Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

Catalytic Asymmetric Cyclopropanation of Sulfoxonium Ylides Catalyzed by a Chiral-at-Metal Rhodium Complex

Siliang Ming[†],[a] Jian Yang[†],[a] Shi Wu,[a] Gang Yao,[a] Hongwei Xiong,[a] Yu Du,[b] and Jun Gong*[a]

[a] School of Pharmacy, Hubei University of Science and Technology, Xianning, Hubei 437100, P. R. China. E-mail: gongjun@hbust.edu.cn

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China.

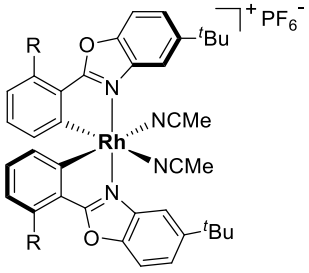
[†] These authors contributed equally to this work.

Contents

1. General Information

All non-aqueous reactions were performed in oven-dried glassware and standard Schlenk tubes under an atmosphere of argon. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from CaH_2 under inert atmosphere. Tetrahydrofuran (THF) and toluene were distilled from sodium and benzophenone under inert atmosphere. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.2~0.3 mm) and visualized by short-wave UV (254 nm) irradiation, potassium permanganate, or iodine stain. Column chromatography was performed with silica gel (200-300 mesh, Yantai Jiangyou Silica Gel Development Co., Ltd). The ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD 400 NMR spectrometer, respectively. Chemical shifts (δ) for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (δ 77.00 ppm) as the internal standard. The infrared spectra were recorded on a VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm^{-1}. Optical rotation was recorded on INESA SGW-1 polarimeter at concentrations of 0.1 g/100 mL or 0.2 g/100 mL. Enantiomeric excess was determined by HPLC analysis on Chiralpak column (Daicel Chemical Industries, LTD) on Shimadzu LC-20AD. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry.

2. Synthesis of Catalysts

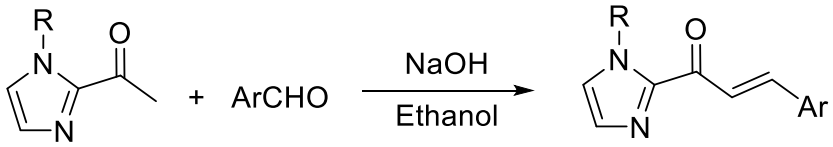


Λ-Rh1 R = 3,5-$Me_2C_6H_3$
Λ-Rh2 R = 3,5-$(CF_3)_2C_6H_3$
Λ-Rh3 R = H

Racemic rhodium catalyst ***rac*-Rh3** and chiral catalyst **Λ-Rh3** were prepared according to reported procedures developed by Meggers' group.[1] **Λ-Rh1**[2], **Λ-Rh2**[3] were synthesized following published procedures.

3. Synthesis of Substrates

3.1 Synthesis of α,β-unsaturated 2-acylimidazoles



α,β-unsaturated 2-acylimidazoles **1** were prepared by *Aldol* reaction according to a reported procedure.[3] 2-acetyl-imidazole (10.0 mmol, 1.0 eq.) and ethanol (50 mL) were added to a 100 mL round-bottom flask followed by the aromatic aldehyde (12 mmol, 1.2 eq.) and NaOH (5 mmol, 0.5 eq.). The solution was stirred at room temperature until the substrates consumption (detected by TLC). The reaction mixture was then quenched with saturated aqueous NH_4Cl and the mixture was extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with 50 mL brine and dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel to afford the desired product **1**.

1n was prepared according to published procedures.[4] **1q** was prepared according to published procedures.[5] **1r** was prepared according to published procedures.[6] **1v** was prepared according to published procedures.[7] **1w** was prepared according to published procedures.[8]

3.2 Synthesis of sulfur ylides

The sulfoxonium ylides **2a-2k** were prepared according to a reported method.[9] **2l** was prepared according to published procedures.[10] **2m** was prepared according to published procedures.[11]

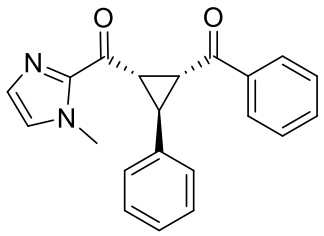
4. Asymmetric Cyclopropanation Reactions

4.1 Synthesis of racemic products as HPLC references

General Procedure: A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazoles **1** (0.20 mmol), sulfoxonium ylides **2** (0.24 mmol) and racemic catalyst *rac*-**Rh3** (1.7 mg, 1.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30ºC for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford racemic products as HPLC reference for determination of enantiomeric excess.

4.2 Substrate Scope

General Procedure: A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazoles **1** (0.20 mmol), sulfoxonium ylides **2** (0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30ºC for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral products.



3aa

Following **General Procedure**, a dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1a** (42.5 mg, 0.20 mmol), sulfoxonium ylide **2a**

(47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3aa** as pale yellow oil (64.1 mg, yield: 97%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 12.841 min, t_r(major) = 15.743 min;

$[\alpha]_D^{25}$ = -175.8° (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 2980, 1671, 1510, 1459, 1432, 1373, 1320, 1284, 1237, 1143 cm^{-1};

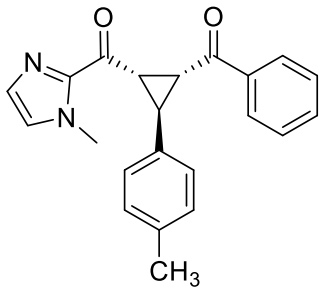
^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.28 – 7.22 (m, 1H), 7.15 (s, 1H), 7.00 (s, 1H), 4.15 – 4.10 (m, 1H), 3.90 (s, 3H), 3.57 (t, *J* = 6.3 Hz, 1H), 3.35 (dd, *J* = 9.6, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.07, 185.90, 143.34, 138.45, 137.02, 133.15, 129.15, 128.70, 128.52, 127.05, 126.70, 38.60, 36.25, 36.14, 30.67;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{18}N_2O_2Na^+$ $[M+Na]^+$: 353.1266, found: 353.1261.

Alternatively, **3aa** can also be synthesized with sulfur ylide **2l**. Following **General Procedure**, a dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1a** (42.5 mg, 0.20 mmol), sulfur ylide **2l** (43.2 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (1.6 mg, 1.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3aa** as pale yellow oil (62.8 mg, yield: 95%). Dr = 8:1 was determined by crude ^1H NMR analysis, *ee* = 98% (for the major diastereoisomer).

In the scale-up synthesis, a dried 25 mL flask was charged with α,β-unsaturated 2-acylimidazole **1a** (424.5 mg, 2.0 mmol), sulfoxonium ylide **2a** (471.0 mg, 2.4 mmol) and chiral catalyst **Λ-Rh3** (8.3 mg, 0.5 mol% or 1.7 mg, 0.1 mol%). The tube was purged with argon, then DCE (5.0 mL) was added. The reaction mixture was stirred at 30°C (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3aa** as pale yellow oil (630.6 mg, 95% yield or 564.0 mg, 85% yield). Enantiomeric excess was determined by HPLC analysis, *ee* = 99%.



3ba

Following **General Procedure**, a dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1b** (45.3 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3ba** as pale yellow oil (66.8 mg, yield: 97%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 12.455 min, t_r(major) = 15.568 min;

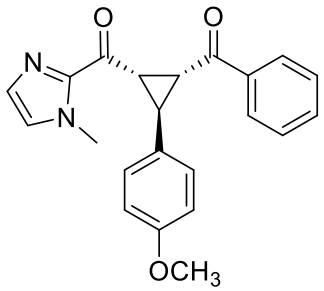
$[\alpha]_D^{25}$ = -48.0° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2924, 1658, 1594, 1579, 1514, 1469, 1456, 1441, 1399, 1311, 1286, 1221, 1178, 1157, 1087 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.97 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.17 – 7.11 (m, 3H), 6.99 (s, 1H), 4.09 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.90 (s, 3H), 3.54 (t, *J* = 6.3 Hz, 1H), 3.31 (dd, *J* = 9.6, 6.6 Hz, 1H), 2.34 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.16, 186.09, 143.47, 137.08, 136.70, 135.41, 133.09, 129.37, 129.24, 128.51, 128.51, 127.00, 126.58, 38.59, 36.18, 36.10, 30.50, 21.08;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 367.1423, found: 367.1417.



3ca

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1c** (48.5 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3ca** as pale yellow oil (67.0 mg, yield: 93%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 24.443 min, t_r(major) = 34.027 min;

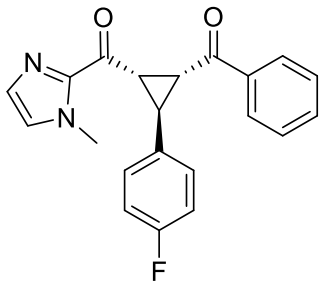
$[\alpha]_D^{25}$ = -62.0° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3141, 2956, 2830, 2050, 1672, 1648, 1613, 1597, 1581, 1518, 1450, 1414, 1399, 1324, 1306, 1282, 1261, 1251, 1224 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.99 (m, 2H), 7.54 – 7.48 (m, 1H), 7.39 (td, *J* = 8.3, 7.1 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.14 (d, *J* = 1.0 Hz, 1H), 6.99 (s, 1H), 6.90 – 6.85 (m, 2H), 4.07 (dd, *J* = 9.5, 6.1 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.53 (t, *J* = 6.3 Hz, 1H), 3.29 (dd, *J* = 9.5, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.16, 186.14, 158.71, 143.52, 137.09, 133.09, 130.47, 129.31, 128.51 (overlap, 4C), 127.84, 127.03, 114.10, 55.35, 38.47, 36.13, 36.11, 30.21;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 383.1372, found: 383.1366.



3da

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1d** (46.1 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3da** as pale yellow oil (66.9 mg, yield: 96%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 19.511 min, t_r(major) = 22.872 min;

$[\alpha]_D^{25}$= -134.2° (*c* = 0.2, $CHCl_3$);

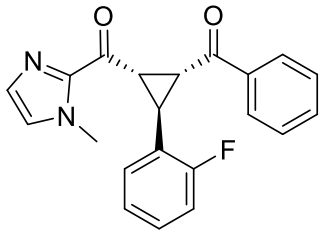
IR (KBr) ν_{max}: 3107, 1681, 1673, 1593, 1577, 1515, 1470, 1445, 1403, 1331, 1314, 1275, 1215, 1166, 1160 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.98 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.16 (s, 1H), 7.06 – 6.98 (m, 3H), 4.09 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.89 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.30 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.88, 185.72, 161.93 (d, *J* = 245.4 Hz, 1C), 143.32, 136.97, 134.18 (d, *J* = 3.2 Hz, 1C), 133.20, 129.28, 128.54, 128.49, 128.36 (d, *J* = 8.0 Hz, 2C), 127.13, 115.56 (d, *J* = 21.6 Hz, 2C), 38.37, 36.19, 36.11, 29.81;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -115.50;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}FN_2O_2Na^+$ $[M+Na]^+$: 371.1172, found: 371.1167.



3ea

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1e** (46.1 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30ºC for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3ea** as pale yellow oil (66.4 mg, yield: 95%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column ID, λ = 254 nm, *n*-hexane/*i*-PrOH = 70:30, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 18.694 min, t_r(major) = 22.170 min;

$[\alpha]_D^{25}$ = -111.4º (*c* = 0.2, $CHCl_3$);

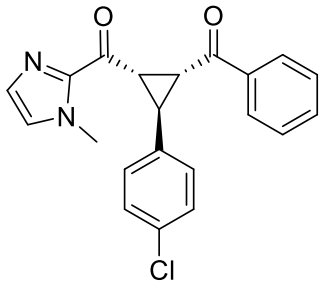
IR (KBr) ν_{max}: 3113, 2923, 1681, 1661, 1598, 1580, 1498, 1454, 1433, 1399, 1364, 1346, 1319, 1294, 1281, 1240, 1219 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 – 8.00 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.18 (m, 2H), 7.16 – 7.02 (m, 3H), 7.00 (s, 1H), 4.16 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.88 (s, 3H), 3.71 (t, *J* = 6.5 Hz, 1H), 3.42 (dd, *J* = 9.6, 6.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.84, 185.72, 161.68 (d, *J* = 247.3 Hz, 1C), 143.39, 136.98, 133.13, 129.38, 128.59, 128.49, 128.47, 127.90 (d, *J* = 3.7 Hz, 1C), 127.15, 125.58 (d, *J* = 13.8 Hz, 1C), 124.21 (d, *J* = 3.6 Hz, 1C), 115.60 (d, *J* = 21.6 Hz, 1C), 36.80 (d, *J* = 1.9 Hz, 1C), 36.07, 34.95 (d, *J* = 1.6 Hz, 1C), 24.87 (d, *J* = 3.9 Hz, 1C);

^{19}F NMR (376 MHz, $CDCl_3$): δ = -117.75;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}FN_2O_2Na^+$ $[M+Na]^+$: 371.1172, found: 371.1167.



3fa

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1f** (49.4 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3fa** as white solid (69.3 mg, yield: 95%), mp 121–122 °C. Enantiomeric excess was determined by HPLC analysis, *ee* > 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, tr(minor) = 14.443 min, tr(major) = 16.722 min;

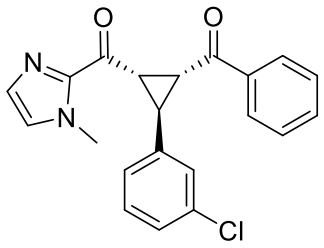
$[\alpha]_D^{25}$= -81.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2923, 1666, 1595, 1577, 1497, 1451, 1407, 1360, 1293, 1270, 1223, 1154, 1110, 1082, 1051, 1015 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 – 7.98 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.35 (m, 2H), 7.32 – 7.21 (m, 4H), 7.15 (d, *J* = 1.0 Hz, 1H), 7.00 (s, 1H), 4.10 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.87 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.29 (dd, *J* = 9.7, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.65, 185.61, 143.41, 137.08, 136.93, 133.22, 132.78, 129.48, 128.81, 128.55, 128.49, 128.13, 127.20, 38.30, 36.12, 36.08, 29.76;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}ClN_2O_2Na^+$ $[M+Na]^+$: 387.0877, found: 387.0870.



3ga

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1g** (49.4 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3ga** as pale yellow oil (70.0 mg, yield: 96%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, 30 °C, tr(minor) = 17.213 min, tr(major) = 19.312 min;

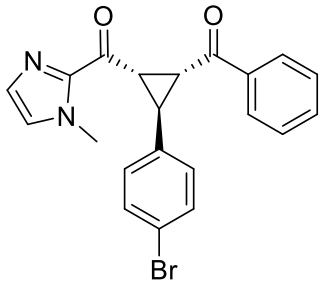
$[\alpha]_D^{25}$ = -109.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2940, 1678, 1605, 1563, 1499, 1430, 1402, 1338, 1291, 1262, 1209, 1169, 1130, 1047 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.98 (m, 2H), 7.54 – 7.48 (m, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.18 (m, 4H), 7.16 (d, *J* = 0.9 Hz, 1H), 7.01 (s, 1H), 4.12 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.87 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.33 (dd, *J* = 9.7, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.61, 185.41, 143.23, 140.62, 136.87, 134.61, 133.27, 129.94, 129.30, 128.56, 128.51, 127.23, 127.19, 126.80, 125.10, 37.56, 36.22, 36.11, 29.89;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}ClN_2O_2Na^+$ $[M+Na]^+$: 387.0877, found: 387.0872.



3ha

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1h** (58.2 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30ºC for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford chiral product **3ha** as white solid (73.7 mg, yield: 90%), mp 104–105 ºC.

Enantiomeric excess was determined by HPLC analysis, *ee* > 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 15.243 min, t_r(major) = 17.464 min;

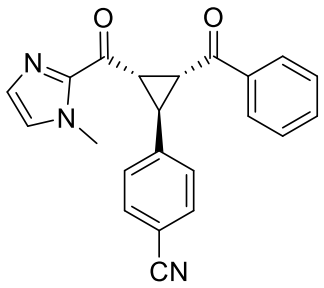
$[\alpha]_D^{25}$ = -128.7º (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 2923, 1677. 1658, 1594, 1580, 1489, 1458, 1440, 1403, 1286, 1221, 1180, 1158 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.97 (m, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.36 (m, 4H), 7.20 – 7.13 (m, 3H), 6.99 (s, 1H), 4.09 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.87 (s, 3H), 3.53 (t, *J* = 6.3 Hz, 1H), 3.29 (dd, *J* = 9.7, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.66, 185.58, 143.37, 137.61, 136.91, 133.24, 131.76, 129.44, 128.56, 128.49, 128.48, 127.20, 120.81, 38.30, 36.09 (overlap, 2C), 29.83;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{18}BrN_2O_2^+$ $[M+H]^+$: 409.0552, found: 409.0546.



3ia

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1i** (47.5 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30^{o}C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ia** as white solid (67.5 mg, yield: 95%), mp 103–104 ^{o}C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 97%, Chiralpak column IA, λ = 254 nm, *n*-hexane/*i*-PrOH = 70:30, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 20.275 min, t_r(minor) = 26.743 min;

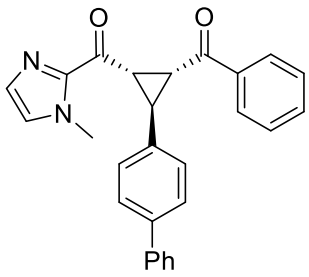
$[\alpha]_D^{25}$= -59.9^{o} (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 2924, 2853, 2225, 1692, 1659, 1609. 1595, 1578, 1512, 1448, 1416, 1398, 1346, 1327, 1310, 1290, 1275, 1220, 1178, 1153 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.18 (s, 1H), 7.03 (s, 1H), 4.20 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.89 (s, 3H), 3.61 (t, *J* = 6.3 Hz, 1H), 3.39 (dd, *J* = 9.8, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.20, 184.83, 144.21, 142.96, 136.67, 133.44, 132.52, 129.21, 128.63, 128.50, 127.50, 127.35, 118.73, 110.81, 38.53, 36.48, 36.16, 29.96;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{17}N_3O_2Na^+$ $[M+Na]^+$: 378.1219, found: 378.1213.



3ja

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1j** (57.7 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30^{o}C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3ja** as pale yellow oil (78.8 mg, yield: 97%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 14.026 min, t_r(major) = 16.803 min;

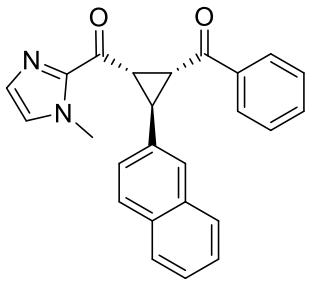
$[\alpha]_D^{25}$ = -71.3^{o} (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3060, 3027, 2285, 1682, 1656, 1597, 1579, 1488, 1445, 1404, 1341, 1287, 1218, 1176, 1155 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.3 Hz, 2H), 7.62 – 7.50 (m, 5H), 7.47 – 7.32 (m, 7H), 7.16 (s, 1H), 7.00 (s, 1H), 4.20 – 4.13 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.91 (s, 3H), 3.62 (t, *J* = 6.3 Hz, 1H), 3.38 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.96, 185.94, 143.52, 140.68, 139.99, 137.64, 137.06, 133.17, 129.43, 128.83, 128.55, 128.54, 127.41, 127.33, 127.13, 127.03, 38.56, 36.31, 36.10, 30.42 (one aryl peak lost for overlap);

HRMS (ESI, *m*/*z*) calcd. for $C_{27}H_{22}N_2O_2Na^+$ $[M+Na]^+$: 429.1579, found: 429.1574.



3ka

.

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1k** (52.5 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30^{o}C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3ka** as white solid (73.9 mg, yield: 97%), mp 139–140 ^{o}C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 13.706 min, t_r(major) = 16.806 min;

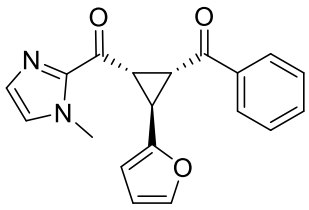
$[\alpha]_D^{25}$ = -67.7^o (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2920, 2852, 1685, 1661, 1598, 1510, 1468, 1451, 1429, 1404, 1285, 1222 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 – 8.01 (m, 2H), 7.85 – 7.75 (m, 4H), 7.54 – 7.37 (m, 6H), 7.16 (s, 1H), 7.00 (s, 1H), 4.25 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.91 (s, 3H), 3.74 (t, *J* = 6.3 Hz, 1H), 3.45 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.91, 185.93, 143.51, 137.01, 135.93, 133.39, 133.15, 132.52, 129.40, 128.52 (overlap, 4C), 128.45, 127.67, 127.57, 127.09, 126.36, 125.74, 125.32, 124.85, 38.72, 36.16, 36.10, 30.76;

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 403.1423, found: 403.1417.



3la

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1l** (40.4 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3la** as pale yellow oil (52.7 mg, yield: 82%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column ID, λ = 254 nm, *n*-hexane/*i*-PrOH =75:25, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 25.252 min, t_r(major) = 28.334 min;

$[\alpha]_D^{25}$ = -170.3° (*c* = 0.2, $CHCl_3$);

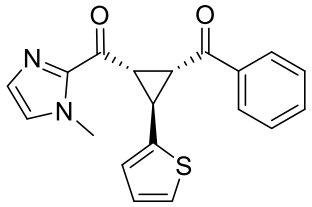
IR (KBr) ν_{max}: 3435, 3138, 3070, 3029, 2922, 1675, 1657, 1597, 1510, 1453, 1423, 1401, 1287, 1249, 1224, 1178, 1152 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 – 7.97 (m, 2H), 7.51 (td, *J* = 7.2, 1.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.15 (s, 1H), 6.99 (s, 1H), 6.35 –

6.30 (m, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 4.18 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.87 (s, 3H), 3.57 (t, *J* = 6.2 Hz, 1H), 3.47 (dd, *J* = 9.7, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.49, 185.49, 151.71, 143.41, 141.46, 136.89, 133.19, 129.47, 128.55, 128.52, 127.12, 110.70, 106.59, 36.22, 36.07, 34.45, 23.97;

HRMS (ESI, *m*/*z*) calcd. for $C_{19}H_{16}N_2O_3Na^+$ $[M+Na]^+$: 343.1059, found: 343.1053.



3ma

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1m** (43.7 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30ºC for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3ma** as pale yellow oil (63.3 mg, yield: 94%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column OD-H, λ = 254 nm, *n*-hexane/*i*-PrOH =90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 11.247 min, t_r(major) = 15.682 min;

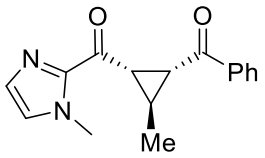
$[\alpha]_D^{25}$ = -235.9º (*c* = 0.3, $CHCl_3$);

IR (KBr) ν_{max}: 3271, 2944, 1703, 1667, 1604, 1527, 1442, 1430, 1407, 1391, 1373, 1352, 1277, 1204, 1157 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 8.00 (m, 2H), 7.55 – 7.48 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.14 (m, 2H), 7.02 – 6.98 (m, 2H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.10 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.89 (s, 3H), 3.74 (t, 1H, *J* = 6.2 Hz), 3.37 (dd, *J* = 9.7, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.45, 185.34, 143.34, 142.41, 136.86, 133.22, 129.43, 128.53 (overlap, 4C), 127.11 (overlap, 2C), 124.70, 123.75, 39.38, 37.29, 36.08, 25.93;

HRMS (ESI, *m*/*z*) calcd. for $C_{19}H_{16}N_2O_2SNa^+$ $[M+Na]^+$: 359.0830, found: 359.0830.



3na

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1n** (30.1 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3na** as colorless oil (45.6 mg, yield: 85%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column ID, λ = 254 nm, *n*-hexane/*i*-PrOH =75:25, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 14.494 min, t_r(minor) = 17.270 min;

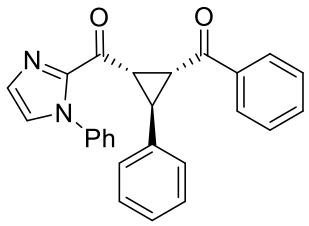
$[\alpha]_D^{25}$= +74.2° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2979, 1681, 1595, 1571, 1549, 1511, 1464, 1456, 1412, 1383, 1339, 1278, 1220, 1189, 1167, 1072 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 – 8.01 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.24 – 7.18 (m, 1H), 7.07 (s, 1H), 4.09 (dd, *J* = 5.7, 4.6 Hz, 1H), 3.99 (s, 3H), 3.45 (dd, *J* = 9.7, 4.7 Hz, 1H), 2.26 (dp, *J* = 9.7, 6.2 Hz, 1H), 1.26 (d, *J* = 6.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.47, 189.60, 143.29, 138.02, 133.02, 129.81, 128.59, 128.26, 127.29, 36.16, 35.36, 32.99, 29.56, 11.30;

HRMS (ESI, *m*/*z*) calcd. for $C_{16}H_{16}N_2O_2Na^+$ $[M+Na]^+$: 291.1109, found: 291.1102.



3oa

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1o** (54.9 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3oa** as pale yellow oil (76.9 mg, yield: 98%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IB, λ = 254 nm, *n*-hexane/*i*-PrOH =90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 11.333 min, t_r(major) = 15.550 min;

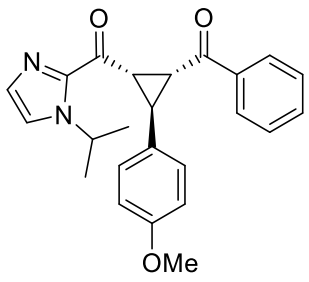
$[\alpha]_D^{25}$ = +21.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3453, 2922, 1677, 1596, 1580, 1503, 1497, 1445, 1429, 1399, 1310, 1274, 1217 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.97 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 – 7.21 (m, 11H), 7.15 – 7.08 (m, 3H), 4.07 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.46 (t, *J* = 6.3 Hz, 1H), 3.37 (dd, *J* = 9.5, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.84, 184.56, 143.28, 138.46, 137.99, 136.96, 133.12, 129.80, 128.87, 128.66, 128.54, 128.50, 128.46, 127.02, 126.98, 126.58, 125.62, 38.58, 36.00, 30.40;

HRMS (ESI, *m*/*z*) calcd. for $C_{26}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 415.1422, found: 415.1417.



3pa

A dried 25 mL Schlenk tube was charged with α,β-unsaturated 2-acylimidazole **1p** (54.1 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3pa** as colorless oil (62.4 mg, yield: 80%).

Enantiomeric excess was determined by HPLC analysis, *ee* > 99%, Chiralpak column IA, λ = 254 nm, *n*-hexane/*i*-PrOH =80:20, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 15.107 min, t_r(minor) = 23.330 min;

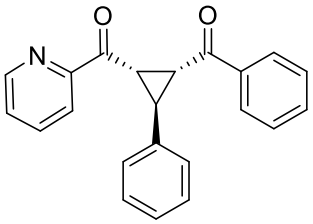
$[\alpha]_D^{25}$ = -49.2° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3439, 2935, 1687, 1659, 1613, 1597, 1580, 1517, 1450, 1414, 1394, 1306, 1279, 1250, 1217, 1197, 1176 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.20 (m, 3H), 7.18 (s, 1H), 6.90 – 6.84 (m, 2H), 5.42 (m, *J* = 6.7 Hz, 1H), 4.14 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.80 (s, 3H), 3.53 (t, *J* = 6.3 Hz, 1H), 3.26 (dd, *J* = 9.6, 6.6 Hz, 1H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.18, 186.16, 158.67, 142.82, 137.08, 133.03, 130.59, 129.79, 128.48, 128.45, 127.87, 121.22, 114.08, 55.34, 49.17, 38.50, 36.60, 30.02, 23.45, 23.40;

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{24}N_2O_3Na^+$ $[M+Na]^+$: 411.1685, found: 411.1682.



3qa

A dried 25 mL Schlenk tube was charged with **1q** (41.9 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3qa** as white solid (49.4 mg, yield: 75%), mp 93–94 °C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH =90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 15.938 min, t_r(major) = 20.009 min;

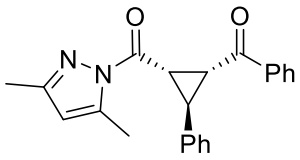
$[\alpha]_D^{25}$ = -143.8° (*c* = 0.3, $CHCl_3$);

IR (KBr) ν_{max}: 3014, 1702, 1649, 1588, 1521, 1469, 1456, 1432, 1417, 1396, 1378, 1335, 1270, 1219, 1165, 1154 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.43 – 7.32 (m, 6H), 7.31 – 7.26 (m, 1H), 4.27 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.60 (t, *J* = 6.2 Hz, 1H), 3.48 (dd, *J* = 9.4, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.81, 194.18, 152.53, 148.19, 138.55, 137.91, 136.83, 133.18, 128.73, 128.52, 128.50, 127.38, 127.07, 126.70, 122.56, 39.19, 34.86, 31.34;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{17}NO_2Na^+$ $[M+Na]^+$: 350.1157, found: 350.1151.



3ra

A dried 25 mL Schlenk tube was charged with α,β-unsaturated *N*-acylpyrazole **1r** (45.3 mg, 0.20 mmol), sulfoxonium ylide **2a** (47.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 50°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 4:1) to afford chiral product **3ra** as white solid (58.0 mg, yield: 84%), mp 103–104 °C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 97%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH =85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 6.441 min, t_r(major) = 7.280 min;

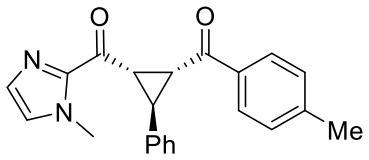
$[\alpha]_D^{25}$= +48.4° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2947, 1687, 1664, 1572, 1483, 1403, 1336, 1290, 1203, 1028 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 5.91 (s, 1H), 3.90 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.37 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.46 (s, 3H), 2.19 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.22, 168.41, 152.21, 144.19, 138.17, 137.04, 133.13, 128.68, 128.49, 128.46, 127.11, 126.79, 111.09, 37.02, 32.86, 30.63, 14.35, 13.79;

HRMS (ESI, *m*/*z*) calculated for $C_{22}H_{21}N_2O_2^+$ $[M+H]^+$: 345.1603, found: 345.1602.



3ab

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2b** (50.4 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ab** as white solid (66.8 mg, yield: 97%), mp 137–138 °C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column ID, λ = 254 nm, *n*-hexane/*i*-PrOH =70:30, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 25.149 min, t_r(major) = 28.060 min;

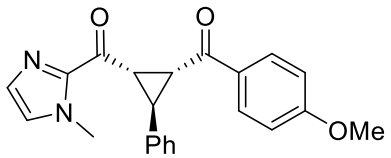
$[\alpha]_D^{25}$ = -141.7° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 2992, 1929, 1817, 1774, 1679, 1660, 1605, 1573, 1504, 1461, 1402, 1349, 1323, 1309, 1276, 1228, 1211, 1176, 1157 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.88 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 7.21 – 7.13 (m, 3H), 7.00 (s, 1H), 4.12 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.91 (s, 3H), 3.55 (t, *J* = 6.2 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.6 Hz, 1H), 2.36 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.57, 185.92, 144.00, 143.28, 138.54, 134.54, 129.22, 128.94, 128.69, 128.66, 127.00, 126.97, 126.70, 38.72, 36.17, 36.15, 30.61, 21.69;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 367.1423, found: 367.1417.



3ac

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2c** (54.3 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to

room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ac** as colorless oil (66.1 mg, yield: 92%).

Enantiomeric excess was determined by HPLC analysis, *ee* > 99%, Chiralpak column OD-H, λ = 254 nm, *n*-hexane/*i*-PrOH =85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 17.359 min, t_r(major) = 18.314 min;

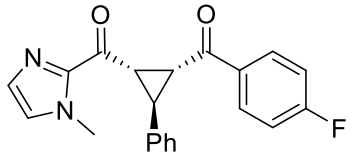
$[\alpha]_D^{25}$ = -83.1° (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 2923, 1677, 1654, 1598, 1510, 1462, 1431, 1400, 1343, 1313, 1281, 1261, 1227, 1162 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.96 (m, 2H), 7.35 – 7.27 (m, 4H), 7.23 (ddd, *J* = 8.5, 5.4, 2.1 Hz, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 0.9 Hz, 1H), 6.87 – 6.82 (m, 2H), 4.08 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.30 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.27, 186.09, 163.49, 143.51, 138.63, 130.77, 130.10, 129.27, 128.63, 127.01, 126.93, 126.64, 113.63, 55.42, 38.50, 36.07, 35.91, 30.41;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 383.1372, found: 383.1366.



3ad

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2d** (51.4 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ad** as colorless oil (67.9 mg, yield: 97%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column OD-H, λ = 254 nm, *n*-hexane/*i*-PrOH =85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 9.872 min, t_r(major) = 11.403 min;

$[\alpha]_D^{25}$ = +45.5° (*c* = 0.1, $CHCl_3$);

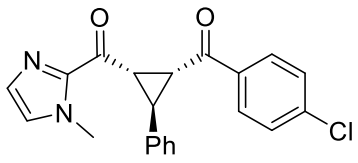
IR (KBr) ν_{max}: 2921, 1683, 1647, 1589, 1504, 1458, 1430, 1401, 1350, 1323, 1278, 1224, 1154 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 – 8.01 (m, 2H), 7.36 – 7.23 (m, 5H), 7.15 (d, *J* = 0.9 Hz, 1H), 7.09 – 7.02 (m, 2H), 7.00 (s, 1H), 4.13 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.89 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.28 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.40, 185.88, 165.75 (d, *J* = 254.7 Hz, 1C), 143.44, 138.33, 133.49 (d, *J* = 3.0 Hz, 1C), 131.14 (d, *J* = 9.4 Hz, 2C), 129.46, 128.72, 127.19, 127.10, 126.68, 115.64 (d, *J* = 21.9 Hz, 2C), 38.33, 36.10 (overlap, 2C), 30.55;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.00;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}FN_2O_2Na^+$ $[M+Na]^+$: 371.1172, found: 371.1166.



3ae

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2e** (55.5 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ae** as white solid (64.2 mg, yield: 88%), mp 119–120 °C.

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column IA, λ = 254 nm, *n*-hexane/*i*-PrOH = 75:25, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 14.628 min, t_r(major) = 17.342 min;

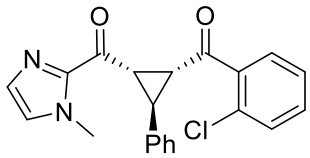
$[\alpha]_D^{25}$ = +31.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3061, 1673, 1659, 1587, 1570, 1502, 1432, 1408, 1337, 1323, 1303, 1281, 1217, 1171, 1156, 1087 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 – 7.94 (m, 2H), 7.39 – 7.23 (m, 7H), 7.15 (s, 1H), 7.01 (s, 1H), 4.14 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.89 (d, *J* = 2.6 Hz, 3H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.27 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.83, 185.80, 143.39, 139.57, 138.25, 135.38, 129.90, 129.49, 128.85, 128.73, 127.22, 127.13, 126.69, 38.26, 36.19, 36.11, 30.59;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}ClN_2O_2Na^+$ $[M+Na]^+$: 387.0877, found: 387.0871.



3af

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2f** (55.5 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3af** as colorless oil (54.1 mg, yield: 74%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 15.279 min, t_r(major) = 19.811 min;

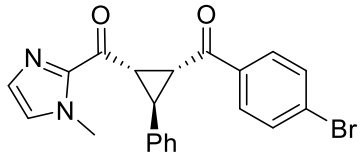
$[\alpha]_D^{25}$ = +57.4° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3132, 3111, 3070, 1684, 1652, 1586, 1502, 1462, 1434, 1400, 1331, 1294, 1273, 1223, 1183, 1157, 1123, 1089, 1074 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.55 (m, 1H), 7.38 – 7.21 (m, 8H), 7.14 (s, 1H), 7.03 (s, 1H), 4.03 – 3.93 (m, 4H), 3.57 (t, *J* = 6.5 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.3 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.76, 185.49, 143.44, 138.79, 138.26, 132.01, 131.67, 130.50, 130.19, 129.41, 128.65, 127.08, 127.06, 126.77, 126.65, 40.82, 38.33, 36.15, 32.31;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}ClN_2O_2Na^+$ $[M+Na]^+$: 387.0877, found: 387.0871.



3ag

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2g** (66.0 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ag** as colorless oil (74.7 mg, yield: 91%).

Enantiomeric excess was determined by HPLC analysis, *ee* > 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 10.740 min, t_r(major) = 13.112 min;

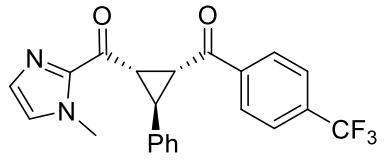
$[\alpha]_D^{25}$ = +59.9° (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 3426, 3055, 1684, 1657, 1603, 1584, 1508, 1502, 1459, 1432, 1403, 1337, 1323, 1308, 1276, 1218, 1171, 1157, 1085, 1069, 1048, 1011 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.85 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.23 (m, 5H), 7.16 (s, 1H), 7.01 (s, 1H), 4.14 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.90 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.27 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.16, 185.87, 143.44, 138.32, 135.86, 131.96, 130.12, 129.57, 128.84, 128.47, 127.33, 127.24, 126.79, 38.38, 36.33, 36.26, 30.72;

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}BrN_2O_2Na^+$ $[M+Na]^+$: 431.0371, found: 431.0364.



3ah

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2h** (63.4 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30^{o}C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ah** as colorless oil (58.3 mg, yield: 73%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column OD-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 9.261 min, t_r(major) = 12.469 min;

$[\alpha]_D^{25}$ = +66.0^o (*c* = 0.1, $CHCl_3$);

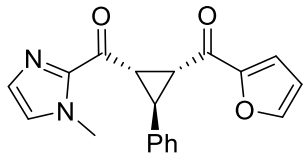
IR (KBr) ν_{max}: 3105, 2914, 1687, 1663, 1601, 1589, 1508, 1456, 1472, 1394, 1362, 1324, 1297, 1282, 1253, 1230, 1183 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.24 (m, 5H), 7.16 (d, *J* = 0.9 Hz, 1H), 7.02 (s, 1H), 4.18 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.90 (s, 3H), 3.58 (t, *J* = 6.3 Hz, 1H), 3.30 (dd, *J* = 9.6, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.29, 185.69, 143.32, 139.73, 138.05, 134.31 (q, *J* = 32.5 Hz, 1C), 129.58, 128.79, 128.77, 127.32, 127.22, 126.70, 125.61 (q, *J* = 3.8 Hz, 2C), 123.59 (q, *J* = 272.6 Hz, 1C), 38.25, 36.39, 36.10, 30.78;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.09;

HRMS (ESI, *m*/*z*) calcd. for $C_{22}H_{17}F_3N_2O_2Na^+$ $[M+Na]^+$: 421.1140, found: 421.1136.



3ai

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2i** (63.4 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (3.4 mg, 2.0 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ai** as colorless oil (50.6 mg, yield: 79%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 12.820 min, t_r(minor) = 17.134 min;

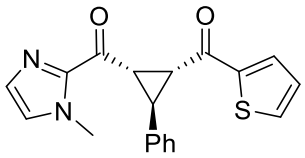
$[\alpha]_D^{25}$ =+101.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3421, 3113, 1668, 1605, 1564, 1510, 1464, 1438, 1401, 1286, 1255, 1224, 1159 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 1.4 Hz, 1H), 7.36 – 7.20 (m, 7H), 7.01 (s, 1H), 6.49 (dt, *J* = 3.2, 1.4 Hz, 1H), 3.98 – 3.93 (m, 4H), 3.56 (t, *J* = 6.4 Hz, 1H), 3.33 (dd, *J* = 9.5, 6.4 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.63, 182.86, 152.82, 146.66, 143.47, 138.41, 129.34, 128.67, 127.06, 127.01, 126.70, 117.79, 112.27, 37.28, 36.31, 36.15, 30.64;

HRMS (ESI, *m*/*z*) calcd. for $C_{19}H_{16}N_2O_3Na^+$ $[M+Na]^+$: 343.1059, found: 343.1053.



3aj

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2j** (48.5 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3aj** as pale yellow oil (63.8 mg, yield: 95%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 97%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 9.161 min, t_r(major) = 10.208 min;

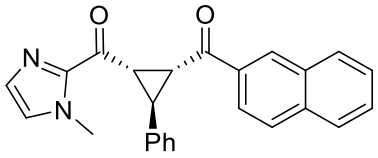
$[\alpha]_D^{25}$ = +57.9° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3448, 2923, 1668, 1640, 1518, 1461, 1435, 1412, 1404, 1364, 1355, 1283, 1242, 1224, 1157 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 2.7 Hz, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.36 – 7.22 (m, 5H), 7.15 (s, 1H), 7.08 – 7.04 (m, 1H), 7.02 (s, 1H), 4.05 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.94 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 1H), 3.33 (dd, *J* = 9.5, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.65, 185.60, 144.15, 143.29, 138.28, 133.80, 132.63, 129.03, 128.69, 128.10, 127.08, 127.01, 126.67, 38.69, 36.15, 35.96, 30.80;

HRMS (ESI, *m*/*z*) calcd. for $C_{19}H_{16}N_2O_2SNa^+$ $[M+Na]^+$: 359.0830, found: 359.0826.



3ak

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfoxonium ylide **2k** (59.1 mg, 0.24 mmol) and chiral catalyst **Λ-Rh3** (0.83 mg, 0.5 mol %). The tube was purged with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30°C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 5:1 to 2:1) to afford chiral product **3ak** as pale yellow oil (72.2 mg, yield: 95%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IA, λ = 254 nm, *n*-hexane/*i*-PrOH = 75:25, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 14.021 min, t_r(minor) = 19.940 min;

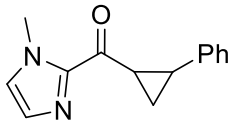
$[\alpha]_D^{25}$ = +143.6° (*c* = 0.2, $CHCl_3$);

IR (KBr) ν_{max}: 3140, 3055, 3020, 1685, 1665, 1647, 1627, 1599, 1576, 1510, 1464, 1428, 1402, 1354, 1322, 1303, 1280, 1251, 1219, 1191, 1155, 1123 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.83 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.54 (dddd, *J* = 23.8, 8.1, 6.9, 1.3 Hz, 2H), 7.36 (d, *J* = 4.3 Hz, 4H), 7.31 – 7.23 (m, 1H), 7.15 (d, *J* = 0.9 Hz, 1H), 6.95 (s, 1H), 4.23 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.84 (s, 3H), 3.65 (t, *J* = 6.3 Hz, 1H), 3.48 (dd, *J* = 9.7, 6.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.81, 185.94, 143.50, 138.57, 135.61, 134.39, 132.44, 130.49, 129.67, 129.42, 128.73, 128.51, 128.38, 127.75, 127.19, 127.06, 126.77, 126.71, 124.13, 38.65, 36.31, 36.06, 30.50;

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 403.1423, found: 403.1417.



3am

A dried 25 mL Schlenk tube was charged with **1a** (42.6 mg, 0.20 mmol), sulfur ylide **2m** (0.24 mmol) and chiral catalyst **Λ-Rh3** (1.6 mg, 1.0 mol %). The tube was purged

with argon, then DCE (0.6 mL) was added. The reaction mixture was stirred at 30^{o}C for indicated time (monitored by TLC) under argon. After cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 5:1) to afford **3am** as pale yellow oil (32.6 mg, yield: 72%). Dr = 7:1 was determined by crude ^{1}H NMR analysis.

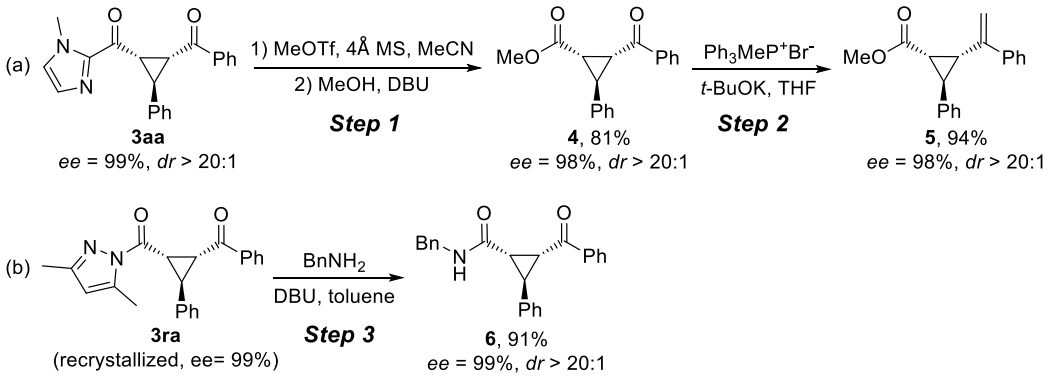
Enantiomeric excess was determined by HPLC analysis, *ee* = 0% (for the major diastereoisomer), Chiralpak column OJH, λ = 254 nm, *n*-hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, 30 °C, t_r = 9.798 min and 12.221 min;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.23 (m, 2H), 7.21 – 7.11 (m, 4H), 7.04 (s, 1H), 4.01 (s, 3H), 3.65 – 3.54 (m, 1H), 2.69 (ddd, *J*=9.2, 6.6, 4.0, 1H), 1.80 (ddd, *J*=9.2, 5.3, 4.0, 1H), 1.52 (ddd, *J*=8.4, 6.6, 4.0, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.48, 140.55, 129.50, 128.54, 127.12, 126.54, 126.38, 126.27, 36.28, 29.78, 29.35, 20.27;

HRMS (ESI, *m*/*z*) calcd. for $C_{14}H_{14}N_2ONa^+$ $[M+Na]^+$: 249.1004, found: 249.0998.

5. Synthetic Transformations



Step 1:

4 Å MS (500 mg, 100 mg/0.1 mmol of **3aa**) was added to a solution of **3aa** (165.2 mg, 0.5 mmol) in dry CH_3CN (5 mL) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 hours at 25ºC. Then methyl trifluoromethansulfonate (226.4 uL, 2.0 mmol, 4.0 eq.) was added. After being stirred at 25ºC for 12 hours, MeOH (2.7 mL) and DBU (113 uL, 0.75 mmol, 1.5 eq.) were subsequently added. After being stirred at 25 ºC for 30 min, the reaction mixture was concentrated and the residue was subjected to a silica gel flash chromatography (petroleum ether/ EtOAc = 10:1 to 4:1) to afford product **4** as colorless oil (113.4 mg, yield: 81%).

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 85:15, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 8.721 min, t_r(major) = 10.920 min;

$[\alpha]_D^{25}$ = -71.4º (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3424, 3051, 3006, 2957, 1975, 1955, 1916, 1892, 1816, 1719, 1673, 1605, 1595, 1579, 1504, 1462, 1449, 1438, 1364, 1341, 1330, 1317, 1313, 1284, 1227, 1205, 1180, 1175, 1156 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.19 (m, 3H), 3.65 (s, 3H), 3.36 (t, *J* = 6.2 Hz, 1H), 3.12 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.66 (dd, *J* = 9.4, 6.1 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.94, 169.73, 137.96, 136.86, 133.42, 128.81, 128.71, 128.42, 127.27, 126.58, 52.29, 35.04, 31.56, 30.11;

HRMS (ESI, *m*/*z*) calculated for $C_{18}H_{16}O_3Na^+$ $[M+Na]^+$: 303.0997, found: 303.0994.

Step 2:

According to a reported procedure [12], under argon atmosphere, potassium *tert*-butoxide (31 mg, 0.28 mmol) powder was added to a solution of methyltriphenylphosphonium bromide (107 mg, 0.3 mmol) in 2 mL THF in ice bath. The reaction mixture was stirred for 30 min. a solution of **4** (54.0 mg, 0.2 mmol) in 1 mL THF was added by syringe. The resulting solution was stirred at 50 °C and monitored by TLC analysis. After 5 h, the reaction was cooled to room temperature and quenched with 5 mL saturated aqueous NH_4Cl in ice bath. The resulting solution was extracted with ethyl acetate (3×5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:15) to afford the desired product **5** as colorless oil (52 mg, 94% yield). The racemic reaction was carried out in the same condition.

Enantiomeric excess was determined by HPLC analysis, *ee* = 98%, Chiralpak column ID, λ = 254 nm, *n*-hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 5.400 min, t_r(major) = 6.329 min;

$[\alpha]_D^{25}$ = -39° (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3382, 3036, 1704, 1697, 1638, 1599, 1568, 1422, 1403, 1367, 1310, 1295, 1205, 1134 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 2H), 7.36 – 7.30 (m, 4H), 7.30 – 7.20 (m, 4H), 5.69 (s, 1H), 5.37 (s, 1H), 3.49 (s, 3H), 3.06 (dd, *J* = 6.7, 5.5 Hz, 1H), 2.68 (t, *J* = 6.4 Hz, 1H), 2.44 (dd, *J* = 9.6, 5.1 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.43, 141.78, 140.14, 139.38, 128.64, 128.29, 127.67, 126.75, 126.64, 125.87, 115.38, 51.71, 34.36, 30.67, 29.65;

HRMS (ESI, *m*/*z*) calculated for $C_{19}H_{18}O_2Na^+$ $[M+Na]^+$: 301.1204, found: 301.1202.

Step 3:

According to a reported procedure [13], a solution of **3ra** (68 mg, 0.2 mmol, recrystallized) benzylamine (42 μL, 0.4 mmol) and DBU (30 uL, 0.2 mmol) in toluene (2 mL) was heated to reflux for overnight. After being cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:5 to 1:3) to afford compound **6** (64 mg, 91%) as a white solid, mp 130–131 ºC. The racemic reaction was carried out in the same condition.

Enantiomeric excess was determined by HPLC analysis, *ee* = 99%, Chiralpak column IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 75:25, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 6.144 min, t_r(major) = 6.926 min;

$[\alpha]_D^{25}$ = -31.7º (*c* = 0.1, $CHCl_3$);

IR (KBr) ν_{max}: 3241, 3017, 2950, 1714, 1680, 1649, 1631, 1593, 1542, 1484, 1460, 1400, 1369, 1315, 1281, 1297, 1185, 1062 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.86 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.21 (m, 5H), 7.16 (d, *J* = 4.6 Hz, 5H), 6.67 (t, *J* = 5.6 Hz, 1H), 4.47 (qd, *J* = 14.7, 5.7 Hz, 2H), 3.66 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.45 (dd, *J* = 10.1, 6.1 Hz, 1H), 3.13 (dd, *J* = 6.2, 4.8 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.68, 170.32, 137.85, 137.49, 134.34, 133.25, 128.85, 128.76, 128.63, 128.35, 128.15, 127.91, 127.62, 127.12, 44.11, 35.41, 34.56, 27.84;

HRMS (ESI, *m*/*z*) calculated for $C_{24}H_{22}NO_2^+$ $[M+H]^+$: 356.1651, found: 356.1648.

6. ^{1}H NMR and ^{13}C NMR Spectra

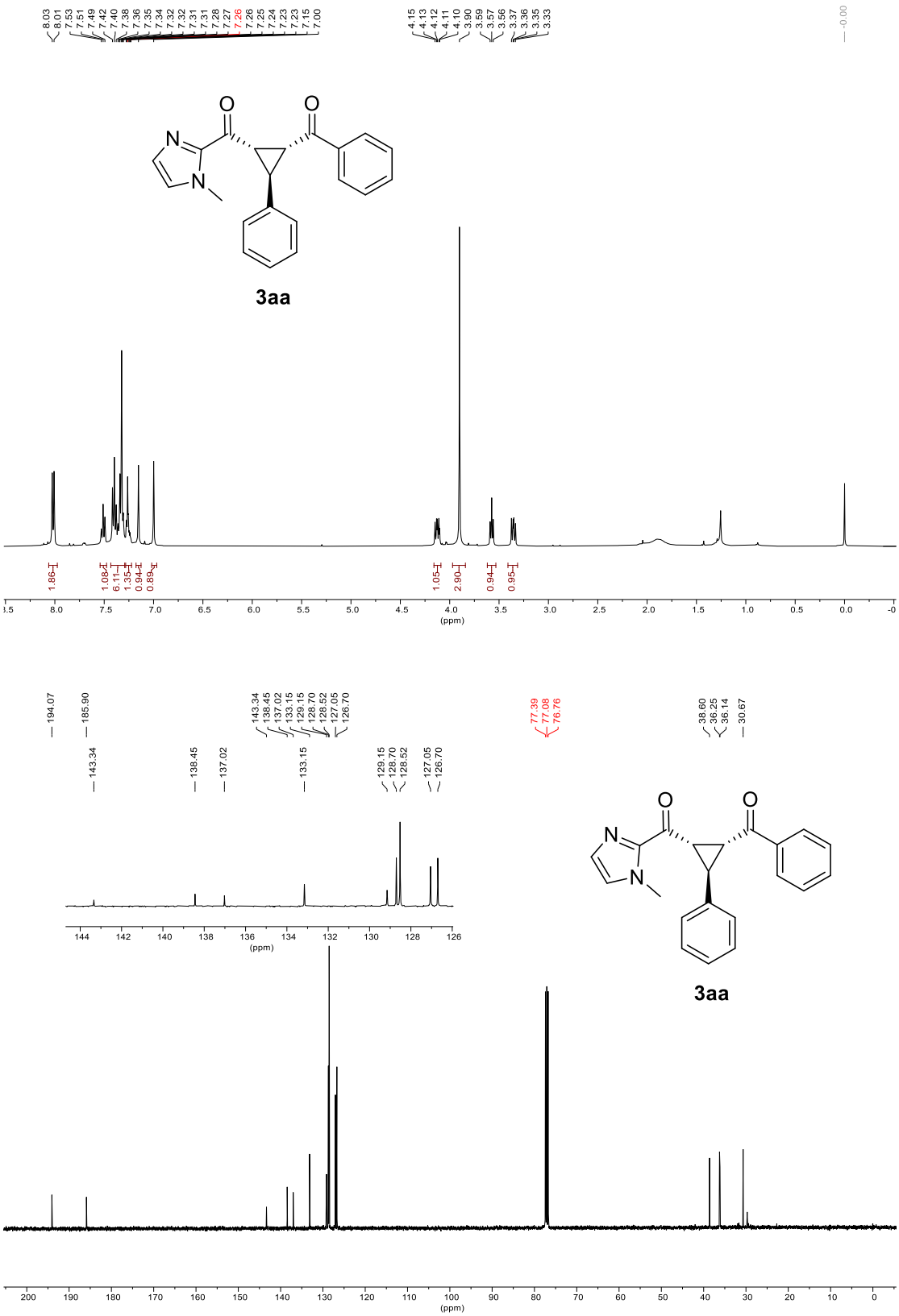


Figure S1. ^{1}H and ^{13}C NMR spectrum of **3aa**.

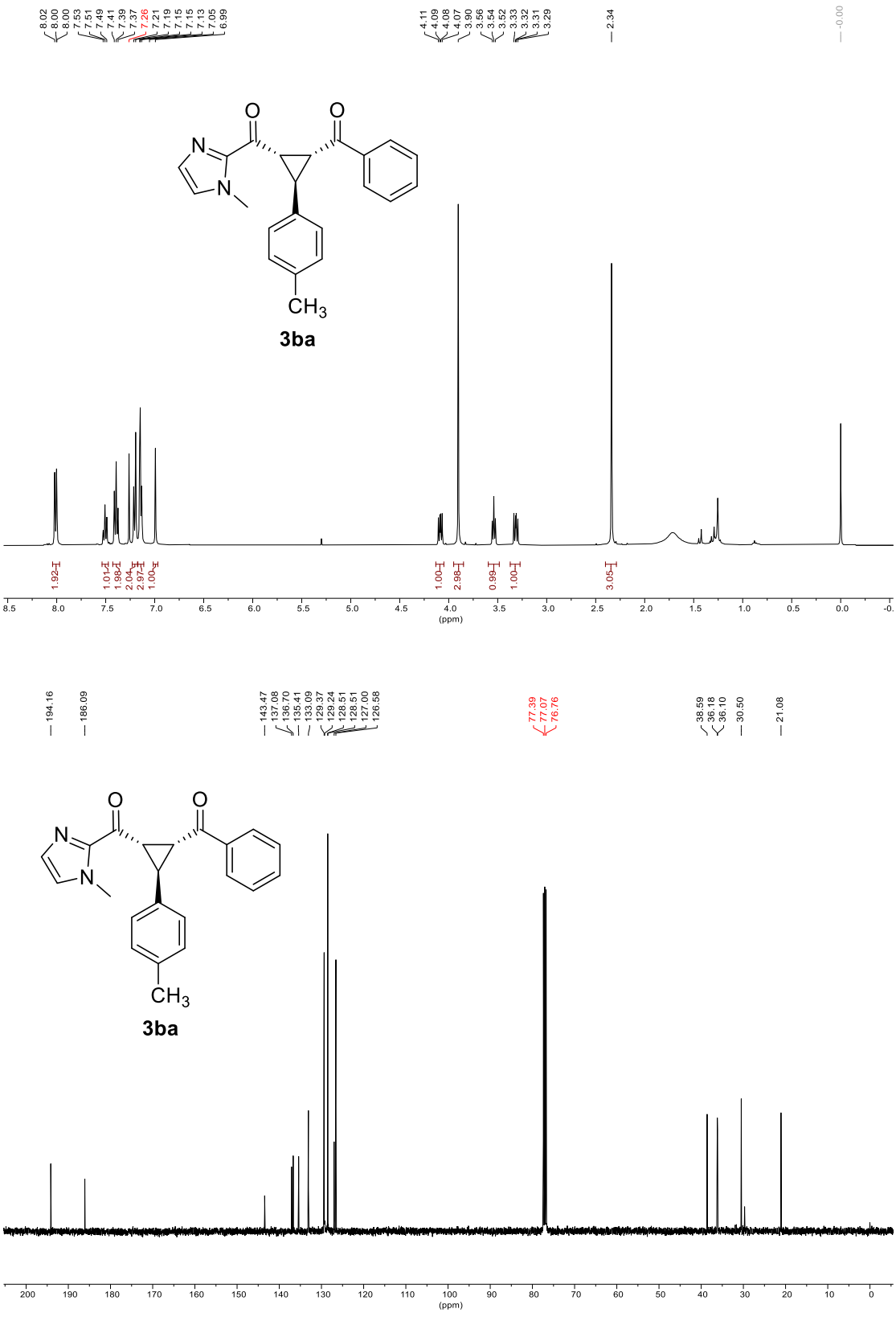


Figure S2. ^{1}H and ^{13}C NMR spectrum of **3ba**.

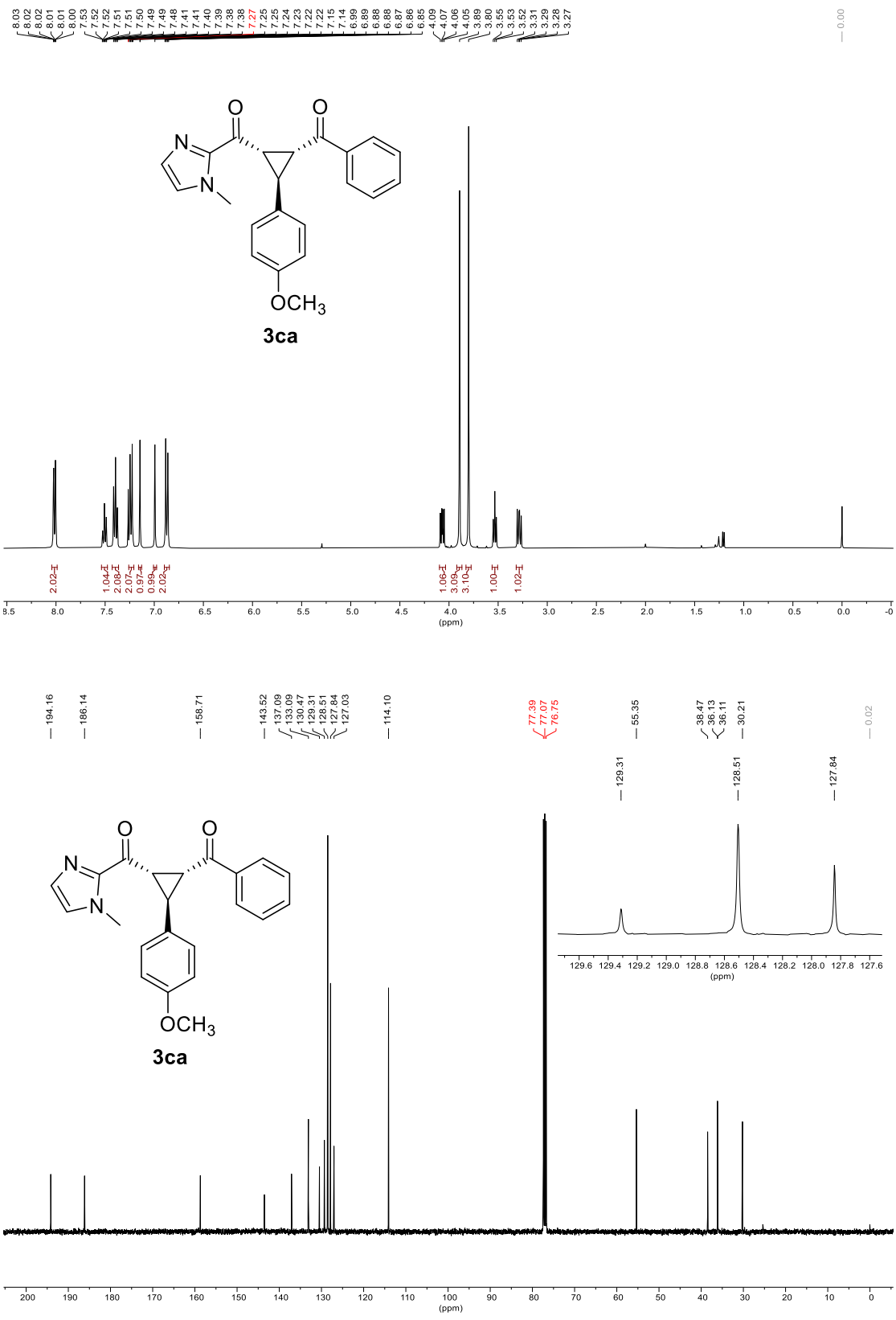
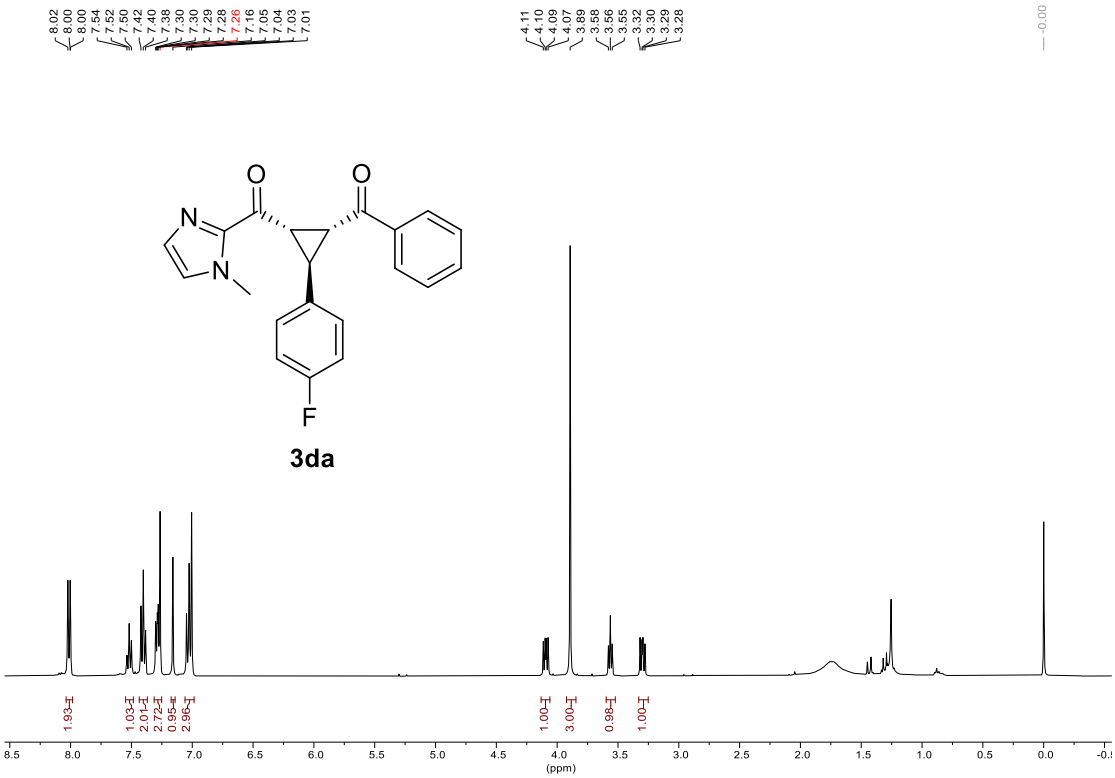
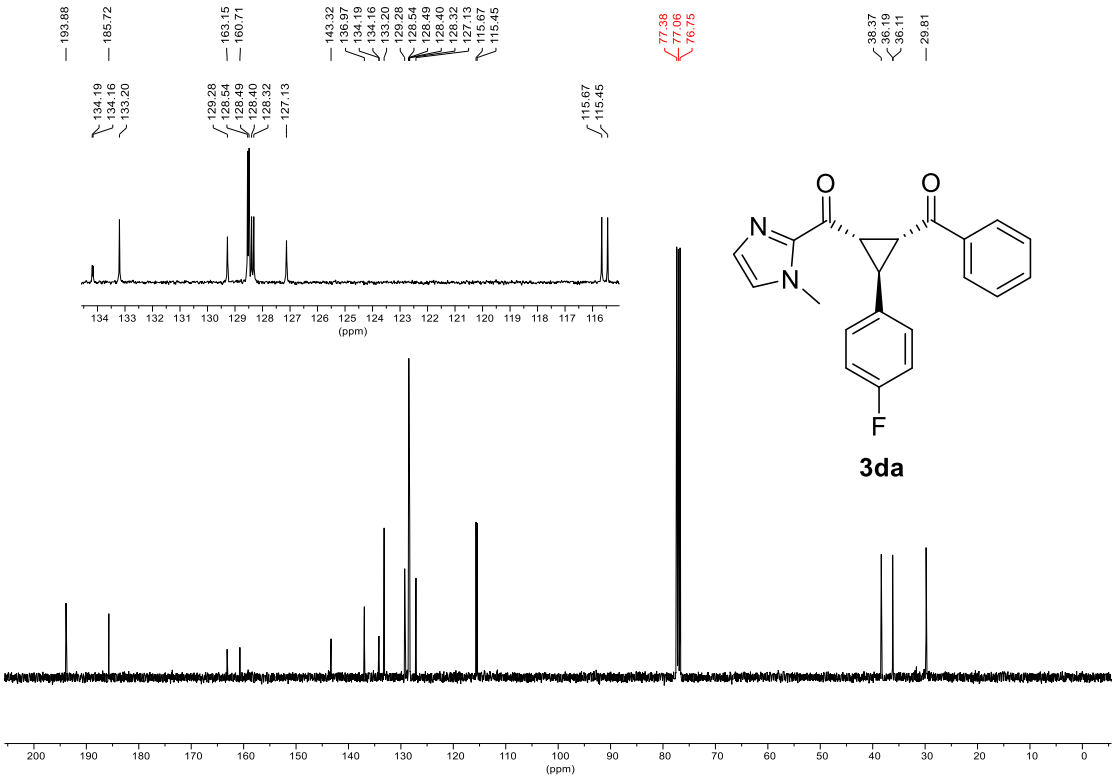


Figure S3. ^{1}H and ^{13}C NMR spectrum of **3ca**.


8.02
8.00
8.00
7.54
7.52
7.50
7.42
7.40
7.38
7.30
7.30
7.29
7.28
7.26
7.16
7.05
7.04
7.03
7.01
4.11
4.10
4.09
4.07
3.89
3.58
3.56
3.55
3.32
3.30
3.29
3.28
0.00
O
O
N
N
F
3da
1.93
1.03
2.01
2.72
0.95
2.96
1.00
3.00
0.98
1.00
(ppm)


193.88
185.72
163.15
160.71
143.32
136.97
134.19
134.16
133.20
129.28
128.54
128.49
128.40
128.32
127.13
115.67
115.45
77.38
77.06
76.75
38.37
36.19
36.11
29.81
O
O
N
N
F
3da
(ppm)

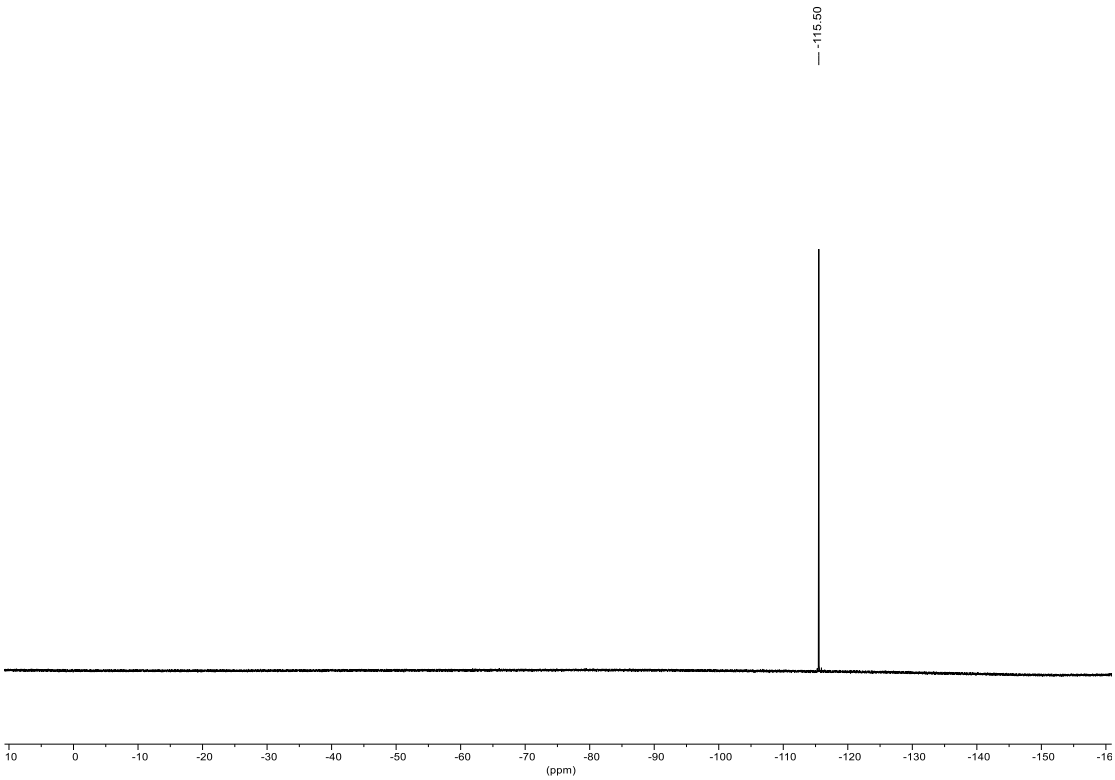
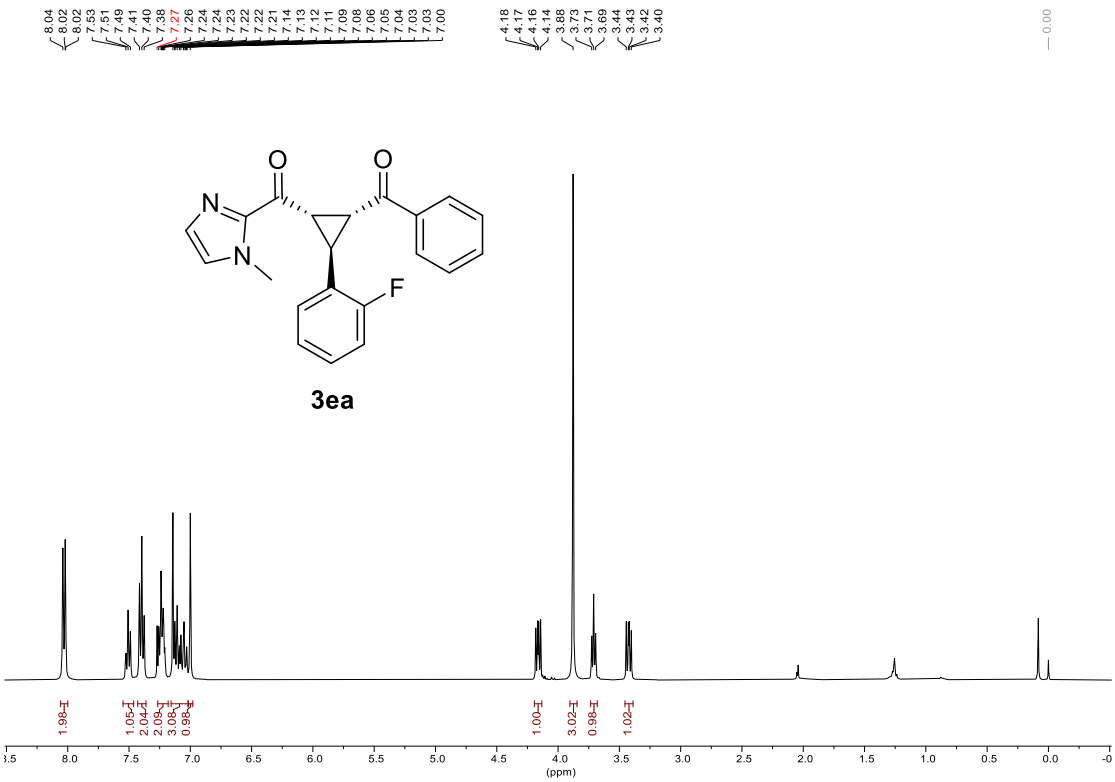
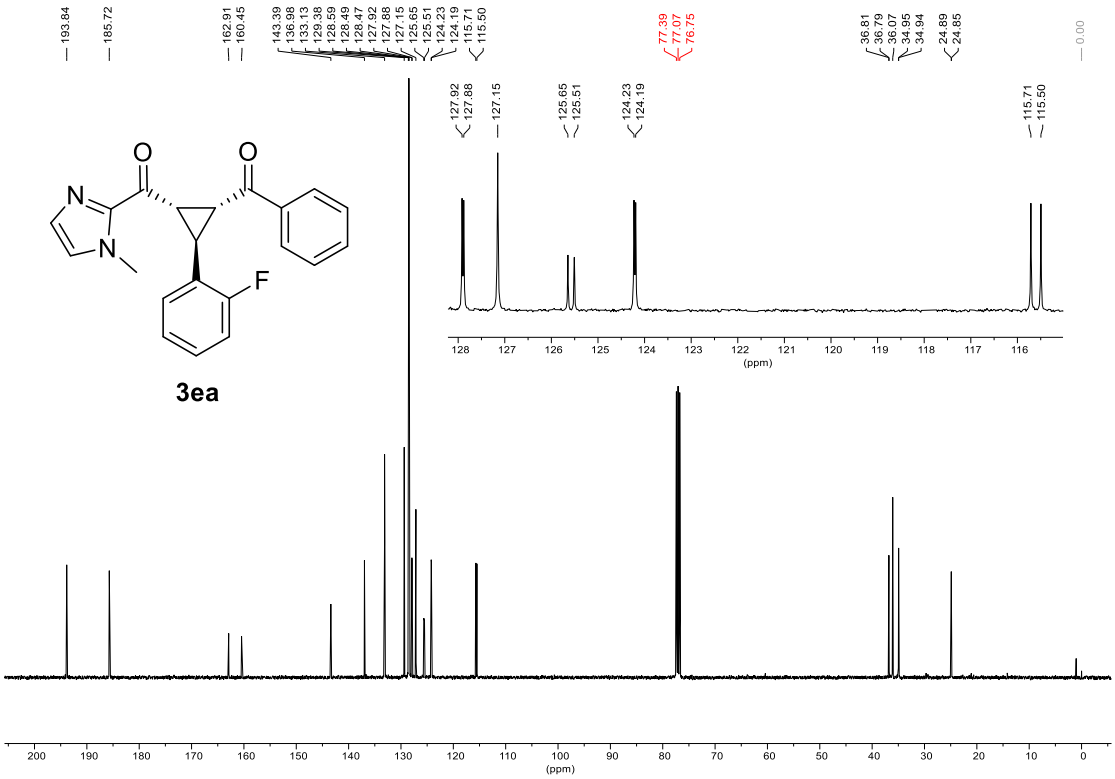


Figure S4. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3da**.


8.04
8.02
8.02
7.53
7.51
7.49
7.41
7.40
7.38
7.27
7.26
7.24
7.24
7.23
7.22
7.22
7.21
7.14
7.13
7.12
7.11
7.09
7.08
7.06
7.05
7.04
7.03
7.03
7.00
4.18
4.17
4.16
4.14
3.88
3.73
3.71
3.69
3.44
3.43
3.42
3.40
0.00
O
O
N
N
F
3ea
1.98
1.05
2.04
2.09
3.08
0.96
1.00
3.02
0.98
1.02
(ppm)


193.84
185.72
162.91
160.45
143.39
136.98
133.13
129.38
128.59
128.49
128.47
127.92
127.88
127.15
125.65
125.51
124.23
124.19
115.71
115.50
77.39
77.07
76.75
36.81
36.79
36.07
34.95
34.94
24.89
24.85
0.00
127.92
127.88
127.15
125.65
125.51
124.23
124.19
115.71
115.50
O
O
N
N
F
3ea
(ppm)
(ppm)

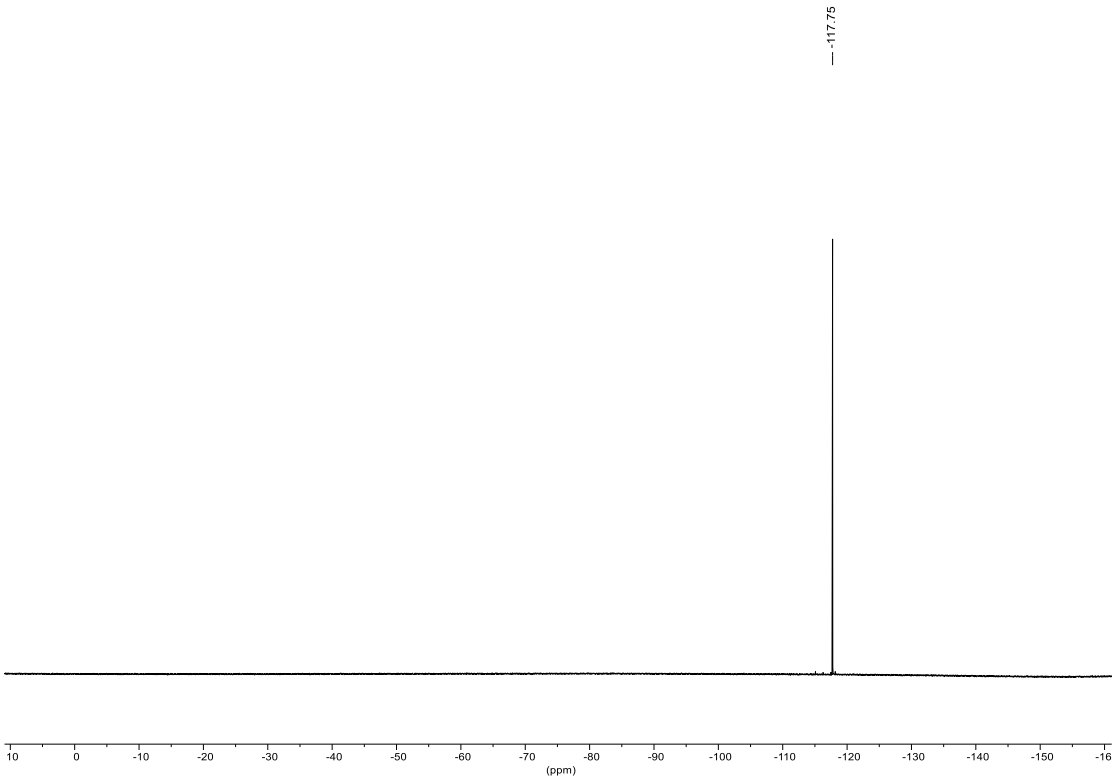


Figure S5. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3ea**.

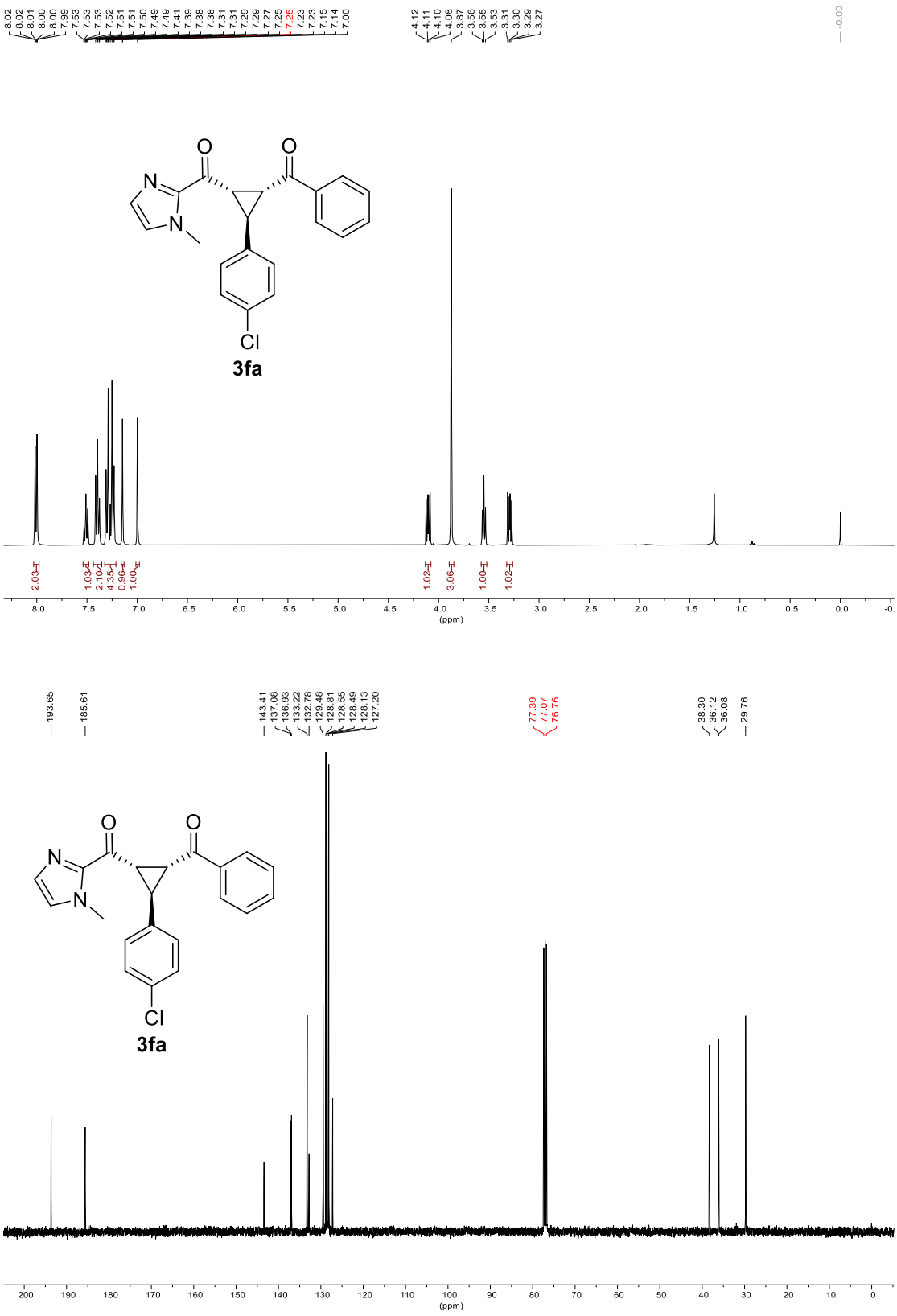


Figure S6. ^{1}H and ^{13}C NMR spectrum of **3fa**.

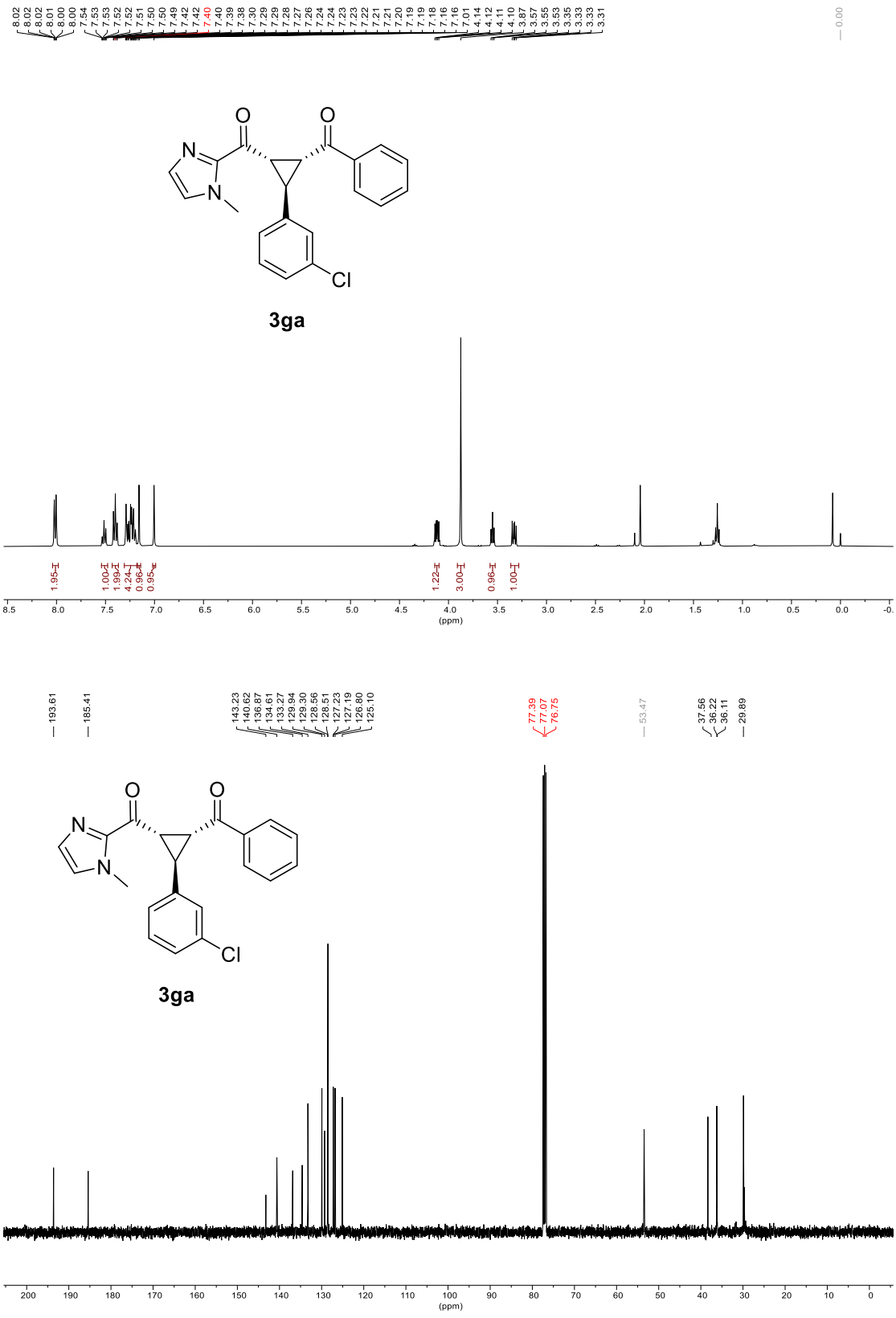


Figure S7. ^{1}H and ^{13}C NMR spectrum of **3ga**.

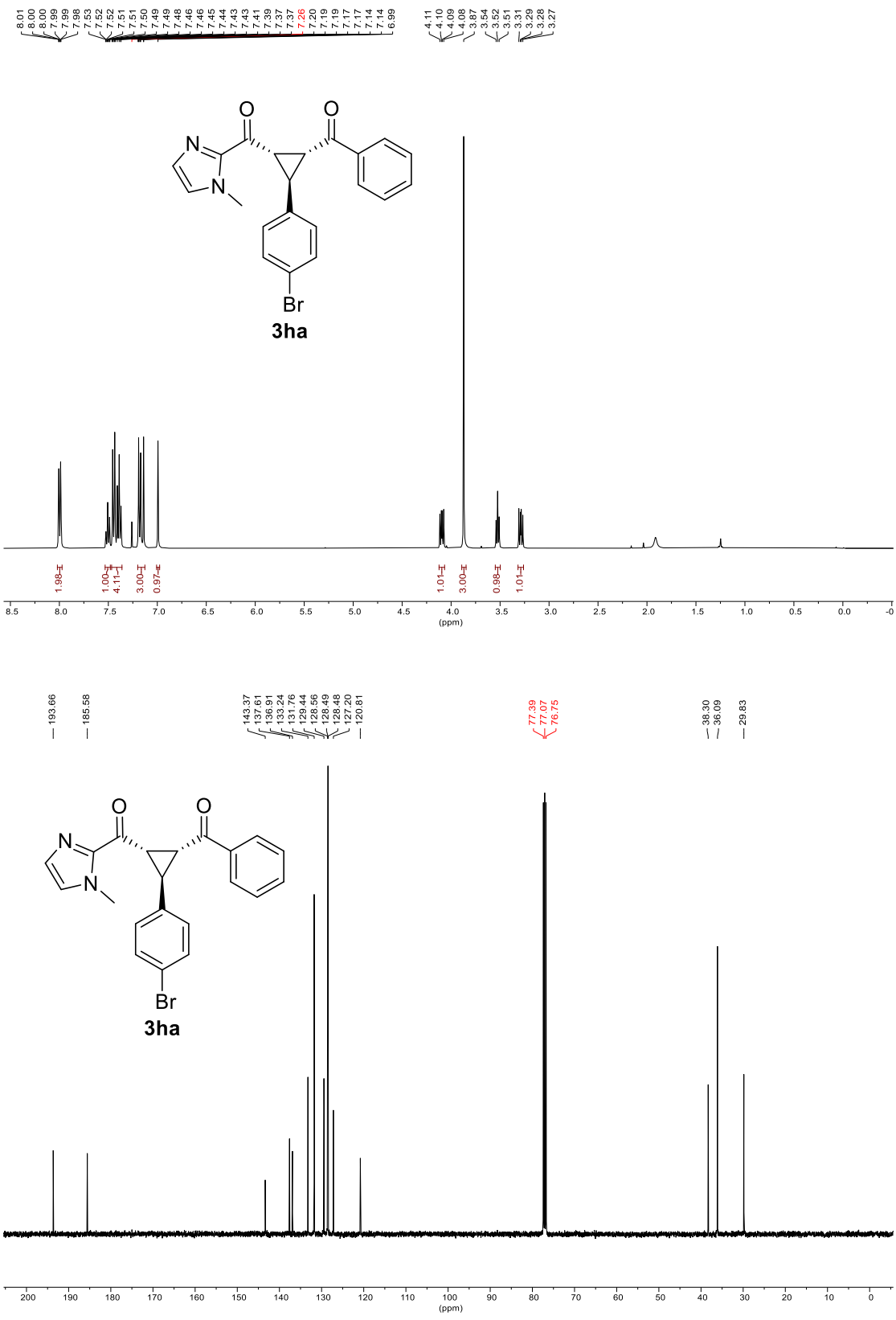


Figure S8. ^{1}H and ^{13}C NMR spectrum of **3ha**.

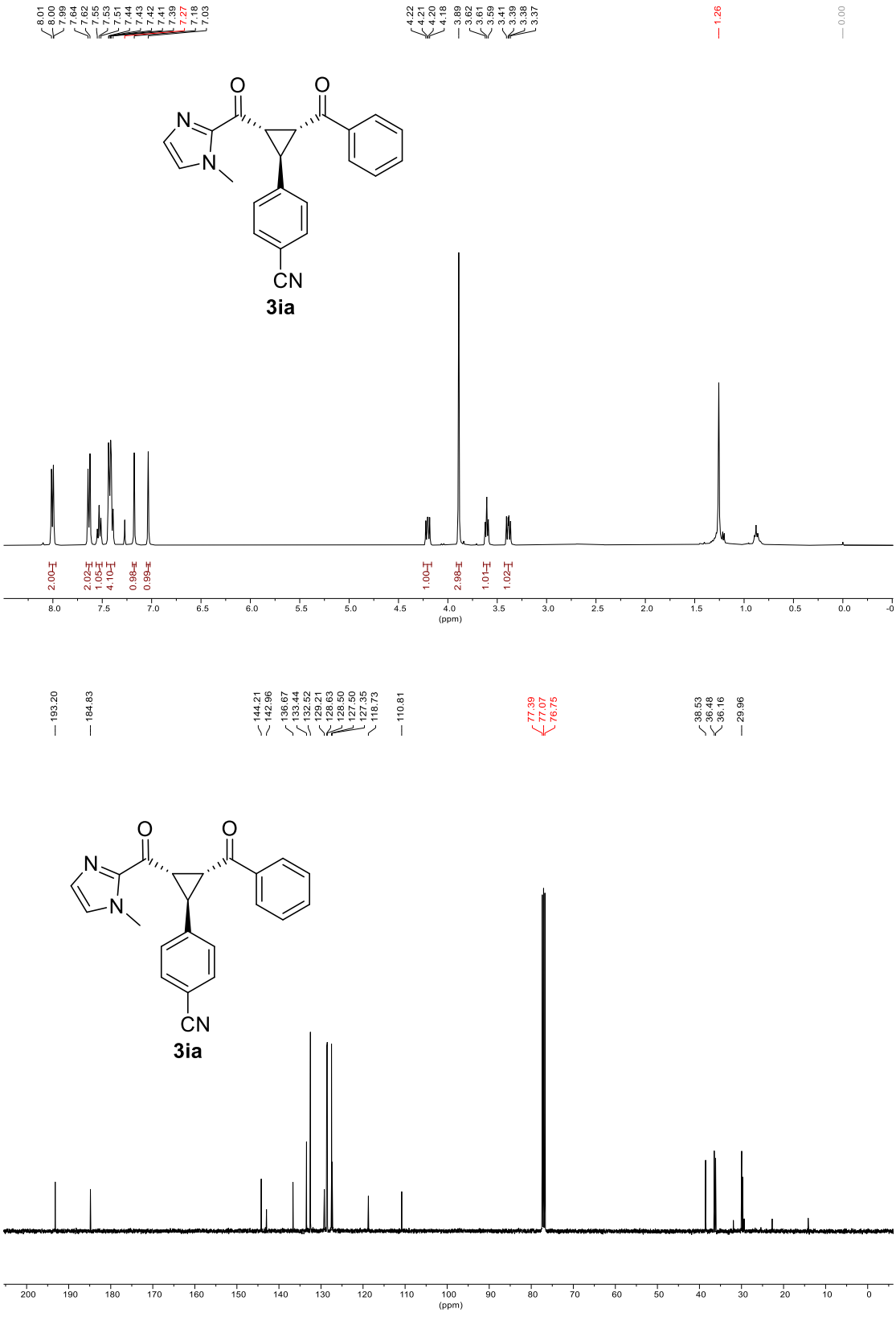


Figure S9. ^{1}H and ^{13}C NMR spectrum of **3ia**.

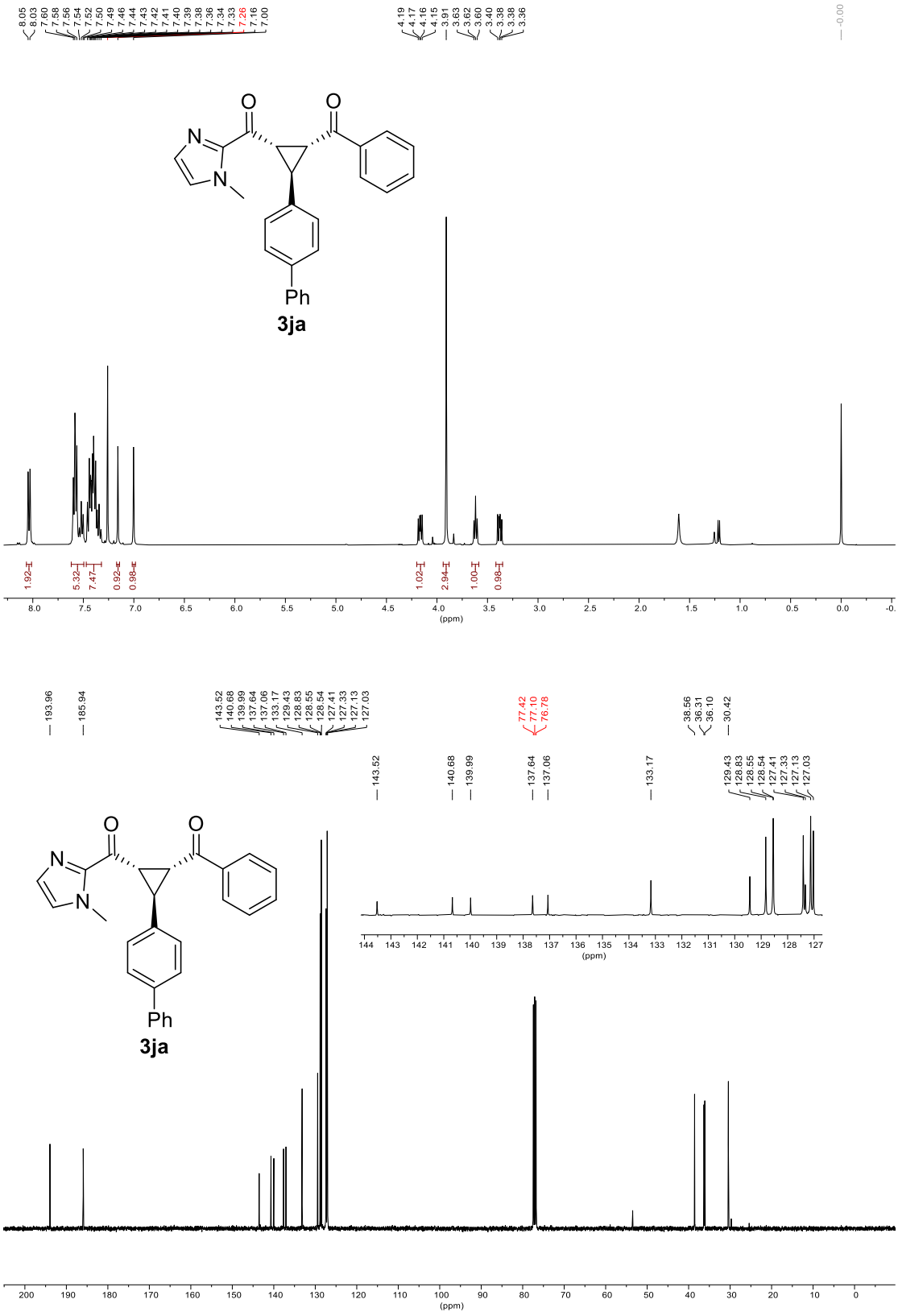


Figure S10. ^{1}H and ^{13}C NMR spectrum of **3ja**.

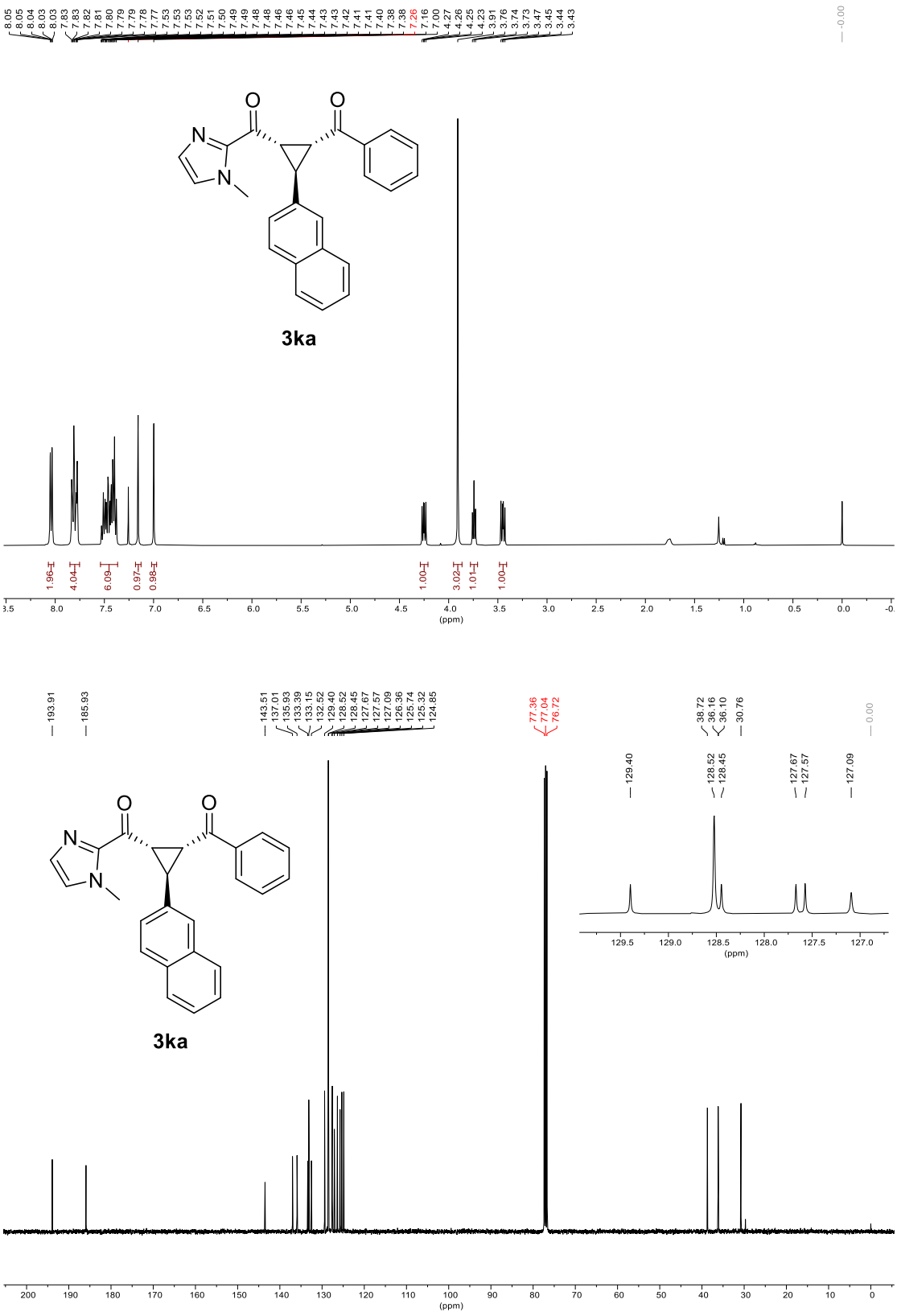


Figure S11. ^{1}H and ^{13}C NMR spectrum of **3ka**.

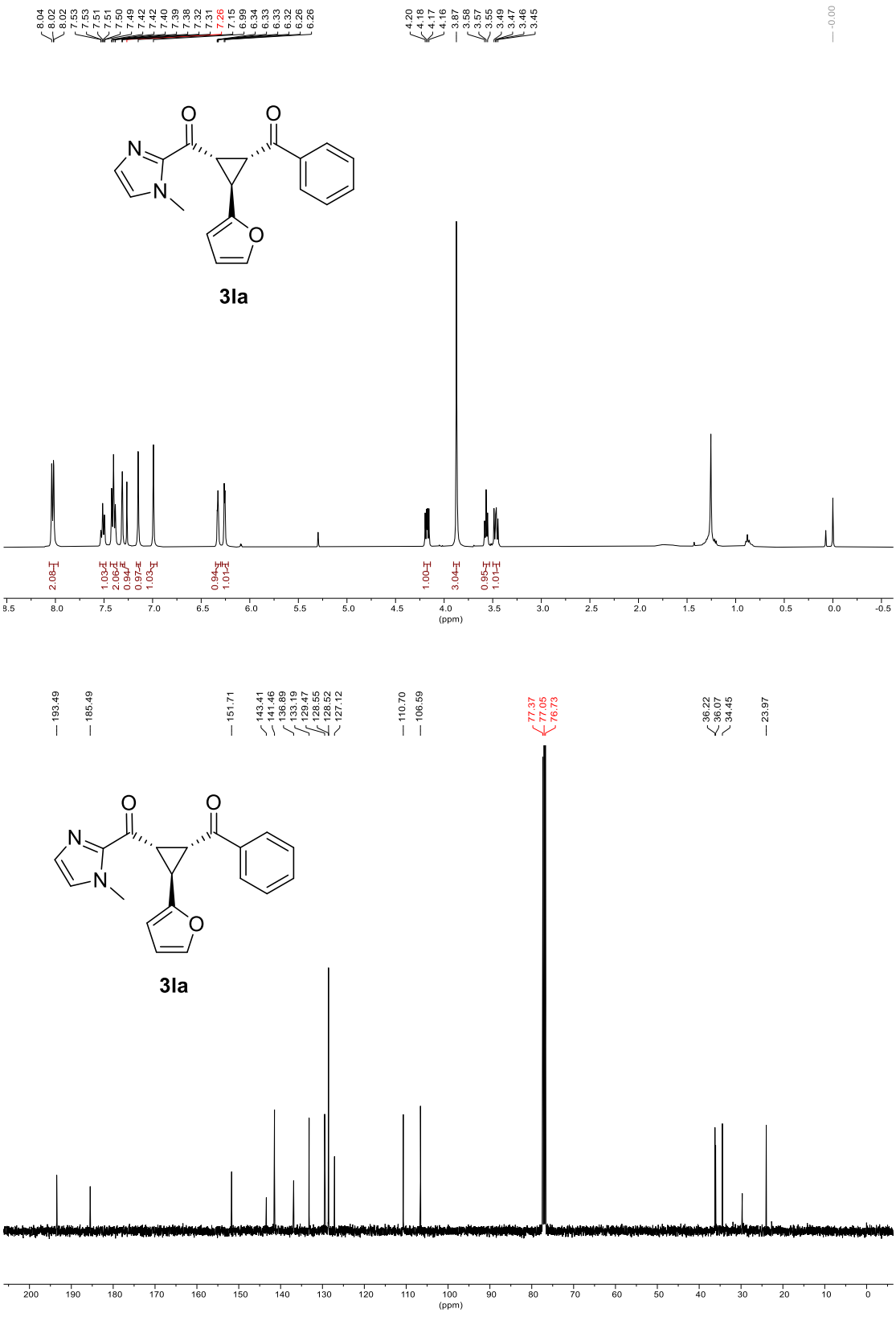


Figure S12. ^{1}H and ^{13}C NMR spectrum of **3la**.

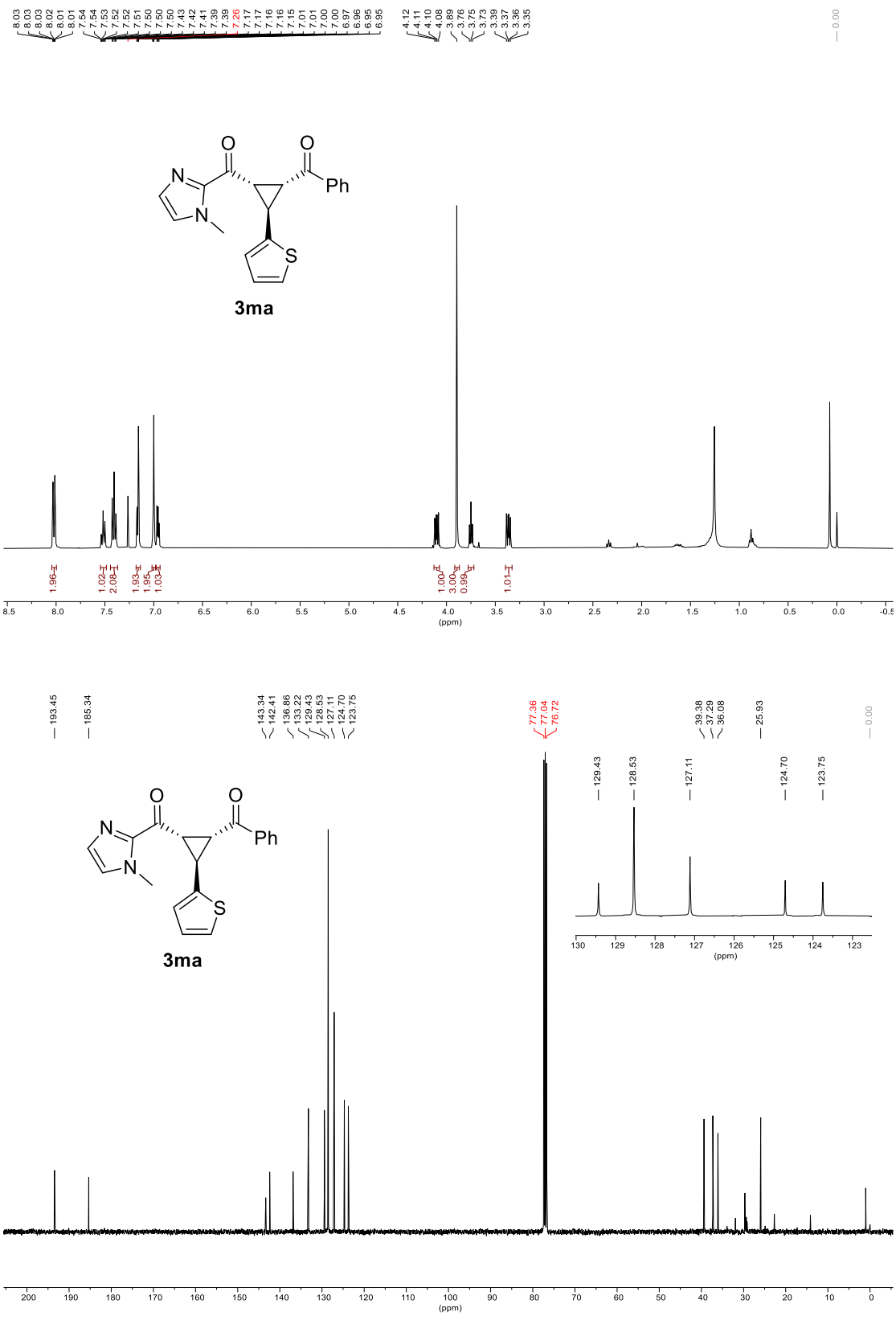


Figure S13. ^{1}H and ^{13}C NMR spectrum of **3ma**.

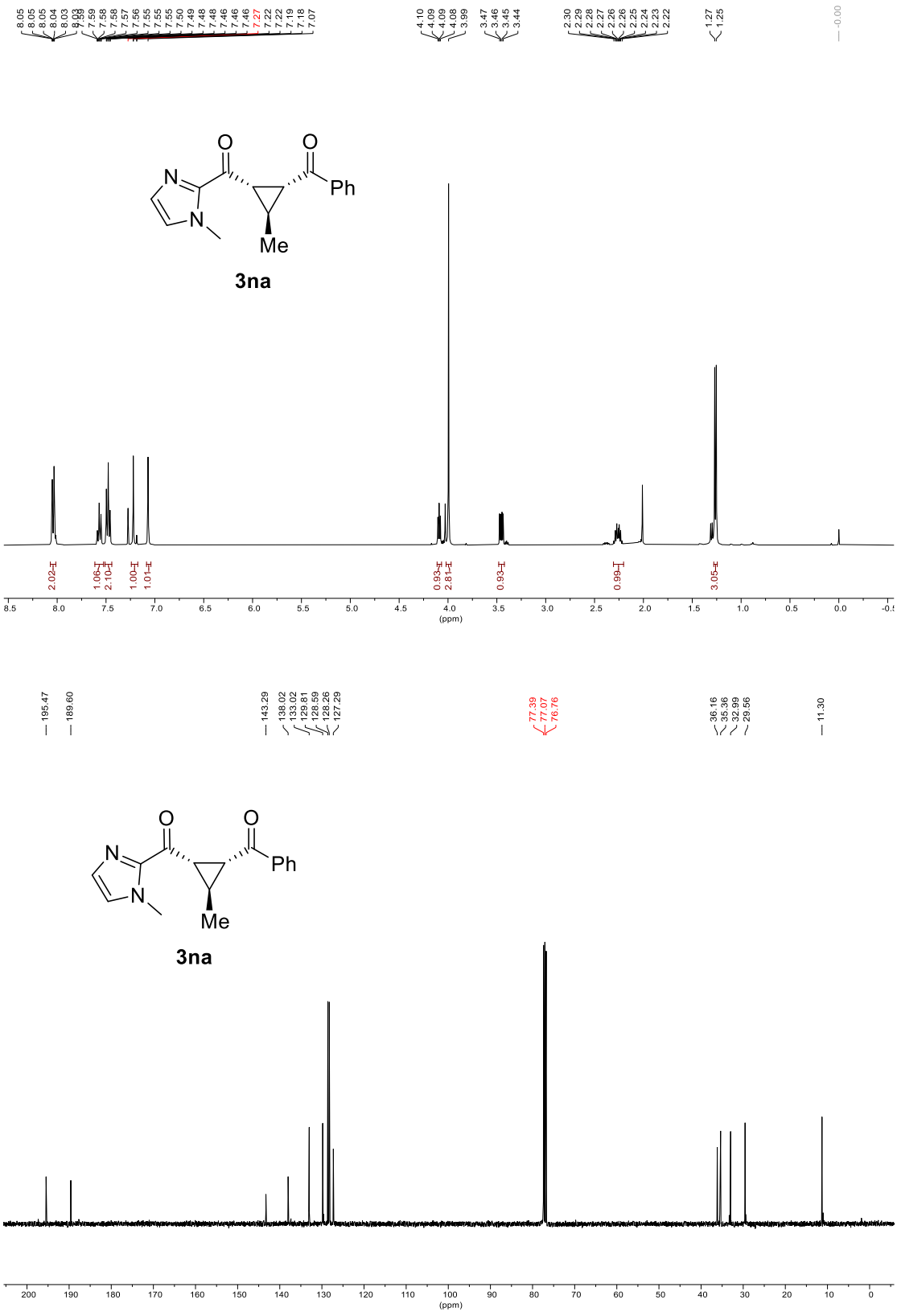


Figure S14. ^{1}H and ^{13}C NMR spectrum of **3na**.

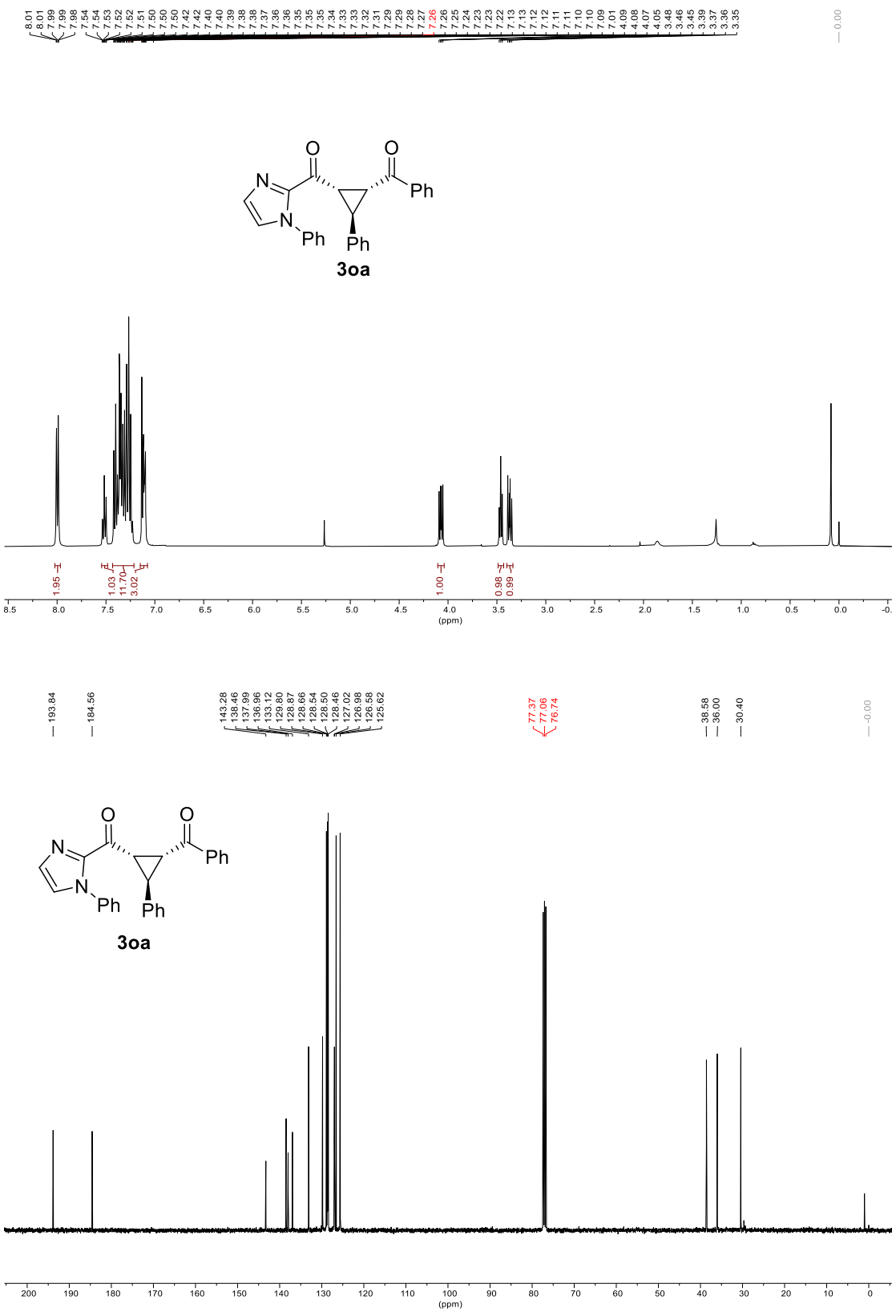


Figure S15. ^{1}H and ^{13}C NMR spectrum of **3oa**.

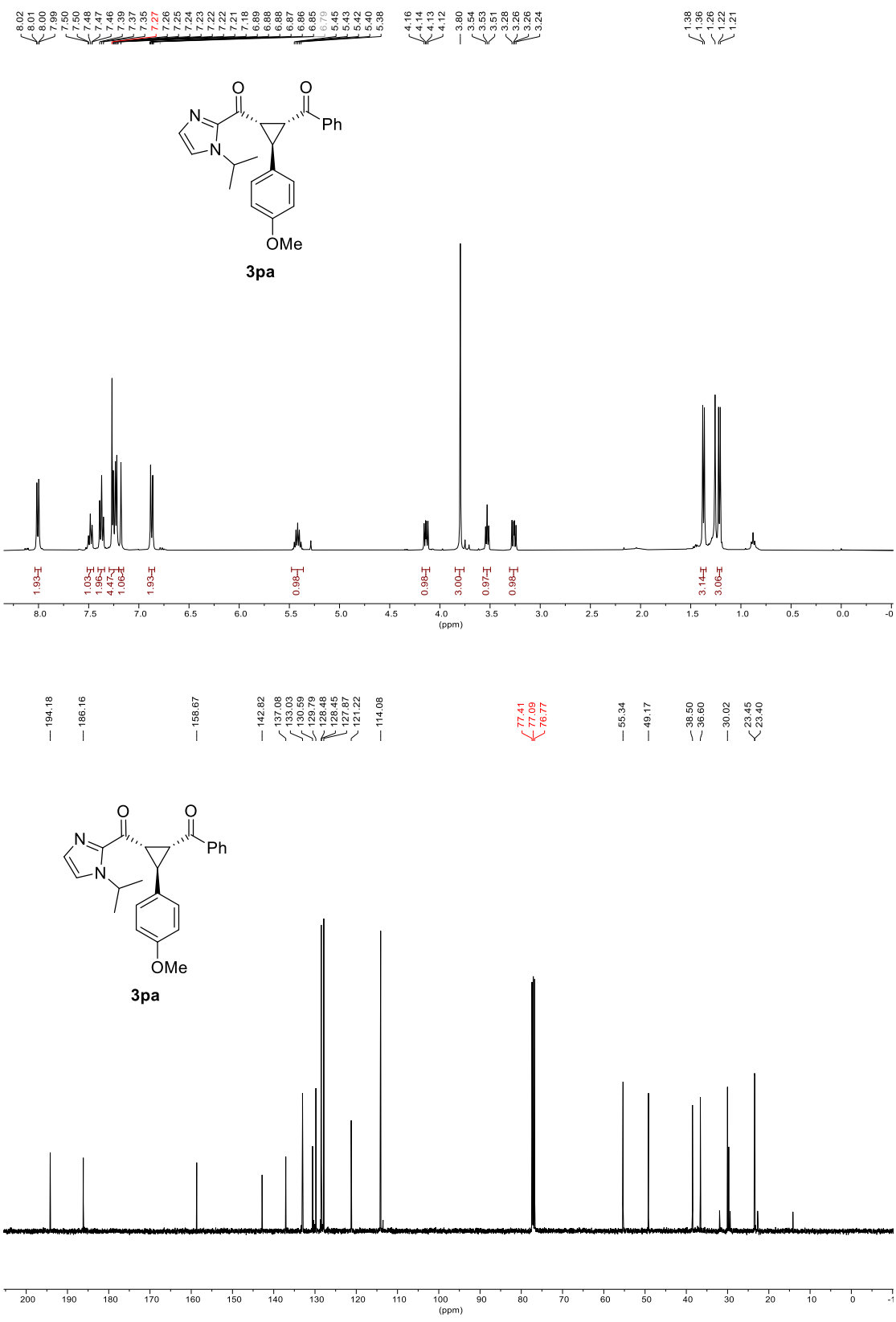


Figure S16. ^{1}H and ^{13}C NMR spectrum of **3pa**.

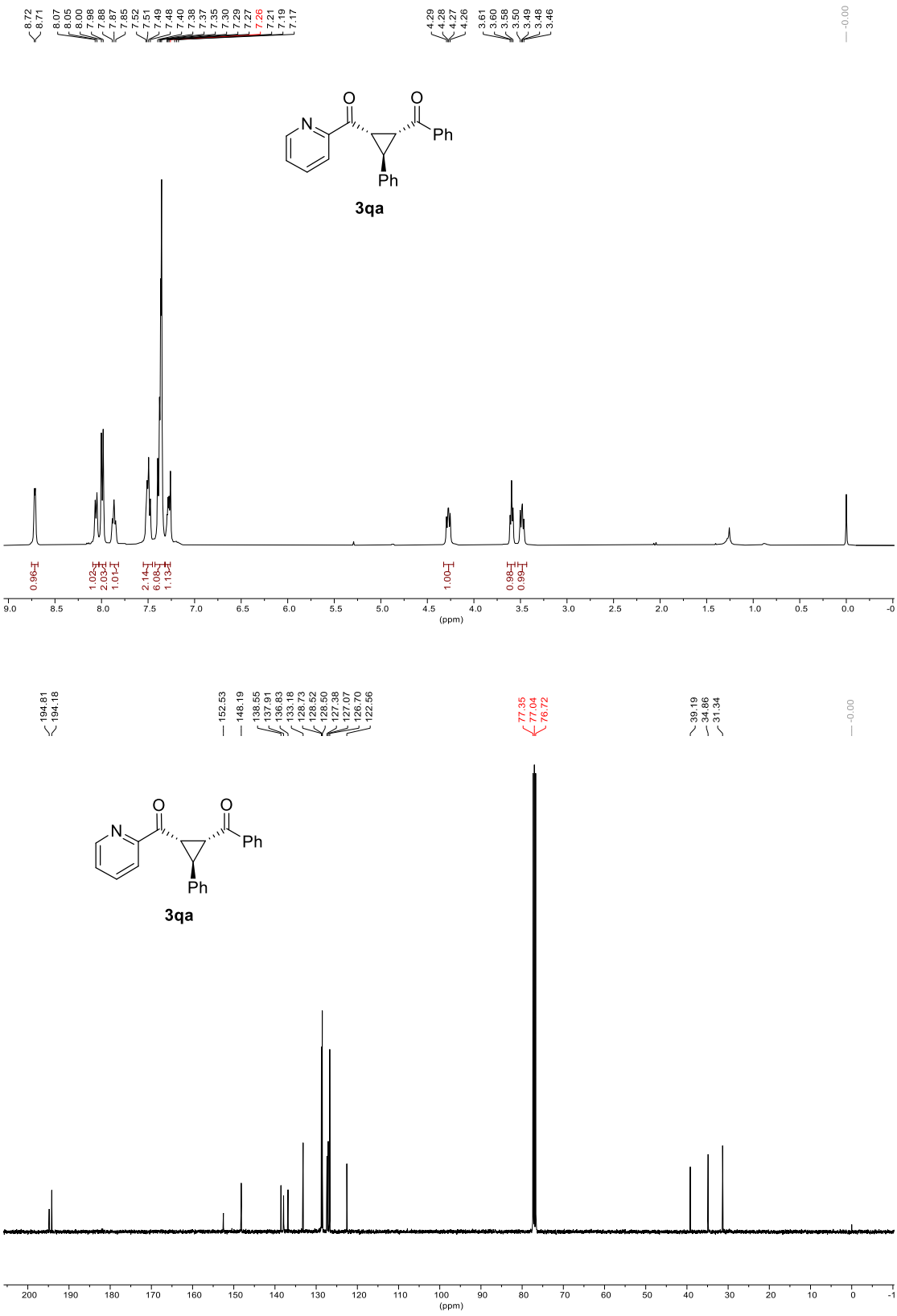


Figure S17. ^{1}H and ^{13}C NMR spectrum of **3qa**.

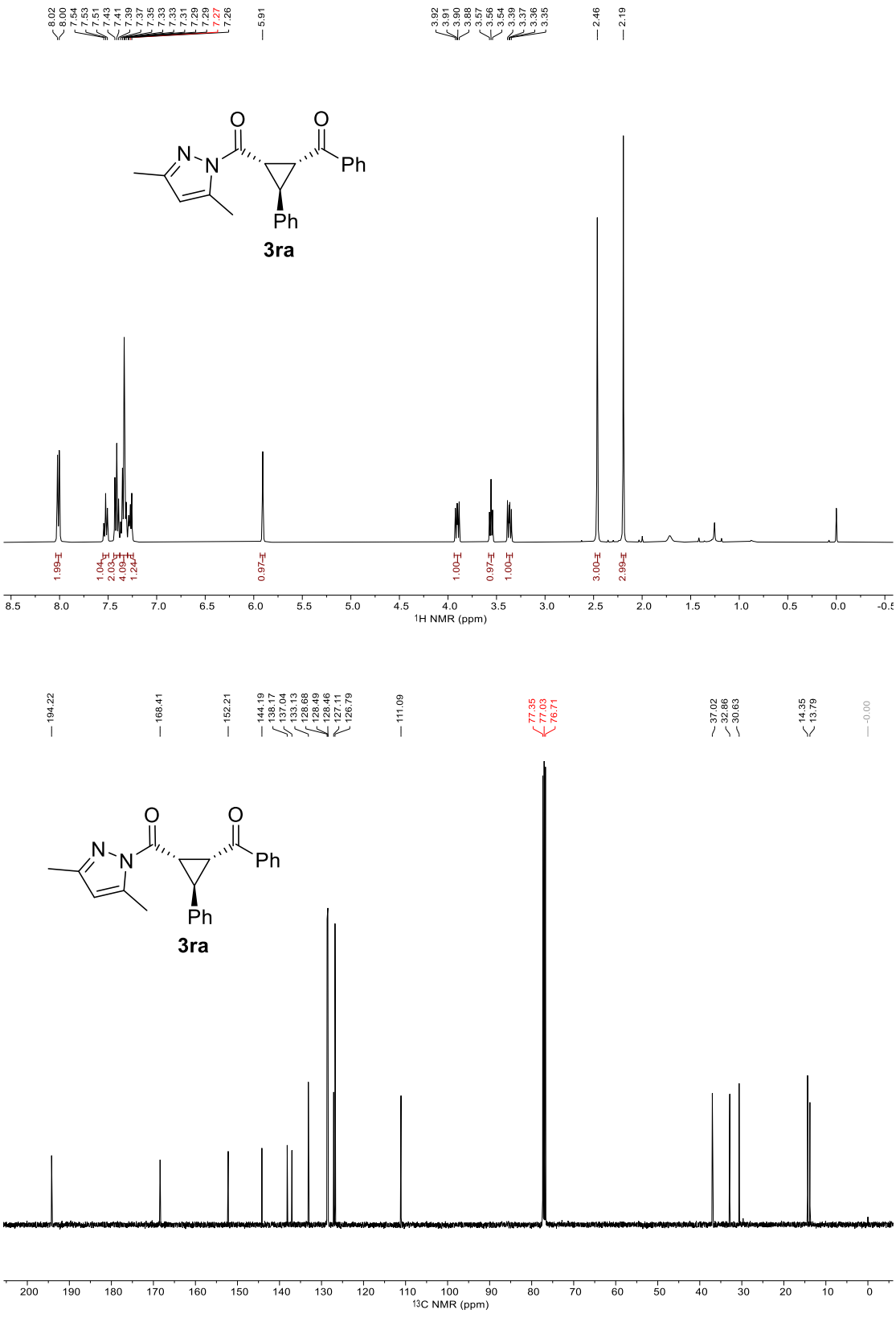


Figure S18. ^{1}H and ^{13}C NMR spectrum of **3ra**.

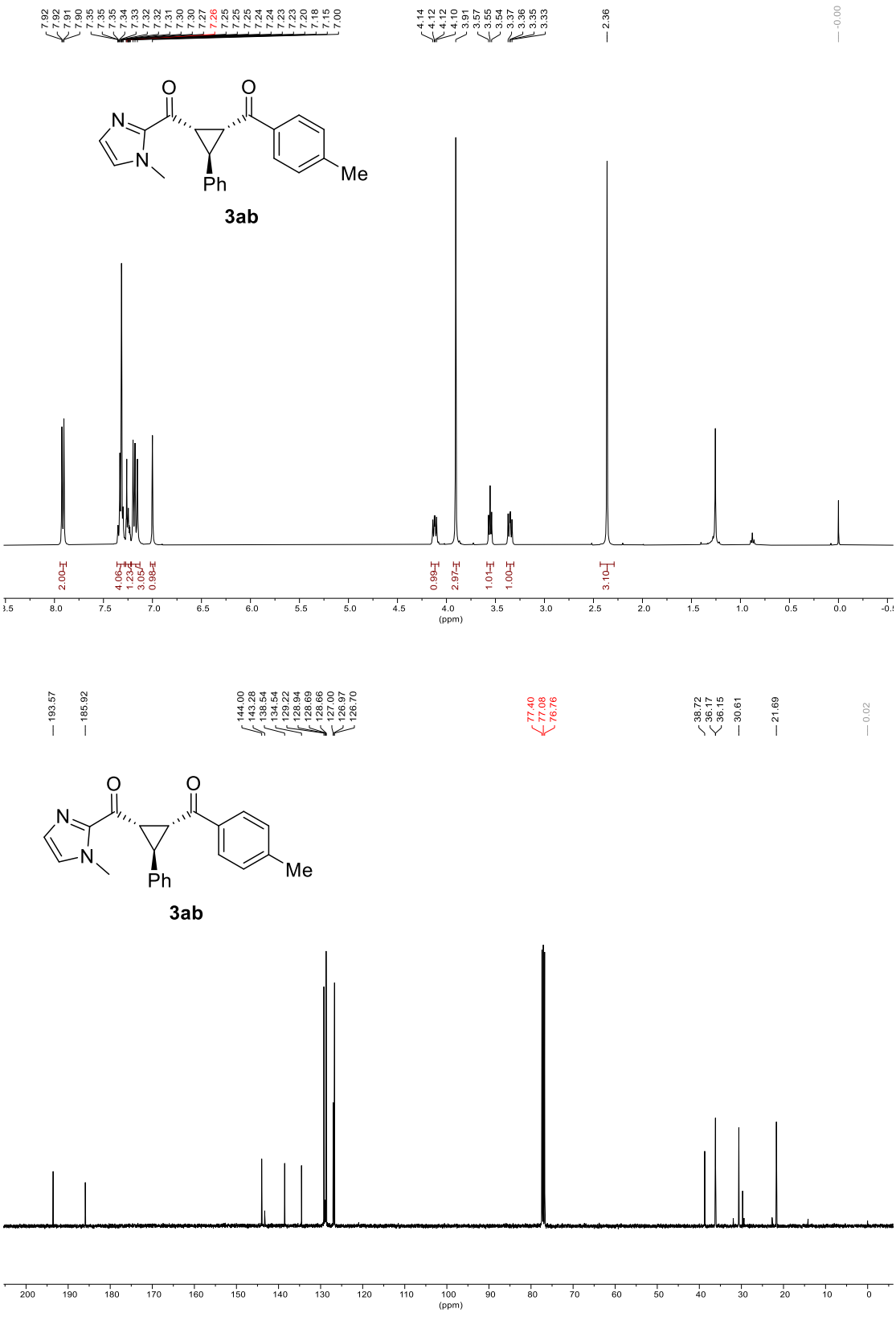


Figure S19. ^{1}H and ^{13}C NMR spectrum of **3ab**.

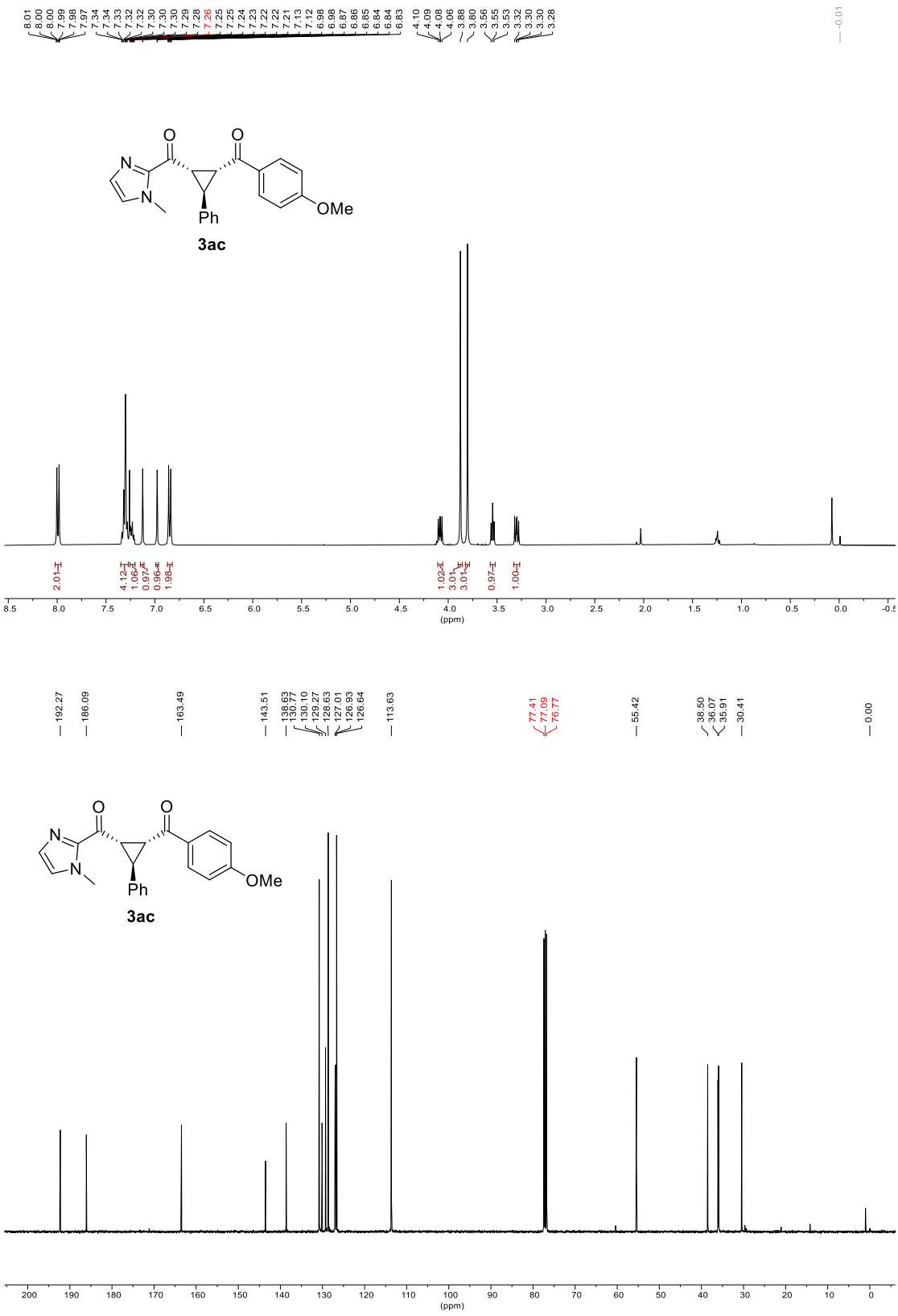
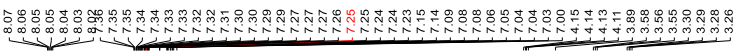
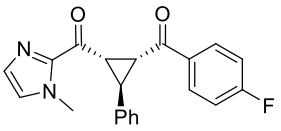
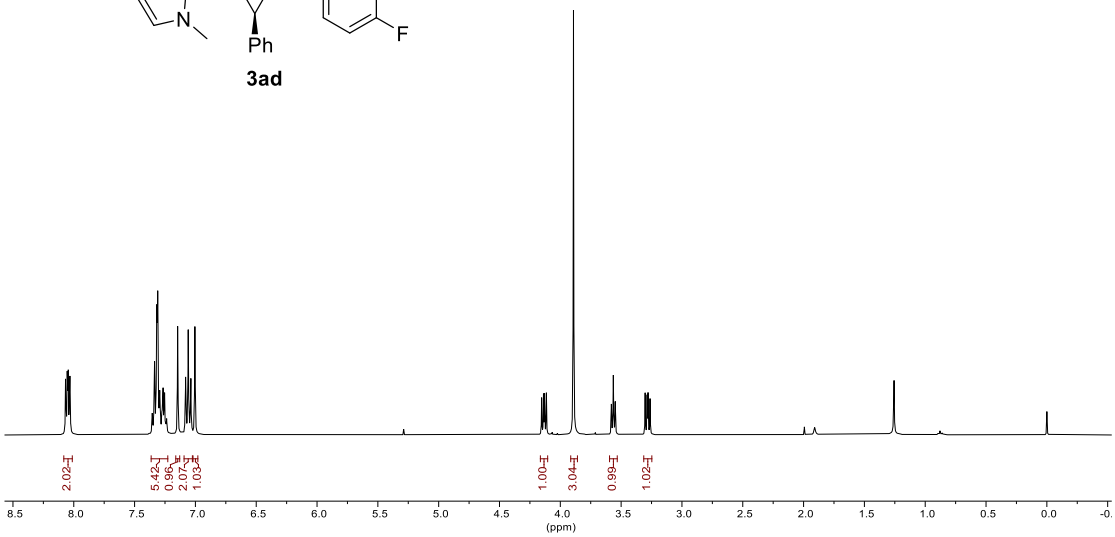


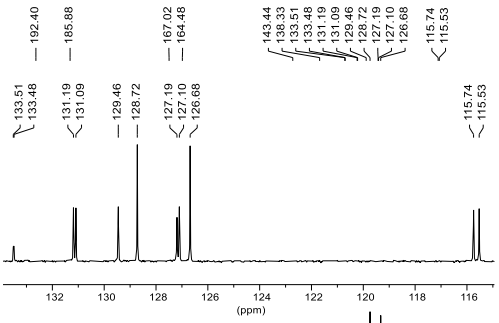
Figure S20. ^{1}H and ^{13}C NMR spectrum of **3ac**.

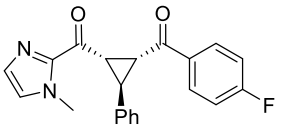




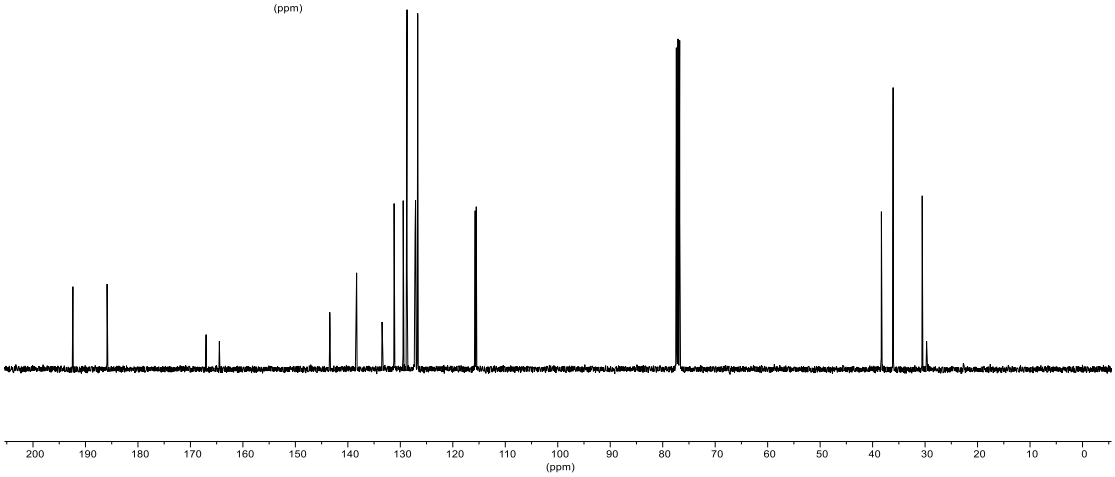
3ad







3ad



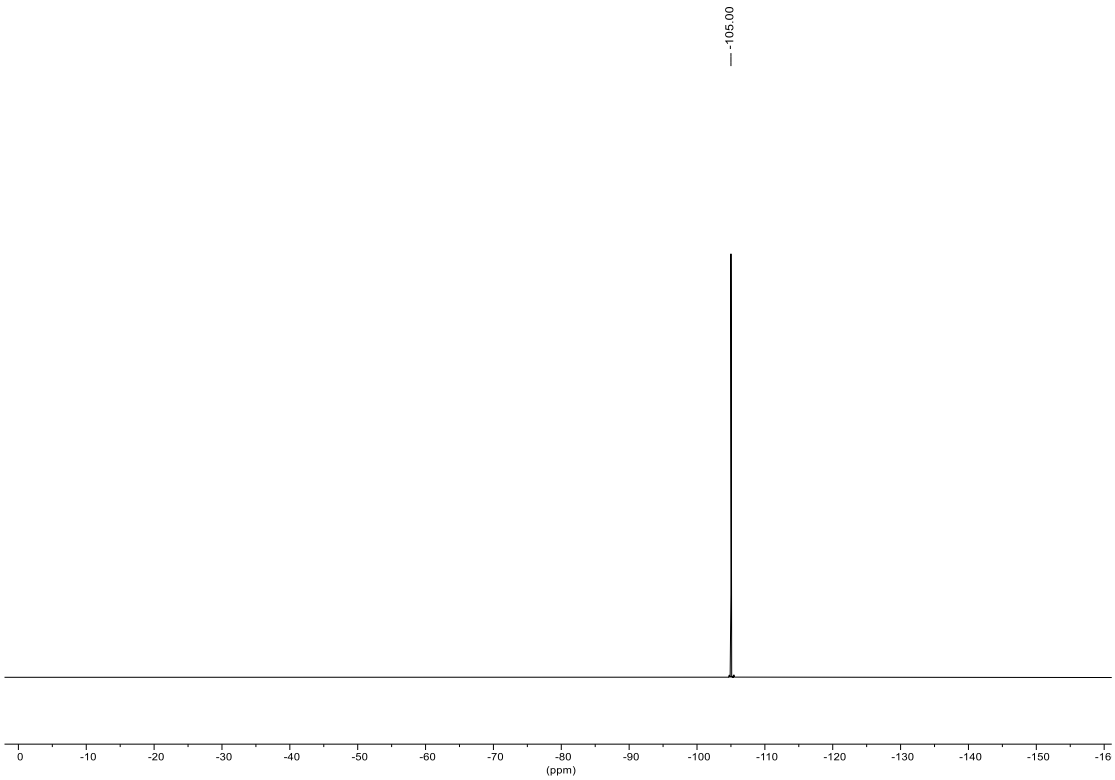


Figure S21. ^{1}H and ^{13}C NMR spectrum of **3ad**.

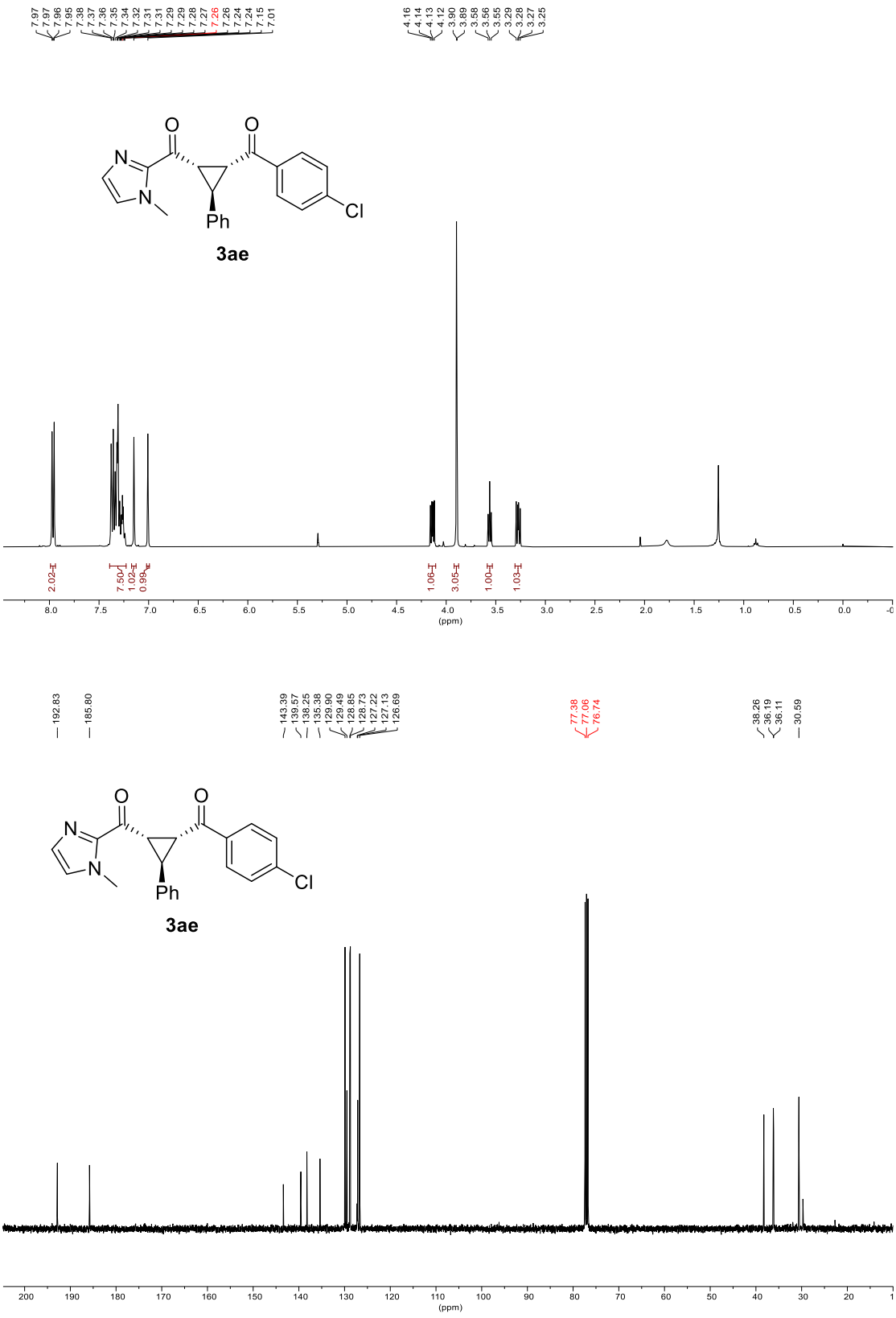


Figure S22. ^{1}H and ^{13}C NMR spectrum of **3ae**.

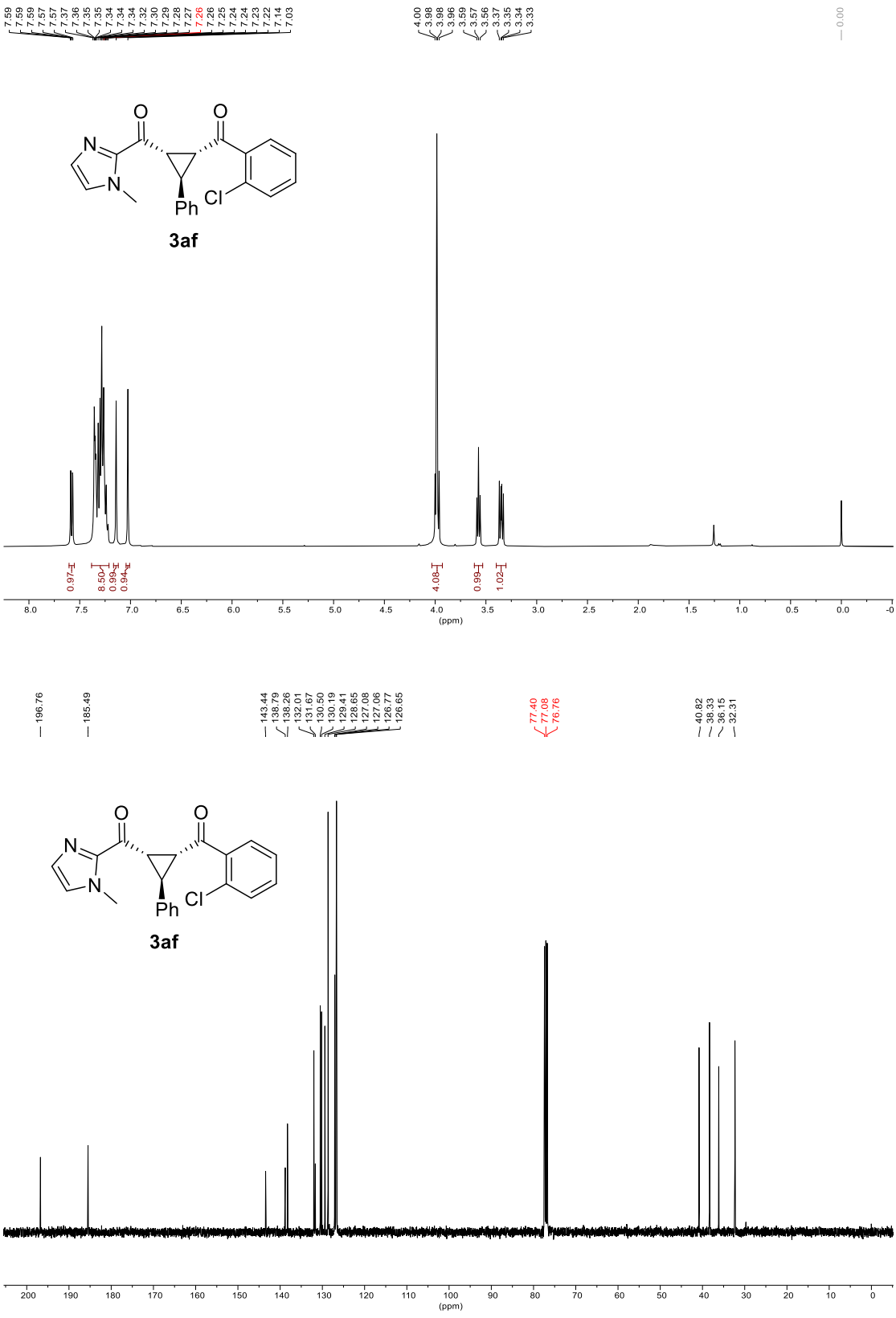


Figure S23. ^{1}H and ^{13}C NMR spectrum of **3af**.

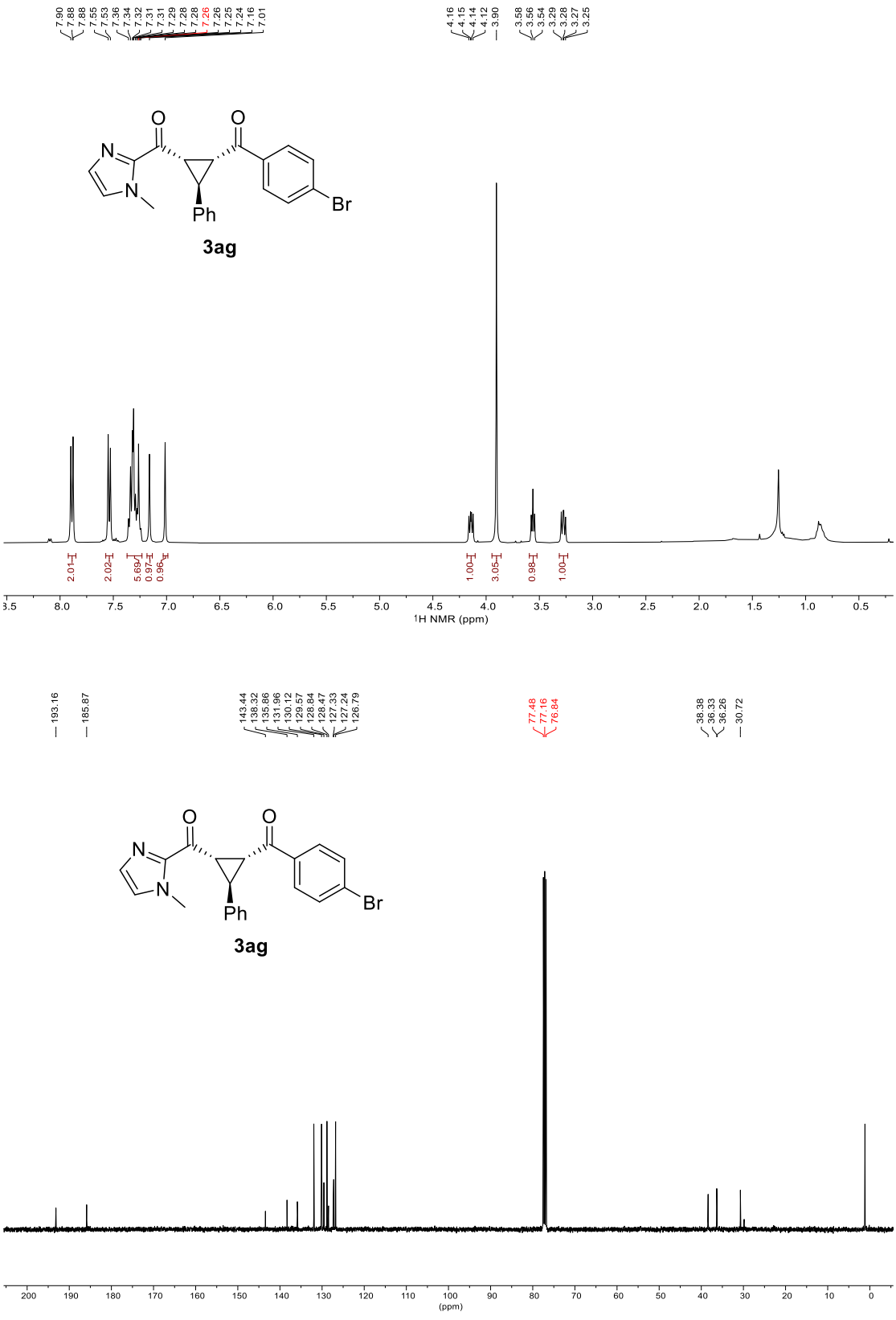
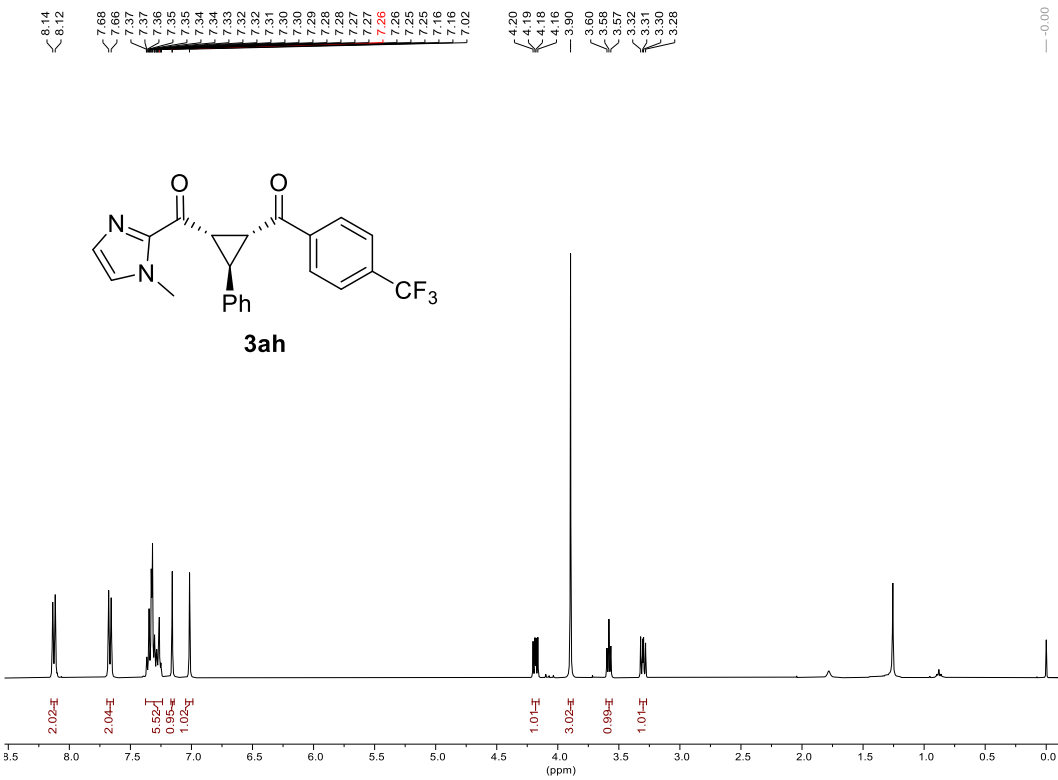
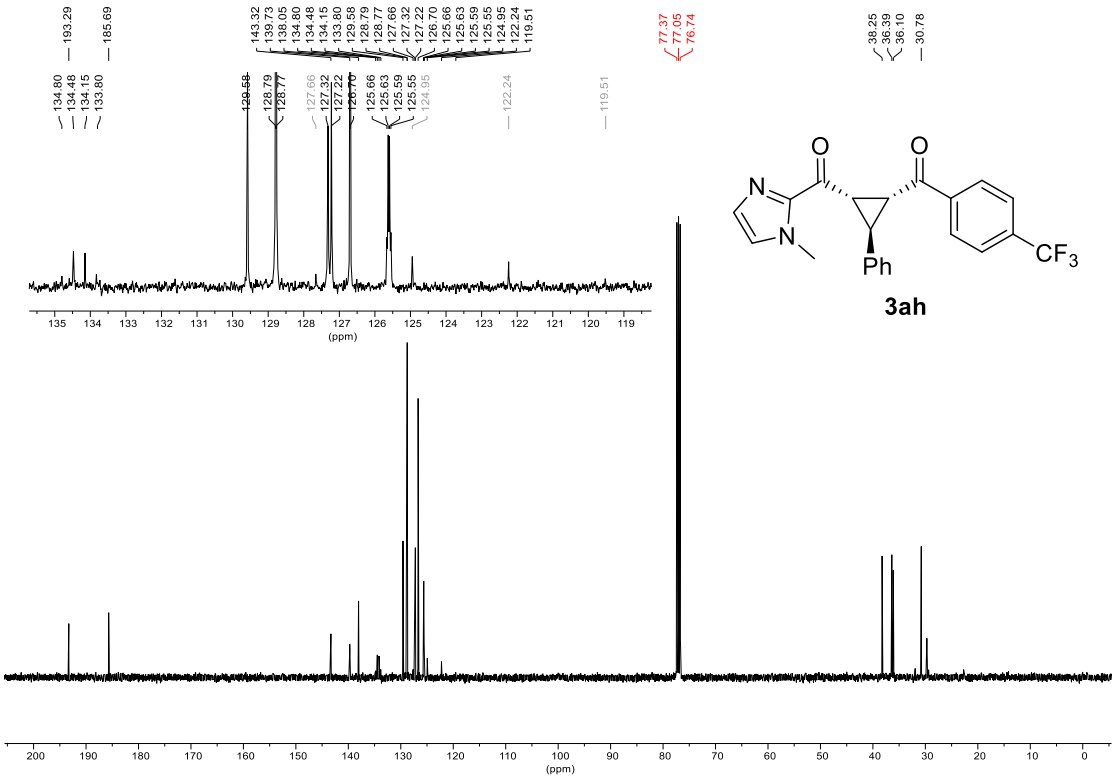


Figure S24. ^{1}H and ^{13}C NMR spectrum of **3ag**.


8.14
8.12
7.68
7.66
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.16
7.16
7.02
4.20
4.19
4.18
4.16
3.90
3.60
3.58
3.57
3.32
3.31
3.30
3.28
-0.00
O
O
N
N
Ph
CF3
3ah
2.02
2.04
5.52
0.95
1.02
1.01
3.02
0.99
1.01
(ppm)


193.29
185.69
143.32
139.73
138.05
134.80
134.48
134.15
133.80
129.58
128.79
128.77
127.66
127.32
127.22
126.70
125.66
125.63
125.59
125.55
124.95
122.24
119.51
77.37
77.05
76.74
38.25
36.39
36.10
30.78
O
O
N
N
Ph
CF3
3ah
(ppm)

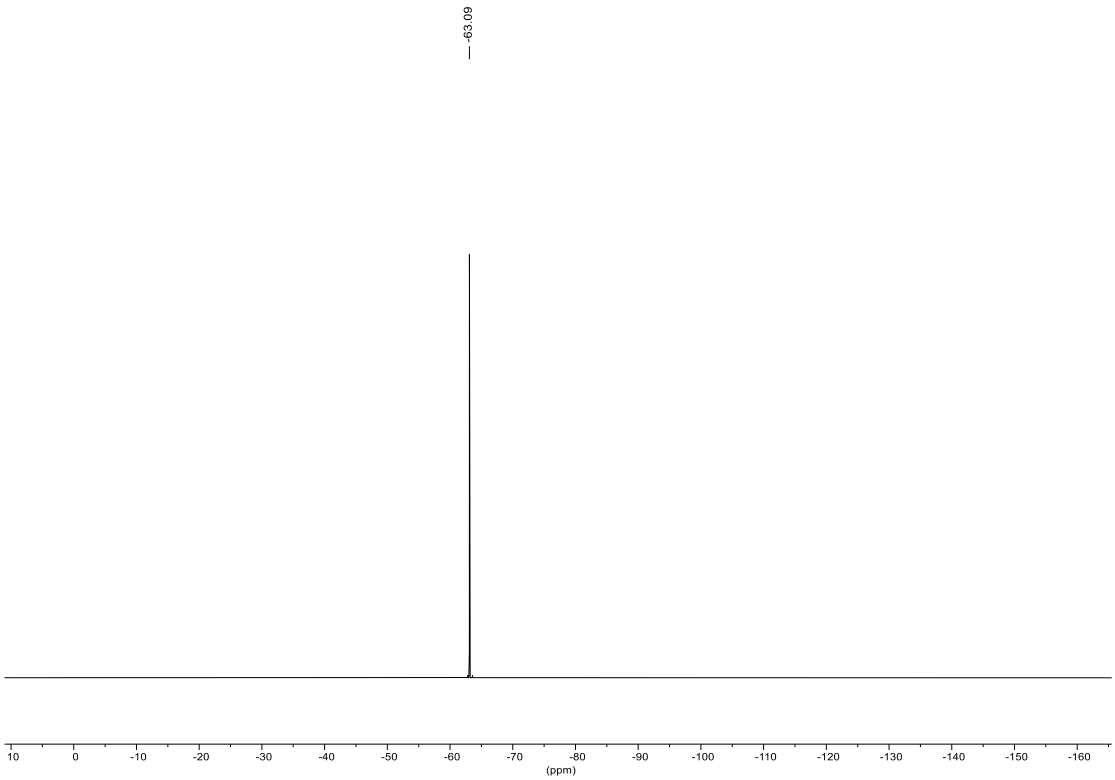


Figure S25. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3ah**.

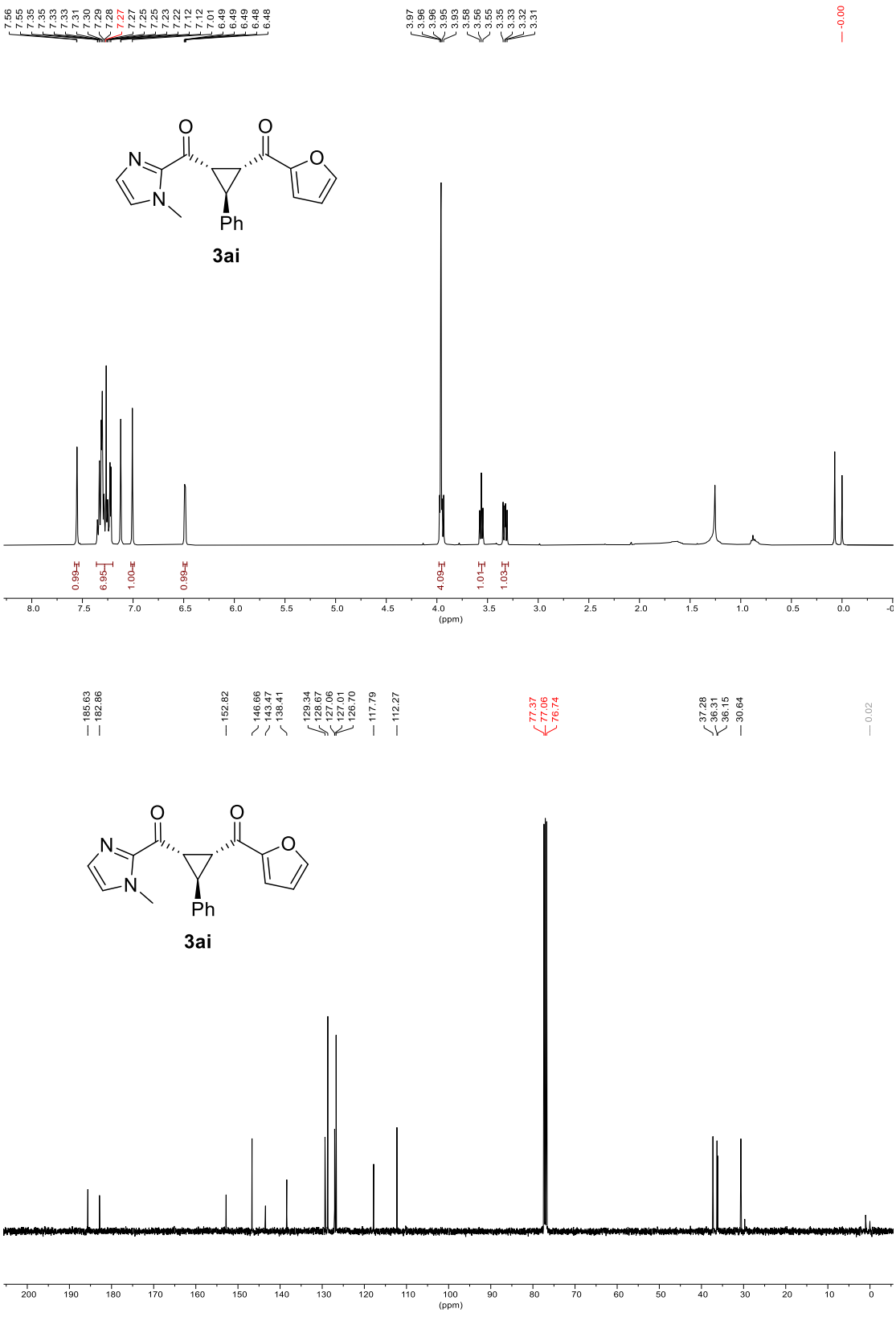


Figure S26. ^{1}H and ^{13}C NMR spectrum of **3ai**.

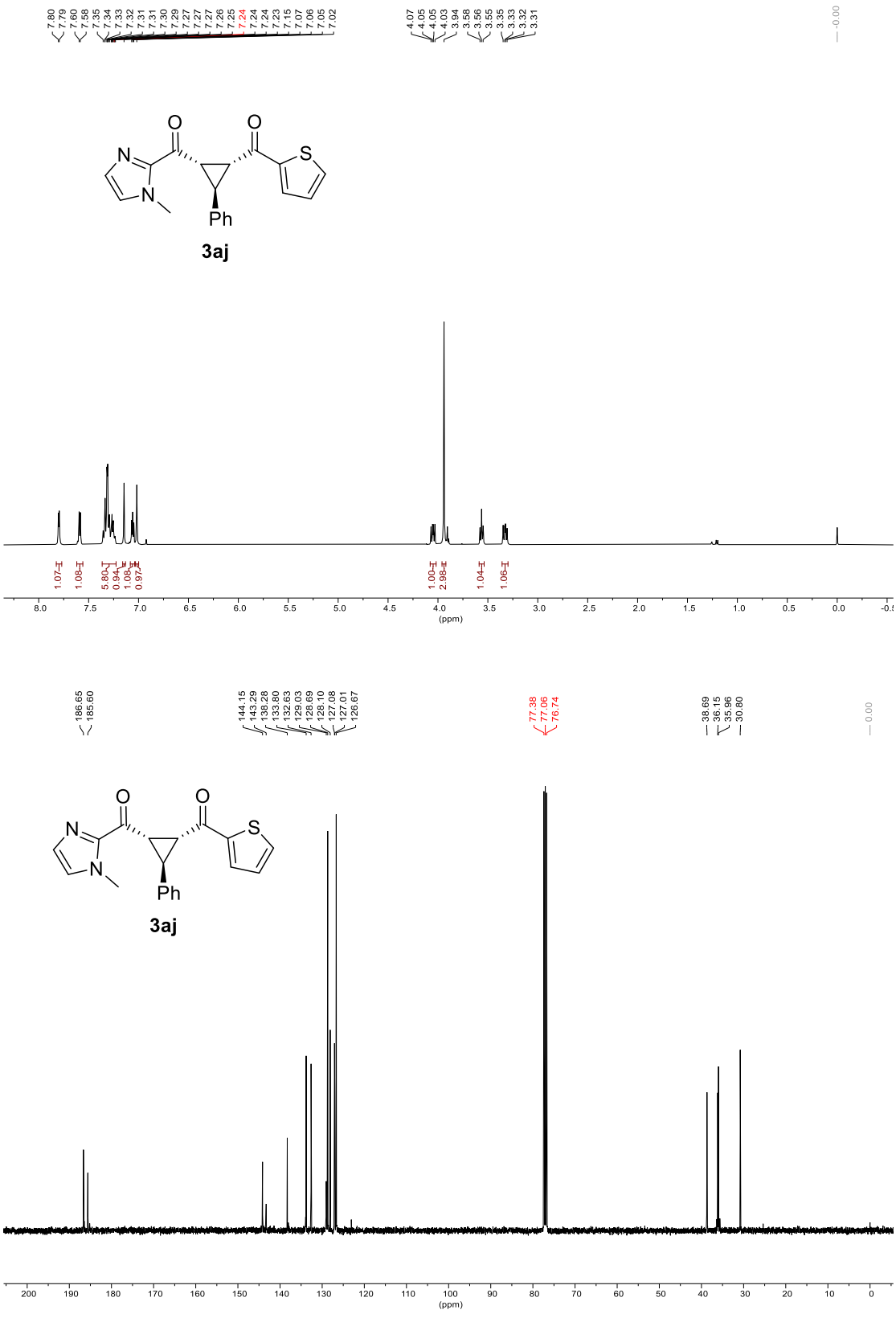


Figure S27. ^{1}H and ^{13}C NMR spectrum of **3aj**.

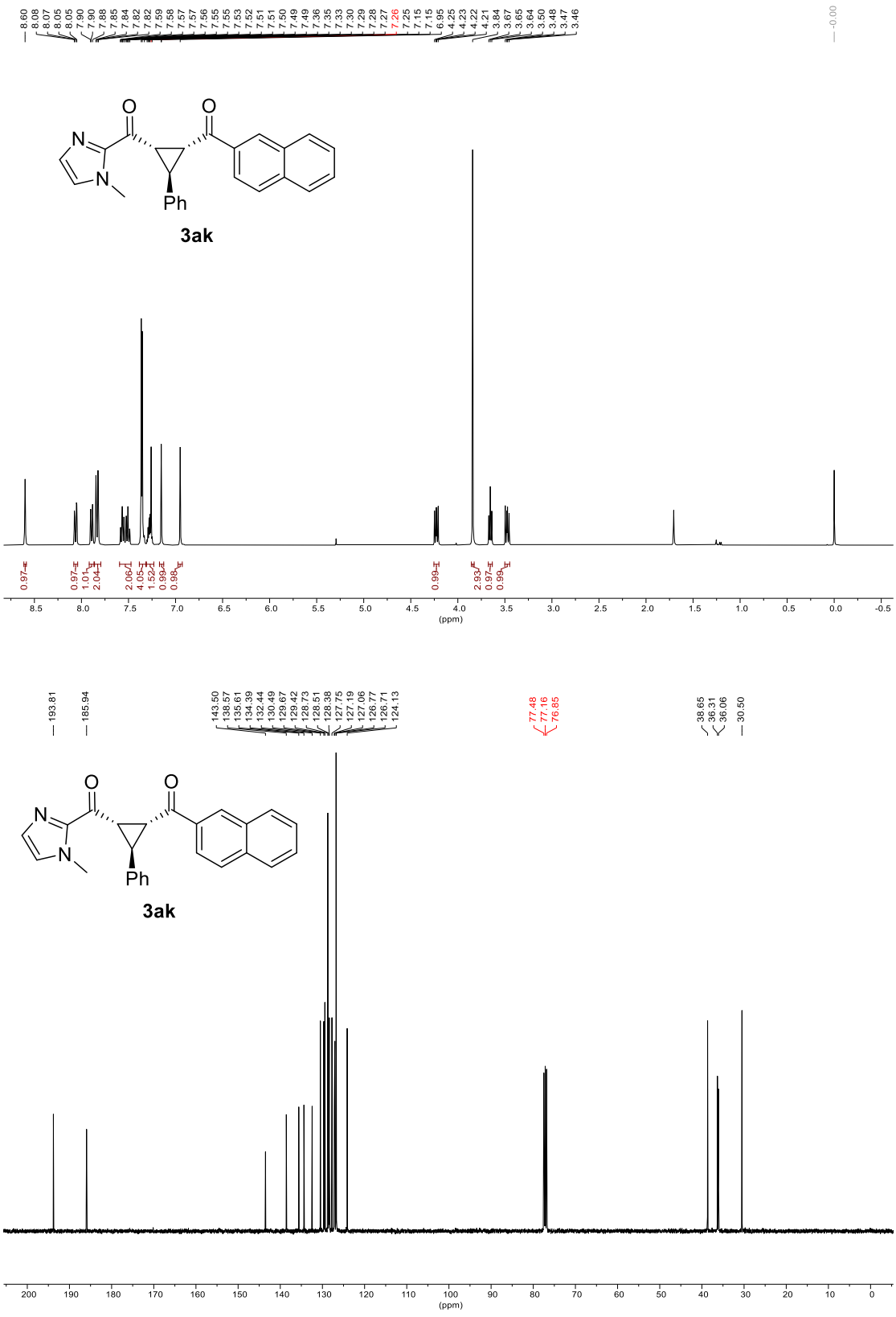


Figure S28. ^{1}H and ^{13}C NMR spectrum of **3ak**.

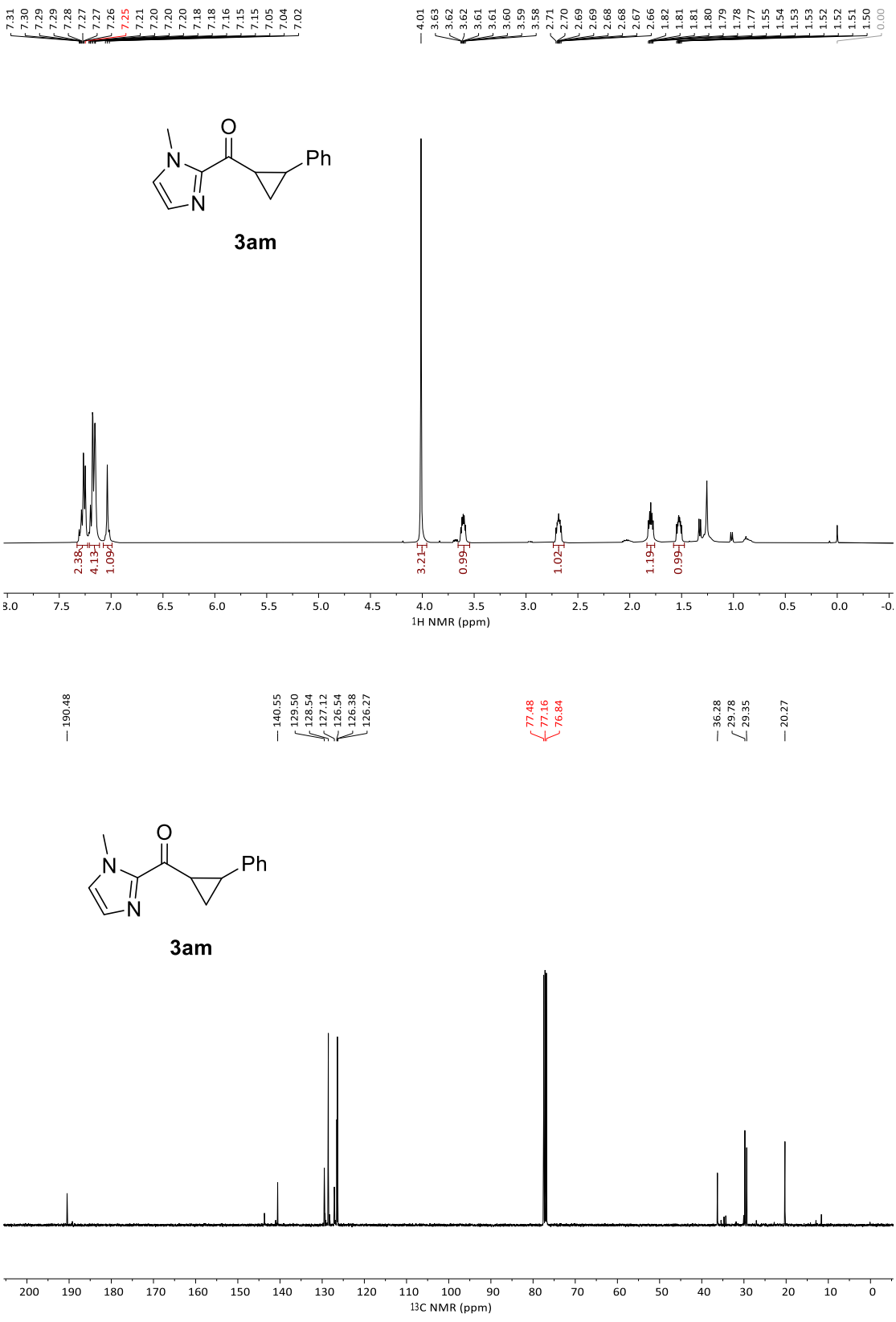


Figure S29. ^{1}H and ^{13}C NMR spectrum of **3am**.

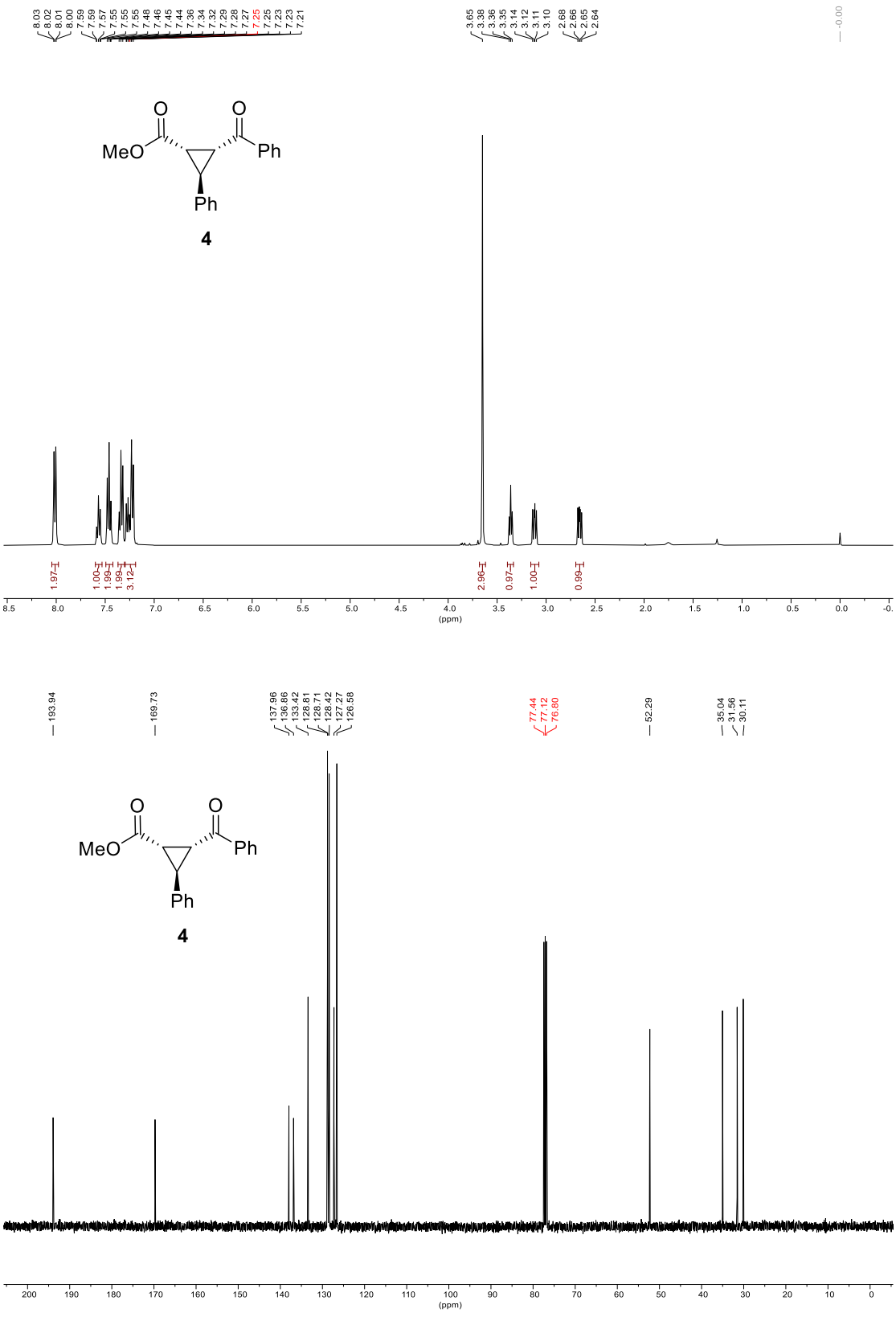


Figure S30. ^{1}H and ^{13}C NMR spectrum of **4**.

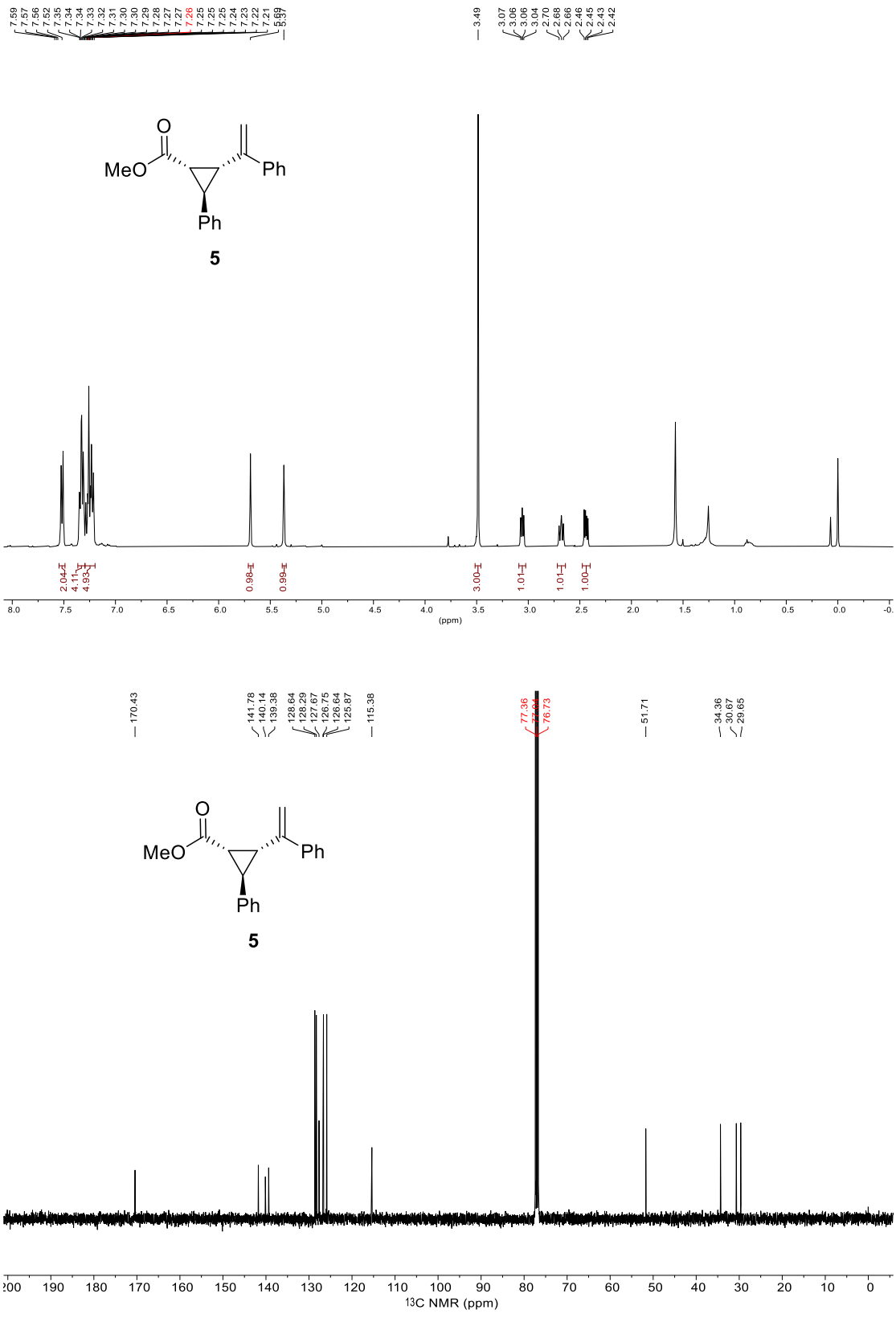


Figure S31. ^{1}H and ^{13}C NMR spectrum of **5**.

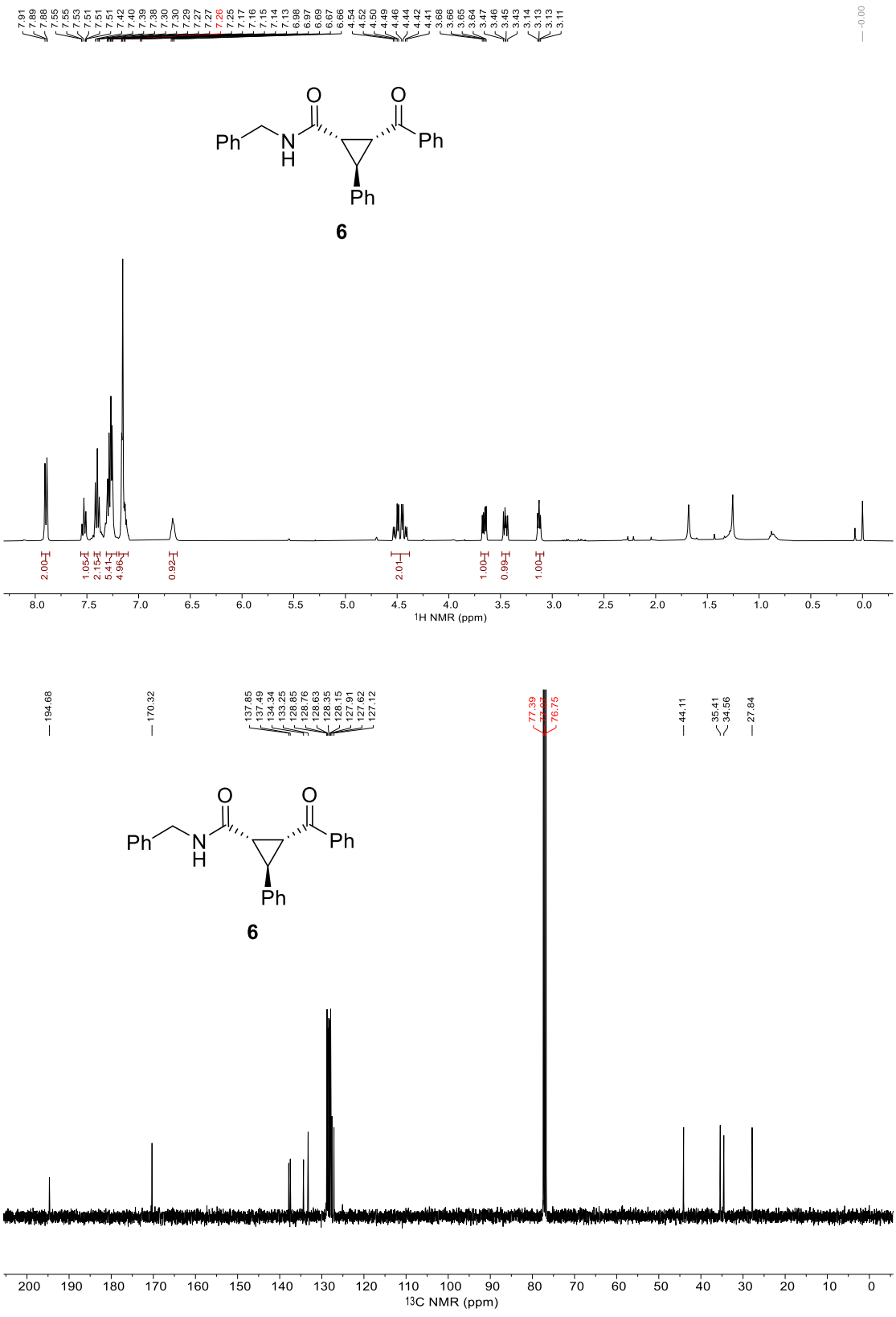
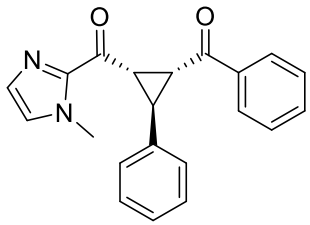
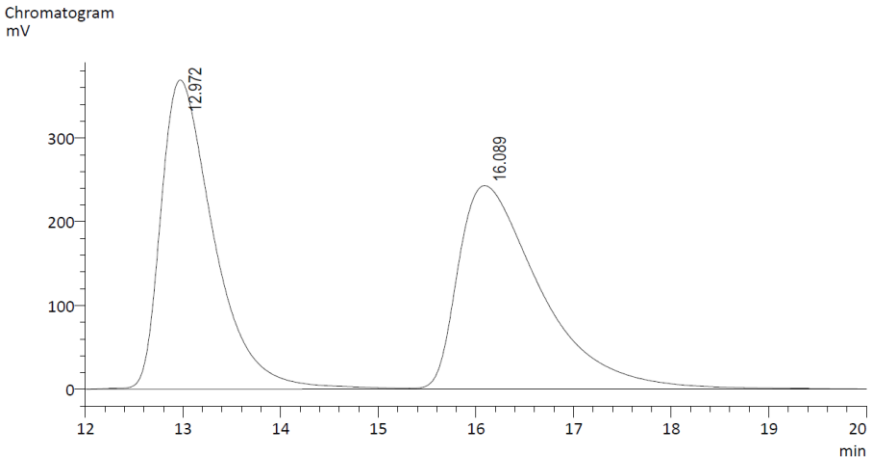


Figure S32. ^{1}H and ^{13}C NMR spectrum of **6**.

7. HPLC Traces on Chiral Stationary Phase

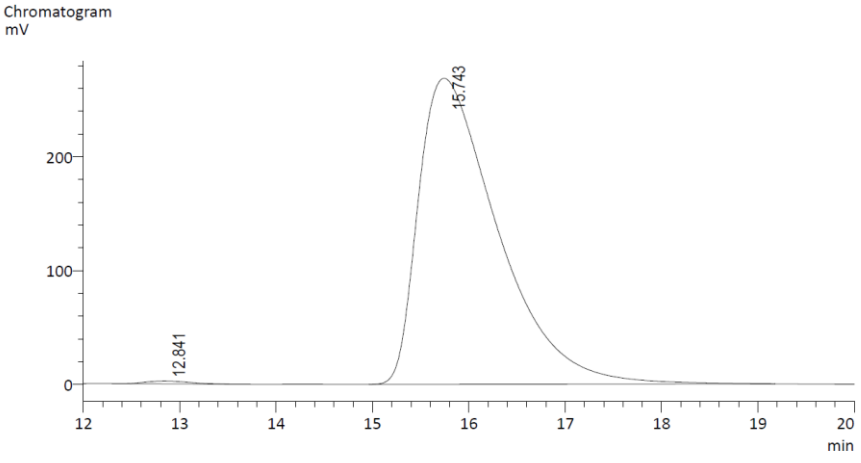


3aa



<Peak Table>
Detector A 254nm

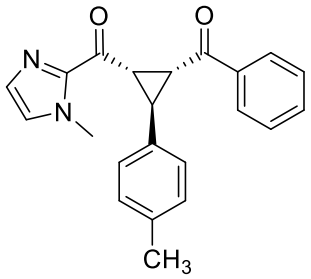
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.972	13950907	369009	49.378
2	16.089	14302356	242882	50.622
Total		28253263	611890	100.000



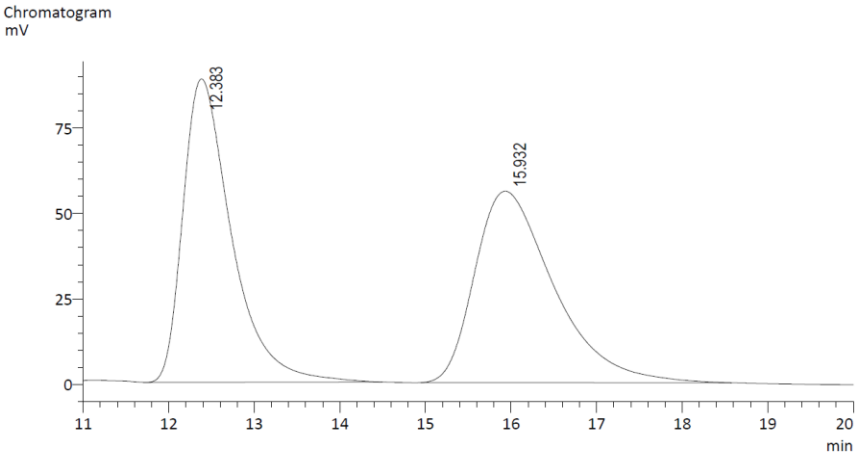
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.841	79879	2552	0.515
2	15.743	15415557	268817	99.485
Total		15495436	271369	100.000

Figure S33. HPLC traces of racemic **3aa** (reference) and chiral **3aa**. Area integration = 0.5: 99.5 (99% ee).

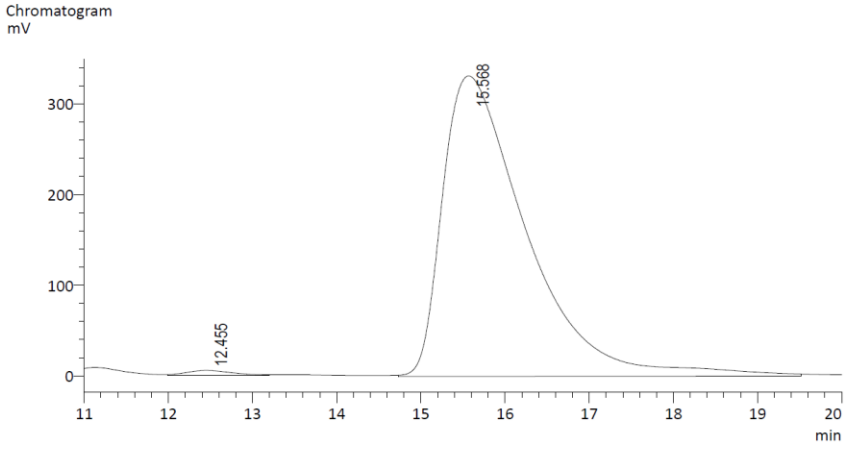


3ba



<Peak Table>
Detector A 254nm

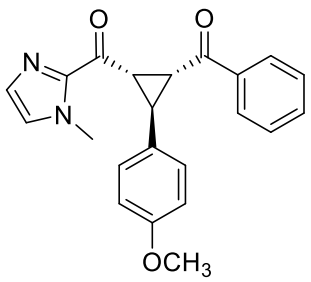
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.383	3497530	88685	49.269
2	15.932	3601323	55963	50.731
Total		7098853	144648	100.000



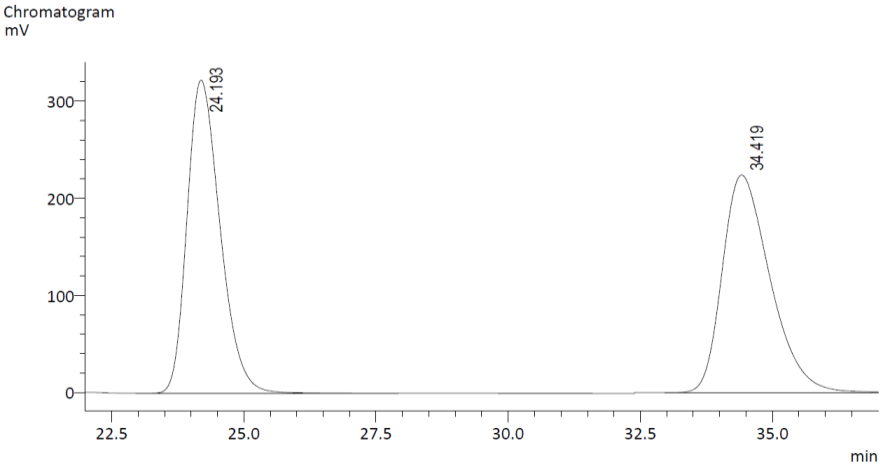
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.455	223859	5650	0.965
2	15.568	22966723	331248	99.035
Total		23190582	336898	100.000

Figure S34. HPLC traces of racemic **3ba** (reference) and chiral **3ba**. Area integration = 1.0:99.0 (98% ee).

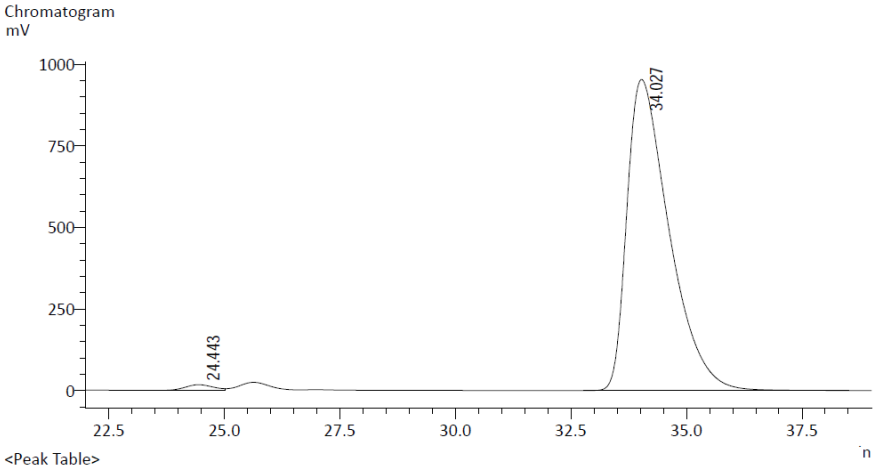


3ca



<Peak Table>
Detector A 254nm

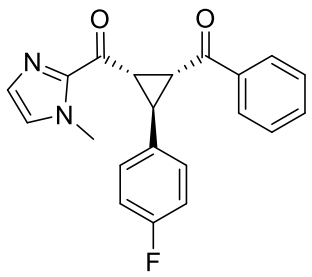
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	24.193	14028512	322458	49.834
2	34.419	14121931	223963	50.166
Total		28150443	546422	100.000



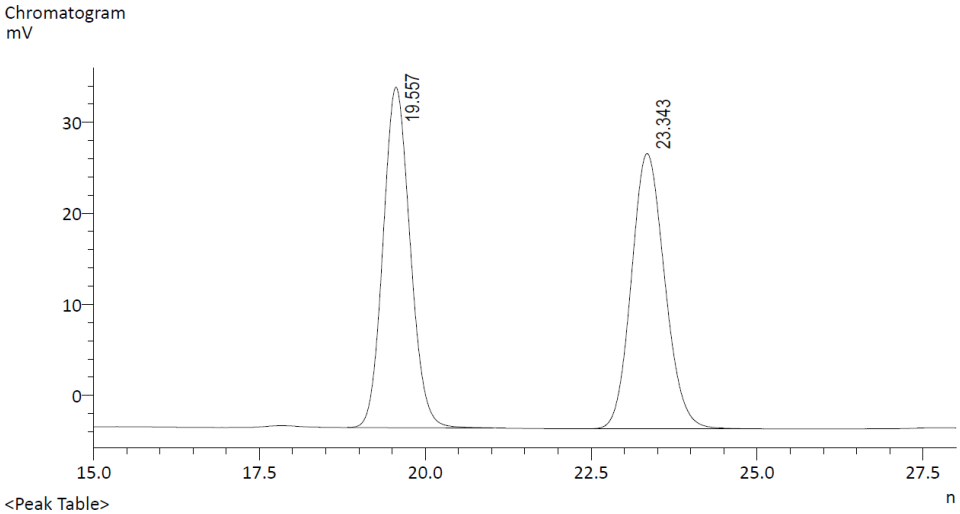
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	24.443	722162	17067	1.179
2	34.027	60520440	953017	98.821
Total		61242602	970085	100.000

Figure S35. HPLC traces of racemic **3ca** (reference) and chiral **3ca**. Area integration = 1.2:98.8 (98% ee).

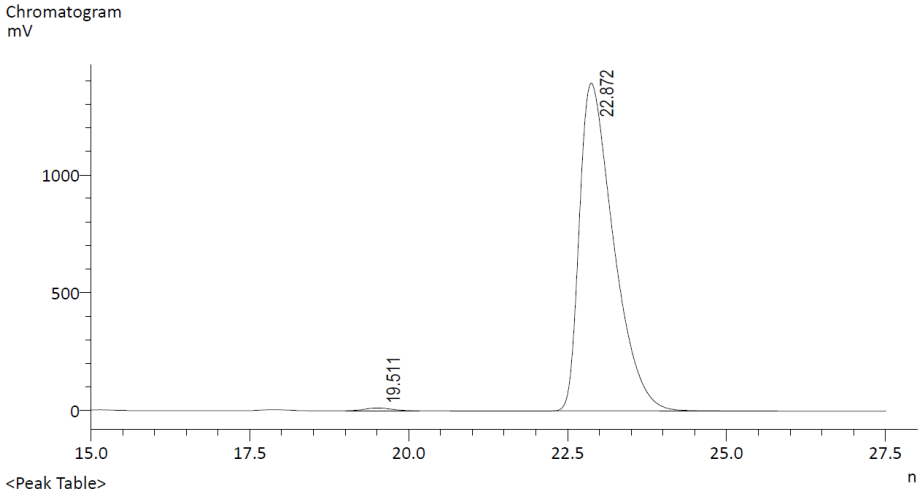


3da



<Peak Table>
Detector A 254nm

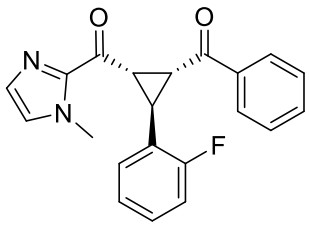
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	19.557	1061930	37418	50.094
2	23.343	1057943	30260	49.906
Total		2119873	67677	100.000



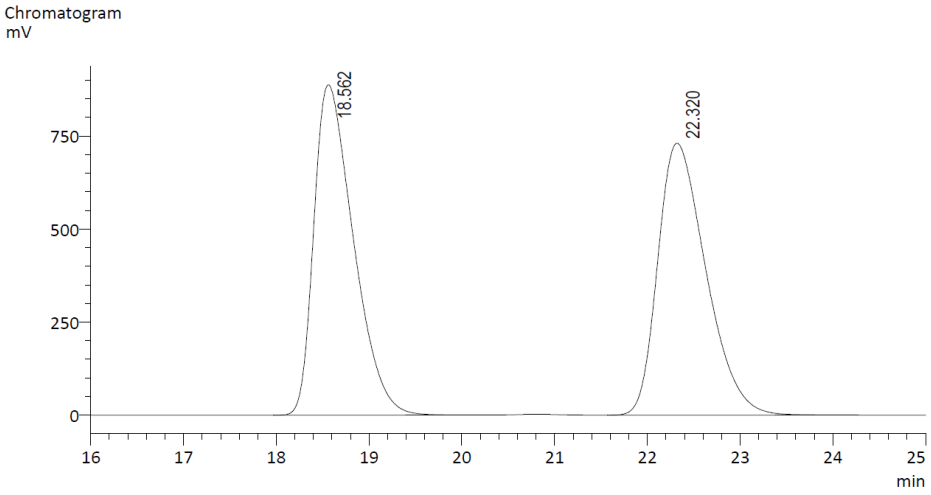
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	19.511	345831	11975	0.661
2	22.872	52009941	1391518	99.339
Total		52355772	1403493	100.000

Figure S36. HPLC traces of racemic **3da** (reference) and chiral **3da**. Area integration = 0.7:99.3 (99% ee).

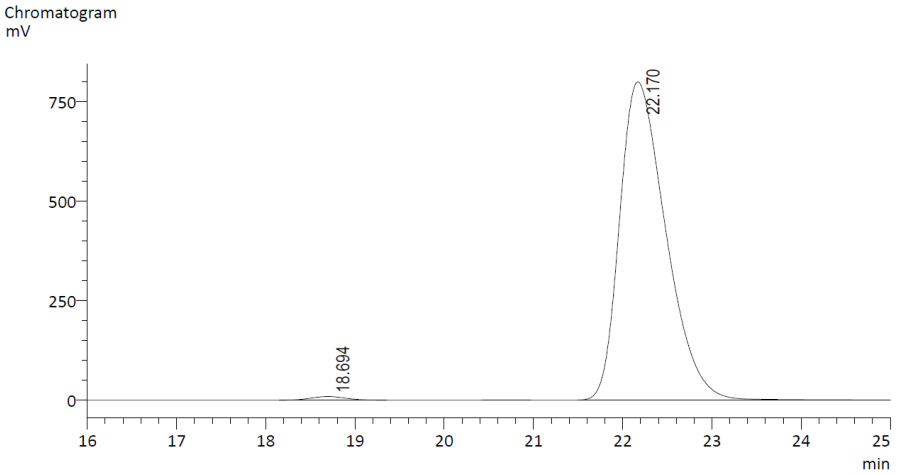


3ea



<Peak Table>
Detector A 254nm

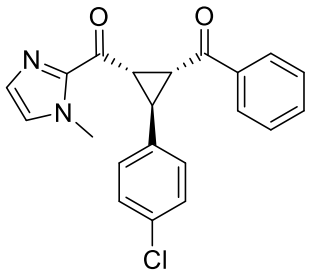
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	18.562	26341894	887944	49.976
2	22.320	26366850	730871	50.024
Total		52708745	1618815	100.000



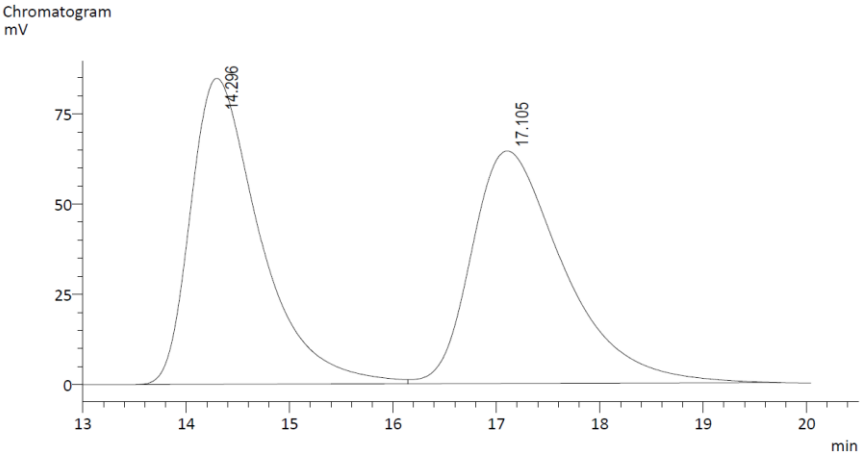
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	18.694	265952	9517	0.914
2	22.170	28835762	799606	99.086
Total		29101714	809123	100.000

Figure S37. HPLC traces of racemic **3ea** (reference) and chiral **3ea**. Area integration = 0.9:99.1 (98% ee).

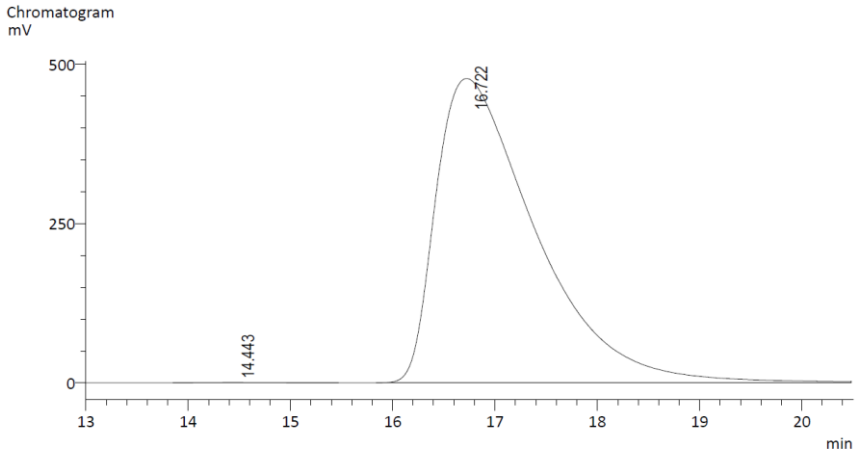


3fa



<Peak Table>
Detector A 254nm

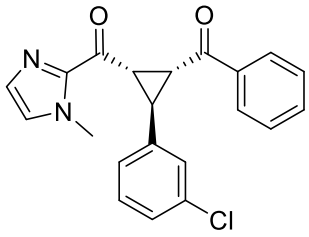
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.296	3959242	84726	49.776
2	17.105	3994878	64383	50.224
Total		7954120	149109	100.000



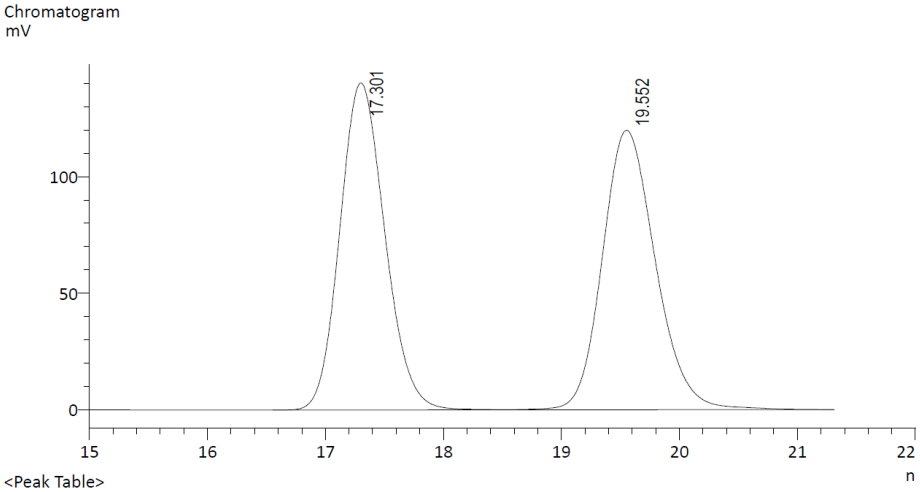
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.443	26981	549	0.083
2	16.722	32420551	477530	99.917
Total		32447532	478079	100.000

Figure S38. HPLC traces of racemic **3fa** (reference) and chiral **3fa**. Area integration = 0.1:99.9 (99.8% ee).

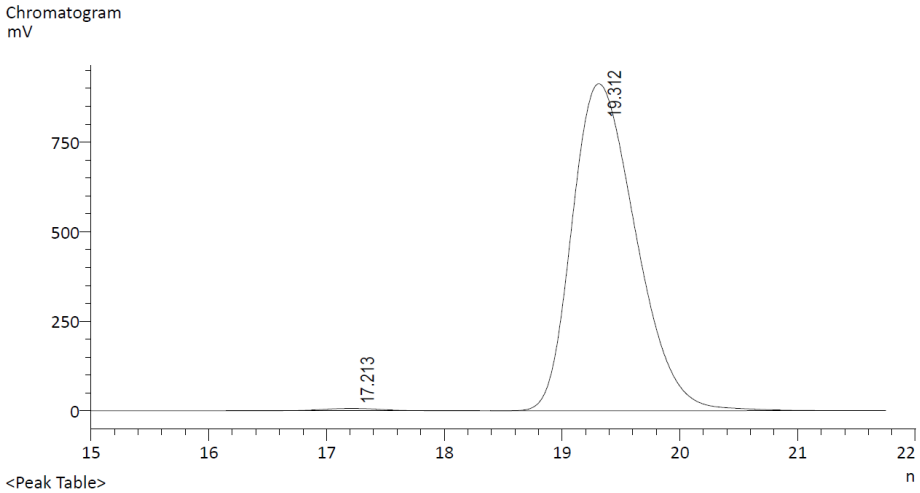


3ga



<Peak Table>
Detector A 254nm

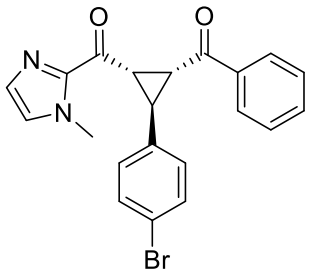
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	17.301	3726799	140468	49.789
2	19.552	3758378	120019	50.211
Total		7485177	260487	100.000



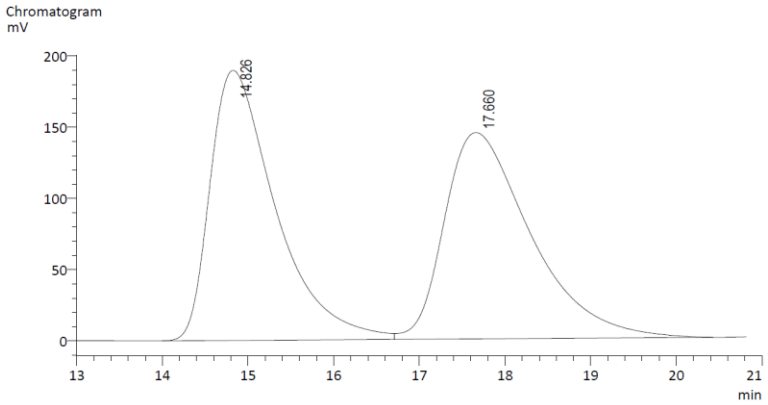
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	17.213	246961	6896	0.715
2	19.312	34293994	912274	99.285
Total		34540955	919169	100.000

Figure S39. HPLC traces of racemic **3ga** (reference) and chiral **3ga**. Area integration = 0.7:99.3 (99% ee).

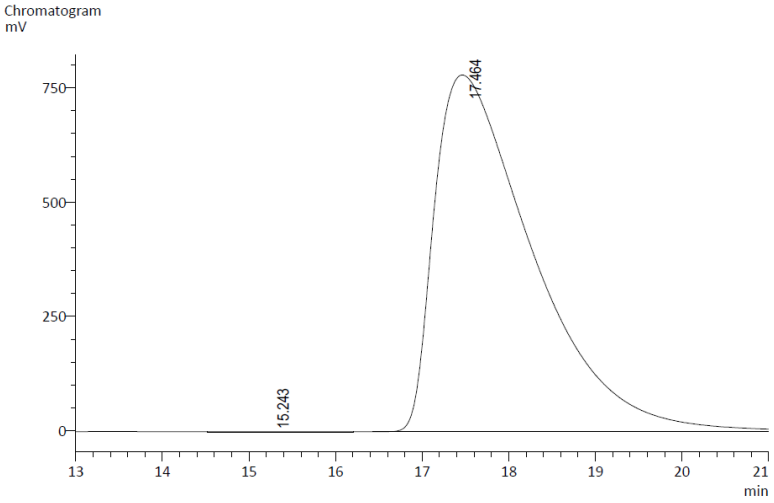


3ha



<Peak Table>
Detector A 254nm

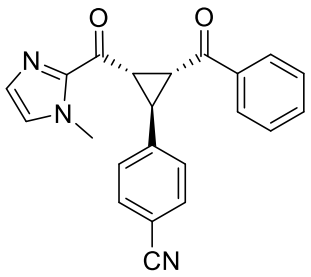
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.826	10062855	189595	49.790
2	17.660	10147925	144835	50.210
Total		20210780	334430	100.000



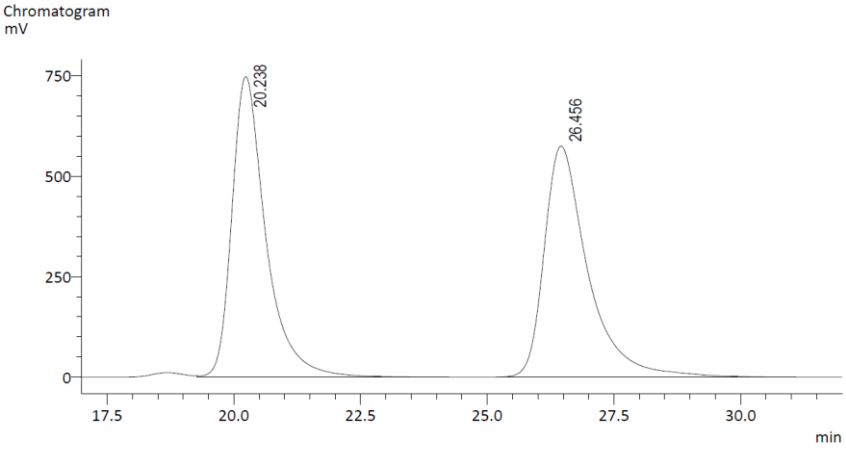
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	15.243	25594	464	0.041
2	17.464	62341981	781181	99.959
Total		62367575	781645	100.000

Figure S40. HPLC traces of racemic **3ha** (reference) and chiral **3ha**. Area integration = 0.1:99.9 (99.8% ee).

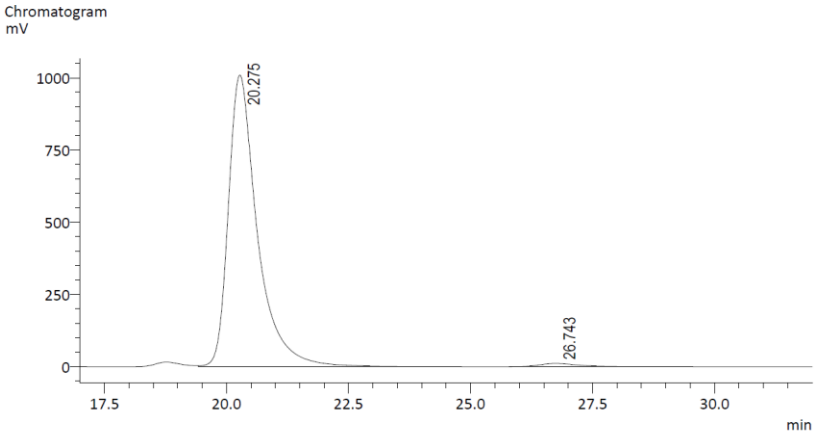


3ia



<Peak Table>
Detector A 254nm

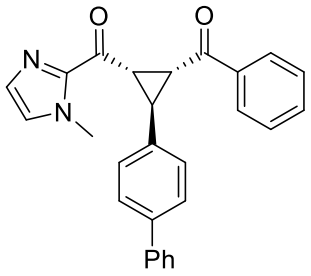
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	20.238	34768446	747729	50.260
2	26.456	34408552	574783	49.740
Total		69176997	1322512	100.000



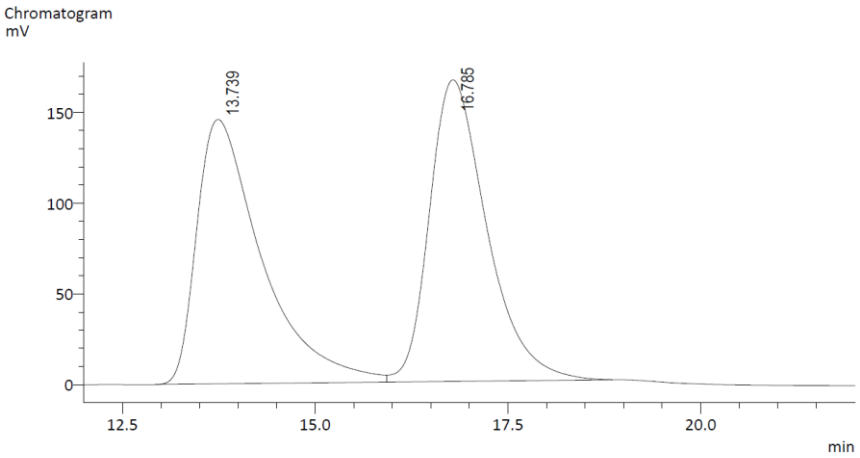
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	20.275	41788223	1009835	98.558
2	26.743	611440	10959	1.442
Total		42399662	1020794	100.000

Figure S41. HPLC traces of racemic **3ia** (reference) and chiral **3ia**. Area integration = 98.6:1.4 (97% ee).

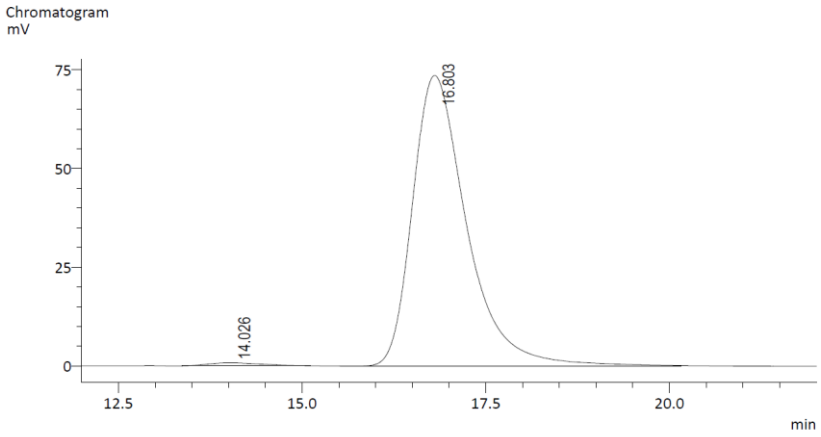


3ja



<Peak Table>
Detector A 254nm

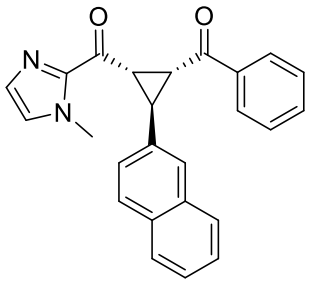
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	13.739	8544925	145738	49.787
2	16.785	8618167	166188	50.213
Total		17163092	311927	100.000



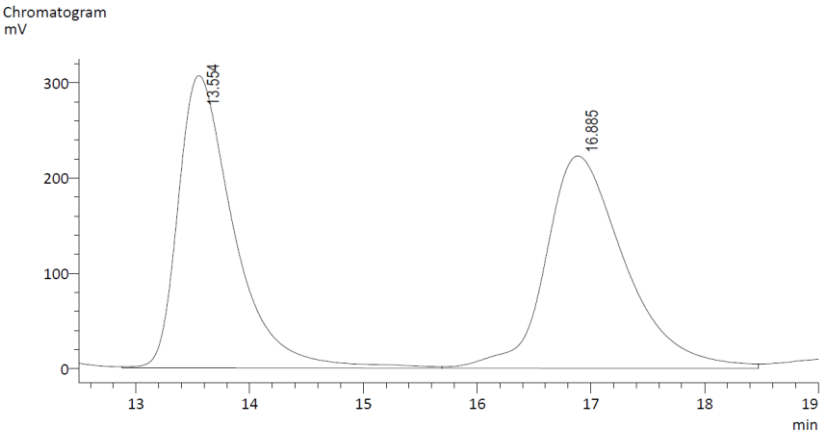
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.026	35402	724	0.924
2	16.803	3794017	73619	99.076
Total		3829419	74343	100.000

Figure S42. HPLC traces of racemic **3ja** (reference) and chiral **3ja**. Area integration = 0.9:99.1 (98% ee).

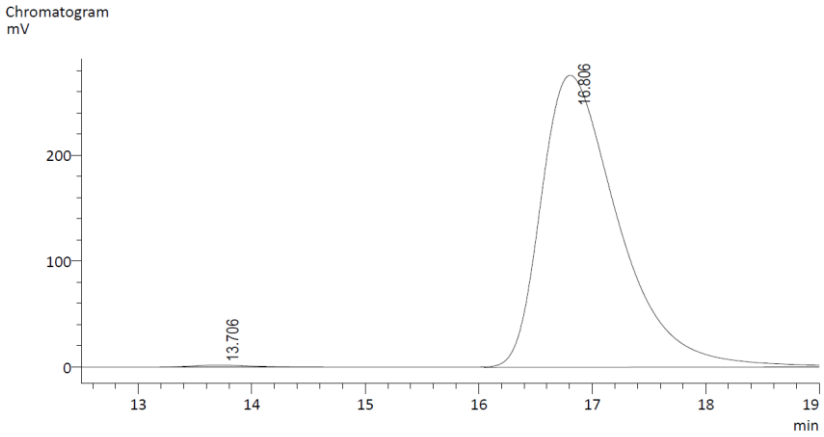


3ka



<Peak Table>
Detector A 254nm

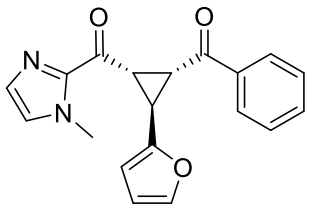
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	13.554	10424418	306489	49.155
2	16.885	10782735	222532	50.845
Total		21207153	529020	100.000



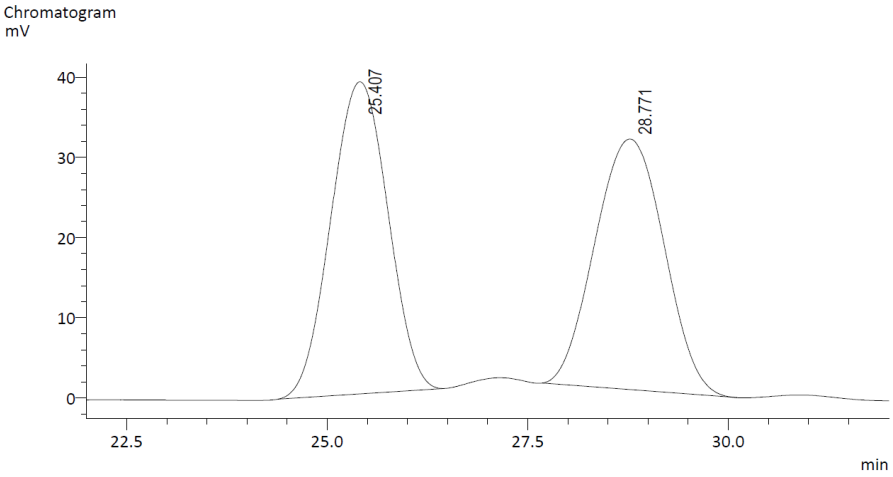
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	13.706	60246	1799	0.457
2	16.806	13117360	275804	99.543
Total		13177606	277603	100.000

Figure S43. HPLC traces of racemic **3ka** (reference) and chiral **3ka**. Area integration = 0.5:99.5 (99% ee).

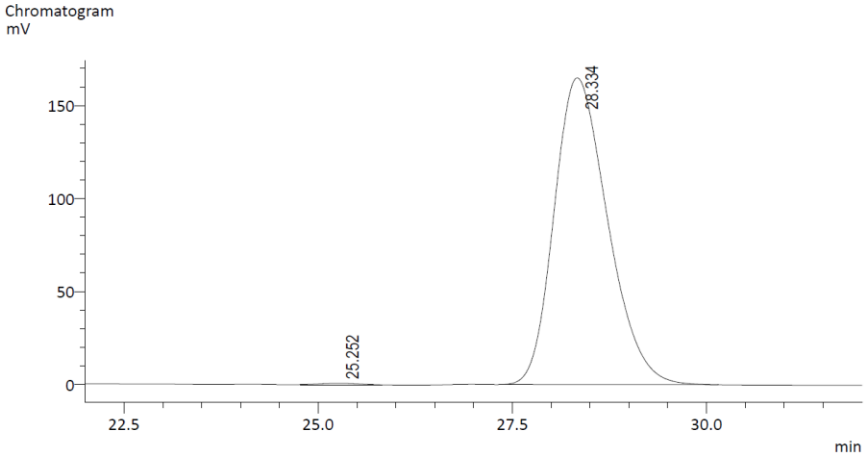


3la



<Peak Table>
Detector A 254nm

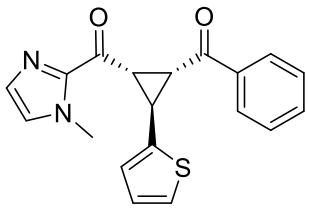
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	25.407	1923401	38922	50.659
2	28.771	1873345	31264	49.341
Total		3796747	70186	100.000



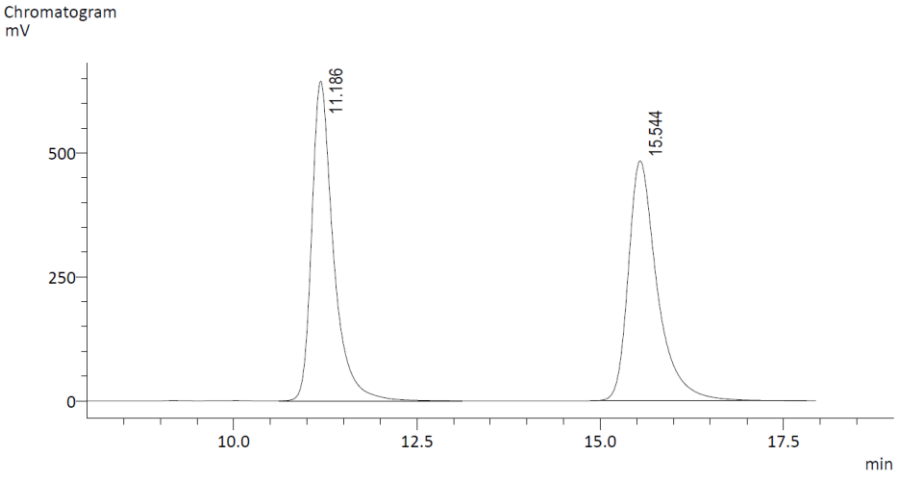
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	25.252	33530	870	0.422
2	28.334	7913863	164969	99.578
Total		7947394	165839	100.000

Figure S44. HPLC traces of racemic **3la** (reference) and chiral **3la**. Area integration = 0.4:99.6 (99% ee).

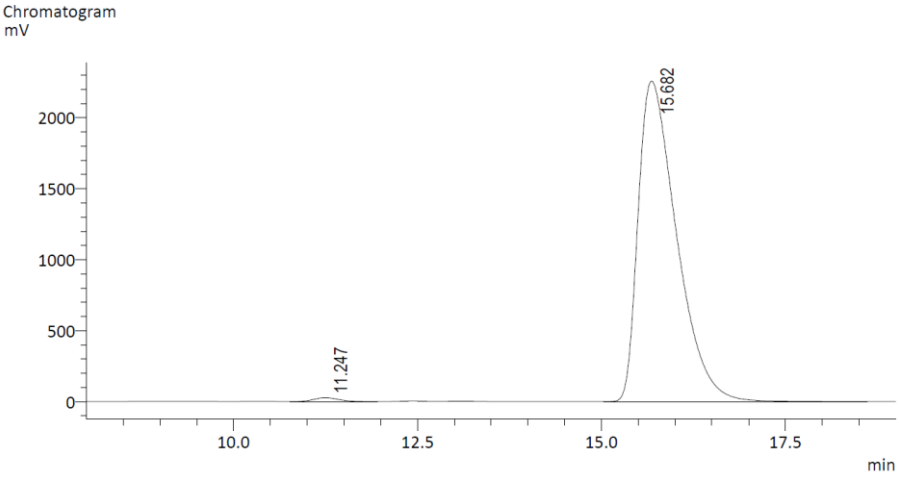


3ma



<Peak Table>
Detector A 254nm

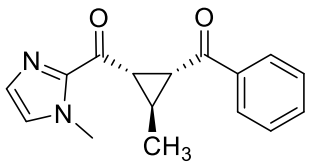
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	11.186	13276812	645231	49.943
2	15.544	13307201	484274	50.057
Total		26584012	1129505	100.000



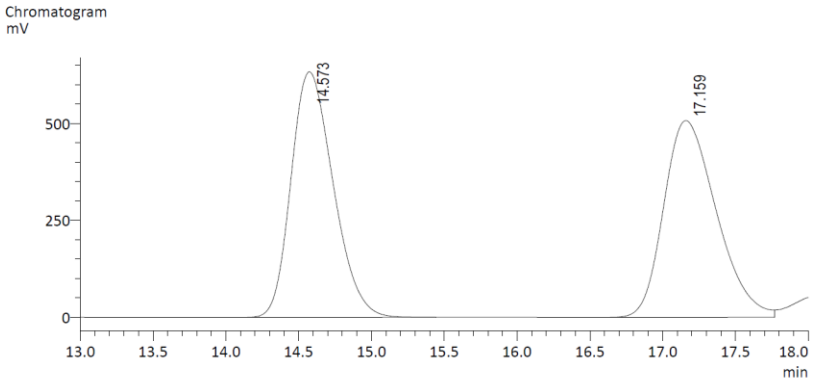
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	11.247	645100	27359	0.780
2	15.682	82108410	2259987	99.220
Total		82753510	2287346	100.000

Figure S45. HPLC traces of racemic **3ma** (reference) and chiral **3ma**. Area integration = 0.8:99.2 (98% ee).

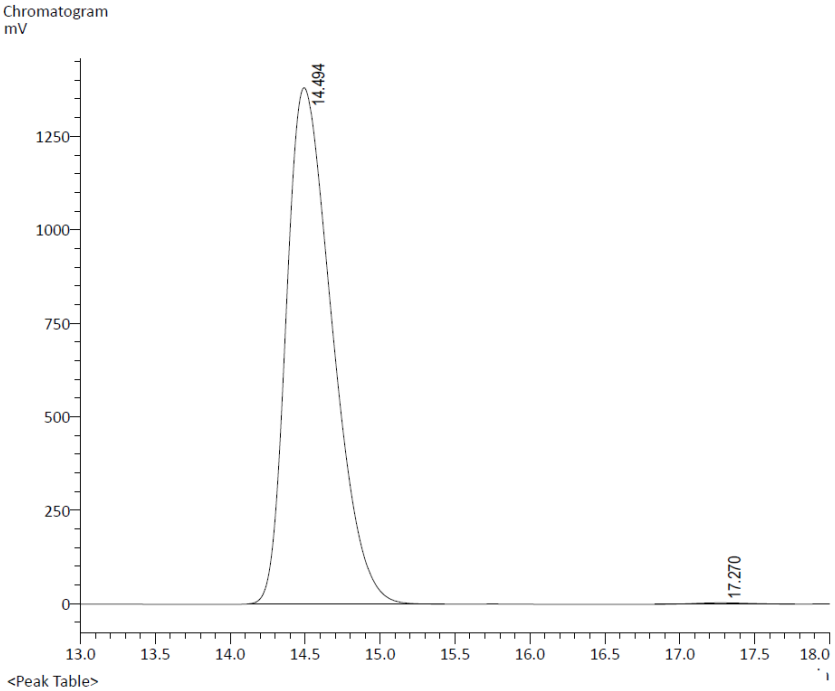


3na



<Peak Table>
Detector A 254nm

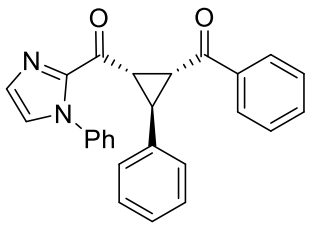
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.573	12747782	633383	49.977
2	17.159	12759561	507479	50.023
Total		25507343	1140862	100.000



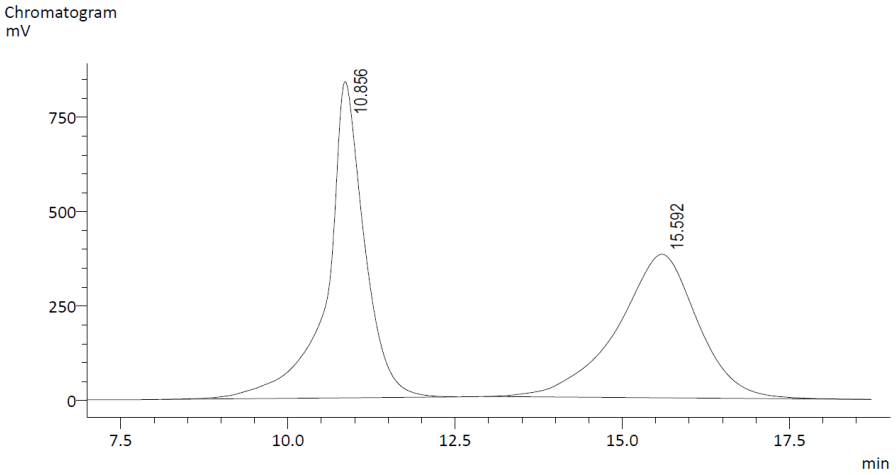
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.494	29272687	1381531	99.646
2	17.270	103999	3659	0.354
Total		29376685	1385191	100.000

Figure S46. HPLC traces of racemic **3na** (reference) and chiral **3na**. Area integration = 99.6:0.4 (99% ee).

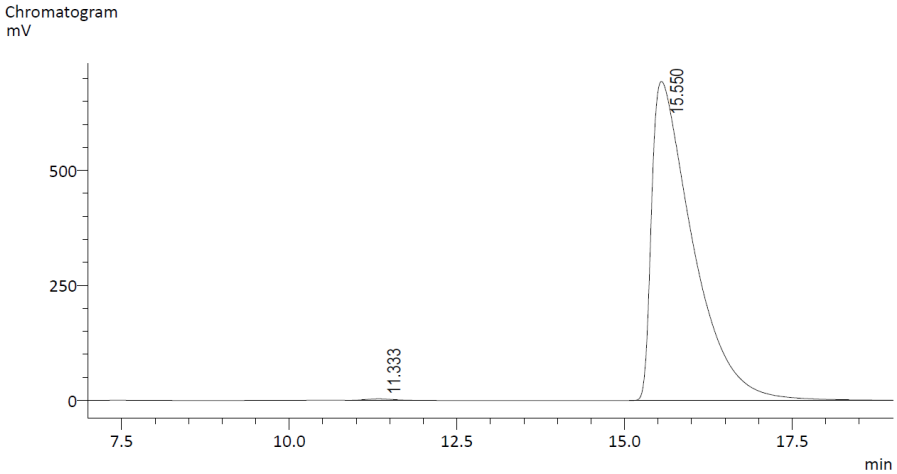


3oa



<Peak Table>
Detector A 254nm

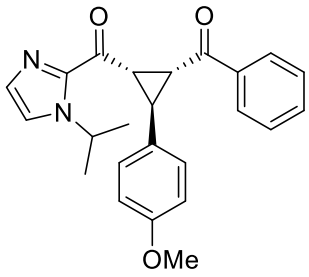
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	10.856	32605399	836893	50.495
2	15.592	31965899	379886	49.505
Total		64571297	1216780	100.000



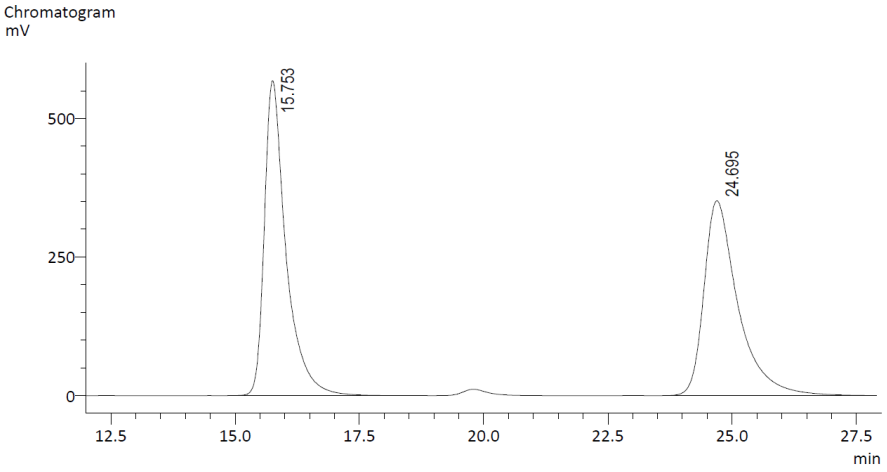
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	11.333	116990	3577	0.391
2	15.550	29809084	694089	99.609
Total		29926073	697666	100.000

Figure S47. HPLC traces of racemic **3oa** (reference) and chiral **3oa**. Area integration =0.4: 99.6 (99% ee).

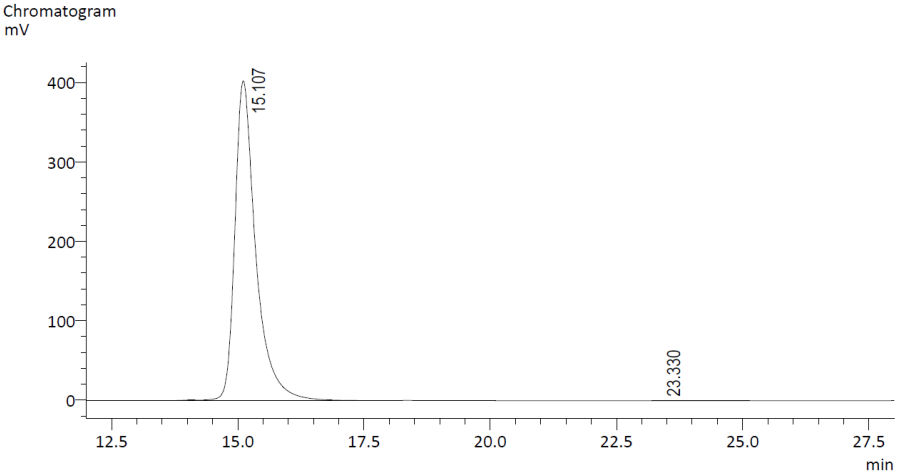


3pa



<Peak Table>
Detector A 254nm

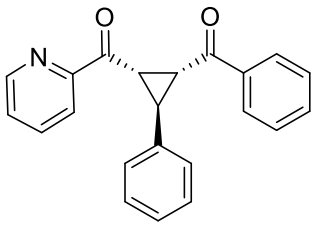
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	15.753	17181530	568130	50.598
2	24.695	16775653	351570	49.402
Total		33957183	919700	100.000



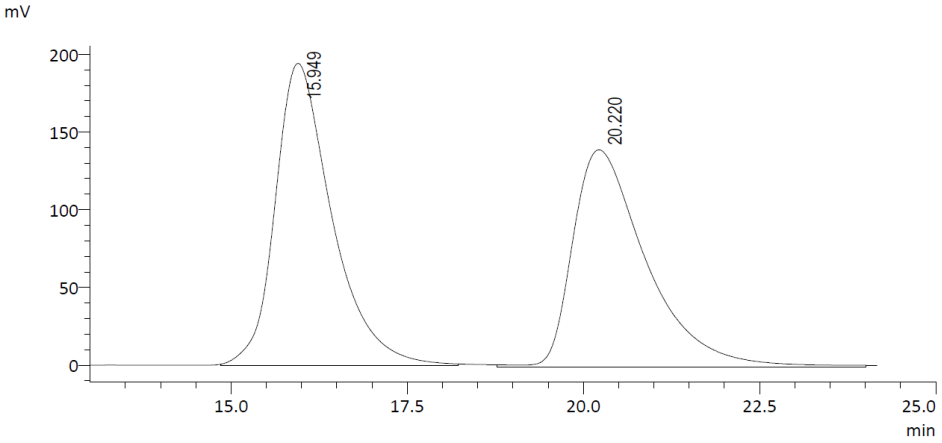
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	15.107	11662887	403049	99.870
2	23.330	15240	145	0.130
Total		11678127	403194	100.000

Figure S48. HPLC traces of racemic **3pa** (reference) and chiral **3pa**. Area integration = 99.9:0.1 (99.8% ee).

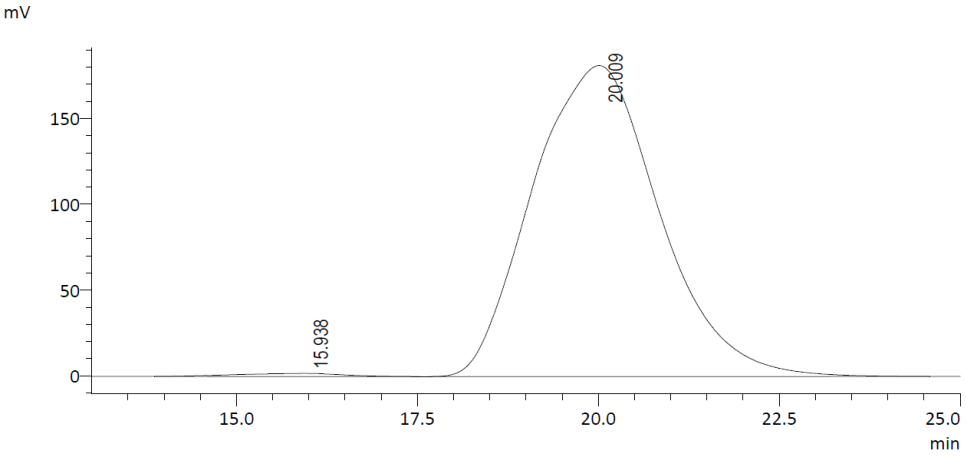


3qa



Integration Table
Detector A 254nm

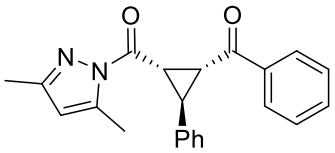
Peak No.	Retention Time (min)	Area (mAU*s)	Height (mAU)	Area Ratio (%)
1	15.949	10896402	194258	51.743
2	20.220	10162401	139665	48.257
总计		21058804	333923	100.000



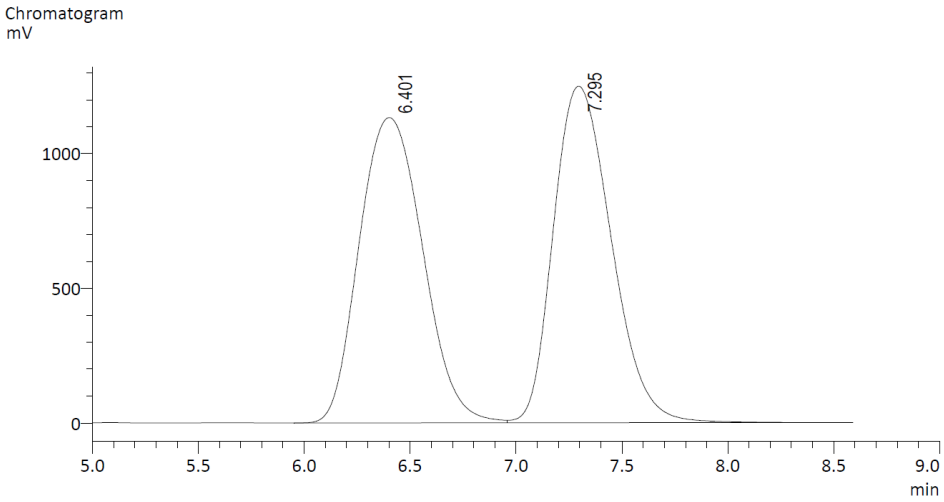
Integration Table
Detector A 254nm

Peak No.	Retention Time (min)	Area (mAU*s)	Height (mAU)	Area Ratio (%)
1	15.938	185047	1827	0.829
2	20.009	22127687	181308	99.171
总计		22312735	183134	100.000

Figure S49. HPLC traces of racemic **3qa** (reference) and chiral **3qa**. Area integration = 0.8:99.2 (98% ee).

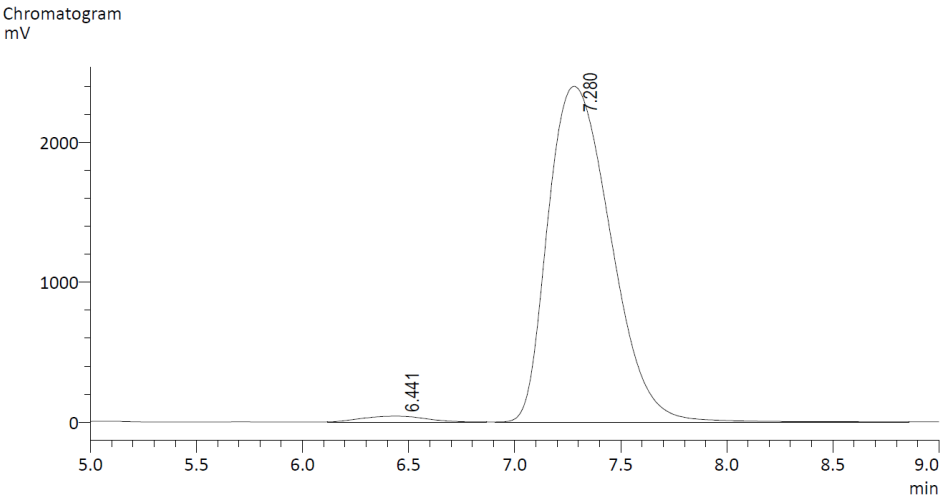


3ra



<Peak Table>
Detector A 254nm

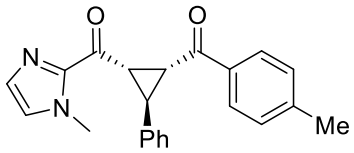
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	6.401	23675969	1134136	49.869
2	7.295	23800576	1249766	50.131
Total		47476545	2383902	100.000



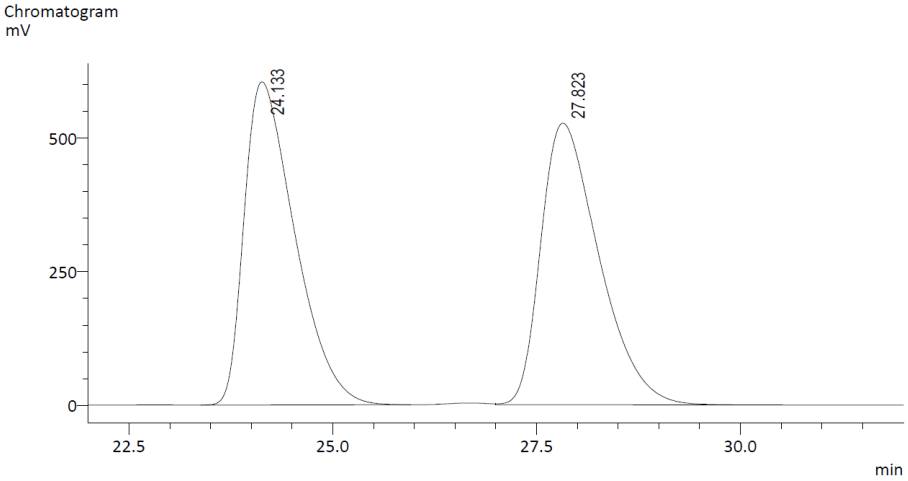
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	6.441	850223	41097	1.690
2	7.280	49448663	2401539	98.310
Total		50298886	2442636	100.000

Figure S50. HPLC traces of racemic **3ra** (reference) and chiral **3ra**. Area integration = 1.7:98.3 (97% ee).

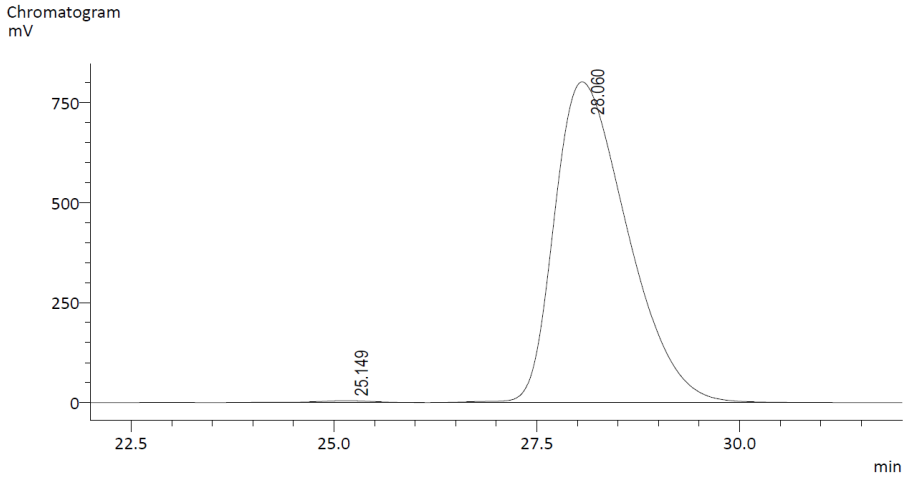


3ab



<Peak Table>
Detector A 254nm

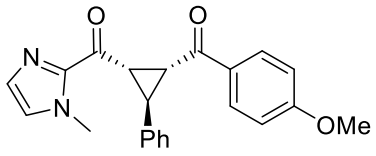
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	24.133	26150534	604431	49.990
2	27.823	26160727	526800	50.010
Total		52311261	1131231	100.000



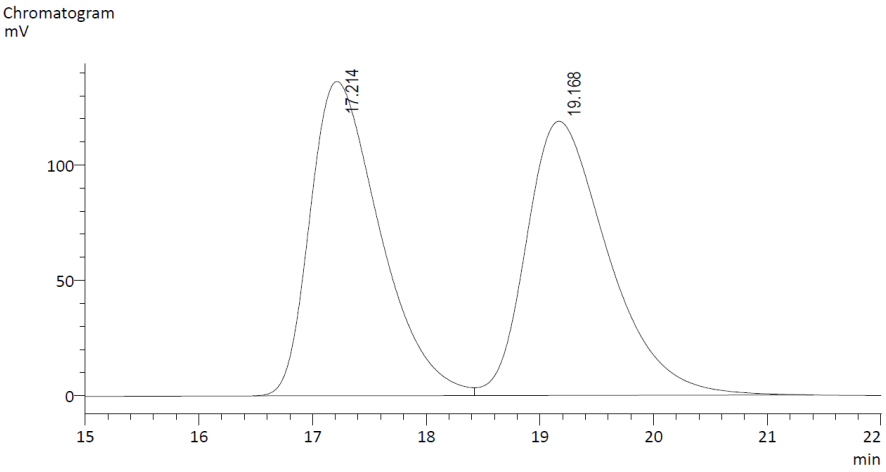
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	25.149	251910	4423	0.501
2	28.060	50005369	801921	99.499
Total		50257279	806345	100.000

Figure S51. HPLC traces of racemic **3ab** (reference) and chiral **3ab**. Area integration = 0.5: 99.5 (99% ee).

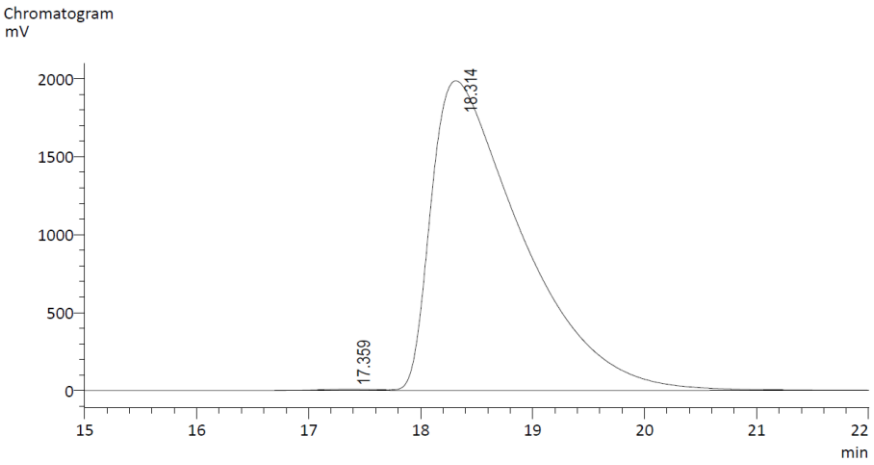


3ac



<Peak Table>
Detector A 254nm

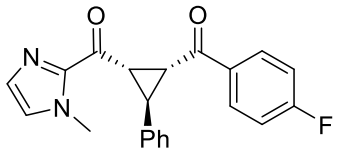
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	17.214	5828263	136230	49.521
2	19.168	5940984	118844	50.479
Total		11769247	255073	100.000



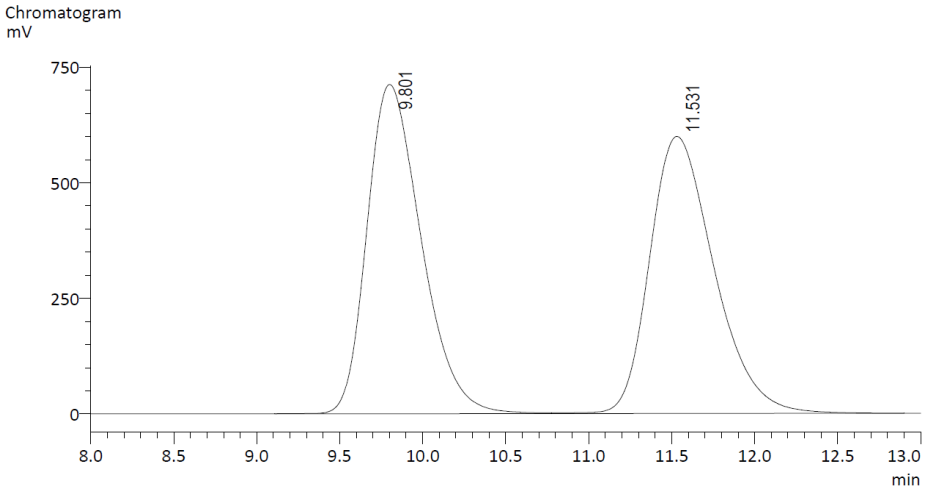
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	17.359	313137	9213	0.279
2	18.314	112084595	1986446	99.721
Total		112397732	1995658	100.000

Figure S52. HPLC traces of racemic **3ac** (reference) and chiral **3ac**. Area integration = 0.3:99.7 (99.4% ee).

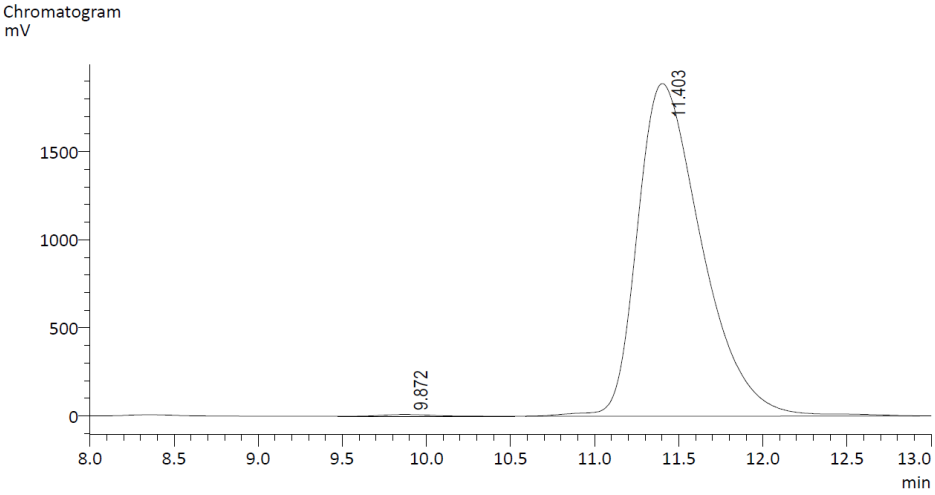


3ad



<Peak Table>
Detector A 254nm

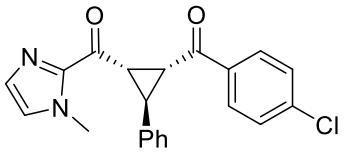
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.801	16171629	712174	49.998
2	11.531	16172640	599272	50.002
Total		32344269	1311446	100.000



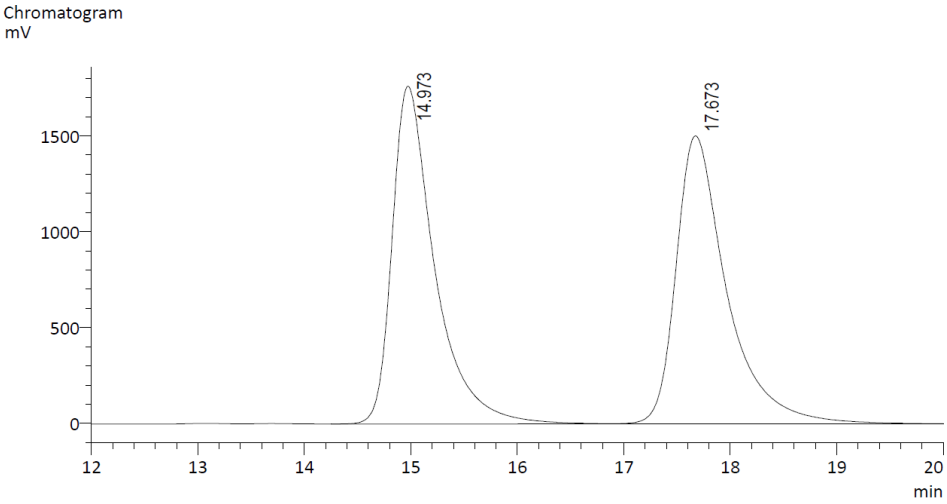
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.872	209086	10093	0.414
2	11.403	50326252	1887432	99.586
Total		50535338	1897525	100.000

Figure S53. HPLC traces of racemic **3ad** (reference) and chiral **3ad**. Area integration = 0.4:99.6 (99% ee).

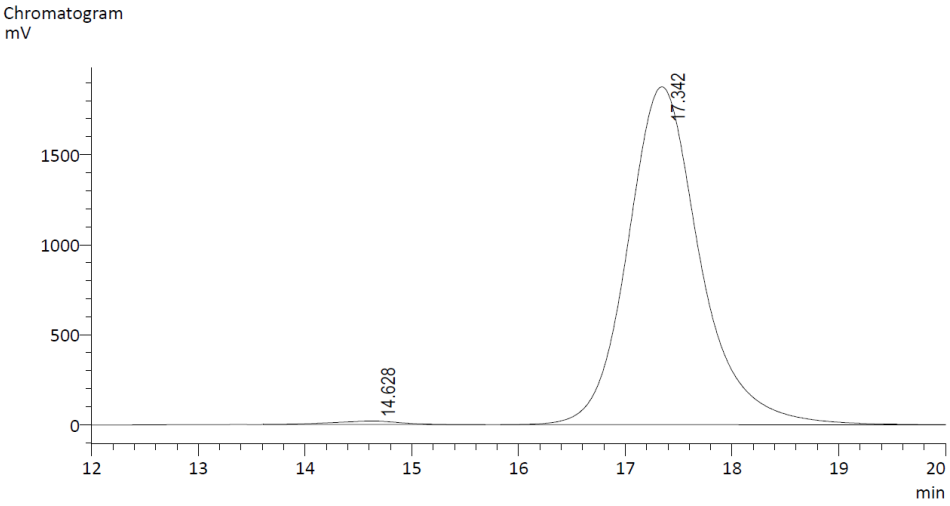


3ae



<Peak Table>
Detector A 254nm

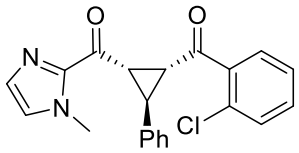
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.973	49079628	1762206	49.638
2	17.673	49795111	1502281	50.362
Total		98874738	3264488	100.000



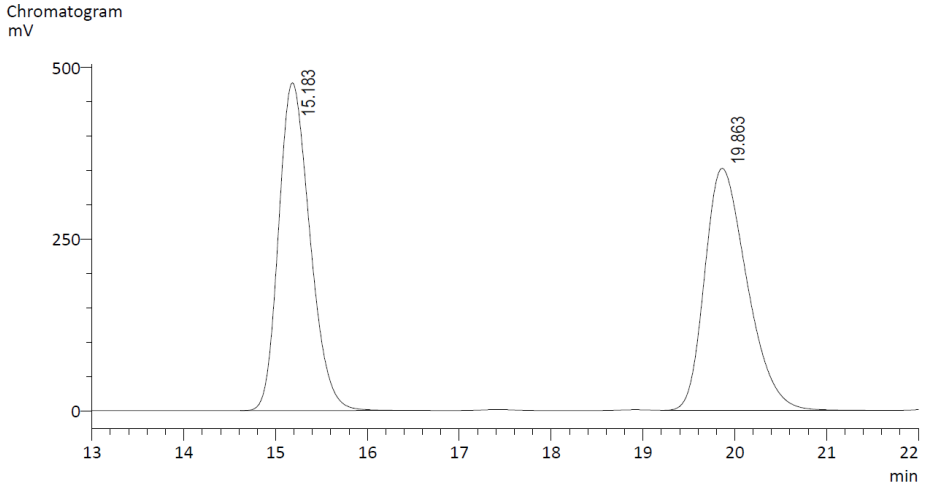
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.628	870879	19675	0.973
2	17.342	88592698	1877694	99.027
Total		89463577	1897369	100.000

Figure S54. HPLC traces of racemic **3ae** (reference) and chiral **3ae**. Area integration = 1.0:99.0 (98% ee).

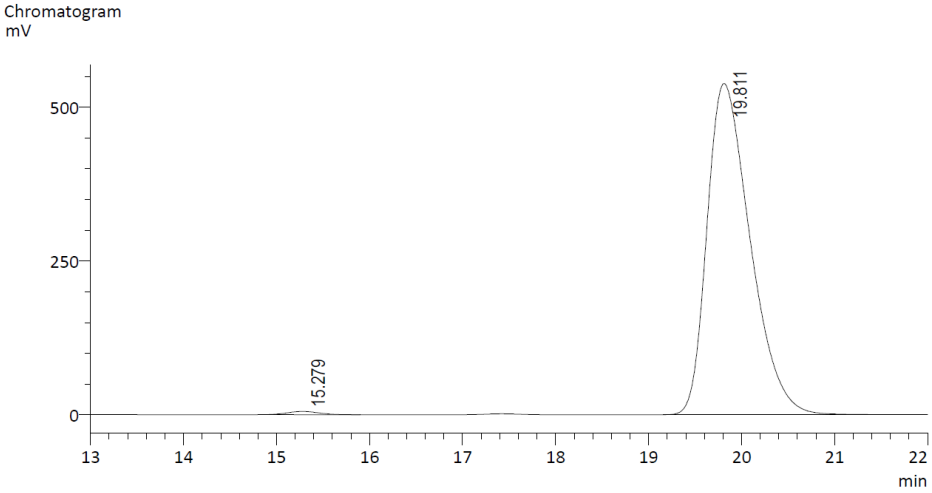


3af



<Peak Table>
Detector A 254nm

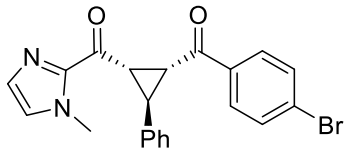
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	15.183	11294842	477507	50.002
2	19.863	11293967	352552	49.998
Total		22588809	830059	100.000



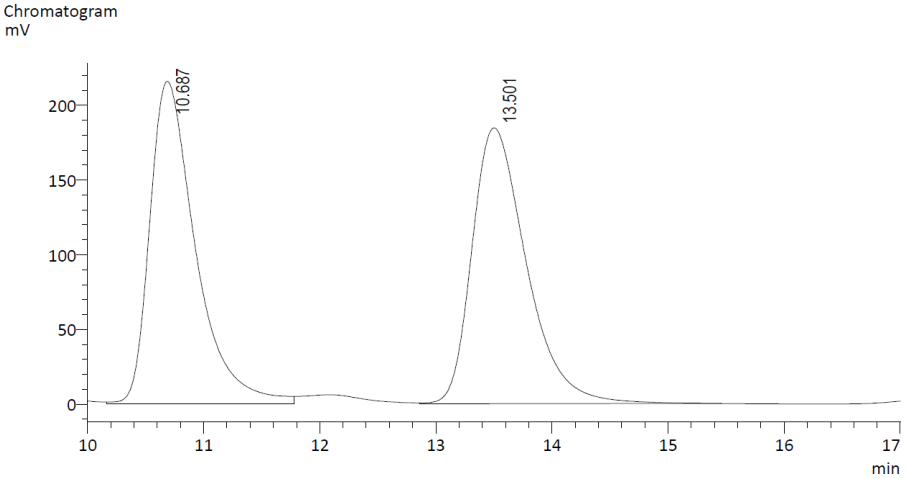
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	15.279	129556	5414	0.740
2	19.811	17381872	538833	99.260
Total		17511428	544247	100.000

Figure S55. HPLC traces of racemic **3af** (reference) and chiral **3af**. Area integration = 0.7:99.3 (99% ee).

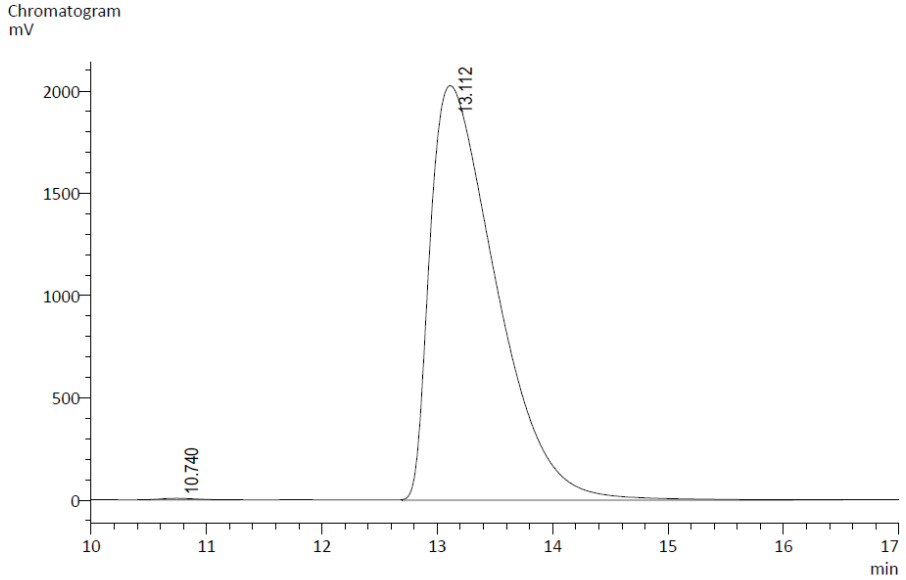


3ag



<Peak Table>
Detector A 254nm

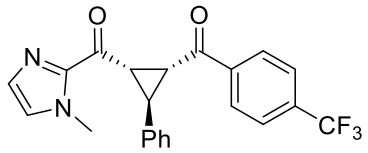
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	10.687	5929295	215889	49.647
2	13.501	6013570	184538	50.353
Total		11942865	400427	100.000



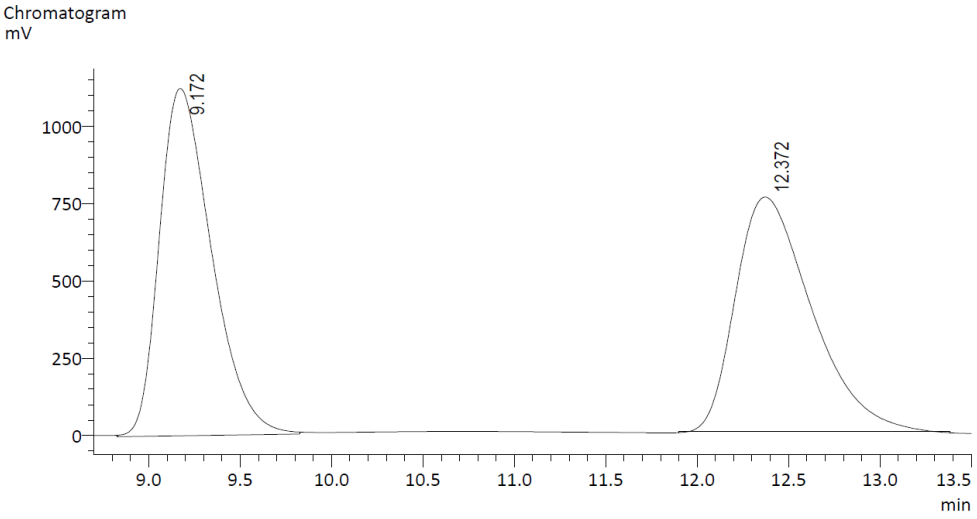
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	10.740	193559	7782	0.239
2	13.112	80787518	2026003	99.761
Total		80981077	2033785	100.000

Figure S56. HPLC traces of racemic **3ag** (reference) and chiral **3ag**. Area integration = 0.2:99.8 (99.6% ee).

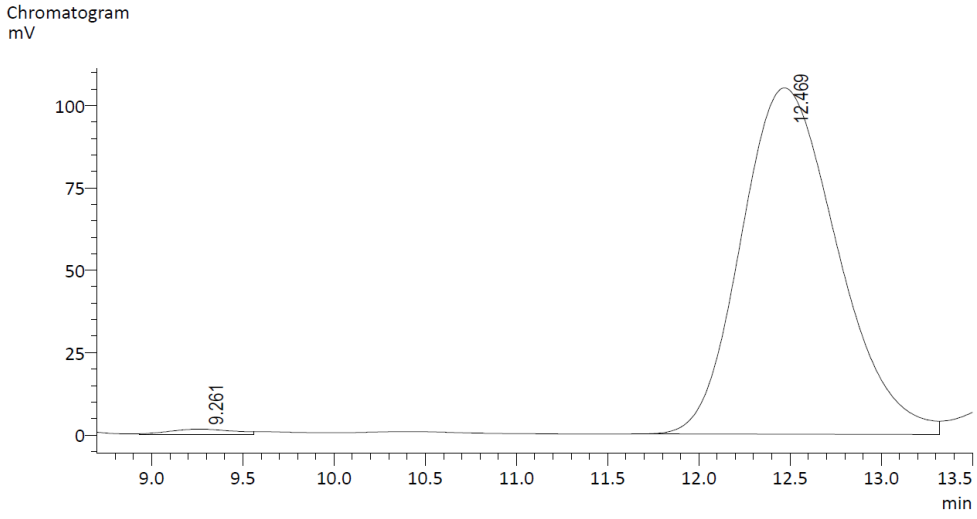


3ah



<Peak Table>
Detector A 254nm

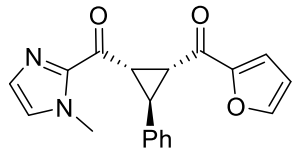
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.172	22316921	1122577	50.440
2	12.372	21927784	758169	49.560
Total		44244705	1880746	100.000



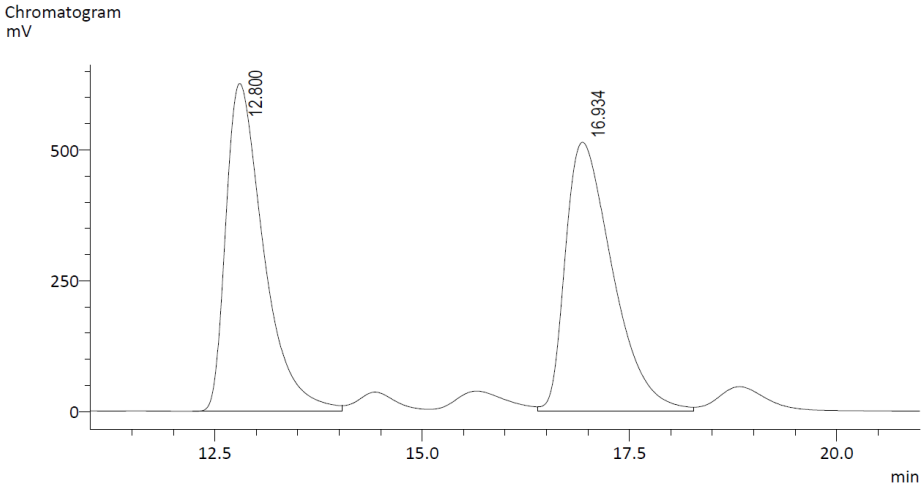
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.261	40860	1638	1.049
2	12.469	3853603	105113	98.951
Total		3894463	106752	100.000

Figure S57. HPLC traces of racemic **3ah** (reference) and chiral **3ah**. Area integration = 1.0:99.0 (98% ee).

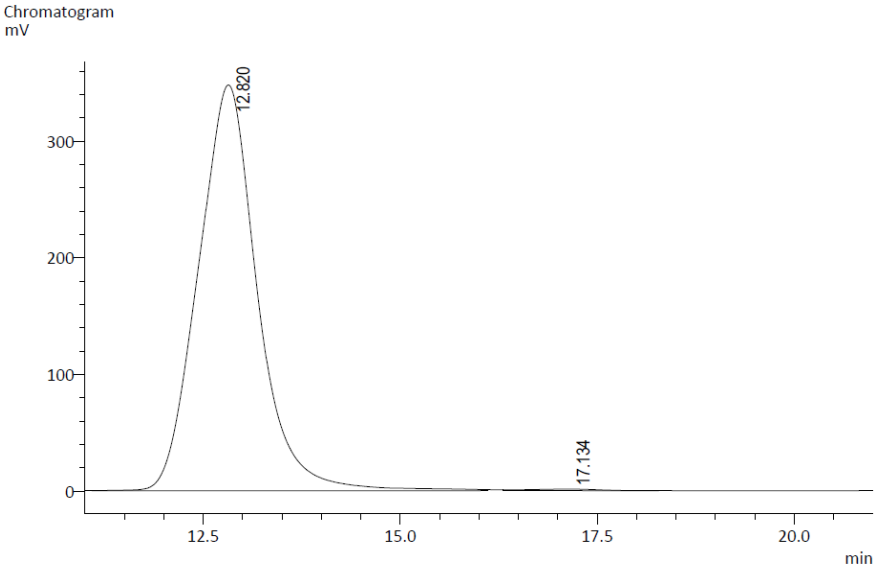


3ai



<Peak Table>
Detector A 254nm

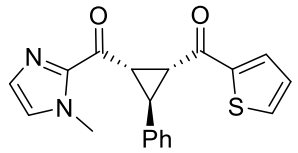
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.800	19902695	626269	49.359
2	16.934	20419976	513884	50.641
Total		40322671	1140153	100.000



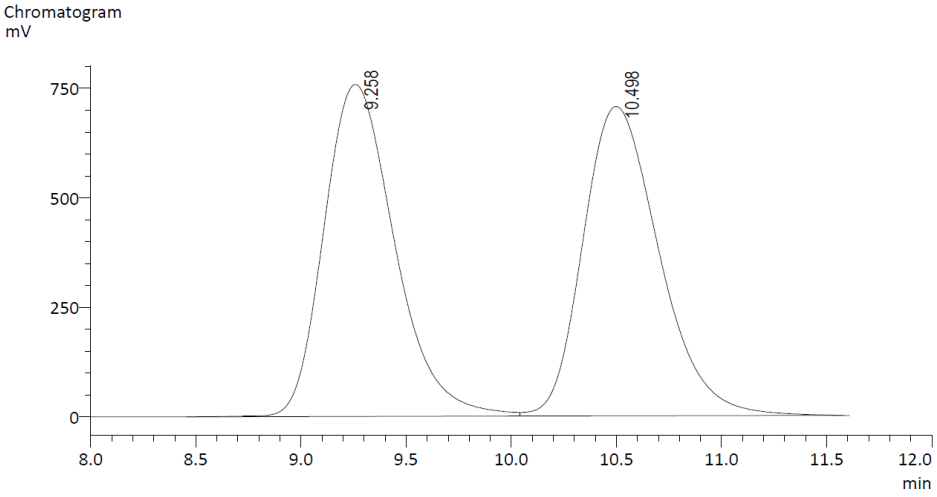
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	12.820	18192948	348149	99.526
2	17.134	86733	1309	0.474
Total		18279682	349458	100.000

Figure S58. HPLC traces of racemic **3ai** (reference) and chiral **3ai**. Area integration = 99.5:0.5 (99% ee).

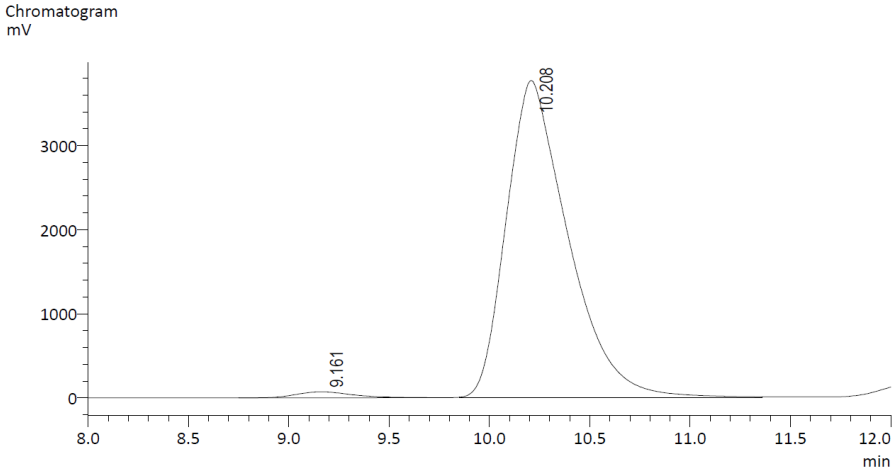


3aj



<Peak Table>
Detector A 254nm

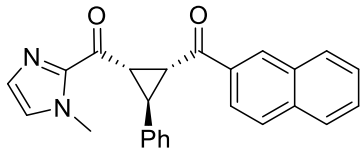
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.258	17763317	758348	49.969
2	10.498	17785114	706668	50.031
Total		35548431	1465015	100.000



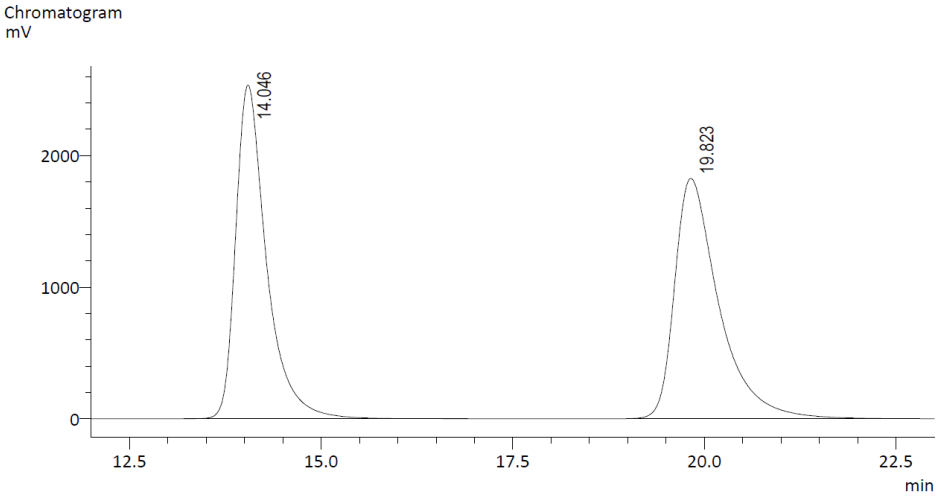
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	9.161	1391434	71143	1.687
2	10.208	81077840	3775654	98.313
Total		82469275	3846797	100.000

Figure S59. HPLC traces of racemic **3aj** (reference) and chiral **3aj**. Area integration = 1.7:98.3 (97% ee).

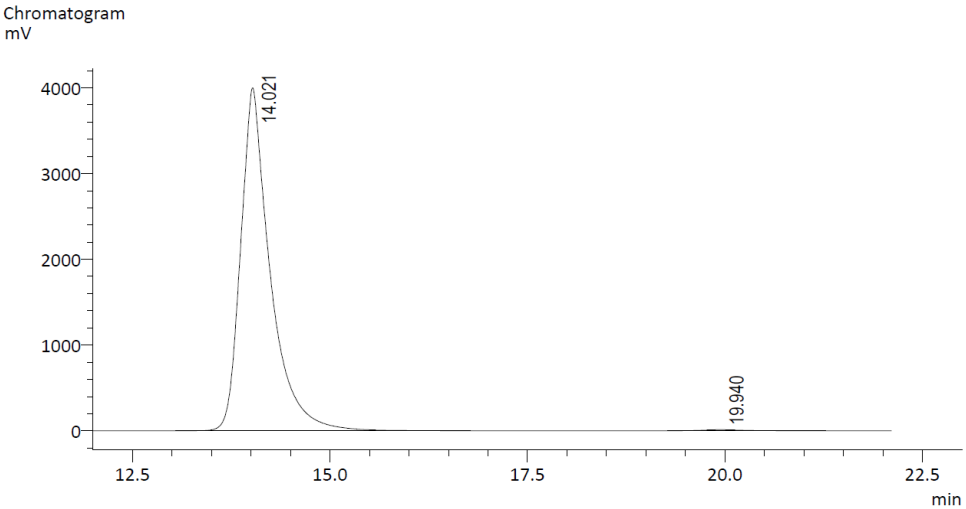


3ak



<Peak Table>
Detector A 254nm

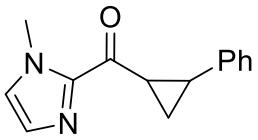
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.046	71037947	2536275	49.210
2	19.823	73317933	1825214	50.790
Total		144355879	4361488	100.000



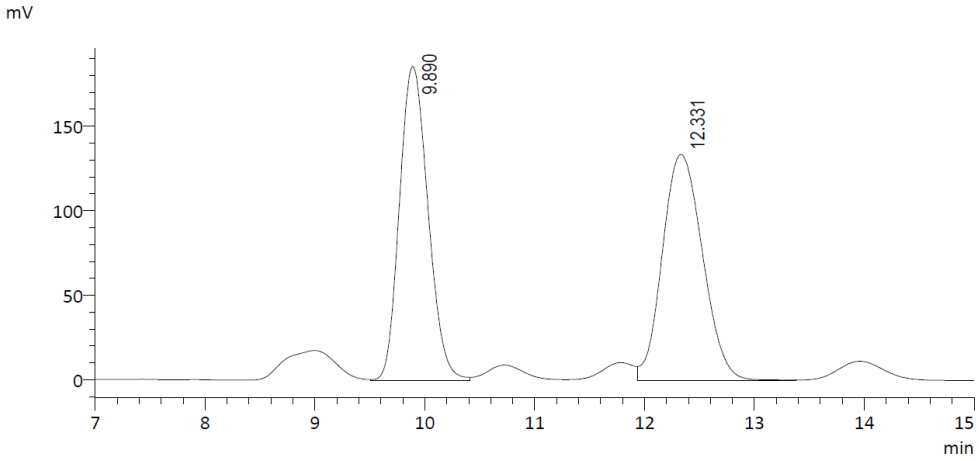
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	14.021	104048916	3999214	99.535
2	19.940	485777	12859	0.465
Total		104534693	4012073	100.000

Figure S60. HPLC traces of racemic **3ak** (reference) and chiral **3ak**. Area integration = 99.5:0.5 (99% ee).

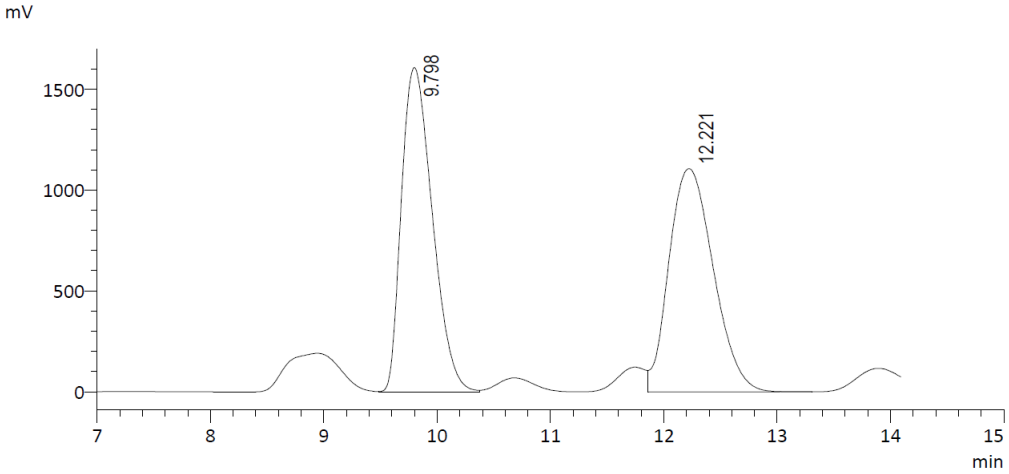


3am



Integration Table
Detector A 254nm

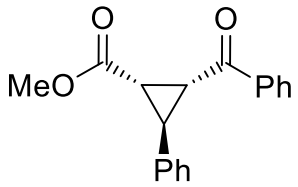
Peak No.	Retention Time (min)	Area (mAU*s)	Height (mAU)	Area Ratio (%)
1	9.890	3360513	185799	49.663
2	12.331	3406137	133717	50.337
总计		6766650	319516	100.000



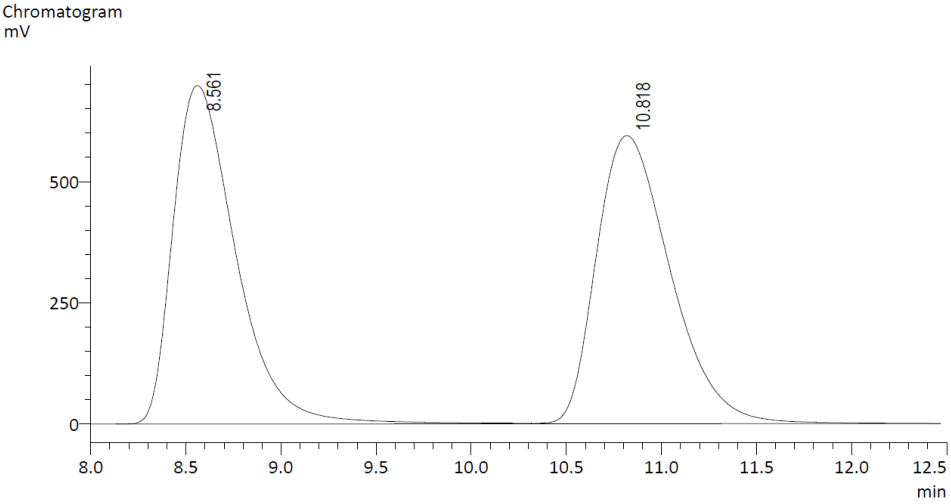
Integration Table
Detector A 254nm

Peak No.	Retention Time (min)	Area (mAU*s)	Height (mAU)	Area Ratio (%)
1	9.798	30534359	1609038	50.323
2	12.221	30141947	1107236	49.677
总计		60676306	2716274	100.000

Figure S61. HPLC traces of racemic **3am** (reference) and chiral **3am**. Area integration = 50:50 (0% ee).

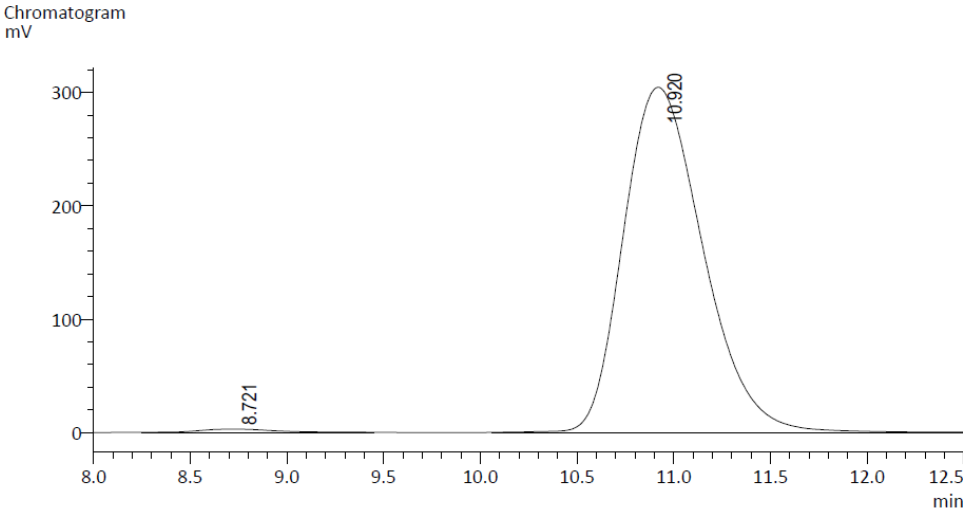


4



<Peak Table>
Detector A 254nm

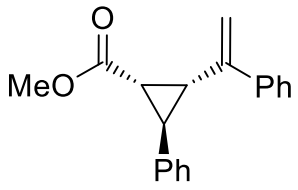
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	8.561	16035823	698368	49.917
2	10.818	16088996	594306	50.083
Total		32124819	1292674	100.000



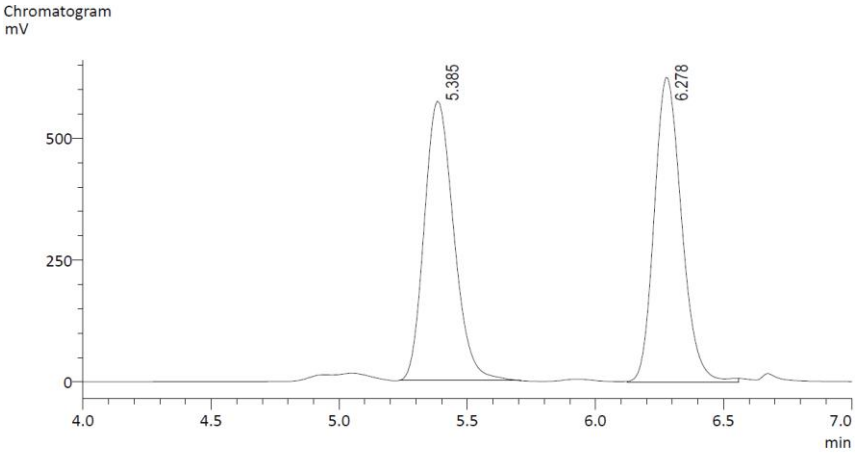
<Peak Table>
Detector A 254nm

Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	8.721	91706	3210	1.039
2	10.920	8732181	304586	98.961
Total		8823886	307796	100.000

Figure S62. HPLC traces of racemic **4** (reference) and chiral **4**. Area integration = 1.0:99.0 (98% ee).

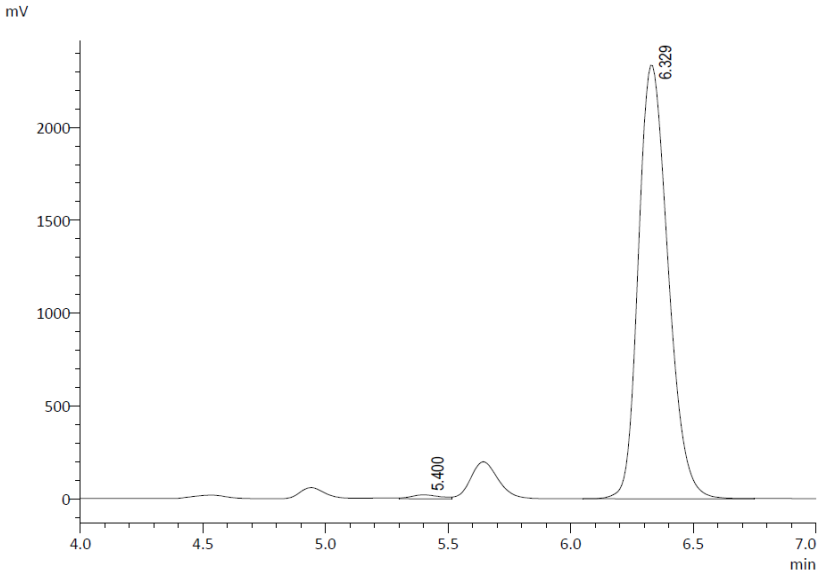


5



<Peak Table>
Detector A 254nm

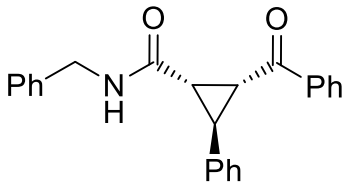
Peak#	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	5.385	4554210	572966	49.388
2	6.278	4666992	626075	50.612
Total		9221203	1199041	100.000



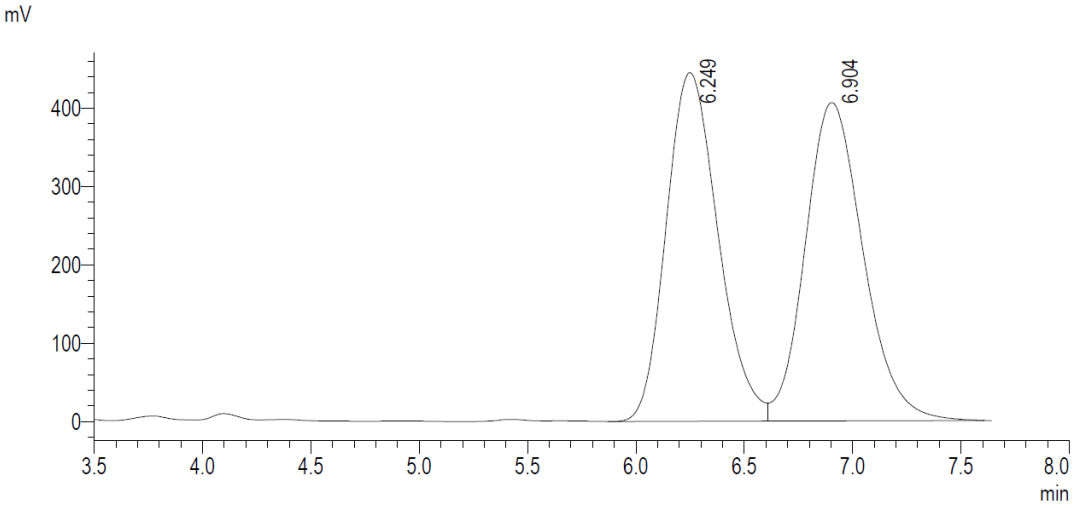
Integration Table
Detector A 254nm

Peak No.	Retention Time (min)	Area (mAU*min)	Height (mAU)	Area Ratio (%)
1	5.400	171206	21066	0.863
2	6.329	19658119	2333428	99.137
Total		19829325	2354495	100.000

Figure S63. HPLC traces of racemic **5** (reference) and chiral **5**. Area integration = 0.9:99.1 (98% ee).

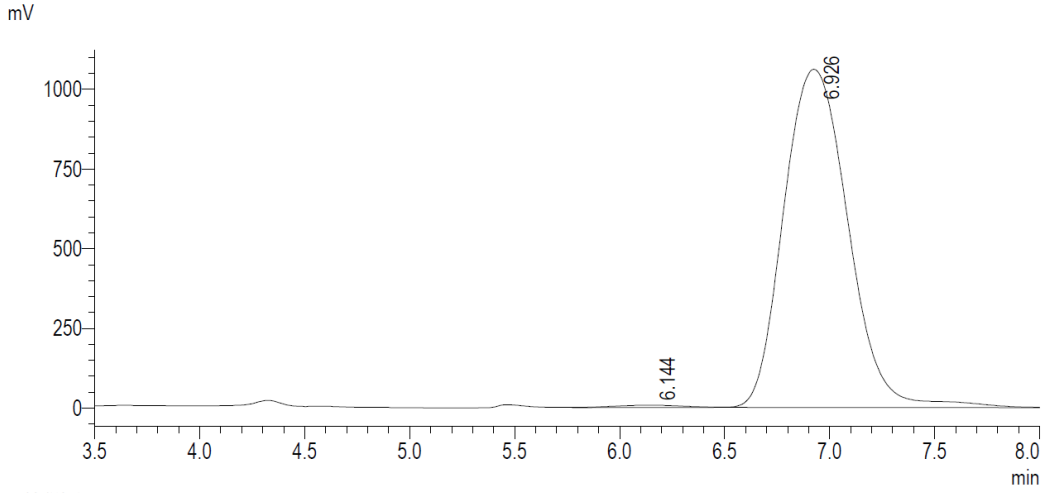


6



检测器A 254nm

Peak#	Retention Time (min)	Area (mAu*min)	Height (mAU)	Area Ratio %
1	6.249	7411262	445177	49.528
2	6.904	7552434	406337	50.472
总计		14963697	851513	100.000



检测器A 254nm

Peak#	Retention Time (min)	Area (mAu*min)	Height (mAU)	Area Ratio %
1	6.144	159636	7169	0.698
2	6.926	22700992	1060776	99.302
总计		22860628	1067945	100.000

Figure S64. HPLC traces of racemic **6** (reference) and chiral **6**. Area integration = 0.7:99.3 (99% ee).

8. Single Crystal X-Ray Diffraction Study

The single crystal for compound **3fa** was prepared from a mixture solvent of ethyl acetate and acetonitrile (v/v = 1:2). The data were collected on a Bruker APEX-II CCD equipped with molybdenum micro-focus X-ray sources (λ = 0.71073 Å) at 150 K. The crystal structures were resolved by direct methods and all calculations were performed on the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in the riding model and refined with isotropic thermal parameters. The data has been deposited at Cambridge Crystallographic Data Centre under **CCDC Deposition Number** 2131834. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

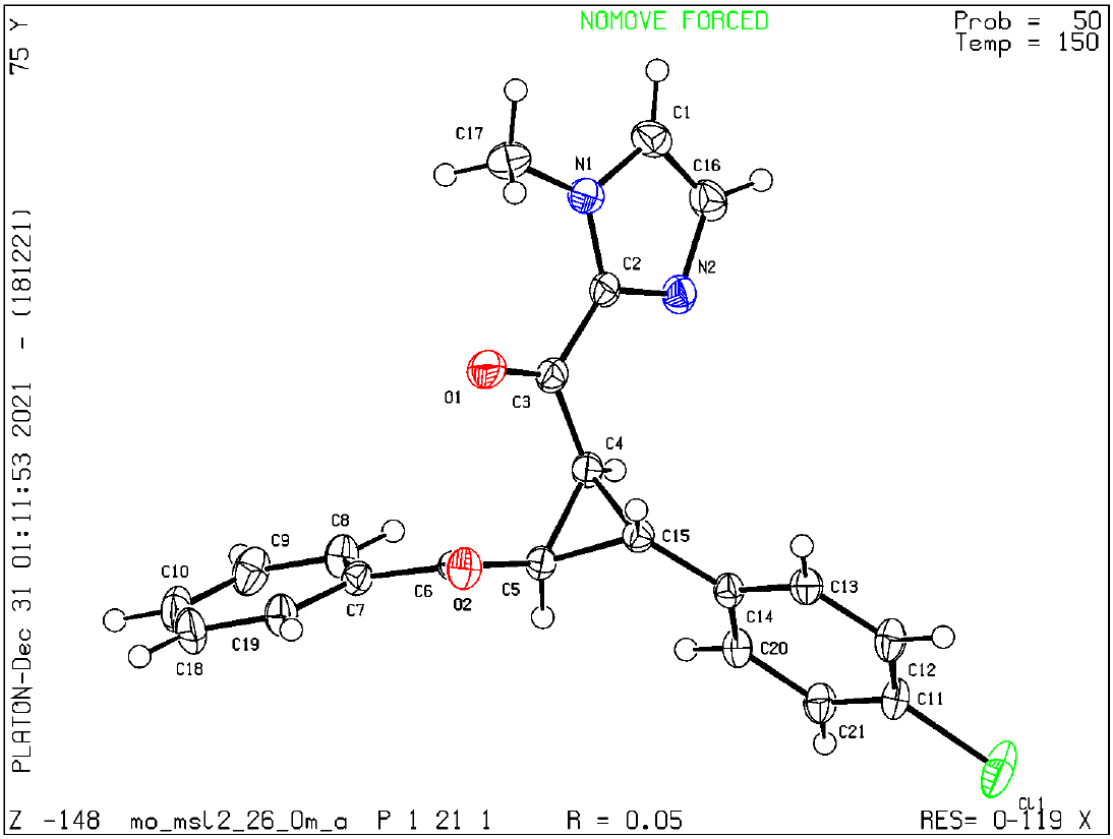


Figure S65. Crystal structure of **3fa** to verify absolute configuration.

Table S1. Crystal data and structure refinement for **3fa**.

Bond precision	**C-C = 0.0052 Å**	**Z**	**2**
Wavelength	0.71073 Å	**μ (mm^{-1})**	0.228
Cell	a = 5.7040(5) b = 17.4146(15) c = 9.2460(8) α = 90 β = 99.371(3) γ = 90	**F000**	380.0
		F000'	380.44
		h, k, l_{max}	7, 22, 12
Temperature	150 K	**N_{ref}**	4155
Volume	906.17(14)	**T_{min}, T_{max}**	0.518, 0.746
Crystal system	monoclinic	**Data completeness**	0.99
Space group	$P2_1$	**θ (max)**	27.508
Hall group	P 2yb	**R(reflections)**	0.0518(3396)
Moiety formula	$C_{21}H_{17}ClN_2O_2$	**wR2(reflections)**	0.1202(4155)
Sum formula	$C_{21}H_{17}ClN_2O_2$	**S**	1.032
Mr	364.82	**Npar**	236
Density (g/cm^3)	1.337		

9. References

[1] Wang, C.; Chen, L.-A.; Huo, H.; Shen, X.; Harms, K.; Gong, L.; Meggers, E. *Chem. Sci.* **2015**, *6*, 1094-1100.

[2] Gong, J.; Li, S.-W.; Saira, Q.; Kang, Q. *Eur. J. Org. Chem.* **2017**, *25*, 3584-3593.

[3] Lin, S.-X.; Sun, G.-J.; Kang, Q. *Chem. Commun*. **2017**, *53*, 7665-7668.

[4] Huo, H.; Fu, C.; Harms, K.; Meggers, E. *J. Am. Chem. Soc.* **2014**, *136*, 2990-2993.

[5] Mukherjee, S.; Mondal, S.; Patra, A.; Gonnade, R. G.; Biju, A. T. *Chem. Commun.* **2015**, *51*, 9559-9562.

[6] Sibi, M.; Itoh, K. *J. Am. Chem. Soc.* **2007**, *129*, 8064-8065.

[7] Nakamura, T.; Oshida, M.; Nomura, T.; Nakazaki, A.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 5533-5536.

[8] Singh, P. K.; Singh, V. K. *Org. Lett.* **2008**, *10*, 4121-4124.

[9] Dias, R. M. P.; Burtoloso, A. C. B. *Org. Lett.* **2016**, *18*, 3034-3037.

[10] Yuan, Z.; Fang, X.; Li, X.; Wu, J.; Yao, H.; Lin, A. *J. Org. Chem.* **2015**, *80*, 11123-11130.

[11] Kakei, H.; Sone, T.; Sohtome, Y.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2007**, *129*, 13410-13411.

[12] Fenster, E.; Fehl, C.; Aube, J. *Org. Lett.* **2011**, *13*, 2614-2617.

[13] Ye, C.-X.; Chen, S.; Han, F.; Xie, X.; Ivlev, S.; Houk, K. N.; Meggers, E. *Angew. Chem. Int. Ed.* **2020**, *59*, 13552-13556.