Supporting Information

Enantioselective Conjugate Addition of Hydroxylamines to α,β-Unsaturated 2-Acyl Imidazoles Catalyzed by Chiral-at-Metal Rh(III) Complex

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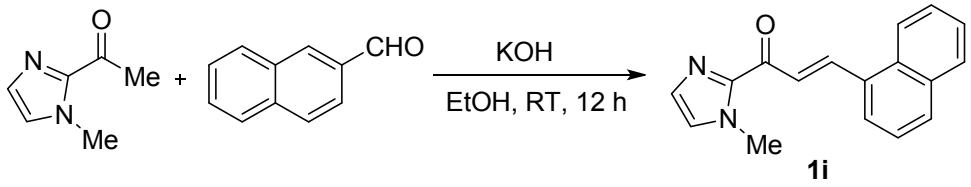
I General Information

Chemicals and solvents were obtained from various commercial sources. Unless otherwise stated, all reactions were carried out under N_2 atmosphere. THF and Toluene were distilled freshly before use over sodium and bezophenone, CH_2Cl_2 and DCE were distilled from CaH_2. Chloroform was distilled over P_2O_5 and stored over 3 Å molecular sieves. ^1H and ^{13}C spectra were recorded on a Bruker Ascend 400 (400 MHz) spectrometer using solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a VERTEX70 IR spectrometer as KBr pellets with absorption in cm^{-1}. For TLC, silica gel plates were used and the spots were visualized by UV light and/or by heating the plate treated with PMA solution. HPLC analyses of the compounds were done using chiralpak IA-IF columns on (Daicel Chemical Industries, LTD) on Shimadzu LC-20AD using hexanes and isopropanol as eluent. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Starna scientific polarimeter (SGW-1) and are reported as follows: $[\alpha]_D^{RT}$ (*c* in g per 100 mL solvent). HRMS data were obtained on a Thermo Fisher Scientific LTQ FT Ultrasystem.

II Experimental Section

Starting materials (**1a, 1b,** [1] **1c**,[3] **1d,**[4] **1e-1k,**[2] **1l-1o**,[1]) were prepared according to literature procedures. N-Boc as well as N-Cbz hydroxyl amines were purchased from "Energy Chemical" company, China. Chiral Ir(III) and Rh(III) complexes, Δ-Ir1, Δ-Ir2 and Δ-Rh were prepared according to literature procedures.[5,6]

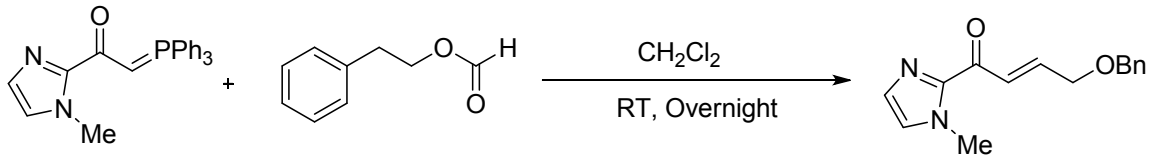
(*E*)-3-(1-naphthyl)-1-(1-methyl-1H-imidazol-2-yl) prop-2-en-1-one (1i)



1i

To a stirred solution of 2-acetyl-1-methylimidazole[2] (5 mmol, 1.0 equiv.) in EtOH (10 mL)were added 1-naphthaldehyde (5.0 mmol, 1.0 equiv.) and KOH (1.0 mmol, 0.2 equiv.). The reaction mixture was allowed to stir at RT. After completion of the reaction, brine solution (30 mL) was added to the reaction mixture then it was extracted with EtOAc (4 x 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 then concentrated in a rotovap. The resulting crude mixture was purified by a flash column chromatography on silica gel using EtOAc/petroleum ether as eluents to get pure product. Yellow solid; Yield = 56%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 15.8 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 15.7 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.59 (ddd, *J* = 6.9, 8.4, 1.3 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.24 (s, 1H), 7.10 (s, 1H), 4.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 144.1, 140.0, 133.8, 132.1, 131.9, 130.8, 129.4, 128.8, 127.3, 126.9, 126.1, 125.5, 125.5, 125.1, 123.4, 36.4; IR (KBr): *ν* 3076, 3042, 2963, 1661, 1598, 1408, 1471, 1346, 1020, 968, 802, 778, 759, 601 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{14}N_2O$ $(M+H)^+$ 263.1184; found 263.1178.

(*E*)-4-(benzyloxy)-1-(1-methyl-1H-imidazol-2-yl)but-2-en-1-one (1o)



1o

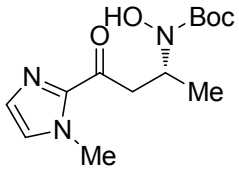
To a stirred solution of phenethyl formate (2.6 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added 3-phenyl-1-propanal (3.12 mmol, 1.2 equiv) at RT. The reaction mixture was allowed to stir at RT. After completion of the reaction, solvent was removed in a rotovap. The residue was loaded on a silica gel column. It was eluted with ethyl acetate/ petroleum ether mixture to get the product. The purified material was diluted in dichloromethane (5 mL) and then DMAP (3.902 mmol, 1.5 equiv) was added to the flask. The flask was sealed with a septum and kept at -23 ºC for 3 d. Then the reaction mixture was diluted with EtOAc (50 mL), washed with saturated NH_4Cl solution (2x30 mL) and brine solution. The combined organic extracts were dried over anhydrous Na_2SO_4 then concentrated in a rotovap. **1o** was obtained as Yellow oil, Yield = 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dt, *J* = 106.8, 2.0 Hz, 1H), 7.35-7.27 (m, 5H), 7.18 (d, *J* = 0.8 Hz, 1H), 7.14 (dt, *J* = 15.6, 4.8 Hz, 1H), 7.05 (s, 1H), 4.59 (s, 2H), 4.28 (dd, *J* = 4.4, 1.6 Hz, 2H),4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2, 143.3, 137.7, 129.3, 128.3, 127.7, 127.7, 127.2, 126.1, 72.6, 69.2, 36.2; IR (KBr): *ν* 3109, 3031, 2860, 1722, 1670, 1625, 1454, 1407,1362, 1276, 1157, 1119, 1027, 917, 842, 738, 699 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{16}N_2NaO_2$ $(M+Na)^+$ 279.1104; found 279.1102.

General procedure for catalytic enantioselective addition of N-protected hydroxylamine to α,β-unsaturated 2-acyl imidazoles

To a solution of α,β-unsaturated 2-acyl imidazole substartes (0.2-0.3 mmol) in $CHCl_3$ (1.0 M), 0.5-2 mol% of chiral metal complex was added under N_2 atmosphere. The reaction mixture was allowed to stir at room temperature for 20 minutes before adding amine nucleophile (1.2 equiv.). Then the reaction mixture was allowed to stir at room temperature or 50 ºC under N_2 atmosphere. After reaction was completed monitored by TLC, the reaction mixture was directly loaded onto a silica gel column. It was eluted with

ethyl acetate/ petroleum ether mixture to get the corresponding conjugated addition product.

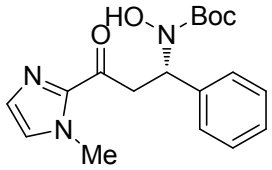
(*R*)-tert-Butyl hydroxy(4-(1-methyl-1H-imidazol-2-yl)-4-oxobutan-2-yl)carbamate (3a)



3a

According to the general procedure, **3a** was obtained as light yellow viscous liquid, 51.5 mg, 91% yield, 92% ee, $[\alpha]_D^{25}$ = -24.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 15.93 min, t_{minor} =14.79 min); Rf = 0.12 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (brs, 1H), 7.08 (s, 1H), 7.00 (s, 1H), 4.64-4.56 (m, 1H), 3.92 (s, 3H), 3.72 (t, *J* = 12.0 Hz, 1H), 2.31 (dd, *J* = 12.4, 2.8 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 155.7, 143.3, 128.6, 127.1, 80.3, 53.8, 43.6, 36.2, 28.0, 18.3; IR (KBr): *v* 3344, 3111, 2977, 2974, 2850, 1709, 1681, 1479, 1406, 1362, 1174, 1106, 1011, 930, 801, 739, 689 cm^{-1}.; HRMS (ESI): calcd for $C_{13}H_{21}N_3NaO_4$ $(M+Na)^+$ 306.1430; found 306.1424.

(*S*)-tert-Butyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-phenylpropyl)-carbamate (3b)

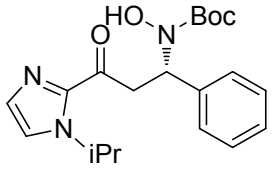


3b

According to the general procedure, **3b** was obtained as a white solid, 34.5 mg, 50% yield, 95% ee, mp = 132.3-134.2 °C, $[\alpha]_D^{25}$ = -121.2 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, t_{major} = 13.52 min, t_{minor} = 17.47 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (brs, 1H), 7.53-7.51 (m, 2H), 7.36-7.27 (m,

3H), 7.16 (s, 1H), 7.07 (s, 1H), 5.63 (d, J = 11.6 Hz, 1H), 4.33 (t, J = 12.4 Hz, 1H), 4.00 (s, 3H), 2.80 (dd, J = 12.8, 2.4 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 156.0, 143.4, 139.7, 128.8, 128.3, 127.6, 127.3, 127.2, 80.8, 61.0，42.7, 36.3, 28.1. IR (KBr): v 3421, 3133, 3116, 2972, 2982, 2918, 1700, 1685, 1416, 1387, 1222, 989, 927, 779, 713, 696 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{23}N_3NaO_4$ $(M+Na)^+$ 368.1586; found 368.1582.

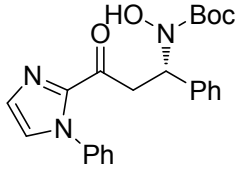
(*S*)-tert-Butyl hydroxy(3-(1-isopropyl-1H-imidazol-2-yl)-3-oxo-1-phenylpropyl)-carbamate (3c)



3c

According to the general procedure, **3c** was obtained as yellow viscous liquid, 64.0 mg, 86% yield, 91% ee, $[\alpha]_D^{25}$ = -55.6 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 11.07 min, t_{minor} = 8.02 min); R_f = 0.17 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (brs, 1H), 7.53-7.51 (m, 2H), 7.36-7.26 (m, 3H), 7.22 (s, 1H), 7.14 (s, 1H), 5.67 (d, J = 10.0 Hz, 1H), 5.53 (m, 1H), 4.31 (t, J = 12.4 Hz, 1H), 2.83 (dd, J = 12.4, 3.2 Hz, 1H), 1.46 (d, J = 6.9 Hz, 6H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 158.6, 155.9, 142.6, 139.6, 129.2, 128.3, 127.5, 127.2, 121.6, 81.9, 80.8, 60.7, 49.5, 43.1, 28.1, 28.0, 23.6, 23.4; IR (KBr): v 3311, 2980, 2933, 1684, 1455, 1396, 1368, 1254, 1167, 1107, 931, 777, 701 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{27}N_3NaO_4$ $(M+Na)^+$ 396.1899; found 396.1896.

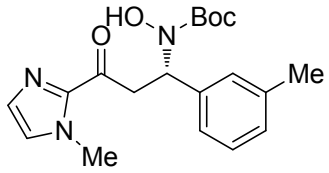
(*S*)-tert-Butyl hydroxy(3-oxo-1-phenyl-3-(1-phenyl-1H-imidazol-2-yl)propyl)-carbamate (3d)



3d

According to the general procedure, **3c** was obtained as a white solid, 57.8 mg, 71% yield, 96% ee, mp = 124.4-126.3 °C, $[\alpha]_D^{25}$ = -121.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 14.10 min, t_{minor} = 9.08 min); R_f = 0.20 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (brs, 1H), 7.51-7.49 (m, 5H), 7.35-7.23 (m, 7H), 5.60 (d, *J* = 11.6 Hz, 1H), 4.33 (t, *J* = 12.4 Hz, 1H), 2.79 (dd, *J* = 12.0, 0.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 156.0, 143.2, 139.6, 137.7, 129.2, 129.1, 129.0, 128.4, 127.6, 127.4, 127.2, 125.7, 81.0, 60.9, 42.7, 28.1; IR (KBr): *v* 3439, 3117, 3064, 2974, 1687, 1594, 1496, 1401, 1308, 1255, 1160, 1095, 907, 762, 697 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{25}N_3NaO_4$ $(M+Na)^+$ 430.1743; found 430.1739.

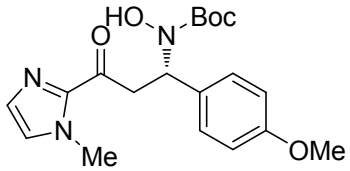
(*S*)-tert-Butyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-p-tolylpropyl)-carbamate (3e)



3e

According to the general procedure, **3e** was obtained as a white solid, 51.0 mg, 71% yield, 90% ee, mp = 85.0-87.0 °C, $[\alpha]_D^{25}$ = -93.5 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 11.16 min, t_{minor} = 9.28 min); R_f = 0.12 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (brs, 1H), 7.34-7.30 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 7.10-7.08 (m, 2H), 5.60 (d, *J* = 10.2 Hz, 1H), 4.31 (t, *J* = 12.5 Hz, 1H), 4.00 (s, 3H), 2.78 (dd, *J* = 12.8, 3.2 Hz, 1H), 2.35 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 156.0, 143.3, 139.5, 137.9, 128.7, 128.3, 128.2, 127.9, 127.3, 124.2, 80.7, 60.8, 42.6, 36.2, 28.0, 21.4; IR (KBr): *v* 3421, 3117, 2975, 2923, 2868, 1689, 1510，1476, 1413, 1367, 1319, 1255, 1164, 1103，989, 931, 785 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{25}N_3NaO_4$ $(M+Na)^+$ 382.1737; found 382.1735.

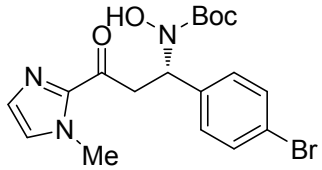
(S)-*tert*-Butyl hydroxy(1-(4-methoxyphenyl)-3-(1-methyl-1H-imidazol-2-yl)-3-oxopropyl)carbamate (3f)



3f

According to the general procedure, **3f** was obtained as a yellow solid, 38.3 mg, 51% yield, 91% ee, mp = 120.3-122.2 ^{o}C, $[\alpha]_D^{25}$ = -95.9 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 8.94 min, t_{minor} = 11.79 min); R_f = 0.10 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (brs, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.17 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 5.57 (d, *J* = 11.6 Hz, 1H), 4.31 (t, *J* = 12.4 Hz, 1H), 4.01 (s, 3H), 3.80 (s, 3H), 2.74 (d, *J* = 12.4 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 158.9, 156.0, 143.4, 131.8, 128.7, 128.5, 127.2, 113.6, 80.8, 60.5, 55.2, 42.7, 36.3, 28.1; IR (KBr): *v* 3446, 3112, 2979, 2920, 1703, 1687, 1616, 1519, 1416, 1324, 1162, 1092, 1032, 931, 831, 743 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{25}N_3NaO_5$ $(M+Na)^+$ 398.1692; found 398.1688.

(*S*)-tert-Butyl 1-(4-bromophenyl)-3-(1-methyl-1H-imidazol-2-yl)-3-oxopropylhydroxycarbamate (3g)

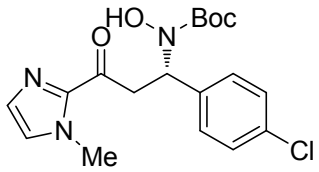


3g

According to the general procedure, **3g** was obtained as a white solid, 65.1 mg, 77% yield, 93% ee, mp = 113.4-115.1 ^{o}C, $[\alpha]_D^{25}$ = -119.7 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min, t_{major} = 8.47 min, t_{minor} = 7.12 min); R_f = 0.08 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (brs, 1H), 7.47-7.40 (m, 4H), 7.16 (s, 1H), 7.08 (s, 1H), 5.59 (d, *J* = 11.2 Hz, 1H), 4.27 (t, *J* = 12.4 Hz, 1H), 3.99 (s, 3H), 2.79 (dd, *J* = 13.2 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.01, 155.9, 143.0, 138.6, 131.4, 129.0, 128.7, 127.3, 121.5, 81.0, 60.0, 42.4, 36.2, 28.0; IR (KBr): *v* 3446, 3125,

3106, 2973, 2929, 1718, 1671, 1457, 1409, 1367, 1321, 1162, 1102, 1012, 933, 802, 536 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{22}BrN_3NaO_4$ $(M+Na)^+$ 446.0691; found 446.0683.

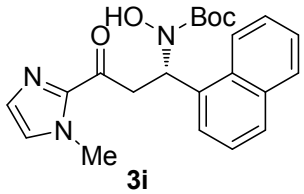
(*S*)-tert-Butyl 1-(4-chlorophenyl)-3-(1-methyl-1H-imidazol-2-yl)-3-oxopropylhydroxycarbamate (3h)



3h

According to the general procedure, **3h** was obtained as a white solid, 64.4 mg, 85% yield, 92% ee, mp = 108.6-110.5 °C, $[\alpha]_D^{25}$ = -73.2 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, t_{major} = 11.09 min, t_{minor} = 9.21 min); R_f = 0.10 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (brs, 1H), 7.54-7.53 (m, 1H), 7.41-7.40 (m, 1H), 7.29-7.27 (m, 2H), 7.18 (s, 1H), 7.09 (s, 1H), 5.58 (d, *J* = 11.2 Hz, 1H), 4.29 (t, *J* = 12.4 Hz, 1H), 4.02 (s, 3H), 2.75 (dd, *J* = 12.8, 3.2 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 155.8, 143.2, 141.6, 134.1, 129.6, 128.8, 127.8, 127.5, 127.4, 125.5, 81.1, 60.4, 42.5, 36.3, 28.0; IR (KBr): *v* 3422, 3129, 2969, 2927, 1708, 1685, 1574, 1478, 1416, 1366, 1221, 1161, 1096, 992, 929, 724 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{22}ClN_3NaO_4$ $(M+Na)^+$ 402.1197; found 402.1192.

(*S*)-tert-Butyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-1-(naphthalen-1-yl)-3-oxopropyl)carbamate (3i)

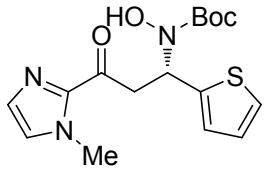


3i

According to the general procedure, **3i** was obtained as yellow viscous liquid, 49.0 mg, 62% yield, 94% ee, $[\alpha]_D^{25}$ = -19.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 13.86 min, t_{minor} = 12.73 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400

MHz, $CDCl_3$): δ 10.14 (brs, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.59-7.55 (m, 1H), 7.51-7.45 (m, 2H), 7.20 (s, 1H), 7.09 (s, 1H), 6.43 (d, *J* = 11.2 Hz, 1H), 4.43 (t, *J* = 12.4 Hz, 1H), 4.03 (s, 3H), 2.91 (dd, *J* = 12.8, 2.8 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 155.7, 143.4, 136.1, 133.8, 130.5, 128.9, 128.9, 128.3, 127.5, 126.5, 125.5, 125.4, 124.4, 123.0, 80.8, 57.4, 42.4, 36.3, 28.0; IR (KBr): *v* 3421, 3119, 2975, 2927, 1687, 1509, 1474, 1416, 1165, 1105, 931, 802, 725 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{25}N_3NaO_4$ $(M+Na)^+$ 418.1743; found 418.1740.

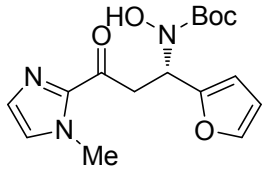
(*S*)-tert-Butyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-(thiophen-2-yl)propyl)carbamate (3j)



3j

According to the general procedure, **3j** was obtained as a yellow solid, 35.1 mg, 50% yield, 94% ee, mp = 125.0-127.0 °C, $[\alpha]_D^{25}$ = -189.1 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, t_{major} = 11.54 min, t_{minor} = 15.72 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (brs, 1H), 7.16-7.15 (m, 1H), 7.09 (s, 1H), 7.05-7.01 (m, 2H), 6.89-6.87 (m, 1H), 5.79 (d, *J* = 10.0 Hz, 1H), 4.23 (t, *J* = 12.4 Hz, 1H), 3.93 (s, 3H), 2.77 (dd, *J* = 12.8, 3.6 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 155.9, 143.3, 141.4, 128.8, 127.3, 126.2, 125.3, 124.8, 81.2, 57.3，43.6, 36.2, 28.0; IR (KBr): *v* 3421, 3136, 3115, 2973, 2926, 1708, 1683, 1458, 1318, 1161, 1091, 988, 930, 808, 695 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{21}N_3NaO_4S$ $(M+Na)^+$ 374.1150; found 374.1145.

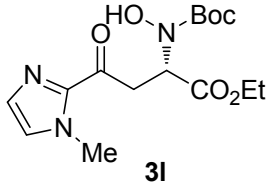
(*S*)-tert-Butyl 1-(furan-2-yl)-3-(1-methyl-1H-imidazol-2-yl)-3-oxopropylhydroxycarbamate (3k)



3k

According to the general procedure, **3k** was obtained as a white solid, 10.7 mg, 16% yield, 99.5% ee, mp = 116.4-118.4 ^{o}C, $[\alpha]_D^{25}$ = -71.6 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IF, λ = 254 nm, hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min, t_{major} = 10.41 min, t_{minor} = 14.30 min); R_f = 0.10 in 1:6 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (brs, 1H), 7.37-7.36 (m, 1H), 7.17 (s, 1H), 7.08 (s, 1H), 6.34-6.32 (m, 2H), 5.70 (d, *J* = 11.6 Hz, 1H), 4.20 (t, *J* = 12.4 Hz, 1H), 4.01 (s, 3H), 2.91 (d, *J* = 12.8 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 156.1, 152.4, 143.4, 141.8, 128.9, 127.3, 110.3, 107.1, 81.2, 55.6，40.3, 36.3, 28.1; IR (KBr): *v* 3422, 3134, 3114, 2979, 2926, 1706, 1678, 1477, 1418, 1362, 1163, 1106, 1090, 1006, 989, 927, 734 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{21}N_3NaO_5$ $(M+Na)^+$ 358.1379; found 358.1373.

(*S*)-Ethyl 2-(tert-butoxycarbonyl)-4-(1-methyl-1H-imidazol-2-yl)-4-oxobutanoate (3l)

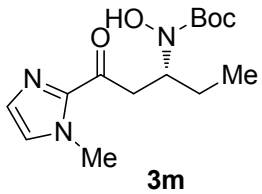


3l

According to the general procedure, **3l** was obtained as a white solid, 59.3 mg, 87% yield, 91% ee, mp = 81.7-83.0 ^{o}C, $[\alpha]_D^{25}$ = -85.8 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 19.36 min, t_{minor} = 28.86 min); R_f = 0.05 in 1:06 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (brs, 1H), 7.16 (s, 1H), 7.07 (s, 1H), 5.28-5.21 (m, 1H), 4.27-4.19 (m, 2H), 3.99 (s, 3H), 3.89 (dd, *J* =14.4, 10.8 Hz, 1H), 3.29 (d, *J* = 10.8 Hz, 1H), 1.44 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 169.7, 156.8, 142.9, 128.8, 127.1, 81.5, 61.7, 59.9, 38.4, 36.2, 28.0, 14.0; IR (KBr): *v* 3492, 3124,

2980, 2926, 1733, 1685, 1420, 1370, 1272, 1164, 1025, 925, 859, 671 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}N_3NaO_6$ $(M+Na)^+$ 364.1485; found 364.1481.

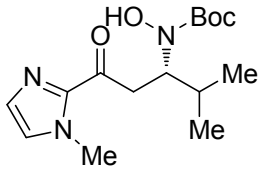
(*R*)-tert-Butyl hydroxy(1-(1-methyl-1H-imidazol-2-yl)-1-oxopentan-3-yl)carbamate (3m)



3m

According to the general procedure, **3m** was obtained as colorless viscous liquid, 54.0 mg, 91% yield, 95% ee, $[\alpha]_D^{25}$ = -50.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IF, λ = 254 nm, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, t_{major} = 11.28 min, t_{minor} = 10.22 min); R_f = 0.08 in 1:06 EtOAc/petroleum ether. ^1H NMR (400 MHz, $CDCl_3$): δ 9.42 (brs, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 4.49-4.42 (m, 1H), 3.99 (s, 3H), 3.75 (t, *J* = 12.0 Hz, 1H), 2.44 (dd, *J* = 12.0, 3.2 Hz, 1H), 1.88-1.79 (m, 1H), 1.62-1.52 (m, 1H), 1.28 (s, 9H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 155.8, 143.5, 128.7, 127.2, 80.2, 59.1, 42.2, 36.3, 28.0, 26.0, 10.8; IR (KBr): *v* 3462, 3108, 2971, 2875, 1709, 1678, 1418, 1367, 1249, 1157, 1165, 1087, 980, 792 686 cm^{-1}.; HRMS (ESI): calcd for $C_{14}H_{23}N_3NaO_4$ $(M+Na)^+$ 320.1586; found 320.1584.

(S)-tert-butyl hydroxy(4-methyl-1-(1-methyl-1H-imidazol-2-yl)-1-oxopentan-3-yl)carbamate (3n)

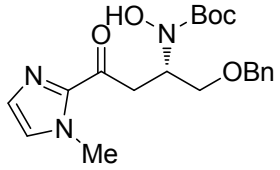


3n

According to the general procedure, **3n** was obtained as yellow viscous liquid, 47.9 mg, 77% yield, 92% ee, $[\alpha]_D^{25}$ = -25.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IC, λ = 254 nm, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, t_{major} = 19.51 min, t_{minor} = 15.41 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^1H NMR (400 MHz, $CDCl_3$): δ 9.63 (brs, 1H), 7.15 (s, 1H), 7.07 (s, 1H), 4.26-4.18 (m, 1H), 3.98 (s, 3H),

3.74 (t, J = 12.4 Hz, 1H), 2.58 (dd, J = 12.0, 2.4 Hz, 1H), 2.09-2.00 (m, 1H), 1.27 (s, 9H), 1.03-0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 155.5, 143.3, 128.5, 127.1, 80.0, **60.3**, 39.8, 36.1, 31.3, 27.9, 19.8, 19.5; IR (KBr): v 3134, 3114, 2970, 2929, 2874, 1705, 1684, 1474, 1410, 1366, 1304, 1256, 1174, 1132, 1094, 966, 930, 790, 750, 695 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{25}N_3NaO_4$ $(M+Na)^+$ 334.1737; found 334.1740.

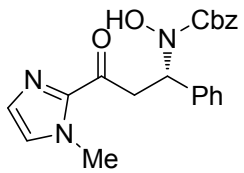
(S)-tert-butyl (1-(benzyloxy)-4-(1-methyl-1H-imidazol-2-yl)-4-oxobutan-2-yl)(hydroxy)carbamate (3o)



3o

According to the general procedure, **3o** was obtained as yellow viscous liquid, 47.5 mg, 61% yield, 98% ee, $[\alpha]_D^{25}$ = -9.9 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, t_{major} = 17.71 min, t_{minor} = 16.54 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (brs, 1H), 7.35-7.27 (m, 5H), 7.14 (s, 1H), 7.04 (s, 1H), 4.84-4.76 (m, 1H), 4.57 (q, J = 12.0, 6.8 Hz, 1H), 3.98 (s, 3H), 3.77-3.67 (m, 2H), 3.60-3.56 (m, 1H), 2.65 (dd, J = 12.4, 3.2 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 155.9, 143.4, 138.1, 128.6, 128.3, 127.7, 127.6, 127.5, 127.1, 80.6, 73.0, 69.5, 57.3, 38.9, 36.2, 28.0; IR (KBr): v 3392, 3123, 2972, 2924, 2866, 1687, 1465, 1409, 1365, 1256, 1168, 1113, 1024, 929, 745, 701 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{27}N_3NaO_5$ $(M+Na)^+$ 412.1843; found 412.1840.

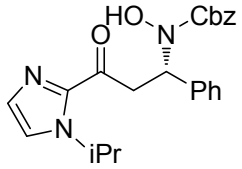
(*S*)-Benzyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-phenylpropyl)carbamate (4a)



4a

According to the general procedure, **4a** was obtained as yellow viscous liquid, 70.5 mg, 93% yield, 95% ee, $[\alpha]_D^{25}$ = -68.2 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IE, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 16.79 min, t_{minor} = 21.71 min); R_f = 0.16 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.70 (brs, 1H), 7.51-7.49 (m, 2H), 7.34-7.26 (m, 6H), 7.21-7.19 (m, 2H), 7.10 (s, 1H), 7.00 (s, 1H), 5.69 (d, *J* = 11.2 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.36 (t, *J* = 12.4 Hz, 1H), 3.95 (s, 3H), 2.75 (dd, *J* = 12.8, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 156.6, 143.2, 139.1, 136.2, 128.5, 128.4, 128.2, 127.8, 127.3, 127.2, 67.3, 60.9, 42.6, 36.3; IR (KBr): *v* 3430, 3120, 3033, 2929, 2848, 1701, 1681, 1406, 1297, 1095, 930, 745, 697 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{22}N_3O_4$ $(M+H)^+$ 380.1610; found 380.1606.

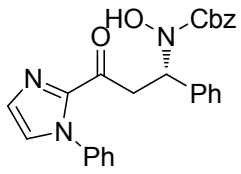
(S)-benzyl hydroxy(3-(1-isopropyl-1H-imidazol-2-yl)-3-oxo-1-phenylpropyl)carbamate (4b)



4b

According to the general procedure, **4b** was obtained as yellow viscous liquid, 52.1 mg, 64% yield, 94% ee, $[\alpha]_D^{25}$ = -64.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 8.30 min, t_{minor} = 9.63 min); R_f = 0.15 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.70 (brs, 1H), 7.51-7.49 (m, 2H), 7.36-7.25 (m, 7H), 7.19-7.17 (m, 3H), 5.68(d, *J* = 11.2 Hz, 1H), 5.53-5.48 (m, 1H), 5.06(d, *J* = 12.8 Hz, 1H), 4.97(d, *J* = 12.8 Hz, 1H), 4.37 (t, *J* = 12.4 Hz, 1H), 2.73 (dd, *J* = 12.4, 2.8 Hz, 1H), 1.44 (t, *J* = 6.8Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 156.5, 142.7, 139.2, 136.3, 128.5, 128.3, 127.8, 127.7, 127.2, 121.6, 67.2, 61.2, 49.6, 43.2, 30.9, 23.5, 23.5; IR (KBr): *v* 3295, 3065, 3033, 2930, 1687, 1498, 1454, 1398, 1307, 1257, 1108, 1030, 986, 746, 699 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{26}N_3O_4$ $(M+H)^+$ 408.1919; found 408.1918.

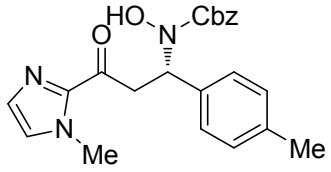
(S)-benzyl hydroxy(3-oxo-1-phenyl-3-(1-phenyl-1H-imidazol-2-yl)propyl)carbamate (4c)



4c

According to the general procedure, **4c** was obtained as yellow viscous liquid, 75.8 mg, 86% yield, 97% ee, $[\alpha]_D^{25}$ = -72.8 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, t_{major} = 25.30 min, t_{minor} = 21.45 min); R_f = 0.15 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (brs, 1H), 7.49-7.45 (m, 5H), 7.35-7.30 (m, 3H), 7.26-7.18 (m, 8H), 7.17 (s, 1H), 5.65 (d, *J* = 10.4 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.37 (t, *J* = 12.4 Hz, 1H), 2.74 (dd, *J* = 12.4, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3): δ 188.8, 158.8, 156.6, 143.1, 139.0, 137.5, 136.1, 135.5, 129.1, 129.1, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.4, 127.2, 125.7, 67.6, 67.4, 60.8, 42.5; IR (KBr): *v* 3453, 3065, 3032, 2955, 2857, 1693, 1501, 1453, 1406, 1262, 1105, 973, 760, 700 cm^{-1}; HRMS (ESI): calcd for $C_{26}H_{24}N_3O_4$ $(M+H)^+$ 442.1764; found 442.1760.

(S)-benzyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-(p-tolyl)propyl)carbamate (4d)

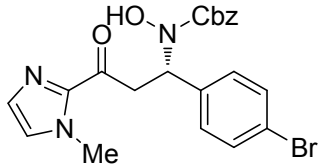


4d

According to the general procedure, **4d** was obtained as colorless viscous liquid, 58.2 mg, 74% yield, 97% ee, $[\alpha]_D^{25}$ = -138.6 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 13.50 min, t_{minor} = 15.94 min); R_f = 0.1 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.58 (brs, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.27-7.26 (m, 3H), 7.21-7.18 (m, 2H), 7.14-7.10 (m, 3H), 7.0 (s, 1H), 5.65 (dd, *J* = 12.3, 2.1 Hz, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 4.98 (d, *J* = 12.4 Hz, 1H), 4.34 (t, *J* = 12.6 Hz, 1H), 3.96 (s, 3H), 2.73 (dd, *J* =

12.6, 3.1 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 156.7, 143.3, 137.5, 136.3, 136.2, 129.1, 128.6, 128.2, 127.9, 127.8, 127.3, 127.1, 67.2, 60.8, 42.6, 36.3, 21.1; IR (KBr): *v* 3132, 3029, 2919, 2860, 1689, 1508, 1464, 1409, 1300, 1219, 1163, 1099, 992, 932, 812, 743, 697 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{24}N_3O_4$ $(M+H)^+$ 394.1759; found 394.1761.

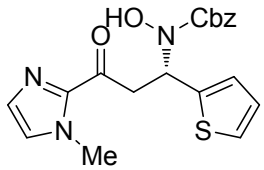
(*S*)-Benzyl 1-(4-bromophenyl)-3-(1-methyl-1H-imidazol-2-yl)-3-oxopropylhydroxycarbamate (4e)



4e

According to the general procedure, **4e** was obtained as a yellow solid, 71.3 mg, 78% yield, 94% ee, mp = 103.4-106.0 °C, $[\alpha]_D^{25}$ = -223.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IE, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 15.27 min, t_{minor} = 19.05 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.76 (brs, 1H), 7.44-7.36 (m, 4H), 7.27-7.20 (m, 5H), 7.08 (s, 1H), 7.00 (s, 1H), 5.63 (d, *J* = 11.6 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 4.31 (t, *J* = 12.8 Hz, 1H), 3.95 (s, 3H), 2.72 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 156.6, 143.0, 138.1, 136.1, 131.5, 129.0, 128.3, 127.9, 127.3, 121.8, 67.4, 60.3, 42.4, 36.3; IR (KBr): *v* 3446, 3129, 3104, 3030, 2921, 1715, 1684, 1671, 1458, 1407, 1301, 1160, 1099, 1012, 932, 796, 762, 700 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}BrN_3O_4$ $(M+H)^+$ 458.0715; found 458.0710.

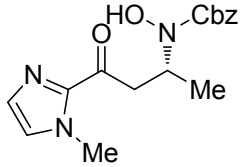
(*S*)-Benzyl hydroxy(3-(1-methyl-1H-imidazol-2-yl)-3-oxo-1-(thiophen-2-yl)propyl)carbamate (4f)



4f

According to the general procedure, **4f** was obtained as yellow viscous liquid, 56.2 mg, 73% yield, 94% ee, $[\alpha]_D^{25}$ = -86.8 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 13.07 min, t_{minor} = 15.71 min); R_f = 0.08 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.61 (brs, 1H), 7.29-7.22 (m, 6H), 7.11 (s, 1H), 7.09-7.08 (m, 1H), 7.01 (s, 1H), 6.95-6.93 (m, 1H), 5.93 (dd, *J* = 12.4, 2.8 Hz, 1H), 5.10 (d, J = 12.4 Hz, 1H), 5.02 (d, *J* = 12.4 Hz, 1H), 4.32 (t, *J* = 12.4 Hz, 1H), 3.96 (s, 3H), 2.81 (dd, *J* = 12.4, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 156.6, 143.2, 140.9, 136.0, 128.6, 128.3, 127.9, 127.3, 126.3, 125.5, 125.1, 67.5, 57.4, 43.6, 36.3; IR (KBr): *v* 3448, 3111, 2923, 2853, 1687, 1409, 1297, 1213, 1098, 986, 927, 694 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{19}N_3O_4NaS$ $(M+Na)^+$ 408.0994; found 408.0987.

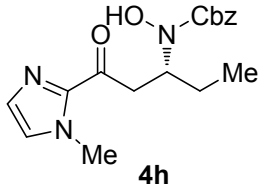
(*R*)-Benzyl hydroxy(4-(1-methyl-1H-imidazol-2-yl)-4-oxobutan-2-yl)carbamate (4g)



4g

According to the general procedure, **4g** was obtained as yellow viscous liquid, 50.7 mg, 80% yield, 92% ee, $[\alpha]_D^{25}$ = -87.1 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, t_{major} = 14.43 min, t_{minor} = 11.51 min); R_f = 0.11 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.0 (s, 1H), 7.32-7.23 (m, 5 H), 7.09 (s, 1H), 6.97 (s, 1H), 5.04 (d, *J* = 12.4 Hz, 1H), 4.98 (d, *J* = 12.4 Hz, 1H), 4.76-4.68 (m, 1H), 3.93 (s, 3H), 3.82 (t, *J* =12.4 Hz, 1H), 2.37 (dd, *J* = 12.0, 2.8 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 156.3, 143.2, 136.3, 128.4, 128.3, 127.9,127.8, 127.2, 67.1, 54.3, 43.6, 36.2, 18.2; IR (KBr): *v* 3434, 3134, 2960, 2929, 1707, 1681, 1406, 1317, 1101, 930, 697 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}N_3NaO_4$ $(M+Na)^+$ 340.1273; found 340.1269.

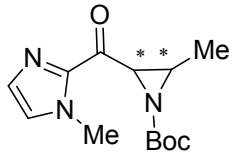
(R)-benzyl hydroxy(1-(1-methyl-1H-imidazol-2-yl)-1-oxopentan-3-yl)carbamate (4h)



4h

According to the general procedure, **4h** was obtained as colorless viscous liquid, 50 mg, 30% yield, 90% ee, $[\alpha]_D^{25}$ = -14.0 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IA, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 10.44 min, t_{minor} = 7.39 min); R_f = 0.08 in 1:3 EtOAc/petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (brs, 1H), 7.30-7.22 (m, 3H), 7.22-7.20 (m, 2H), 7.08 (s, 1H), 6.95 (s, 1H), 5.02 (d, *J* = 12.4 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.54-4.47 (m, 1H), 3.91 (s, 3H), 3.76 (t, *J* = 12.0 Hz, 1H), 2.42 (dd, *J* = 12.4, 3.2 Hz, 1H), 1.92-1.81 (m, 1H), 1.64-1.54(m, 1H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 156.5, 143.3, 136.5, 128.4, 128.2, 128.0, 127.8, 127.2, 67.0, 60.0, 42.2, 41.8, 36.3, 26.0, 10.6; IR (KBr): *v* 3330, 3113,3032, 2963, 2926, 2855, 1680, 1454, 1406, 1327, 1261, 1086, 1025, 775, 746, 696 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{21}N_3NaO_4$ $(M+Na)^+$ 354.1424; found 354.1426.

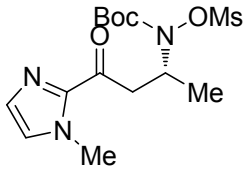
tert-butyl 2-methyl-3-(1-methyl-1H-imidazole-2-carbonyl)aziridine-1-carboxylate (6)



To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **Δ-Rh** (2.0 mol%) was added along with α,β-unsaturated 2-acyl imidazole **1a** (0.1 mmol) and toluene (0.2 mL). After being stirred at room temperature for 5 min, sulfonyl hydroxycarbamate **5** (1.2 equiv) was added at room temperature followed by Na_2HPO_4 (1.2 equiv). The reaction was stirring at 50 °C for 24 hours. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:6) to afford aziridine **6** as yellow oil, 19.5 mg, 37% yield, 81% ee, $[\alpha]_D^{25}$ = +19.4 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column IE, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 8.20 min, t_{minor} = 12.25 min); R_f = 0.38 in 1:3 EtOAc/petroleum ether. ^{1}H NMR

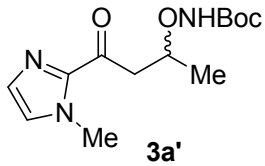
(400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 7.11(s, 1H), 4.34 (d, *J* = 2.6 Hz, 1H), 4.01 (s, 3H), 2.87-2.83 (m, 1H), 1.46 (s, 9H), 1.41 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.5, 159.5, 143.0, 130.0, 127.5, 81.3, 44.4, 41.7, 36.0, 28.0, 16.9; IR (KBr): *v* 3111, 2976, 2932, 1723, 1672, 1458, 1402, 1368, 1307, 1156, 1015, 912, 823, 780, 695 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}N_3NaO_3$ $(M+Na)^+$ 288.1319; found 288.1317.

(R)-tert-butyl (4-(1-methyl-1H-imidazol-2-yl)-4-oxobutan-2-yl)((methylsulfonyl)oxy)carbamate (7)



To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **Δ-Rh** (2.0 mol%) was added along with α,β-unsaturated 2-acyl imidazole **1a** (0.1 mmol) and toluene (0.2 mL). After being stirred at room temperature for 5 min, sulfonyl hydroxycarbamate **5** (1.2 equiv or 2.0 equiv) was added at room temperature followed by Na_2HPO_4 (1.2 equiv). The reaction was stirring at 50 ^oC for 24 hours. The solution directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:6) to afford aziridine **7** as yellow oil, 6.3 mg, 9% yield, 47% ee, $[\alpha]_D^{25}$ = -10.8 (c = 0.5, $CHCl_3$); The ee was determined by HPLC (Chiralpak column ID, λ = 254 nm, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, t_{major} = 9.53 min, t_{minor} = 8.61 min); R_f = 0.15 in 1:3 EtOAc/petroleum ether. ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 1H), 7.03(s, 1H), 4.08-4.75 (m, 1H), 3.99 (s, 3H), 3.50-3.44 (m, 1H), 3.17 (s, 1H), 1.53 (s, 9H), 1.36 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 155.8**,** 142.7, 129.1, 127.0, 84.3, 55.8, 42.6, 37.9, 36.0, 28.0; IR (KBr): *v* 3111, 2963, 2928, 1717, 1702, 1684, 1507, 1519, 1457, 1402, 1367, 1239, 1192, 1054, 963, 783, 758 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{23}N_3NaO_6S$ $(M+Na)^+$ 384.1200; found 384.1198.

***tert*-Butyl 4-(1-methyl-1H-imidazol-2-yl)-4-oxobutan-2-yloxycarbamate (3a')**



3a'

Prepared by following general procedure. **3a'** was obtained as a colorless viscous liquid; Yield = 86%; R_f = 0.1 in 1:3 EtOAc/petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (brs, 1H), 7.14 (s, 1H), 7.04 (s, 1H), 4.53-4.49 (m, 1H), 4.00 (s, 3H), 3.36 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.26 (dd, *J* = 14.8, 5.2 Hz, 1H), 1.46 (s, 9H), 1.35 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 156.8, 143.3, 129.0, 127.2, 81.2, 78.5, 44.0, 36.2, 28.2, 18.6; IR (KBr): υ 3341, 2979, 2934, 1734, 1681, 1412, 1370, 1252, 1163, 1104, 997, 913, 784 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{21}N_3NaO_4$ $(M+Na)^+$ 306.1430; found 306.1425

III References

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

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

3. Evans, D. A.; Fandrick, K. *Org. Lett*. **2006**, *8*, 2249.

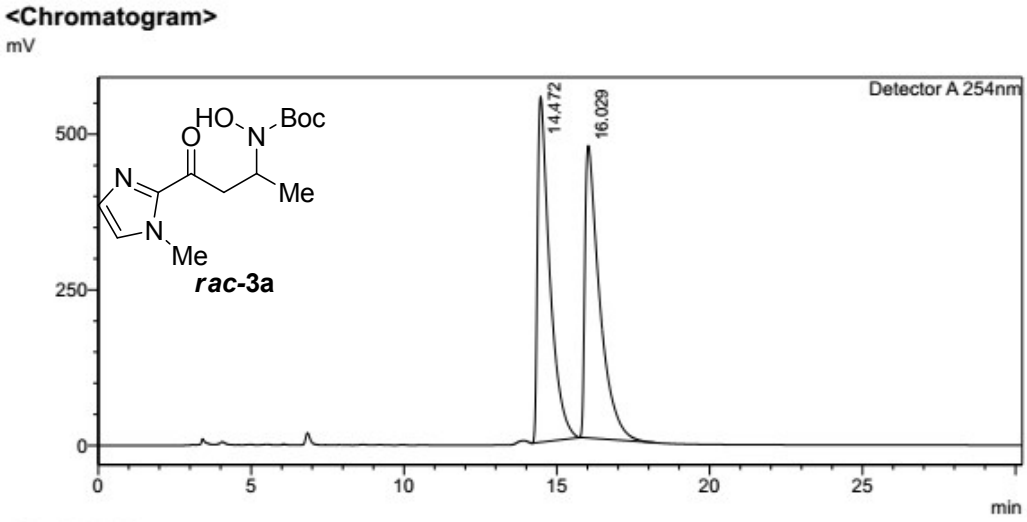
4. Trost, B. M.; Lam, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 11319.

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

6. (a) Huo, H.; Shen, X.; Wang, C.; Zhang, L.; Rose, P.; Chen, L.-A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E. *Nature* **2014**, *515*, 100. (b) Shen, X.; Huo, H.; Wang, C.; Zhang, B.; Harms, K.; Meggers, E. *Chem. Eur. J*. **2015**, *21*, 9720.

IV. Chiral HPLC analysis trace

rac-**3a**

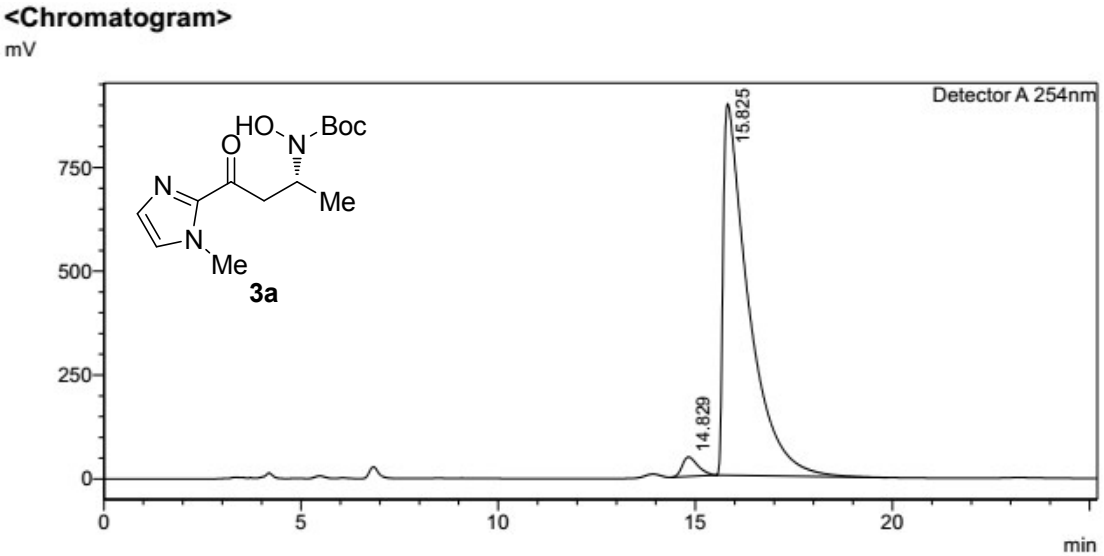


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.472	15481404	554916	49.669			
2	16.029	15687454	469131	50.331		M	
Total		31168858	1024047				

chiral **3a**



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.829	1305220	46947	3.163		M	
2	15.825	39965104	894525	96.837		M	
Total		41270324	941472				

rac-**3b**

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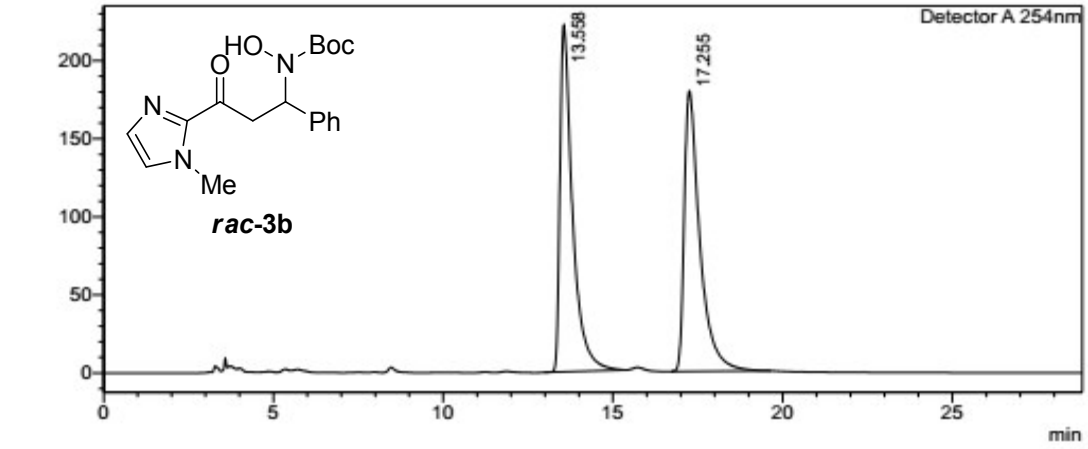


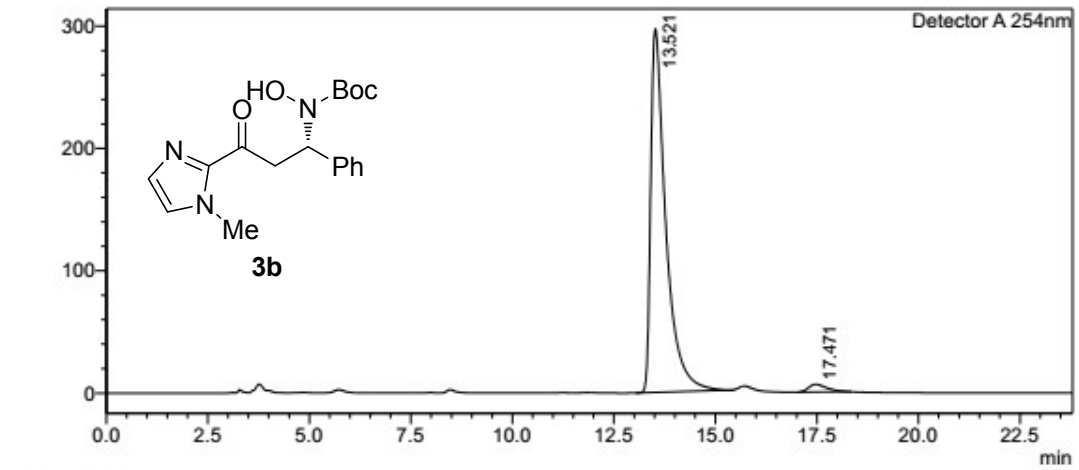
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.558	5719613	221855	49.908		M	
2	17.255	5740657	179591	50.092		M	
Total		11460269	401446				

Chiral **3b**

<Chromatogram>



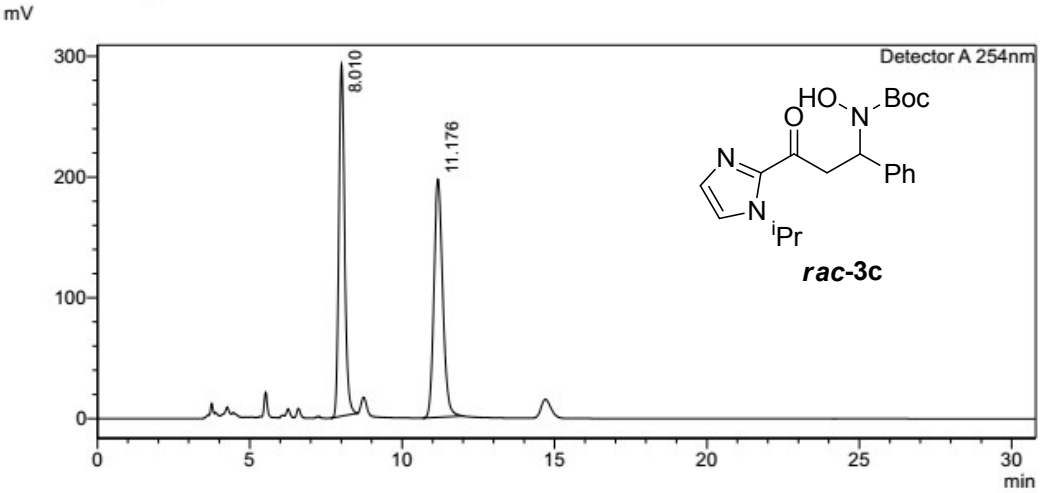
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.521	7667858	296845	97.513		M	
2	17.471	195580	6241	2.487		M	
Total		7863438	303086				

rac-**3c**

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.010	3834646	290970	49.227		M	
2	11.176	3955051	197263	50.773		M	
Total		7789697	488232				

Chiral **3c**

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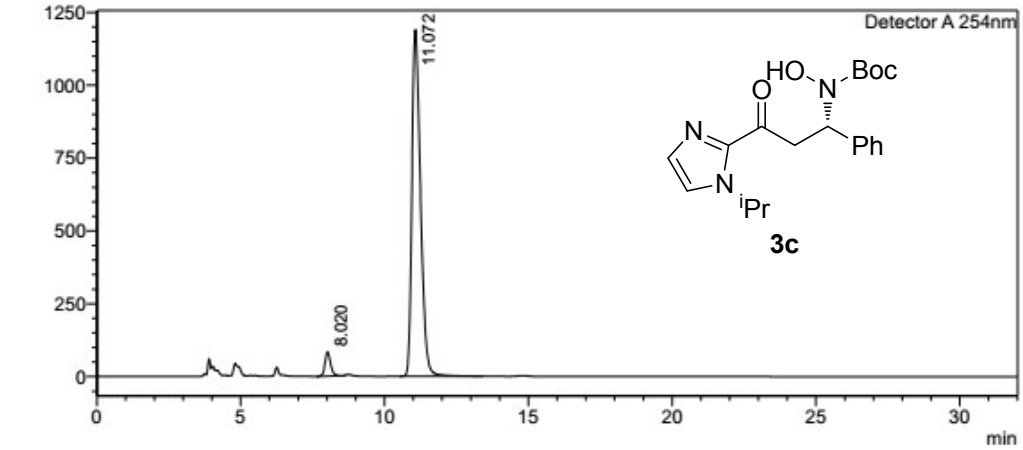
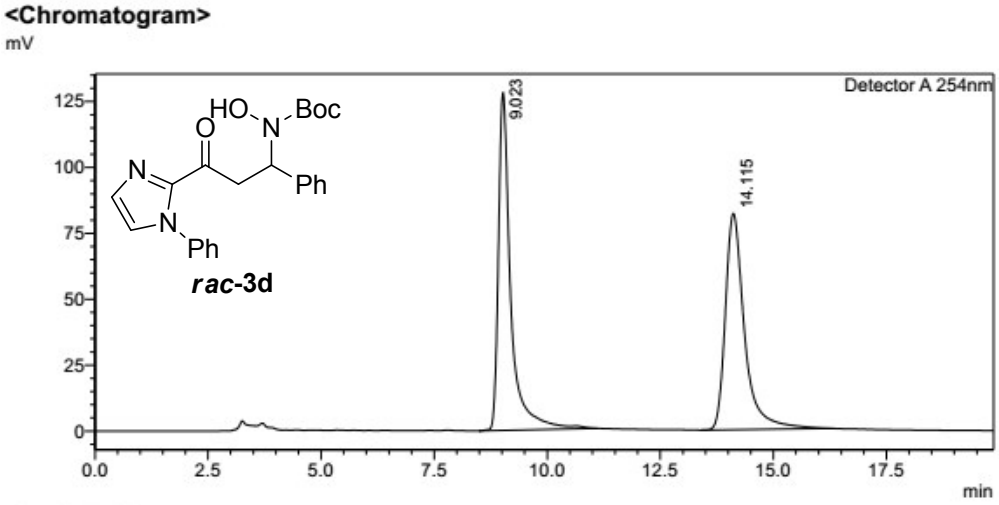


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.020	1137483	83581	4.396		M	
2	11.072	24735466	1189506	95.604		M	
Total		25872949	1273087				

rac-**3d**

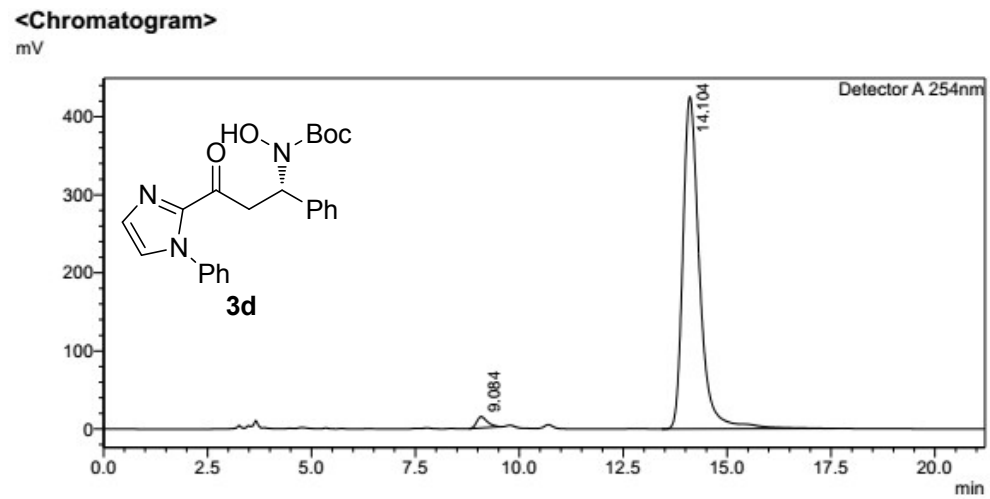


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.023	2431183	128015	50.087		M	
2	14.115	2422767	82029	49.913		M	
Total		4853949	210044				

Chiral-**3d**



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.084	258052	14481	2.128		M	
2	14.104	11865945	425456	97.872		M	
Total		12123997	439937				

rac-**3e**

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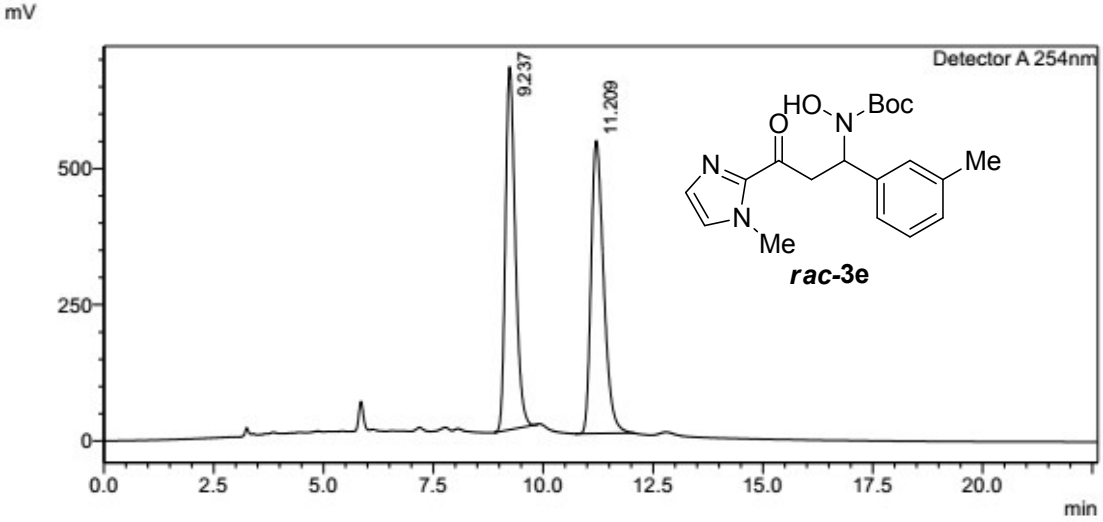

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.237	10356451	665817	49.242		M	
2	11.209	10675268	537109	50.758		M	
Total		21031718	1202926				

Chiral-**3e**

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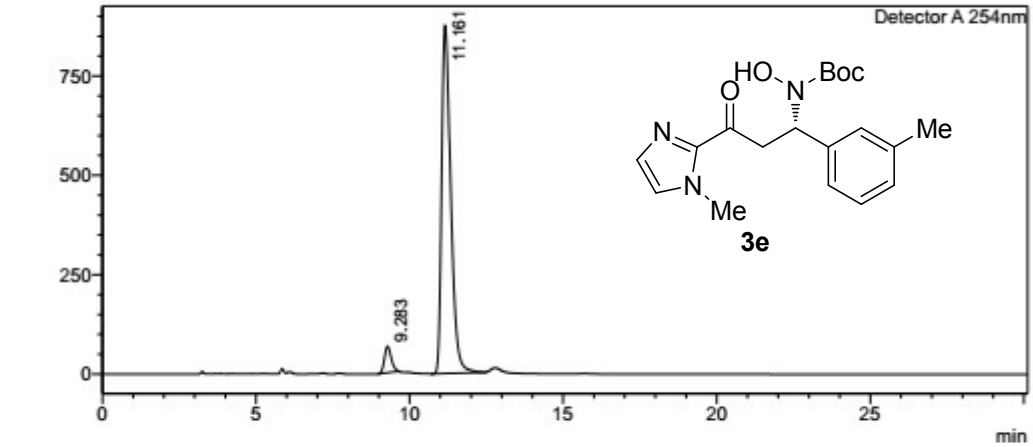


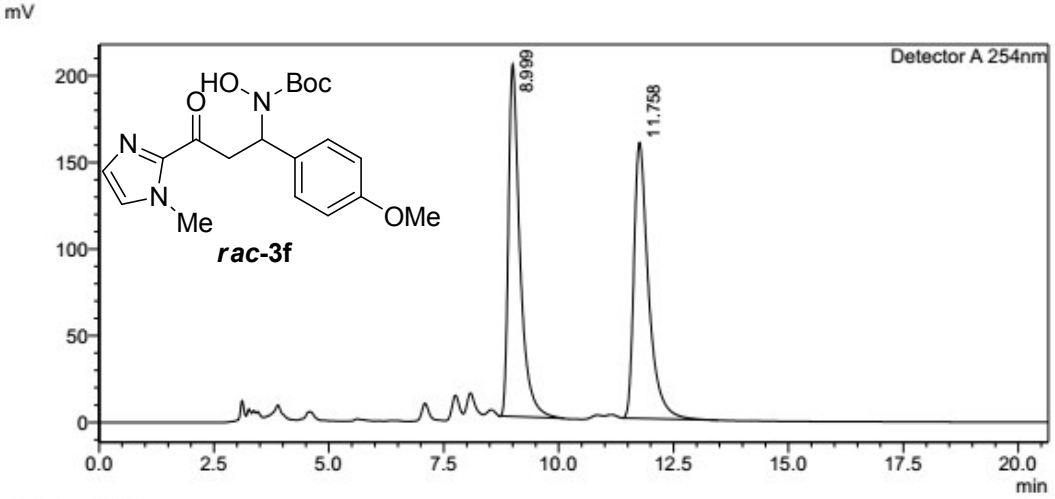
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.283	1019961	66088	5.400		M	
2	11.161	17867844	874779	94.600		M	
Total		18887804	940867				

rac-**3f**

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.999	3519734	203049	50.073		M	
2	11.758	3509441	159147	49.927		M	
Total		7029174	362195				

Chiral-**3f**

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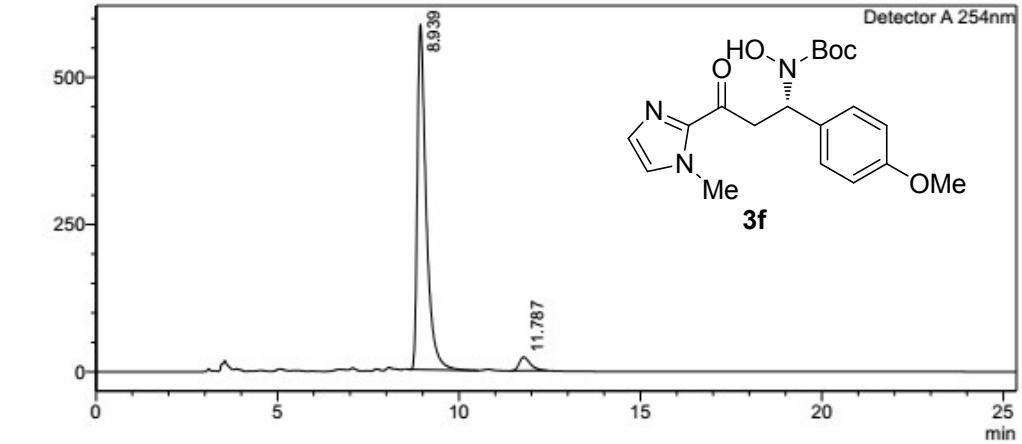

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.939	9966866	585341	95.320		M	
2	11.787	489329	23127	4.680		M	
Total		10456196	608468				

rac-**3g**

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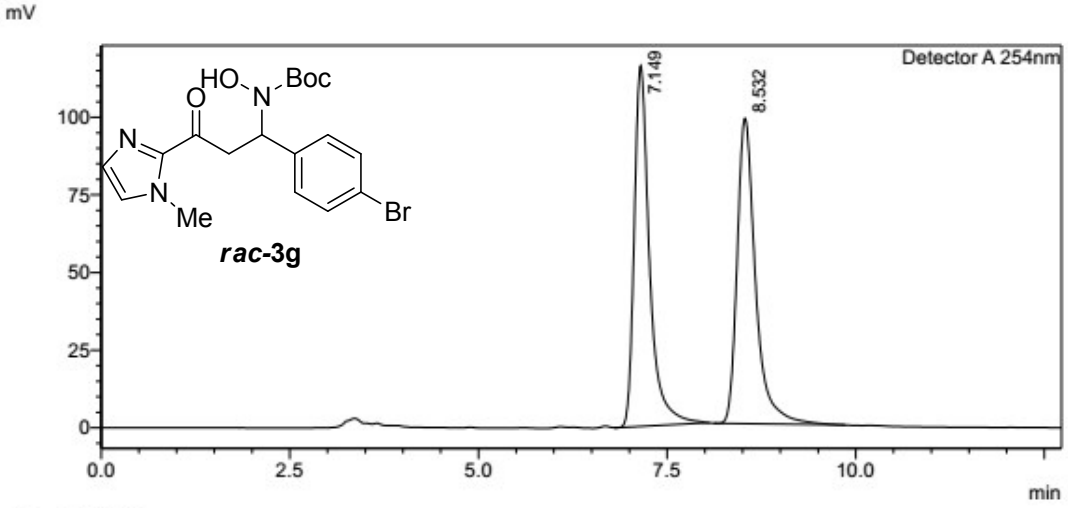

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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.149	1639143	116118	49.499		M	
2	8.532	1672321	98354	50.501		M	
Total		3311464	214473				

Chiral-**3g**

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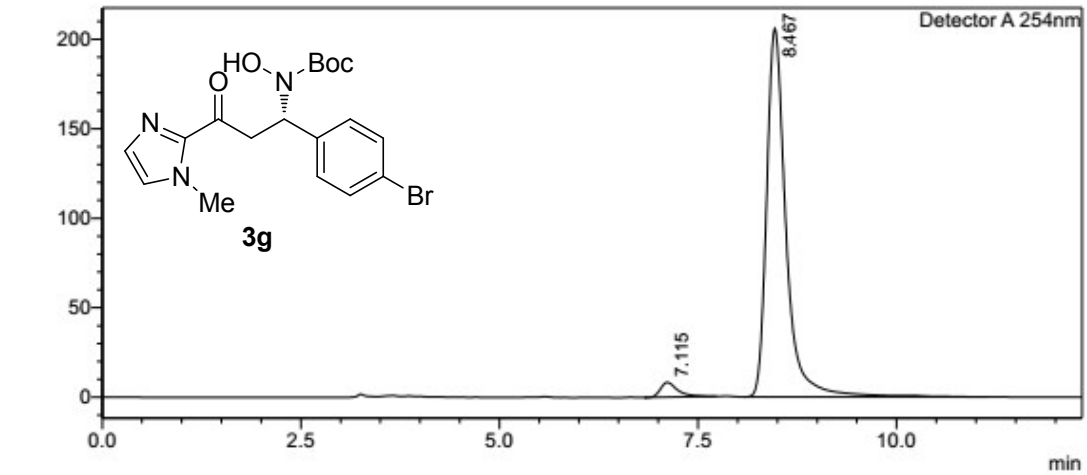

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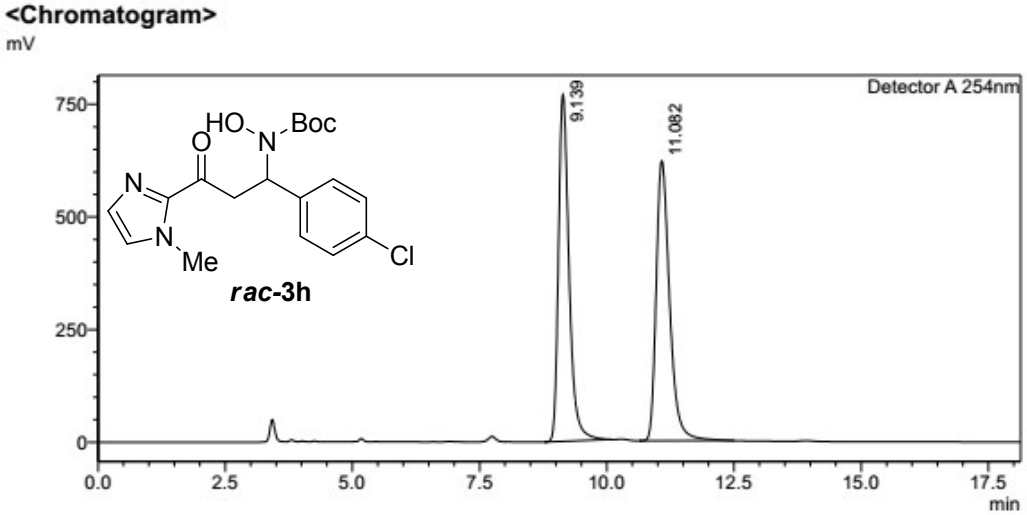
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.115	127905	8264	3.525		M	
2	8.467	3500280	205735	96.475		M	
Total		3628185	213999				

rac-**3h**

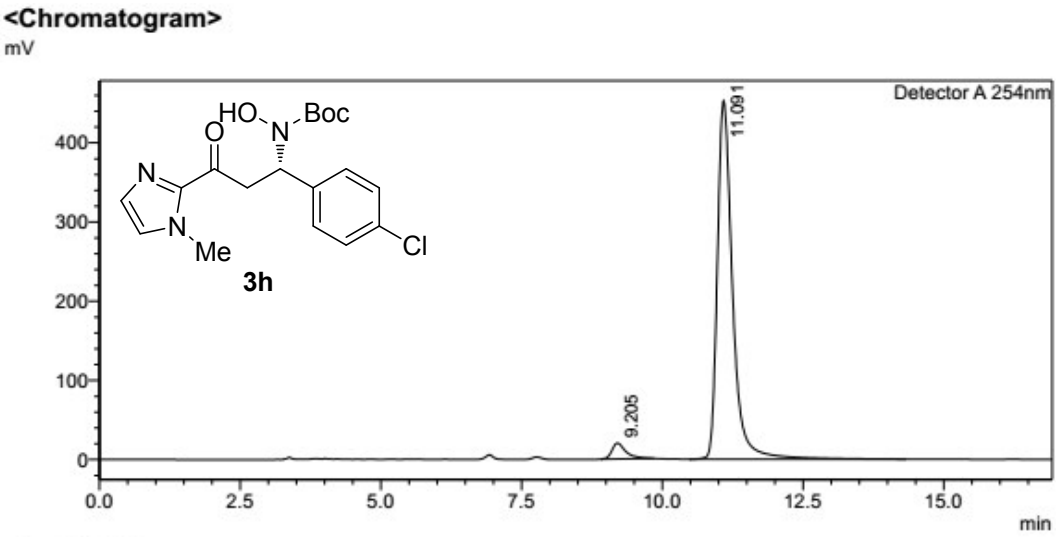


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.139	11196847	769504	49.576		M	
2	11.082	11388463	621575	50.424		M	
Total		22585310	1391080				

Chiral-**3h**



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.205	341991	19979	3.856		M	
2	11.091	8526023	452680	96.144		M	
Total		8868014	472659				

rac-**3i**

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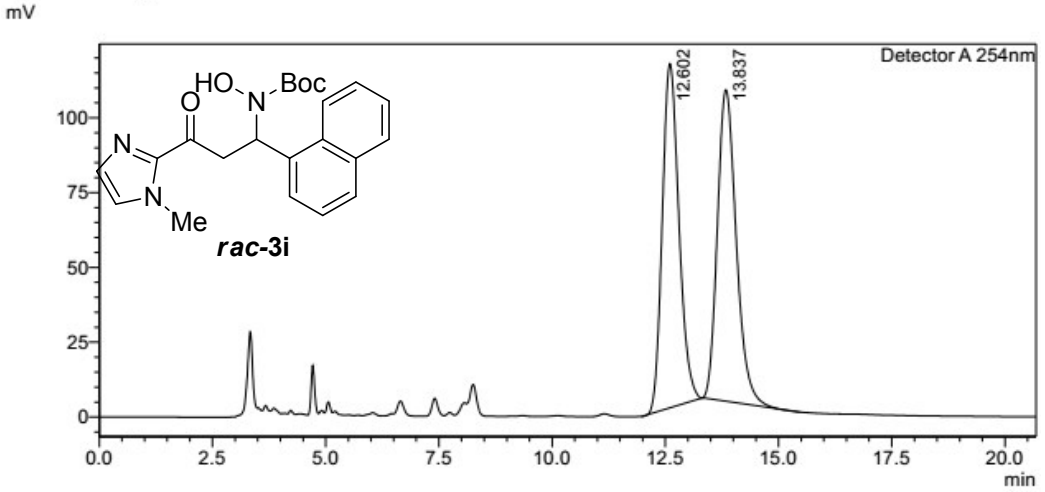


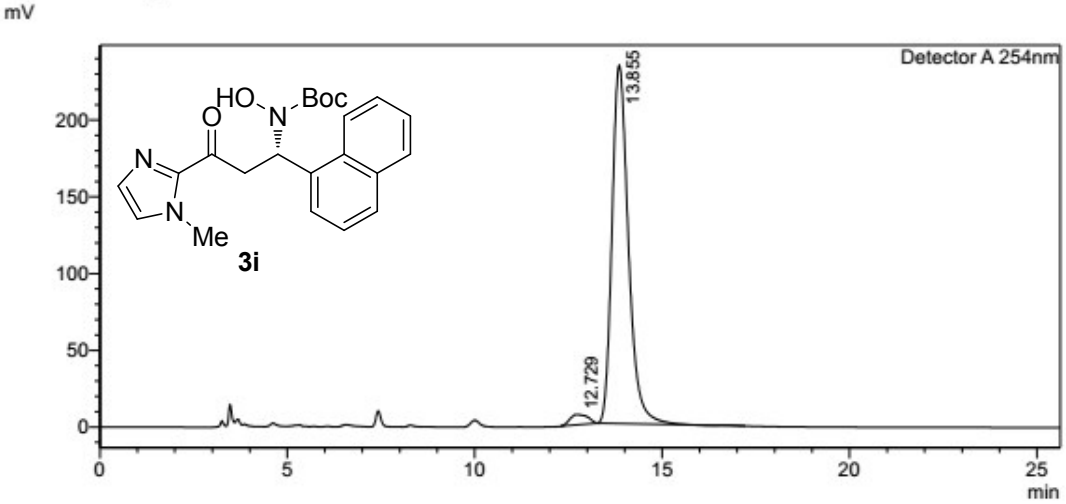
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.602	2937809	114978	49.368		M	
2	13.837	3013017	104128	50.632		M	
Total		5950827	219106				

Chiral-**3i**

<Chromatogram>



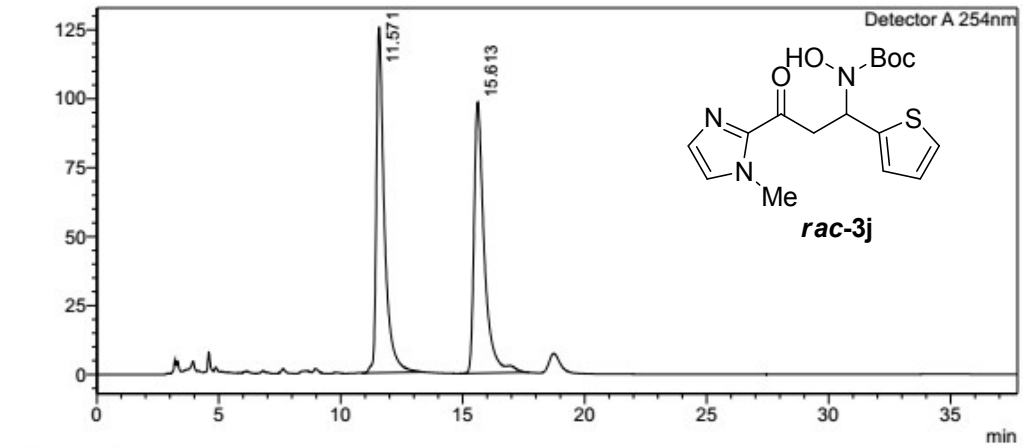
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.729	219491	6680	2.998		M	
2	13.855	7101886	233318	97.002		M	
Total		7321377	239998				

rac-**3j**

<Chromatogram>



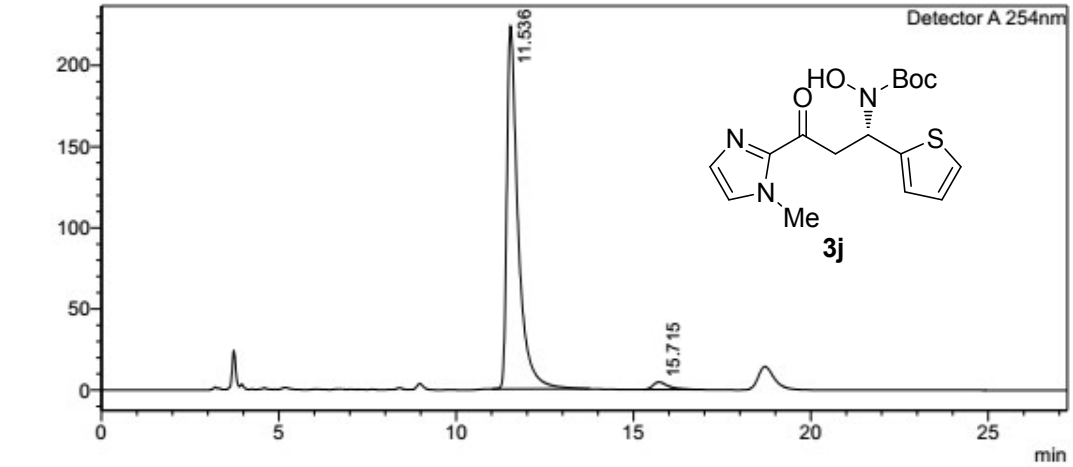
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.571	2862365	125276	49.923		M	
2	15.613	2871187	98307	50.077		M	
Total		5733552	223583				

Chiral-**3j**

<Chromatogram>



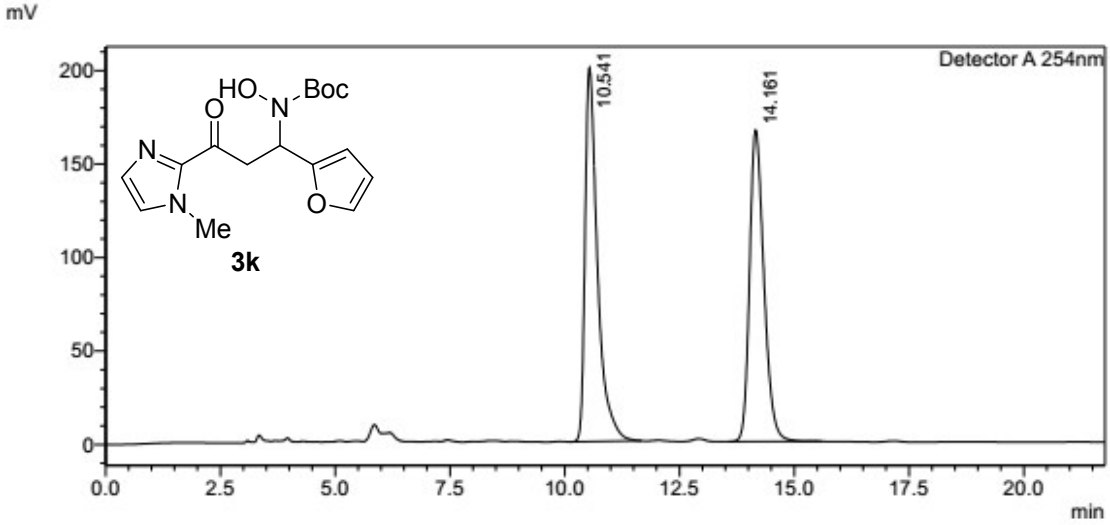
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.536	4927554	223443	97.165		M	
2	15.715	143788	4658	2.835		M	
Total		5071342	228101				

rac-**3k**

<Chromatogram>



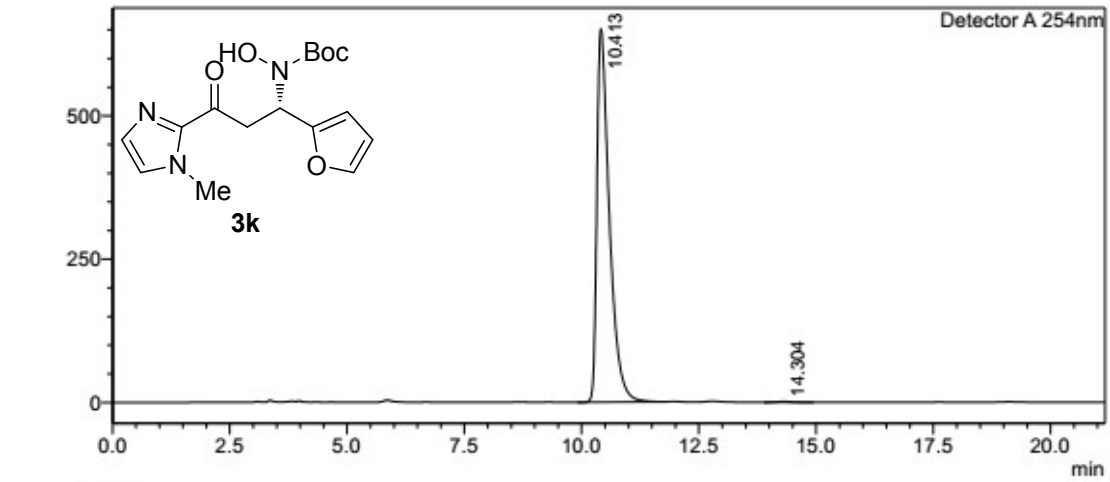
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.541	3766387	199925	50.976		M	
2	14.161	3622118	166607	49.024		M	
Total		7388505	366532				

Chiral-**3k**

<Chromatogram>



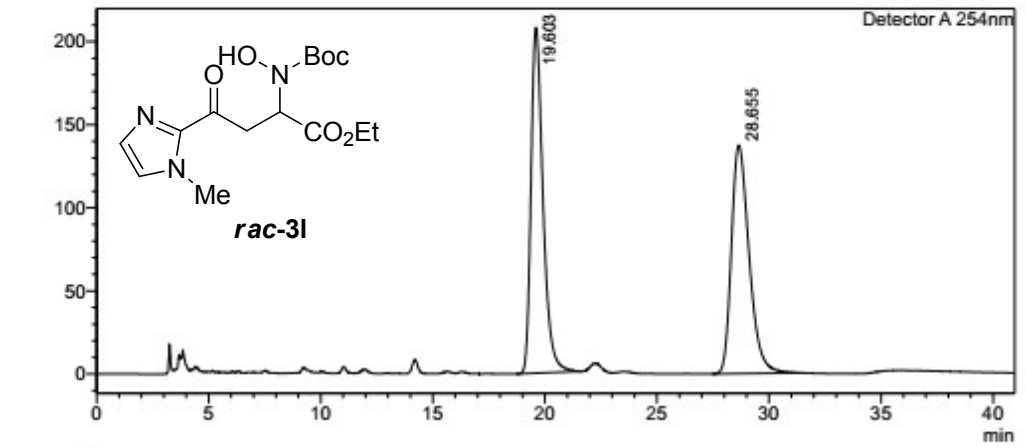
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.413	12073802	651551	99.756		M	
2	14.304	29567	1381	0.244		M	
Total		12103369	652931				

rac-**3l**

<Chromatogram>



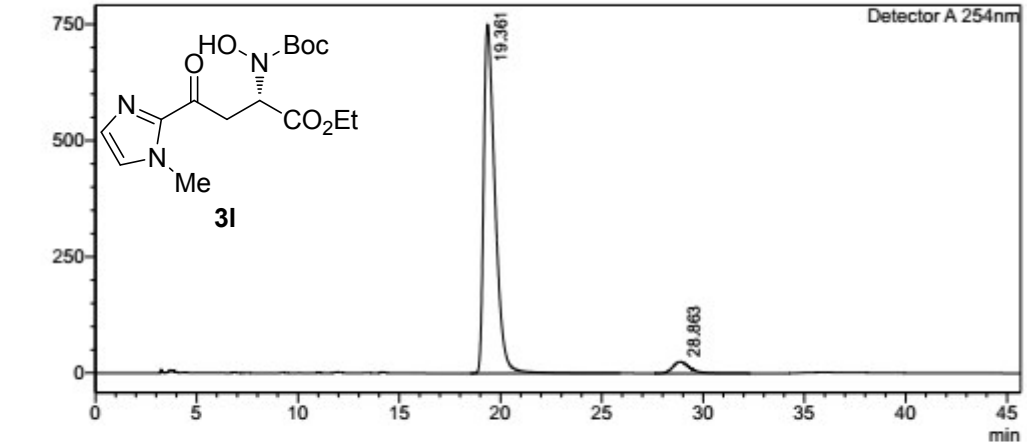
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.603	7741237	207736	50.588		M	
2	28.655	7561248	137398	49.412		M	
Total		15302486	345134				

Chiral-**3l**

<Chromatogram>

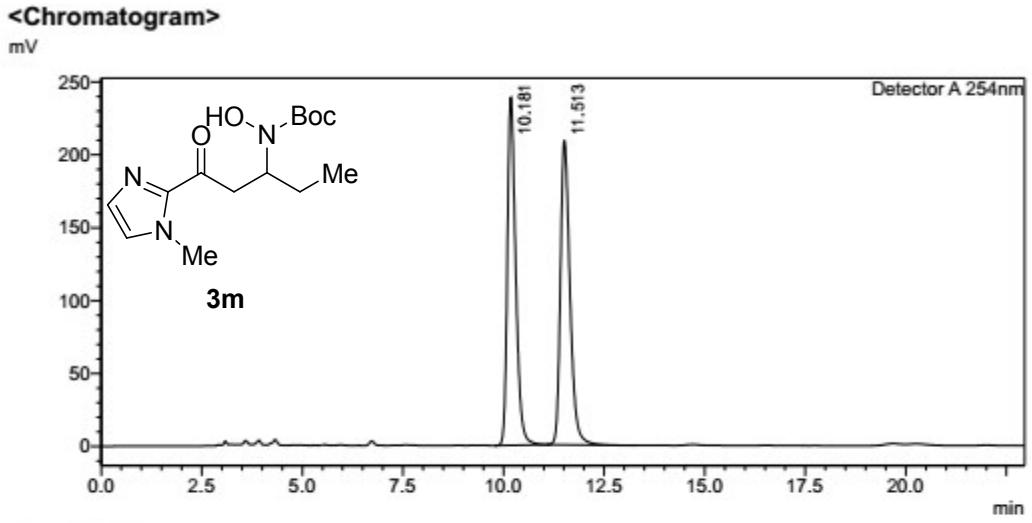


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.361	29079559	749796	95.302		M	
2	28.863	1433547	24713	4.698		M	
Total		30513106	774509				

rac-**3m**

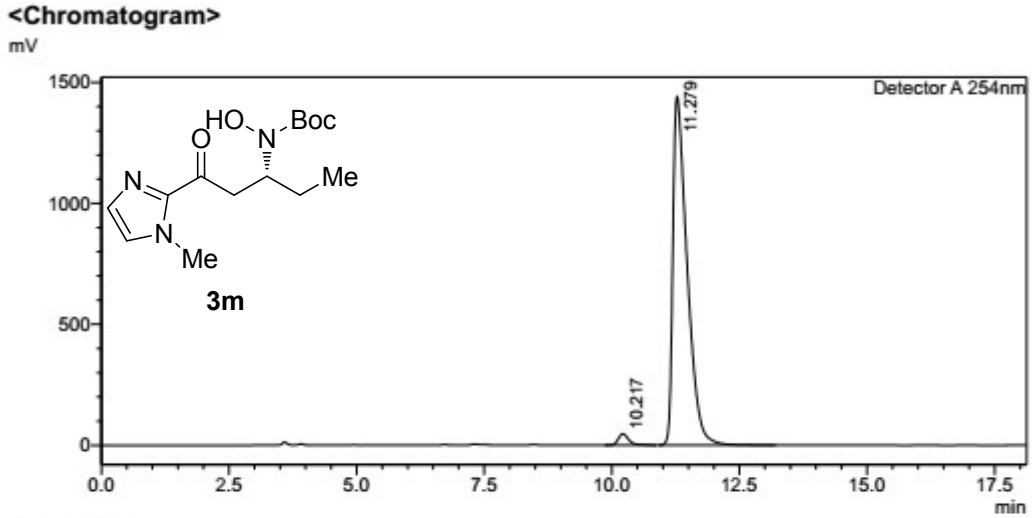


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.181	3441860	238620	49.918			
2	11.513	3453228	208691	50.082		M	
Total		6895088	447311				

Chiral-**3m**



<Peak Table>

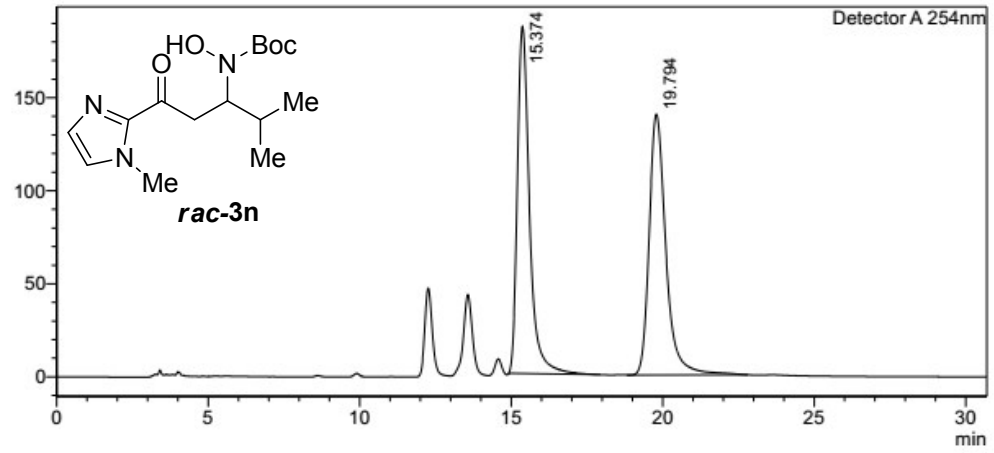
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.217	671284	46742	2.343		M	
2	11.279	27982447	1440063	97.657		M	
Total		28653730	1486805				

rac-**3n**

<Chromatogram>

mV



<Peak Table>

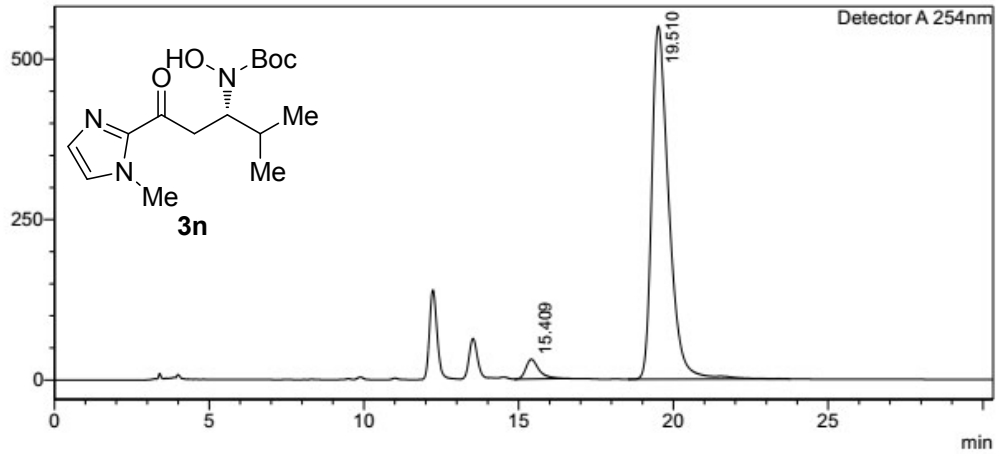
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.374	5199928	186630	49.175		M	
2	19.794	5374469	140083	50.825		M	
Total		10574396	326713				

Chiral-**3n**

<Chromatogram>

mV



<Peak Table>

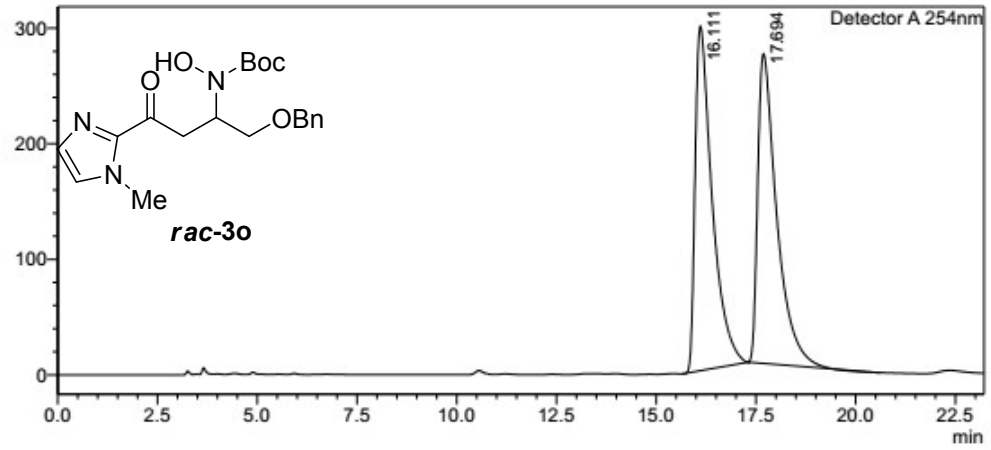
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.409	905109	30667	4.085		M	
2	19.510	21250926	550347	95.915		M	
Total		22156035	581013				

rac-**3o**

<Chromatogram>

mV



<Peak Table>

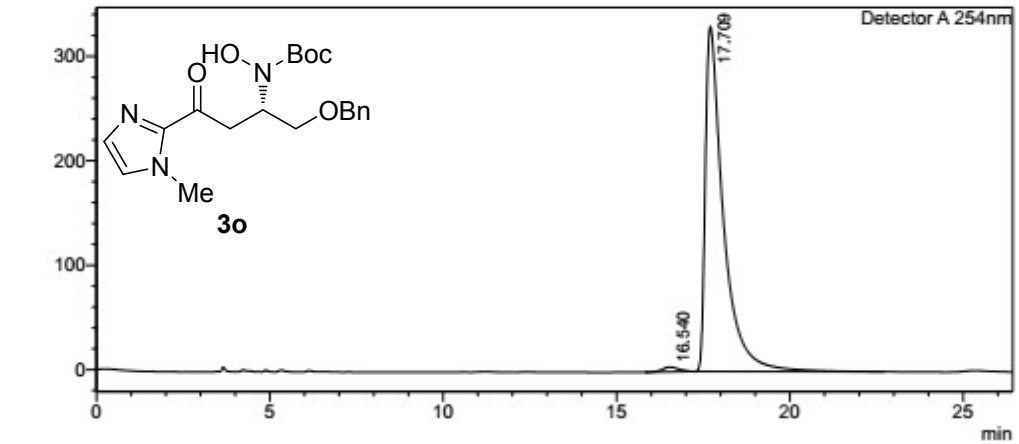
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.111	8881586	298117	50.061		M	
2	17.694	8859929	267969	49.939		M	
Total		17741515	566086				

Chiral-**3o**

<Chromatogram>

mV



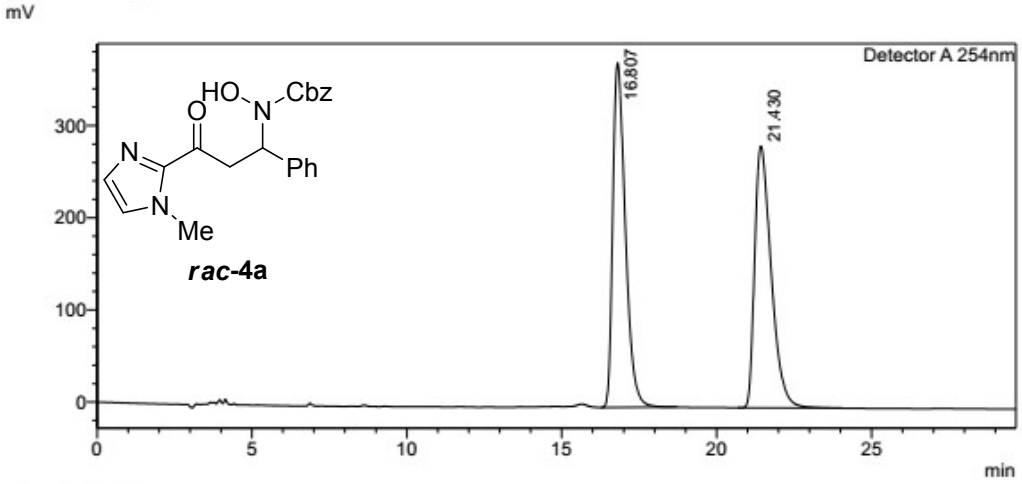
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.540	148455	4546	1.230			
2	17.709	11922132	329997	98.770		M	
Total		12070588	334544				

rac-**4a**

<Chromatogram>



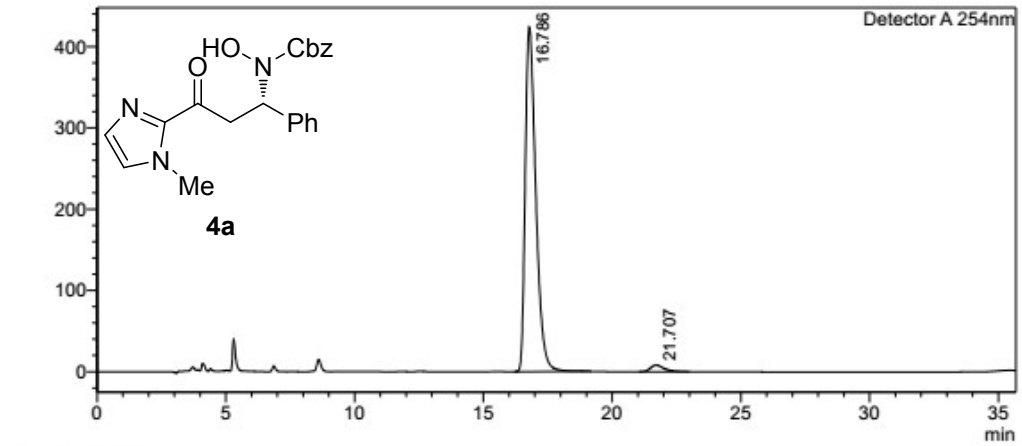
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.807	10562233	373702	50.012		M	
2	21.430	10557252	284206	49.988		M	
Total		21119484	657908				

Chiral-**4a**

<Chromatogram>

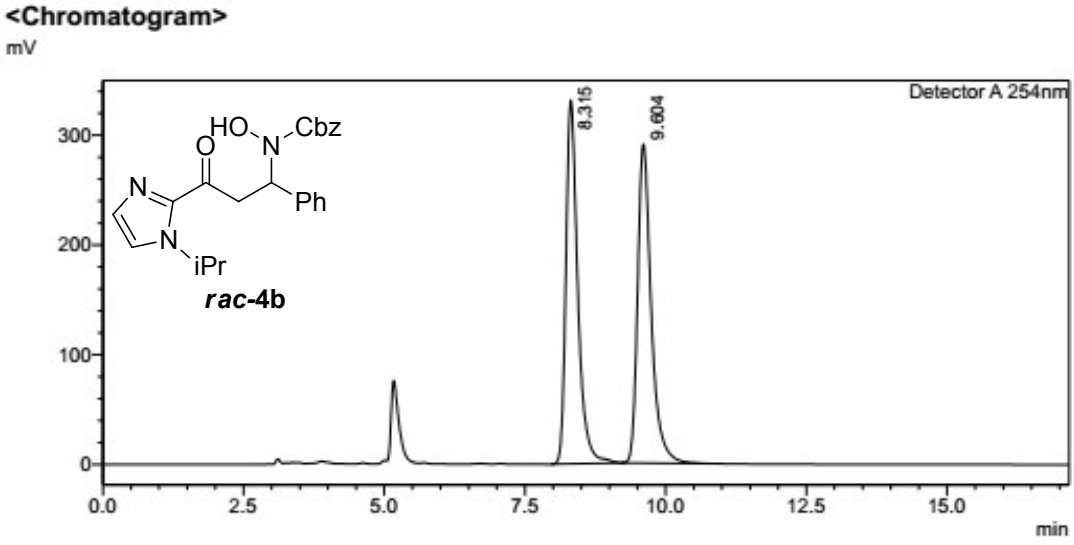


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.786	12122191	424139	97.567		M	
2	21.707	302351	8123	2.433		M	
Total		12424542	432262				

rac-**4b**

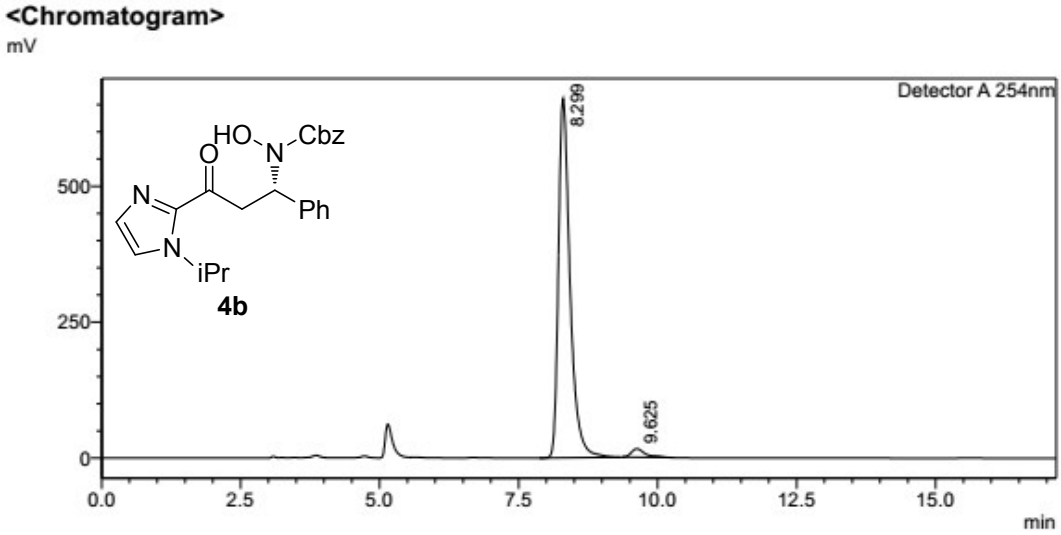


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.315	4837637	330792	49.871		M	
2	9.604	4862608	290251	50.129		M	
Total		9700245	621043				

Chiral-**4b**



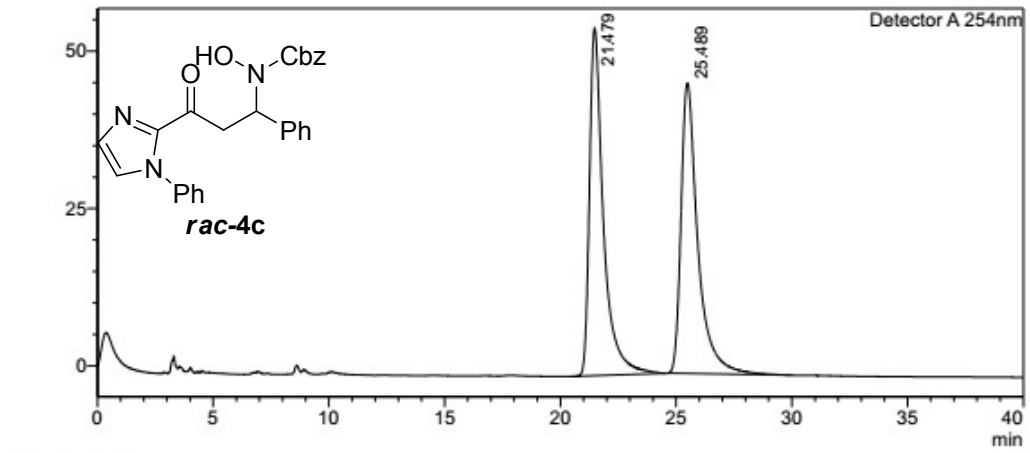
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.299	9587486	660384	97.216		M	
2	9.625	274573	15500	2.784		M	
Total		9862059	675884				

rac-**4c**

<Chromatogram>



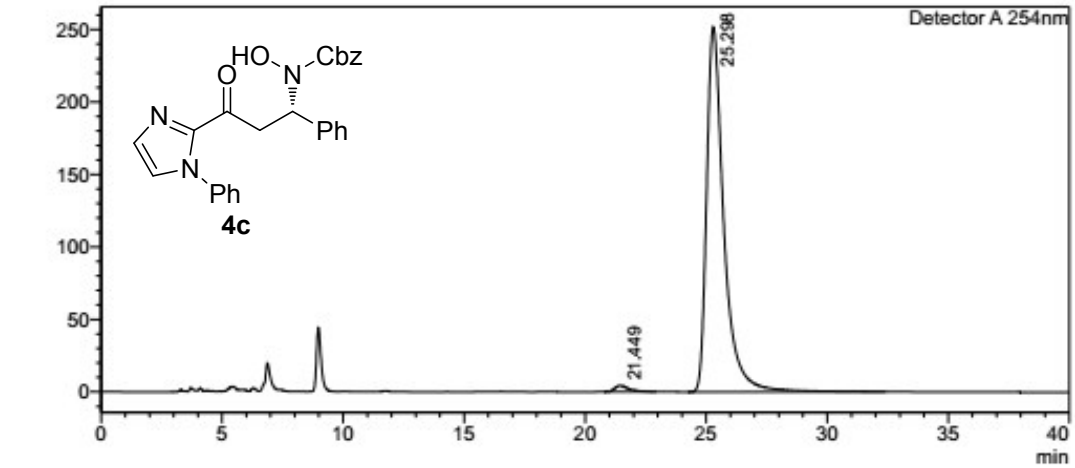
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.479	2313635	55255	49.826		M	
2	25.489	2329749	46158	50.174		M	
Total		4643384	101413				

Chiral-**4c**

<Chromatogram>



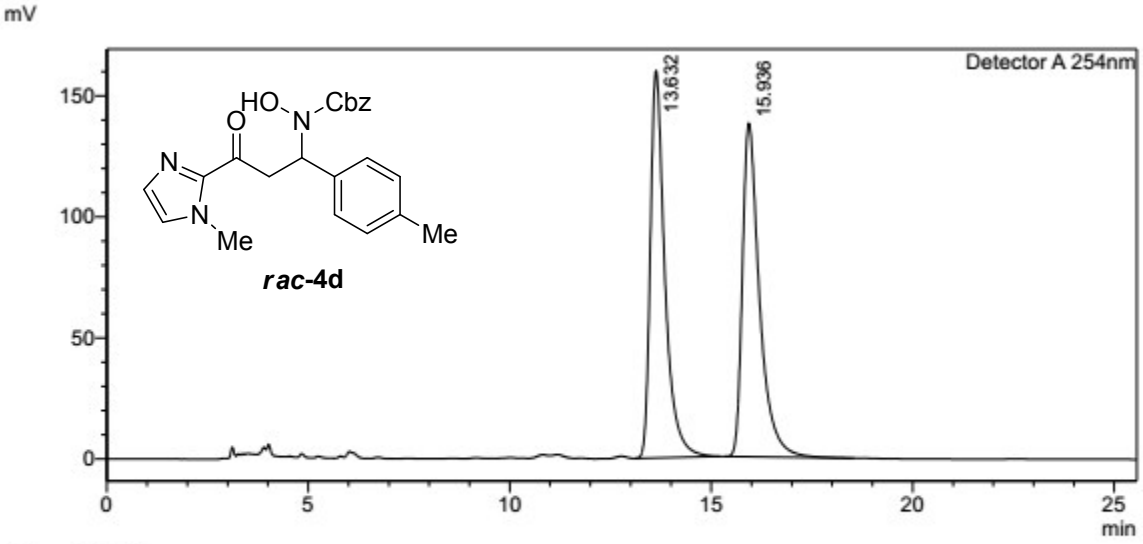
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.449	174029	4259	1.381		M	
2	25.298	12424141	251694	98.619		M	
Total		12598171	255953				

rac-**4d**

<Chromatogram>



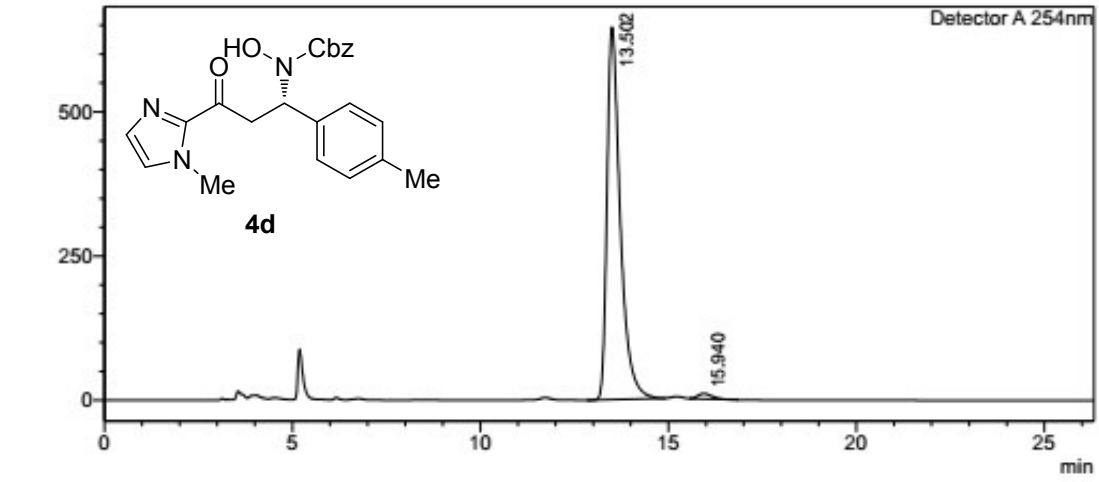
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.632	4013676	159916	49.590		M	
2	15.936	4080002	137789	50.410		M	
Total		8093678	297705				

Chiral-**4d**

<Chromatogram>



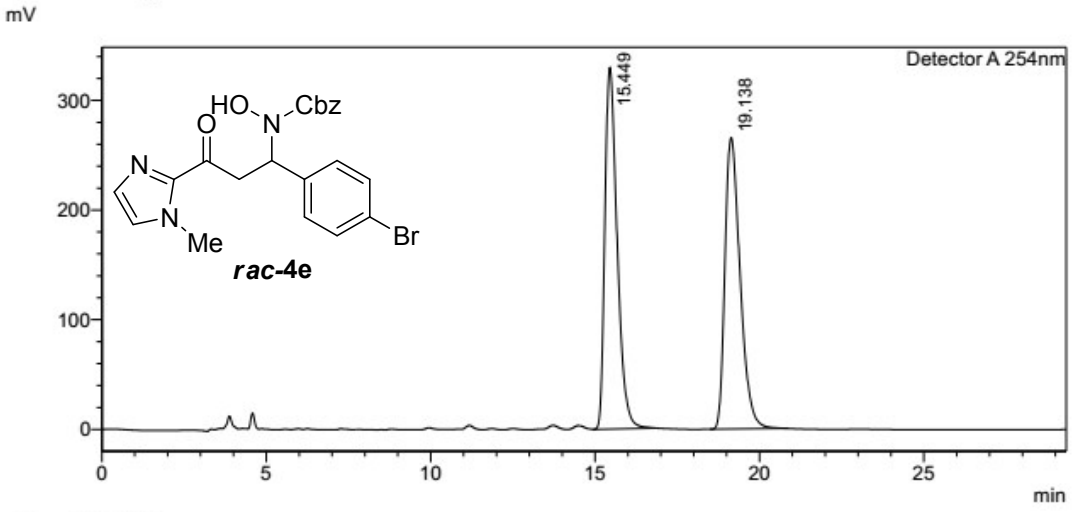
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.502	15776629	644911	98.505		M	
2	15.940	239391	9207	1.495		M	
Total		16016021	654117				

rac-**4e**

<Chromatogram>



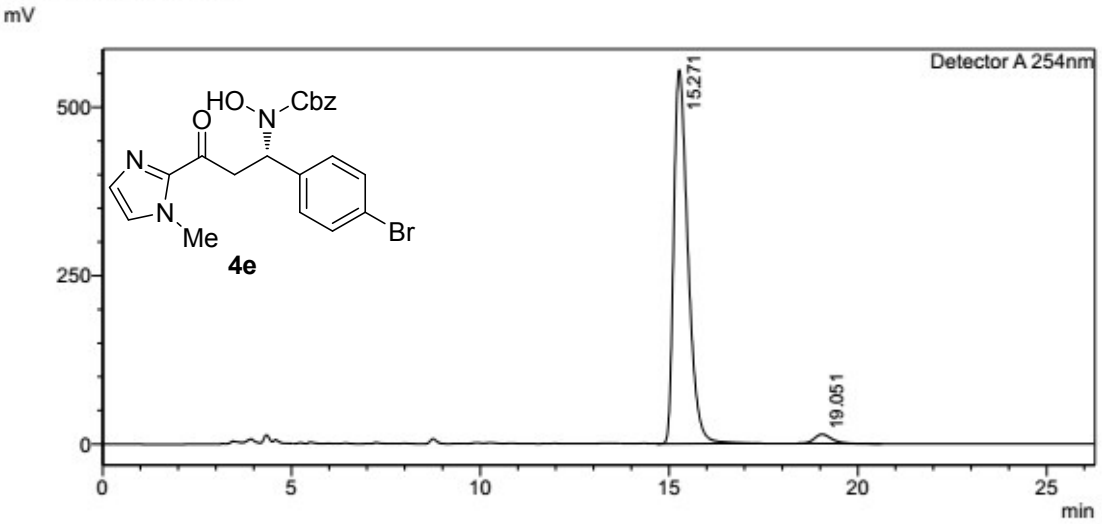
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.449	8560350	329522	50.082		M	
2	19.138	8532448	265571	49.918		M	
Total		17092798	595093				

Chiral-**4e**

<Chromatogram>



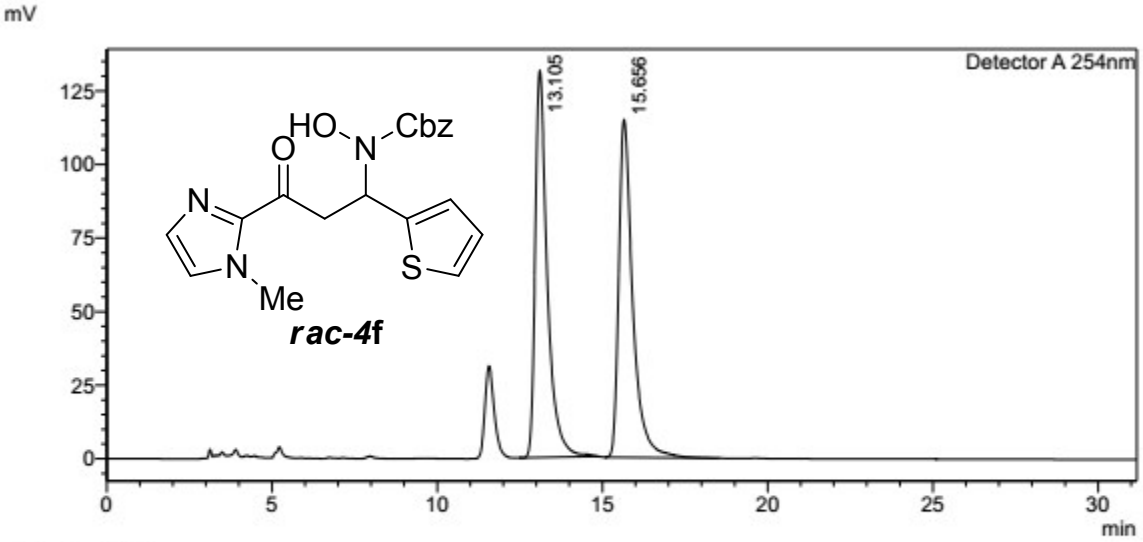
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.271	14500688	554452	97.067		M	
2	19.051	438185	13657	2.933		M	
Total		14938873	568109				

rac-**4f**

<Chromatogram>



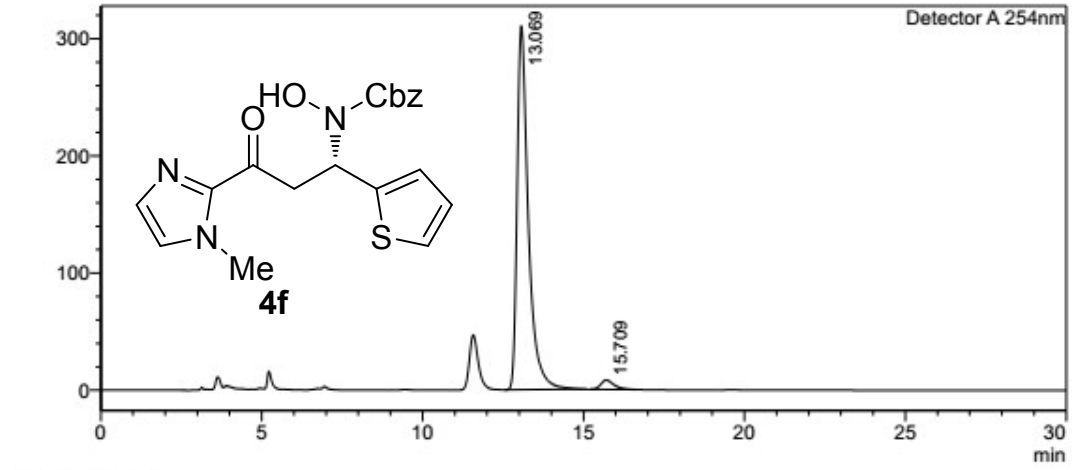
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.105	3347446	131383	49.828		M	
2	15.656	3370581	114687	50.172		M	
Total		6718027	246070				

Chiral-**4f**

<Chromatogram>



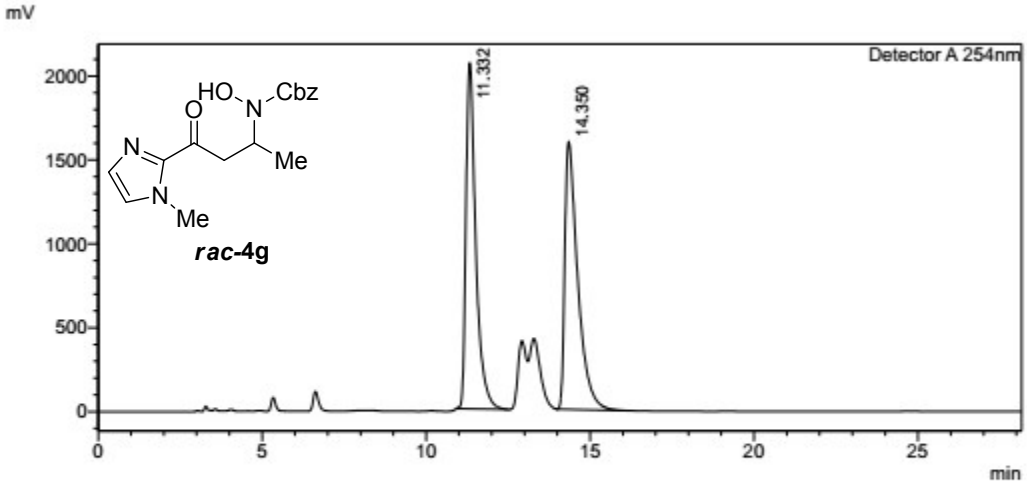
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.069	7571946	310201	97.130		M	
2	15.709	223773	7904	2.870		M	
Total		7795719	318105				

rac-**4g**

<Chromatogram>



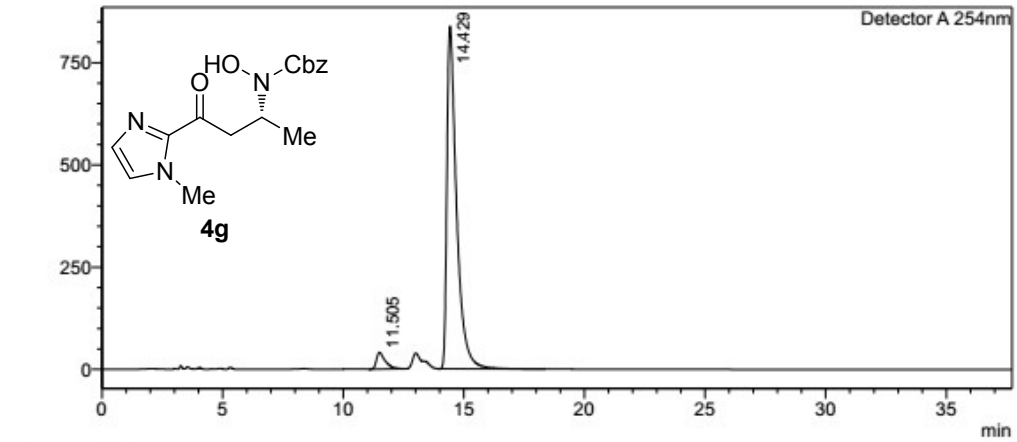
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.332	42979395	2058812	49.509		M	
2	14.350	43831500	1593067	50.491		M	
Total		86810895	3651878				

Chiral-**4g**

<Chromatogram>



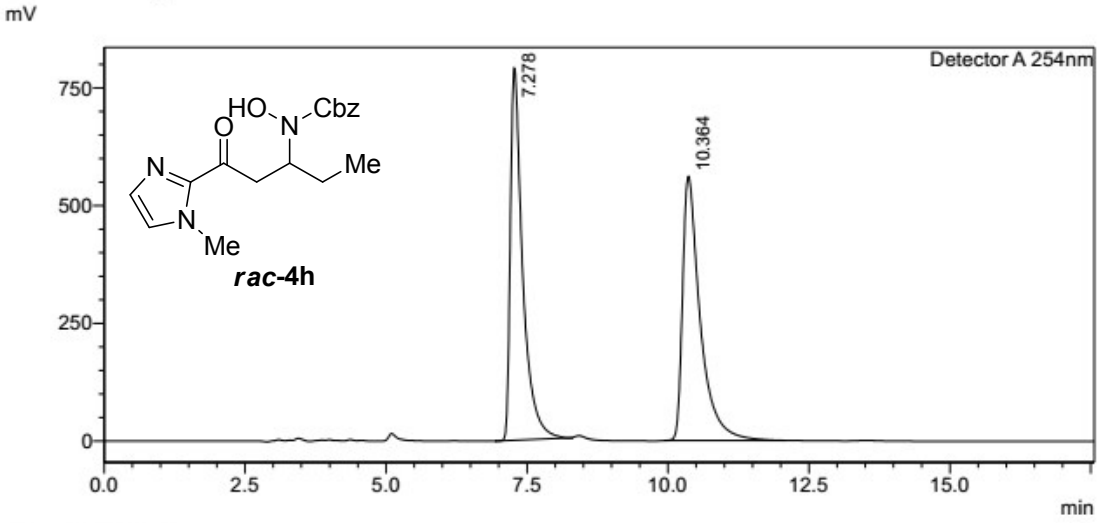
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.505	1037988	40674	4.262		M	
2	14.429	23315391	837442	95.738		M	
Total		24353379	878116				

rac-**4h**

<Chromatogram>



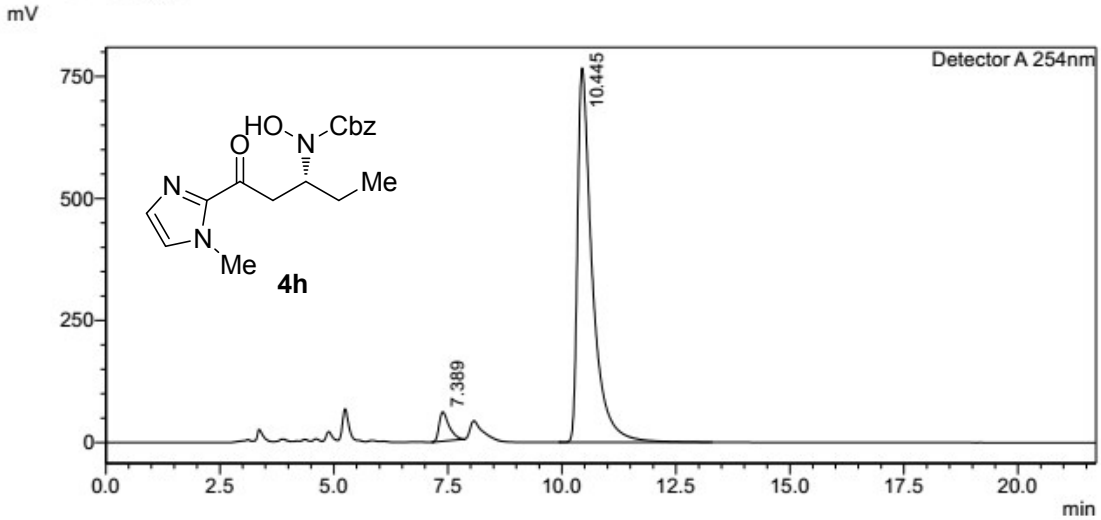
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.278	11988501	789880	49.521		M	
2	10.364	12220629	560933	50.479		M	
Total		24209130	1350813				

Chiral-**4h**

<Chromatogram>



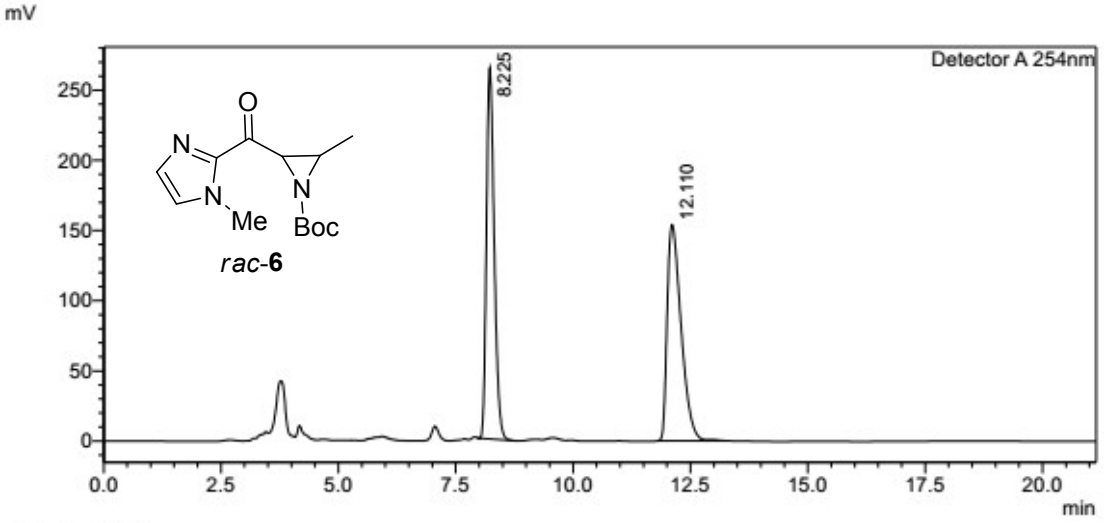
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.389	913926	59707	5.024		M	
2	10.445	17276885	766651	94.976		M	
Total		18190811	826358				

rac-**6**

<Chromatogram>

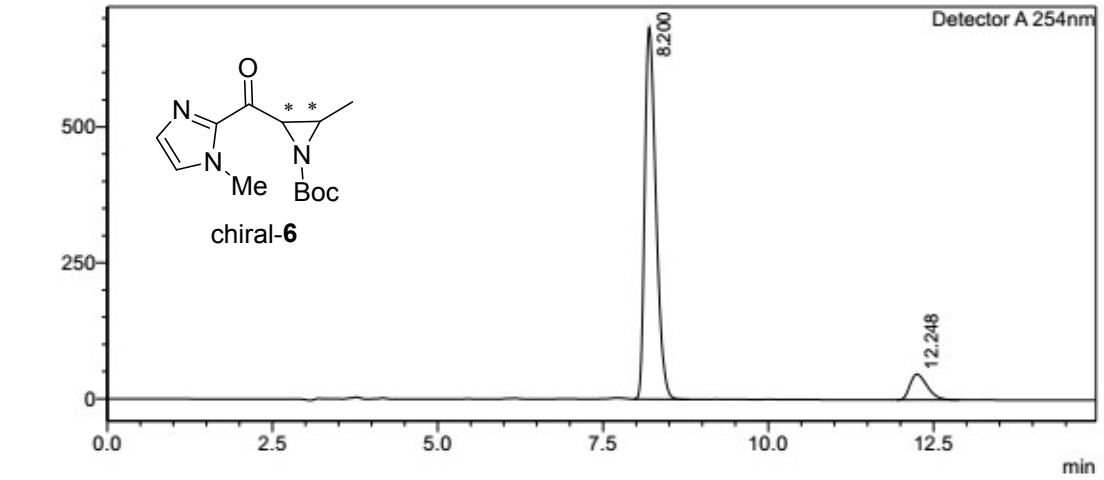


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.225	3044074	264511	48.955		M	
2	12.110	3174056	154014	51.045		M	
Total		6218130	418525				

<Chromatogram>



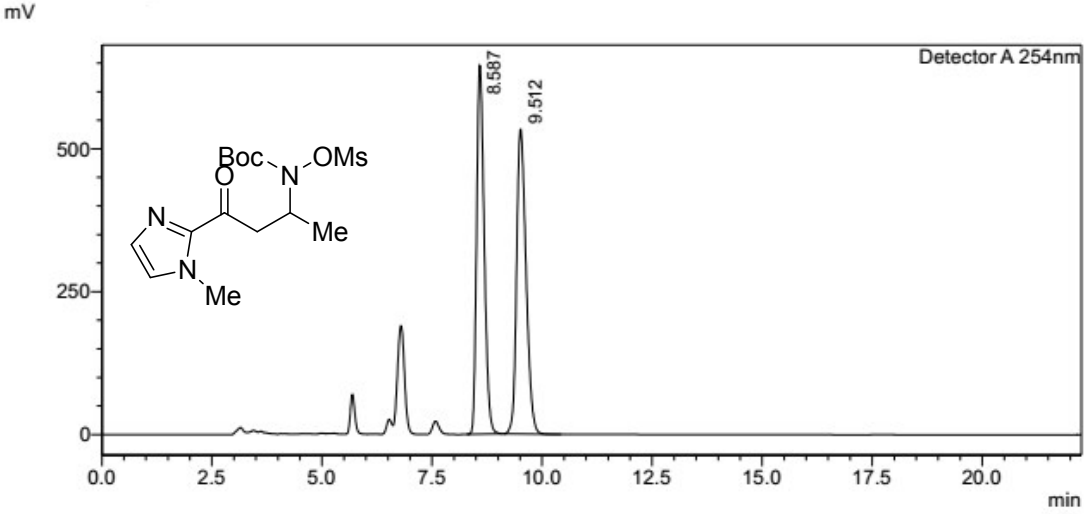
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.200	8112286	683722	90.495		M	
2	12.248	852092	47090	9.505		M	
Total		8964377	730812				

rac-**7**

<Chromatogram>



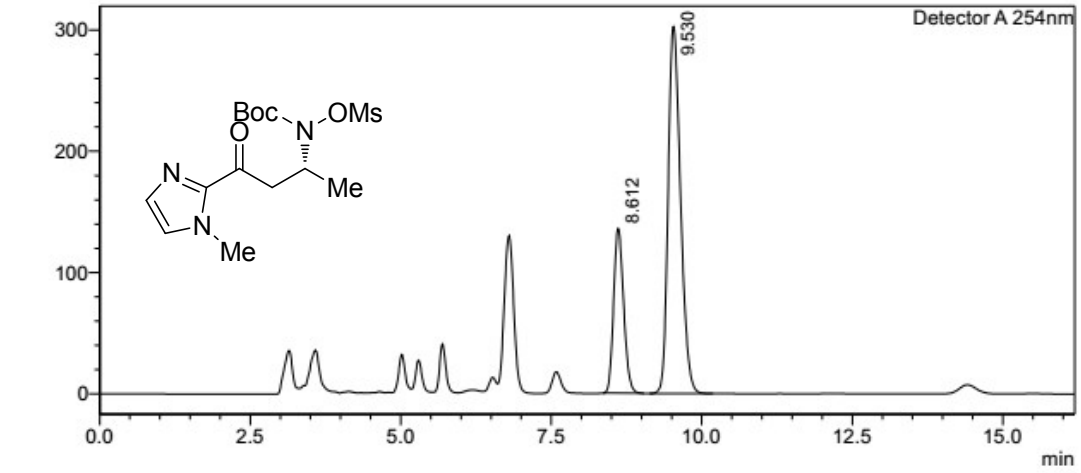
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.587	7713978	644745	49.212		M	
2	9.512	7960888	533267	50.788		M	
Total		15674865	1178013				

Chiral-**7**

<Chromatogram>

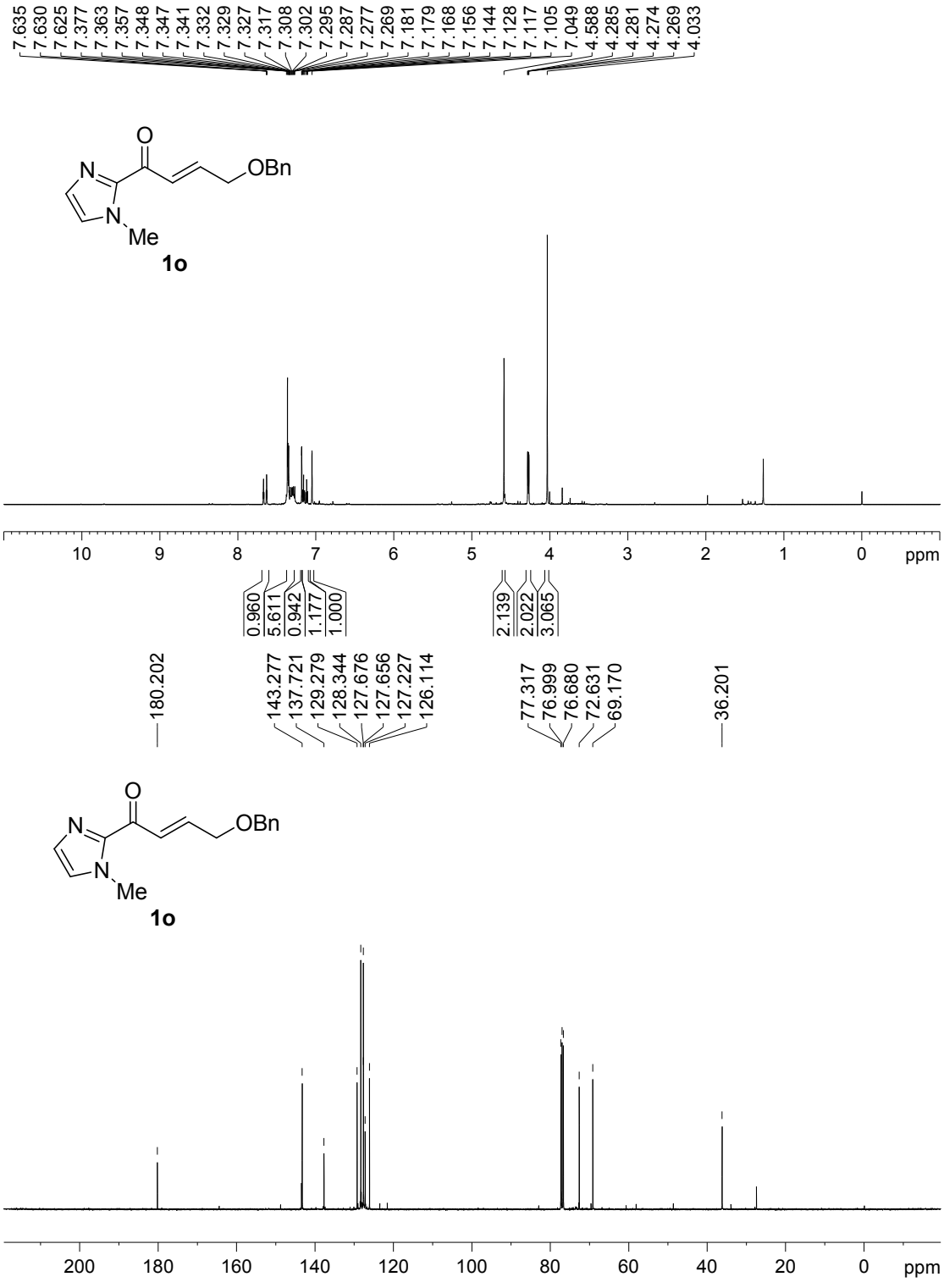


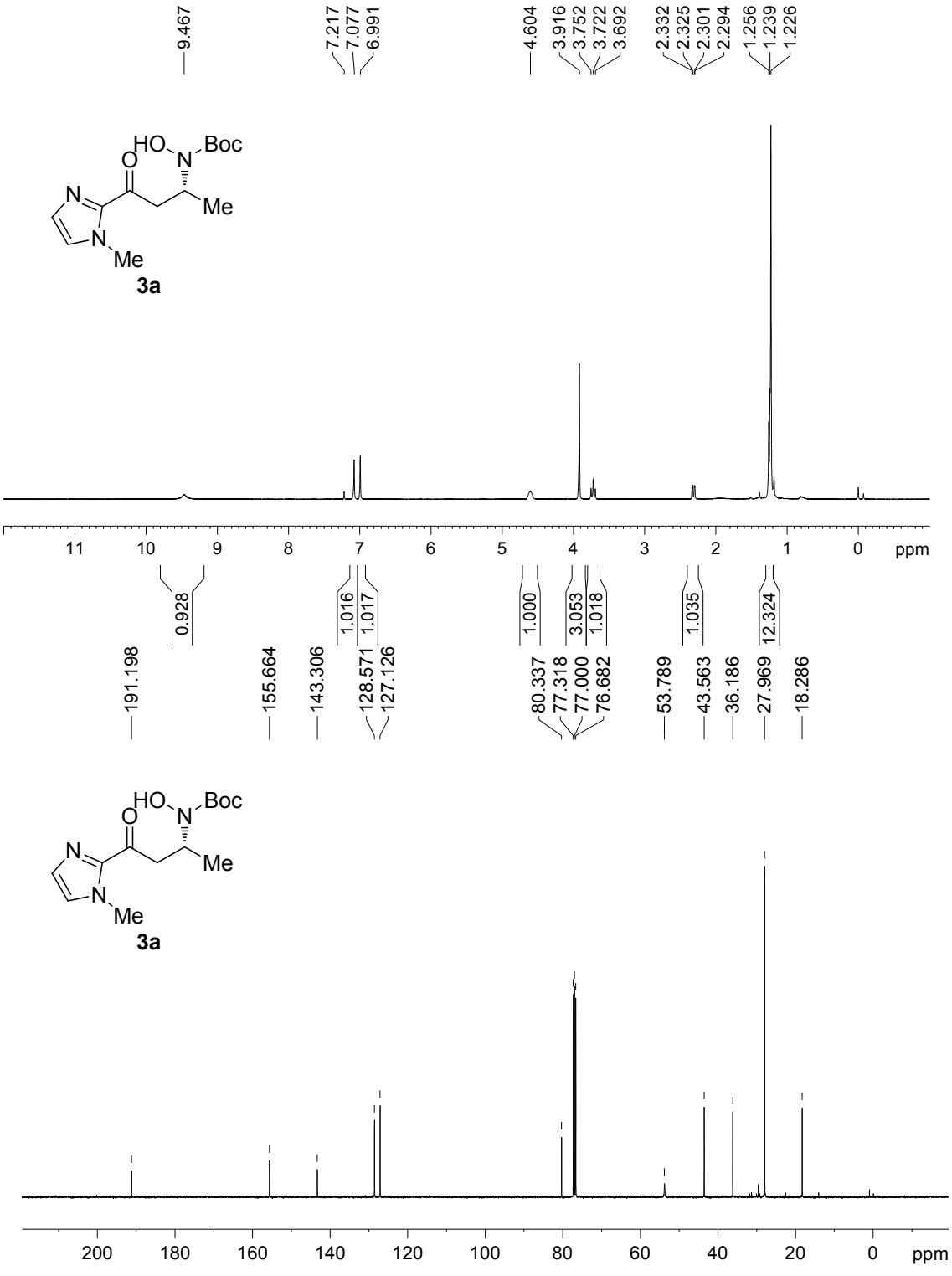
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.612	1574683	135747	26.636		M	
2	9.530	4337247	302606	73.364		M	
Total		5911930	438353				

V NMR Spectra of Products

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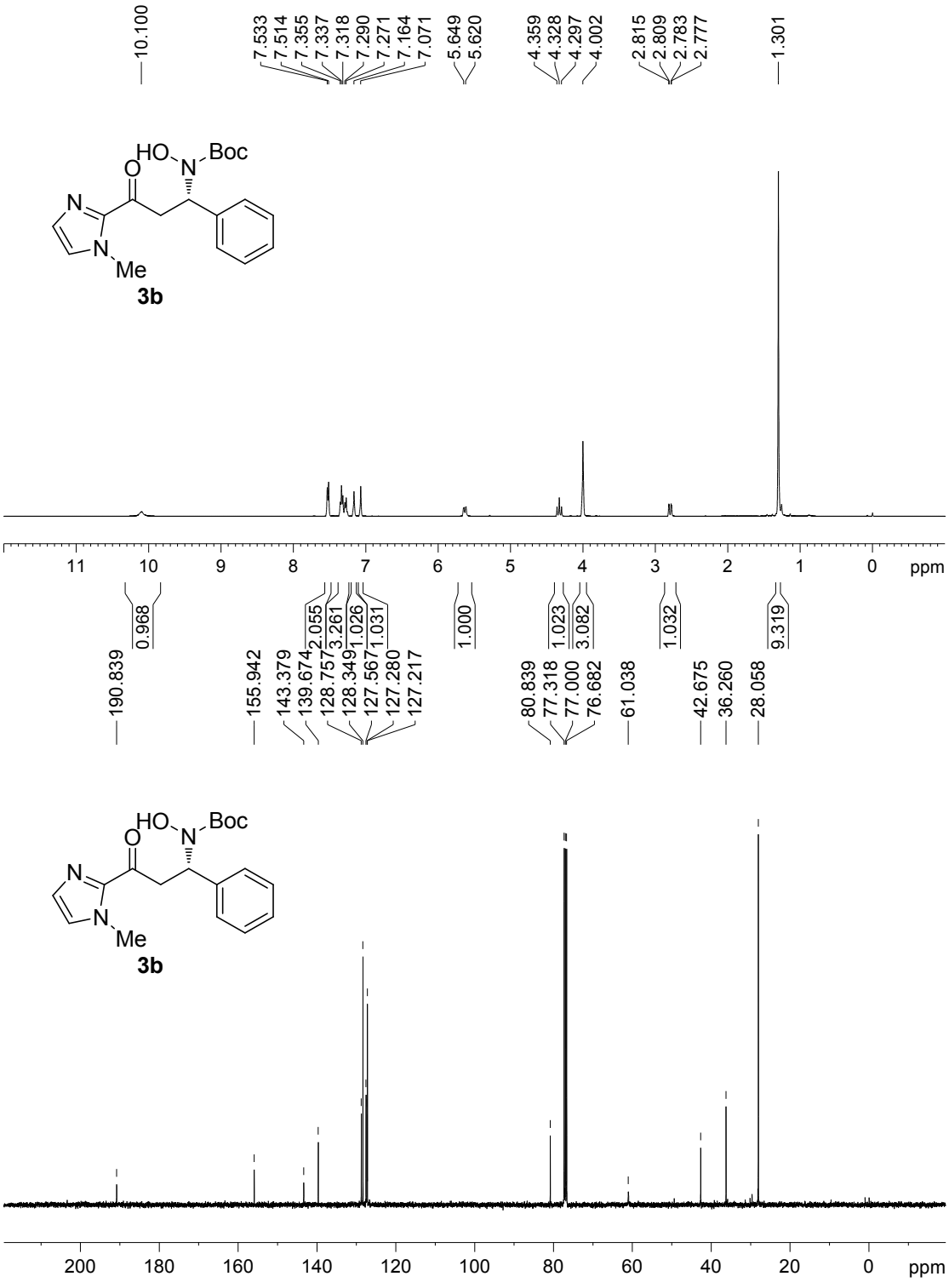
7.077
6.991
4.604
3.916
3.752
3.722
3.692
2.332
2.325
2.301
2.294
1.256
1.239
1.226
HO
N
Boc
O
N
Me
N
Me
3a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.928
1.016
1.017
1.000
3.053
1.018
1.035
12.324
191.198
155.664
143.306
128.571
127.126
80.337
77.318
77.000
76.682
53.789
43.563
36.186
27.969
18.286
HO
N
Boc
O
N
Me
N
Me
3a
200
180
160
140
120
100
80
60
40
20
0
ppm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7.514
7.355
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7.290
7.271
7.164
7.071
5.649
5.620
4.359
4.328
4.297
4.002
2.815
2.809
2.783
2.777
1.301
HO
N
Boc
O
N
N
Me
3b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.968
2.055
3.261
1.026
1.031
1.000
1.023
3.082
1.032
9.319
190.839
155.942
143.379
139.674
128.757
128.349
127.567
127.280
127.217
80.839
77.318
77.000
76.682
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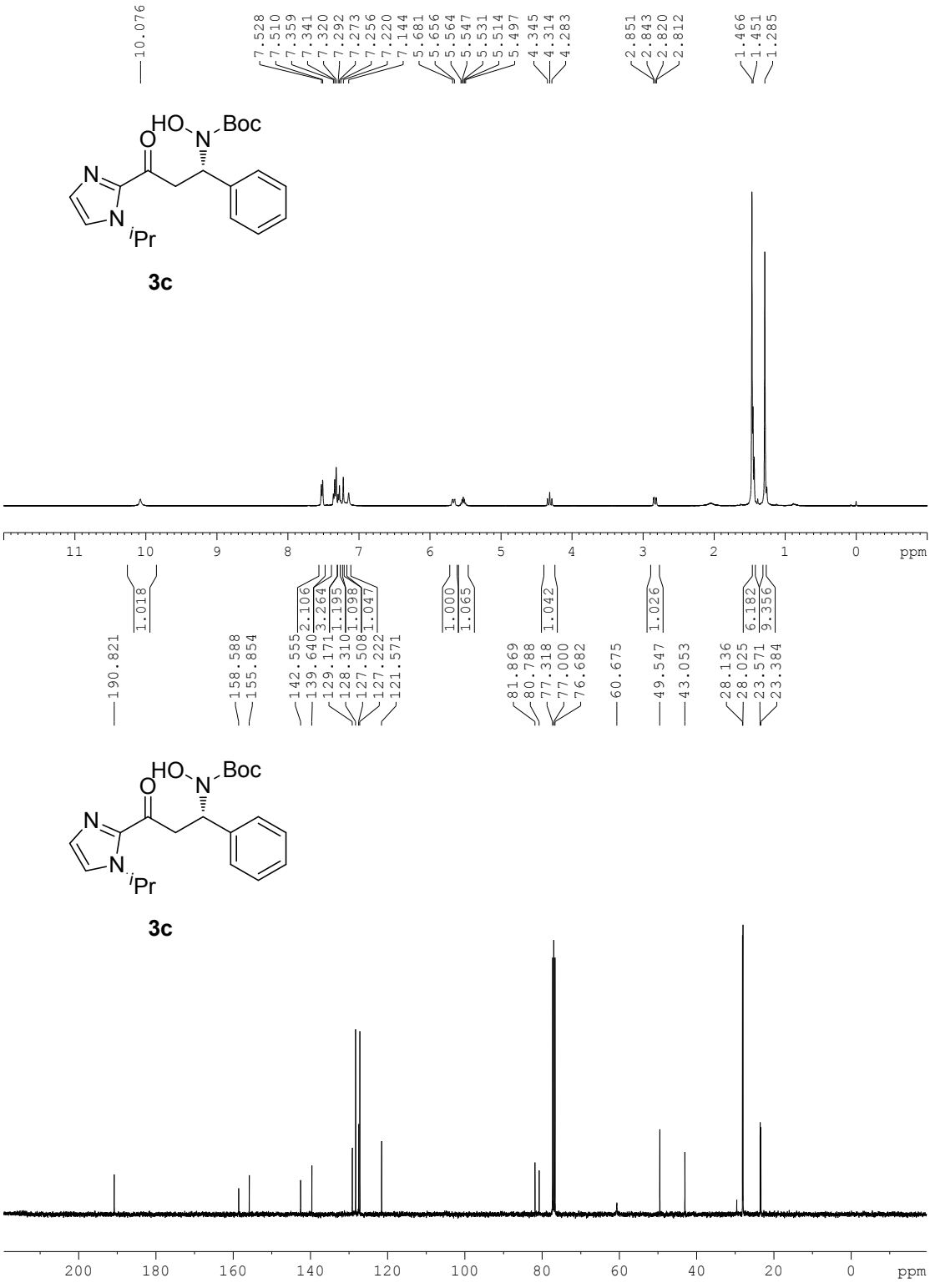
28.058
200
180
160
140
120
100
80
60
40
20
0
ppm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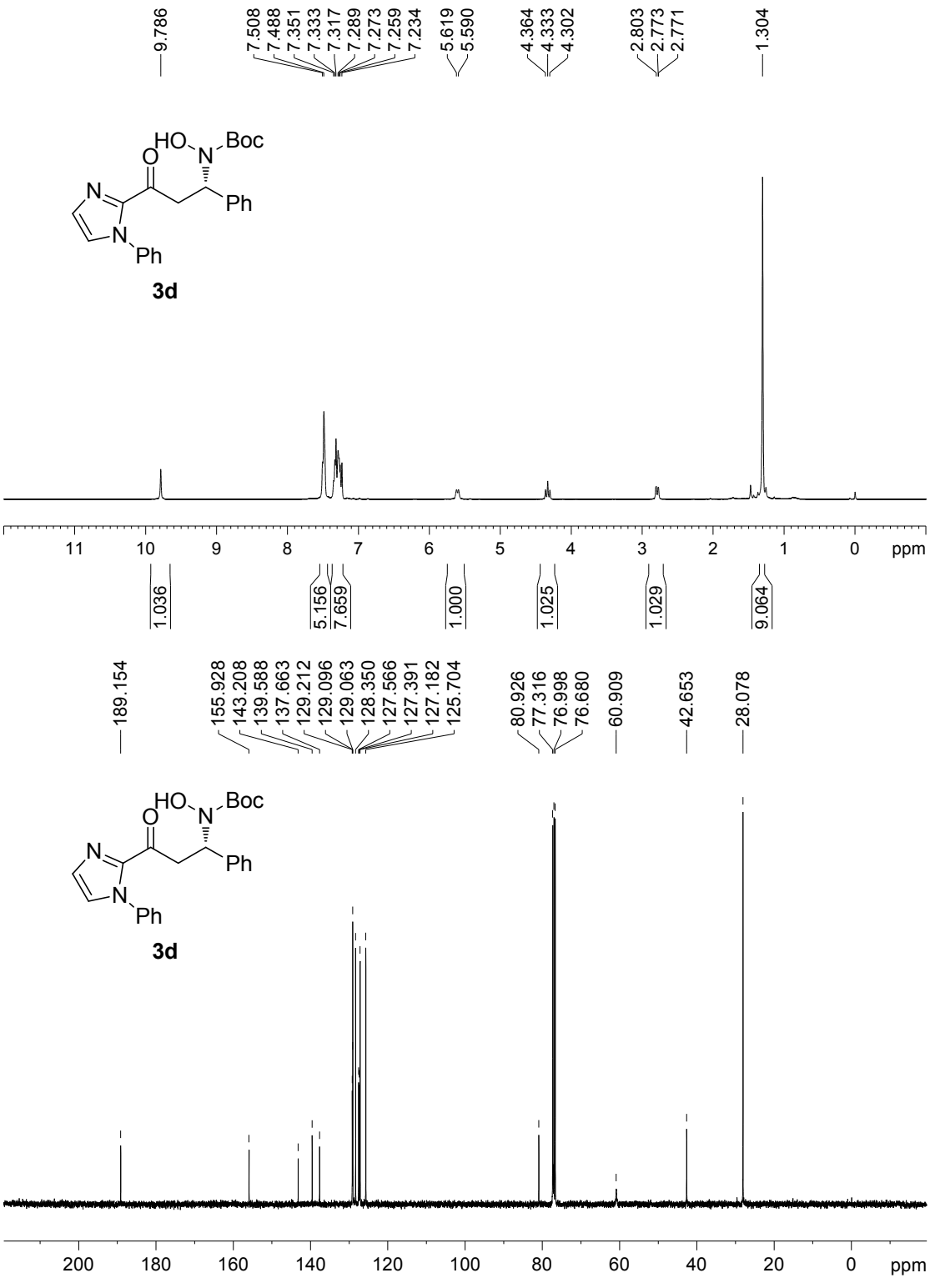
7.359
7.341
7.320
7.292
7.273
7.256
7.220
7.144
5.681
5.656
5.564
5.547
5.531
5.514
5.497
4.345
4.314
4.283
2.851
2.843
2.820
2.812
1.466
1.451
1.285
HO
N
Boc
O
N
N
iPr
3c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.018
2.106
3.264
1.195
1.098
1.047
1.000
1.065
1.042
1.026
6.182
9.356
190.821
158.588
155.854
142.555
139.640
129.171
128.310
127.508
127.222
121.571
81.869
80.788
77.318
77.000
76.682
60.675
49.547
43.053
28.136
28.025
23.571
23.384
HO
N
Boc
O
N
N
iPr
3c
200
180
160
140
120
100
80
60
40
20
0
ppm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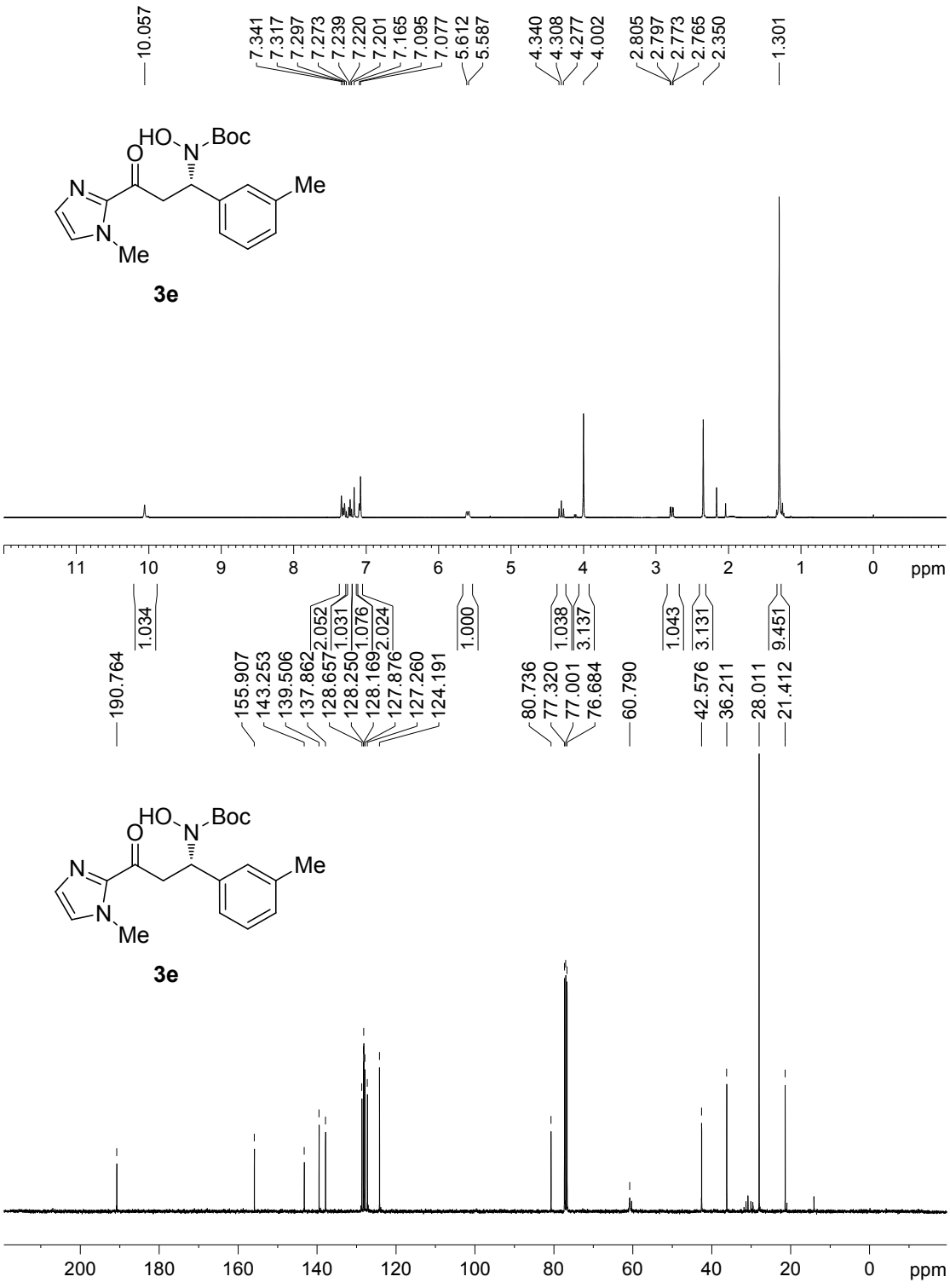
7.351
7.333
7.317
7.289
7.273
7.259
7.234
5.619
5.590
4.364
4.333
4.302
2.803
2.773
2.771
1.304
HO
O
N
Boc
Ph
N
N
Ph
3d
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.036
5.156
7.659
1.000
1.025
1.029
9.064
189.154
155.928
143.208
139.588
137.663
129.212
129.096
129.063
128.350
127.566
127.391
127.182
125.704
80.926
77.316
76.998
76.680
60.909
42.653
28.078
HO
O
N
Boc
Ph
N
N
Ph
3d
200
180
160
140
120
100
80
60
40
20
0
ppm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7.317
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7.239
7.220
7.201
7.165
7.095
7.077
5.612
5.587
4.340
4.308
4.277
4.002
2.805
2.797
2.773
2.765
2.350
1.301
HO
N
Boc
O
N
Me
N
Me
3e
ppm
1.034
2.052
1.031
1.076
2.024
1.000
1.038
3.137
1.043
3.131
9.451
190.764
155.907
143.253
139.506
137.862
128.657
128.250
128.169
127.876
127.260
124.191
80.736
77.320
77.001
76.684
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36.211
28.011
21.412
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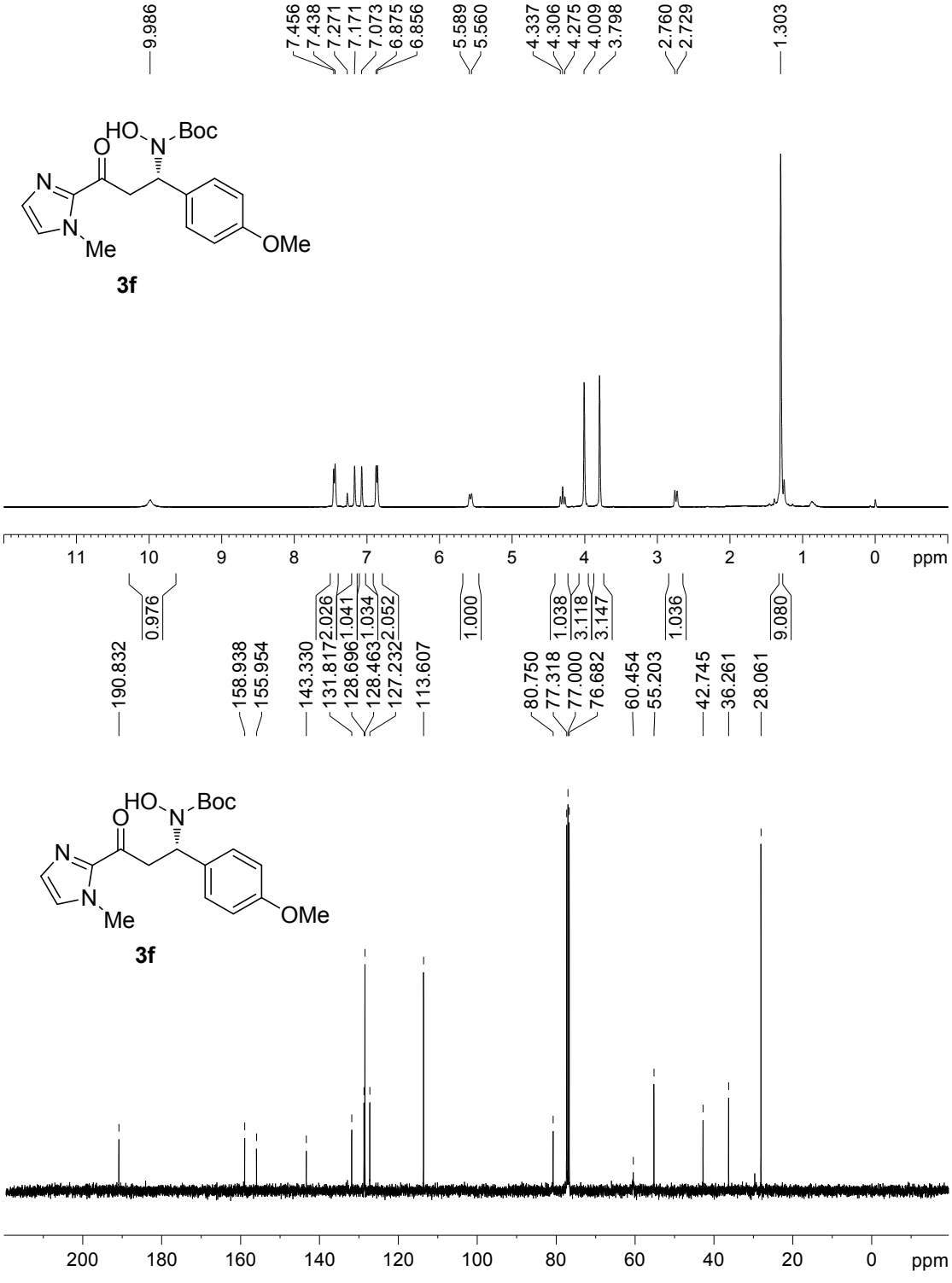
Boc
O
N
Me
N
Me
3e
ppm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7.438
7.271
7.171
7.073
6.875
6.856
5.589
5.560
4.337
4.306
4.275
4.009
3.798
2.760
2.729
1.303
HO
N
Boc
O
N
N
Me
OMe
3f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.976
2.026
1.041
1.034
2.052
1.000
1.038
3.118
3.147
1.036
9.080
190.832
158.938
155.954
143.330
131.817
128.696
128.463
127.232
113.607
80.750
77.318
77.000
76.682
60.454
55.203
42.745
36.261
28.061
HO
N
Boc
O
N
N
Me
OMe
3f
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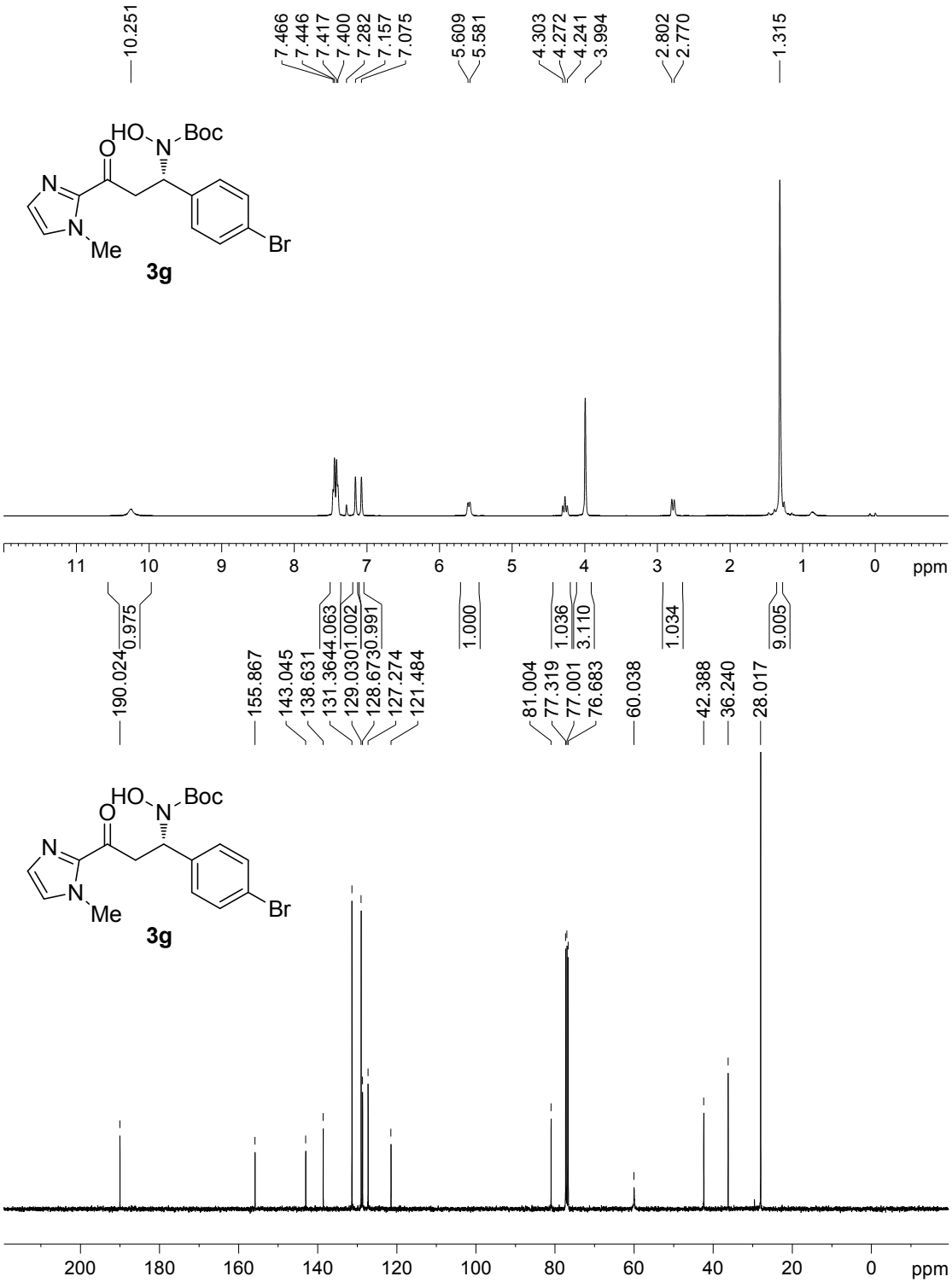
160
140
120
100
80
60
40
20
0
ppm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7.446
7.417
7.400
7.282
7.157
7.075
5.609
5.581
4.303
4.272
4.241
3.994
2.802
2.770
1.315
HO
N
Boc
O
N
Me
Br
3g
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.975
1.000
3.644
1.002
30.991
1.036
3.110
1.034
9.005
190.024
155.867
143.045
138.631
131.363
129.030
128.673
127.274
121.484
81.004
77.319
77.001
76.683
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36.240
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120
100
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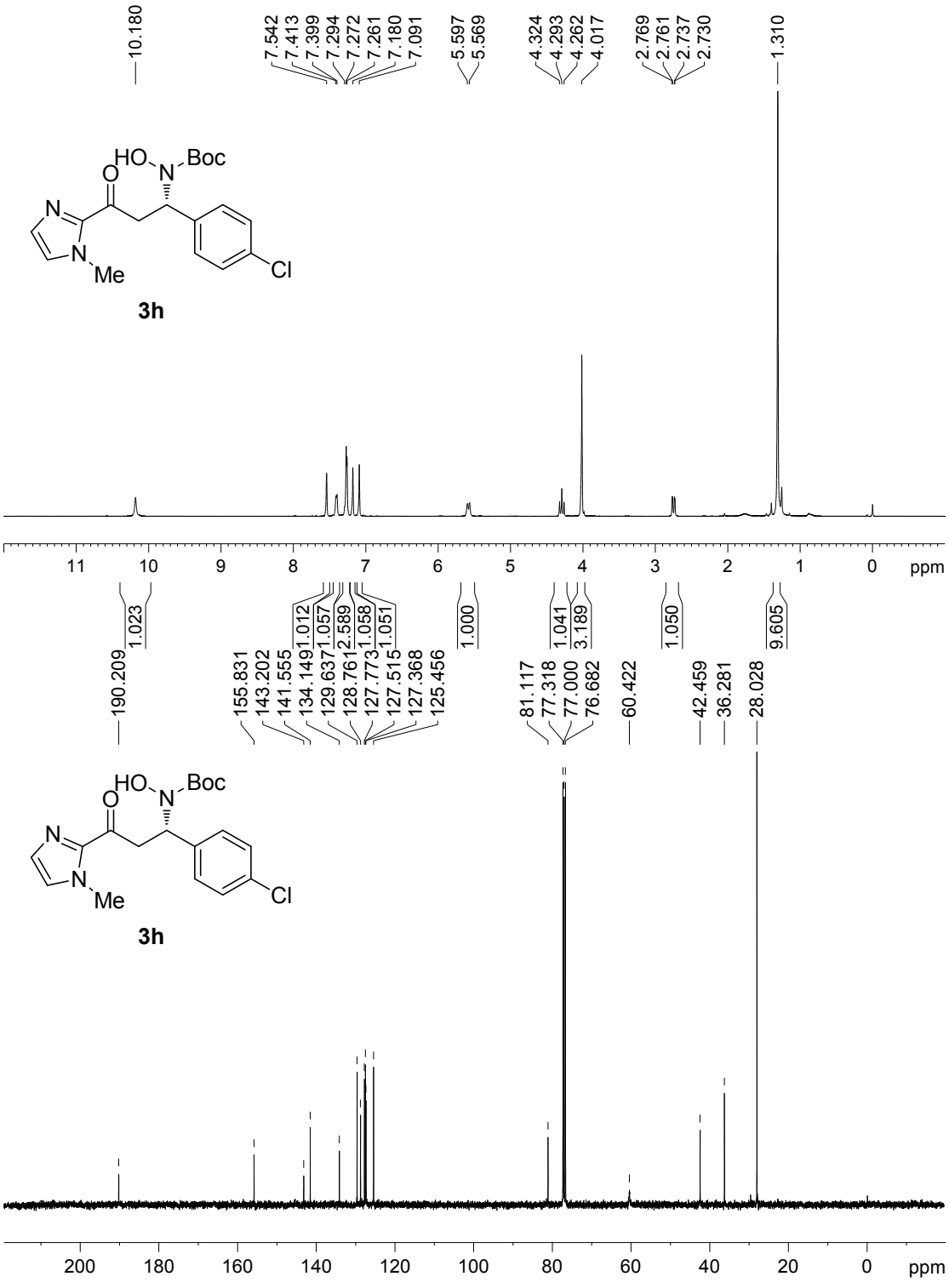
60
40
20
0
ppm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7.272
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7.180
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4.324
4.293
4.262
4.017
2.769
2.761
2.737
2.730
1.310
HO
N
Boc
O
N
N
Me
Cl
3h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.023
1.012
1.057
2.589
1.058
1.051
1.000
1.041
3.189
1.050
9.605
190.209
155.831
143.202
141.555
134.149
129.637
128.761
127.773
127.515
127.368
125.456
81.117
77.318
77.000
76.682
60.422
42.459
36.281
28.028
HO
N
Boc
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Me
Cl
3h
200
180
160
140
120
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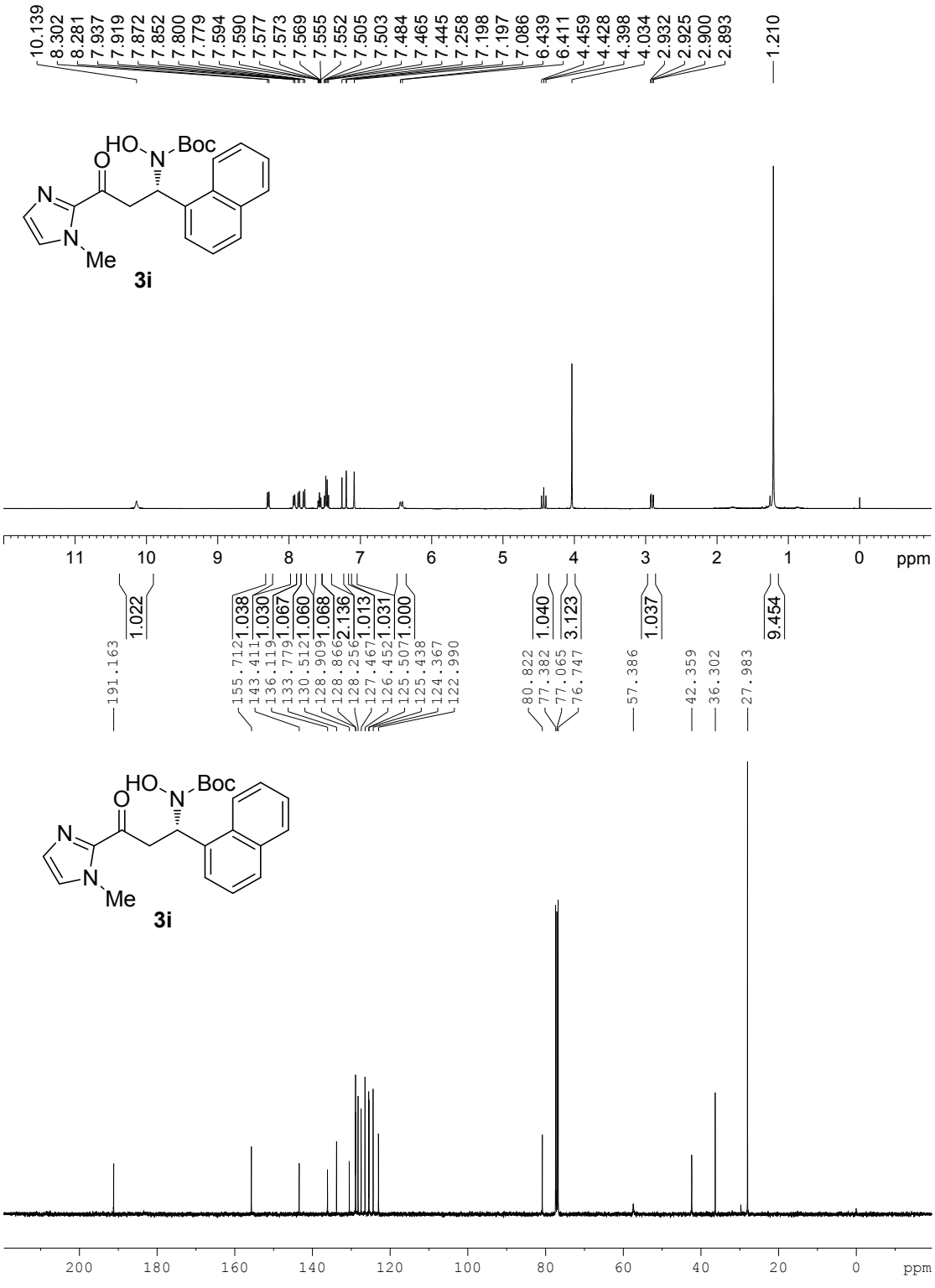
80
60
40
20
0
ppm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8.281
7.937
7.919
7.872
7.852
7.800
7.779
7.594
7.590
7.577
7.573
7.569
7.555
7.552
7.505
7.503
7.484
7.465
7.445
7.258
7.198
7.197
7.086
6.439
6.411
4.459
4.428
4.398
4.034
2.932
2.925
2.900
2.893
1.210
HO
N
Boc
O
N
N
Me
3i
ppm
1.022
1.038
1.030
1.067
1.060
1.068
2.136
1.013
1.031
1.000
1.040
3.123
1.037
9.454
191.163
155.712
143.411
136.119
133.779
130.512
128.909
128.866
128.256
127.467
126.452
125.507
125.438
124.367
122.990
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77.382
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Boc
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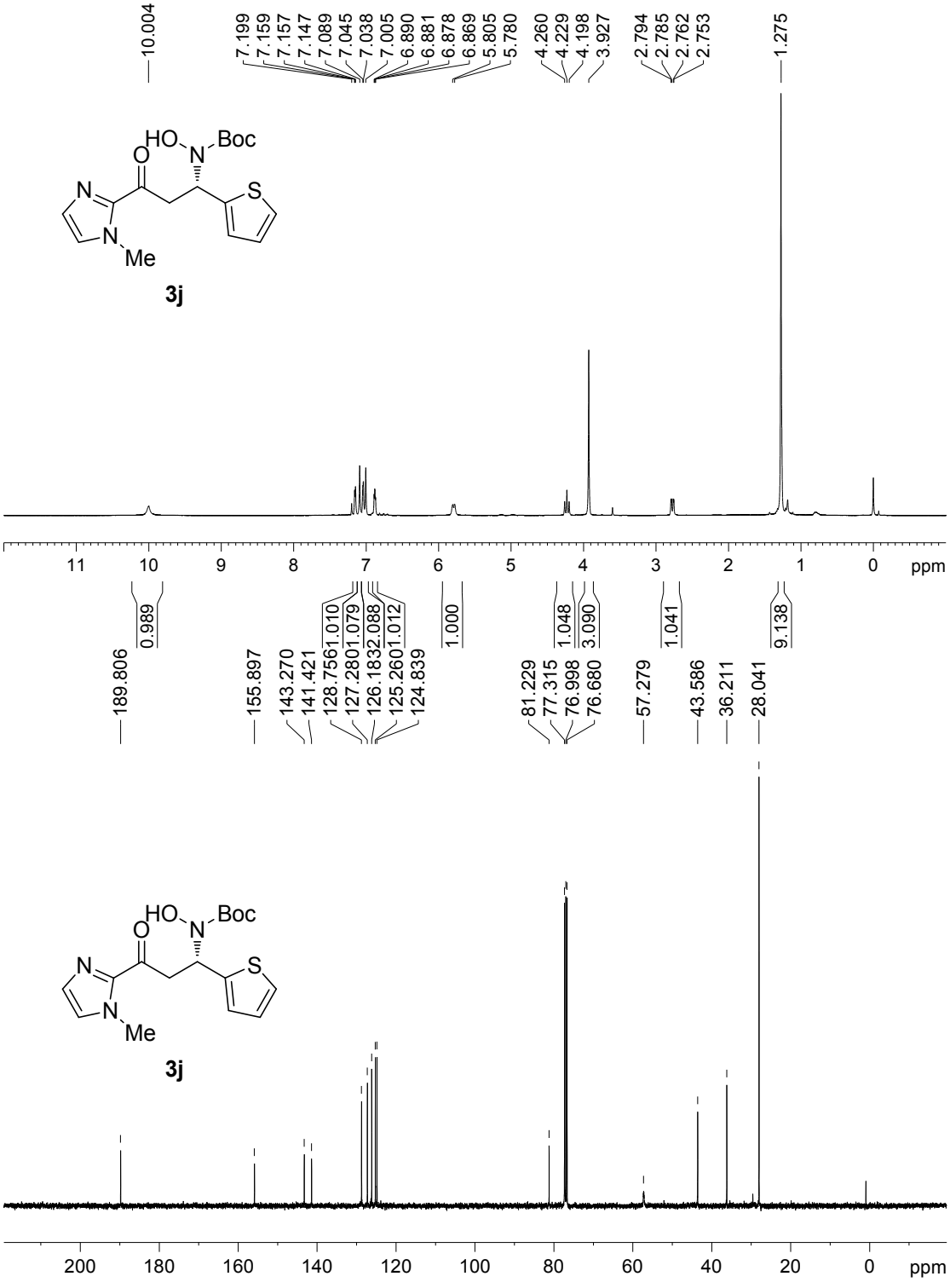
N
N
Me
3i
ppm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7.157
7.147
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7.045
7.038
7.005
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6.878
6.869
5.805
5.780
4.260
4.229
4.198
3.927
2.794
2.785
2.762
2.753
1.275
HO
O
N
Boc
N
S
N
Me
3j
ppm
0.989
1.010
1.079
2.088
1.012
1.000
1.048
3.090
1.041
9.138
189.806
155.897
143.270
141.421
128.756
127.280
126.183
125.260
124.839
81.229
77.315
76.998
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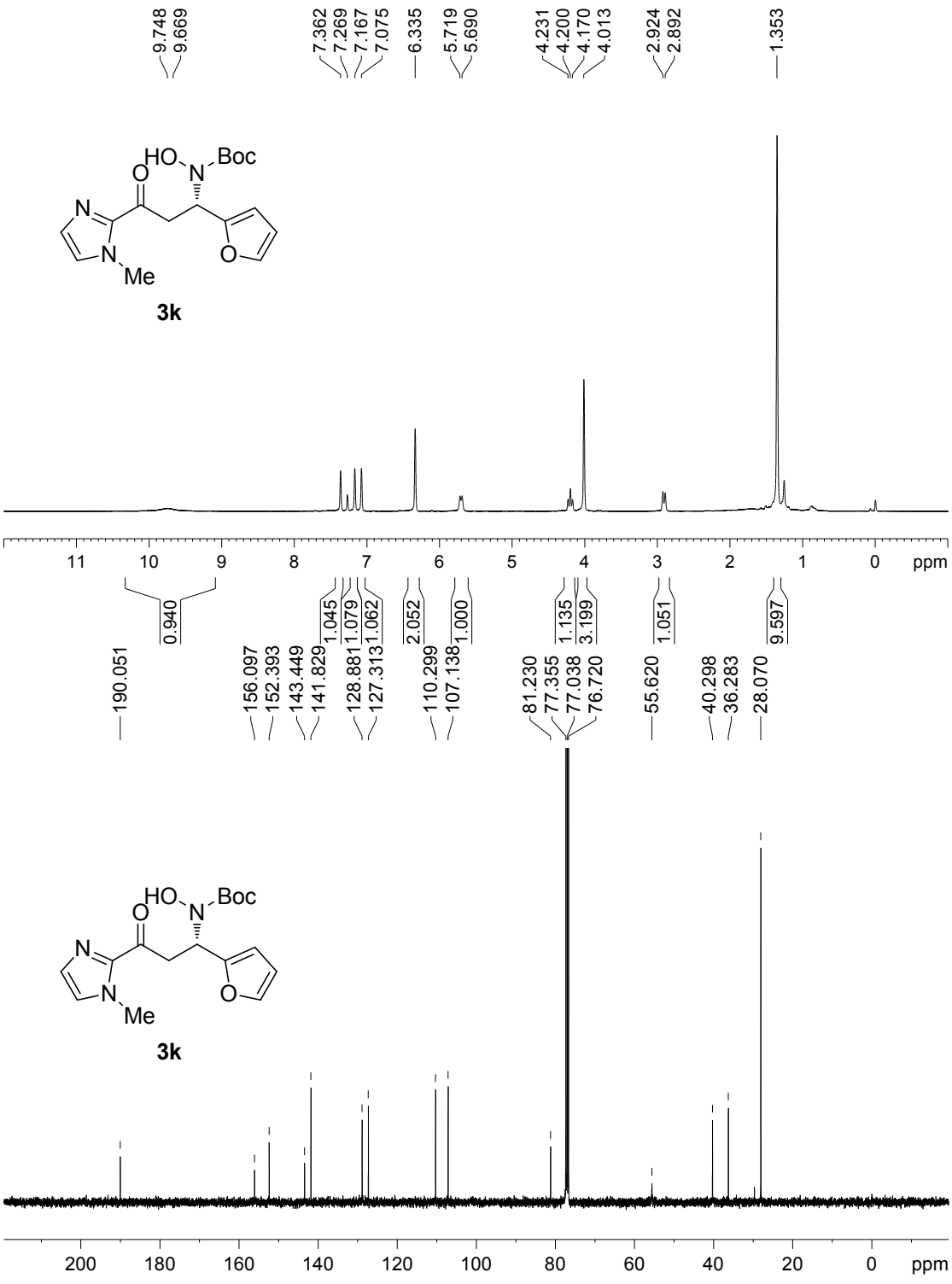
57.279
43.586
36.211
28.041
HO
O
N
Boc
N
S
N
Me
3j
ppm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7.269
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7.075
6.335
5.719
5.690
4.231
4.200
4.170
4.013
2.924
2.892
1.353
HO
N
Boc
O
N
N
Me
O
3k
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.940
1.045
1.079
1.062
2.052
1.000
1.135
3.199
1.051
9.597
190.051
156.097
152.393
143.449
141.829
128.881
127.313
110.299
107.138
81.230
77.355
77.038
76.720
55.620
40.298
36.283
28.070
HO
N
Boc
O
N
N
Me
O
3k
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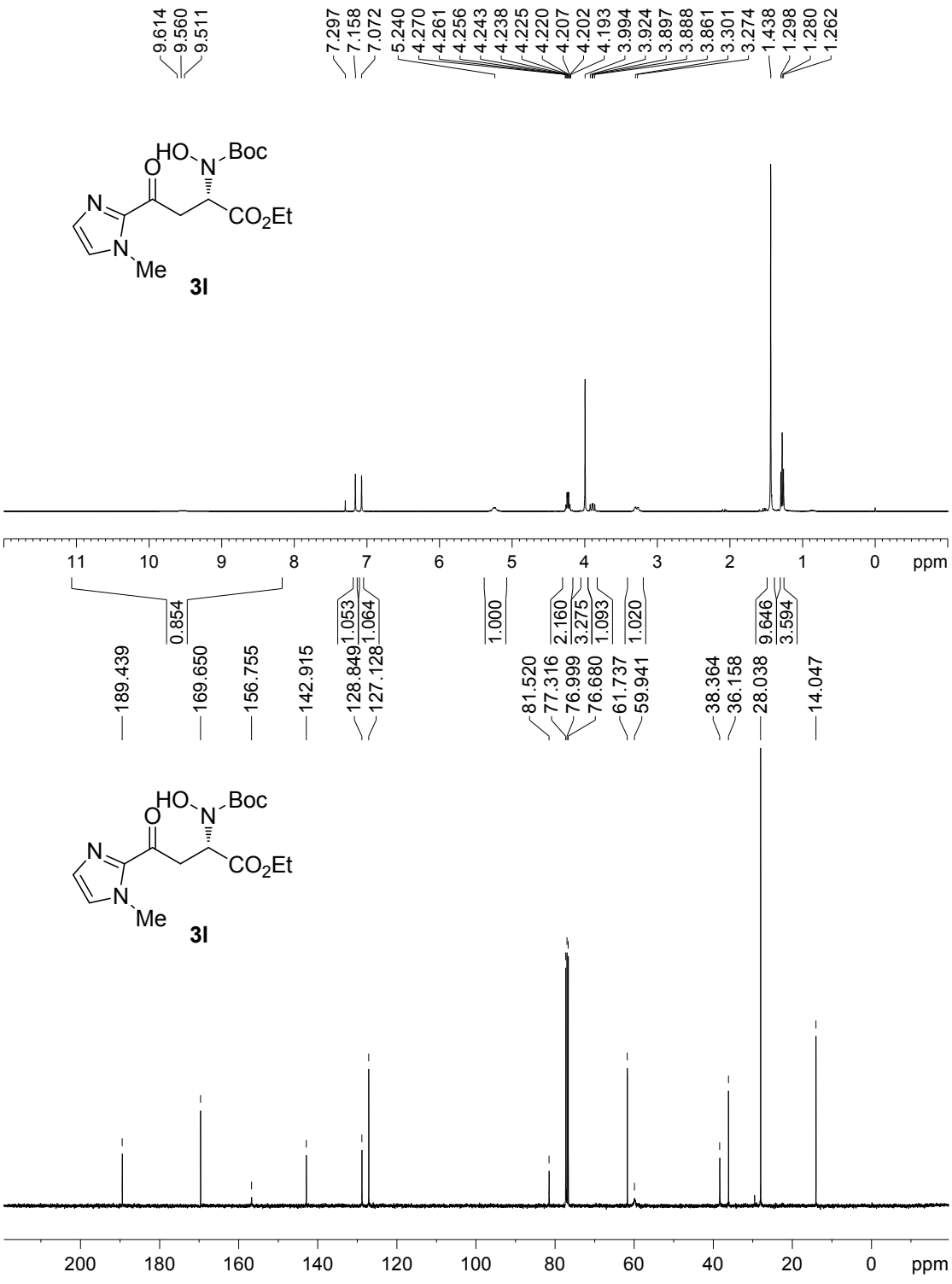
160
140
120
100
80
60
40
20
0
ppm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9.511
7.297
7.158
7.072
5.240
4.270
4.261
4.256
4.243
4.238
4.225
4.220
4.207
4.202
4.193
3.994
3.924
3.897
3.888
3.861
3.301
3.274
1.438
1.298
1.280
1.262
HO
N
Boc
O
N
CO2Et
N
Me
3l
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.854
1.053
1.064
1.000
2.160
3.275
1.093
1.020
9.646
3.594
189.439
169.650
156.755
142.915
128.849
127.128
81.520
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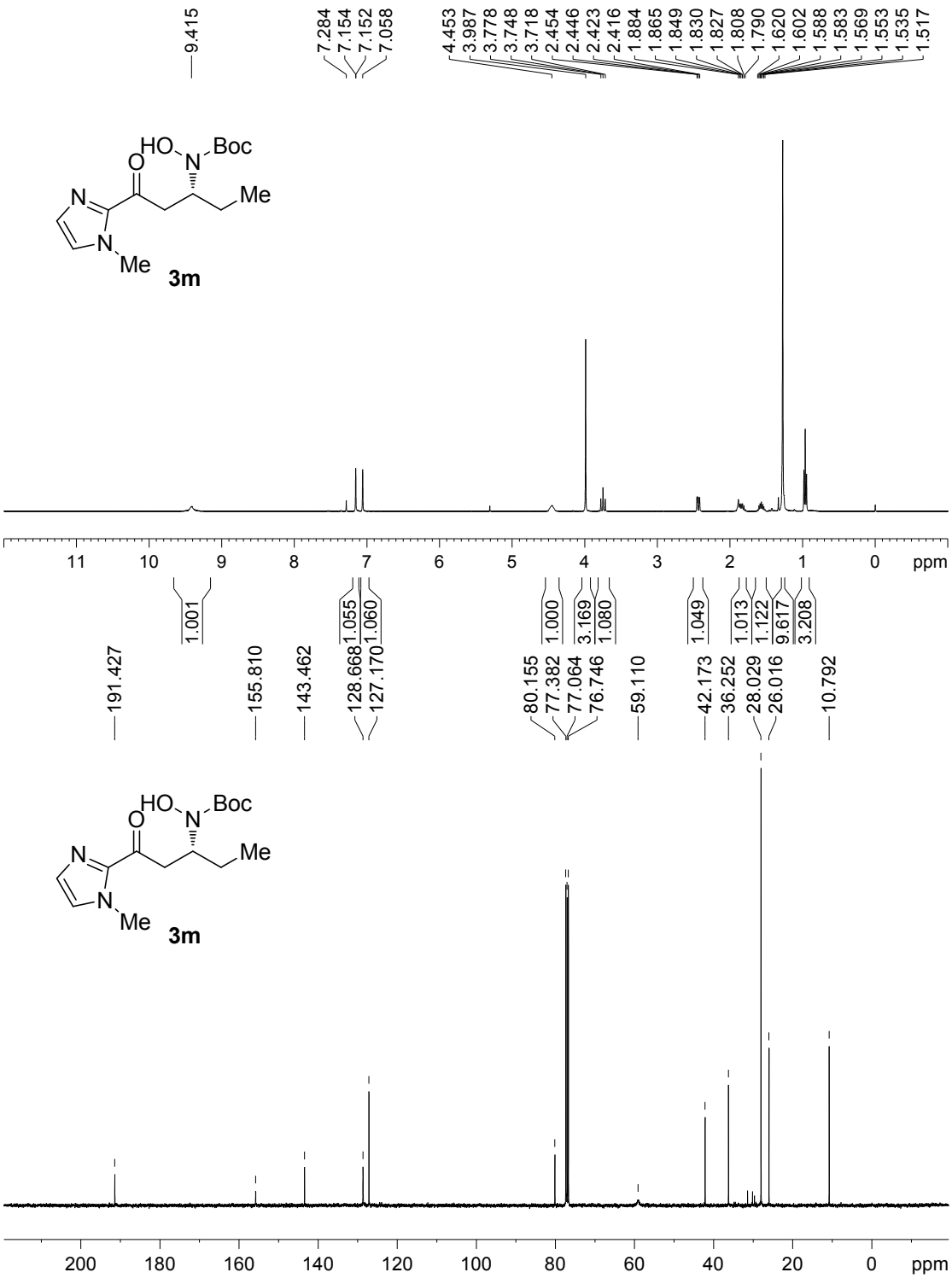
76.999
76.680
61.737
59.941
38.364
36.158
28.038
14.047
200 180 160 140 120 100 80 60 40 20 0 ppm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3.718
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2.446
2.423
2.416
1.884
1.865
1.849
1.830
1.827
1.808
1.790
1.620
1.602
1.588
1.583
1.569
1.553
1.535
1.517
HO
N
Boc
O
N
Me
N
Me
3m
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.001
1.055
1.060
1.000
3.169
1.080
1.049
1.013
1.122
9.617
3.208
191.427
155.810
143.462
128.668
127.170
80.155
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59.110
42.173
36.252
28.029
26.016
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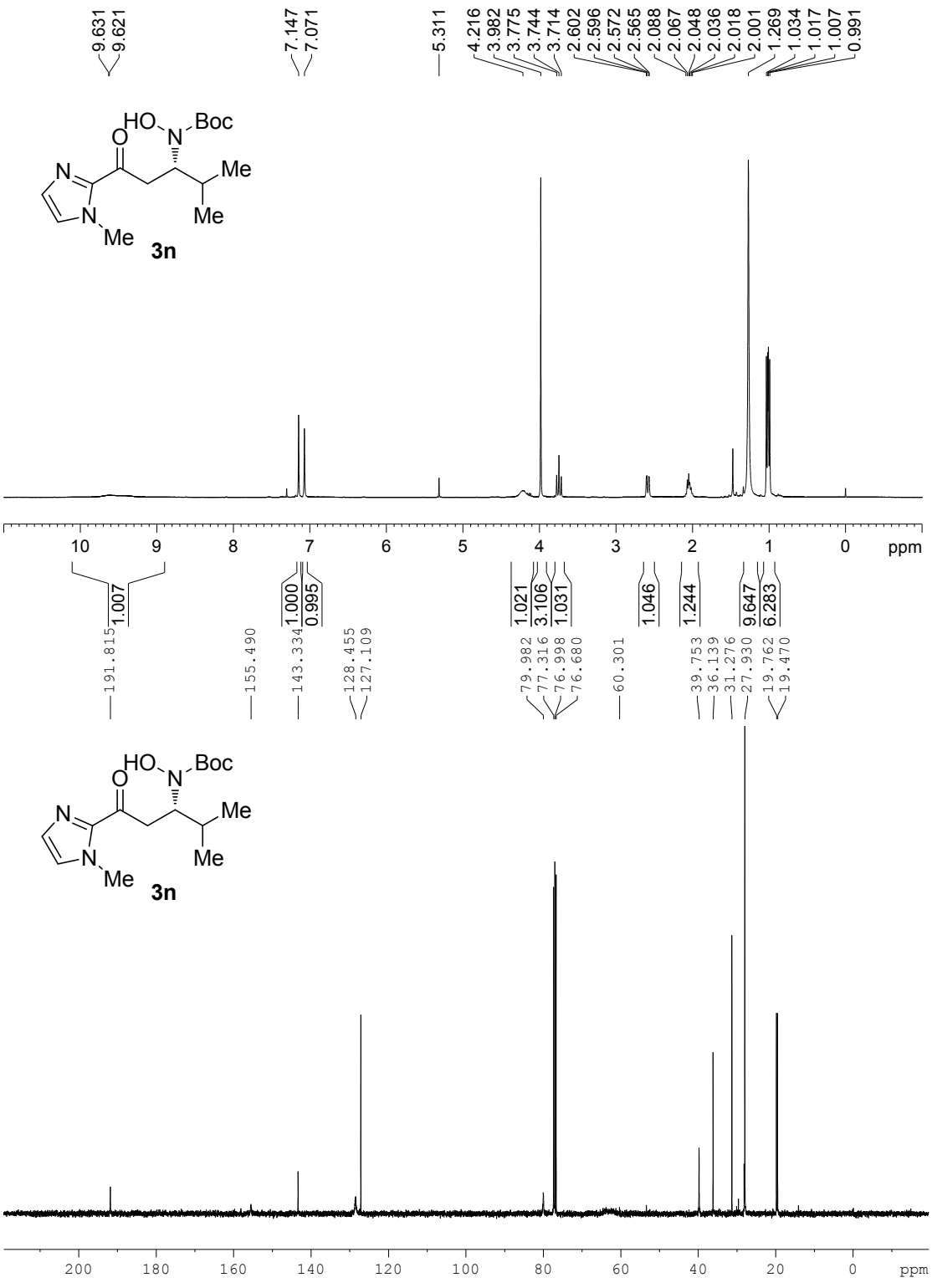
200 180 160 140 120 100 80 60 40 20 0 ppm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3.775
3.744
3.714
2.602
2.596
2.572
2.565
2.088
2.067
2.048
2.036
2.018
2.001
1.269
1.034
1.017
1.007
0.991
HO
N
Boc
O
N
Me
Me
N
Me
3n
10
9
8
7
6
5
4
3
2
1
0
ppm
1.007
1.000
0.995
1.021
3.106
1.031
1.046
1.244
9.647
6.283
191.815
155.490
143.334
128.455
127.109
79.982
77.316
76.998
76.680
60.301
39.753
36.139
31.276
27.930
19.762
19.470
HO
N
Boc
O
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Me
Me
N
Me
3n
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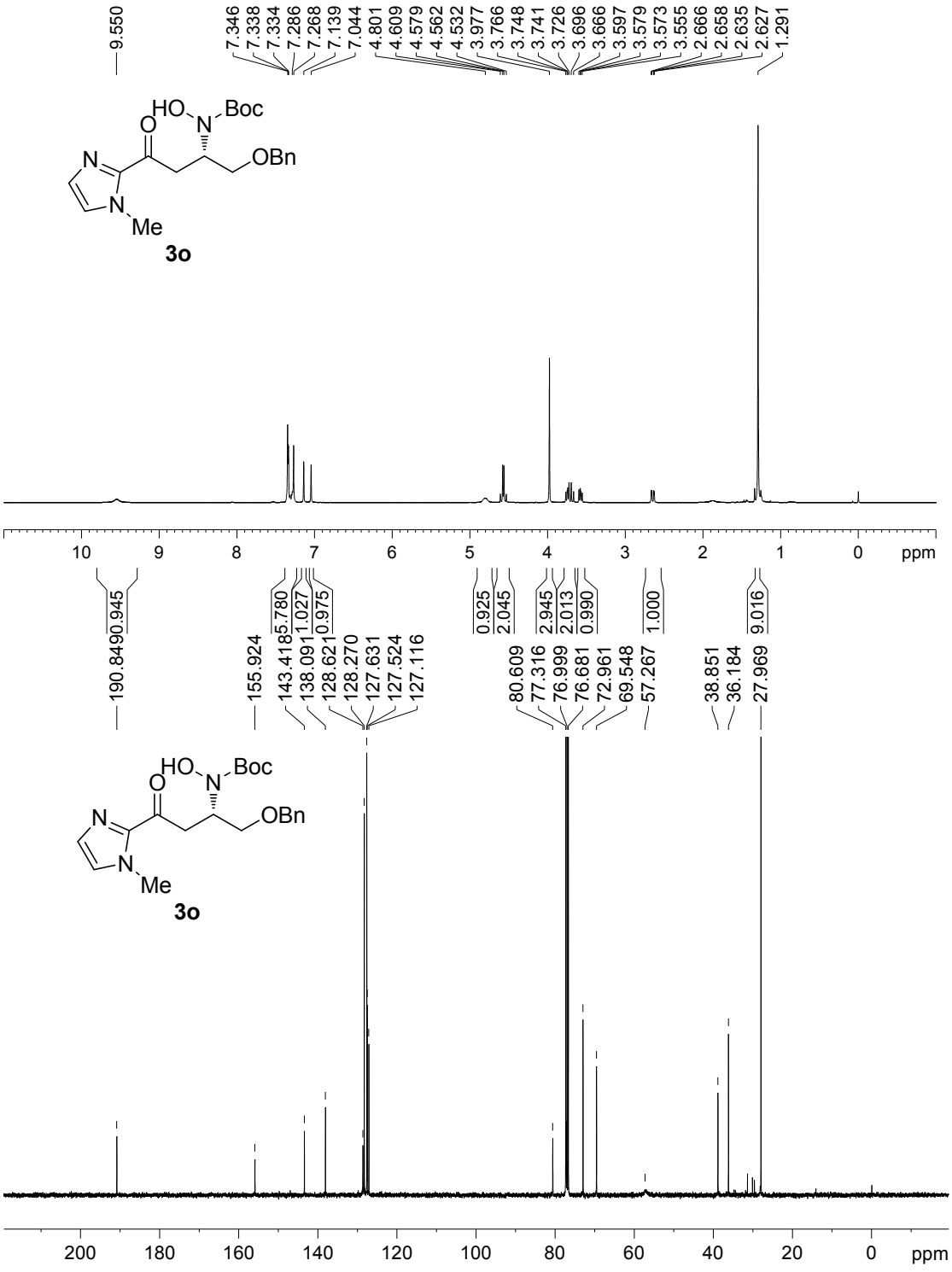
160
140
120
100
80
60
40
20
0
ppm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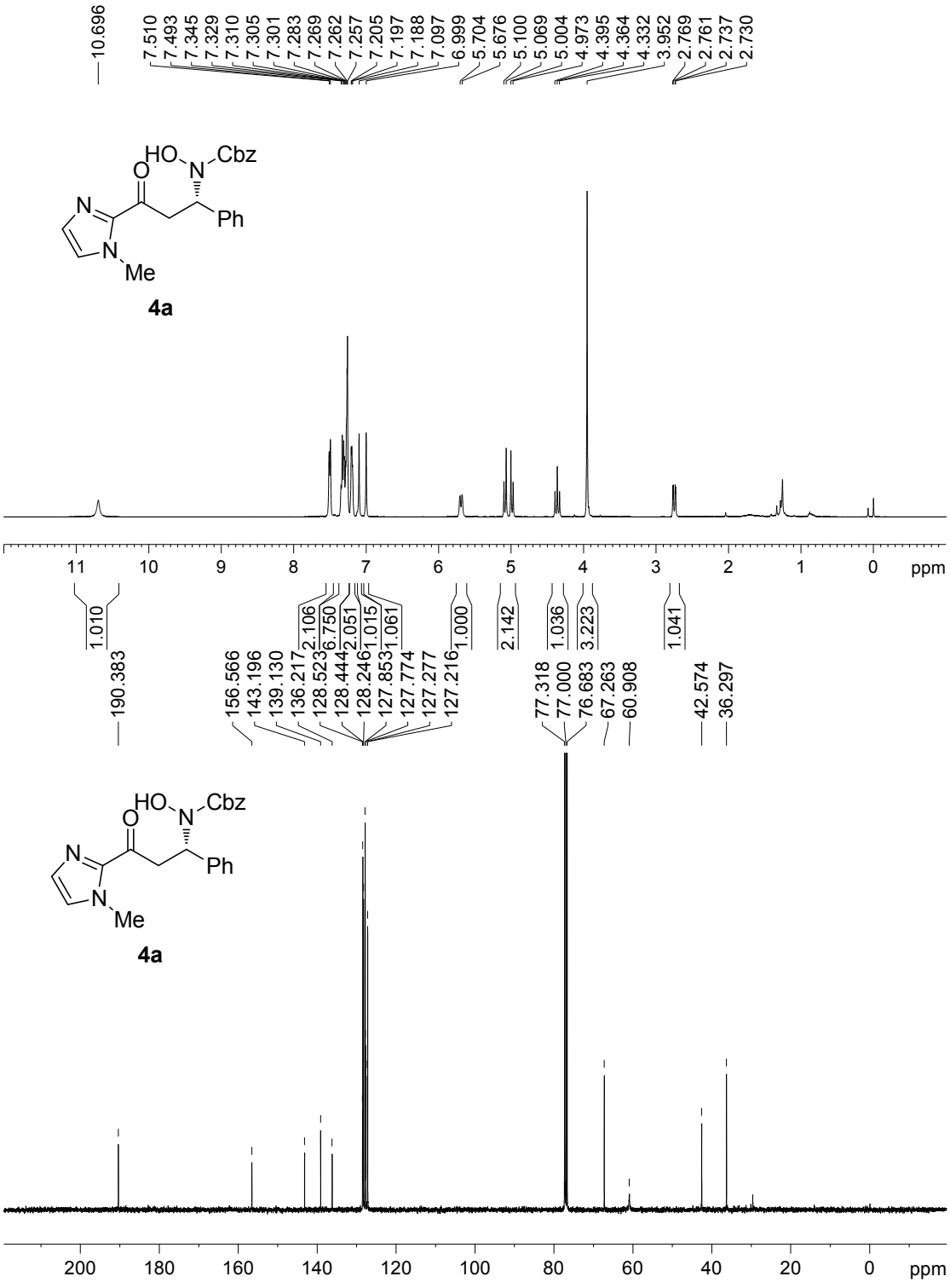
7.286
7.268
7.139
7.044
4.801
4.609
4.579
4.562
4.532
3.977
3.766
3.748
3.741
3.726
3.696
3.666
3.597
3.579
3.573
3.555
2.666
2.658
2.635
2.627
1.291
HO
N
Boc
O
N
OBn
N
Me
3o
10
9
8
7
6
5
4
3
2
1
0
ppm
0.945
5.780
1.027
0.975
0.925
2.045
2.945
2.013
0.990
1.000
9.016
190.849
155.924
143.418
138.091
128.621
128.270
127.631
127.524
127.116
80.609
77.316
76.999
76.681
72.961
69.548
57.267
38.851
36.184
27.969
HO
N
Boc
O
N
OBn
N
Me
3o
200
180
160
140
120
100
80
60
40
20
0
ppm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7.493
7.345
7.329
7.310
7.305
7.301
7.283
7.269
7.262
7.257
7.205
7.197
7.188
7.097
6.999
5.704
5.676
5.100
5.069
5.004
4.973
4.395
4.364
4.332
3.952
2.769
2.761
2.737
2.730
HO
N
Cbz
O
N
Ph
N
Me
4a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.010
2.106
6.750
2.051
1.015
1.061
1.000
2.142
1.036
3.223
1.041
190.383
156.566
143.196
139.130
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128.444
128.246
127.853
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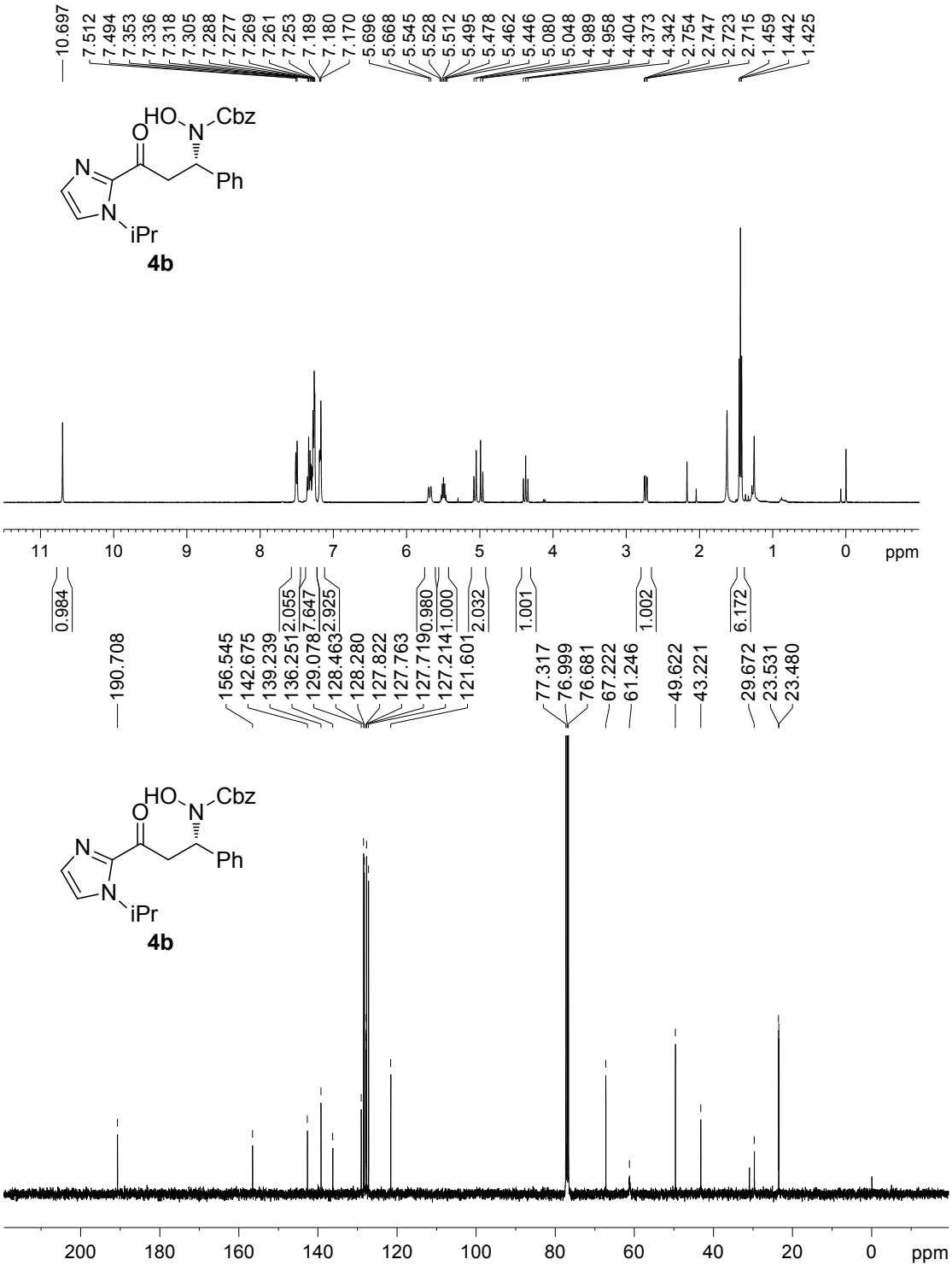
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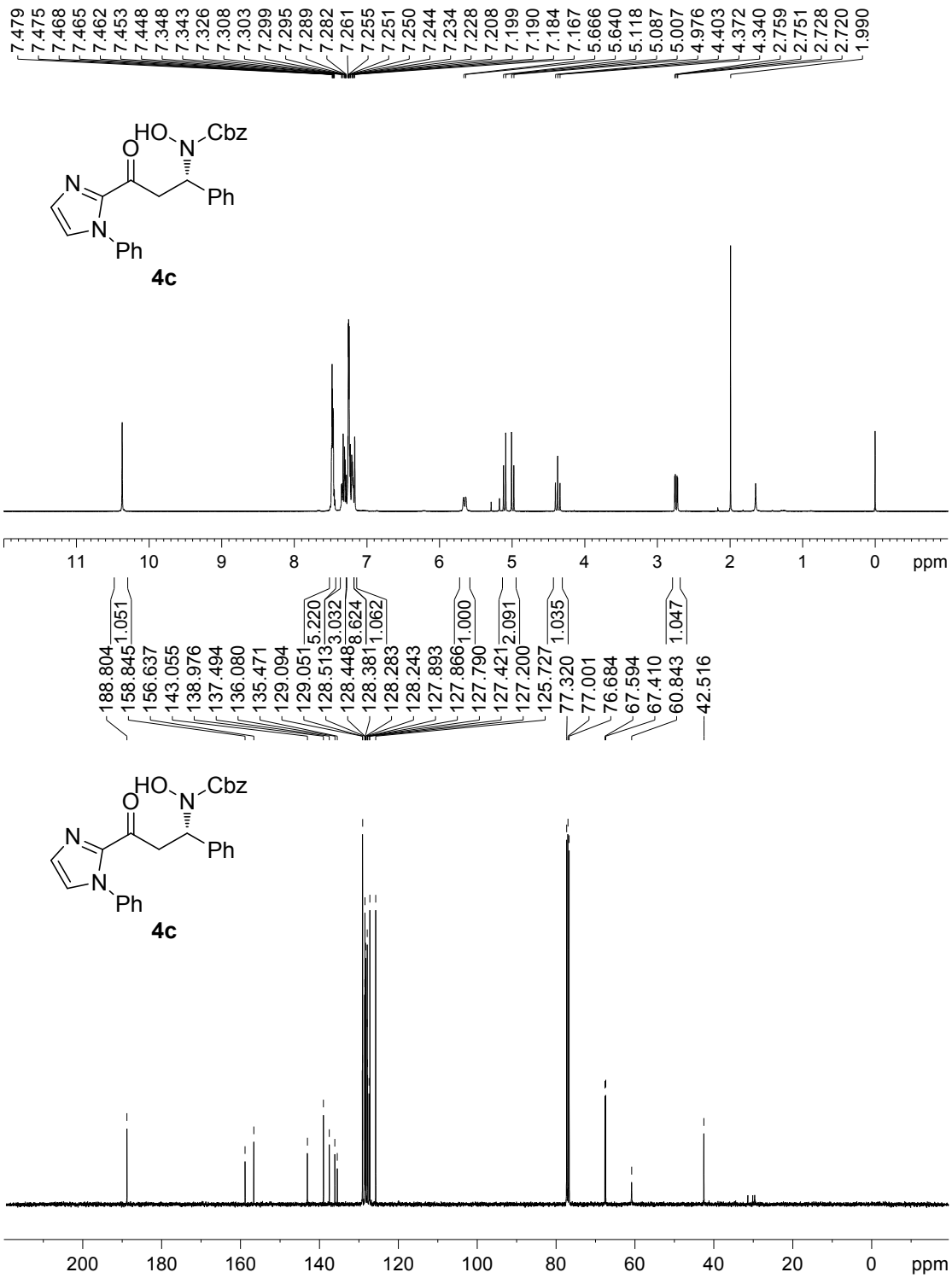
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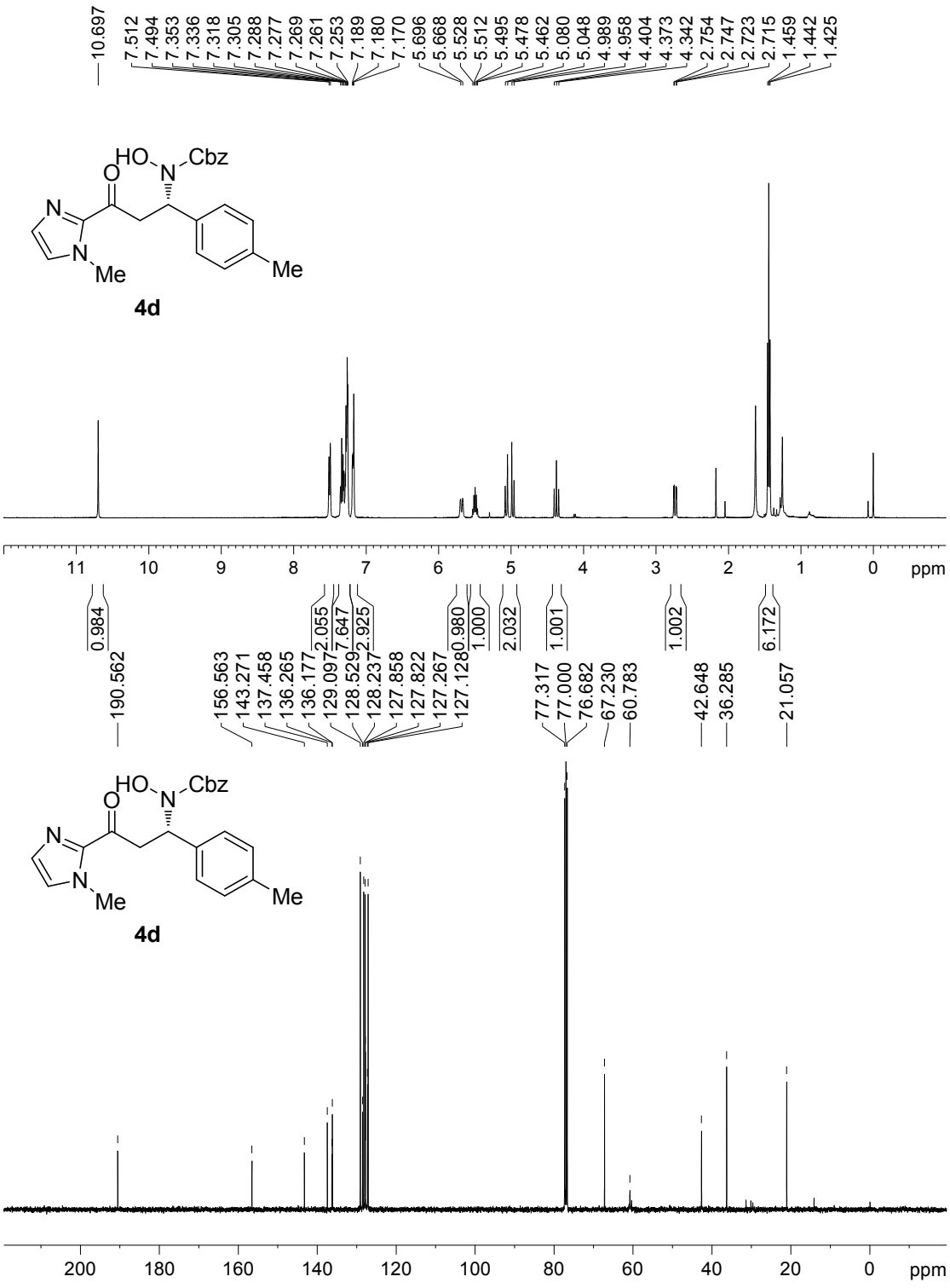
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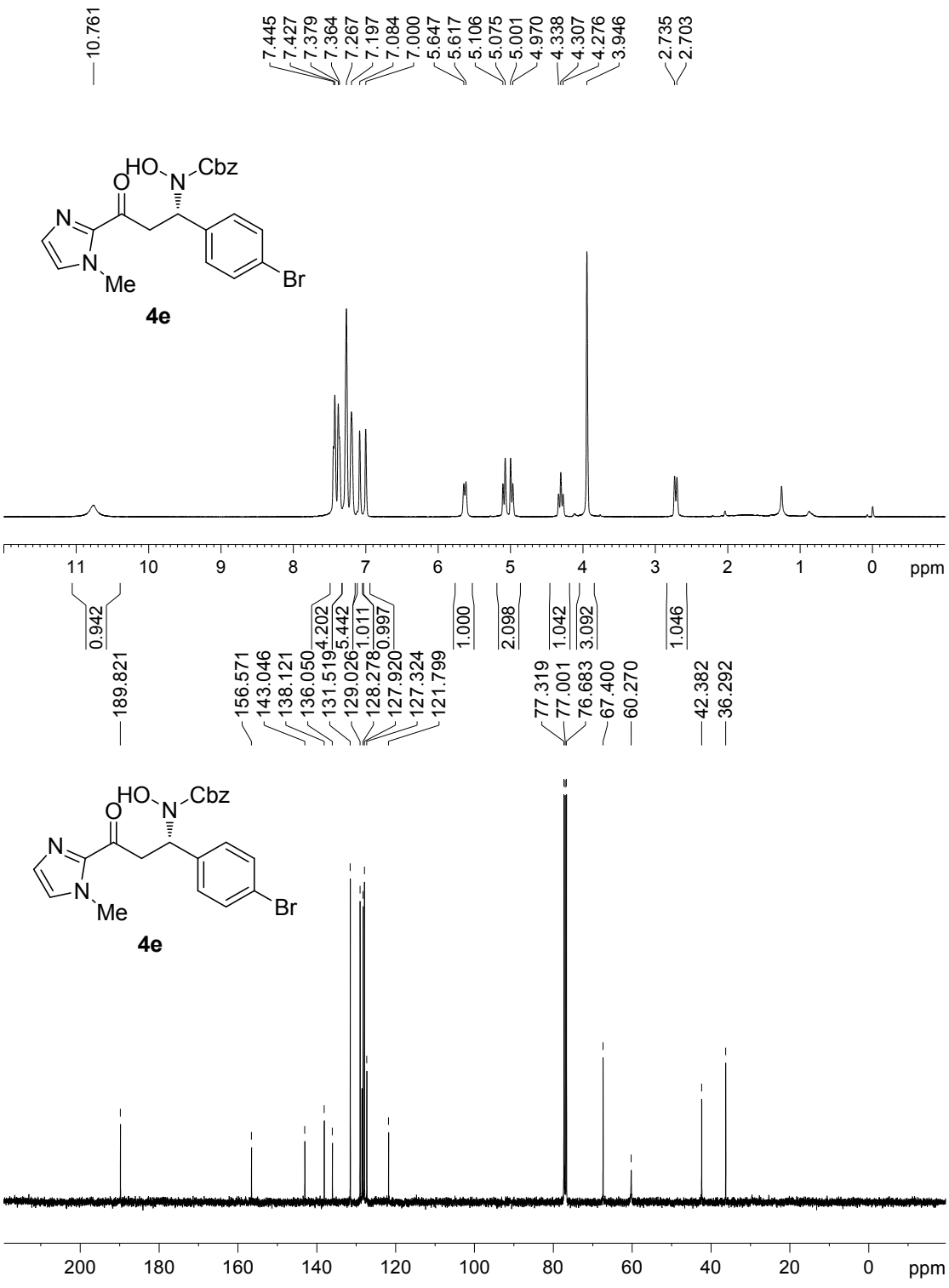
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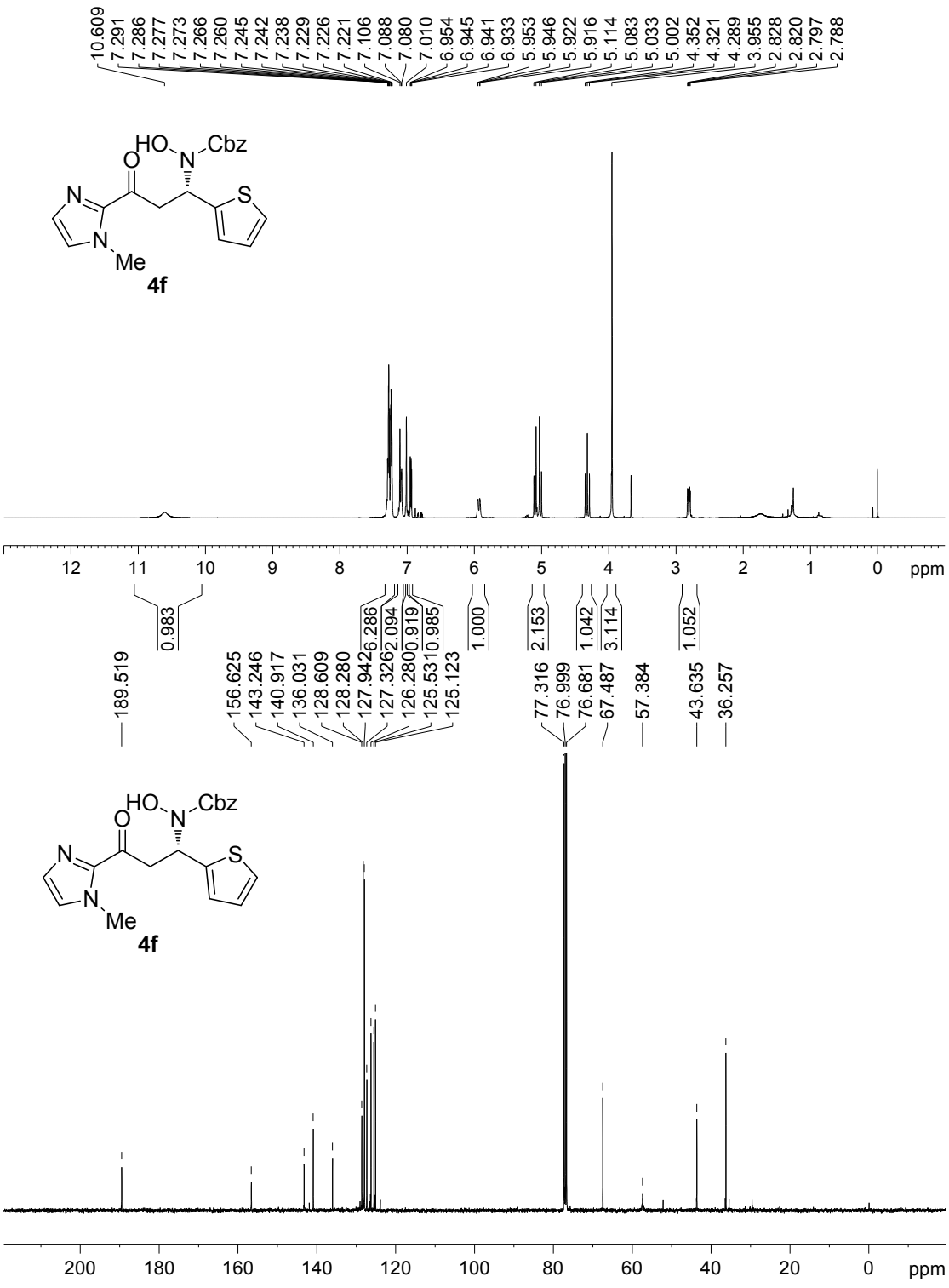
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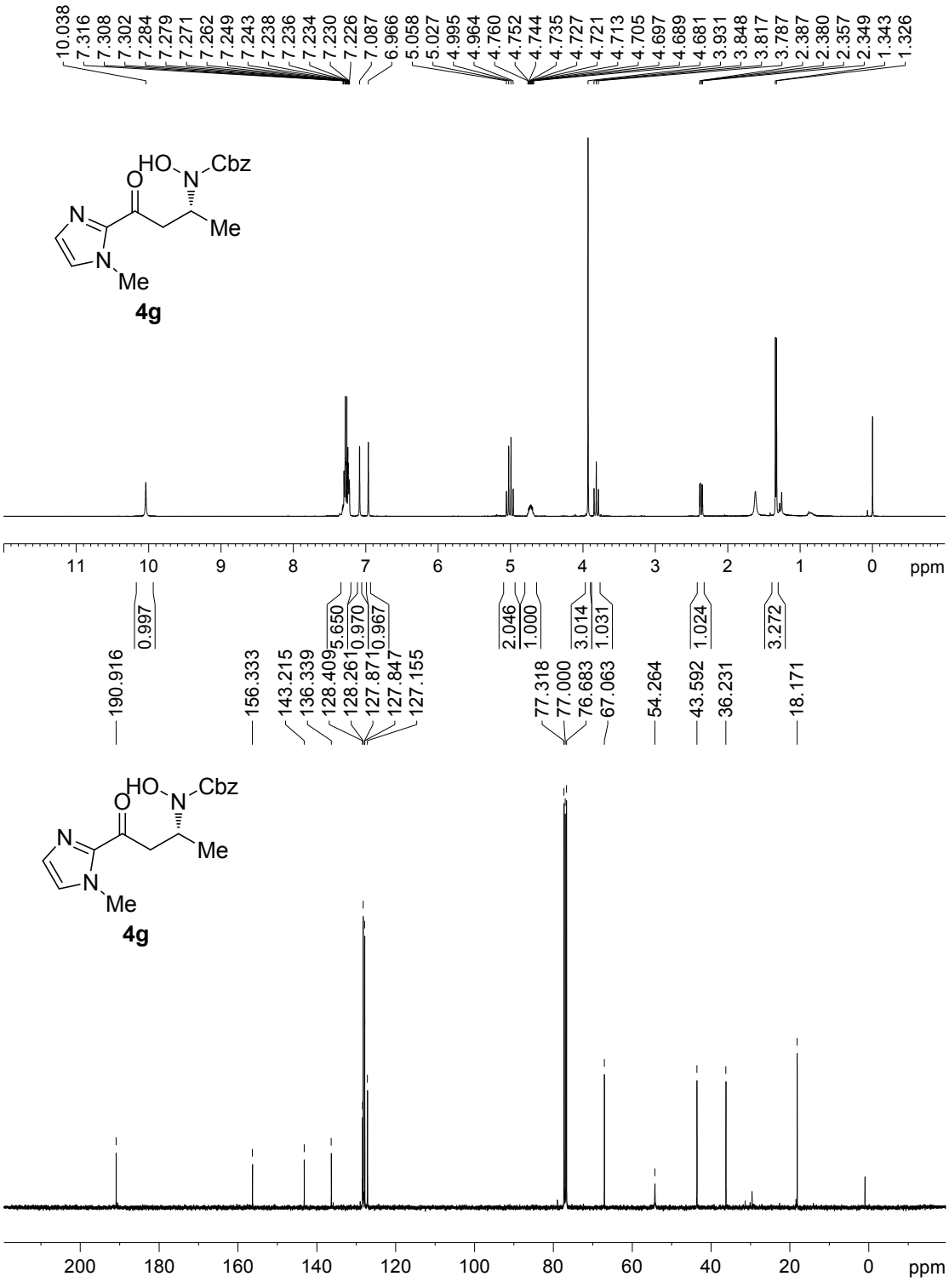
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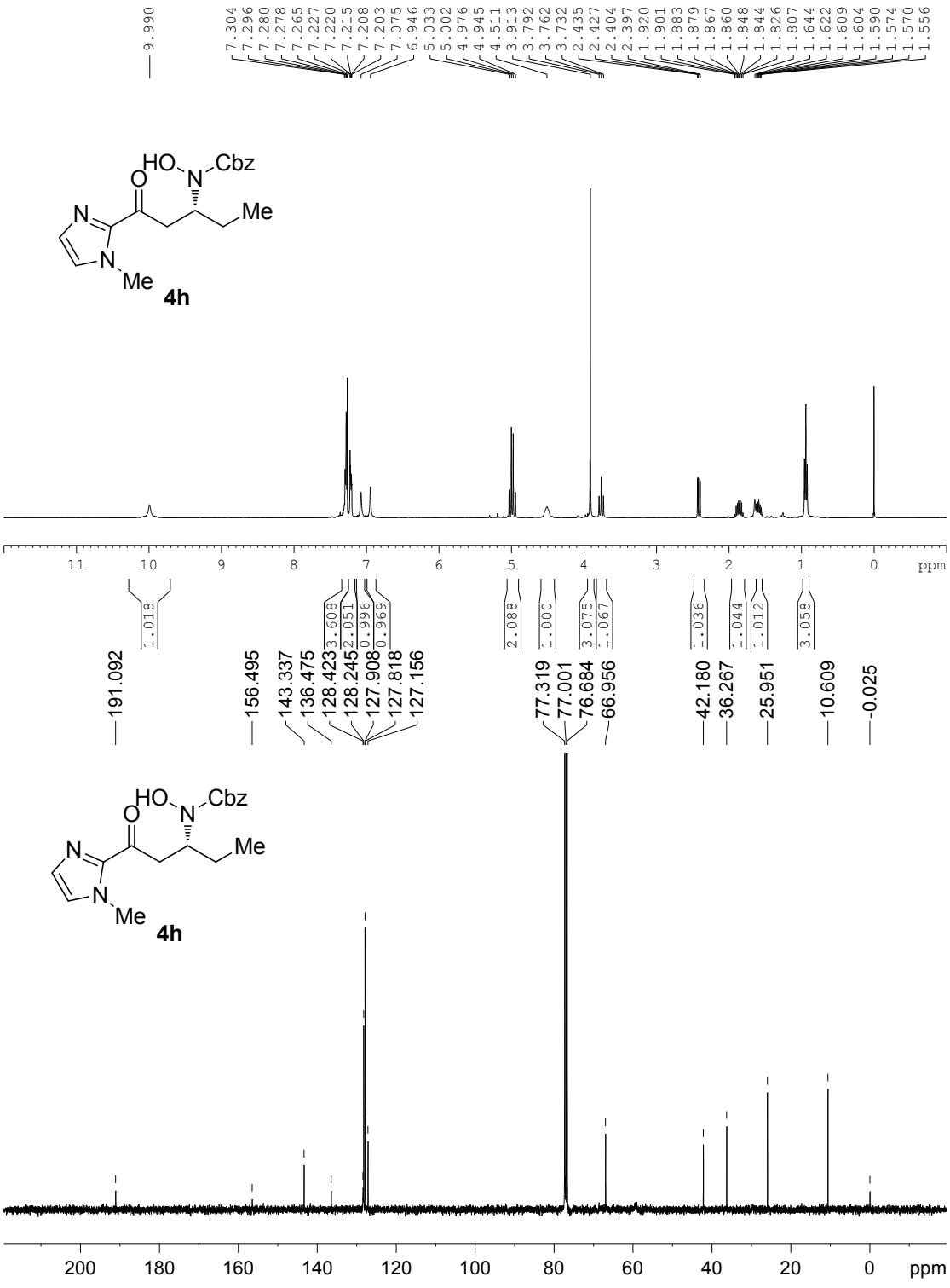
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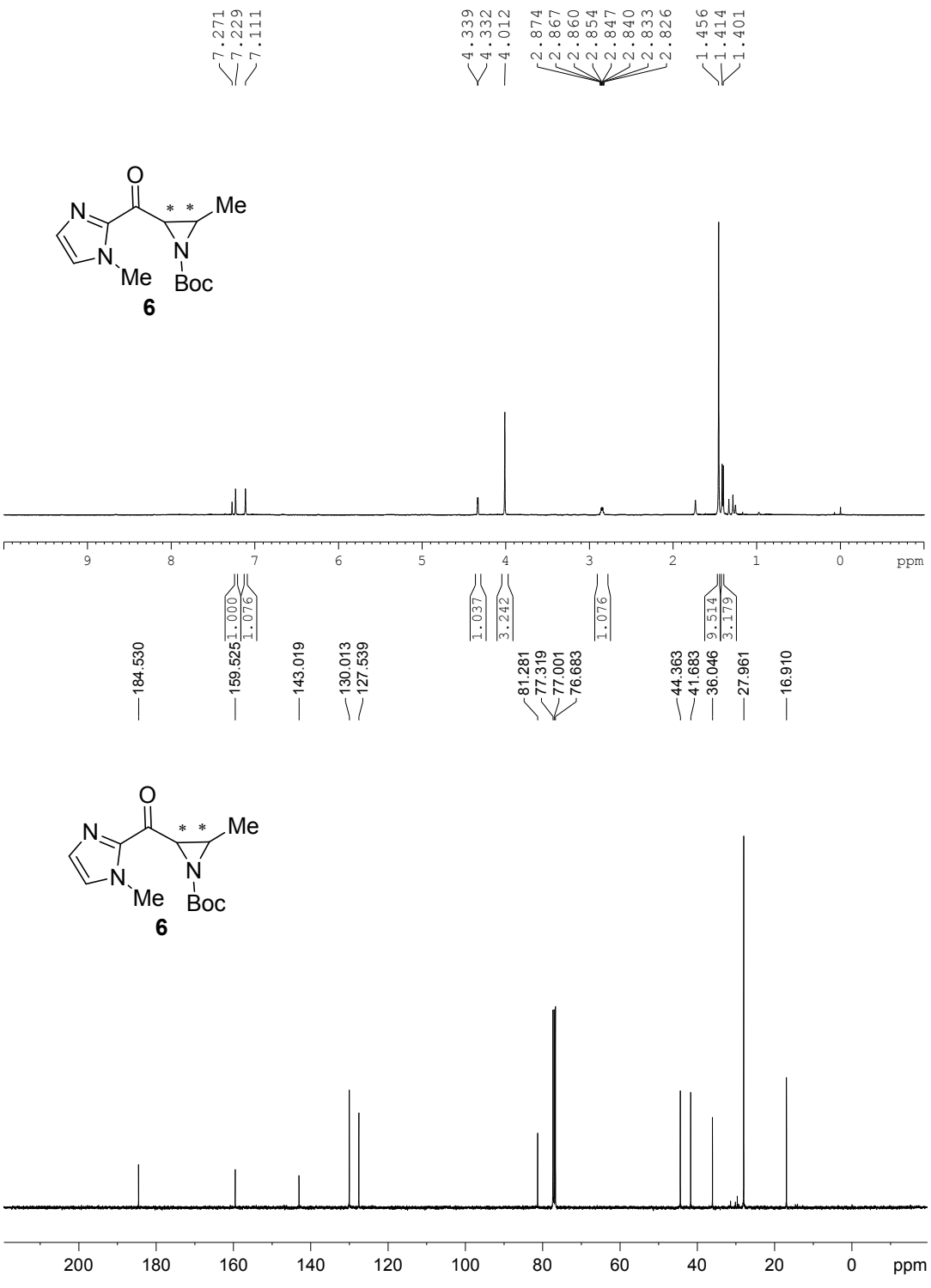
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* *
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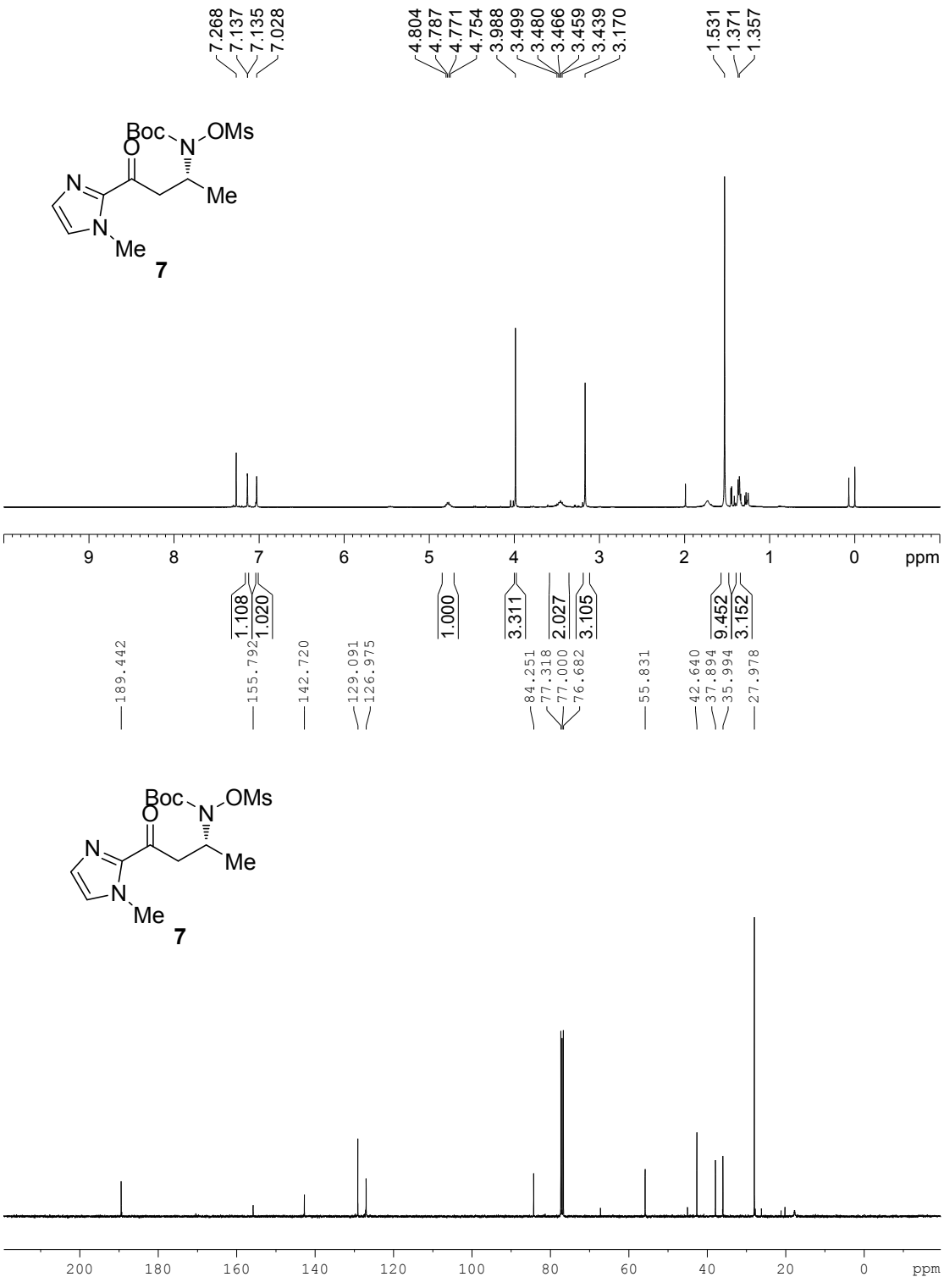
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VI Single Crystal X-Ray Diffraction of *ent*-3k.

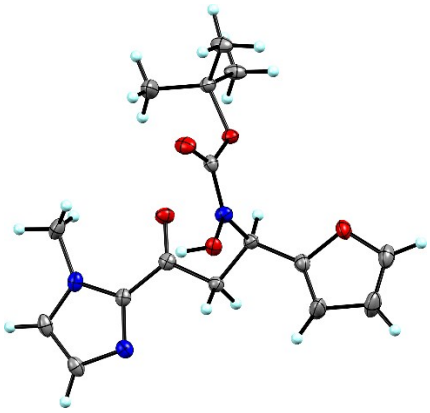

Figure S1 Crystal structure of *ent*-**3k** with thermal ellipsoids shown at the 40% probability level

Table S1. Crystal data and structure refinement for *ent*-**3k**.

Identification code	*ent*-**3k**	
Empirical formula	C16 H21 N3 O5	
Formula weight	335.36	
Temperature	100.0(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.4855(4) Å	α= 90°.
	b = 15.8870(7) Å	β= 90°.
	c = 25.5299(13) Å	γ = 90°.
Volume	3441.7(3) $Å^3$	
Z	8	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	0.812 mm^{-1}	
F(000)	1424	
Crystal size	0.150 x 0.120 x 0.040 mm^3	
Theta range for data collection	3.276 to 73.374°.	
Index ranges	-10<=h<=3, -19<=k<=19, -31<=l<=30	
Reflections collected	8887	
Independent reflections	5845 [R(int) = 0.0365]	
Completeness to theta = 67.684°	99.8 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.74145
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5845 / 0 / 443
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0804
R indices (all data)	R1 = 0.0489, wR2 = 0.0857
Absolute structure parameter	-0.06(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.190 and -0.194 e.$Å^{-3}$