Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


Supporting Information for

# Rhodium(III)/Amine Synergistically Catalyzed Enantioselective Michael addition of cyclohexanone with α,β-Unsaturated 2-Acyl Imidazoles

## Table of contents

Contents

## General Information

All non-aqueous reactions were performed in oven-dried glassware and standard Schlenk tubes under an atmosphere of nitrogen. 1,2-Dichloroethane (DCE) and dichloromethane (DCM) were distilled from $CaH_2$ under inert atmosphere. Tetrahydrofuran (THF) and toluene (PhMe) were distilled from sodium and benzophenone under inert atmosphere. Iridium and rhodium catalysts **Δ-Ir1**,[1] **Δ-Ir2**,[2] **Δ-Rh1**,[3] **Λ-Rh2**, **Δ-Rh3**[4] were prepared according to the reported procedures. 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 NMR spectra were obtained in $CDCl_3$ using a Bruker Avance III spectrometer at 400 and 100 MHz for $^1H$ and $^{13}C$ NMR, respectively. Chemical shifts (δ) for $^1H$ 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, dd = double doublet), 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 $cm^{-1}$. HRMS data were obtained on a Thermo Fisher Scientific LTQ FT Ultrasystem. Optical rotation was recorded on INESA SGW-1 polarimeter at concentrations of 1.0g/100mL. Enantiomeric excess was determined by HPLC analysis on Chiralpak ID, OJ column, IC column (Daicel Chemical Industries, LTD) on Shimadzu LC-

20AD. The crystallographic measurement was made on an Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer. The structure was solved by direct method and refined to convergence by least squares method on F2 using the SHELXTL-2014 software suit.

## Synthesis of Substrates

*α,β*-Unsaturated 2-acyl imidazoles **1a-1g**,[5] **1i-1o**,[5] **1p** and **1q**[6] were prepared according to reported procedures.

**1h** was prepared according to a general procedure.[5] Accordingly, 2-acetyl-1-methylimidazole[4] (621 mg, 5.0 mmol, 1.0 eq) and EtOH (10 mL) were added to a 50 mL round-bottom flask followed by the aromatic aldehyde (5.0 mmol, 1.0 eq) and a catalytic amount of KOH (56.1 mg, 1.0 mmol, 0.2 eq). After stirring at room temperature for 12 h, an aqueous saturated NaCl solution (15 mL) and $H_2O$ (5 mL) were added, and the mixture was extracted with EtOAc (4 × 30 mL). Then the combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by a flash column chromatography on silica gel.

## General Procedure for the Catalytic Reactions

### Synthesis of racemic products as HPLC references

General Procedure: In distilled anhydrous DCE (0.2 mL) the *α,β*-unsaturated 2-acyl imidazoles **1a-1q** (0.20 mmol) was added and the resulting solution was stirred for 2 min followed by the addition of racemic catalyst *rac*-**RhO** (2.0 mol%) in a Schlenk tube. Then the Schlenk tube was sealed and allowed to stir at room temperature for 20 min. On the other hand, to a solution of secondary amine (0.04 mmol) in anhydrous DCE (0.2 mL) was added the respected cyclohexanone (0.60 mmol) in a glass vial and the mixture was stirred at room temperature for 10 min. Then the solution in the glass vial was transferred to the Schlenk tube containing *α,β*-unsaturated 2-acyl imidazole. The reaction mixture was stirred at 50 ℃ for 12-24 hours (conversion monitored by TLC) under argon atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 2:1) to afford the racemic products as HPLC references for determination of enantiomeric excess. The ee values were determined by chiral HPLC chromatography using a Daicel Chiralpak ID, OJ column or IC column (250 × 4.6 mm).

### Substrate Scope for chiral products

**General Procedure A**: In distilled anhydrous DCM (0.2 mL) the α,β-unsaturated 2-acyl imidazoles **1a-1q** (0.20 mmol) was added and the resulting solution was stirred for 2 min followed by the addition of chiral catalyst **Λ-Rh3** (2.0 mol%) in a Schlenk tube. Then the Schlenk tube was sealed and allowed to stir at room temperature for 20 min. On the other hand, to a solution of secondary amine (0.04 mmol) in anhydrous DCM (0.2 mL) was added the respected cyclohexanone (0.60

mmol) in a glass vial and the mixture was stirred at room temperature for 10 min. Then the solution in the glass vial was transferred to the Schlenk tube containing α,β-unsaturated 2-acyl imidazole. The reaction mixture was stirred at 25 ℃ for the indicated time (conversion monitored by TLC) under argon atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 10:1 to 2:1) to afford the desired products. The dr values were determined by $^{1}$H NMR analysis, and the ee values were determined by chiral HPLC chromatography using a Daicel Chiralpak ID, OJ column or IC column (250 × 4.6 mm).

**General Procedure B for transformation:**

**3v** (0.08 mmol) was added to anhydrous DCM (0.1 mL) in a Schlenk tube and the resulting solution was cooled to 0 ℃ followed by the addition of methyl trifluoromethansulfonate (0.4 mmol). Then the Schlenk tube was sealed and allowed to stir at room temperature for 12 hours. Monitored by TLC, DBU (1equiv.) and MeOH (2 equiv.) were added. After being stirred at 20 ℃ for 90 min, the reaction mixture was concentrated and the residue was subjected to a silica gel flash chromatography (petroleum ether/ EtOAc = 20:1 to 10:1) to afford the product. The ee value was determined by chiral HPLC chromatography using a Daicel Chiralpak IC column (250 × 4.6 mm).

**Stereochemistry Determination via Single Crystal X-Ray Diffraction**

The data have been assigned to the Cambridge Crystallographic Data Centre with a deposition number CCDC 1837613.

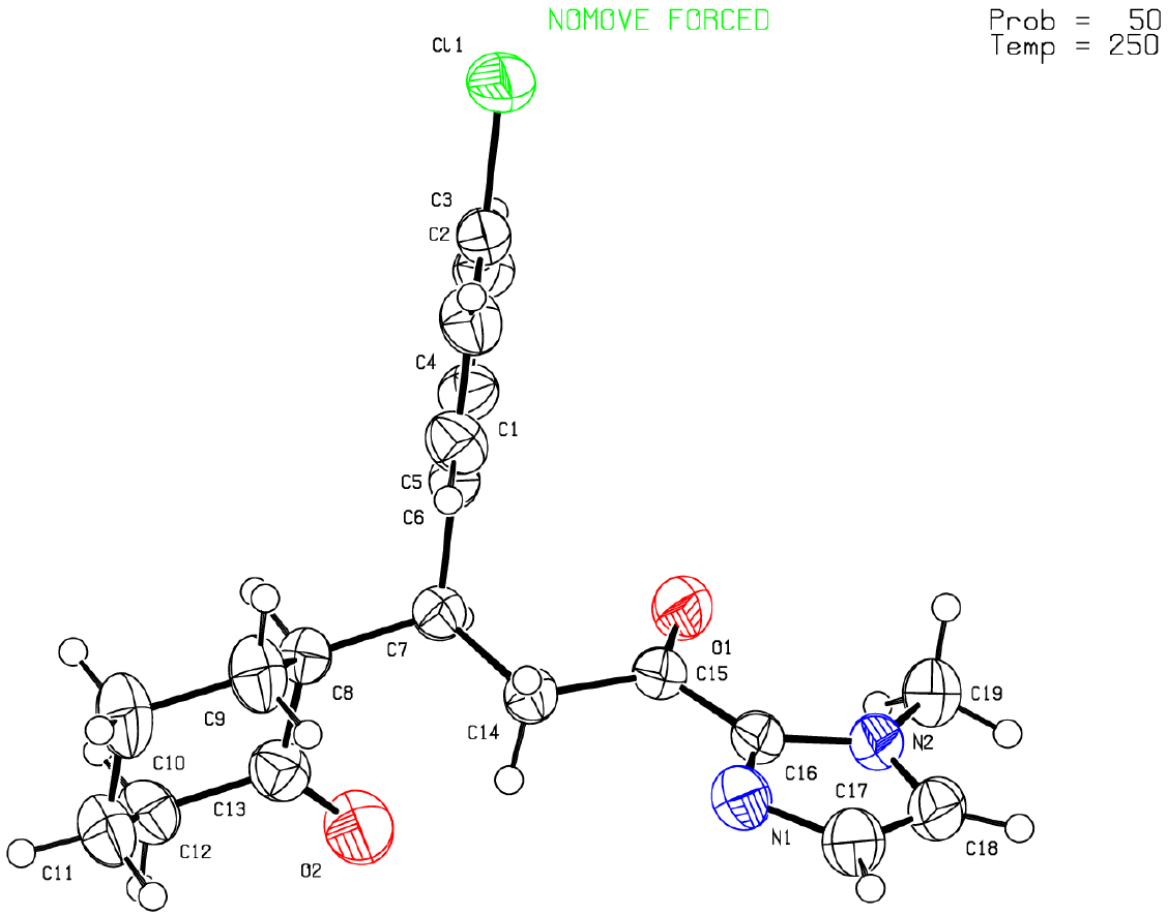


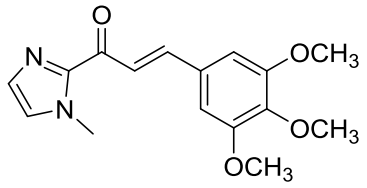

**Table 1.** Crystal data and structure refinement for **3k**.

| | |
|---|---|
| Identification code | XXX |
| Empirical formula | $C_{19}H_{21}ClN_2O_2$ |
| Formula weight | 344.83 |
| Temperature (K) | 250.0(1) |
| Wavelength (Å) | 1.54184 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |

| | | |
|---|---|---|
| Unit cell dimensions (Å, °) | $a$ = 9.2234(2) | α = 90 |
| | $b$ = 10.9322(2) | β = 90 |
| | $c$ = 17.6251(3) | γ = 90 |
| Volume (Å) | 1777.17(6) | |
| $Z$ | 4 | |
| Calculated density (g cm$^{-3}$) | 1.289 | |
| Absorption coefficient (mm$^{-1}$) | 2.007 | |
| $F_{000}$ | 728 | |
| Crystal size (mm$^3$) | 0.13 × 0.10 × 0.09 | |
| θ range for data collection (°) | 4.760 to 71.882 | |
| Miller index ranges | $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$ | |
| Reflections collected | 26755 | |
| Independent reflections | 3479 [$R_{int}$ = 0.0413] | |
| Completeness to $\theta_{max}$ (%) | 0.997 | |
| Max. and min. transmission | 0.71339 and 1.00000 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3479 / 0 / 218 | |
| Goodness-of-fit on $F^2$ | 0.970 | |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0336, $wR2$ = 0.0931 | |
| R indices (all data) | $R1$ = 0.0366, $wR2$ = 0.0964 | |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.368 and -0.290 | |
| Absolute structure parameter | .011(6) | |

## Characterization of Products

Compound **1h:**




**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 15.9 Hz, 1H), 7.76 (d, *J* = 15.9 Hz, 1H), 7.23 (d, *J* = 0.6 Hz, 1H), 7.10 (s, 1H), 6.92 (s, 2H), 4.10 (s, 3H), 3.92 (s, 6H), 3.90 (s, 3H).

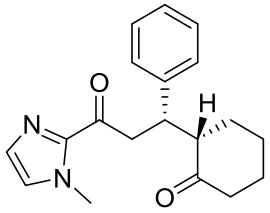
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 179.9, 153.10, 143.7, 143.3, 140.0, 130.2, 128.9, 127.1, 121.6, 105.6, 60.7, 56.0, 36.1.

**IR** (film) $\nu_{max}$: 3113, 2950, 2834, 1662, 1607, 1583, 1507, 1472, 1410, 1345, 1273, 1132, 1032, 966, 619 $cm^{-1}$.

**HRMS** (ESI, *m/z*) calcd. for $C_{16}H_{18}N_2O_4Na^+$ $[M+Na]^+$: 325.1159, found: 325.1159.

**Mp** 134–135 ℃.

Compound **3a**



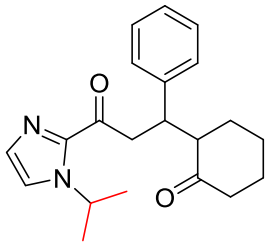
Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3a** as a white solid (60.95mg, 0.20 mmol, yield: 98%). The diastereomeric ratio was determined as 7:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +15.6; **Mp** 95–96 ℃; **IR** (film) $\nu_{max}$: 2924, 2855, 1706 (C=O), 1678 (C=O), 1452, 1409 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{19}H_{22}N_2O_2Na^+$ $[M+Na]^+$: 333.1573, found: 333.1574.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.10 (m, 5H), 7.11 (s, 1H), 6.96 (s, 1H), 4.05 (ddd, *J* = 10.3, 4.5, 4.2 Hz, 1H), 3.86 (s, 3H), 3.83 (dd, *J* = 17.3, 10.3 Hz, 1H), 3.34 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.62 (m, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 2.10–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.4, 191.0, 143.2, 142.5, 128.7, 128.2, 128.1, 126.7, 126.1, 56.3, 42.2, 39.4, 38.3, 36.0, 28.8, 27.5, 24.8; **HPLC**: 99% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 17.9 min, tr(2) = 51.4 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.10 (m, 5H), 7.06 (s, 1H), 6.93 (s, 1H), 3.85 (s, 3H), 3.77 (ddd, *J* = 9.5, 9.3, 4.4 Hz, 1H), 3.64 (dd, *J* = 17.2, 9.3 Hz, 1H), 3.48 (dd, *J* = 17.2, 4.4 Hz, 1H), 2.68 (m, 1H), 2.46 (m, 1H), 2.32 (m, 1H), 2.10–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 213.1, 190.8, 143.1, 128.6, 128.5, 128.3, 126.5, 126.3, 55.8, 44.3, 42.4, 39.7, 35.9, 32.5, 28.5, 24.5; **HPLC**: 17%

ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 38.1 min, tr(2) = 64.4 min.

Compound **3b**



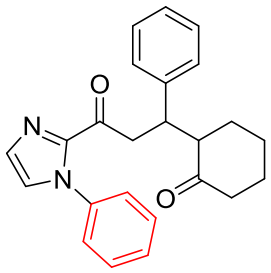
Following **General Procedure A**, the reaction of **1b** (48.06 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3b** as a colorless oil (60.19 mg, 0.177 mmol, yield: 89%). The diastereomeric ratio was determined as 1.2:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +9.15; **IR** (film) $\nu_{max}$: 2925, 2860, 1707, 1678, 1453, 1395, 1256, 1129, 977, 916, 770 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{21}H_{26}N_2O_2Na^+$ $[M+Na]^+$: 361.1886, found: 361.1885; **$^{13}$C NMR** (100 MHz, $CDCl_3$, for diastereomeric mixture) δ 213.0, 211.4, 191.2, 191.0, 143.2, 142.5, 142.4, 142.3, 129.2, 129.1, 128.5, 128.22, 128.2, 128.1, 126.3, 126.1, 120.8, 120.6, 56.3, 55.9, 48.9, 48.85, 44.8, 42.3, 42.2, 40.2, 39.9, 38.6, 32.5, 28.9, 28.5, 27.5, 24.7, 24.4, 23.5, 23.3, 23.27.

Diastereoisomer 1: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 7H), 5.38 (heptet, *J* = 6.6 Hz, 1H), 3.78 (ddd, *J* = 9.7, 9.4, 4.5 Hz, 1H), 3.64 (dd, *J* = 17.0, 9.4 Hz, 1H), 3.50 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.68 (m, 1H), 2.50–1.50 (m, 8H), 1.35 (dd, *J* = 6.6, 1.4 Hz, 6H); **HPLC**: 96% ee (ID, 254 nm, n-hexane/isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 12.7 min, tr(2) = 13.8 min.

Diastereoisomer 2: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 7H), 5.38 (m, 1H), 4.05 (ddd, *J* = 10.5, 4.7, 4.3 Hz, 1H), 3.82 (dd, *J* = 17.1, 10.5 Hz, 1H), 3.37

(dd, *J* = 17.1, 4.3 Hz, 1H), 2.63 (m, 1H), 2.50–1.50 (m, 8H), 1.28 (dd, *J* = 6.7, 2.0 Hz, 6H); **HPLC**: 33% ee (ID, 254 nm, n-hexane/isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 11.4 min, tr(2) = 12.0 min.

Compound **3c**



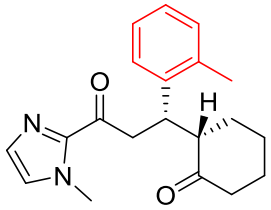

Following **General Procedure A**, the reaction of **1c** (54.86 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3c** as a yellow oil (67 mg, 0.18 mmol, yield: 92%). The diastereomeric ratio was determined as 1.7:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = –5.55; **IR** (film) $\nu_{max}$: 2926, 2856, 1705, 1688, 1493, 1447, 1407, 1311, 764, 701 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{24}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 395.1730, found: 395.1728.

Diastereoisomer 1: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40–6.98 (m, 12H), 3.98 (ddd, *J* = 10.1, 5.1, 4.6 Hz, 1H), 3.80 (dd, *J* = 16.7, 10.1 Hz, 1H), 3.39 (dd, *J* = 16.7, 4.6 Hz, 1H), 2.63 (m, 1H), 2.35 (m, 1H), 2.21 (m, 1H), 2.10–1.40 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.3, 189.6, 143.1, 142.9, 138.0, 129.2, 128.7, 128.5, 128.3, 128.1, 126.7, 126.1, 125.5, 56.2, 42.1, 40.0, 38.9, 29.2, 27.5, 24.6; **HPLC**: 90% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 30.4 min, tr(2) = 99.8 min.

Diastereoisomer 2: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40–6.98 (m, 12H), 3.74 (ddd, *J* = 9.3, 8.7, 5.2 Hz, 1H), 3.60 (dd, *J* = 16.7, 8.7 Hz, 1H), 3.50 (dd, *J* = 16.7, 5.2 Hz,

1H), 2.67 (m, 1H), 2.46 (m, 1H), 2.30 (m, 1H), 2.10–1.40 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 213.0, 189.3, 143.0, 142.2, 138.1, 129.2, 128.7, 128.4, 128.3, 128.2, 126.5, 126.3, 125.5, 55.9, 44.4, 42.0, 40.0, 32.1, 28.3, 24.0; **HPLC**: 33% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 36.4 min, tr(2) = 45.1 min.

Compound **3d**

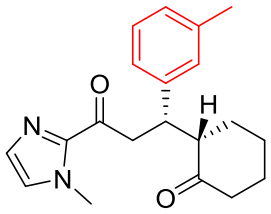



Following **General Procedure A**, the reaction of **1d** (45.25 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3d** as a yellow oil (59.0 mg, 0.18 mmol, yield: 93%). The diastereomeric ratio was determined as 9:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +17.1; **IR** (film) $\nu_{max}$: 2935, 2861, 1706, 1677, 1448, 1410, 1290, 1128, 981, 915, 768 cm$^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{20}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 347.1730, found: 347.1725.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.00 (m, 5H), 6.95 (s, 1H), 4.34 (ddd, *J* = 10.3, 4.6, 4.4 Hz, 1H), 3.85 (s, 3H), 3.83 (dd, *J* = 17.3, 10.3 Hz, 1H), 3.29 (dd, *J* = 17.3, 4.4 Hz, 1H), 2.50 (m, 1H), 2.41 (s, 3H), 2.38 (m, 1H), 2.25 (m, 1H), 2.15–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.3, 191.0, 143.2, 141.6, 136.2, 130.5, 128.6, 126.6, 126.3, 125.9, 125.6, 54.5, 42.2, 39.5, 36.0, 33.0, 28.6, 27.5, 25.1, 19.6; **HPLC**: 95% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 8.1 min, tr(2) = 18.4 min.

Minor isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.00 (m, 5H), 6.91 (s, 1H), 4.00 (ddd, *J* = 9.0, 9.0, 4.4 Hz, 1H), 3.87 (s, 3H), 3.63 (dd, *J* = 17.3, 9.0 Hz, 1H), 3.53 (dd, *J* = 17.3, 4.4 Hz, 1H), 2.72 (m, 1H), 2.45 (s, 3H), 2.40–1.45 (m, 8H); **HPLC**: 24% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 20.0 min, tr(2) = 31.0 min.

Compound **3e**

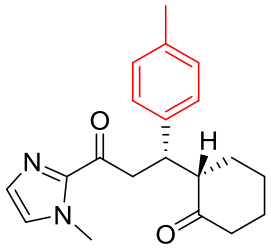



Following **General Procedure A**, the reaction of **1e** (45.25 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3e** as a yellow oil (59.52 mg, 0.18 mmol, yield: 93%). The diastereomeric ratio was determined as 3.4:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +24.6; **IR** (film) $\nu_{max}$: 2930, 2861, 1706, 1677, 1462, 1408, 1290, 1261, 1040, 1018, 915, 804, 707 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{20}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 347.1730, found: 347.1731.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.17–6.92 (m, 6H), 4.03 (ddd, *J* = 10.3, 5.1, 4.1 Hz, 1H), 3.87 (s, 3H), 3.82 (dd, *J* = 17.5, 10.3 Hz, 1H), 3.32 (dd, *J* = 17.5, 4.1 Hz, 1H), 2.59 (m, 1H), 2.38 (m, 1H), 2.29 (s, 3H), 2.24 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.4, 191.0, 143.14, 143.1, 137.7, 128.9, 128.7, 128.0, 126.9, 126.6, 124.9, 56.3, 42.2, 39.3, 38.0, 36.0, 28.6, 27.5, 24.8, 21.4; **HPLC**: 98% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 18.3 min, tr(2) = 46.1 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.17–6.92 (m, 6H), 3.86 (s, 3H), 3.72 (ddd, *J* = 9.4, 9.1, 4.3 Hz, 1H), 3.62 (dd, *J* = 17.2, 9.1 Hz, 1H), 3.47 (dd, *J* = 17.2, 4.3 Hz, 1H), 2.66 (m, 1H), 2.46 (m, 1H), 2.35–2.25 (m, 1H), 2.30 (s, 3H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 213.2, 190.8, 143.0, 142.5, 137.7, 129.1, 128.6, 128.1, 127.1, 126.5, 125.5, 55.9, 44.3, 42.4, 39.6, 35.9, 32.5, 28.5, 24.4; **HPLC**: 25% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 38.4 min, tr(2) = 58.3 min.

Compound **3f**



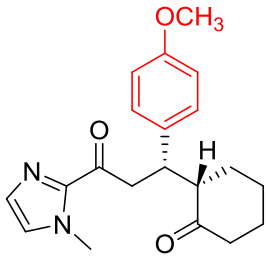

Following **General Procedure A**, the reaction of **1f** (45.25 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3f** as a yellow oil (58.8 mg, 0.18 mmol, yield: 92%). The diastereomeric ratio was determined as 3:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +19.2; **IR** (film) $\nu_{max}$: 2925, 2858, 1705, 1677, 1463, 1409, 1290, 1261, 1128, 1096, 1020, 820 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{20}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 347.1730, found: 347.1729.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.02 (m, 5H), 6.96 (s, 1H), 4.02 (ddd, *J* = 10.5, 5.1, 4.1 Hz, 1H), 3.88 (s, 3H), 3.81 (dd, *J* = 17.4, 10.5 Hz, 1H), 3.32 (dd, *J* = 17.4, 4.1 Hz, 1H), 2.59 (m, 1H), 2.38 (m, 1H), 2.27 (s, 3H), 2.23 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.6, 191.1, 143.2, 140.1, 135.6, 129.0, 128.7, 127.9, 126.7, 56.4, 42.2, 39.5, 37.9, 36.1, 28.8, 27.5, 24.8,

21.0; **HPLC**: 97% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 17.2 min, tr(2) = 60.1 min.

Minor isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.02 (m, 6H), 6.93 (s, 1H), 3.87 (s, 3H), 3.73 (ddd, *J* = 9.5, 9.3, 4.2 Hz, 1H), 3.62 (dd, *J* = 17.2, 9.3 Hz, 1H), 3.46 (dd, *J* = 17.2, 4.2 Hz, 1H), 2.65 (m, 1H), 2.46 (m, 1H), 2.35–2.25 (m, 1H), 2.28 (s, 3H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 213.2, 190.9, 143.1, 139.4, 135.8, 129.0, 128.7, 128.3, 126.5, 56.0, 44.4, 42.4, 39.3, 36.0, 32.5, 28.6, 24.5, 21.0; **HPLC**: 27% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 42.2 min, tr(2) = 76.8 min.

Compound **3g**



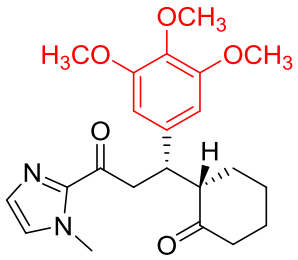

Following **General Procedure A**, the reaction of **1g** (48.45 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3g** as a white solid (59.9 mg, 0.18 mmol, yield: 88%). The diastereomeric ratio was determined as 4.5:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +22.9; **Mp** 122–124 ℃; **IR** (film) $\nu_{max}$: 2927, 2855, 1705, 1677, 1513, 1408, 1248, 1034 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{20}H_{24}N_2O_3Na^+$ $[M+Na]^+$: 363.1679, found: 363.1678.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 7.11 (s, 1H), 6.97 (s, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.99 (ddd, *J* = 10.5, 5.1, 4.1 Hz, 1H), 3.87 (s, 3H), 3.79 (dd, *J* = 17.2, 10.5 Hz, 1H), 3.74 (s, 3H), 3.31 (dd, *J* = 17.2, 4.1 Hz, 1H),

2.59 (m, 1H), 2.37 (m, 1H), 2.23 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.6, 191.1, 157.8, 143.1, 135.1, 129.0, 128.7, 126.7, 113.5, 56.4, 55.0, 42.1, 39.8, 37.6, 36.0, 28.9, 27.5, 24.6; **HPLC**: 98% ee (IC, 254 nm, n-hexane/ isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 16.2 min, tr(2) = 49.2 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 7.06 (s, 1H), 6.94 (s, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H), 3.71 (ddd, *J* = 9.9, 9.5, 4.2 Hz, 1H), 3.61 (dd, *J* = 17.1, 9.5 Hz, 1H), 3.42 (dd, *J* = 17.1, 4.2 Hz, 1H), 2.63 (m, 1H), 2.46 (m, 1H), 2.32 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 213.2, 190.9, 157.9, 143.0, 134.4, 129.3, 128.6, 126.5, 113.6, 56.0, 55.0, 44.3, 42.3, 38.9, 35.9, 32.3, 28.5, 24.4; **HPLC**: 22% ee (IC, 254 nm, n-hexane/ isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 32.9 min, tr(2) = 56.6 min.

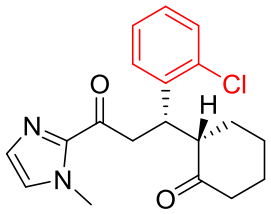
Compound **3h**




Following **General Procedure A**, the reaction of **1h** (60.46 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3h** as a yellow oil (67 mg, 0.17 mmol, yield: 85%). The diastereomeric ratio was determined as 9:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +28.3; **IR** (film) $\nu_{max}$: 2933, 2856, 1708, 1680, 1580, 1506, 1406, 1272, 1025 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{22}H_{28}N_2O_5Na^+$ $[M+Na]^+$: 423.1890, found: 423.1890. Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 6.99 (s, 1H), 6.48 (s, 2H), 4.04

(ddd, *J* = 10.6, 4.4, 4.1 Hz, 1H), 3.92 (dd, *J* = 16.6, 10.6 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 9H), 3.18 (dd, *J* = 16.6, 4.1 Hz, 1H), 2.59 (m, 1H), 2.42 (m, 1H), 2.28 (m, 1H), 2.12–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.4, 191.2, 152.8, 143.3, 138.9, 136.0, 128.7, 126.9, 105.0, 60.7, 56.4, 56.0, 42.3, 38.9, 38.8, 36.1, 28.8, 27.5, 24.9; **HPLC**: 99% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 15.7 min, tr(2) = 25.2 min.

Compound **3i**

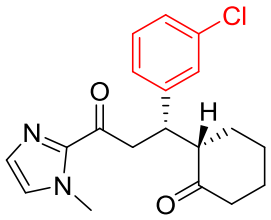



Following **General Procedure A**, the reaction of **1i** (49.3 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3i** as a colorless oil (64 mg, 0.19 mmol, yield: 94%). The diastereomeric ratio was determined as 10:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +40.7; **IR** (film) $\nu_{max}$: 2936, 2863, 1706, 1678, 1474, 1410, 1290, 1033, 1015, 915, 765 cm$^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{19}H_{21}ClN_2O_2Na^+$ $[M+Na]^+$: 367.1184, found: 367.1181.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.23 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.12 (m, 3H), 6.99 (s, 1H), 4.58 (ddd, *J* = 10.8, 4.1, 4.0 Hz, 1H), 3.88 (s, 3H), 3.87 (dd, *J* = 17.6, 10.8 Hz, 1H), 3.39 (dd, *J* = 17.6, 4.0 Hz, 1H), 2.67 (m, 1H), 2.42 (m, 1H), 2.29 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.9, 190.4, 143.0, 140.3, 133.9, 129.9, 128.7, 128.2, 127.3, 126.8, 126.4, 53.2, 42.0, 38.3, 36.0, 34.2, 28.1, 27.3, 24.9; **HPLC**: 98% ee (IC, 254

nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 8.4 min, tr(2) = 30.4 min.

Compound **3j**



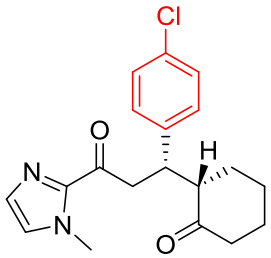

Following **General Procedure A**, the reaction of **1j** (49.3 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3j** as a yellow oil (61 mg, 0.18 mmol, yield: 90%). The diastereomeric ratio was determined as 2.3:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +24.5; **IR** (film) $\nu_{max}$: 2925, 2856, 1707, 1677, 1462, 1410, 1289 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{19}H_{21}ClN_2O_2Na^+$ $[M+Na]^+$: 367.1184, found: 367.1182.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 4H), 7.12 (s, 1H), 6.99 (s, 1H), 4.01 (ddd, *J* = 10.3, 4.5, 4.2 Hz, 1H), 3.88 (s, 3H), 3.77 (dd, *J* = 17.5, 10.3 Hz, 1H), 3.35 (dd, *J* = 17.5, 4.2 Hz, 1H), 2.60 (m, 1H), 2.38 (m, 1H), 2.26 (m, 1H), 2.10–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.9, 190.6, 145.5, 142.9, 134.0, 129.4, 128.8, 128.2, 126.8, 126.4, 126.3, 56.0, 42.2, 39.3, 38.2, 36.0, 28.9, 27.5, 24.9; **HPLC**: 96% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 8.0 min, tr(2) = 16.0 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.12 (m, 4H), 7.08 (s, 1H), 6.96 (s, 1H), 3.88 (s, 3H), 3.75 (m, 1H), 3.61 (dd, *J* = 17.5, 9.2 Hz, 1H), 3.48 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.66 (m, 1H), 2.45 (m, 1H), 2.34 (m, 1H), 2.10–1.50 (m, 6H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.5, 190.3, 144.7, 142.9, 134.0, 129.5, 128.7, 128.5, 126.7, 126.6, 55.5, 44.0, 42.5, 39.4, 36.0, 32.5, 28.5, 24.7; **HPLC**: 13% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 12.2 min, tr(2) = 20.6 min.

Compound **3k**

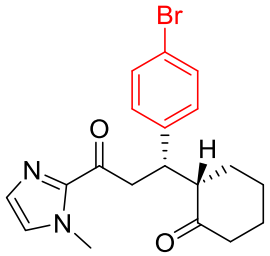



Following **General Procedure A**, the reaction of **1k** (49.3 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3k** as an off-white solid (65 mg, 0.19 mmol, yield: 95%). The diastereomeric ratio was determined as 2:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +10.4; **Mp** 108–109 ℃; **IR** (film) $\nu_{max}$: 2933, 2861, 1702, 1679, 1491, 1411, 1289, 1128, 1110, 1013, 915, 834, 775 cm$^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{19}H_{21}ClN_2O_2Na^+$ $[M+Na]^+$: 367.1184, found: 367.1188.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 4H), 7.11 (s, 1H), 6.99 (s, 1H), 3.99 (ddd, *J* = 10.4, 5.0, 4.1 Hz, 1H), 3.88 (s, 3H), 3.79 (dd, *J* = 17.3, 10.4 Hz, 1H), 3.33 (dd, *J* = 17.3, 4.1 Hz, 1H), 2.59 (m, 1H), 2.38 (m, 1H), 2.25 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.1, 190.7, 143.0, 141.8, 131.8, 129.5, 128.8, 128.3, 126.9, 56.1, 42.2, 39.5, 38.1, 36.0, 29.1, 27.5, 24.8; **HPLC**: 95% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 7.8 min, tr(2) = 20.4 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 7.07 (s, 1H), 6.96 (s, 1H), 3.88 (s, 3H), 3.76 (ddd, *J* = 9.5, 9.4, 4.2 Hz, 1H), 3.64 (dd, *J* = 17.3, 9.5 Hz, 1H), 3.46 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.64 (m, 1H), 2.45 (m, 1H), 2.33 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.5, 190.5, 142.9, 141.0, 131.9, 129.9, 128.7, 128.4, 126.7, 55.6, 44.0, 42.5, 39.1, 36.0, 32.4, 28.4, 24.6; **HPLC**: 19% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 14.1 min, tr(2) = 27.9 min.

Compound **3l**



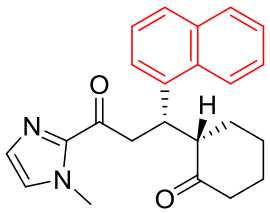

Following **General Procedure A**, the reaction of **1l** (58.2 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3l** as a white solid (73.9 mg, 0.19 mmol, yield: 95%). The diastereomeric ratio was determined as 3.4:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +15.9; **Mp** 120–122 ℃; **IR** (film) $\nu_{max}$: 2936, 2862, 1705, 1676, 1488, 1410, 1289, 1073, 1009, 915, 831, 770 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{19}H_{21}BrN_2O_2Na^+$ $[M+Na]^+$: 411.0679, found: 411.0678.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.11 (s, 1H), 6.98 (s, 1H), 3.98 (ddd, *J* = 10.6, 5.2, 4.1 Hz, 1H), 3.88 (s, 3H), 3.79 (dd, *J* = 17.4, 10.6 Hz, 1H), 3.33 (dd, *J* = 17.4, 4.1 Hz, 1H), 2.59 (m, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$)

δ 211.1, 190.7, 143.0, 142.3, 131.3, 129.9, 128.8, 126.9, 120.0, 56.0, 42.3, 39.5, 38.1, 36.1, 29.1, 27.5, 24.9; **HPLC**: 97% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 8.0 min, tr(2) = 21.0 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 1H), 6.96 (s, 1H), 3.88 (s, 3H), 3.75 (ddd, *J* = 9.6, 9.2, 4.2 Hz, 1H), 3.64 (dd, *J* = 17.3, 9.6 Hz, 1H), 3.45 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.64 (m, 1H), 2.44 (m, 1H), 2.33 (m, 1H), 2.10–1.45 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.5, 190.5, 142.9, 141.5, 131.4, 130.3, 128.8, 126.7, 120.1, 55.5, 43.9, 42.5, 39.1, 36.0, 32.4, 28.5, 24.7; **HPLC**: 15% ee (IC, 254 nm, n-hexane/isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 14.3 min, tr(2) = 28.5 min.

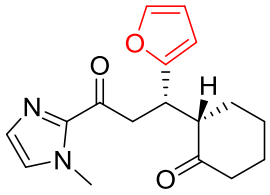
Compound **3m**




Following **General Procedure A**, the reaction of **1m** (52.5 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3m** as a colorless oil (60.5 mg, 0.17 mmol, yield: 84%). The diastereomeric ratio was determined as 9:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +23.6; **IR** (film) $\nu_{max}$: 2935, 2862, 1703, 1677, 1409, 1289, 1261, 1223, 1203, 1128, 966, 915, 779 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{23}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 383.1730, found: 383.1734. Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.48 (m, 2H), 7.32 (m, 2H), 7.12 (s, 1H), 6.92 (s, 1H), 5.10 (ddd, *J* = 10.5, 4.1, 3.6 Hz, 1H), 4.12 (dd, *J* = 17.3,

10.5 Hz, 1H), 3.76 (s, 3H), 3.36 (dd, *J* = 17.3, 4.1 Hz, 1H), 2.64 (m, 1H), 2.43 (m, 1H), 2.24 (m, 1H), 2.02–1.32 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.1, 190.7, 143.1, 138.8, 134.1, 131.3, 128.9, 128.7, 126.8, 126.7, 126.1, 125.3, 124.9, 123.5, 123.1, 54.4, 42.0, 38.4, 35.9, 32.0, 28.0, 27.1, 24.9; **HPLC**: 94% ee (IC, 254 nm, n-hexane/ isopropanol 60/40, 1.0 mL/min, 25 ℃) tr(1)= 8.4 min, tr(2) = 16.1 min.

Compound **3n**

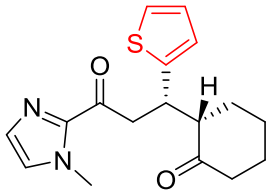



Following **General Procedure A**, the reaction of **1n** (40.4 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3n** as a yellow oil (52.2 mg, 0.17 mmol, yield: 87%). The diastereomeric ratio was determined as 2.5:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +9.15; **IR** (film) $\nu_{max}$: 2935, 2863, 1705, 1678, 1410, 1262, 1014, 915, 801 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{17}H_{20}N_2O_3Na^+$ $[M+Na]^+$: 323.1366, found: 323.1363.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.13 (s, 1H), 7.01 (s, 1H), 6.23 (m, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 4.17 (ddd, *J* = 10.4, 3.8, 3.7 Hz, 1H), 3.96 (s, 3H), 3.76 (dd, *J* = 17.4, 10.4 Hz, 1H), 3.21 (dd, *J* = 17.4, 3.7 Hz, 1H), 2.79 (m, 1H), 2.42 (m, 1H), 2.30 (m, 1H), 2.10–1.55 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.9, 190.5, 156.7, 143.0, 140.9, 128.9, 126.8, 110.0, 105.6, 53.5, 42.1, 38.2, 36.1, 32.2, 28.8, 27.4, 25.0; **HPLC**: 93% ee (OJ, 254 nm, n-hexane/ isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 8.6 min, tr(2) = 86.2 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.10 (s, 1H), 6.98 (s, 1H), 6.23 (m, 1H), 6.10 (d, *J* = 3.1 Hz, 1H), 3.97 (ddd, *J* = 9.3, 9.0, 4.6 Hz, 1H), 3.94 (s, 3H), 3.68 (dd, *J* = 17.4, 9.3 Hz, 1H), 3.37 (dd, *J* = 17.4, 4.6 Hz, 1H), 2.70 (m, 1H), 2.42 (m, 1H), 2.30 (m, 1H), 2.10–1.55 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 211.8, 190.5, 155.7, 142.9, 141.0, 128.9, 126.7, 109.9, 106.8, 54.4, 42.4, 41.6, 36.1, 33.1, 31.8, 28.1, 24.9; **HPLC**: 30% ee (OJ, 254 nm, n-hexane/ isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 9.3 min, tr(2) = 15.1 min.

Compound **3o**



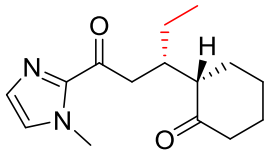

Following **General Procedure A**, the reaction of **1o** (43.7 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3o** as a colorless oil (60 mg, 0.19 mmol, yield: 96%). The diastereomeric ratio was determined as 4.3:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +10.5; **IR** (film) $\nu_{max}$: 2935, 2862, 1705, 1677, 1410, 1289, 1014, 915 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{17}H_{20}N_2O_2SNa^+$ $[M+Na]^+$: 339.1138, found: 339.1137.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.13–7.06 (m, 2H), 6.99 (s, 1H), 6.89–6.83 (m, 2H), 4.35 (ddd, *J* = 10.2, 4.1, 4.0 Hz, 1H), 3.92 (s, 3H), 3.82 (dd, *J* = 17.4, 10.2 Hz, 1H), 3.33 (dd, *J* = 17.4, 4.0 Hz, 1H), 2.68 (m, 1H), 2.41 (m, 1H), 2.28 (m, 1H), 2.20–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.8, 190.3, 146.9, 143.0, 128.8, 126.8, 126.4, 124.5, 123.1, 56.4, 42.2, 41.1, 36.0, 34.0, 29.0,

27.4, 25.0; **HPLC**: 99% ee (OJ, 254 nm, n-hexane/isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 9.5 min, tr(2) = 32.9 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.13–7.06 (m, 2H), 6.97 (s, 1H), 6.89–6.83 (m, 2H), 4.19 (ddd, *J* = 9.0, 8.7, 4.8 Hz, 1H), 3.91 (s, 3H), 3.67 (dd, *J* = 17.3, 9.0 Hz, 1H), 3.47 (dd, *J* = 17.3, 4.8 Hz, 1H), 2.63 (m, 1H), 2.44 (m, 1H), 2.32 (m, 1H), 2.20–1.50 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.0, 190.2, 145.8, 142.9, 128.8, 126.7, 126.3, 125.2, 123.4, 56.2, 44.7, 42.3, 36.0, 34.8, 31.6, 28.1, 24.6; **HPLC**: 36% ee (OJ, 254 nm, n-hexane/isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 11.3 min, tr(2) = 14.5 min.

Compound **3p**

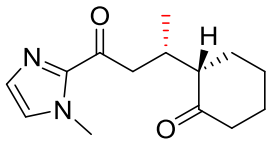



Following **General Procedure A**, the reaction of **1p** (32.84 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3p** as a yellow oil (43.55 mg, 0.17 mmol, yield: 83%). The diastereomeric ratio was determined as 2:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +3.51; **IR** (film) $\nu_{max}$: 2935, 2864, 1705, 1674, 1408, 1014, 914, 774 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{15}H_{22}N_2O_2Na^+$ $[M+Na]^+$: 285.1573, found: 285.1572; **$^{13}$C NMR** (100 MHz, $CDCl_3$, for diastereomeric mixture) δ 212.6, 212.4, 192.8, 192.4, 143.3, 143.2, 128.8, 128.6, 126.8, 126.7, 53.3, 52.3, 42.2, 42.15, 40.54, 40.5, 36.2, 33.8, 33.6, 28.7, 28.3, 27.47, 27.5, 27.3, 24.9, 24.85, 24.83, 23.9, 11.8, 11.6.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.02 (s, 1H), 4.01 (s, 3H), 3.13 (dd, *J* = 17.1, 7.7 Hz, 1H), 3.03 (dd, *J* = 17.1, 4.9 Hz, 1H), 2.62 (m, 1H), 2.40 (m, 2H), 2.26 (m, 1H), 2.12–1.40 (m, 8H), 0.89 (t, *J* = 7.4 Hz, 3H); **HPLC**: 94% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 14.5 min, tr(2) = 29.0 min.

Minor isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.02 (s, 1H), 3.99 (s, 3H), 3.21 (dd, *J* = 17.1, 5.7 Hz, 1H), 3.06 (dd, *J* = 17.1, 7.4 Hz, 1H), 2.62 (m, 1H), 2.40 (m, 2H), 2.26 (m, 1H), 2.12–1.40 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 3H); **HPLC**: 74% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 19.1 min, tr(2) = 27.9 min.

Compound **3q**



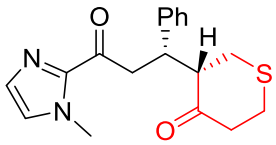

Following **General Procedure A**, the reaction of **1q** (30.0 mg, 0.20 mmol) and cyclohexanone **2a** (58.9 mg, 62 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3q** as a yellow oil (47.61 mg, 0.19 mmol, yield: 96%). The diastereomeric ratio was determined as 2:1 by $^1$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = –18.4; **IR** (film) $\nu_{max}$: 2925, 2854, 1706, 1676, 1409, 1377, 1290, 1155 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{14}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 271.1417, found: 271.1415.

Major isomer: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.03 (s, 1H), 4.01 (s, 3H), 3.20–1.50 (m, 12H), 0.99 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.2, 192.3, 143.2, 128.6, 126.7, 55.4, 42.4, 42.0, 36.0, 29.4, 27.8, 27.5, 24.5,

18.0; **HPLC**: 99% ee (IC, 254 nm, n-hexane/ isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 10.4 min, tr(2) = 20.4 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.03 (s, 1H), 4.00 (s, 3H), 3.20–1.50 (m, 12H), 0.95 (d, *J* = 6.8 Hz, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 212.2, 192.2, 143.1, 128.7, 126.8, 54.5, 43.8, 42.1, 28.4, 24.7, 16.5; **HPLC**: 84% ee (IC, 254 nm, n-hexane/ isopropanol 80/20, 1.0 mL/min, 25 ℃) tr(1)= 13.7 min, tr(2) = 14.5 min.

Compound **3r**

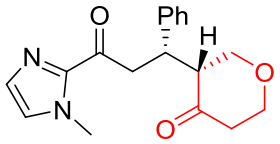



Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and tetrahydrothiopyran-4-one **2r** (69.7 mg, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3r** as a colorless oil (60.5 mg, 0.18 mmol, yield: 92%). The diastereomeric ratio was determined as 3.2:1 by $^{1}$HNMR. **Opt. Rot.**: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +6.55; **IR** (film) $\nu_{max}$: 2954, 2919, 1705, 1676, 1409, 1289, 1154, 1001, 915, 773 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{18}H_{20}N_2O_2SNa^+$ $[M+Na]^+$: 351.1138, found: 351.1137.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 5H), 7.11 (d, *J* = 0.8 Hz, 1H), 6.98 (s, 1H), 4.21 (ddd, *J* = 10.1, 4.6, 4.4 Hz, 1H), 3.87 (s, 3H), 3.80 (dd, *J* = 17.1, 10.1 Hz, 1H), 3.37 (dd, *J* = 17.1, 4.4 Hz, 1H), 3.06–2.53 (m, 7H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 208.7, 190.3, 142.9, 141.9, 128.8, 128.4, 128.1, 126.9, 126.6, 58.4, 44.1, 39.9, 38.9, 36.0, 32.0, 30.6; **HPLC**: 98% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 13.0 min, tr(2) = 29.1 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.13 (m, 5H), 7.07 (d, *J* = 0.8 Hz, 1H), 6.94 (s, 1H), 4.05 (ddd, *J* = 9.8, 9.4, 4.4 Hz, 1H), 3.85 (s, 3H), 3.63 (dd, *J* = 17.2, 9.4 Hz, 1H), 3.37 (dd, *J* = 17.2, 4.4 Hz, 1H), 3.06–2.38 (m, 7H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.6, 190.2, 142.8, 141.1, 128.6, 128.4, 128.1, 126.8, 126.7, 58.0, 43.9, 43.8, 39.7, 35.9, 34.9, 31.5; **HPLC**: 35% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 27.8 min, tr(2) = 35.5 min.

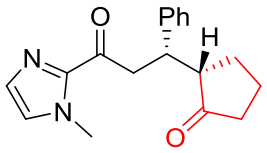
Compound **3s**




Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and tetrahydro-4H-pyran-4-one **2s** (60.07 mg, 55 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3s** as a colorless oil (58.16 mg, 0.19 mmol, yield: 93%). The diastereomeric ratio was determined as 2.5:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +7.53; **IR** (film) $\nu_{max}$: 2963, 2922, 2855, 1711, 1676, 1410, 1289, 1153, 977, 914, 703 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{18}H_{20}N_2O_3Na^+$ $[M+Na]^+$: 335.1366, found: 335.1368. Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 5H), 7.11 (d, *J* = 0.8 Hz, 1H), 6.98 (s, 1H), 4.07 (m, 3H), 3.88 (s, 3H), 3.92–3.80 (m, 2H), 3.81 (dd, *J* = 17.3, 10.0 Hz, 1H), 3.40 (dd, *J* = 17.3, 4.5 Hz, 1H), 2.87 (m, 1H), 2.48–2.37 (m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 206.9, 190.2, 142.9, 141.8, 128.9, 128.4, 128.0, 126.9, 126.6, 69.6, 68.4, 56.9, 42.5, 40.2, 37.2, 36.0; **HPLC**: 98% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 14.1 min, tr(2) = 24.9 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 5H), 7.08 (d, *J* = 0.8 Hz, 1H), 6.95 (s, 1H), 3.99 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.86 (s, 3H), 3.92–3.80 (m, 2H), 3.64 (dd, *J* = 17.3, 9.0 Hz, 1H), 3.61 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.51 (dd, *J* = 17.3, 4.9 Hz, 1H), 3.35 (dd, *J* = 11.5, 7.2 Hz, 1H), 2.80 (m, 1H), 2.70 (m, 1H), 2.53 (m, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 208.5, 190.3, 142.9, 141.1, 128.8, 128.6, 128.3, 126.8, 126.7, 71.3, 68.9, 57.0, 44.0, 42.5, 37.9, 36.0; **HPLC**: 29% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 29.9 min, tr(2) = 39.9 min.

Compound **3t**

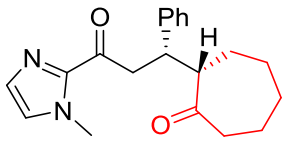



Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and cyclopentanone **2t** (50.47 mg, 53 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3t** as a brown oil (53.4 mg, 0.18 mmol, yield: 90%). The diastereomeric ratio was determined as 2.3:1 by $^{1}$HNMR. **Opt. Rot.**: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +6.63; **IR** (film) $\nu_{max}$: 2924, 1731, 1676, 1409, 1154, 915, 774, 704 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{18}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 319.1417, found: 319.1419.

Major isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 7.11 (d, *J* = 2.6 Hz, 1H), 6.97 (s, 1H), 3.96–3.65 (m, 6H), 2.50–1.46 (m, 7H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 219.5, 190.8, 143.1, 141.9, 128.8, 128.4, 128.2, 126.7, 126.4, 53.3, 42.7, 39.8, 38.7, 36.0, 26.9, 20.2; **HPLC**: 30% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 32.5 min, tr(2) = 48.4 min.

Minor isomer: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 7.11 (s, 1H), 6.97 (s, 1H), 3.96–3.65 (m, 5H), 3.30 (m, 1H), 2.50–1.46 (m, 7H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 219.3, 190.8, 143.0, 142.9, 128.3, 127.9, 126.8, 126.3, 54.8, 39.9, 39.5, 39.0, 25.9, 20.3; **HPLC**: 25% ee (IC, 254 nm, n-hexane/ isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 18.4 min, tr(2) = 28.5 min.

Compound **3u**

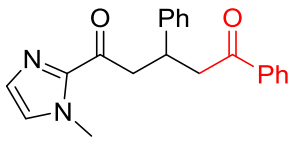



Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and cycloheptanone **2u** (67.30 mg, 71 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3u** as a colorless oil (45.47 mg, 0.14 mmol, yield: 70%). The diastereomeric ratio was determined as 2:1 by $^{1}$HNMR. **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +2.88; **IR** (film) $\nu_{max}$: 2928, 2855, 1696, 1677, 1453, 1410, 915, 771 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{20}H_{24}N_2O_2Na^+$ $[M+Na]^+$: 347.1730, found: 347.1727; **$^{13}$C NMR** (100 MHz, $CDCl_3$, for diastereomeric mixture) δ 216.2, 215.4, 191.1, 190.8, 143.12, 143.1, 142.3, 142.2, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 126.8, 126.7, 126.55, 126.5, 57.9, 57.7, 44.0, 43.5, 43.1, 42.7, 42.5, 41.3, 36.1, 36.0, 29.6, 29.2, 29.1, 28.44, 28.4, 28.1, 25.0, 24.7.

Diastereoisomer 1: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 5H), 7.12 (s, 1H), 6.97 (s, 1H), 3.87 (s, 3H), 3.80–3.48 (m, 3H), 2.90–1.10 (m, 11H); **HPLC**: 59% ee (IC, 254 nm, n-hexane/isopropanol 90/10, 1.0 mL/min, 25 ℃) tr(1)= 104.7 min, tr(2) = 124.6 min.

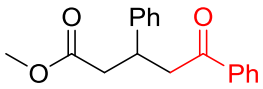
Diastereoisomer 2: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.13 (m, 5H), 7.07 (s, 1H), 6.94 (s, 1H), 3.86 (s, 3H), 3.80–3.48 (m, 2H), 3.37 (dd, *J* = 16.9, 5.0 Hz, 1H), 2.90–1.10 (m, 11H); **HPLC**: 1% ee (IC, 254 nm, n-hexane/isopropanol 90/10, 1.0 mL/min, 25 ℃) tr(1)= 147.5 min, tr(2) = 161.8 min.

Compound **3v**




Following **General Procedure A**, the reaction of **1a** (42.5 mg, 0.20 mmol) and acetophenone **2v** (72.09 mg, 69.9 μL, 0.60 mmol) catalyzed by **Λ-Rh3** (4.15 mg, 0.004 mmol) and pyrrolidine (3.3 μL, 0.04 mmol) afforded the product **3v** as a white solid (62.55 mg, 0.19 mmol, yield: 94%). **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +8.83; **Mp** 89–92 ℃; **IR** (film) $\nu_{max}$: 2923, 2853, 1730, 1674, 1596, 1408, 1156, 990, 913, 793 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{21}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 355.1417, found: 355.1414; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (s, 1H), 6.97 (s, 1H), 4.10 (quint, *J* = 7.1 Hz, 1H), 3.91 (s, 3H), 3.67 (dd, *J* = 16.9, 7.6 Hz, 1H), 3.53 (dd, *J* = 16.9, 6.8 Hz, 1H), 3.43 (dd, *J* = 16.9, 7.1 Hz, 1H), 3.33 (dd, *J* = 16.9, 7.0 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 198.3, 190.8, 144.0, 143.0, 136.9, 132.9, 128.8, 128.4, 127.9, 127.5, 126.8, 126.4, 45.1, 44.9, 36.4, 36.0; **HPLC**: 86% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 13.8 min, tr(2) = 22.4 min.

Compound **4**



Following **General Procedure B**, in distilled anhydrous DCM (0.1 mL) the moiety **3v** (0.08 mmol) was added and stir the solution for 2 hours at 0 ℃ followed by the addition of methyl trifluoromethansulfonate (0.4 mmol) in a Schlenk tube. Then the Schlenk tube was sealed and allowed to stir at room temperature for 12 hours. Monitor the reaction by TLC, then add DBU (90 μL) and MeOH (180 μL). After being stirred at 20 ℃ for 90 min, the reaction mixture was concentrated and the residue was subjected to a silica gel flash chromatography (petroleum ether/ EtOAc = 20:1 to 10:1) to afford the product **4** as a white solid (16.8 mg, 0.06 mmol, yield: 74%). **Opt. Rot**.: $[\alpha]_D^{25}$ (*c* 1.0, $CHCl_3$) = +5.55; **Mp** 88–90 ℃; **IR** (film) $\nu_{max}$: 2950, 2923, 1732, 1682, 1446, 1266, 1153, 1006, 701, 687 $cm^{-1}$; **HRMS** (ESI, *m/z*) calcd. for $C_{18}H_{18}O_3Na^+$ $[M+Na]^+$: 305.1148, found: 305.1146; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.32–7.16(m, 5H), 3.88 (quint, *J* = 7.2 Hz, 1H), 3.58 (s, 3H), 3.40 (dd, *J* = 16.9, 7.0 Hz, 1H), 3.33 (dd, *J* = 16.9, 7.0 Hz, 1H), 2.82 (dd, *J* = 15.4, 7.0 Hz, 1H), 2.69 (dd, *J* = 15.4, 7.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 198.1, 172.3, 143.3, 136.8, 133.1, 128.6, 128.5, 128.0, 127.3, 126.8, 51.5, 44.5, 40.5, 37.4; **HPLC**: 81% ee (IC, 254 nm, n-hexane/isopropanol 70/30, 1.0 mL/min, 25 ℃) tr(1)= 8.2 min, tr(2) = 10.4 min.

## Reference

1. H. Huo, C. Fu, K. Harms and E. Meggers, *J. Am. Chem. Soc.*, 2014, **136**, 2990.

2. H. Huo, X. Shen, C. Wang, L. Zhang, P. Rose, L.-A. Chen, K. Harms, M. Marsch, G. Hilt and E. Meggers, *Nature*, 2014, **515**, 100.

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

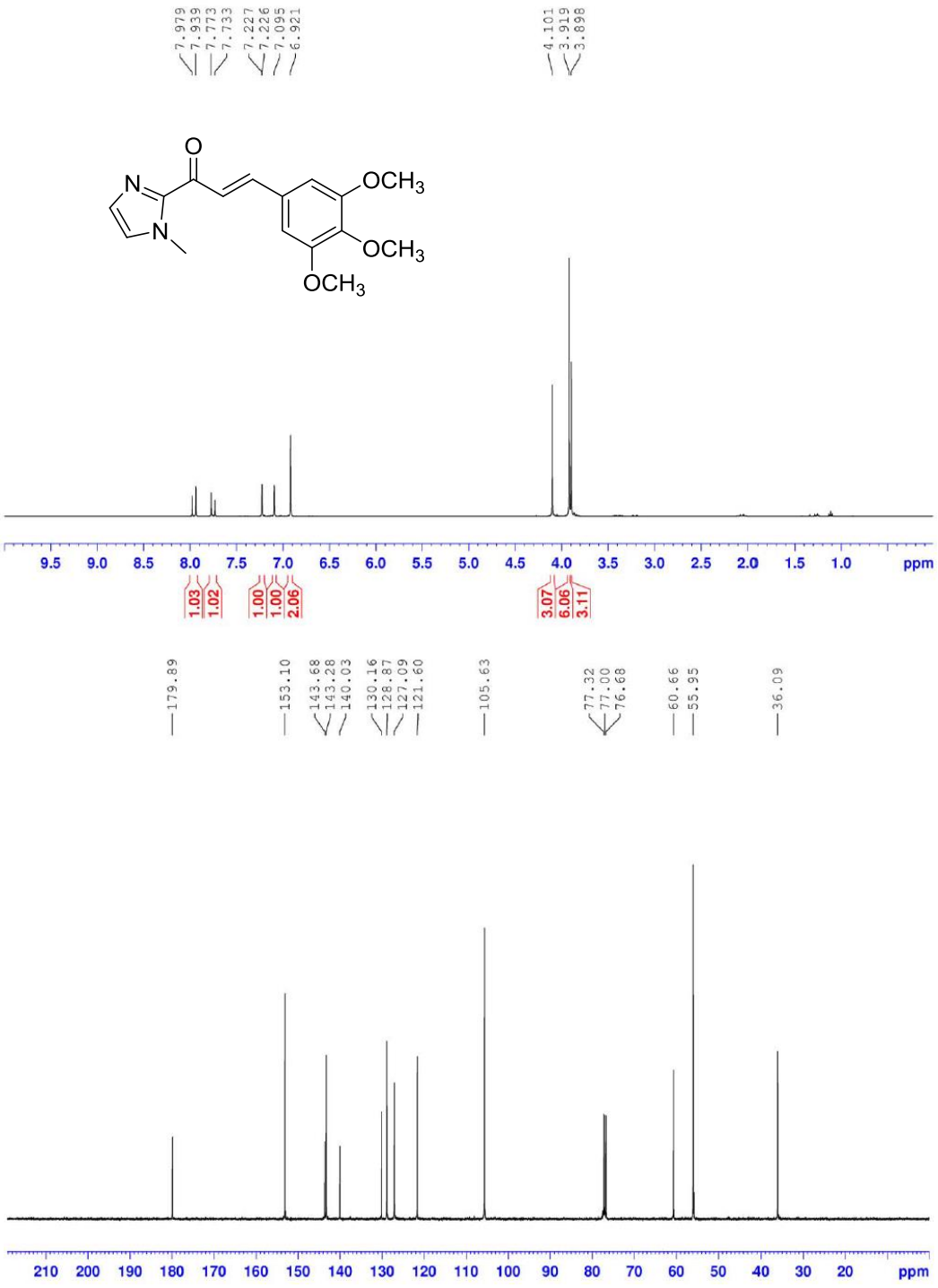
4. S.-W. Li, J. Gong and Q. Kang, *Org. Lett.*, 2017, **19**, 1350.

5. M. C. Myers, A. R. Bharadwaj, B. C. Milgram and K. A. Scheidt, *J. Am. Chem. Soc.*, 2005, **127**, 14675.

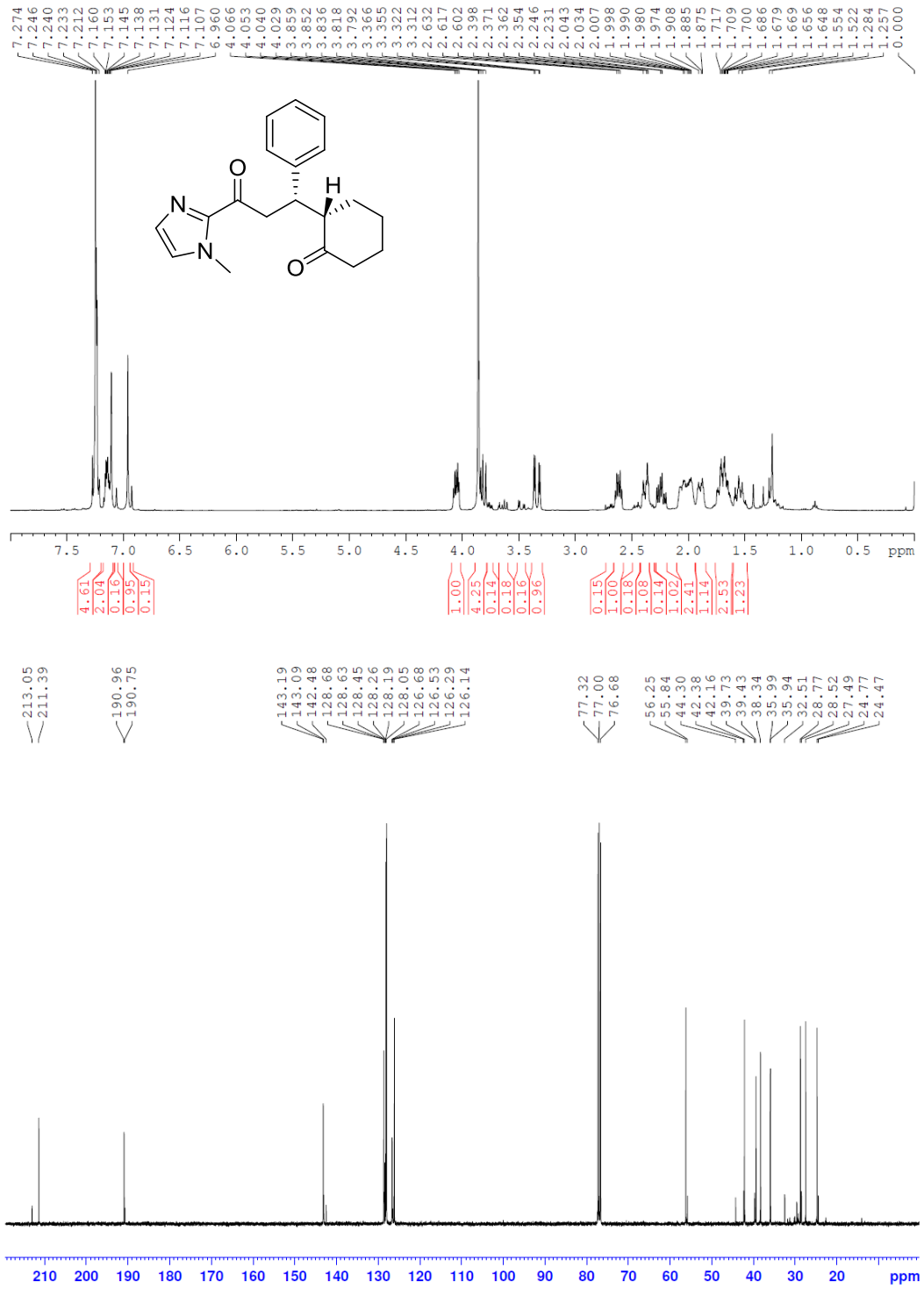
6. D. A. Evans, K. R. Fandrick and H.-J. Song, *J. Am. Chem. Soc.*, 2005, **127**, 8942.

## NMR Spectra

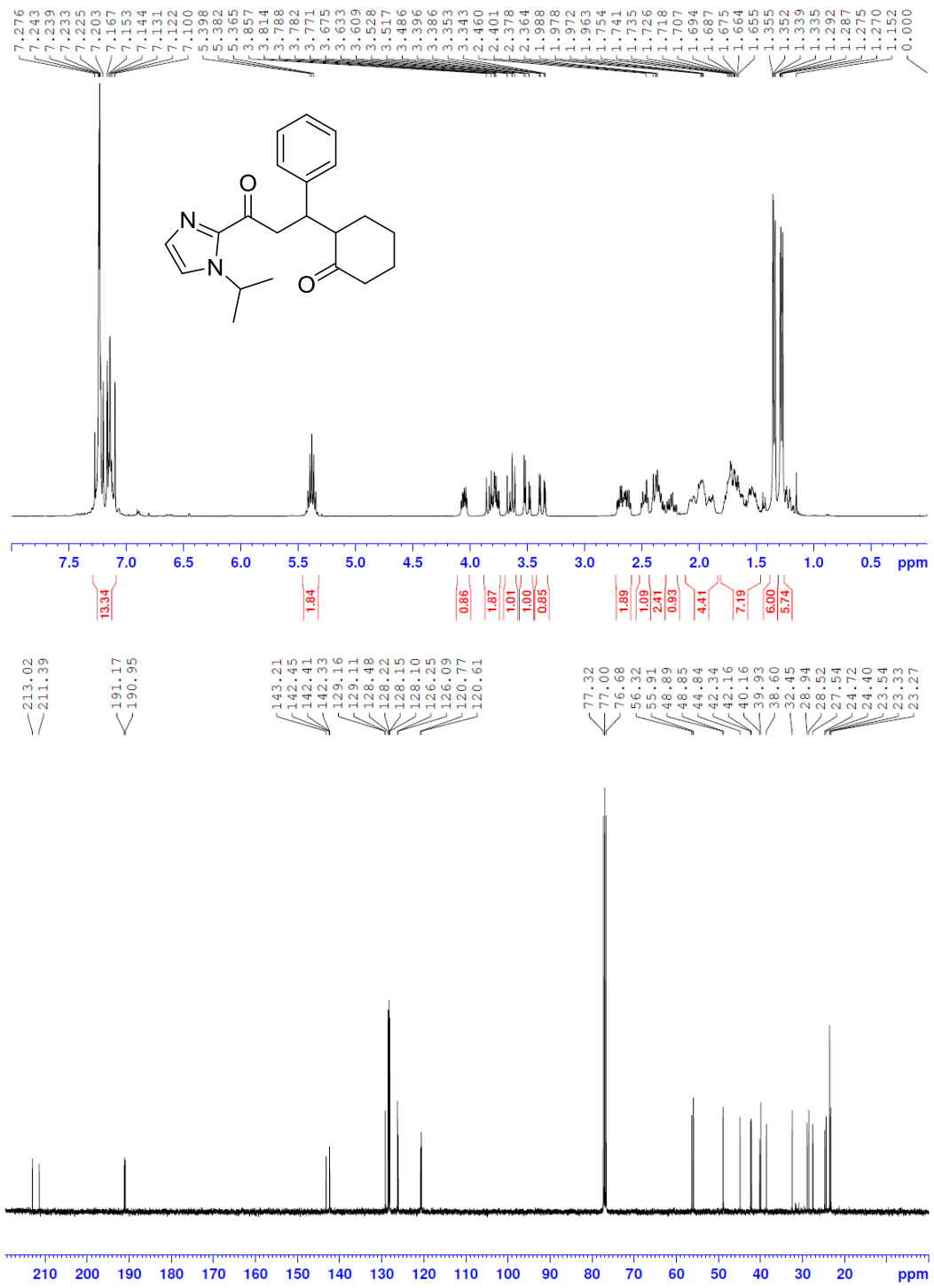
### 1h



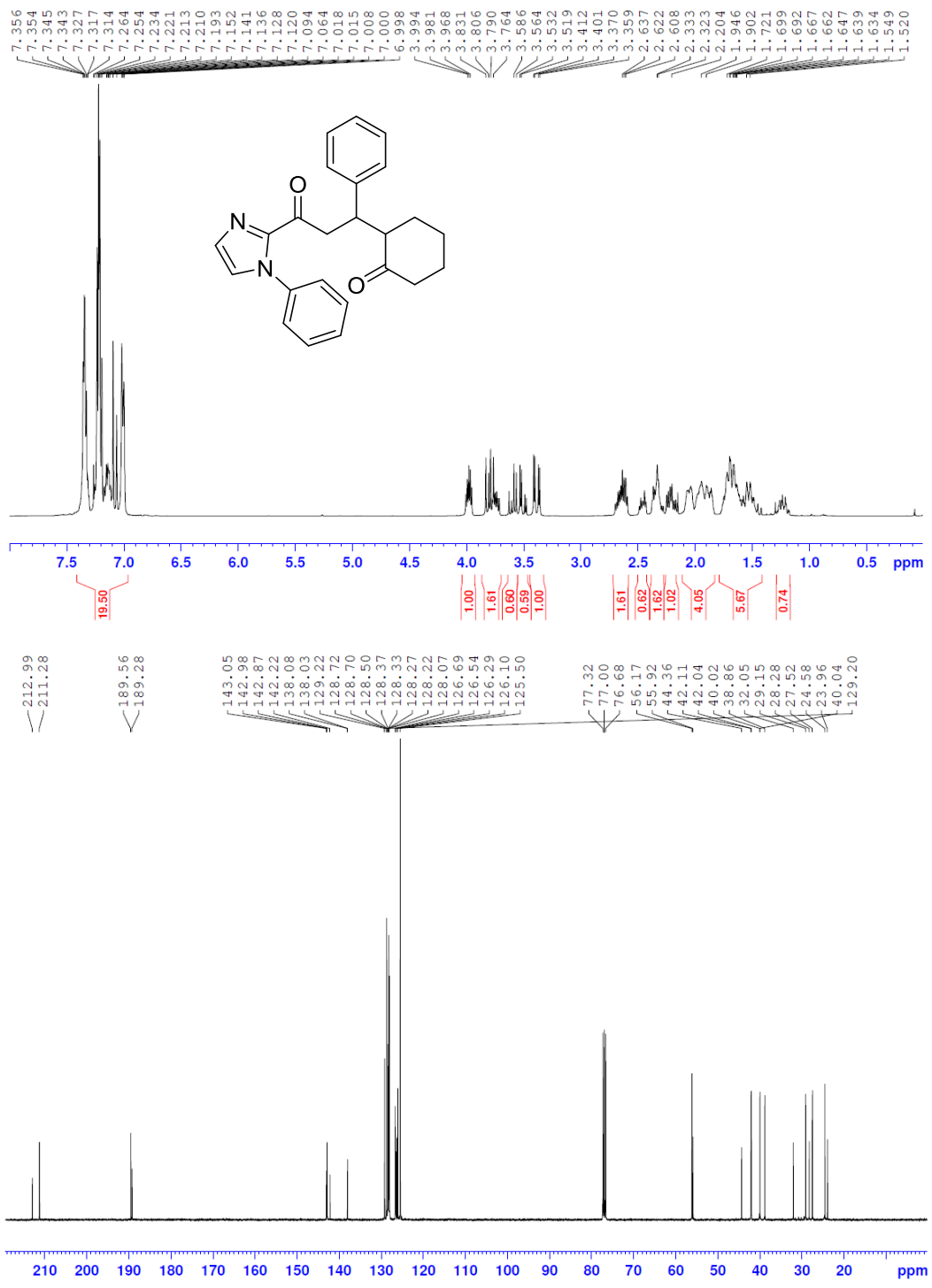
**3a**


7.274
7.246
7.240
7.233
7.212
7.160
7.153
7.145
7.138
7.131
7.124
7.116
7.107
6.960
4.066
4.053
4.040
4.029
3.859
3.852
3.836
3.818
3.792
3.366
3.355
3.322
3.312
2.632
2.617
2.602
2.398
2.371
2.362
2.354
2.246
2.231
2.043
2.034
2.007
1.998
1.990
1.980
1.974
1.908
1.885
1.875
1.717
1.709
1.700
1.686
1.679
1.669
1.656
1.648
1.554
1.522
1.284
1.257
0.000
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.61
2.04
0.16
0.95
0.15
1.00
4.25
0.14
0.18
0.16
0.96
0.15
1.00
0.18
1.08
0.14
1.02
2.41
1.14
2.53
1.23
213.05
211.39
190.96
190.75
143.19
143.09
142.48
128.68
128.63
128.45
128.26
128.19
128.05
126.68
126.53
126.29
126.14
77.32
77.00
76.68
56.25
55.84
44.30
42.38
42.16
39.73
39.43
38.34
35.99
35.94
32.51
28.77
28.52
27.49
24.77
24.47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

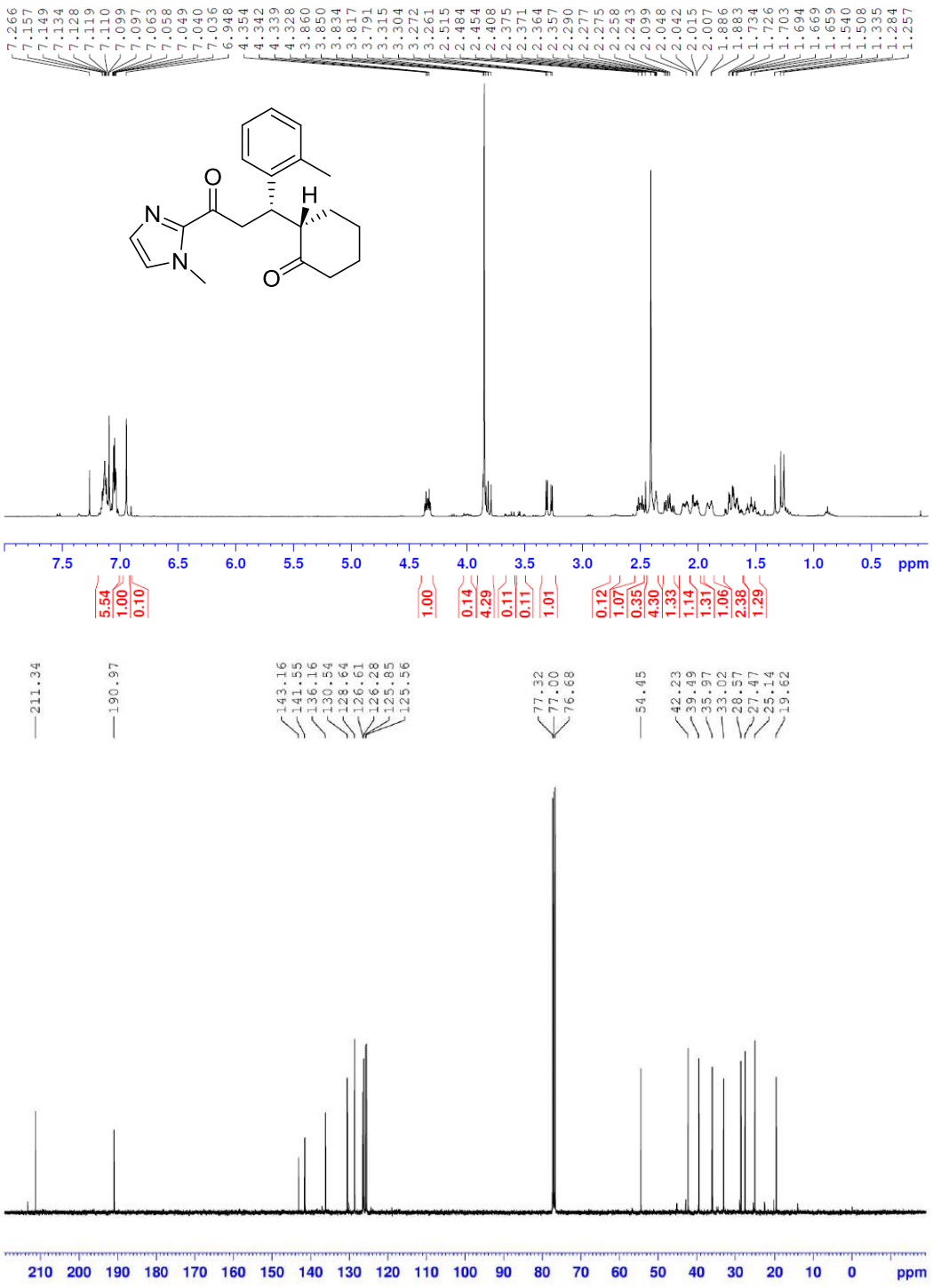
**3b**


7.276
7.243
7.239
7.233
7.225
7.203
7.167
7.153
7.144
7.131
7.122
7.100
5.398
5.382
5.365
3.857
3.814
3.788
3.782
3.771
3.675
3.633
3.609
3.528
3.517
3.486
3.396
3.386
3.353
3.343
2.460
2.401
2.378
2.364
1.988
1.978
1.972
1.963
1.754
1.741
1.735
1.726
1.718
1.707
1.694
1.687
1.675
1.664
1.655
1.355
1.352
1.339
1.335
1.292
1.287
1.275
1.270
1.152
0.000
O
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
13.34
1.84
0.86
1.87
1.01
1.00
0.85
1.89
1.09
2.41
0.93
4.41
7.19
6.00
5.74
213.02
211.39
191.17
190.95
143.21
142.45
142.41
142.33
129.16
129.11
128.48
128.22
128.15
128.10
126.25
126.09
120.77
120.61
77.32
77.00
76.68
56.32
55.91
48.89
48.85
44.84
42.34
42.16
40.16
39.93
38.60
32.45
28.94
28.52
27.54
24.72
24.40
23.54
23.33
23.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

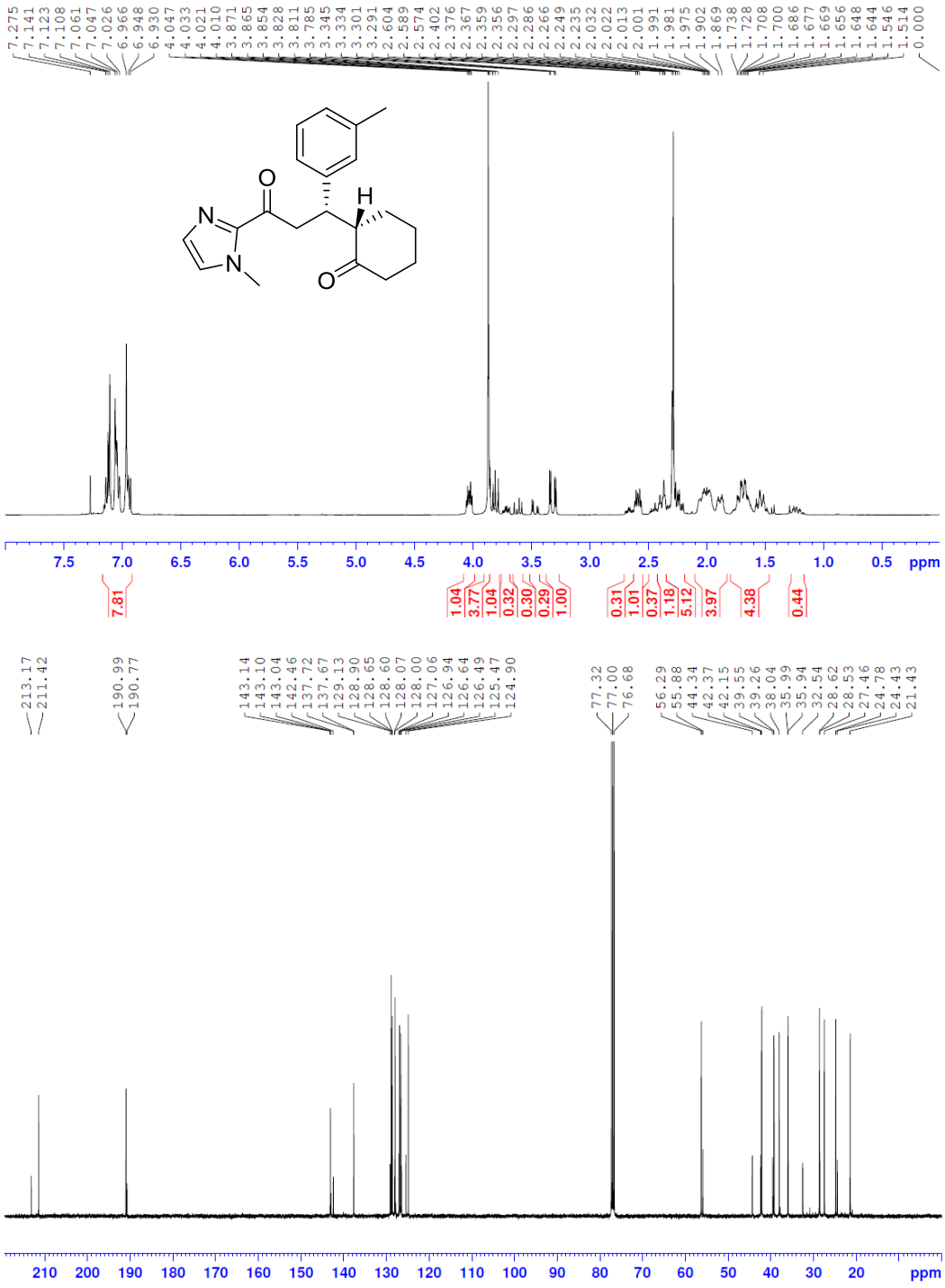
**3c**


7.356
7.354
7.345
7.343
7.327
7.317
7.314
7.264
7.254
7.234
7.221
7.213
7.210
7.193
7.152
7.141
7.136
7.128
7.120
7.094
7.064
7.018
7.015
7.008
7.000
6.998
3.994
3.981
3.968
3.831
3.806
3.790
3.764
3.586
3.564
3.532
3.519
3.412
3.401
3.370
3.359
2.637
2.622
2.608
2.333
2.323
2.204
1.946
1.902
1.721
1.699
1.692
1.667
1.662
1.647
1.639
1.634
1.549
1.520
O
N
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
19.50
1.00
1.61
0.60
0.59
1.00
1.61
0.62
1.62
1.02
4.05
5.67
0.74
212.99
211.28
189.56
189.28
143.05
142.98
142.87
142.22
138.08
138.03
129.22
128.72
128.70
128.50
128.37
128.33
128.27
128.22
128.07
126.69
126.54
126.29
126.10
125.50
77.32
77.00
76.68
56.17
55.92
44.36
42.11
42.04
40.02
38.86
32.05
29.15
28.28
27.52
24.58
23.96
40.04
129.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

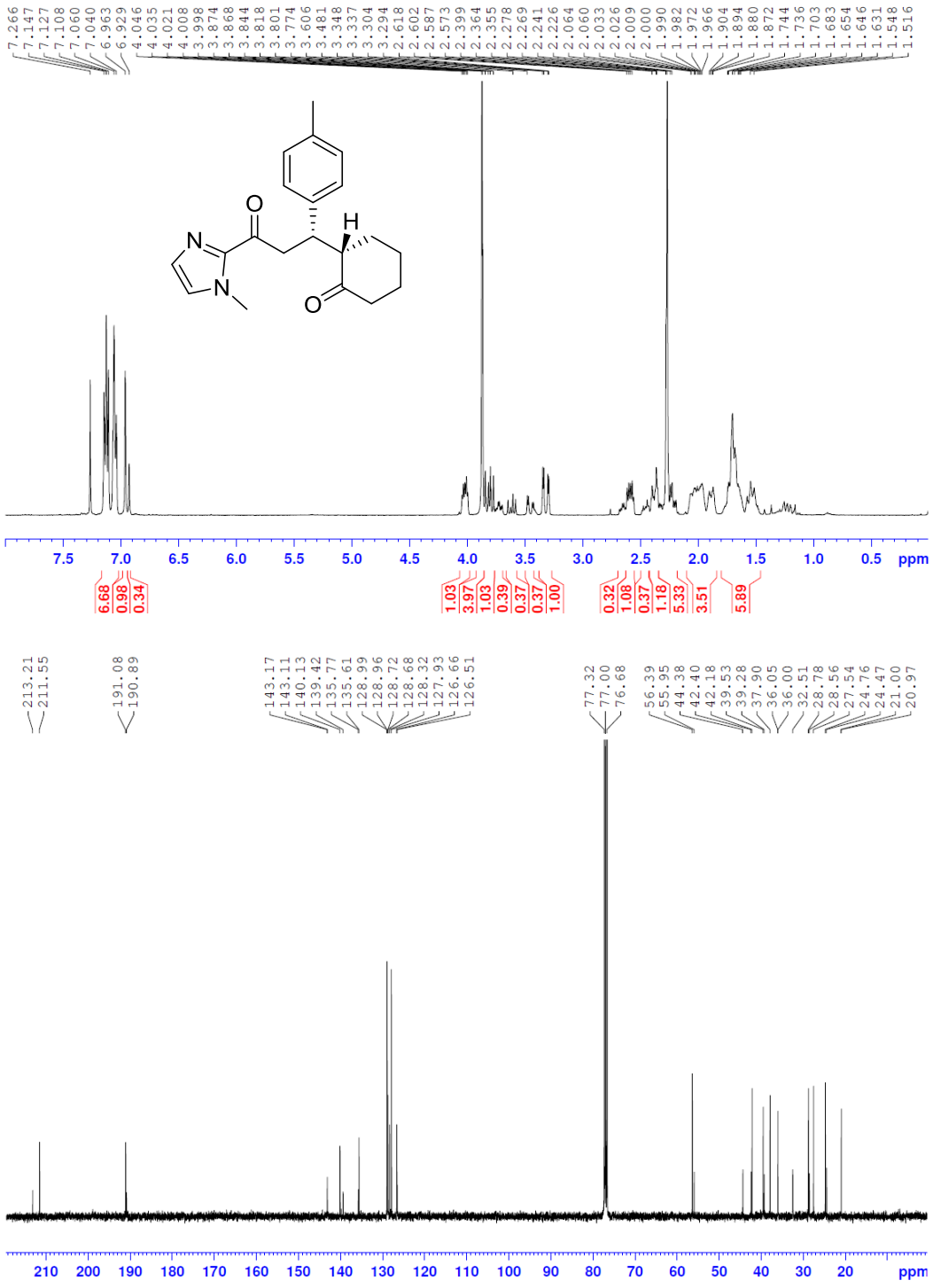
**3d**


7.266
7.157
7.149
7.134
7.128
7.119
7.110
7.099
7.097
7.063
7.058
7.049
7.040
7.036
6.948
4.354
4.342
4.339
4.328
3.860
3.850
3.834
3.817
3.791
3.315
3.304
3.272
3.261
2.515
2.484
2.454
2.408
2.375
2.371
2.364
2.357
2.290
2.277
2.275
2.258
2.243
2.099
2.048
2.042
2.015
2.007
1.886
1.883
1.734
1.726
1.703
1.694
1.669
1.659
1.540
1.508
1.335
1.284
1.257
O
H
N
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.54 1.00 0.10 1.00 0.14 4.29 0.11 0.11 1.01 0.12 1.07 0.35 4.30 1.33 1.14 1.31 1.06 2.38 1.29
211.34
190.97
143.16
141.55
136.16
130.54
128.64
126.61
126.28
125.85
125.56
77.32
77.00
76.68
54.45
42.23
39.49
35.97
33.02
28.57
27.47
25.14
19.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

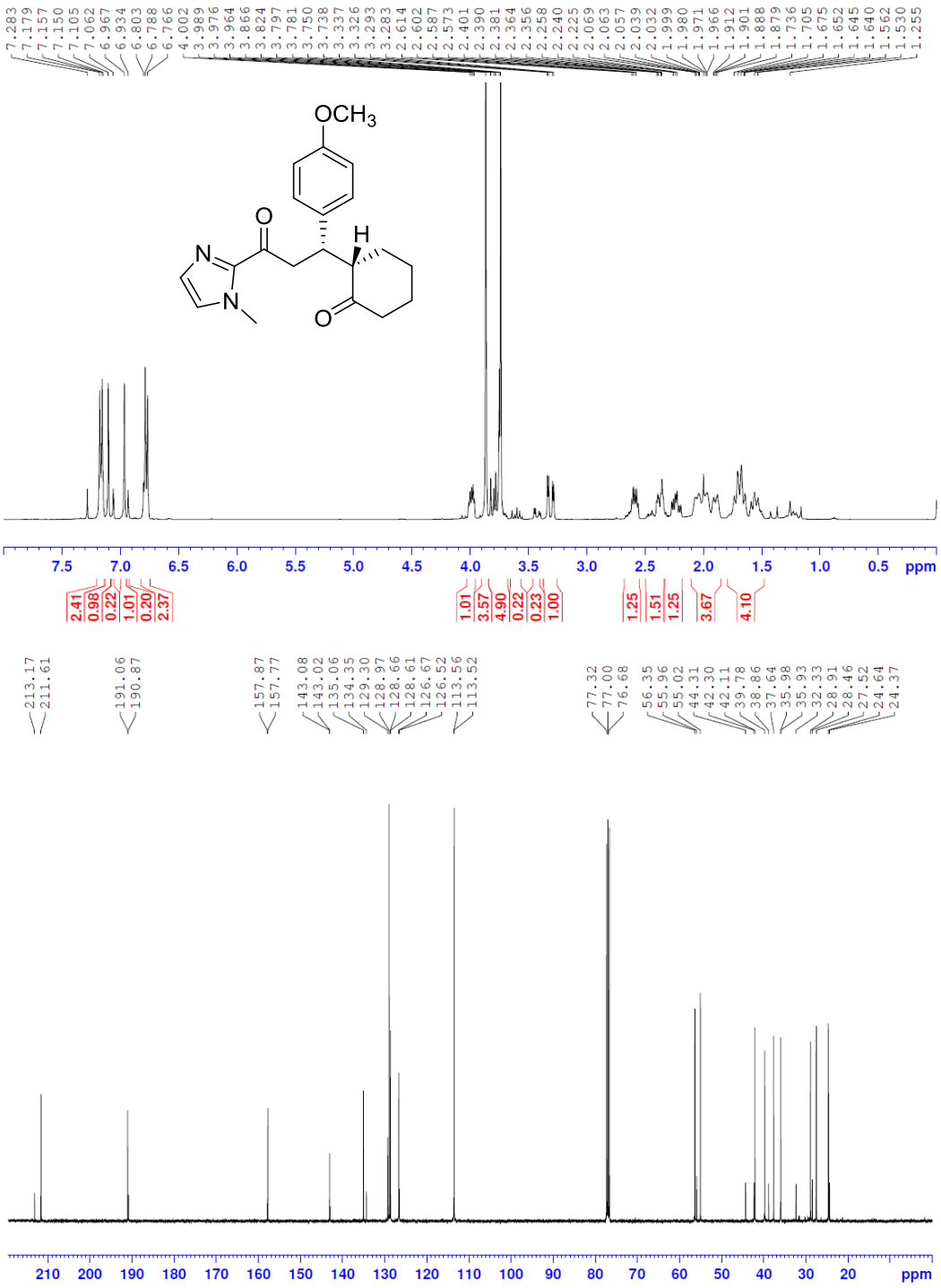
**3e**


7.275
7.141
7.123
7.108
7.061
7.047
7.026
6.966
6.948
6.930
4.047
4.033
4.021
4.010
3.871
3.865
3.854
3.828
3.811
3.785
3.345
3.334
3.301
3.291
2.604
2.589
2.574
2.402
2.376
2.367
2.359
2.356
2.297
2.286
2.266
2.249
2.235
2.032
2.022
2.013
2.001
1.991
1.981
1.975
1.902
1.869
1.738
1.728
1.708
1.700
1.686
1.677
1.669
1.656
1.648
1.644
1.546
1.514
0.000
O
N
N
H
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.81
1.04
3.77
1.04
0.32
0.30
0.29
1.00
0.31
1.01
0.37
1.18
5.12
3.97
4.38
0.44
213.17
211.42
190.99
190.77
143.14
143.10
143.04
142.46
137.72
137.67
129.13
128.90
128.65
128.60
128.07
128.00
127.06
126.94
126.64
126.49
125.47
124.90
77.32
77.00
76.68
56.29
55.88
44.34
42.37
42.15
39.55
39.26
38.04
35.99
35.94
32.54
28.62
28.53
27.46
24.78
24.43
21.43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

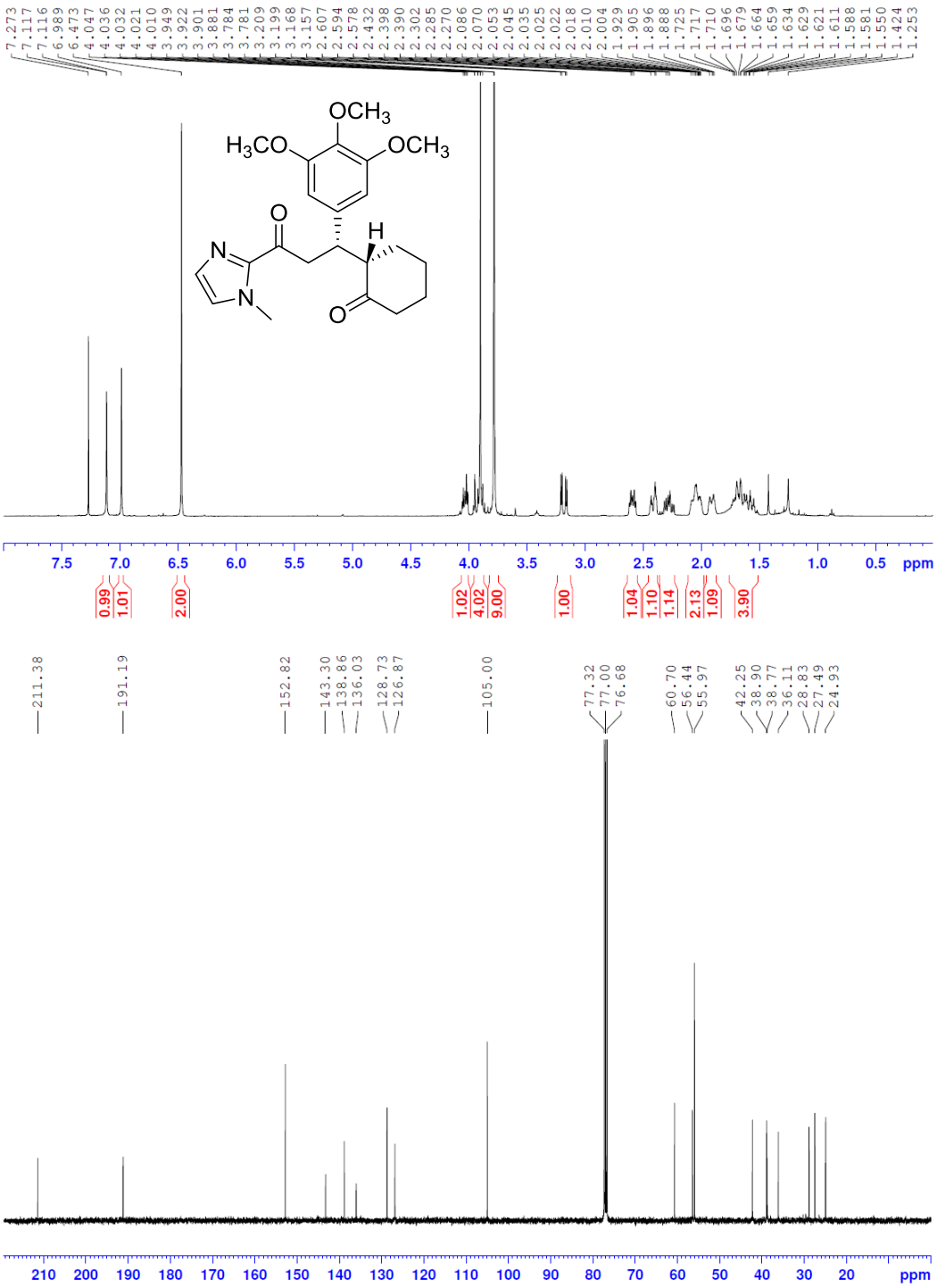
**3f**


7.266
7.147
7.127
7.108
7.060
7.040
6.963
6.929
4.046
4.035
4.021
4.008
3.998
3.874
3.868
3.844
3.818
3.801
3.774
3.606
3.481
3.348
3.337
3.304
3.294
2.618
2.602
2.587
2.573
2.399
2.364
2.355
2.278
2.269
2.241
2.226
2.064
2.060
2.033
2.026
2.009
2.000
1.990
1.982
1.972
1.966
1.904
1.894
1.880
1.872
1.744
1.736
1.703
1.683
1.654
1.646
1.631
1.548
1.516
O
N
N
H
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.68 0.98 0.34 1.03 3.97 1.03 0.39 0.37 0.37 1.00 0.32 1.08 0.37 1.18 5.33 3.51 5.89
213.21
211.55
191.08
190.89
143.17
143.11
140.13
139.42
135.77
135.61
128.99
128.96
128.72
128.68
128.32
127.93
126.66
126.51
77.32
77.00
76.68
56.39
55.95
44.38
42.40
42.18
39.53
39.28
37.90
36.05
36.00
32.51
28.78
28.56
27.54
24.76
24.47
21.00
20.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

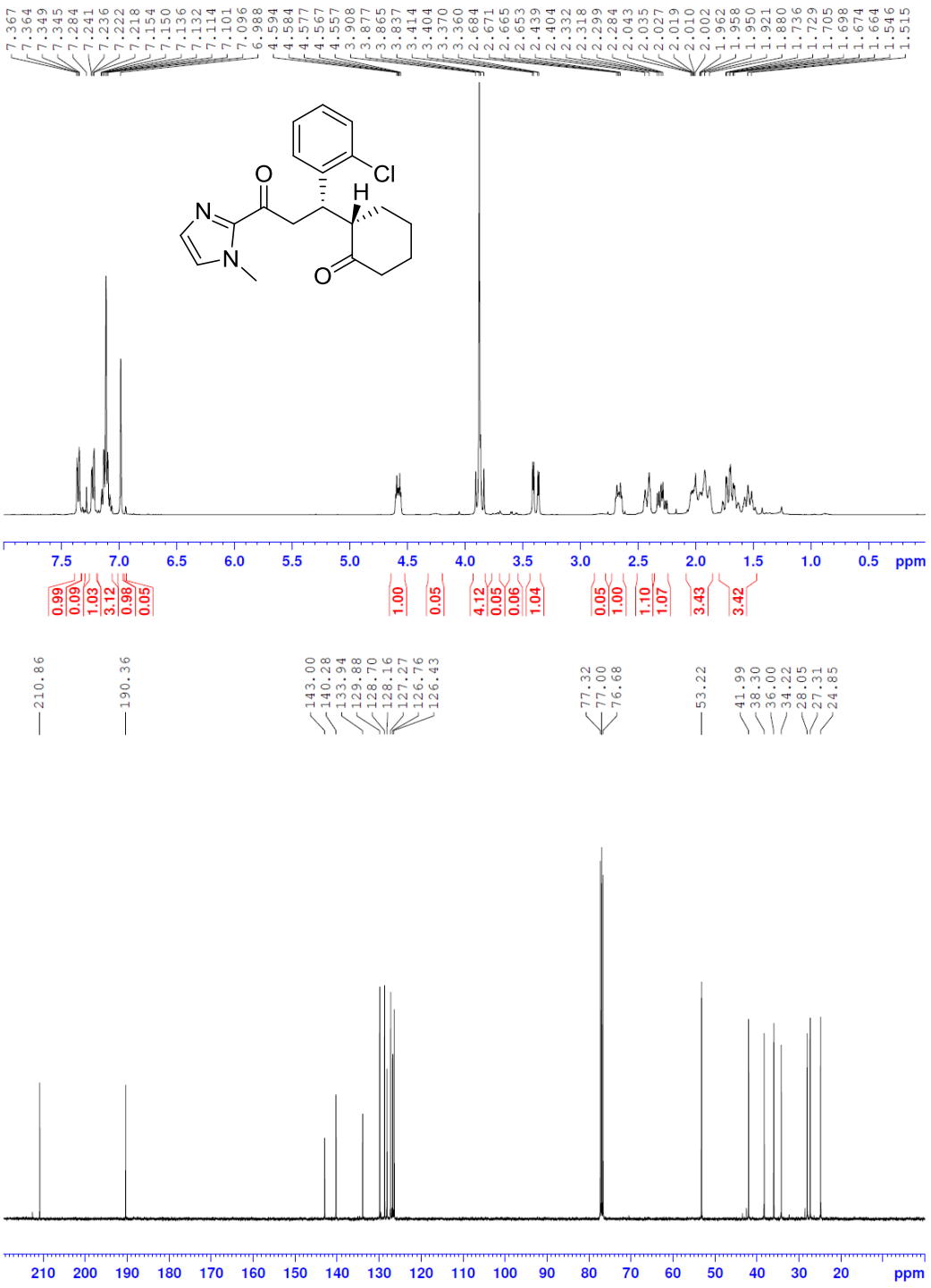
**3g**


7.283
7.179
7.157
7.150
7.105
7.062
6.967
6.934
6.803
6.788
6.766
4.002
3.989
3.976
3.964
3.866
3.824
3.797
3.781
3.750
3.738
3.337
3.326
3.293
3.283
2.614
2.602
2.587
2.573
2.401
2.390
2.381
2.364
2.356
2.258
2.240
2.225
2.069
2.063
2.057
2.039
2.032
1.999
1.980
1.971
1.966
1.912
1.901
1.888
1.879
1.736
1.705
1.675
1.652
1.645
1.640
1.562
1.530
1.255
OCH3
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.41
0.98
0.22
1.01
0.20
2.37
1.01
3.57
4.90
0.22
0.23
1.00
1.25
1.51
1.25
3.67
4.10
213.17
211.61
191.06
190.87
157.87
157.77
143.08
143.02
135.06
134.35
129.30
128.97
128.66
128.61
126.67
126.52
113.56
113.52
77.32
77.00
76.68
56.35
55.96
55.02
44.31
42.30
42.11
39.78
38.86
37.64
35.98
35.93
32.33
28.91
28.46
27.52
24.64
24.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

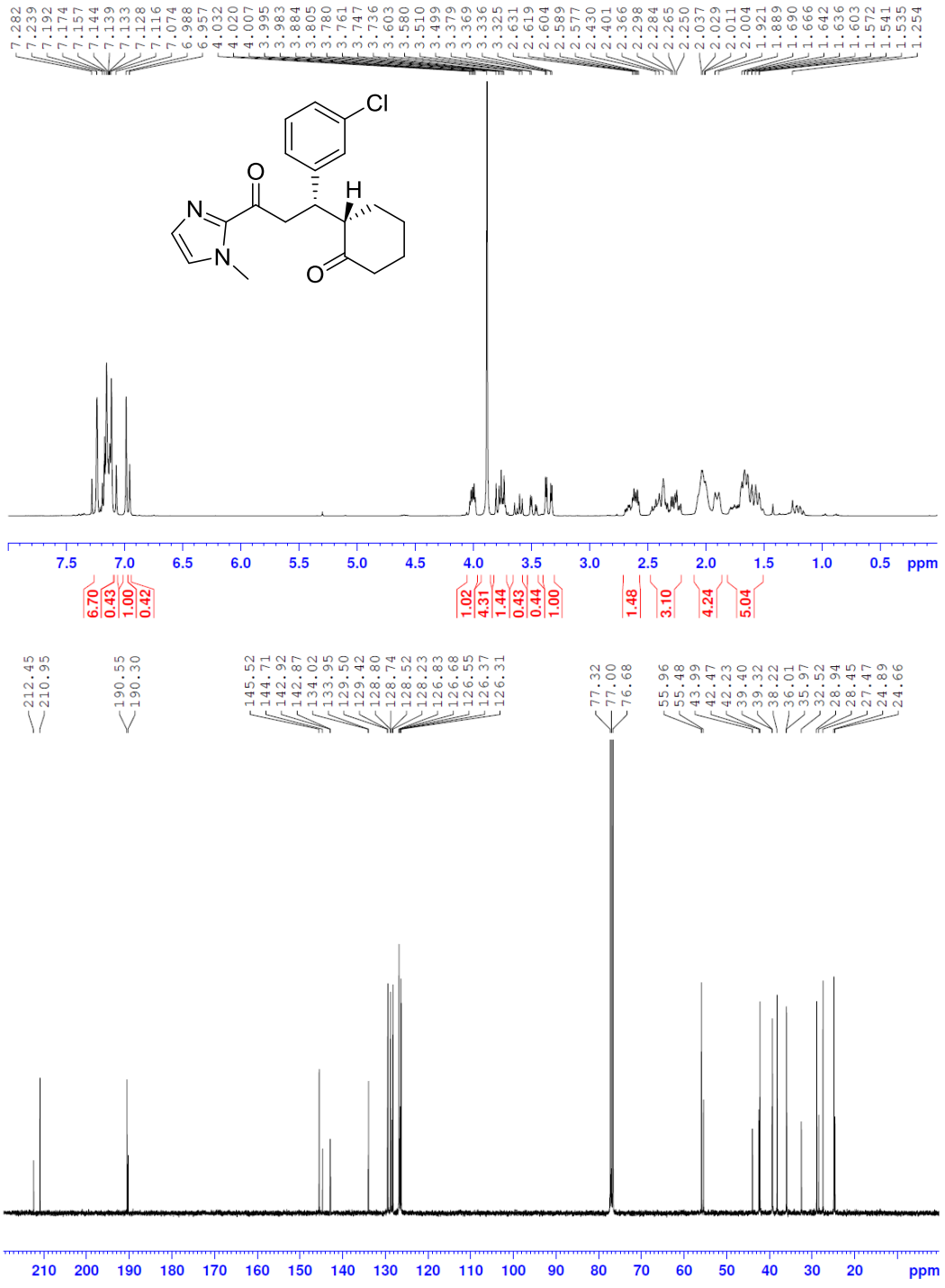
**3h**


7.273
7.117
7.116
6.989
6.473
4.047
4.036
4.032
4.021
4.010
3.949
3.922
3.901
3.881
3.784
3.781
3.209
3.199
3.168
3.157
2.607
2.594
2.578
2.432
2.398
2.390
2.302
2.285
2.270
2.086
2.070
2.053
2.045
2.035
2.025
2.022
2.018
2.010
2.004
1.929
1.905
1.896
1.888
1.725
1.717
1.710
1.696
1.679
1.664
1.659
1.634
1.629
1.621
1.611
1.588
1.581
1.550
1.424
1.253
OCH3
H3CO
OCH3
O
H
N
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99 1.01 2.00 1.02 4.02 9.00 1.00 1.04 1.10 1.14 2.13 1.09 3.90
211.38
191.19
152.82
143.30
138.86
136.03
128.73
126.87
105.00
77.32
77.00
76.68
60.70
56.44
55.97
42.25
38.90
38.77
36.11
28.83
27.49
24.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

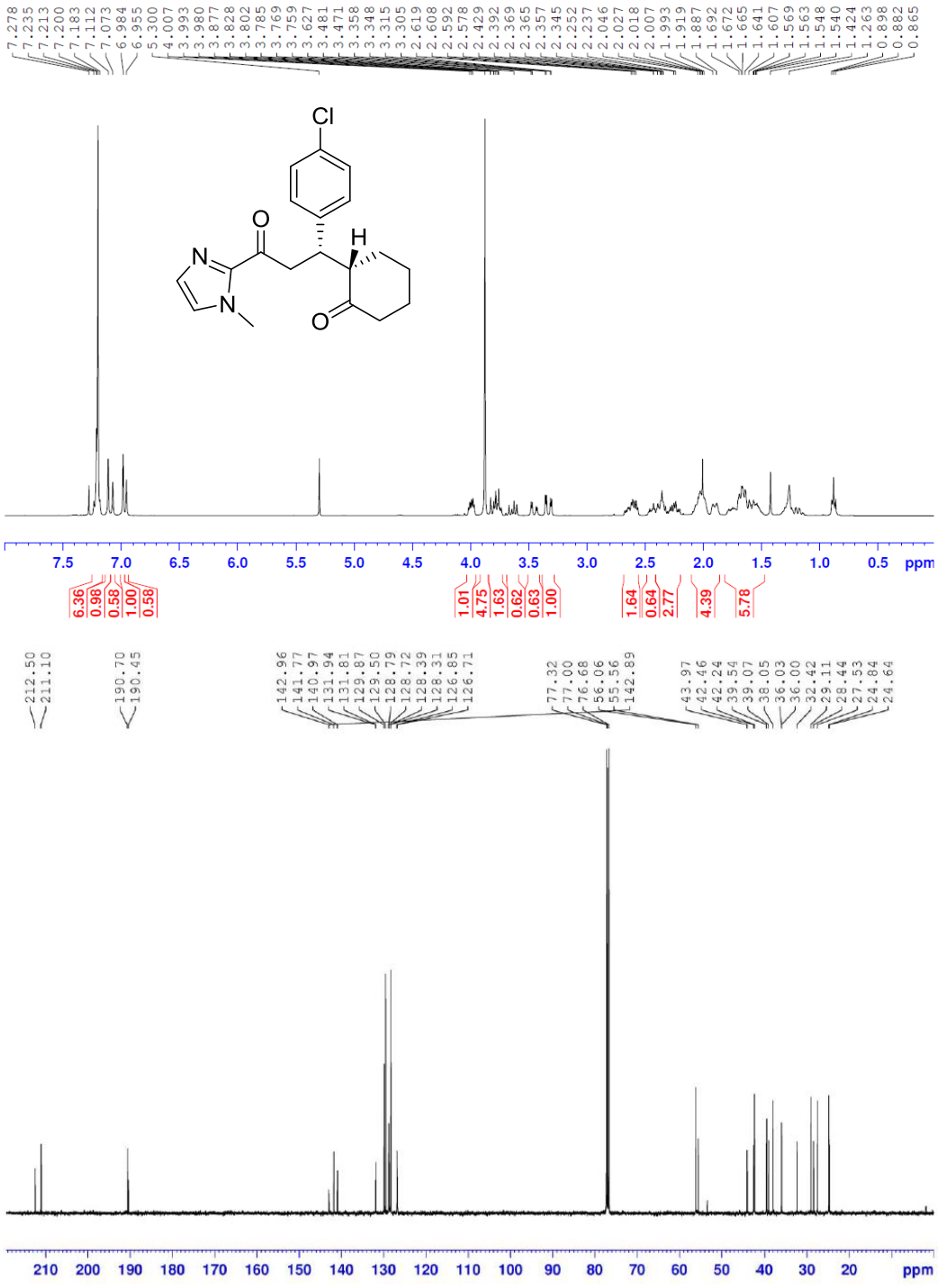
**3i**


7.367
7.364
7.349
7.345
7.284
7.241
7.236
7.222
7.218
7.154
7.150
7.136
7.132
7.114
7.101
7.096
6.988
4.594
4.584
4.577
4.567
4.557
3.908
3.877
3.865
3.837
3.414
3.404
3.370
3.360
2.684
2.671
2.665
2.653
2.439
2.404
2.332
2.318
2.299
2.284
2.043
2.035
2.027
2.019
2.010
2.002
1.962
1.958
1.950
1.921
1.880
1.736
1.729
1.705
1.698
1.674
1.664
1.546
1.515
O
Cl
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.99
0.09
1.03
3.12
0.98
0.05
1.00
0.05
4.12
0.05
0.06
1.04
0.05
1.00
1.10
1.07
3.43
3.42
210.86
190.36
143.00
140.28
133.94
129.88
128.70
128.16
127.27
126.76
126.43
77.32
77.00
76.68
53.22
41.99
38.30
36.00
34.22
28.05
27.31
24.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

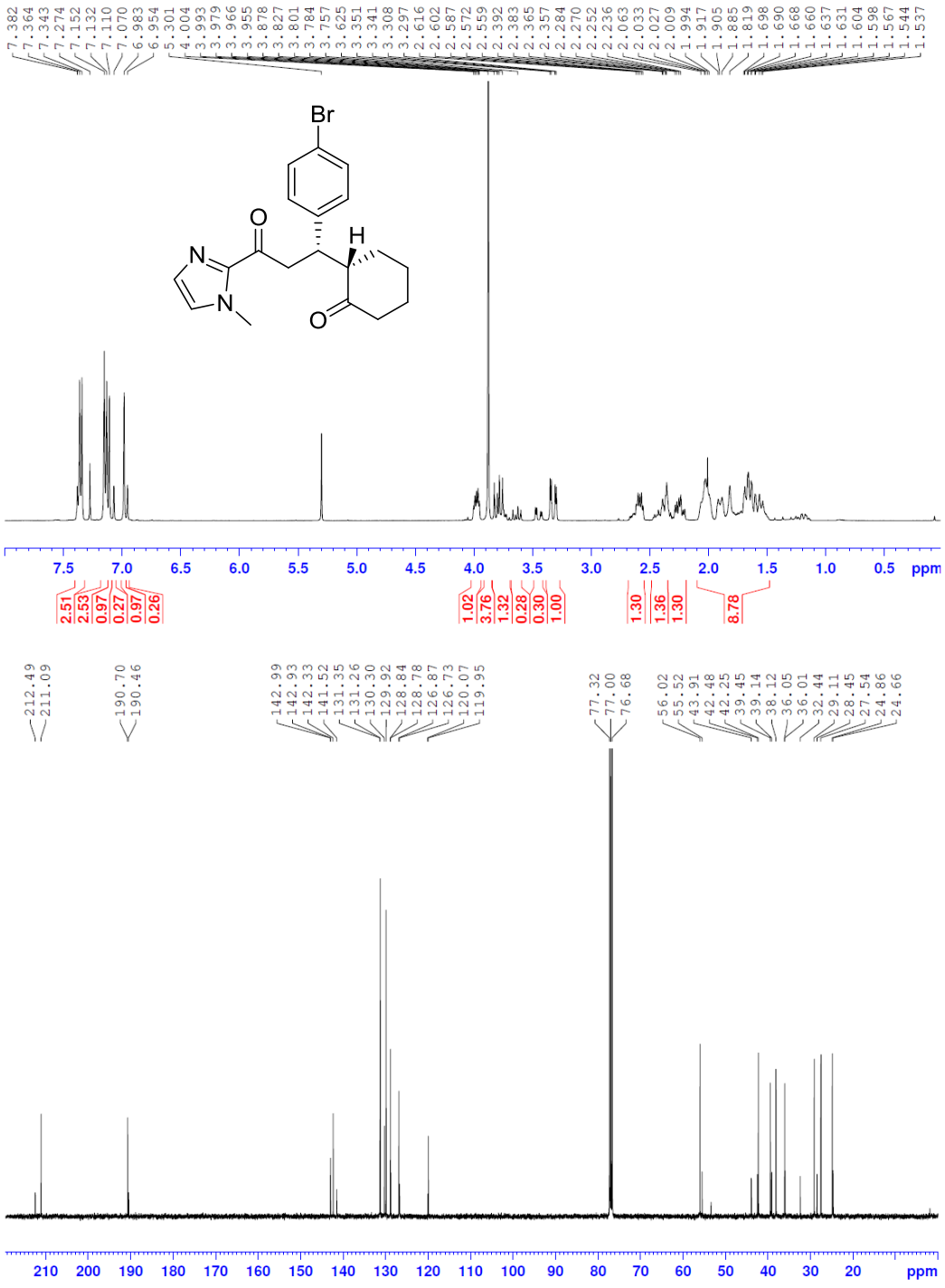
**3j**


7.282
7.239
7.192
7.174
7.157
7.144
7.139
7.133
7.128
7.116
7.074
6.988
6.957
4.032
4.020
4.007
3.995
3.983
3.884
3.805
3.780
3.761
3.747
3.736
3.603
3.580
3.510
3.499
3.379
3.369
3.336
3.325
2.631
2.619
2.604
2.589
2.577
2.430
2.401
2.366
2.298
2.284
2.265
2.250
2.037
2.029
2.011
2.004
1.921
1.889
1.690
1.666
1.642
1.636
1.603
1.572
1.541
1.535
1.254
Cl
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.70
0.43
1.00
0.42
1.02
4.31
1.44
0.43
0.44
1.00
1.48
3.10
4.24
5.04
212.45
210.95
190.55
190.30
145.52
144.71
142.92
142.87
134.02
133.95
129.50
129.42
128.80
128.74
128.52
128.23
126.83
126.68
126.55
126.37
126.31
77.32
77.00
76.68
55.96
55.48
43.99
42.47
42.23
39.40
39.32
38.22
36.01
35.97
32.52
28.94
28.45
27.47
24.89
24.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

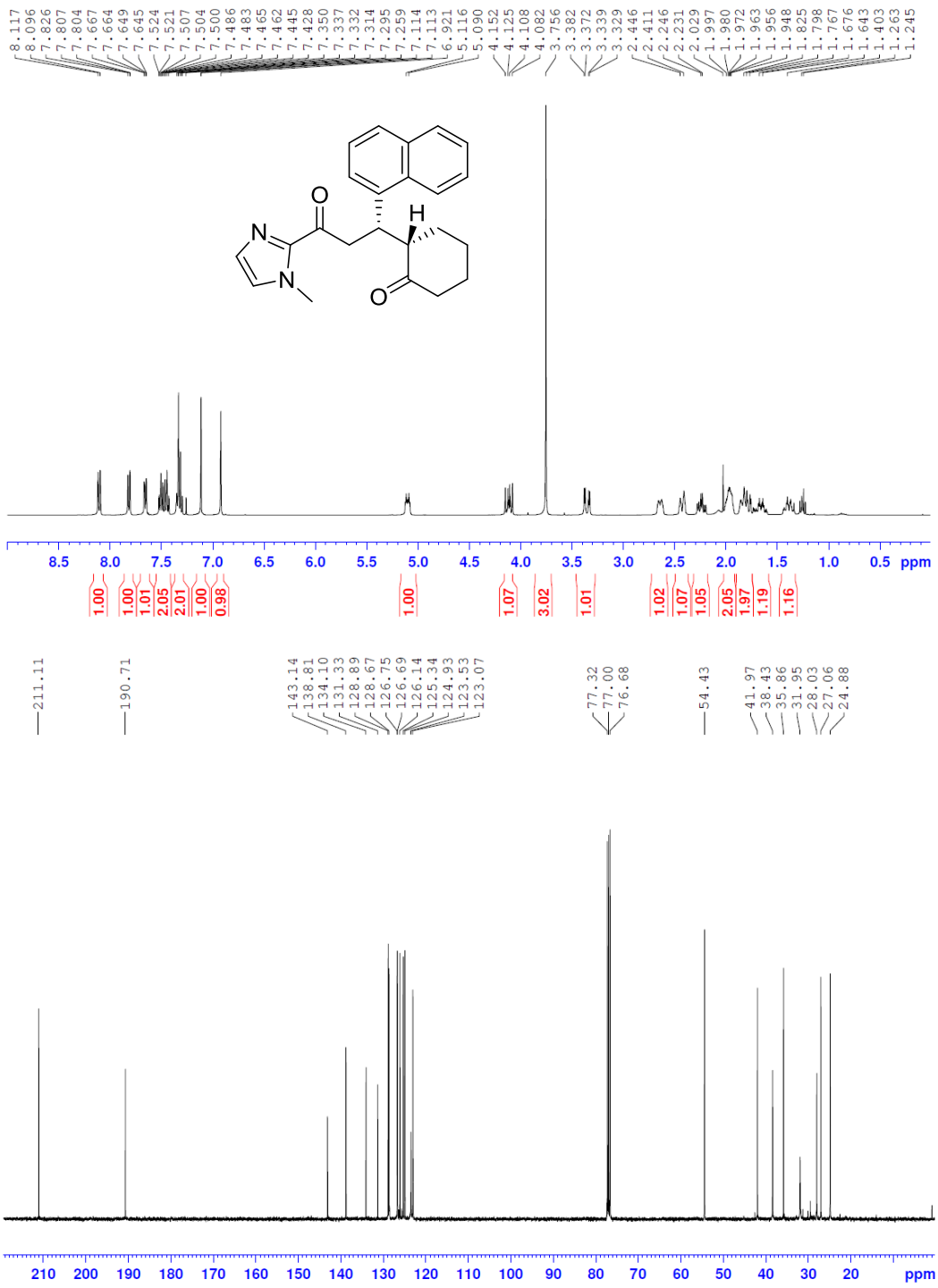
**3k**


7.278
7.235
7.213
7.200
7.183
7.112
7.073
6.984
6.955
5.300
4.007
3.993
3.980
3.877
3.828
3.802
3.785
3.769
3.759
3.627
3.481
3.471
3.358
3.348
3.315
3.305
2.619
2.608
2.592
2.578
2.429
2.392
2.369
2.365
2.357
2.345
2.252
2.237
2.046
2.027
2.018
2.007
1.993
1.919
1.887
1.692
1.672
1.665
1.641
1.607
1.569
1.563
1.548
1.540
1.424
1.263
0.898
0.882
0.865
Cl
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.36
0.98
0.58
1.00
0.58
1.01
4.75
1.63
0.62
0.63
1.00
1.64
0.64
2.77
4.39
5.78
212.50
211.10
190.70
190.45
142.96
141.77
140.97
131.94
131.81
129.87
129.50
128.79
128.72
128.39
128.31
126.85
126.71
77.32
77.00
76.68
56.06
55.56
142.89
43.97
42.46
42.24
39.54
39.07
38.05
36.03
36.00
32.42
29.11
28.44
27.53
24.84
24.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

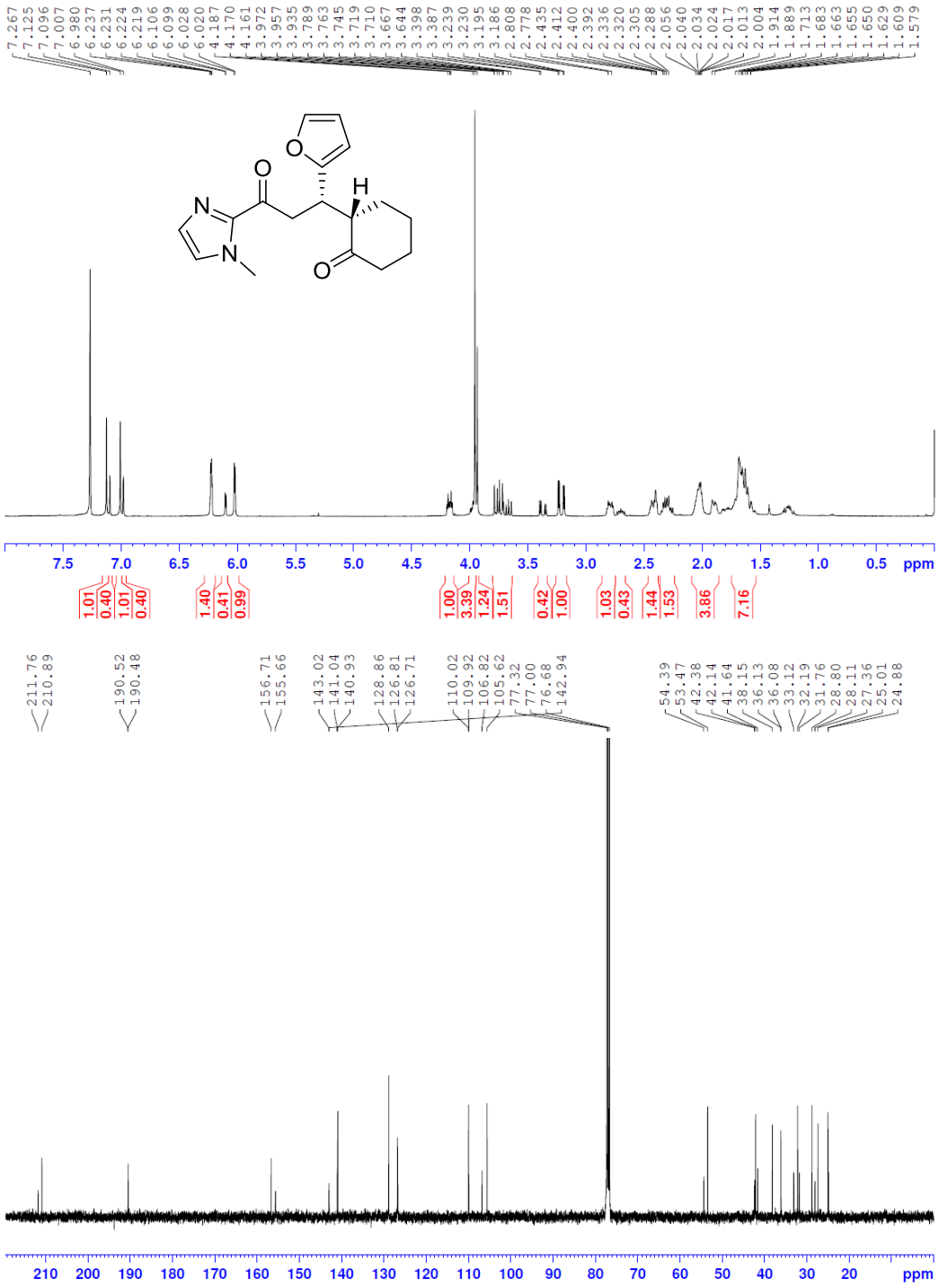
**3l**


7.382
7.364
7.343
7.274
7.152
7.132
7.110
7.070
6.983
6.954
5.301
4.004
3.993
3.979
3.966
3.955
3.878
3.827
3.801
3.784
3.757
3.625
3.351
3.341
3.308
3.297
2.616
2.602
2.587
2.572
2.559
2.392
2.383
2.365
2.357
2.284
2.270
2.252
2.236
2.063
2.033
2.027
2.009
1.994
1.917
1.905
1.885
1.819
1.698
1.690
1.668
1.660
1.637
1.631
1.604
1.598
1.567
1.544
1.537
Br
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.51
2.53
0.97
0.27
0.97
0.26
1.02
3.76
1.32
0.28
0.30
1.00
1.30
1.36
1.30
8.78
212.49
211.09
190.70
190.46
142.99
142.93
142.33
141.52
131.35
131.26
130.30
129.92
128.84
128.78
126.87
126.73
120.07
119.95
77.32
77.00
76.68
56.02
55.52
43.91
42.48
42.25
39.45
39.14
38.12
36.05
36.01
32.44
29.11
28.45
27.54
24.86
24.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

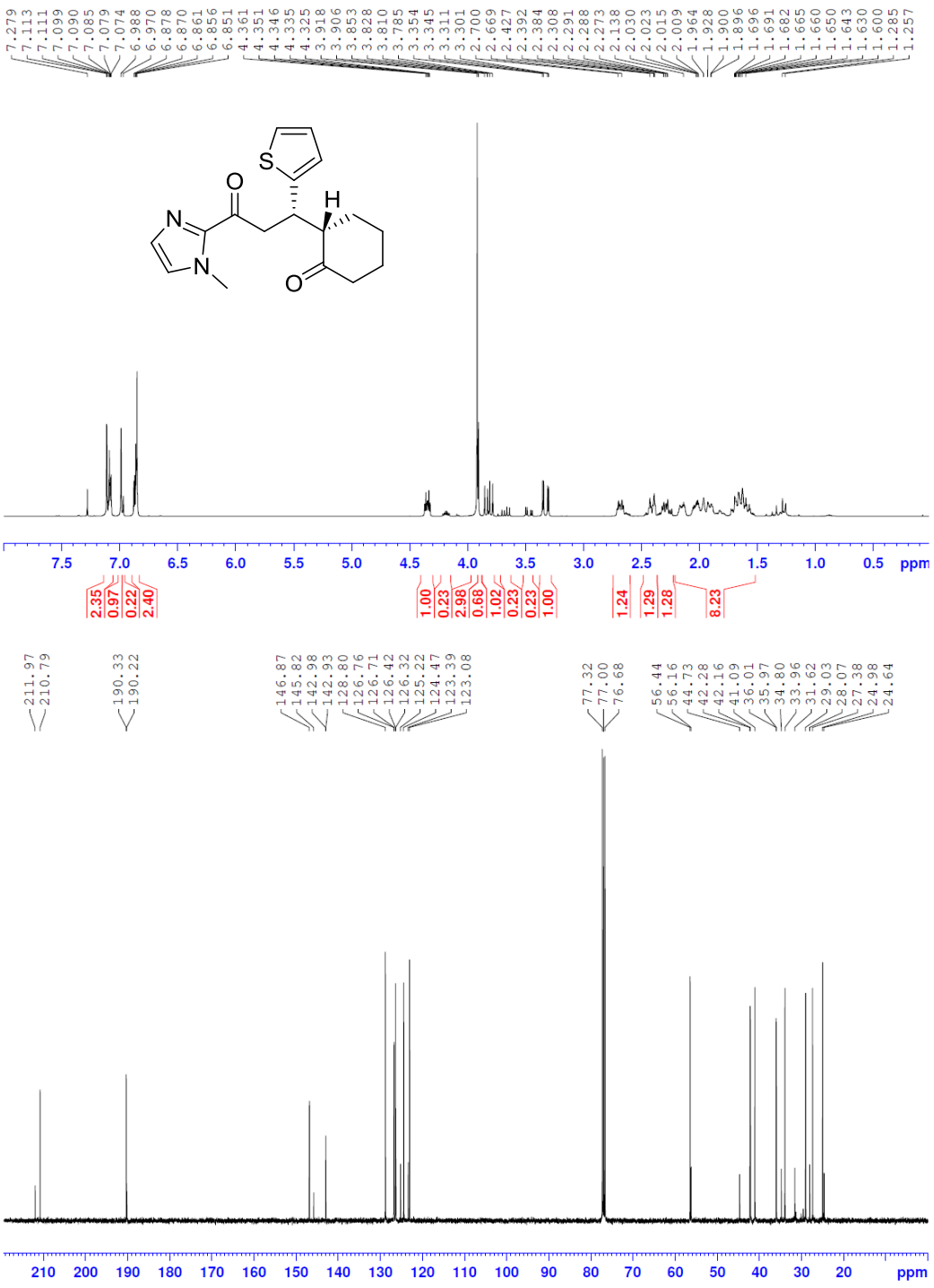
**3m**


8.117
8.096
7.826
7.807
7.804
7.667
7.664
7.649
7.645
7.524
7.521
7.507
7.504
7.500
7.486
7.483
7.465
7.462
7.445
7.428
7.350
7.337
7.332
7.314
7.295
7.259
7.114
7.113
6.921
5.116
5.090
4.152
4.125
4.108
4.082
3.756
3.382
3.372
3.339
3.329
2.446
2.411
2.246
2.231
2.029
1.997
1.980
1.972
1.963
1.956
1.948
1.825
1.798
1.767
1.676
1.643
1.403
1.263
1.245
O
N
N
H
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.00 1.01 2.05 2.01 1.00 0.98 1.00 1.07 3.02 1.01 1.02 1.07 1.05 2.05 1.97 1.19 1.16
211.11
190.71
143.14
138.81
134.10
131.33
128.89
128.67
126.75
126.69
126.14
125.34
124.93
123.53
123.07
77.32
77.00
76.68
54.43
41.97
38.43
35.86
31.95
28.03
27.06
24.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

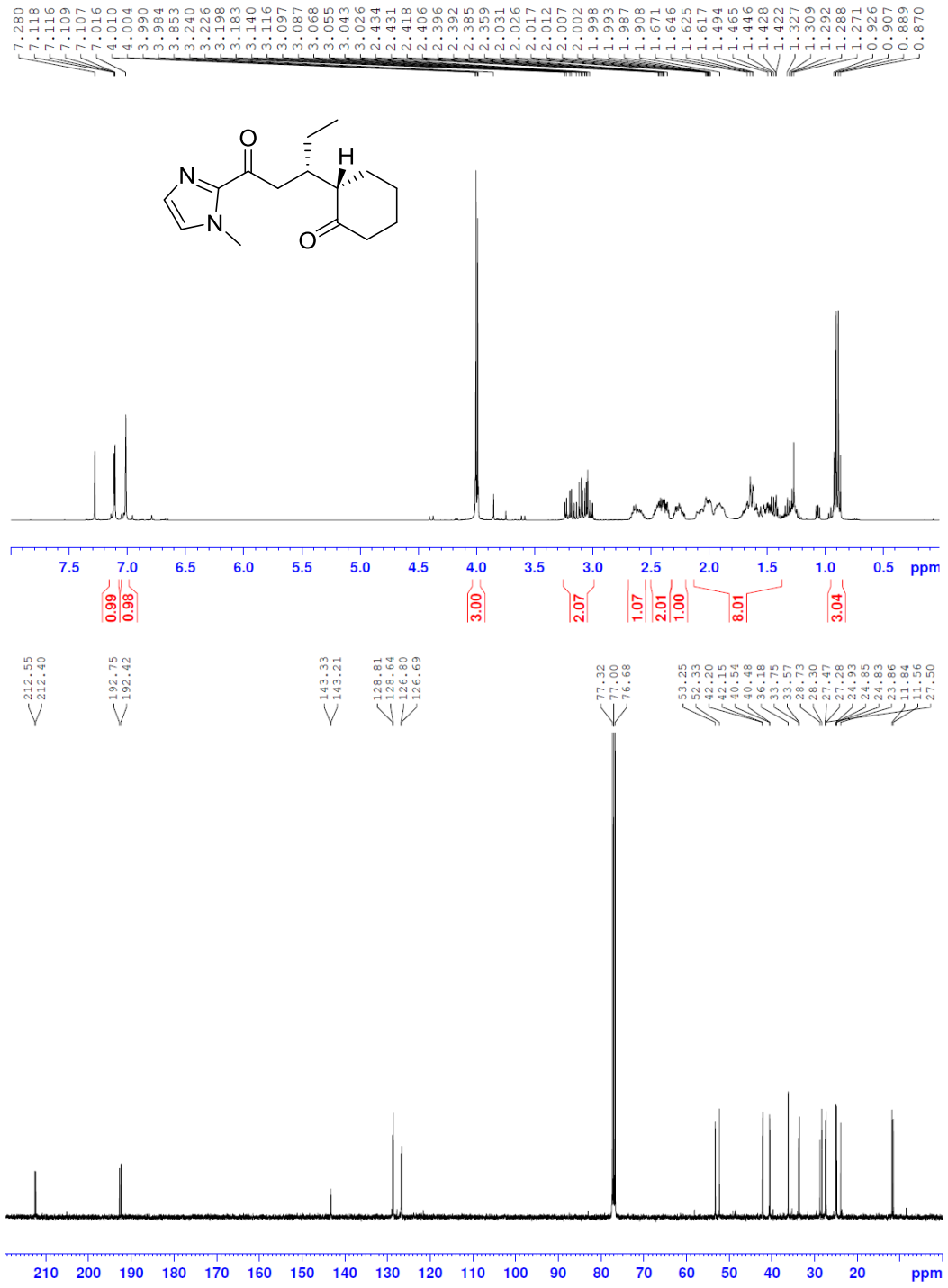
**3n**


7.267
7.125
7.096
7.007
6.980
6.237
6.231
6.224
6.219
6.106
6.099
6.028
6.020
4.187
4.170
4.161
3.972
3.957
3.935
3.789
3.763
3.745
3.719
3.710
3.667
3.644
3.398
3.387
3.239
3.230
3.195
3.186
2.808
2.778
2.435
2.412
2.400
2.392
2.336
2.320
2.305
2.288
2.056
2.040
2.034
2.024
2.017
2.013
2.004
1.914
1.889
1.713
1.683
1.663
1.655
1.650
1.629
1.609
1.579
O
O
N
N
H
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01 0.40 1.01 0.40 1.40 0.41 0.99 1.00 3.39 1.24 1.51 0.42 1.00 1.03 0.43 1.44 1.53 3.86 7.16
211.76
210.89
190.52
190.48
156.71
155.66
143.02
141.04
140.93
128.86
126.81
126.71
110.02
109.92
106.82
105.62
77.32
77.00
76.68
142.94
54.39
53.47
42.38
42.14
41.64
38.15
36.13
36.08
33.12
32.19
31.76
28.80
28.11
27.36
25.01
24.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

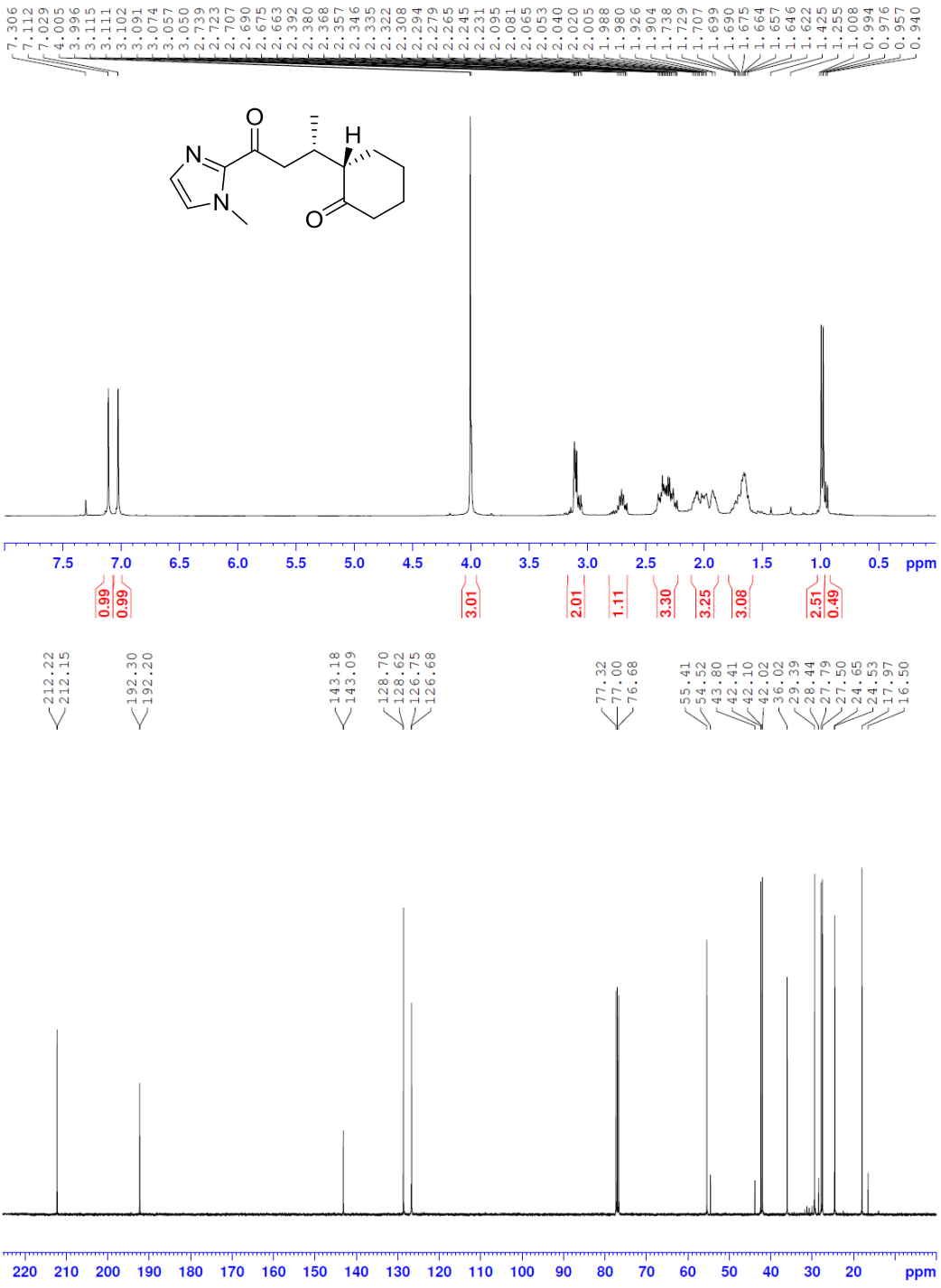
**3o**


7.279
7.113
7.111
7.099
7.090
7.085
7.079
7.074
6.988
6.970
6.878
6.870
6.861
6.856
6.851
4.361
4.351
4.346
4.335
4.325
3.918
3.906
3.853
3.828
3.810
3.785
3.354
3.345
3.311
3.301
2.700
2.669
2.427
2.392
2.384
2.308
2.291
2.288
2.273
2.138
2.030
2.023
2.015
2.009
1.964
1.928
1.900
1.896
1.696
1.691
1.682
1.665
1.660
1.650
1.643
1.630
1.600
1.285
1.257
S
O
H
N
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.35
0.97
0.22
2.40
1.00
0.23
2.98
0.68
1.02
0.23
0.23
1.00
1.24
1.29
1.28
8.23
211.97
210.79
190.33
190.22
146.87
145.82
142.98
142.93
128.80
126.76
126.71
126.42
126.32
125.22
124.47
123.39
123.08
77.32
77.00
76.68
56.44
56.16
44.73
42.28
42.16
41.09
36.01
35.97
34.80
33.96
31.62
29.03
28.07
27.38
24.98
24.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

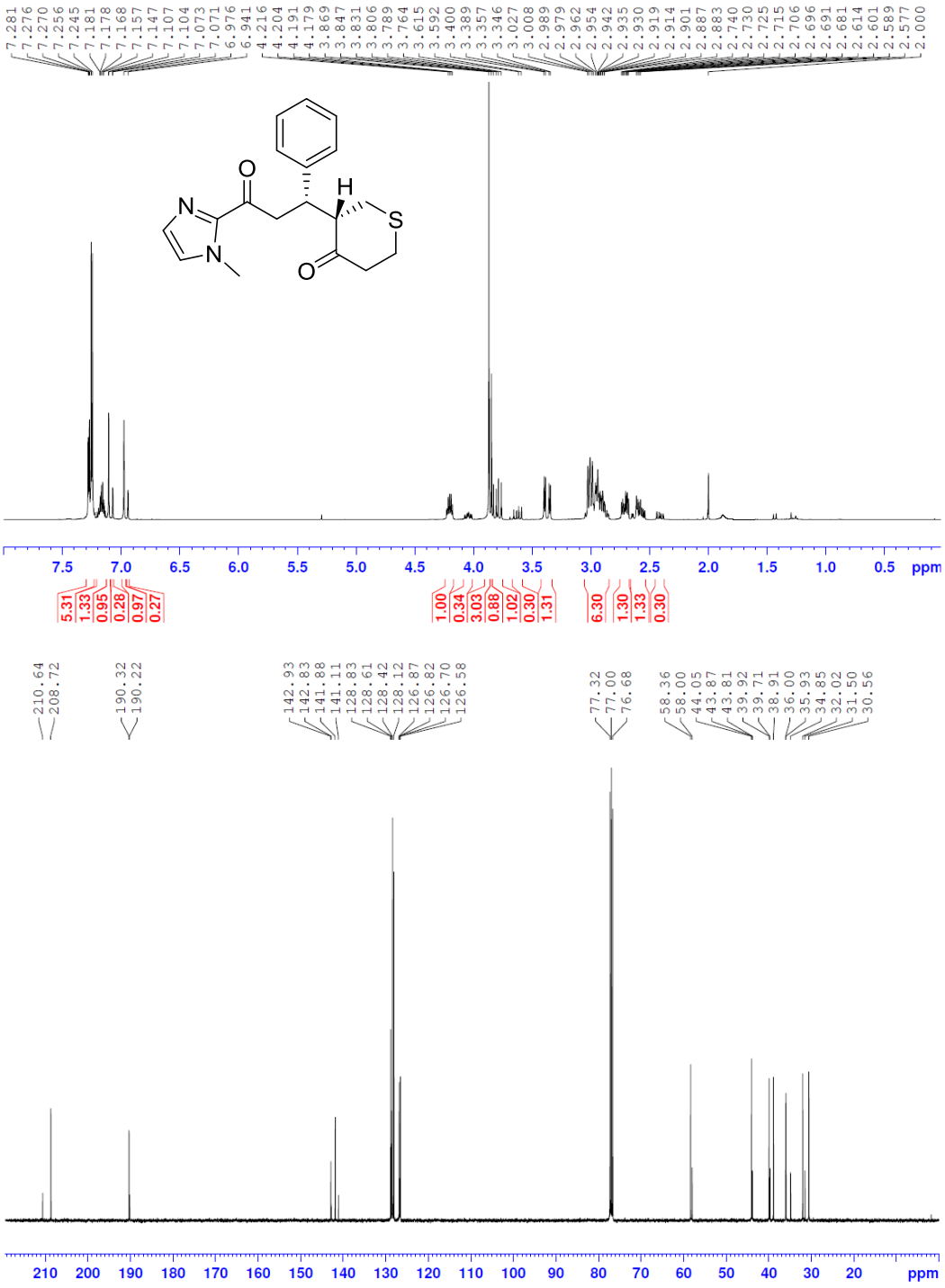
**3p**


7.280
7.118
7.116
7.109
7.107
7.016
4.010
4.004
3.990
3.984
3.853
3.240
3.226
3.198
3.183
3.140
3.116
3.097
3.087
3.068
3.055
3.043
3.026
2.434
2.431
2.418
2.406
2.396
2.392
2.385
2.359
2.031
2.026
2.017
2.012
2.007
2.002
1.998
1.993
1.987
1.908
1.671
1.646
1.625
1.617
1.494
1.465
1.446
1.428
1.422
1.327
1.309
1.292
1.288
1.271
0.926
0.907
0.889
0.870
O
H
N
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
0.98
3.00
2.07
1.07
2.01
1.00
8.01
3.04
212.55
212.40
192.75
192.42
143.33
143.21
128.81
128.64
126.80
126.69
77.32
77.00
76.68
53.25
52.33
42.20
42.15
40.54
40.48
36.18
33.75
33.57
33.13
28.30
27.47
27.28
24.93
24.85
24.83
23.86
11.84
11.56
27.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

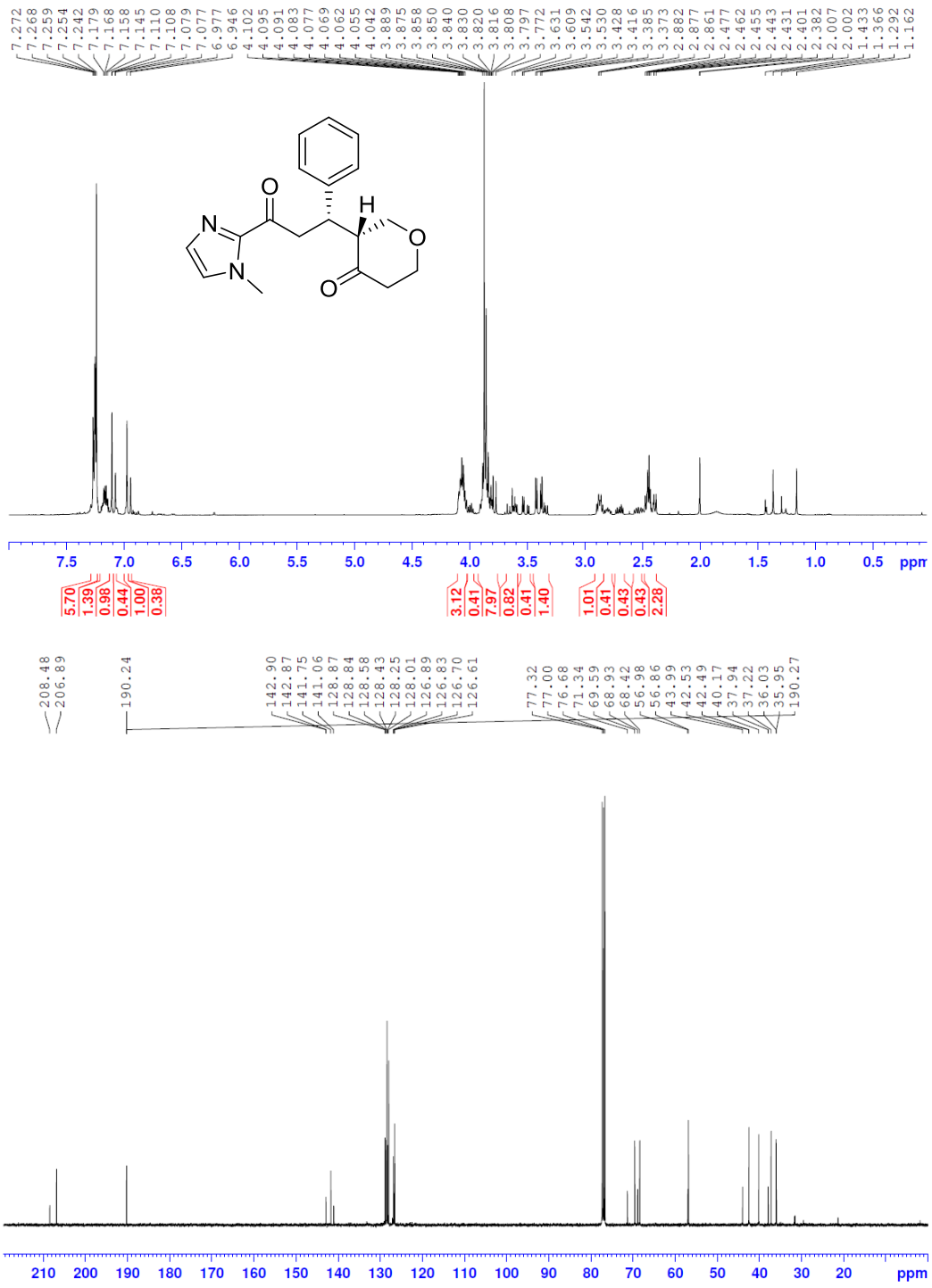
**3q**


7.306
7.112
7.029
4.005
3.996
3.115
3.111
3.102
3.091
3.074
3.057
3.050
2.739
2.723
2.707
2.690
2.675
2.663
2.392
2.380
2.368
2.357
2.346
2.335
2.322
2.308
2.294
2.279
2.265
2.245
2.231
2.095
2.081
2.065
2.053
2.040
2.020
2.005
1.988
1.980
1.926
1.904
1.738
1.729
1.707
1.699
1.690
1.675
1.664
1.657
1.646
1.622
1.425
1.255
1.008
0.994
0.976
0.957
0.940
O
H
N
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
0.99
3.01
2.01
1.11
3.30
3.25
3.08
2.51
0.49
212.22
212.15
192.30
192.20
143.18
143.09
128.70
128.62
126.75
126.68
77.32
77.00
76.68
55.41
54.52
43.80
42.41
42.10
42.02
36.02
29.39
28.44
27.79
27.50
24.65
24.53
17.97
16.50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

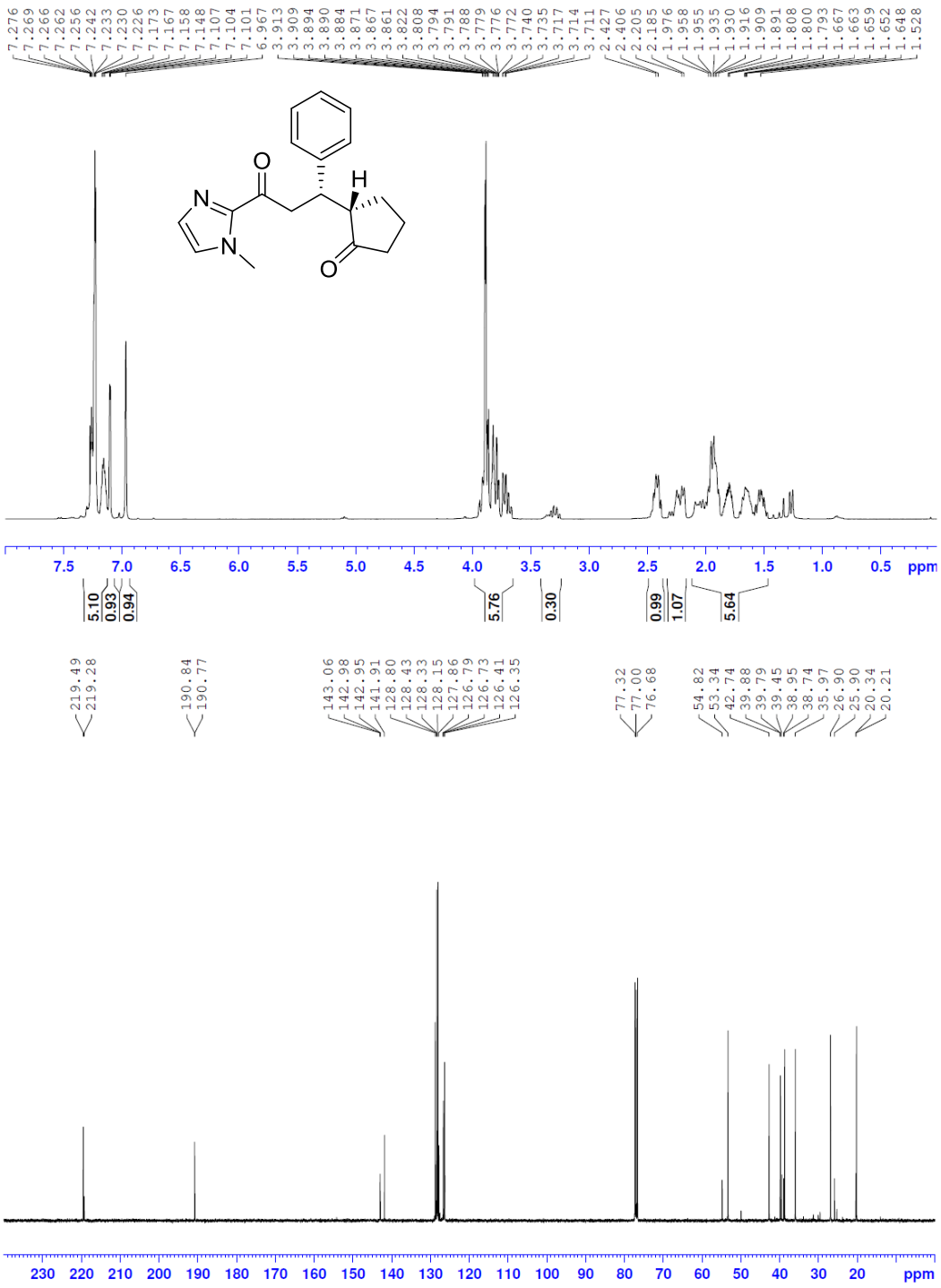
**3r**


7.281
7.276
7.270
7.256
7.245
7.181
7.178
7.168
7.157
7.147
7.107
7.104
7.073
7.071
6.976
6.941
4.216
4.204
4.191
4.179
3.869
3.847
3.831
3.806
3.789
3.764
3.615
3.592
3.400
3.389
3.357
3.346
3.027
3.008
2.989
2.979
2.962
2.954
2.942
2.935
2.930
2.919
2.914
2.901
2.887
2.883
2.740
2.730
2.725
2.715
2.706
2.696
2.691
2.681
2.614
2.601
2.589
2.577
2.000
O
N
N
H
S
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.31 1.33 0.95 0.28 0.97 0.27
1.00 0.34 3.03 0.88 1.02 0.30 1.31
6.30 1.30 1.33 0.30
210.64
208.72
190.32
190.22
142.93
142.83
141.88
141.11
128.83
128.61
128.42
128.12
126.87
126.82
126.70
126.58
77.32
77.00
76.68
58.36
58.00
44.05
43.87
43.81
39.92
39.71
38.91
36.00
35.93
34.85
32.02
31.50
30.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

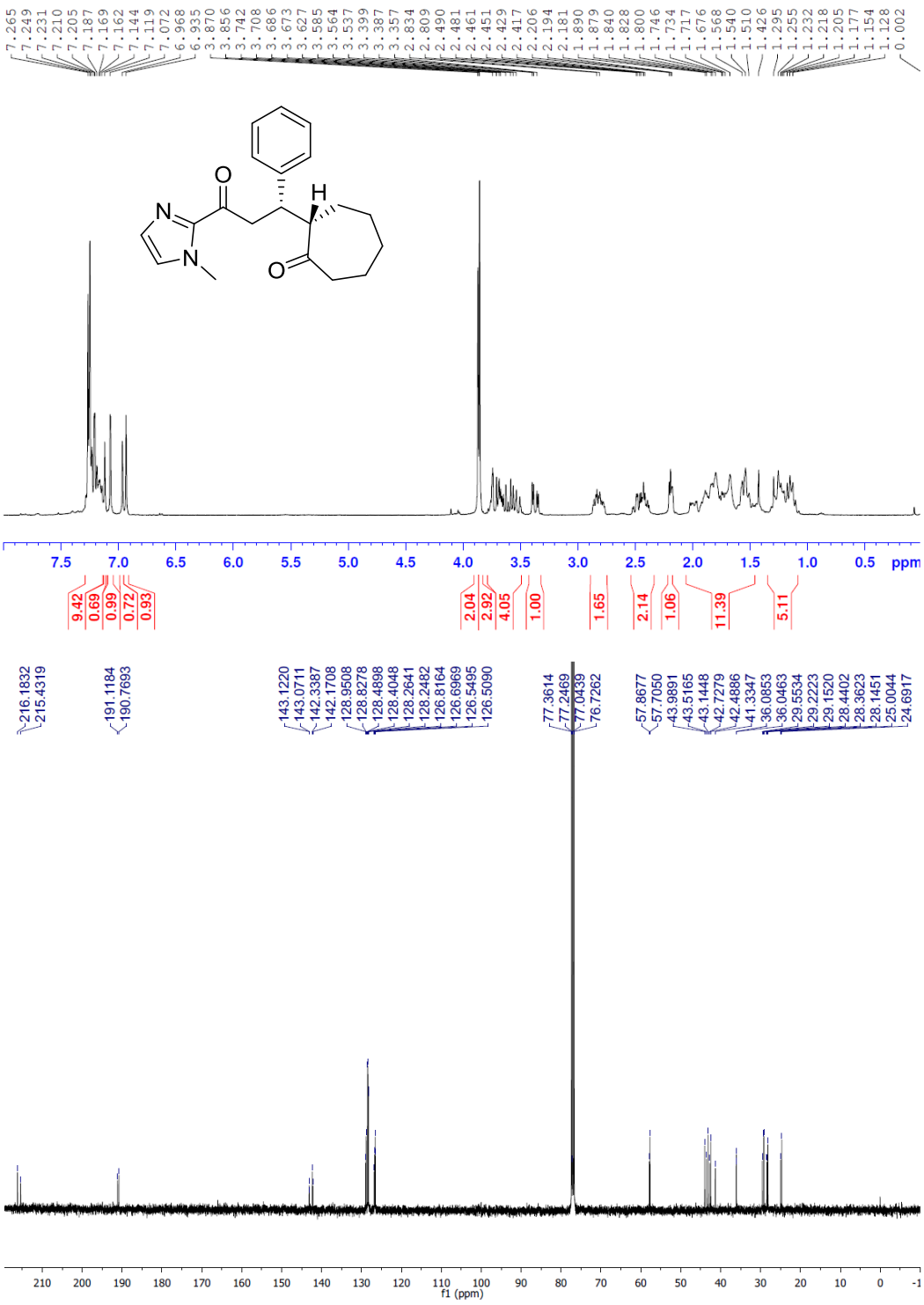
**3s**


7.272
7.268
7.259
7.254
7.242
7.179
7.168
7.158
7.145
7.110
7.108
7.079
7.077
7.077
6.977
6.946
4.102
4.095
4.091
4.083
4.077
4.069
4.062
4.055
4.042
3.889
3.875
3.858
3.850
3.840
3.830
3.820
3.816
3.808
3.797
3.772
3.631
3.609
3.542
3.530
3.428
3.416
3.385
3.373
2.882
2.877
2.861
2.477
2.462
2.455
2.443
2.431
2.401
2.382
2.007
2.002
1.433
1.366
1.292
1.162
O
H
N
O
N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.70
1.39
0.98
0.44
1.00
0.38
3.12
0.41
7.97
0.82
0.41
1.40
1.01
0.41
0.43
0.43
2.28
208.48
206.89
190.24
142.90
142.87
141.75
141.06
128.87
128.84
128.58
128.43
128.25
128.01
126.89
126.83
126.70
126.61
77.32
77.00
76.68
71.34
69.59
68.93
68.42
56.98
56.86
43.99
42.53
42.49
40.17
37.94
37.22
36.03
35.95
190.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

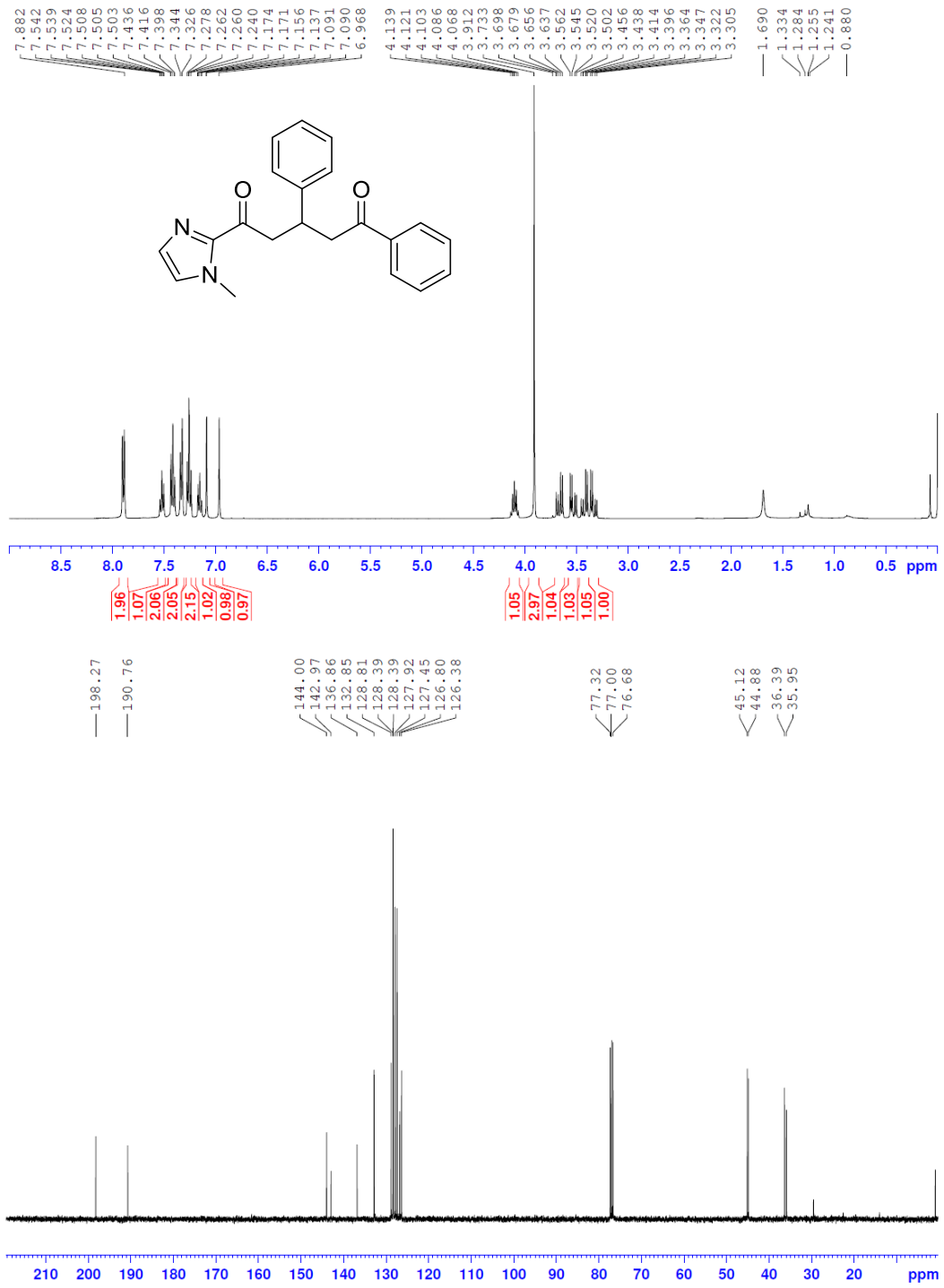
**3t**


7.276
7.269
7.266
7.262
7.256
7.242
7.233
7.230
7.226
7.173
7.167
7.158
7.148
7.107
7.104
7.101
6.967
3.913
3.909
3.894
3.890
3.884
3.871
3.867
3.861
3.822
3.808
3.794
3.791
3.788
3.779
3.776
3.772
3.740
3.735
3.717
3.714
3.711
2.427
2.406
2.205
2.185
1.976
1.958
1.955
1.935
1.930
1.916
1.909
1.891
1.808
1.800
1.793
1.667
1.663
1.659
1.652
1.648
1.528
O
N
H
N
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.10
0.93
0.94
5.76
0.30
0.99
1.07
5.64
219.49
219.28
190.84
190.77
143.06
142.98
142.95
141.91
128.80
128.43
128.33
128.15
127.86
126.79
126.73
126.41
126.35
77.32
77.00
76.68
54.82
53.34
42.74
39.88
39.79
39.45
38.95
38.74
35.97
26.90
25.90
20.34
20.21
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

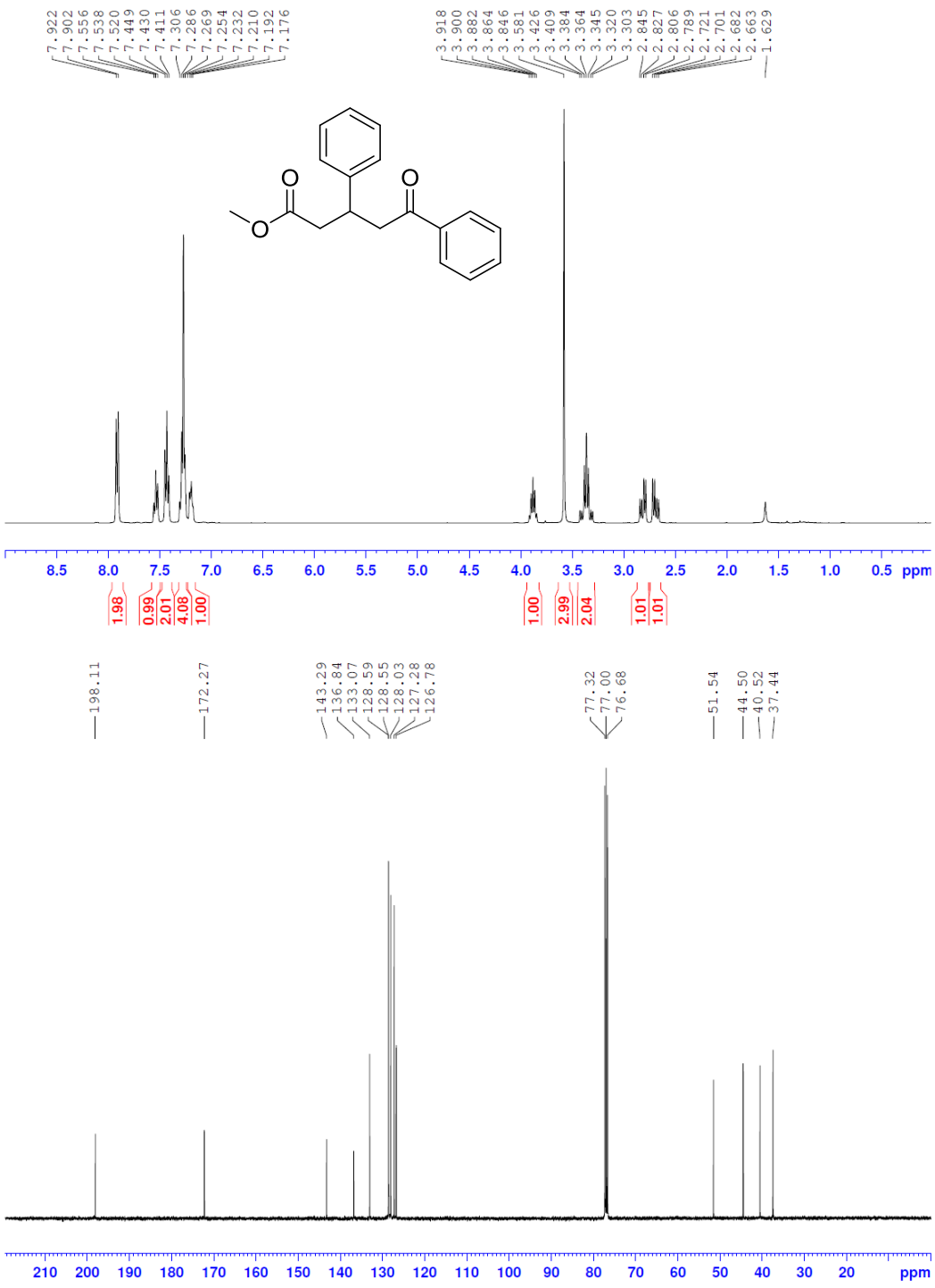
**3u**


7.265
7.249
7.231
7.210
7.205
7.187
7.169
7.162
7.144
7.119
7.072
6.968
6.935
3.870
3.856
3.742
3.708
3.686
3.673
3.627
3.585
3.564
3.537
3.399
3.387
3.357
2.834
2.809
2.490
2.481
2.461
2.451
2.429
2.417
2.206
2.194
2.181
1.890
1.879
1.840
1.828
1.800
1.746
1.734
1.717
1.676
1.568
1.540
1.510
1.426
1.295
1.255
1.232
1.218
1.205
1.177
1.154
1.128
0.002
O
N
N
H
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
9.42
0.69
0.99
0.72
0.93
2.04
2.92
4.05
1.00
1.65
2.14
1.06
11.39
5.11
216.1832
215.4319
191.1184
190.7693
143.1220
143.0711
142.3387
142.1708
128.9508
128.8278
128.4898
128.4048
128.2641
128.2482
126.8164
126.6969
126.5495
126.5090
77.3614
77.2469
77.0439
76.7262
57.8677
57.7050
43.9891
43.5165
43.1448
42.7279
42.4886
41.3347
36.0853
36.0463
29.5534
29.2223
29.1520
28.4402
28.3623
28.1451
25.0044
24.6917
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

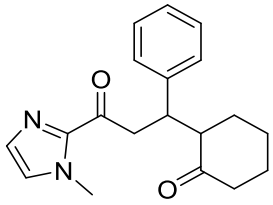
**3v**


7.882
7.542
7.539
7.524
7.508
7.505
7.503
7.436
7.416
7.398
7.344
7.326
7.278
7.262
7.260
7.240
7.174
7.171
7.156
7.137
7.091
7.090
6.968
4.139
4.121
4.103
4.086
4.068
3.912
3.733
3.698
3.679
3.656
3.637
3.562
3.545
3.520
3.502
3.456
3.438
3.414
3.396
3.364
3.347
3.322
3.305
1.690
1.334
1.284
1.255
1.241
0.880
O
O
N
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.96 1.07 2.06 2.05 2.15 1.02 0.98 0.97
1.05 2.97 1.04 1.03 1.05 1.00
198.27
190.76
144.00
142.97
136.86
132.85
128.81
128.39
128.39
127.92
127.45
126.80
126.38
77.32
77.00
76.68
45.12
44.88
36.39
35.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Compound **4**

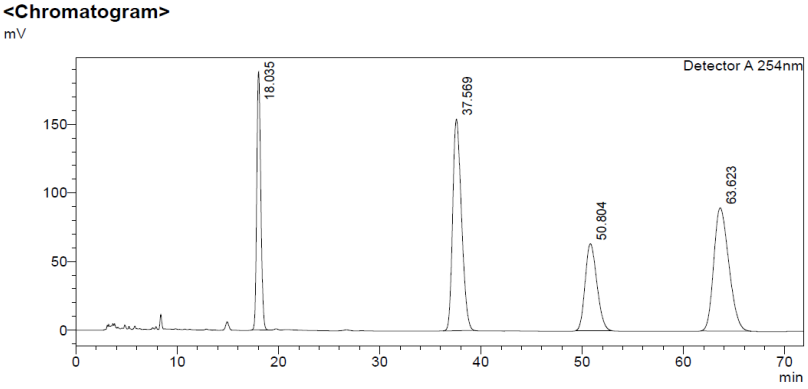

7.922
7.902
7.556
7.538
7.520
7.449
7.430
7.411
7.306
7.286
7.269
7.254
7.232
7.210
7.192
7.176
3.918
3.900
3.882
3.864
3.846
3.581
3.426
3.409
3.384
3.364
3.345
3.320
3.303
2.845
2.827
2.806
2.789
2.721
2.701
2.682
2.663
1.629
O
O
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98
0.99
2.01
4.08
1.00
1.00
2.99
2.04
1.01
1.01
198.11
172.27
143.29
136.84
133.07
128.59
128.55
128.03
127.28
126.78
77.32
77.00
76.68
51.54
44.50
40.52
37.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

## HPLC Spectra



Racemic **3a**

**<Chromatogram>**



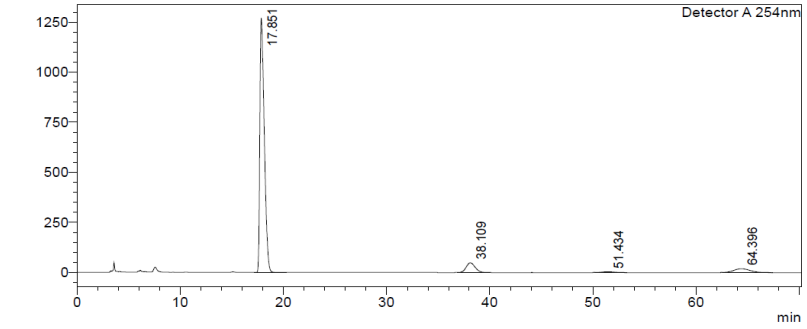

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18.035 | 5199889 | 187973 | 17.967 | | M | |
| 2 | 37.569 | 9329339 | 154138 | 32.235 | | M | |
| 3 | 50.804 | 5116891 | 63428 | 17.680 | | M | |
| 4 | 63.623 | 9295687 | 89734 | 32.119 | | M | |
| Total | | 28941807 | 495272 | | | | |

Chiral **3a**

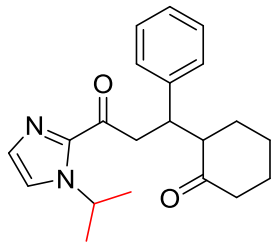
**<Chromatogram>**



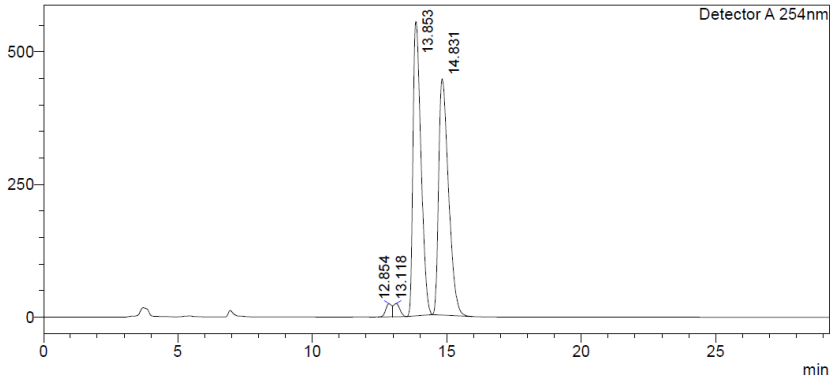

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17.851 | 38183756 | 1267854 | 87.975 | | M | |
| 2 | 38.109 | 2887182 | 48301 | 6.652 | | M | |
| 3 | 51.434 | 284620 | 3684 | 0.656 | | M | |
| 4 | 64.396 | 2047302 | 19397 | 4.717 | | M | |
| Total | | 43402860 | 1339237 | | | | |



Racemic **3b**




**<Peak Table>**

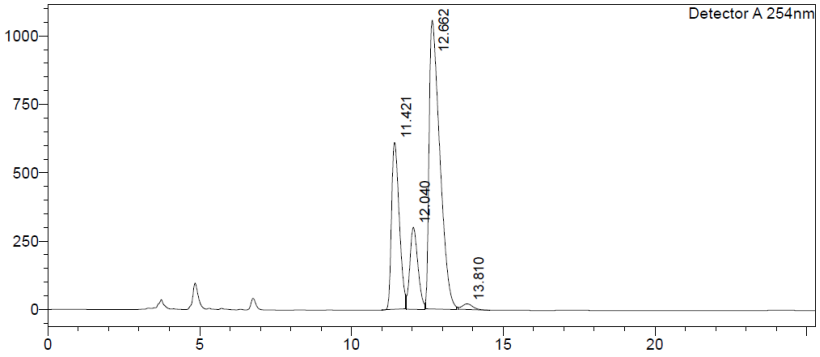
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.854 | 391147 | 24588 | 1.654 | | | |
| 2 | 13.118 | 420452 | 24931 | 1.778 | | V | |
| 3 | 13.853 | 11434660 | 554308 | 48.353 | | | |
| 4 | 14.831 | 11402050 | 444968 | 48.215 | | M | |
| Total | | 23648309 | 1048795 | | | | |

Chiral **3b**

**<Chromatogram>**

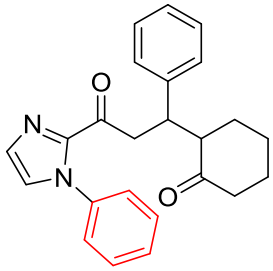
mV



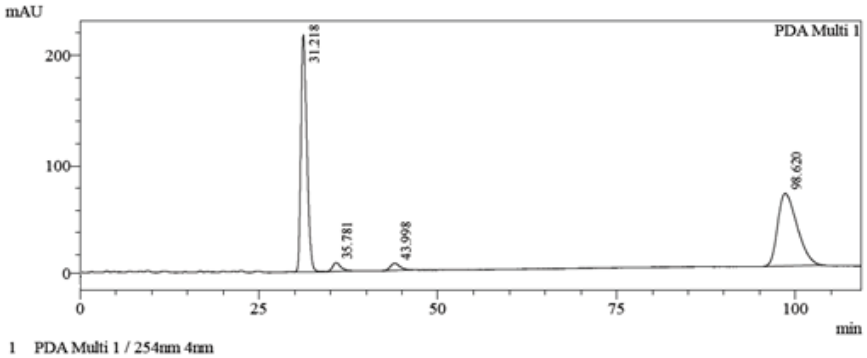

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.421 | 10748164 | 610347 | 25.210 | | M | |
| 2 | 12.040 | 5467349 | 299138 | 12.824 | | M | |
| 3 | 12.662 | 25927816 | 1054711 | 60.814 | | M | |
| 4 | 13.810 | 491590 | 20395 | 1.153 | | M | |
| Total | | 42634918 | 1984592 | | | | |




Racemic **3c**



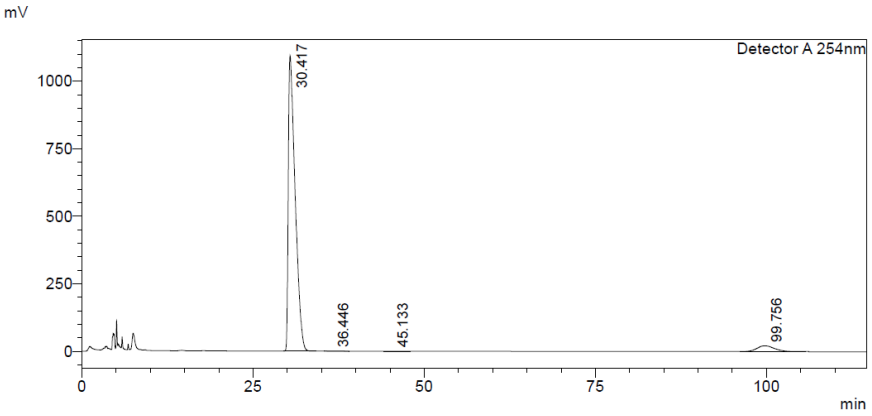

1 PDA Multi 1 / 254nm 4nm

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 31.218 | 12483458 | 214203 | 47.843 |
| 2 | 35.781 | 596732 | 7680 | 2.287 |
| 3 | 43.998 | 610434 | 6563 | 2.340 |
| 4 | 98.620 | 12401819 | 65562 | 47.530 |
| Total | | 26092444 | 294009 | 100.000 |

Chiral **3c**

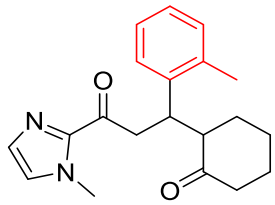
**<Chromatogram>**




**<Peak Table>**

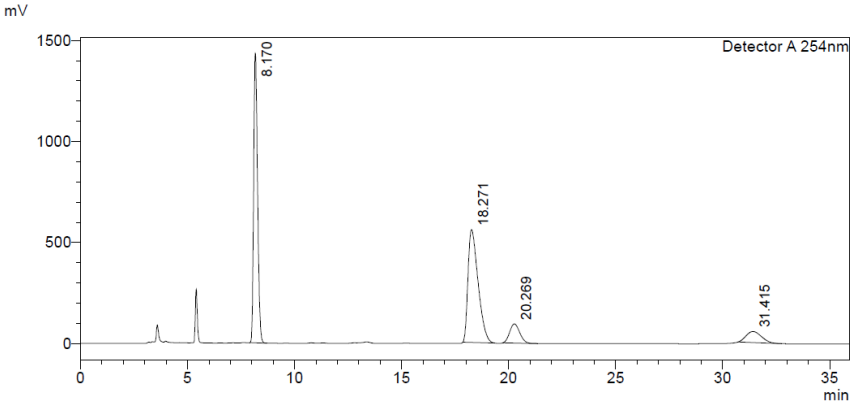
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 30.417 | 76272517 | 1093190 | 95.069 | | M | |
| 2 | 36.446 | 61625 | 695 | 0.077 | | M | |
| 3 | 45.133 | 31382 | 313 | 0.039 | | M | |
| 4 | 99.756 | 3862773 | 21560 | 4.815 | | M | |
| Total | | 80228298 | 1115758 | | | | |



Racemic **3d**

**<Chromatogram>**

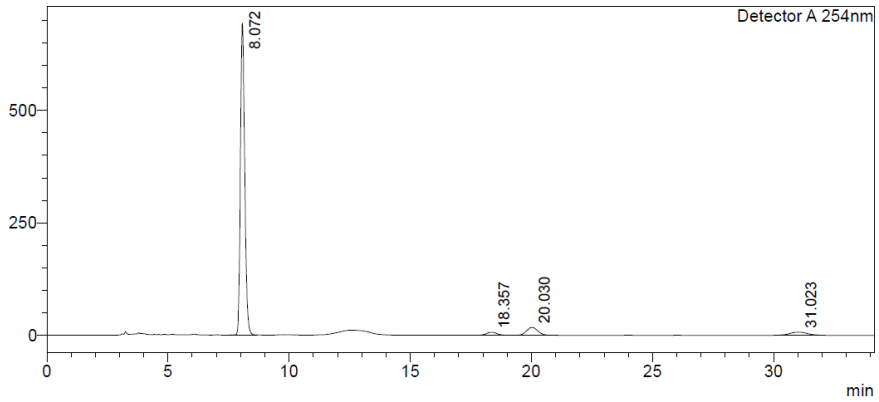



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.170 | 18110314 | 1433389 | 42.829 | | M | |
| 2 | 18.271 | 18329813 | 558709 | 43.348 | | M | |
| 3 | 20.269 | 3077920 | 94687 | 7.279 | | M | |
| 4 | 31.415 | 2767259 | 55256 | 6.544 | | M | |
| Total | | 42285307 | 2142040 | | | | |

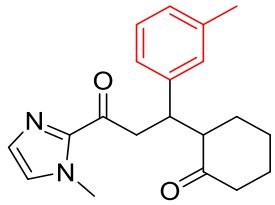
Chiral **3d**



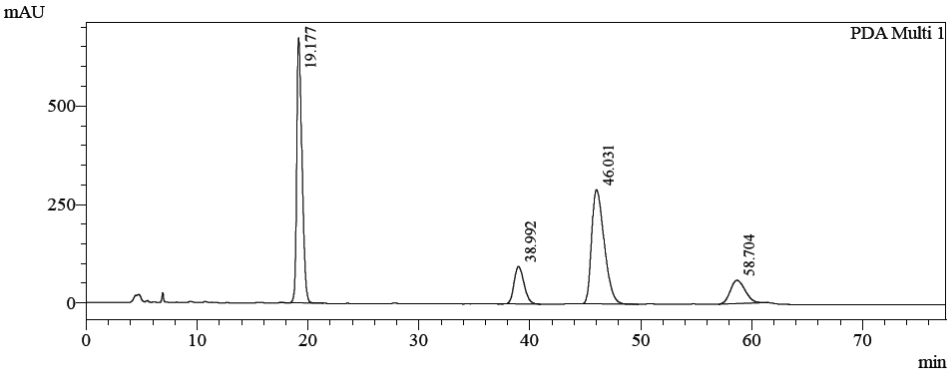

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.072 | 8617935 | 691815 | 88.296 | | M | |
| 2 | 18.357 | 210422 | 6926 | 2.156 | | M | |
| 3 | 20.030 | 575989 | 17707 | 5.901 | | M | |
| 4 | 31.023 | 355919 | 7035 | 3.647 | | M | |
| Total | | 9760265 | 723483 | | | | |



Racemic **3e**

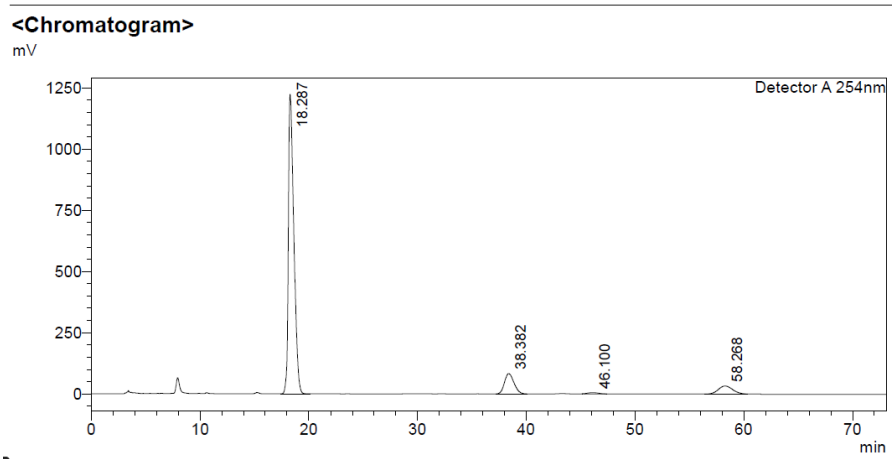



1 PDA Multi 1 / 254nm 4nm

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 19.177 | 22468680 | 674204 | 39.648 |
| 2 | 38.992 | 5884008 | 94807 | 10.383 |
| 3 | 46.031 | 22809413 | 289507 | 40.250 |
| 4 | 58.704 | 5507624 | 58976 | 9.719 |
| Total | | 56669725 | 1117494 | 100.000 |

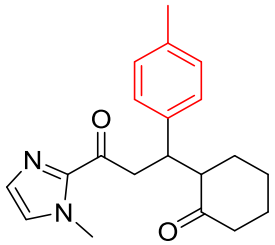
Chiral **3e**




**<Peak Table>**

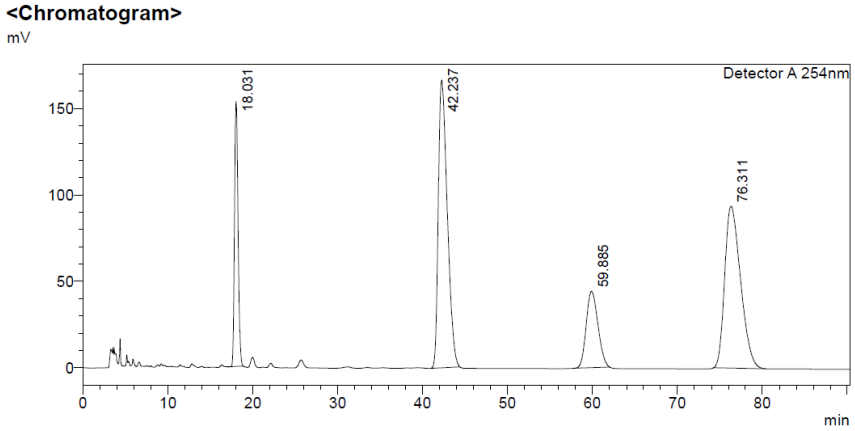
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18.287 | 42878515 | 1223289 | 83.429 | | M | |
| 2 | 38.382 | 5094534 | 83352 | 9.913 | | M | |
| 3 | 46.100 | 366982 | 5428 | 0.714 | | M | |
| 4 | 58.268 | 3054907 | 33241 | 5.944 | | M | |
| Total | | 51394937 | 1345310 | | | | |



Racemic **3f**

**<Chromatogram>**



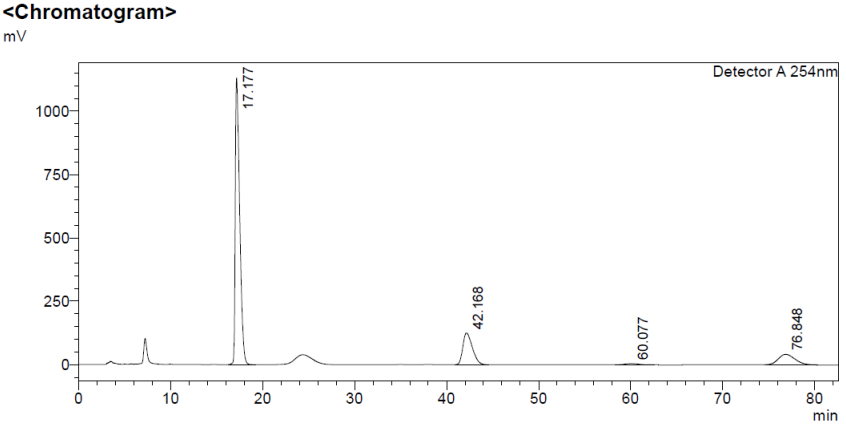

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18.031 | 4366611 | 153254 | 13.248 | | M | |
| 2 | 42.237 | 12179068 | 166547 | 36.952 | | M | |
| 3 | 59.885 | 4247602 | 44271 | 12.887 | | M | |
| 4 | 76.311 | 12166024 | 93710 | 36.912 | | M | |
| Total | | 32959306 | 457783 | | | | |

Chiral **3f**

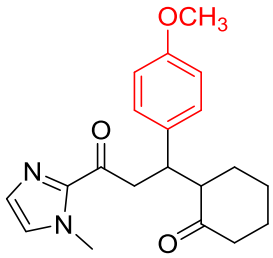
**<Chromatogram>**



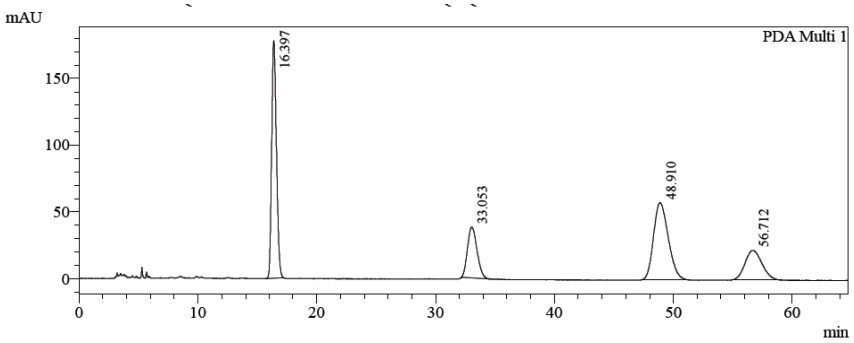

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17.177 | 37800899 | 1129296 | 71.999 | | M | |
| 2 | 42.168 | 9024655 | 125286 | 17.189 | | M | |
| 3 | 60.077 | 481404 | 5093 | 0.917 | | M | |
| 4 | 76.848 | 5195250 | 41285 | 9.895 | | M | |
| Total | | 52502209 | 1300959 | | | | |



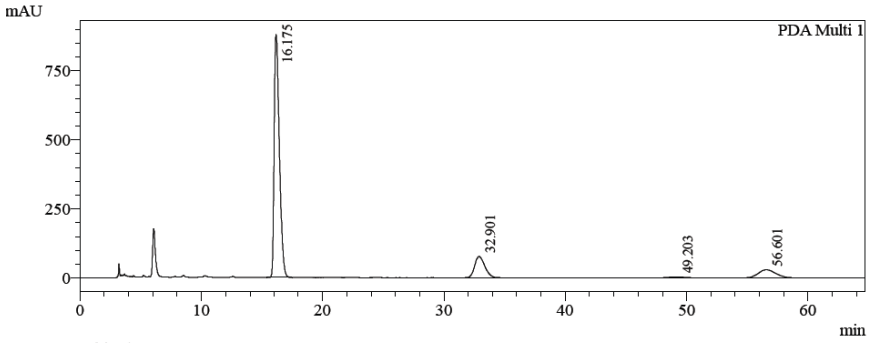

Racemic **3g**




PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 16.397 | 4964489 | 178122 | 34.771 |
| 2 | 33.053 | 2115820 | 38073 | 14.819 |
| 3 | 48.910 | 4978491 | 57866 | 34.869 |
| 4 | 56.712 | 2218933 | 22330 | 15.541 |
| Total | | 14277734 | 296391 | 100.000 |

Chiral **3g**

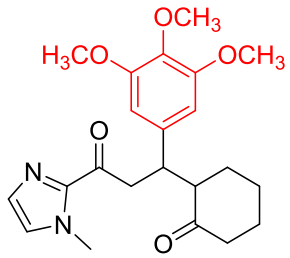



1 PDA Multi 1 / 254nm 4nm

PeakTable

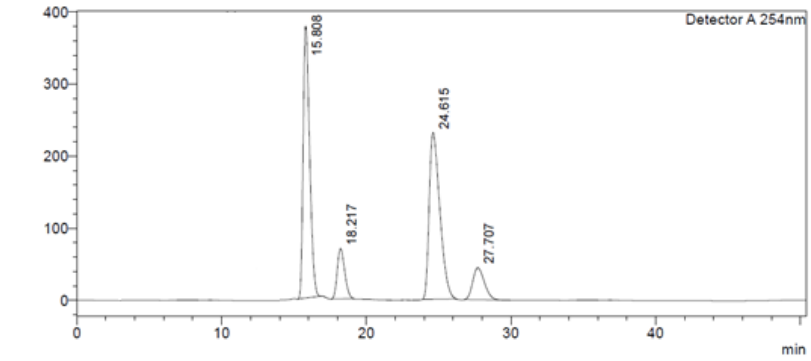
PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 16.175 | 26223087 | 880308 | 77.505 |
| 2 | 32.901 | 4449348 | 76636 | 13.150 |
| 3 | 49.203 | 313287 | 3818 | 0.926 |
| 4 | 56.601 | 2848347 | 28679 | 8.419 |
| Total | | 33834069 | 989441 | 100.000 |




Racemic **3h**

<Chromatogram>



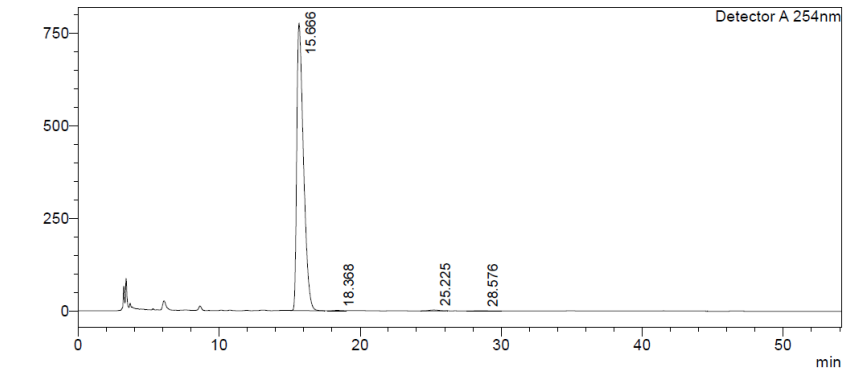

<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.808 | 11669797 | 377026 | 41.043 | | M | |
| 2 | 18.217 | 2494639 | 69599 | 8.774 | | M | |
| 3 | 24.615 | 11799756 | 231163 | 41.501 | | M | |
| 4 | 27.707 | 2468577 | 44303 | 8.682 | | M | |
| Total | | 28432768 | 722090 | | | | |

Chiral **3h**

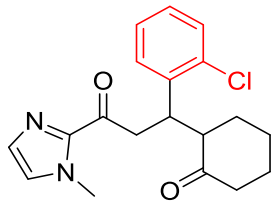
<Chromatogram>




<Peak Table>

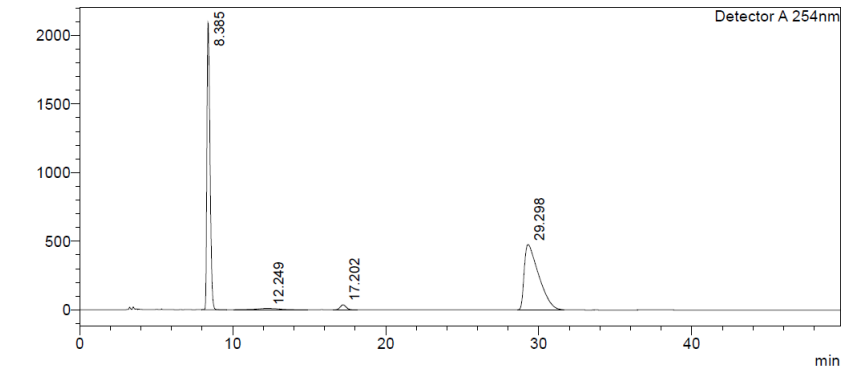
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 15.666 | 25767420 | 775946 | 99.349 | | M | |
| 2 | 18.368 | 33799 | 947 | 0.130 | | M | |
| 3 | 25.225 | 114027 | 2326 | 0.440 | | M | |
| 4 | 28.576 | 21101 | 300 | 0.081 | | M | |
| Total | | 25936347 | 779519 | | | | |




Racemic **3i**

**<Chromatogram>**



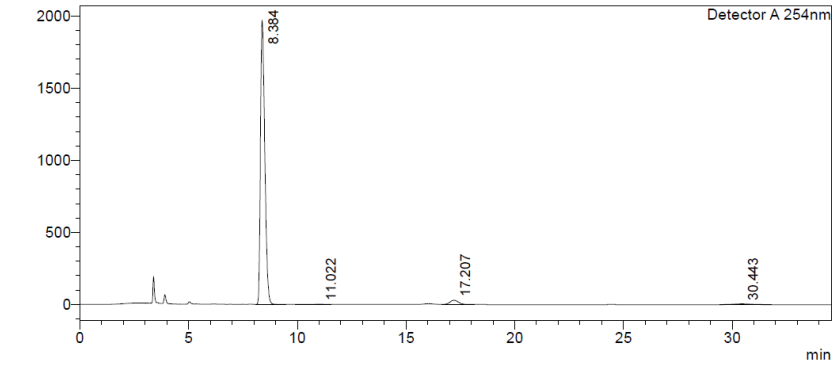

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.385 | 29250943 | 2089284 | 46.846 | | M | |
| 2 | 12.249 | 1060773 | 10567 | 1.699 | | M | |
| 3 | 17.202 | 1016934 | 36445 | 1.629 | | M | |
| 4 | 29.298 | 31112290 | 476420 | 49.827 | | M | |
| Total | | 62440939 | 2612715 | | | | |

Chiral **3i**

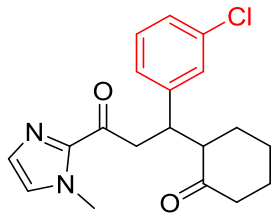
**<Chromatogram>**




**<Peak Table>**

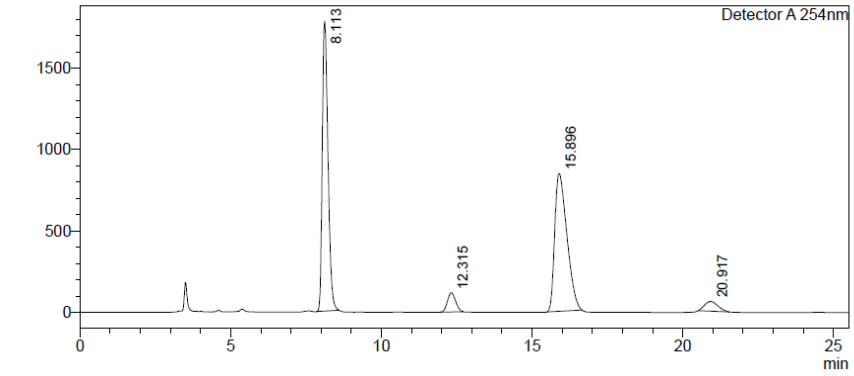
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.384 | 27389049 | 1962459 | 96.031 | | M | |
| 2 | 11.022 | 60136 | 1952 | 0.211 | | M | |
| 3 | 17.207 | 823925 | 29914 | 2.889 | | M | |
| 4 | 30.443 | 247799 | 4759 | 0.869 | | M | |
| Total | | 28520910 | 1999084 | | | | |




Racemic **3j**

**<Chromatogram>**



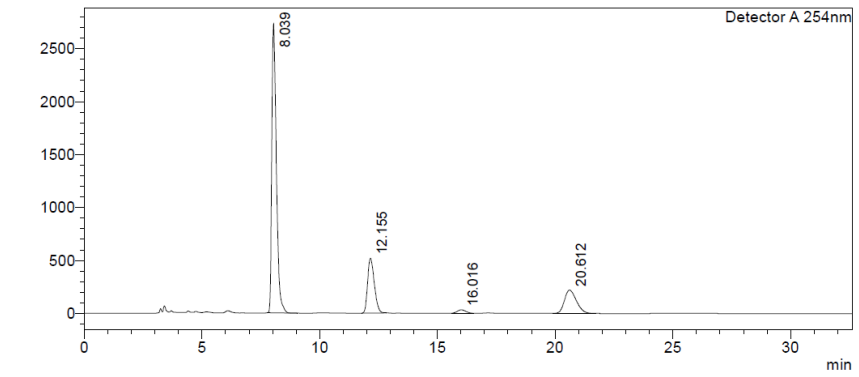

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.113 | 23358157 | 1776722 | 45.613 | | M | |
| 2 | 12.315 | 2243302 | 118500 | 4.381 | | M | |
| 3 | 15.896 | 23769675 | 845630 | 46.417 | | M | |
| 4 | 20.917 | 1838008 | 59526 | 3.589 | | M | |
| Total | | 51209142 | 2800378 | | | | |

Chiral **3j**

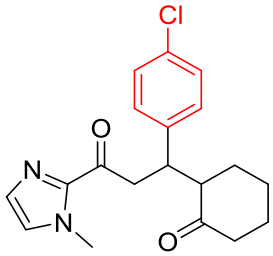
**<Chromatogram>**




**<Peak Table>**

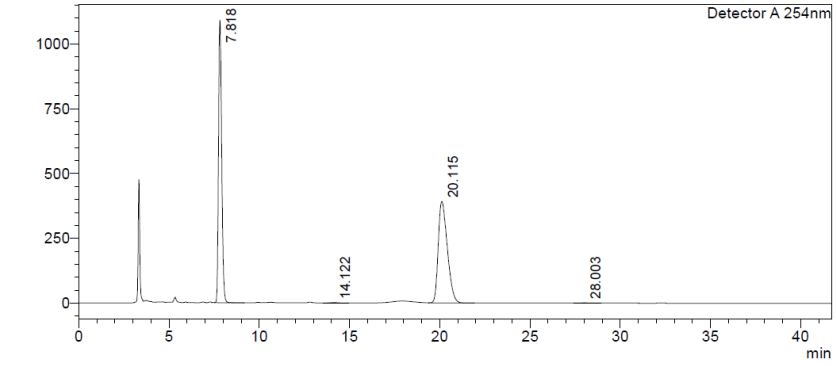
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.039 | 36782009 | 2727650 | 66.171 | | M | |
| 2 | 12.155 | 10197705 | 517697 | 18.346 | | M | |
| 3 | 16.016 | 834608 | 33639 | 1.501 | | M | |
| 4 | 20.612 | 7772271 | 220417 | 13.982 | | M | |
| Total | | 55586593 | 3499404 | | | | |




Racemic **3k**

**<Chromatogram>**



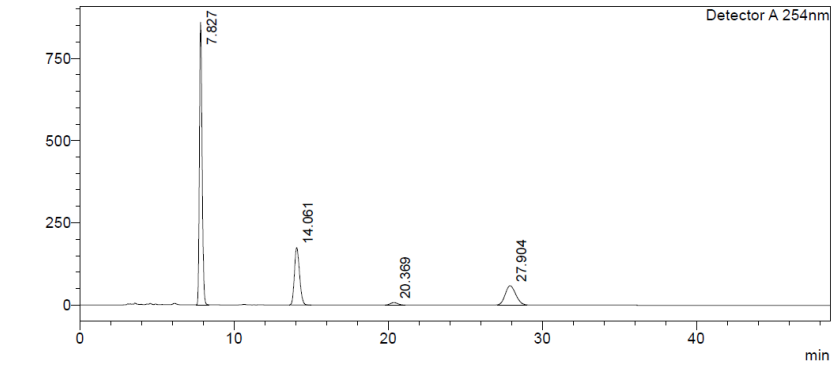

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 7.818 | 13346756 | 1092053 | 49.187 | | M | |
| 2 | 14.122 | 40212 | 1673 | 0.148 | | M | |
| 3 | 20.115 | 13717468 | 391860 | 50.553 | | M | |
| 4 | 28.003 | 30314 | 706 | 0.112 | | M | |
| Total | | 27134749 | 1486292 | | | | |

Chiral **3k**

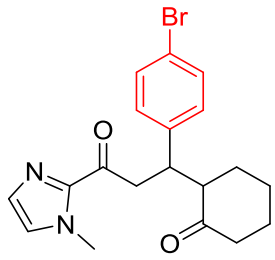
**<Chromatogram>**




**<Peak Table>**

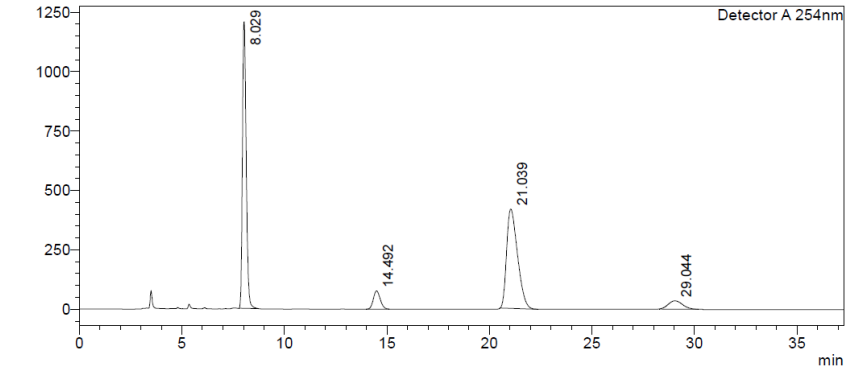
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 7.827 | 10487472 | 860200 | 59.997 | | M | |
| 2 | 14.061 | 4011840 | 174481 | 22.951 | | M | |
| 3 | 20.369 | 244742 | 7585 | 1.400 | | M | |
| 4 | 27.904 | 2735876 | 58368 | 15.652 | | M | |
| Total | | 17479930 | 1100636 | | | | |




Racemic **3l**

**<Chromatogram>**



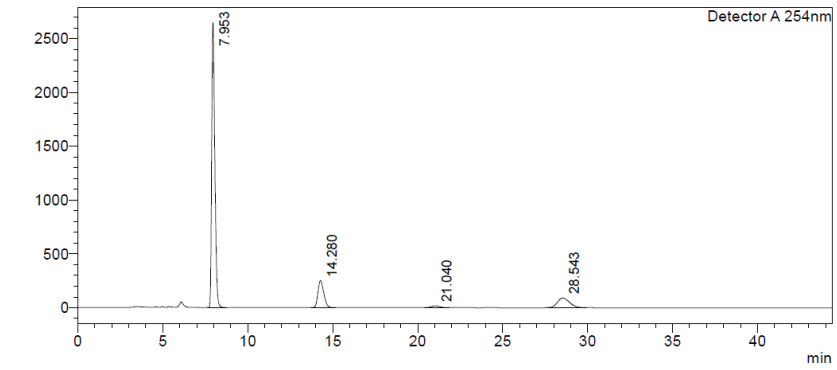

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.029 | 15359234 | 1205525 | 44.750 | | M | |
| 2 | 14.492 | 1806524 | 76795 | 5.263 | | M | |
| 3 | 21.039 | 15458297 | 418560 | 45.038 | | M | |
| 4 | 29.044 | 1698404 | 35472 | 4.948 | | M | |
| Total | | 34322458 | 1736353 | | | | |

Chiral **3l**

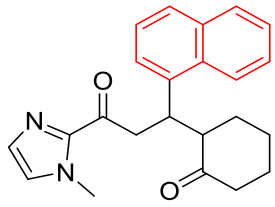
**<Chromatogram>**




**<Peak Table>**

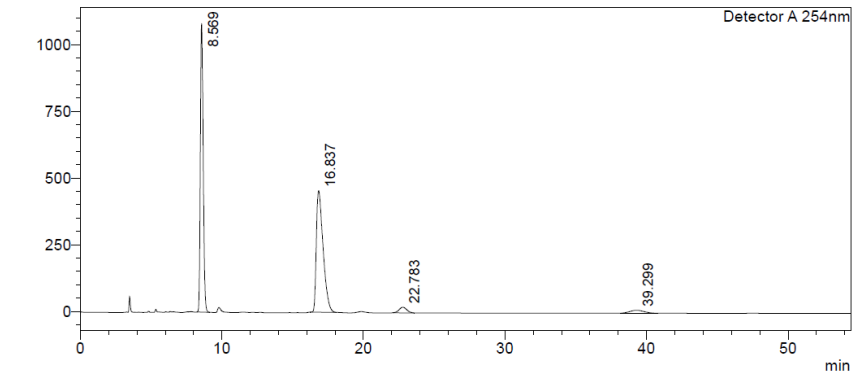
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 7.953 | 34057695 | 2641999 | 75.633 | | M | |
| 2 | 14.280 | 5973964 | 250782 | 13.267 | | M | |
| 3 | 21.040 | 570633 | 16626 | 1.267 | | M | |
| 4 | 28.543 | 4427958 | 89346 | 9.833 | | M | |
| Total | | 45030250 | 2998753 | | | | |



Racemic **3m**

**<Chromatogram>**

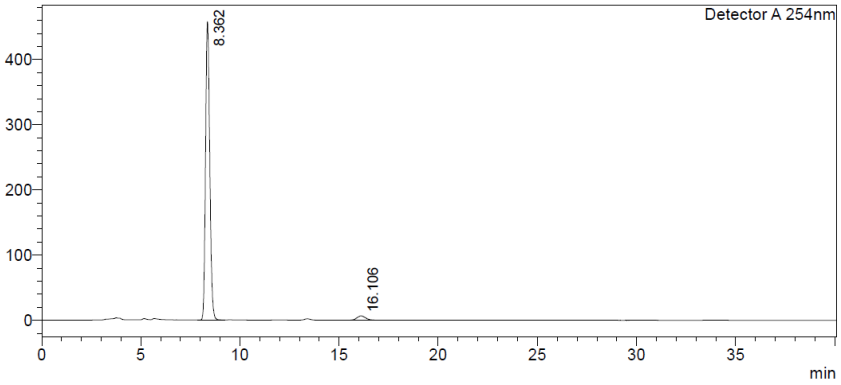



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.569 | 15069751 | 1081838 | 47.402 | | M | |
| 2 | 16.837 | 15151856 | 455501 | 47.660 | | M | |
| 3 | 22.783 | 798551 | 21080 | 2.512 | | M | |
| 4 | 39.299 | 771301 | 11406 | 2.426 | | M | |
| Total | | 31791460 | 1569825 | | | | |

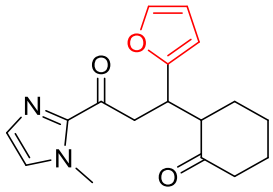
Chiral **3m**




**<Peak Table>**

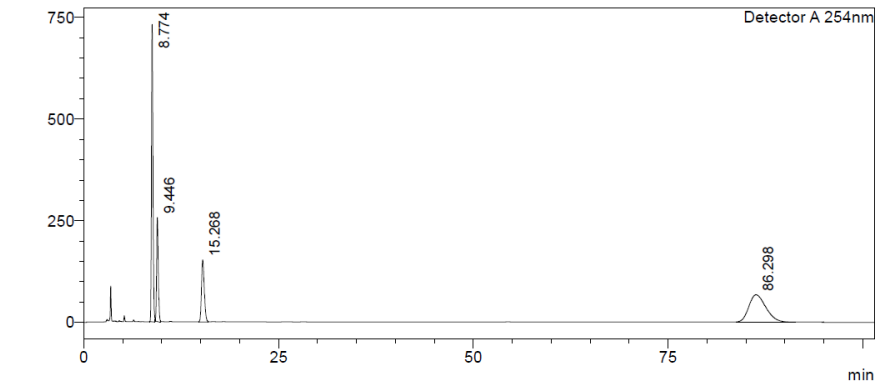
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.362 | 6804834 | 457283 | 97.091 | | M | |
| 2 | 16.106 | 203896 | 6577 | 2.909 | | M | |
| Total | | 7008731 | 463861 | | | | |



Racemic **3n**

**<Chromatogram>**



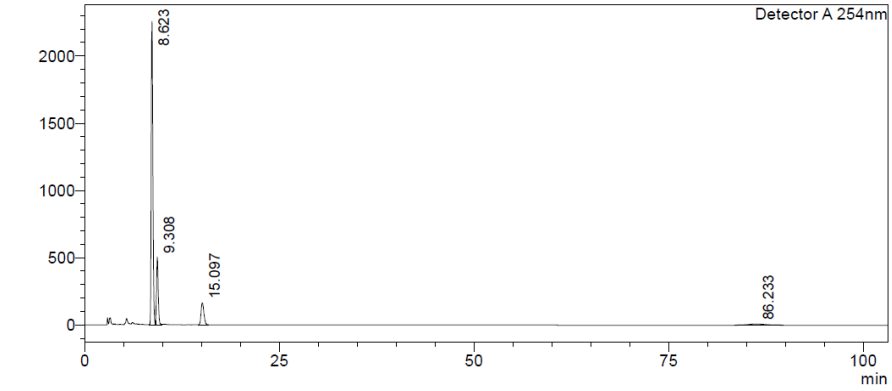

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.774 | 10031535 | 732149 | 35.877 | | M | |
| 2 | 9.446 | 3827933 | 256193 | 13.690 | | M | |
| 3 | 15.268 | 3867265 | 152984 | 13.831 | | M | |
| 4 | 86.298 | 10234274 | 67237 | 36.602 | | M | |
| Total | | 27961008 | 1208563 | | | | |

Chiral **3n**

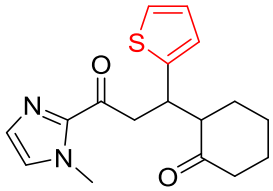
**<Chromatogram>**




**<Peak Table>**

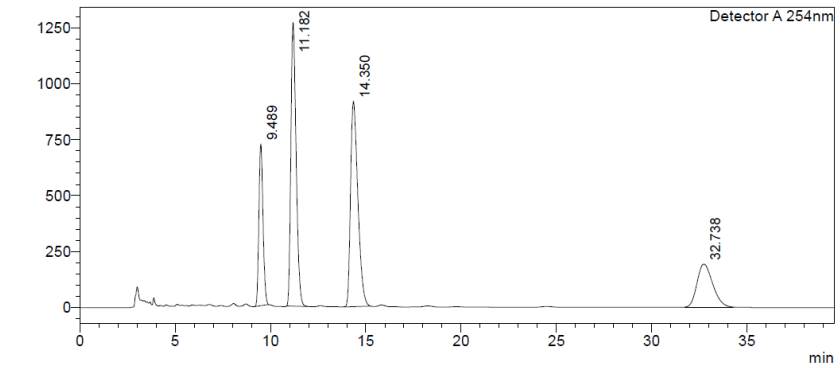
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.623 | 32134182 | 2255173 | 71.376 | | M | |
| 2 | 9.308 | 7611350 | 500549 | 16.906 | | M | |
| 3 | 15.097 | 4130912 | 163967 | 9.176 | | M | |
| 4 | 86.233 | 1144352 | 7891 | 2.542 | | M | |
| Total | | 45020795 | 2927580 | | | | |




Racemic **3o**

**<Chromatogram>**



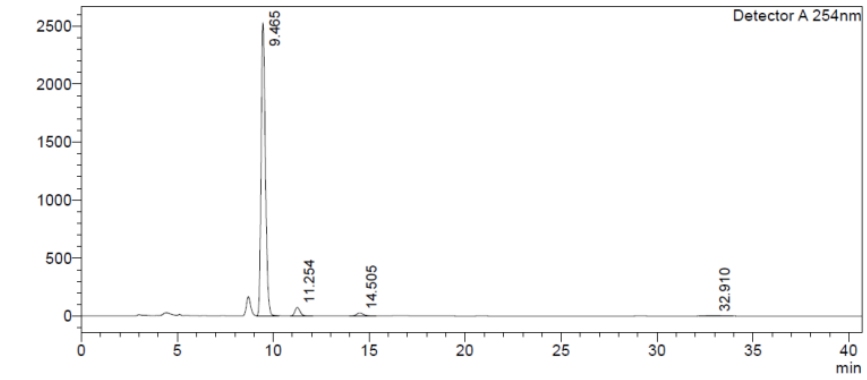

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.489 | 10866689 | 722679 | 15.373 | | M | |
| 2 | 11.182 | 24356498 | 1265592 | 34.457 | | M | |
| 3 | 14.350 | 24518716 | 916318 | 34.686 | | M | |
| 4 | 32.738 | 10944960 | 192725 | 15.484 | | M | |
| Total | | 70686864 | 3097314 | | | | |

Chiral **3o**

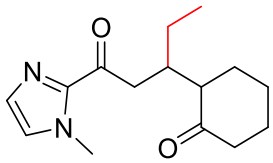
**<Chromatogram>**




**<Peak Table>**

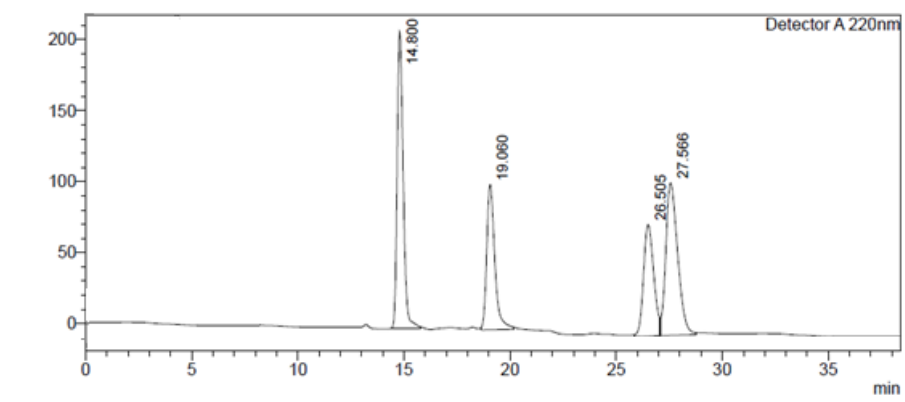
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.465 | 38950415 | 2526241 | 94.756 | | M | |
| 2 | 11.254 | 1365187 | 74531 | 3.321 | | M | |
| 3 | 14.505 | 638029 | 25190 | 1.552 | | M | |
| 4 | 32.910 | 152390 | 2996 | 0.371 | | M | |
| Total | | 41106021 | 2628957 | | | | |



Racemic **3p**

**<Chromatogram>**



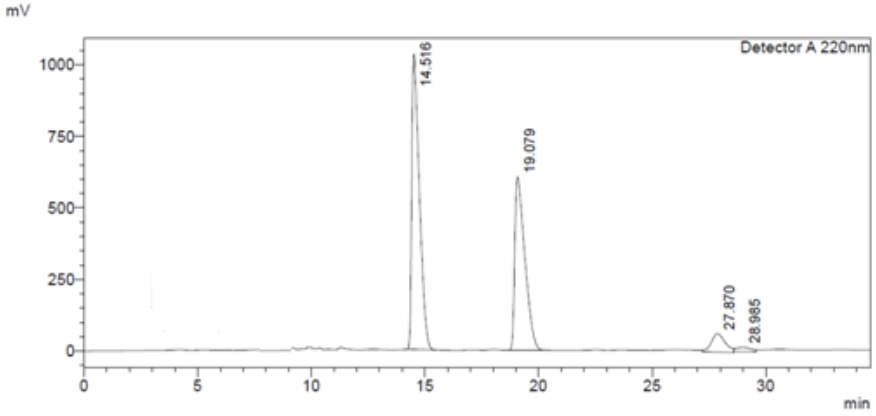

**<Peak Table>**

Detector A 220nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.800 | 4139506 | 208928 | 30.423 | | M | |
| 2 | 19.060 | 2695952 | 102304 | 19.814 | | M | |
| 3 | 26.505 | 2623180 | 78642 | 19.279 | | M | |
| 4 | 27.566 | 4148001 | 107124 | 30.485 | | M | |
| Total | | 13606639 | 496998 | | | | |

Chiral **3p**

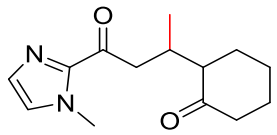
**<Chromatogram>**




**<Peak Table>**

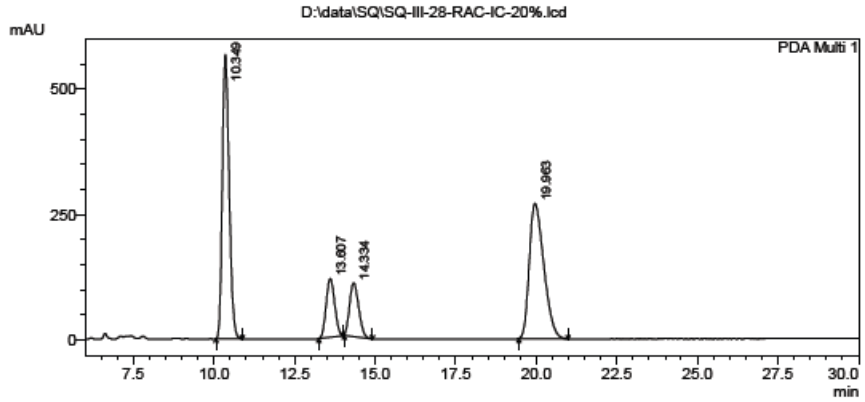
Detector A 220nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.516 | 24114668 | 1030173 | 52.243 | | M | |
| 2 | 19.079 | 18627533 | 605589 | 40.355 | | M | |
| 3 | 27.870 | 2725074 | 64268 | 5.904 | | M | |
| 4 | 28.985 | 691359 | 15083 | 1.498 | | M | |
| Total | | 46158634 | 1715113 | | | | |



Racemic **3q**

<Chromatogram>

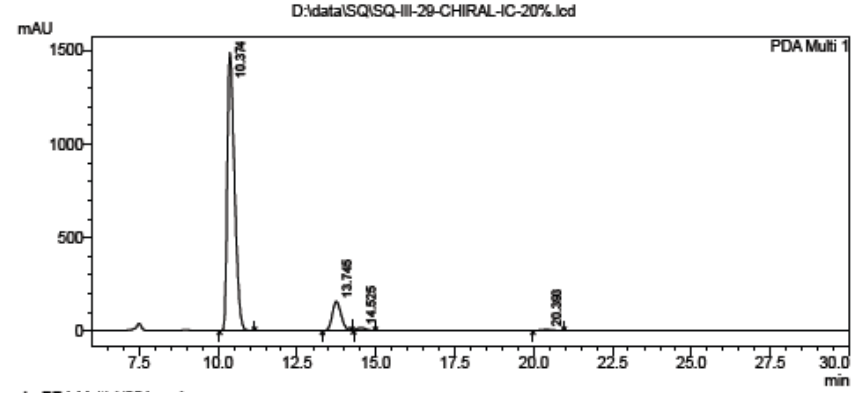



PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.349 | 8360847 | 566631 | 39.670 |
| 2 | 13.607 | 2149538 | 117114 | 10.199 |
| 3 | 14.334 | 2108152 | 106944 | 10.003 |
| 4 | 19.963 | 8457489 | 269401 | 40.128 |
| Total | | 21076026 | 1060090 | 100.000 |

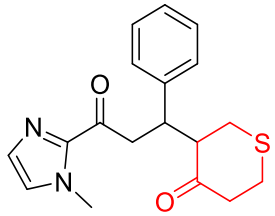
Chiral **3q**

<Chromatogram>



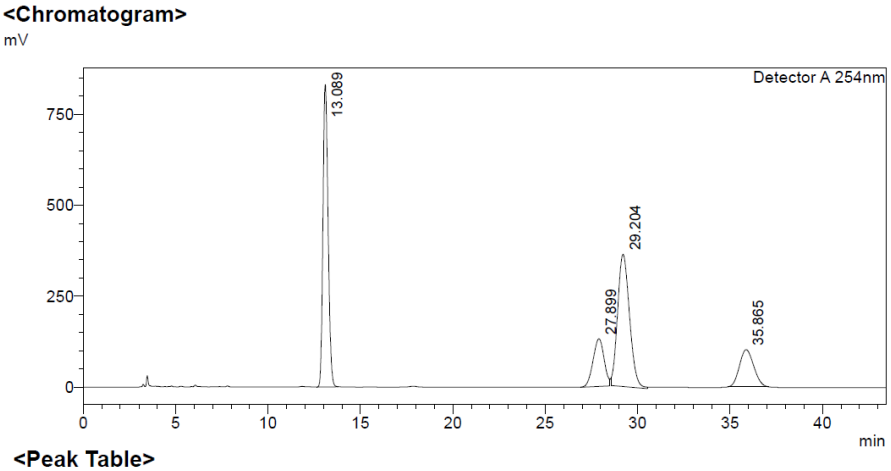

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.374 | 23704833 | 1486769 | 87.425 |
| 2 | 13.745 | 3023138 | 156383 | 11.150 |
| 3 | 14.525 | 263019 | 14847 | 0.970 |
| 4 | 20.393 | 123537 | 4463 | 0.456 |
| Total | | 27114526 | 1662463 | 100.000 |




Racemic **3r**

**<Chromatogram>**



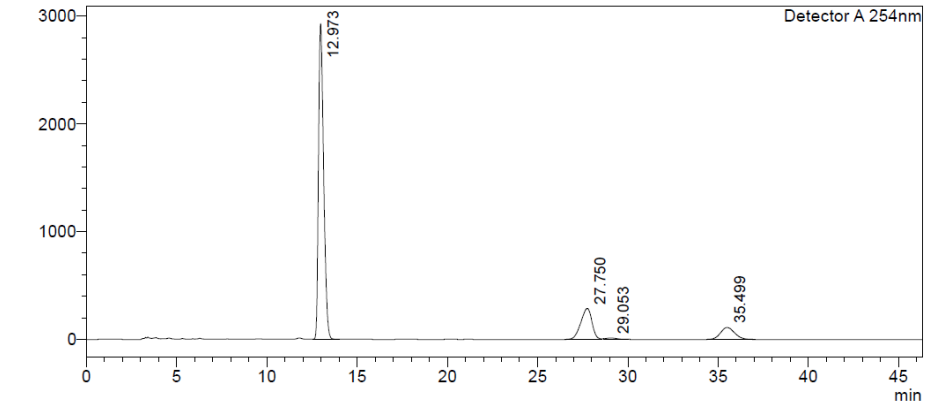

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.089 | 16049279 | 831286 | 37.151 | | M | |
| 2 | 27.899 | 5402501 | 131039 | 12.506 | | M | |
| 3 | 29.204 | 16253222 | 363286 | 37.623 | | M | |
| 4 | 35.865 | 5495631 | 102191 | 12.721 | | M | |
| Total | | 43200634 | 1427802 | | | | |

Chiral **3r**

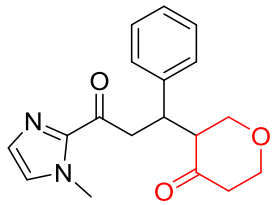
**<Chromatogram>**




**<Peak Table>**

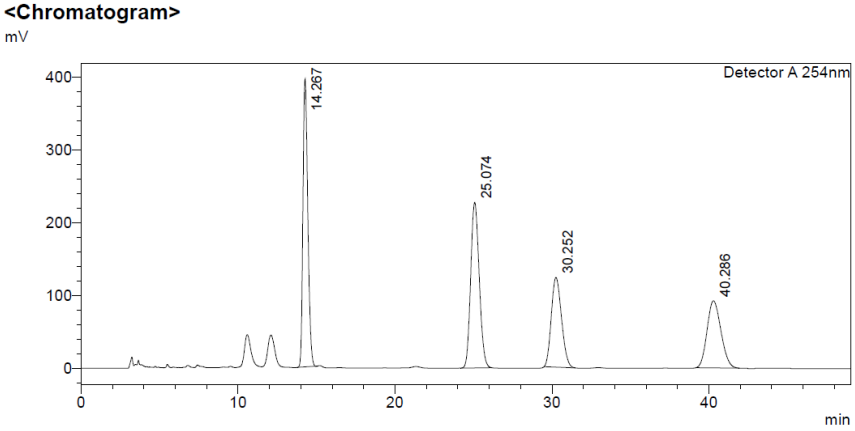
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 12.973 | 57902852 | 2930103 | 75.513 | | M | |
| 2 | 27.750 | 12317814 | 287574 | 16.064 | | M | |
| 3 | 29.053 | 499124 | 12214 | 0.651 | | M | |
| 4 | 35.499 | 5959210 | 109952 | 7.772 | | M | |
| Total | | 76679000 | 3339842 | | | | |



Racemic **3s**

**<Chromatogram>**



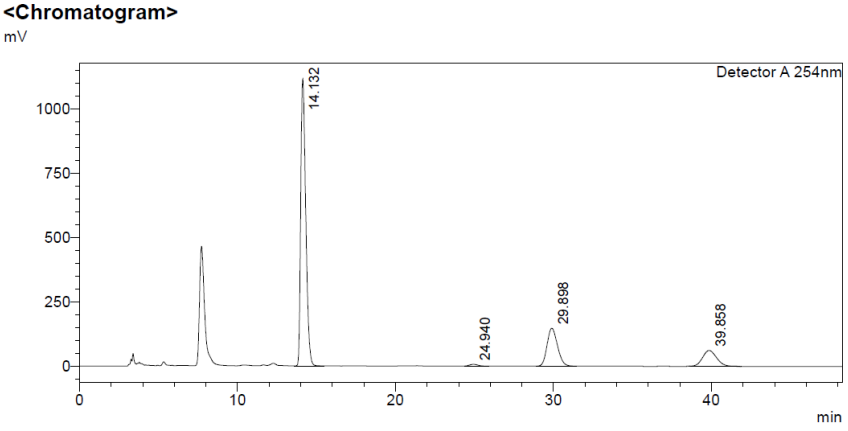

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.267 | 8496592 | 394685 | 29.996 | | M | |
| 2 | 25.074 | 8597275 | 227376 | 30.352 | | M | |
| 3 | 30.252 | 5574087 | 123124 | 19.679 | | M | |
| 4 | 40.286 | 5657445 | 92105 | 19.973 | | M | |
| Total | | 28325399 | 837290 | | | | |

Chiral **3s**

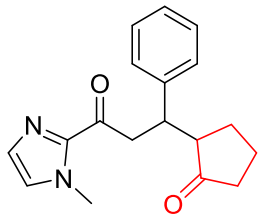
**<Chromatogram>**




**<Peak Table>**

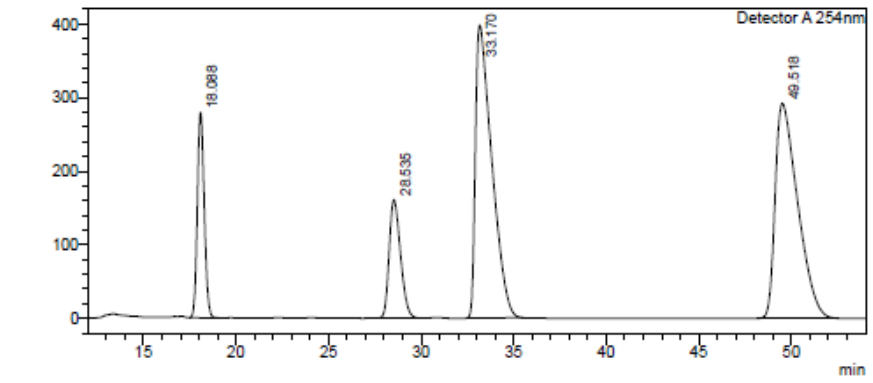
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.132 | 24695306 | 1115629 | 69.663 | | M | |
| 2 | 24.940 | 252058 | 7030 | 0.711 | | M | |
| 3 | 29.898 | 6754725 | 147527 | 19.055 | | M | |
| 4 | 39.858 | 3747362 | 61393 | 10.571 | | M | |
| Total | | 35449451 | 1331579 | | | | |



Racemic **3t**

<Chromatogram>

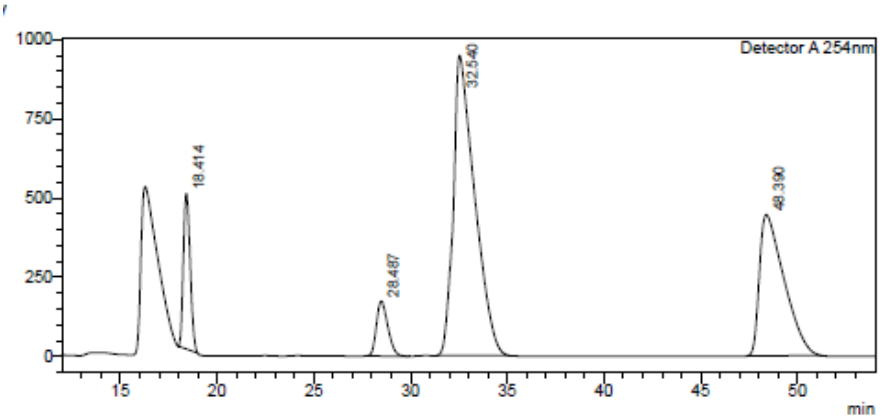



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18.088 | 7223301 | 278739 | 11.437 | | M | |
| 2 | 28.535 | 6849929 | 161009 | 10.846 | | M | |
| 3 | 33.170 | 24447012 | 397669 | 38.709 | | M | |
| 4 | 49.518 | 24635923 | 291971 | 39.008 | | M | |
| Total | | 63156165 | 1129388 | | | | |

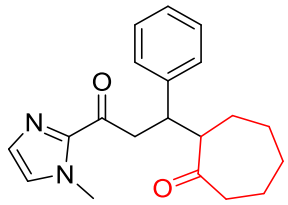
Chiral **3t**




**<Peak Table>**

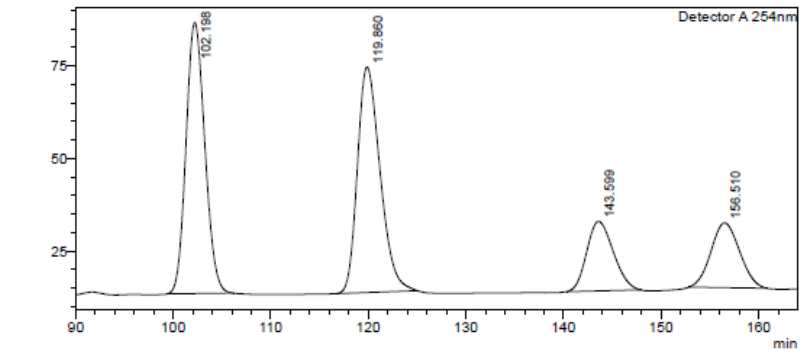
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 18.414 | 11970824 | 489527 | 9.132 | | M | |
| 2 | 28.487 | 7117492 | 173251 | 5.430 | | M | |
| 3 | 32.540 | 72590710 | 947009 | 55.376 | | M | |
| 4 | 48.390 | 39407191 | 445098 | 30.062 | | M | |
| Total | | 131086217 | 2054886 | | | | |



Racemic **3u**

<Chromatogram>



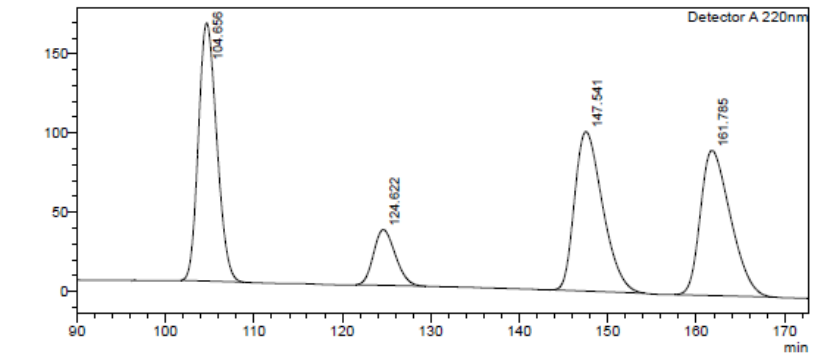

<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 102.198 | 9815545 | 73243 | 36.601 | | M | |
| 2 | 119.860 | 9868659 | 60994 | 36.799 | | M | |
| 3 | 143.599 | 3561101 | 18781 | 13.279 | | M | |
| 4 | 156.510 | 3572513 | 17484 | 13.321 | | M | |
| Total | | 26817818 | 170502 | | | | |

Chiral **3u**

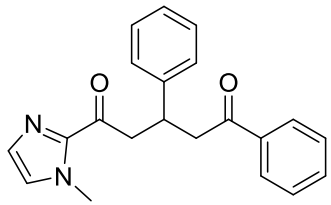
<Chromatogram>




<Peak Table>

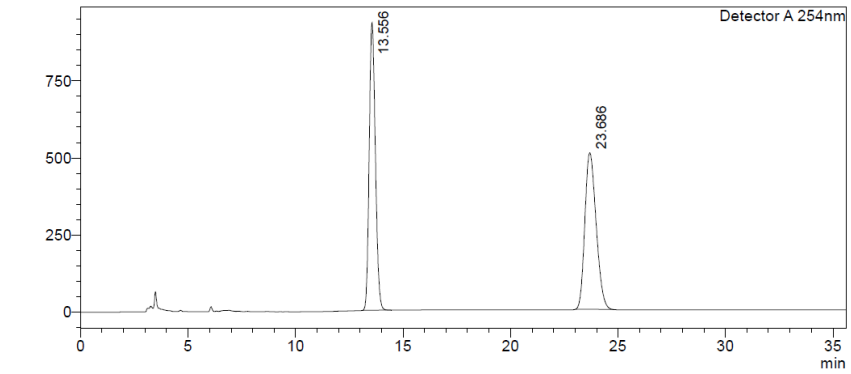
Detector A 220nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 104.656 | 23530324 | 163055 | 31.947 | | M | |
| 2 | 124.622 | 6036244 | 35164 | 8.195 | | M | |
| 3 | 147.541 | 22315045 | 100767 | 30.297 | | M | |
| 4 | 161.785 | 21773572 | 91720 | 29.561 | | M | |
| Total | | 73655185 | 390706 | | | | |



Racemic **3v**

**<Chromatogram>**



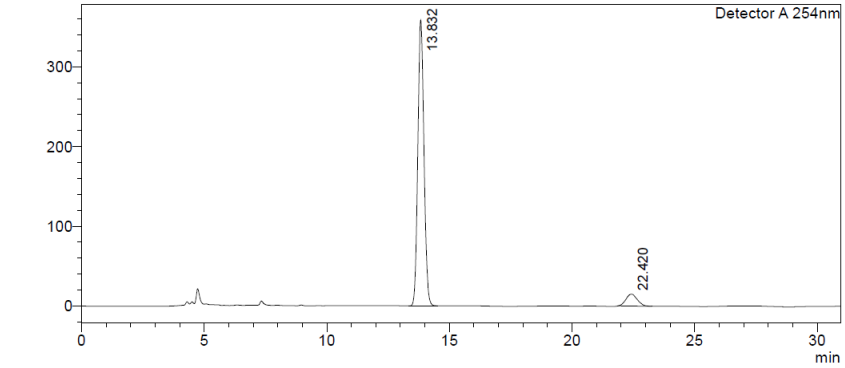

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.556 | 18602984 | 932082 | 50.135 | | M | |
| 2 | 23.686 | 18502993 | 507702 | 49.865 | | M | |
| Total | | 37105977 | 1439784 | | | | |

Chiral **3v**

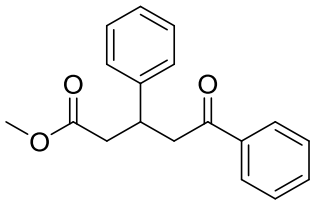
**<Chromatogram>**




**<Peak Table>**

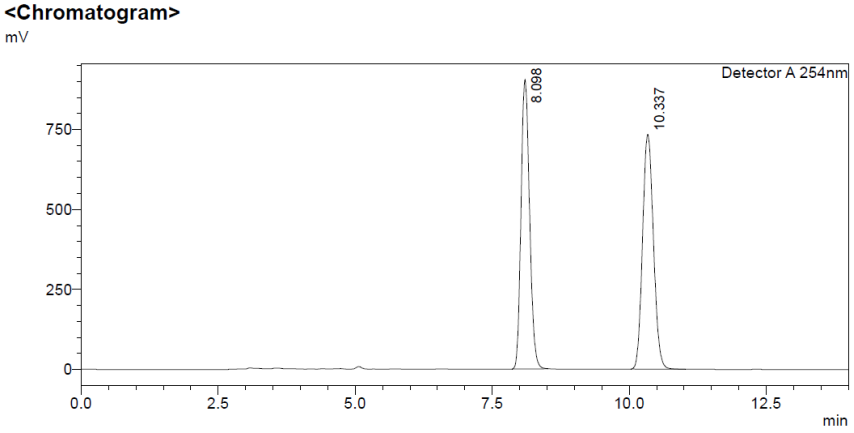
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.832 | 6265529 | 358049 | 92.838 | | M | |
| 2 | 22.420 | 483338 | 15056 | 7.162 | | M | |
| Total | | 6748867 | 373105 | | | | |



Racemic **4**

**<Chromatogram>**



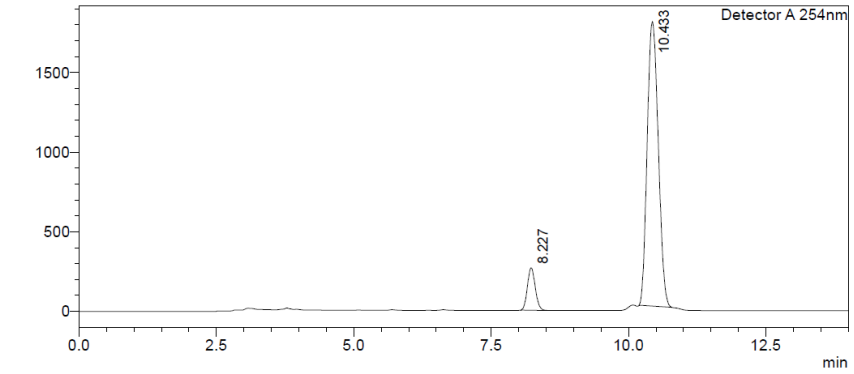

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.098 | 9822740 | 904580 | 49.203 | | M | |
| 2 | 10.337 | 10140932 | 734068 | 50.797 | | M | |
| Total | | 19963672 | 1638648 | | | | |

Chiral **4**

**<Chromatogram>**




**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.227 | 2628929 | 266197 | 9.487 | | M | |
| 2 | 10.433 | 25082548 | 1786503 | 90.513 | | M | |
| Total | | 27711477 | 2052700 | | | | |