Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible-Light-Activated Rhodium Complex in Enantioselective Conjugate Addition of α-Amino Radicals with Michael Acceptors

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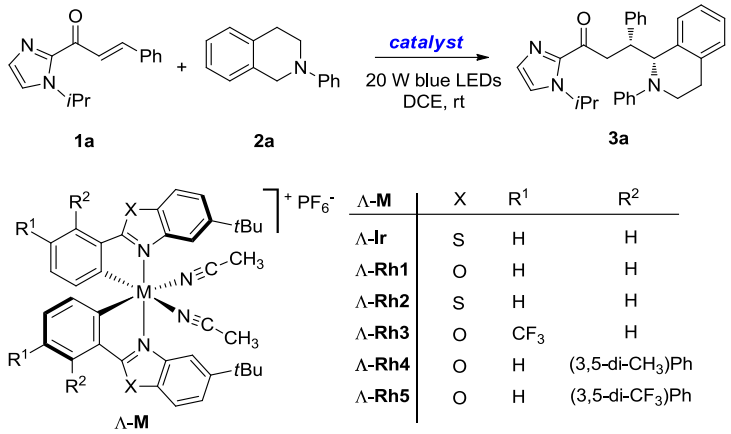
I General Information

All reactions were performed in Schlenk tubes under an atmosphere of argon using oven-dried glassware. Commercially obtained reagents were used without further purification, unless otherwise noted. THF and toluene were distilled freshly before using over sodium and benzophenone. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) from CaH_2. Reactions were checked for completion by TLC analysis and plates were visualized with short-wave UV light (254 nm). The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 400 and 100 MHz respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, mul-tiplet. Coupling constants (*J*) are given in hertz (Hz). HPLC analysis of the compounds were done using IA-IF and AD-H columns using hexane and isopropanol as eluent. The infrared spectra were recorded on a Bruker VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm^{-1}. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry.

II Optimization of Reaction Conditions

Table S1. Screening Catalysts.[a]

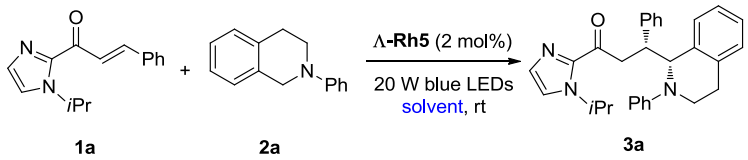


Λ-M	X	R^1	R^2
Λ-Ir	S	H	H
Λ-Rh1	O	H	H
Λ-Rh2	S	H	H
Λ-Rh3	O	CF_3	H
Λ-Rh4	O	H	(3,5-di-CH_3)Ph
Λ-Rh5	O	H	(3,5-di-CF_3)Ph

Entry	Λ-M	d.r.[b]	Yield(%)[c]	ee (%)[d]
1	**Λ-Ir**	53:47	36	0
2	**Λ-Rh1**	74:26	72	93
3	**Λ-Rh2**	64:36	84	91
4	**Λ-Rh3**	75:25	67	50
5	**Λ-Rh4**	82:18	65	91
6	***Λ-Rh5***	***83:17***	***90***	***95***

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (2 mol%), DCE (0.4 mL) under irradiation with 20W blue LEDs. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]NMR yields using 1,3,5-trimethoxybenzene as internal standard. [d]Determined by chiral HPLC analysis.

Table S2. Screening Solvents.[a]

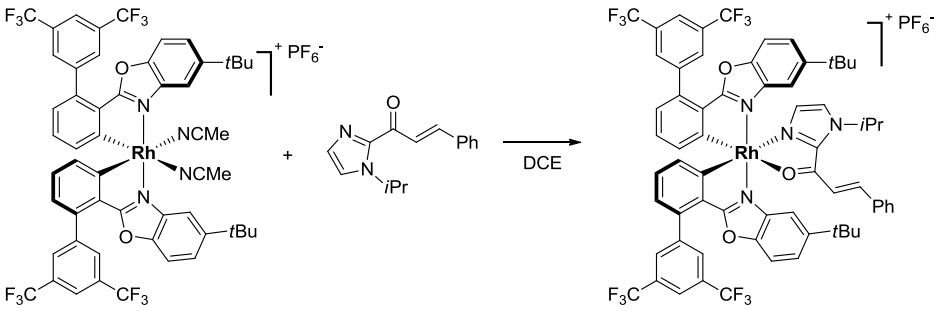


Entry	Solvent	d.r.[b]	Yield(%)[c]	ee (%)[d]
1	***DCE***	***83:17***	***90***	***95***
2	THF	76:24	33	85
3	toulene	86:14	36	94
4	DCM	84:16	73	95
5	$CHCl_3$	71:29	21	85
6	MeCN	87:13	69	89

[a]Reaction conditions:**1a** (0.1mmol), **2a** (0.2mmol), **Λ-Rh5**(2 mol%) in 0.4 mL solvent under 20W blue LEDs. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]NMR yields using 1,3,5-trimethoxybenzene as internal standard. [d]Determined by chiral HPLC analysis.

III Mechanism Investigation

a) Substrate-Coordinated Rhodium Complex *rac*-Rh-IM



Procedure: To a Mixture of Michael acceptor **1a** (12.0 mg, 0.05mmol) and *rac*-**Rh5** (63.0 mg, 0.05 mmol) was added DCE (1.0 mL) at room temperature and stirred for 3 mins. Afterwards, the solution was evaporated for the crude ^{1}H NMR (figure S1). The labile ligands (CH_3CN) were completely removed.

- Signals of *t*-Bu in complex of *rac*-**Rh5**
- Signals of *t*-Bu in complex of *rac*-**Rh5-IM**
- Signals of CH_3CN in complex of *rac*-**Rh5**
- Signals of *i*-Pr in complex of *rac*-**Rh5-IM**

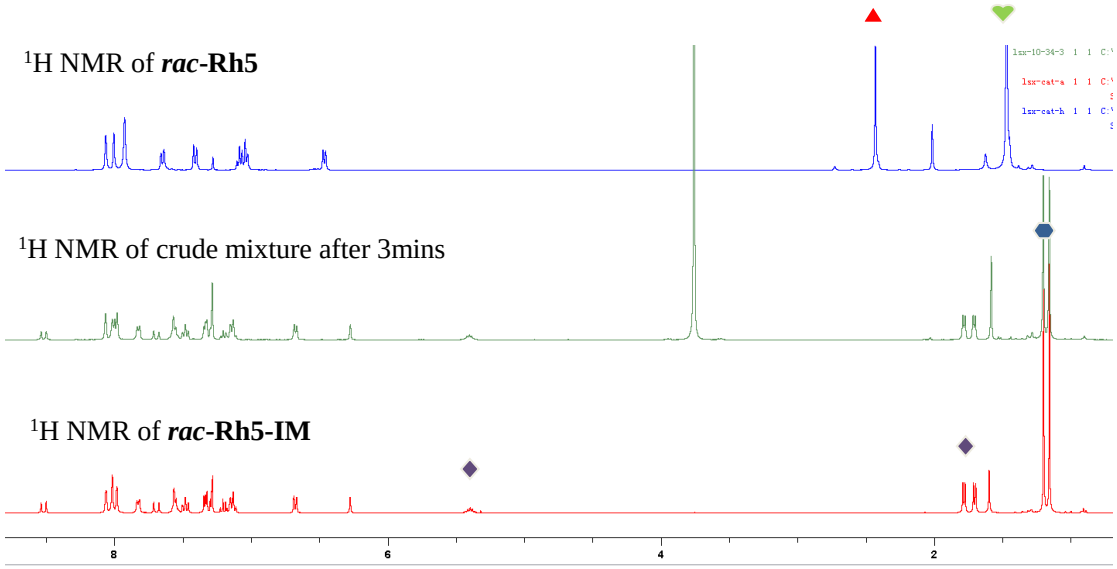
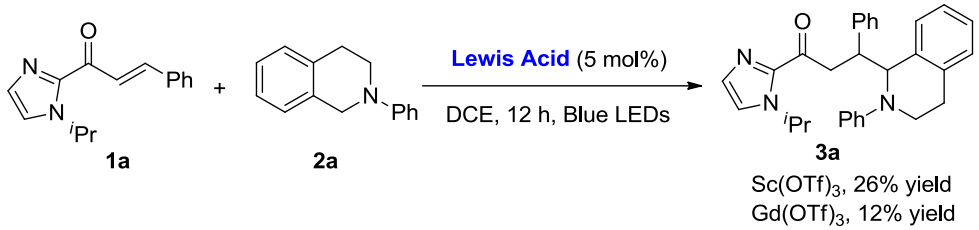


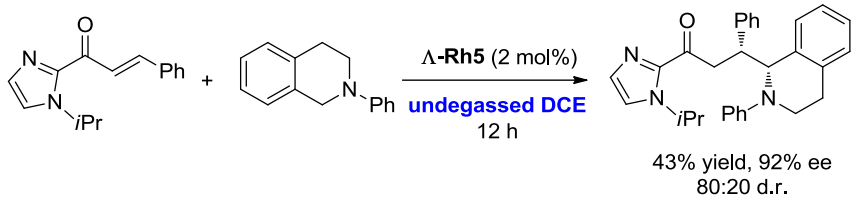
Figure S1. ^{1}H NMR spectra of ***rac*-Rh5**, ***rac*-Rh5-IM** and the crude mixture.

b) Control experiment with other Lewis catalysts instead of Λ-Rh5



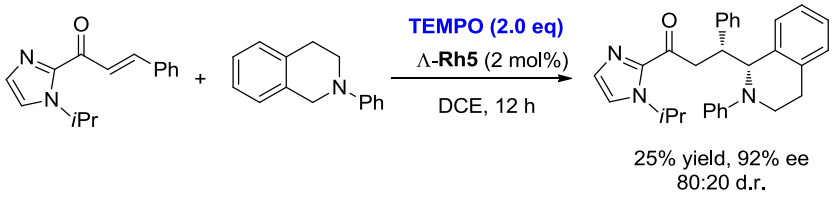
Other Lewis acid catalysts such as $Sc(OTf)_3$ and $Gd(OTf)_3$ were introduced to the reaction instead of **Λ-Rh5**, resulting in sluggish transformations, gave product **3a** in 26% and 12% yield, respectively.

c) Control experiment in the presence of air



Performed in analogy to entry 6 of Table S1 by using undegassed DCE as solvent. Product **3a** was obtained in 43% yield with 80:20 dr, 92% *ee* after 12 h.

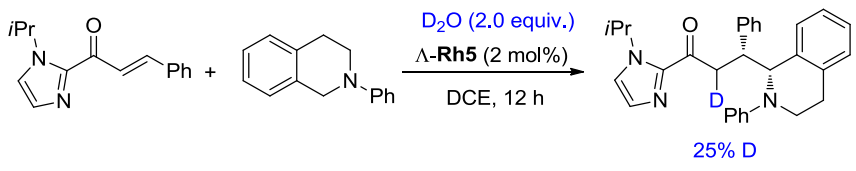
d) Control experiment with radical inhibitor TEMPO



Under the identical conditions, 2.0 equivalent radical inhibitor TEMPO was added to reaction mixture. Product **3a** was offered with 25% yield, 80:20 dr and 92% *ee* after 12 h.

e) Control experiments in deuterated solvent

The deuterium labeling experiments were performed according to general procedure. The ratios of H/D was calculated by ^{1}H NMR analysis.



f) UV/Vis-Absorption Spectra

The absorption spectra of the catalyst *rac*-**Rh5** and *rac*-**Rh5-IM** were measured in solution of DCE. As shown in Figure S2.

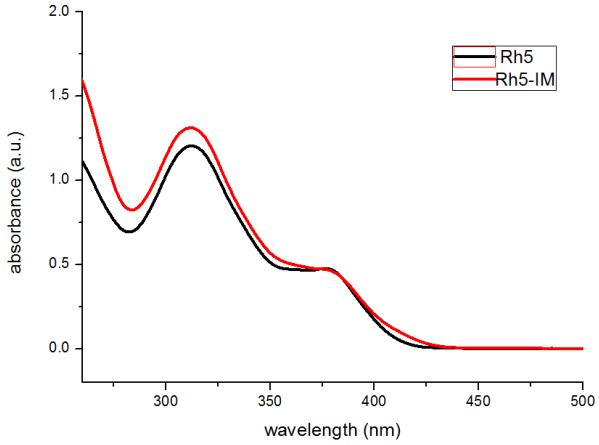


Figure S2. UV/Vis-absorption spectra of the catalyst *rac*-**Rh5** and *rac*-**Rh5-IM**. Measured as solutions in THF ($2*10^{-5}$ M). a.u. = absorbance units.

g) Luminescence Quenching Experiments

The luminescence quenching experiments were investigated in the presence of catalyst *rac*-**Rh5** and *rac*-**Rh5-IM**. Emission intensities were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette. All the solutions were excited at 280 nm and the emission was measured at 420 nm. The concentration of the photoredox catalyst solution (*rac*-**Rh5** and *rac*-**Rh5-IM**) was 0.2 mM in DCE. The concentration of the quencher (2-phenyl-1,2,3,4-tetrahydroisoquinoline **2a**) stock solution was 0.18 M in DCE. For each quenching experiment, 10 µL of this stock solution were titrated to a solution (3.0 mL) of rhodium complex in a screw-top quartz cuvette. The addition of 10 µL stock solution refers to an increase of the quencher concentration of 0.6 mM. After degassing with an argon stream for 5 minutes, the emission intensity was collected.

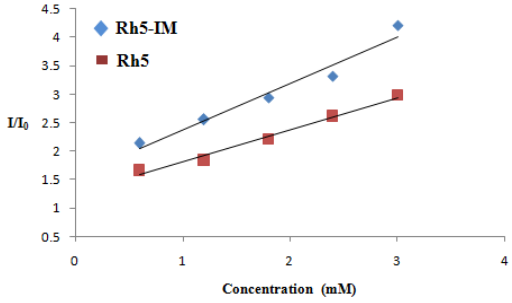


Figure S3. Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the quencher (2-phenyl-1,2,3,4-tetrahydroisoquinoline **2a**).

h) Quantum Yield Measurement

1) Measurement of light intensity at 420 nm

The photon flux of the spectrophotomete was measured by standard ferrioxalateactinometry[1]. A 0.15 M solution of ferrioxalate was prepared by dissolving 1.47 g of potassium ferrioxalate hydrate in 20 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 5.0 mg of phenanthroline and 1.125 g of sodium acetate in 5 mL of 0.5 M H_2SO_4. Both solutions were prepared and stored in the dark.

To determine the photon flux of the spectrophotometer, 2.5 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 420 nm with an emission slit width at 10.0 nm. After irradiation, 0.44 mL of the phenanthroline solution was added to the cuvette. The solution was kept in dark for 1 h to make sure the complete coordination. The absorbance of the actinometry solution was monitored at 510 nm. The absorbance of a non-irradiated (in dark) sample was also measured at 510 nm. The moles of Fe^{2+} formed was determined using Beer's Law:

$$\text{mol } Fe^{2+} = \frac{V \bullet \Delta A}{l \bullet \varepsilon}$$

Where V is the total volume (0.00294 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and the ε is the molar absorptivity at 510 nm (11,100 $mol^{-1}cm^{-1}$). ε (510 nm) is the molar absorptivity of $Fe(phen)_3^{2+}$ (11100 L $mol^{-1}cm^{-1}$). The photon flux can be calculated as:

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \bullet t \bullet f}$$

Where Φ is the quantum yield for the ferrioxalateactinometer (1.05 for a 0.15 solution at 412 nm; 1.04 for a 0.15 solution at 422 nm; 1.03 for a 0.15 solution at 433 nm)[1], t is the irradiated time (90 s), and f is the fraction of light absorbed at λ = 420 nm ($f = 1-10^{-A}$). The measurement of the fraction of the light at 420 nm for the ferrioxalate solution was shown in Figure S4. The absorbance of the ferrioxalate solution at 420 nm is >3

indicating f (f = 1–10^{-A}) is >0.999. The photon flux was calculated (average of three experiments) to be 8.42×10^{-10}einstein s^{-1}.

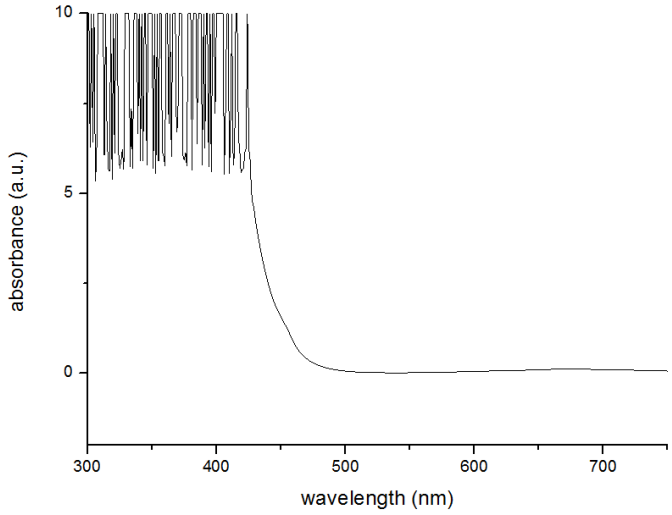


Figure S4. Absorbance of the ferrioxalateactinometer solution (0.15 M).

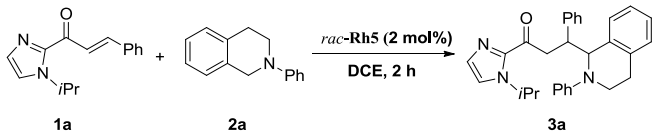
Sample calculation:

$$\text{mol } Fe^{2+} = \frac{0.00294\ \text{L} \times 0.297}{1.0\ \text{cm} \times 11{,}100\ \text{mol}^{-1}\text{cm}^{-1}} = 7.86\times10^{-8}$$

$$\text{photon flux} = \frac{7.86\times10^{-8}}{1.04 \times 90\ \text{s} \times 1} = 8.40 \times10^{-10}\ \text{einstein}\ \text{s}^{-1}$$

2) Measurement of quantum yield:

Model reaction:



1a 2a 3a

A screw-top cuvette (10.0 mm) was charged with **1a** (0.1 mmol, 1.0 eq.), **2a** (0.2 mmol, 2.0 eq.), catalyst *rac*-**Rh5** (2 mol%) and 0.4 mL DCE (0.25 M). The sample was stirred and irradiated (λ = 420 nm, slit width = 10.0 nm) for 7200 s (2 h). After irradiation, the yield of product formed was determined by ^{1}H NMR base on 1,3,5-trimethoxybenzene as internal standard. The quantum yield was determined as following:

$$\Phi = \frac{\text{mole of product formed}}{\text{mole of photo absorbed}} = \frac{0.1\times10^{-3}\times0.12}{8.42\times10^{-10}\times2\times3600\times1} = 2.0$$

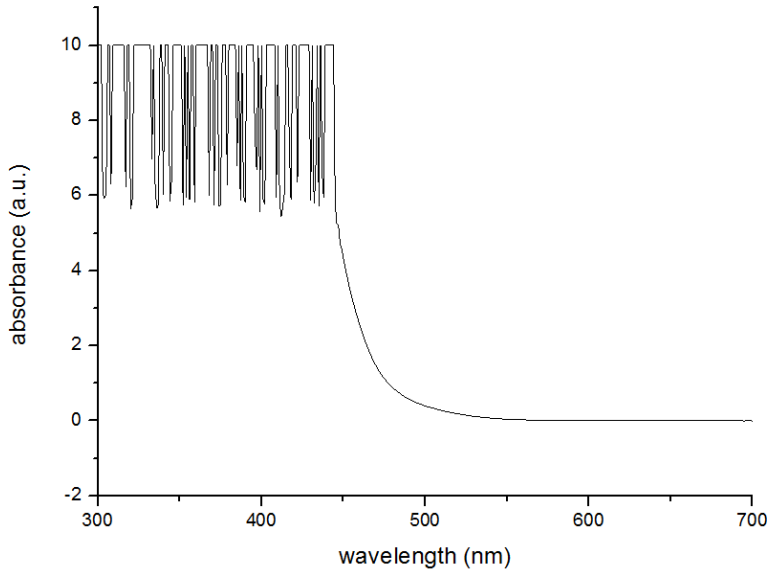


Figure S5. Absorbance of a 1.0×10^{-2} M solution of *rac*-**Rh5-IM** in DCE. Absorbance at 420 nm (>3) demonstrating that the fraction of light absorbed is >0.999 ($f = 1\text{-}10^{A(420\ nm)}$).

i) Explanation of proposed mechanism.

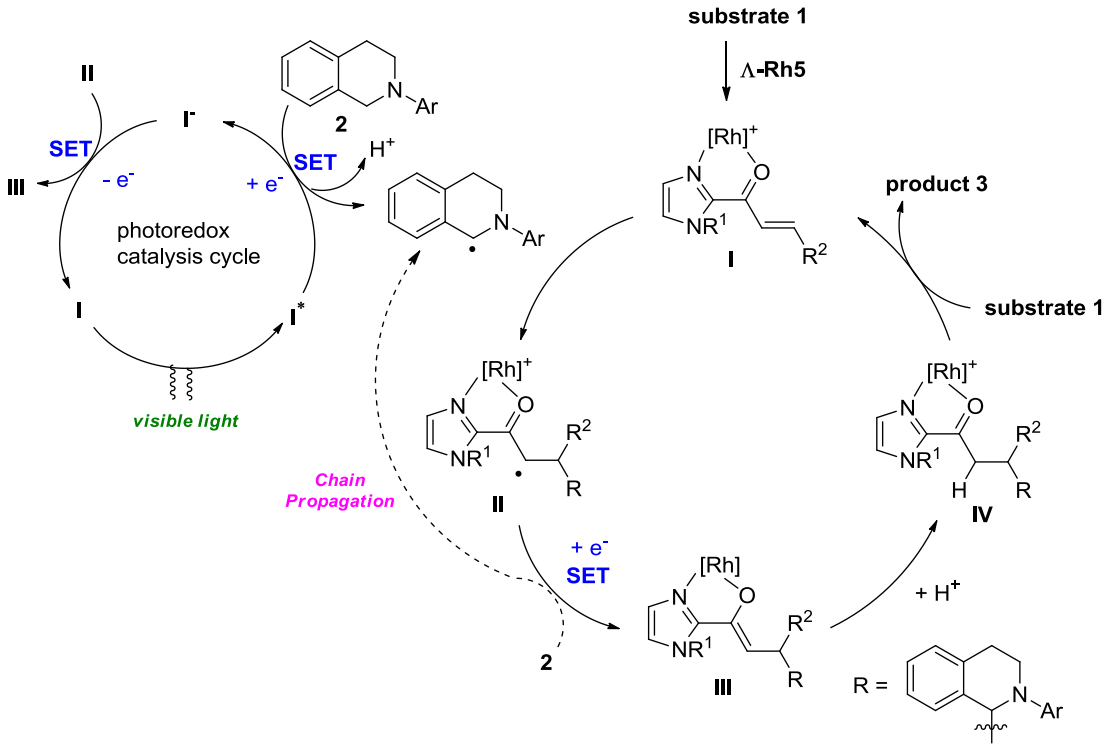


Figure S6. Proposed mechanism.

The proposed mechanism is shown in Figure S6. Substrate **1** first coordinates with

rhodium complex in bidentate fashion to generate intermediate **I**. Then, *N*,*O*-rhodium-coordinated α, β-unsaturated 2-acyl imidazoles complex (intermediate **I**) is photoexcited and reduced by tetrahydroisoquinoline **2**, thus generating an α-amino radical, which subsequently added to intermediate **I** to generate the secondary radical intermediate **II**. Intermediate **III** (rhodium enolate), which generated from intermediate **II** via single electron transfer (SET) process results in rhodium-coordinated product **IV** by protonation with H^+. The desired product is released by replacement of the coordinated product **IV** by **1a**. However, a quantum yield measurement shows that a quantum yield of this reaction is over 2, which indicates that radical intermediate **II** might not only accept a single electron from the reduced photosensitizer $\mathbf{I}^-$, but also from substrate **2**, thus leading to a chain propagation cycle (M. A. Cismesia and T. P. Yoon, *Chem. Sci*., **2015**, *6*, 5426-5434).

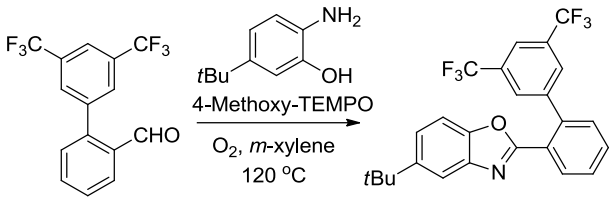
IV Experimental Section

1. Synthesis of chiral catalysts.

(a) **Λ-Ir**[2]**, Λ-Rh1**[2]**, Λ-Rh2**[2]**, Λ-Rh3**[3] and **Λ-Rh4**[4] were prepared according to reported procedure.

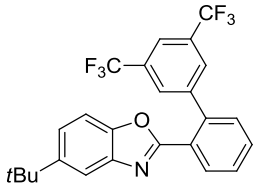
(b) General procedure to synthesize **Λ-Rh5**.

Ligand synthesis:



Ligand

A solution of 2-amino-4-*tert*-butylphenol (0.825 g, 5.0 mmol) and 3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-carbaldehyde (1.59 g, 5.0 mmol) in *m*-xylene (16.0 mL) was stirred at 120 °C for 30 mins. 4-Methoxy-TEMPO (46.5 mg, 5 mol%) was added to the mixture and the reaction was stirred at this temperature for further 8 h under oxygen atmosphere. Then the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:20) to obtain the product (1.97 g, 85% yield).

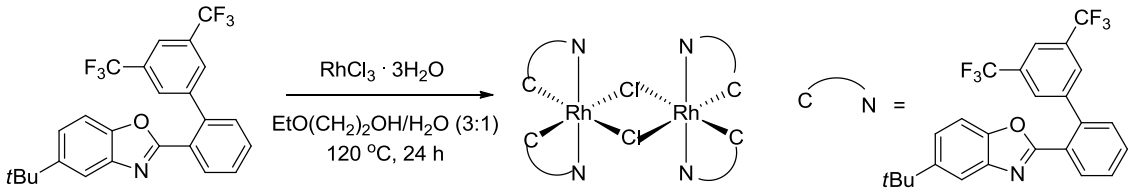


Ligand

White solid, mp = 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30-8.28 (m, 1H), 7.91 (s, 1H), 7.82 (s, 2H), 7.68-7.68 (d, *J* = 1.2 Hz, 1H), 7.63-7.57 (m, 2H), 7.45-7.43 (m, 1H), 7.37-7.34 (dd, *J* = 8.8 Hz, 1.5 Hz, 1H), 7.23-7.21 (d, *J* = 8.4 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.2, 148.5, 148.3, 143.1, 141.4, 139.0, 131.3, 131.2, 131.1 (q, *J* = 33.2 Hz), 130.8, 129.6 (q, *J* = 2.7 Hz), 129.0, 126.2, 123.4 (q, *J* =

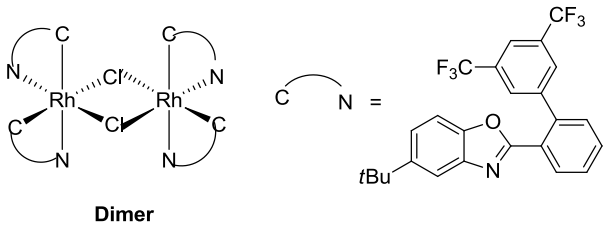
271.0 Hz), 123.3, 121.1 (q, J = 3.9 Hz), 116.7, 109.5, 34.9, 31.7. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = -62.8. IR (KBr): ν(cm^{-1}) 3026, 2962, 2870, 1581, 1549, 1481, 1463, 1394, 1380, 1366, 1334, 1275, 1179, 1162, 1131, 1115, 1045, 904, 774, 680. HRMS (ESI, m/z) calcd for $C_{25}H_{20}F_6NO[M+H]^+$: 464.1444, found: 464.1442.

Precursor rhodium complex (Dimer):



Ligand Dimer

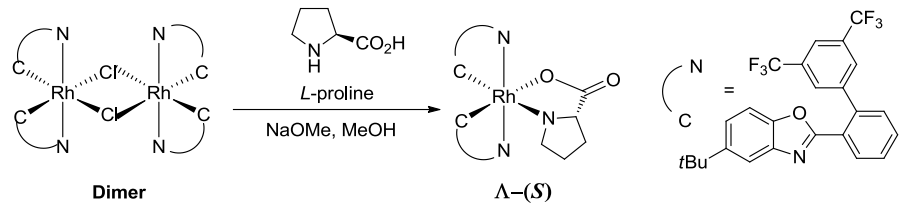
Ligand (1.9 g, 4.1 mmol) was added to $RhCl_3$•$3H_2O$ (418.5 mg, 2.0 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 92 mL). The reaction mixture was heated at 120 °C for 24 h under argon atmosphere. The resulting precipitate was collected by filtration, washed with methanol and dried to obtain the product dimer (1.7 g, 81% yield).



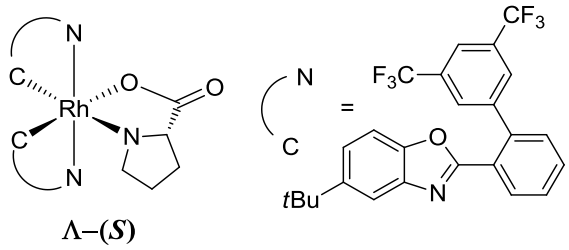
Dimer

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 4H), 7.99 (s, 4H), 7.92 (s, 8H), 7.02-7.00 (d, J = 8.8 Hz, 4H), 6.91-6.85 (m, 8H), 6.79-6.77 (d, J = 8.8 Hz, 4H), 6.34-6.33 (d, J = 7.2 Hz, 4H), 0.88 (s, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.1, 169.0, 167.1, 166.8, 148.5, 147.0, 141.8, 138.3, 137.7, 133.8, 130.3, 127.2, 125.8, 124.2, 123.5 (q, J = 271.0 Hz), 121.2 (q, J = 4.1 Hz), 121.2 (q, J = 3.5 Hz), 115.2, 109.8, 34.7, 31.1. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.5, -62.7. IR (KBr): ν(cm^{-1}) 2966, 2908, 2871, 1619, 1606, 1566, 1516, 1483, 1468, 1444, 1414, 1395, 1377, 1355, 1281, 1252, 1178, 1136, 1106, 1057, 933, 900, 846, 806, 710, 682. HRMS (ESI, m/z) calcd for $C_{100}H_{72}ClF_{24}N_4O_4Rh_2[M-Cl]^+$: 2090.3042, found: 2090.2991.

Rhodium Auxiliary Complexes



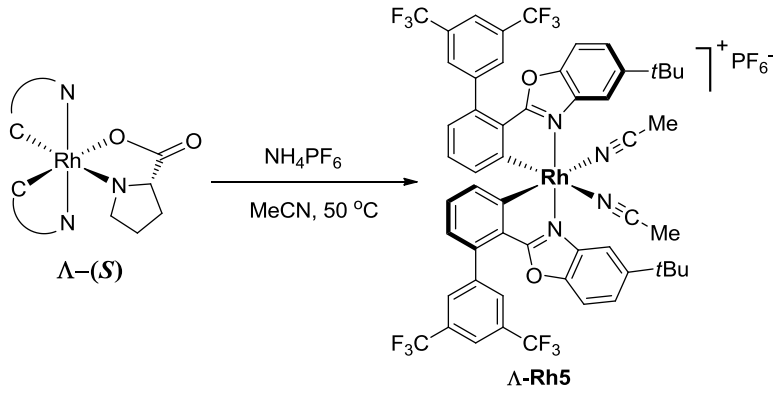
To a solution of NaOMe (230 mg, 2.0 mmol) in methanol (120 mL), *L*-proline (108 mg, 2.0 mmol) was added in one portion. The mixture was stirred for 10 min, to which a suspension of rhodium dimer (2.08 g, 1.0 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h. After the mixture cooled to room temperature, CH_2Cl_2 (16.0 mL) was added. The reaction mixture was stirred for a further 12 h. The solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc/DCM = 1:5) to obtain the product **Λ-(*S*)** (752 mg, 33% yield).



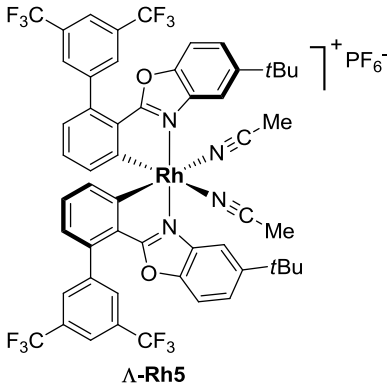
Yellow solid. $[\alpha]_D^{25}$ = +123.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19-8.18 (d, *J* = 1.2 Hz, 1H), 8.05 (s, 1H), 7.99-7.95 (d, *J* = 16.4 Hz, 4H), 7.55-7.52 (m, 2H), 7.35-7.31 (t, *J* = 8.4 Hz, 2H), 7.28-7.28 (d, *J* = 1.2 Hz, 1H), 7.04-6.9 (m, 4H), 6.85-6.83 (d, *J* = 7.2 Hz, 1H), 6.48-6.46 (d, *J* = 7.6 Hz, 1H), 4.29-4.24 (q, *J* = 7.6 Hz, 1H), 4.07-4.01 (m, 1H), 2.86-2.81 (m, 1H), 2.26-2.21 (m, 2H), 2.09-1.99 (m, 1H), 1.75-1.70 (m, 1H), 1.61-1.49 (m, 1H), 1.40 (s, 9H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 180.6, 171.5, 171.4,169.9, 169.9, 169.1, 168.8, 168.5, 168.1, 151.5, 150.4, 147.9, 147.9, 142.0, 141.6, 138.7, 138.6, 137.5, 137.1, 135.3, 134.2, 131.3 (q, *J* = 33.1 Hz), 131.0 (q, *J* = 32.5 Hz), 130.5, 130.4, 129.8, 129.8, 127.7, 127.5, 125.9, 125.4, 124.3, 124.2, 123.5 (q, *J* = 271.1 Hz), 123.4 (q, *J* = 271.1 Hz), 121.6 (q, *J* = 3.4 Hz), 121.6 (q, *J* = 4.3 Hz), 121.2 (q, *J* = 4.3 Hz), 121.2 (q, *J* = 3.1 Hz), 115.3, 111.7, 110.6, 110.5, 63.9, 49.4, 35.4, 35.2, 31.7, 31.7, 29.7, 26.9. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.7. IR (KBr): *v*(cm^{-1}) 1618, 1571, 1560, 1507, 1376, 1363, 1278, 1135, 1057, 709, 682. HRMS (ESI, *m*/*z*) calcd for $C_{55}H_{44}F_{12}N_3O_4Rh[M+H]^+$: 1142.2222, found:

1142.2254.

Synthesis of Non-Racemic Rhodium Catalysts.



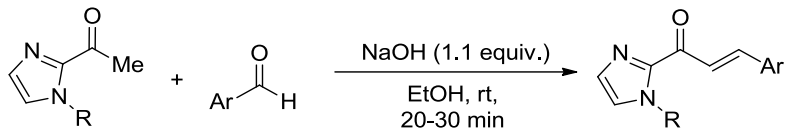
A suspension of the rhodium auxiliary complex **Λ-(*S*)** (239.0 mg, 0.28 mmol) and NH_4PF_6 (163.0 mg, 2.80 mmol) in acetonitrile (56.0 mL) was heated at 50 °C for 24 h under argon in the dark. Then removed the solvent under reduced pressure and subjected to flash silica gel chromatography (100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 20:1) to give the enantiopure catalyst Λ-**Rh5** (132.7 mg, 49% yield).



Pale yellow solid. $[\alpha]_D^{25}$ = +115.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 2H), 7.98 (s, 2H), 7.90 (s, 4H), 7.64-7.61 (d, *J* = 8.8 Hz, 2H), 7.40-7.38 (d, *J* = 8.8 Hz, 2H), 7.08-7.00 (s, 4H), 6.45-6.43 (d, *J* = 7.6 Hz, 2H),2.41 (s, 6H), 1.45 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.9, 167.9, 160.8, 160.4, 149.6, 145.8, 139.2, 136.8, 135.0, 131.1, 129.5 (q, *J* = 33.2 Hz), 129.4, 128.0, 128.0, 125.4, 124.9, 123.5, 121.5 (q, *J* = 271.2 Hz), 120.5 (q, *J* = 3.4 Hz), 119.9 (q, *J* = 3.6 Hz), 119.9 (q, *J*= 4.0 Hz), 111.4, 109.4, 33.5, 29.6, 1.4. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.7, -71.6, -73.5. IR (KBr): *ν*(cm^{-1}) 3056, 2965, 2872, 2289, 1620, 1578, 1517, 1483, 1417, 1378, 1280, 1180, 1135,

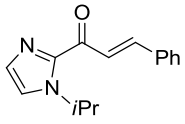
1107, 847, 709, 682, 558. HRMS (ESI, *m*/*z*) calcd for $C_{54}H_{42}F_{12}N_4O_2Rh[M+H]^+$: 1110.2244, found: 1110.2187.

2. General procedure (A) to synthesize *α, β*-unsaturated 2-acyl imidazoles 1a-1m, 1p, 1q.



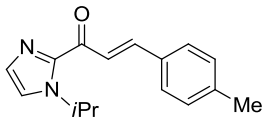
S1 **1a-1m, 1p, 1q**

2-Acetyl-imidazole **S1**(10.0 mmol, 1.0 equiv.) and EtOH (20 mL) were added to a 50 mL RBF followed by corresponding aromatic aldehyde (10.5 mmol, 1.05 equiv.) and NaOH (11.0 mmol, 1.1 equiv.). The solution was stirred until the substrates consumption (detect by TLC), then transferred to separatory funnel. Saturated NaCl (30 mL) and H_2O (10 mL) were added and the mixture was extracted with DCM (3 x 25 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated on a rotatory evaporator. The resulting residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:9) to give the desired products (65-88% yields).



1a

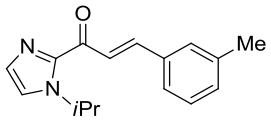
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15-8.11 (d, *J* = 16 Hz, 1H), 7.83-7.79 (d, *J* = 16 Hz, 1H), 7.71-7.69 (m, 2H), 7.40-7.39 (m, 3H), 7.32 (s, 1H), 7.26 (s, 1H), 5.78-5.68 (m, 1H), 1.50-1.48 (d, *J* = 8.0 Hz, 6H).



1b

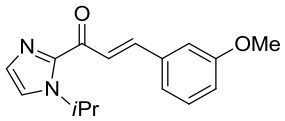
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.06 (d, *J* = 16.0 Hz, 1H), 7.81-7.77 (d, *J* = 16.0 Hz, 1H), 7.61-7.59 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 1H), 7.25 (s, 1H), 7.22-7.20 (d, *J* = 8.0

Hz, 2H), 5.77-5.70 (m, 1H), 2.39 (s, 3H), 1.50-1.48 (d, *J* = 6.8 Hz, 6H).



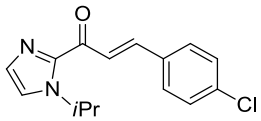
1c

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13-8.09 (d, *J* = 16.0 Hz, 1H), 7.80-7.76 (d, *J* = 16.0 Hz, 1H), 7.55 (s, 1H), 7.49-7.47 (d, *J* = 7.6 Hz, 1H), 7.32-7.26 (m, 3H), 7.22-7.20 (d, *J* = 7.6 Hz, 1H), 5.77-5.70 (m, 1H), 2.39 (s, 3H), 1.50-1.49 (d, *J* = 6.8 Hz, 6H).



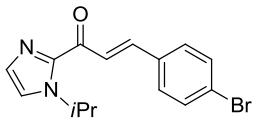
1d

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12-8.08 (d, *J* = 15.6 Hz, 1H), 7.80-7.76 (d, *J* = 16.0 Hz, 1H), 7.33-7.22 (s, 5H), 6.96-6.93 (m, 1H), 5.76-5.69 (m, 1H), 3.85 (s, 3H), 1.50-1.48 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 180.4, 159.8, 143.2, 143.1, 136.3, 129.7, 123.6, 121.6, 121.4, 116.6, 112.9, 55.3, 49.3, 23.6. IR (KBr): *v*(cm^{-1}) 1658, 1600, 1593, 1452, 1404, 1390, 1378, 1255, 1012, 813, 781, 753, 718. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2O_3[M+H]^+$: 271.1441, found: 271.1441.



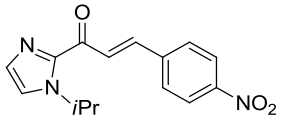
1e

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.07 (d, *J* = 16.0 Hz, 1H), 7.76-7.72 (d, *J* = 16.0 Hz, 1H), 7.64-7.62 (d, *J* = 8.4 Hz, 2H), 7.38-7.36 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.26 (s, 1H), 5.75-5.68 (m, 1H), 1.50-1.49 (d, *J* = 6.8 Hz, 6H).



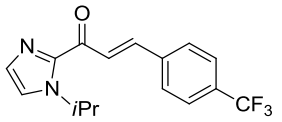
1f

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13-8.09 (d, *J* = 16.0 Hz, 1H), 7.74-7.70 (d, *J* = 16.0 Hz, 1H), 7.57-7.52 (m, 4H), 7.33 (s, 1H), 7.27 (s, 1H), 5.75-5.68 (m, 1H), 1.50-1.49 (d, *J* = 6.8 Hz, 6H).



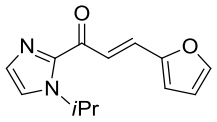
1g

Yellow solid, mp = 142-144ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27-8.22 (m, 3H), 7.84-7.77 (m, 3H), 7.37 (s, 1H), 7.29-7.27 (d, *J* = 6.4 Hz, 1H), 5.73-5.66 (m, 1H), 1.52-1.50 (d, *J* =6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.5, 148.4, 143.0, 141.2, 139.7, 130.2, 129.1, 127.5, 124.1, 122.1, 49.5, 23.6. IR (KBr): *v*(cm^{-1}) 1659, 1610, 1592, 1511, 1393, 1379, 1342, 1150, 1109, 1006, 842, 777, 765, 732. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{15}N_3O_3[M+H]^+$: 286.1186, found: 286.1185.



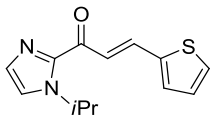
1h

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.17 (d, *J* = 16.0 Hz, 1H), 7.81-7.77 (m, 3H), 7.67-7.65 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 1H), 7.28 (s, 1H), 5.74-5.68 (m, 1H), 1.51-1.50 (d, *J* = 6.8 Hz, 6H).



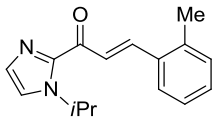
1i

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.94 (d, *J* = 15.6 Hz, 1H), 7.59-7.55 (d, *J* = 16.0 Hz, 1H), 7.52 (s, 1H), 7.31 (s, 1H), 7.25 (s, 1H), 6.74-6.73 (d, *J* = 3.2 Hz, 1H), 6.50-6.49 (q, *J* =1.6 Hz, 1H), 5.75-5.68 (m, 1H), 1.49-1.47 (d, *J* = 6.8 Hz, 6H).



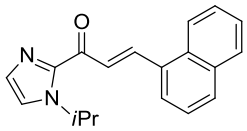
1j

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.86 (m, 2H), 7.42-7.41 (d, *J* = 4.8 Hz, 1H), 7.38-7.38 (d, *J* = 3.6 Hz, 1H), 7.32 (s, 1H), 7.25 (s, 1H), 7.09-7.07 (m, 1H), 5.75-5.69 (m, 1H), 1.50-1.48 (d, *J* = 6.8 Hz, 6H).



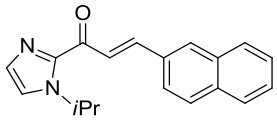
1k

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16-8.04 (q, *J* = 16.0 Hz, 2H), 7.83-7.82 (d, *J* = 7.6 Hz, 1H), 7.33-7.21 (m, 5H), 5.77-5.70 (m, 1H), 2.50 (s, 3H), 1.51-1.49 (d, *J* = 6.8 Hz, 6H).



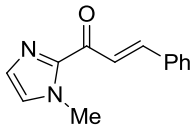
1l

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72-8.68 (d, *J* = 15.6 Hz, 1H), 8.33-8.31 (d, *J* = 8.4 Hz, 1H), 8.25-8.21 (d, *J* = 16.0 Hz, 1H), 8.05-8.03 (d, *J* = 7.2 Hz, 1H), 7.92-7.88 (t, *J* = 9.4 Hz, 2H), 7.59-7.49 (m, 3H), 7.35 (s, 1H), 7.28 (s, 1H), 5.81-5.74 (m, 1H), 1.53-1.52 (d, *J* = 6.8 Hz, 6H).



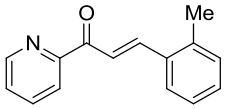
1m

Yellow solid, mp =103-105ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26-8.22 (d, *J* = 16.0 Hz, 1H), 8.09 (s, 1H), 7.99-7.95 (d, *J* = 16.0 Hz, 1H), 7.89-7.83 (m, 4H), 7.53-7.50 (m, 2H), 7.34 (s, 1H), 7.28 (s, 1H), 5.79-5.73 (m, 1H), 1.52-1.50 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 180.5, 143.3, 143.2, 134.3, 133.3, 132.5, 130.5, 129.8, 128.6, 128.5, 127.7, 127.2, 126.5, 124.3, 123.6, 121.4, 49.3, 23.6. IR (KBr): *v*(cm^{-1}) 2920, 1658, 1598, 1567, 1560, 1510, 1400, 1391, 1379, 1011, 811, 734. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{18}N_2O[M+H]^+$: 291.1492, found: 291.1495.



1p

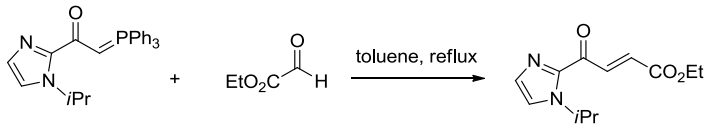
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.06 (d, *J* = 16.0 Hz, 1H), 7.70 (s, 2H), 7.40 (s, 3H), 7.22 (s, 1H), 7.09 (s, 1H), 4.10 (s, 3H).



1q

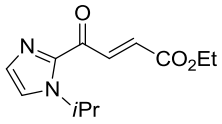
White solid, mp = 68-70 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75-8.74 (d, *J* = 4.0 Hz, 1H), 8.25-8.25 (d, *J* = 1.2 Hz, 2H), 8.21-8.19 (d, *J* = 8.0 Hz, 1H), 7.90-7.84 (m, 2H), 7.50-7.17 (m, 1H), 7.32-7.22 (m, 3H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.5, 154.3, 148.8, 142.2, 138.5, 137.0, 134.0, 130.8, 130.3, 126.8, 126.2, 122.9, 121.8, 19.8. IR (KBr): *v*(cm^{-1}) 3055, 1670, 1610, 1599, 1578, 1332, 1220, 1027, 994, 986, 748. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{13}NO[M+Na]^+$: 246.0889, found: 246.0890.

3. General procedure (B) to synthesize *α, β*-unsaturated 2-acyl imidazole 1o.



1o

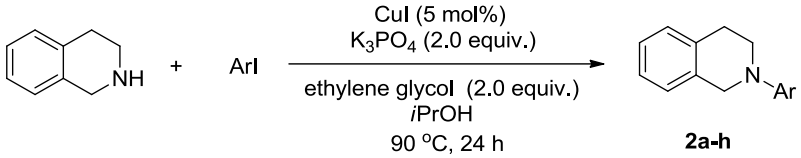
To a solution of Wittig reagent (1.24 g, 3.0 mmol) in toluene (15 mL) was added aldehyde (766 mg, 7.5 mmol, 2.5 equiv.), the reaction was stirred in reflux condition overnight (18 h). Then DMAP (0.1 equiv.) was added to the reaction mixture. The reaction was stirred at -5 °C for 24 h and concentrated *in vacuo*. The material was directly subjected to flash silica chromatography (EtOAc/Petroleum ether = 1:3) to give the desired compounds. ^{1}H NMR showed that the material is a mixture of *E*:*Z* isomers in a ratio of >20:1[6].



1o

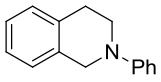
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 15.8 Hz, 1H), 7.36-7.28 (m, 2H), 6.91 (d, *J* = 15.8 Hz, 1H), 5.66-5.56 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.48 (d, *J* = 6.7 Hz, 6H), 1.34 (t, *J* = 5.9 Hz, 3H).

4. General procedure to synthesis *N*-aryl-1,2,3,4-tetrahydroisoquinolines 2a-h.



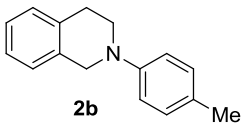
2a-h

Copper(I) iodide (190 mg, 1.0 mmol) and potassium phosphate (4.24 g, 20.0 mmol) were put into a 50 mL three-neck flask. The three-neck flask was evacuated and backfilled with argon. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 30.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (1.2 mL, 10 mmol) and aryl iodide (10.0 mmol, 1.0 equiv.) were added successively by syringe at room temperature. The reaction mixture was heated at 90 °C for 24 h and then allowed to cool to room temperature. DCM (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (PE/EA = 20:1), and the fraction with R_f = 0.5 was collected to give the desired products **2a-h** with 52-86% isolated yields[7].



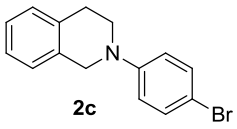
2a

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 2H), 7.18-7.14 (m, 4H), 7.00-6.98 (d, *J* = 7.6 Hz, 2H), 6.85-6.81 (t, *J* = 7.2 Hz, 1H), 4.41 (s, 2H), 3.58-3.55 (t, *J* = 5.6 Hz, 2H), 3.00-2.97 (t, *J* = 5.8 Hz, 2H).



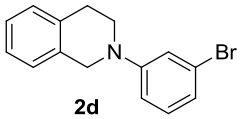
2b

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.03 (m, 4H), 7.11-7.09 (d, *J* = 8.4 Hz, 2H), 6.93-6.91 (d, *J* = 8.4 Hz, 2H), 4.36 (s, 2H), 3.52-3.50 (t, *J* = 5.8 Hz, 2H), 3.00-2.97 (t, *J* = 5.6 Hz, 2H).



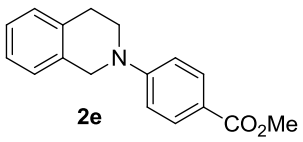
2c

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.34 (d, *J* = 9.2 Hz, 2H), 7.21-7.15 (m, 4H), 6.84-6.82 (d, *J* = 8.8 Hz, 2H), 4.38 (s, 2H), 3.55-3.52 (t, *J* = 5.8 Hz, 2H), 2.99-2.96 (t, *J* = 5.6 Hz, 2H).



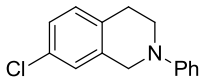
2d

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.11 (m, 4H), 7.09-7.07 (d, *J* = 8.4 Hz, 1H), 7.05-7.04 (t, *J* = 2.0 Hz, 1H), 6.90-6.88 (m, 1H), 6.84-6.81 (m, 1H), 4.36 (s, 2H), 3.52-3.49 (t, *J* = 6.0 Hz, 2H), 2.95-2.92 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.4, 134.7, 133.9, 130.3, 128.4, 126.5, 126.5, 126.1, 123.3, 120.8, 117.2, 113.0, 49.9, 45.8, 29.0. IR (KBr): *v*(cm^{-1}) 1591, 1560, 1508, 1489, 1458, 1474, 1418, 1387. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{14}BrN[M+H]^+$: 288.0382, found: 288.0373.



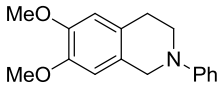
2e

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.1 Hz, 1H), 7.23-7.17 (m, 4H), 6.87 (d, *J* = 9.0 Hz, 1H), 4.52 (s, 2H), 3.87 (s, 3H), 3.65 (t, *J* = 5.8 Hz, 2H), 2.99 (t, *J* = 5.8 Hz, 2H).



2g

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 4.27 (s, 2H), 3.55 (t, *J* = 5.8 Hz, 3H), 2.94 (t, *J* = 5.7 Hz, 2H).

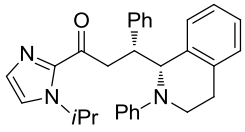


2h

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.27 (t, *J* = 8.0 Hz, 2H), 7.00-6.98 (d, *J* = 8.0 Hz, 2H), 6.85-6.81 (t, *J* = 7.2 Hz, 2H), 6.66-6.65 (d, *J* = 4.4 Hz, 2H), 4.34 (s, 2H), 3.88-3.87 (t, *J* = 3.2 Hz, 6H), 3.57-3.54 (t, *J* = 5.8 Hz, 2H), 2.92-2.89 (t, *J* = 5.6 Hz, 2H).

5. General procedure for chiral Rhodium (III) complex catalyzed enantioselective α-amino radical addition reaction:

To an oven-dried 25 mL Schlenk tube equipped with a stir bar, Λ-**Rh5** (2.5 mg, 2 mol%) was added along with *α, β*-unsaturated 2-acyl imidazoles **1** (0.1 mmol, 1.0 equiv.), *N*-aryl-1,2,3,4-tetrahydroisoquinolines **2** (2.0 equiv.) and DCE (0.4 mL). After degassing via three freeze-pump-thaw cycles, the Schlenk tube was sealed and positioned at a distance of 5-10 cm from 20 W blue LEDs. The reaction was stirred at room temperature for 12 h under argon, and then the mixture directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:10) to afford title products **3**.

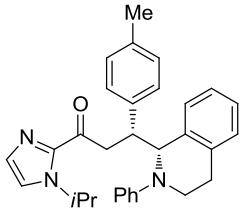


3a

According to the general procedure, **3a** was obtained as yellowish oil; 92% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 96:4, flow rate 1.0 mL/min, t_r1 (major) = 17.93 min, t_r1 (minor) = 16.03 min; t_r2 (major) = 13.58 min, t_r2 (minor) = 10.39 min); $[\alpha]_D^{25}$ = -88.3 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.25-7.00 (m, 13H), 6.69-6.67 (d, *J* = 8.0 Hz, 2H), 6.61-6.57 (t, *J* = 7.2 Hz, 1H), 5.24-5.17 (m,1H), 5.02-5.00 (d, *J* = 7.6 Hz, 1H),

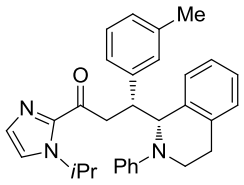
4.13-4.07 (q, *J* = 7.6 Hz, 1H), 3.80-3.74 (dd, *J* = 16.8, *J* = 8.0Hz, 1H), 3.65-3.53 (m, 2H), 3.44-3.38 (m, 1H), 2.97-2.93 (t, *J* = 6.4 Hz, 2H), 1.28-1.22 (q, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =191.2, 150.0, 142.4, 141.7, 136.7, 135.7, 129.2, 128.8, 128.6, 128.5, 128.5, 127.9, 126.7, 126.3, 125.2, 120.7, 117.1, 114.2, 63.6, 48.9, 46.2, 42.8, 42.1, 26.7, 23.4, 23.4. IR (KBr): *v*(cm^{-1}) 3420, 2919, 2850, 1676, 1654, 1597, 1502, 1453, 1395, 1255, 981, 750, 698. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{31}N_3O$ $[M+H]^+$: 450.2540, found: 450.2535.



3b

According to the general procedure, **3b** was obtained as yellowish oil; 92% yield, 92% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 96:4, flow rate 1.0 mL/min, t_r1 (major) = 17.86 min, t_r1 (minor) = 16.97 min; t_r2 (major) = 14.82 min, t_r2 (minor) = 11.73 min); $[\alpha]_D^{25}$ = -59.3 (c = 0.5, $CHCl_3$) (major).

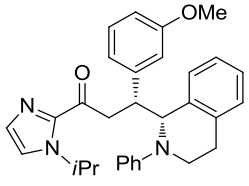
^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.17-7.00 (m, 10H), 6.95-6.93 (d, *J* = 8.0 Hz, 2H), 6.71-6.69 (d, *J* = 8.0 Hz, 2H), 6.62-6.58 (t, *J* = 7.2 Hz, 1H), 5.26-5.19 (m, 1H), 5.00-4.98 (d, *J* = 7.2 Hz, 1H), 4.10-4.04 (q, *J* = 7.2 Hz, 1H), 3.78-3.71 (dd, *J* = 17.2, *J* = 8.0 Hz, 1H), 3.65-3.51 (m, 2H), 3.45-3.39 (m, 1H), 2.97-2.87 (m, 2H), 2.22 (s, 3H), 1.28-1.24 (q, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.3, 150.1, 142.4, 138.6, 136.7, 135.7, 135.7, 129.2, 128.8, 128.6, 128.5, 128.5, 126.6, 125.1, 120.7, 114.3, 63.7, 48.9, 45.8, 42.7, 42.2, 26.6, 23.5, 23.4, 21.0. IR (KBr): *v*(cm^{-1}) 3402, 2918, 2849, 1684, 1654, 1560, 1507, 1473, 1458, 1395, 1387. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_3O$ $[M+H]^+$: 464.2696, found: 464.2691.



3c

According to the general procedure, **3c** was obtained as yellowish oil; 87% yield, 91% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r1 (major) = 32.32 min, t_r1 (minor) = 30.37 min; t_r2 (major) = 20.87 min, t_r2 (minor) = 17.57 min); $[\alpha]_D^{25}$ = -53.6 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.14-7.00 (m, 11H), 6.88-6.87 (d, *J* = 6.0 Hz, 1H), 6.70-6.68 (d, *J* = 8.4 Hz, 2H), 6.60-6.57 (t, *J* = 7.2 Hz, 1H), 5.25-5.18 (m, 1H), 5.02-5.00 (d, *J* = 7.2 Hz, 1H), 4.09-4.03 (q, *J* = 7.2 Hz,1H), 3.75-3.54 (m, 3H), 3.44-3.39 (m, 1H), 2.98-2.95 (t, *J* = 6.4 Hz, 2H), 2.19 (s, 3H), 1.29-1.23 (q, *J* =6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.2, 149.9, 142.4, 141.6, 137.3, 136.7, 135.6, 129.4, 129.2, 128.7, 128.6, 128.4, 127.7, 127.0, 126.7, 125.7, 125.1, 120.7, 117.0, 114.1, 63.7, 48.9, 46.0, 42.7, 42.1, 26.7, 23.4, 23.4, 21.3. IR (KBr): *ν*(cm^{-1}) 3419, 2918, 2850, 1684, 1676, 1654, 1500, 1490, 1458, 1405, 1395, 1387. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_3O$ $[M+H]^+$: 464.2696, found: 464.2694.



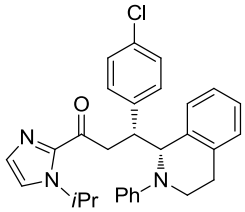
3d

According to the general procedure, **3d** was obtained as yellowish oil; 78% yield, 92% ee (HPLC: chiralpak AD-H column, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, t_r1 (major) = 19.70 min, t_r1(minor) = 12.39 min; t_r2 (major) = 11.46 min, t_r2 (minor) = 17.69 min); $[\alpha]_D^{25}$ = -23.1 (c =1.0, $CHCl_3$) (major), $[\alpha]_D^{25}$ = +14.1 (c = 0.5, $CHCl_3$) (minor).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.17-7.01 (m, 9H), 6.84 (d, *J* = 8.3 Hz, 1H),

6.70 (d, *J* = 8.4 Hz, 3H), 6.64-6.58 (m, 2H), 5.26-5.20 (m, 1H), 5.02 (d, *J* = 7.3 Hz, 1H), 4.11-4.06 (m, 1H), 3.78 (dd, *J* = 17.0 Hz, *J* = 8.1 Hz, 1H), 3.61-3.51 (m, 5H), 3.44-3.38 (m, 1H), 2.95 (t, *J* = 6.4 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.25 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =191.2, 159.1, 150.0, 143.3, 142.5, 136.7, 135.7, 129.3, 128.9, 128.6, 126.8, 125.2, 121.2, 120.8, 117.2, 114.3, 114.1, 112.4, 63.6, 55.1, 49.0, 46.4, 42.8, 42.0. 26.7, 23.5, 23.4. IR (KBr): *v*(cm^{-1}) 3419, 2963, 2919, 1672, 1654, 1597, 1502, 1490, 1454, 1436, 1395, 1260, 1088, 1037, 802, 748, 694. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_3O_2[M+H]^+$: 480.2646, found: 480.2645.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.21-7.15 (m, 3H), 7.10-7.06 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.89-6.87 (m, 3H), 6.73-6.69 (m, 2H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.46-6.41 (m, 2H), 5.43-5.35 (m, 1H), 4.87 (d, *J* = 8.1 Hz, 1H), 4.02-3.90 (m, 2H), 3.70-3.63 (m, 4H), 3.54-3.48 (m, 1H), 2.81-3.74 (m, 1H), 2.42-2.35 (m, 1H), 1.36-1.31 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.1, 159.2, 149.4, 143.1, 142.5, 135.7, 135.6, 129.3, 129.1, 128.9, 128.5, 127.9, 126.7, 125.0, 121.9, 120.7, 117.4, 114.5, 114.0, 112.8, 63.8, 55.2, 49.0, 48.0, 43.2, 42.8, 26.6, 23.6. IR (KBr): *v*(cm^{-1}) 2923, 2852, 1671, 1654, 1596, 1501, 1490, 1465, 1458, 1395, 1255, 748, 693. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_3O_2[M+H]^+$: 480.2646, found: 480.2647.

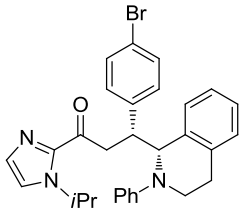


3e

According to the general procedure, **3e** was obtained as yellowish oil; 89% yield, 93% ee (HPLC: chiralpak IA column, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, t_r1 (major) = 14.76 min, t_r1 (minor) = 12.10 min; t_r2 (major) = 10.56 min, t_r2 (minor) = 13.18 min); $[\alpha]_D^{25}$ = -77.0 (c = 1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.19-7.03 (m,12H), 6.71-6.69 (d, *J* = 8.0 Hz, 2H), 6.65-6.61 (t, *J* = 7.2 Hz, 1H), 5.26-5.19 (m, 1H), 4.99-4.97 (d, *J* = 7.6Hz, 1H),

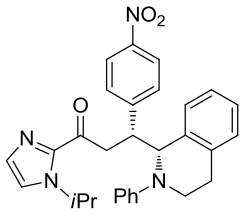
4.09-4.03 (q, *J* = 7.2 Hz, 1H), 3.80-3.74 (dd, *J* = 16.8, *J* = 8.4 Hz, 1H), 3.60-3.39 (m, 3H), 2.99-2.85 (m, 2H), 1.29-1.25 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.9, 150.0, 142.4, 140.3, 136.4, 135.6, 132.1, 130.0, 129.4, 128.9, 128.7, 128.5, 128.0, 126.9, 125.3, 120.9, 117.6, 114.6, 63.4, 49.0, 45.9, 42.9, 42.1, 26.5, 23.4, 23.4. IR (KBr): *v*(cm^{-1}) 2923, 2851, 1672, 1654, 1596, 1490, 1458, 1394, 1363, 1255, 752, 689. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}ClN_3O[M+H]^+$: 484.2150, found: 484.2144.



3f

According to the general procedure, **3f** was obtained as yellowish oil; 91% yield, 94% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, t_r1 (major) = 14.13 min, t_r1 (minor) = 27.04 min; t_r2 (major) = 15.83 min, t_r2 (minor) = 10.83 min); $[\alpha]_D^{25}$= -72.6 (c = 0.5, $CHCl_3$) (major).

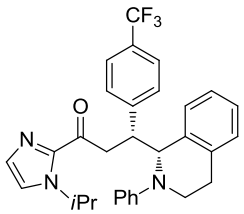
^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.26-7.24 (t, *J* = 3.4 Hz, 2H), 7.19-7.03 (m, 10H), 6.71-6.69 (d, *J* = 8.0 Hz, 2H), 6.65-6.61 (t, *J* = 7.6 Hz, 1H), 5.26-5.19 (m, 1H), 4.99-4.97 (d, *J* = 7.2Hz, 1H), 4.07-4.02 (q, *J* = 7.2 Hz, 1H), 3.81-3.74 (dd, *J* = 16.8, *J*= 8.4 Hz, 1H), 3.59-3.39 (m, 3H), 2.99-2.86 (m, 2H), 1.29-1.25 (dd, *J* = 8.4, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.9, 150.0, 142.3, 140.8, 136.3, 135.6, 130.9, 130.4, 129.4, 128.9, 128.7, 128.5, 126.9, 125.3, 121.0, 120.2, 117.6, 114.6, 63.3, 49.0, 45.9, 42.9, 42.0, 26.5, 23.4, 23.3. IR (KBr): *v*(cm^{-1}) 2923, 1673, 1596, 1502, 1488, 1393, 747. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}BrN_3O[M+H]^+$: 528.1645, found: 528.1637.



3g

According to the general procedure, **3g** was obtained as brown oil; 66% yield, 99.1% ee (HPLC: chiralpak AD-H column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 17.44 min, t_r1(minor) = 14.50 min; t_r2 (major) = 12.21 min, t_r2 (minor) = 19.03 min); $[\alpha]_D^{25}$ = -61.6 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 8.01-7.99 (d, *J* = 8.8 Hz, 2H), 7.43-7.40 (d, *J* = 8.4 Hz, 2H), 7.26-7.04 (m, 8H), 6.68-6.61 (m, 3H), 5.25-5.18 (m, 1H), 5.04-5.02 (d, *J* = 8.0 Hz, 1H), 4.20-4.14 (m, 1H), 3.92-3.85 (q, *J* = 8.8 Hz, 1H), 3.63-3.52 (m, 2H), 3.47-3.41 (m, 1H), 3.01-2.92 (m, 2H), 1.30-1.28 (d, *J*= 6.8 Hz, 3H), 1.27-1.25 (d, *J*= 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.2, 150.0, 149.7, 146.5, 142.1, 135.9, 135.5, 129.5, 129.4, 128.9, 128.9, 128.4, 127.2, 125.5, 123.0, 121.3, 118.0, 114.7, 63.1, 49.1, 46.4, 43.0, 42.0, 26.4, 23.4, 23.3. IR (KBr): *v*(cm^{-1}) 2923, 2852, 1675, 1596, 1517, 1507, 1395, 1344, 1255, 750, 693. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}N4O_3$ $[M+H]^+$: 495.2391, found: 495.2390.

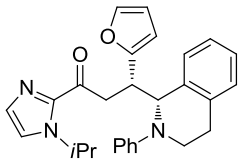


3h

According to the general procedure, **3h** was obtained as yellowish oil; 70% yield, 91% ee (HPLC: chiralpak IA column, 254 nm, hexane/isopropanol = 92:8, flow rate 1.0 mL/min, t_r1 (major) = 9.57 min, t_r1 (minor) = 7.81 min; t_r2 (major) = 6.94 min, t_r2 (minor) = 8.31 min); $[\alpha]_D^{25}$ = -50.4 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.42-7.33 (m, 4H), 7.20-7.02 (m, 8H), 6.68-6.60 (m, 3H), 5.24-5.27 (m, 1H), 5.02-5.01 (d, *J* = 7.6 Hz, 1H), 4.17-4.11 (m, 1H), 3.86-3.79 (dd, *J* = 8.4 Hz, *J* = 17.2 Hz, 1H), 3.62-3.61 (d, *J* = 6.4 Hz, 1H), 3.58-3.51 (m, 1H), 3.47-3.40 (m, 1H), 3.02-2.89 (m, 2H), 1.28-1.27 (d, *J* = 6.8 Hz, 3H), 1.25-1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.6, 149.9, 146.0, 142.2, 136.2, 135.6, 129.4, 128.9, 128.9, 128.8, 128.5, 128.4, 127.0, 125.3, 124.8, 124.7, 122.8, 121.0, 117.7,

114.6, 63.4, 49.0, 46.2, 42.8, 42.0, 26.5, 23.4, 23.3. IR (KBr): ν(cm^{-1}) 2923, 1676, 1655, 1508, 1396, 1324.1121. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{30}F_3N_3O[M+H]^+$: 518.2414, found: 518.2410.



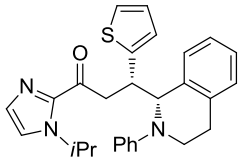
3i

According to the general procedure, **3i** was obtained as yellowish oil; 80% yield, 94% ee (HPLC: chiralpak ID column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 9.99 min, t_r1(minor) = 11.46 min; t_r2 (major) = 12.75 min, t_r2 (minor) = 9.37 min); $[\alpha]_D^{25}$ = -4.5 (c = 1.0, $CHCl_3$) (major), $[\alpha]_D^{25}$ = +71.0 (c =1.0, $CHCl_3$) (minor).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.60 (m,1H), 7.19-7.13 (m, 6H), 7.10-7.02 (m, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.13-6.12 (m, 1H), 5.87 (d, *J* = 3.2 Hz, 1H), 5.36-5.26 (m, 1H), 5.11 (d, *J* = 6.8 Hz, 1H), 4.18-4.13 (m, 1H), 3.74 (dd, *J* = 17.2 Hz, *J* = 9.0 Hz, 1H), 3.58-3.52 (m, 1H), 3.50-3.36 (m, 2H), 3.12-3.05 (m, 1H), 3.01-2.94 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8, 155.1, 149.6, 142.3, 140.9, 136.1, 135.7, 129.4, 129.0, 128.3, 128.1, 126.9, 125.5, 121.0, 117.2, 113.8, 110.3, 107.1, 62.0, 49.1, 43.2, 40.2, 39.5, 27.5, 23.5. IR (KBr): ν(cm^{-1}) 2923, 2852, 1677, 1597, 1508, 1406, 1385, 747, 693. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{30}N_3O_2[M+H]^+$: 440.2333, found: 440.2329.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.36 (d, *J* = 1.0 Hz, 1H), 7.18-7.14 (m, 3H), 7.09-7.03 (m, 3H), 6.01-6.87 (m, 3H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.21 (dd, *J* = 3.0 Hz, *J* = 1.84 Hz, 1H),5.84 (d, *J* = 3.0 Hz, 1H), 5.47-5.37 (m, 1H), 4.99 (d, *J* = 9.5 Hz, 1H), 4.11-4.05 (m, 1H), 3.88 (dd, *J* = 15.8 Hz, *J* = 6.1 Hz, 1H), 3.73-3.67 (m, 1H), 3.55-3.45 (m, 2H), 2.98-2.90 (m, 1H), 2.67-2.60 (m, 1H), 1.36 (d, *J* = 6.7 Hz, 3H), 1.35 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.6, 149.4, 142.3, 141.1, 136.1, 135.0, 129.4, 129.1, 128.3, 127.8, 126.7, 125.1, 120.7, 117.8, 114.6, 110.3, 107.9, 61.8, 49.0, 42.3, 42.0, 41.9, 26.0, 23.6, 23.6. IR (KBr): ν(cm^{-1}) 2923, 2852, 1674,

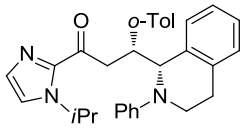
1597, 1504, 1455, 1394, 1255, 748, 692. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{30}N_3O_2[M+H]^+$: 440.2333, found: 440.2332.



3j

According to the general procedure, **3j** was obtained as brown oil; 80% yield, 92% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 12.54 min, t_r2 (minor) = 7.81 min; t_r2 (major) = 9.34 min, t_r2 (minor) = 7.09 min); $[\alpha]_D^{25}$ = -22.6 (c =0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.18-7.02 (m, 9H), 6.79-6.74 (m, 4H), 6.66-6.62 (t, *J* = 7.2 Hz, 1H), 5.33-5.26 (m, 1H), 5.01-4.99 (d, *J* = 7.2 Hz, 1H), 4.37-4.31 (q, *J* = 6.8 Hz, 1H), 3.87-3.81 (dd, *J* = 17.2, *J* = 8.0 Hz, 1H), 3.68-3.62 (dd, *J* = 17.2, *J* = 6.4 Hz, 1H), 3.52-3.42 (m, 2H), 2.95-2.91 (m, 2H), 1.32-1.29 (dd, *J* = 6.8, *J* = 2.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =190.7, 150.1, 145.0, 142.3, 136.3, 135.9, 129.4, 128.9, 128.5, 128.4, 126.9, 126.2, 125.5, 124.9, 123.8, 120.9, 117.5, 114.5, 63.7, 49.0, 43.3, 42.6, 41.9, 26.8, 23.4. IR (KBr): *ν*(cm^{-1}) 2923, 1286, 1596, 1502, 1459, 1396, 1254, 751, 692. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{30}N_3OS[M+H]^+$: 456.2104, found: 456.2103.

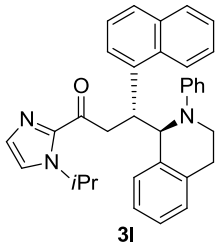


3k

According to the general procedure, **3k** was obtained as white solid; m.p. = 91-93 ^{o}C, 81% yield, 93% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, t_r1 (major) = 11.35 min, t_r1(minor) = 14.63 min; t_r2 (major) = 10.29 min, t_r2 (minor) = 8.13 min); $[\alpha]_D^{25}$ = -58.4 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.46-7.44 (d, *J* = 8.0 Hz, 1H), 7.24-7.22 (d, *J*

= 7.2 Hz, 1H), 7.11-7.06 (m, 5H), 7.01-6.92 (m, 5H), 6.60-6.54 (m, 3H), 5.12-5.05 (m, 2H), 4.45-4.39 (q, *J* = 7.6 Hz, 1H), 3.70-3.61 (m, 2H), 3.50-3.38 (m, 2H), 3.03-2.92 (m, 2H), 2.21 (s, 3H), 1.23-1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.0, 149.7, 142.4, 141.0, 137.1, 136.9, 135.8, 130.1, 129.2, 128.8, 128.7, 128.1, 126.8, 126.1, 125.9, 125.3, 120.6, 117.0, 113.7, 64.2, 48.8, 44.1, 43.7, 26.9, 23.4, 23.3, 19.8. IR (KBr): *v*(cm^{-1}) 3445, 2923, 2851, 1673, 1650, 1596, 1503, 1454, 1393, 1255, 744. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_3O[M+H]^+$: 464.2696, found: 464.2696.



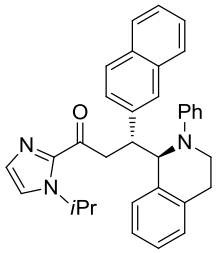
3l

According to the general procedure, **3l** was obtained as yellowish oil; 87% yield, 92% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 9.27 min, t_r1(minor) = 11.04 min; t_r2 (major) = 8.19 min, t_r2 (minor) = 7.06 min); $[\alpha]_D^{25}$ = -28.7 (c = 1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 8.13 (d, *J* = 7.8 Hz, 3H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60-7.58 (m, 2H), 7.39-7.30 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.11 (s, 1H), 7.08-7.07 (m, 3H), 6.98-6.93 (m, 3H), 6.60-6.53 (m, 3H), 5.18 (d, *J* = 7.8 Hz, 1H), 5.06-4.96 (m, 2H), 3.88 (dd, *J* = 16.4 Hz, *J* = 6.7 Hz, 1H), 3.65-3.59 (m, 2H), 3.35-3.29 (m, 1H), 3.13-3.06 (m, 1H), 2.99-2.92 (m, 1H), 1.13-1.12 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8, 149.7, 142.3, 139.0, 137.0, 135.6, 133.7, 132.5, 129.2, 128.8, 128.7, 128.6, 126.9, 125.5, 125.3, 125.1, 125.0, 123.4, 120.7, 117.4, 114.7, 63.9, 48.9, 44.1, 43.4, 26.8, 23.4, 23.3. IR (KBr): *v*(cm^{-1}) 2923, 2852, 1675, 1671, 1654, 1597, 1502, 1491, 1405, 1394, 1254, 748, 690. HRMS (ESI, *m*/*z*)calcd for $C_{34}H_{33}N_3O[M+H]^+$: 500.2696, found: 500.2693.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.71-7.66 (m,2H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.37-7.35 (m, 2H), 7.30-7.21 (m, 4H), 7.12-7.09 (m, 3H), 6.94-6.91 (m, 4H), 6.73 (t, *J*

= 7.2 Hz, 1H), 6.67-6.62 (m, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 5.29-5.23 (m, 1H), 5.12-5.05 (m, 2H), 4.11 (dd, *J* = 15.6 Hz, *J* = 5.7 Hz, 1H), 3.62 (dd, *J* = 15.5 Hz, *J* = 7.8 Hz, 1H), 3.47-3.41 (m, 2H), 3.31-3.25 (m, 1H), 2,71-2.64 (m, 1H), 2.25-2.18 (m, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.2, 149.4, 142.4, 138.3, 135.6, 135.4, 133.4, 133.2, 129.3, 129.2, 128.1, 127.9, 127.7, 127.1, 126.7, 125.5, 125.1, 125.0, 123.4, 120.7, 117.2, 113.5, 70.6, 64.5, 48.9, 43.7, 43.3, 40.5, 26.8, 26.5, 23.5, 23.4. IR (KBr): *v*(cm^{-1}) 2923, 2851, 1675, 1596, 1501, 1491, 1394, 1255, 776, 747, 690. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{33}N_3O[M+H]^+$: 500.2696, found: 500.2693.

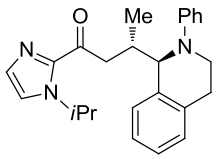


3m

According to the general procedure, **3m** was obtained as yellowish oil; 90% yield, 93% ee (HPLC: chiralpak IA column, 254 nm, hexane/isopropanol = 96:4, flow rate 1.0 mL/min, t_r1 (major) = 20.21 min, t_r1 (minor) = 16.78 min; t_r2 (major) = 14.96 min, t_r2 (minor) = 17.79 min); $[\alpha]_D^{25}$ = -44.5 (c = 1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.71-7.67 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.40-7.35 (m, 3H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.13-7.00 (m, 7H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 5.23-5.14 (m, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 1H), 3.90 (dd, *J* = 17.0 Hz, *J* = 8.2 Hz, 1H), 3.72 (dd, *J* = 17.0 Hz, *J* = 8.2 Hz, 1H), 3.60-3.52 (m, 1H), 3.25-3.39 (m, 1H), 2.99-2.83 (m, 2H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.2, 150.1, 142.5, 139.5, 136.7, 135.7, 133.3, 132.3, 129.3, 128.9, 128.7, 128.7, 127.8, 127.5, 127.5, 127.3, 127.2, 126.8, 125.6, 125.3, 125.2, 120.9, 117.4, 114.6, 63.5, 49.0, 46.5, 42.8, 42.4, 26.5, 23.5, 23.3. IR (KBr): *v*(cm^{-1}) 2920, 2851, 1654, 1508, 1490, 1458, 1395, 1260, 745, 689. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{33}N_3O[M+H]^+$: 500.2696, found: 500.2696.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.78-7.76 (m,1H), 7.68-7.64 (m, 2H), 7.43-7.40 (m, 3H), 7.24-7.17 (m, 3H), 7.13 (s, 1H), 7.07-7.98 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.78-6.71 (m, 2H), 6.33 (d, *J* = 7.6 Hz, 1H), 5.38-5.32 (m, 1H), 4.99 (d, *J* = 8.4 Hz, 1H), 4.21-4.15 (m, 1H), 4.04 (dd, *J* = 15.9 Hz, *J* = 6.4 Hz, 1H), 3.73-3.58 (m,2H), 3.41-3.33 (m, 1H), 2.78-2.72 (m, 1H), 2.39-2.32 (m, 1H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.0, 149.5, 142.5, 139.2, 135.7, 135.5, 133.2, 132.5, 129.3, 129.2, 128.5, 128.0, 128.0, 127.8, 127.7, 127.5, 127.5, 126.7, 125.7, 125.4, 125.0, 120.7, 117.5, 114.0, 63.8, 49.0, 48.1, 43.2, 43.1, 26.7, 23.6, 23.5. IR (KBr): *v*(cm^{-1}) 2923, 2852, 1672, 1596, 1501, 1452, 1394, 1255, 746, 689. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{33}N_3O[M+H]^+$: 500.2696, found: 500.2694.



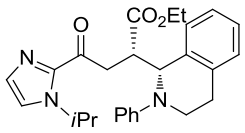
3n

According to the general procedure, **3n** was obtained as yellowish oil; 54% yield, 97 % ee (HPLC: chiralpak IE column, 254 nm, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, t_r1 (major) = 21.04 min, t_r1 (minor) = 18.18 min; t_r2 (major) = 19.36 min, t_r2 (minor) = 16.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ =7.26-7.02 (m, 8H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.69-6.62 (m, 1H), 5.39-5.33 (m, 1H), 4.68 (d, *J* = 8.8 Hz, 1H), 3.81-3.69 (m, 1H), 3.55-3.48 (m, 1H), 3.25 (d, *J* = 6.4 Hz, 2H), 3.15-2.92 (m, 2H), 2.86-2.74 (m, 1H), 1.40 (s, 1H), 1.38 (s, 1H), 1.09 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.2, 150.2, 142.7, 137.6, 135.6, 129.3, 129.1, 128.4, 128.1, 126.7, 125.4, 121.0, 116.8, 113.6, 62.6, 49.1, 43.7, 43.3, 35.9, 27.0, 23.7, 23.5, 18.0.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.26-7.02 (m, 8H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.69-6.62 (m, 1H), 5.50-5.43 (m, 1H), 4.49 (d, *J* = 9.3 Hz, 1H), 3.81-3.69 (m, 1H), 3.55-3.48 (m, 1H), 3.43-3.37(m, 1H), 3.15-2.92 (m, 3H), 2.86-2.74 (m, 1H), 1.36 (s, 3H), 1.34 (s, 3H), 1.04 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.3, 149.6, 142.7, 137.1, 135.4, 129.2, 128.9, 128.7, 128.5, 126.8, 125.2, 120.6, 117.2, 114.1, 63.6,

49.1, 43.5, 42.9, 36.7, 26.7, 23.8, 23.5, 18.4. IR (KBr): ν(cm^{-1}) 2965, 2931, 1677, 1596, 1503, 1458, 1393, 752, 691. HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{29}N_3O[M+H]^+$: 388.2383, found: 388.2382.

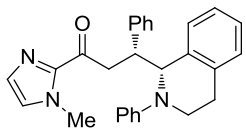


3o

According to the general procedure, **3o** was obtained as yellowish oil; 54% yield, 92 % ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 18.54 min, t_r1(minor) = 26.05 min; t_r2 (major) = 16.54 min, t_r2 (minor) = 27.58 min); $[\alpha]_D^{25}$ = -6.7 (c = 1.0, $CHCl_3$) (major), $[\alpha]_D^{25}$ = +51.1 (c = 1.0, $CHCl_3$) (minor).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.22-7.09 (m, 8H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.42-5.32 (m, 1H), 5.09 (d, *J* = 9.0 Hz, 1H), 4.03-3.78 (m, 4H), 3.54-3.44 (m, 2H), 3.35 (dd, *J* = 18.0 Hz, *J* = 3.9 Hz, 1H), 3.24-3.16 (m, 1H), 3.08-3.01 (m, 1H), 1.37 (d, *J* = 6.6 Hz, 3H),1.32 (d, *J* = 6.6 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.3, 173.4, 148.9, 141.9, 136.0, 135.4, 129.6, 129.1, 128.7, 127.8, 127.4, 125.8, 121.0, 117.6, 113.9, 60.7, 60.2, 49.1, 46.8, 43.1, 40.2, 39.6, 27.1, 26.9, 23.6, 23.5, 14.0. IR (KBr): ν(cm^{-1})2978, 2930, 1734, 1675, 1597, 1502, 1458, 1395, 1256, 748, 692. HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_3O_3[M+Na]^+$: 468.2258, found: 468.2255.

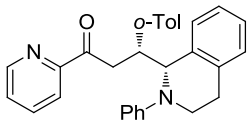
^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.19-7.08 (m, 8H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 5.49-5.39 (m, 1H), 5.15 (d, *J* = 8.5 Hz, 1H), 4.07-3.92 (m, 2H), 3.73-3.55 (m, 5H), 3.03-2.95 (m, 1H), 2.89-2.82 (m, 1H), 1.38 (d, *J* = 6.7 Hz, 6H) 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.5, 173.8, 149.6, 141.9, 136.1, 135.1, 129.5, 129.0, 128.8, 127.2, 127.1, 125.7, 120.8, 118.4, 115.5, 60.5, 59.5, 49.0, 48.6, 43.0, 40.2, 26.0, 23.6, 23.5, 13.9. IR (KBr): ν(cm^{-1}) 2924, 2852, 1731, 1673, 1597, 1503, 1396, 748, 693. HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_3O_3[M+Na]^+$: 468.2258, found: 468.2253.



3p

According to the general procedure, **3p** was obtained as yellowish oil; 91% yield, 91% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 95:15, flow rate 1.0 mL/min, t_r1 (major) = 20.78 min, t_r1 (minor) = 11.90 min; t_r2 (major) = 15.79 min, t_r2 (minor) = 8.25 min); $[\alpha]_D^{25}$ = -72.0 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.25-7.23 (m, 2H), 7.16-6.97 (m, 10H), 6.90 (s, 1H), 6.68-6.66 (d, *J* = 8.4 Hz, 2H), 6.61-6.58 (t, *J* = 7.2 Hz, 1H), 5.00-4.98 (d, *J* = 7.6 Hz, 1H), 4.13-4.07 (q, *J* = 7.56 Hz, 1H), 3.77-3.68 (m, 1H), 3.71 (s, 3H), 3.63-3.55 (m, 2H), 3.44-3.37 (m, 1H), 2.98-2.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.9, 149.9, 143.1, 141.7, 136.6, 135.7, 128.8, 128.6, 128.5, 128.4, 127.9, 126.8, 126.6, 126.4, 125.1, 117.2, 114.2, 63.7, 46.0, 42.9, 41.5, 35.9, 26.7. IR (KBr): *v*(cm^{-1}) 2919, 2850, 1676, 1654, 1596, 1507, 1490, 1473, 1458, 1405, 1387, 1374, 751, 698. HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_3O_3[M+H]^+$: 422.2224, found: 422.2227.



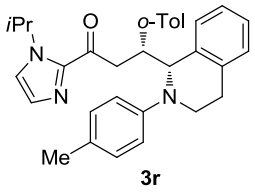
3q,

According to the general procedure, **3q** was obtained as yellowish oil; 73% yield, 92% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 96:4, flow rate 1.0 mL/min, t_r1 (major) = 14.12 min, t_r1(minor) = 20.01 min; t_r2 (major) = 13.12 min, t_r2 (minor) = 8.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 8.62 (d, *J* = 4.5 Hz, 1H), 7.73-7.67 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.39-7.36 (m, 1H), 7.30-7.21 (m, 1H), 7.12-6.94 (m, 7H), 6.76-6.72 (m, 1H), 6.66-6.61 (m, 2H), 6.56 (t, *J* = 7.2 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H), 4.48-4.42 (m, 1H), 3.78 (dd, *J* = 7.5 Hz, *J* = 17.5 Hz, 1H), 3.61-3.55 (m, 2H), 3.39-3.33 (m, 1H), 2.92-2.89 (m, 2H), 2.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 200.2, 153.3,

149.8, 148.7, 141.2, 137.3, 137.0, 136.6, 135.8, 130.2, 128.8, 128.2, 127.9, 126.9, 126.9, 126.2, 125.9, 125.5, 121.7, 117.0, 113.8, 63.9, 43.9, 43.0, 42.2, 26.8, 19.9.

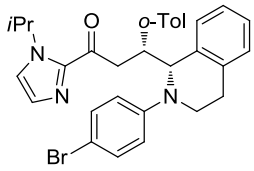
^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 8.43 (d, *J* = 4.3 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.73-7.67 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.30-7.21 (m, 1H), 7.12-6.94 (m, 8H), 6.76-6.72 (m, 1H), 6.66-6.61 (m, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 9.4 Hz, 1H), 4.40-4.29 (m, 2H), 3.61-3.55 (m, 1H), 3.32-3.25 (m, 1H), 3.22-3.17 (m, 1H), 2.86-2.72 (m, 2H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 199.0, 153.4, 149.3, 148.7, 140.9, 138.0, 136.5, 135.4, 130.0, 128.9, 128.1, 127.9, 127.4, 126.7, 126.3, 126.1, 125.0, 121.5, 117.6, 114.2, 64.3, 43.5, 42.2, 40.7, 26.4, 19.3. HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_3O_3[M+H]^+$: 455.2094, found: 455.2097.



3r

According to the general procedure, **3r** was obtained as white solid; 74% yield, 96% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 96:4, flow rate 1.0 mL/min, t_r1 (major) = 14.12 min, t_r1 (minor) = 20.01 min; t_r2 (major) = 13.12 min, t_r2 (minor) = 8.81 min); $[\alpha]_D^{25}$ = -46.4 (c =1.0, $CHCl_3$) (major).

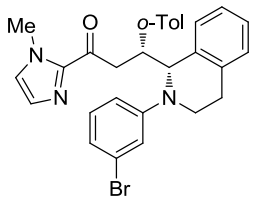
^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.43 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.52 Hz, 1H), 7.11-7.05 (m, 5H), 7.01-6.94 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.6 Hz, 2H), 5.15-5.05 (m, 1H), 4.96 (d, *J* = 7.8 Hz, 1H), 4.43-4.37 (m, 1H), 3.68-3.61 (m, 2H), 3.47 (dd, *J* = 16.7 Hz, *J* = 7.4 Hz, 1H), 3.41-3.34 (m, 1H), 2.99-2.87 (m, 2H), 2.21 (s, 3H), 2.13 (s, 3H), 1.22 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.1, 147.9, 142.4, 141.2, 137.1, 137.0, 135.9, 130.1, 129.3, 129.2, 128.9, 128.3, 126.7, 126.5, 126.0, 125.9, 125.2, 120.6, 114.5, 64.7, 48.9, 44.1, 44.0, 26.7, 23.5, 23.4, 20.2, 19.9. IR (KBr): *v*(cm^{-1}) 2963, 2919, 1670, 1517, 1457, 1395, 1256, 757. HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{35}N_3O[M+H]^+$: 478.2853, found: 478.2855.



3s

According to the general procedure, **3s** was obtained as white solid; m.p. = 75-77 ^{o}C, 86% yield, 94% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, t_r1 (major) = 14.13 min, t_r1 (minor) = 27.04 min; t_r2 (major) = 15.88 min, t_r2 (minor) = 10.83 min; $[\alpha]_D^{25}$ = -67.2 (c =1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.46 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.13-7.06 (m, 5H), 7.04-6.95 (m, 4H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.40-6.36 (m, 2H), 5.12-5.02 (m, 1H), 4.96 (d, *J* = 8.5 Hz, 1H), 4.42-4.36 (m, 1H), 3.70-3.64 (m, 1H), 3.59 (dd, *J* = 16.6 Hz, *J* = 7.5 Hz, 1H), 3.44 (dd, *J* = 16.6 Hz, *J* = 7.3 Hz, 1H), 3.33-3.27 (m, 1H), 3.17-3.10 (m, 1H), 2.98-2.91 (m, 1H), 2.21 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8, 148.4, 142.3, 140.9, 136.9, 136.8, 135.6, 131.2, 130.3, 129.3, 128.8, 127.1, 126.3, 126.1, 125.5, 120.7, 114.8, 108.6, 64.5, 48.9, 44.0, 26.9, 23.4, 23.4, 19.8. IR (KBr): *v*(cm^{-1}) 2964, 2924, 1671, 1587, 1491, 1463, 1393, 1256, 759, 725.HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{32}BrN_3O[M+H]^+$: 542.1802, found: 542.1803.

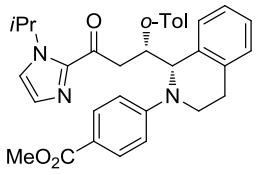


3t

According to the general procedure, **3t** was obtained as yellowish solid, m.p. = 79-81 ^{o}C, 93% yield, 93% ee (HPLC: chiralpak AD-H column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 7.69 min, t_r1 (minor) = 6.20 min; t_r2 (major) = 5.23 min, t_r2 (minor) = 9.30 min); $[\alpha]_D^{25}$ = -42.9 (c = 0.5, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.49-7.47 (d, *J* = 7.6 Hz, 1H), 7.25-7.25 (d, *J* = 2.0 Hz, 1H), 7.16-7.07 (m, 5H), 7.01-7.00 (t, *J* = 7.2 Hz, 2H), 6.93-6.92 (d, *J* = 7.2

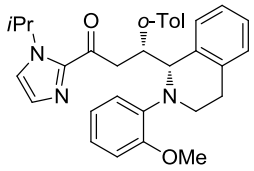
Hz, 1H), 6.81-6.77 (m, 1H), 6.63-6.63 (m, 2H), 6.42-6.39 (m, 1H), 5.12-5.06 (m, 1H), 5.01-4.99 (d, *J* = 8.4 Hz, 1H), 4.43-4.37 (q, *J* = 8.0 Hz, 1H), 3.69-3.57 (m, 2H), 3.48-3.42 (dd, *J* = 7.2 Hz, *J* = 16.4 Hz, 1H), 3.32-3.26 (m, 1H), 3.19-3.11 (m, 1H), 2.20 (s, 3H), 1.23-1.21 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.7, 150.4, 142.1, 140.6, 136.8, 136.8, 135.5, 130.2, 129.7, 129.2, 128.7, 127.9, 127.1, 126.3, 126.1, 125.5, 122.9, 120.7, 119.2, 115.6, 111.2, 64.3, 48.8, 44.1, 43.9, 27.0, 23.4, 23.3, 19.7. IR (KBr): *v*(cm^{-1}) 2919, 2850, 1684, 1676, 1587, 1550, 1507, 1458, 1405. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{32}BrN_3O[M+H]^+$: 542.1802, found: 542.1792.



3u

According to the general procedure, **3u** was obtained as yellowish oil; 78% yield, 90% ee (HPLC: chiralpak AD-H column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 24.36 min, t_r1 (minor) = 31.01 min; t_r2 (major) = 18.37 min, t_r2 (minor) = 19.17 min; $[\alpha]_D^{25}$ = -52.0 (c = 0.5, $CHCl_3$) (major).

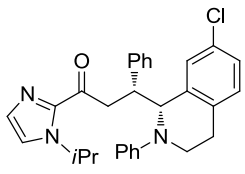
^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.63-7.60 (d, *J* = 9.2 Hz, 2H), 7.51-7.49 (d, *J* = 7.2 Hz, 1H), 7.28-7.27 (d, *J* = 7.2 Hz, 1H), 7.14-7.08 (m, 5H), 7.03-6.94 (m, 2H), 6.88-6.86 (d, *J* = 7.2 Hz, 1H), 6.45-6.43 (d, *J* = 9.2 Hz, 2H), 5.18-5.15 (d, *J* = 8.8 Hz, 1H), 5.09-5.03 (m, 1H), 4.46-4.41 (q, *J* = 7.6 Hz, 1H), 3.85-3.75 (m, 1H), 3.78 (s, 3H), 3.61-3.55 (dd, *J* = 7.2 Hz, *J* = 16.8 Hz, 1H), 3.49-3.27 (m, 3H), 3.02-2.96 (m, 1H), 2.18 (s, 3H), 1.21-1.19 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.4, 167.2, 152.1, 142.1, 140.3, 136.8, 136.7, 135.3, 130.6, 130.2, 129.2, 128.6, 127.8, 127.3, 126.4, 126.1, 125.6, 120.7, 117.0, 110.9, 63.8, 51.3, 48.8, 44.1, 43.9, 27.2, 23.3, 23.2, 19.5. IR (KBr): *v*(cm^{-1}) 2919, 2850, 1701, 1672, 1603, 1517, 1434, 1394, 1283, 1186, 767. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{35}N_3O_3[M+Na]^+$: 544.2571, found: 544.2573.



3v

According to the general procedure, **3v** was obtained as yellowish oil; 82% yield, 97% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, t_r1 (major) = 7.46 min, t_r1 (minor) = 13.00 min; t_r2 (major) = 8.51 min, t_r2 (minor) = 23.33 min); $[\alpha]_D^{25}$ = +44.7 (c = 1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.49-7.47 (d, *J* = 7.2 Hz, 2H), 7.19-7.07 (m, 3H), 7.04-6.94 (m, 3H), 6.90-6.80 (m, 3H), 6.70-6.61 (m, 3H), 5.80-5.78 (d, *J* = 7.6 Hz, 1H), 5.32-5.25 (m, 1H), 4.39-4.37 (d, *J* = 10.8 Hz, 1H), 4.31-4.24 (m, 1H), 4.20-4.15 (dd, *J* = 4.8 Hz, *J* = 16.4 Hz, 1H), 3.92-3.85 (m, 1H), 3.76 (s, 3H), 3.73-3.61 (m, 2H), 2.88-2.79 (m, 1H), 2.71-2.66 (dd, *J* = 4.0 Hz, *J* = 16.8 Hz, 1H), 1.27-1.24 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.9, 152.7, 142.8, 140.8, 138.4, 136.7, 134.9, 129.6, 129.0, 128.5, 127.8, 126.0, 126.0, 125.9, 124.4, 122.1, 121.1, 120.7, 120.2, 111.6, 65.6, 55.5, 48.8, 44.4, 41.8, 41.6, 25.6, 23.5, 23.3, 19.1. IR (KBr): *ν*(cm^{-1}) 2923, 2852, 1672, 1497, 1458, 1405, 1387, 1238, 1027, 744. HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{35}N_3O_2[M+Na]^+$: 494.2802, found: 494.2802.



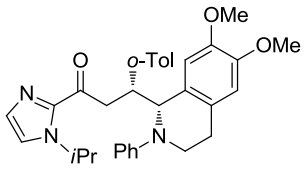
3w

According to the general procedure, **3w** was obtained as yellowish oil; 96% yield, 99% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r1 (major) = 14.20 min, t_r1 (minor) = 18.45 min; t_r2 (major) = 16.64 min, t_r2 (minor) = 12.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.42 (d, *J* = 7.8 Hz, 1H), 7.25-7.22 (m, 2H), 7.18-7.09 (m, 3H), 7.04-6.95 (m, 5H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.60 (t, *J* = 7.2 Hz, 1H),

6.62-6.58 (m, 2H), 5.17-5.07 (m, 1H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.45-4.40 (m, 1H), 3.82 (dd, *J* = 8.2 Hz, *J* = 16.8 Hz, 1H), 3.67-3.61 (m, 1H), 3.51-3.31 (m, 2H), 2.98-2.84 (m, 2H), 2.22 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =190.7, 149.6, 142.2, 140.7, 139.0, 136.6, 134.3, 131.1, 129.6, 129.5, 129.1, 128.8, 128.1, 126.8, 126.3, 126.0, 120.9, 117.6, 114.2, 64.2, 49.0, 43.4, 42.1, 26.1, 23.5, 23.3, 19.9.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.47 (d, *J* = 7.7 Hz, 1H), 7.25-7.22 (m, 1H), 7.18-7.09 (m, 4H), 7.04-6.95 (m, 5H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 5.41-5.33 (m, 5.41-5.33), 4.67 (d, *J* = 9.9 Hz, 1H), 4.36-4.30 (m, 1H), 4.02 (dd, *J* = 6.4 Hz, *J* = 15.9 Hz, 1H), 3.81-3.75 (m, 1H), 3.59-3.53 (m, 1H), 3.51-3.31 (m, 1H), 2.98-2.84 (m, 1H), 2.68-2.60 (m, 1H), 1.65 (s, 3H), 1.31-1.29 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.2, 149.5, 142.5, 139.9, 138.0, 137.5, 133.6, 130.2, 130.0, 129.4, 129.3, 128.5, 127.4, 126.7, 126.6, 126.4, 120.6, 118.4, 115.2, 63.8, 49.0, 43.9, 42.4, 25.4, 23.6, 23.5, 19.2. IR (KBr): *v*(cm^{-1}) 2965, 2928, 1671, 1596, 1502, 1464, 1394, 1255, 746, 691. HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{35}N_3O_2$ $[M+H]^+$: 498.2307, found: 498.2307.



3x

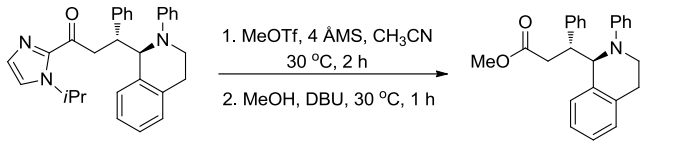
According to the general procedure, **3x** was obtained as white solid; m.p. = 63-65 °C. 78% yield, 94% ee (HPLC: chiralpak IA column, 254 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, t_r1 (major) = 10.10 min, t_r1(minor) = 7.38 min; t_r2 (major) = 8.35 min, t_r2 (minor) = 9.36 min); $[\alpha]_D^{25}$ = +62.9 (c = 1.0, $CHCl_3$) (major), $[\alpha]_D^{25}$ = -38.0 (c = 1.0, $CHCl_3$) (minor).

^{1}H NMR (400 MHz, $CDCl_3$) (major): δ = 7.58-7.56 (d, *J* = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 7.15-7.11 (t, *J* = 7.2 Hz, 3H), 7.08-7.05 (t, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.94-6.92 (d, *J* = 7.6 Hz, 1H), 6.85-6.83 (d, *J* = 8.4 Hz, 2H), 6.71-6.68 (t, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 5.44 (s, 1H), 5.40-5.33 (m, 1H), 4.64-4.61 (d, *J* = 11.2 Hz, 1H), 4.39-4.33 (dd, *J* = 16.8 Hz, *J* = 7.2 Hz, 1H), 4.11-4.05 (dd, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 3.85-3.79 (m,

1H), 3.77 (s, 3H), 3.63-3.59 (m, 1H), 3.44-3.38 (q, *J* = 7.6 Hz, 1H), 3.23 (s, 3H), 2.93-2.85 (m, 1H), 2.63-2.59 (d, *J* = 16.0 Hz, 1H), 1.67 (s, 3H), 1.31-1.29 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.0, 149.7, 147.2, 145.4, 142.2, 140.8, 138.3, 129.9, 129.0, 128.9, 127.5, 127.5, 126.5, 126.2, 126.1, 120.4, 118.2, 115.6, 110.8, 110.6, 63.9, 55.5, 54.9, 48.8, 43.7, 42.2, 42.0, 25.1, 23.4, 23.4, 19.4. IR (KBr): *v*(cm^{-1}) 2933, 2833, 1670, 1596, 1502, 1463, 1393, 1250, 1210, 749. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{37}N_3O_3[M+H]^+$: 524.2908, found: 524.2908.

^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ = 7.41-7.19 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.14-7.00 (m, 5H), 5.11-5.04 (m, 1H), 4.92-4.90 (d, *J* = 8.0 Hz, 1H), 4.52-4.46 (m, 1H), 3.99-3.93 (dd, *J*= 8.4 Hz, *J*= 16.8 Hz, 1H), 3.80 (s, 3H), 3.71-3.62 (m, 1H), 3.66 (s, 3H), 3.44-3.37 (m, 1H), 3.32-3.27 (dd, *J* = 6.0 Hz, *J*= 16.8 Hz, 1H), 3.04-2.97 (m, 1H), 2.92-2.85 (m, 1H), 2.29 (s, 3H), 1.26-1.23 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.4, 149.7, 147.5, 146.2, 142.2, 141.3, 136.6, 130.1, 129.1, 128.7, 128.7, 128.1, 127.7, 126.0, 125.9, 120.8, 117.2, 114.1, 111.8, 111.0, 64.0, 55.7, 55.6, 48.9, 43.8, 43.6, 26.4, 23.5, 23.1, 19.9. IR (KBr): *v*(cm^{-1}) 2919, 2850, 1676, 1596, 1507, 1465, 1395, 1254, 747. HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{37}N_3O_3[M+H]^+$: 524.2908, found: 524.2908.

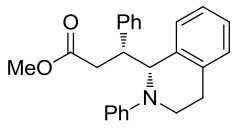
6. General procedure for Synthetic Transformation:



3a, 97% ee　　**4**, 60% yield, 97% ee

To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **3a** (90.0 mg, 0.2 mmol, 1.0 equiv.) was added along with 4Å molecular sieves (100 mg) and acetonitrile (1.5 mL). The suspension was stirred vigorously at 30 °C for 2 hours. Then methyl trifluoromethanesulfonate (49.2 mg, 0.3 mmol, 34 µL, 1.5 equiv.) was added. The mixture was stirred for 1 hour. An additional 10 µL of methyl trifluoromethanesulfonate was added to Schlenk tube and the resulting solution was stirred for 1 hour. TLC at this point showed only trace amounts of **3a** remained. 1.2 mL

of methanol and 0.4 mL of DBU was added to the tube. The reaction was stirred at 30 ^{o}C for 30 min. The reaction was directly loaded on flash silica chromatography (R_f = 0.3, EtOAc/Petroleum ether = 1:20) to afford **4**[8] (44.5 mg, 60% yield).



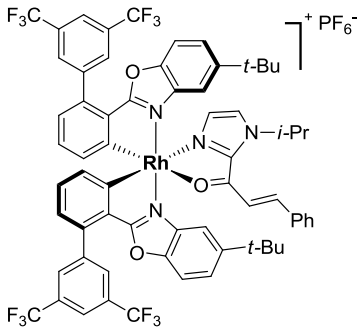
4

According to the general procedure, **4** was obtained as white solid; m.p. = 78-80 ^{o}C. 60% yield, 97% ee (HPLC: chiralpak IA column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r1 (major) = 10.21 min, t_r2 (minor) = 8.18 min; t_r2 (major) = 8.92 min, t_r2 (minor) = 7.13 min); $[\alpha]_D^{25}$ = -31.6 (c = 1.0, $CHCl_3$) (major).

^{1}H NMR (400 MHz, $CDCl_3$) (major) δ = 7.34-7.02 (m, 10H), 6.97-6.91 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 5.0 (d, *J* = 6.3 Hz, 1H), 3.90-3.84 (m, 1H), 3.46 (d, *J* = 0.6 Hz, 3H), 3.42-3.28 (m, 2H), 2.93-2.86 (m, 2H), 2.79-2.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.8, 150.2, 141.0, 136.1, 135.8, 129.0, 128.6, 128.4, 128.4, 128.1, 126.9, 126.7, 125.5, 117.7, 114.8, 63.1, 51.5, 47.3, 43.2, 37.3, 26.7.

^{1}H NMR (400 MHz, $CDCl_3$) (major) δ = 7.34-7.02 (m, 11H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.79-6.77 (m, 1H), 6.34 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 8.4 Hz, 1H), 3.77-3.71 (m, 1H), 3.65-3.61 (m, 1H), 3.55 (d, *J* = 0.6 Hz, 3H), 3.42-3.28 (m, 1H), 3.07 (dd, *J* = 6.7 Hz, *J* = 15.7 Hz, 1H), 2.79-2.70 (m, 2H), 2.39-2.31 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 712.9, 149.6, 141.2, 135.8, 135.4, 129.3, 129.0, 128.3, 128.2, 128.0, 127.0, 126.9, 125.0, 117.4, 113.5, 63.3, 51.5, 48.1, 43.5, 37.9, 26.8. IR (KBr): *v*(cm^{-1}) 2951, 2926, 2836, 1716, 1594, 1502, 1429, 1320, 1258, 743, 698. HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}NO_2[M+H]^+$: 372.1958, found: 372.1956.

7. Synthesis of Intermediate Complexe *rac*-Rh5-IM.



rac-**Rh5-IM**

The racemic complex *rac*-**Rh5-IM** was obtained by reacting Michael acceptor **1a** (12.0 mg, 0.05 mmol) with *rac*-**Rh5** (63.0 mg, 0.05mmol) at room temperature for 3 mins in CH_2Cl_2 (1.0 mL). Afterwards, the solution was evaporated and the resulting solid was dissolved in CH_2Cl_2 (1.0 mL) follow by concentrated under vacuum. The labile ligands (CH_3CN) were completely removed via dissolved-evaporated for three cycles. The orange solid was obtained (70.0 mg, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51-8.47 (d, *J* = 15.2 Hz, 1H), 8.04-7.96 (t, *J* = 22.5 Hz, 7H), 7.81-7.79 (m, 2H), 7.69-7.65 (d, *J* = 12.8 Hz, 1H), 7.54-7.52 (m, 3H), 7.48-7.42 (td, J_1 = 1.6 Hz, J_2 = 8.8 Hz, J_3 = 13.2 Hz, 2H), 7.32-7.26 (m, 5H), 7.20-7.09 (m, 4H), 6.66-6.64 (t, *J* = 6.4 Hz, 2H), 6.25-6.25 (d, *J* = 1.2 Hz, 1H), 5.40-5.34 (m, 1H), 1.77-1.75 (d, *J* = 6.4 Hz, 3H), 1.69-1.67 (d, *J* = 6.4 Hz, 3H), 1.17 (s, 9H), 1.13 (s, 9H).
^{19}F NMR (376.4 MHz, $CDCl_3$) δ = -62.7, 62.7, -72.0, 73.9.

Reference:

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2) X. Shen, H. Huo, C. Wang, B. Zhang, K. Harms and E. Meggers, *Chem. - Eur. J.*, **2015,** *21*, 9720-9726.

3) C. Wang, L.-A. Chen, H. Huo, X. Shen, K. Harms, L Gong and E, Meggers, *Chem. Sci*., **2015**, *6*, 1094-1100.

4) J. Ma, X. Shen, K. Harmsa and E. Meggers, *Dalton Trans.*, **2016**, *45*, 8320-8323.

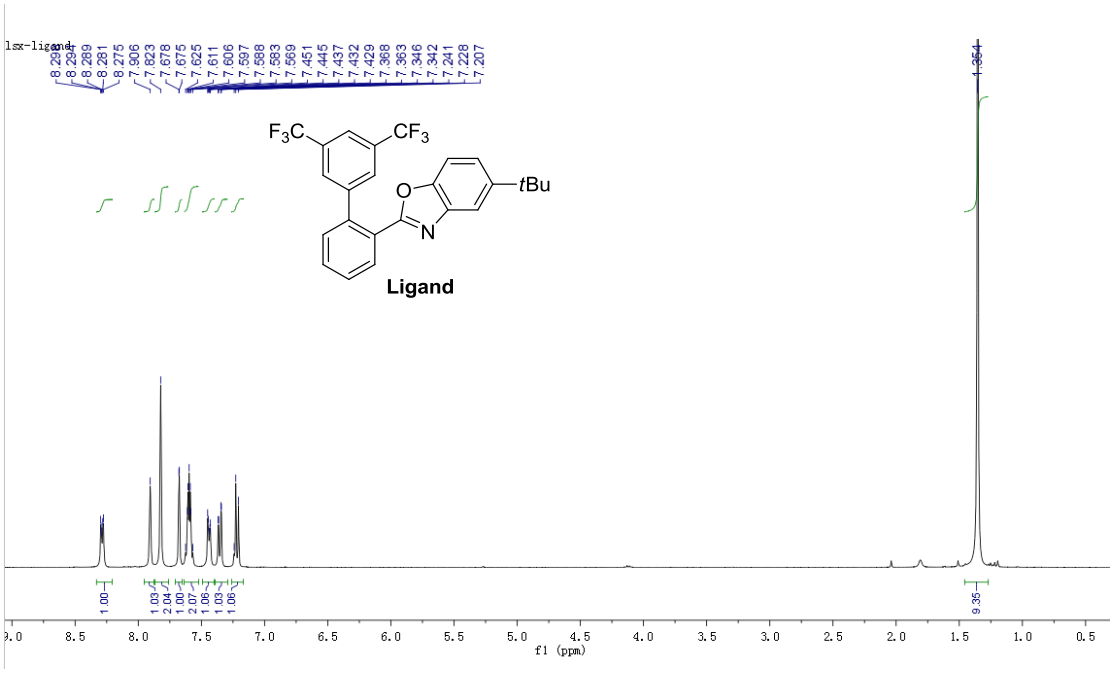
5) G.-J. Sun, J. Gong and Q. Kang, *J. Org. Chem*., **2017**, *82*, 796-803.

6) S.-W. Li, J. Gong and Q. Kang, *Org. Lett.*, **2017**, *19*, 1350-1353.

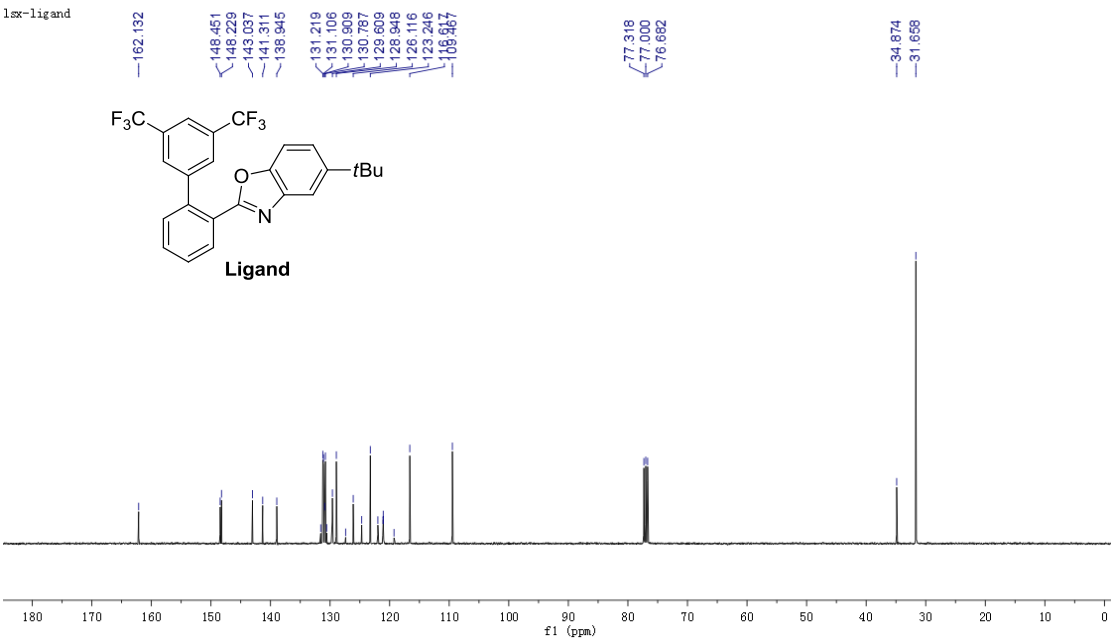
7) X.-Z. Shu, Y.-F. Yang, X.-F. Xia, K.-G. Ji, X.-Y. Liu and Y.-M. Liang, *Org. Biomol. Chem.*, **2010**, *8*, 4077-4079.

8) D. A. Evans, H.-J. Song and K. R. Fandrick, *Org. Lett*., **2006**, *8*, 3351-3554.

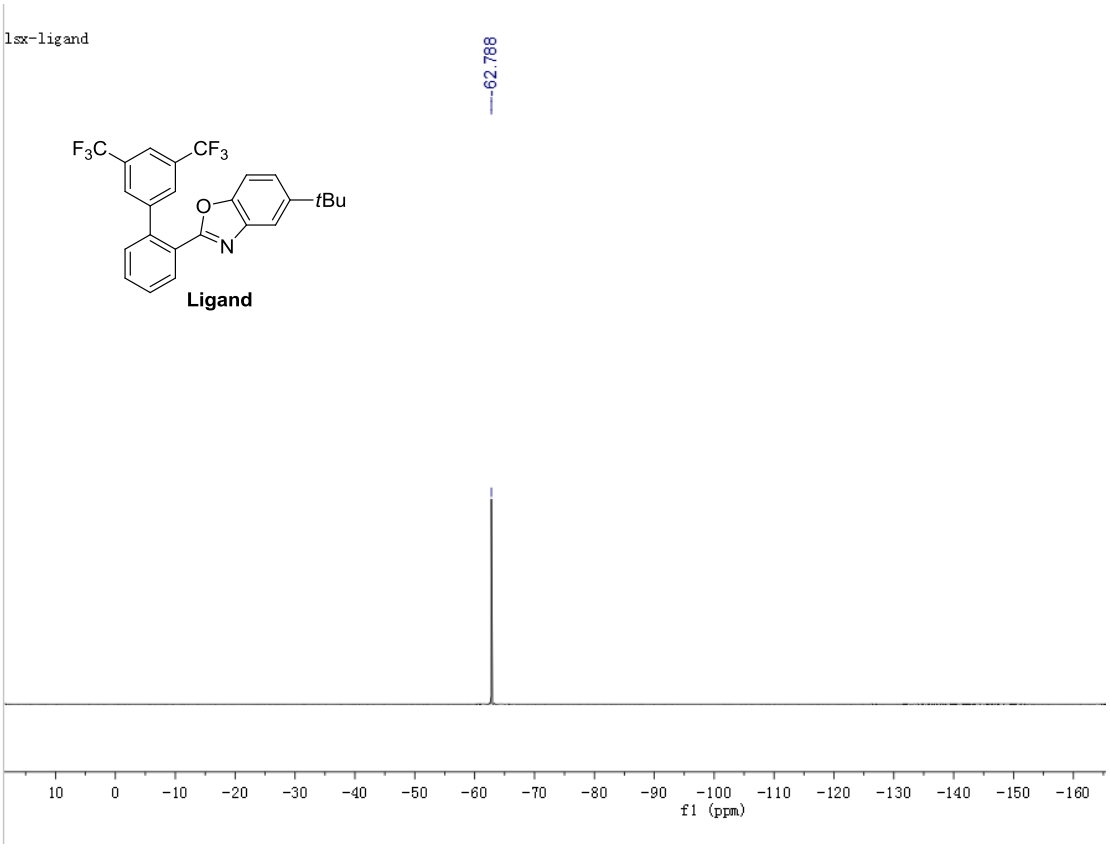
V. NMR Spectra of Substrates and Products



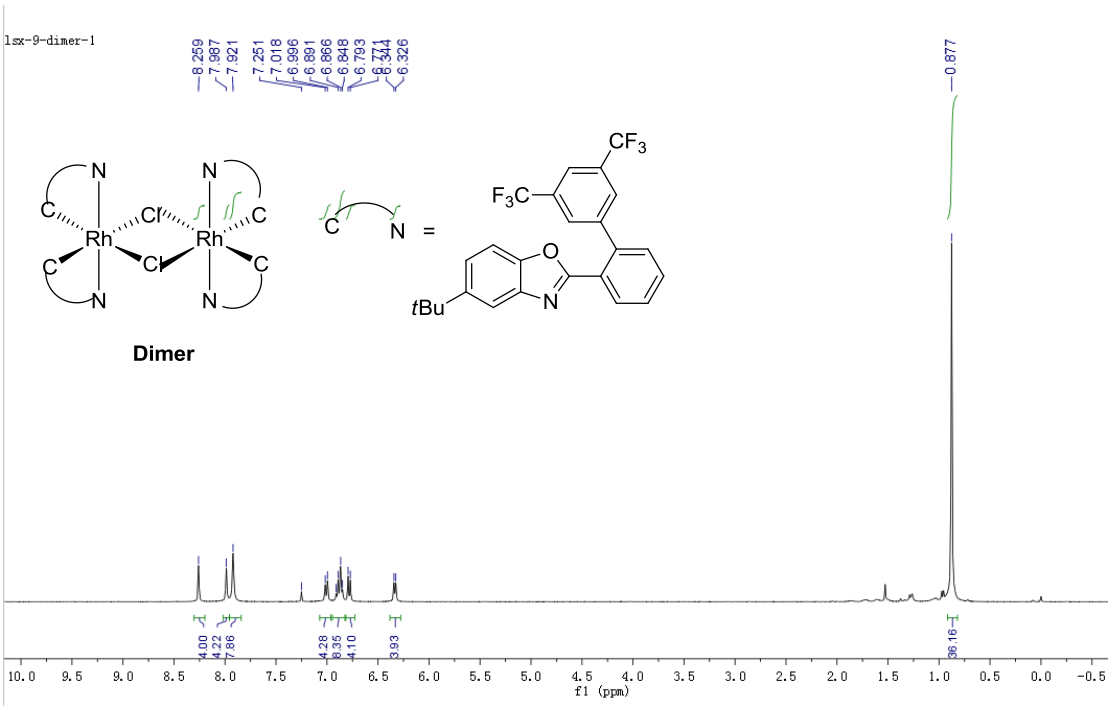
^{1}H NMR spectra of **Ligand**



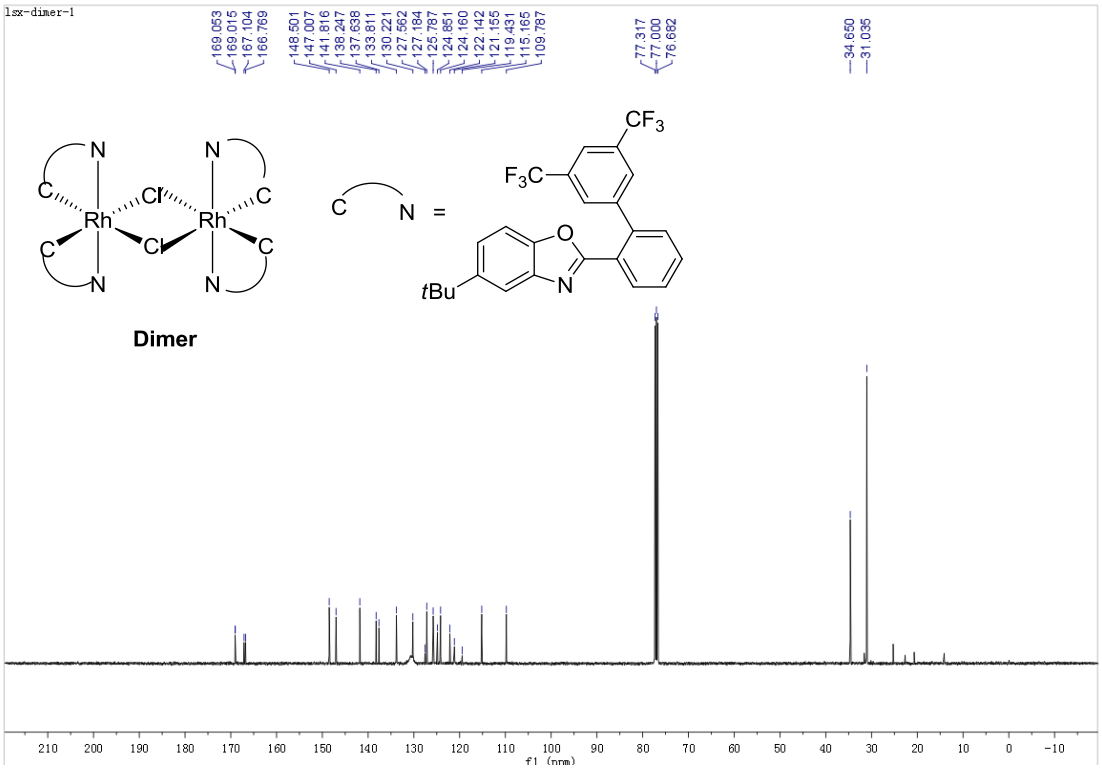
^{13}C NMR spectra of **Ligand**



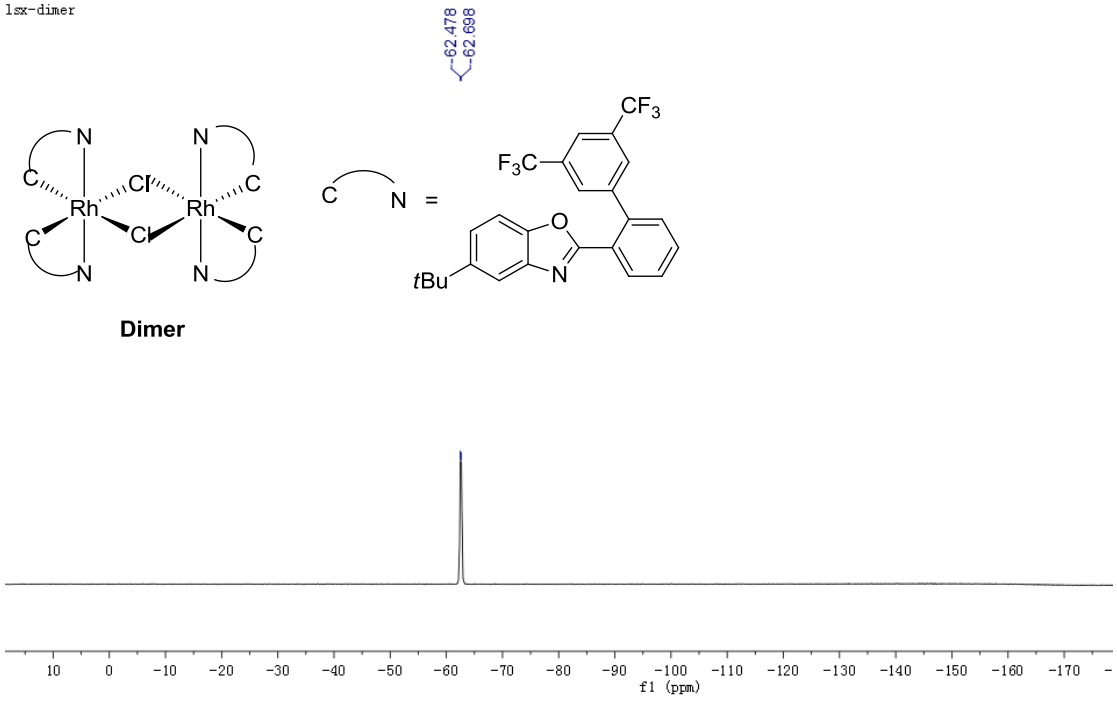
^{19}F NMR spectra of **Ligand**



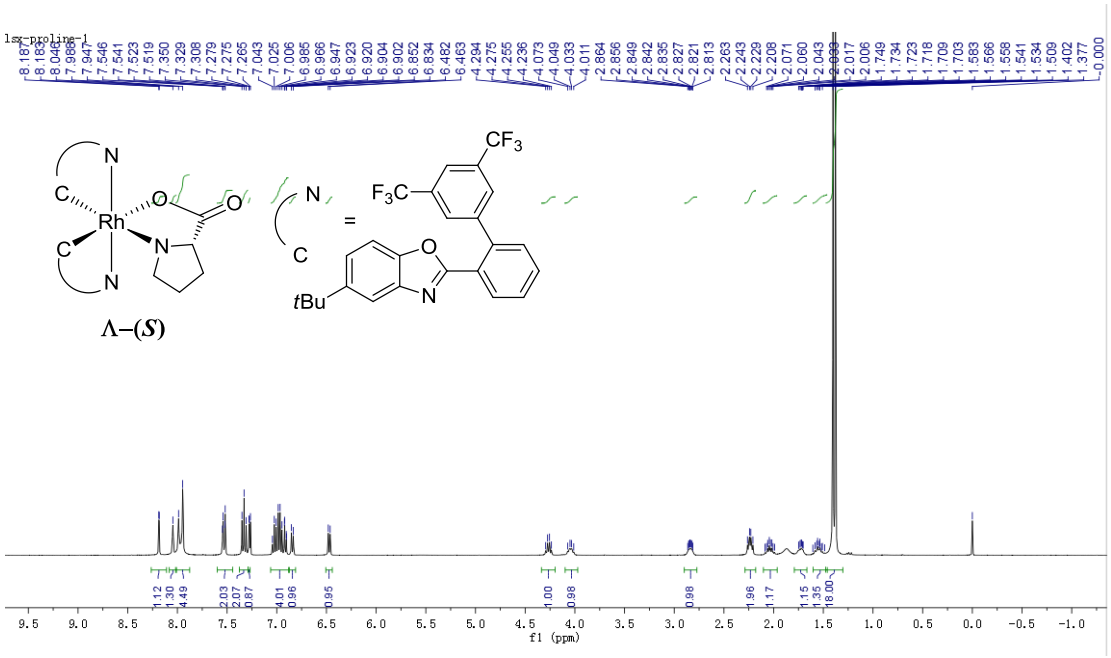
^{1}H NMR spectra of **Dimer**



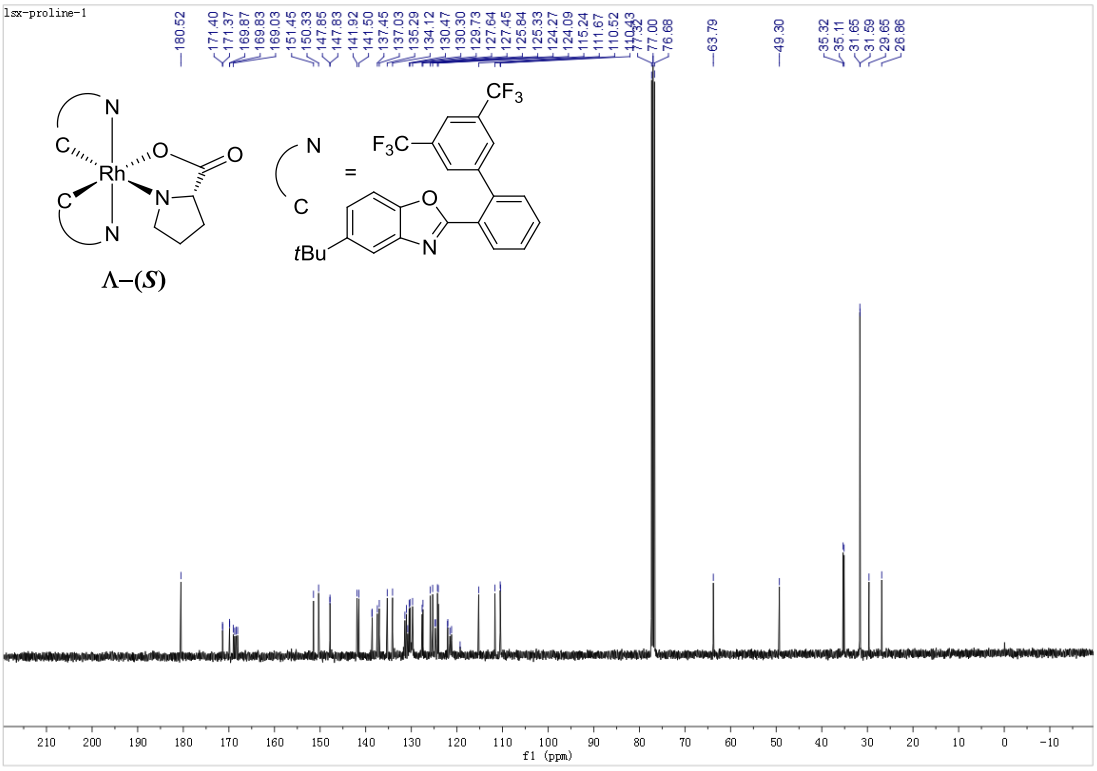
^{13}C NMR spectra of **Dimer**



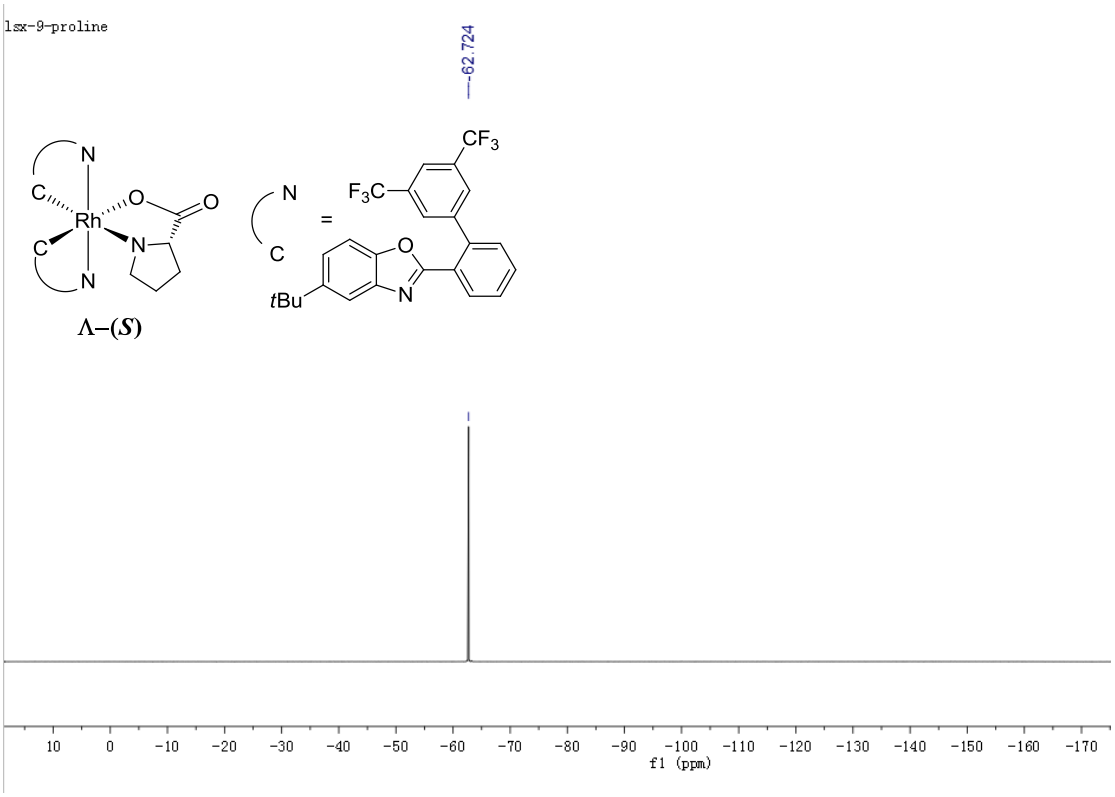
^{19}F NMR spectra of **Dimer**



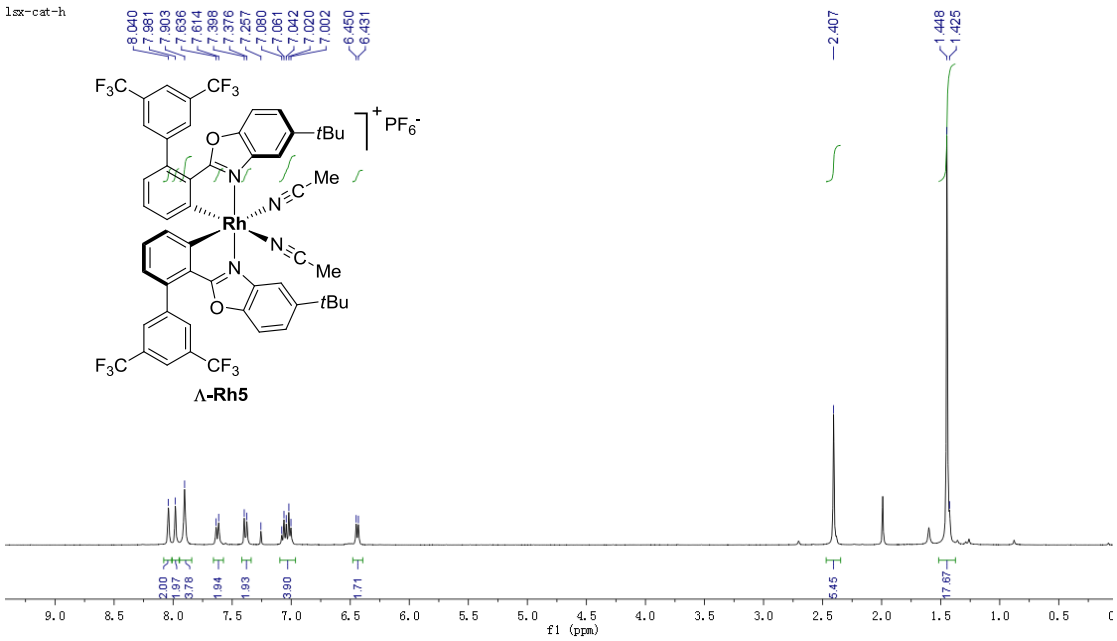
^{1}H NMR spectra of **Λ-(*S*)-Rh complex**



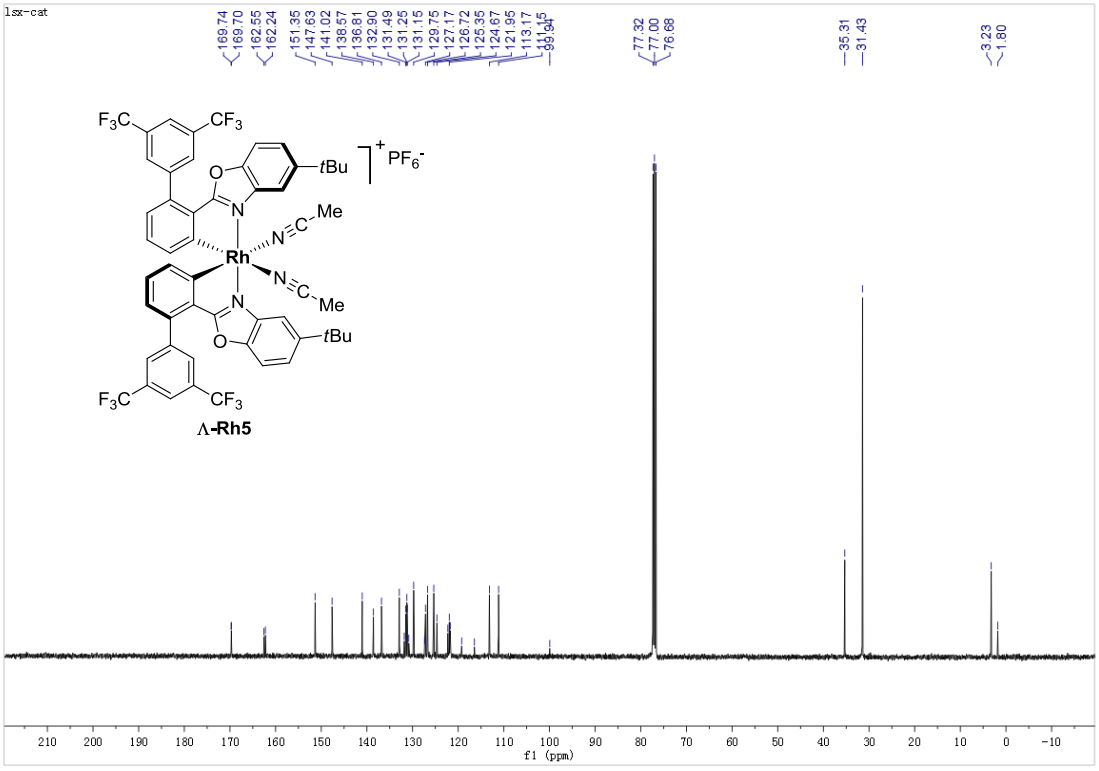
^{13}C NMR spectra of **Λ-(*S*)-Rh complex**



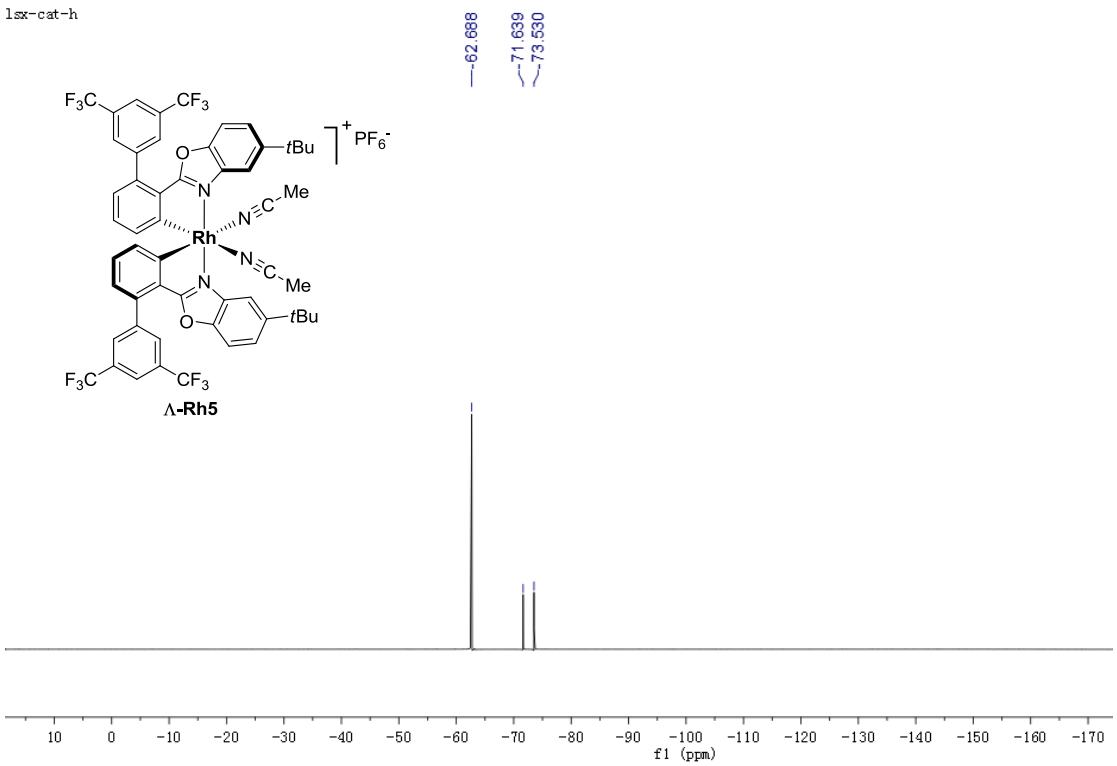
^{19}F NMR spectra of **Λ-(*S*)-Rh complex**



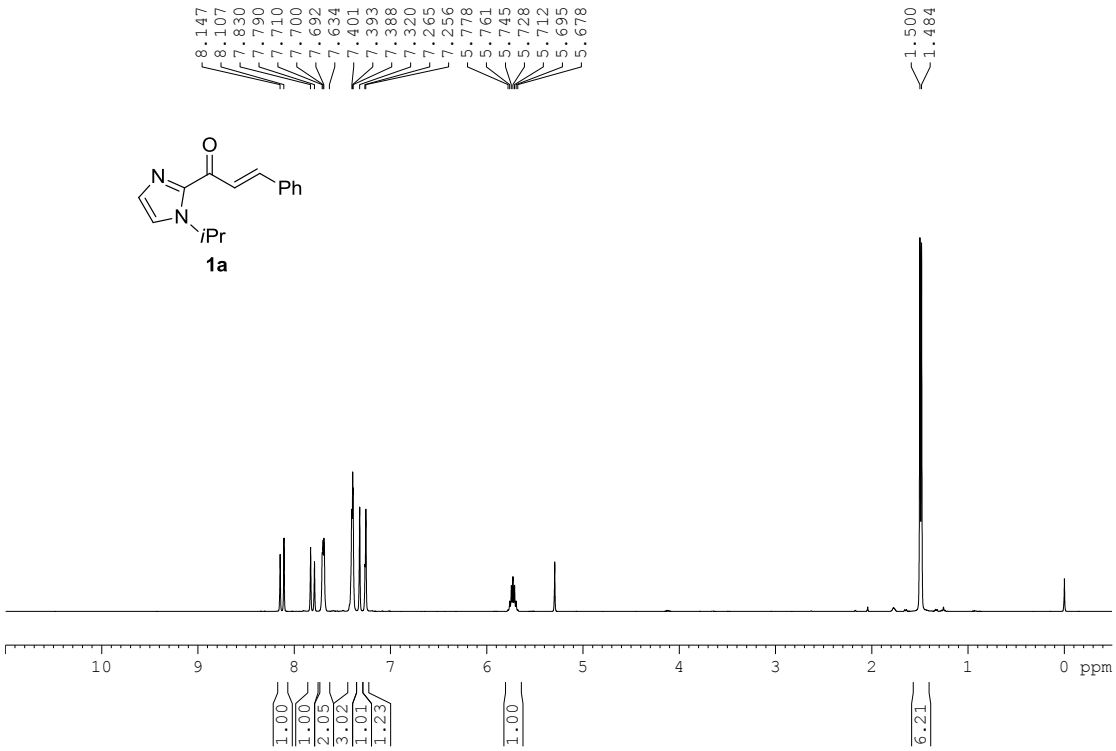
^{1}H NMR spectra of catalyst **Λ-Rh5**



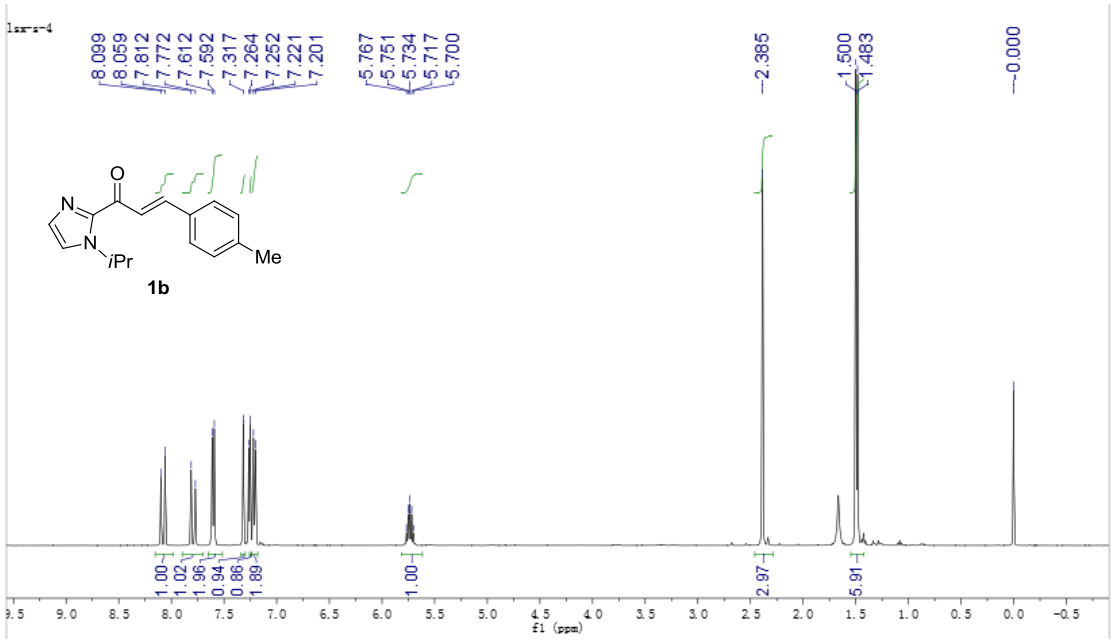
^{13}C NMR spectra of catalyst **Λ-Rh5**



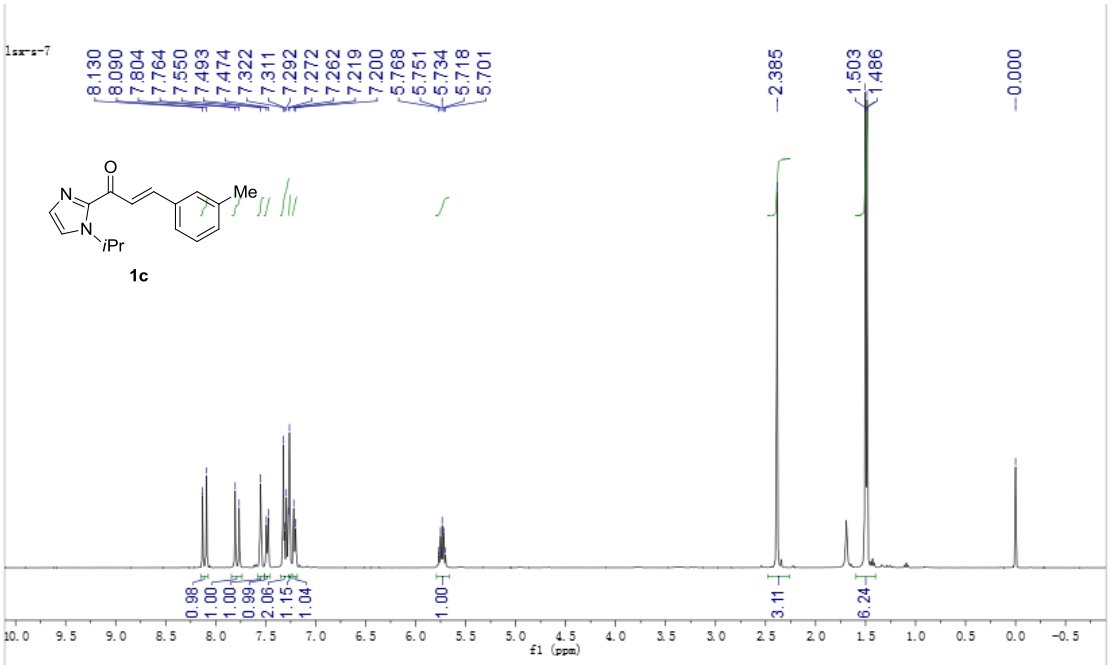
^{19}F NMR spectra of **catalyst Λ-Rh5**



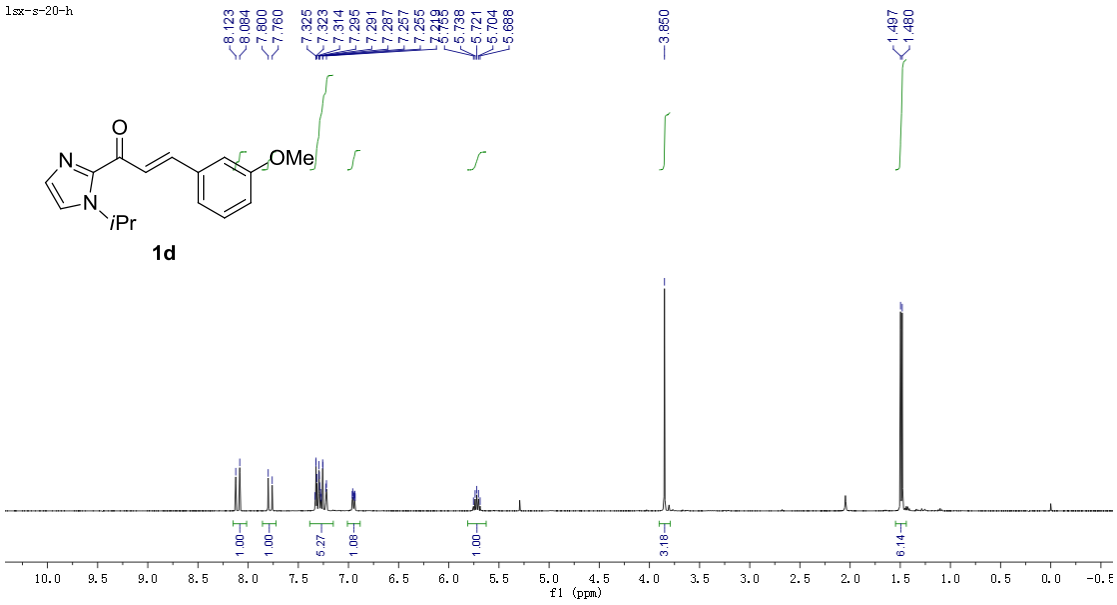
^{1}H NMR spectra of compound **1a**



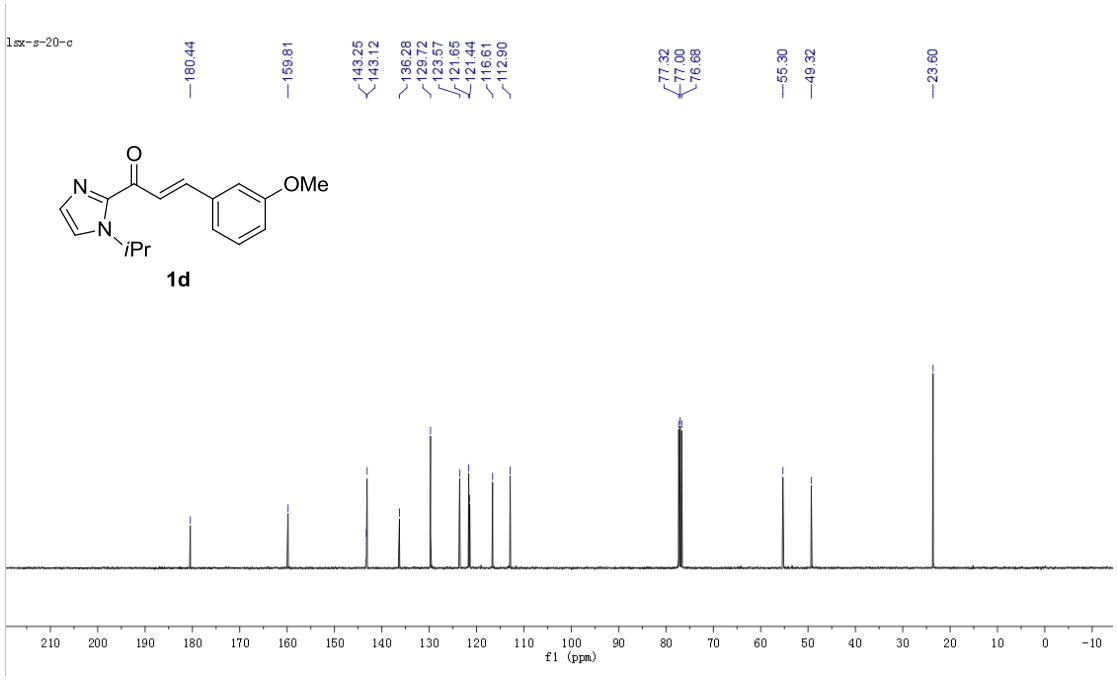
^{1}H NMR spectra of compound **1b**



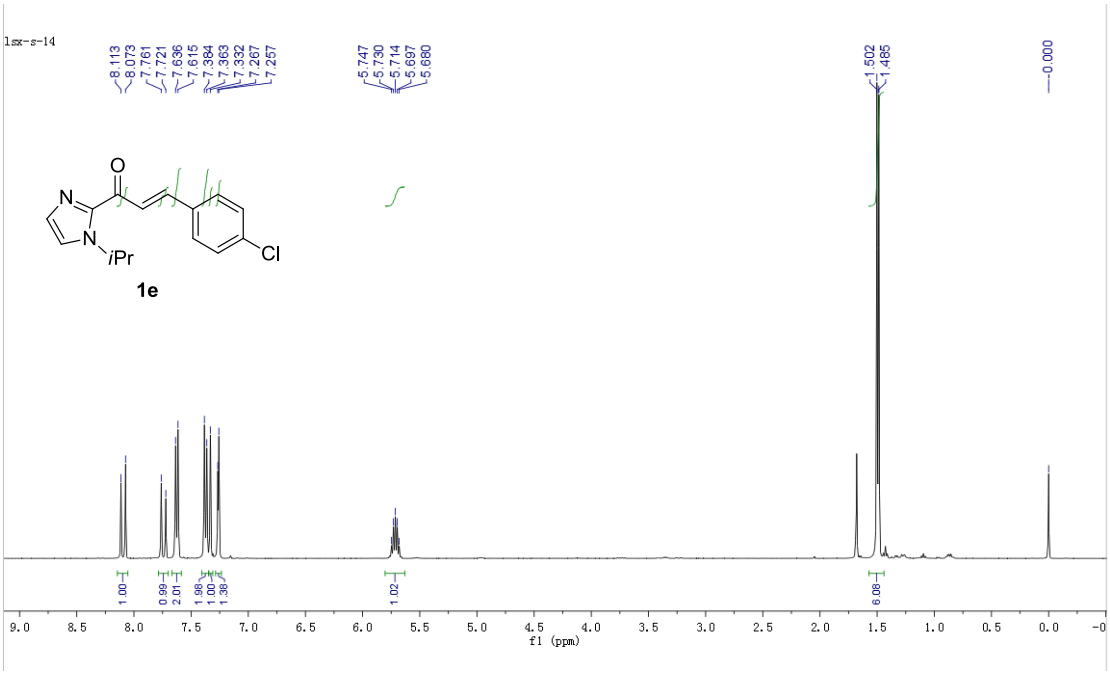
^{1}H NMR spectra of compound **1c**



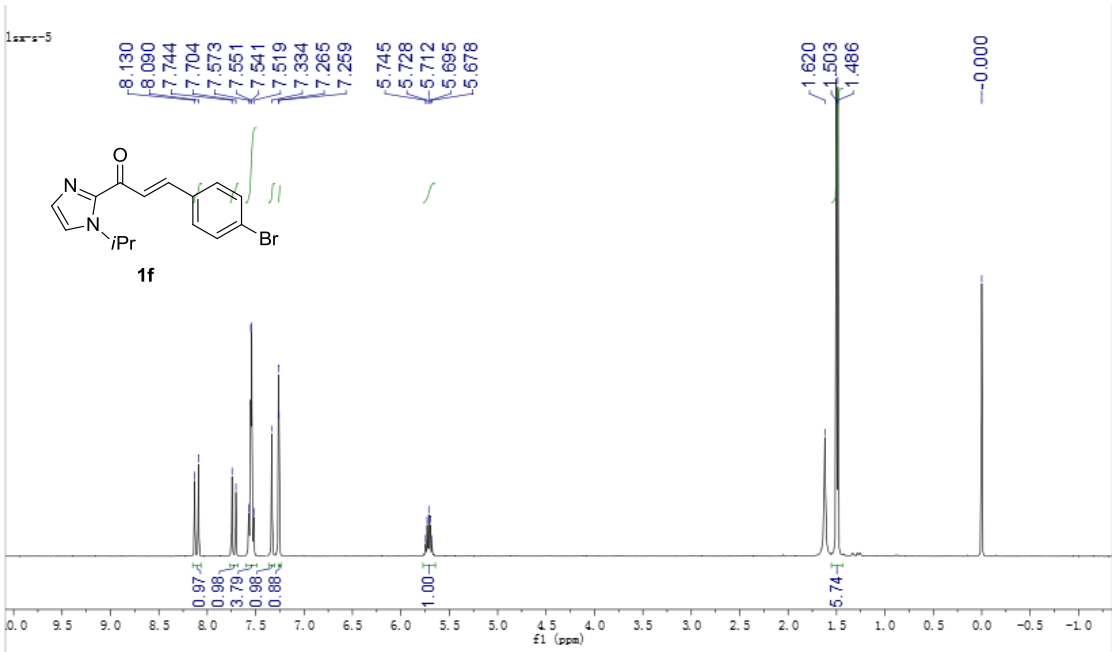
^{1}H NMR spectra of compound **1d**



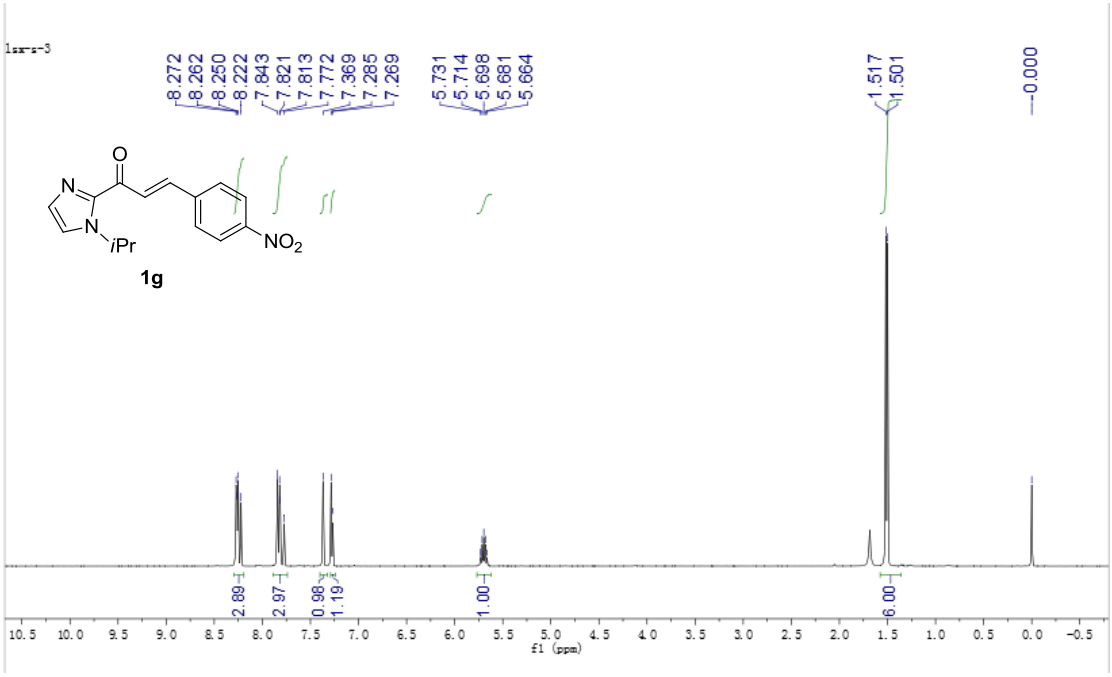
^{13}C NMR spectra of compound **1d**



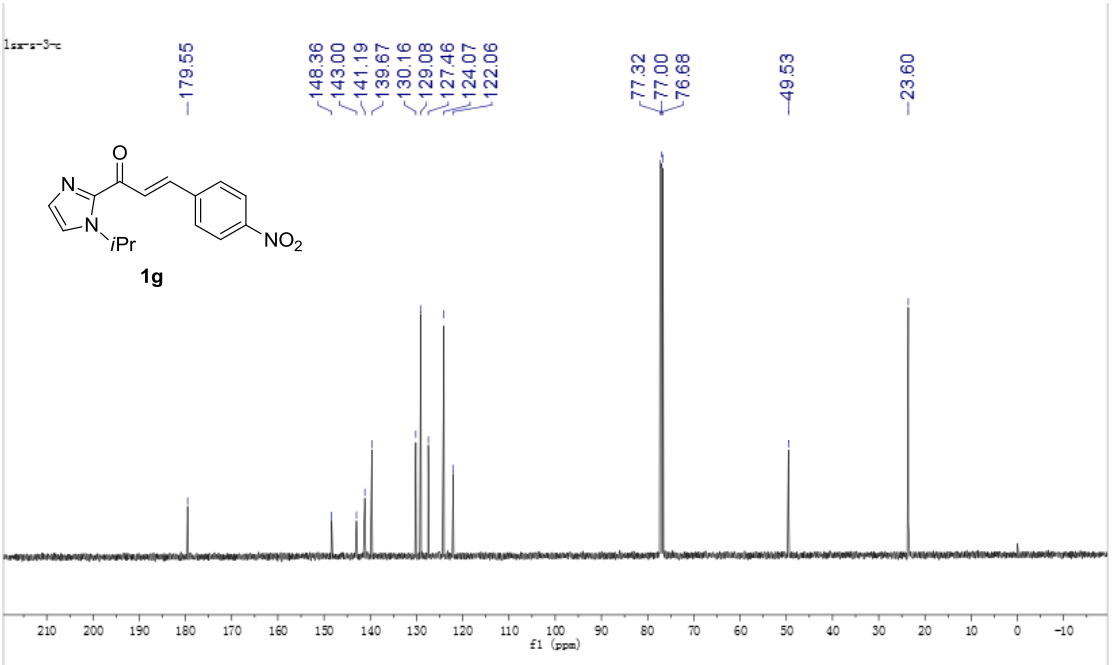
^{1}H NMR spectra of compound **1e**



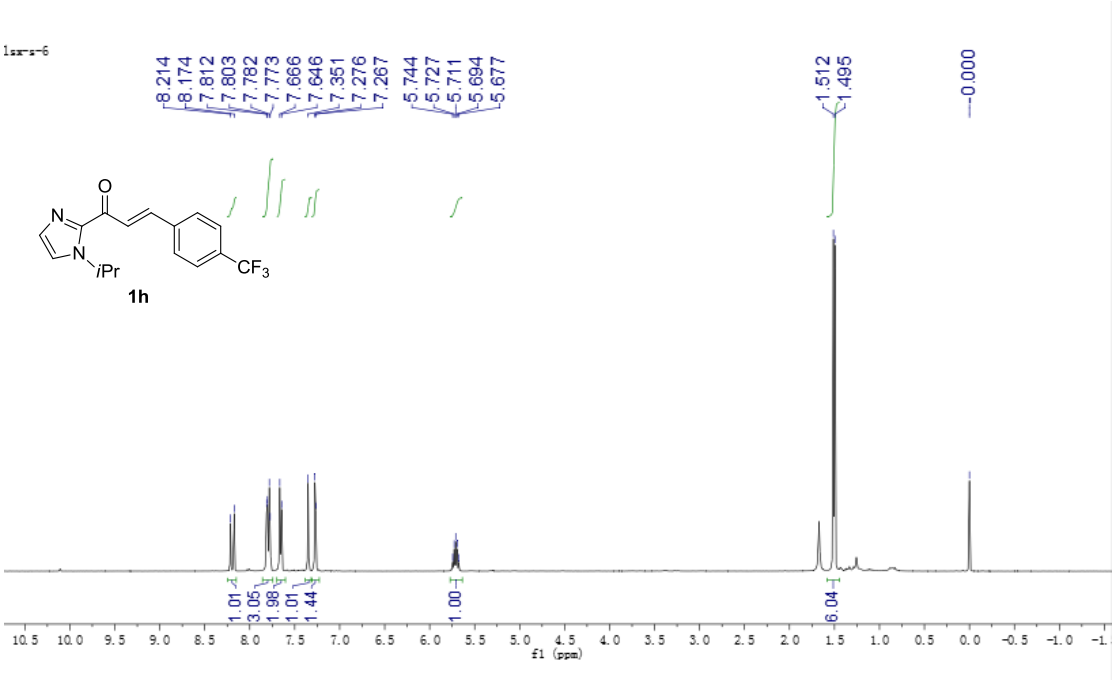
^{1}H NMR spectra of compound **1f**



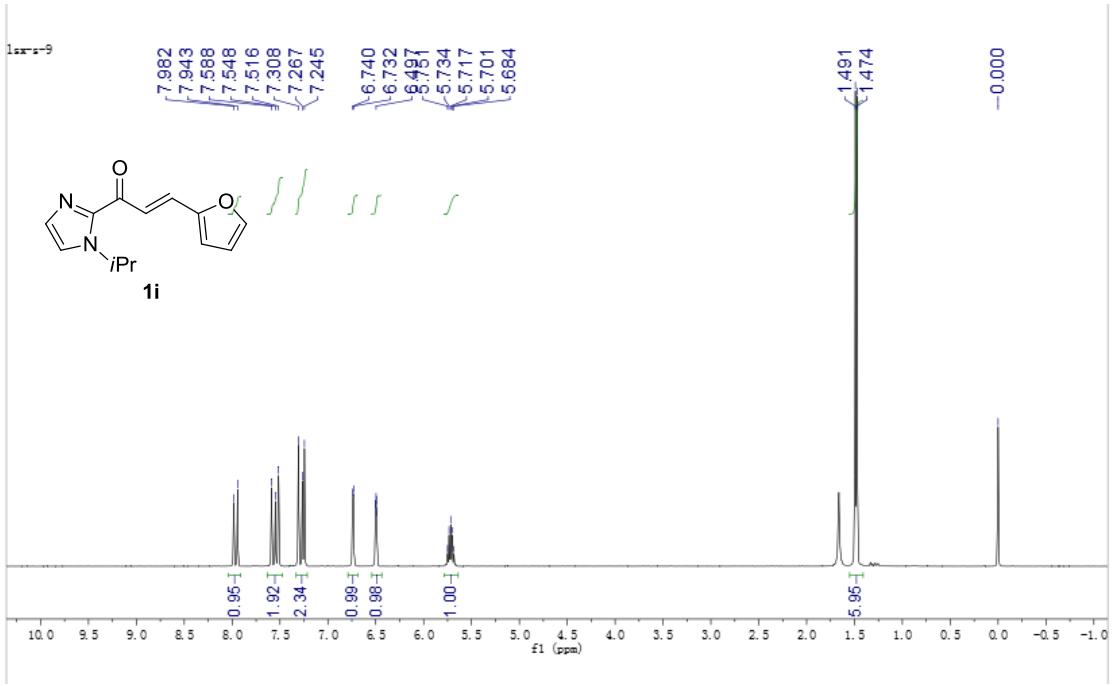
^{1}H NMR spectra of compound **1g**



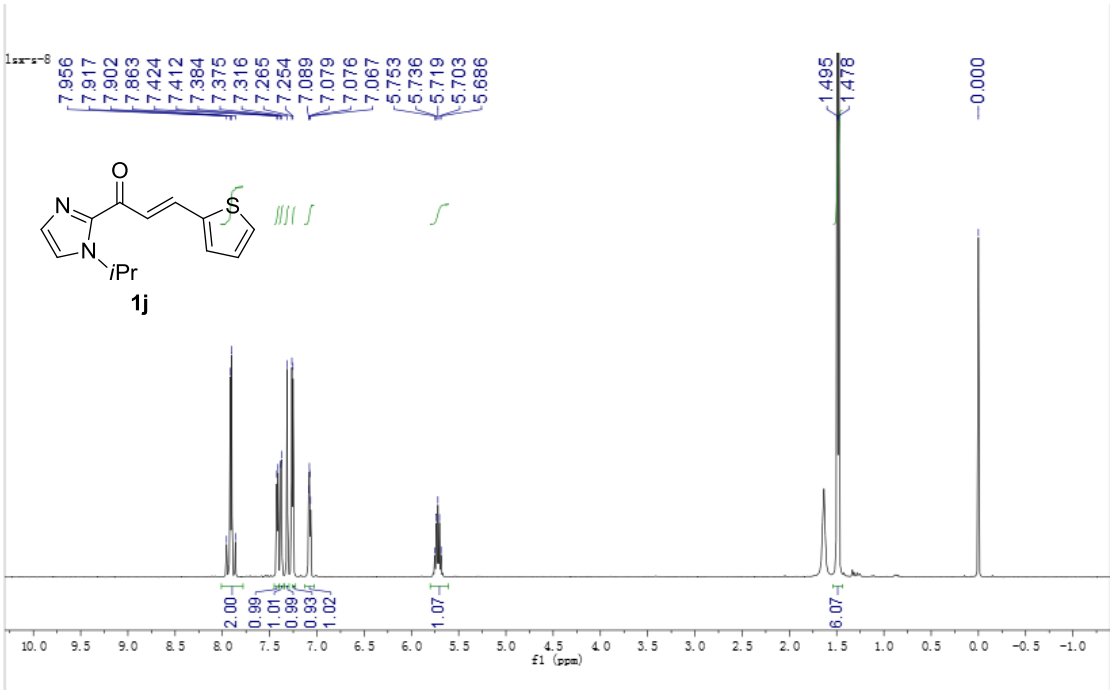
^{13}C NMR spectra of compound **1g**



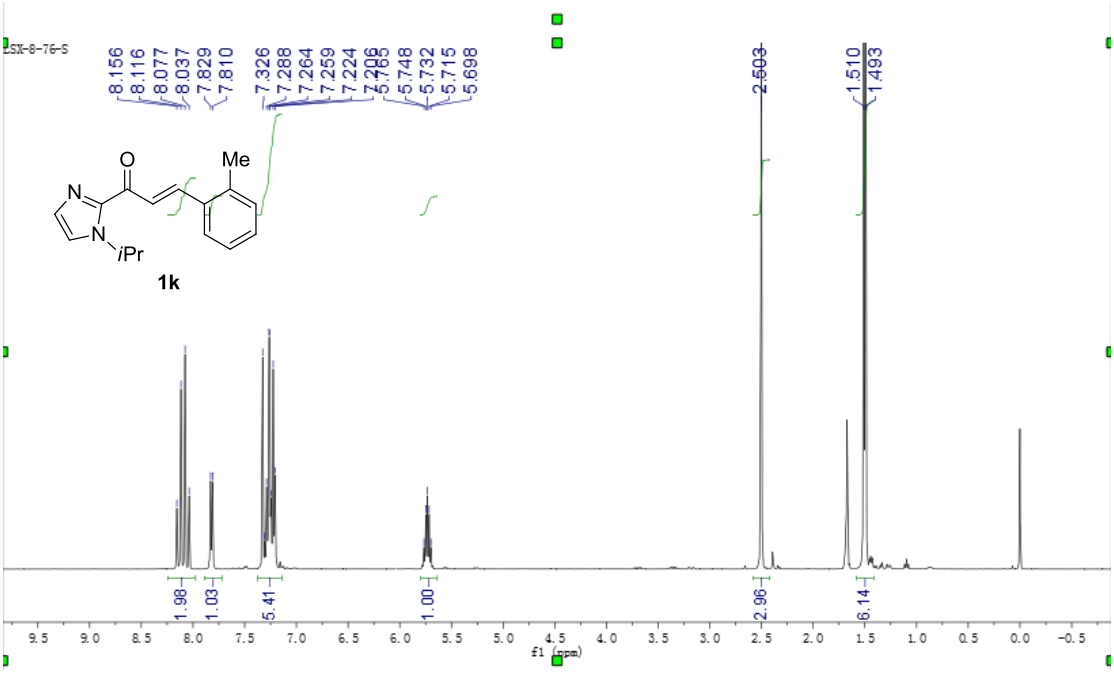
^{1}H NMR spectra of compound **1h**



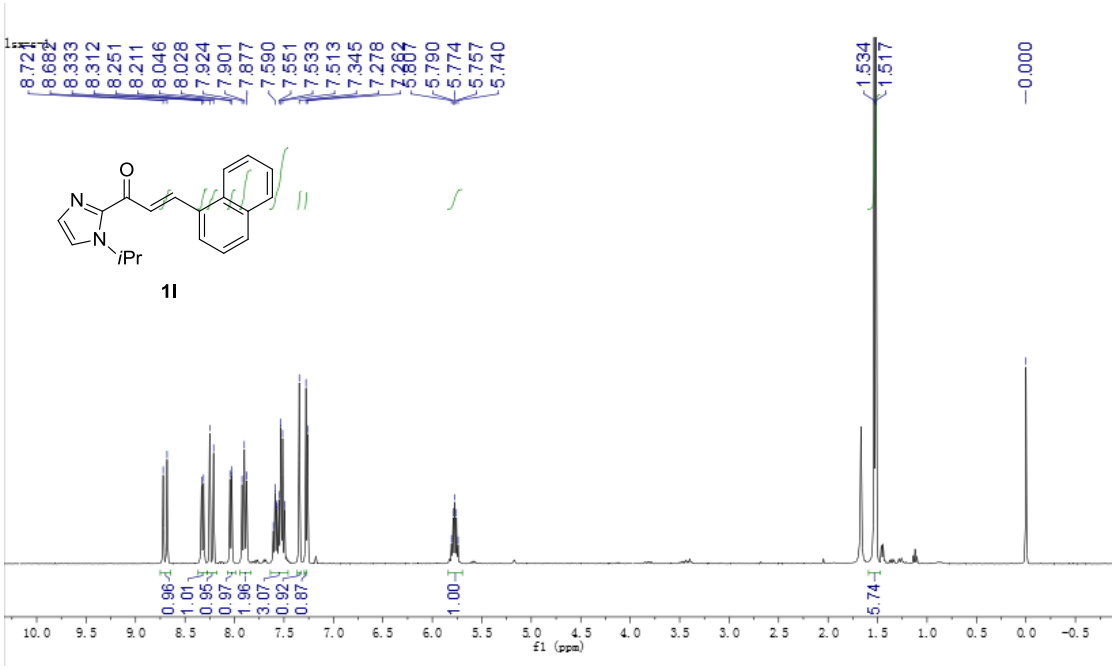
^{1}H NMR spectra of compound **1i**



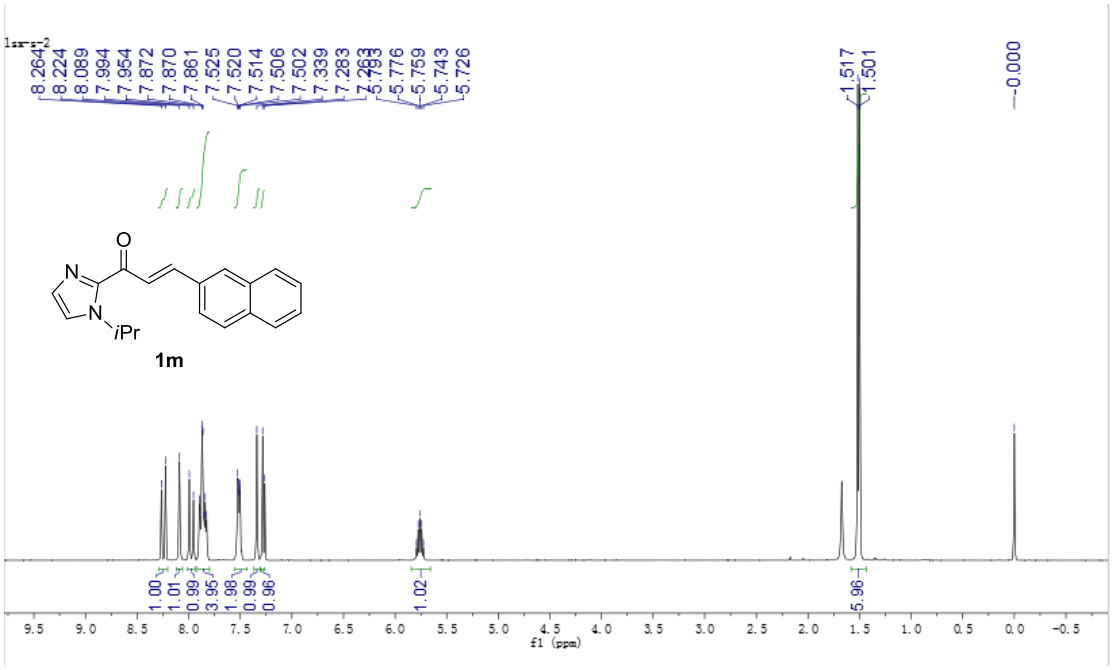
^{1}H NMR spectra of compound **1j**



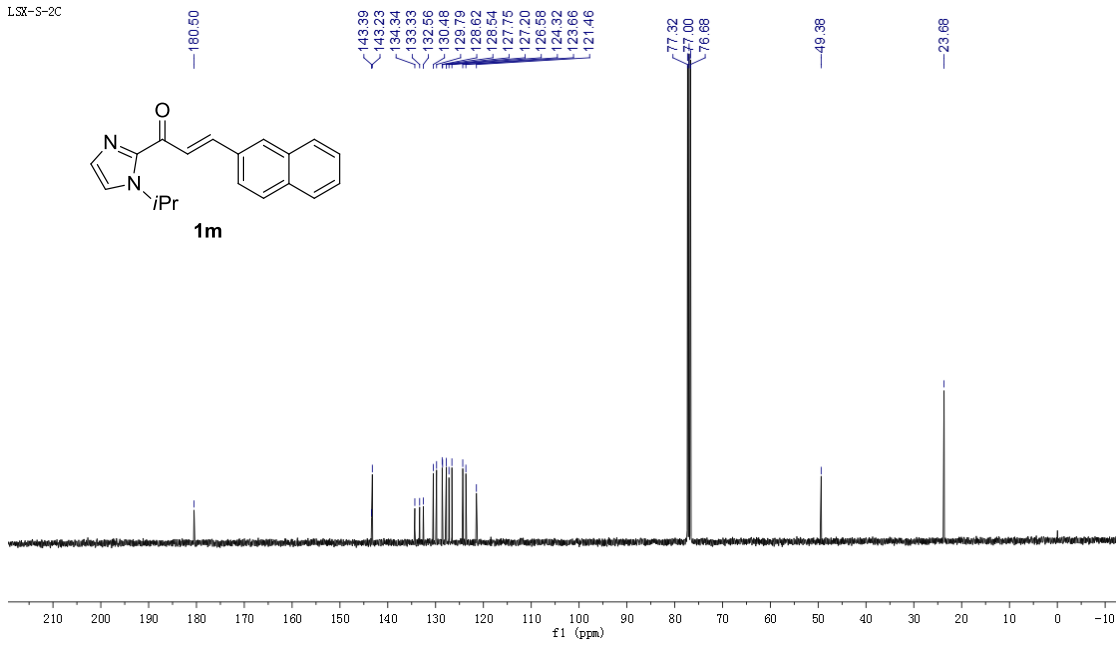
^{1}H NMR spectra of compound **1k**



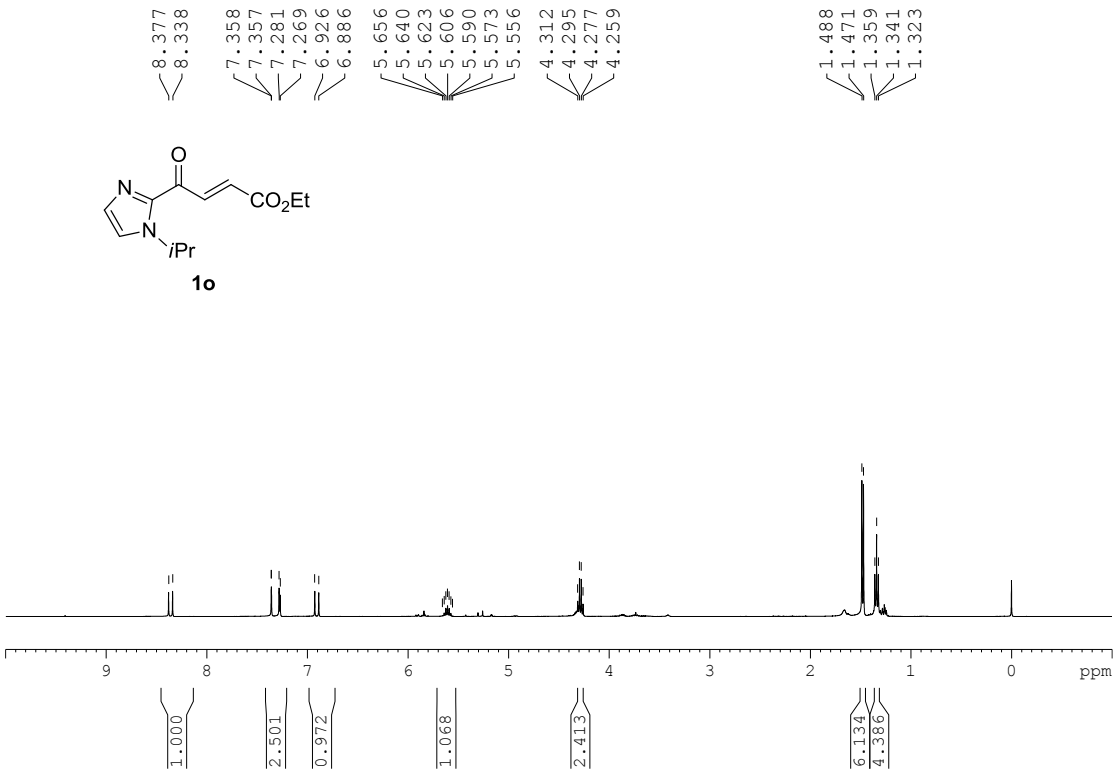
^{1}H NMR spectra of compound **1l**



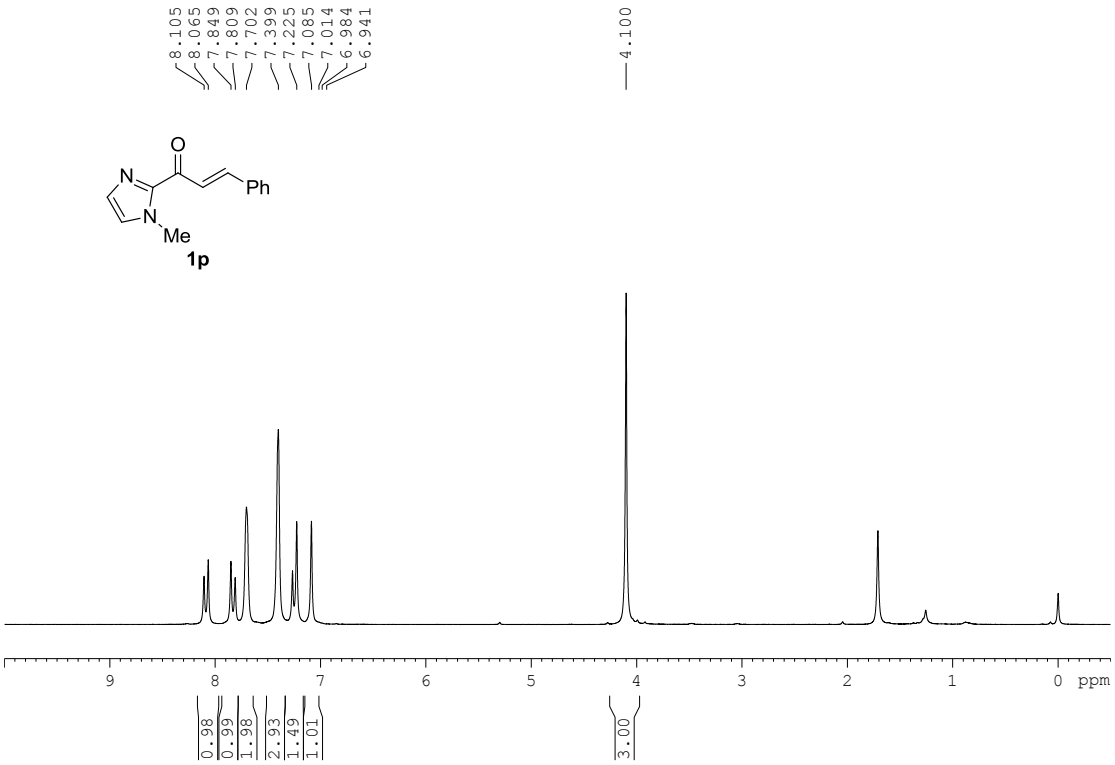
^{1}H NMR spectra of compound **1m**



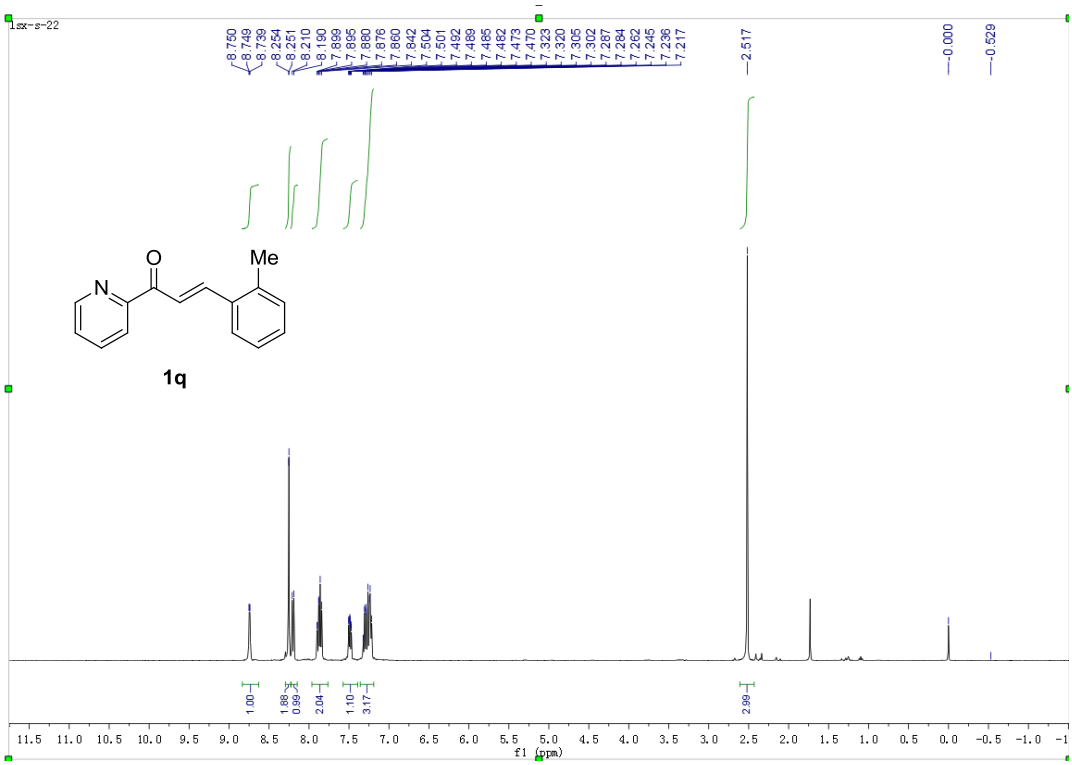
^{13}C NMR spectra of compound **1m**



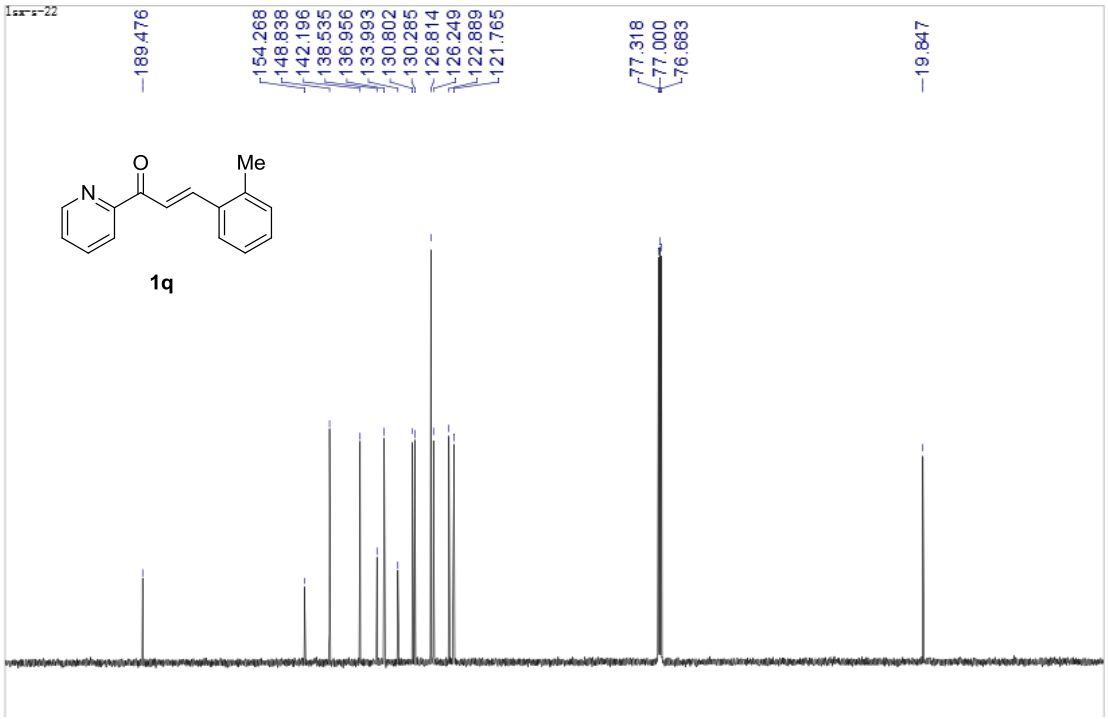
^{1}H NMR spectra of compound **1o**



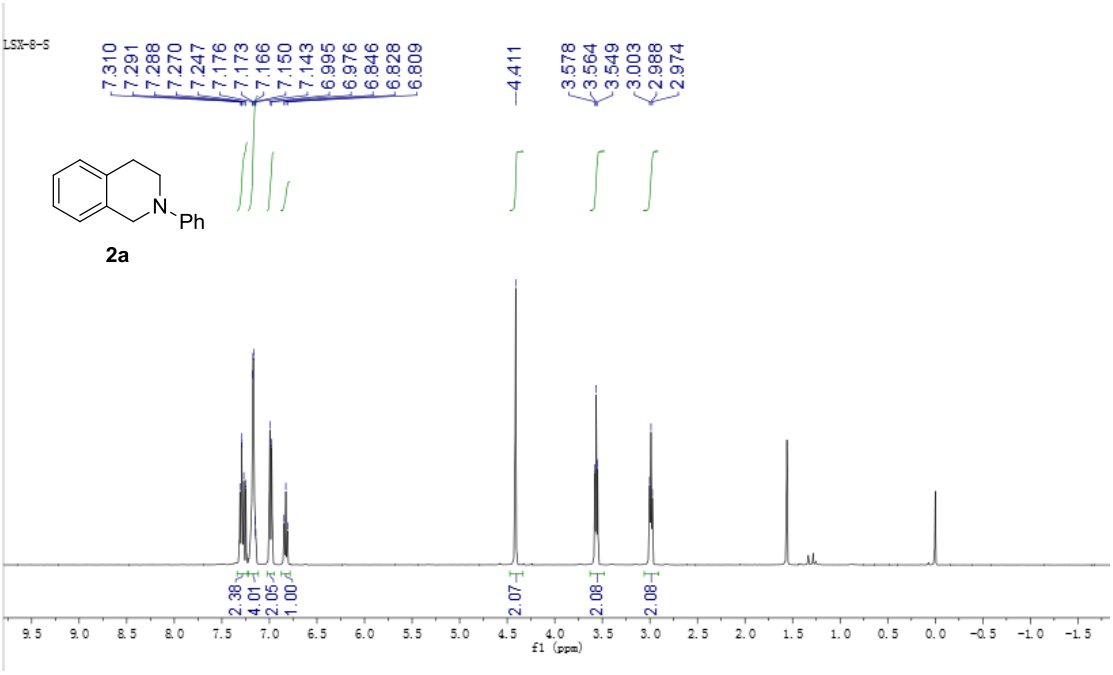
^{1}H NMR spectra of compound **1p**



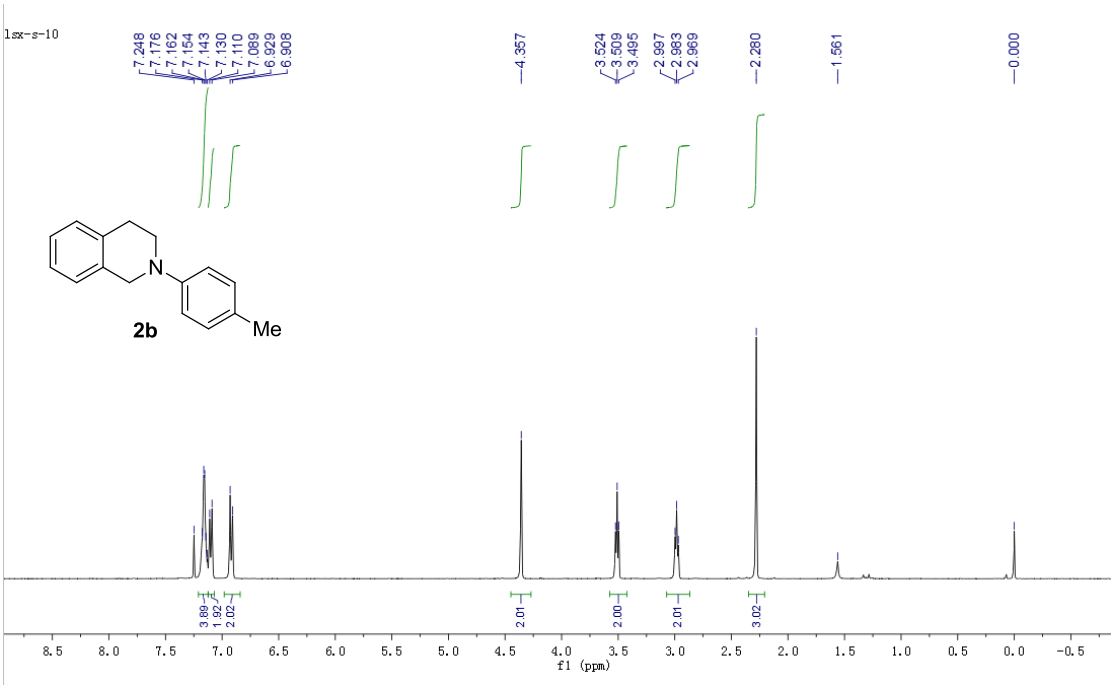
^{1}H NMR spectra of compound **1q**



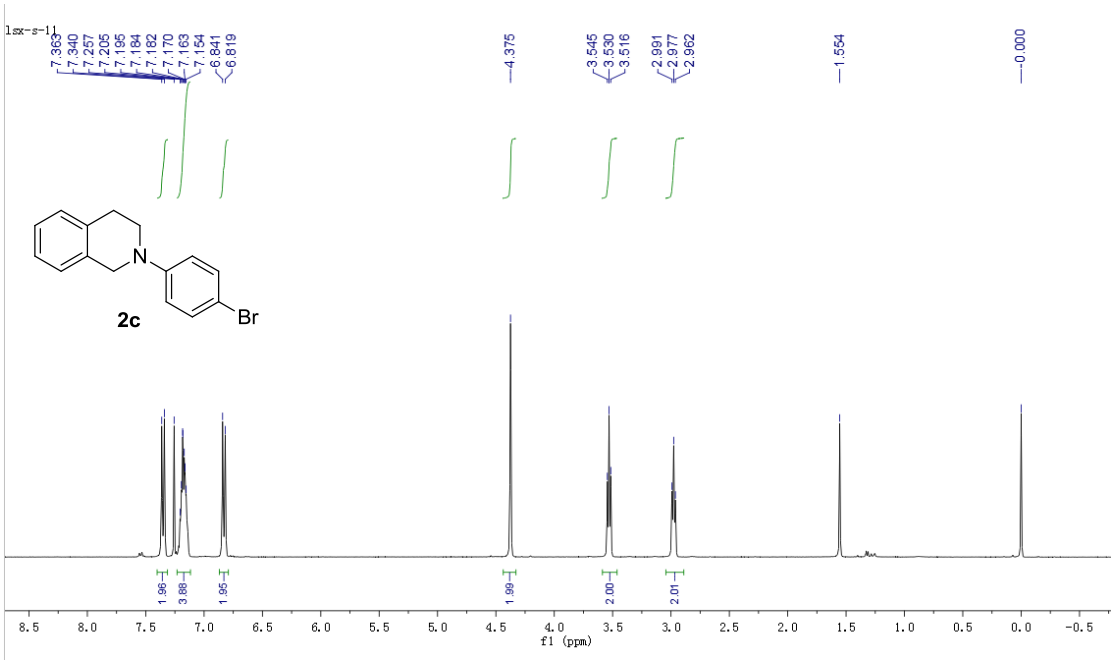
^{13}C NMR spectra of compound **1q**



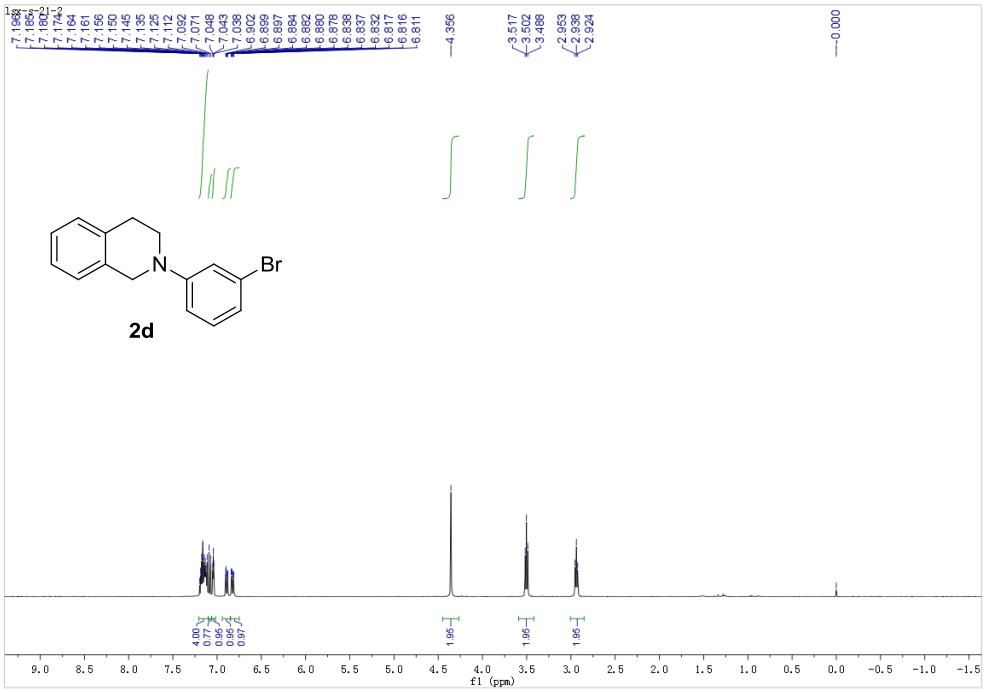
^{1}H NMR spectra of compound **2a**



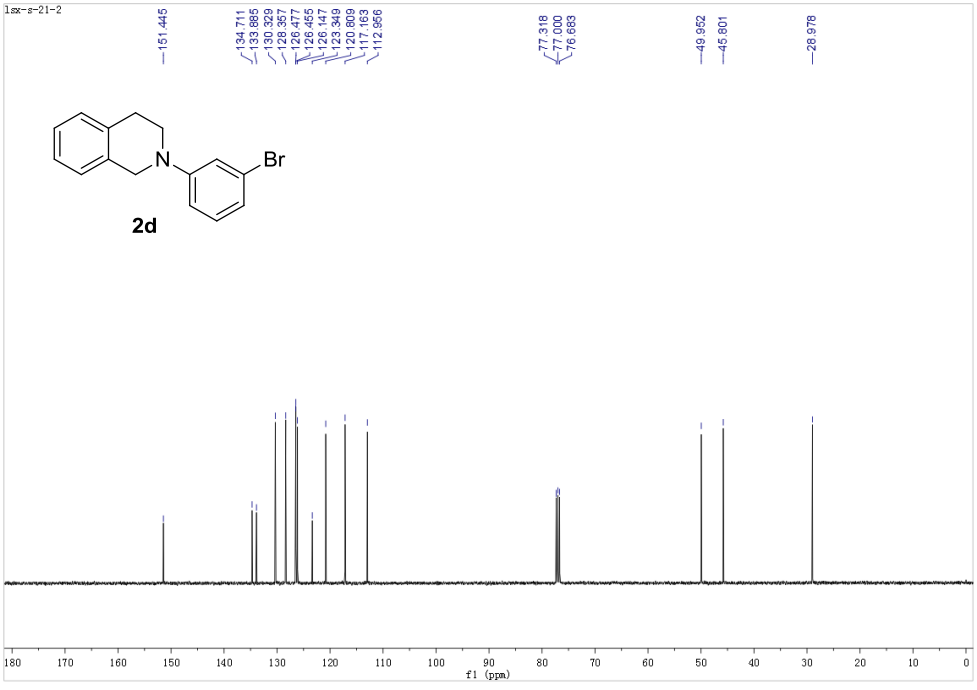
^{1}H NMR spectra of compound **2b**



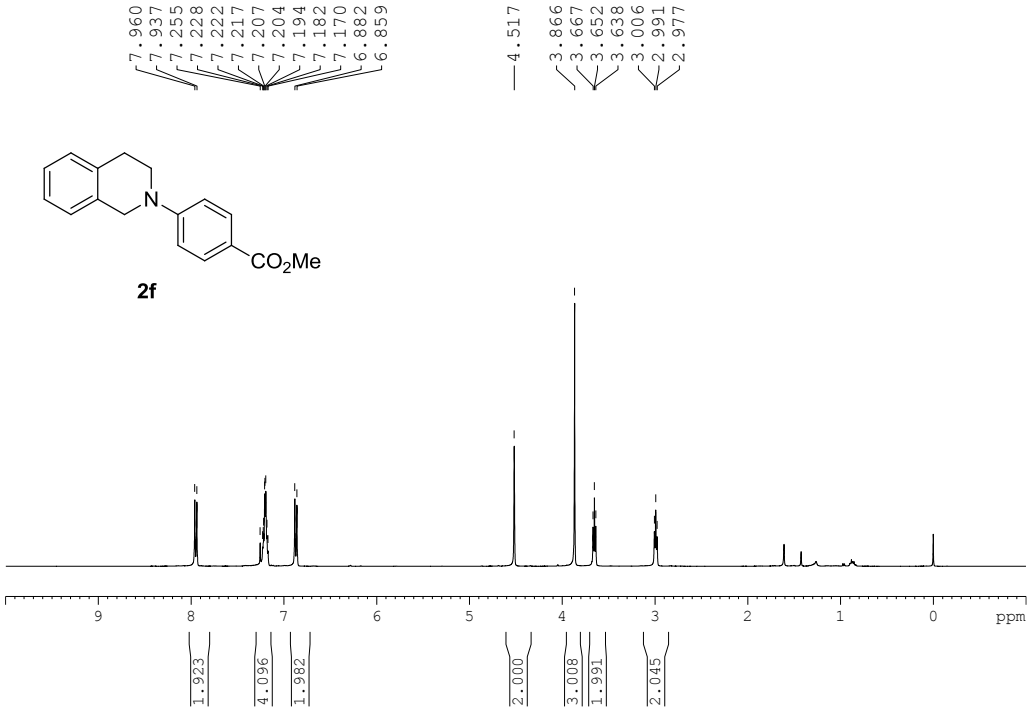
^{1}H NMR spectra of compound **2c**



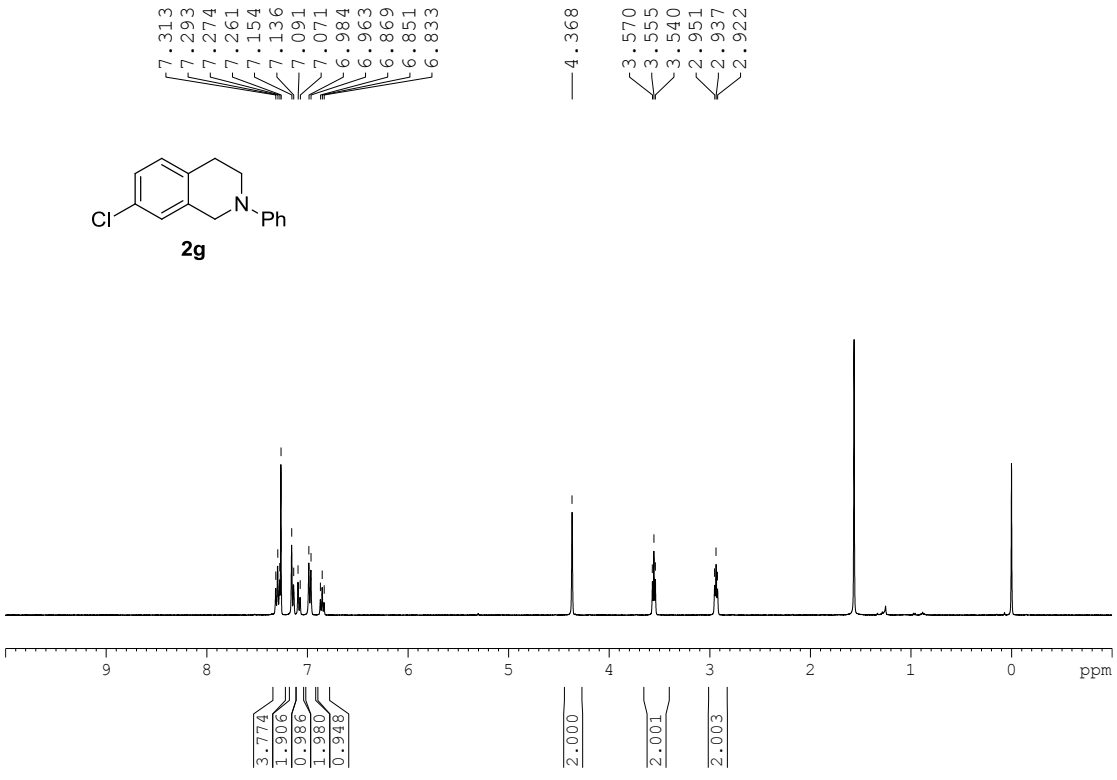
^{1}H NMR spectra of compound **2d**



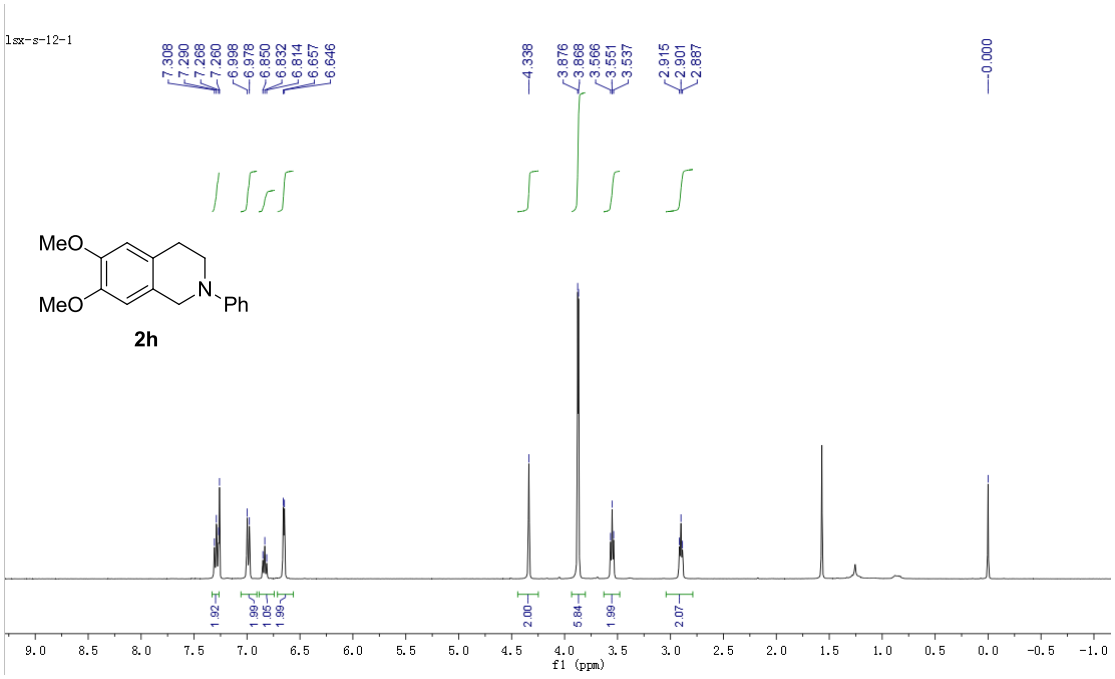
^{13}C NMR spectra of compound **2d**



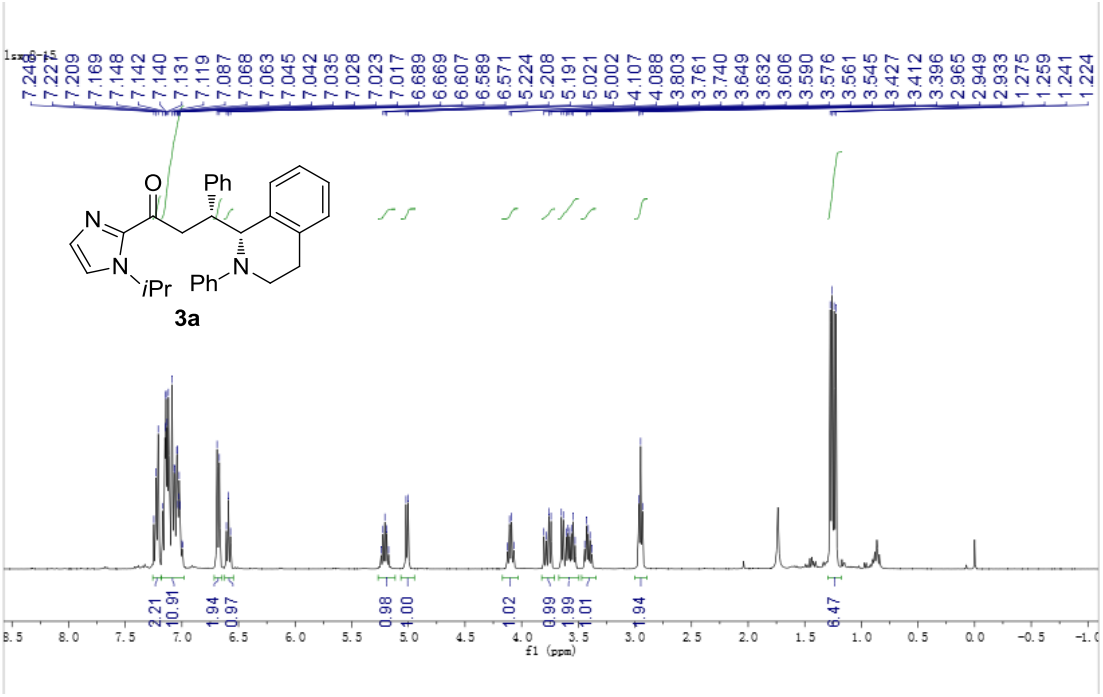
^{1}H NMR spectra of compound **2f**



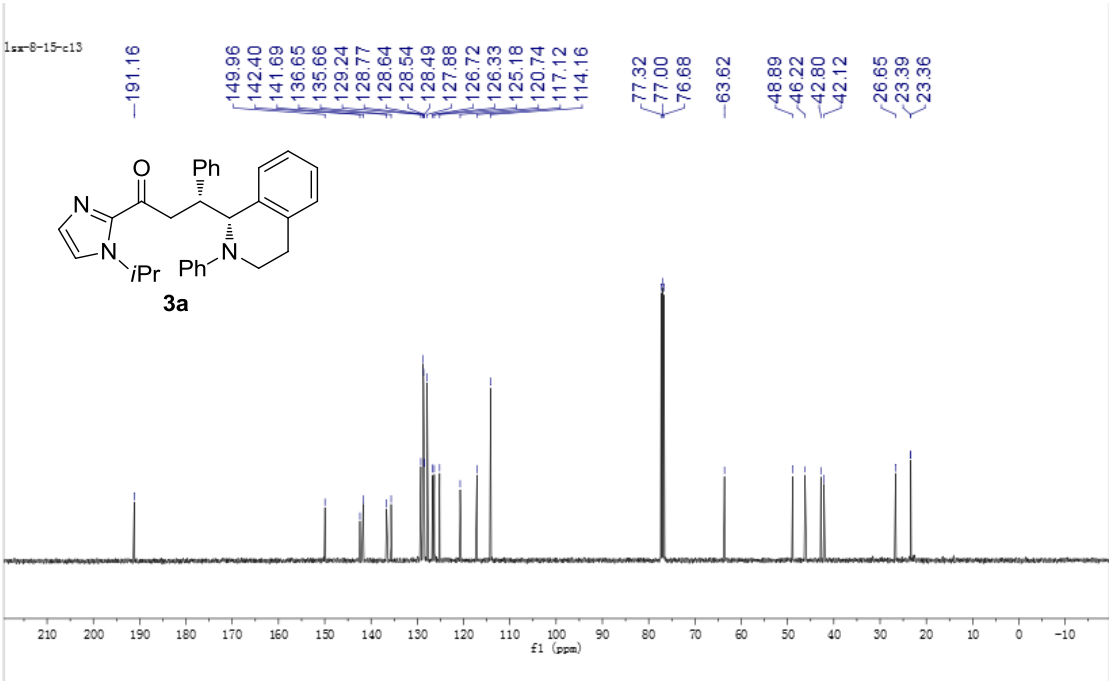
^{1}H NMR spectra of compound **2g**



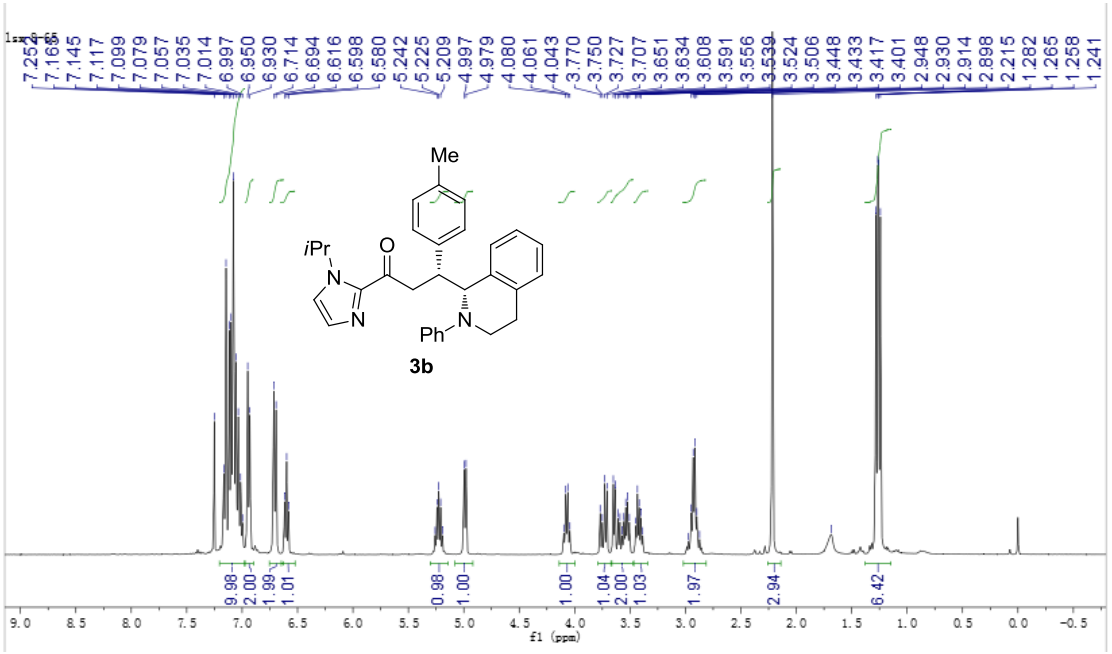
^{1}H NMR spectra of compound **2h**



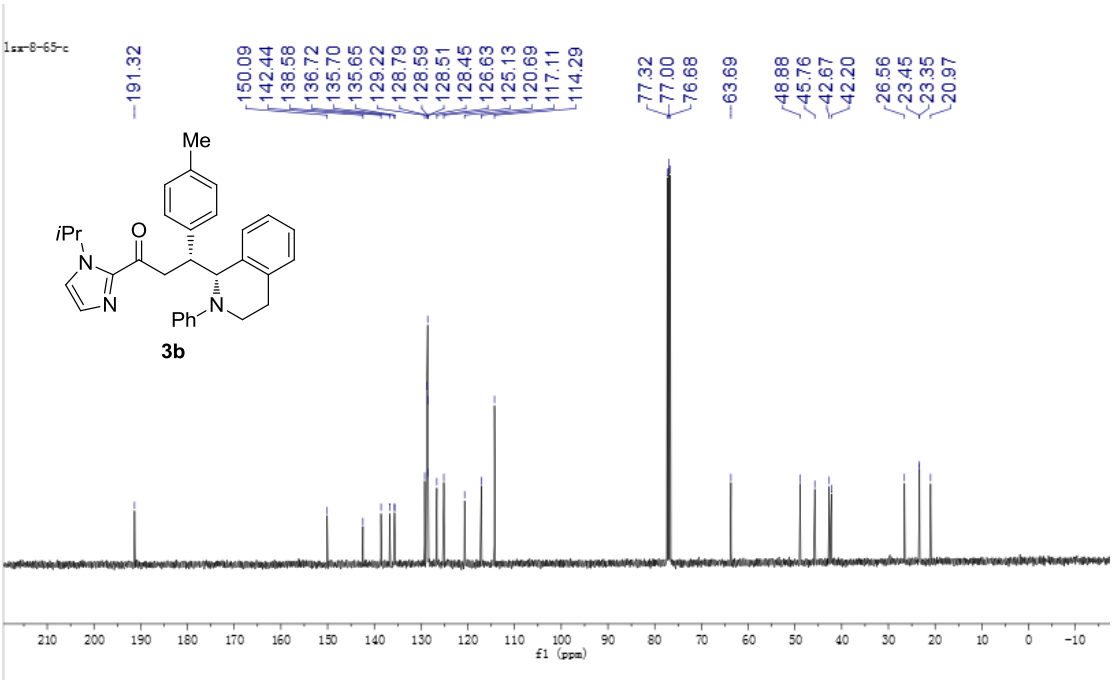
^{1}H NMR spectra of compound **3a**



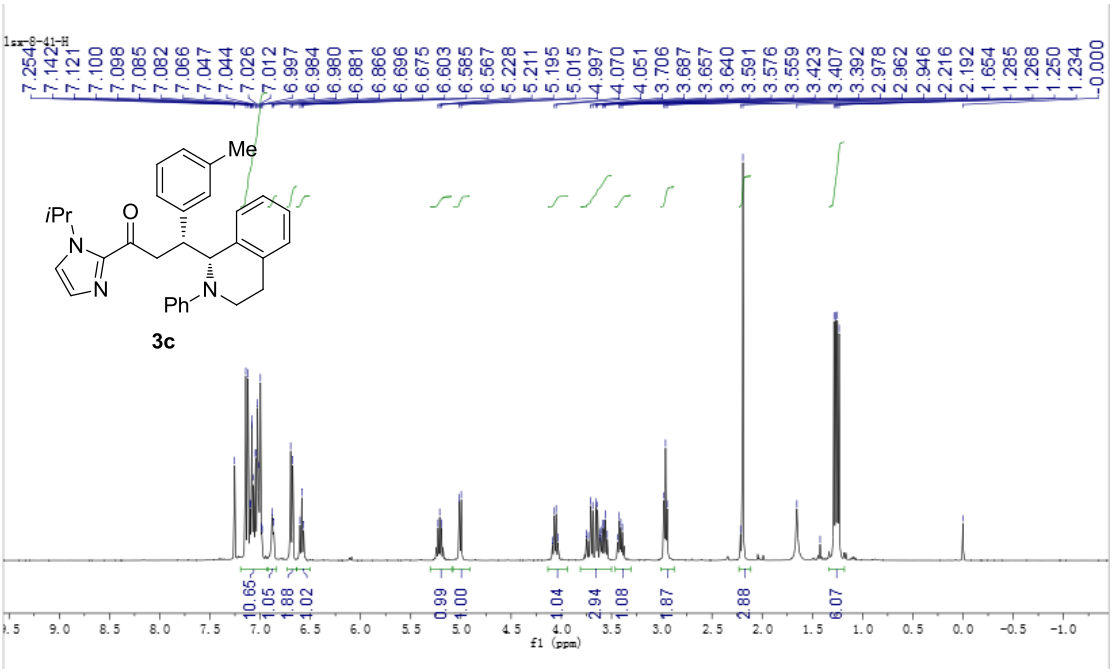
^{13}C NMR spectra of compound **3a**



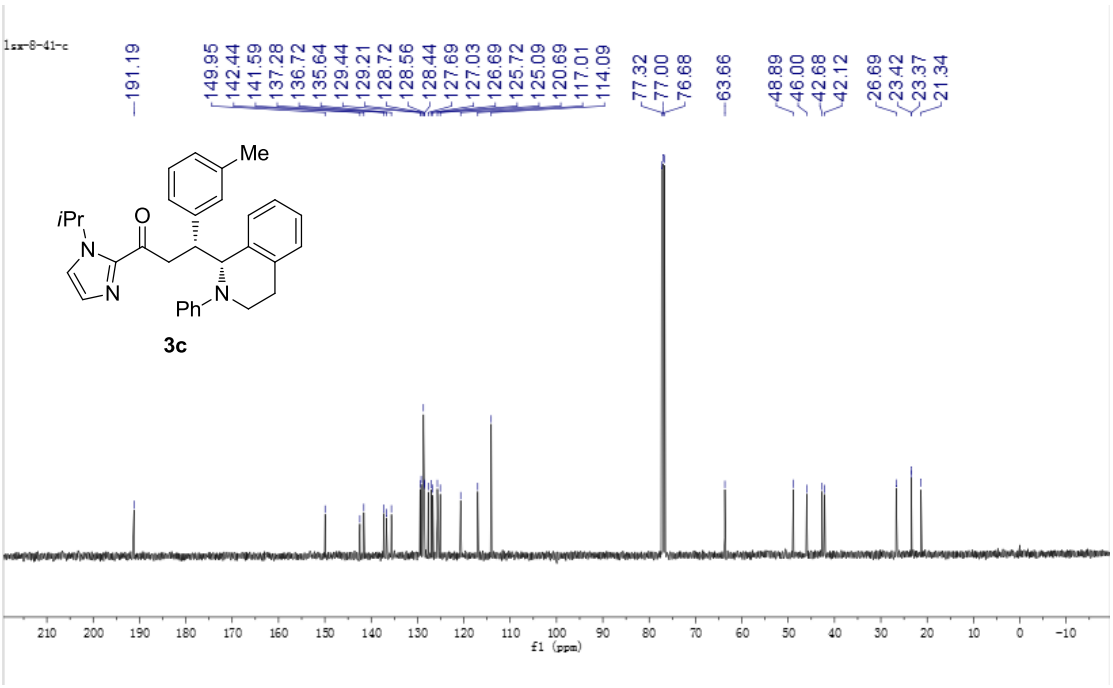
^{1}H NMR spectra of compound **3b**



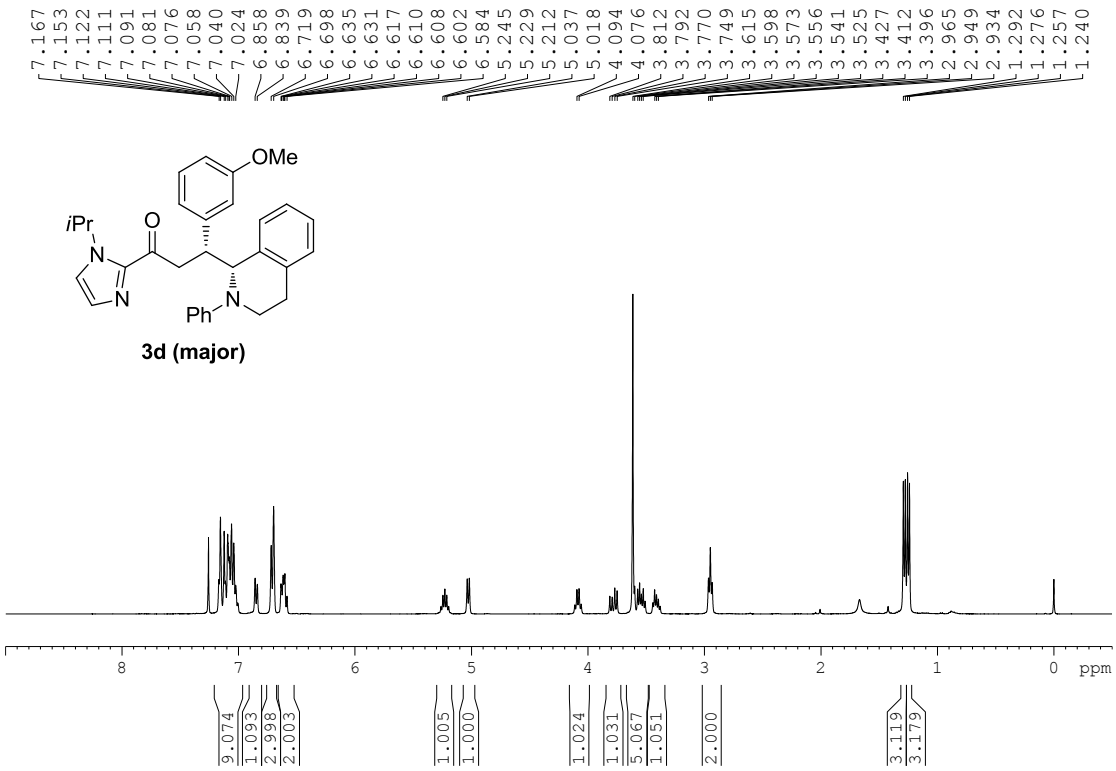
^{13}C NMR spectra of compound **3b**



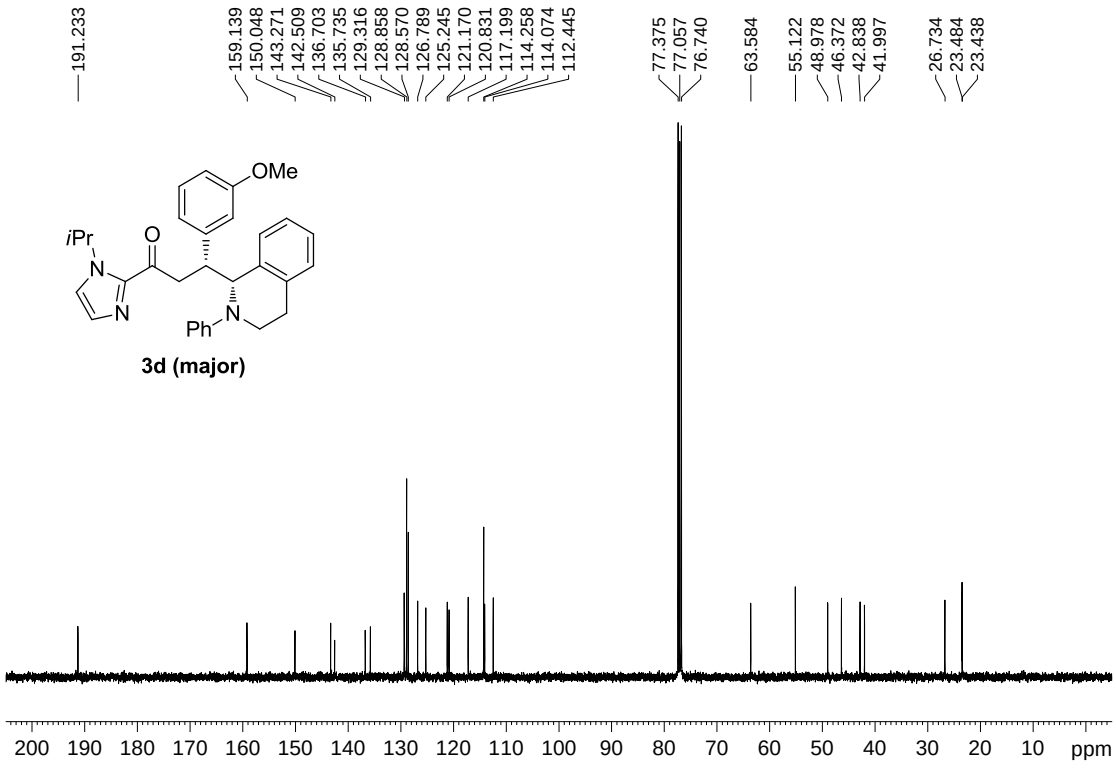
^{1}H NMR spectra of compound **3c**



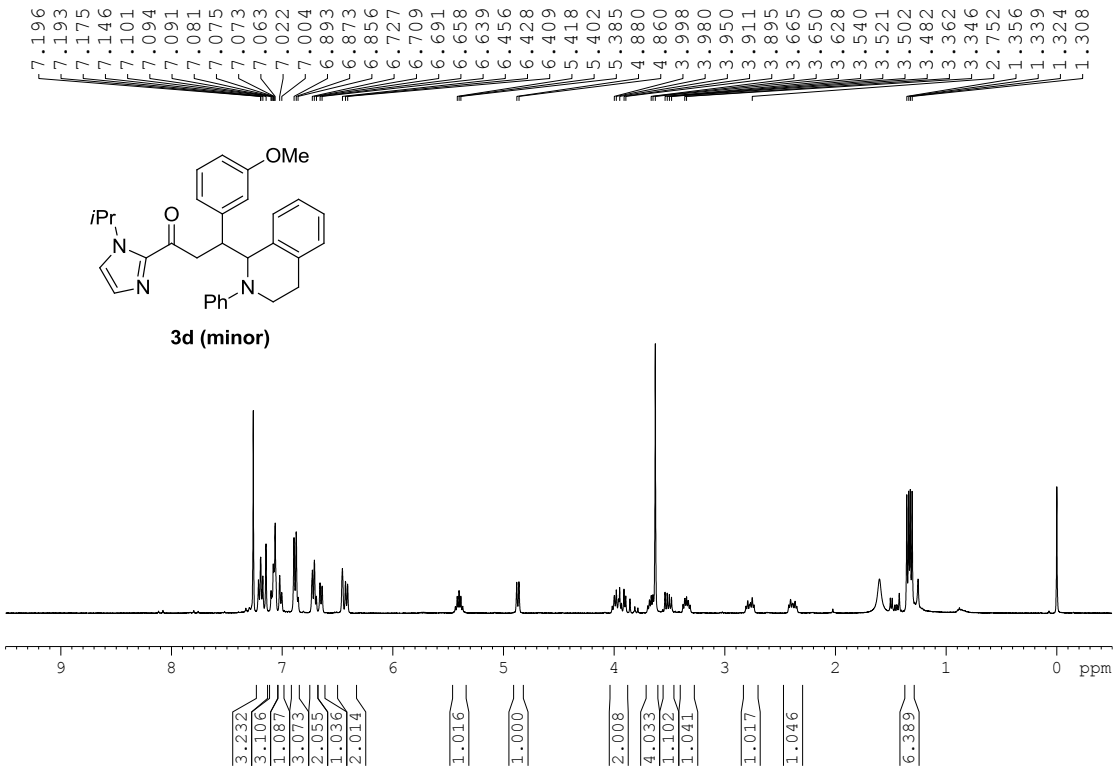
^{13}C NMR spectra of compound **3c**



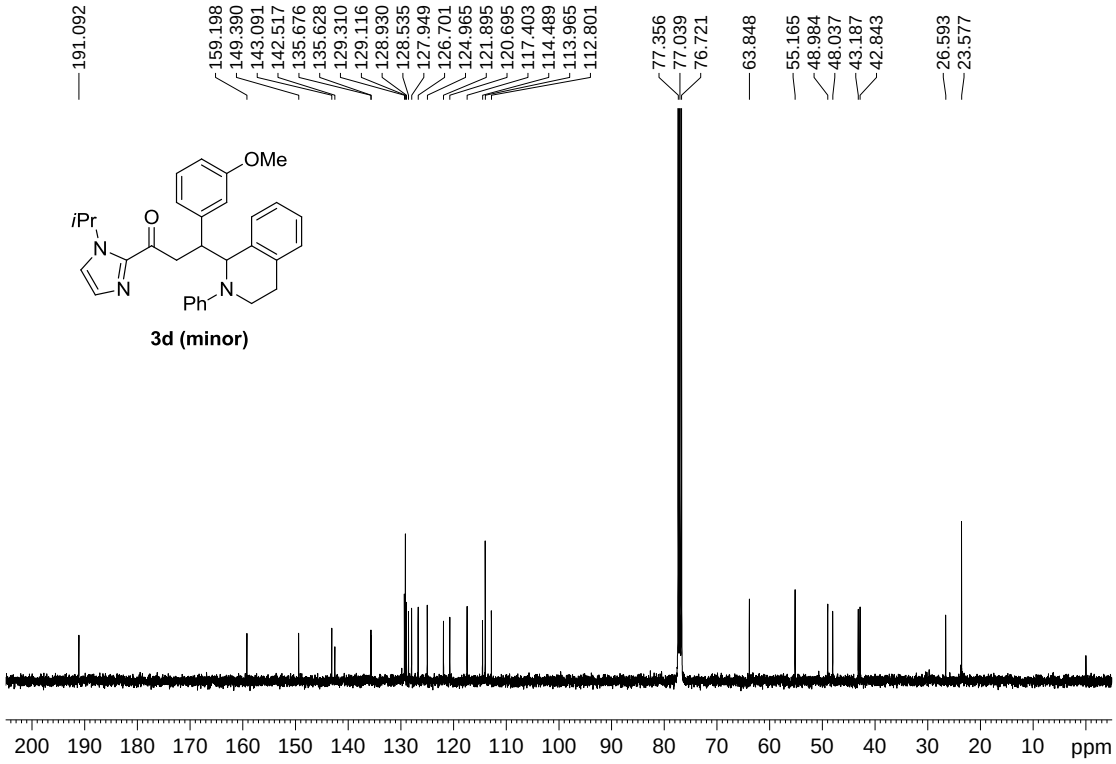
^{1}H NMR spectra of compound **3d**



^{13}CNMR spectra of compound **3d**



^{1}H NMR spectra of compound **3d**



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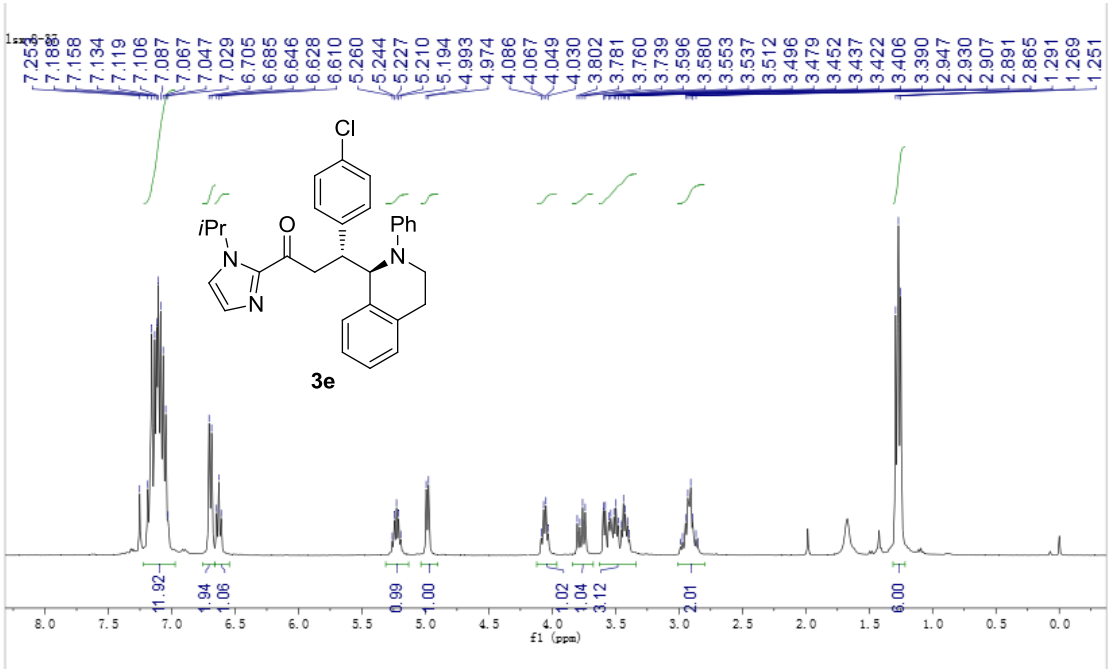
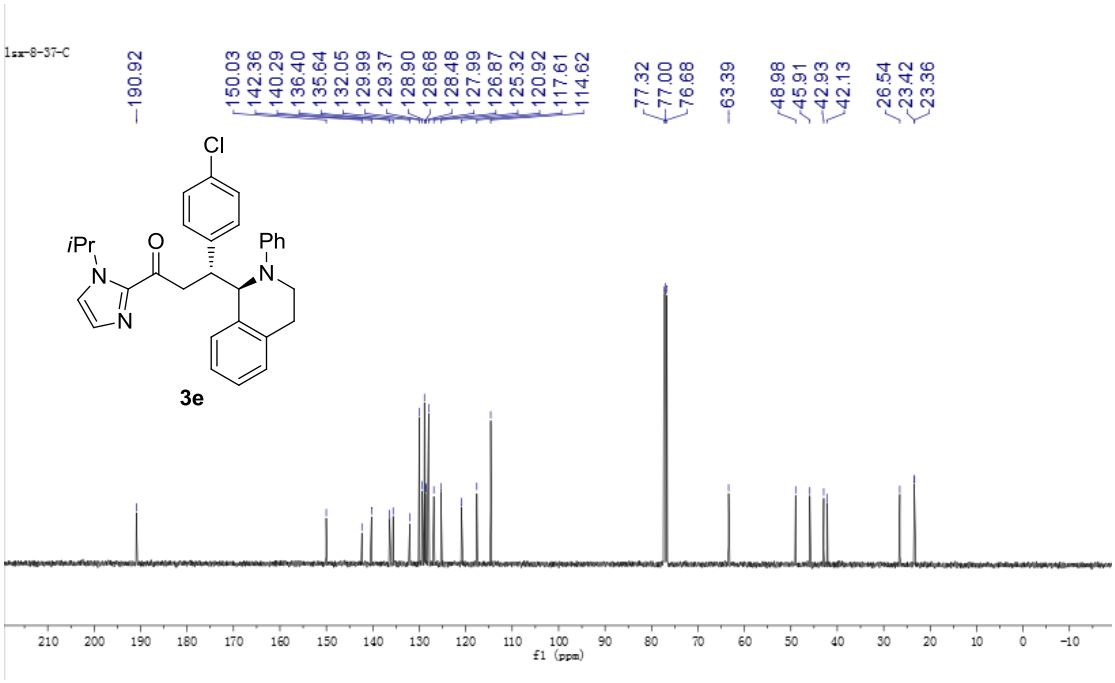
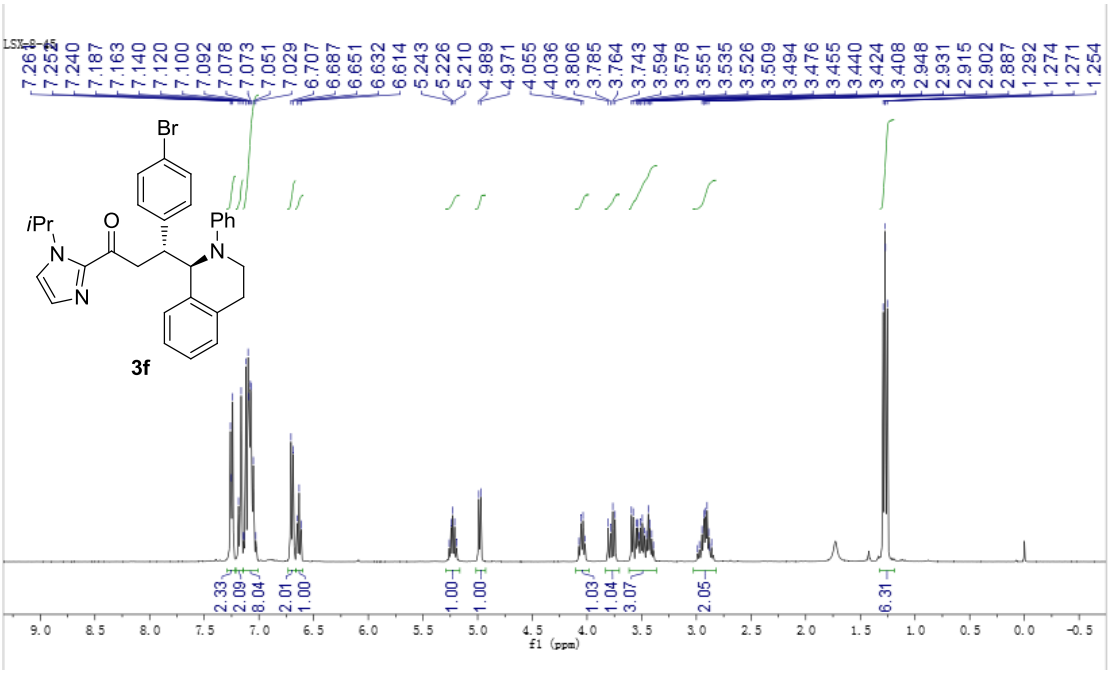


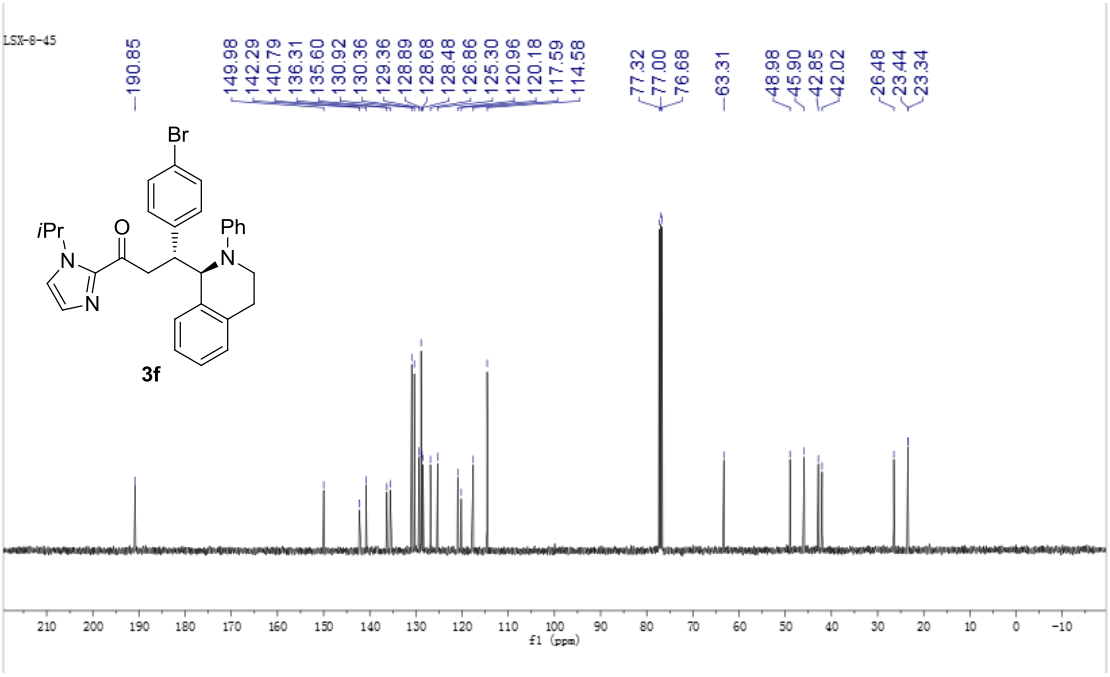
^{1}H NMR spectra of compound **3e**



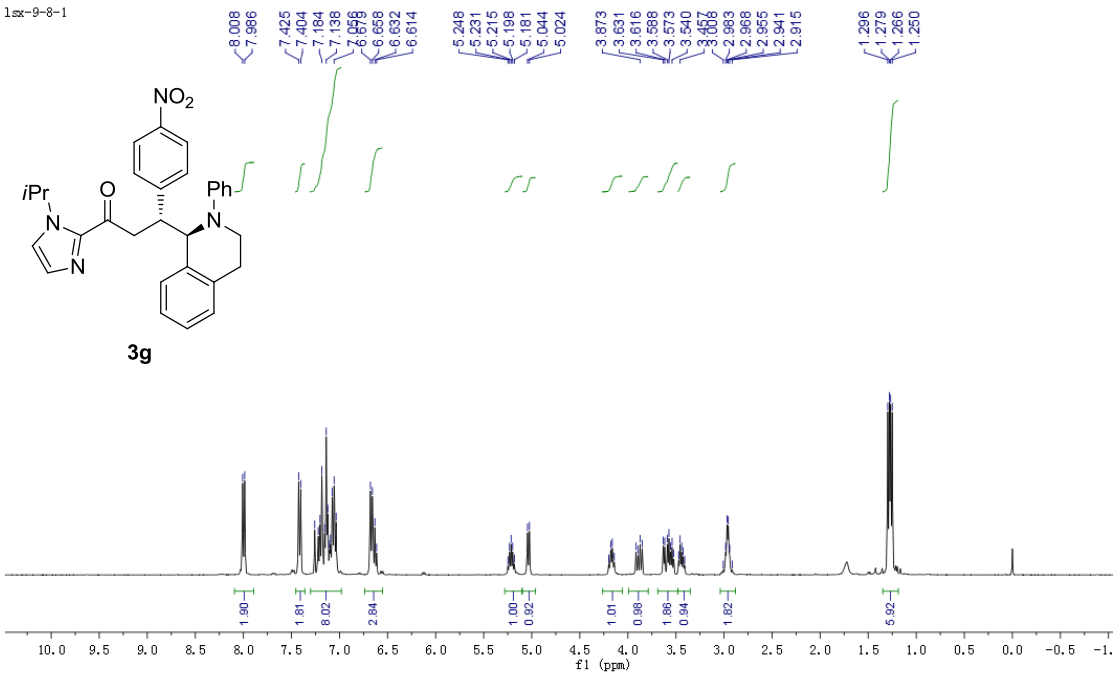
^{13}CNMR spectra of compound **3e**



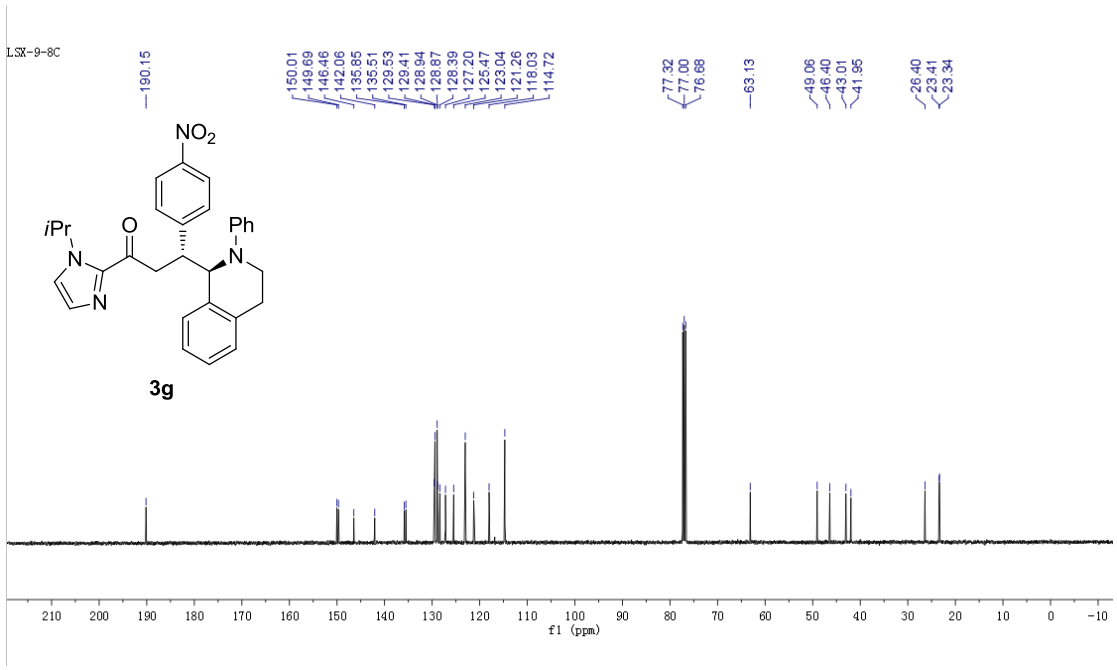
^{1}H NMR spectra of compound **3f**



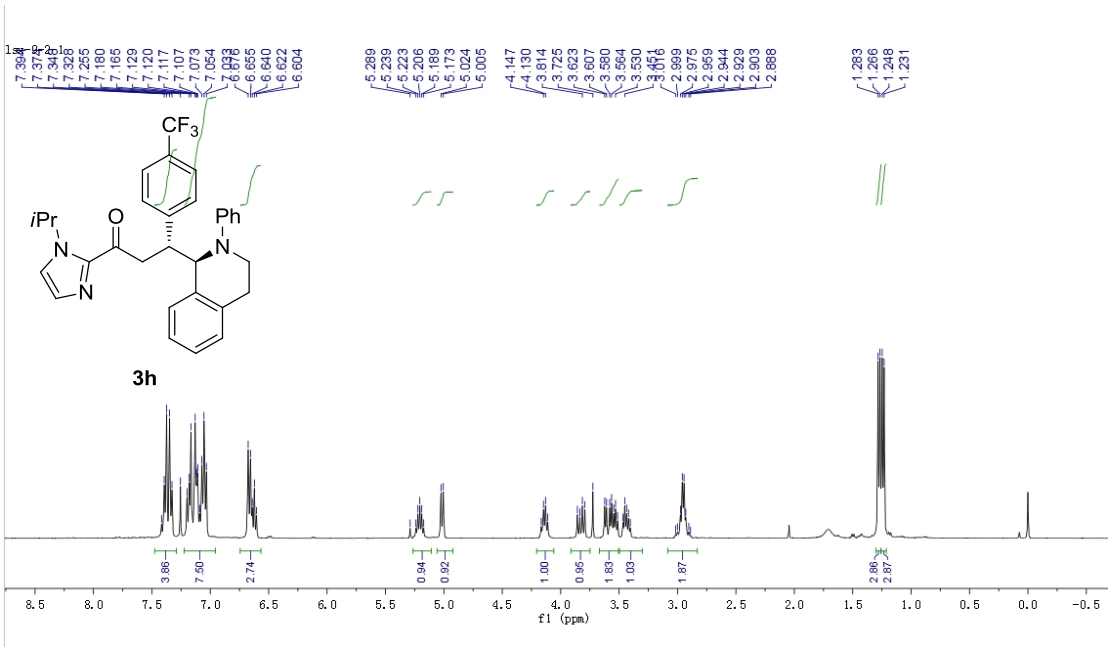
^{13}CNMR spectra of compound **3f**



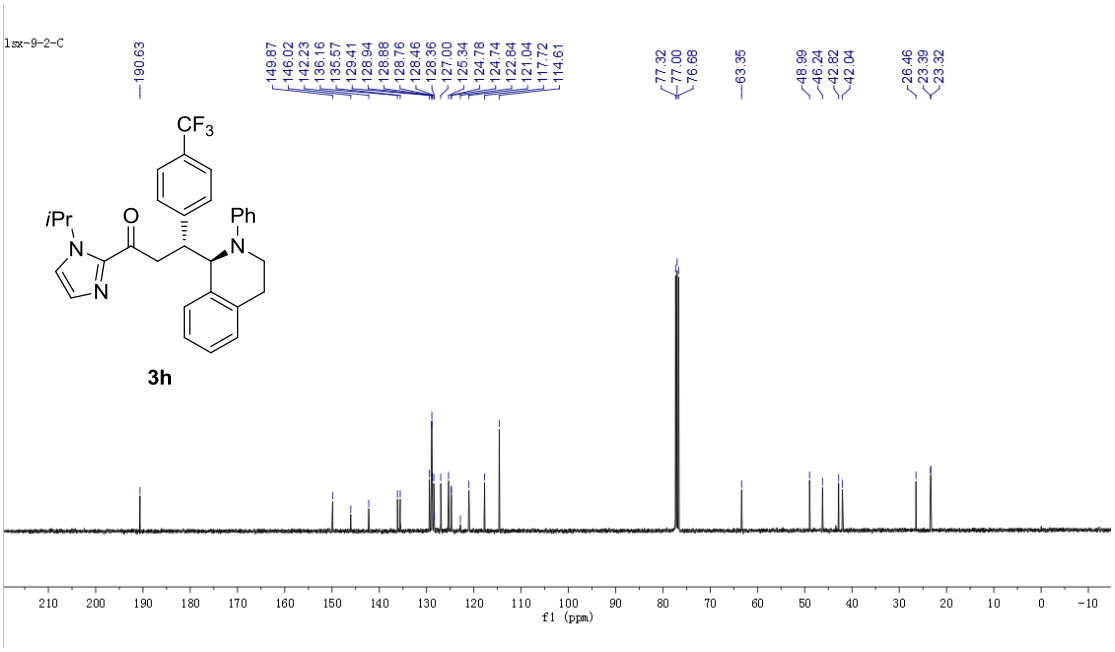
^{1}H NMR spectra of compound **3g**



^{13}CNMR spectra of compound **3g**



^{1}H NMR spectra of compound **3h**



^{13}C NMR spectra of compound **3h**

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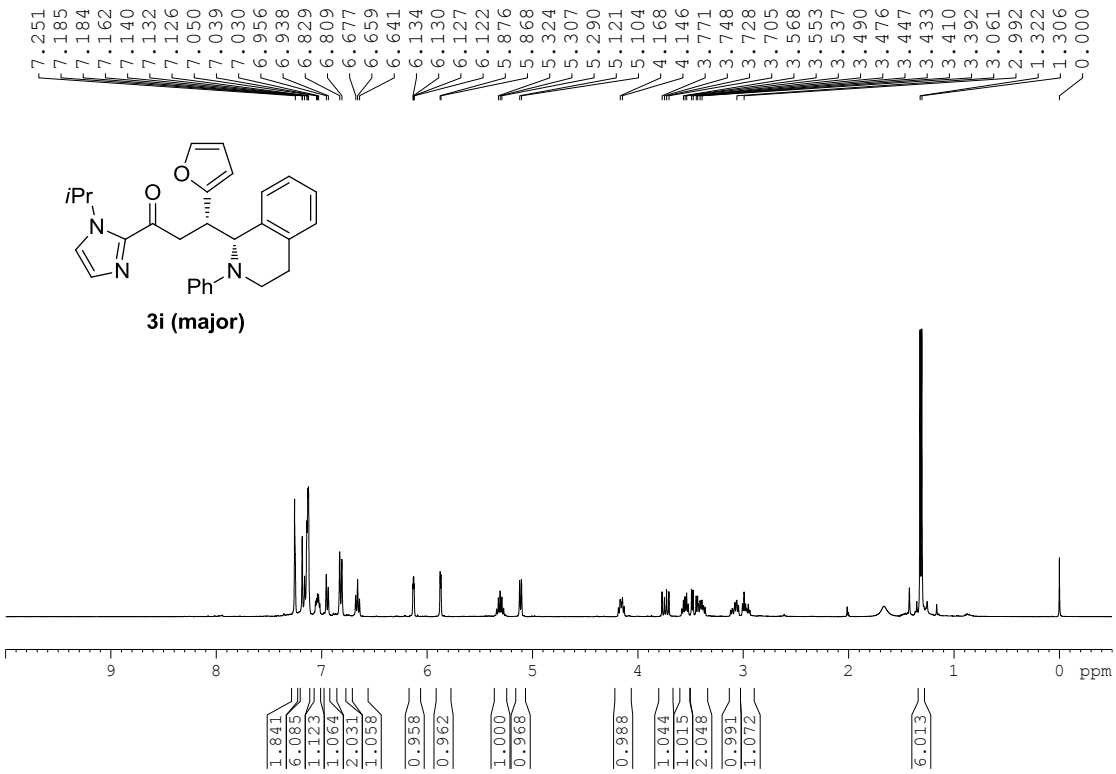
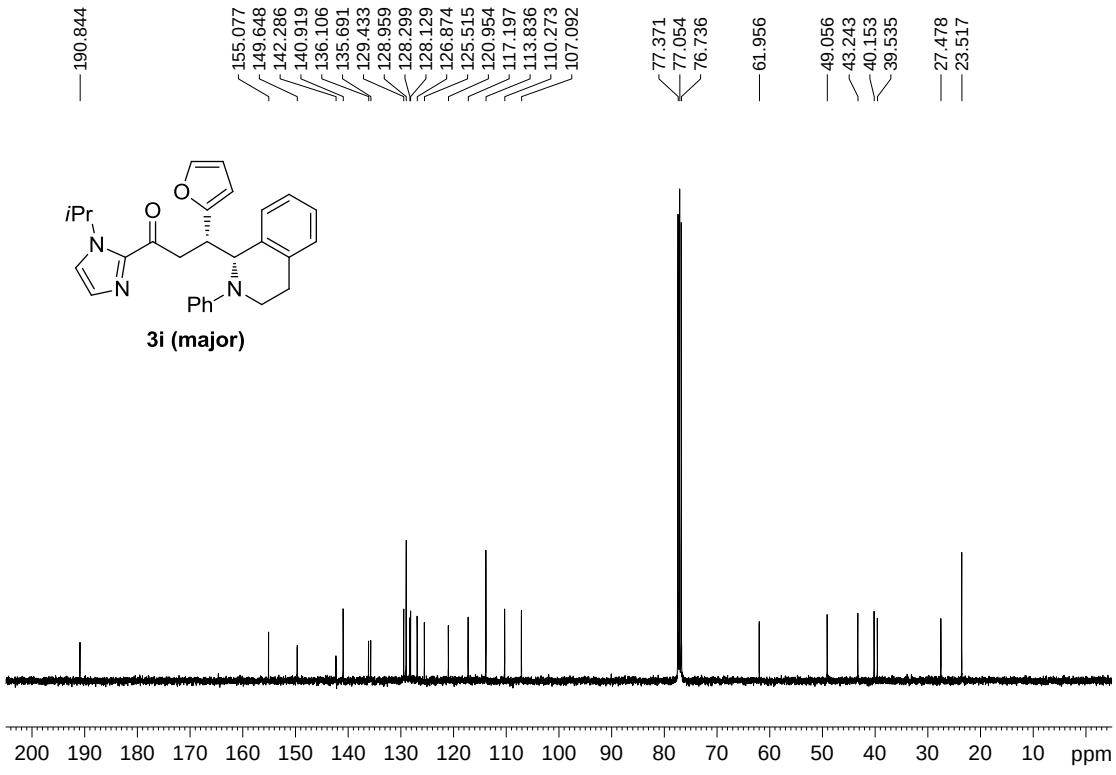
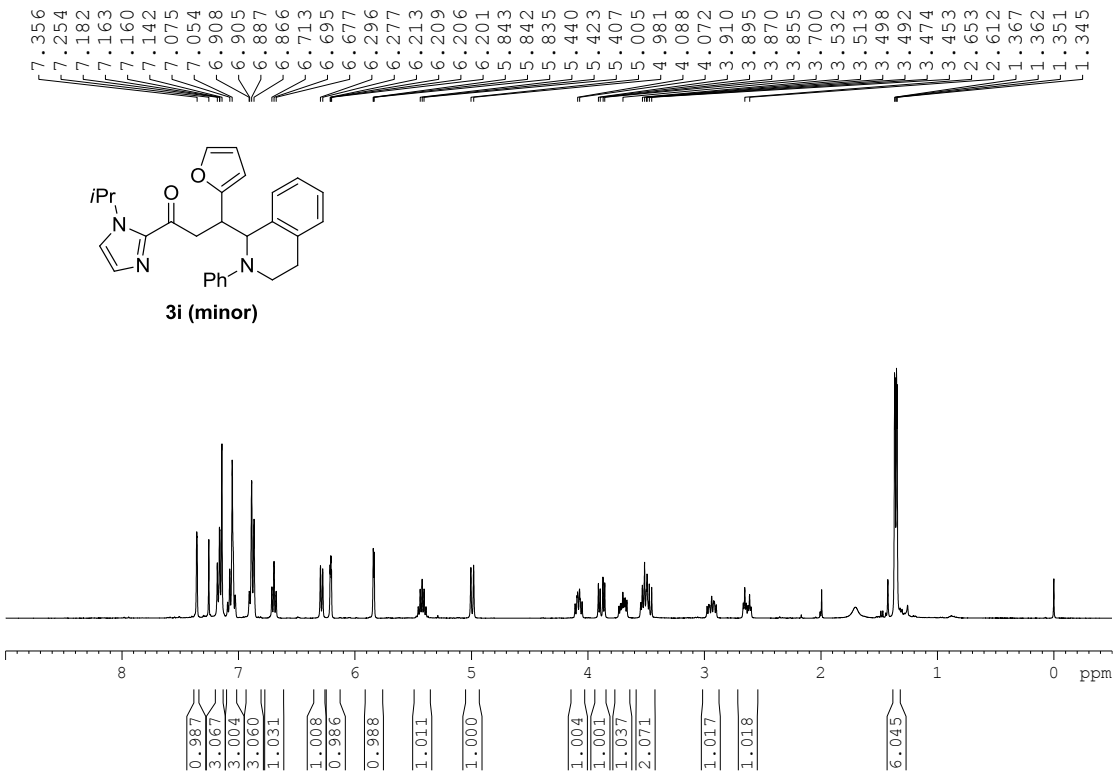


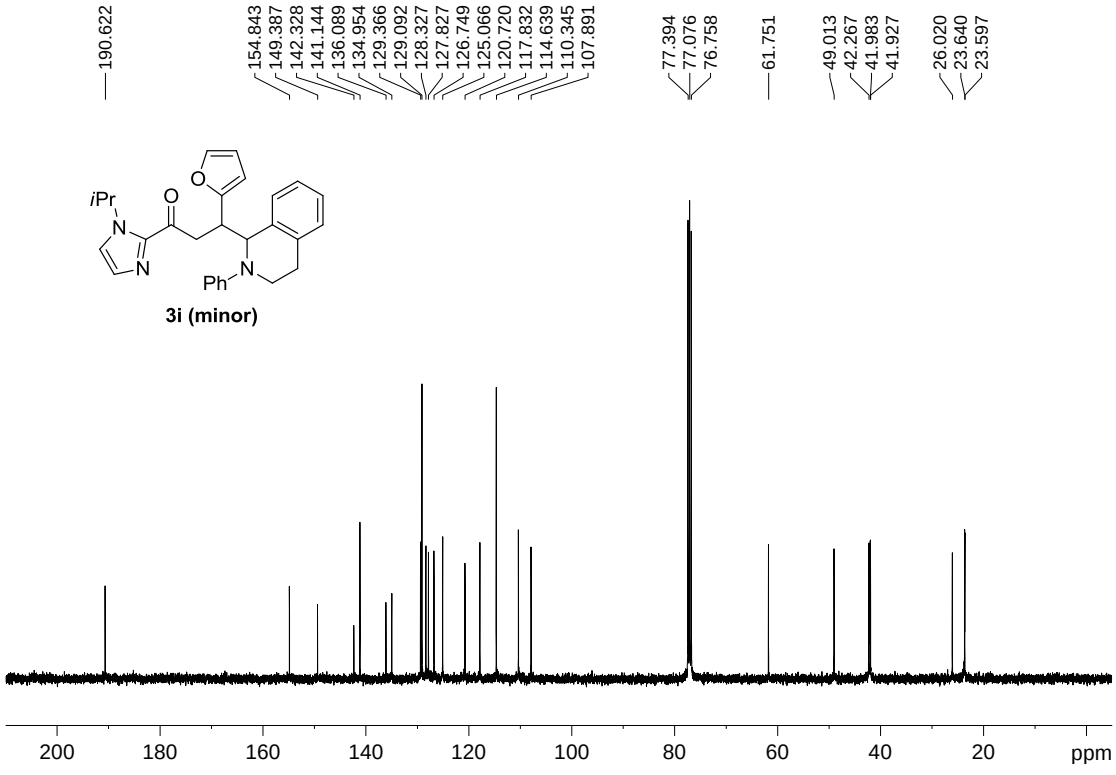
^{1}H NMR spectra of compound **3i**



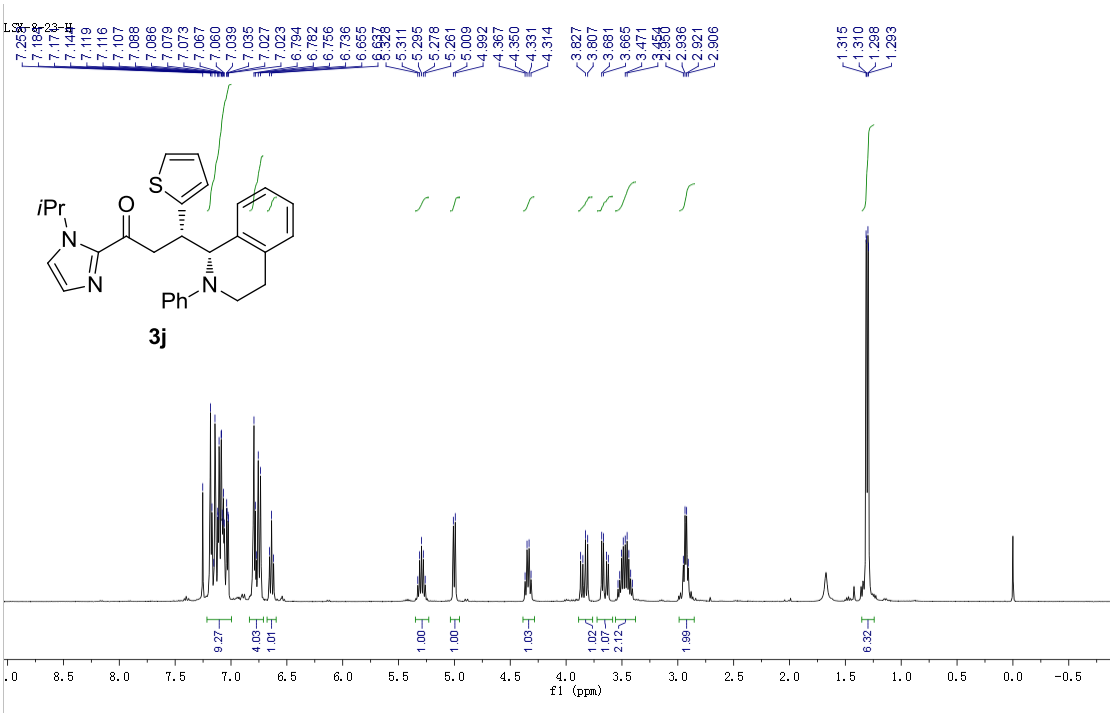
^{13}C NMR spectra of compound **3i**



^{1}H NMR spectra of compound **3i**



^{13}C NMR spectra of compound **3i**



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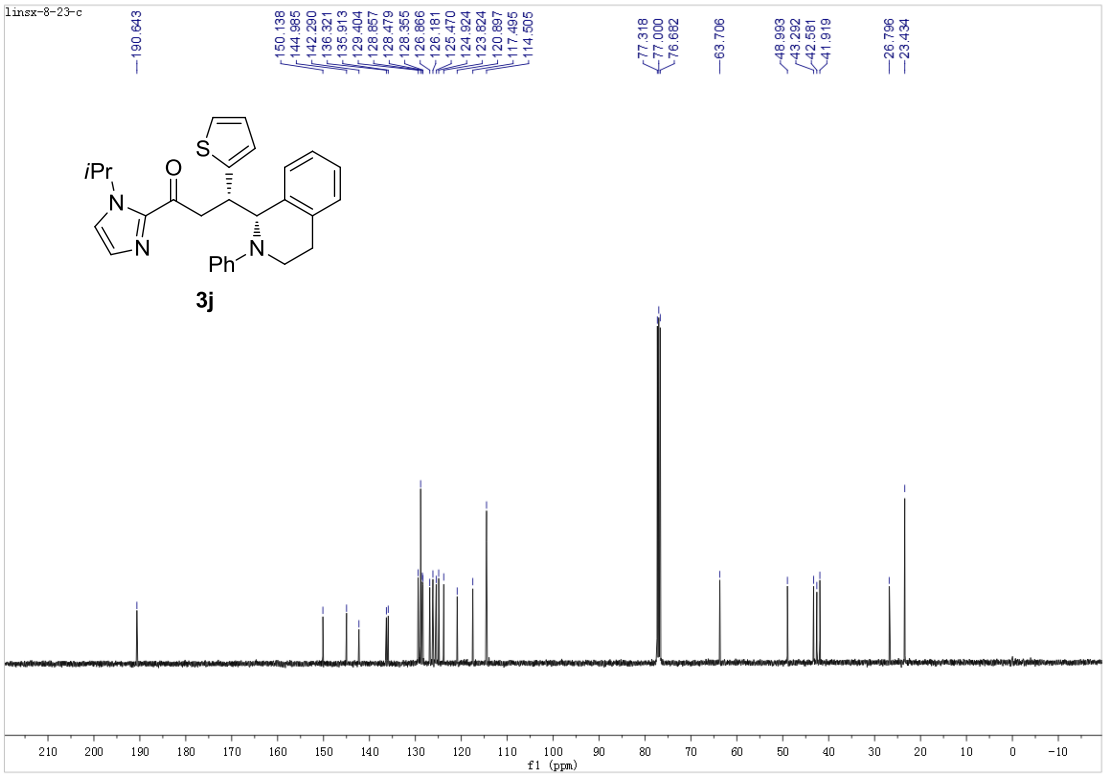

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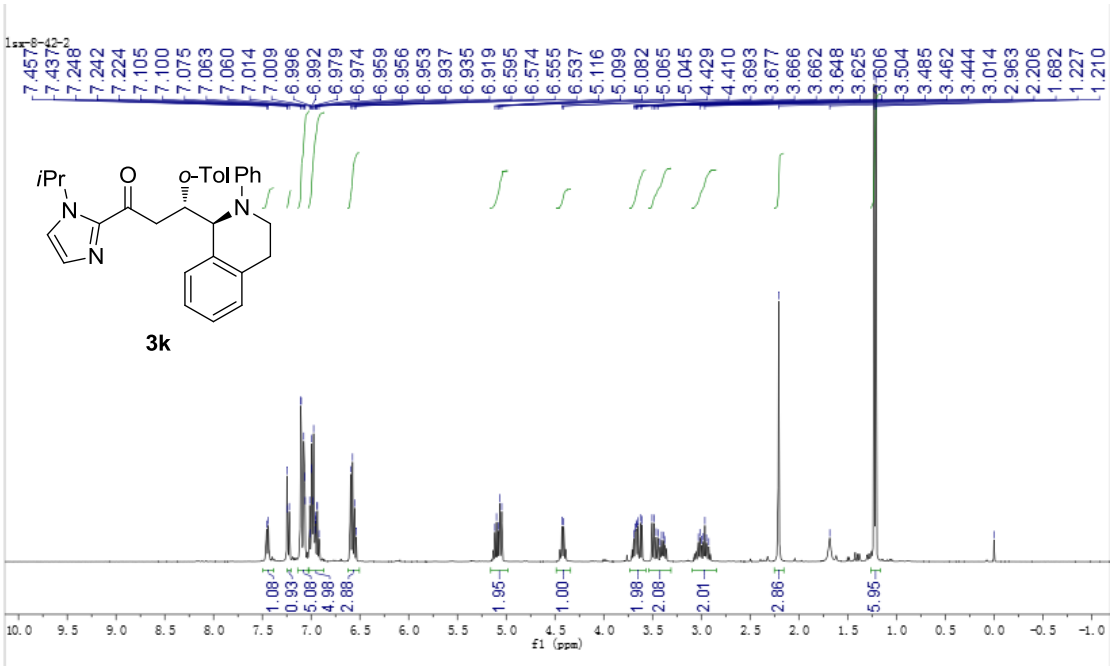
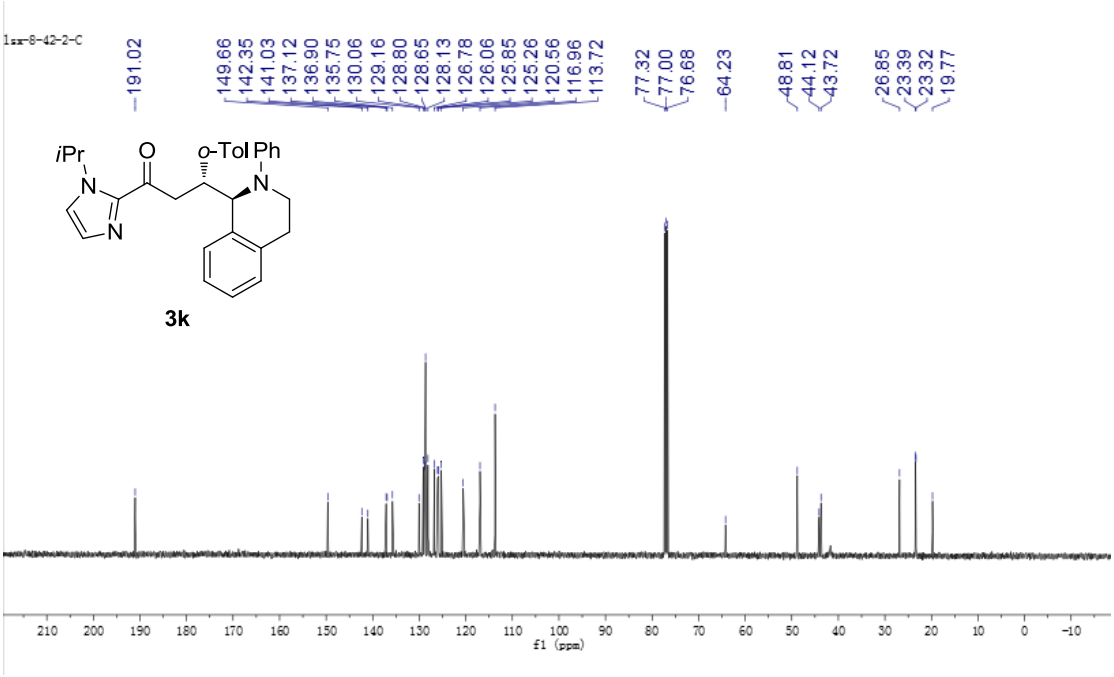
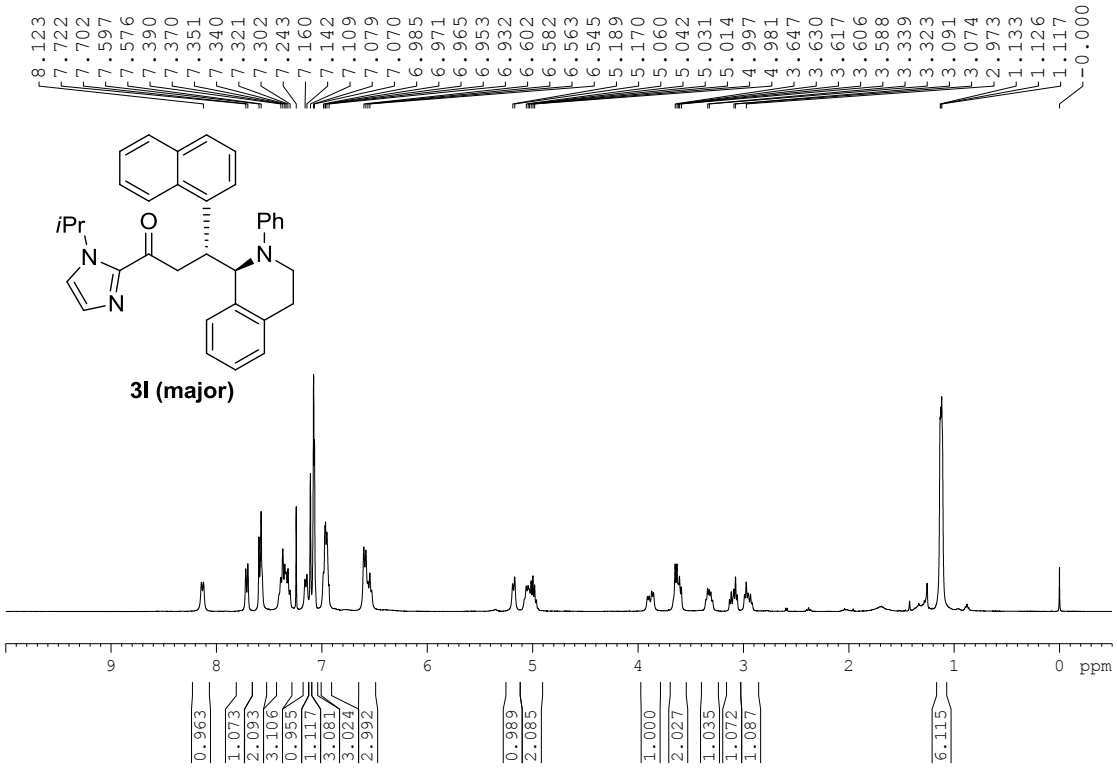


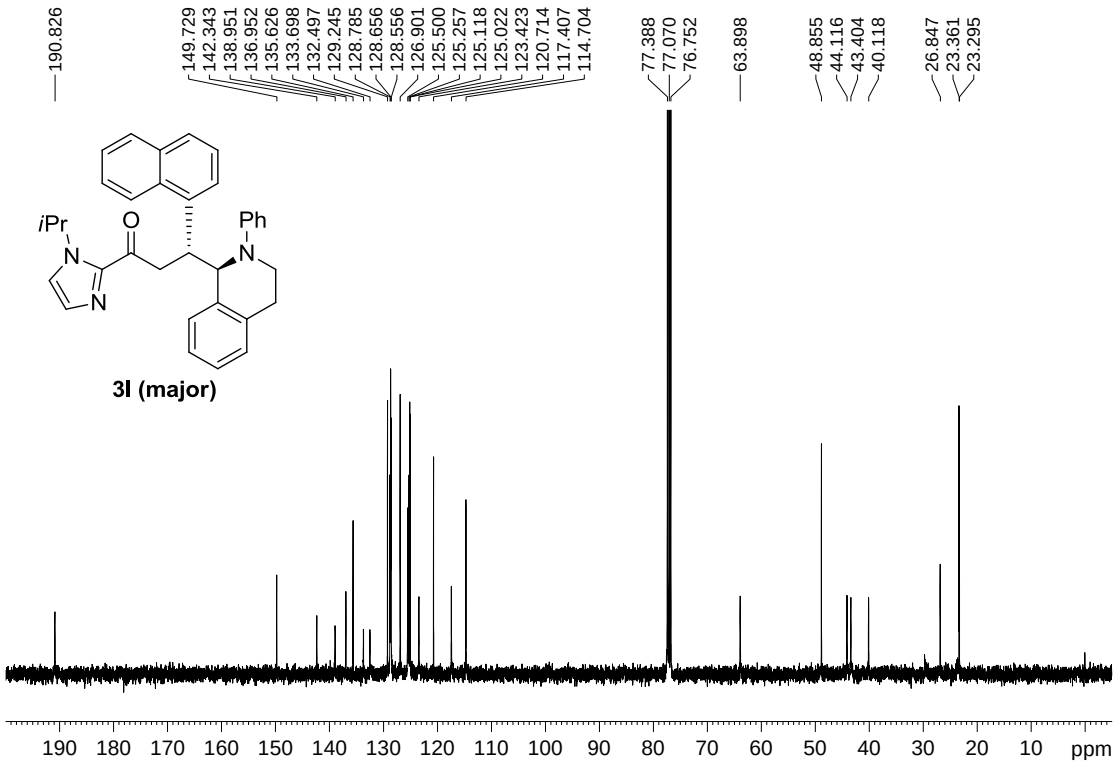
^{1}H NMR spectra of compound **3k**



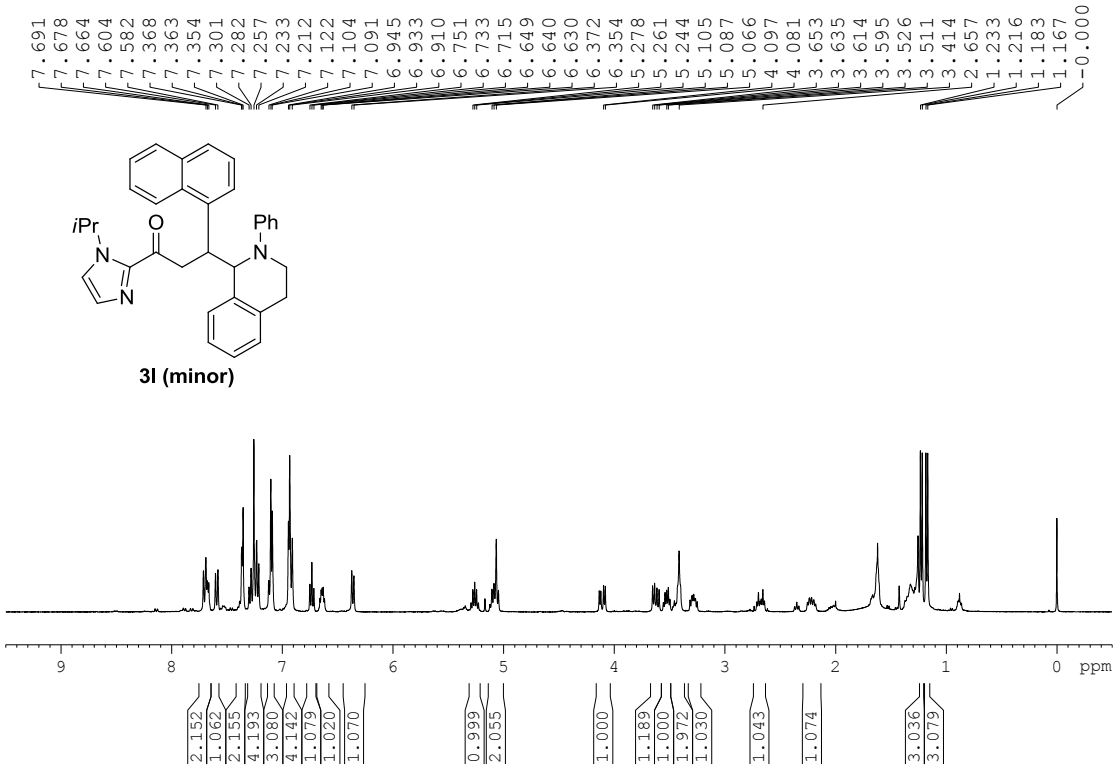
^{13}C NMR spectra of compound **3k**



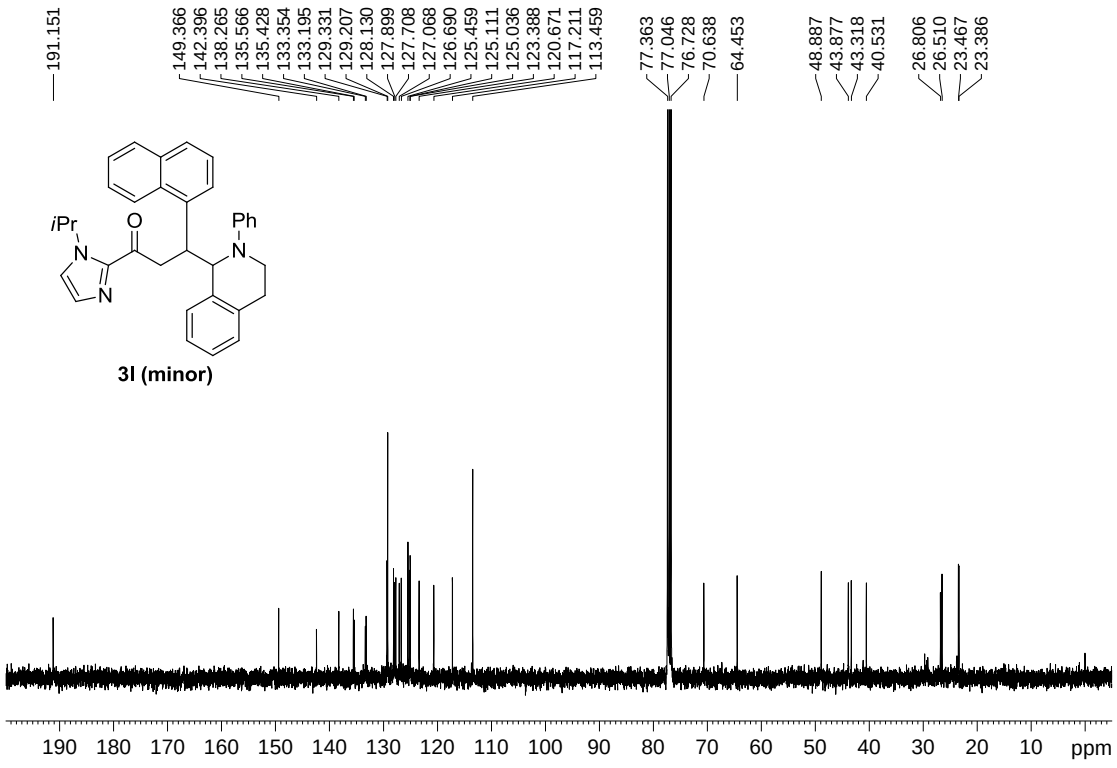
^{1}H NMR spectra of compound **3l**



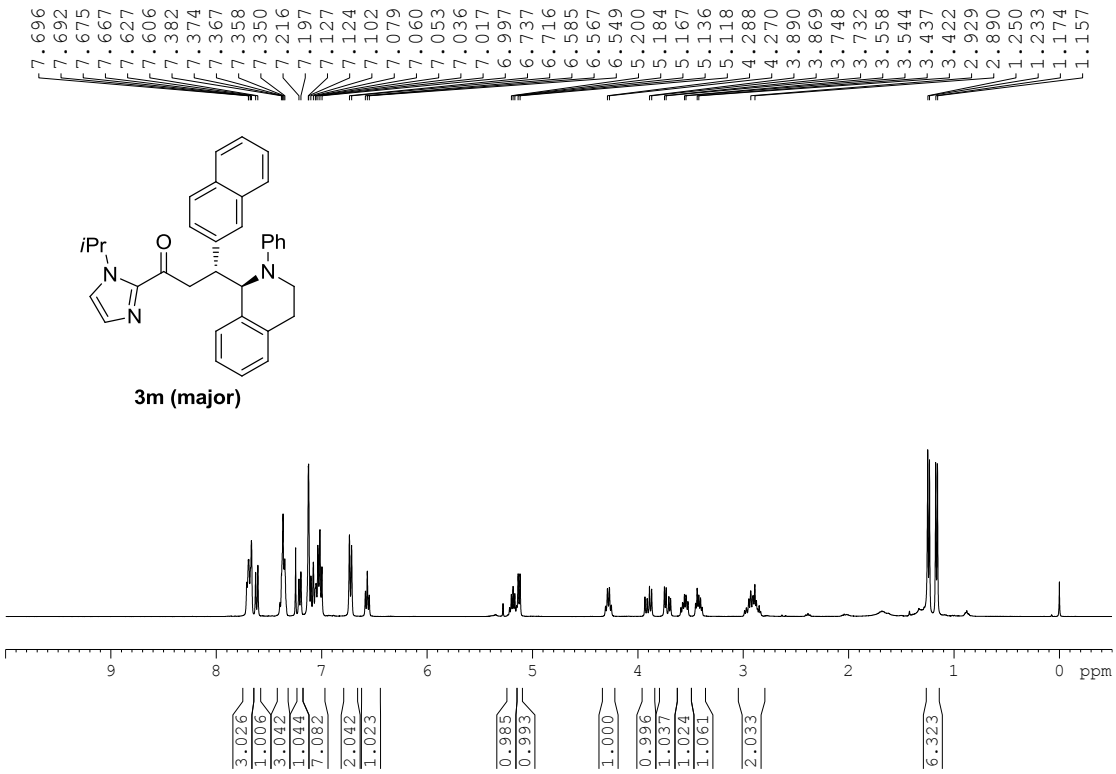
^{13}C NMR spectra of compound **3l**



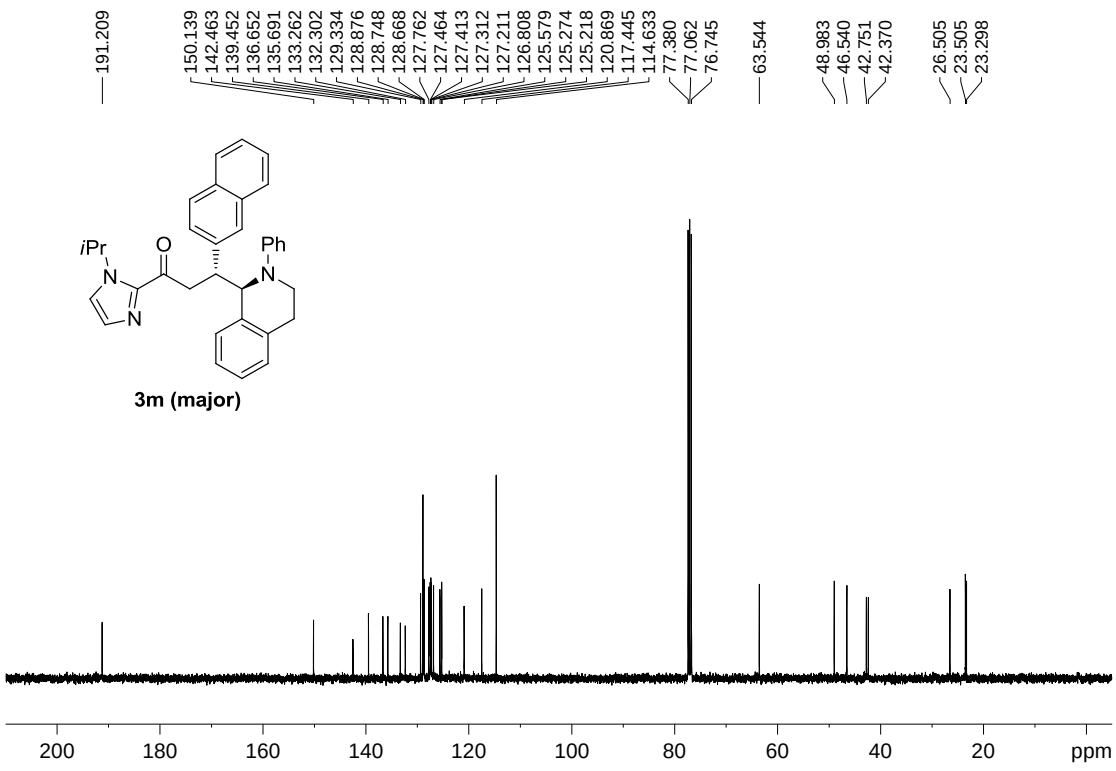
^{1}H NMR spectra of compound **3l**



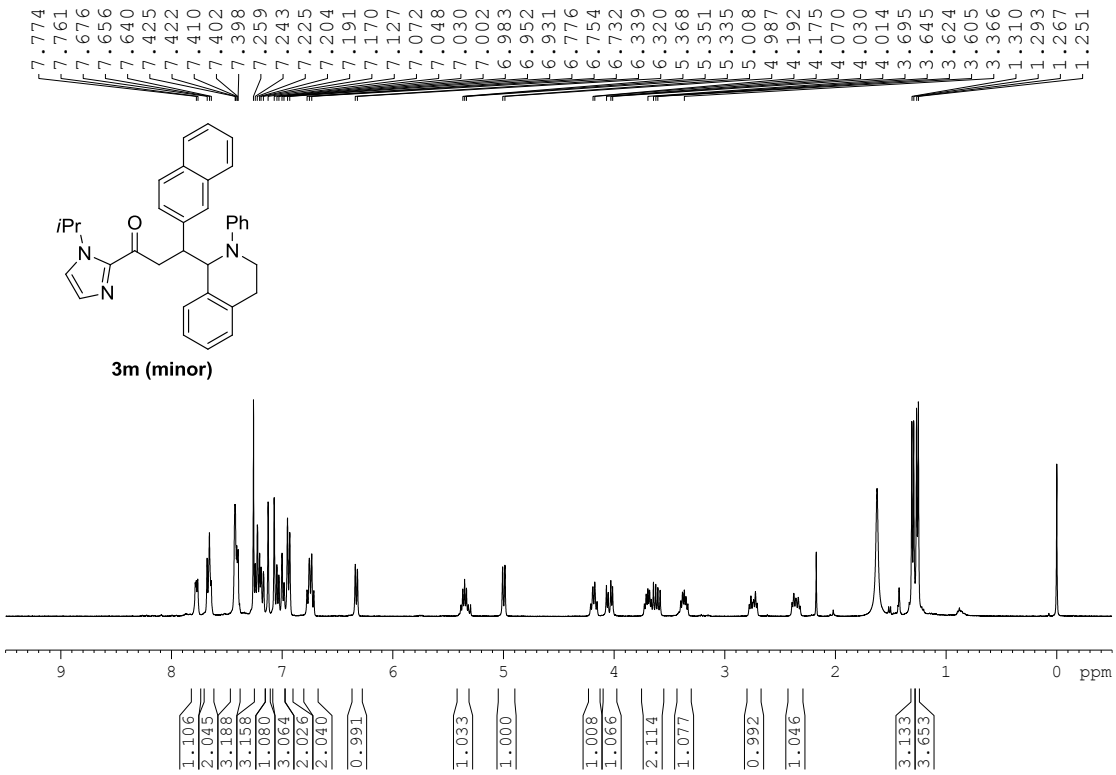
^{13}C NMR spectra of compound **3l**



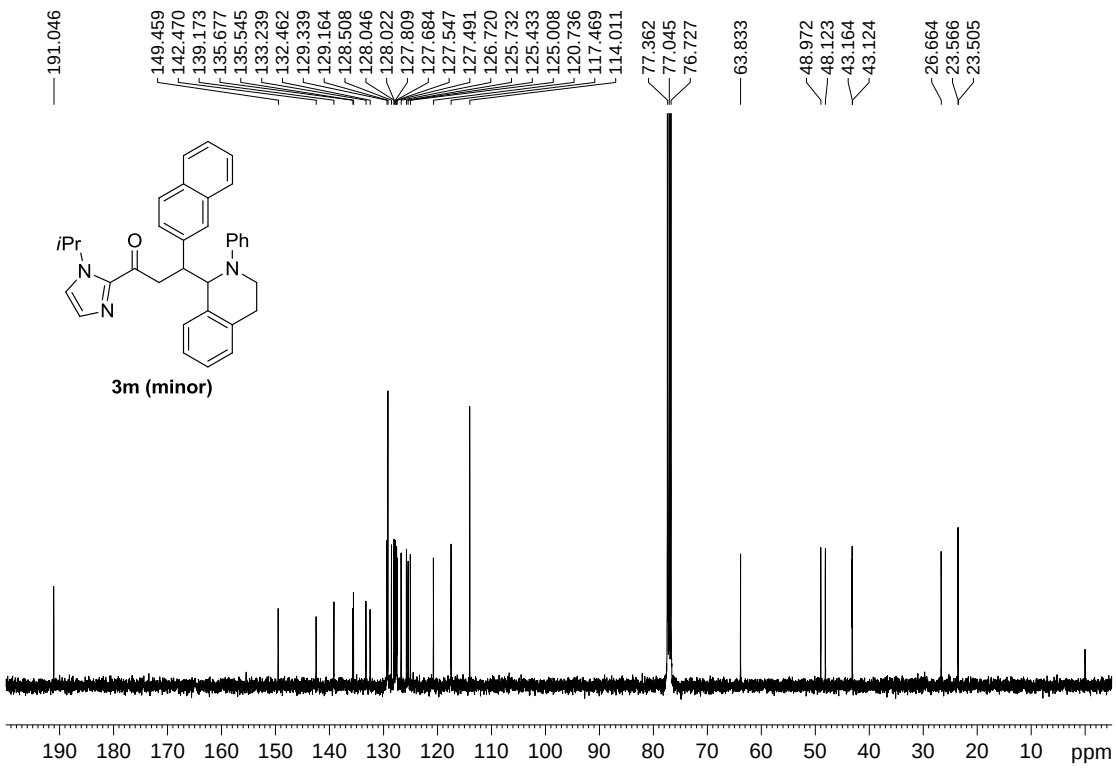
^{1}H NMR spectra of compound **3m**



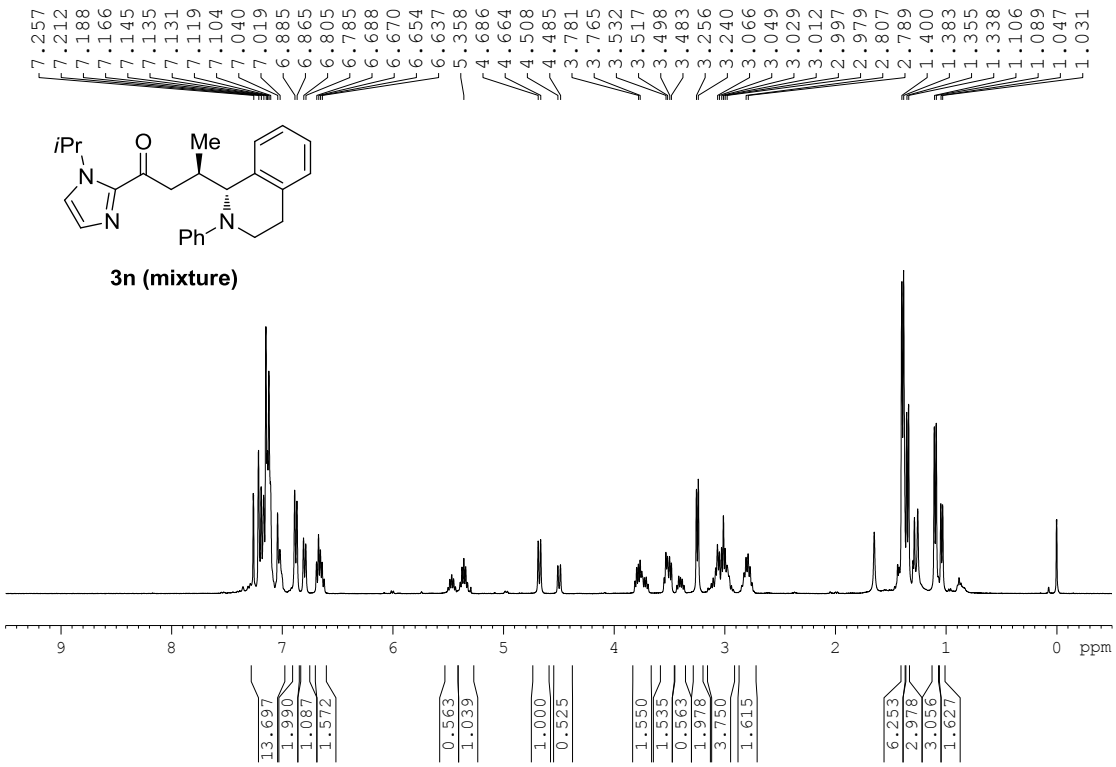
^{13}C NMR spectra of compound **3m**



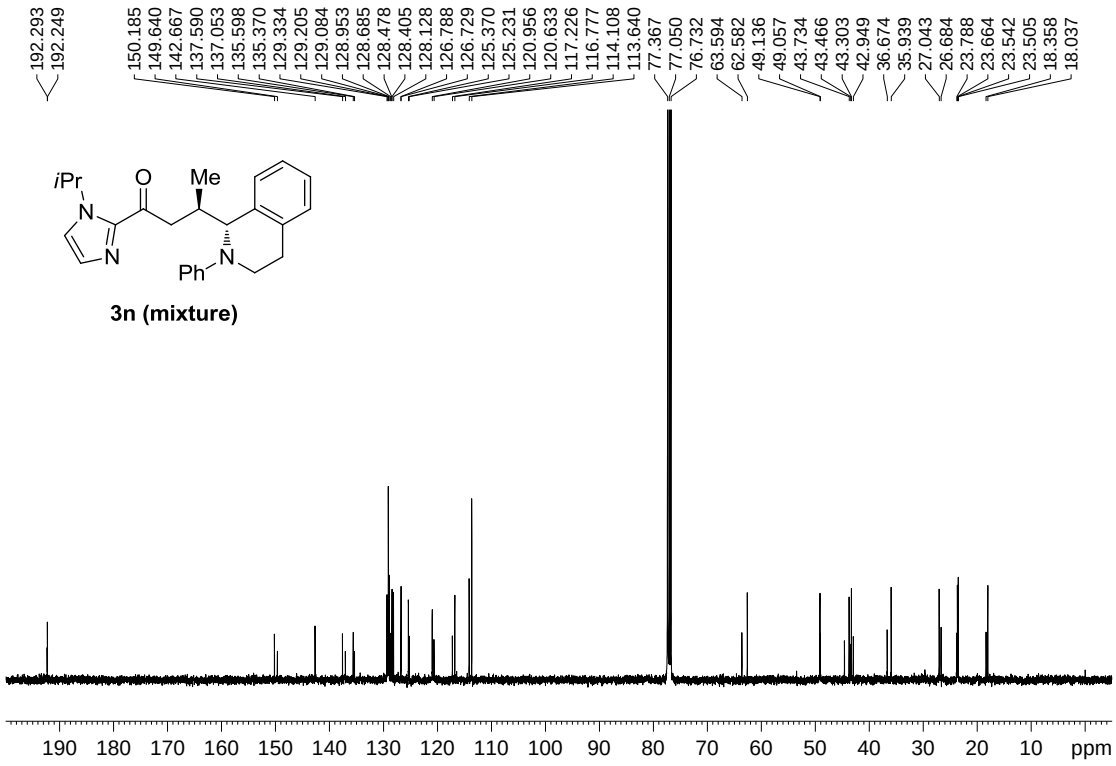
^{1}H NMR spectra of compound **3m**



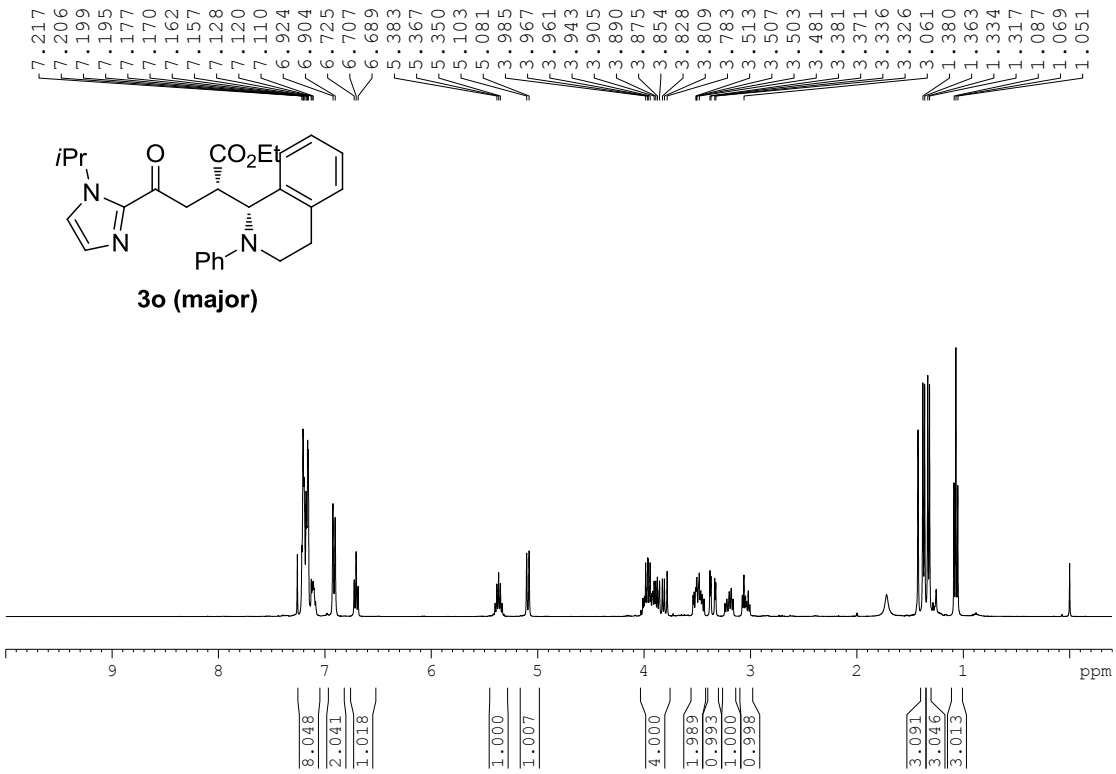
^{13}C NMR spectra of compound **3m**



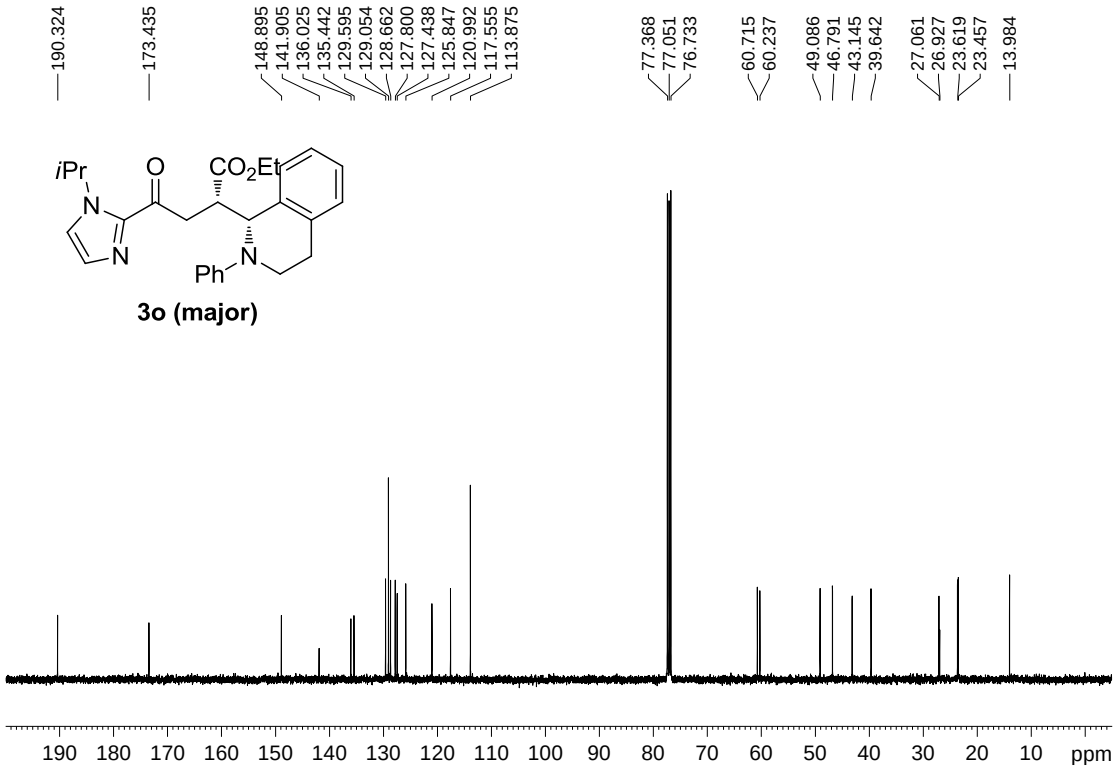
^{1}H NMR spectra of compound **3n**



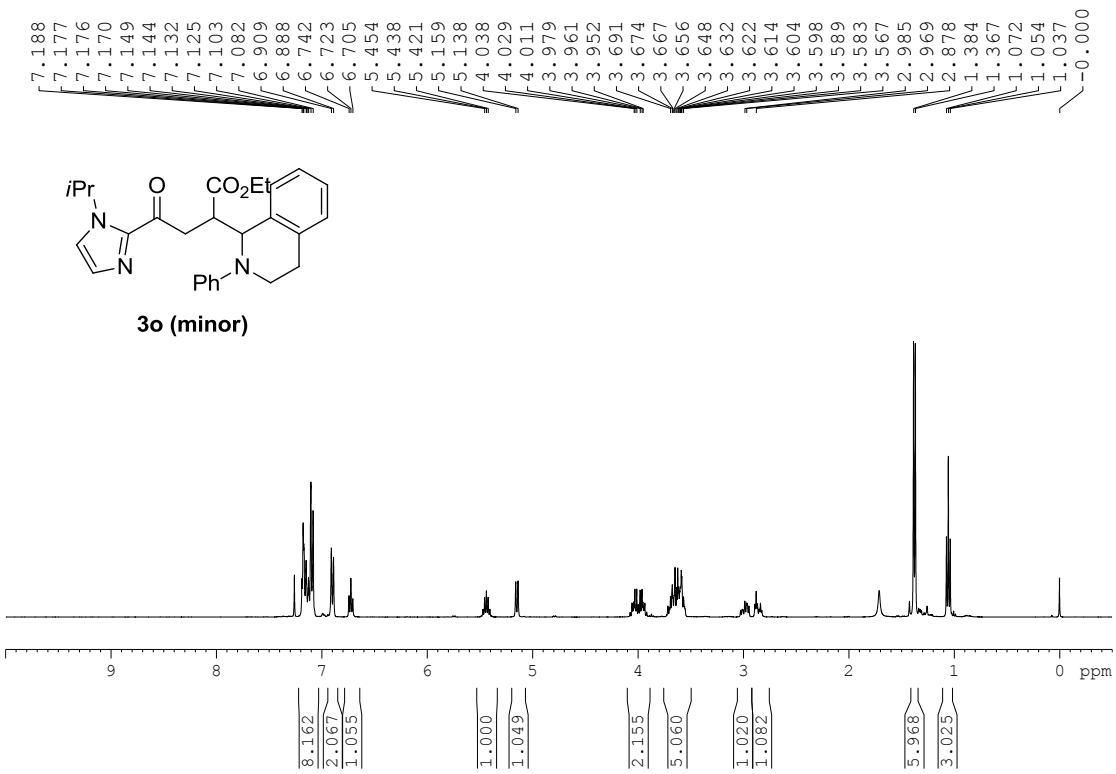
^{13}C NMR spectra of compound **3n**



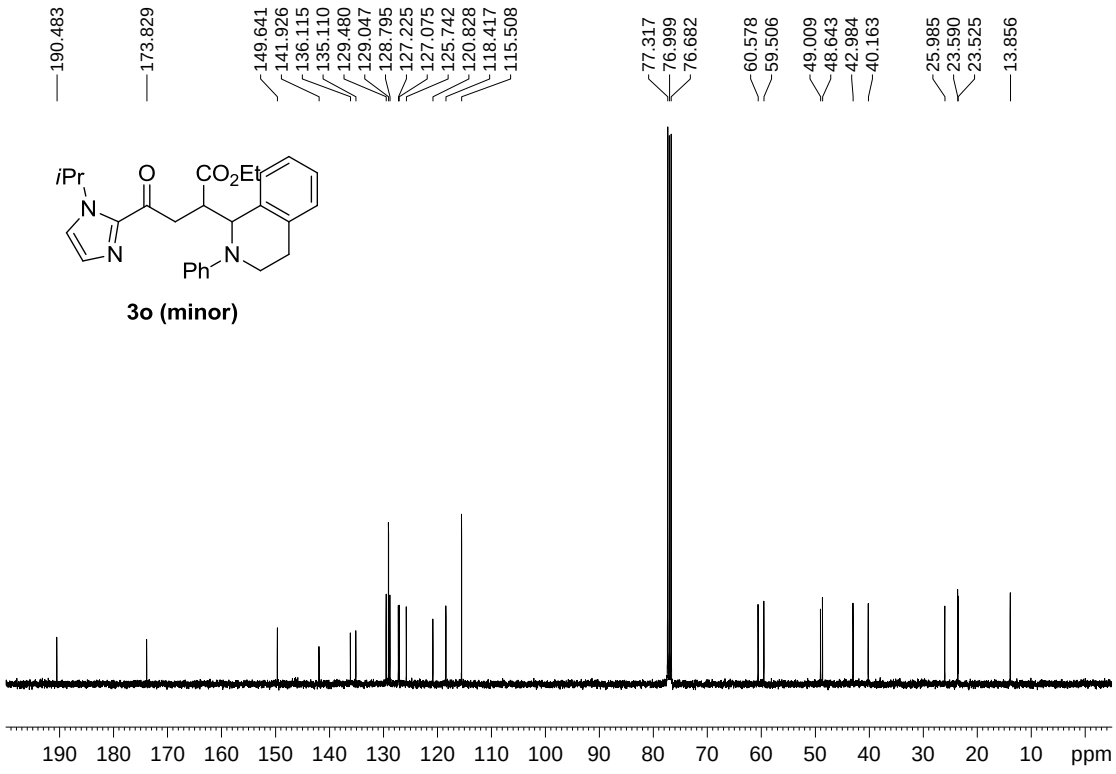
^{1}H NMR spectra of compound **3o**



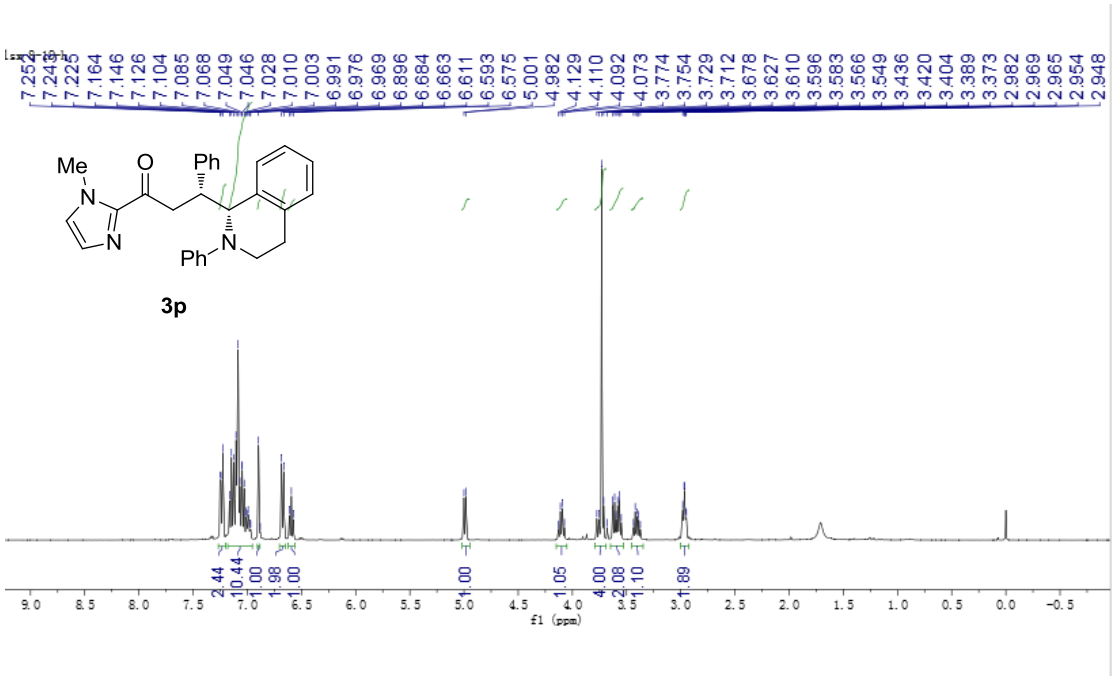
^{13}C NMR spectra of compound **3o**



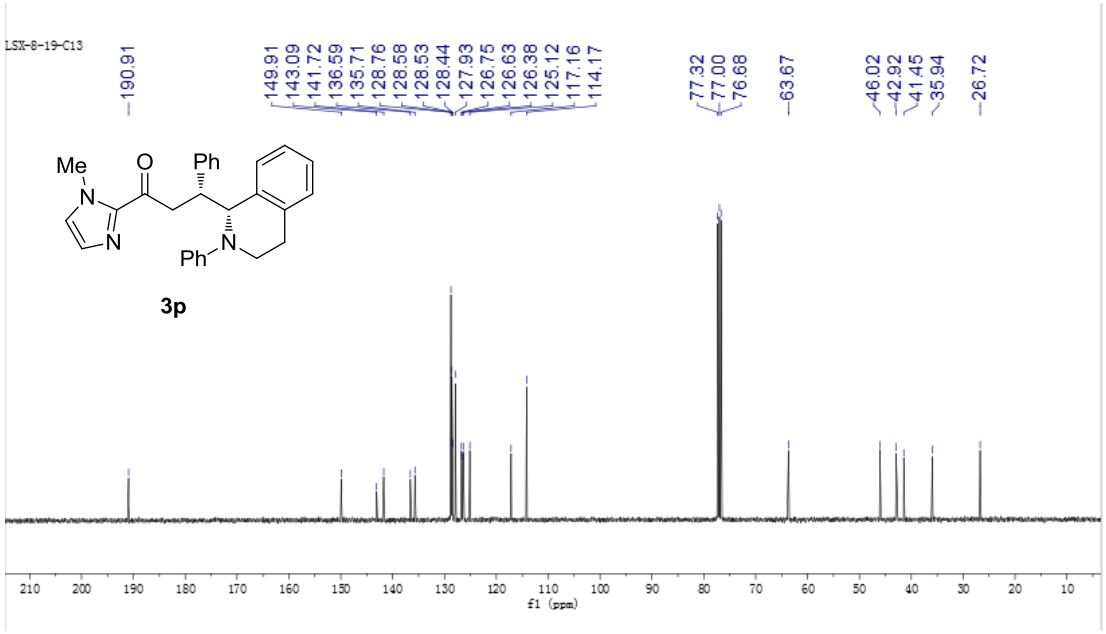
^{1}H NMR spectra of compound **3o**



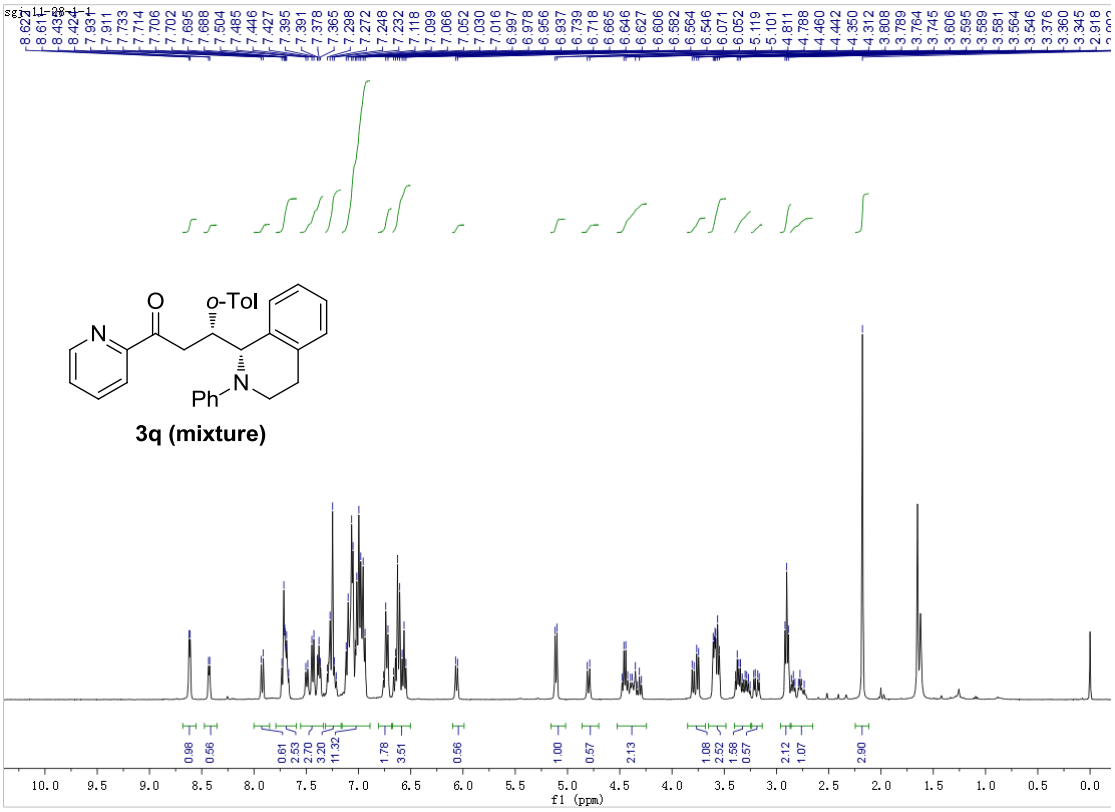
^{13}C NMR spectra of compound **3o**



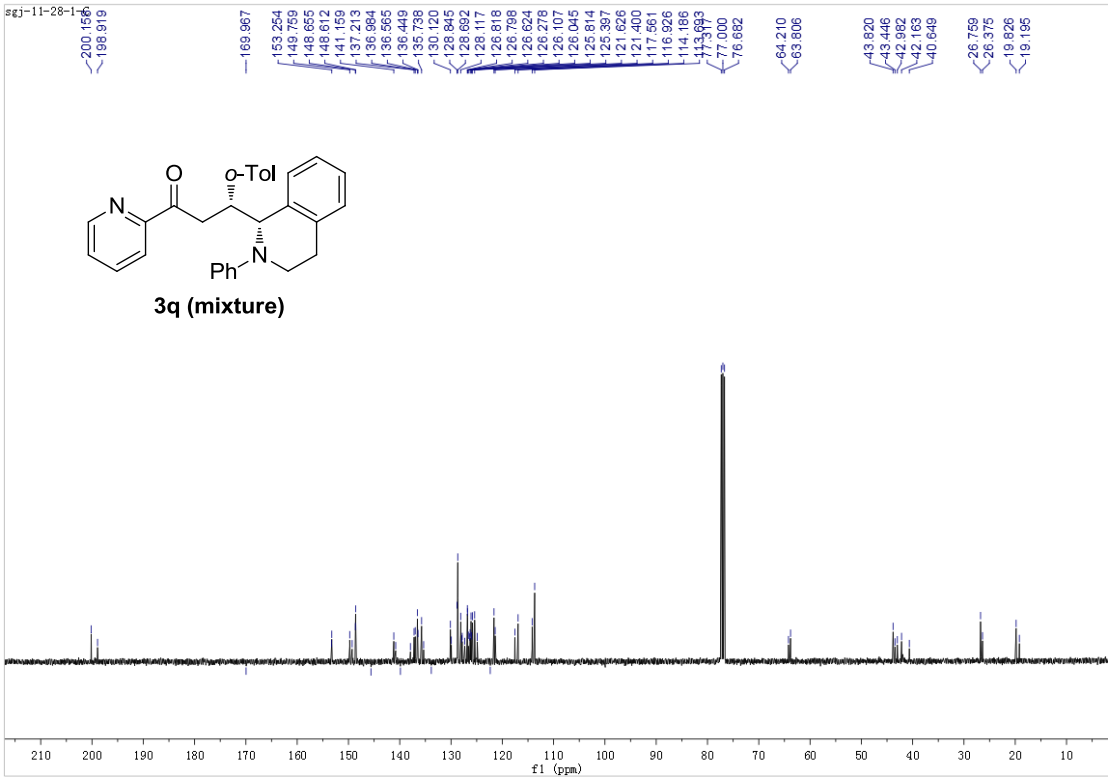
^{1}H NMR spectra of compound **3p**



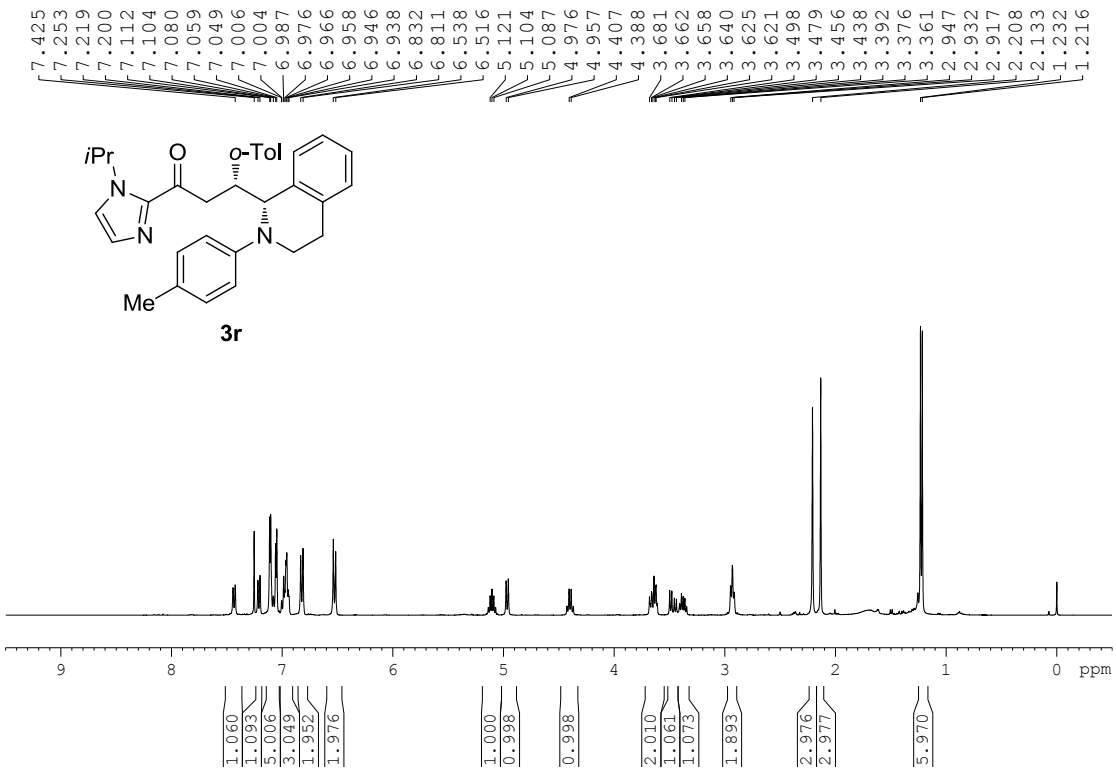
^{13}C NMR spectra of compound **3p**



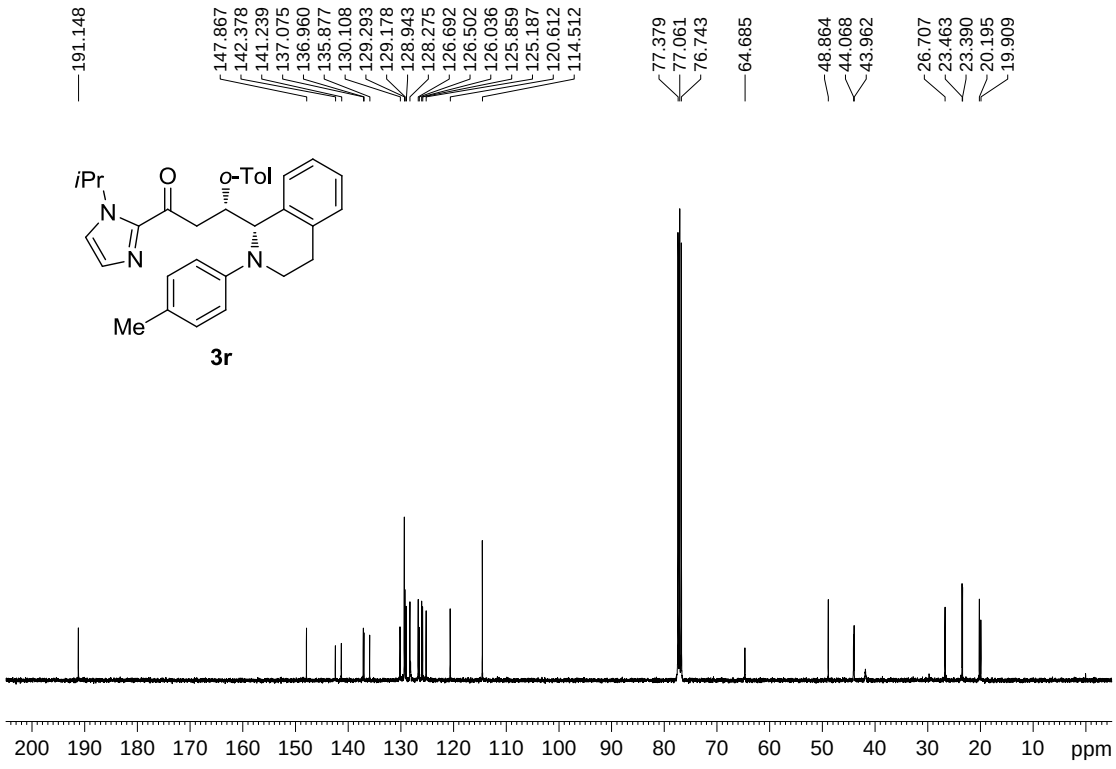
^{1}H NMR spectra of compound **3q**



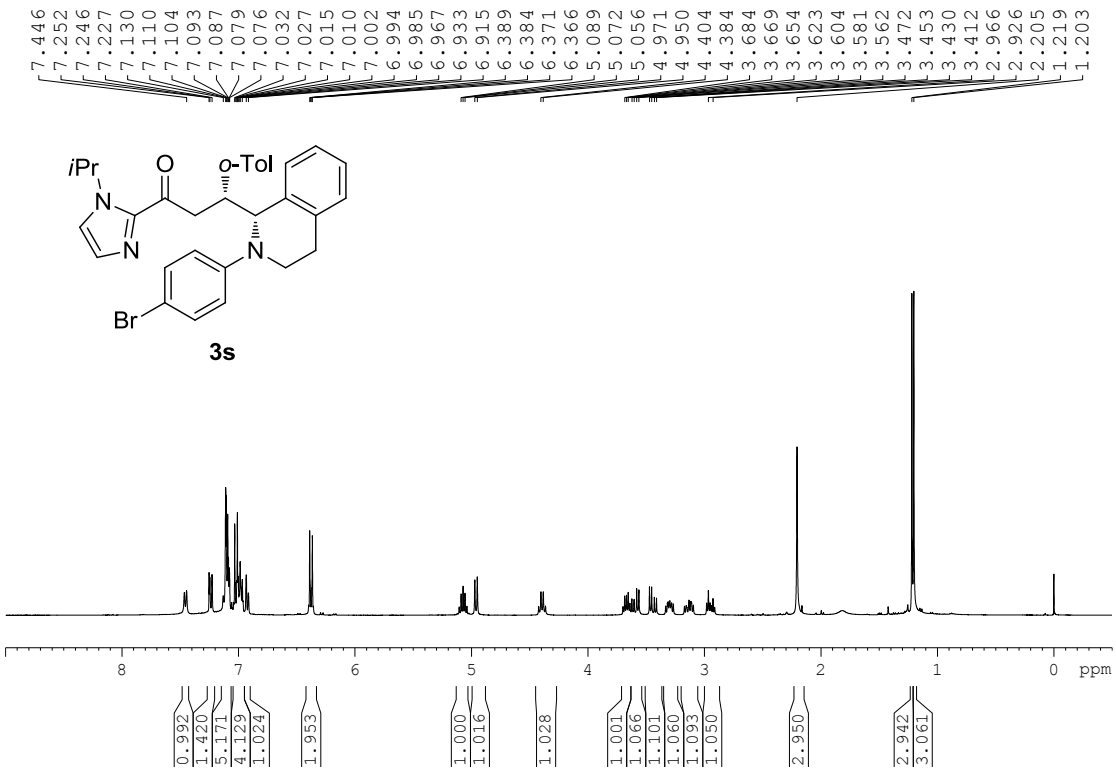
^{13}C NMR spectra of compound **3q**



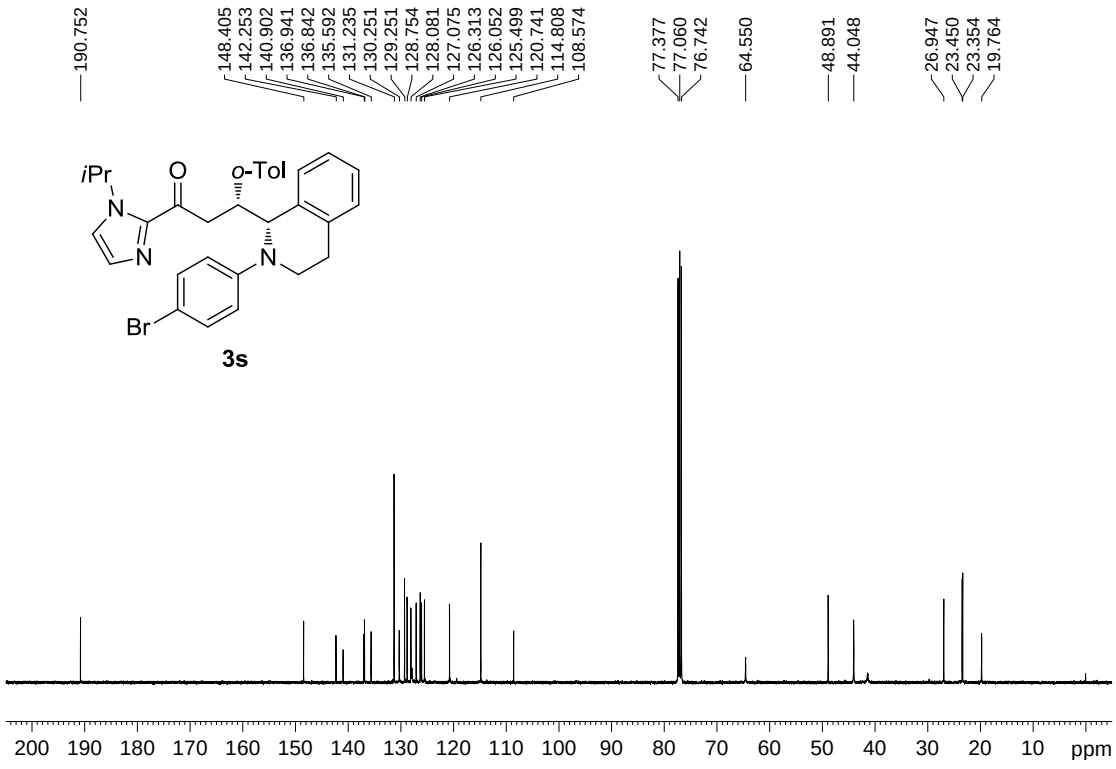
^{1}H NMR spectra of compound **3r**



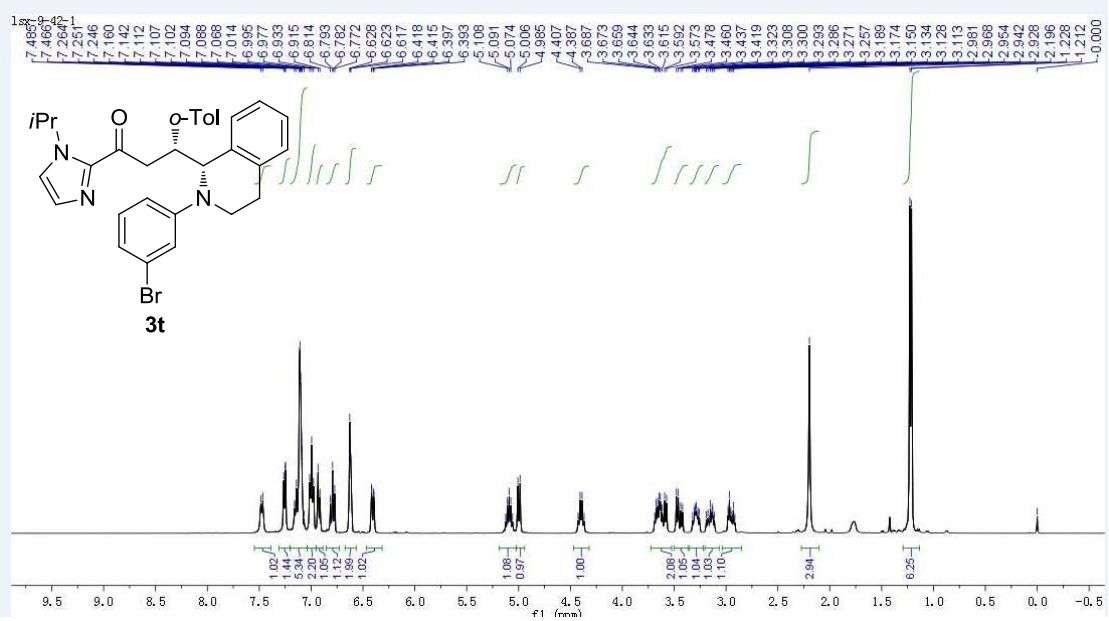
^{13}C NMR spectra of compound **3r**



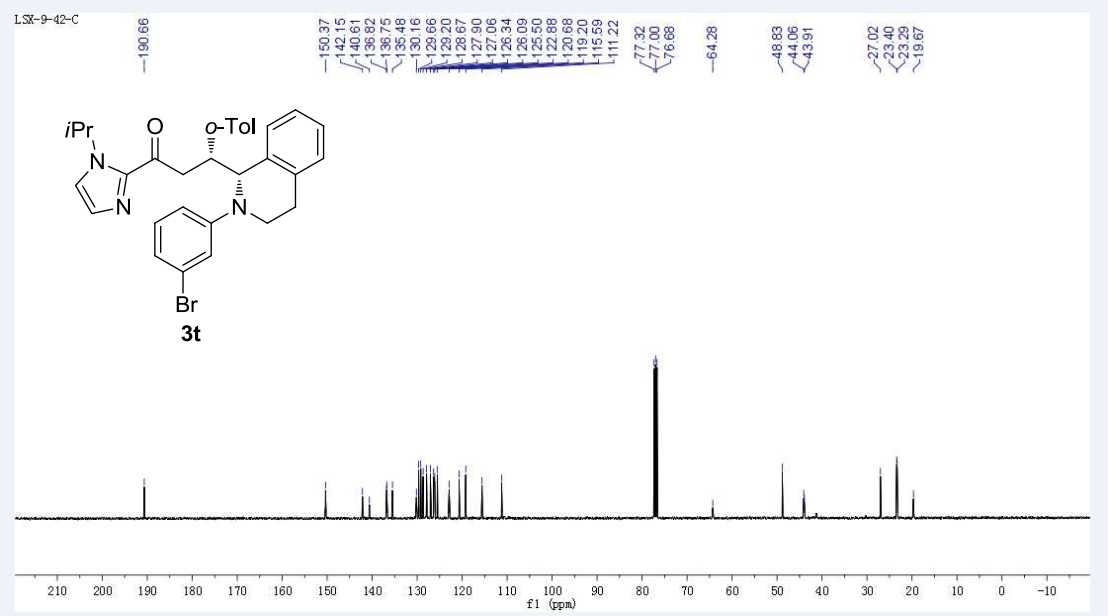
^{1}H NMR spectra of compound **3s**



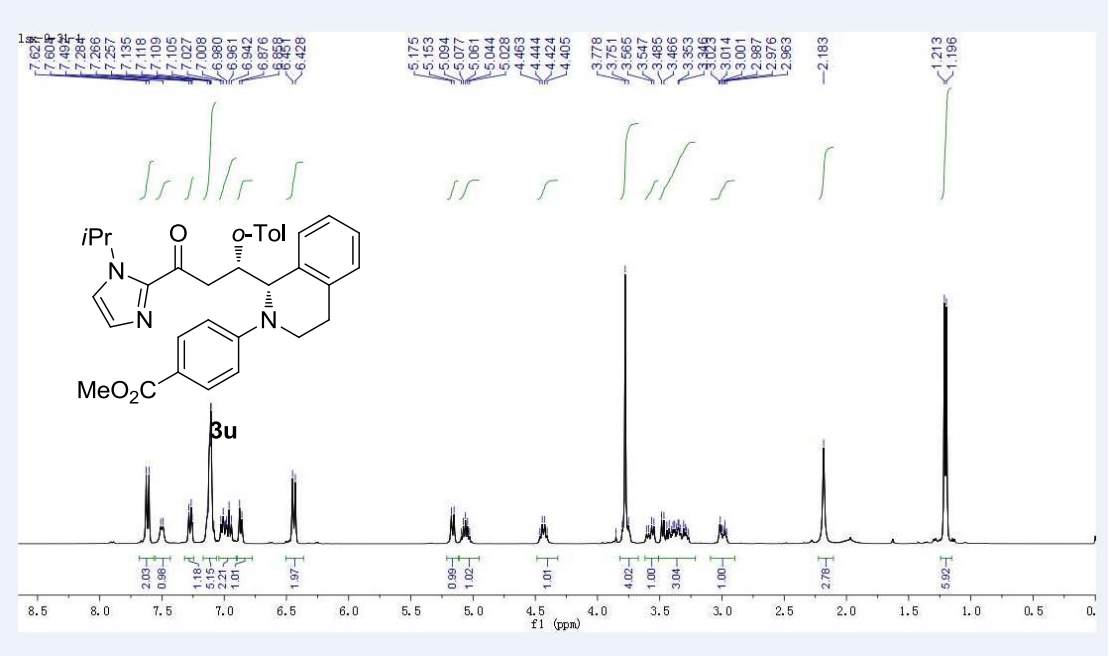
^{13}C NMR spectra of compound **3s**



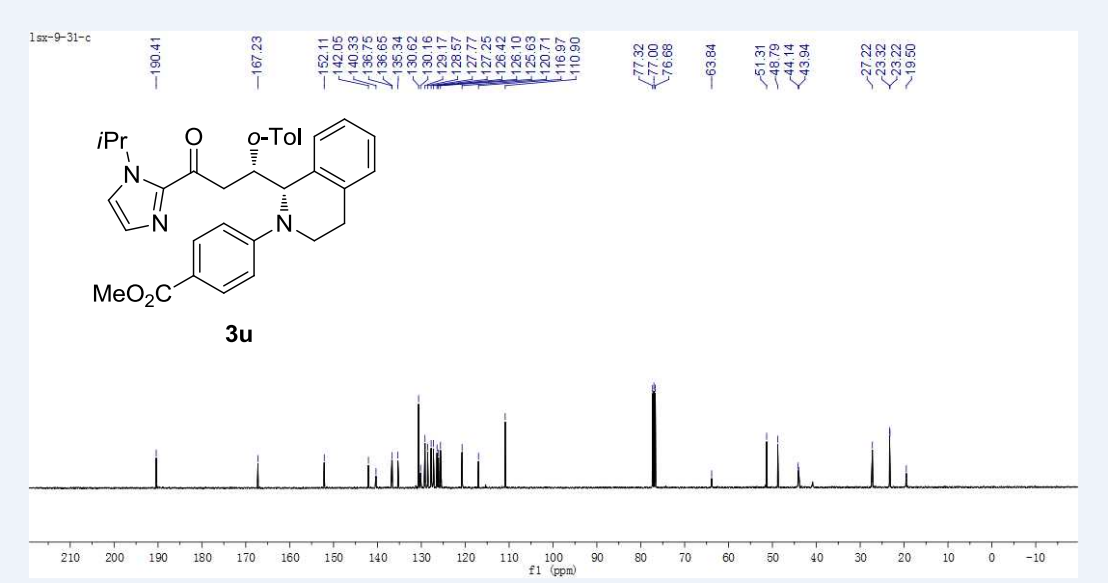
^{1}H NMR spectra of compound **3t**



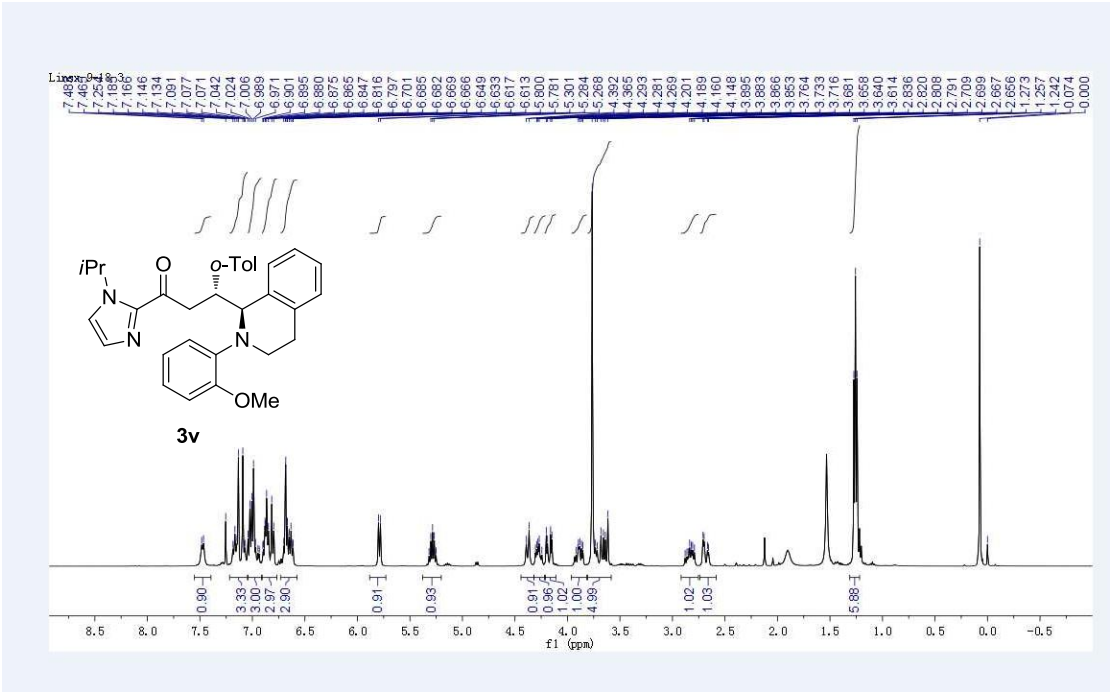
^{13}C NMR spectra of compound **3t**



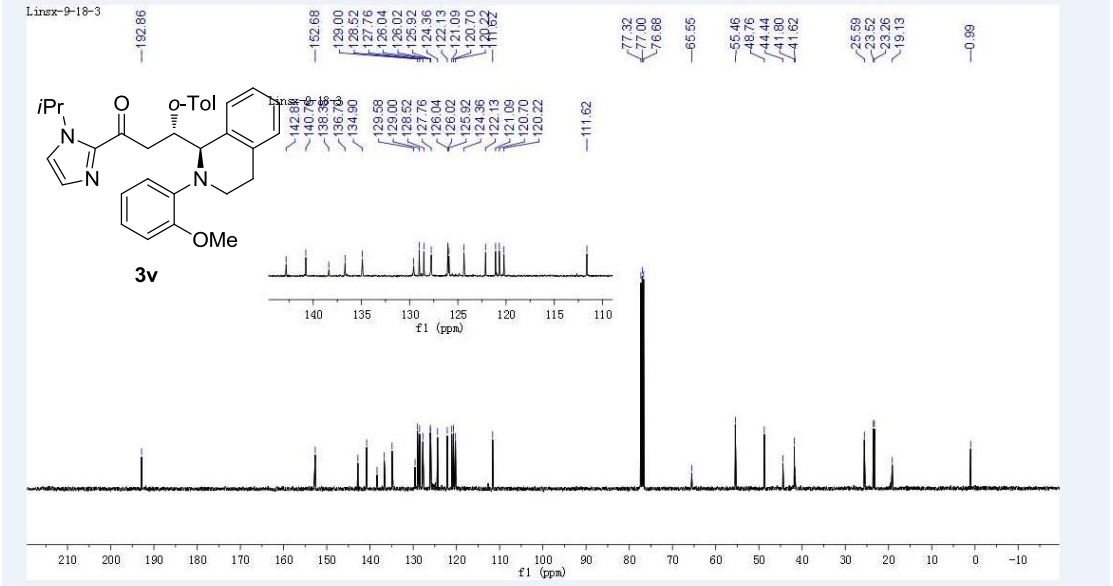
^{1}H NMR spectra of compound **3u**



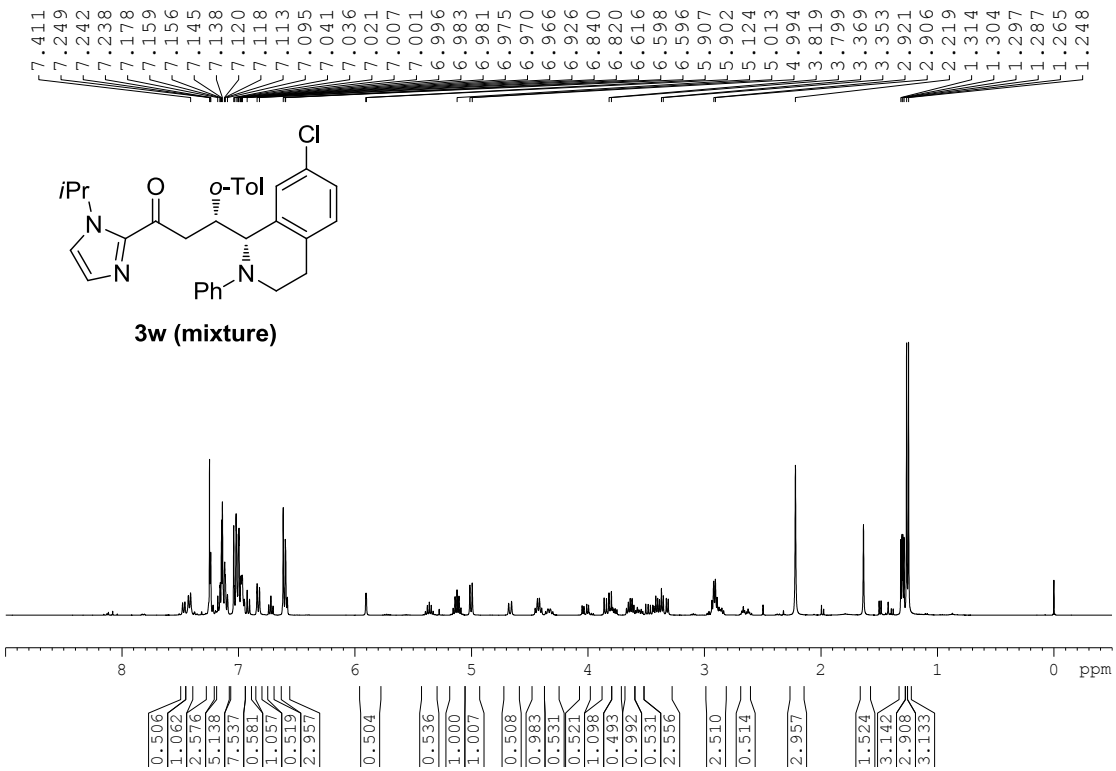
^{13}C NMR spectra of compound **3u**



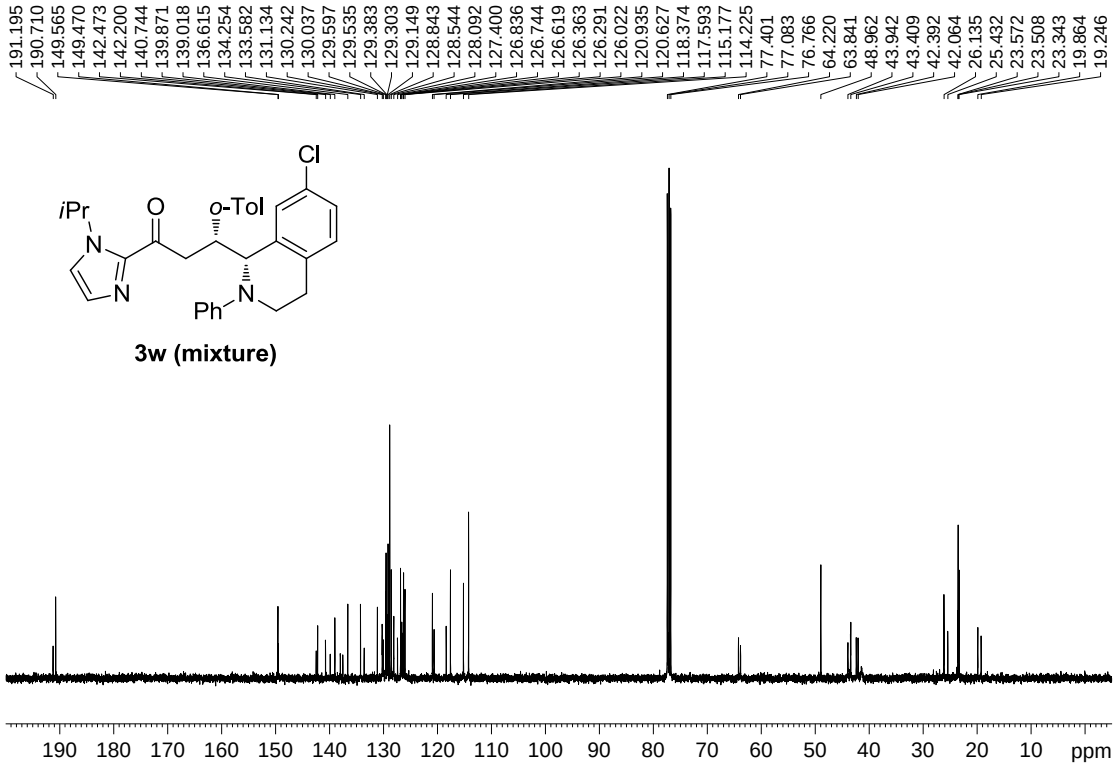
^{1}H NMR spectra of compound **3v**



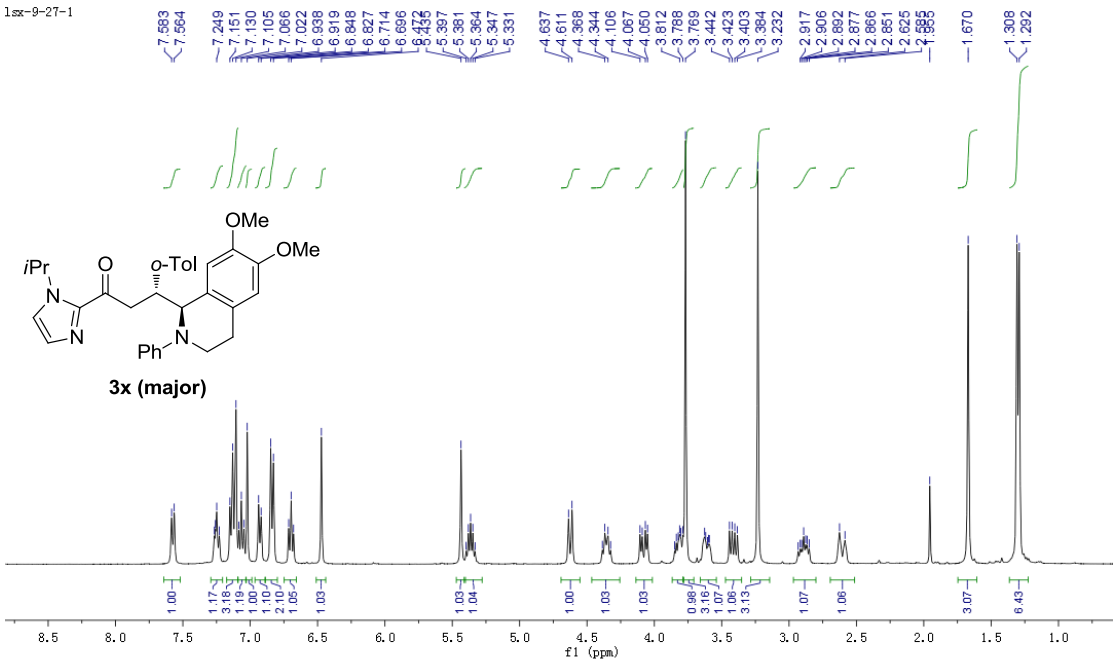
^{13}C NMR spectra of compound **3v**



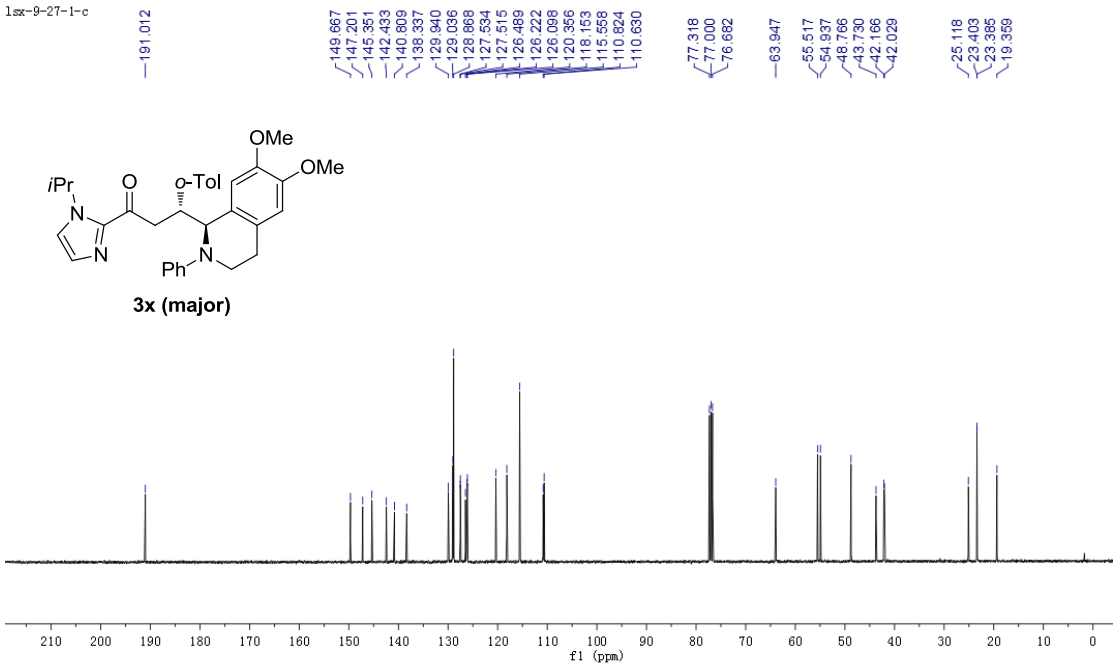
^{1}H NMR spectra of compound **3w**



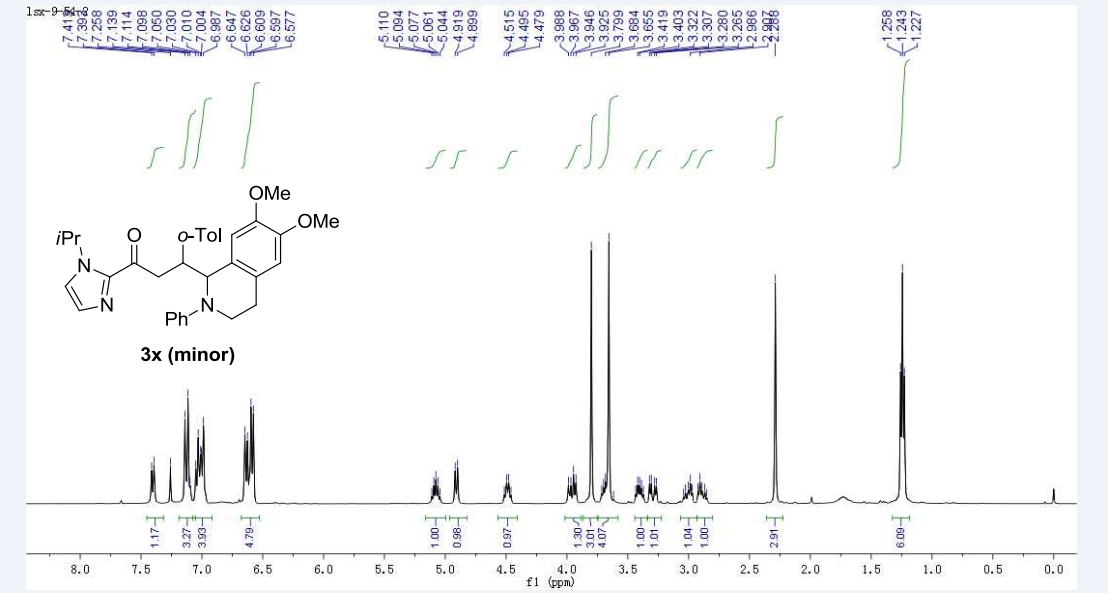
^{13}C NMR spectra of compound **3w**



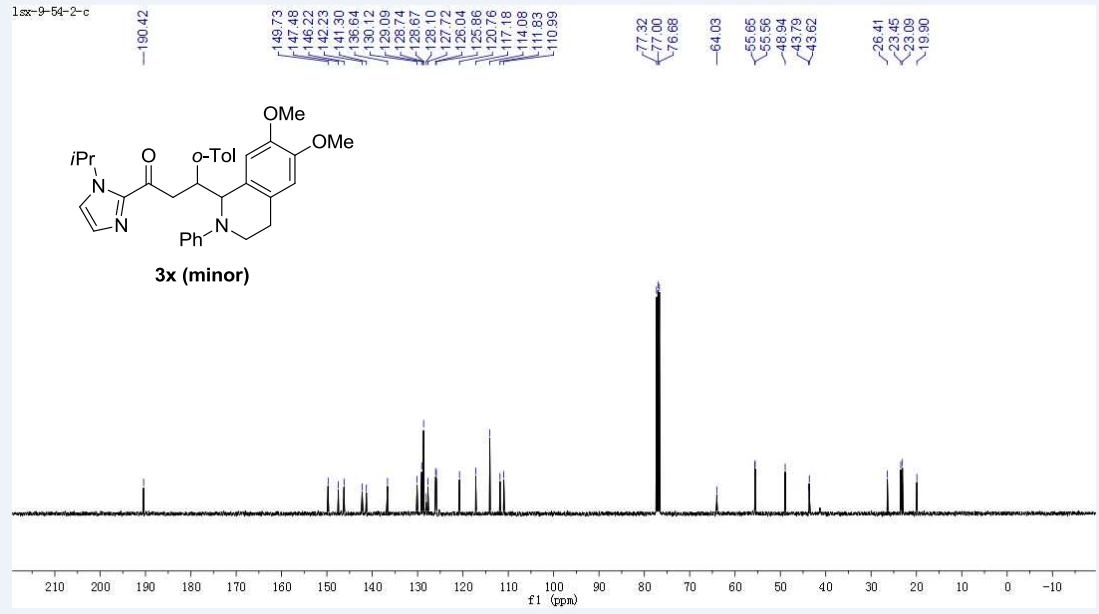
^{1}H NMR spectra of compound **3x**



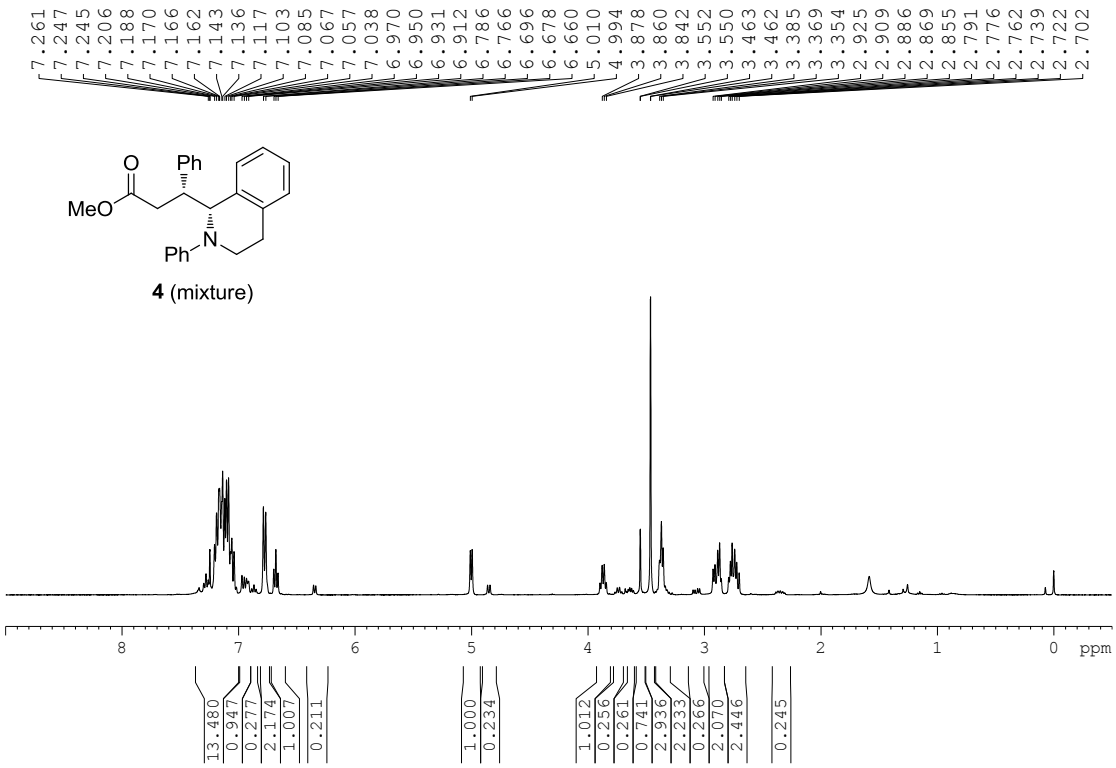
^{13}C NMR spectra of compound **3x**



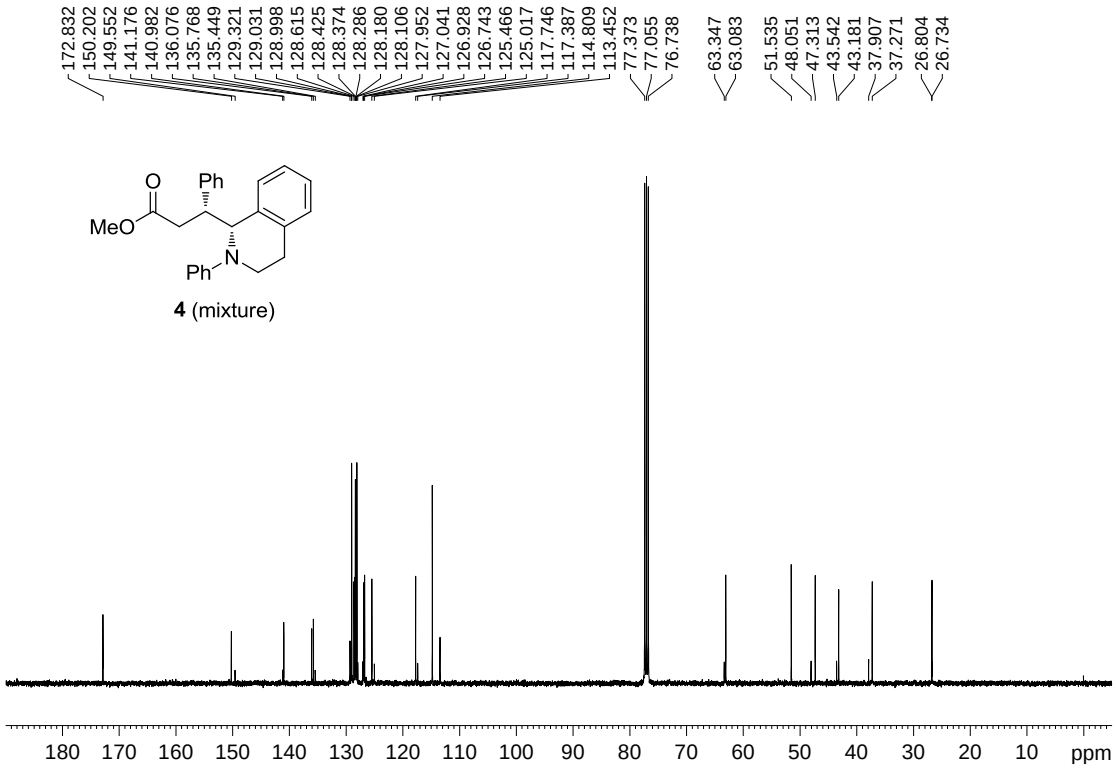
^{1}H NMR spectra of compound **3x**



^{13}C NMR spectra of compound **3x**



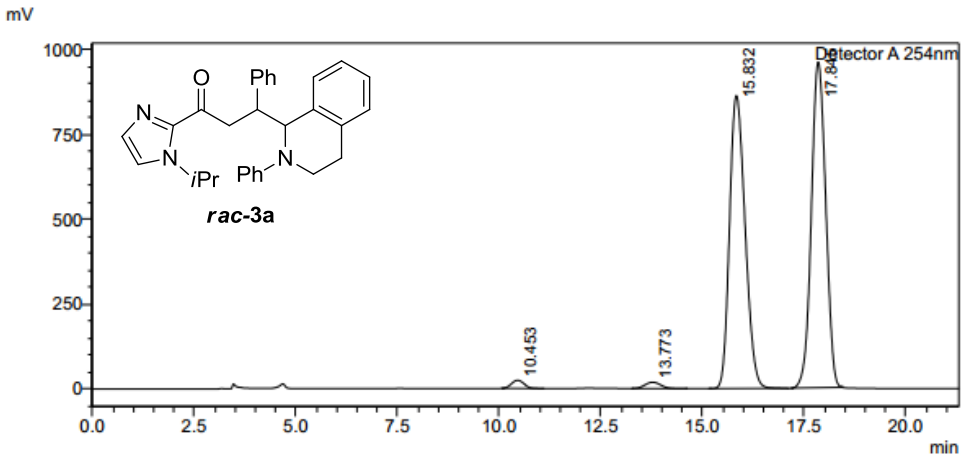
^{1}H NMR spectra of compound **4**



^{13}C NMR spectra of compound **4**

VI Chiral HPLC analysis trace

Racemic **3a**:

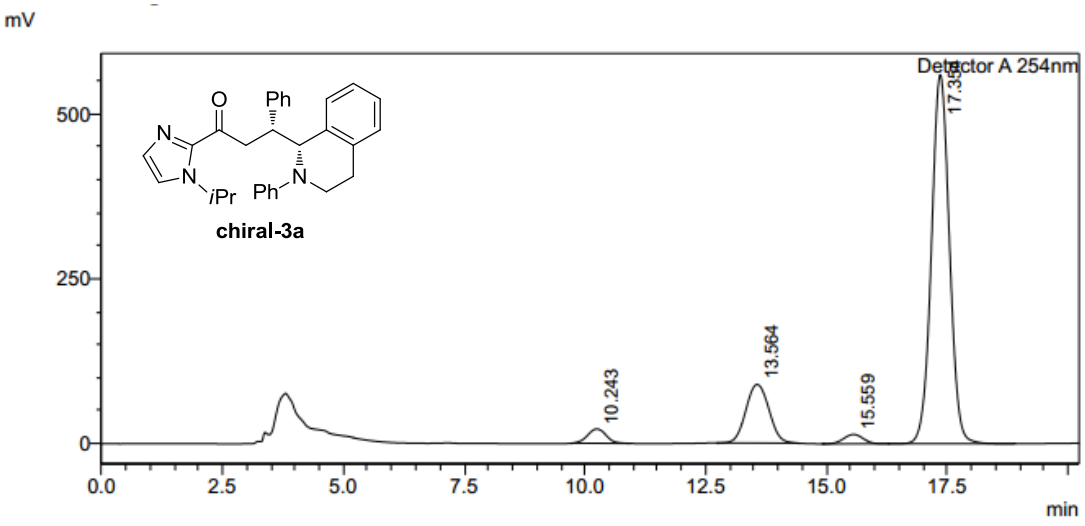


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.453	508036	23781	1.068
2	13.773	496287	18531	1.043
3	15.832	23011812	863520	48.384
4	17.845	23544212	960044	49.504
Total		47560347	1865876	100.000

Chiral **3a**:



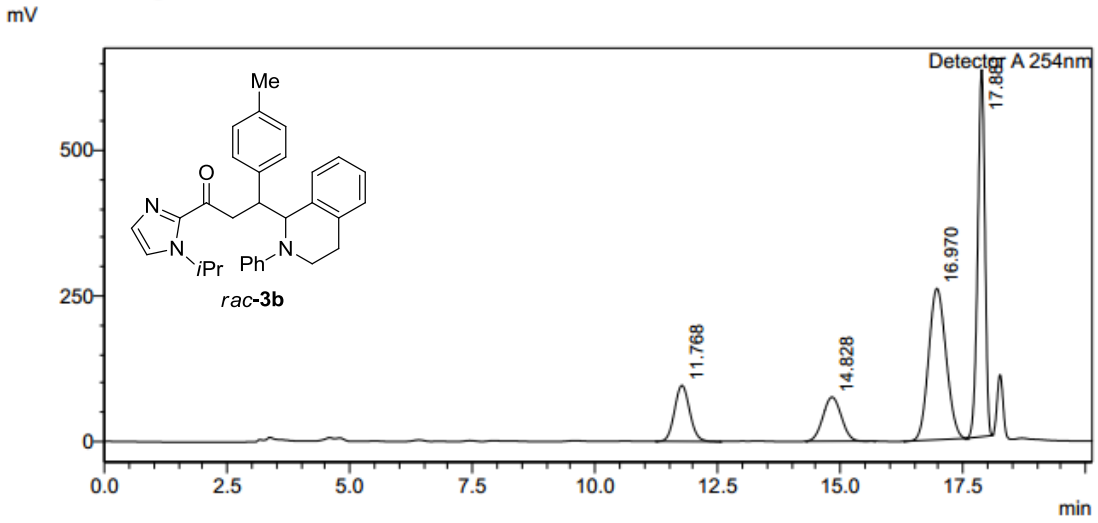
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.243	583240	21706	3.166
2	13.564	2946615	88744	15.994
3	15.559	400146	14198	2.172
4	17.354	14493351	559317	78.668
Total		18423353	683965	100.000

HPLC traces of *rac*-**3a** (reference) and chiral-**3a**. Area integration = 2.2:78.7 (95% ee).

Racemic **3b**:

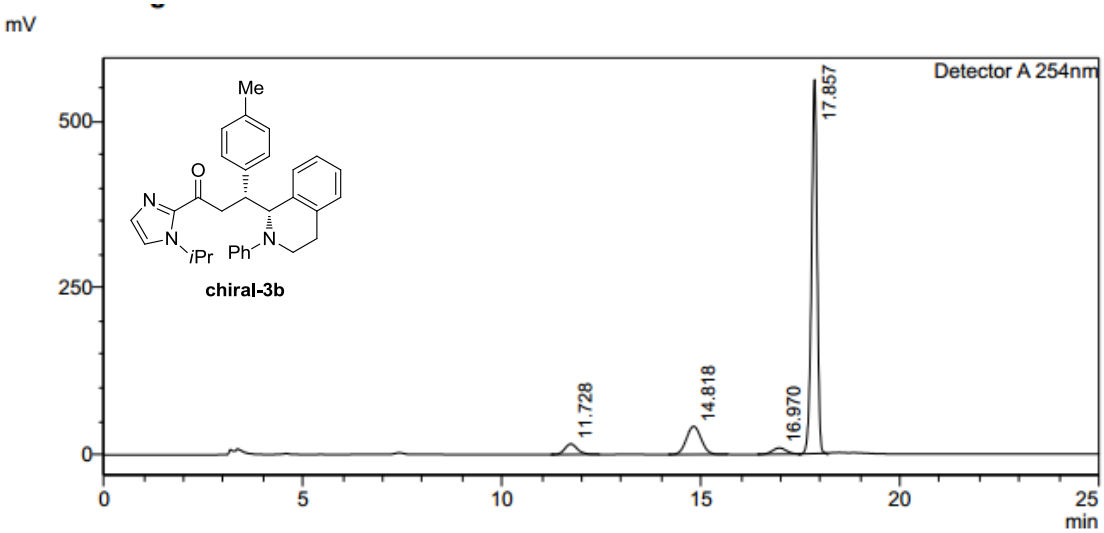


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.768	2059376	96151	12.166
2	14.828	1973687	75674	11.660
3	16.970	6444537	260021	38.073
4	17.881	6449125	630659	38.100
Total		16926725	1062505	100.000

Chiral **3b**:



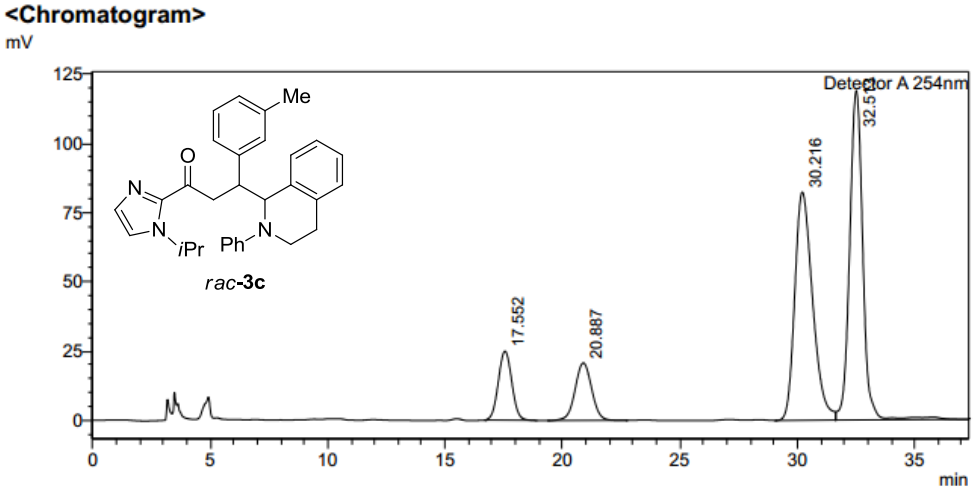
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.728	346265	15808	4.853
2	14.818	1088150	42210	15.249
3	16.970	225374	9356	3.158
4	17.857	5476004	559971	76.740
Total		7135793	627345	100.000

HPLC traces of *rac*-**3b** (reference) and chiral-**3b**. Area integration = 3.2:76.7 (92% ee).

Racemic **3c**:

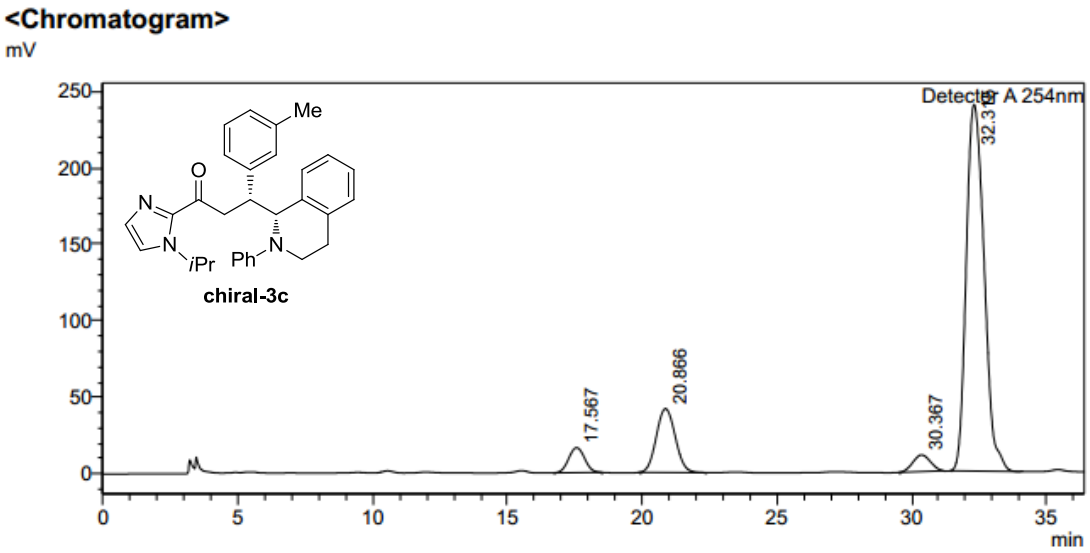


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	17.552	996520	24933	9.029
2	20.887	1023650	20794	9.275
3	30.216	4361132	82454	39.516
4	32.513	4655160	118933	42.180
Total		11036462	247114	100.000

Chiral **3c**:



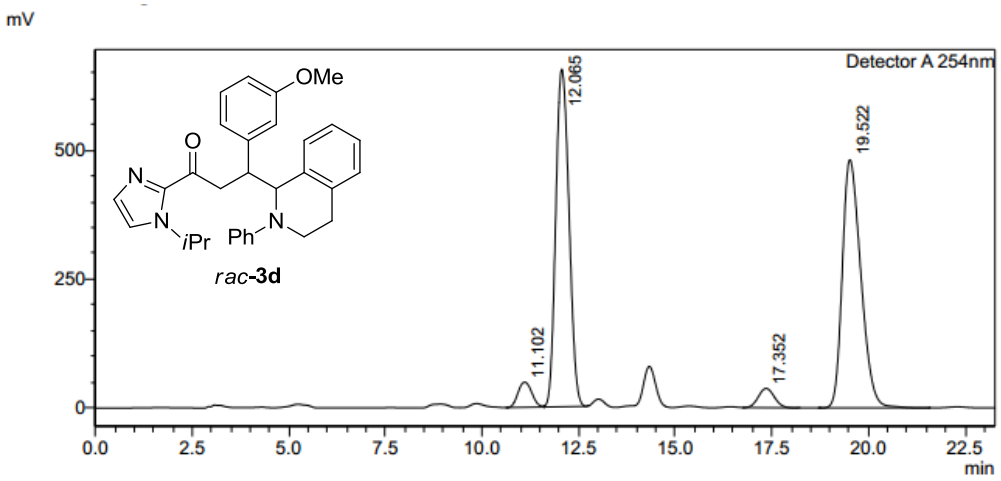
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	17.567	667741	16272	4.680
2	20.866	2039289	41689	14.292
3	30.367	493722	10864	3.460
4	32.315	11067931	239650	77.568
Total		14268683	308474	100.000

HPLC traces of *rac*-**3c** (reference) and chiral-**3c**. Area integration = 3.5:77.6 (91% ee).

Racemic **3d**:

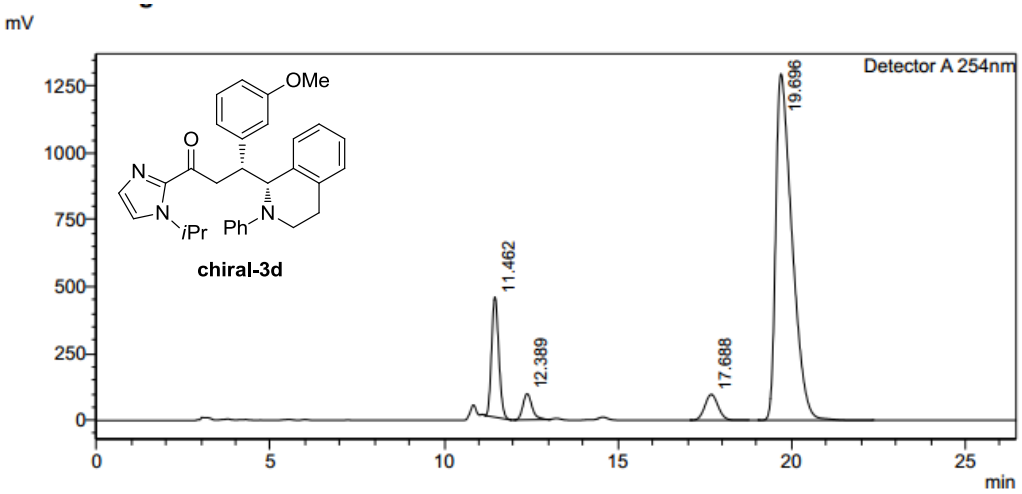


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.102	1210725	48813	3.562
2	12.065	15632772	654922	45.991
3	17.352	1075488	37445	3.164
4	19.522	16072142	481509	47.283
Total		33991127	1222689	100.000

Chiral **3d**:



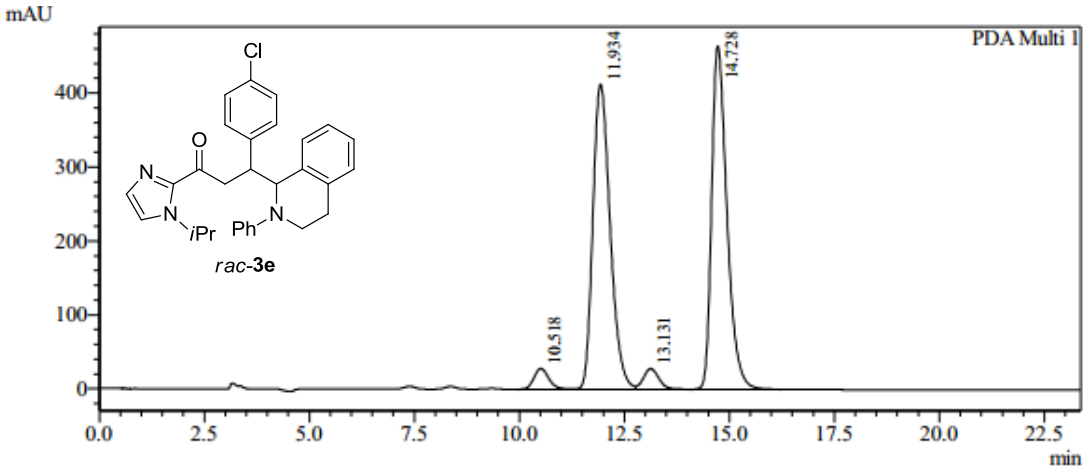
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.462	6474911	448614	12.182
2	12.389	1793468	97622	3.374
3	17.688	2564023	96527	4.824
4	19.696	42319910	1296095	79.620
Total		53152312	1938858	100.000

HPLC traces of *rac*-**3d** (reference) and chiral-**3d**. Area integration = 3.4:79.6 (92% ee).

Racemic **3e**:



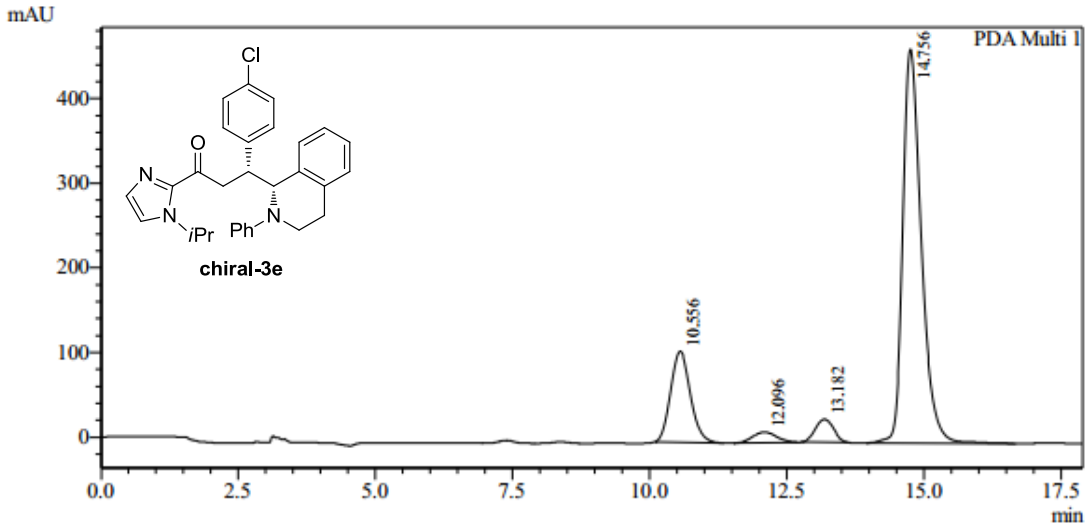
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT10.518	10.518	684892	28051	2.739
2	RT11.934	11.934	11817776	412720	47.255
3	RT13.131	13.131	710931	27835	2.843
4	RT14.728	14.728	11794671	464523	47.163
Total			25008270	933128	100.000

Chiral **3e**:



1 PDA Multi 1 / 254nm 4nm

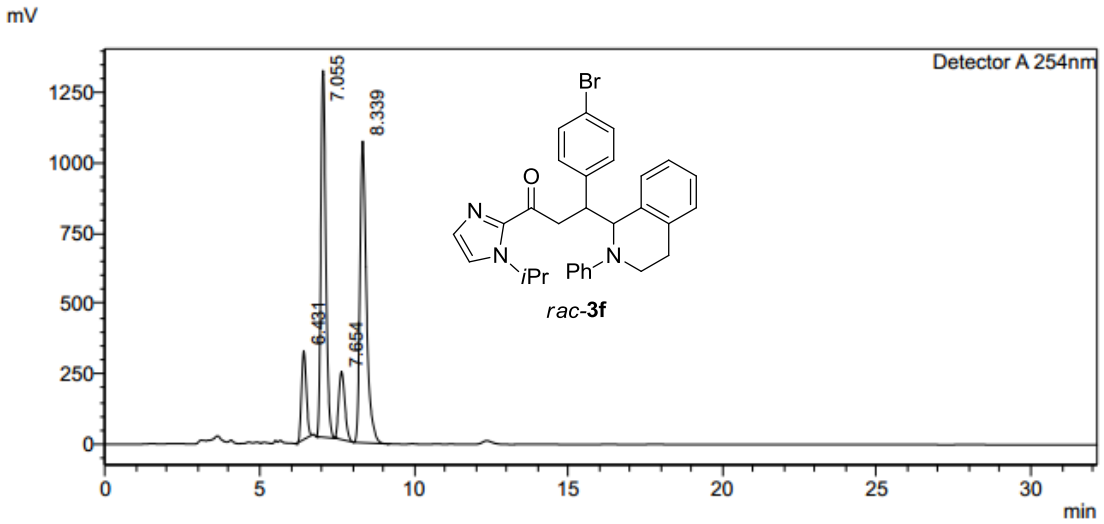
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT10.556	10.556	2688114	107440	18.469
2	RT12.096	12.096	381507	12530	2.621
3	RT13.182	13.182	623397	27100	4.283
4	RT14.756	14.756	10862034	465290	74.627
Total			14555053	612359	100.000

HPLC traces of *rac*-**3e** (reference) and chiral-**3e**. Area integration = 2.6:74.6 (93% ee).

Racemic **3f**:

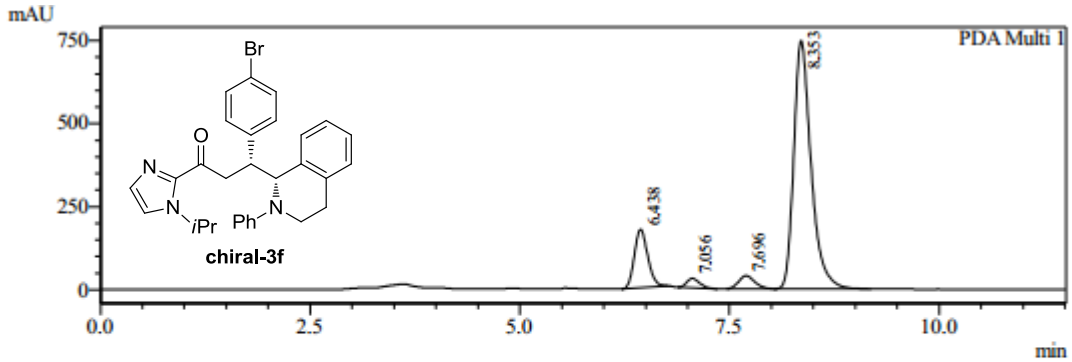


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	6.431	3425400	315764	9.244
2	7.055	14593516	1305049	39.382
3	7.654	3343818	242182	9.024
4	8.339	15693597	1073117	42.351
Total		37056330	2936112	100.000

Chiral **3f**:



1 PDA Multi 1 / 254nm 4nm

PeakTable

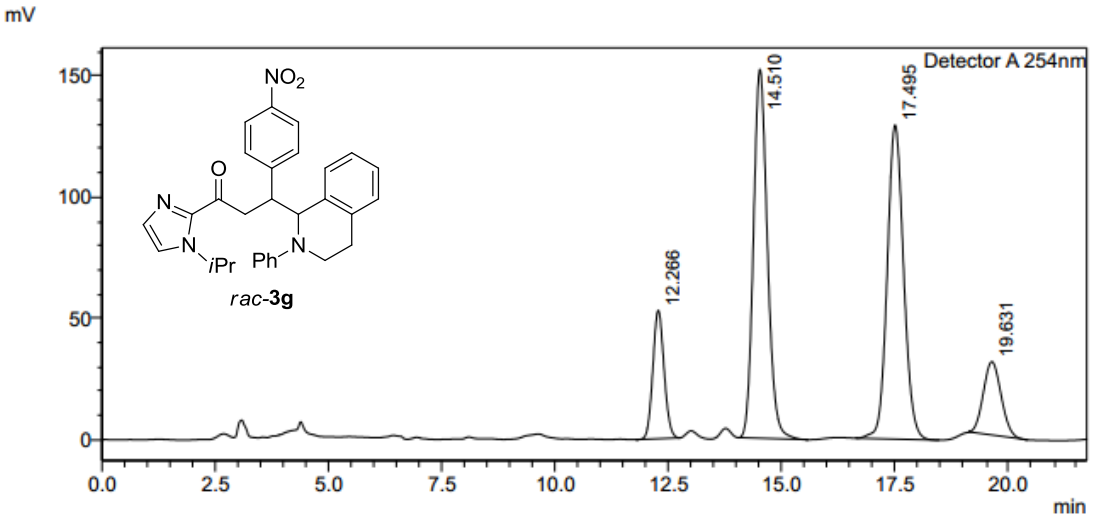
PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT6.438	6.438	1960330	176120	14.511
2	RT7.056	7.056	302839	28349	2.242
3	RT7.696	7.696	513592	39310	3.802
4	RT8.353	8.353	10732768	746451	79.446
Total			13509529	990231	100.000

HPLC traces of *rac*-**3f** (reference) and chiral-**3f**. Area integration = 2.2:79.4 (94% ee).

Racemic **3g**:

<Chromatogram>

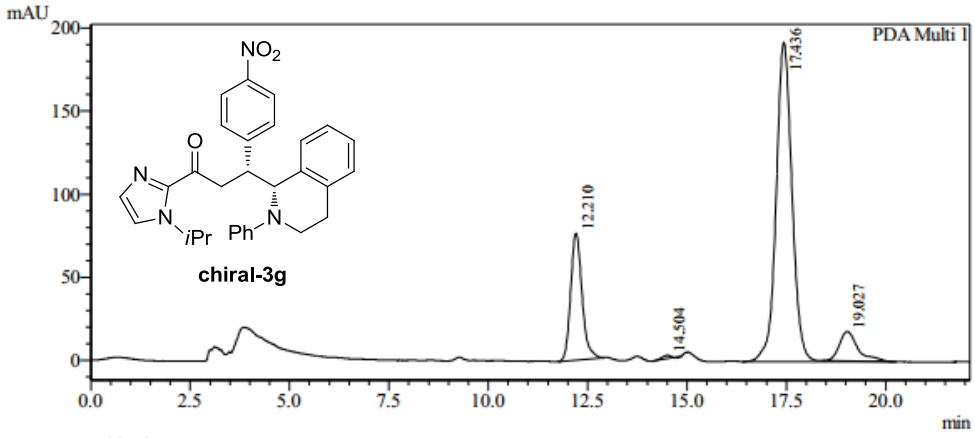


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	12.266	913493	53015	11.038
2	14.510	3262192	152266	39.420
3	17.495	3273968	129610	39.562
4	19.631	825924	30235	9.980
Total		8275578	365126	100.000

Chiral **3g**:



1 PDA Multi 1 / 254nm 4nm

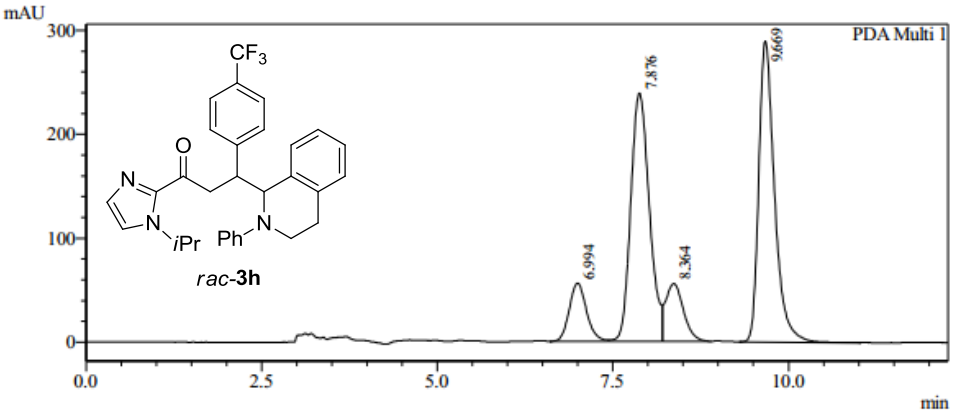
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT12.210	12.210	1516763	76385	20.278
2	RT14.504	14.504	24023	1934	0.321
3	RT17.436	17.436	5353042	192316	71.568
4	RT19.027	19.027	585861	17859	7.833
Total			7479689	288495	100.000

HPLC traces of *rac*-**3g** (reference) and chiral-**3g**. Area integration = 0.3:71.6 (99.1% ee).

Racemic **3h**



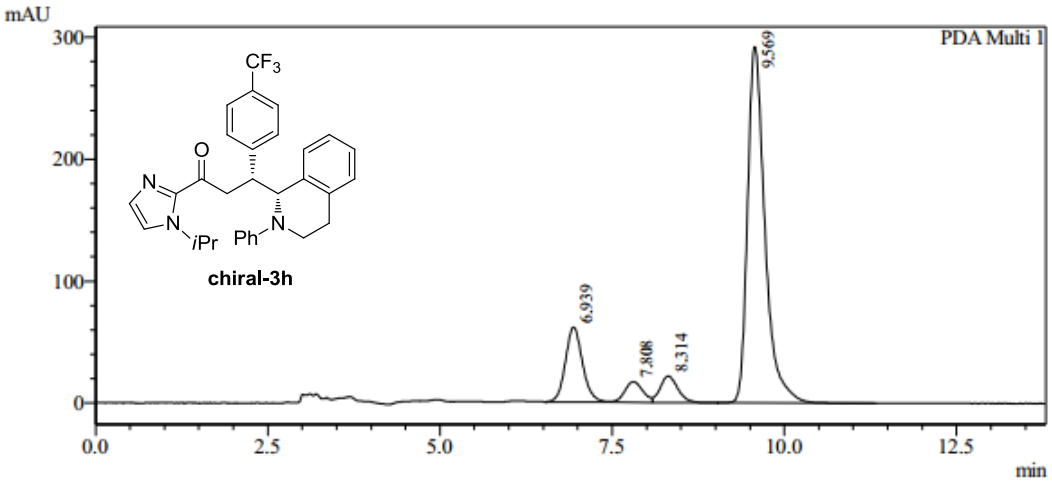
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT6.994	6.994	952937	55950	8.786
2	RT7.876	7.876	4397701	238843	40.548
3	RT8.364	8.364	985858	55498	9.090
4	RT9.669	9.669	4509194	289633	41.576
Total			10845690	639925	100.000

Chiral **3h**:



1 PDA Multi 1 / 254nm 4nm

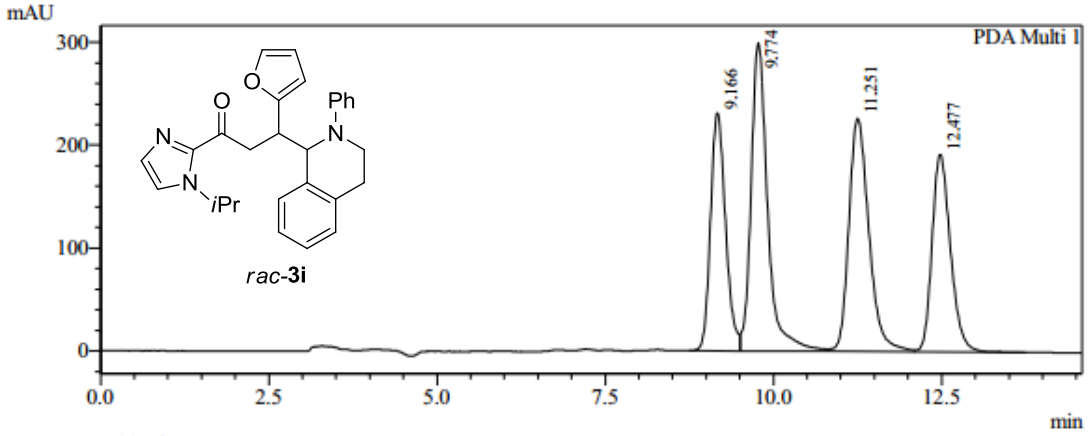
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT6.939	6.939	1059682	61347	15.363
2	RT7.808	7.808	309243	16923	4.483
3	RT8.314	8.314	384979	21651	5.581
4	RT9.569	9.569	5143807	292118	74.573
Total			6897711	392038	100.000

HPLC traces of *rac*-**3h** (reference) and chiral-**3h**. Area integration = 4.5:74.6 (91% ee).

Racemic **3i**



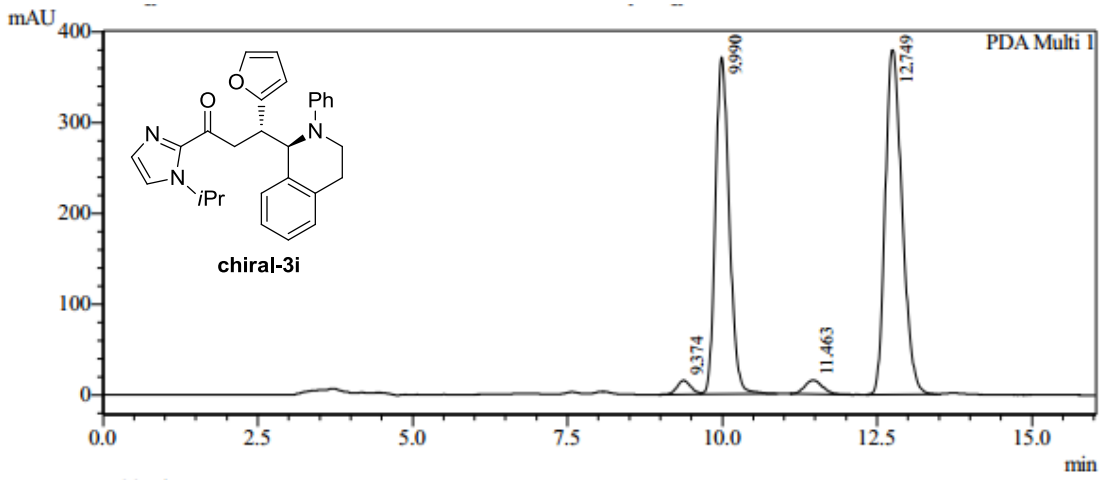
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT9.166	9.166	3600961	231076	21.037
2	RT9.774	9.774	5134411	299376	29.996
3	RT11.251	11.251	4708959	226658	27.511
4	RT12.477	12.477	3672572	191976	21.456
Total			17116903	949086	100.000

Chiral **3i**:



1 PDA Multi 1 / 254nm 4nm

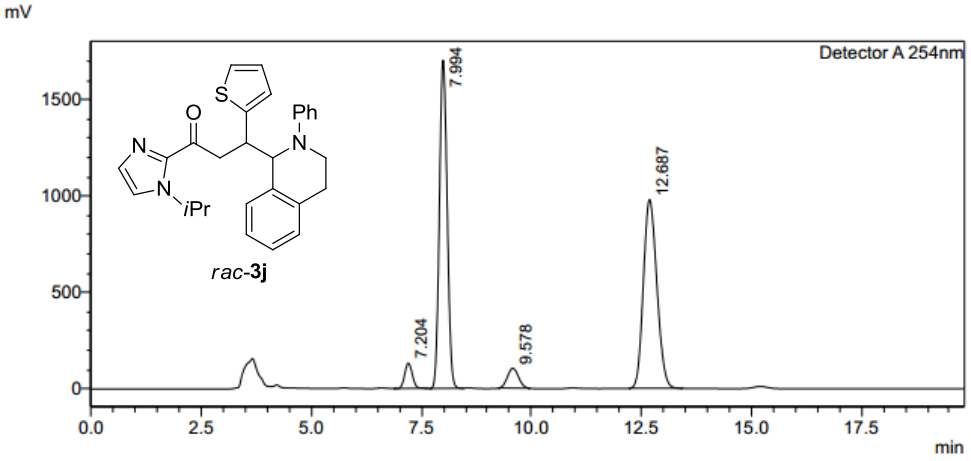
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT9.374	9.374	241027	15400	1.779
2	RT9.990	9.990	5772824	371441	42.603
3	RT11.463	11.463	300389	15271	2.217
4	RT12.749	12.749	7235877	379816	53.401
Total			13550116	781929	100.000

HPLC traces of *rac*-**3i** (reference) and chiral-**3i**. Area integration = 1.8:53.4(94% ee).

Racemic **3j**:

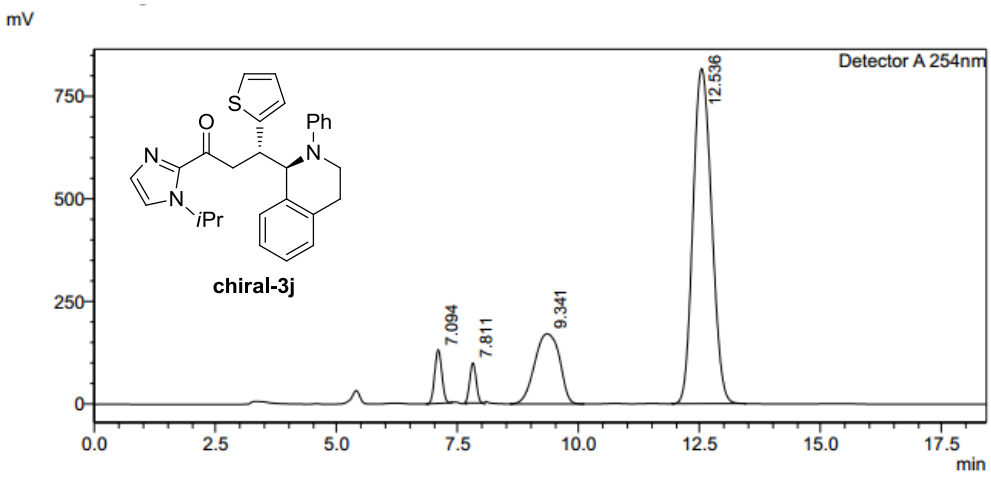


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.204	1581136	130668	3.504
2	7.994	20869568	1702290	46.244
3	9.578	1800557	102621	3.990
4	12.687	20877913	978694	46.263
Total		45129174	2914273	100.000

Chiral **3j**:



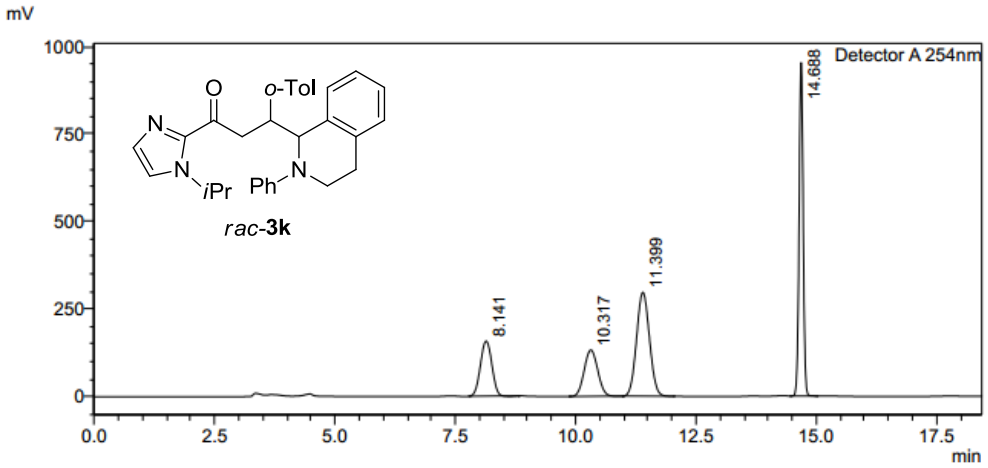
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.094	1348233	130540	4.471
2	7.811	903813	97534	2.997
3	9.341	6117378	170733	20.285
4	12.536	21788031	815424	72.248
Total		30157455	1214230	100.000

HPLC traces of *rac*-**3j** (reference) and chiral-**3j**. Area integration = 3.0:72.3 (92% ee).

Racemic **3k**:

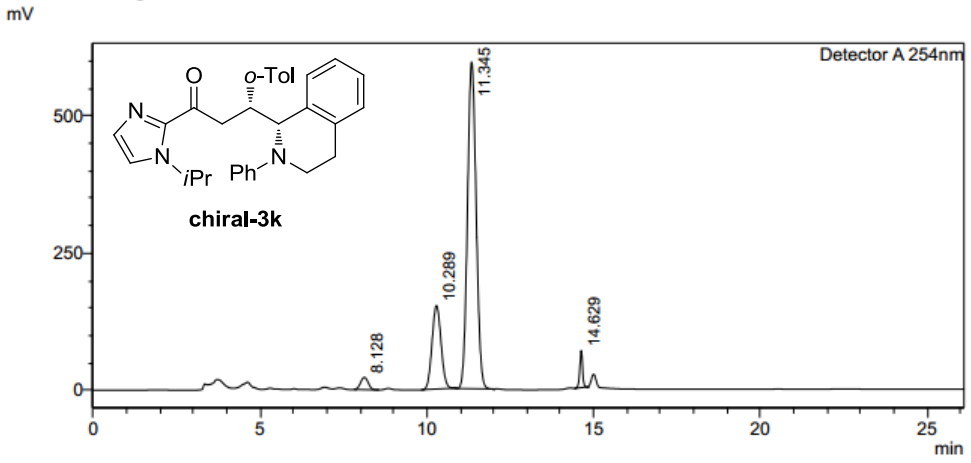


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	8.141	2588932	157248	15.836
2	10.317	2596605	132446	15.883
3	11.399	5550807	296815	33.953
4	14.688	5612237	950829	34.329
Total		16348581	1537337	100.000

Chiral **3k**:



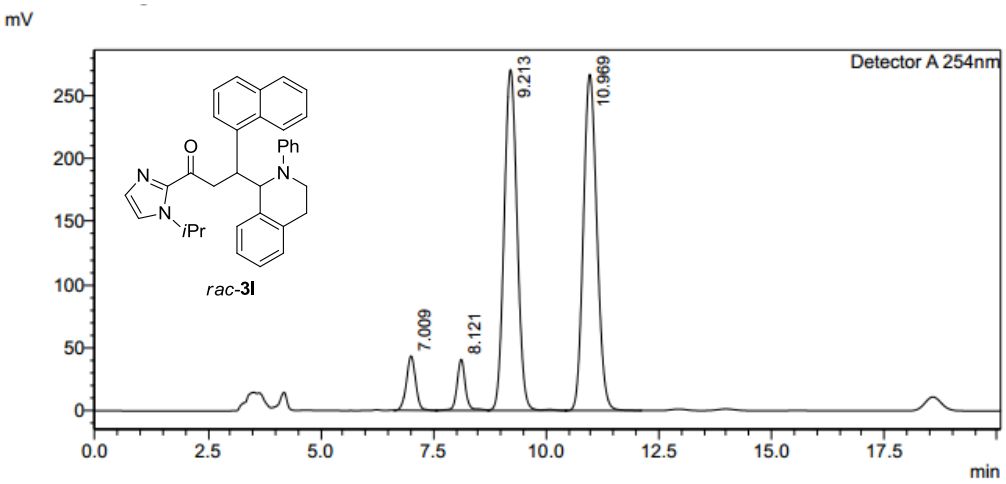
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	8.128	349794	22213	2.429
2	10.289	2866888	152399	19.910
3	11.345	10785874	595982	74.906
4	14.629	396566	67891	2.754
Total		14399121	838484	100.000

HPLC traces of *rac*-**3k** (reference) and chiral-**3k**. Area integration = 74.9:2.8 (93%ee).

Racemic **3l**:



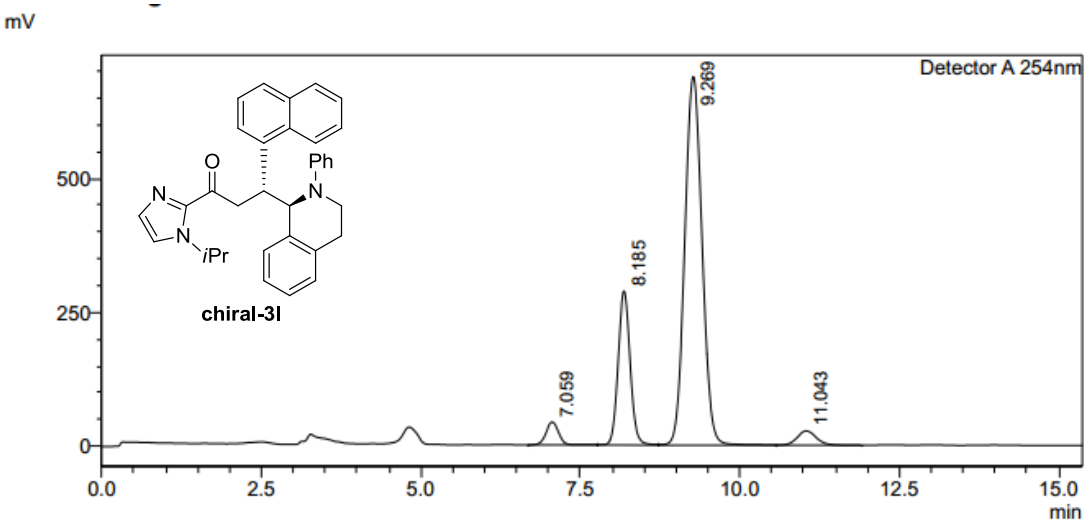
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.009	611158	43168	5.060
2	8.121	522373	40383	4.325
3	9.213	5389257	270194	44.623
4	10.969	5554452	266486	45.991
Total		12077240	620232	100.000

l

Chiral **3l**:



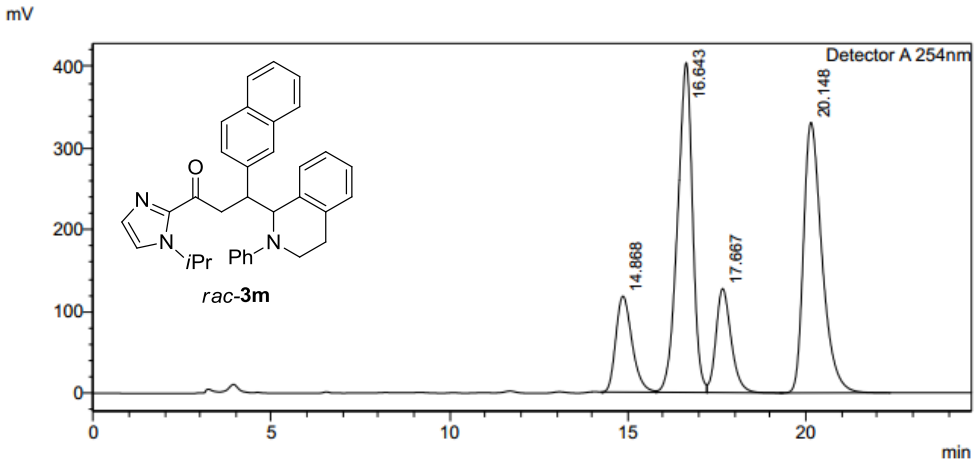
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.059	597877	42976	3.341
2	8.185	3765354	287634	21.044
3	9.269	12969260	687766	72.484
4	11.043	560037	26698	3.130
Total		17892528	1045074	100.000

HPLC traces of *rac*-**3l** (reference) and chiral-**3l**. Area integration = 72.5:3.1 (92% ee).

Racemic **3m**:

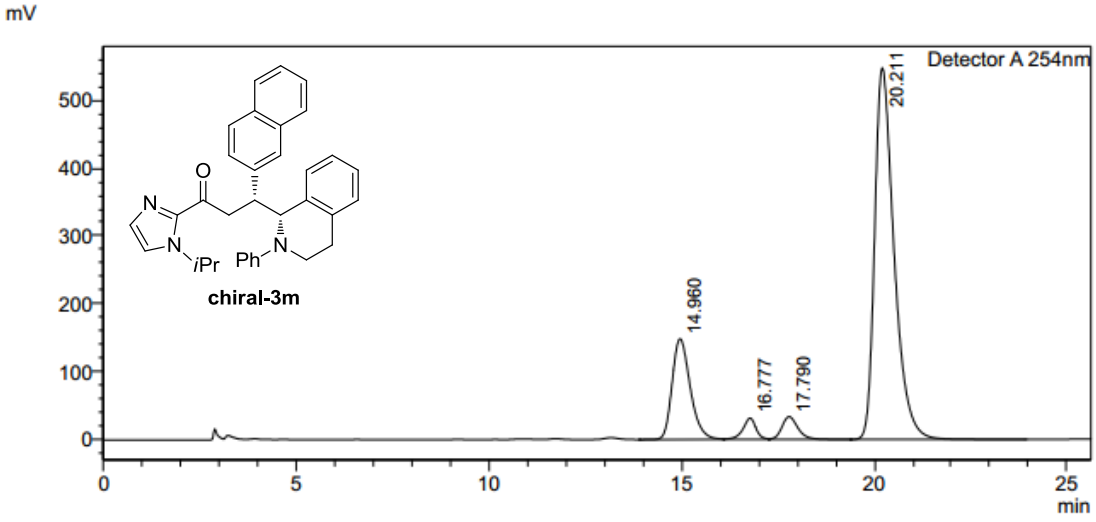


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.868	3733503	117481	11.917
2	16.643	11865173	403649	37.874
3	17.667	3788071	127179	12.092
4	20.148	11941374	330857	38.117
Total		31328120	979166	100.000

Chiral **3m**:



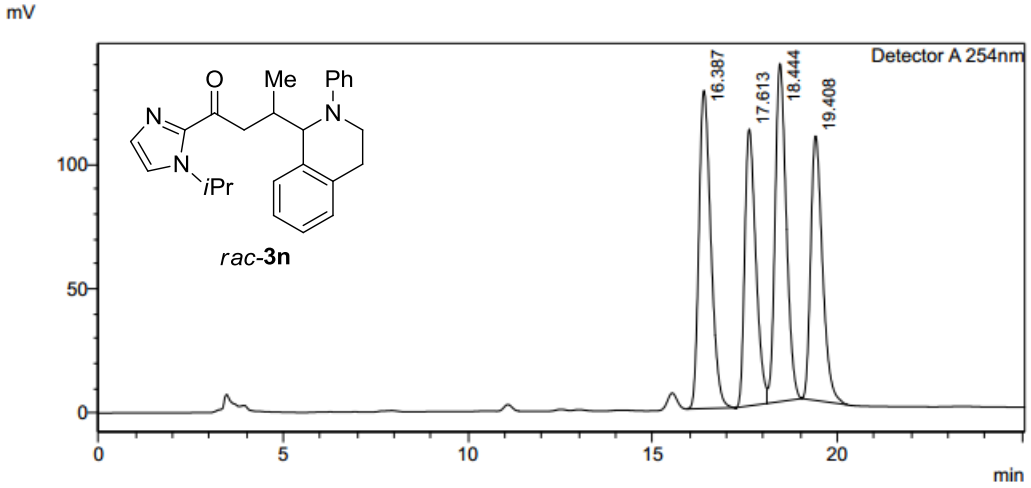
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.960	4858598	148250	18.821
2	16.777	752181	31538	2.914
3	17.790	985492	33678	3.818
4	20.211	19217927	547057	74.447
Total		25814198	760523	100.000

HPLC traces of *rac*-**3m** (reference) and chiral-**3m**. Area integration = 2.9:74.4 (93% ee).

Racemic **3n**:

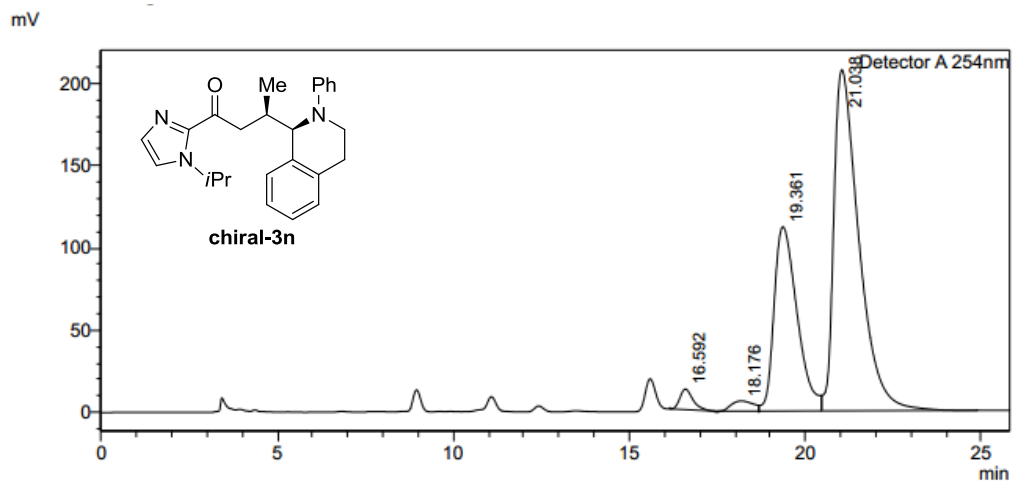


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	16.387	2872886	127786	27.580
2	17.613	2330296	111188	22.371
3	18.444	2857536	135797	27.432
4	19.408	2355933	106242	22.617
Total		10416651	481013	100.000

Chiral **3n**:



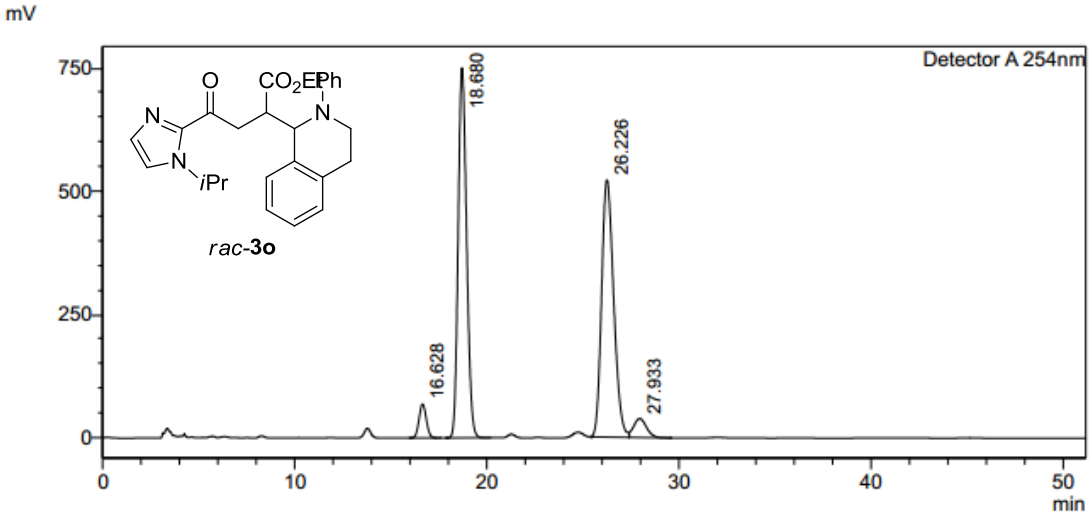
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	16.592	322206	12536	2.018
2	18.176	268785	6114	1.684
3	19.361	5079515	111790	31.817
4	21.038	10294108	206915	64.481
Total		15964614	337354	100.000

HPLC traces of *rac*-**3n** (reference) and chiral-**3n**. Area integration = 1.7:64.5 (97% ee).

Racemic **3o**:

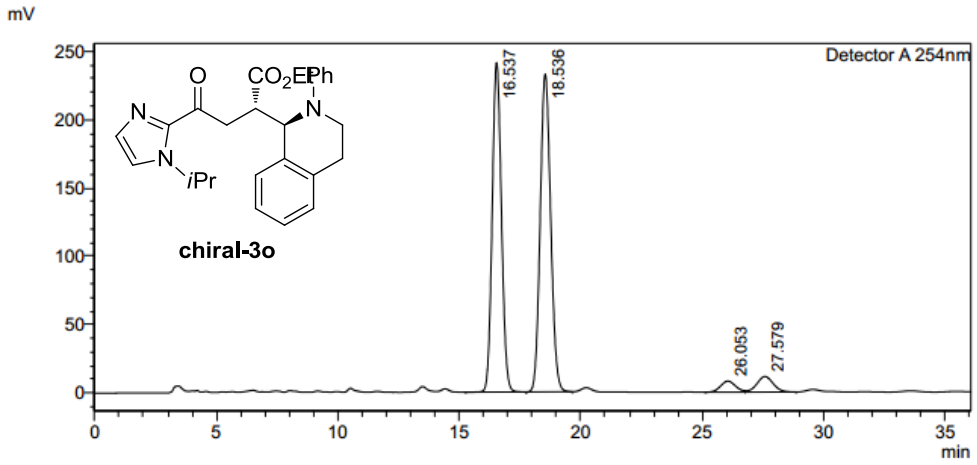


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	16.628	1811694	68881	3.676
2	18.680	22896687	750643	46.460
3	26.226	22753838	522106	46.170
4	27.933	1820315	38486	3.694
Total		49282534	1380116	100.000

Chiral **3o**:



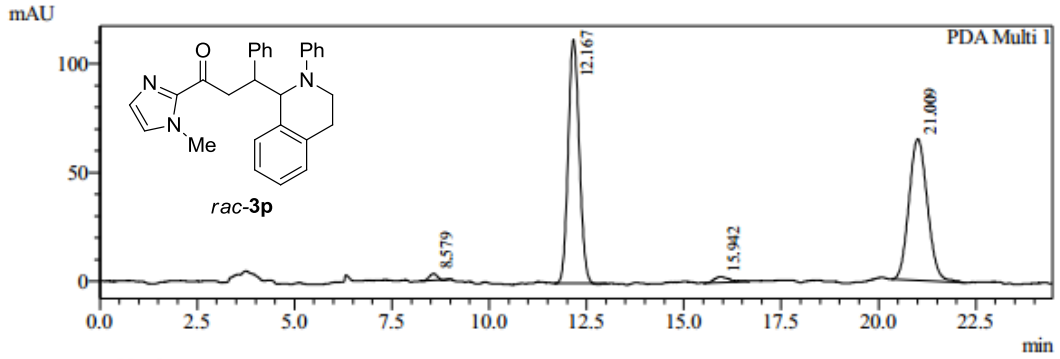
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	16.537	6354512	241042	44.793
2	18.536	6962070	232491	49.076
3	26.053	344742	8052	2.430
4	27.579	525067	11364	3.701
Total		14186391	492948	100.000

HPLC traces of *rac*-**3o** (reference) and chiral-**3o**. Area integration = 49.1:2.4 (92% ee).

Racemic **3p**:



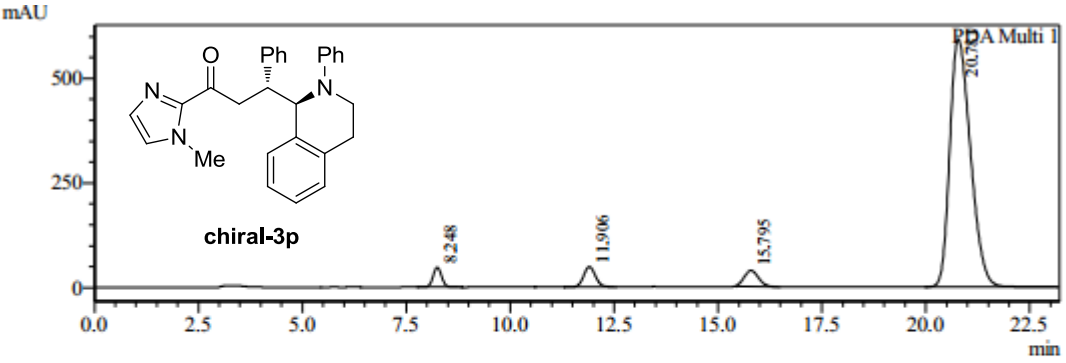
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT8.579	8.579	43329	3115	0.970
2	RT12.167	12.167	2206330	112007	49.395
3	RT15.942	15.942	65814	2643	1.473
4	RT21.009	21.009	2151257	65062	48.162
Total			4466730	182826	100.000

Chiral **3p**:



1 PDA Multi 1 / 254nm 4nm

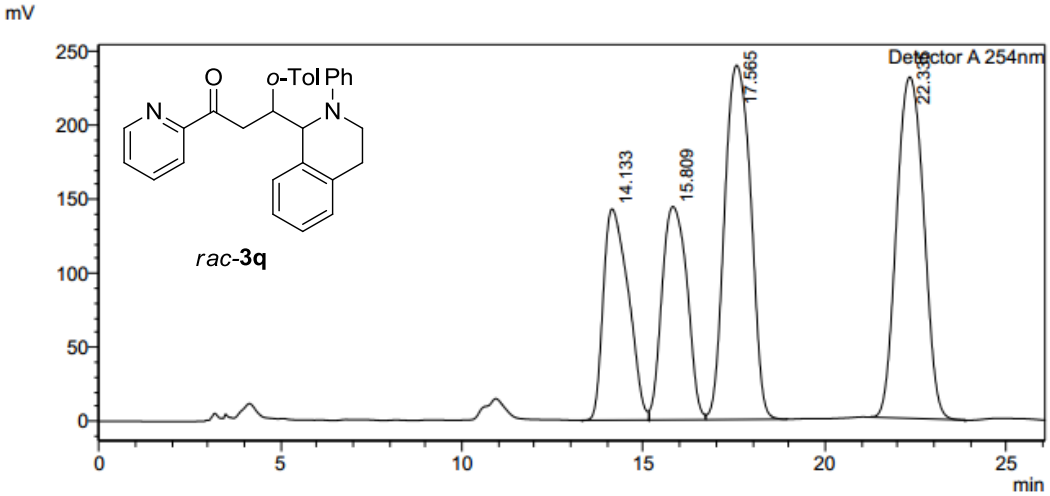
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT8.248	8.248	657350	46885	2.863
2	RT11.906	11.906	942949	48371	4.107
3	RT15.795	15.795	900405	37829	3.922
4	RT20.781	20.781	20457124	592306	89.107
Total			22957828	725391	100.000

HPLC traces of *rac*-**3p** (reference) and chiral-**3p**. Area integration = 4.1:89.1 (91% ee).

Racemic **3q**:

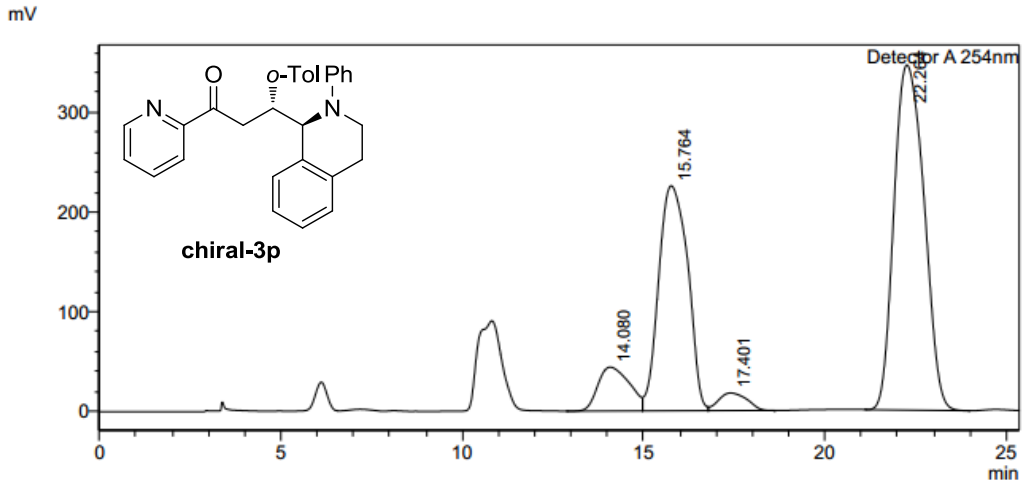


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.133	6828326	142863	18.048
2	15.809	6975414	144222	18.437
3	17.565	12008554	239575	31.740
4	22.335	12021314	230854	31.774
Total		37833608	757514	100.000

Chiral **3q**:



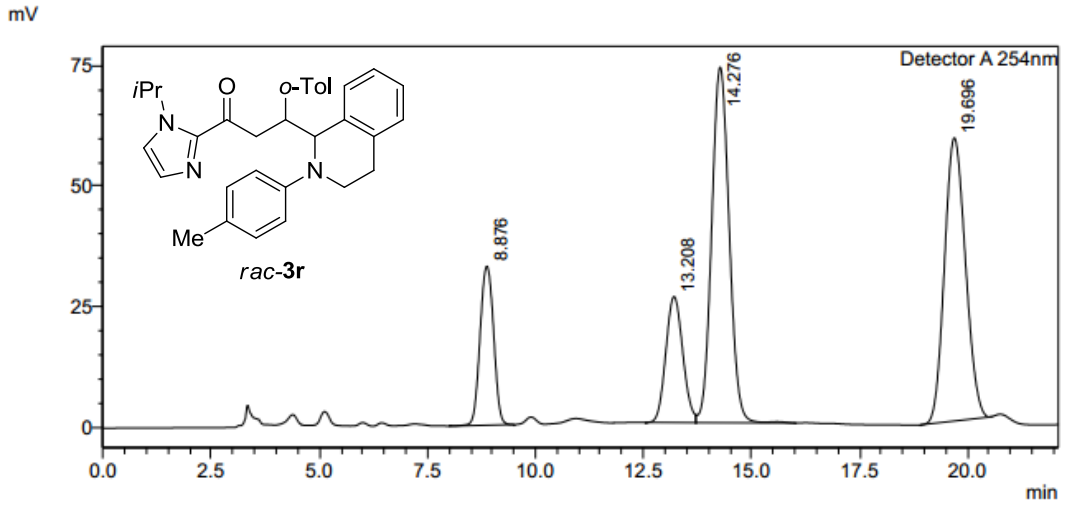
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.080	2662739	44011	7.354
2	15.764	12633859	225526	34.894
3	17.401	963028	17720	2.660
4	22.264	19947142	345830	55.092
Total		36206768	633087	100.000

HPLC traces of *rac*-**3q** (reference) and chiral-**3q**. Area integration = 2.7:55.1 (91% ee).

Racemic **3r**:

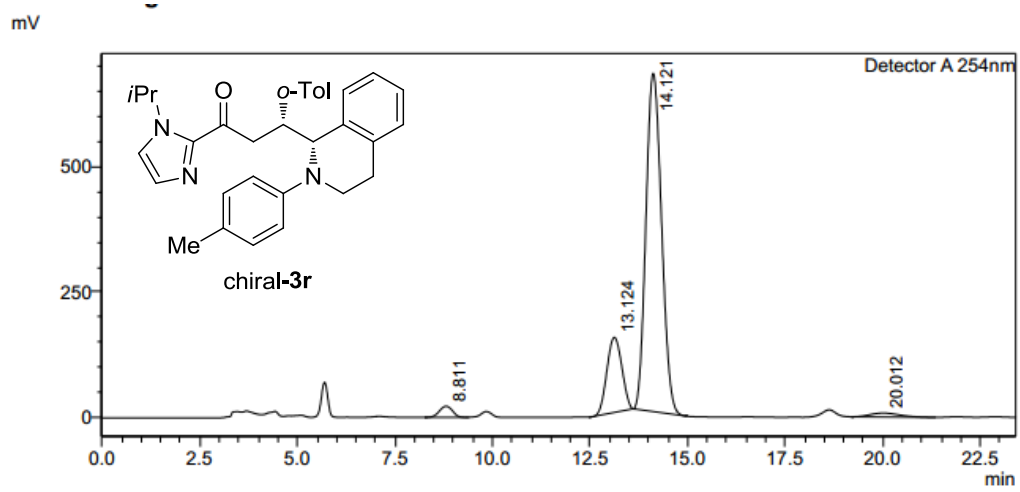


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	8.876	716408	32847	13.076
2	13.208	713963	26038	13.031
3	14.276	2072193	73486	37.822
4	19.696	1976274	58519	36.071
Total		5478838	190891	100.000

Chiral **3r**:



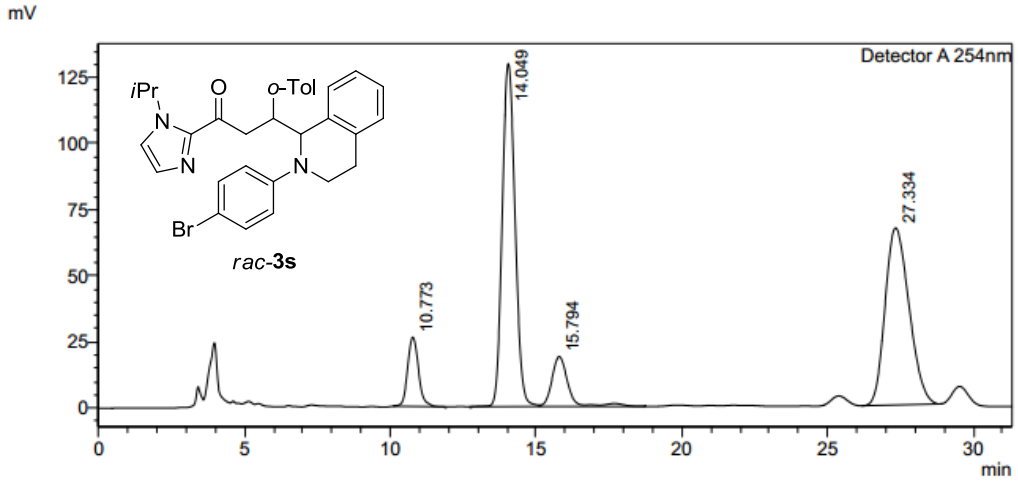
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	8.811	513143	21963	2.174
2	13.124	3985875	149364	16.885
3	14.121	18701808	673261	79.227
4	20.012	404667	7787	1.714
Total		23605492	852375	100.000

HPLC traces of *rac*-**3r** (reference) and chiral-**3r**. Area integration = 79.2:1.7 (96% ee).

Racemic **3s**:

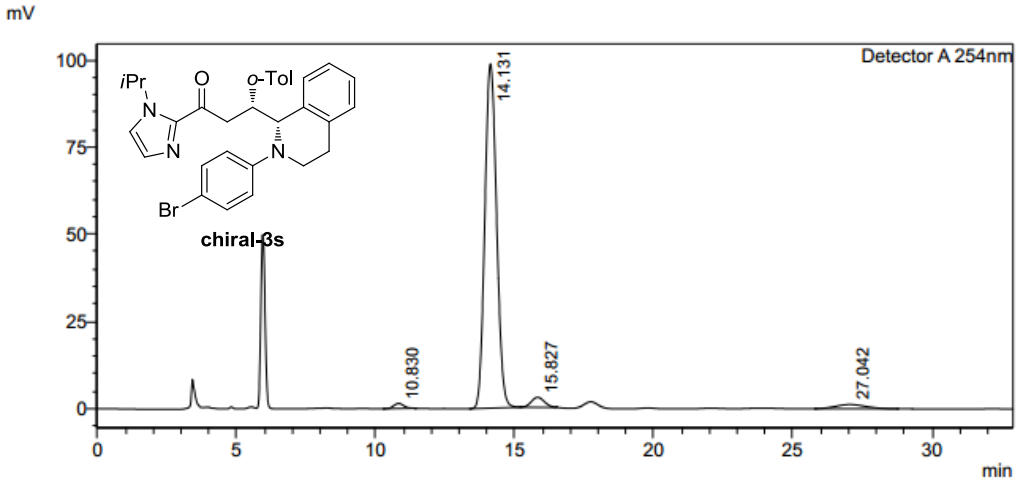


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.773	676688	26155	7.338
2	14.049	3967114	129668	43.017
3	15.794	743693	18912	8.064
4	27.334	3834700	66952	41.581
Total		9222196	241687	100.000

Chiral **3s**:



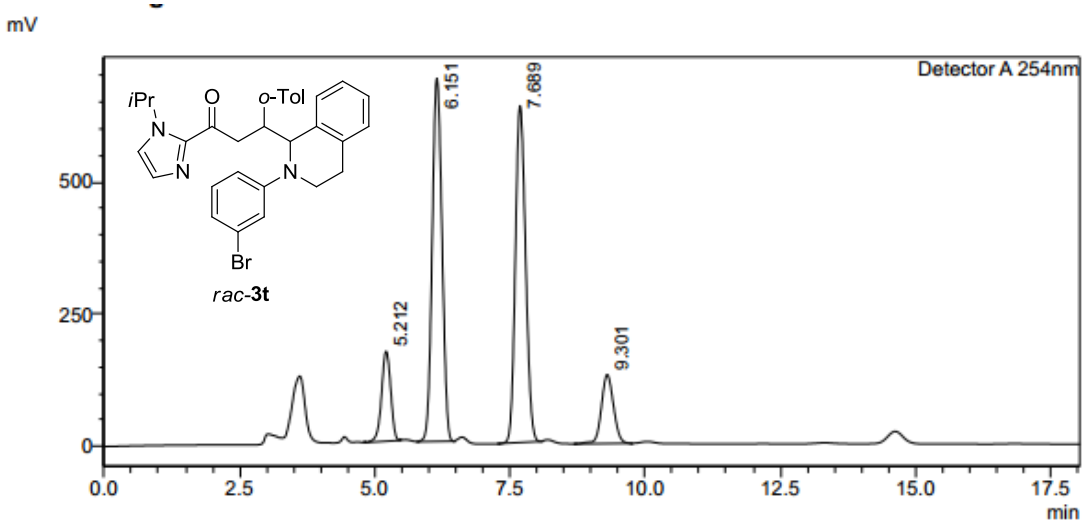
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.830	35217	1420	1.135
2	14.131	2885932	98625	92.976
3	15.827	93108	2867	3.000
4	27.042	89687	1208	2.889
Total		3103945	104120	100.000

HPLC traces of *rac*-**3s** (reference) and chiral-**3s**. Area integration = 93.0:2.9 (94% ee).

Racemic **3t**:

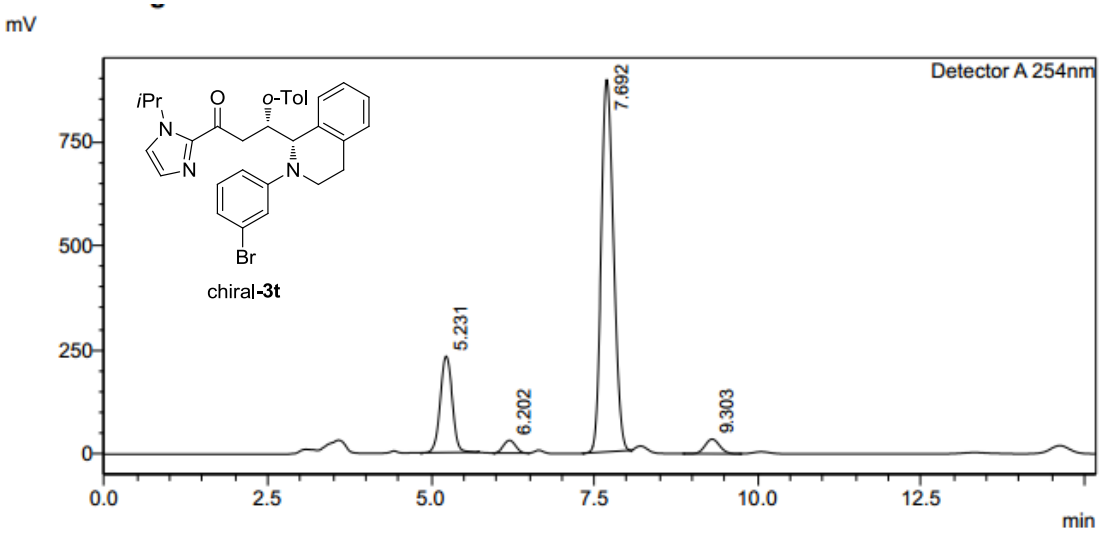


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	5.212	2006791	169895	9.528
2	6.151	8632933	686187	40.988
3	7.689	8393601	636698	39.852
4	9.301	2028772	129928	9.632
Total		21062098	1622708	100.000

Chiral **3t**:



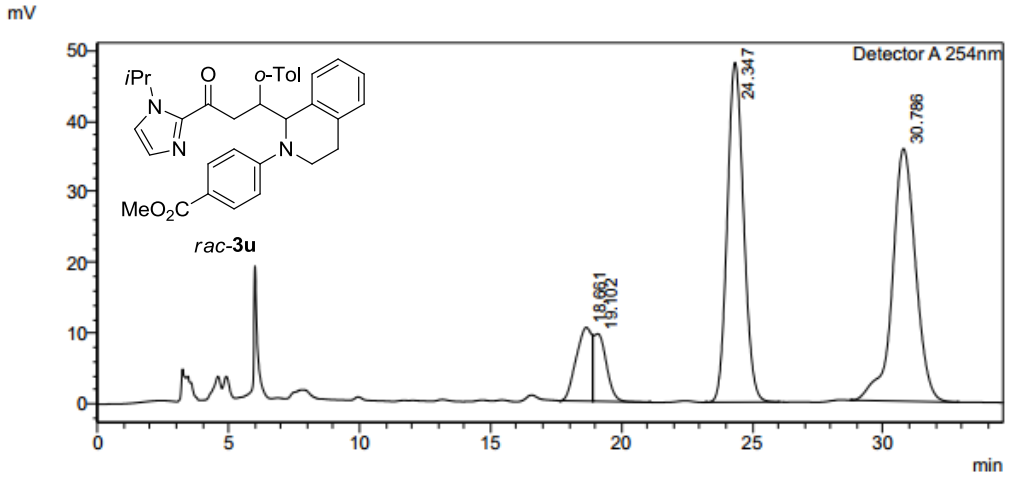
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	5.231	2965195	230882	18.898
2	6.202	395844	30461	2.523
3	7.692	11786254	893219	75.117
4	9.303	543210	35021	3.462
Total		15690503	1189582	100.000

HPLC traces of *rac*-**3t** (reference) and chiral-**3t**. Area integration = 2.5:75.1(93% ee).

Racemic **3u**:

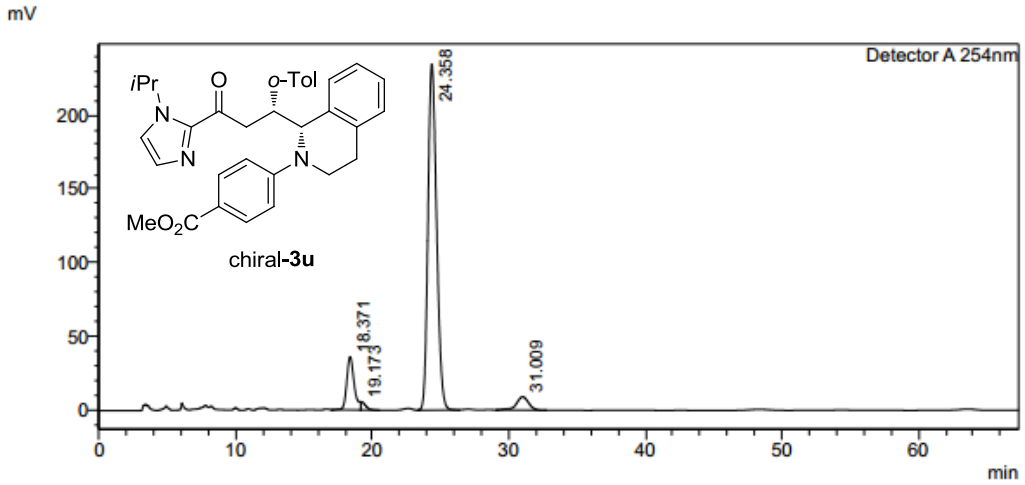


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	18.661	448243	10433	8.879
2	19.102	307437	9560	6.090
3	24.347	2084889	48045	41.297
4	30.786	2207899	35737	43.734
Total		5048468	103775	100.000

Chiral**3u**:



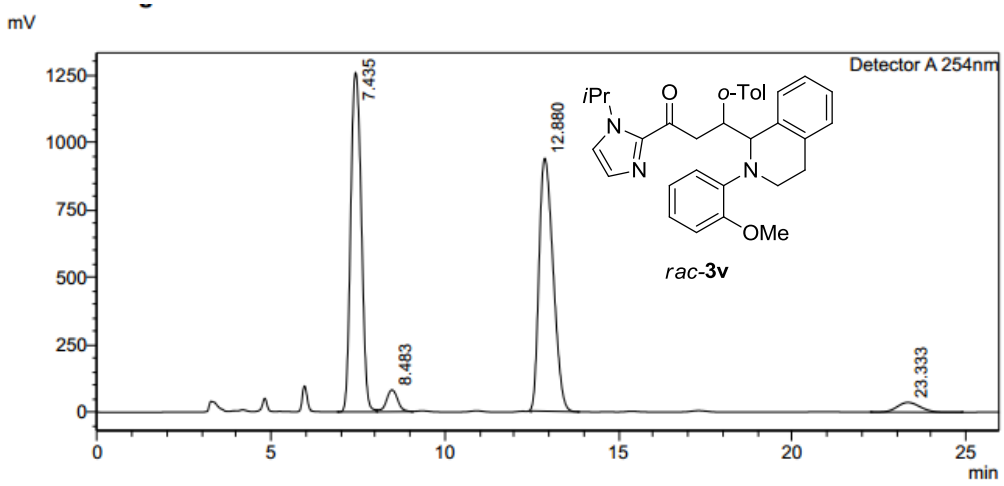
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	18.371	1336807	35947	10.882
2	19.173	157613	5520	1.283
3	24.358	10230637	234056	83.280
4	31.009	559618	8995	4.555
Total		12284675	284518	100.000

HPLC traces of *rac*-**3u** (reference) and chiral-**3u**. Area integration = 83.3:4.6 (90% ee).

Racemic **3v**:

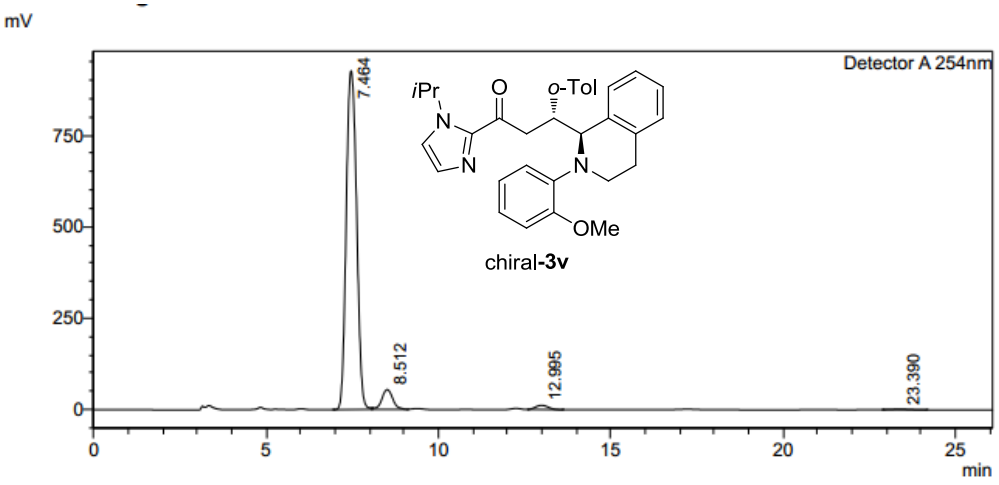


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.435	26633479	1257347	47.162
2	8.483	1787146	80181	3.165
3	12.880	26411823	936846	46.770
4	23.333	1639334	35960	2.903
Total		56471782	2310334	100.000

Chiral**3v**:



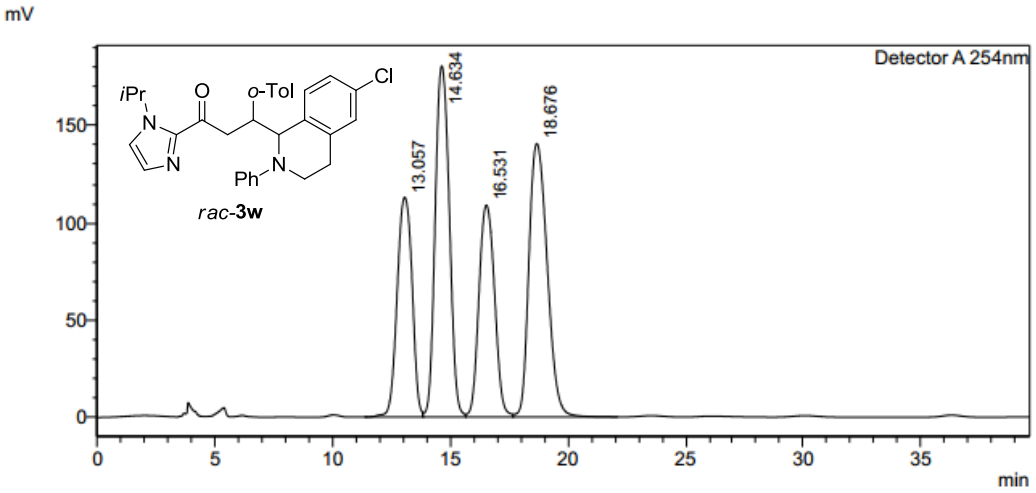
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.464	19296187	924896	92.637
2	8.512	1187314	53879	5.700
3	12.995	290841	11498	1.396
4	23.390	55439	1394	0.266
Total		20829782	991668	100.000

HPLC traces of *rac*-**3v** (reference) and chiral-**3v**. Area integration = 92.6:1.4(97% ee).

Racemic **3w**:

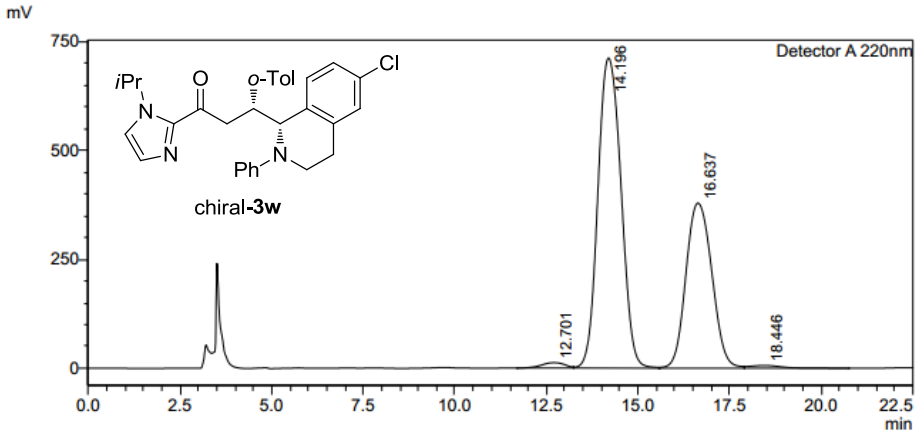


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.
1	13.057	5010488	112961	19.918
2	14.634	7521627	180524	29.900
3	16.531	5052508	108889	20.085
4	18.676	7571277	140571	30.097
Total		25155900	542945	100.000

Chiral**3w**:



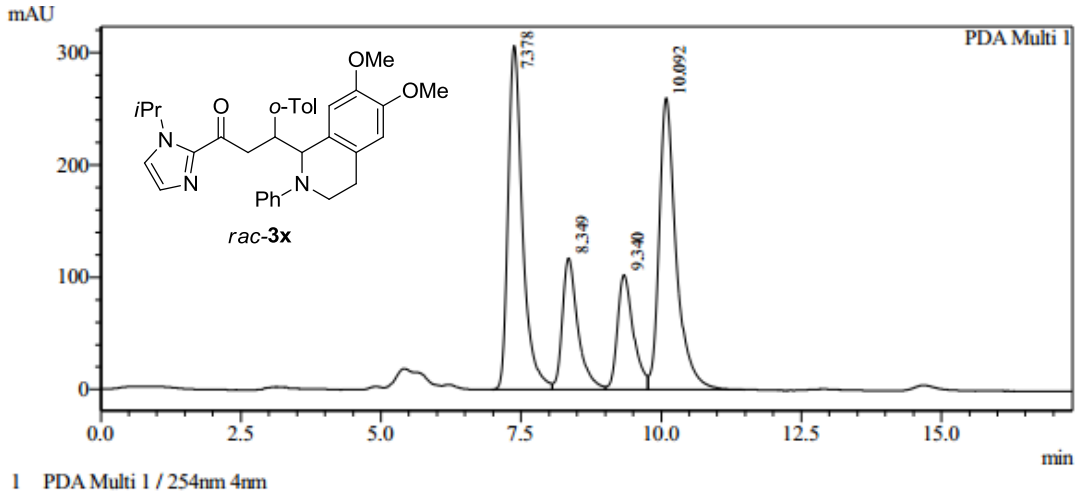
<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.
1	12.701	551476	12402	1.085
2	14.196	31212269	711282	61.387
3	16.637	18692570	378758	36.764
4	18.446	388522	6257	0.764
Total		50844838	1108698	100.000

HPLC traces of *rac*-**3w** (reference) and chiral-**3w**. Area integration = 61.4:0.8 (99%).

Racemic **3x**:



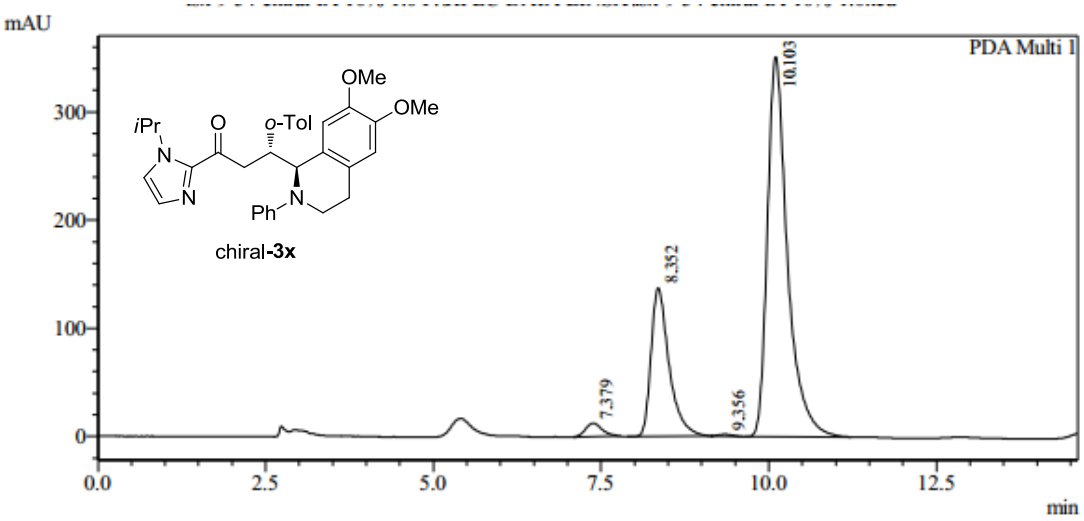
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT7.378	7.378	5541886	306186	36.084
2	RT8.349	8.349	2276885	117053	14.825
3	RT9.340	9.340	2018568	102036	13.143
4	RT10.092	10.092	5521158	259478	35.949
Total			15358497	784753	100.000

Chiral**3x**:



1 PDA Multi 1 / 254nm 4nm

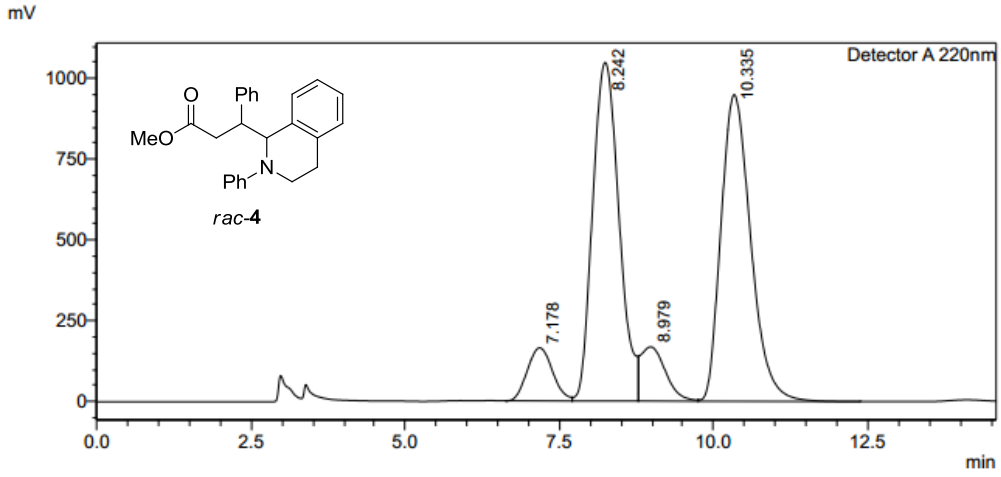
PeakTable

PDA Ch1 254nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %
1	RT7.379	7.379	209693	12239	2.074
2	RT8.352	8.352	2565994	136826	25.377
3	RT9.356	9.356	23616	1732	0.234
4	RT10.103	10.103	7312040	350980	72.315
Total			10111343	501778	100.000

HPLC traces of *rac*-**3x** (reference) and chiral-**3x**. Area integration = 2.1:72.3 (94%).

Racemic **4**:

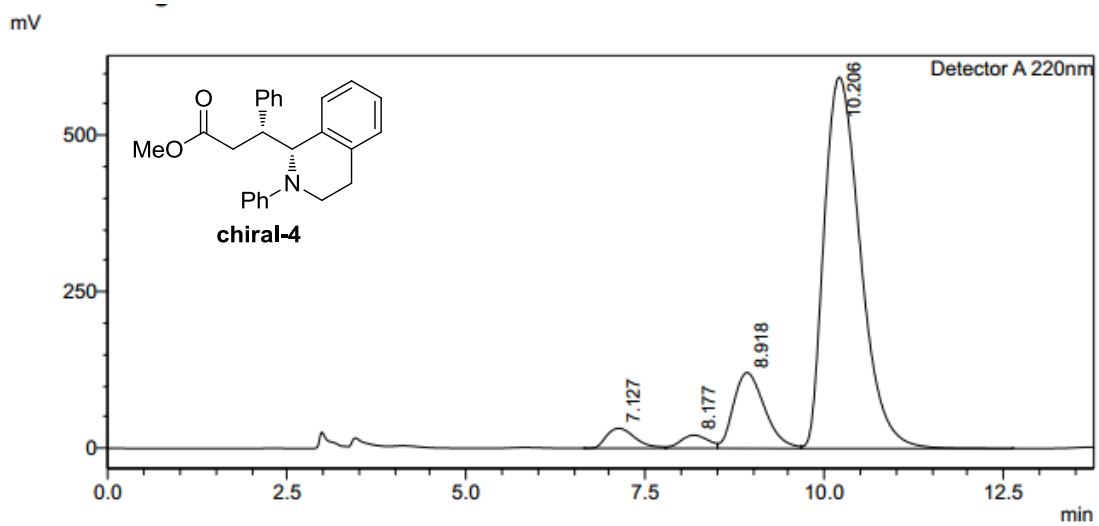


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.178	4693008	164052	6.471
2	8.242	31138273	1047517	42.937
3	8.979	4795600	167834	6.613
4	10.335	31893974	949142	43.979
Total		72520856	2328545	100.000

Chiral **4**:



<Peak Table>

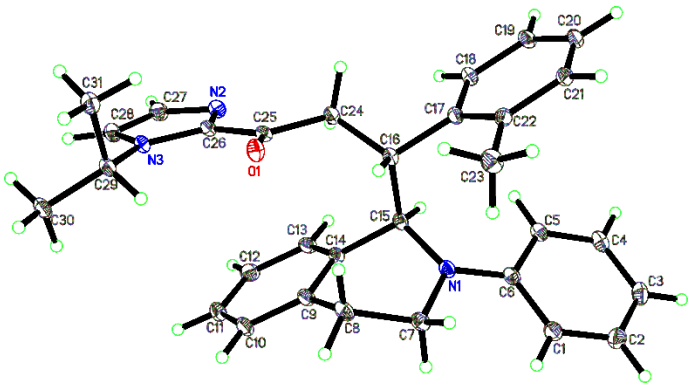
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.
1	7.127	898288	31875	3.454
2	8.177	565788	21032	2.176
3	8.918	3649919	121145	14.035
4	10.206	20891000	593577	80.335
Total		26004995	767629	100.000

HPLC traces of *rac*-**4**(reference) and chiral-**4**. Area integration = 2.2:80.3 (97%).

Ⅶ Single Crystal X-Ray Diffraction of 3k

Table S3. Crystal data and structure refinement for **3k**.



Identification code	**3k**
Empirical formula	C31 H33 N3 O
Formula weight	463.60
Temperature	100.0(3) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	a = 12.5308(3) Å = 90°.
	b = 7.8842(2) Å = 98.906(2)°.
	c = 12.7592(3) Å = 90°.
Volume	1245.35(5) $Å^3$
Z	2
Density (calculated)	1.236 Mg/m^3
Absorption coefficient	0.583 mm^{-1}
F(000)	496
Crystal size	0.140 x 0.130 x 0.100 mm^3
Theta range for data collection	3.506 to 73.359°.
Index ranges	-15<=h<=15, -9<=k<=8, -14<=l<=15
Reflections collected	4859
Independent reflections	3345 [R(int) = 0.0225]
Completeness to theta = 67.684°	99.8 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	1.00000 and 0.81204
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3345 / 1 / 319
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0852
R indices (all data)	R1 = 0.0347, wR2 = 0.0868
Absolute structure parameter	0.1(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.146 and -0.193 e. $Å^{-3}$