

Supplemental information

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1. Experimental section regarding 2-(*N*-benzoylamino)cyclohexanecarboxylic acid derivatives

Ethyl 2-(N-benzoylamino)cyclohexene-1-carboxylate (6a)

To a mixture of **5a** (80.00 g, 472.8 mmol), pyridine (37.4 g, 472.8 mmol) and MeCN (190 mL) was added benzoyl chloride (63.14 g, 449.2 mmol) in MeCN (126 mL) solution at 40-50°C. The mixture was stirred at 50-60°C for 1.5 h. After cooling to 20-30°C, water (631 mL) was added for 30 minutes. The resultant mixture was stirred for additional 30 minutes and filtered. The filtrate was washed with water (631 mL), and dried under reduced pressure (60 °C) to afford the titled compound **6a** (119.62 g, 97%) as a white solid.

mp:97-99°C

¹H NMR (500MHz, CDCl₃, TMS): 1.31 (3H, t, *J*=7.3 Hz), 1.60-1.75 (4H, m), 2.35-2.42 (2H, m), 3.10-3.19 (2H, m), 4.22 (2H, q, *J*=7.3 Hz), 7.44-7.55 (3H, m), 7.94-8.01 (2H, m), 12.54 (1H, brs) ppm.

¹³C NMR (125 MHz, CDCl₃, TMS): 14.3, 21.8, 22.0, 24.4, 28.8, 60.4, 105.4, 127.6, 128.7, 131.9, 134.9, 152.6, 165.3, 170.3 ppm.

IR (ATR, cm⁻¹): 3186, 2941, 2853, 1682, 1651, 1618, 1580, 1512, 1454, 1437, 1267, 1238, 1221, 1179, 1159, 1144, 1121, 1094, 1074, 1055, 1016, 986, 968, 797, 775, 748

Anal. calcd. for C₁₆H₁₉NO₃, C; 70.31, H; 7.01, N; 5.12. found C; 70.29, H; 7.15, N; 5.08.

HRMS calcd. for C₁₆H₁₉NO₃, 274.1438 [M+H]⁺; found, 274.1428 [M+H]⁺.

Ethyl (1S, 2R)-2-(N-benzoylamino)cyclohexane-1-carboxylate (1a) by asymmetric hydrogenation of 6a using [Ru(cod)(methallyl)₂] and (S)-BINAP (run 2, Table 1)

(All operations were carried out under argon atmosphere)

To a 15 mL Schlenk tube were added (*S*)-BINAP (73.9 mg, 91.4 × 10⁻⁶ mol), [Ru(cod)(methallyl)₂] (29.2 mg, 91.4 × 10⁻⁶ mol) and degassed dichloromethane (4.5 mL), and the mixture was stirred at 0°C. HBF₄·Et₂O (32 μL) was added to the mixture, and then the mixture was stirred at room temperature for 30 minutes. The reaction mixture was concentrated *in vacuo* to afford crude metal complex as a yellow-brown solid.

To a 120 mL pressure-resistant vessel was added **6a** (500 mg, 1.83 mmol). To the vessel was added the crude metal complex prepared above in degassed MeOH (25 mL) by cannulation. To the mixture was purged H₂ (5MPa), then stirred for 18 h at 50°C. H₂ pressure was released, and then the reaction mixture was concentrated to afford the diastereomer/enantiomer mixture of crude titled compounds **1a** (500 mg, 100%) as a pale-brown solid/oil.

Conversion: 96.9%, 71.0%ee.

Pure **1a** (300 mg, 60.0%) was obtained by silica-gel chromatography purification

(Hexane/AcOEt=2:1, R_f 0.66) as a white solid.

mp: 88-90°C

^1H NMR (CDCl_3 , 500MHz, TMS): 1.25-1.40 (4H, m), 1.40-1.60 (2H,m), 1.60-1.85 (4H, m), 2.10-2.30 (1H, m), 2.80-3.00 (1H, m), 4.10-4.30 (2H, m), 4.30-4.40 (1H, m), 7.30 (1H, d, $J=7.6$ Hz), 7.40-7.60 (3H, m), 7.70-7.80 (2H, m) ppm.

^{13}C NMR (CDCl_3 , 500MHz, TMS): 14.2, 22.4, 24.3, 27.5, 29.4, 44.4, 48.3, 60.6, 126.9, 128.5, 131.3, 134.8, 166.3, 174.4 ppm.

IR (ATR, cm^{-1}): 3323, 2951, 2936, 2922, 2862, 1719, 1634, 1605, 1580, 1533, 1491, 1445, 1408, 1329, 1277, 1260, 1238, 1188, 1157, 1130, 1111, 1070, 1024, 864, 723, 692, 677, 656

Anal. calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_3$, C; 69.79, H; 7.69, N; 5.09. found C; 69.79, H; 7.77, N; 4.98.

HRMS calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_3$, 276.1594 ($\text{M}+\text{H}$) $^+$; found, 276.1596 ($\text{M}+\text{H}$) $^+$.

Ethyl (1S, 2R)-2-(N-benzoylamino)cyclohexane-1-carboxylate (1a) by asymmetric hydrogenation of 6a using [Ru(cod)(methallyl) $_2$] and (S)-C $_3$ -TunaPhos (run 4, Table 1)

(All operations were carried out at argon atmosphere)

To a 15 mL Schlenk tube were added (S)-C $_3$ -TunaPhos (54.4 mg, 91.5×10^{-6} mol), [Ru(cod)(methallyl) $_2$] (29.2 mg, 91.4×10^{-6} mol) and degassed dichloromethane (4.5 mL), and the mixture was stirred at 0°C. $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (32 μL) was added to the mixture, and then the mixture was stirred at room temperature for 30 minutes. The reaction mixture was concentrated *in vacuo* to afford crude metal complex as a yellow-brown solid.

To a 120 mL pressure-resistant vessel was added **6a** (500 mg, 1.83 mmol). To the vessel was added the crude metal complex prepared above in degassed MeOH (25 mL) by cannulation. To the mixture was purged H_2 (5MPa), then stirred for 18 h at 50°C. H_2 pressure was released, and then the reaction mixture was concentrated to afford the diastereomer/enantiomer mixture of crude titled compounds **1a** (500 mg, 100%) as a pale-brown solid/oil.

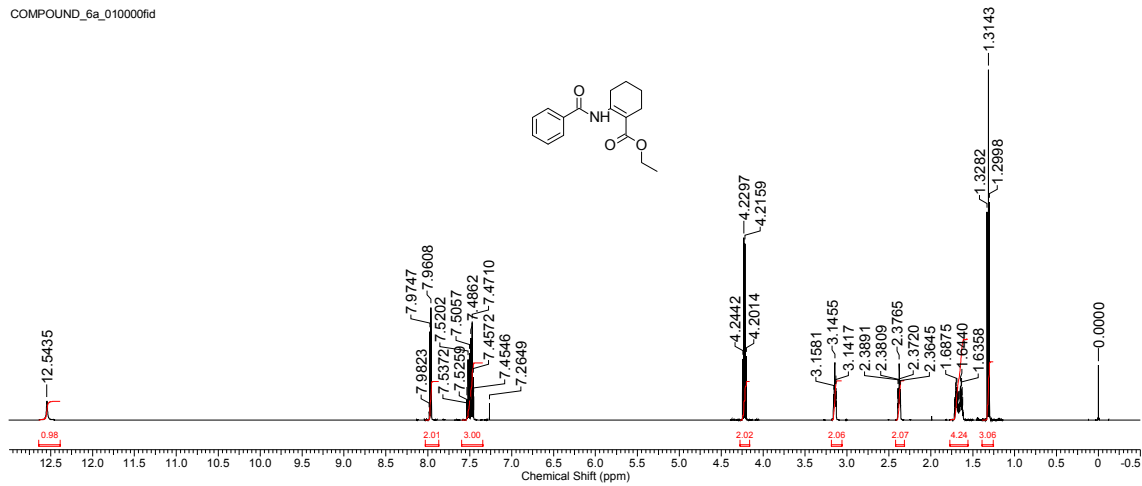
Conversion: 94.3%, 70.3%ee.

2, NMR data

2-1. Compound 6a

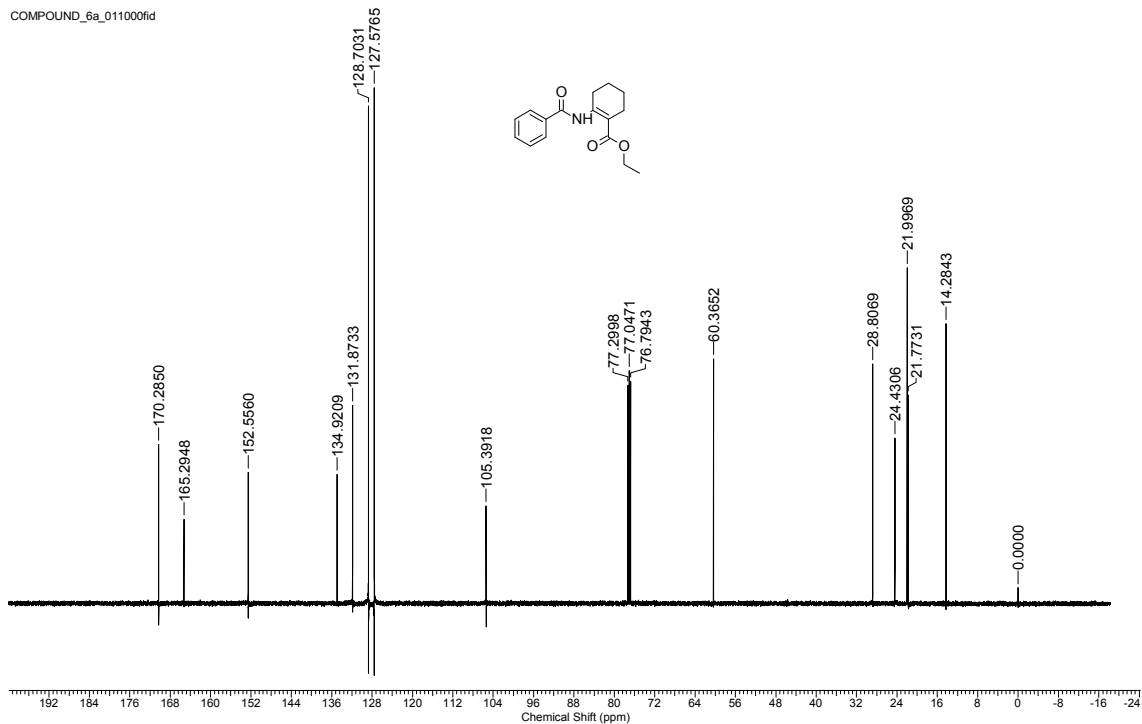
¹H NMR spectra (Compound 6a)

COMPOUND_6a_010000fid



¹³C NMR spectra (Compound 6a)

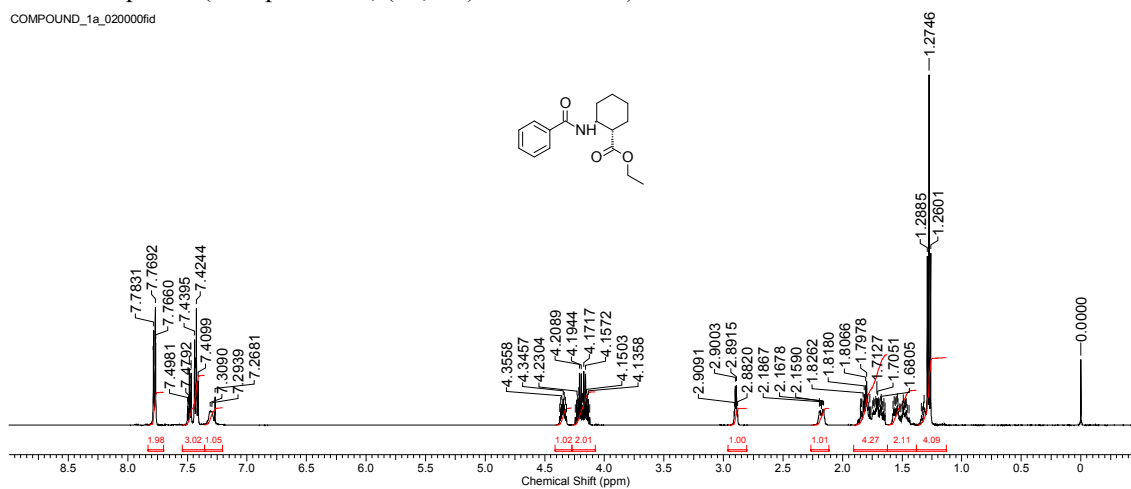
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2-2. Compound 1a

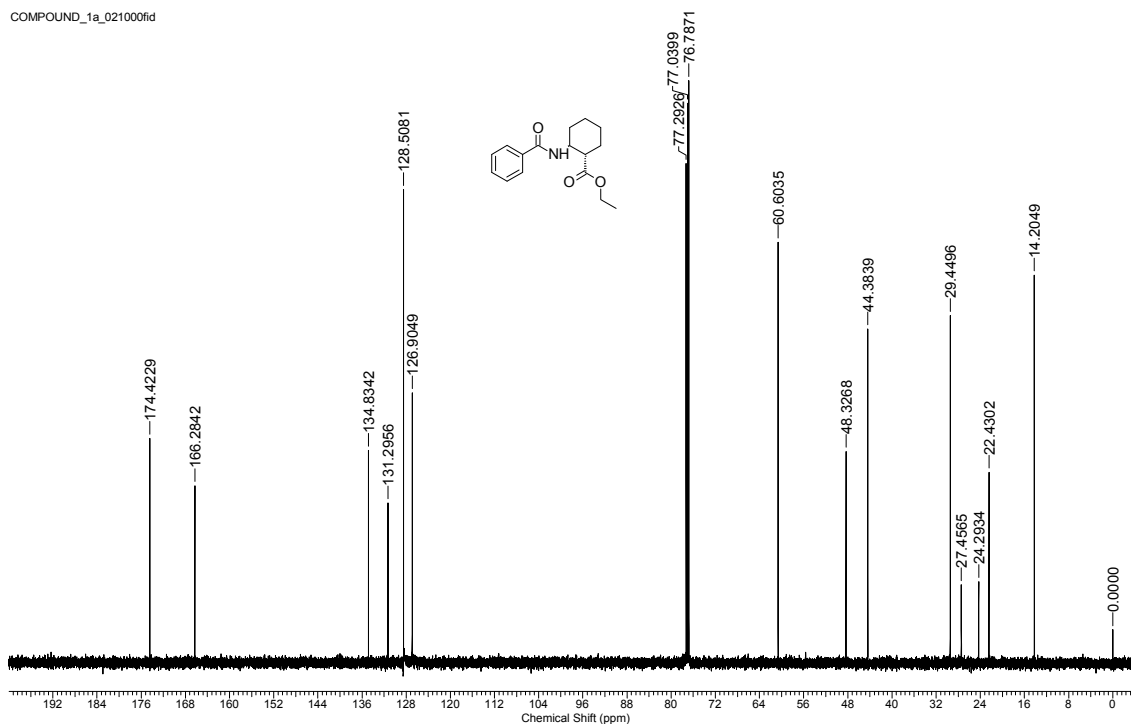
¹H NMR spectra (Compound 1a, (1*S*, 2*R*) stereoisomer)

COMPOUND_1a_021000fid



¹³C NMR spectra (Compound 1a)

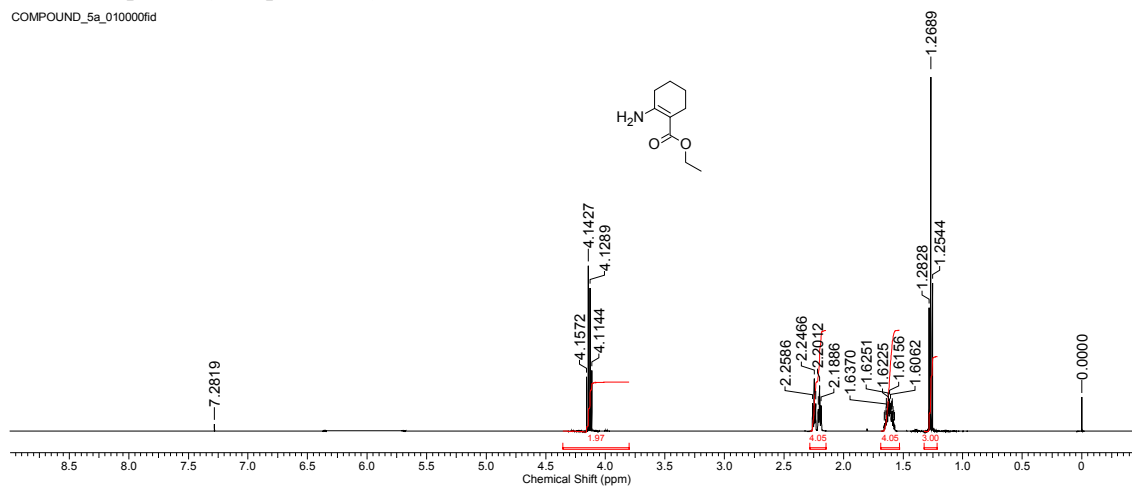
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2-3. Compound 5a

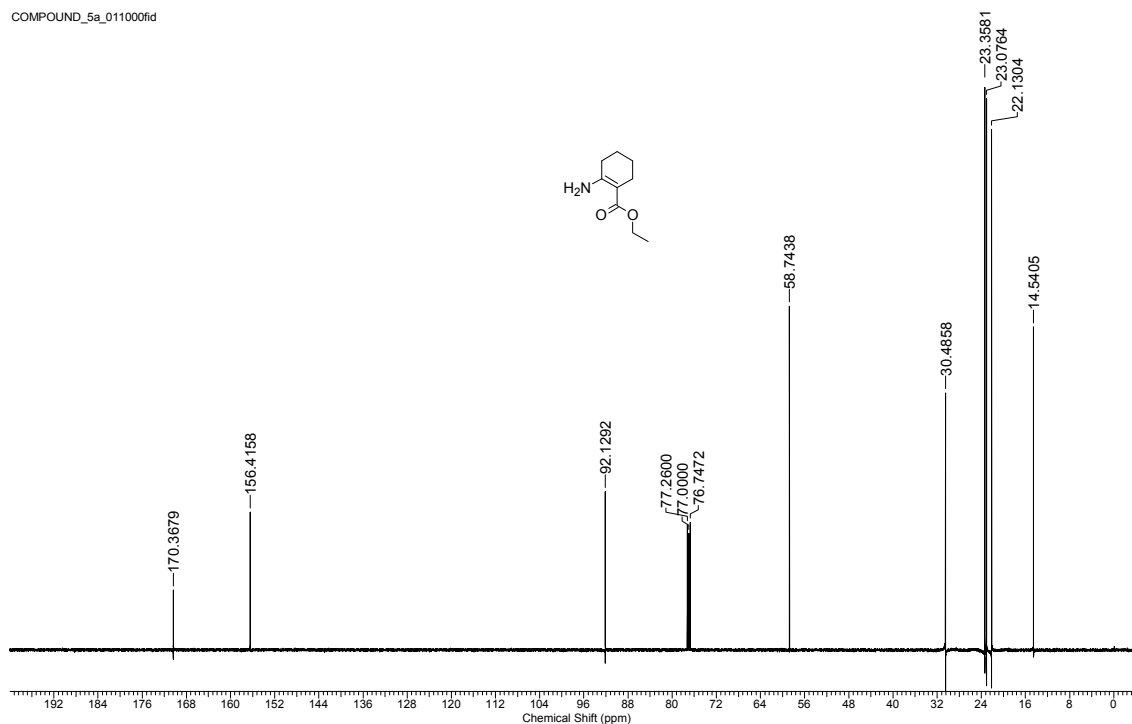
¹H NMR spectra (Compound 5a)

COMPOUND_5a_010000fid



¹³C NMR spectra (Compound 5a)

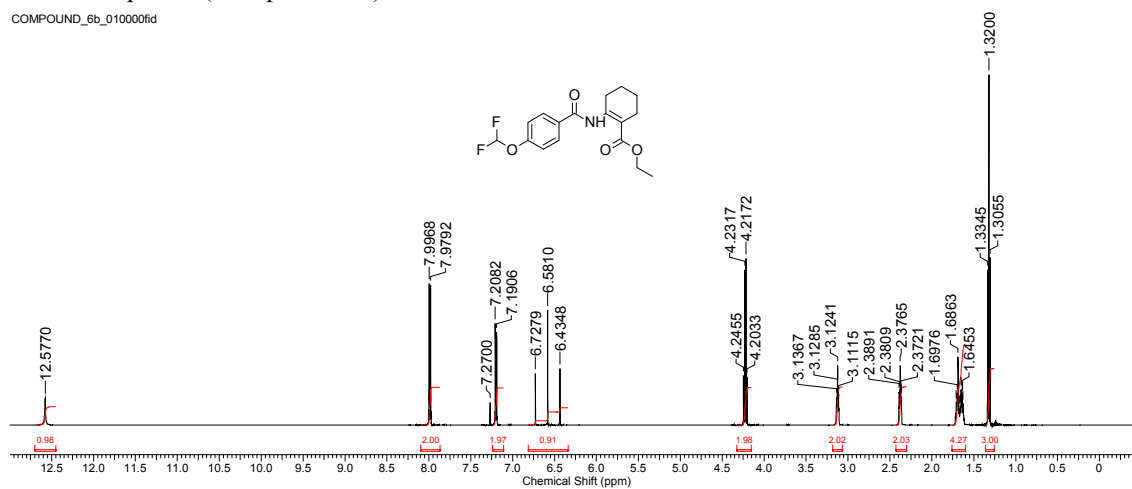
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2-4. Compound **6b**

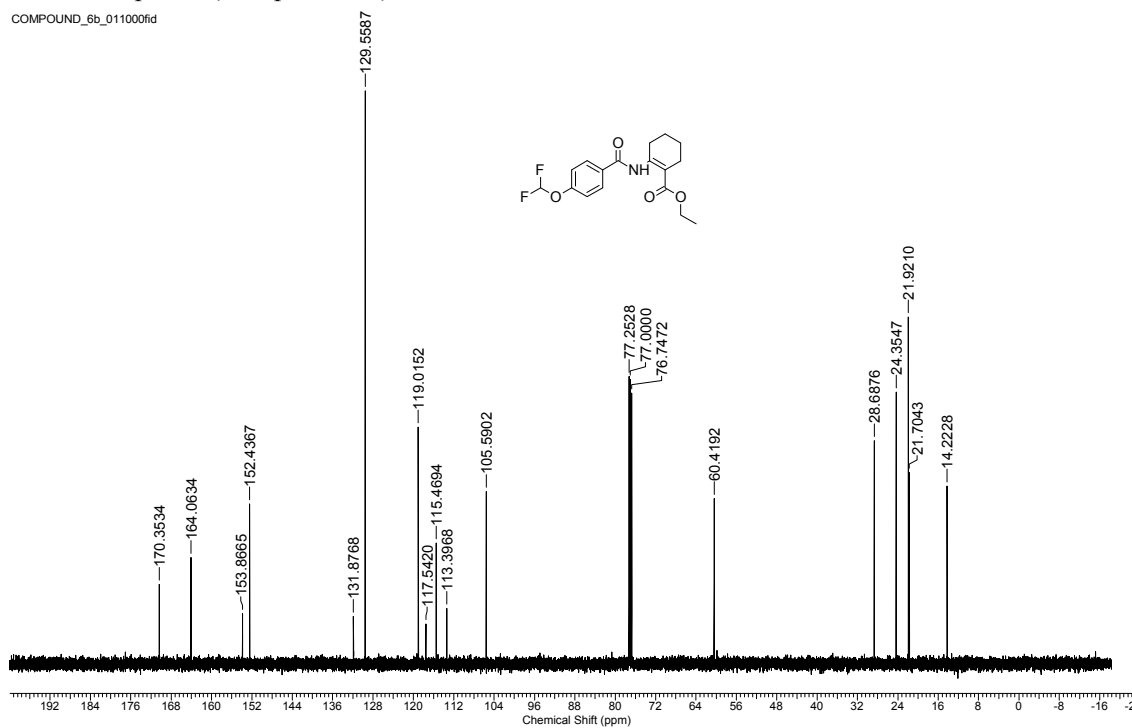
¹H NMR spectra (Compound **6b**)

COMPOUND_6b_010000fid



¹³C NMR spectra (Compound **6b**)

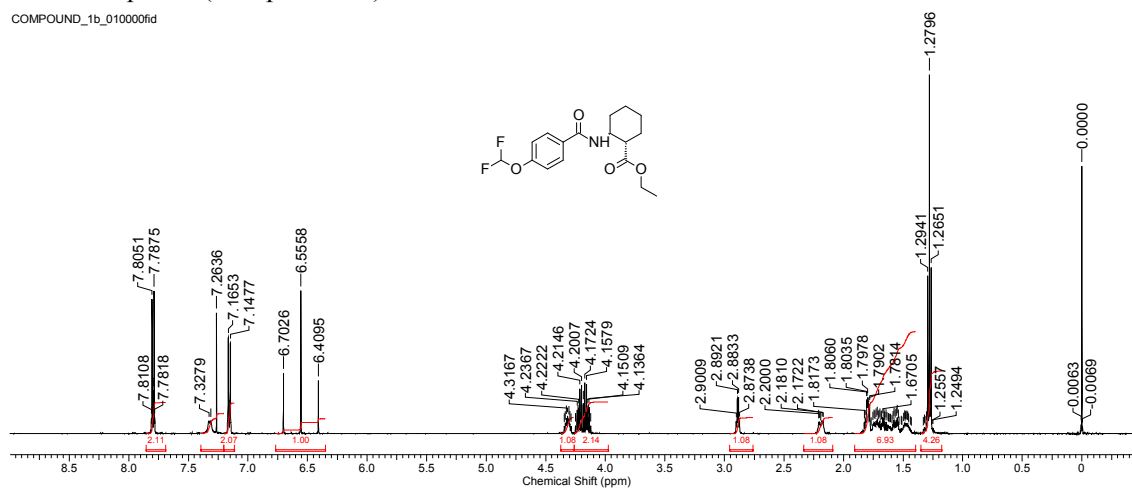
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2-5. Compound 1b

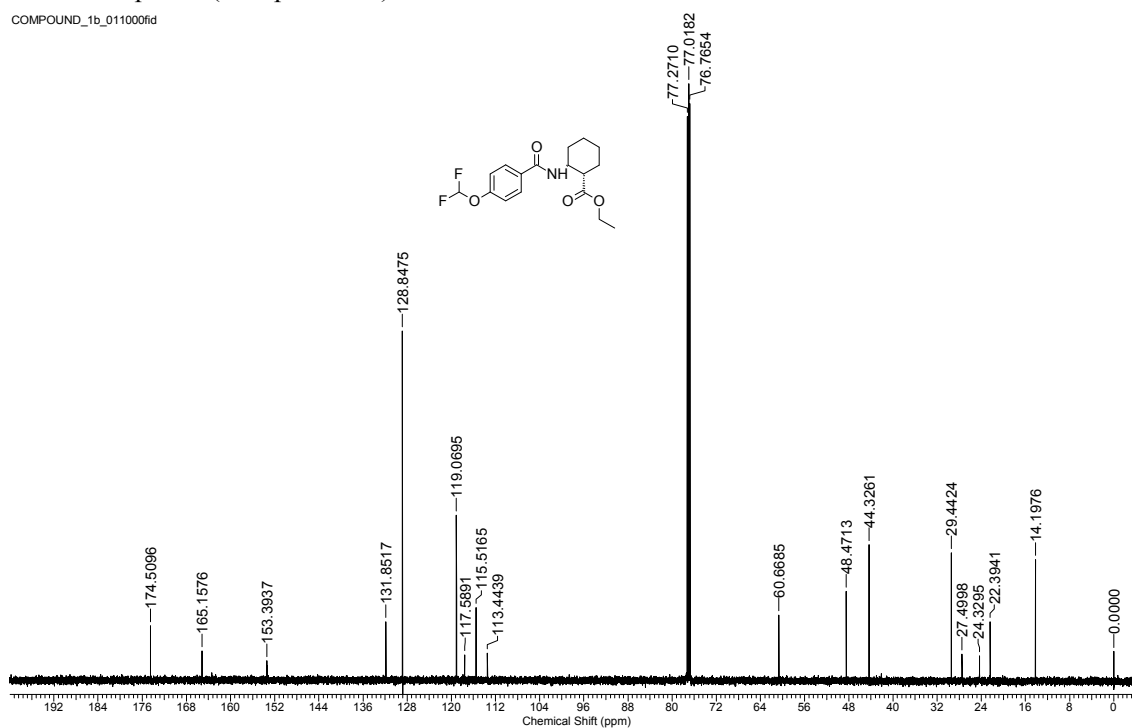
¹H NMR spectra (Compound 1b)

COMPOUND_1b_010000fid



¹³C NMR spectra (Compound 1b)

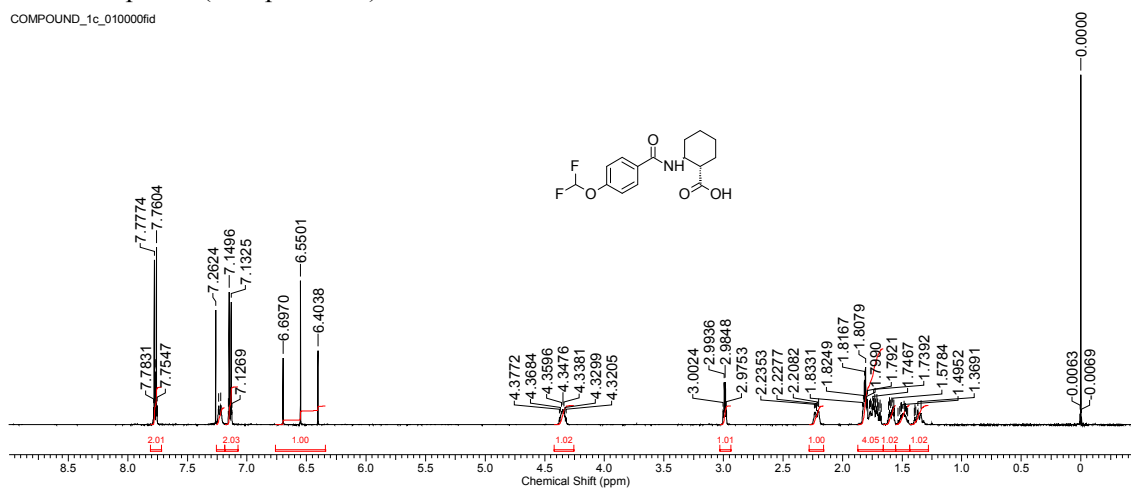
COMPOUND_1b_011000fid



2-6. Compound 1c

¹H NMR spectra (Compound 1c)

COMPOUND_1c_0110000fid



¹³C NMR spectra (Compound 1c)

COMPOUND_1c_0110000fid

