

Supporting Information

Convergent paired electrolysis for zinc-mediated diastereoselective cinnamylation α -amino esters

Hahyoun Park, Minjun Kim, Jungtaek Kang, Hyunjoon Song* and Hyunwoo Kim*

*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST),
Daejeon 34141, Republic of Korea*

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1. General information

All reactions were conducted under an argon atmosphere unless otherwise noted. Commercially available compounds were purchased from Sigma Aldrich, Alfa Aesar, and TCI. Anhydrous solvents in a sure seal bottle were used with fresh activated 3Å molecular sieves. Tetrabutylammonium hexafluorophosphate (>99% purity) was stored in the glove box. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short-wave ultraviolet light (254 nm or 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). Thin layer chromatography plates were visualized by exposure to ultraviolet light. ¹H NMR (400 or 500 MHz), ¹³C{¹H} NMR (100 or 126 MHz), and ¹⁹F{¹H} NMR (376 MHz) were recorded on a Bruker Avance Neo 400 or 500, or a Bruker Avance III HD spectrometer and were reported in ppm, relative to residual protonated solvent peak (CDCl₃). All coupling constants (*J* values) were reported in Hertz (Hz). Mass spectra were obtained using a Bruker Daltonik micro TOF-Q II high-resolution mass spectrometer (ESI) at the KAIST Analyst Center for Research Advancement.

Electrolysis experiments were performed using a Biologics VMP3 multichannel potentiostat or a DC power supply. Electrodes were purchased from Alfa Aesar and Goodfellow. Graphite rod anode (6.15 mm diameter) was cut into 50 mm long before use. Nickel foam cathode (Ni, 99.5%) was cut into 1.6 x 8.0 x 15.0 mm³ pieces before use. Electrodes were connected to electrical feed through the Teflon cap of the electrochemical cell via stainless steel or a piece of graphite (4H pencil lead, 2 mm in diameter).

Scanning electron microscope (SEM) images were acquired from Magellan400 (KAIST, 10 kV, 100 pA). X-ray photoelectron spectroscopy (XPS) was measured by Thermo VG Scientific K-alpha. The nickel and zinc contents were measured using the inductively coupled plasma-optical emission spectroscopy (ICP-OES, 5110 ICP-OES, Agilent).

2. Preparation of starting materials

2.1 Synthesis of substituted cinnamyl chlorides **2i-m**¹

Benzaldehyde (5 mmol) was dissolved in anhydrous THF (5 mL) under N₂. Vinyl magnesium (6 mmol) was added to the reaction tube at 0 °C. After completion, the reaction was quenched with saturated NH₄Cl solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). Then the organic layer was dried with Na₂SO₄ and filtered. After evaporating, the resulting crude product was purified by column chromatography.

An oven-dried round bottom flask equipped with a magnetic stir bar was charged with dichloromethane (6 mL) and synthesized alcohol (1 equiv.) under an N₂ atmosphere. The solution was cooled to 0 °C, and SOCl₂ (10 equiv.) was added dropwise. The solution was stirred at 0 °C for 2 h, then warmed to rt for 1 h. The reaction was quenched with ice water (10 mL), extracted into CH₂Cl₂ (3 x 20 mL) dried over Na₂SO₄, filtered, and concentrated in vacuum.

2.2 Synthesis of alkyl *N*-aryl glycine esters **4b-e**²

Substituted aniline (20 mmol) was added to the solution of alkyl bromoacetate (20 mmol) in ethanol (3 mL) and anhydrous sodium acetate (20 mmol). The reaction mixture was refluxed for 6-10 h under N₂. After cooling, the mixture was filtered, and the filtrate was cooled in ice bath to precipitate. The precipitation was recrystallized from ethanol-hexane, giving the desired ethyl *N*-aryl glycine ester.

2.3 Synthesis of 1-phenyl-2-(phenylamino)ethenone **4f**³

Aniline (7 mmol) was added to the solution of bromoacetophenone (3.5 mmol) in acetonitrile (7 mL). The reaction mixture was stirred for 24 h. Solid aniline salt was filtered off, and the filtrate was concentrated under a vacuum. The evaporated reaction mixture was dissolved in ethyl acetate and washed sequentially with H₂O (5 mL), 5% citric acid (5 mL), and brine (2.5 mL). The organic layer was dried with Na₂SO₄ and filtered. The filtrate was evaporated to yield the product.

2.4 Synthesis of 1-(phenylamino)propan-2-one **4g**⁴

Aniline (3 mmol) and anhydrous K₂CO₃ (4.5 mmol) were mixed in dry acetone (3 mL) and heated to 60 °C for 1 h under an N₂ atmosphere. Then, chloroacetone was added dropwise to the mixture and stirred for 12 h at 60 °C. Afterward, the mixture was filtered, and the solvent was evaporated under vacuum. The resulting crude product was purified by column chromatography.

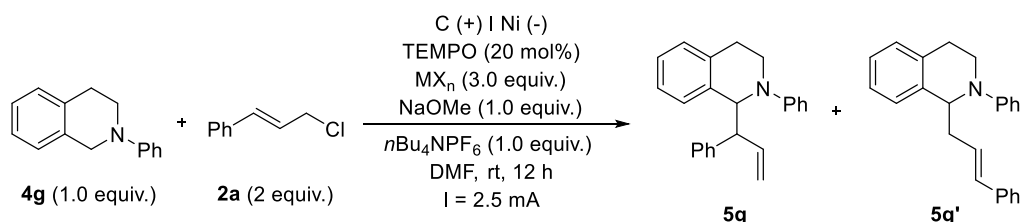
2.5 Synthesis of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **4h**⁵

With an oven-dried round bottom flask (50 mL), Pd₂(dba)₃ (0.2 mmol), BINAP (0.4 mmol) were introduced into the flask and degassed three times with argon, then anhydrous toluene (15 mL) was added into the flask through a syringe. The reaction mixture was stirred at 110 °C for 30 minutes. After cooling down to room temperature, NaOtBu (9.5 mmol), bromobenzene (5 mmol), and 1,2,3,4-tetrahydroisoquinoline (10 mmol) were added to the solution. The mixture was then degassed three times with argon and stirred under reflux for 10 h. After cooling down to room temperature, the reaction

mixture was filtered by celite and washed with CH₂Cl₂ (5 x 3 mL). The combined organic layer was evaporated to remove the solvent. The resulting crude product was purified by column chromatography.

3. Condition optimization

Table S1. Screening of metal salt

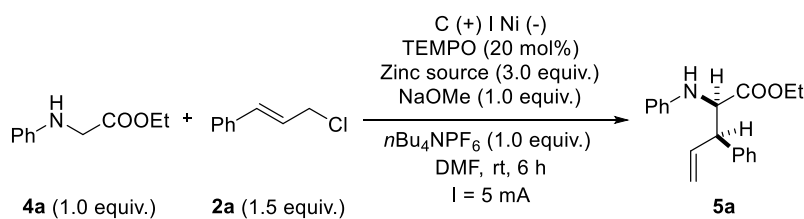


Entry	Metal source (3.0 equiv.)	Yield (%) ^b	5g: 5g'
1	ZnCl ₂	27	>19:1
2	PbBr ₂	40	1:3
3	BiCl ₃	-	-
4	InCl ₃	10	>19:1

^a Reaction conditions: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.3 mmol) and cinnamyl chloride (0.6 mmol) in 6 mL of DMF.

^b Yields were determined by ¹H NMR using mesitylene as an internal standard

Table S2. Screening of zinc source



Entry	Zinc source (3.0 equiv.)	Yield (%) ^b
1	ZnCl ₂	46
2	Zn(OAc) ₂	32
3	ZnF ₂	-
4	Zn(OTf) ₂	34

^a Reaction conditions: *N*-phenyl glycine ethyl ester (0.3 mmol) and cinnamyl chloride (0.45 mmol) in 6 mL of DMF.

^b Yields were determined by ¹H NMR using mesitylene as an internal standard

4. General procedure for electrochemical reaction

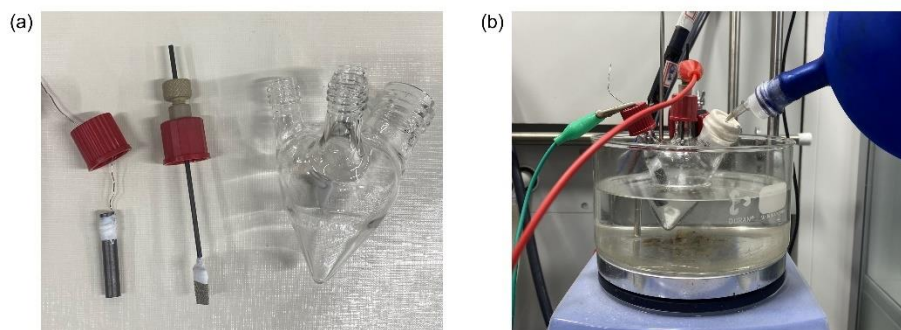
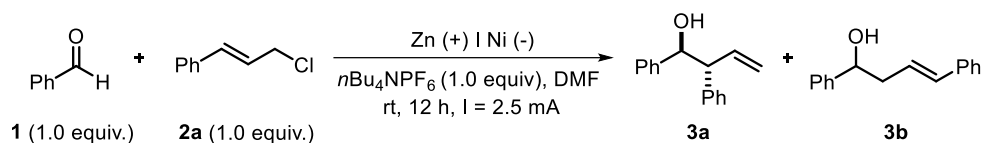


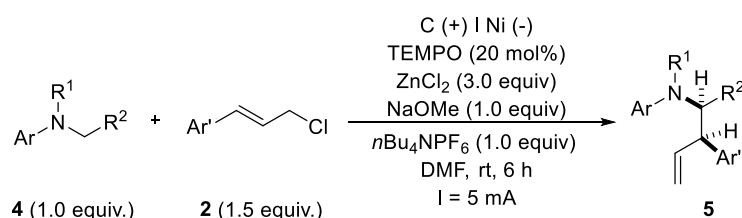
Fig S1. Set up for electrochemical reaction (a) electrodes and reactor (b) reaction in progress

Cinnamylation of aldehyde



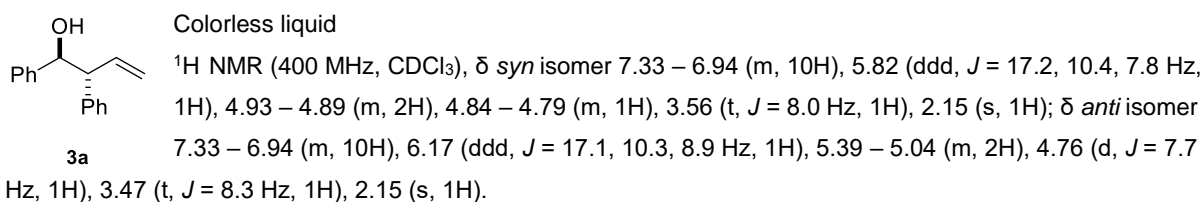
In a glove box filled with argon, the oven-dried undivided electrochemical cell with zinc anode (0.25 x 6.0 x 15.0 mm³) and nickel foam cathode (1.6 x 8.0 x 15.0 mm³) was charged with benzaldehyde (31.8 mg, 0.3 mmol, 1.0 equiv.), cinnamyl chloride (45.8 mg, 0.3 mmol, 1.0 equiv.) and *n*Bu₄NPF₆ (116.2 mg, 0.3 mmol) in anhydrous DMF (6 mL). Electrolysis was then performed at 2.5 mA of constant current at ambient temperature for 12 h. The reaction mixture was then treated with an aqueous saturated NH₄Cl solution (6 mL), and both electrodes were washed and sonicated with ethyl acetate (2 x 5 mL). The washings were added to the reaction mixture, and the combined phases were then extracted with ethyl acetate (3 x 10 mL). The organic phase was washed with aqueous saturated NH₄Cl solution (3 x 20 mL), dried over MgSO₄, and evaporated to remove the solvents. Finally, column chromatography on silica gel (*n*-hexane: ethyl acetate = 10: 1) afforded the corresponding products.

Cinnamylation of amines using paired electrolysis

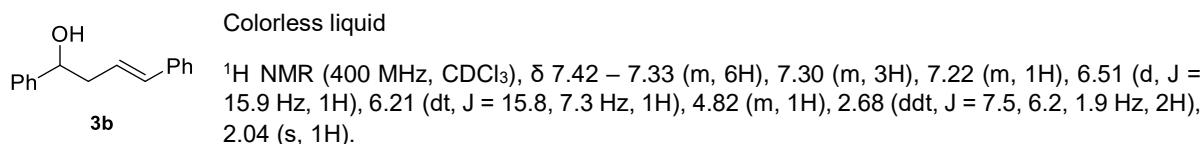


An undivided electrochemical cell with a graphite rod anode and a nickel foam cathode was used in a glove box filled with argon. In an oven-dried undivided electrochemical cell, *N*-phenyl glycine ethyl ester (0.3 mmol, 1.0 equiv.), cinnamyl chloride (0.45 mmol, 1.5 equiv.), TEMPO (9.4 mg, 0.06 mmol),

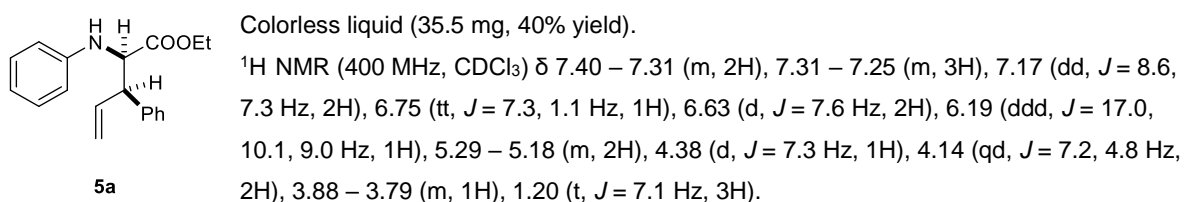
ZnCl₂ (122.7 mg, 0.9 mmol), NaOMe (16.2 mg, 0.3 mmol) and *n*Bu₄NPF₆ (116.2 mg, 0.3 mmol) was charged in anhydrous DMF (6.0 mL). Electrocatalysis was then performed at 5 mA of constant current at ambient temperature for 6 h. The reaction mixture was subsequently treated with an aqueous saturated NH₄Cl solution (6 ml). Both electrodes were washed and sonicated thoroughly with ethyl acetate (2 x 5 mL). The washings were added to the reaction mixture, and the combined phases were extracted with ethyl acetate (3 x 10 mL). Then, the organic phases were washed with an aqueous saturated NH₄Cl solution (3 x 20 mL) and dried over MgSO₄. Evaporation of the solvents and subsequent column chromatography on silica gel (*n*-hexane: ethyl acetate = 20: 1) afforded the corresponding products **5**. The NMR data was utilized to establish the diastereomeric ratio by comparing the data to the reference values, and the reported data was used to identify the diastereomer.^{9,11}



¹³C{¹H} NMR (126 MHz, CDCl₃) δ *syn* isomer 142.0, 140.4, 137.8, 128.9, 128.8, 128.3, 128.0, 127.9, 127.2, 117.4, 77.7, 58.6; δ *anti* isomer 142.0, 140.8, 138.0, 128.5, 128.5, 128.0, 127.5, 126.8, 126.7, 118.5, 77.4, 59.3. Data is in accordance with the literature.^{6,7}



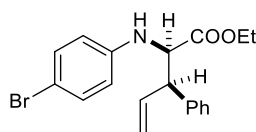
¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.0, 137.3, 133.6, 128.7, 128.6, 127.8, 127.5, 126.3, 126.0, 126.0, 73.9, 43.2. Data is in accordance with the literature.⁸



¹³C{¹H} NMR (126 MHz, CDCl₃) δ 172.8, 146.8, 139.5, 137.0, 129.4, 128.9, 128.1, 127.4, 118.7, 118.0, 113.9, 61.4, 61.1, 53.3, 14.3.

HRMS (ESI) calculated for C₁₉H₂₁NO₂ [M+Na]⁺: 318.1465, Found: 318.1465

Data is in accordance with the literature.⁹



5b

White solid (52.6 mg, 47% yield). Mp: 89-91 °C

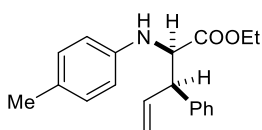
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 2H), 7.31 – 7.20 (m, 5H), 6.54 – 6.45 (m, 2H), 6.16 (ddd, $J = 16.9, 10.2, 9.0$ Hz, 1H), 5.27 – 5.17 (m, 2H), 4.31 (d, $J = 7.3$ Hz, 1H), 4.14 (qd, $J = 7.1, 4.4$ Hz, 2H), 3.85 – 3.78 (m, 1H), 1.20 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.5, 145.9, 139.2, 136.8, 132.1, 128.9, 128.1, 127.5,

118.1, 115.5, 110.4, 61.3, 61.3, 53.2, 14.3.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{20}\text{BrNO}_2$ $[\text{M}+\text{Na}]^+$: 396.0570, Found: 396.0577

Data is in accordance with the literature.⁹



5c

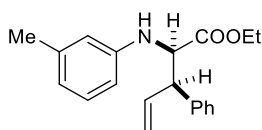
Colorless solid (33.8 mg, 36% yield). MP: 67-69 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.17 (m, 5H), 6.95 (d, $J = 7.9$ Hz, 2H), 6.54 (d, $J = 8.4$ Hz, 2H), 6.16 (ddd, $J = 17.0, 10.1, 9.0$ Hz, 1H), 5.26 – 5.15 (m, 2H), 4.32 (d, $J = 7.3$ Hz, 1H), 4.10 (qd, $J = 7.1, 5.2$ Hz, 2H), 3.86 – 3.73 (m, 1H), 2.21 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.0, 144.5, 139.6, 137.1, 129.9, 128.8, 128.1, 128.0, 127.3, 117.9, 114.1, 61.8, 61.0, 53.3, 20.5, 14.3.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 332.1621, Found: 332.1621

Data is in accordance with the literature.⁹



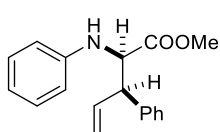
5d

Colorless liquid (21.3 mg, 23% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.55 (d, $J = 7.4$ Hz, 1H), 6.42 (m, 2H), 6.16 (ddd, $J = 16.9, 10.1, 9.0$ Hz, 1H), 5.25 – 5.16 (m, 2H), 4.34 (d, $J = 7.3$ Hz, 1H), 4.11 (dddd, $J = 17.9, 10.8, 7.1, 3.6$ Hz, 2H), 3.80 (dd, $J = 9.0, 7.2$ Hz, 1H), 2.24 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.7, 146.4, 139.5, 139.2, 136.8, 129.3, 128.9, 128.1, 127.4, 120.0, 118.1, 115.1, 111.3, 61.6, 61.1, 53.1, 21.7, 14.3.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 332.1621, Found: 332.1613



5e

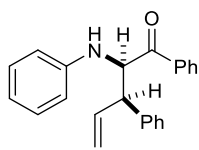
White solid (19.4 mg, 23% yield). MP: 71-74 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 7.14 (dd, $J = 8.6, 7.3$ Hz, 2H), 6.73 (t, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 2H), 6.15 (ddd, $J = 16.9, 10.1, 9.0$ Hz, 1H), 5.25 – 5.17 (m, 2H), 4.37 (d, $J = 7.4$ Hz, 1H), 3.84 – 3.78 (m, 1H), 3.65 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 173.3, 146.6, 139.4, 136.9, 129.4, 129.0, 128.1, 127.5, 118.9, 117.9, 114.0, 61.5, 53.3, 52.0.

HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 304.1308, Found: 304.1311

Data is in accordance with the literature.¹⁰



5f

Yellow solid (18.8 mg, 19% yield).

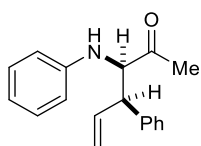
^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.84 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H), 7.31 – 7.28 (m, 1H), 7.28 – 7.08 (m, 5H), 6.81 – 6.69 (m, 2H), 6.60 – 6.51 (m, 1H), 6.37 – 6.12 (m, 1H), 5.38 (d, J = 5.0 Hz, 0.5H), 5.29 (d, J = 4.9 Hz, 0.5H), 5.28 – 5.19 (m, 1.5H), 5.02 (dt, J = 17.1, 1.3 Hz, 0.5H), 4.02 (dd, J = 9.1, 4.9 Hz, 0.5H), 3.90 (dd,

J = 8.5, 4.9 Hz, 0.5H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 199.9, 199.6, 147.5, 146.8, 140.6, 138.9, 137.3, 136.3, 136.1, 135.9, 133.6, 133.6, 129.5, 129.3, 128.9, 128.9, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 127.4, 127.3, 119.0, 118.7, 118.6, 117.8, 114.7, 114.5, 63.9, 62.9, 53.3, 52.9.

HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{21}\text{NO}$ $[\text{M}+\text{Na}]^+$: 350.1515, Found: 350.1512

Data is in accordance with the literature.¹¹



5g

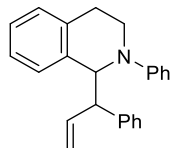
Yellow liquid (11.7 mg, 15% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.25 (m, 5H), 7.17 (m, 2H), 6.87 – 6.72 (m, 1H), 6.56 (m, 2H), 6.12 (m, 1H), 5.35 – 5.05 (m, 2H), 4.25 (m, 1H), 3.81 (t, J = 8.1 Hz, 0.7H), 3.74 (t, J = 8.1 Hz, 0.3H), 2.05 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 210.09, 209.54, 146.80, 146.08, 139.45, 138.91, 136.89, 136.46, 129.43, 129.37, 129.09, 128.92, 128.14, 128.03, 127.59, 127.43, 119.07, 118.72,

118.40, 117.99, 113.93, 113.71, 67.93, 67.86, 52.68, 52.01, 27.74, 27.47.

HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{19}\text{NO}$ $[\text{M}+\text{H}]^+$: 266.1539, Found: 266.1529



5h

Colorless liquid (22.7 mg, 23% yield).

^1H NMR (400 MHz, CDCl_3) δ (*R,S*)-**5g** 7.35 – 6.82 (m, 12H), 6.79 – 6.74 (m, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.29 (ddd, J = 17.0, 10.2, 8.8 Hz, 1H), 5.23 – 5.10 (m, 2H), 5.06 (m, 1H), 3.91 (dd, J = 8.7, 7.0 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.48 – 3.30 (m, 1H), 2.72 (dt, J = 15.9, 5.7 Hz, 1H),

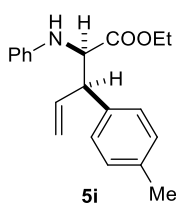
2.13 (ddd, J = 15.1, 8.5, 5.8 Hz, 1H). δ (*R,R*)-**5g** 7.35 – 6.82 (m, 13H), 6.74 – 6.70 (m, 1H), 6.11 (dt, J = 16.9, 9.8 Hz, 1H), 5.05 – 4.94 (m, 3H), 3.97 (dd, J = 9.5, 5.9 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.48 – 3.30 (m, 1H), 2.92 (td, J = 6.4, 3.5 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (*R,S*)-**5g** 149.5, 141.5, 139.5, 136.0, 135.9, 129.4, 129.3, 128.3, 128.1, 128.1, 127.0, 126.8, 125.3, 117.0, 116.1, 113.1, 64.7, 56.6, 43.0, 27.1.

δ (*R,R*)-**5g** 149.8, 142.2, 139.1, 136.0, 135.6, 129.2, 129.0, 128.5, 128.4, 128.4, 126.9, 126.5, 125.1, 117.5, 117.2, 114.5, 64.1, 56.4, 42.6, 27.3.

HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{23}\text{N}$ $[\text{M}+\text{H}]^+$: 326.1903, Found: 326.1910

The information of each isomer, which is in accordance with the literature, was identified based on literature reference.¹¹



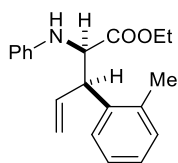
5i

Yellow gum (18.4 mg, 20% yield).

^1H NMR (500 MHz, CDCl_3) δ 7.18 – 7.09 (m, 6H), 6.76 – 6.69 (m, 1H), 6.61 (d, J = 8.0 Hz, 2H), 6.14 (dt, J = 17.1, 9.6 Hz, 1H), 5.25 – 5.11 (m, 2H), 4.32 (d, J = 7.3 Hz, 1H), 4.18 – 4.04 (m, 2H), 3.78 (t, J = 8.2 Hz, 1H), 2.32 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.8, 146.6, 137.1, 137.1, 136.3, 129.6, 129.4, 128.0, 119.0, 117.8, 114.2, 61.6, 61.2, 52.8, 21.2, 14.3.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 332.1621, Found: 332.1615



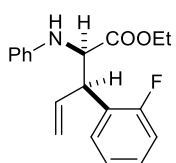
5j

White solid (25.1 mg, 27% yield). MP: 87-90 °C

^1H NMR (500 MHz, CDCl_3) δ 7.24 – 7.11 (m, 6H), 6.74 (tt, J = 7.3, 1.2 Hz, 1H), 6.64 – 6.58 (m, 2H), 6.03 (dt, J = 17.3, 9.3 Hz, 1H), 5.26 – 5.02 (m, 2H), 4.37 (d, J = 8.5 Hz, 1H), 4.17 – 4.06 (m, 2H), 4.03 (t, J = 8.7 Hz, 1H), 2.39 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.3, 146.7, 137.4, 136.7, 136.5, 131.0, 129.4, 127.0, 126.8, 126.5, 118.8, 118.0, 114.0, 61.1, 60.7, 49.0, 19.8, 14.3.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 332.1621, Found: 332.1613



5k

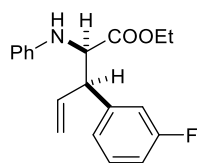
Yellow liquid (30.1 mg, 32% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.18 (m, 2H), 7.18 – 7.00 (m, 4H), 6.72 (tt, J = 7.3, 1.1 Hz, 1H), 6.63 (d, J = 7.5 Hz, 2H), 6.18 (dddd, J = 16.8, 10.3, 9.1, 1.2 Hz, 1H), 5.29 – 5.18 (m, 2H), 4.44 (d, J = 7.5 Hz, 1H), 4.17 – 4.03 (m, 3H), 1.16 (t, J = 7.1 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.7, 161.9, 159.9, 146.6, 135.2, 129.4, 129.3, 129.3, 128.9, 128.8, 126.9, 126.8, 124.4, 124.4, 119.0, 118.7, 115.9, 115.7, 114.0, 61.2, 60.3, 60.3, 46.5, 14.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -117.4.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{20}\text{FNO}_2$ $[\text{M}+\text{Na}]^+$: 336.1370, Found: 336.1364



5l

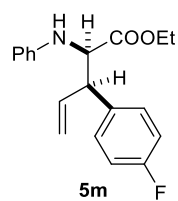
Yellow liquid (32.9 mg, 35% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.24 (m, 1H), 7.16 (dd, J = 8.6, 7.3 Hz, 2H), 7.04 (dt, J = 7.7, 1.3 Hz, 1H), 7.02 – 6.90 (m, 2H), 6.75 (tt, J = 7.3, 1.1 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.13 (ddd, J = 16.6, 10.5, 9.1 Hz, 1H), 5.29 – 5.18 (m, 2H), 4.35 (d, J = 7.1 Hz, 1H), 4.11 (qd, J = 7.2, 2.2 Hz, 2H), 3.81 (dd, J = 9.1, 7.0 Hz, 1H), 1.18 (t, J = 7.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.5, 164.0, 162.1, 146.6, 142.2, 142.1, 136.3, 130.3, 130.3, 129.4, 123.8, 123.8, 118.9, 118.5, 115.2, 115.1, 114.4, 114.2, 114.1, 61.4, 61.3, 53.0, 52.9, 14.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -112.6.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{20}\text{FNO}_2$ $[\text{M}+\text{Na}]^+$: 336.1370, Found: 336.1369



5m

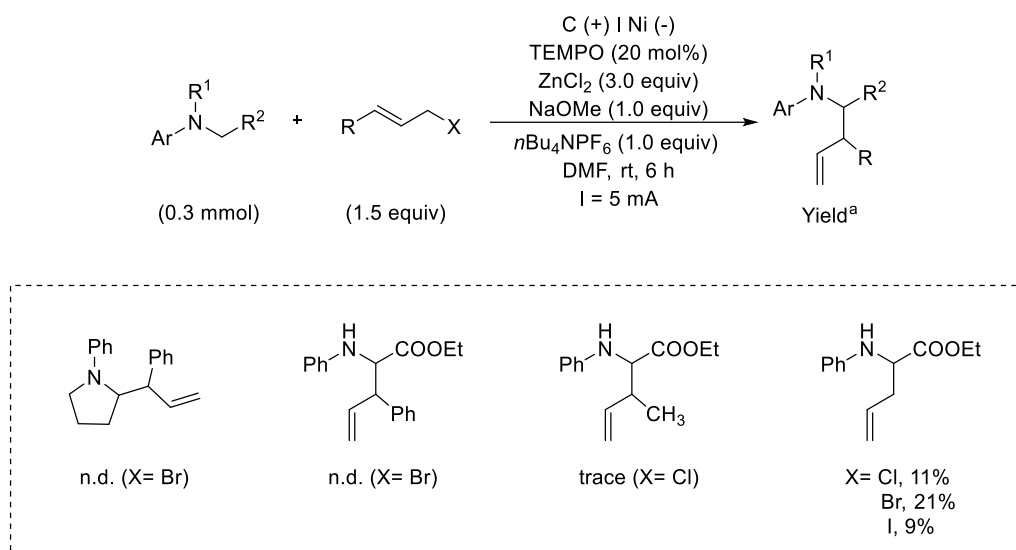
Brown solid (28.3 mg, 30% yield). MP: 75-77 °C

^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.15 (m, 2H), 7.19 – 7.10 (m, 2H), 7.07 – 6.96 (m, 2H), 6.74 (tt, J = 7.3, 1.1 Hz, 1H), 6.65 – 6.57 (m, 2H), 6.20 – 6.06 (m, 1H), 5.27 – 5.16 (m, 2H), 4.33 (d, J = 7.1 Hz, 1H), 4.11 (qd, J = 7.1, 4.4 Hz, 2H), 3.81 (dd, J = 9.0, 7.1 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.6, 163.1, 161.1, 146.7, 136.8, 135.3, 135.2, 129.7, 129.6, 129.4, 118.9, 118.2, 115.8, 115.6, 114.0, 61.5, 61.2, 52.5, 14.3.

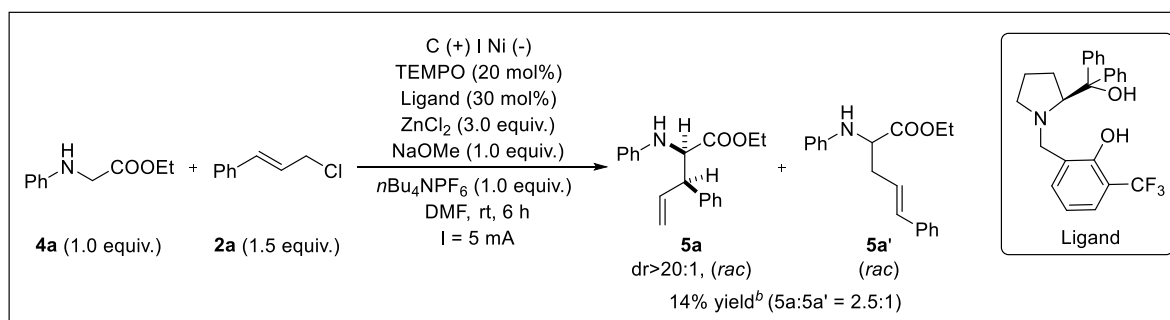
$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -115.4.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{20}\text{FNO}_2$ $[\text{M}+\text{Na}]^+$: 336.1370, Found: 336.1363



^aYields were determined by ¹H NMR using mesitylene as an internal standard

Scheme S1. Unsuccessful substrate scopes.



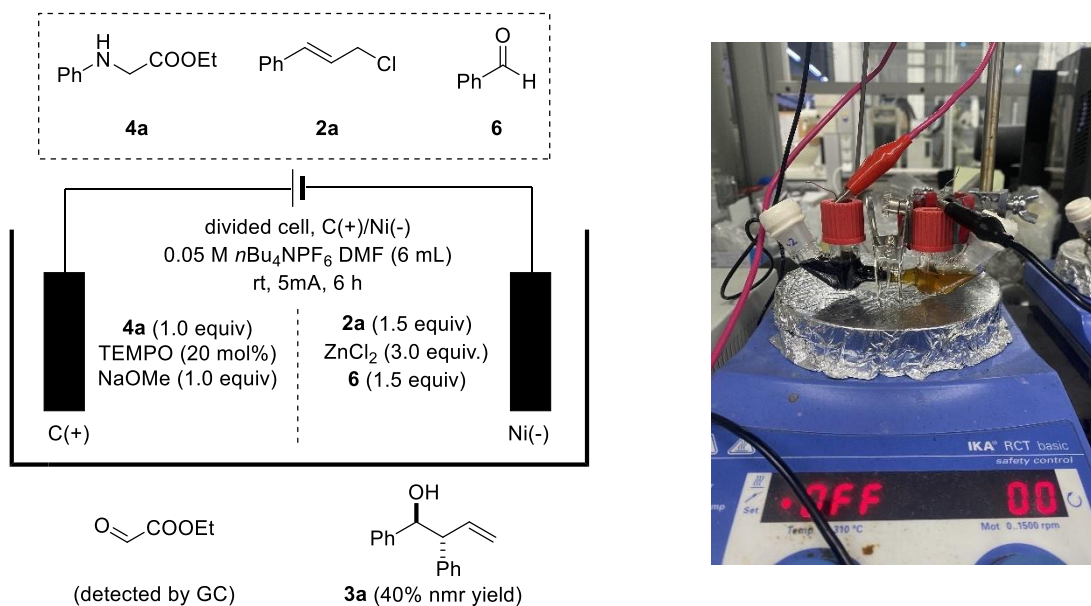
^a Reaction conditions: *N*-phenyl glycine ethyl ester (0.3 mmol) and cinnamyl chloride (0.6 mmol) in 6 mL of DMF.

^b Yields were determined by ¹H NMR using mesitylene as an internal standard.

^c ee was measured with chiral cobalt complex in ¹H NMR.¹²

^d Ligand was synthesized according to the reference.¹³

Scheme S2. Reaction with chiral ligand



^aYields were determined by ¹H NMR using mesitylene as an internal standard

Scheme S3. Reaction with divided cell

5. Cyclic voltammetry experiments

The cyclic voltammetry measurements were conducted in a 10 mL glass vial with Ag/Ag⁺ as the reference electrode. A glassy carbon (3 mm diameter) was used as the working electrode and a platinum wire as the counter electrode. The solution was bubbled with argon gas for 5 minutes before data collection. The redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured and used to provide an internal reference. The measurements were recorded at a scan rate of 10 mVs⁻¹.

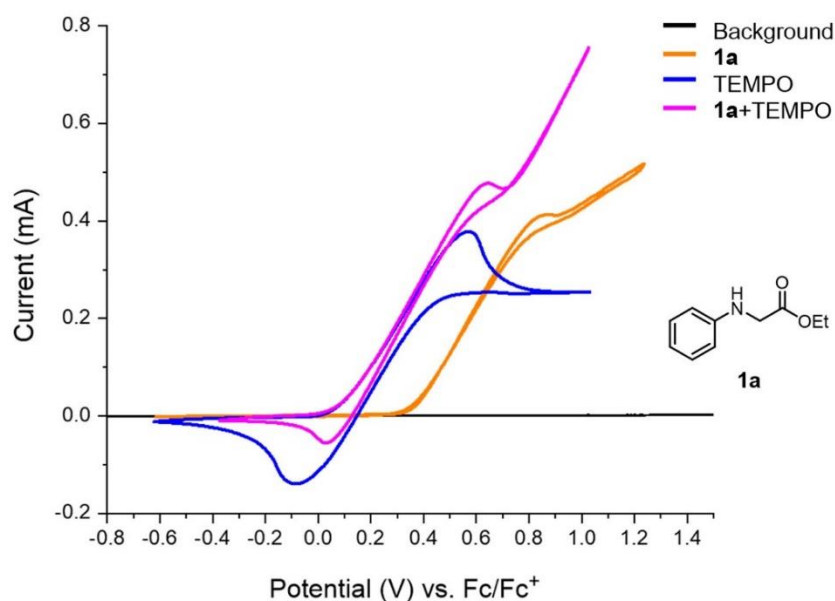


Fig S2. Cyclic voltammetry (CV) study of in 0.05 M $\text{KPF}_6/\text{CH}_3\text{CN}$ supporting electrolyte

6. Identification of reduced zinc

The inductively coupled plasma-optical emission spectroscopy (ICP-OES)

After the reaction, the electrodes were removed from the electrolyte solution and washed with ethanol and acetone. The electrodes were placed in the concentrated HCl solution for complete etching to prepare the sample solutions. The ICP-OES (5110 ICP-OES, Agilent) was used to accurately measure the Ni and Zn contents.

X-ray photoelectron spectroscopy (XPS) analysis

After the reaction, the electrodes were removed from the electrolyte solution and washed with ethanol and acetone. The electrodes were characterized by XPS to identify the zinc surface deposition. The measurements were performed using the XPS system (Thermo VG Scientific K-alpha)

The XPS spectra of nickel electrodes were measured that underwent a general procedure for cinnamylation of amines using paired electrolysis. The XPS spectra of (a) and (b) were measured after the reaction with both **1a** and **2a**.

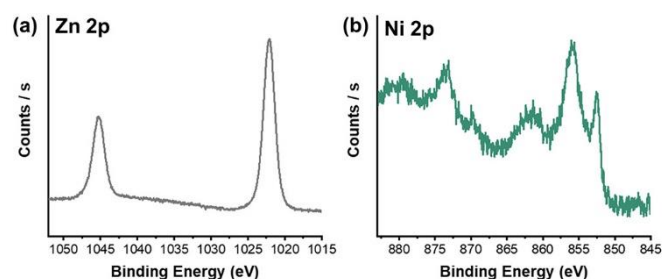


Fig S3. XPS spectra of nickel electrode after reaction

Scanning electron microscopy (SEM)

After the reaction, the electrodes were removed from the electrolyte solution and washed with ethanol and acetone. The electrodes were analyzed by SEM to confirm their surface morphology. The SEM images were acquired from Magellan400 (KAIST, 10 kV, 100 pA)

The SEM images were taken of the nickel electrode that underwent a general procedure for cinnamylation of amines using paired electrolysis with only **1a** (without **2a**).

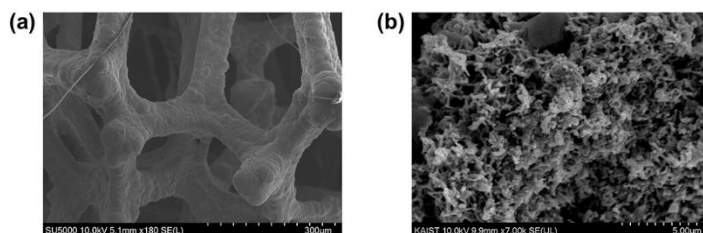
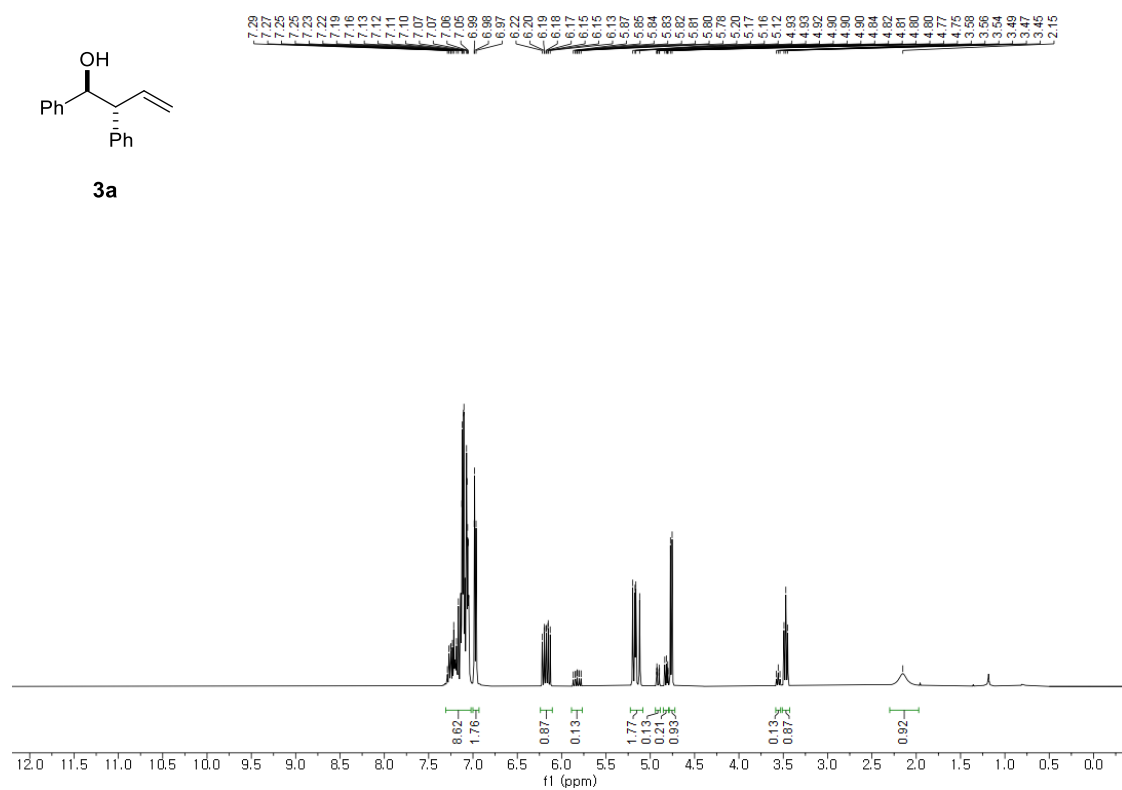


Fig S4. SEM image of nickel electrode (a) before reaction (b) after reaction without 2a

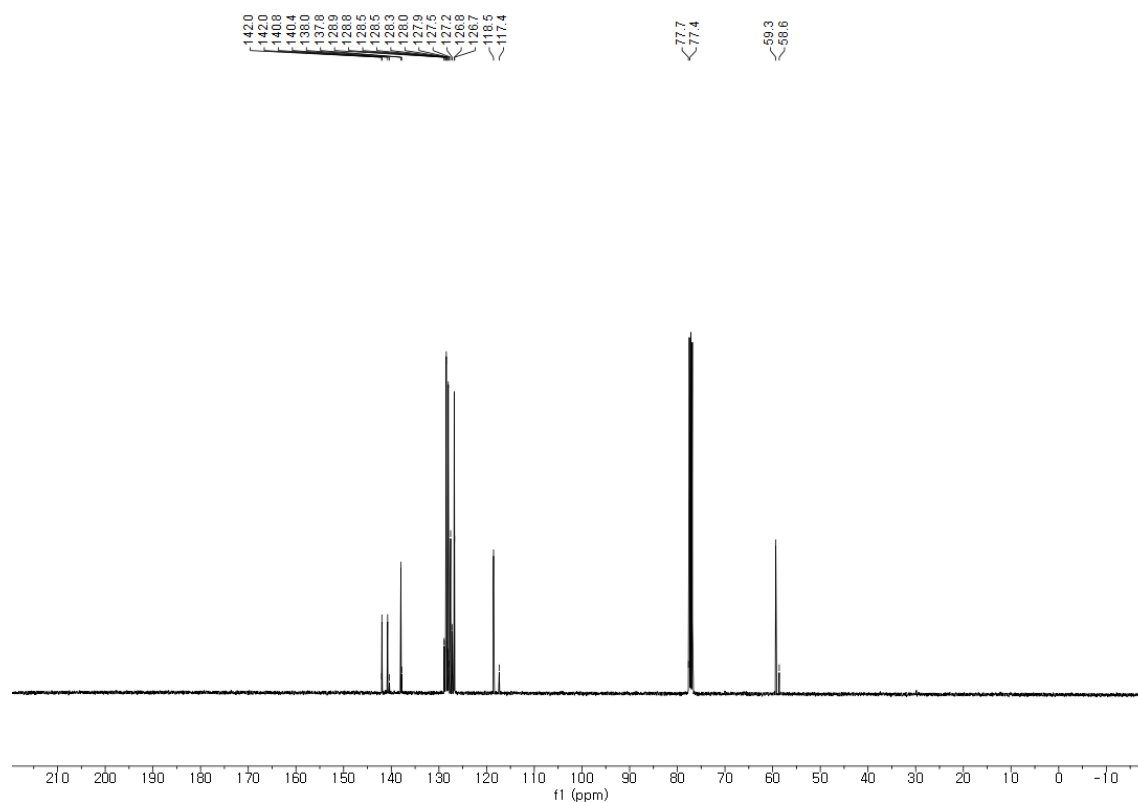
7. References

1. L. A. Brozek, M. J. Ardolino, J. P. Morken, *J. Am. Chem. Soc.*, 2011, **42**, 16778.
2. J. Xie, Z. Huang, *Angew. Chem.*, 2010, **122**, 10379.
3. F. J. Lankner, M. A. Parker, B. Rogovoy, A. Khvat, A. Ivachtchenko, *Synthesis*, 2009, **12**, 1987.
4. M. C. Cruz, F. Jimenez, F. Delgado, J. Tamariz, *Synlett*, 2006, **5**, 749.
5. L. Yang, Z. Qiu, J. Wu, J. Zhao, T. Shen, X. Huang, Z. Liu, *Org. Lett.*, 2021, **23**, 3207.
6. S. Araki, T. Kamei, T. Hirashita, H. Yamamura, M. Kawai, *Org. Lett.*, 2000, **2**, 847.
7. J. M. Coxon, S. J. Van Eyk, P. J. Steel, *Tetrahedron*, 1989, **45**, 1029.
8. S. Teng, M. E. Tessensohn, R. D. Webster, J. S. Zhou, *ACS Catal.*, 2018, **8**, 7439.
9. N. A. Aslam, V. Rajkumar, C. Reddy, M. Yasuda, A. Baba, S. A. Babu, *Eur. J. Org. Chem.*, 2012, **23**, 4395.
10. R. K. Everett, J. P. Wolfe, *J. Org. Chem.*, 2015, **80**, 9041.
11. J. Zhang, B. Breit, *Angew. Chem. Int. Ed.*, 2019, **58**, 3392.
12. S. Jang, H. Kim, *Org. Lett.*, 2020, **22**, 4185.
13. K. Li, X. Sun, S. Zhao, T. Li, Z. Zha, Z. Wang, *Chem. Commun.*, 2022, 58, 2156.

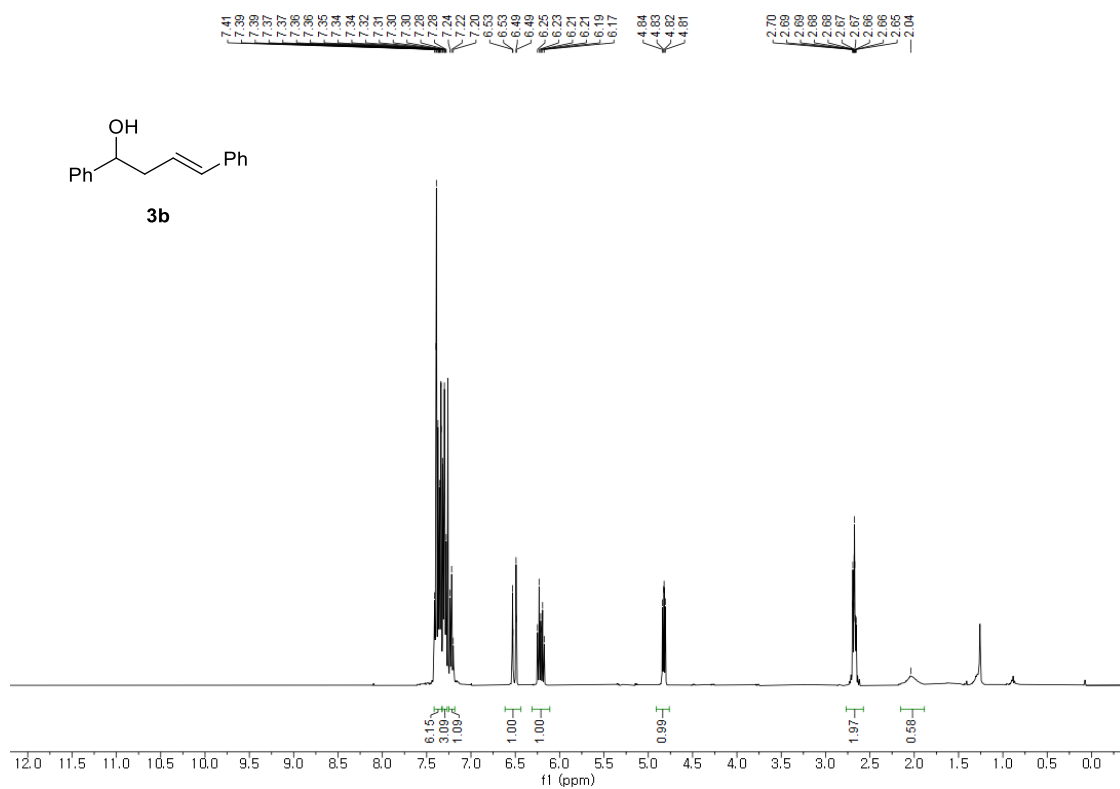
8. NMR spectra



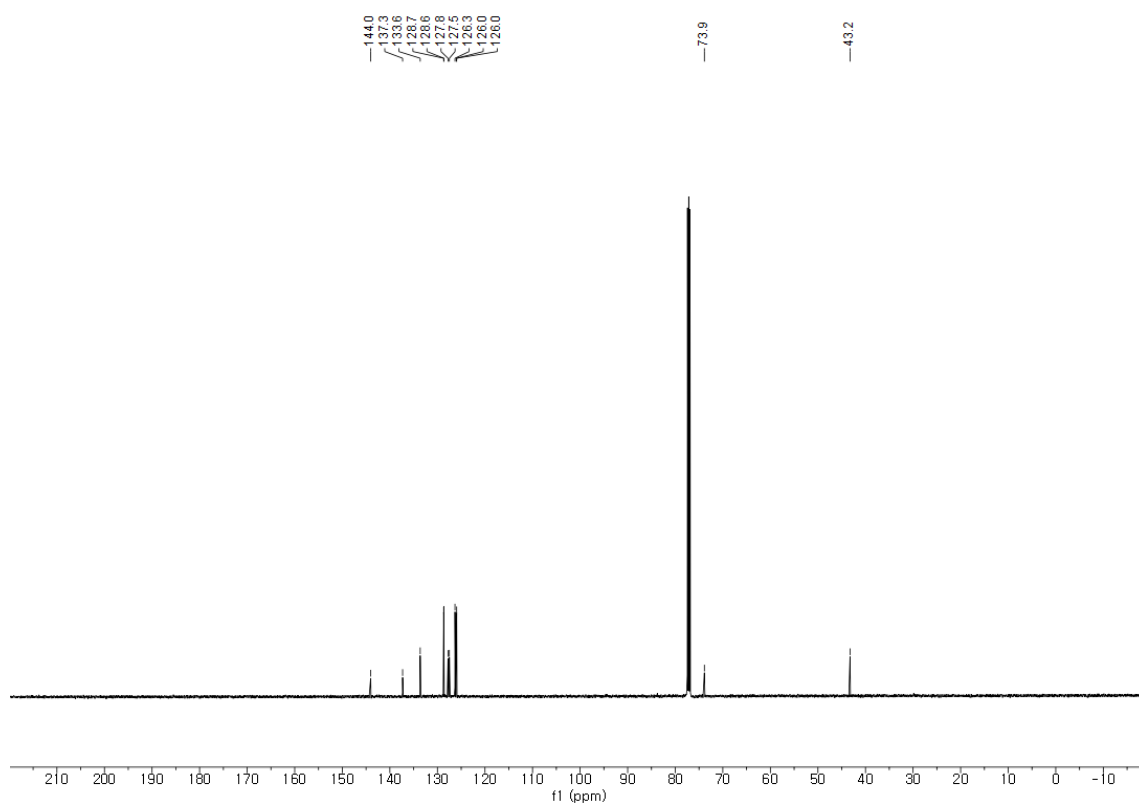
¹H NMR spectrum (400 MHz, CDCl₃) of **3a**



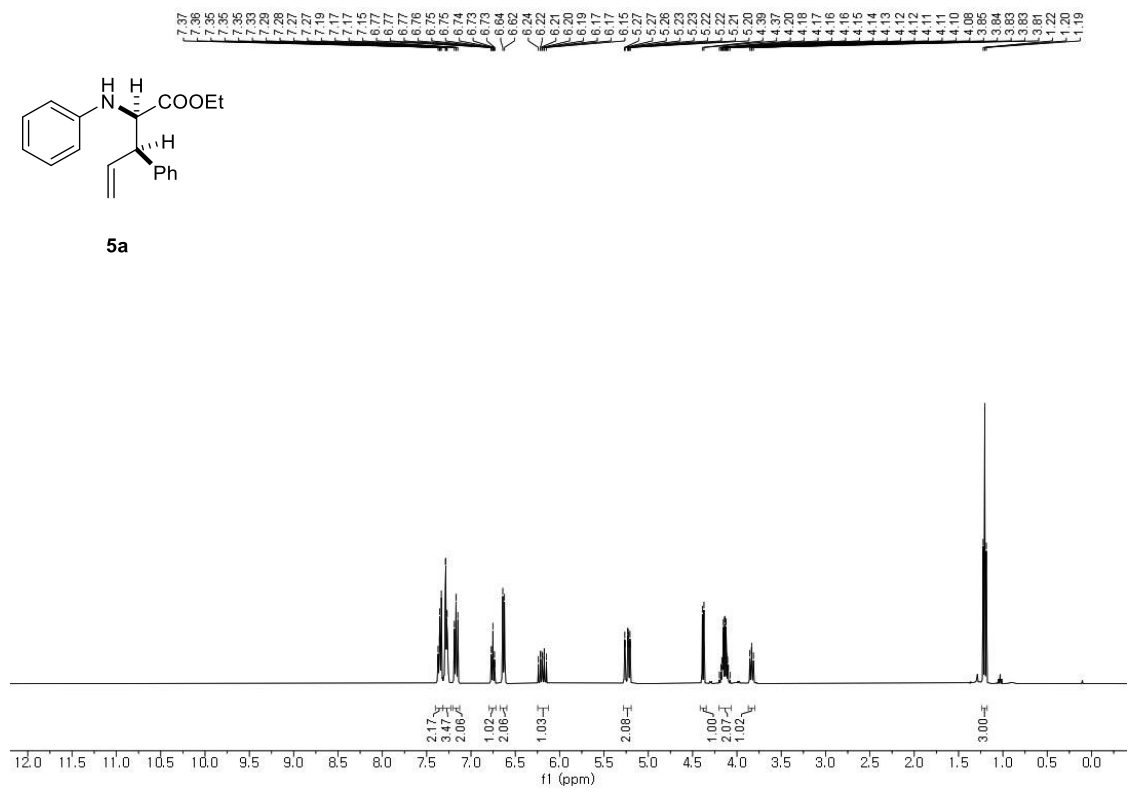
¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **3a**



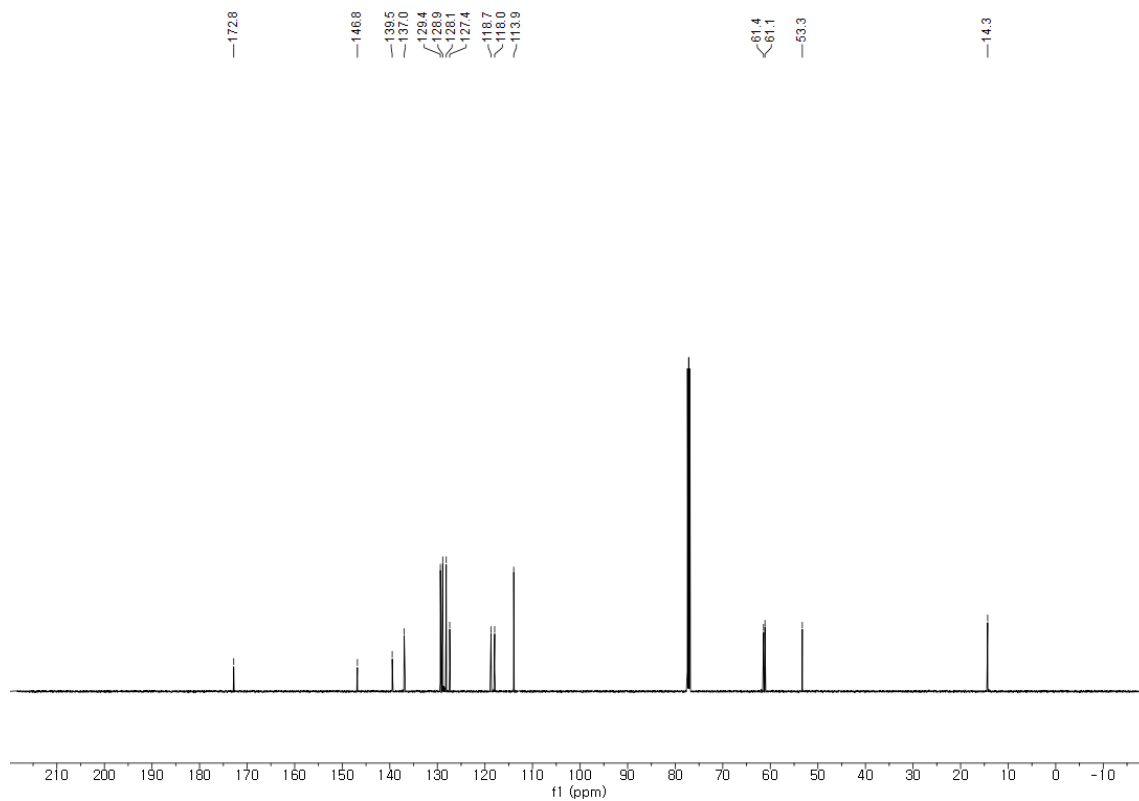
¹H NMR spectrum (400 MHz, CDCl₃) of **3b**



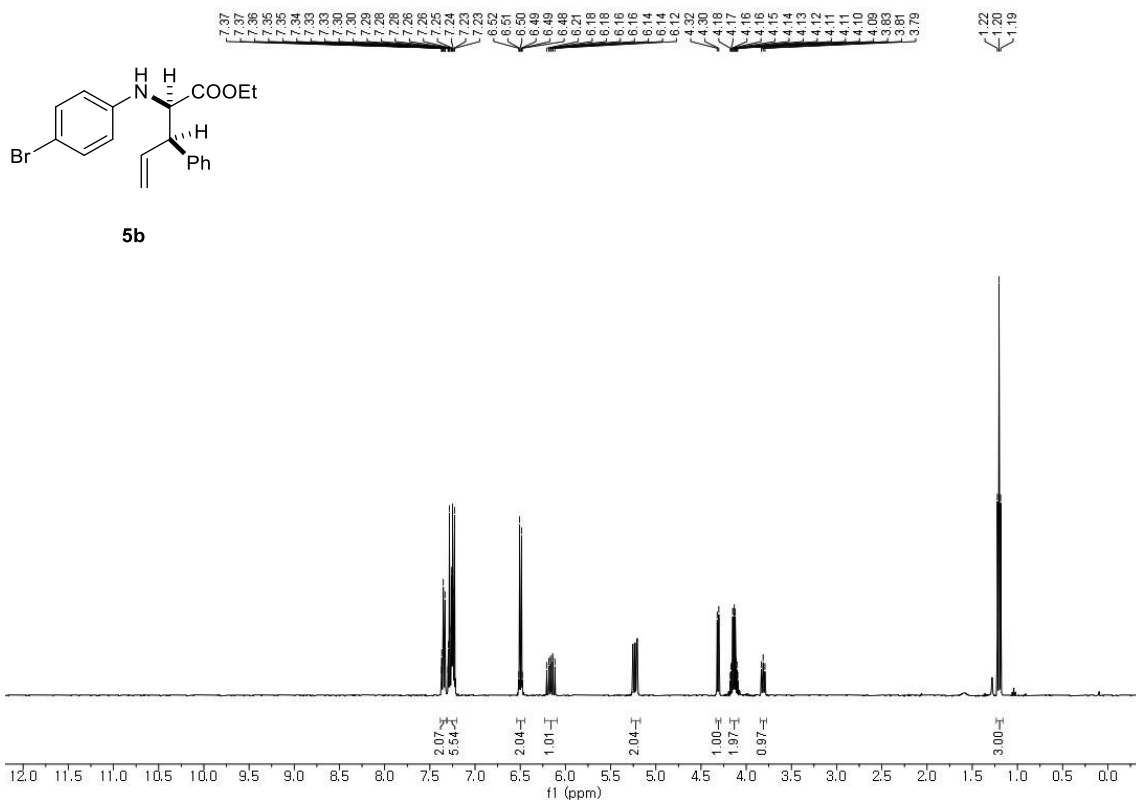
¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **3b**



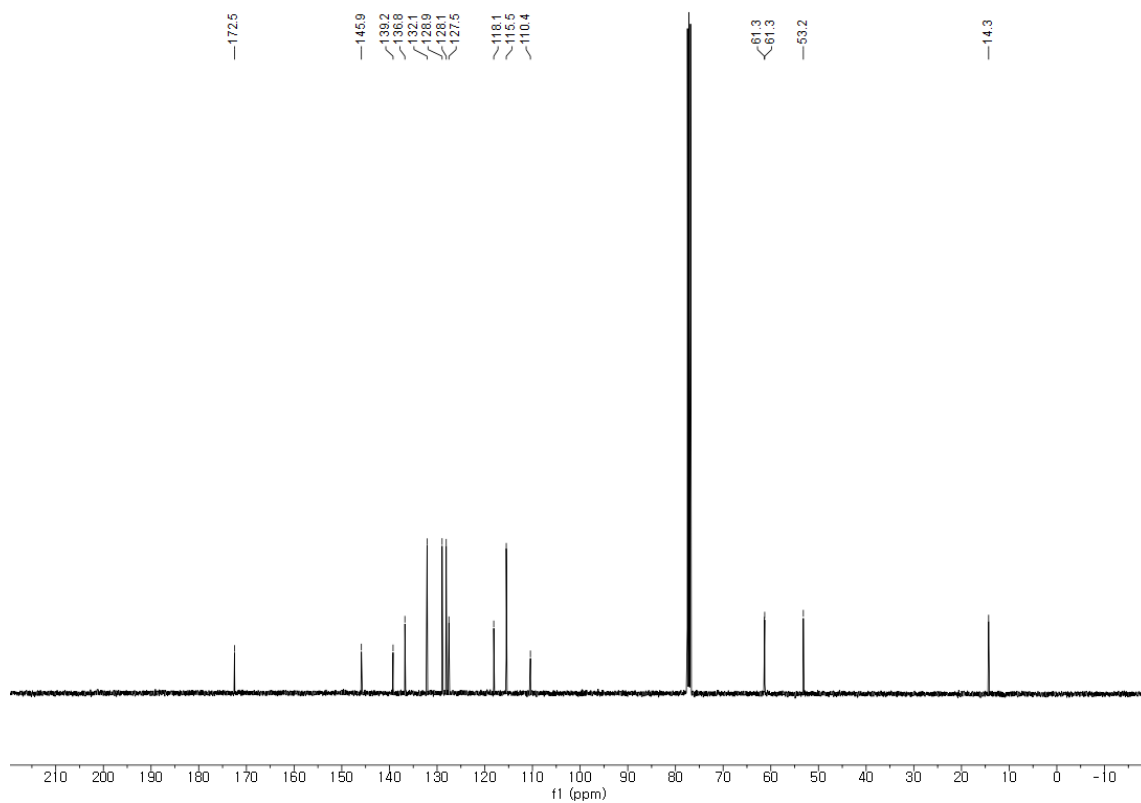
¹H NMR spectrum (400 MHz, CDCl₃) of **5a**



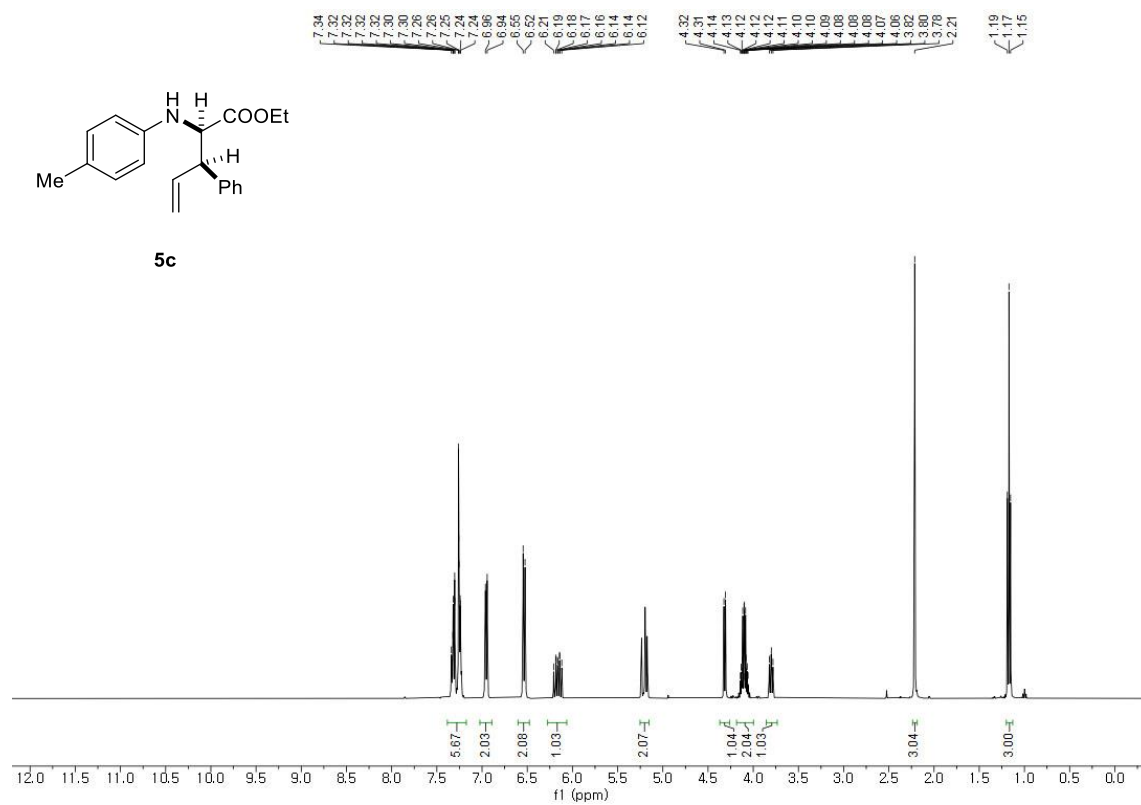
¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **5a**



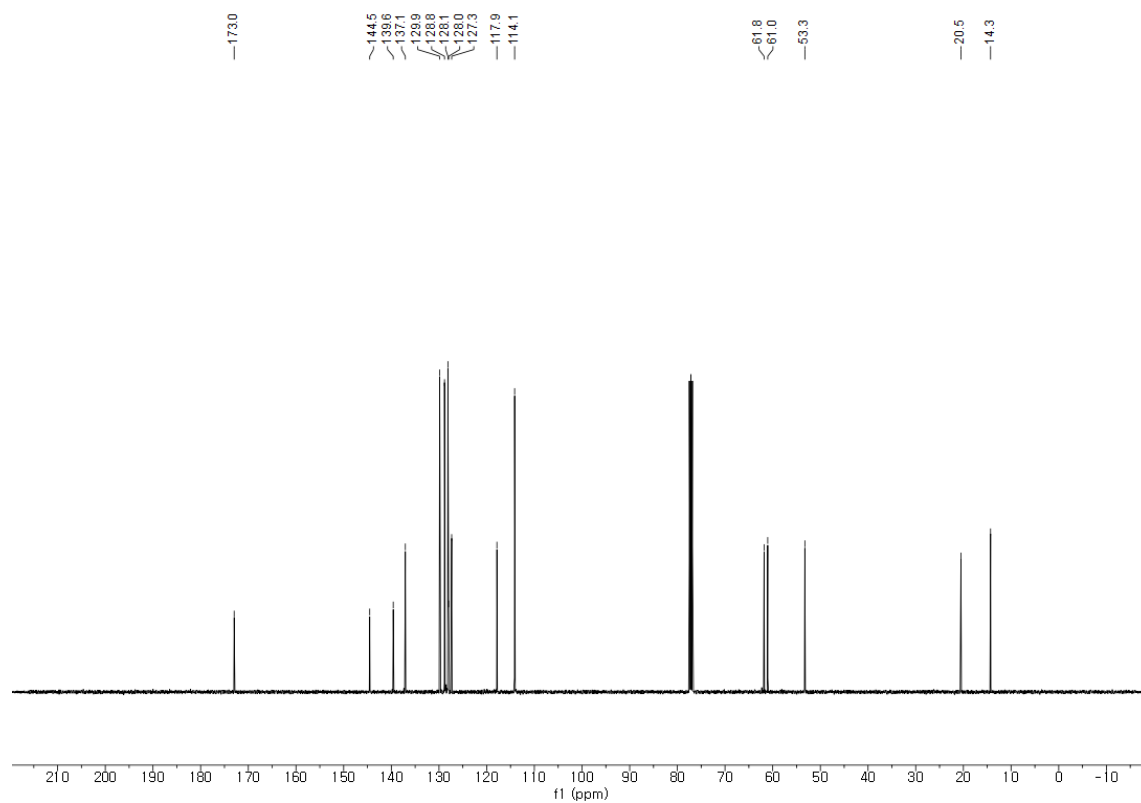
^1H NMR spectrum (400 MHz, CDCl_3) of **5b**



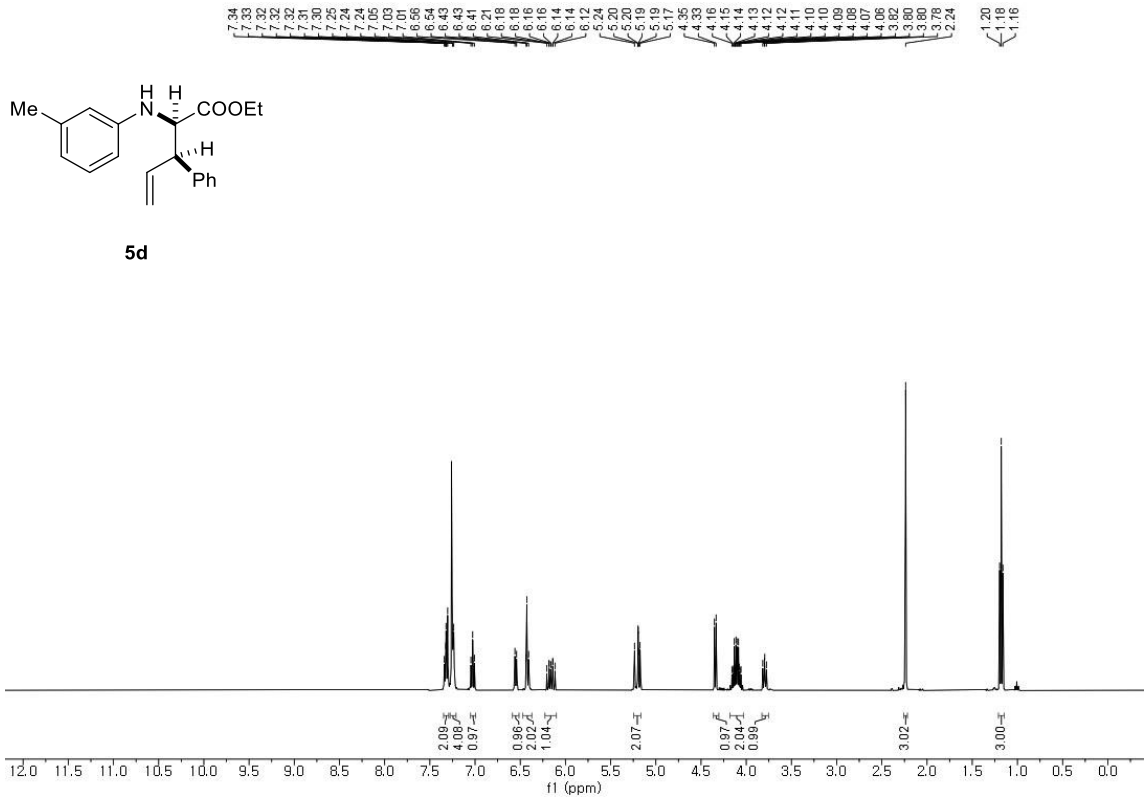
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **5b**



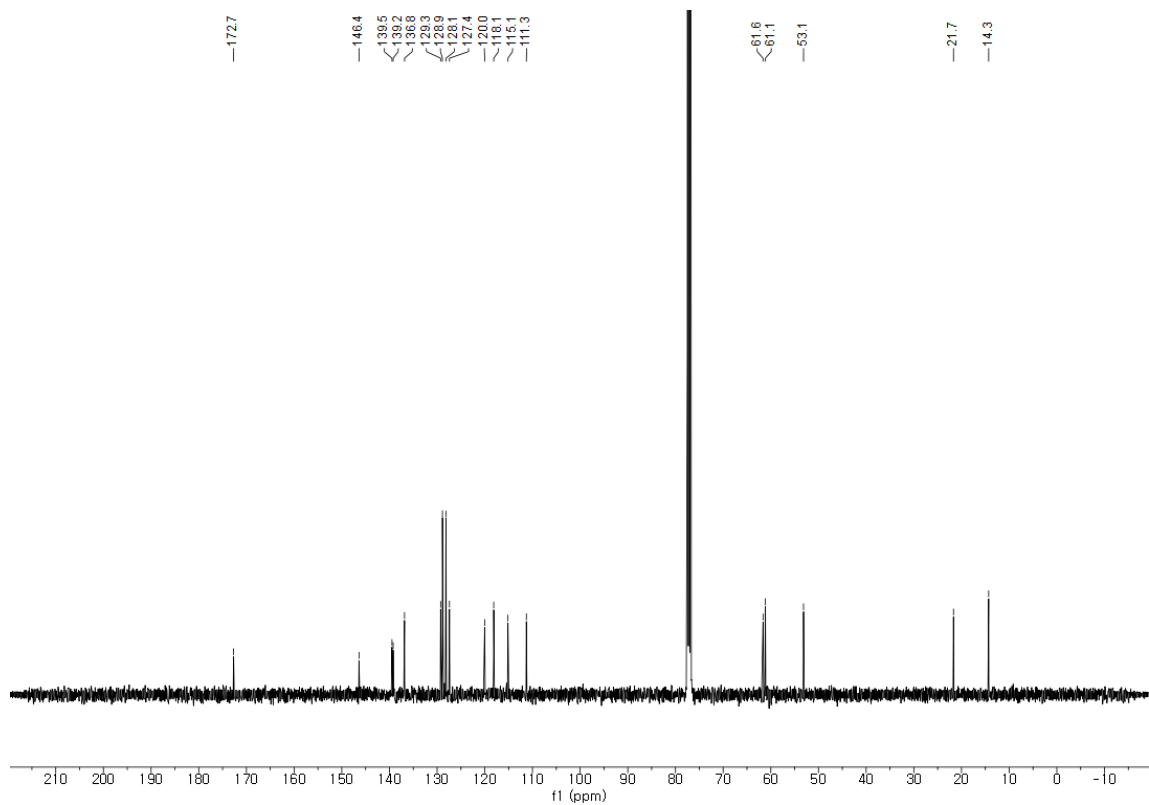
^1H NMR spectrum (400 MHz, CDCl_3) of **5c**



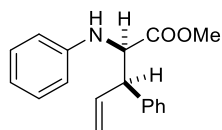
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **5c**



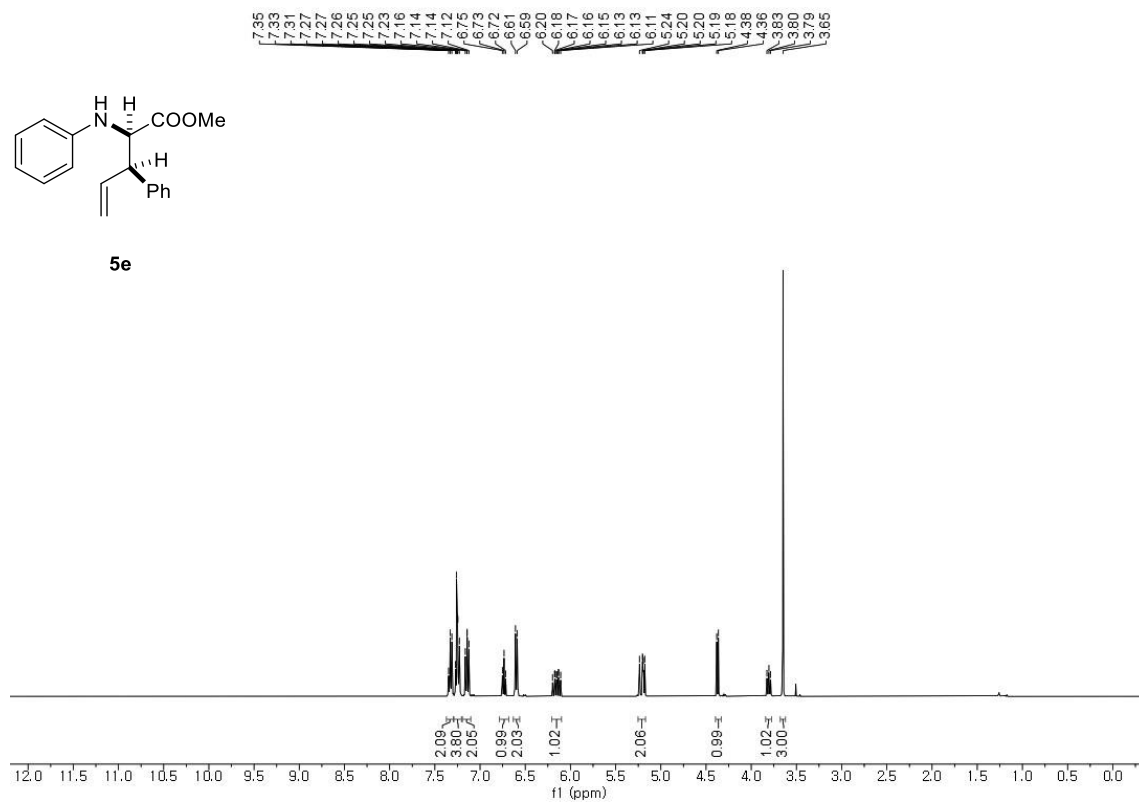
^1H NMR spectrum (400 MHz, CDCl_3) of **5d**



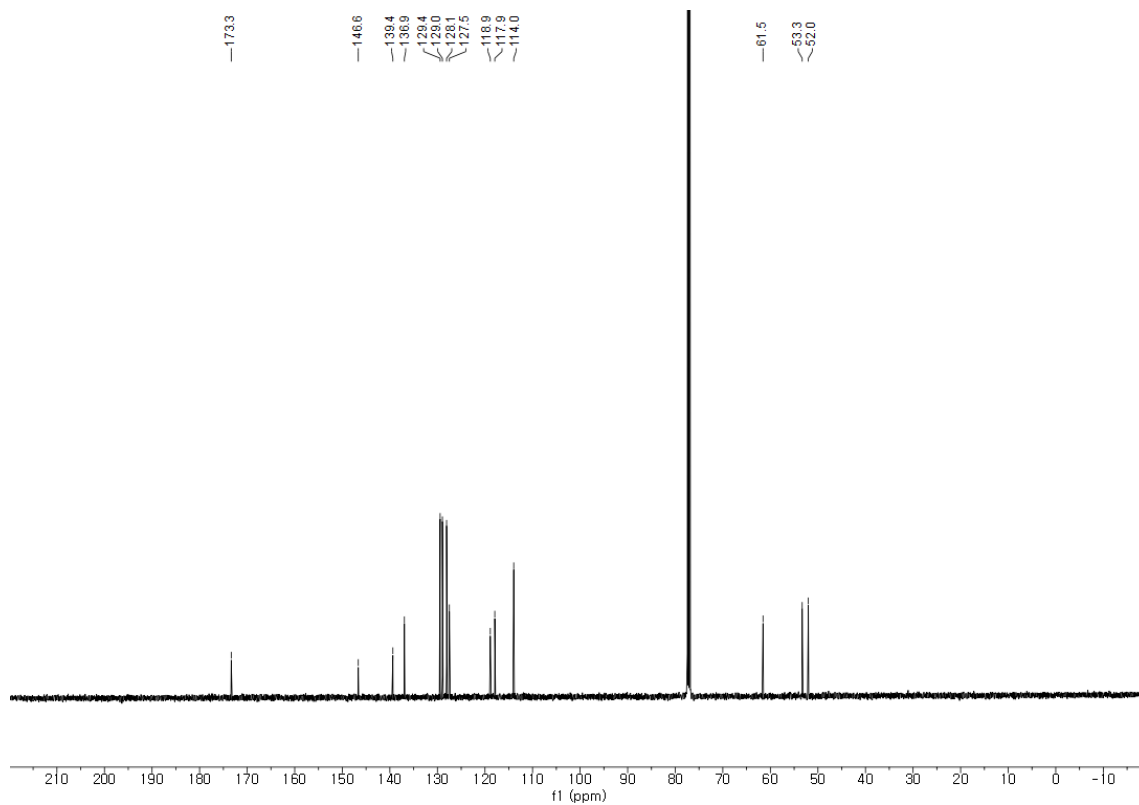
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3) of **5d**



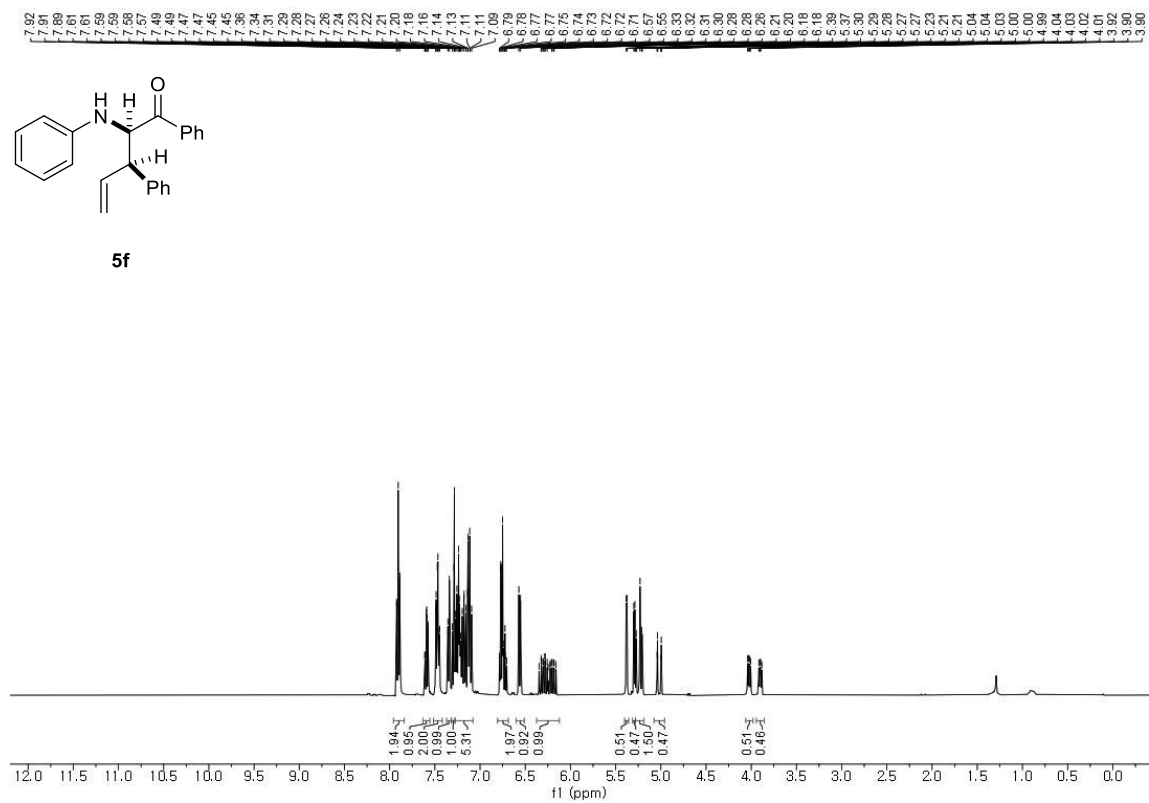
5e



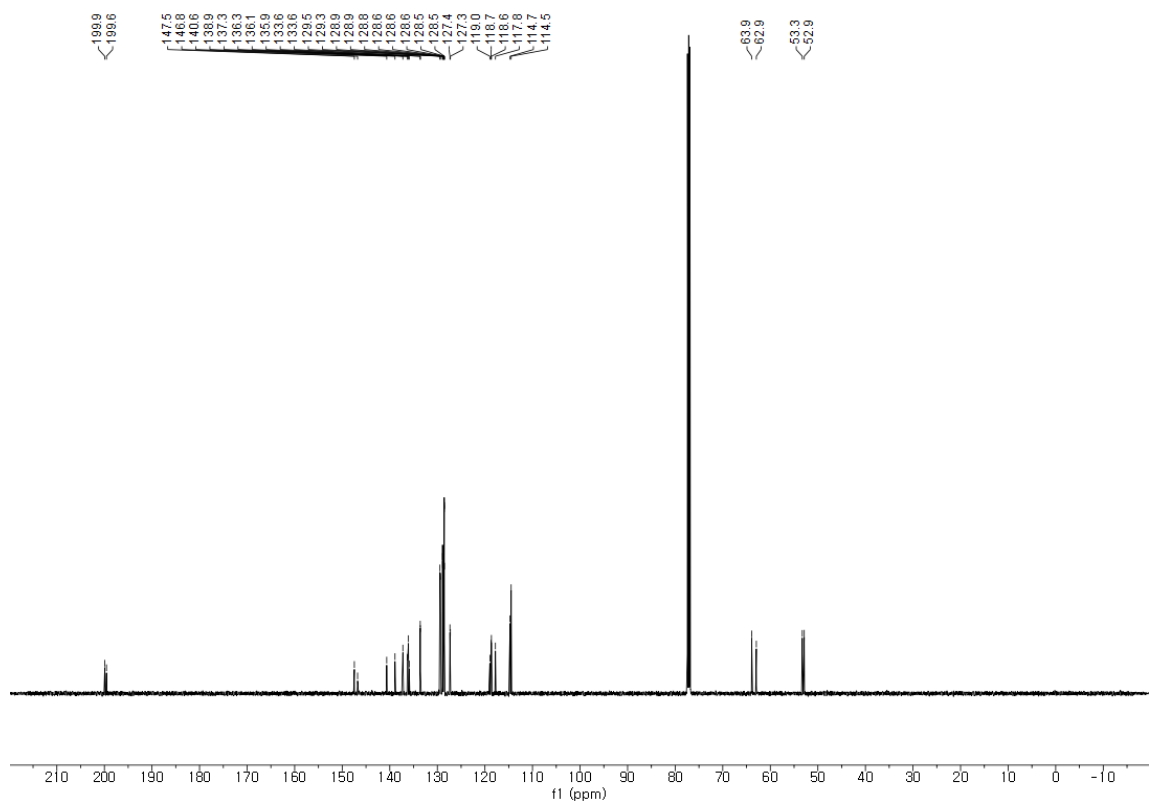
^1H NMR spectrum (400 MHz, CDCl_3) of **5e**



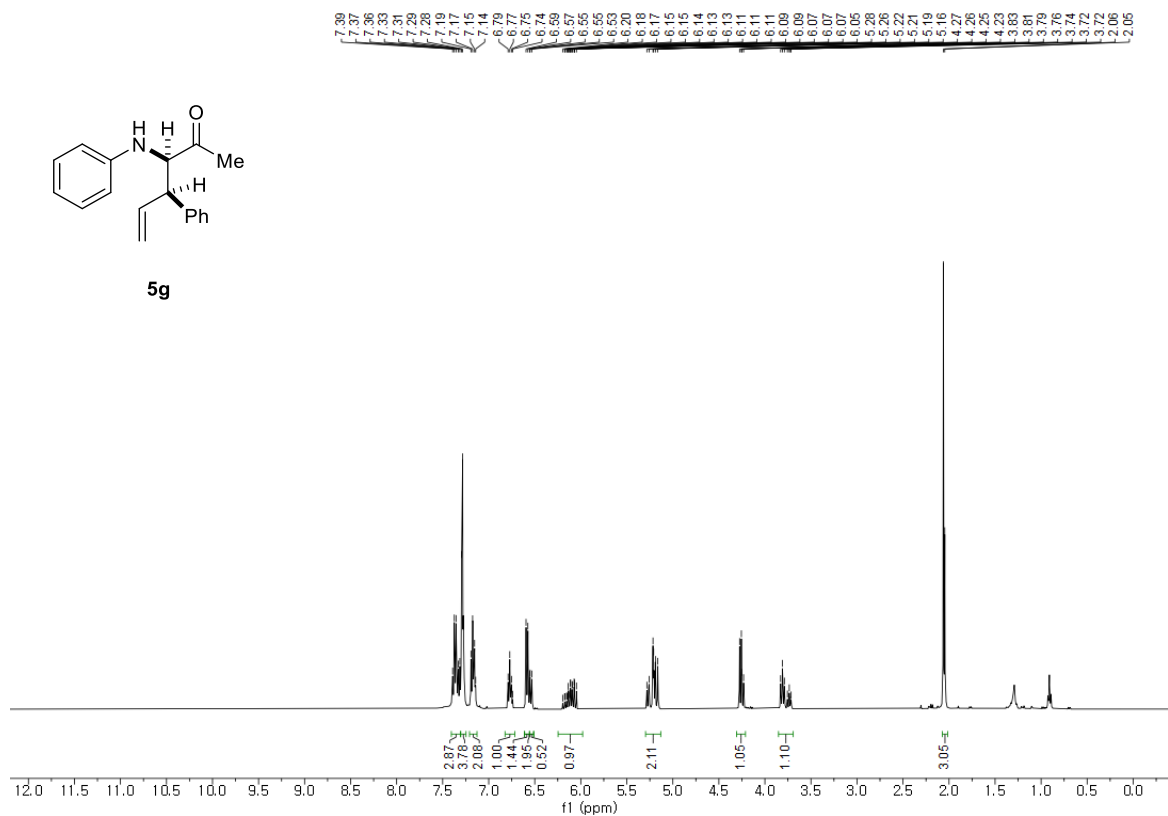
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **5e**



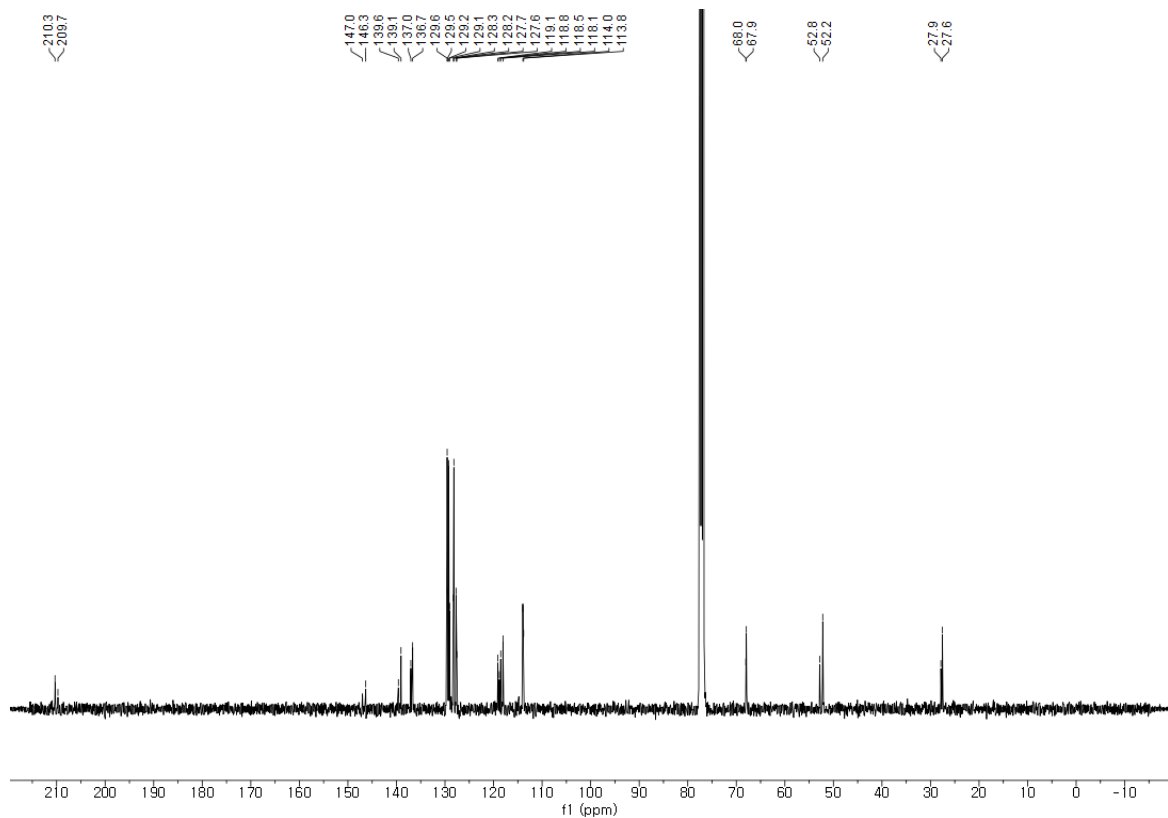
^1H NMR spectrum (400 MHz, CDCl_3) of **5f**



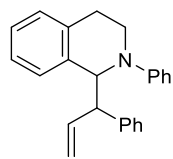
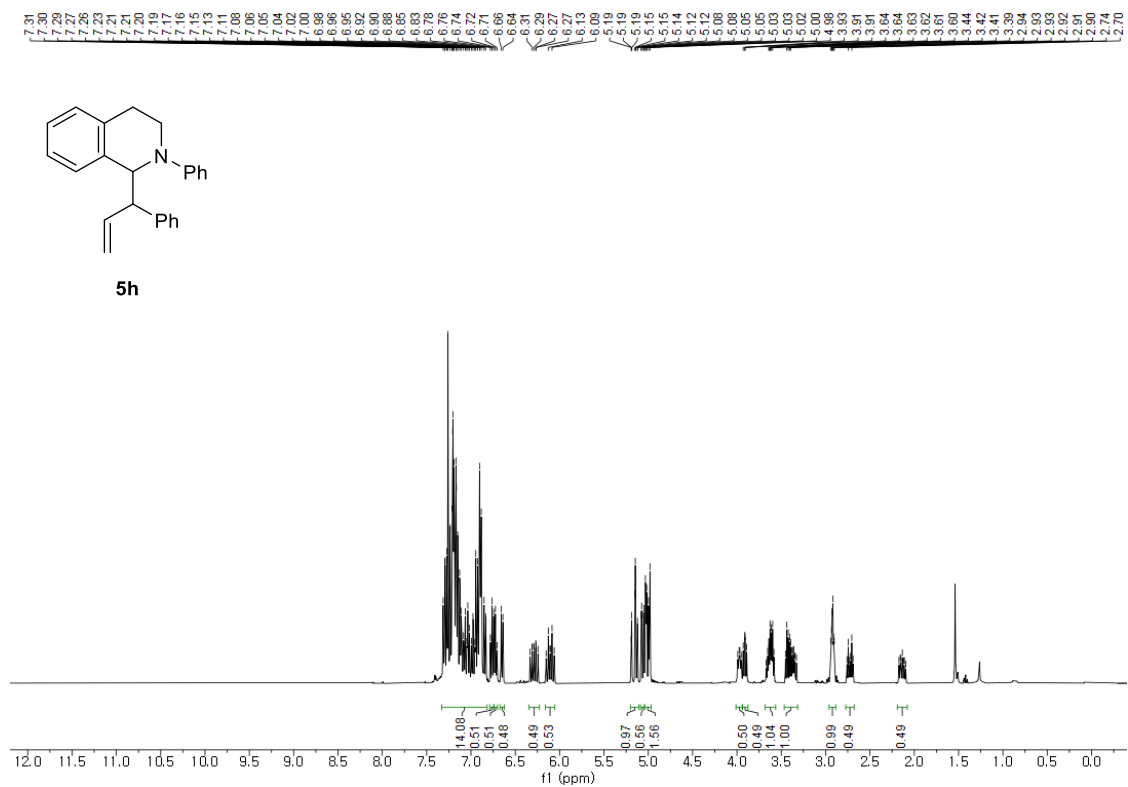
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **5f**



1H NMR spectrum (400 MHz, CDCl₃) of 5g

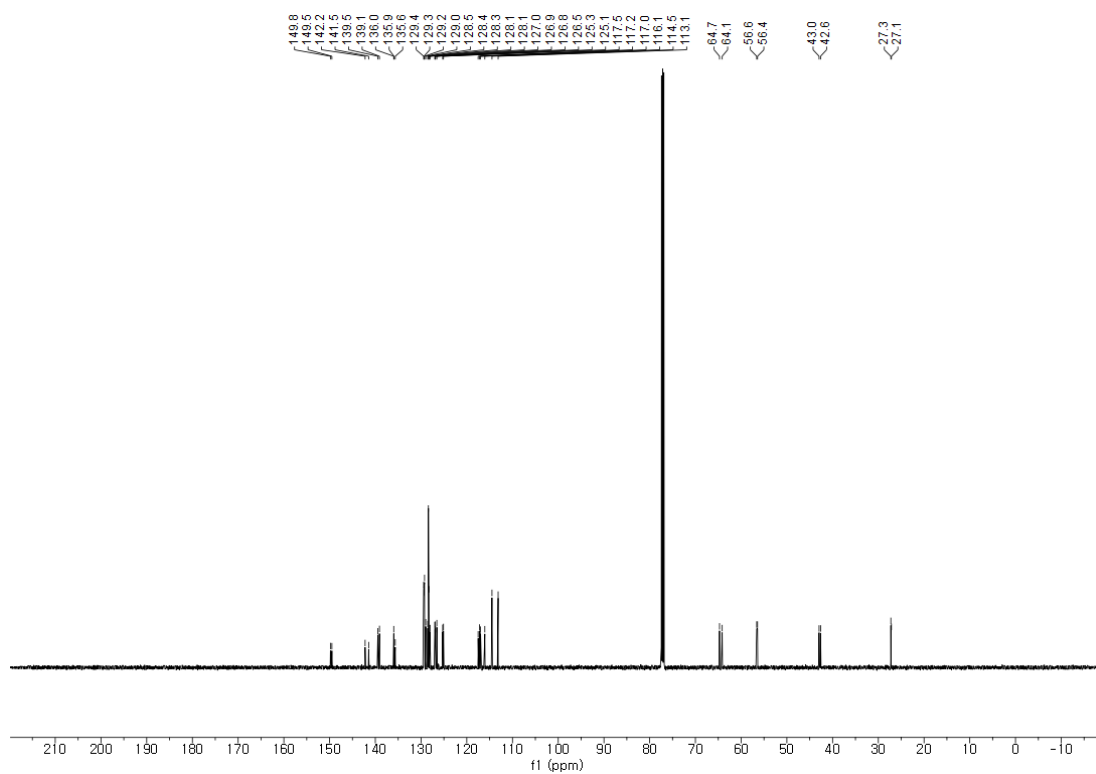


¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of 5g

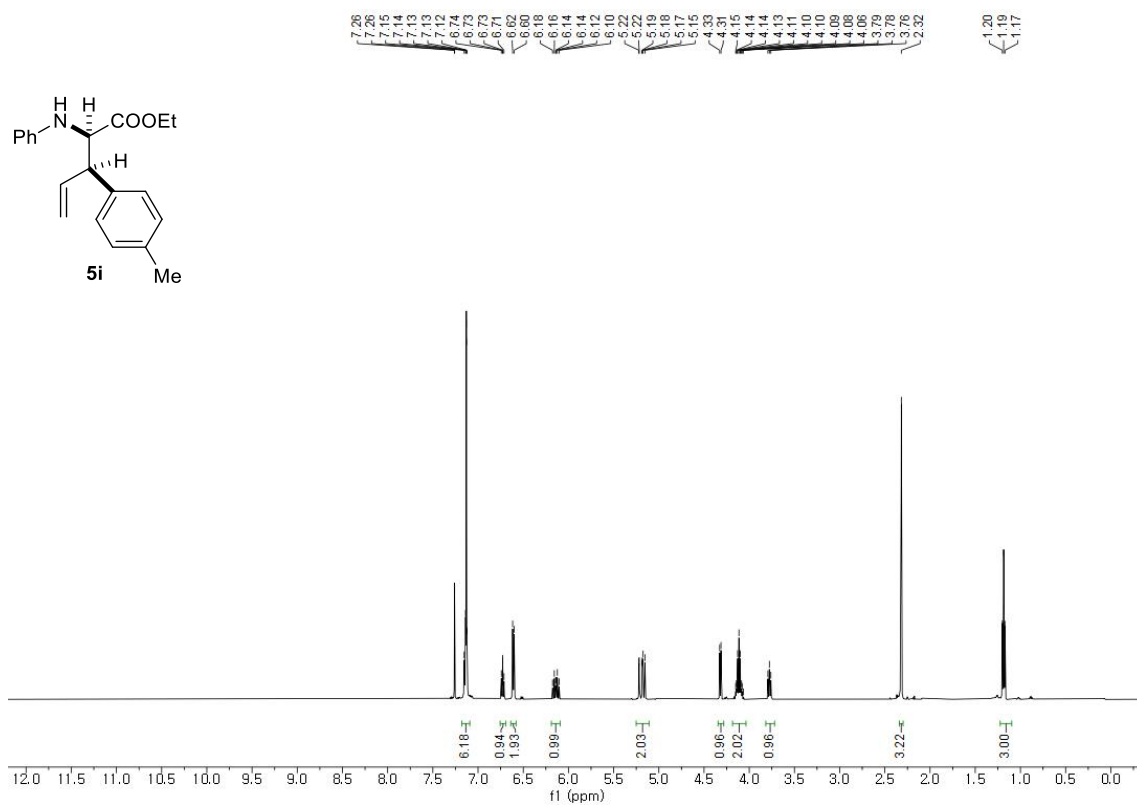


5h

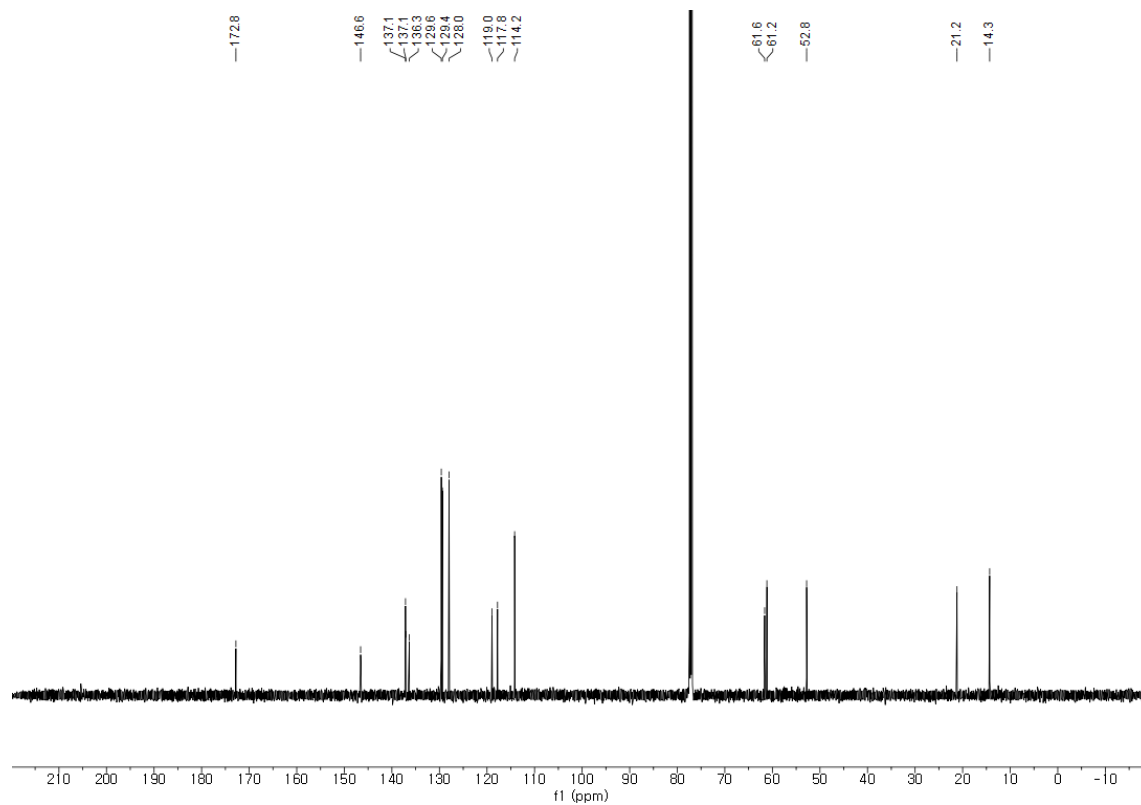
^1H NMR spectrum (400 MHz, CDCl_3) of 5h



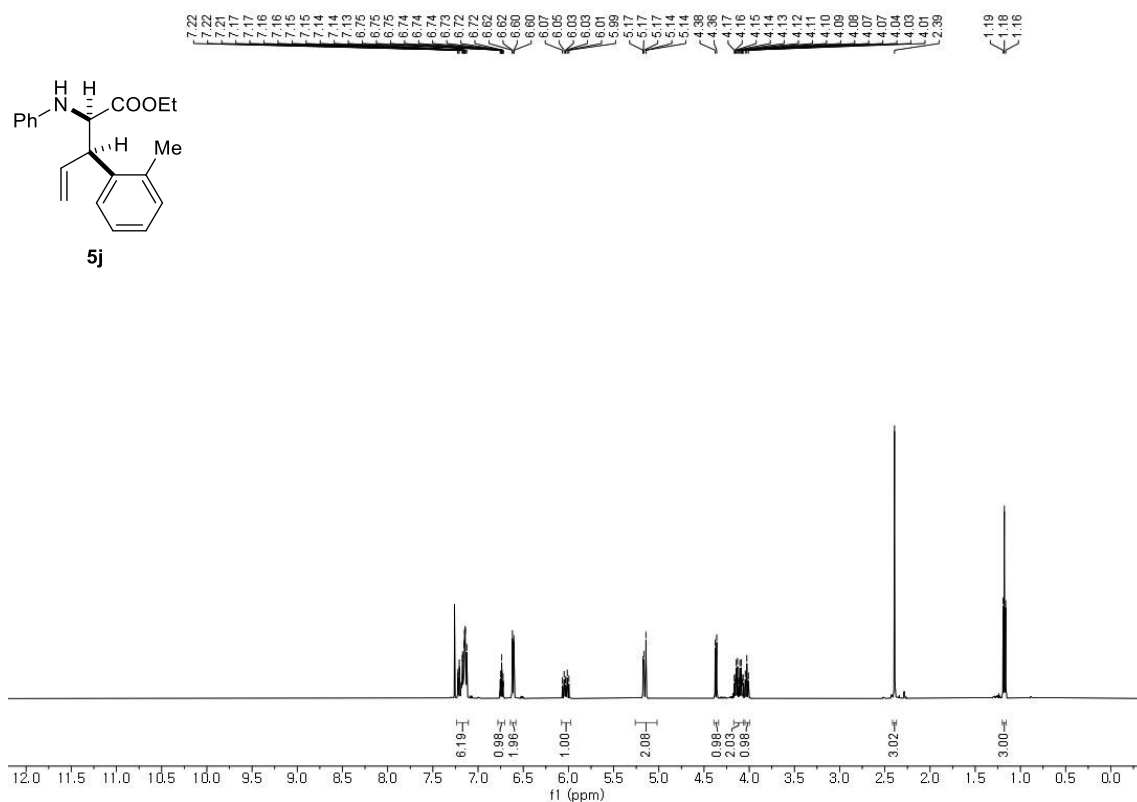
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of 5h



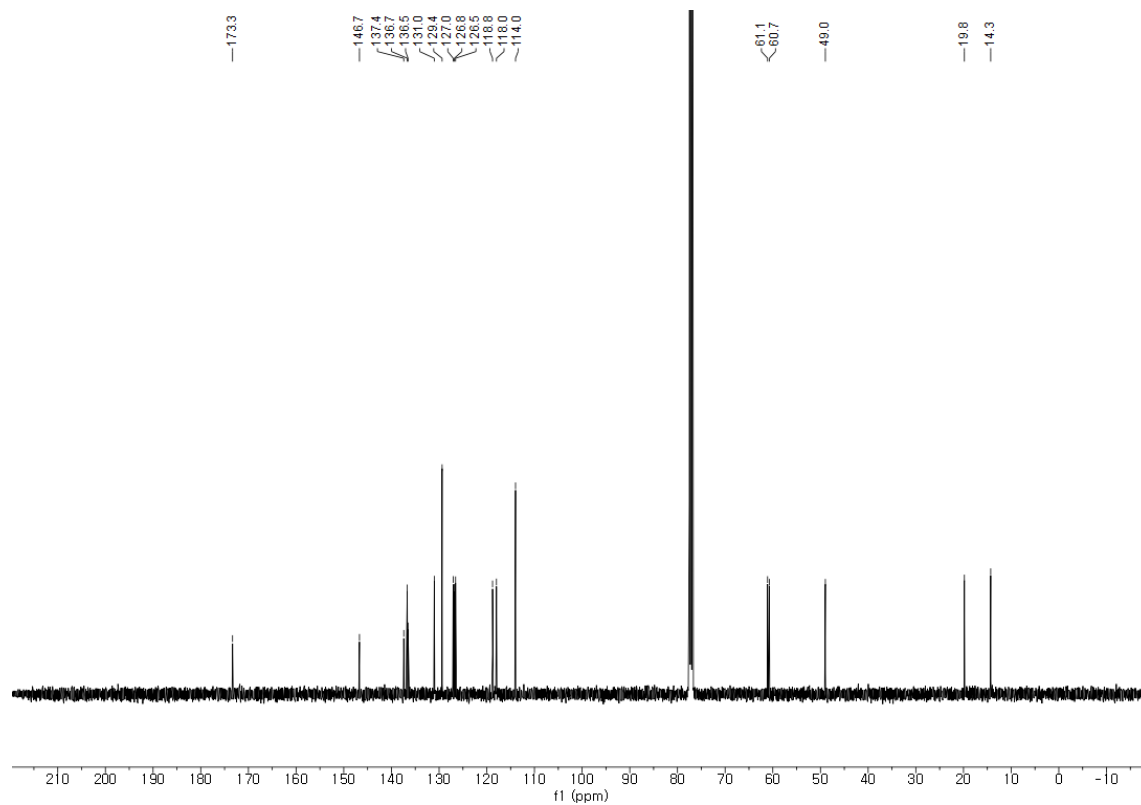
¹H NMR spectrum (500 MHz, CDCl₃) of **5i**



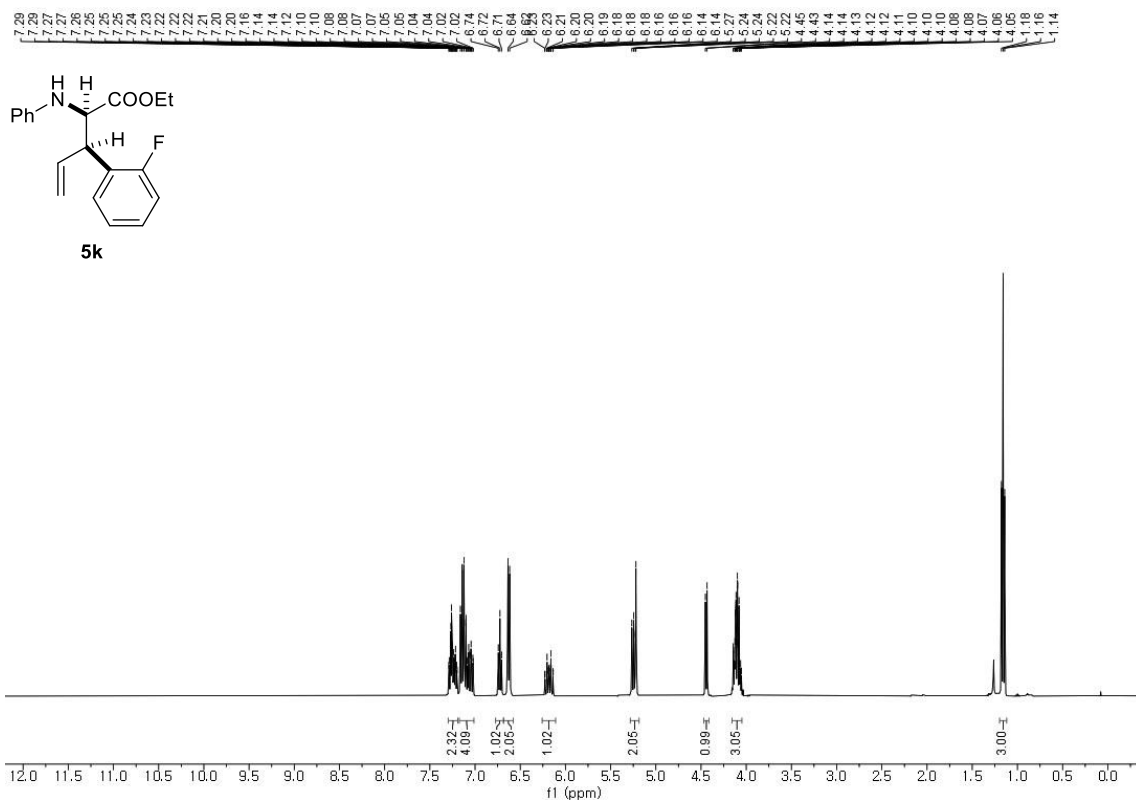
¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **5i**



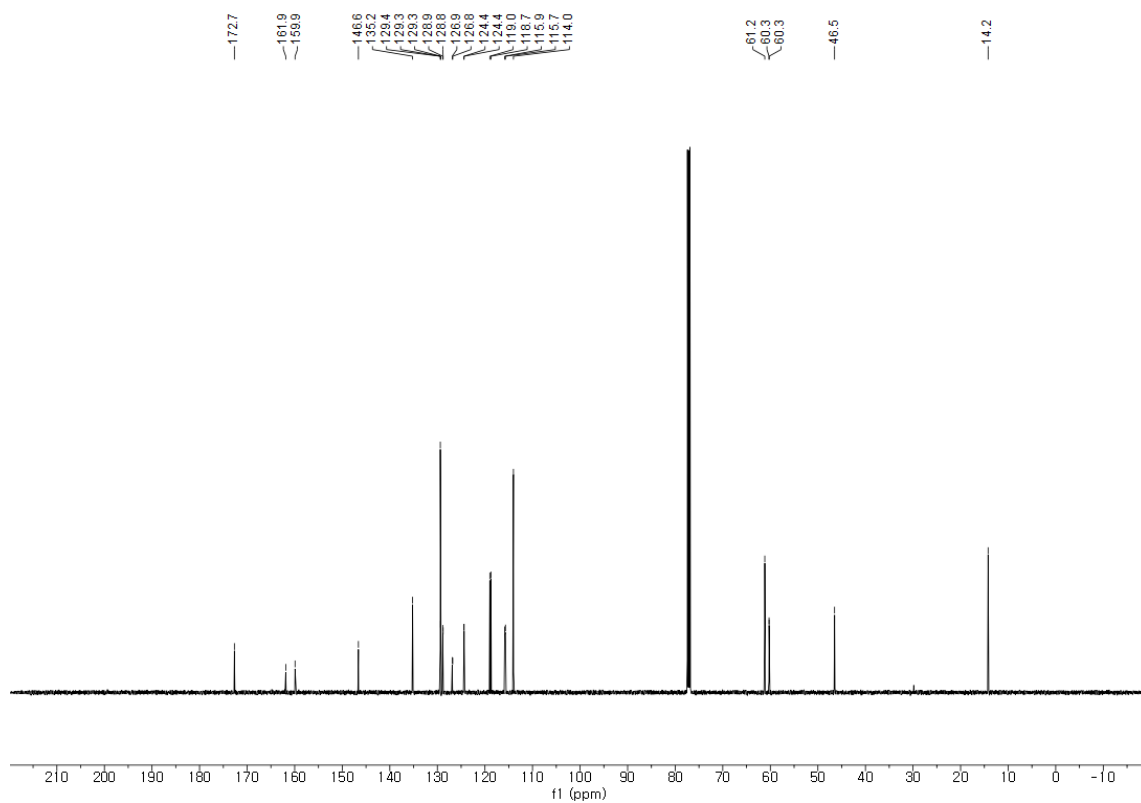
¹H NMR spectrum (500 MHz, CDCl₃) of **5j**



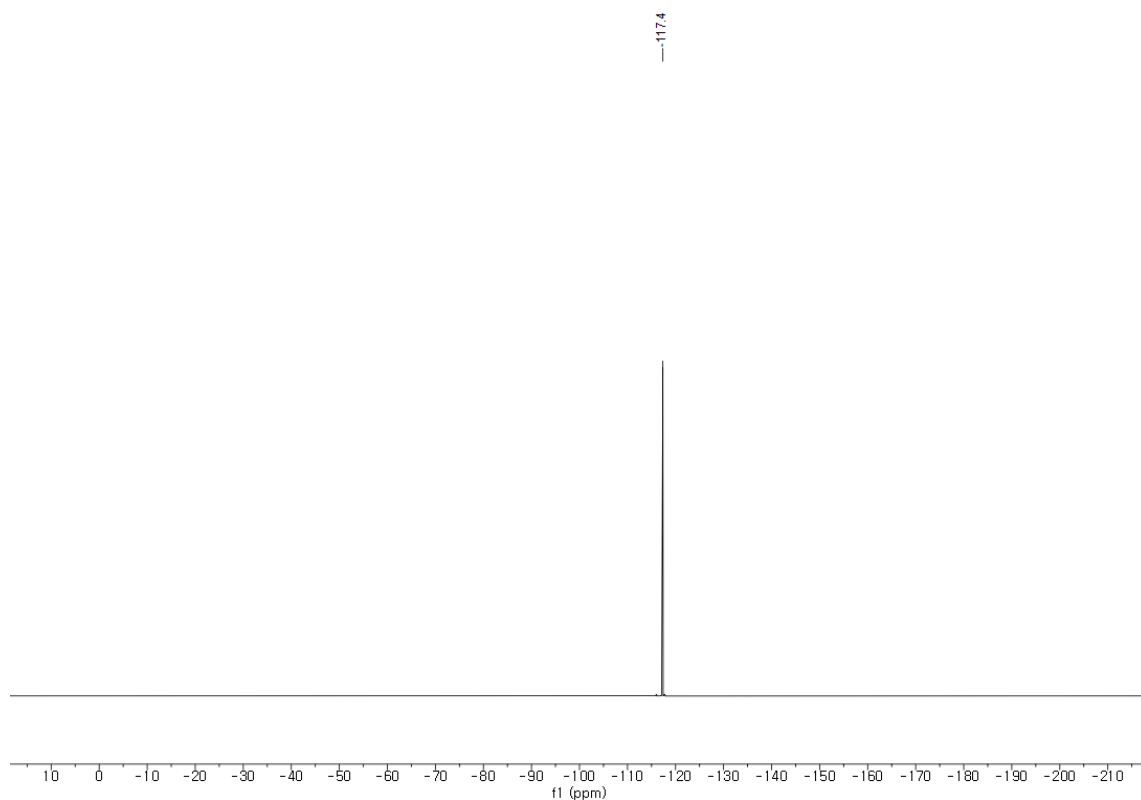
¹³C{¹H} NMR spectrum (100 MHz, CDCl₃) of **5j**



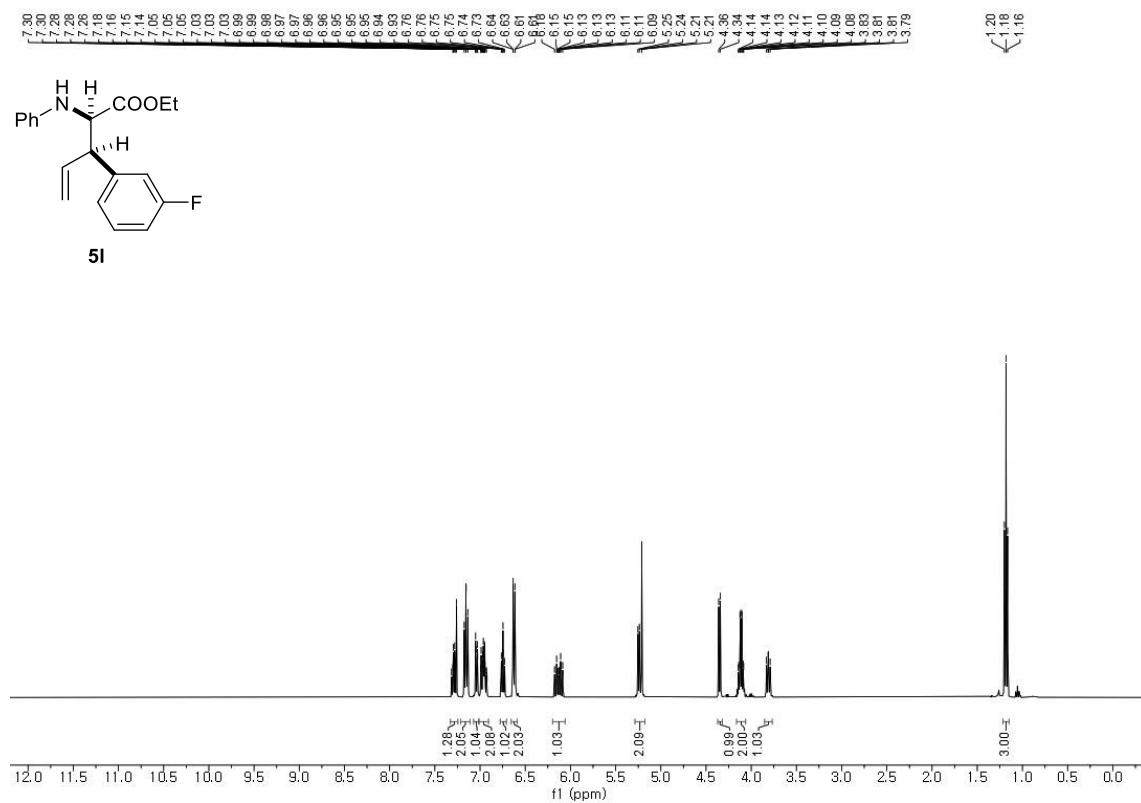
^1H NMR spectrum (400 MHz, CDCl_3) of **5k**



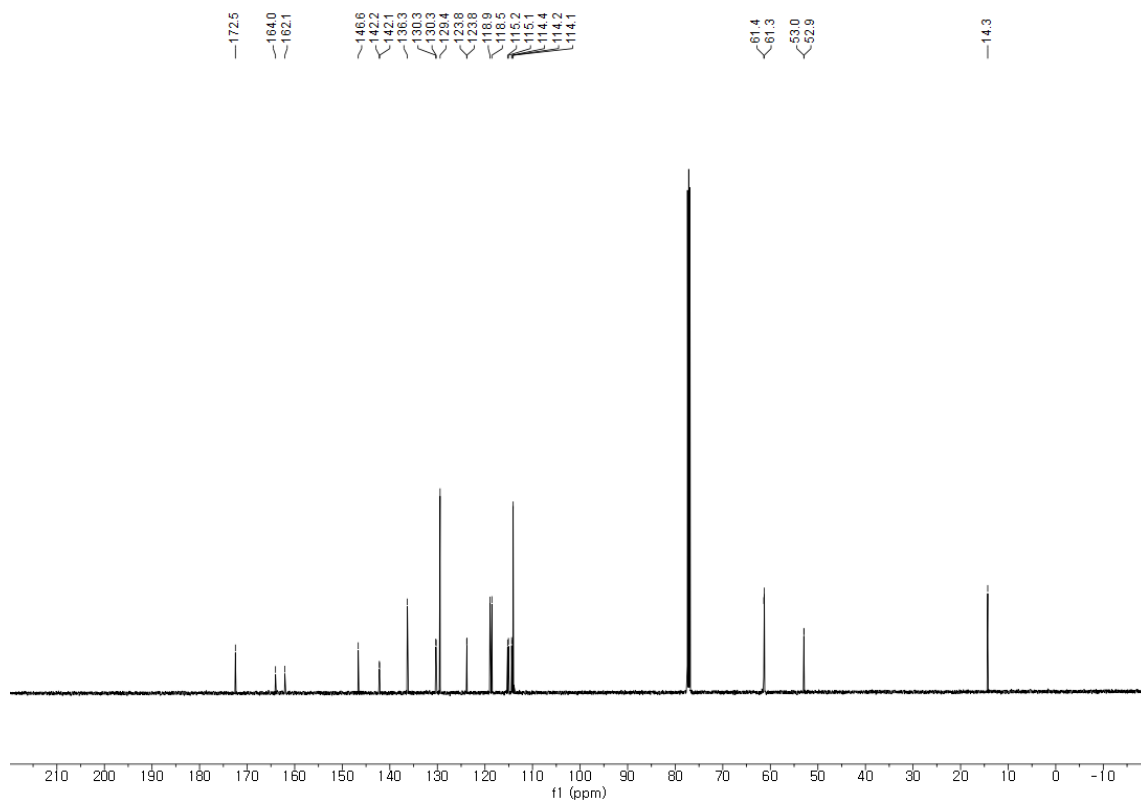
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **5k**



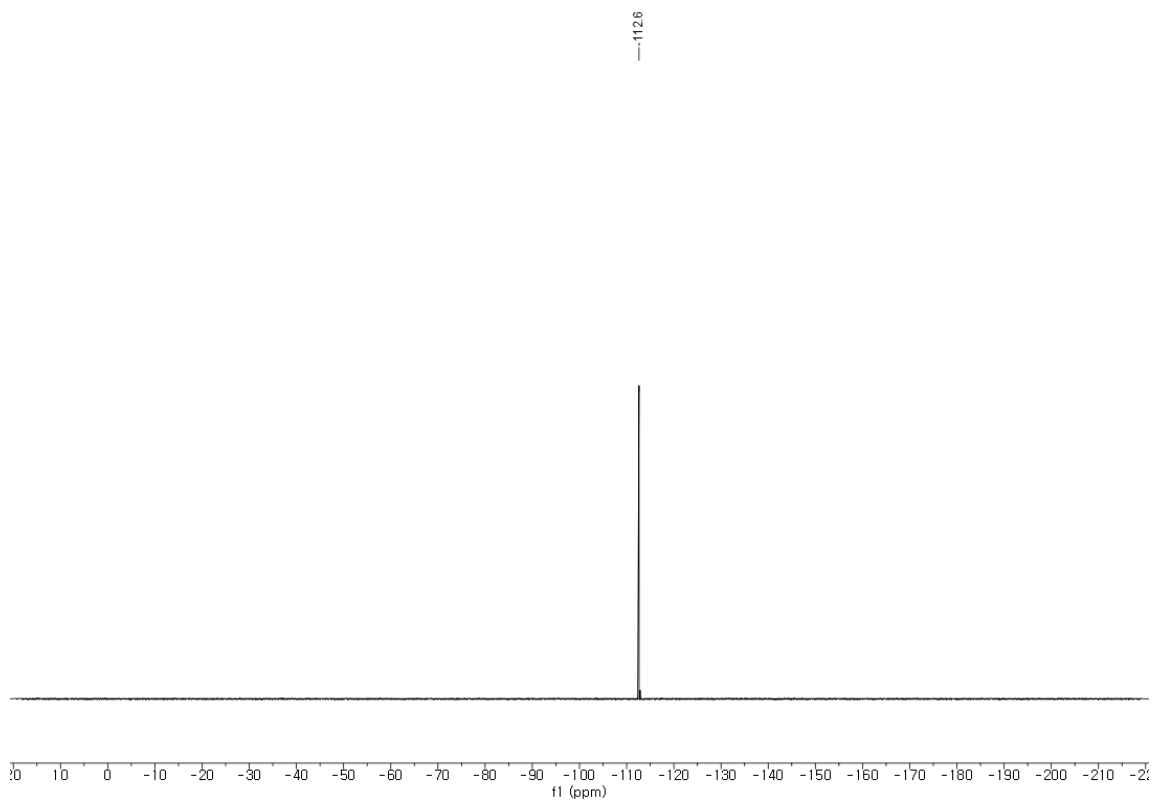
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz, CDCl_3) of **5k**



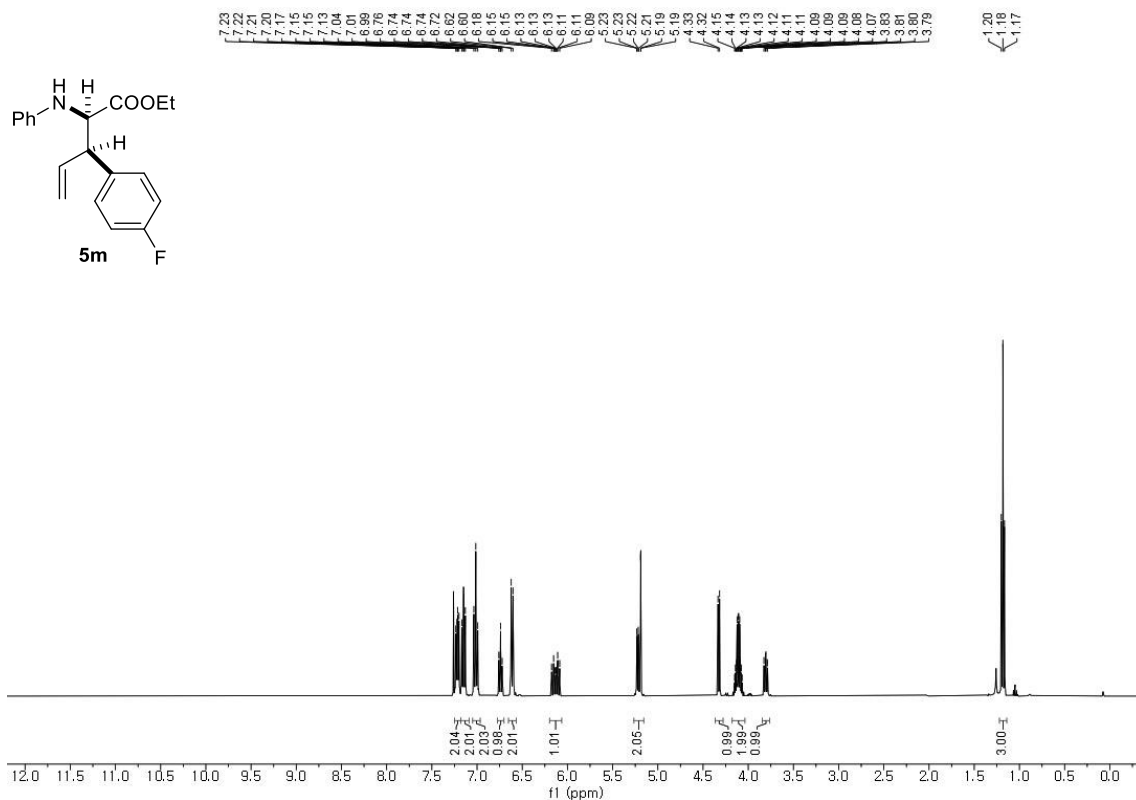
^1H NMR spectrum (400 MHz, CDCl_3) of **5l**



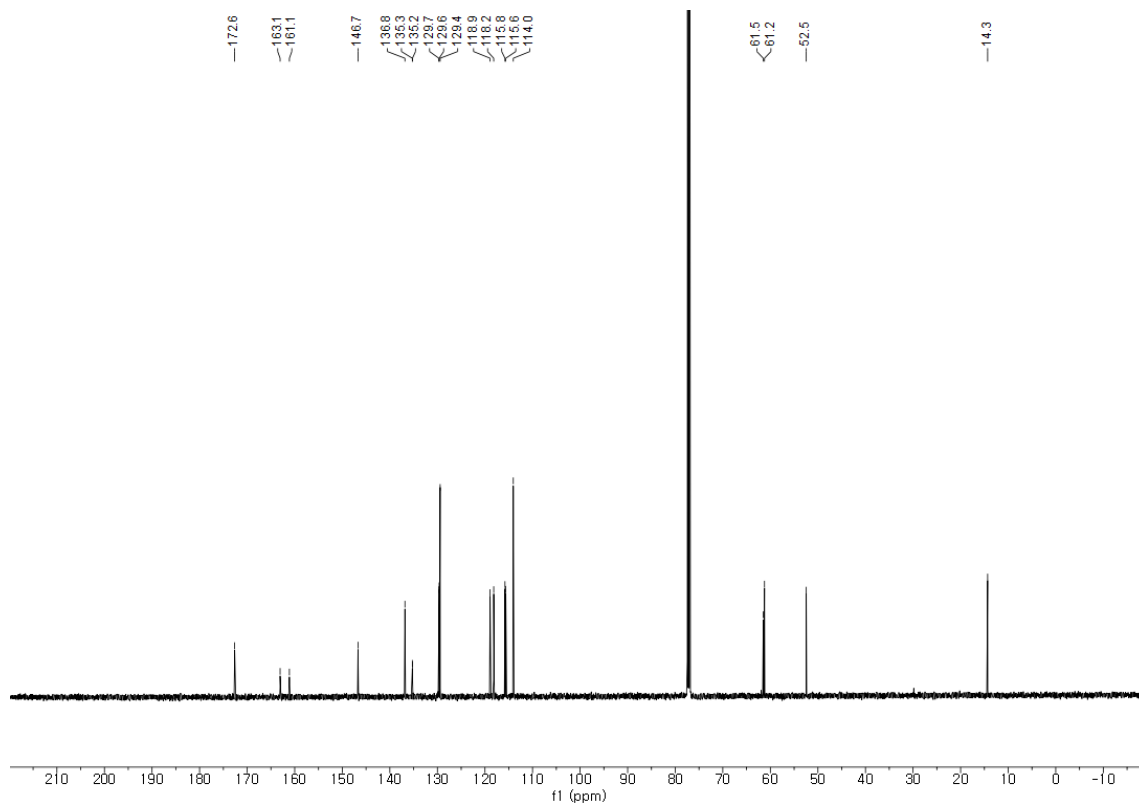
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **5I**



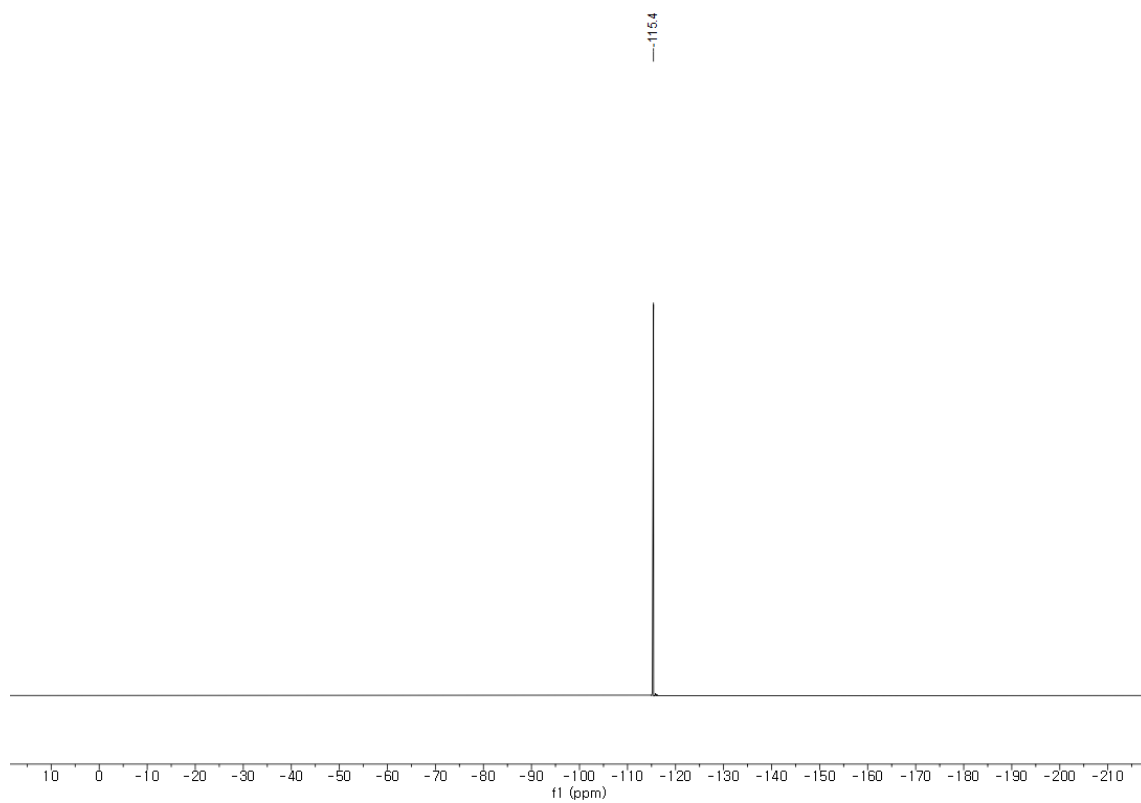
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz, CDCl_3) of **5I**



¹H NMR spectrum (400 MHz, CDCl₃) of **5m**



¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **5m**



$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz, CDCl_3) of **5m**