

Supporting Information

Expeditious Preparation of β -*sec*-Alkyl Vicinal Amino Alcohols Used for Chiral Ligand Synthesis

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Table of Contents

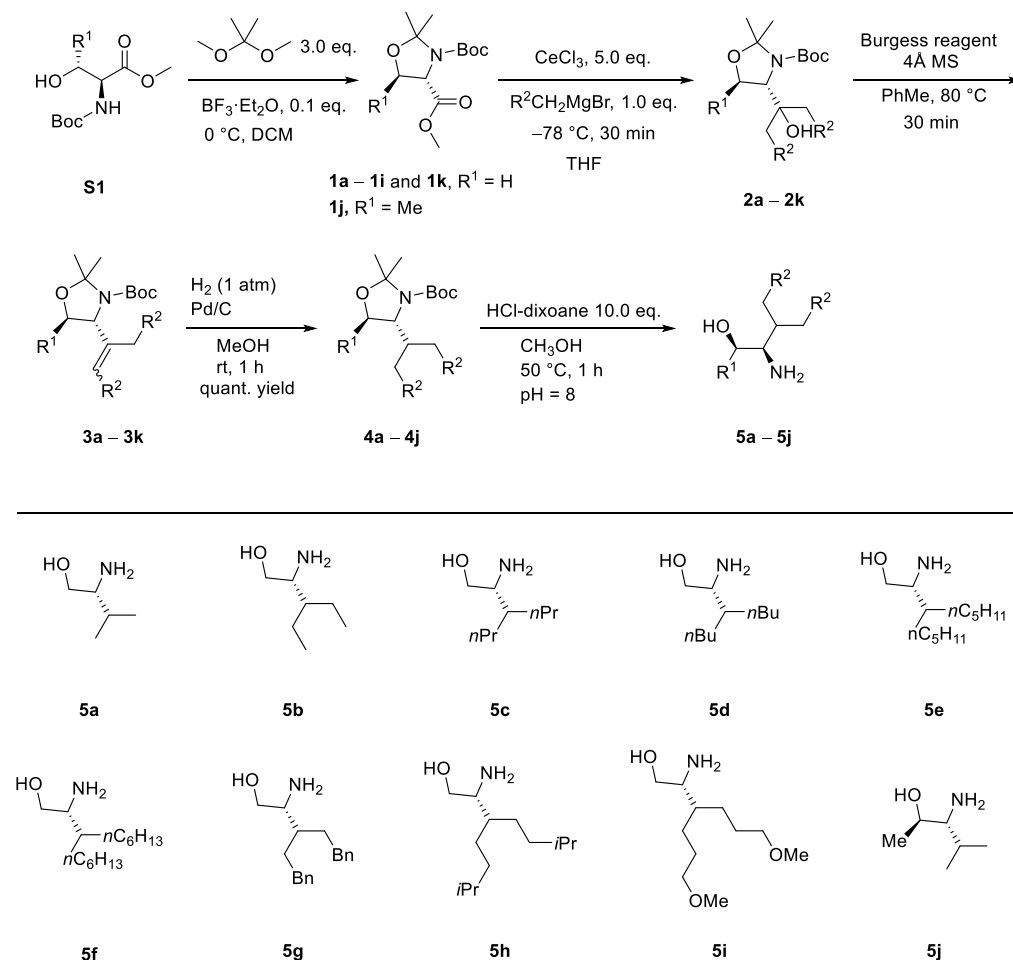
General Information	1
Synthetic Route A	2
I. Protection of the Hydroxy and <i>N</i> -Boc Amino Groups in S1	2
II. Grignard Reaction of Compound 1	3
III. Burgess Dehydration Reaction of Compound 2	6
IV. Hydrogenation of Compound 3	7
V. Deprotection of Compound 4	10
Ee and dr Determination of the Chiral Amino Alcohols	11
Synthetic Route B	25
Synthetic Route C	28
Synthesis of Ligands	31
I. Synthesis of <i>i</i> Pr-BiOx	31
II. Synthesis of (<i>R</i>)-PyOx-5d	33
III Synthesis of (<i>R,R</i>)-BiOx-5d	34
IV Application of BiOx-5d	35
Spectroscopic Data (NMR Spectra)	38
References	66

General Information

Anhydrous THF and toluene was distilled after treated with sodium/benzophenone prior to use. Anhydrous DCM was distilled after treated with calcium hydride. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Boc-L-serine methyl ester (CAS: 2766-43-0, purchased from Adamas), Burgess reagent (CAS: 29684-56-8, purchased from Adamas), MeMgBr (3.0 M solution in 2-methyl-THF, purchased from Adamas), magnesium chips (purchased from Sinopharm Chemical Reagent Co., Ltd.). All reagents and starting materials were purchased from commercial sources without further purification, except for specific instructions.

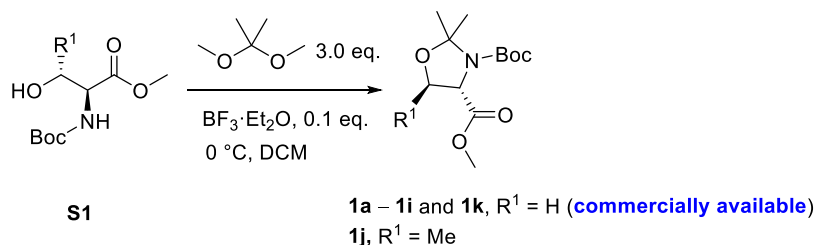
Column chromatography was performed using silica gel (Huanghai, 300-400 mesh) as the stationary phase. All NMR spectra were recorded on JEOL 400 MHz spectrometer or Bruker 600 MHz spectrometer. ^1H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. Ultra-Fast liquid chromatography was performed on Shimadzu Chromatographs using Daicel Chiralcel columns (250 mm). Optical rotations were measured on a JASCO P1030 using a 100 mm pathlength cell at 589 nm with $[\alpha]_{\text{D}}$ values reported in degrees. Mass spectrometry data were obtained from Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI⁺) mode or atmospheric pressure chemical ionization (APCI⁻) mode. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Synthetic Route A



Scheme S1 Synthetic route A and scope investigation of this pathway.

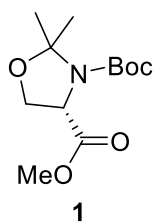
I. Protection of the Hydroxy and *N*-Boc Amino Groups in S1



General Procedure 1: The synthetic method of **1a** was reported in previous work.¹ To a solution of Boc-L-serine methyl ester (14 g, 64 mmol, 1.0 equiv.) in DCM (100 mL) were added 2,2-dimethoxypropane (20 g, 192 mmol, 3.0 equiv.) and BF₃·Et₂O (48% wt, 4.5 g, 6.4 mmol, 0.1 equiv.) at 0 °C. The color of the reaction solution changed from

light yellow to dark red. After the reaction mixture was warmed to room temperature, it was allowed to stir at 25 °C for 3 hours. After that, TLC analysis showed no remaining starting material and clean formation of a single product. The reaction was quenched with saturated NaOH aqueous solution, and the aqueous layer was extracted with two portions of ethyl acetate. The combined organic layer was washed with 10% NaCl aqueous solution, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (10% ethyl acetate in hexane).

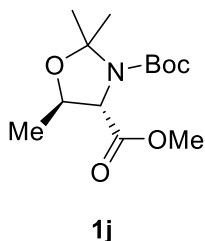
3-(*tert*-Butyl) 4-methyl (*S*)-2,2-dimethyloxazolidine-3,4-dicarboxylate (**1**).



The title compound is commercially available. It was prepared according to the **general procedure 1**. After purification by a flash column chromatography (silica gel: 10% ethyl acetate in petroleum ether), the product **1** was obtained as a pale-yellow oil (16.4 g, yield 99%).

¹H NMR (600 MHz, Chloroform-*d*) δ 4.42 (ddd, *J* = 65.1, 6.9, 2.8 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.07 – 3.99 (m, 1H), 3.74 (d, *J* = 1.5 Hz, 3H), 1.73 – 1.30 (m, 15H).

3-(*tert*-Butyl) 4-methyl (4*S*,5*R*)-2,2,5-trimethyloxazolidine-3,4-dicarboxylate (**1j**).



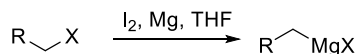
The title compound was prepared according to the **general procedure 1** using Boc-L-threonine methyl ester (2.0 g, 8.78 mmol) as the starting material. After purification by a flash column chromatography (silica gel: 10% ethyl acetate in petroleum ether), the product **1j** was obtained as a pale-yellow oil (2.3 g, yield 96%).

¹H NMR (600 MHz, Chloroform-*d*) δ 4.12 – 3.78 (m, 2H), 3.68 (s, 3H), 1.60 – 1.26 (m, 18H).

HRMS (ESI) *m/z* calcd for C₁₃H₂₄NO₅⁺ [(M+H)⁺] 274.1649, found 274.1653.

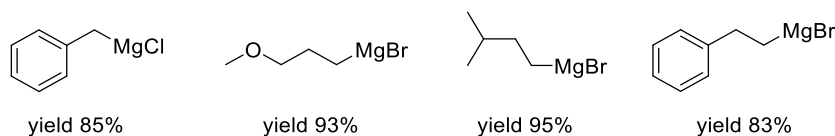
II. Grignard Reaction of Compound 1

Grignard reagent synthesis:

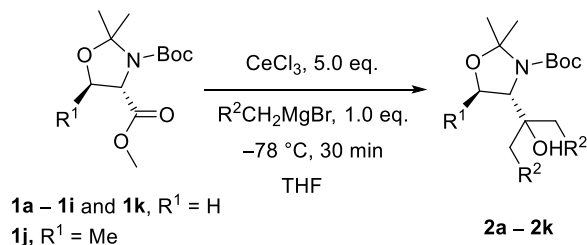


X = Cl, Br

The preparation of Grignard reagents was adapted from procedures described by Repo.² Magnesium (1.1 equiv., 2.16 g, 90 mmol) was activated by washing with 1 M HCl, then washed with water, ethanol, and ether before transferring to a flame-dried 250 mL 3-neck flask, equipped with a reflux condenser and a stir bar. The Mg was stirred under vacuum for 60 min. Under nitrogen atmosphere alkyl halide (RBr or RCl, 1 equiv., 82 mmol) was dissolved in anhydrous THF (40 mL), then 1 mL of alkyl halide solution was added and a fleck of I₂ was added, and then the stirring mixture was periodically heated to reflux with a heat gun over 2 minutes, until the brown solution turned colorless. Then the remaining alkyl halide in dry THF was added to the reaction in an addition funnel slowly over 40 minutes, while a mild reflux was maintained. After addition of alkyl halide, the reaction was stirred at 75 °C until the magnesium chips are completely consumed, then it was cooled to room temperature and titrated. Yields of some Grignard reagent was listed as shown below. The result indicated that it's easy to prepare these 1° alkyl Grignard reagents in high yields.



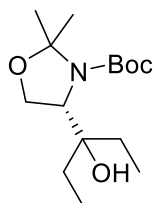
Grignard Reaction:



General Procedure 2: The synthesis of **2a – 2k** was adapted from procedure described by Ledoussal.³ A suspension of cerium (III) chloride (1.4 g, 5.8 mmol, 1.0 equiv.) in THF (80 mL) at room temperature was stirred vigorously for 2 hours. (*S*)-3-*tert*-butyl 4-methyl 2,2-dimethyloxazolidine-3,4-dicarboxylate (**1**, 1.5 g, 5.8 mmol, 1.0 equiv.) in

THF (10 mL) was then added. The suspension was cooled to $-78\text{ }^{\circ}\text{C}$ and Grignard reagent 1.0 M (29 mL, 29 mmol, 5.0 equiv.) was added dropwise. The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 minutes and then warmed to room temperature, after that GCMS analysis showed no remaining starting material and clean formation of a single product. The reaction was quenched with saturated NH_4Cl , diluted further with water and extracted twice with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered and concentrated. After column chromatography (silica gel: 5% ethyl acetate in petroleum ether) purification, the reaction afforded product **2** (yield: 87%–95%).

***tert*-Butyl (*S*)-4-(3-hydroxypentan-3-yl)-2,2-dimethyloxazolidine-3-carboxylate (2b).**



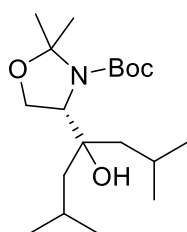
2b

The title compound was prepared according to the **general procedure 2** using **1a** (1.5 g, 5.79 mmol) as the starting material. After purification by a flash column chromatography (silica gel: 5% ethyl acetate in petroleum ether), the product **2b** was obtained as a colorless oil (1.58 g, yield 95%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 5.07 (s, 1H), 4.16 (d, $J = 7.3$ Hz, 1H), 4.00 (t, $J = 8.5$ Hz, 1H), 3.82 (d, $J = 8.5$ Hz, 1H), 1.62 – 1.33 (m, 19H), 0.91 (t, $J = 7.5$ Hz, 6H).

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{30}\text{NO}_4^+$ [(M+H) $^+$] 288.2169, found 288.2187.

***tert*-Butyl (*S*)-4-(4-hydroxy-2,6-dimethylheptan-4-yl)-2,2-dimethyloxazolidine-3-carboxylate (2k).**



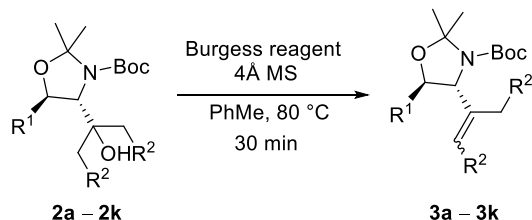
2k

The title compound was prepared according to the **general procedure 2** using **1a** (810 mg, 3.13 mmol) as the starting material. After purification by a flash column chromatography (silica gel: 5% ethyl acetate in petroleum ether), the product **2k** was obtained as a colorless oil (0.98 g, yield 91%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 5.09 (s, 1H), 4.21 (d, $J = 7.6$ Hz, 1H), 4.07 – 3.92 (m, 1H), 3.84 – 3.66 (m, 1H), 1.95 – 1.45 (m, 21H), 1.13 – 0.90 (m, 12H).

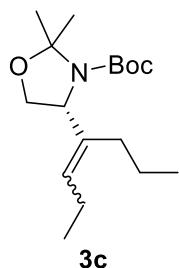
HRMS (ESI) m/z calcd for $C_{19}H_{38}NO_4^+$ [(M+H)⁺] 344.2795, found 344.2797.

III. Burgess Dehydration Reaction of Compound 2



General Procedure 3: The synthesis of **3b – 3k** was adapted from procedures described by Reissig.⁴ A 100 mL round-bottom flask charged with **2** (0.3 mmol, 1.0 equiv.), Burgess reagent (178.5 mg, 0.75 mmol, 2.5 equiv.) and 4Å molecular sieves (activated powder which had been further dried overnight at 140 °C in vacuo) was evacuated and backfilled with N₂ for three times before anhydrous toluene (10 mL) was added. The resulting mixture was heated to 80 °C and allowed to stir at this temperature for 30 min. Upon completion (detected by TLC or GCMS), the reaction solution was concentrated directly under reduced pressure. After purification by column chromatography (silica gel: 2% ethyl acetate in petroleum ether), the product **3** was isolated as a pale-yellow oil (yield: 61%–91%).

tert-Butyl (*R*)-4-(hept-3-en-4-yl)-2,2-dimethyloxazolidine-3-carboxylate (**3c**).



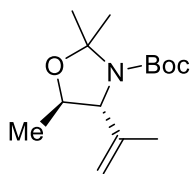
The title compound was prepared according to the **general procedure 3** using **2c** (1.73 g, 5.5 mmol) as the starting material. After purification by flash column chromatography (silica gel: 2% ethyl acetate in petroleum ether), the product **3c** was obtained as a pale-yellow oil (998 mg, yield 61%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.28 – 5.19 (m, 1H), 4.38 – 3.99 (m, 2H), 3.75 – 3.57 (m, 1H), 2.08 – 1.97 (m, 2H), 1.70 – 1.57 (m, 3H), 1.56 – 1.31 (m, 16H), 0.97 – 0.88 (m, 6H).

HRMS (ESI) m/z calcd for $C_{17}H_{32}NO_3^+$ [(M+H)⁺] 298.2377, found 298.2368.

tert-Butyl (4*R*,5*R*)-2,2,5-trimethyl-4-(prop-1-en-2-yl)oxazolidine-3-carboxylate

(3j).



3j

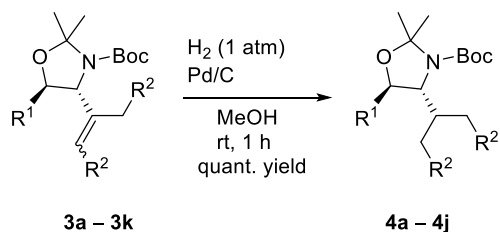
The title compound was prepared according to the **general procedure 3** using **2j** (1.3 g, 4.76 mmol) as the starting material. After purification by a flash column chromatography (silica gel: 2% ethyl acetate in petroleum ether), the product **3j** was obtained as a pale-

yellow oil (0.87 g, yield 86%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.85 (d, $J = 25.6$ Hz, 2H), 3.93 – 3.44 (m, 2H), 1.66 – 1.30 (m, 18H), 1.21 (d, $J = 5.5$ Hz, 3H).

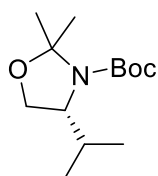
HRMS (ESI) m/z calcd for $C_{14}H_{25}NO_3Na^+$ [(M+Na)⁺] 278.1727, found 278.1742.

IV. Hydrogenation of Compound 3



General Procedure 4: The synthesis of **4a – 4j** was adapted from procedures described by Hirota.⁵ A 50 mL Schlenk flask was charged with MeOH (15 mL), Pd/C (10% Pd, 424 mg, H₂O 55%), and **3a** (500 mg, 2.0 mmol, 1.0 equiv.). The stopcock of the Schlenk flask was closed and the side arm connected to a vacuum manifold. The flask was evacuated and back-filled with a balloon of hydrogen for three times, then the mixture was stirred at room temperature until the starting materials was consumed. At the end of the reaction, the mixture was transferred to a funnel filled with Celite for filtration to remove solid impurities and the cake was washed three times with ethyl acetate. Compounds **4** were obtained after the filtrate was concentrated by vacuum (yield: 94%–99%). Most of the alkenes can be hydrogenated using Pd/C (10% Pd, 10 wt %, H₂O 55%).

***tert*-Butyl (*R*)-4-isopropyl-2,2-dimethyloxazolidine-3-carboxylate (**4a**).**



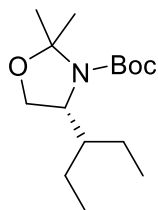
4a

The title compound was prepared according to the **general procedure 4**, using **3a** (2.0 mmol, 1.0 equiv.) as the starting material. The product **4a** was obtained as a colorless oil (0.48 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 3.87 – 3.61 (m, 3H), 2.20 – 1.97 (m, 1H), 1.62 – 1.40 (m, 15H), 0.96 – 0.81 (m, 6H).

HRMS (ESI) m/z calcd for C₁₃H₂₆NO₃⁺ [(M+H)⁺] 244.1907, found 244.1877.

***tert*-Butyl (*R*)-2,2-dimethyl-4-(pentan-3-yl)oxazolidine-3-carboxylate (**4b**).**



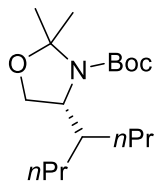
4b

The title compound was prepared according to the **general procedure 4**, using **3b** (2.0 mmol, 1.0 equiv.) as the starting material. The product **4b** was obtained as a colorless oil (0.54 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.09 – 3.70 (m, 3H), 1.85 – 1.35 (m, 20H), 0.88 (m, 6H).

HRMS (ESI) m/z calcd for C₁₅H₃₀NO₃⁺ [(M+H)⁺] 272.2220, found 272.2215.

***tert*-Butyl (*R*)-4-(heptan-4-yl)-2,2-dimethyloxazolidine-3-carboxylate (**4c**).**



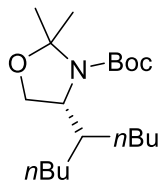
4c

The title compound was prepared according to the **general procedure 4**, using **3c** (2.0 mmol, 1.0 equiv.) as the starting material. The product was obtained as a colorless oil (0.60 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.03 – 3.72 (m, 3H), 1.96 – 1.77 (m, 1H), 1.63 – 1.22 (m, 23H), 0.86 (d, $J = 6.5$ Hz, 6H).

HRMS (ESI) m/z calcd for C₁₇H₃₄NO₃⁺ [(M+H)⁺] 300.2533, found 300.2512.

***tert*-Butyl (*R*)-2,2-dimethyl-4-(nonan-5-yl)oxazolidine-3-carboxylate (**4d**).**



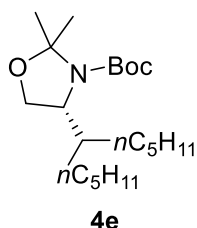
4d

The title compound was prepared according to the **general procedure 4**, using **3d** (2.0 mmol, 1.0 equiv.) as the starting material. The product **4d** was obtained as a colorless oil (0.65 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.03 – 3.74 (m, 3H), 1.95 – 1.74 (m, 1H), 1.65 – 1.12 (m, 27H), 0.85 (t, $J = 6.7$ Hz, 6H).

HRMS (ESI) m/z calcd for C₁₉H₃₈NO₃⁺ [(M+H)⁺] 328.2846, found 328.2848.

***tert*-Butyl (R)-2,2-dimethyl-4-(undecan-6-yl)oxazolidine-3-carboxylate (4e).**



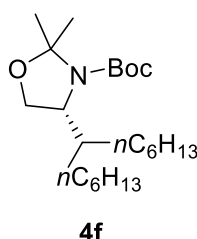
The title compound was prepared according to the **general procedure 4**, using **3e** (2.0 mmol, 1.0 equiv.) as the starting material.

The product **4e** was obtained as a colorless oil (0.67 g, 94%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.44 – 3.53 (m, 3H), 1.96 – 1.70 (m, 1H), 1.65 – 1.13 (m, 31H), 0.84 (t, *J* = 6.8 Hz, 6H).

HRMS (ESI) *m/z* calcd for C₂₁H₄₂NO₃⁺ [(M+H)⁺] 356.3159, found 356.3153.

***tert*-Butyl (R)-2,2-dimethyl-4-(tridecan-7-yl)oxazolidine-3-carboxylate (4f).**



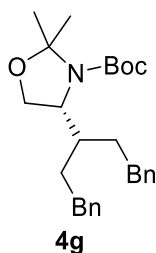
The title compound was prepared according to the **general procedure 4**, using **3f** (2.0 mmol, 1.0 equiv.) as the starting material.

The product **4f** was obtained as a colorless oil (0.73 g, 95%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.00 – 3.72 (m, 3H), 1.83 (d, *J* = 43.8 Hz, 1H), 1.65 – 1.10 (m, 35H), 0.84 (t, *J* = 6.6 Hz, 6H).

HRMS (ESI) *m/z* calcd for C₂₃H₄₆NO₃⁺ [(M+H)⁺] 384.3472, found 384.3479.

***tert*-Butyl (R)-4-(1,5-diphenylpentan-3-yl)-2,2-dimethyloxazolidine-3-carboxylate (4g).**

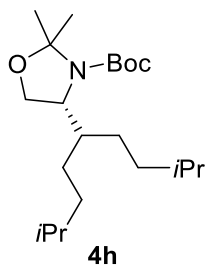


The title compound was prepared according to the **general procedure 4**, using **3g** (2.0 mmol, 1.0 equiv.) as the starting material. The product **4g** was obtained as a colorless oil (0.84 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.18 (m, 10H), 5.33 – 3.74 (m, 3H), 3.09 – 2.43 (m, 4H), 2.34 – 1.19 (m, 20H).

HRMS (ESI) *m/z* calcd for C₂₇H₃₈NO₃⁺ [(M+H)⁺] 424.2846, found 424.2848.

***tert*-Butyl (R)-4-(2,8-dimethylnonan-5-yl)-2,2-dimethyloxazolidine-3-carboxylate (4h).**



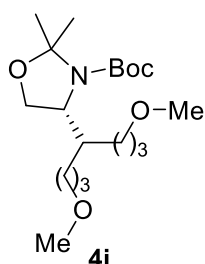
The title compound was prepared according to the **general procedure 4**, using **3h** (2.0 mmol, 1.0 equiv.) as the starting material.

The product **4h** was obtained as a colorless oil (0.70 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.06 – 3.73 (m, 3H), 1.91 – 1.67 (m, 1H), 1.64 – 0.93 (m, 25H), 0.82 (t, $J = 7.3$ Hz, 12H).

HRMS (ESI) m/z calcd for $C_{21}H_{42}NO_3^+$ [(M+H)⁺] 356.3159, found 356.3156.

***tert*-Butyl (*R*)-4-(1,7-dimethoxyheptan-4-yl)-2,2-dimethyloxazolidine-3-carboxylate (**4i**).**



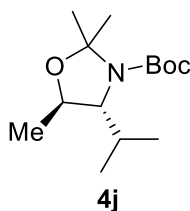
The title compound was prepared according to the **general procedure 4**, using **3i** (2.0 mmol, 1.0 equiv.) as the starting material.

The product **4i** was obtained as a colorless oil (0.71 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 3.96 – 3.72 (m, 3H), 3.38 – 3.17 (m, 10H), 1.92 – 1.73 (m, 1H), 1.70 – 1.03 (m, 23H).

HRMS (ESI) m/z calcd for $C_{19}H_{38}NO_5^+$ [(M+H)⁺] 360.2744, found 360.2726.

***tert*-Butyl (4*R*,5*R*)-4-isopropyl-2,2,5-trimethyloxazolidine-3-carboxylate (**4j**).**



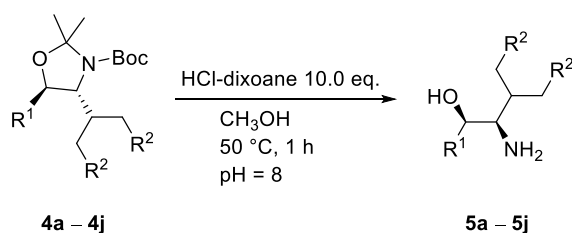
The title compound was prepared according to the **general procedure 4**, using **3j** (2.0 mmol, 1.0 equiv) as the starting material.

The product **4j** was obtained as a colorless oil (0.51 g, 99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.04 – 3.89 (m, 1H), 3.34 (d, $J = 69.2$ Hz, 1H), 2.16 (d, $J = 89.5$ Hz, 1H), 1.53 – 1.15 (m, 18H), 0.85 – 0.73 (m, 6H).

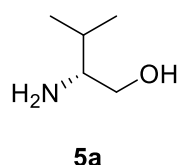
HRMS (ESI) m/z calcd for $C_{14}H_{28}NO_3^+$ [(M+H)⁺] 258.2064, found 258.2059.

V. Deprotection of Compound 4



General Procedure 5: The deprotection of **4** was adapted from procedure described by Ledoussal.³ A 50 mL Schlenk flask was charged with in MeOH (10 mL) and **4a** (2 mmol, 486 mg, 1.0 equiv.) at room temperature, 4 M HCl/dioxane (10 equiv.) was added. The reaction was stirred for 1 hour at 50 °C and the color turned light amber. After that it was cooled to room temperature and added concentrated sodium hydroxide solution to the reaction mixture until the pH = 8. The aqueous layer was extracted three times with a 3:1 mixture of CHCl₃:*i*-PrOH. The organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The crude amino alcohol was purified by column chromatography using silica gel pre-saturated with 3% Et₃N in EtOAc and eluting with 10% MeOH in DCM to obtain the product **5a** (202 mg, yield 98%).

(*R*)-2-Amino-3-methylbutan-1-ol (5a).



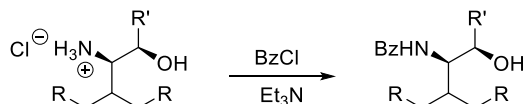
The title compound was prepared according to the **general procedure 5** using **4a** (486 mg, 2 mmol) as the starting material, and the product **5a** was obtained as a colorless oil (202 mg, yield 98%).

¹H NMR (400 MHz, Chloroform-*d*) δ 3.57 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.25 (dd, *J* = 10.6, 8.6 Hz, 1H), 2.51 (ddd, *J* = 8.5, 6.3, 3.8 Hz, 1H), 2.41 (s, 2H), 1.61 – 1.47 (m, *J* = 6.8 Hz, 1H), 0.86 (dd, *J* = 6.8, 4.2 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 64.6, 58.5, 31.2, 19.4, 18.4.

Ee and dr Determination of the Chiral Amino Alcohols

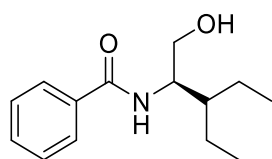
The ee or dr of the chiral amino alcohols was determined after converting them to their corresponding benzamides.



General procedure 6: The crude amino alcohol hydrochloride product was obtained by deprotection of **4** (0.3 mmol, 1.0 equiv.) according to **general procedure 5**, and it was not necessary to carry out the next purification to participate directly in the reaction. The crude amino alcohol hydrochloride was placed in a round bottom flask containing 10 ml of dichloromethane at 0 °C, and triethylamine (0.9 mmol, 3.0 equiv.) and benzoyl

chloride (0.3 mmol, 1.0 equiv.) were added in turn. After they were added into the reaction mixture dropwise, the reaction was allowed to warm to room temperature and stirred for 30 min. After completion of the reaction (monitored by TLC), it was quenched by sodium bicarbonate aqueous solution, and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography (yields over two steps: 74%–91%).

(R)-N-(3-Ethyl-1-hydroxypentan-2-yl)benzamide (6b).



6b

The title compound was prepared according to the **general procedure 5 and 6** using **4b** (81.3 mg, 0.3 mmol) as the starting material of the first step, and the product **6b** was obtained as a white solid (56.6 mg, over 2 steps: 80% yield, >99% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 1H), 4.38 – 4.05 (m, 1H), 3.93 – 3.52 (m, 2H), 1.65 – 1.52 (m, 1H), 1.51 – 1.23 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 6H).

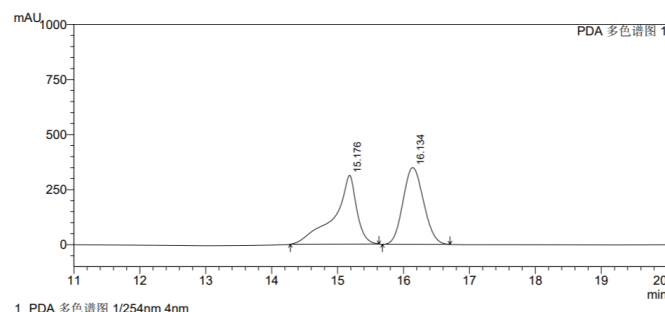
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.5, 134.6, 131.6, 128.6, 127.0, 63.8, 53.8, 41.7, 22.1, 21.8, 11.4, 11.1.

HRMS (ESI) *m/z* calcd for C₁₄H₂₂NO₂⁺ [(M+H)⁺] 236.1645, found 236.1644.

[α]_D²⁶ = +1.7 (*c* = 1, CHCl₃); >99% ee.

M.p. : 83.4 – 85.1 °C.

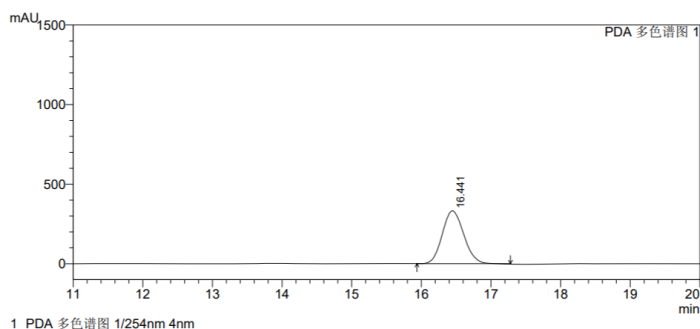
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, *t*_R (minor) = 15.2 min, *t*_R (major) = 16.1 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

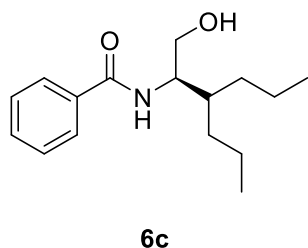
Peak#	Retention Time	Area	Height	Area %	Height %
1	15.176	7448957	312589	49.604	47.290
2	16.134	7568004	348421	50.396	52.710
总计		15016961	661010	100.000	100.000



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm					
Peak#	Resolution Time	Area	Height	Area %	Height %
1	16.441	7106185	332071	100.000	100.000
总计		7106185	332071	100.000	100.000

(R)-N-(1-Hydroxy-3-propylhexan-2-yl)benzamide (6c).



The title compound was prepared according to the **general procedure 5 and 6** using **4c** (89.7 mg, 0.3 mmol) as the starting material of the first step, and the product **6c** was obtained as a white solid (69.0 mg, over 2 steps: 87% yield, 98% ee).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 7.7$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 6.54 (d, $J = 8.5$ Hz, 1H), 4.19 – 4.13 (m, 1H), 3.71 (d, $J = 5.4$ Hz, 2H), 3.66 – 3.54 (m, 1H), 1.75 – 1.69 (m, 1H), 1.42 – 1.24 (m, 8H), 0.88 (t, $J = 6.8$ Hz, 6H).

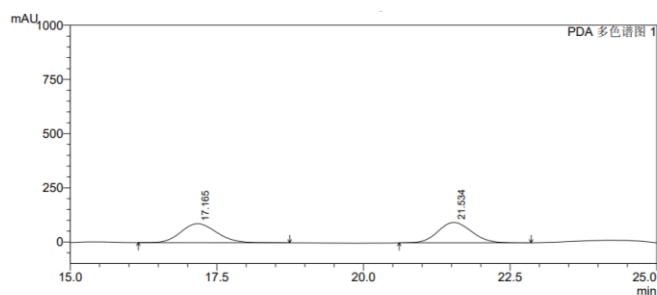
$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 168.6, 134.6, 131.6, 128.6, 127.0, 63.9, 54.4, 38.6, 32.8, 32.3, 20.4, 20.1, 14.5.

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_2^+$ [(M+H) $^+$] 264.1958, found 264.1959.

$[\alpha]_{\text{D}}^{26} = +0.3$ ($c = 1$, CHCl_3); 98% ee.

M.p. : 78.1 – 80.3 °C.

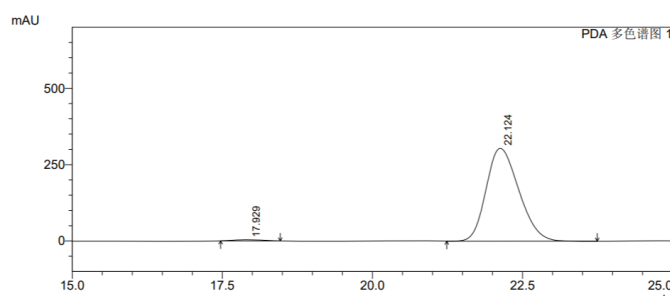
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_{R} (minor) = 17.9 min, t_{R} (major) = 22.1 min



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	17.165	3684188	87438	49.861	48.260
2	21.534	3704725	93744	50.139	51.740
总计		7388912	181182	100.000	100.000

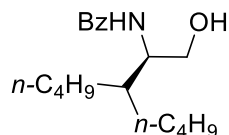


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	17.929	133974	4075	1.150	1.323
2	22.124	11516343	304024	98.850	98.677
总计		11650317	308099	100.000	100.000

(R)-N-(3-butyl-1-hydroxyheptan-2-yl)benzamide (6d).



6d

The title compound was prepared according to the **general procedure 5** and **6** using **4d** (98.1 mg, 0.3 mmol) as the starting material of the first step, and the product **6d** was obtained as a white solid (79.4 mg, over 2 steps: 91% yield, 97% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 7.5$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 1H), 4.19 – 4.12 (m, 1H), 3.71 (d, $J = 5.0$ Hz, 2H), 1.88 – 1.64 (m, 1H), 1.58 – 1.13 (m, 12H), 0.87 (q, $J = 6.9$ Hz, 6H).

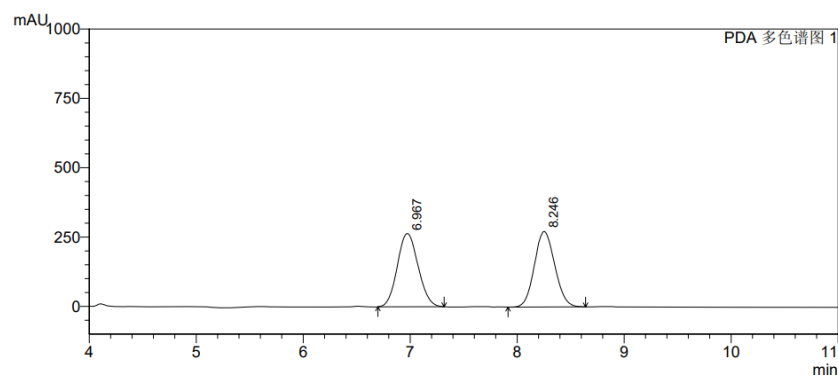
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.6, 134.6, 131.5, 128.6, 127.0, 63.8, 54.4, 38.9, 30.1, 29.7, 29.4, 29.0, 23.1, 14.1.

HRMS (ESI) m/z calcd for $C_{18}H_{30}NO_2^+$ [(M+H)⁺] 292.2271, found 292.2273.

$[\alpha]_D^{26} = +0.22$ ($c = 1$, CHCl_3); 97% ee.

M.p. : 101 – 102 °C.

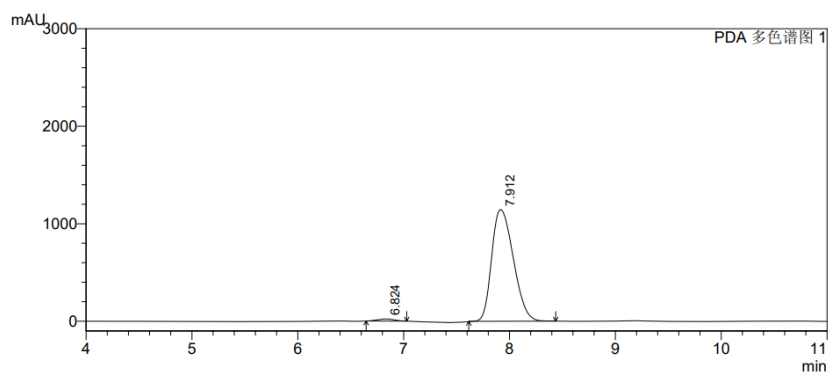
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 6.8 min, t_R (major) = 7.9 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	6.967	3569062	264333	49.752	49.248
2	8.246	3604583	272400	50.248	50.752
总计		7173645	536733	100.000	100.000

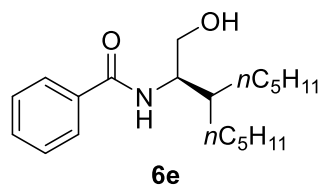


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	6.824	250171	21933	1.511	1.877
2	7.912	16309696	1146566	98.489	98.123
总计		16559867	1168499	100.000	100.000

(R)-N-(1-Hydroxy-3-pentyl octan-2-yl)benzamide (6e).



The title compound was prepared according to the **general procedure 5 and 6** using **4e** (106.5 mg, 0.3 mmol) as the starting material of the first step, and the product **6e** was obtained as a white solid (81.6 mg, over 2 steps: 85% yield,

96% ee).

^1H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 7.7$ Hz, 2H), 7.43 (t, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 2H), 6.61 (d, $J = 8.5$ Hz, 1H), 4.22 – 4.12 (m, 1H), 3.71 (d, $J = 5.1$ Hz, 2H), 1.69 (s, 1H), 1.35 – 1.19 (m, 16H), 0.88 – 0.83 (m, 6H).

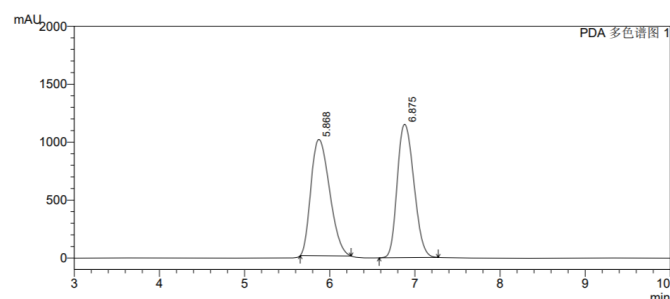
^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 134.6, 131.5, 128.6, 127.1, 63.8, 54.4, 38.9, 32.3, 30.3, 29.9, 26.9, 26.5, 22.7, 14.1.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{34}\text{NO}_2^+$ [(M+H) $^+$] 320.2584, found 320.2585.

$[\alpha]_{\text{D}}^{26} = +0.9$ ($c = 1$, CHCl_3); 97% ee.

M.p. : 89.2 – 90.6 °C.

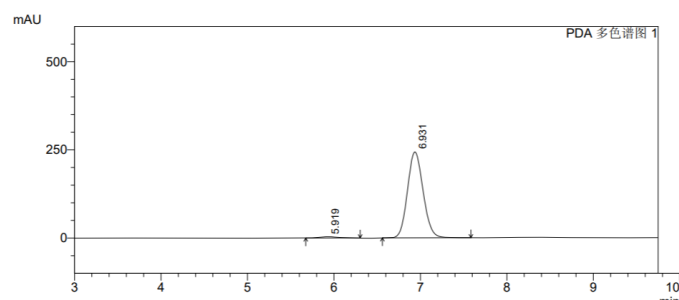
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_{R} (minor) = 5.9 min, t_{R} (major) = 6.9 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.868	15380682	1003260	49.521	46.551
2	6.875	15678302	1151939	50.479	53.449
总计		31058984	2155198	100.000	100.000

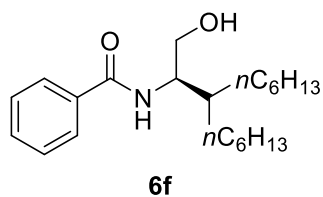


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.919	50018	3431	1.611	1.389
2	6.931	3054622	243582	98.389	98.611
总计		3104641	247013	100.000	100.000

(*R*)-*N*-(3-Hexyl-1-hydroxynonan-2-yl)benzamide (6f).



The title compound was prepared according to the **general procedure 5** and **6** using **4f** (115 mg, 0.3 mmol) as the starting material of the first step, and the product **6f** was obtained as a white solid (88.0 mg, over 2 steps: 85% yield,

96% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 6.32 (d, $J = 3.6$ Hz, 1H), 4.29 – 4.13 (m, 1H), 3.94 – 3.66 (m, 2H), 1.69 (d, $J = 5.6$ Hz, 1H), 1.54 – 1.13 (m, 20H), 1.02 – 0.78 (m, 6H).

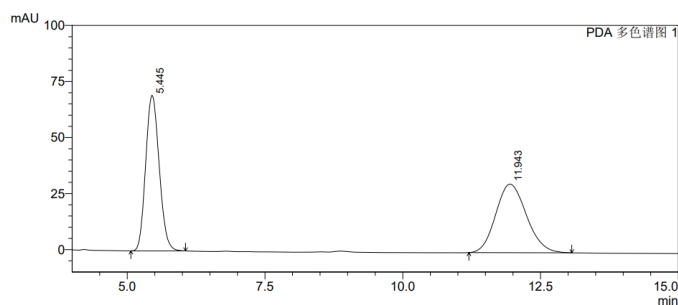
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.8, 134.6, 131.8, 128.8, 127.1, 64.8, 54.8, 39.3, 31.9, 30.6, 30.1, 29.8, 29.8, 27.4, 27.0, 22.8, 22.8, 14.2.

HRMS (ESI) m/z calcd for $C_{22}H_{38}NO_2^+$ [(M+H)⁺] 348.2897, found 348.2896.

$[\alpha]_D^{26} = +2.5$ ($c = 1$, $CHCl_3$); 96% ee.

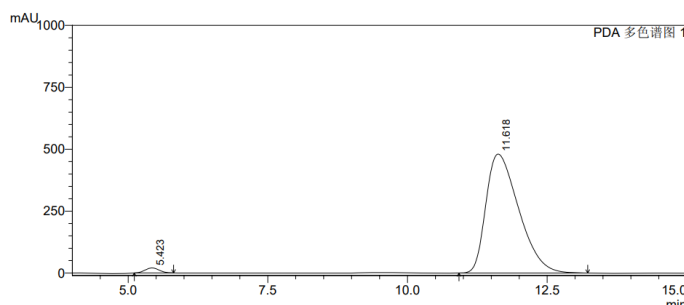
M.p. : 65.9 – 67.8 °C.

HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 5.4 min, t_R (major) = 11.6 min.



Ch1 254nm 4nm

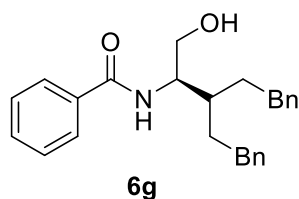
Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.445	1184974	69425	50.008	69.416
2	11.943	1184611	30588	49.992	30.584
总计		2369586	100013	100.000	100.000



Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.423	354445	20214	1.774	4.037
2	11.618	19619997	480492	98.226	95.963
总计		19974442	500707	100.000	100.000

(R)-N-(1-Hydroxy-3-phenethyl-5-phenylpentan-2-yl)benzamide (6g).



The title compound was prepared according to the **general procedure 5 and 6** using **4g** (127 mg, 0.3 mmol) as the starting material of the first step, and the product **6g** was obtained as a white solid (88.0 mg, over 2 steps: 76% yield,

89% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, $J = 7.7$ Hz, 2H), 7.58 – 7.06 (m, 13H), 6.45 (d, $J = 8.6$ Hz, 1H), 4.46 – 4.23 (m, 1H), 3.74 (d, $J = 5.0$ Hz, 2H), 2.96 – 2.51 (m, 4H), 1.92 – 1.57 (m, 5H).

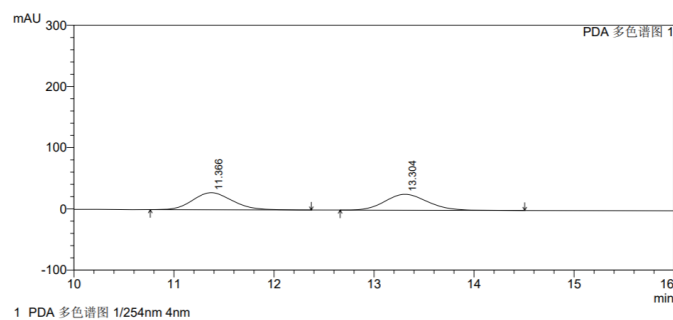
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.6, 142.2, 142.2, 134.4, 131.7, 128.6, 128.5, 128.5, 128.5, 127.0, 126.0, 63.6, 53.8, 38.1, 33.3, 33.2, 32.5, 32.1.

HRMS (ESI) m/z calcd for $C_{26}H_{30}NO_2^+$ [(M+H)⁺] 388.2271, found 388.2269.

$[\alpha]_D^{26} = +0.2$ ($c = 1$, $CHCl_3$); 89% ee.

M.p. : 108.5 – 110.3 °C.

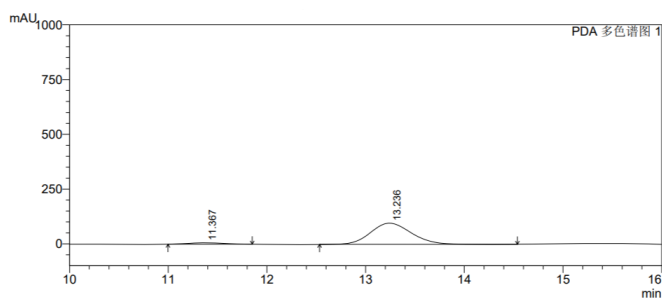
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 11.4 min, t_R (major) = 13.2 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	11.366	767044	27899	49.904	51.790
2	13.304	770007	25970	50.096	48.210
总计		1537051	53869	100.000	100.000

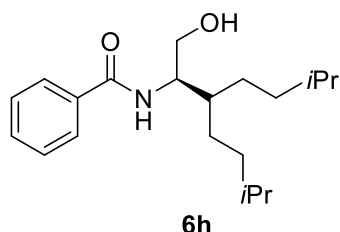


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	11.367	157833	6401	5.379	6.216
2	13.236	2776242	96574	94.621	93.784
总计		2934075	102976	100.000	100.000

(R)-N-(1-Hydroxy-3-isopentyl-6-methylheptan-2-yl)benzamide (6h).



The title compound was prepared according to the **general procedure 5 and 6** using **4h** (106.5 mg, 0.3 mmol) as the starting material of the first step, and the product **6h** was obtained as a white solid (71 mg, over 2 steps: 74% yield, 96% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 7.6$ Hz, 2H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 2H), 6.59 (d, $J = 8.4$ Hz, 1H), 4.16 (t, $J = 6.7$ Hz, 1H), 3.72 (d, $J = 4.7$ Hz, 2H), 1.71 – 1.63 (m, 1H), 1.49 – 1.15 (m, 10H), 0.88 – 0.82 (m, 12H).

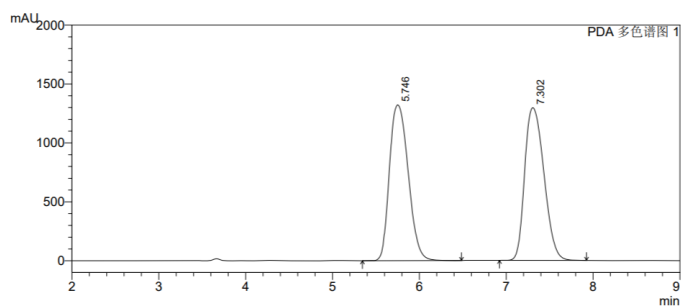
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.6, 134.6, 131.5, 128.6, 127.0, 63.8, 54.4, 39.2, 36.3, 35.89, 28.4, 27.9, 27.5, 22.8, 22.5.

HRMS (ESI) m/z calcd for $C_{20}H_{34}NO_2^+$ [(M+H)⁺] 320.2584, found 320.2576.

$[\alpha]_D^{26} = +1.8$ ($c = 1$, $CHCl_3$); 96% ee.

M.p. : 68.1 – 75.4 °C.

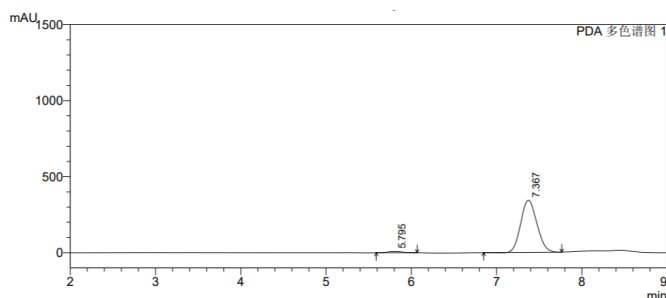
HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 5.8 min, t_R (major) = 7.4 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.746	19867272	1322594	49.873	50.516
2	7.302	19968294	1295587	50.127	49.484
总计		39835566	2618181	100.000	100.000

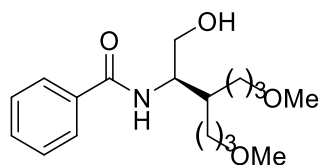


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	5.795	93543	7540	2.032	2.153
2	7.367	4510655	342678	97.968	97.847
总计		4604198	350217	100.000	100.000

(R)-N-(1-Hydroxy-6-methoxy-3-(3-methoxypropyl)hexan-2-yl)benzamide (6i).



6i

The title compound was prepared according to the **general procedure 5** and **6** using **4i** (107.7 mg, 0.3 mmol) as the starting material of the first step, and the product **6i** was obtained as a white solid (85.5 mg, over 2 steps: 88% yield, >99% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, $J = 7.7$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 4.14 – 4.07 (m, 1H), 3.70 – 3.64 (m, 2H), 3.35 – 3.27 (m, 4H), 3.23 (d, $J = 2.9$ Hz, 6H), 1.74 – 1.31 (m, 9H).

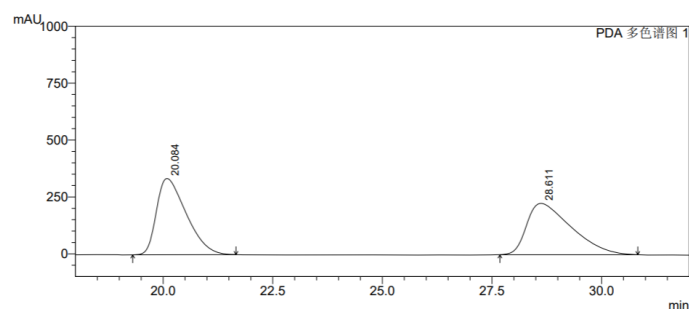
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.3, 134.5, 131.4, 128.4, 127.0, 72.8, 72.7, 63.1, 58.4, 58.4, 54.2, 38.2, 26.9, 26.7, 26.5.

HRMS (ESI) m/z calcd for $C_{18}H_{30}NO_4^+$ [(M+H)⁺] 324.2169, found 324.2169.

$[\alpha]_D^{26} = +1.9$ ($c = 1$, $CHCl_3$); >99% ee.

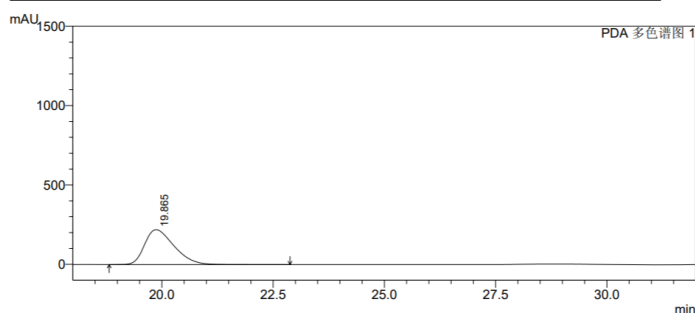
M.p. : 76.5 – 78.1 °C.

HPLC analysis CHIRALCEL IC-H column, 20% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (major) = 20.1 min, t_R (minor) = 28.6 min.



Ch1 254nm 4nm

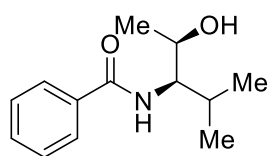
Peak#	Retention Time	Area	Height	Area %	Height %
1	20.084	15805228	335061	49.817	59.750
2	28.611	15921573	225712	50.183	40.250
总计		31726801	560773	100.000	100.000



Ch1 254nm 4nm

Peak#	Retention Time	Area	Height	Area %	Height %
1	19.865	10111291	219800	100.000	100.000
总计		10111291	219800	100.000	100.000

***N*-((2*R*,3*R*)-2-Hydroxy-4-methylpentan-3-yl)benzamide (**6j**).**



6j

The title compound was prepared according to the **general procedure 5 and 6** using **4j** (77.1 mg, 0.3 mmol) as the starting material of the first step, and the product **6j** was obtained as a white solid (59.3 mg, over 2 steps: 89% yield, dr > 99:1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, $J = 7.7$ Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 6.70 (dd, $J = 10.2, 5.5$ Hz, 1H), 4.15 – 4.09 (m, 1H), 3.67 (t, $J = 10.4$ Hz, 1H), 3.18 – 3.00 (m, 1H), 2.01 – 1.92 (m, 1H), 1.17 (d, $J = 6.4$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 3H).

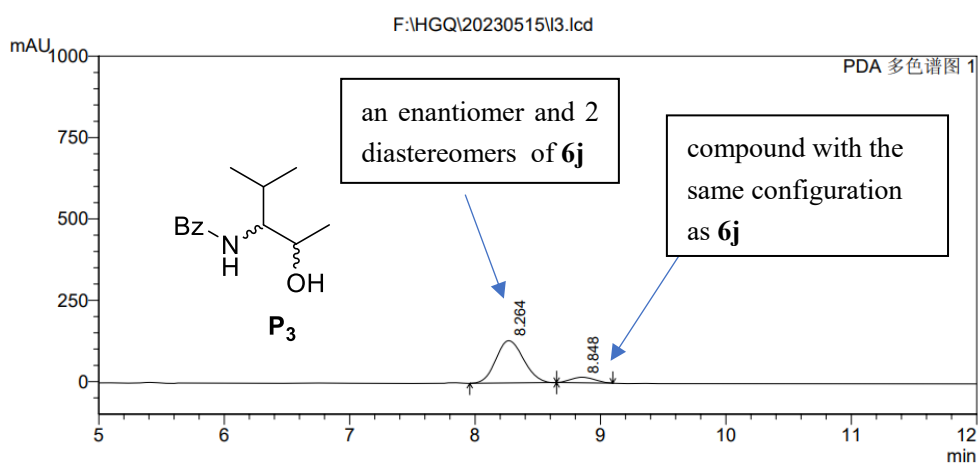
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.5, 168.5, 134.6, 131.5, 128.5, 127.0, 66.4, 60.5, 60.5, 30.2, 21.4, 19.9, 19.6.

HRMS (ESI) m/z calcd for $C_{13}H_{20}NO_2^+$ [(M+H)⁺] 222.1489, found 222.1480.

$[\alpha]_D^{26} = +4.5$ ($c = 1$, CHCl_3); $\text{dr} > 99:1$.

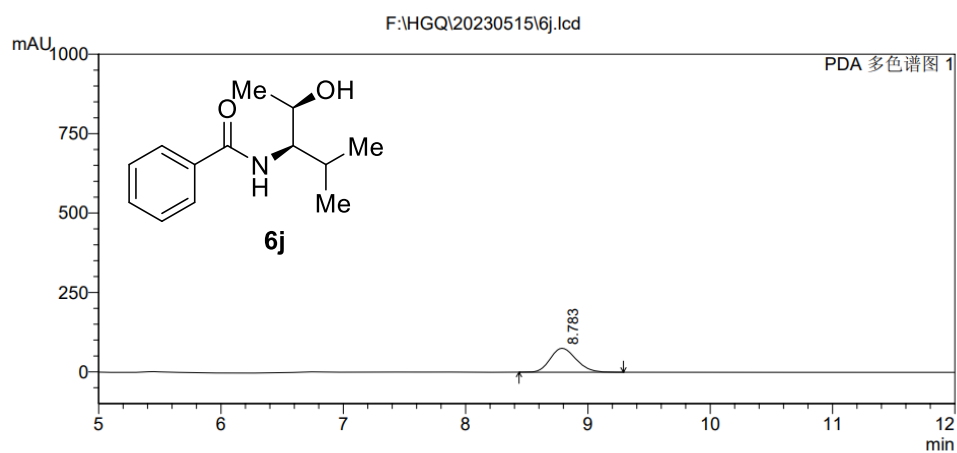
M.p. : 118.7 – 119.5 °C.

HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (diastereomer and enantiomer) = 8.3 min, t_R (**6j**) = 8.8 min.



Ch1 254nm 4nm

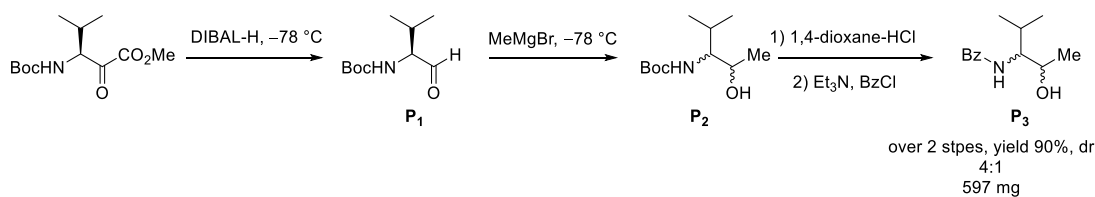
Peak#	Resolution Time	Area	Height	Area %	Height %
1	8.264	1990615	130119	89.808	88.271
2	8.848	225910	17290	10.192	11.729
总计		2216526	147408	100.000	100.000



Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	8.783	1100620	75282	100.000	100.000
总计		1100620	75282	100.000	100.000

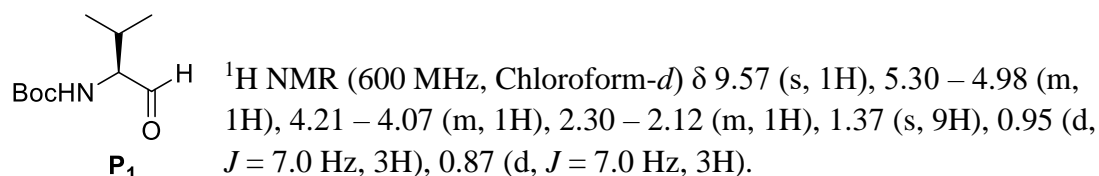
Synthesis of the reference compound for **6j:**



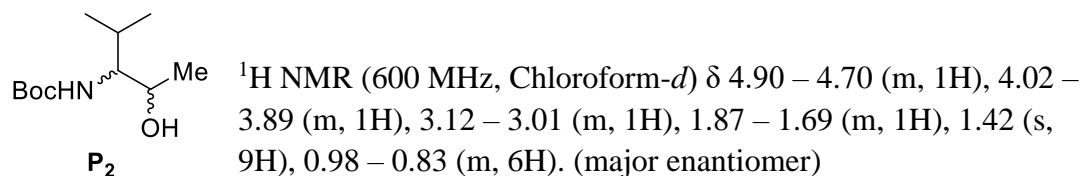
Scheme S2 Preparation of reference compound **P₃**.

Reference compound **P₃** was prepared through 4 steps: 1. DIBAL-H reduction;⁶ 2. Grignard reaction;⁷ 3. Deprotection (**General Procedure 5**); 4. Amidation (**General Procedure 6**). (Scheme S2)

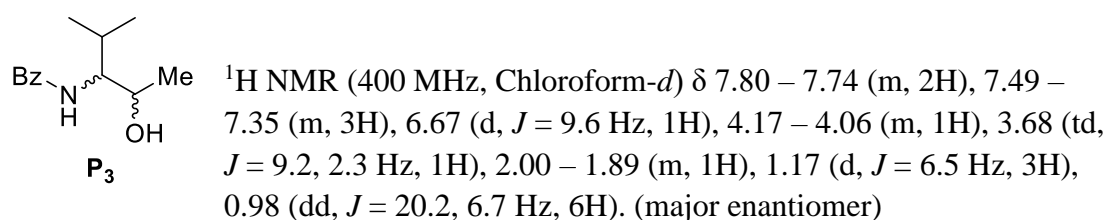
tert-Butyl (*S*)-(3-methyl-1-oxobutan-2-yl)carbamate (**P₁**).

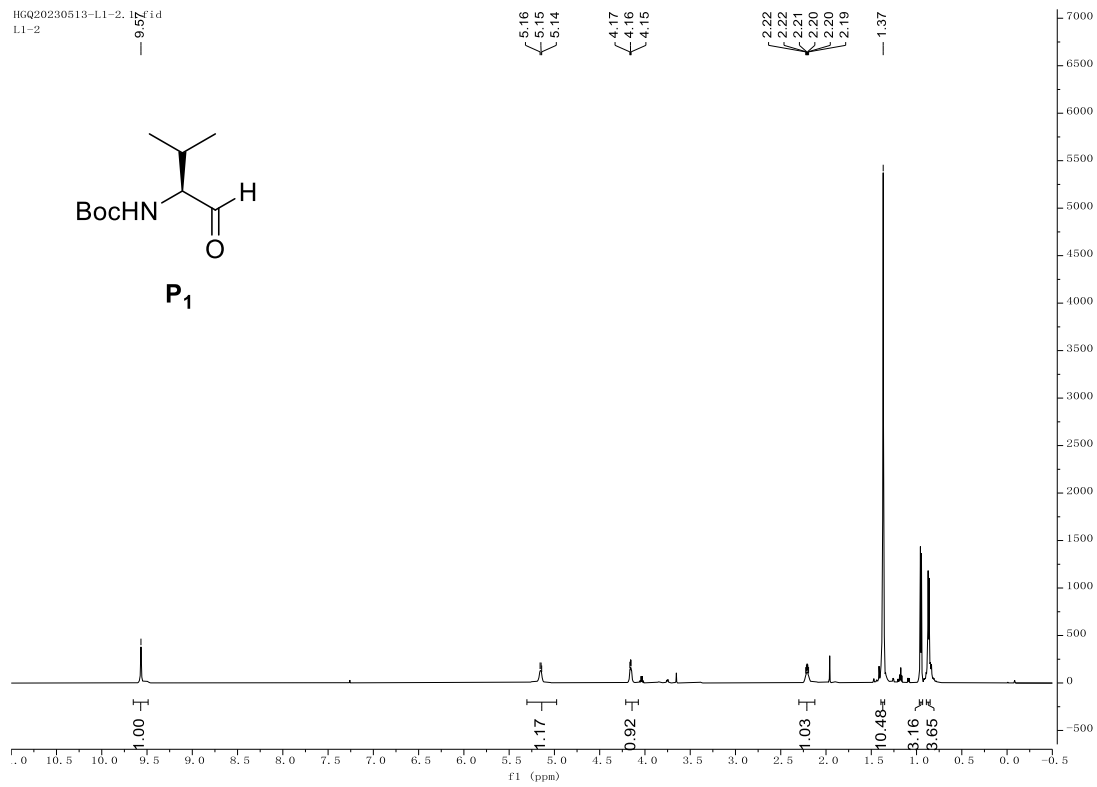


tert-Butyl (2-hydroxy-4-methylpentan-3-yl)carbamate (**P₂**).

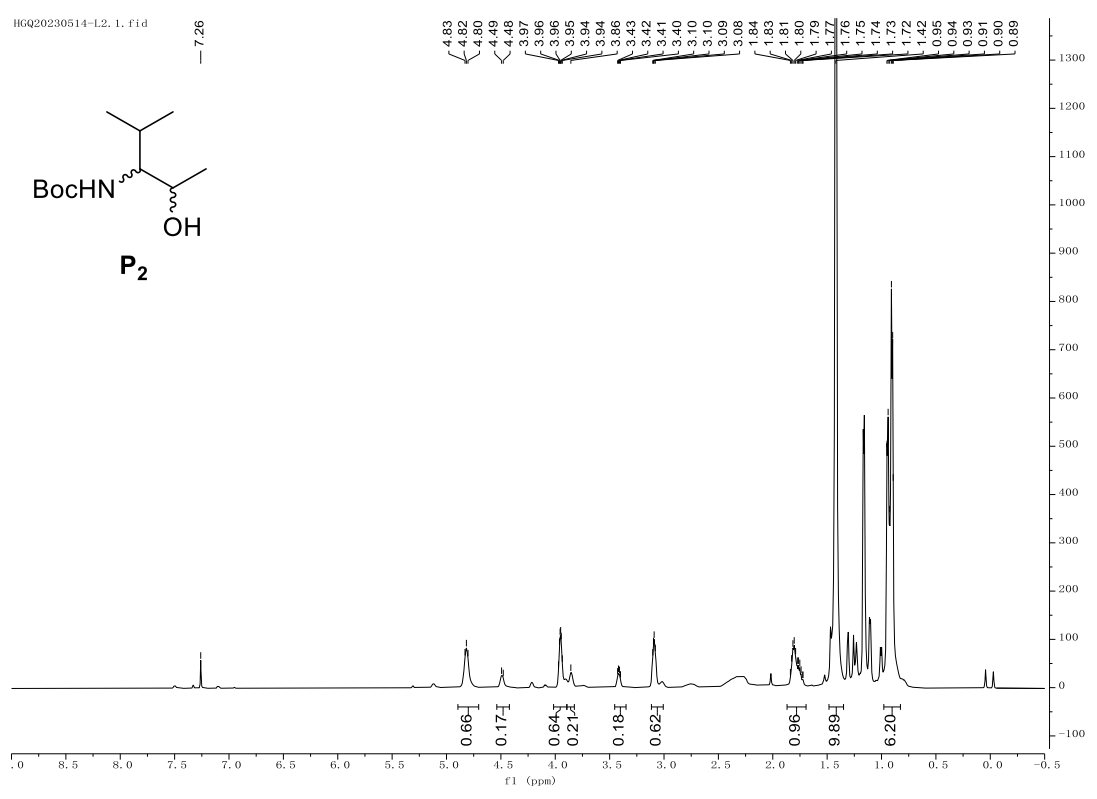


N-(2-Hydroxy-4-methylpentan-3-yl)benzamide (**P₃**).

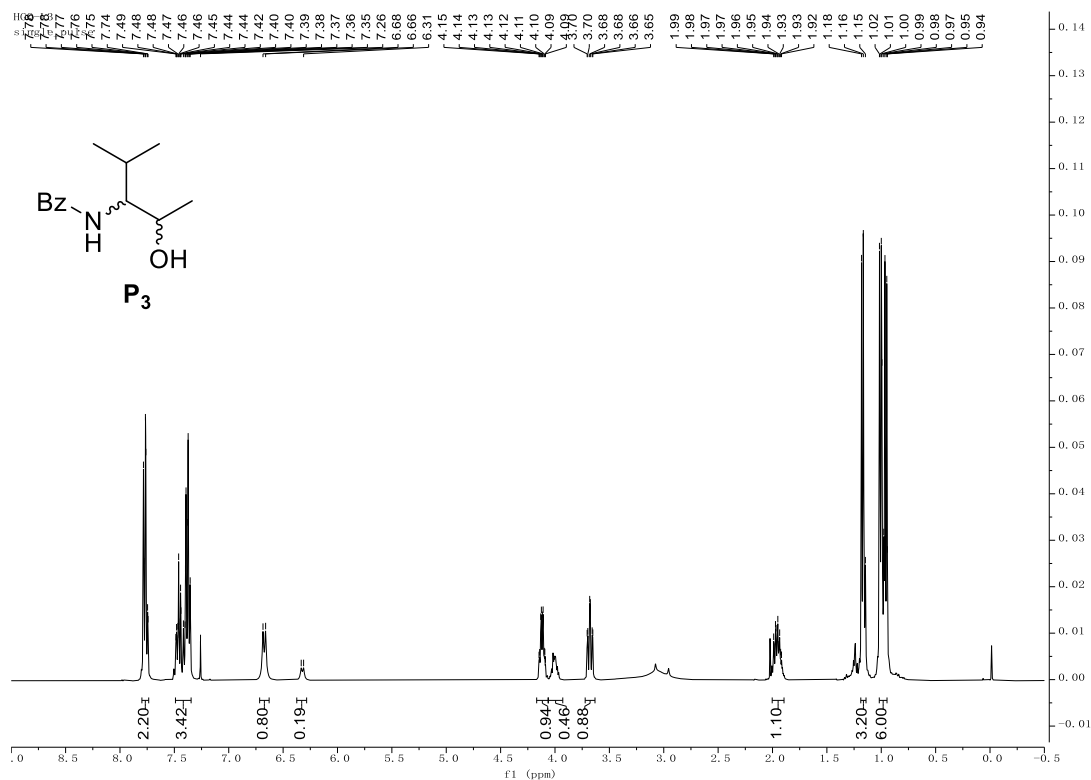




¹H NMR (600 MHz, CDCl₃) spectrum for **P₁**



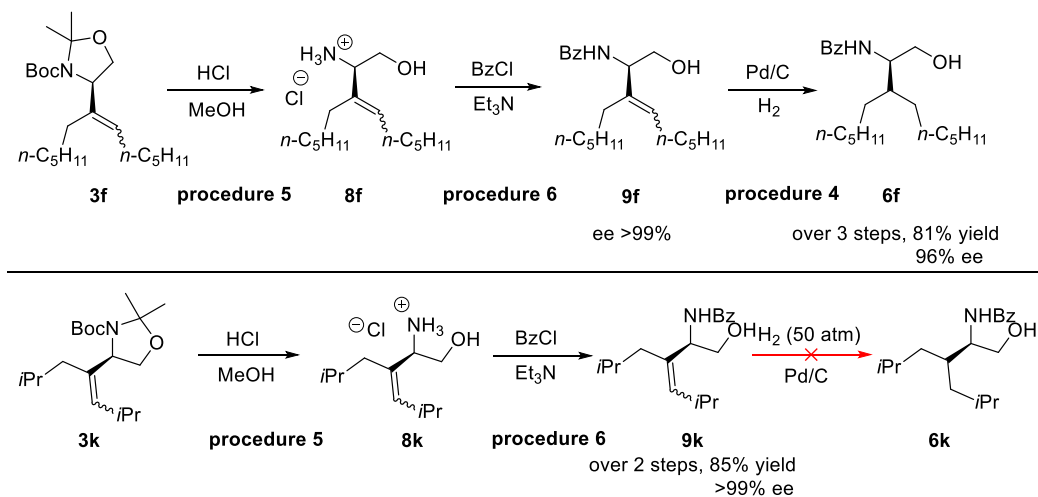
¹H NMR (600 MHz, CDCl₃) spectrum for **P₂**



^1H NMR (600 MHz, CDCl_3) spectrum for the reference compound **P3**.

Synthetic Route B

Synthetic route B to chiral amino alcohols:

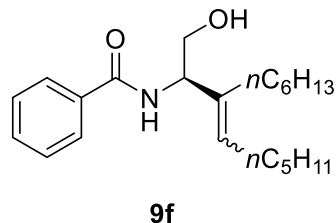


Scheme S3 Synthetic route B.

Synthetic route B used the same sub-procedure as route A (**General Procedure 4, 5** and **6**) start from compound **3**, but it used these reactions in an order of **General**

Procedure 5 to 6 to 4.

(*R*)-*N*-(3-Hexyl-1-hydroxynon-3-en-2-yl)benzamide (**9f**).



The title compound was prepared according to the **general procedure 5** and **6** using **3f** (106 mg, 0.3 mmol) as the starting material of the first step, and the product **9f** was obtained as a white solid (80.0 mg, over 2 steps: 77% yield, >99% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, $J = 7.7$ Hz, 2H), 7.53 – 7.43 (m, 1H), 7.43 – 7.34 (m, 2H), 6.69 (d, $J = 22.4$ Hz, 1H), 5.61 – 5.31 (m, 1H), 4.72 – 4.42 (m, 1H), 3.73 (t, $J = 4.3$ Hz, 2H), 2.25 – 1.90 (m, 4H), 1.60 – 1.13 (m, 14H), 0.96 – 0.76 (m, 6H).

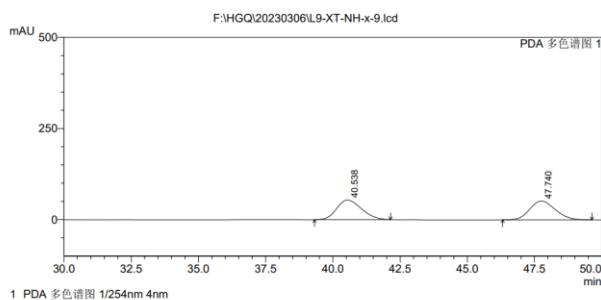
¹³C NMR (151 MHz, Chloroform-*d*) δ 167.9, 136.9, 134.4, 131.7, 128.7, 127.5, 127.1, 64.7, 56.5, 31.7, 29.9, 29.63, 29.6, 28.9, 27.8, 22.7, 22.6, 14.1, 14.1.

HRMS (ESI) m/z calcd for $C_{22}H_{36}NO_2^+$ [(M+H)⁺] 346.2741, found 346.2740.

$[\alpha]_D^{26} = +1.1$ ($c = 1$, $CHCl_3$); >99% ee.

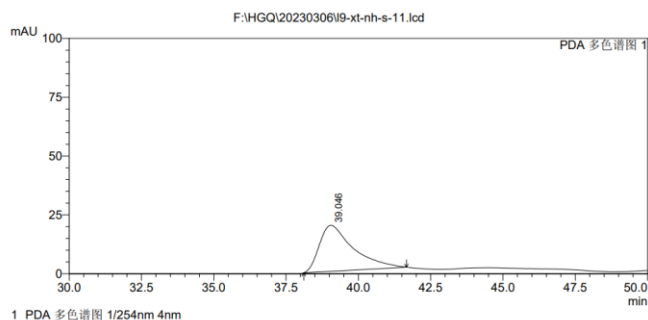
M.p. : 64.7 – 66.9 °C.

HPLC analysis CHIRALCEL OD-H column, 3% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_R (major) = 40.5 min, t_R (minor) = 47.7 min.



Ch1 254nm 4nm

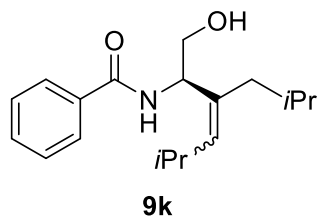
Peak#	Resolution Time	Area	Height	Area %	Height %
1	40.538	3465229	53797	50.330	51.024
2	47.740	3419783	51637	49.670	48.976
总计		6885012	105434	100.000	100.000



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm					
Peak#	Resolution Time	Area	Height	Area %	Height %
1	39.046	1596536	19577	100.000	100.000
总计		1596536	19577	100.000	100.000

(R)-N-(1-Hydroxy-3-isobutyl-5-methylhex-3-en-2-yl)benzamide (9k).



The title compound was prepared according to the **general procedure 5 and 6** using **3k** (98 mg, 0.3 mmol) as the starting material of the first step, the product **9k** was obtained as a white solid (78.3 mg, over 2 steps: 90% yield, >99% ee).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 2H), 7.49 – 7.42 (m, 1H), 7.41 – 7.33 (m, 2H), 6.74 – 6.61 (m, 1H), 5.24 (d, $J = 9.7$ Hz, 1H), 4.59 – 4.51 (m, 1H), 3.77 – 3.60 (m, 2H), 3.47 – 3.30 (m, 1H), 2.76 – 2.52 (m, 1H), 2.11 – 2.03 (m, 1H), 1.92 – 1.76 (m, 2H), 0.97 – 0.84 (m, 12H).

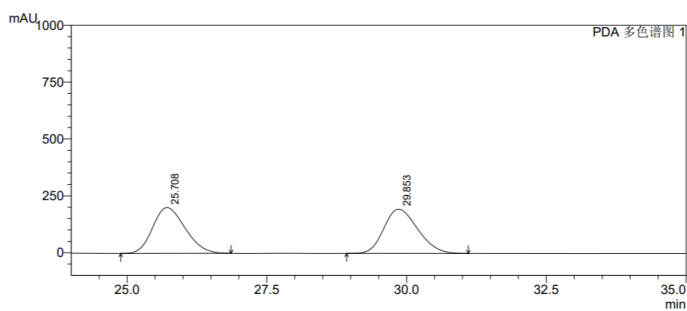
¹³C NMR (151 MHz, Chloroform-*d*) δ 168.0, 135.5, 134.4, 133.6, 131.6, 128.6, 127.0, 64.8, 55.7, 39.0, 27.2, 27.0, 23.3, 23.1, 22.8, 22.5.

HRMS (ESI) m/z calcd for $C_{18}H_{28}NO_2^+$ [(M+H)⁺] 290.2115, found 290.2117.

$[\alpha]_D^{26} = +3.6$ ($c = 1$, $CHCl_3$); > 99% ee.

M.p. : 86.6 – 88.2 °C.

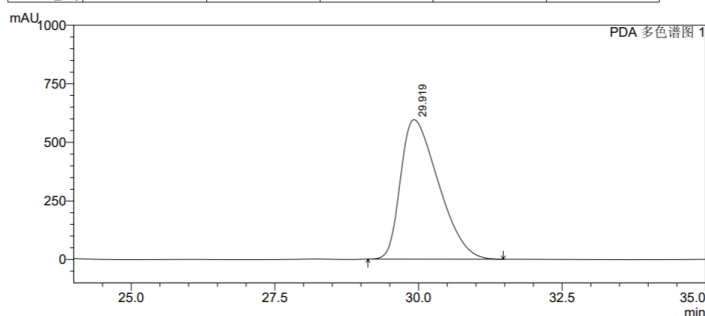
HPLC analysis CHIRALCEL OD-H column, 5% *i*PrOH in hexanes, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 25.7 min, t_R (major) = 29.8 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	25.708	8179207	201593	49.848	50.845
2	29.853	8229076	194892	50.152	49.155
总计		16408282	396485	100.000	100.000

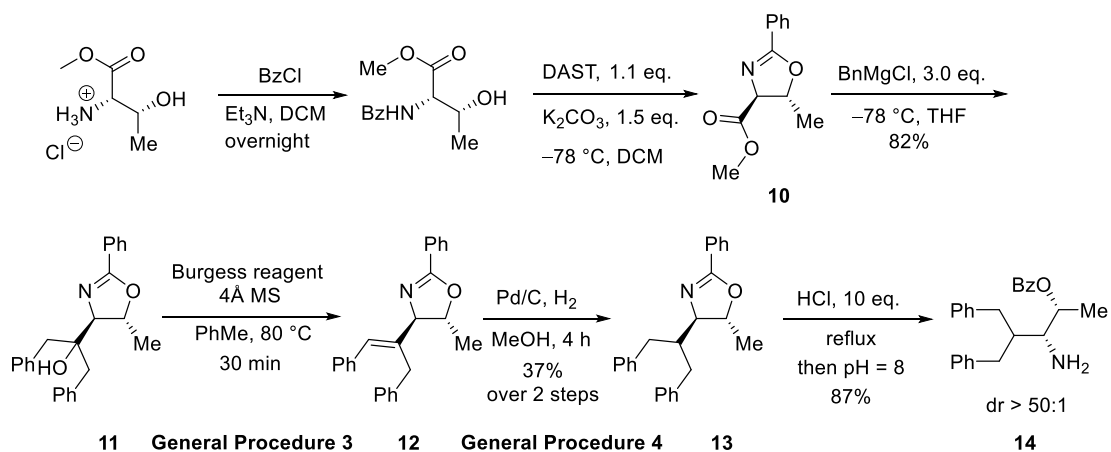


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	29.919	27311699	595136	100.000	100.000
总计		27311699	595136	100.000	100.000

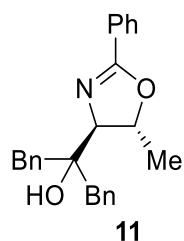
Synthetic Route C



Scheme S4 Preparation of 12.

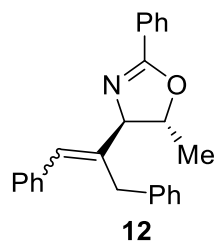
2-((4*R*,5*R*)-5-Methyl-2-phenyl-4,5-dihydrooxazol-4-yl)-1,3-diphenylpropan-2-ol (11).

A method of two-step preparation of compound **10** was reported by Pàmies.⁸ The NMR spectra of **10** and **11** have been reported by Pfaltz.⁹ **10** (1.5 g, 6.8mmol, 1.0 equiv.) was dissolved in anhydrous tetrahydrofuran (50 mL) at -78 °C. A solution of benzyl magnesium chloride (1.0 M, 20.5 mL, 20.5 mmol, 3.0 equiv.) was added slowly. After completion of the addition, the reaction mixture was slowly stirred at room temperature for 4 hours. After the raw material was completely consumed (monitored by TLC), the reaction mixture was poured into 10 mL mixture of NH_4Cl aqueous solution and ice to quench the reaction. The mixture was further diluted with water and extracted with ethyl acetate (50 mL \times 3). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel: 10% ethyl acetate/petroleum ether and 1% triethylamine), and the product **11** was obtained as a colorless oil (2.1 g, yield 82%).



$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.54 – 7.44 (m, 3H), 7.41 – 7.27 (m, 10H), 4.92 – 4.80 (m, 1H), 4.18 – 4.15 (m, 1H), 3.24 (d, $J = 13.8$ Hz, 1H), 3.16 (d, $J = 13.9$ Hz, 1H), 2.99 (d, $J = 13.8$ Hz, 1H), 2.74 (d, $J = 13.8$ Hz, 1H), 2.15 (s, 1H), 1.77 (dd, $J = 6.9, 1.1$ Hz, 3H).

(4R,5R)-4-(1,3-Diphenylprop-1-en-2-yl)-5-methyl-2-phenyl-4,5-dihydrooxazole (12).



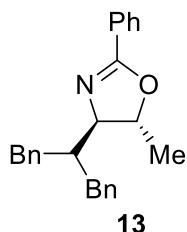
The title compound was prepared according to the **general procedure 3**, and the product **12** was obtained as a colorless oil (yield see compound **13**).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.06 – 7.90 (m, 2H), 7.53 – 7.38 (m, 3H), 7.36 – 7.09 (m, 10H), 6.22 (s, 1H), 5.44 (d, $J = 10.0$ Hz, 1H), 5.02 – 4.89 (m, 1H), 3.61 (dd, $J = 16.7, 1.8$ Hz, 1H), 3.38 (dd, $J = 16.8, 1.7$ Hz, 1H), 1.54 (d, $J = 6.7$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 164.2, 139.6, 137.6, 131.4, 130.4, 129.9, 128.4, 128.4, 128.3, 128.2, 127.9, 126.7, 126.1, 79.9, 68.8, 39.9, 16.4.

HRMS (ESI) m/z calcd for $C_{25}H_{24}NO^+$ [(M+H)⁺] 354.1852, found 354.1849.

(4*R*,5*R*)-4-(1,3-Diphenylpropan-2-yl)-5-methyl-2-phenyl-4,5-dihydrooxazole (13).



The title compound was prepared according to the **general procedure 4** using **12** (186 mg, 0.5 mmol) as the starting material, and the product **13** was obtained as a white solid (66.0 mg, over 2 steps, yield 37%).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, $J = 7.5$ Hz, 2H), 7.46 – 7.30 (m, 3H), 7.24 – 7.15 (m, 6H), 7.15 – 7.06 (m, 4H), 4.72 – 4.65

(m, 1H), 4.09 – 4.04 (m, 1H), 2.89 – 2.82 (m, 1H), 2.68 – 2.57 (m, 2H), 2.57 – 2.45 (m, 1H), 2.23 (s, 1H), 1.43 (d, $J = 6.7$ Hz, 3H).

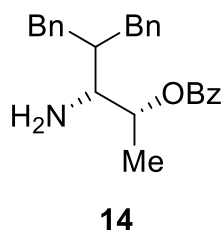
¹³C NMR (151 MHz, Chloroform-*d*) δ 163.5, 141.0, 140.7, 131.3, 129.6, 129.4, 128.5, 128.5, 128.4, 128.4, 126.1, 126.1, 79.2, 68.5, 42.6, 37.2, 36.5, 14.8.

HRMS (ESI) m/z calcd for $C_{25}H_{26}NO^+$ [(M+H)⁺] 356.2009, found 356.2005.

$[\alpha]_D^{26} = +4.1$ ($c = 1$, $CHCl_3$).

M.p. : 66.7 – 69.5 °C.

(2*R*,3*R*)-3-Amino-4-benzyl-5-phenylpentan-2-yl benzoate (14).



The title compound was prepared according to the **General procedure 5** using **13** (35.6 mg, 0.1 mmol) as the starting material, and the product **14** was obtained as a pale-yellow oil (32.5 mg, yield 87%, dr > 50:1). The diastereomeric ratio (dr) was determined based on the characteristic NMR peak of the α -H of OBz group

(5.19 ppm).

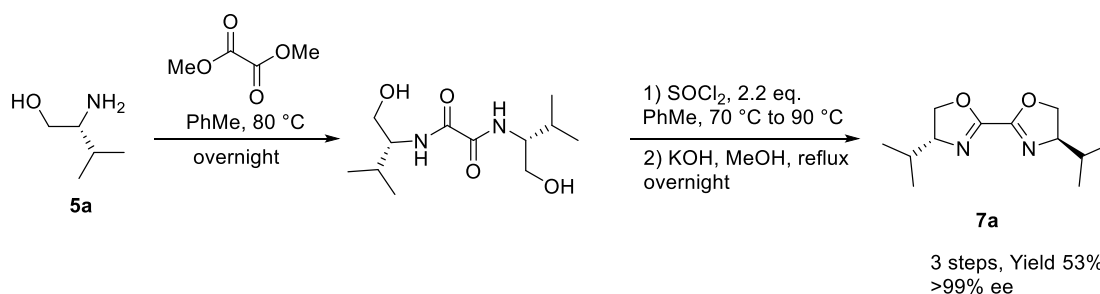
¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.60 – 7.55 (m, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.27 – 7.10 (m, 8H), 7.06 (d, $J = 7.1$ Hz, 2H), 5.28 – 5.13 (m, 1H), 2.98 (dd, $J = 13.2, 3.4$ Hz, 1H), 2.84 (dd, $J = 8.0, 2.5$ Hz, 1H), 2.73 – 2.64 (m, 1H), 2.64 – 2.53 (m, 1H), 2.42 (dd, $J = 13.2, 10.6$ Hz, 1H), 2.36 – 2.22 (m, 1H), 1.32 (d, $J = 6.2$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.0, 140.9, 133.1, 130.5, 129.7, 129.4, 129.1, 128.6, 128.5, 128.47, 126.1, 72.8, 55.4, 43.2, 36.4, 35.1, 17.6.

HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_2^+$ [(M+H)⁺] 374.2115, found 374.2110.

Synthesis of Ligands

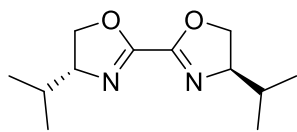
I. Synthesis of *i*Pr-BiOx



Scheme S5 Preparation of **7a**.

The synthesis of **7a** was adapted from procedures described by Reisman.¹⁰ **5a** (2 equiv., 198 mg, 1.9 mmol) and dimethyloxalate (112 mg, 0.95 mmol, 1 equiv.) were dissolved in dry PhMe (20 mL) and heated to 80 °C. The reaction was allowed to stir overnight with the diamide precipitating out of solution as a white solid. Reaction was cooled to room temperature and concentrated in vacuo to afford the crude diol as a sticky white solid. The crude diol was added PhMe (60 mL) and heated to 70 °C, whereupon thionyl chloride (249 mg, 2.1 mmol, 2.2 equiv.) was added. Reaction was stirred at 70 °C for 0.5 h then heated to 90 °C for 1.5 h. The reaction was cooled to room temperature and poured into 20% KOH solution cooled to 0 °C. The aqueous layer was separated and extracted (3 × 20 mL) with DCM and the combined organic layers were washed with 20% KOH solution, NaHCO₃ and brine. The organic layer was dried over Na₂SO₄, filtered through a pad of Celite, and concentrated in vacuo to afford the dichloride as a sticky brown solid. The crude dichloride was immediately dissolved in MeOH (9 mL) and KOH (133 mg, 2.4 mmol, 2.5 equiv.) was added. The reaction was heated to reflux for 14 hours. The reaction was cooled to room temperature and concentrated to remove MeOH. The crude mixture was loaded directly onto a silica gel column and eluted with 10–40% EtOAc/PE. The pure ligand was obtained as an off-white solid (113 mg, 53% yield over 3 steps, >99% ee).

(4*R*,4'*R*)-4,4'-Diisopropyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (7a).



7a

¹H NMR (400 MHz, Chloroform-*d*) δ 4.59 – 4.31 (m, 2H), 4.20 – 3.96 (m, 4H), 2.00 – 1.67 (m, *J* = 6.8 Hz, 2H), 0.98 (d, *J* = 6.8 Hz, 6H), 0.88 (d, *J* = 6.8 Hz, 6H).

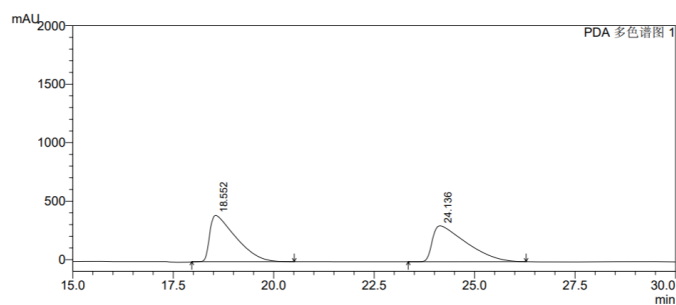
¹³C NMR (101 MHz, Chloroform-*d*) δ 154.6, 73.2, 71.1,

32.5, 19.0, 18.3.

*R*_f = 0.2 (silica gel, 20% EtOAc/PE, UV).

HPLC analysis CHIRALCEL IC-H column, 10% *i*PrOH in hexanes, 1.0 mL/min,

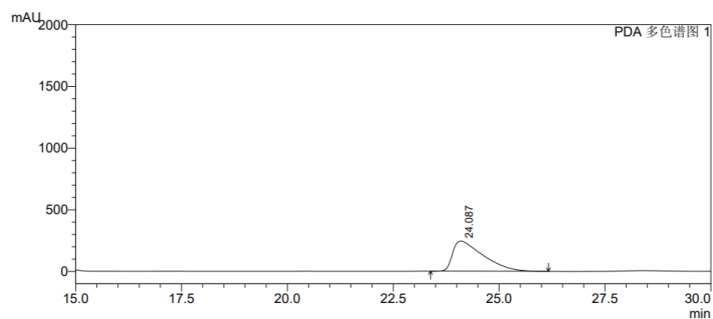
254 nm UV detector, *t*_R (minor) = 18.5 min, *t*_R (major) = 24.1 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	18.552	17686396	394250	49.724	56.212
2	24.136	17882682	307116	50.276	43.788
总计		35569079	701366	100.000	100.000

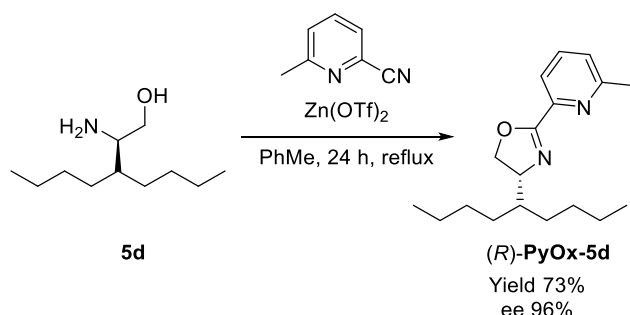


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	24.087	12138147	243023	100.000	100.000
总计		12138147	243023	100.000	100.000

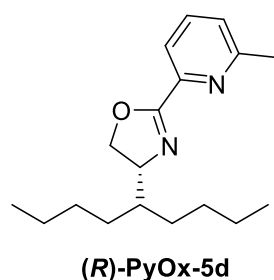
II. Synthesis of (*R*)-PyOx-5d



Scheme S6 Preparation of (*R*)-PyOx-5d.

The synthesis of (*R*)-PyOx-5d was adapted from procedures described by Huang.¹¹ The prepared amino alcohol **5d** (0.5 g, 2.6 mmol, 1.0 equiv.) was added to a mixture of 6-methylpyridine nitrile (189 mg, 1.6 mmol, 0.6 equiv.) and Zn(OTf)₂ (57 mg, 0.15 mmol, 0.06 equiv.) in toluene 20 mL. The solution was refluxed and stirred for 24 hours, and then concentrated in vacuo. The crude product was purified by column chromatography with PE/EtOAc (2/1, 1% Et₃N added) as the eluent, the target compound (*R*)-PyOx-5d was obtained as a white solid at 0 °C (562 mg, yield 73%, 96% ee).

(*R*)-2-(6-Methylpyridin-2-yl)-4-(nonan-5-yl)-4,5-dihydrooxazole ((*R*)-PyOx-5d).



(R)-PyOx-5d

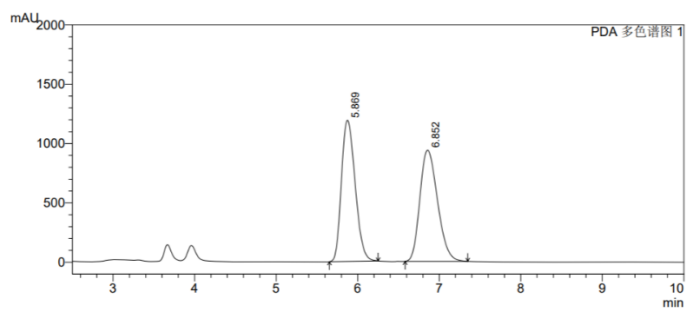
¹H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.50 (m, 1H), 7.22 – 7.12 (m, 1H), 4.53 – 4.41 (m, 1H), 4.42 – 4.34 (m, 1H), 4.28 – 4.12 (m, 1H), 2.59 (d, *J* = 3.1 Hz, 3H), 1.72 – 1.56 (m, 1H), 1.46 – 1.08 (m, 12H), 0.93 – 0.76 (m, 6H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 162.6, 158.7, 146.5, 136.7, 125.3, 121.2, 70.7, 69.7, 42.2, 30.2, 29.4, 29.3, 29.3, 24.7, 23.1, 23.1, 14.1.

HRMS (ESI) *m/z* calcd for C₁₈H₂₉N₂O⁺ [(M+H)⁺] 289.2274, found 289.2262.

[α]_D²⁶ = +4.5 (*c* = 1, CHCl₃); 96% ee.

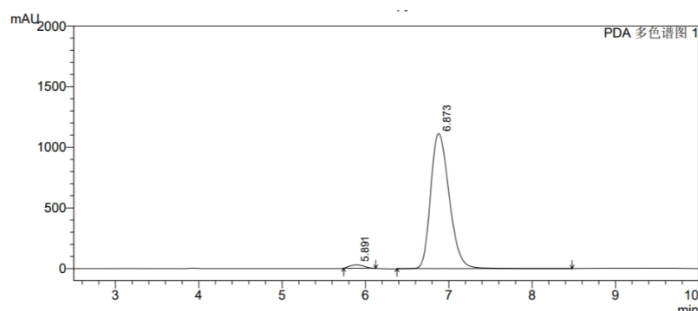
HPLC analysis CHIRALCEL OD-H column, 20% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, *t*_R (minor) = 5.9 min, *t*_R (major) = 6.9 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
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2	6.852	14111973	937978	50.420	44.081
总计		27988955	2127838	100.000	100.000

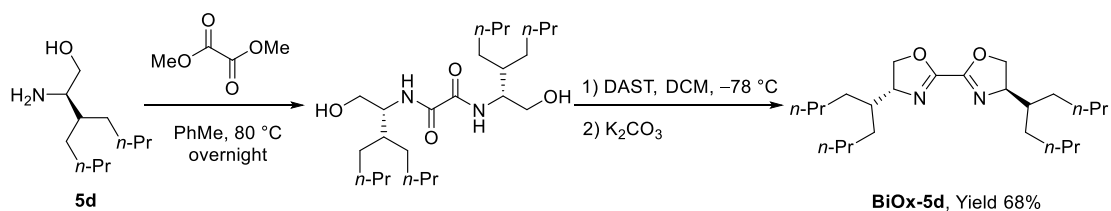


1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
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2	6.873	17232910	1112202	98.137	97.587
总计		17560008	1139709	100.000	100.000

III Synthesis of (*R,R*)-BiOx-5d

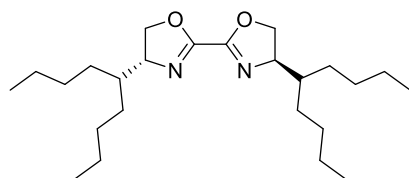


Scheme S7 Preparation of (*R,R*)-BiOx-5d.

Amino alcohol (100 mg, 0.53 mmol, 2.0 equiv.) and dimethyloxalate (31.6 mg, 0.27 mmol, 1.0 equiv.) were dissolved in PhMe (7 mL) and heated to 80 °C. After stir overnight, the reaction mixture was concentrated in vacuo to afford the crude diamide. To an oven-dried 50 mL round bottom flask crude diamide (109 mg, 0.25 mmol, 1.0 equiv.) was added under N₂ atmosphere, DCM (4 mL) was added and the flask was cooled to -78 °C, and diethylaminosulfur trifluoride (DAST, 114 mg, 0.71 mmol, 2.8

equiv.) was added dropwise. The reaction was stirred for 1 h, then K_2CO_3 (138 mg, 1.0 mmol, 4.0 equiv.) was added and the flask was warmed to rt. After 45 min, the mixture was diluted with DCM (5 mL) and water (7 mL) was added. After transferring to a separatory funnel, the organic layer was washed with sat. NaHCO_3 (aq.) (15 mL), and brine (15 mL), and dried over MgSO_4 . The dried organic layer was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel to afford ligand **BiOx-5d** as a colorless solid (yield 68%, 66.6 mg).

(4*R*,4'*R*)-4,4'-Di(nonan-5-yl)-4,4',5,5'-tetrahydro-2,2'-bioxazole (BiOx-5d)

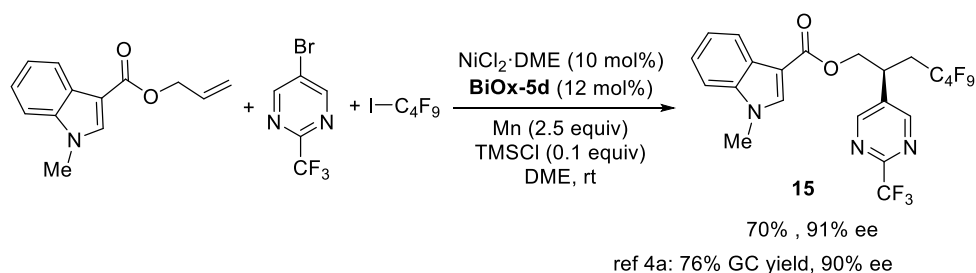


(*R,R*)-**BiOx-5d**

^1H NMR (600 MHz, Chloroform-*d*) δ 4.73 – 4.29 (m, 4H), 4.14 (t, $J = 7.9$ Hz, 2H), 1.66 – 1.56 (m, 2H), 1.44 – 1.12 (m, 24H), 0.93 – 0.74 (m, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.5, 71.0, 69.9, 41.9, 29.8, 29.3, 29.2, 29.2, 23.1, 23.0, 14.1, 14.1.

IV Application of **BiOx-5d**

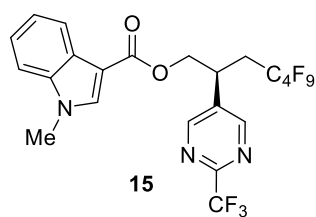


Scheme S8 Application of **BiOx-5d**.

To a flame-dried 10 mL reaction vial was charged with $\text{NiCl}_2 \cdot \text{glyme}$ (2.2 mg, 0.01 mmol, 10 mol%), **BiOx-5d** (4.7 mg, 0.012 mmol, 12 mol%) [Note: 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy) for the corresponding racemic reactions], Mn (13.8 mg, 0.25 mmol, 2.5 equiv.), alkene (43 mg, 0.2 mmol, 2.0 equiv.), and aryl halide (22.6 mg, 0.1

mmol, 1.0 equiv.). After evacuated and backfilled nitrogen three times, DME 0.2 mL was added via a syringe. The reaction mixture was allowed to stir for approximately 30 minutes before fluoroalkyl iodide (69.2 mg, 0.2 mmol, 2.0 equiv.) and TMSCl (1.1 mg, 0.01 mmol, 0.1 equiv.) were added. The reaction mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 24 h. The reaction was quenched with saturated ammonium chloride solution, extracted with ethyl acetate three times. The combined organic layers were dried over MgSO_4 , filtered, and concentrated in vacuo. The crude material was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1). The product as a white solid (40.7 mg, 70%, 91% ee).

(S)-4,4,5,5,6,6,7,7,7-nonafluoro-2-(2-(trifluoromethyl)pyrimidin-5-yl)heptyl 1-methyl-1H-indole-3-carboxylate (15)

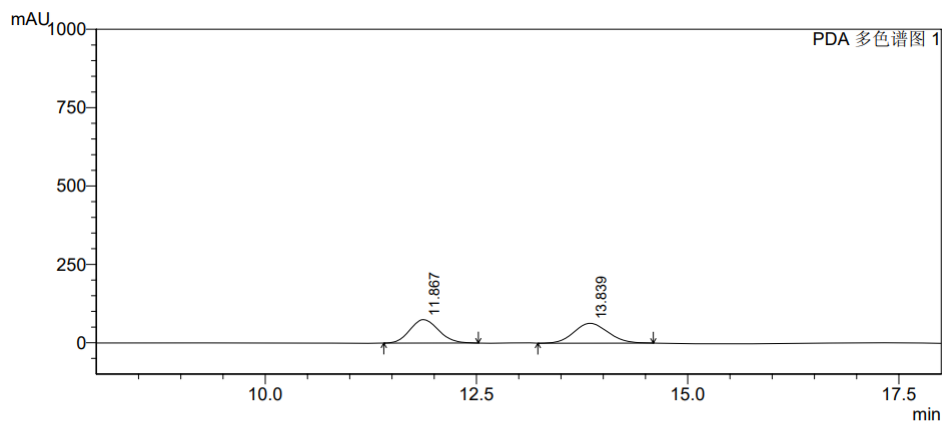


$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.91 (s, 2H), 7.95 (d, $J = 7.9$ Hz, 1H), 7.70 (s, 1H), 7.39 – 7.35 (m, 1H), 7.35 – 7.29 (m, 1H), 7.29 – 7.27 (m, 1H), 4.78 – 4.36 (m, 2H), 3.85 (s, 3H), 3.80 – 3.73 (m, 1H), 2.87 – 2.76 (m, 1H), 2.73 – 2.60 (m, 1H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 163.9, 157.5, 156.4, 137.4, 136.2, 135.6, 126.5, 123.4, 121.3, 119.4, 110.2, 105.6, 65.2, 34.4, 33.7, 32.9.

$^{19}\text{F NMR}$ (565 MHz, Chloroform-*d*) δ -70.24, -80.96 (d, $J = 10.1$ Hz), -108.62 – -112.35 (m), -112.20 – -114.22 (m), -121.55 – -127.52 (m).

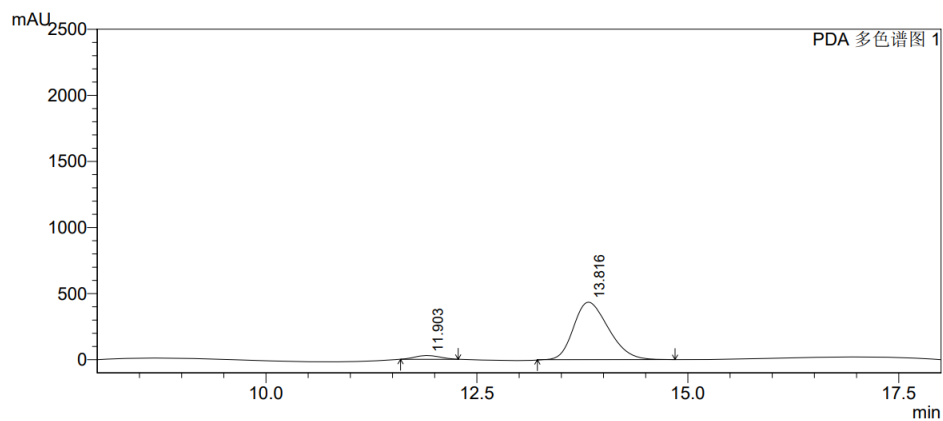
HPLC analysis CHIRALCEL IC-H column, 15% *i*PrOH in hexanes, 1.0 mL/min, 254 nm UV detector, t_{R} (minor) = 11.9 min, t_{R} (major) = 13.8 min.



1 PDA 多色谱图 1/254nm 4nm

Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
1	11.867	1767171	74989	49.874	54.204
2	13.839	1776122	63357	50.126	45.796
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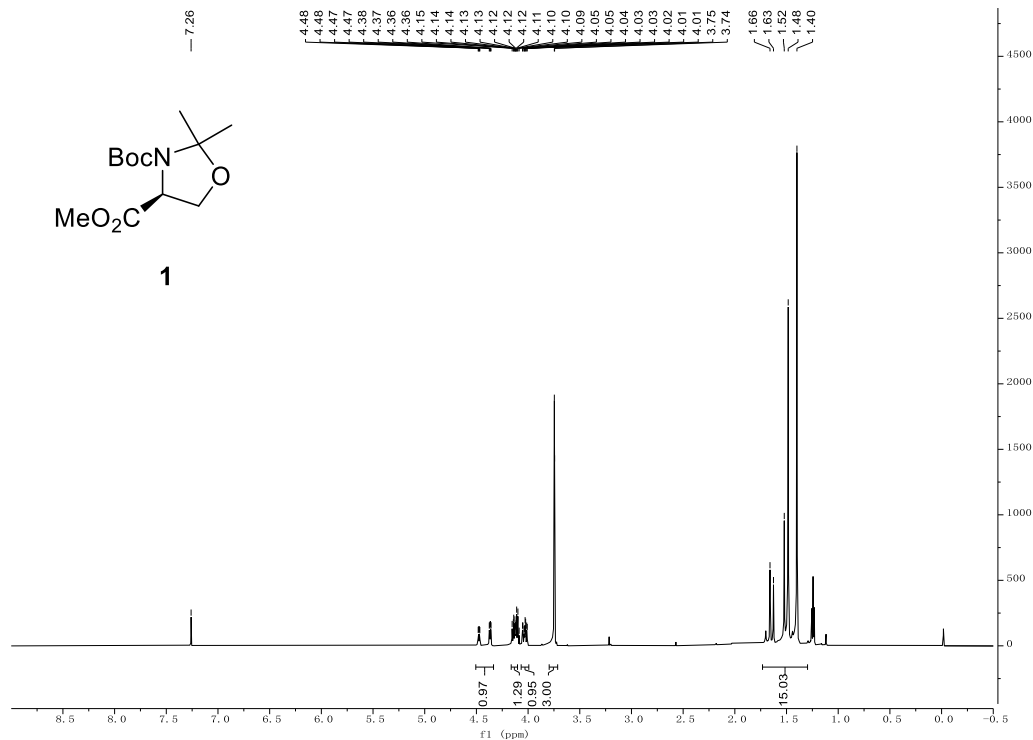


1 PDA 多色谱图 1/254nm 4nm

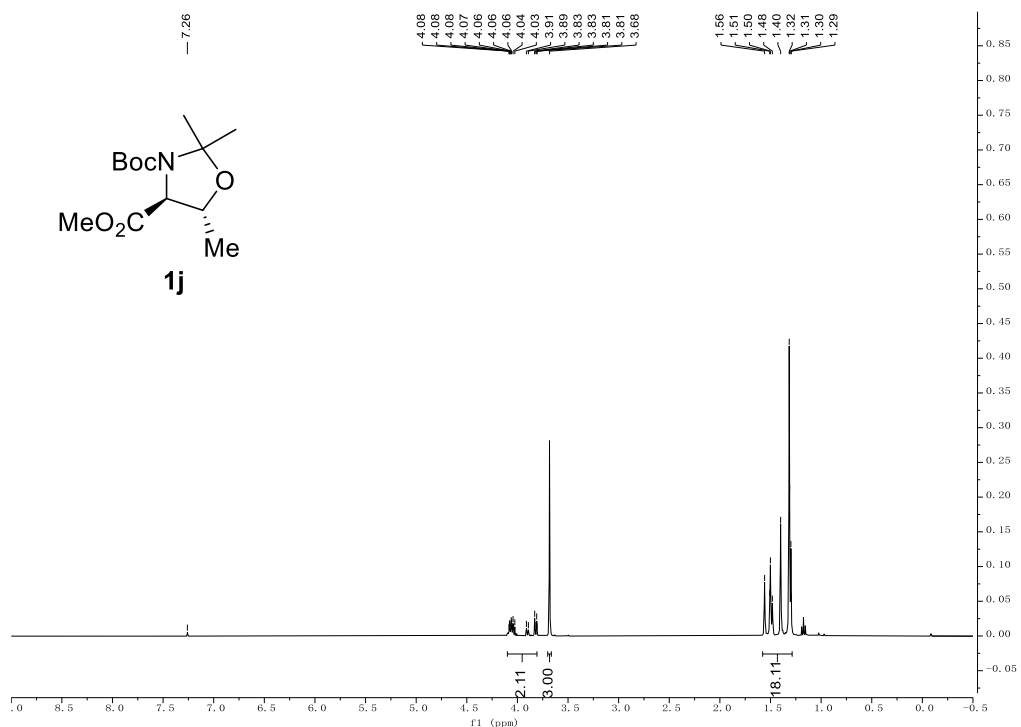
Ch1 254nm 4nm

Peak#	Resolution Time	Area	Height	Area %	Height %
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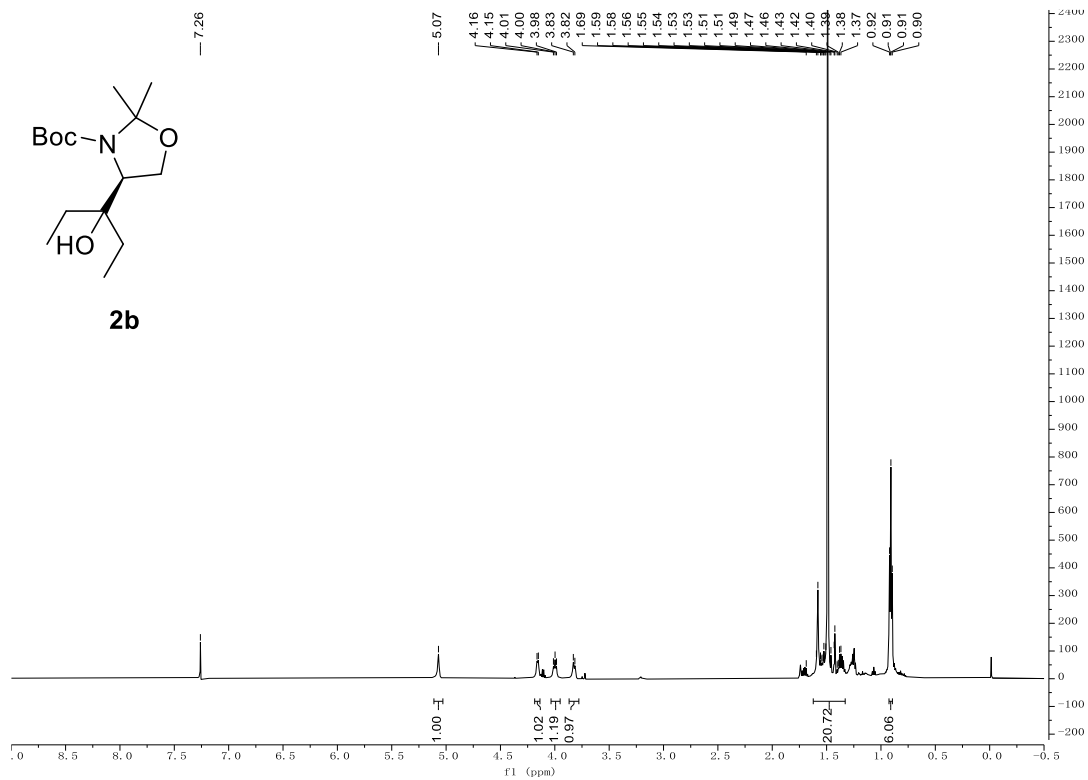
Spectroscopic Data (NMR Spectra)



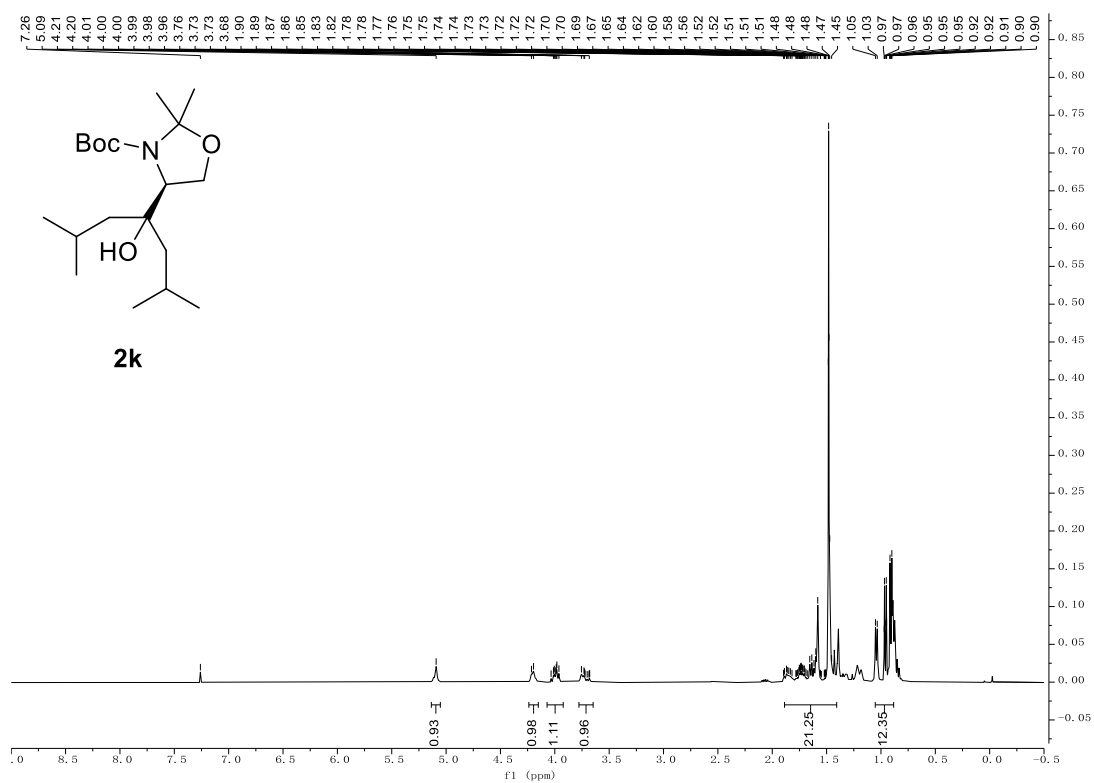
¹H NMR (600 MHz, CDCl₃) spectrum for **1**



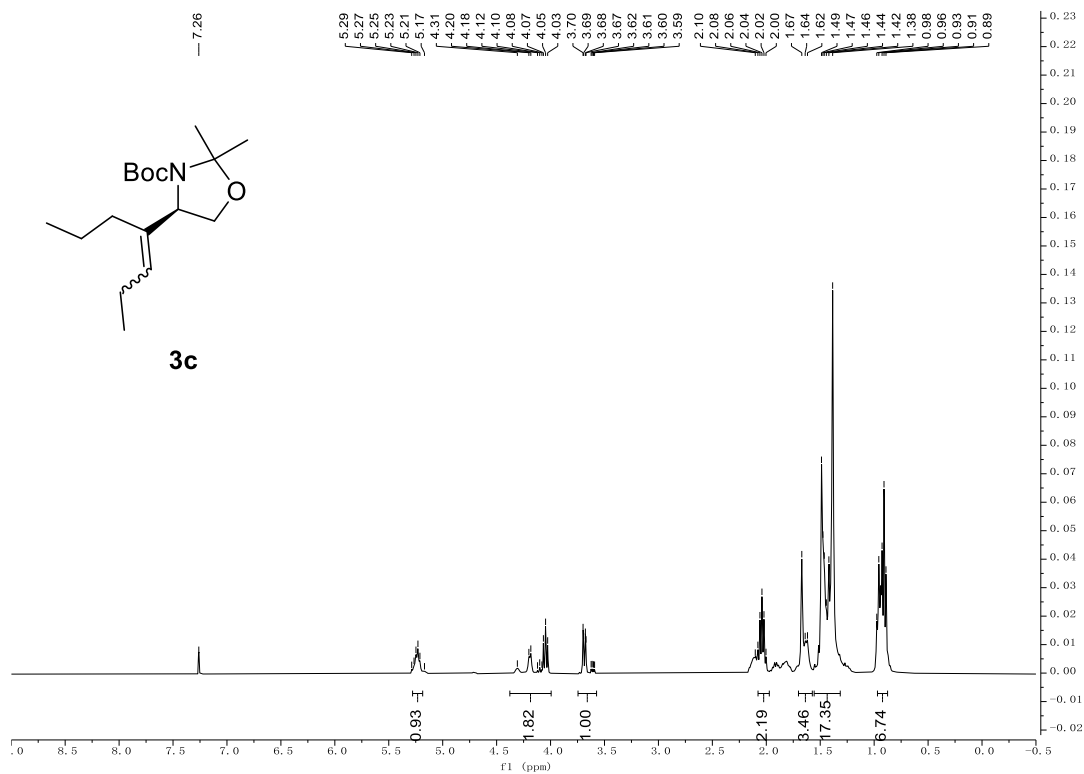
¹H NMR (600 MHz, CDCl₃) spectrum for **1j**



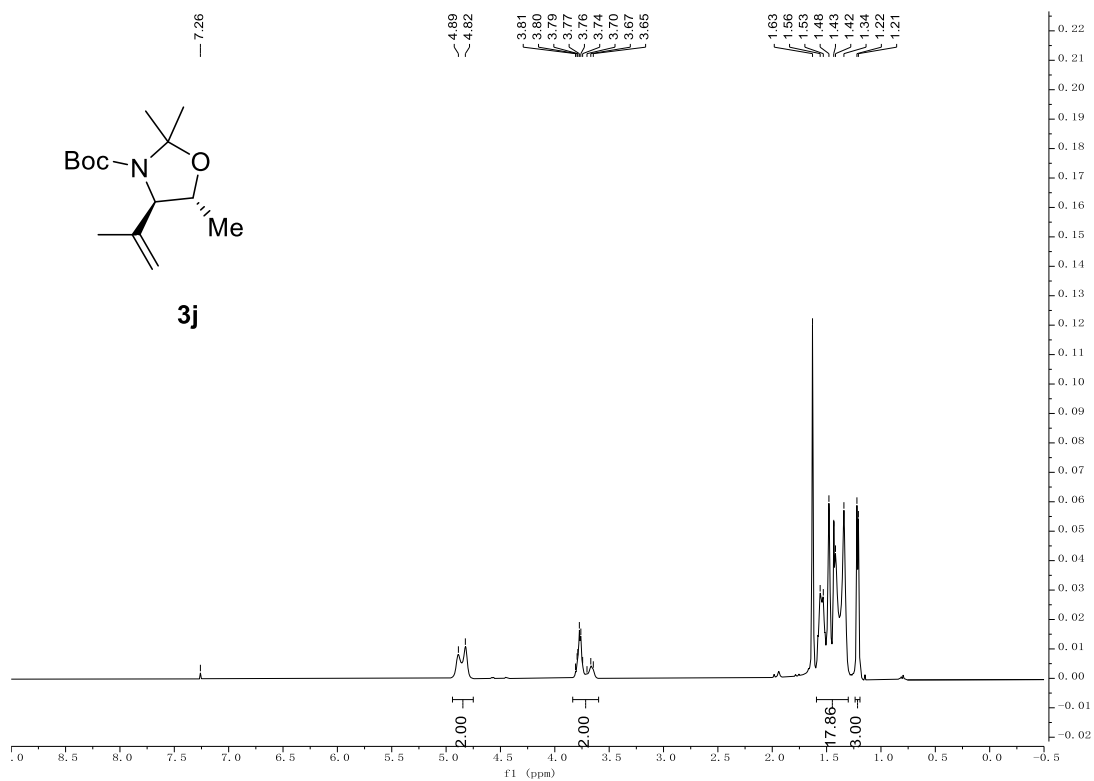
^1H NMR (600 MHz, CDCl_3) spectrum for **2b**



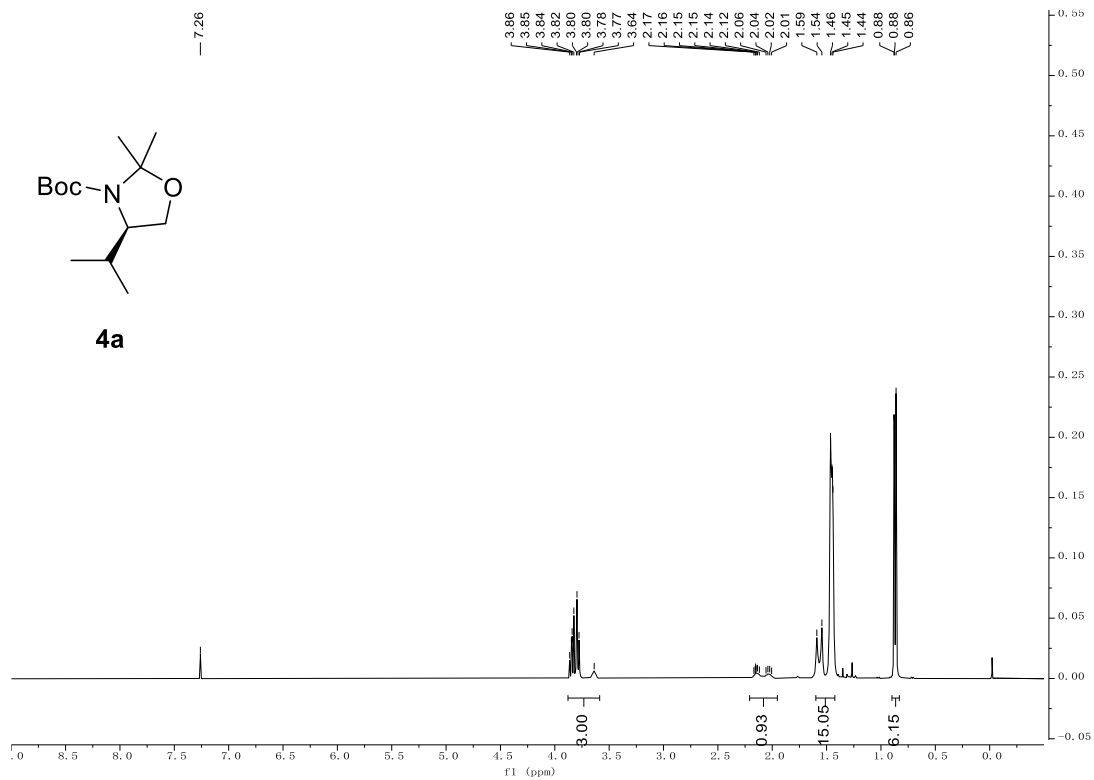
^1H NMR (600 MHz, CDCl_3) spectrum for **2k**



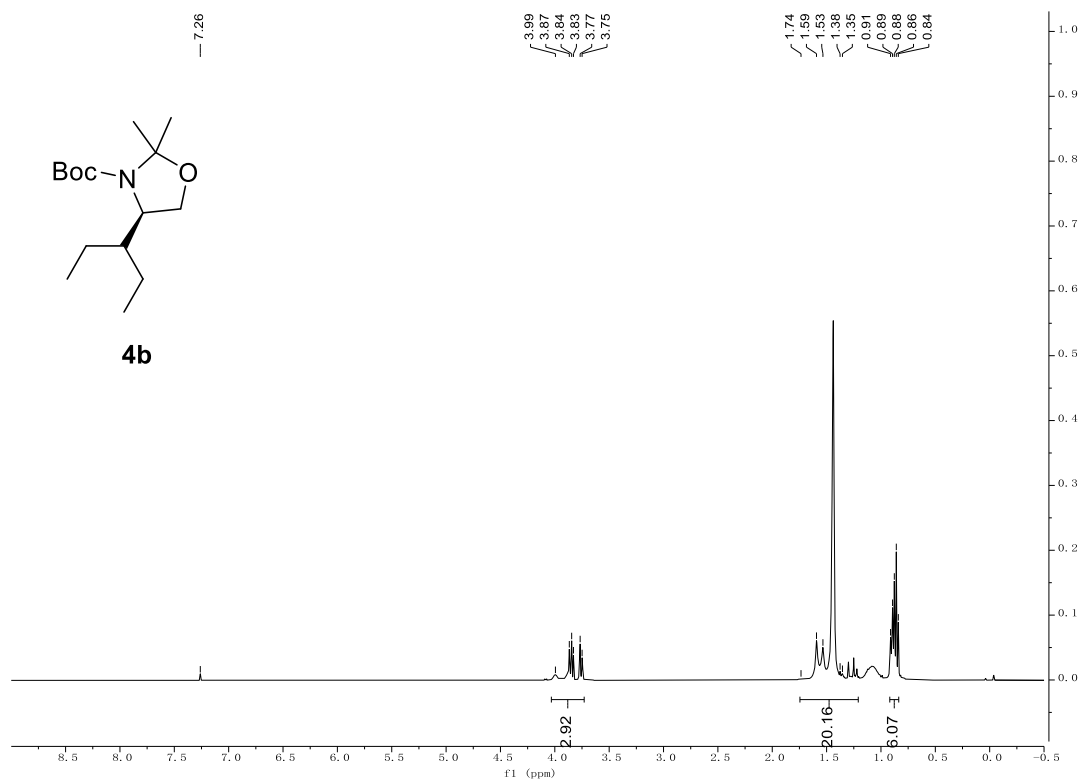
^1H NMR (400 MHz, CDCl_3) spectrum for **3c**



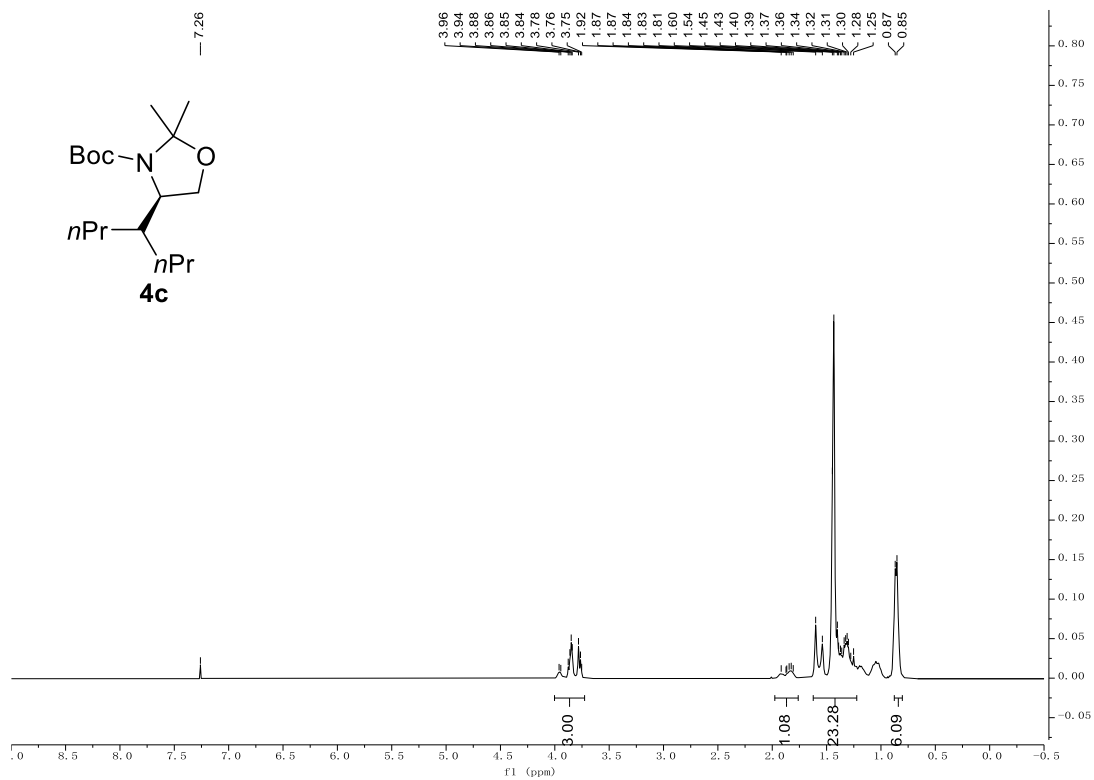
^1H NMR (400 MHz, CDCl_3) spectrum for **3j**



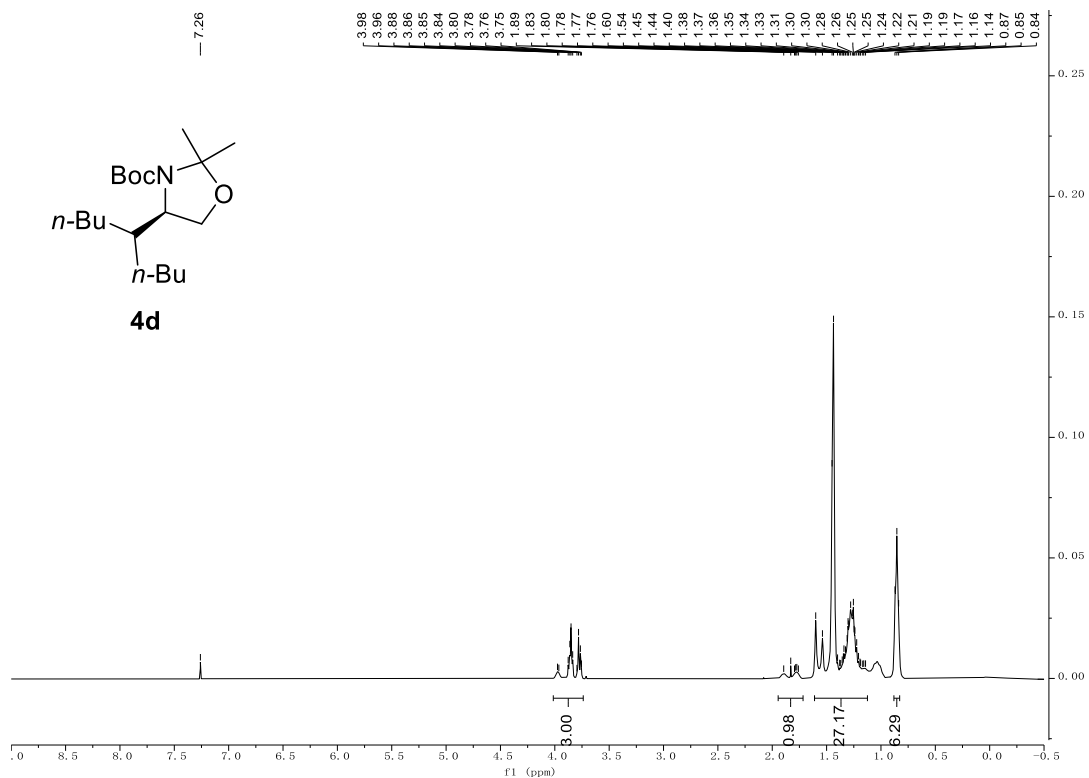
^1H NMR (400 MHz, CDCl_3) spectrum for **4a**



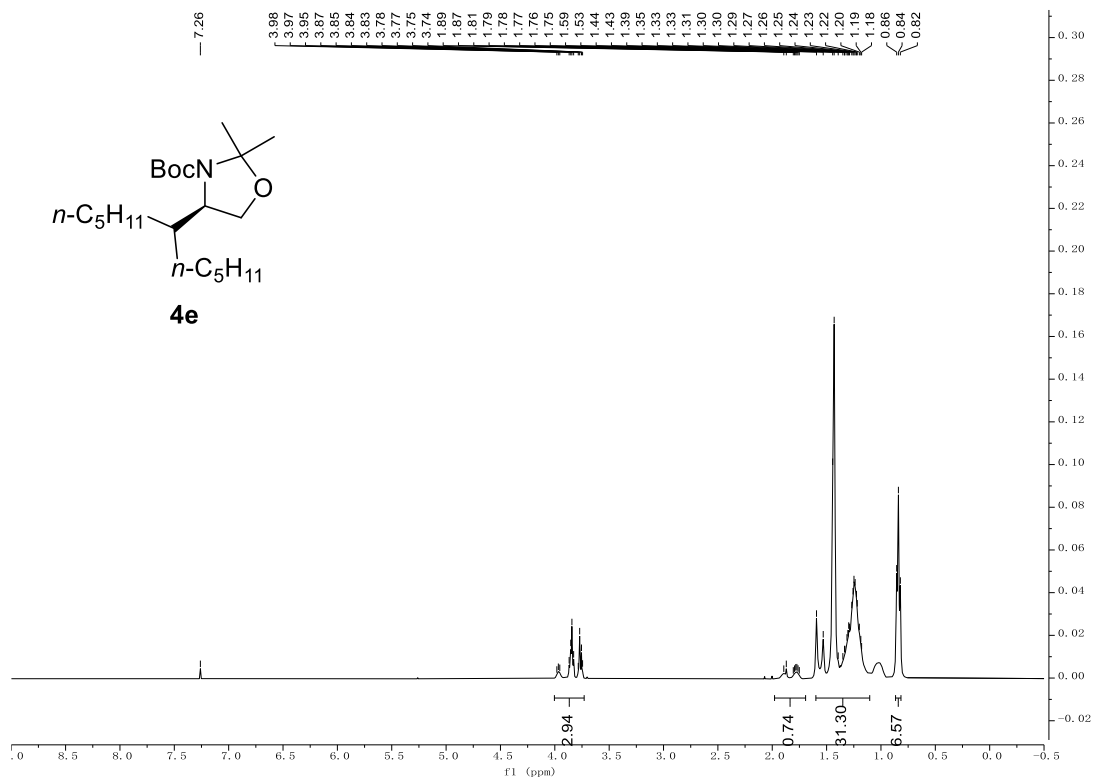
^1H NMR (400 MHz, CDCl_3) spectrum for **4b**



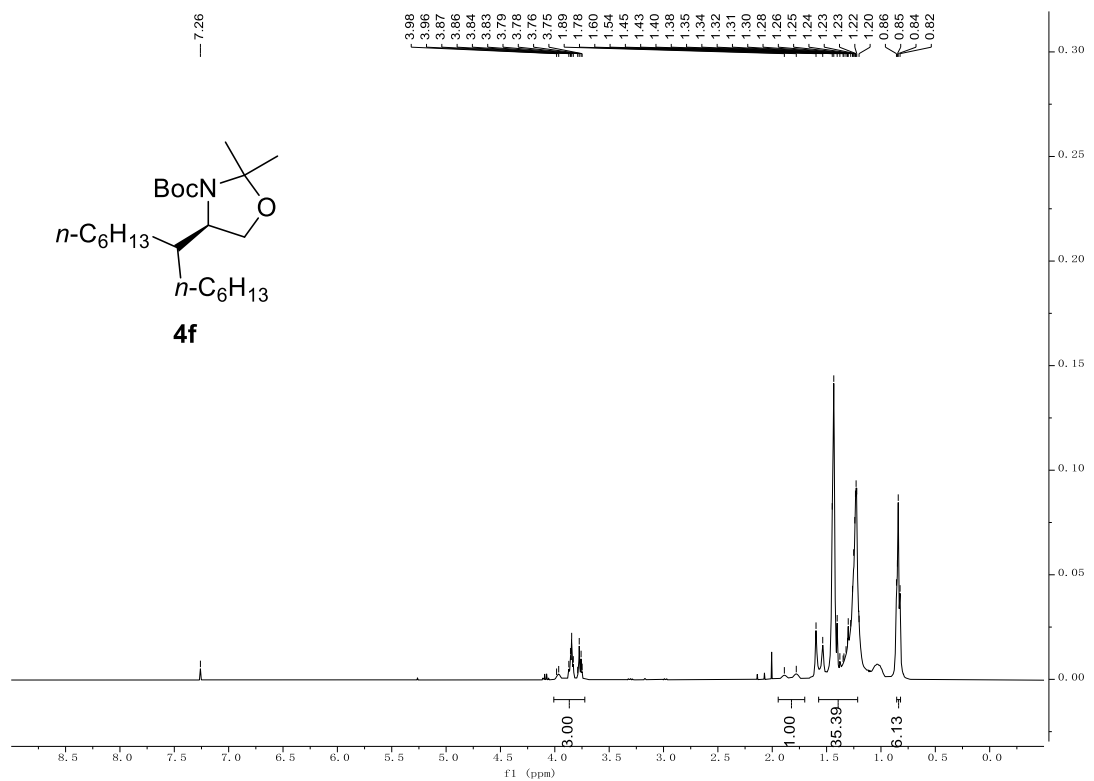
¹H NMR (400 MHz, CDCl₃) spectrum for **4c**



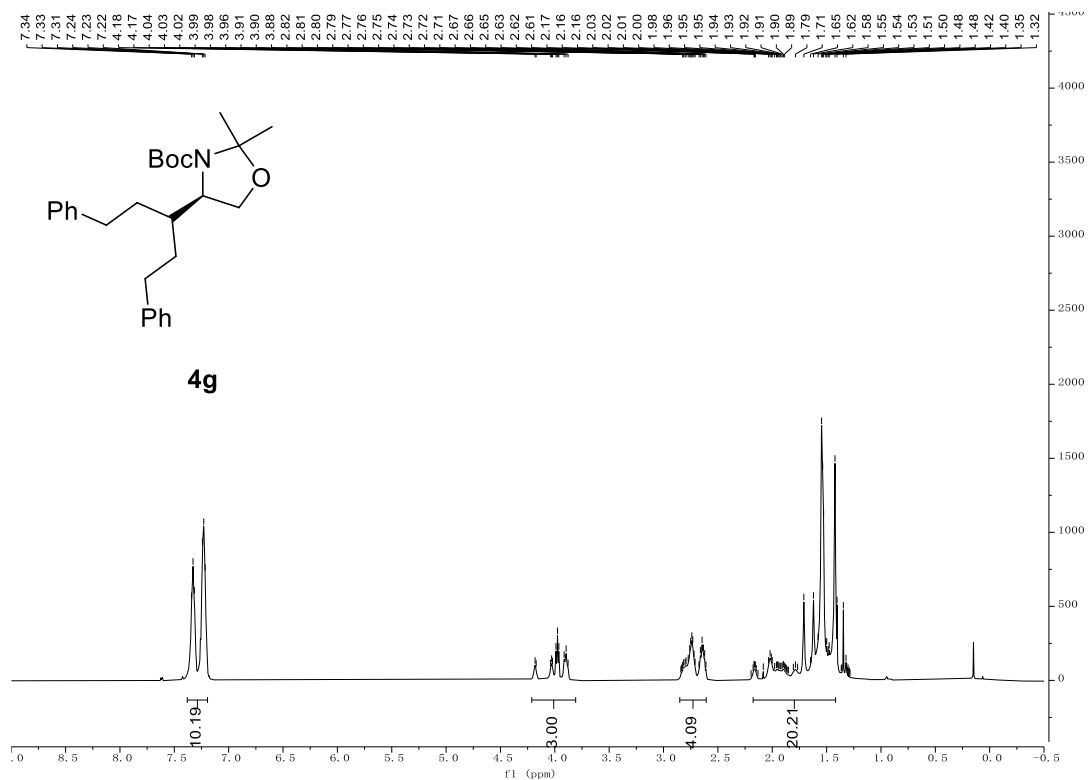
¹H NMR (400 MHz, CDCl₃) spectrum for **4d**



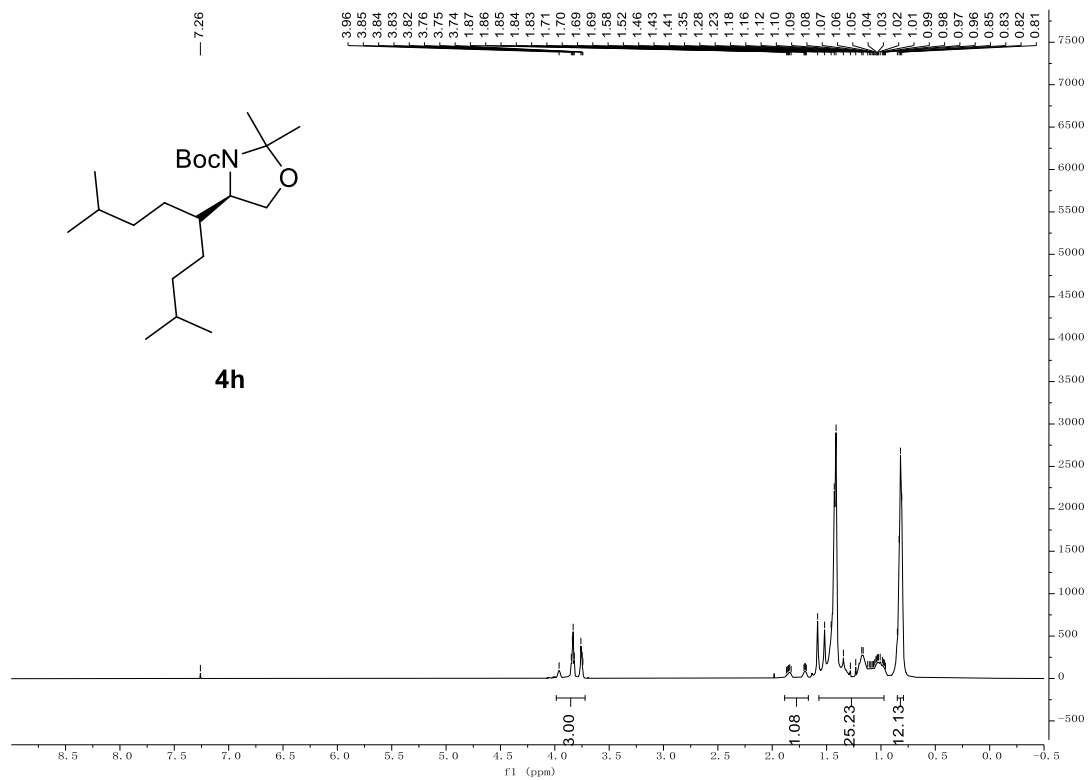
¹H NMR (400 MHz, CDCl₃) spectrum for **4e**



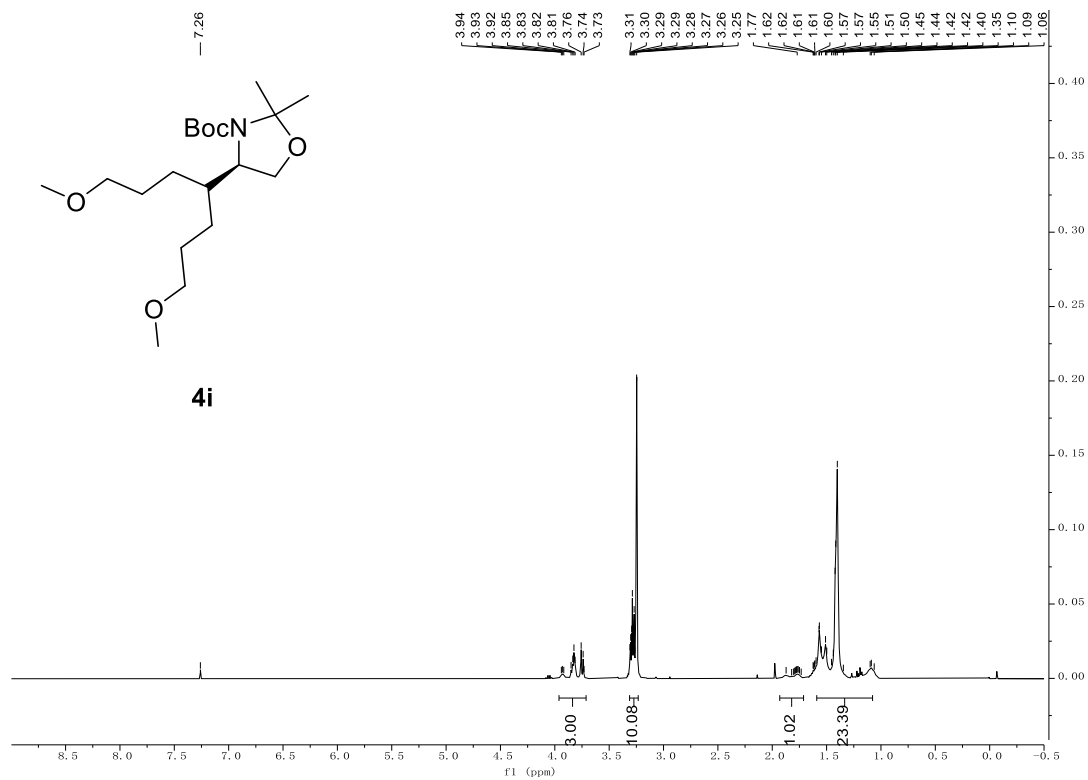
¹H NMR (400 MHz, CDCl₃) spectrum for **4f**



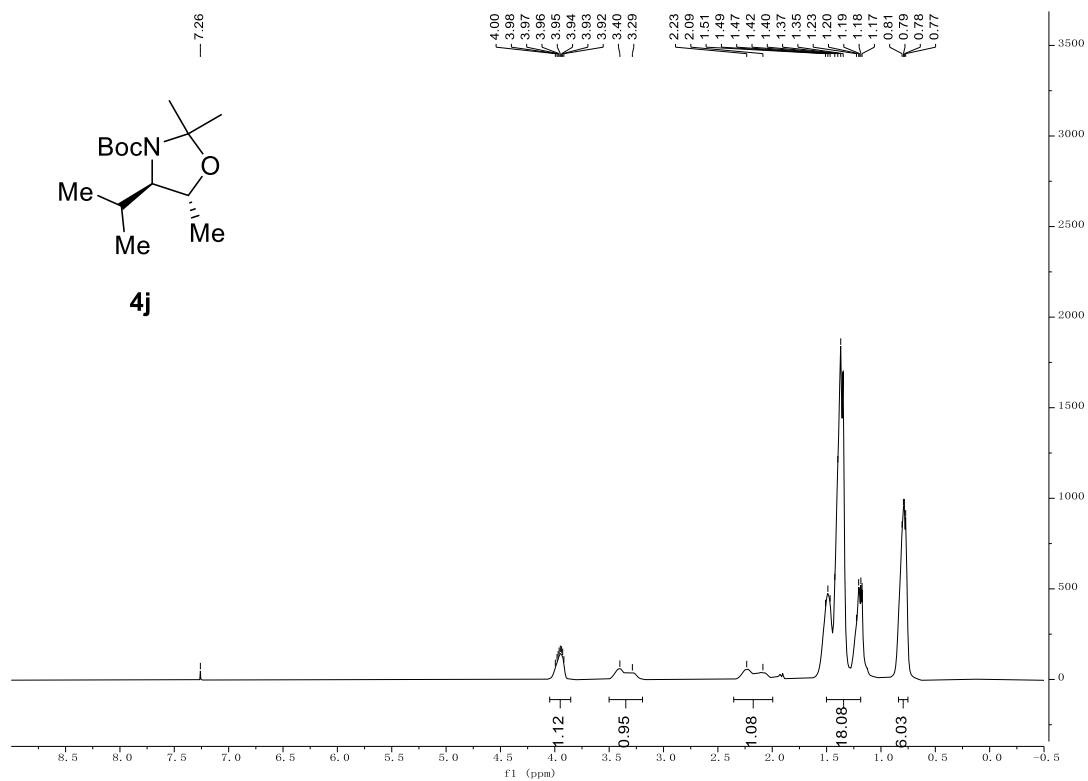
¹H NMR (400 MHz, CDCl₃) spectrum for **4g**



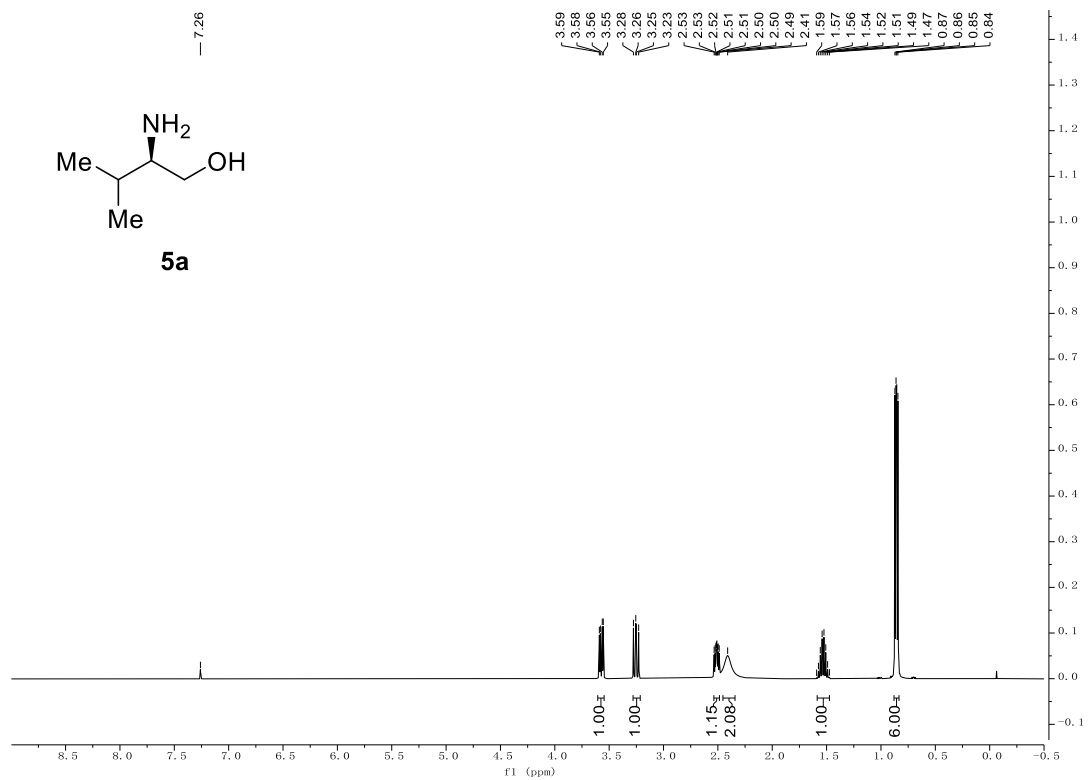
¹H NMR (400 MHz, CDCl₃) spectrum for **4h**



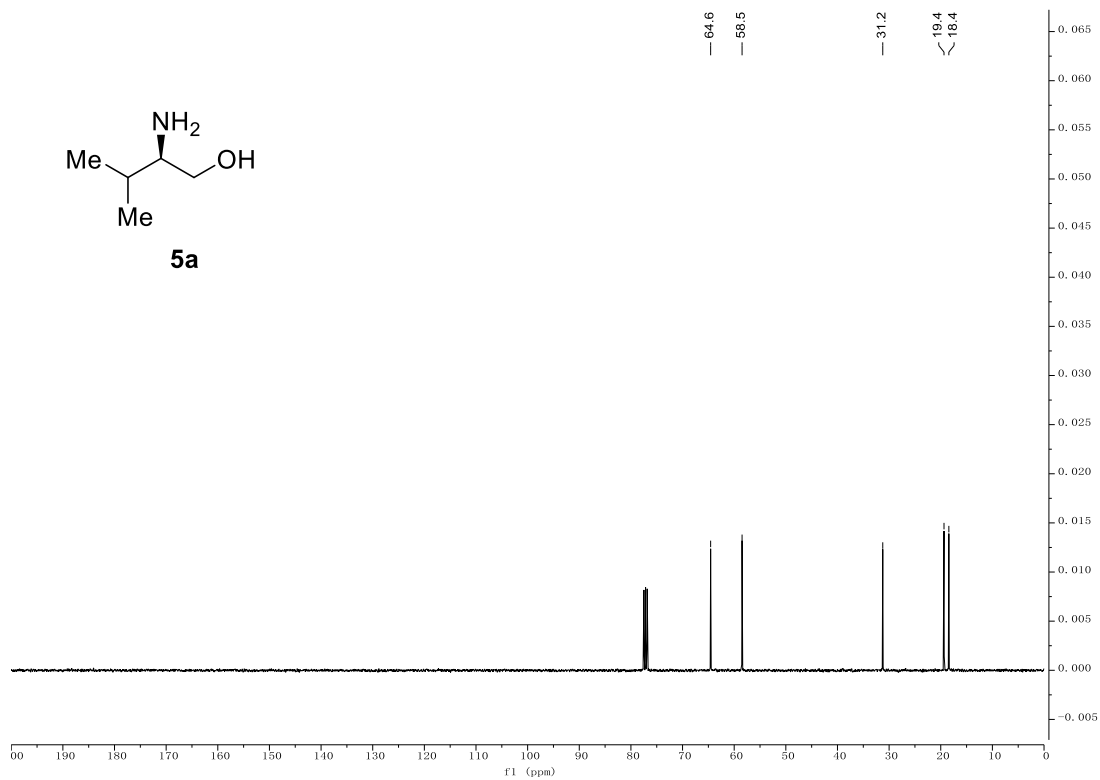
^1H NMR (400 MHz, CDCl_3) spectrum for **4i**



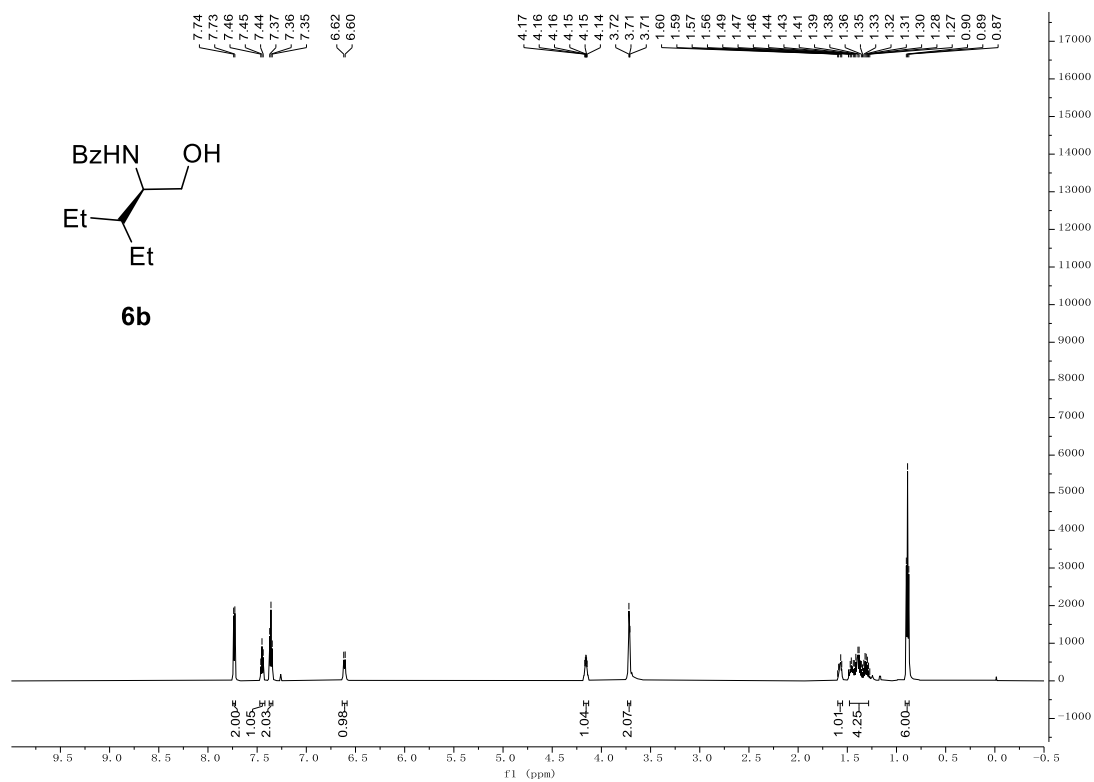
^1H NMR (400 MHz, CDCl_3) spectrum for **4j**



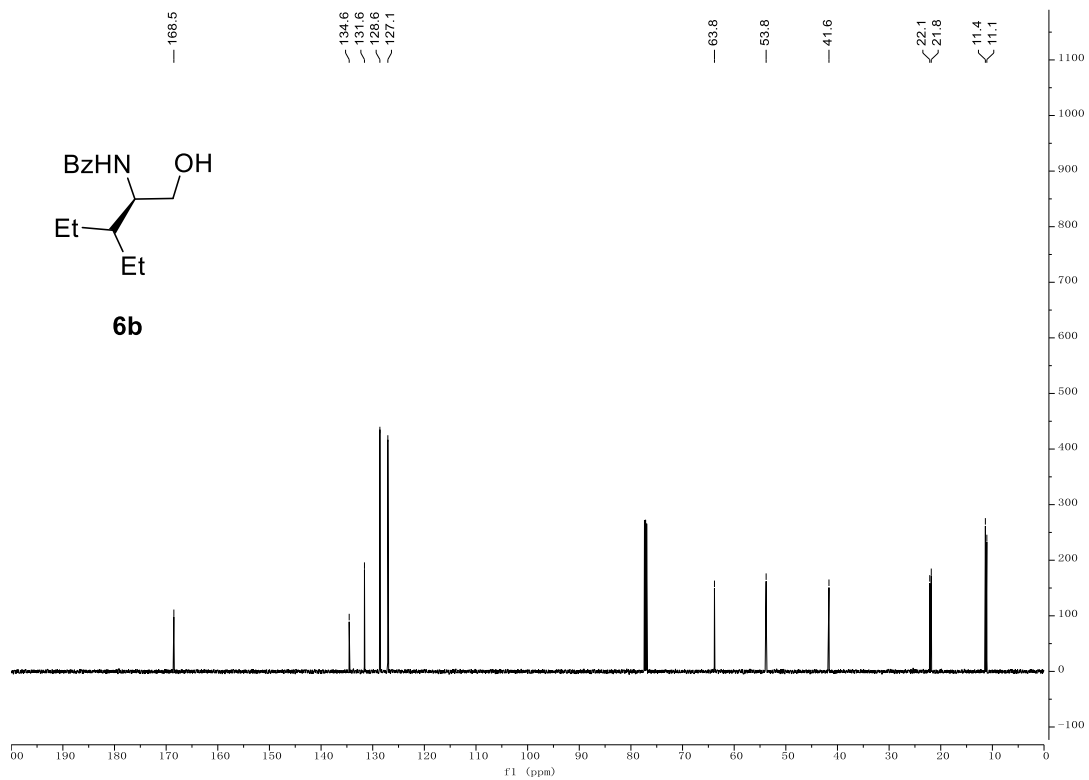
^1H NMR (400 MHz, CDCl_3) spectrum for **5a**



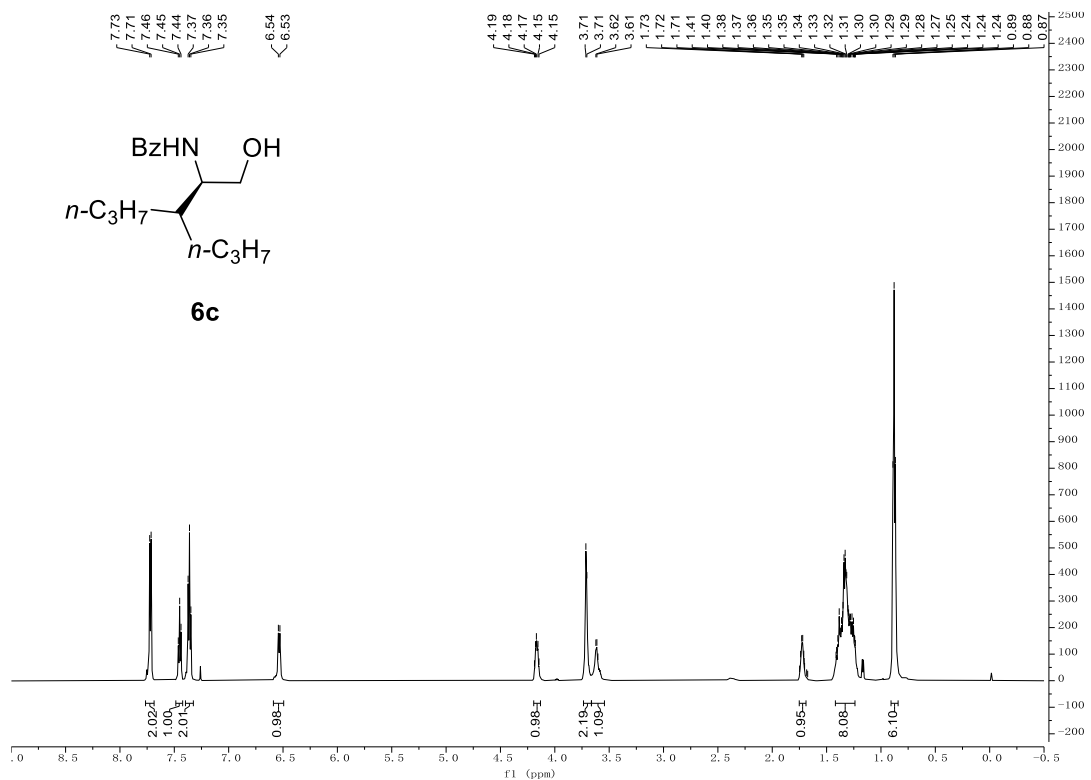
^{13}C NMR (101 MHz, CDCl_3) spectrum for **5a**



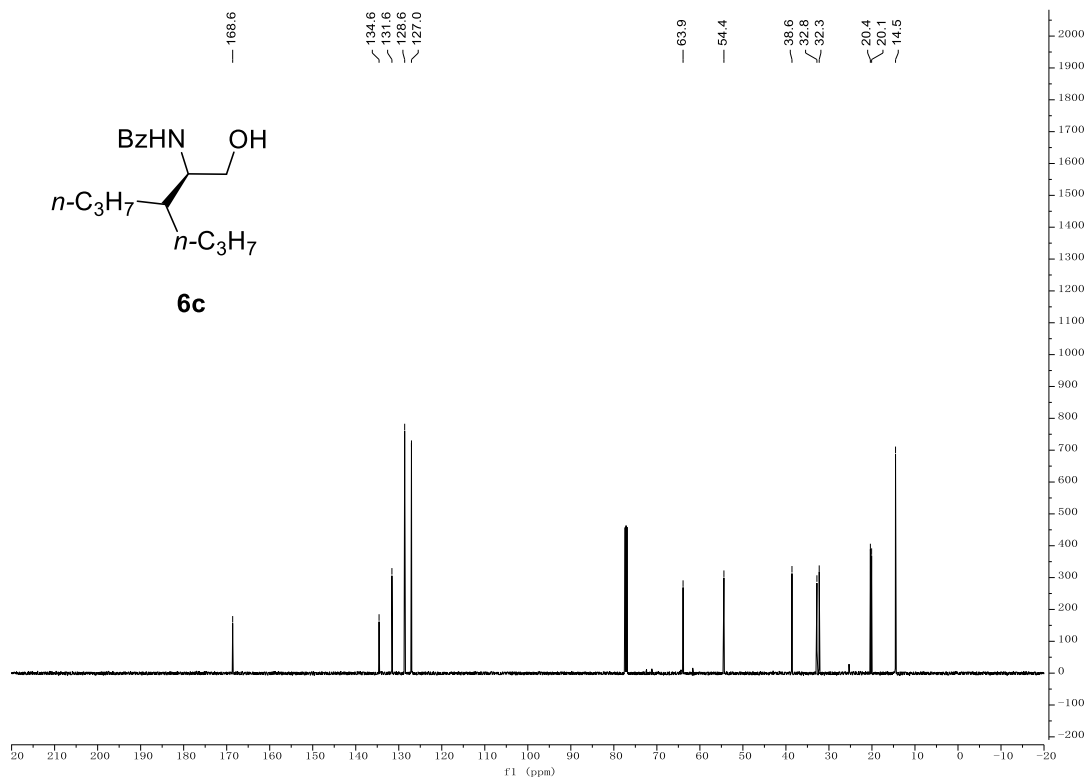
^1H NMR (600 MHz, CDCl_3) spectrum for **6b**



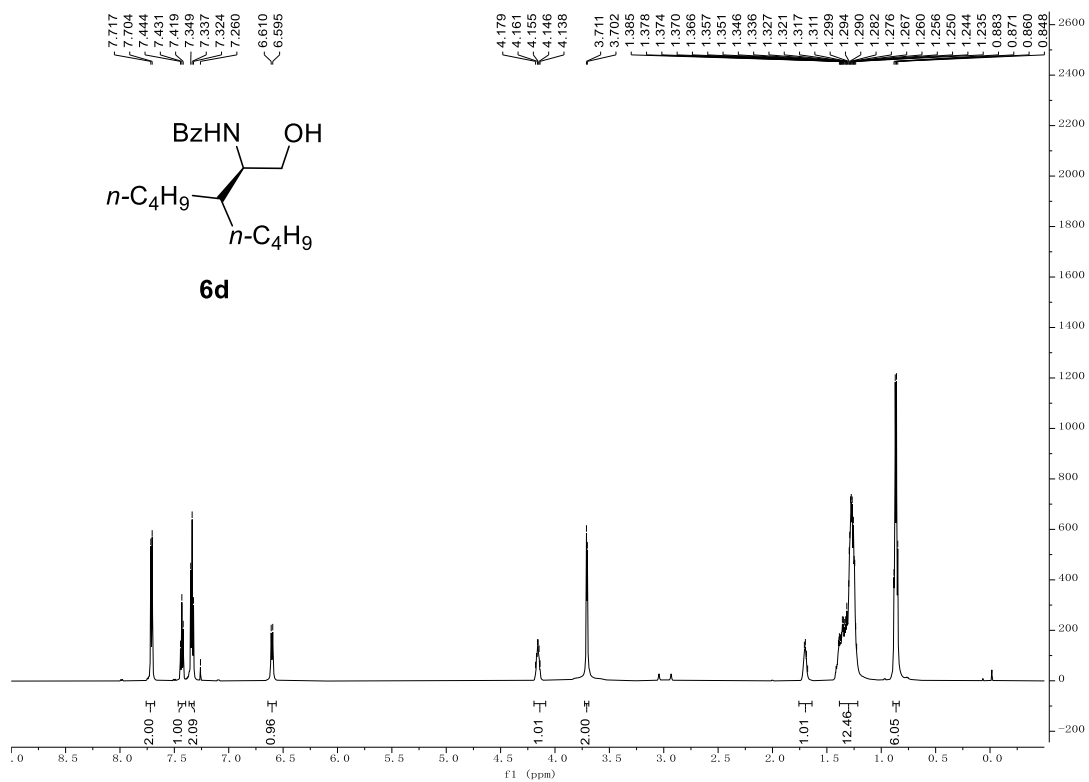
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6b**



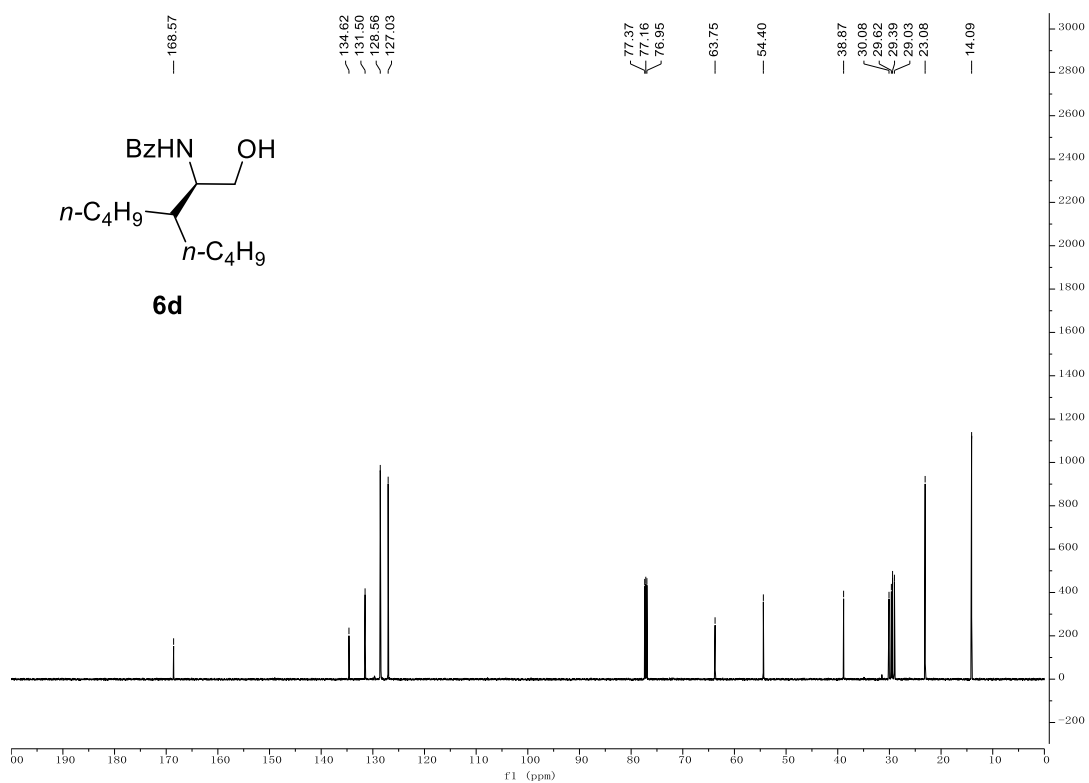
¹H NMR (600 MHz, CDCl₃) spectrum for **6c**



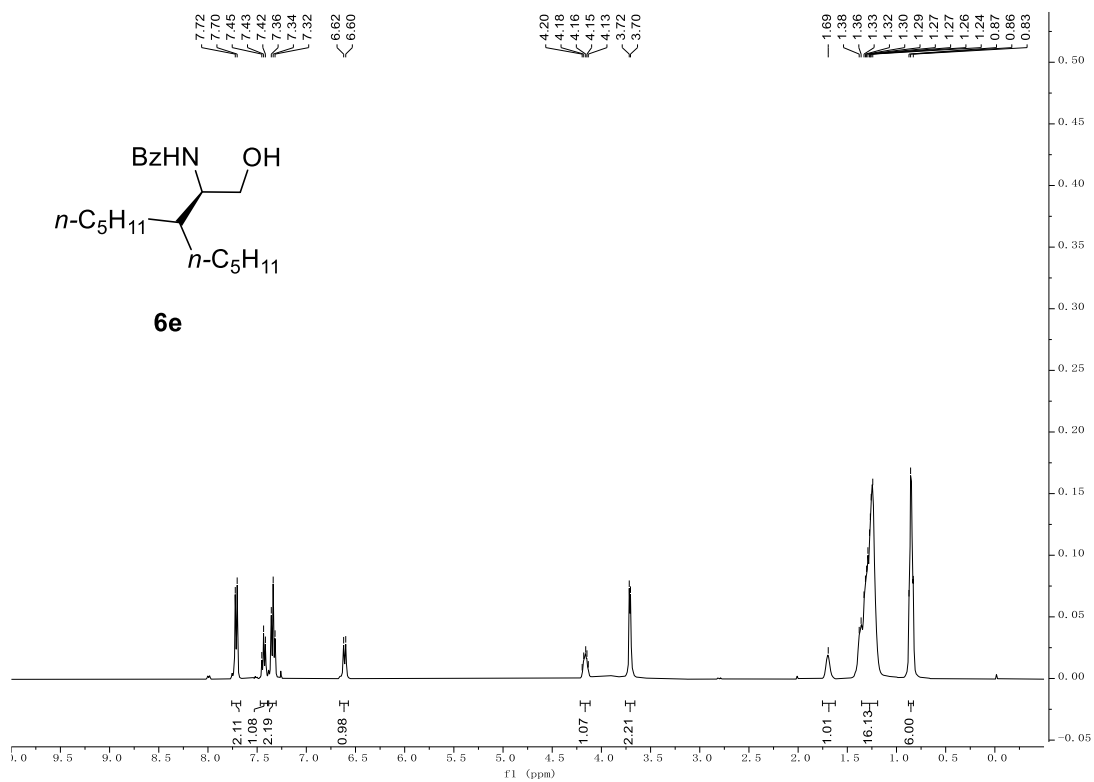
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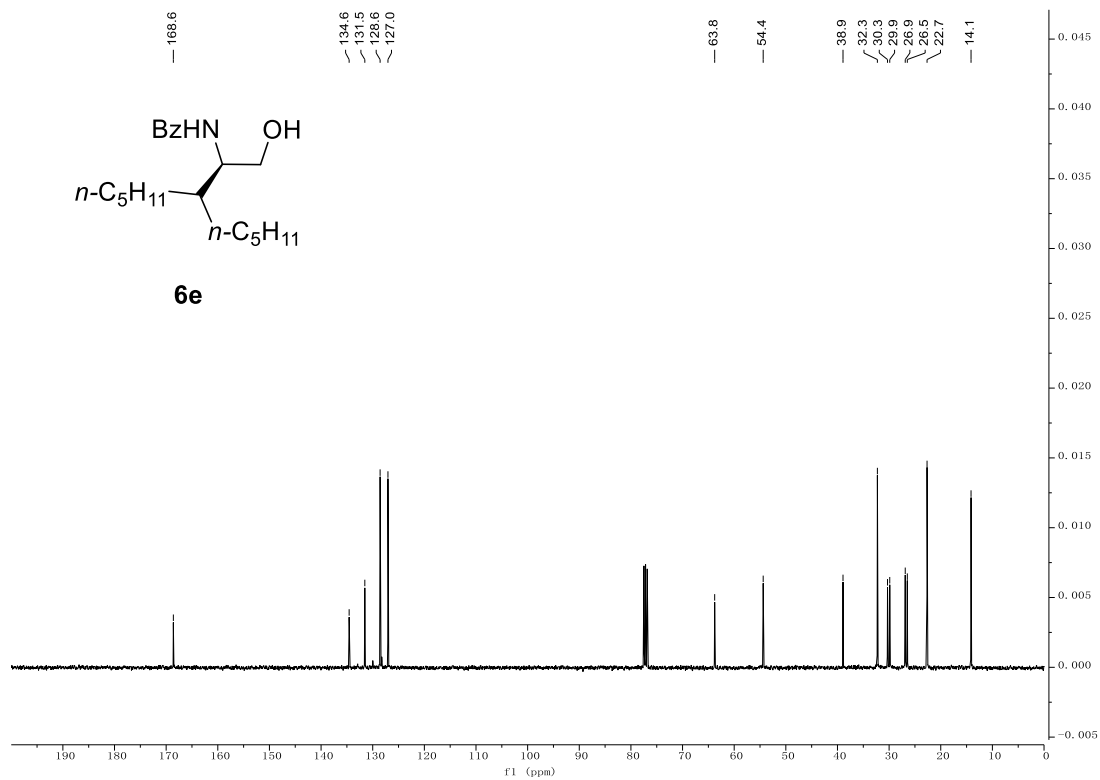
^1H NMR (600 MHz, CDCl_3) spectrum for **6d**



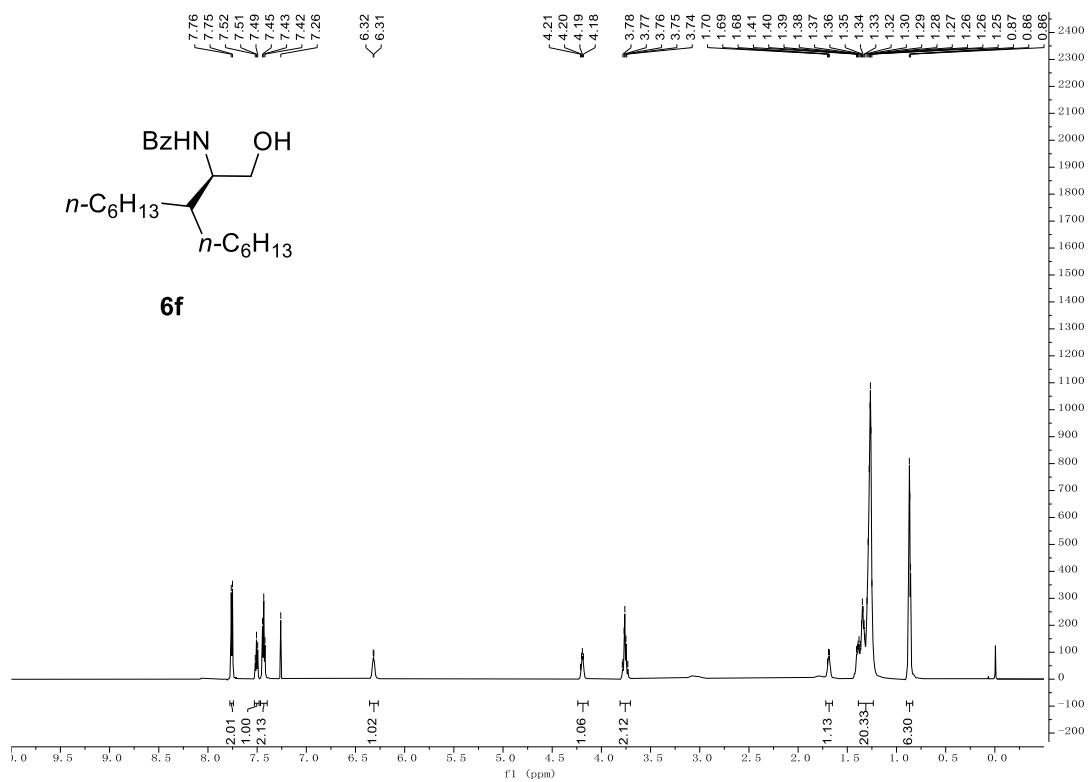
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6d**



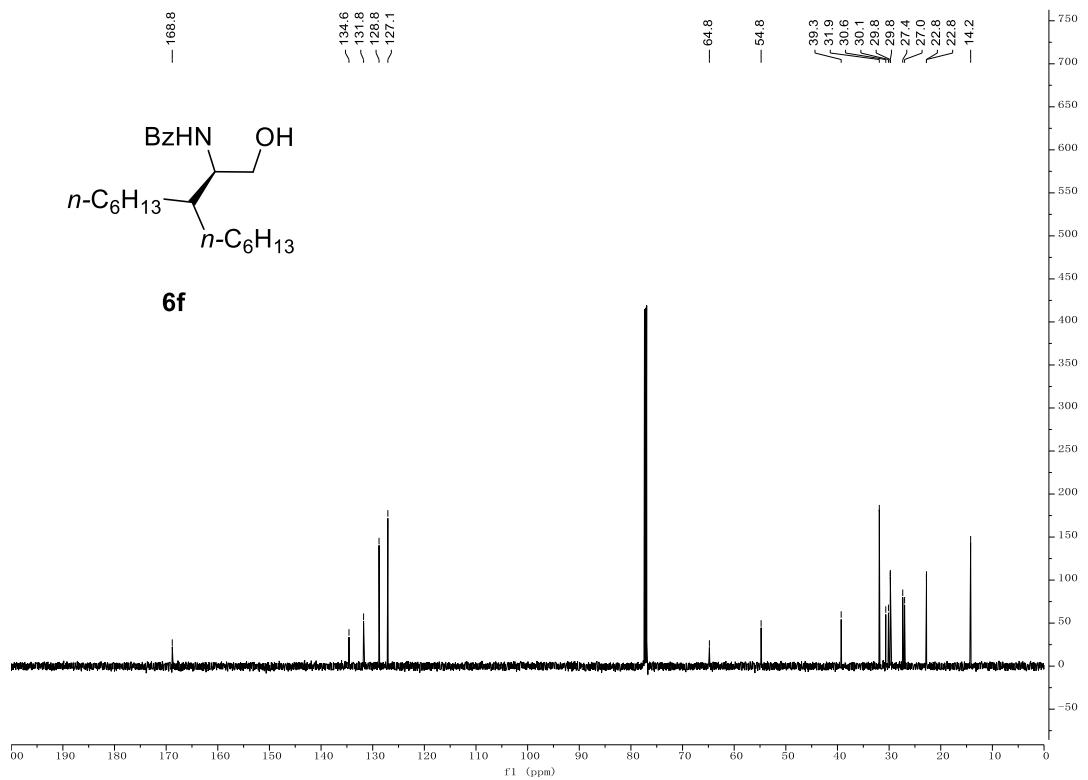
^1H NMR (600 MHz, CDCl_3) spectrum for **6e**



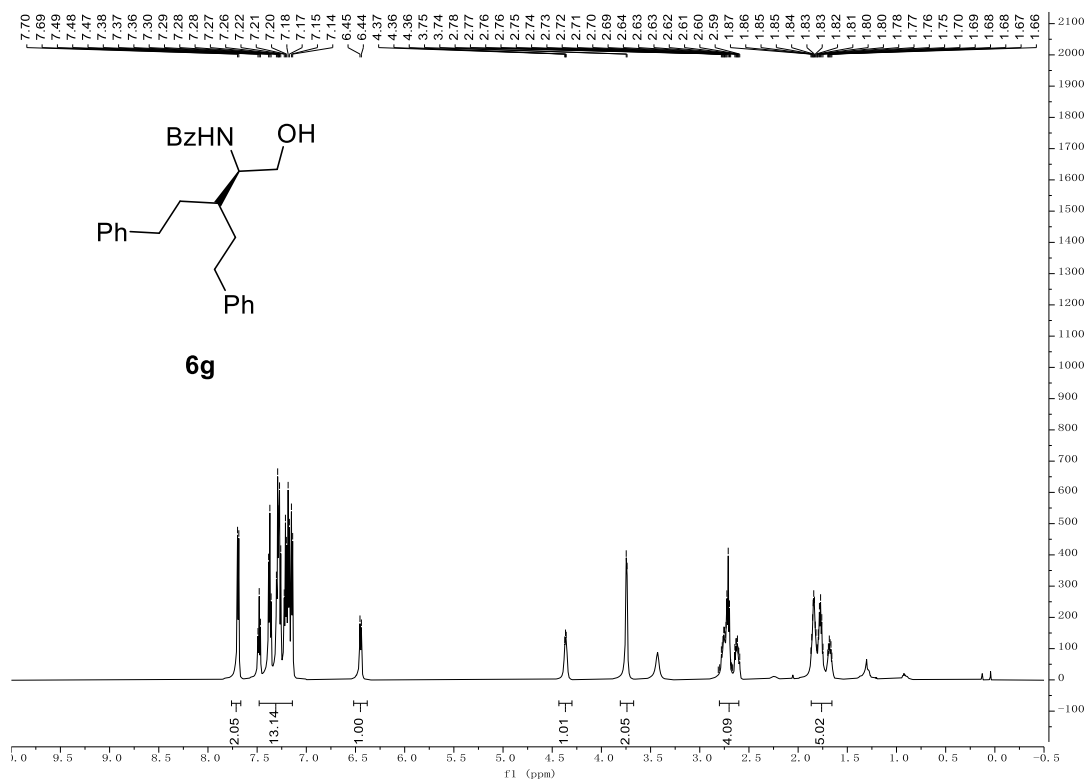
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6e**



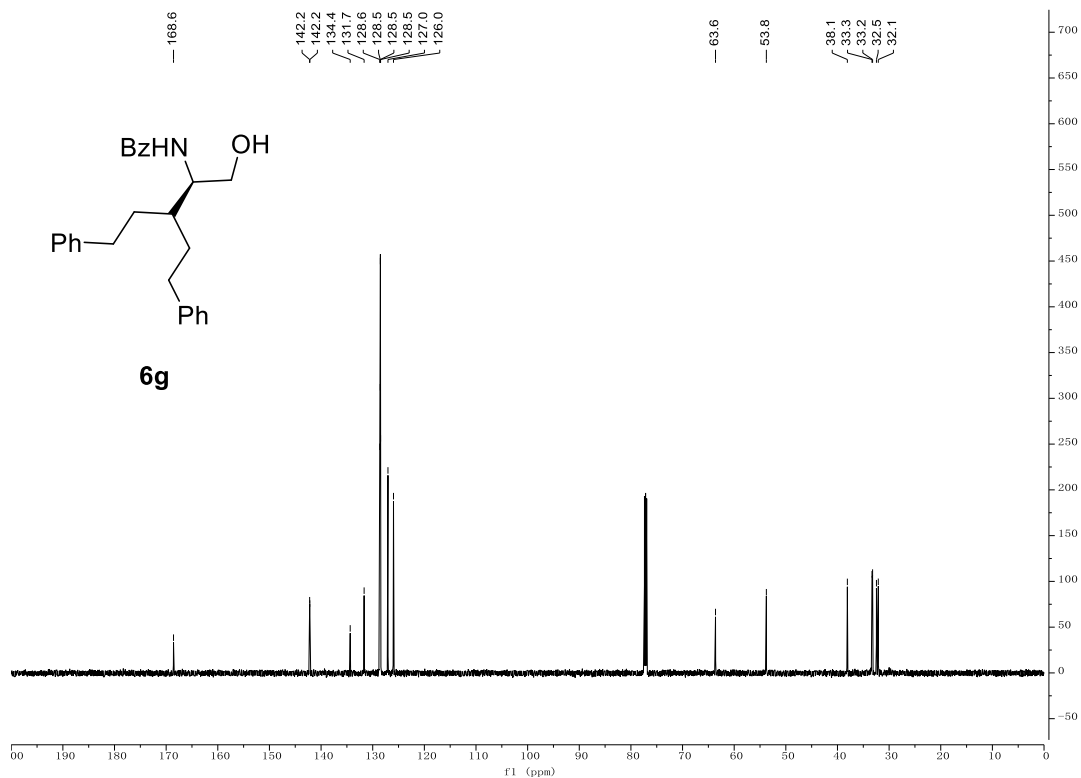
^1H NMR (600 MHz, CDCl_3) spectrum for **6f**



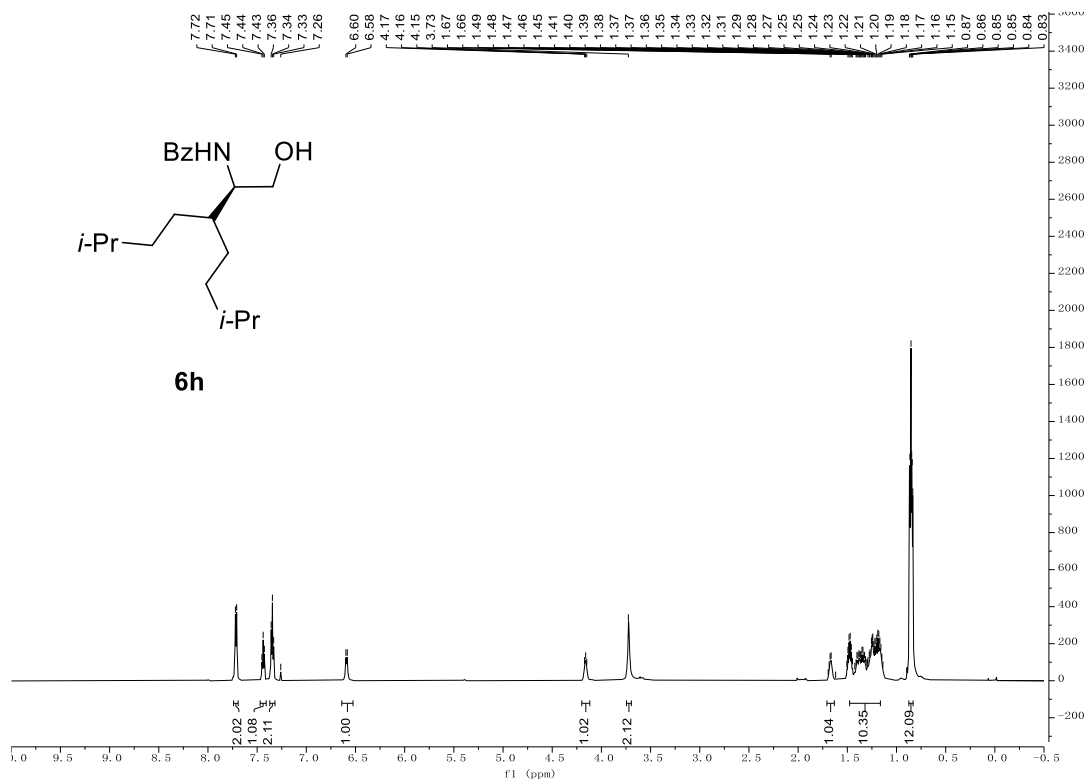
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6f**



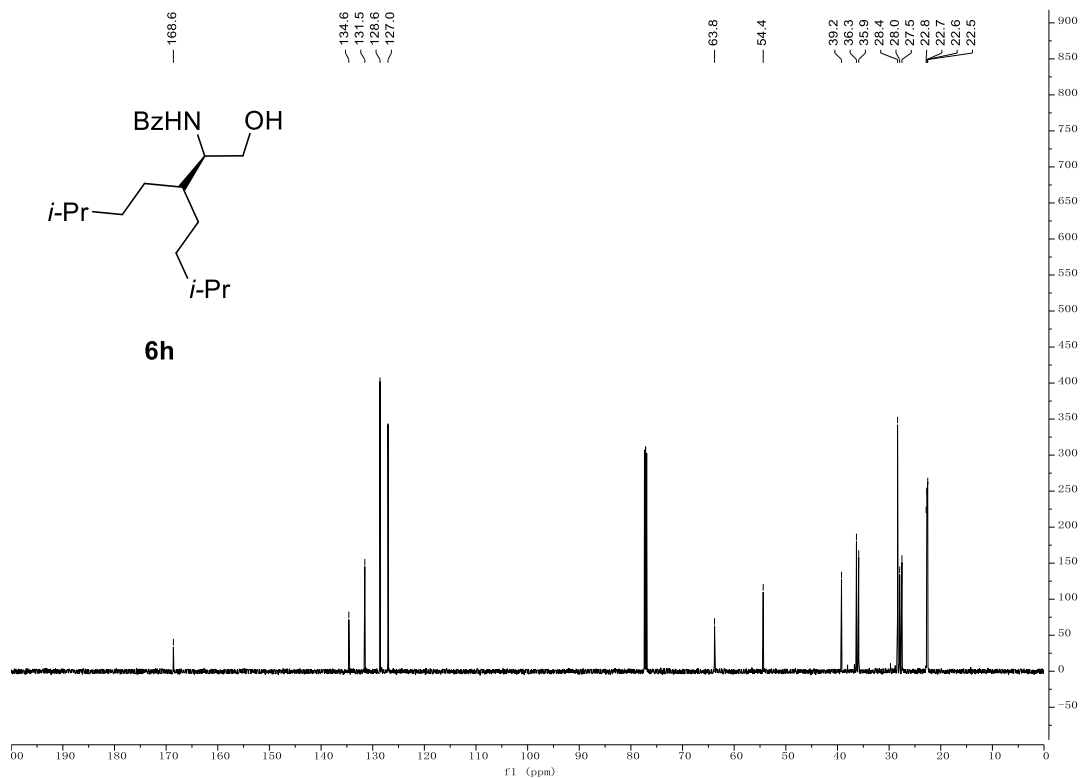
^1H NMR (600 MHz, CDCl_3) spectrum for **6g**



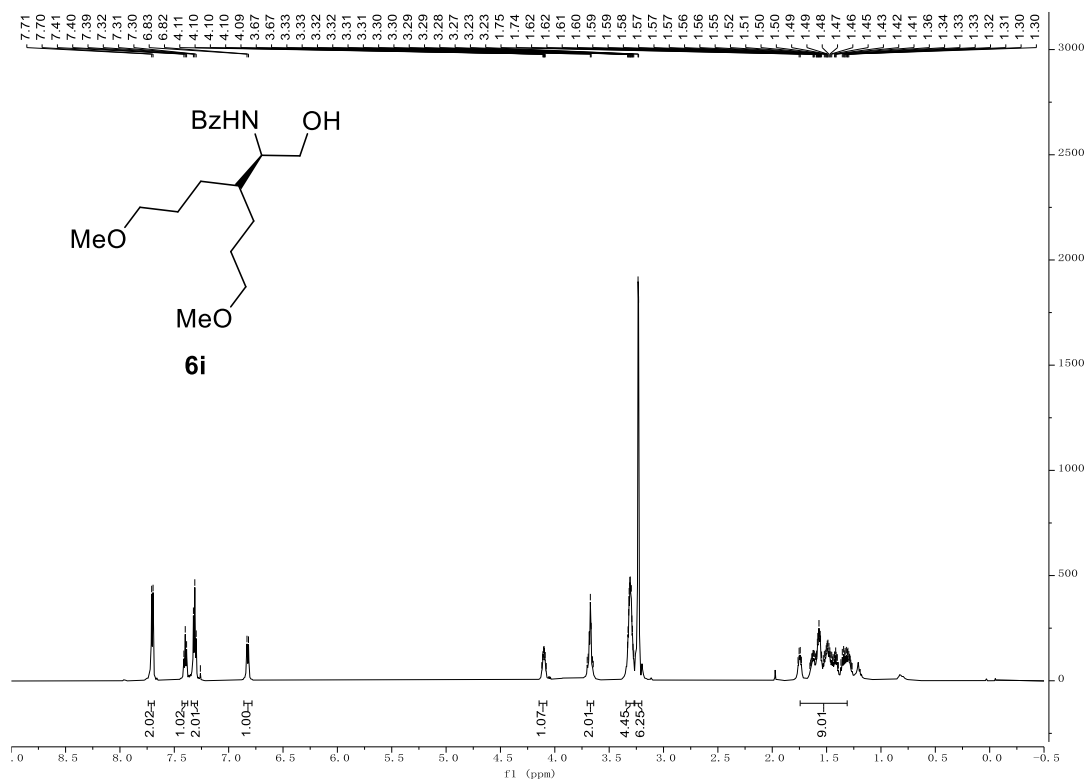
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6g**



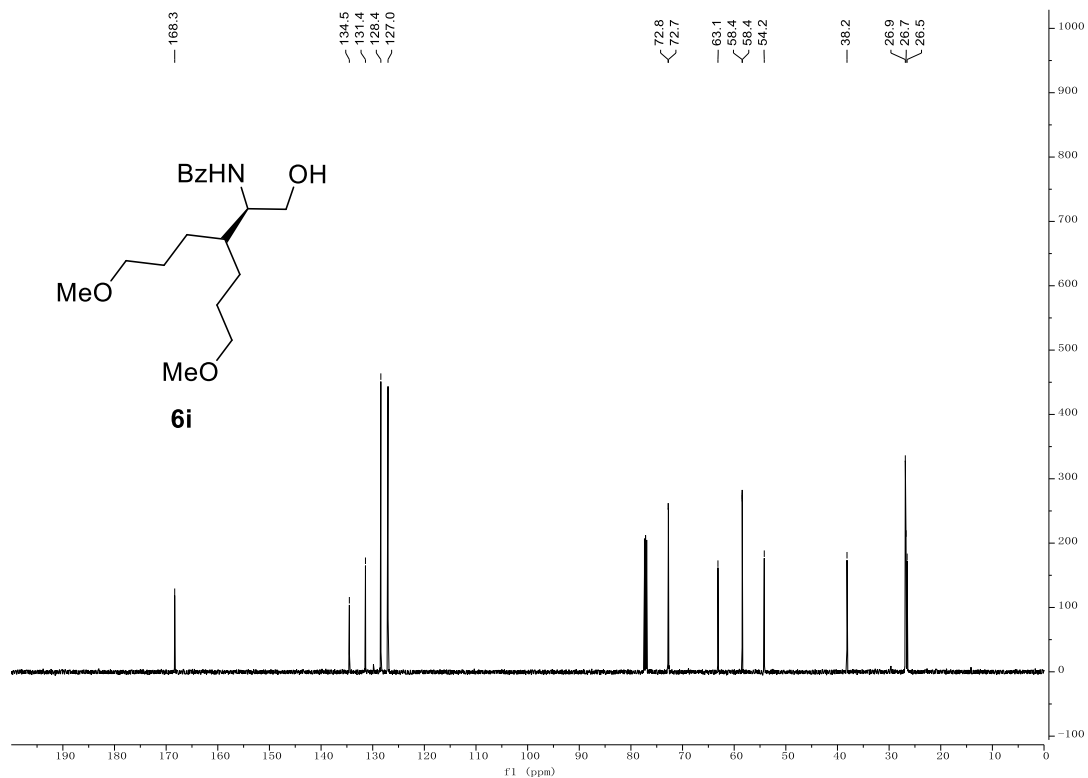
^1H NMR (600 MHz, CDCl_3) spectrum for **6h**



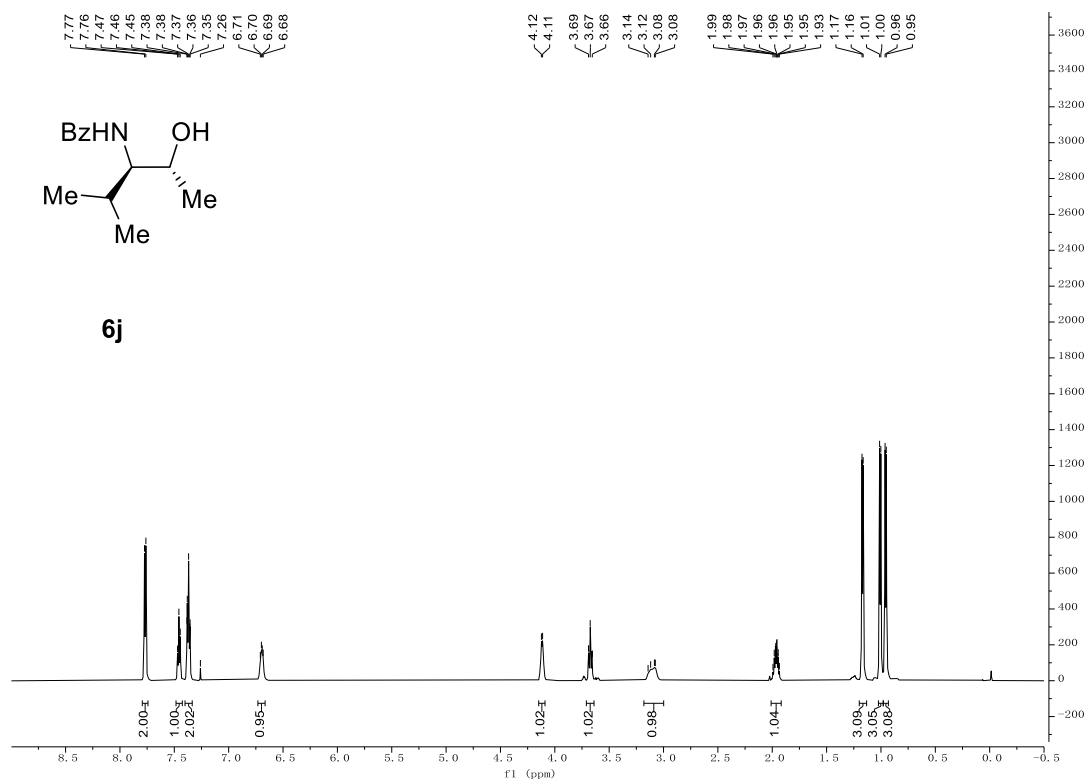
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6h**



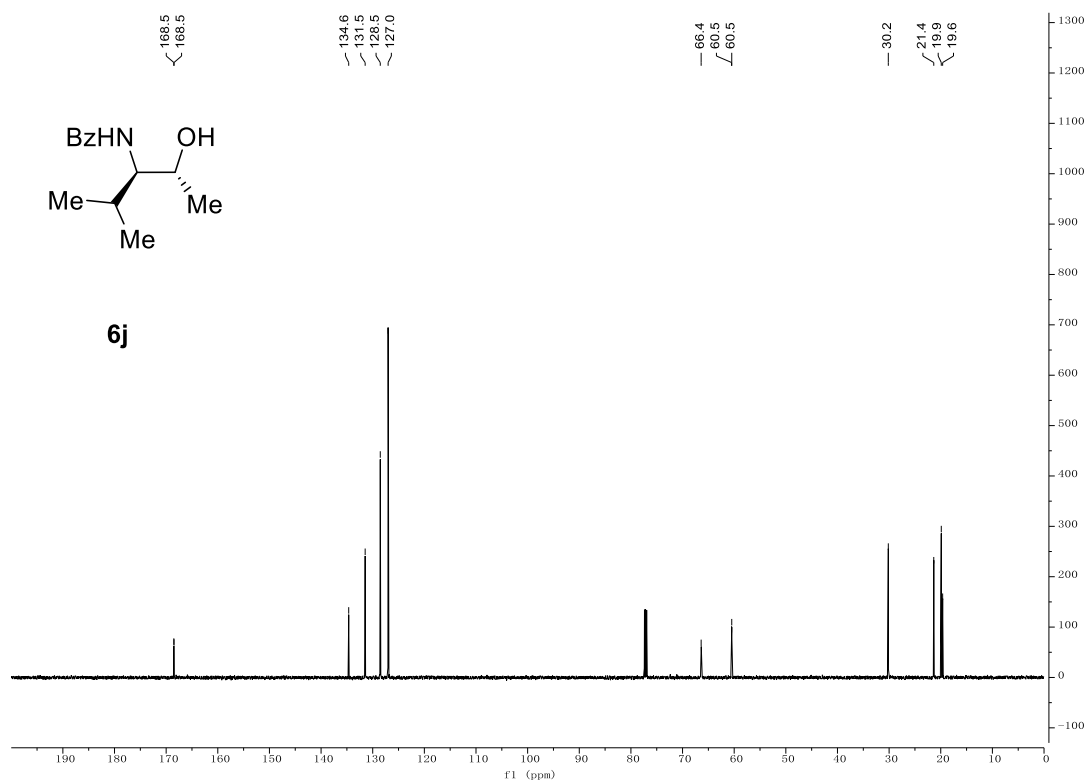
¹H NMR (600 MHz, CDCl₃) spectrum for **6i**



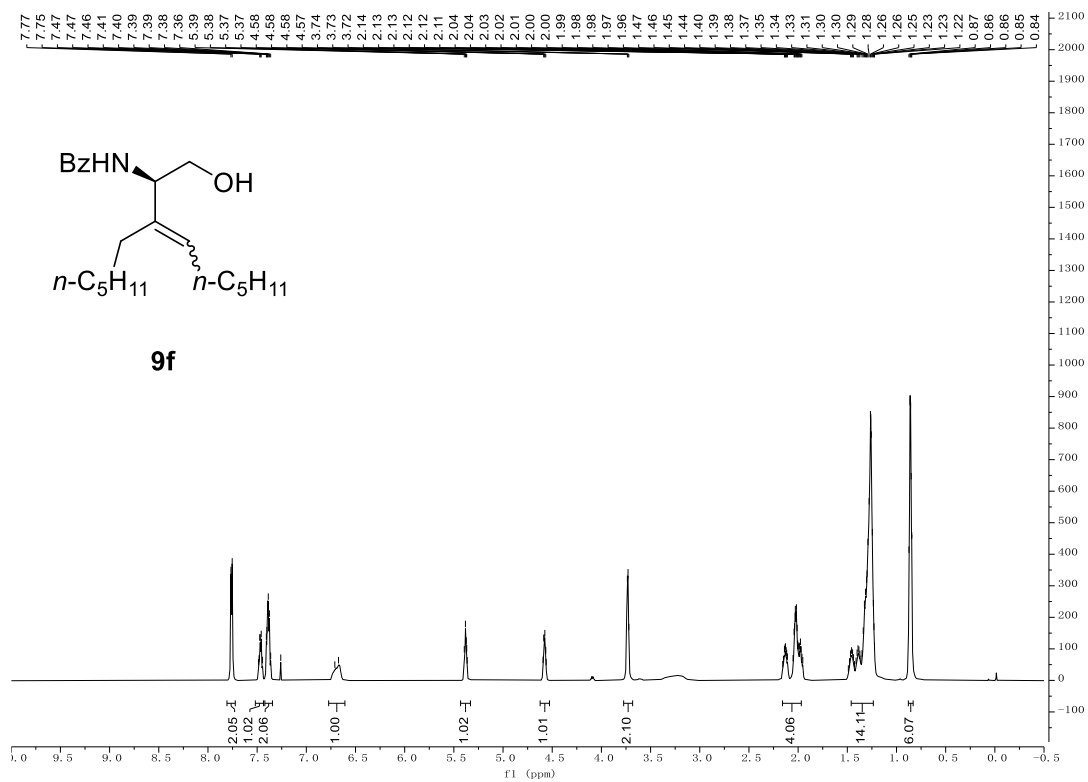
¹³C NMR (151 MHz, CDCl₃) spectrum for **6i**



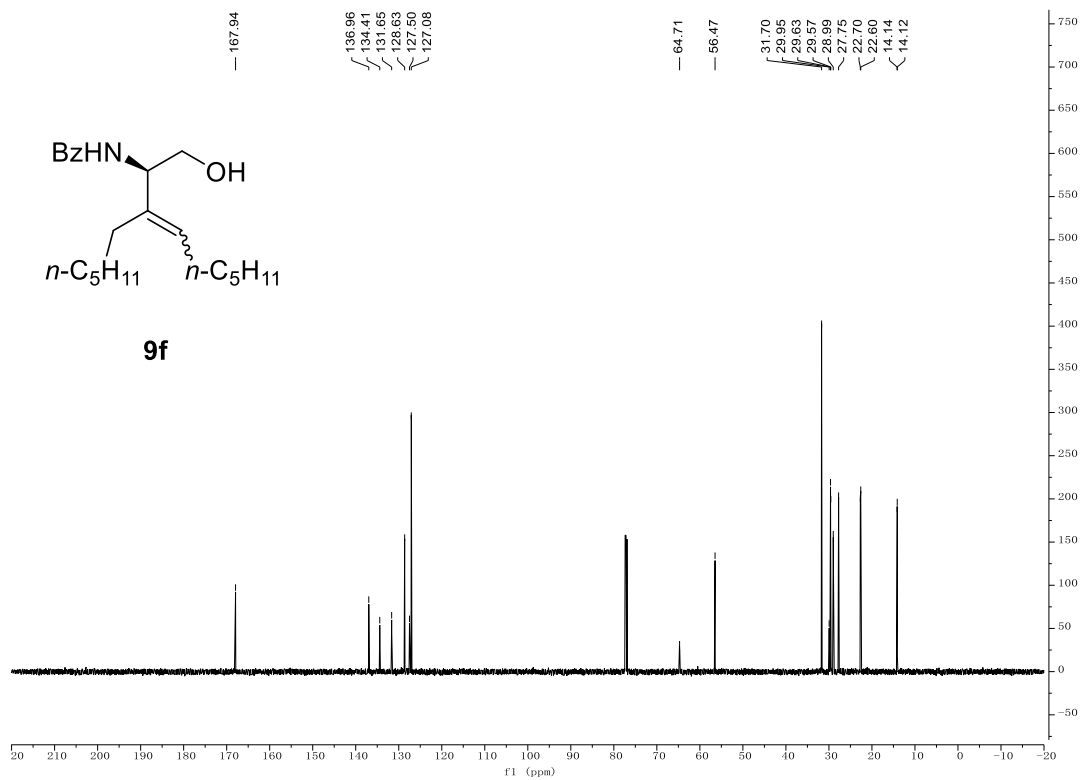
^1H NMR (600 MHz, CDCl_3) spectrum for **6j**



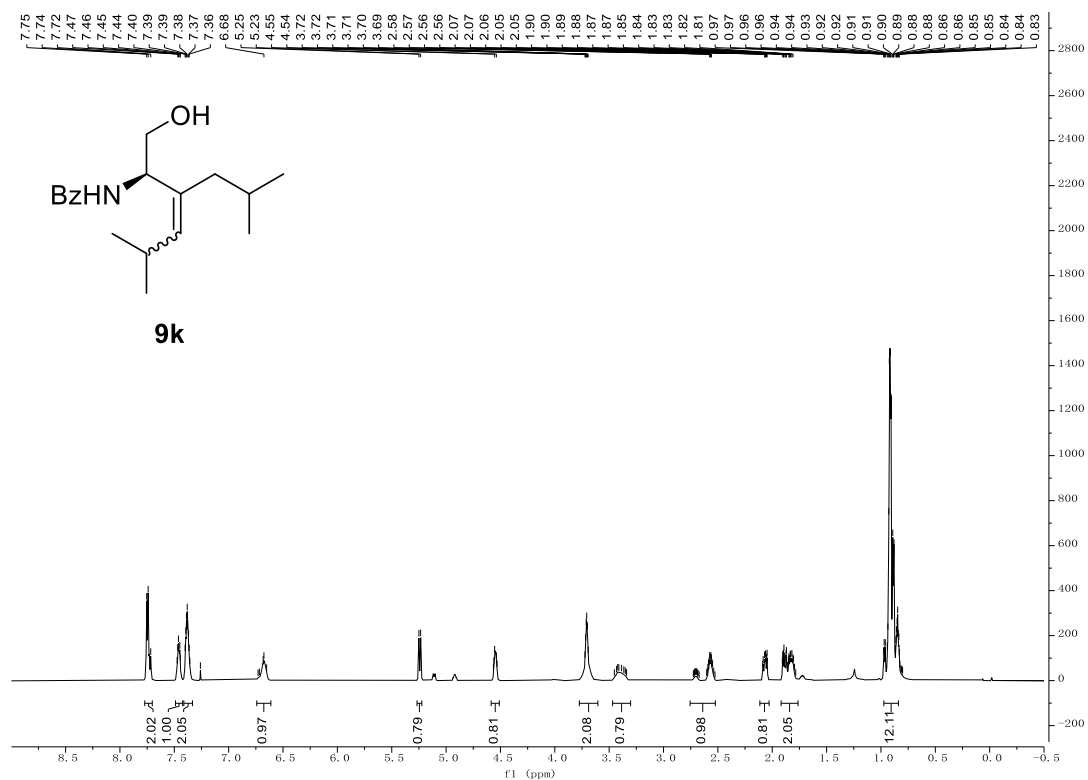
^{13}C NMR (151 MHz, CDCl_3) spectrum for **6j**



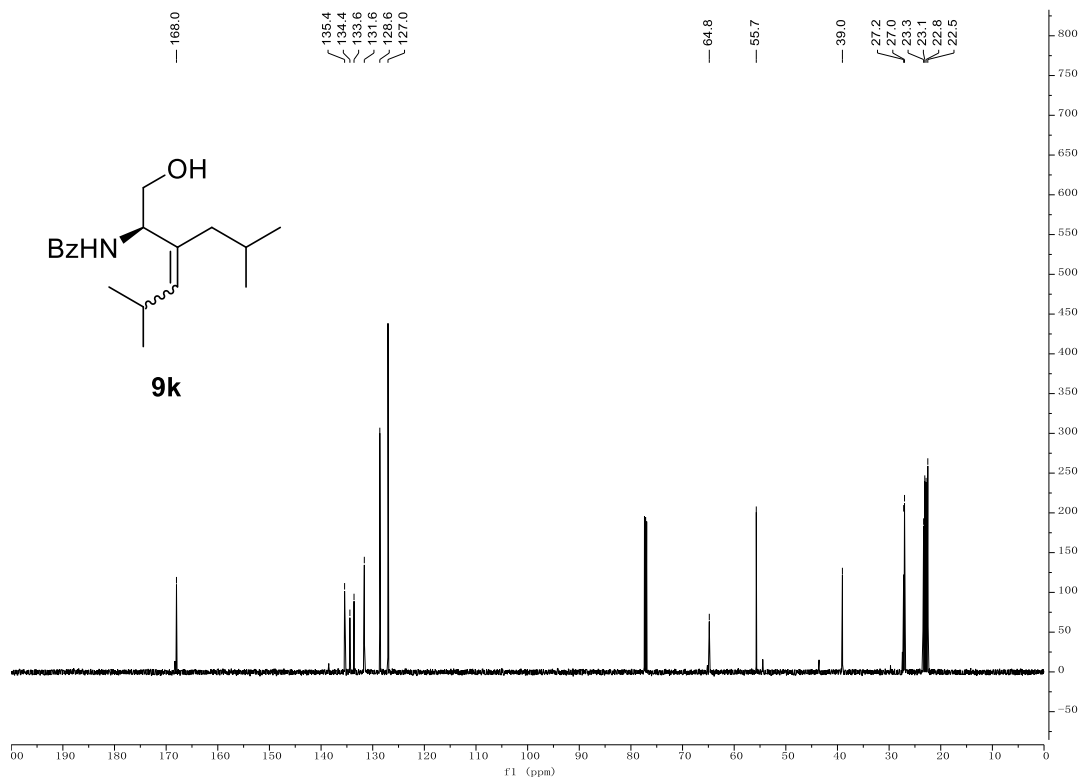
$^1\text{H NMR}$ (600 MHz, CDCl_3) spectrum for **9f**



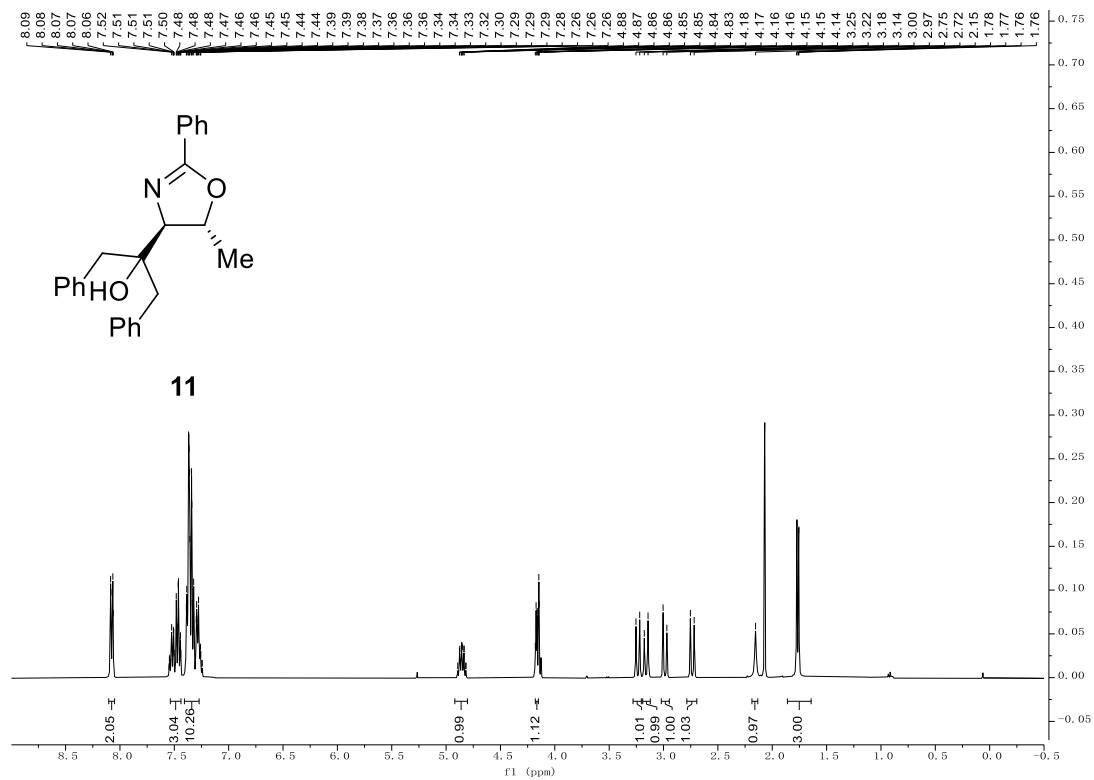
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) spectrum for **9f**



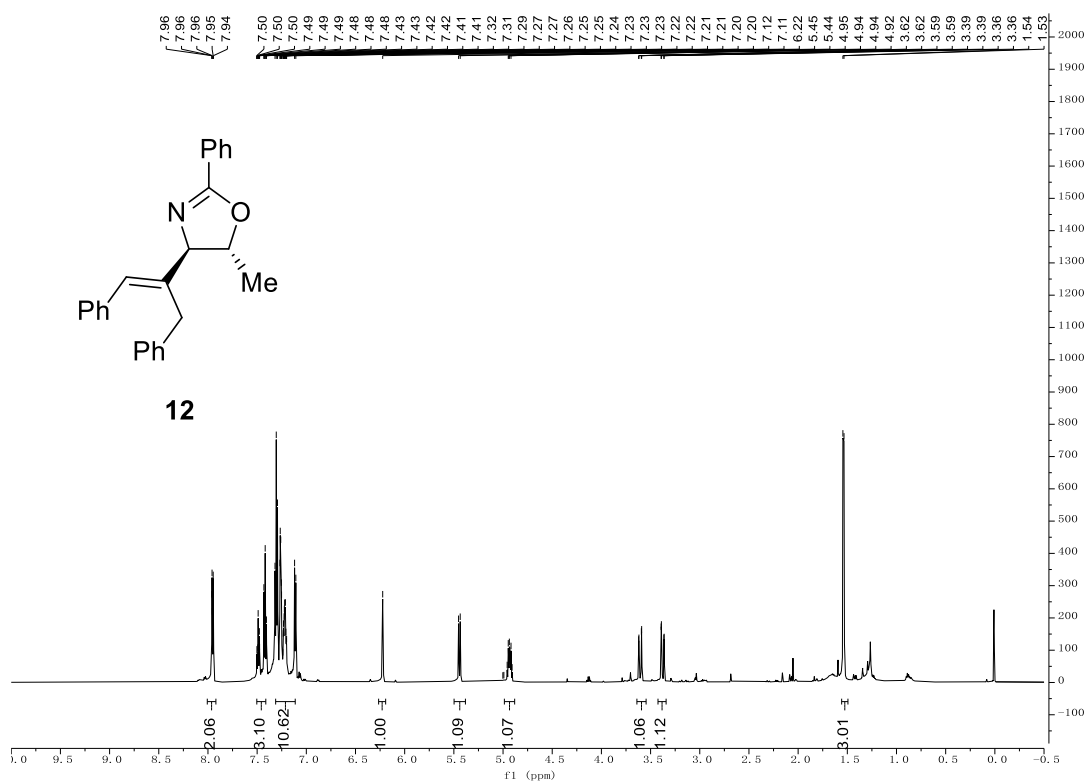
$^1\text{H NMR}$ (600 MHz, CDCl_3) spectrum for **9k**



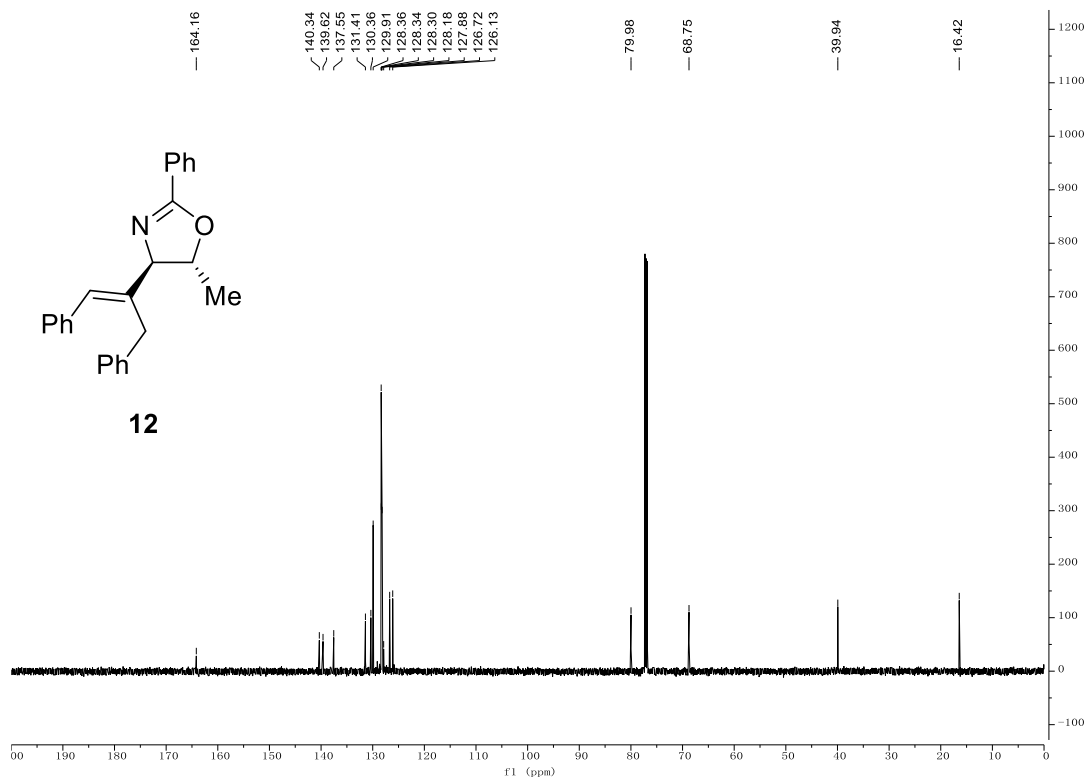
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) spectrum for **9k**



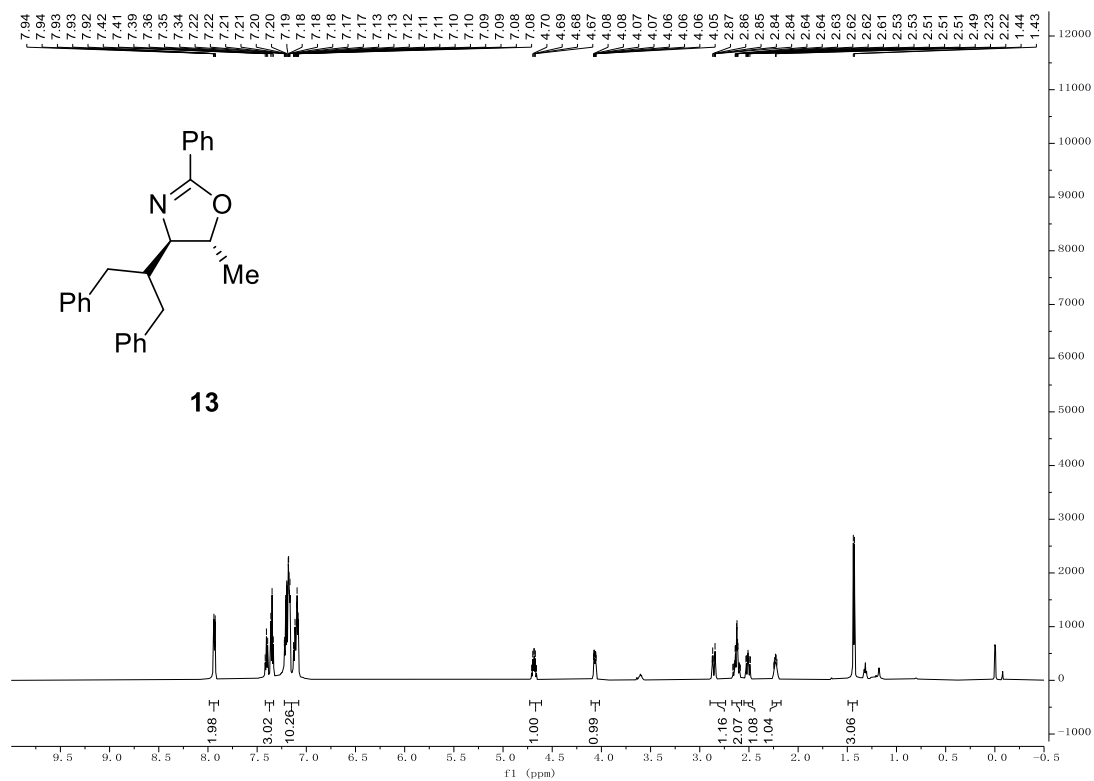
^1H NMR (600 MHz, CDCl_3) spectrum for **11**



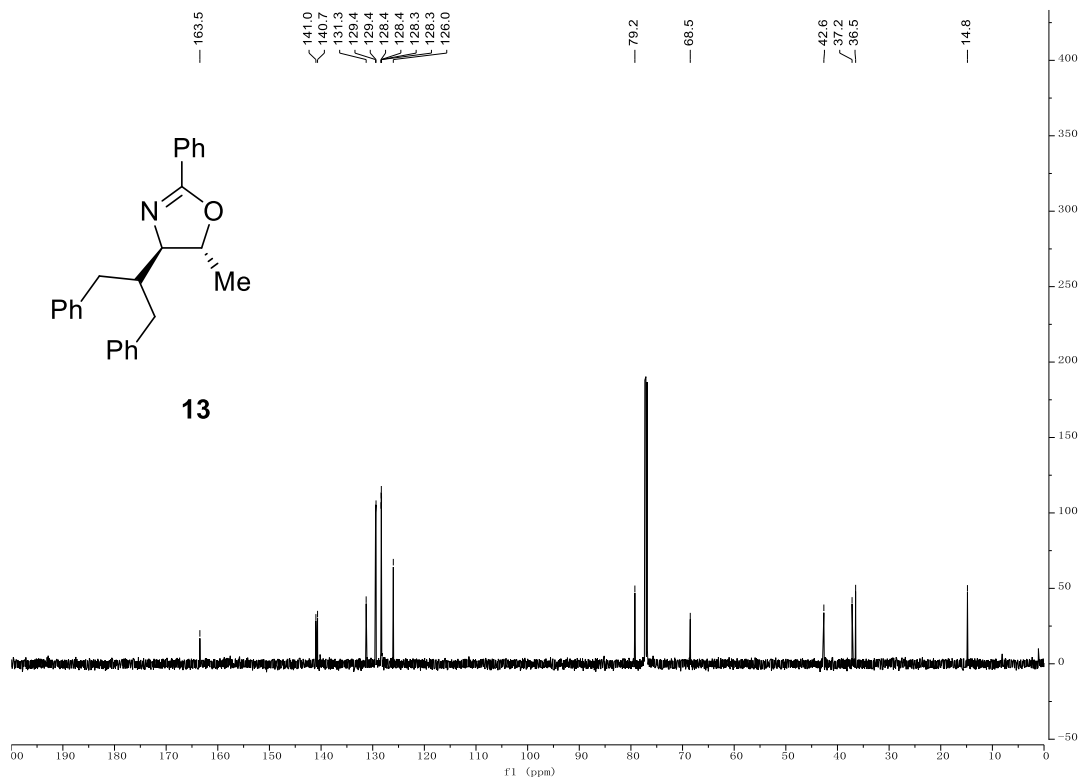
^1H NMR (600 MHz, CDCl_3) spectrum for **12**



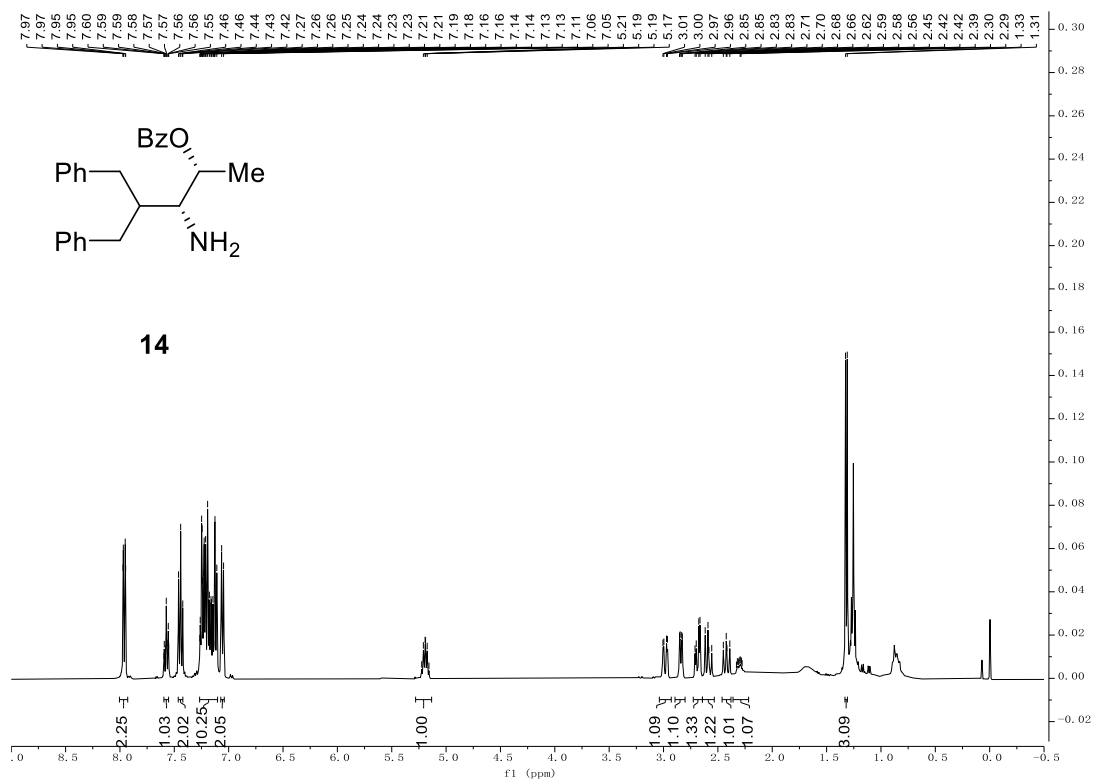
¹³C NMR (151 MHz, CDCl₃) spectrum for **12**



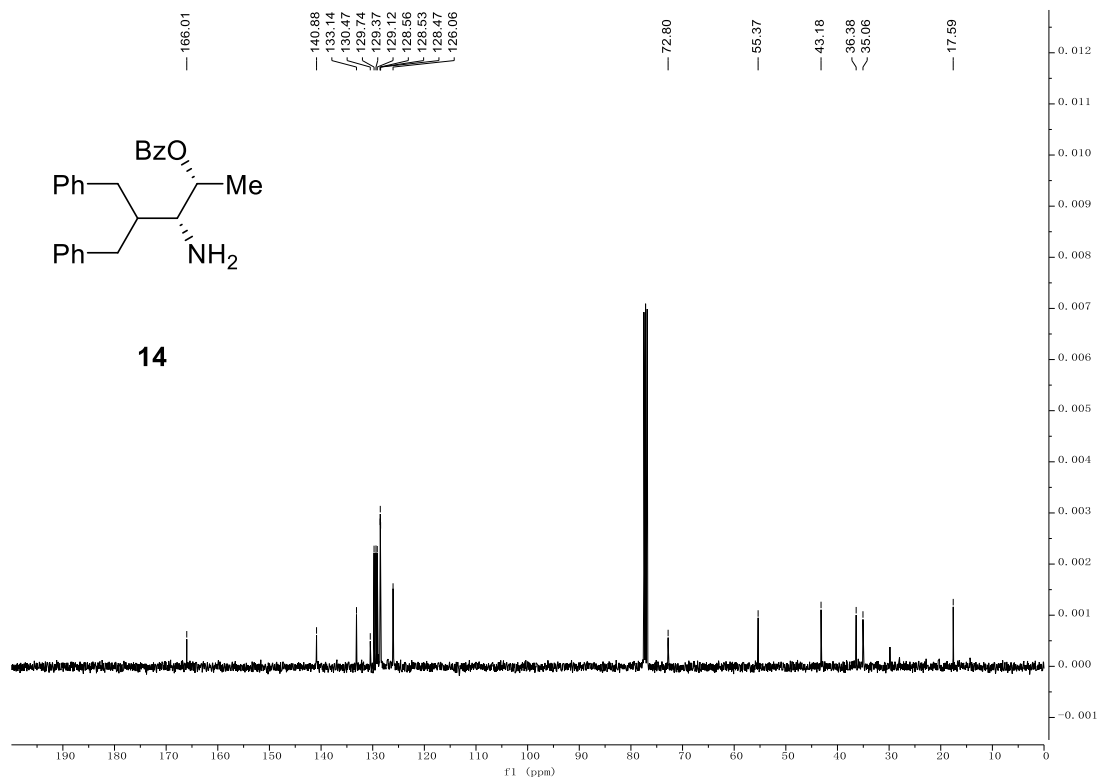
¹H NMR (600 MHz, CDCl₃) spectrum for **13**



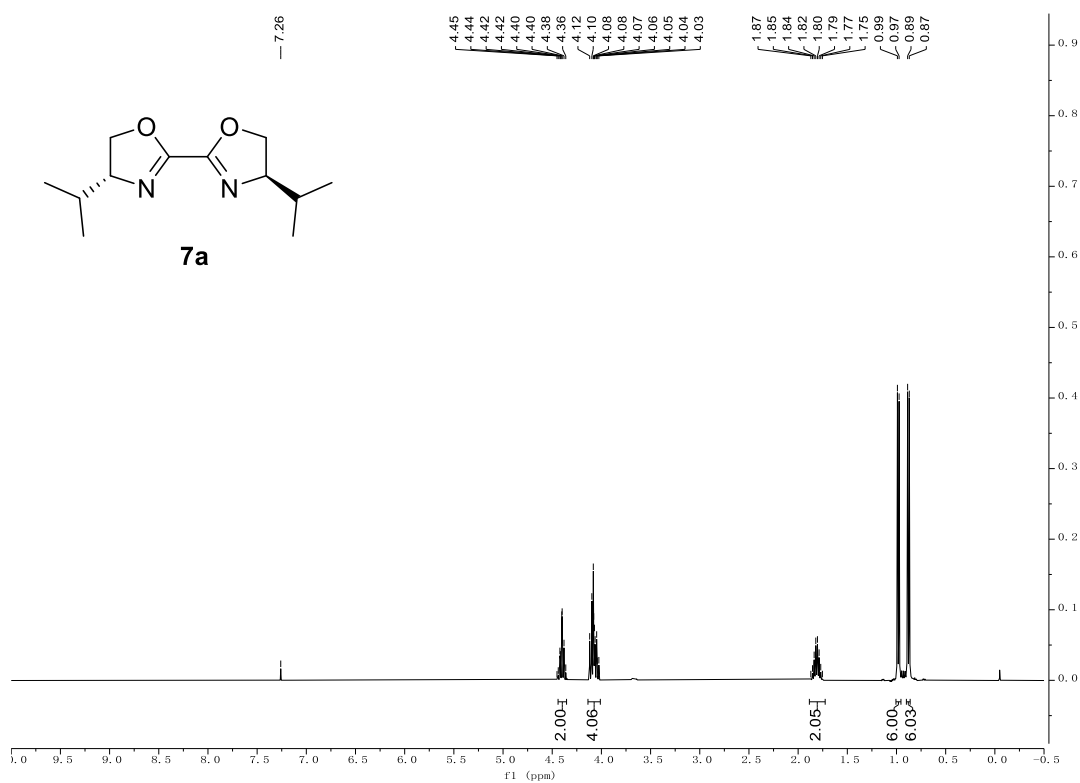
^{13}C NMR (151 MHz, CDCl_3) spectrum for **13**



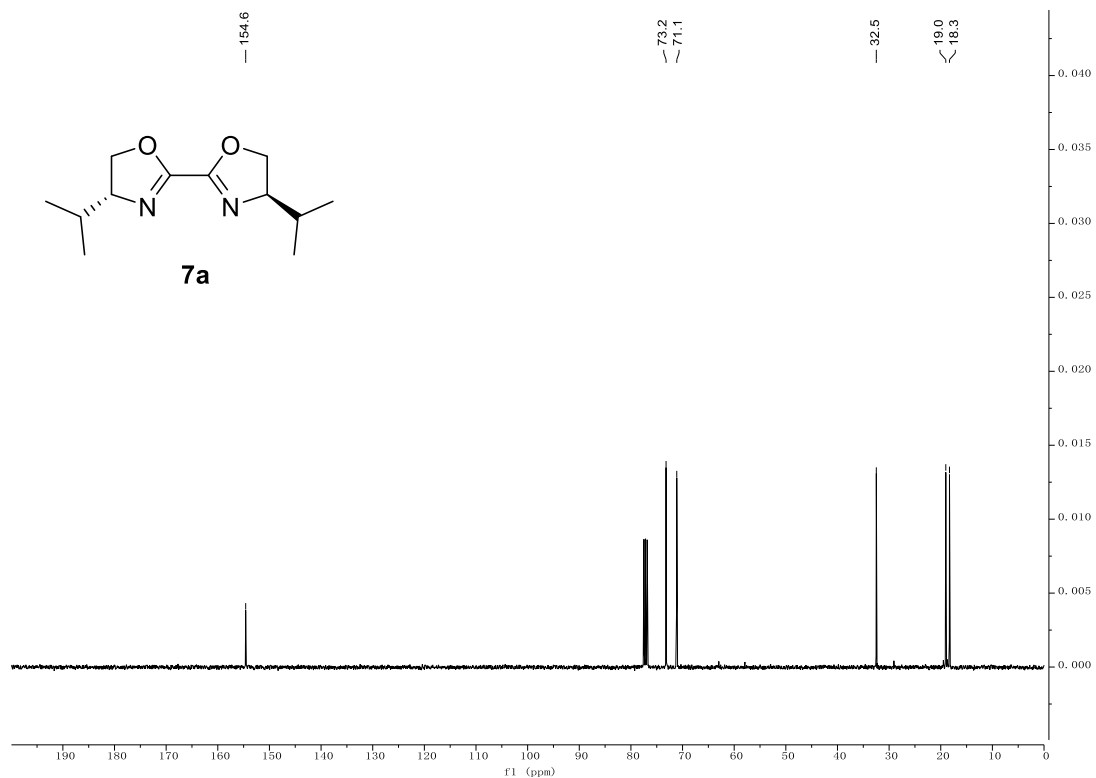
^1H NMR (400 MHz, CDCl_3) spectrum for **14**



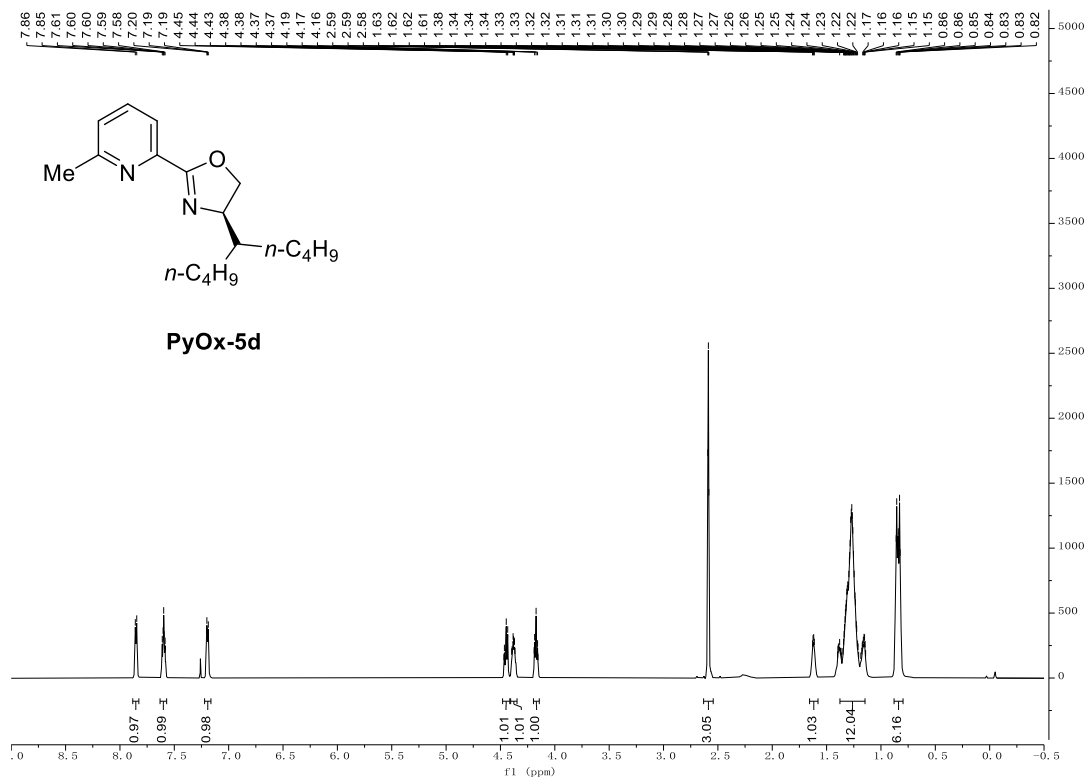
^{13}C NMR (101 MHz, CDCl_3) spectrum for **14**



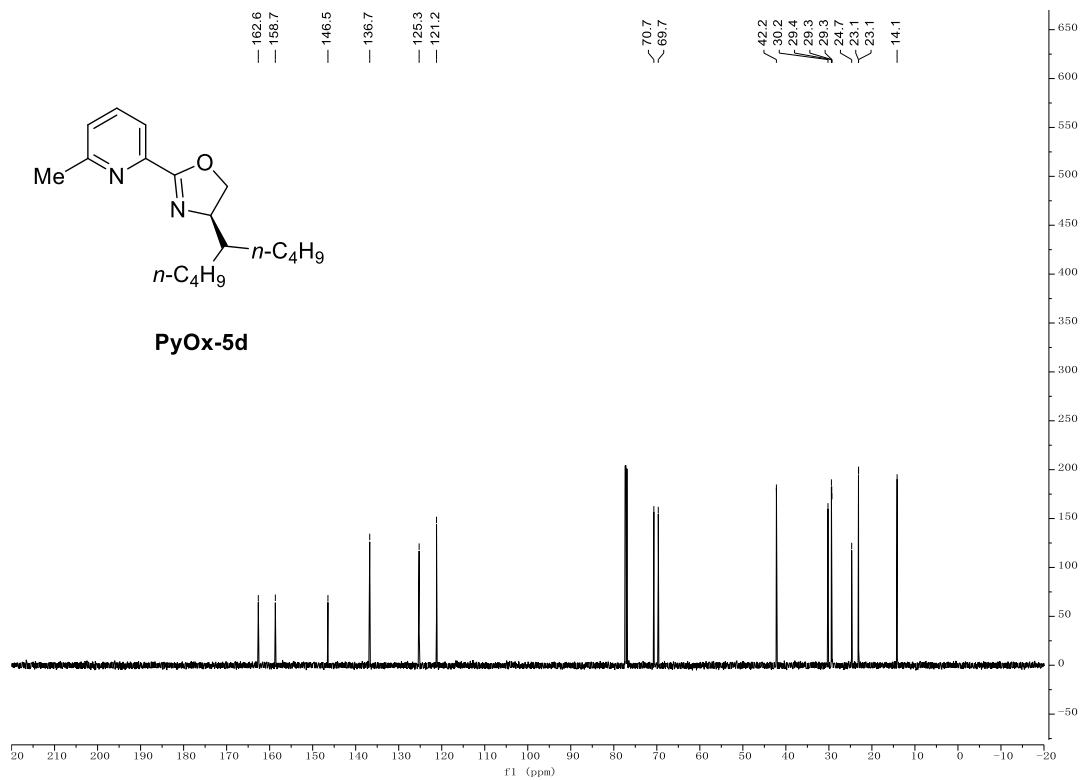
^1H NMR (400 MHz, CDCl_3) spectrum for **7a**



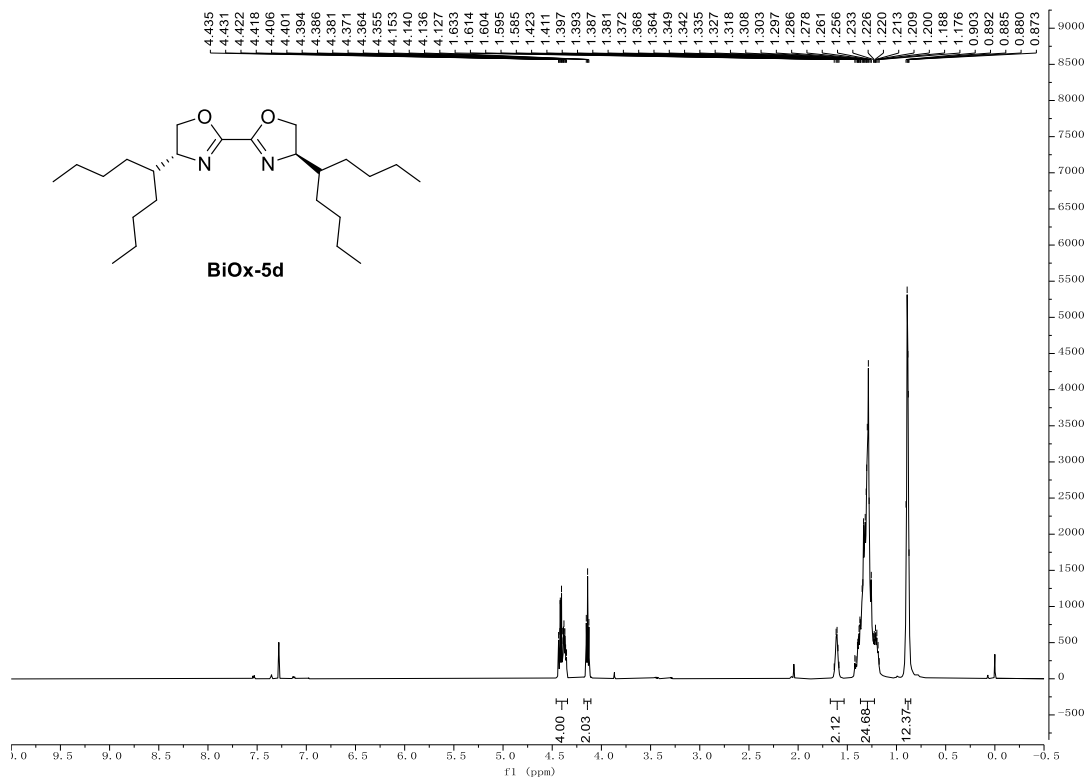
^{13}C NMR (101 MHz, CDCl_3) spectrum for **7a**



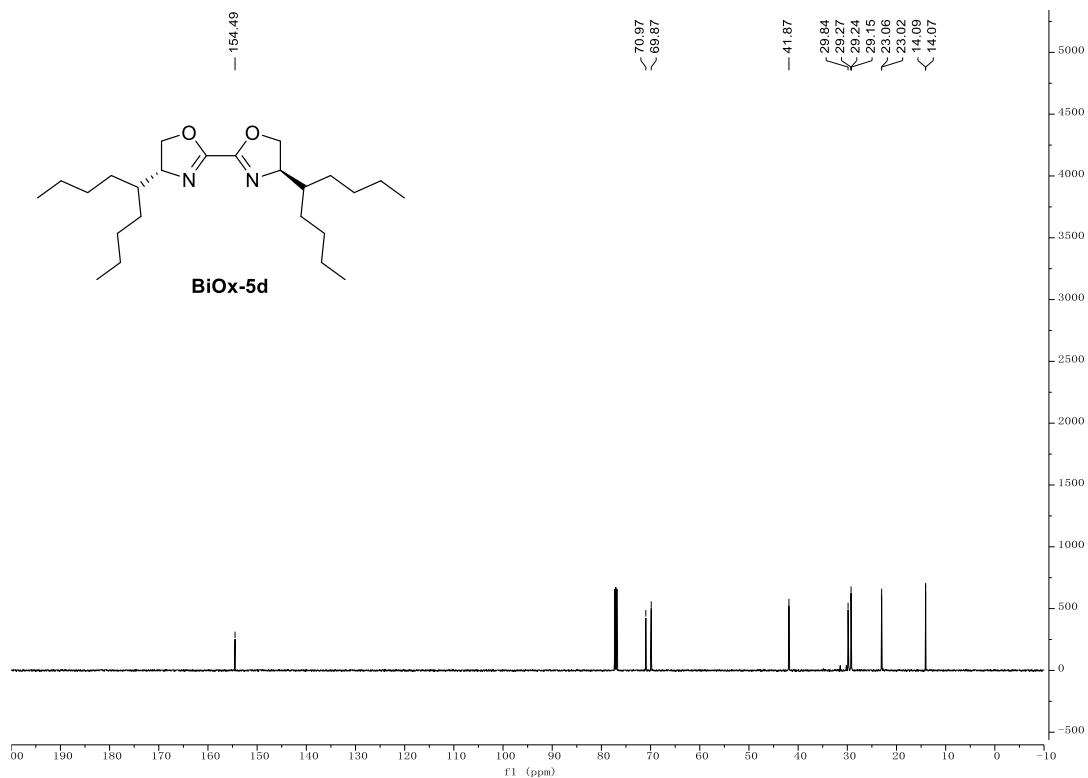
^1H NMR (600 MHz, CDCl_3) spectrum for **PyOx-5d**



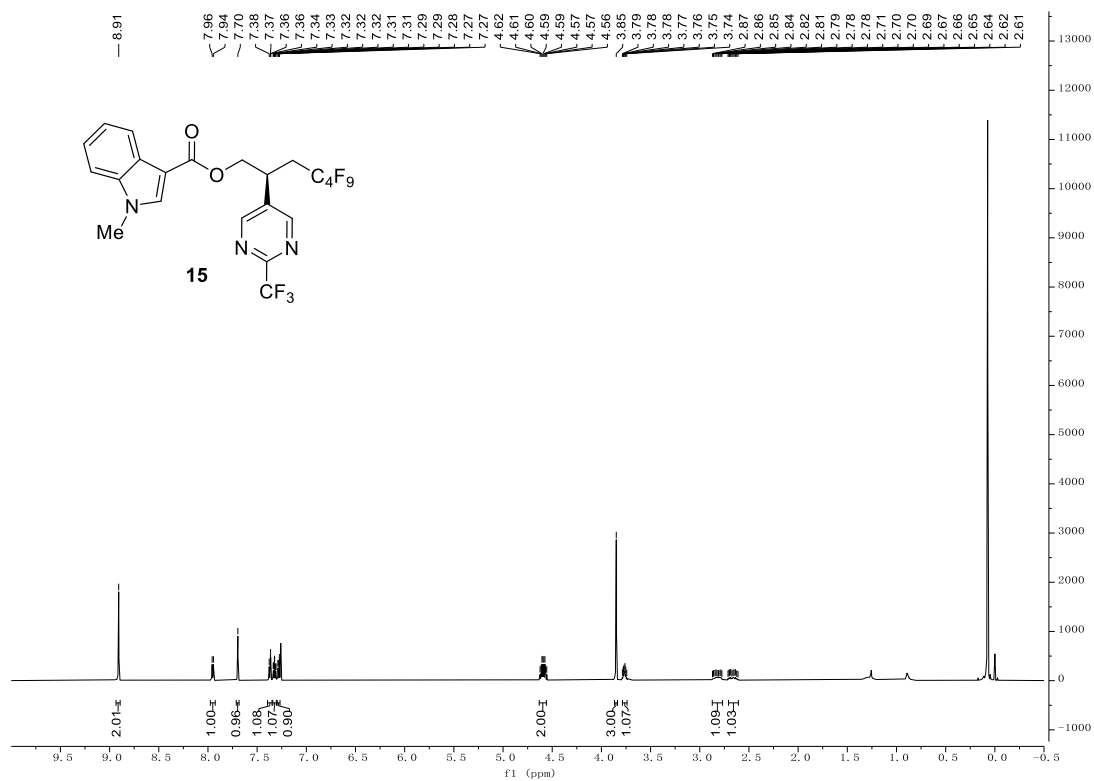
^{13}C NMR (151 MHz, CDCl_3) spectrum for **PyOx-5d**



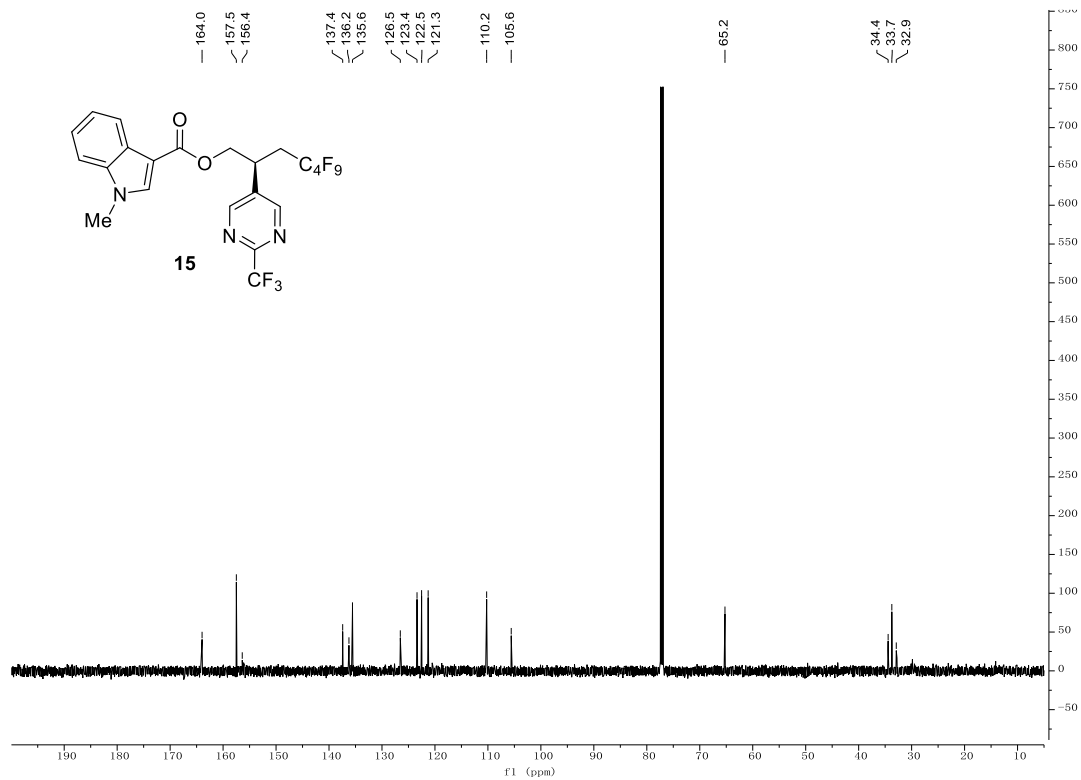
^1H NMR (600 MHz, CDCl_3) spectrum for **BiOx-5d**



^{13}C NMR (151 MHz, CDCl_3) spectrum for **BiOx-5d**



^1H NMR (600 MHz, CDCl_3) spectrum for **15**



¹³C NMR (151 MHz, CDCl₃) spectrum for **15**



¹⁹F NMR (565 MHz, CDCl₃) spectrum for **15**

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