Supporting Information

for

Access to Dialkylated Allylic Stereogenic Centers by Ni-Catalysed Enantioselective Hydrovinylation of Unactivated Alkenes

Jian-Xin Zhang,[†] Peng-Fei Yang,[†] and Wei Shu[†,*]

[†]*Shenzhen Grubbs Institute, Department of Chemistry, and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, Guangdong, P. R. China*

[*]E-mail: shuw@sustech.edu.cn

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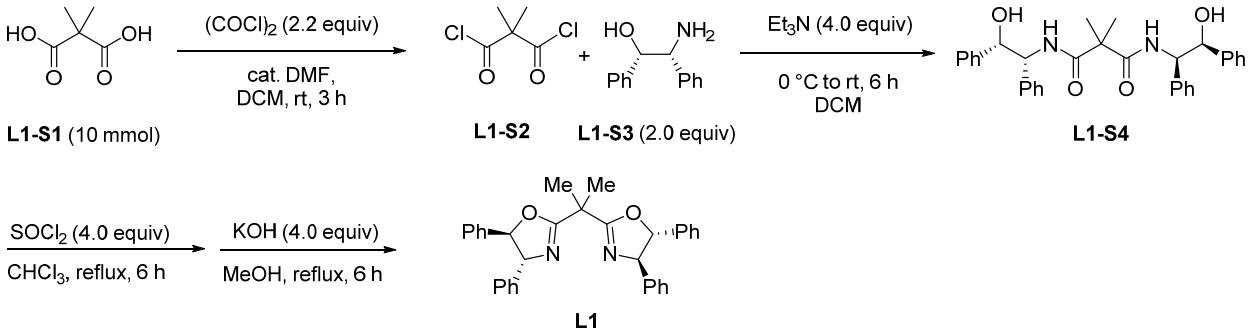
I. General information

General words: NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual 1H and 13C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a Thermo Scientific Q Exactive mass spectrometer (mass analyzer type: Orbitrap). A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 <l PEG200, 2 <l PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100 mL MeOH (HPLC Supra grade, Scharlau, E-Barcelona) as internal standard.

Materials and Methods: Unless otherwise noted, commercial reagents were purchased from Energy-Chemical Limited, J&K, Adamas-beta®, Aladdin, Macklin Reagent, Bidepharm and used directly without further purification. Solvents were purchased in HPLC quality, degassed by purging with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Conversion was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ethanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (300-400 mesh).

II. Preparation of chiral ligands

(*4R,4'R,5R,5'R*)-2,2'-(propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (L1)



L1-S1 (10 mmol) **L1-S2** **L1-S3** (2.0 equiv) **L1-S4**

L1

General procedure of preparation of chiral ligand,[1] a mixture of dimethylmalonic acid **L1-S1** (1.32 g, 10.0 mmol) in dry DCM (20.0 mL) was stirred at room temperature, oxalyl chloride (2.8 g, 22.0 mmol, 2.2 equiv) was added, then 1 drop DMF was added. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to afford the corresponding crude acid chloride, which was directly used for the next step without further purification.

L1-S2 (obtained in previous step) dissolved in dry DCM (10.0 mL) was added dropwise to a solution of chiral (1*S*,2*R*)-2-amino-1,2-diphenylethan-1-ol **L1-S3** (4.26 g, 20.0 mmol) and Et_3N (4.1 g, 40.0 mmol) in dry DCM (40.0 mL) cooled to 0 °C. Then the reaction mixture was allowed warm to room temperature and stirred for 6 h. The mixture was washed with H_2O, dried with Na_2SO_4, filtered and concentrated in vacuo, which was directly used for the next step without further purification.

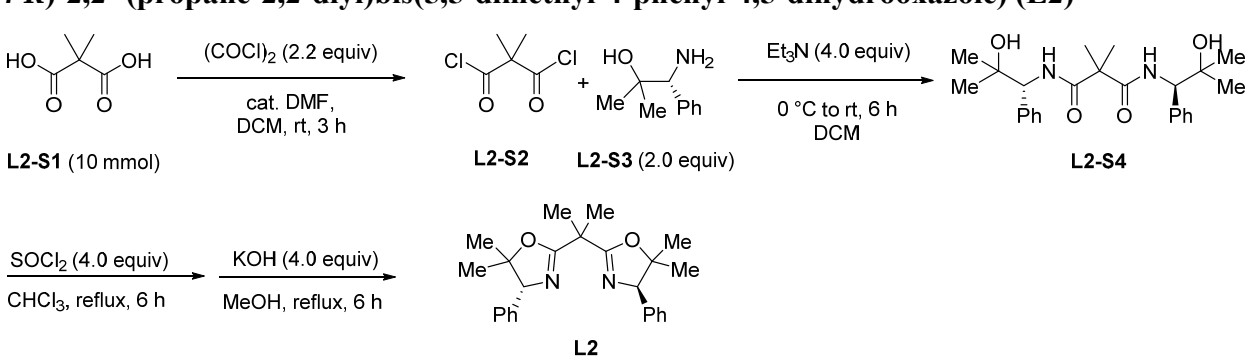
The chiral amide **L1-S4** (5.2 g, 10.0 mmol) was dissolved in $CHCl_3$ (50.0 mL), and the solution was cooled to 0 °C. A solution of $SOCl_2$ (4.8 g, 40.0 mmol, 4.0 equiv) was added dropwise. The reaction mixture was stirred at 70 °C for 6 h, then cooled to room temperature. The reaction mixture was quenched by H_2O, then extracted with DCM. Then solvent was removed under reduced pressure to afford the corresponding crude product, which was directly used for the next step without further purification. Then dissolved in MeOH (40.0 mL), and KOH (2.3 g, 40.0 mmol, 4.0 equiv) was added. The suspension was stirred at reflux for 6 h, When the reaction was complete, H_2O was added, and the mixture was extracted with DCM. The combined organic phase was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE: EtOAc = 6: 1) to afford chiral ligand **L1** as a white solid (3.1 g, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.22 (m, 20H), 5.36 (d, *J* = 7.6 Hz, 2H), 5.16 (d, *J* = 7.6 Hz, 2H), 1.93 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 142.1, 140.5, 128.9, 128.9, 128.5, 127.8, 126.8, 126.0, 89.9, 78.7, 39.5, 25.0.

HRMS (ESI-TOF) Calcd for $C_{33}H_{31}N_2O_2$ $(M+H)^+$ 487.2380. Found 487.2374.

(*4R,4'R*)-2,2'-(propane-2,2-diyl)bis(5,5-dimethyl-4-phenyl-4,5-dihydrooxazole) (L2)



General procedure of preparation of chiral ligand,[2] a mixture of dimethylmalonic acid **L2-S1** (1.32 g, 10.0 mmol, 1.0 equiv) in dry DCM (20.0 mL) was stirred at room temperature, oxalyl chloride (2.8g, 22.0 mmol, 2.2 equiv) was added, then 1 drop DMF was added. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to afford the corresponding crude acid chloride, which was directly used for the next step without further purification.

L2-S2 (obtained in previous step) dissolved in dry DCM (10.0 mL) was added dropwise to a solution of chiral **L2-S3** (4.26 g, 20.0 mmol) and Et_3N (4.1 g, 40.0 mmol) in dry DCM (40.0 mL) cooled to 0 °C. Then the reaction mixture was allowed warm to room temperature and stirred for 6 h. The mixture was washed

with H_2O, dried with Na_2SO_4, filtered and concentrated in vacuo, which was directly used for the next step without further purification.

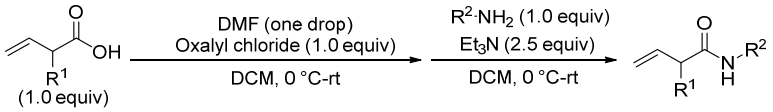
The chiral amide **L2-S4** (5.2 g, 10.0 mmol) was dissolved in $CHCl_3$ (50.0 mL), and the solution was cooled to 0 °C. A solution of $SOCl_2$ (4.8 g, 40.0 mmol, 4.0 equiv) was added dropwise. The reaction mixture was stirred at 70 °C for 6 h, then cooled to room temperature. The reaction mixture was quenched by H_2O, then extracted with DCM. Then solvent was removed under reduced pressure to afford the corresponding crude product, which was directly used for the next step without further purification. Then dissolved in MeOH (40.0 mL), and KOH (2.3 g, 40.0 mmol, 4.0 equiv) was added. The suspension was stirred at reflux for 6 h. When the reaction was complete, H_2O was added, and the mixture was extracted with DCM. The combined organic phase was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (PE: EtOAc = 6: 1) to afford chiral ligand **L2** as a white solid (1.97 g, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.07 (m, 10H), 4.77 (s, 2H), 1.61 (s, 6H), 1.49 (s, 6H), 0.79 (s, 6H).

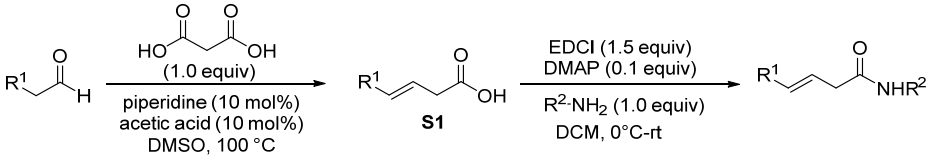
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 139.0, 128.2, 127.5, 127.4, 78.0, 39.0, 29.2, 24.1, 23.8.

HRMS (ESI-TOF) Calcd for $C_{25}H_{31}N_2O_2$ $(M+H)^+$ 391.2380. Found 391.2375.

III.Preparation of olefins and electrophiles



General procedure (A) for preparation of terminal olefins. To a solution of vinylacetic acid (5.0mmol，1.0 equiv) in dry CH_2Cl_2 was added one drop DMF, then oxalyl chloride (1.0 equiv) in dry CH_2Cl_2 was added dropwise to the above solution at 0 ºC. The resulting mixture was stirred at room temperature for 3 h. Then the resulting solution was added dropwise to a solution of amine (1.0 equiv) and Et_3N (2.5 equiv) in dry CH_2Cl_2 at 0 ºC, the mixture was then stirred at room temperature for 3 h. The mixture was diluted with CH_2Cl_2 and washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and purified by flash chromatography to afford the desired olefins.

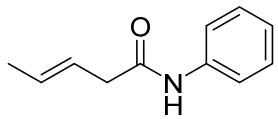


General procedure (B) for preparation of internal olefins. Acid (**S1**) was prepared following the literature procedure. To a solution of aldehyde (10.0 mmol, 1.0 equiv) and malonic acid (2.08 g, 20.0 mmol, 2.0 equiv) in DMSO was added piperidine (85.0 mg, 1.0 mmol, 10 mol%) and acetic acid (60.0 mg, 1.0 mmol, 10 mol%). The resulting mixture was heated to 100 ˚C and stirred for overnight. Then the mixture

was cooled to room temperature, diluted with water and ethyl acetate. The organic phase was washed with brine, dried with anhydrous Na_2SO_4, filtered, and purified by flash chromatography to afford acid (**S1**).

To a solution of β,γ-unsaturated carboxylic acid (5.0 mmol, 1.0 equiv.) in dichloromethane (10.0 mL) were added 1-ethyl-3-(3-(dimethylamino) propyl)-carbodiimide hydrochloride (EDCI) (1.4 g, 7.5 mmol, 1.5 equiv), DMAP (61.0 mg, 0.50 mmol, 0.1 equiv) and amine (5.5 mmol, 1.1 equiv). The reaction was stirred at room temperature for 12 h. After completion of the reaction, DCM (50.0 mL) was added to the mixture and washed with 1% HCl (10.0 mL) and brine (20.0 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/PE mixture as eluent.

(*E*)-*N*-phenylpent-3-enamide (1a)



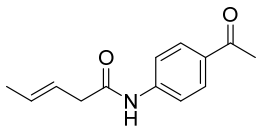
Following the GP-B, **1a** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.77 g, 88% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.43 (m, 2H), 7.32 (s, 1H), 7.25 – 7.23 (m, 2H), 7.04 – 7.02 (m, 1H), 5.69 – 5.65 (m, 1H), 5.59 – 5.54 (m, 1H), 3.03 (d, *J* = 7.1 Hz, 2H), 1.71 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.6, 137.9, 132.1, 129.1, 124.5, 123.6, 119.9, 41.8, 18.2.

HRMS (ESI-TOF) Calcd for $C_{11}H_{14}NO$ $(M+H)^+$ 176.1070. Found 176.1069.

(*E*)-*N*-(4-acetylphenyl)pent-3-enamide (1b)



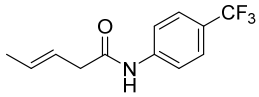
Following the GP-B, **1b** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.79 g, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 5.81 – 5.67 (m, 1H), 5.67 – 5.57 (m, 1H), 3.12 (d, *J* = 6.9 Hz, 2H), 2.55 (s, 3H), 1.74 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.2, 170.1, 142.4, 132.8, 131.9, 129.7, 123.0, 118.9, 41.6, 26.5, 18.1.

HRMS (ESI-TOF) Calcd for $C_{13}H_{16}NO_2$ $(M+H)^+$ 218.1176. Found 218.1174.

(*E*)-*N*-(4-(trifluoromethyl)phenyl)pent-3-enamide (1c)



Following the GP-B, **1c** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.95 g, 78% yield).

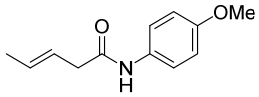
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.65 – 5.58 (m, 1H), 5.55 – 5.47 (m, 1H), 3.02 (d, *J* = 6.4 Hz, 2H), 1.72 – 1.56 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 141.0, 132.4, 128.3, 126.3 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.7 Hz), 123.1, 119.5, 41.7, 18.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.14 (s, 3F).

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}F_3NO$ $(M+H)^+$ 244.0944. Found 244.0941.

(*E*)-*N*-(4-methoxyphenyl)pent-3-enamide (1d)



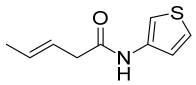
Following the GP-B, **1d** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.71 g, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 3H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.73 – 5.60 (m, 1H), 5.60 – 5.50 (m, 1H), 3.71 (s, 3H), 3.00 (d, *J* = 6.9 Hz, 2H), 1.69 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 156.6, 131.8, 131.0, 123.7, 121.9, 114.2, 55.6, 41.5, 18.2.

HRMS (ESI-TOF) Calcd for $C_{12}H_{16}NO_2$ $(M+H)^+$ 206.1176. Found 206.1175.

(*E*)-*N*-(thiophen-3-yl)pent-3-enamide (1e)



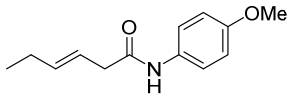
Following the GP-B, **1e** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.62 g, 71% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.47 – 7.46 (m, 1H), 7.11 – 7.10 (m, 1H), 6.95 – 6.94 (m, 1H), 5.64 – 5.55 (m, 1H), 5.55 – 5.43 (m, 1H), 2.99 (d, *J* = 6.9 Hz, 2H), 1.64 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 135.7, 131.3, 124.4, 123.4, 121.3, 110.4, 40.9, 18.1.

HRMS (ESI-TOF) Calcd for $C_9H_{12}NOS$ $(M+H)^+$ 182.0634. Found 182.0633.

(*E*)-*N*-(4-methoxyphenyl)hex-3-enamide (1f)



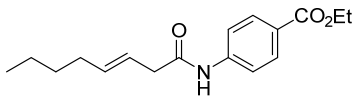
Following the GP-B, **1f** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.75 g, 68% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 5.80 – 5.65 (m, 1H), 5.65 – 5.51 (m, 1H), 3.76 (s, 3H), 3.06 (d, *J* = 7.0 Hz, 2H), 2.12 – 2.05 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 156.4, 138.3, 131.1, 121.9, 121.6, 114.1, 55.5, 41.3, 25.7, 13.6.

HRMS (ESI-TOF) Calcd for $C_{13}H_{18}NO_2$ $(M+H)^+$ 220.1332. Found 220.1330.

Ethyl (*E*)-4-(oct-3-enamido)benzoate (1g)



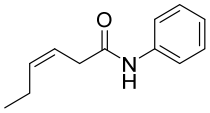
Following the GP-B, **1g** was purified by flash chromatography (PE/EA = 5: 1), white solid (1.0 g, 72% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.60 (m, 3H), 5.79 – 5.75 (m, 1H), 5.66 – 5.61 (m, 1H), 4.40 – 4.36 (q, *J* = 7.1 Hz, 2H), 3.15 (d, *J* = 7.1 Hz, 2H), 2.14 (q, *J* = 7.1 Hz, 2H), 1.46 – 1.34 (m, 7H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.8, 166.3, 142.0, 138.1, 130.9, 126.1, 122.0, 118.7, 61.0, 41.9, 32.4, 31.4, 22.4, 14.5, 14.0.

HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NO_3$ $(M+H)^+$ 290.1751. Found 290.1752.

(*Z*)-*N*-phenylhex-3-enamide (1h)



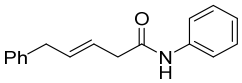
Following the GP-A, **1h** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.83 g, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.03 – 6.99 (m, 1H), 5.80 – 5.61 (m, 1H), 5.61 – 5.47 (m, 1H), 3.09 (d, *J* = 7.5 Hz, 2H), 2.07 – 2.00 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*)) δ 169.4, 137.9, 137.5, 129.0, 124.4, 120.9, 119.9, 36.1, 20.8, 14.0.

HRMS (ESI-TOF) Calcd for $C_{12}H_{16}NO$ $(M+H)^+$ 190.1227. Found 190.1226.

(*E*)-*N*,5-diphenylpent-3-enamide (1l)



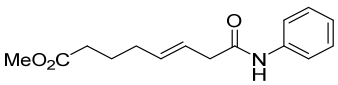
Following the GP-B, **1l** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.76 g, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.38 – 7.36 (m, 2H), 7.23 – 7.17 (m, 4H), 7.14 – 7.09 (m, 3H), 7.01 – 6.97 (m, 1H), 5.85 – 5.70 (m, 1H), 5.64 – 5.56 (m, 1H), 3.32 (d, *J* = 6.8 Hz, 2H), 3.02 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 140.0, 137.9, 135.6, 129.0, 128.7, 128.6, 126.4, 124.4, 123.9, 119.9, 41.4, 39.1.

HRMS (ESI-TOF) Calcd for $C_{17}H_{18}NO$ $(M+H)^+$ 252.1383. Found 252.1381.

Methyl (*E*)-8-oxo-8-(phenylamino)oct-5-enoate (1j)



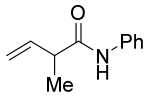
Following the GP-B, **1j** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.81 g, 62% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 3H), 7.32 – 7.26 (m, 2H), 7.11 – 7.09 (m, 1H), 5.70 – 5.62 (m, 2H), 3.67 (s, 3H), 3.11 (d, *J* = 5.4 Hz, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.15 – 2.13 (m, 2H), 1.79 – 1.74 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 169.4, 138.0, 135.8, 129.1, 124.4, 123.6, 120.0, 51.7, 41.7, 33.5, 32.0, 24.3.

HRMS (ESI-TOF) Calcd for $C_{15}H_{20}NO_3$ $(M+H)^+$ 262.1438. Found 262.1435.

2-Ethyl-*N*-phenylbut-3-enamide (1l)

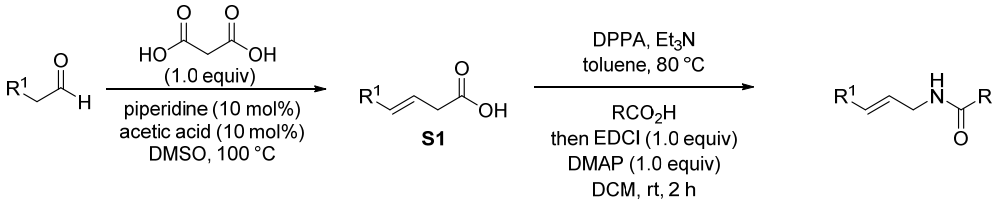


Following the GP-A, **1l** was purified by flash chromatography (PE/EA = 5: 1), white solid (0.73 g, 77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) 7.55 – 7.47 (m, 2H), 7.41 – 7.27 (m, 3H), 7.14 – 7.06 (m, 1H), 6.10 – 5.89 (m, 1H), 5.45 – 5.15 (m, 2H), 3.21 – 3.09 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) 172.2, 138.2, 138.0, 129.0, 124.4, 119.9, 117.6, 46.5, 16.8.

HRMS (ESI-TOF) Calcd for $C_{12}H_{14}NO$ $(M+H)^+$ 176.1070. Found 176.1073.

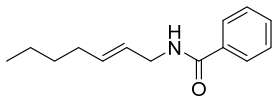


General procedure (C) for preparation of γ-substituted allylic amide.[3] To a 250-mL round bottomed flask was charged with malonic acid (2.1 g, 20.0 mmol, 2.0 equiv), piperidine (85.0 mg, 1.0 mmol, 10 mol%), acetic acid (60.0 mg, 1.0 mmol, 10 mol%), and aldehyde hydrocarbon (10.0 mmol, 1.0 equiv) in DMSO (20.0 mL). After the reaction mixture was stirred at 40 °C for 2 h, the solution was heated in an oil bath at 100 °C. A rapid evolution of carbon dioxide was observed. Heating was maintained until the evolution of carbon dioxide ceased. The solution was cooled to room temperature, poured into cold water (50.0 mL), and extracted with diethyl ether (3 × 20.0 mL). The combined organic phase was washed with water (30.0 mL), brine (30.0 mL), and then dried over anhydrous $MgSO_4$, After removal of the solvent, the crude β,γ-unsaturated acid **S1**was used for the next step without further purification.

To a solution of the crude acid **S1** in toluene (30.0 mL) was slowly added diphenylphosphoryl azide (DPPA) (2.75 g, 10.0 mmol) followed by addition of Et_3N (1.12 g, 11.0 mmol). The resulting solution was stirred at 80 °C for 2 h. After cooling to room temperature, 1 M NaOH (20.0 mL) was added and the mixture was allowed to stir at rt for 2 h. The organic phase was then separated and concentrated. The residue was dissolved in CH_2Cl_2 (20.0 mL) followed by sequential addition of RCO_2H (10.0 mmol), EDCI (1.92 g, 10.0 mmol, 1.0 equiv) and DMAP (1.22 g, 1.0 mmol, 1.0 equiv) at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stir at this temperature for additional 2 h. The reaction was then quenched by saturated aq. $NaHCO_3$ (50 mL) and extracted with diethyl ether twice (2 × 50.0 mL). The combined

ethereal solution was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc as the eluent to afford the corresponding γ-substituted allylic amide. The yield is based on RCO_2H.

(*E*)-*N*-(hept-2-en-1-yl)benzamide (1n)



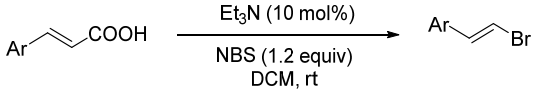
Following the GP-C, **1n** was purified by flash chromatography (PE/EA = 5: 1), white solid (1.52 g, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.71 (m, 2H), 7.52 – 7.45 (m, 1H), 7.47 – 7.39 (m, 2H), 6.20 (s, 1H), 5.73 – 5.65 (m, 1H), 5.59 – 5.47 (m, 1H), 4.01 (t, *J* = 5.8 Hz, 2H), 2.04 (q, *J* = 7.0 Hz, 2H), 1.39 – 1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 134.8, 134.4, 131.5, 128.7, 127.0, 125.5, 42.1, 32.1, 31.4, 22.3, 14.0.

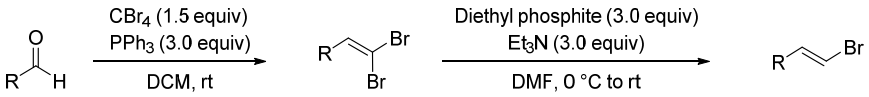
HRMS (ESI-TOF) Calcd for $C_{14}H_{20}NO$ $(M+H)^+$ 218.1540. Found 215.1538.

General procedure D for the preparation of *E*-alkenyl bromides



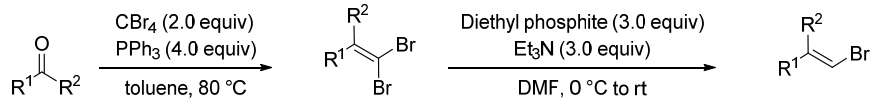
Following literature procedure,[4] a round-bottom flask was charged with cinnamic acid (10 mmol, 1.0 equiv), catalytic amounts of Et_3N (1.0 mmol, 101.0 mg) and DCM (50.0 mL). The mixture was stirred at room temperature for 10 minutes before the addition of NBS (4.3 g, 24.0 mmol, 1.2 equiv). Then, the mixture was stirred for 5 min at room temperature and monitored by TLC analysis. After total conversion of the substrate, the solvent was evaporated and the alkenyl bromide product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 100: 1).

General procedure E for the preparation of *E*-alkenyl bromides from aldehydes and ketones



Following literature procedure,[4] to a flame-dried round-bottom flask was added aldehyde (10.0 mmol, 1.0 equiv), CBr_4 (15.0 mmol, 1.5 equiv), and CH_2Cl_2 (40.0 mL). The flask was cooled to 0 °C, after which a solution of PPh_3 (30.0 mmol, 3.0 equiv) in CH_2Cl_2 (30.0 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C for 1 h. About half the volume of CH_2Cl_2 was then removed under reduced pressure. Hexane (50.0 mL) was added, and phosphine oxide was precipitated out. After filtration and evaporation of the solvent, the residue was dissolved in hexane (30.0 mL) which led to further precipitation. Filtration and evaporation of the solvent afforded the crude dibromide which was directly used in the next step.

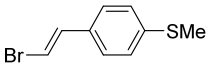
To a solution of the crude dibromide (~ 5.0 mmol, 1 equiv) and NEt_3 (15.0 mmol, 3.0 equiv) in DMF (5 mL) was added diethyl phosphite (15.0 mmol, 3.0 equiv). The solution was stirred overnight at room temperature. Water (15.0 mL) was added to the mixture, which was extracted with hexane (2 × 25.0 mL). The combined organic phases were washed with an aqueous solution of HCl (1 M, 10.0 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by silica gel chromatography.



Following literature procedure,[4] A Schlenk flask was charged with ketone (5.0 mmol), CBr_4 (10.0 mmol, 2.0 equiv) and PPh_3 (20.0 mmol, 4.0 equiv). After degassing and refilling with N_2 twice, toluene (35.0 mL) was added through syringe. The flask was sealed and heated at 80 °C overnight. After cooling to room temperature, the mixture was filtered through a pad of silica gel and washed with hexanes. The solvent was then under reduced pressure and the product was purified by silica gel chromatography.

To a solution of the crude dibromide (~ 5.0 mmol, 1 equiv) and NEt_3 (15.0 mmol, 3.0 equiv) in DMF (5 mL) was added diethyl phosphite (15.0 mmol, 3.0 equiv). The solution was stirred overnight at room temperature. Water (15.0 mL) was added to the mixture, which was extracted with hexane (2 × 25.0 mL). The combined organic phases were washed with an aqueous solution of HCl (1 M, 10.0 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by silica gel chromatography.

(*E*)-(4-(2-bromovinyl)phenyl)(methyl)sulfane (2c)



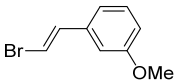
Following the GP-E, **2c** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.07 (m, 4H), 6.96 (d, *J* = 14.0 Hz, 1H), 6.64 (d, *J* = 14.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 136.6, 132.8, 126.61, 126.56, 105.9, 15.7.

HRMS (ESI-TOF) Calcd for $(M+H)^+$ $C_9H_{10}BrS$ 228.9681. Found 228.9673.

(*E*)-1-(2-bromovinyl)-2-methoxybenzene (2i)



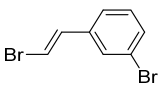
Following the GP-E, **2i** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.01 (m, 3H), 6.81 – 6.74 (m, 3H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.6, 133.1, 129.4, 128.0, 124.8, 120.8, 111.0, 108.0, 55.4.

HRMS (ESI-TOF) Calcd for $(M+H)^+$ $C_9H_{10}BrO$ 219.9910. Found 219.9907.

(*E*)-1-bromo-3-(2-bromovinyl)benzene (2j)



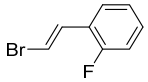
Following the GP-D, **2j** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.37 (m, 2H), 7.23 – 7.17 (m, 2H), 7.03 (d, *J* = 14.0 Hz, 1H), 6.80 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.9, 135.8, 131.2, 130.3, 129.0, 124.7, 122.9, 108.2.

HRMS (ESI-TOF) Calcd for $(M+H)^+$ $C_8H_7Br^{81}Br$ 262.8889. Found 262.8885.

(*E*)-1-(2-bromovinyl)-2-fluorobenzene (2l)



Following the GP-E, **2l** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

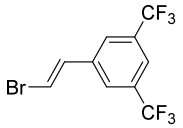
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.16 (m, 2H), 7.11 (d, *J* = 14.0 Hz, 1H), 7.05 – 6.94 (m, 2H), 6.85 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9 (d, *J* = 250.7 Hz), 130.6 (d, *J* = 2.4 Hz), 129.7 (d, *J* = 8.5 Hz), 128.1 (d, *J* = 3.4 Hz), 124.5 (d, *J* = 3.6 Hz), 123.8 (d, *J* = 12.6 Hz), 116.2 (d, *J* = 21.9 Hz), 109.8 (d, *J* = 8.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.25 - -116.19 (m, 1F).

HRMS (ESI-TOF) Calcd for $(M+H)^+$ C_8H_7BrF 200.9710. Found 200.9706.

(*E*)-1-(2-bromovinyl)-3,5-bis(trifluoromethyl)benzene (2m)



Following the GP-E, **2m** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

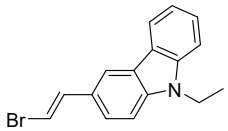
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.63 (s, 2H), 7.08 (d, *J* = 14.0 Hz, 1H), 6.93 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.0, 134.7, 132.5 (q, *J* = 33.4 Hz), 126.1 (d, *J* = 3.3 Hz), 123.2 (q, *J* = 272.7 Hz), 121.8 (p, *J* = 3.9 Hz), 111.3.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -63.2 (s, 6F).

HRMS (ESI-TOF) Calcd for $(M+H)^+$ $C_{10}H_6BrF_6$ 318.9552. Found 318.9550.

(*E*)-3-(2-bromovinyl)-9-ethyl-9*H*-carbazole (2p)



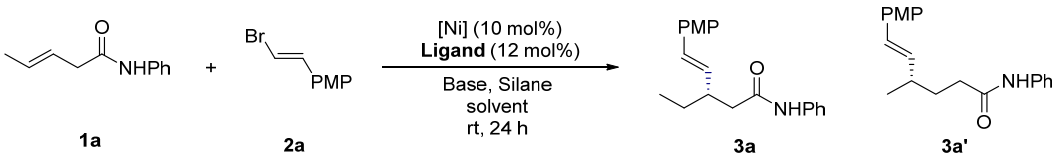
Following the GP-E, **2p** was purified by flash chromatography (PE), white solid (1.52 g, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.87 (s, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.10 (m, 5H), 6.61 (d, *J* = 13.9, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.5, 139.9, 138.0, 127.2, 126.1, 123.9, 123.3, 122.9, 120.6, 119.3, 118.5, 108.82, 108.80, 103.3, 37.7, 13.9.

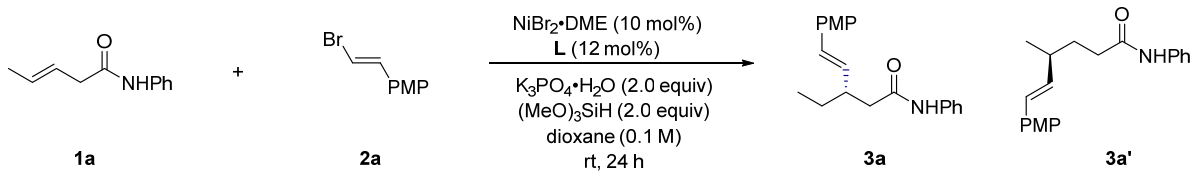
HRMS (ESI-TOF) Calcd for $(M+H)^+$ $C_{16}H_{15}BrN$ 300.0383. Found 300.0378.

IV. Evaluation of reaction parameters

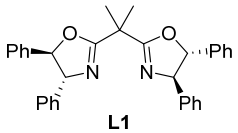


General procedure: In a nitrogen-filled glovebox, [Ni] (10 mol%) and **Ligand** (12 mol%) were dissolved in solvent in Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 15 min, then alkene **1a** (0.1 mmol, 1.0 equiv), alkenyl bromides **2a**, and base were sequentially added, then silane was added dropwise. The resulting mixture was stirred at room temperature for 24 h. Then the reaction mixture was diluted with saturated NH_4Cl (aqueous solution, 0.5 mL) and EtOAc (3.0 mL). Dodecane (23.0 μL, 0.1 mmol) was added as an internal standard and a small aliquot of the organic phase was removed for GC analysis to confirm yield and regio-isomeric ratio. For the remaining mixture, the aqueous phase was extracted with EtOAc (2 × 3.0 mL). The combined organic phase was dried over Na_2SO_4, and the volatiles were removed to afford the crude product. Then, the mixture was purified by PTLC and the enantiomeric excess was determined by HPLC analysis.

Table S1. Effect of ligands[a]

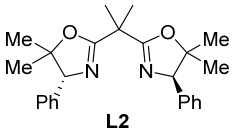


1a **2a** **3a** **3a'**



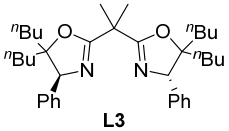
L1

50% yield, 79% ee
rr = 13: 1



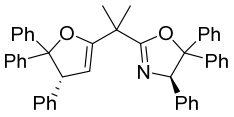
L2

26% yield, 2% ee
rr = 6: 1



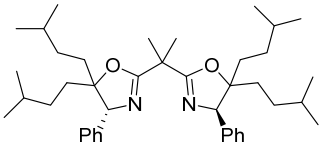
L3

60% yield, -70% ee
rr = 12: 1



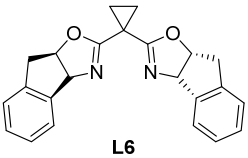
L4

76% yield, 69% ee
rr = 13: 1



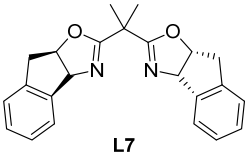
L5

68% yield, 63% ee
rr = 12: 1



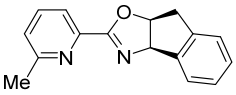
L6

14% yield, 11% ee
rr = 6: 1



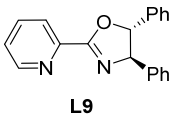
L7

trace



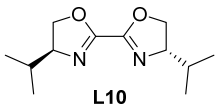
L8

23% yield, 11% ee
rr = 6: 1



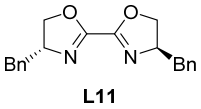
L9

36% yield, 15% ee
rr = 6: 1



L10

30% yield, 2% ee
rr = 5: 1

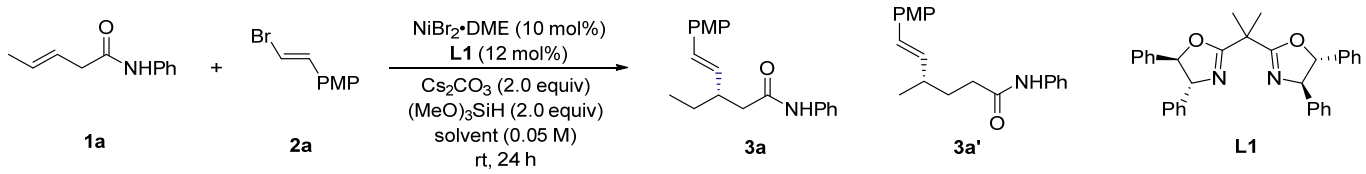


L11

21% yield, 30% ee
rr = 4: 1

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (0.01 mmol), ligand (0.012 mmol), K_3PO_4·H_2O (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in dioxane (1.0 mL) under N_2 atmosphere at room temperature for 24 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

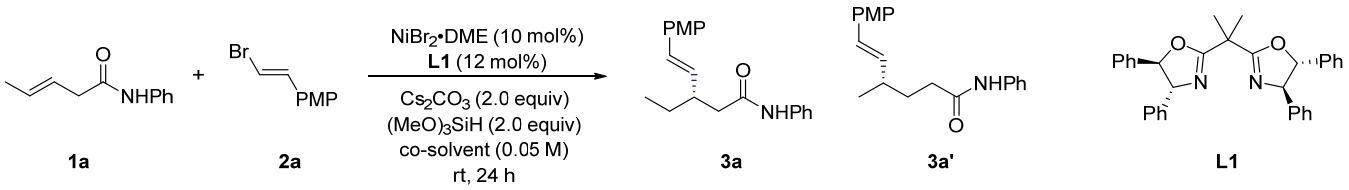
Table S2. Effect of solvent



entry	solvent	yield of **3a** (ee)[a]	rr[b]
1	THF	40% yield (76% ee)	7: 1
2	2-Me-THF	60% yield (76% ee)	7: 1
3	THP	63% yield (69% ee)	7: 1
4	1,3-dioxolane	36% yield (80% ee)	8: 1
5	Et_2O	32% yield (60% ee)	5: 1
6	DME	45% yield (81% ee)	7: 1
7	Diglyme	47% yield (80% ee)	7: 1
8	$PhCF_3$	trace	--
9	DMA	trace	--
10	DMSO	trace	--
11	Hexane	trace	--

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (10 mol%), **L1** (12 mol%), Cs_2CO_3 (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in dioxane (2.0 mL) under N_2 atmosphere at room temperature for 24 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

Table S3. Effect of co-solvent

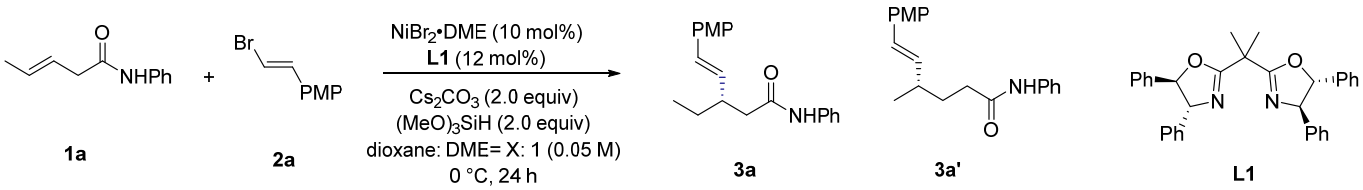


1a 2a 3a 3a' L1

entry	co-solvent	yield of **3a** (ee)[a]	rr[b]
1	dioxane: THF= 3: 1	45% yield (82% ee)	10: 1
2	dioxane: 2-Me-THF= 3: 1	75% yield (83% ee)	11: 1
3	dioxane: THP= 3: 1	72% yield (82% ee)	10: 1
4	dioxane: Et_2O= 3: 1	52% yield (82% ee)	11: 1
5	dioxane: 1,3-dioxolane= 3: 1	72% yield (82% ee)	11: 1
6	**dioxane: DME= 3: 1**	**71% yield (85% ee)**	**10: 1**
7	dioxane: diglyme= 3: 1	76% yield (83% ee)	10: 1
8	dioxane: triethyleneglycol dimethyl ether= 3: 1	67% yield (82% ee)	9: 1
9	dioxane: isopropyl ether= 3: 1	58% yield (84% ee)	11: 1
10	dioxane: ethylene glycol diethyl ether= 3: 1	73% yield (82% ee)	10: 1
11	dioxane: tetraethylene glycol dimethyl ether= 3: 1	43% yield (79% ee)	12: 1
12	dioxane: $PhCF_3$= 3: 1	55% yield (82% ee)	12: 1
13	dioxane: DMA= 3: 1	32% yield (74% ee)	8: 1
14	dioxane: toluene= 3: 1	40% yield (82% ee)	12: 1
15	dioxane: ACN = 3: 1	10% yield (33% ee)	7: 1
16	dioxane: *t*-BuOH= 3: 1	73% yield (79% ee)	11: 1
17	dioxane: DCE= 3: 1	31% yield (64% ee)	10: 1
18	dioxane: DCM= 3: 1	trace	--
19	dioxane: hexane= 3: 1	50% yield (85% ee)	11: 1

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (0.01 mmol), **L1** (0.012 mmol), Cs_2CO_3 (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in co-solvent (3: 1, 2.0 mL) under N_2 atmosphere at room temperature for 24 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

Table S4. Effect of co-solvent ratio

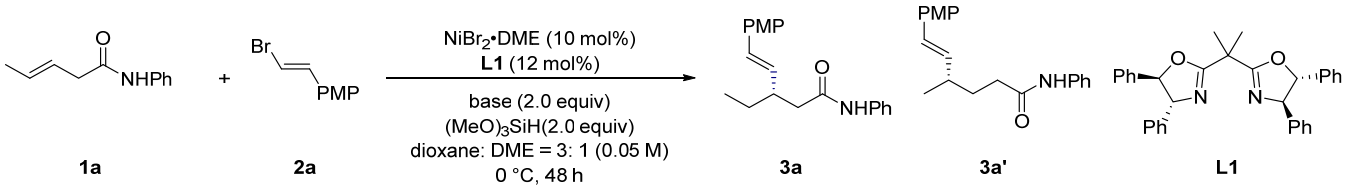


1a 2a 3a 3a' L1

Entry	ratio of co-solvent	yield of **3a** (ee)[a]	rr[b]
1	dioxane: DME= 1: 1	45% yield (88% ee)	10: 1
2	**dioxane: DME= 3: 1**	**55% yield (90% ee)**	**12: 1**
3	dioxane: DME= 6: 1	36% yield (90% ee)	12: 1
4	dioxane: DME= 9: 1	21% yield (84% ee)	16: 1

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (0.01 mmol), **L1** (0.012 mmol), Cs_2CO_3 (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in dioxane: DME (X: 1, 2.0 mL) under N_2 atmosphere at 0 °C for 24 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

Table S5. Effect of base

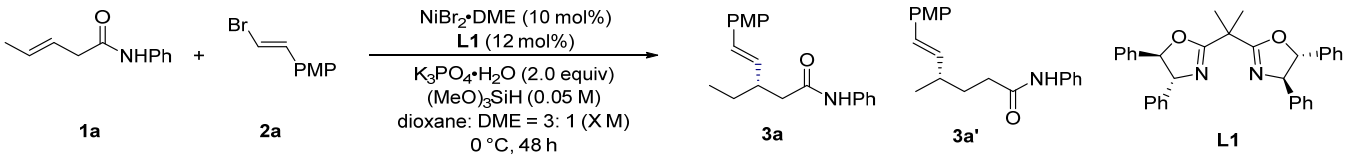


1a 2a 3a 3a' L1

entry	base	yield of **3a** (ee)[a]	rr[b]
1	Na_2CO_3	71% yield (85% ee)	10: 1
2	$NaHCO_3$	22% yield (84% ee)	9: 1
3	K_2CO_3	24% yield (86% ee)	12: 1
4	$KHCO_3$	30% yield (86% ee)	11: 1
5	**K_3PO_4·H_2O**	**84% yield (91% ee)**	**10: 1**

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (0.01 mmol), **L1** (0.012 mmol), base (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in dioxane: DME (3: 1, 2.0 mL) under N_2 atmosphere at 0 °C for 48 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

Table S6. Effect of concentration

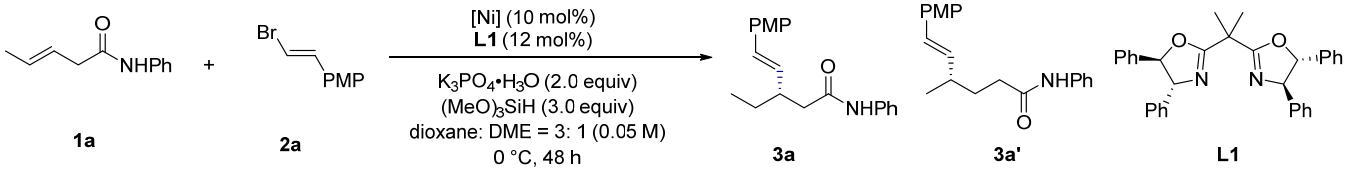


1a 2a 3a 3a' L1

entry	concentration	yield of **3a** (ee)[a]	rr[b]
1	0.1 M	80% yield (88% ee)	9: 1
2	0.067 M	80% yield (90% ee)	11: 1
3	**0.05 M**	**84% yield (91% ee)**	**10: 1**
4	0.04 M	67% yield (90% ee)	12: 1
5	0.033 M	60% yield (90% ee)	13: 1

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.2 mmol), $NiBr_2$·DME (0.01 mmol), **L1** (0.012 mmol), K_3PO_4·H_2O (0.2 mmol), $(MeO)_3SiH$ (0.2 mmol) in dioxane: DME (3: 1, X M) under N_2 atmosphere at 0 °C for 48 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

Table S7. Effect of precatalyst



1a 2a 3a 3a' L1

entry	precatalyst	yield of **3a** (ee)[a]	rr[b]
1	$NiCl_2$·glyme	84% yield (91% ee)	10: 1
2	$NiBr_2$	trace	--
3	$NiBr_2$·diglyme	79% yield (90% ee)	10: 1
4	$Ni(OTf)_2$	n.d.	--
5	$Ni(OAc)_2$	n.d.	--
6	**$Ni(COD)_2$**	**84% yield (92% ee)**	**10: 1**

[a]The reaction was conducted using **1a** (0.1 mmol), **2a** (0.25 mmol), [Ni] (0.01 mmol), **L1** (0.012 mmol), K_3PO_4·H_2O (0.2 mmol), $(MeO)_3SiH$ (0.3 mmol) in dioxane: DME (3: 1, 2.0 mL) under N_2 atmosphere at 0 °C for 48 h. Yields were determined by GC using *n*-dodecane as the internal standard. Enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. [b]rr = ratio of regioisomers (**3a**: **3a'**) was determined by GC.

V. General procedures for enantioselective hydroalkenylations of alkenes

Method A: In a nitrogen-filled glovebox, $Ni(COD)_2$ (5.5 mg, 0.02 mmol, 10 mol%) and **L1** (12.0 mg, 0.024 mmol, 12 mol%) were dissolved in co-solvent (dioxane: DME = 3:1, 4.0 mL) in a 10.0 mL Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 15 min, then alkene (0.2 mmol, 1.0 equiv), alkenyl bromides (0.5 mmol, 2.5 equiv), K_3PO_4•H_2O (92.0 mg, 0.4 mmol, 2.0 equiv) were sequentially added. The mixture was cooled to 0 ℃ before $(MeO)_3SiH$ (73.2 mg, 0.6 mmol, 3.0 equiv) was added dropwise and stirred at 0 ℃ for 48 h. The mixture was quenched with H_2O (2.0 mL) and extracted with ethyl acetate (20.0 mL), then filtered through a pad of silica gel. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, ratio of main product and other isomers was determined by GC. The crude mixture was purified by flash column chromatography on silica gel to obtain the desired product.

Method B: In a nitrogen-filled glovebox, $NiBr_2$•DME (6.2 mg, 0.02 mmol, 10 mol%) and **L1** (12.0 mg, 0.024 mmol, 12 mol%) were dissolved in dioxane (4.0 mL) in Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 15 min, then alkene (0.2 mmol, 1.0 equiv), alkenyl bromides (0.5 mmol, 2.5 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), NaI (30.0 mg, 0.2 mmol, 1.0 equiv) were sequentially added, then HBpin (90.0 mg, 0.7 mmol, 3.5 equiv) was added dropwise. The resulting mixture was stirred at room temperature for 48 h. The mixture was quenched H_2O (2.0 mL) and extracted with ethyl acetate (20.0 mL), then filtered through a pad of silica gel. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, ratio of main product and other isomers was determined by GC. The crude mixture was purified by flash column chromatography on silica gel to obtain the desired product.

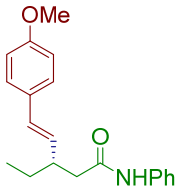
Method C: In a nitrogen-filled glovebox, $NiBr_2$•DME (6.2 mg, 0.02 mmol, 10 mol%) and **L1** (12.0 mg, 0.024 mmol, 12 mol%) were dissolved in dioxane (4.0 mL) in Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 15 min, then alkene (0.2 mmol, 1.0 equiv), alkenyl bromides (0.5 mmol, 2.5 equiv), NaI (6.0 mg, 0.04 mmol, 0.2 equiv), K_3PO_4•H_2O (92.0 mg, 0.4 mmol, 2.0 equiv) were sequentially added, then $(MeO)_3SiH$ (73.2 mg, 0.6 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at room temperature for 24 h. The mixture was quenched with H_2O (2.0 mL) and extracted with ethyl acetate (20.0 mL), then filtered through a pad of silica gel. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, ratio of main product and other isomers was determined by GC. The crude mixture was purified by flash column chromatography on silica gel to obtain the desired product.

Method D: In a nitrogen-filled glovebox, $NiBr_2$•DME (6.2 mg, 0.02 mmol, 10 mol%) and **L1** (12.0 mg, 0.024 mmol, 12 mol%) were dissolved in dioxane (4.0 mL) in Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 10 min, then alkene (0.4 mmol, 2.0 equiv), alkenyl bromides (0.2 mmol, 1.0 equiv), NaI (15.0 mg, 0.1 mmol, 0.5 equiv), KCl (7.5 mg, 0.1

mmol, 0.5 equiv), CsF (60.8 mg, 0.4 mmol, 2.0 equiv) were sequentially added, then HBpin (90.0 mg, 0.7 mmol, 3.5 equiv) was added dropwise. The resulting mixture was stirred at room temperature for 24 h. The mixture was quenched with H_2O (2.0 mL) and extracted with ethyl acetate (20.0 mL), then filtered through a pad of silica gel. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, ratio of main product and other isomers was determined by GC. The crude mixture was purified by flash column chromatography on silica gel to obtain the desired product.

VI. Characterization of products

(*S*,*E*)-3-Ethyl-5-(4-methoxyphenyl)-*N*-phenylpent-4-enamide (3a)



3a

Following **method A**, **3a** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (48.8 mg, 79% yield, 92% ee). rr = 10: 1.

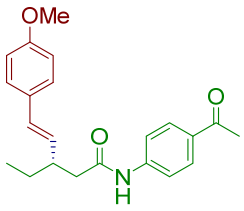
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.35 (m, 2H), 7.35 – 7.19 (m, 5H), 7.08 – 7.04 (m, 1H), 6.89 – 6.69 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.91 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.78 (s, 3H), 2.79 – 2.57 (m, 1H), 2.48 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.38 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.65 – 1.55 (m, 1H), 1.49 – 1.38 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 159.1, 137.9, 130.8, 130.7, 130.1, 129.1, 127.4, 124.4, 120.1, 114.1, 55.4, 43.9, 42.1, 28.2, 11.9.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO_2$ $(M+H)^+$ 310.1802. Found 310.1799.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 14.8 min (major) and 17.7min (minor).

(*S*,*E*)-*N*-(4-acetylphenyl)-3-ethyl-5-(4-methoxyphenyl)pent-4-enamide (3b)



3b

Following **method A**, **3b** was obtained as white solid after flash chromatography (PE: EtOAc = 3: 1) (49.8 mg, 71% yield, 90% ee). rr = 12: 1.

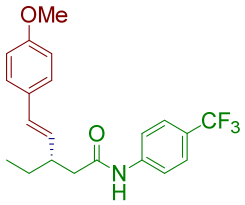
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.64 – 7.48 (m, 3H), 7.31– 7.29 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 5.94 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.82 (s, 3H), 2.69 – 2.61 (m, 1H), 2.61 – 2.52 (m, 4H), 2.46 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.68 – 1.59 (m, 1H), 1.54 – 1.44 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.0, 170.6, 159.2, 142.3, 133.0, 131.1, 130.4, 129.8, 128.9, 127.4, 119.0, 114.2, 55.4, 44.0, 42.0, 28.2, 26.6, 11.9.

HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_3$ $(M+H)^+$ 352.1907. Found 352.1908.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 17.6 min (major) and 18.5 min (minor).

(*S*,*E*)-3-Ethyl-5-(4-methoxyphenyl)-*N*-(4-(trifluoromethyl)phenyl)pent-4-enamide (3c)



3c

Following **method A**, **3c** was obtained as white solid after flash chromatography (PE: EtOAc = 8: 1) (56.5 mg, 75% yield, 91% ee). rr = 10: 1.

^{1}H NMR (400 MHz, Chloroform-*d***)** δ 7.54 (s, 1H), 7.52 – 7.42 (m, 4H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.82 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.71 (s, 3H), 2.62 – 2.54 (m, 1H), 2.44 (dd, *J* = 14.4, 5.5 Hz, 1H), 2.33 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.57 – 1.47 (m, 1H), 1.43 – 1.32 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

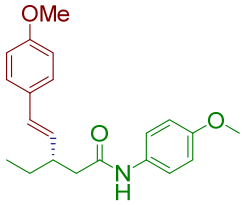
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 159.2, 141.0, 132.5, 131.1, 130.4, 129.9, 127.4, 126.3 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.7 Hz), 119.6, 114.1, 55.4, 43.9, 42.1, 28.2, 11.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.1 (s, 3F).

HRMS (ESI-TOF) Calcd for $C_{21}H_{23}F_3NO_2$ $(M+H)^+$ 378.1676. Found 378.1677.

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 8.9 min (major) and 10.3 min (minor).

(*S*,*E*)-3-Ethyl-*N*,5-bis(4-methoxyphenyl)pent-4-enamide (3d)



3d

Following **method A**, **3d** was obtained as white solid after flash chromatography (PE: EtOAc= 3: 1) (49.5 mg, 73% yield, 90% ee). rr = 10: 1.

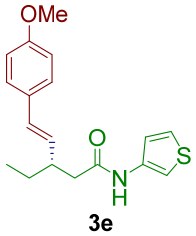
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (s, 1H), 7.26 – 7.24 (m, 2H), 7.20 – 7.18 (m, 2H), 6.80 – 6.67 (m, 4H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.83 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.62 – 2.53 (m, 1H), 2.39 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.29 (dd, *J* = 14.2, 8.4 Hz, 1H), 1.57 – 1.47 (m, 1H), 1.40 –1.29 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 159.1, 156.5, 131.0, 130.8, 130.7, 130.2, 127.4, 122.1, 114.2, 114.1, 55.6, 55.4, 43.7, 42.1, 28.2, 11.9.

HRMS (ESI-TOF) Calcd for $C_{21}H_{26}NO_3$ $(M+H)^+$ 340.1907. Found 340.1907.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 85/15, flow rate = 1 mL/min, detection at 254 nm) retention time = 22.2 min (major) and 25.0 min (minor).

(*S*,*E*)-3-Ethyl-5-(4-methoxyphenyl)-*N*-(thiophen-3-yl)pent-4-enamide (3e)



3e

Following **method A**, **3e** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (44.1 mg, 70% yield, 92% ee). rr = 11: 1.

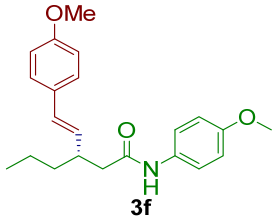
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.44 – 7.43 (m, 1H), 7.19 – 7.17 (m, 2H), 7.09 – 7.07 (m, 1H), 6.85 – 6.83 (m, 1H), 6.76– 6.73 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.71 (s, 3H), 2.62 – 2,53 (m, 1H), 2.38 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.30 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.54 – 1.48 (m, 1H), 1.38 – 1.30 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 159.1, 135.7, 130.7, 130.6, 130.1, 127.4, 124.5, 121.2, 114.1, 110.4, 55.4, 43.2, 42.0, 28.1, 11.8.

HRMS (ESI-TOF) Calcd for $C_{18}H_{22}NO_2S$ $(M+H)^+$ 316.1366. Found 316.1366.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 13.2 min (major) and 14.4 min (minor).

(*S*,*E*)-*N*-(4-methoxyphenyl)-3-(4-methoxystyryl)hexanamide (3f)



3f

Following **method A**, **3f** was obtained as white solid after flash chromatography (PE: EtOAc = 3: 1) (38.1 mg, 54% yield, 88% ee). rr = 9: 1.

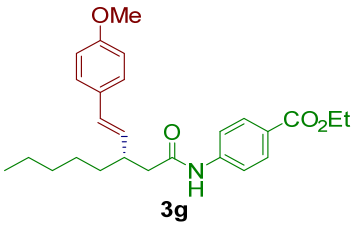
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.38 – 7.30 (m, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.87 – 6.76 (m, 4H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.78 – 2.72 (m, 1H), 2.44 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.35 (dd, *J* = 14.2, 8.3 Hz, 1H), 1.56 – 1.47 (m, 1H), 1.43 – 1.37 (m, 2H), 1.34 – 1.32 (m, 1H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.3, 159.0, 156.5, 131.07, 131.05, 130.4, 130.2, 127.4, 122.2, 114.2, 114.1, 55.6, 55.4, 44.0, 40.3, 37.5, 20.5, 14.1.

HRMS (ESI-TOF) Calcd for $C_{22}H_{28}NO_3$ $(M+H)^+$ 354.2064. Found 354.2066.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 22.2 min (major) and 24.3 min (minor).

Ethyl (*S*,*E*)-4-(3-(4-methoxystyryl)octanamido)benzoate (3g)



3g

Following **method A**, **3g** was obtained as white solid after flash chromatography (PE: EtOAc = 3: 1) (66.0 mg, 78% yield, 88% ee). rr = 10: 1.

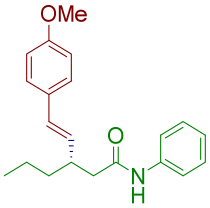
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 2H), 7.80 (s, 1H), 7.47 – 7.45 (m, 2H), 7.17 – 7.15 (m, 2H), 6.75 – 6.73 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.8, 8.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.70 – 2.61 (m, 1H), 2.42 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.33 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.48 – 1.38 (m, 1H), 1.36 – 1.26 (m, 5H), 1.22 – 1.16 (m, 5H), 0.77 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 166.3, 159.1, 142.2, 130.8, 130.6, 130.0, 127.4, 125.8, 119.0, 114.1, 61.0, 55.4, 44.2, 40.4, 35.3, 31.9, 27.0, 22.7, 14.4, 14.2.

HRMS (ESI-TOF) Calcd for $C_{26}H_{34}NO_4$ $(M+H)^+$ 424.2483. Found 424.2485.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 18.6 min (minor) and 21.5 min (major).

(*S*,*E*)-3-(4-Methoxystyryl)-*N*-phenylhexanamide (3h)



3h

Following **method A**, **3h** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (42.0 mg, 65% yield, 71% ee). rr = 9: 1.

Following **method B**, **3h** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (35.5 mg, 55% yield, 88% ee). rr = 12: 1.

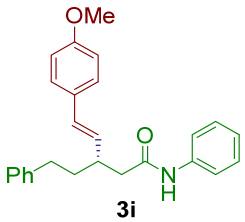
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.50 – 7.48 (m, 2H), 7.34 – 7.24 (m, 4H), 7.12 – 7.08 (m, 1H), 6.87 – 6.85 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.82 (s, 3H), 2.87 – 2.73 (m, 1H), 2.50 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.41 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.61 – 1.50 (m, 1H), 1.50 – 1.33 (m, 3H), 0.93 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 159.1, 137.9, 131.0, 130.6, 130.1, 129.1, 127.4, 124.4, 120.1, 114.1, 55.4, 44.3, 40.2, 37.5, 20.5, 14.2.

HRMS (ESI-TOF) Calcd for $C_{21}H_{26}NO_2$ $(M+H)^+$ 324.1958. Found 324.1957.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 15.9 min (major) and 17.6 min (minor).

(*S*,*E*)-5-(4-Methoxyphenyl)-3-phenethyl-*N*-phenylpent-4-enamide (3i)



3i

Following **method A**, **3i** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (60.0 mg, 78% yield, 91% ee). rr = 9: 1.

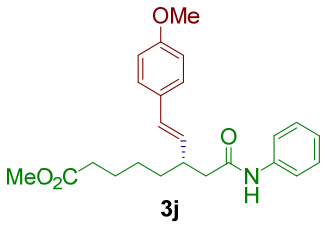
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.42 (m, 2H), 7.36 – 7.27 (m, 7H), 7.20 – 7.17 (m, 3H), 7.10 – 7.07 (m, 1H), 6.87 – 6.85 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.82 (s, 3H), 2.86 – 2.77 (m, 1H), 2.77 – 2.69 (m, 1H), 2.68 – 2.57 (m, 1H), 2.52 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.44 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.79 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 159.2, 142.1, 137.8, 131.2, 130.4, 130.0, 129.1, 128.56, 128.51, 127.5, 126.0, 124.4, 120.1, 114.1, 55.4, 44.2, 40.2, 36.9, 33.7.

HRMS (ESI-TOF) Calcd for $C_{26}H_{28}NO_2$ $(M+H)^+$ 386.2115. Found 386.2117.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 30.1 min (minor) and 35.7 min (major).

Methyl (*S*,*E*)-8-(4-methoxyphenyl)-6-(2-oxo-2-(phenylamino)ethyl)oct-7-enoate (3j)



3j

Following **method A**, **3j** was obtained as white solid after flash chromatography (PE: EtOAc = 3: 1) (58.5 mg, 74% yield, 90% ee). rr = 9: 1.

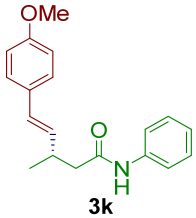
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.06 – 7.02 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.86 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 2.77 – 2.68 (m, 1H), 2.43 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.35 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.26 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.47 (m, 3H), 1.47 – 1.26 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 170.3, 159.1, 137.9, 130.64, 130.59, 130.0, 129.0, 127.4, 124.3, 120.1, 114.1, 55.4, 51.6, 44.0, 40.2, 34.7, 34.0, 26.8, 24.9.

HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NO_4$ $(M+H)^+$ 396.2170. Found 396.2172.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 21.6 min (major) and 23.7 min (minor).

(*S*,*E*)-5-(4-Methoxyphenyl)-3-methyl-*N*-phenylpent-4-enamide (3k)



3k

Following **method A**, **3k** was obtained as white solid after flash chromatography (PE: EtOAc = 8: 1) (44.2 mg, 75% yield, 88% ee). rr = 11: 1.

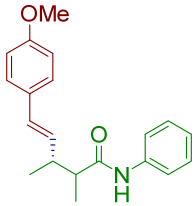
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.40 – 7.38 (m, 2H), 7.22 – 7.16 (m, 4H), 7.02 – 6.98 (m, 1H), 6.76 – 6.74 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.71 (s, 3H), 2.89 – 2.82 (m, 1H), 2.37 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.29 (dd, *J* = 14.3, 6.9 Hz, 1H), 1.11 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.3, 159.1, 137.9, 132.3, 130.1, 129.1, 128.8, 127.4, 124.4, 120.1, 114.1, 55.4, 45.3, 34.5, 20.4.

HRMS (ESI-TOF) Calcd for $C_{19}H_{22}NO_2$ $(M+H)^+$ 296.1645. Found 296.1646.

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 37.8 min (major) and 45.8 min (minor).

(3*S*,*E*)-2-Ethyl-5-(4-methoxyphenyl)-3-methyl-*N*-phenylpent-4-enamide (3l)



3l

Following **method B**, **3l** was obtained as white solid after flash chromatography (PE: EtOAc = 6: 1) (44.4 mg, 72% yield, rr = 18:1, d.r. = 1.05 (89% ee): 1 (87% ee) was determined by GC and HPLC.

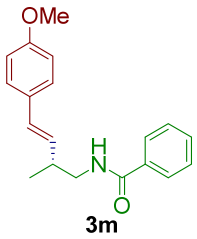
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.12 (m, 5H), 7.04 – 6.94 (m, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 6.32 (dd, *J* = 15.9, 11.9 Hz, 1H), 6.01 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.73 (s, 3H), 2.64 – 2.47 (m, 1H), 2.29 – 2.22 (m, 1H), 1.19 – 1.13 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.2, 159.0, 138.0, 131.1, 130.3, 129.5, 129.1, 127.4, 124.4, 120.4, 114.1, 55.4, 48.6, 41.2, 19.0, 16.3.

HRMS (ESI-TOF) Calcd for $C_{21}H_{26}NO_2$ $(M+H)^+$ 310.1802. Found 310.1806.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 10.2 min (minor) and 11.7 min (major), 10.8 min (major) and 13.0 min (minor)

(*S*,*E*)-*N*-(4-(4-methoxyphenyl)-2-methylbut-3-en-1-yl)benzamide (3m)



3m

Following **method A**, **3m** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (36.6 mg, 62% yield, 85% ee). rr = 5: 1.

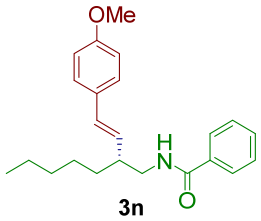
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.70 (m, 2H), 7.48 – 7.44 (m, 1H), 7.41 – 7.38 (m, 2H), 7.30 – 7.28 (m, 2H), 6.86 – 6.84 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.29 (s, 1H), 5.96 (dd, *J* = 15.8, 8.1 Hz, 1H), 3.80 (s, 3H), 3.65 – 3.61 (m, 1H), 3.29 – 3.24 (m, 1H), 2.65 – 2.58 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6, 159.2, 134.9, 131.4, 131.0, 130.2, 130.0, 128.7, 127.4, 126.9, 114.1, 55.4, 45.4, 37.8, 18.4.

HRMS (ESI-TOF) Calcd for $C_{19}H_{22}NO_2$ $(M+H)^+$ 296.1645. Found 296.1647.

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 17.6 min (minor) and 27.5 min (major).

(*S*,*E*)-*N*-(2-(4-methoxystyryl)hexyl)benzamide (3n)



3n

Following **method A**, **3n** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (52.6 mg, 78% yield, 92% ee). rr = 7: 1.

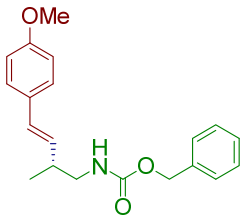
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.69 (m, 2H), 7.47 – 7.43 (m, 1H), 7.40 – 7.36 (m, 2H), 7.31 – 7.29 (m, 2H), 6.87 – 6.85 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.26 (s, 1H), 5.86 (dd, *J* = 15.8, 9.1 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.68 (m, 1H), 3.20 – 3.13 (m, 1H), 2.48 – 2.39 (m, 1H), 1.57 – 1.50 (m, 1H), 1.45 – 1.25 (m, 7H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 159.2, 134.9, 131.5, 131.4, 130.1, 130.0, 128.6, 127.4, 126.9, 114.1, 55.4, 44.2, 43.9, 33.1, 32.0, 26.9, 22.7, 14.2.

HRMS (ESI-TOF) Calcd for $C_{22}H_{30}NO_2$ $(M+H)^+$ 352.2271. Found 352.2275.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 11.9 min (major) and 14.4 min (minor).

Benzyl (*S*,*E*)-(4-(4-methoxyphenyl)-2-methylbut-3-en-1-yl)carbamate (3o)



3o

Following **method A**, **3o** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (39.0mg, 60% yield, 85% ee). rr = 6: 1.

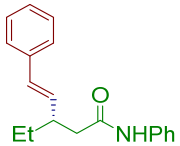
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 – 7.17 (m, 7H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 15.8 Hz, 1H), 5.80 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.00 (s, 2H), 4.76 (s, 1H), 3.72 (s, 3H), 3.24 – 3.20 (m, 1H), 3.05 – 2.95 (m, 1H), 2.42 – 2.38 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.1, 156.5, 136.7, 130.7, 130.1, 128.6, 128.22, 128.18, 127.7, 127.4, 114.1, 66.7, 55.4, 46.7, 38.0, 18.1.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO_3$ $(M+H)^+$ 326.1751. Found 326.1752.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 9.5 min (major) and 11.3 min (minor).

(*S*,*E*)-3-Ethyl-*N*,5-diphenylpent-4-enamide (4a)



4a

Following **method A**, **4a** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (36.2 mg, 65% yield, 90% ee). rr = 13: 1.

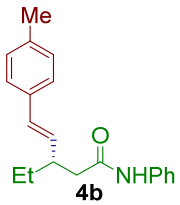
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.18 (m, 6H), 7.16 – 7.12 (m, 1H), 7.03 – 7.00 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.43 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.34 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.58 – 1.50 (m, 1H), 1.44 – 1.31 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 137.9, 137.3, 132.9, 131.3, 129.0, 128.6, 127.4, 126.3, 124.4, 120.2, 43.7, 42.0, 28.0, 11.8.

HRMS (ESI-TOF) Calcd for $C_{19}H_{22}NO$ $(M+H)^+$ 280.1696. Found 280.1697.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 10.5 min (major) and 12.9 min (minor).

(*S*,*E*)-3-Ethyl-*N*-phenyl-5-(*p*-tolyl)pent-4-enamide (4b)



4b

Following **method A**, **4b** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (43.9 mg, 75% yield, 89% ee). rr = 12: 1.

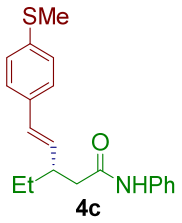
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.12 (m, 5H), 7.03 – 6.97 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.41 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.32 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.24 (s, 3H), 1.59 – 1.47 (m, 1H), 1.48 – 1.31 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 137.9, 137.2, 134.5, 131.9, 131.2, 129.3, 129.1, 126.2, 124.4, 120.1, 43.8, 42.0, 28.1, 21.3, 11.8.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO$ $(M+H)^+$ 294.1853. Found 294.1853.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 9.9 min (major) and 10.7 min (minor).

(*S*,*E*)-3-Ethyl-5-(4-(methylthio)phenyl)-*N*-phenylpent-4-enamide (4c)



4c

Following **method A**, **4c** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (35.7 mg, 55% yield, 89% ee). rr = 12: 1.

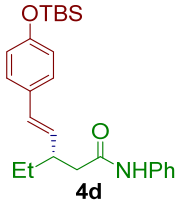
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.33 (s, 1H), 7.26 – 7.22 (m, 4H), 7.18 – 7.10 (m, 2H), 7.06 – 7.02 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.49 – 2.43 (m, 4H), 2.36 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.63 – 1.53 (m, 1H), 1.49 – 1.36 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 137.9, 137.4, 134.4, 132.4, 130.7, 129.1, 126.9, 126.7, 124.4, 120.1, 43.7, 42.0, 28.0, 16.1, 11.9.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NOS$ $(M+H)^+$ 326.1573. Found 326.1572.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 16.4 min (major) and 18.2 min (minor).

(*S*,*E*)-5-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-ethyl-*N*-phenylpent-4-enamide (4d)



4d

Following **method A**, **4d** was obtained as colorless oil after flash chromatograph (PE: EtOAc = 8: 1) (40.9 mg, 50% yield, 86% ee). rr = 12: 1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.04 (m, 3H), 7.09 – 7.06 (m, 2H), 7.03 – 7.01 (m, 2H), 6.90 – 6.86 (m, 1H), 6.58 – 6.57 (m, 2H), 6.22 (d, *J* = 15.8 Hz, 1H), 5.72 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.50 – 2.44

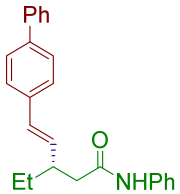
(m, 1H), 2.29 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.20 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.45 – 1.38 (m, 1H), 1.29 – 1.22 (m, 1H), 0.79 (s, 9H), 0.74 (t, *J* = 7.4 Hz, 3H), 0.00 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 155.2, 137.9, 130.9, 130.8, 130.7, 129.0, 127.3, 124.3, 120.3, 120.1, 43.9, 42.0, 28.1, 25.8, 18.3, 11.9, -4.3.

HRMS (ESI-TOF) Calcd for $C_{25}H_{36}NO_2Si$ $(M+H)^+$ 410.2510. Found 410.2510.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 5.5 min (major) and 6.1 min (minor).

(*S*,*E*)-5-([1,1'-Biphenyl]-4-yl)-3-ethyl-*N*-phenylpent-4-enamide (4e)



4e

Following **method A**, **4e** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (42.6 mg, 60% yield, 97% ee). rr = 14: 1.

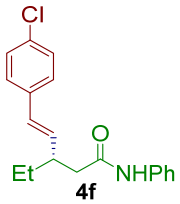
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 2H), 7.55 – 7.53 (m, 2H), 7.47 – 7.41 (m, 6H), 7.36 – 7.34 (m, 1H), 7.33 – 7.26 (m, 3H), 7.11 – 7.06 (m, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.53 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.43 (dd, *J* = 14.2, 8.2 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.55 – 1.44 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 140.9, 140.2, 137.9, 136.4, 133.0, 130.9, 129.1, 128.9, 127.4, 127.12, 127.05, 126.7, 124.5, 120.1, 43.8, 42.1, 28.1, 11.9.

HRMS (ESI-TOF) Calcd for $C_{25}H_{26}NO$ $(M+H)^+$ 356.2009. Found 356.2008.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 15.9 min (major) and 18.9 min (minor).

(*S*,*E*)-5-(4-Chlorophenyl)-3-ethyl-*N*-phenylpent-4-enamide (4f)



4f

Following **method A**, **4f** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (34.4 mg, 55% yield, 87% ee). rr = 8: 1.

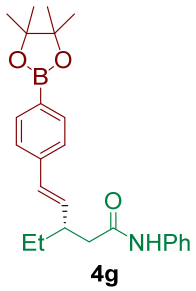
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.18 (m, 7H), 7.03 – 6.99 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.43 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.32 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.58 – 1.49 (m, 1H), 1.43 – 1.35 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 137.8, 135.8, 133.6, 133.0, 130.1, 129.1, 128.8, 127.5, 124.5, 120.1, 43.7, 42.0, 28.0, 11.9.

HRMS (ESI-TOF) Calcd for $C_{19}H_{21}ClNO$ $(M+H)^+$ 314.1306. Found 314.1303.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 21.0 min (major) and 24.7 min (minor).

(*S*,*E*)-3-Ethyl-*N*-phenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-4-enamide (4g)



4g

Following **method B**, **4g** was obtained as colorless oil after flash chromatograph (PE: EtOAc = 6: 1) (48.6 mg, 60% yield, 85% ee). rr = 9: 1.

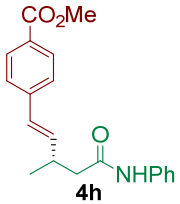
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.65 (m, 2H), 7.37 – 7.35 (m, 2H), 7.28 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 7.03 – 7.00 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.70 – 2.58 (m, 1H), 2.42 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.33 (dd, *J* = 14.2, 8.2 Hz, 1H), 1.58 – 1.52 (m, 1H), 1.43 – 1.37 (m, 1H), 1.26 (s, 12H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.2, 140.0, 137.8, 135.2, 134.0, 131.4, 129.1, 125.6, 124.4, 120.14, 120.12, 83.9, 43.7, 42.1, 28.0, 25.0, 11.9.

HRMS (ESI-TOF) Calcd for $C_{25}H_{33}BNO_3$ $(M+H)^+$ 406.2548. Found 406.2542.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 0.7 mL/min, detection at 254 nm) retention time = 12.3 min (major) and 14.4 min (minor).

Methyl (*S*,*E*)-4-(3-methyl-5-oxo-5-(phenylamino)pent-1-en-1-yl)benzoate (4h)



4h

Following **method B**, **4h** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (35.5 mg, 55% yield, 88% ee). rr = 8: 1.

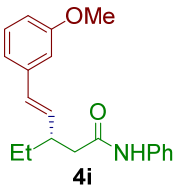
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.94 (m, 2H), 7.50 – 7.48 (m, 2H), 7.45 (s, 1H), 7.38 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.11 – 7.07 (m, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.90 (s, 3H), 3.06 – 2.96 (m, 1H), 2.48 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.40 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.21 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.9, 167.1, 142.0, 137.9, 137.3, 130.0, 129.1, 128.7, 128.5, 126.1, 124.5, 120.1, 52.2, 45.0, 34.5, 20.1.

HRMS (ESI-TOF) Calcd for $C_{20}H_{22}NO_3$ $(M+H)^+$ 324.1594. Found 324.1590.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, detection at 254 nm) retention time = 69.8 min (major) and 76.2 min (minor).

(*S*,*E*)-3-Ethyl-5-(3-methoxyphenyl)-*N*-phenylpent-4-enamide (4i)



4i

Following **method A**, **4i** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (32.1 mg, 52% yield, 90% ee). rr = 8: 1.

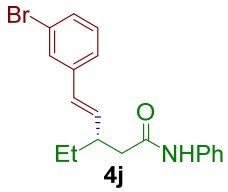
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 2H), 7.30 (s, 1H), 7.22 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 7.02 – 6.98 (m, 1H), 6.87 – 6.85 (m, 1H), 6.80 – 6.79 (m, 1H), 6.71 – 6.68 (m, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.71 (s, 3H), 2.67 – 2.58 (m, 1H), 2.42 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.32 (dd, *J* = 14.2, 8.2 Hz, 1H), 1.60 – 1.50 (m, 1H), 1.46 – 1.31 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 159.9, 138.8, 137.9, 133.2, 131.2, 129.6, 129.1, 124.4, 120.2, 118.9, 113.0, 111.7, 55.3, 43.7, 42.0, 28.0, 11.8.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO_2$ $(M+H)^+$ 310.1802. Found 310.1802.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 13.3 min (major) and 16.9 min (minor).

(*S*,*E*)-5-(4-Bromophenyl)-3-ethyl-*N*-phenylpent-4-enamide (4j)



4j

Following **method A**, **4j** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (47.8 mg, 67% yield, 90% ee). rr = 10: 1.

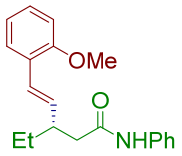
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.38 – 7.37 (m, 2H), 7.25 – 7.18 (m, 4H), 7.15 – 7.14 (m, 1H), 7.08 – 7.06 (m, 1H), 7.03 – 7.01 (m, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.42 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.31 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.57 – 1.52 (m , 1H), 1.42 – 1.35 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.0, 139.5, 137.8, 134.5, 130.23, 130.18, 129.9, 129.1, 129.0, 125.1, 124.5, 122.9, 120.2, 43.6, 42.0, 27.9, 11.9.

HRMS (ESI-TOF) Calcd for $C_{19}H_{21}BrNO$ $(M+H)^+$ 358.0801. Found 358.0799.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 12.2 min (major) and 13.7 min (minor).

(*S*,*E*)-3-Ethyl-5-(2-methoxyphenyl)-*N*-phenylpent-4-enamide (4k)



4k

Following **method A**, **4k** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (43.2 mg, 70% yield, 89% ee). rr = 12: 1.

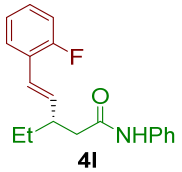
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.40 – 7.38 (m, 2H), 7.33 – 7.31 (m, 1H), 7.20 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 7.00 – 6.96 (m, 1H), 6.84 – 6.80 (m, 1H), 6.77 – 6.75 (m, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 5.98 (dd, *J* = 16.0, 8.7 Hz, 1H), 3.70 (s, 3H), 2.65 – 2.56 (m, 1H), 2.44 – 2.32 (m, 2H), 1.59 – 1.48 (m, 1H), 1.44 – 1.33 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 156.6, 138.0, 133.7, 129.0, 128.5, 126.7, 126.4, 126.2, 124.3, 120.7, 120.2, 111.0, 55.5, 43.7, 42.4, 28.1, 11.8.

HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO_2$ $(M+H)^+$ 310.1802. Found 310.1802.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 13.0 min (major) and 15.9 min (minor).

(*S*,*E*)-3-Ethyl-5-(2-fluorophenyl)-*N*-phenylpent-4-enamide (4l)



4l

Following **method A**, **4l** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (37.5 mg, 63% yield, 93% ee). rr = 9: 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.46 (m, 2H), 7.40 – 7.36 (m, 1H), 7.35 (s, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.14 (m, 1H), 7.12 – 7.05 (m, 2H), 7.05 – 6.96 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 8.7 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.51 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.43 (dd, *J* = 14.2, 8.1 Hz, 1H), 1.69 – 1.59 (m, 1H), 1.55 – 1.41 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

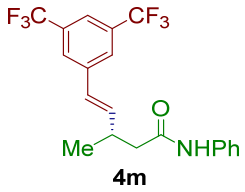
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 160.2 (d, *J* = 248.7 Hz), 137.9, 135.8 (d, *J* = 4.9 Hz), 129.1, 128.6 (d, *J* = 8.4 Hz), 127.6 (d, *J* = 4.0 Hz), 125.1 (d, *J* = 12.3 Hz), 124.4, 124.2 (d, *J* = 3.6 Hz), 123.7 (d, *J* = 3.2 Hz), 120.2, 115.8 (d, *J* = 2.2 Hz), 43.6, 42.4, 27.9, 11.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.15 – -118.22 (m, 1F).

HRMS (ESI-TOF) Calcd for $C_{19}H_{21}FNO$ $(M+H)^+$ 298.1602. Found 298.1601.

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 15.2 min (minor) and 16.9 min (major).

(*S*,*E*)-5-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-*N*-phenylpent-4-enamide (4m)



4m

Following **method A**, **4m** was obtained as white solid after flash chromatograph (PE: EtOAc = 8: 1) (64.1 mg, 80% yield, 87% ee). rr = 9: 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.54 (m, 4H), 7.42 – 7.40 (m, 2H), 7.21 – 7.17 (m, 2H), 7.02 – 6.99 (m, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.23 (dd, *J* = 15.8, 7.3 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.42 – 2.30 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 3H).

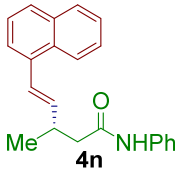
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 139.5, 138.6, 137.8, 131.9 (q, *J* = 33.2 Hz), 129.1, 126.8, 126.0 (d, *J* = 4.0 Hz), 124.7, 123.4 (q, *J* = 273.7 Hz), 120.6 (p, *J* = 3.4 Hz), 120.3, 44.6, 34.5, 20.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.0 (s, 6F).

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_6NO$ $(M+H)^+$ 402.1287. Found 402.1284.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 10.7 min (minor) and 13.5 min (major).

(*S*,*E*)-3-Methyl-5-(naphthalen-1-yl)-*N*-phenylpent-4-enamide (4n)



4n

Following **method B**, **4n** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (49.2 mg, 78% yield, 85% ee). rr = 7: 1.

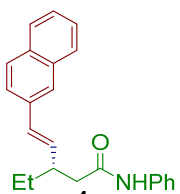
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 1H), 7.73 – 7.71 (m, 1H), 7.66 – 7.64 (m, 1H), 7.49 – 7.29 (m, 7H), 7.20 – 7.16 (m, 2H), 7.09 (d, *J* = 15.6 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.06 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.05 – 2.95 (m, 1H), 2.45 – 2.29 (m, 2H), 1.17 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 137.9, 137.7, 135.3, 133.6, 131.2, 129.1, 128.5, 127.7, 126.9, 126.0, 125.8, 125.7, 124.5, 124.0, 123.8, 120.2, 45.3, 35.0, 20.4.

HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO$ $(M+H)^+$ 316.1696. Found 316.1695.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 13.3 min (major) and 14.7 min (minor).

(*S*,*E*)-3-Ethyl-5-(naphthalen-2-yl)-*N*-phenylpent-4-enamide (4o)



4o

Following **method B**, **4o** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (48.7 mg, 74% yield, 87% ee). rr = 13: 1.

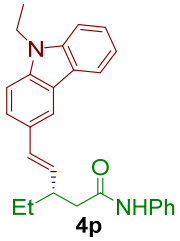
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.64 (m, 3H), 7.59 (s, 1H), 7.49 – 7.47 (m, 1H), 7.41 – 7.28 (m, 5H), 7.22 – 7.15 (m, 2H), 7.00 – 6.96 (m, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.45 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.36 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.49 – 1.38 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.2, 137.8, 134.7, 133.7, 133.2, 132.9, 131.4, 129.0, 128.2, 127.9, 127.7, 126.3, 125.9, 125.7, 124.3, 123.5, 120.1, 43.7, 42.1, 28.0, 11.8.

HRMS (ESI-TOF) Calcd for $C_{23}H_{24}NO$ $(M+H)^+$ 330.1853. Found 330.1852.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 15.2 min (major) and 16.7 min (minor).

(*S*,*E*)-3-Ethyl-5-(9-ethyl-*9H*-carbazol-3-yl)-*N*-phenylpent-4-enamide (4p)



4p

Following **method B**, **4p** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (49.9 mg, 63% yield, 91% ee). rr = 9: 1.

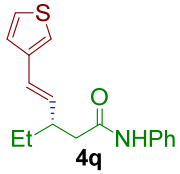
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.10 (m, 2H), 7.58 – 7.39 (m, 6H), 7.38 – 7.19 (m, 4H), 7.11 – 7.06 (m, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 8.7 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.81 – 2.72 (m, 1H), 2.58 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.49 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.60 – 1.52 (m, 1H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 140.4, 139.6, 138.0, 132.2, 130.2, 129.1, 128.5, 125.9, 124.3, 124.2, 123.3, 123.1, 120.6, 120.1, 119.0, 118.3, 108.7, 108.6, 44.1, 42.3, 37.7, 28.3, 13.9, 11.9.

HRMS (ESI-TOF) Calcd for $C_{27}H_{29}N_2O$ $(M+H)^+$ 397.2275. Found 397.2273.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 95/5, flow rate = 1 mL/min, detection at 254 nm) retention time = 48.7 min (major) and 52.9 min (minor).

(*S*,*E*)-3-Ethyl-*N*-phenyl-5-(thiophen-3-yl)pent-4-enamide (4q)



4q

Following **method A**, **4q** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (31.9 mg, 56% yield, 89% ee). rr = 11: 1.

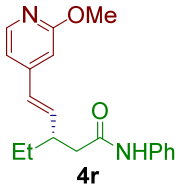
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38– 7.36 (m, 3H), 7.24 – 7.14 (m, 3H), 7.11 – 7.10 (m , 1H), 7.02 – 6.98 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.83 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.40 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.31 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.58 – 1.48 (m, 1H), 1.42 – 1.30 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 139.8, 137.8, 132.6, 129.0, 126.0, 125.4, 124.9, 124.3, 121.4, 120.1, 43.6, 41.8, 27.9, 11.7.

HRMS (ESI-TOF) Calcd for $C_{17}H_{20}NOS$ $(M+H)^+$ 286.1260. Found 286.1259.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 13.1 min (major) and 16.2 min (minor).

(*S*,*E*)-3-Ethyl-5-(2-methoxypyridin-4-yl)-*N*-phenylpent-4-enamide (4r)



4r

Following **method A**, **4r** was obtained as white solid after flash chromatograph (PE: EtOAc = 6: 1) (40.3 mg, 65% yield, 89% ee). rr = 9: 1.

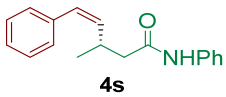
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.97 (m, 1H), 7.53 – 7.51 (m, 2H), 7.39 – 7.37 (m, 2H), 7.21 – 7.17 (m, 2H), 7.01 – 6.98 (m, 1H), 6.61 – 6.58 (m, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 5.85 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.84 (s, 3H), 2.68 – 2.56 (m, 1H), 2.41 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.31 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.57 – 1.49 (m, 1H), 1.41 – 1.30 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 163.4, 145.0, 137.9, 135.7, 132.4, 129.1, 127.1, 126.6, 124.4, 120.1, 110.9, 53.7, 43.6, 42.0, 28.0, 11.8.

HRMS (ESI-TOF) Calcd for $C_{19}H_{23}N_2O_2$ $(M+H)^+$ 311.1754. Found 311.1752.

HPLC (IA, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 14.3 min (major) and 16.4 min (minor).

(*S*,*Z*)-3-Methyl-*N*,5-diphenylpent-4-enamide (4s)



4s

Following **method B**, **4s** was obtained as colorless oil after flash chromatograph (PE: Et_2O = 4: 1) (26.6 mg, 51% yield, 93% ee). rr = 5: 1.

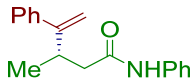
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.31 (m, 2H), 7.27 – 7.24 (m, 2H), 7.23 – 7.20 (m, 3H), 7.20 – 7.15 (m, 2H), 7.06 (s, 1H), 7.02 – 6.99 (m, 1H), 6.40 (d, *J* = 11.0 Hz, 1H), 5.47 (t, *J* = 11.0 Hz, 1H), 3.34 – 3.26 (m, 1H), 2.35 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.29 (dd, *J* = 14.4, 6.6 Hz, 1H), 1.12 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.8, 137.9, 137.1, 136.7, 129.3, 129.1, 128.7, 128.6, 127.1, 124.4, 120.0, 45.6, 30.2, 21.3.

HRMS (ESI-TOF) Calcd for $C_{18}H_{20}NO$ $(M+H)^+$ 266.1540. Found 266.1536.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 9.7 min (minor) and 10.3min (major).

(*S*)-3-Methyl-*N*,4-diphenylpent-4-enamide (4t)



4t

Following **method C**, **4t** was obtained as colorless oil after flash chromatography (PE: Et_2O = 4: 1) (21.7 mg, 41% yield, 93% ee). rr = 5: 1.

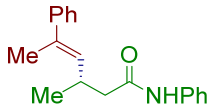
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 (m, 4H), 7.15 – 7.13 (m, 1H), 7.05 – 6.98 (m, 1H), 5.19 (s, 1H), 5.05 (s, 1H), 3.33 – 3.25 (m, 1H), 2.53 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.19 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 153.7, 142.1, 138.1, 129.3, 128.7, 128.0, 127.9, 127.1, 120.2, 112.2, 44.4, 35.4, 20.0.

HRMS (ESI-TOF) Calcd for $C_{18}H_{20}NO$ $(M+H)^+$ 266.1540. Found 266.1538.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 8.6 min (major) and 12.1 min (minor).

(*S*,*E*)-3-Methyl-*N*,5-diphenylhex-4-enamide (4u)



4u

Following **method C**, **4u** was obtained as white solid after flash chromatography (PE: Et_2O = 4: 1) (25.6 mg, 46% yield, 94% ee). rr = 5: 1.

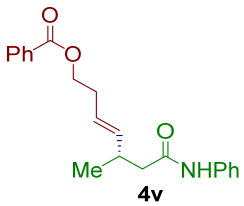
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.45 (m, 2H), 7.37 – 7.35 (m, 2H), 7.32 – 7.29 (m, 4H), 7.25 – 7.23 (m, 1H), 7.18 (s, 1H), 7.11 – 7.07 (m, 1H), 5.62 (d, *J* = 9.5 Hz, 1H), 3.23 – 3.16 (m, 1H), 2.46 – 2.36 (m, 2H), 2.09 (s, 3H), 1.17 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 143.6, 138.0, 135.7, 132.6, 129.1, 128.4, 127.0, 125.9, 124.4, 120.0, 45.7, 31.1, 21.4, 16.3.

HRMS (ESI-TOF) Calcd for $C_{19}H_{22}NO$ $(M+H)^+$ 280.1696. Found 280.1695.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 8.3 min (major) and 9.7 min (minor).

(*S*,*E*)-5-Methyl-7-oxo-7-(phenylamino)hept-3-en-1-yl benzoate (4v)



4v

Following **method D**, **4v** was obtained as white solid after flash chromatography (PE: EtOAc = 10: 1) (28.4 mg, 42% yield, 87% ee). rr = 3: 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.94 (m, 2H), 7.49 – 7.46 (m, 1H), 7.41 – 7.40 (m, 2H), 7.37 – 7.34 (m, 2H), 7.23 – 7.18 (m, 4H) 5.53 – 5.47 (m, 2H), 4.27 – 4.23 (m, 2H), 2.73 – 2.67 (m, 1H), 2.41 – 2.38 (m, 2H), 2.26 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.19 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H).

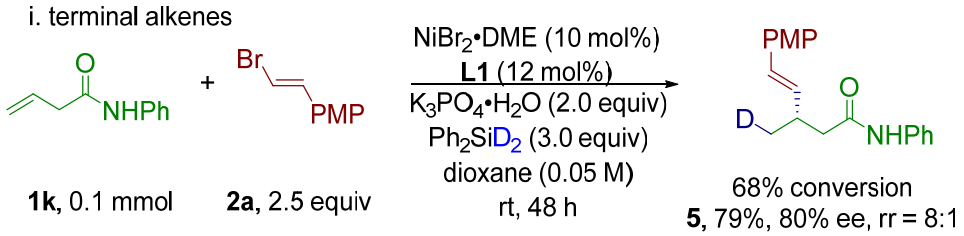
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 166.6, 137.8, 137.4, 132.9, 130.3, 129.5, 129.0, 128.4, 125.0, 124.3, 119.8, 64.3, 45.2, 34.0, 32.1, 20.3.

HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_3$ $(M+H)^+$ 338.1751. Found 338.1749.

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 16.7 min (major) and 21.2 min (minor).

VII. Mechanistic experiments

7.1 Isotope experiments



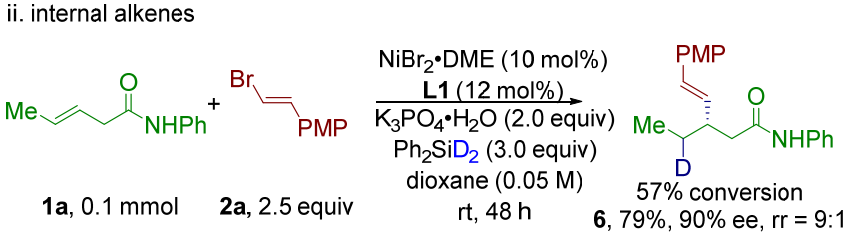
In a nitrogen-filled glovebox, $NiBr_2$•DME (3.1 mg, 0.01 mmol, 10 mol%) and **L1** (5.8 mg, 0.012 mmol, 12 mol%) were dissolved in dioxane (2.0 mL, 0.05 M) in a 10 mL Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 10 min, then alkene **1k** (16.0 mg, 0.1 mmol, 1.0 equiv), **2a** (55.0 mg, 0.25 mmol, 2.5 equiv), K_3PO_4•H_2O (46.0 mg, 0.2 mmol, 2.0 equiv) and Ph_2SiD_2 (56.0 mg, 0.3 mmol, 3.0 equiv) were sequentially added. The mixture was stirred at room temperature for 48 h. The mixture was quenched with H_2O (2.0 mL) and extracted with ethyl acetate (10 mL), then filtered through a pad of diatomite. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel using a mixture of PE: EtOAc= 8:1 as eluent to give **5** as white solid (16.1 mg, 79% yield, 80% ee). Yield was calculated based on the recovery of alkene and the deuterated ratio was confirmed by ^{1}H NMR (96 % D).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 –7.38 (m, 2H), 7.22 – 7.19 (m, 5H), 7.02 – 7.00 (m, 1H), 6.77 – 6.75 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.72 (s, 3H), 2.89 – 2.83 (m, 1H), 2.39 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.30 (dd, *J* = 14.4, 6.9 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 159.0, 137.8, 132.1, 130.0, 129.0, 128.8, 127.3, 124.3, 120.0, 114.0, 55.3, 45.3, 34.3, 20.1 (t, *J* = 20.2 Hz).

HRMS (ESI-TOF) Calcd for $C_{19}H_{21}DNO_2$ $(M+H)^+$ 297.1708. Found 297.1706.

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 39.5 min (major) and 47.2 min (minor).



In a nitrogen-filled glovebox, $NiBr_2$•DME (3.1 mg, 0.01 mmol, 10 mol%) and **L1** (5.8 mg, 0.012 mmol, 12 mol%) were dissolved in dioxane (2.0 mL, 0.05 M) in a 10 mL Schlenk tube with screw-cap equipped with a magnetic stirrer. The mixture was stirred at room temperature for 10 min, then **1a** (17.5 mg, 0.1 mmol, 1.0 equiv), **2a** (55.0 mg, 0.25 mmol, 2.5 equiv), K_3PO_4•H_2O (46.0 mg, 0.2 mmol, 2.0 equiv) and Ph_2SiD_2 (55.0 mg, 0.3 mmol, 3.0 equiv) were sequentially added. The mixture was stirred at room temperature for 48 h. The mixture was quenched with H_2O (2.0 mL), extracted with ethyl acetate (10.0 mL), filtered through a pad of diatomite. The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel using a mixture of PE: EtOAc= 8:1 as eluent to give **6** as white solid (14.0 mg, 79% yield, 90% ee). Yield was calculated based on the recovery of alkene and the deuterated ratio was confirmed by ^{1}H NMR (98% D).

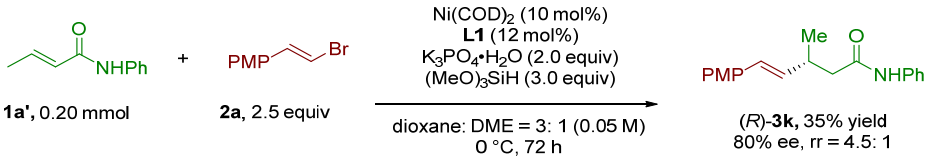
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 2H), 7.24 – 7.19 (m, 5H), 7.01 – 6.99 (m, 1H), 6.80 – 6.73 (m, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.85 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.72 (s, 3H), 2.59 (m, 1H), 2.42 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.32 (dd, *J* = 14.4, 8.3 Hz, 1H), 1.56 – 1.47 (m, 1H), 0.86 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 159.0, 137.8, 130.7, 130.6, 130.0, 129.0, 127.3, 124.3, 120.0, 114.0, 55.3, 43.8, 41.9, 27.7 (t, *J* = 19.2 Hz), 11.6.

HRMS (ESI-TOF) Calcd for $C_{20}H_{23}DNO_2$ $(M+H)^+$ 311.1865. Found 311.1862.

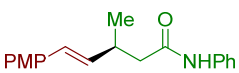
HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 15.1 min (major) and 17.9 min (minor).

7.2 Control experiments



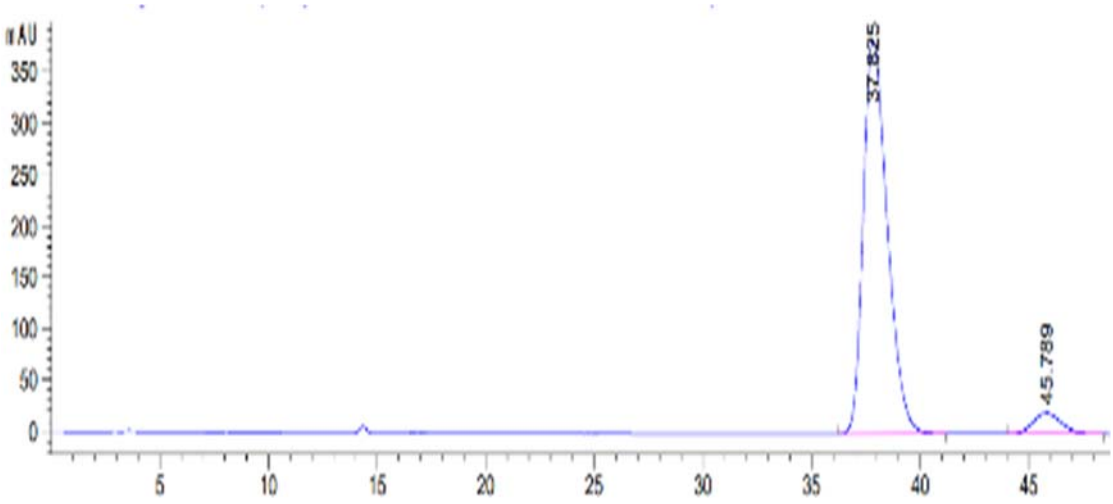
1a', 0.20 mmol **2a**, 2.5 equiv (*R*)-**3k**, 35% yield 80% ee, rr = 4.5: 1

To an oven-dried 10 mL Teflon-screw cap tube containing a magnetic stir was charged with $Ni(COD)_2$ (5.5 mg, 0.02 mmol, 10 mol%) and ligand **L1** (12.0 mg, 0.024 mmol, 12 mol%) in a nitrogen-filled glove-box. Subsequently, anhydrous dioxane (3.0 mL) and DME (1.0 mL) were added, and the mixture was stirred for 15 min at room temperature. Then olefin **1a′** (350.0 mg, 0.20 mmol, 1.0 equiv), **2a** (110.0 mg, 0.50 mmol, 2.5 equiv), K_3PO_4•H_2O (92.0 mg, 0.4 mmol, 2.0 equiv) were sequentially added. The tube was sealed and removed from the glove box and stirred at 0 ˚C for 10 min, then $(MeO)_3SiH$ (75.4 mg, 0.60 mmol, 3.0 equiv) added dropwise under N_2 atmosphere. The resulting mixture was stirred at 0 ˚C for 48 h. After the reaction was completed, the reaction mixture was quenched with H_2O and extracted with EtOAc (3 × 20.0 mL) and the combined organic phase was concentrated in vacuum. The crude mixture was purified by flash column chromatography on silica gel using a mixture of PE: EtOAc= 10:1 as eluent to give (*R*)-**3k** (20.7 mg, 35% yield, 80% ee, rr = 4.5: 1).

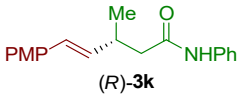


(*S*)-**3k**

HPLC data of (*S*)-**3k** using **L1**

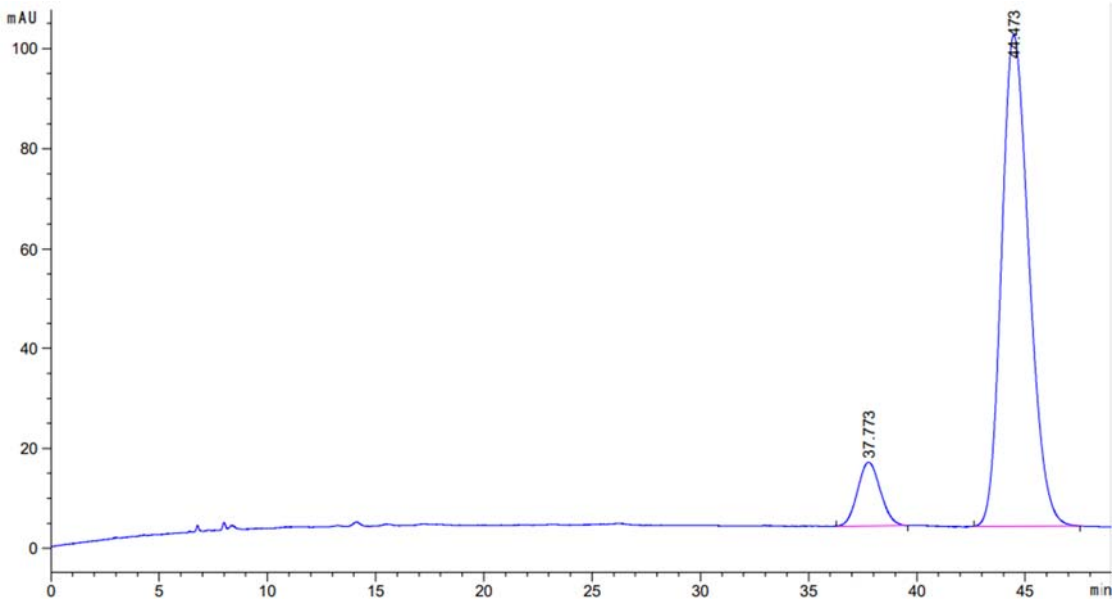


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.825	BB	1.1701	2.94184e4	382.13712	94.1948
2	45.789	BB	1.0761	1813.06152	20.18155	5.8052



(*R*)-**3k**

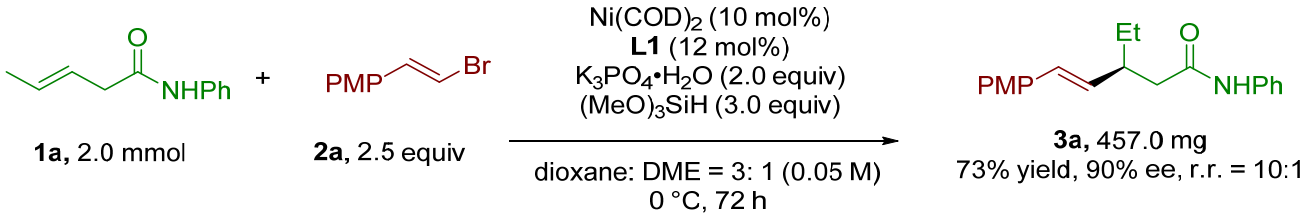
HPLC data of (*R*)-**3k** using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.773	BB	0.9007	932.39642	12.72687	9.7066
2	44.473	BB	1.3283	8673.40625	98.21320	90.2934

VIII. Scale-up reaction and derivatization of coupling products

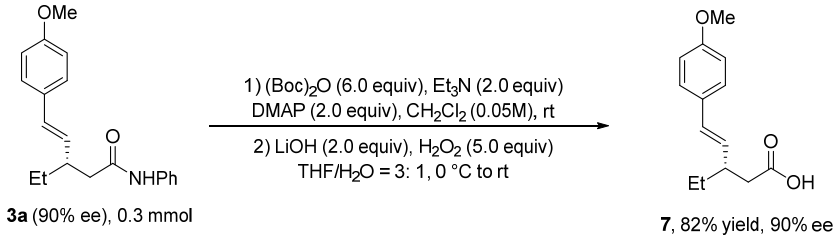
8.1 Scale-up reaction



1a, 2.0 mmol **2a,** 2.5 equiv **3a,** 457.0 mg
73% yield, 90% ee, r.r. = 10:1

To an oven-dried 100 mL Teflon-screw cap tube containing a magnetic stir was charged with $Ni(COD)_2$ (55.0 mg, 0.2 mmol, 10 mol%) and ligand **L1** (120.0 mg, 0.24 mmol, 12 mol%) in a nitrogen-filled glove-box. Subsequently, anhydrous dioxane (30.0 mL) and DME (10.0 mL) were added, and the mixture was stirred for 15 min at room temperature. Then olefin **1a** (350.0 mg, 2.0 mmol, 1.0 equiv), **2a** (1.1 g, 5.0 mmol, 2.5 equiv), K_3PO_4•H_2O (920.0 mg, 4.0 mmol, 2.0 equiv) were sequentially added. The tube was sealed and removed from the glove box and stirred at 0 ˚C for 10 min, then $(MeO)_3SiH$ (754.0 mg, 6.0 mmol, 3.0 equiv) added dropwise under N_2 atmosphere. The resulting mixture was stirred at 0 ˚C for 72 h. After the reaction was completed, the reaction mixture was quenched with H_2O and extracted with EtOAc (3 × 20.0 mL) and the combined organic phase was concentrated in vacuum. The crude mixture was purified by flash column chromatography on silica gel using a mixture of PE: EtOAc= 10:1 as eluent to give **3a** (457.0 mg, 73% yield, 90% ee).

8.2 Derivatization of coupling products

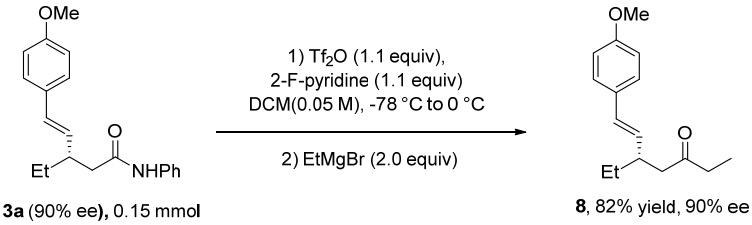


3a (90% ee), 0.3 mmol **7**, 82% yield, 90% ee

Following literature procedure,[5,6] to a solution of **3a** (93.0 mg, 0.3 mmol, 1.0 equiv) in dry DCM (20.0 mL) was added triethylamine (64.2 mg, 0.6 mmol, 2.0 equiv), $(Boc)_2O$ (261.6 mg, 1.2 mmol, 6.0 equiv) and DMAP (48.8 mg,0.4 mmol, 2.0 equiv), the resulting reaction mixture was stirred at room temperature for 2 h. The resulting solution was quenched with water (30.0 mL). The aqueous layer was extracted with DCM (2 × 30.0 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified on flash column to afford the product.

A round-bottom flask equipped with a magnetic stirring bar was charged with 0.05 M solution of the product obtained above (82.0 mg, 0.20 mmol, 1.0 equiv) in THF: H_2O = 3:1. The solution was cooled to 0 °C followed by adding 30% (by wt.) aqueous solution of H_2O_2 (113.3 mg, 1.0 mmol, 5.0 equiv) and LiOH (9.6 mg, 0.40 mmol, 2.0 equiv). The mixture was warmed slowly to room temperature and stirred for 3 h until completion as judged by TLC analysis. The reaction was cooled to 0 ºC and treated with 1.5 N aqueous solution of Na_2SO_3 (1.1 equiv). The mixture was stirred for 5 min at room temperature and was diluted with

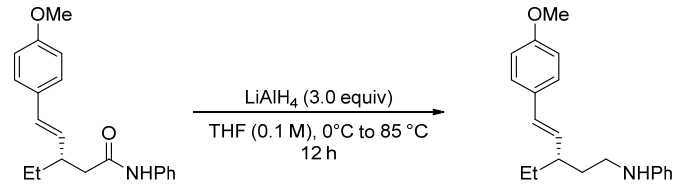
H_2O. The mixture was extracted with CH_2Cl_2 to remove HN(Boc)Ph. The remaining basic aqueous layer was acidified to pH = 4 and extracted with CH_2Cl_2. The organic layer was concentrated in vacuum and chromatographed on a silica column (PE: EtOAc = 1:1) to afford **7** as white solid (39.0 mg, 82% yield, 91% ee). (ee value was determined by corresponding arylamide). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.87 (dd, *J* = 15.8, 8.6 Hz, 1H), 3.80 (s, 3H), 2.61 – 2.55 (m, 1H), 2.48 (dd, *J* = 15.0, 6.4 Hz, 1H), 2.41 (dd, *J* = 15.0, 8.0 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.46 – 1.40 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 178.3, 159.0, 130.33, 130.27, 130.25, 127.4, 114.1, 55.4, 41.3, 40.0, 27.9, 11.7. **HRMS (ESI-TOF)** Calcd for $C_{14}H_{19}O_3$ $(M+H)^+$ 235.1329. Found 235.1333. HPLC trace was obtained by the corresponding arylamide. **HPLC** (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 14.9 min (major) and 17.7 min (minor).



3a (90% ee), 0.15 mmol

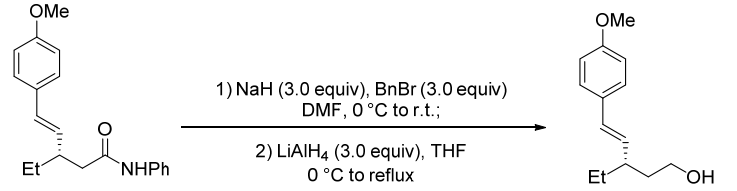
8, 82% yield, 90% ee

Following literature procedure,[7] to a flame-dried and nitrogen-flushed 10 mL round-bottom flask equipped with a stir bar and a septum was added **3a** (46.5 mg, 0.15 mmol, 1.0 equiv), anhydrous DCM (3.0 mL), and 2-fluoropyridine (16.5 mg, 0.17 mmol, 1.1 equiv). The solution was then cooled to –78 ˚C and stirred for 2 min. Tf_2O (48.0 mg, 0.17 mmol, 1.1 equiv) was added dropwise using a syringe at –78 ˚C and the reaction was stirred for 15 min. The solution was warmed to 0 ˚C and stirred for 15 min. EtMgBr (0.3 mmol, 150.0 μL, 2.0 equiv, 2.0 M in Et_2O) was added in one portion to the reaction at 0 ˚C, and the reaction was stirred for 25 min at 0 ˚C. The reaction was quenched by the addition of 1.6 mL of an aqueous solution of HCl (0.5 M). The biphasic mixture was gently heated to 65 ℃ (keeping the flask ventilated for DCM evaporation) for 2 h to ensure complete hydrolysis to the ketone. The aqueous layer was extracted with EtOAc (2 × 10.0 mL) and the organic layers were combined. The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The ketones were purified by column chromatography on silica gel (PE: EtOAc = 30:1) to provide the title compound **8** as a colorless oil (30.2 mg, 82% yield, 90% ee). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 6.85 – 6.83 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.84 (dd, *J* = 15.8, 8.6 Hz, 1H), 3.80 (d, *J* = 1.2 Hz, 3H), 2.63 (m, 1H), 2.50 (d, *J* = 7.1 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.49 (m, 1H), 1.36 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 210.9, 158.9, 131.0, 130.3, 129.7, 127.2, 113.9, 55.3, 48.1, 40.7, 36.8, 28.1, 11.7, 7.7. **HRMS (ESI-TOF)** Calcd for $C_{16}H_{23}O_2$ $(M+H)^+$ 247.1693. Found 247.1698. **HPLC** (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 4.6 min (major) and 5.0 min (minor).



3a (90% ee), 0.2 mmol **9**, 84% yield, 91% ee

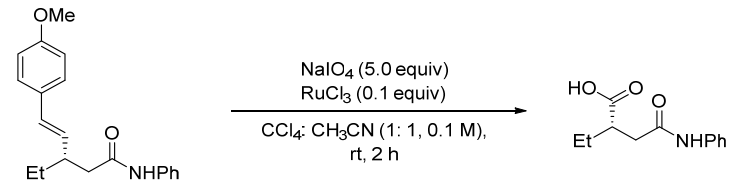
Following literature procedure,[8] lithium aluminum hydride (23.0 mg, 1.0 M in Et_2O, 3.0 equiv) was added dropwise to a solution of **3a** (62.0 mg, 0.2 mmol, 1.0 equiv) in THF (2.0 mL) at 0 ˚C in a 10-mL Schlenk tube. Next, the reaction mixture was allowed to warm to room temperature, and then it was heated to 85 ˚C. After being stirred at 85 ˚C in the sealed Schlenk tube overnight, the reaction mixture was diluted with Et_2O (10.0 mL) and cooled to 0 °C. The reaction was then quenched in turn with H_2O (36.0 mg, 0.2 mmol, 1.0 equiv), 15% aqueous NaOH (36.0 mg, 0.2 mmol, 1.0 equiv), and H_2O (108 mg, 0.6 mmol, 3.0 equiv). Next, the suspension was filtered through a sintered funnel to remove the white solid. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EtOAc = 10:1) to afford the pure product **9** as colorless oil (50.0 mg, 84% yield, 91% ee). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.7 Hz, 2H), 7.08 – 7.04 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.61 – 6.57 (m, 1H), 6.51 – 6.49 (m, 2H), 6.24 (d, *J* = 15.8 Hz, 1H), 5.75 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.69 (s, 3H), 3.13 – 2.96 (m, 2H), 2.11 – 2.02 (m, 1H), 1.72 – 1.64 (m, 1H), 1.58 – 1.47 (m, 1H), 1.47 – 1.37 (m, 1H), 1.34 – 1.24 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.9, 148.4, 132.3, 130.5, 129.9, 129.3, 127.2, 117.2, 114.0, 112.9, 55.4, 43.3, 42.4, 35.0, 28.6, 11.9. **HRMS (ESI-TOF)** Calcd for $C_{20}H_{26}NO$ $(M+H)^+$ 296.2009. Found 296.2015. **HPLC** (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 7.3 min (major) and 8.0 min (minor).



3a (90% ee), 0.3 mmol **10**, 70% yield, 87% ee

Following literature procedure,[9] a solution of **3a** (93.0 mg, 0.3 mmol, 1.0 equiv) in dry DMF (3.0 mL) was added into a suspension of NaH (60% dispersion in mineral oil, 18.0 mg, 0.6 mmol) in dry DMF (1.0 mL) at 0 ºC (in an ice-water bath). After stirring the resulting solution for 15 min, benzyl bromide (150.0 mg, 0.9 mmol, 3.0 equiv) was added dropwise. The ice bath was then removed, and the reaction mixture was stirred at room temperature monitored by TLC analysis (3 h). Then DMF was removed under reduced pressure, and the resulting yellow residual was treated with water (20.0 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried over anhydrous sodium sulfate, and the volatile components were removed under reduced pressure. The residual was treated with silica gel column chromatography (PE: EtOAc = 8: 1) to give the pure product.

Lithium aluminum hydride (23.0 mg, 1.0 M in Et_2O, 3.0 equiv) was added dropwise to a solution of the product obtained above (80.0 mg, 0.2 mmol, 1.0 equiv) in THF (2.0 mL) at 0 ˚C in a 10-mL Schlenk tube. Next, the reaction mixture was allowed to warm to room temperature, and then it was heated to 85 ˚C. After being stirred at 85 ˚C in the sealed Schlenk tube overnight, the reaction mixture was diluted with Et_2O (10.0 mL) and cooled to 0 °C. The reaction was then quenched in turn with H_2O (38.0 μL), 15% aqueous NaOH (38 μL), and H_2O (114.0 μL). Next, the suspension was filtered through a sintered funnel to remove the white solid. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE: EtOAc = 10:1) to afford the pure product **10** as colorless oil (31.0 mg, 69% yield, 87% ee). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.82 (dd, *J* = 15.8, 9.1 Hz, 1H), 3.80 (s, 3H), 3.74 – 3.61 (m, 2H), 2.19 – 2.09 (m, 1H), 1.81 – 1.71 (m, 1H), 1.66 – 1.53 (m, 2H), 1.41 – 1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.9, 132.5, 130.5, 129.8, 127.2, 114.1, 61.6, 55.5, 42.2, 38.2, 28.7, 11.9. **HRMS (ESI-TOF)** Calcd for $C_{14}H_{21}O_2$ $(M+H)^+$ 221.1536. Found 221.1541. **HPLC** (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow rate = 1 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 7.2 min (minor).



3a (90% ee), 0.1 mmol

11, 73% yield, 87% ee

Following literature procedure,[10] olefin **3a** (31.0 mg, 0.1 mmol, 1.0 equiv) and $NaIO_4$ (107.0 mg, 0.5 mmol) in a 1:1 mixture of CCl_4 and CH_3CN (2.0 mL). Add a solution of $RuCl_3$ (1.0 mg, 0.001 mol) in H_2O (1.0 mL) to the flask. Stir the reaction mixture vigorously. After completion of the reaction (2.0 hour), add EtOAc (20.0 mL) and $NaHCO_3$ (saturated aqueous solution, 20.0 mL) to the reaction. Extract the organic phase with $NaHCO_3$ (saturated aqueous solution, 4 × 10.0 mL). The combined aqueous phase was acidified with concentrated HCl aq. until pH value reached 2, which was extracted with EtOAc (4 × 10.0 mL). The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE: EtOAc: CH_3COOH = 80: 20: 1) to afford the pure product **11** as white solid (16.0 mg, 73% yield, 90% ee). (ee value was determined by corresponding methyl ester). **^{1}H NMR** (400 MHz, Acetonitrile-d_3) δ 9.50 (s, 1H), 8.40 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.05 (m, 1H), 2.88 – 2.73 (m, 1H), 2.66 (dd, *J* = 15.6, 9.0 Hz, 1H), 2.49 (dd, *J* = 15.6, 4.9 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.46 – 1.41 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Acetonitrile-d_3) δ 175.5, 170.0, 138.4, 128.5, 123.4, 119.1, 42.0, 37.3, 24.3, 10.4. **HRMS (ESI-TOF)** Calcd for $C_{12}H_{16}NO_3$ $(M+H)^+$ 222.1125. Found 222.1131. **HPLC** (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 85/15, flow rate = 1 mL/min, detection at 254 nm) retention time = 6.4 min (major) and 7.4 min (minor).

IX. X-Ray diffraction data of 4q

X-ray structure of 4q (CCDC 2131923)

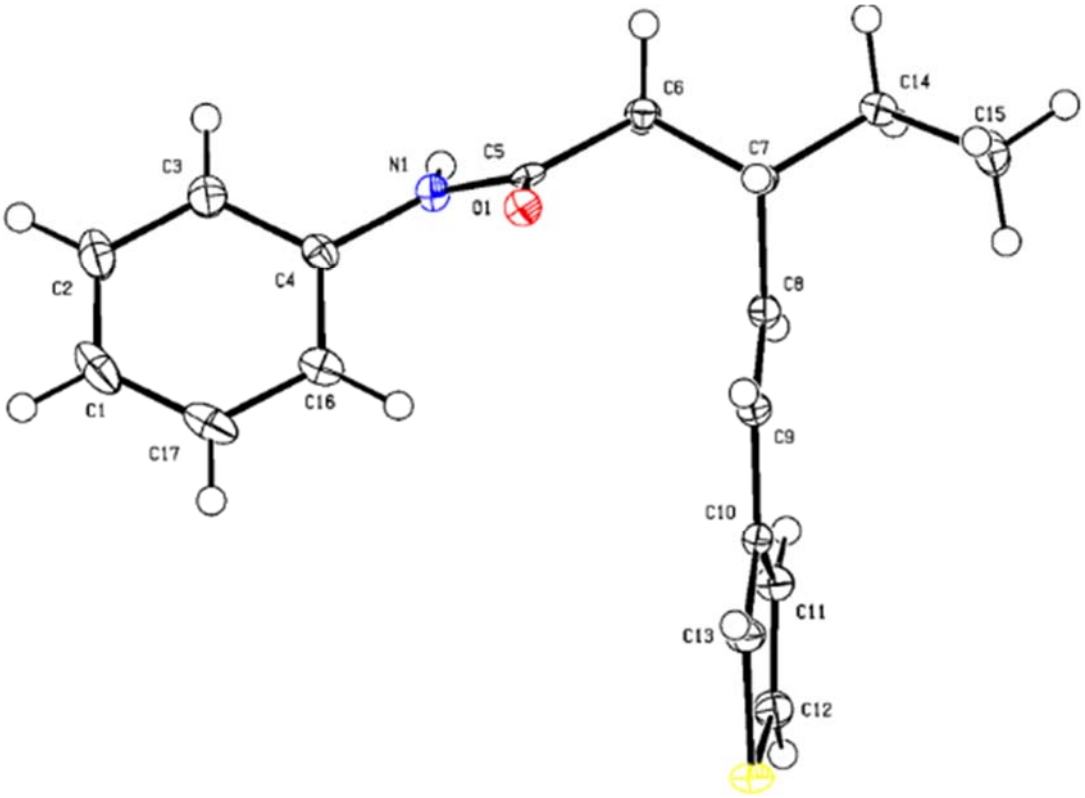


Table S8.Crystal data and structure refinement for cxy3456_0m (4q)

Identification code	cxy3456_0m
Empirical formula	$C_{17}H_{19}NOS$
Formula weight	285.39
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.8663(14)
b/Å	8.7930(14)
c/Å	10.1594(16)
α/°	90
β/°	108.871(5)
γ/°	90
Volume/Å^3	749.5(2)
Z	2
ρ_{calc}g/cm^3	1.265

μ/mm^{-1}	1.865
F(000)	304.0
Crystal size/mm^3	0.42 × 0.42 × 0.38
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.198 to 136.874
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$
Reflections collected	11797
Independent reflections	2740 [R_{int}= 0.0341, R_{sigma}= 0.0297]
Data/restraints/parameters	2740/1/183
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0657
Final R indexes [all data]	R_1 = 0.0262, wR_2 = 0.0658
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.18
Flack parameter	-0.001(7)

X. References

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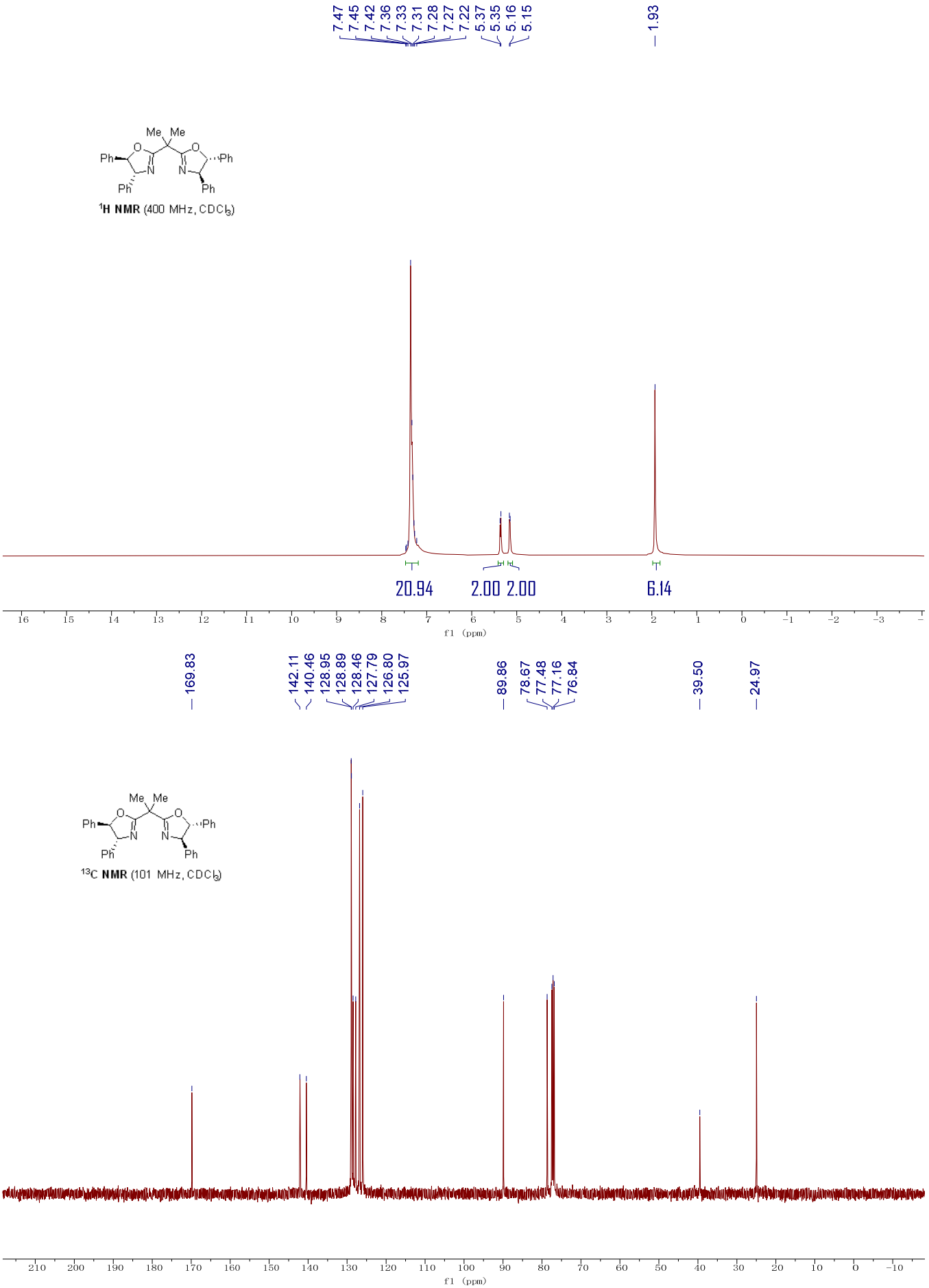
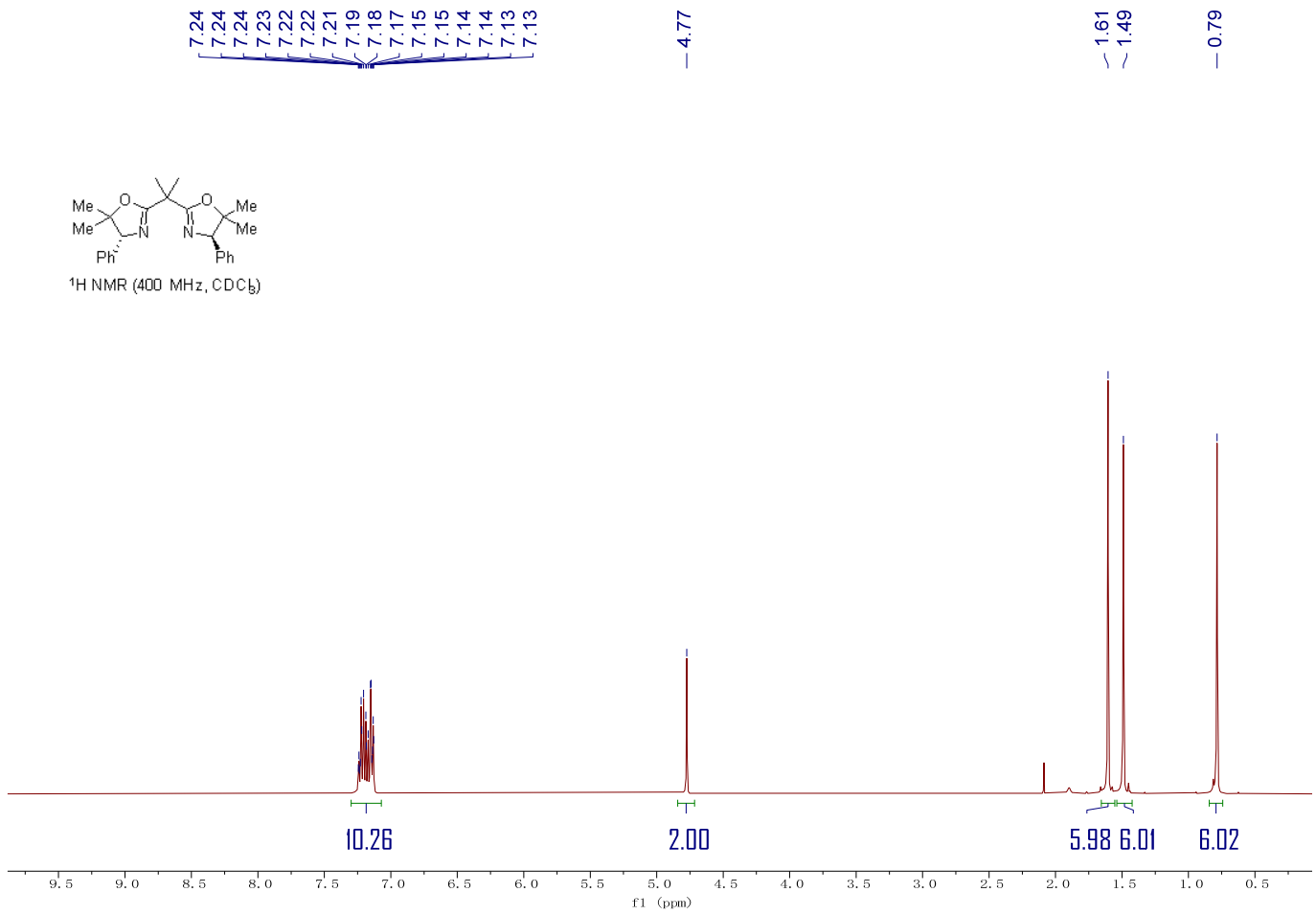
XI.^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

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7.24
7.24
7.23
7.22
7.22
7.21
7.19
7.18
7.17
7.15
7.15
7.14
7.14
7.13
7.13
4.77
1.61
1.49
0.79
Me
Me
O
N
O
Me
Me
Ph
Ph
1H NMR (400 MHz, CDCl3)
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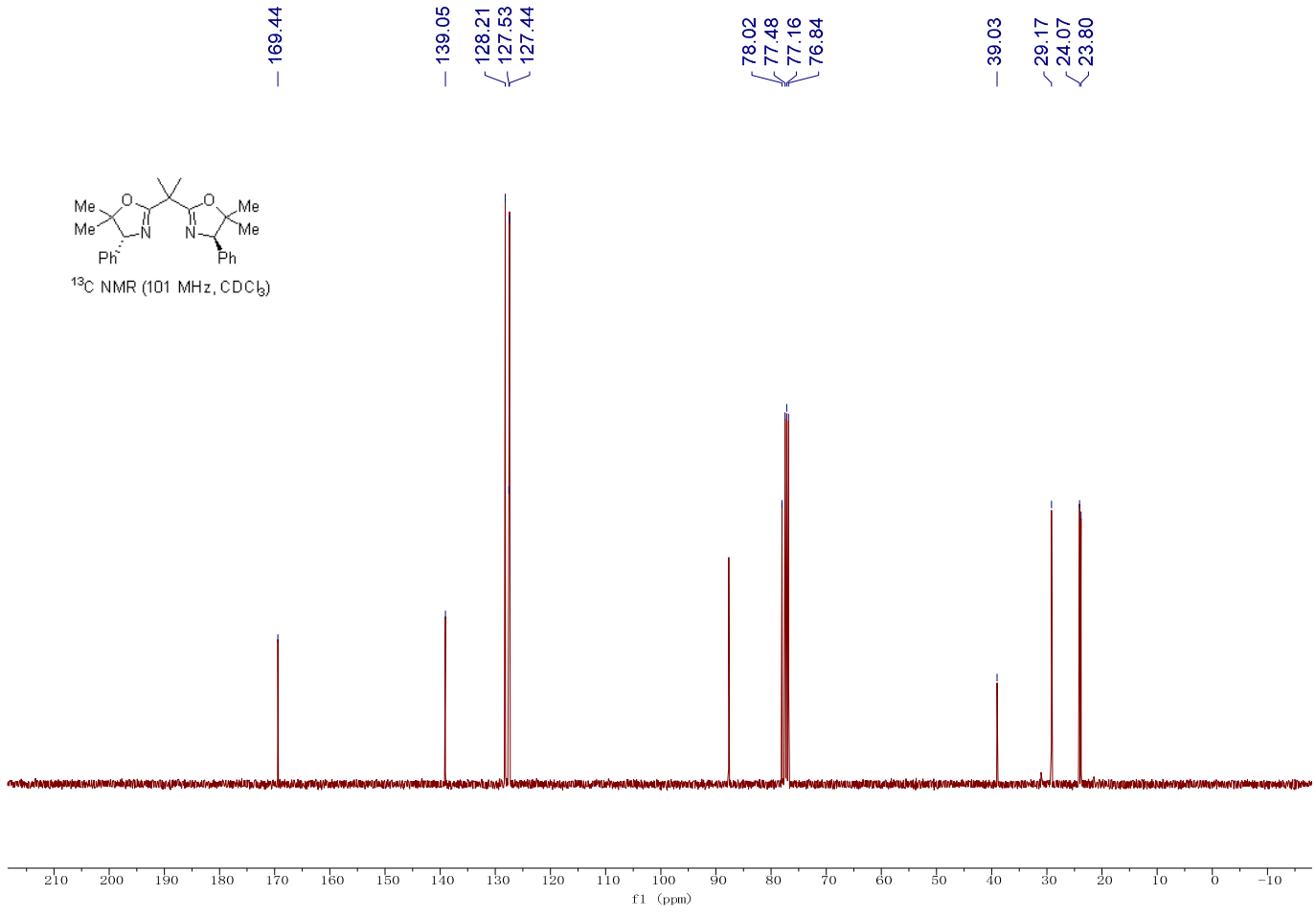
2.00
5.98
6.01
6.02
f1 (ppm)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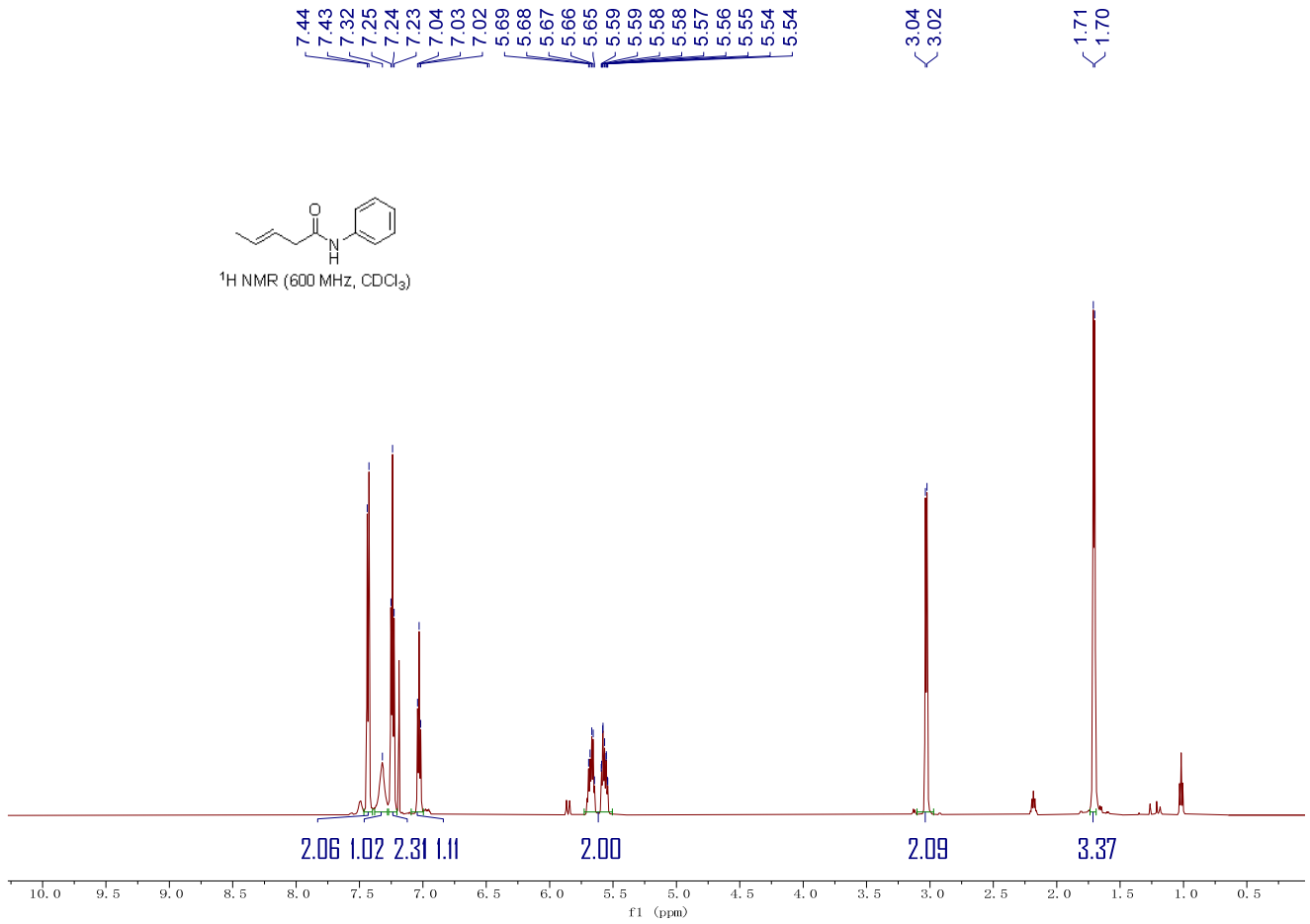
Me
Me
O
N
O
Me
Me
Ph
Ph
13C NMR (101 MHz, CDCl3)
f1 (ppm)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7.43
7.32
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7.03
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5.69
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5.65
5.59
5.59
5.58
5.58
5.57
5.56
5.55
5.54
5.54
3.04
3.02
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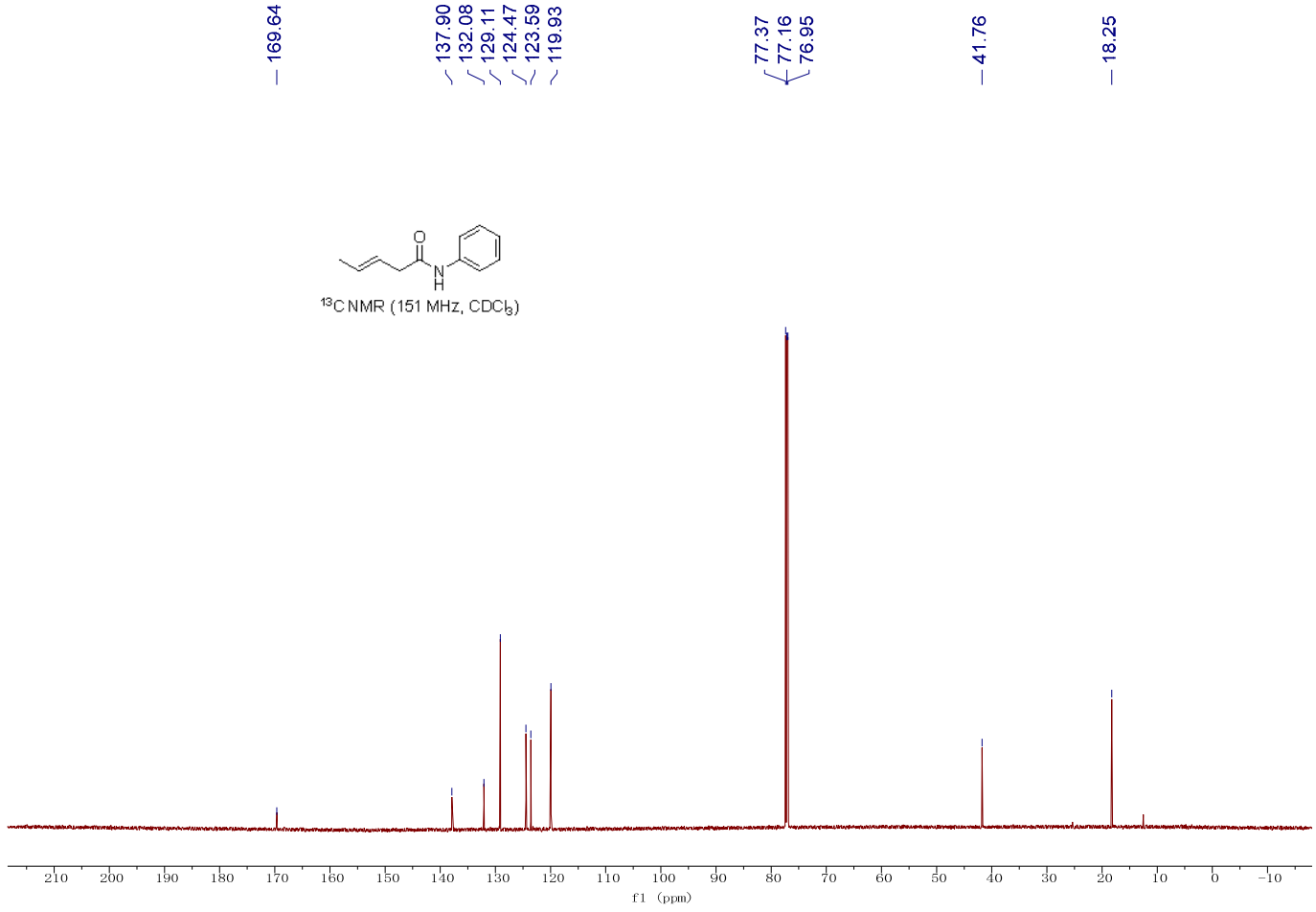
2.00
2.09
3.37
f1 (ppm)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41.76
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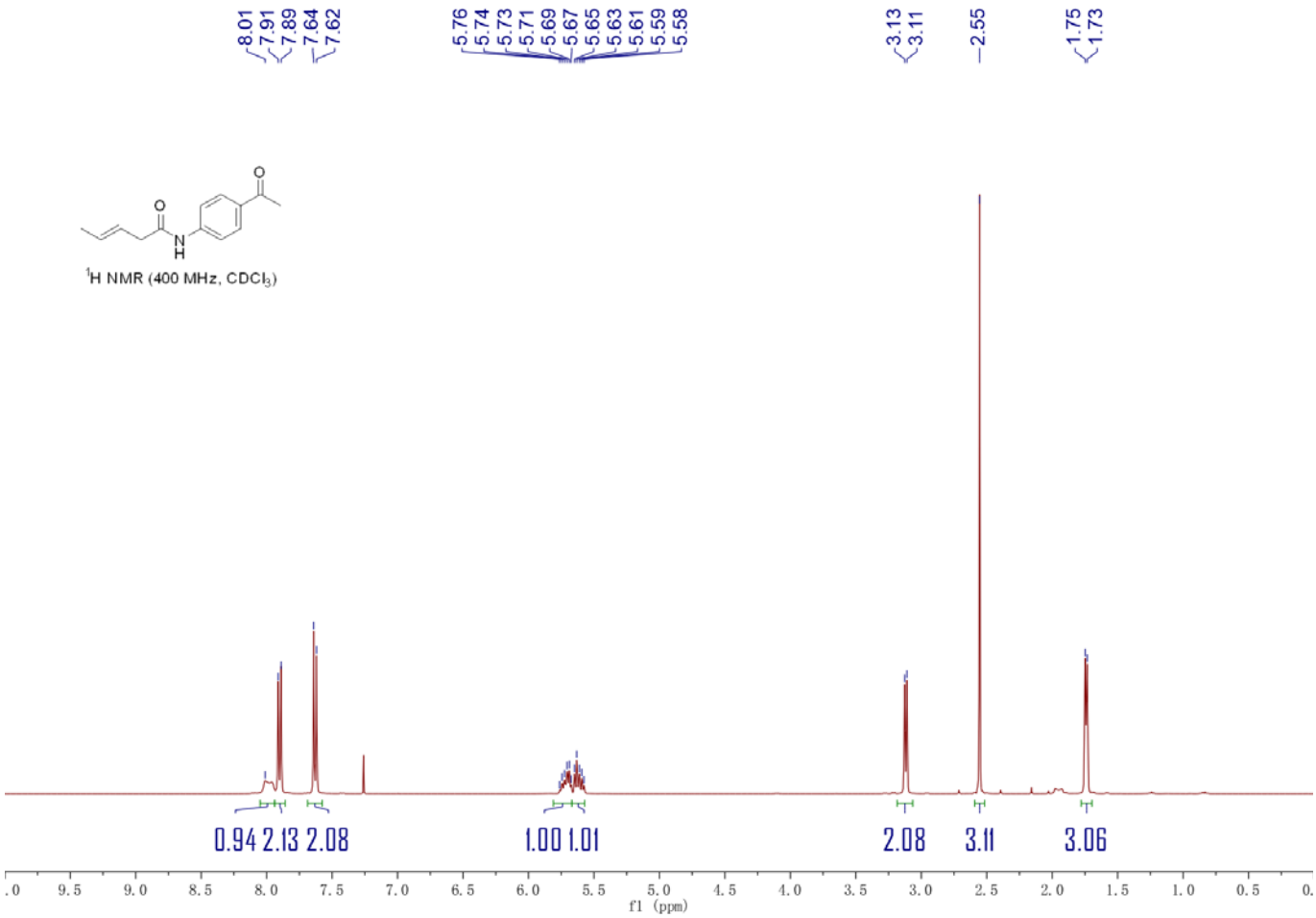
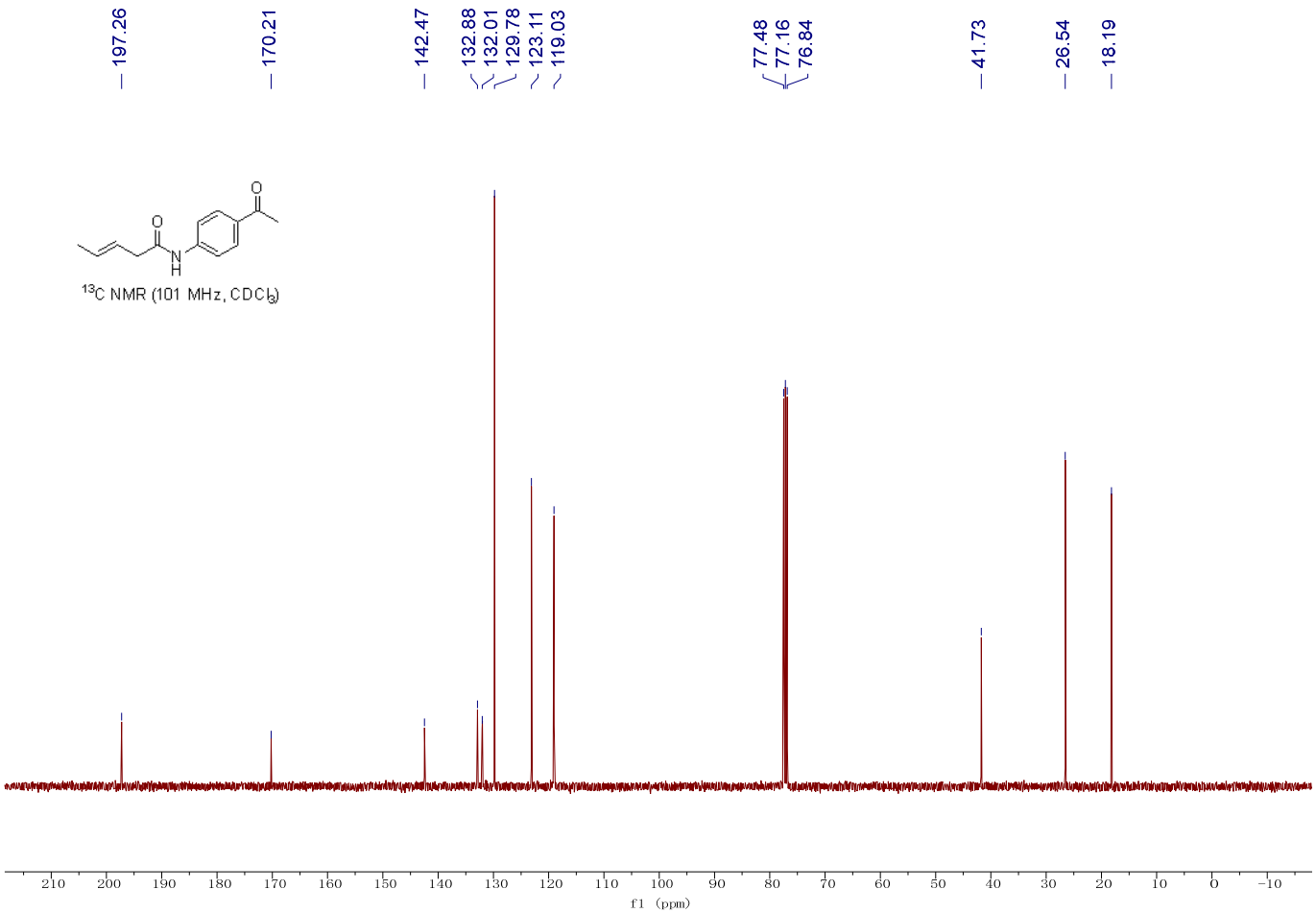
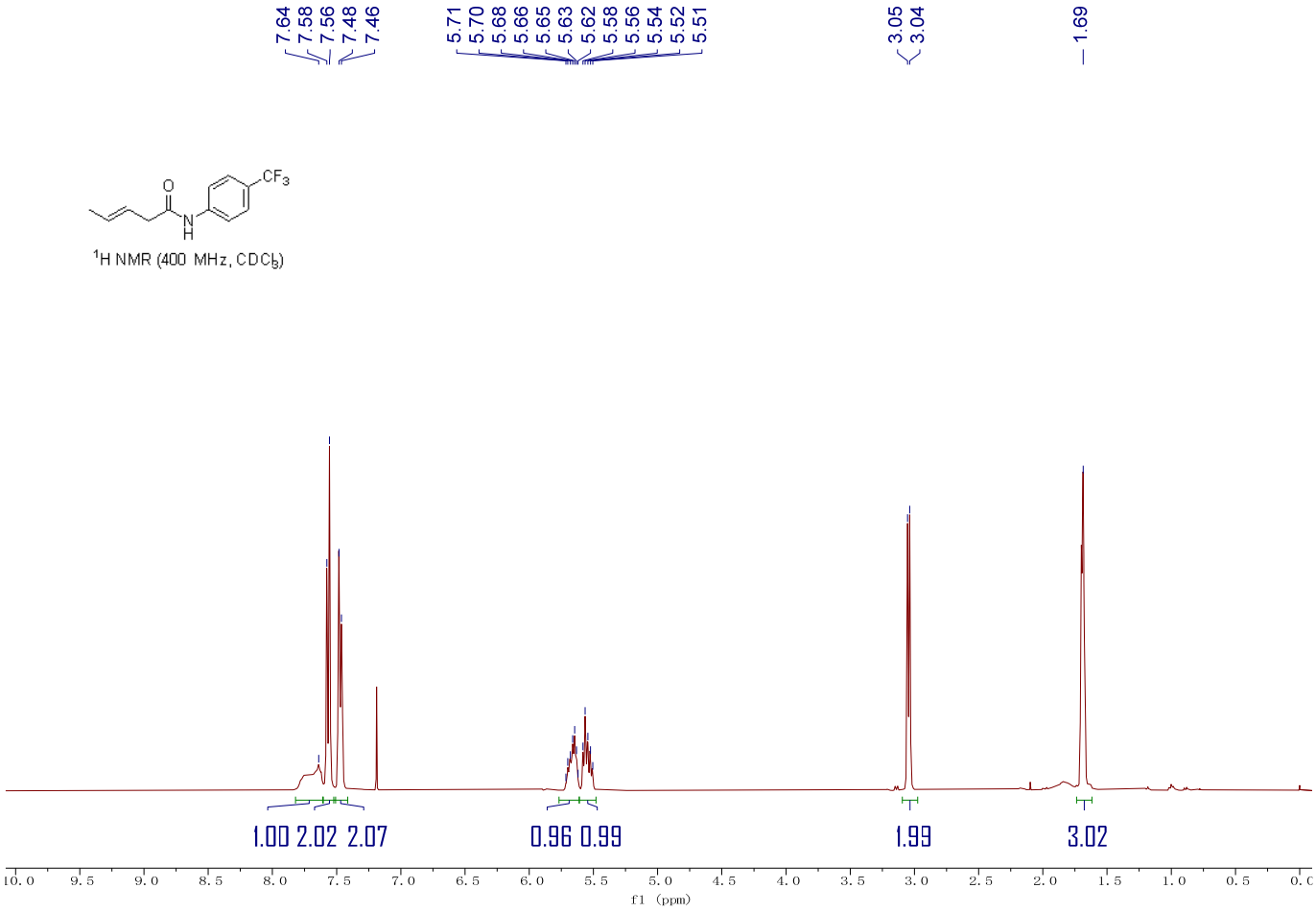
13C NMR (151 MHz, CDCl3)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)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5.70
5.68
5.66
5.65
5.63
5.62
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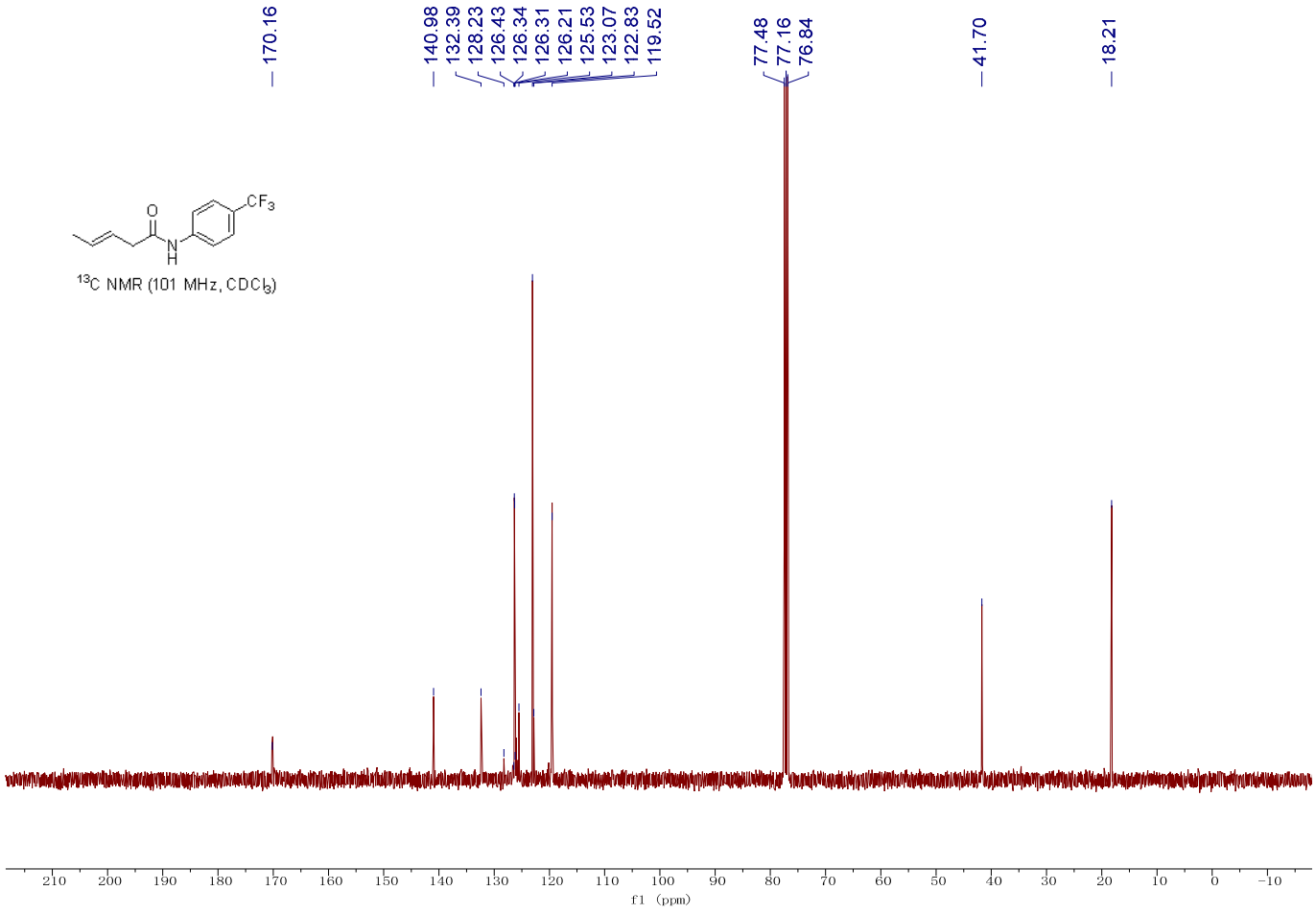
5.56
5.54
5.52
5.51
3.05
3.04
1.69
CF3
O
N
H
1H NMR (400 MHz, CDCl3)
1.00 2.02 2.07
0.96 0.99
1.99
3.02
f1 (ppm)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123.07
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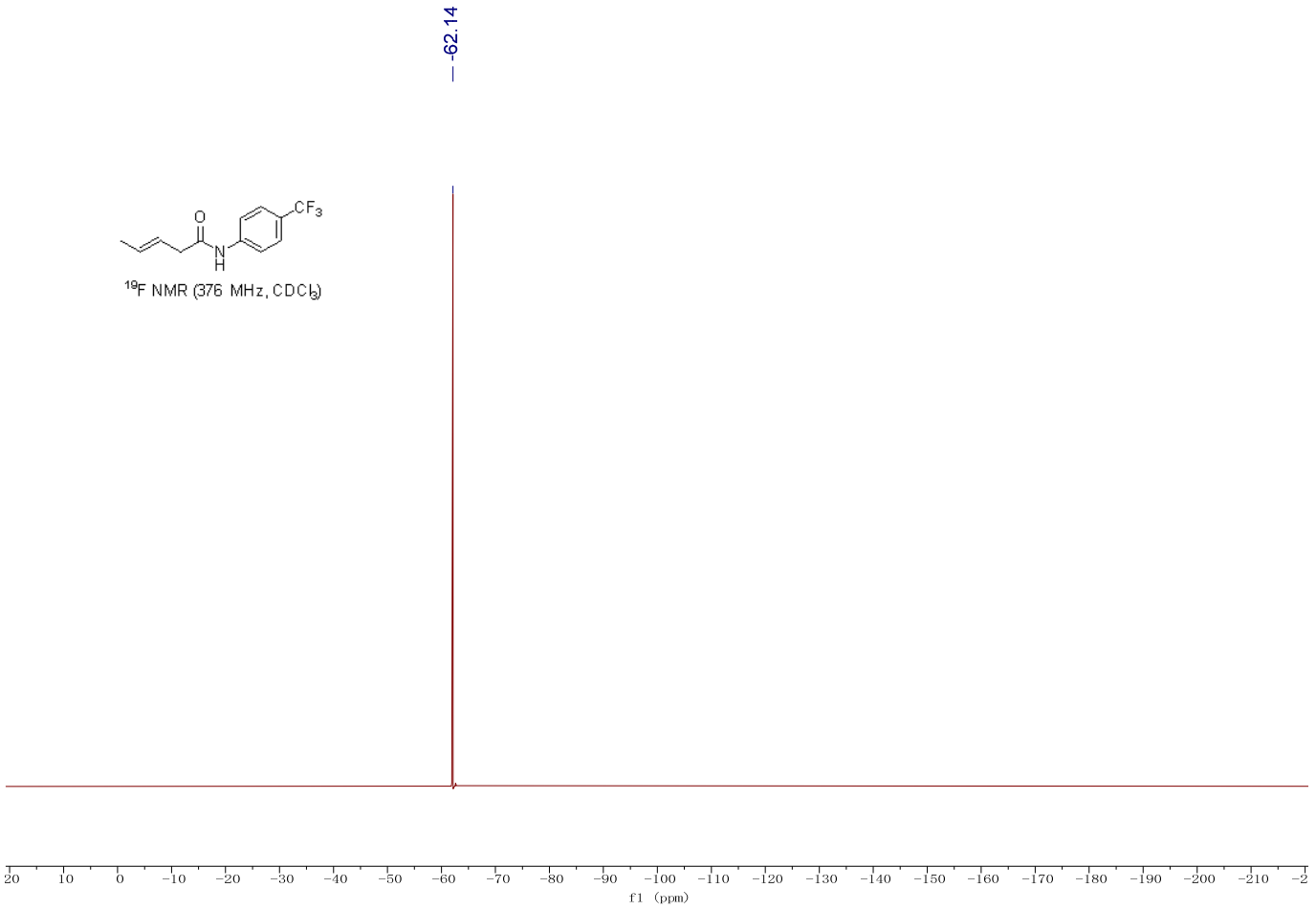
18.21
CF3
O
N
H
13C NMR (101 MHz, CDCl3)
f1 (ppm)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N
H
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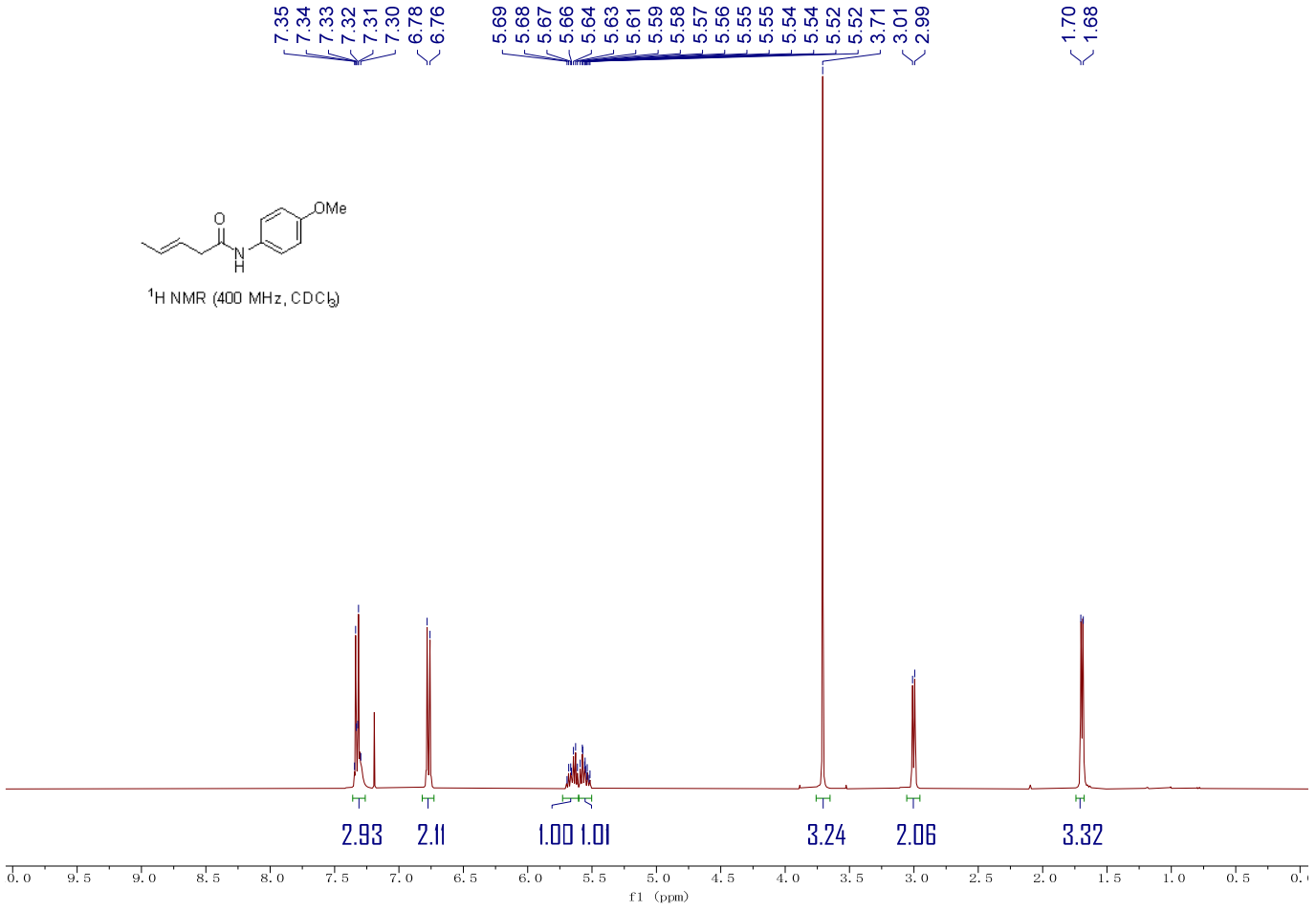
f1 (ppm)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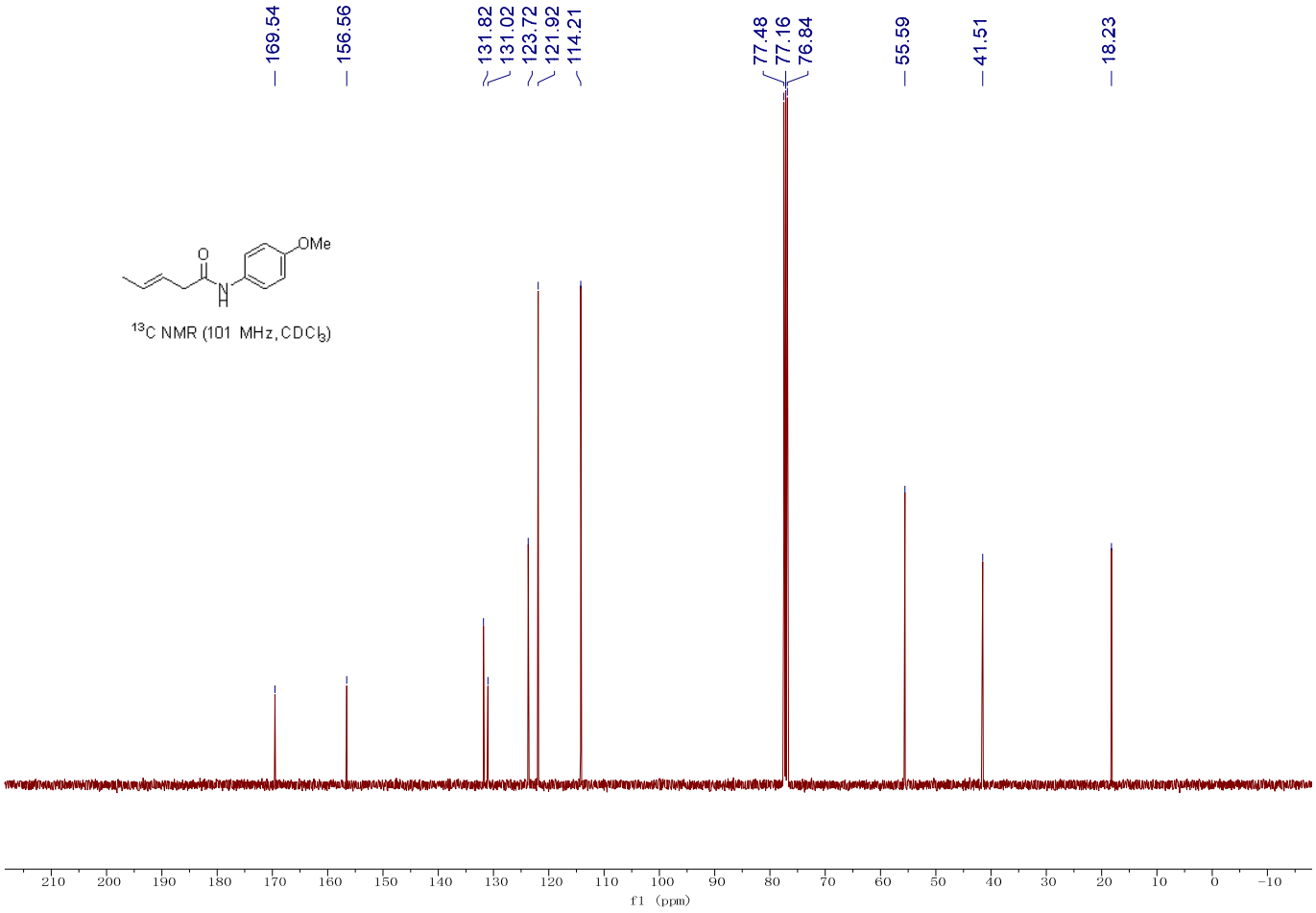
1.70 1.68
OMe
O
N
H
1H NMR (400 MHz, CDCl3)
2.93 2.11 1.00 1.01 3.24 2.06 3.32
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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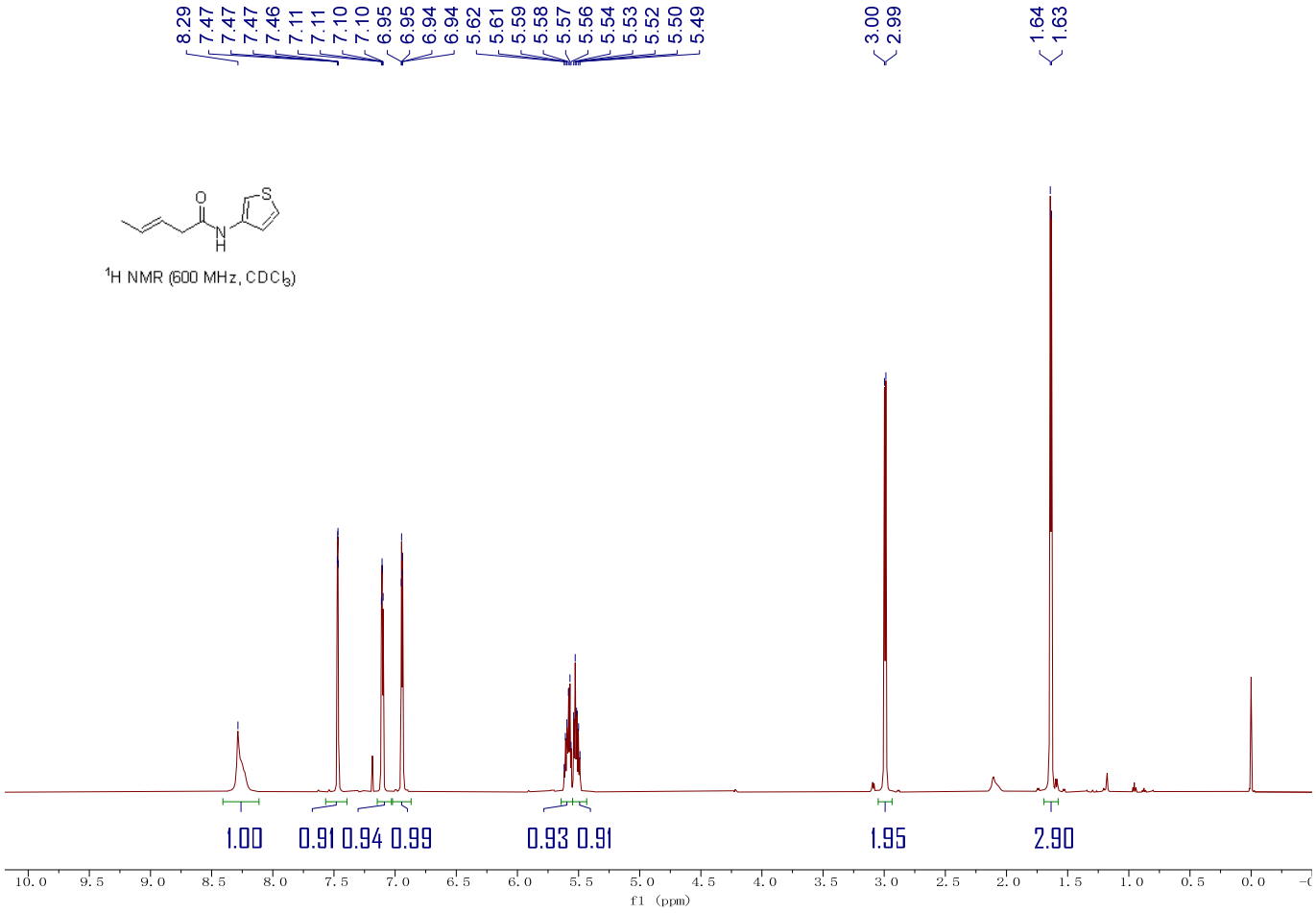
O
N
H
13C NMR (101 MHz, CDCl3)
f1 (ppm)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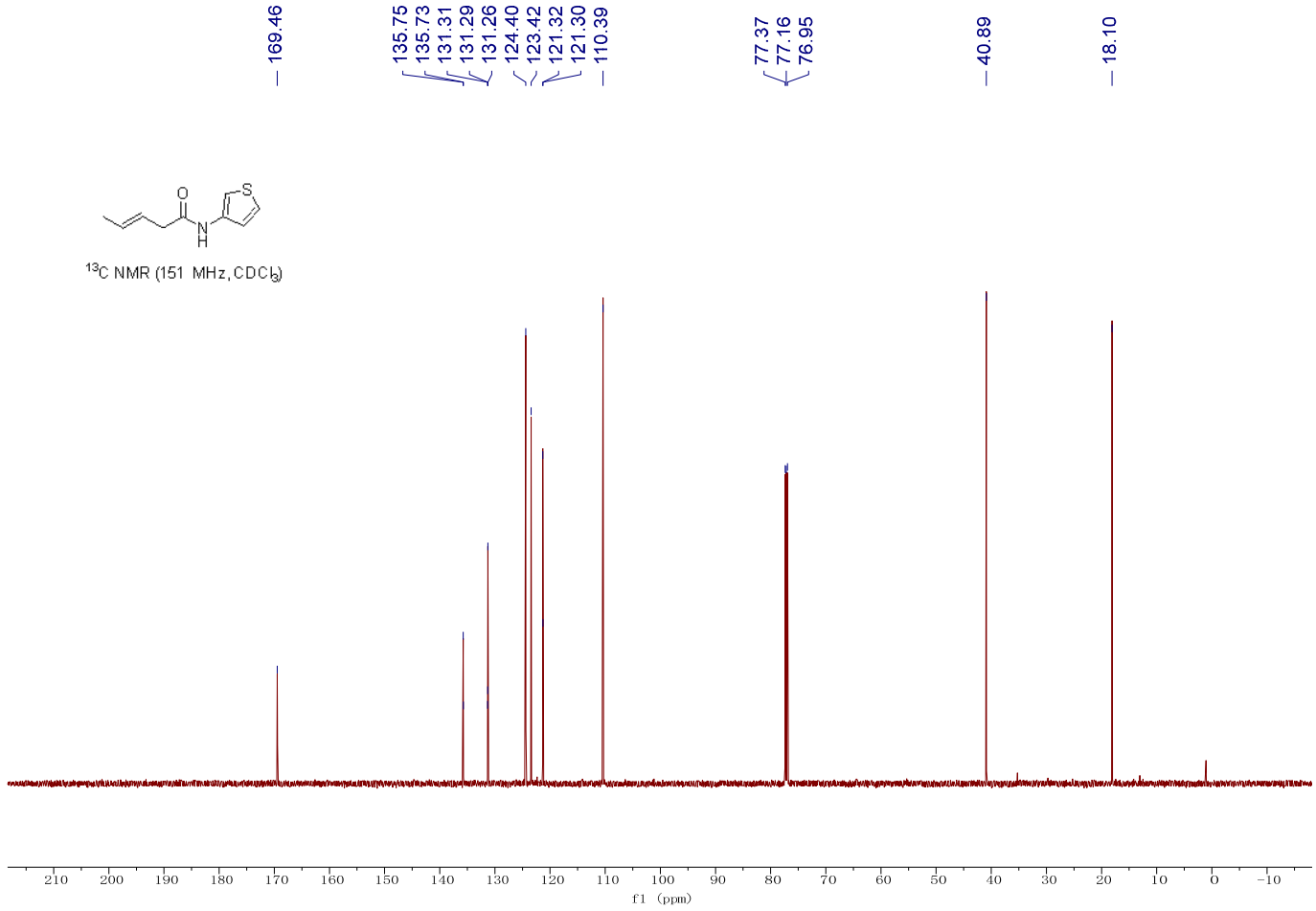
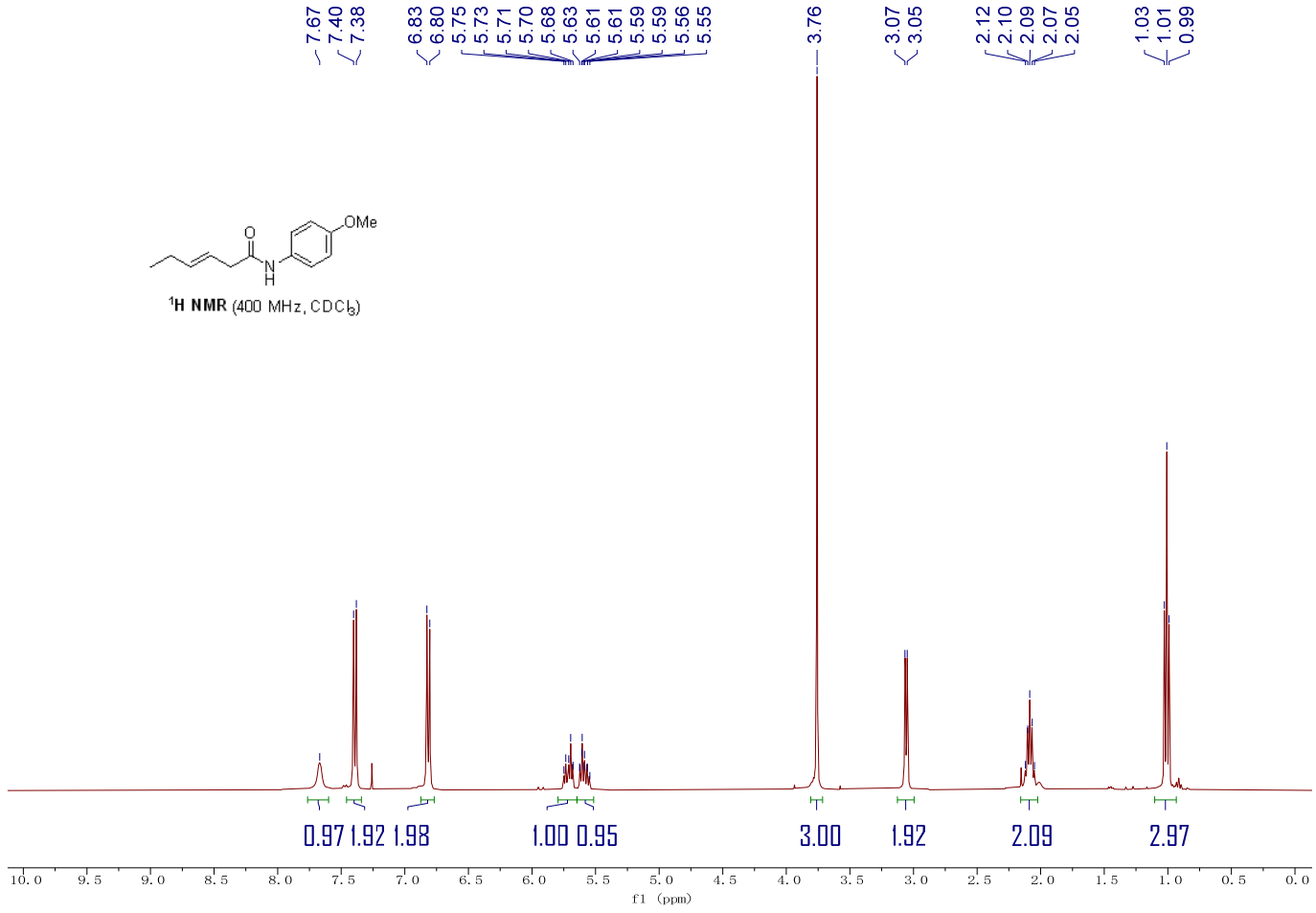
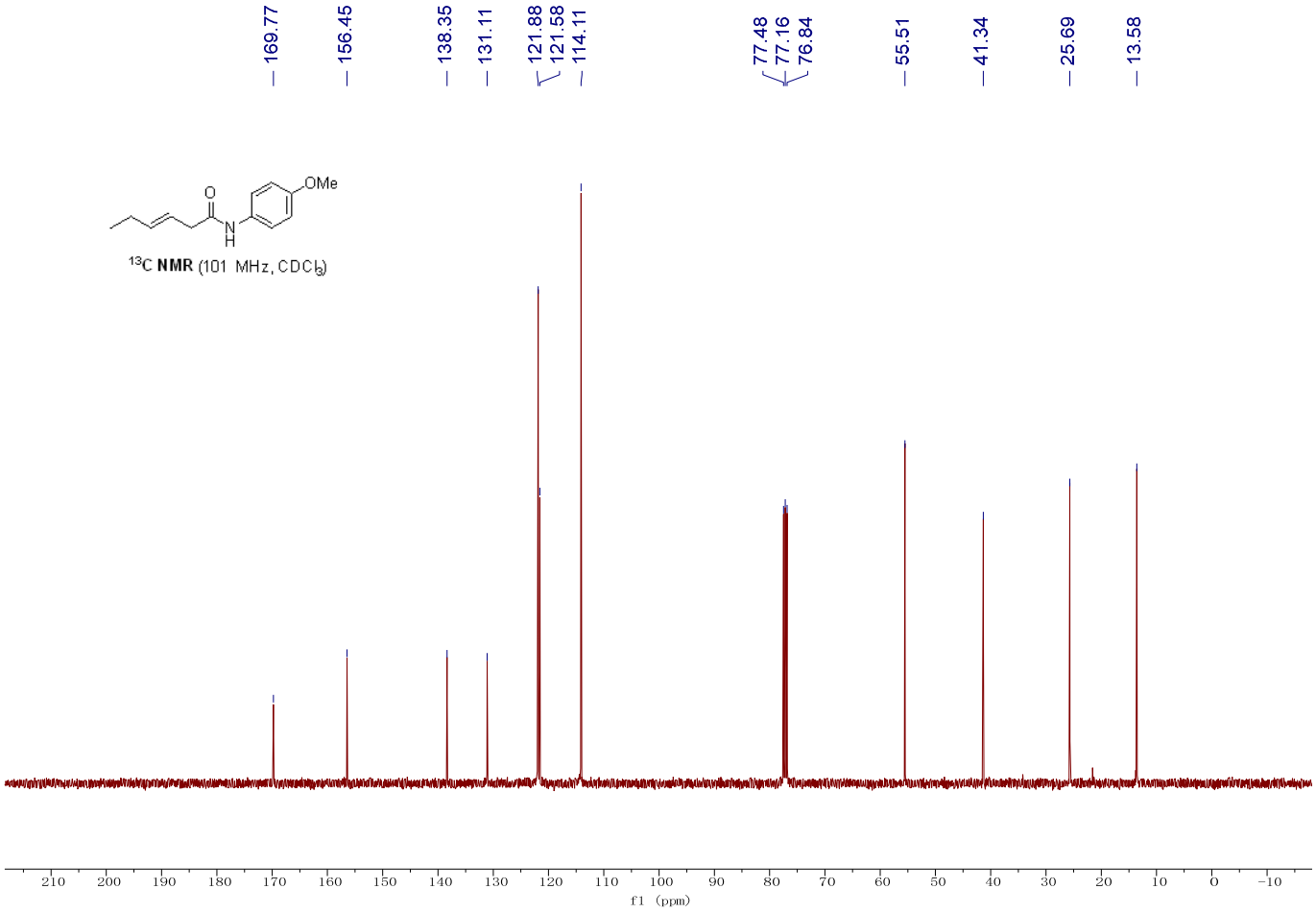
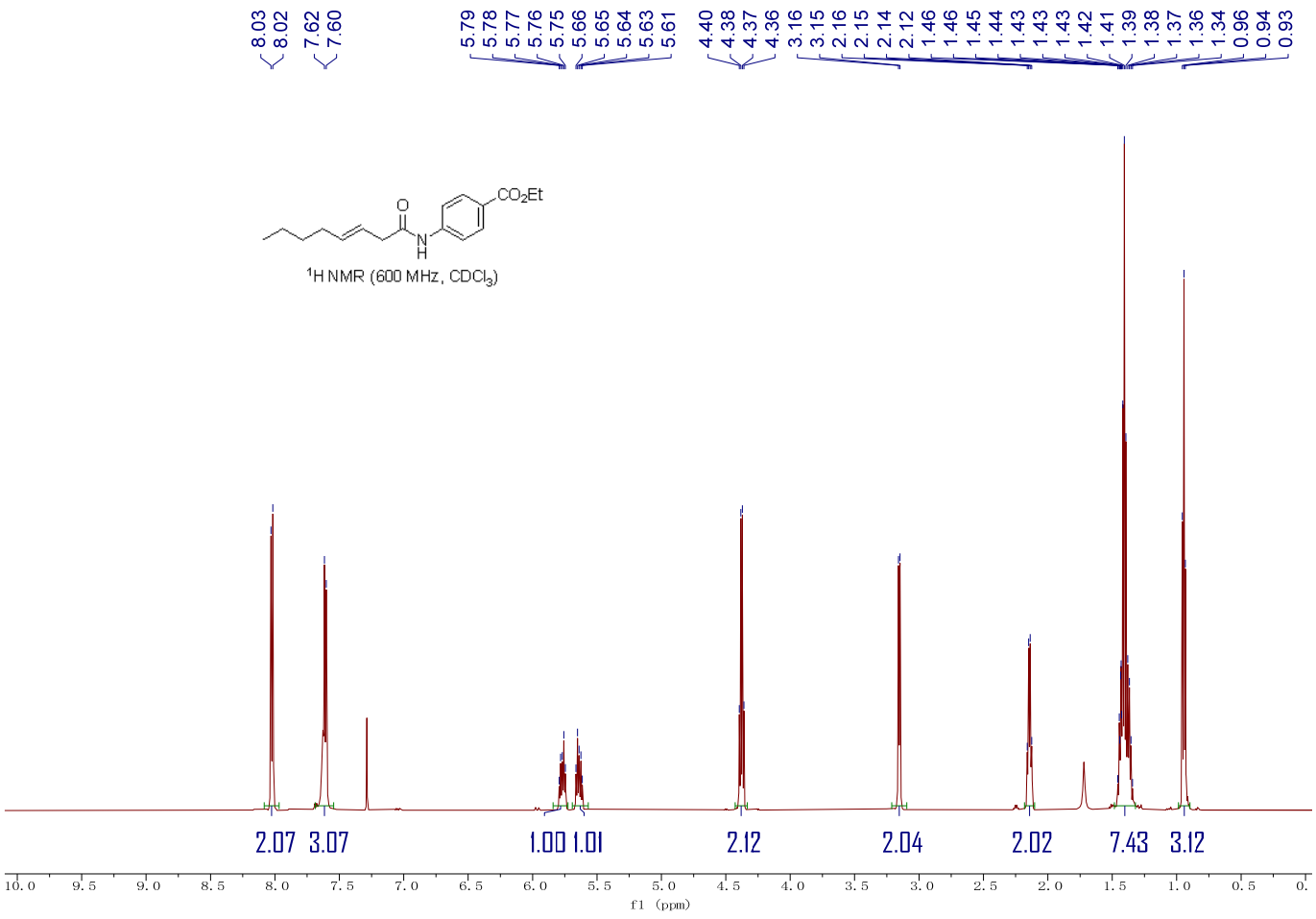
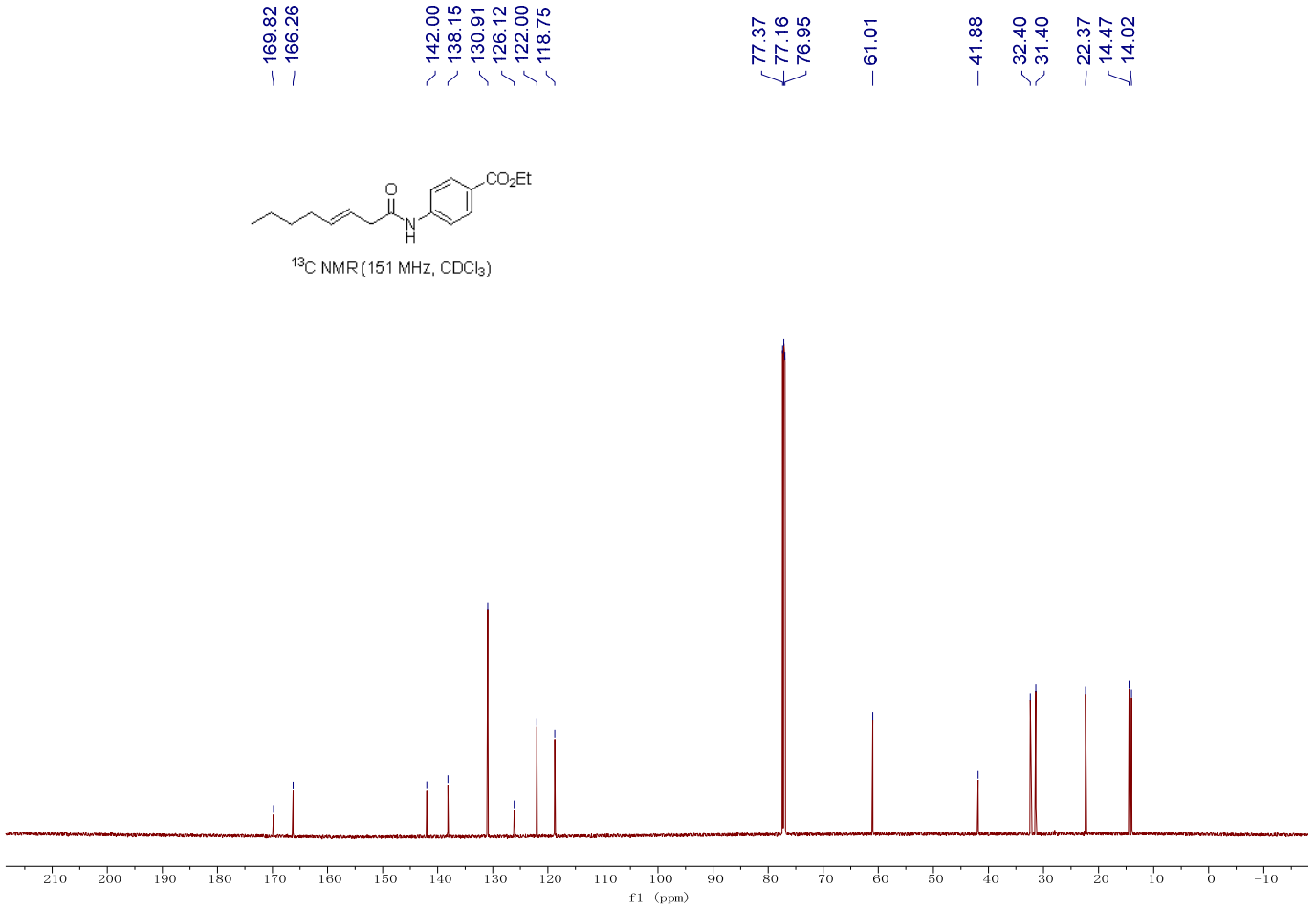
7.10
7.10
6.95
6.95
6.94
6.94
5.62
5.61
5.59
5.58
5.57
5.56
5.54
5.53
5.52
5.50
5.49
3.00
2.99
1.64
1.63
O
S
N
H
1H NMR (600 MHz, CDCl3)
1.00
0.91
0.94
0.99
0.93
0.91
1.95
2.90
f1 (ppm)

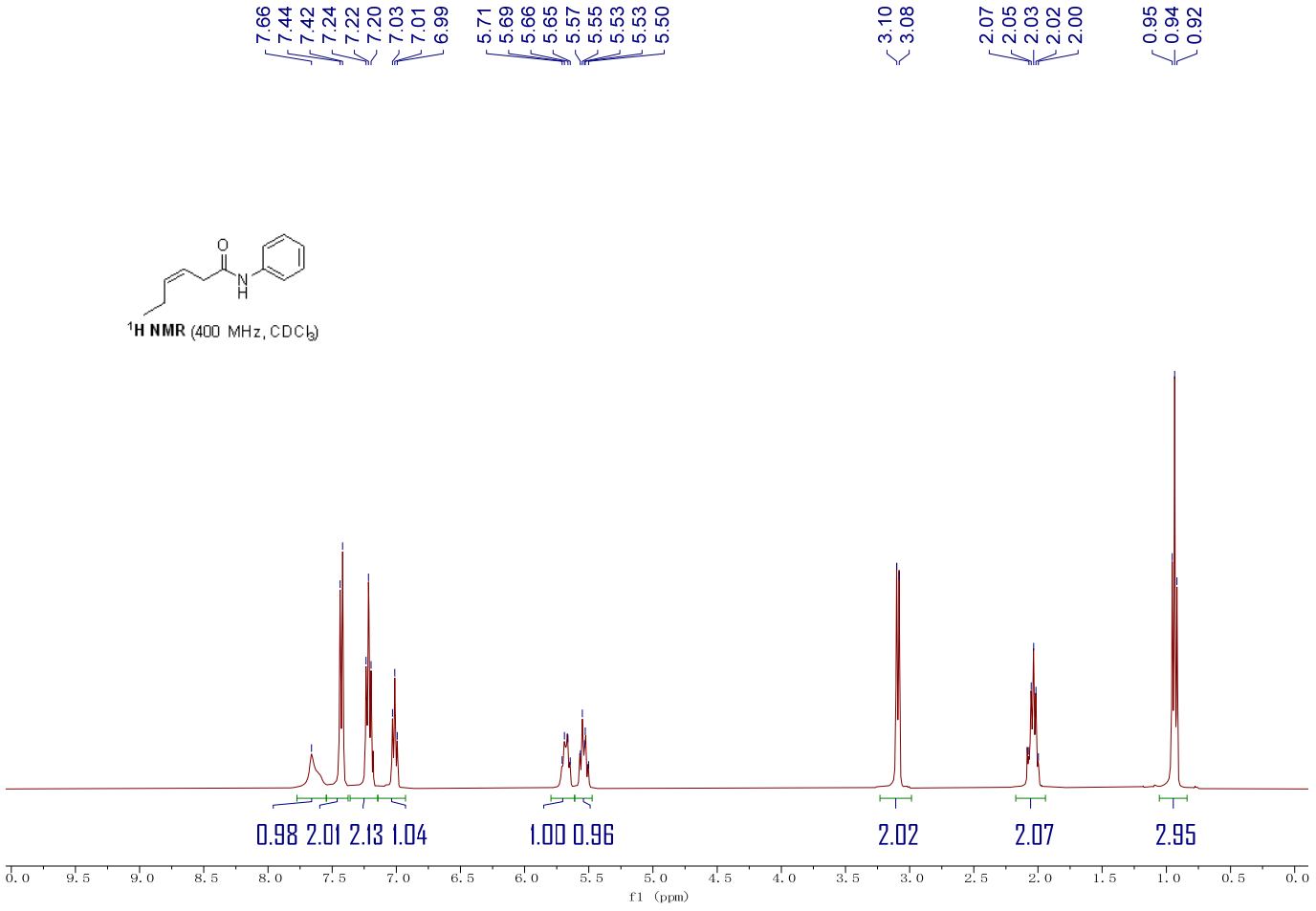

169.46
135.75
135.73
131.31
131.29
131.26
124.40
123.42
121.32
121.30
110.39
77.37
77.16
76.95
40.89
18.10
O
S
N
H
13C NMR (151 MHz, CDCl3)
f1 (ppm)

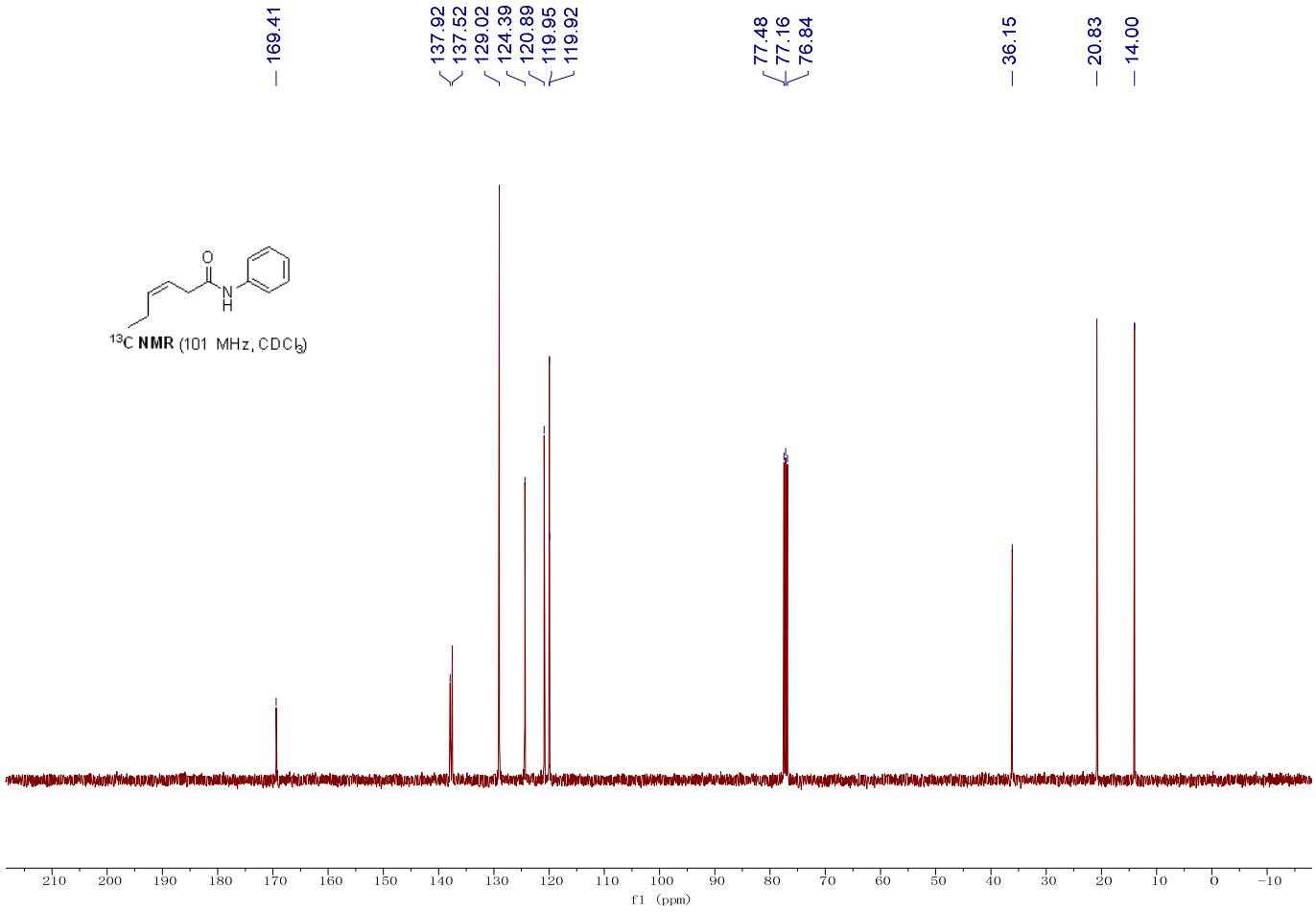

7.67
7.40
7.38
6.83
6.80
5.75
5.73
5.71
5.70
5.68
5.63
5.61
5.61
5.59
5.59
5.56
5.55
3.76
3.07
3.05
2.12
2.10
2.09
2.07
2.05
1.03
1.01
0.99
OMe
O
N
H
1H NMR (400 MHz, CDCl3)
0.97
1.92
1.98
1.00
0.95
3.00
1.92
2.09
2.97
f1 (ppm)

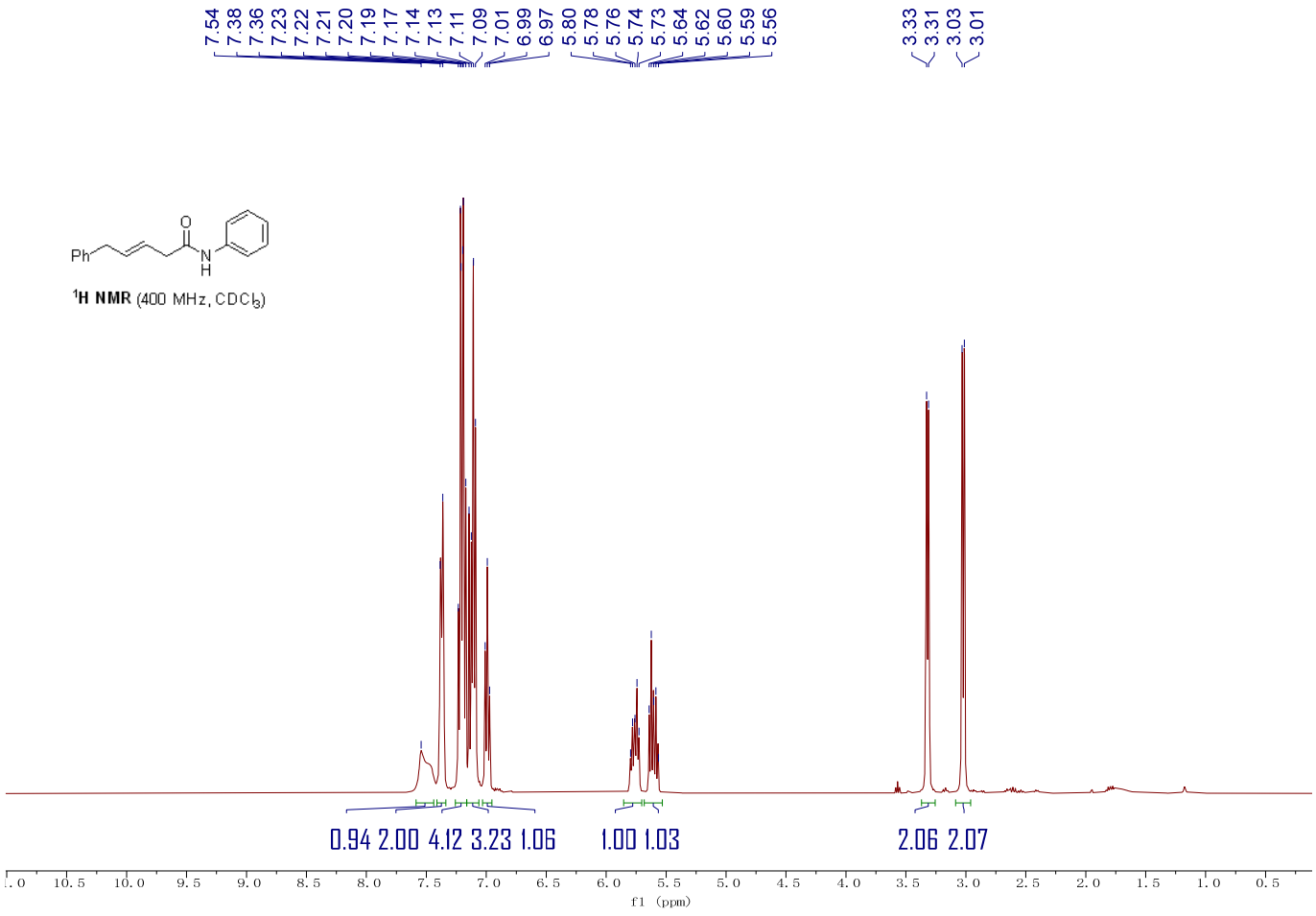

169.77
156.45
138.35
131.11
121.88
121.58
114.11
77.48
77.16
76.84
55.51
41.34
25.69
13.58
OMe
O
N
H
13C NMR (101 MHz, CDCl3)
f1 (ppm)

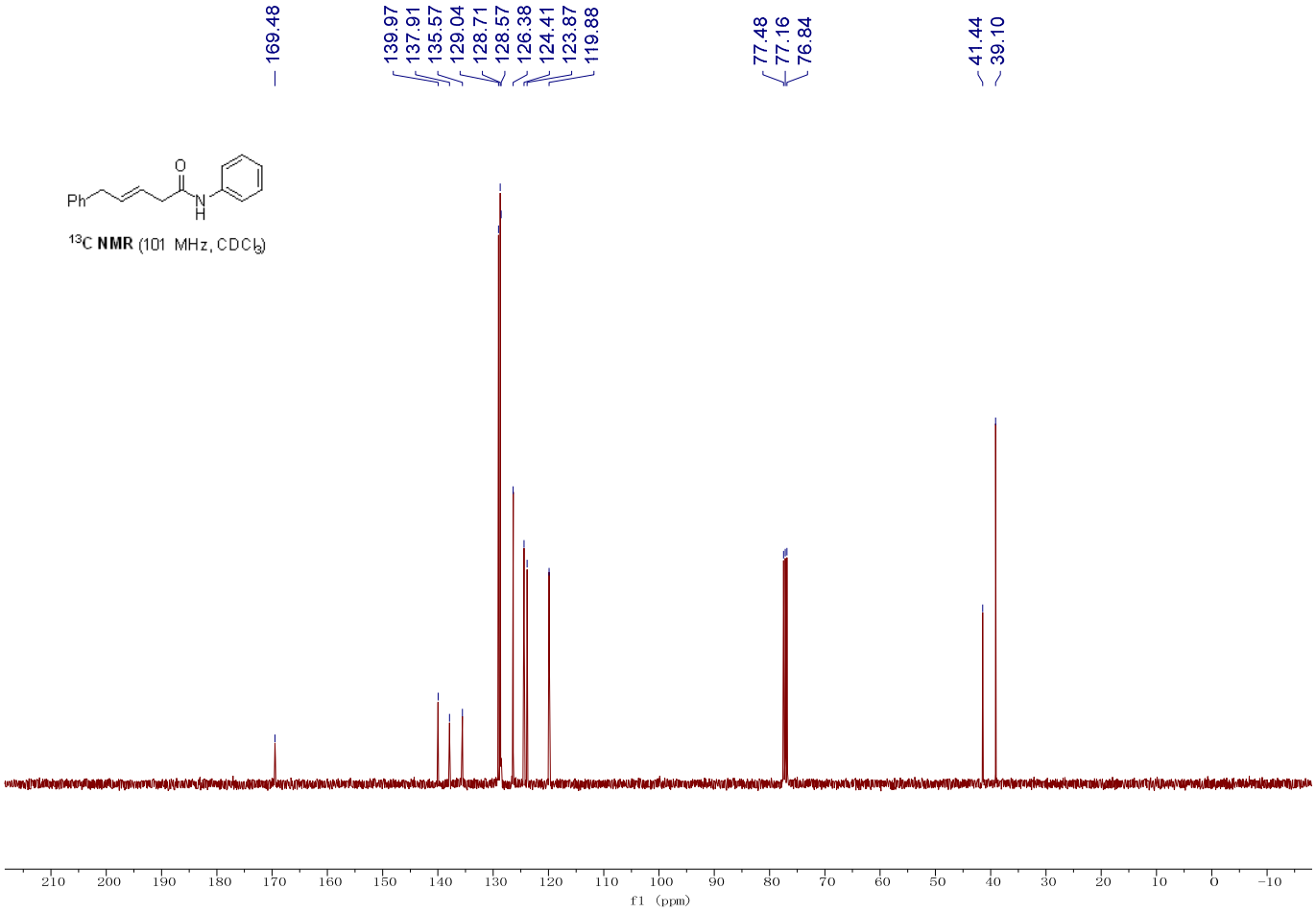

8.03
8.02
7.62
7.60
5.79
5.78
5.77
5.76
5.75
5.66
5.65
5.64
5.63
5.61
4.40
4.38
4.37
4.36
3.16
3.15
2.16
2.15
2.14
2.12
1.46
1.45
1.44
1.43
1.43
1.43
1.42
1.41
1.39
1.38
1.37
1.36
1.34
0.96
0.94
0.93
CO2Et
O
N
H
1H NMR (600 MHz, CDCl3)
2.07
3.07
1.00
1.01
2.12
2.04
2.02
7.43
3.12
f1 (ppm)

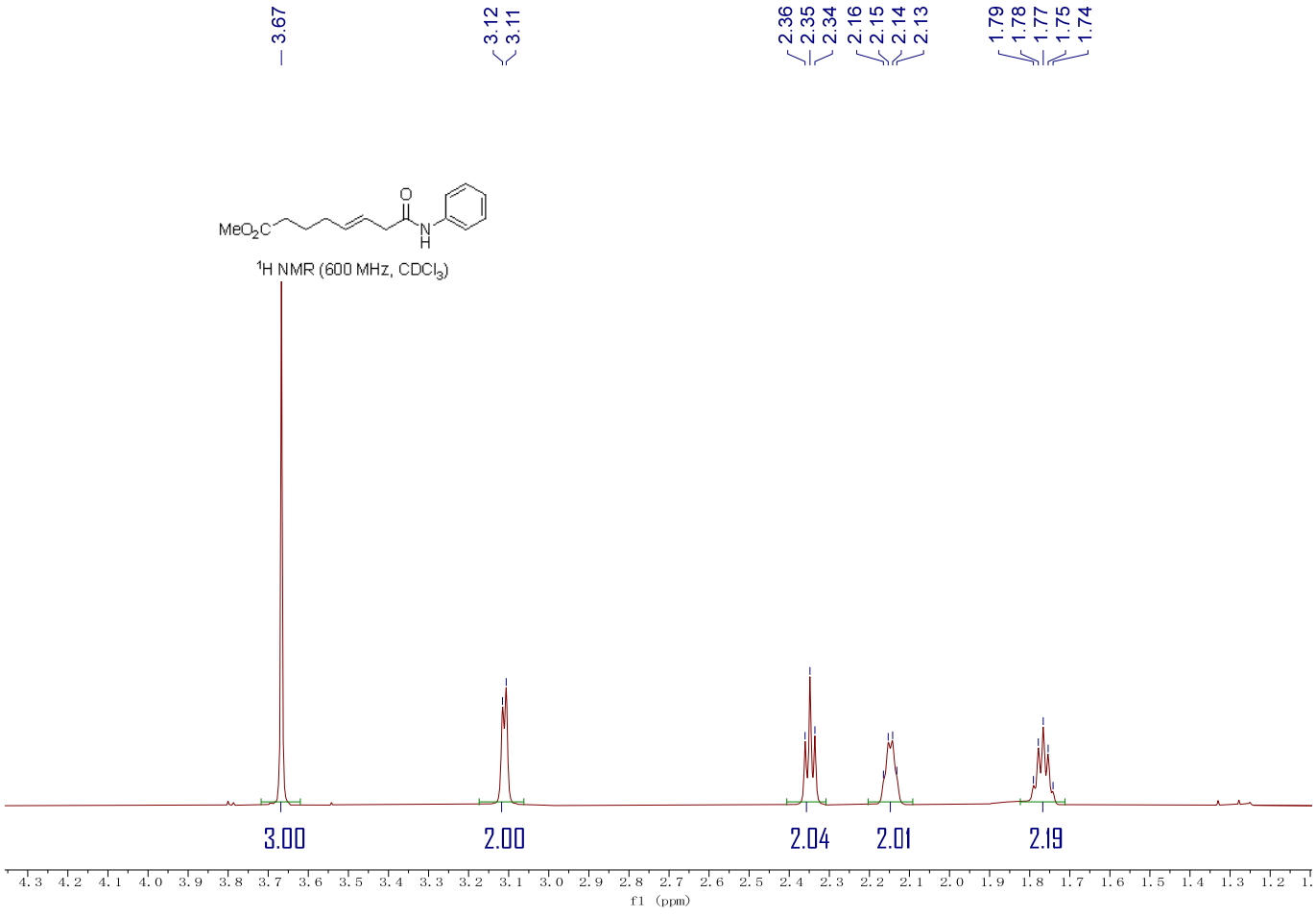

169.82
166.26
142.00
138.15
130.91
126.12
122.00
118.75
77.37
77.16
76.95
61.01
41.88
32.40
31.40
22.37
14.47
14.02
CO2Et
O
N
H
13C NMR (151 MHz, CDCl3)
f1 (ppm)

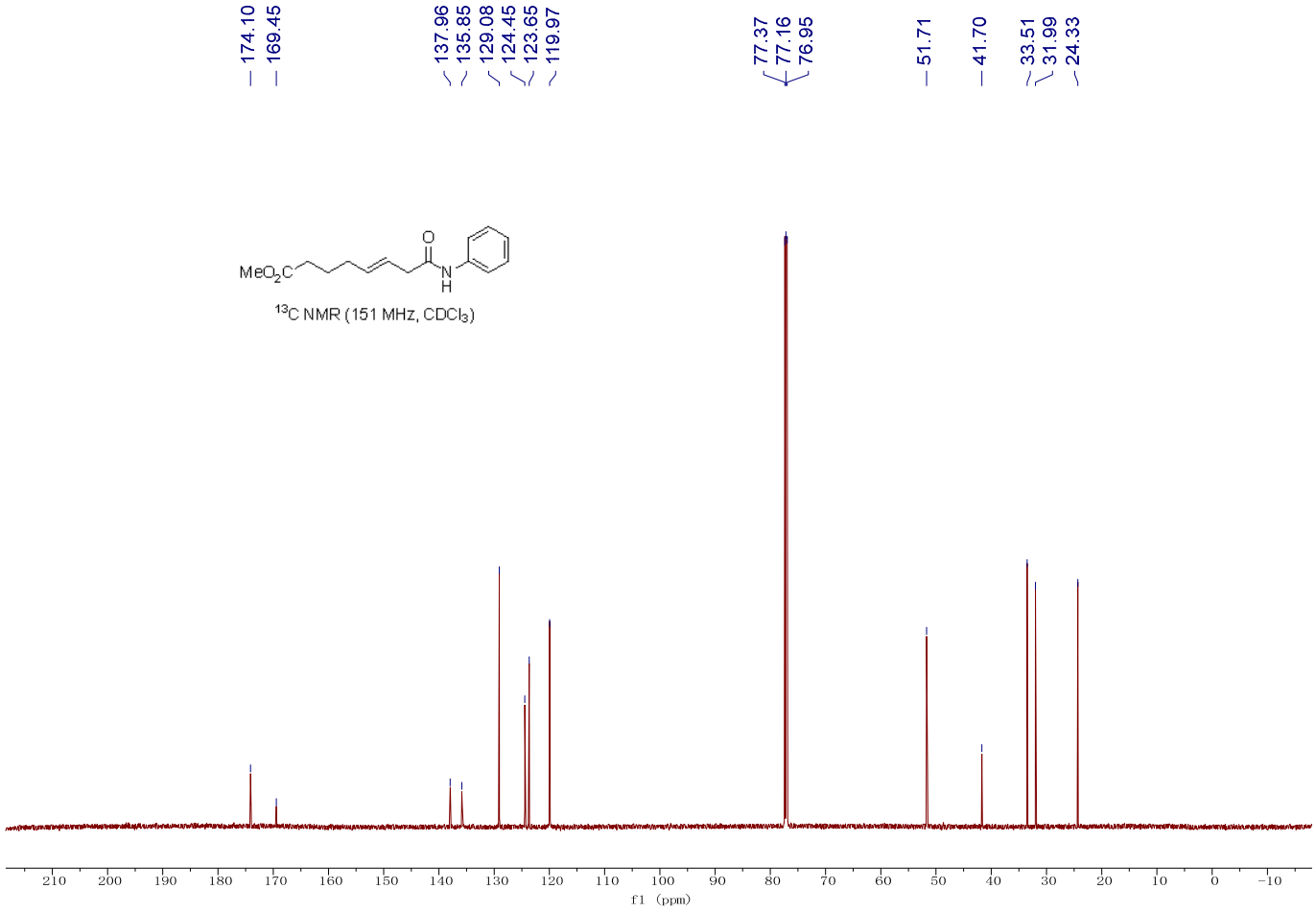

7.66
7.44
7.42
7.24
7.22
7.20
7.03
7.01
6.99
5.71
5.69
5.66
5.65
5.57
5.55
5.53
5.53
5.50
3.10
3.08
2.07
2.05
2.03
2.02
2.00
0.95
0.94
0.92
O
N
H
1H NMR (400 MHz, CDCl3)
0.98
2.01
2.13
1.04
1.00
0.96
2.02
2.07
2.95
f1 (ppm)

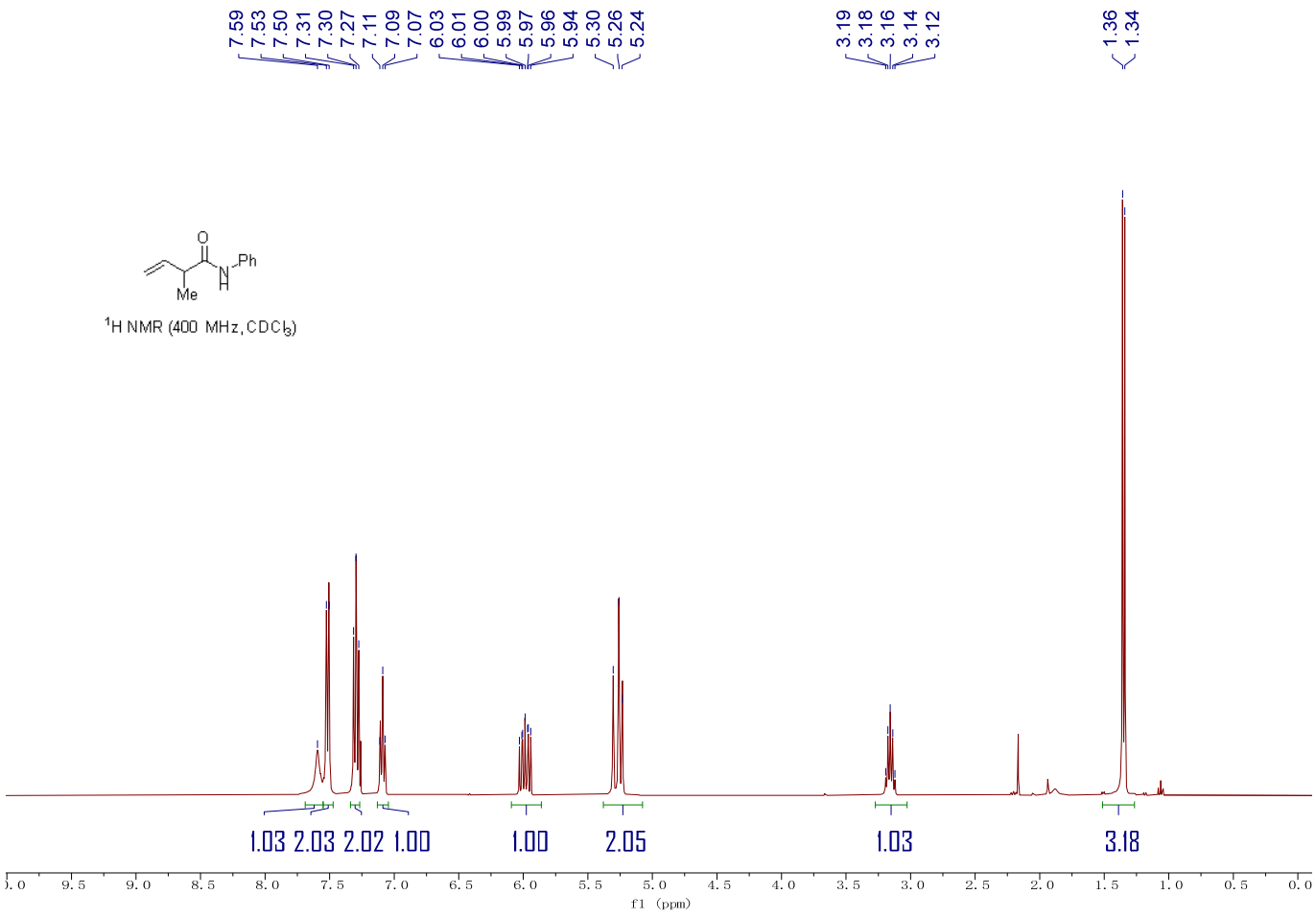

169.41
137.92
137.52
129.02
124.39
120.89
119.95
119.92
77.48
77.16
76.84
36.15
20.83
14.00
13C NMR (101 MHz, CDCl3)
f1 (ppm)

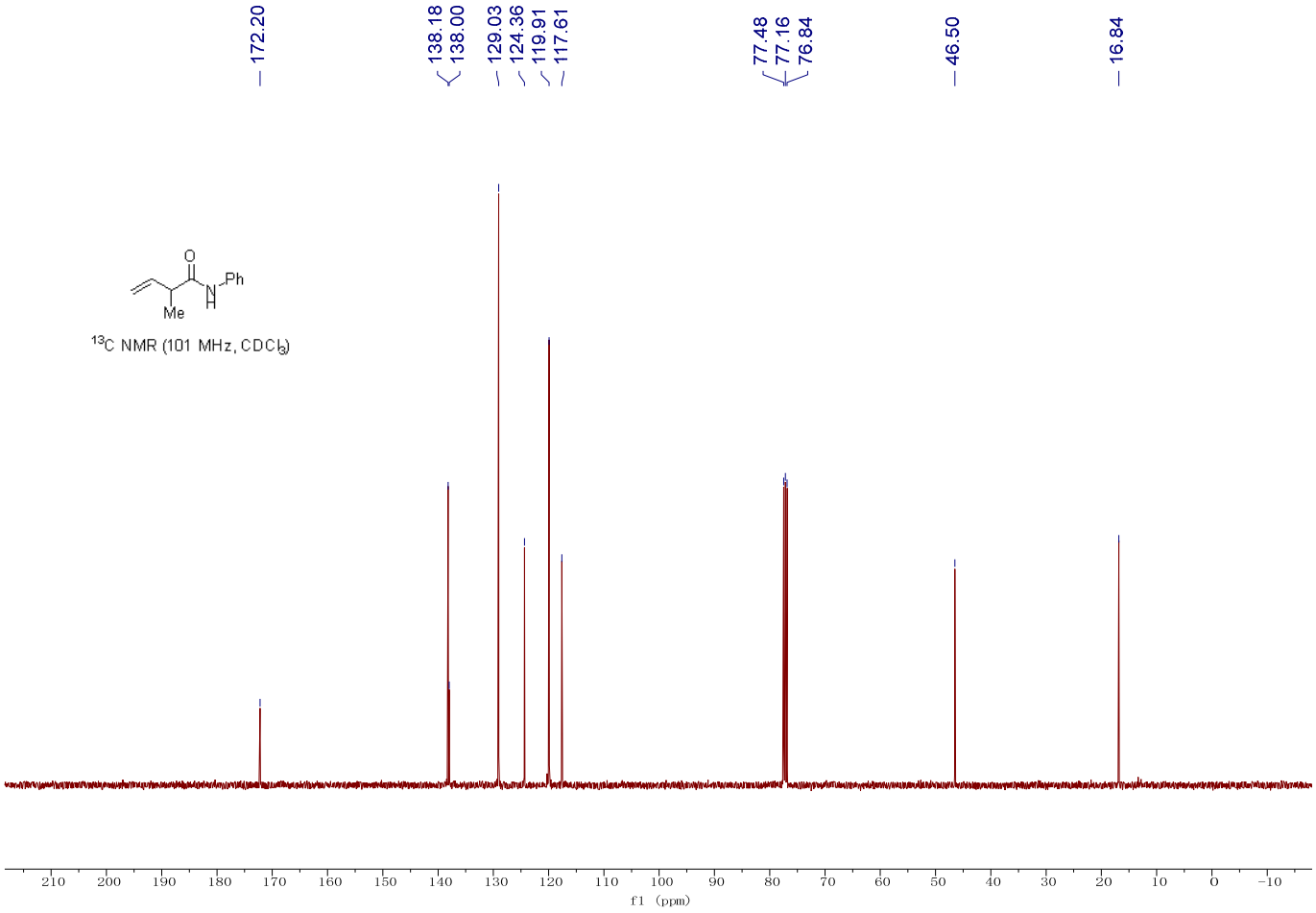

7.54
7.38
7.36
7.23
7.22
7.21
7.20
7.19
7.17
7.14
7.13
7.11
7.09
7.01
6.99
6.97
5.80
5.78
5.76
5.74
5.73
5.64
5.62
5.60
5.59
5.56
3.33
3.31
3.03
3.01
Ph
1H NMR (400 MHz, CDCl3)
0.94 2.00 4.12 3.23 1.06
1.00 1.03
2.06 2.07
f1 (ppm)


169.48
139.97
137.91
135.57
129.04
128.71
128.57
126.38
124.41
123.87
119.88
77.48
77.16
76.84
41.44
39.10
Ph
O
N
H
13C NMR (101 MHz, CDCl3)
f1 (ppm)

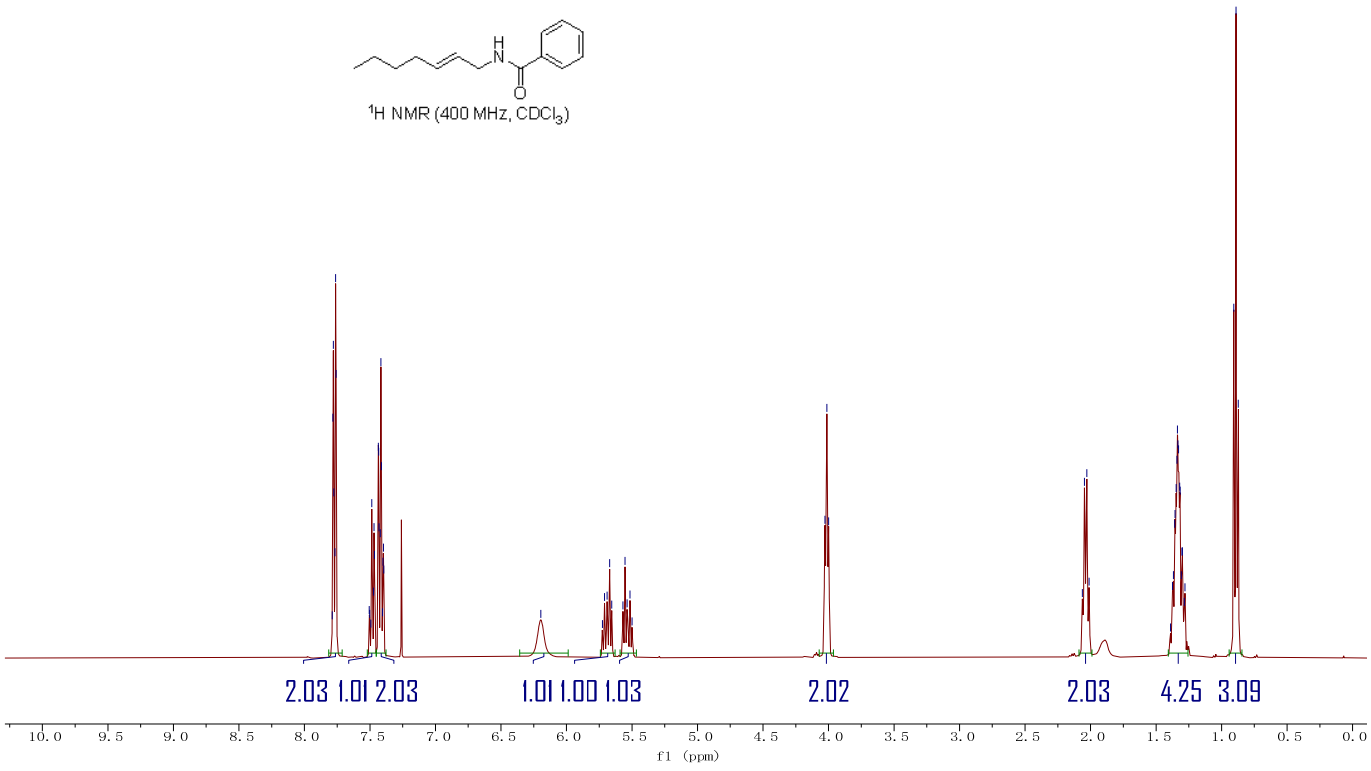

3.67
3.12
3.11
2.36
2.35
2.34
2.16
2.15
2.14
2.13
1.79
1.78
1.77
1.75
1.74
MeO2C
O
N
H
1H NMR (600 MHz, CDCl3)
3.00
2.00
2.04
2.01
2.19
f1 (ppm)

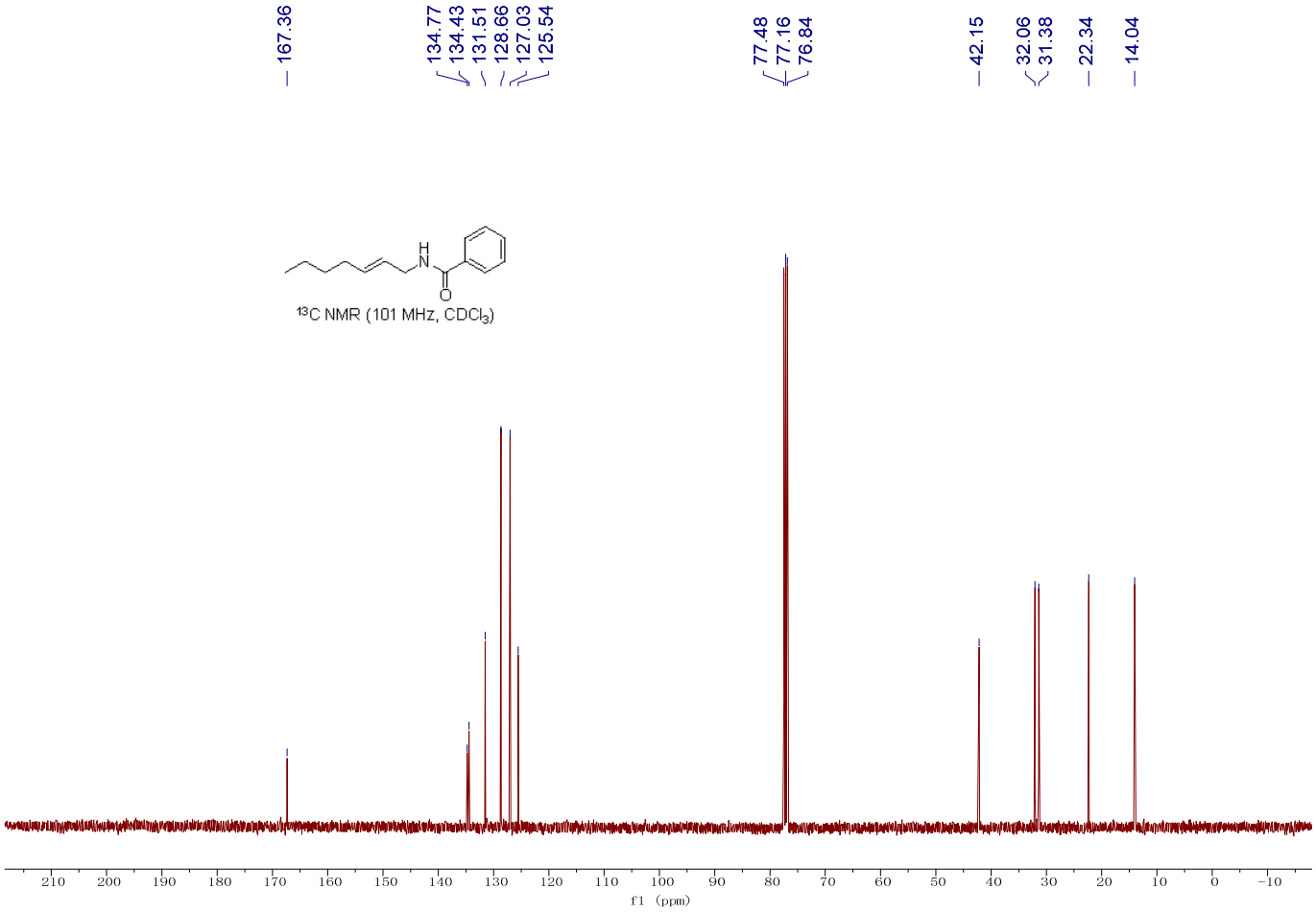

174.10
169.45
137.96
135.85
129.08
124.45
123.65
119.97
77.37
77.16
76.95
51.71
41.70
33.51
31.99
24.33
MeO2C
O
N
H
13C NMR (151 MHz, CDCl3)
f1 (ppm)

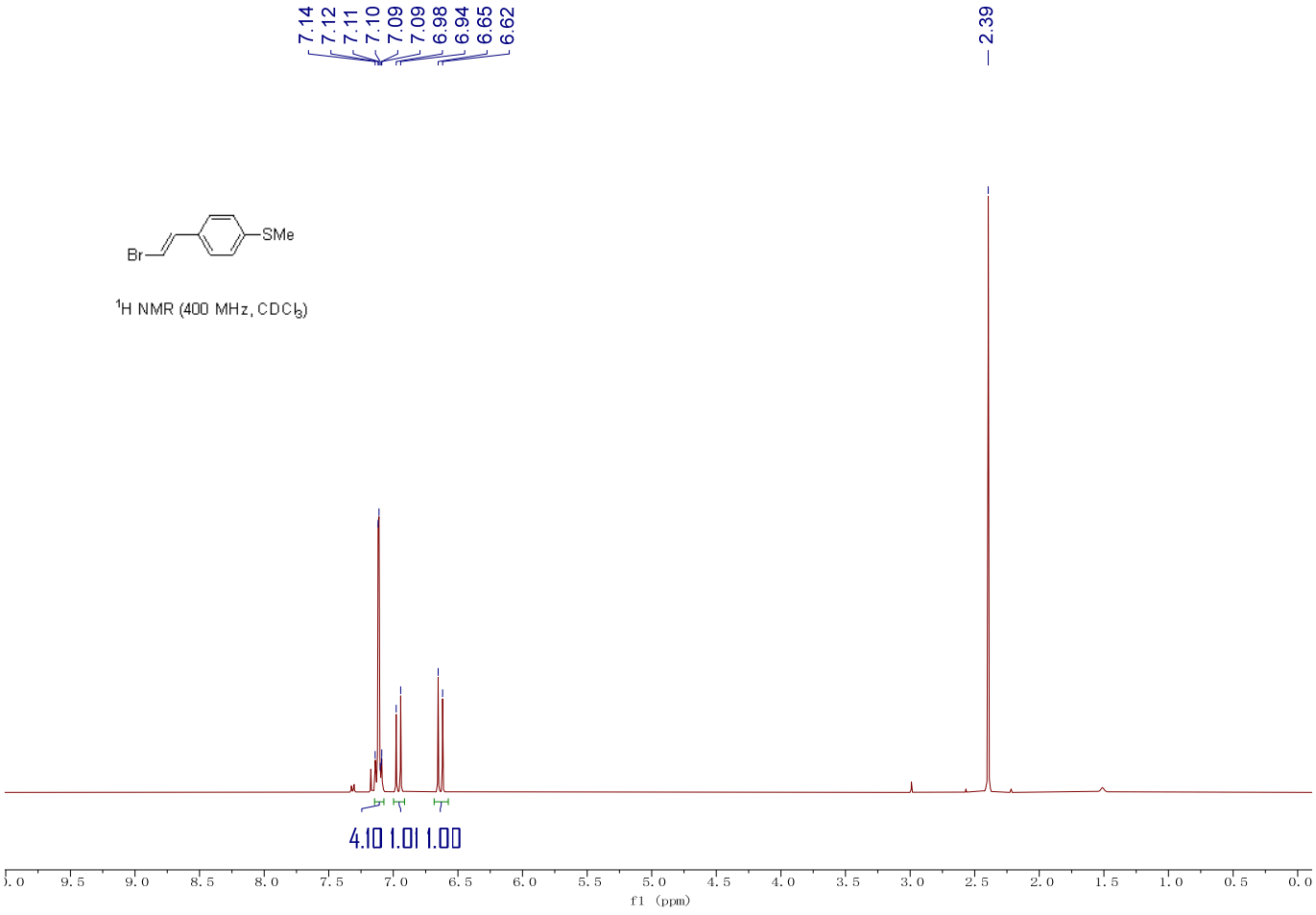

7.59
7.53
7.50
7.31
7.30
7.27
7.11
7.09
7.07
6.03
6.01
6.00
5.99
5.97
5.96
5.94
5.30
5.26
5.24
3.19
3.18
3.16
3.14
3.12
1.36
1.34
O
N
Ph
H
Me
1H NMR (400 MHz, CDCl3)
1.03
2.03
2.02
1.00
1.00
2.05
1.03
3.18
f1 (ppm)

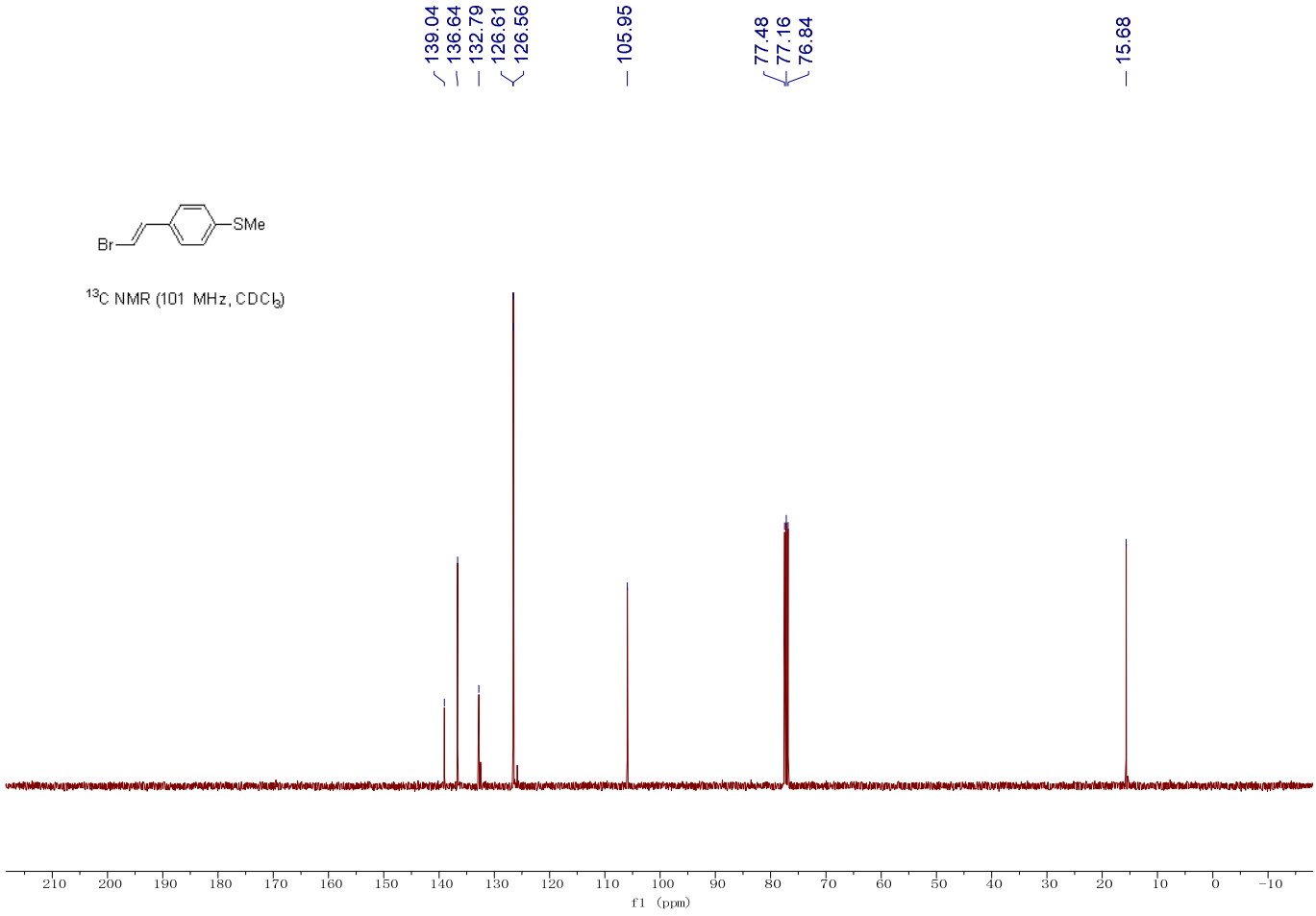

172.20
138.18
138.00
129.03
124.36
119.91
117.61
77.48
77.16
76.84
46.50
16.84
O
N
H
Ph
Me
13C NMR (101 MHz, CDCl3)
f1 (ppm)

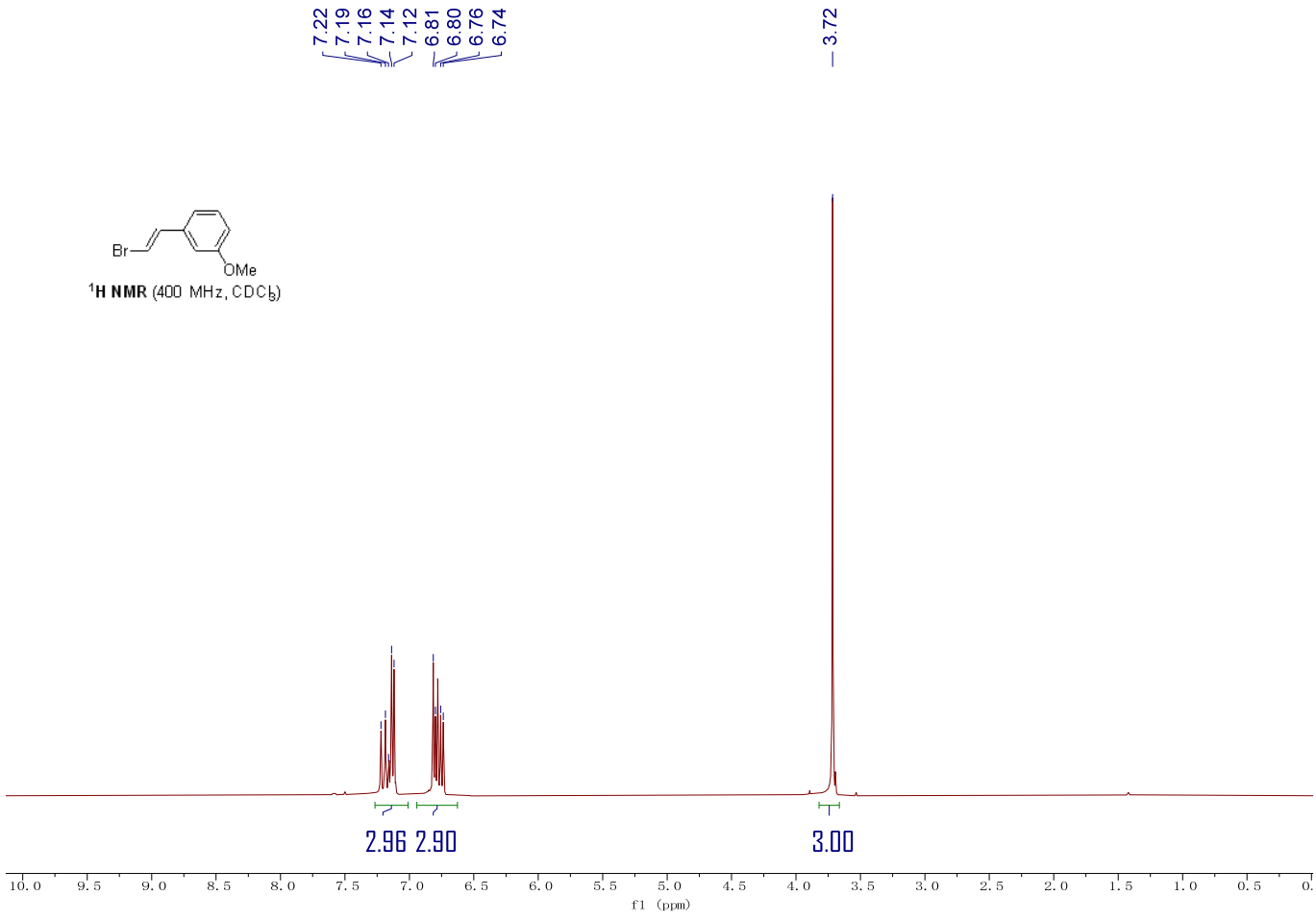

7.79
7.78
7.78
7.78
7.77
7.76
7.76
7.51
7.50
7.49
7.47
7.47
7.46
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.39
6.20
5.71
5.69
5.67
5.65
5.57
5.55
5.54
5.51
4.03
4.01
4.00
2.06
2.05
2.03
2.01
1.38
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.33
1.32
1.32
1.31
1.30
1.30
1.28
1.28
0.91
0.89
0.87

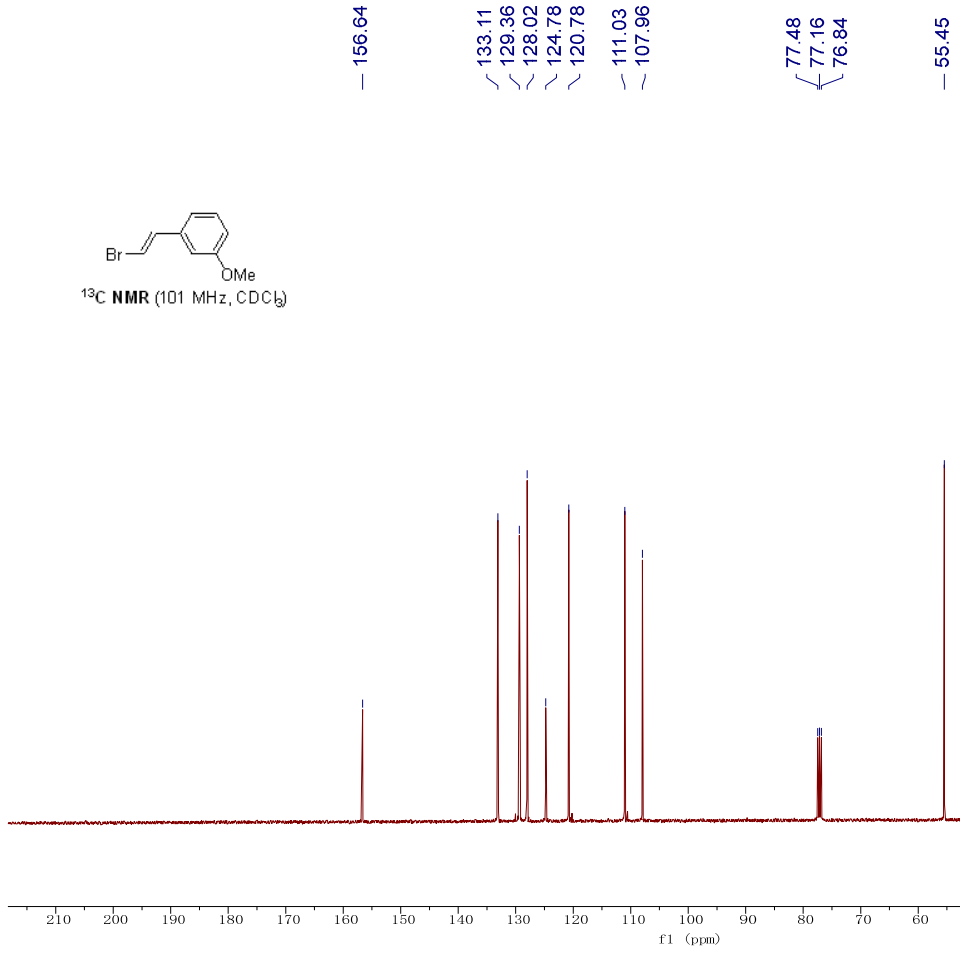

H
N
O
1H NMR (400 MHz, CDCl3)
2.03 1.01 2.03
1.01 1.00 1.03
2.02
2.03
4.25
3.09
f1 (ppm)

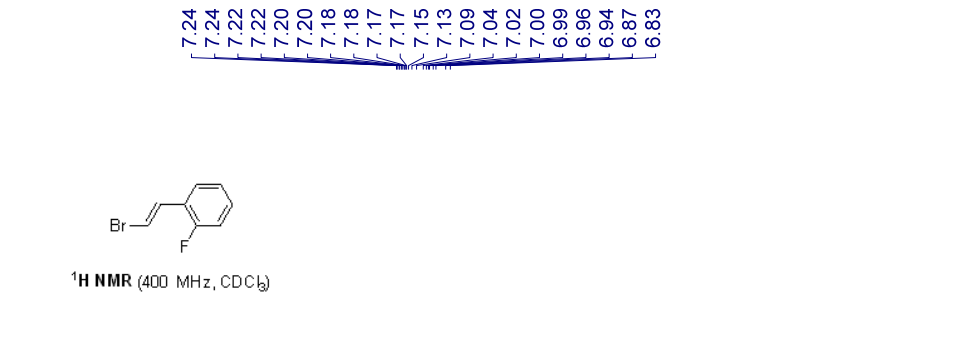

167.36
134.77
134.43
131.51
128.66
127.03
125.54
77.48
77.16
76.84
42.15
32.06
31.38
22.34
14.04
13C NMR (101 MHz, CDCl3)
f1 (ppm)

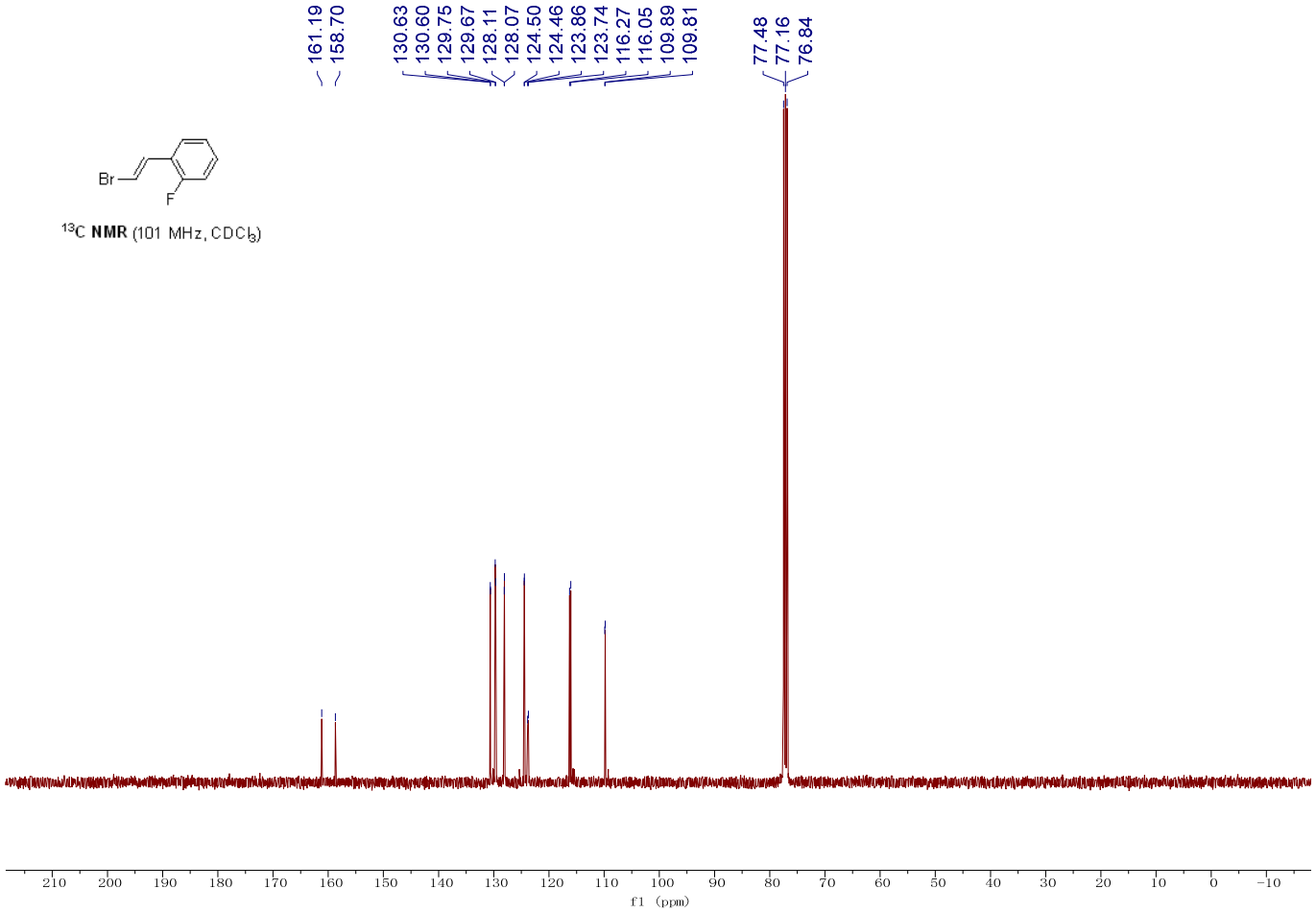

7.14
7.12
7.11
7.10
7.09
7.09
6.98
6.94
6.65
6.62
2.39
Br
SMe
1H NMR (400 MHz, CDCl3)
4.10 1.01 1.00
f1 (ppm)


139.04
136.64
132.79
126.61
126.56
105.95
77.48
77.16
76.84
15.68
Br
SMe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

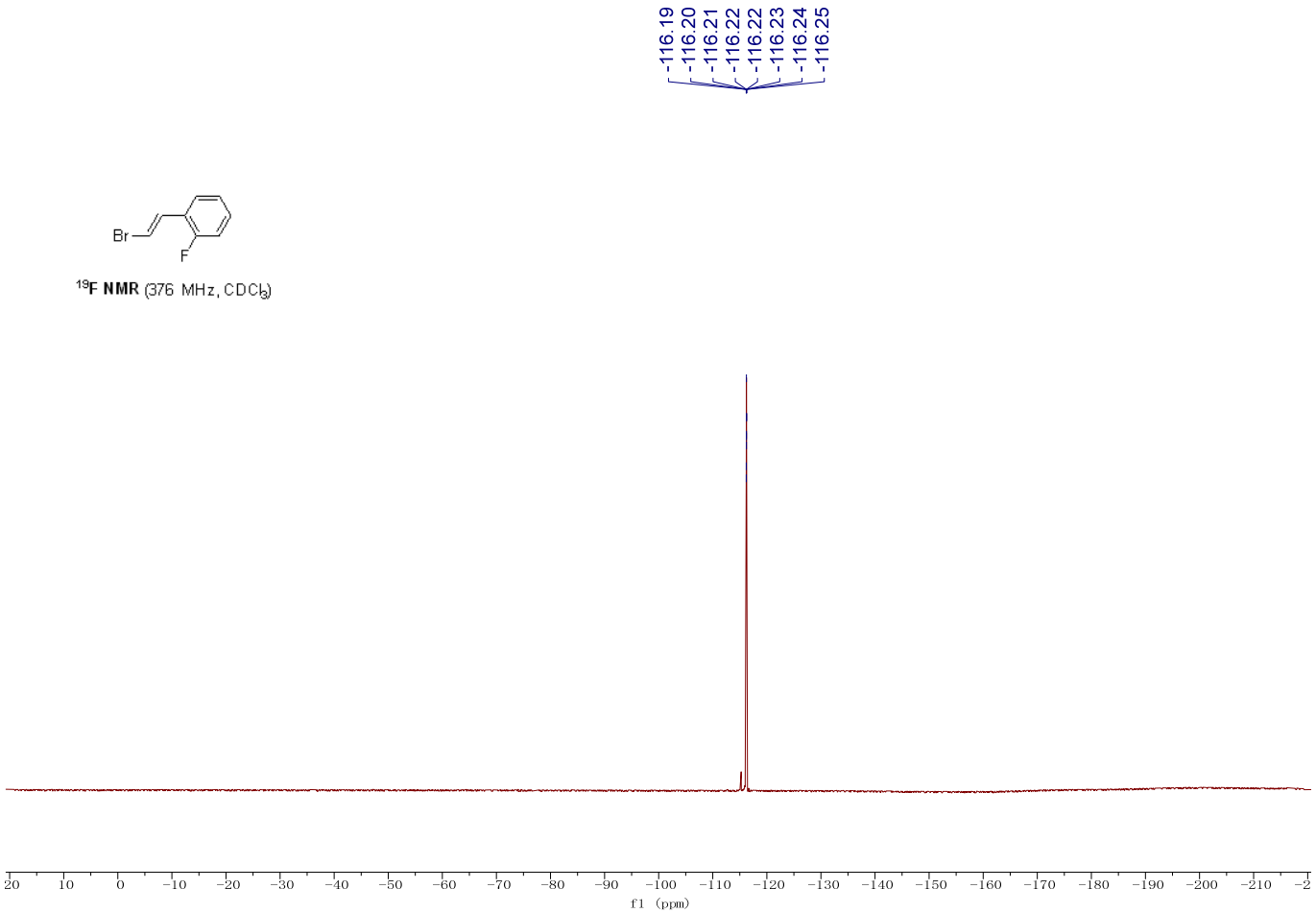

7.22
7.19
7.16
7.14
7.12
6.81
6.80
6.76
6.74
3.72
Br
OMe
1H NMR (400 MHz, CDCl3)
2.96 2.90
3.00
f1 (ppm)


156.64
133.11
129.36
128.02
124.78
120.78
111.03
107.96
77.48
77.16
76.84
55.45
Br
OMe
13C NMR (101 MHz, CDCl3)
f1 (ppm)

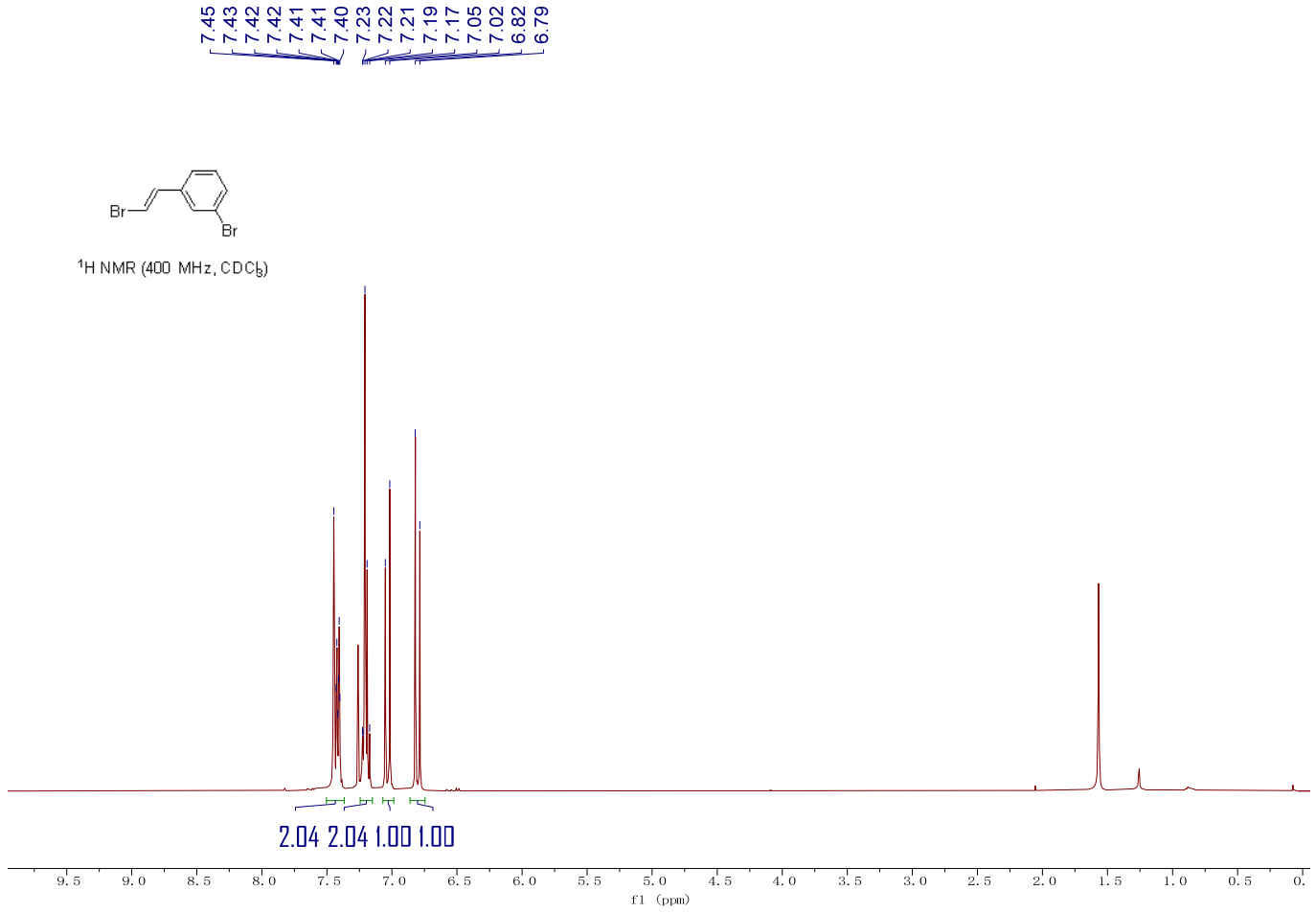

7.24
7.24
7.22
7.22
7.20
7.20
7.18
7.18
7.17
7.17
7.15
7.13
7.09
7.04
7.02
7.00
6.99
6.96
6.94
6.87
6.83
Br
F
1H NMR (400 MHz, CDCl3)
2.24 1.06 2.02 1.00
f1 (ppm)

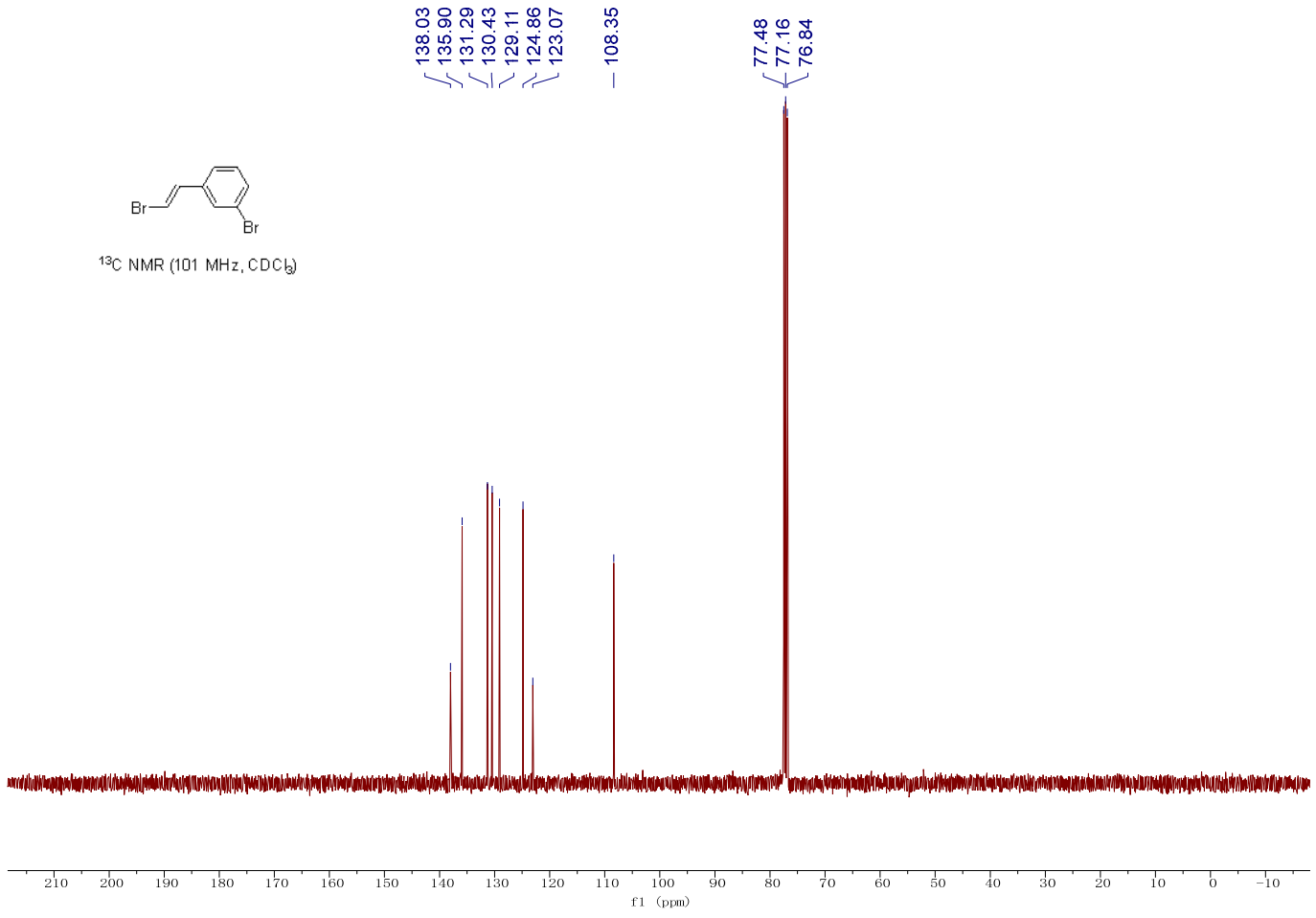


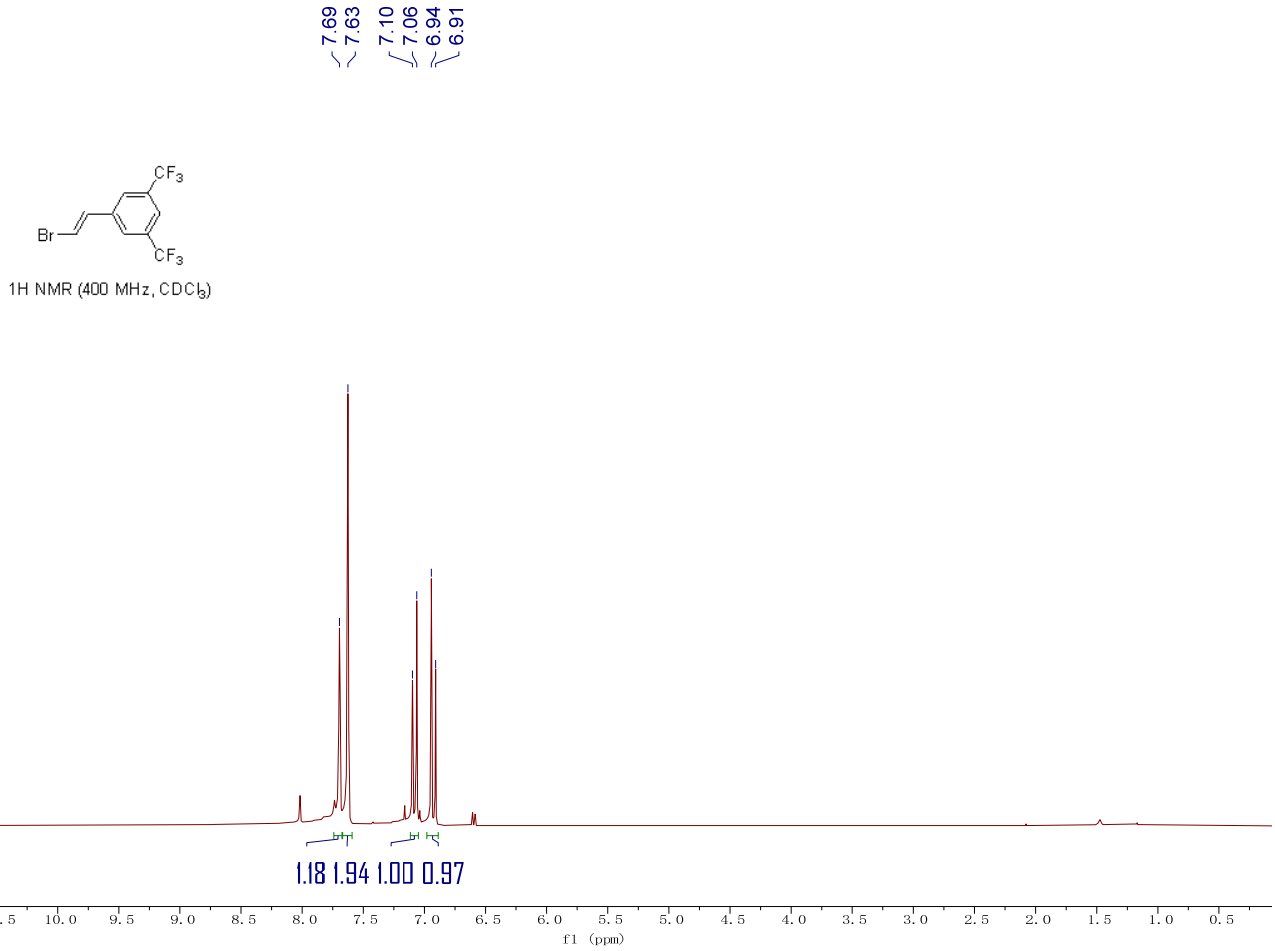
^{13}C **NMR** (101 MHz, $CDCl_3$)

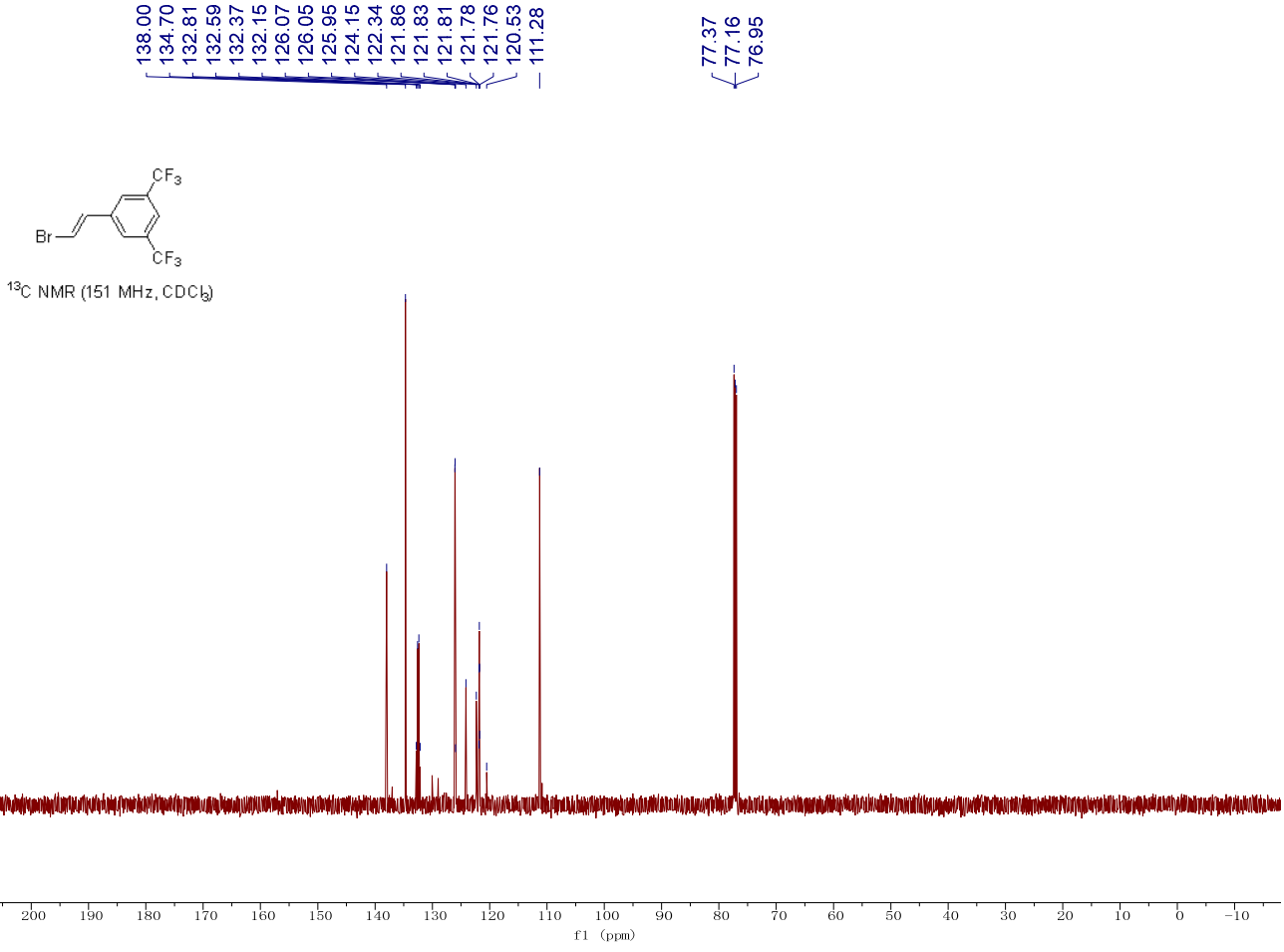


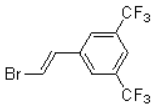
^{19}F **NMR** (376 MHz, $CDCl_3$)


7.45
7.43
7.42
7.42
7.41
7.41
7.40
7.23
7.22
7.21
7.19
7.17
7.05
7.02
6.82
6.79
Br
Br
1H NMR (400 MHz, CDCl3)
2.04 2.04 1.00 1.00
f1 (ppm)

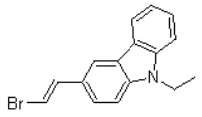

138.03
135.90
131.29
130.43
129.11
124.86
123.07
108.35
77.48
77.16
76.84
Br
Br
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.69
7.63
7.10
7.06
6.94
6.91
CF3
Br
CF3
1H NMR (400 MHz, CDCl3)
1.18 1.94 1.00 0.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

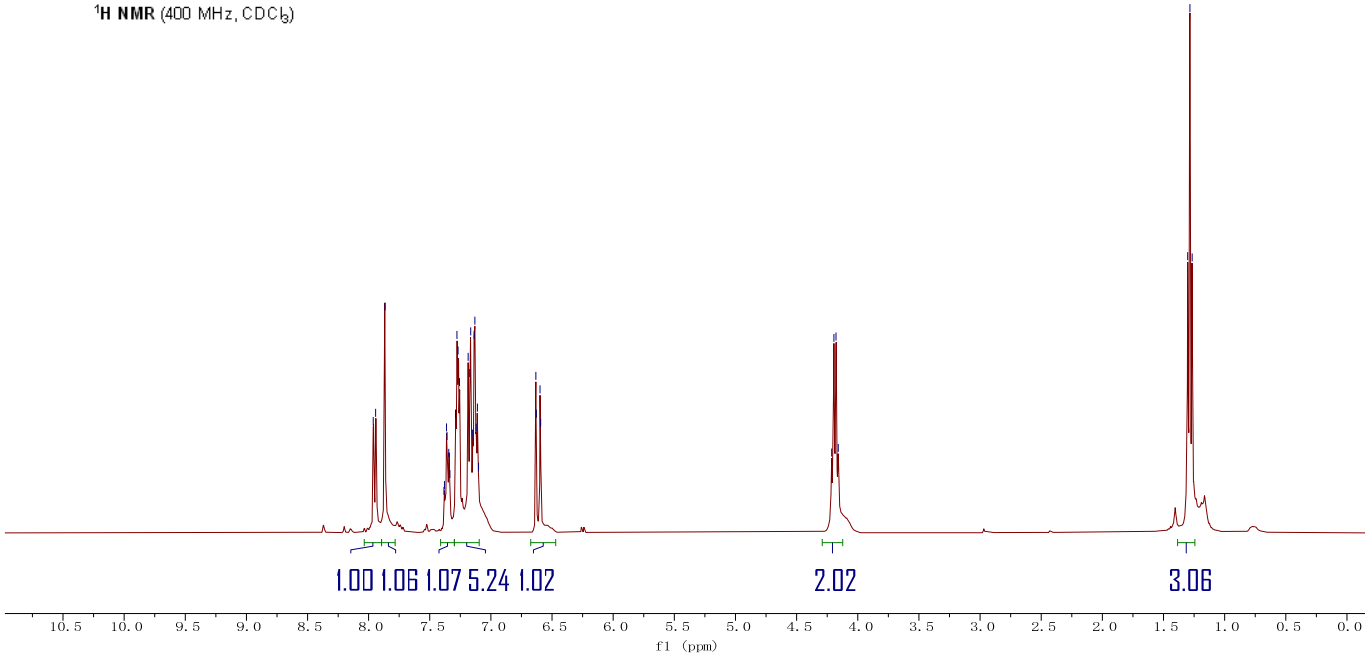

138.00
134.70
132.81
132.59
132.37
132.15
126.07
126.05
125.95
124.15
122.34
121.86
121.83
121.81
121.78
121.76
120.53
111.28
77.37
77.16
76.95
CF3
Br
CF3
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

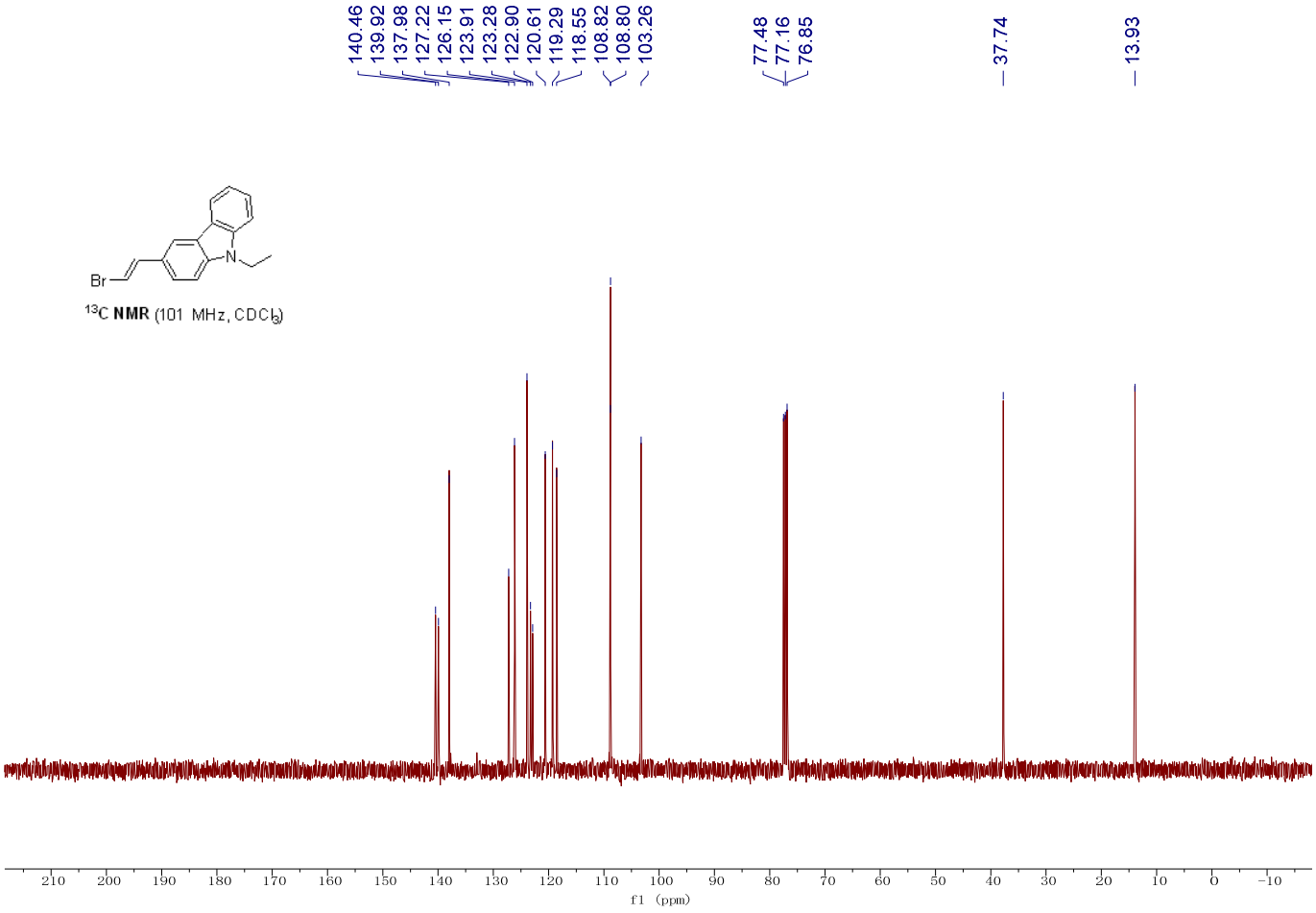


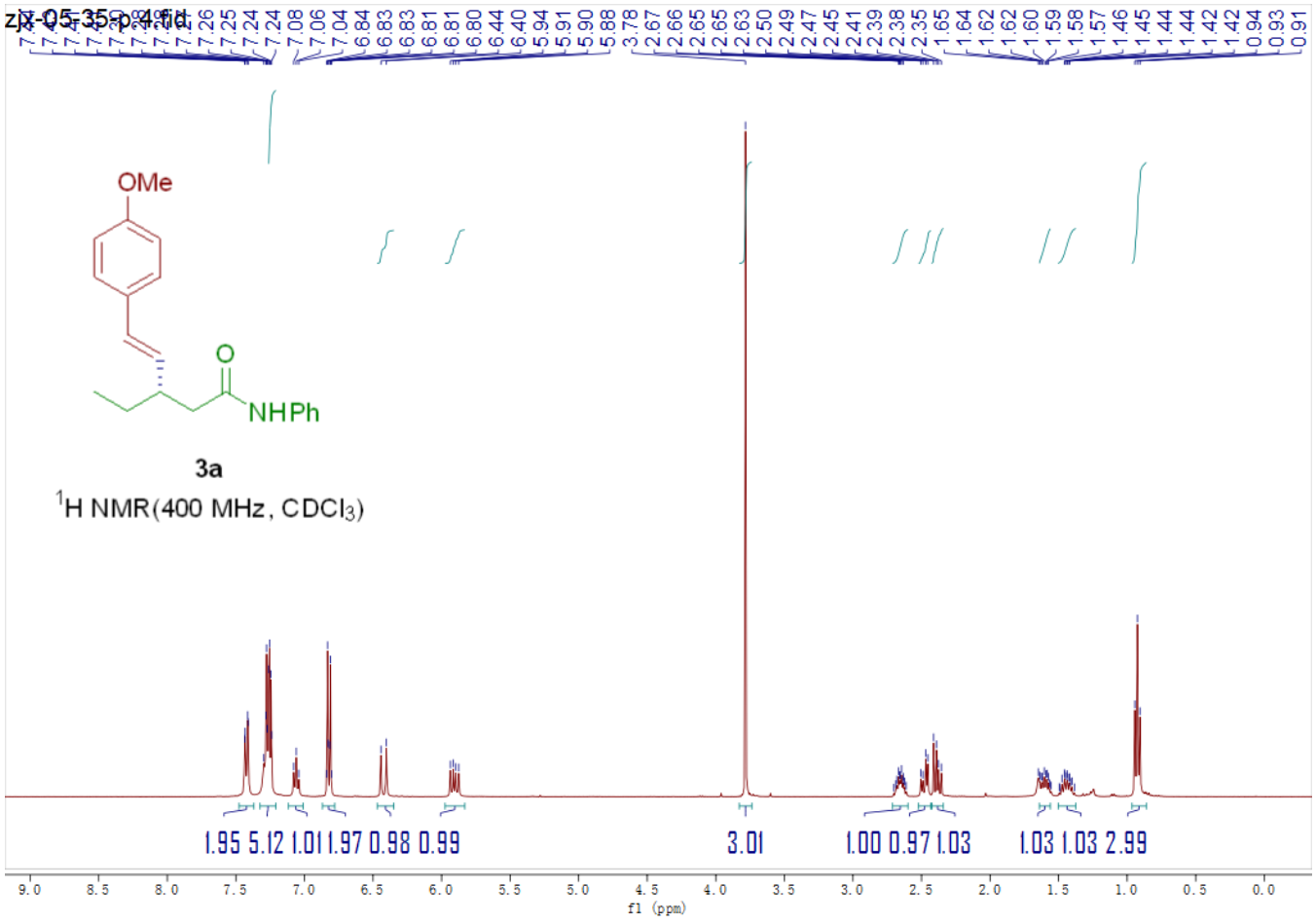
^{19}FF NMR (376 MHz, $CDCl_3$)

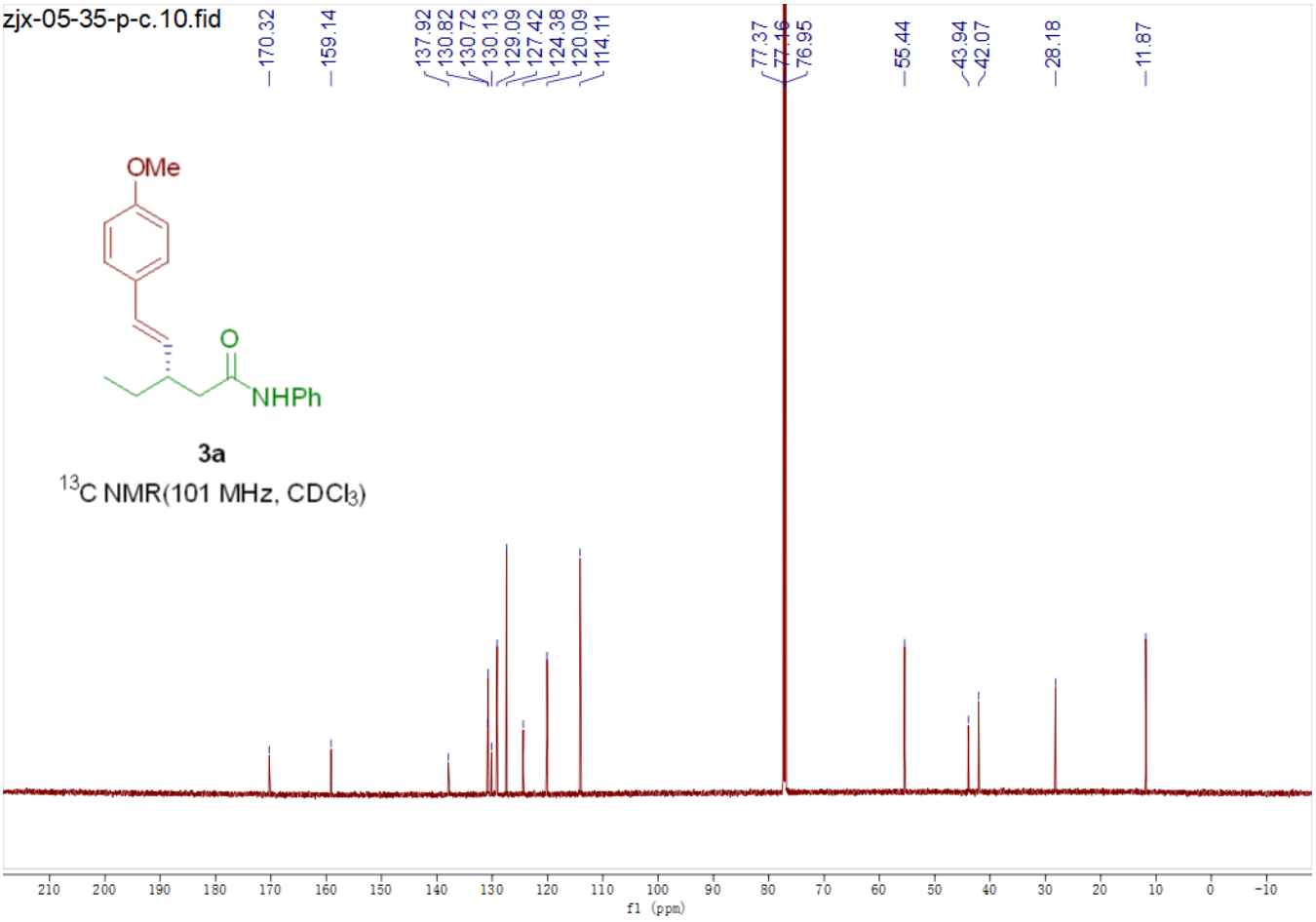


^{1}H NMR (400 MHz, $CDCl_3$)



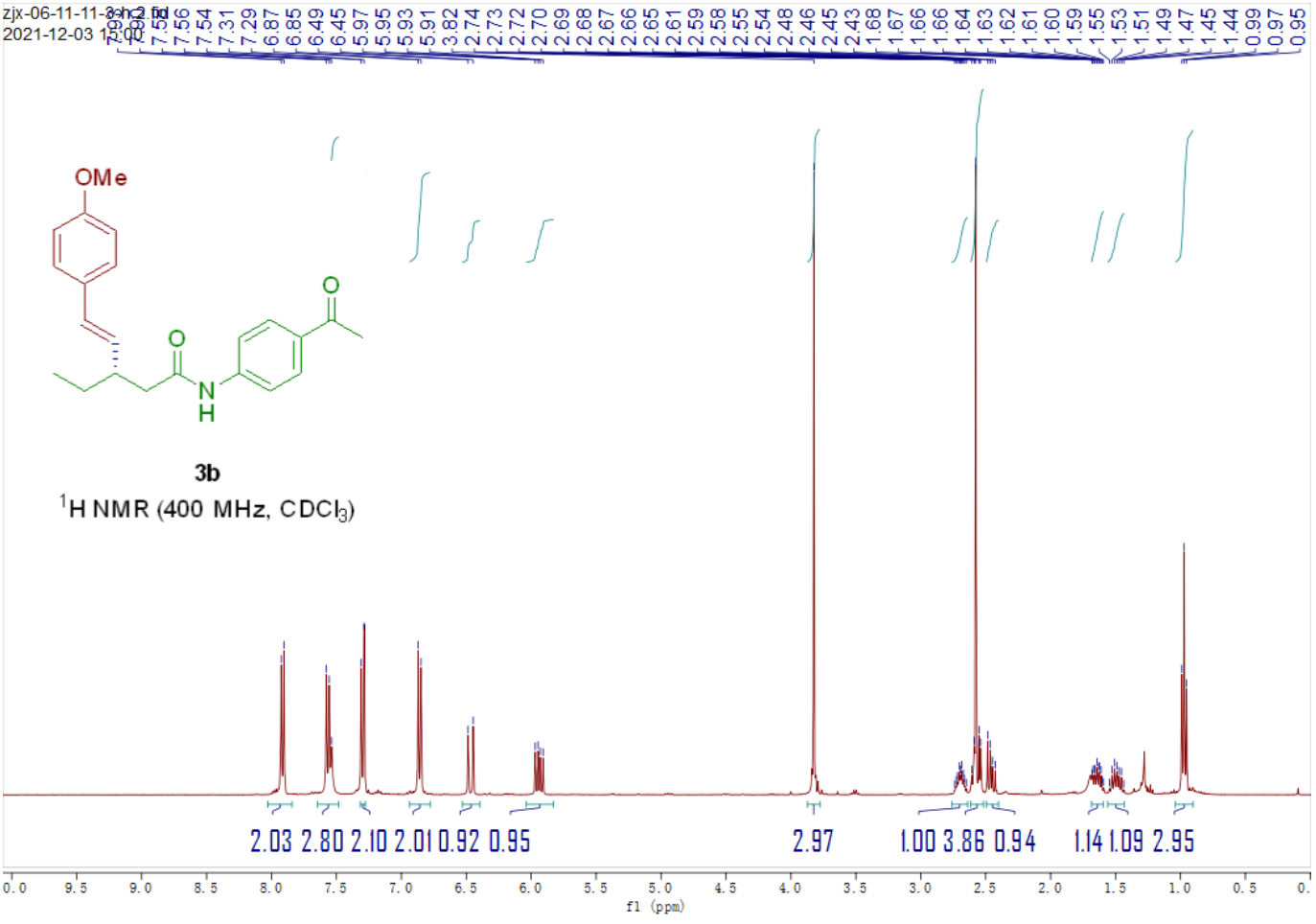

140.46
139.92
137.98
127.22
126.15
123.91
123.28
122.90
120.61
119.29
118.55
108.82
108.80
103.26
77.48
77.16
76.85
37.74
13.93
Br
N
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-05-35-p-4-fid
OMe
O
NHPh
3a
1H NMR(400 MHz, CDCl3)
1.95 5.12 1.01 1.97 0.98 0.99
3.01
1.00 0.97 1.03
1.03 1.03 2.99
f1 (ppm)



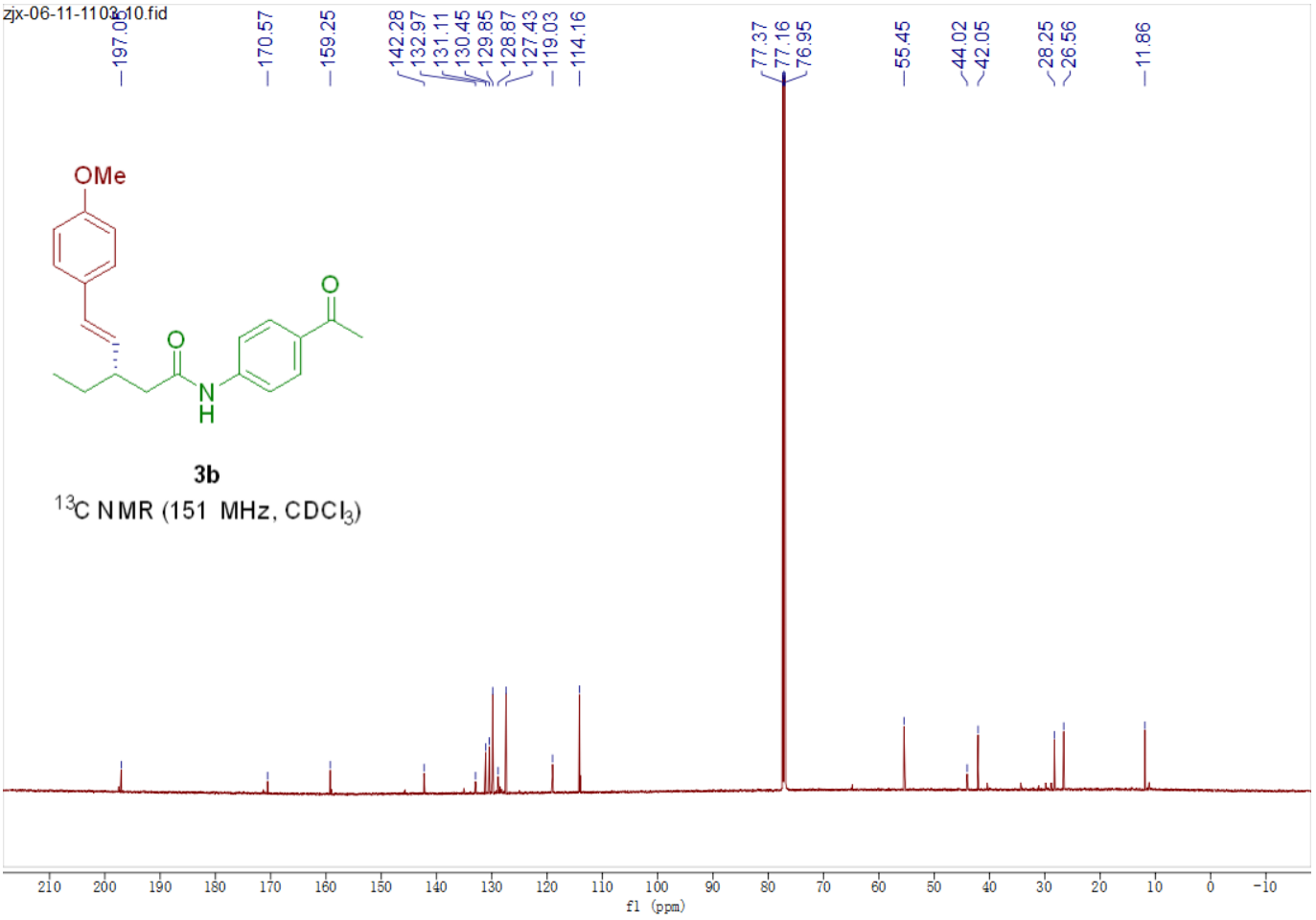
3a

^{13}C NMR(101 MHz, $CDCl_3$)



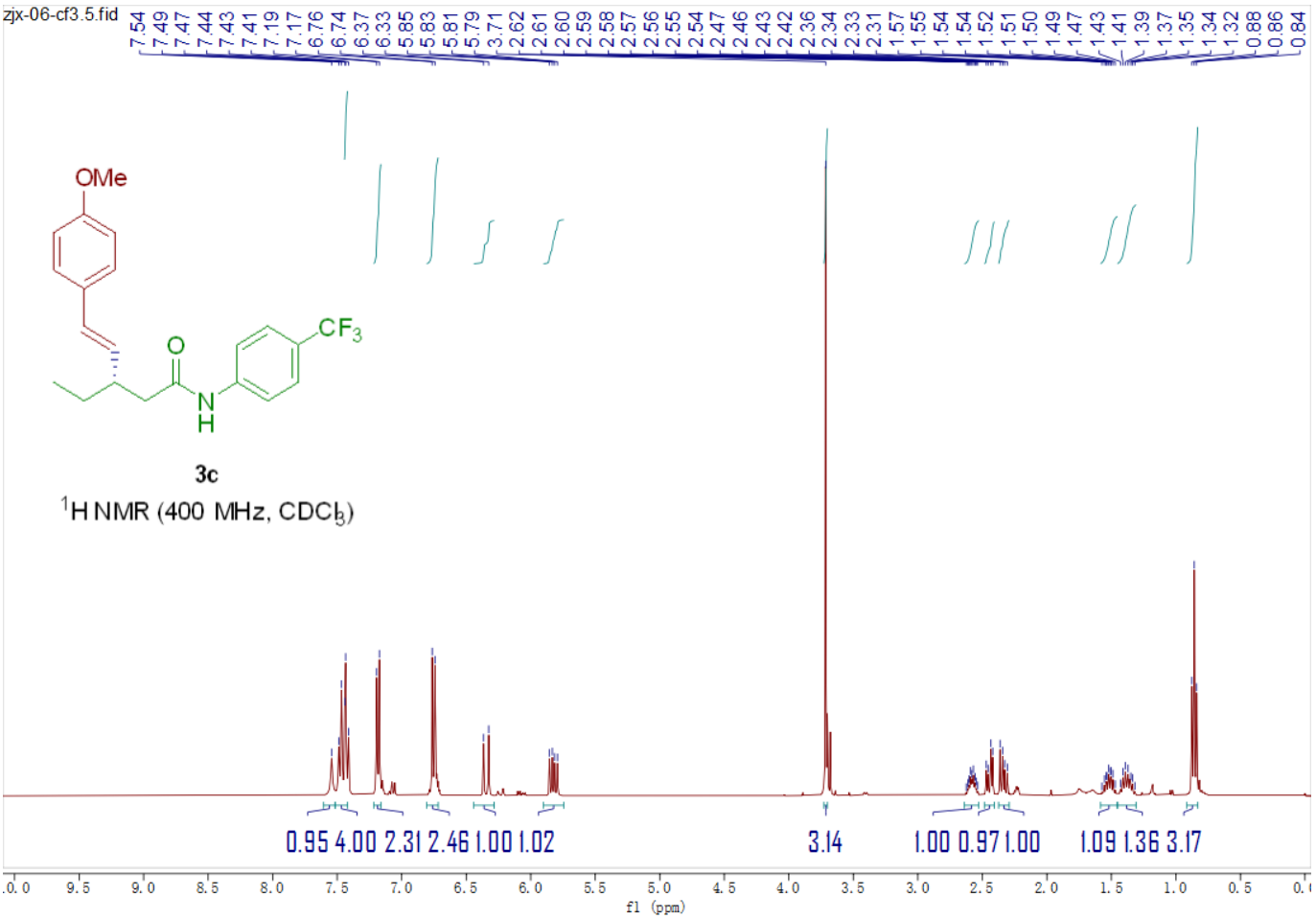
3b

^{1}H NMR (400 MHz, $CDCl_3$)



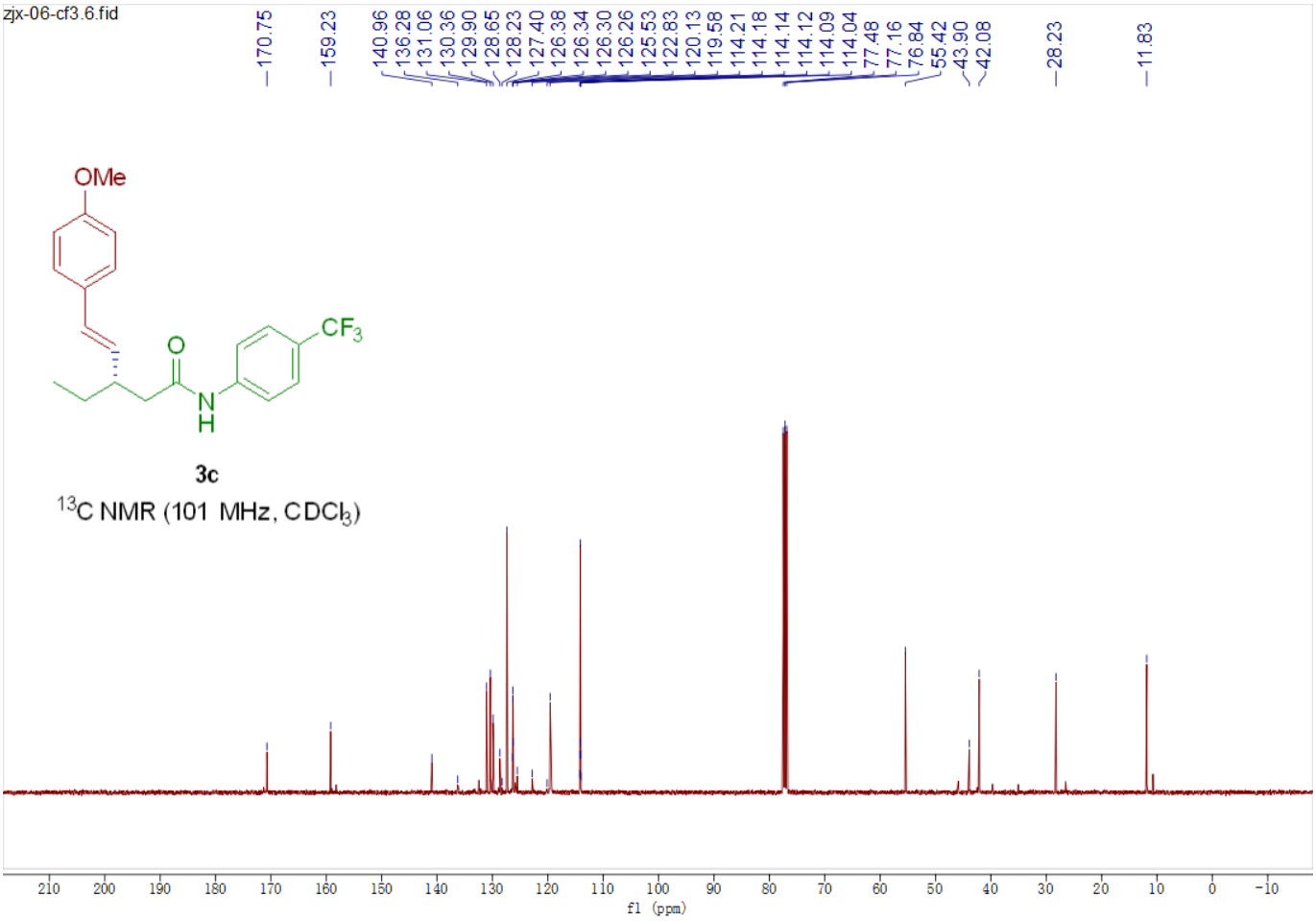
3b

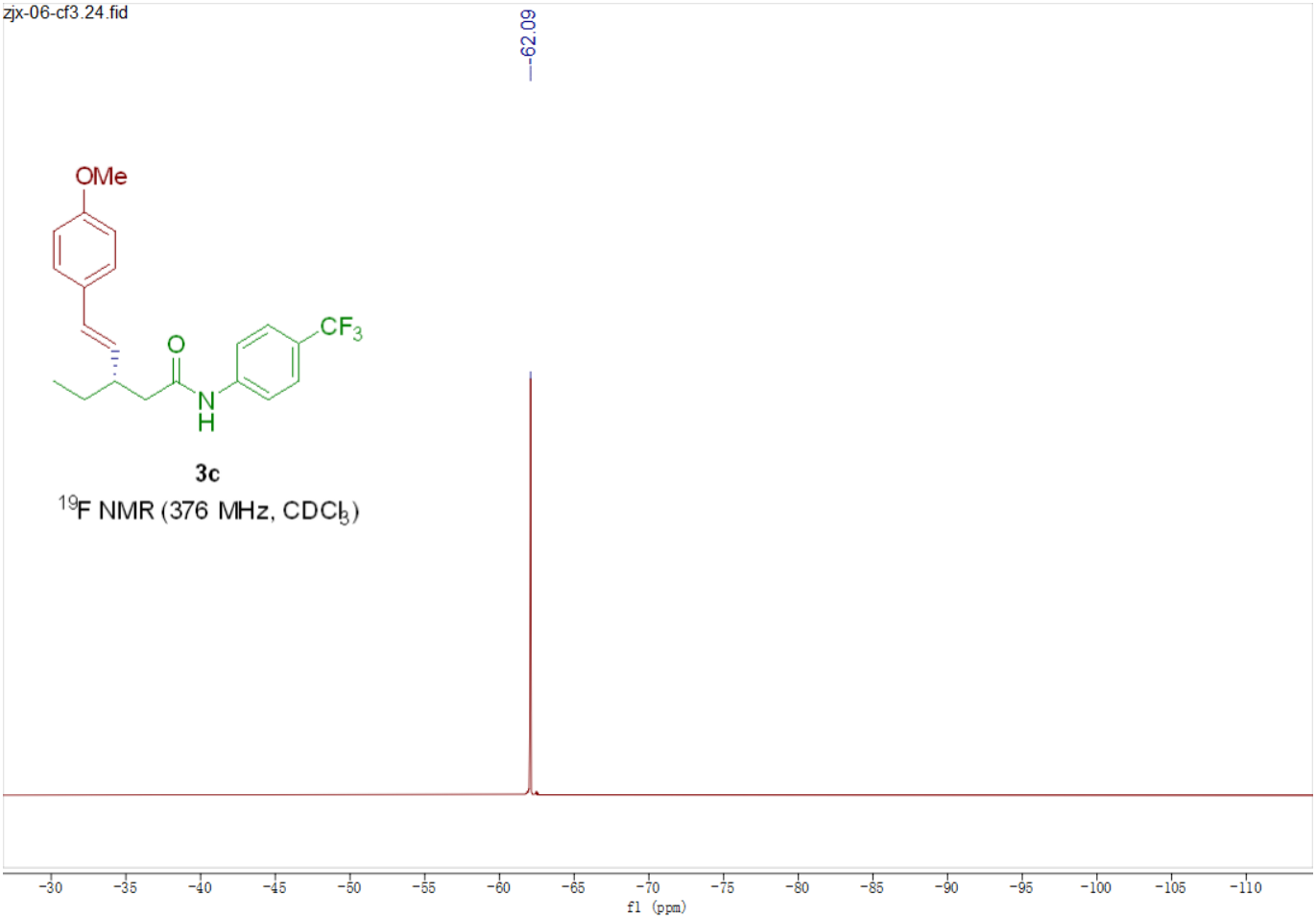
^{13}C NMR (151 MHz, $CDCl_3$)

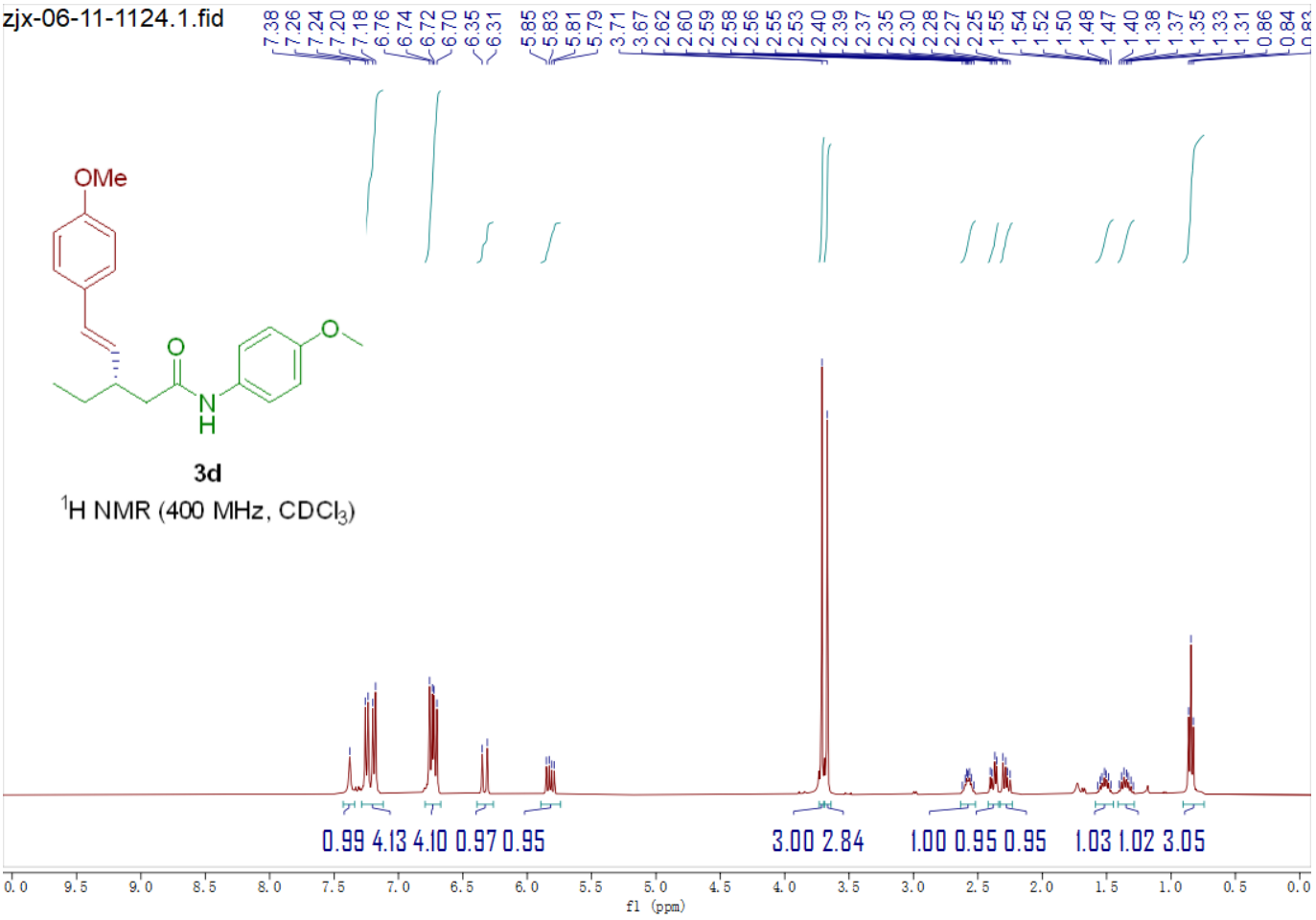


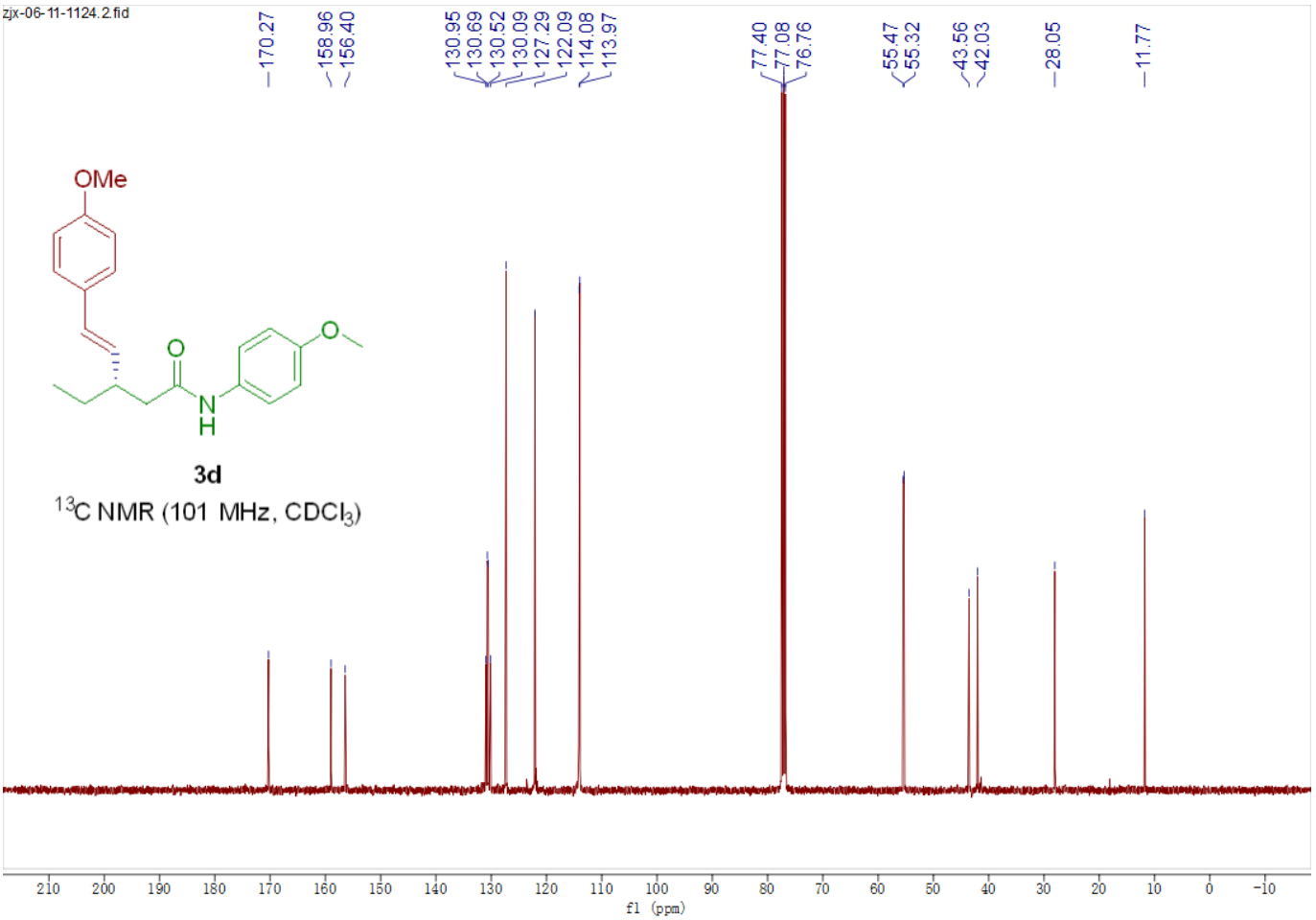
3c

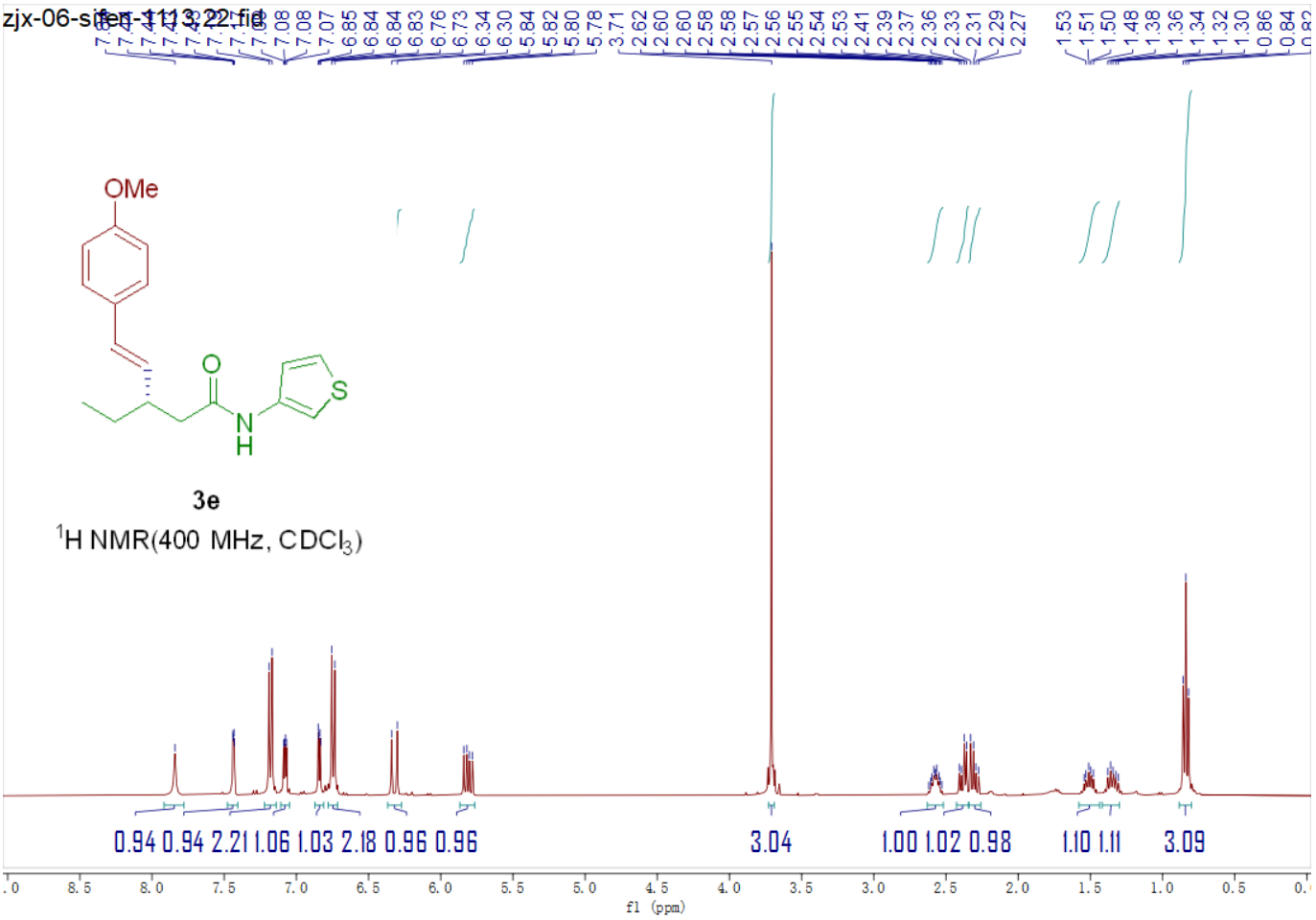
^{1}H NMR (400 MHz, $CDCl_3$)

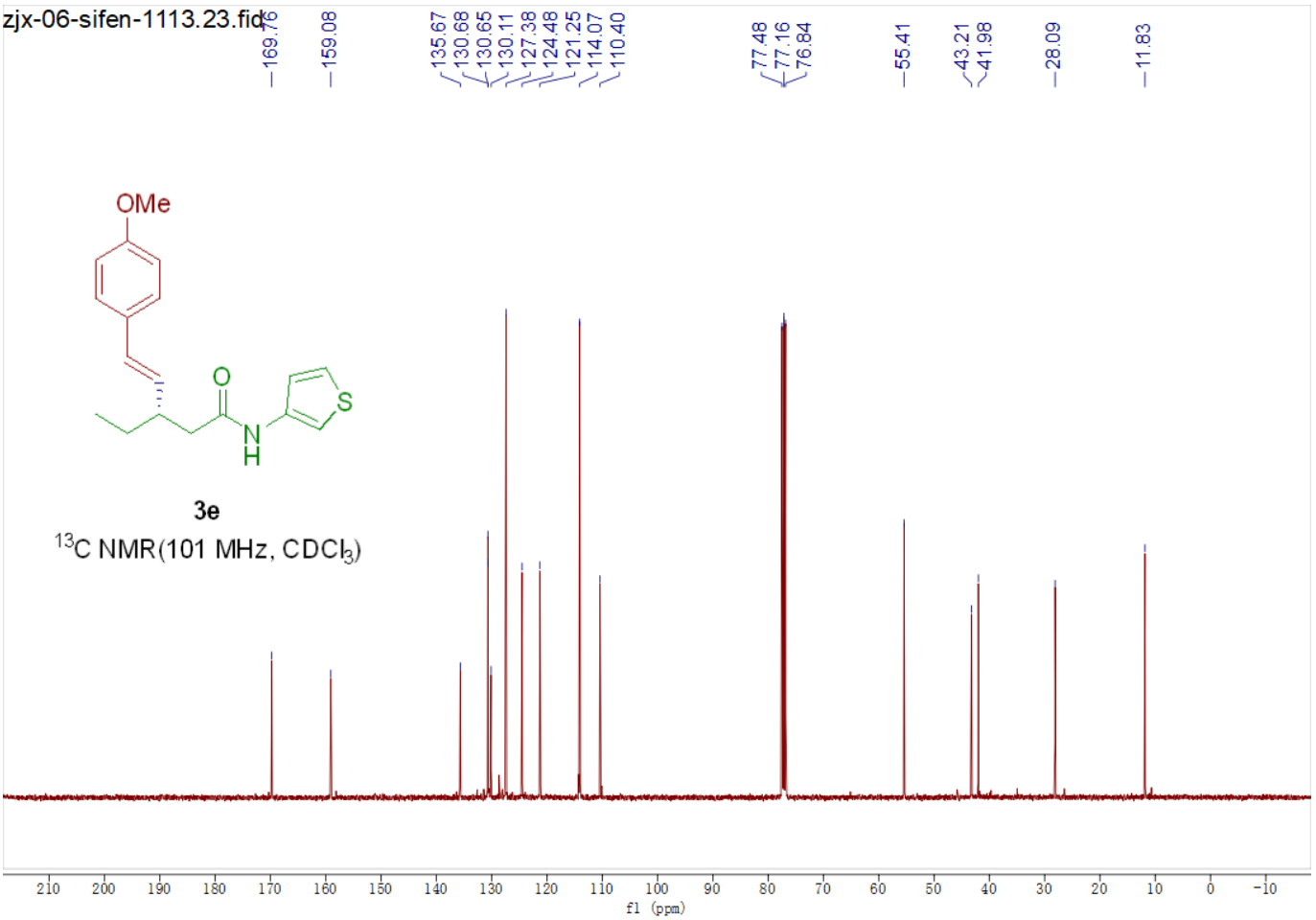

zjx-06-cf3.6.fid
170.75
159.23
140.96
136.28
131.06
130.36
129.90
128.65
128.23
127.40
126.38
126.34
126.30
126.26
125.53
122.83
120.13
119.58
114.21
114.18
114.14
114.12
114.09
114.04
77.48
77.16
76.84
55.42
43.90
42.08
28.23
11.83
OMe
CF3
O
N
H
3c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

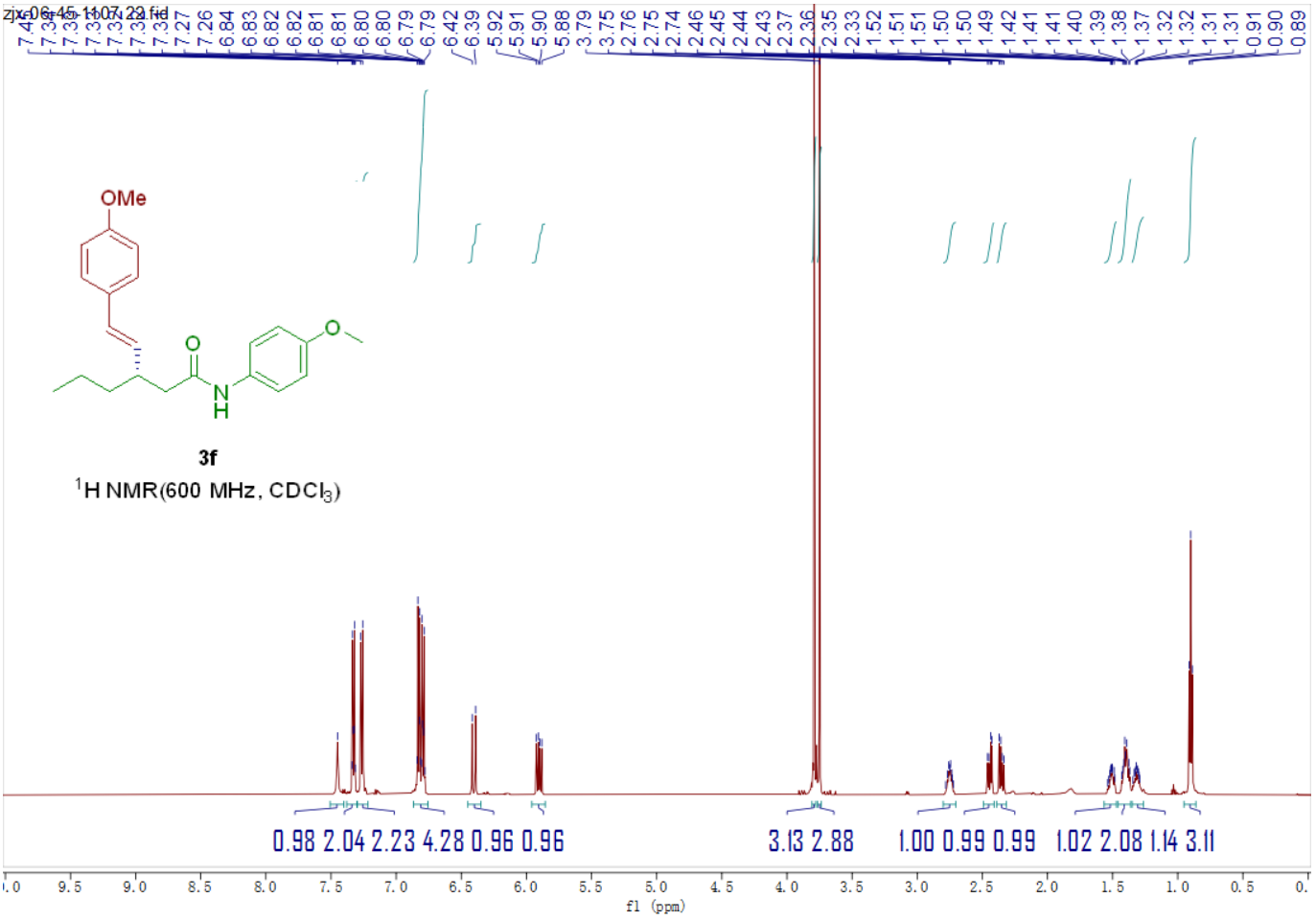

zjx-06-cf3.24.fid
-62.09
OMe
CF3
O
N
H
3c
19F NMR (376 MHz, CDCl3)
f1 (ppm)

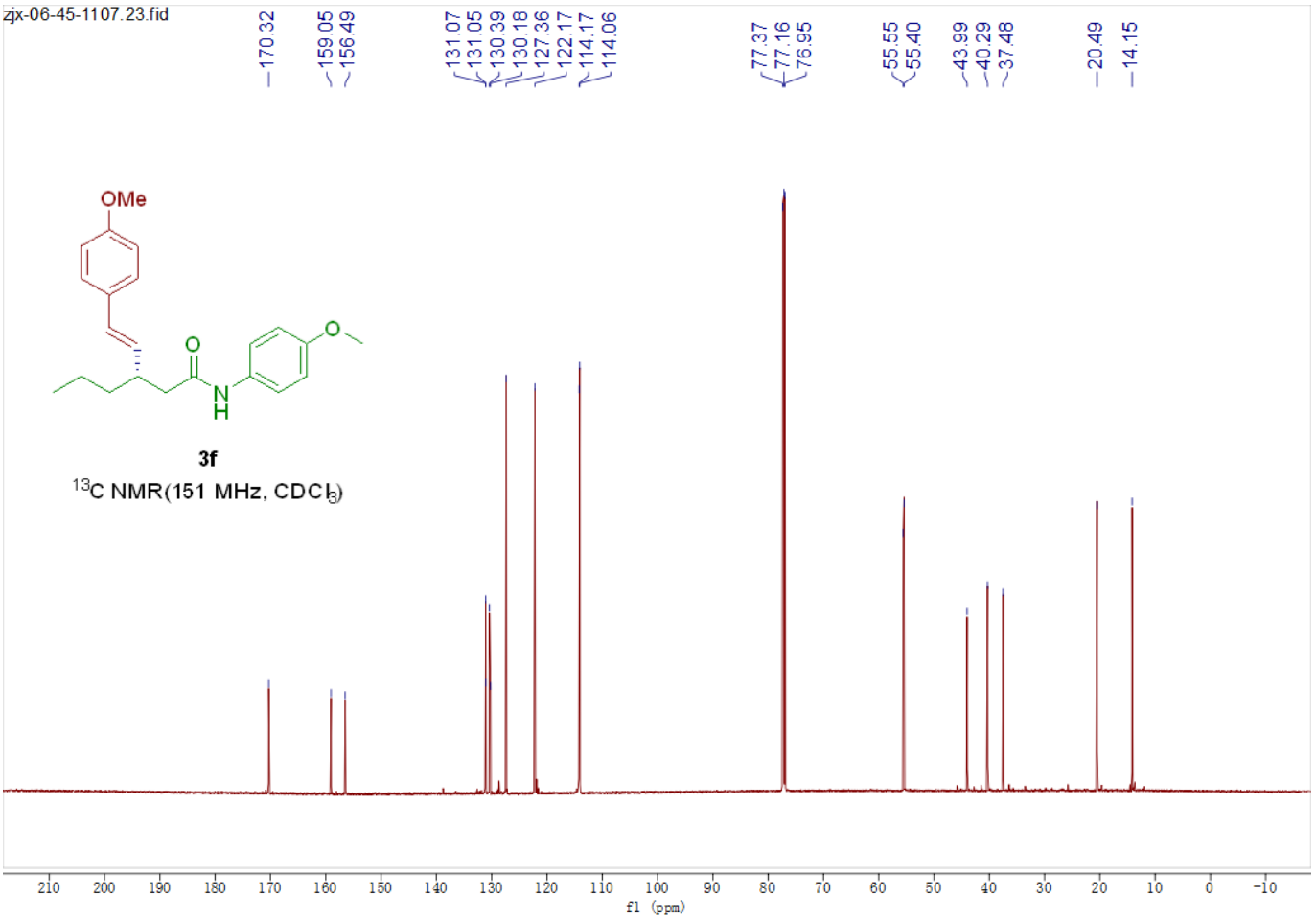

zjx-06-11-1124.1.fid
OMe
O
N
H
O
3d
^{1}H NMR (400 MHz, $CDCl_3$)
0.99 4.13 4.10 0.97 0.95
3.00 2.84
1.00 0.95 0.95
1.03 1.02 3.05
f1 (ppm)


zjx-06-11-1124.2.fid
OMe
O
N
H
O
3d
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


zjx-06-sifen-1113.22.fid
OMe
O
N
H
S
3e
1H NMR(400 MHz, CDCl3)
0.94 0.94 2.21 1.06 1.03 2.18 0.96 0.96
3.04
1.00 1.02 0.98
1.10 1.11
3.09
f1 (ppm)


zjx-06-sifen-1113.23.fid
169.76
159.08
135.67
130.68
130.65
130.11
127.38
124.48
121.25
114.07
110.40
77.48
77.16
76.84
55.41
43.21
41.98
28.09
11.83
OMe
O
N
H
S
3e
13C NMR(101 MHz, CDCl3)
f1 (ppm)


zjx-06-45-1107.23.fid
OMe
O
N
H
O
3f
1H NMR(600 MHz, CDCl3)
0.98 2.04 2.23 4.28 0.96 0.96
3.13 2.88
1.00 0.99 0.99
1.02 2.08 1.14 3.11
f1 (ppm)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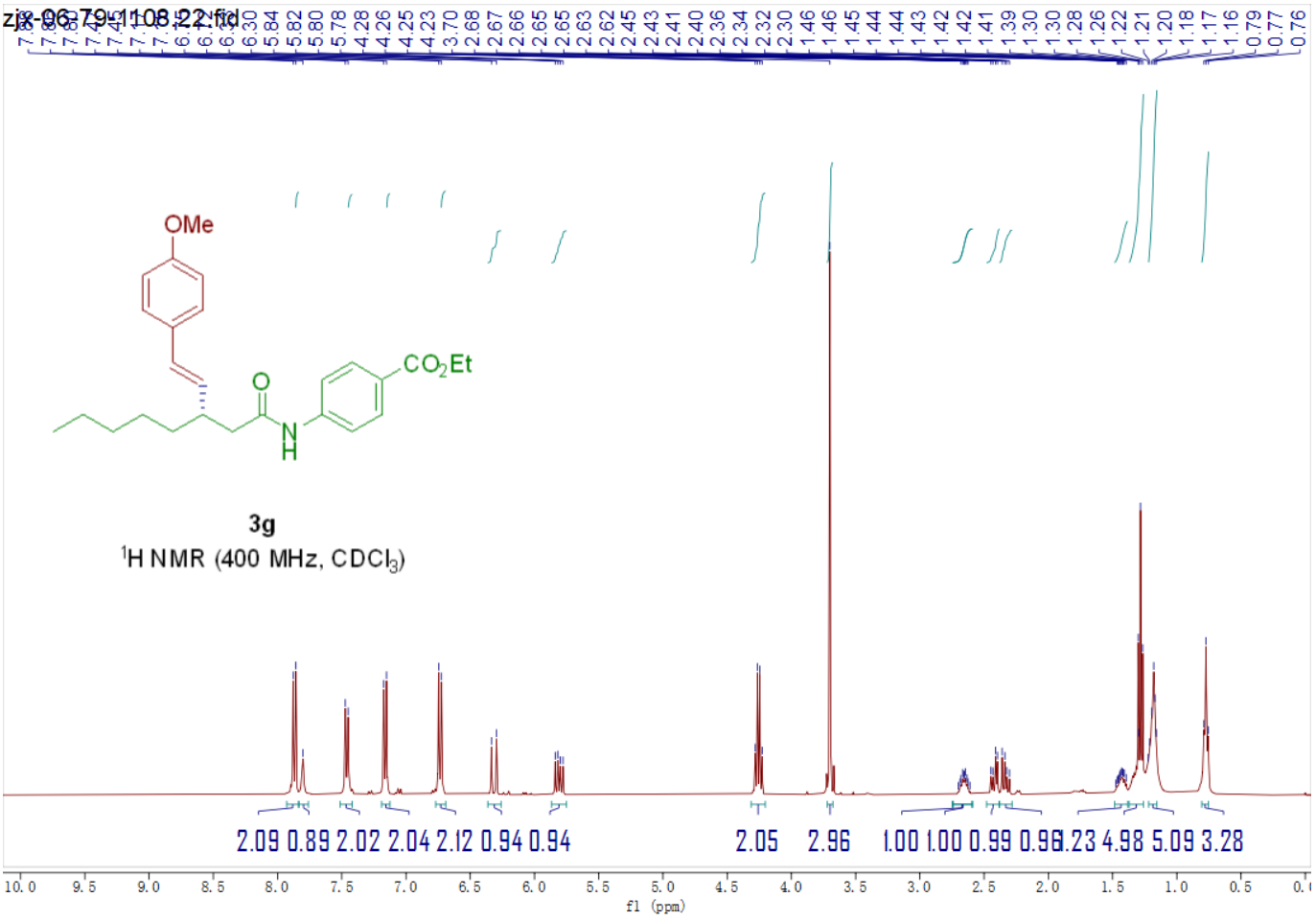
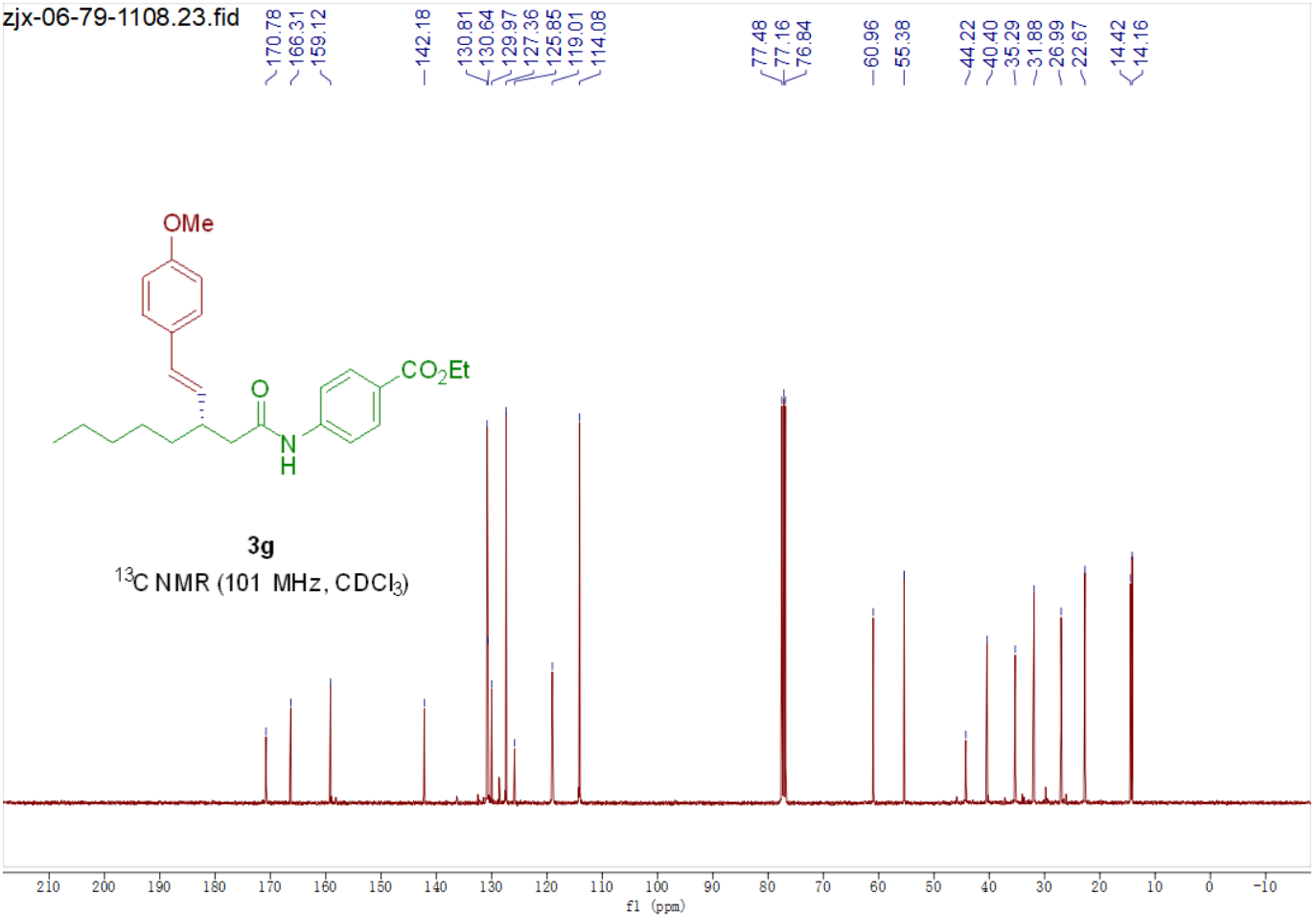
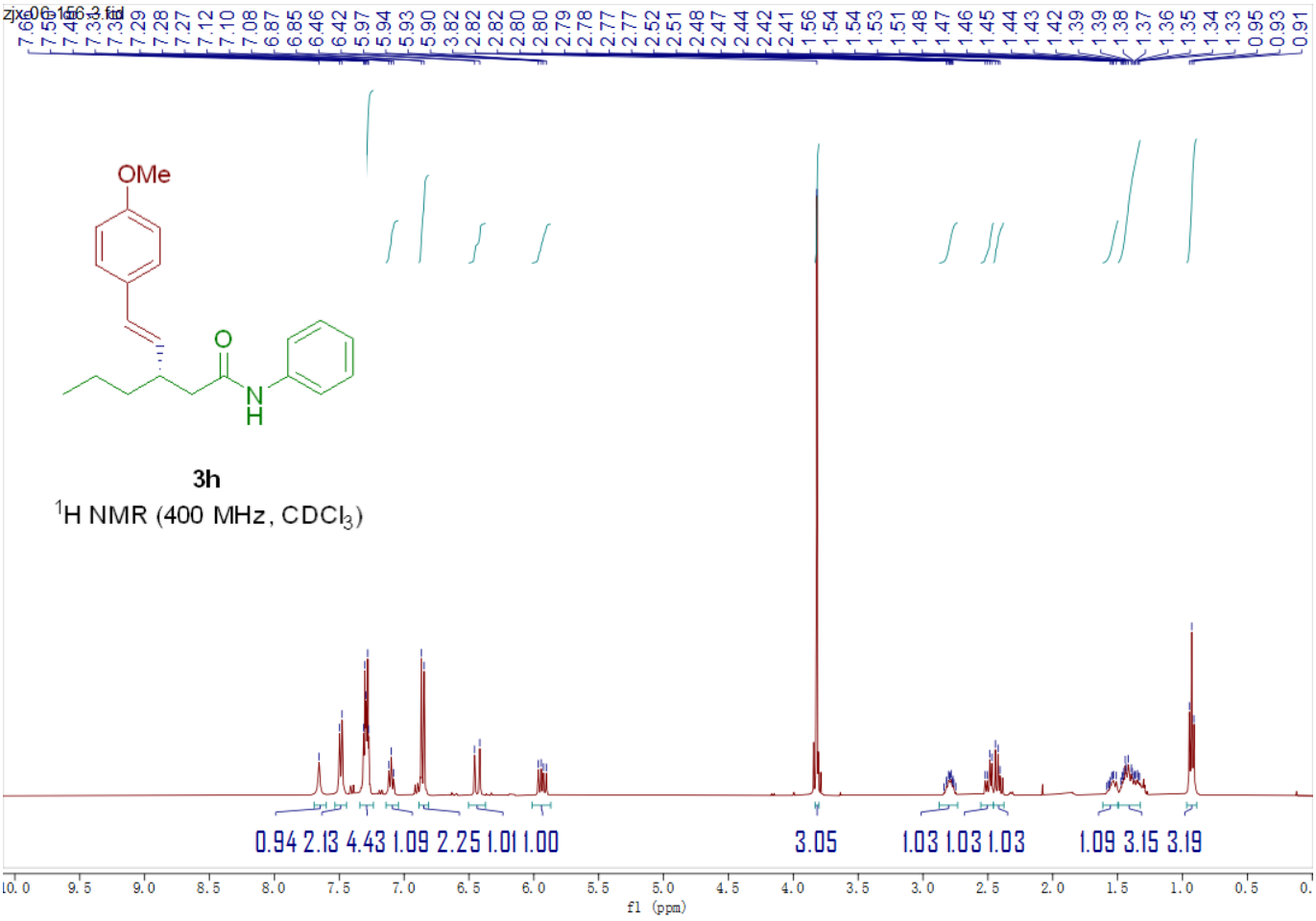
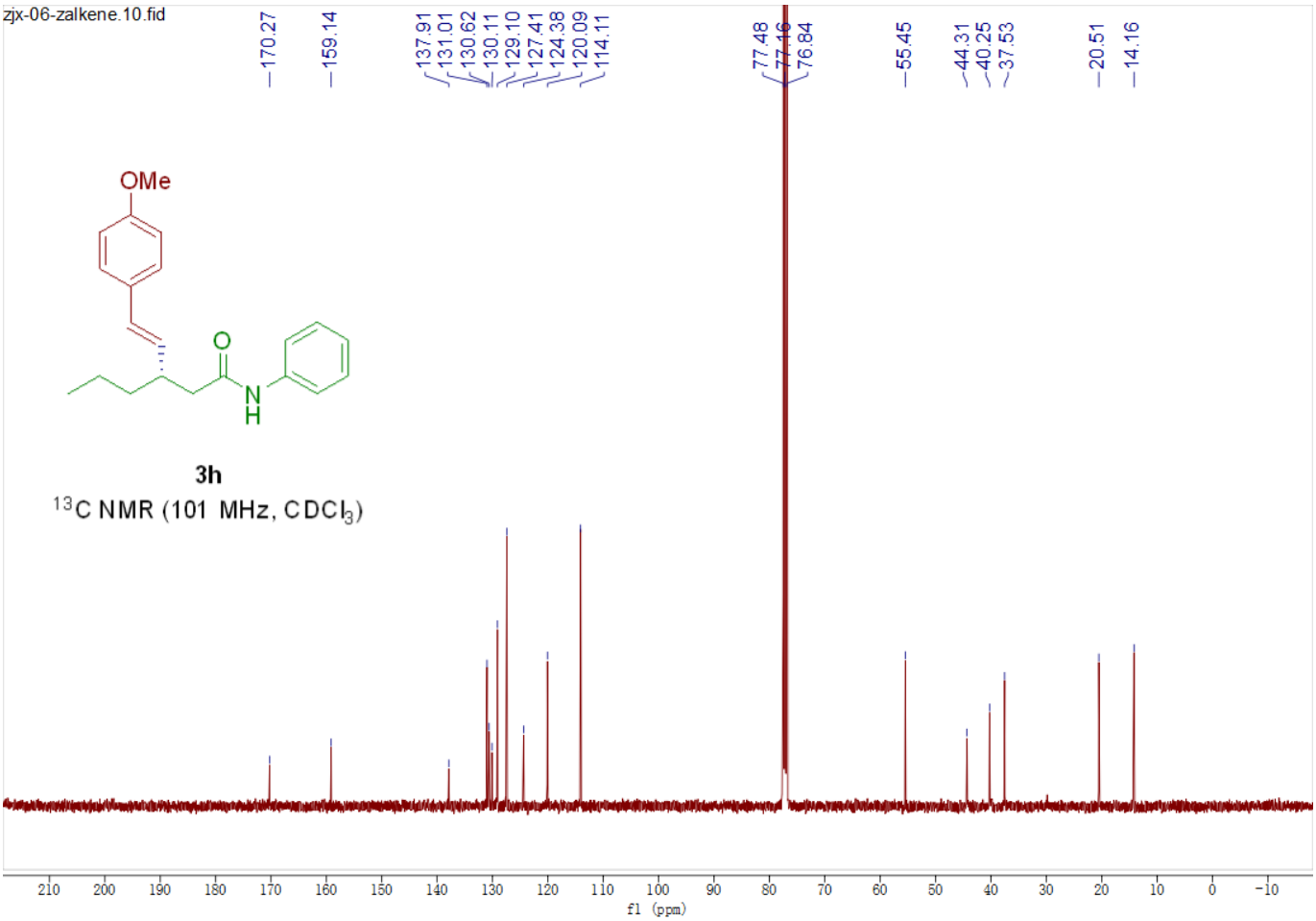
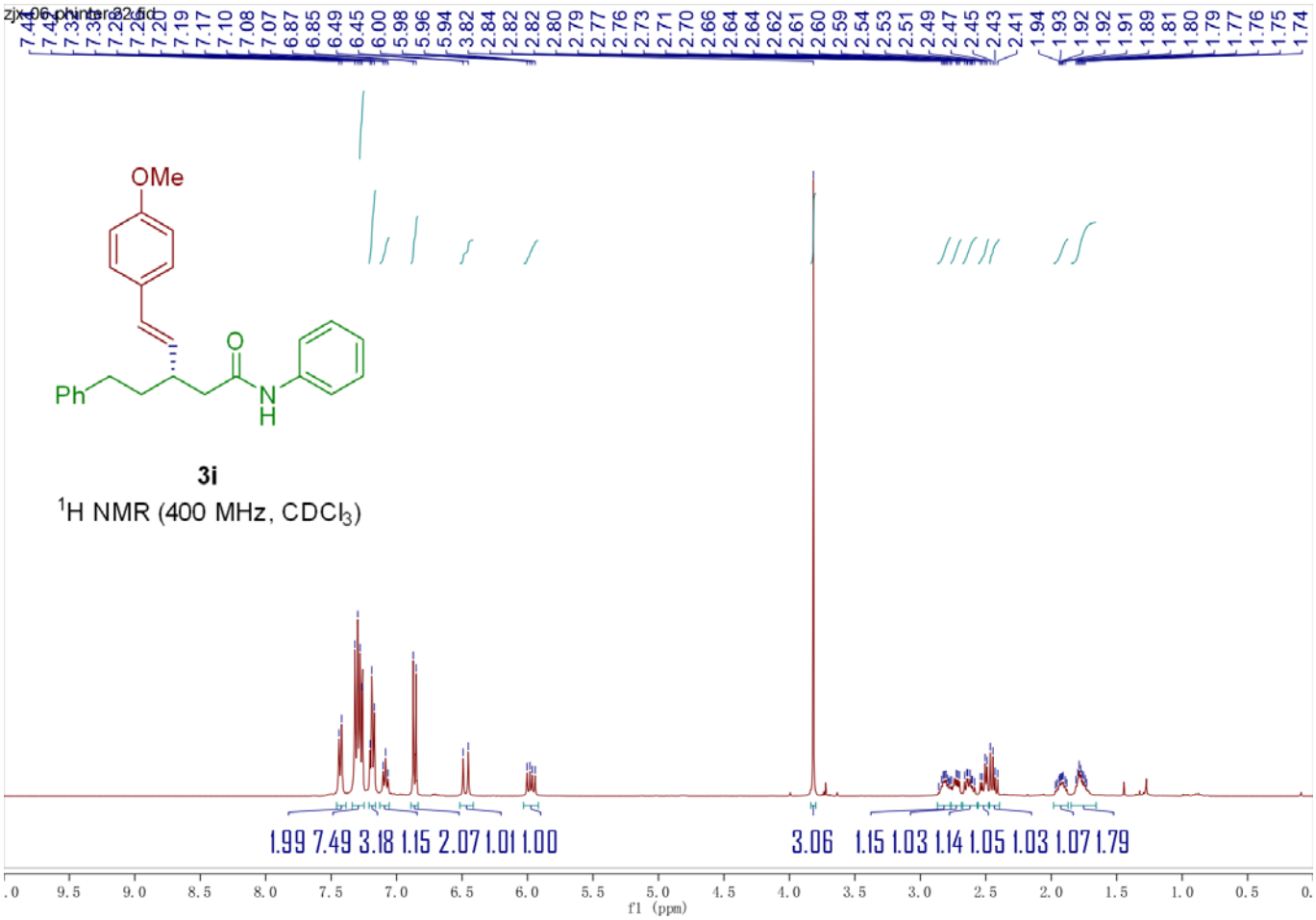
159.05
156.49
131.07
131.05
130.39
130.18
127.36
122.17
114.17
114.06
77.37
77.16
76.95
55.55
55.40
43.99
40.29
37.48
20.49
14.15
OMe
O
N
H
O
3f
13C NMR(151 MHz, CDCl3)
f1 (ppm)

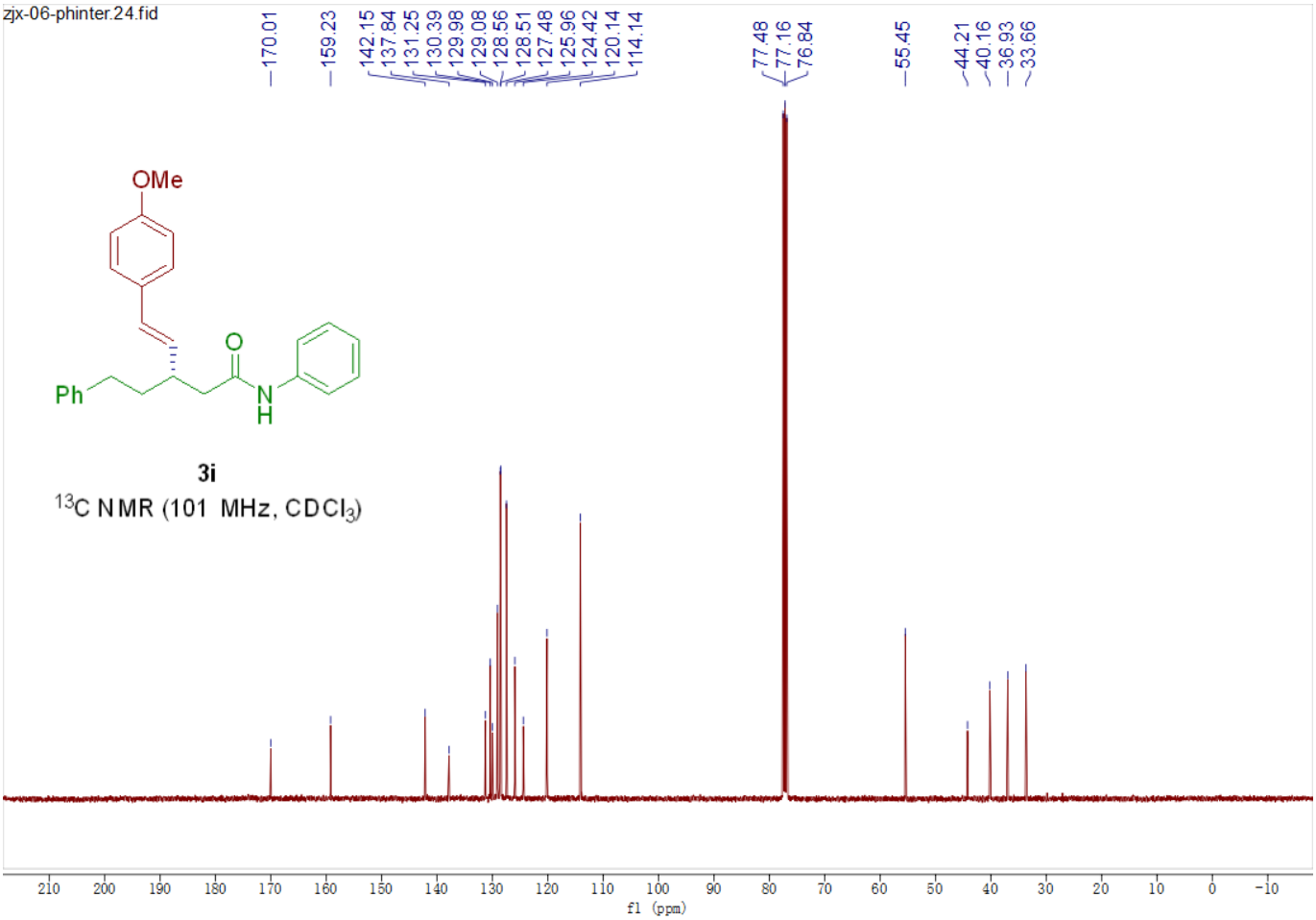

zjx-06-79-1108.22.fid
OMe
CO2Et
O
N
H
3g
1H NMR (400 MHz, CDCl3)
2.09 0.89 2.02 2.04 2.12 0.94 0.94
2.05 2.96 1.00 1.00 0.99 0.98 3.23 4.98 5.09 3.28
f1 (ppm)

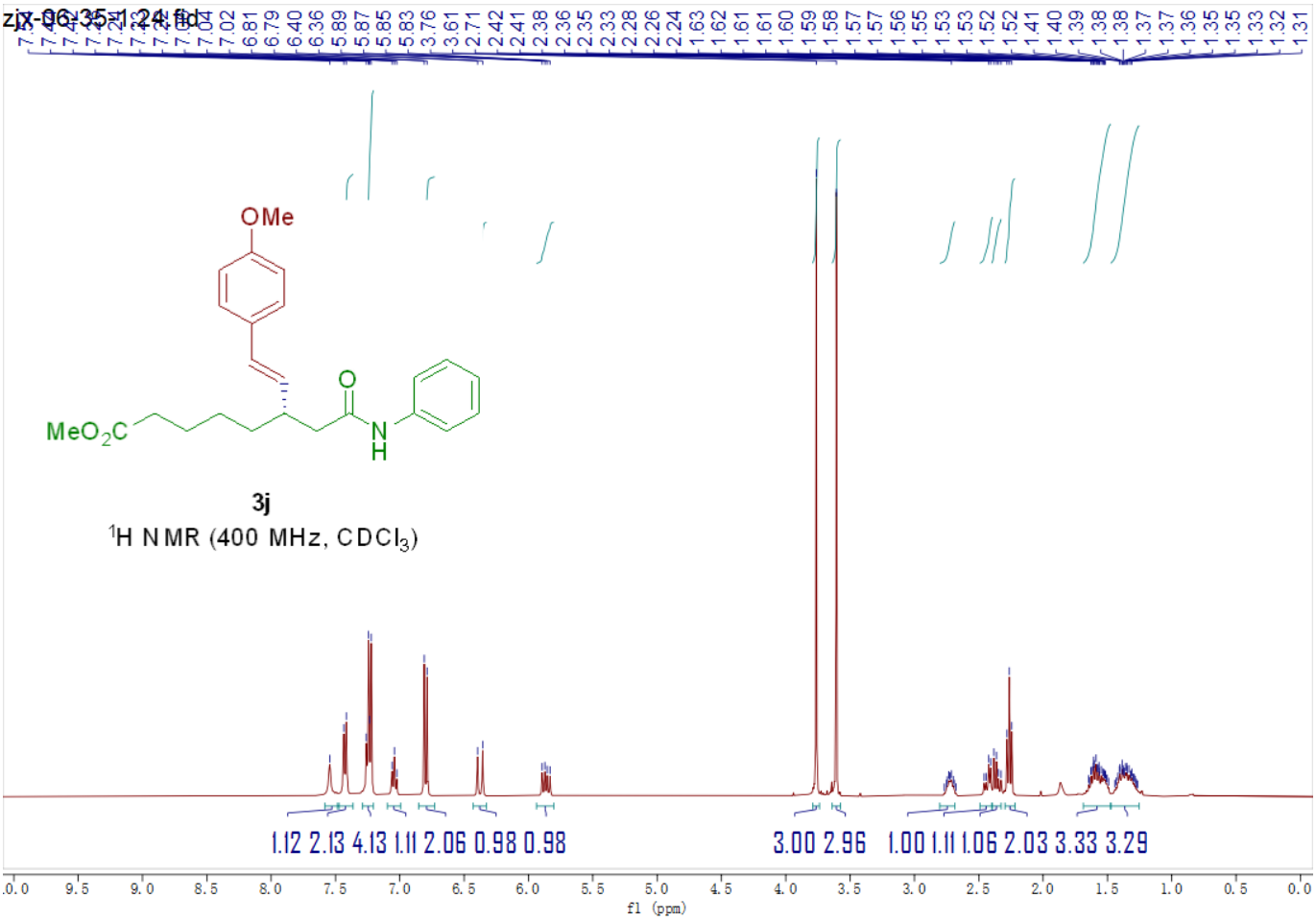

zjx-06-79-1108.23.fid
170.78
166.31
159.12
142.18
130.81
130.64
129.97
127.36
125.85
119.01
114.08
77.48
77.16
76.84
60.96
55.38
44.22
40.40
35.29
31.88
26.99
22.67
14.42
14.16
OMe
CO2Et
O
N
H
3g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

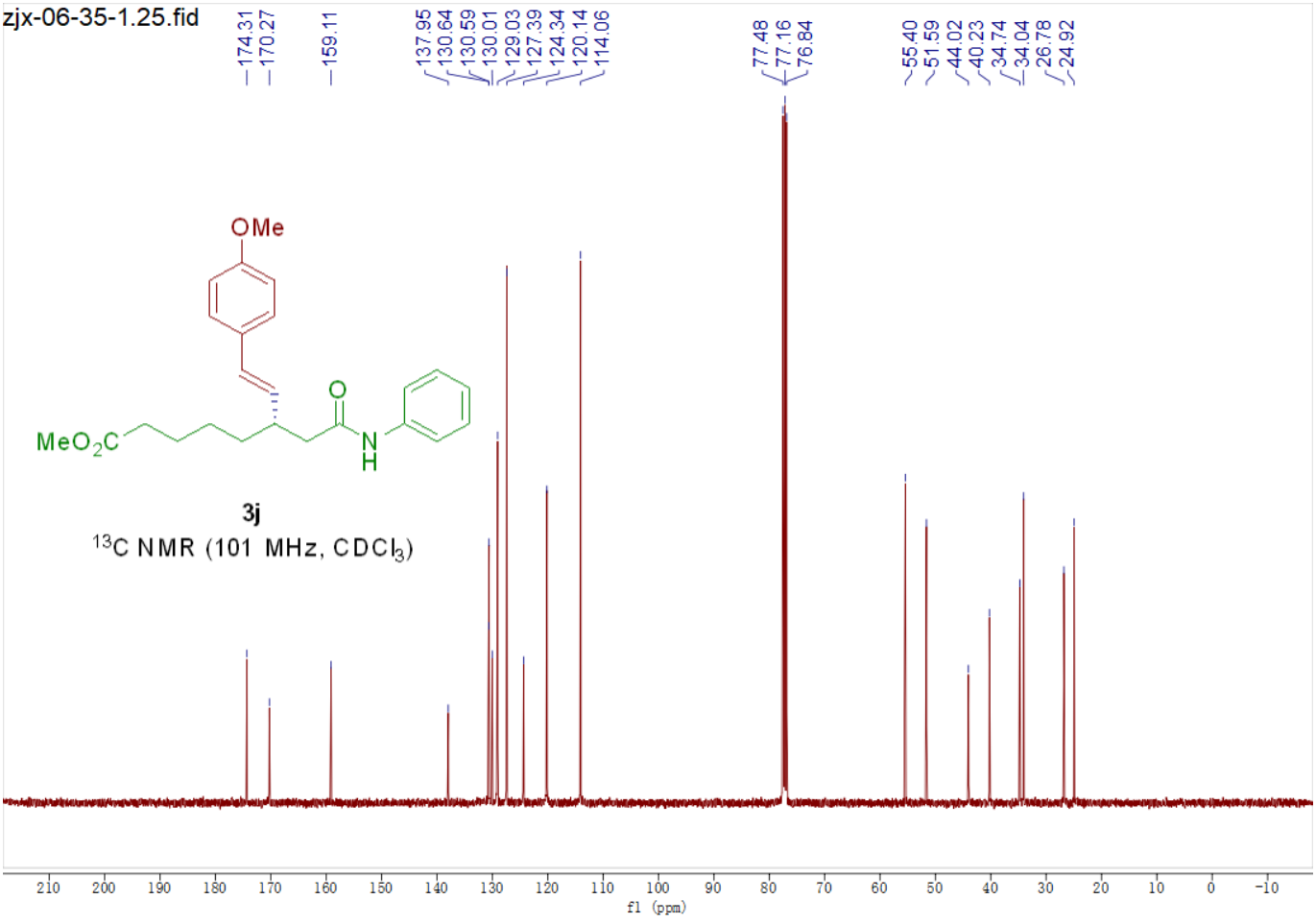

zjx-06-150.3.fid
OMe
O
N
H
3h
1H NMR (400 MHz, CDCl3)
0.94 2.13 4.43 1.09 2.25 1.01 1.00
3.05
1.03 1.03 1.03
1.09 3.15 3.19
f1 (ppm)

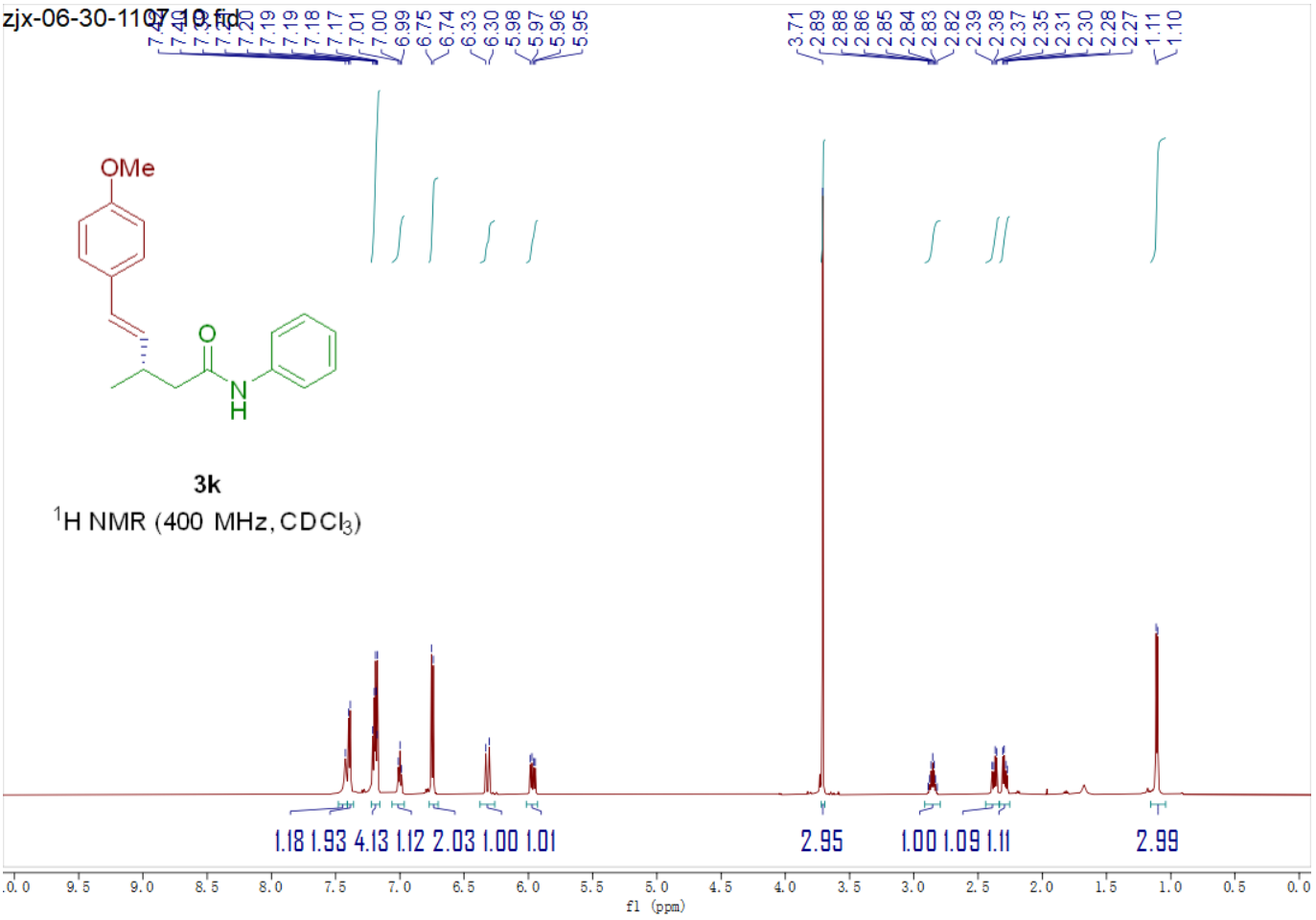

zjx-06-zalkene.10.fid
170.27
159.14
137.91
131.01
130.62
130.11
129.10
127.41
124.38
120.09
114.11
77.48
77.16
76.84
55.45
44.31
40.25
37.53
20.51
14.16
OMe
O
N
H
3h
13C NMR (101 MHz, CDCl3)
f1 (ppm)

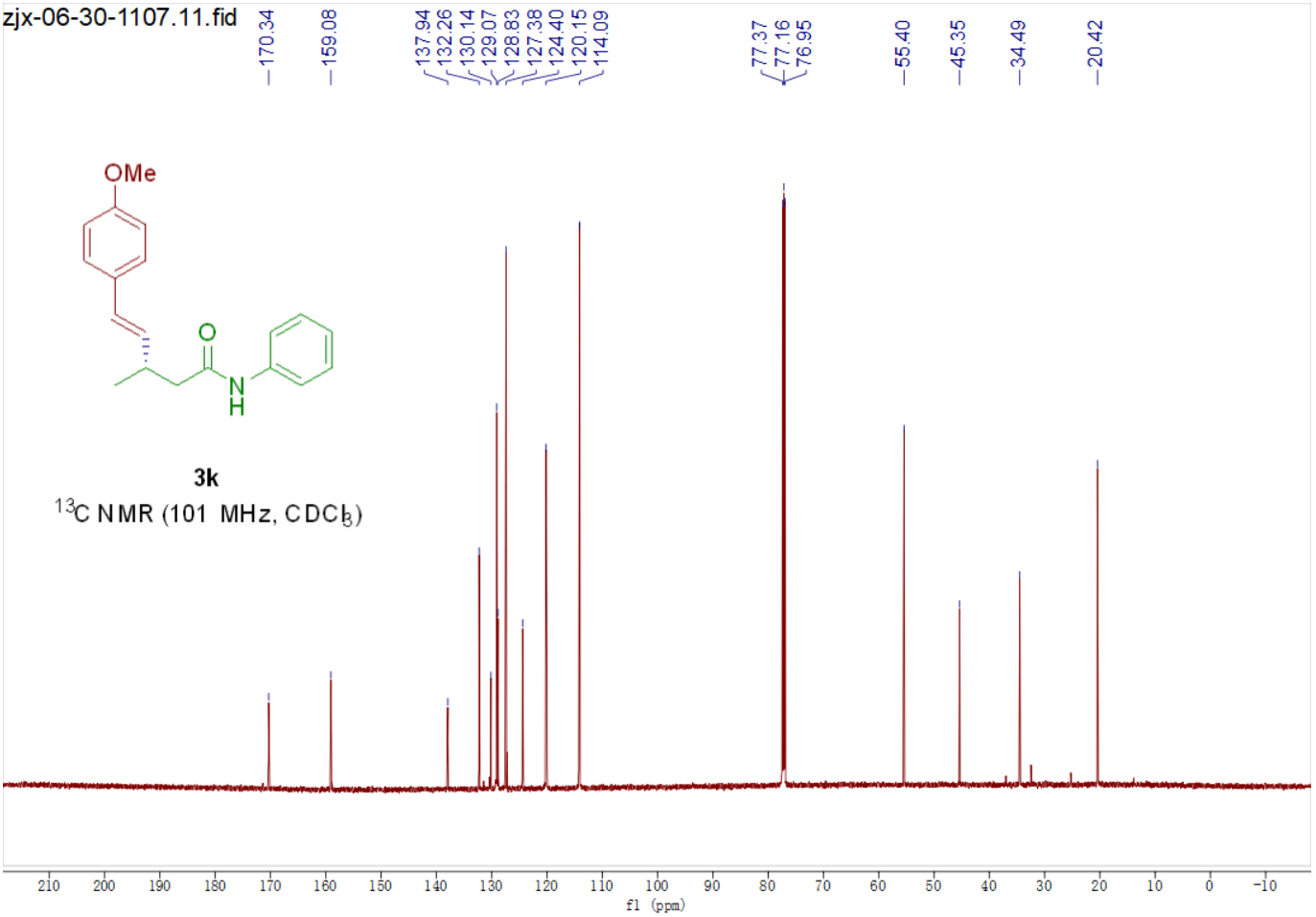

zjx-06-phinter.32.fid
OMe
O
N
H
Ph
3i
1H NMR (400 MHz, CDCl3)
1.99 7.49 3.18 1.15 2.07 1.01 1.00
3.06 1.15 1.03 1.14 1.05 1.03 1.07 1.79
f1 (ppm)

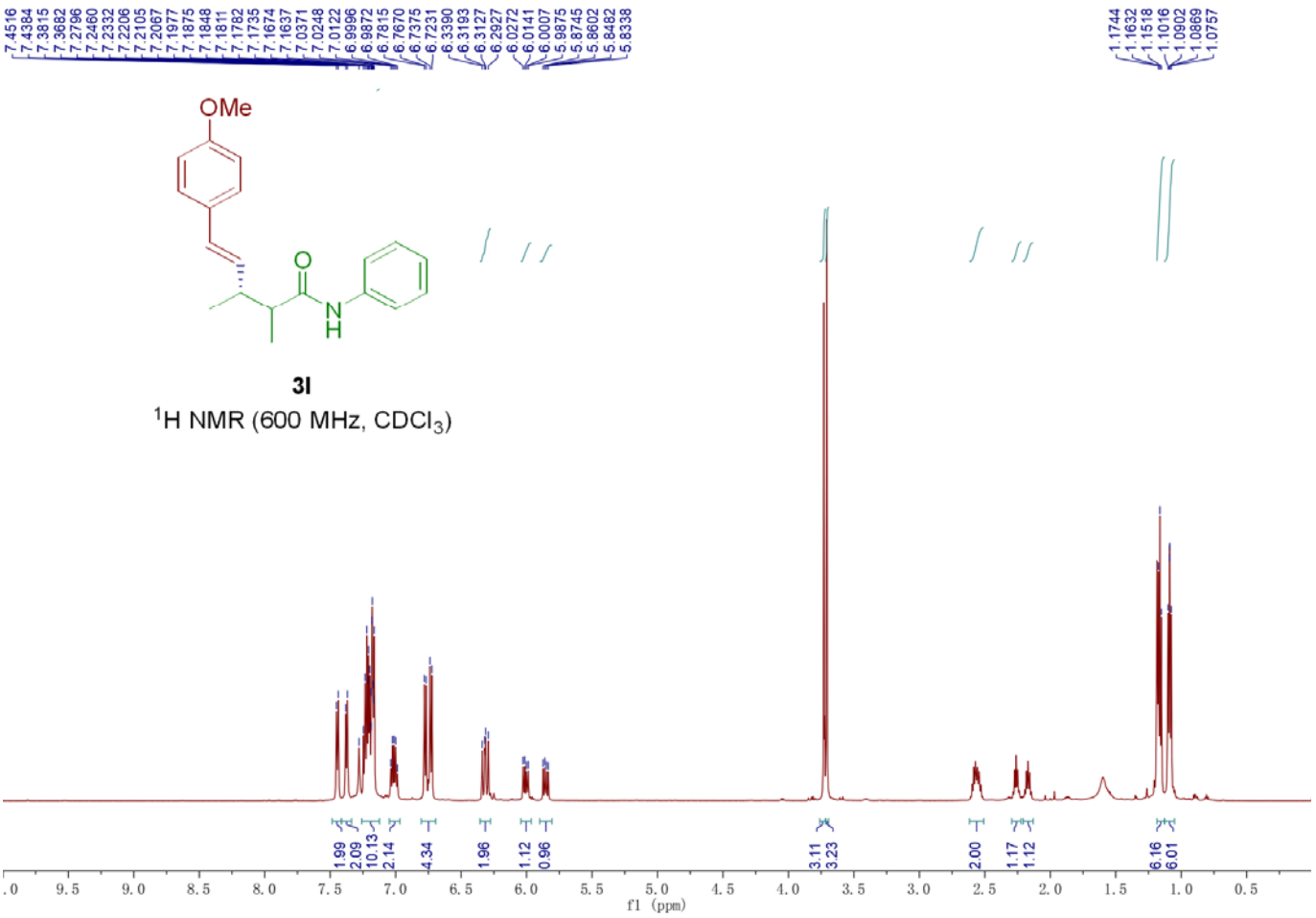

zjx-06-phinter.24.fid
170.01
159.23
142.15
137.84
131.25
130.39
129.98
129.08
128.56
128.51
127.48
125.96
124.42
120.14
114.14
77.48
77.16
76.84
55.45
44.21
40.16
36.93
33.66
OMe
O
N
H
Ph
3i
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-06-35-1.24.fid
OMe
O
N
H
MeO2C
3j
1H NMR (400 MHz, CDCl3)
1.12 2.13 4.13 1.11 2.06 0.98 0.98
3.00 2.96 1.00 1.11 1.06 2.03 3.33 3.29
f1 (ppm)


zjx-06-35-1.25.fid
174.31
170.27
159.11
137.95
130.64
130.59
130.01
129.03
127.39
124.34
120.14
114.06
77.48
77.16
76.84
55.40
51.59
44.02
40.23
34.74
34.04
26.78
24.92
OMe
O
N
H
MeO2C
3j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

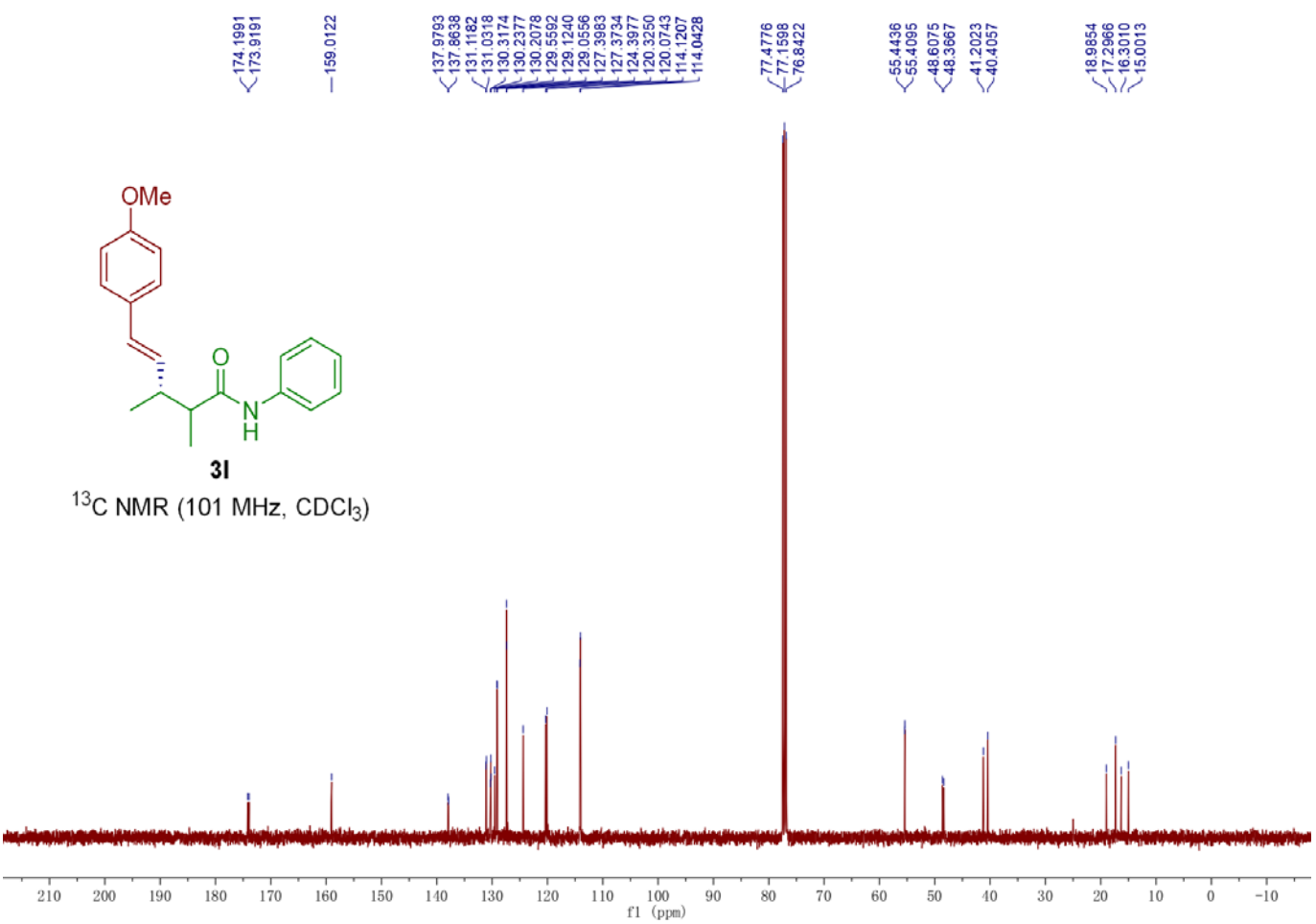

zjx-06-30-1107.10.fid
7.41 7.40 7.39 7.38 7.20 7.19 7.19 7.18 7.17 7.01 7.00 6.99 6.75 6.74 6.33 6.30 5.98 5.97 5.96 5.95
3.71 2.89 2.88 2.86 2.85 2.84 2.83 2.82 2.39 2.38 2.37 2.35 2.31 2.30 2.28 2.27 1.11 1.10
OMe
O
N
H
3k
1H NMR (400 MHz, CDCl3)
1.18 1.93 4.13 1.12 2.03 1.00 1.01
2.95
1.00 1.09 1.11
2.99
f1 (ppm)


zjx-06-30-1107.11.fid
170.34 159.08 137.94 132.26 130.14 129.07 128.83 127.38 124.40 120.15 114.09
77.37 77.16 76.95
55.40 45.35 34.49 20.42
OMe
O
N
H
3k
13C NMR (101 MHz, CDCl3)
f1 (ppm)



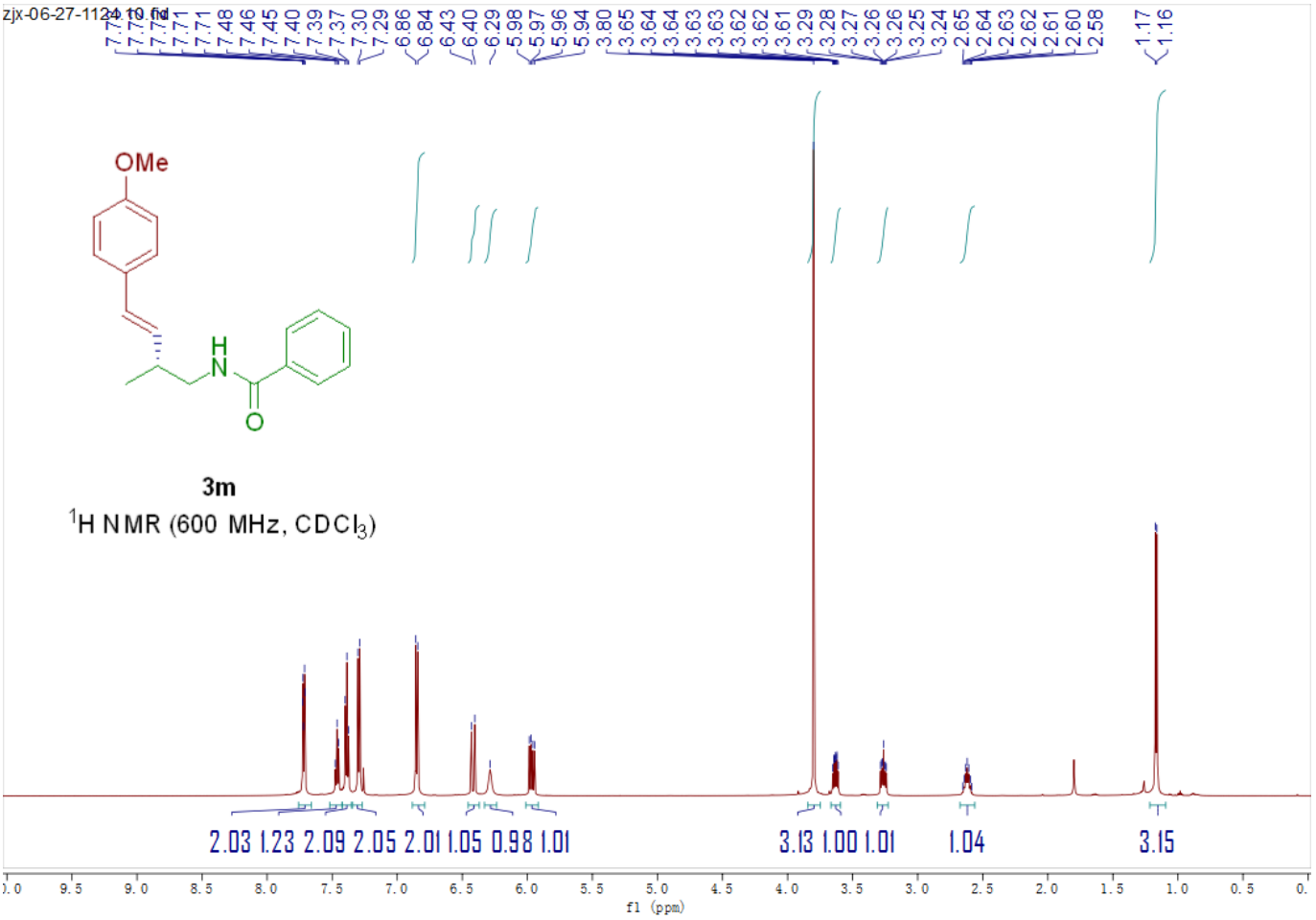
3l

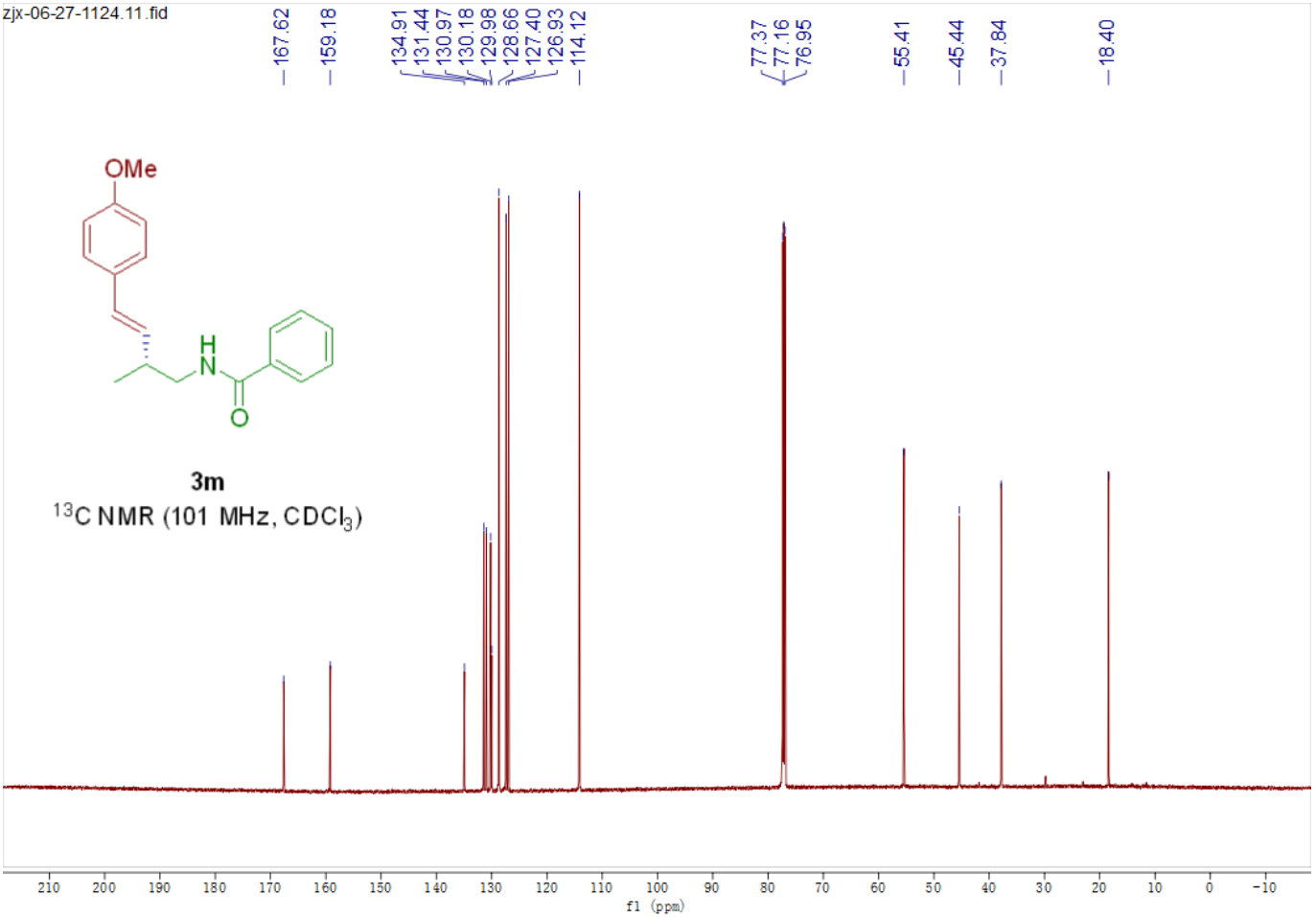
^{1}H NMR (600 MHz, $CDCl_3$)

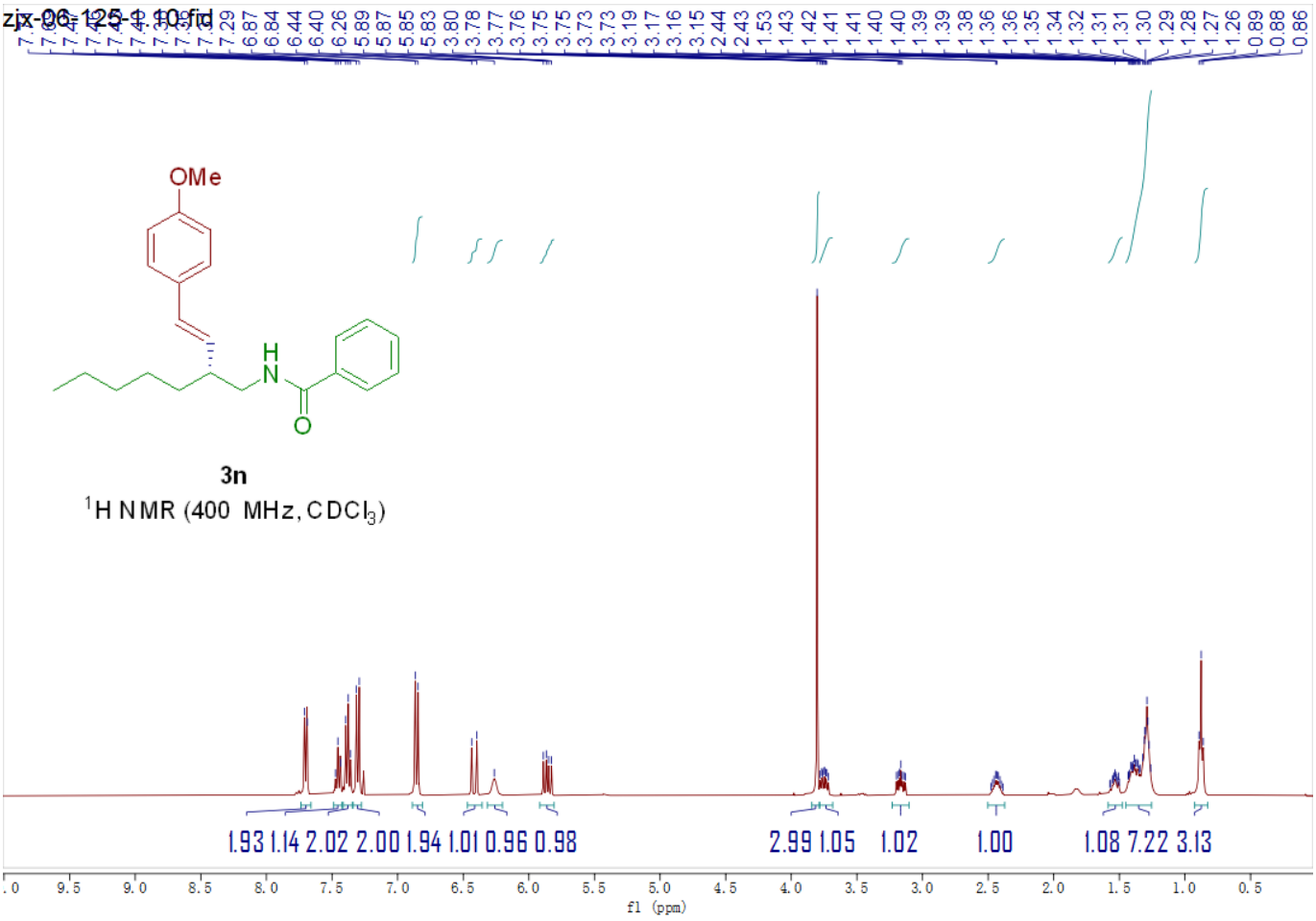


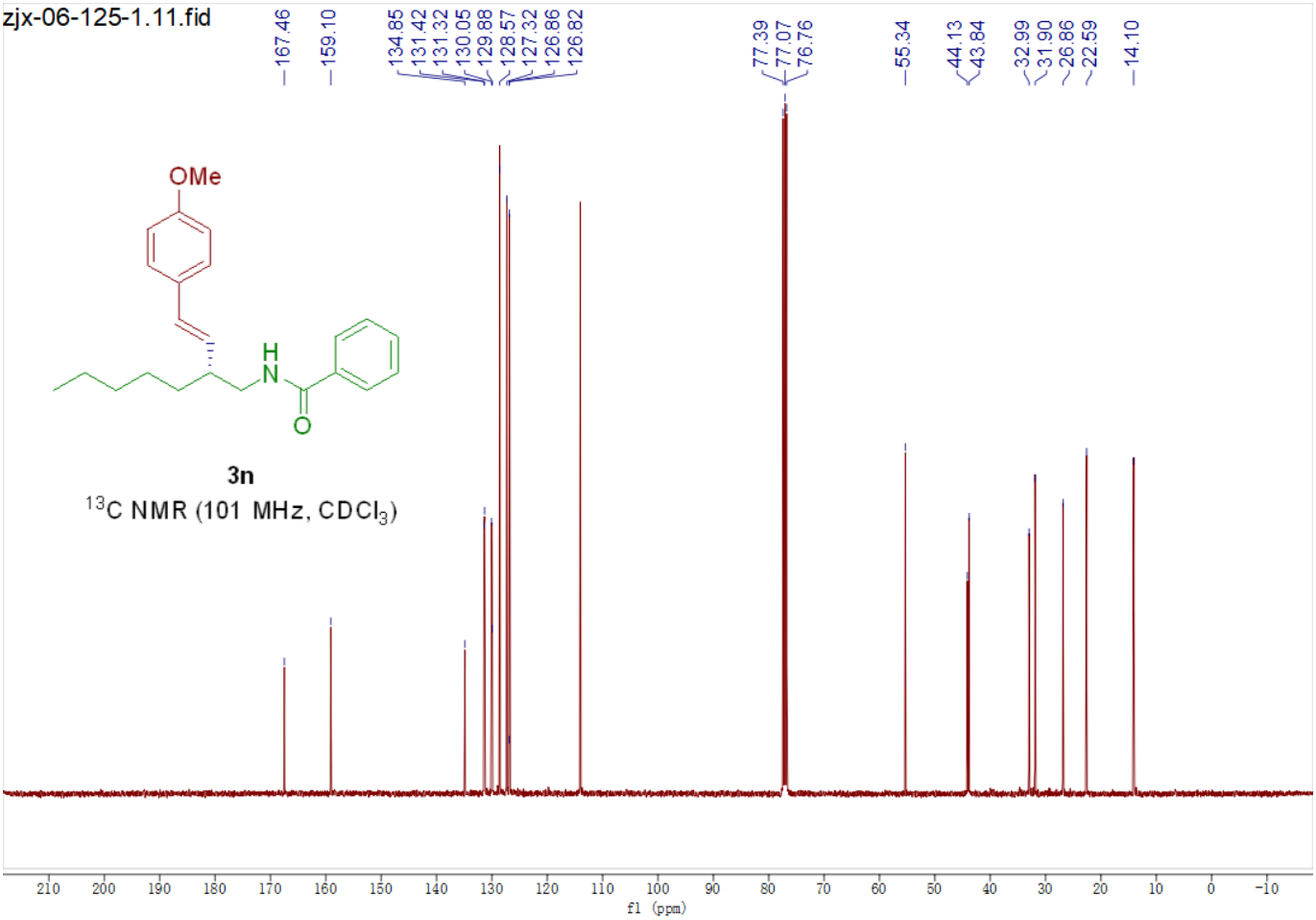
3l

^{13}C NMR (101 MHz, $CDCl_3$)

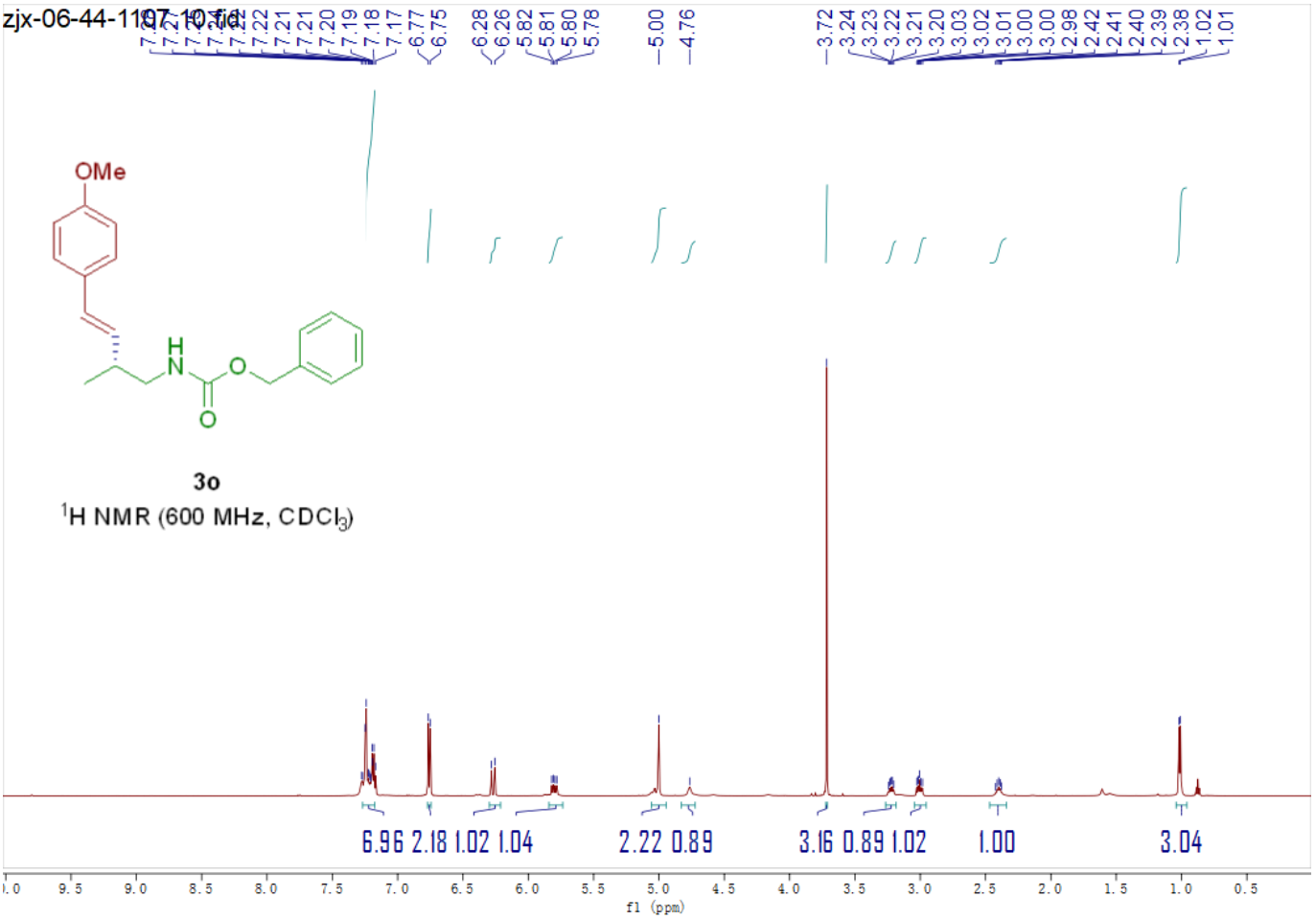

zjx-06-27-1124.10.fid
OMe
H
N
O
3m
1H NMR (600 MHz, CDCl3)
2.03 1.23 2.09 2.05 2.01 1.05 0.98 1.01
3.13 1.00 1.01
1.04
3.15
f1 (ppm)


zjx-06-27-1124.11.fid
167.62
159.18
134.91
131.44
130.97
130.18
129.98
128.66
127.40
126.93
114.12
77.37
77.16
76.95
55.41
45.44
37.84
18.40
OMe
H
N
O
3m
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-06-125-1.10.fid
OMe
H
N
O
3n
^{1}H NMR (400 MHz, CDCl$_3$)
1.93 1.14 2.02 2.00 1.94 1.01 0.96 0.98
2.99 1.05 1.02 1.00 1.08 7.22 3.13
f1 (ppm)


zjx-06-125-1.11.fid
167.46
159.10
134.85
131.42
131.32
130.05
129.88
128.57
127.32
126.86
126.82
77.39
77.07
76.76
55.34
44.13
43.84
32.99
31.90
26.86
22.59
14.10
OMe
H
N
O
3n
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

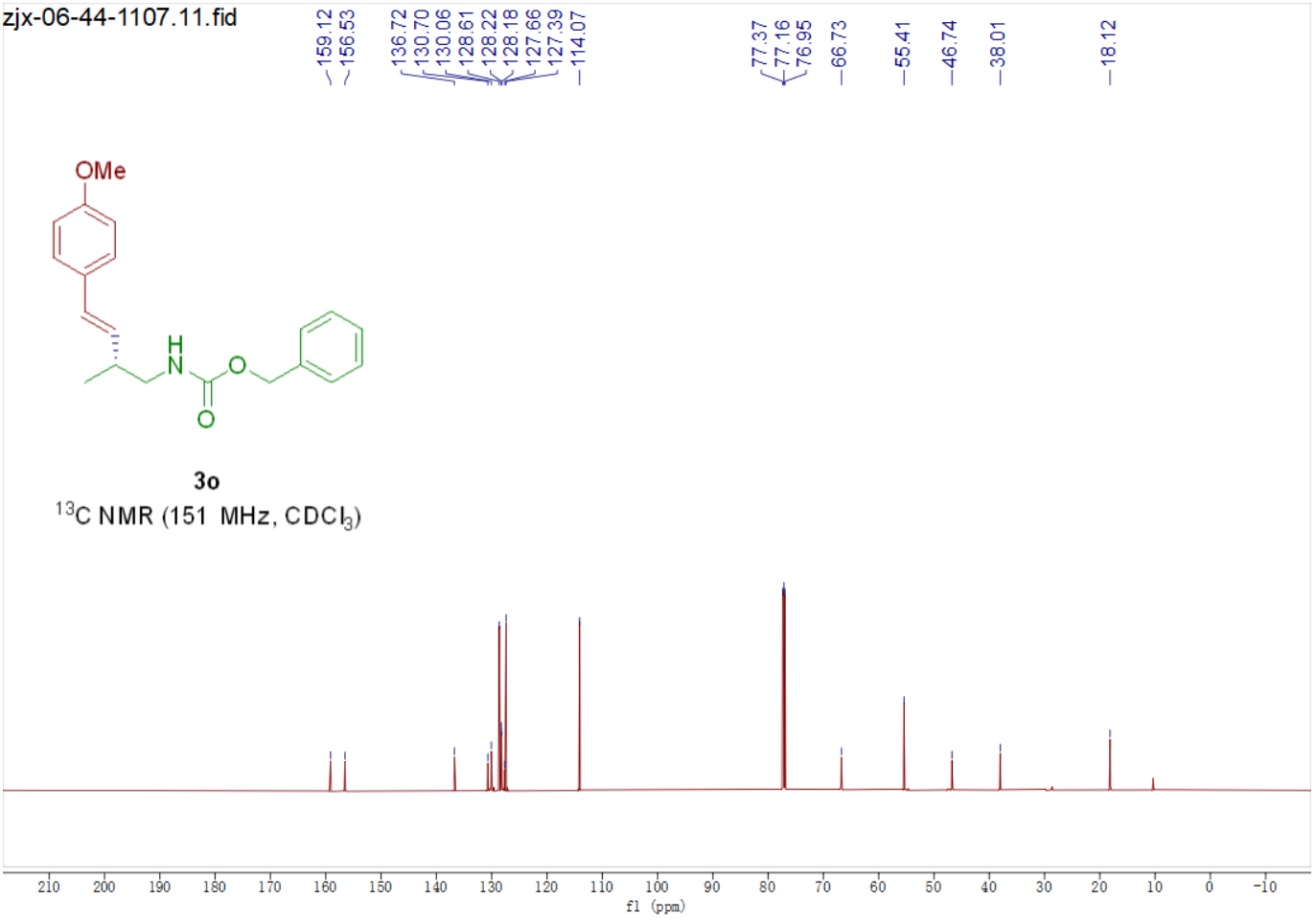
zjx-06-44-1107.10.fid



3o

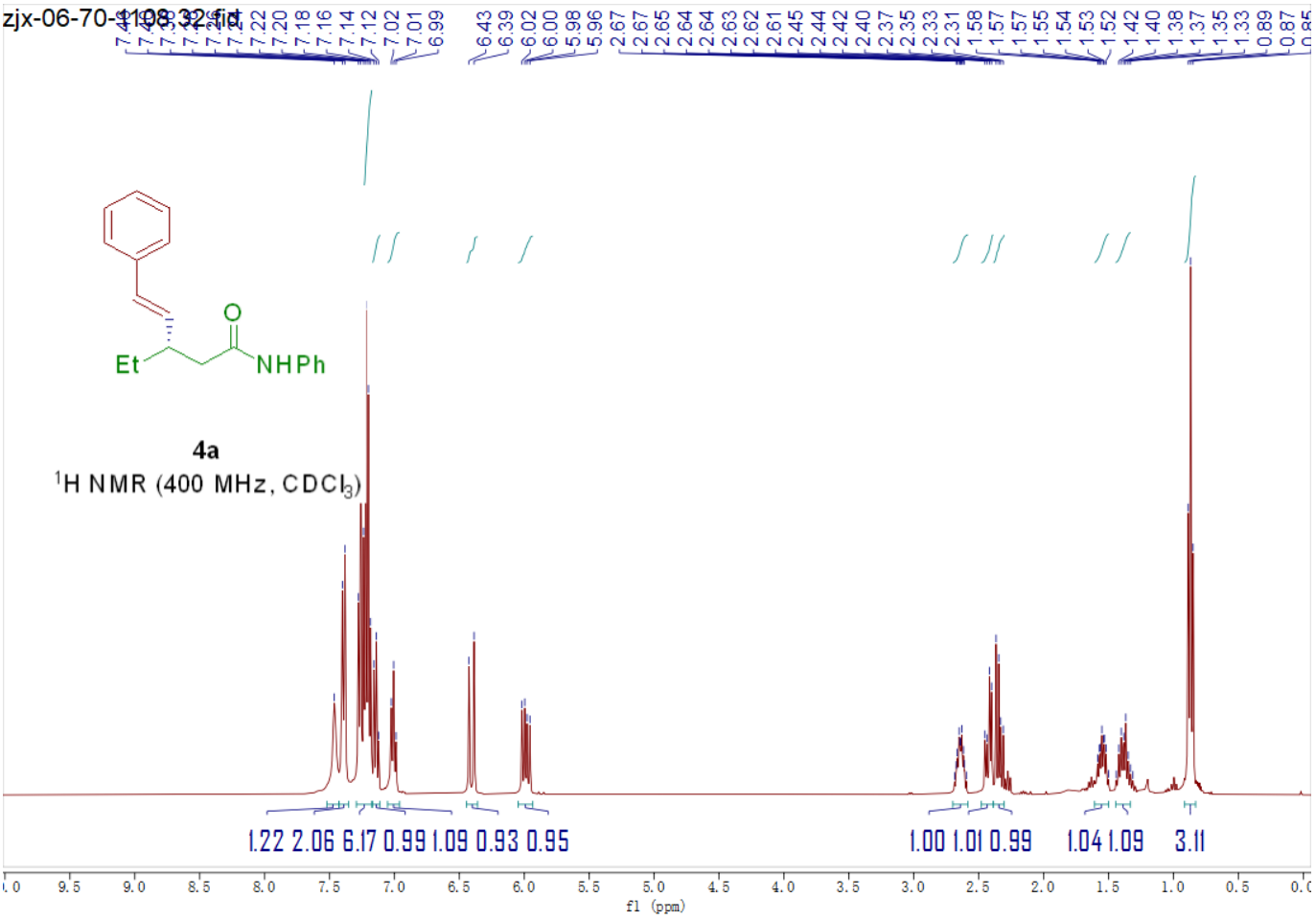
^{1}H NMR (600 MHz, $CDCl_3$)

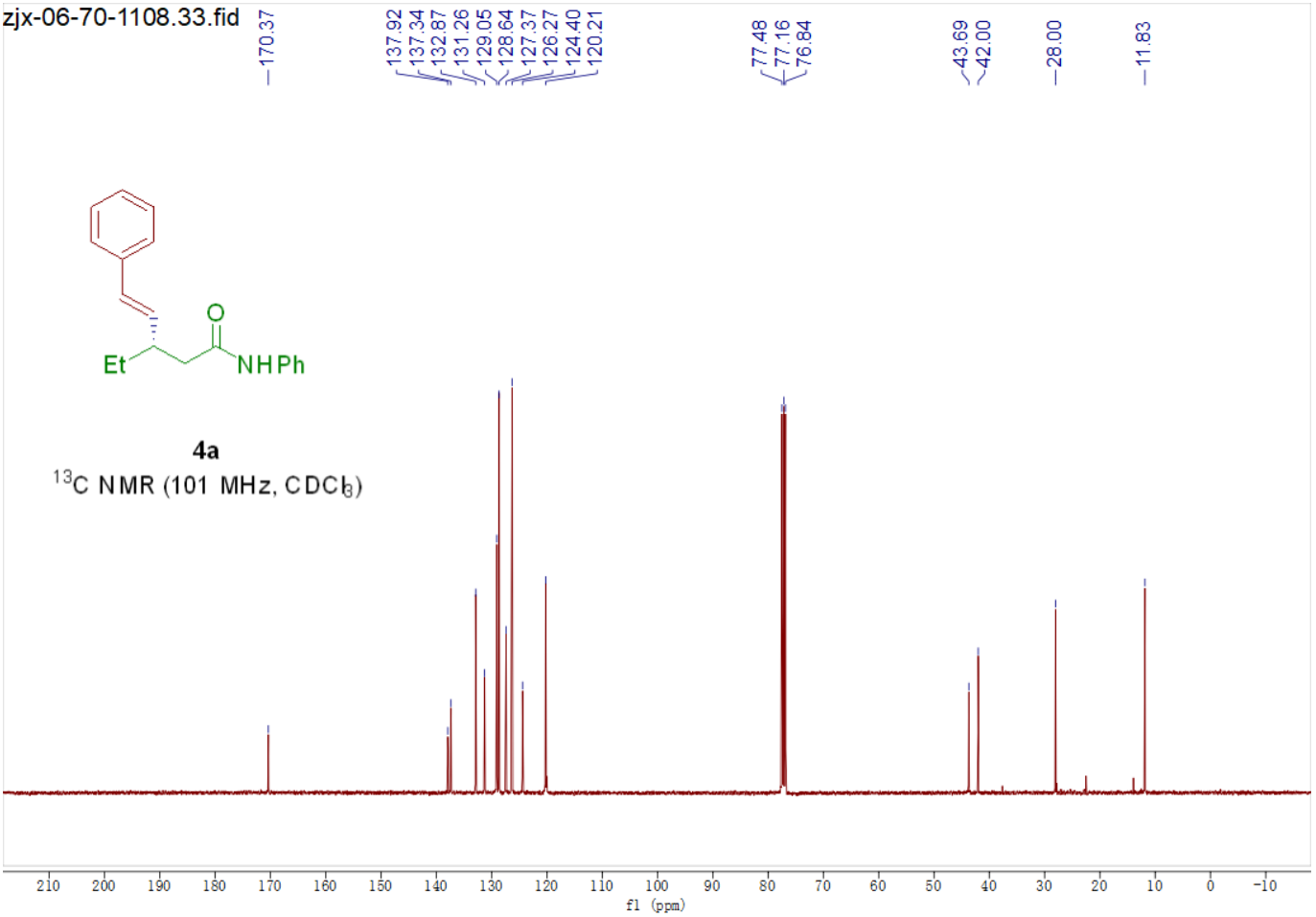
zjx-06-44-1107.11.fid



3o

^{13}C NMR (151 MHz, $CDCl_3$)


zjx-06-70-1108.32.fid
Et
NHPh
O
4a
1H NMR (400 MHz, CDCl3)
1.22 2.06 6.17 0.99 1.09 0.93 0.95
1.00 1.01 0.99 1.04 1.09 3.11
f1 (ppm)


zjx-06-70-1108.33.fid
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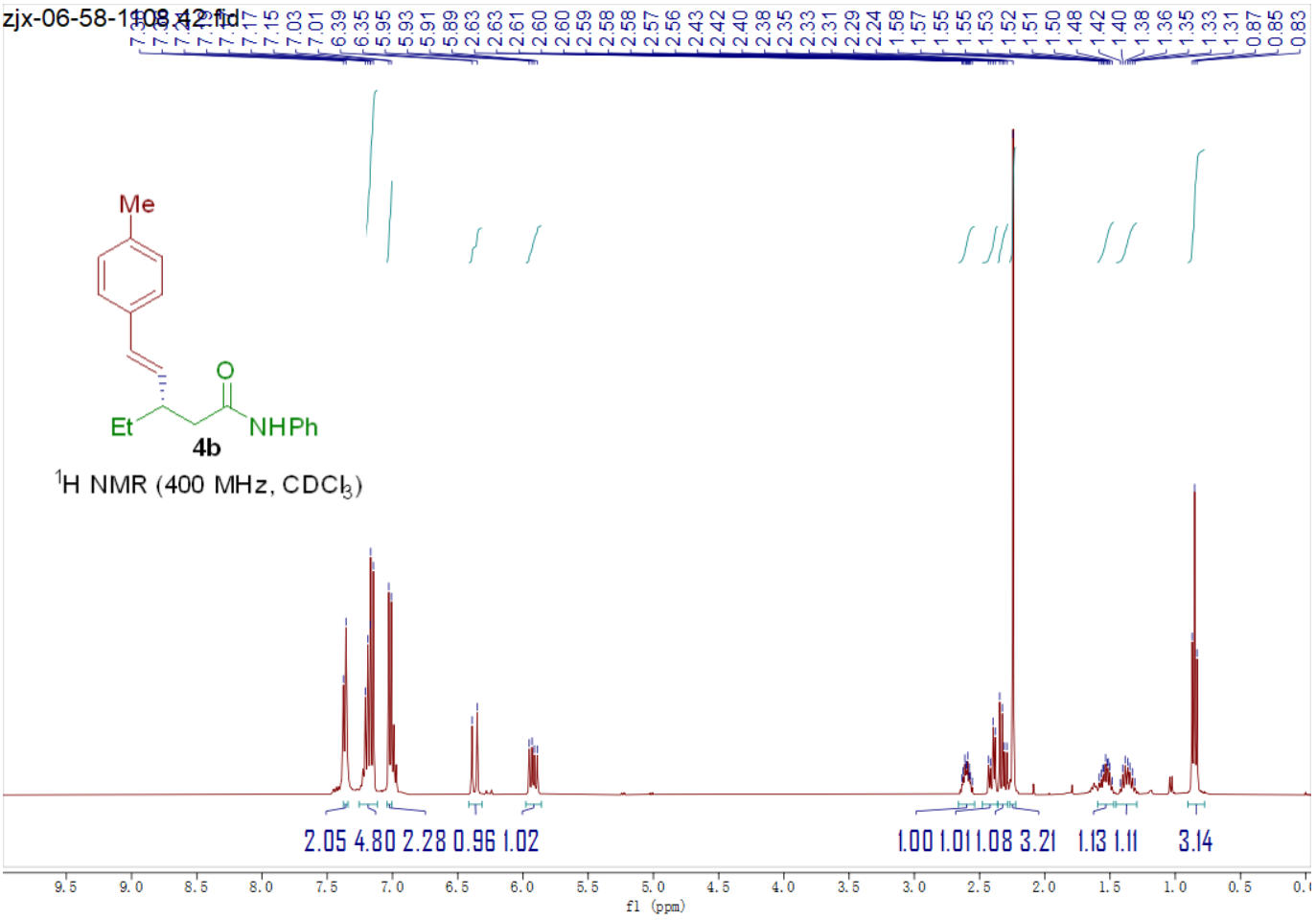
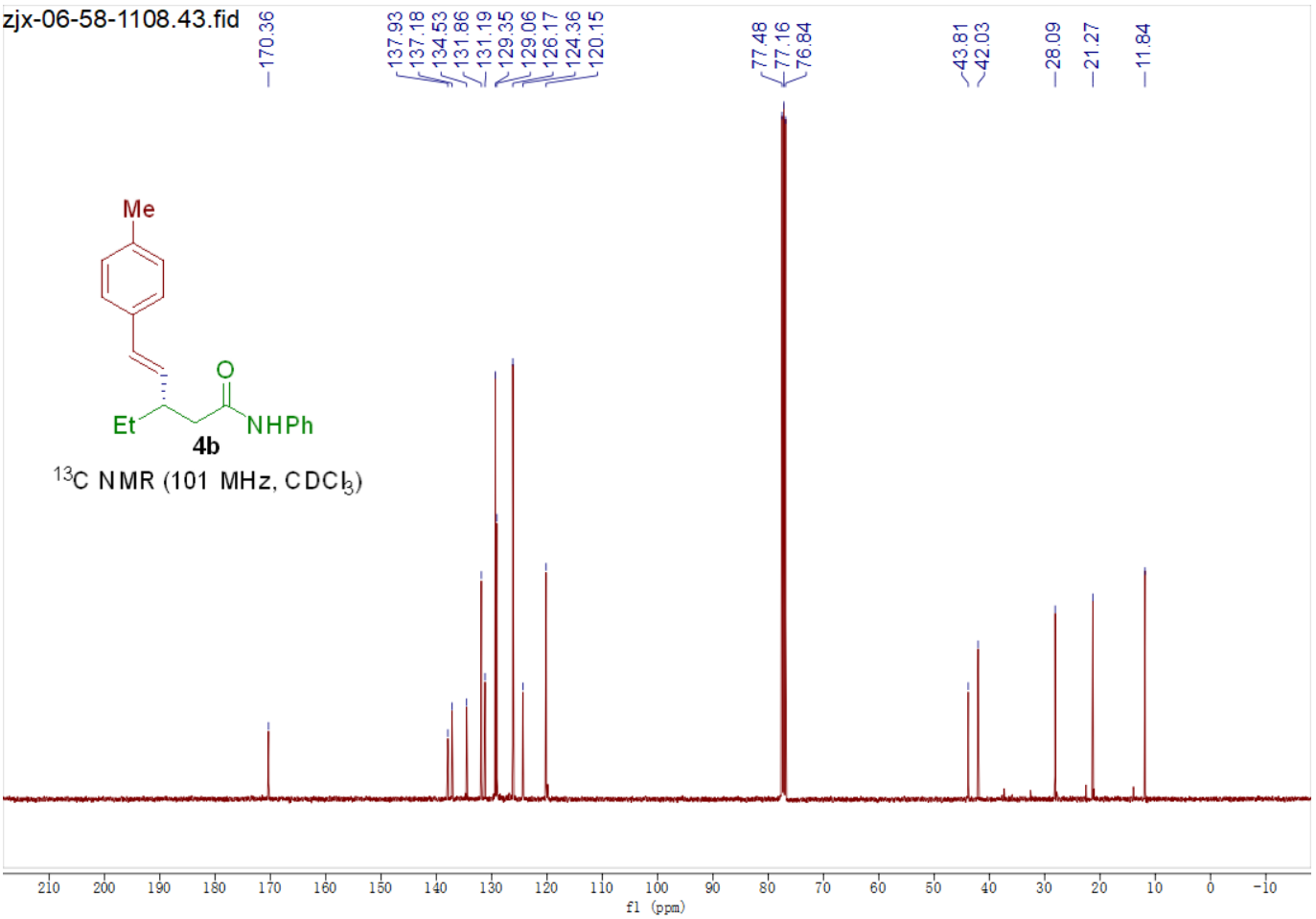
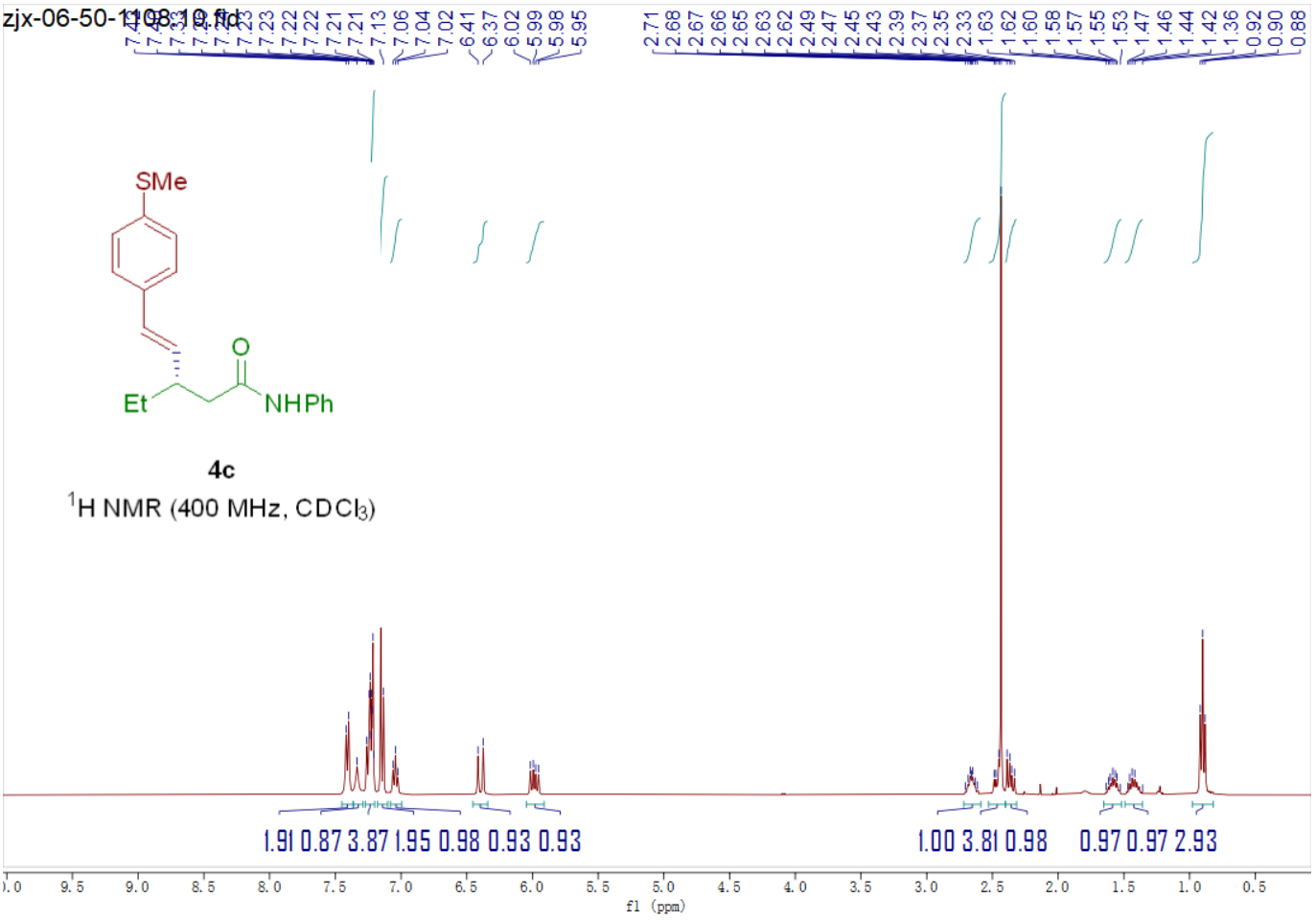
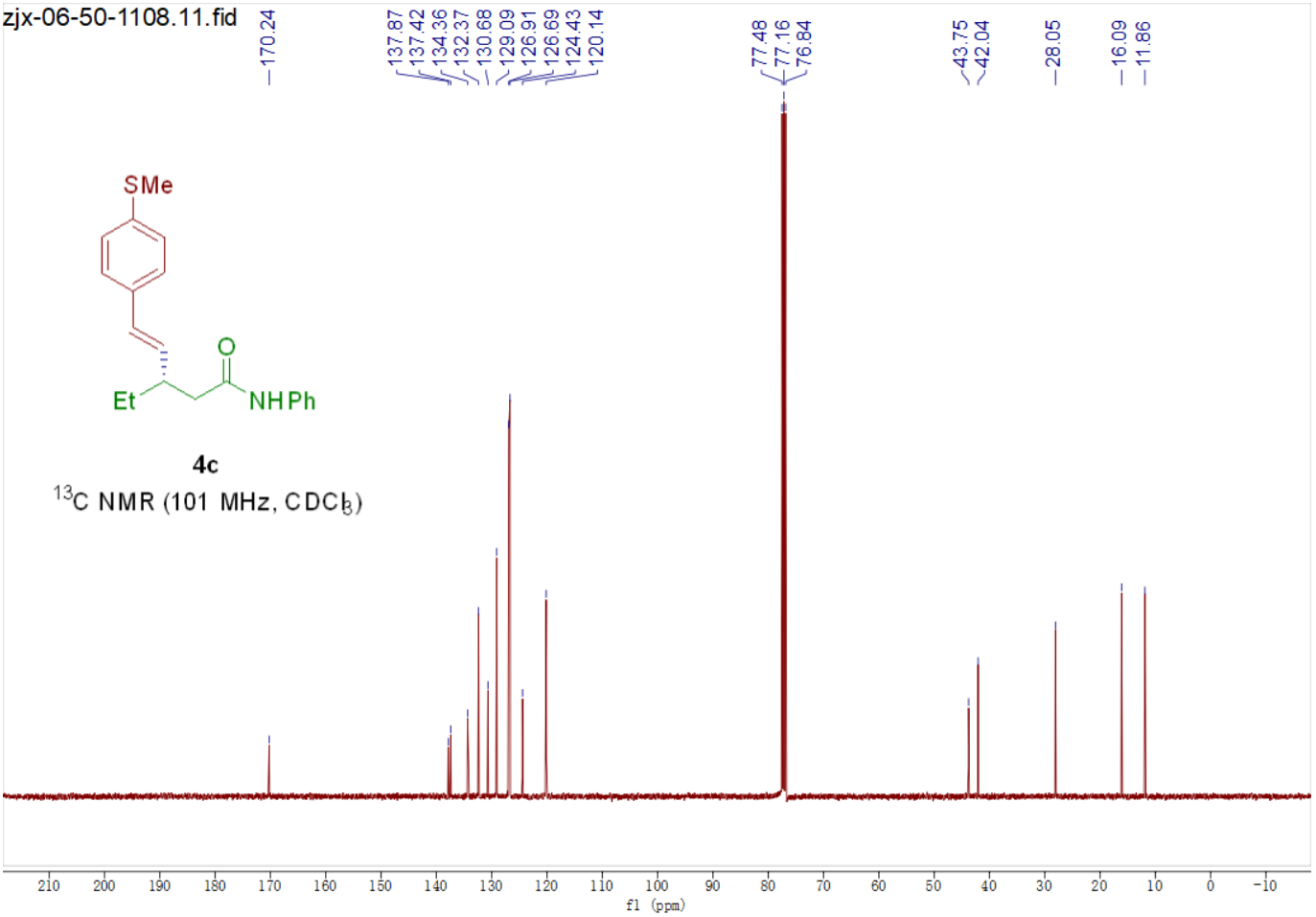
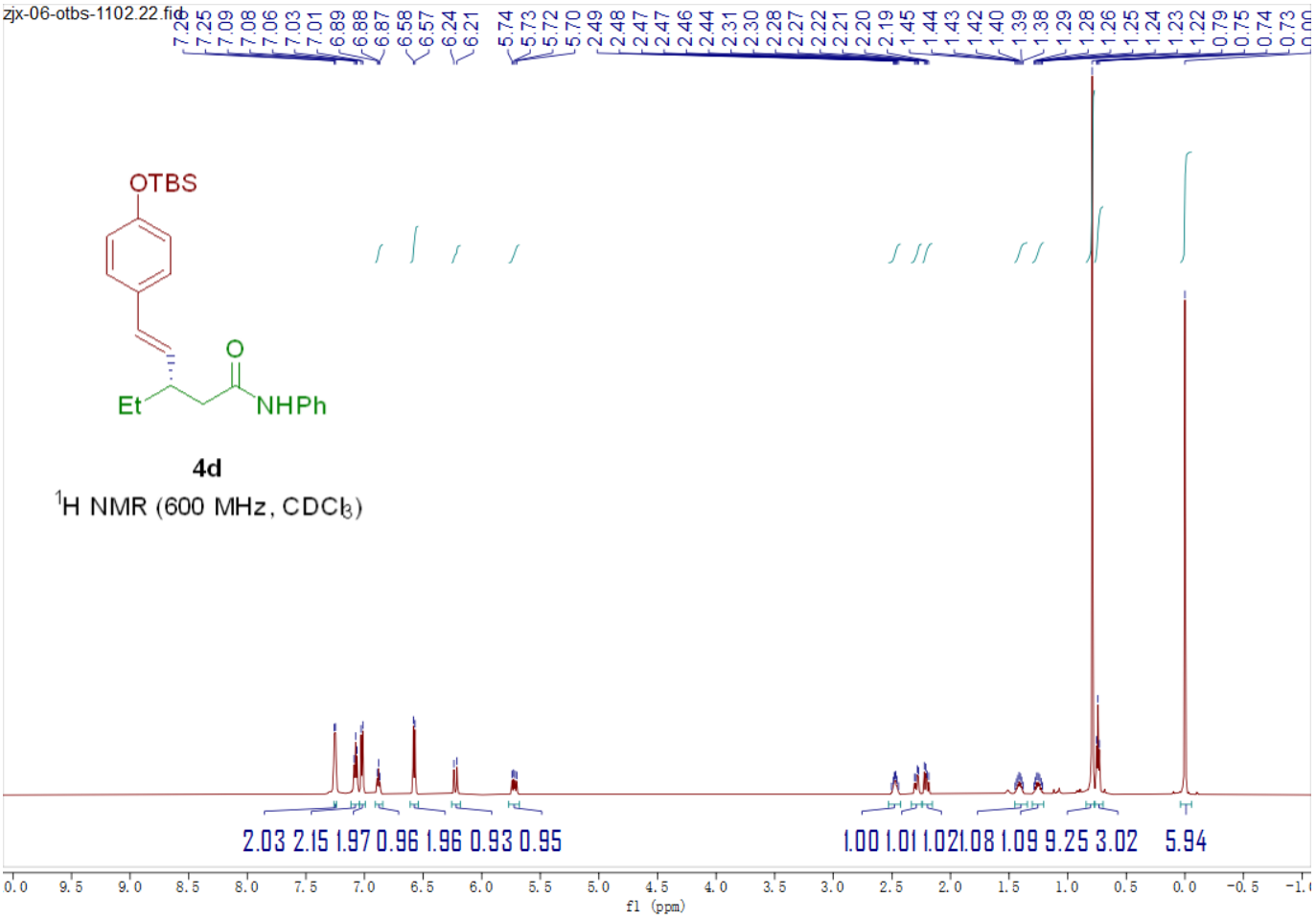
137.92
137.34
132.87
131.26
129.05
128.64
127.37
126.27
124.40
120.21
77.48
77.16
76.84
43.69
42.00
28.00
11.83
Et
NHPh
O
4a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

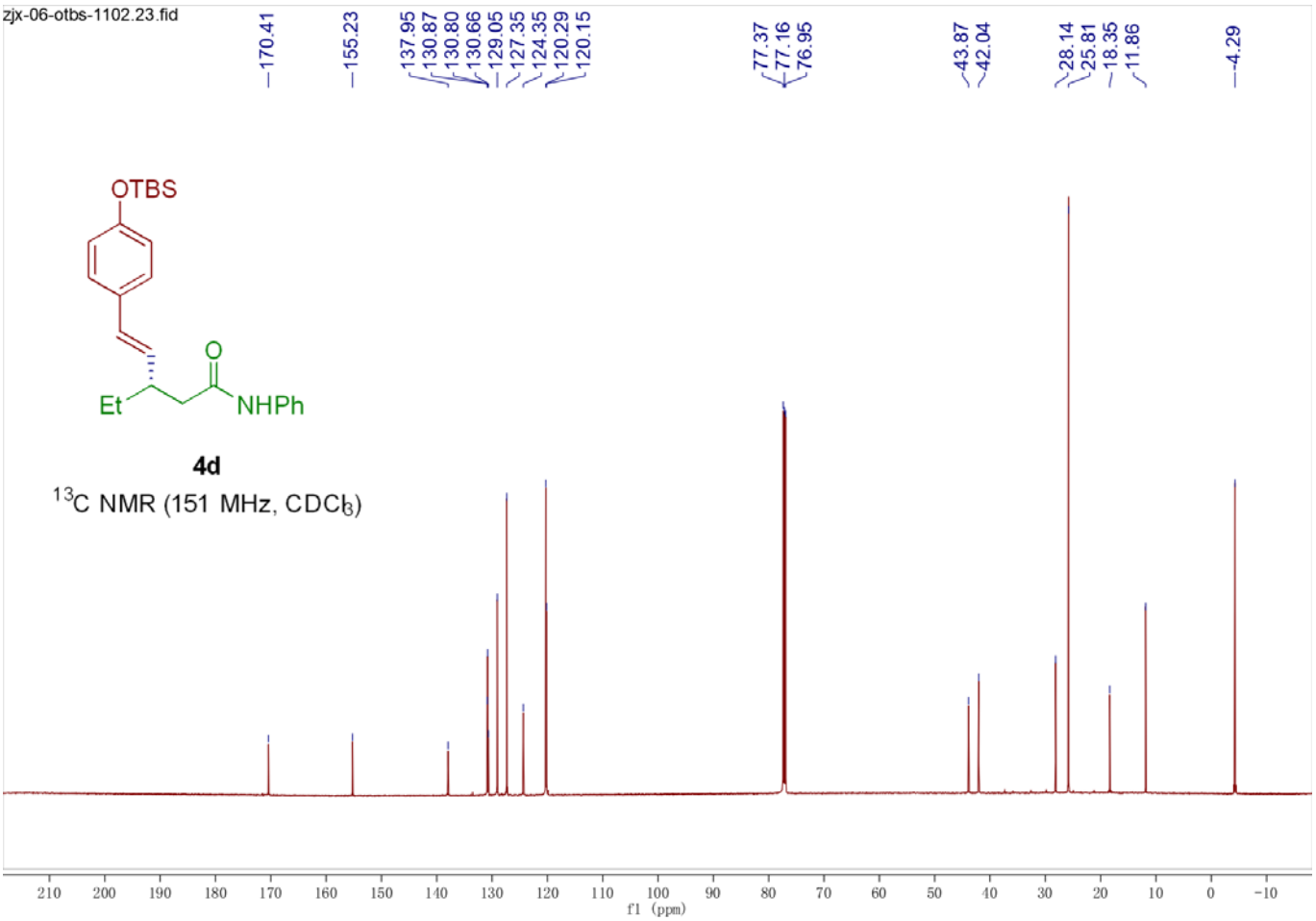

zjx-06-58-1108.42.fid
Me
O
Et
NHPh
4b
1H NMR (400 MHz, CDCl3)
2.05 4.80 2.28 0.96 1.02
1.00 1.01 1.08 3.21 1.13 1.11 3.14
f1 (ppm)

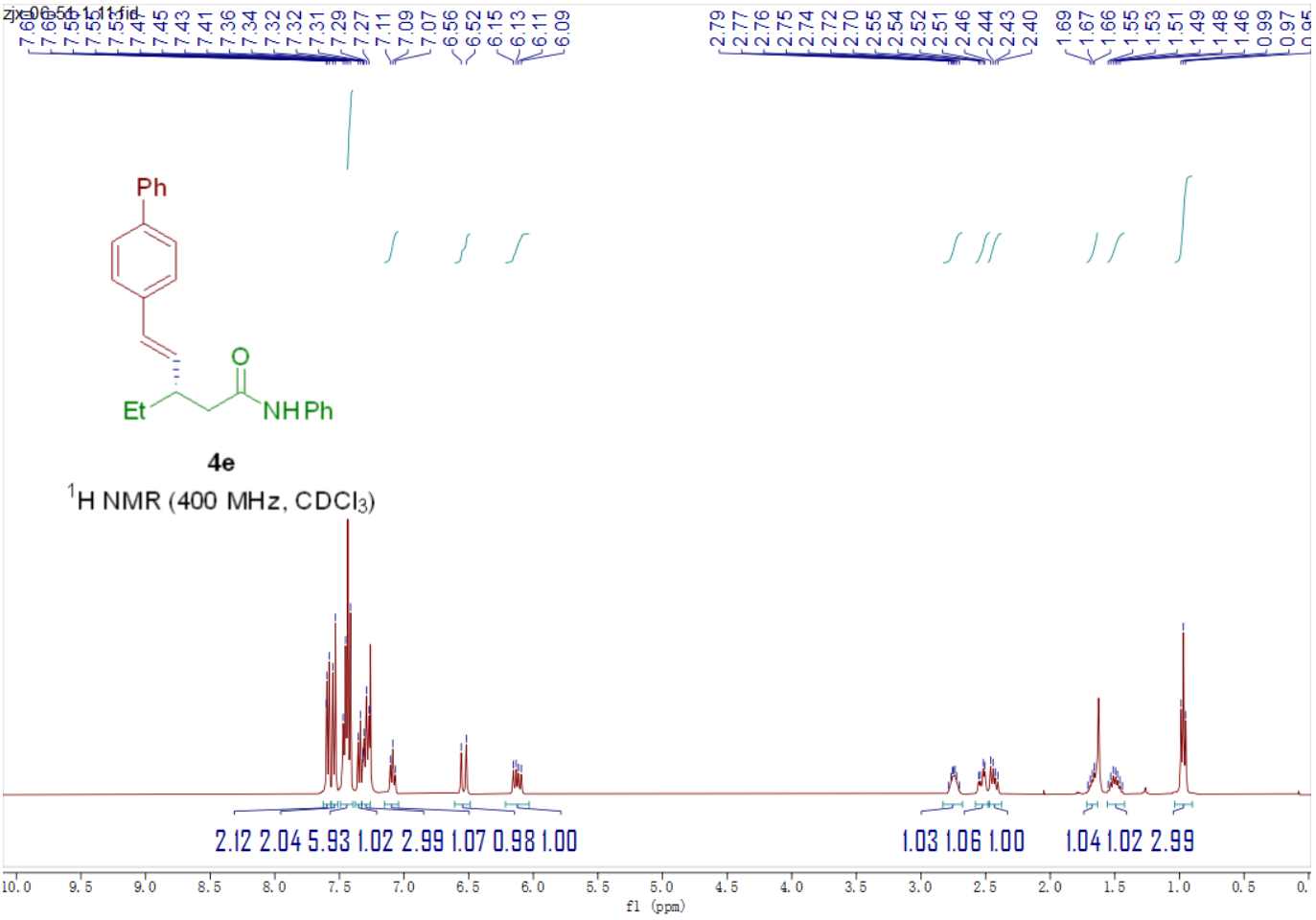

zjx-06-58-1108.43.fid
170.36
137.93
137.18
134.53
131.86
131.19
129.35
129.06
126.17
124.36
120.15
77.48
77.16
76.84
43.81
42.03
28.09
21.27
11.84
Me
O
Et
NHPh
4b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

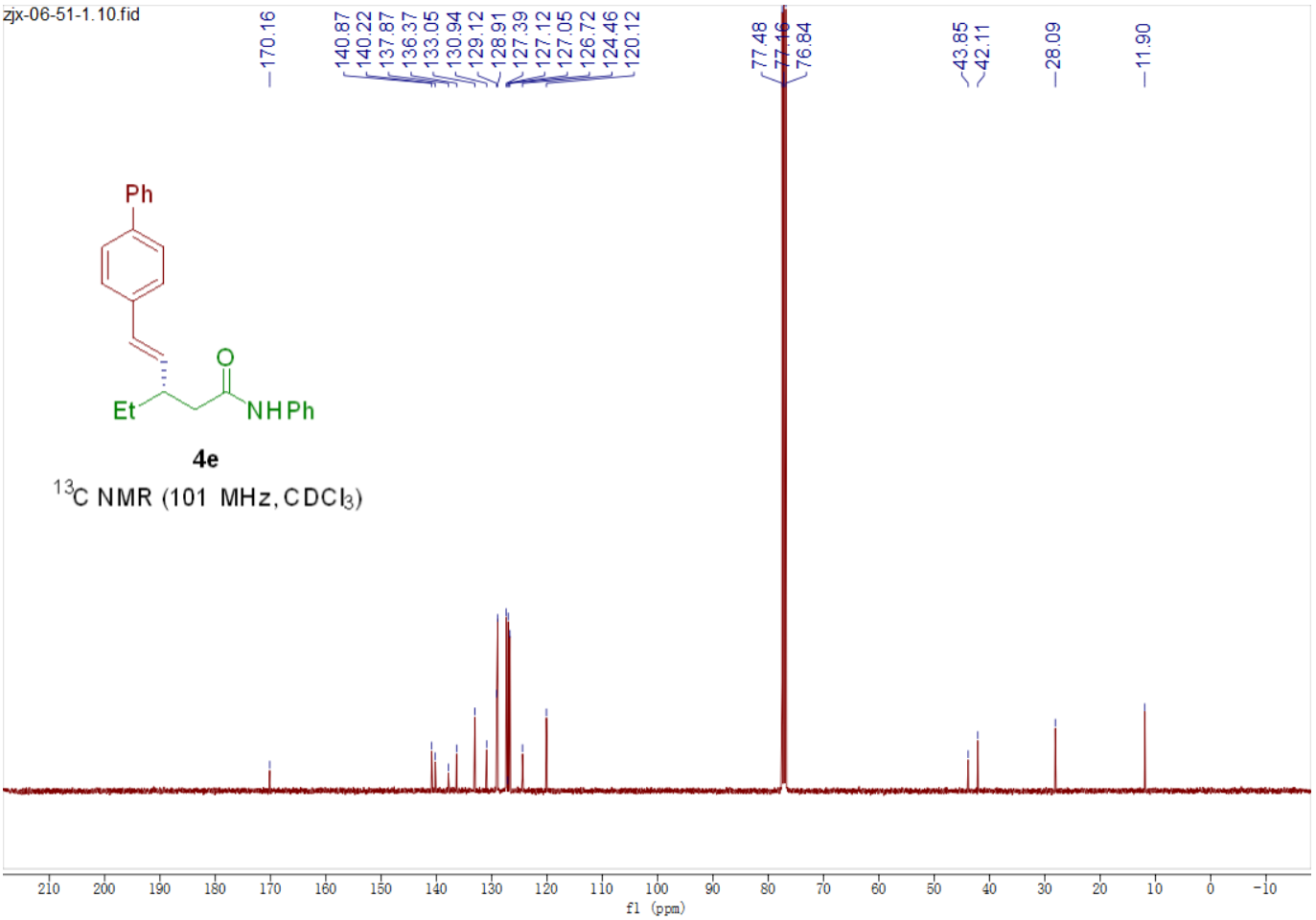

zjx-06-50-1108.10.fid
SMe
O
Et
NHPh
4c
1H NMR (400 MHz, CDCl3)
1.91 0.87 3.87 1.95 0.98 0.93 0.93
1.00 3.81 0.98 0.97 0.97 2.93
f1 (ppm)

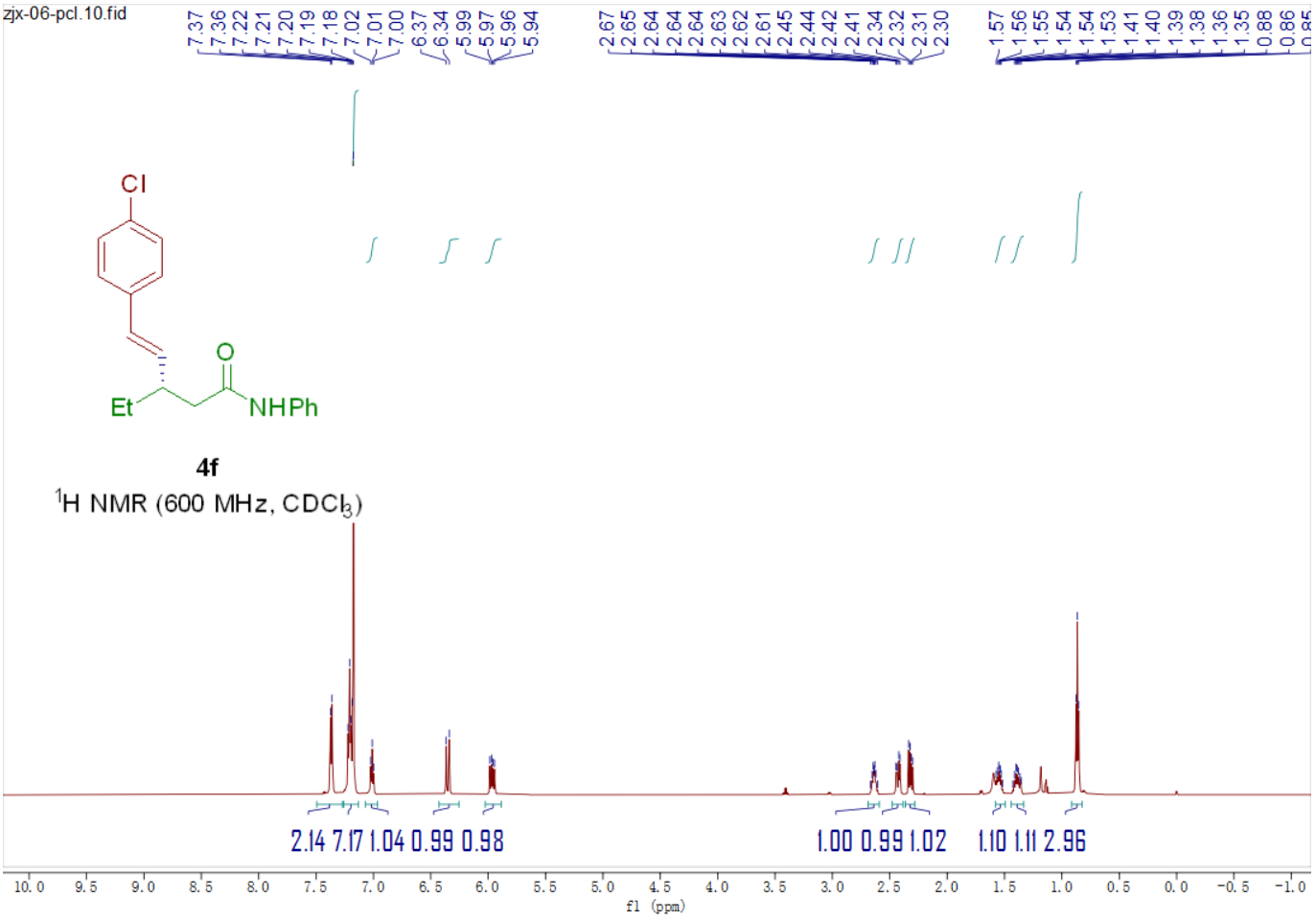

zjx-06-50-1108.11.fid
SMe
O
Et
NHPh
4c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

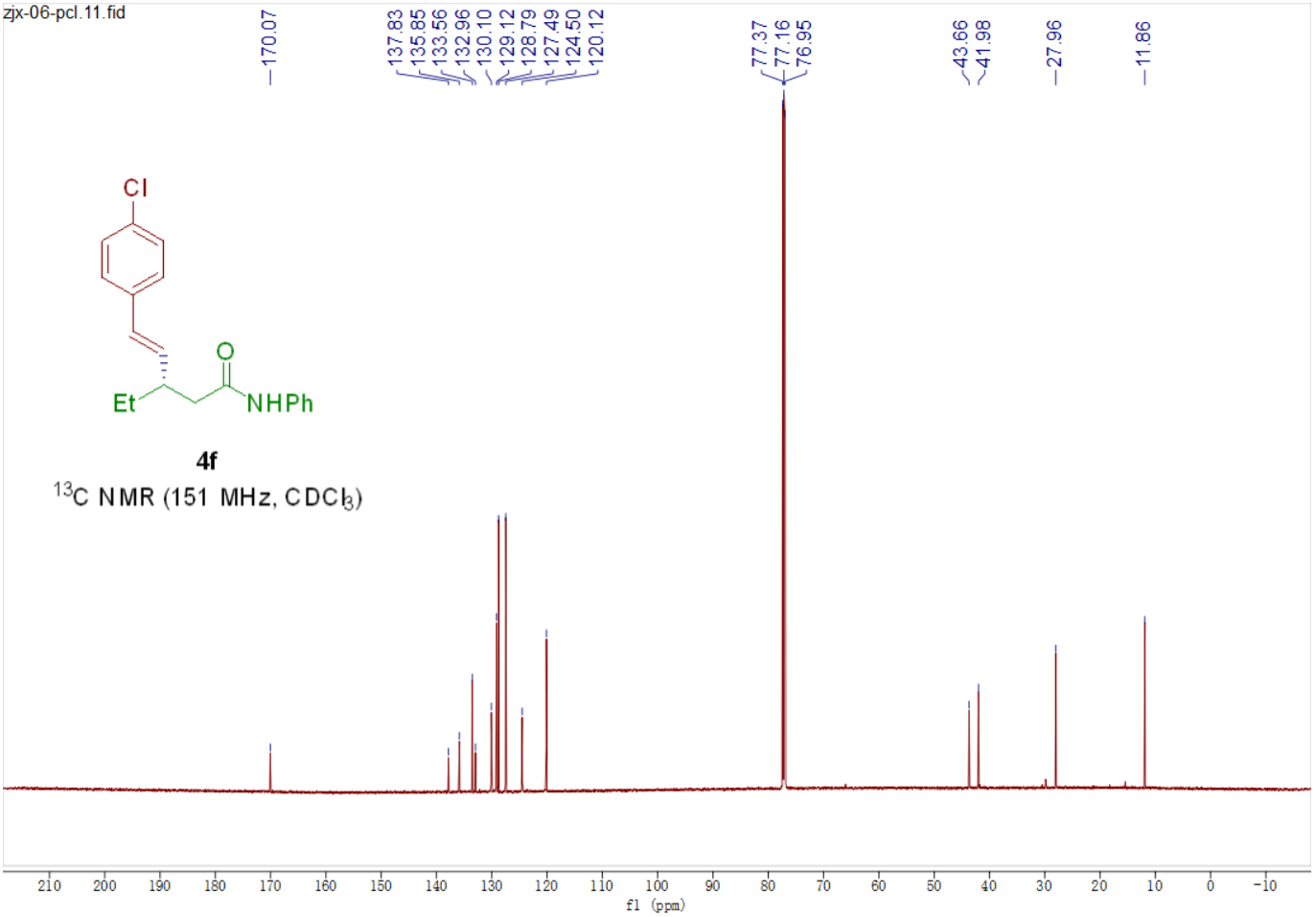

zjx-06-otbs-1102.22.fid
OTBS
O
Et
NHPh
4d
1H NMR (600 MHz, CDCl3)
2.03 2.15 1.97 0.96 1.96 0.93 0.95
1.00 1.01 1.02 1.08 1.09 9.25 3.02 5.94
f1 (ppm)

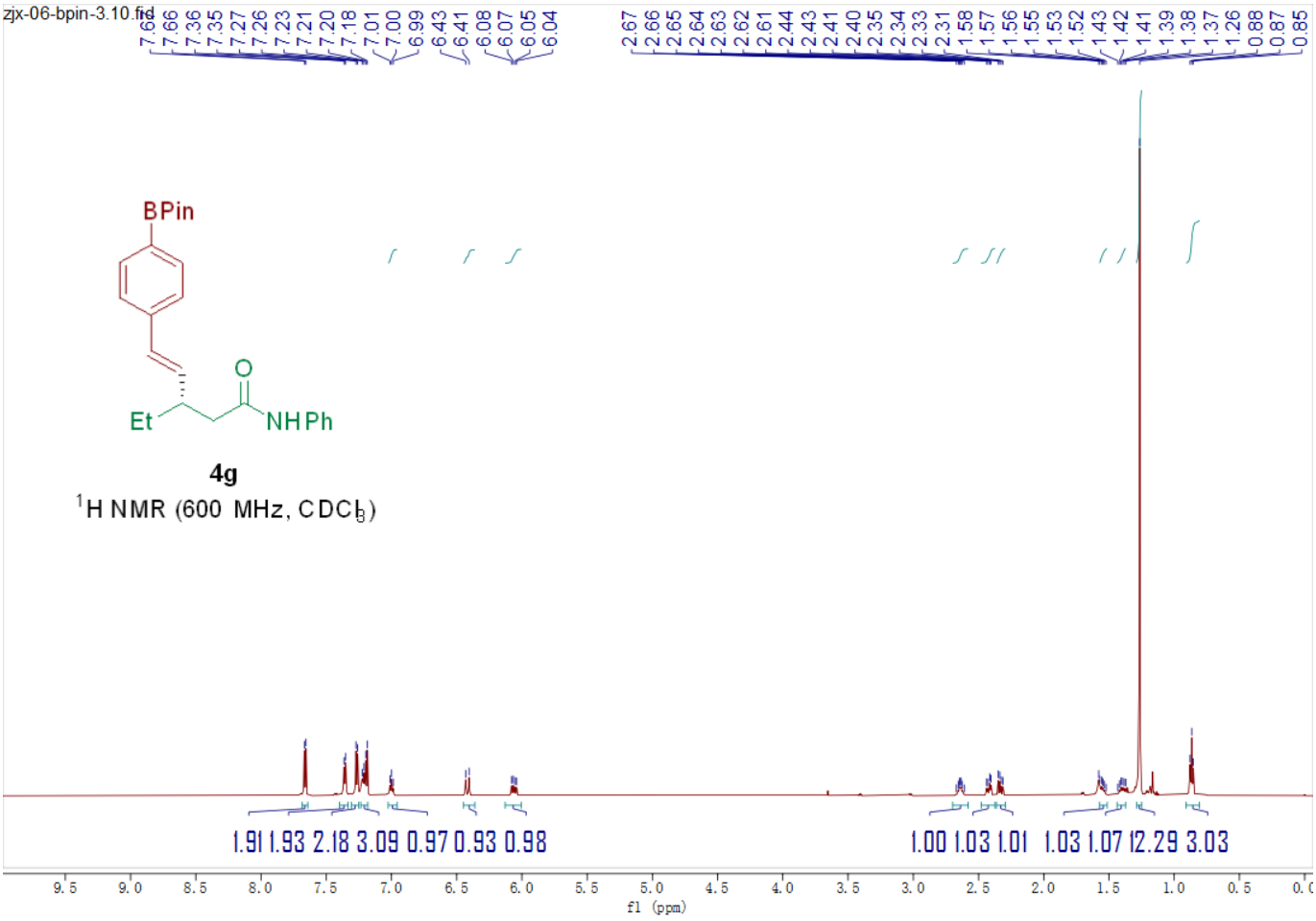

zjx-06-otbs-1102.23.fid
OTBS
O
Et
NHPh
4d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

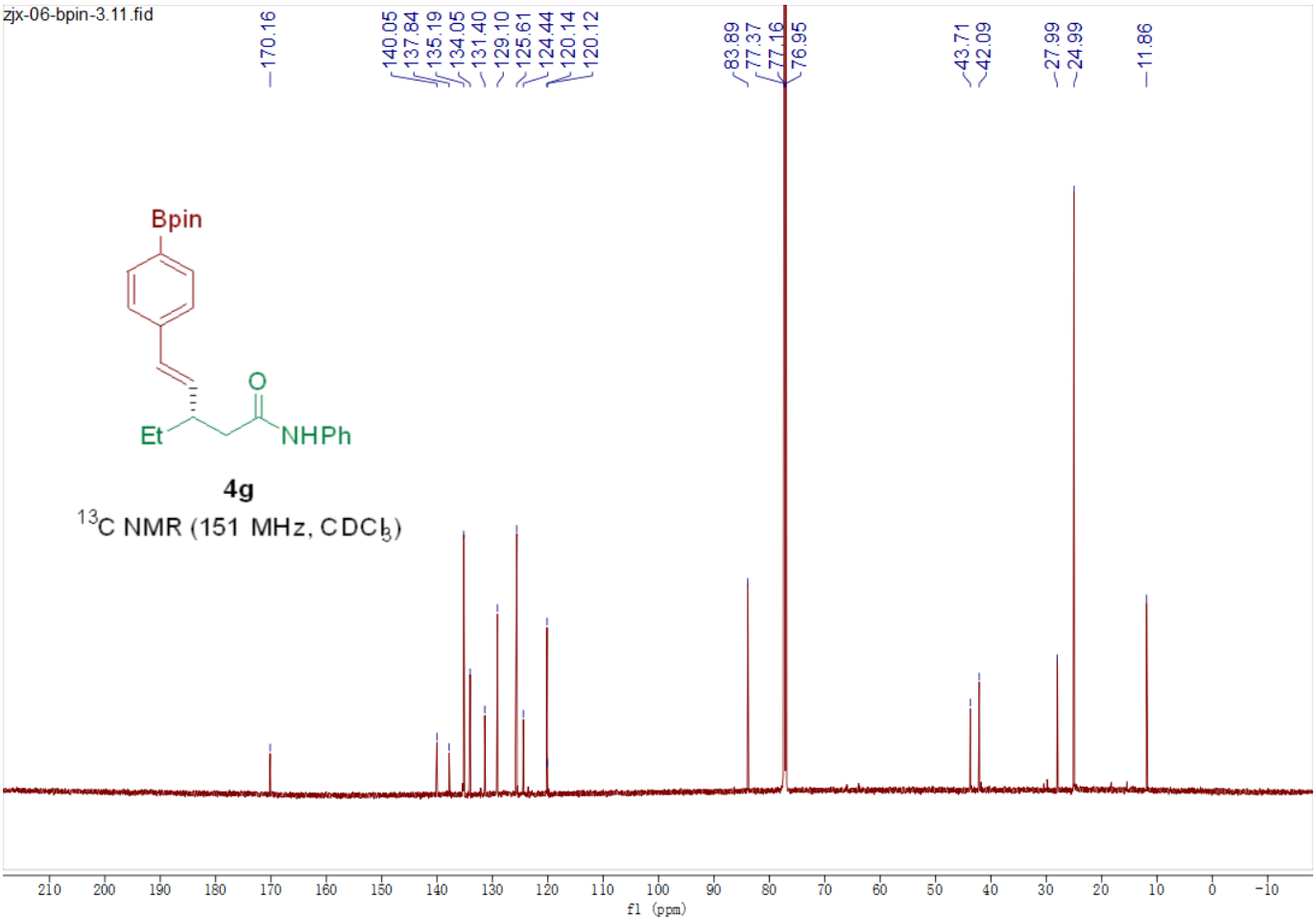

zjx-06-51-1.11.fid
Ph
Et
O
NHPh
4e
1H NMR (400 MHz, CDCl3)
2.12 2.04 5.93 1.02 2.99 1.07 0.98 1.00
1.03 1.06 1.00
1.04 1.02 2.99
f1 (ppm)

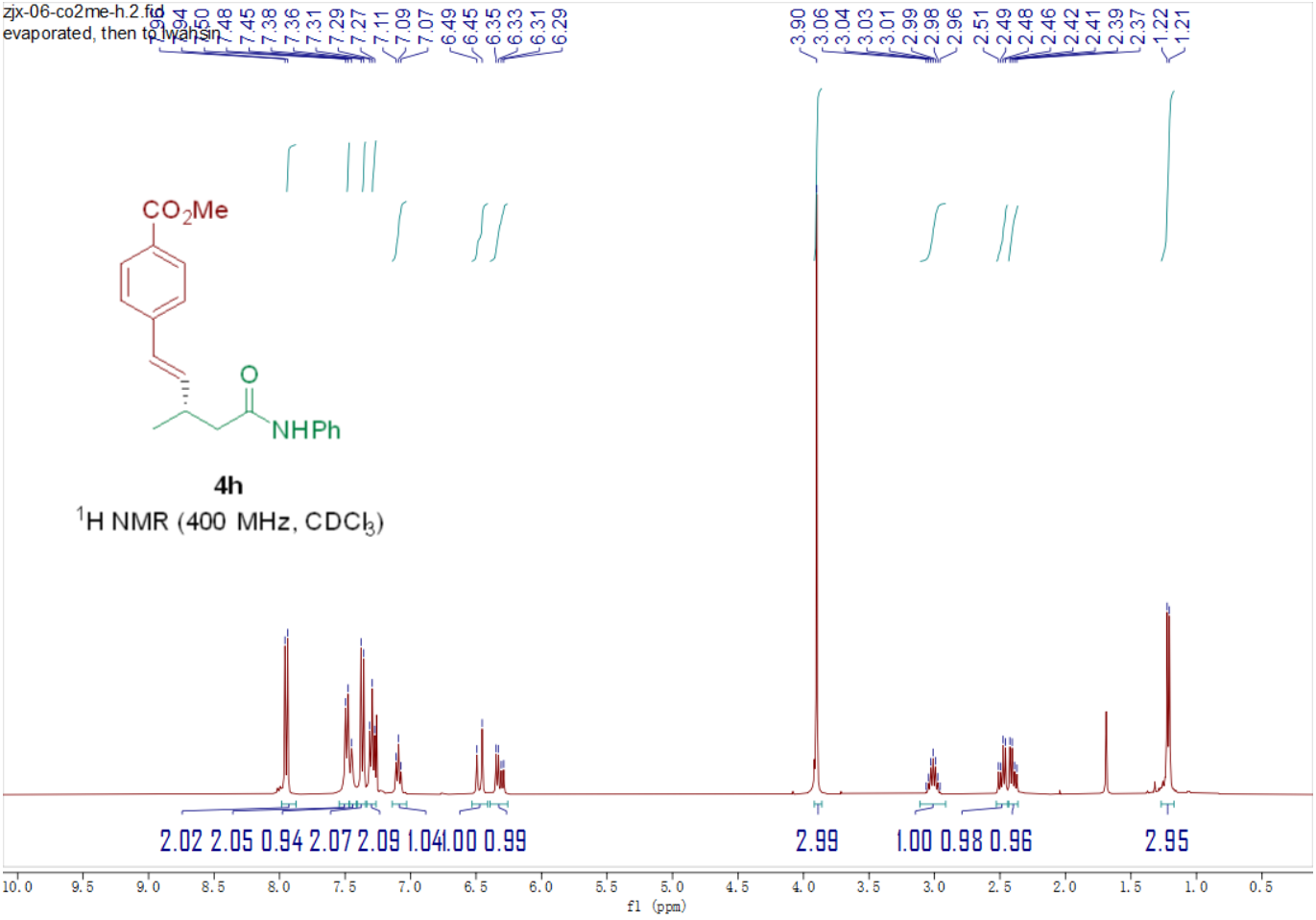

zjx-06-51-1.10.fid
Ph
Et
O
NHPh
4e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

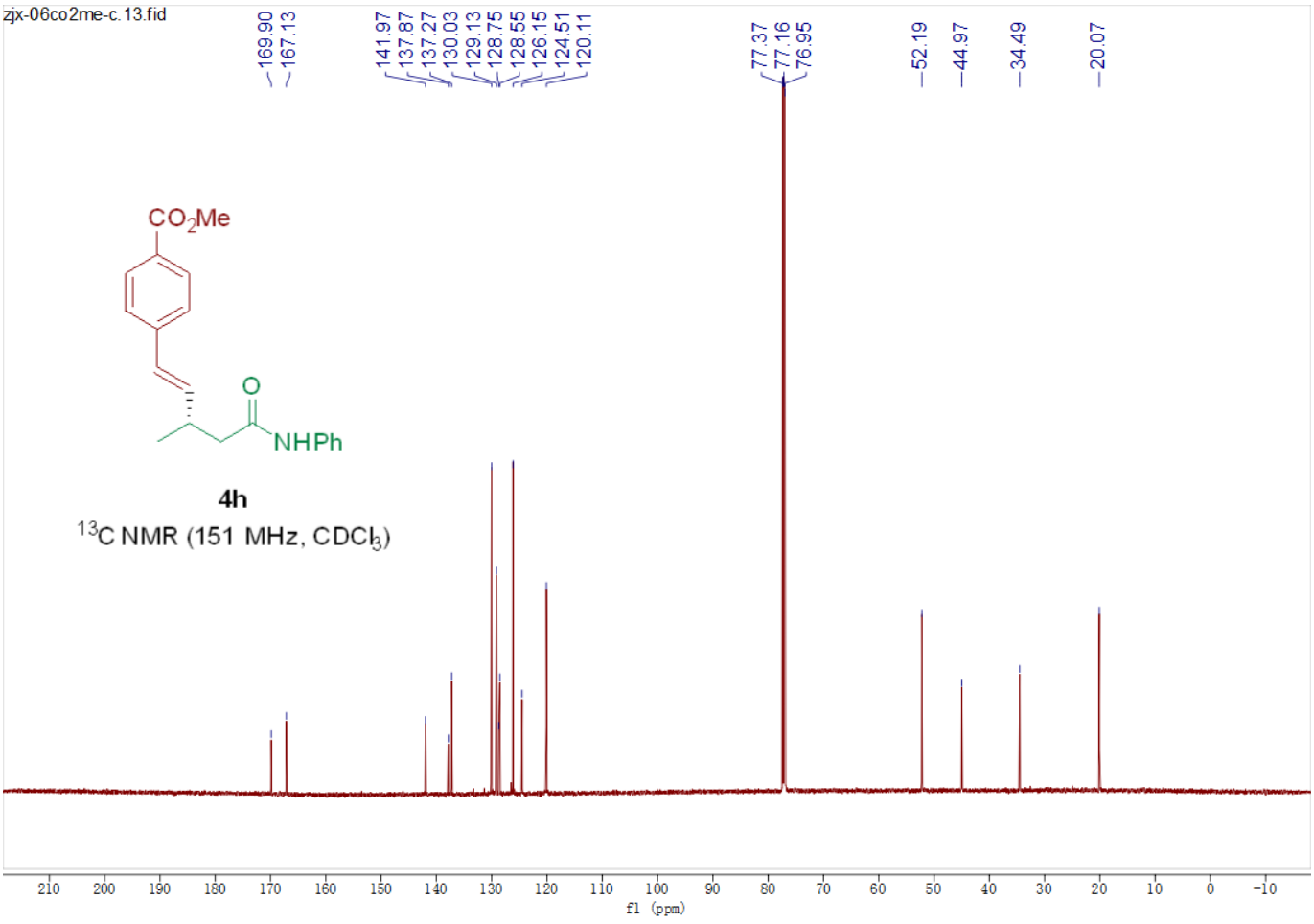

zjx-06-pcl.10.fid
7.37 7.36 7.22 7.21 7.20 7.19 7.18 7.02 7.01 7.00 6.37 6.34 5.99 5.97 5.96 5.94
2.67 2.65 2.64 2.64 2.64 2.63 2.62 2.61 2.45 2.44 2.42 2.41 2.34 2.32 2.31 2.30
1.57 1.56 1.55 1.54 1.54 1.53 1.41 1.40 1.39 1.38 1.36 1.35 0.88 0.86
Cl
O
Et
NHPh
4f
1H NMR (600 MHz, CDCl3)
2.14 7.17 1.04 0.99 0.98
1.00 0.99 1.02 1.10 1.11 2.96
f1 (ppm)

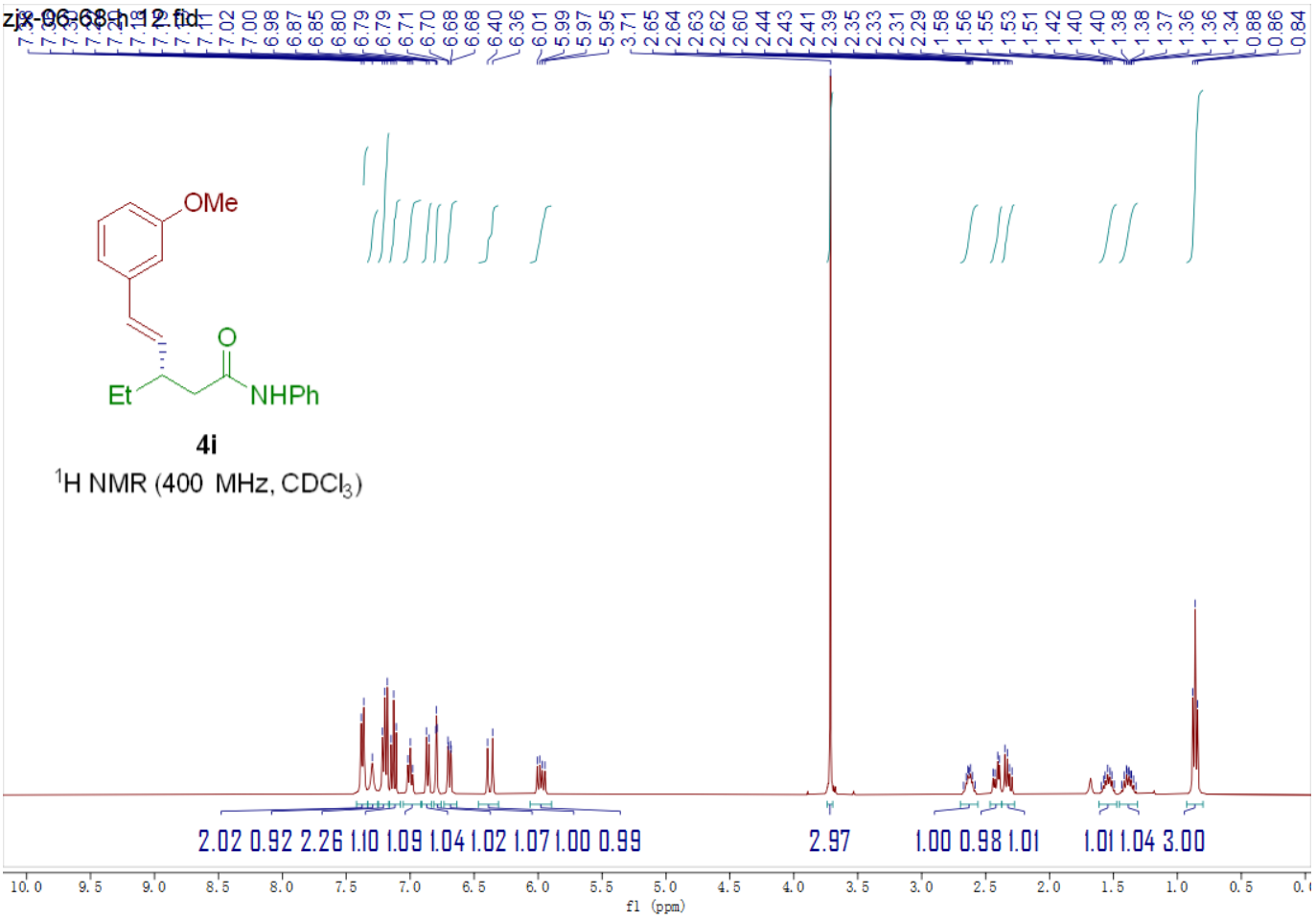

zjx-06-pcl.11.fid
170.07
137.83 135.85 133.56 132.96 130.10 129.12 128.79 127.49 124.50 120.12
77.37 77.16 76.95
43.66 41.98
27.96
11.86
Cl
O
Et
NHPh
4f
13C NMR (151 MHz, CDCl3)
f1 (ppm)

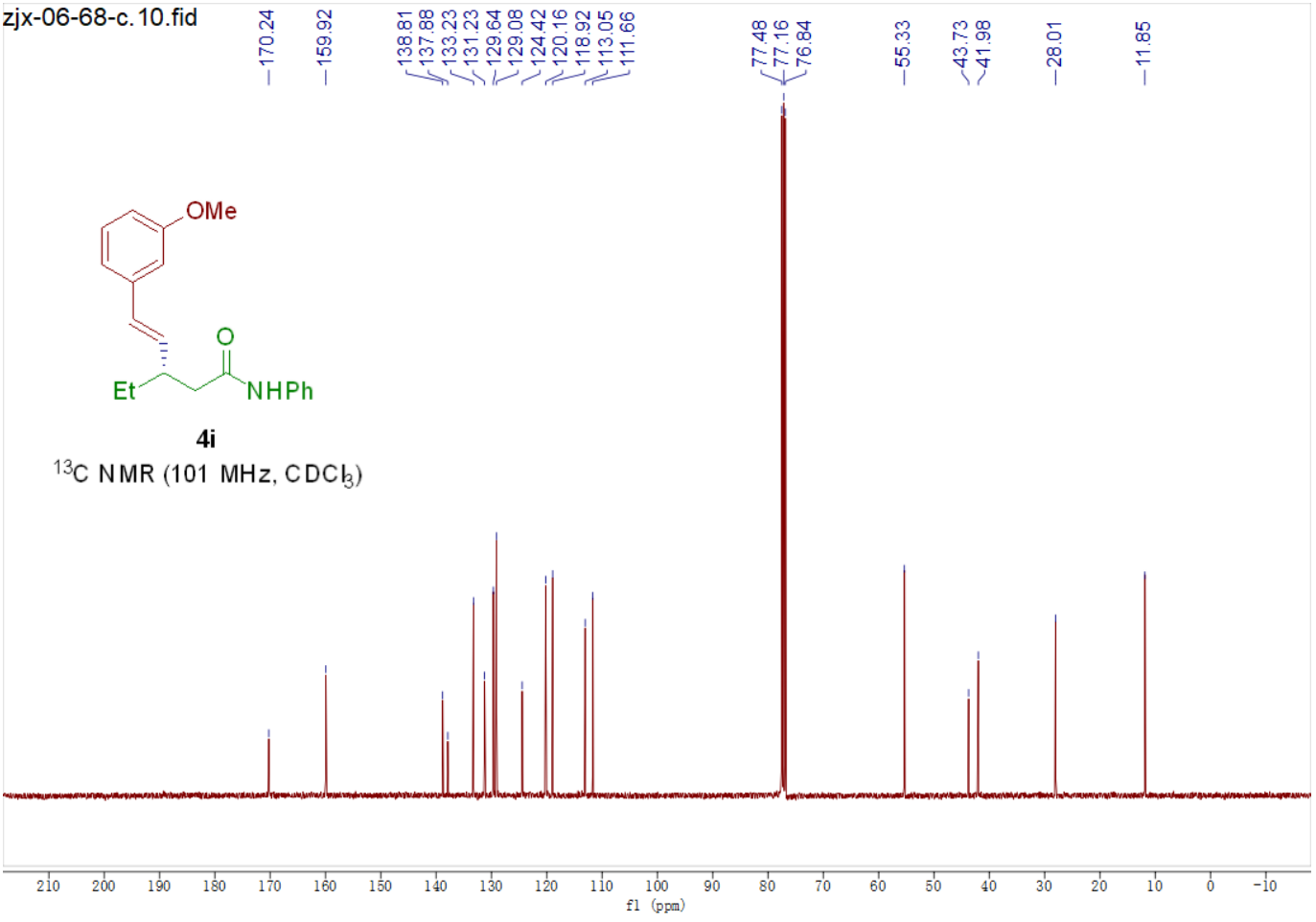

zjx-06-bpin-3.10.fid
BPin
O
Et
NHPh
4g
1H NMR (600 MHz, CDCl3)
1.91 1.93 2.18 3.09 0.97 0.93 0.98
1.00 1.03 1.01 1.03 1.07 12.29 3.03
f1 (ppm)

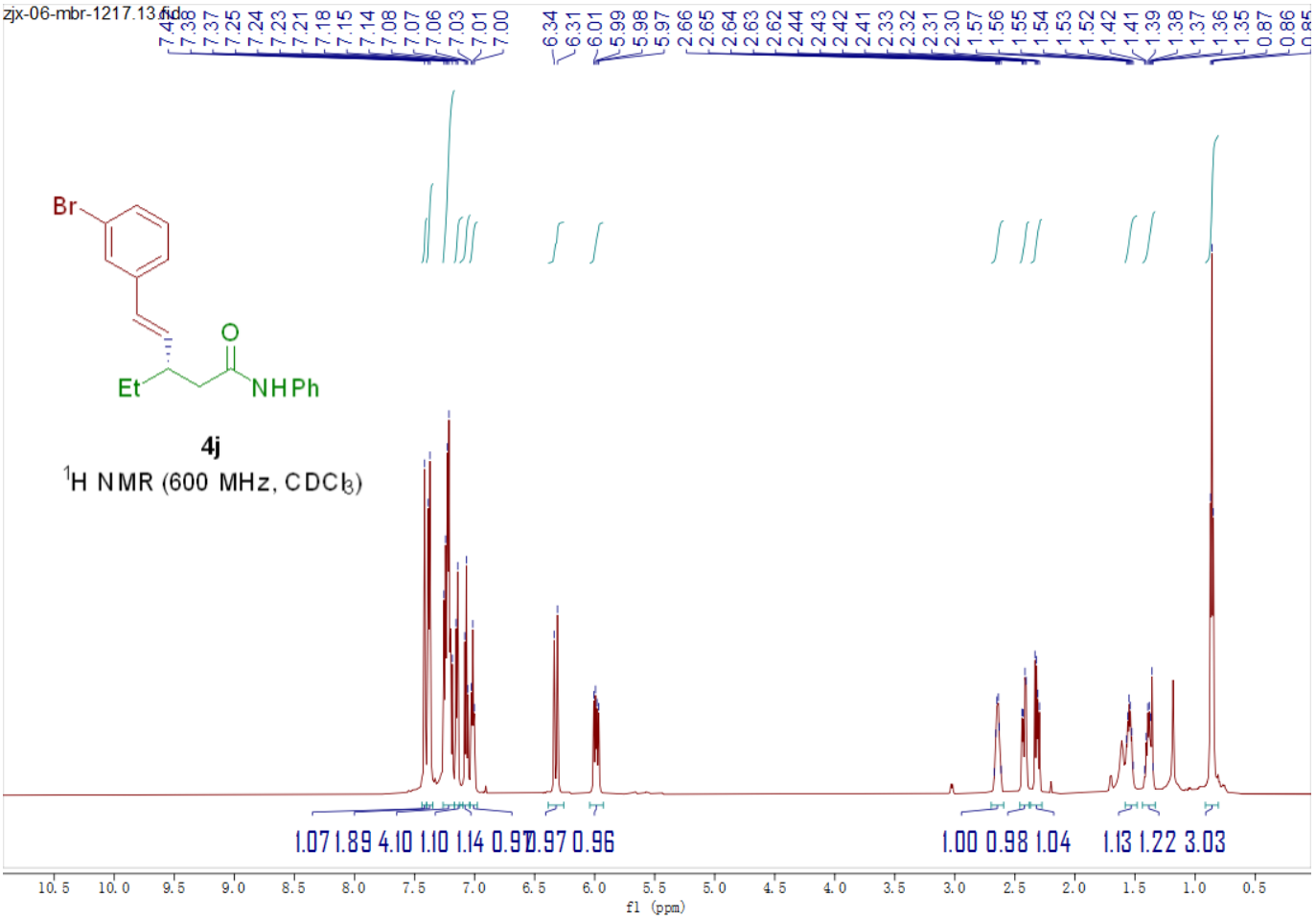

zjx-06-bpin-3.11.fid
Bpin
O
Et
NHPh
4g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

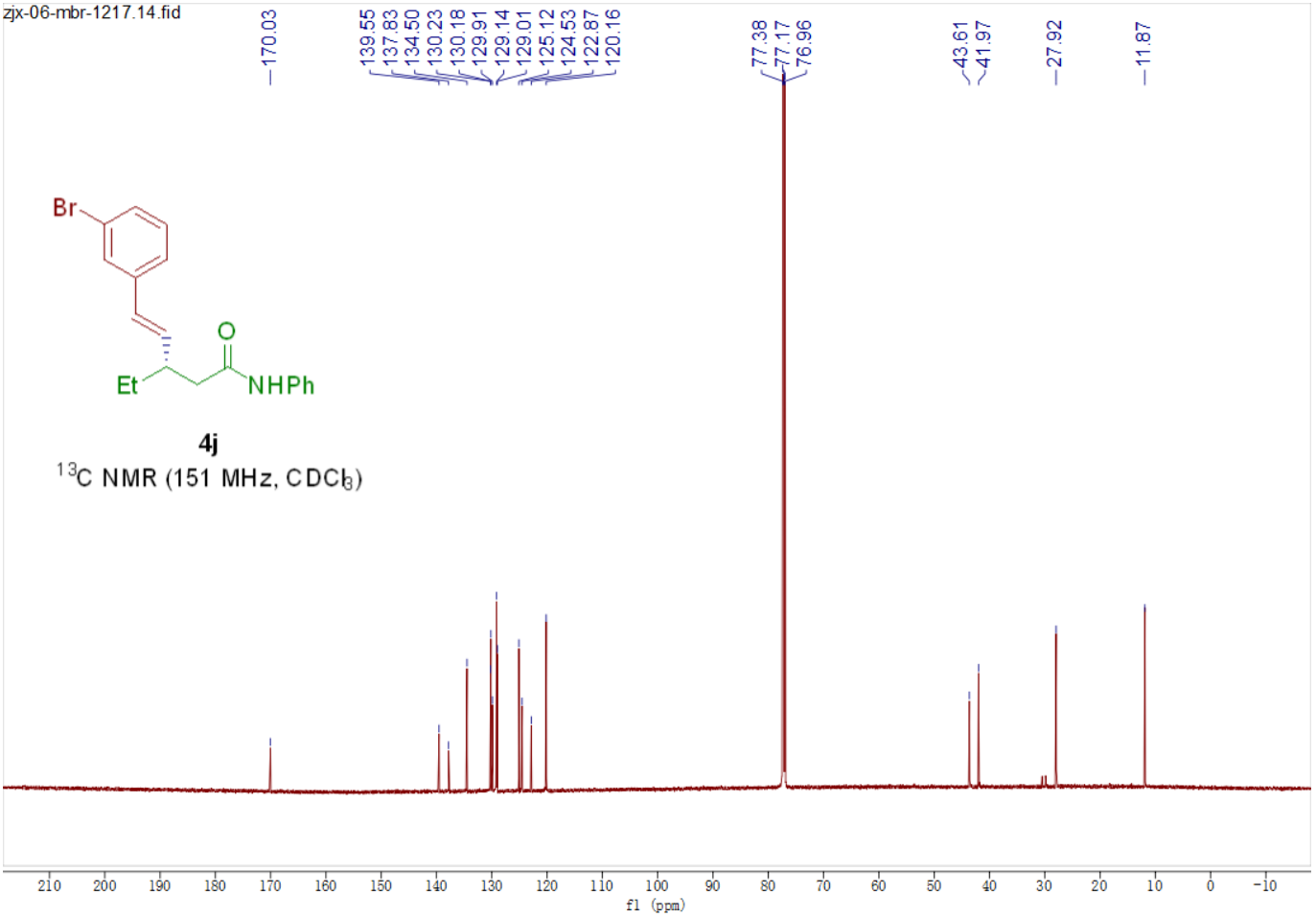

zjx-06-co2me-h.2.fid
evaporated, then to Iwan sin
9.94 7.50 7.48 7.45 7.38 7.36 7.31 7.29 7.27 7.11 7.09 7.07 6.49 6.45 6.35 6.33 6.31 6.29
3.90 3.06 3.04 3.03 3.01 2.99 2.98 2.96 2.51 2.49 2.48 2.46 2.42 2.41 2.39 2.37 1.22 1.21
CO2Me
O
NHPh
4h
1H NMR (400 MHz, CDCl3)
2.02 2.05 0.94 2.07 2.09 1.04 1.00 0.99
2.99 1.00 0.98 0.96 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

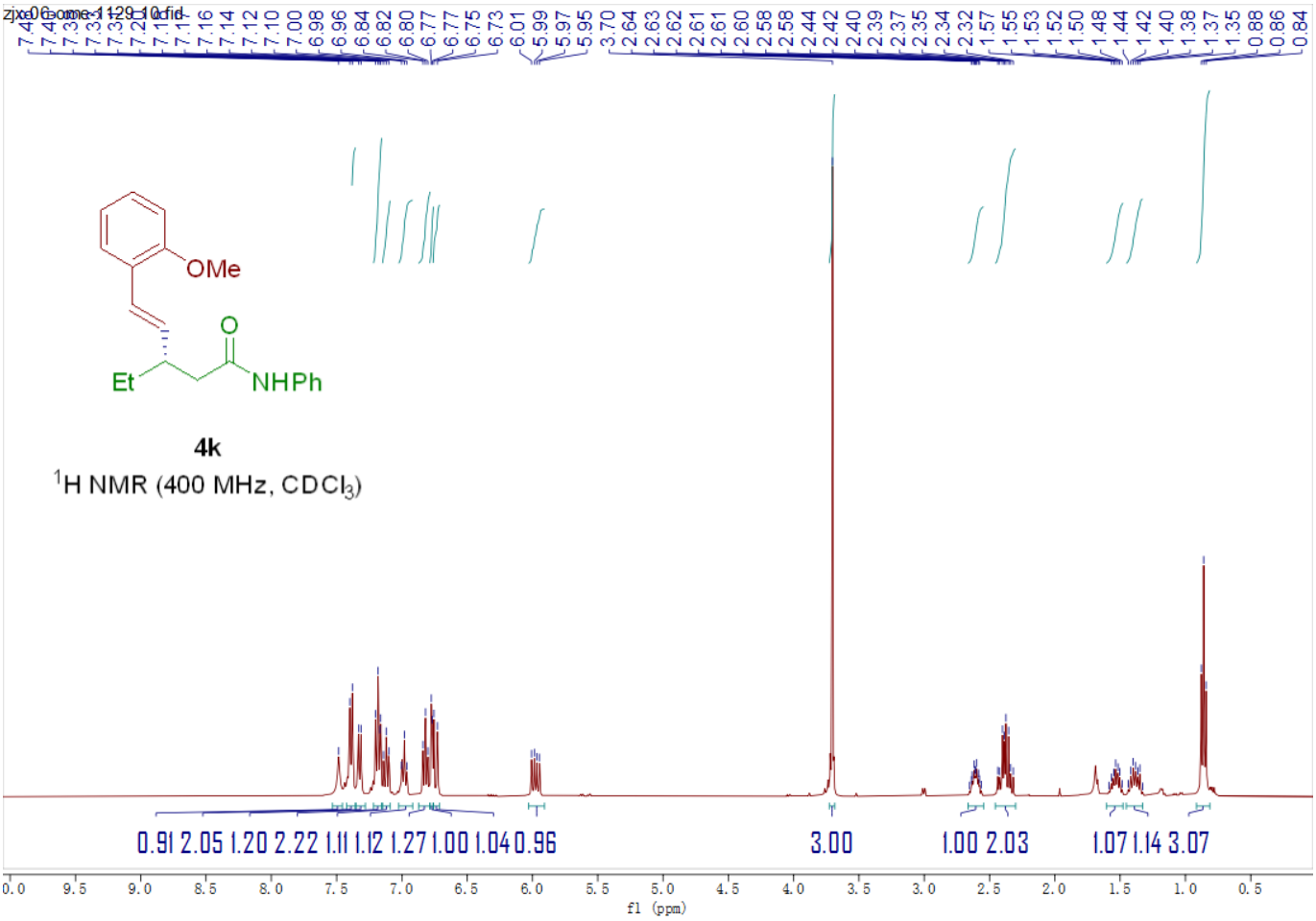

zjx-06co2me-c.13.fid
169.90 167.13 141.97 137.87 137.27 130.03 129.13 128.75 128.55 126.15 124.51 120.11
77.37 77.16 76.95 52.19 44.97 34.49 20.07
CO2Me
O
NHPh
4h
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

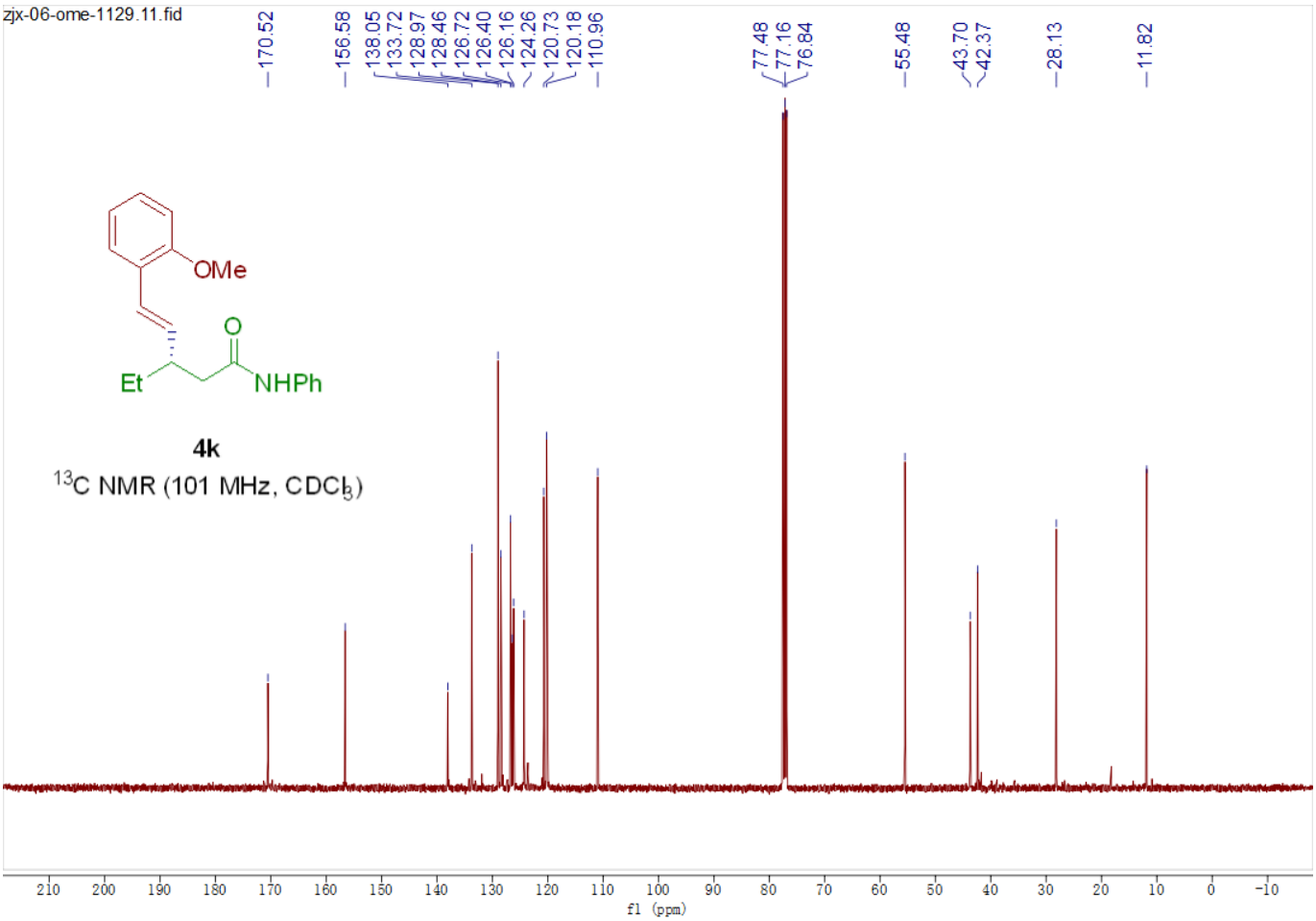

zjx-06-68-h.12.fid
OMe
O
Et
NHPh
4i
1H NMR (400 MHz, CDCl3)
2.02 0.92 2.26 1.10 1.09 1.04 1.02 1.07 1.00 0.99
2.97
1.00 0.98 1.01
1.01 1.04 3.00
f1 (ppm)

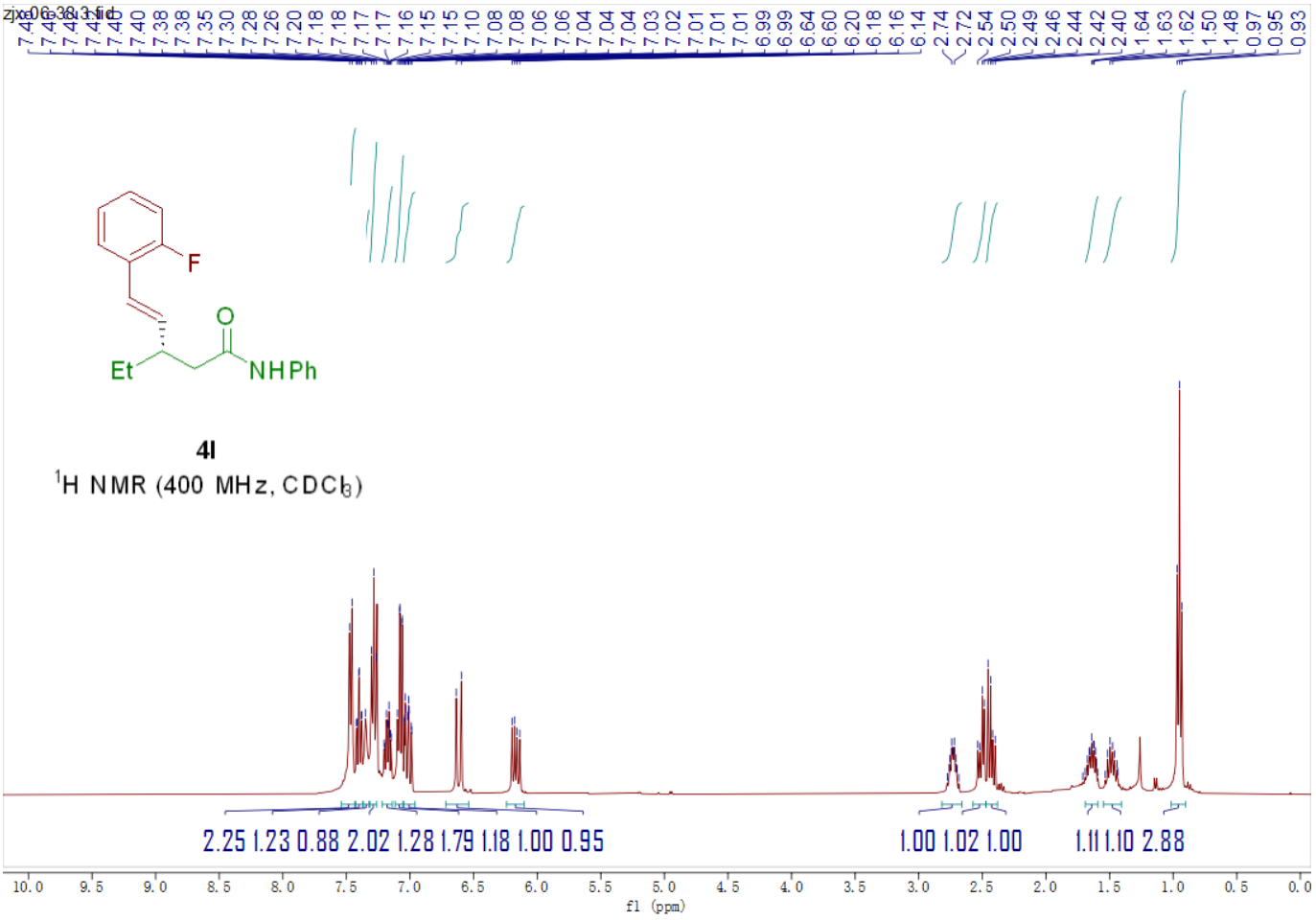

zjx-06-68-c.10.fid
170.24
159.92
138.81
137.88
133.23
131.23
129.64
129.08
124.42
120.16
118.92
113.05
111.66
77.48
77.16
76.84
55.33
43.73
41.98
28.01
11.85
OMe
O
Et
NHPh
4i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

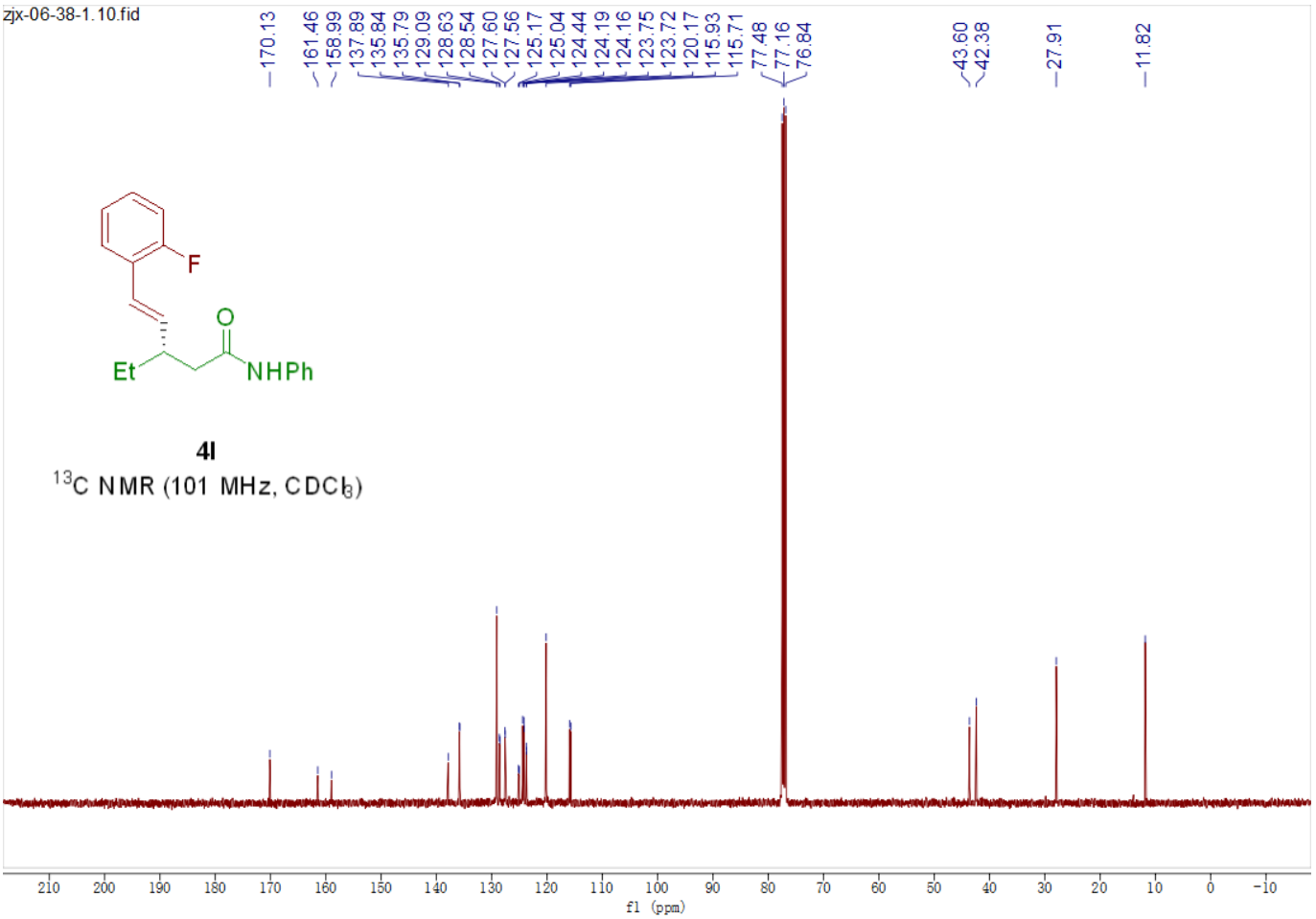

zjx-06-mbr-1217.13.fid
Br
O
Et
NHPh
4j
1H NMR (600 MHz, CDCl3)
1.07 1.89 4.10 1.10 1.14 0.97 0.97 0.96
1.00 0.98 1.04 1.13 1.22 3.03
f1 (ppm)

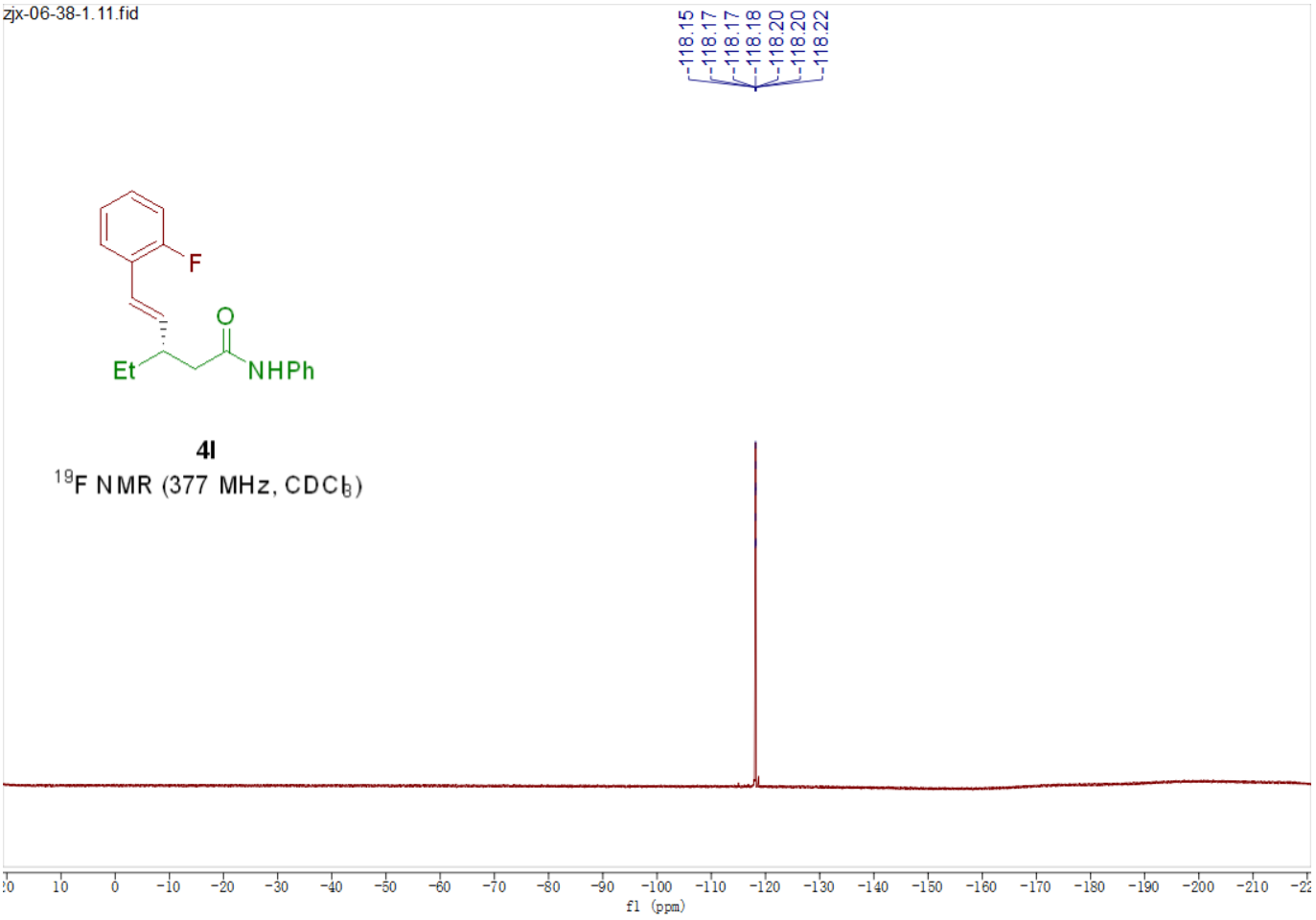

zjx-06-mbr-1217.14.fid
170.03
139.55
137.83
134.50
130.23
130.18
129.91
129.14
129.01
125.12
124.53
122.87
120.16
77.38
77.17
76.96
43.61
41.97
27.92
11.87
Br
O
Et
NHPh
4j
13C NMR (151 MHz, CDCl3)
f1 (ppm)

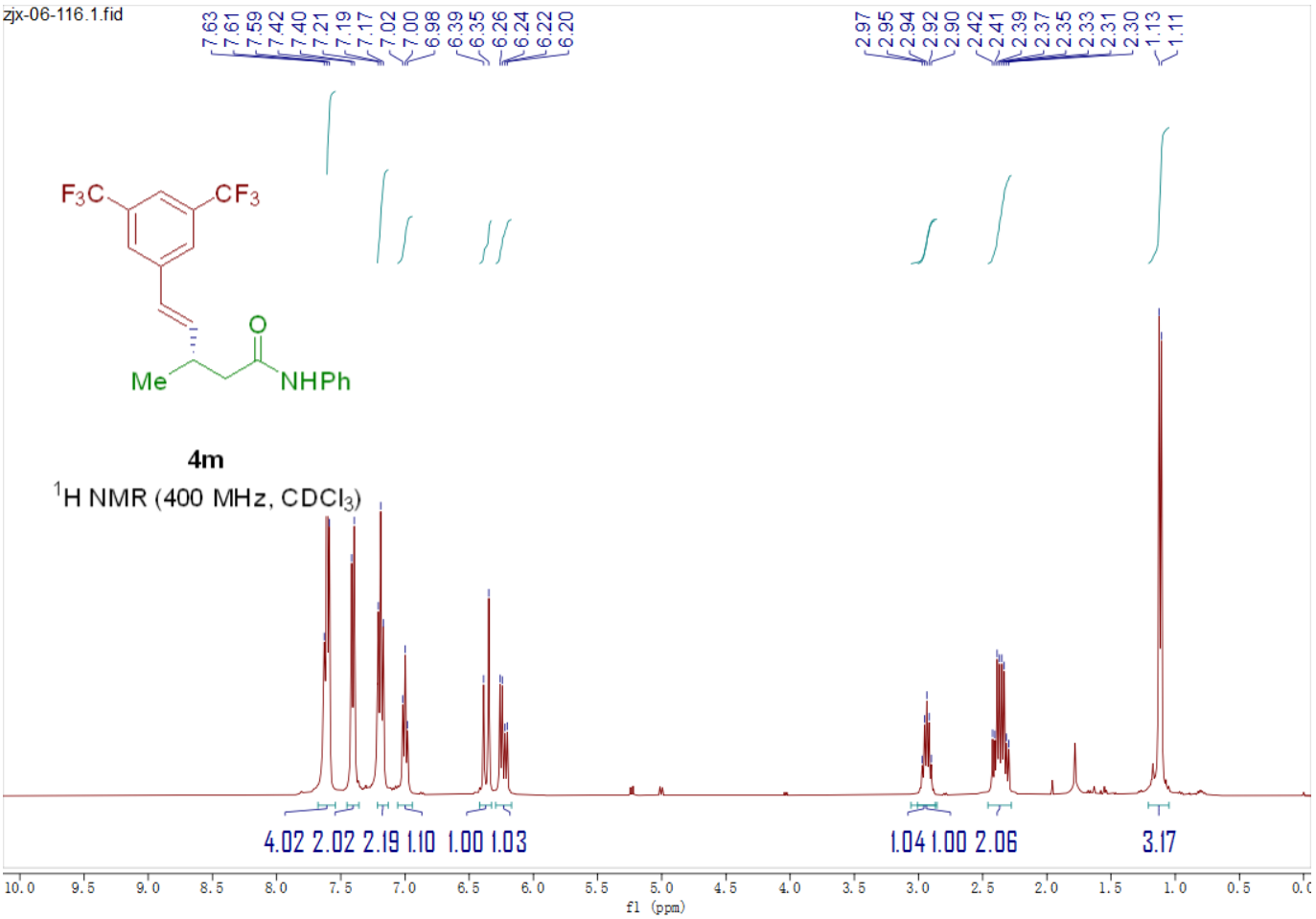

zjx-06-ome-1129.10.fid
OMe
O
Et
NHPh
4k
1H NMR (400 MHz, CDCl3)
0.91 2.05 1.20 2.22 1.11 1.12 1.27 1.00 1.04 0.96
3.00
1.00 2.03
1.07 1.14 3.07
f1 (ppm)

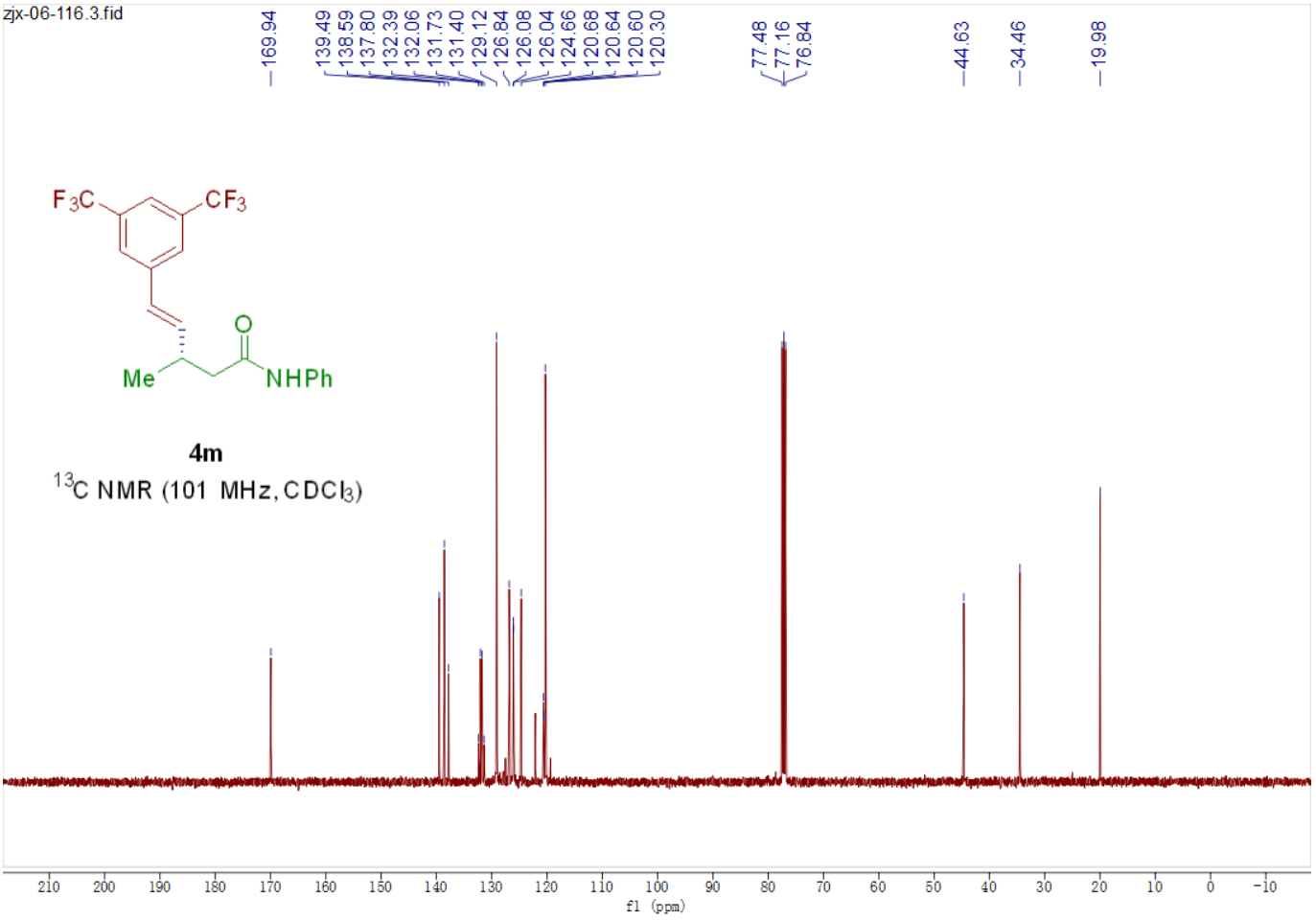

zjx-06-ome-1129.11.fid
170.52
156.58
138.05
133.72
128.97
128.46
126.72
126.40
126.16
124.26
120.73
120.18
110.96
77.48
77.16
76.84
55.48
43.70
42.37
28.13
11.82
OMe
O
Et
NHPh
4k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

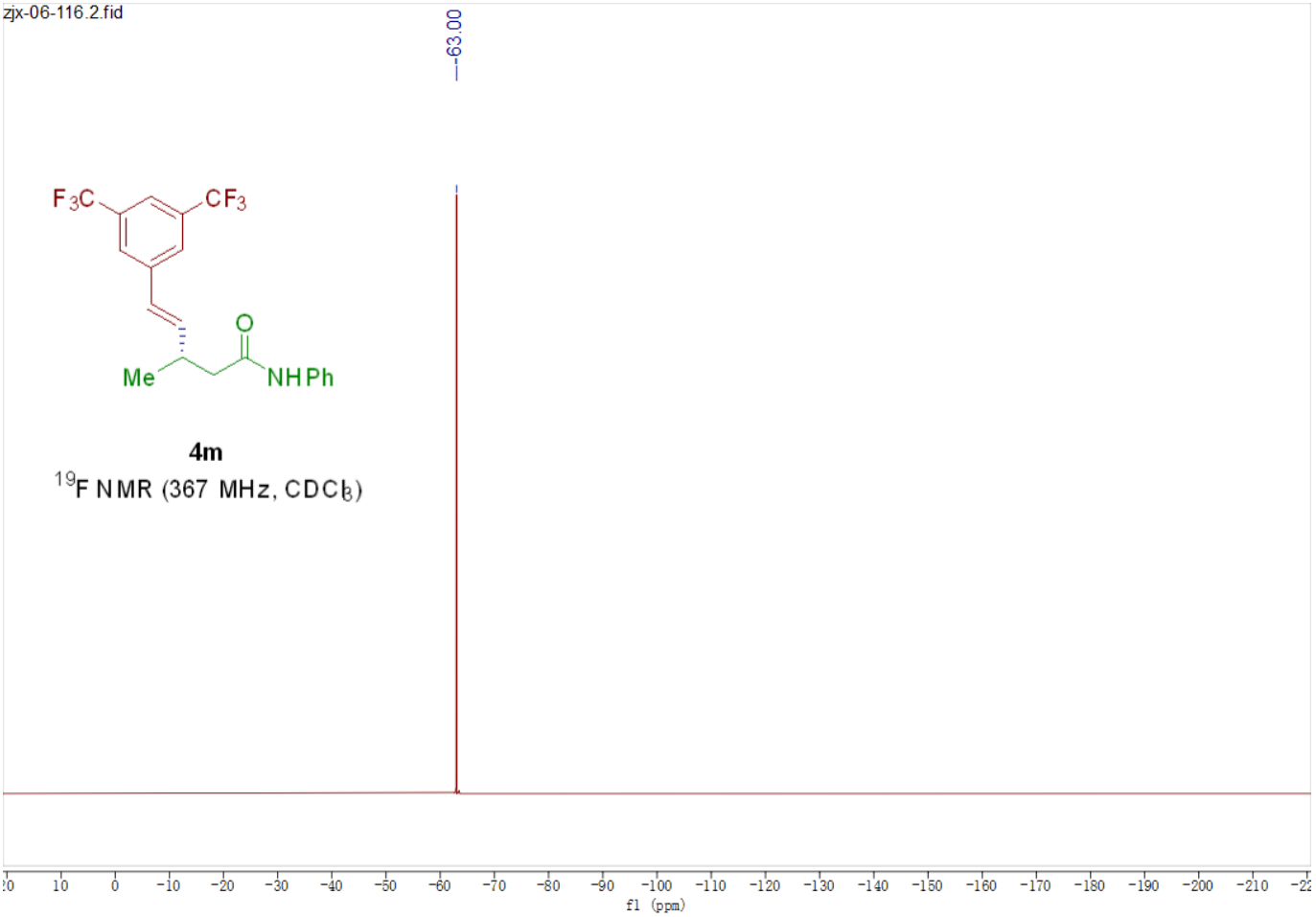

zjx-06-38-3.fid
F
O
Et
NHPh
4l
1H NMR (400 MHz, CDCl3)
2.25 1.23 0.88 2.02 1.28 1.79 1.18 1.00 0.95
1.00 1.02 1.00
1.11 1.10 2.88
f1 (ppm)

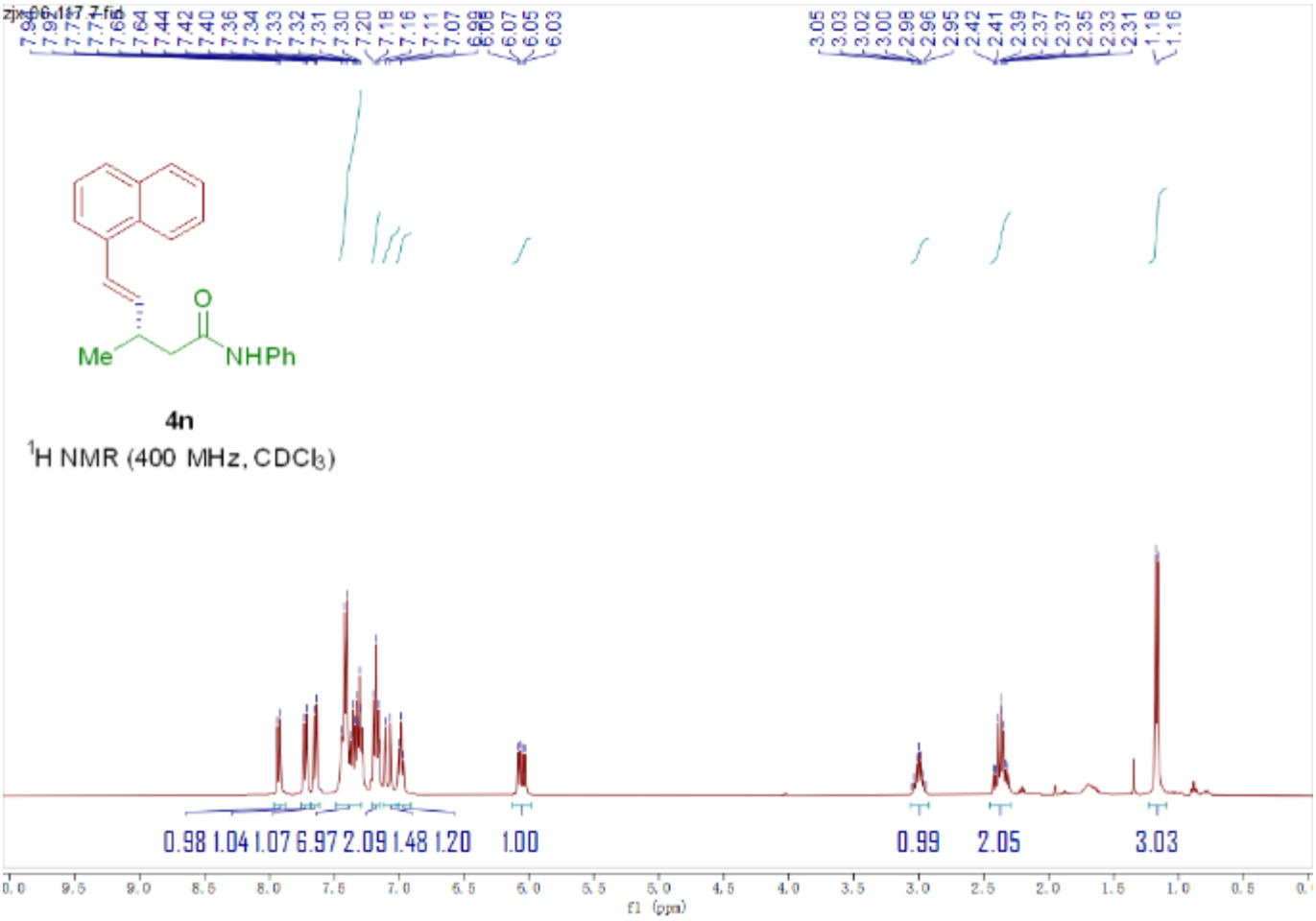

zjx-06-38-1.10.fid
170.13
161.46
158.99
137.89
135.84
135.79
129.09
128.63
128.54
127.60
127.56
125.17
125.04
124.44
124.19
124.16
123.75
123.72
120.17
115.93
115.71
77.48
77.16
76.84
43.60
42.38
27.91
11.82
F
O
Et
NHPh
4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-06-38-1.11.fid
-118.15
-118.17
-118.17
-118.18
-118.20
-118.20
-118.22
F
O
Et
NHPh
4l
19F NMR (377 MHz, CDCl3)
f1 (ppm)


zjx-06-116.1.fid
7.63
7.61
7.59
7.42
7.40
7.21
7.19
7.17
7.02
7.00
6.98
6.39
6.35
6.26
6.24
6.22
6.20
2.97
2.95
2.94
2.92
2.90
2.42
2.41
2.39
2.37
2.35
2.33
2.31
2.30
1.13
1.11
F3C
CF3
O
Me
NHPh
4m
1H NMR (400 MHz, CDCl3)
4.02 2.02 2.19 1.10 1.00 1.03
1.04 1.00 2.06
3.17
f1 (ppm)

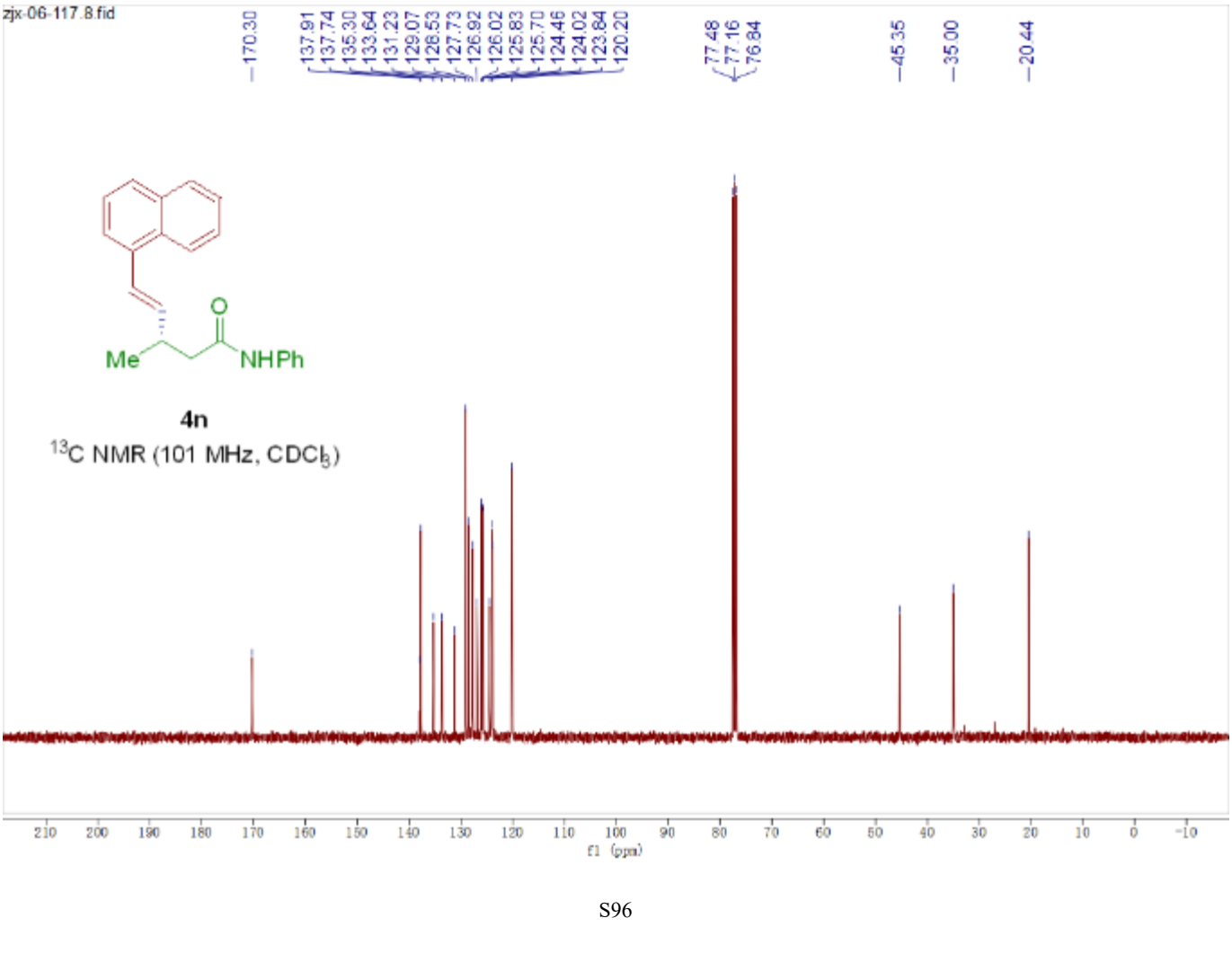

zjx-06-116.3.fid
169.94
139.49
138.59
137.80
132.39
132.06
131.73
131.40
129.12
126.84
126.08
126.04
124.66
120.68
120.64
120.60
120.30
77.48
77.16
76.84
44.63
34.46
19.98
F3C
CF3
O
Me
NHPh
4m
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-06-116.2.fid
-63.00
F3C
CF3
O
Me
NHPh
4m
19F NMR (367 MHz, CDCl3)
f1 (ppm)



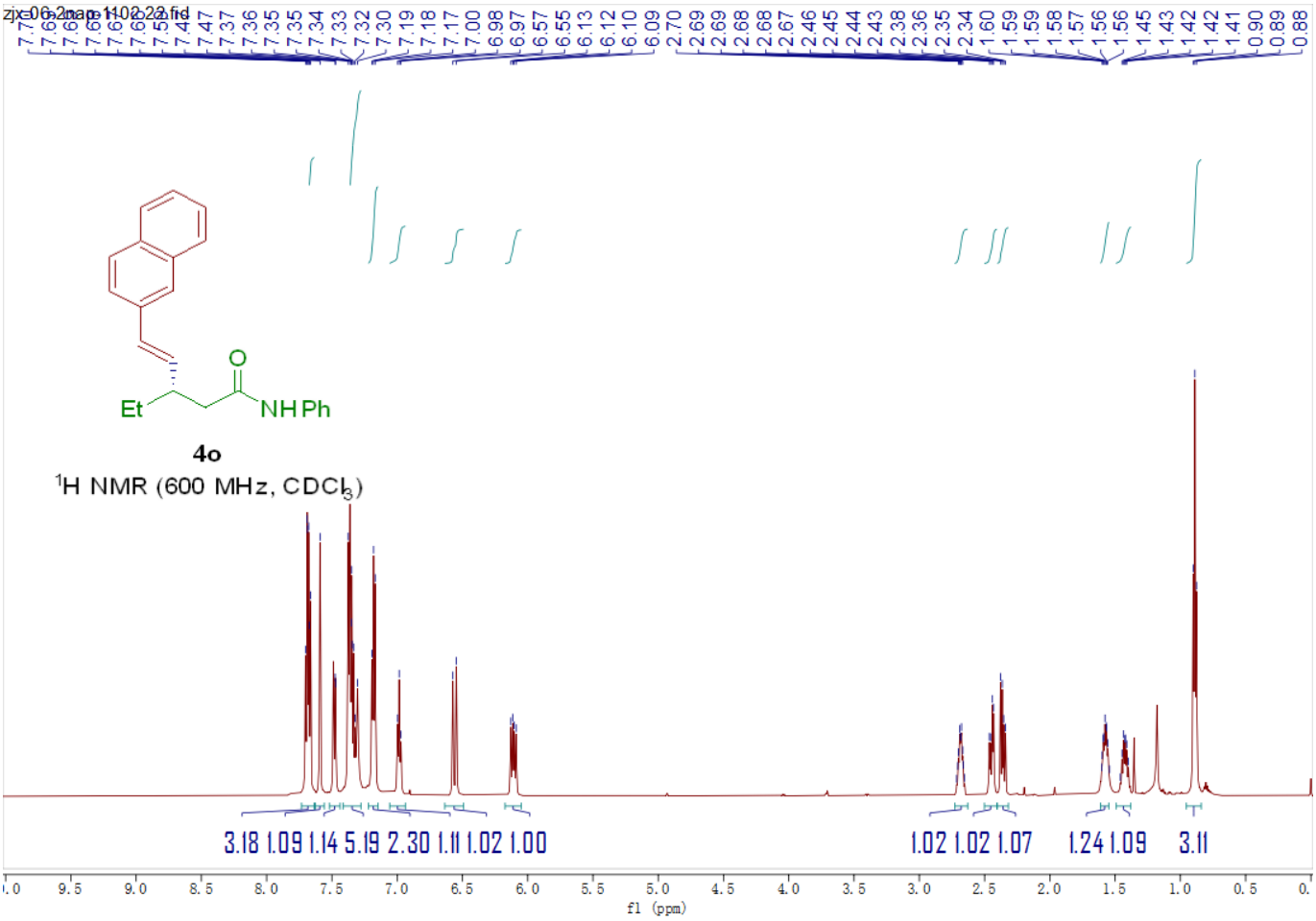
4n

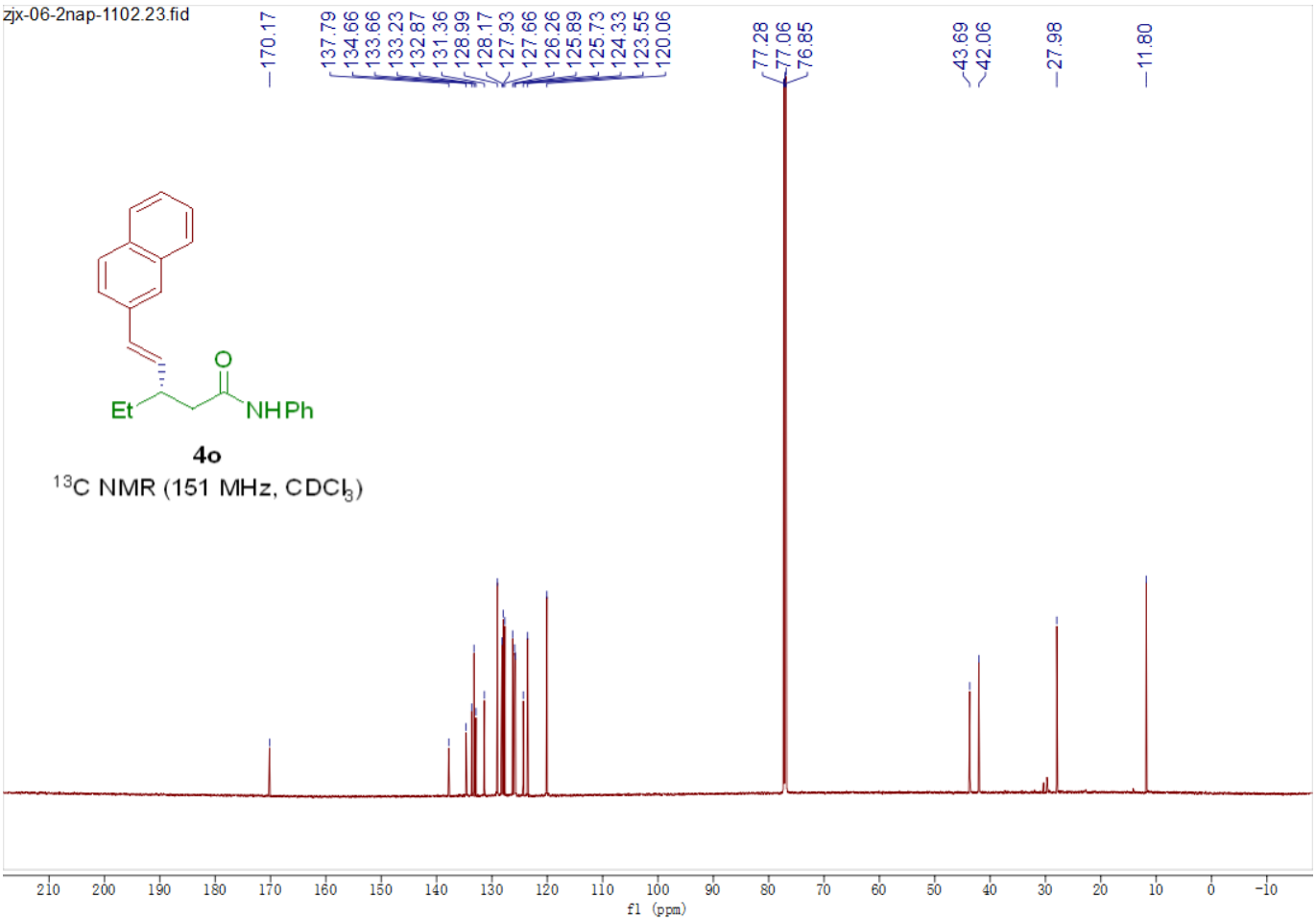
^{1}H NMR (400 MHz, $CDCl_3$)

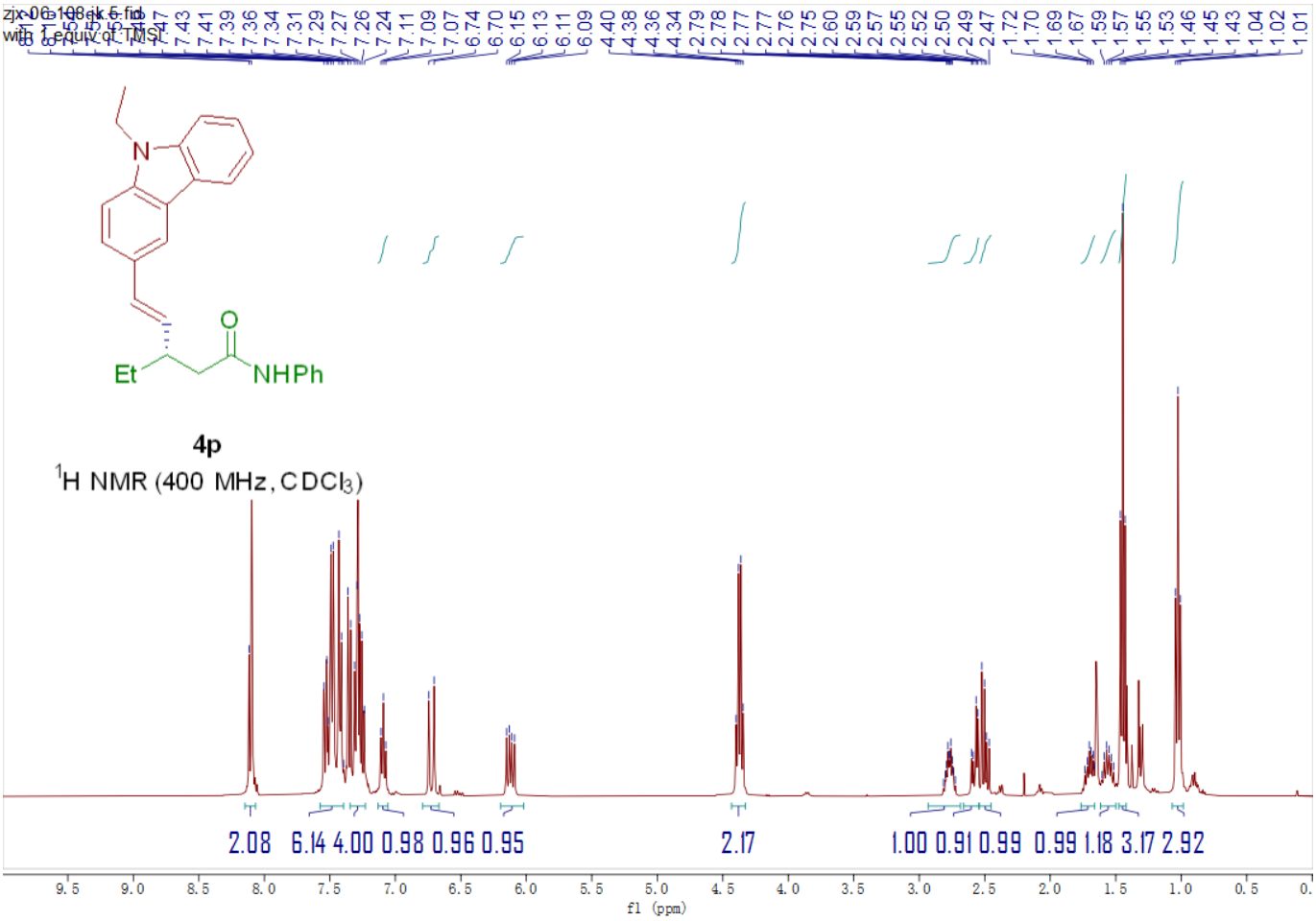


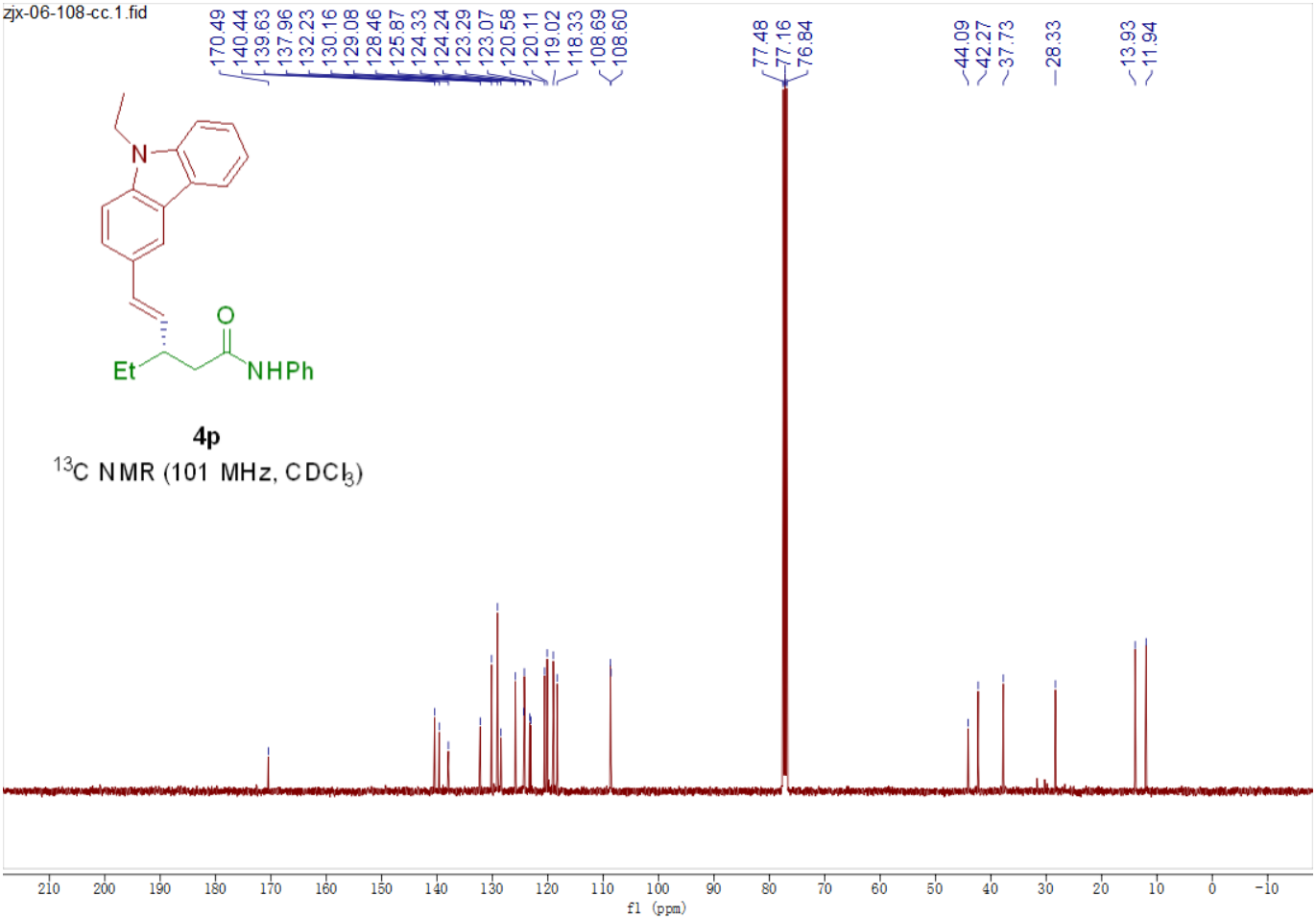
4n

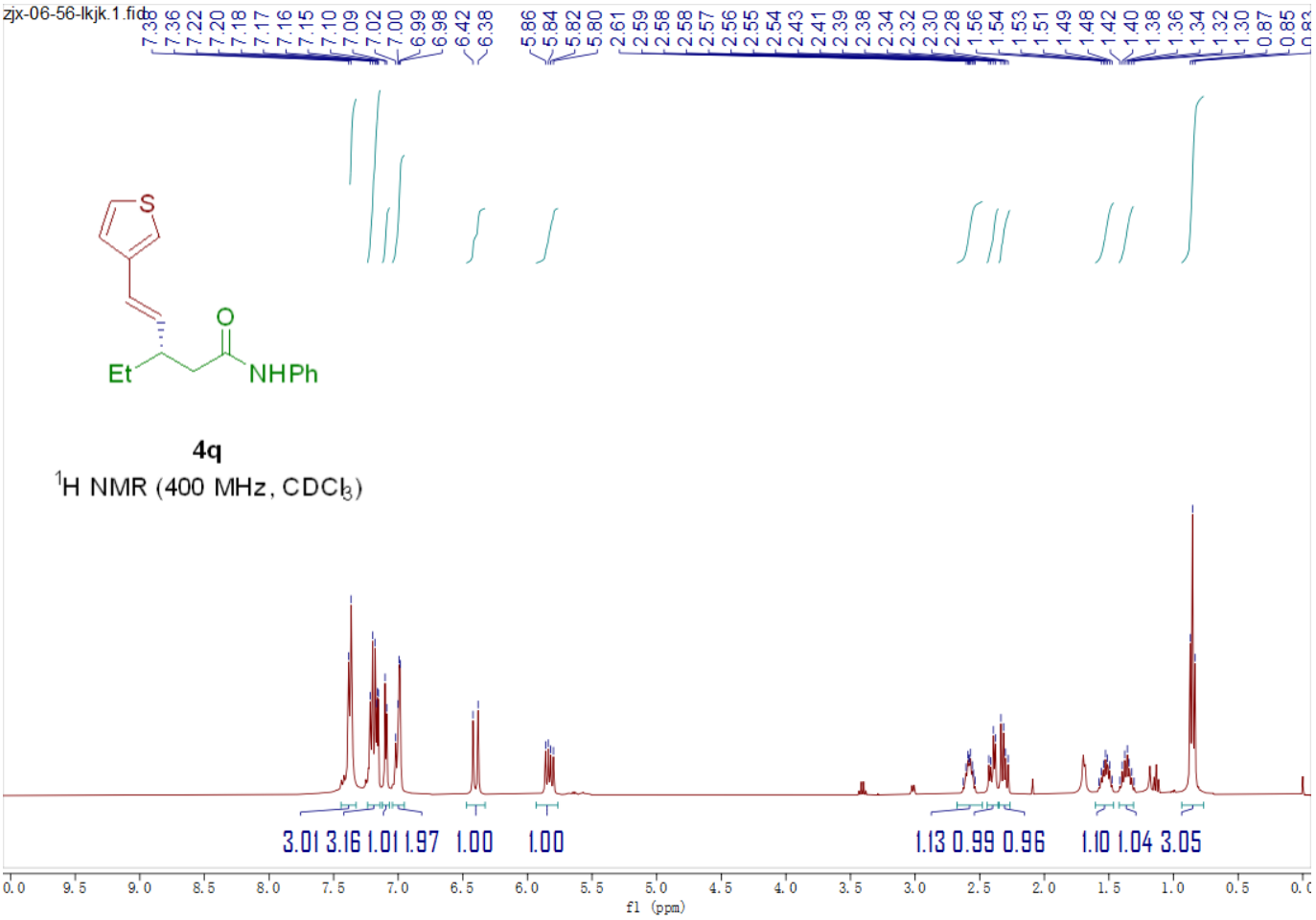
^{13}C NMR (101 MHz, $CDCl_3$)

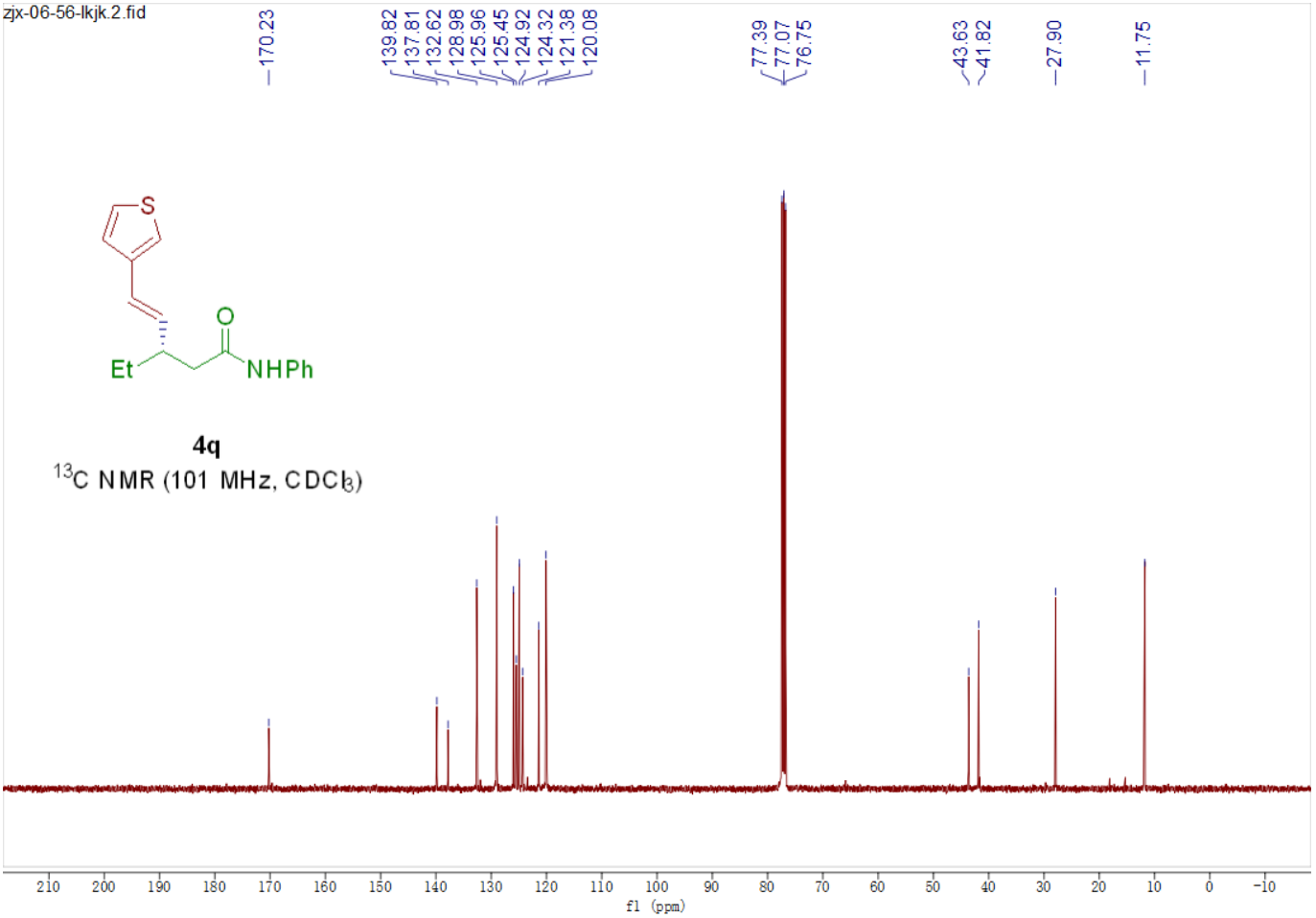

zjx-06-2nap-1102.22.fid
Et
O
NHPh
4o
1H NMR (600 MHz, CDCl3)
3.18 1.09 1.14 5.19 2.30 1.11 1.02 1.00
1.02 1.02 1.07 1.24 1.09 3.11
f1 (ppm)

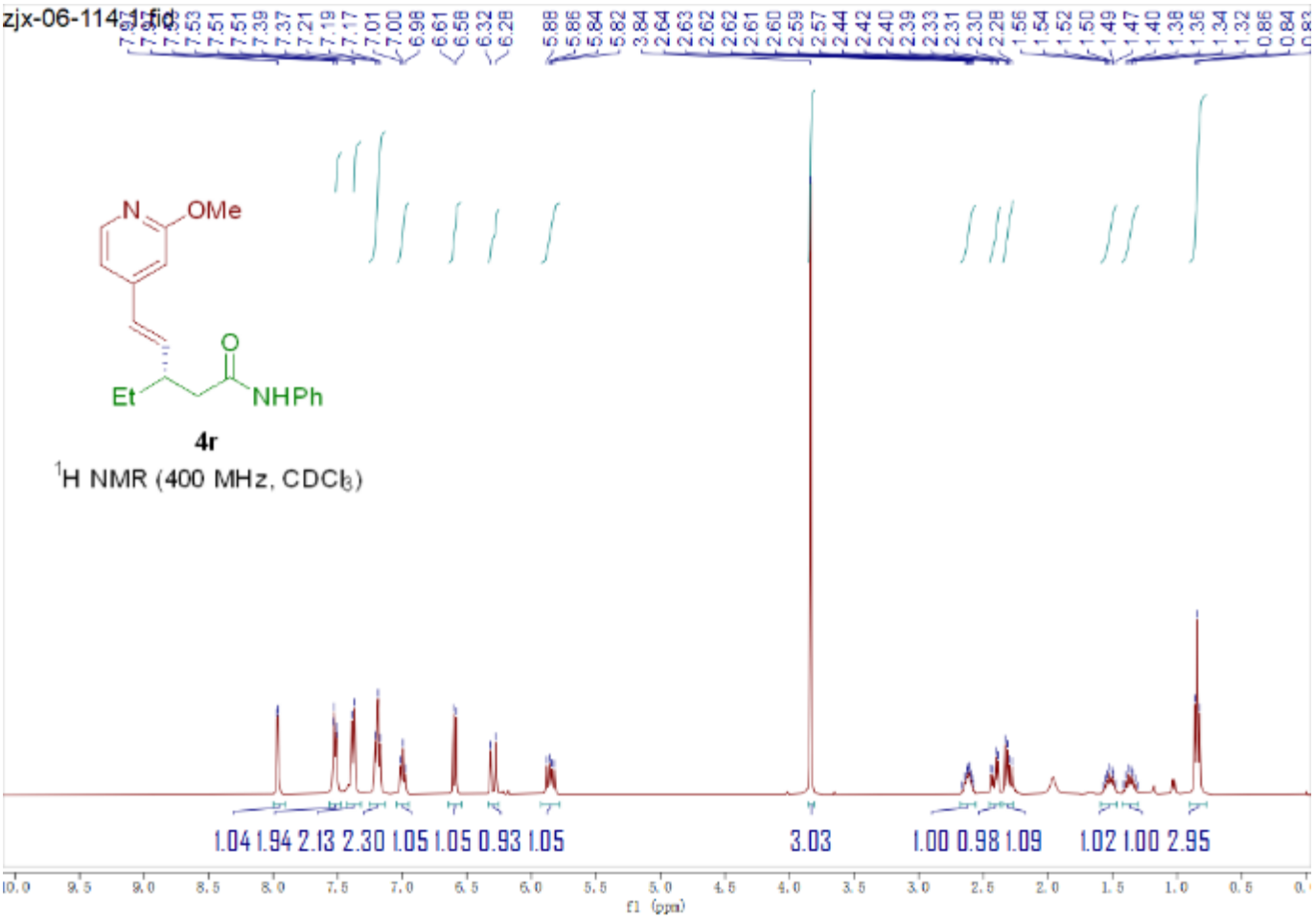

zjx-06-2nap-1102.23.fid
Et
O
NHPh
4o
13C NMR (151 MHz, CDCl3)
f1 (ppm)

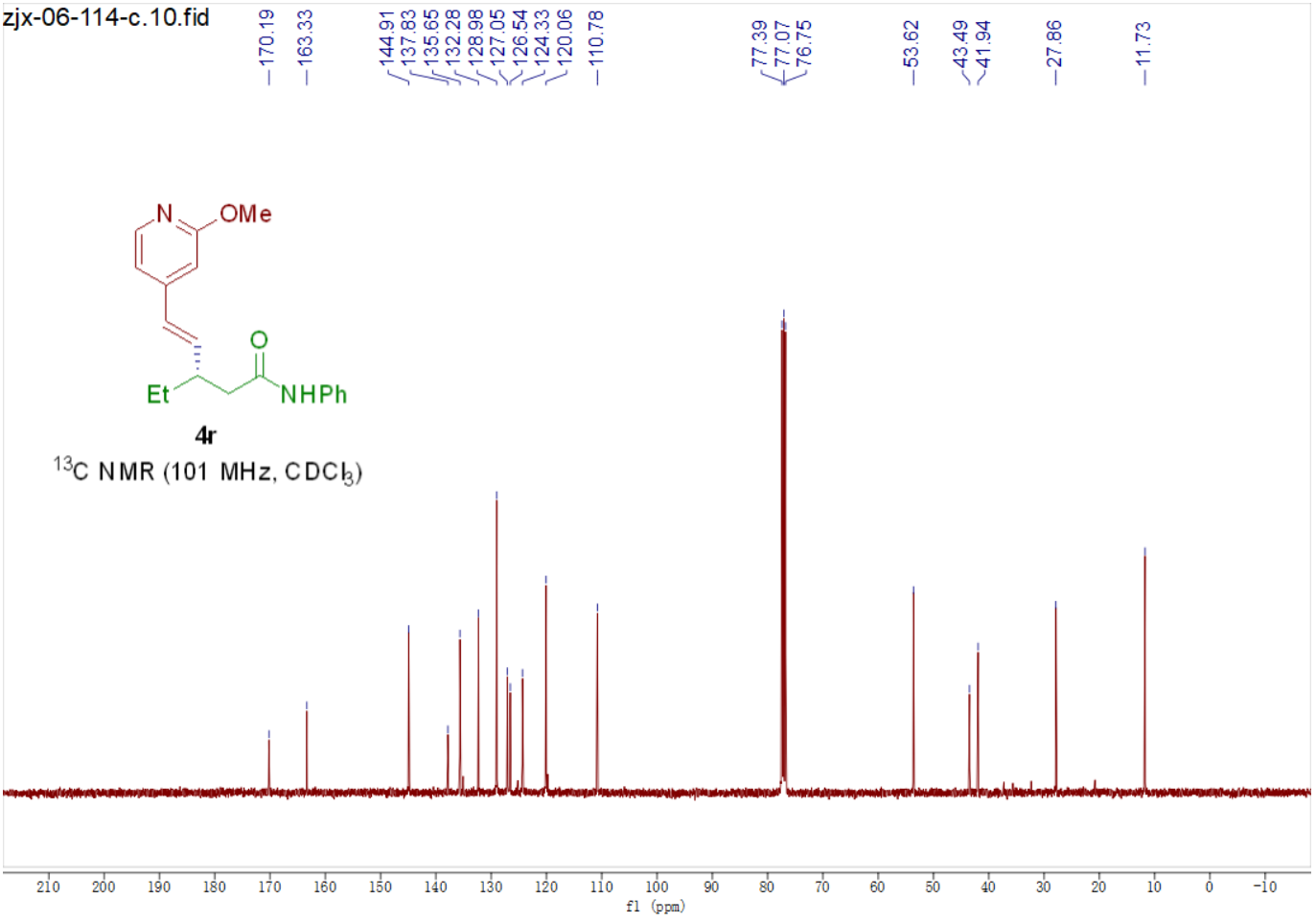

zjx-06-108-jk-5.fid
with 1 equiv of TMSI
7.55 7.53 7.47 7.43 7.41 7.39 7.36 7.34 7.31 7.29 7.27 7.26 7.24 7.11 7.09 7.07 6.74 6.70 6.15 6.13 6.11 6.09 4.40 4.38 4.36 4.34 2.79 2.78 2.77 2.76 2.75 2.60 2.59 2.57 2.55 2.52 2.50 2.49 2.47 1.72 1.70 1.69 1.67 1.59 1.57 1.55 1.53 1.46 1.45 1.43 1.04 1.02 1.01
N
O
Et
NHPh
4p
1H NMR (400 MHz, CDCl3)
2.08 6.14 4.00 0.98 0.96 0.95 2.17 1.00 0.91 0.99 0.99 1.18 3.17 2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

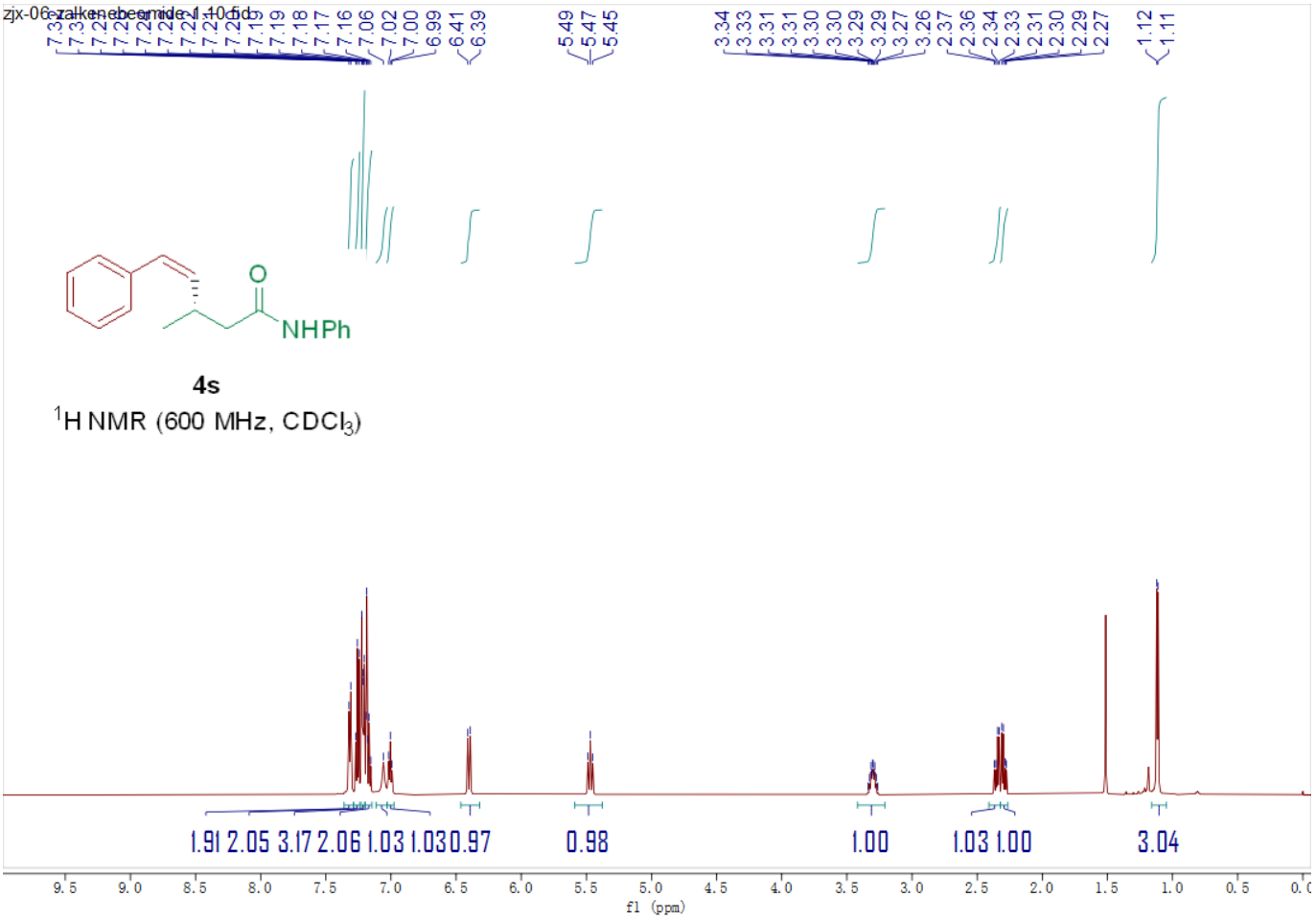

zjx-06-108-cc.1.fid
170.49 140.44 139.63 137.96 132.23 130.16 129.08 128.46 125.87 124.33 124.24 123.29 123.07 120.58 120.11 119.02 118.33 108.69 108.60
77.48 77.16 76.84
44.09 42.27 37.73 28.33 13.93 11.94
N
O
Et
NHPh
4p
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

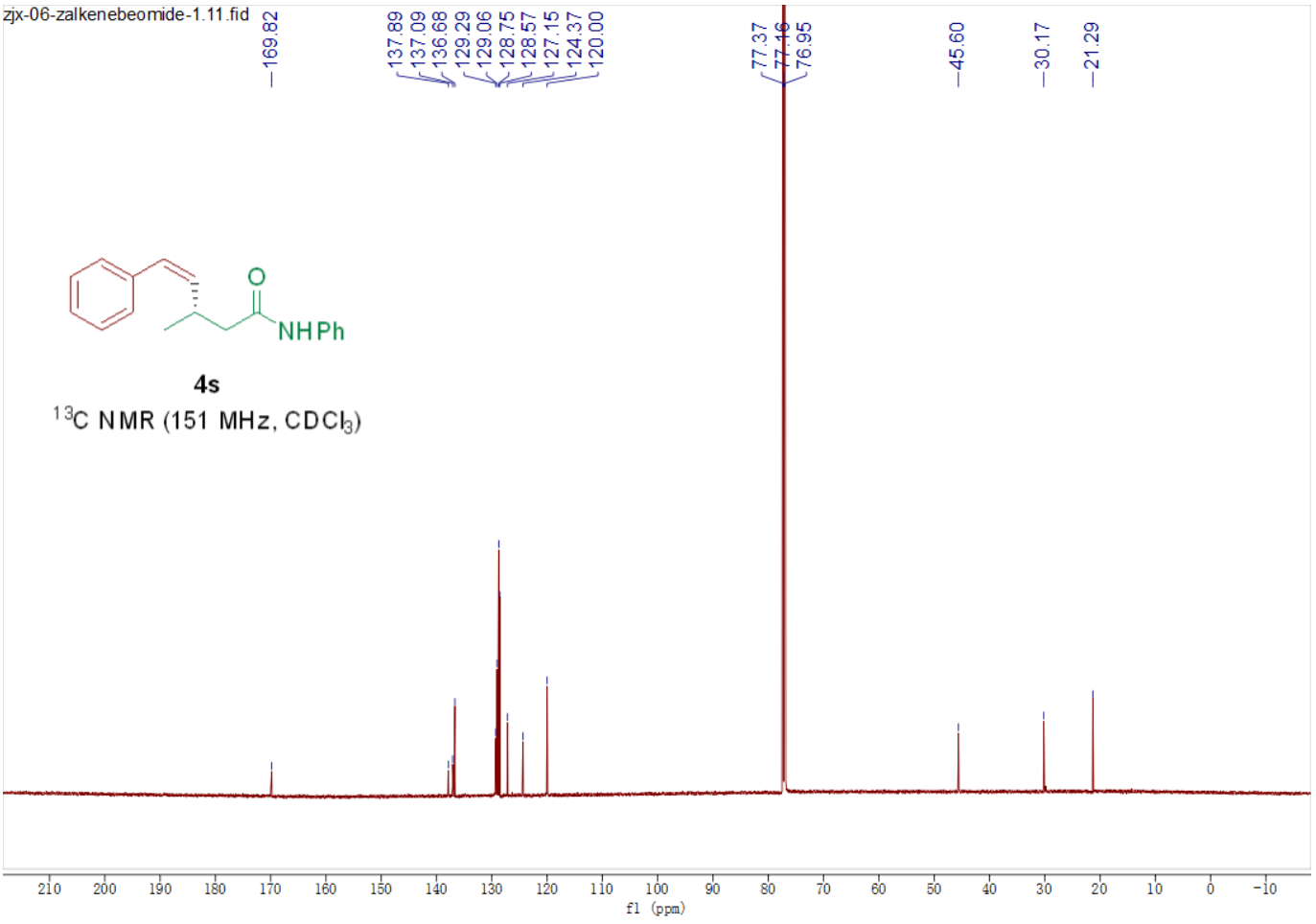

zjx-06-56-lkjk.1.fid
7.38 7.36 7.22 7.20 7.18 7.17 7.16 7.15 7.10 7.09 7.02 7.00 6.99 6.98 6.42 6.38
5.86 5.84 5.82 5.80
2.61 2.59 2.58 2.58 2.57 2.56 2.55 2.54 2.43 2.41 2.39 2.38 2.34 2.32 2.30 2.28 1.56 1.54 1.53 1.51 1.49 1.48 1.42 1.40 1.38 1.36 1.34 1.32 1.30 0.87 0.85
S
O
Et
NHPh
4q
1H NMR (400 MHz, CDCl3)
3.01 3.16 1.01 1.97 1.00 1.00 1.13 0.99 0.96 1.10 1.04 3.05
f1 (ppm)

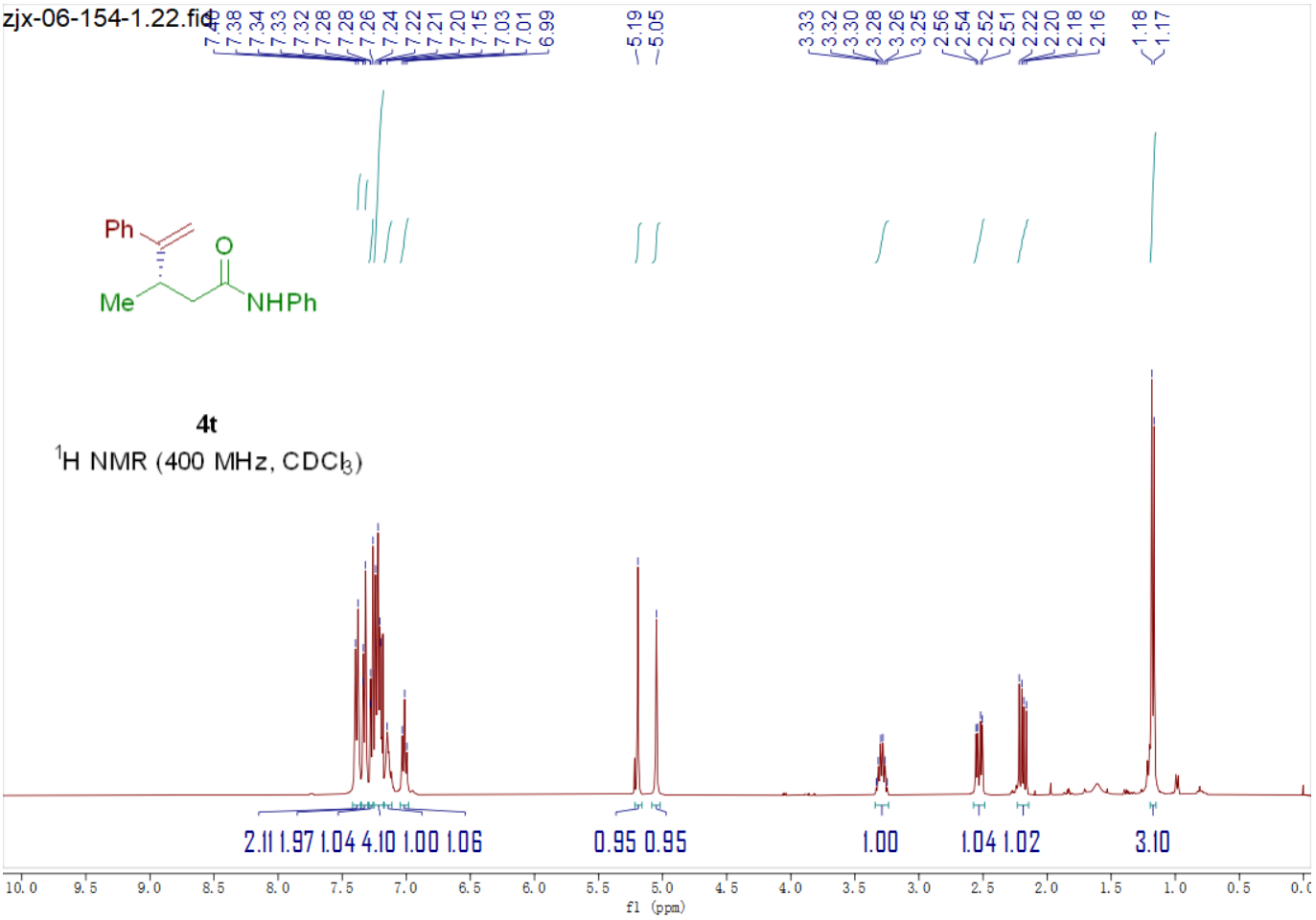

zjx-06-56-lkjk.2.fid
170.23
139.82 137.81 132.62 128.98 125.96 125.45 124.92 124.32 121.38 120.08
77.39 77.07 76.75
43.63 41.82
27.90
11.75
S
O
Et
NHPh
4q
13C NMR (101 MHz, CDCl3)
f1 (ppm)

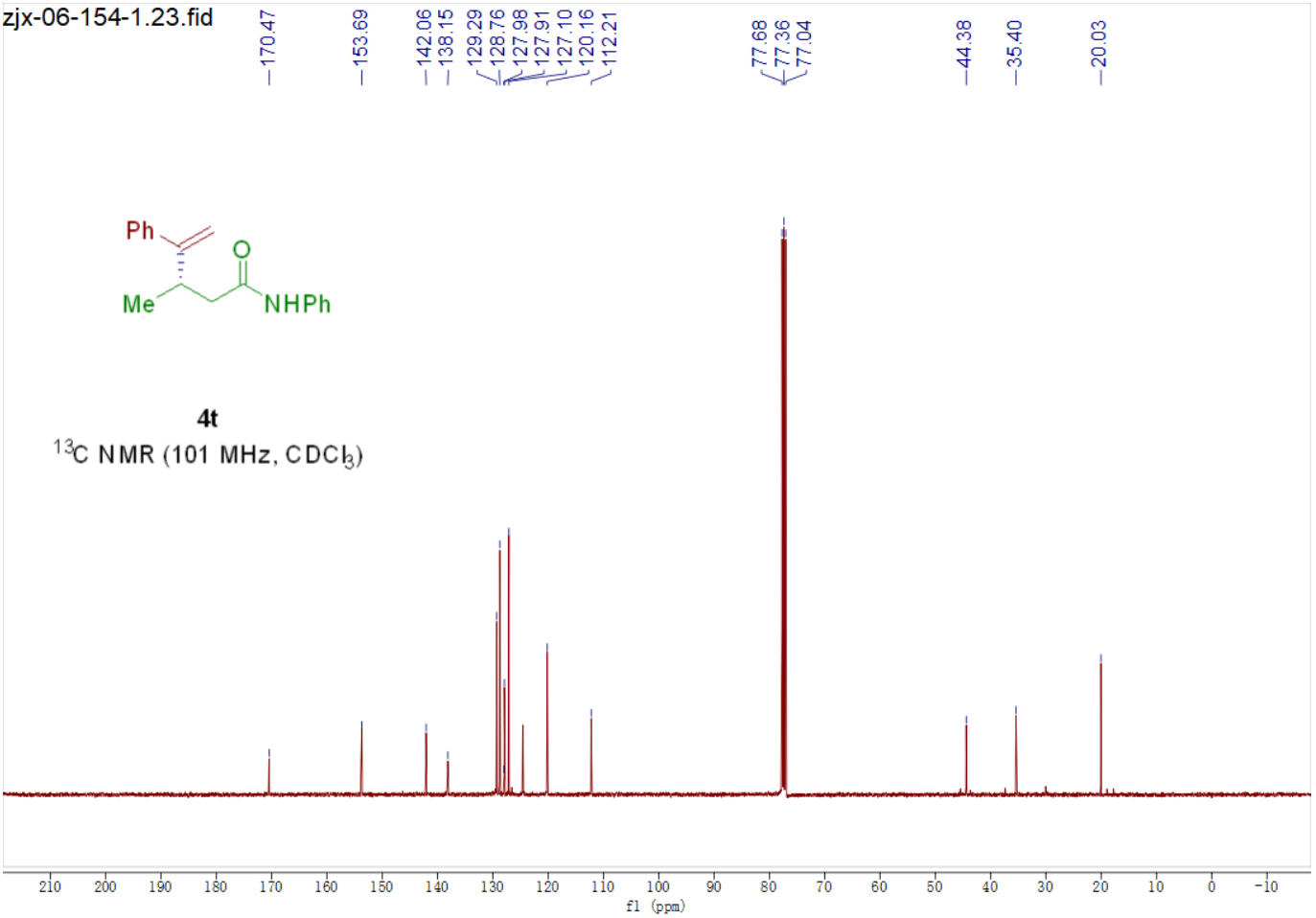

zjx-06-114-1.fid
N
OMe
O
Et
NHPh
4r
1H NMR (400 MHz, CDCl3)
1.04 1.94 2.13 2.30 1.05 1.05 0.93 1.05
3.03
1.00 0.98 1.09
1.02 1.00 2.95
f1 (ppm)

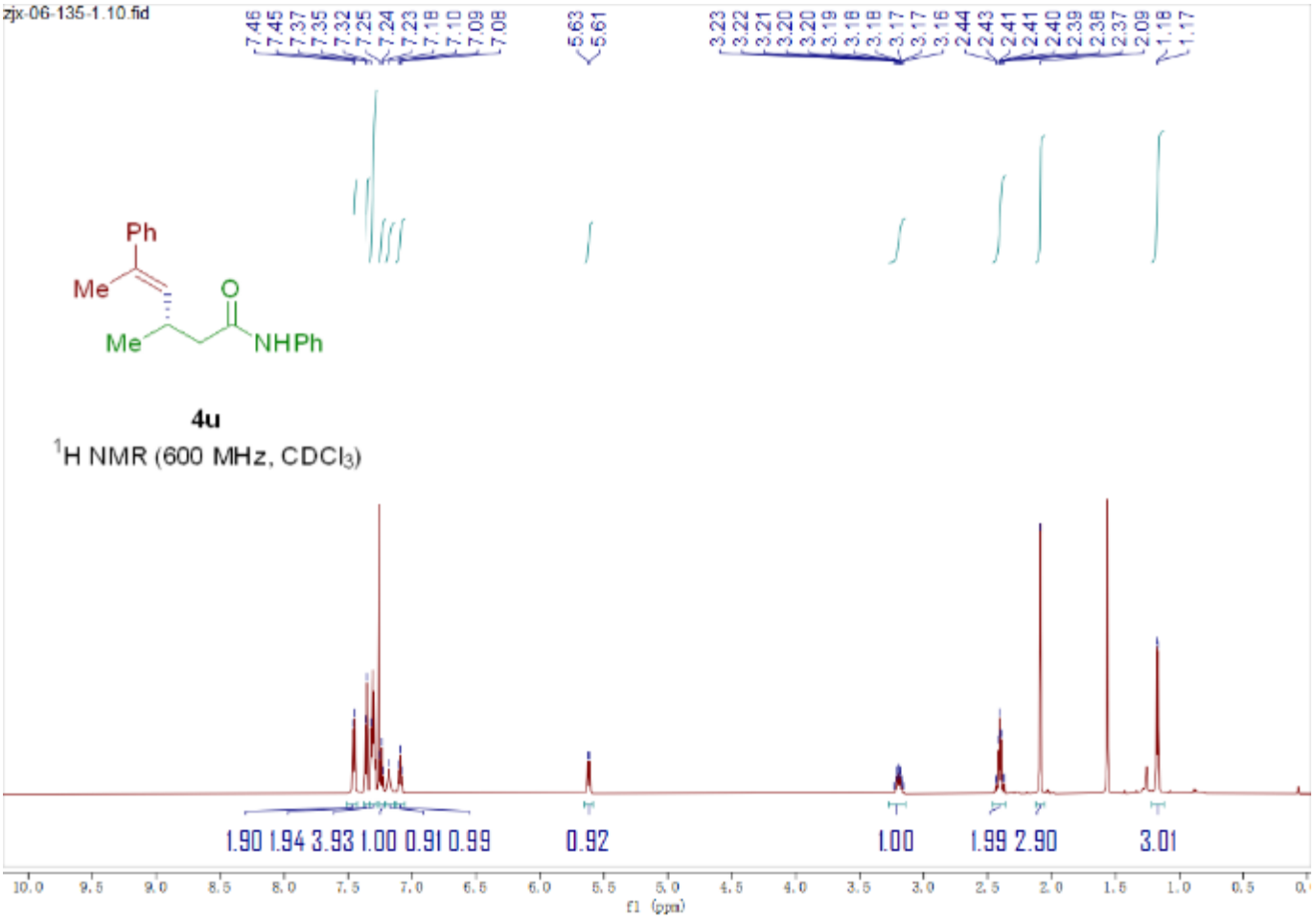

zjx-06-114-c.10.fid
170.19
163.33
144.91
137.83
135.65
132.28
128.98
127.05
126.54
124.33
120.06
110.78
77.39
77.07
76.75
53.62
43.49
41.94
27.86
11.73
N
OMe
O
Et
NHPh
4r
13C NMR (101 MHz, CDCl3)
f1 (ppm)

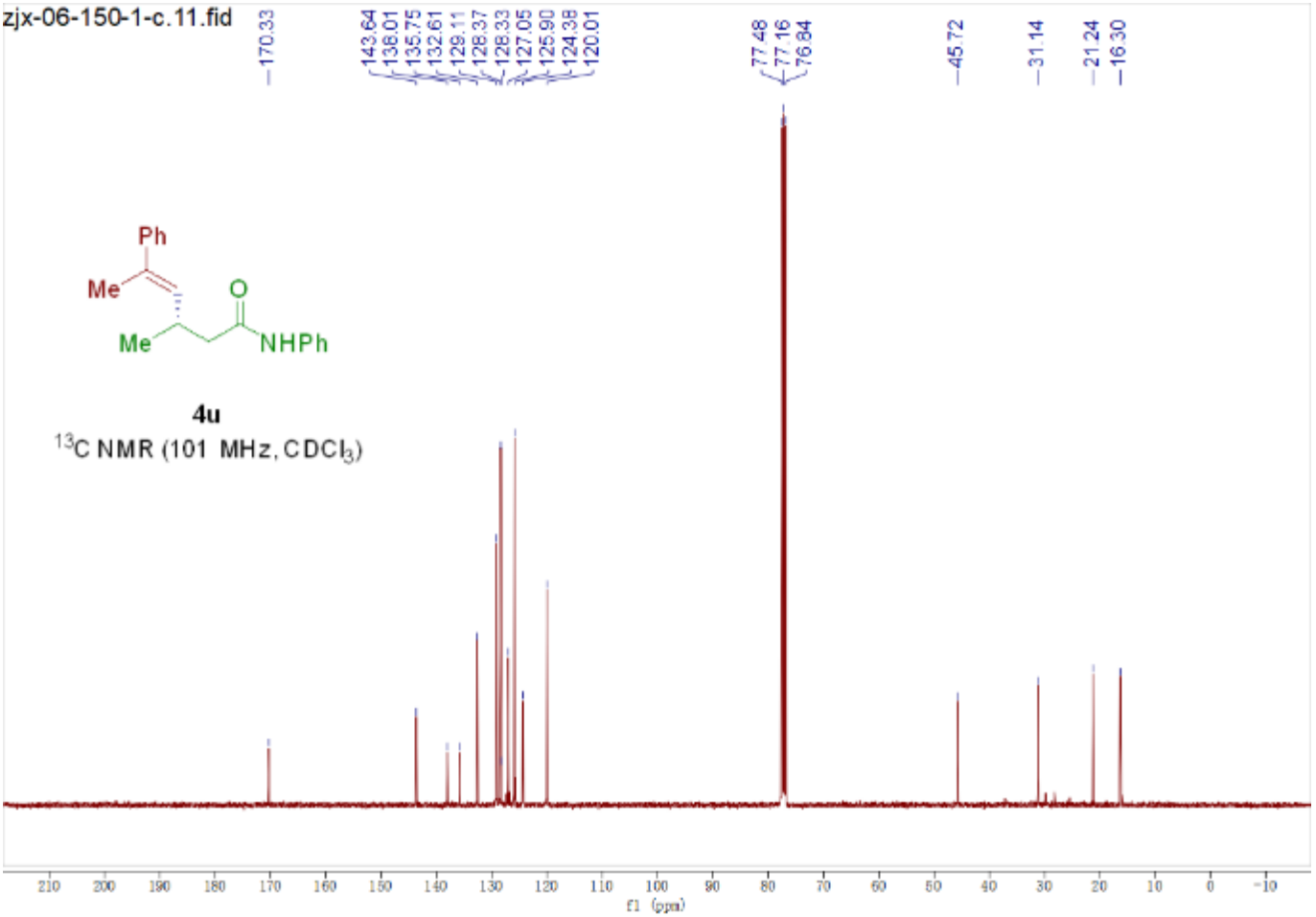

zjx-06-zalkenebeomide-1.10.fid
7.32 7.31 7.24 7.24 7.24 7.24 7.23 7.21 7.20 7.19 7.18 7.17 7.16 7.06 7.02 7.00 6.99 6.41 6.39
5.49 5.47 5.45
3.34 3.33 3.31 3.31 3.30 3.30 3.29 3.29 3.27 3.26 2.37 2.36 2.34 2.33 2.31 2.30 2.29 2.27
1.12 1.11
O
NHPh
4s
1H NMR (600 MHz, CDCl3)
1.91 2.05 3.17 2.06 1.03 1.03 0.97 0.98 1.00 1.03 1.00 3.04
f1 (ppm)

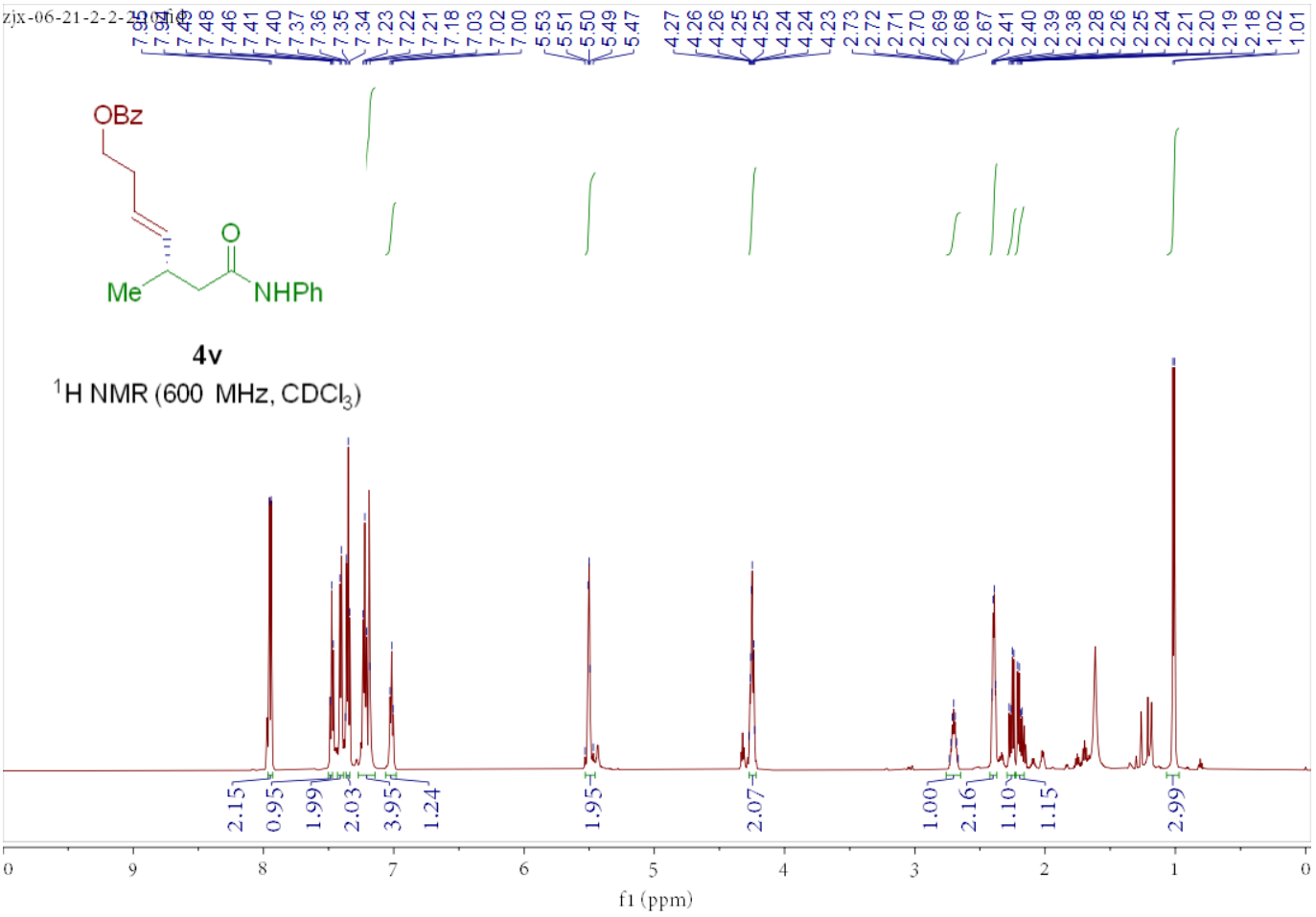

zjx-06-zalkenebeomide-1.11.fid
169.82
137.89 137.09 136.68 129.29 129.06 128.75 128.57 127.15 124.37 120.00
77.37 77.16 76.95
45.60
30.17
21.29
O
NHPh
4s
13C NMR (151 MHz, CDCl3)
f1 (ppm)

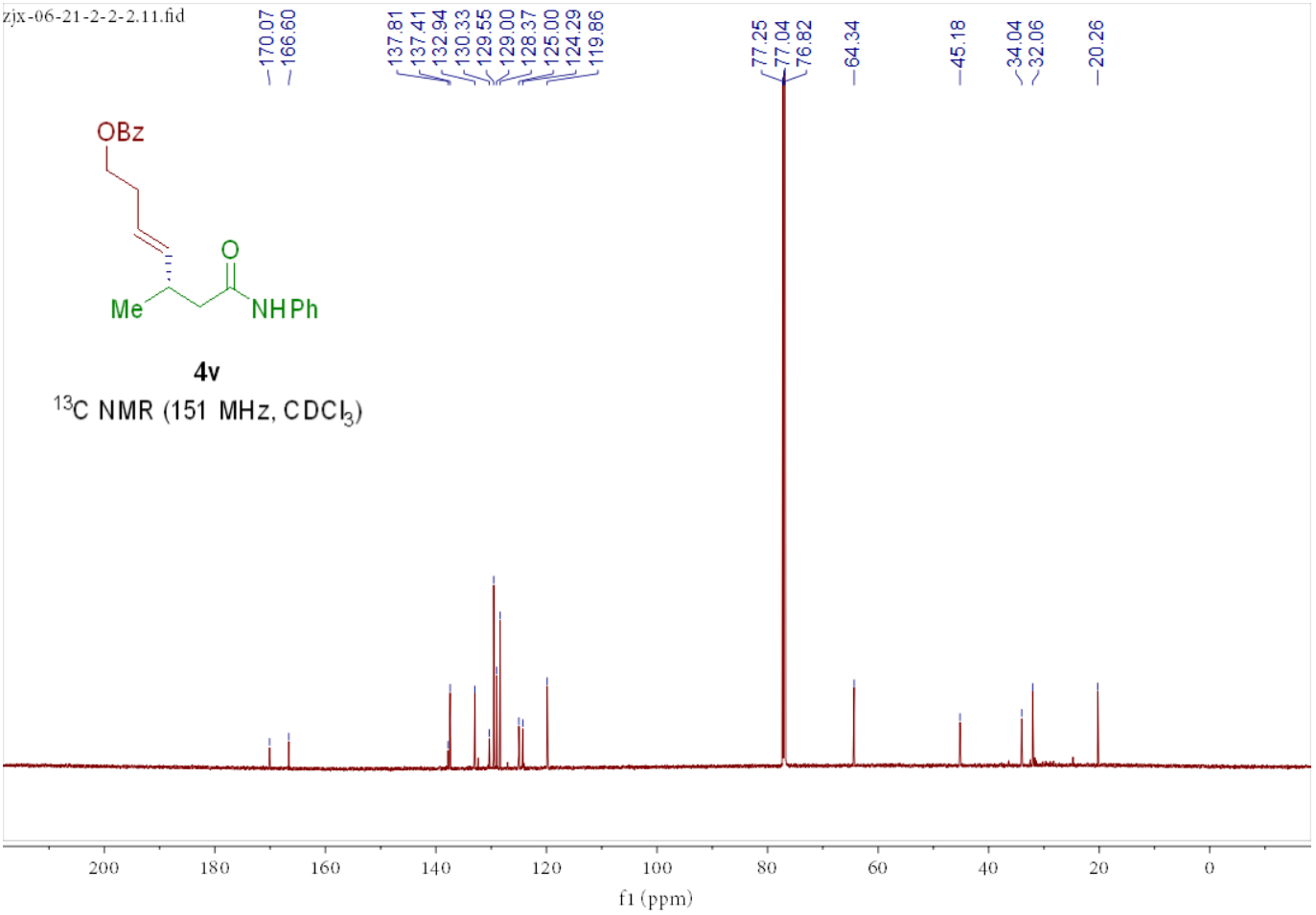

zjx-06-154-1.22.fid
7.40
7.38
7.34
7.33
7.32
7.28
7.28
7.26
7.24
7.22
7.21
7.20
7.15
7.03
7.01
6.99
5.19
5.05
3.33
3.32
3.30
3.28
3.26
3.25
2.56
2.54
2.52
2.51
2.22
2.20
2.18
2.16
1.18
1.17
Ph
O
Me
NHPh
4t
1H NMR (400 MHz, CDCl3)
2.11 1.97 1.04 4.10 1.00 1.06
0.95 0.95
1.00
1.04 1.02
3.10
f1 (ppm)

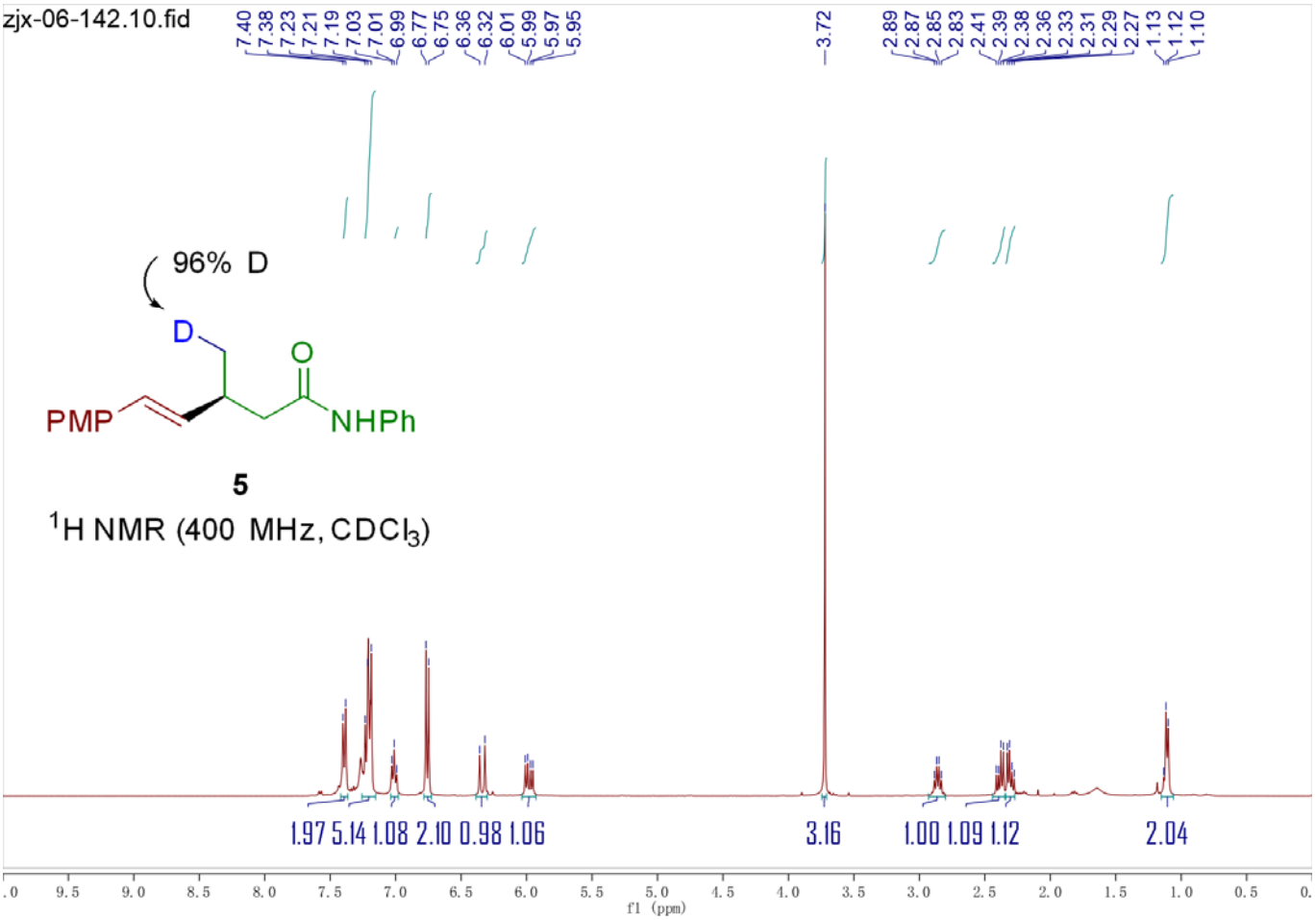

zjx-06-154-1.23.fid
170.47
153.69
142.06
138.15
129.29
128.76
127.98
127.91
127.10
120.16
112.21
77.68
77.36
77.04
44.38
35.40
20.03
Ph
O
Me
NHPh
4t
13C NMR (101 MHz, CDCl3)
f1 (ppm)

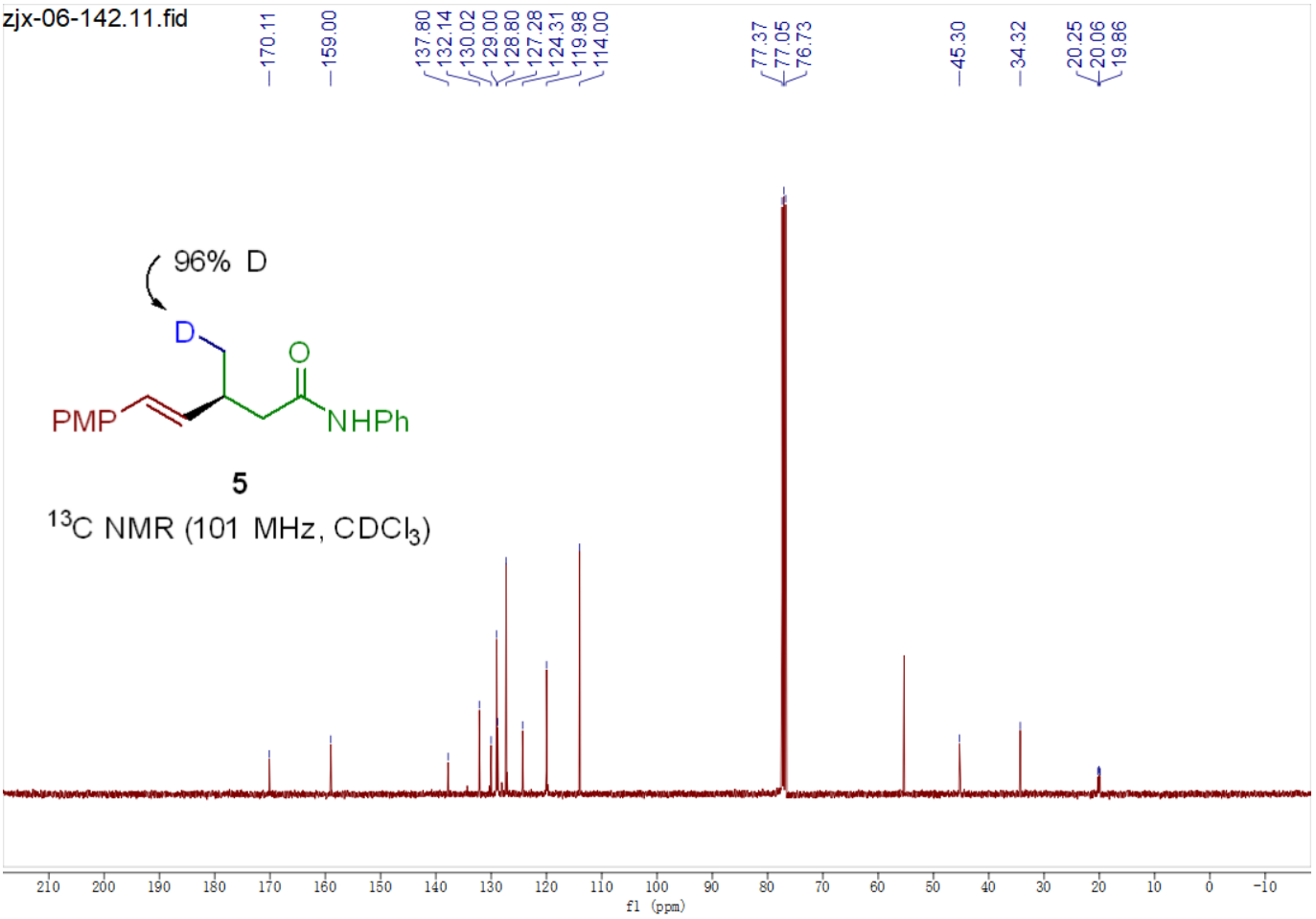

zjx-06-135-1.10.fid
7.46
7.45
7.37
7.35
7.32
7.25
7.24
7.23
7.18
7.10
7.09
7.08
5.63
5.61
3.23
3.22
3.21
3.20
3.20
3.19
3.18
3.18
3.17
3.17
3.16
2.44
2.43
2.41
2.41
2.40
2.39
2.38
2.37
2.09
1.18
1.17
Ph
Me
O
Me
NHPh
4u
1H NMR (600 MHz, CDCl3)
1.90 1.94 3.93 1.00 0.91 0.99
0.92
1.00
1.99 2.90
3.01
f1 (ppm)

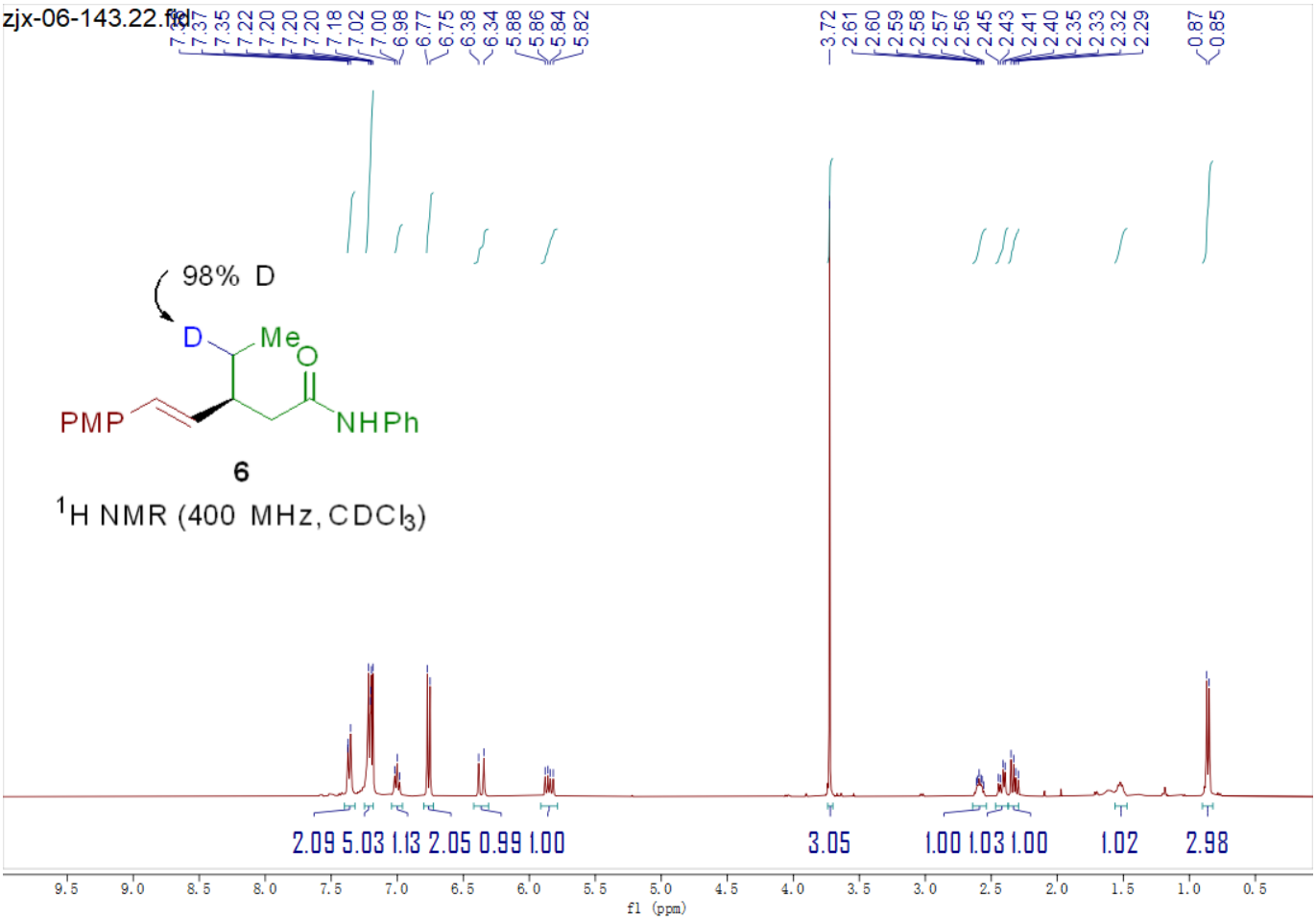

zjx-06-150-1-c.11.fid
170.33
143.64
136.01
135.75
132.61
129.11
128.37
128.33
127.05
125.90
124.38
120.01
77.48
77.16
76.84
45.72
31.14
21.24
16.30
Ph
Me
O
Me
NHPh
4u
13C NMR (101 MHz, CDCl3)
f1 (ppm)

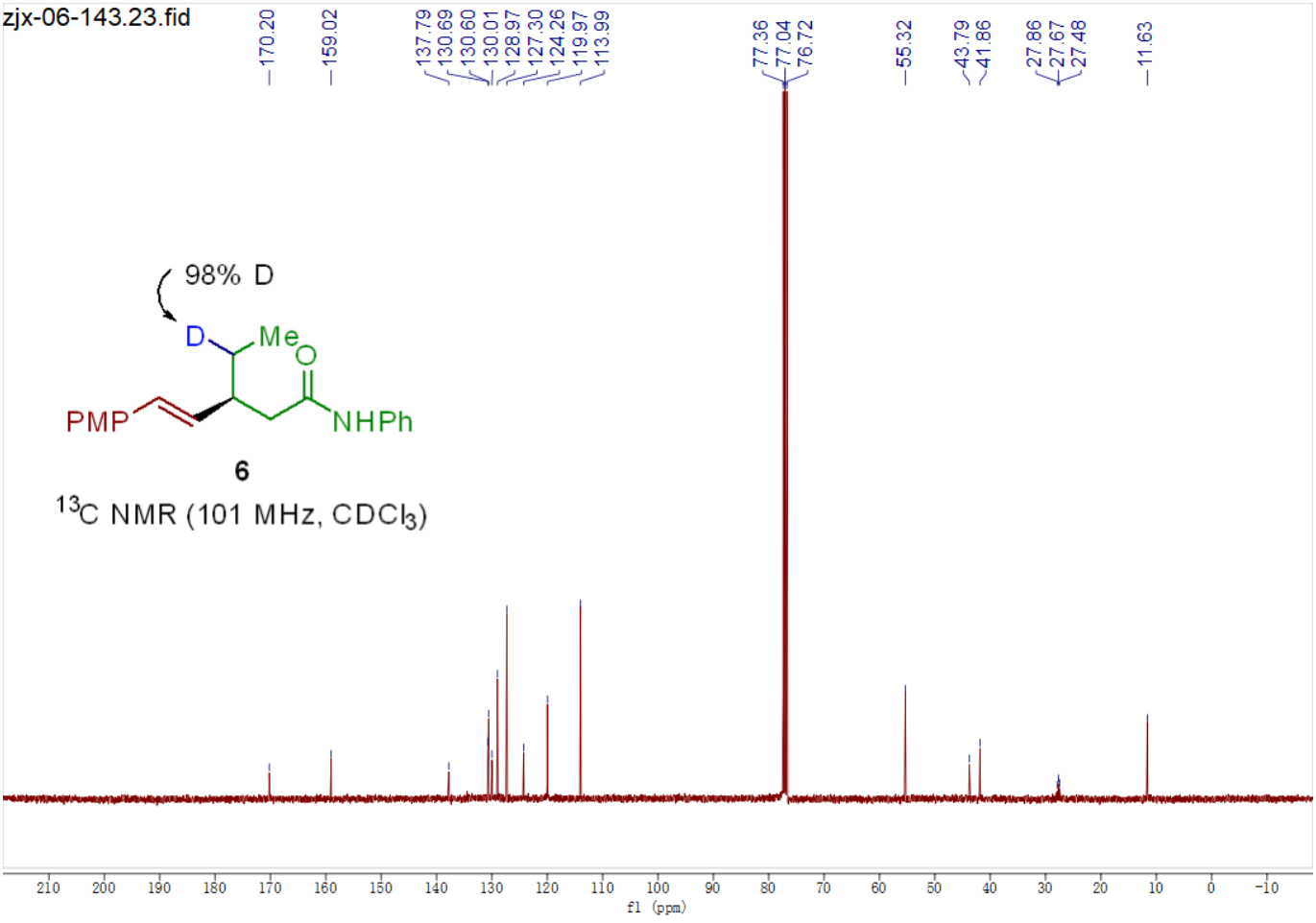

OBz
O
Me
NHPh
4v
1H NMR (600 MHz, CDCl3)
2.15
0.95
1.99
2.03
3.95
1.24
1.95
2.07
1.00
2.16
1.10
1.15
2.99
f1 (ppm)

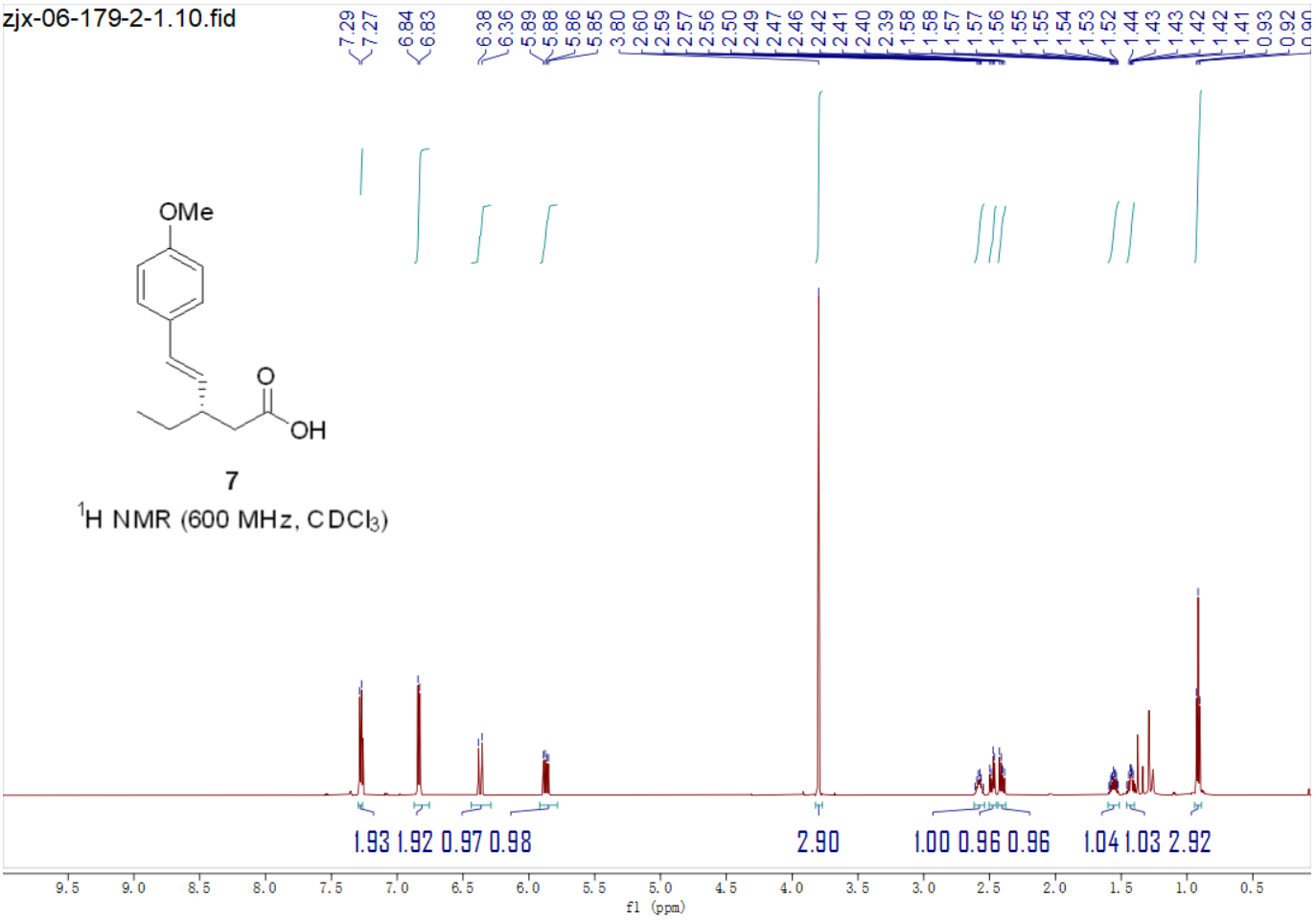

OBz
O
Me
NHPh
4v
13C NMR (151 MHz, CDCl3)
f1 (ppm)

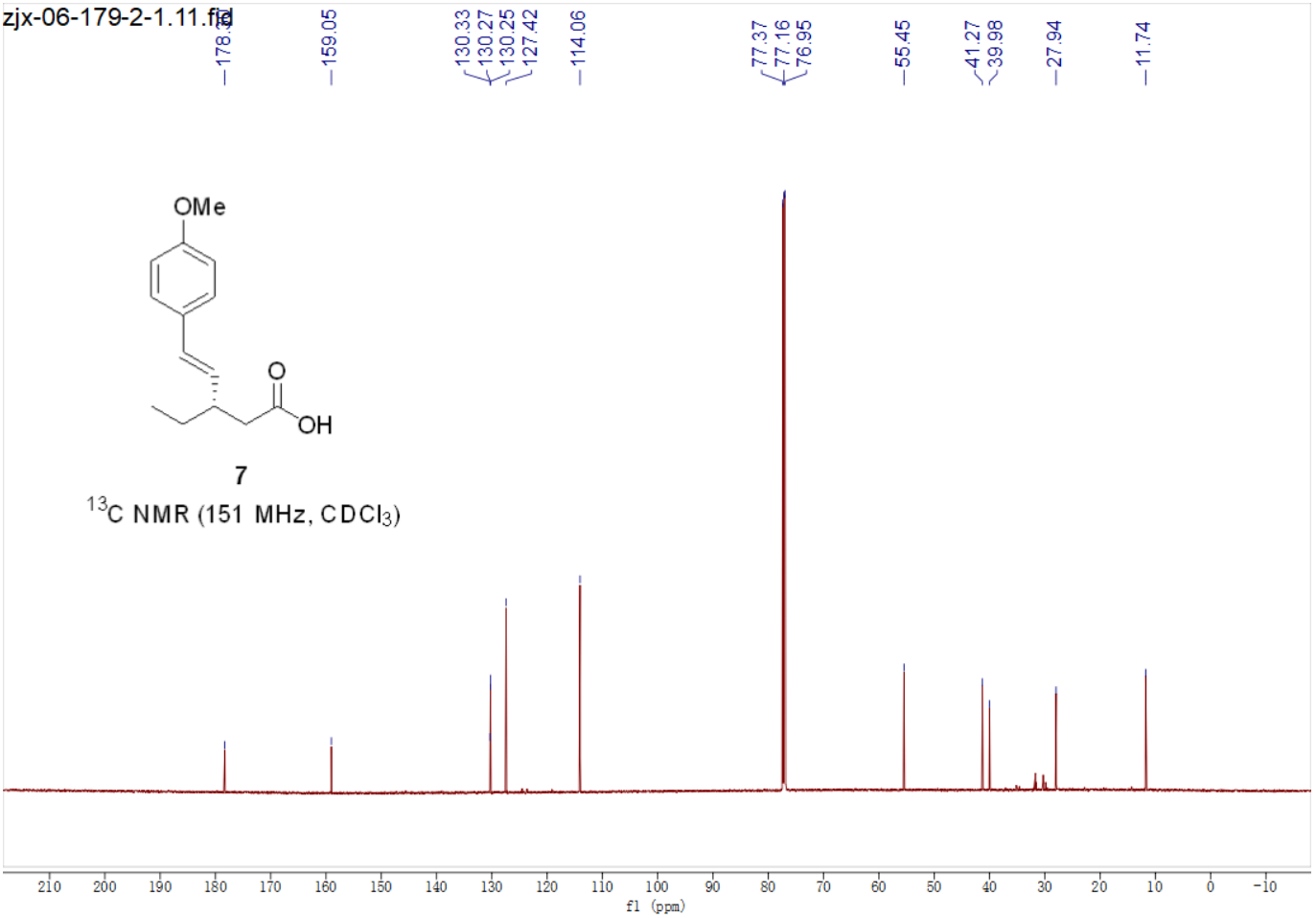

zjx-06-142.10.fid
7.40 7.38 7.23 7.21 7.19 7.03 7.01 6.99 6.77 6.75 6.36 6.32 6.01 5.99 5.97 5.95
3.72
2.89 2.87 2.85 2.83 2.41 2.39 2.38 2.36 2.33 2.31 2.29 2.27 1.13 1.12 1.10
96% D
D
O
PMP
NHPh
5
1H NMR (400 MHz, CDCl3)
1.97 5.14 1.08 2.10 0.98 1.06
3.16
1.00 1.09 1.12
2.04
f1 (ppm)

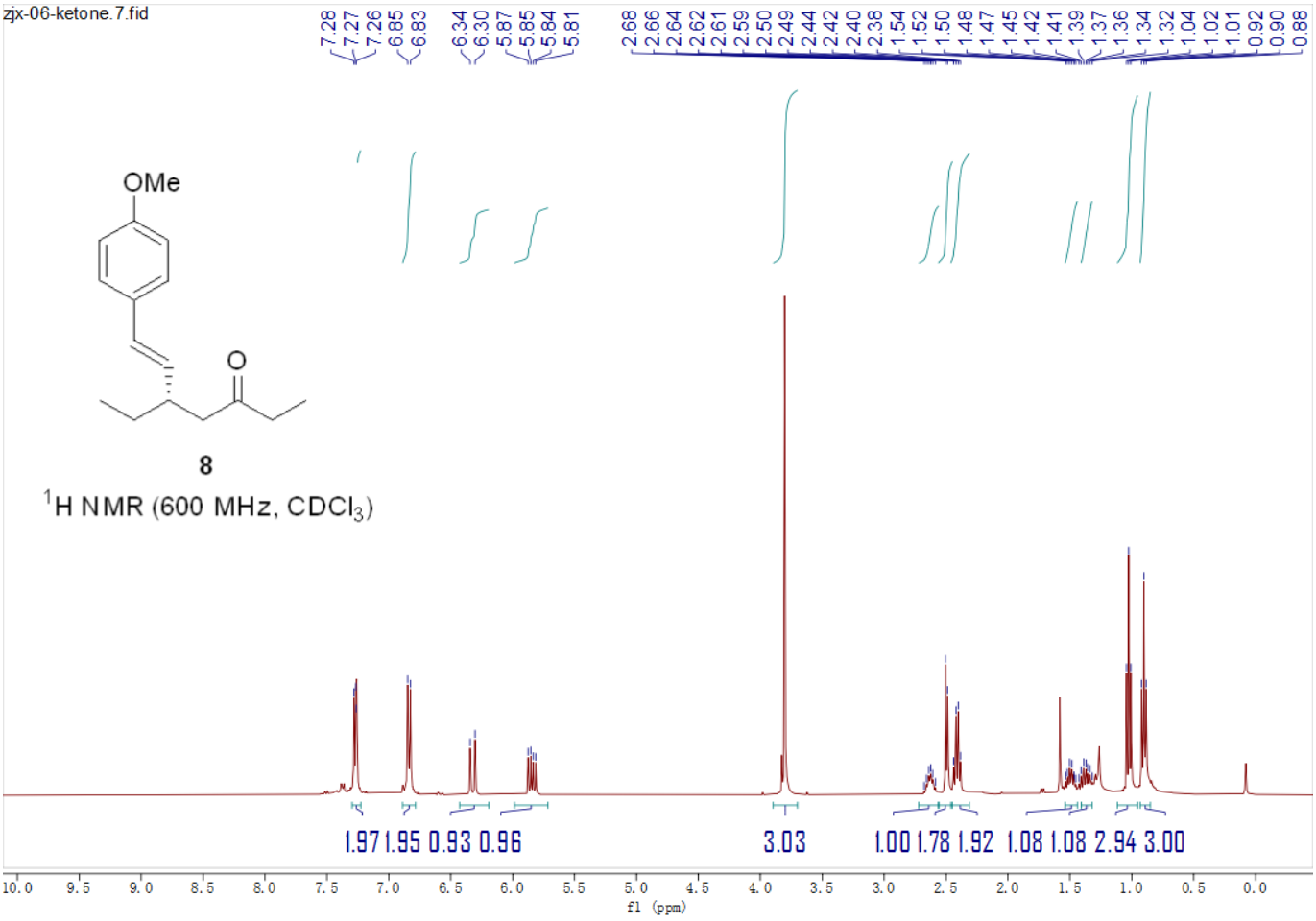

zjx-06-142.11.fid
170.11
159.00
137.80 132.14 130.02 129.00 128.80 127.28 124.31 119.98 114.00
77.37 77.05 76.73
45.30
34.32
20.25 20.06 19.86
96% D
D
O
PMP
NHPh
5
13C NMR (101 MHz, CDCl3)
f1 (ppm)

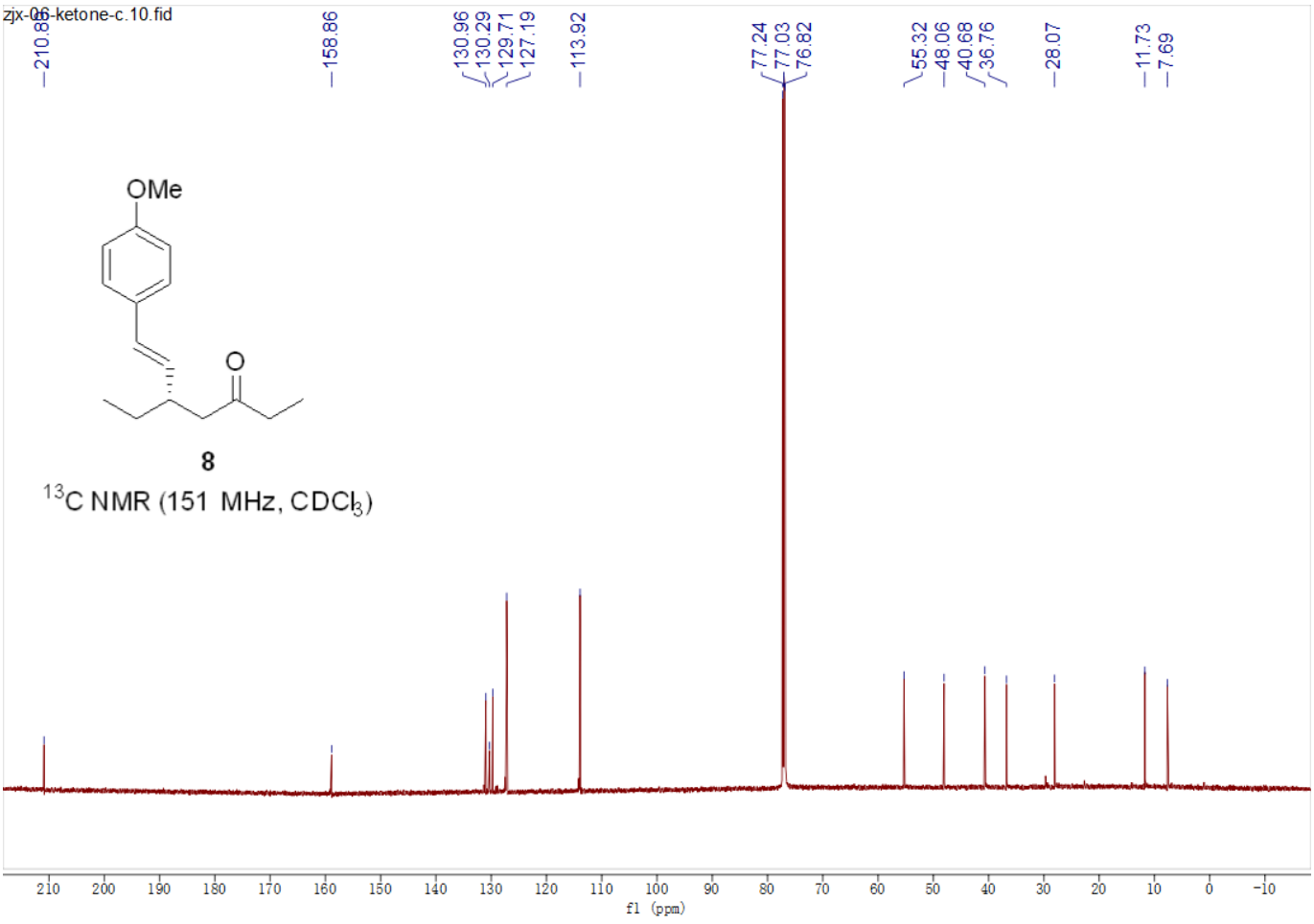

zjx-06-143.22.fid
98% D
D
Me
O
PMP
NHPh
6
1H NMR (400 MHz, CDCl3)
2.09 5.03 1.13 2.05 0.99 1.00
3.05
1.00 1.03 1.00
1.02
2.98
f1 (ppm)

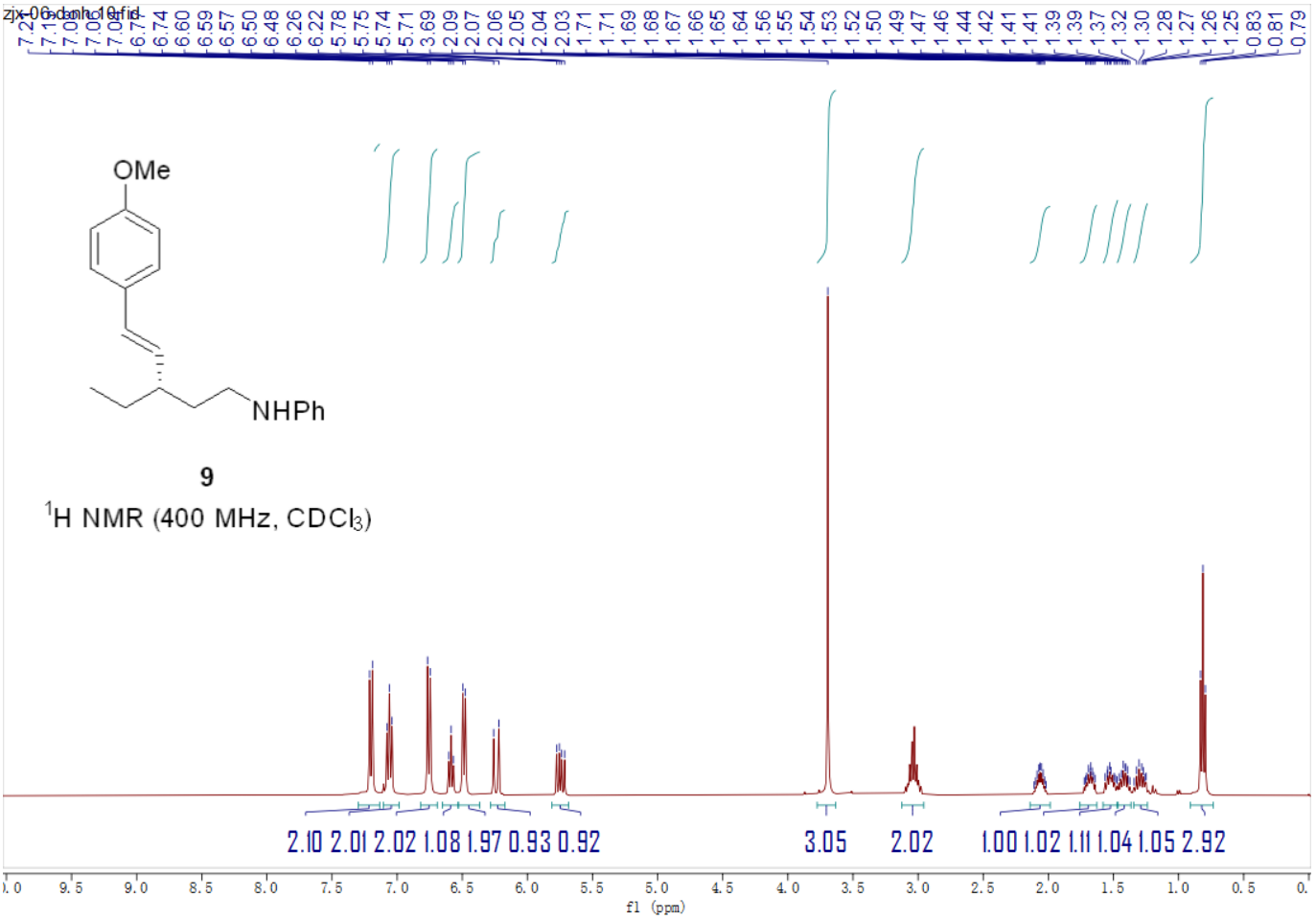

zjx-06-143.23.fid
98% D
D
Me
O
PMP
NHPh
6
13C NMR (101 MHz, CDCl3)
f1 (ppm)

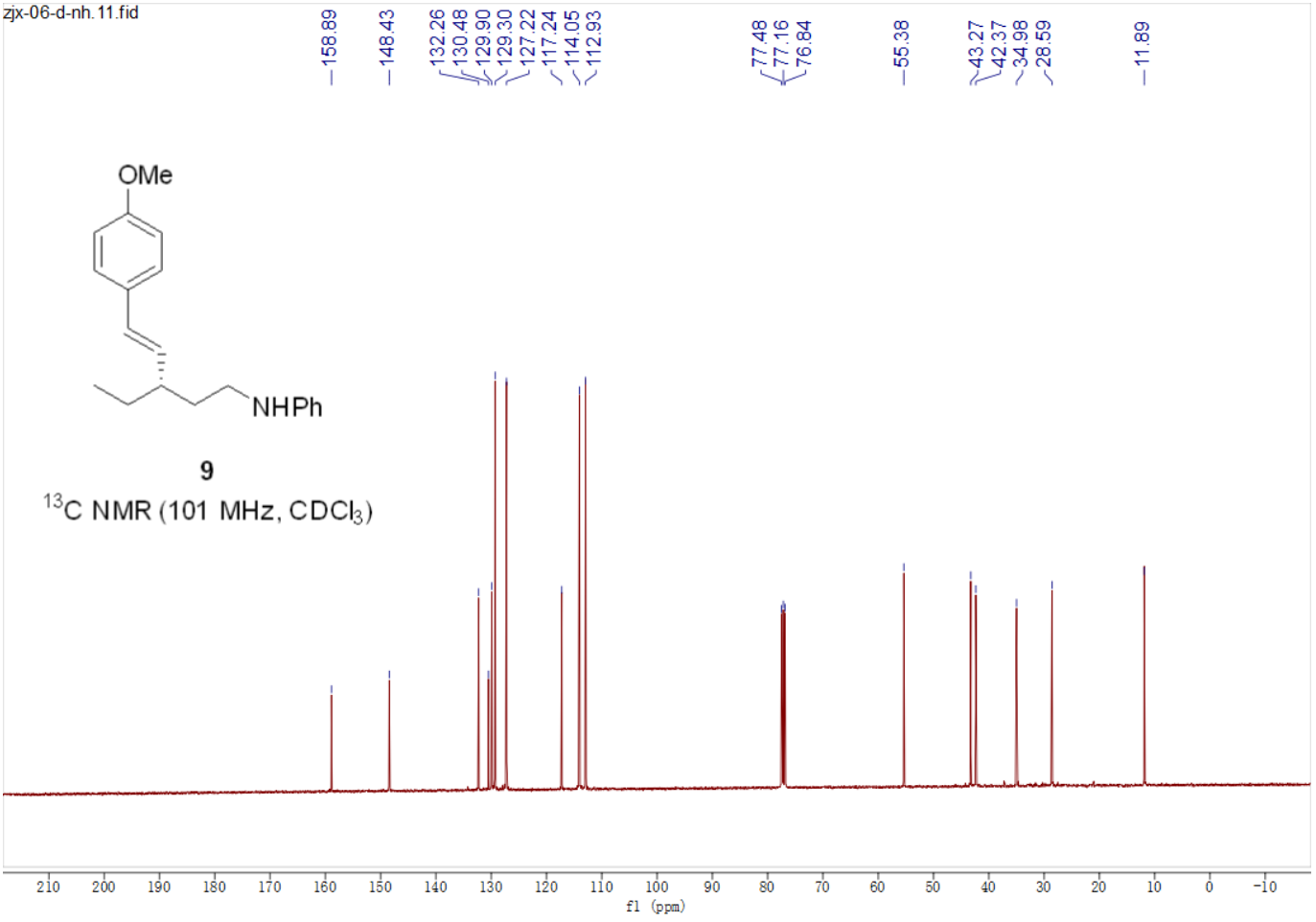

zjx-06-179-2-1.10.fid
7.29
7.27
6.84
6.83
6.38
6.36
5.89
5.88
5.86
5.85
3.80
2.60
2.59
2.57
2.56
2.50
2.49
2.47
2.46
2.42
2.41
2.40
2.39
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.52
1.44
1.43
1.43
1.42
1.42
1.41
0.93
0.92
OMe
O
OH
7
1H NMR (600 MHz, CDCl3)
1.93 1.92 0.97 0.98
2.90
1.00 0.96 0.96
1.04 1.03 2.92
f1 (ppm)

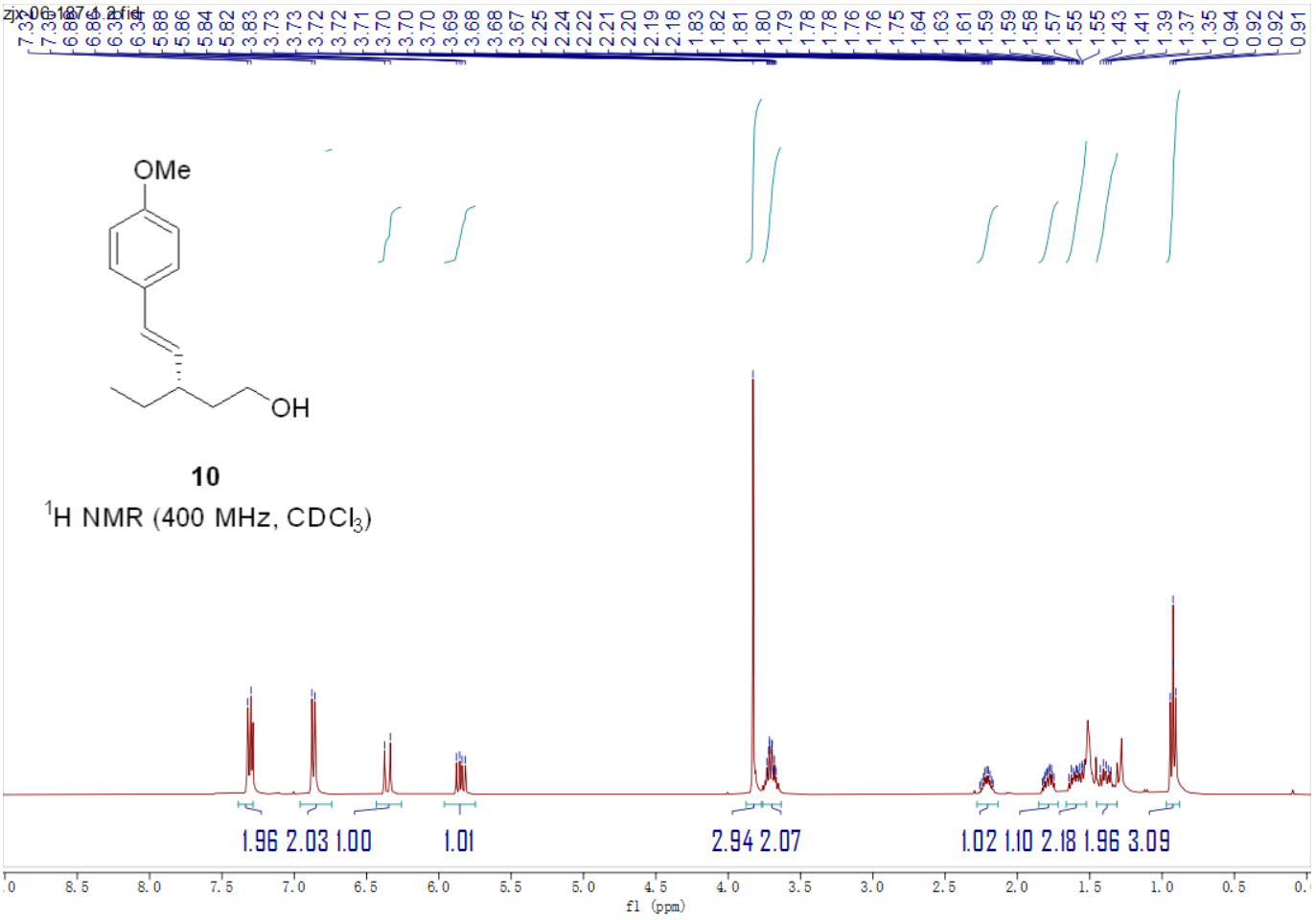

zjx-06-179-2-1.11.fid
178.
159.05
130.33
130.27
130.25
127.42
114.06
77.37
77.16
76.95
55.45
41.27
39.98
27.94
11.74
OMe
O
OH
7
13C NMR (151 MHz, CDCl3)
f1 (ppm)

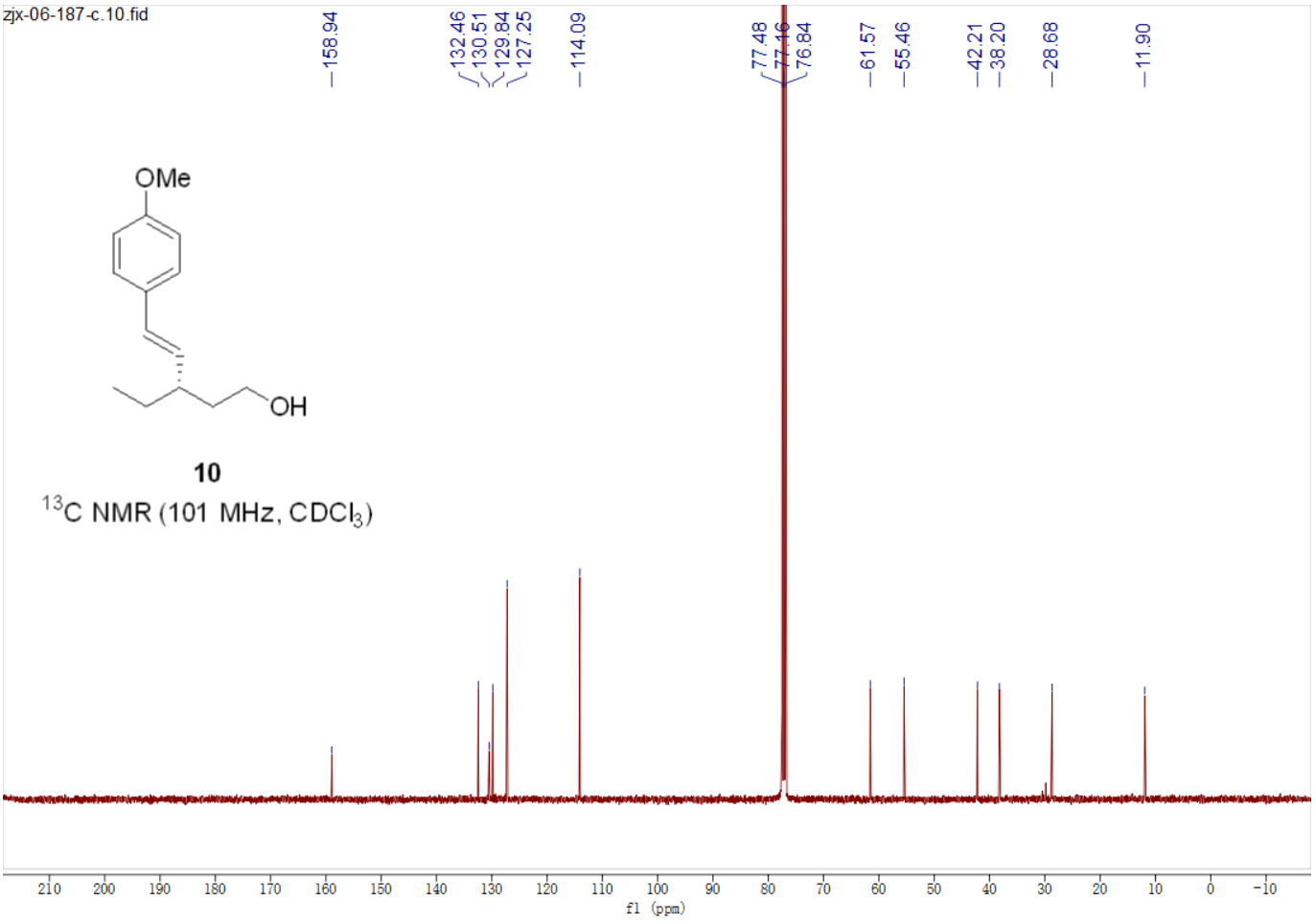

zjx-06-ketone.7.fid
OMe
O
8
1H NMR (600 MHz, CDCl3)
1.97 1.95 0.93 0.96
3.03
1.00 1.78 1.92 1.08 1.08 2.94 3.00
f1 (ppm)

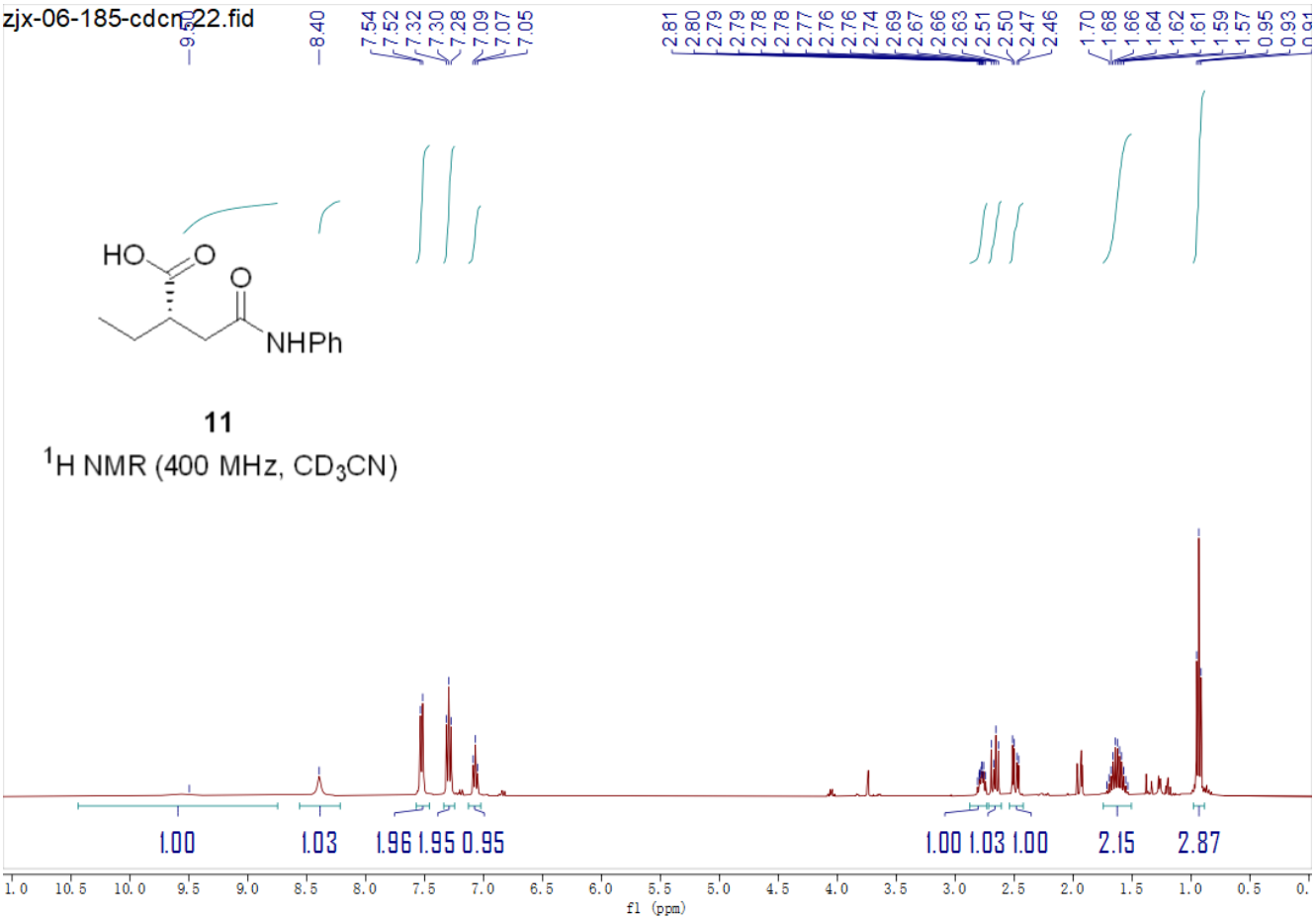

zjx-06-ketone-c.10.fid
OMe
O
8
13C NMR (151 MHz, CDCl3)
f1 (ppm)

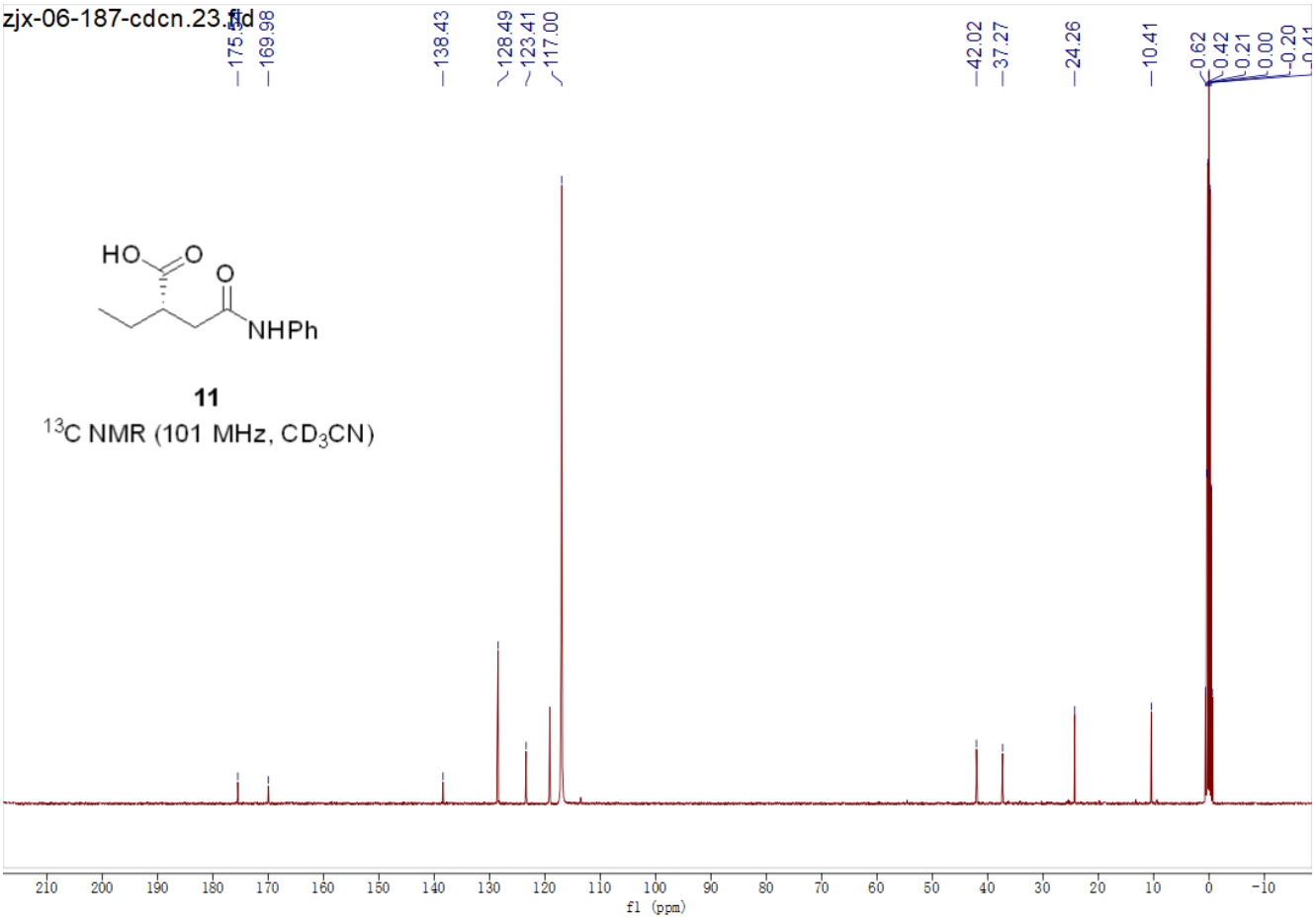

zjx-06-dnh.10.fid
OMe
NHPh
9
1H NMR (400 MHz, CDCl3)
2.10 2.01 2.02 1.08 1.97 0.93 0.92
3.05
2.02
1.00 1.02 1.11 1.04 1.05 2.92
f1 (ppm)


zjx-06-d-nh.11.fid
158.89
148.43
132.26
130.48
129.90
129.30
127.22
117.24
114.05
112.93
77.48
77.16
76.84
55.38
43.27
42.37
34.98
28.59
11.89
OMe
NHPh
9
13C NMR (101 MHz, CDCl3)
f1 (ppm)

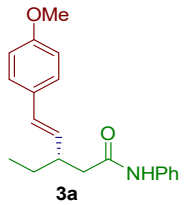

zjx-06-187-c.2.fid
OMe
OH
10
1H NMR (400 MHz, CDCl3)
1.96 2.03 1.00
1.01
2.94 2.07
1.02 1.10 2.18 1.96 3.09
f1 (ppm)


zjx-06-187-c.10.fid
158.94
132.46
130.51
129.84
127.25
114.09
77.48
77.16
76.84
61.57
55.46
42.21
38.20
28.68
11.90
OMe
OH
10
13C NMR (101 MHz, CDCl3)
f1 (ppm)


zjx-06-185-cdcn-22.fid
HO
O
O
NHPh
11
1H NMR (400 MHz, CD3CN)
1.00
1.03
1.96
1.95
0.95
1.00
1.03
1.00
2.15
2.87
f1 (ppm)

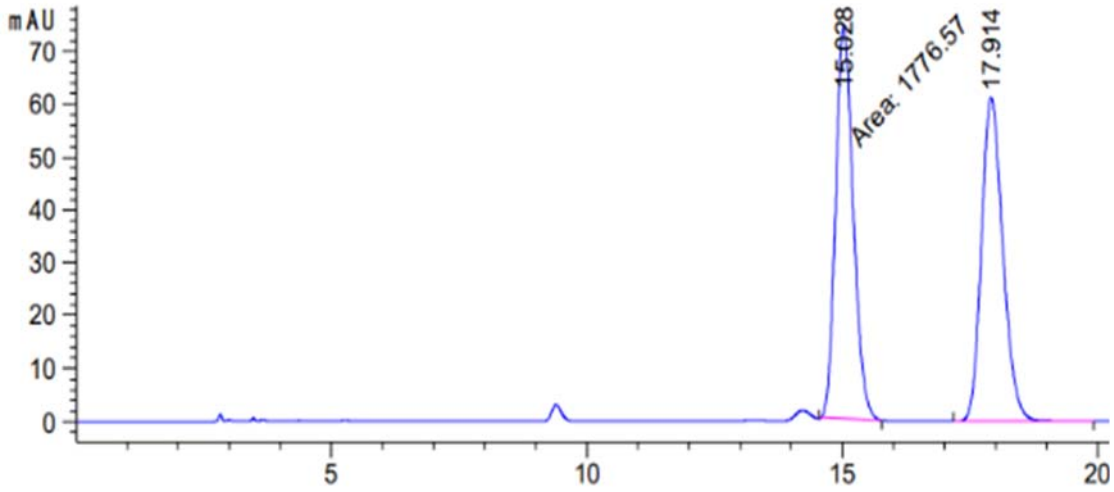

zjx-06-187-cdcn.23.fid
175.49
169.98
138.43
128.49
123.41
117.00
42.02
37.27
24.26
10.41
0.62
0.42
0.21
0.00
-0.20
HO
O
O
NHPh
11
13C NMR (101 MHz, CD3CN)
f1 (ppm)

XII.HPLC traces



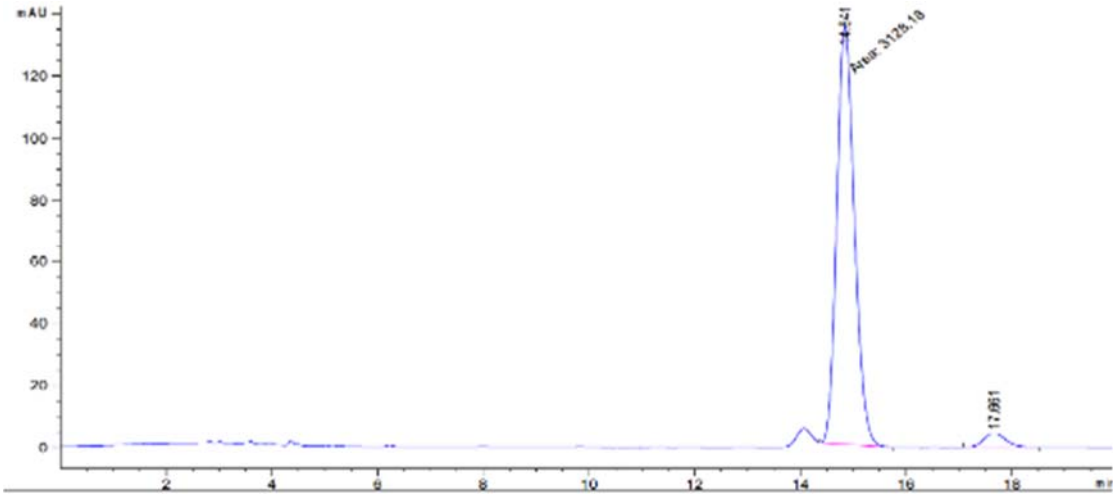
3a

HPLC data using rac-**L1**

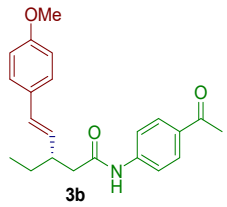


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.028	MM	0.3985	1776.57129	74.30415	49.8469
2	17.914	BB	0.4489	1787.48767	61.16855	50.1531

HPLC data using **L1**

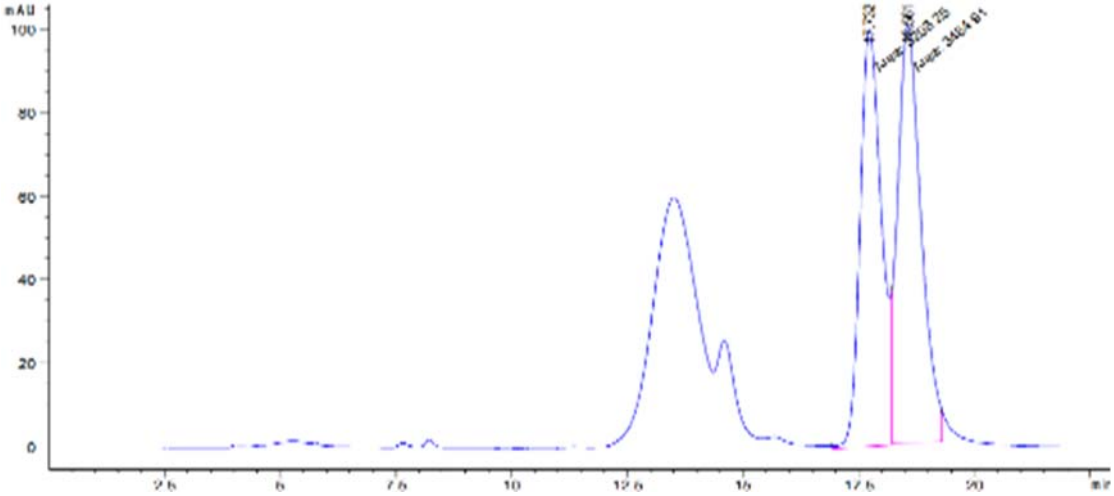


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.841	MM	0.3862	3128.18408	135.00490	95.9728
2	17.661	BB	0.4186	131.26450	4.71746	4.0272



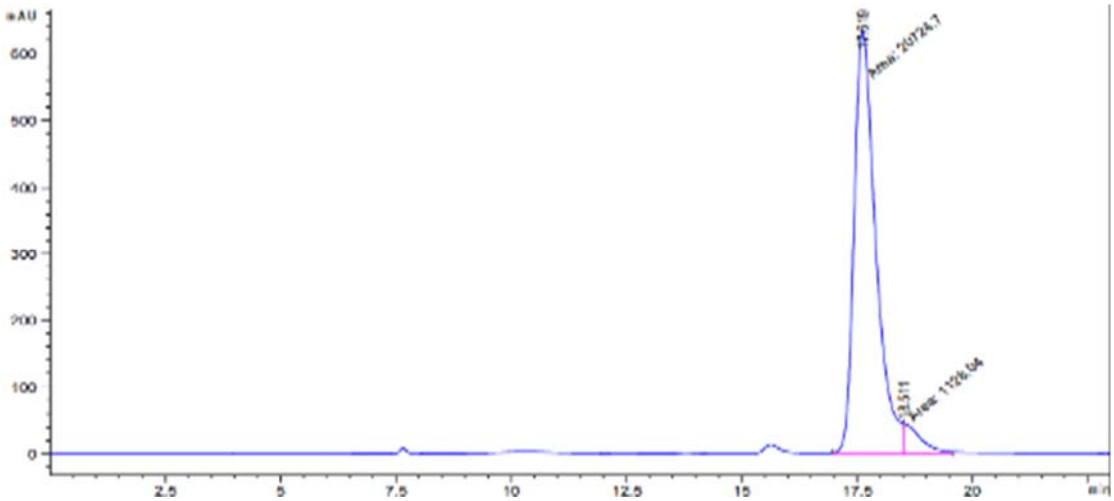
3b

HPLC data using rac-**L1**

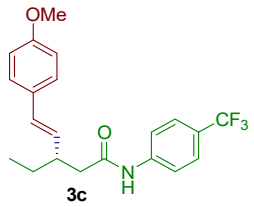


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.732	MM	0.5357	3208.25342	99.82164	47.9333
2	18.561	MM	0.5801	3484.91431	100.12344	52.0667

HPLC data using **L1**

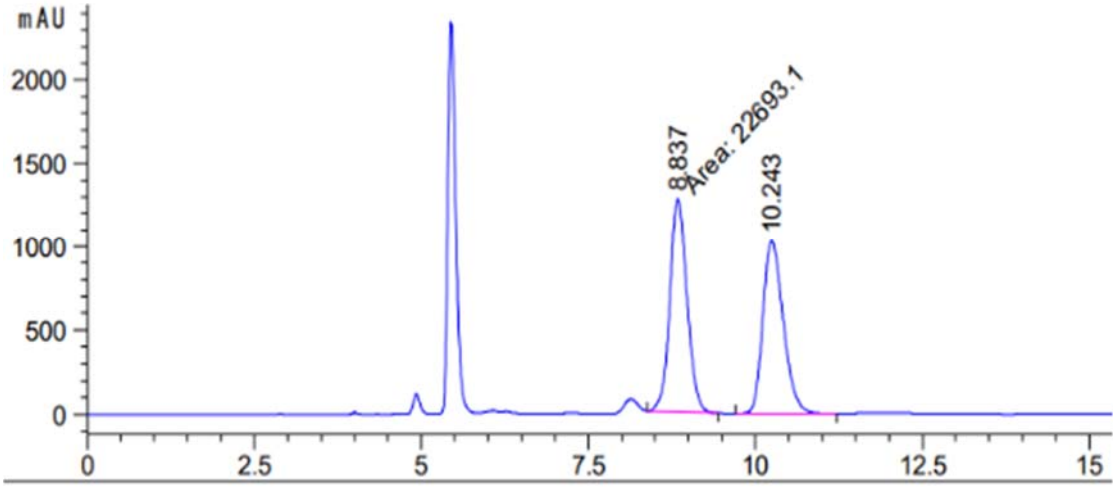


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.619	MM	0.5449	2.07247e4	633.87415	94.8380
2	18.511	MM	0.4184	1128.03503	44.93483	5.1620



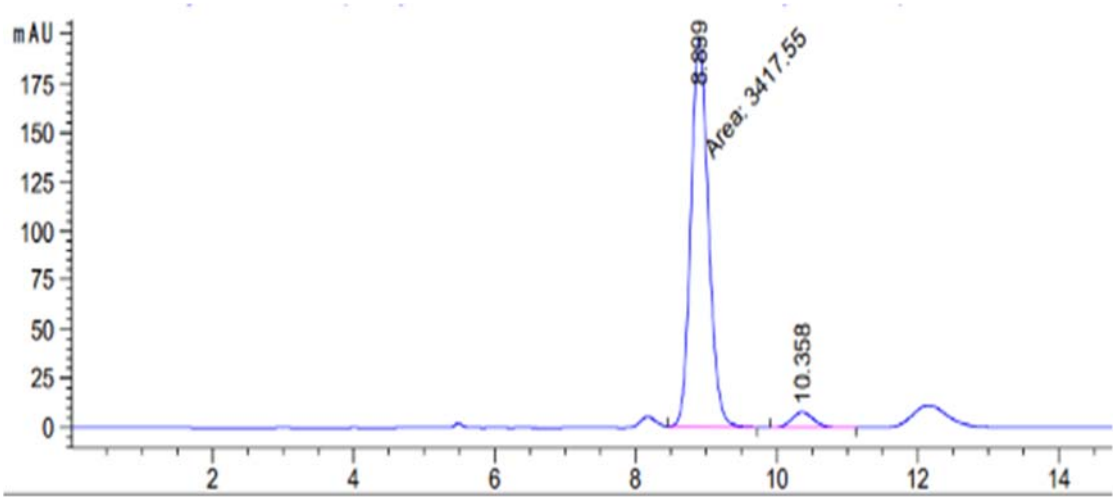
3c

HPLC data using rac-**L1**

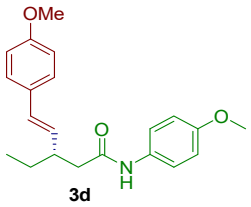


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.837	MM	0.2967	2.26931e4	1274.68542	50.9733
2	10.243	BB	0.3274	2.18265e4	1029.26038	49.0267

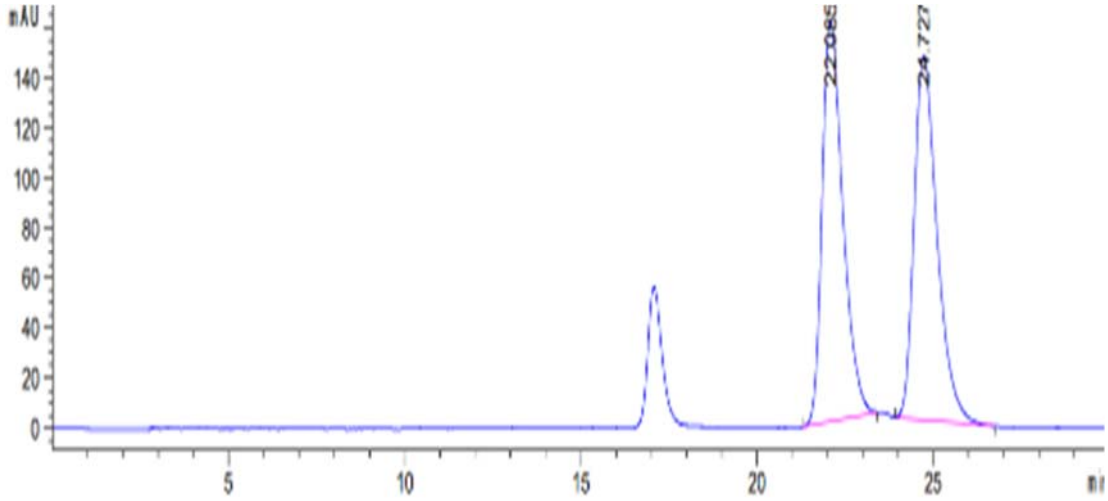
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.899	MM	0.2887	3417.55225	197.26672	95.3075
2	10.358	BB	0.3305	168.26343	7.83668	4.6925

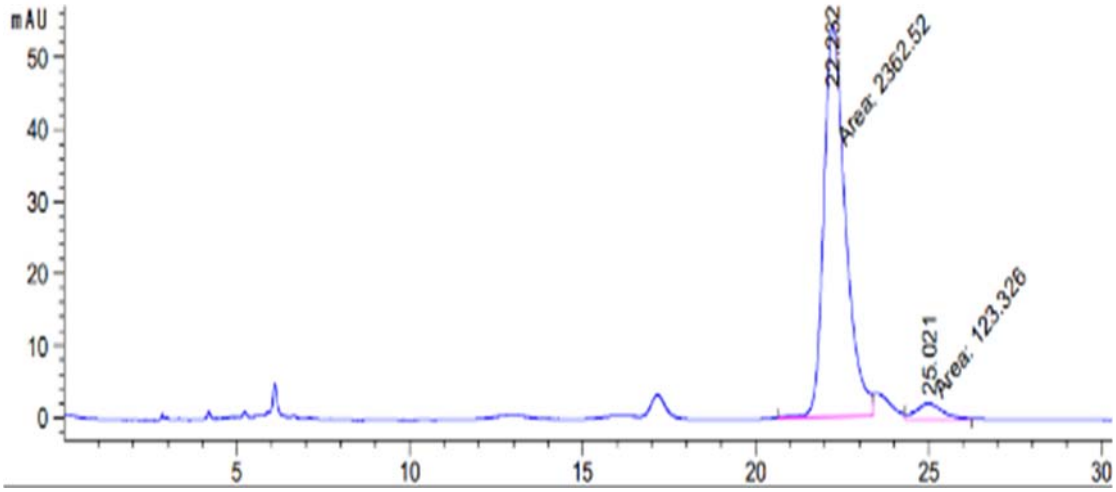


HPLC data using rac-**L1**

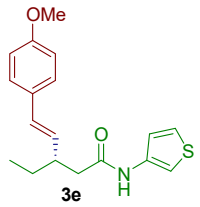


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.085	BB	0.6218	6523.32715	159.96231	49.7113
2	24.727	BB	0.6920	6599.08594	145.25883	50.2887

HPLC data using **L1**

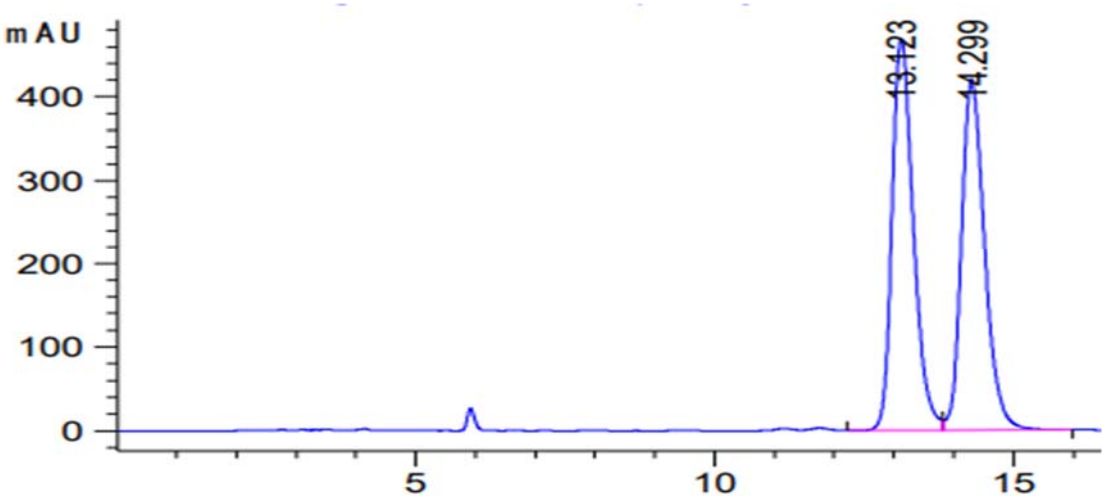


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.232	MM	0.7248	2362.52051	54.32397	95.0389
2	25.021	MM	0.9242	123.32573	2.22413	4.9611



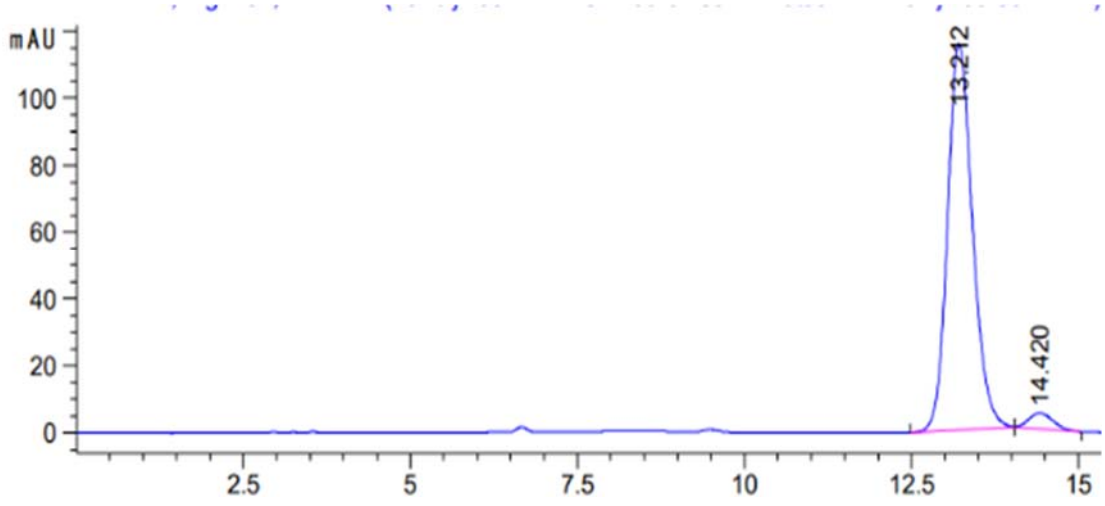
3e

HPLC data using rac-**L1**

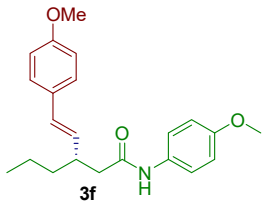


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.123	BV	0.3836	1.16361e4	468.71271	50.7074
2	14.299	VB	0.4140	1.13114e4	420.29257	49.2926

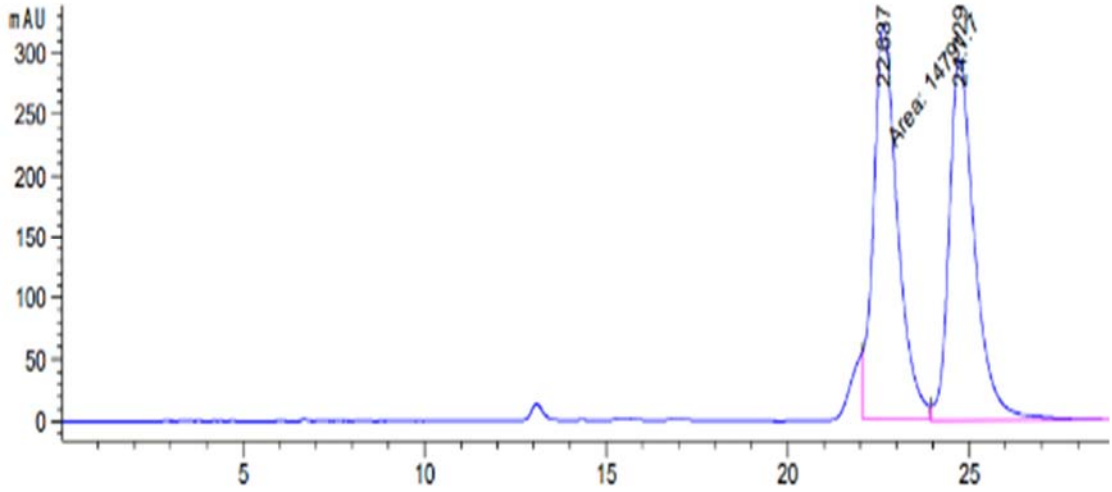
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.212	BB	0.4006	2988.12817	115.20288	96.3331
2	14.420	BB	0.3878	113.74168	4.57962	3.6669

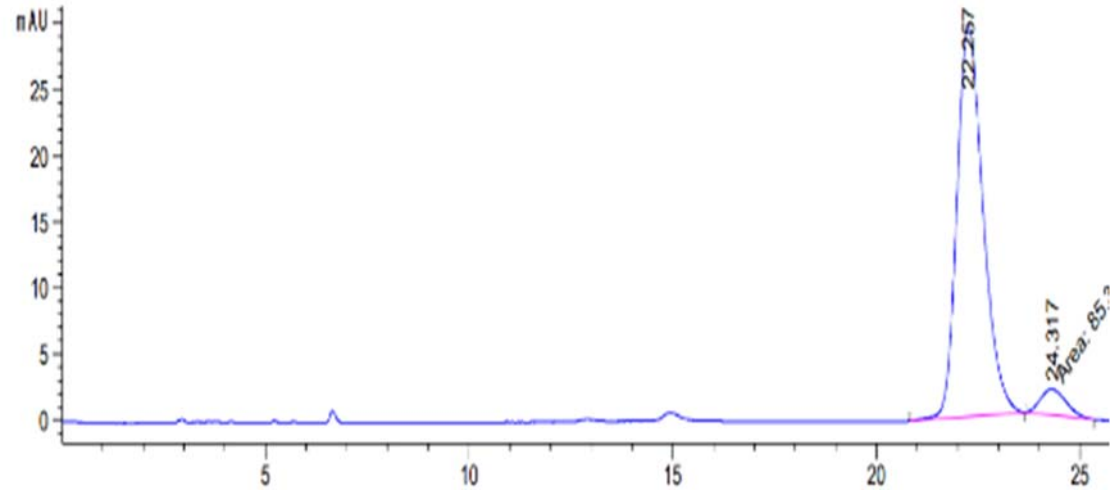


HPLC data using rac-**L1**

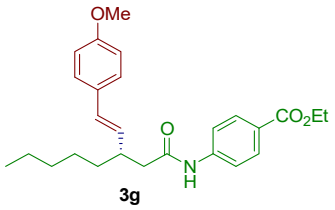


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.637	MM	0.7676	1.47917e4	321.15363	50.4893
2	24.729	VB	0.7368	1.45050e4	294.40417	49.5107

HPLC data using **L1**

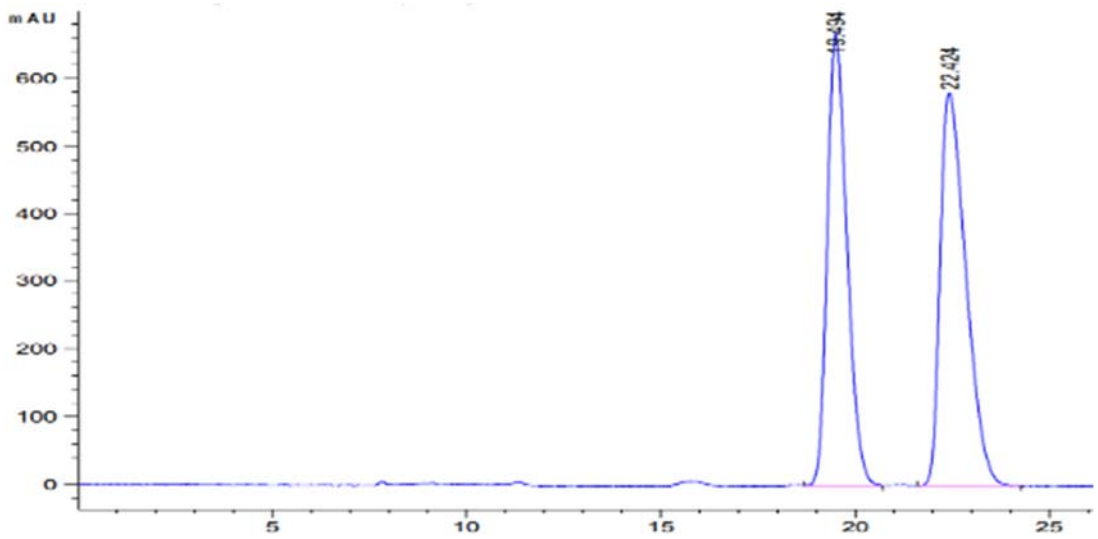


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.257	BB	0.6889	1318.62415	29.53568	93.9210
2	24.317	MM	0.7313	85.34719	1.94502	6.0790



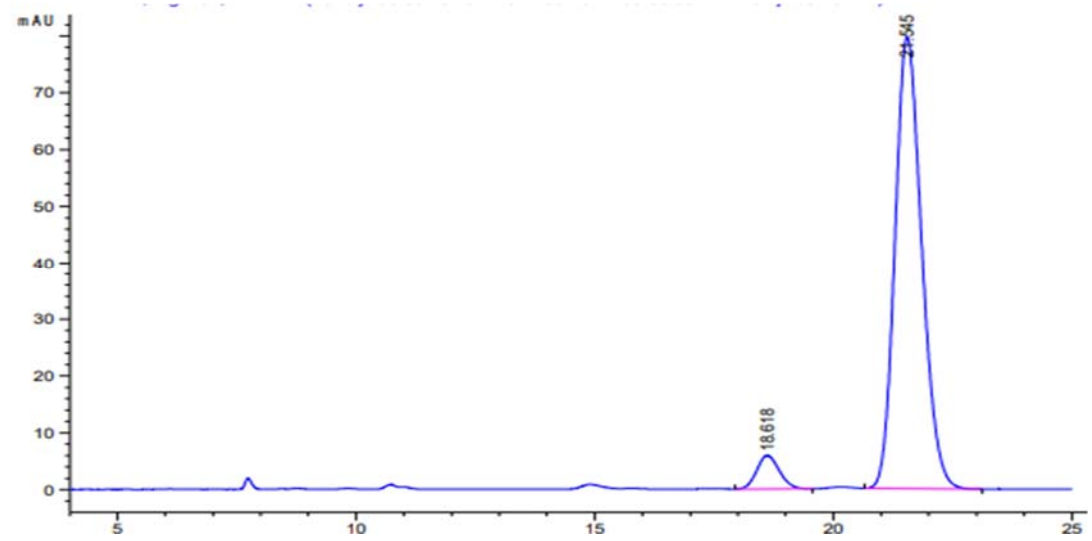
3g

HPLC data using rac-**L1**

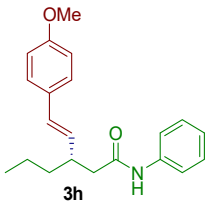


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.494	VB R	0.5024	2.34901e4	667.73126	46.8739
2	22.424	VV R	0.6171	2.66232e4	580.44238	53.1261

HPLC data using **L1**

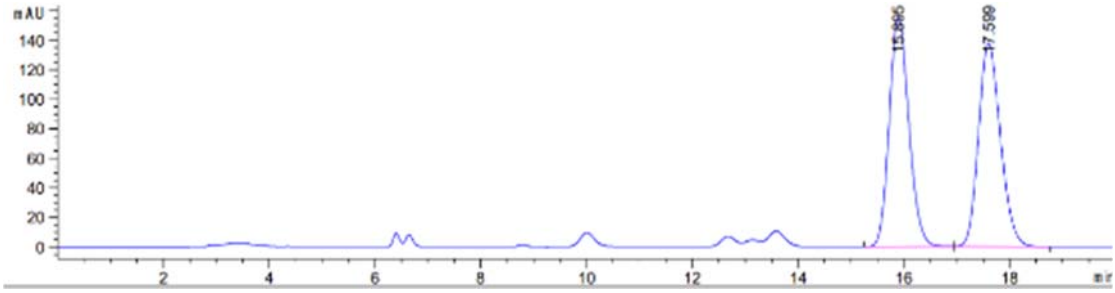


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.618	BB	0.4841	194.31361	5.90164	5.9023
2	21.545	BB	0.5957	3097.84985	79.66009	94.0977



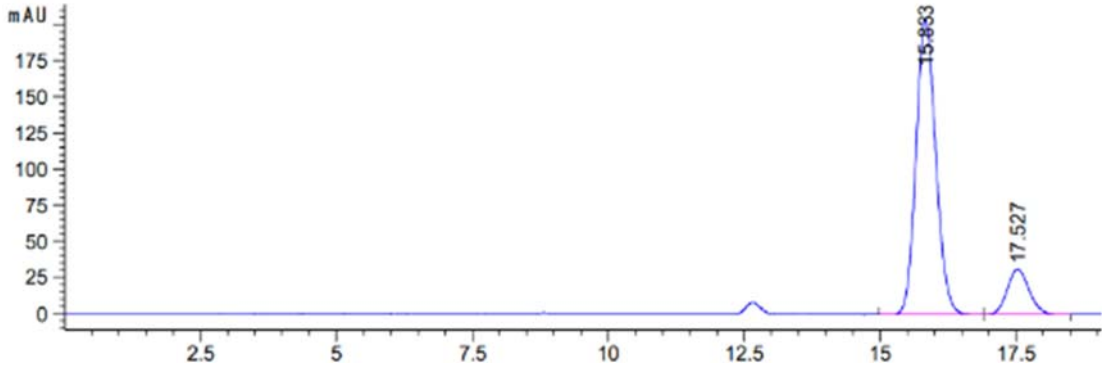
3h

HPLC data using rac-**L1**



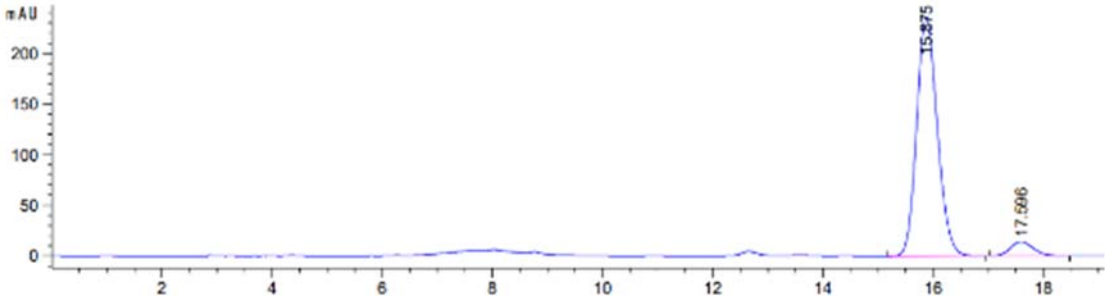
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.895	BB	0.3980	4002.25757	155.62849	50.2386
2	17.599	BB	0.4461	3964.24829	137.58749	49.7614

HPLC data using **L1**(**Method A**)

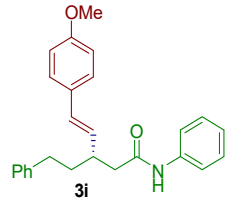


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.833	BB	0.3923	5158.70703	204.48750	85.5132
2	17.527	BB	0.4276	873.93866	31.31697	14.4868

HPLC data using **L1**(**Method B**)

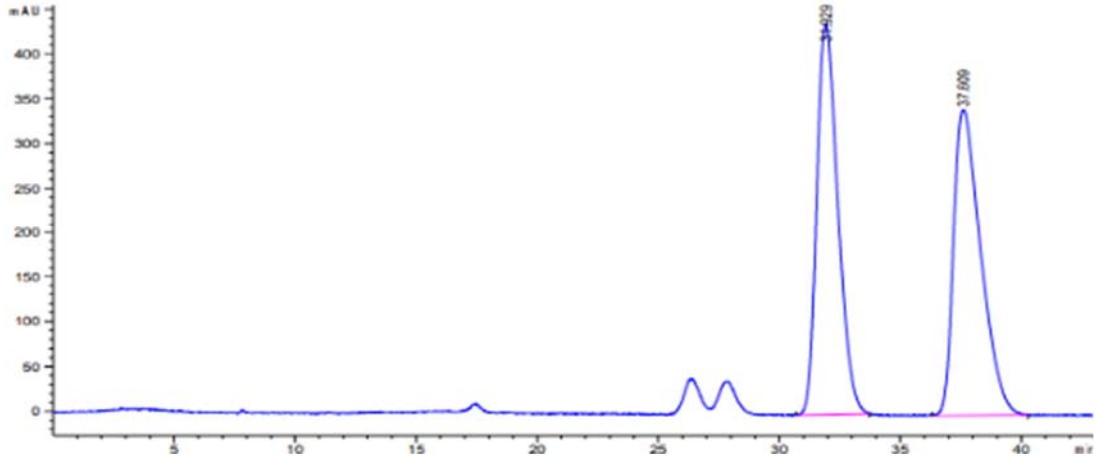


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.875	BB	0.4026	6118.38965	235.91379	93.9067
2	17.596	BB	0.4431	396.99948	13.99044	6.0933



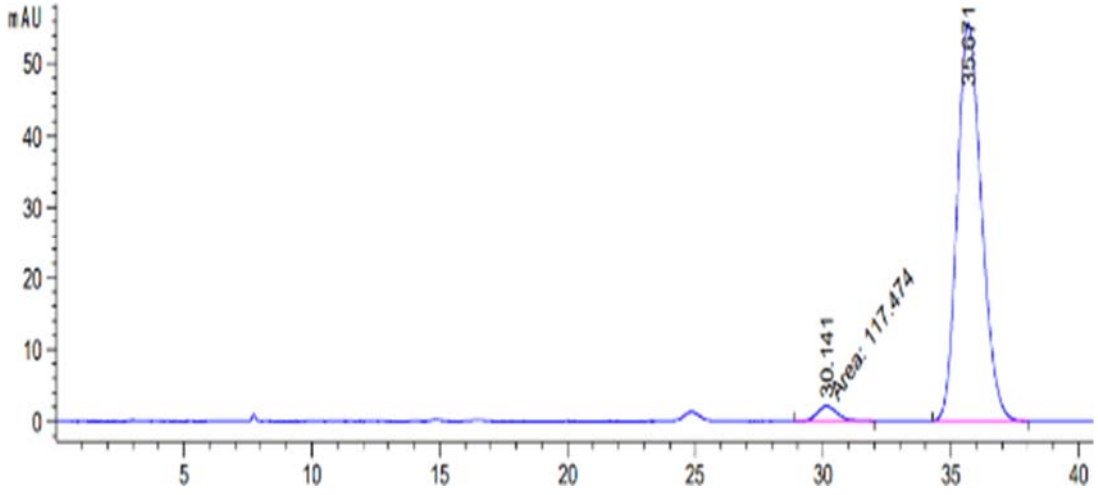
3i

HPLC data using rac-**L1**

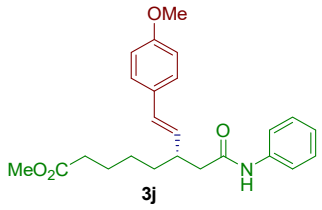


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.929	VV R	0.7313	2.64739e4	436.67569	49.8419
2	37.609	VV R	0.9140	2.66419e4	342.30954	50.1581

HPLC data using **L1**

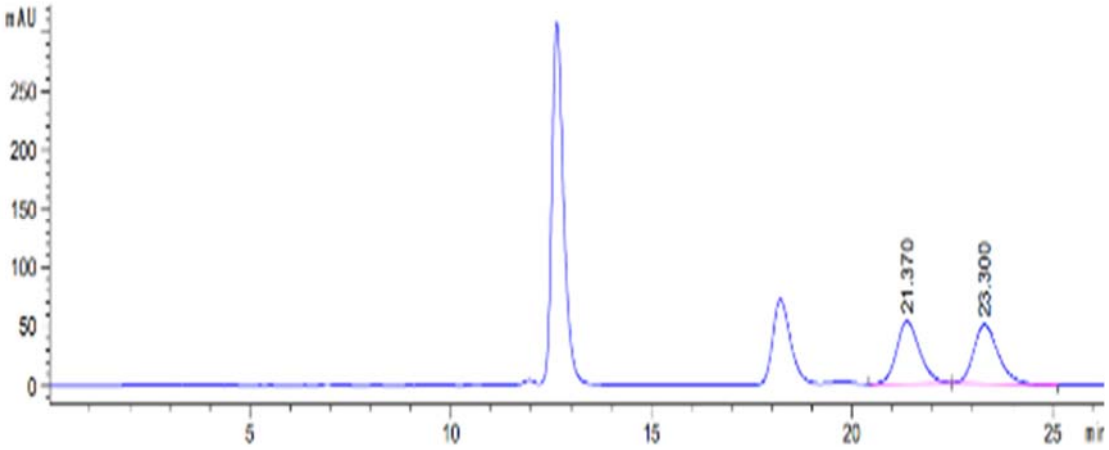


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.141	MM	0.9365	117.47357	2.09075	3.1062
2	35.671	BB	1.0098	3664.40503	55.53914	96.8938



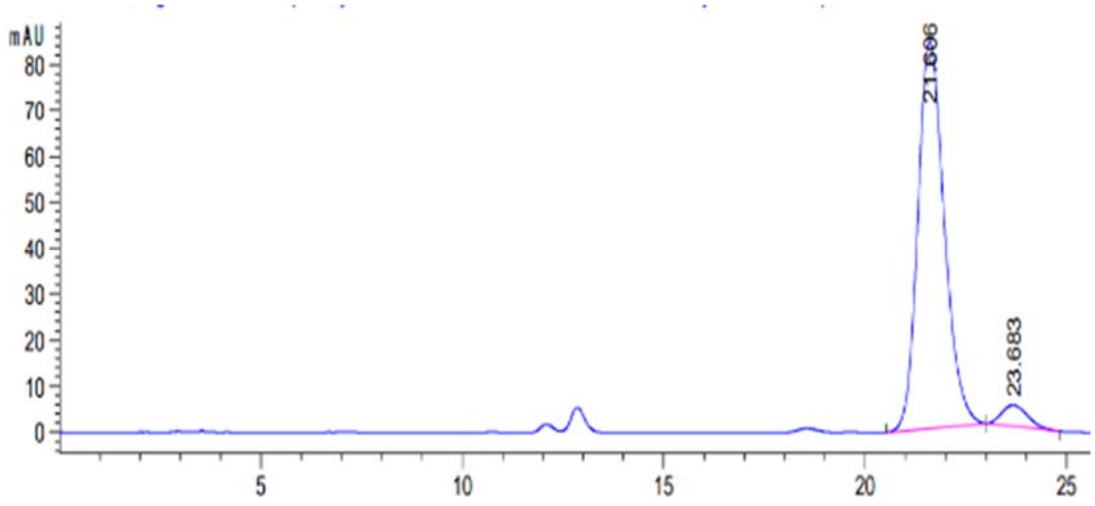
3j

HPLC data using rac-**L1**

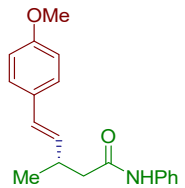


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.370	BB	0.6081	2106.78540	52.50605	49.8947
2	23.300	BB	0.6548	2115.68042	49.68749	50.1053

HPLC data using **L1**

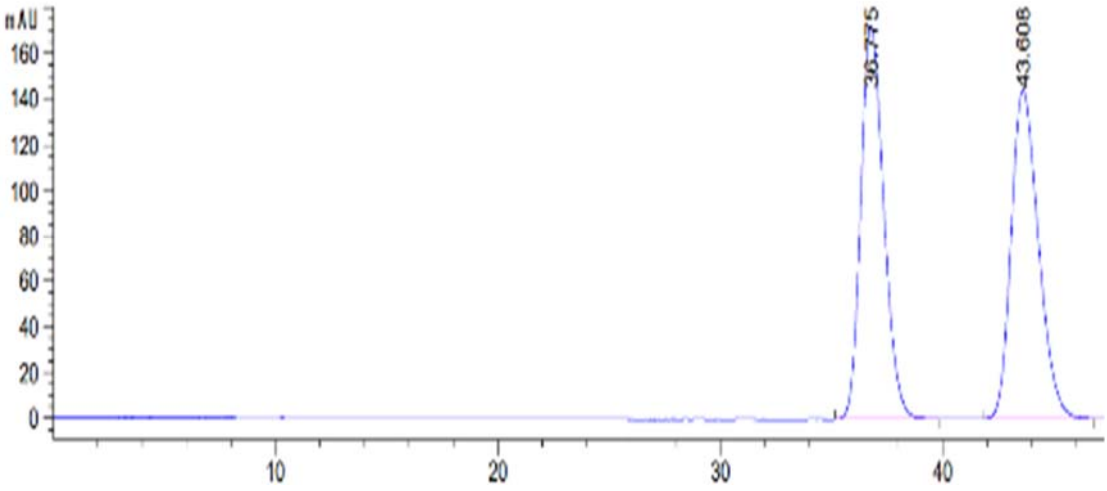


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.606	BB	0.7045	3847.72168	84.29404	94.9649
2	23.683	BB	0.5597	204.00734	4.59734	5.0351



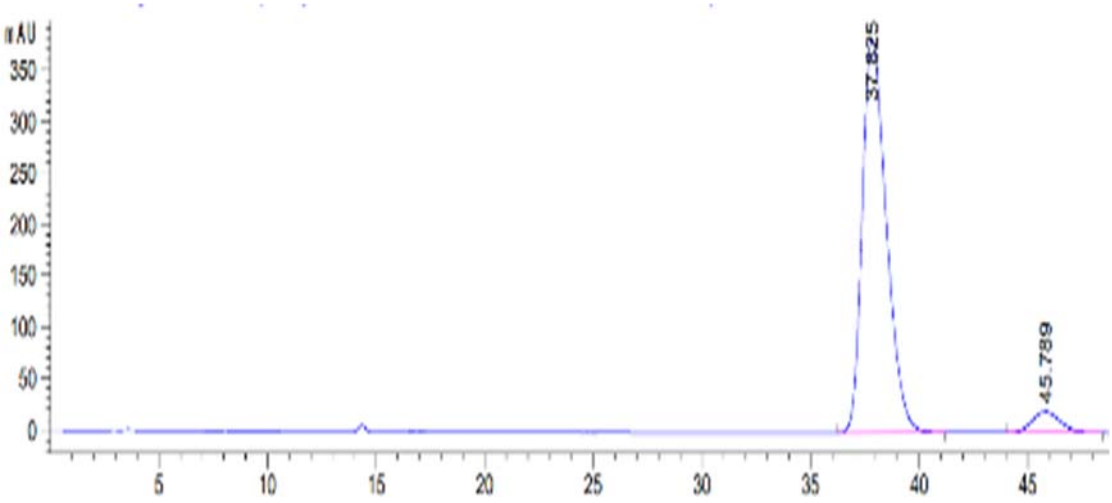
3k

HPLC data using rac-**L1**

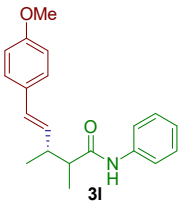


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.775	BB	1.0691	1.23655e4	172.32986	50.1251
2	43.608	BB	1.2509	1.23038e4	143.99590	49.8749

HPLC data using **L1**

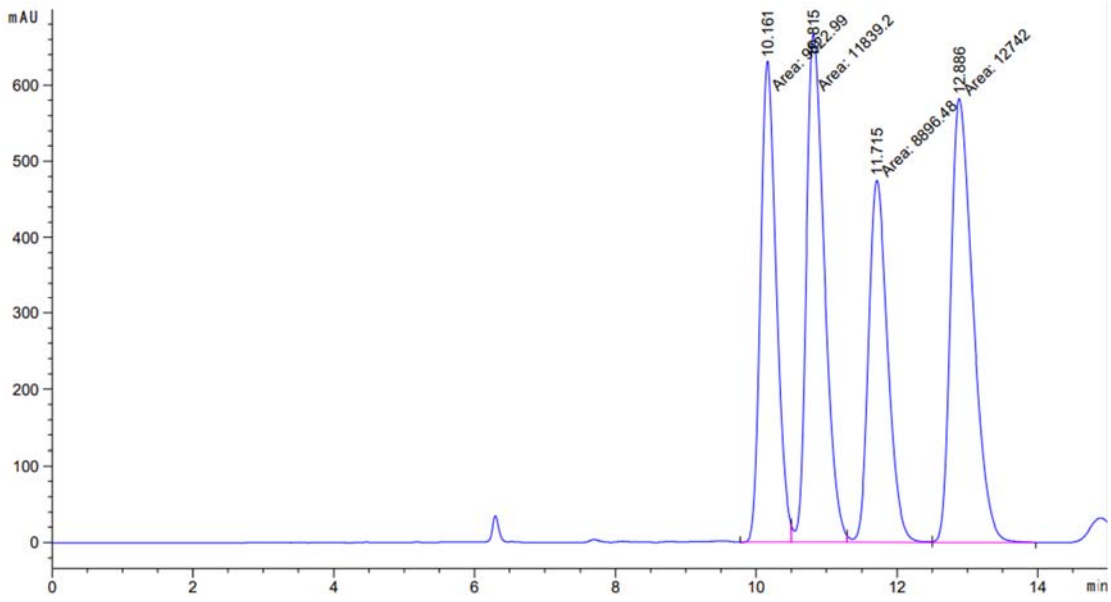


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.825	BB	1.1701	2.94184e4	382.13712	94.1948
2	45.789	BB	1.0761	1813.06152	20.18155	5.8052



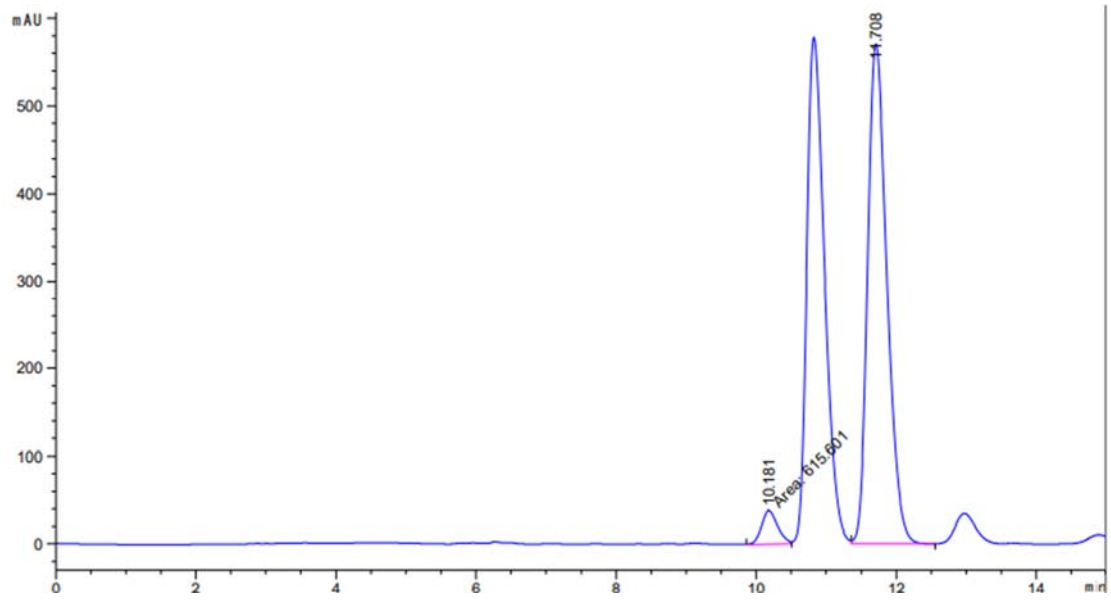
3l

HPLC data using rac-**L1**

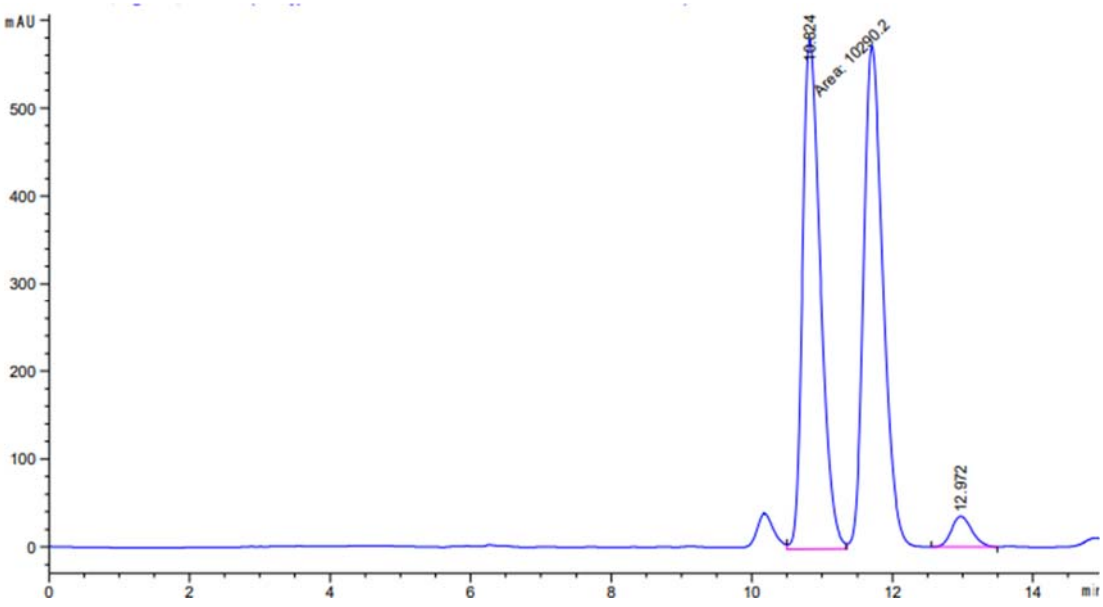


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.161	MF	0.2594	9822.99219	631.17651	22.6855
2	10.815	FM	0.2963	1.18392e4	665.86530	27.3418
3	11.715	MM	0.3125	8896.47949	474.49716	20.5458
4	12.886	MM	0.3649	1.27420e4	582.00397	29.4268

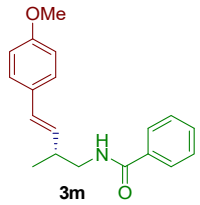
HPLC data using **L1**



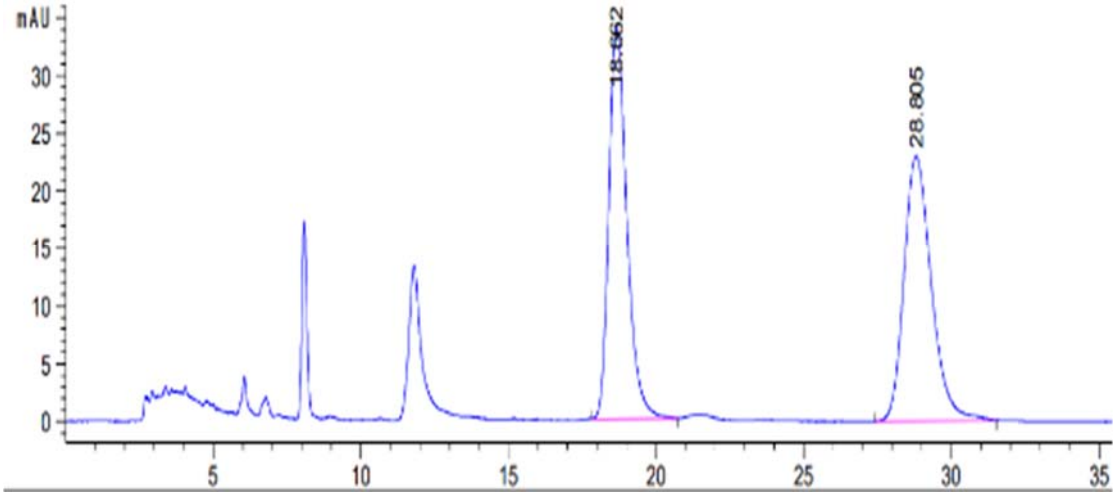
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.181	MM	0.2654	615.60052	38.66043	5.3615
2	11.708	VB	0.2921	1.08662e4	570.85498	94.6385



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.824	MM	0.2953	1.02902e4	580.76996	93.6606
2	12.972	BB	0.3127	696.49036	34.61568	6.3394

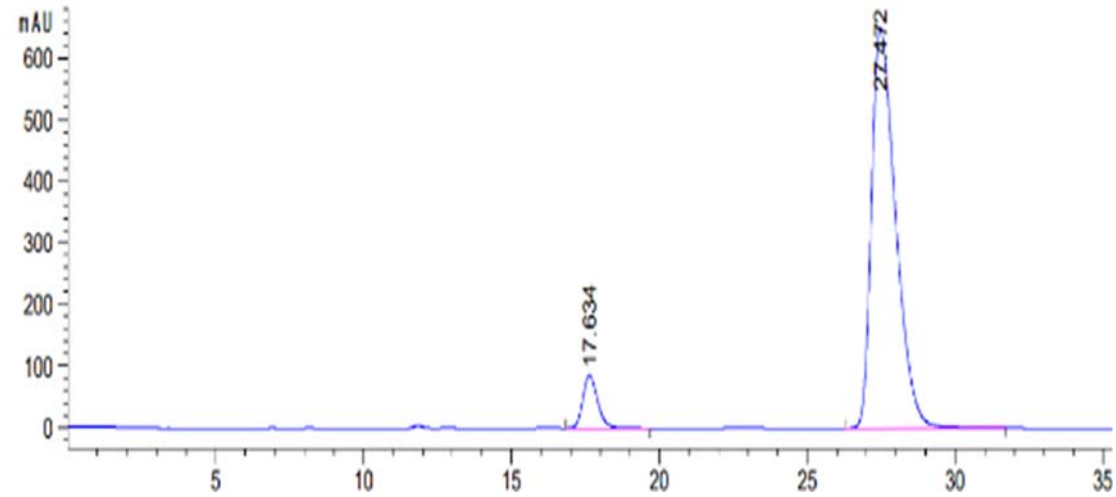


HPLC data using rac-**L1**

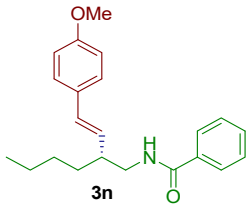


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.662	BB	0.6380	1440.01636	34.14860	49.3292
2	28.805	BB	0.8858	1479.18225	23.01514	50.6708

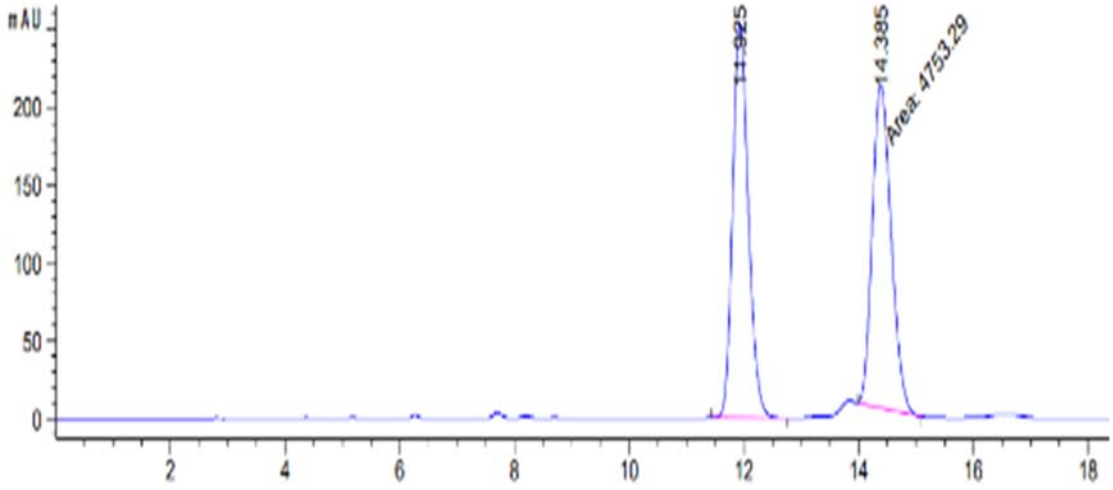
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.634	BB	0.5224	2924.10132	85.62224	7.3891
2	27.472	BB	0.8680	3.66491e4	649.82788	92.6109

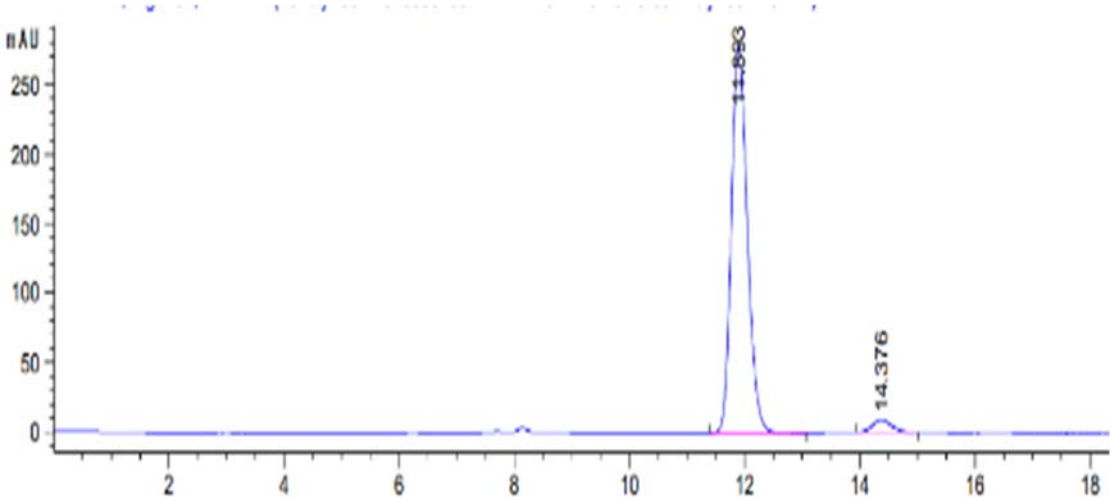


HPLC data using rac-**L1**

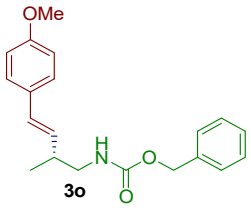


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.925	BB	0.2936	4805.69580	253.04465	50.2741
2	14.385	MM	0.3808	4753.29053	208.02565	49.7259

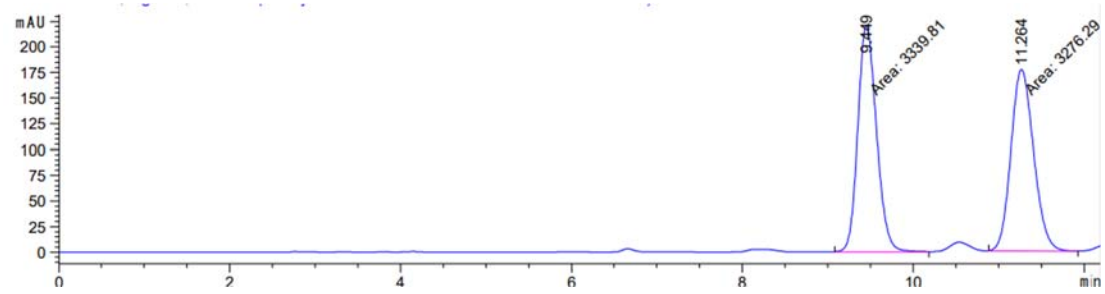
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.893	BB	0.2954	5338.65527	278.82727	96.2485
2	14.376	BB	0.3517	208.08792	9.06777	3.7515

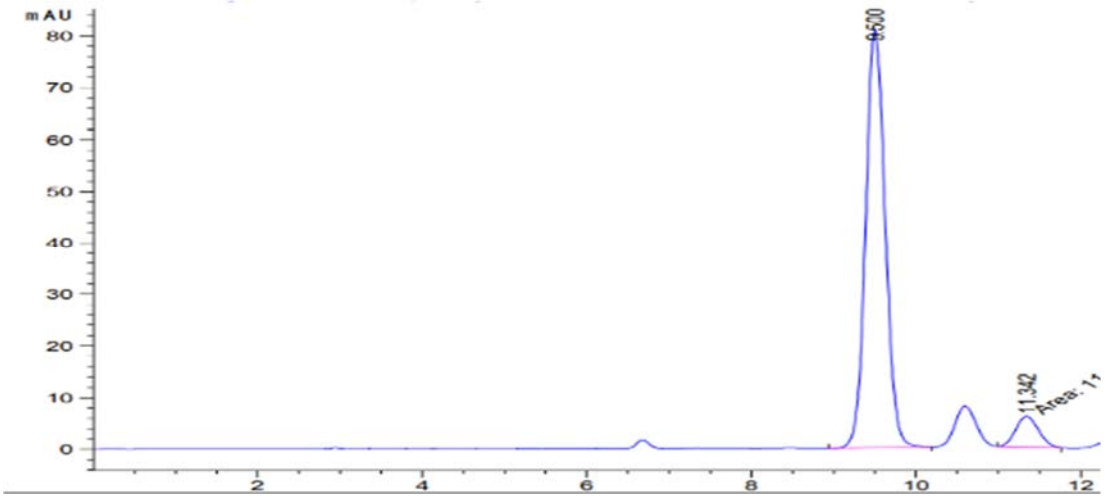


HPLC data using rac-**L1**

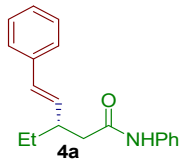


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.449	MM	0.2522	3339.81006	220.67616	50.4800
2	11.264	MM	0.3087	3276.29272	176.90694	49.5200

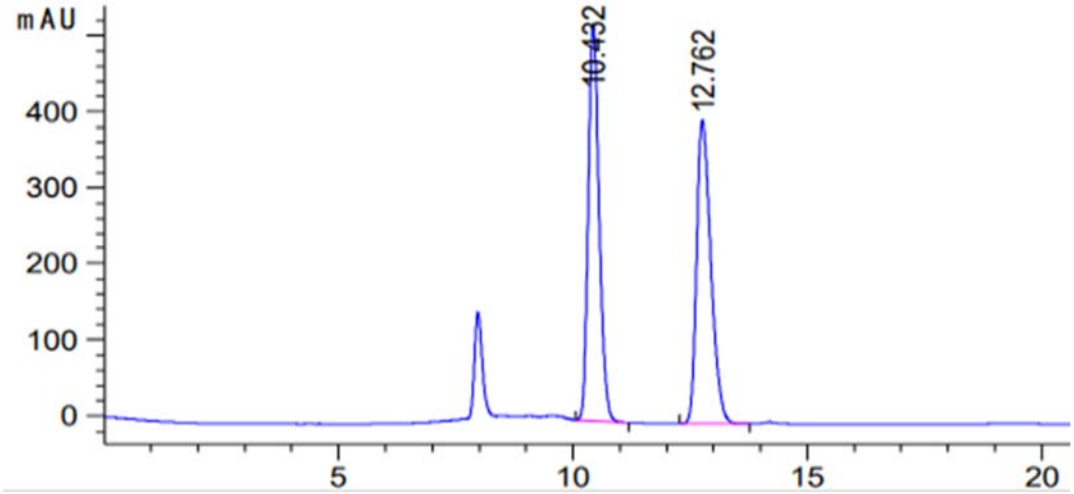
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.500	BB	0.2580	1331.25269	80.89272	92.0573
2	11.342	MM	0.3235	114.86008	5.91831	7.9427

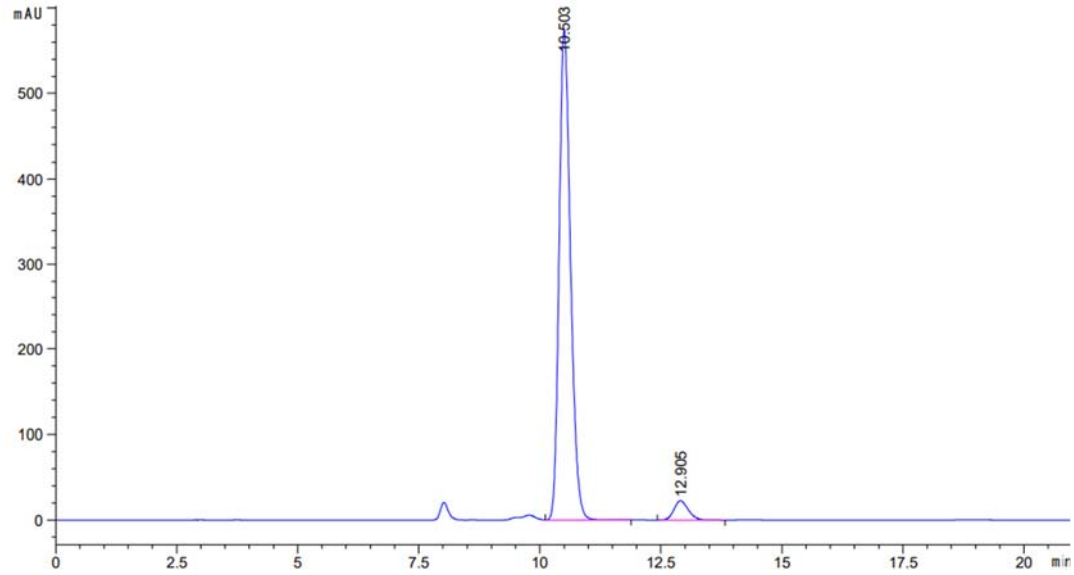


HPLC data using rac-**L1**

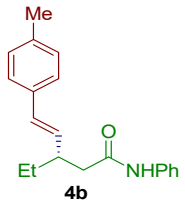


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.432	BB	0.2476	8351.00293	519.43225	49.8438
2	12.762	BB	0.3245	8403.34375	397.64615	50.1562

HPLC data using **L1**

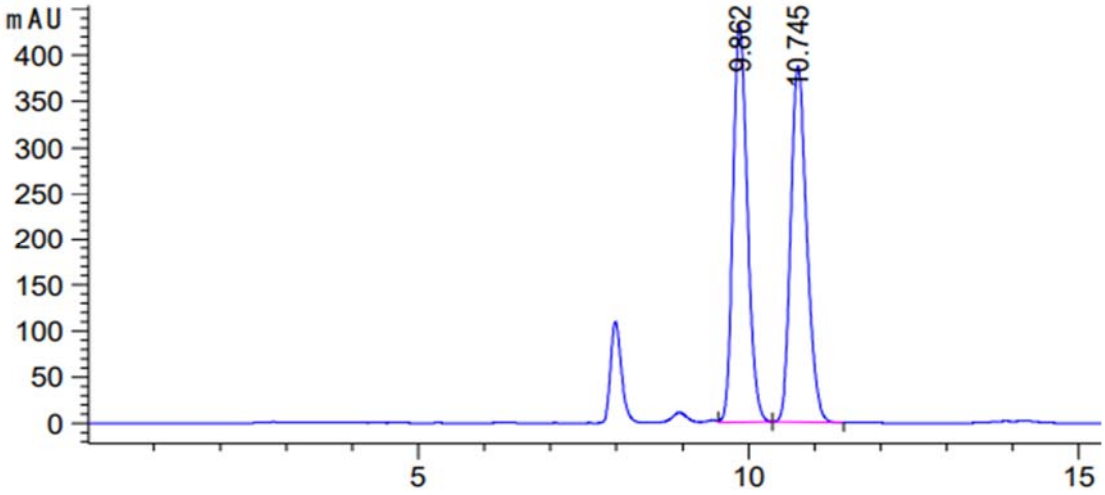


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.503	VB	0.2513	9414.79199	574.18719	95.2982
2	12.905	BB	0.3162	464.50330	22.55820	4.7018



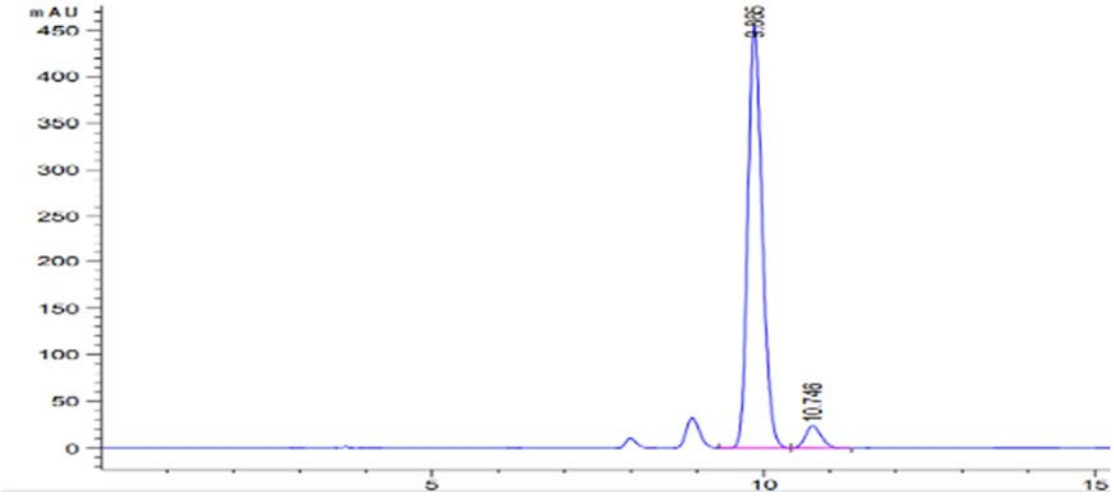
4b

HPLC data using rac-**L1**

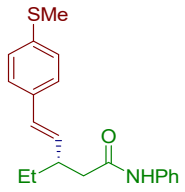


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.862	VB	0.2339	6517.29736	432.35846	49.8786
2	10.745	BB	0.2613	6549.02148	387.20273	50.1214

HPLC data using **L1**

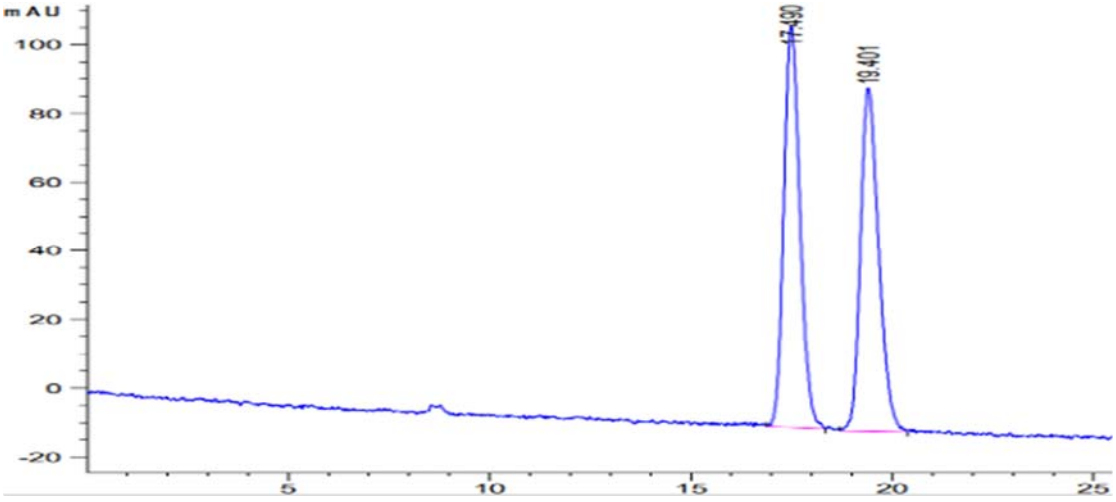


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.865	BV	0.2321	6853.49268	453.97610	94.4885
2	10.746	VB	0.2575	399.76559	23.85170	5.5115



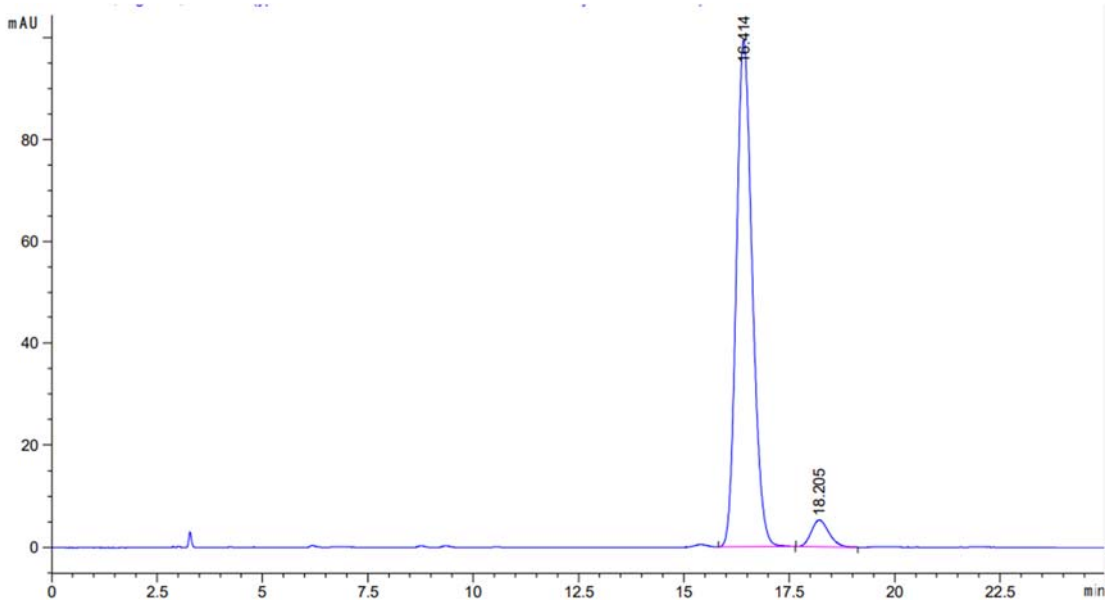
4c

HPLC data using rac-**L1**

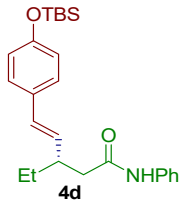


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.490	VV R	0.3893	3239.34619	116.90580	50.6718
2	19.401	VV R	0.4224	3153.45752	99.85294	49.3282

HPLC data using **L1**

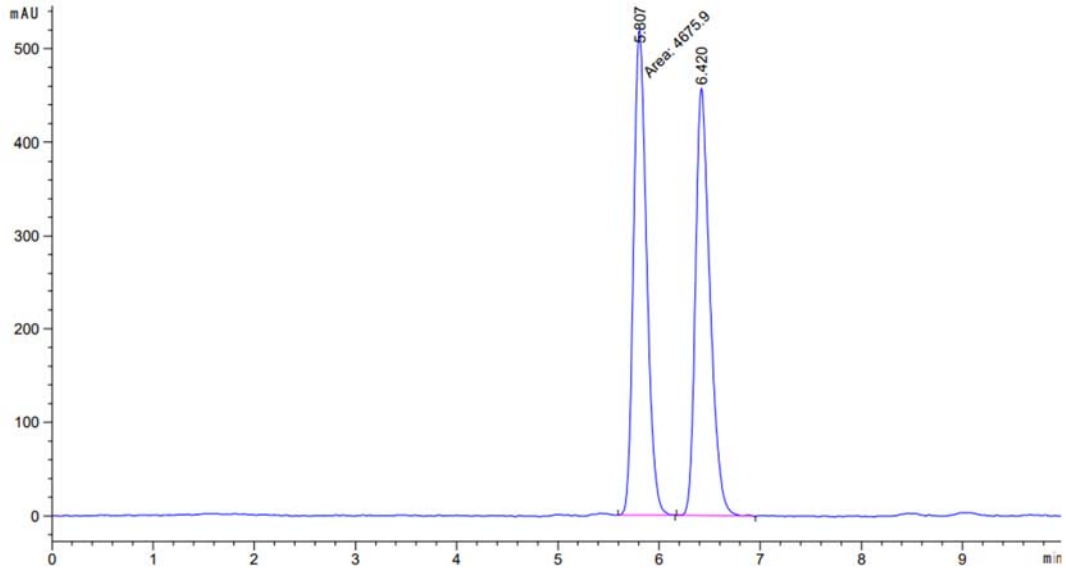


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.414	BB	0.4046	2610.75586	99.34956	94.4788
2	18.205	BB	0.4329	152.56882	5.25273	5.5212



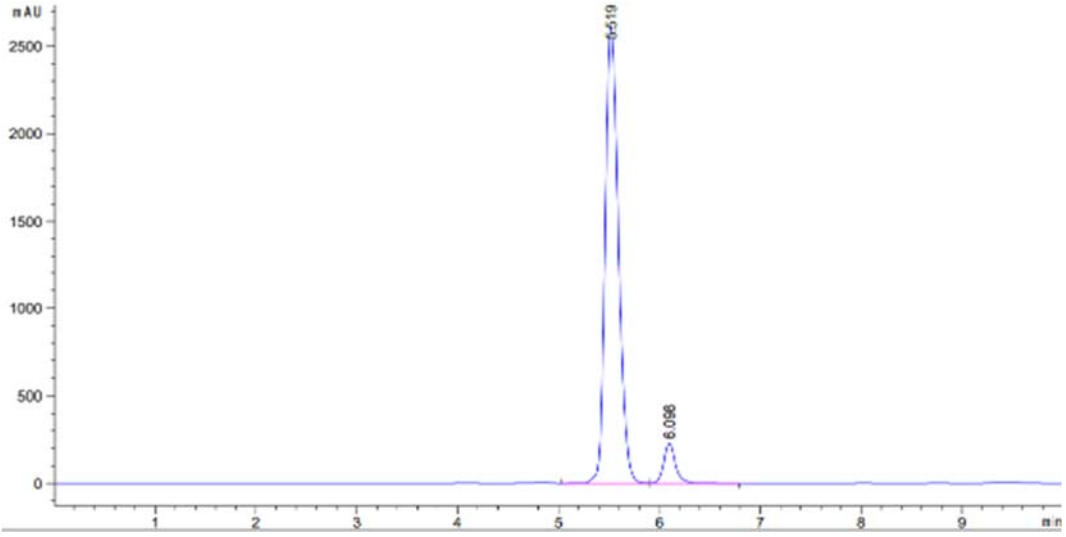
4d

HPLC data using rac-**L1**

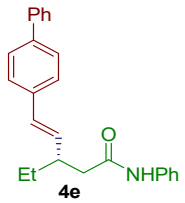


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.807	MM	0.1499	4675.90234	519.73724	50.5750
2	6.420	VV R	0.1507	4569.57324	456.97687	49.4250

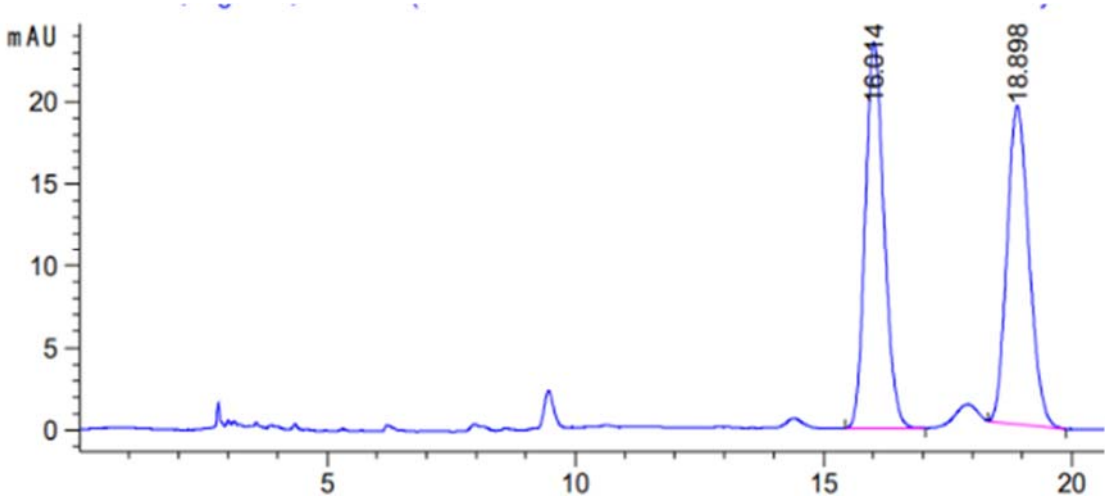
HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.519	BV	0.1429	2.38781e4	2605.44238	92.8442
2	6.098	VB	0.1215	1840.35376	229.63184	7.1558

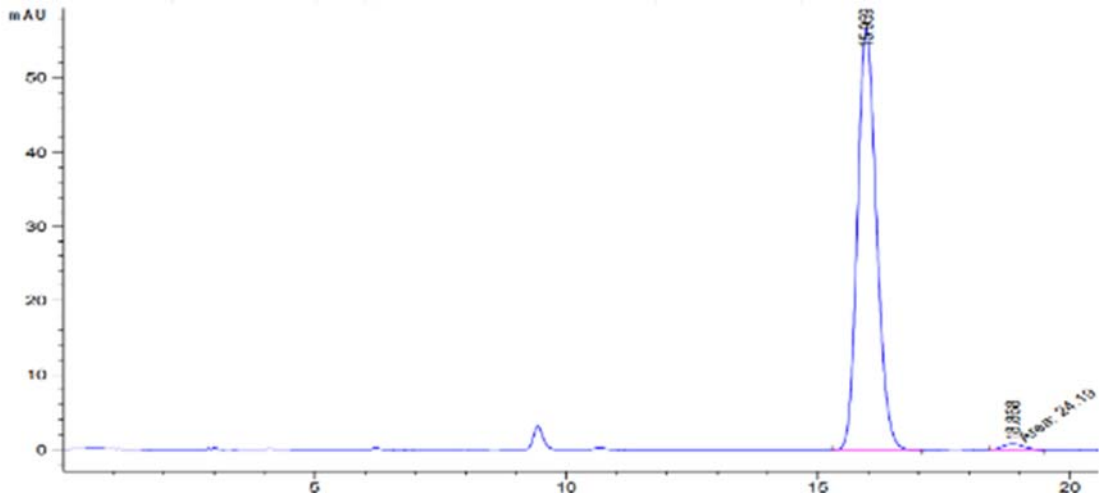


HPLC data using rac-**L1**

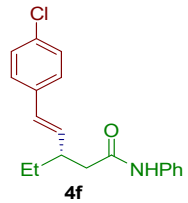


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.014	BB	0.4054	619.01019	23.49388	50.8779
2	18.898	BB	0.4717	597.64850	19.38445	49.1221

HPLC data using **L1**

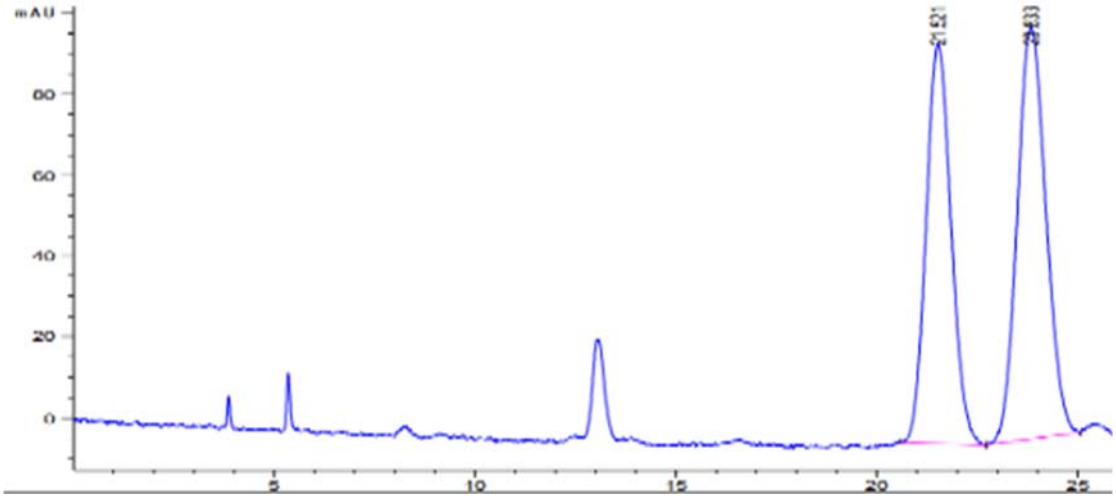


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.959	BB	0.4052	1491.02014	56.62566	98.4035
2	18.868	MM	0.5096	24.19000	7.91201e-1	1.5965



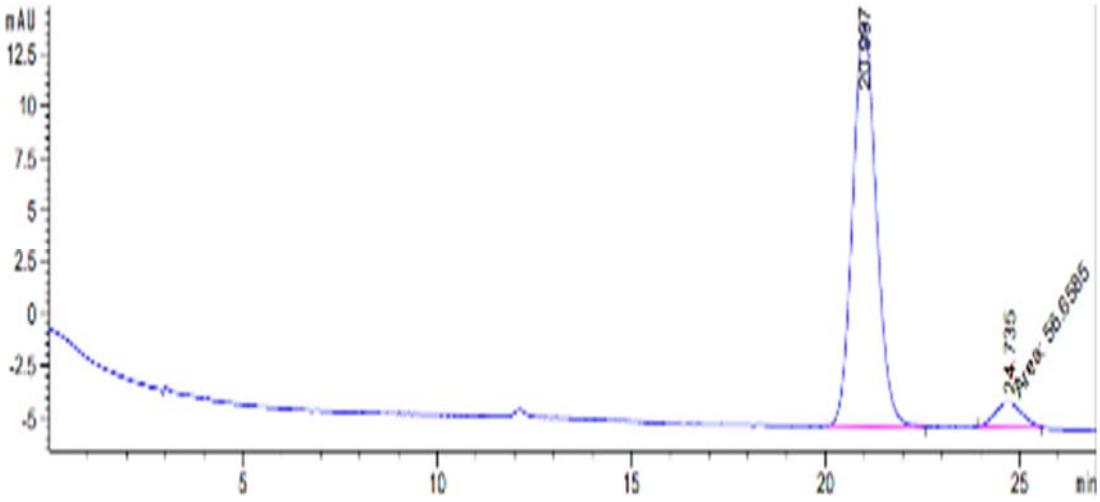
4f

HPLC data using rac-**L1**

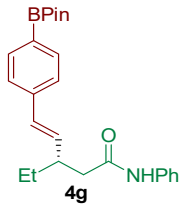


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.521	VB R	0.5517	4264.06592	98.76539	45.9304
2	23.833	BV R	0.5899	5019.69141	101.69619	54.0696

HPLC data using **L1**

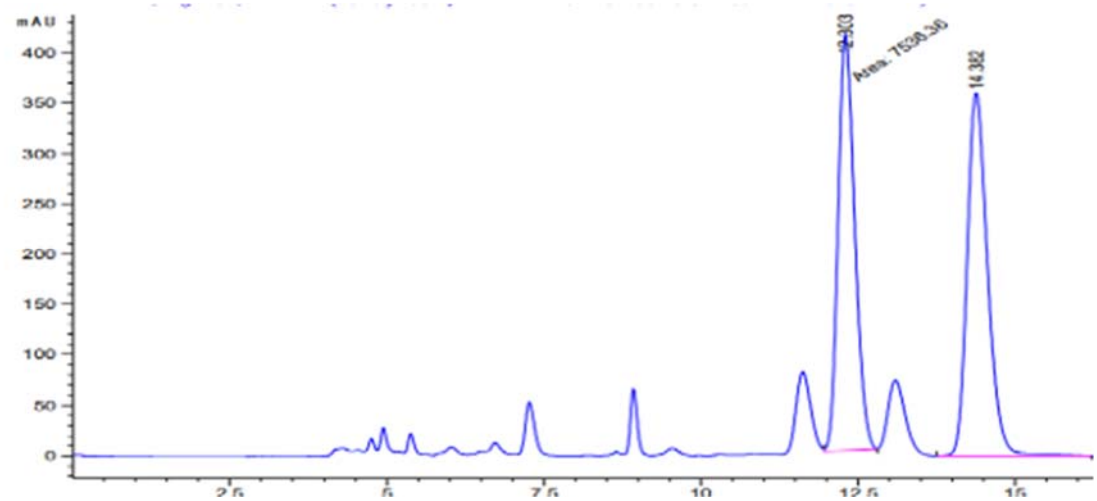


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.997	BB	0.6288	816.76758	19.25692	93.5131
2	24.735	MM	0.8066	56.65855	1.17076	6.4869



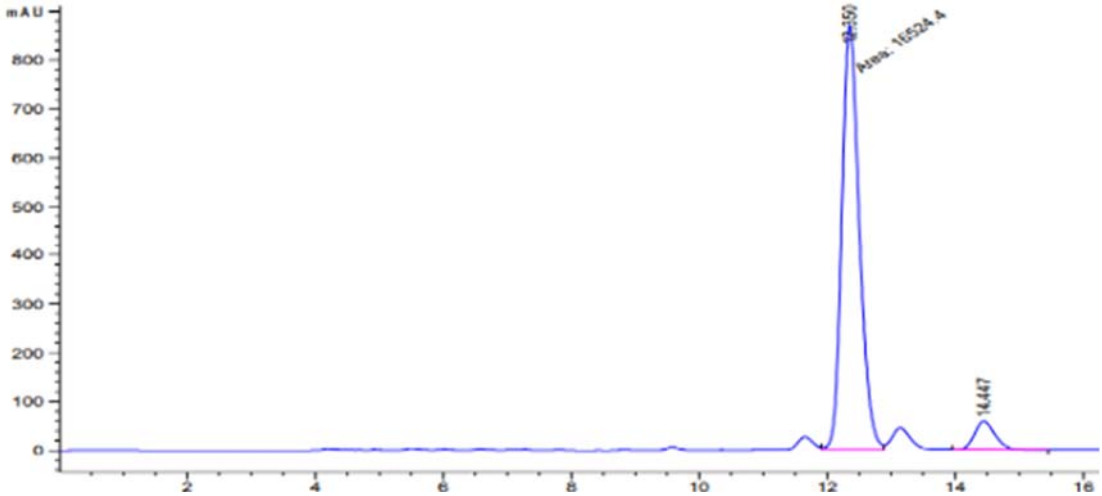
4g

HPLC data using rac-**L1**

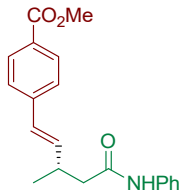


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.303	MM	0.3052	7536.36133	411.49503	48.0883
2	14.382	BB	0.3478	8135.55713	359.84979	51.9117

HPLC data using **L1**

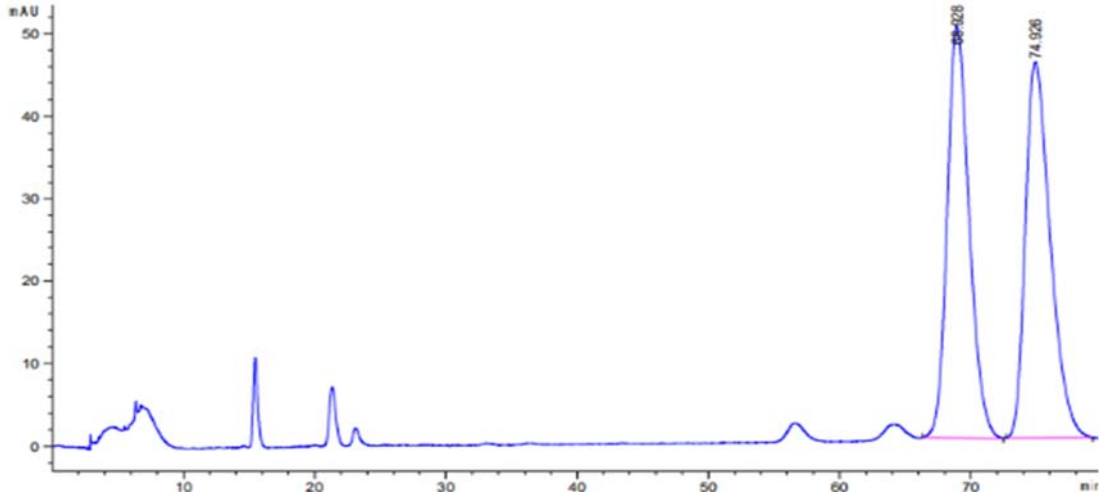


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.350	FM	0.3173	1.65244e4	867.85724	92.8245
2	14.447	BB	0.3397	1277.37390	57.83045	7.1755



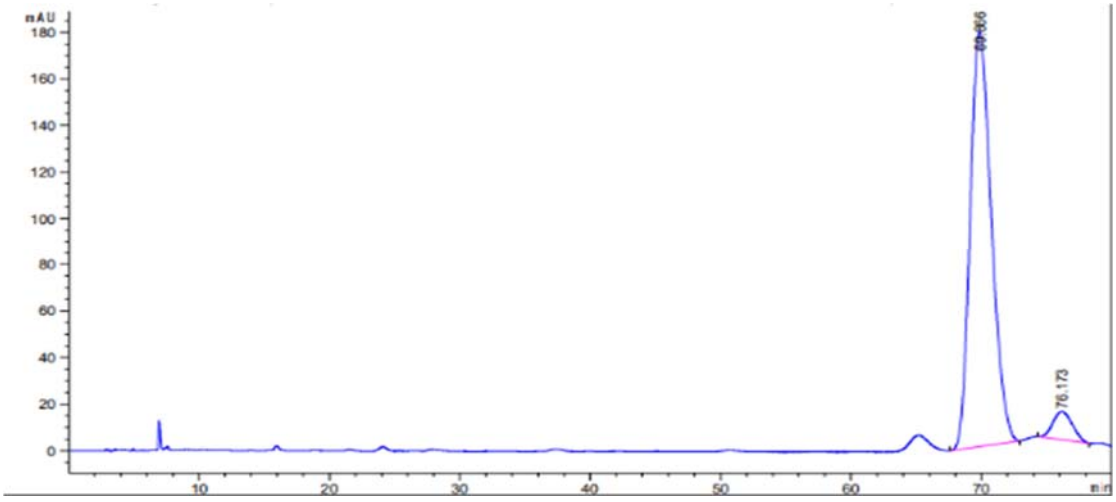
4h

HPLC data using rac-**L1**

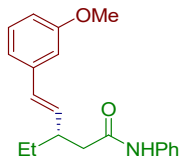


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.928	BB	1.4193	5792.40723	49.93583	49.1996
2	74.926	BB	1.5815	5980.87402	45.56237	50.8004

HPLC data using **L1**

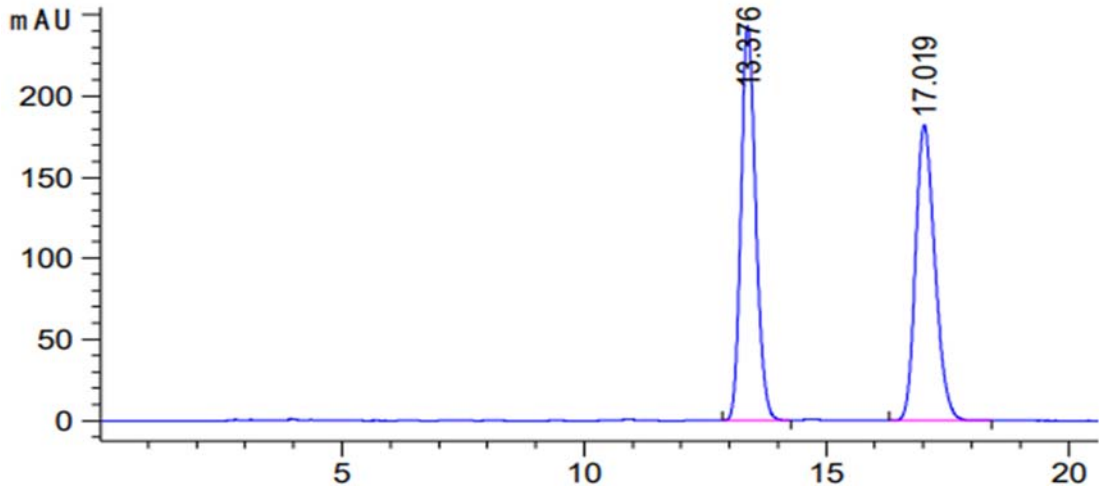


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.866	BB	1.6506	2.01325e4	178.40144	94.1465
2	76.173	BB	1.2180	1251.73022	12.04880	5.8535



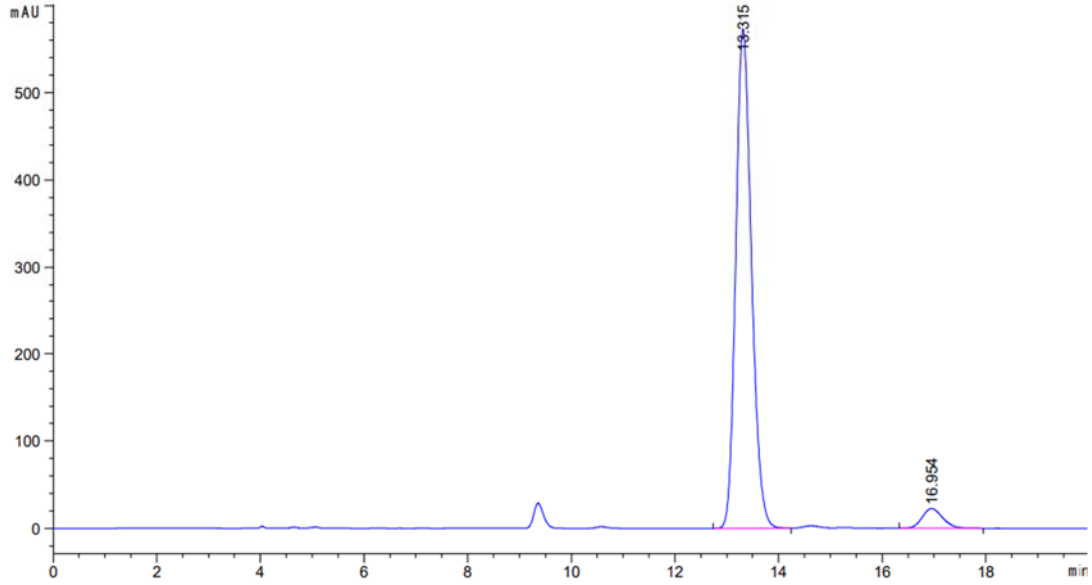
4i

HPLC data using rac-**L1**

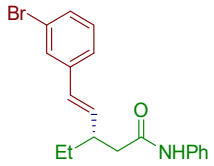


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.376	BB	0.3274	5147.11182	242.69609	50.4371
2	17.019	BB	0.4297	5057.89502	182.28032	49.5629

HPLC data using **L1**

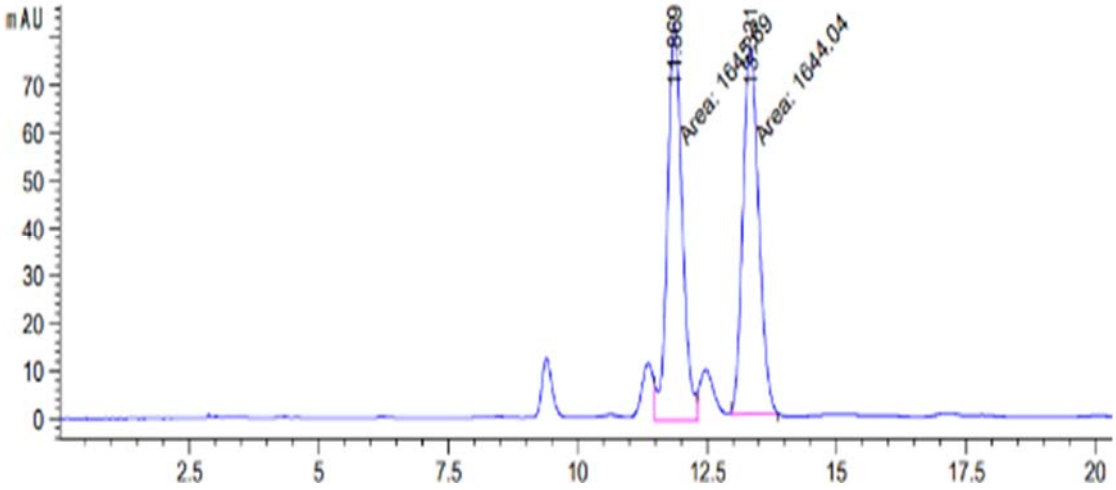


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.315	BB	0.3231	1.20344e4	572.84308	95.1125
2	16.954	BB	0.4234	618.40680	22.59113	4.8875



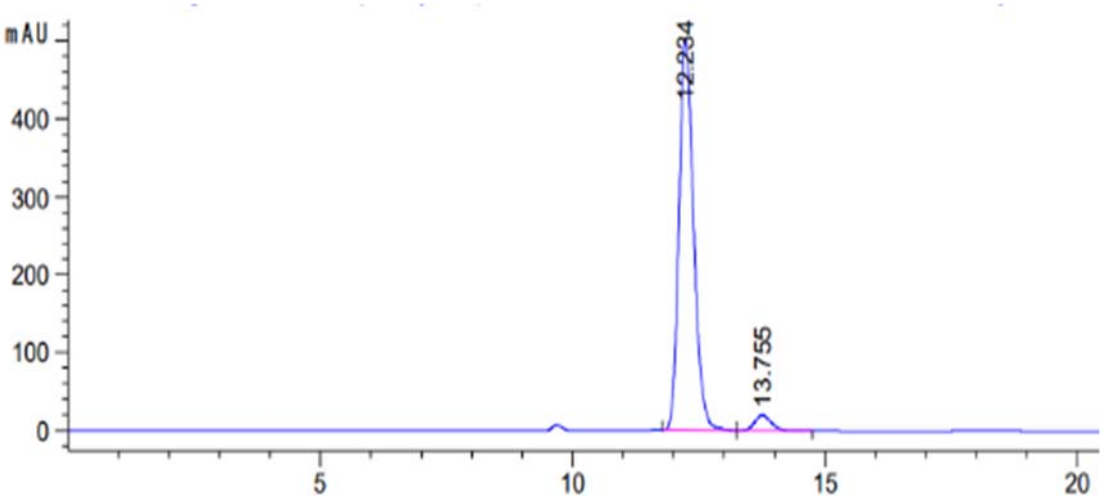
4j

HPLC data using rac-**L1**

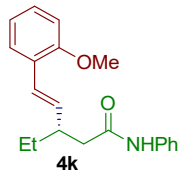


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.869	MM	0.3298	1645.68799	83.17652	50.0251
2	13.331	MM	0.3542	1644.03674	77.35761	49.9749

HPLC data using **L1**

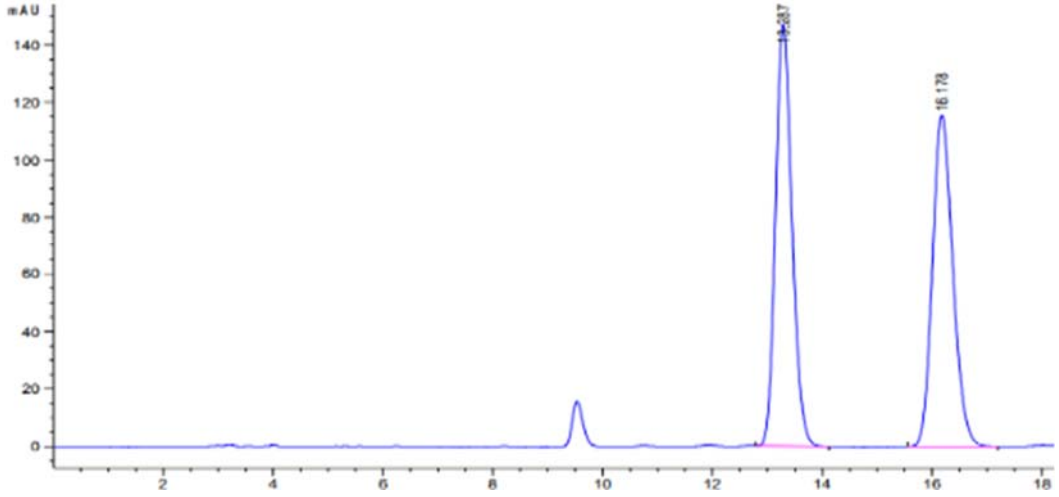


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.234	BB	0.3081	1.00475e4	500.67984	95.8478
2	13.755	BB	0.3415	435.26822	19.57161	4.1522



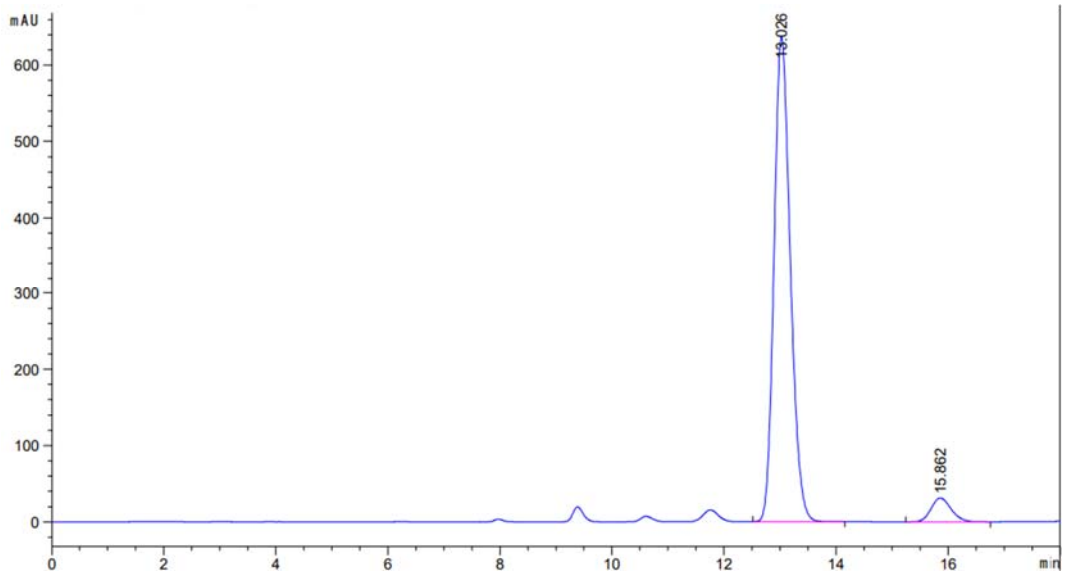
4k

HPLC data using rac-**L1**

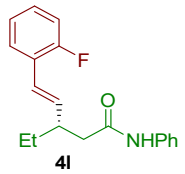


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.287	BB	0.3218	3069.93750	146.90334	50.7151
2	16.178	BB	0.3972	2983.36743	115.54459	49.2849

HPLC data using **L1**

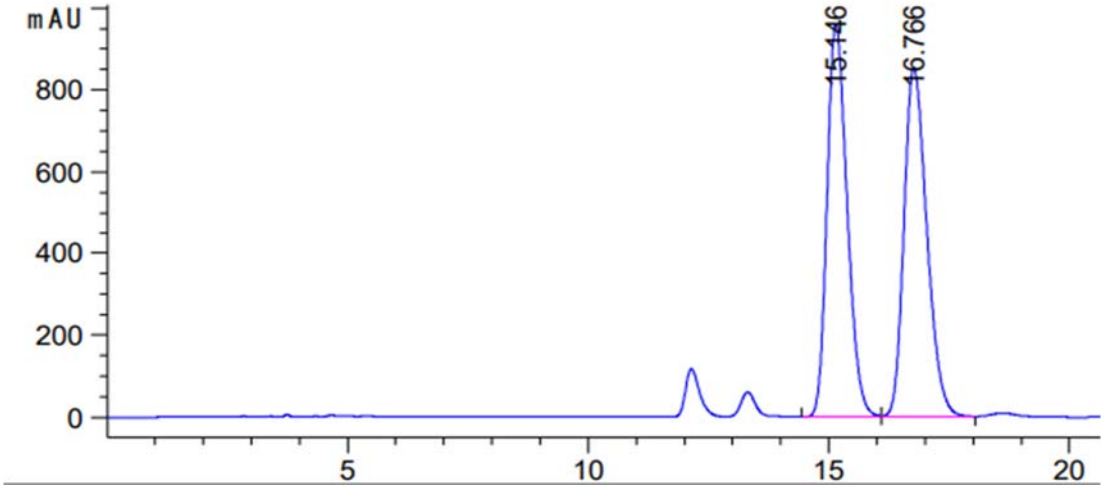


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.026	BB	0.3112	1.28431e4	636.93695	94.2841
2	15.862	BB	0.3839	778.59900	31.33191	5.7159



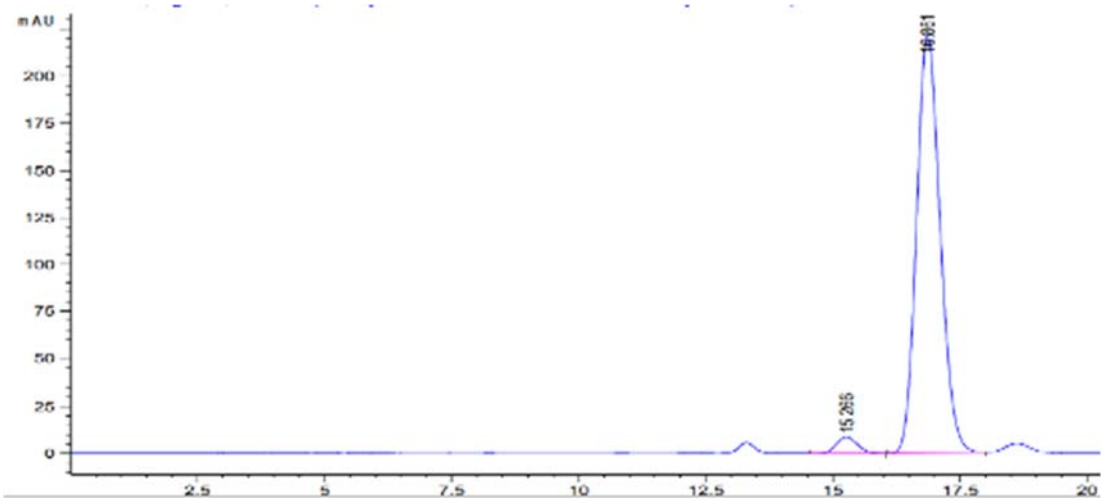
4l

HPLC data using rac-**L1**

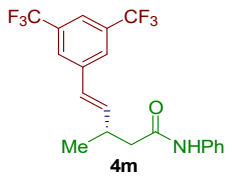


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.146	BV	0.4476	2.77799e4	959.87793	49.6877
2	16.766	VB	0.5087	2.81292e4	853.01227	50.3123

HPLC data using **L1**

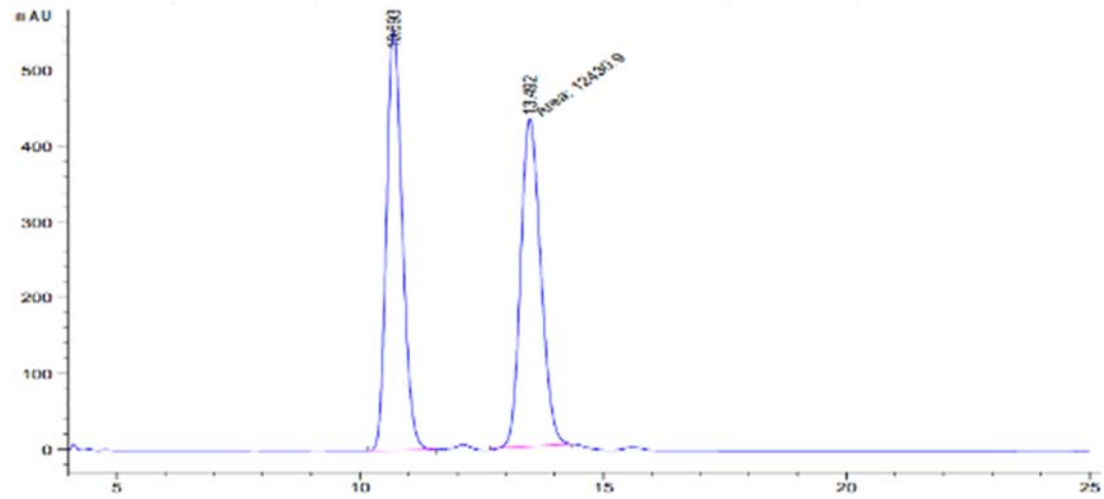


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.266	BB	0.4405	260.63910	8.98206	3.5164
2	16.861	BB	0.5024	7151.48438	221.64267	96.4836



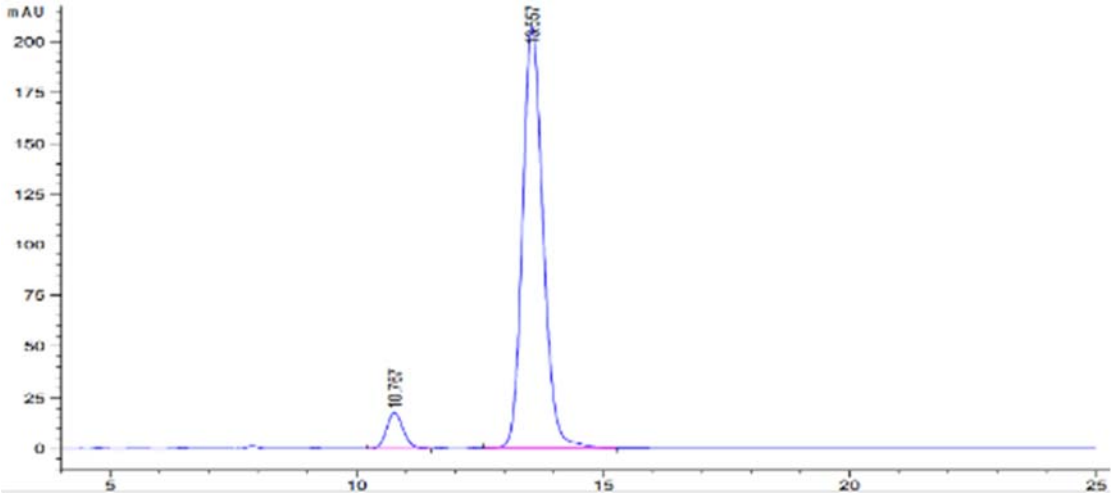
4m

HPLC data using rac-**L1**

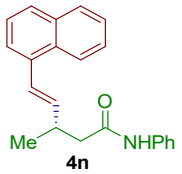


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.693	BB	0.3502	1.25611e4	554.75110	50.2605
2	13.492	MM	0.4782	1.24309e4	433.27512	49.7395

HPLC data using **L1**

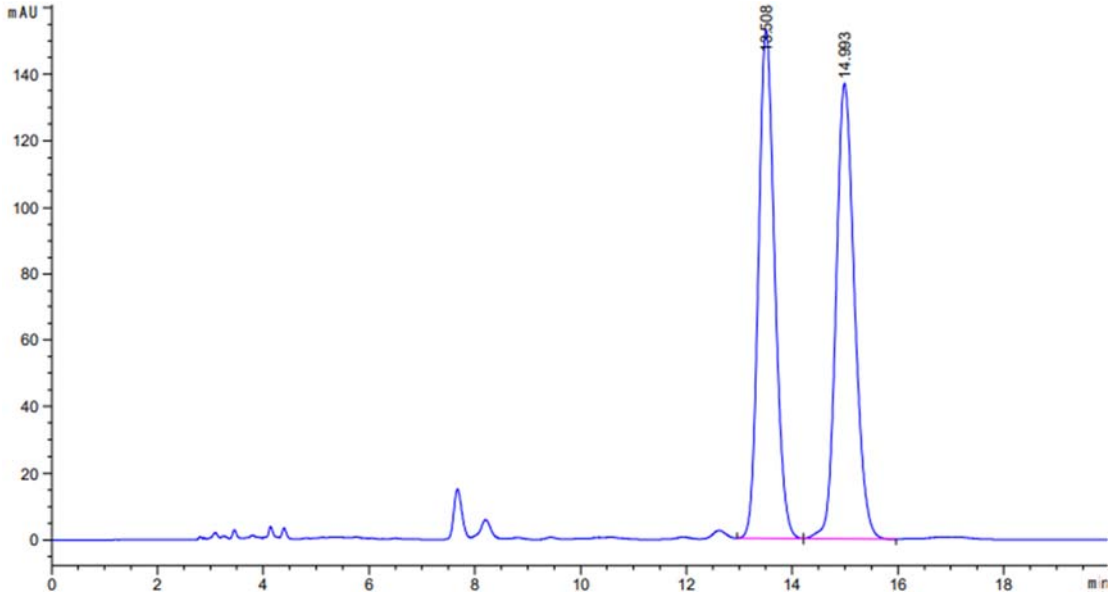


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.767	BB	0.3590	411.02695	17.82857	6.4185
2	13.557	BB	0.4472	5992.78955	207.33090	93.5815



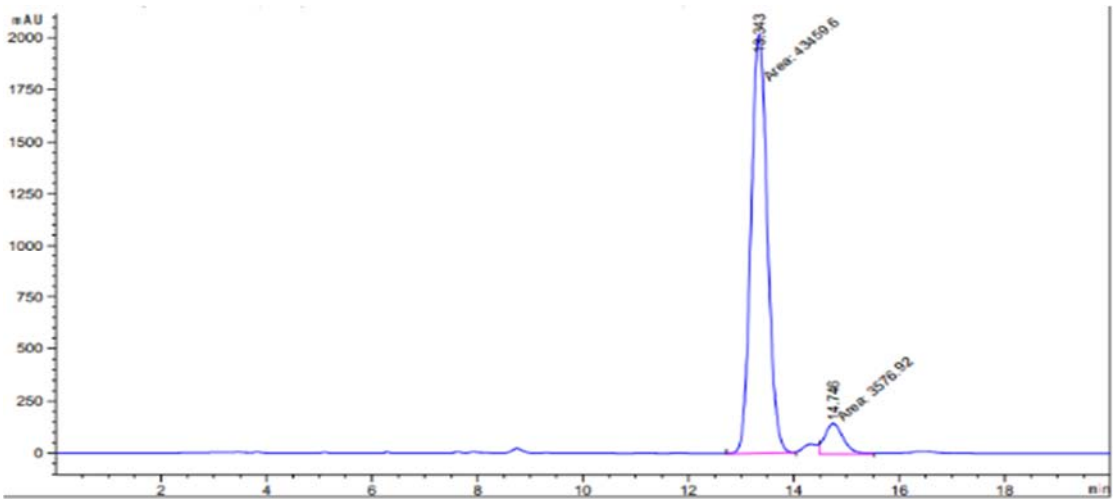
4n

HPLC data using rac-**L1**

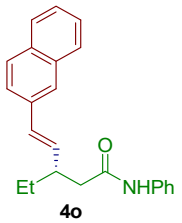


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.508	BB	0.3286	3256.51660	152.83232	49.5212
2	14.993	BB	0.3729	3319.48584	136.88239	50.4788

HPLC data using **L1**

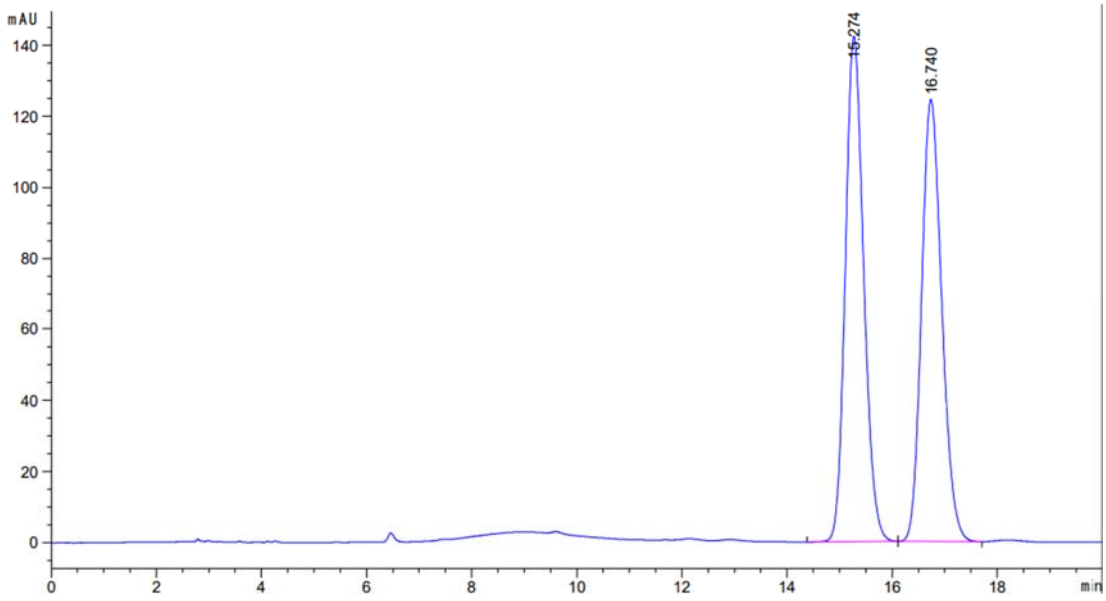


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.343	MM	0.3590	4.34596e4	2017.49365	92.3954
2	14.746	MM	0.4066	3576.92285	146.62115	7.6046



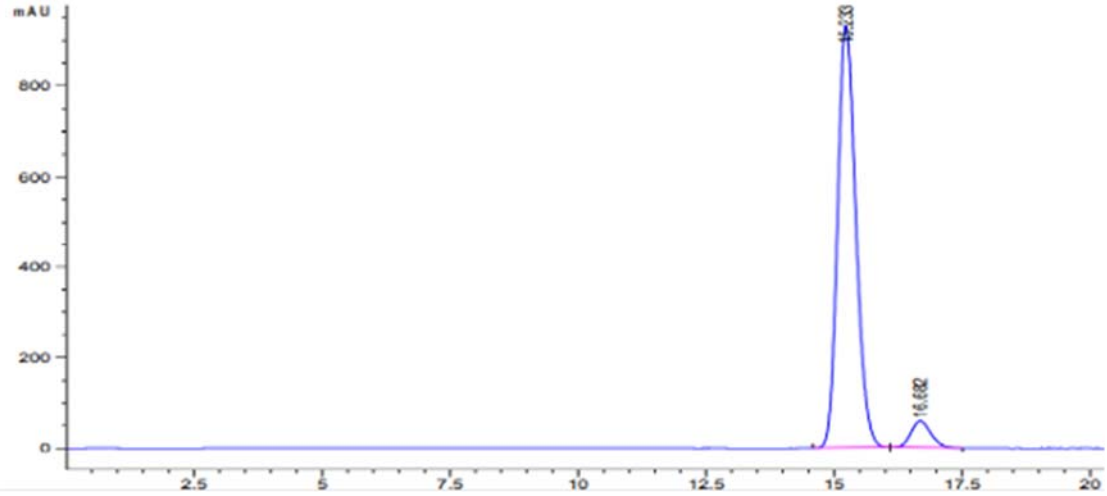
4o

HPLC data using rac-**L1**

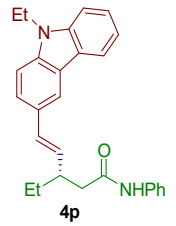


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.274	BB	0.3743	3442.92163	142.26883	50.8996
2	16.740	BB	0.4135	3321.22363	124.39402	49.1004

HPLC data using **L1**

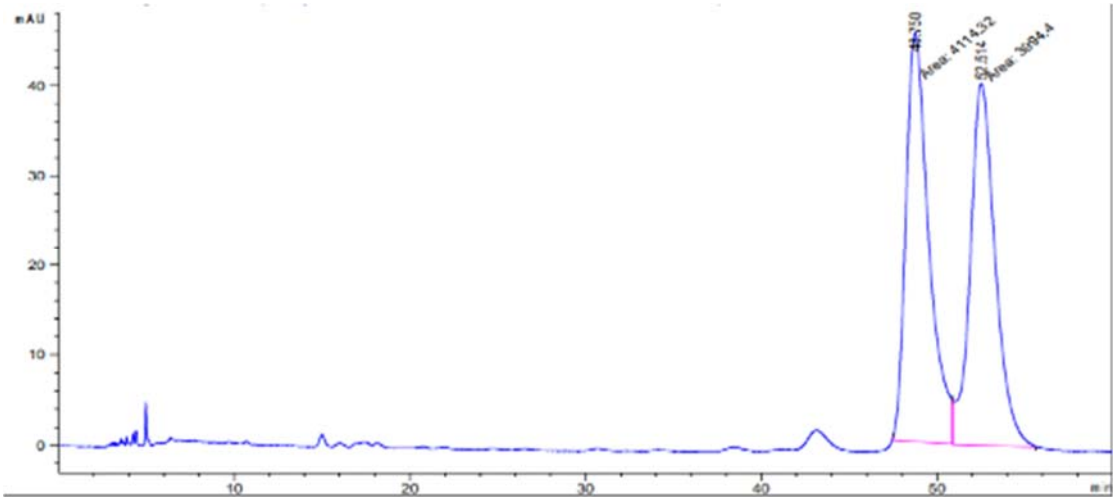


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.233	BB	0.3829	2.30509e4	930.88837	93.5490
2	16.682	BB	0.4184	1589.55383	58.98816	6.4510



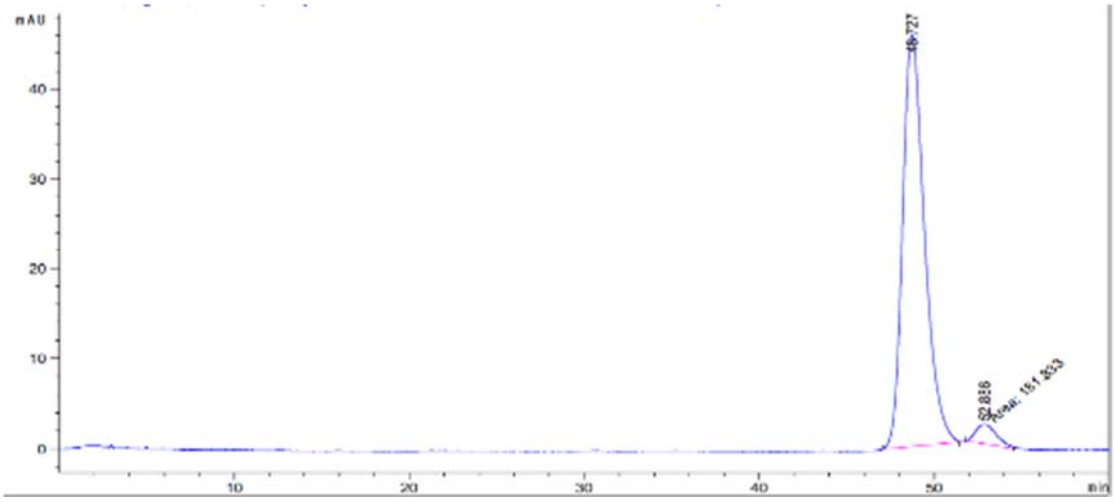
4p

HPLC data using rac-**L1**

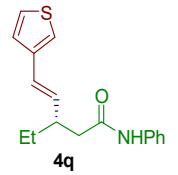


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.750	MM	1.5086	4114.31787	45.45294	50.7394
2	52.514	MM	1.6542	3994.40015	40.24456	49.2606

HPLC data using **L1**

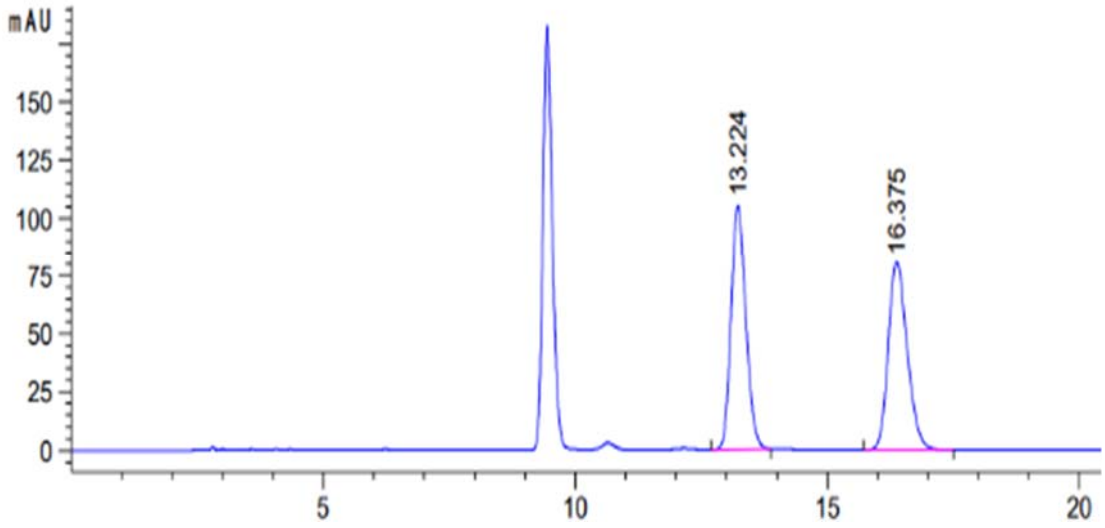


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.727	BB	1.2415	3965.62695	45.83137	95.6158
2	52.886	MM	1.3884	181.83350	2.18285	4.3842



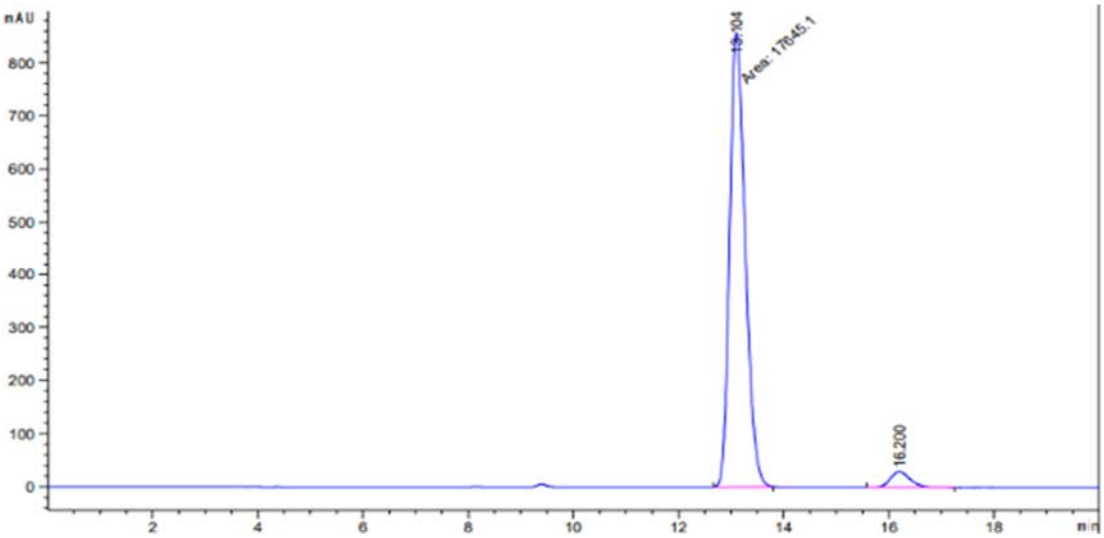
4q

HPLC data using rac-**L1**

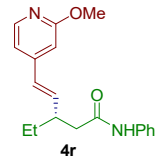


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.224	BB	0.3126	2129.33862	105.01877	50.3266
2	16.375	BB	0.4001	2101.70459	80.63589	49.6734

HPLC data using **L1**

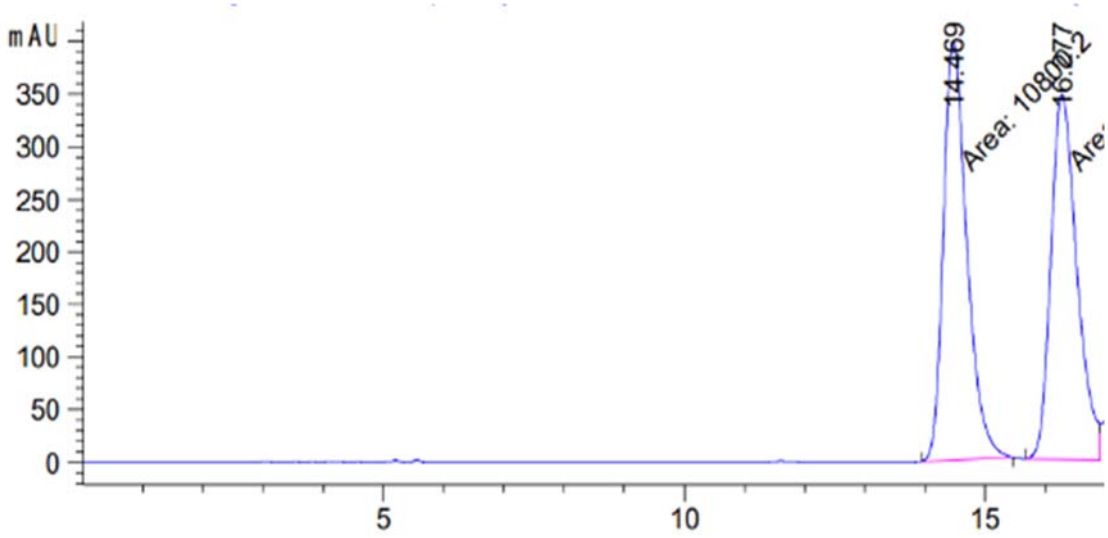


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.104	MM	0.3434	1.76451e4	856.40411	95.9371
2	16.200	BB	0.3947	747.26495	29.19026	4.0629



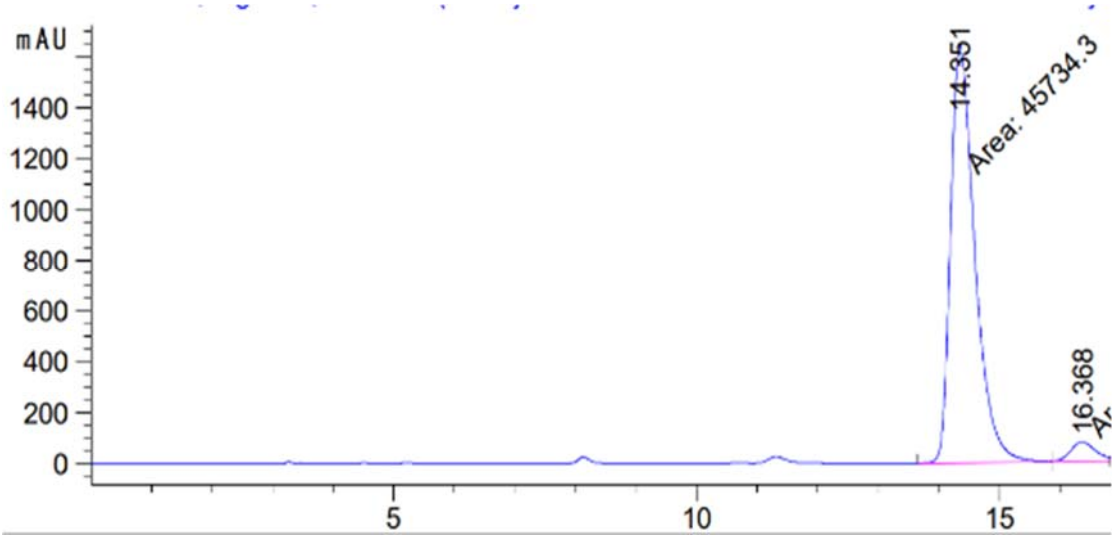
4r

HPLC data using rac-**L1**

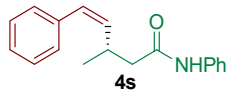


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.469	MM	0.4532	1.08002e4	397.16122	50.8509
2	16.277	MM	0.5025	1.04388e4	346.22037	49.1491

HPLC data using **L1**

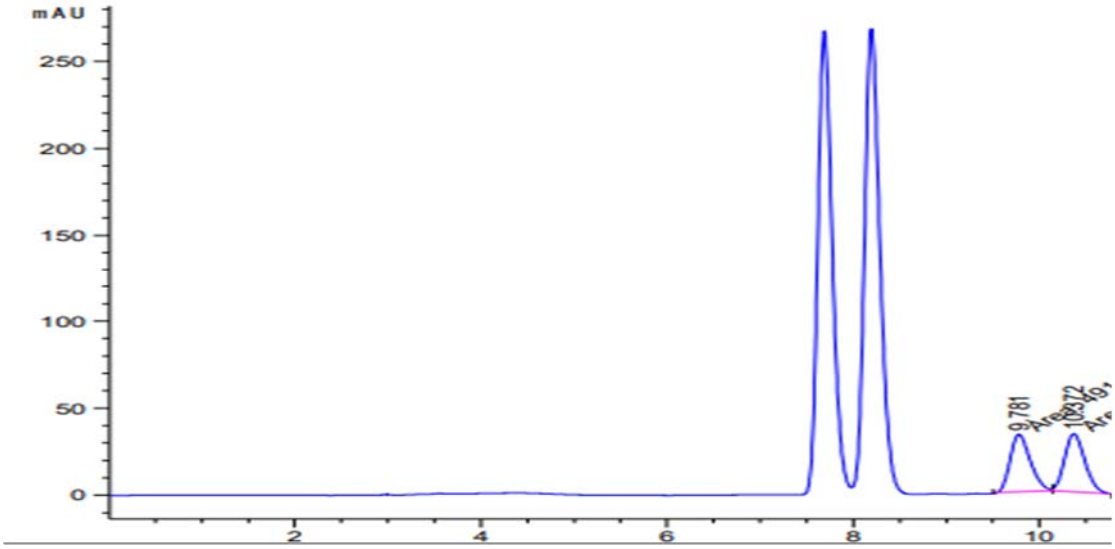


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.351	MM	0.4639	4.57343e4	1643.26831	95.3211
2	16.368	MM	0.4879	2244.90503	76.68397	4.6789



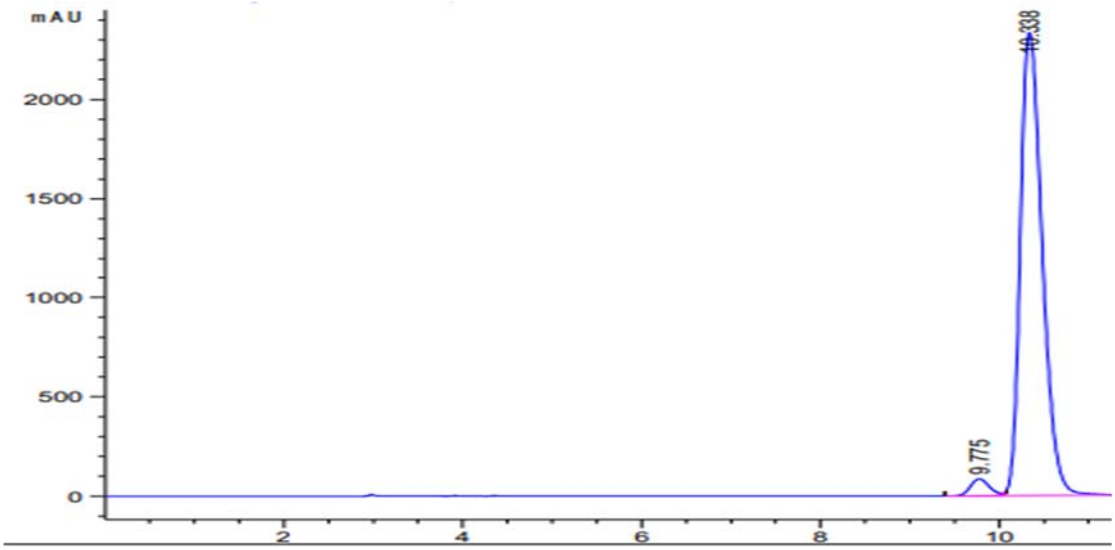
4s

HPLC data using rac-**L1**

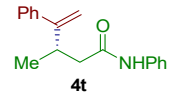


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.781	MM	0.2488	491.83655	32.94780	49.6161
2	10.372	MM	0.2502	499.44687	33.26496	50.3839

HPLC data using **L1**

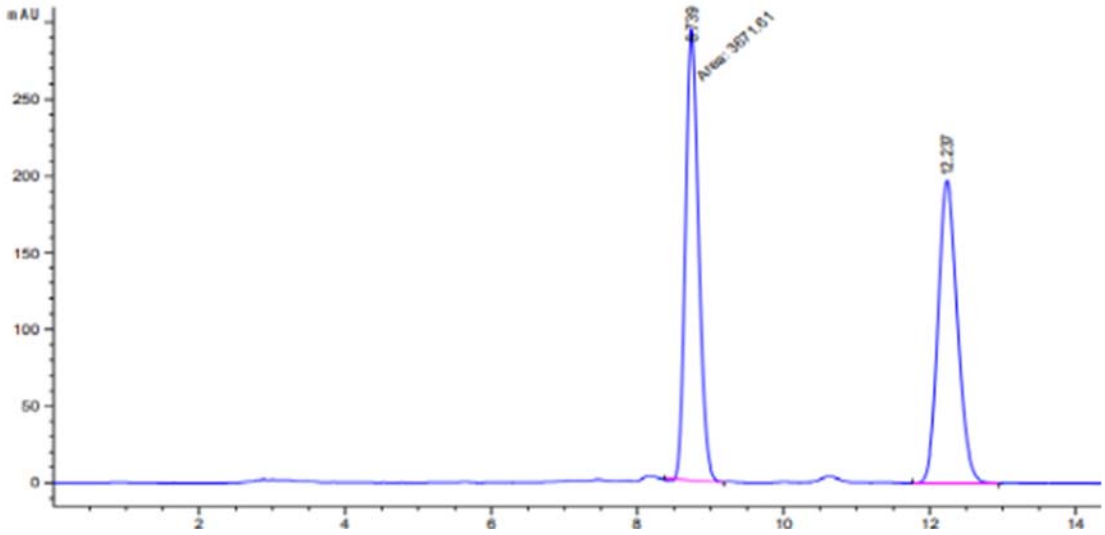


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.775	BV E	0.2244	1253.56628	85.82412	3.0706
2	10.338	VB R	0.2640	3.95713e4	2331.97681	96.9294



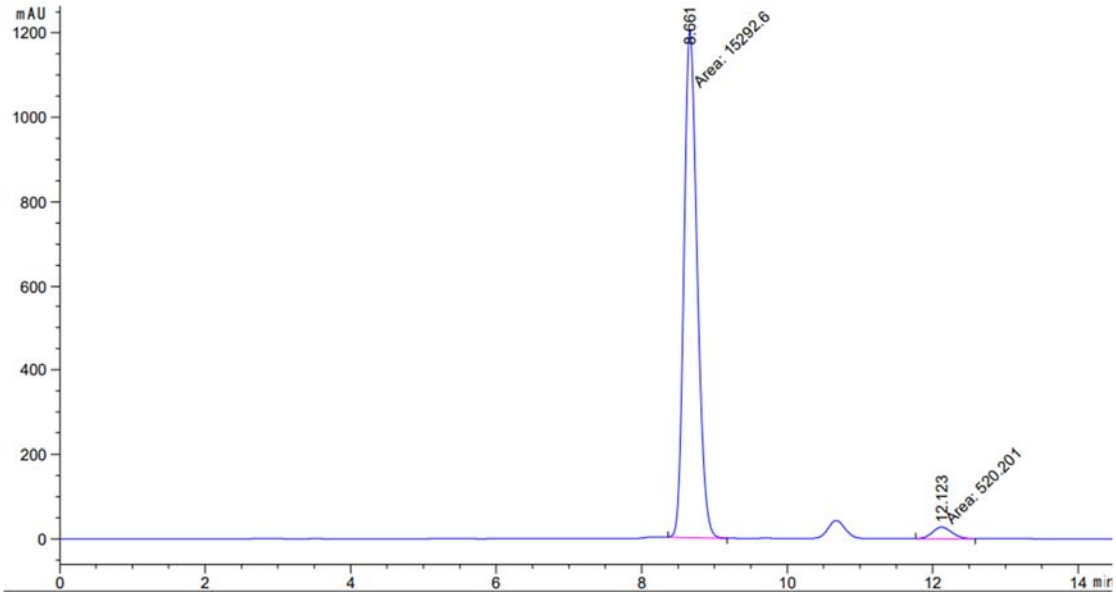
4t

HPLC data using rac-**L1**

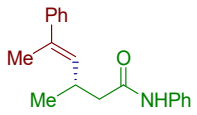


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.739	MM	0.2086	3671.61377	293.38538	50.2478
2	12.237	BB	0.2849	3635.40332	197.36060	49.7522

HPLC data using **L1**

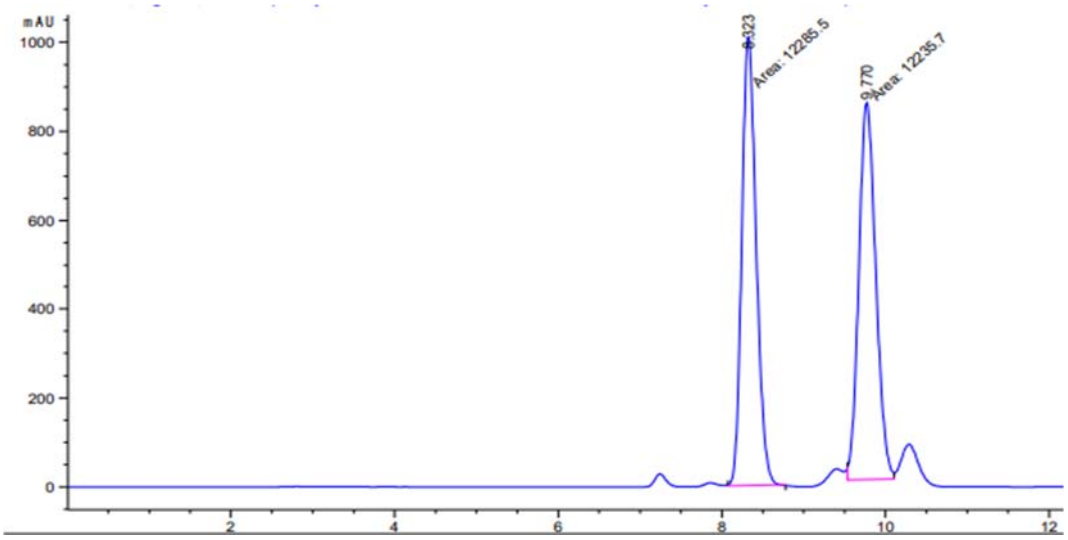


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.661	MM	0.2120	1.52926e4	1202.25500	96.7102
2	12.123	MM	0.3115	520.20117	27.83016	3.2898



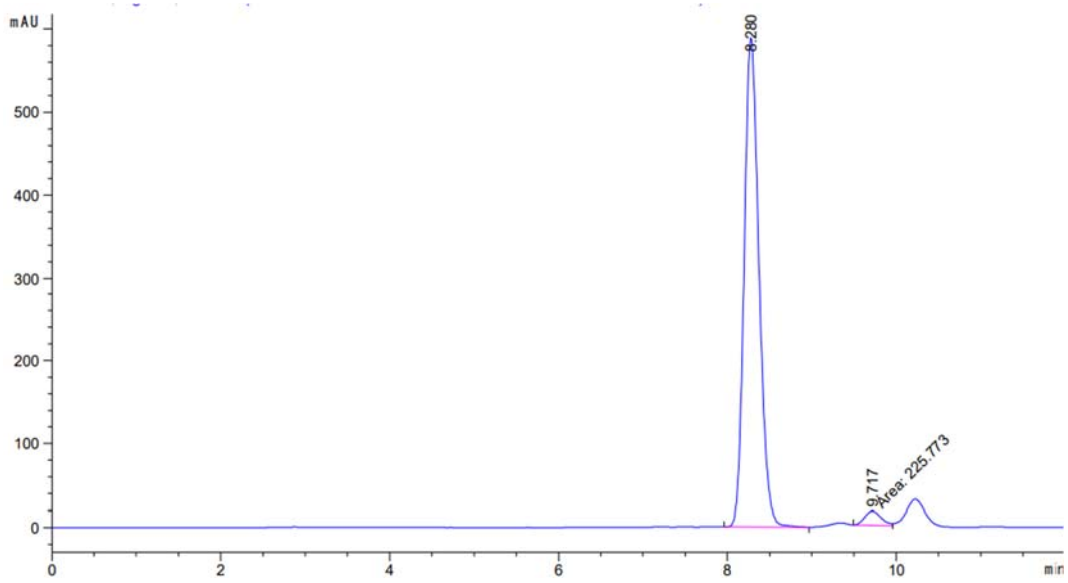
4u

HPLC data using rac-**L1**

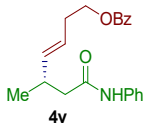


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.323	MM	0.2030	1.22855e4	1008.77563	50.1014
2	9.770	MM	0.2406	1.22357e4	847.73724	49.8986

HPLC data using **L1**

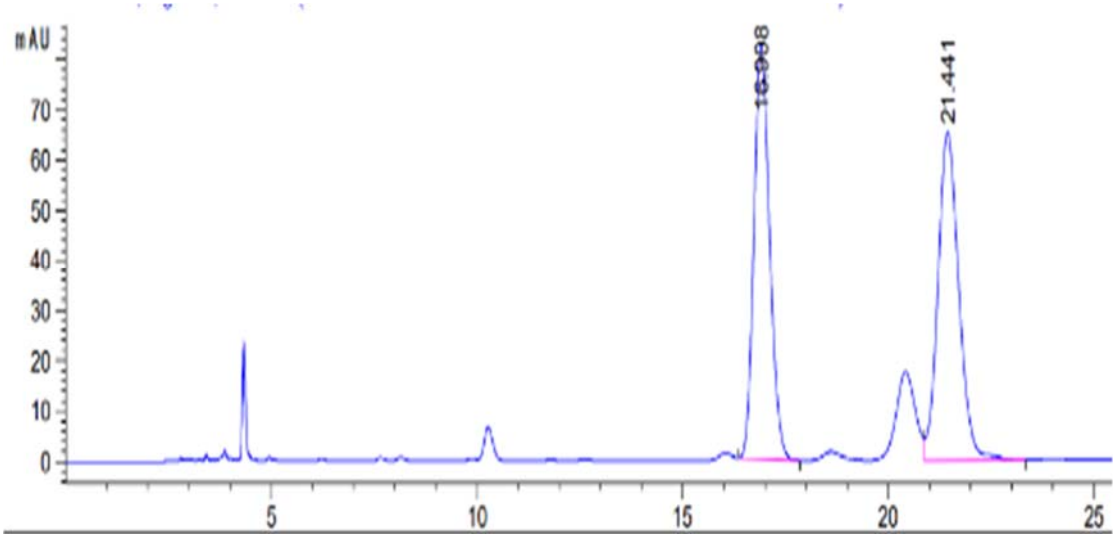


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.280	BB	0.1879	7153.40186	588.33716	96.9404
2	9.717	MM	0.2259	225.77325	16.65383	3.0596



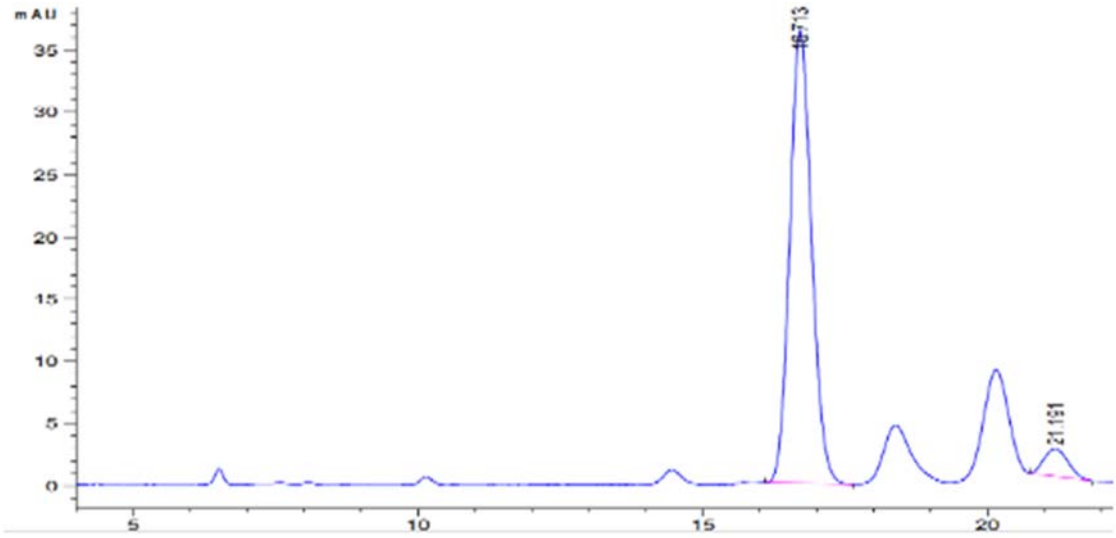
4v

HPLC data using rac-**L1**

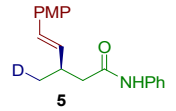


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.908	BB	0.4107	2190.93066	82.27848	48.7534
2	21.441	VB	0.5401	2302.97021	65.19888	51.2466

HPLC data using **L1**

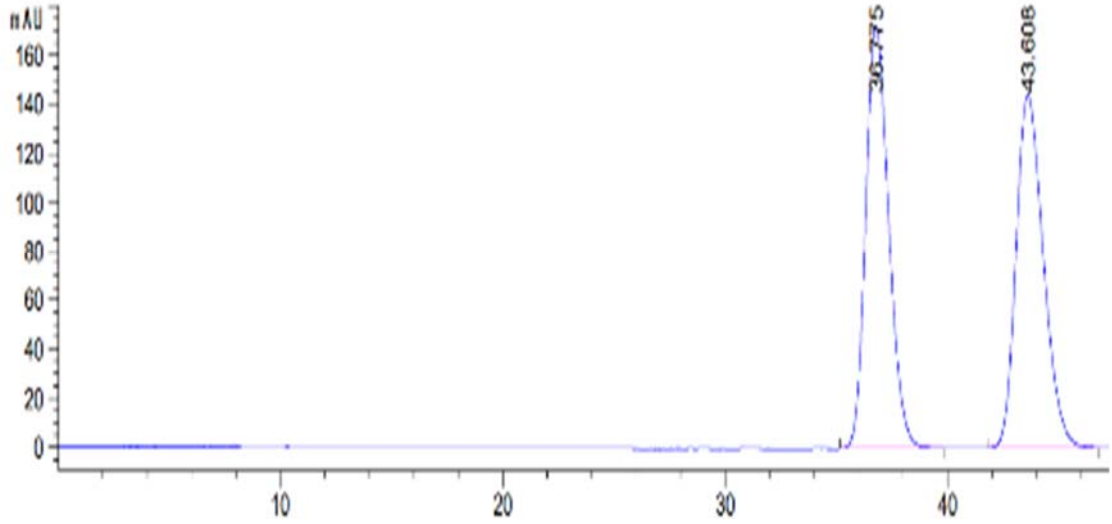


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.713	BB	0.4145	967.07593	36.33714	93.7120
2	21.191	BB	0.3785	64.89010	2.21005	6.2880



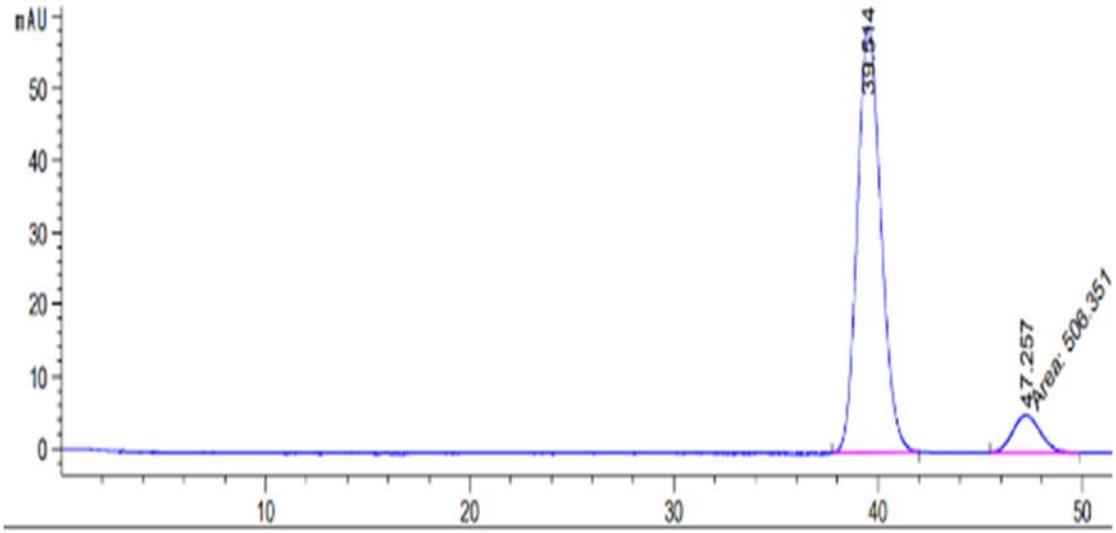
5

HPLC data using rac-**L1**

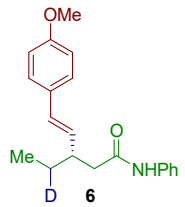


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.775	BB	1.0691	1.23655e4	172.32986	50.1251
2	43.608	BB	1.2509	1.23038e4	143.99590	49.8749

HPLC data using **L1**

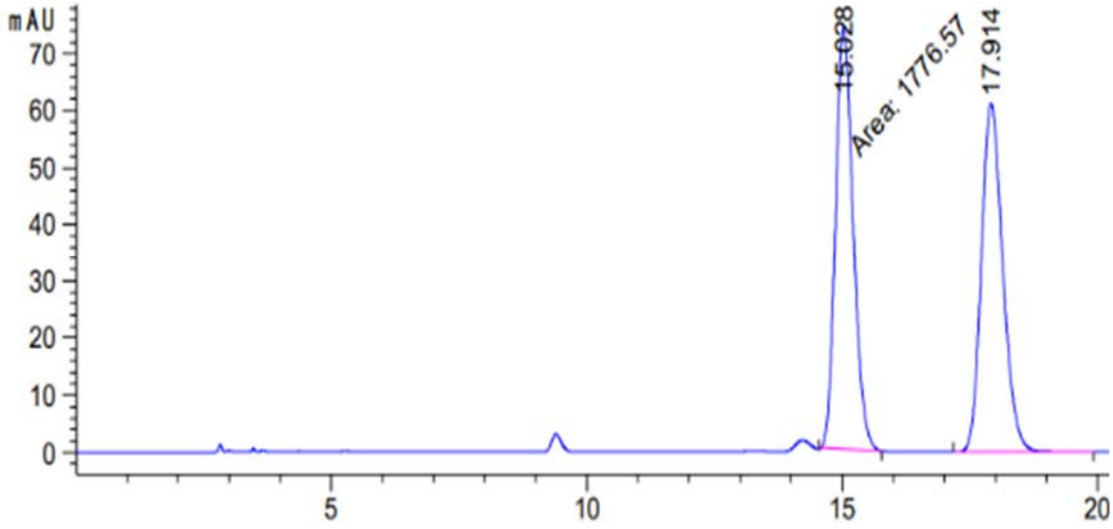


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.514	BB	1.1706	4752.14746	59.06883	90.3708
2	47.257	MM	1.6034	506.35052	5.26343	9.6292



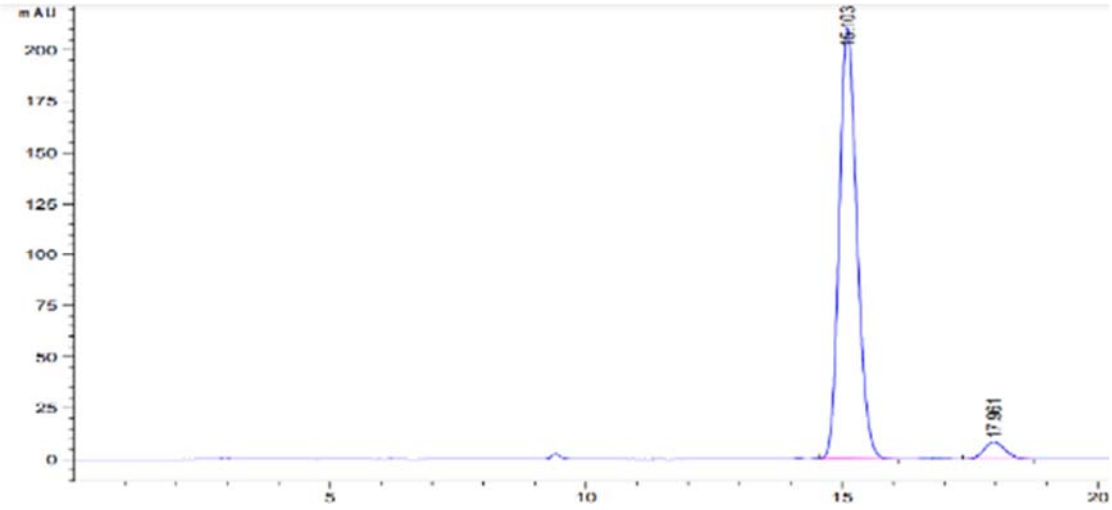
6

HPLC data using rac-**L1**

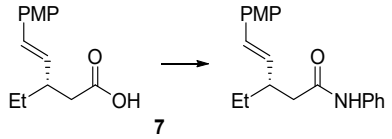


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.028	MM	0.3985	1776.57129	74.30415	49.8469
2	17.914	BB	0.4489	1787.48767	61.16855	50.1531

HPLC data using **L1**

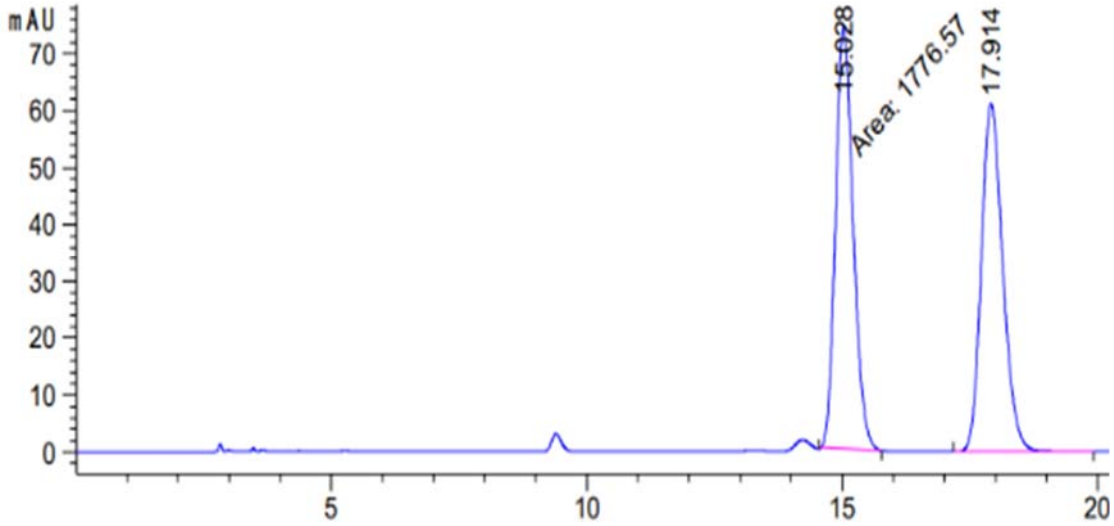


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.103	BB	0.3694	5042.65283	210.52457	95.3798
2	17.961	BB	0.4240	244.26556	8.43241	4.6202



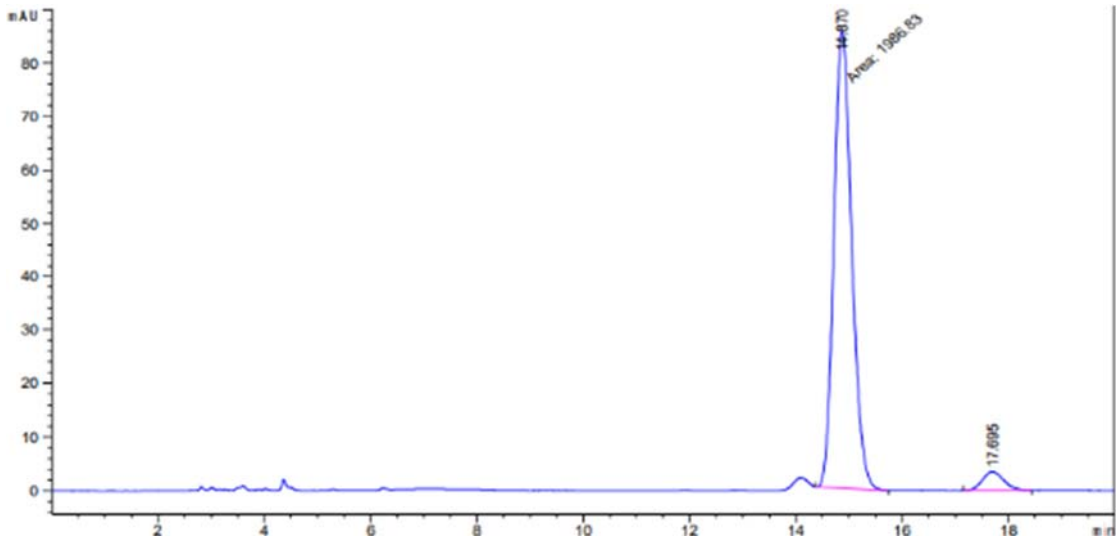
7

HPLC data using rac-**L1**

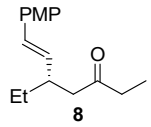


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.028	MM	0.3985	1776.57129	74.30415	49.8469
2	17.914	BB	0.4489	1787.48767	61.16855	50.1531

HPLC data using **L1**

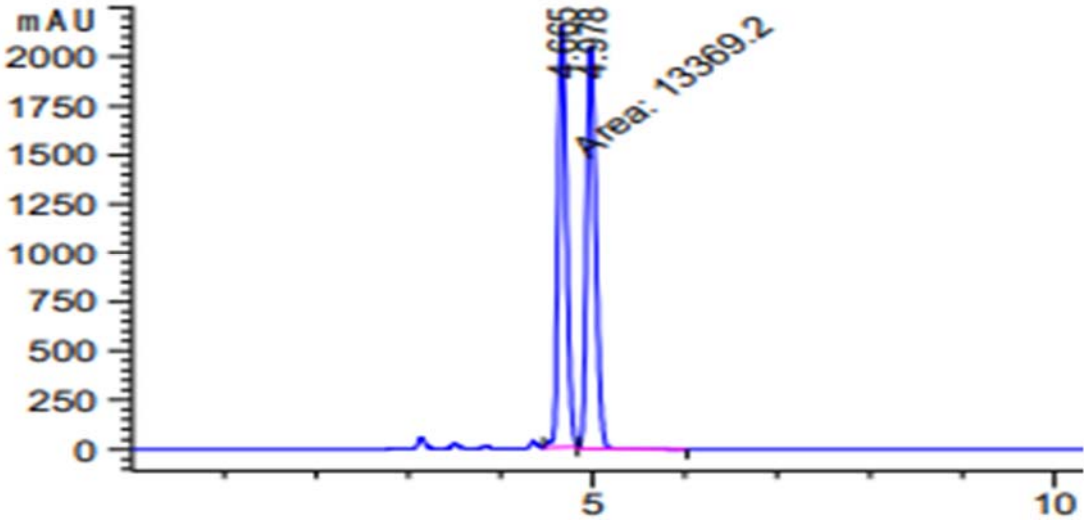


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.870	MM	0.3879	1986.83167	85.36097	95.3408
2	17.695	BB	0.4143	97.09464	3.49297	4.6592



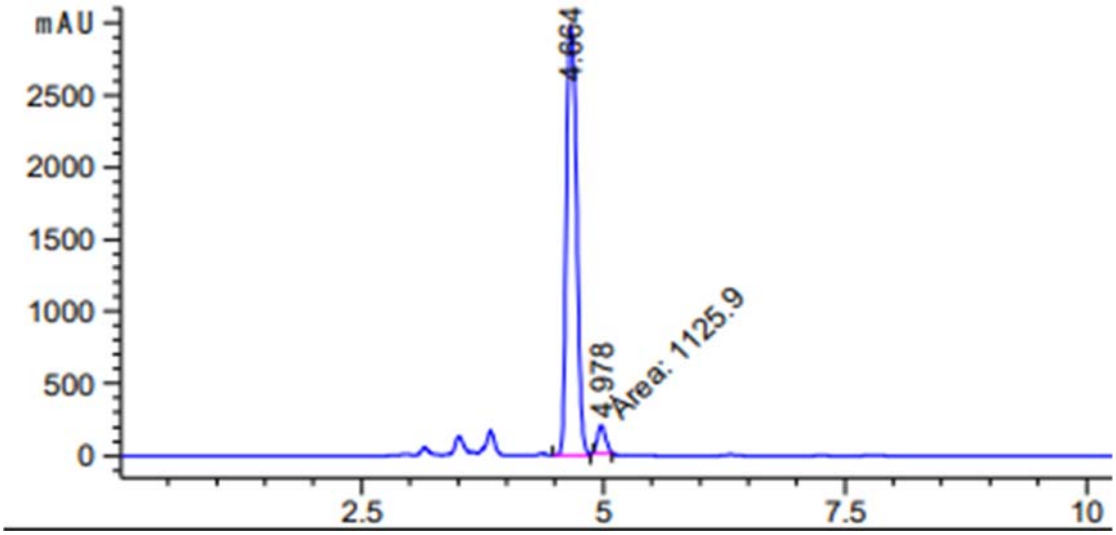
8

HPLC data using rac-**L1**

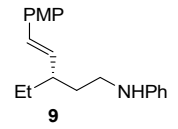


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.665	MM	0.1037	1.33692e4	2149.03027	49.4716
2	4.978	VB	0.1034	1.36548e4	2057.75488	50.5284

HPLC data using **L1**

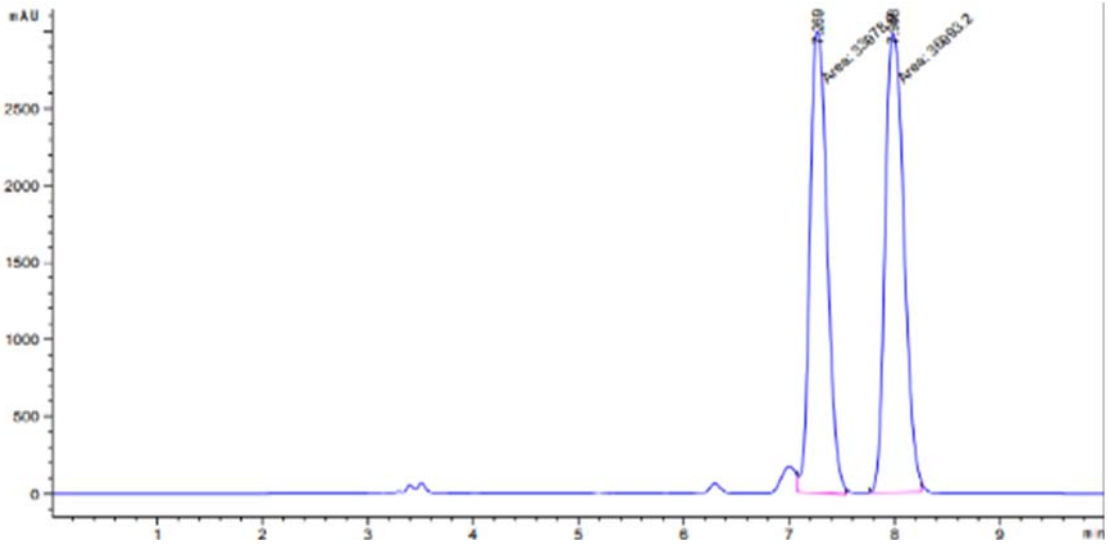


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.664	BV	0.1185	2.19687e4	2961.44995	95.1248
2	4.978	MM	0.0965	1125.90076	194.41954	4.8752



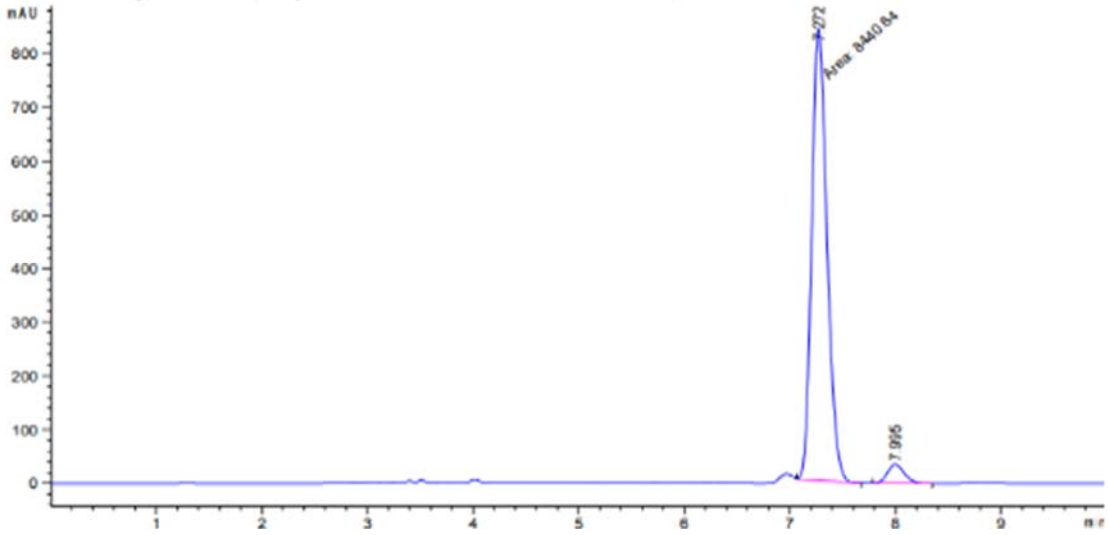
9

HPLC data using rac-**L1**

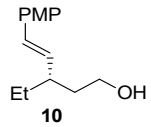


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.269	MM	0.1892	3.39788e4	2992.93701	47.8763
2	7.988	MM	0.2071	3.69932e4	2976.55273	52.1237

HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.272	MM	0.1672	8440.64355	841.51349	95.7080
2	7.995	BB	0.1673	378.51392	34.68337	4.2920



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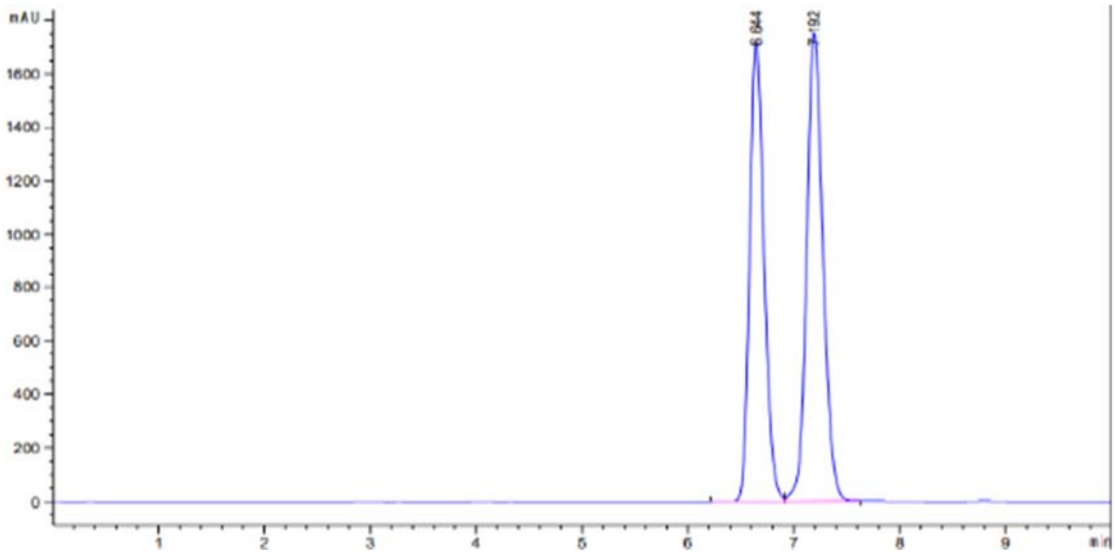
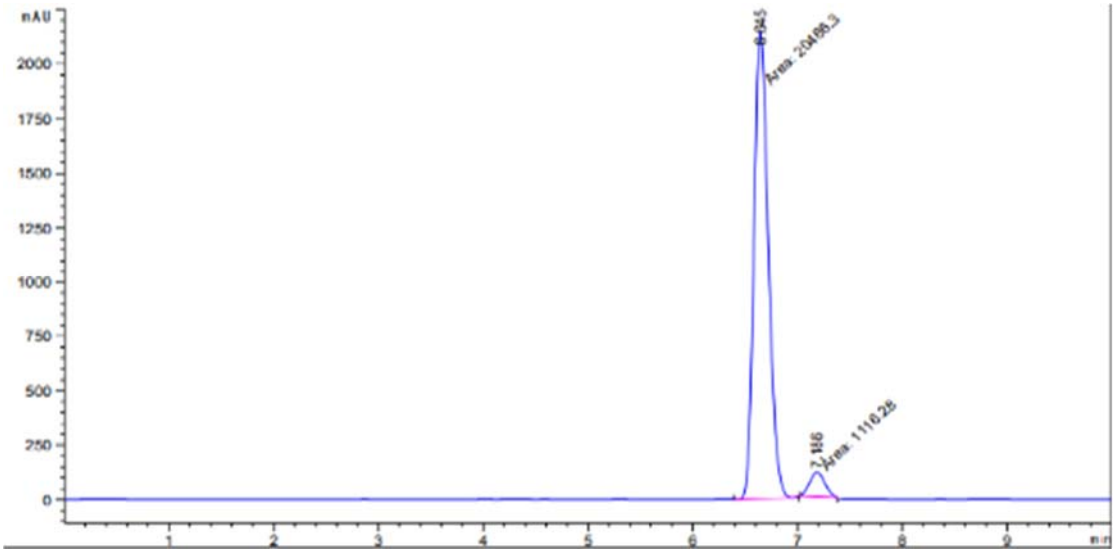
HPLC data using rac-**L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.644	BV	0.1463	1.62722e4	1721.32983	46.5244
2	7.192	VB	0.1647	1.87034e4	1750.43640	53.4756

HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.645	MM	0.1594	2.04863e4	2142.05957	94.8327
2	7.186	MM	0.1677	1116.28076	110.93472	5.1673

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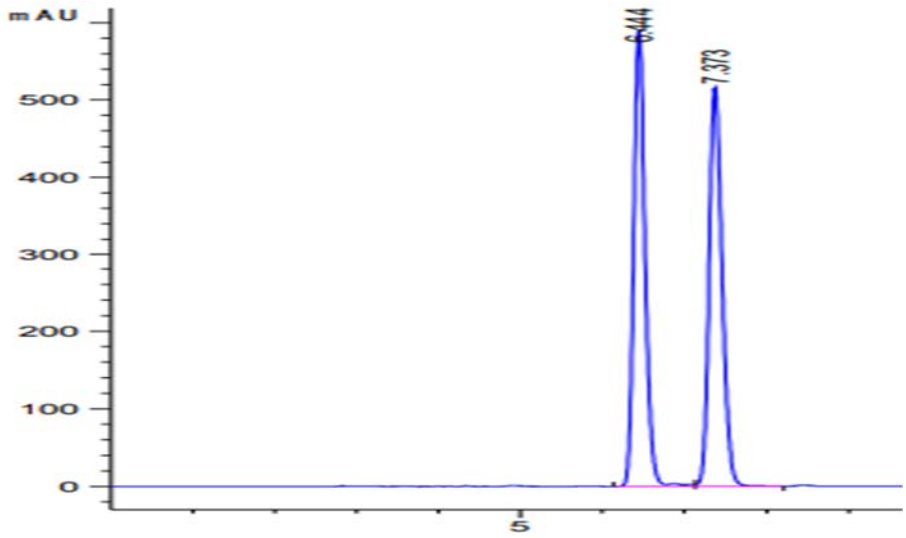
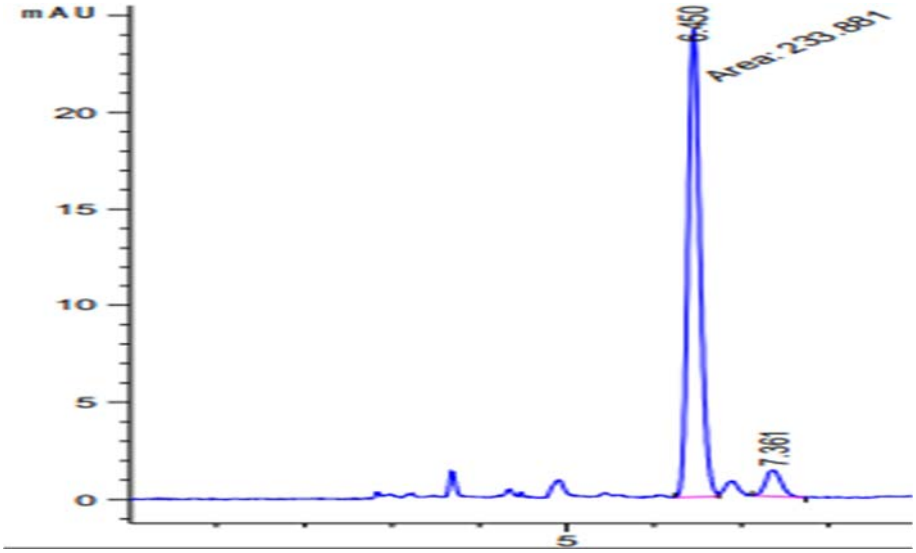
HPLC data using rac-**L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.444	BV R	0.1471	5678.30566	590.26971	50.2580
2	7.373	VB	0.1671	5620.00537	515.67517	49.7420

HPLC data using **L1**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.450	MF	0.1610	233.88072	24.20433	93.4002
2	7.361	BB	0.1832	16.52632	1.34620	6.5998