Supplementary Information for

Enantioselective and Diastereoselective Boron Conjugate Addition to α-Alkyl α,β-Unsaturated Esters

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I. General Information

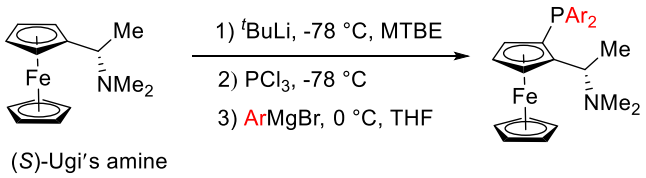
All air or moisture sensitive reactions were conducted in oven-dried glassware under an atmosphere of argon using dry solvents. Anhydrous solvents were obtained by distillation over Na/benzophenone (MTBE, toluene). Unless otherwise noted, other anhydrous solvents (including deuterated solvents) and reagents were obtained from commercial sources (Adamas-beta®, Energy Chemical®) and used without further purification. For product purification, flash column chromatography was performed on silica gel (200~300 and 300~400 mesh). Analytical thin layer chromatography (TLC) was visualized with UV light, or stained with $KMnO_4$ and phosphomolybdic acid hydrate solutions or I_2. NMR data including ^1H NMR or ^{13}C NMR spectra were recorded on Bruker Ascend 500 MHz or Bruker AVANCE III 400 MHz NMR. ^1H NMR chemical shifts were recorded in ppm relative to residual signals of the solvent ($CDCl_3$ at 7.26 ppm). ^{13}C NMR chemical shifts were recorded in ppm relative to the solvent ($CDCl_3$ at 77.16 ppm). The substrates (**1**) and the chiral ligands (**L1**–**L5**) were prepared according to the literature procedures. The known compounds were characterized by ^1H NMR. The new compounds were characterized by ^1H, ^{13}C NMR and HRMS. Coupling constants (*J*) were reported in Hz.

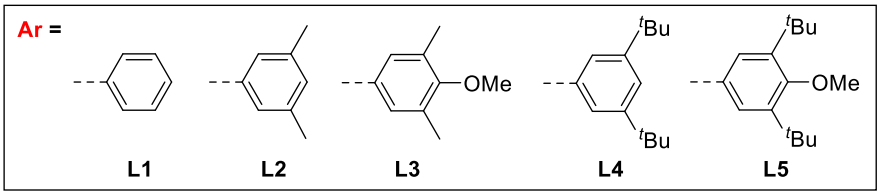
High resolution mass spectra were obtained from Thermo Scientific LTQ Orbitrap XL. High-pressure liquid chiral chromatography (HPLC) was performed on Agilent 1100 Series using a chiral column (25 cm) as noted for each chiral compound. Enantiomer excess was determined by HPLC analysis employing Chiralpak AD-H and OD-H column with ^{n}hexane/^{i}PrOH (or ^{n}hexane/EtOH) as the eluent. Optical rotations were measured on an Anton Paar's high-precision digital polarimeter MCP 300 series using a sodium lamp (589 nm) as the light source over a path length of 10 cm.

X-ray diffraction data collection of **3e** was recorded by Bruker D8 VENTURE system with PHOTON II CPAD detector and a Ga-target Liquid METALJET D2 PLUS X-ray Source (λ = 1.34139 Å). The structure was solved by SHELXT (version 2018/2) and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3) through the OLEX2 graphical interface.

II. Preparation of the Chiral Ligands and Substrates

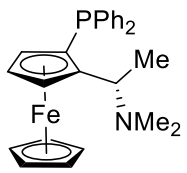
a). Preparation of the Ligands[1]





Typical procedure for the synthesis of *ent*-L4: A dried 100 mL Schlenk tube was charged with (*R*)-Ugi's amine (1.0 g, 3.89 mmol) and methyl *tert*-butyl ether (MTBE, 10 mL) under the protection of argon. 1.3 M ^{t}BuLi solution in ^{n}pentane (3.14 mL, 4.08 mmol) was added dropwise and the resulting mixture was stirred at –78 ℃ for one hour. The mixture was warmed to room temperature and then stirred for another hour. Then, the mixture was cooled to –78 ℃ again, and PCl_3 (distilled prior to use) (614 mg, 4.47 mmol) was added and the mixture was stirred at –78 ℃ for one hour. Grignard reagent freshly prepared (see the details below, 5 equivalents) was added dropwise at 0 ℃ and the reaction was stirred overnight. The resulting mixture was quenched by 2 M NaOH solution and stirred for 30 min, and then extracted with CH_2Cl_2 for three times. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate/ Et_3N = 10:1:0.1) to afford *ent*-**L4** as a yellow solid (1.9 g, 73%).

Preparation of the Grignard reagent: A dried 100 mL three-necked flask was charged with magnesium chips (567 mg, 23.3 mmol) and tetrahydrofuran (THF, 5 mL). A dried 25 mL dropping funnel was charged 3,5-di-*tert*-butylbromobenzene (5.2 g, 19.4 mmol) and 10 mL THF. A grain of iodine was added under the protection of argon. Then, 4~5 drops of the aryl bromide solution was added at 65 ℃. After the reaction was initiated, the aryl bromide solution was added slowly (2~3 s/drop). The mixture was then stirred for 2~3 hours at 65 ℃. The resulting suspension was cooled to room temperature, and then used in the synthesis of *ent*-**L4**.

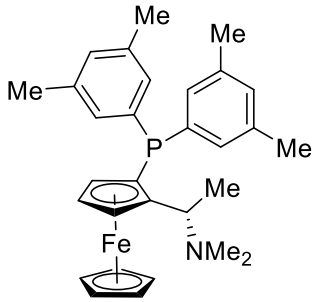


L1

(*S*, R_p)-*N*, *N*-Dimethyl-2-(diphenylphosphinoferrocenyl) ethylamine (L1)[1d]:

Orange solid (280 mg, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2H, Ar–H), 7.36–7.34 (m, 3H, Ar–H), 7.20–7.16 (m, 5H, Ar–H), 4.38 (s, 1H, Cp–H), 4.25 (s, 1H, Cp–H), 4.17–4.14 (q, *J* = 4.9 Hz, 1H, CH), 3.94 (s, 5H, Cp–H), 3.86 (s, 1H, Cp–H), 1.77 (s, 6H, NCH_3), 1.27 (d, *J* = 7.1 Hz, 3H, CH_3).

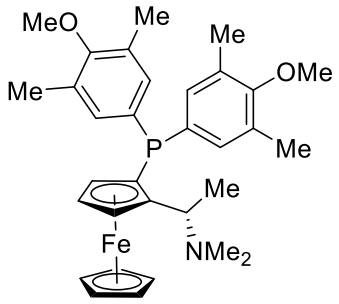


L2

(*S*, R_p)-*N*, *N*-Dimethyl-2-di(3,5-bis(methyl) phosphinoferrocenyl) ethylamine (L2)[1a]:

Orange solid (715 mg, 37% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H, Ar–H), 6.99 (s, 1H, Ar–H), 6.79 (d, *J* = 7.2 Hz, 3H, Ar–H), 4.36 (s, 1H, Cp–H), 4.24 (s, 1H, Cp–H), 4.11–4.07 (q, *J* = 6.8 Hz, 1H, CH), 3.92 (s, 5H, Cp–H), 3.88 (s, 1H, Cp–H), 2.32 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 1.81 (s, 6H, NCH_3), 1.29 (d, *J* = 6.8 Hz, 3H, CH_3).

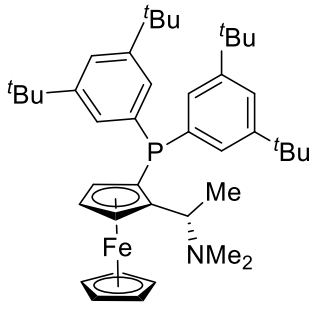


L3

(*S*, R_p)-*N*, *N*-Dimethyl-2-di(3,5-bis(methyl)-4-methoxyphenyl) phosphinoferrocenyl) ethylamine (L3):

Orange solid (778 mg, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H, Ar–H), 6.82 (d, *J* = 7.8 Hz, 2H, Ar–H), 4.36 (s, 1H, Cp–H), 4.24 (s, 1H, Cp–H), 4.13–4.07 (q, *J* = 7.0 Hz, 1H, CH), 3.92 (s, 5H, Cp–H), 3.88 (s, 1H, Cp–H), 3.74 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.29 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 1.80 (s, 6H, NCH_3).

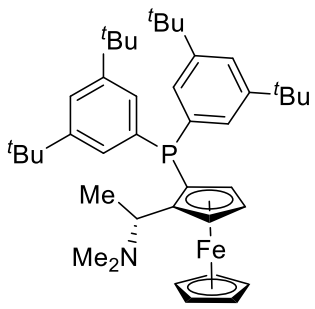


L4

(*S, R*$_p$)-*N, N*-Dimethyl-2-di(3,5-bis(*tert*-butyl)) phosphinoferrocenyl) ethylamine (L4):

Yellow foam solid (967 mg, 31% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H, Ar–H), 7.39 (s, 1H, Ar–H), 7.19 (d, J = 7.4 Hz, 3H, Ar–H), 4.32 (s, 1H, Cp–H), 4.21 (s, 1H, Cp–H), 3.92 (s, 5H, Cp–H), 3.85 (s, 1H, Cp–H), 1.68 (s, 6H, NCH_3), 1.31 (s, 18H, ^{t}Bu). 1.21 (s, 18H, ^{t}Bu).

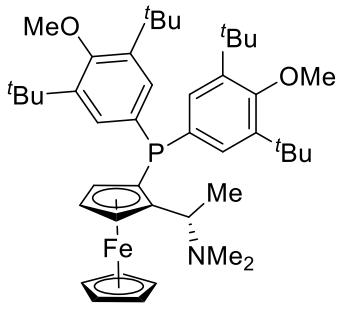


ent-**L4**

(*R, S*$_p$)-*N, N*-Dimethyl-2-di(3,5-bis(*tert*-butyl)) phosphinoferrocenyl) ethylamine (*ent*-L4)[1a]**:**

Yellow foam solid (1.9 g, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.52 (dd, J = 1.9 Hz, 8.4 Hz, 2H, Ar–H), 7.39 (s, 1H, Ar–H), 7.20–7.18 (m, 3H, Ar–H), 4.35 (s, 1H, Cp–H), 4.23 (s, 1H, Cp–H), 4.14–4.10 (q, J = 7.1 Hz, 1H, CH), 3.92 (s, 5H, Cp–H), 3.87 (s, 1H, Cp–H), 1.70 (s, 6H, NCH_3), 1.31 (s, 18H, ^{t}Bu). 1.21 (s, 18H, ^{t}Bu).



L5

(*S,R*$_p$)-*N,N*-Dimethyl-2-di(3,5-bis(*tert*-butyl)-4-methoxyphenyl)phosphinoferrocenyl)

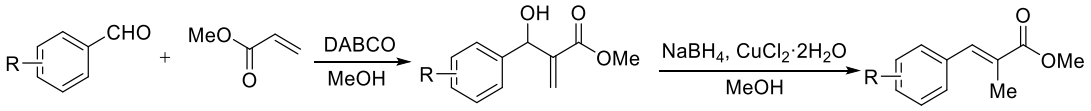
ethylamine (L5)[1e]**:**

Orange solid (930 mg, 33% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 2H, Ar–H), 7.21 (d, J = 8.4 Hz, 2H, Ar–H), 4.14–4.10 (q, J = 7.1 Hz, 1H, CH), 3.93 (s, 5H, Cp–H), 3.70 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 2.17 (s, 9H, CH_3), 1.41 (s, 18H, ^{t}Bu), 1.31 (s, 18H, ^{t}Bu).

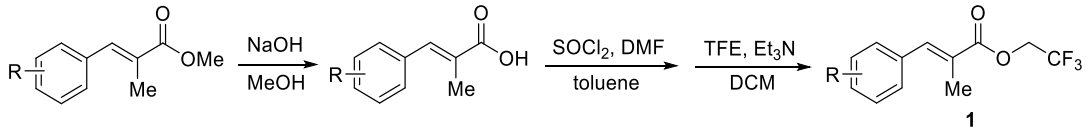
b). Preparation of the Substrates

General Procedure



A solution of mono-substituted benzaldehyde (843 mg, 6 mmol), methyl acrylate (1.0 g, 12 mmol), triethylenediamine (DABCO, 1.4 g, 12 mmol) in methanol (2 mL) was stirred at room temperature. After completion of reaction as monitored by TLC, the mixture was washed with water and extracted with CH_2Cl_2 for three times. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to afford the desired product[2a,b].

The above product (500 mg, 2.2 mmol) and $CuCl_2·2H_2O$ (563 mg, 3.3 mmol) were dissolved in methanol (5 mL), and then stirred for 15 min at room temperature. After that, $NaBH_4$ (250 mg, 6.6 mmol) was added and the mixture was stirred for 2 hours at 35~40 ℃. The resulting mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc for three times. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the desired product[2c].

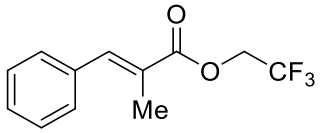


A dried 50 mL round-bottomed flask was charged with methyl cinnamate (0.92 mmol), NaOH solution (1.84 mmol, 2 mol/L) and methanol (2 mL). After completion, the mixture was adjusted to acidic with 1 M HCl and extracted with CH_2Cl_2 for three times. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum to afford the acid as a white solid.

The above acid (173 mg, 0.88 mmol) was dissolved in toluene (5 mL), and then $SOCl_2$ (126 mg, 1.06 mmol) and one drop of *N*,*N*-dimethylformamide (DMF) were added. The mixture was stirred for 7 hours at 90 °C, concentrated in vacuum to remove the solvent and residual thionyl chloride, and then used directly to the next step.

The acyl chloride was treated with TFE (131 mg, 1.32 mmol), Et_3N (267 mg, 2.64 mmol) and CH_2Cl_2 (5 mL). After completion, the mixture was diluted with water and extracted with CH_2Cl_2 for three times. The organic phase was washed with saturated $NaHCO_3$ and the aqueous phase was

back-extracted with CH_2Cl_2. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford the desired product.

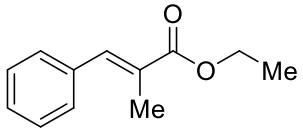


1a

2,2,2-trifluoroethyl (*E*)-2-methyl-3-phenylacrylate (1a)[3]:

Colorless liquid (2.8 g, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H, Alkenyl–H), 7.42–7.34 (m, 5H, Ar–H), 4.63–4.57 (q, J = 8.5 Hz, 2H, CH_2), 2.16 (s, 3H, CH_3).

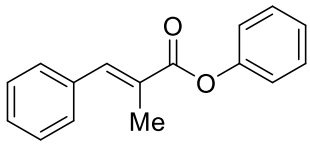


1b

Ethyl (*E*)-2-methyl-3-phenylacrylate (1b)[4]:

Light yellow liquid (1.1 g, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H, Alkenyl–H), 7.41–7.37 (m, 4H, Ar–H), 4.34–4.29 (m, 1H, Ar–H), 4.30–4.25 (q, J = 7.1 Hz, 2H, CH_2), 2.12 (d, J = 1.6 Hz, 3H, CH_3), 1.35 (t, J = 7.2 Hz, 3H, CH_3).

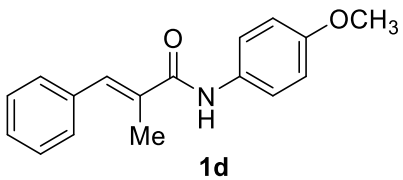


1c

Phenyl (*E*)-2-methyl-3-phenylacrylate (1c)[5]:

Light yellow solid (2.8 g, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H, Alkenyl–H, Ar–H), 7.43–7.31 (m, 8H, Ar–H), 7.14 (t, J = 7.4 Hz, 1H, Ar–H), 2.22 (d, J = 1.4 Hz, 3H, CH_3).

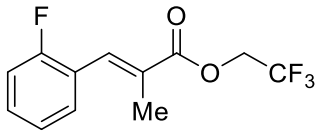


1d

(*E*)-*N*-(4-methoxyphenyl)-2-methyl-3-phenylacrylamide (1d)[6]:

White solid (1.4 g, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.49 (m, 3H), 7.42–7.37 (m, 5H), 7.34–7.31 (m, 1H, Ar–H), 6.90 (d, J = 9.1 Hz, 2H, Ar–H), 3.82 (s, 3H, CH_3), 2.21 (s, 3H, CH_3).



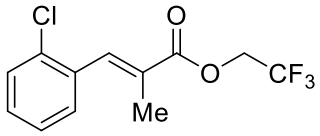
1e

2,2,2-trifluoroethyl (*E*)-3-(2-fluorophenyl)-2-methylacrylate (1e):

Light yellow liquid (502 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H, Alkenyl–H), 7.29–7.22 (m, 2H, Ar–H), 7.08 (t, J = 7.5 Hz, 2H, Ar–H), 7.01 (t, J = 8.6 Hz, 2H, Ar–H), 4.55–4.48 (q, J = 8.4 Hz, 2H, CH_2), 1.98 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.4, 160.5 (d, J = 251.3 Hz), 134.0 (d, J = 4.0 Hz), 130.8 (d, J = 9.1 Hz), 130.6 (d, J = 3.0 Hz), 129.3, 124.0 (d, J = 4.0 Hz), 123.3 (d, J = 14.1 Hz), 123.3 (q, J = 278.3 Hz), 115.9 (d, J = 22.2 Hz), 61.0 (q, J = 36.4 Hz), 14.3.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}F_4O_2Na^+$ $(M+Na)^+$ 285.0509; found 285.0508.



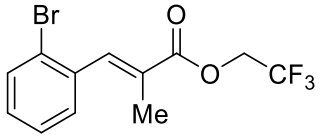
1f

2,2,2-trifluoroethyl (*E*)-3-(2-chlorophenyl)-2-methylacrylate (1f):

Yellow liquid (430 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H, Alkenyl–H), 7.45–7.42 (m, 1H, Ar–H), 7.34–7.26 (m, 3H, Ar–H), 4.65–4.59 (q, J = 8.4 Hz, 2H, CH_2), 2.03 (d, J = 1.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.8, 138.3, 134.3, 133.9, 130.5, 130.0, 129.8, 129.0, 126.7, 123.2 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 14.1.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}ClF_3O_2Na^+$ $(M+Na)^+$ 301.0214; found 301.0213.



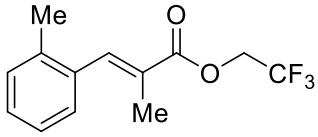
1g

2,2,2-trifluoroethyl (*E*)-3-(2-bromophenyl)-2-methylacrylate (1g):

Yellow liquid (871 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H, Alkenyl–H), 7.54 (d, J = 8.0 Hz, 1H, Ar–H), 7.28–7.20 (m, 2H, Ar–H), 7.14–7.10 (m, 1H, Ar–H), 4.57–4.50 (q, J = 8.5 Hz, 2H, CH_2), 1.93 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.4, 140.5, 135.7, 133.0, 130.6, 130.1, 128.6, 127.2, 124.3, 123.2 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 14.0.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}BrF_3O_2Na^+$ $(M+Na)^+$ 344.9708; found 344.9709.



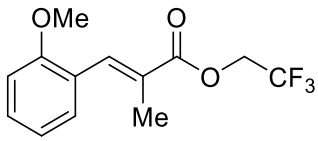
1h

2,2,2-trifluoroethyl (*E*)-2-methyl-3-(*o*-tolyl) acrylate (1h):

Light yellow liquid (342 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H, Alkenyl–H), 7.25–7.20 (m, 4H, Ar–H), 4.64–4.57 (q, J = 8.5 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.00 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.8, 140.7, 137.1, 134.6, 130.3, 128.9, 128.7, 127.6, 125.7, 123.3 (q, J = 278.3 Hz), 60.9 (q, J = 37.4 Hz), 19.9, 13.9.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 281.0760; found 281.0759.



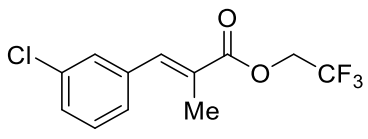
1i

2,2,2-trifluoroethyl (*E*)-3-(2-methoxyphenyl)-2-methylacrylate (1i):

Light yellow liquid (616 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H, Alkenyl–H), 7.28–7.21 (m, 2H, Ar–H), 6.90 (t, J = 7.5 Hz, 1H, Ar–H), 6.84 (d, J = 8.2 Hz, 1H, Ar–H), 4.54–4.48 (q, J = 8.5 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 2.00 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 157.8, 137.4, 130.5, 130.3, 126.8, 124.4, 123.4 (q, J = 278.3 Hz), 120.3, 110.7, 60.8 (q, J = 37.4 Hz), 55.6, 14.2.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_3Na^+$ $(M+Na)^+$ 297.0709; found 297.0710.



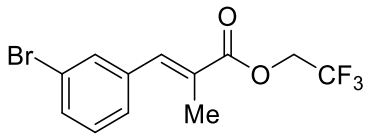
1j

2,2,2-trifluoroethyl (*E*)-3-(3-chlorophenyl)-2-methylacrylate (1j):

Light yellow liquid (437 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H, Alkenyl–H), 7.30–7.18 (m, 4H, Ar–H), 4.55–4.49 (q, J = 8.4 Hz, 2H, CH_2), 2.05 (d, J = 1.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 139.8, 137.1, 134.6, 129.9, 129.6, 128.9, 128.2, 127.9, 123.2 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 14.1.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}ClF_3O_2Na^+$ $(M+Na)^+$ 301.0214; found 301.0213.



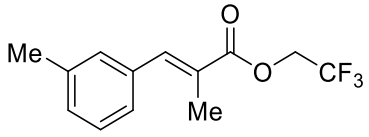
1k

2,2,2-trifluoroethyl (*E*)-3-(3-bromophenyl)-2-methylacrylate (1k):

Light yellow liquid (770 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, Alkenyl–H), 7.54 (s, 1H, Ar–H), 7.48 (d, J = 7.8 Hz, 1H, Ar–H), 7.34–7.26 (m, 2H, Ar–H), 4.63–4.57 (q, J = 8.4 Hz, 2H, CH_2), 2.13 (d, J = 1.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 139.4, 137.4, 132.5, 131.8, 130.1, 128.3, 123.2 (q, J = 278.3 Hz), 122.7, 61.0 (q, J = 36.4 Hz), 14.1.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}BrF_3O_2Na^+$ $(M+Na)^+$ 344.9708; found 344.9710.



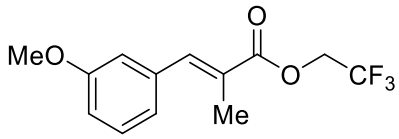
1l

2,2,2-trifluoroethyl (*E*)-2-methyl-3-(*m*-tolyl) acrylate (1l):

Yellow liquid (230 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H, Alkenyl–H), 7.32–7.15 (m, 4H, Ar–H), 4.62–4.56 (q, J= 8.5 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.15 (d, J=1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 141.4, 138.3, 135.4, 130.7, 129.8, 128.5, 127.0, 126.6, 123.3 (q, J = 277.9 Hz), 60.9 (q, J = 36.4 Hz), 21.5, 13.7.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 281.0760; found 281.0760.



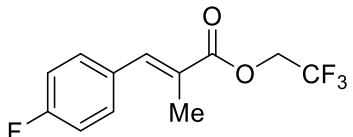
1m

2,2,2-trifluoroethyl (*E*)-3-(3-methoxyphenyl)-2-methylacrylate (1m):

Light yellow liquid (725 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H, Alkenyl–H), 7.32 (t, J = 8.2 Hz, 1H, Ar–H), 7,00 (d, J = 8.5 Hz, 1H, Ar–H), 6.94–6.88 (m, 2H, Ar–H), 4.63–4.56 (q, J = 8.5 Hz, 2H, CH_2), 3.82 (s, 3H, OCH_3), 2.15 (d, J = 1.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.4, 160.1, 141.5, 137.2, 130.0, 127.6, 123.8 (q, J = 278.2 Hz), 123.1, 115.8, 115.0, 61.4 (q, J = 37.4 Hz), 55.8, 14.6.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_3Na^+$ $(M+Na)^+$ 297.0709; found 297.0710.



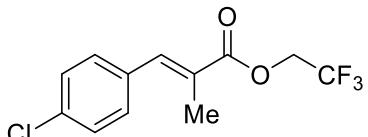
1n

2,2,2-trifluoroethyl (*E*)-3-(4-fluorophenyl)-2-methylacrylate (1n):

Light yellow liquid (706 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H, Alkenyl–H), 7.43–7.39 (m, 2H, Ar–H), 7.10 (t, J = 8.7 Hz, 2H, Ar–H), 4.63–4.57 (q, J = 8.5 Hz, 2H, CH_2), 2.14 (d, J = 1.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 162.9 (d, J = 251.3 Hz), 139.6, 131.9 (d, J = 8.1 Hz), 131.5 (d, J = 3.0 Hz), 126.6 (d, J = 2.0 Hz), 123.3 (q, J = 278.3 Hz), 115.7 (d, J = 21.2 Hz), 61.0 (q, J = 36.4 Hz), 14.0.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}F_4O_2Na^+$ $(M+Na)^+$ 285.0509; found 285.0508.



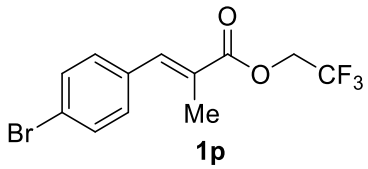
1o

2,2,2-trifluoroethyl (*E*)-3-(4-chlorophenyl)-2-methylacrylate (1o):

Light yellow liquid (213 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H, Alkenyl–H), 7.31–7.25 (dd, J = 8.5 Hz, 16.0 Hz, 4H, Ar–H), 4.55–4.48 (q, J = 8.5 Hz, 2H, CH_2), 2.05 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.8, 139.8, 134.9, 133.8, 131.2, 128.9, 127.4, 123.3 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 14.1.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}ClF_3O_2Na^+$ $(M+Na)^+$ 301.0214; found 301.0211.



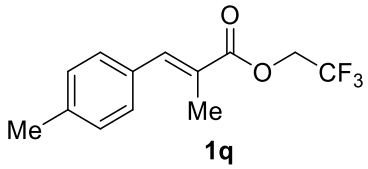
1p

2,2,2-trifluoroethyl (*E*)-3-(4-bromophenyl)-2-methylacrylate (1p):

Yellow liquid (611 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H, Alkenyl–H), 7.46 (d, J = 8.5 Hz, 2H, Ar–H), 7.20 (d, J = 8.5 Hz, 2H, Ar–H), 4.55–4.49 (q, J = 8.5 Hz, 2H, CH_2), 2.04 (d, J = 1.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.8, 139.9, 134.3, 131.9, 131.4, 127.6, 123.2, 123.2 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 13.7.

HRMS (ESI) m/z: calcd for $C_{12}H_{10}BrF_3O_2Na^+$ $(M+Na)^+$ 344.9708; found 344.9708.



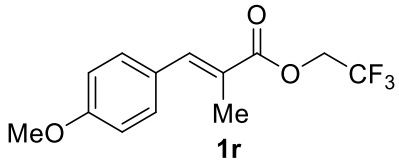
1q

2,2,2-trifluoroethyl (*E*)-2-methyl-3-(*p*-tolyl) acrylate (1q):

Yellow liquid, (597 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H, Alkenyl–H), 7.24 (d, J = 8.2 Hz, 2H, Ar–H), 7.13 (d, J = 8.2 Hz, 2H, Ar–H), 4.53–4.47 (q, J = 8.5 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.07 (d, J = 1.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.2, 141.3, 139.2, 132.6, 130.1, 129.3, 125.8, 123.4 (q, J = 278.3 Hz), 60.9 (q, J = 36.4 Hz), 21.4, 14.1.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 281.0760; found 281.0759.



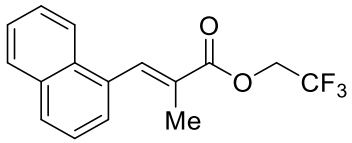
1r

2,2,2-trifluoroethyl (*E*)-3-(4-methoxyphenyl)-2-methylacrylate (1r):

White solid (474 mg, 62% yield), m.p. 66.3–68.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H, Alkenyl–H), 7.42 (d, J = 8.8 Hz, 2H, Ar–H), 6.94 (d, J = 8.9 Hz, 2H, Ar–H), 4.62–4.56 (q, J = 8.5 Hz, 2H, CH_2), 3.85 (s, 3H, CH_3), 2.17 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.8, 160.7, 141.4, 132.3, 128.5, 124.9, 123.8 (q, J = 278.3 Hz), 114.6, 61.4 (q, J = 36.4 Hz), 55.9, 14.6.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_3Na^+$ $(M+Na)^+$ 297.0709; found 297.0710.



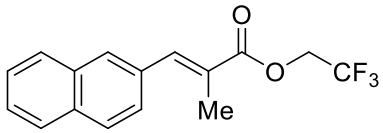
1s

2,2,2-trifluoroethyl (*E*)-2-methyl-3-(naphthalen-1-yl) acrylate (1s):

Yellow liquid (435 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, Alkenyl–H), 7.90–7.83 (m, 3H, Np–H), 7.55–7.46 (m, 3H, Np–H), 7.39 (d, J = 7.1 Hz, 1H, Np–H), 4.69–4.63 (q, J = 8.5 Hz, 2H, CH_2), 2.03 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.7, 139.9, 133.6, 132.6, 131.5, 129.2, 129.1, 128.7, 126.9, 126.7, 126.4, 125.2, 124.6, 123.3 (q, J = 278.3 Hz), 61.0 (q, J = 36.4 Hz), 14.3.

HRMS (ESI) m/z: calcd for $C_{16}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 317.0760; found 317.0761.



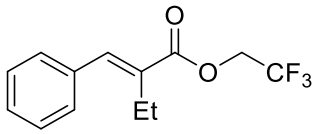
1t

2,2,2-trifluoroethyl (*E*)-2-methyl-3-(naphthalen-2-yl) acrylate (1t):

White solid (171 mg, 32% yield), m.p. 54–60 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H, Alkenyl–H), 7.82–7.76 (m, 4H, Np–H), 7.46–7.42 (m, 3H, Np–H), 4.58–4.52 (q, J = 8.5 Hz, 2H, CH_2), 2.17 (d, J = 1.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 141.3, 133.3, 133.2, 132.9, 130.0, 128.5, 128.2, 127.8, 127.1, 127.1, 127.0, 126.7, 61.0 (q, J = 36.4 Hz), 14.3.

HRMS (ESI) m/z: calcd for $C_{16}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 317.0760; found 317.0760.



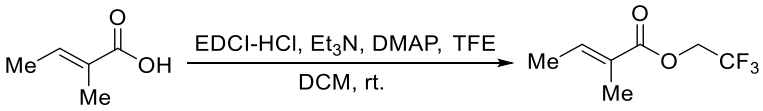
1v

2,2,2-trifluoroethyl (*E*)-2-benzylidenebutanoate (1v):

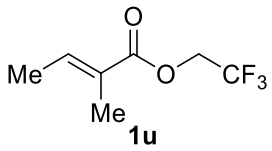
Light yellow liquid (488 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H, Alkenyl–H), 7.43–7.34 (m, 5H, Ar–H), 4.65–4.58 (q, J = 8.5 Hz, 2H, CH_2), 2.63–2.57 (q, J = 7.5 Hz, 2H, CH_2), 1.22 (t, J = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.7, 140.9, 135.3, 133.2, 129.4, 128.9, 128.7, 123.4 (q, J = 278.3 Hz), 60.8 (q, J = 36.4 Hz), 20.9, 13.7.

HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3O_2Na^+$ $(M+Na)^+$ 281.0760; found 281.0774.



A dried 100 mL round-bottomed flask was charged with (*E*)-2-methylbut-2-enoic acid (1g, 10.0 mmol), EDCI-HCl (2.3 g, 12.0 mmol), DMAP (244 mg, 2.0 mol) and CH_2Cl_2 (20 mL). Et_3N (1.2 g, 12.0 mmol) and TFE (1.1 g, 11.0 mmol) were added and the mixture was stirred for 18 hours at room temperature. The resulting mixture was washed with H_2O, and extracted with CH_2Cl_2 for three times. The combined organic solution was washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum.

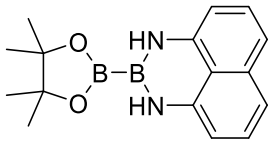


1u

2,2,2-trifluoroethyl (*E*)-2-methylbut-2-enoate (1u):

Colorless liquid (1.5 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02–6.96 (qq, J = 1.4 Hz, 7.1 Hz, 1H, Alkenyl–H), 4.55–4.48 (q, J = 8.5 Hz, 2H, CH_2), 1.88–1.86 (q, J = 1.4 Hz, 2H, Ar–H), 1.85–1.83 (dq, J = 7 Hz, 1.2 Hz, 3H, CH_3).



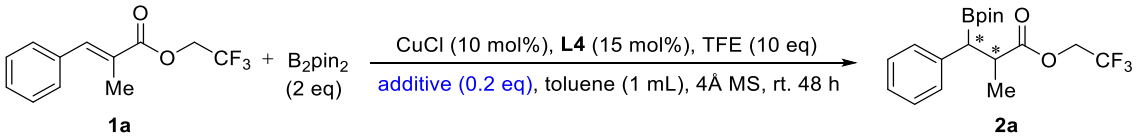
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2] diazaborinine (Bpin-Bdan):

The compound was synthesized according to the literature procedure[7]. White solid (145 mg, 46% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, J = 8.2 Hz, 1H, Ar–H), 7.05 (d, J = 8.2 Hz, 1H, Ar–H), 6.97 (d, J = 8.4 Hz, 2H, Ar–H), 6.26 (d, J = 7.4 Hz, 2H, Ar–H), 6.17 (s, 2H, NH), 1.28 (s, 12H, CH_3).

III. Optimizations of the Conditions

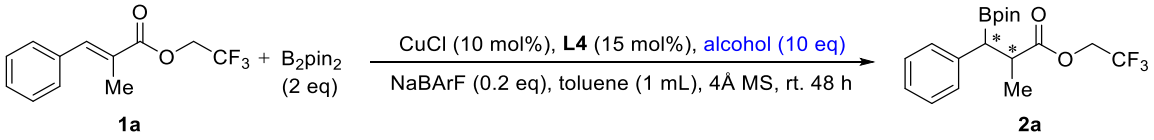
a). Additives (CuCl as the catalyst precursor)



Additive	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
$AgNTf_2$	46	1.6:1
AgOTf	-	-
$AgBF_4$	<5	-
$AgPF_6$	trace	-
Ag_2O	trace	-
$AgNO_3$	trace	-
NaBArF	42	10:1

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), CuCl (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), additive (0.024 mmol, 20 mol%), TFE (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^1H NMR analyses of the crude mixtures.

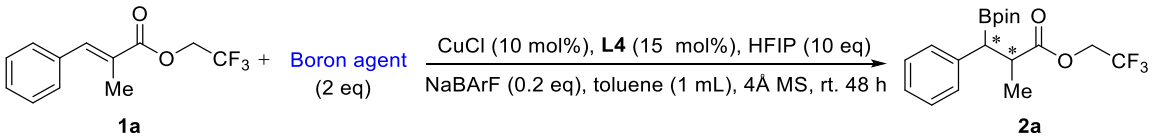
b). Alcohols



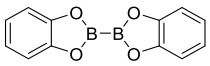
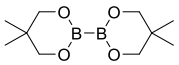
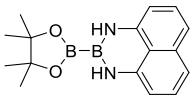
Alcohol	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
TFE	42	10:1
HFIP	52	6:1
EtOH	trace	-
^{i}PrOH	trace	-

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), CuCl (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), alcohol (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^1H NMR analyses of the crude mixtures.

c). Boron Agents

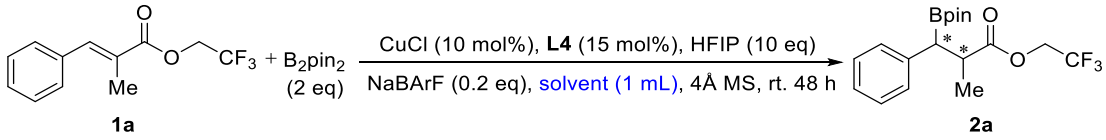


1a **2a**

Protic agent	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
	trace	-
	trace	-
	trace	-

[a] Reaction conditions: **1a** (0.122 mmol), Boron agent (2 equiv), CuCl (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures.

d). Solvents

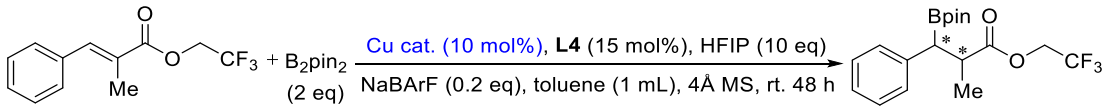


1a **2a**

Solvent	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
Toluene	54	6:1
$PhCF_3$	44	2.3:1
THF	trace	-
CH_2Cl_2	56	1.2:1
CH_3CN	trace	-
Dioxane	trace	-

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 eq), CuCl (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in solvent (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures.

e). Copper Precursors

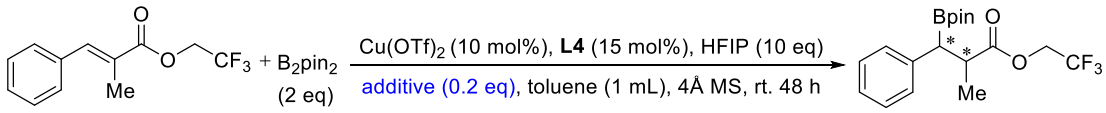


1a **2a**

Cu catalyst	Conv. /%[a][b]	ee /%[c]	dr (*syn* : *anti*)[b]
$Cu(OTf)_2$	84	97	7:1
$Cu(OAc)_2$	15	-	2.4:1
CuTc	45	98	6:1
$CuBr{\cdot}Me_2S$	17	-	6:1
CuOAc	47	91	3:1
CuI	<5	-	2.3:1
$Cu(acac)_2$	79	>99	5:1
$Cu(acac\text{-}F_6)_2$[d]	trace	-	-
(CuOTf)·1/2 Toluene	80	98	5:1
$CuSO_4{\cdot}5H_2O$	8	-	4:1
$CuCl_2{\cdot}2H_2O$	35	-	14:1
1/2 $CuCO_3$·1/2 CuH_2O_2	61	90	4:1

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), Cu precursor (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^1H NMR analyses of the crude mixtures; [c] Determined by transforming **2a** into corresponding alcohol using $NaBO_3{\cdot}4H_2O$ as oxidant and then analyzed by chiral HPLC; [d] $Cu(acac\text{-}F_6)_2$: copper(II) hexafluoropentanedionate.

f). Additives ($Cu(OTf)_2$ as the copper precursor)



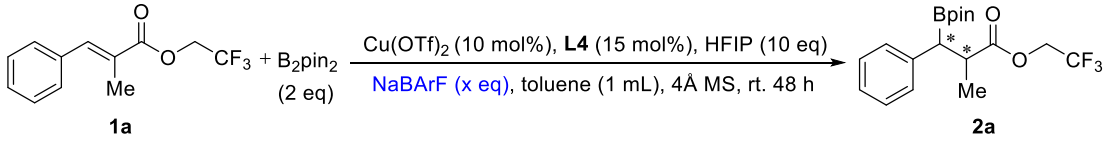
1a **2a**

Additive	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
CsOPiv	trace	-
KOAc	trace	-
CsF	22	3:1
KF	25	3:1
NaO^tBu	20	1.2:1
-	44	3:1

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), $Cu(OTf)_2$ (0.012 mmol, 10 mol%) and

L4 (0.018 mmol, 15 mol%), additive (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures.

g). NaBArF Dosage

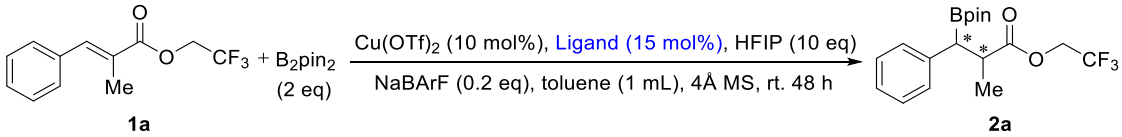


1a **2a**

NaBArF Dosage /eq	Conv. /%[a][b]	dr (*syn* : *anti*)[b]
0.2	84	7:1
0.3	83	6:1
0.4	83	5:1

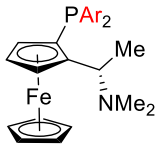
[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), $Cu(OTf)_2$ (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (x equiv), HFIP (10 equiv), in toluene (1 mL), 4Å MS, rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures.

h). Ligands



1a **2a**

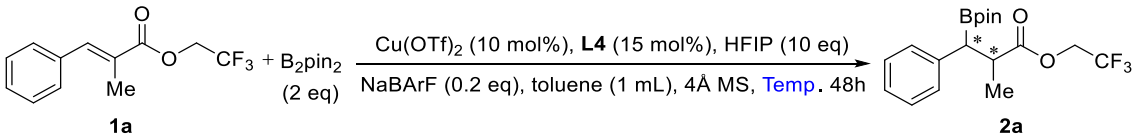
Ligand	Conv. /%[a][b]	ee /%[c]	dr (*syn* : *anti*)[b]
L1	69	90	4:1
L2	36	89	5:1
L3	63	90	6:1
L4	84	97	7:1
L5	62	97	10:1



Ar = Ph, (S,R_p)-**L1**
Ar = 3,5-di-methylbenzene, (S,R_p)-**L2**
Ar = 3,5-di-methyl-4-methoxybenzene, (S,R_p)-**L3**
Ar = 3,5-di-*tert*-butylbenzene, (S,R_p)-**L4**
Ar = 3,5-di-*tert*-butyl-4-methoxybenzene, (S,R_p)-**L5**

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), $Cu(OTf)_2$ (0.012 mmol, 10 mol%) and Ligand (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures; [c] Determined by transforming **2a** into corresponding alcohol using $NaBO_3 \cdot 4H_2O$ as oxidant and then analyzed by chiral HPLC.

i). **Temperatures**

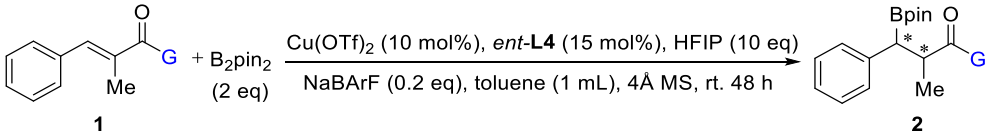


1a **2a**

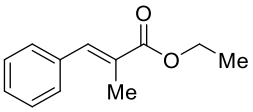
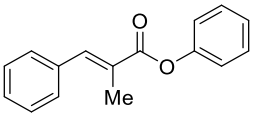
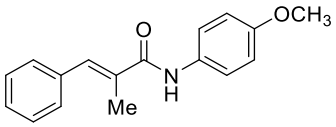
Temperature /°C	Conv. /%[a][b]	ee /%[c]	dr (*syn* : *anti*)[b]
0	94	96	11:1
20	84	97	7:1
40	63	93	6:1
60	44	92	6:1

[a] Reaction conditions: **1a** (0.122 mmol), B_2pin_2 (2 equiv), $Cu(OTf)_2$ (0.012 mmol, 10 mol%) and **L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), Temperature, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures; [c] Determined by transforming **2a** into corresponding alcohol using $NaBO_3 \cdot 4H_2O$ as oxidant and then analyzed by chiral HPLC.

j). **Substrates**



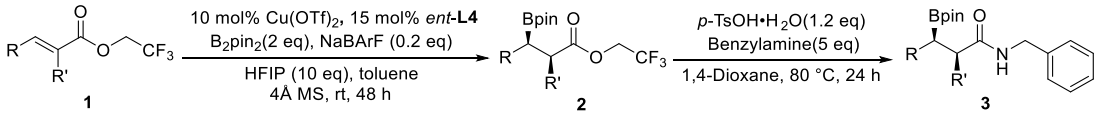
1 **2**

Substrate	Conv. /%[a][b]	ee /%[c]	dr (*syn* : *anti*)[b]
	42	–91	10:1
	>99	–94	1.5:1
	4	-	-

[a] Reaction conditions: **1** (0.122 mmol), B_2pin_2 (2 equiv), $Cu(OTf)_2$ (0.012 mmol, 10 mol%) and *ent*-**L4** (0.018 mmol, 15 mol%), NaBArF (0.024 mmol, 20 mol%), HFIP (10 equiv), in toluene (1 mL), 4Å MS (30 mg), rt, 48 h; [b] Determined by ^{1}H NMR analyses of the crude mixtures; [c] Determined by ^{1}H NMR analyses of the crude mixtures; [c] Determined by transforming **2** (excluding **2c**) into corresponding alcohol using $NaBO_3 \cdot 4H_2O$ as oxidant and then analyzed by chiral HPLC.

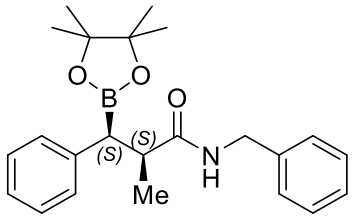
IV. Experimental Procedures

a). General Procedure A for the asymmetric synthesis.



Procedure A-I: A dried 10 mL Schlenk tube was charged with B_2pin_2 (62.0 mg, 0.244 mmol), $Cu(OTf)_2$ (4.4 mg, 0.012 mmol), *ent*-**L4** (12.2 mg, 0.018 mmol), NaBArF (21.6 mg, 0.024 mmol), 4Å MS (30 mg) and toluene (1 mL) under the protection of argon, and then stirred at room temperature for 30 min. Then, **1** (0.122 mmol) and $(CF_3)_2CHOH$ (HFIP, 205 mg, 0.13 mL, 1.22 mmol) were added and the mixture was stirred for 48 hours. The resulting suspension was filtered through Celite, rinsed with EtOAc for three times and concentrated in vacuum. The crude product was analyzed by ^{1}H NMR.

Procedure A-II: Another Schlenk tube was charged with the above crude product, *p*-TsOH·H_2O (27.8 mg, 0.146 mmol), benzylamine (65.4 mg, 66.7 μL, 0.61 mmol) and 1,4-dioxane (1 mL) under the protection of argon, and then stirred at 80 ℃ for 24 hours. After evaporation of the volatiles under vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the corresponding product **3**, which was analyzed by ^{1}H NMR, ^{13}C NMR, HRMS and chiral HPLC.



3a

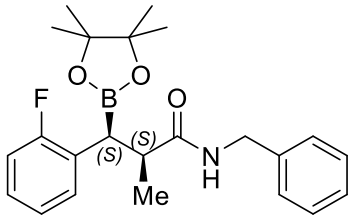
(2*S*,3*S*)-*N*-benzyl-2-methyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3a):

Colorless oily liquid (32.4 mg, 70% yield), 90% ee, 7:1 dr. $[\alpha]_D^{25}$ = +23.7 (c = 0.37, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.24–7.16 (m, 8H, Ar–H), 6.75–6.74 (m, 2H, Ar–H), 5.34 (t, *J* = 5.9 Hz, 1H, NH), 4.27 (dd, *J* = 6.4 Hz, 14.9 Hz, 1H, CH_2), 4.05 (dd, *J* = 5.0 Hz, 14.9 Hz, 1H, CH_2), 2.74–2.63 (m, 2H, CH, B–CH), 1.29 (d, *J* = 3.8 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.5, 140.8, 138.2, 129.2, 128.7, 128.5, 127.5, 127.2, 126.0, 83.7, 45.4, 43.3, 24.7, 24.7, 18.2. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.02 (s, 1H, NH), 4.46 (d, *J* = 5.9 Hz, 2H, CH_2), 2.83–2.79 (m, 1H, CH), 2.44 (d, *J* = 11.1 Hz, 1H, B–CH), 1.15 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 1.02 (d, *J* = 6.9 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{30}BNO_3Na^+$ $(M+Na)^+$ 402.2211; found 402.2213.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 12.8 min, t_2 (major) = 13.4 min.



3e

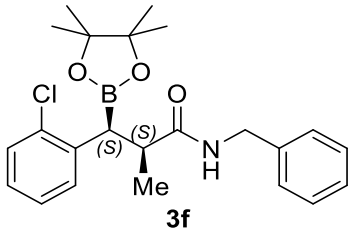
(2*S*,3*S*)-*N*-benzyl-3-(2-fluorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3e):

Yellow solid (37.3 mg, 77% yield), m.p. 120–125 ℃, 93% ee, 17:1 dr. $[\alpha]_D^{25}$ = +9.4 (c = 0.56, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.31–7.13 (m, 5H, Ar–H), 7.02 (t, *J* = 7.6 Hz, 1H, Ar–H), 6.94 (t, *J* = 8.2 Hz, 1H, Ar–H), 6.89–6.87 (m, 2H, Ar–H), 5.69 (t, *J* = 6.2 Hz, 1H, NH), 4.30 (dd, *J* = 6.4 Hz, 14.7 Hz, 1H, CH_2), 4.13 (dd, *J* = 4.9 Hz, 14.8 Hz, 1H, CH_2), 2.88–2.78 (m, 2H, CH, B–CH), 1.30 (d, *J* = 3.9 Hz, 3H, CH_3), 1.21 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.4, 161.1 (d, *J* = 245.0 Hz), 138.3, 132.0 (d, *J* = 5.0 Hz), 128.6, 127.6, 127.2, 124.3 (d, *J* = 4.0 Hz), 115.3 (d, *J* = 23.2 Hz), 83.8, 43.4, 43.2, 24.8, 24.6, 17.9. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.12 (s, 1H, NH), 4.45 (d, *J* = 5.2 Hz, 2H, CH_2), 1.03 (d, *J* = 7.1 Hz, 3H, CH_3).

HRMS(ESI) m/z: calcd for $C_{23}H_{29}BFNO_3Na^+$ $(M+Na)^+$ 420.2117; found 420.2119.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 11.3 min, t_2 (major) = 12.4 min.



3f

(2*S*,3*S*)-*N*-benzyl-3-(2-chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3f):

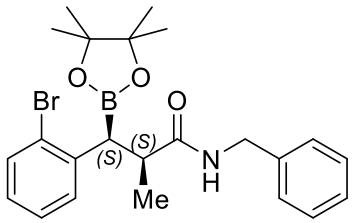
Light yellow solid (35.0 mg, 69% yield), m.p. 150–152 ℃, 87% ee, 9:1 dr. $[\alpha]_D^{25}$ = +19.1 (c = 0.59, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.35–7.08 (m, 7H, Ar–H), 6.90–6.89 (m, 2H, Ar–H), 5.63 (t, *J* = 6.0 Hz, 1H, NH), 4.28 (dd, *J* = 6.4 Hz, 14.9 Hz, 1H, CH_2), 4.16 (dd, *J* = 5.5 Hz, 15.0 Hz, 1H,

CH_2), 3.05 (d, *J* = 10 Hz, 1H, B–CH), 2.99–2.93 (m, 1H, CH), 1.33 (d, *J* = 4.4 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.20 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.4, 138.9, 138.3, 134.2, 131.4, 129.7, 128.6, 127.6, 127.3, 127.0, 83.7, 43.4, 43.0, 24.9, 24.7, 17.8. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.13 (s, 1H, NH), 4.47 (s, 2H, CH_2), 1.17 (s, 6H, CH_3), 1.13 (s, 6H, CH_3), 1.03 (d, *J* = 6.8 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BClNO_3Na^+$ $(M+Na)^+$ 436.1821; found 436.1828.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 9.6 min, t_2 (minor) = 10.0 min.



3g

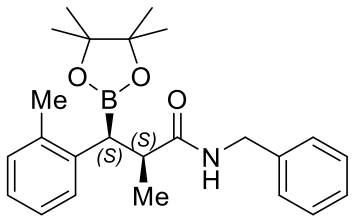
(2*S*,3*S*)-*N*-benzyl-3-(2-bromophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3g):

Light yellow solid (39.4 mg, 70% yield), m.p. 142–150 ℃, 92% ee, 4:1 dr. $[\alpha]_D^{25}$ = +13.3 (c = 0.62, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 1.5 Hz, 8.0 Hz, 1H, Ar–H), 7.36 (dd, *J* = 1.8 Hz, 7.8 Hz, 1H, Ar–H), 7.22–7.19 (m, 4H, Ar–H), 7.01 (td, *J* = 1.7 Hz, 7.5 Hz, 1H, Ar–H), 6.94–6.91 (m, 2H, Ar–H), 5.67 (t, *J* = 5.8 Hz, 1H, NH), 4.29 (dd, *J* = 6.0 Hz, 14.9 Hz, 1H, CH_2), 4.24 (dd, *J* = 5.4 Hz, 14.8 Hz, 1H, CH_2), 3.10 (d, *J* = 9.6 Hz, 1H, B–CH), 3.00–2.92 (m, 1H, CH), 1.31 (d, *J* = 6.9 Hz, 3H, CH_3), 1.23 (s, 6H, CH_3), 1.20 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.3, 140.5, 138.3, 133.1, 128.6, 127.7, 127.5, 127.5, 127.3, 83.7, 43.4, 43.3, 24.9, 24.7, 17.6. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.15 (s, 1H, NH), 4.48–4.46 (dd, *J* = 3.0 Hz, 5.6 Hz, 2H, CH_2), 3.06 (d, *J* = 10.4 Hz, 1H, B–CH), 2.90–2.85 (m, 1H, CH), 1.16 (s, 6H, CH_3), 1.13 (s, 6H, CH_3), 1.07 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BBrNO_3Na^+$ $(M+Na)^+$ 480.1316; found 480.1320.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 8.7 min, t_2 (minor) = 9.9 min.



3h

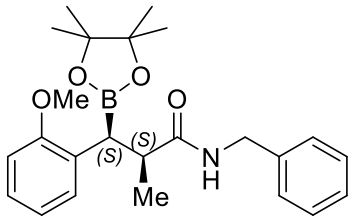
(2*S*,3*S*)-*N*-benzyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl) propenamide (3h):

Yellow oily liquid (35.0 mg, 73% yield), 99% ee, 4:1 dr. $[\alpha]_D^{25}$ = +22.7 (c = 0.62, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 2.2 Hz, 7.4 Hz, 1H, Ar–H), 7.17–7.15 (m, 3H, Ar–H), 7.11 (dd, *J* = 2.6 Hz, 6.8 Hz, 1H, Ar–H), 7.07–7.04 (m, 2H, Ar–H), 5.37 (t, *J* = 5.8 Hz, 2H, NH), 4.28 (dd, *J* = 6.4 Hz, 15.0 Hz, 1H, CH_2), 4.03 (dd, *J* = 4.9 Hz, 15.0 Hz, 1H, CH_2), 2.94 (d, *J* = 11.2 Hz, 1H, B–CH), 2.80–2.73 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.31 (d, *J* = 6.8 Hz, CH_3), 1.19 (s, 6H, CH_3), 1.14 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.8, 139.4, 138.3, 137.2, 130.8, 128.5, 127.9, 127.4, 127.1, 125.9, 125.6, 83.5, 44.7, 43.4, 24.7, 24.6, 20.4, 18.3. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 6.13 (s, 1H, NH), 4.47–4.46 (dd, *J* = 3.2 Hz, 5.7 Hz, 2H, CH_2), 2.36(s, 3H, CH_3), 1.11 (s, 6H, CH_3), 1.07 (s, 6H, CH_3), 1.00 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_3Na^+$ $(M+Na)^+$ 416.2368; found 416.2369.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 220 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 10.2 min, t_2 (minor) = 13.2 min.



3i

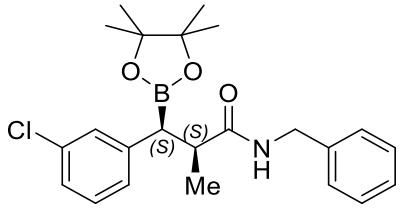
(2*S*,3*S*)-*N*-benzyl-3-(2-methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3i):

Colorless oily liquid (41.9 mg, 84% yield), 90% ee, 2:1 dr. $[\alpha]_D^{25}$ = +29.8 (c = 0.25, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 1H, Ar–H), 7.23–7.18 (m, 5H, Ar–H), 7.15 (t, *J* = 7.9 Hz, 1H, Ar–H), 6.85–6.83 (m, 2H, Ar–H), 5.70 (t, *J* = 5.8 Hz, 2H, NH), 4.16 (d, *J* = 5.5 Hz, 2H, CH_2), 3.64 (s, 3H, O–CH_3), 2.92–2.86 (m, 1H, CH), 2.75 (d, *J* = 10.4 Hz, 1H, B–CH), 1.32 (d, *J* = 6.8 Hz, CH_3), 1.21 (s, 6H, CH_3), 1.17 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 176.0, 156.9, 138.6, 131.2, 128.9, 128.6, 127.7, 127.2, 127.2, 121.2, 110.4, 83.4, 55.2, 43.4, 43.3, 25.0, 24.9, 18.4. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 6.10 (s, 1H, NH), 4.44 (d, *J* = 5.8 Hz, 2H, CH_2), 3.80 (s, 3H, O–CH_3), 1.12 (d, *J* = 7.2 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_4Na^+$ $(M+Na)^+$ 432.2317; found 432.2320.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t_1 (major) = 11.4 min, t_2 (minor) = 13.6 min.



3j

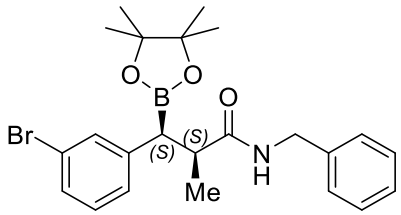
(2*S*,3*S*)-*N*-benzyl-3-(3-chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3j):

Colorless solid (33.8 mg, 67% yield), m.p. 99–107 ℃, 91% ee, 7:1 dr. $[\alpha]_D^{25}$ = +18.1 (c = 0.33, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.26 (s, 1H, Ar–H), 7.20 (dd, *J* = 1.6 Hz, 4.6 Hz, 2H, Ar–H), 7.16–7.10 (m, 4H, Ar–H), 6.82–6.80 (m, 2H, Ar–H), 5.44 (t, *J* = 6.0 Hz, 1H, NH), 4.36 (dd, *J* = 6.6 Hz, 14.9 Hz, 1H, CH_2), 4.06 (dd, *J* = 4.8 Hz, 14.9 Hz, 1H, CH_2), 2.72–2.62 (m, 2H, CH, B–CH), 1.28 (d, *J* = 6.2 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.19 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.0, 143.0, 138.1, 134.3, 129.8, 129.0, 128.6, 127.6, 127.5, 127.3, 126.2, 83.9, 45.2, 43.3, 24.7, 24.7, 18.2. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.03 (s, 1H, NH), 4.47 (t, *J* = 5.8 Hz, 2H, CH_2), 2.84–2.76 (m, 1H, CH), 2.39 (d, *J* = 11.3 Hz, 1H, B–CH), 1.14 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.04 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BClNO_3Na^+$ $(M+Na)^+$ 436.1821; found 436.1827.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 230 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t_1 (major) = 9.8 min, t_2 (minor) = 11.1 min.



3k

(2*S*,3*S*)-*N*-benzyl-3-(3-bromophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3k):

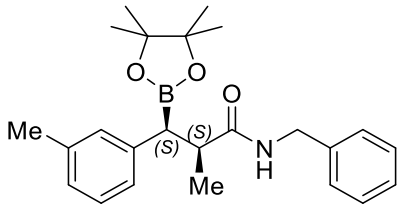
Colorless solid (37.7 mg, 67% yield), m.p. 104–110 ℃, 90% ee, 6:1 dr. $[\alpha]_D^{25}$ = +17.4 (c = 0.47, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 1.9 Hz, 1H, Ar–H), 7.30 (dt, *J* = 1.3 Hz, 7.9 Hz,

1H, Ar–H), 7.22–7.16 (m, 4H, Ar–H), 7.08 (t, *J* = 7.8 Hz, 1H, Ar–H), 6.83–6.80 (m, 2H, Ar–H), 5.45 (t, *J* = 5.4 Hz, 1H, NH), 4.36 (dd, *J* = 6.6 Hz, 14.9 Hz, 1H, CH_2), 4.05 (dd, *J* = 4.8 Hz, 14.8 Hz, 1H, CH_2), 2.70–2.61 (m, 2H, CH, B–CH), 1.27 (d, *J* = 6.4 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.19 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.0, 143.3, 138.1, 131.9, 130.2, 129.2, 128.7, 128.0, 127.5, 127.3, 122.6, 83.9, 45.2, 43.3, 24.7, 24.7, 18.2. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.07 (s, 1H, NH), 4.47 (t, *J* = 5.8 Hz, 2H, CH_2), 2.84–2.76 (m, 1H, CH), 2.37 (d, *J* = 11.2 Hz, 1H, B–CH), 1.14 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.04 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BBrNO_3Na^+$ $(M+Na)^+$ 480.1316; found 480.1317.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 10.0 min, t_2 (minor) = 11.1 min.



3l

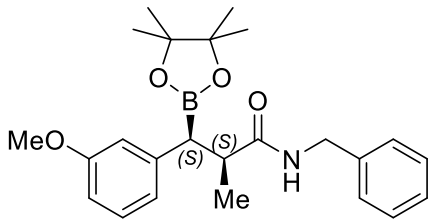
(2*S*,3*S*)-*N*-benzyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*m*-tolyl) propenamide (3l):

White solid (28.8 mg, 60% yield), m.p. 112–114 ℃, 91% ee, 2:1 dr. $[\alpha]_D^{25}$ = +21.5 (c = 0.46, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.17–7.10 (m, 4H, Ar–H), 7.04 (s, 1H, Ar–H), 7.04 (d, *J* = 7.2 Hz, 1H, Ar–H), 6.99 (d, *J* = 7.4 Hz, 1H, Ar–H), 6.74–6.73 (m, 2H, Ar–H), 5.34 (t, *J* = 5.7 Hz, 1H, NH), 4.30 (dd, *J* = 6.5 Hz, 15.0 Hz, 1H, CH_2), 4.04 (dd, *J* = 4.9 Hz, 15.0 Hz, 1H, CH_2), 2.73–2.66 (m, 1H, CH), 2.59 (d, *J* = 11.0 Hz, 1H, B–CH), 2.27 (s, 3H, CH_3), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.6, 140.7, 138.3, 138.15, 130.0, 128.5, 127.5, 127.2, 126.8, 126.0, 83.7, 45.3, 43.3, 24.7, 24.7, 21.5, 18.2. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 6.02 (s, 1H, NH), 4.46 (d, *J* = 5.6 Hz, 2H, CH_2), 2.82–2.75 (m, 1H, CH), 2.40 (d, *J* = 11.2 Hz, 1H, B–CH), 2.30 (s, 3H, CH_3), 1.15 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 1.02 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_3Na^+$ $(M+Na)^+$ 416.2368; found 416.2371.

HPLC conditions: hexane/ ethanol = 95/5, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 9.9 min, t_2 (major) = 12.0 min.



3m

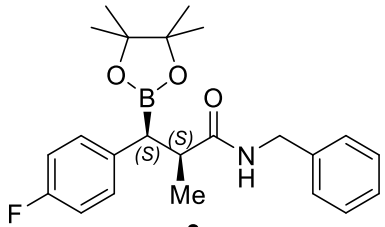
(2*S*,3*S*)-*N*-benzyl-3-(3-methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3m):

Light yellow solid (36.4 mg, 73% yield), m.p. 88–95 ℃, 92% ee, 4:1 dr. $[\alpha]_D^{25}$ = +18.1 (c = 0.50, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.19–7.12 (m, 4H, Ar–H), 6.83–6.78 (m, 4H, Ar–H), 6.72 (dd, *J* = 2.8 Hz, 8.2 Hz, 1H, Ar–H), 5.37 (t, *J* = 5.8 Hz, 1H, NH), 4.29 (dd, *J* = 6.4 Hz, 15.0 Hz, 1H, CH_2), 4.07 (dd, *J* = 4.9 Hz, 14.8 Hz, 1H, CH_2), 3.73 (s, 3H, O–CH_3), 2.73–2.66 (m, 1H, CH), 2.61 (d, *J* = 10.8 Hz, 1H, B–CH), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.5, 159.9, 142.5, 138.3, 129.6, 128.6, 127.5, 127.2, 121.6, 114.5, 111.9, 83.7, 55.2, 45.3, 43.4, 24.7, 24.7, 18.2. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 5.99 (s, 1H, NH), 4.46 (d, *J* = 5.7 Hz, 2H, CH_2), 3.77 (s, 3H, O–CH_3), 2.82–2.76 (m, 1H, CH), 2.41 (d, *J* = 11.2 Hz, 1H, B–CH), 1.16 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.03 (d, *J* = 6.9 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_4Na^+$ $(M+Na)^+$ 432.2317; found 432.2318.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 15.6 min, t_2 (minor) = 16.9 min.



3n

(2*S*,3*S*)-*N*-benzyl-3-(4-fluorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3n):

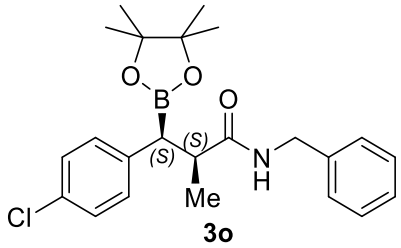
Colorless solid (31.5 mg, 65% yield), m.p. 90–105 ℃, 93% ee, 8:1 dr. $[\alpha]_D^{25}$ = +20.8 (c= 0.42, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.21–7.18 (m, 5H, Ar–H), 6.90 (t, *J* = 8.8 Hz, 2H, Ar–H), 6.78–6.76 (m, 2H, Ar–H), 5.42 (t, *J* = 6.2 Hz, 1H, NH), 4.35 (dd, *J* = 6.9 Hz, 15.0 Hz, 1H, CH_2), 4.03 (dd, *J* = 4.4 Hz, 14.9 Hz, 1H, CH_2), 2.69–2.61 (m, 2H, CH, B–CH), 1.27 (d, *J* = 6.2 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.2, 161.5

(d, *J* = 244.7 Hz), 138.2, 136.5 (d, *J* = 4.0 Hz), 130.6 (d, *J* = 8.1 Hz), 128.6, 127.5, 127.3, 115.4 (d, *J* = 18.2 Hz), 83.8, 45.6, 43.3, 24.7, 24.7, 18.3. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 6.03 (s, 1H, NH), 4.45 (d, *J* = 5.9 Hz, 2H, CH_2), 2.80–2.73 (m, 1H, CH), 2.41 (d, *J* = 11.2 Hz, 1H, B–CH), 1.15 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 1.03 (d, *J* = 7.2 Hz, 3H, CH_3).

HRMS(ESI) m/z: calcd for $C_{23}H_{29}BFNO_3Na^+$ $(M+Na)^+$ 420.2117; found 420.2119.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 11.3 min, t_2 (major) = 12.0 min.



3o

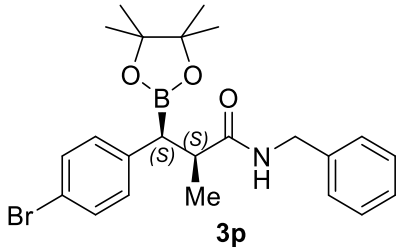
(2*S*,3*S*)-*N*-benzyl-3-(4-chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3o):

Yellow oily liquid (31.6 mg, 62% yield), 92% ee, 7:1 dr. $[\alpha]_D^{25}$ = +12.6 (c = 0.28, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 7H, Ar–H), 6.75–6.73 (m, 2H, Ar–H), 5.39 (t, *J* = 6.0 Hz, 1H, NH), 4.40 (dd, *J* = 6.9 Hz, 14.9 Hz, 1H, CH_2), 4.00 (dd, *J* = 4.6 Hz, 14.9 Hz, 1H, CH_2), 2.68–2.61 (m, 2H, CH, B–CH), 1.28 (d, *J* = 6.2 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.1, 139.4, 138.1, 131.8, 130.6, 128.8, 128.6, 127.5, 127.4, 83.8, 45.4, 43.3, 24.7, 24.7, 18.3. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 5.99 (s, 1H, NH), 4.48–4.46 (dd, *J* = 2.0 Hz, 5.8 Hz, 2H, CH_2), 2.82–2.74 (m, 1H, CH), 2.40 (d, *J* = 11.1 Hz, 1H, B–CH), 1.14 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BClNO_3Na^+$ $(M+Na)^+$ 436.1821; found 436.1828.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 230 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 28.5 min, t_2 (major) = 31.5 min.



3p

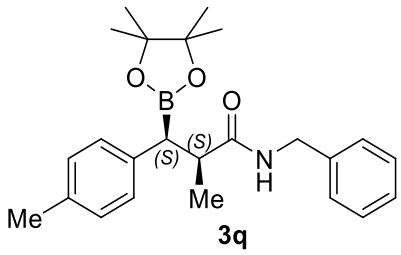
(2*S*,3*S*)-*N*-benzyl-3-(4-bromophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3p):

Colorless oily liquid (36.6 mg, 66% yield), 91% ee, 5:1 dr. $[\alpha]_D^{25}$ = +10.9 (c = 0.22, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.24–7.22 (m, 3H, Ar–H), 7.11 (d, *J* = 8.5 Hz, 2H, Ar–H), 6.76–6.74 (m, 2H, Ar–H), 5.38 (t, *J* = 6.0 Hz, 1H, NH), 4.40 (dd, *J* = 6.9 Hz, 14.9 Hz, 1H, CH_2), 4.00 (dd, *J* = 4.6 Hz, 14.9 Hz, 1H, CH_2), 2.70–2.60 (m, 2H, CH, B–CH), 1.27 (d, *J* = 6.2 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.1, 140.0, 138.1, 131.7, 131.0, 128.7, 127.5, 127.4, 119.9, 83.9, 45.4, 43.3, 24.7, 24.7, 18.3. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 5.98 (s, 1H, NH), 4.48–4.46 (dd, *J* = 2.1 Hz, 5.6 Hz, 2H, CH_2), 2.82–2.74 (m, 1H, CH), 2.39 (d, *J* = 11.2 Hz, 1H, B–CH), 1.14 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{23}H_{29}BBrNO_3Na^+$ $(M+Na)^+$ 480.1316; found 480.1317.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 11.5 min, t_2 (major) = 12.5 min.



3q

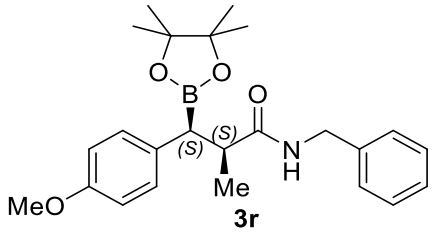
(2*S*,3*S*)-*N*-benzyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl) propenamide (3q):

White solid (36.9 mg, 77% yield), m.p. 98–105 ℃, 92% ee, 5:1 dr. $[\alpha]_D^{25}$ = +21.8 (c = 0.35, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.18–7.15 (m, 3H, Ar–H), 7.11 (d, *J* = 8.2 Hz, 2H, Ar–H), 7.03 (d, *J* = 8.0 Hz, 2H, Ar–H), 6.77–6.76 (m, 2H, Ar–H), 5.31 (t, *J* = 6.1 Hz, 1H, NH), 4.30 (dd, *J* = 6.4 Hz, 14.8 Hz, 1H, CH_2), 4.04 (dd, *J* = 4.9 Hz, 14.8 Hz, 1H, CH_2), 2.70–2.64 (m, 1H, CH), 2.58 (d, *J* = 10.8 Hz, 1H, B–CH), 2.31 (s, 3H, CH_3), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.6, 138.4, 137.7, 135.3, 129.4, 129.0, 128.5, 127.6, 127.2, 83.6, 45.4, 43.4, 24.8, 24.7, 21.2, 18.2.

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_3Na^+$ $(M+Na)^+$ 416.2368; found 416.2361.

HPLC conditions: hexane/ ethanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 11.2 min, t_2 (major) = 11.7 min.



3r

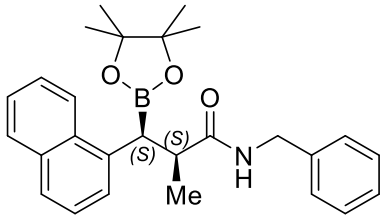
(2*S*,3*S*)-*N*-benzyl-3-(4-methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3r):

White solid (38.4 mg, 77% yield), m.p. 95–98 ℃, 98% ee, 4:1 dr. $[\alpha]_D^{25}$ = +20.8 (c = 0.28, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.18–7.14 (m, 5H, Ar–H), 6.78–6.76 (m, 4H, Ar–H), 5.32 (t, *J* = 5.8 Hz, 1H, NH), 4.33 (dd, *J* = 6.6 Hz, 15.0 Hz, 1H, CH_2), 4.04 (dd, *J* = 4.9 Hz, 15.0 Hz, 1H, CH_2), 3.78 (s, 3H, O–CH_3), 2.67–2.61 (m, 1H, CH), 2.57 (d, *J* = 10.8 Hz, 1H, B–CH), 1.27 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.6, 158.0, 138.4, 132.8, 130.1, 128.5, 127.6, 127.2, 114.1, 83.7, 55.3, 45.6, 43.4, 24.8, 24.7, 18.2. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 5.99 (s, 1H, NH), 4.46 (d, *J* = 5.7 Hz, 2H, CH_2), 3.77 (s, 3H, O–CH_3), 2.82–2.76 (m, 1H, CH), 2.41 (d, *J* = 11.2 Hz, 1H, B–CH), 1.16 (s, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.03 (d, *J* = 6.9 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{24}H_{32}BNO_4Na^+$ $(M+Na)^+$ 432.2317; found 432.2318.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 220 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 10.4 min, t_2 (major) = 16.8 min.



3s

(2*S*,3*S*)-*N*-benzyl-2-methyl-3-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3s):

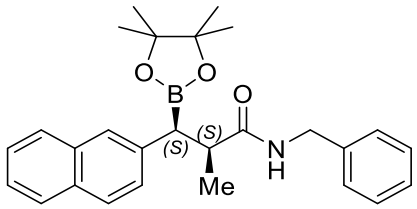
Yellow oily liquid (26.2 mg, 50% yield), 92% ee, 4:1 dr. $[\alpha]_D^{25}$ = +16.6 (c = 0.52, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.83 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.68 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.48–7.31 (m, 6H, Np–H, Ar–H), 7.10 (t, J= 7.4 Hz, 1H, Ar–H), 7.05 (t, *J* = 7.8 Hz, 1H, Ar–H), 6.52 (d, *J* = 7.4 Hz, 2H, Ar–H), 5.20 (br, 1H, NH), 3.99 (dd, *J* = 6.0 Hz, 14.8 Hz, 1H, CH_2), 3.94 (dd, *J* = 5.2 Hz, 14.8 Hz, 1H, CH_2), 3.44 (d, *J* = 8.0 Hz, 1H, B–CH), 2.99–2.93 (m, 1H, CH), 1.40 (d, *J* = 6.8 Hz, 3H, CH_3), 1.21 (s, 6H, CH_3), 1.14 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.4, 138.5, 138.0, 134.0, 132.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.6, 127.2, 127.0, 126.0, 125.3, 83.8, 45.4, 43.3, 24.8, 24.7, 18.4. **^{1}H NMR (*anti*,**

500 MHz, $CDCl_3$) δ 6.10 (s, 1H, NH), 4.50–4.48 (dd, *J* = 2.7 Hz, 5.7 Hz, 2H, CH_2), 3.31 (d, *J* = 11.0 Hz, 1H, B–CH), 3.07–3.00 (m, 1H, CH).

HRMS (ESI) m/z: calcd for $C_{27}H_{32}BNO_3Na^+$ $(M+Na)^+$ 452.2368; found 452.2368.

HPLC conditions: hexane/ ethanol = 95/5, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 11.2 min, t_2 (major) = 14.1 min.



3t

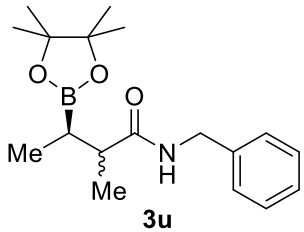
(2*S*,3*S*)-*N*-benzyl-2-methyl-3-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (3t):

Yellow oily liquid (31.4 mg, 60% yield), 92% ee, 6:1 dr. $[\alpha]_D^{25}$ = +11.9 (c = 0.52, CH_2Cl_2).

^{1}H NMR (*syn*, 500 MHz, $CDCl_3$) δ 7.81–7.70 (m, 4H, Ar–H), 7.45–7.39 (m, 3H, Ar–H), 6.97 (t, *J* = 3.0 Hz, 1H, Ar–H), 6.74 (t, *J* = 7.8 Hz, 1H, Ar–H), 6.42 (d, *J* = 7.0 Hz, 2H, Ar–H), 5.34 (t, *J* = 6.0 Hz, 1H, NH), 4.28 (dd, *J* = 7.0 Hz, 15.0 Hz, 1H, CH_2), 3.91 (dd, *J* = 4.6 Hz, 15.0 Hz, 1H, CH_2), 2.85–2.79 (m, 2H, CH, B–CH), 1.34 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.17 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 126 MHz, $CDCl_3$) δ 175.3, 138.4, 137.8, 133.9, 132.2, 128.2, 128.1, 127.8, 127.6, 127.5, 127.5, 127.1, 126.9, 125.8, 125.2, 83.7, 45.3, 43.2, 24.6, 24.6, 18.2. **^{1}H NMR (*anti*, 500 MHz, $CDCl_3$)** δ 6.06 (s, 1H, NH), 4.49–4.48 (dd, *J* = 2.6 Hz, 5.6 Hz, 2H, CH_2), 2.97–2.91 (m, 1H, CH), 2.61 (d, *J* = 11.2 Hz, 1H, B–CH), 1.15 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 1.05 (d, *J* = 7.0 Hz, 3H, CH_3).

HRMS (ESI) m/z: calcd for $C_{27}H_{32}BNO_3Na^+$ $(M+Na)^+$ 452.2368; found 452.2363.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 220 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 19.3 min, t_2 (minor) = 23.0 min.



3u

***N*-benzyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butanamide (3u):**

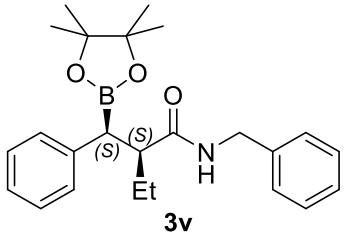
White solid (30.4 mg, 78% yield), m.p. 92–103 ℃, 90% ee, 1:1 dr. $[\alpha]_D^{25}$ = +9.2 (c = 0.53, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 5H, Ar–H), 6.16–6.10 (m, 1H, NH), 4.49–4.37 (m,

2H, CH_2), 3.78 (s, 3H, O–CH_3), 2.67–2.61 (m, 1H, CH), 2.57 (d, *J* = 10.8 Hz, 1H, B–CH), 1.27 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 176.9, 176.2, 138.7, 138.6, 128.8, 128.0, 128.0, 127.5, 83.4, 83.1, 44.0, 43.8, 43.6, 43.6, 24.9, 24.8, 24.8, 24.7, 17.3, 16.6, 13.1, 13.0.

HRMS (ESI) m/z: calcd for $C_{18}H_{28}BNO_3Na^+$ $(M+Na)^+$ 340.2054; found 340.2053.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 8.4 min, t_2 (major) = 9.9 min.



3v

(2*S*,3*S*)-*N*-benzyl-2-phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)butanamide (3v):

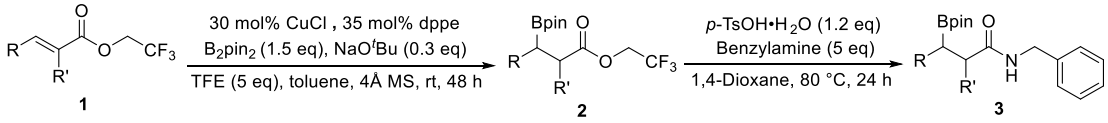
White solid (38.6 mg, 45% yield), m.p. 148–161 ℃, 90% ee, 6:1 dr. $[\alpha]_D^{25}$ = +15.6 (c = 0.32, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.24–7.15 (m, 8H, Ar–H), 6.74–6.72 (m, 2H, Ar–H), 5.31 (t, *J* = 5.9 Hz, 1H, NH), 4.25 (dd, *J* = 6.5 Hz, 14.9 Hz, 1H, CH_2), 4.06 (dd, *J* = 5.0 Hz, 14.9 Hz, 1H, CH_2), 2.67 (d, *J* = 11.4 Hz, 1H, B–CH), 2.51–2.45 (td, *J* = 10.8 Hz, 3.5 Hz, 1H, CH), 1.85–1.74 (m, 1H, CH_2), 1.65–1.56 (m, 1H, CH_2), 1.21 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.95 (t, *J* = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ174.5, 140.7, 138.3, 129.2, 128.6, 128.5, 127.6, 127.2, 126.0, 83.7, 53.5, 43.3, 26.2, 24.7, 12.7. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 5.96 (s, 1H, NH), 4.56 (dd, *J* = 6.0 Hz, 14.8 Hz, 1H, CH_2), 4.42 (dd, *J* = 5.4 Hz, 14.8 Hz, 1H, CH_2), 1.15 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 0.81 (t, *J* = 7.2 Hz, 3H, CH_3).

HRMS(ESI) m/z: calcd for $C_{24}H_{32}BNO_3Na^+$ $(M+Na)^+$ 416.2373; found 416.2375.

HPLC conditions: hexane/EtOH = 95/5, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (minor) = 19.4 min, t_2 (major) = 21.7 min.

b). General Procedure B for the preparation of racemic products.

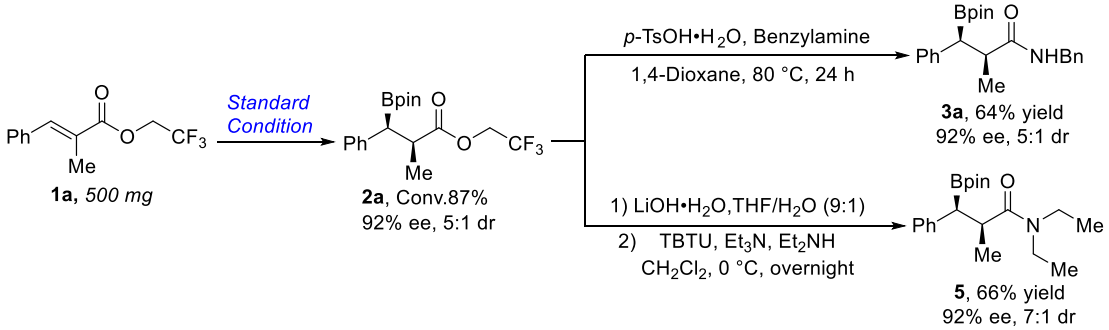


Procedure B-I: A dried 10 mL Schlenk tube was charged with **1** (0.122 mmol), B_2pin_2 (46.5 mg,

0.183 mmol), CuCl (3.6 mg, 0.037 mmol), 1,2-bis(diphenylphosphino)ethane (17.0 mg, 0.043 mmol), NaO^{t}Bu (3.5 mg, 0.037 mmol), CF_3CH_2OH (TFE, 61.0 mg, 43.9 μL, 0.61 mmol), 4Å MS (30 mg) and toluene (1 mL) under the protection of argon, and then stirred at room temperature for 48 hours. The suspension was filtered through Celite, rinsed with EtOAc for three times and concentrated in vacuum. The crude product was analyzed by ^{1}H NMR.

Procedure B-II: Refer to the **Procedure A-II**.

c). Applications of stereospecific transformation.



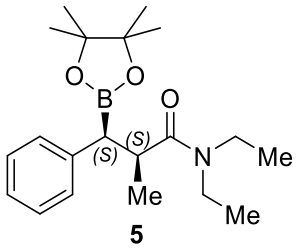
A dried 50 mL Schlenk tube was charged with B_2pin_2 (1.0 g, 4.094 mmol), $Cu(OTf)_2$ (74.0 mg, 0.205 mmol), *ent*-**L4** (163.5 mg, 0.246 mmol), NaBArF (181.4 mg, 0.205 mmol), 4Å MS and toluene (10 mL) under the protection of argon, and then stirred at room temperature for 30 min. Then, **1a** (500 mg, 2.047 mmol) and HFIP (3.4 g, 2.16 mL, 20.47 mmol) were added and the mixture was stirred for 48 hours. The resulting suspension was filtered through Celite, rinsed with EtOAc for three times and concentrated in vacuum. The crude product was analyzed by ^{1}H NMR.

Half of the above crude product was used for the **Procedure A-II**: Another Schlenk tube was charged with the above crude product, *p*-TsOH·H_2O (233 mg, 1.224 mmol), benzylamine (546 mg, 0.56 mL, 5.1 mmol) and 1,4-dioxane under the protection of argon, and then stirred at 80 ℃ for 24 hours. After evaporation of the volatiles under vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 2:1) to afford **3a** as a colorless oily liquid (246 mg, 64% yield), which was analyzed by ^{1}H NMR, ^{13}C NMR, HRMS and chiral HPLC.

The other half of the crude product was treated with LiOH·H_2O (107 mg, 2.55 mmol) and a mixed solution (THF/H_2O = 9:1), and then the reaction mixture was stirred for 24 hours. The solvent was removed under reduced pressure. Then, petroleum ether and water were added, and the aqueous phase was extracted with MTBE. After adjusting the pH of the aqueous phase with 1M HCl solution, the aqueous phase was extracted with MTBE for three times. The combined organic solution was dried with anhydrous sodium sulfate and concentrated in vacuum.

A dried 25 mL Schlenk tube was charged with Et_2NH (373 mg, 0.53 mL, 5.1 mmol) and CH_2Cl_2 under the protection of argon. Then, Et_3N (619 mg, 0.85 mL, 6.12 mmol) was added dropwise at 0 ℃ and stirred for 30 min. TBTU (982 mg, 3.06 mmol) and the above acid were added at 0 ℃ and stirred overnight. The solvent was removed under reduced pressure. Then, ethyl acetate and water were added, and the organic phase was successively washed with diluted HCl and 2% aqueous K_2CO_3. The aqueous phase was back-extracted with ethyl acetate. The combined

organic solutions were washed with brine, dried with anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10: 1 to 2:1) to afford **5** as a colorless oily liquid (232 mg, 66% yield).



5

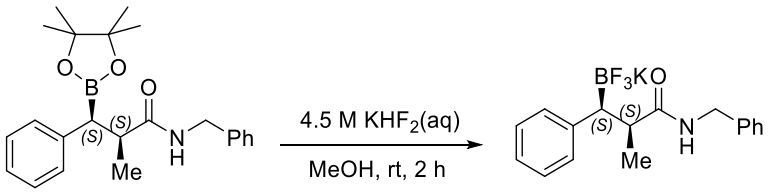
(2*S*,3*S*)-*N*,*N*-diethyl-2-methyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propenamide (5)：

Colorless oily liquid (232 mg, 66% yield), 92% ee, 7:1 dr. $[\alpha]_D^{25}$ = +43.3 (c = 0.85, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.29 (d， J = 7.5 Hz, 2H, Ar–H), 7.21–7.17 (t, J = 7.3 Hz, 2H, Ar–H), 7.11–7.08 (t, J = 7.2 Hz, 1H, Ar–H), 3.40–3.31 (m, 1H, N–CH_2), 3.21–2.92 (m, 4H, N–CH_2, CH), 2.73 (d, J = 10.5 Hz, 1H, B–CH), 1.25 (s, 6H, CH_3), 1.21 (d, J = 7.3 Hz, 3H, CH_3), 1.20 (s, 6H, CH_3), 0.99 (t, J = 7.1 Hz, 3H, CH_3), 0.82 (t, J = 7.1 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$) δ 175.9, 141.0, 129.7, 128.0, 125.6, 83.0, 41.7, 40.3, 39.6, 24.8, 24.8, 18.1, 14.7, 12.8. **^{1}H NMR (*anti*, 400 MHz, $CDCl_3$)** δ 3.57–3.48 (m, 1H, N–CH_2), 2.43 (d, J = 9.4 Hz, 1H, B–CH), 1.14 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 1.06 (d, J = 7.0 Hz, 3H, CH_3).

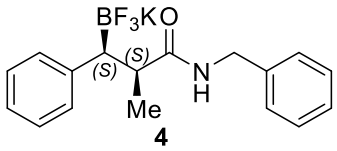
HRMS (ESI) m/z: calcd for $C_{20}H_{32}BNO_3Na^+$ $(M+Na)^+$ 368.2368; found 368.2368.

HPLC conditions: hexane/2-propanol = 90/10, 1 mL/min, λ = 210 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_1 (major) = 5.5 min, t_2 (minor) = 6.2 min.



3a **4**, *82%, 8:1 dr*

A solution of **3a** (100 mg, 0.264 mmol) in MeOH (1.2 mL) was treated with 4.5 M aqueous KHF_2 (0.29 mL, 1.32 mmol), and then the reaction mixture was stirred for 2 hours at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in toluene and concentrated in vacuum for three times to remove the residual water. The crude mixture was then dissolved in acetone and filtered. The combined organic solution was concentrated in vacuum. The pale solid obtained was dissolved in minimum amount of acetone and then hexanes were added to the solution. The participates were collected and dried in vacuum to afford **4** (77.4 mg, 82%) as a white solid [8].

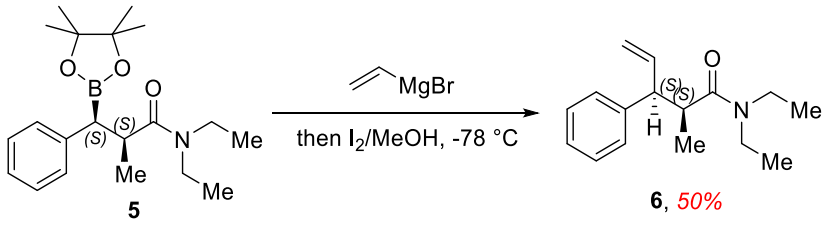


4

(2*S*,3*S*)-*N*-benzyl-2-methyl-3-phenyl-3-(trifluoro-λ^4-boranyl) propanamide, potassium salt (4):

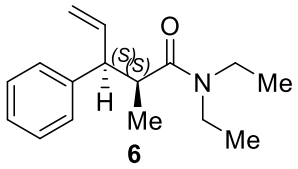
White solid (77.4 mg, 82% yield), 8:1 dr.

^{1}H NMR (*syn*, 400 MHz, $(CD_3)_2CO$) δ 7.23–7.21 (m, 1H, Ar–H), 7.13–7.05 (m, 5H, Ar–H), 6.99–6.92 (m, 2H, Ar–H), 6.76–6.74 (m, 2H, Ar–H), 4.23 (dd, J = 6.64 Hz, 15.4 Hz, 1H, CH_2), 4.01 (dd, J = 5.52 Hz, 15.4 Hz, 1H, CH_2), 2.89–2.81 (m, 1H, CH), 2.09–2.02 (m, 1H, B–CH), 1.27 (d, J = 6.88 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $(CD_3)_2CO$) δ 178.6, 149.5, 140.3, 129.6, 128.4, 127.6, 127.4, 126.5, 123.6, 45.4, 42.5, 18.5. $^{19}F\{^1H\}$ NMR (*syn*, 376 MHz, $(CD_3)_2CO$) δ –138.96.



5 **6**, *50%*

A dried 25 mL Schlenk tube was charged with **5** (66.5 mg, 0.192 mmol) and THF (1.5 mL) under the protection of argon. Then, vinylmagnesium bromide (0.96 mL of a 1 M solution in THF, 0.96 mmol) was added dropwise at –78 ℃ and stirred for 30 min. The reaction mixture was warmed to 0 ℃ for 30 min, a solution of iodine (97.5 mg, 0.384 mmol) in methanol (2 mL) was added dropwise and stirred for one hour. The resulting mixture was filtered through Celite, rinsed with CH_2Cl_2 for three times and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) to afford **6** as a colorless oily liquid (23.7 mg, 50% yield)[9].



6

(2*S*,3*S*)-*N*,*N*-diethyl-2-methyl-3-phenylpent-4-enamide (6):

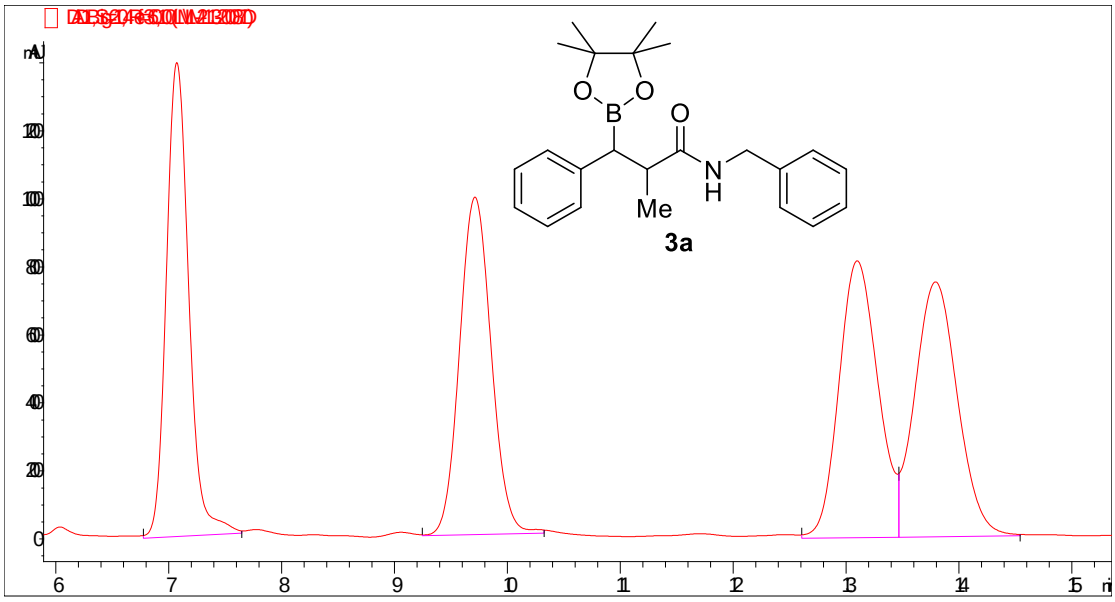
Colorless oily liquid (23.7 mg, 50% yield). $[\alpha]_D^{25}$ = +1.8 (c = 0.39, CH_2Cl_2).

^{1}H NMR (*syn*, 400 MHz, $CDCl_3$) δ 7.25–7.11 (m, 5H, Ar–H), 6.02 (dt, J = 9.88 Hz, 17.0 Hz, 1H, CH_2=**CH**), 5.19–5.11 (m, 2H, **CH_2**=CH), 3.58 (t, J = 9.88 Hz, 1H, CH), 3.46–3.37 (m, 1H, N–CH_2), 3.20–3.11 (m, 1H, N–CH_2), 2.96–2.81 (m, 3H, N–CH_2, CH), 1.20 (d, J = 6.64 Hz, 3H, CH_3), 0.96 (t, J = 7.28 Hz, 3H, CH_3), 0.73 (t, J = 7 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (*syn*, 101 MHz, $CDCl_3$)

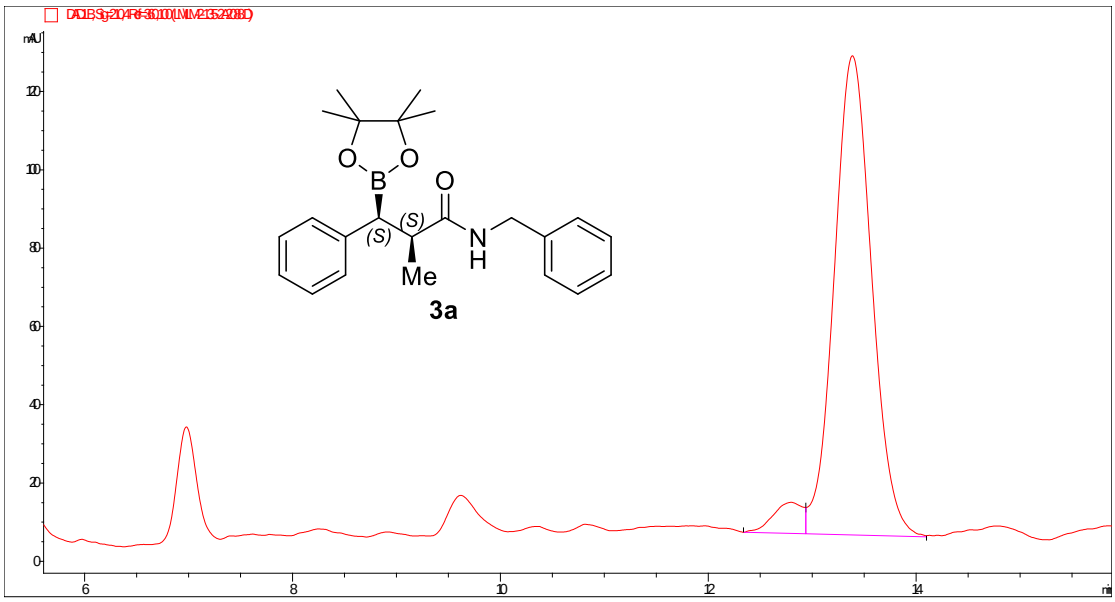
δ 174.4, 143.3, 139.2, 128.4, 128.0, 126.4, 116.9, 54.2, 41.8, 41.1, 40.3, 17.3, 14.7, 12.7.

HRMS (ESI) m/z: calcd for $C_{16}H_{23}NONa^+$ $(M+Na)^+$ 268.1672; found 268.1670.

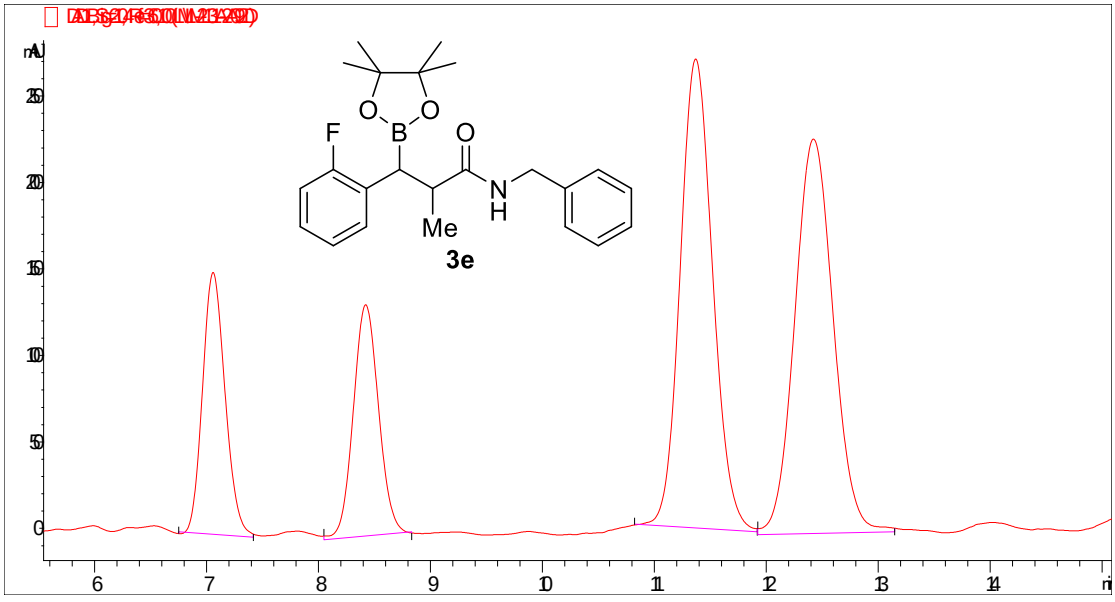
V. HPLC Spectra



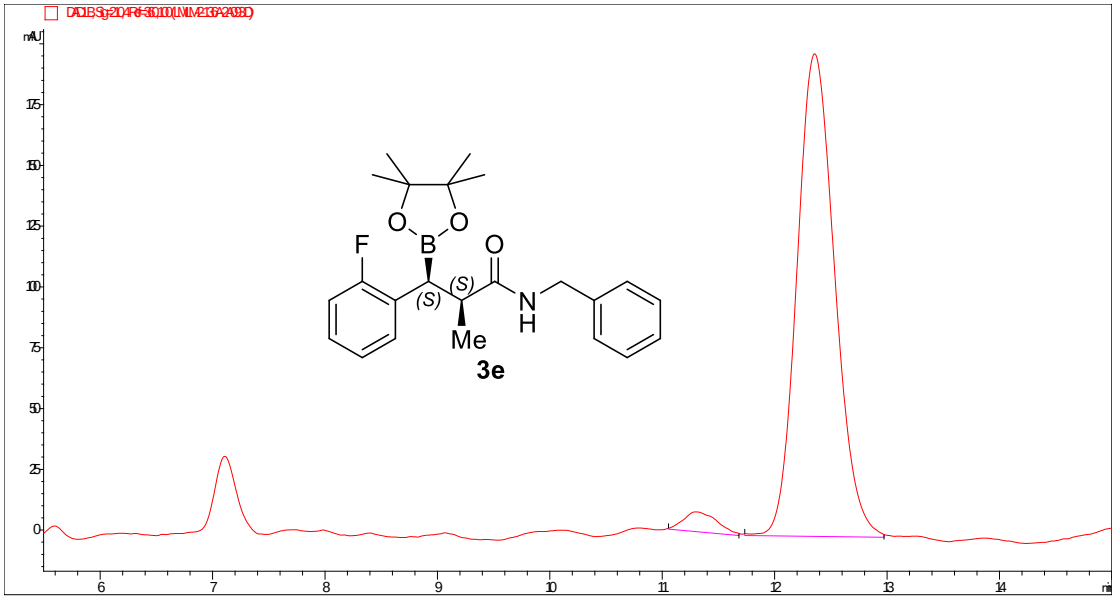
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.703	19293.1	1394.5	0.2306	0.835	24.784
2	9.714	19331.2	992.7	0.3246	0.911	24.833
3	13.099	19600.7	814.2	0.4012	0.853	25.179
4	13.794	19619.7	749.6	0.4362	0.899	25.204



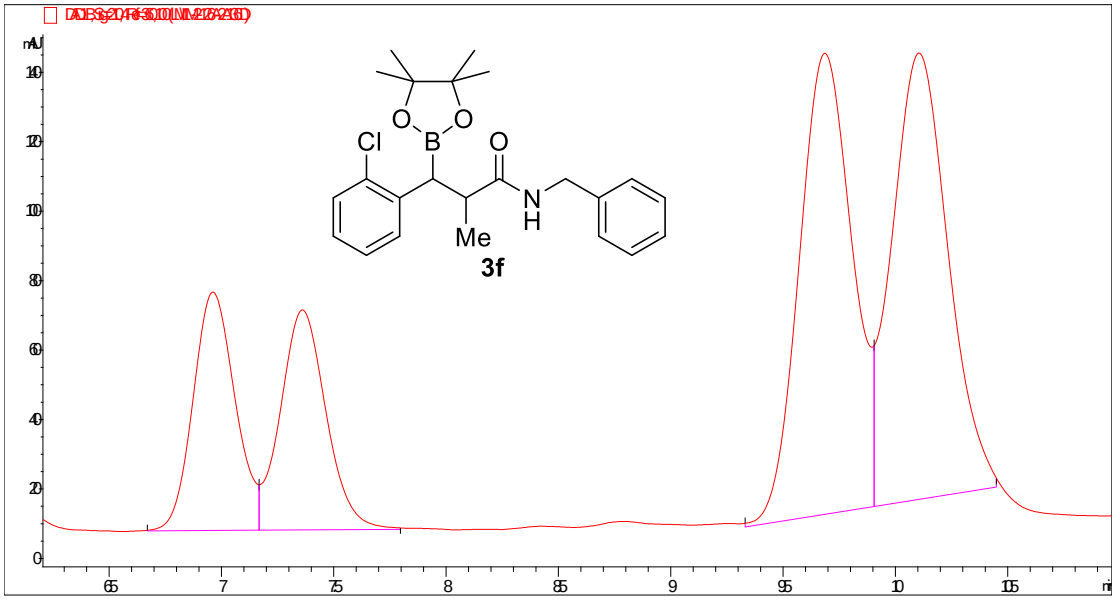
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	12.801	157.8	8	0.2868	1.651	4.877
2	13.388	3077.5	122.4	0.3873	0.908	95.123



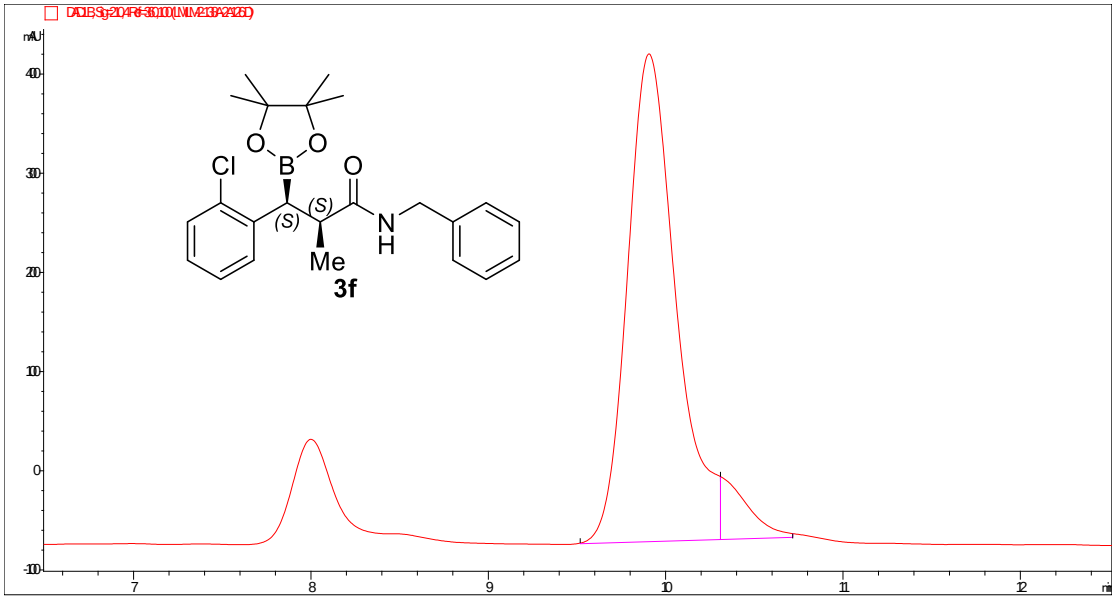
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.055	2117.2	151.4	0.2331	0.842	13.988
2	8.418	2094.5	133.8	0.2609	0.937	13.839
3	11.366	5468.3	271.2	0.336	0.881	36.129
4	12.418	5455.5	228.1	0.3986	0.914	36.044



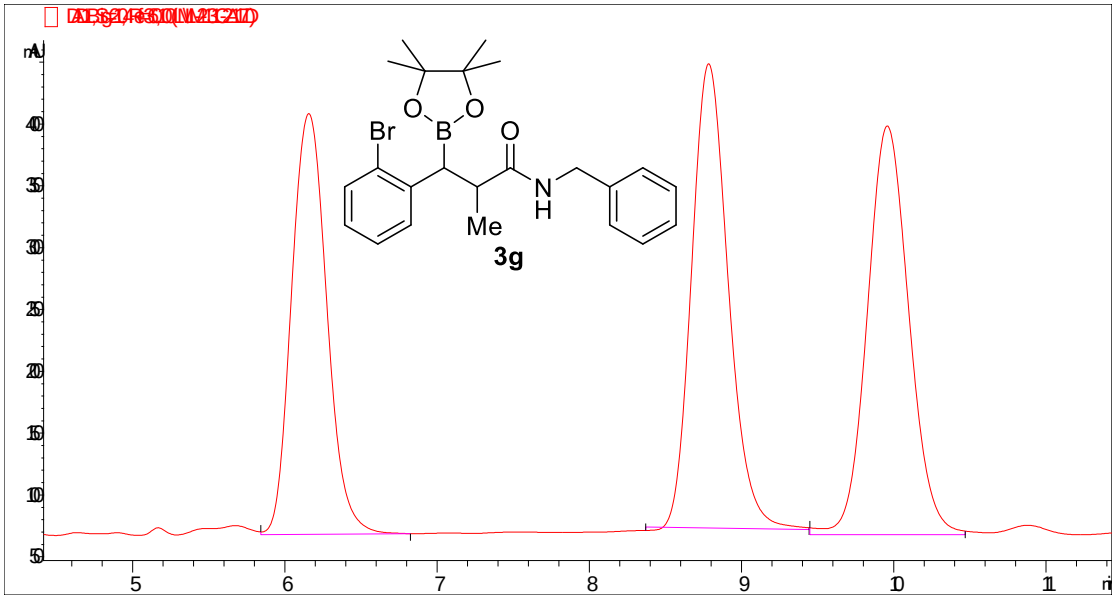
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.308	172	8.2	0.351	0.519	3.573
2	12.355	4641.4	198.5	0.3897	0.853	96.427



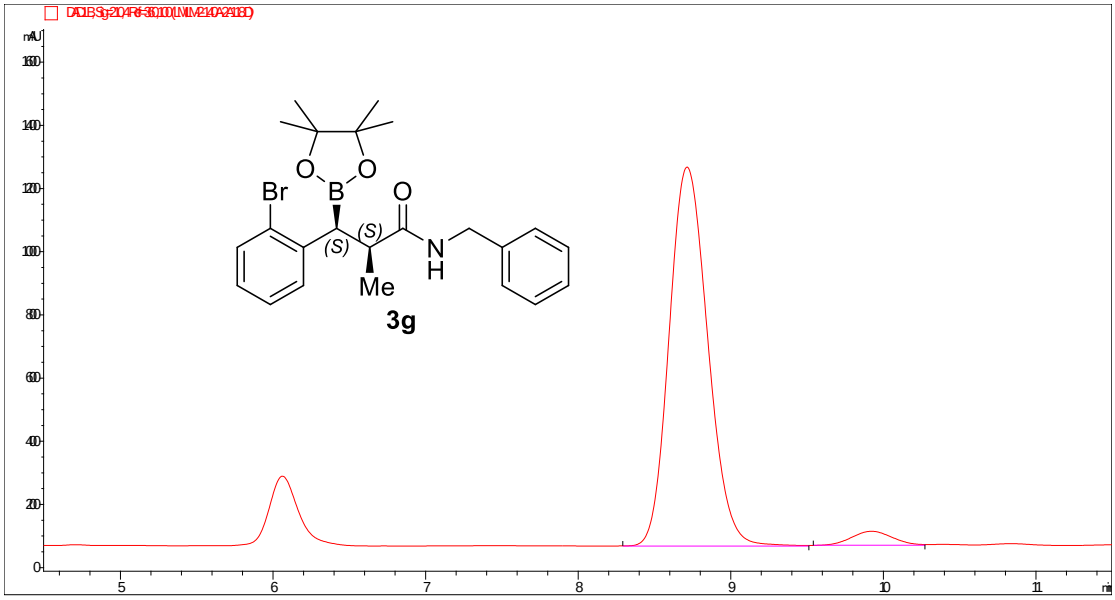
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	6.961	893.3	68.7	0.1997	0.863	14.406
2	7.359	896.1	63.4	0.2169	0.88	14.451
3	9.684	2188.8	132.8	0.2746	0	35.299
4	10.104	2222.6	128.6	0.288	0.895	35.843



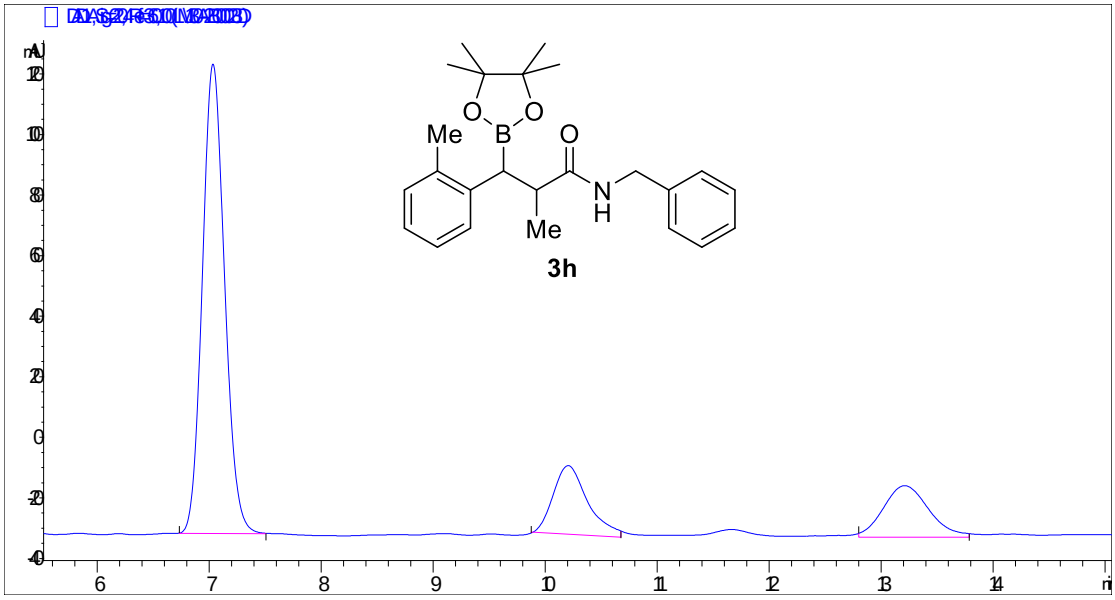
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.559	5143.2	318.6	0.2686	0.886	93.555
2	9.978	353.7	25.7	0.229	0.836	6.445



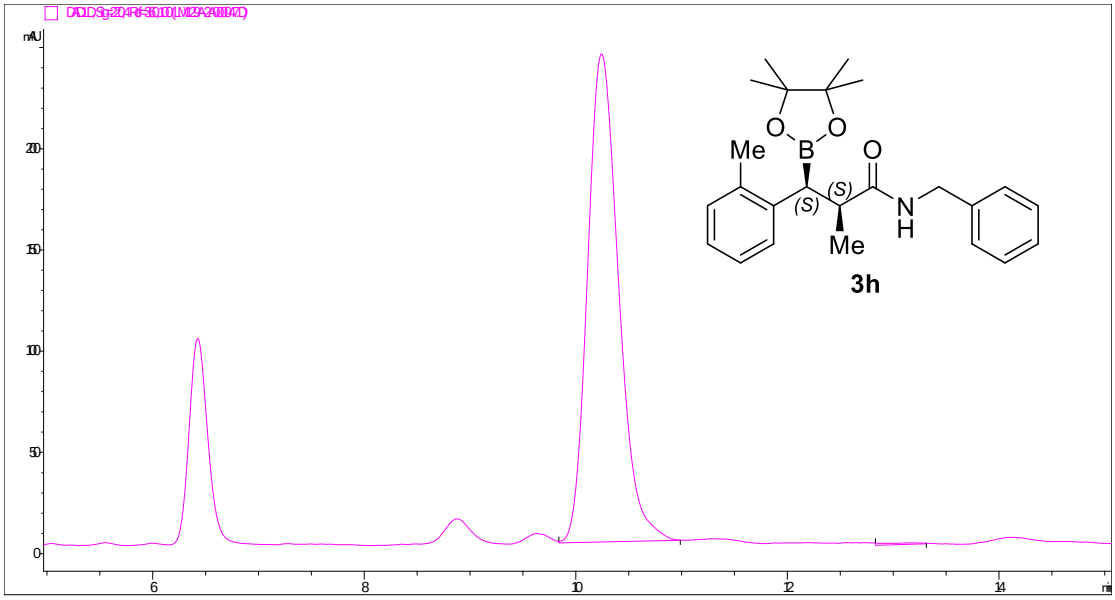
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	6.154	5481.3	340.3	0.2559	0.893	30.361
2	8.781	6282.7	375.5	0.2788	0.826	34.800
3	9.954	6289.7	330.7	0.317	0.904	34.839



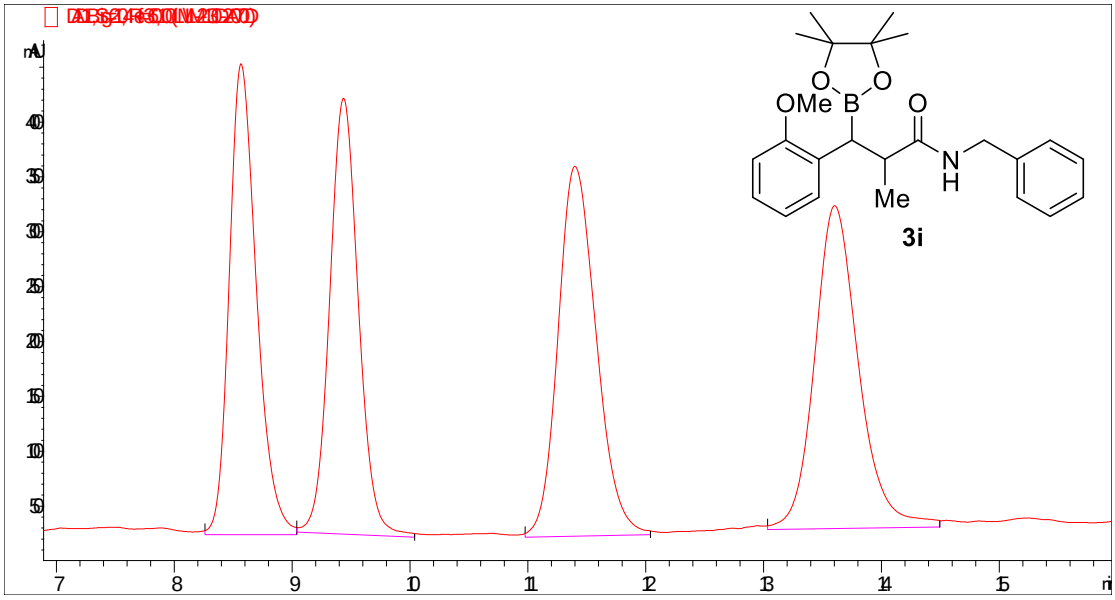
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	8.716	21047.7	1199.9	0.2746	0.818	96.208
2	9.924	829.6	44.4	0.3114	0.918	3.792



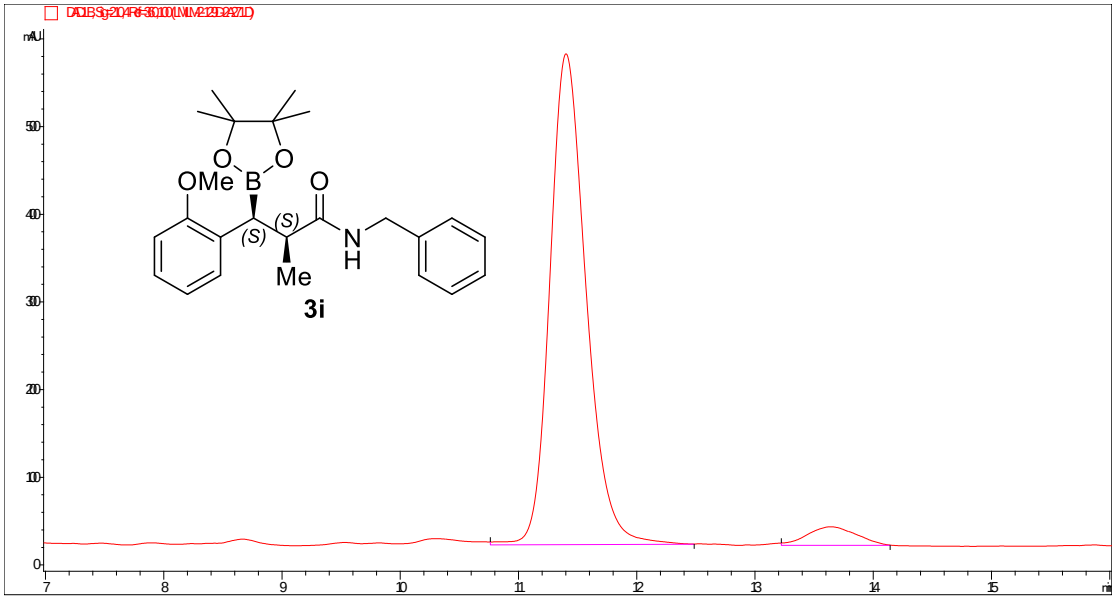
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.033	2136.6	155.1	0.2147	0.863	68.743
2	10.206	486.6	22.7	0.3574	0.725	15.655
3	13.211	484.9	17.1	0.474	0.863	15.602



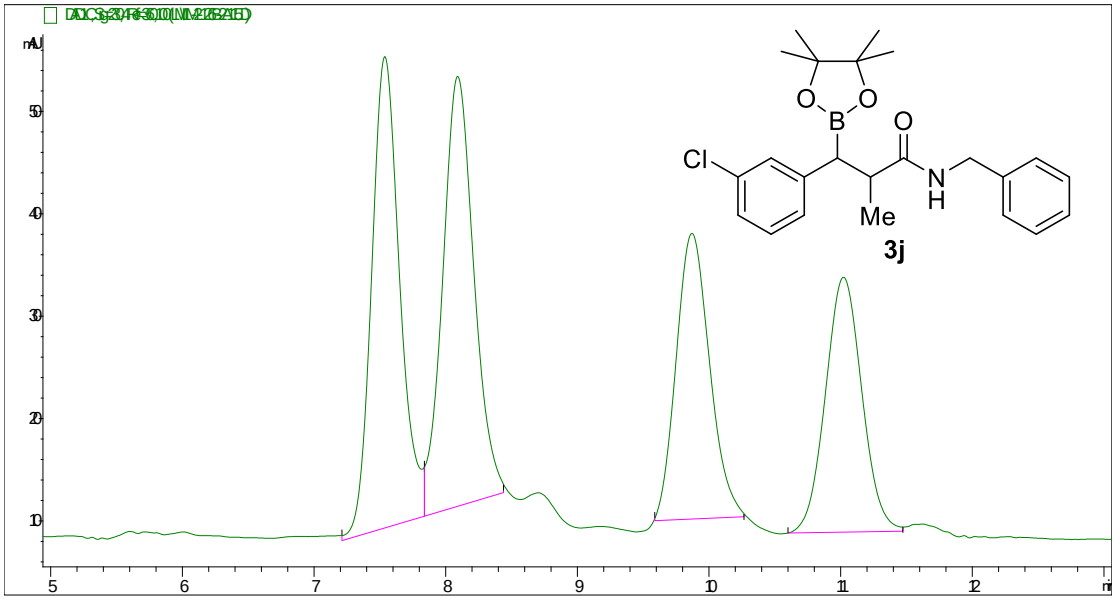
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	10.243	4913.9	241.2	0.3157	0.769	99.573
2	13.156	21.1	7.7E-1	0.3315	0	0.427



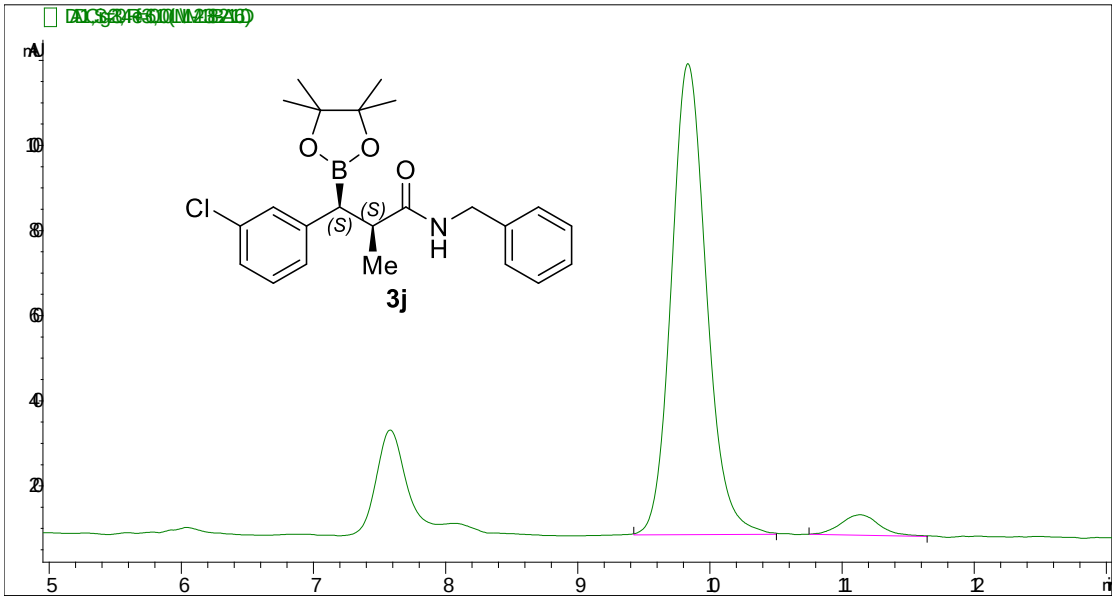
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	8.566	6902.7	429.3	0.268	0.733	23.900
2	9.435	6749.1	397.5	0.283	0.903	23.368
3	11.398	7591.5	337.2	0.3752	0.773	26.285
4	13.602	7638.2	294.3	0.4325	0.811	26.447



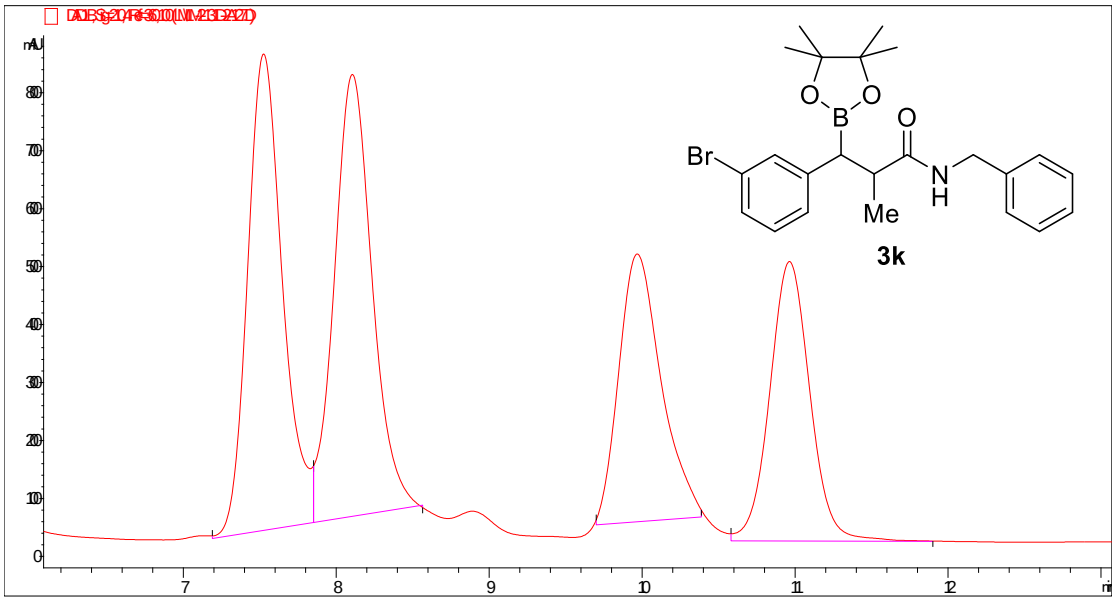
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.405	11933.3	559.9	0.3266	0.761	95.086
2	13.644	616.7	21.3	0.4826	0.913	4.914



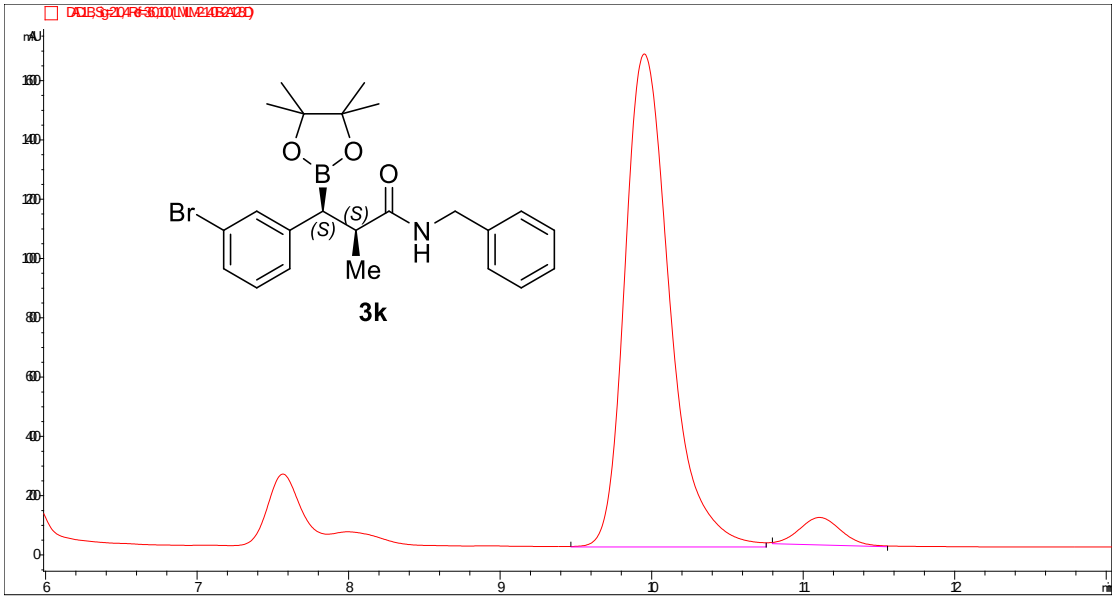
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.535	684.1	46.1	0.2473	0	29.152
2	8.809	691.8	42.1	0.2742	0.9	29.480
3	9.868	492	27.9	0.2936	0.861	20.968
4	11.019	478.7	24.9	0.3003	0.948	20.400



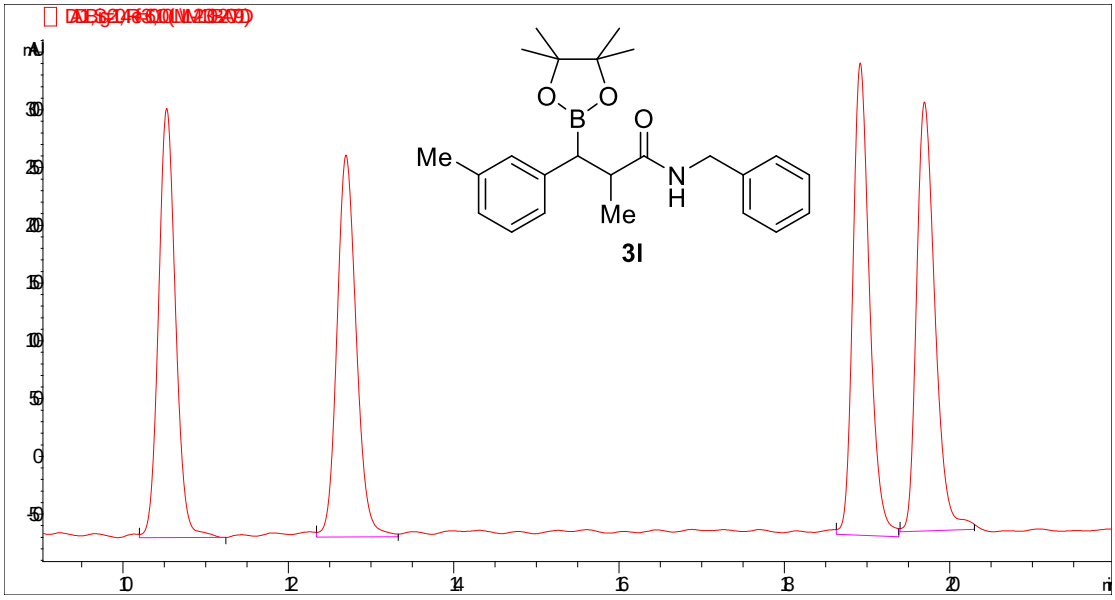
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.831	2035.2	110.7	0.2825	0.843	95.381
2	11.136	98.6	4.8	0.3088	0.954	4.619



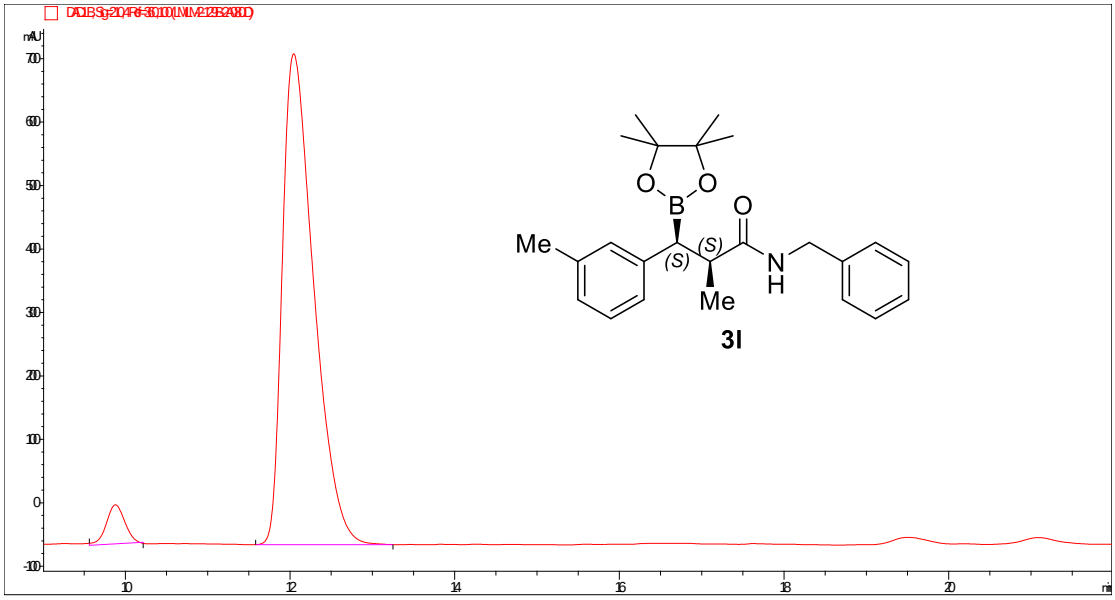
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.526	13054.3	822.4	0.2645	0	29.775
2	8.106	13114	762.8	0.2865	0.888	29.911
3	9.969	8861.2	462.1	0.3196	0.744	20.212
4	10.964	8813	482.3	0.2812	0.92	20.102



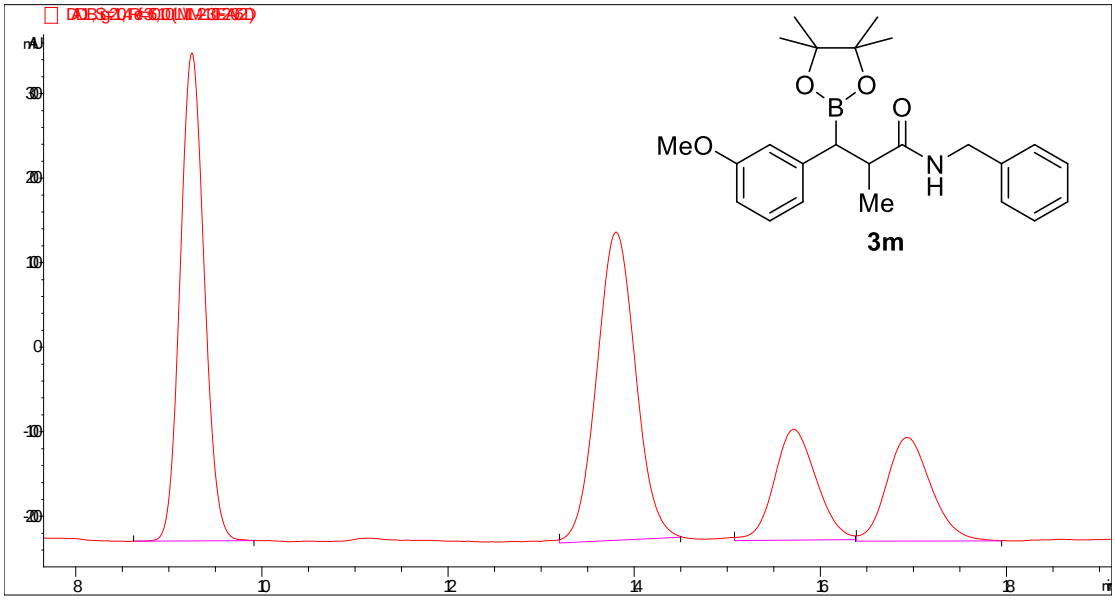
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.952	34349.9	1663.5	0.3189	0.713	95.070
2	11.107	1781.4	92.7	0.3202	0.885	4.930



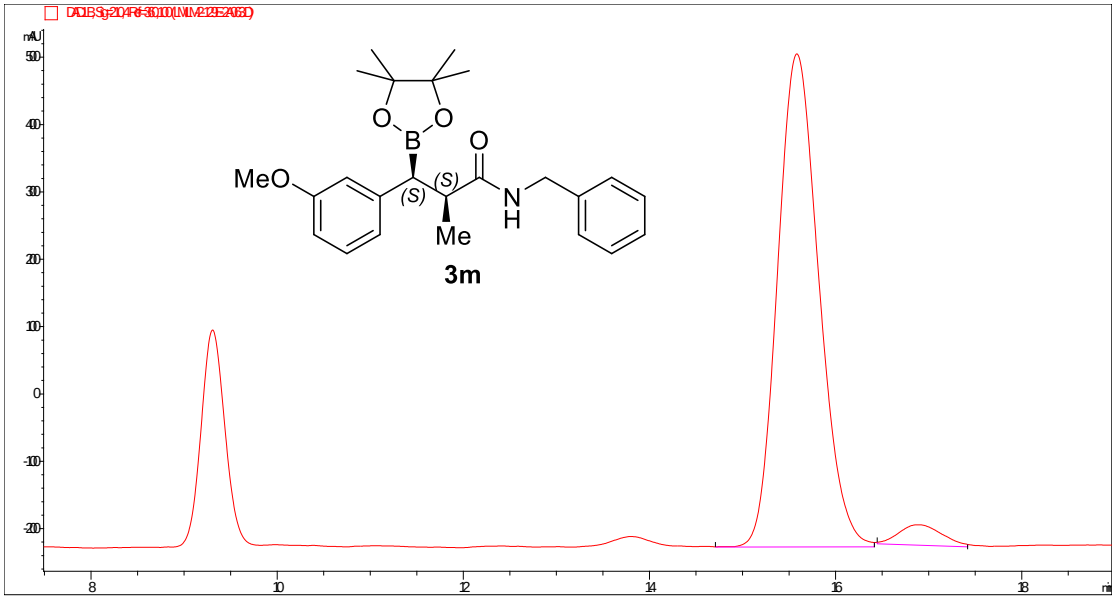
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	10.529	5333.4	371.6	0.2195	0.861	23.989
2	12.698	5370.7	330.7	0.2515	0.827	24.157
3	18.918	5767.2	408.9	0.2351	0.756	25.940
4	19.694	5761.7	371.5	0.2585	0.709	25.915



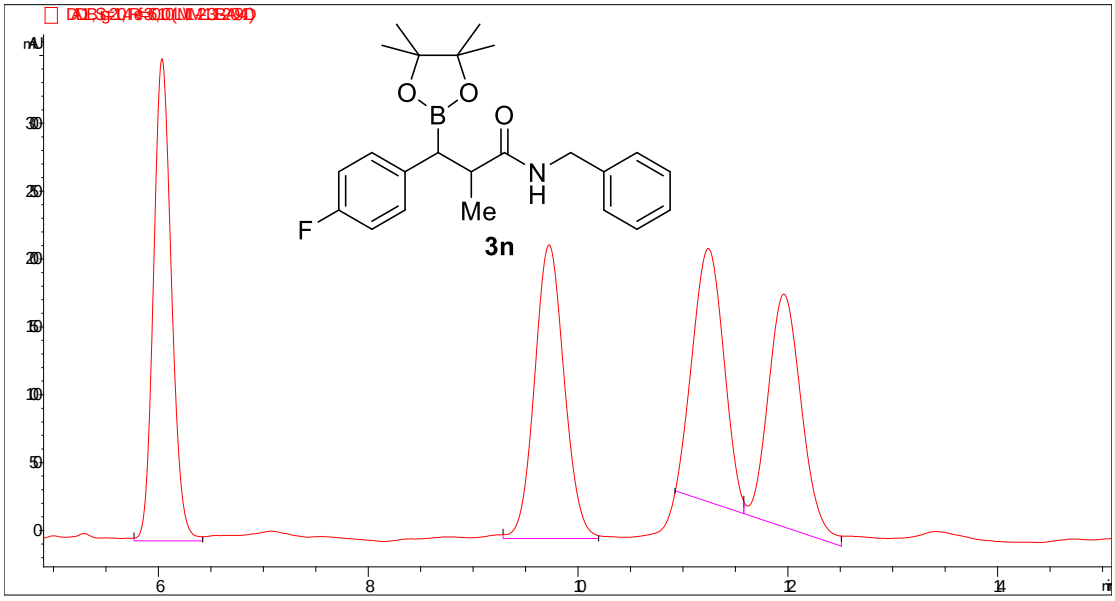
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.876	956.8	61.7	0.2586	0.973	4.448
2	12.041	20554.7	773.7	0.4	0.526	95.552



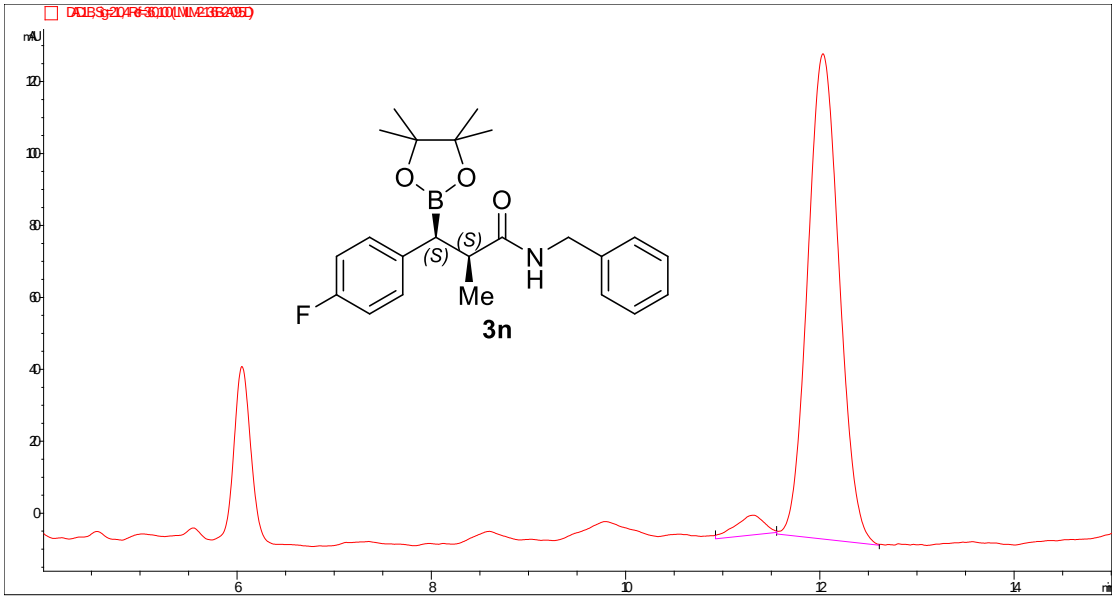
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.249	10411.7	577.5	0.2824	0.902	35.705
2	13.806	10555.8	364.6	0.4826	0.962	36.200
3	15.714	4114.3	131	0.5233	0.841	14.109
4	16.932	4078.3	122.6	0.506	0.818	13.986



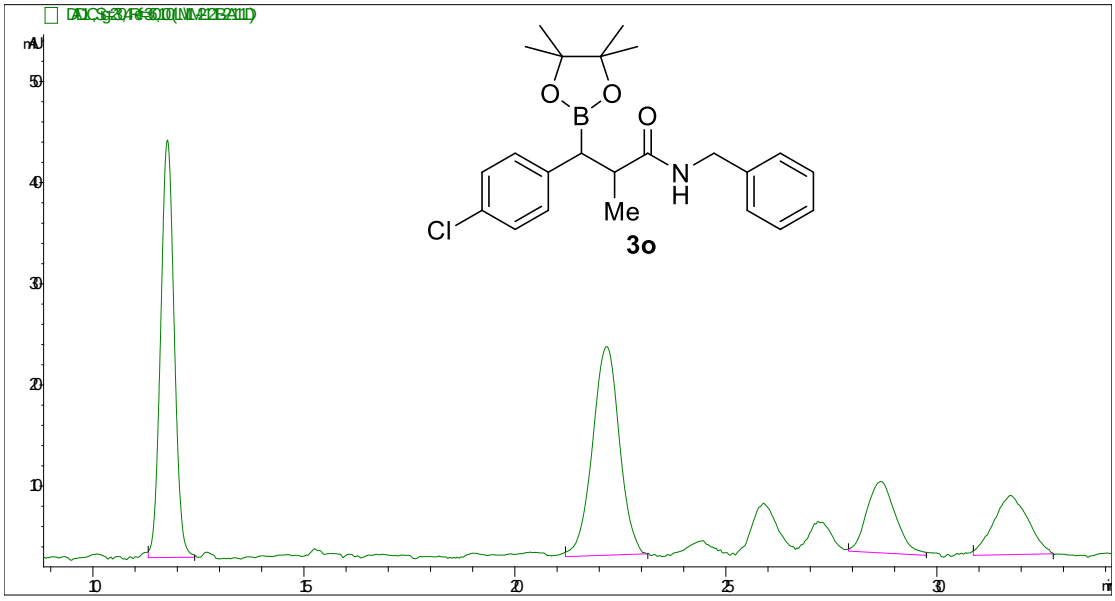
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	15.581	22553.6	732.2	0.4754	0.834	95.819
2	16.908	984.2	30.3	0.5406	0.7	4.181



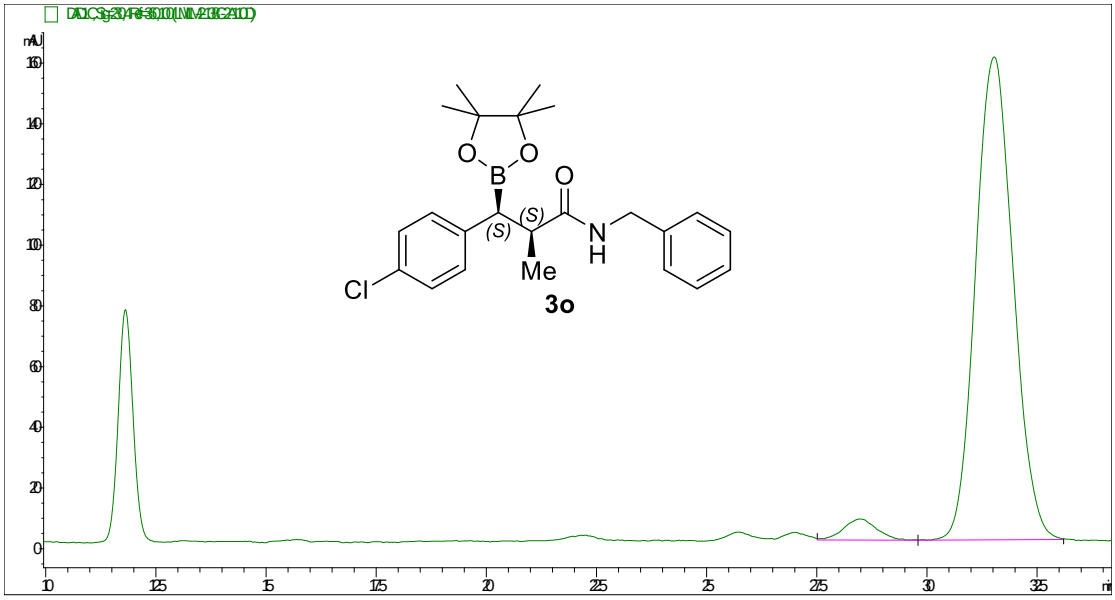
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	6.036	4241.3	355.5	0.1852	0.84	26.267
2	9.725	4246.1	216.5	0.3269	0.925	26.297
3	11.247	3855.1	186.8	0.3439	0.952	23.875
4	11.967	3804.4	171.7	0.3694	0.835	23.561



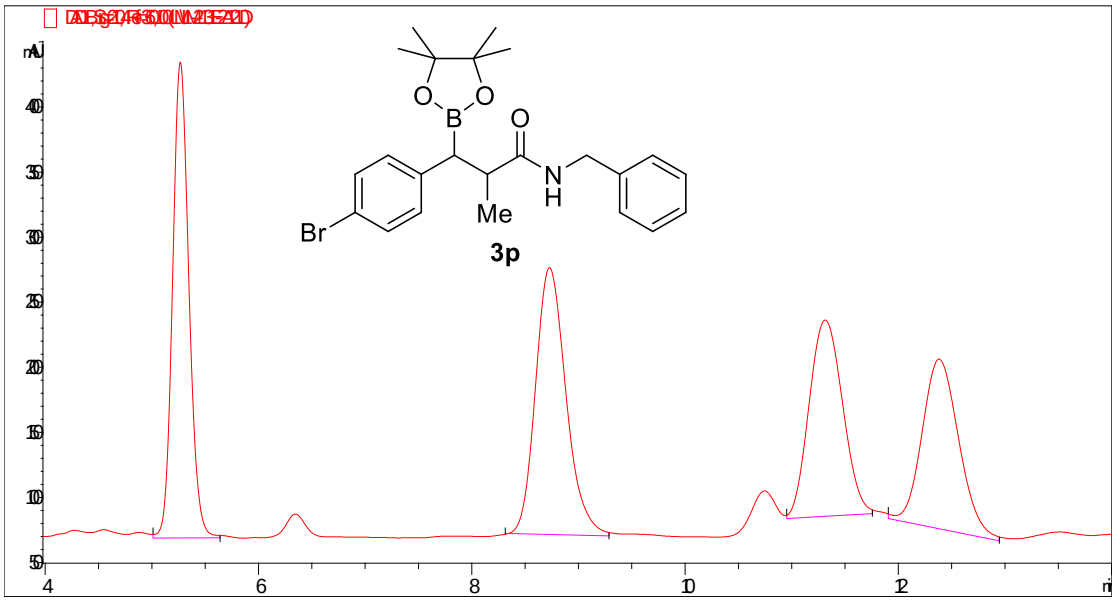
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.314	114.6	5.5	0.3481	1.7	3.630
2	12.033	3043.4	134.9	0.3759	0.906	96.370



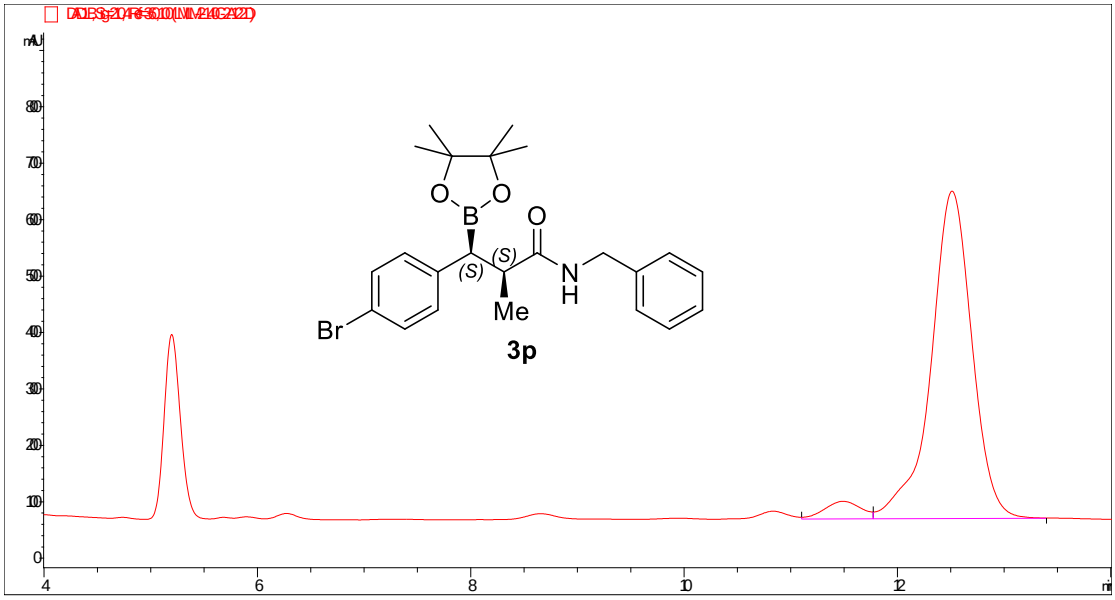
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.768	924	41.3	0.3411	0.956	36.828
2	22.177	917.7	20.6	0.741	1.079	36.577
3	28.685	334.8	7.1	0.7905	0.941	13.344
4	31.755	332.5	5.9	0.9453	0.975	13.251



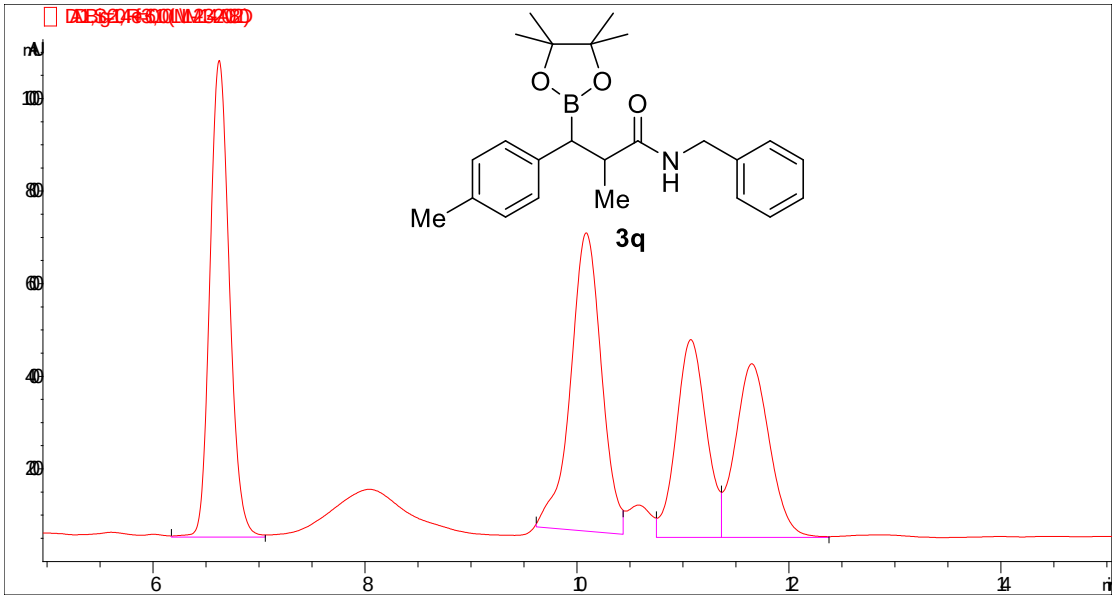
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	28.483	369.7	7	0.6705	0.966	3.770
2	31.527	9438.4	159.1	0.9002	0.937	96.230



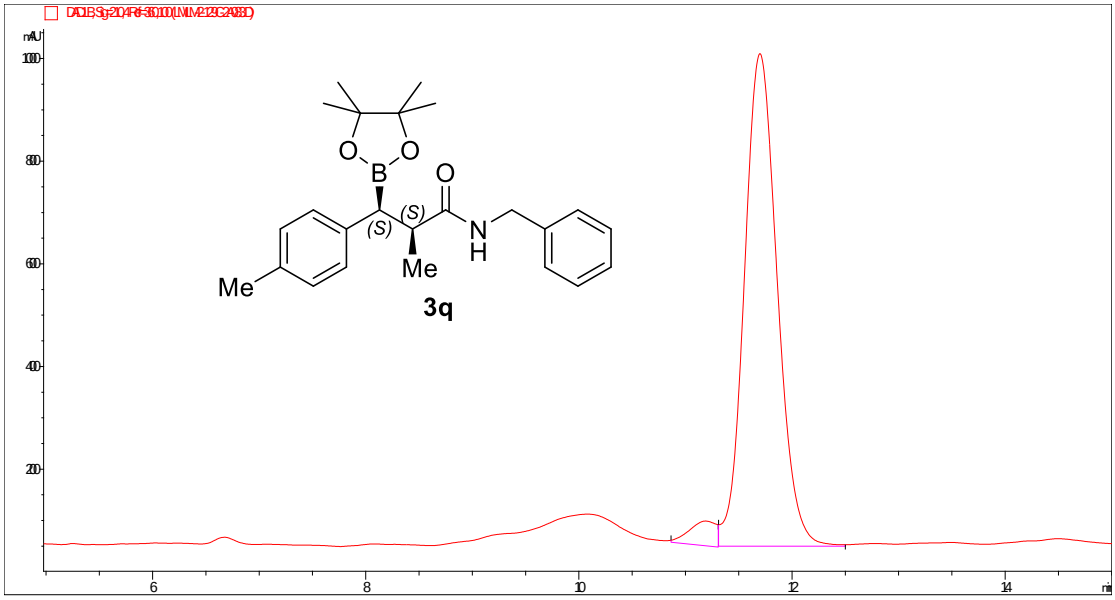
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	5.268	3879.5	365.5	0.1638	0.848	27.055
2	8.73	4065.7	204.8	0.3308	0.81	28.353
3	11.315	3283.5	150.7	0.3631	0.894	22.899
4	12.386	3110.6	130.2	0.3981	0.834	21.693



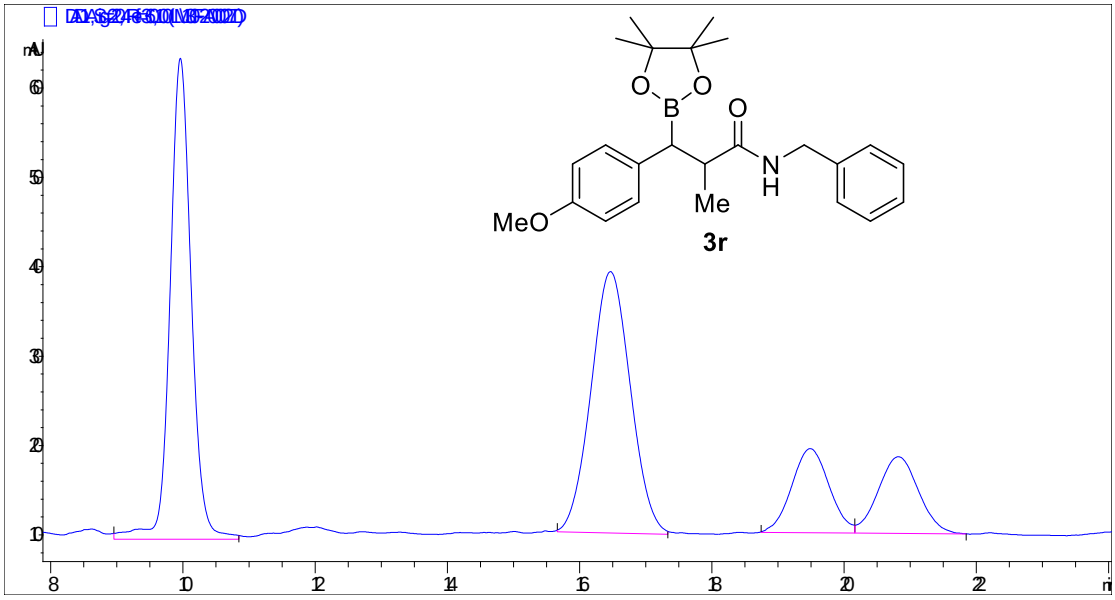
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.493	738.4	31.1	0.3709	1.043	4.554
2	12.515	15474.2	580.2	0.4052	1.057	95.446



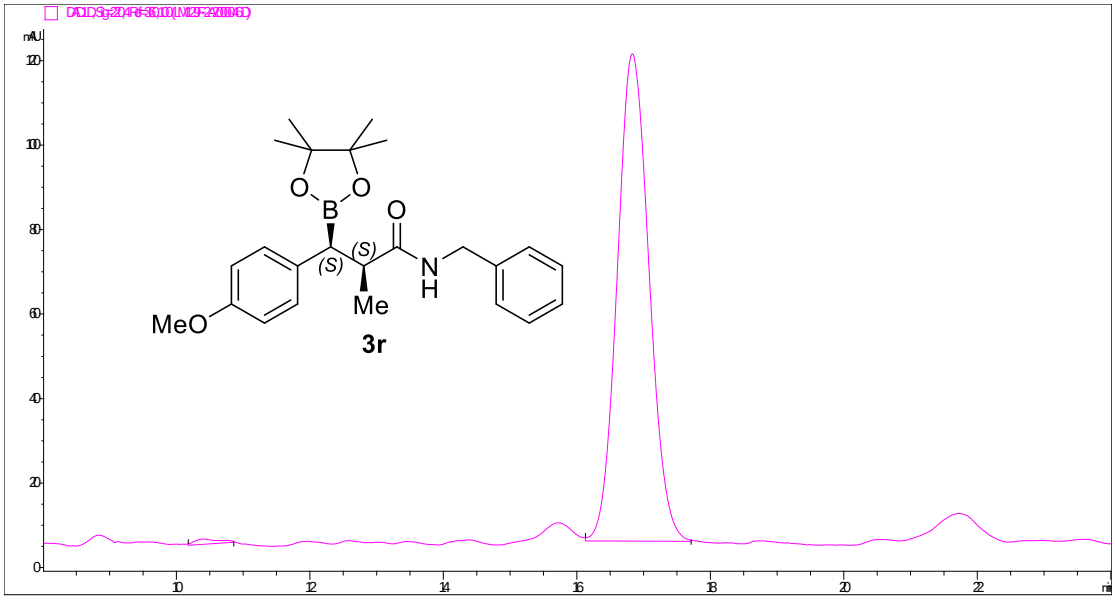
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	6.622	13172	1030	0.1992	0.854	30.524
2	10.085	13084.2	644.6	0.3383	1.002	30.321
3	11.071	8443.6	427.2	0.3026	0.92	19.567
4	11.647	8453	375.3	0.3448	0.866	19.589



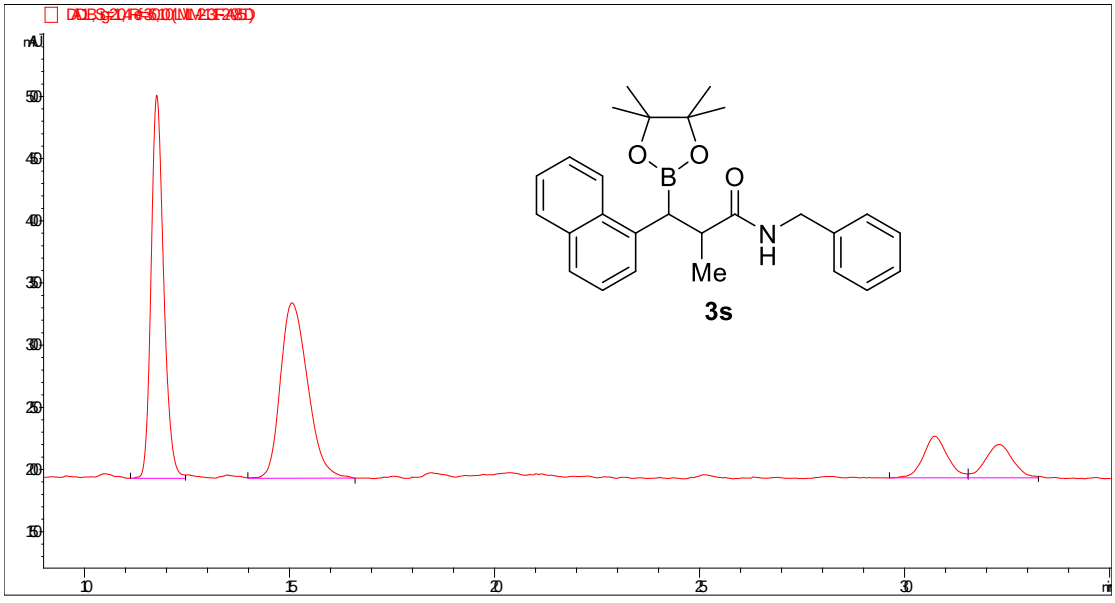
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.194	844	48.3	0.2915	1.452	3.947
2	11.696	20540	959.4	0.3298	0.855	96.053



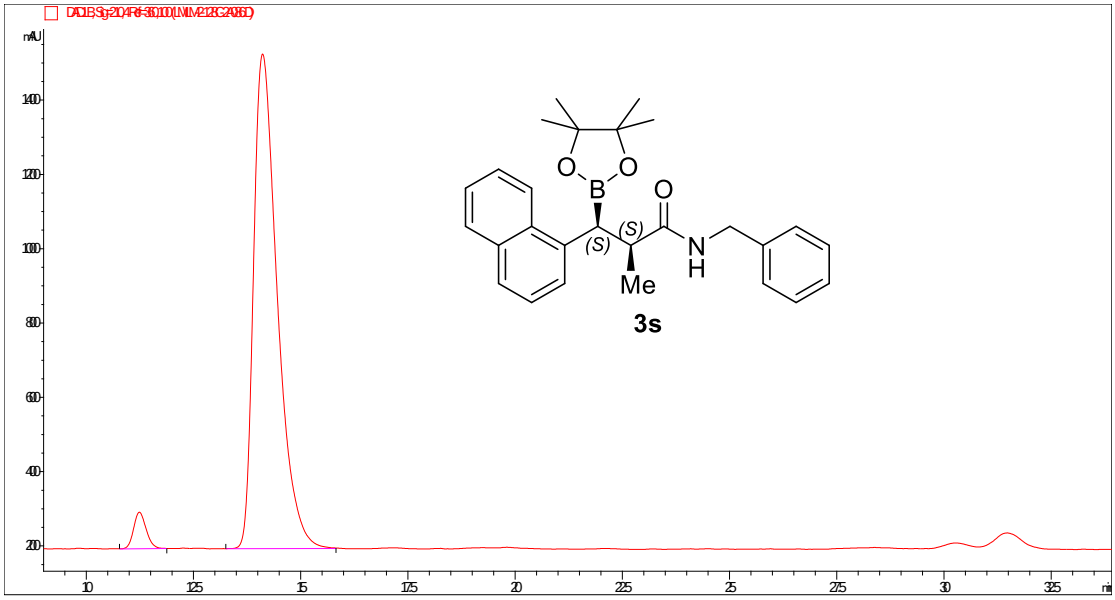
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	9.959	1205.6	53.8	0.3733	0.928	38.205
2	16.463	1213.1	29.3	0.6911	0.948	38.411
3	19.482	371.6	9.4	0.6025	0.931	11.774
4	20.819	365.4	8.6	0.6122	0.955	11.580



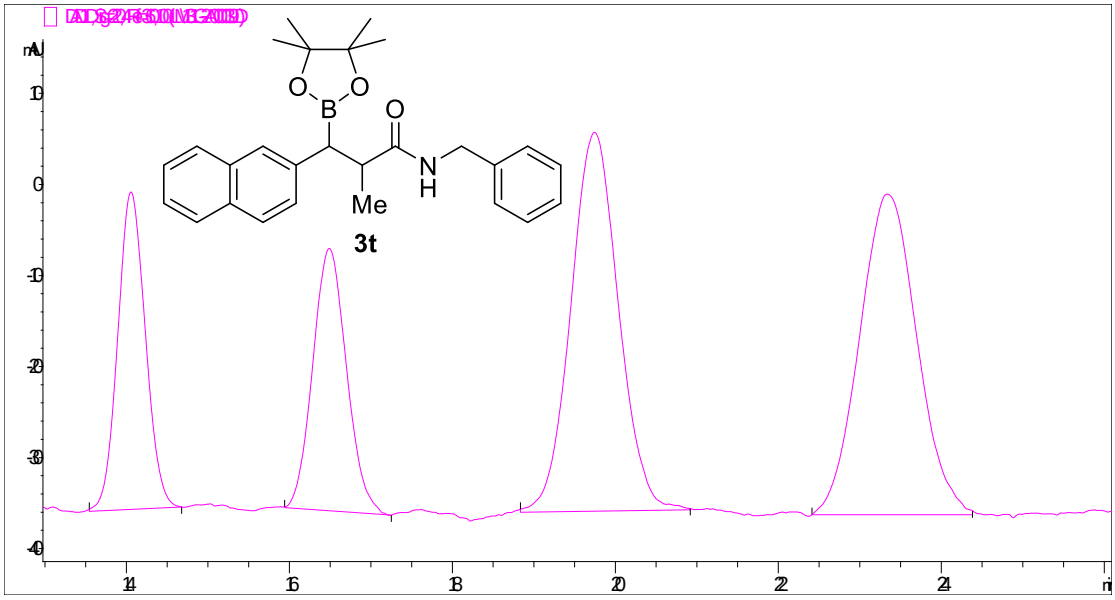
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	10.396	31.7	1.2	0.4238	0.572	0.822
2	16.834	3828.1	115.4	0.5171	0.873	99.178



No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.765	6573.6	308.1	0.3269	0.77	41.902
2	15.063	6496.7	141	0.6957	0.702	41.412
3	30.732	1375.5	33.4	0.6	0.856	8.768
4	32.301	1242	26.8	0.6344	0.954	7.917

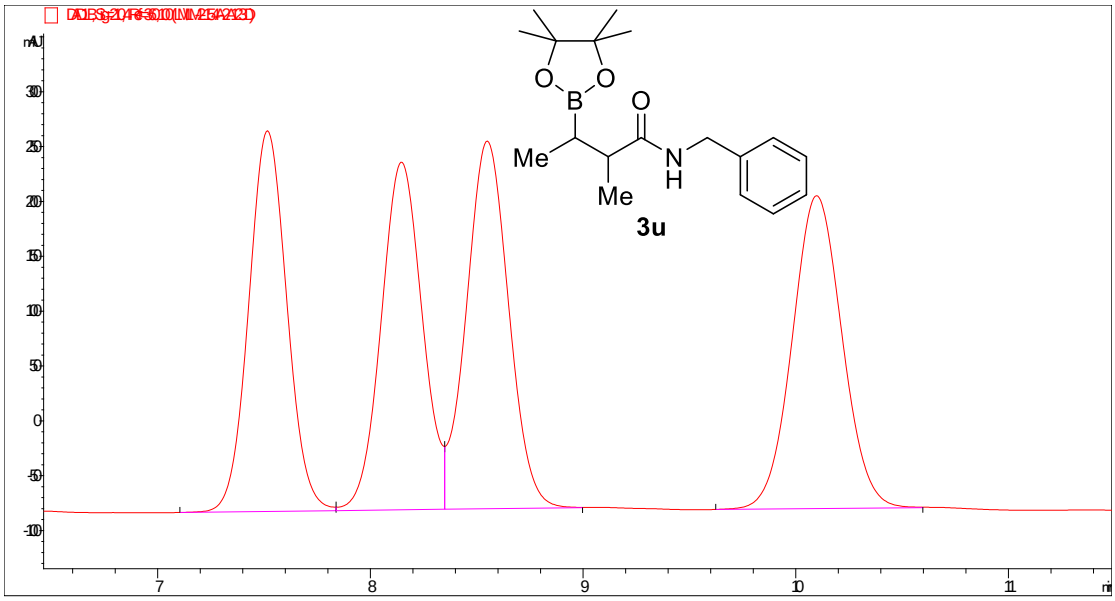


No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	11.238	2004.6	98.4	0.3098	0.817	3.769
2	14.112	51186.3	1331.6	0.5845	0.568	96.231

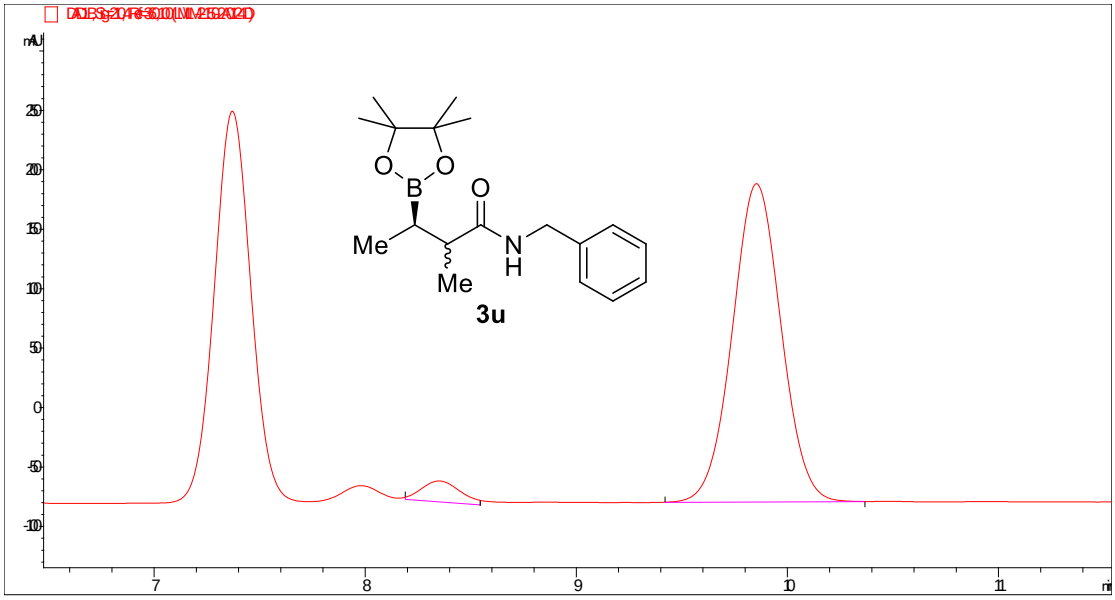


No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	14.053	821.6	34.9	0.3629	0.892	16.248
2	16.485	829.4	28.8	0.4298	0.911	16.402
3	19.741	1687.7	41.6	0.6759	0.96	33.375
4	23.334	1718.1	35.2	0.8132	0.92	33.976

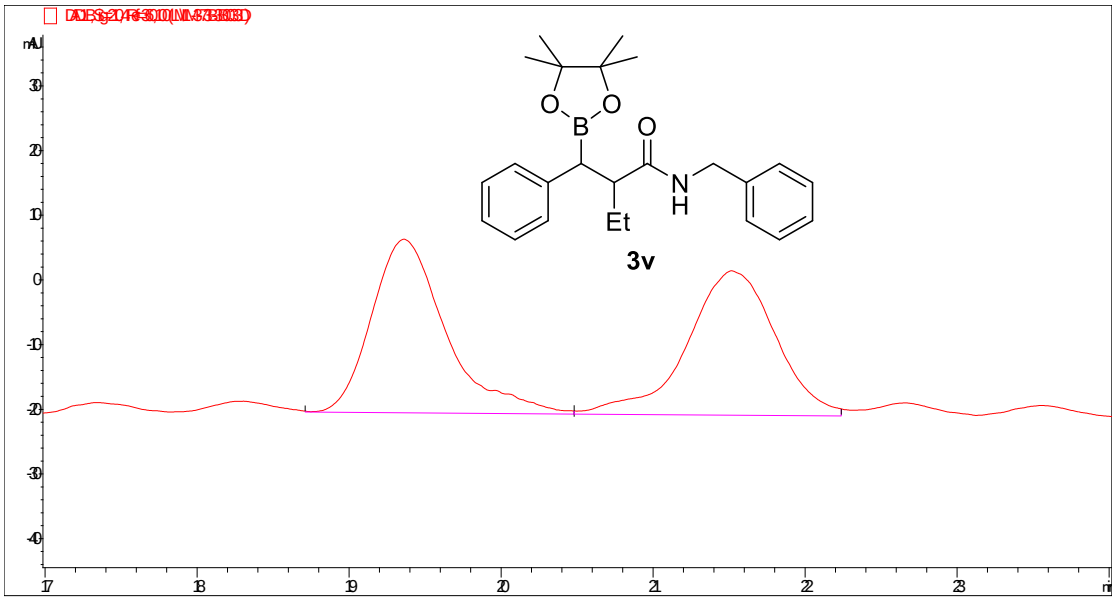
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	19.31	18322.1	450.6	0.6144	0.842	95.795
2	23.011	804.3	16.8	0.7998	0.99	4.205



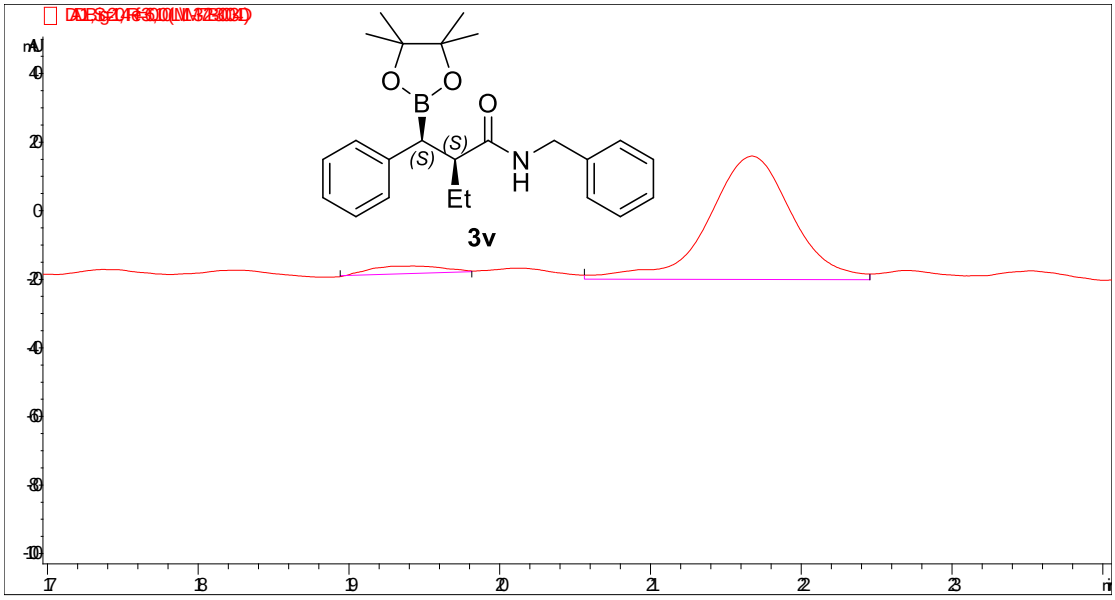
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	7.516	4328.1	347	0.1955	0.929	24.225
2	8.147	4251.5	317.1	0.2064	0.955	23.797
3	8.55	4636.4	335.2	0.2134	0.939	25.951
4	10.099	4649.8	285.2	0.2542	0.929	26.026



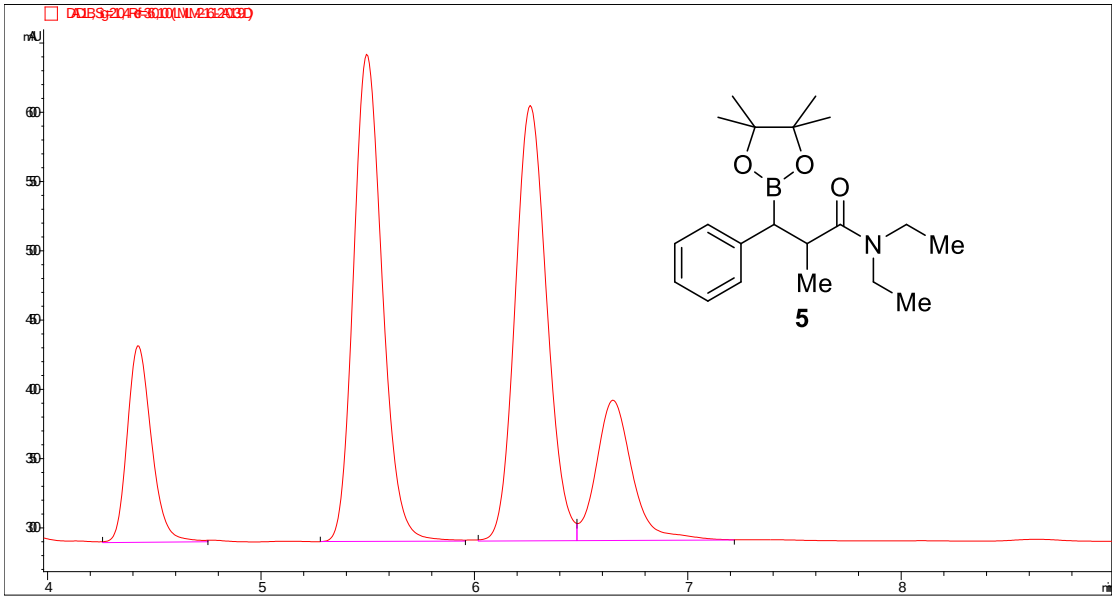
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	8.354	224	17.6	0.2117	0.754	4.949
2	9.851	4301	267.9	0.2493	0.953	95.051



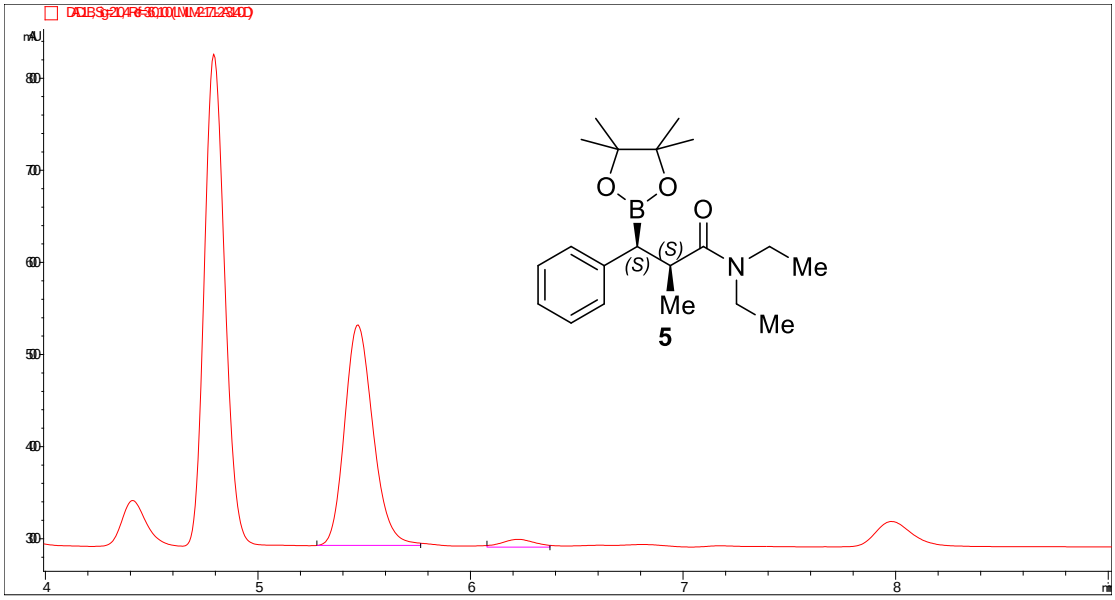
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	19.359	912.8	26.8	0.5669	0.737	50.243
2	21.515	903.9	22.3	0.6749	1.02	49.757



No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	19.422	75.5	2.2	0.5729	1.412	5.148
2	21.673	1390.7	36	0.5866	1.077	94.852



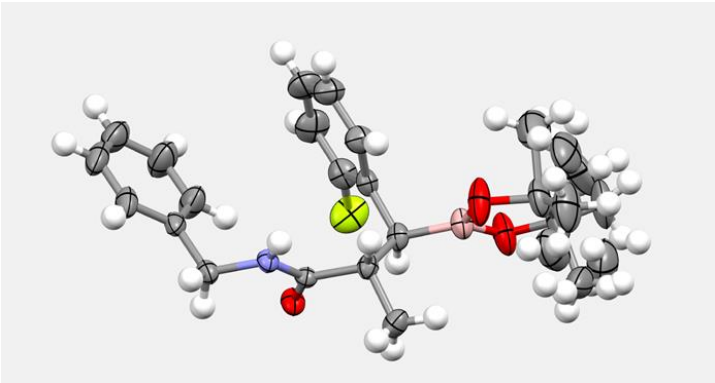
No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	4.421	1119.4	142.1	0.1199	0.758	12.645
2	5.493	3306.5	351.8	0.1456	0.803	37.350
3	6.258	3249.8	314.3	0.1606	0.861	36.709
4	6.646	1177.1	101.2	0.1776	0.795	13.296



No.	Time	Peak Area	Peak Height	Peak Width	Symmetry Factor	Peak Area %
1	5.47	2221.6	239.7	0.1545	0.813	96.068
2	6.224	90.9	8.4	0.1806	0.923	3.932

VI. X-ray Analysis of 3e

The single crystal of **3e** could be obtained by slow evaporation of the solvent (*n*-hexane and methyl *tert*-butyl ether) at room temperature. Crystallographic data (excluding structure factors) for the structure has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number (CCDC 2171509).



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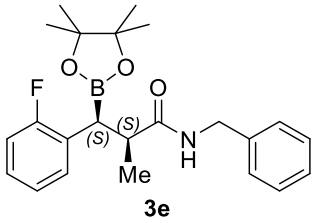
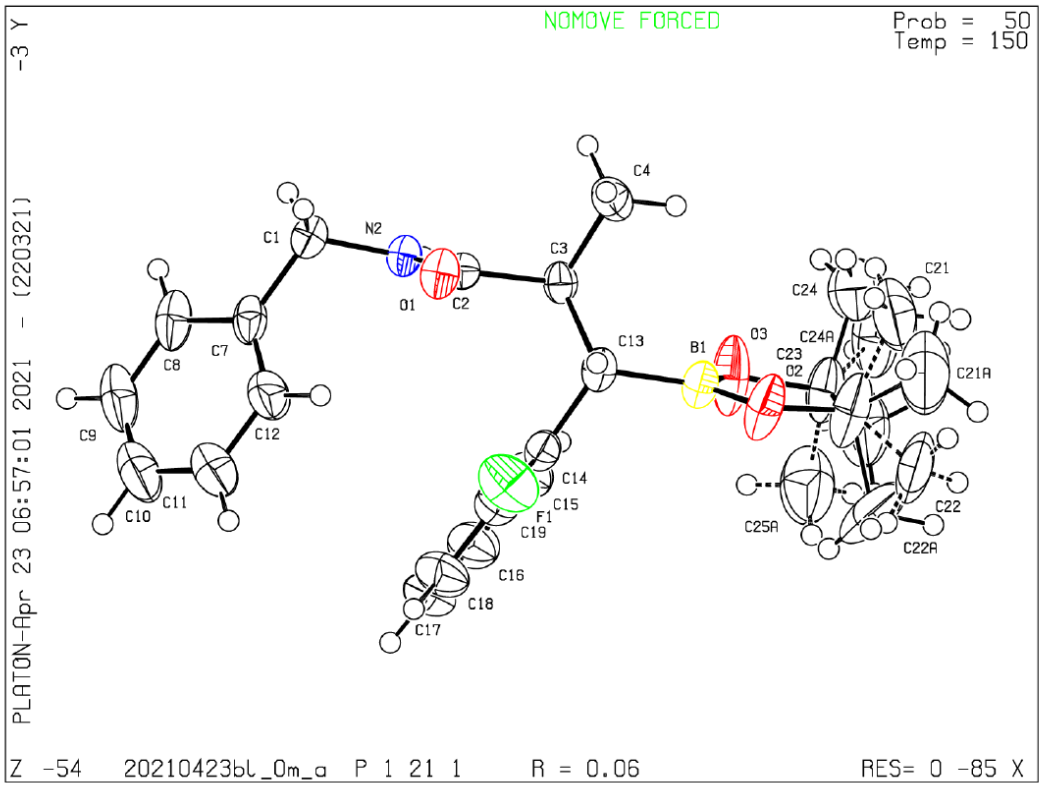




The above figure was showed as ellipsoids at 50% probability level.

Bond precision: C-C = 0.0057 A Wavelength=1.34139

Cell: a=10.0208 (5) b=9.4096 (5) c=12.1630 (7)
alpha=90 beta=93.034(2) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1145.26(11)	1145.26(11)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C23 H29 B F N O3	C23 H29 B F N O3
Sum formula	C23 H29 B F N O3	C23 H29 B F N O3
Mr	397.28	397.28
Dx, g cm- 3	1.152	1.152
Z	2	2
Mu (mm- 1)	0.413	0.416
F000	424 .0	424 .0
F000'	424.98	
h, k, l max	12, 11, 14	12, 11, 14
Nref	4232 [2256]	4152
Tmin, Tmax	0.920, 0.920	0.577, 0.751
Tmin'	0.920	

Correction method= # Reported T Limits: Tmin= 0.577 Tmax=0. 751
AbsCorr = MULTI - SCAN

Data completeness= 1.84/ 0.98 Theta(max)= 54 .101

R(reflections)= 0.0577(3897) wR2(reflections)= 0.1659(4152)

S = 1.039 Npar = 308

VII. Reference

[1] For selected examples for the syntheses of chiral ligands, see: (a) Nie, H. F., Yao, L., Li, B., Zhang, S. Y., Cheng, W. P. Very simple and highly modular synthesis of ferrocene-based chiral phosphines with a wide variety of substituents at the phosphorus atom(s). *Organometallics* **2014**, *33*, 2109−2114. (b) Itoh, T., Kanzaki, Y., Shimizu, Y., Kanai, M. Copper(I)-catalyzed enantio- and diastereodivergent borylative coupling of styrenes and imines. *Angew*. *Chem*., *Int*. *Ed*. **2018**, *57*, 8265–8269. (c) Yu, J. F., Long, J., Yang, Y. H., Wu, W. L., Xue, P., CHUNG, L. W., Dong, X. Q., Zhang, X. M. Iridium-catalyzed asymmetric hydrogenation of ketones with accessible and modular ferrocene-based amino-phosphine-acid (f-ampha) ligands. *Org*. *Lett*. **2017**, *19*, 690−693. (d) How, R. C., Hembre, R., Ponasik, J. A., Tolleson, G. S., Clarke, M. L. A modular family of phosphine-phosphoramidite ligands and their hydroformylation catalysts: steric tuning impacts upon the coordination geometry of trigonal bipyramidal complexes of type [Rh(H)(CO)2(P^P*)]. *Catal*. *Sci*. *Technol*. **2016**, *6*, 118−124. (e) Sawano, T., Ou., Nishimura, T., Hayashi, T. Cobalt-catalyzed asymmetric addition of silylacetylenes to 1,1- disubstituted allenes. *J*. *Org*. *Chem*. **2013**, *78*, 8986−8993.

[2] For selected examples for the syntheses of methyl ester compounds, see: (a) Fort, Y., Berthe, M. C., Caubere, P. The 'Baylis-Hillman Reaction' Mechanism and applications revisited. *Tetrahedron* **1992**, *48*, 6371−6384. (b) Singh, D., Hazra, C. K., Malakar, C. C., Pandey, S. K., Kaith, B. S., Singh, V. Indium-mediated domino allylation-lactonisation approach: diastereoselective synthesis of β-Carboline C-3 Tethered α-Methylene γ-Butyrolactones. *ChemistrySelect*. **2018**, *3*, 4859–4864. (c) Das, B., Banerjee, J., Majhi, A., Mahender, G. An efficient stereoselective synthesis of (*E*)- and (*Z*)-trisubstituted alkenes from unactivated Baylis–Hillman adducts using $NaBH_4/CuCl_2{\cdot}2H_2O$. *Tetrahedron Lett*. **2004**, *45*, 9225–9227.

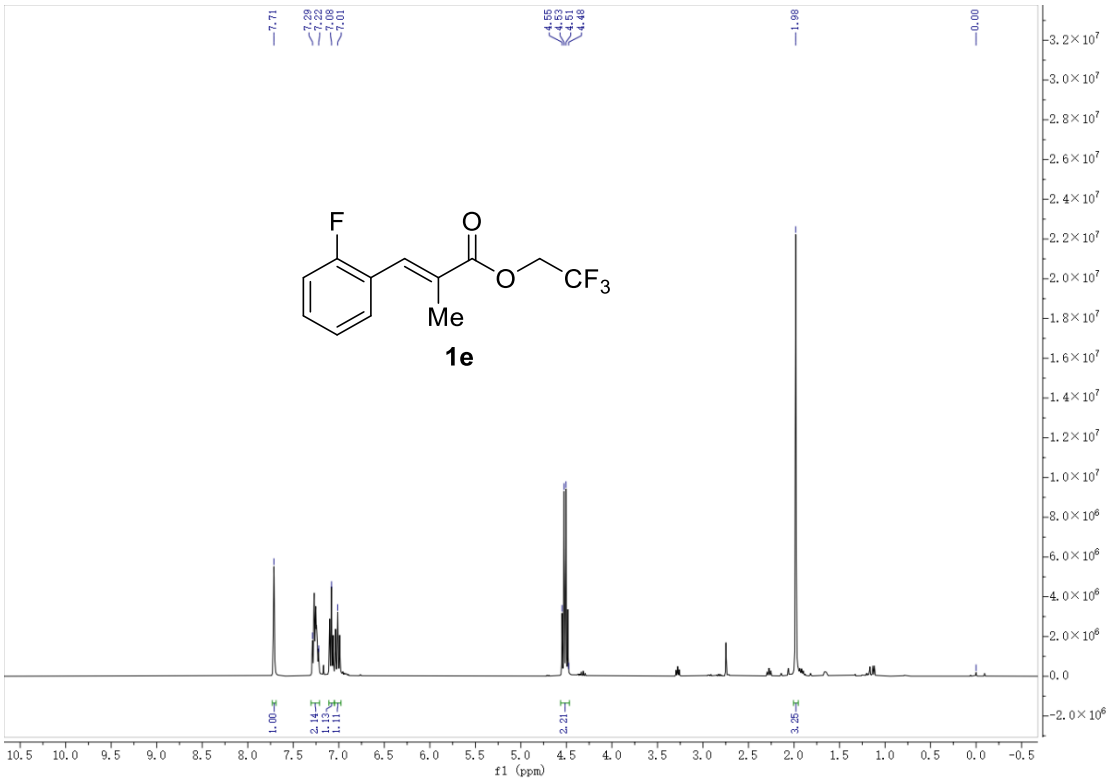
[3] Pandey, A. K., Kirberger, S. E., Johnson, J. A., Kimbrough, J. R., Partridge, D. K. D., Pomerantz, W. C. K. Efficient synthesis of 1,4-thiazepanones and 1,4-thiazepanes as 3D-fragments for screening libraries. *Org*. *Lett*. **2020**, *22*, 3946−3950.

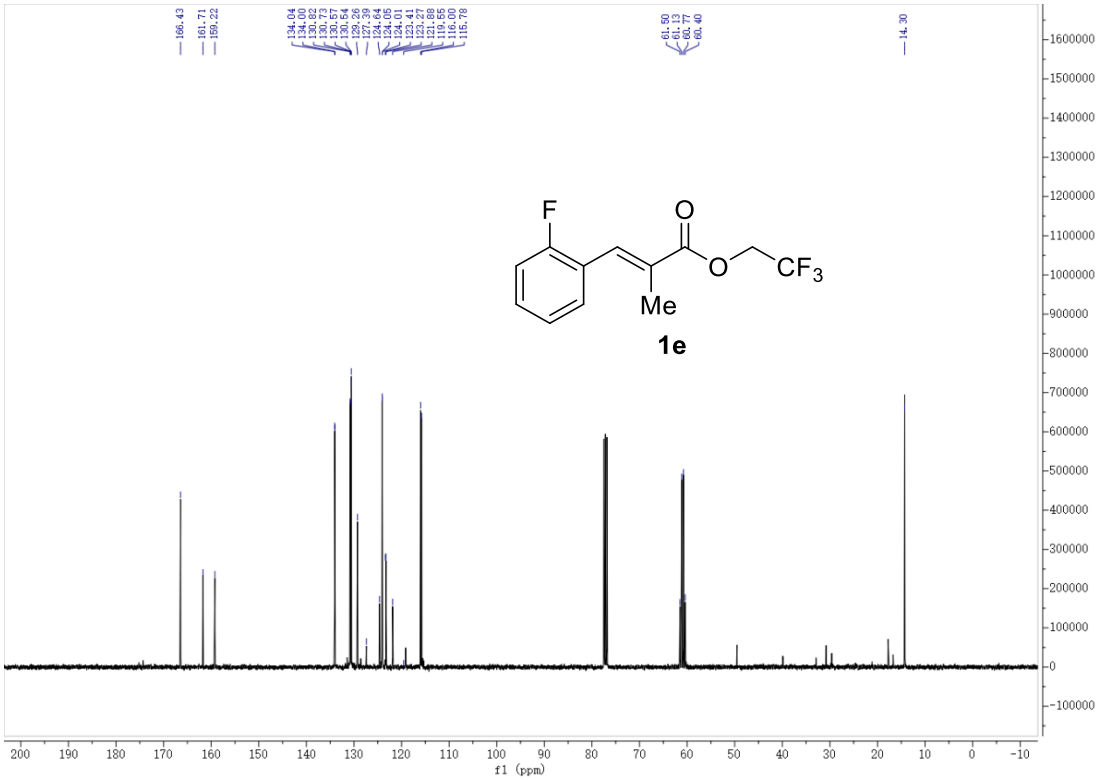
[4] Green, J. E., Bender, D. M., Jackson, S., O'Donnell, M. J., McCarthy, J. R. Mitsunobu approach to the synthesis of optically active α,α-disubstituted amino acids. *Org*. *Lett*. **2009**, *11*, 807−810.

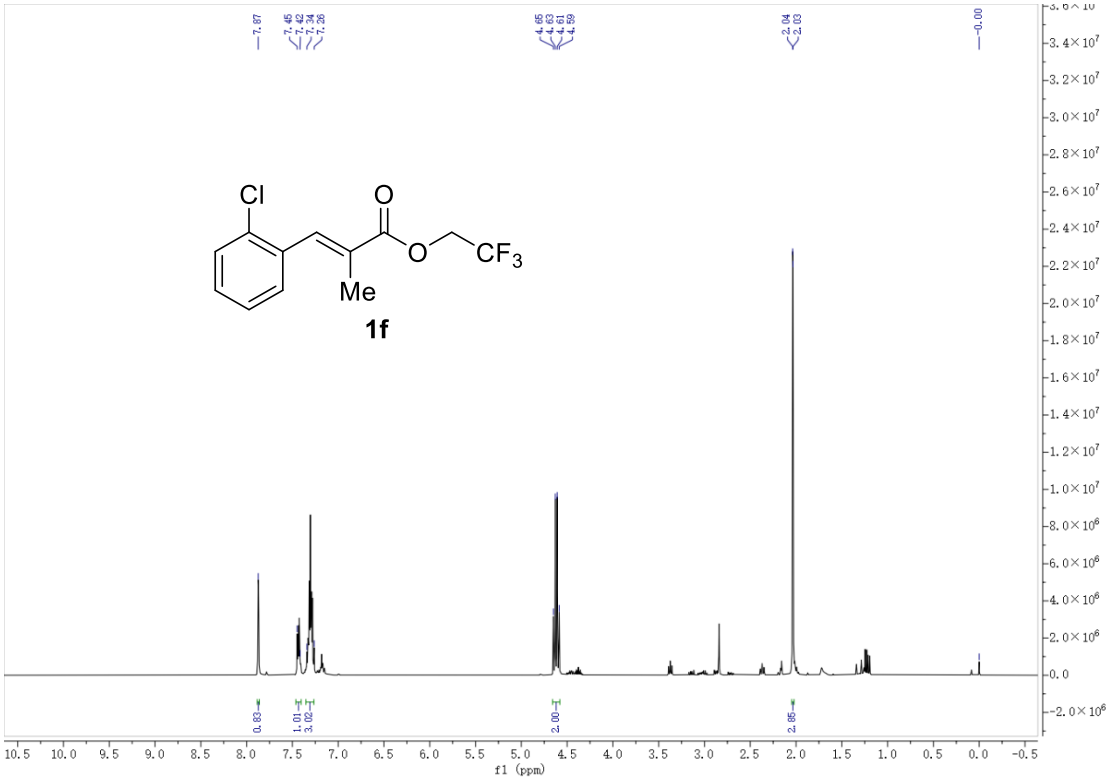
[5] Katafuchi, Y., Fujihara, T., Iwai, T., Terao, J., Tsuji, Y. Palladium-catalyzed hydroesterification

of alkynes employing aryl formates without the use of external carbon monoxide. *Adv*. *Synth*. *Catal*. **2011**, *353*, 475–482.
[6] Fan, T., Wang, Ao., Li, J. Q., Ye, J. L., Zheng, X., Huang, P. Q. Versatile one-pot synthesis of polysubstituted cyclopent-2-enimines from α,β-unsaturated amides: Imino-Nazarov reaction. *Angew*. *Chem*., *Int*. *Ed*. **2018**, *57*, 10352–10356.
[7] Iwadate, N., Suginome, M. Differentially protected diboron for regioselective diboration of alkynes: internal-selective cross-coupling of 1-alkene-1,2-diboronic acid derivatives. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 2548−2549.
[8] Lyu, H., Kevlishvili, I., Yu, X., Liu, P., Dong, G. B. Boron insertion into alkyl ether bonds via zinc/nickel tandem catalysis. *Science*. **2021**, *372*, 175−182.
[9] Aggarwal, V. K., Binanzer, M., de Ceglie, M. C., Gallanti, M., Glasspoole, B. W., Kendrick, S. J. F., Sonawane, R. P., Vázquez-Romero, A., Webster, M. P. Asymmetric synthesis of tertiary and quaternary allyl- and crotylsilanes via the borylation of lithiated carbamates. *Org*. *Lett*. **2011**, *13*, 1490−1493.

VIII. NMR Spectra



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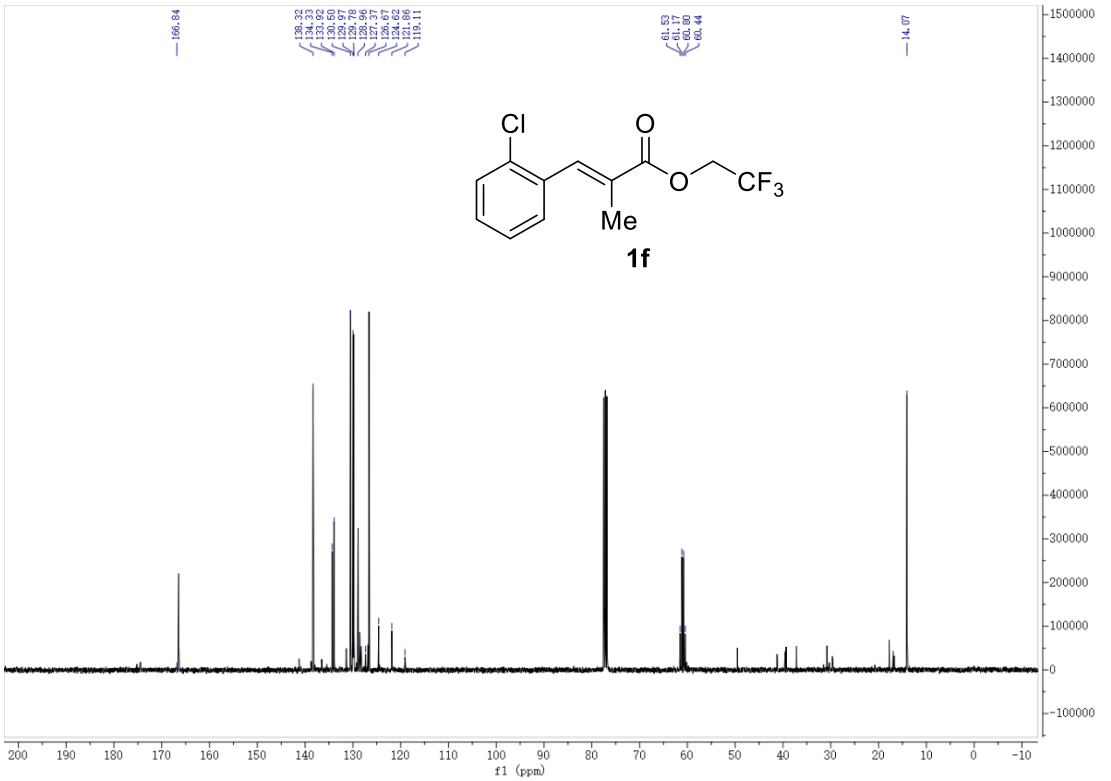
O
CF3
Me
1f
f1 (ppm)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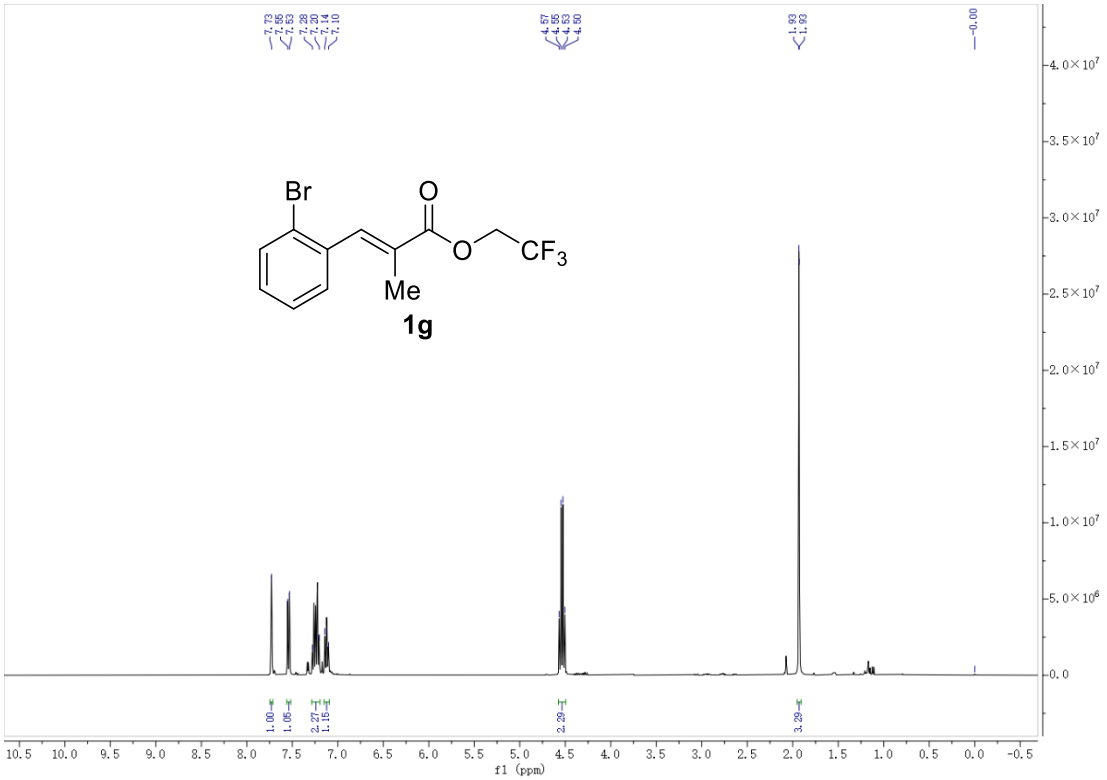
CF3
Me
1f
f1 (ppm)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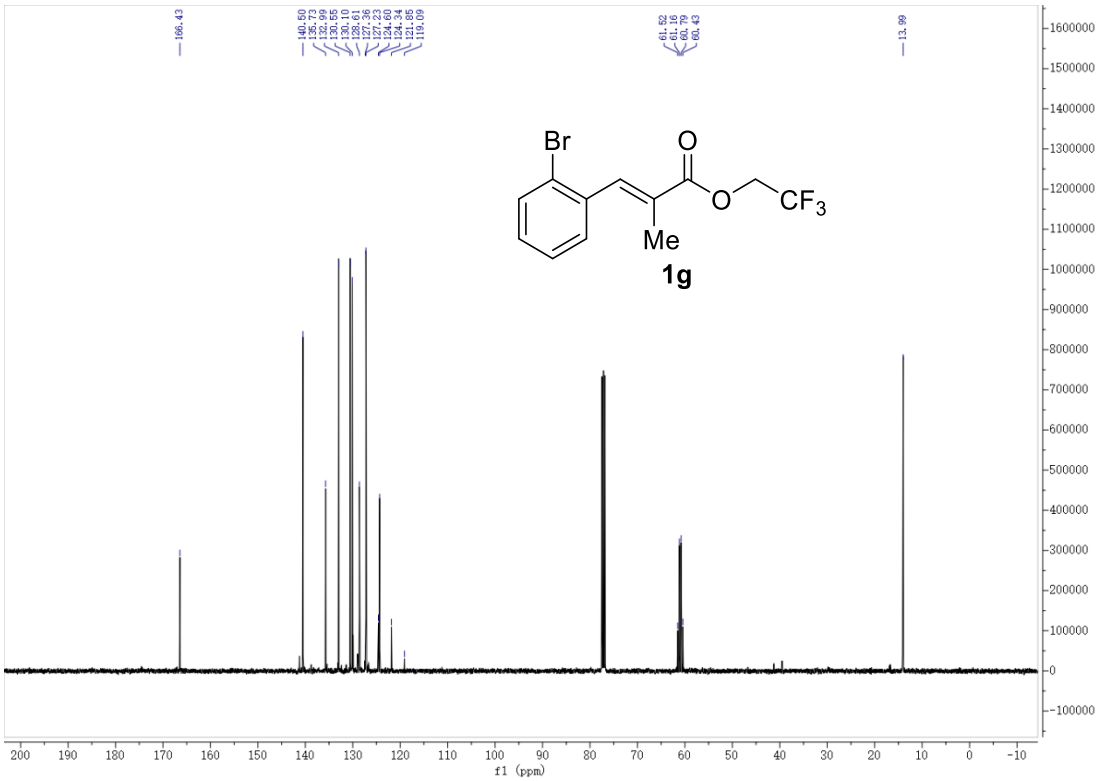
O
CF3
Me
1g
f1 (ppm)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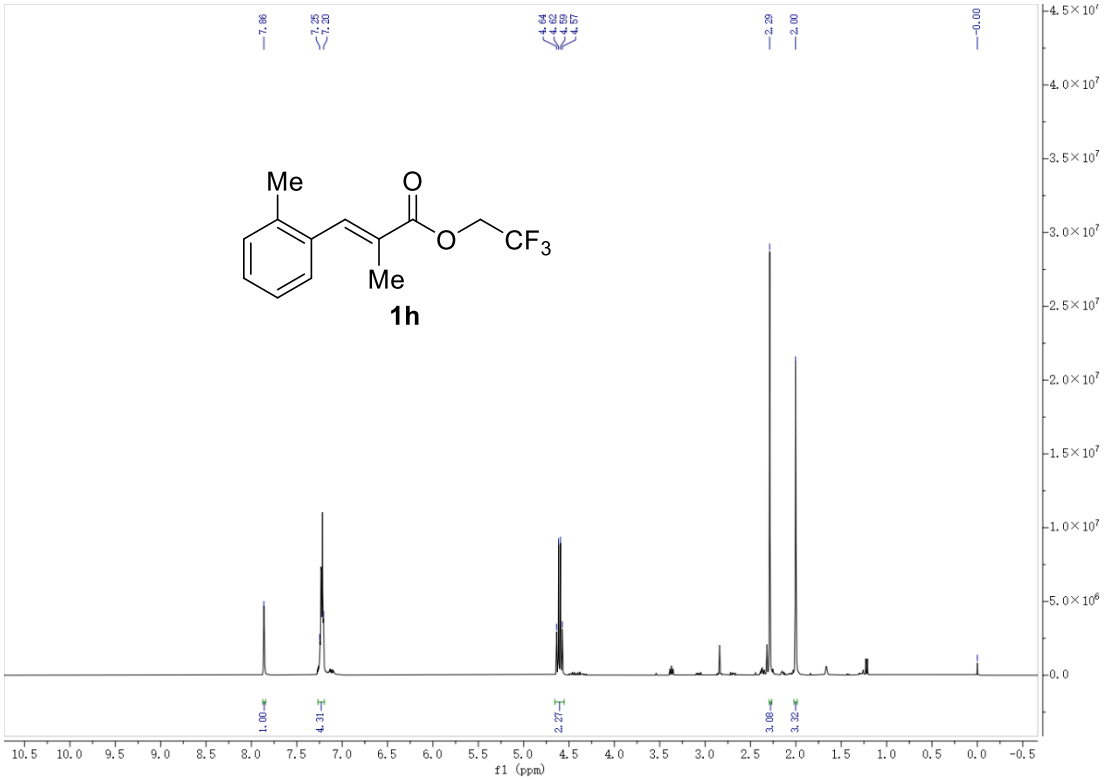
CF3
Me
1g
f1 (ppm)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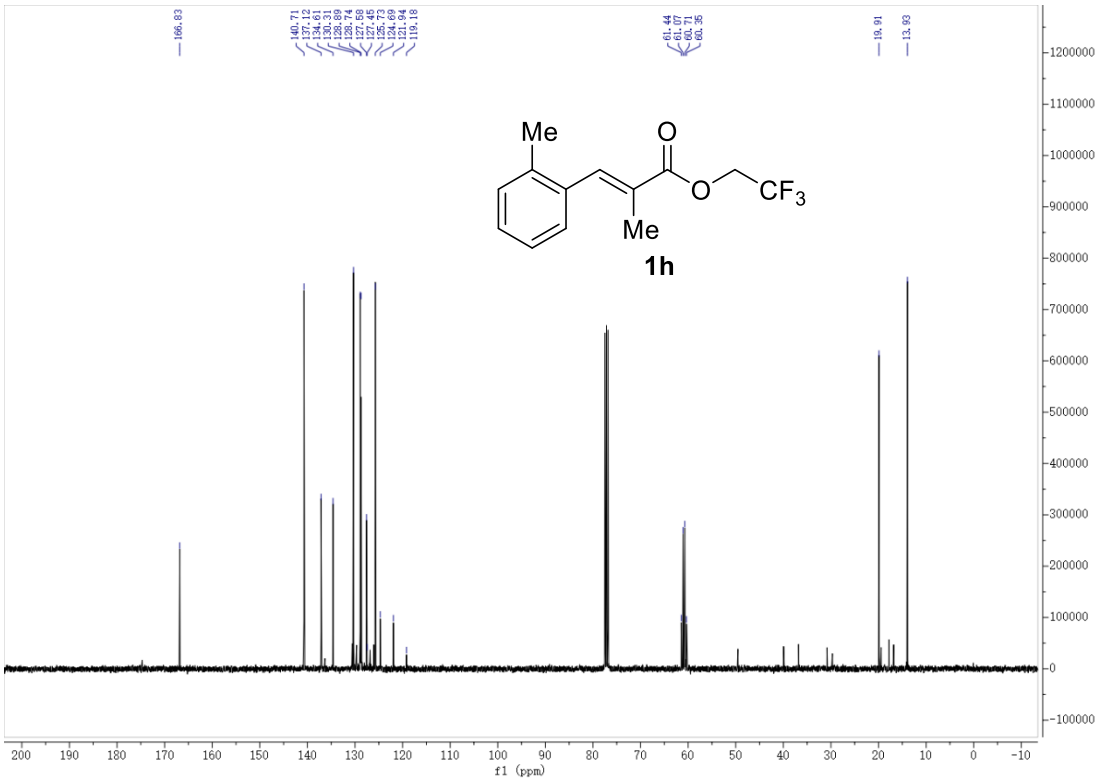
O
CF3
Me
1h
f1 (ppm)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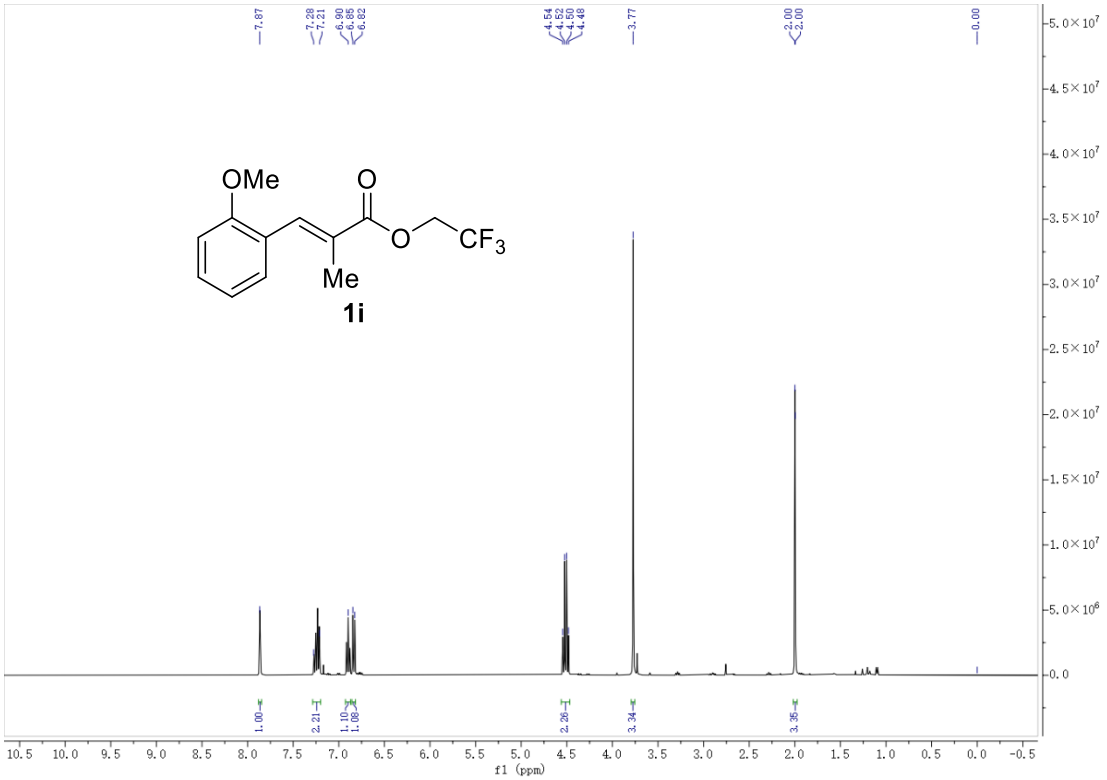
O
O
CF3
Me
1h
f1 (ppm)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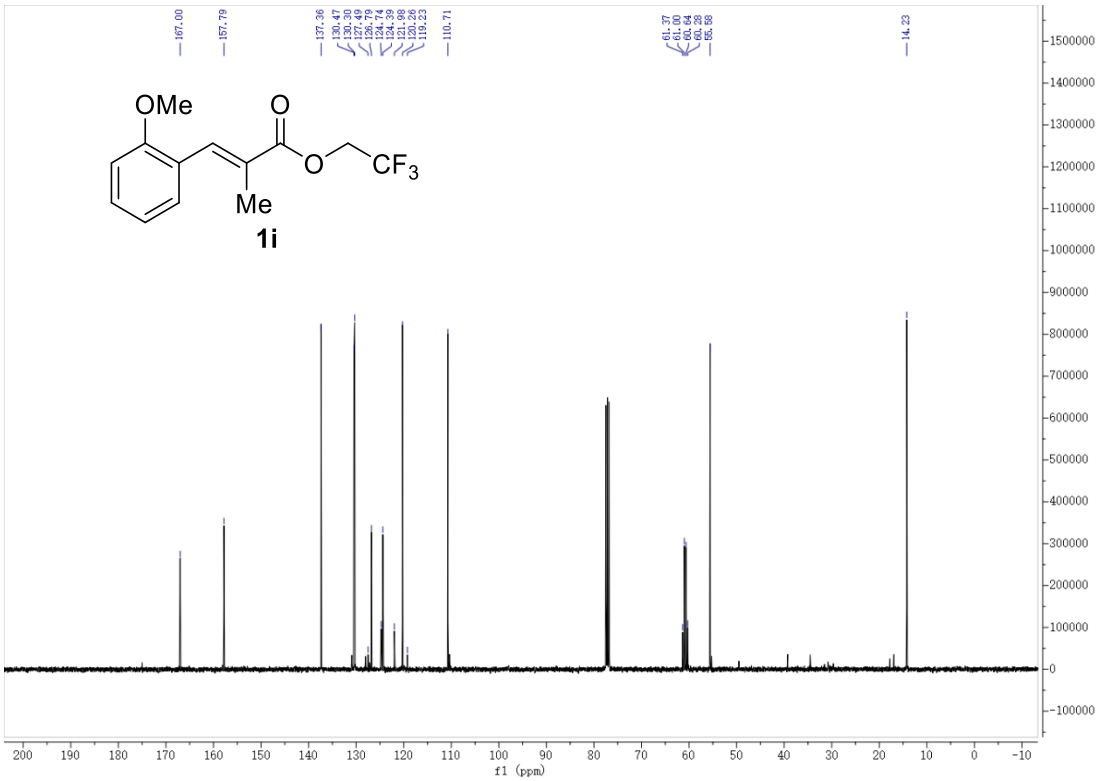
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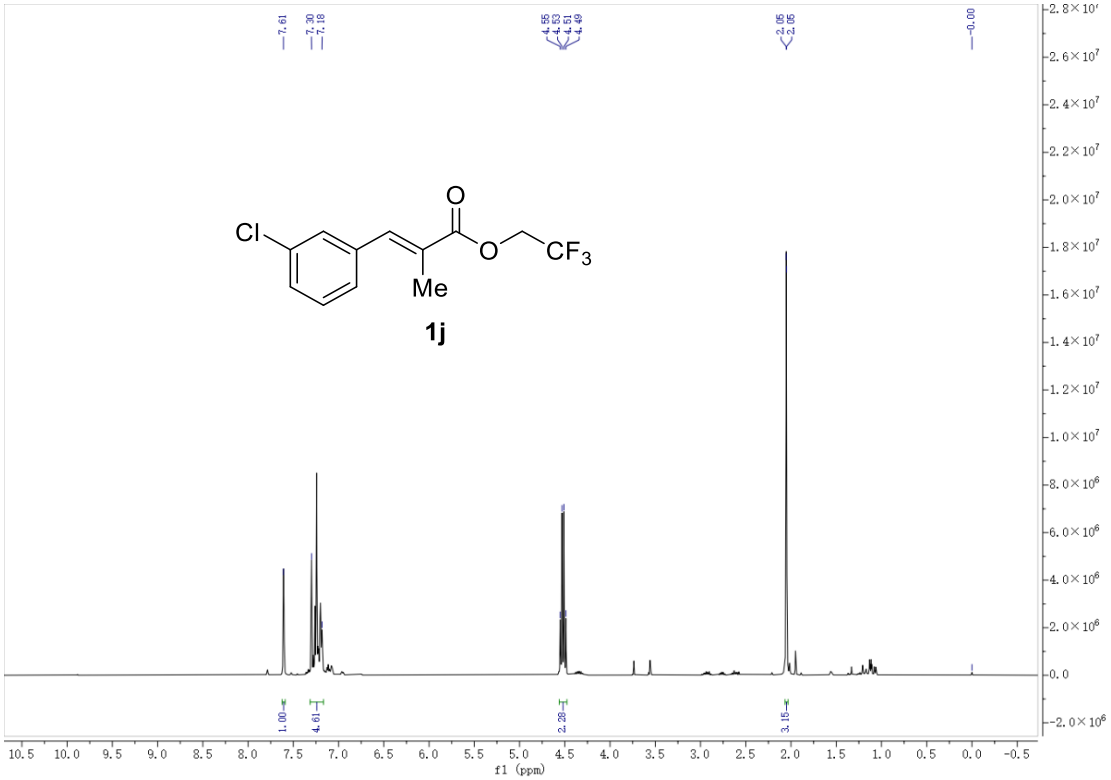
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1j
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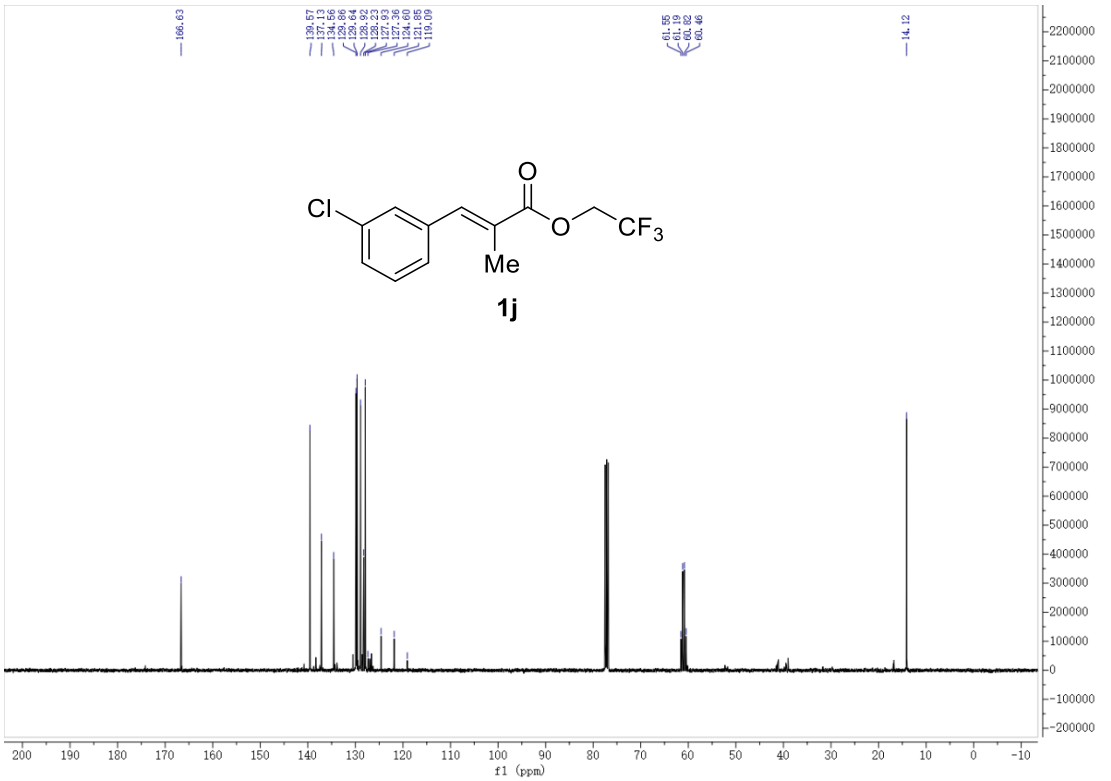
f1 (ppm)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Cl
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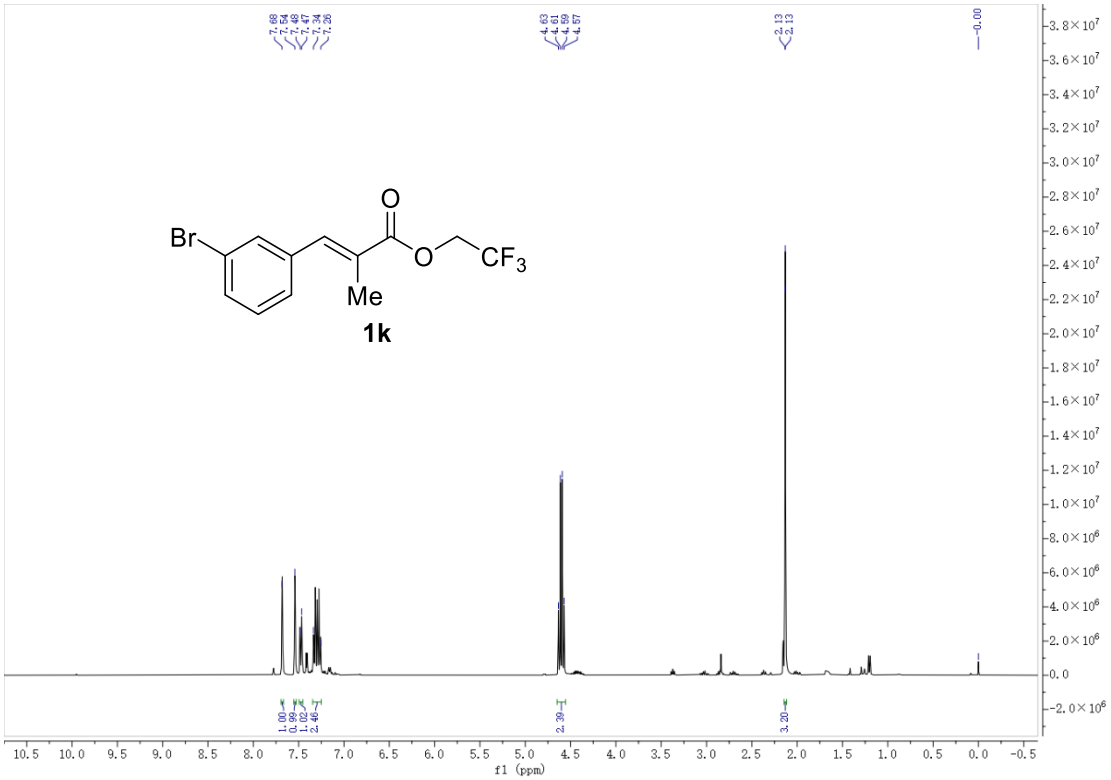
O
CF3
Me
1j
f1 (ppm)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CF3
Me
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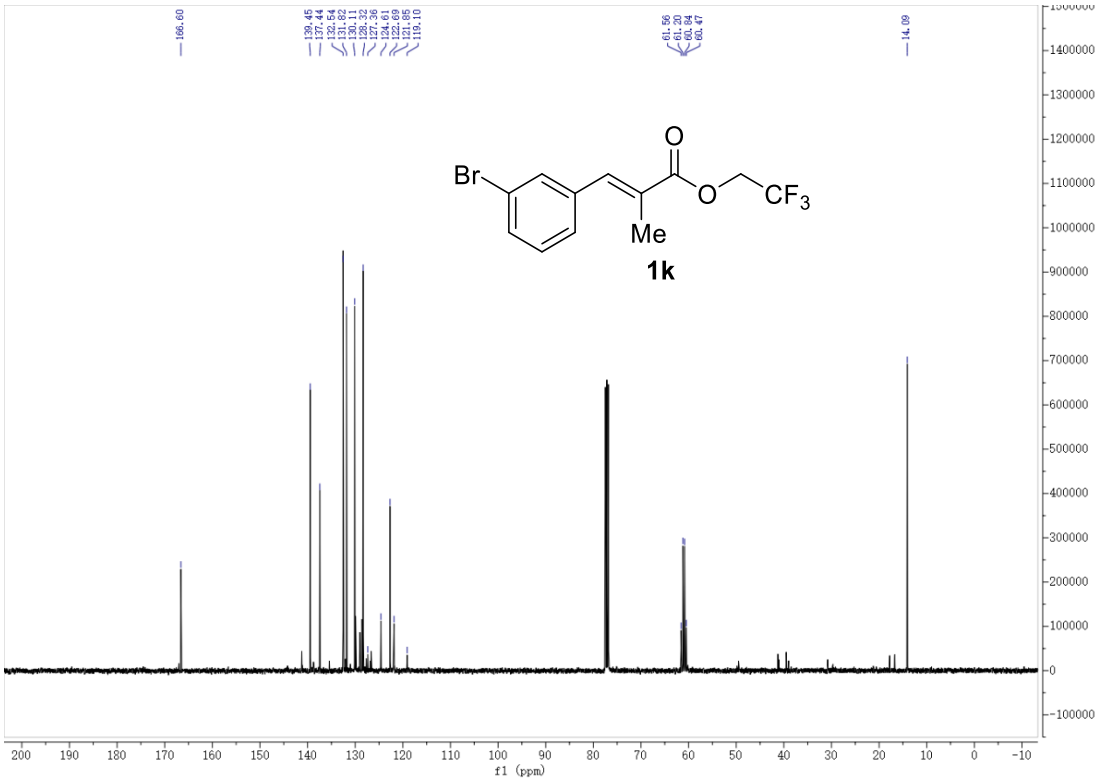
f1 (ppm)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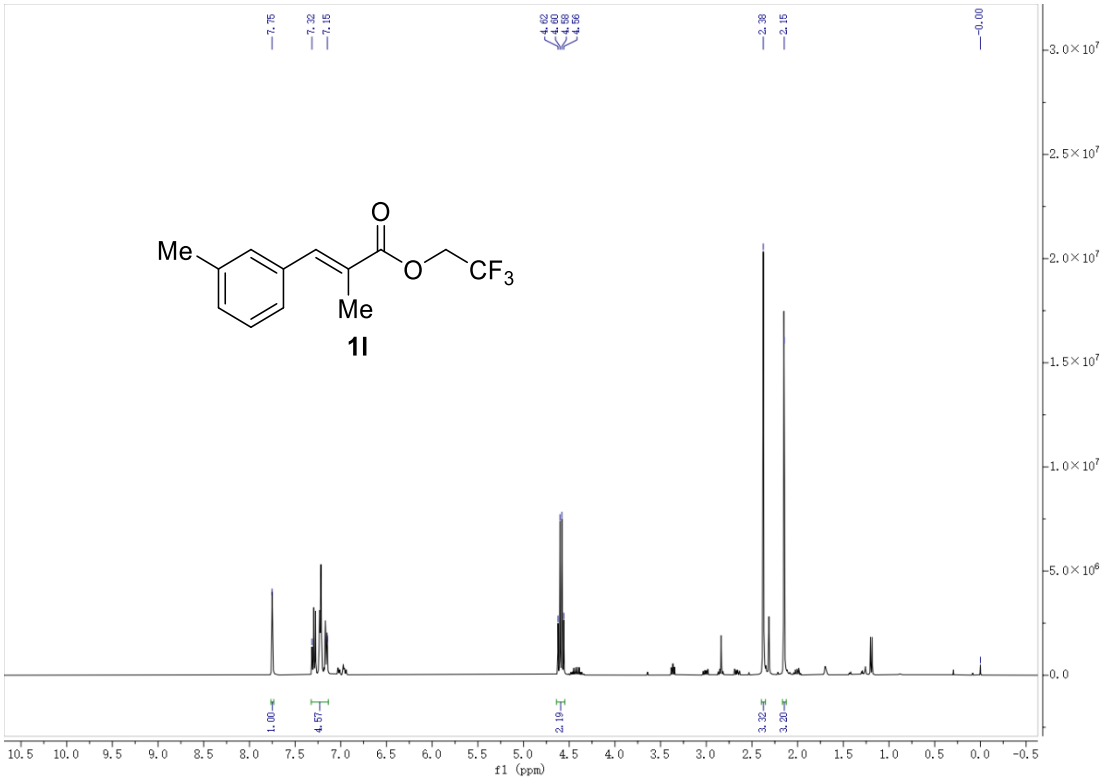
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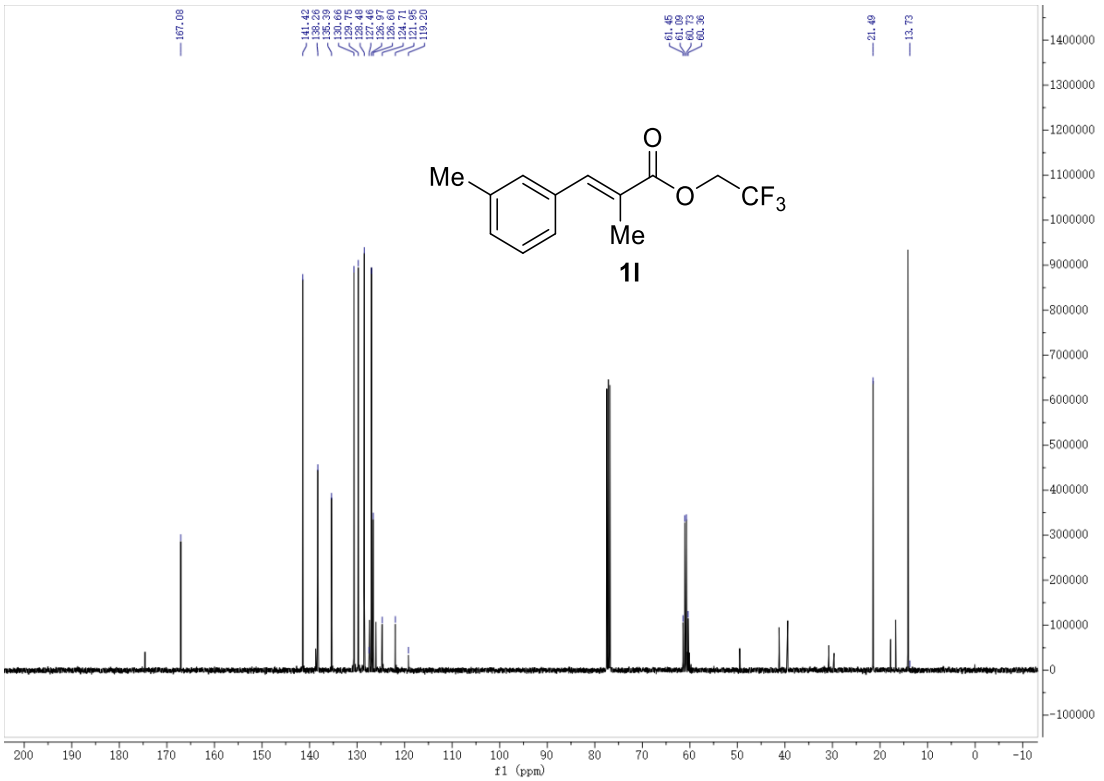
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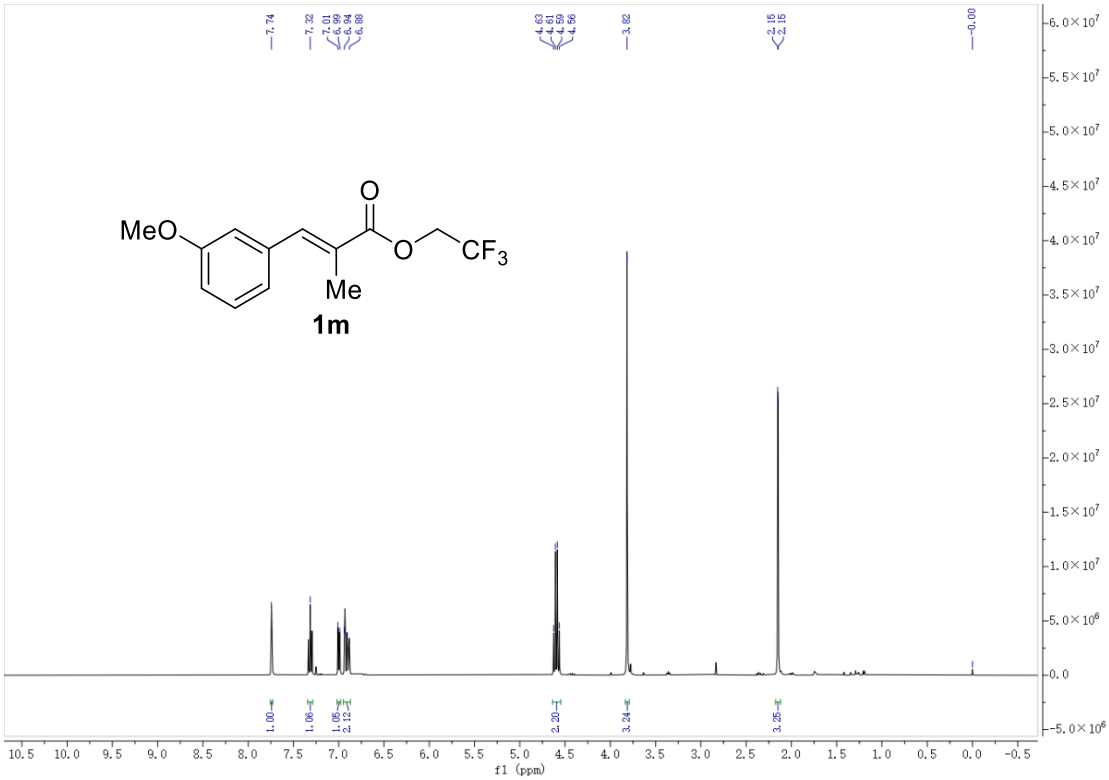
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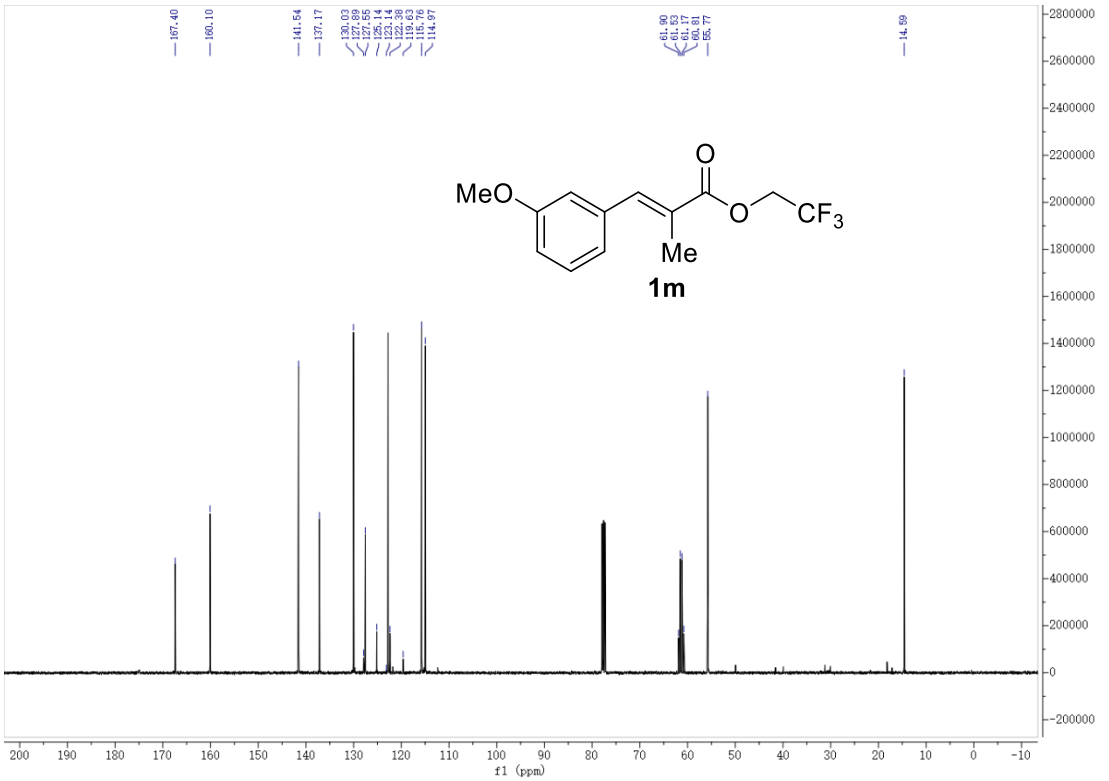
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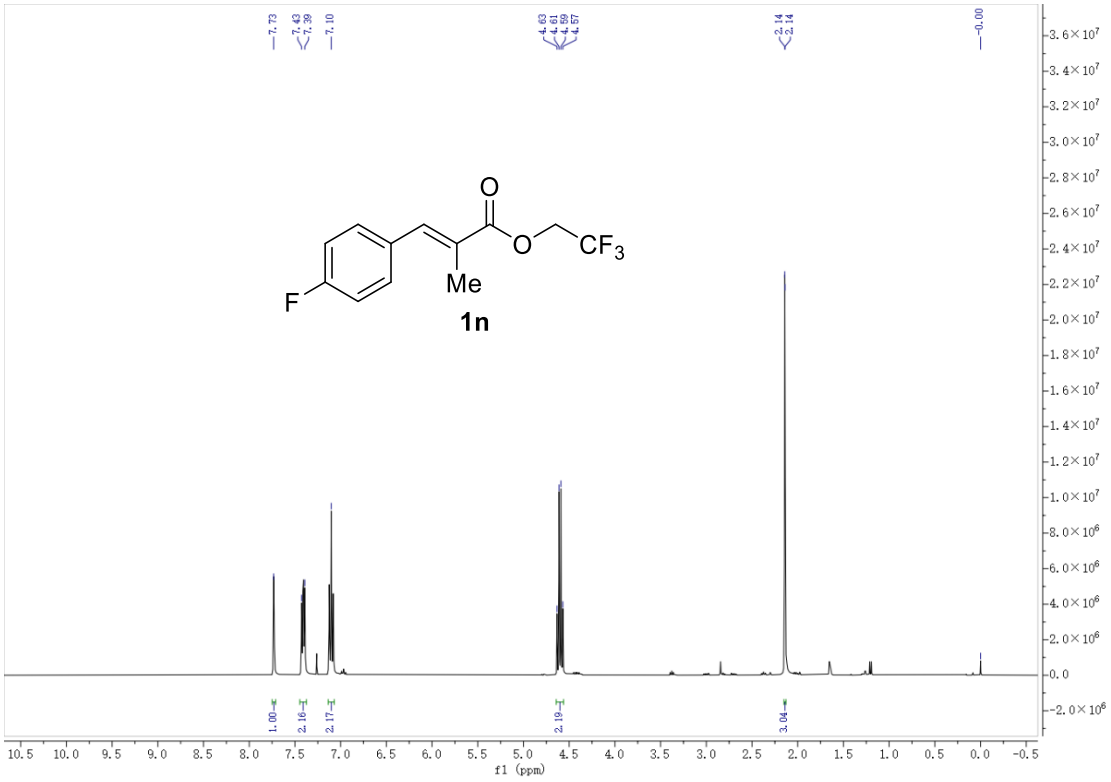
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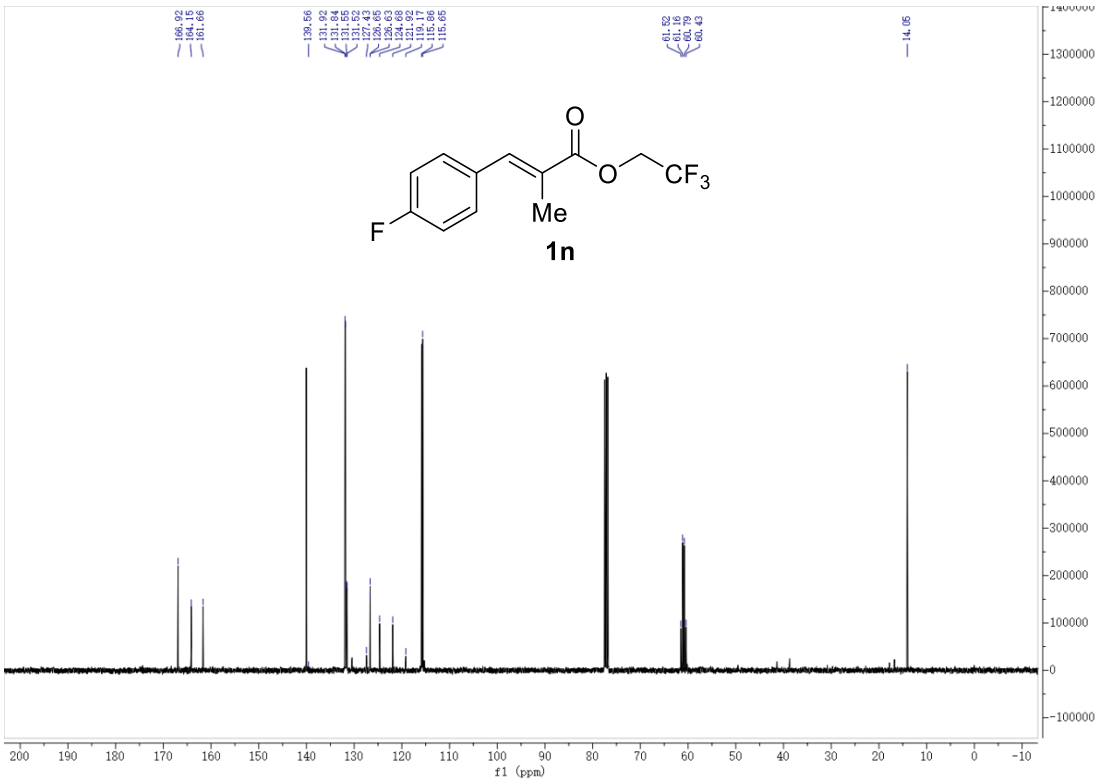
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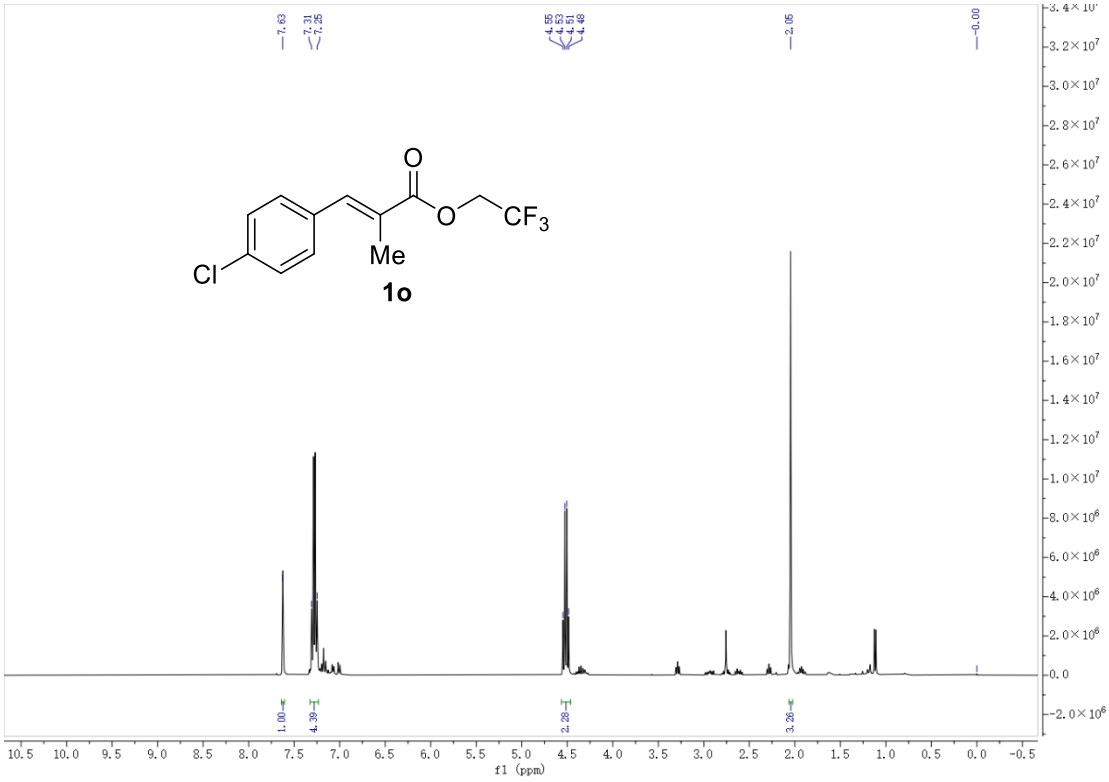
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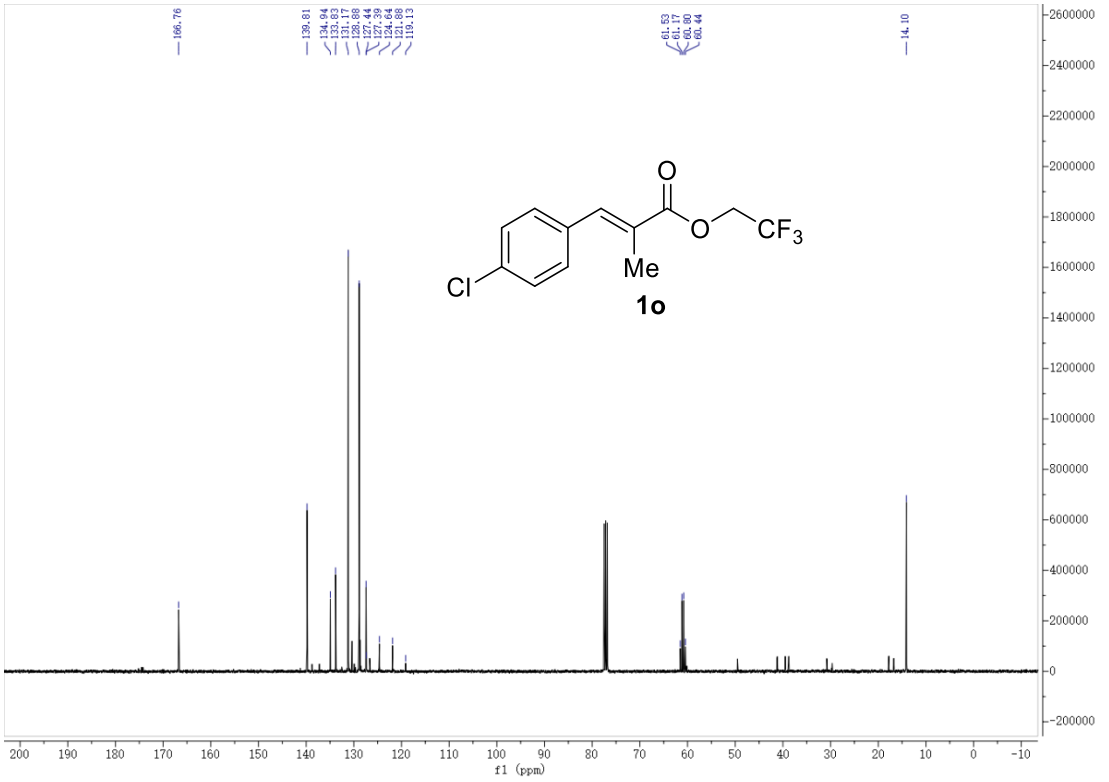
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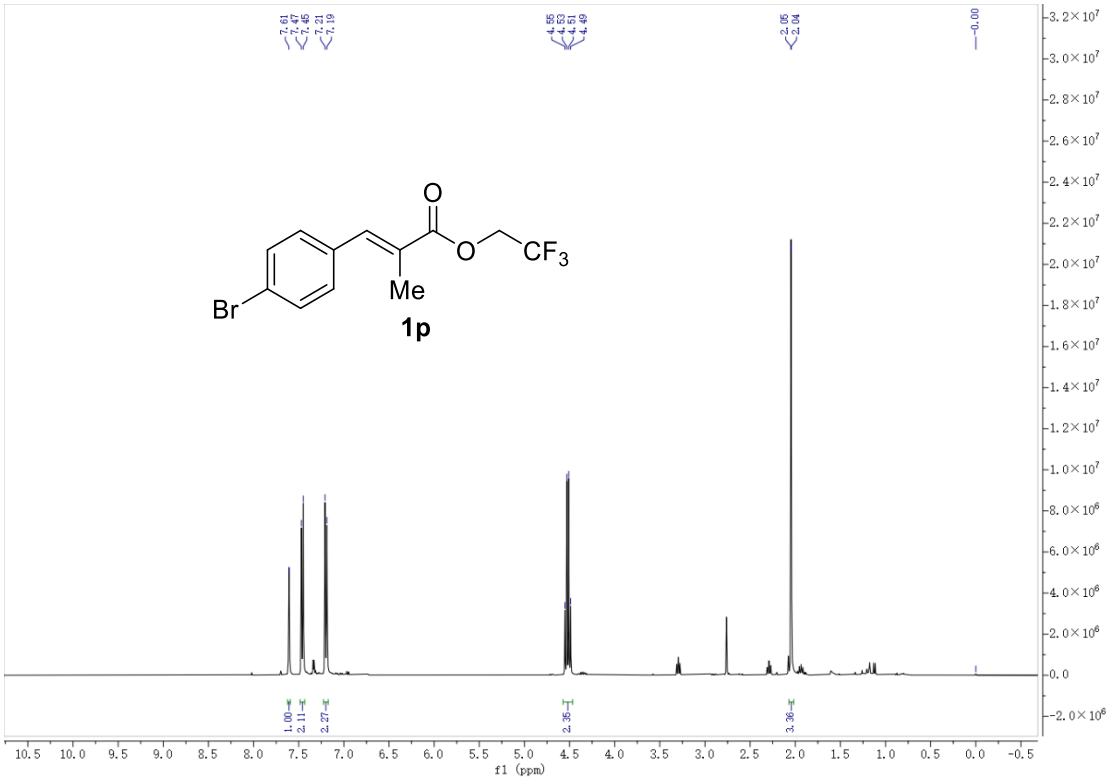
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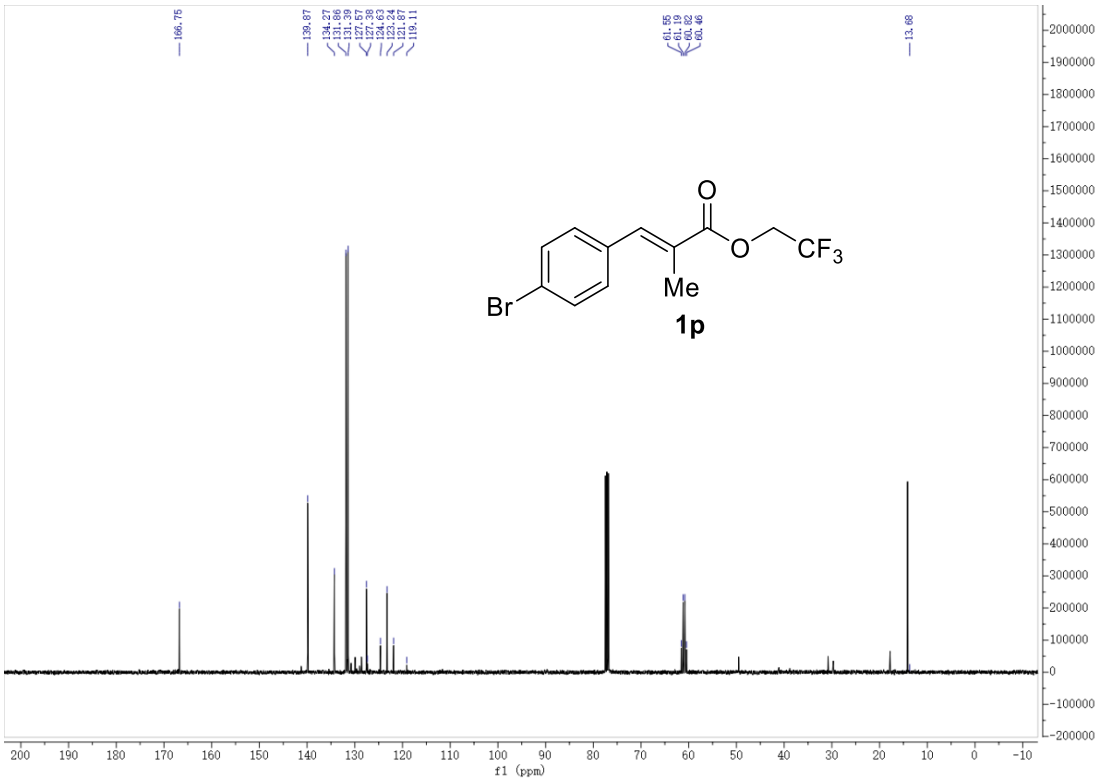
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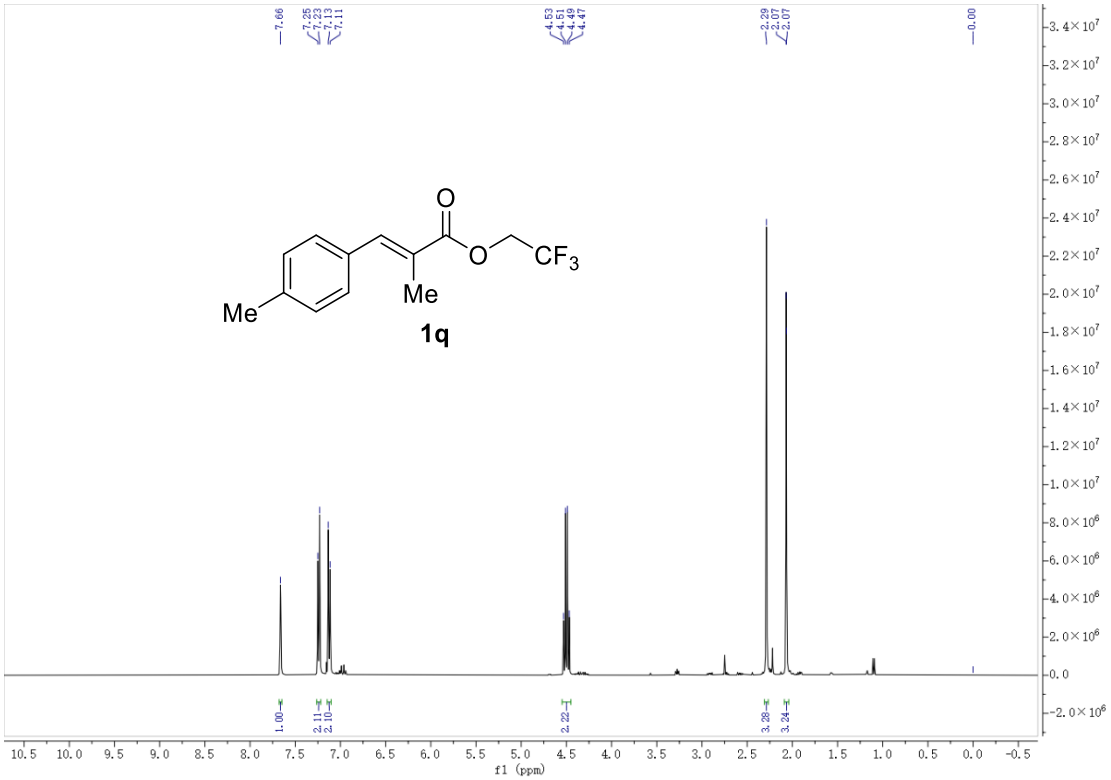
f1 (ppm)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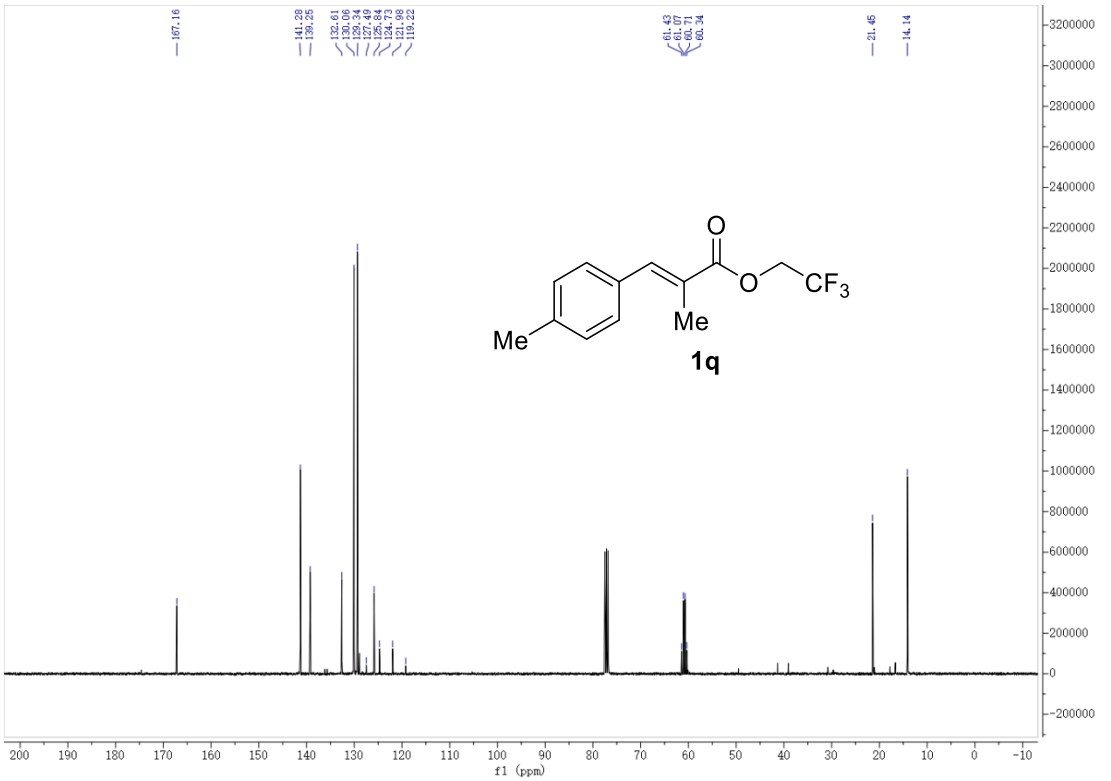
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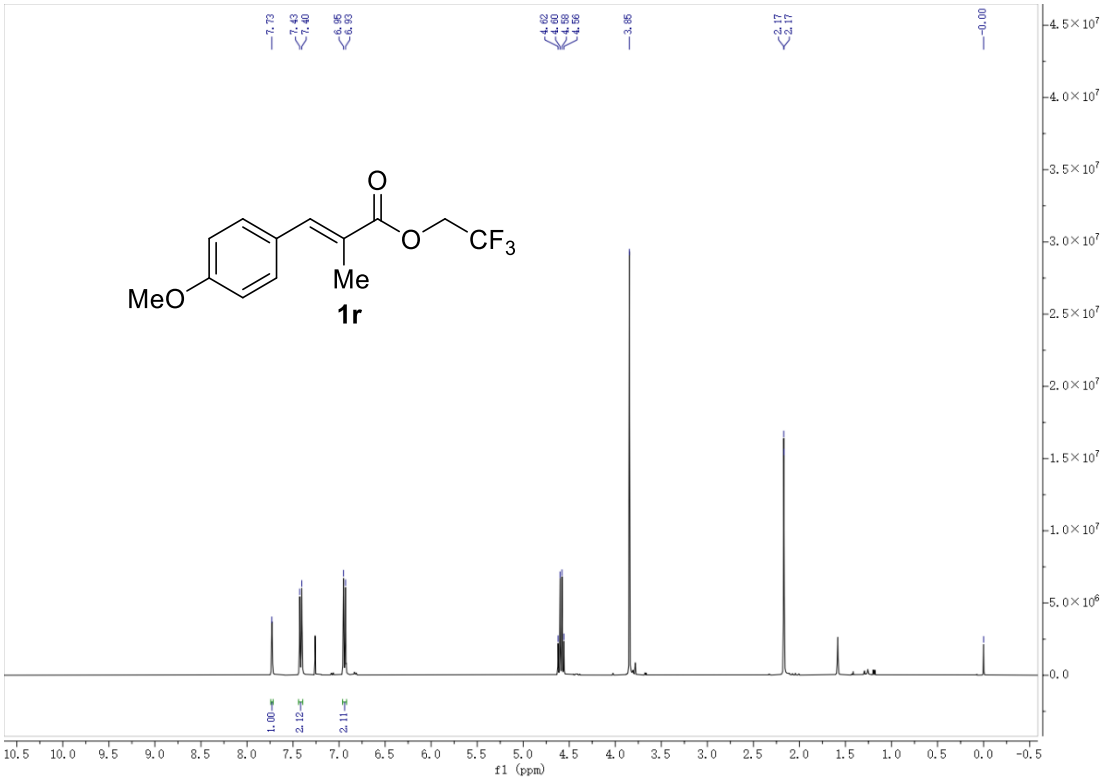
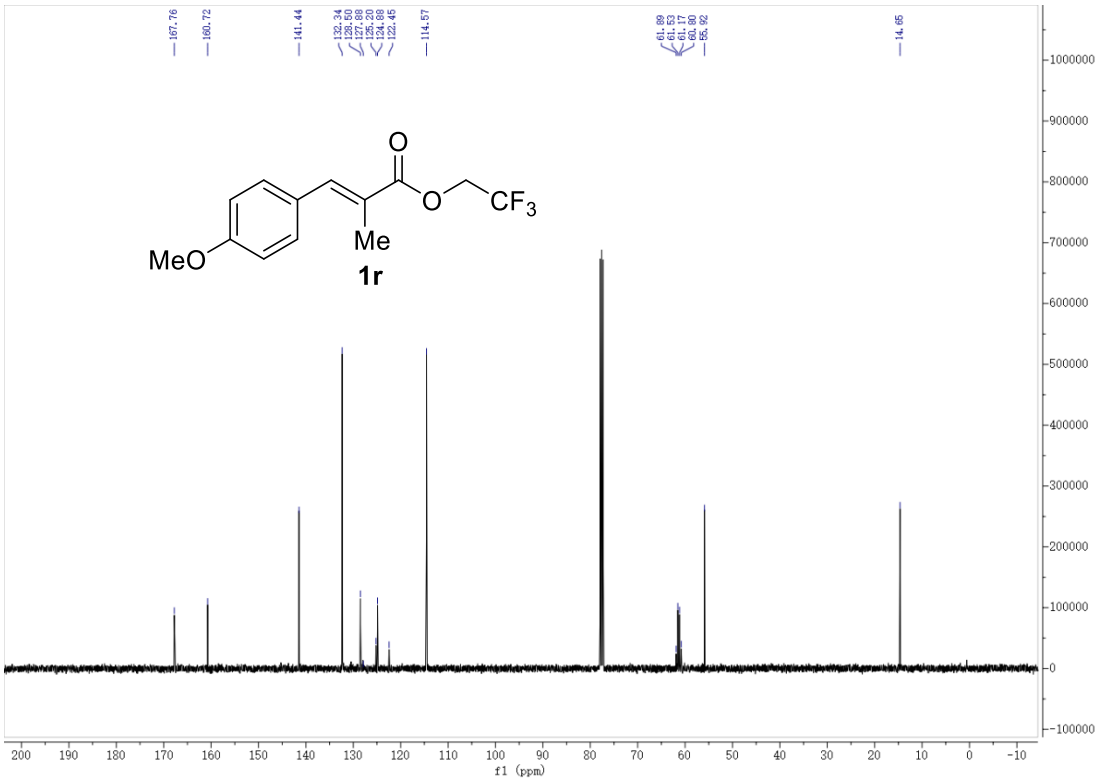
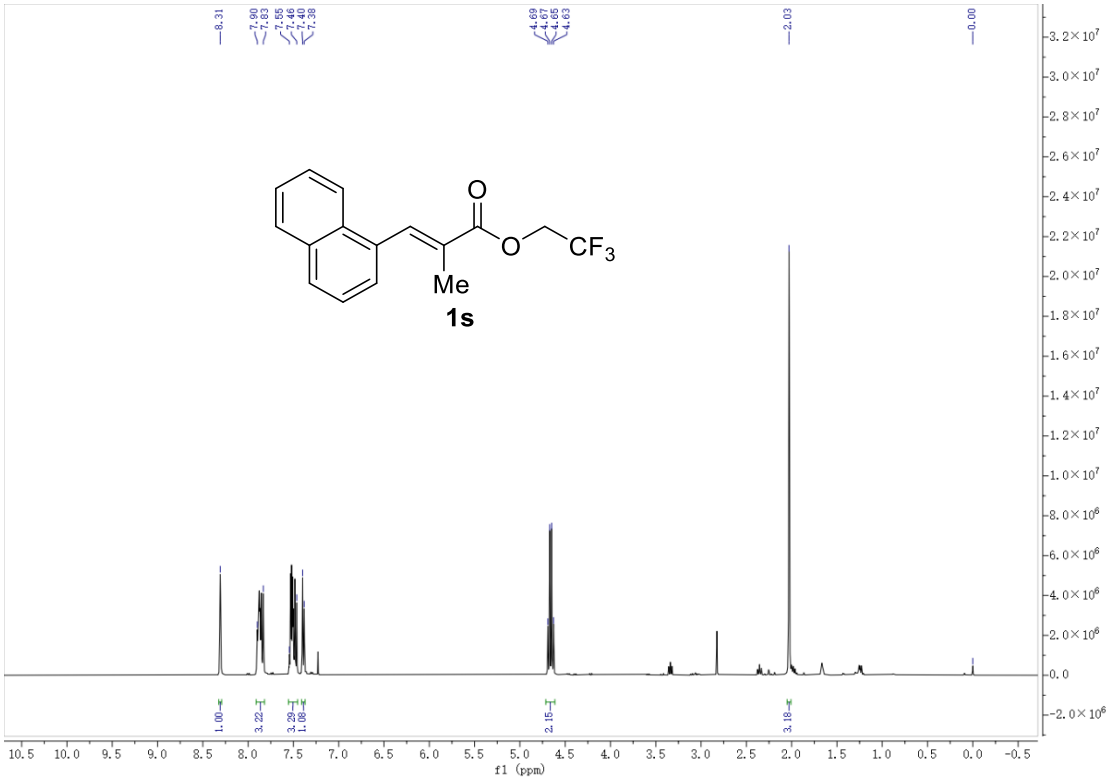
Me
Me
1q
f1 (ppm)


MeO
Me
CF3
1r
f1 (ppm)


MeO
Me
CF3
1r
f1 (ppm)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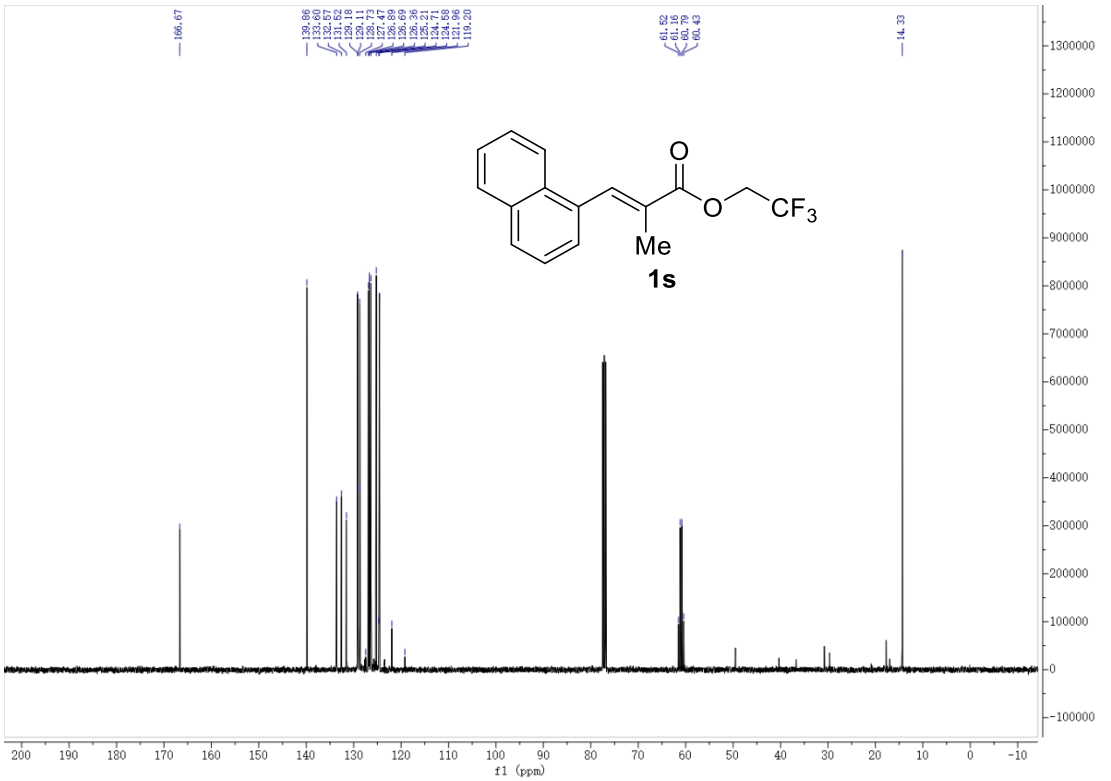
7.90
7.83
7.55
7.46
7.40
7.38
4.69
4.67
4.65
4.63
2.03
0.00
O
O
CF3
Me
1s
1.00
3.22
3.29
1.08
2.15
3.18
f1 (ppm)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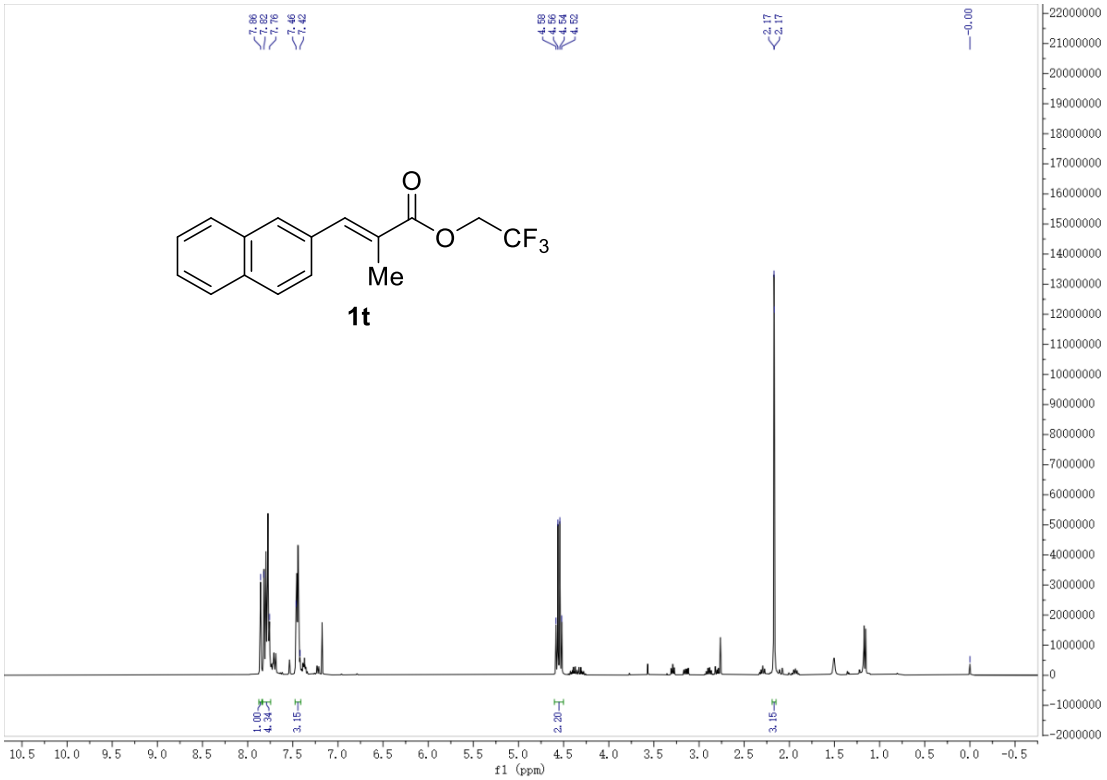
139.86
133.60
132.67
131.52
129.18
129.11
128.73
127.47
126.89
126.69
126.36
125.21
124.71
124.58
121.96
119.20
61.62
61.45
61.29
60.43
14.33
O
O
CF3
Me
1s
f1 (ppm)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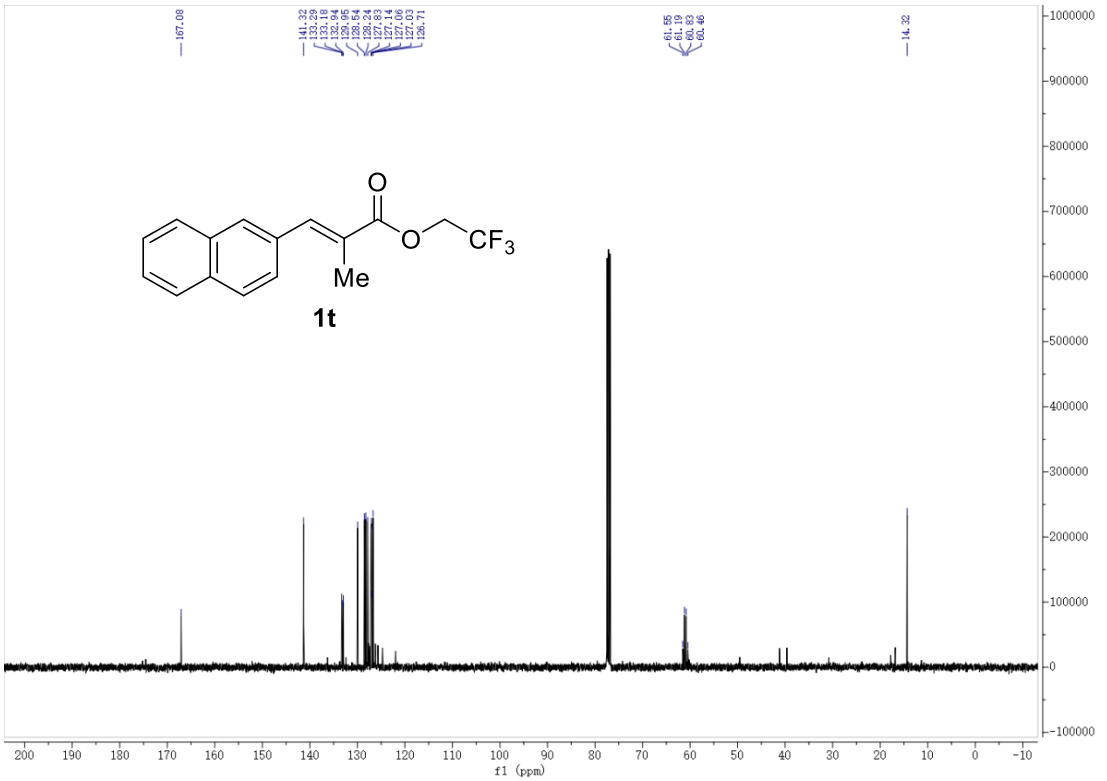
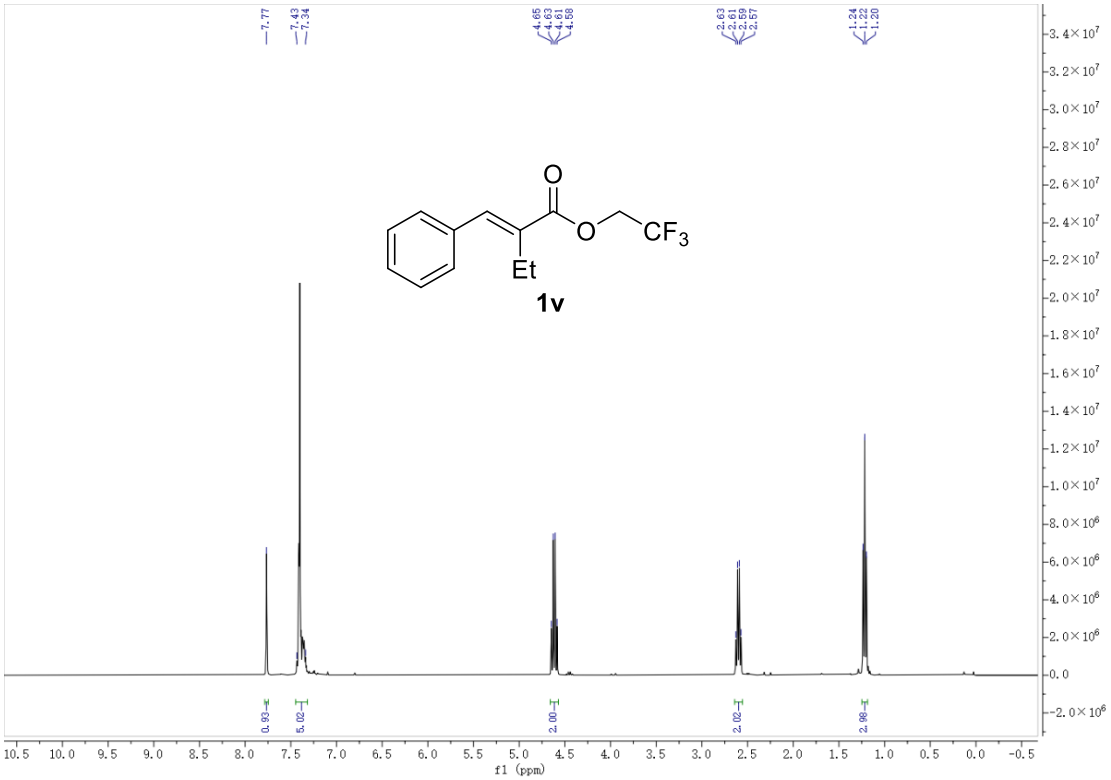
7.82
7.76
7.46
7.42
4.58
4.56
4.54
4.52
2.17
2.17
0.00
O
O
CF3
Me
1t
1.00
4.34
3.15
2.20
3.15
f1 (ppm)


167.08
141.32
133.29
133.18
132.04
129.95
128.54
128.23
127.33
127.14
127.06
127.03
126.71
61.55
61.19
60.83
60.46
14.32
O
O
CF3
Me
1t
f1 (ppm)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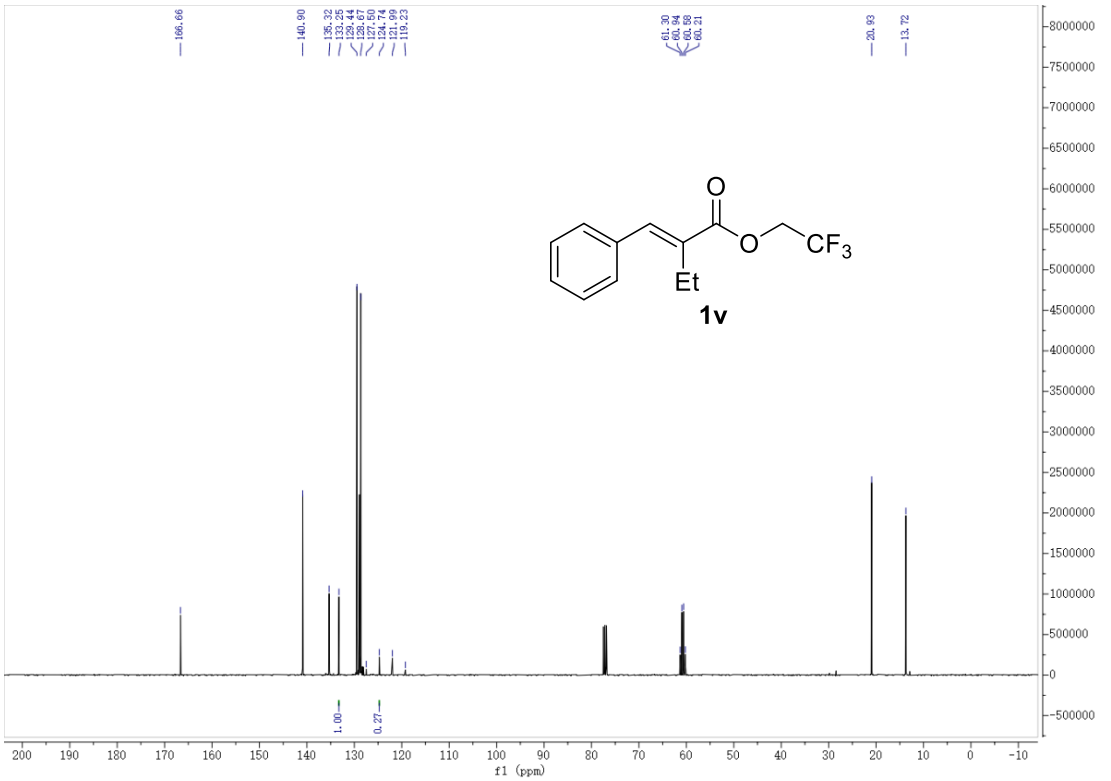
7.43
7.34
4.65
4.63
4.61
4.58
2.63
2.61
2.59
2.57
1.24
1.22
1.20
O
O
CF3
Et
1v
0.93
5.02
2.00
2.02
2.98
f1 (ppm)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133.25
130.44
128.67
127.50
124.74
121.99
119.23
61.30
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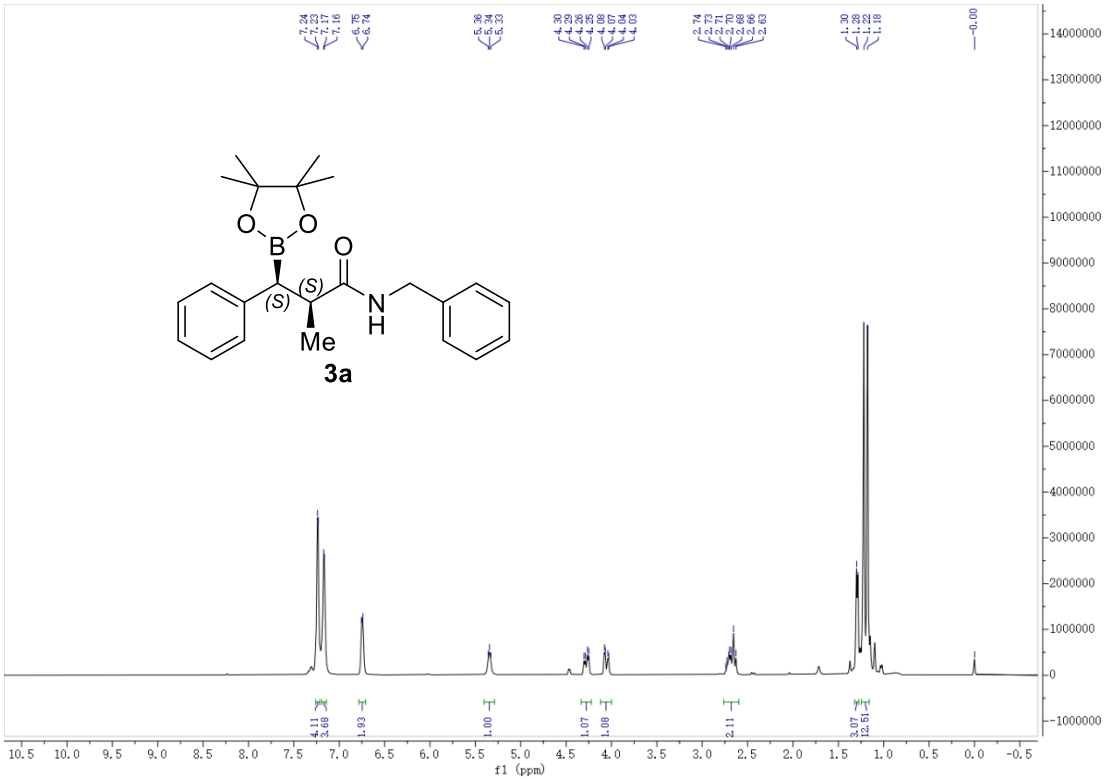
60.58
60.21
20.93
13.72
O
O
CF3
Et
1v
1.00
0.27
f1 (ppm)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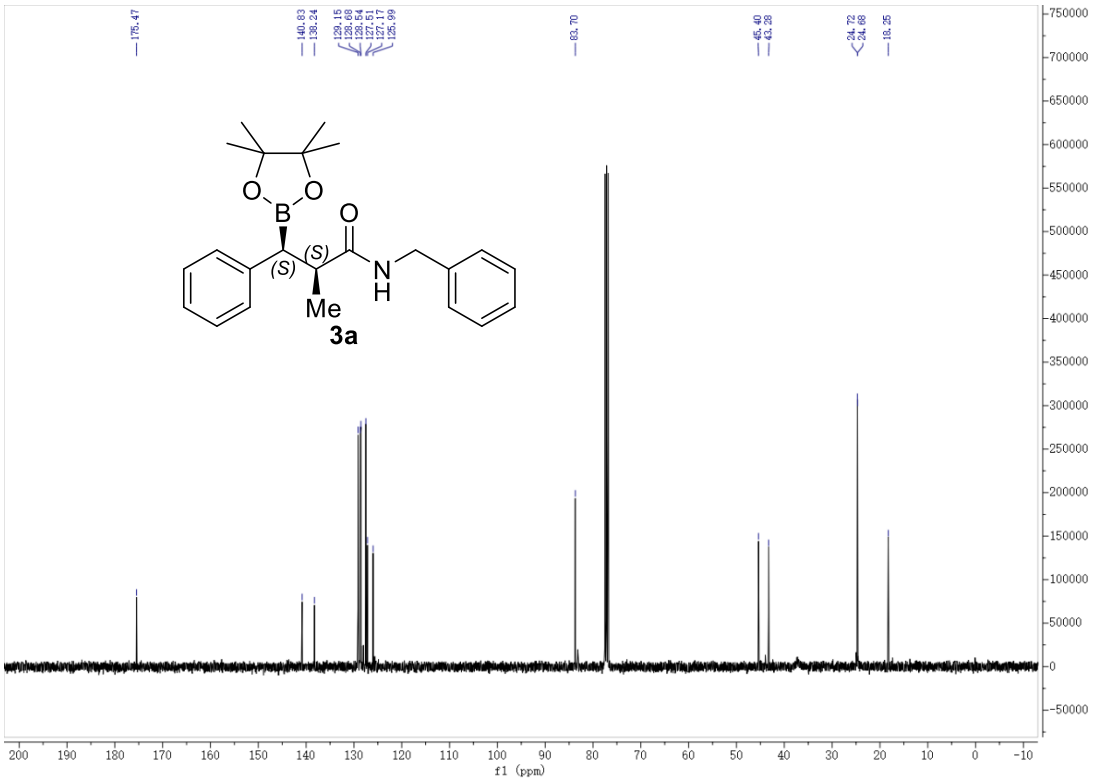
7.17
7.16
6.75
6.74
5.36
5.34
5.33
4.30
4.29
4.26
4.25
4.08
4.07
4.04
4.03
2.74
2.73
2.71
2.70
2.68
2.66
2.63
1.30
1.28
1.22
1.18
0.00
O
B
O
O
(S)
(S)
N
H
Me
3a
4.11
3.68
1.93
1.00
1.07
1.08
2.11
3.07
12.51
f1 (ppm)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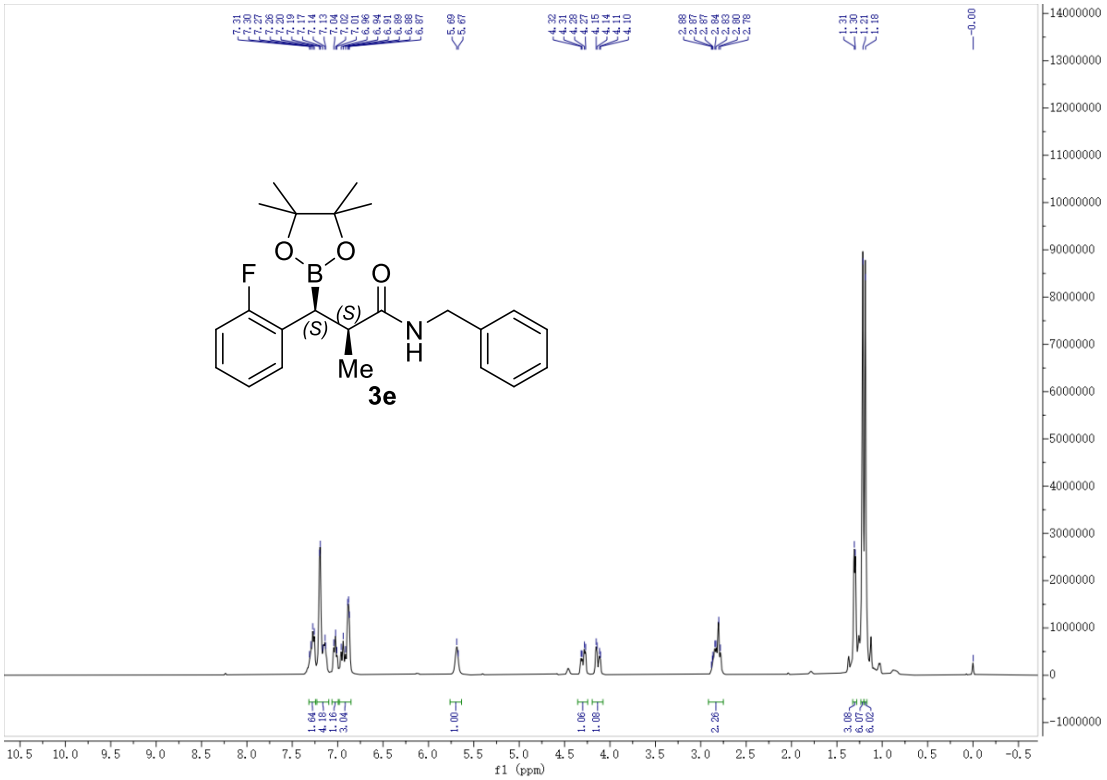
138.24
129.15
128.68
128.54
127.51
127.17
126.99
83.70
65.40
63.38
24.72
24.68
18.25
O
B
O
O
(S)
(S)
N
H
Me
3a
f1 (ppm)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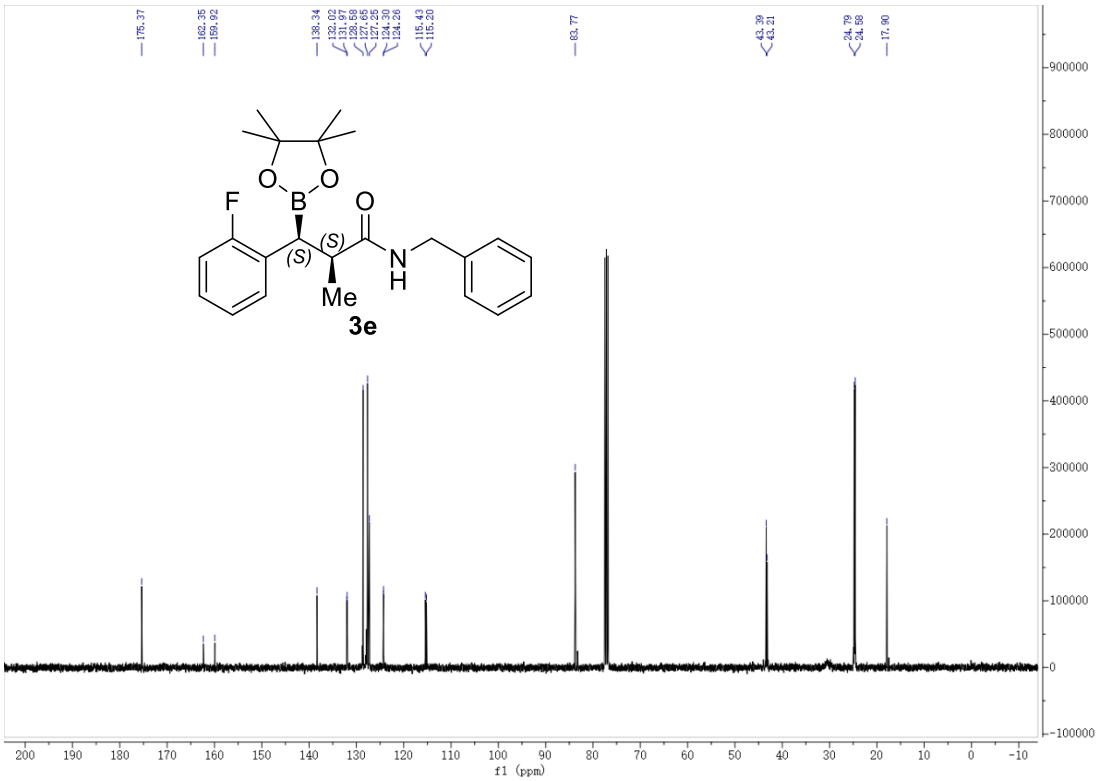
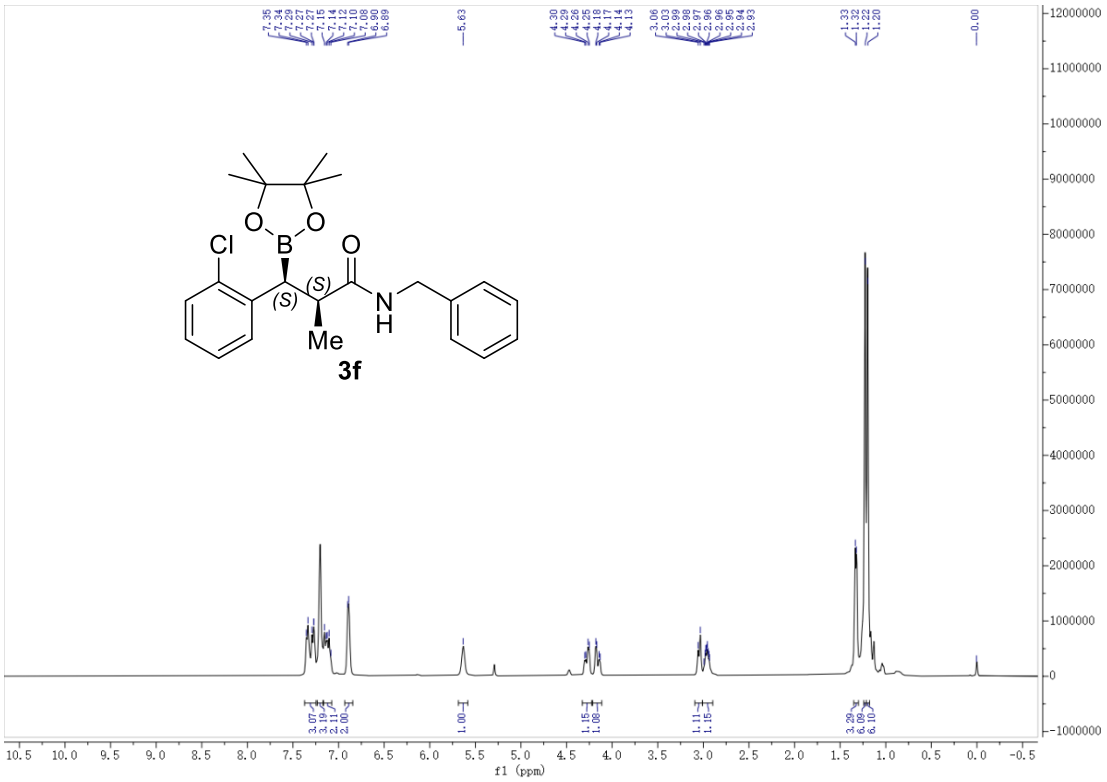
B
O
O
(S)
(S)
N
H
Me
3e
f1 (ppm)


F
O
B
O
O
(S)
(S)
N
H
Me
3e
f1 (ppm)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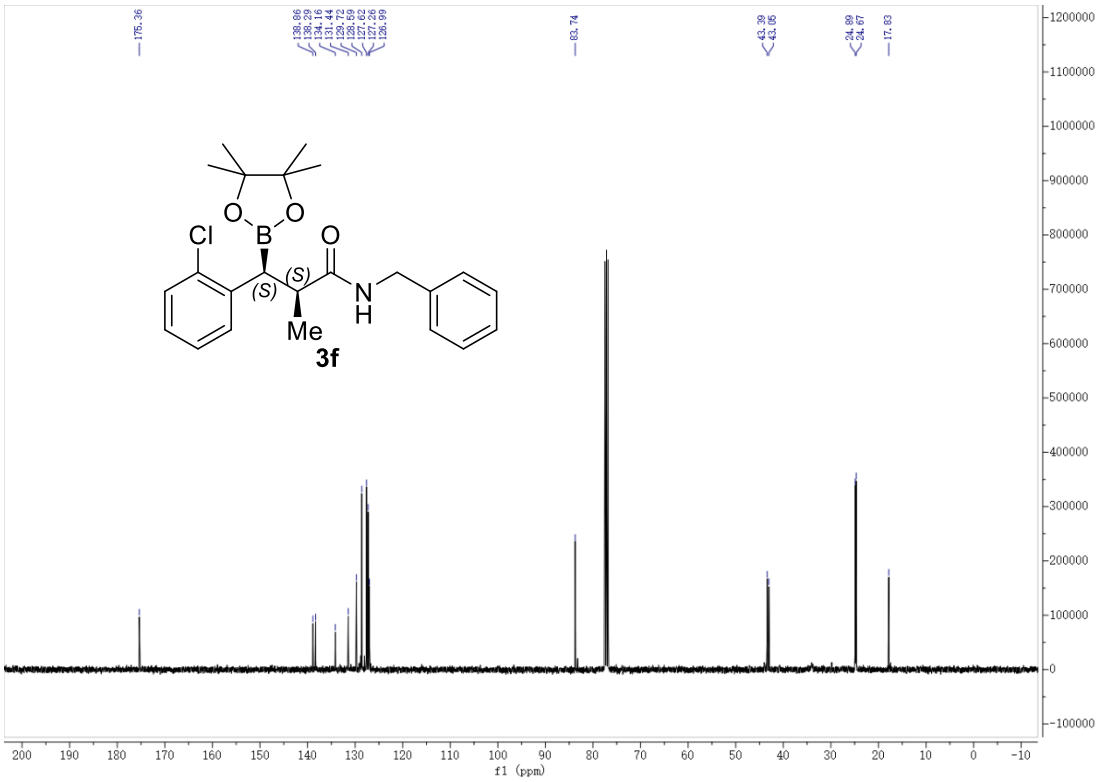
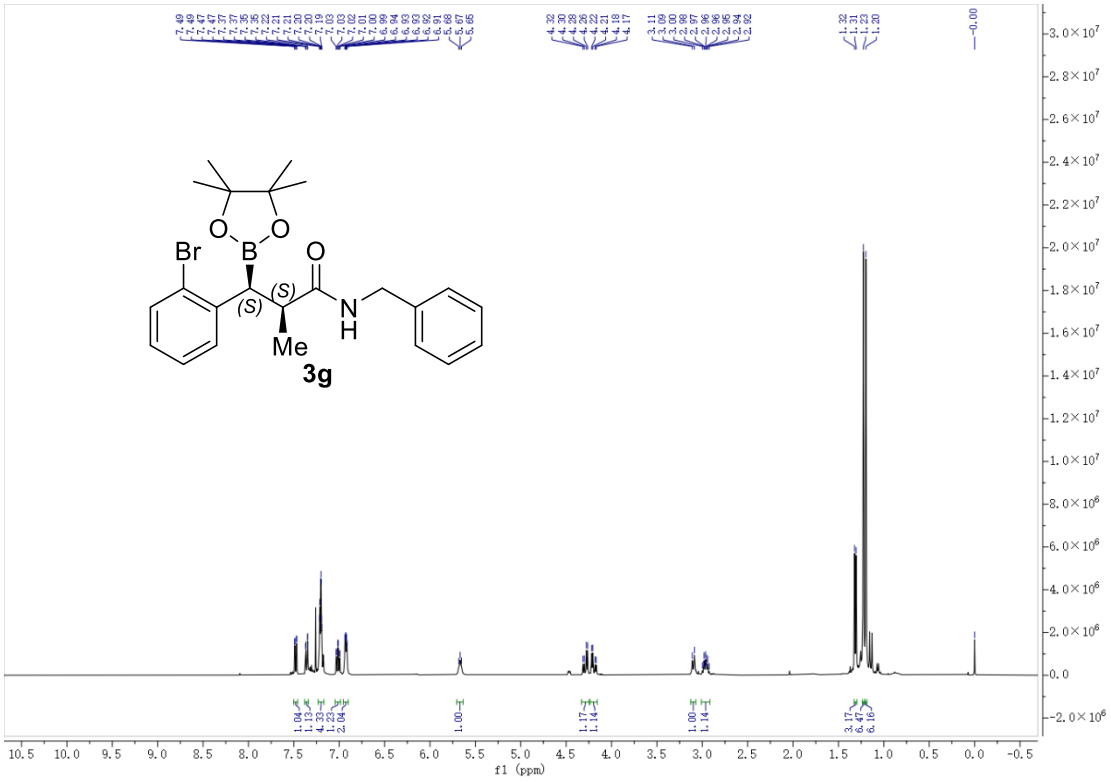
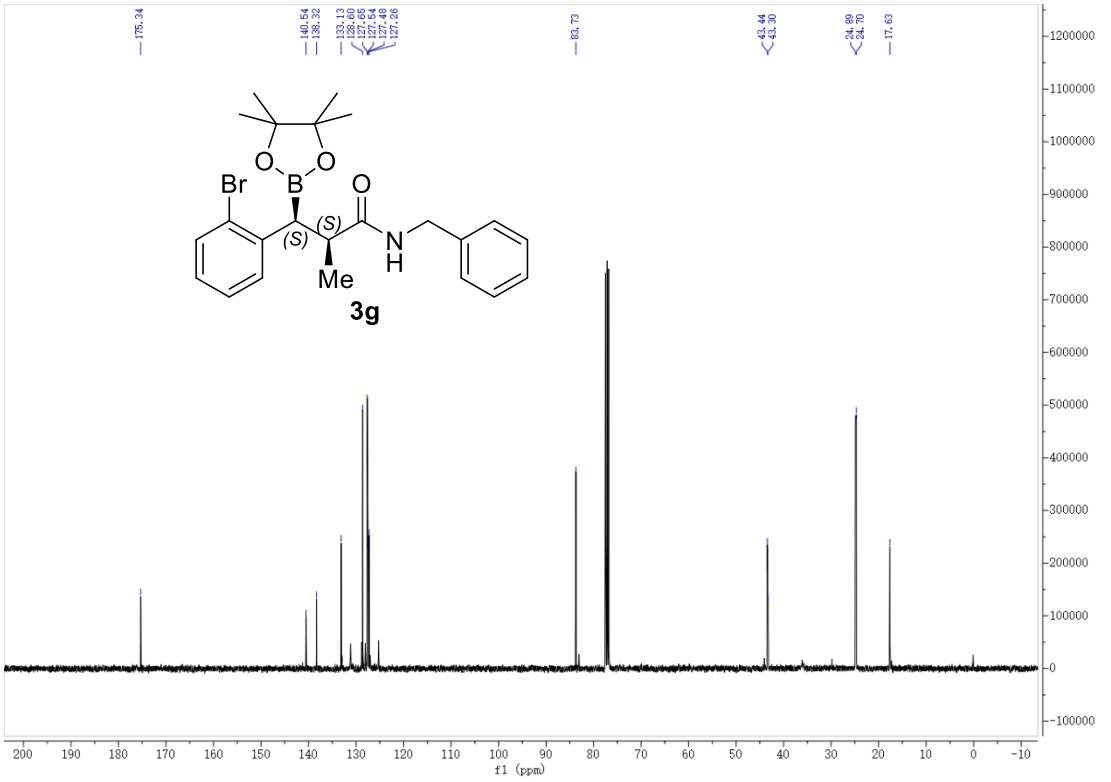
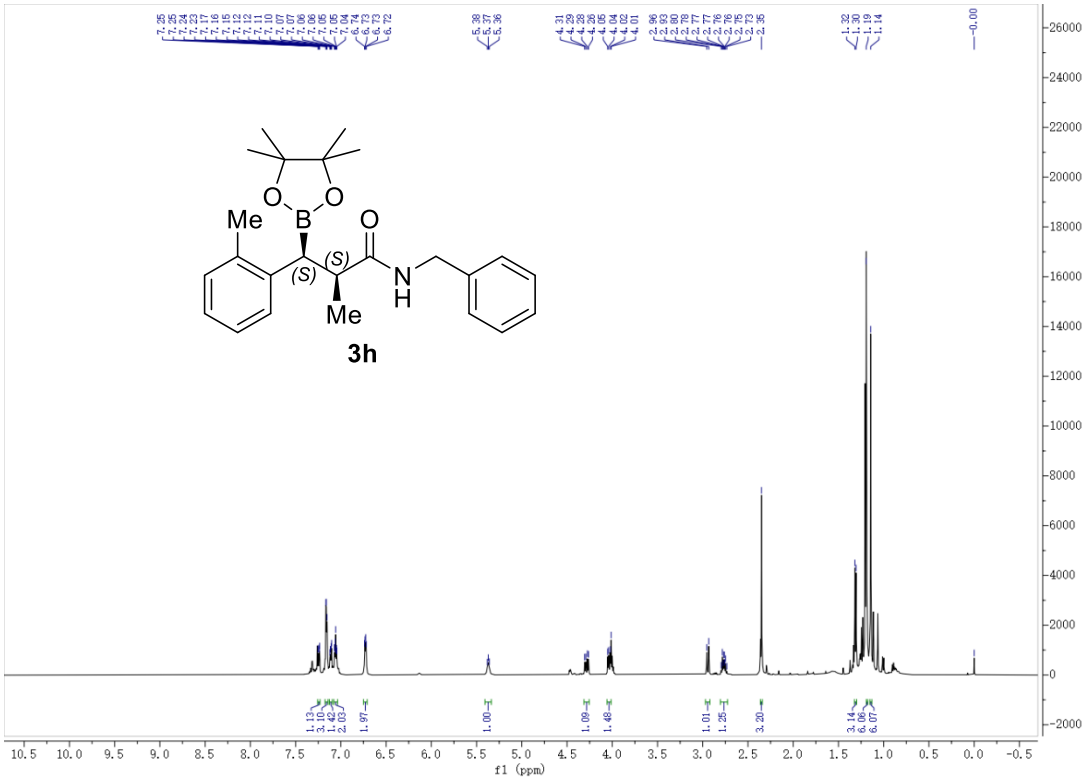
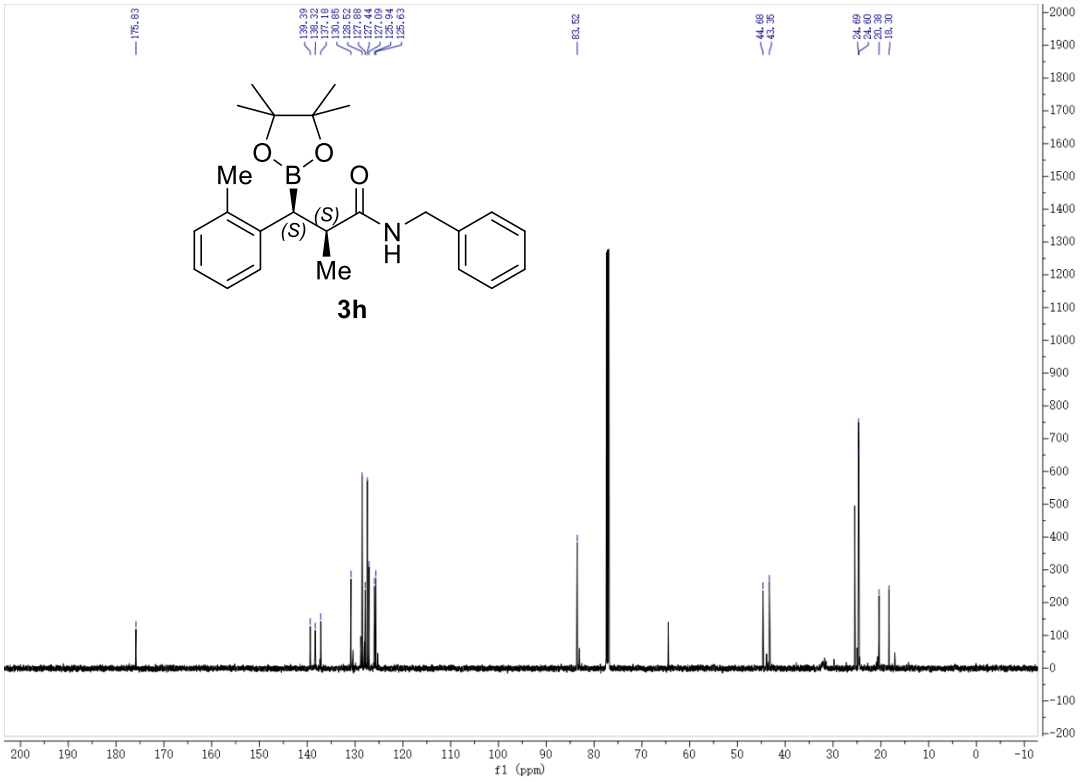
7.34
7.29
7.27
7.27
7.15
7.14
7.12
7.10
7.08
6.90
6.89
5.63
4.30
4.29
4.26
4.25
4.18
4.17
4.14
4.13
3.06
3.03
2.99
2.98
2.97
2.96
2.96
2.95
2.94
2.93
1.33
1.32
1.22
1.20
0.00
3.07
3.04
2.11
2.00
1.00
1.15
1.08
1.11
1.15
3.29
6.09
6.10
f1 (ppm)
Cl
B
O
O
O
(S)
(S)
N
H
Me
3f

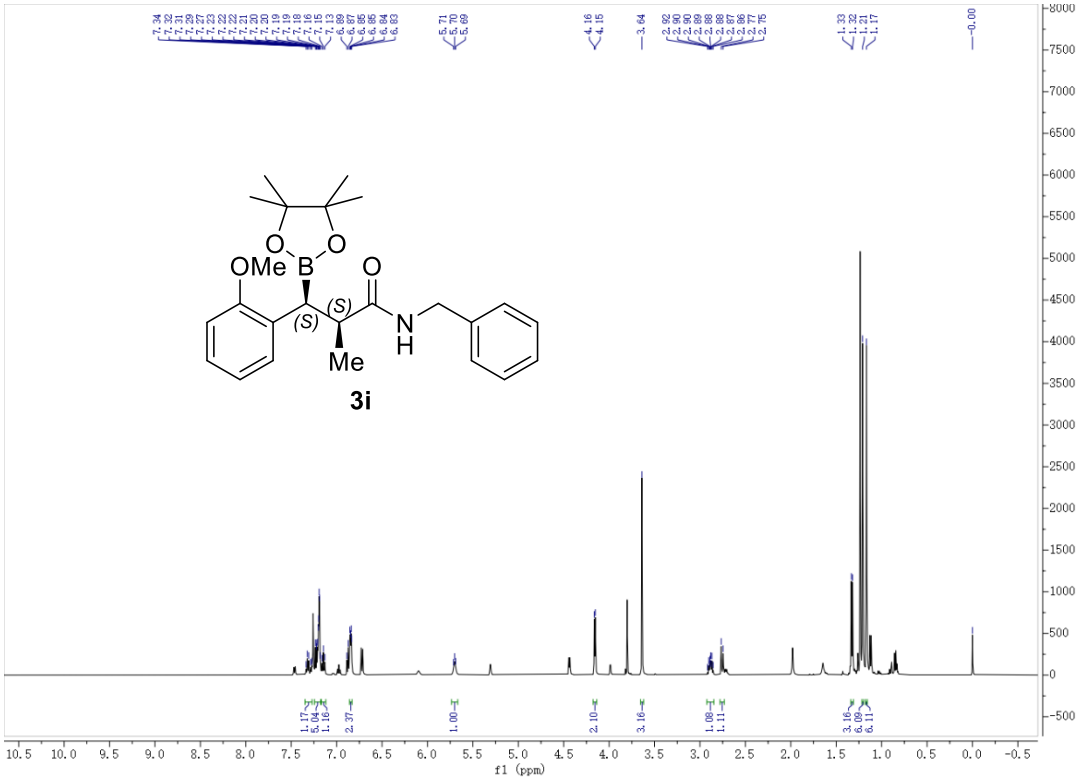

175.36
138.86
138.29
134.16
131.44
129.72
128.89
128.69
127.62
127.26
126.99
83.74
63.39
63.05
24.89
24.67
17.83
f1 (ppm)
Cl
B
O
O
O
(S)
(S)
N
H
Me
3f


Br
B
O
O
O
(S)
(S)
N
H
Me
3g
f1 (ppm)


Br
B
O
O
O
(S)
(S)
N
H
Me
3g
f1 (ppm)


Me
B
O
O
O
(S)
(S)
N
H
Me
3h
f1 (ppm)


Me
B
O
O
O
(S)
(S)
N
H
Me
3h
f1 (ppm)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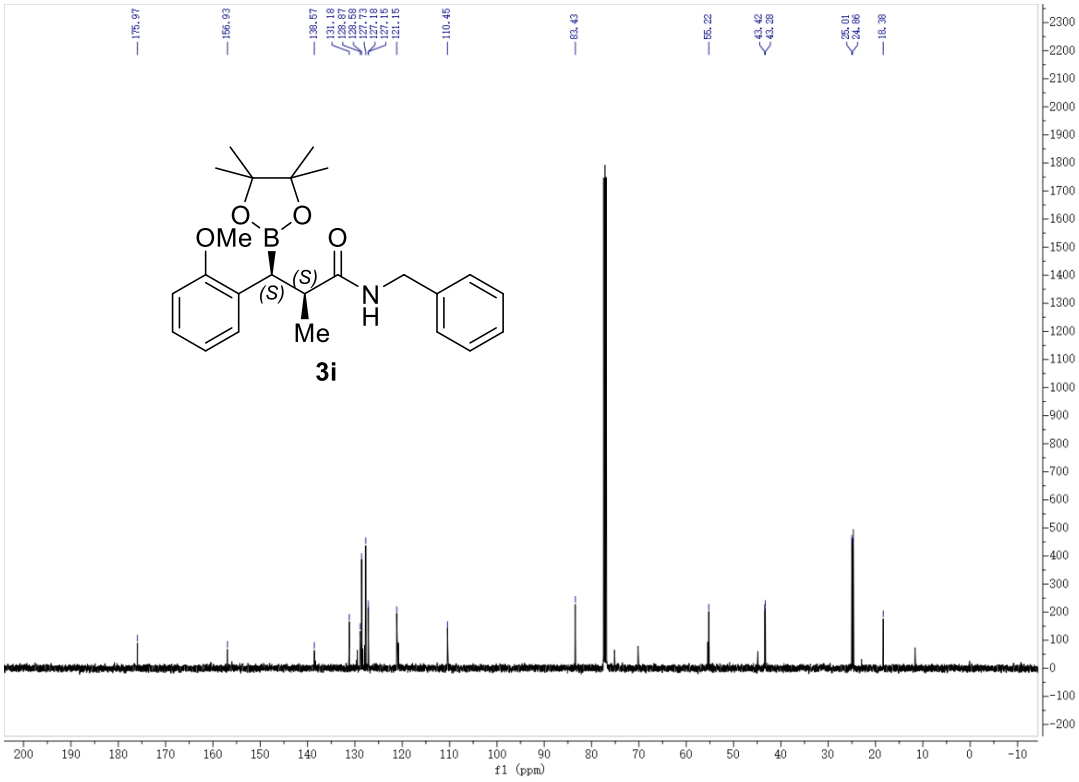
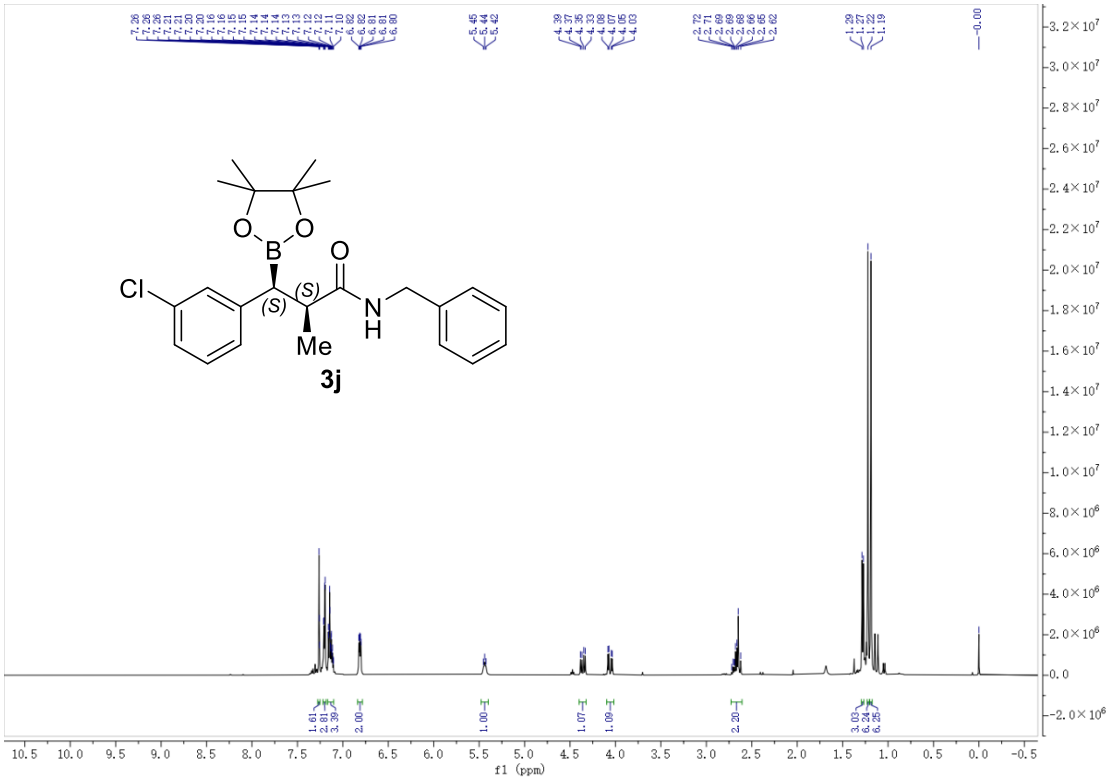
B
O
O
O
(S)
(S)
N
H
Me
3i
f1 (ppm)


OMe
B
O
O
O
(S)
(S)
N
H
Me
3i
f1 (ppm)


Cl
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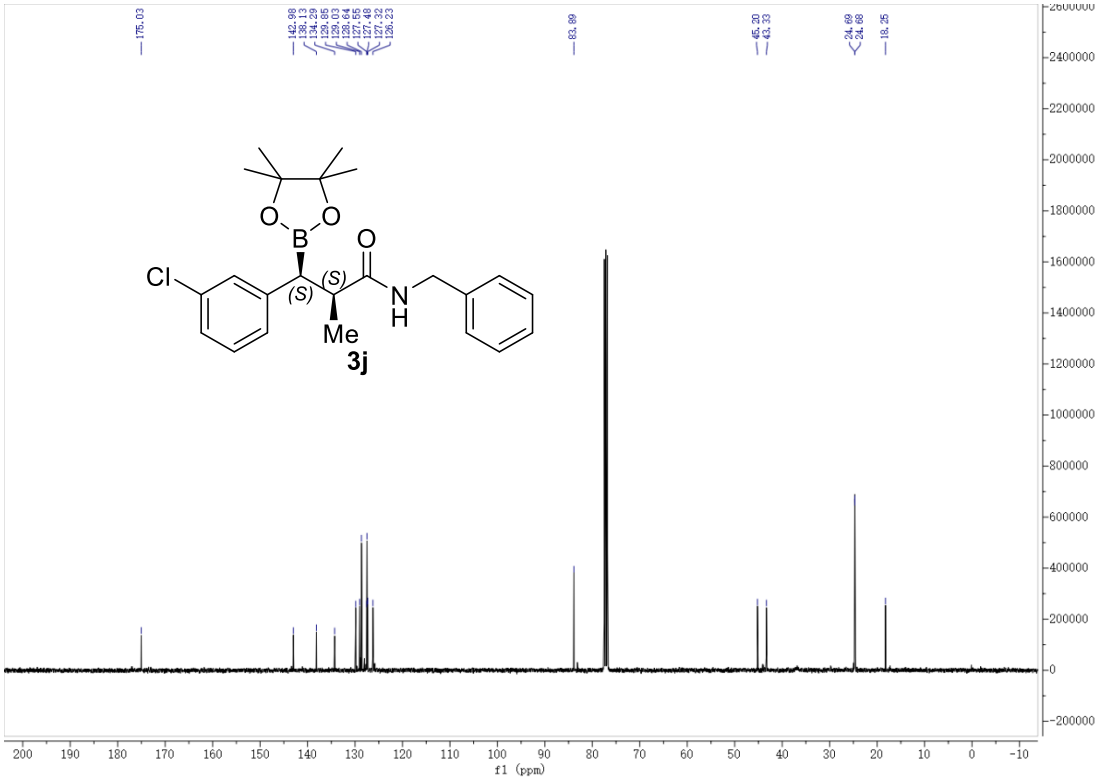
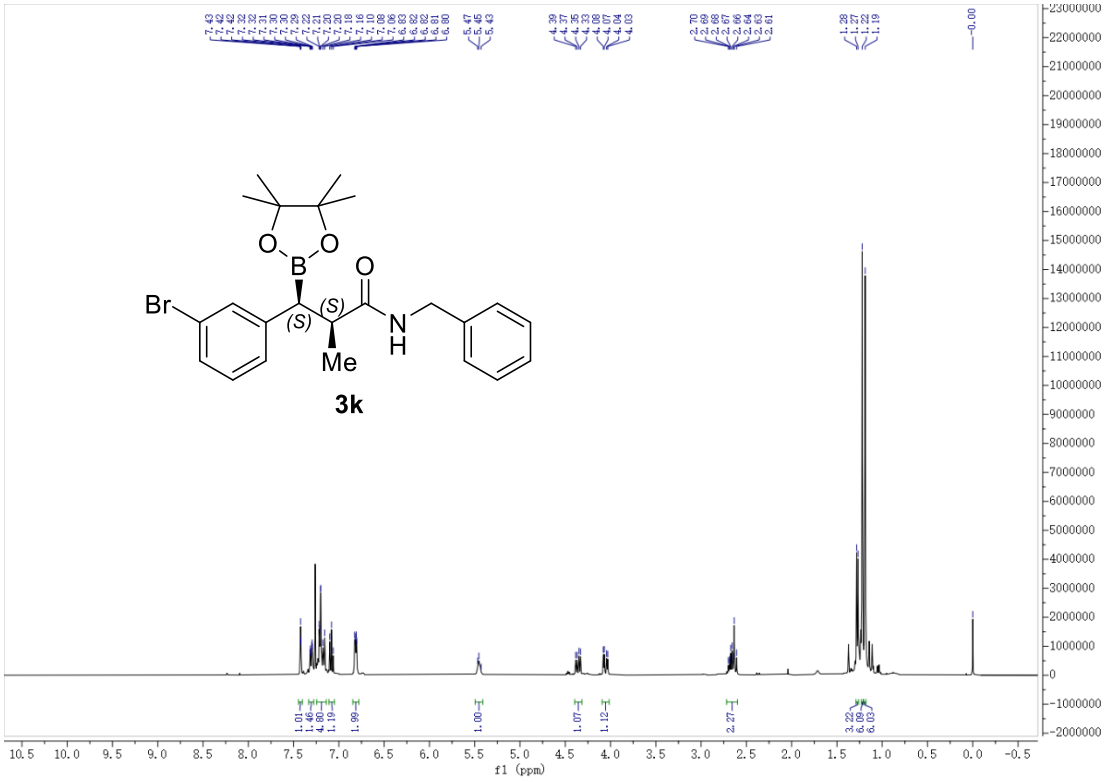
(S)
Me
N
H
O
B
O
O
3j
f1 (ppm)


Cl
(S)
(S)
Me
N
H
O
B
O
O
3j
f1 (ppm)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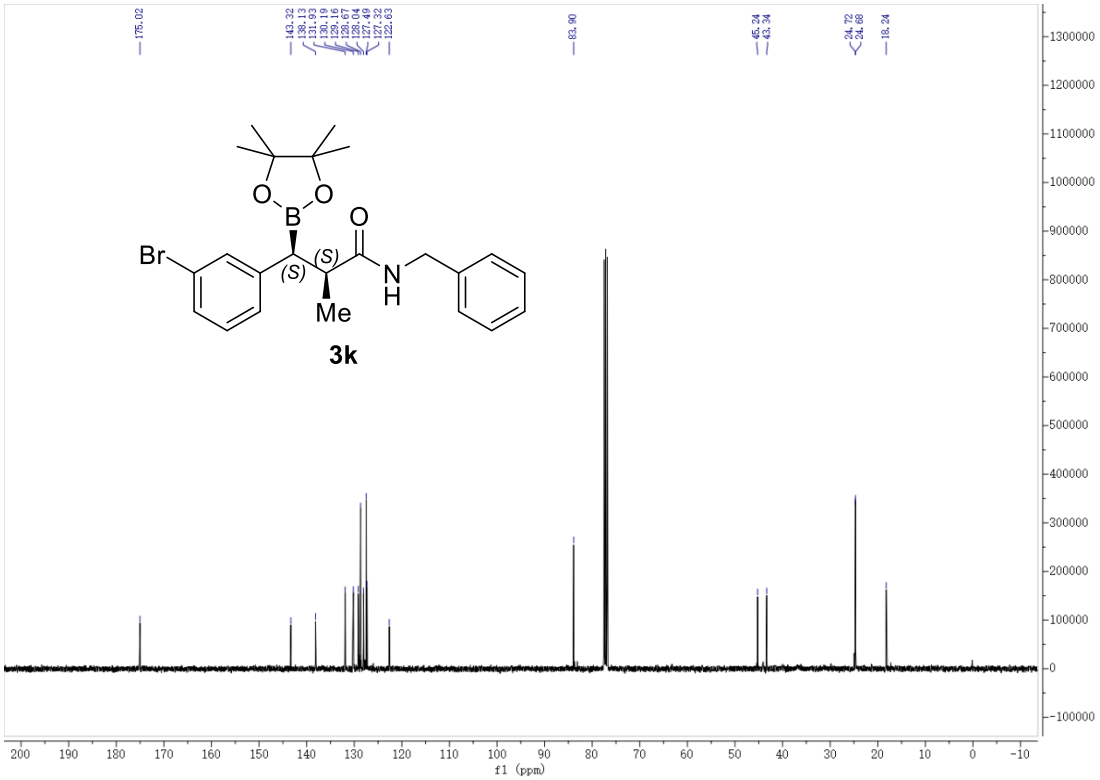
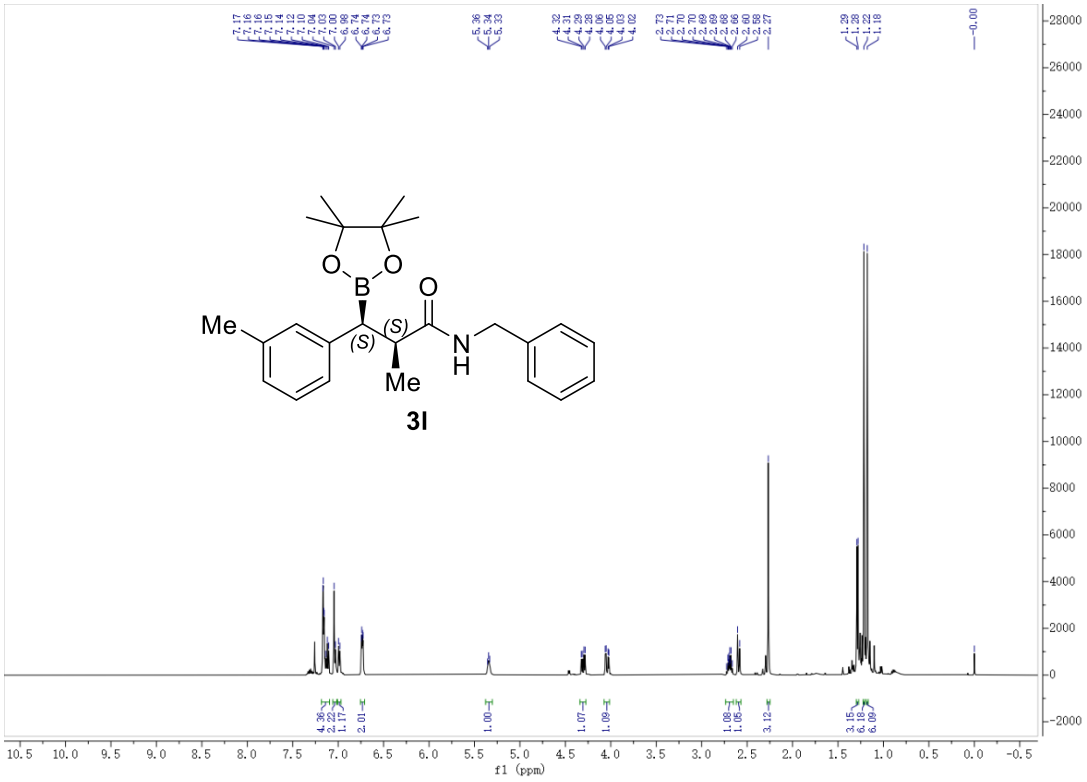
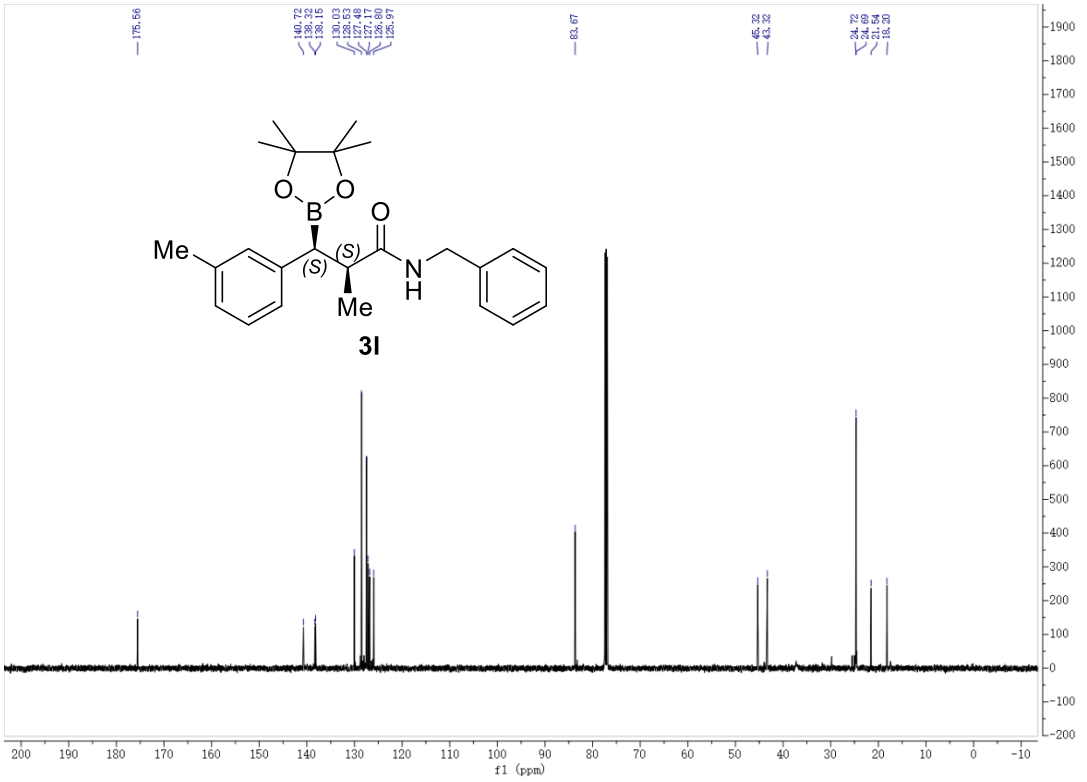
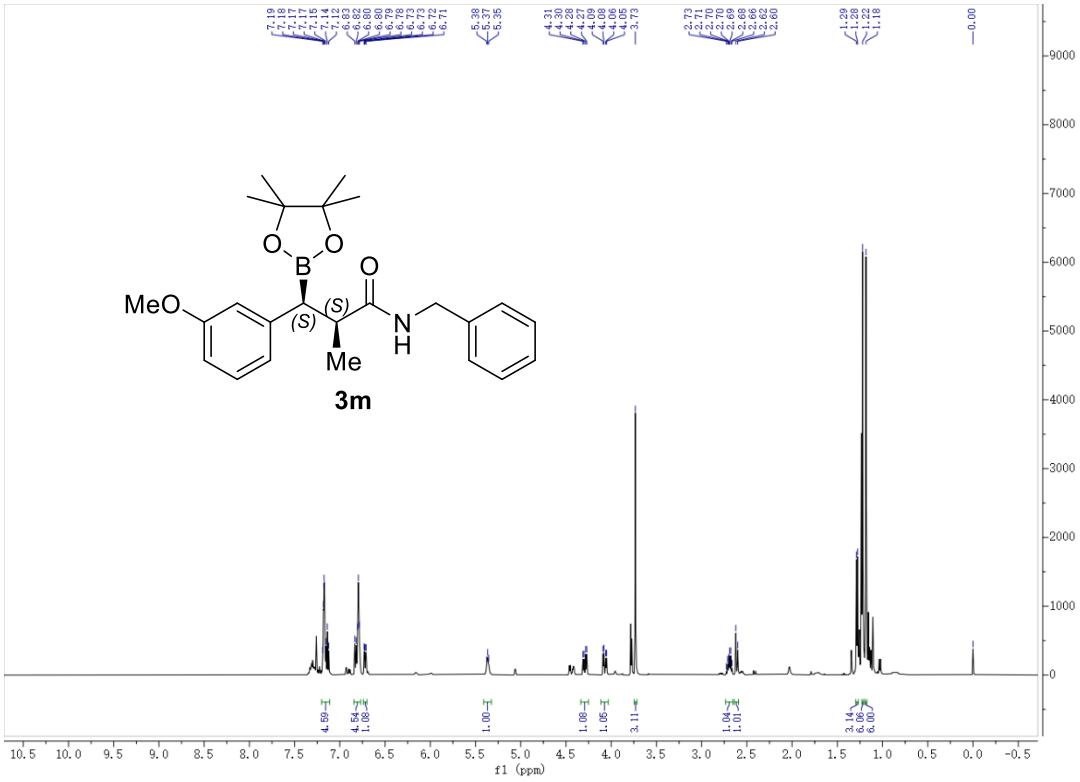
(S)
Me
O
N
H
B
O
O
3k
f1 (ppm)


Br
(S)
(S)
Me
O
N
H
B
O
O
3k
f1 (ppm)


Me
(S)
(S)
Me
N
H
O
B
O
O
3l
f1 (ppm)


Me
(S)
(S)
Me
N
H
O
B
O
O
3l
f1 (ppm)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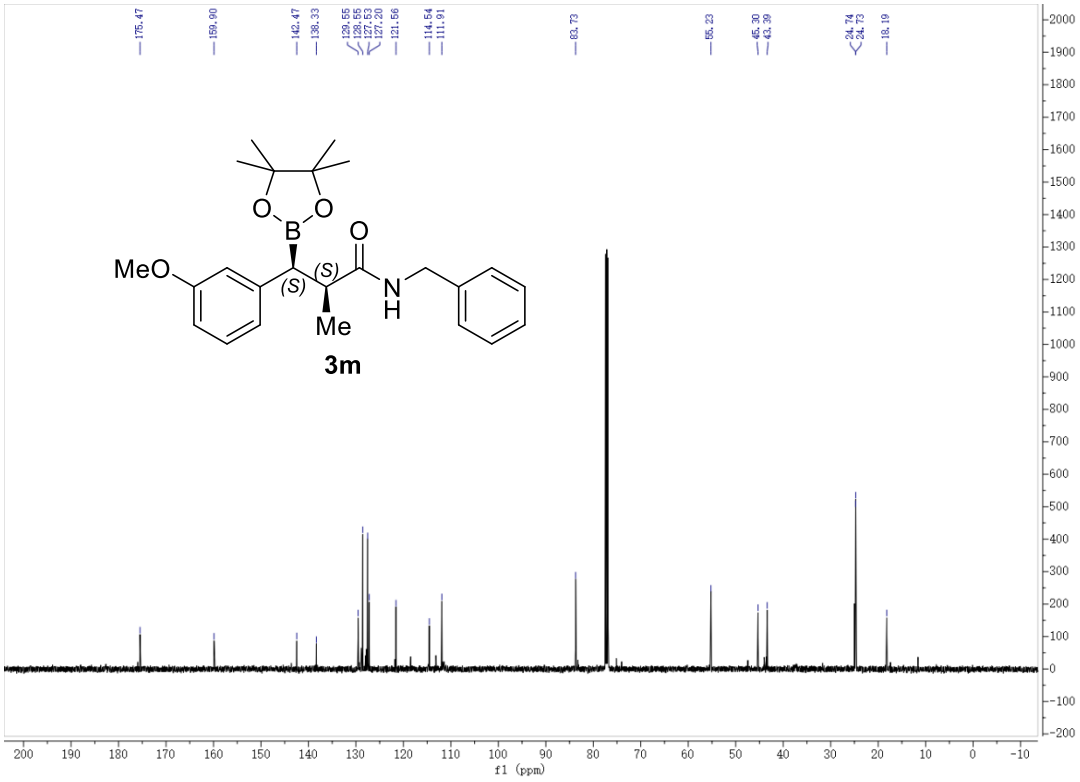
(S)
(S)
Me
O
N
H
3m
f1 (ppm)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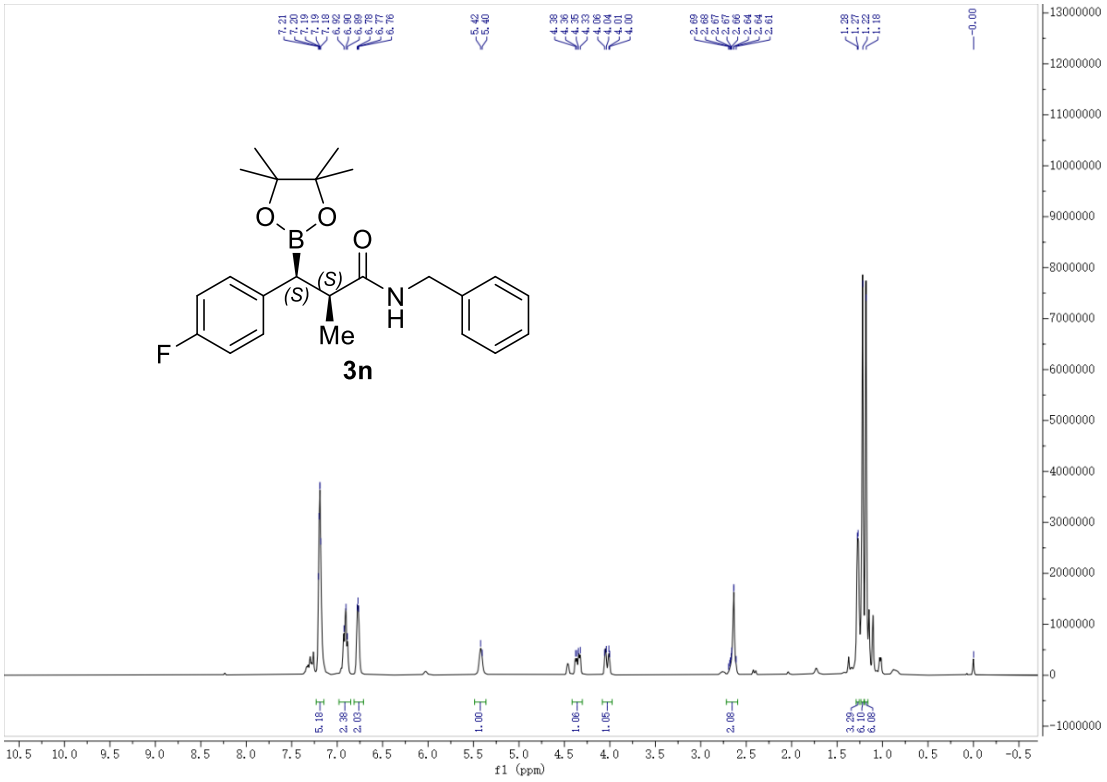
(S)
(S)
Me
O
N
H
3m
f1 (ppm)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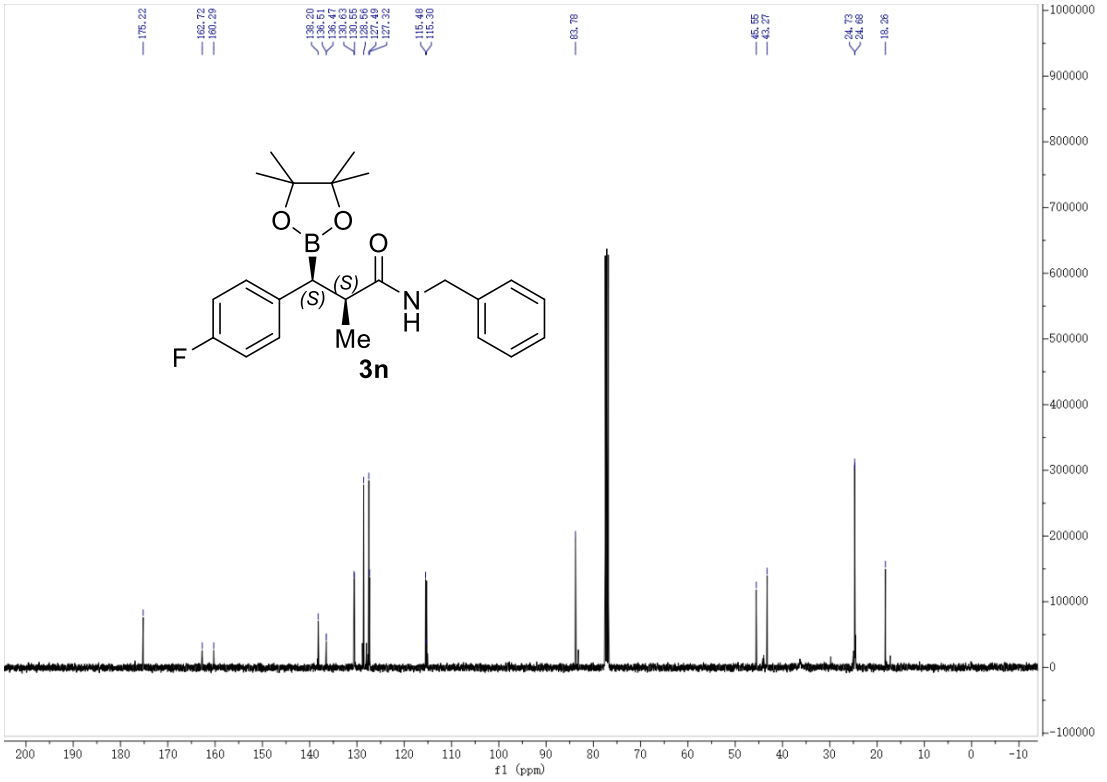
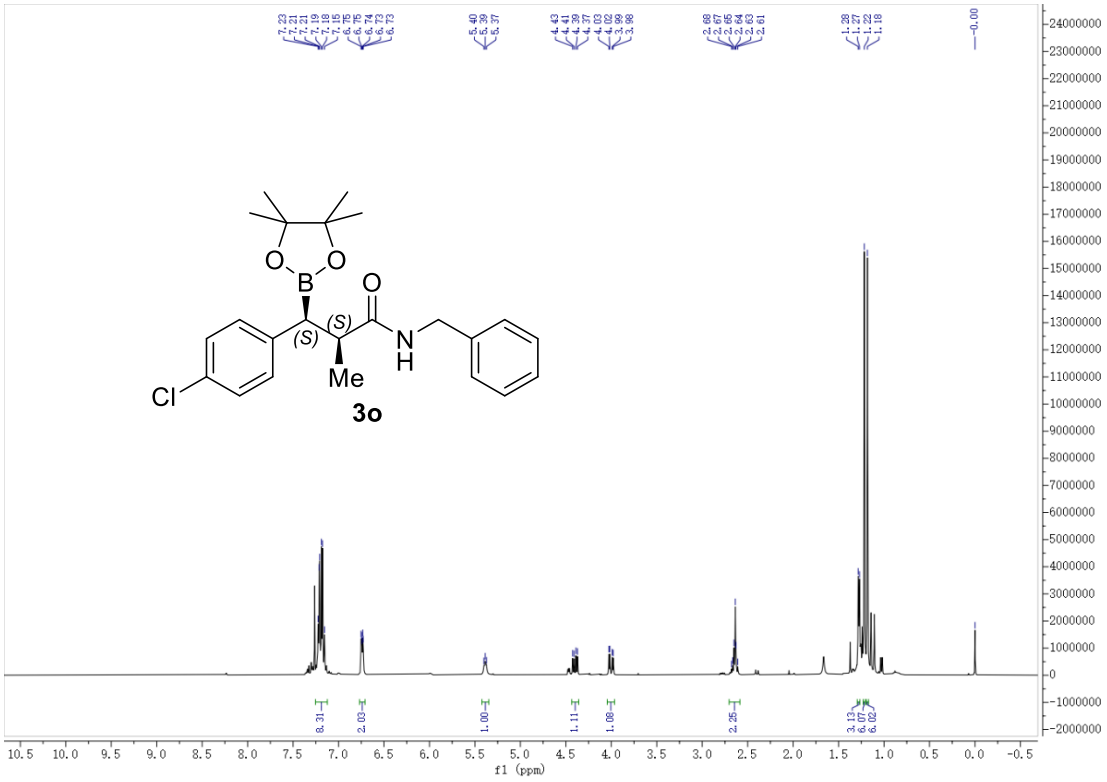
(S)
O
B
O
O
N
H
f1 (ppm)


3n
F
Me
(S)
(S)
O
B
O
O
N
H
f1 (ppm)


7.23
7.21
7.21
7.19
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7.15
6.75
6.74
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6.73
5.40
5.39
5.37
4.43
4.41
4.39
4.37
4.03
4.02
3.89
3.88
2.68
2.67
2.65
2.64
2.63
2.61
1.28
1.27
1.22
1.18
0.00
O
B
O
O
(S)
(S)
N
H
Me
Cl
3o
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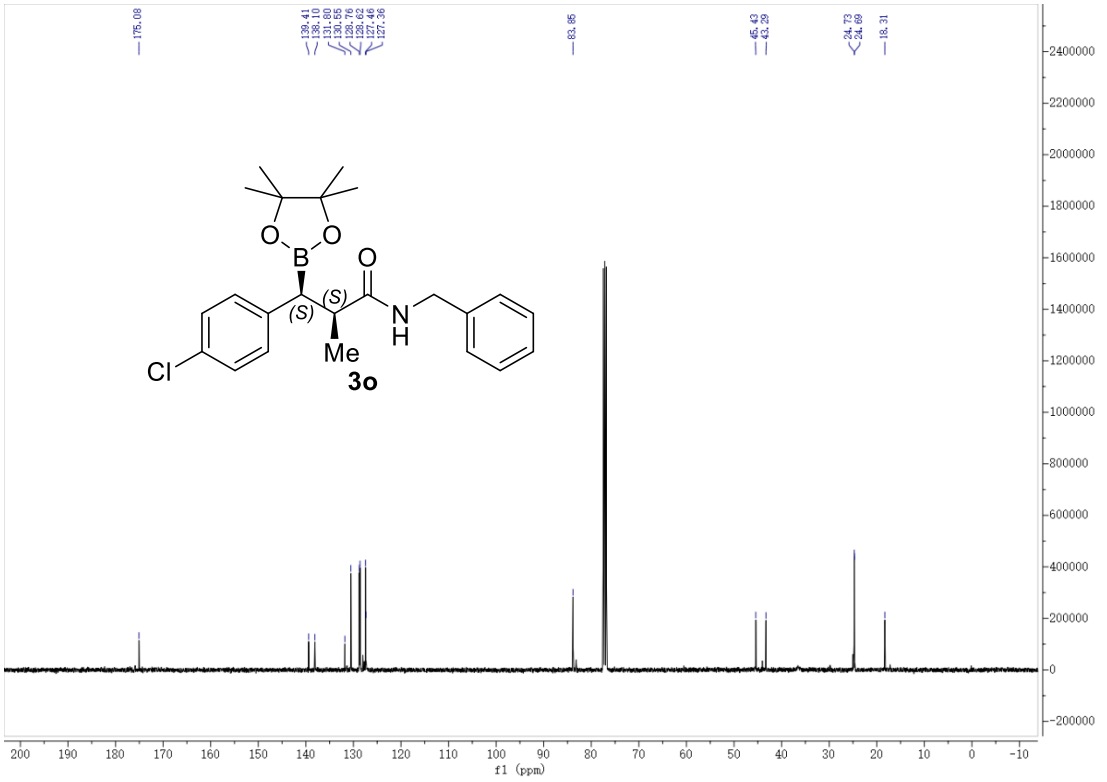
2.03
1.00
1.11
1.08
2.25
3.13
6.07
6.02
f1 (ppm)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131.80
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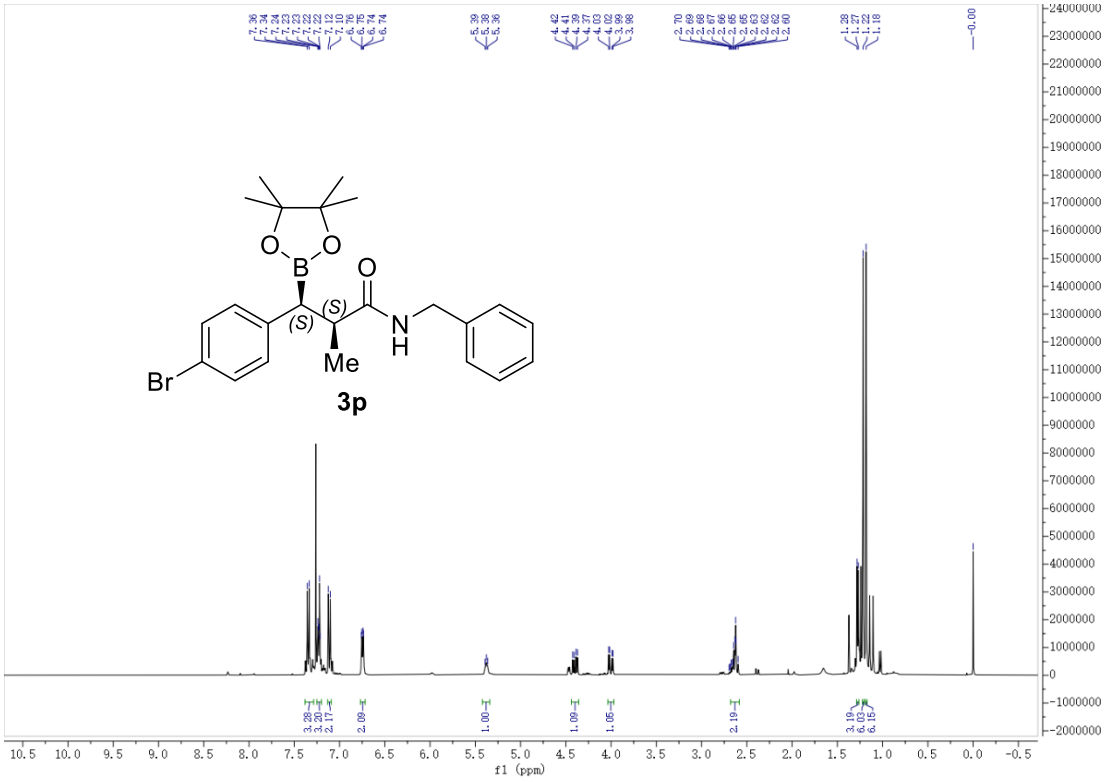
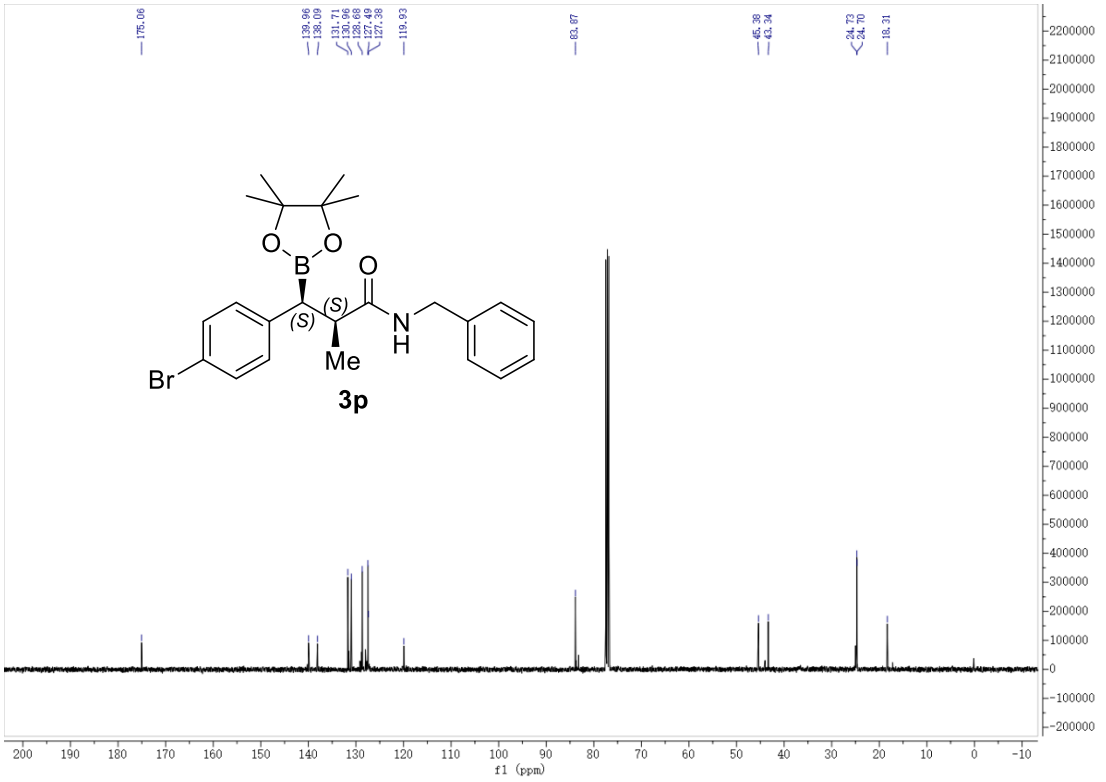
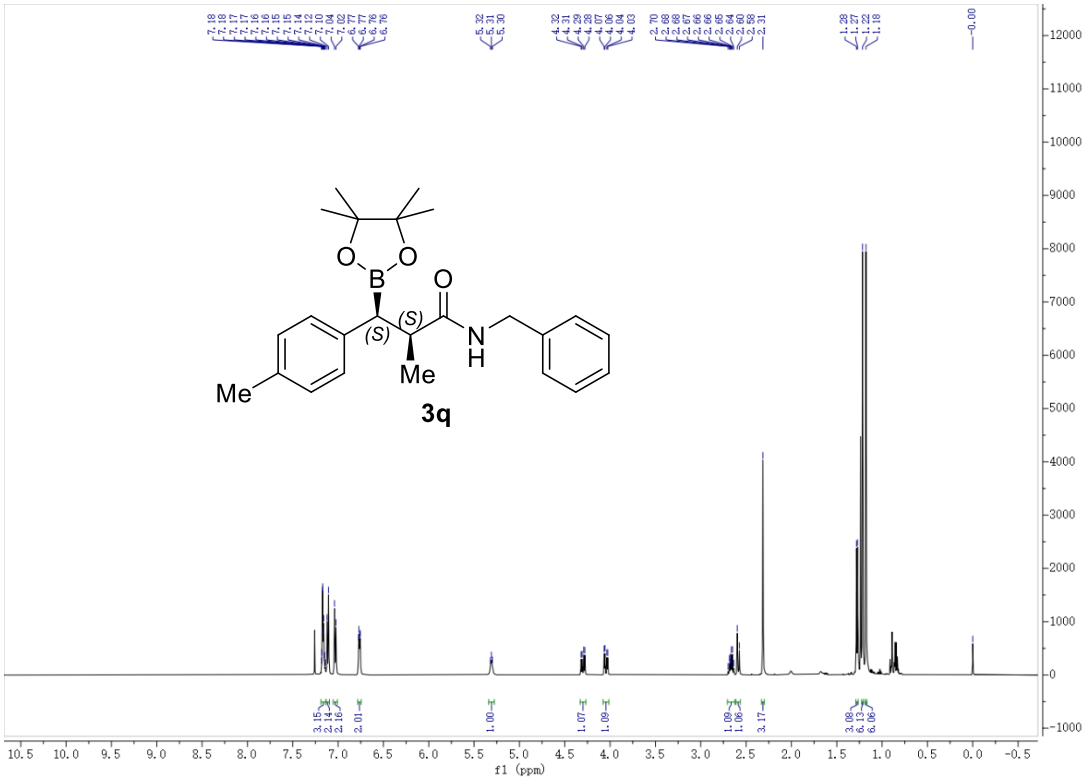
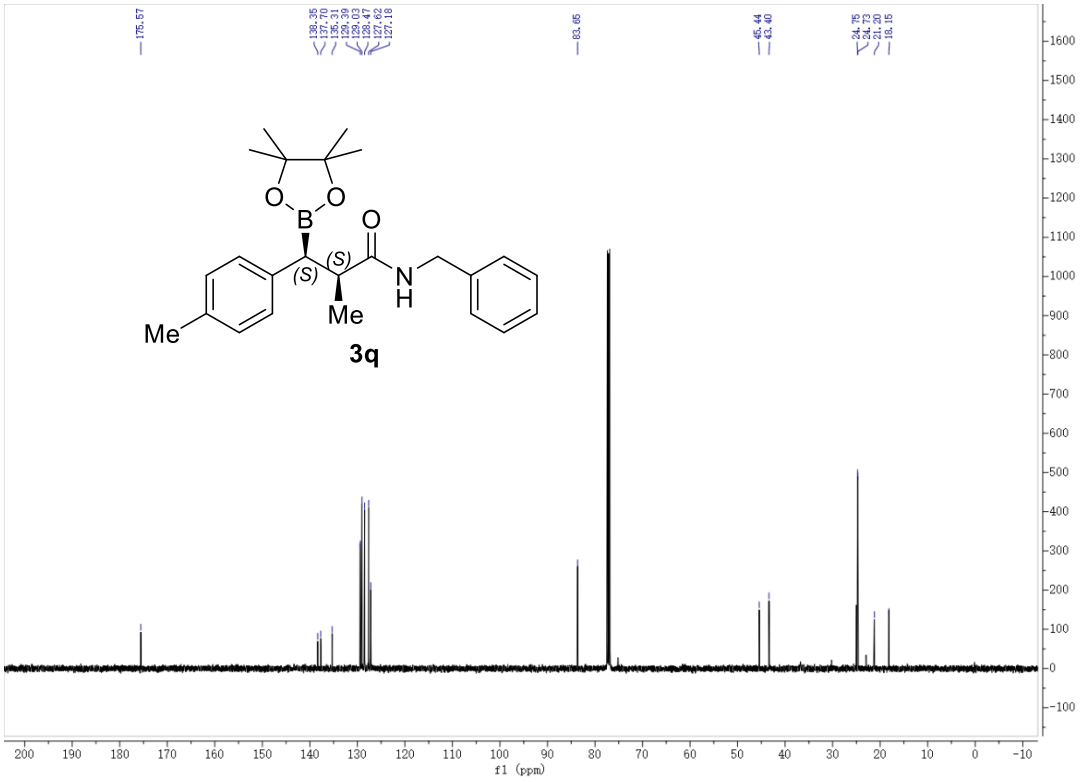
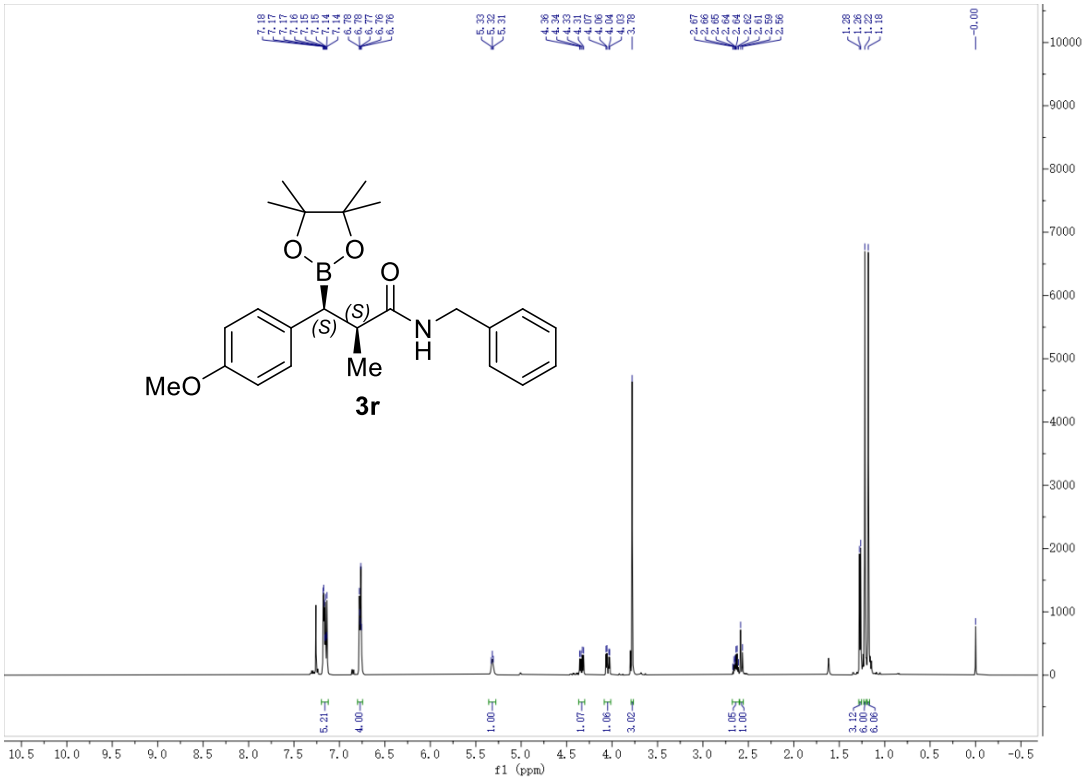
128.76
128.62
127.46
127.36
83.85
65.43
63.29
24.73
24.69
18.31
O
B
O
O
(S)
(S)
N
H
Me
Cl
3o
f1 (ppm)

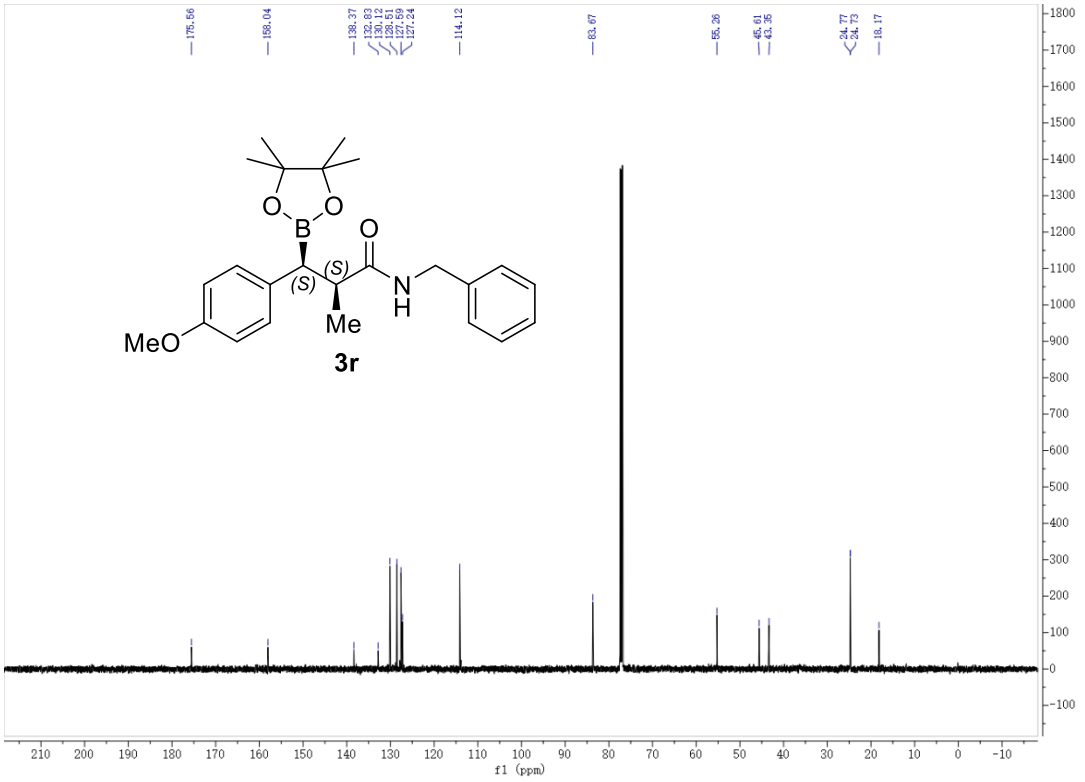

3p
f1 (ppm)

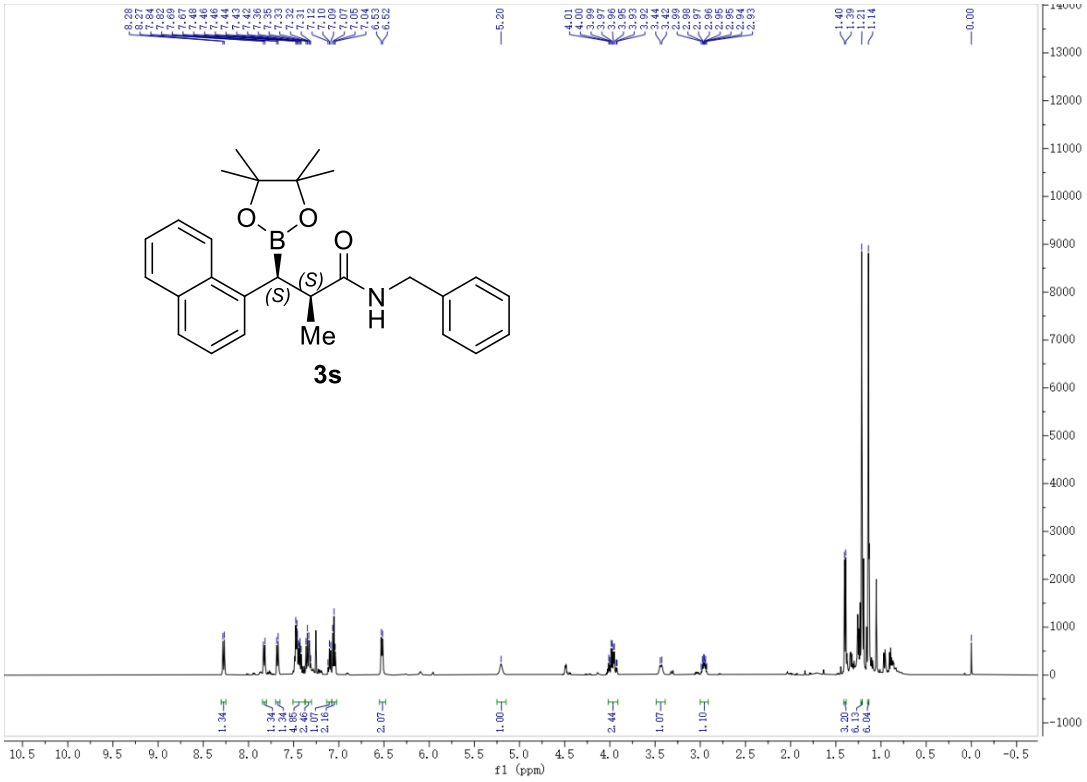

3p
f1 (ppm)

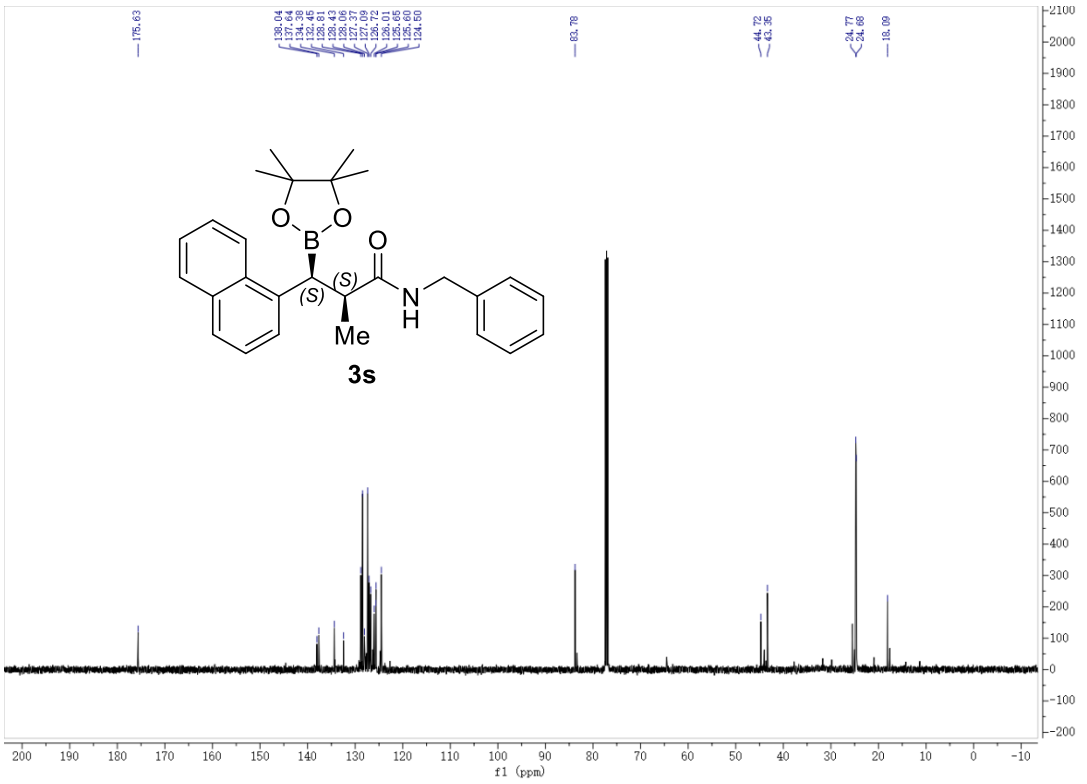

3q
f1 (ppm)

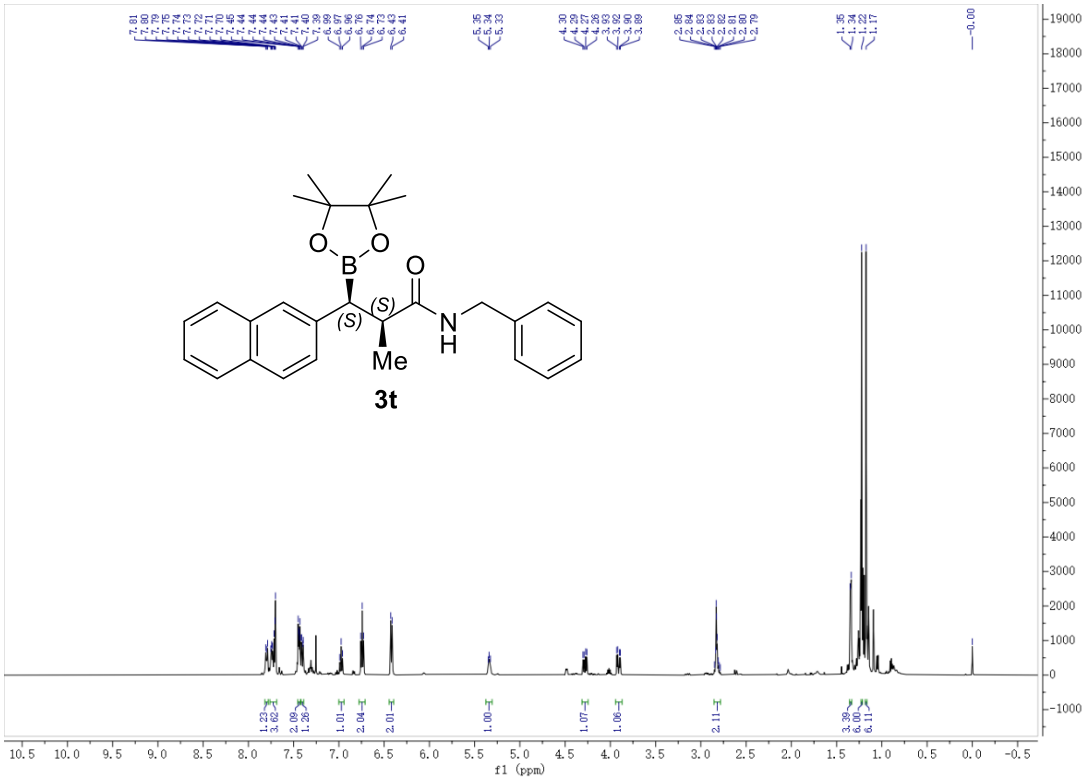

3q
f1 (ppm)

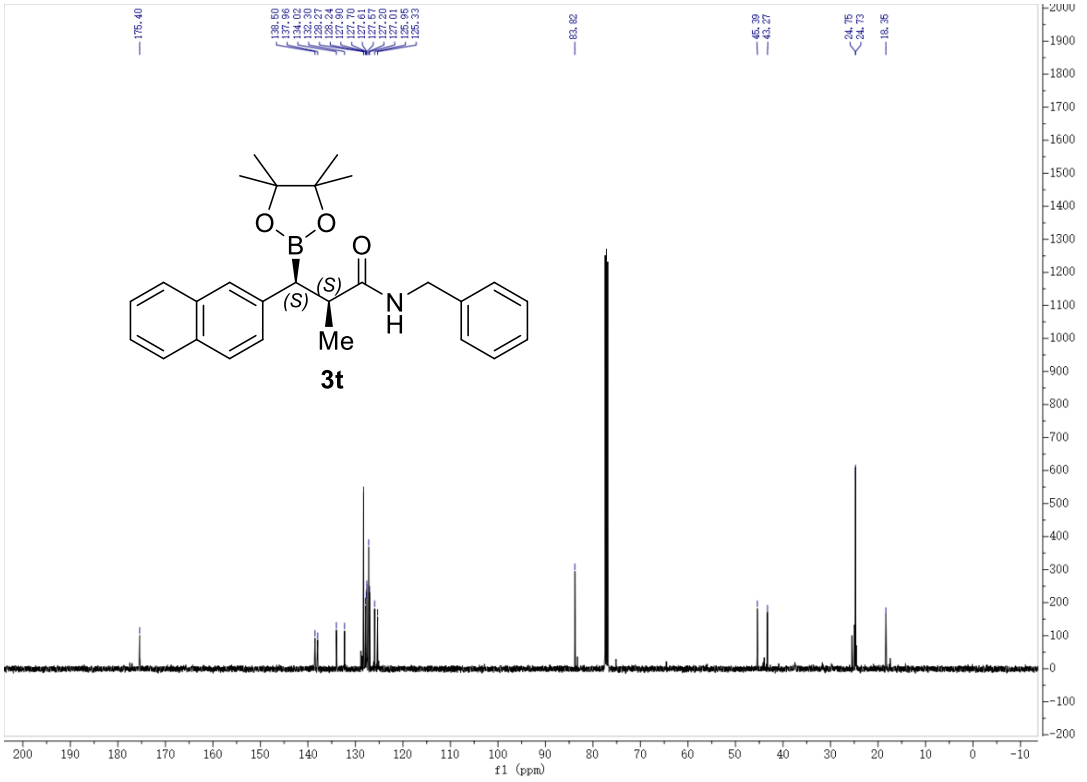

MeO
Me
(S)
(S)
O
B
O
O
N
H
3r
f1 (ppm)

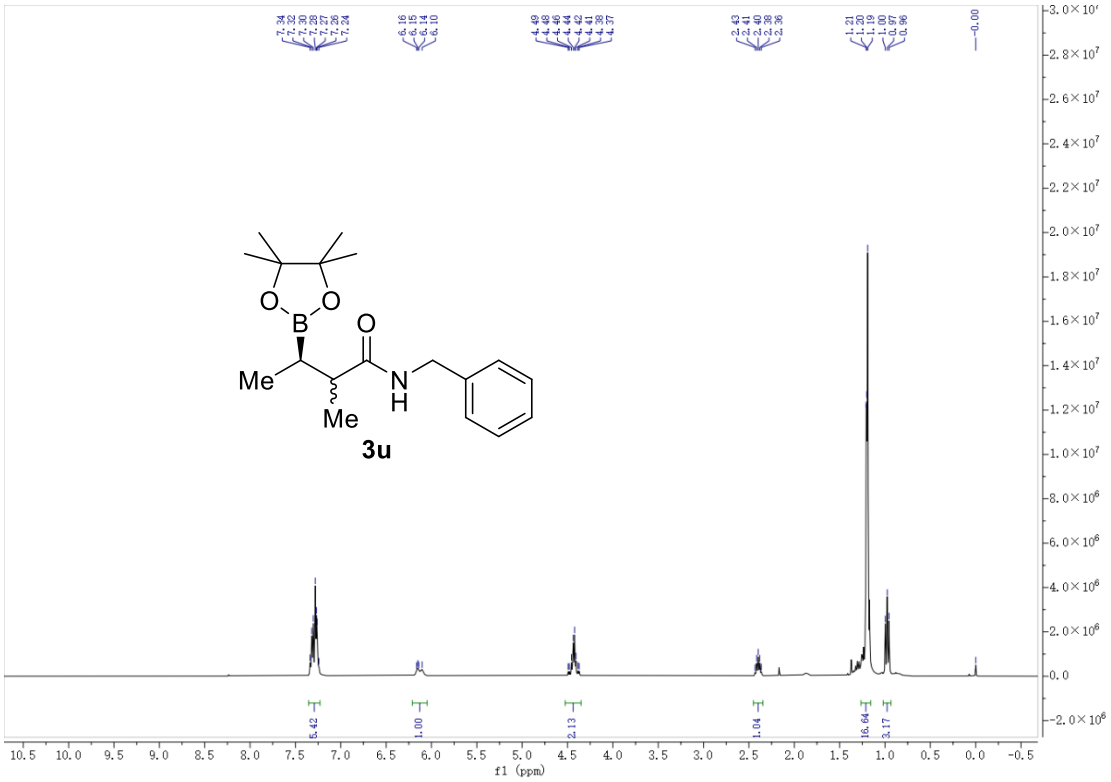

MeO
Me
(S)
(S)
O
B
O
O
N
H
3r
f1 (ppm)

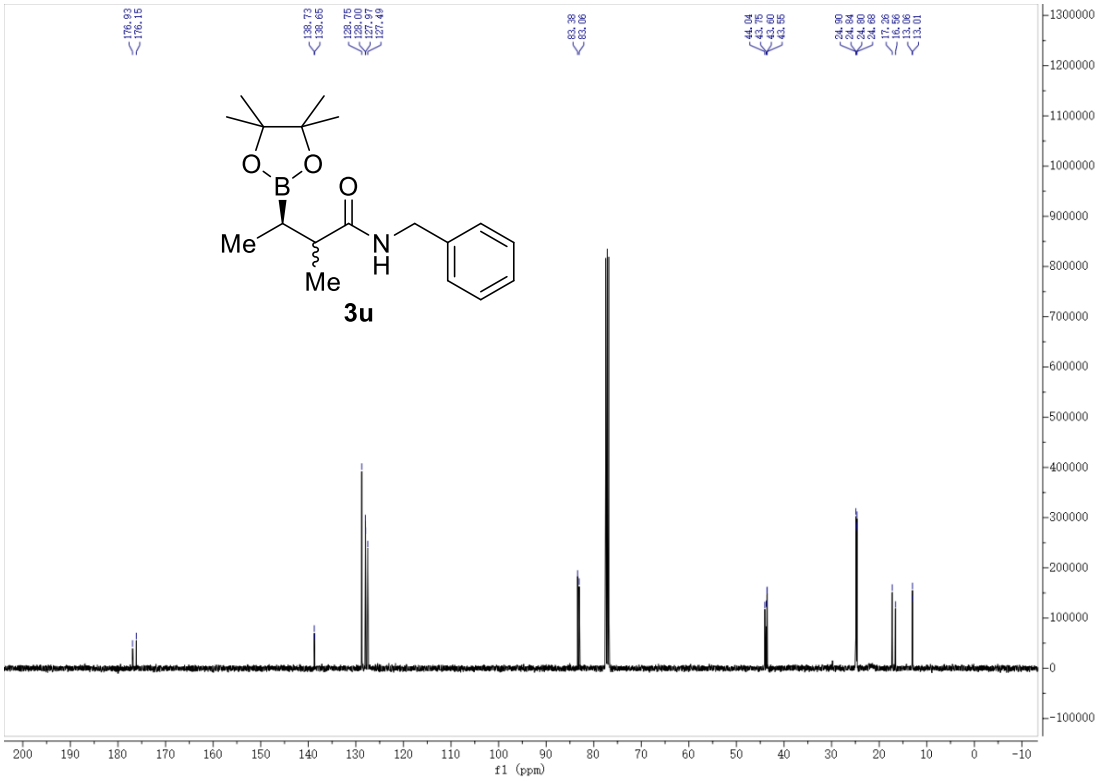

3s
f1 (ppm)

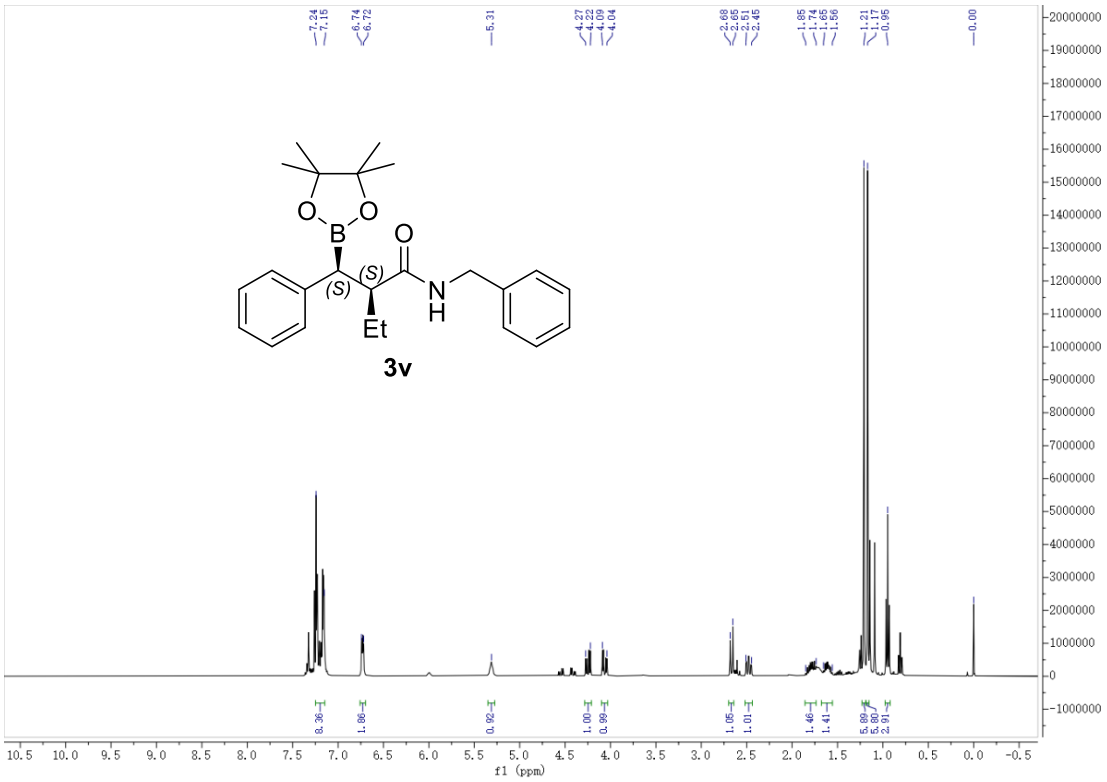

3s
f1 (ppm)

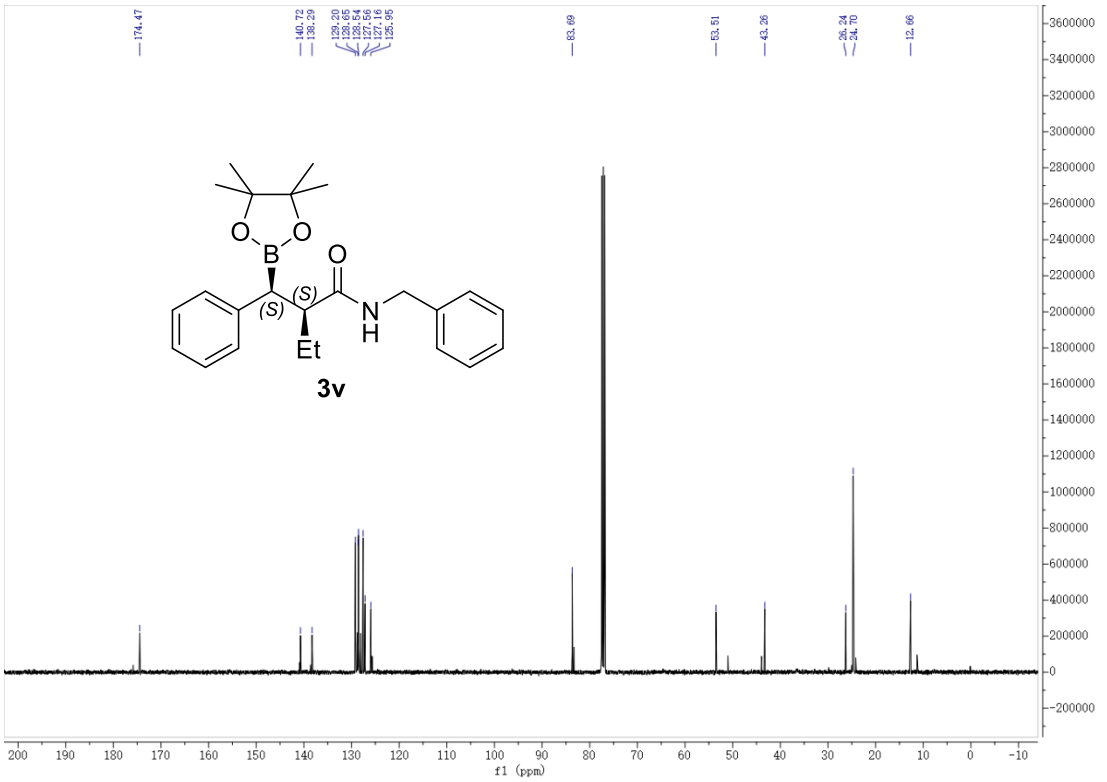

3t
f1 (ppm)

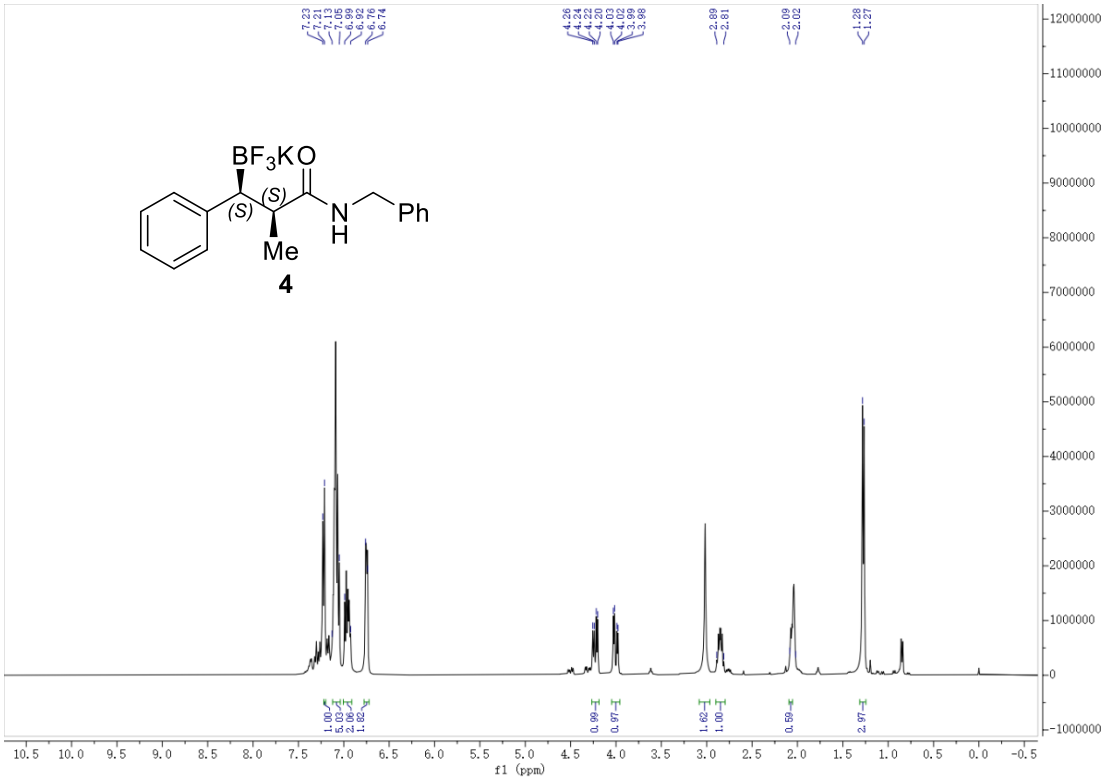

3t
f1 (ppm)

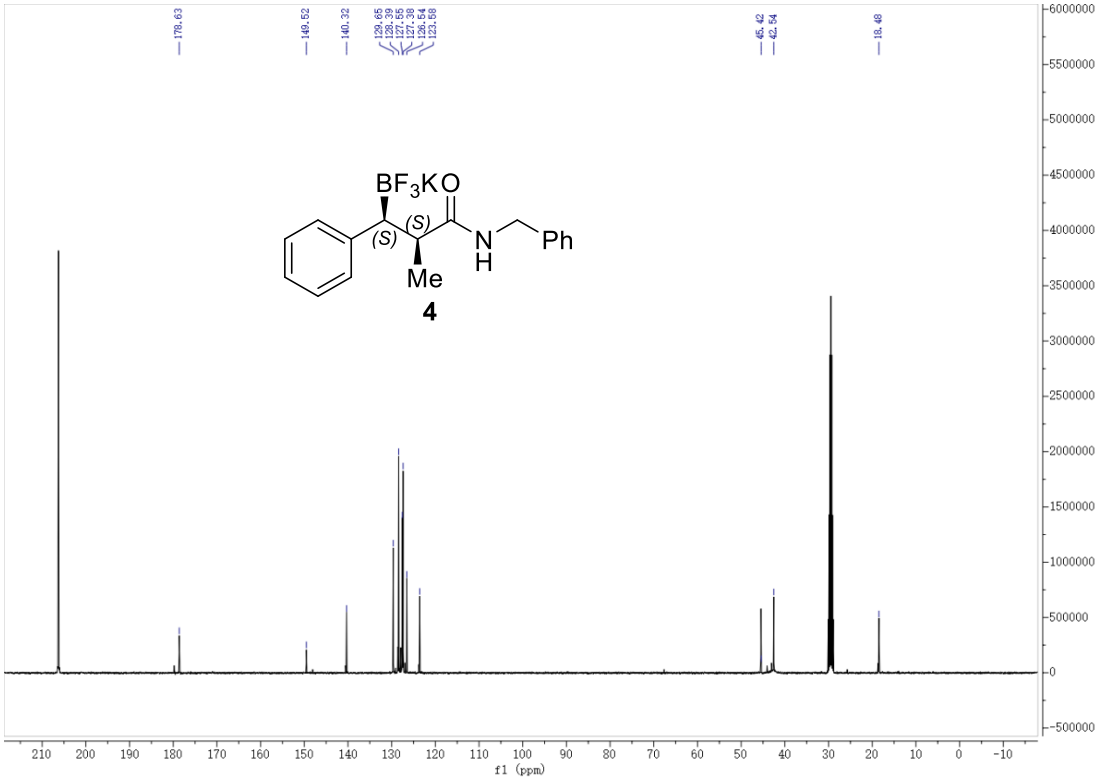

Me
Me
3u
f1 (ppm)

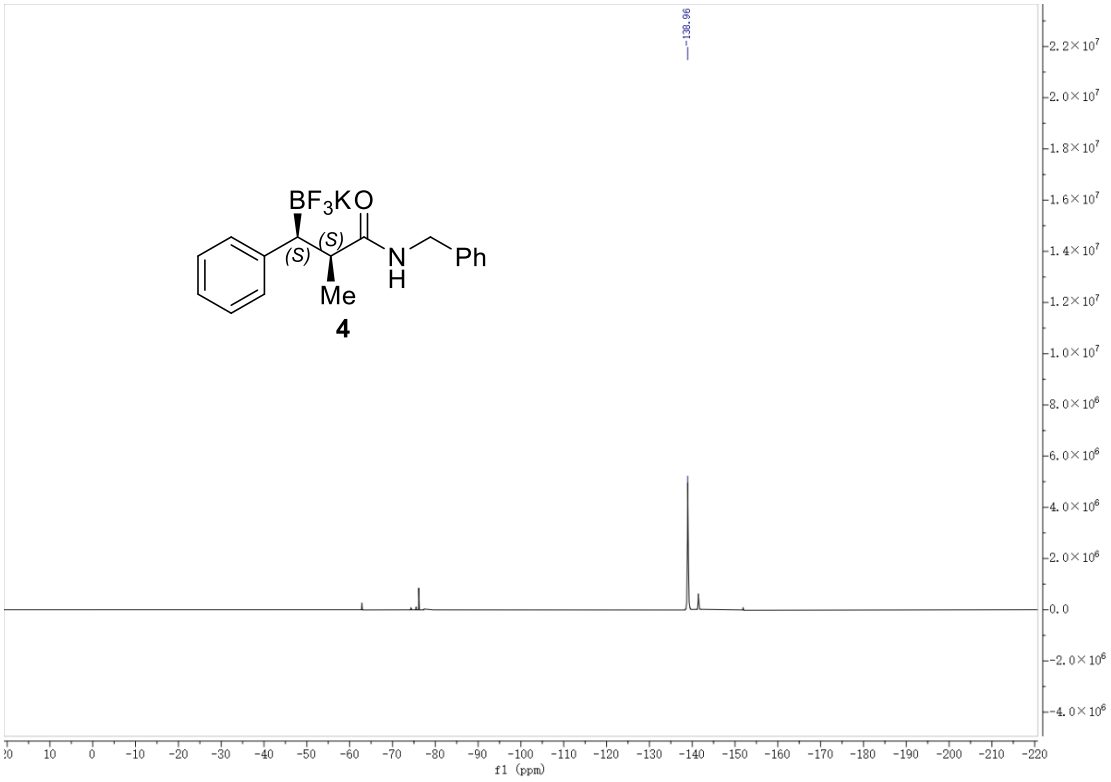

Me
Me
3u
f1 (ppm)

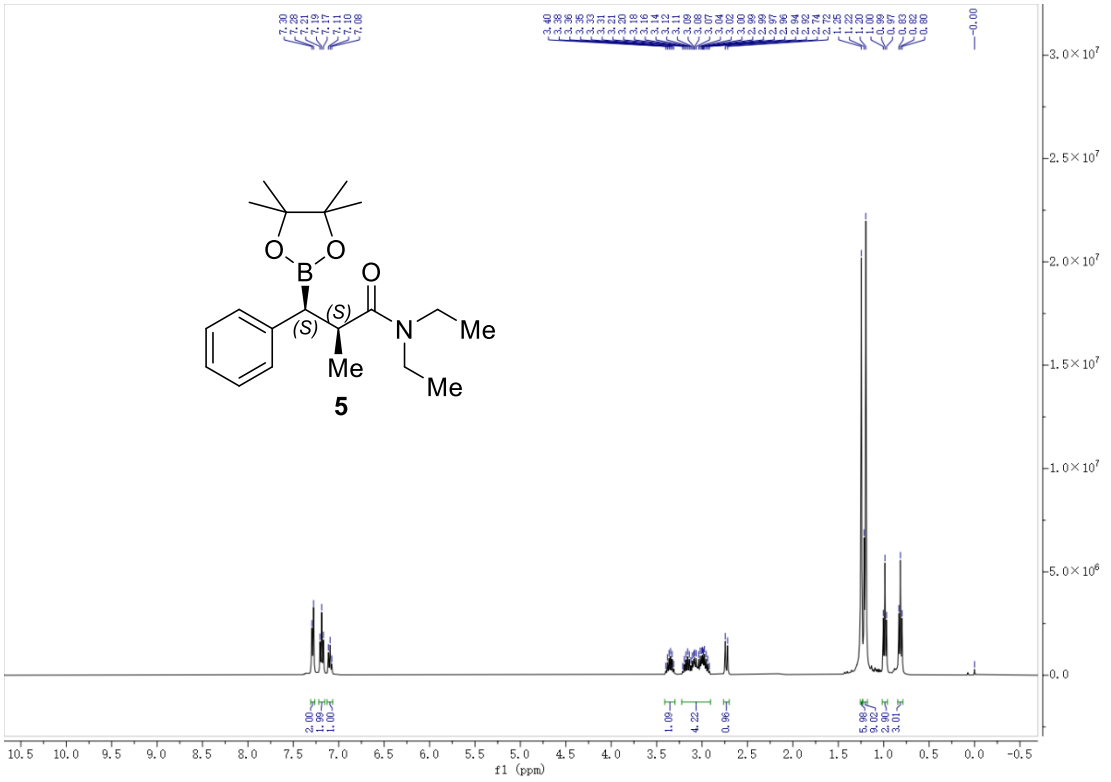

7.24
7.15
6.74
6.72
5.31
4.27
4.23
4.09
4.04
2.68
2.65
2.51
2.45
1.85
1.74
1.65
1.56
1.21
1.17
0.95
0.00
O
B
O
(S)
(S)
O
N
H
Et
3v
8.36
1.86
0.92
1.00
0.99
1.05
1.01
1.46
1.41
5.89
5.80
2.91
f1 (ppm)

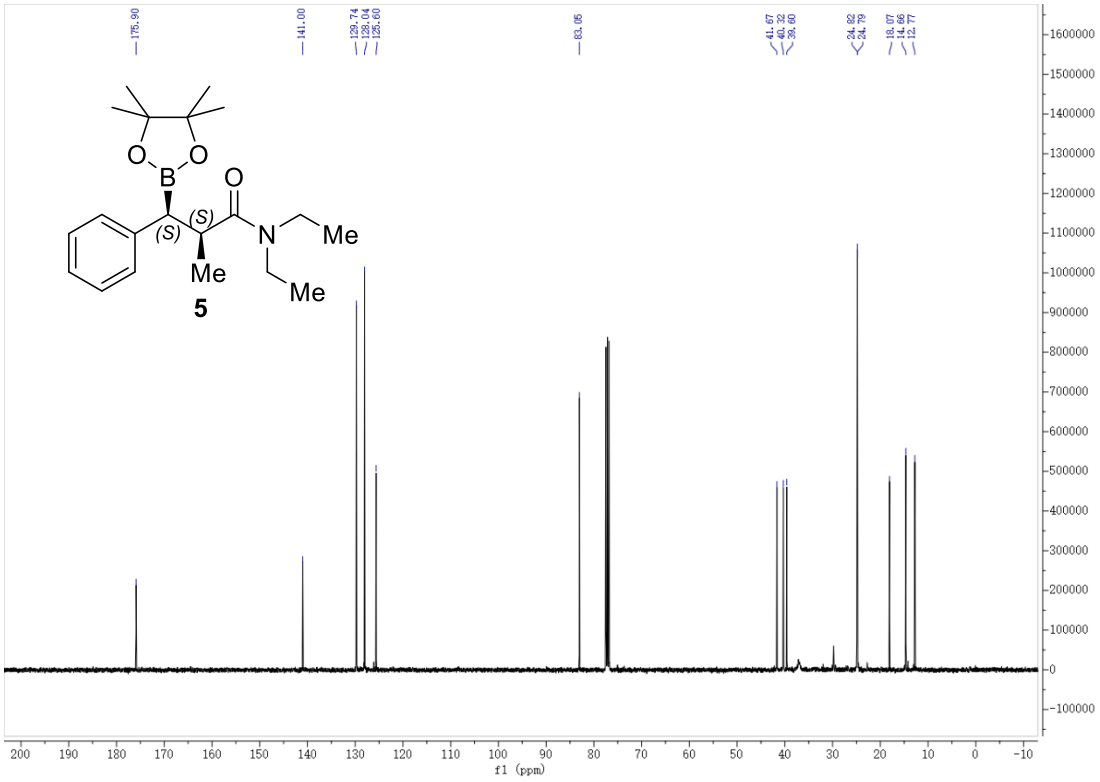

174.47
140.72
138.29
129.20
128.65
128.54
127.66
127.10
125.95
83.89
53.51
43.26
26.24
24.70
12.66
O
B
O
(S)
(S)
O
N
H
Et
3v
f1 (ppm)

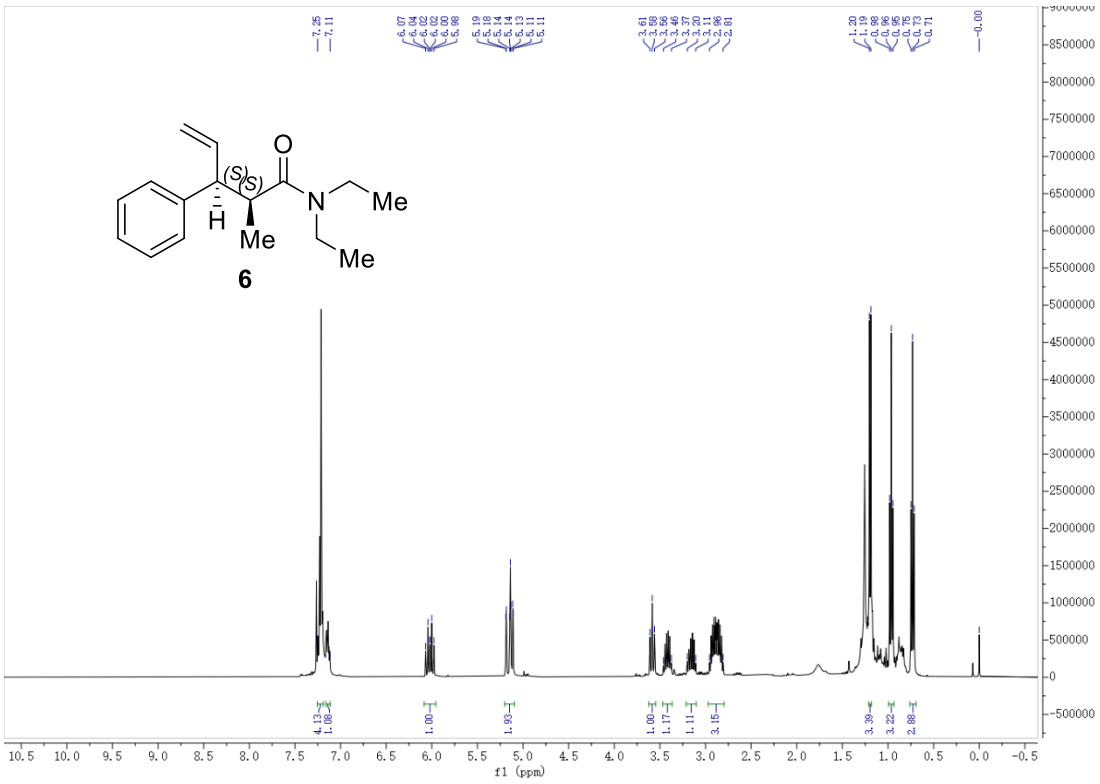

BF3KO
(S)
(S)
N
H
Ph
Me
4
f1 (ppm)

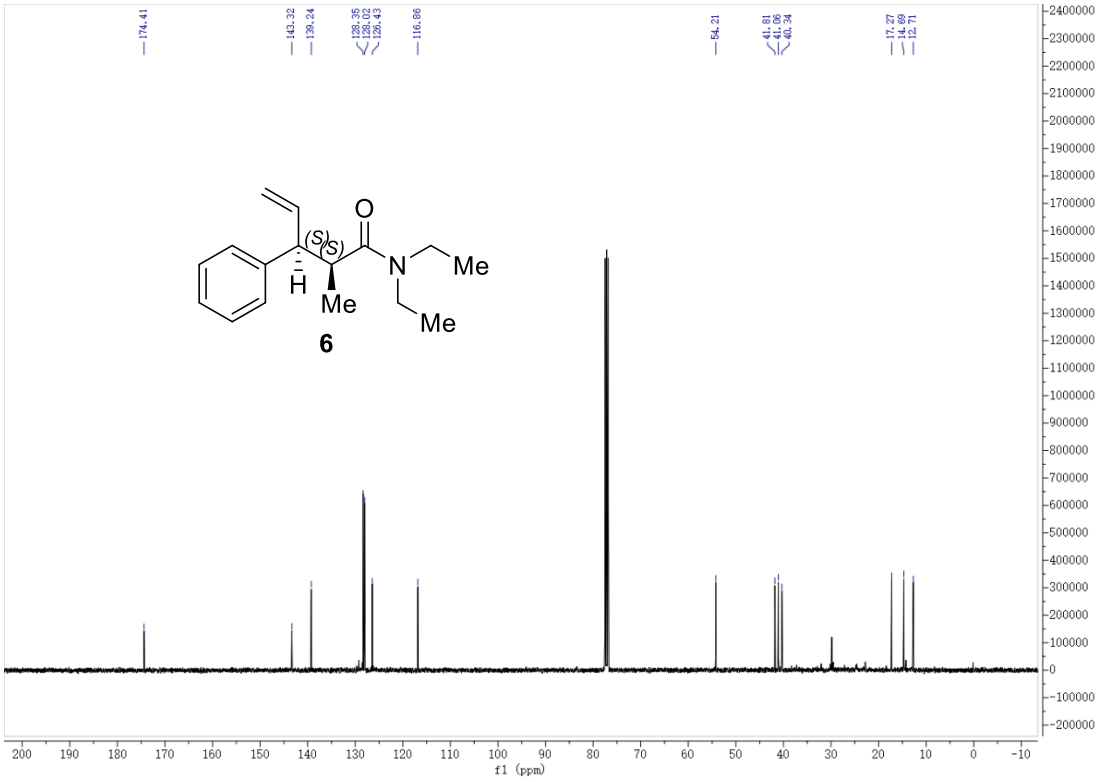

BF3KO
(S)
(S)
N
H
Ph
Me
4
f1 (ppm)


BF3KO
(S)
(S)
N
H
Ph
Me
4
f1 (ppm)


O
O
B
O
(S)
(S)
N
Me
Me
Me
5
f1 (ppm)


175.90
141.00
129.74
129.04
125.60
83.05
41.67
40.32
39.60
24.82
24.79
18.07
14.66
12.77
O
B
O
O
(S)
(S)
N
Me
Me
Me
5
f1 (ppm)


7.25
7.11
6.07
6.04
6.02
6.02
6.00
5.98
5.19
5.18
5.14
5.13
5.11
5.11
3.61
3.59
3.56
3.46
3.37
3.20
3.11
2.96
2.81
1.20
1.19
0.98
0.96
0.95
0.75
0.73
0.71
0.00
O
(S)
(S)
H
N
Me
Me
Me
6
4.13
1.08
1.00
1.93
1.00
1.17
1.11
3.15
3.39
3.22
2.88
f1 (ppm)


174.41
143.32
139.24
128.35
128.03
126.43
116.86
54.21
41.81
41.06
40.34
17.27
14.69
12.71
O
(S)
(S)
H
Me
N
Me
Me
6
fl (ppm)