Conversion of trifluoromethyl into ester along with polyethers upcycling by cation-transfer catalyzed C–O/C–F metathesis

Zhuojun Li, Xiangqian Shi, Dongke Zhang, Qian Wu*

State Key Laboratory of Medicinal Chemical Biology, College of Pharmacy, Academy for Advanced Interdisciplinary Studies and Tianjin Key Laboratory of Molecular Drug Research, Nankai University, 38 Tongyan Road, Jinnan District, Tianjin, 300350, China

E-mail: wuqian@nankai.edu.cn

Supplementary Information

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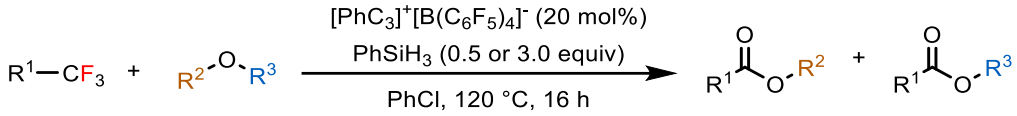
1 General information

Methods: NMR characterization data were collected on Bruker ASCEND^{TM} operating at 400 MHz for ^{1}H NMR, 101 MHz or 151 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR (with complete proton decoupling). Chemical shifts are reported in parts per million (ppm). ^{1}H NMR spectra data were assigned $CDCl_3$ resonance as 7.26 ppm and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant (*J* values) in Hz, and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm with the central peak of residue $CDCl_3$ (77.16 ppm) as the internal standard. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). Gas-Chromatography Mass Spectrometry (GC-MS) data were obtained using a Shimadzu Nexis GC-2030 gas chromatograph connected to a GCMS-QP2020 NX gas chromatograph mass spectrometer (electrospray ionization: EI), equipped with an AOC-20i Plus auto injector. The column was a CD-5MS capillary column (30 m x 0.25 mm x 0.25 μm), with helium as the carrier gas. The sample injection volume was 1 μL, and separations run over a 5-minute period with an increasing oven temperature (gradient) between 50-280 °C. Results were visualised and manipulated using LabSolutions GCMS solution version 4.50. High resolution mass spectral (HRMS) data were acquired on waters G2-S Qtof spectrometer (electrospray ionization: ESI). X-ray crystallography studies were carried out on Rigaku ROD, Synergy Custom DW system using Cu-K_α radiation (λ = 1.54184 Å).
Materials: Unless otherwise stated, all starting materials were commercially available. The starting compounds **1p**[1],**1q**[2], **1r**[2], **1s**[2], **1t**[2], **1u**[2], **1v**[2], **1w**[2], **1x**[2], **1y**[2], **1z**[2], **1aa**[3],**1ab**[4], **1ac**[4], **1ad**[3], **1ae**[5], **1af**[2], **1ag**[6], **1aj**[7], **1ak**[8], **1al**[9], **1am**[10] and **1an**[10] were prepared according to the literature procedure. Flash chromatography was performed using 200-300 mesh silica gel (Yantai Xinnuo Chemicals) with the indicated eluents according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on glass-backed silica gel plates (Yantai Xinnuo Chemicals or Energy Chemical). $[Ph_3C]^+[B(C_6F_5)_4]^-$ was purchased from HEOWNS. All liquid substrates, silanes, and solvent (chlorobenzene, toluene, dichlorobenzene) were dried over calcium hydride, distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Other solid substrates were degassed under vacuum for 2 hours, and stored in a glovebox before use.

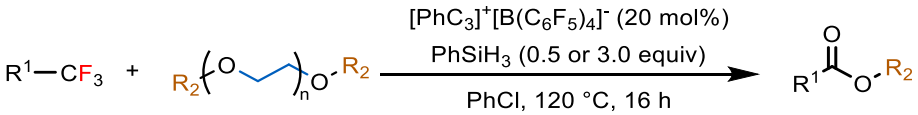
2 General Procedure for the Intermolecular C–O/C–F Metathesis of Ethers with Trifluoromethyl Group

2.1 General Procedure A for Simple Ethers



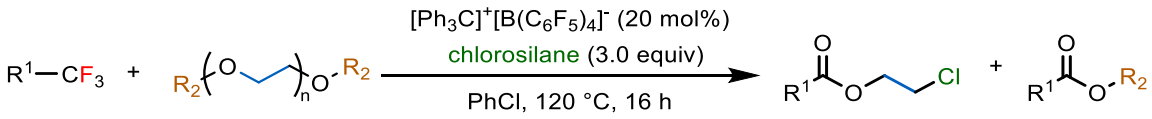
Under argon atmosphere, the sealed tube is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (0.1 mmol or 0.6 mmol, 0.5 equiv or 3.0 equiv) and PhCl (0.2 mL). After stirring the reaction mixture for 15 min at room temperature, ether (0.4 mL) and trifluoromethyl substrates (0.2 mmol, 1.0 equiv) are added to the reaction system in turn by syringe. Then the reaction mixture is heated to 120 ℃ and stirring for 16 h. The products are purified by flash column chromatography after removing the solvent under vacuum. The ratio of the two products is determined by the ratio of their yields.

2.2 General Procedure B for Oligoethers using Hydrosilane



Under argon atmosphere, the sealed tube is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (0.1 mmol or 0.6 mmol, 0.5 equiv or 3.0 equiv) and PhCl (0.2 mL). After stirring the reaction mixture for 15 min at room temperature, ether (0.4 mL) and trifluoromethyl substrates (0.2 mmol, 1.0 equiv) are added to the reaction system in turn by syringe. Then the reaction mixture is heated to 120 ℃ and stirring for 16 h. The product is obtained and purified by flash column chromatography after removing the solvent under vacuum. Notably, the reaction using dioxane, ethyl ester product was obtained.

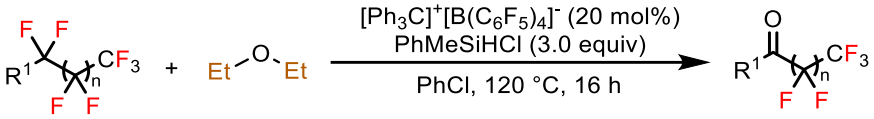
2.3 General Procedure C for Oligoethers using Chlorosilane



Under argon atmosphere, the sealed tube is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), indicated chlorosilane (0.6 mmol, 3.0 equiv) and PhCl (0.2 mL). After stirring the reaction mixture for

15 min at room temperature, oligoether (0.4 mL) and trifluoromethyl substrates (0.2 mmol, 1.0 equiv) are added to the reaction system in turn by syringe. Then the reaction mixture is heated to 120 ℃ and stirring for 16 h. The products are purified by flash column chromatography after removing the solvent under vacuum. The ratio of the two products is determined by the ratio of their yields.

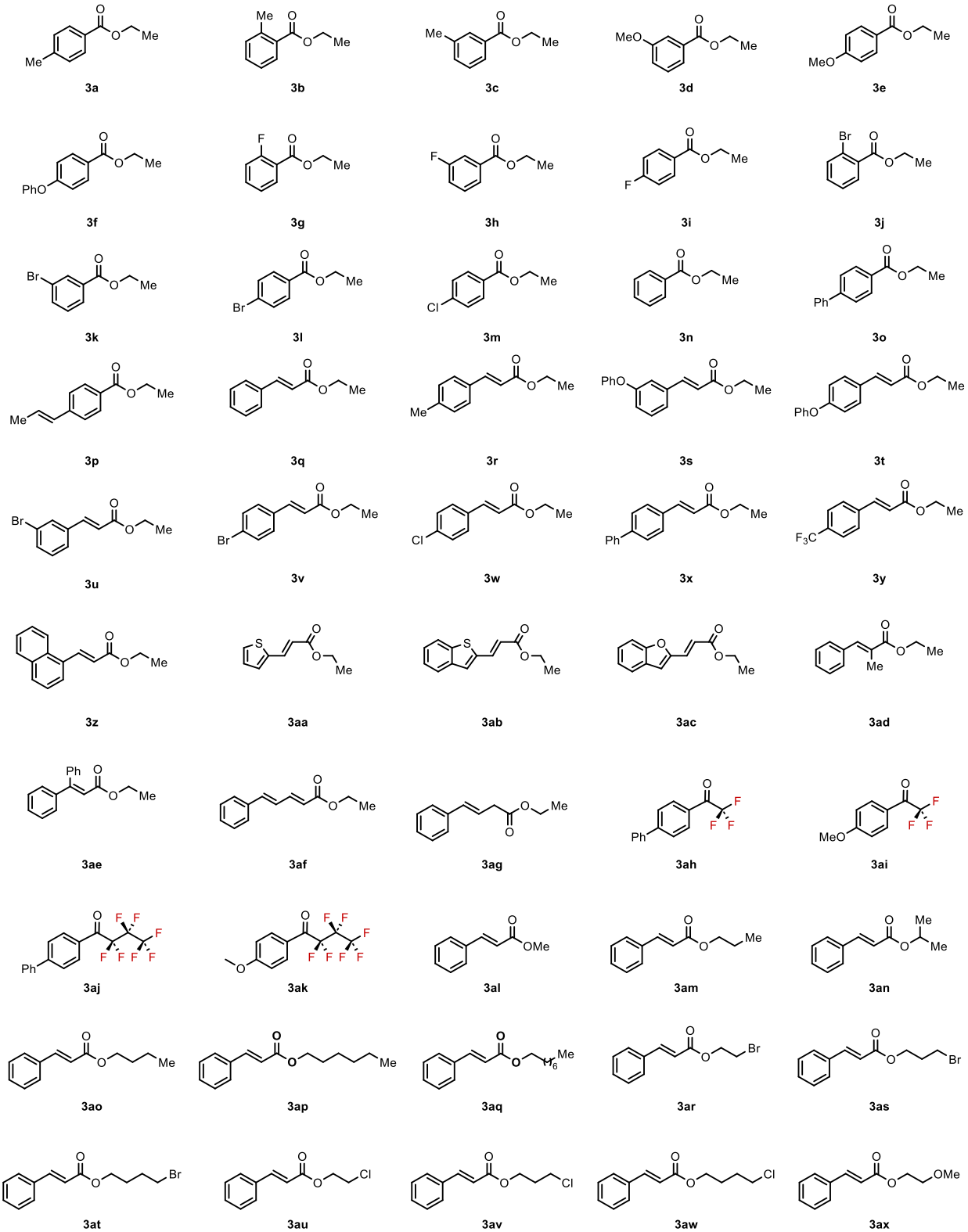
2.4 General Procedure D for Polyfluoroethers



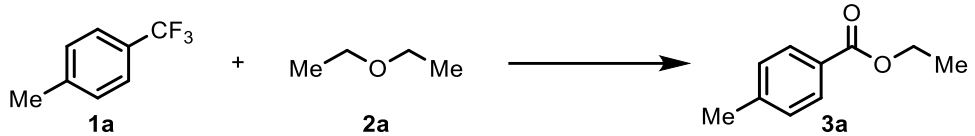
Under argon atmosphere, the sealed tube is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), PhMeSiHCl (90.0 μL, 0.6 mmol, 3.0 equiv) and PhCl (0.2 mL), After stirring the reaction mixture for 15 min, diethyl ether (0.4 mL), polyfluoroalkane (0.2 mmol, 1.0 equiv) are added to the reaction system in turn by syringe. Then the reaction mixture is heated to 120 ℃ and stirring for 16 h. The product is obtained and purified by flash column chromatography after removing the solvent under vacuum.

3 Experimental Details for the Intermolecular C–O/C–F Metathesis of Ethers with Trifluoromethyl Group Enabled by Cation Transfer

Table S1. Summary of products in this work.



3.1 Metathesis of 1-methyl-4-(trifluoromethyl)benzene (1a) with ethyl ether (2a)



1a
$C_8H_7F_3$
M = 160.1392 g/mol

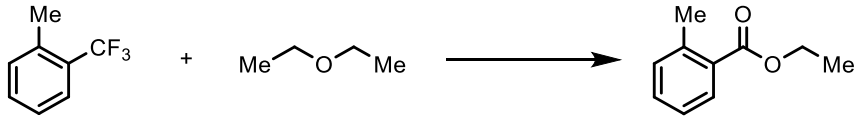
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3a
$C_{10}H_{12}O_2$
M = 164.2040 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methyl-4-(trifluoromethyl)benzene (32.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3a** as yellow liquid (29.2 mg, 89%).

Ethyl 4-methylbenzoate (3a). $\mathbf{R_f}$ = 0.62 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.93 (d, *J* = 13.8 Hz, 2H), 7.22 (d, *J* = 14.3 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.8, 143.5, 129.7, 129.1, 127.9, 60.8, 21.7, 14.3 ppm. **GC-MS (EI)** *m*/*z*: 164.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[11]

3.2 Reaction of 1-methyl-2-(trifluoromethyl)benzene (1b) with ethyl ether (2a)



1b
$C_8H_7F_3$
M = 160.1392 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

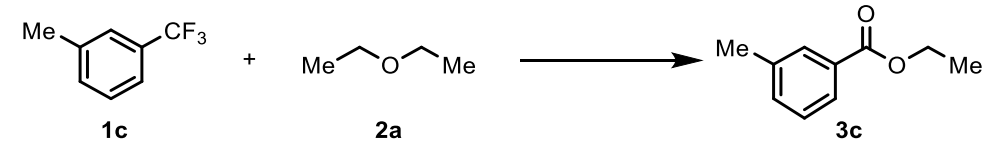
3b
$C_{10}H_{12}O_2$
M = 164.2040 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methyl-2-(trifluoromethyl)benzene (32.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3b** as colourless liquid (26.0 mg, 79%).

Ethyl 2-methylbenzoate (3b). $\mathbf{R_f}$ = 0.65 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz,

$CDCl_3$, 298 K): δ = 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (dt, *J* = 7.2, 3.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.9, 140.1, 131.9, 131.8, 130.6, 130.1, 125.8, 60.8, 21.8, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 164.10 $[M]^+$. The ^1H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[12]

3.3 Reaction of 1-methyl-3-(trifluoromethyl)benzene (1c) with ethyl ether (2a)



1c
$C_8H_7F_3$
M = 160.1392 g/mol

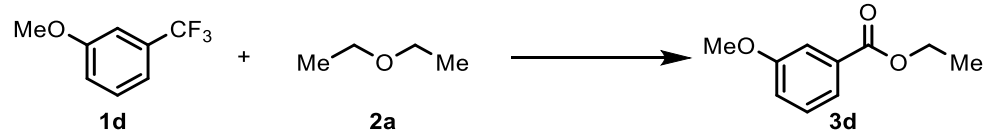
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3c
$C_{10}H_{12}O_2$
M = 164.2040 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methyl-3-(trifluoromethyl)benzene (32.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3c** as colourless liquid (24.6 mg, 75%).

Ethyl 3-methylbenzoate (3c). $\mathbf{R}_f$ = 0.62 (petroleum ether/ethyl acetate, 95/5). **^1H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.85 (d, *J* = 9.3 Hz, 2H), 7.41 – 7.27 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.0, 138.2, 133.7, 130.6, 130.2, 128.3, 126.8, 61.0, 21.4, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 164.10 $[M]^+$. The ^1H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[11]

3.4 Reaction of 1-methoxy-3-(trifluoromethyl)benzene (1d) with ethyl ether (2a)



1d
$C_8H_7F_3O$
M = 176.1382 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

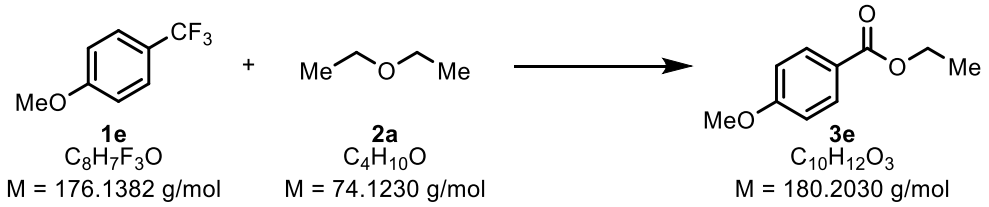
3d
$C_{10}H_{12}O_3$
M = 180.2030 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methoxy-3-(trifluoromethyl)benzene (35.3 mg, 0.2 mmol, 1.0 equiv) were

added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3d** as colourless liquid (31.2 mg, 87%).

Ethyl 3-methoxybenzoate (3d). $\mathbf{R_f}$ = 0.48 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.64 (d, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.6, 159.6, 131.9, 129.5, 122.0, 119.4, 114.1, 61.2, 55.5, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 180.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[13]

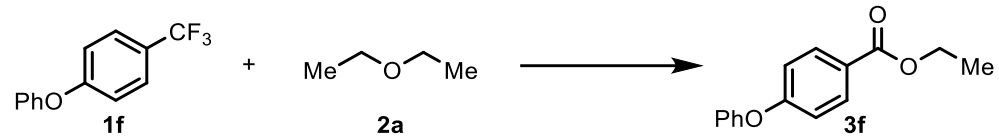
3.5 Reaction of 1-methoxy-4-(trifluoromethyl)benzene (1e) with ethyl ether (2a)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methoxy-4-(trifluoromethyl)benzene (35.3 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3e** as colourless liquid (34.0 mg, 94%).

Ethyl 4-methoxybenzoate (3e). $\mathbf{R_f}$ = 0.50 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = δ 8.00 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.5, 163.4, 131.7, 123.1, 113.7, 60.8, 55.5, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 180.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[11]

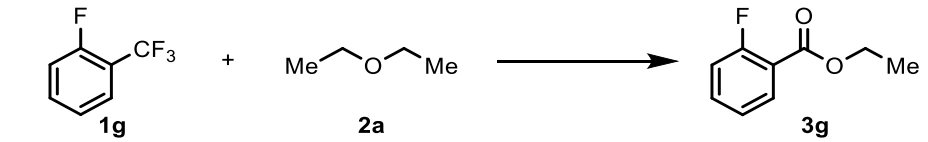
3.6 Reaction of 1-phenoxy-4-(trifluoromethyl)benzene (1f) with ethyl ether (2a)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-phenoxy-4-(trifluoromethyl)benzene (47.6 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3f** as colourless liquid (41.0 mg, 85%). **GC-MS (EI)** *m/z*: 242.10 $[M]^+$. The ^1H, and ^{13}C NMR spectroscopic data is in accordance with literature report.[14]

4-phenoxybenzoic acid ethyl ester (3f). R_f = 0.49 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.28, 161.83, 155.86, 131.77, 130.15, 125.01, 124.57, 120.18, 117.46, 60.96, 14.51 ppm.

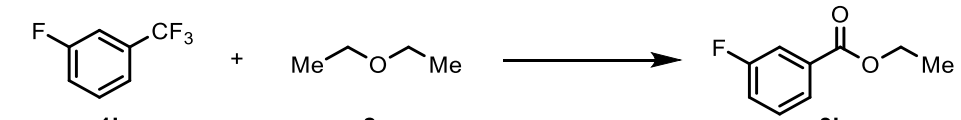
3.7 Reaction of 1-fluoro-2-(trifluoromethyl)benzene (1g) with ethyl ether (2a)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-fluoro-2-(trifluoromethyl)benzene (32.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3g** as yellow liquid (11.8 mg, 35% yield).

Ethyl 2-fluorobenzoate (3g). R_f = 0.57 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.91 (t, *J* = 6.7 Hz, 1H), 7.49 (q, *J* = 8.8, 7.7 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.06 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 164.5 (d, *J* = 3.7 Hz), 162.0 (d, *J* = 259.7 Hz), 134.4 (d, *J* = 9.1 Hz), 124.0 (d, *J* = 4.1 Hz), 119.1 (d, *J* = 9.8 Hz), 117.0 (d, *J* = 22.4 Hz), 61.4, 14.3 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −109.8 ppm. **GC-MS (EI)** *m/z*: 168.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[15]

3.8 Reaction of 1-fluoro-3-(trifluoromethyl)benzene (1h) with ethyl ether (2a)



1h $C_7H_4F_4$ M = 164.1026 g/mol

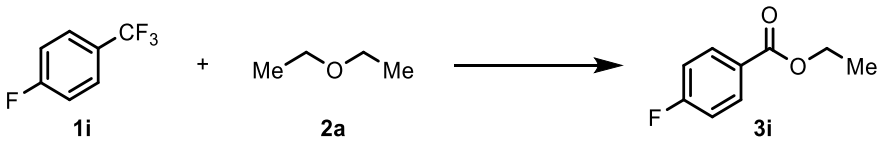
2a $C_4H_{10}O$ M = 74.1230 g/mol

3h $C_9H_9FO_2$ M = 168.1674 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 µL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-fluoro-3-(trifluoromethyl)benzene (32.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3h** as yellow liquid (13.3 mg, 40%).

Ethyl 3-fluorobenzoate (3h). R_f = 0.61 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.84 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.46 – 7.36 (m, 1H), 7.30 – 7.20 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 165.6 (d, *J* = 3.0 Hz), 162.7 (d, *J* = 247.0 Hz), 132.8 (d, *J* = 7.3 Hz), 130.1 (d, *J* = 7.8 Hz), 125.4 (d, *J* = 3.0 Hz), 120.0 (d, *J* = 21.4 Hz), 116.6 (d, *J* = 23.0 Hz), 61.5, 14.4 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −112.6 ppm. **GC-MS (EI)** *m/z*: 168.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[16]

3.9 Reaction of 1-fluoro-4-(trifluoromethyl)benzene (1i) with ethyl ether (2a)



1i $C_7H_4F_4$ M = 164.1026 g/mol

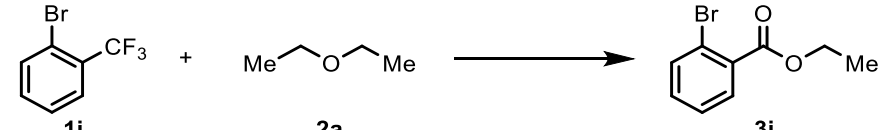
2a $C_4H_{10}O$ M = 74.1230 g/mol

3i $C_9H_9FO_2$ M = 168.1674 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-fluoro-4-(trifluoromethyl)benzene (32.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3i** as yellow liquid (13.1 mg, 39%).

Ethyl 4-fluorobenzoate (3i). $\mathbf{R_f}$ = 0.61 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.06 (s, 2H), 7.14 – 7.06 (m, 2H), 4.40 – 4.33 (m, 2H), 1.39 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 165.8, 165.8 (d, *J* = 253.4 Hz), 132.2 (d, *J* = 9.3 Hz), 115.6 (d, *J* = 21.8 Hz), 61.2, 14.5 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −106.0 ppm. **GC-MS (EI)** *m/z*: 168.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[16]

3.10 Reaction of 1-bromo-2-(trifluoromethyl)benzene (1j) with ethyl ether (2a)



1j $C_7H_4BrF_3$ M = 225.0082 g/mol

2a $C_4H_{10}O$ M = 74.1230 g/mol

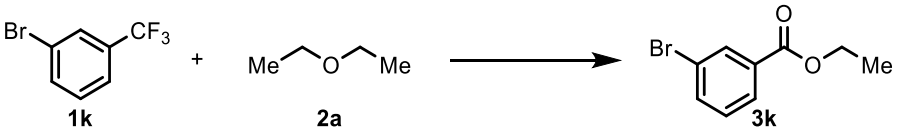
3j $C_9H_9BrO_2$ M = 229.0730 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-bromo-2-(trifluoromethyl)benzene (45.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3j** as yellow liquid (17.7 mg, 39%).

Ethyl 2-bromobenzoate (3j). $\mathbf{R_f}$ = 0.60 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz,

$CDCl_3$, 298 K): δ = 7.78 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.39 – 7.29 (m, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.4, 134.4, 132.6, 132.5, 131.3, 127.2, 121.6, 61.8, 14.3 ppm. **GC-MS (EI)** *m*/*z*: 227.95 $[M]^+$. The ^1H and ^{13}C NMR spectroscopic data is in accordance with literature report.[17]

3.11 Reaction of 1-bromo-3-(trifluoromethyl)benzene (1k) with ethyl ether (2a)



1k $C_7H_4BrF_3$ M = 225.0082 g/mol

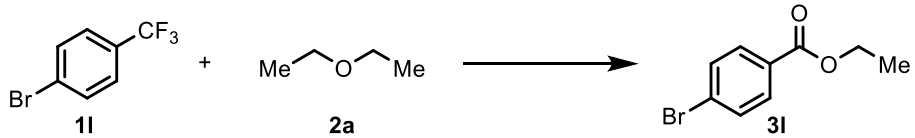
2a $C_4H_{10}O$ M = 74.1230 g/mol

3k $C_9H_9BrO_2$ M = 229.0730 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-bromo-3-(trifluoromethyl)benzene (45.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3k** as yellow liquid (15.3 mg, 34%).

Ethyl 3-bromobenzoate (3k). R_f = 0.65 (petroleum ether/ethyl acetate, 95/5). **^1H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.18 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 165.4, 135.9, 132.7, 132.5, 130.0, 128.3, 122.5, 61.5, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 227.95 $[M]^+$. The ^1H and ^{13}C NMR spectroscopic data is in accordance with literature report.[18]

3.12 Reaction of 1-bromo-4-(trifluoromethyl)benzene (1l) with ethyl ether (2a)



1l $C_7H_4BrF_3$ M = 225.0082 g/mol

2a $C_4H_{10}O$ M = 74.1230 g/mol

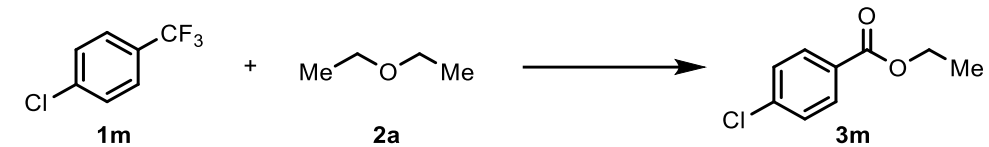
3l $C_9H_9BrO_2$ M = 229.0730 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-bromo-4-(trifluoromethyl)benzene (45.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction,

the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3l** as yellow liquid (21.8 mg, 48%).

Ethyl 4-bromobenzoate (3l). R_f = 0.60 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.90 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.0, 131.8, 131.2, 129.5, 128.0, 61.4, 14.4 ppm. **GC-MS (EI)** *m/z*: 227.95 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[11]

3.13 Reaction of 1-chloro-4-(trifluoromethyl)benzene (1m) with ethyl ether (2a)



1m $C_7H_4ClF_3$ M = 180.5542 g/mol

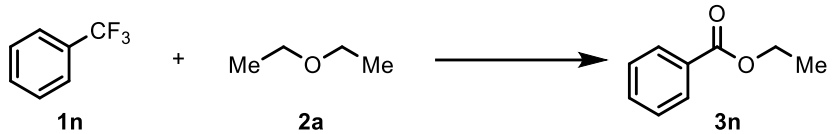
2a $C_4H_{10}O$ M = 74.1230 g/mol

3m $C_9H_9ClO_2$ M = 184.6190 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-chloro-4-(trifluoromethyl)benzene (36.1 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3m** as yellow liquid (13.8 mg, 38%).

Ethyl 4-chlorobenzoate (3m). R_f = 0.65 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.97 (d, *J* = 5.7 Hz, 2H), 7.40 (d, *J* = 5.8 Hz, 2H), 4.37 (q, *J* = 7.3, 6.1 Hz, 2H), 1.39 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 165.9, 139.3, 131.1, 129.0, 128.8, 61.3, 14.4 ppm. **GC-MS (EI)** *m/z*: 184.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[11]

3.14 Reaction of trifluorotoluene (1n) with ethyl ether (2a)



1n
$C_7H_5F_3$
M = 146.1122 g/mol

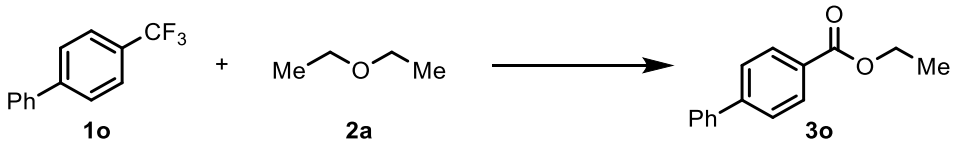
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3n
$C_9H_{10}O_2$
M = 150.1770 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and trifluorotoluene (29.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3n** as colourless liquid (23.3 mg, 78%).

Ethyl benzoate (3n). $\mathbf{R_f}$ = 0.6 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.05 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.8, 132.9, 130.6, 129.6, 128.4, 61.1, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 152.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[19]

3.15 Reaction of 4-(trifluoromethyl)-1,1'-biphenyl (1o) with ethyl ether (2a)



1o
$C_{13}H_9F_3$
M = 222.2102 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

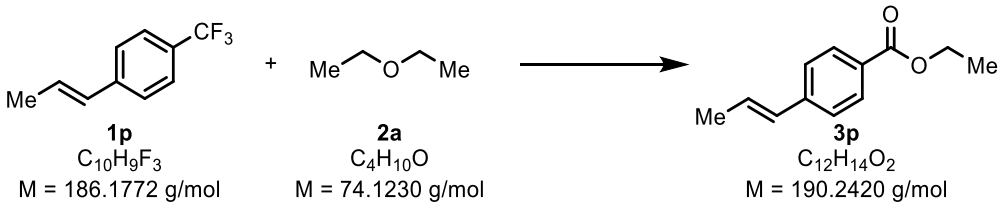
3o
$C_{15}H_{14}O_2$
M = 226.2750 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 4-(trifluoromethyl)-1,1'-biphenyl (44.5 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3o** as yellow liquid (38.0 mg, 84%).

Ethyl 4-phenylbenzoate (3o). $\mathbf{R_f}$ = 0.50 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ 8.12 (d, *J* = 11.4 Hz, 2H), 7.65 (d, *J* = 19.1 Hz, 4H), 7.53 – 7.43 (m, 2H), 7.41 (m, 1H),

4.40 (q, 2H), 1.42 (t, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.7, 145.7, 140.2, 130.2, 129.4, 129.1, 128.2, 127.4, 127.1, 61.1, 14.5 ppm. The ^1H and ^{13}C NMR spectroscopic data is in accordance with literature report.[20]

3.16 Reaction of 1-(prop-1-en-1-yl)-4-(trifluoromethyl)benzene (1p) with ethyl ether (2a)



1p
$C_{10}H_9F_3$
M = 186.1772 g/mol

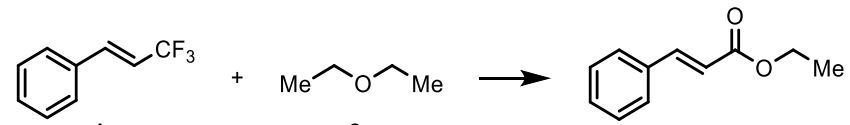
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3p
$C_{12}H_{14}O_2$
M = 190.2420 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-(prop-1-en-1-yl)-4-(trifluoromethyl)benzene (37.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3p** as yellow liquid (22.0 mg, 58%).

Ethyl 4-(propen-1-yl)benzoate (3p). $\mathbf{R_f}$ = 0.54 (petroleum ether/ethyl acetate, 95/5). **^1H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.48 – 6.30 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.91 (d, *J* = 5.9 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.7, 142.5, 130.5, 130.0, 128.8, 128.7, 125.8, 60.9, 18.8, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 190.10 $[M]^+$. The ^1H and ^{13}C NMR spectroscopic data is in accordance with literature report.[21]

3.17 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with ethyl ether (2a)



1q
$C_9H_7F_3$
M = 172.1502 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

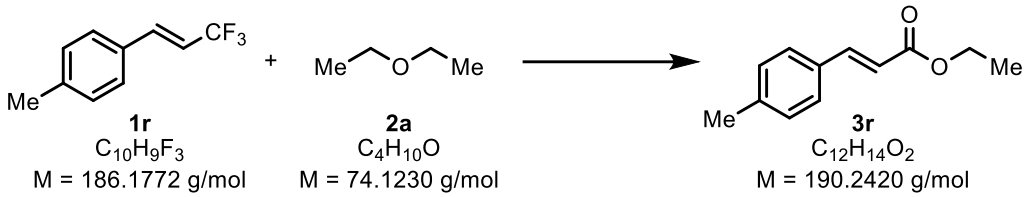
3q
$C_{11}H_{12}O_2$
M = 176.2150 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the

reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as colorless liquid (27.0 mg, 77%).

Ethyl cinnamate (3q). R_f = 0.53 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.53 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.42 – 7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.1, 144.7, 134.6, 130.4, 129.0, 128.2, 118.4, 60.6, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 176.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

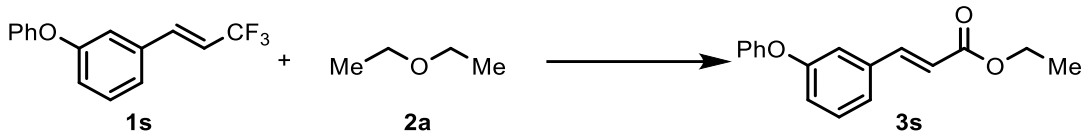
3.18 Reaction of (*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1r) with ethyl ether (2a)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (37.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3r** as yellow liquid (31.0 mg, 82%).

Ethyl (*E*)-3-(4-methylphenyl)acrylate (3r). R_f = 0.54 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.66 (d, *J* = 16.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.4, 144.7, 140.8, 131.8, 129.7, 128.2, 117.3, 60.6, 21.6, 14.5 ppm. **GC-MS (EI)** *m*/*z*:190.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

3.19 Reaction of (*E*)-1-phenoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1s) with ethyl ether (2a)



1s
$C_{15}H_{11}F_3O$
M = 264.2472 g/mol

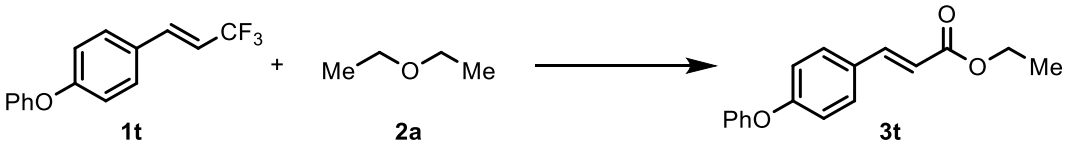
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3s
$C_{17}H_{16}O_3$
M = 268.3120 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-phenoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (52.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3s** as yellow liquid (30.1 mg, 56%).

Ethyl (*E*)-3-(3-phenoxyphenyl)-2-propenoate (3s). R_f = 0.47 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.65 (d, *J* = 16.0 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.28 (s, 1H), 7.20 – 7.13 (m, 2H), 7.08 – 7.02 (m, 3H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.3, 159.6, 156.2, 144.0, 130.0, 129.8, 129.3, 124.2, 119.8, 118.5, 117.0, 60.6, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 268.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

3.20 Reaction of (*E*)-1-phenoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1t) with ethyl ether (2a)



1t
$C_{15}H_{11}F_3O$
M = 264.2472 g/mol

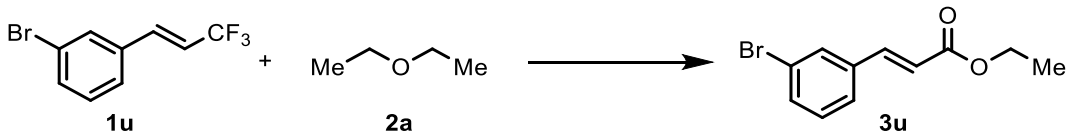
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3t
$C_{17}H_{16}O_3$
M = 268.3120 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-phenoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (52.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3t** as yellow liquid (28.0 mg, 52%).

Ethyl (*E*)-3-(4-phenoxyphenyl)-2-propenoate (3t). R_f = 0.48 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.77 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 4.2, 2.1 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 158.0, 156.8, 144.0, 136.4, 130.3, 130.0, 123.8, 123.1, 120.6, 119.3, 119.1, 117.7, 60.7, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 268.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[23]

3.21 Reaction of (*E*)-1-bromo-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1u) with ethyl ether (2a)



1u
$C_9H_6BrF_3$
M = 251.0462 g/mol

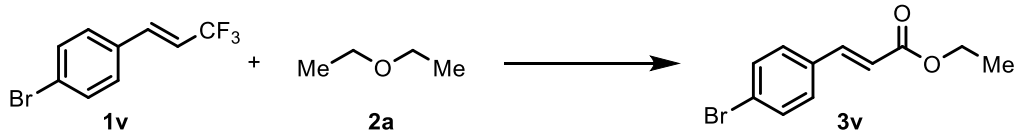
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3u
$C_{11}H_{11}BrO_2$
M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-bromo-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (50.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3u** as yellow solid (45.5 mg, 89%).

Ethyl (*E*)-3-(3-bromophenyl)prop-2-enoate (3u). R_f = 0.48 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.60 (s, 1H), 7.53 (d, *J* = 18.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.6, 142.9, 136.6, 133.1, 130.8, 130.5, 126.7, 119.8, 60.8, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 254.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

3.22 Reaction of (*E*)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1v) with ethyl ether (2a)



1v
$C_9H_6BrF_3$
M = 251.0462 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

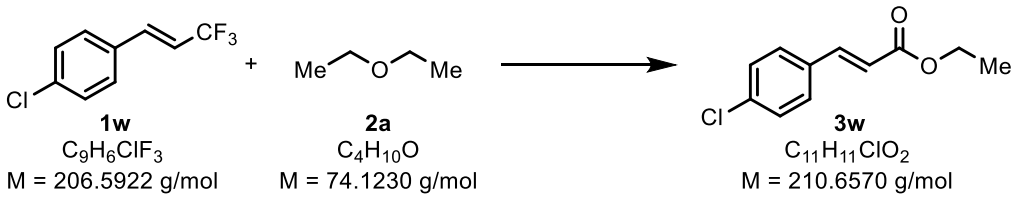
3v
$C_{11}H_{11}BrO_2$
M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%),

$PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (50.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3v** as yellow liquid (44.5 mg, 87%).

Ethyl (*E*)-3-(4-bromophenyl)prop-2-enoate (3v). $\mathbf{R_f}$ = 0.49 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.61 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 143.3, 133.5, 132.3, 129.6, 124.6, 119.1, 60.8, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 254.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

3.23 Reaction of (*E*)-1-chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1w) with ethyl ether (2a)



1w $C_9H_6ClF_3$ M = 206.5922 g/mol

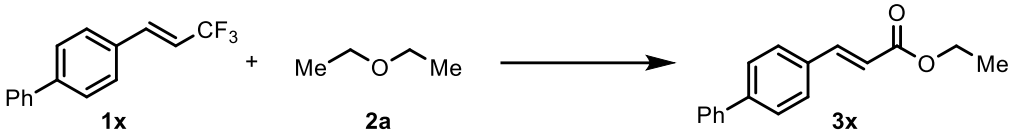
2a $C_4H_{10}O$ M = 74.1230 g/mol

3w $C_{11}H_{11}ClO_2$ M = 210.6570 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (41.3 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3w** as yellow liquid (31.7 mg, 75%).

Ethyl (*E*)-3-(4-chlorophenyl)prop-2-enoate (3w). $\mathbf{R_f}$ = 0.58 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.61 (d, *J* = 16.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 16.1 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.8, 143.2, 136.2, 133.0, 129.3, 129.2, 119.0, 60.7, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 210.05 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[22]

3.24 Reaction of (*E*)-4-(3,3,3-trifluoroprop-1-en-1-yl)-1,1'-biphenyl (1x) with ethyl ether (2a)



1x
$C_{15}H_{11}F_3$
M = 248.2482 g/mol

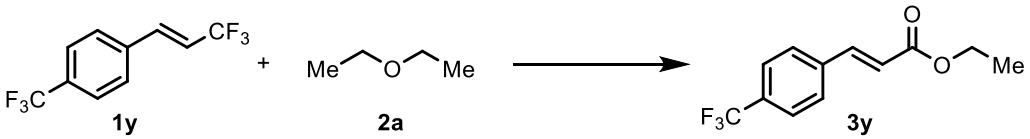
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3x
$C_{17}H_{16}O_2$
M = 252.3130 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-4-(3,3,3-trifluoroprop-1-en-1-yl)-1,1'-biphenyl (41.3 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3x** as white solid (38.6 mg, 77 %).

Ethyl (*E*)-3-([1,1'-biphenyl]-4-yl)acrylate (3x). $\mathbf{R_f}$ = 0.46 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.73 (d, *J* = 18.7 Hz, 1H), 7.67 – 7.58 (m, 6H), 7.45 (t, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 5.6 Hz, 1H), 6.48 (d, *J* = 18.9 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 1.35 (t, *J* = 8.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.2, 144.3, 143.1, 140.3, 135.1, 133.6, 129.1, 128.7, 127.7, 127.2, 118.3, 60.7, 14.5 ppm. **GC-MS (EI)** *m/z*: 252.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[24]

3.25 Reaction of (*E*)-1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1y) with ethyl ether (2a)



1y
$C_{10}H_6F_6$
M = 240.1484 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

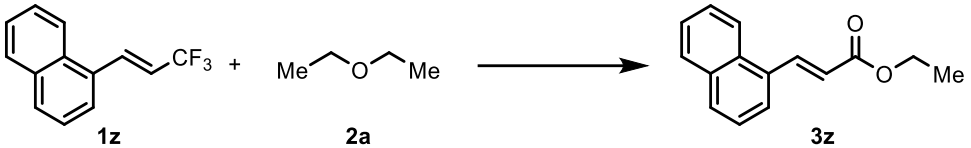
3y
$C_{12}H_{11}F_3O_2$
M = 244.2132 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (48.0 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford

compound **3y** as yellow liquid (32.4 mg, 66%).

Ethyl (*E*)-4-trifluoromethylcinnamate (3y). R_f = 0.34 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.74 – 7.59 (m, 5H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.6, 142.9, 138.0, 132.0, 128.3, 126.0 (q, *J* = 3.9 Hz), 121.0, 61.0, 14.4 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −62.8 ppm. **GC-MS (EI)** *m*/*z*: 244.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[25]

3.26 Reaction of (*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (1z) with ethyl ether (2a)



1z
$C_{13}H_9F_3$
M = 222.2102 g/mol

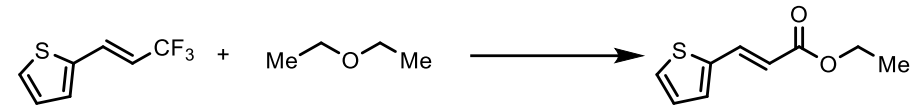
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3z
$C_{15}H_{14}O_2$
M = 226.2750 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (44.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3z** as colourless liquid (33.2 mg, 73%).

Ethyl (*E*)-3-(naphthalen-1-yl)acrylate (3z). R_f = 0.56 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.54 (d, *J* = 17.9 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.89 (t, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.45 (m, 3H), 6.54 (d, *J* = 15.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.0, 141.7, 133.7, 131.9, 131.5, 130.5, 128.8, 126.9, 126.3, 125.5, 125.1, 123.5, 121.0, 60.7, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 226.15 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[22]

3.27 Reaction of (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (1aa) with ethyl ether (2a)



1aa
$C_7H_5F_3S$
M = 178.1722 g/mol

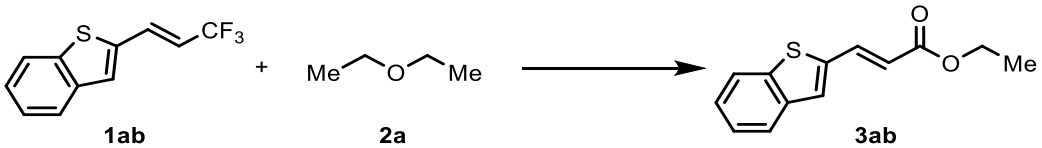
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3aa
$C_9H_{10}O_2S$
M = 182.2370 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (35.6 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3aa** as white solid (27.0 mg, 74%).

Ethyl (*E*)-3-(thiophen-2-yl)acrylate (3aa). $\mathbf{R_f}$ = 0.41 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.7 (dd, *J* = 15.8, 4.1 Hz, 1H), 7.3 – 7.3 (m, 1H), 7.2 – 7.1 (m, 1H), 7.0 (q, *J* = 4.4 Hz, 1H), 6.2 (dd, *J* = 15.8, 3.7 Hz, 1H), 4.2 – 4.1 (m, 2H), 1.3 – 1.2 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 139.7, 137.1, 130.9, 128.4, 128.2, 117.1, 60.6, 14.4 ppm. **GC-MS (EI)** *m*/*z*: 182.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[26]

3.28 Reaction of (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzo[*b*]thiophene (1ab) with ethyl ether (2a)



1ab
$C_{11}H_7F_3S$
M = 228.2322 g/mol

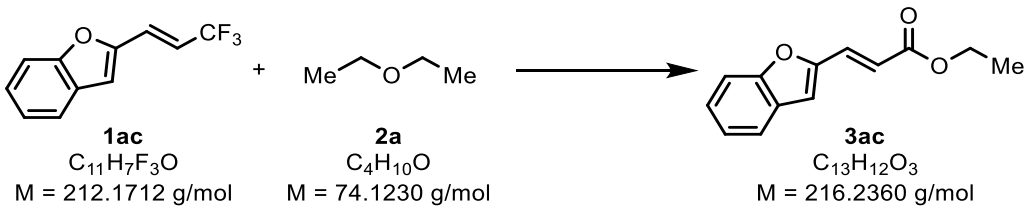
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3ab
$C_{13}H_{12}O_2S$
M = 232.2970 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 µL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzo[*b*]thiophene (45.7 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ab** as white solid (32.5 mg, 70%).

Ethyl (*E*)-3-(benzo[*b*]thiophen-2-yl)acrylate (3ab). R_f = 0.47 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.87 (d, *J* = 15.7 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.46 (s, 1H), 7.42 – 7.31 (m, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 4.28 (q, *J* = 6.3, 5.4 Hz, 2H), 1.35 (t, *J* = 6.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.7, 140.3, 139.7, 137.7, 128.7, 126.3, 125.0, 124.5, 122.6, 119.7, 60.8, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 232.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[27]

3.29 Reaction of (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzofuran (1ac) with ethyl ether (2a)



1ac
$C_{11}H_7F_3O$
M = 212.1712 g/mol

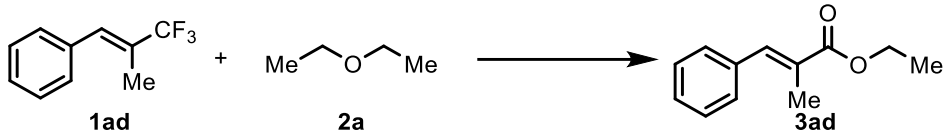
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3ac
$C_{13}H_{12}O_3$
M = 216.2360 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)benzofuran (42.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ac** as white solid (29.0 mg, 67%).

Ethyl (*E*)-3-(benzofuran-3-yl)acrylate (3ac). R_f = 0.50 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.53 – 7.42 (m, 2H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.32 – 7.23 (m, 1H), 7.20 – 7.12 (m, 1H), 6.85 (s, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 155.7, 152.5, 131.4, 128.5, 126.6, 123.5, 121.9, 119.2, 111.6, 111.2, 60.8, 14.5 ppm. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[27]

3.30 Reaction of (*E*)-(3,3,3-trifluoro-2-methylprop-1-en-1-yl)benzene (1ad) with ethyl ether (2a)



1ad $C_{10}H_9F_3$ M = 186.1772 g/mol

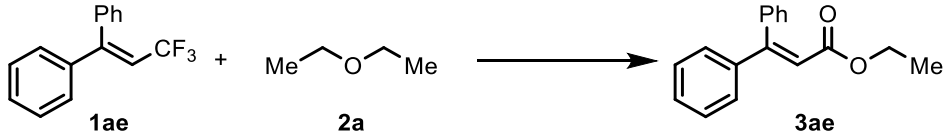
2a $C_4H_{10}O$ M = 74.1230 g/mol

3ad $C_{13}H_{14}O_2$ M = 190.2420 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoro-2-methylprop-1-en-1-yl)benzene (37.6 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ad** as yellow liquid (29.7 mg, 78%).

Ethyl (*E*)-2-methyl-3-phenyl-2-propenoate (3ad). $\mathbf{R}_f$ = 0.62 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ =7.70 (s, 1H), 7.43 – 7.36 (m, 4H), 7.35 – 7.28 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 168.8, 138.8, 136.1, 129.8, 128.7, 128.5, 128.4, 61.0, 14.5, 14.2 ppm. **GC-MS (EI)** *m/z*: 190.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[28]

3.31 Reaction of (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (1ae) with ethyl ether (2a)



1ae $C_{15}H_{11}F_3$ M = 248.2482 g/mol

2a $C_4H_{10}O$ M = 74.1230 g/mol

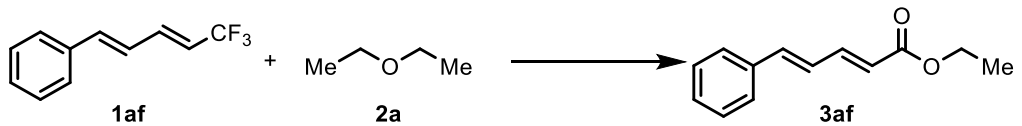
3ae $C_{17}H_{16}O_2$ M = 252.3130 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (49.7 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ae** as yellow liquid (41.0 mg, 81%).

Ethyl 3,3-diphenylacrylate (3ae). $\mathbf{R}_f$ = 0.37 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz,

$CDCl_3$, 298 K): δ = 7.42 – 7.29 (m, 8H), 7.23 – 7.18 (m, 2H), 6.37 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.3, 156.6, 141.0, 139.2, 129.5, 129.3, 128.5, 128.4, 128.2, 128.0, 117.6, 60.2, 14.1 ppm. **GC-MS (EI)** *m*/*z*: 252.10 $[M]^+$. The ^1H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[29]

3.32 Reaction of ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (1af) with ethyl ether (2a)



1af
$C_{11}H_9F_3$
M = 198.1882 g/mol

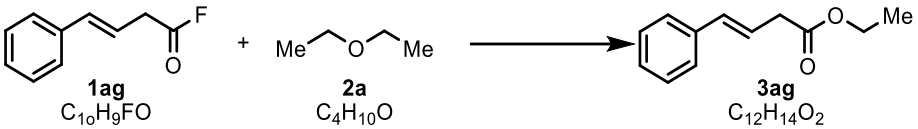
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3af
$C_{13}H_{14}O_2$
M = 202.2530 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (39.6 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3af** as yellow liquid (30.5 mg, 75%).

Ethyl (2*E*,4*E*)-5-phenyl-penta-2,4-dienoate (3af). R_f = 0.44 (petroleum ether/ethyl acetate, 95/5). **^1H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.50 – 7.27 (m, 6H), 6.95 – 6.81 (m, 2H), 5.99 (d, *J* = 15.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.2, 144.7, 140.5, 136.2, 129.2, 128.9, 127.3, 126.4, 121.5, 60.5, 14.5 ppm. **GC-MS (EI)** *m*/*z*: 202.10 $[M]^+$. The ^1H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[22]

3.33 Reaction of (*E*)-4-phenylbut-3-enoyl fluoride (1ag) with ethyl ether (2a)



1ag
$C_{10}H_9FO$
M = 164.1794 g/mol

2a
$C_4H_{10}O$
M = 74.1230 g/mol

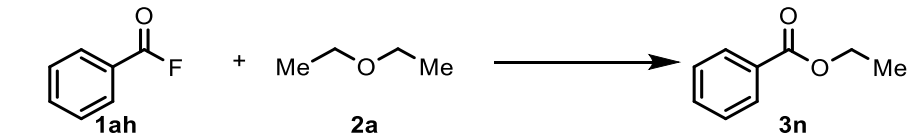
3ag
$C_{12}H_{14}O_2$
M = 190.2420 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and (*E*)-4-phenylbut-3-enoyl fluoride (32.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the

solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ag** as colourless liquid (28.5 mg, 75%).

Ethyl (*E*)-4-phenylbut-3-enoate (3ag). R_f = 0.41 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.46 – 7.39 (m, 3H), 7.40 – 7.32 (m, 2H), 7.33 – 7.24 (m, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.42 – 6.30 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.29 (d, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 171.7, 137.0, 133.5, 128.6, 127.6, 126.4, 122.0, 60.9, 38.6, 14.3 ppm. **GC-MS (EI)** *m*/*z*: 190.15 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[30]

3.34 Reaction of benzoyl fluoride (1ah) with ethyl ether (2a)

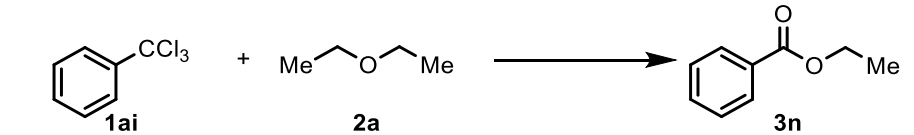


1ah C_7H_5FO M = 124.1144 g/mol | **2a** $C_4H_{10}O$ M = 74.1230 g/mol | **3n** $C_9H_{10}O_2$ M = 150.1770 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and benzoyl fluoride (24.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3n** as colourless liquid (25.0 mg, 83%).

Ethyl benzoate (3n). R_f = 0.60 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.14**.

3.35 Reaction of trichloromethylbenzene (1ai) with ethyl ether (2a)



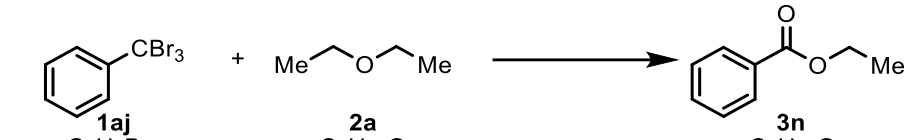
1ai $C_7H_5Cl_3$ M = 195.4670 g/mol | **2a** $C_4H_{10}O$ M = 74.1230 g/mol | **3n** $C_9H_{10}O_2$ M = 150.1770 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and trichloromethylbenzene (39.1 mg, 0.2 mmol, 1.0 equiv) were added to the

sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3n** as colourless liquid (19.2 mg, 64%).

Ethyl benzoate (3n). $\mathbf{R_f}$ = 0.60 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.14**.

3.36 Reaction of tribromomethylbenzene (1aj) with ethyl ether (2a)



1aj $C_7H_5Br_3$ M = 328.8290 g/mol

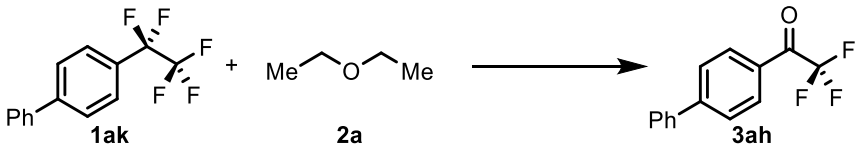
2a $C_4H_{10}O$ M = 74.1230 g/mol

3n $C_9H_{10}O_2$ M = 150.1770 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and tribromomethylbenzene (65.8 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 99/1) to afford compound **3n** as colourless liquid (16.6 mg, 55%).

Ethyl benzoate (3n). $\mathbf{R_f}$ = 0.60 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.14**.

3.37 Reaction of 4-(perfluoroethyl)-1,1'-biphenyl (1ak) with ethyl ether (2a)



1ak $C_{14}H_9F_5$ M = 272.2180 g/mol

2a $C_4H_{10}O$ M = 74.1230 g/mol

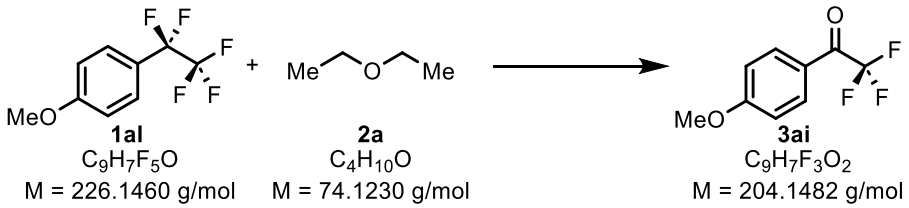
3ah $C_{14}H_9F_3O$ M = 250.2202 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), PhMeSiHCl (90.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 4-(perfluoroethyl)-1,1'-biphenyl (54.4 mg, 0.2 mmol, 1.0 equiv) were

added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ah** as white solid (22.5 mg, 45%).

1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one (3ah). R_f = 0.49 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.16 (d, *J* = 7.7 Hz, 2H), 7.81 – 7.73 (m, 2H), 7.69 – 7.62 (m, 2H), 7.55 – 7.40 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 180.2 (d, *J* = 34.8 Hz), 139.3, 130.9 (q, *J* = 2.4 Hz), 129.3, 129.1, 128.7, 127.8, 127.5, 116.9 (q, *J* = 291.3 Hz) ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −71.3 ppm. **GC-MS (EI)** *m/z*: 250.10 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[31]

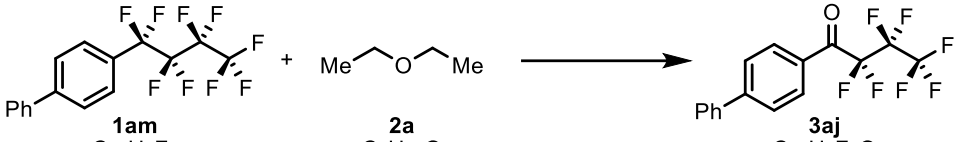
3.38 Reaction of 1-methoxy-4-(pentafluoroethyl)benzene (1al) with ethyl ether (2a)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), PhMeSiHCl (90.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methoxy-4-(pentafluoroethyl)benzene (45.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ai** as colourless liquid (17.8 mg, 44%).

4'-Methoxy-2,2,2-trifluoroacetophenone (3ai). R_f = 0.54 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ =8.06 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 179.1 (q, *J* = 34.5 Hz), 165.6, 132.9 (q, *J* = 2.4 Hz), 122.9, 117.1 (q, *J* = 291.3 Hz), 114.6, 55.8 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −71.0 ppm. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[31]

3.39 Reaction of 4-(perfluorobutyl)-1,1'-biphenyl (1am) with ethyl ether (2a)



1am
$C_{16}H_9F_9$
M = 372.2336 g/mol

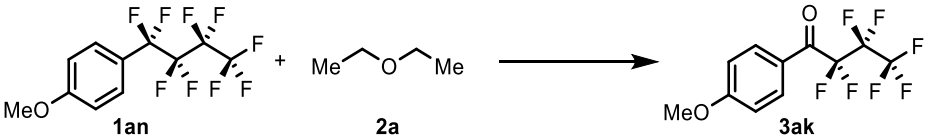
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3aj
$C_{16}H_9F_7O$
M = 350.2358 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 4-(perfluorobutyl)-1,1'-biphenyl (74.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3aj** as colourless liquid (14.8 mg, 21%).

1-[1,1'-Biphenyl]-4-yl-2,2,3,3,4,4,4-heptafluoro-1-butanone (3aj). $\mathbf{R_f}$ = 0.45 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.16 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.55 – 7.41 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 139.2, 131.1 (t, *J* = 3.8 Hz), 130.3, 129.3, 129.1, 127.7, 127.5 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −80.1 (t, *J* = 9.2 Hz), −113.5 (q, *J* = 9.0 Hz), −125.4 ppm. **HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{10}F_7O$: 351.0620; found: 351.0619**.

3.40 Reaction of 1-methoxy-4-(perfluorobutyl)benzene (1an) with ethyl ether (2a)



1an
$C_{11}H_7F_9O$
M = 326.1616 g/mol

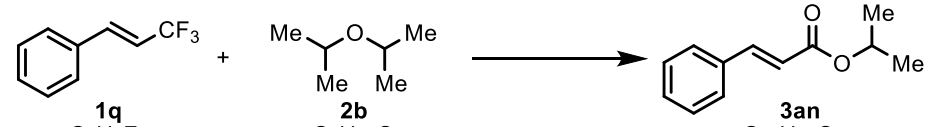
2a
$C_4H_{10}O$
M = 74.1230 g/mol

3ak
$C_{11}H_7F_7O_2$
M = 304.1638 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, ethyl ether (0.4 mL) and 1-methoxy-4-(perfluorobutyl)benzene (65.2 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ak** as yellow liquid (25.7 mg, 42%).

Heptafluoro-1-(4-methoxyphenyl)butan-1-one (3ak). R_f = 0.51 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 8.08 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 9.1 Hz, 2H), 3.92 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 165.6, 133.1 (t, *J* = 3.8 Hz), 124.6, 114.5, 55.9 ppm. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ = −80.1 (t, *J* = 9.2 Hz), −113.3 (q, *J* = 8.9 Hz), −125.5 ppm. **GC-MS (EI)** *m*/*z*: 304.05 $[M]^+$. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data is in accordance with literature report.[32]

3.41 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with diisopropyl etherr (2b)

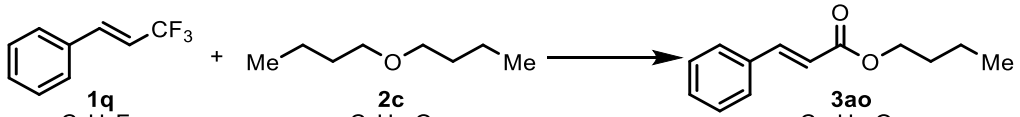


1q $C_9H_7F_3$ M = 172.1502 g/mol + **2b** $C_6H_{14}O$ M = 102.1770 g/mol → **3an** $C_{12}H_{14}O_2$ M = 190.2420 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, diisopropyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3an** as yellow liquid (23.1 mg, 61%).

(*E*)-isopropyl cinnamate (3an). R_f = 0.49 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.67 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.43 – 7.34 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.21 – 5.07 (m, 1H), 1.32 (d, *J* = 6.3 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.7, 144.4, 134.6, 130.3, 129.0, 128.1, 118.9, 67.9, 22.1 ppm. **GC-MS (EI)** *m*/*z*: 190.05 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[33]

3.42 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with dibutyl ether (2c)



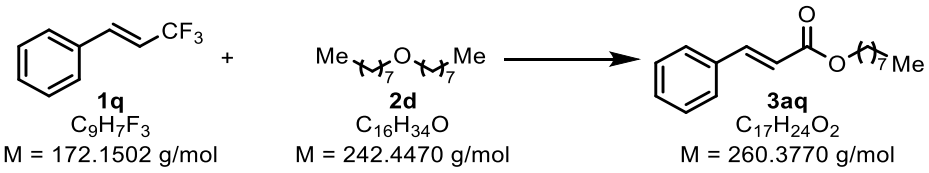
1q $C_9H_7F_3$ M = 172.1502 g/mol + **2c** $C_8H_{18}O$ M = 130.2310 g/mol → **3ao** $C_{13}H_{16}O_2$ M = 204.2690 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min,

dibutyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ao** as yellow liquid (29.5 mg, 72%).

(*E*)-butyl cinnamate (3ao). $\mathbf{R}_f$ = 0.55 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.68 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.44 – 7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.49 – 1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.3, 144.7, 134.6, 130.4, 129.0, 128.2, 118.4, 64.6, 30.9, 19.4, 13.9 ppm. **GC-MS (EI)** *m*/*z*: 204.15 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[33]

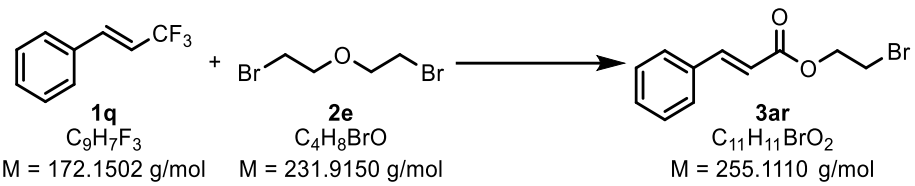
3.43 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with octyl ether (2d)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, octyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3aq** as yellow liquid (35.8 mg, 69%).

(*E*)-octyl cinnamate (3aq). $\mathbf{R}_f$ = 0.60 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.68 (d, *J* = 16.0 Hz, 1H), 7.53 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.70 (p, *J* = 6.8 Hz, 2H), 1.45 – 1.20 (m, 10H), 0.91 – 0.85 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.3, 144.7, 134.6, 130.4, 129.0, 128.2, 118.5, 64.9, 31.9, 29.4, 29.3, 28.9, 26.1, 22.8, 14.2 ppm. **GC-MS (EI)** *m*/*z*: 260.20 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[33]

3.44 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 2,2'-Dibromodiethyl ether (2e)



1q $C_9H_7F_3$ M = 172.1502 g/mol

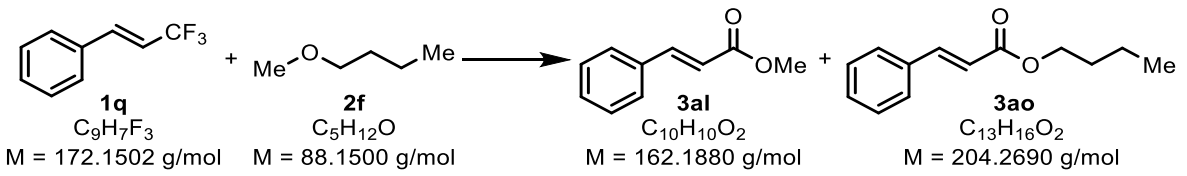
2e C_4H_8BrO M = 231.9150 g/mol

3ar $C_{11}H_{11}BrO_2$ M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 2,2'-Dibromodiethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ar** as yellow liquid (42.0 mg, 82%).

(*E*)-2-bromoethyl cinnamate (3ar). $\mathbf{R_f}$ = 0.36 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.74 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.43 – 7.37 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.52 (t, *J* = 6.2 Hz, 2H), 3.59 (t, *J* = 6.2 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.5, 145.9, 134.3, 130.7, 129.1, 128.3, 117.4, 64.0, 28.9 ppm. **GC-MS (EI)** *m*/*z*: 254.05 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[34]

3.45 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1-Methoxybutane (2f)



1q $C_9H_7F_3$ M = 172.1502 g/mol

2f $C_5H_{12}O$ M = 88.1500 g/mol

3al $C_{10}H_{10}O_2$ M = 162.1880 g/mol

3ao $C_{13}H_{16}O_2$ M = 204.2690 g/mol

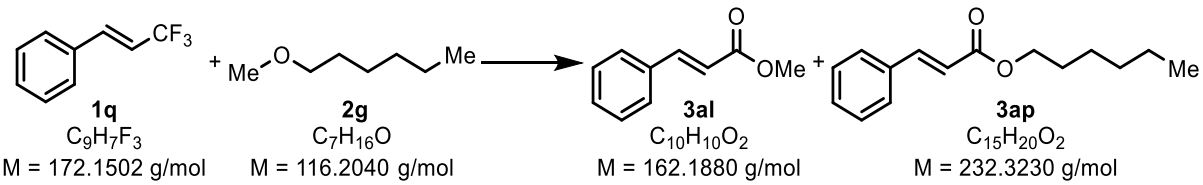
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1-methoxybutane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (4.8 mg, 15%) and compound **3ao** as yellow liquid (21.7 mg, 53%). The yield ratio

of the two regioselective products is **3al**:**3ao** = 22:78.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.70 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.5, 145.0, 134.5, 130.4, 129.0, 128.2, 117.9, 51.8 ppm. **GC-MS (EI)** *m*/*z*: 162.10 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[33]

(*E*)-butyl cinnamate (3ao). $\mathbf{R}_f$ = 0.55 (petroleum ether/ethyl acetate, 95/5). $\mathbf{R}_f$ = 0.6 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.42**.

3.46 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with hexylmethyl ether (2g)



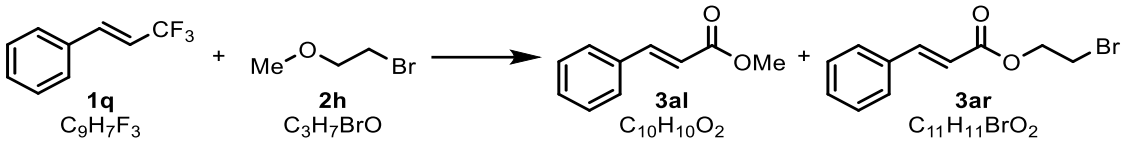
1q $C_9H_7F_3$ M = 172.1502 g/mol; **2g** $C_7H_{16}O$ M = 116.2040 g/mol; **3al** $C_{10}H_{10}O_2$ M = 162.1880 g/mol; **3ap** $C_{15}H_{20}O_2$ M = 232.3230 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, hexylmethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (9.6 mg, 30%) and compound **3ap** as yellow liquid (26.0 mg, 56%). The yield ratio of the two regioselective products is **3al**:**3ap** =35:65.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-hexyl cinnamate (3ap). $\mathbf{R}_f$ = 0.63 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.68 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.42 – 7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.70 (p, *J* = 6.8 Hz, 2H), 1.46 – 1.27 (m, 6H), 0.93 – 0.88 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.3, 144.7, 134.6, 130.4, 129.0, 128.2, 118.5, 64.9, 31.6, 28.8, 25.8, 22.7, 14.2 ppm. **GC-MS (EI)** *m*/*z*: 232.15 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[33]

3.47 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1-bromo-2-methoxyethane (2h)



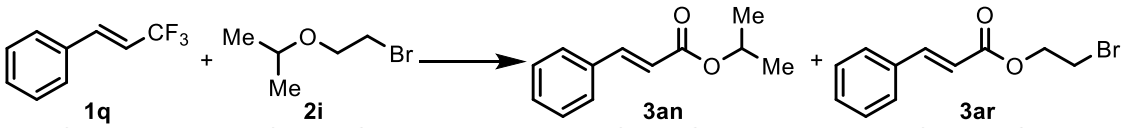
1q $C_9H_7F_3$ M = 172.1502 g/mol + **2h** C_3H_7BrO M = 138.9920 g/mol → **3al** $C_{10}H_{10}O_2$ M = 162.1880 g/mol + **3ar** $C_{11}H_{11}BrO_2$ M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1-bromo-2-methoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (4.0 mg, 12%) and compound **3ar** as yellow liquid (39.2 mg, 77%). The yield ratio of the two regioselective products is **3al**:**3ar** = 13:87.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-2-bromoethyl cinnamate (3ar). $\mathbf{R}_f$ = 0.36 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.44**.

3.48 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 2-(2-bromoethoxy)propane (2i)



1q $C_9H_7F_3$ M = 172.1502 g/mol + **2i** $C_5H_{11}BrO$ M = 167.0460 g/mol → **3an** $C_{12}H_{14}O_2$ M = 190.2420 g/mol + **3ar** $C_{11}H_{11}BrO_2$ M = 255.1110 g/mol

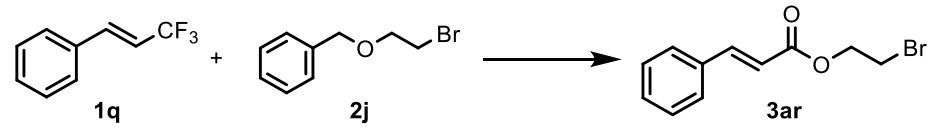
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 2-(2-bromoethoxy)propane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford

compound **3an** as yellow liquid (5.0 mg, 13%) and compound **3ar** as yellow liquid (18.6 mg, 36%). The yield ratio of the two regioselective products is **3an**:**3ar** = 27:73.

(*E*)-isopropyl cinnamate (3an). R_f = 0.49 (petroleum ether/ethyl acetate, 95/5). The ^{1}H spectroscopic data is in accordance with those in reaction **3.41**.

(*E*)-2-bromoethyl cinnamate (3ar). R_f = 0.36 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.44**.

3.49 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with benzyl 2-bromoethyl ether (2j)



1q $C_9H_7F_3$ M = 172.1502 g/mol

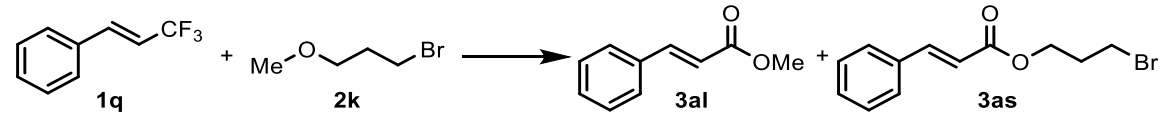
2j $C_9H_{11}BrO$ M = 215.0900 g/mol

3ar $C_{11}H_{11}BrO_2$ M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, benzyl 2-bromoethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ar** as yellow liquid (35.7 mg, 70%), which is the only ester product in the reaction.

(*E*)-2-bromoethyl cinnamate (3ar). R_f = 0.36 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.44**.

3.50 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1-bromo-3-methoxypropane (2k)



1q $C_9H_7F_3$ M = 172.1502 g/mol

2k C_4H_9BrO M = 153.0190 g/mol

3al $C_{10}H_{10}O_2$ M = 162.1880 g/mol

3as $C_{12}H_{13}BrO_2$ M = 269.1380 g/mol

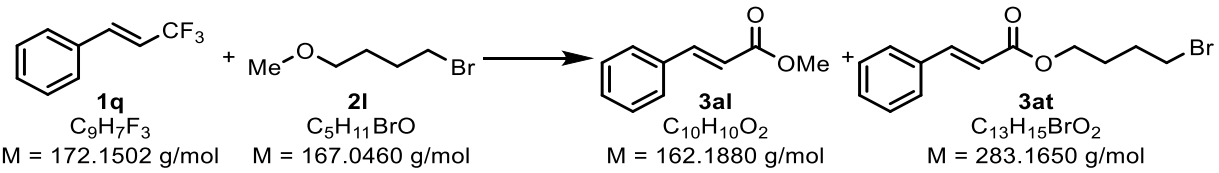
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1-bromo-3-methoxypropane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At

the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (3.2 mg, 10%) and compound **3as** as yellow liquid (40.0 mg, 74%). The yield ratio of the two regioselective products is **3al**:**3as** = 12:88.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-3-bromopropyl cinnamate (3as). $\mathbf{R}_f$ = 0.38 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.70 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.42 – 7.37 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.36 (t, *J* = 6.1 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.26 (p, *J* = 6.4 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 145.3, 134.4, 130.5, 129.0, 128.2, 117.8, 62.3, 31.9, 29.7 ppm. **GC-MS (EI)** *m*/*z*: 267.95 $[M]^+$. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[34]

3.51 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1-bromo-4-methoxybutane (2l)



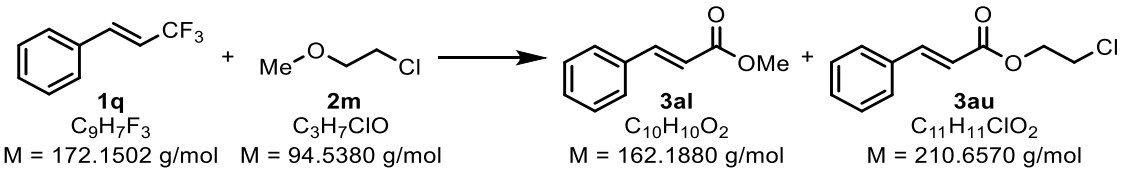
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1-bromo-4-methoxybutane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (15.6 mg, 48%) and compound **3at** as yellow liquid (12.8 mg, 23%). The yield ratio of the two regioselective products is **3al**:**3as** = 68:32.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-4-bromobutyl cinnamate (3at). 3at: $\mathbf{R}_f$ = 0.30 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.43 – 7.35 (m, 3H), 6.44 (d,

J = 16.0 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.51 – 3.42 (m, 2H), 2.06 – 1.94 (m, 2H), 1.94 – 1.82 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.0, 145.0, 134.4, 130.5, 129.0, 128.2, 118.0, 63.6, 33.3, 29.4, 27.5 ppm. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[34]

3.52 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 2-chloroethylmethyl ether (2m)

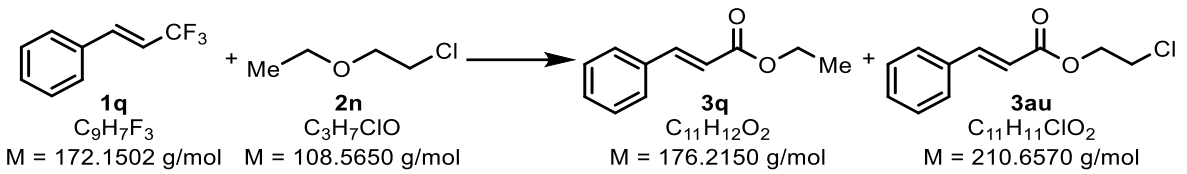


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 2-chloroethylmethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (3.6 mg, 11%) and compound **3au** as yellow liquid (30.0 mg, 71%). The yield ratio of the two regioselective products is **3al**:**3au =** 13:87.

Methyl cinnamate (3al). R_f = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-2-chloroethyl cinnamate (3au). R_f = 0.34 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.74 (d, *J* = 16.0 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.43 – 7.37 (m, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.47 (t, *J* = 5.7 Hz, 2H), 3.77 (t, *J* = 5.7 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.7, 145.9, 134.3, 130.7, 129.1, 128.3, 117.4, 64.2, 41.8 ppm. **HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{12}ClO_2$: 211.0526; found: 211.0529**. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report[35].

3.53 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 2-chloroethylethyl ether (2n)



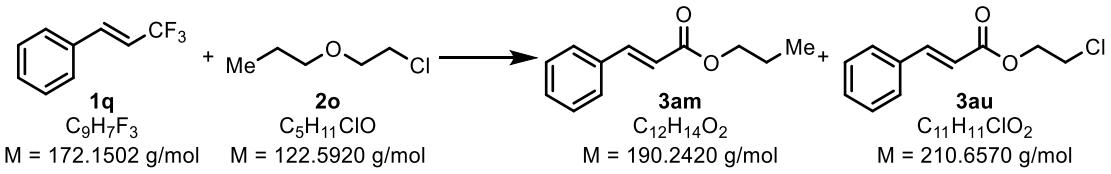
1q	2n	3q	3au
$C_9H_7F_3$	C_3H_7ClO	$C_{11}H_{12}O_2$	$C_{11}H_{11}ClO_2$
M = 172.1502 g/mol	M = 108.5650 g/mol	M = 176.2150 g/mol	M = 210.6570 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 2-chloroethylethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (4.8 mg, 14%) and compound **3au** as yellow liquid (24.0 mg, 57%). The yield ratio of the two regioselective products is **3q**:**3au** = 20:80.

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.52**.

3.54 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 2-chloroethylpropyl ether (2o)



1q	2o	3am	3au
$C_9H_7F_3$	$C_5H_{11}ClO$	$C_{12}H_{14}O_2$	$C_{11}H_{11}ClO_2$
M = 172.1502 g/mol	M = 122.5920 g/mol	M = 190.2420 g/mol	M = 210.6570 g/mol

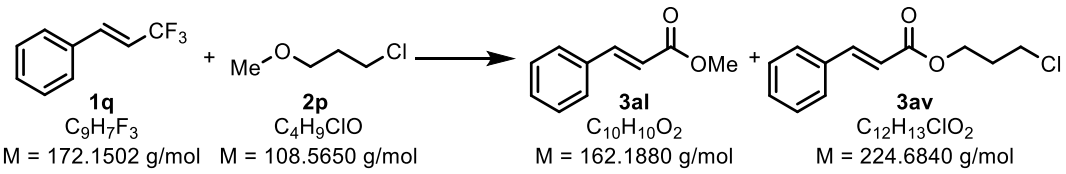
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 2-chloroethylpropyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3am** as yellow liquid (3.6 mg, 9%) and compound **3au** as yellow liquid (19.8 mg, 47%). The yield ratio

of the two regioselective products is **3am**:**3au** = 16:84.

(*E*)-propyl cinnamate (3am). R_f = 0.44 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.53 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 1.74 (h, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.2, 144.7, 134.6, 130.3, 129.0, 128.2, 118.4, 66.3, 22.2, 10.6 ppm. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[27]

(*E*)-2-chloroethyl cinnamate (3au). R_f = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.55 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 3-chloropropylmethyl ether (2p)

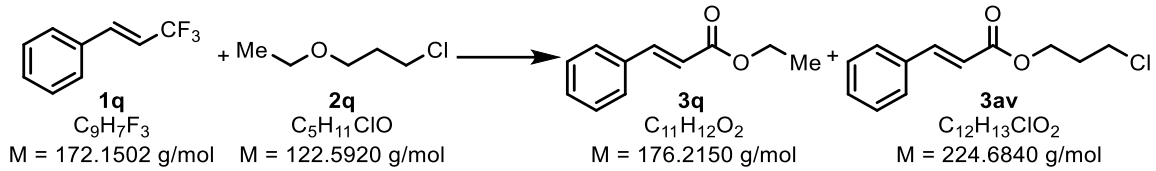


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 3-chloropropylmethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (6.4 mg, 20%) and compound **3av** as yellow liquid (25.0 mg, 56%). The yield ratio of the two regioselective products is **3al**:**3av** = 26:74.

Methyl cinnamate (3al). R_f = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-3-chloropropyl cinnamate (3av). R_f = 0.38 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.70 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.42 – 7.36 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.37 (t, *J* = 6.1 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.18 (p, *J* = 6.2 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 166.9, 145.3, 134.4, 130.5, 129.1, 128.2, 117.9, 61.4, 41.4, 31.9 ppm. **HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClO_2Na$: 247.0502; found: 247.0507**. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report[36].

3.56 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1-chloro-3-ethoxypropane (2q)



1q $C_9H_7F_3$ M = 172.1502 g/mol

2q $C_5H_{11}ClO$ M = 122.5920 g/mol

3q $C_{11}H_{12}O_2$ M = 176.2150 g/mol

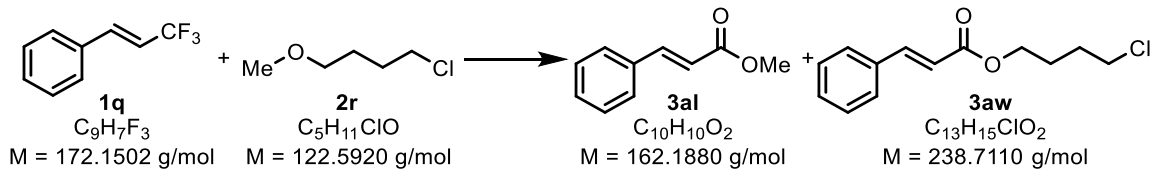
3av $C_{12}H_{13}ClO_2$ M = 224.6840 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1-chloro-3-ethoxypropane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (4.0 mg, 11%) and compound **3av** as yellow liquid (20.6 mg, 46%). The yield ratio of the two regioselective products is **3q**:**3av** = 19:81.

Ethyl cinnamate (3q). $\mathbf{R_f}$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

(*E*)-3-chloropropyl cinnamate (3av). $\mathbf{R_f}$ = 0.38 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.55**.

3.57 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 4-chlorobutylmethyl ether (2r)



1q $C_9H_7F_3$ M = 172.1502 g/mol

2r $C_5H_{11}ClO$ M = 122.5920 g/mol

3al $C_{10}H_{10}O_2$ M = 162.1880 g/mol

3aw $C_{13}H_{15}ClO_2$ M = 238.7110 g/mol

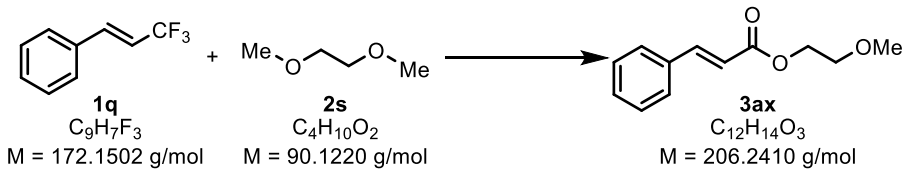
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 4-chlorobutylmethyl ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound

3al as yellow liquid (18.6 mg, 57%) and compound **3aw** as yellow liquid (19.5 mg, 41%). The yield ratio of the two regioselective products is **3al**:**3aw =** 58:42.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-4-chlorobutyl cinnamate (3aw). $\mathbf{R}_f$ = 0.49 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, *J* = 16.2 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.43 – 7.37 (m, 3H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 5.7 Hz, 2H), 3.61 (t, *J* = 5.9 Hz, 2H), 2.10 – 1.75 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.1, 145.1, 134.5, 130.5, 129.0, 128.2, 118.1, 63.8, 44.7, 29.3, 26.3 ppm. **HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}ClO_2Na$: 261.0658; found: 261.0662**. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report[37].

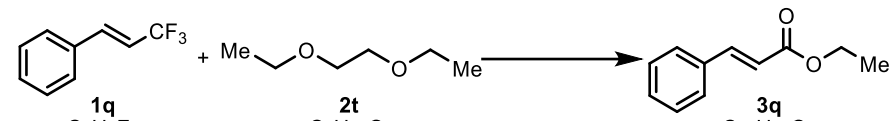
3.58 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-dimethoxyethane (2s)



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-dimethoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ax** as yellow liquid (22.1 mg, 54%).

(*E*)-2-methoxyethyl 3-(phenyl)-2-propenoate (3ax). $\mathbf{R}_f$ = 0.23 (petroleum ether/ethyl acetate, 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 7.72 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.41 – 7.34 (m, 3H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.40 – 4.33 (m, 2H), 3.70 – 3.63 (m, 2H), 3.42 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 167.1, 145.2, 134.4, 130.4, 129.0, 128.2, 117.9, 70.7, 63.7, 59.2 ppm. The ^{1}H and ^{13}C NMR spectroscopic data is in accordance with literature report.[38]

3.59 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-diethoxyethane (2t)



1q $C_9H_7F_3$ M = 172.1502 g/mol

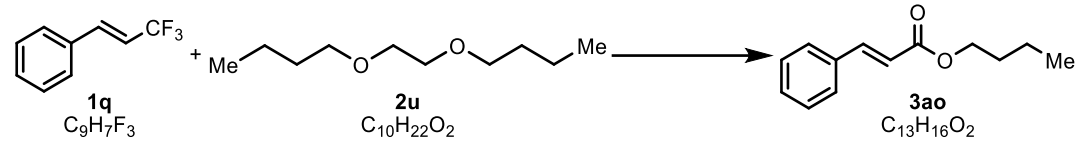
2t $C_6H_{14}O_2$ M = 118.1760 g/mol

3q $C_{11}H_{12}O_2$ M = 176.2150 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-diethoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (14.2 mg, 40%).

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

3.60 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-dibutoxyethane (2u)



1q $C_9H_7F_3$ M = 172.1502 g/mol

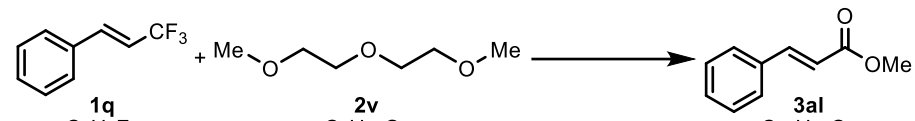
2u $C_{10}H_{22}O_2$ M = 174.2840 g/mol

3ao $C_{13}H_{16}O_2$ M = 204.2690 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-dibutoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ao** as yellow liquid (13.1 mg, 32%).

(*E*)-butyl cinnamate (3ao). $\mathbf{R}_f$ = 0.55 (petroleum ether/ethyl acetate, 95/5). $\mathbf{R}_f$ = 0.6 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.42**.

3.61 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis(2-methoxyethyl)ether (2v)



1q
$C_9H_7F_3$
M = 172.1502 g/mol

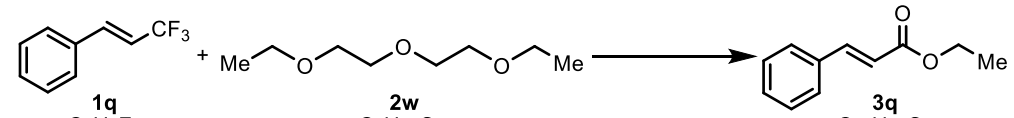
2v
$C_6H_{14}O_3$
M = 134.1750 g/mol

3al
$C_{10}H_{10}O_2$
M = 162.1880 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis(2-methoxyethyl)ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (16.0 mg, 49%).

Methyl cinnamate (3al). $\mathbf{R_f}$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

3.62 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis(2-ethoxyethyl)ether (2w)



1q
$C_9H_7F_3$
M = 172.1502 g/mol

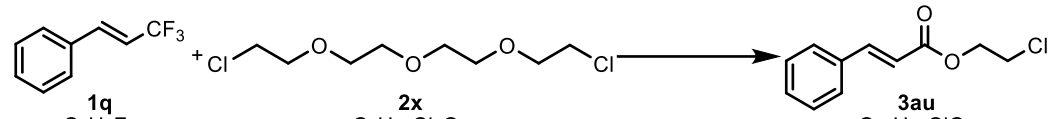
2w
$C_8H_{18}O_3$
M = 162.2290 g/mol

3q
$C_{11}H_{12}O_2$
M = 176.2150 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis(2-ethoxyethyl)ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (11.4 mg, 32%).

Ethyl cinnamate (3q). $\mathbf{R_f}$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

3.63 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis(2-(2-chloroethoxy)ethyl)ether (2x)



1q
$C_9H_7F_3$
M = 172.1502 g/mol

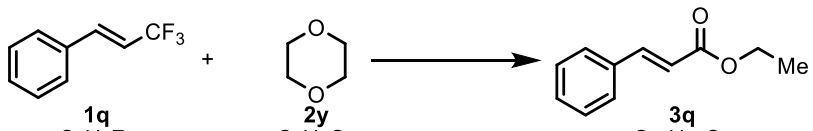
2x
$C_8H_{16}Cl_2O_3$
M = 231.1131 g/mol

3au
$C_{11}H_{11}ClO_2$
M = 210.6570 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (12.0 μL, 0.1 mmol, 0.5 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis(2-(2-chloroethoxy)ethyl)ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3au** as yellow liquid (20.0 mg, 47%).

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.64 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,4-dioxane (2y)



1q
$C_9H_7F_3$
M = 172.1502 g/mol

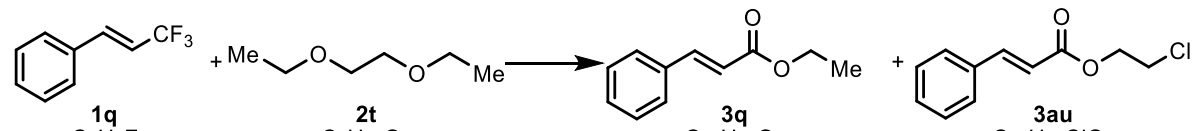
2y
$C_4H_8O_2$
M = 88.1060 g/mol

3q
$C_{11}H_{12}O_2$
M = 176.2150 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $PhSiH_3$ (74.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,4-dioxane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as colourless liquid (18.8 mg, 53%).

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

3.65 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-diethoxyethane (2t) by $MeSiHCl_2$



1q $C_9H_7F_3$ M = 172.1502 g/mol

2t $C_6H_{14}O_2$ M = 118.1760 g/mol

3q $C_{11}H_{12}O_2$ M = 176.2150 g/mol

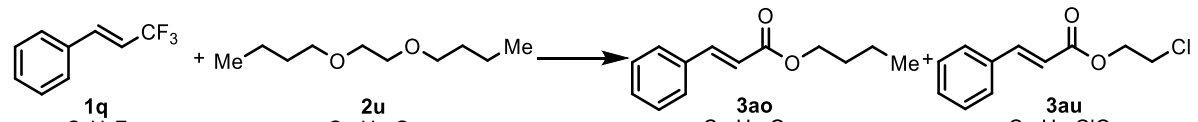
3au $C_{11}H_{11}ClO_2$ M = 210.6570 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-diethoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (8.0 mg, 23%) and compound **3au** as yellow liquid (25.6 mg, 61%). The yield ratio of the two regioselective products is **3q**:**3au** = 27:73.

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.66 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-dibutoxyethane (2u) by $MeSiHCl_2$



1q $C_9H_7F_3$ M = 172.1502 g/mol

2u $C_{10}H_{22}O_2$ M = 174.2840 g/mol

3ao $C_{13}H_{16}O_2$ M = 204.2690 g/mol

3au $C_{11}H_{11}ClO_2$ M = 210.6570 g/mol

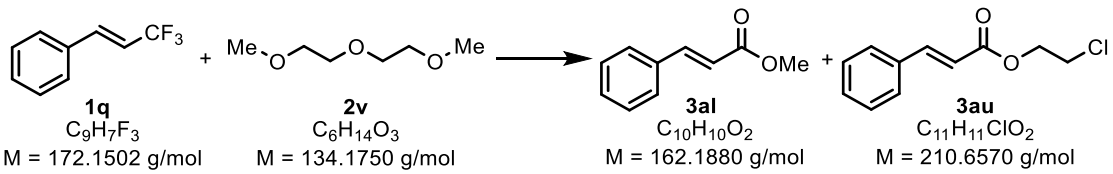
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-dibutoxyethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound

3ao as yellow liquid (3.2 mg, 8%) and compound **3au** as yellow liquid (28.2 mg, 67%). The yield ratio of the two regioselective products is **3ao**:**3au** = 11:89.

(*E*)-butyl cinnamate (3ao). $\mathbf{R}_f$ = 0.55 (petroleum ether/ethyl acetate, 95/5). $\mathbf{R}_f$ = 0.6 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.42**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.67 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis(2-methoxyethyl)ether (2v) by $MeSiHCl_2$

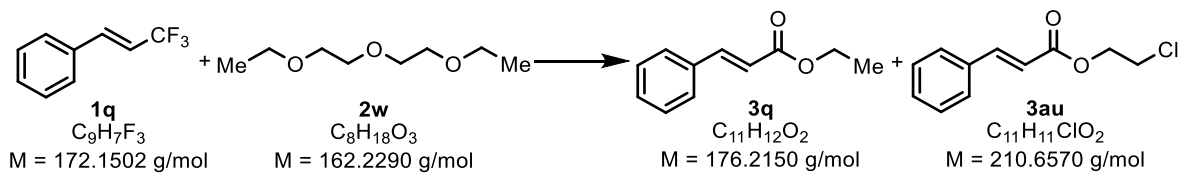


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis(2-methoxyethyl)ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 ℃ for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (6.0 mg, 19%) and compound **3au** as yellow liquid (19.0 mg, 45%). The yield ratio of the two regioselective products is **3al**:**3au** = 30:70.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.68 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis(2-ethoxyethyl)ether (2w) by $MeSiHCl_2$



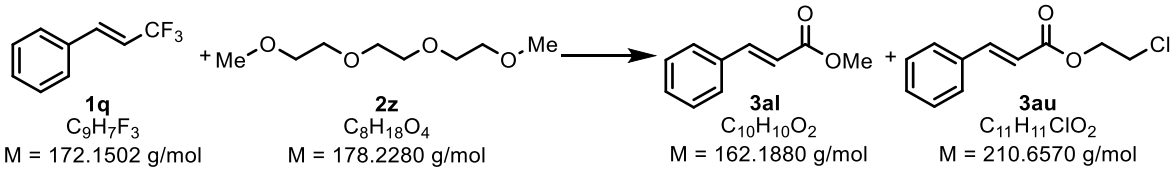
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%),

$MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis(2-ethoxyethyl)ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (7.0 mg, 20%) and compound **3au** as yellow liquid (21.0 mg, 50%). The yield ratio of the two regioselective products is **3q**:**3au** = 29:71.

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.17**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5).The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.69 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,2-bis(2-methoxyethoxy)ethane (2z) by $MeSiHCl_2$

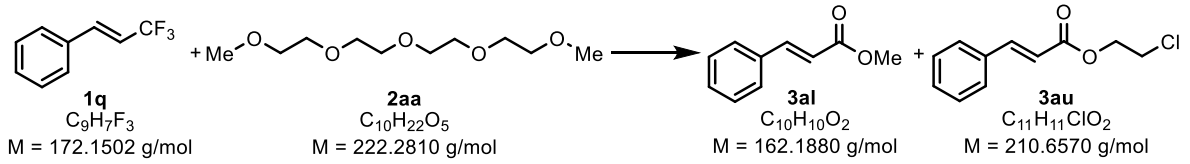


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,2-bis(2-methoxyethoxy)ethane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (9.5 mg, 29%) and compound **3au** as yellow liquid (15.3 mg, 36%). The yield ratio of the two regioselective products is **3al**:**3au** = 45:55.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.70 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with bis[2-(2-methoxyethoxy)ethyl] ether (2aa) by $MeSiHCl_2$

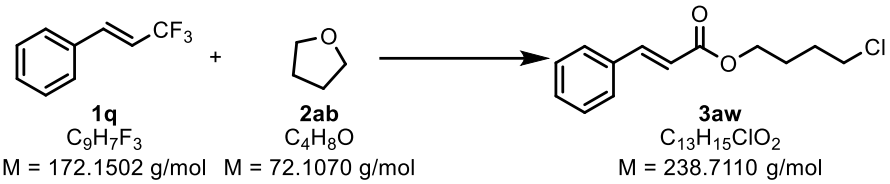


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, bis[2-(2-methoxyethoxy)ethyl] ether (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3al** as yellow liquid (10.2 mg, 31%) and compound **3au** as yellow liquid (21.8 mg, 52%). The yield ratio of the two regioselective products is **3al**:**3au** = 37:63.

Methyl cinnamate (3al). $\mathbf{R}_f$ = 0.42 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.45**.

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

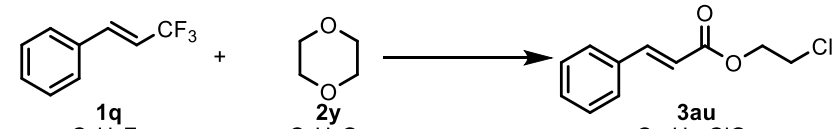
3.71 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with THF (2ab) by $MeSiHCl_2$



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, THF (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3aw** as yellow liquid (26.4 mg, 55%).

(*E*)-4-chlorobutyl cinnamate (3aw). R_f = 0.49 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.57**.

3.72 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,4-dioxane (2y) by $MeSiHCl_2$



1q $C_9H_7F_3$ M = 172.1502 g/mol

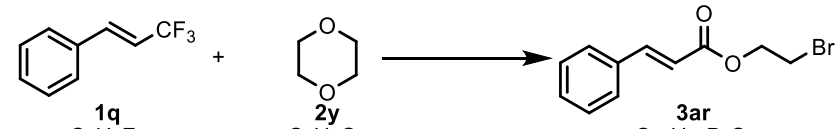
2y $C_4H_8O_2$ M = 88.1060 g/mol

3au $C_{11}H_{11}ClO_2$ M = 210.6570 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,4-dioxane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3au** as yellow liquid (32.2 mg, 76%).

(*E*)-2-chloroethyl cinnamate (3au). R_f = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.73 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 1,4-dioxane (2y) by Me_3SiBr



1q $C_9H_7F_3$ M = 172.1502 g/mol

2y $C_4H_8O_2$ M = 88.1060 g/mol

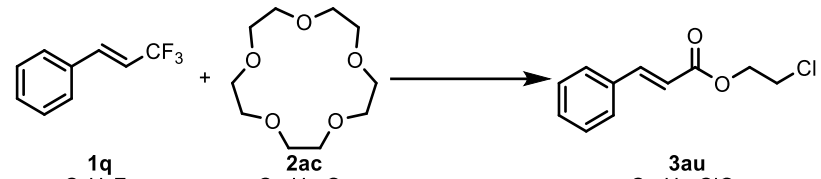
3ar $C_{11}H_{11}BrO_2$ M = 255.1110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), Me_3SiBr (79.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 1,4-dioxane (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3ar** as yellow liquid (30.2 mg, 59%).

(*E*)-2-bromoethyl cinnamate (3ar). R_f = 0.36 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR

spectroscopic data is in accordance with those in reaction **3.44**.

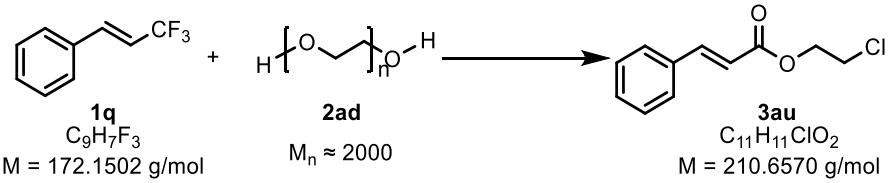
3.74 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with 15-Crown-5 (2ac) by $MeSiHCl_2$



Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, 15-Crown-5 (0.4 mL) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3au** as yellow liquid (22.5 mg, 53%).

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R_f}$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.53**.

3.75 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with PEG (2ad) by $SiCl_4$

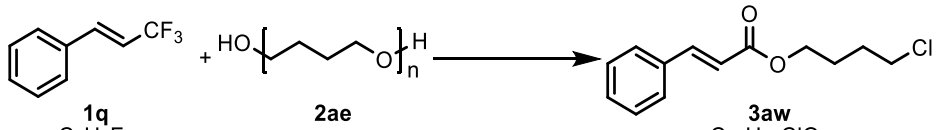


Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $SiCl_4$ (69.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, PEG (90.0 mg, 2 mmol, 10.0 equiv) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3au** as yellow liquid (29.2 mg, 69%).

(*E*)-2-chloroethyl cinnamate (3au). $\mathbf{R_f}$ = 0.34 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR

spectroscopic data is in accordance with those in reaction **3.53**.

3.76 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with PTMG (2ae) by $SiCl_4$



1q
$C_9H_7F_3$
M = 172.1502 g/mol

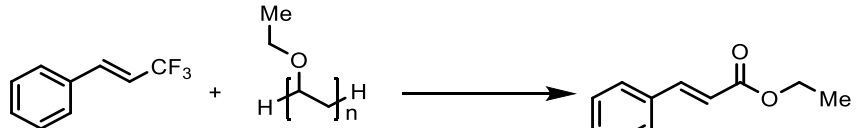
2ae
$M_n \approx 2000$

3aw
$C_{13}H_{15}ClO_2$
M = 238.7110 g/mol

Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $SiCl_4$ (69.0 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, PTMG (146.0 mg, 2 mmol, 10.0 equiv) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3aw** as yellow liquid (28.1 mg, 59%).

(*E*)-4-chlorobutyl cinnamate (3aw). $\mathbf{R}_f$ = 0.49 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data is in accordance with those in reaction **3.57**.

3.77 Reaction of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1q) with Poly(ethylvinyl ether) (2af) by $MeSiHCl_2$



1q
$C_9H_7F_3$
M = 172.1502 g/mol

2af
$M_n \approx 933$

3q
$C_{11}H_{12}O_2$
M = 176.2150 g/mol

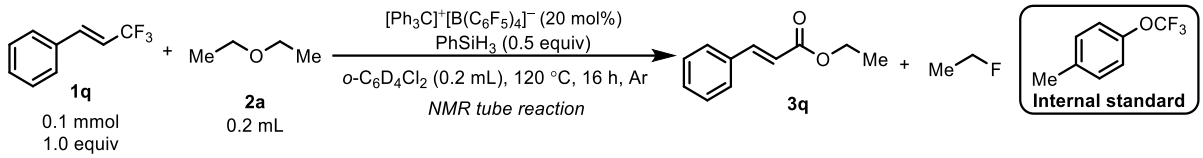
Under argon atmosphere, the sealed tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (36.4 mg, 20 mol%), $MeSiHCl_2$ (62.5 μL, 0.6 mmol, 3.0 equiv) in PhCl (0.2 mL). After stirring the reaction mixture for 15 min, Poly(ethylvinyl ether) (146.0 mg, 2 mmol, 10.0 equiv) and (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was stirred at 120 °C for 16 h. At the end of the reaction, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate, 65/1) to afford compound **3q** as yellow liquid (19.0 mg, 54%). $\mathbf{R}_f$ = 0.5 (petroleum ether/ethyl acetate, 95/5).

Ethyl cinnamate (3q). $\mathbf{R}_f$ = 0.53 (petroleum ether/ethyl acetate, 95/5). The ^{1}H NMR spectroscopic data

is in accordance with those in reaction **3.17**.

4 Mechanism Studies

4.1 Detection of Fluoroalkane with NMR



Under argon atmosphere, a J. Young-valve NMR tube was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (18.4 mg, 20 mol%), *o*-$C_6D_4Cl_2$ (0.2 mL), $PhSiH_3$ (6.0 μL, 0.05 mmol, 0.5 equiv). Then Et_2O (**2a**, 0.2 mL), (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) and 4-trifluoromethoxytoluene (17.6 mg, 0.1 mmol, internal standard) were added to the NMR tube. The reaction mixture was heated at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was directly subjected to NMR spectroscopic analysis. ^{1}H NMR (**Figure S1**, top) shows a signal of 4.47 ppm (dq, J = 47.1, 7.0 Hz, 2H),^{19}F NMR (**Figure S1**, bottom) shows a signal of –211.5 ppm (EtF), which is in accordance with literature report,[39] suggesting that the trifluoromethyl metathesis with ether to form alkyl fluorine. By calculating the ratio between the internal standard and fluoroethane, the amount of fluoroethane is approximately 0.07 mmol.

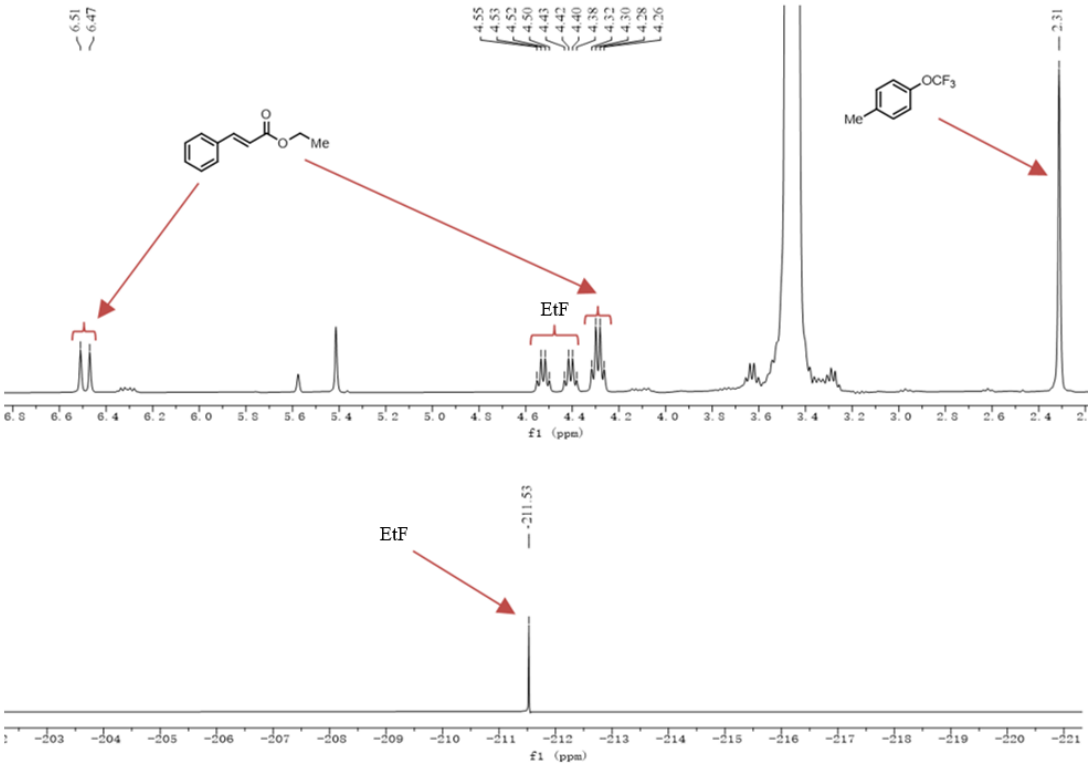
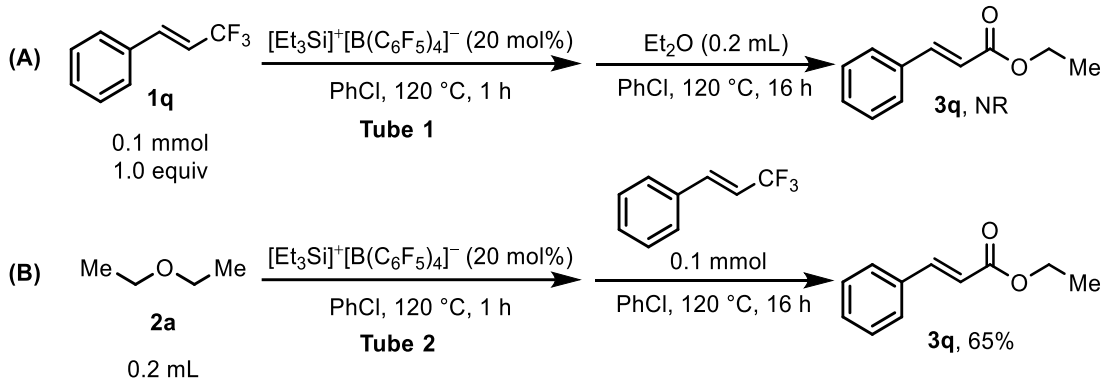
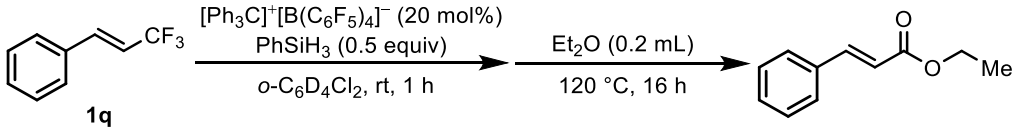


Figure S1. Monitoring the reaction of EtF in *o*-$C_6D_4Cl_2$ by ^{1}H NMR (400 MHz, 298 K) (top) and ^{19}F NMR (376 MHz, 298 K) spectroscopy(bottom).

4.2 Reactive Intermediate Investigation



Under argon atmosphere, two sealed tubes equipped with a stirring bar were charged with $[Et_3Si]^+[B(C_6F_5)_4]^-$ (16.0 mg, 20 mol%), PhCl (0.1 mL). Then, (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) was added to sealed tube 1, and Et_2O (**2a**, 0.2 mL) was added to sealed tubes 2 via syringy, The reaction mixture were stirred for 1 hours at 120 ℃. Subsequently, Et_2O (**2a**, 0.2 mL) was injected to sealed tube 1, and (3,3,3-Trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) was added to sealed tubes 2. Both reaction mixtures were stirred for 16 hours at 120 ℃. Finally, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether) to afford compound **3q**. Product **3q** could not be obtained in sealed tube 1, while the reaction underwent smoothly in sealed tube 2 (**3q**: 65% yield).



Under an argon atmosphere, a sealed tube equipped with a stir bar was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (18.4 mg, 20 mol%), *o*-$C_6D_4Cl_2$ (0.2 mL), and $PhSiH_3$ (6.0 μL, 0.05 mmol, 0.5 equiv). (3,3,3-Trifluoro-1-propen-1-yl)benzene (1q, 15.0 μL, 0.1 mmol, 1.0 equiv) was then added, and the mixture was stirred at room temperature for 1 hour. NMR analysis at this stage revealed the formation of an allylic isomer[40]: ^{19}F NMR δ –88.55 (d, *J* = 45.0 Hz) and –91.71 (d, *J* = 45.5 Hz); ^1H NMR δ 4.20 (dt, *J* = 24.9, 8.0 Hz, 1H) and 3.12 (d, *J* = 8.1 Hz, 3H). Subsequently, Et_2O (**2a**, 0.2 mL) was injected, and the mixture was heated at 120 °C for 16 hours. NMR analysis after heating showed only trace amounts of ester product,

along with residual starting material and silicon–fluorine species (see Figure S2).

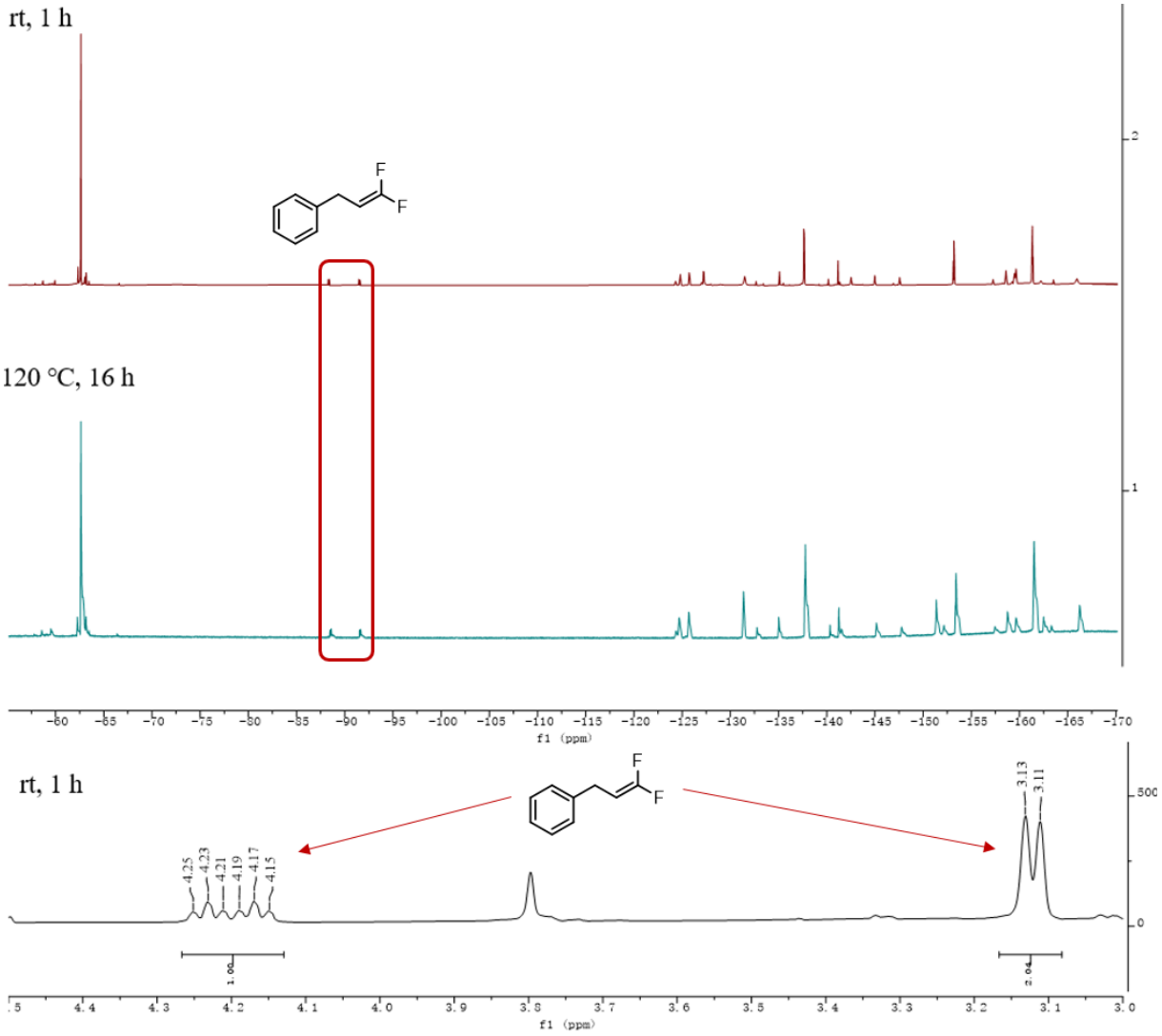
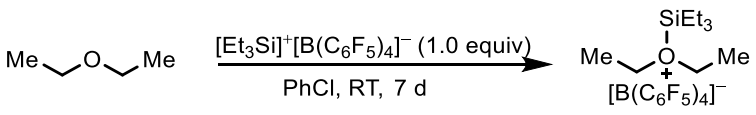


Figure S2. Monitoring the reaction of (3,3-difluoroallyl)benzene in *o*-$C_6D_4Cl_2$ by ^{19}F NMR (376 MHz, 298 K) (top) and ^{1}H NMR (400 MHz, 298 K) (bottom) spectroscopy.

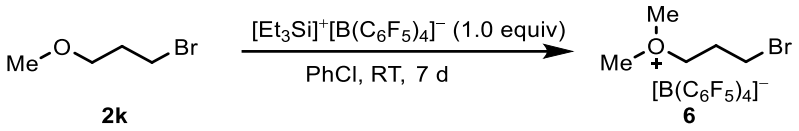
4.3 The Adducts of Silylium Ion and Ethers



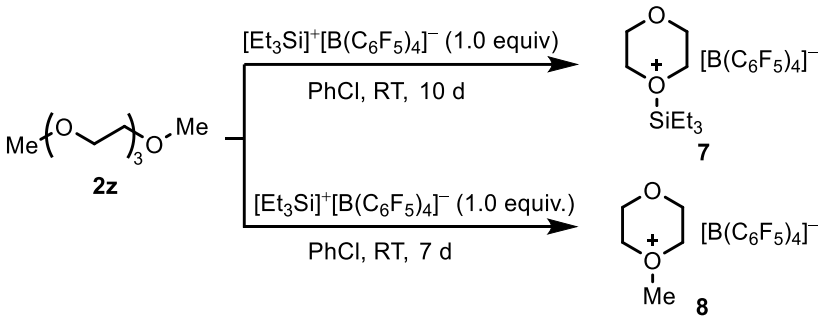
2a **5**

Under argon atmosphere, the NMR tube were charged with $[Et_3Si]^+[B(C_6F_5)_4]^-$ (16.0 mg, 0.02 mmol, 1.0 equiv), PhCl (0.5 mL). Then Et_2O (**2a**, 2.0 μL, 0.02 mmol, 1.0 equiv) was injected to NMR tube, followed by shaking the NMR tube violently for 10 min. Afterwards, dried *n*-hexane (1.0 mL) was added dropwise. Single crystals of intermediates **5** suitable for X-ray diffraction were obtained via layer diffusion from a solution in chlorobenzene by layer diffusion with n-hexane after 7 days at room

temperature (cf. Figure S2 in **5.1**). CCDC 2453488 contains the supplementary crystallographic data. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

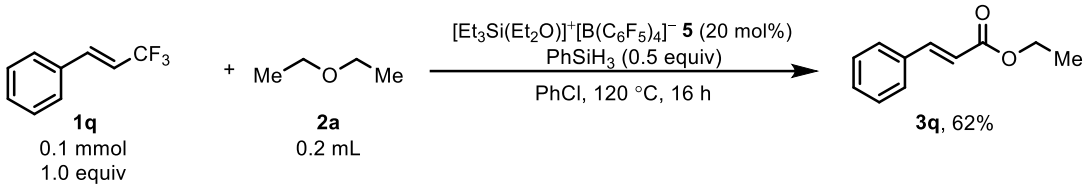


Under argon atmosphere, the NMR tube were charged with $[Et_3Si]^+[B(C_6F_5)_4]^-$ (16.0 mg, 0.02 mmol, 1.0 equiv), PhCl (0.5 mL). Then 1-Bromo-3-methoxypropane (**2k**, 2.5 μL, 0.02 mmol, 1.0 equiv) was added to NMR tube, followed by shaking the NMR tube violently for 10 min. Afterwards, dried *n*-hexane (1.0 mL) was added dropwise. Single crystals of intermediates **6** suitable for X-ray diffraction were obtained via layer diffusion from a solution in chlorobenzene by layer diffusion with n-hexane after 7 days at room temperature (cf. Figure S3 in **5.2**). CCDC 2453037 contains the supplementary crystallographic data. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

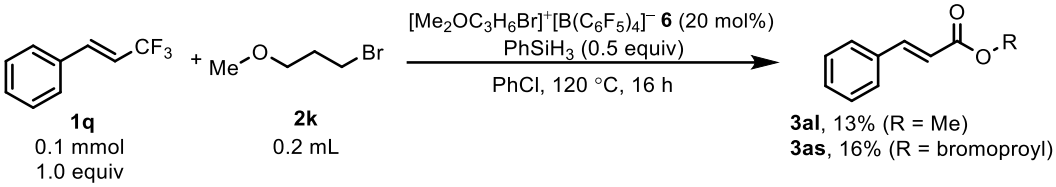


Under argon atmosphere, the NMR tube were charged with $[Et_3Si]^+[B(C_6F_5)_4]^-$ (16.0 mg, 0.02 mmol, 1.0 equiv), PhCl (0.5 mL). Then 1,2-bis(2-methoxyethoxy)ethan**e** (**2z**, 3.5 μL, 0.02 mmol, 1.0 equiv) was added to NMR tube, followed by shaking the NMR tube violently for 10 min. Afterwards, dried *n*-hexane (1.0 mL) was added dropwise. Single crystals of intermediates **7** and **8** suitable for X-ray diffraction were obtained via layer diffusion from a solution in chlorobenzene by layer diffusion with *n*-hexane at room temperature after 10 days and 7 days, respectively (cf. Figure S4 in **5.3** and Figure S5 in **5.4**). CCDC 2453036 of **7** and CCDC 2453038 of **8** contain the supplementary crystallographic data. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

4.4 Investigation of Reactivity of Different Oxonium Ions

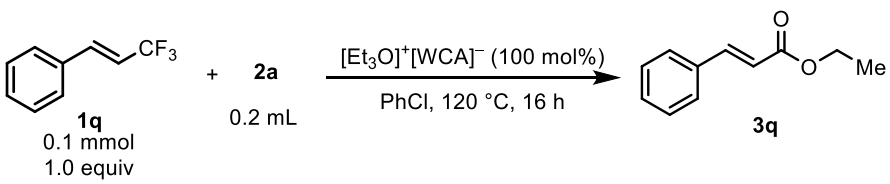


Under argon atmosphere, the sealed tube was charged with $[Et_3Si(Et_2O)]^+[B(C_6F_5)_4]^-$ (17.4 mg, 20 mol%), PhCl (0.1 mL), $PhSiH_3$ (6.0 μL, 0.05 mmol, 0.5 equiv). After stirring the reaction mixture for 15 min, Et_2O (**2a**, 0.2 mL) and (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) were subjected to the sealed tube. The reaction mixture was heated at 120 °C for 16 h. After cooling the reaction mixture to room temperature, the solvent was removed by evaporation under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether) to afford compound **3q** (62% yield).



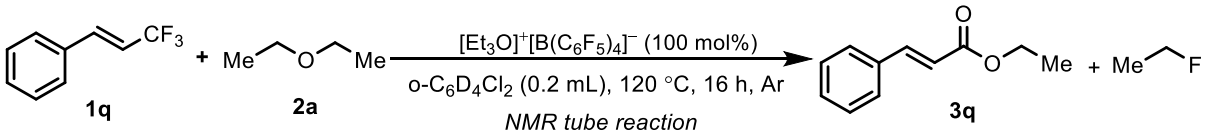
Under argon atmosphere, the sealed tube was charged with $[Me_2OC_3H_6Br]^+[B(C_6F_5)_4]^-$ (17.0 mg, 20 mol%), PhCl (0.1 mL), $PhSiH_3$ (6.0 μL, 0.05 mmol, 0.5 equiv). After stirring the reaction mixture for 15 min, 1-bromo-3-methoxypropane (**2k**, 0.2 mL) and (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) were added to the sealed tube. The reaction mixture was heated at 120 °C for 16 h. After cooling the reaction mixture to room temperature, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether) to afford compounds **3al** (13%) and **3as** (16%), in 13% and 16% yields, respectively.

Table S2. Reaction of Stoichiometric Meerwein-Type Salt

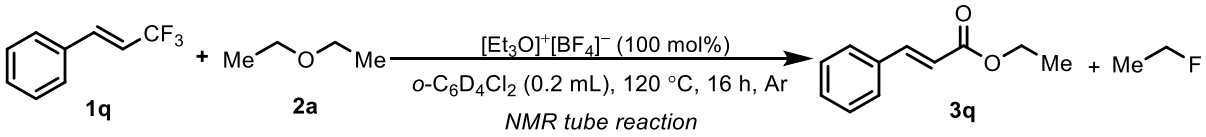


entry	[WCA]⁻	yield
1	$[BF_4]^-$	34%
2	$[B(C_6F_5)_4]^-$	48%

Under argon atmosphere, the sealed tubes equipped with a stirring bar were charged with components as indicated in Table S2. Then PhCl (0.1 mL), (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) and Et_2O (0.2 mL) were added to sealed tubes. The reaction mixture was stirred for 16 hours at 120 ℃. Afterwards, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether) to afford compound **3q**. The yields obtained were shown in Table 2.



Under argon atmosphere, a J. Young-valve NMR tube was charged with $[Et_3O]^+[B(C_6F_5)_4]^-$ (78.2 mg, 100 mol%), *o*-$C_6D_4Cl_2$ (0.2 mL). Then Et_2O (**2a**, 0.2 mL), (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) were added to the NMR tube. The reaction mixture was heated at 120 °C for 16 h. Subsequently, the reaction mixture was directly subjected to NMR spectroscopic analysis, ^{19}F NMR shows a signal of –211.7 ppm (see Figure S3).



Under argon atmosphere, a J. Young-valve NMR tube was charged with $[Et_3O]^+[BF_4]^-$ (19.0 mg, 100 mol%), *o*-$C_6D_4Cl_2$ (0.2 mL). Then Et_2O (**2a**, 0.2 mL), (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) were added to the NMR tube. The reaction mixture was heated at 120 °C for 16 h. Subsequently, the reaction mixture was directly subjected to NMR spectroscopic analysis, ^{19}F NMR shows a signal of –211.0 ppm (see Figure S3).

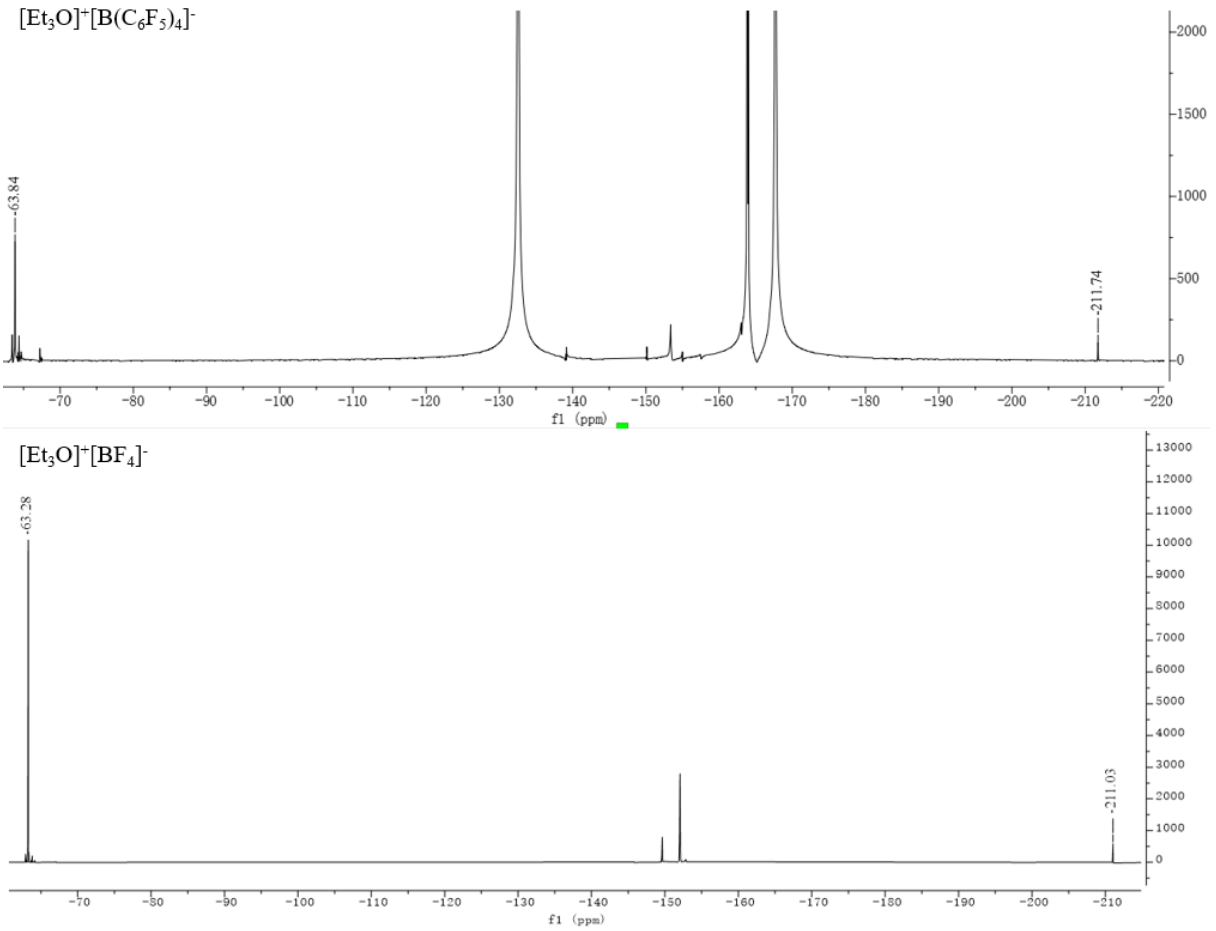
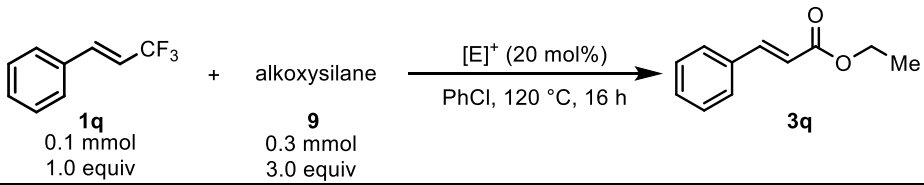


Figure S3. Monitoring the reaction mixture with $[Et_3O]^+[B(C_6F_5)_4]^-$ (top) and $[Et_3O]^+[BF_4]^-$ (bottom) in *o*-$C_6D_4Cl_2$ by ^{19}F NMR (376 MHz, 298 K) spectroscopy.

4.5 Reactions with Alkoxysilane

Table S3. Reaction of alkoxysilane



1q
0.1 mmol
1.0 equiv

9
0.3 mmol
3.0 equiv

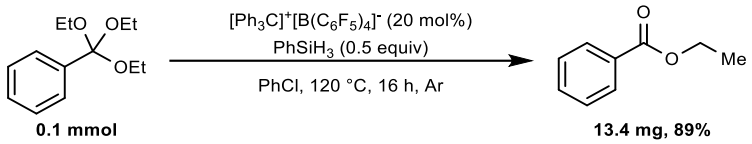
3q

entry	$[E]^+$	alkoxysilane	yield
1	none	$PhSi(OEt)_3$	N.R.
2	$[Ph_3C]^+[B(C_6F_5)_4]^-$	$PhSi(OEt)_3$	73%

Under argon atmosphere, the sealed tubes equipped with a stirring bar were charged with components as indicated in table (**Table S3**). Then PhCl (0.1 mL), (3,3,3-trifluoro-1-propen-1-yl)benzene (**1q**, 15.0 μL, 0.1 mmol, 1.0 equiv) were added to sealed tubes. The reaction mixture was stirred for 16 hours at 120 ℃. Afterwards, the solvent was removed by evaporation under vacuum and the residue was purified

by flash chromatography on silica gel (eluting with petroleum ether) to afford compound **3q**. The yields obtained were shown in Table S3.

4.6 Reaction of (Triethoxymethyl)benzene



0.1 mmol **13.4 mg, 89%**

Under argon atmosphere, the sealed tube equipped with a stirring bar were charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (18.4 mg, 20 mol%), PhCl (0.1 mL), $PhSiH_3$ (6.0 μL, 0.05 mmol, 0.5 equiv). Then, (triethoxymethyl)benzene (22.4 mg, 0.1 mmol, 1.0 equiv) was added to sealed tubes. The reaction mixture was stirred for 16 hours at 120 ℃. Afterwards, the solvent was removed by evaporation under vacuum and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether) to afford compound **3n** (13.4 mg, 89%).

5 Crystallographic Data

Data for the single-crystal structure determination were collected with Rigaku ROD, Synergy Custom DW system using Cu-K_α radiation (λ = 1.54184 Å). Software packages used: Olex 2 for structure solution and refinement, and Mercury for graphics. Hydrogen atoms and solvent molecules, *et al*. are omitted for clarity.

5.1 Molecular Structure of 5 (CCDC 2453488)

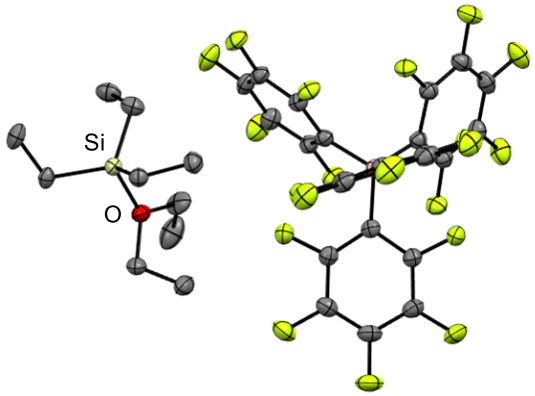


Figure S4. Molecular structure of **5**. Thermal ellipsoids at 50% probability level; H atoms omitted for clarity.

Empirical formula	$C_{37.35}H_{33.04}BF_{20}OSi$
Formula weight	916.78
Temperature/K	99.8(8)
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.62180(10)
b/Å	17.44020(10)
c/Å	21.7686(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7449.39(9)
Z	8
ρ_{calc}g/cm^3	1.635
μ/mm^{-1}	1.789
F(000)	3713.0
Crystal size/mm^3	0.12 × 0.12 × 0.08
Radiation	Cu K_α (λ = 1.54184)
2Θ range for data collection/°	10.144 to 151.872
Index ranges	-20 ≤ h ≤ 24, -21 ≤ k ≤ 21, -27 ≤ l ≤ 24
Reflections collected	35826
Independent reflections	7437 [R_{int} = 0.0347, R_{sigma} = 0.0264]
Data/restraints/parameters	7437/78/670
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	0.53/-0.37

5.2 Molecular Structure of 6 (CCDC 2453037)

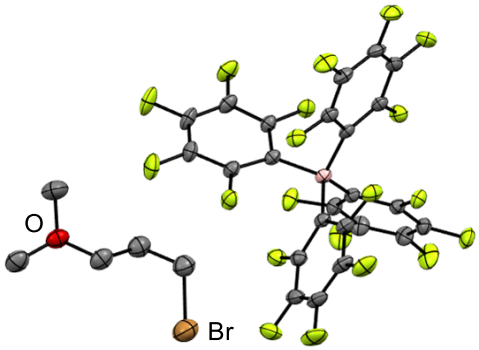


Figure S5. Molecular structure of **6**. Thermal ellipsoids at 50% probability level; H atoms omitted for clarity.

Empirical formula	$C_{29}H_{12}BBrF_{20}O$
Formula weight	847.11
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.57950(10)
b/Å	11.37660(10)
c/Å	17.94160(10)
α/°	90
β/°	90.4630(10)
γ/°	90
Volume/Å^3	2975.79(4)
Z	4
ρ_{calc}g/cm^3	1.891
μ/mm^{-1}	3.323
F(000)	1656.0
Crystal size/mm^3	0.42 × 0.26 × 0.24
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.062 to 149.006
Index ranges	$-18 \le h \le 18$, $-13 \le k \le 12$, $-22 \le l \le 22$
Reflections collected	50879
Independent reflections	6034 [R_{int} = 0.0362, R_{sigma} = 0.0141]
Data/restraints/parameters	6034/0/471
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0687, wR_2 = 0.2108
Final R indexes [all data]	R_1 = 0.0694, wR_2 = 0.2113
Largest diff. peak/hole / e Å^{-3}	0.81/-2.01

5.3 Molecular Structure of 7 (CCDC 2453036)

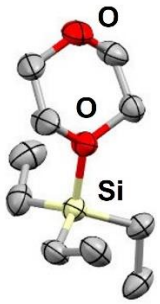


Figure S6. Molecular structure of **7**. Thermal ellipsoids at 50% probability level; H atoms and counter anion omitted for clarity.

Empirical formula	$C_{34}H_{23}BF_{20}O_2Si$
Formula weight	882.42
Temperature/K	138.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.11530(10)
b/Å	20.54670(10)
c/Å	17.47430(10)
α/°	90
β/°	108.4470(10)
γ/°	90
Volume/Å^3	3785.77(5)
Z	4
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	1.759
F(000)	1768.0
Crystal size/mm^3	0.46 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.852 to 136.496
Index ranges	$-13 \leq h \leq 13$, $-24 \leq k \leq 24$, $-20 \leq l \leq 19$
Reflections collected	58348
Independent reflections	6895 [R_{int} = 0.0419, R_{sigma} = 0.0190]
Data/restraints/parameters	6895/0/526
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0478, wR_2 = 0.1366
Final R indexes [all data]	R_1 = 0.0492, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	0.89/-0.62

5.4 Molecular Structure of 8 (CCDC 2453038)

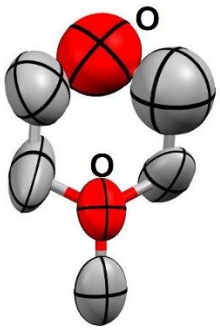


Figure S7. Molecular structure of **8**. Thermal ellipsoids at 50% probability level; H atoms and counter anion omitted for clarity.

Empirical formula	$C_{30.32}H_{14.32}BF_{20}O_{2.66}$
Formula weight	812.02
Temperature/K	138.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7733(6)
b/Å	11.3227(4)
c/Å	17.8844(6)
α/°	90
β/°	90.076(4)
γ/°	90
Volume/Å^3	2991.59(19)
Z	4
ρ_{calc}g/cm^3	1.803
μ/mm^{-1}	1.811
F(000)	1610.0
Crystal size/mm^3	0.42 × 0.32 × 0.24
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.982 to 136.5
Index ranges	$-17 \leq h \leq 17$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	27977
Independent reflections	5463 [R_{int} = 0.0375, R_{sigma} = 0.0239]
Data/restraints/parameters	5463/50/510
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0861, wR_2 = 0.2456
Final R indexes [all data]	R_1 = 0.0973, wR_2 = 0.2595
Largest diff. peak/hole / e Å^{-3}	0.53/-0.66

6 References

1. Y.-H. Li, C.-H. Wang, S.-Q. Gao, F.-M. Qi, S.-D. Yang, *Chem. Commun.,* 2019, **55**, 11888–11891.
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7 NMR Spectra

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-methylbenzoate **(3a)**.

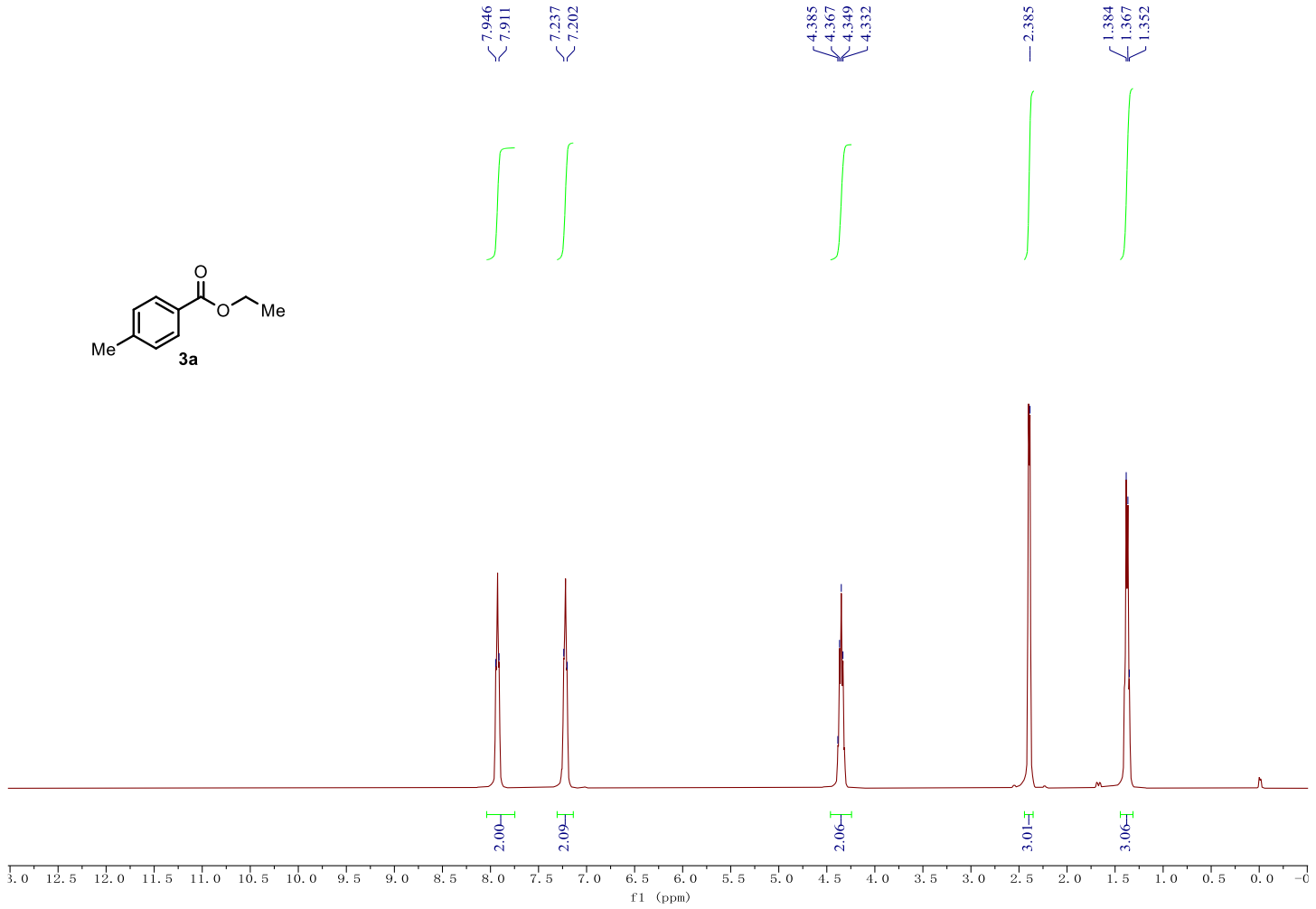

Figure S2. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-methylbenzoate **(3a)**.

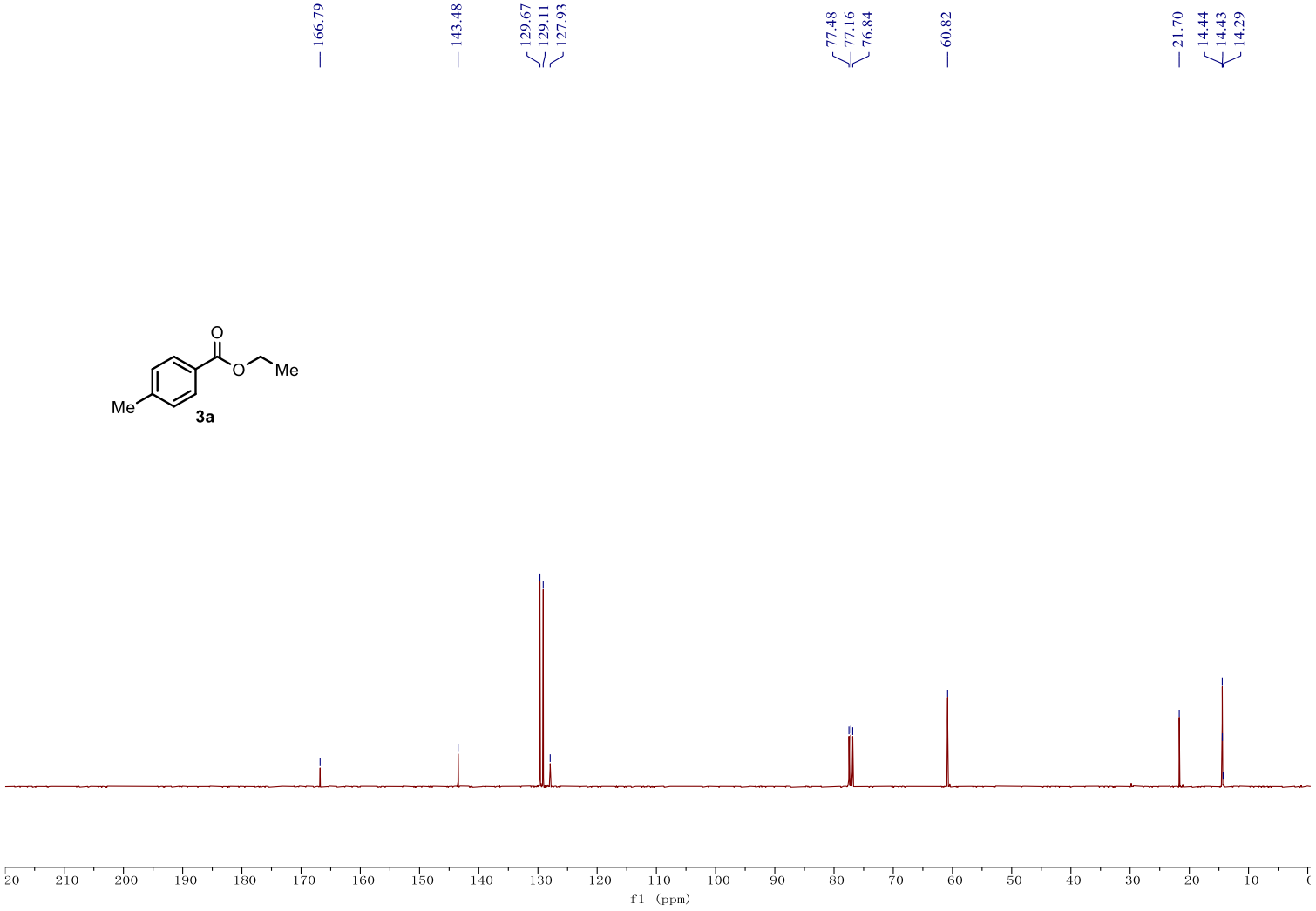

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 2-methylbenzoate **(3b)**.

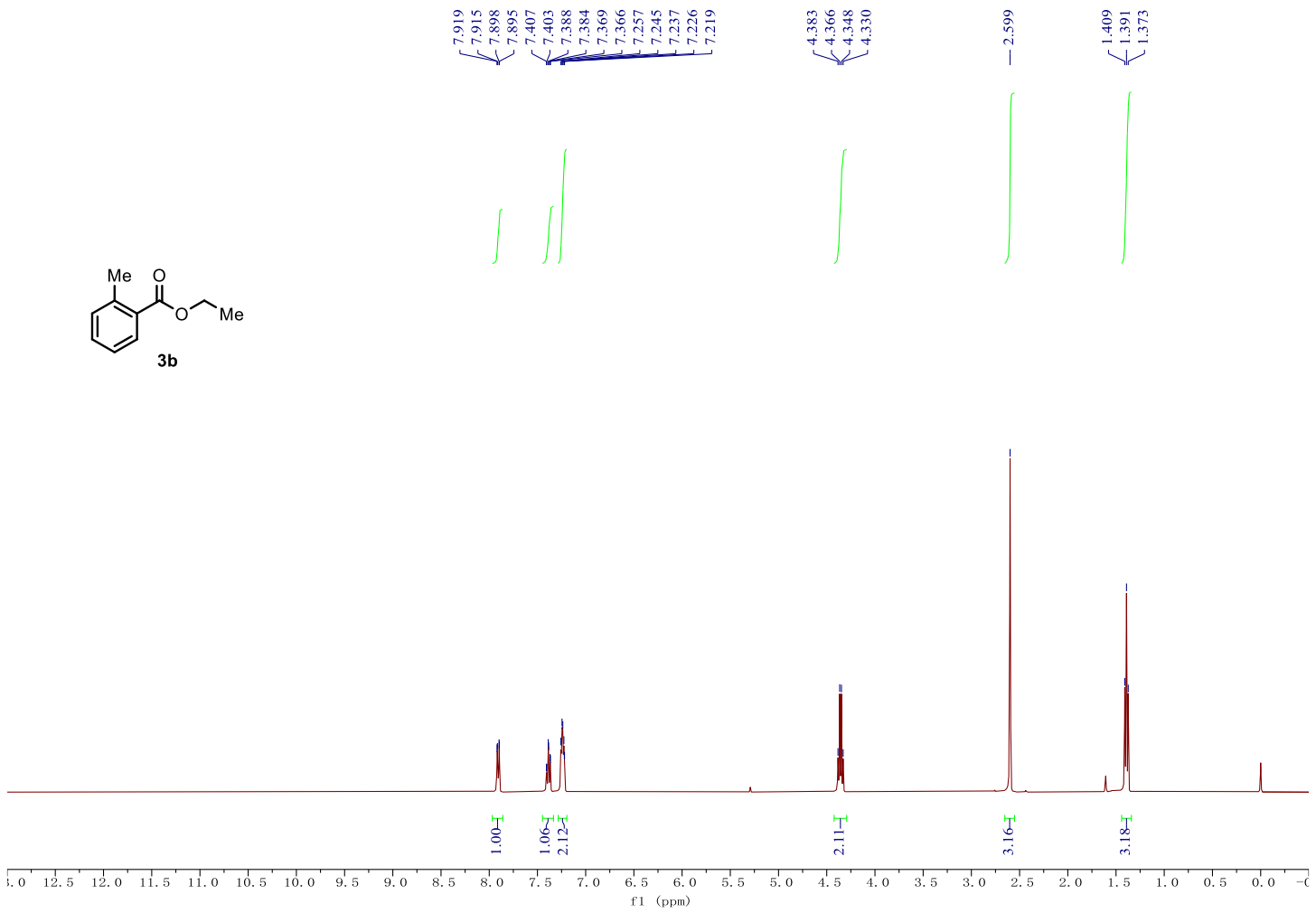

Figure S4. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 2-methylbenzoate **(3b)**.

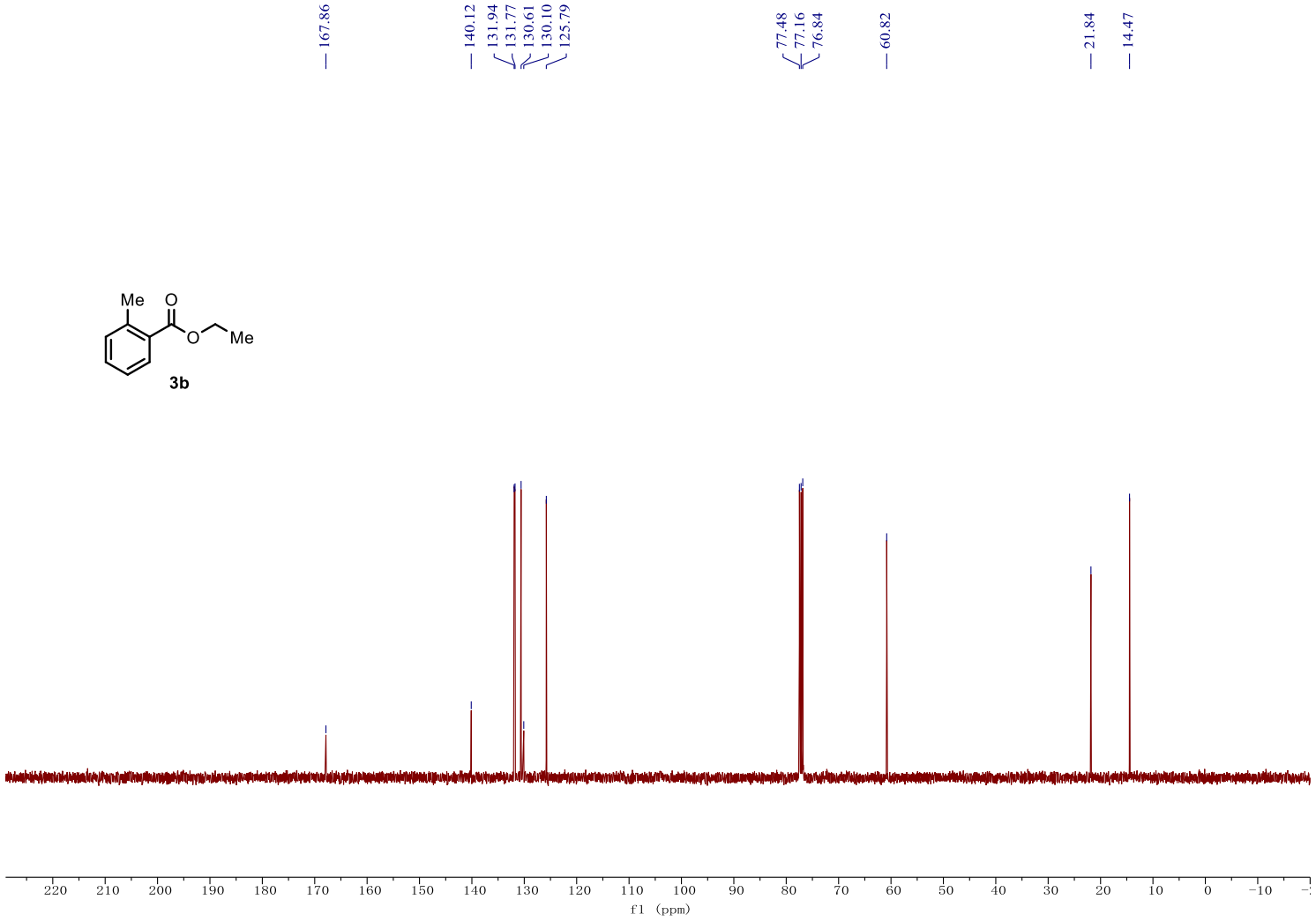

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 3-methylbenzoate **(3c)**.

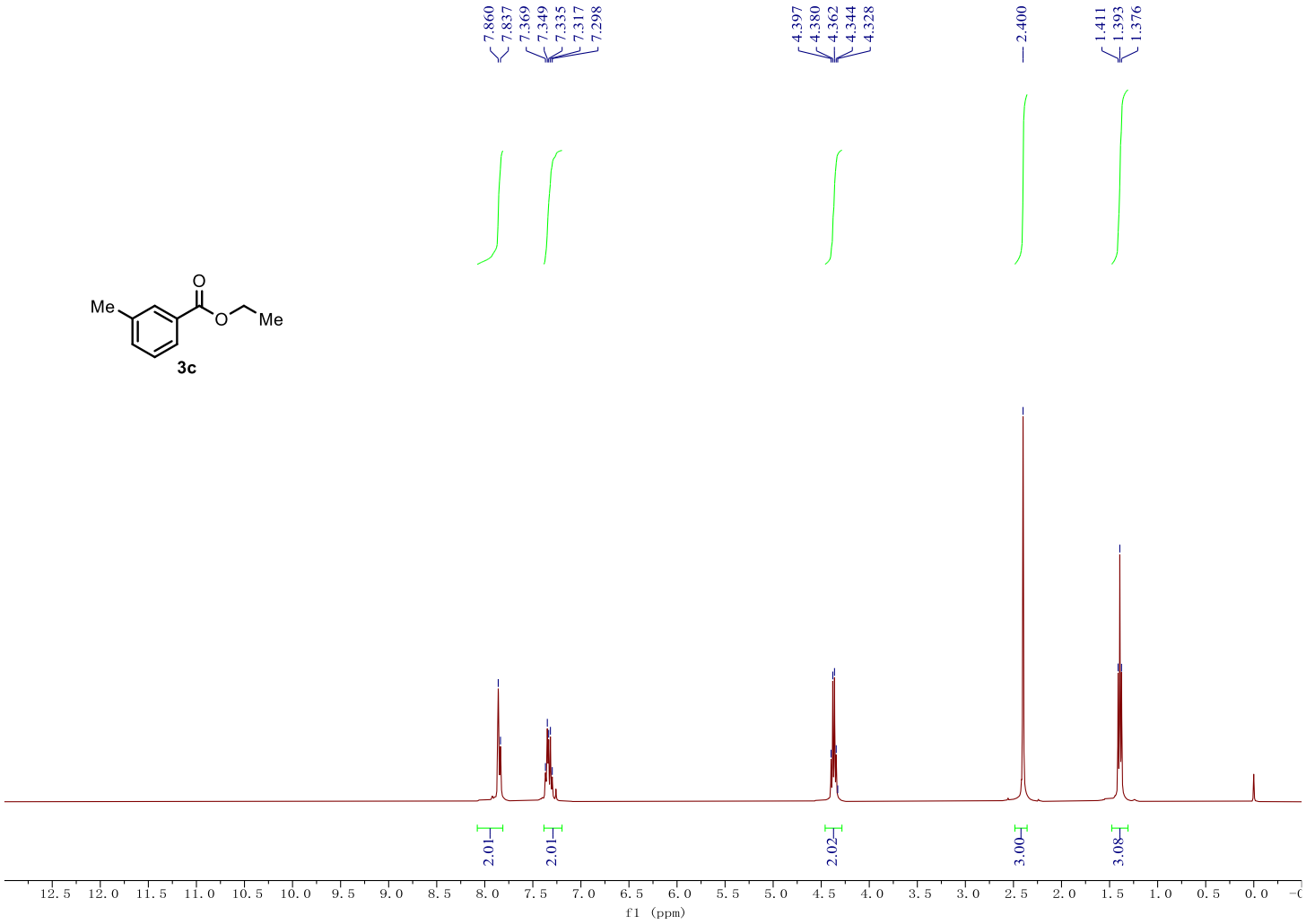

Figure S6. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 3-methylbenzoate **(3c)**.

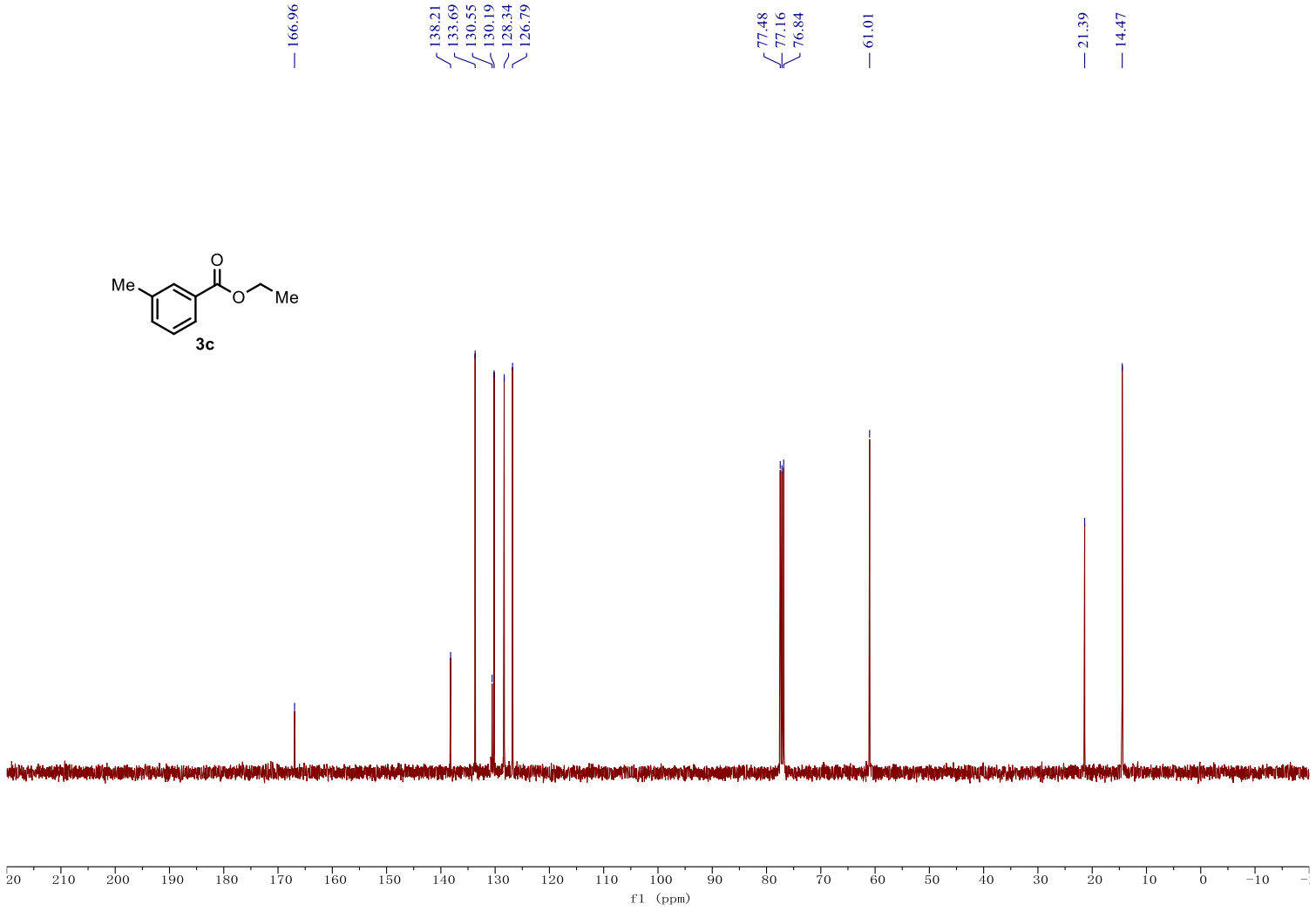

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 3-methoxybenzoate **(3d)**.

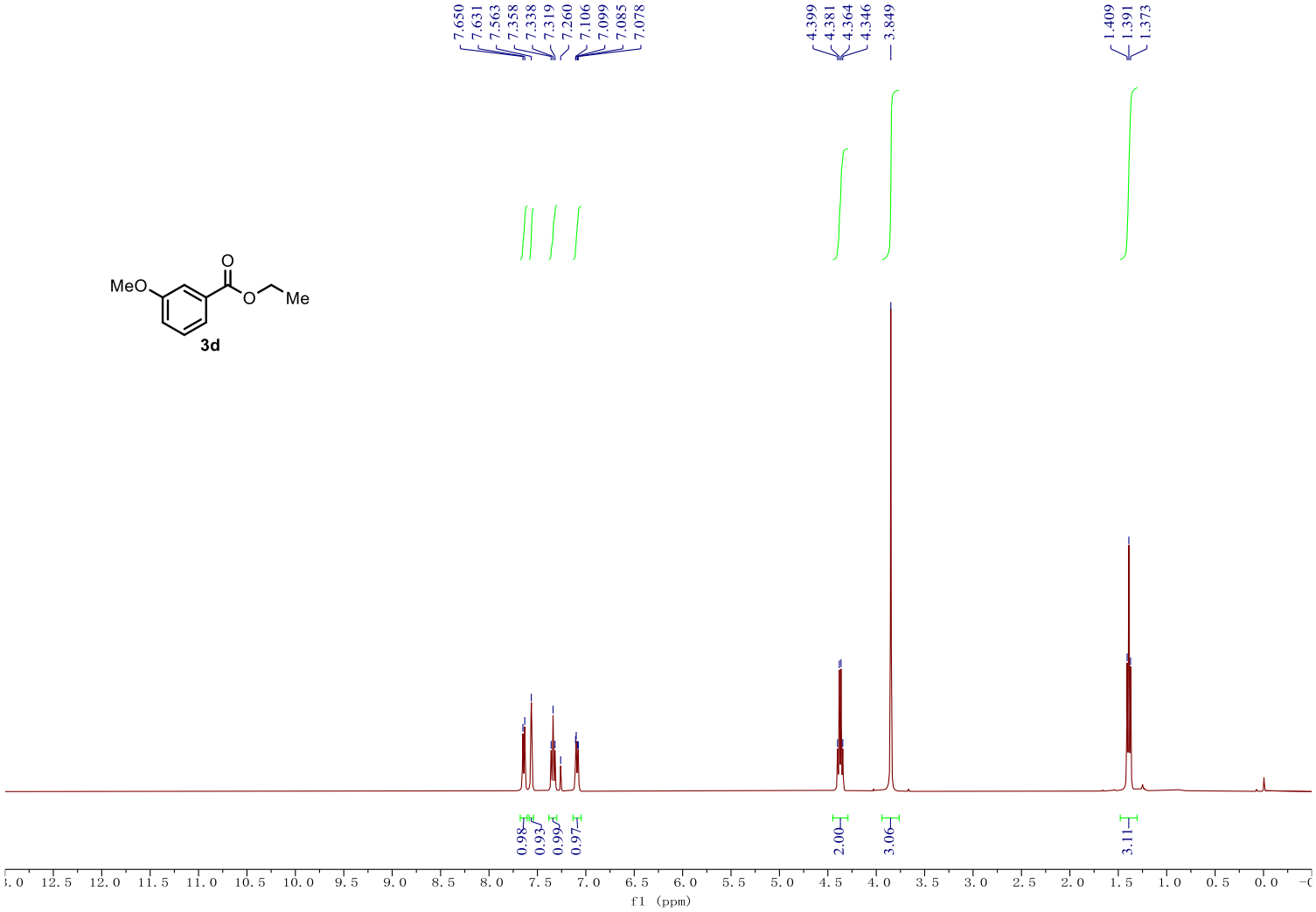

Figure S8. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 3-methoxybenzoate **(3d)**.

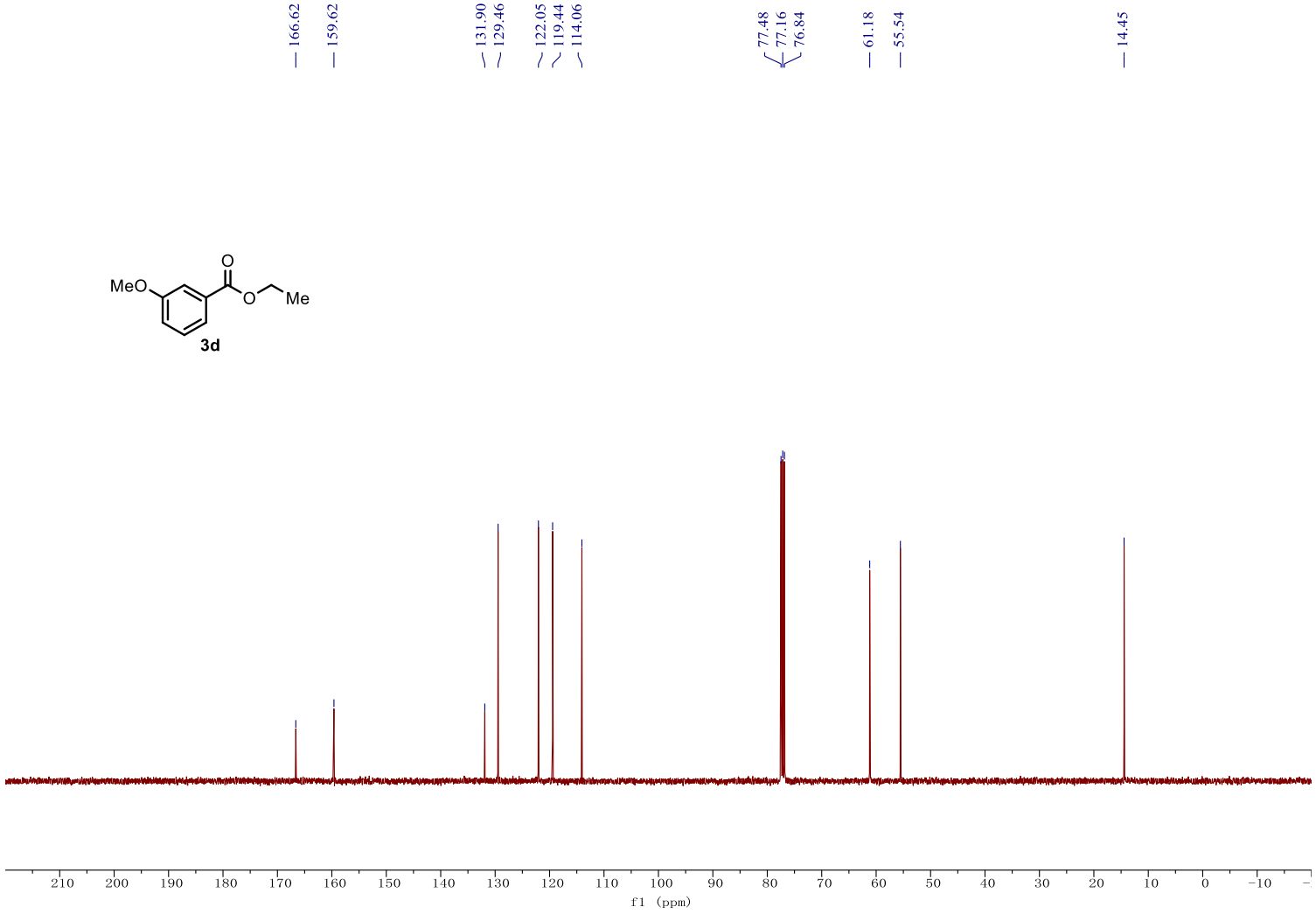

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-methoxybenzoate **(3e)**.

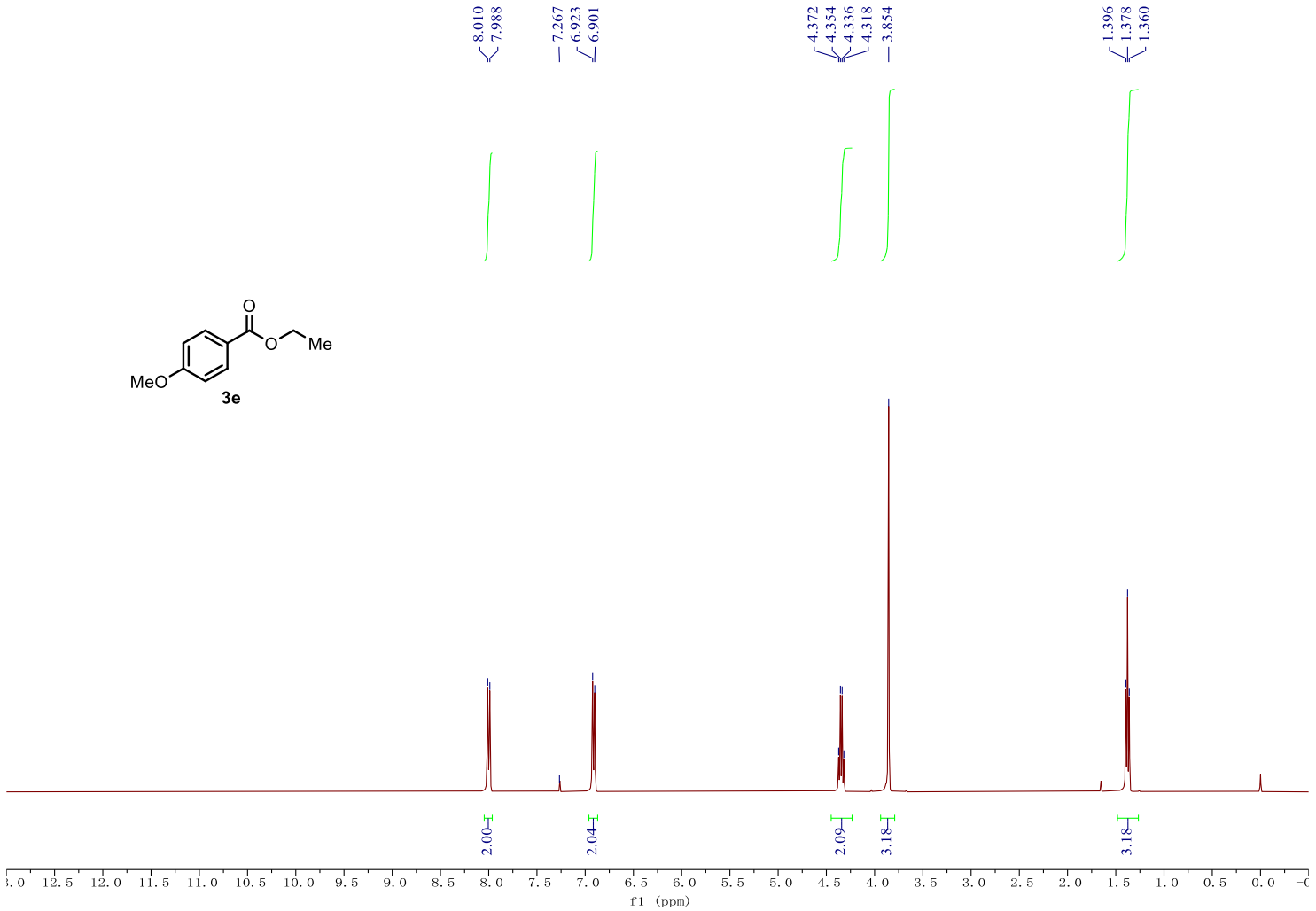

Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-methoxybenzoate **(3e)**.

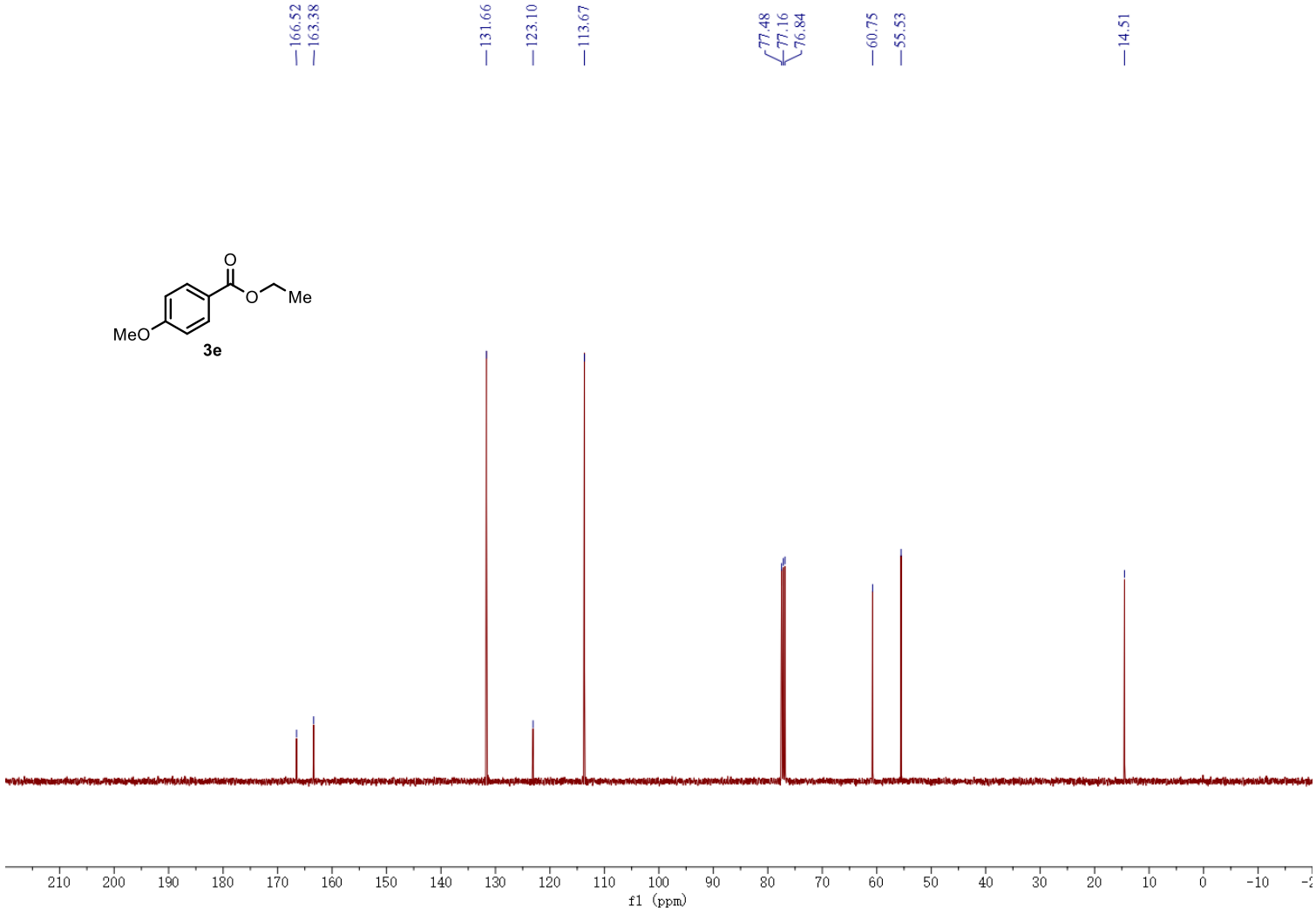

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 4-phenoxybenzoic acid ethyl ester **(3f)**.

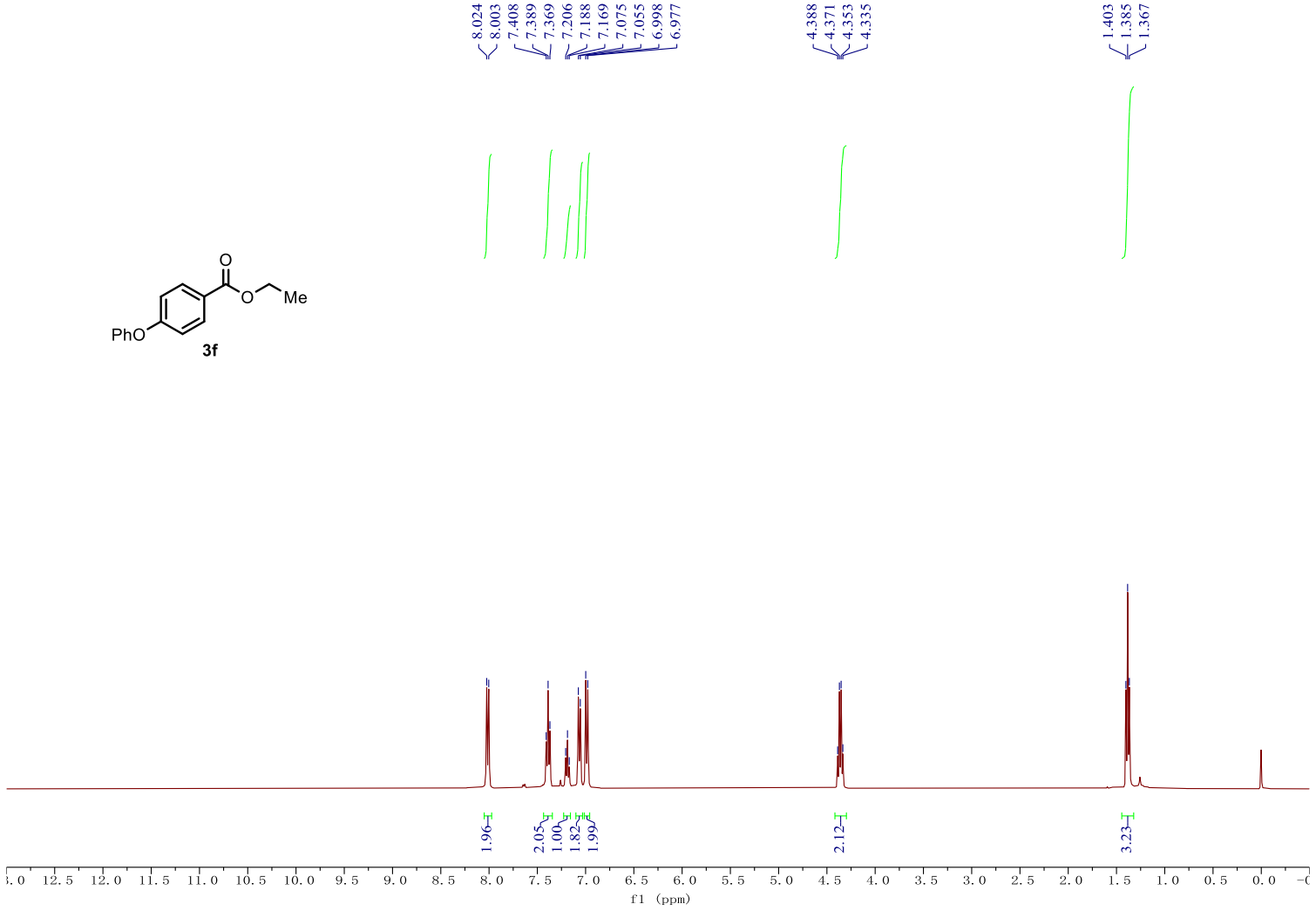

Figure S12. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 4-phenoxybenzoic acid ethyl ester **(3f)**.

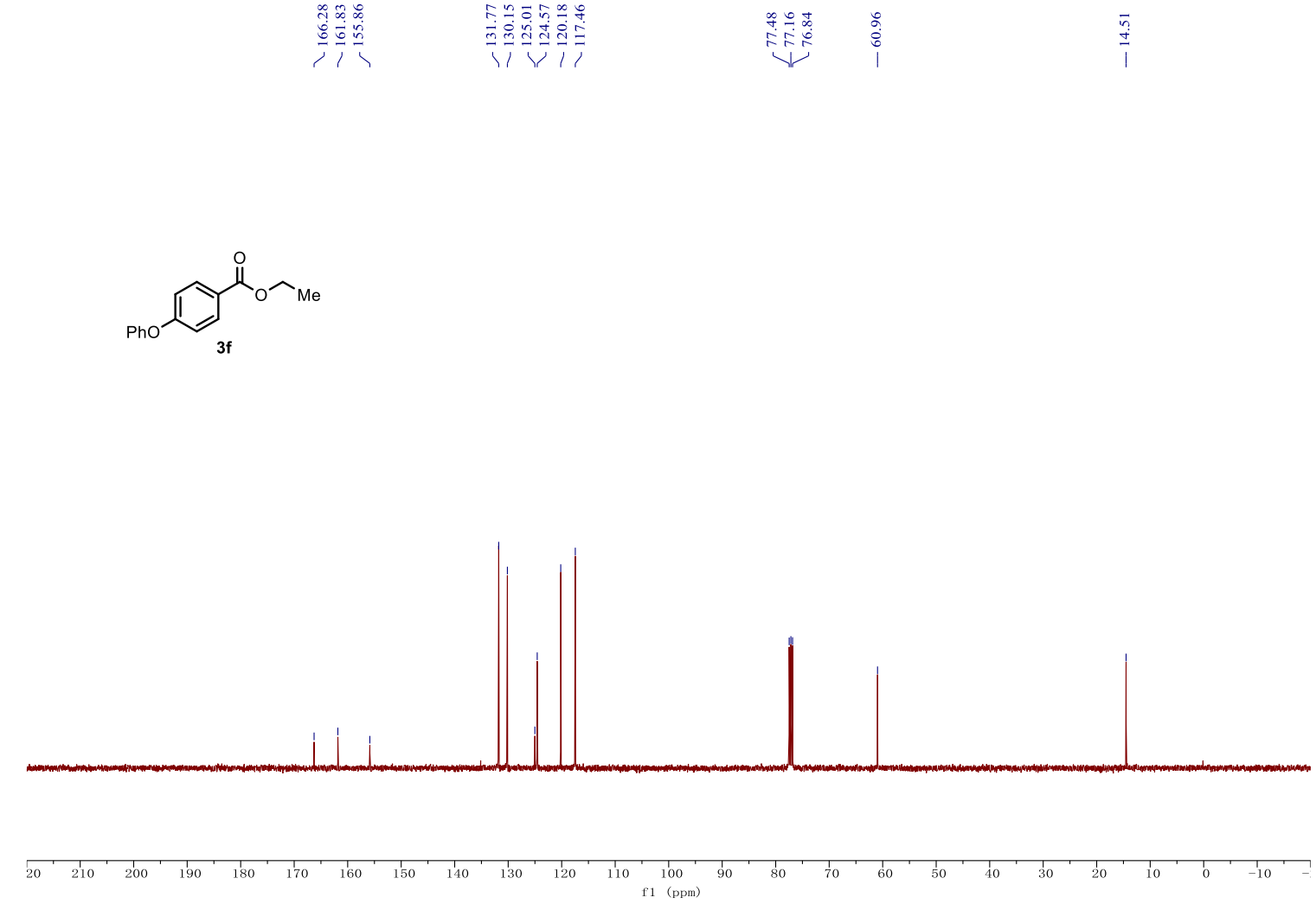

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 2-fluorobenzoate **(3g)**.

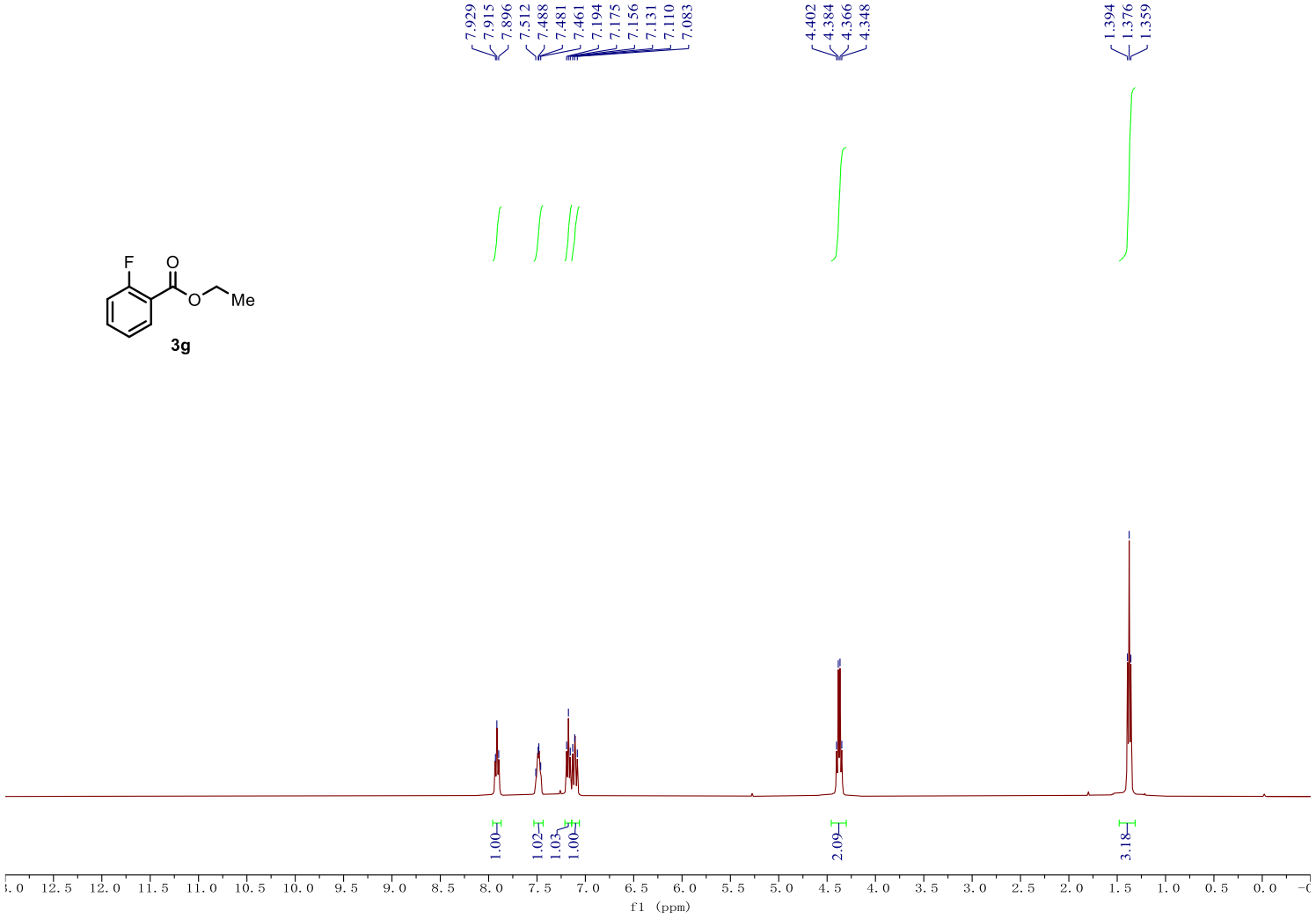

Figure S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 2-fluorobenzoate **(3g)**.

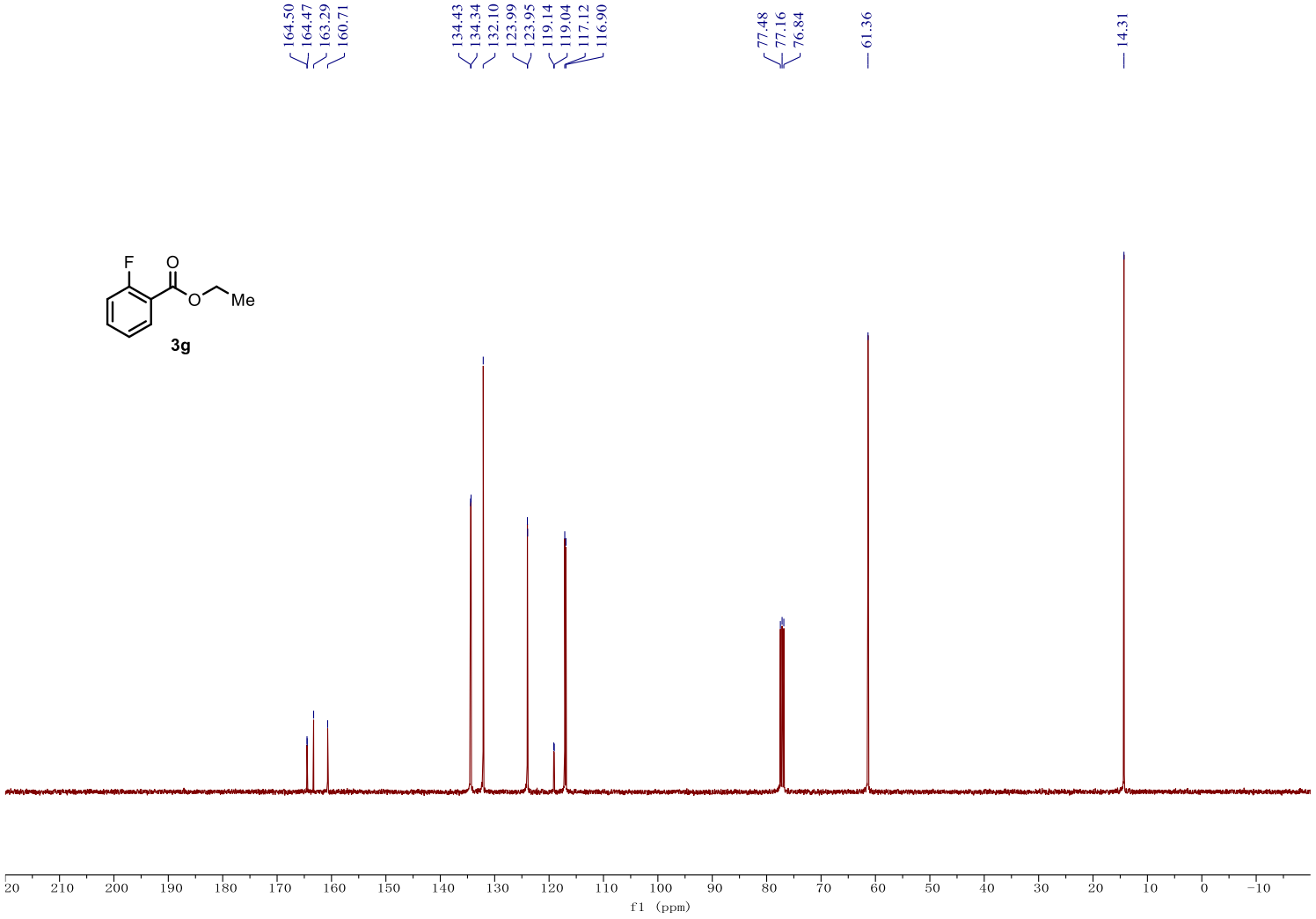

Figure S15. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of ethyl 2-fluorobenzoate **(3g)**.

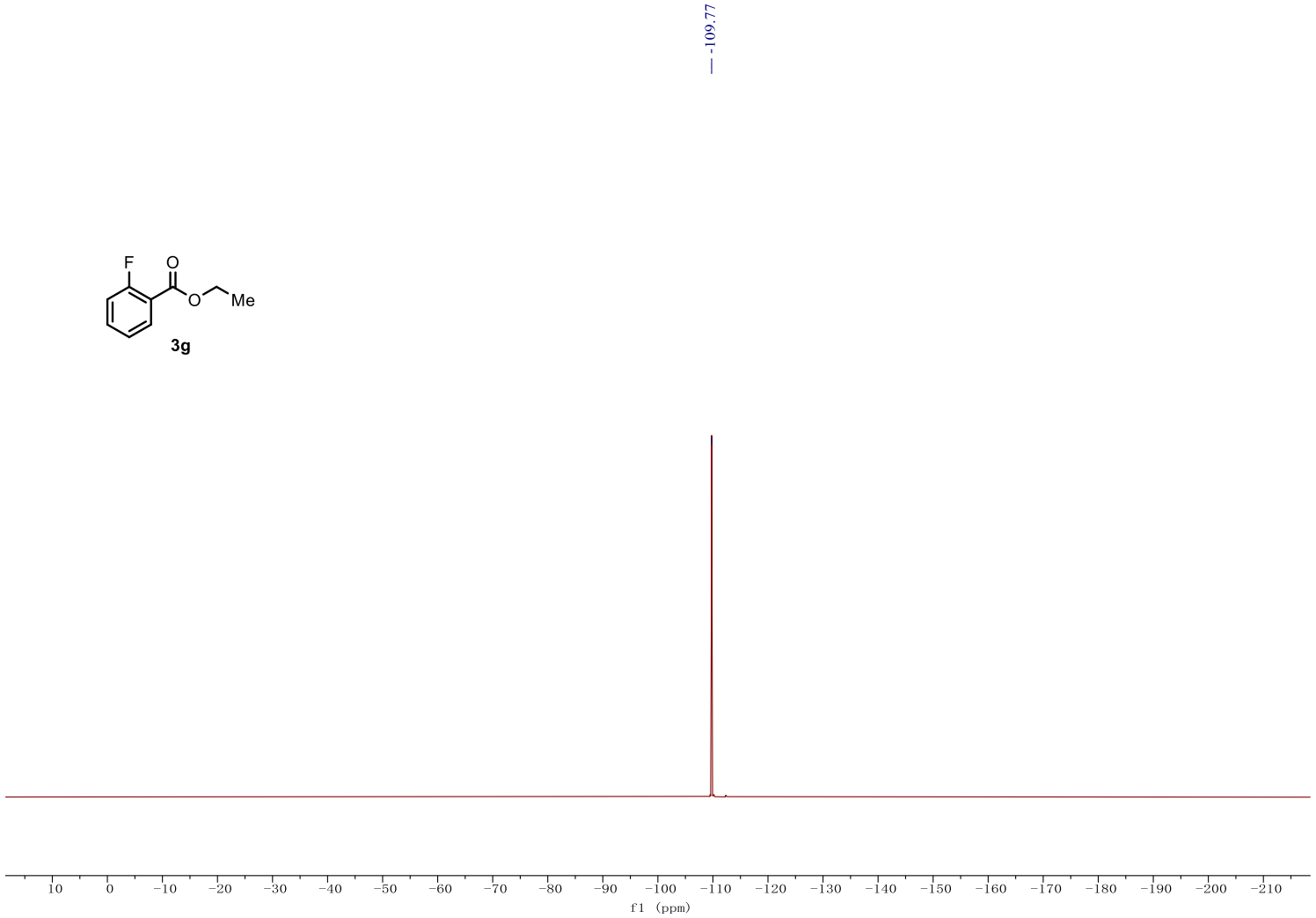

Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 3-fluorobenzoate **(3h)**

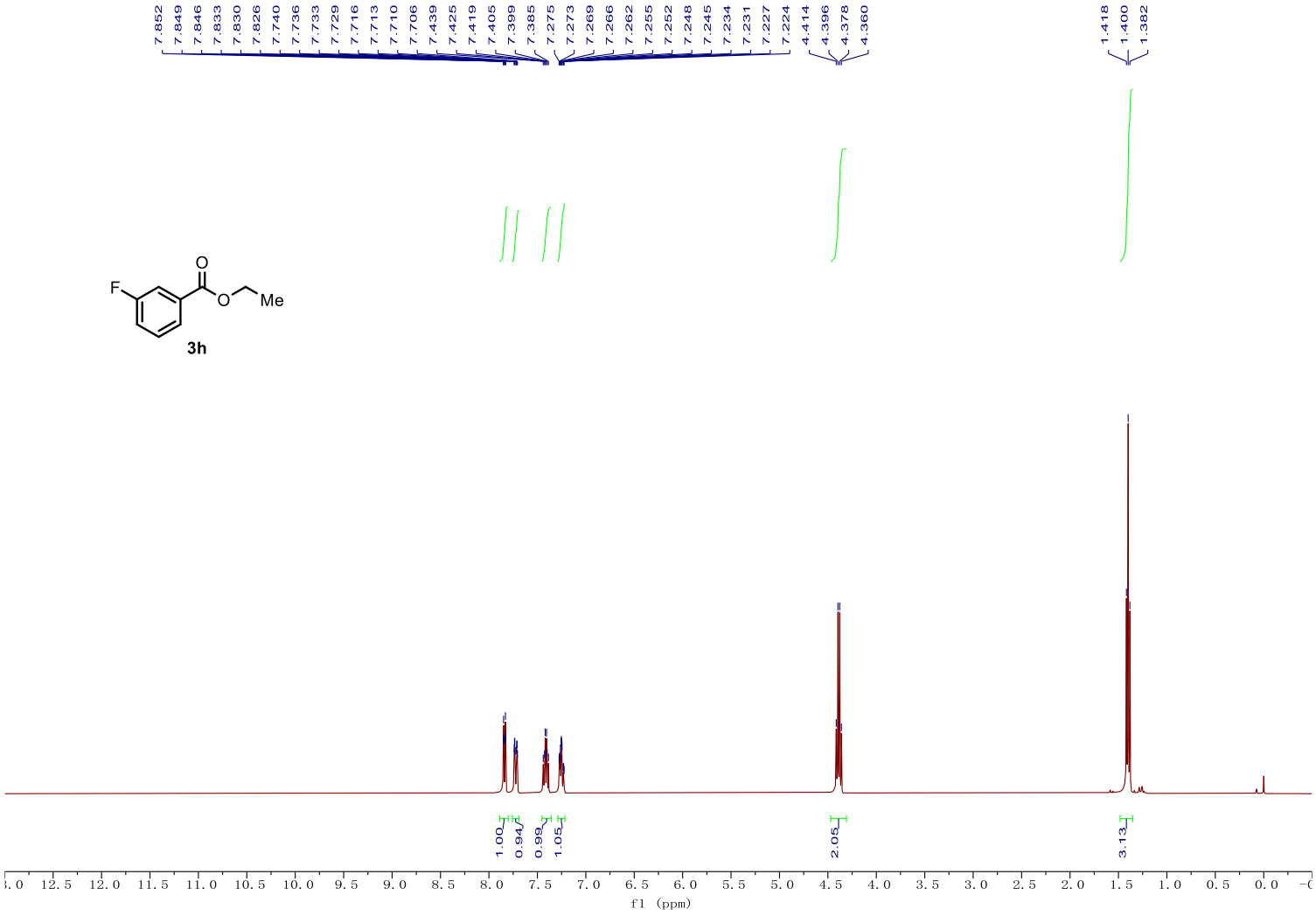

Figure S17. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 3-fluorobenzoate **(3h)**.

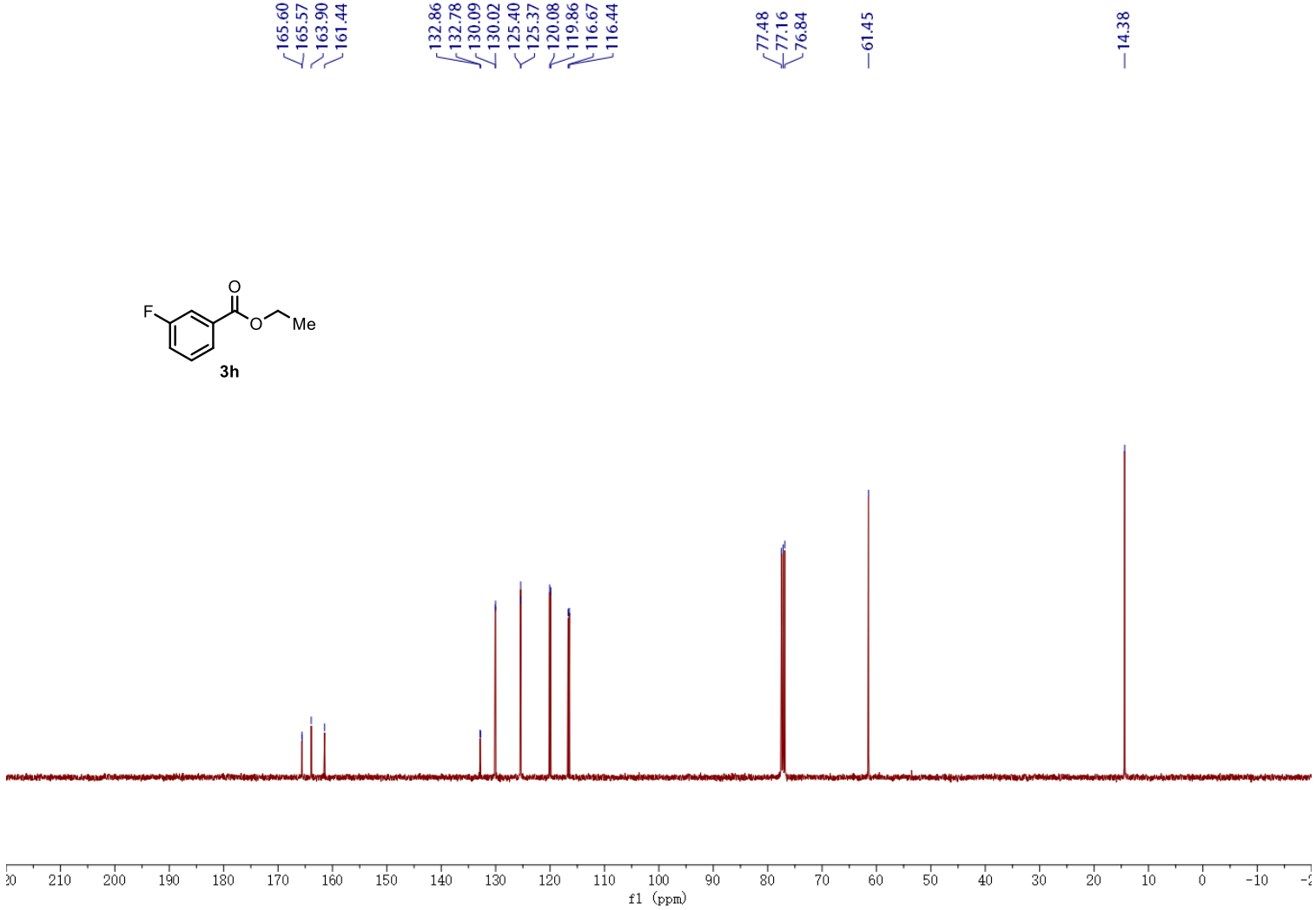

Figure S18. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of 3-fluorobenzoate **(3h)**.

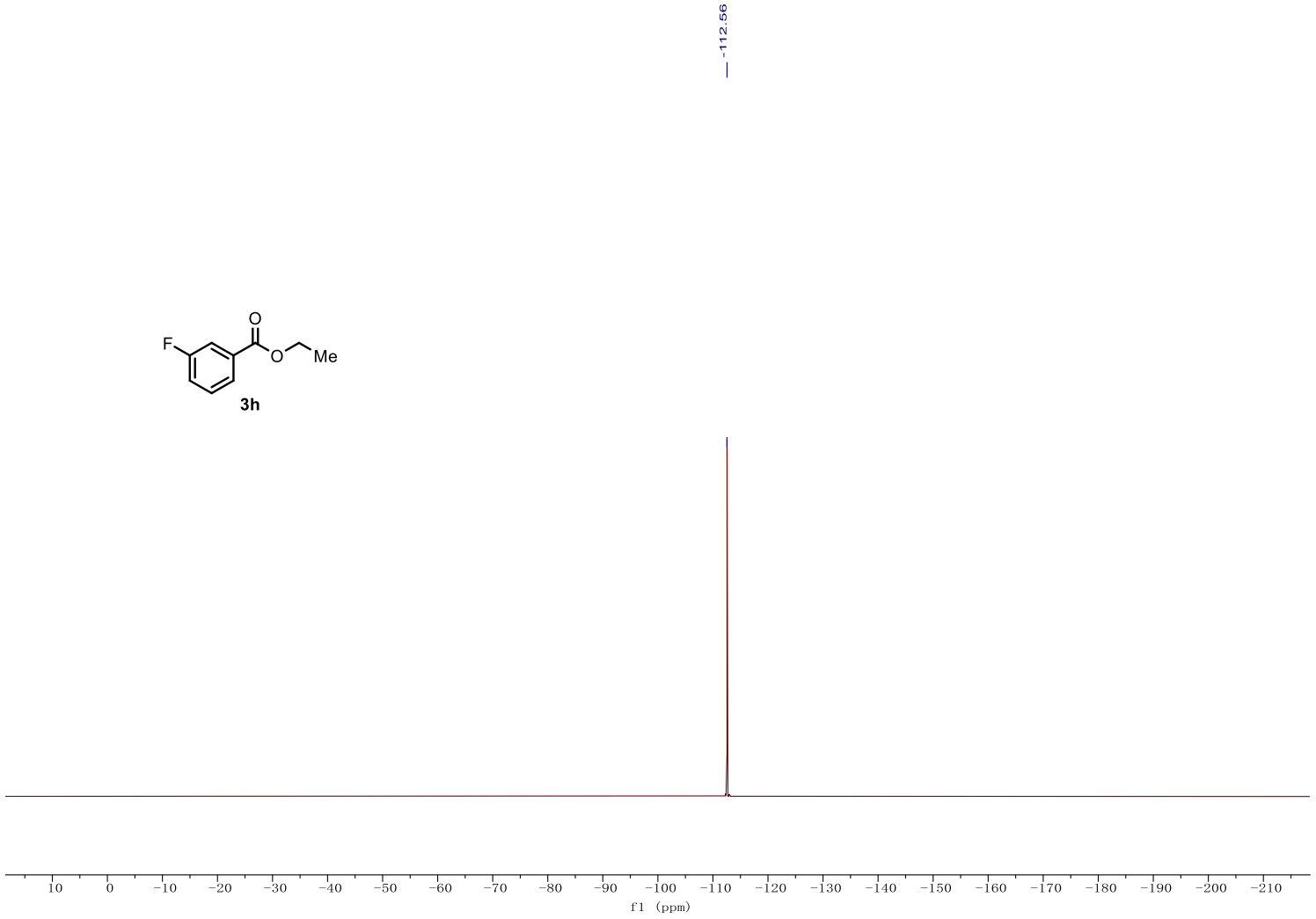

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-fluorobenzoate **(3i)**.

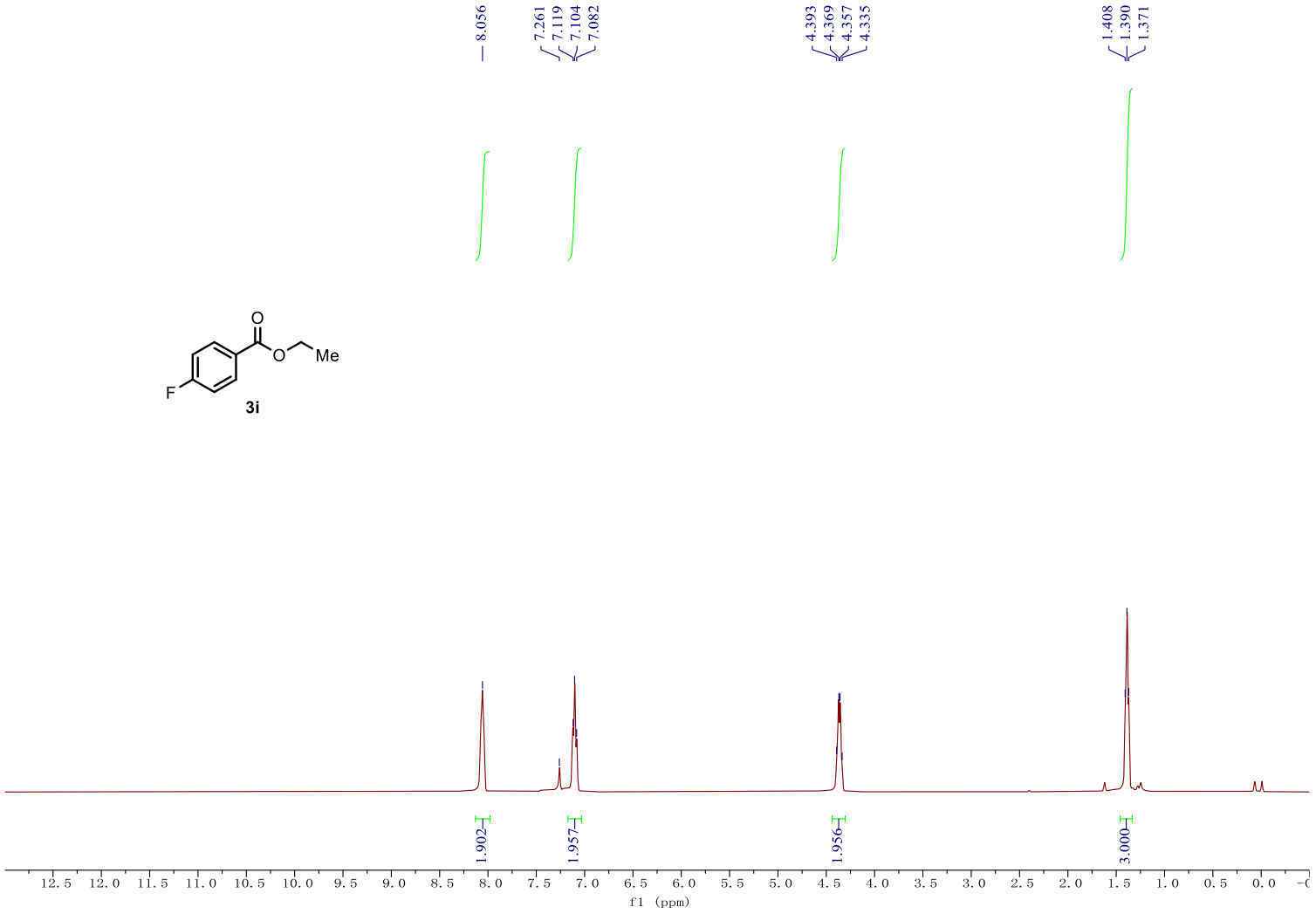

Figure S20. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 4-fluorobenzoate **(3i)**.

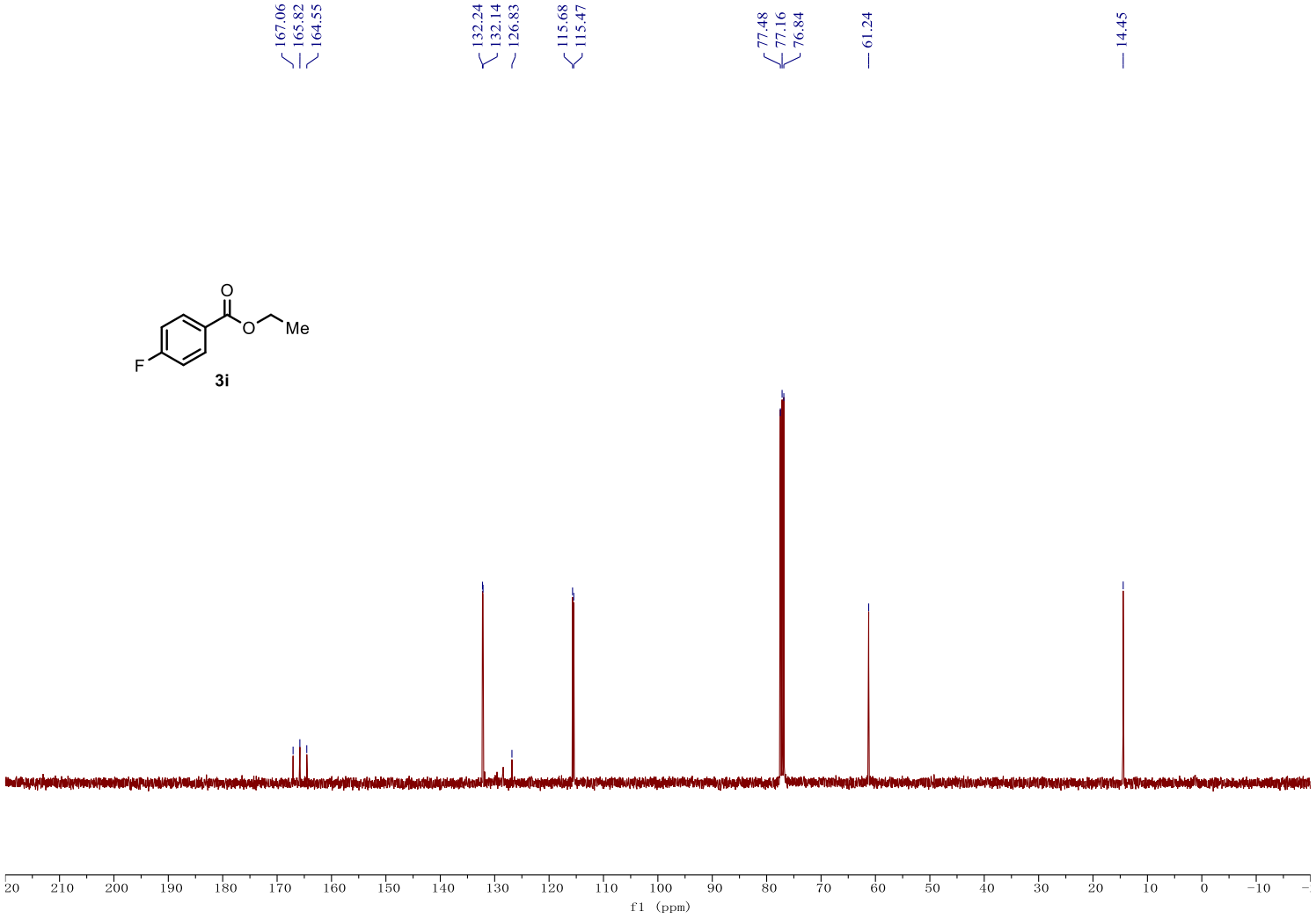

Figure S21. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of 4-fluorobenzoate **(3i)**.

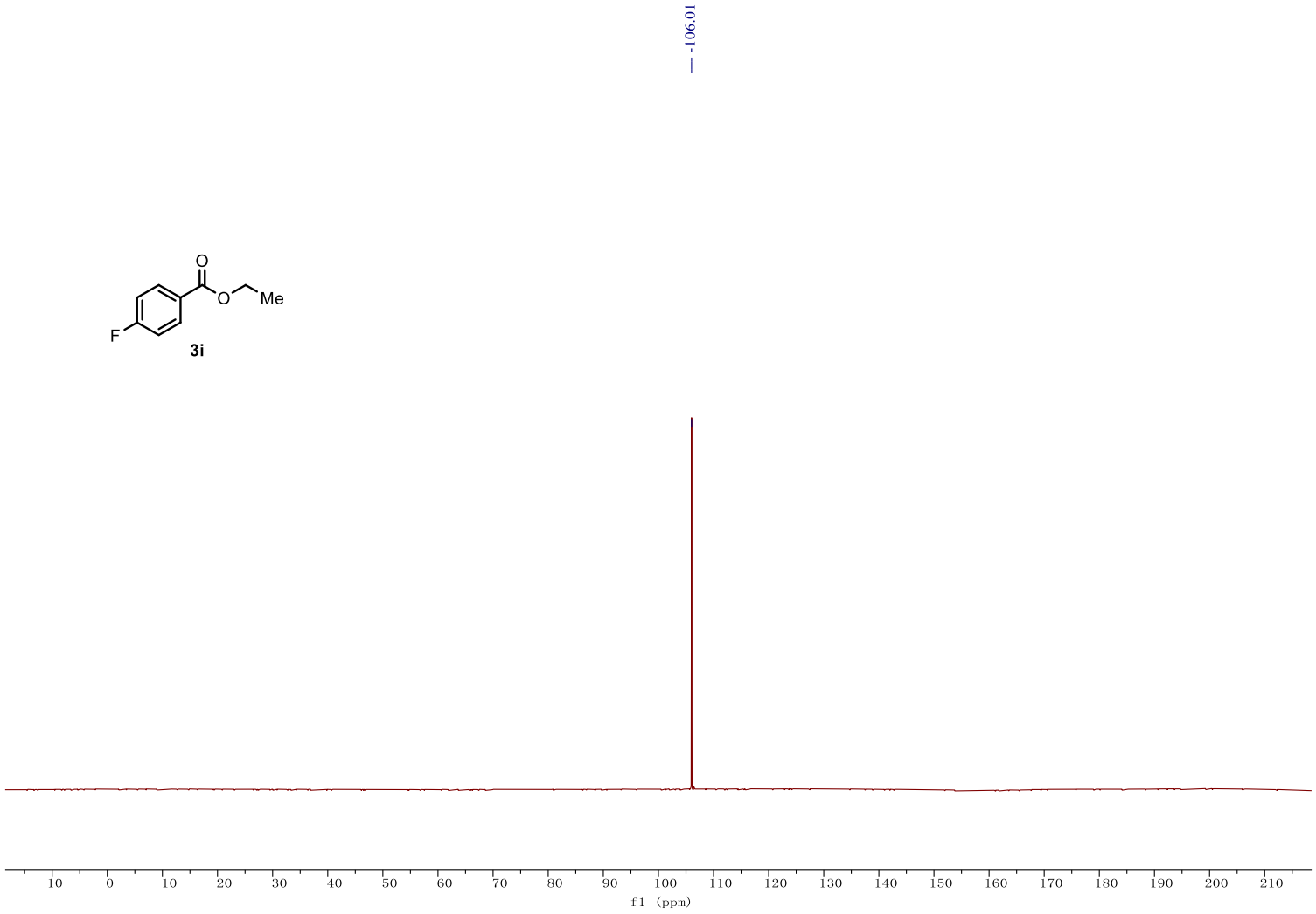

Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 2-bromobenzoate **(3j)**.

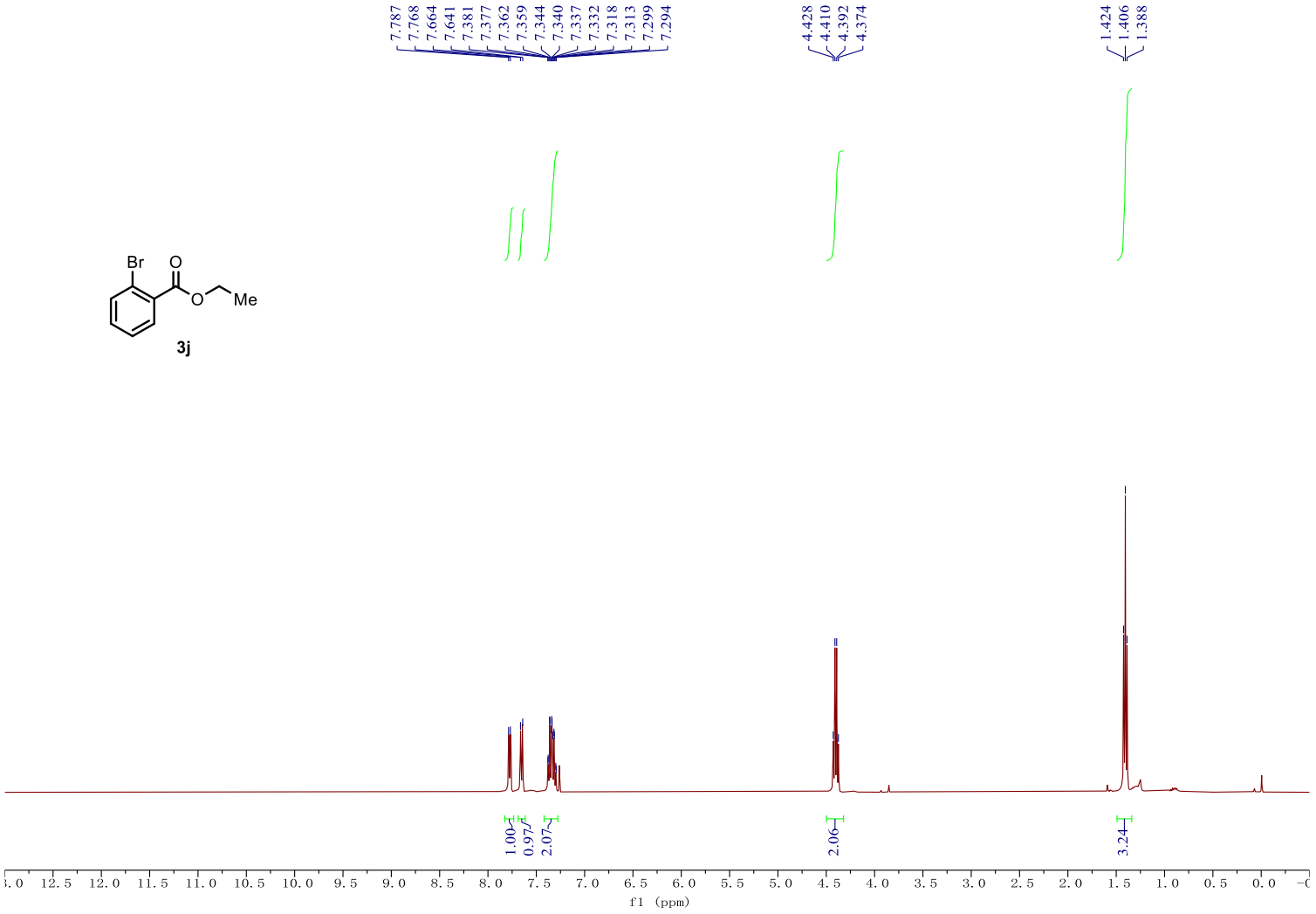

Figure S23. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 2-bromobenzoate **(3j)**.

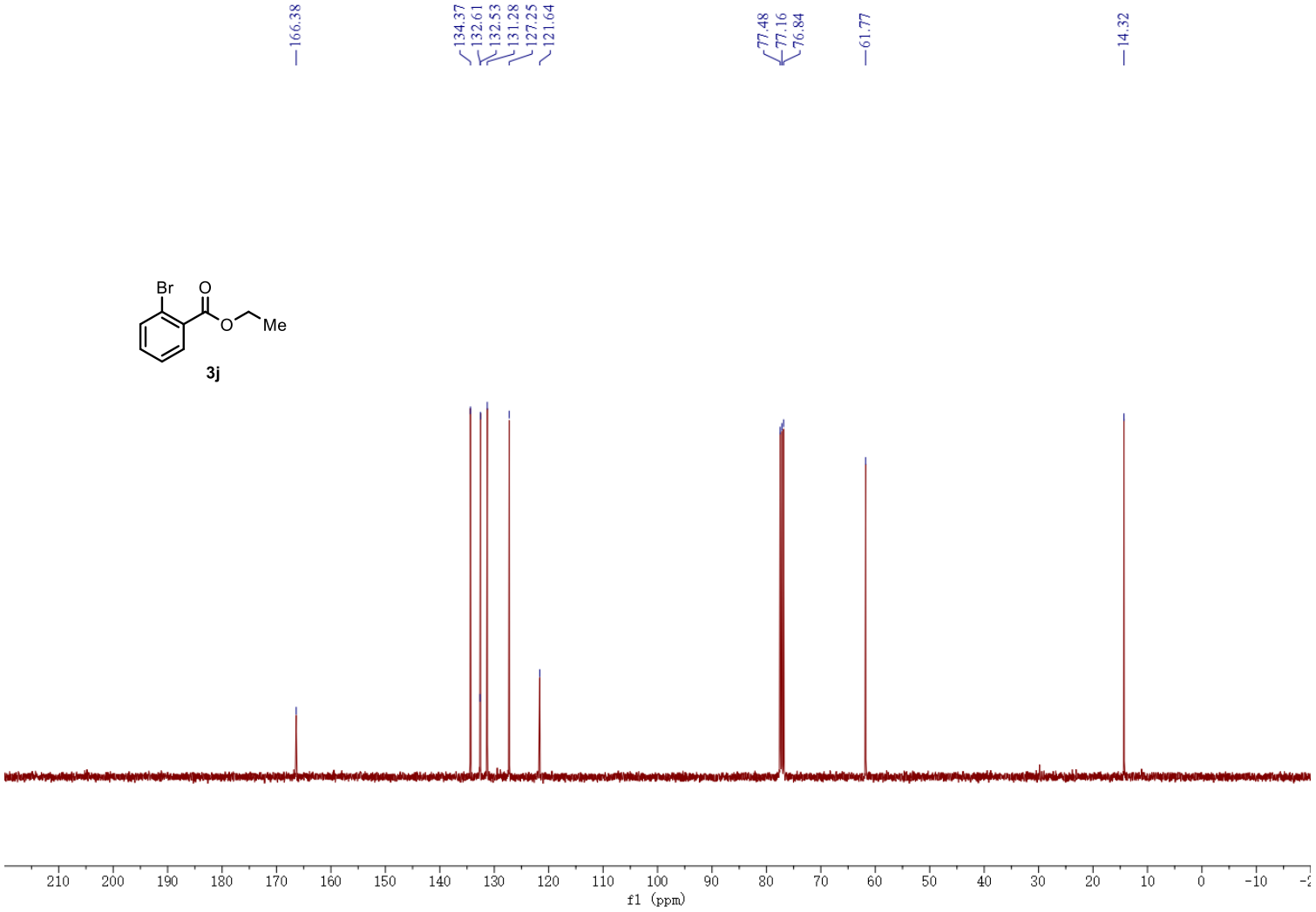

Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 3-bromobenzoate **(3k)**.

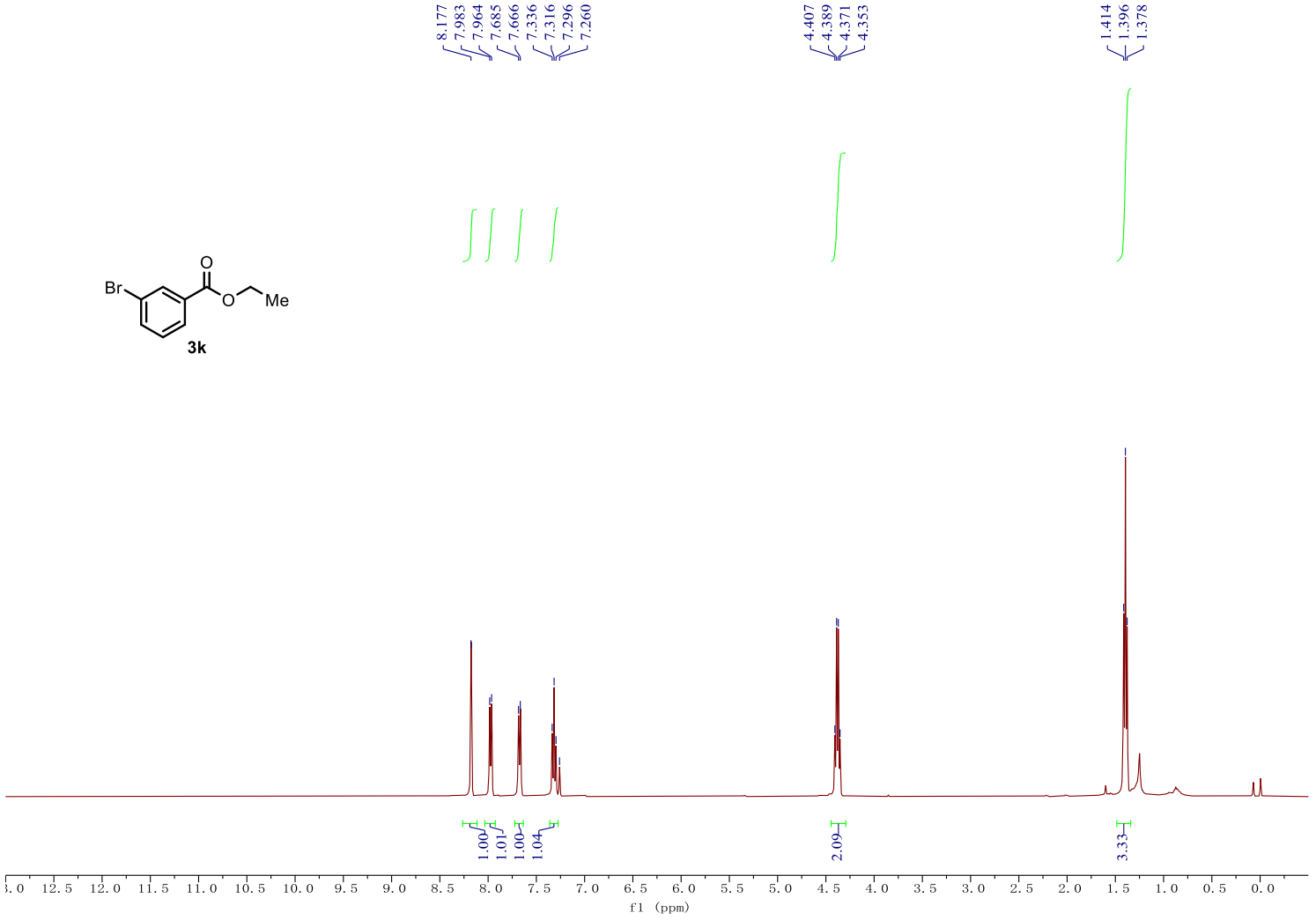

Figure S25. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 3-bromobenzoate **(3k)**.

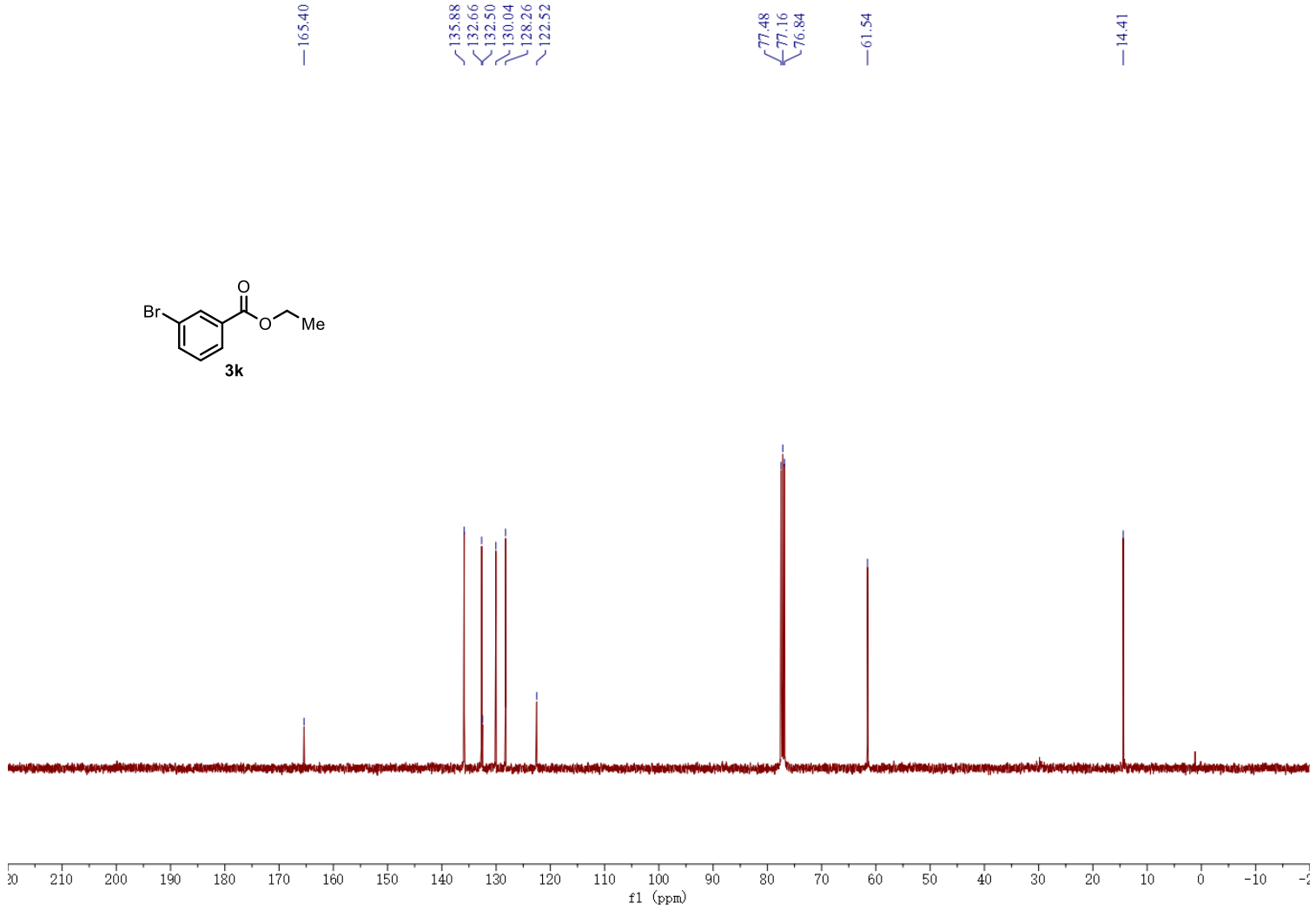

Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-bromobenzoate **(3l)**.

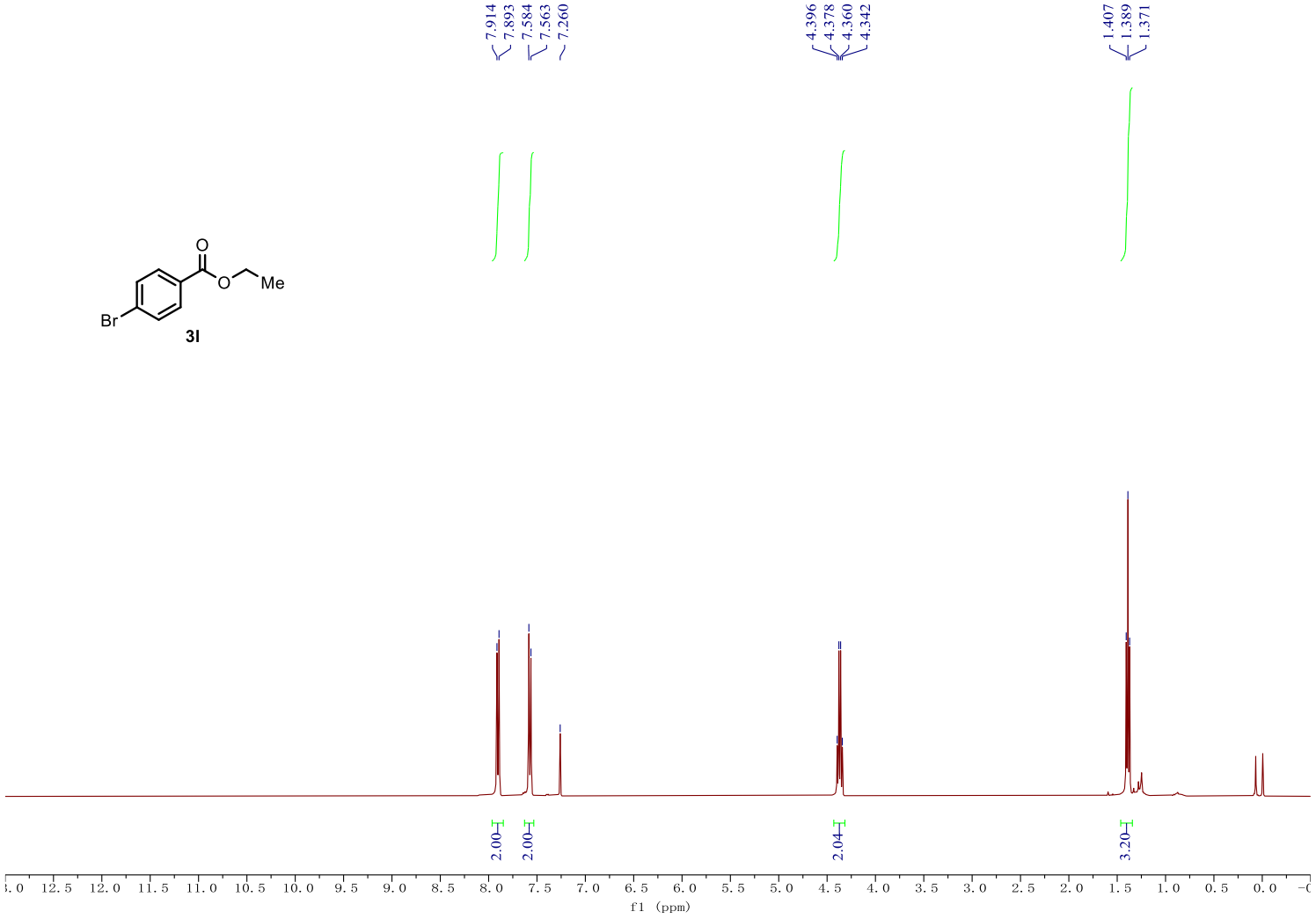

Figure S27. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-bromobenzoate **(3l)**.

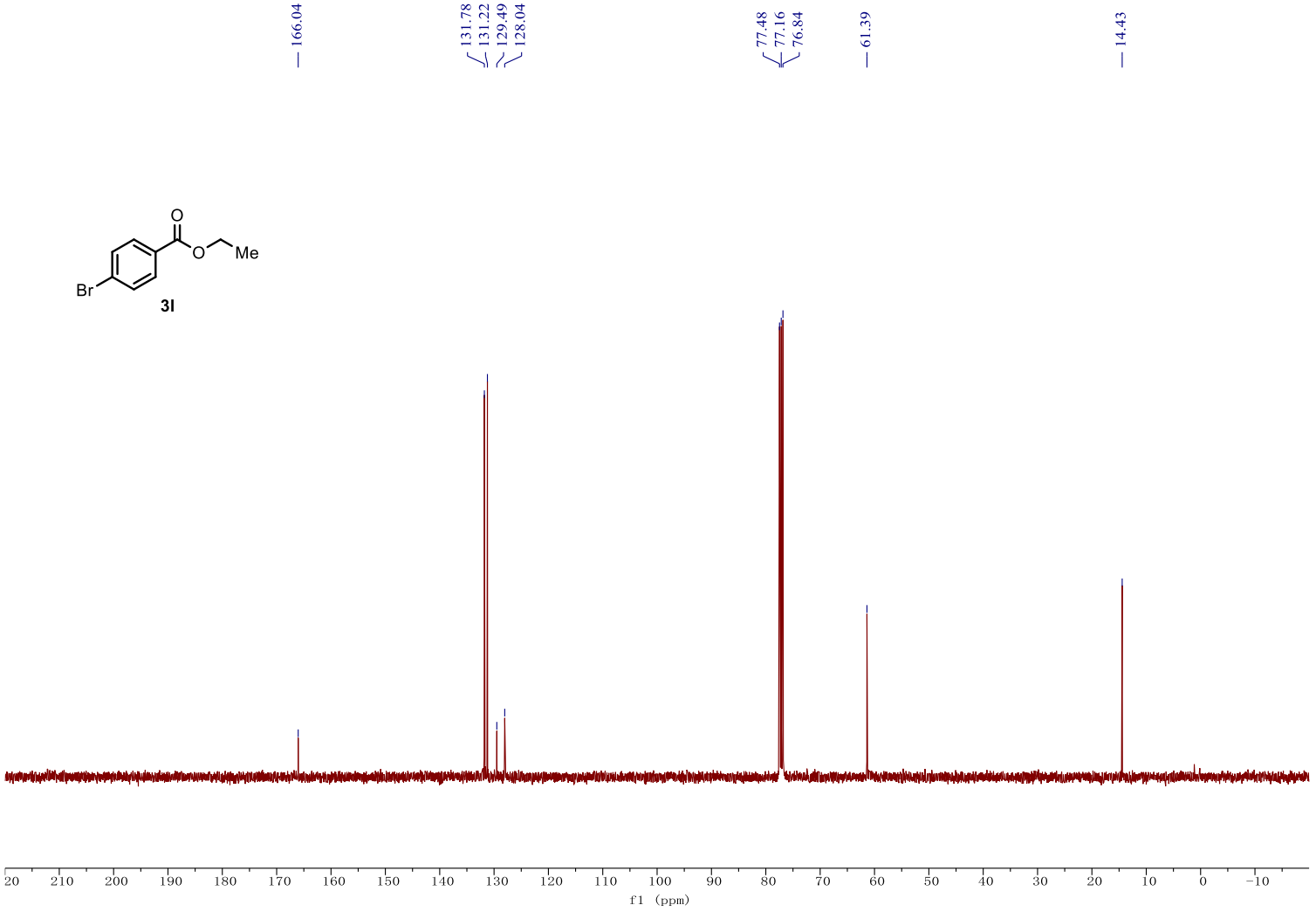

Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-chlorobenzoate **(3m)**.

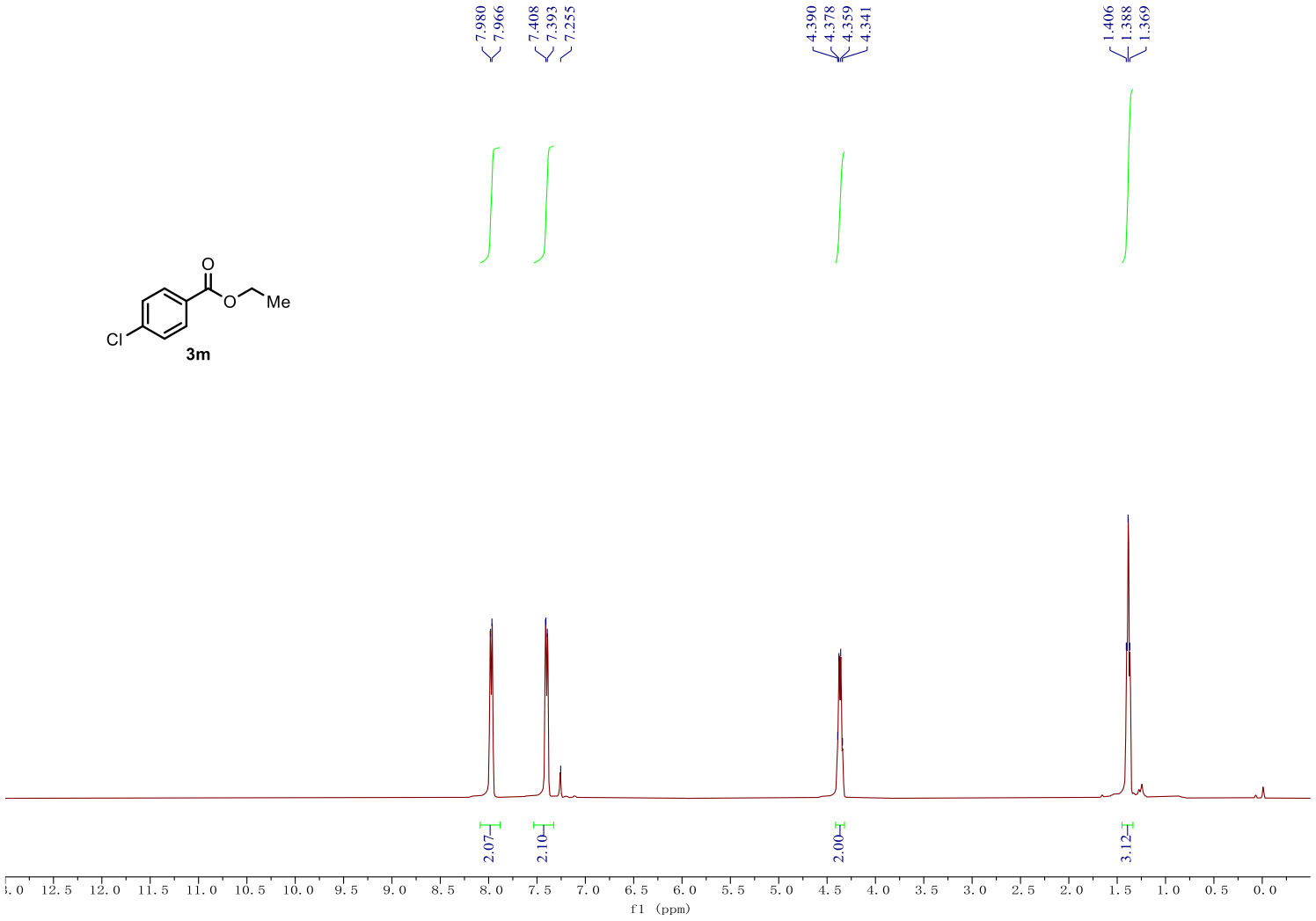

Figure S29. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-chlorobenzoate **(3m)**.

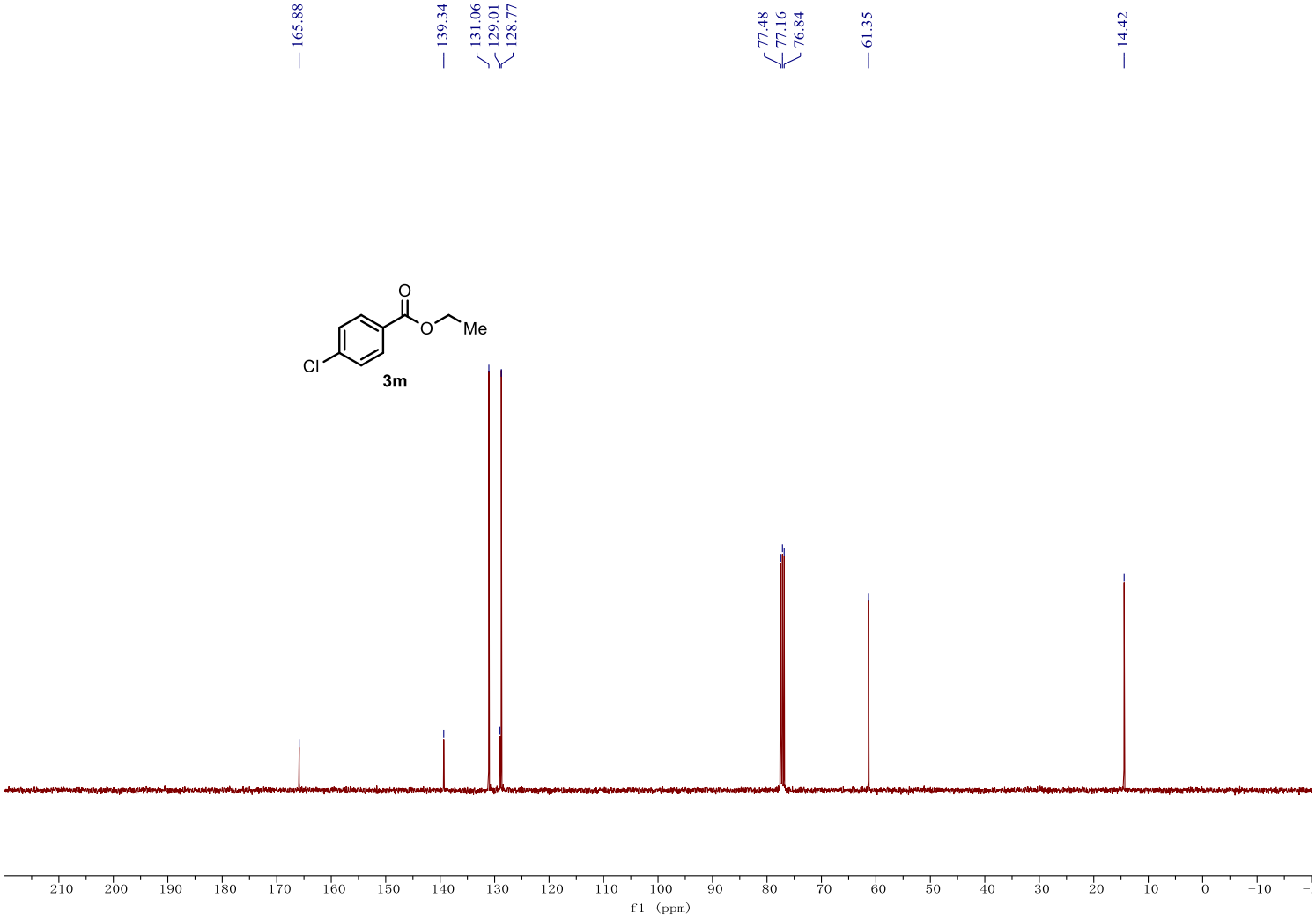

Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl benzoate **(3n)**.

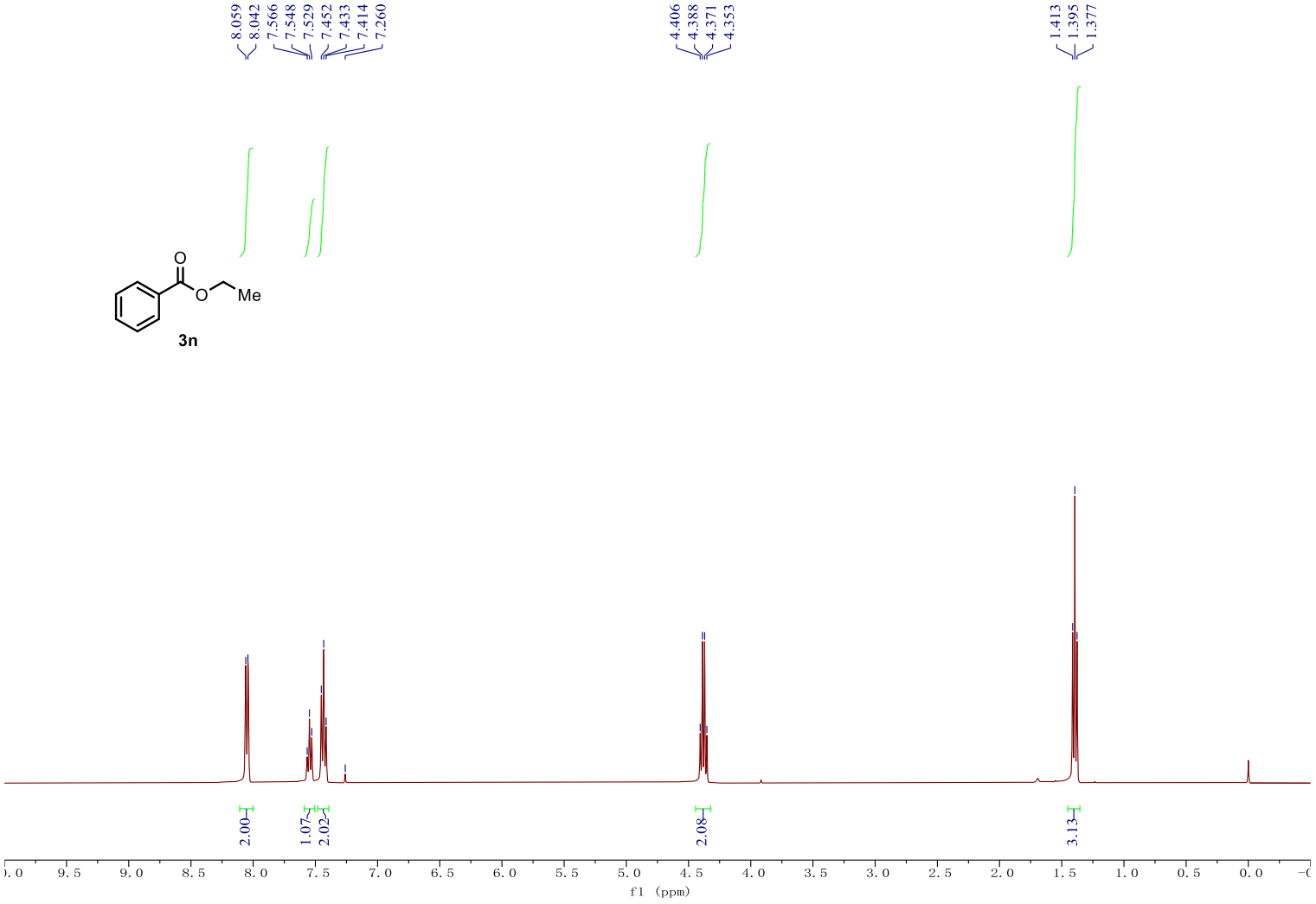

Figure S31. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl benzoate **(3n)**.

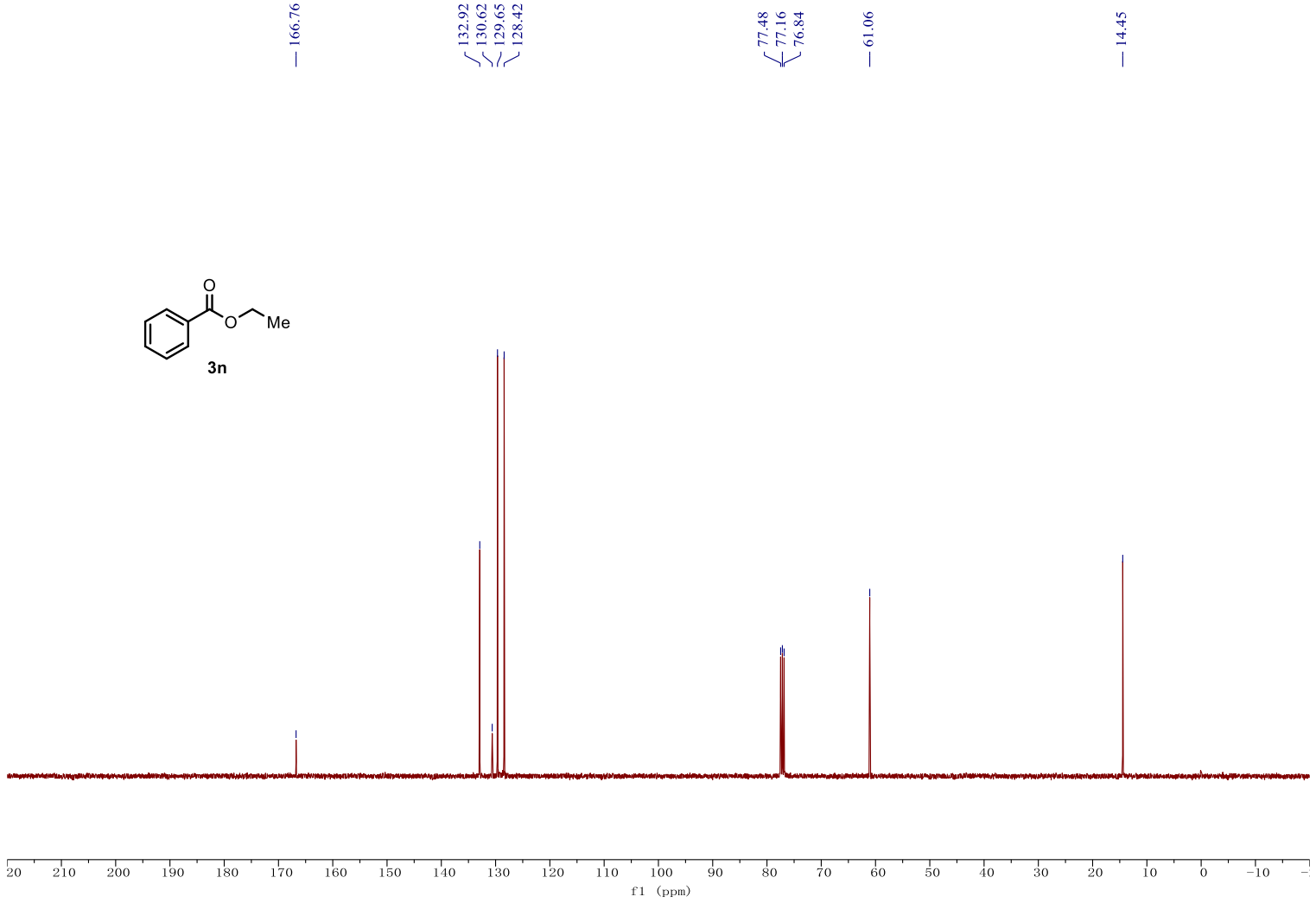

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-phenylbenzoate **(3o)**.

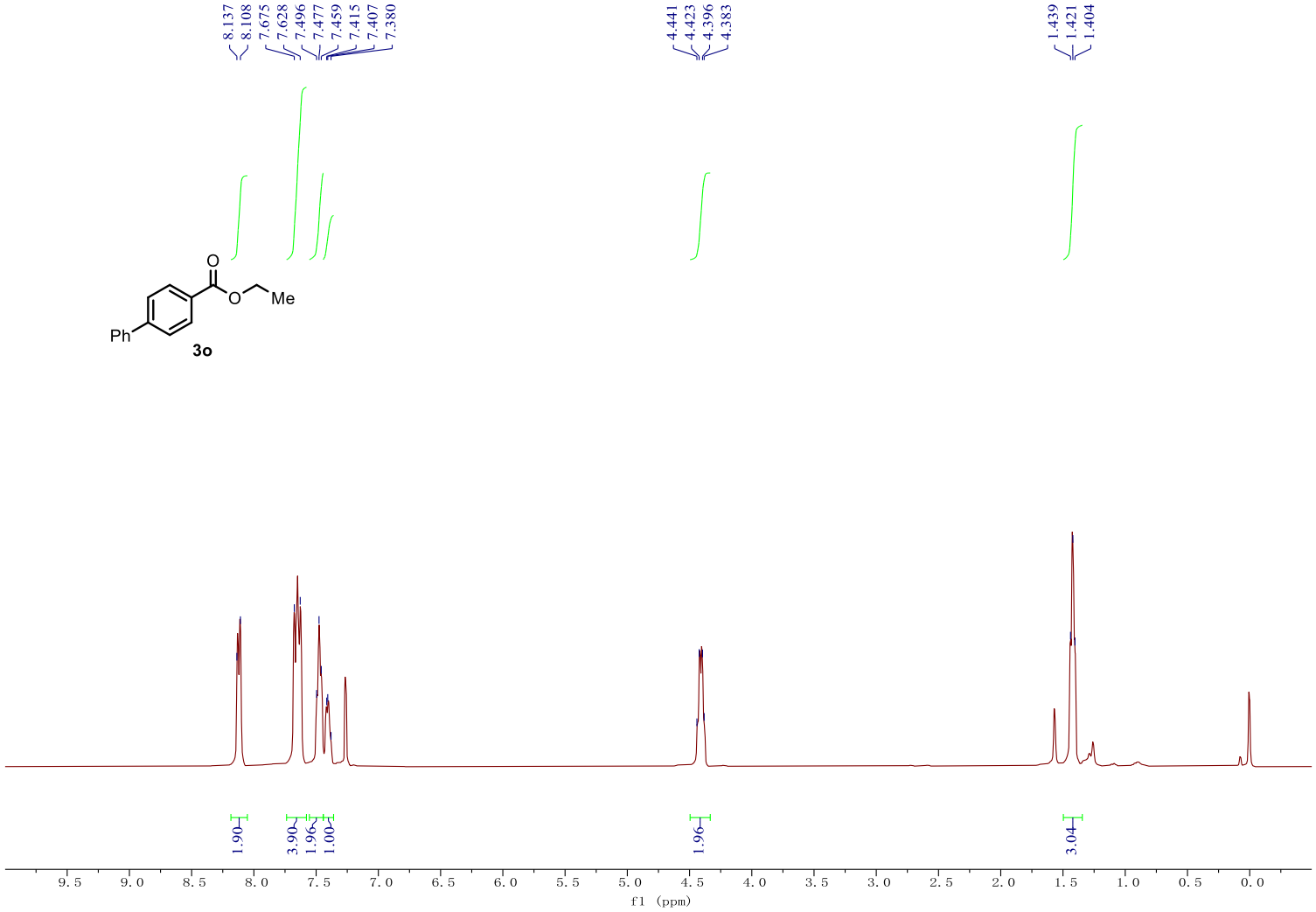

Figure S33. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-phenylbenzoate **(3o)**.

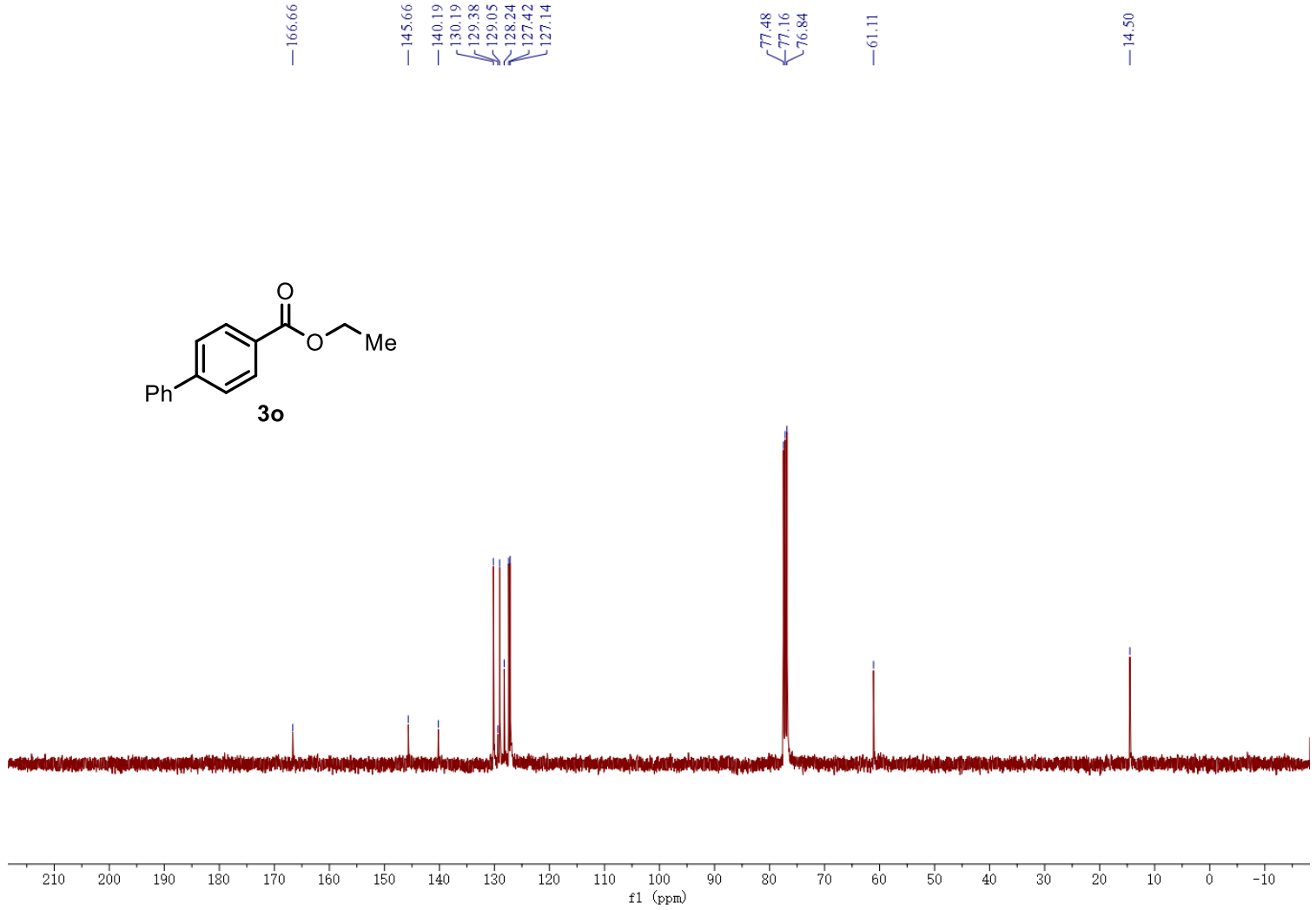

Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 4-(propen-1-yl)benzoate **(3p)**.

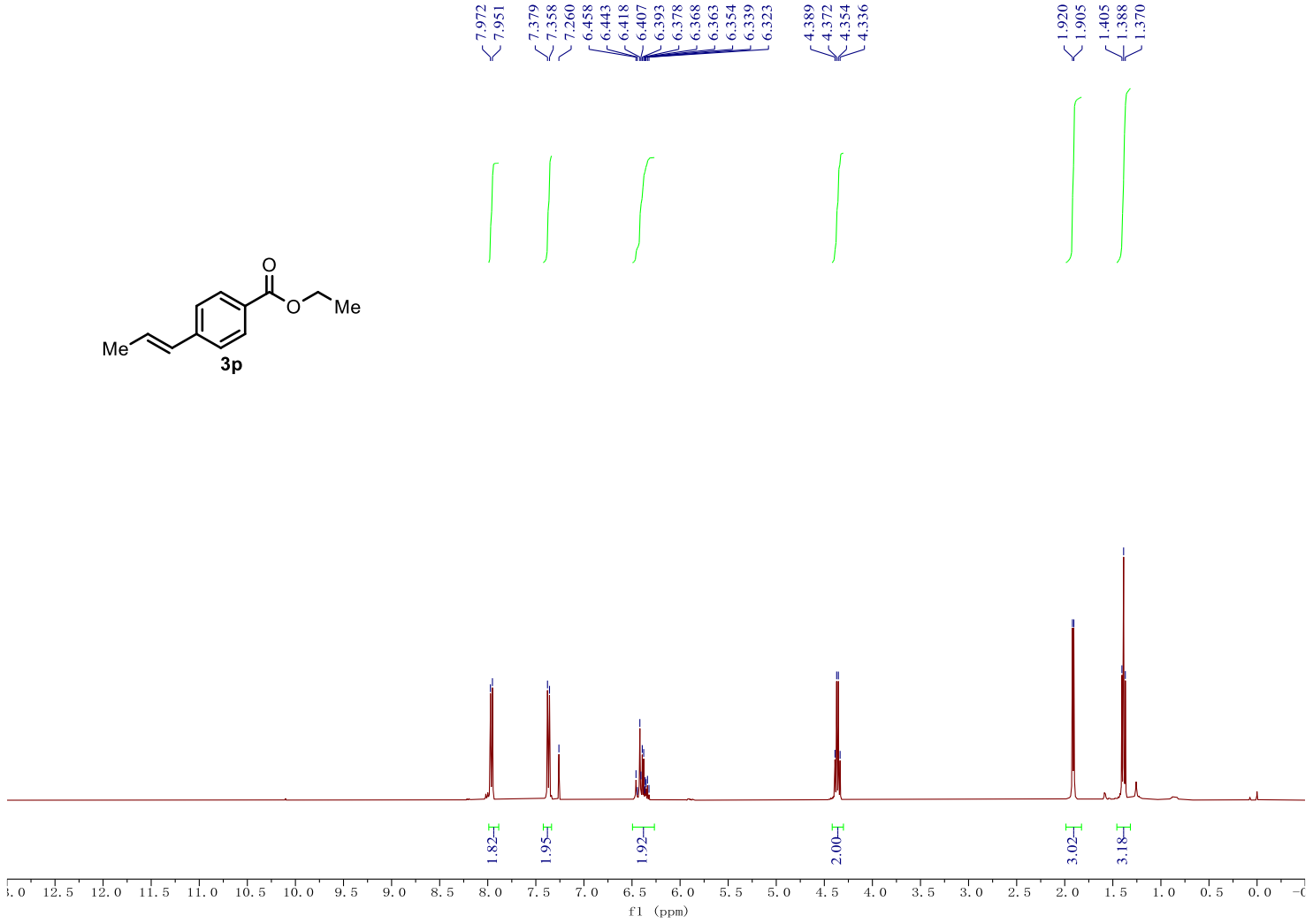

Figure S35. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 4-(propen-1-yl)benzoate **(3p)**.

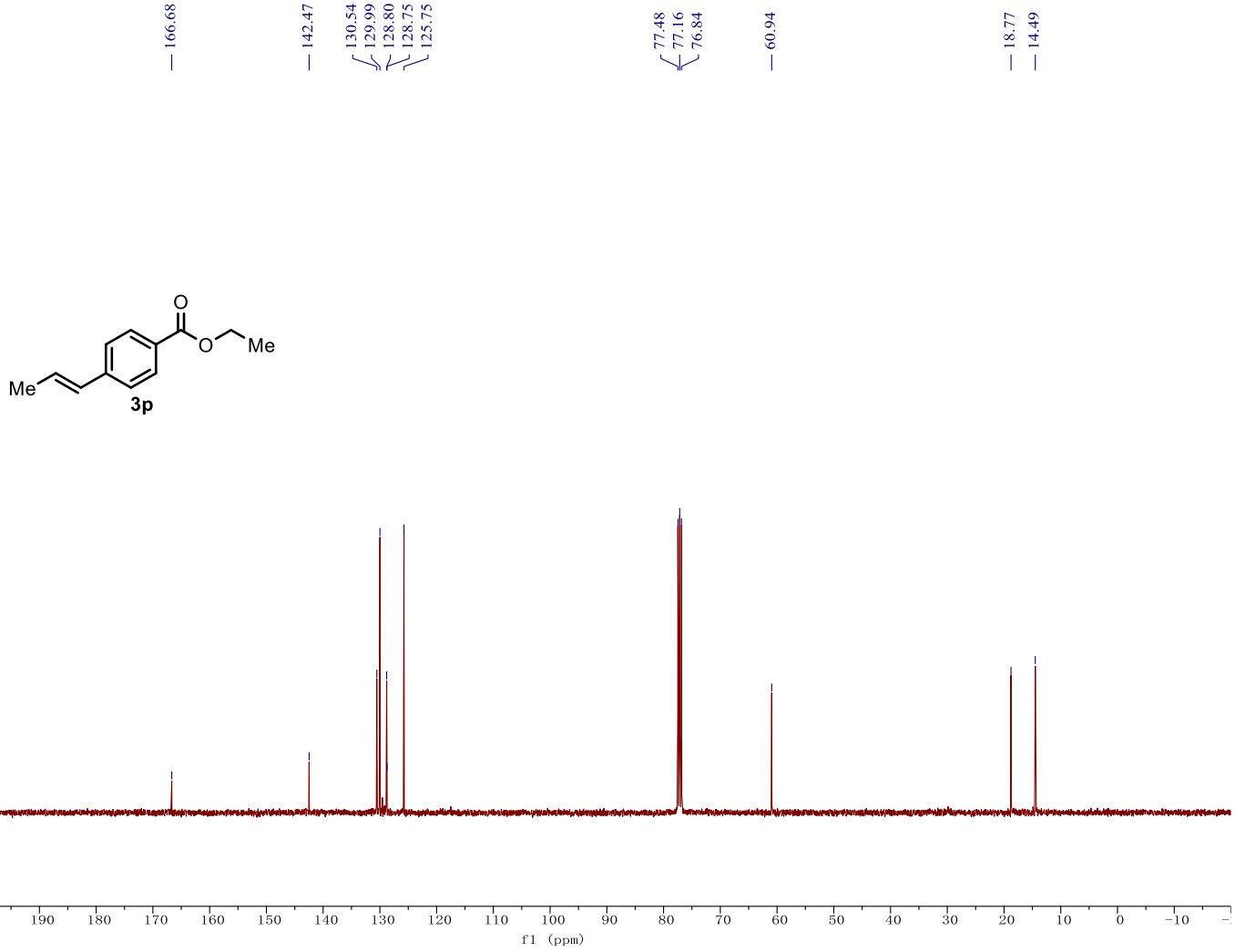

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl cinnamate **(3q)**.

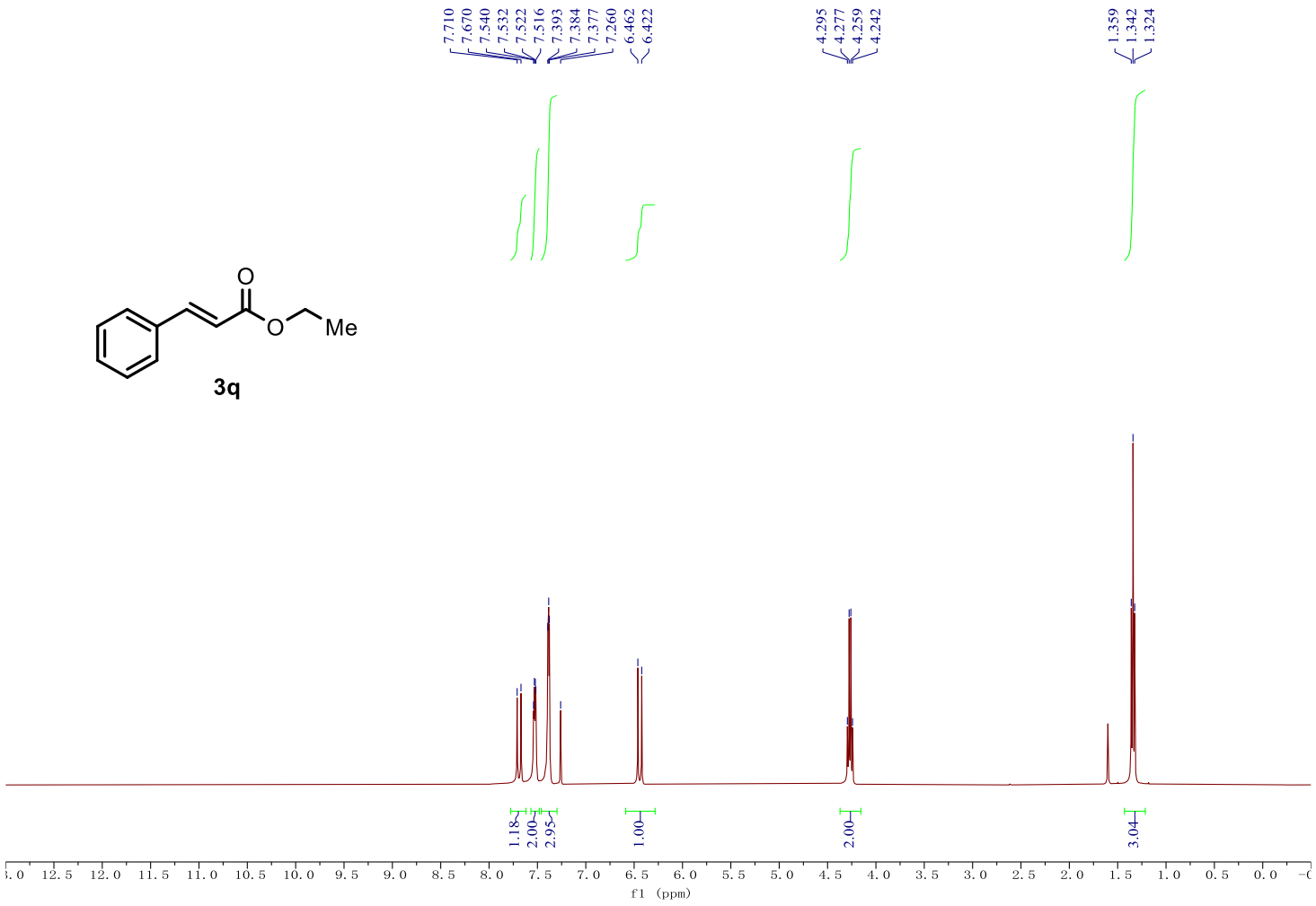

Figure S37. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl cinnamate **(3q)**.

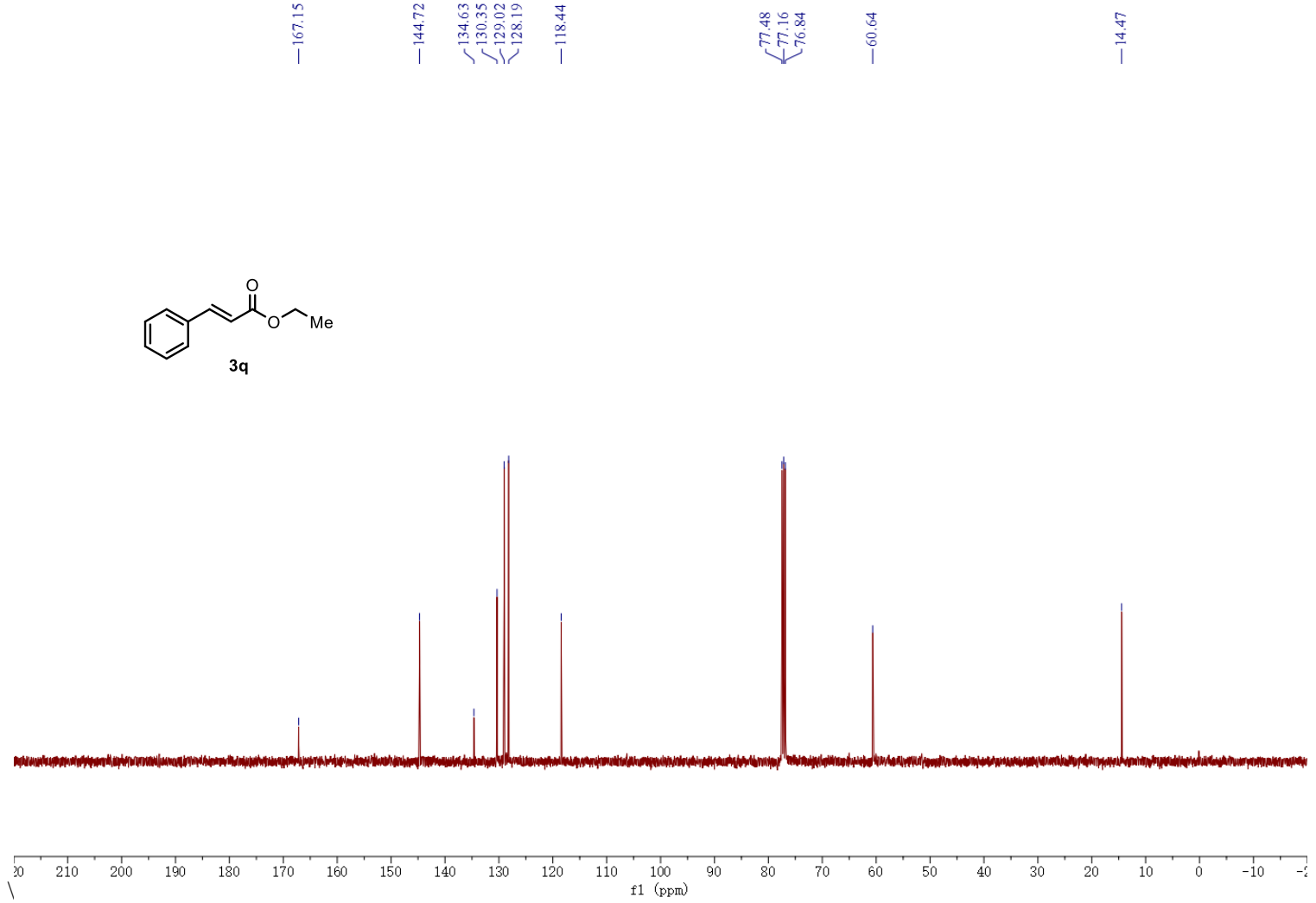

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-methylphenyl)acrylate **(3r)**.

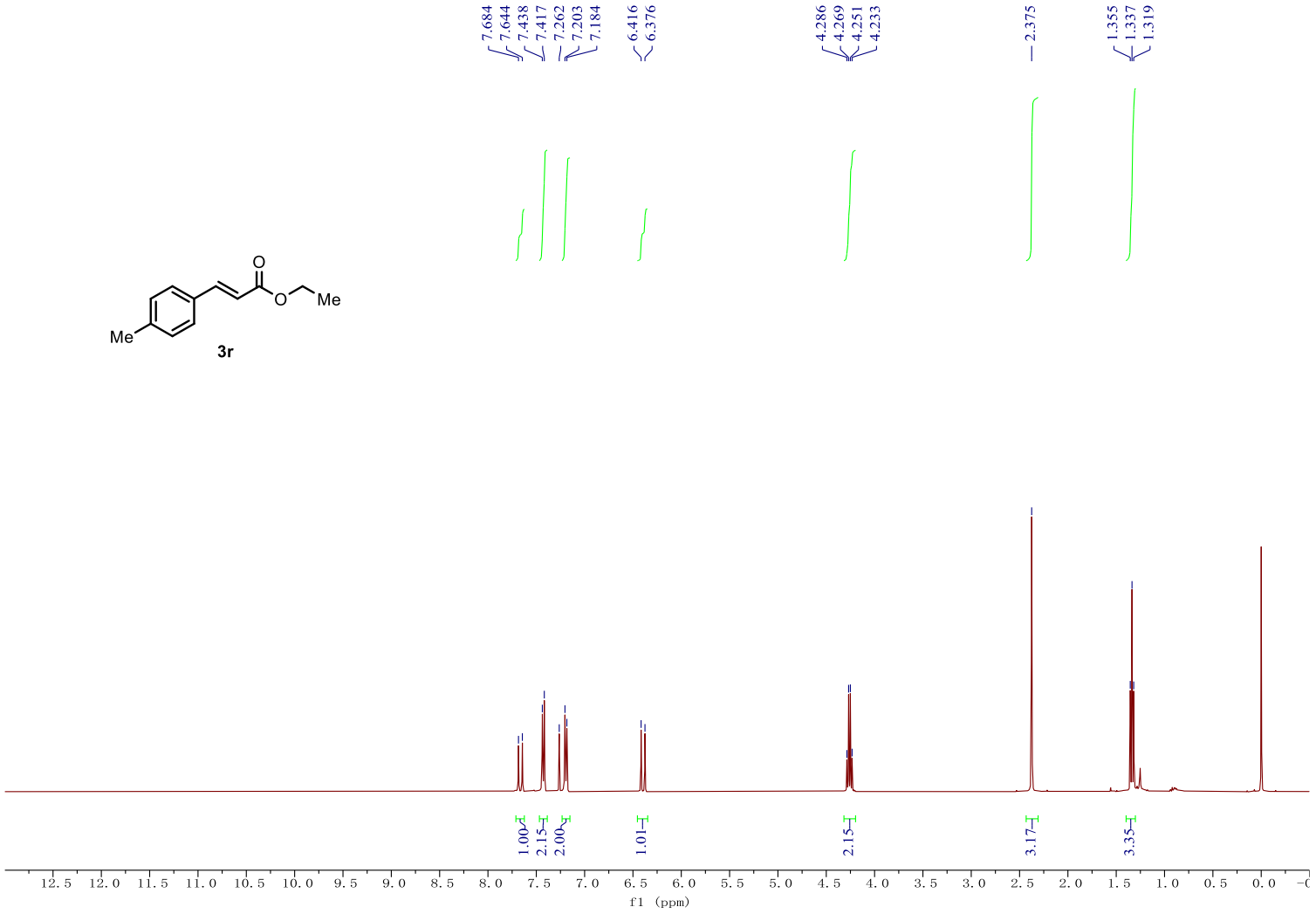

Figure S39. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-methylphenyl)acrylate **(3r)**.

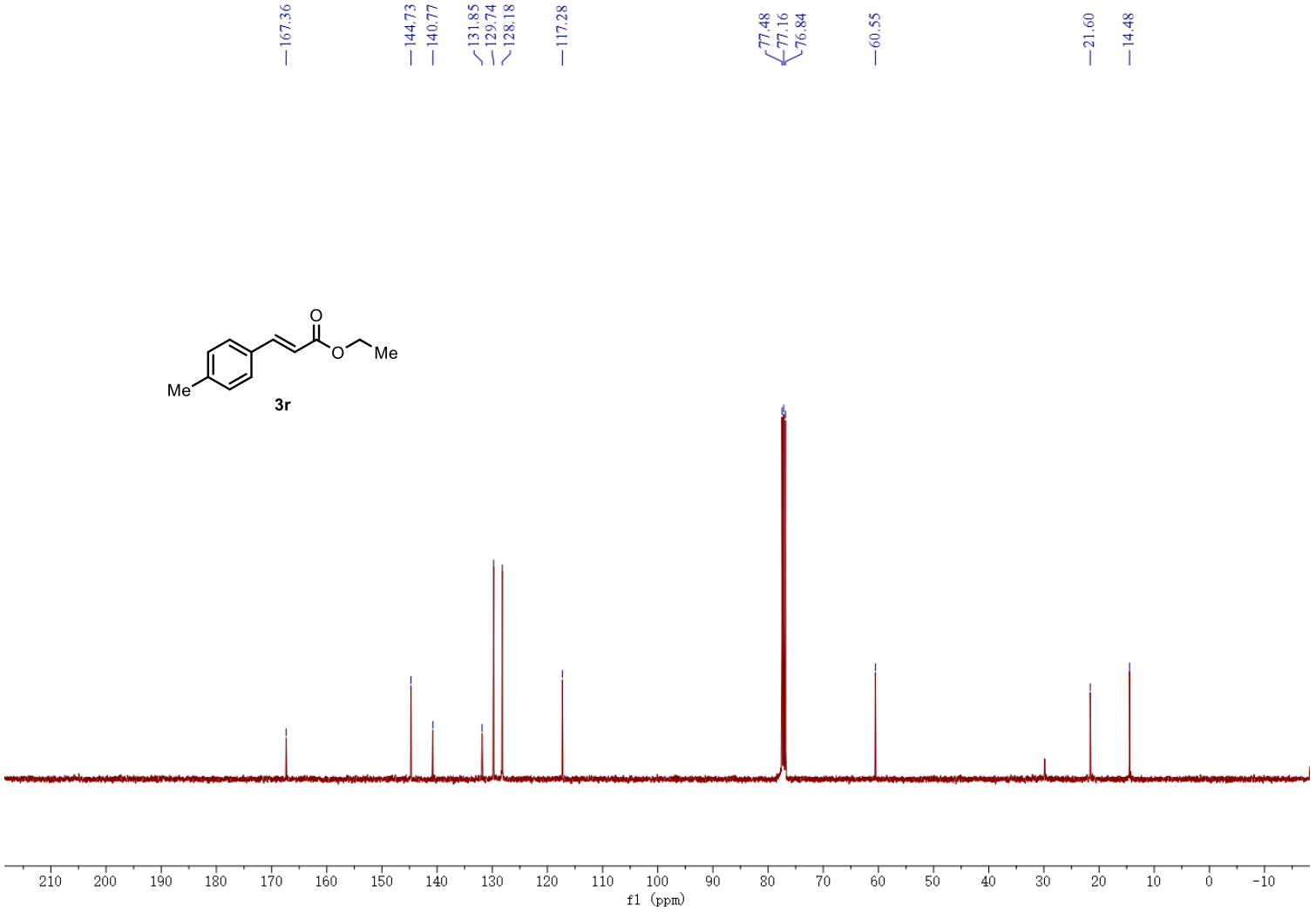

Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(3-phenoxyphenyl)-2-propenoate **(3s)**.

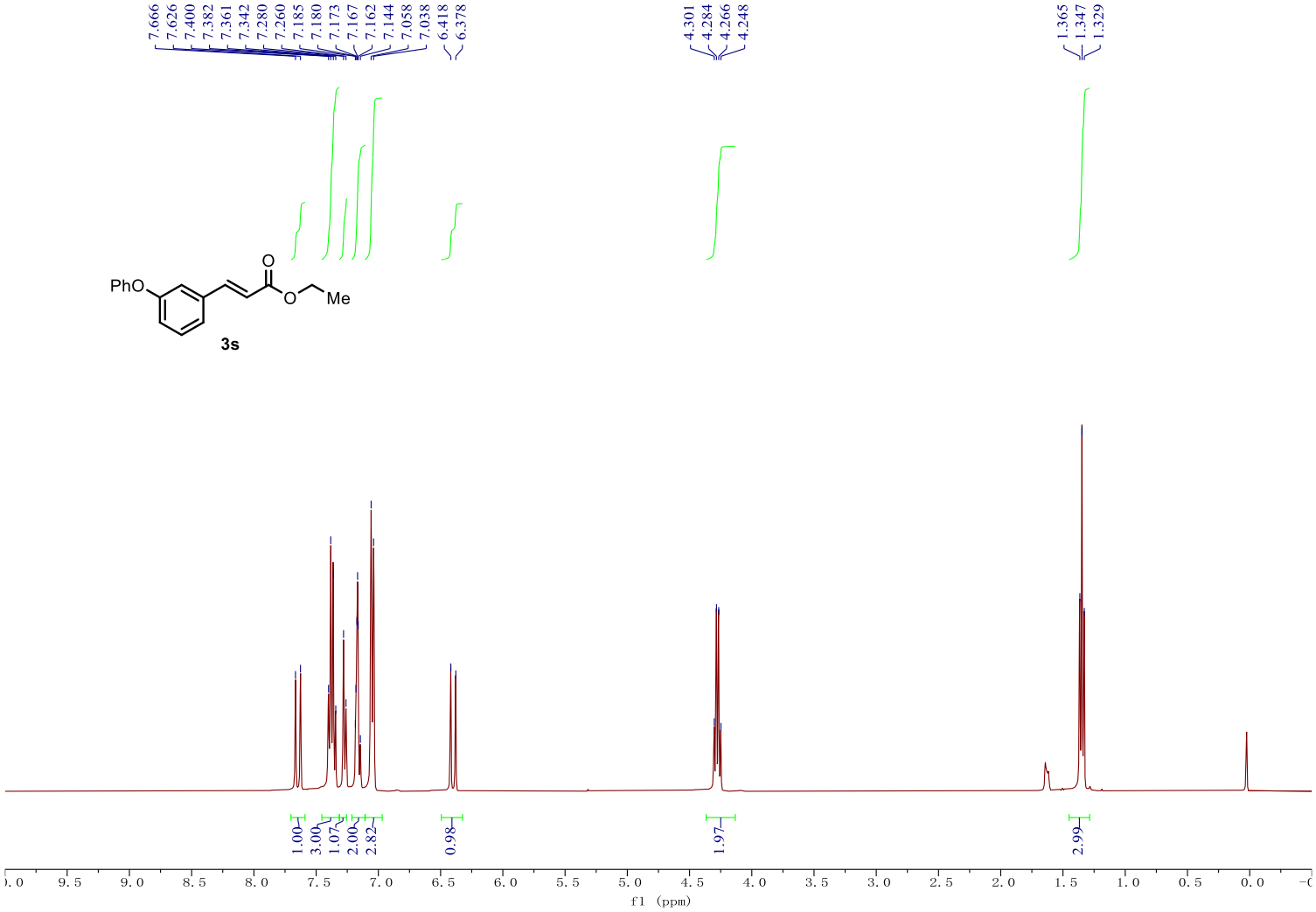

Figure S41. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(3-phenoxyphenyl)-2-propenoate **(3s)**.

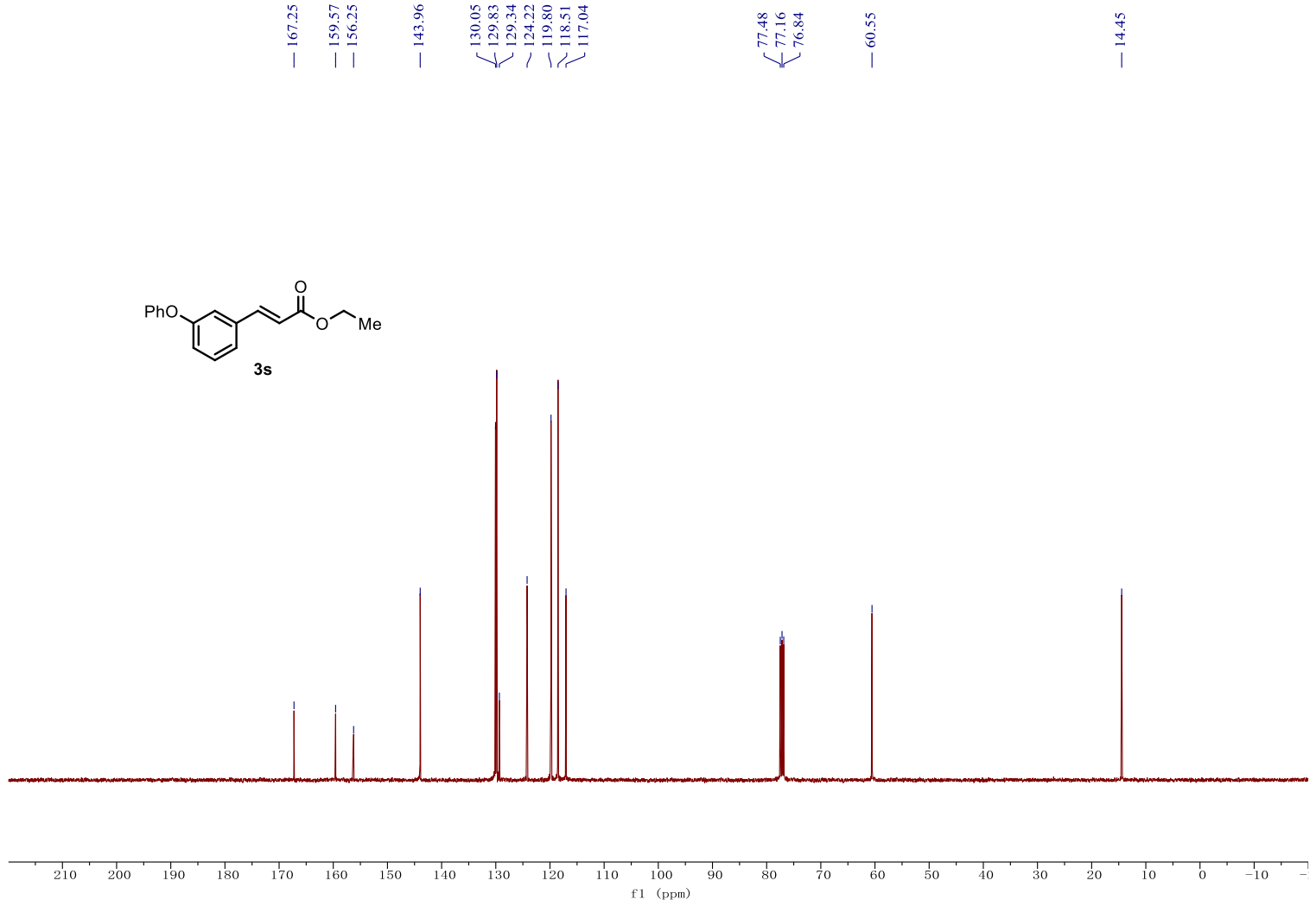

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3 -(4-phenoxyphenyl)-2-propenoate **(3t)**.

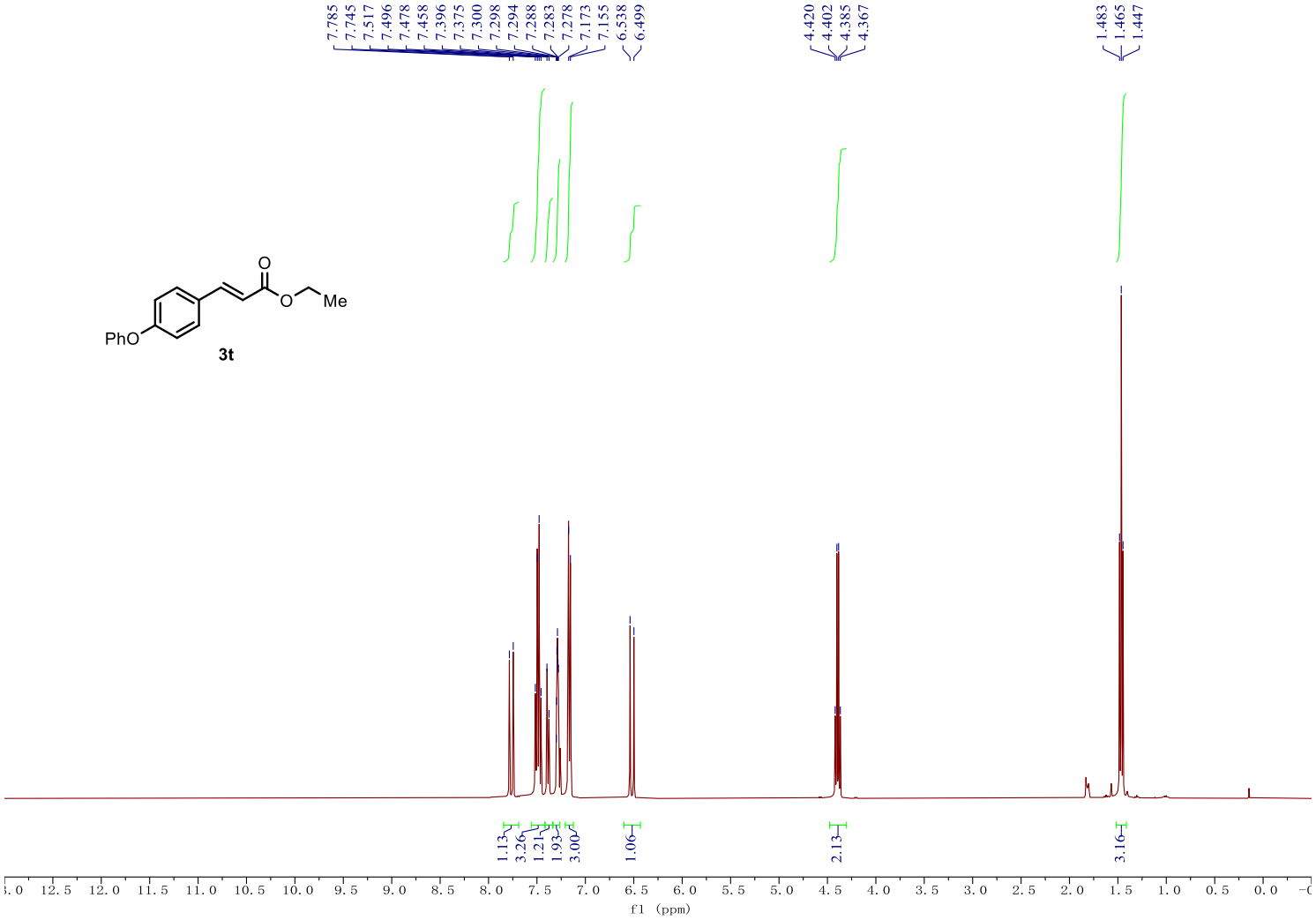

Figure S43. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3 -(4-phenoxyphenyl)-2-propenoate **(3t)**.

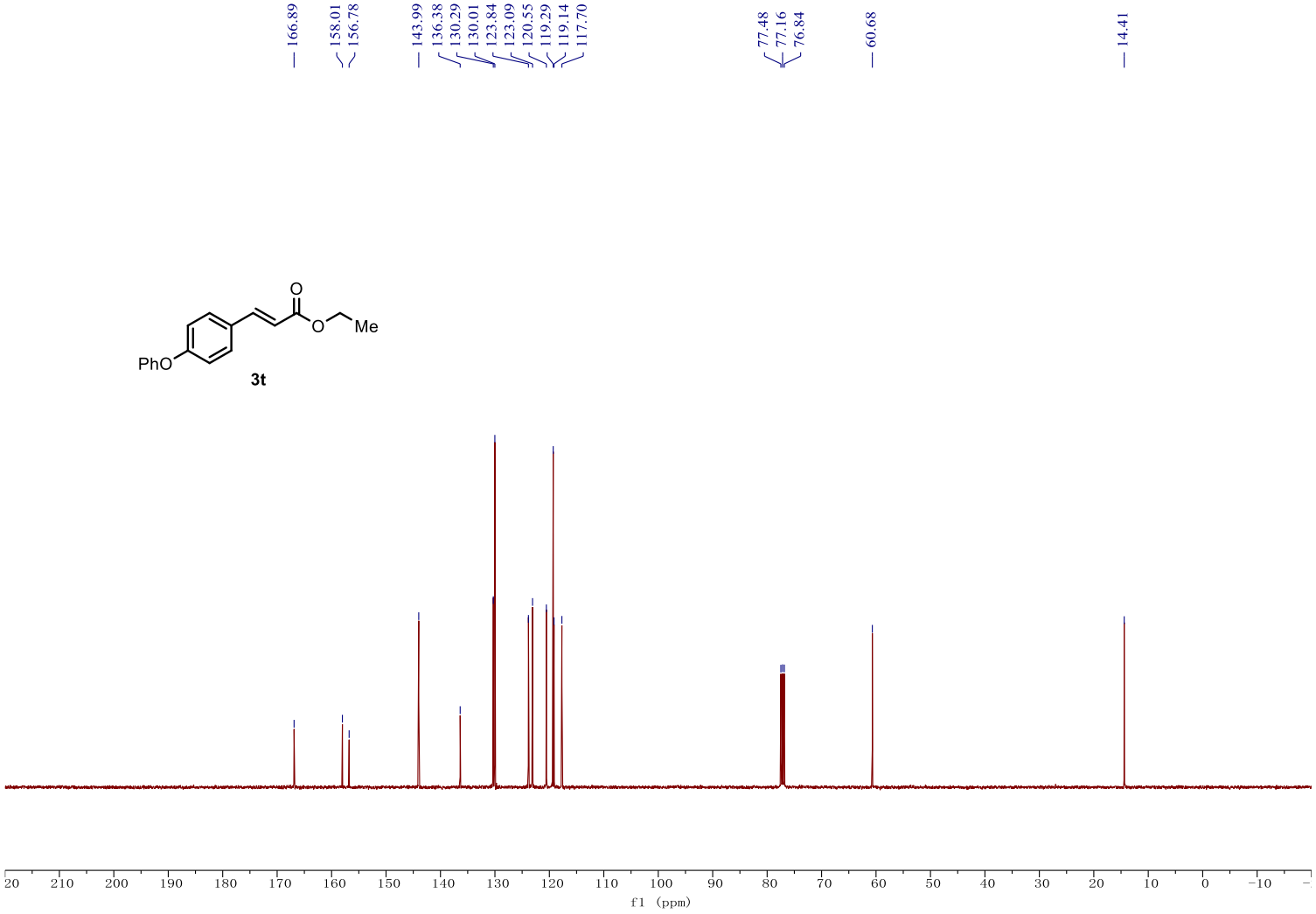

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(3-bromophenyl)prop-2-enoate **(3u)**.

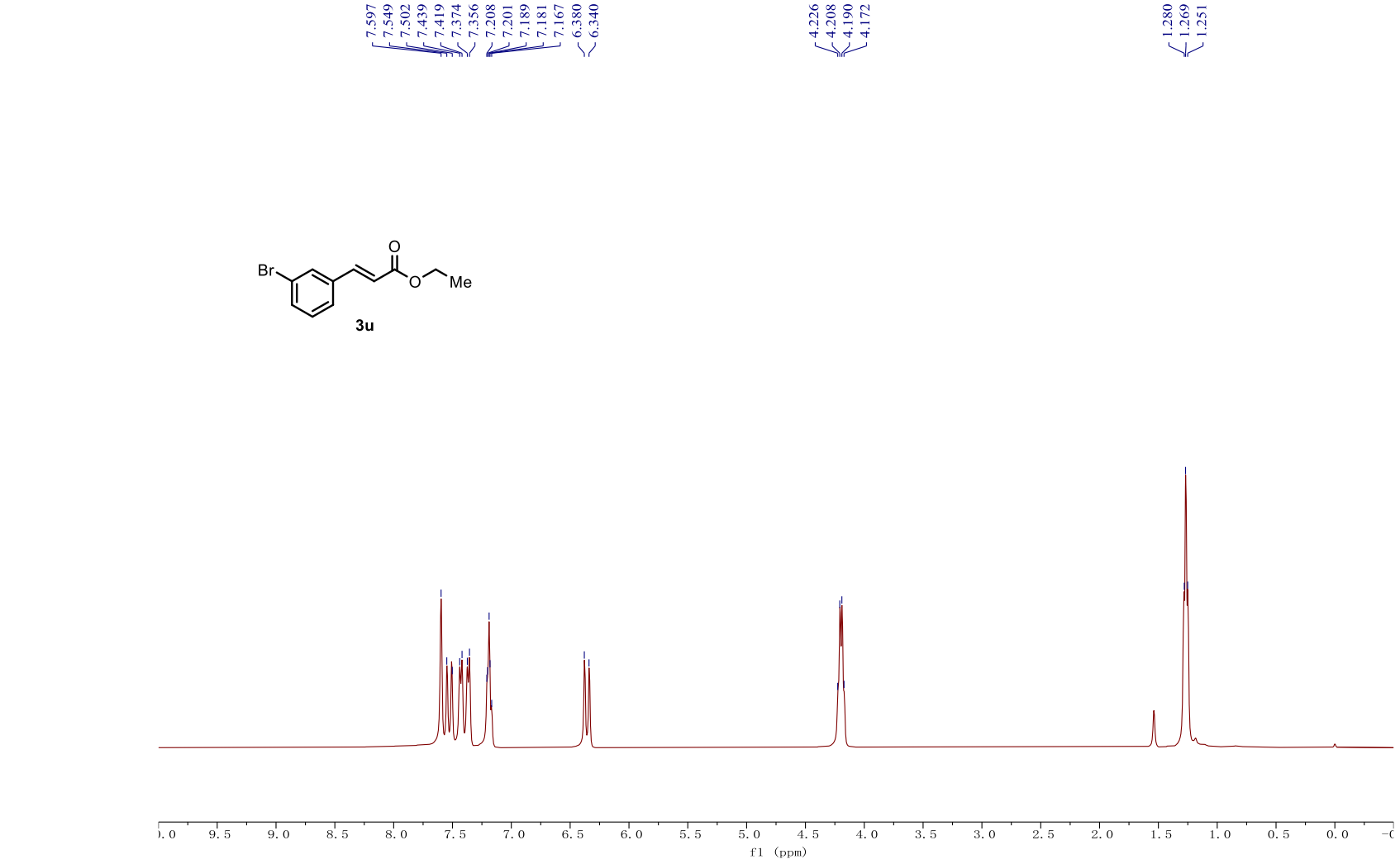

Figure S45. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(3-bromophenyl)prop-2-enoate **(3u)**.

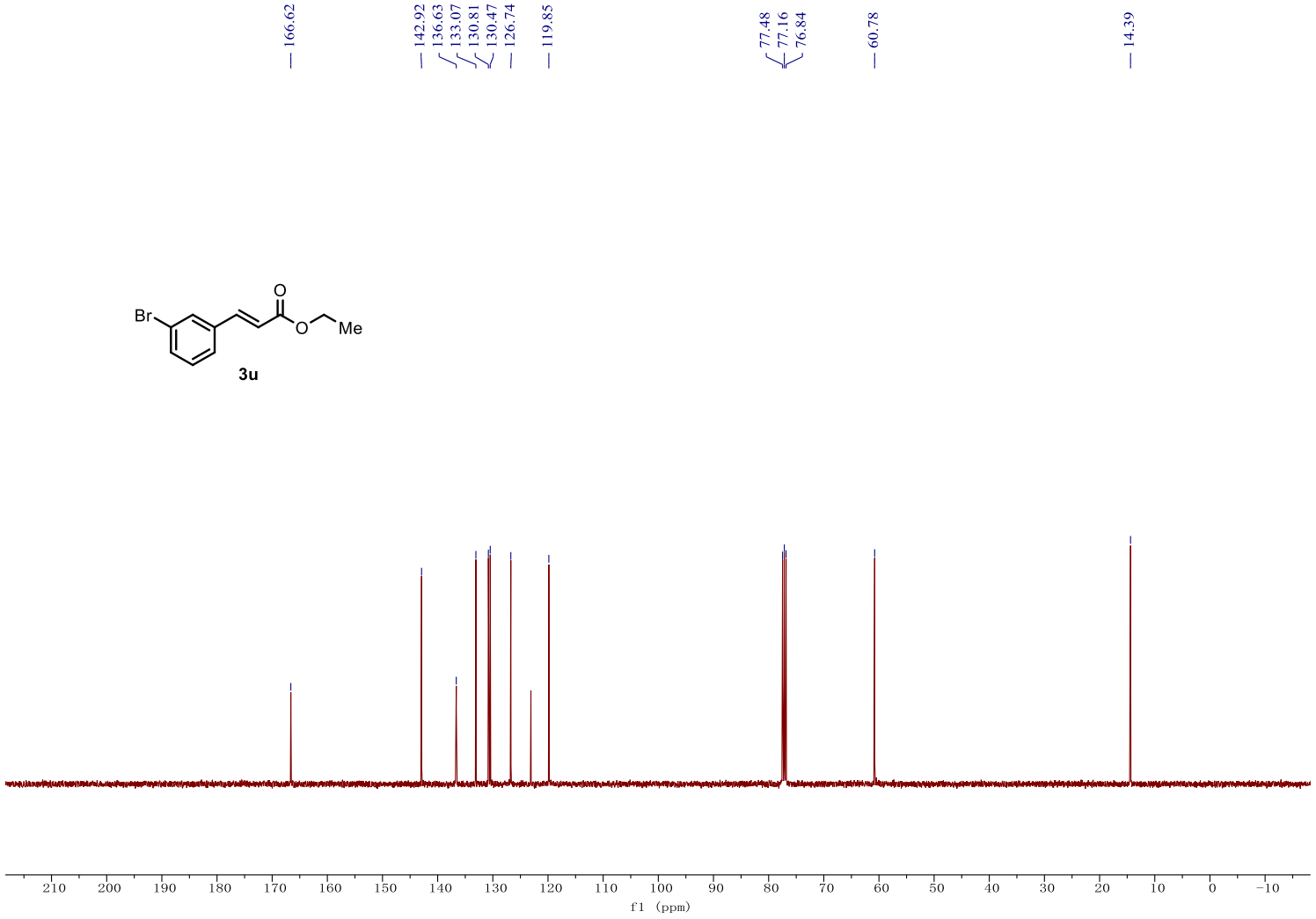

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-bromophenyl)prop-2-enoate **(3v)**.

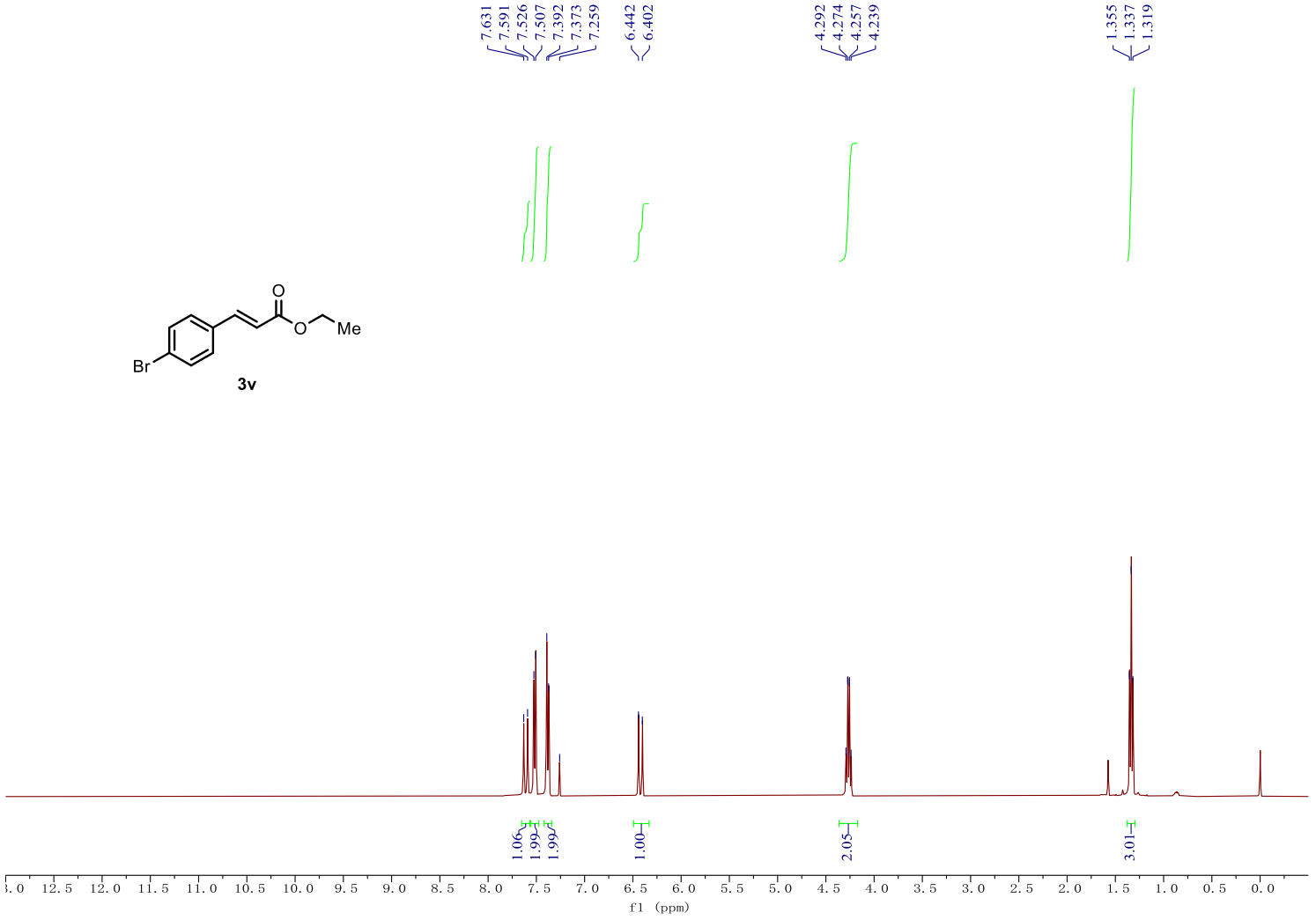

Figure S47. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-bromophenyl)prop-2-enoate **(3v)**.

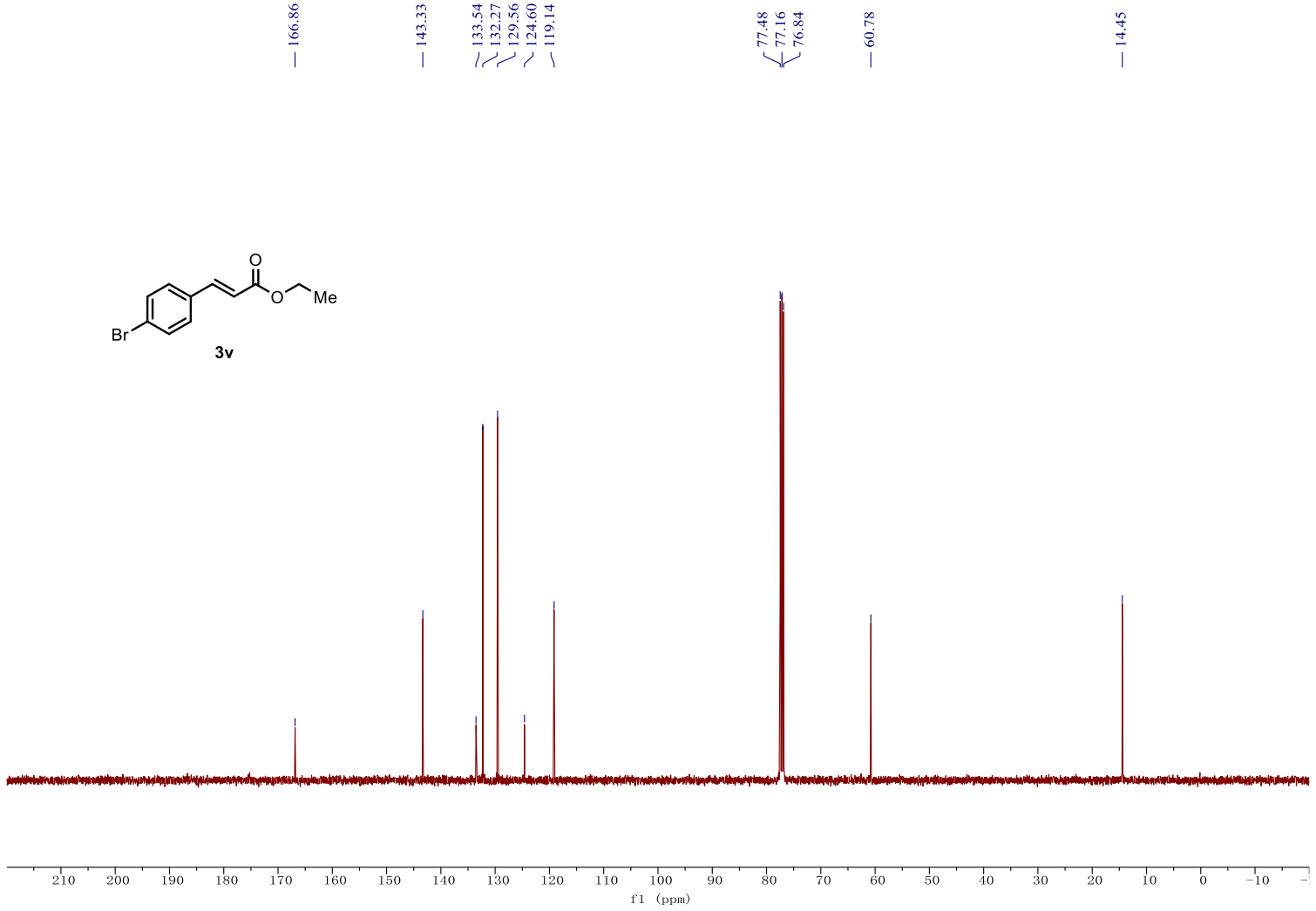

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-chlorophenyl)prop-2-enoate **(3w)**.

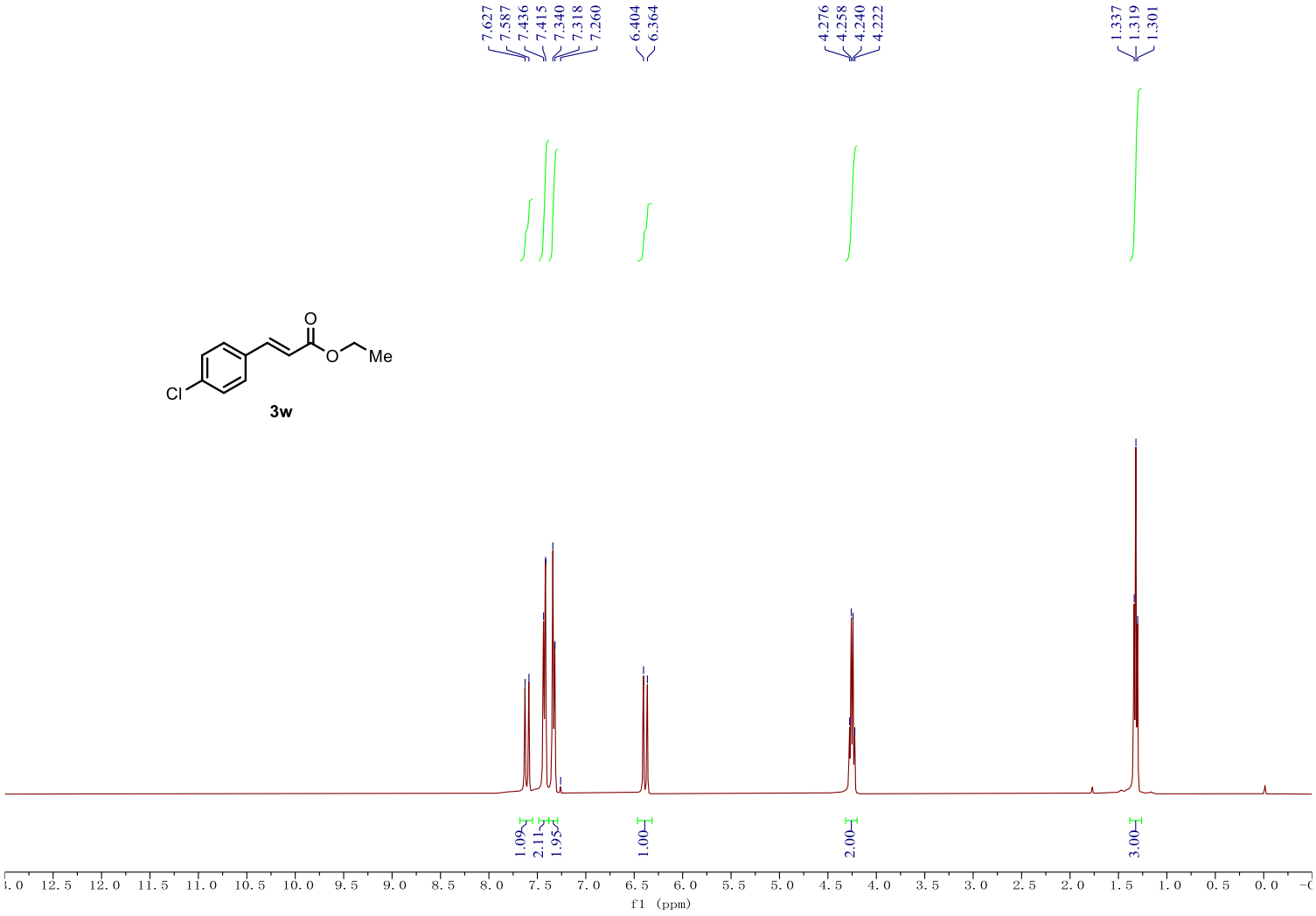

Figure S49. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(4-chlorophenyl)prop-2-enoate **(3w)**.

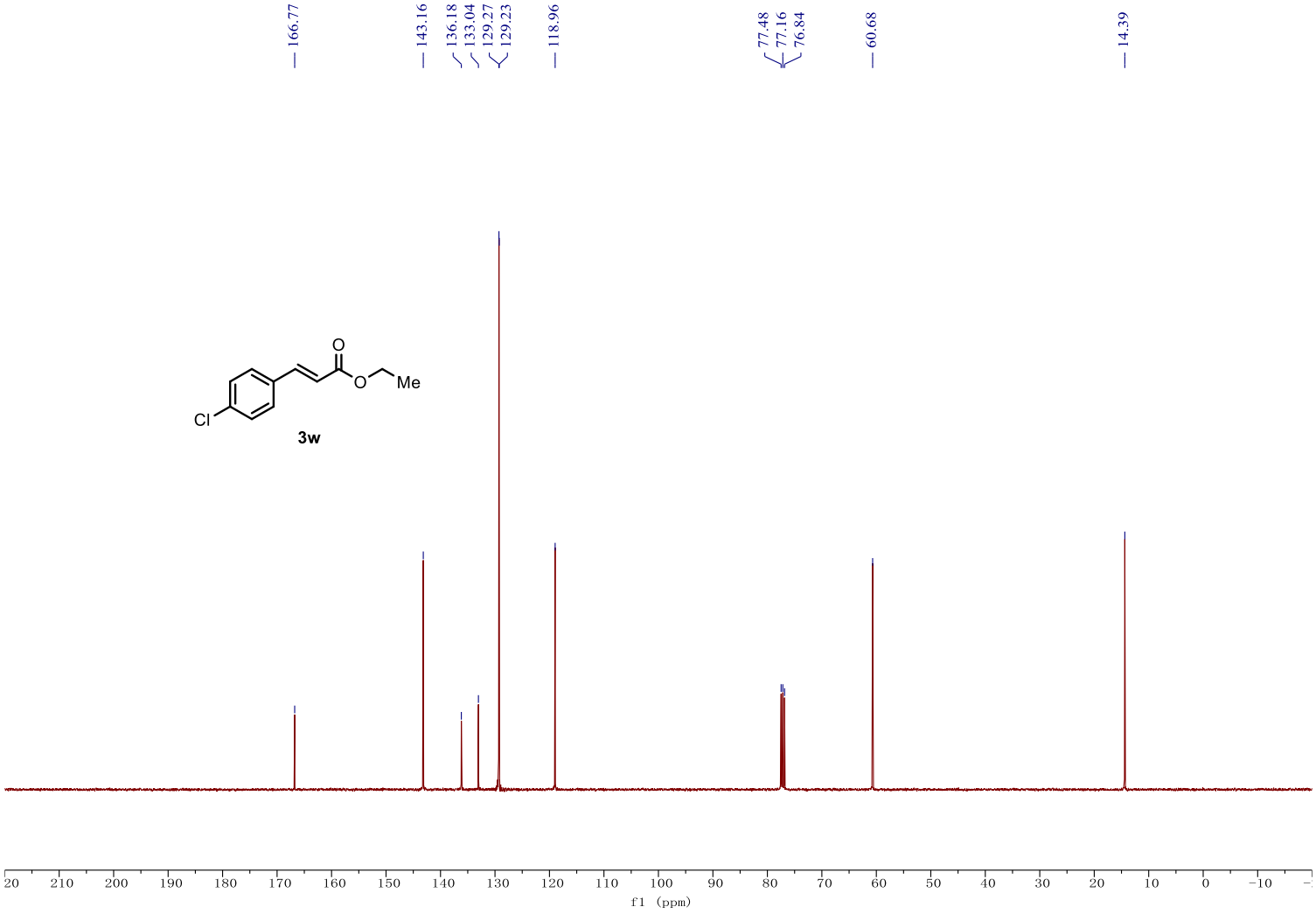

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-([1,1'-biphenyl]-4-yl)acrylate **(3x)**.

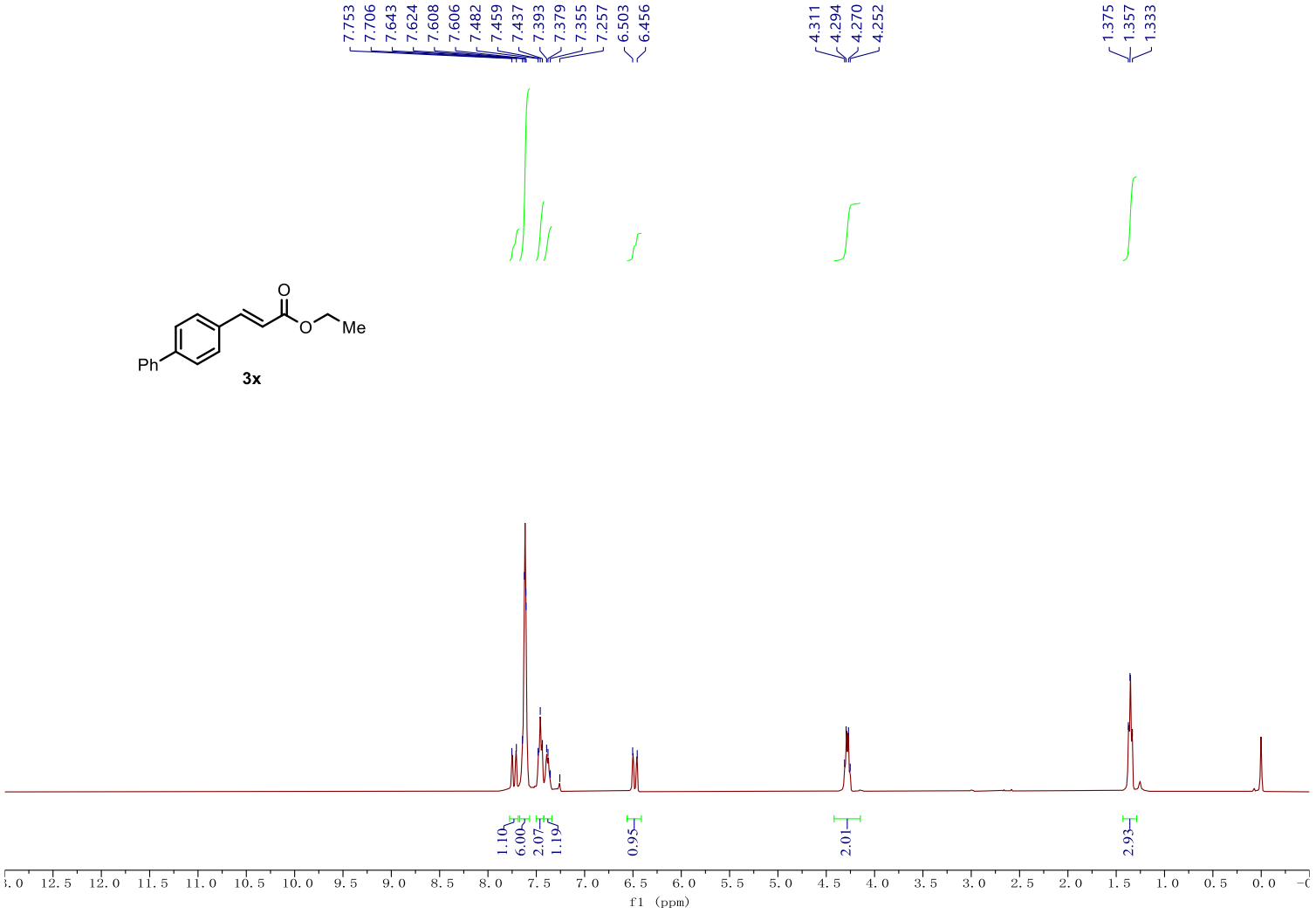

Figure S51. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-([1,1'-biphenyl]-4-yl)acrylate **(3x)**.

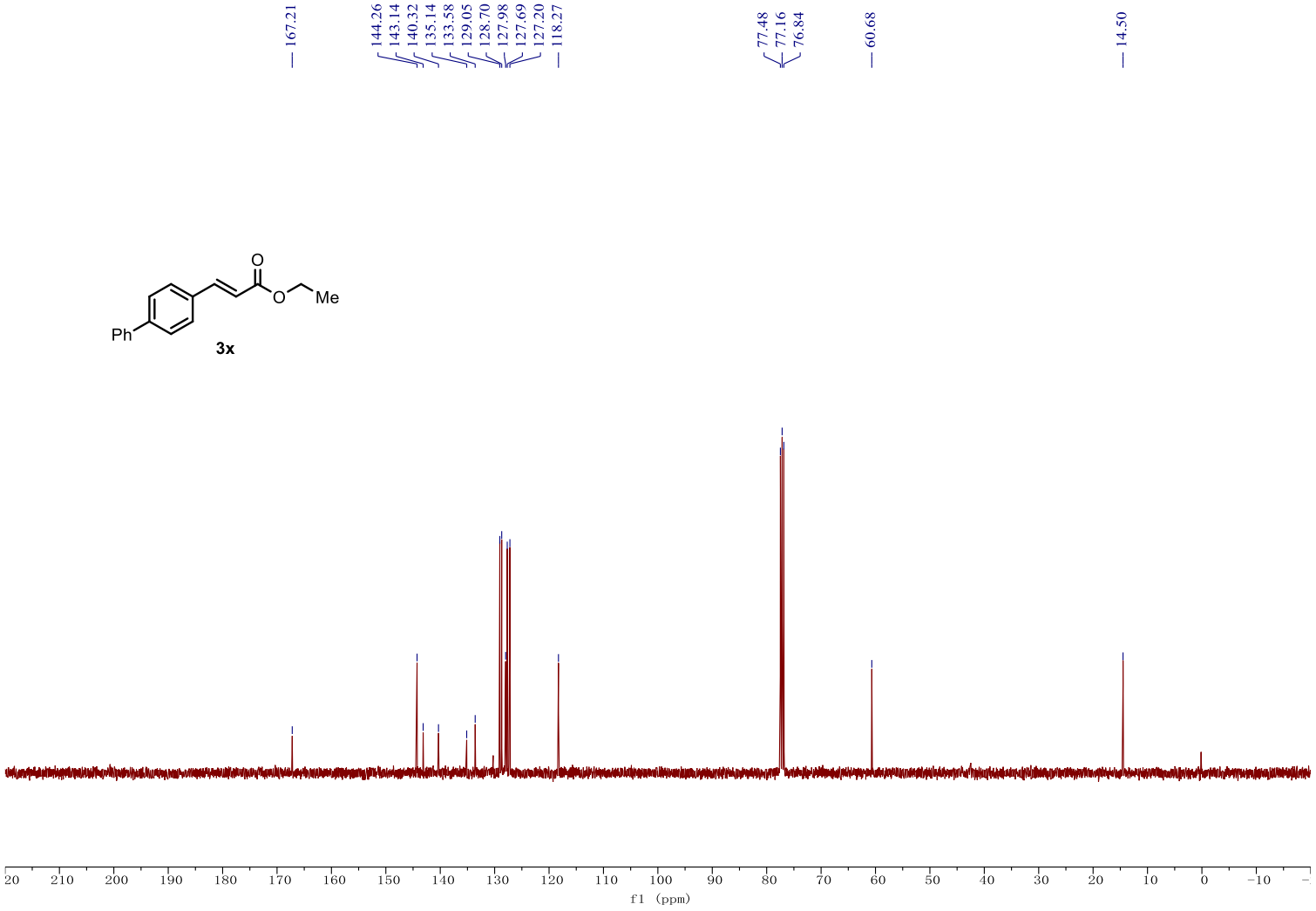

Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-4-trifluoromethylcinnamate **(3y)**.

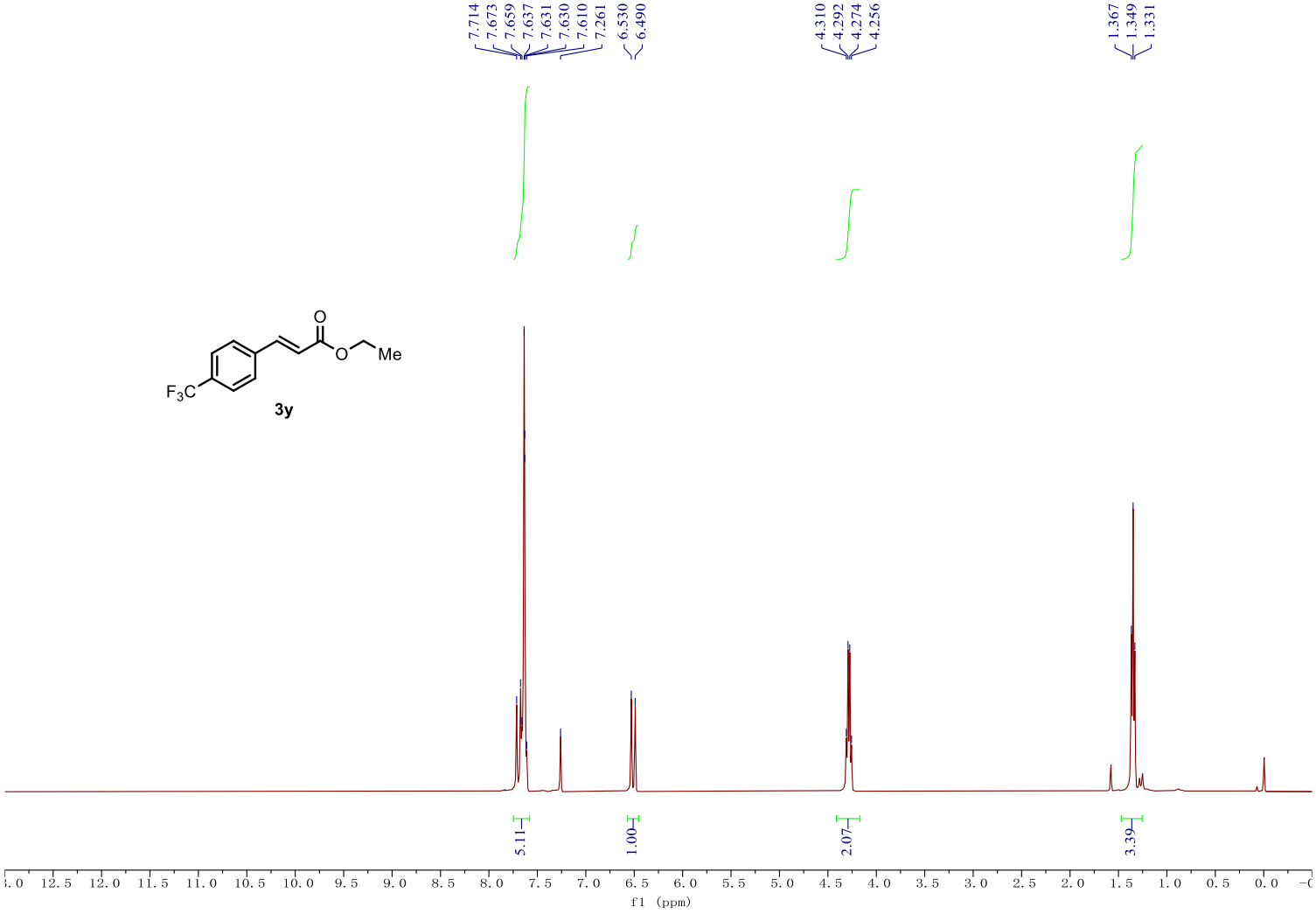

Figure S53. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-4-trifluoromethylcinnamate **(3y)**.

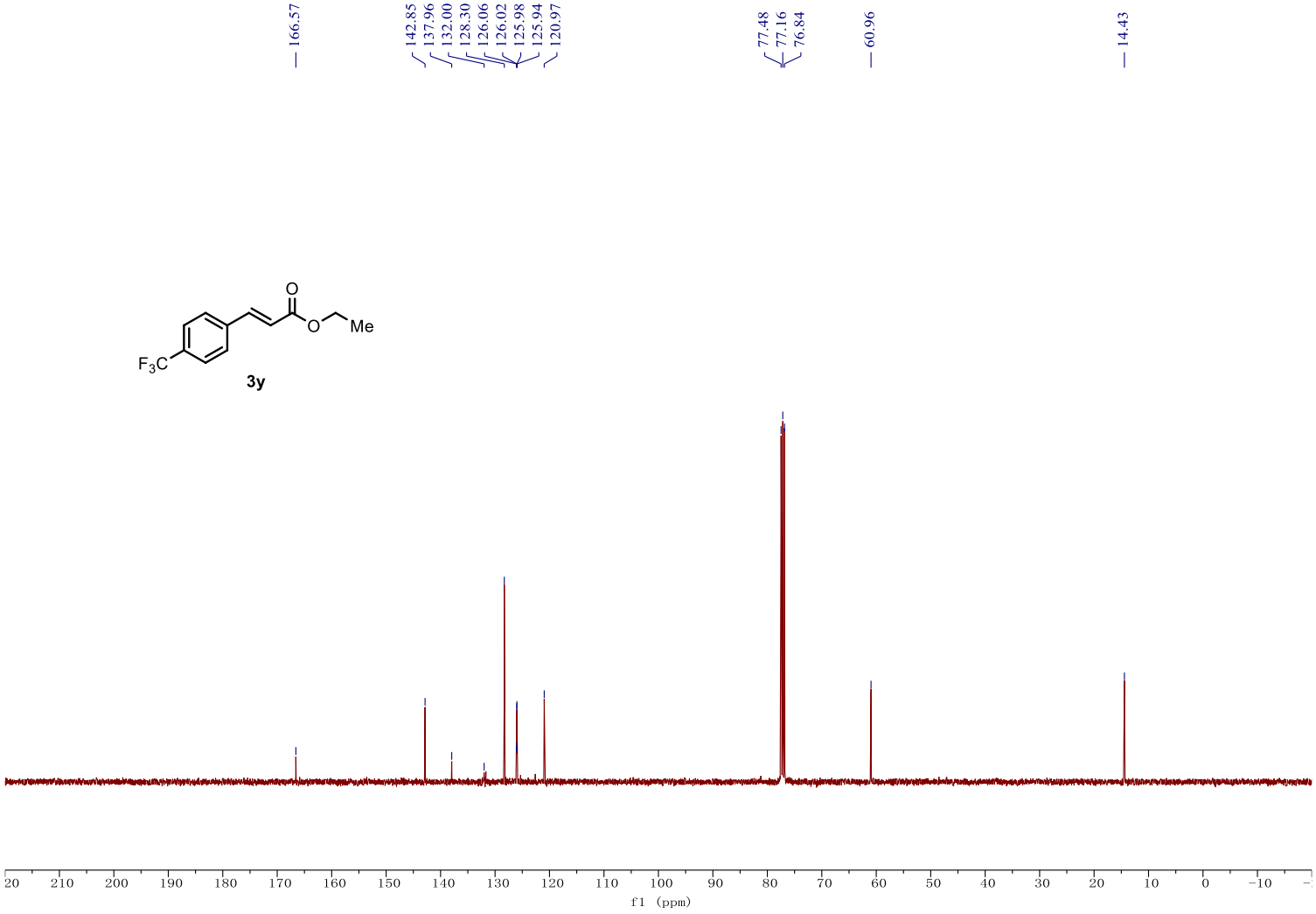

Figure S54. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-4-trifluoromethylcinnamate **(3y)**

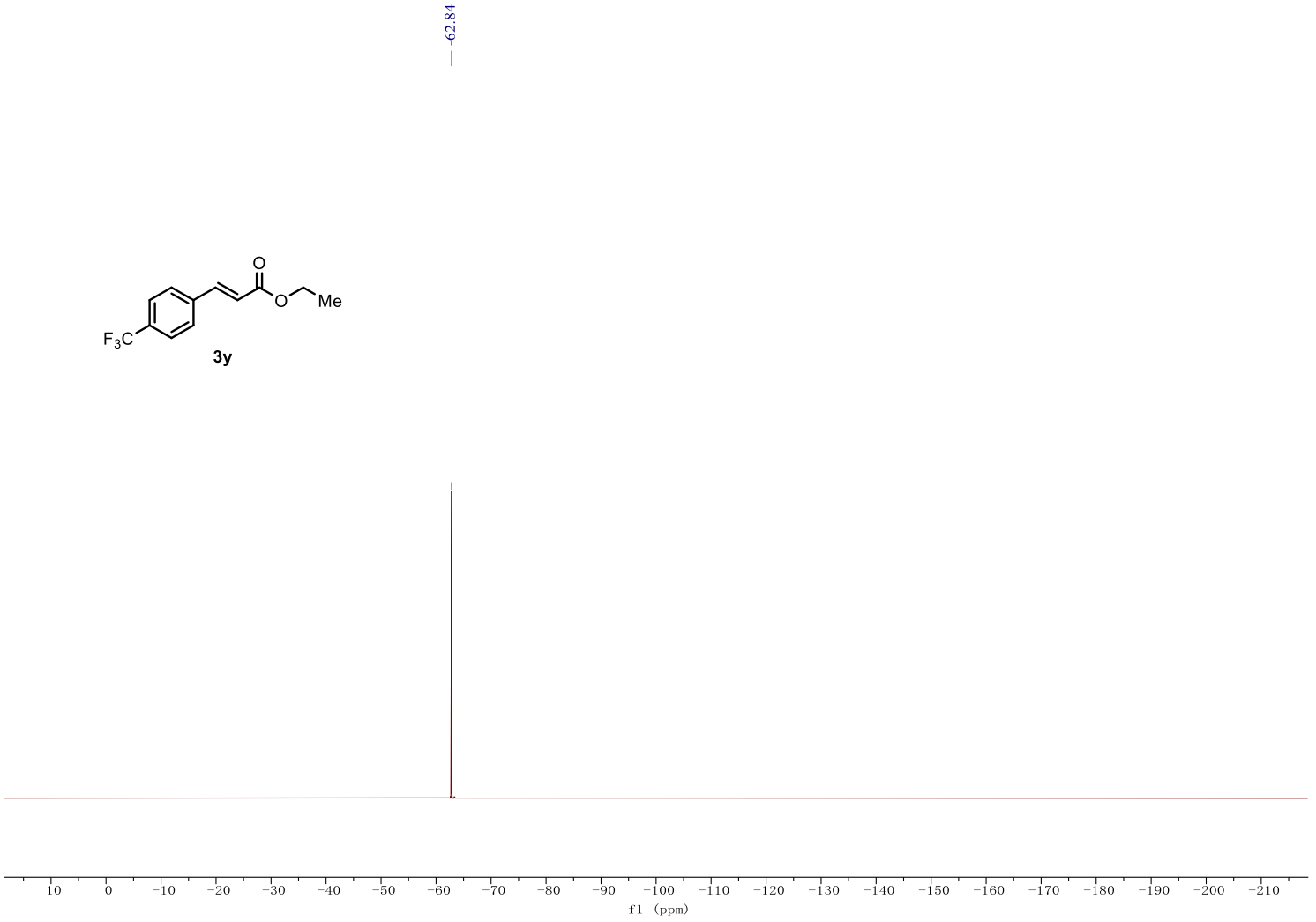

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of *(E)*-ethyl 3-(naphthalen-1-yl)acrylate **(3z)**.

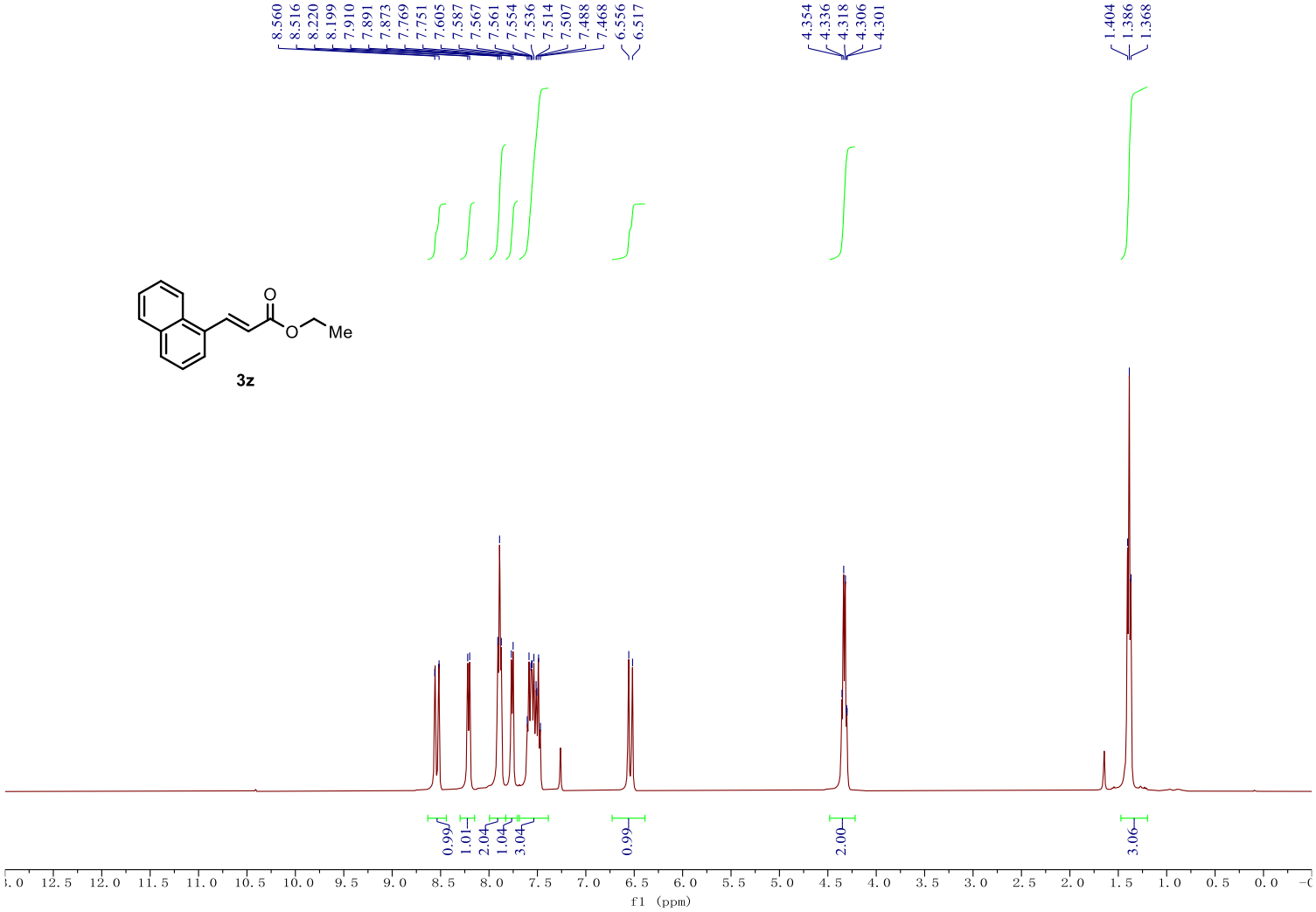

Figure S56. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of *(E)*-ethyl 3-(naphthalen-1-yl)acrylate **(3z)**.

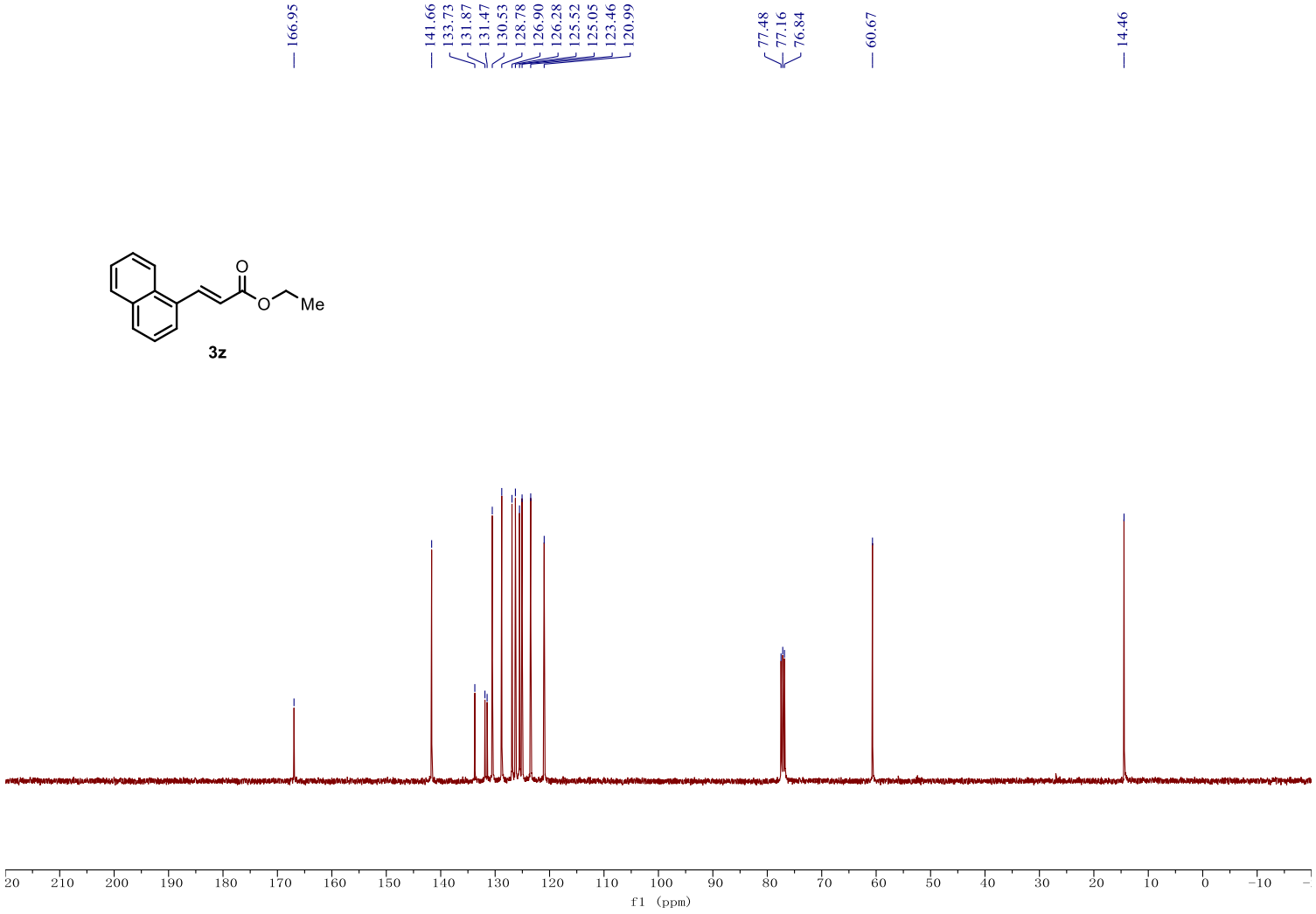

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(thiophen-2-yl)acrylate **(3aa)**.

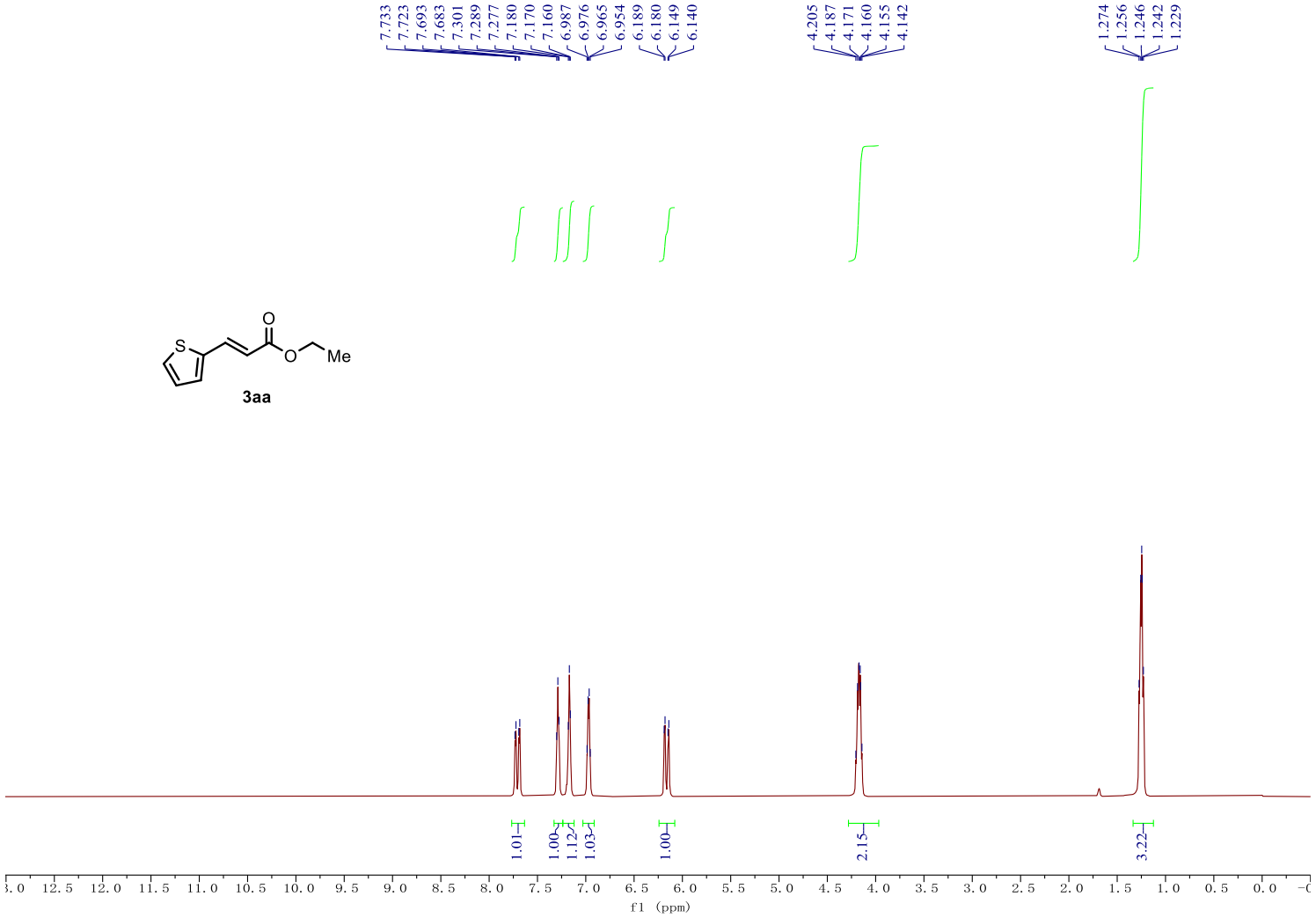

Figure S58. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(thiophen-2-yl)acrylate **(3aa)**.

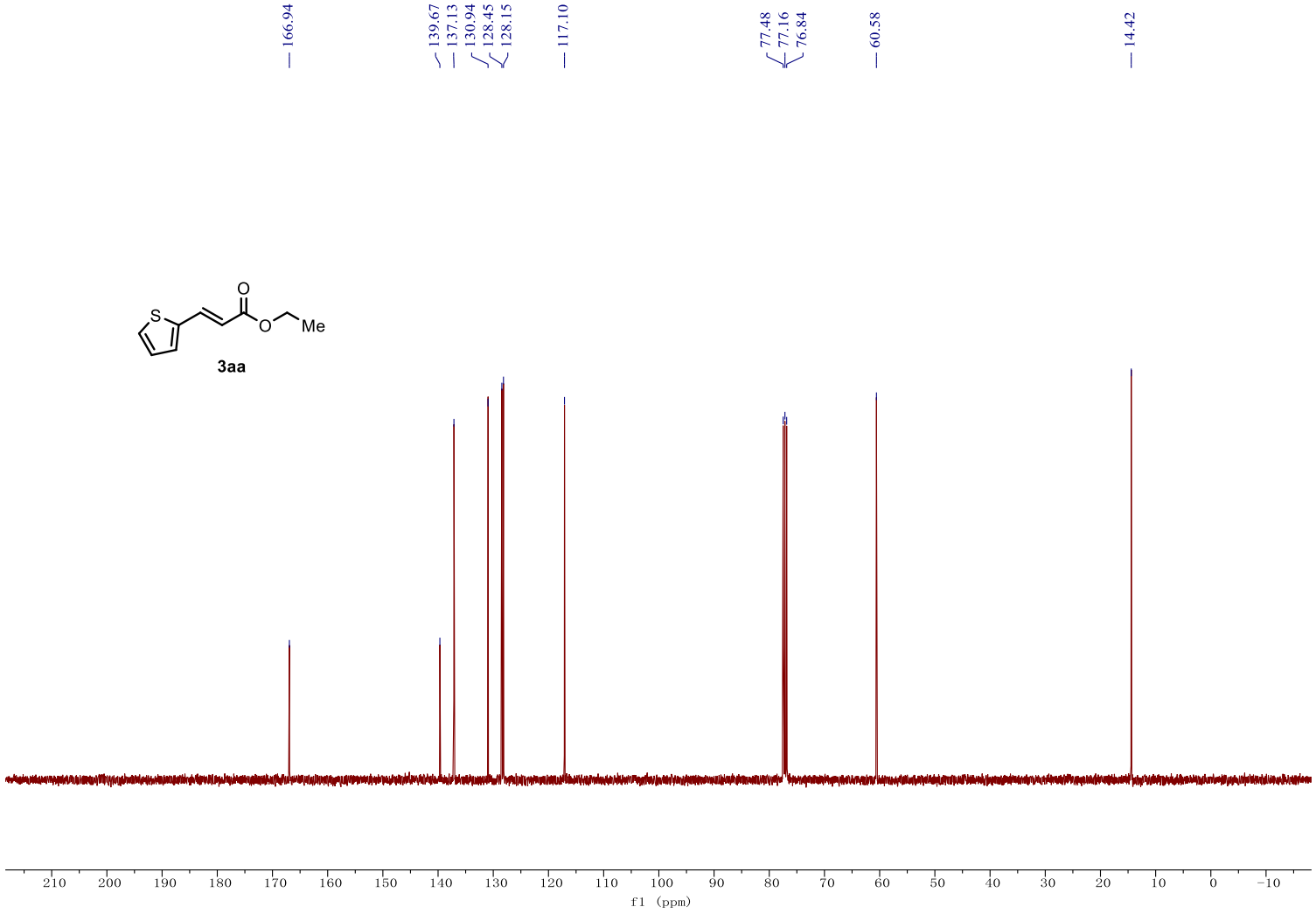

Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(benzo[b]thiophen-2-yl)acrylate **(3ab)**.

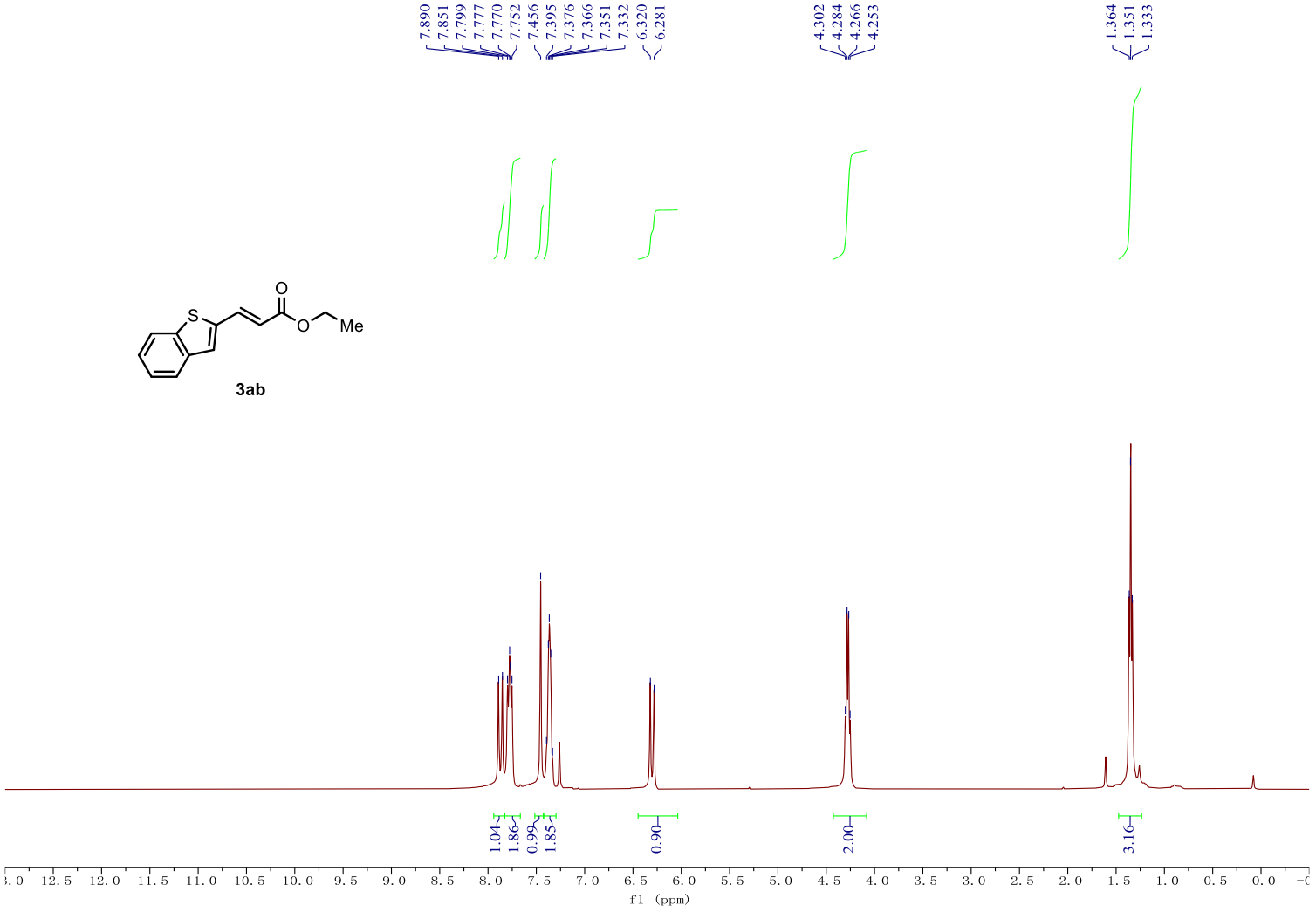

Figure S60. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-3-(benzo[b]thiophen-2-yl)acrylate **(3ab)**.

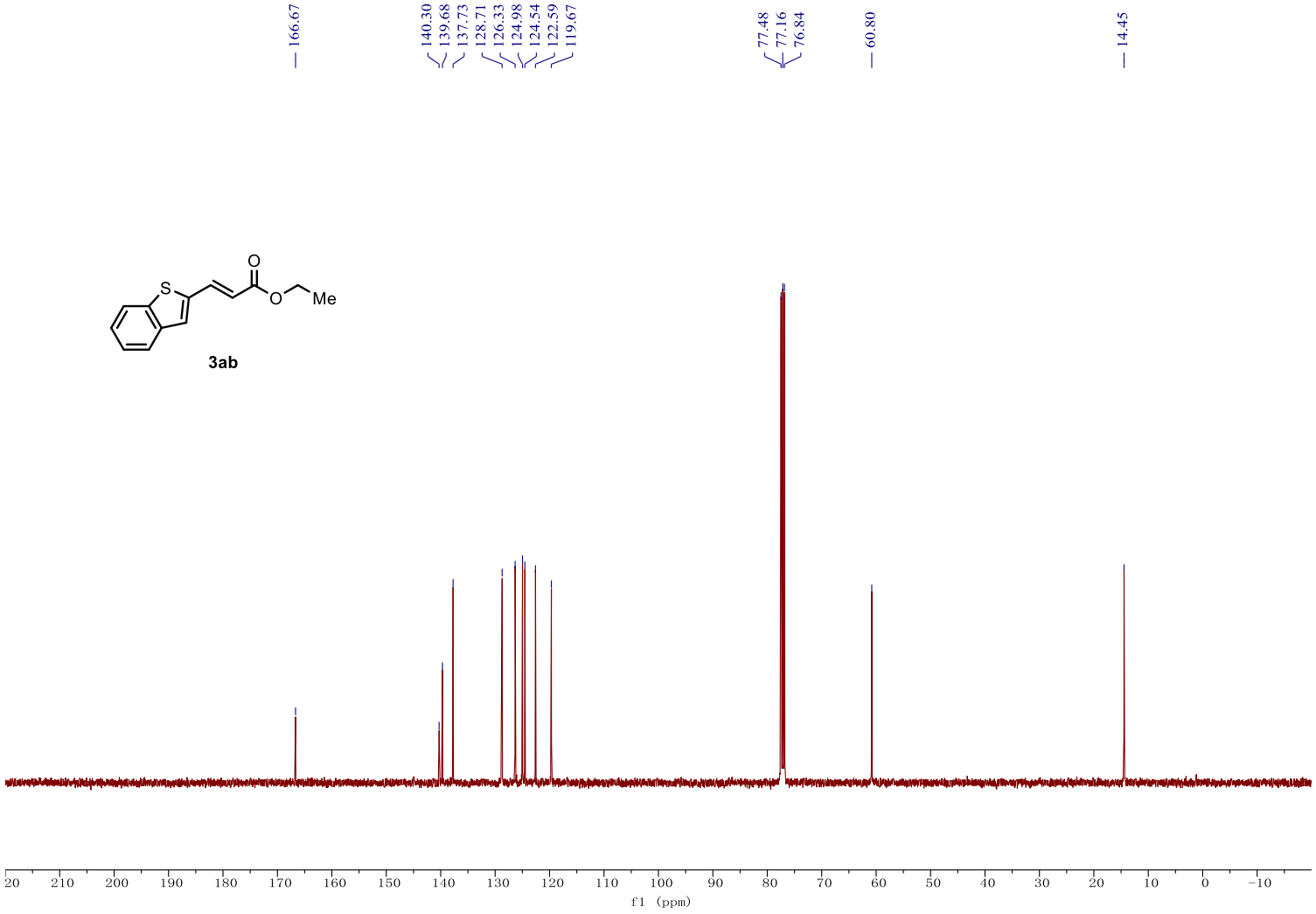

Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of *(E)*-3-benzofuran-3-yl-acrylic acid ethyl ester **(3ac)**.

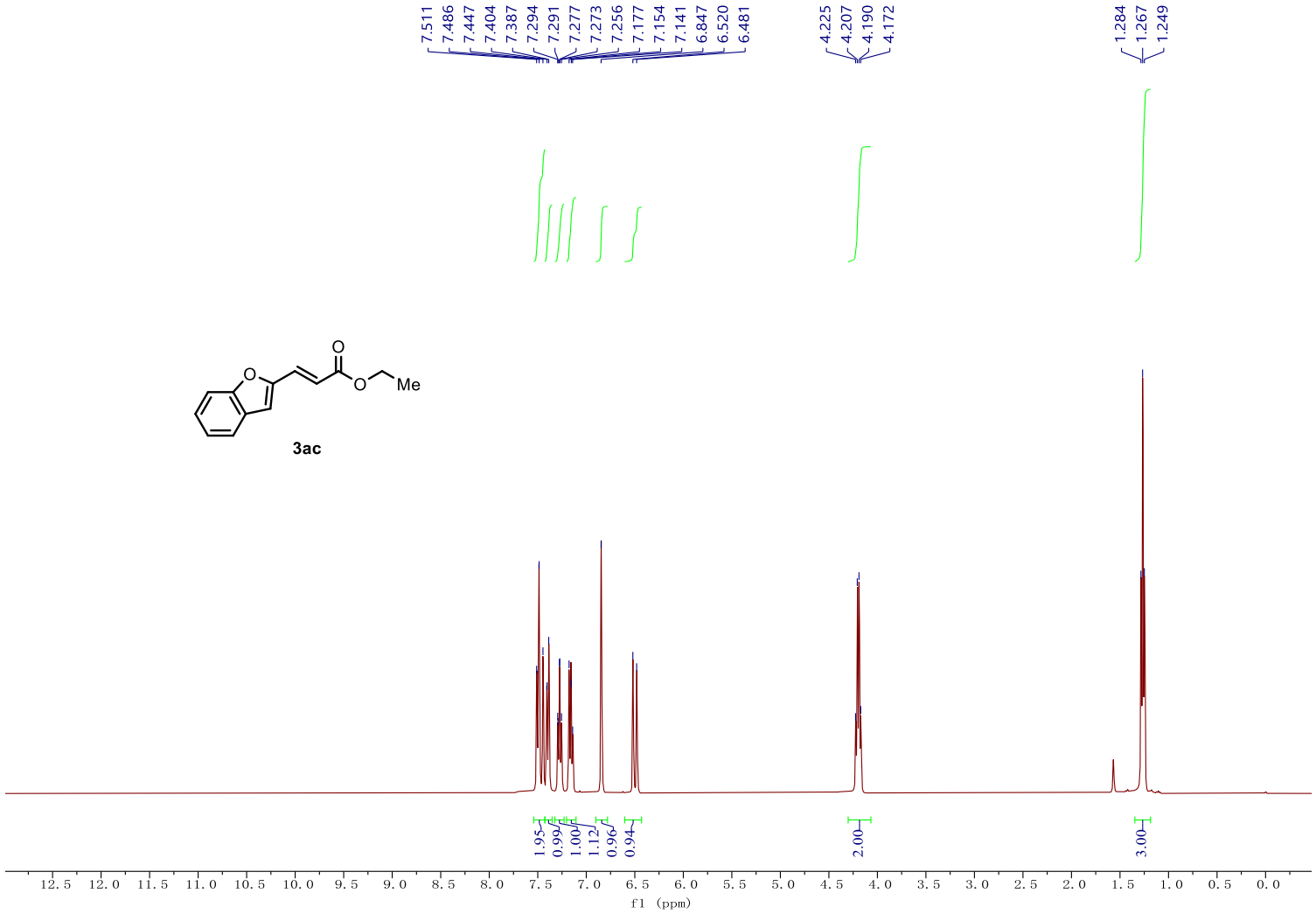

Figure S62. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of *(E)*-3-benzofuran-3-yl-acrylic acid ethyl ester **(3ac)**.

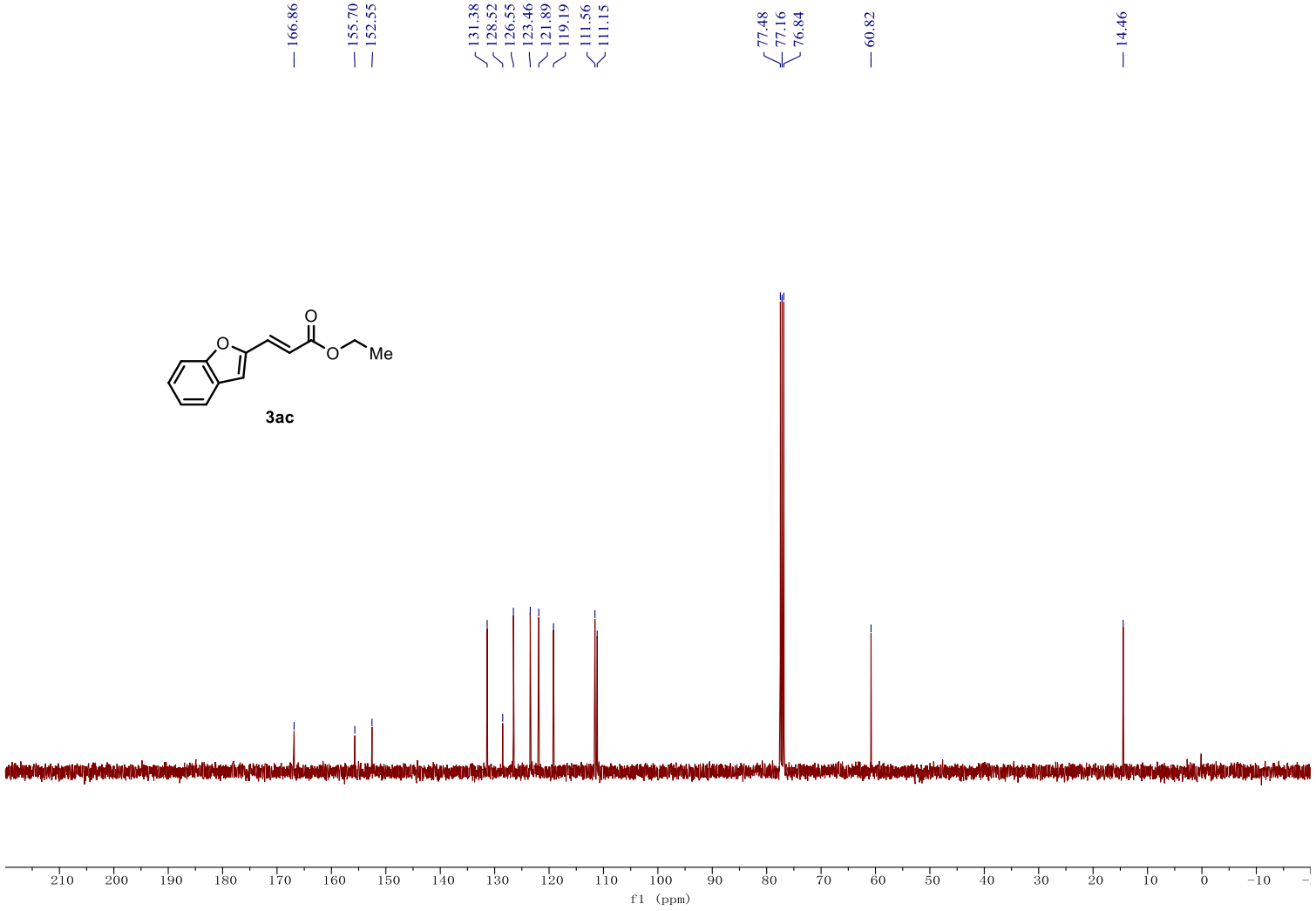

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-2-methyl-3-phenyl-2-propenoate **(3ad)**.

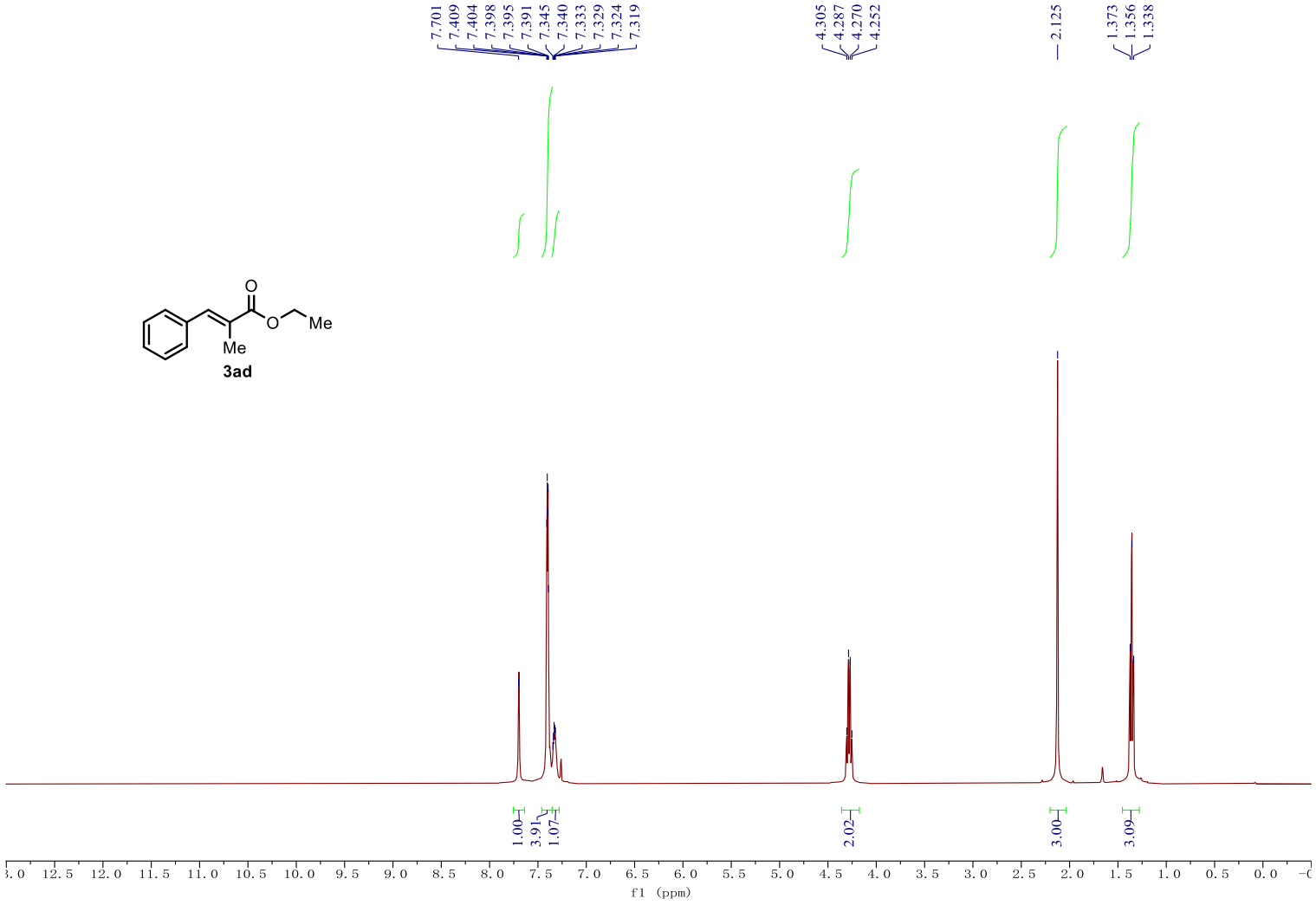

Figure S64. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-2-methyl-3-phenyl-2-propenoate **(3ad)**.

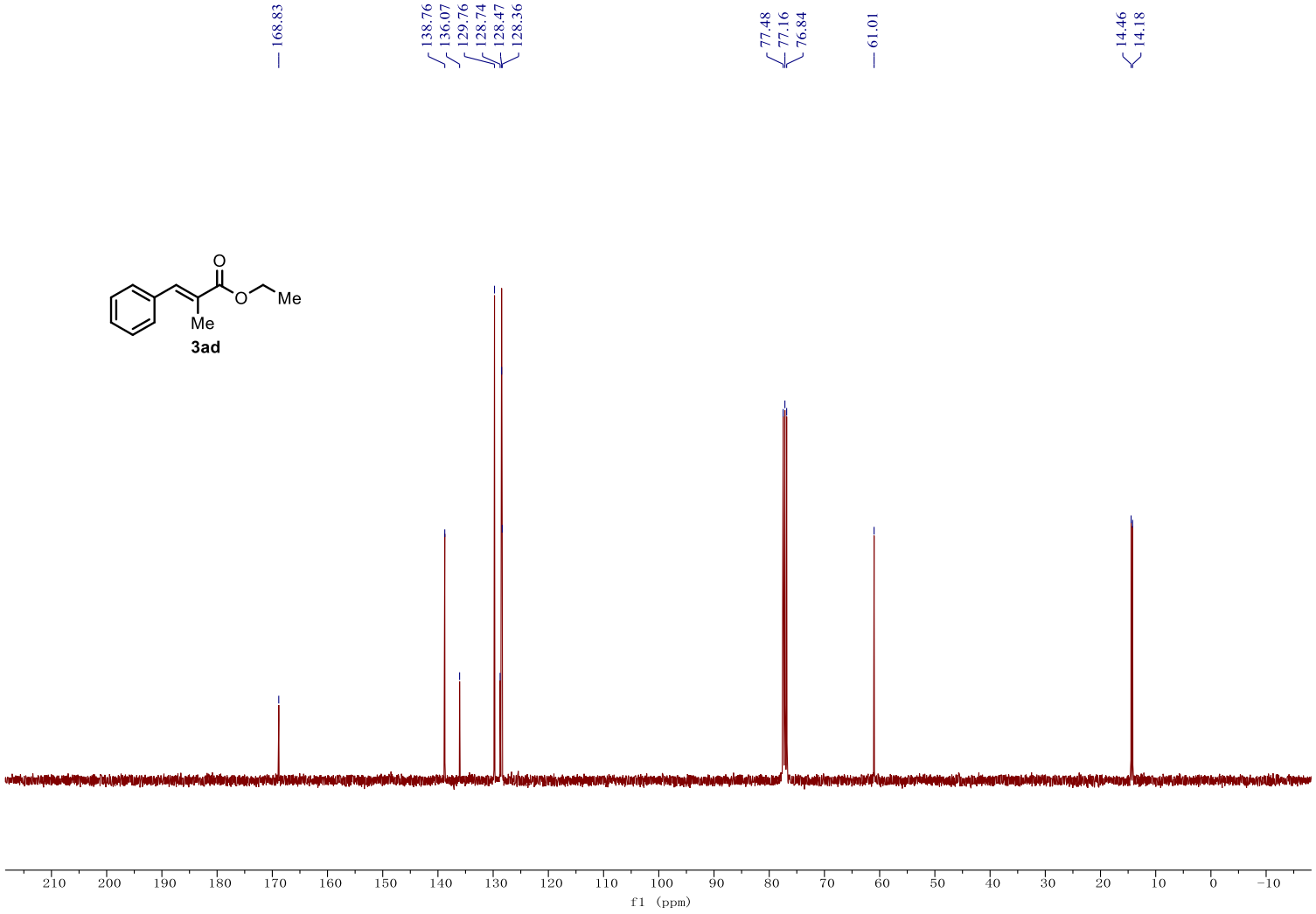

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl 3,3-diphenylacrylate **(3ae)**.

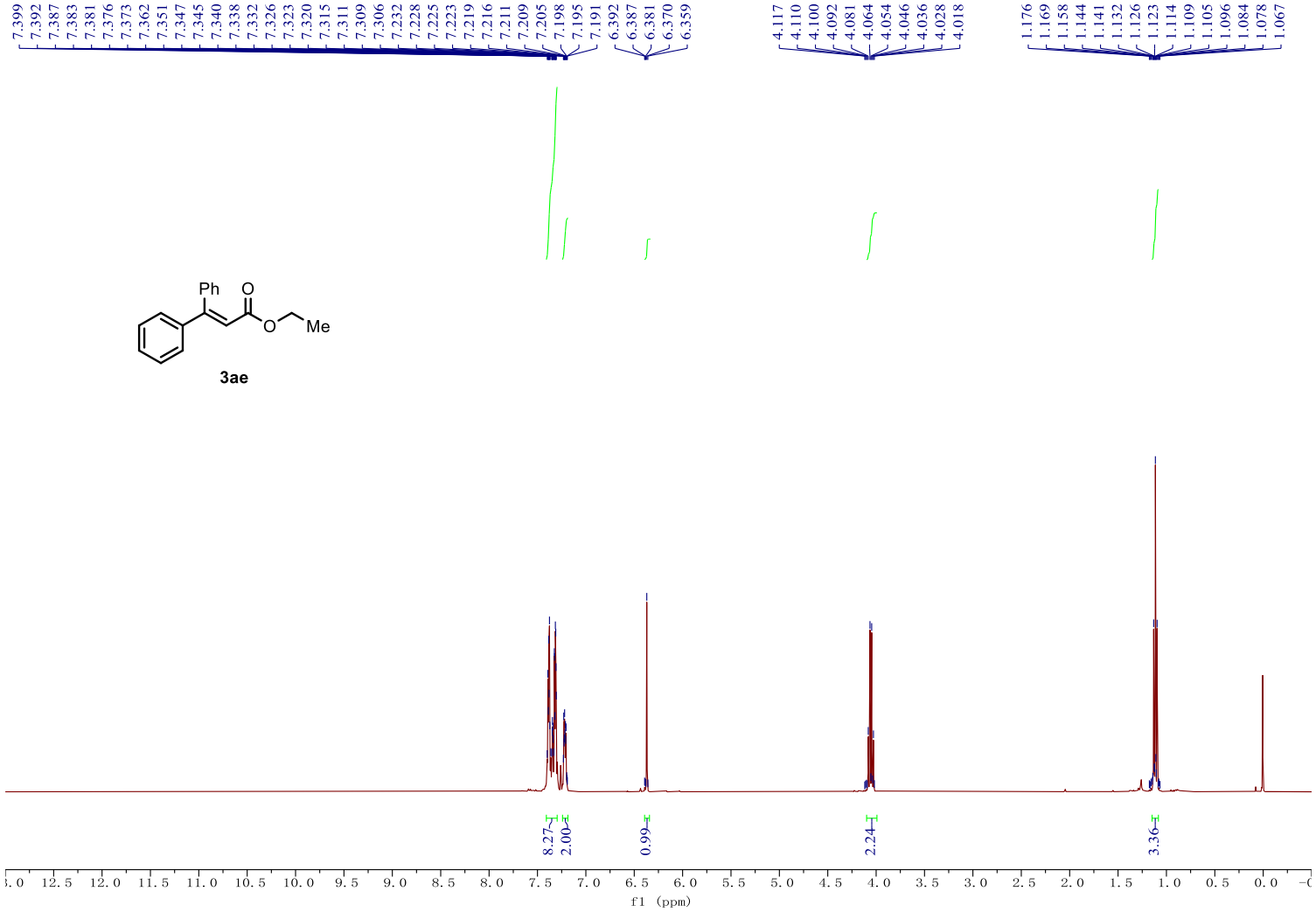

Figure S66. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl 3,3-diphenylacrylate **(3ae)**.

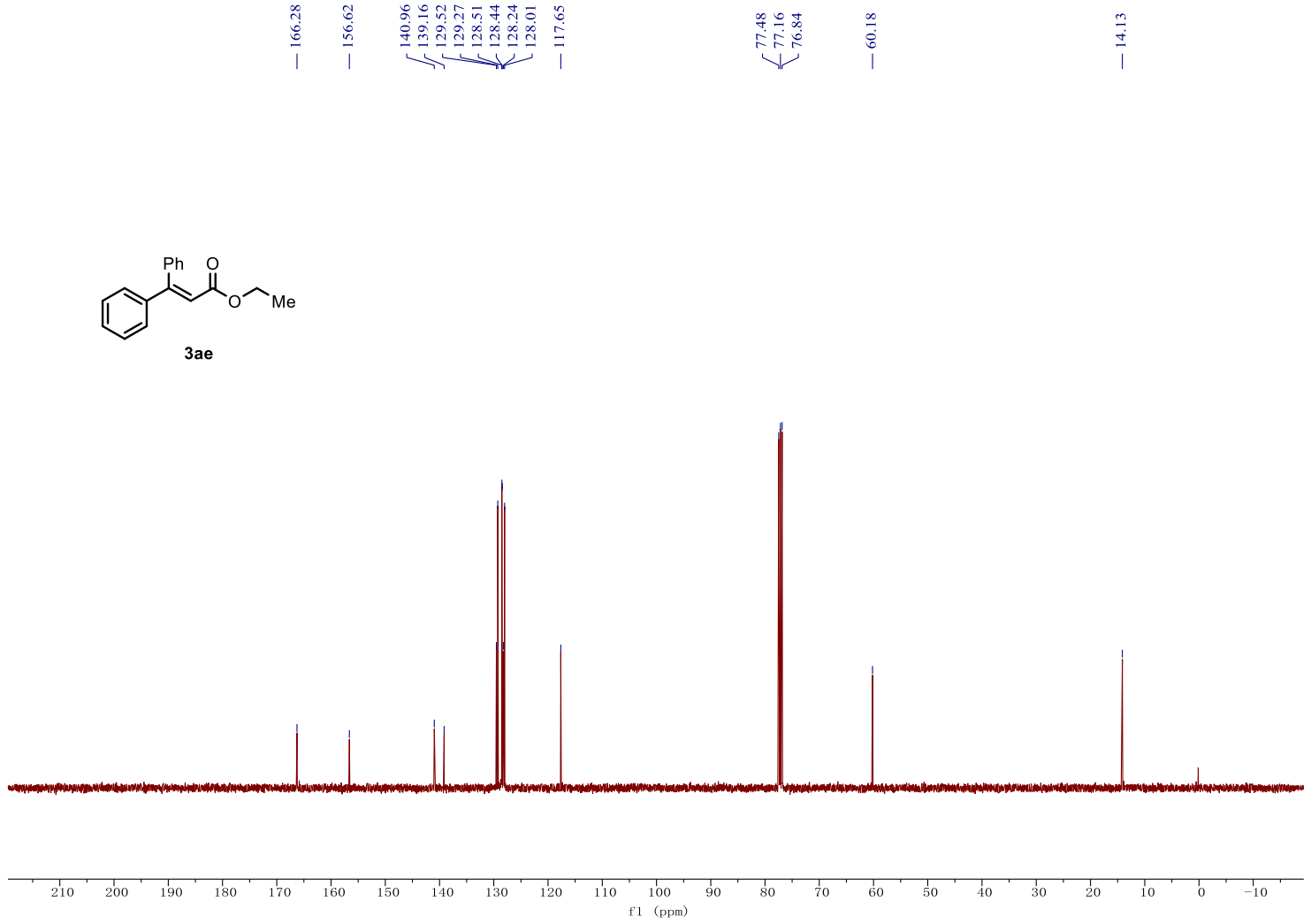

Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl (2E,4E)-5-phenyl-penta-2,4-dienoate **(3af)**.

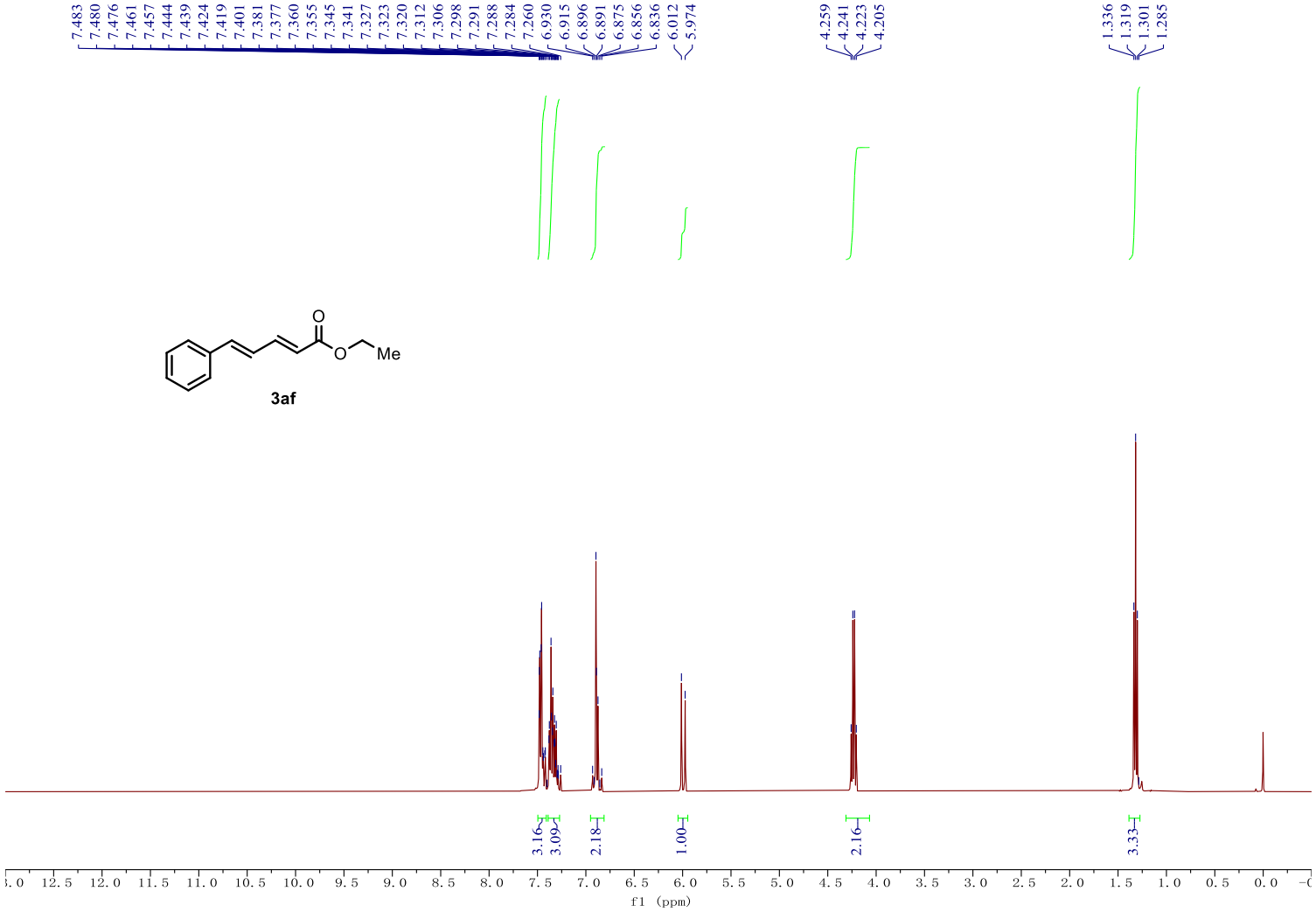

Figure S68. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl (2E,4E)-5-phenyl-penta-2,4-dienoate **(3af)**.

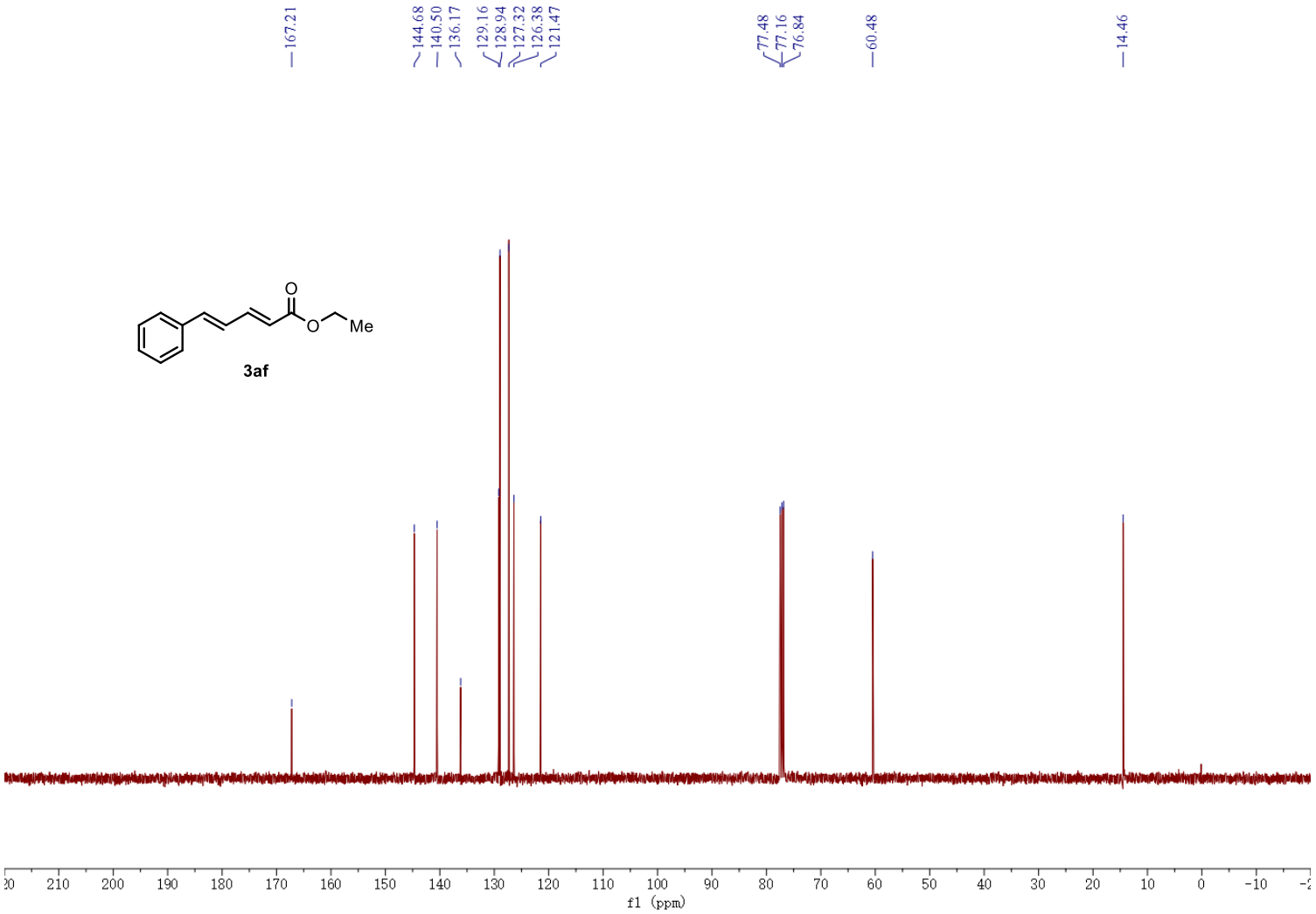

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-4-phenylbut-3-enoate **(3ag)**.

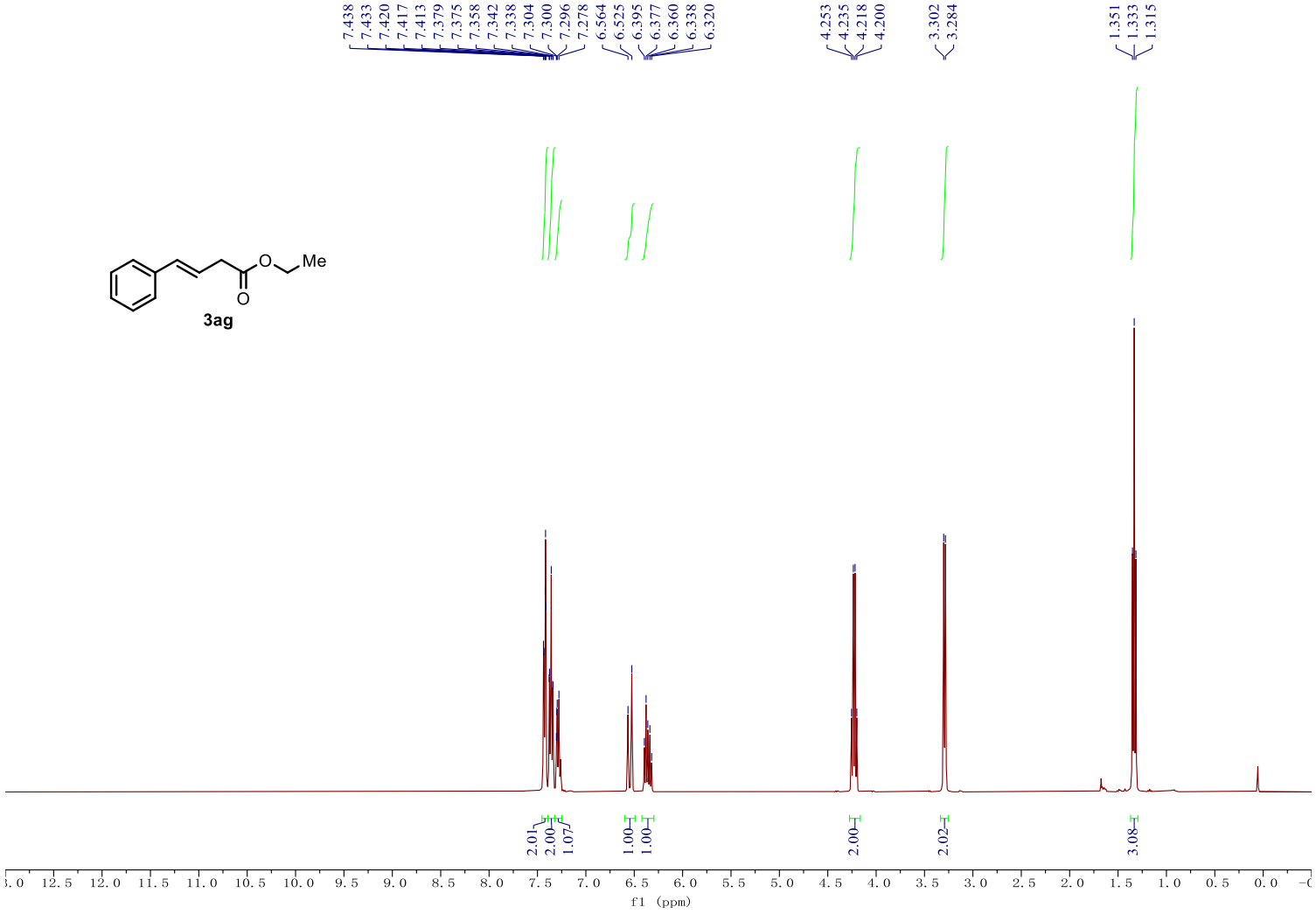

Figure S70. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of ethyl *(E)*-4-phenylbut-3-enoate **(3ag)**.

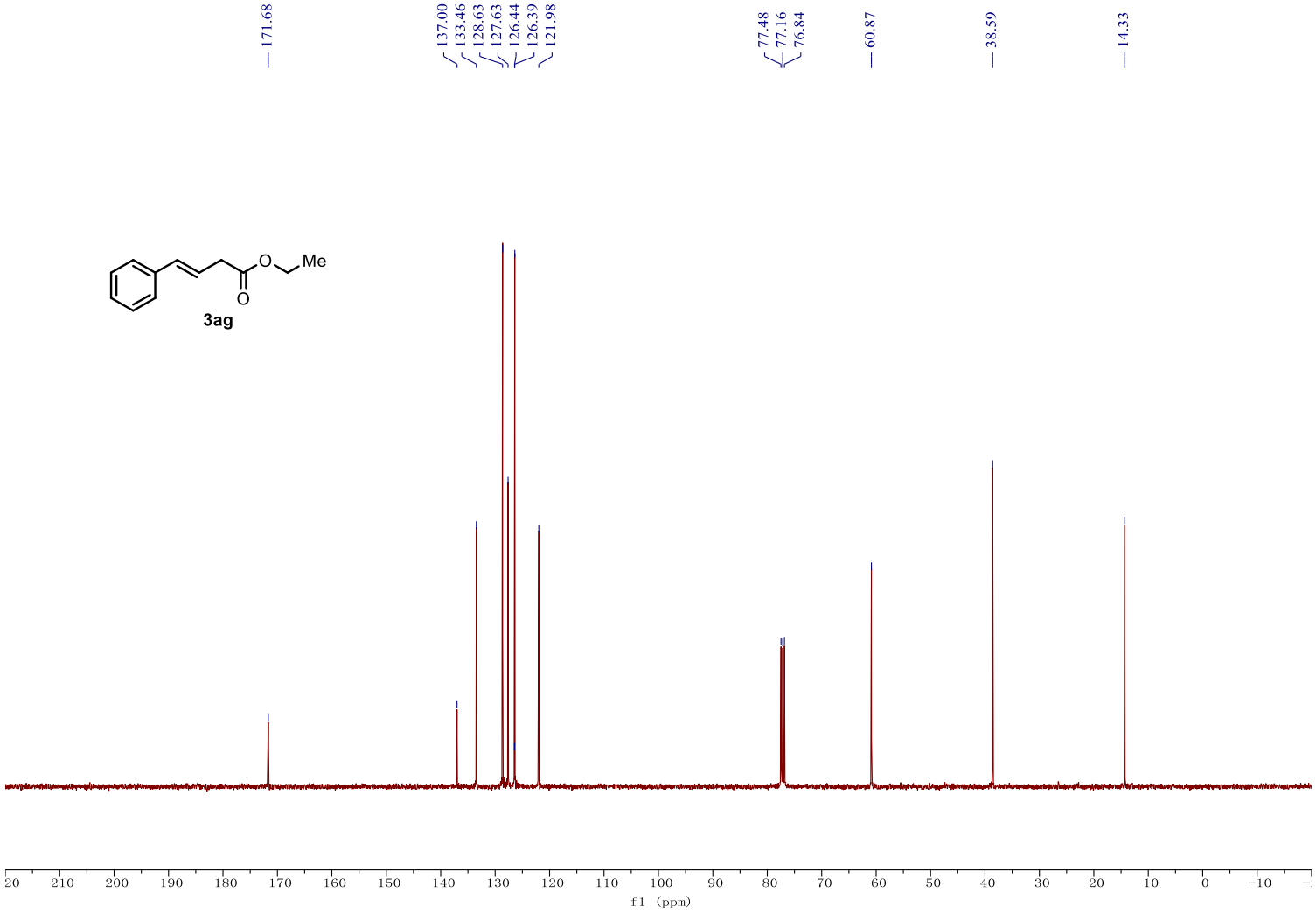

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one **(3ah)**.

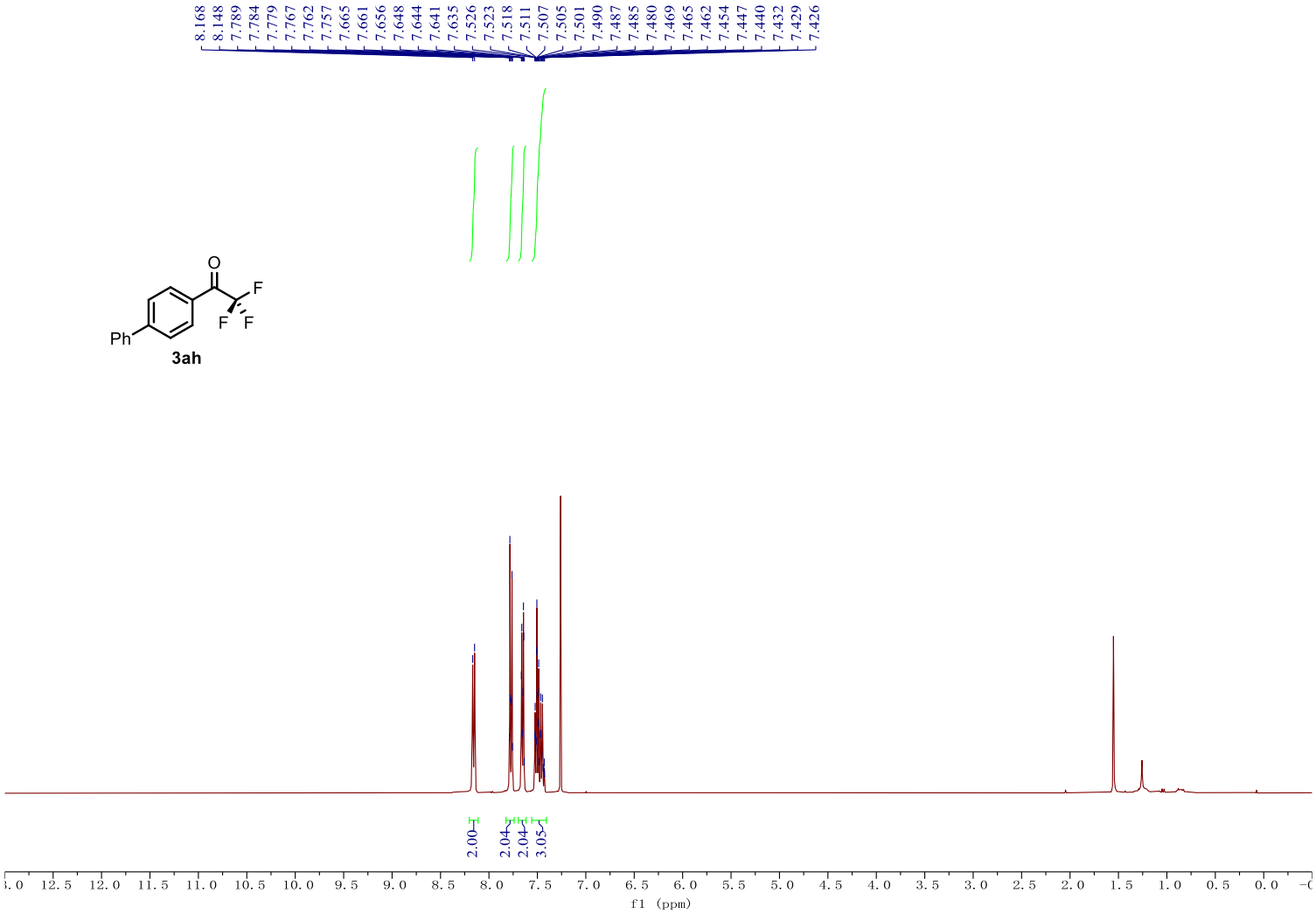

Figure S72. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one **(3ah)**.

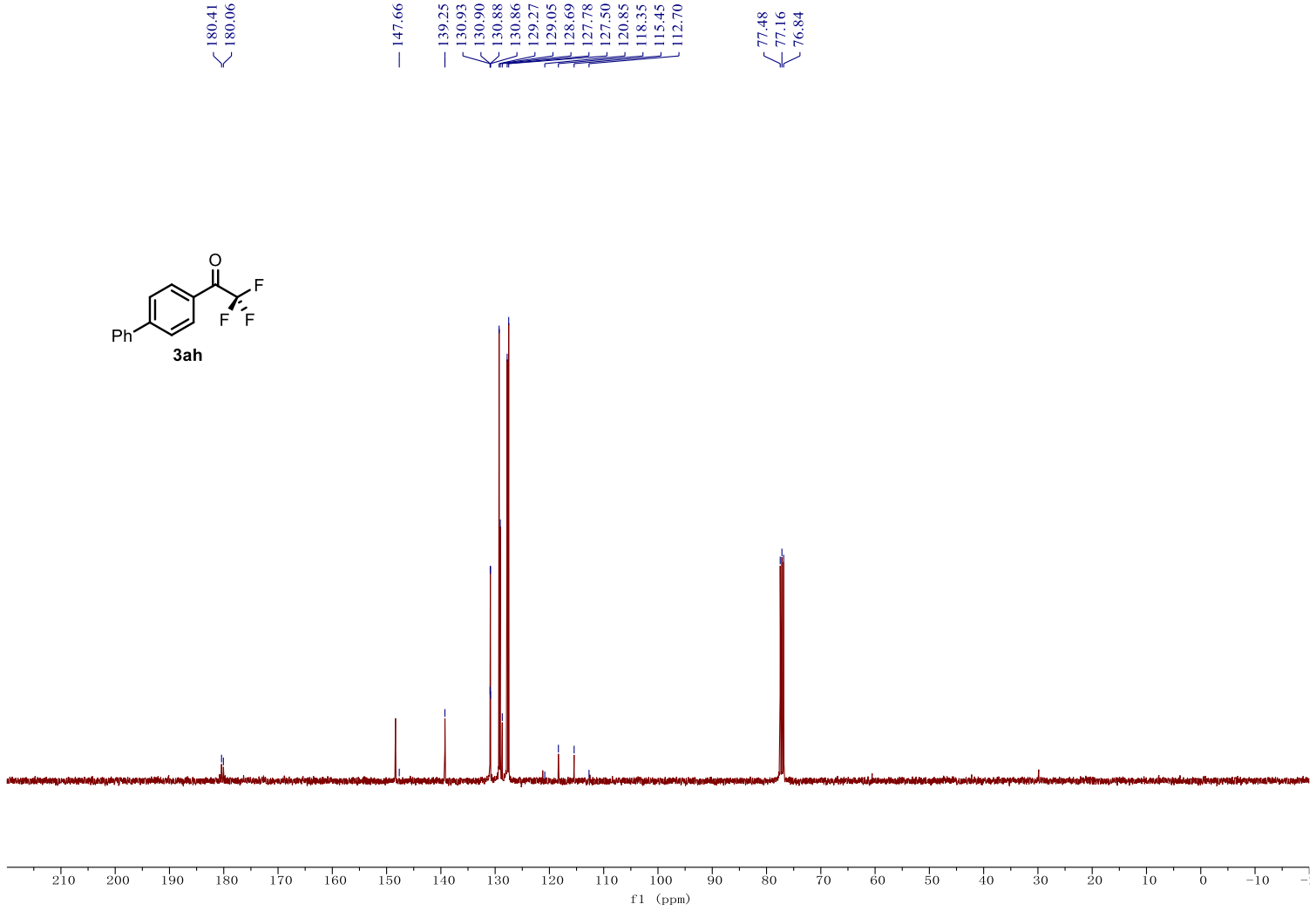

Figure S73. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one **(3ah)**

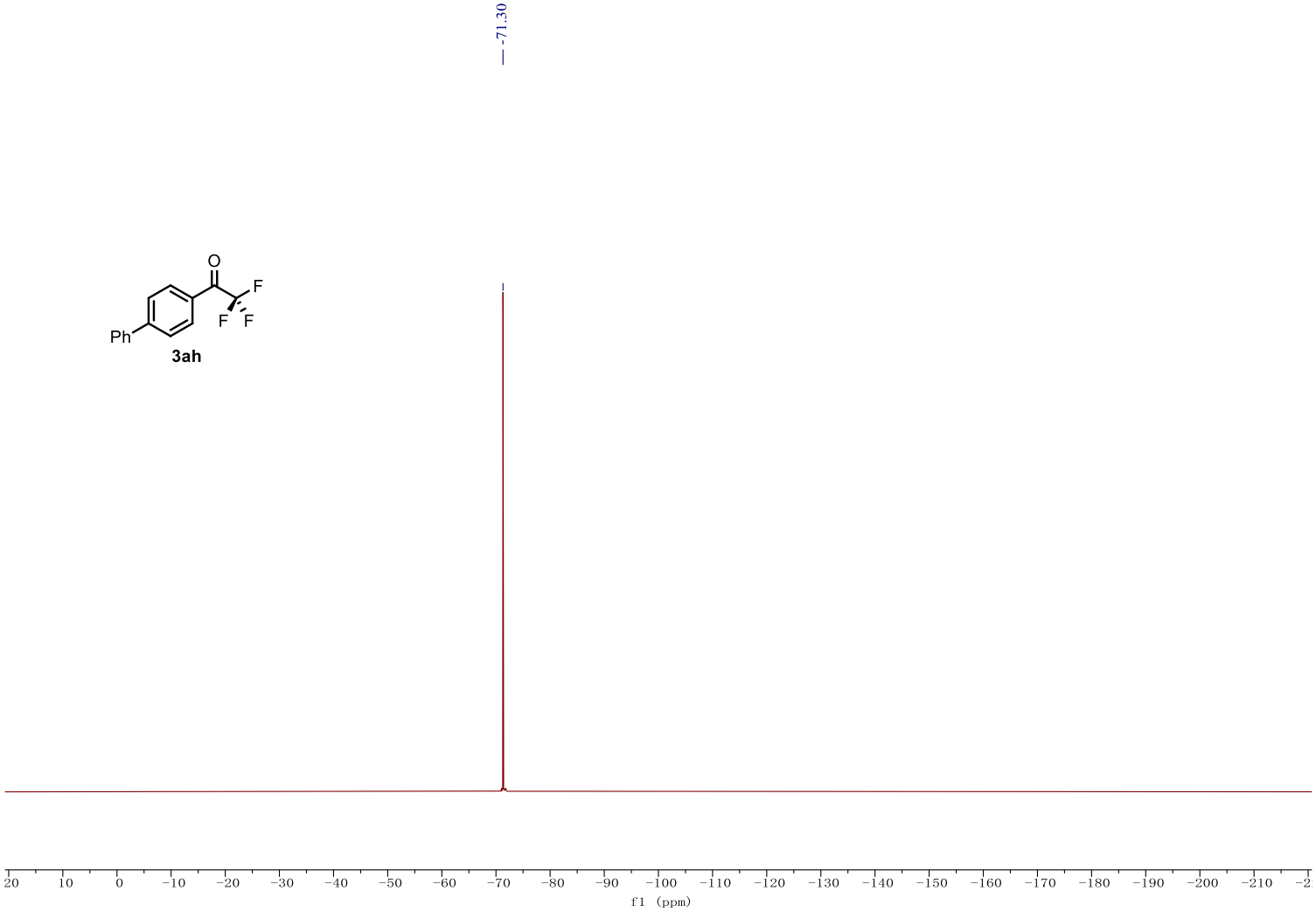

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 4'-methoxy-2,2,2-trifluoroacetophenone **(3ai)**.

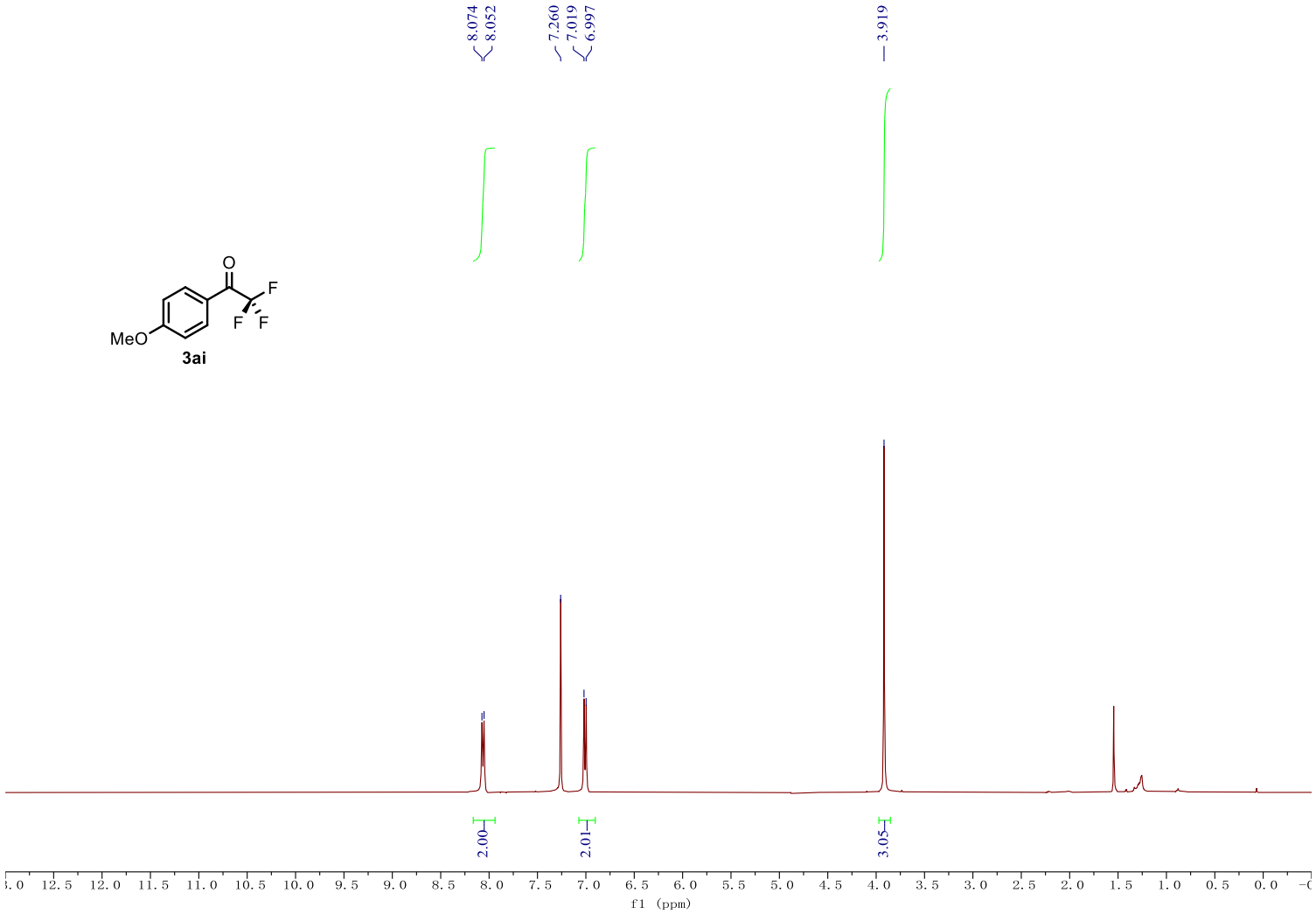

Figure S75. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 4'-methoxy-2,2,2-trifluoroacetophenone **(3ai)**.

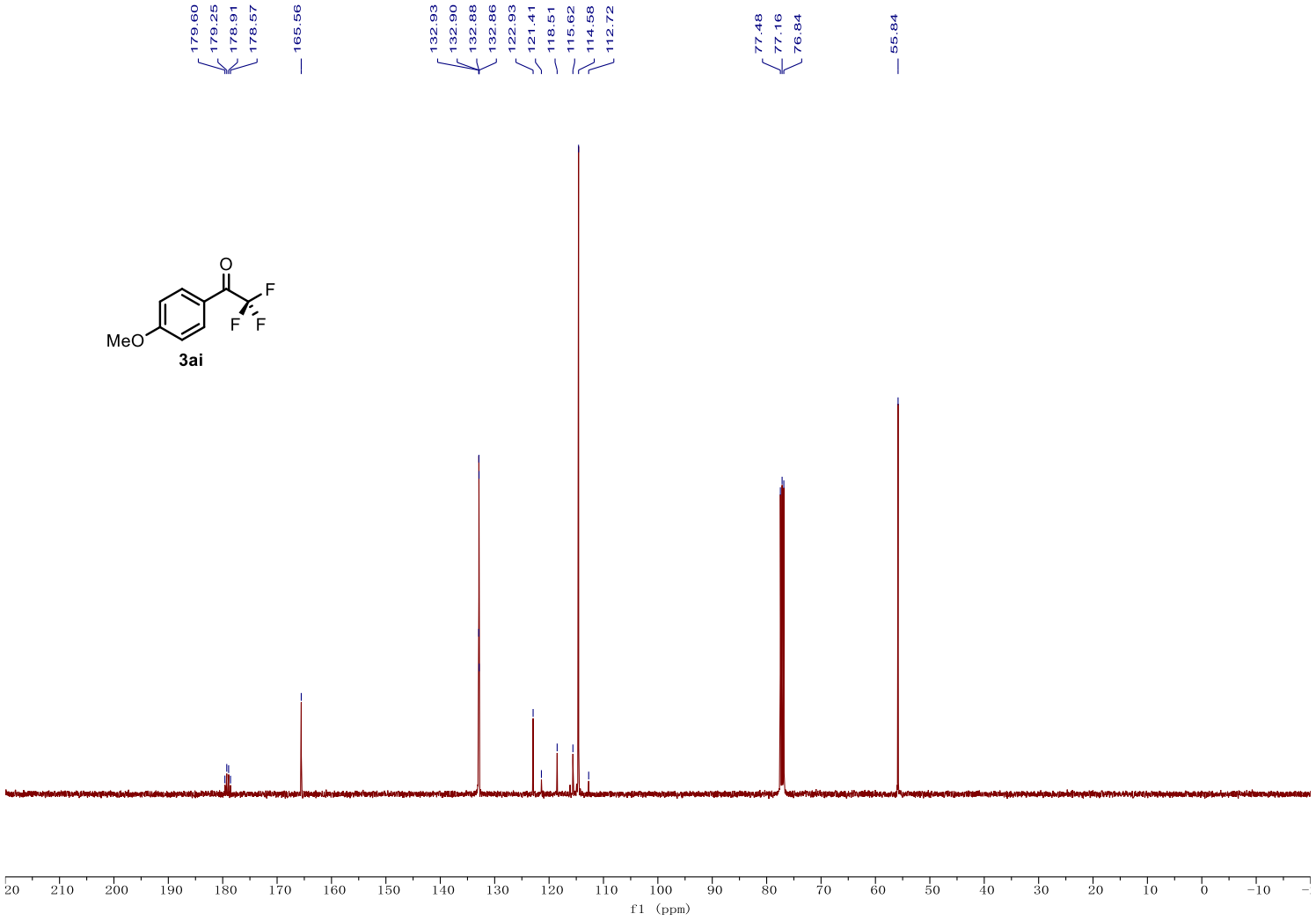

Figure S76. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of 4'-methoxy-2,2,2-trifluoroacetophenone **(3ai)**

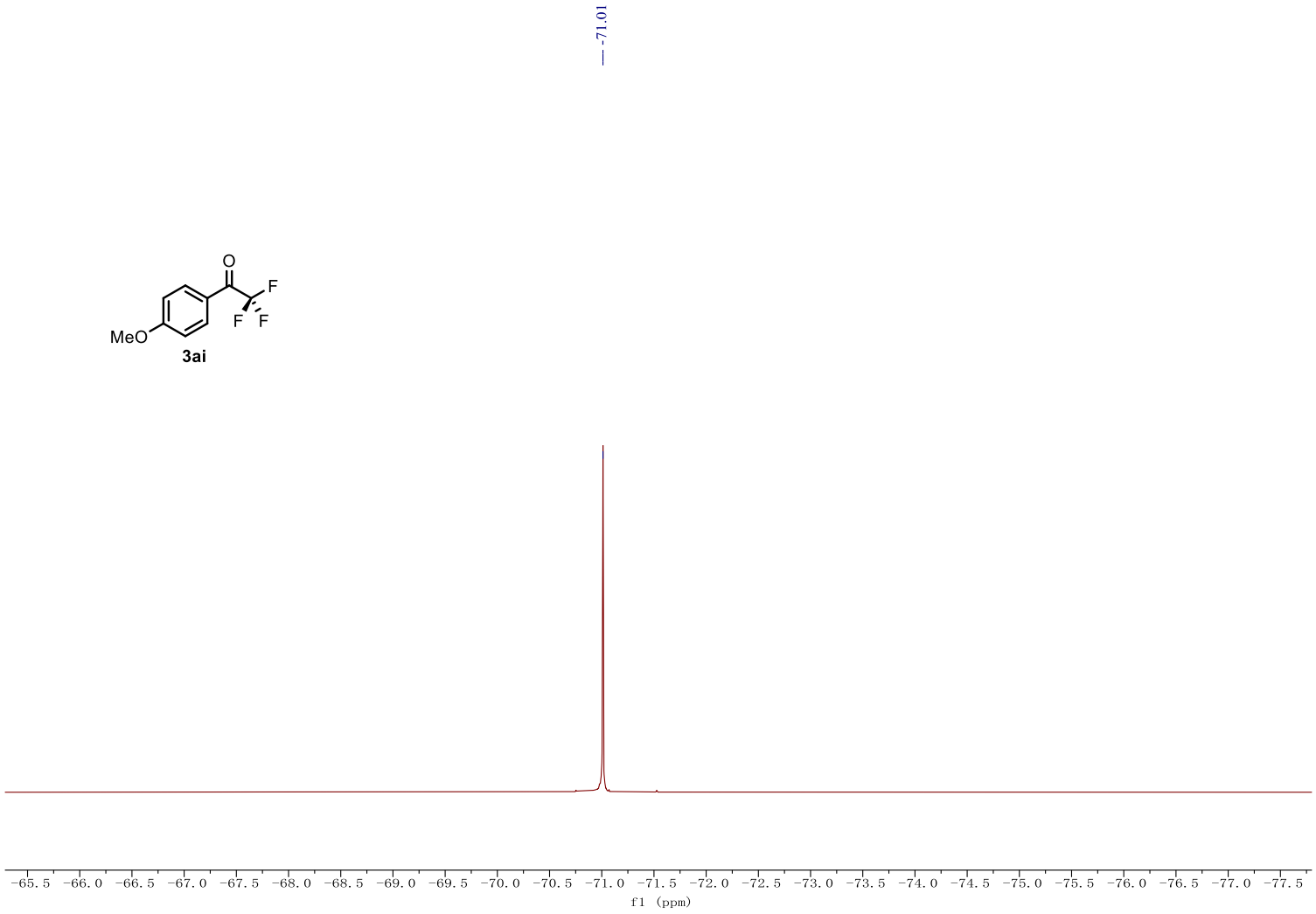

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 1-[1,1'-Biphenyl]-4-yl-2,2,3,3,4,4,4-heptafluoro-1-butanone **(3aj)**.

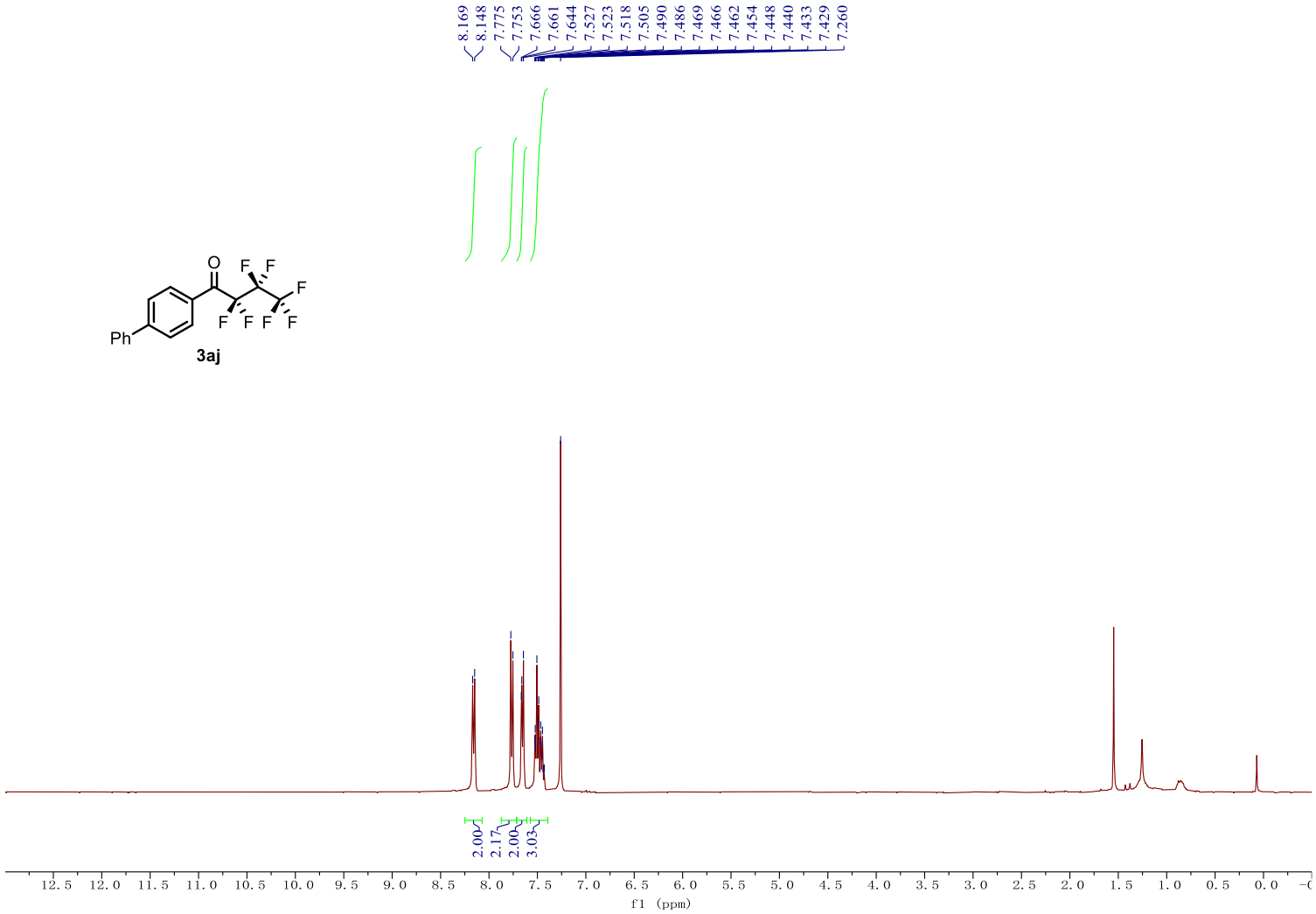

Figure S78. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 1-[1,1'-Biphenyl]-4-yl-2,2,3,3,4,4,4-heptafluoro-1-butanone **(3aj)**.

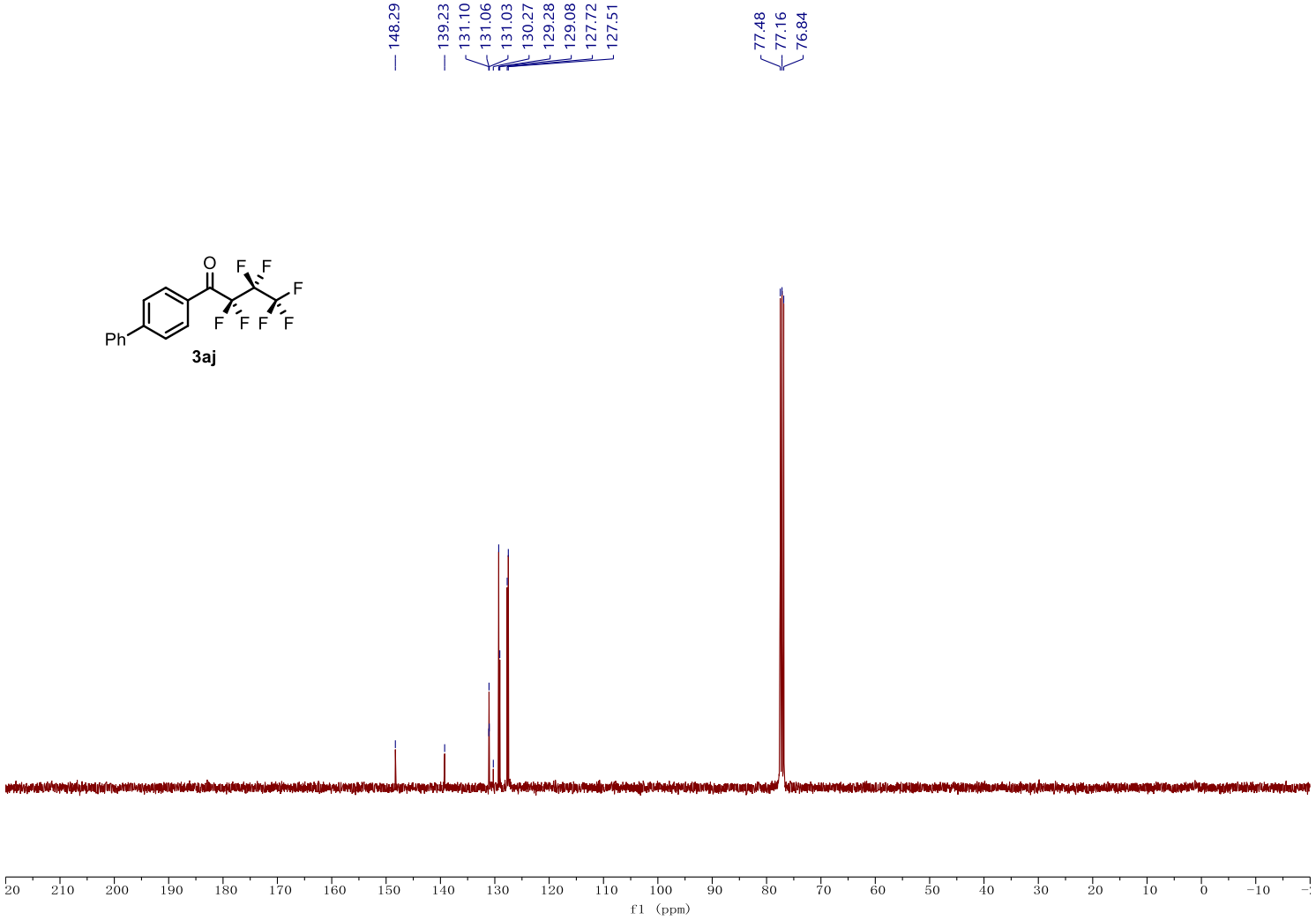

Figure S79. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of 1-[1,1'-Biphenyl]-4-yl-2,2,3,3,4,4,4-heptafluoro-1-butanone **(3aj)**

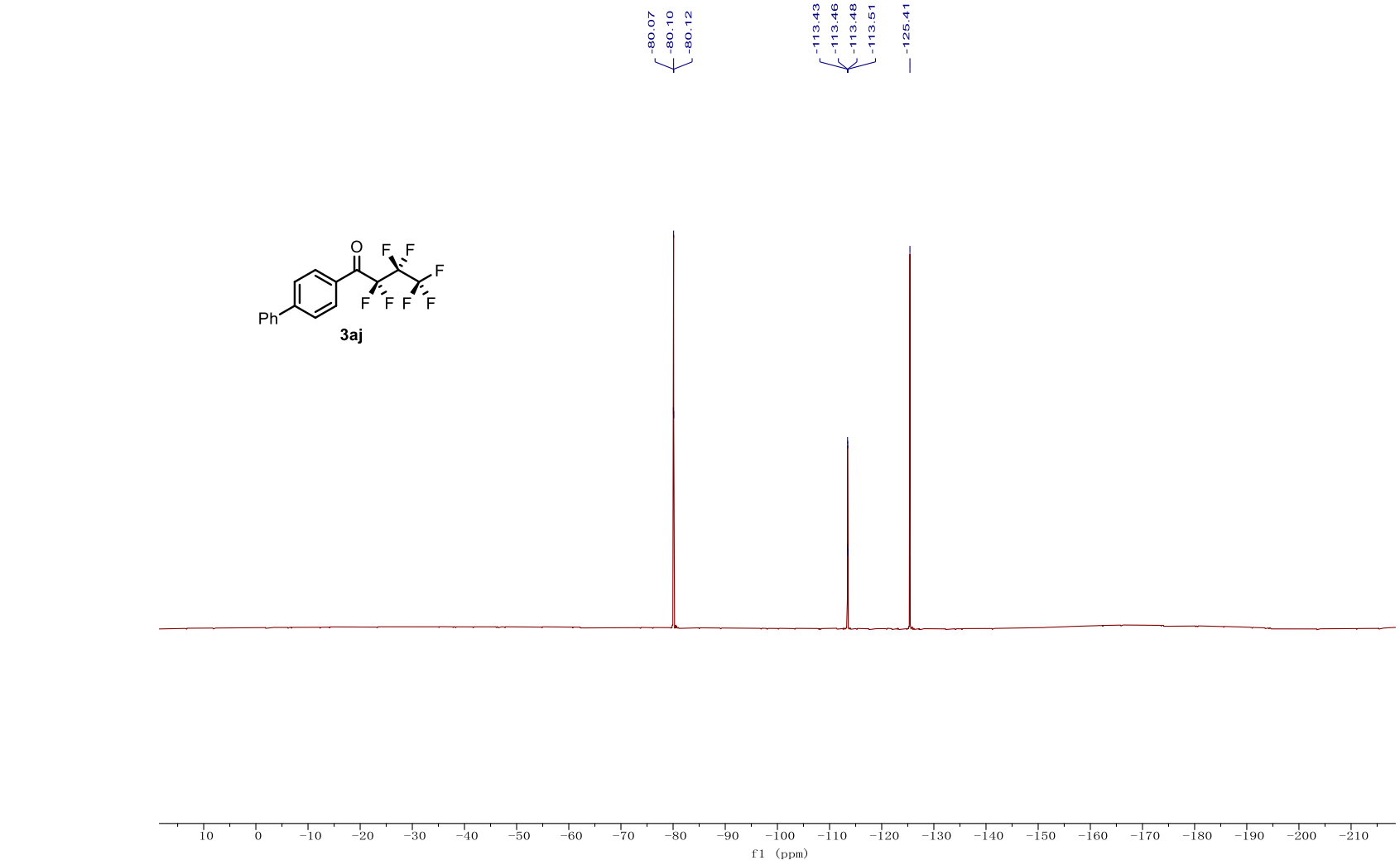

Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of heptafluoro-1-(4-methoxyphenyl)butan-1-one **(3ak)**.

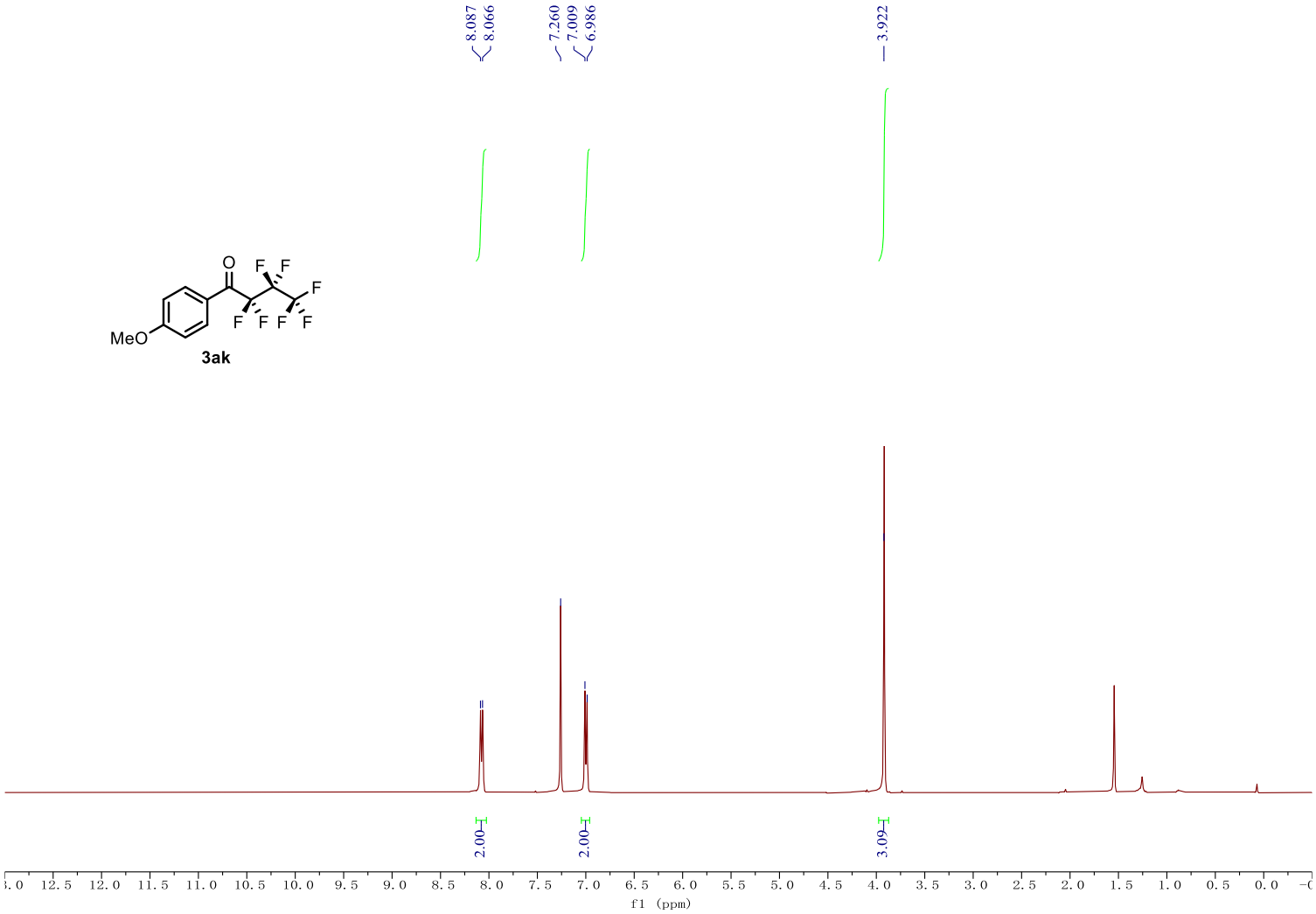

Figure S81. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of heptafluoro-1-(4-methoxyphenyl)butan-1-one **(3ak)**.

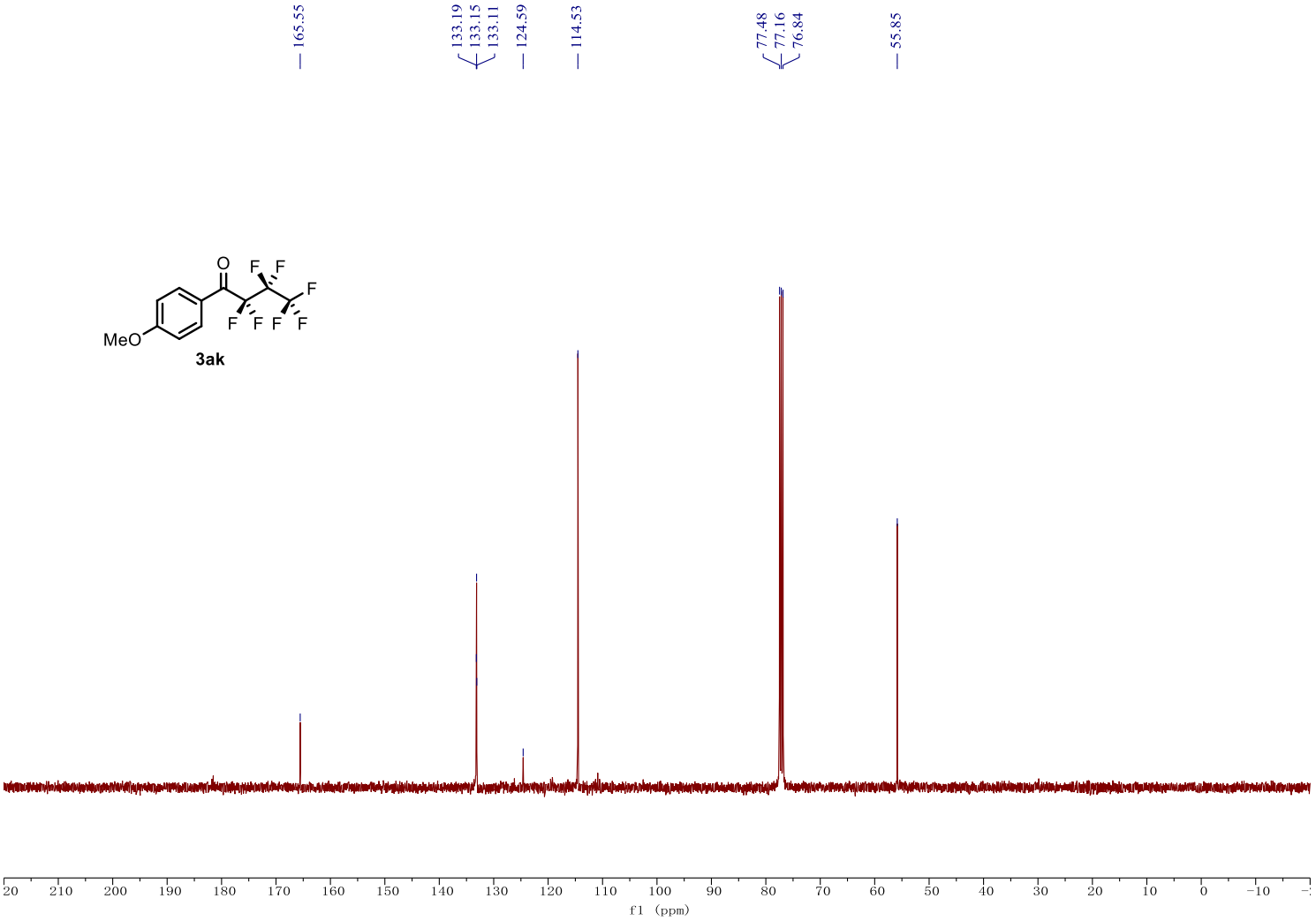

Figure S82. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K) of heptafluoro-1-(4-methoxyphenyl)butan-1-one **(3ak)**

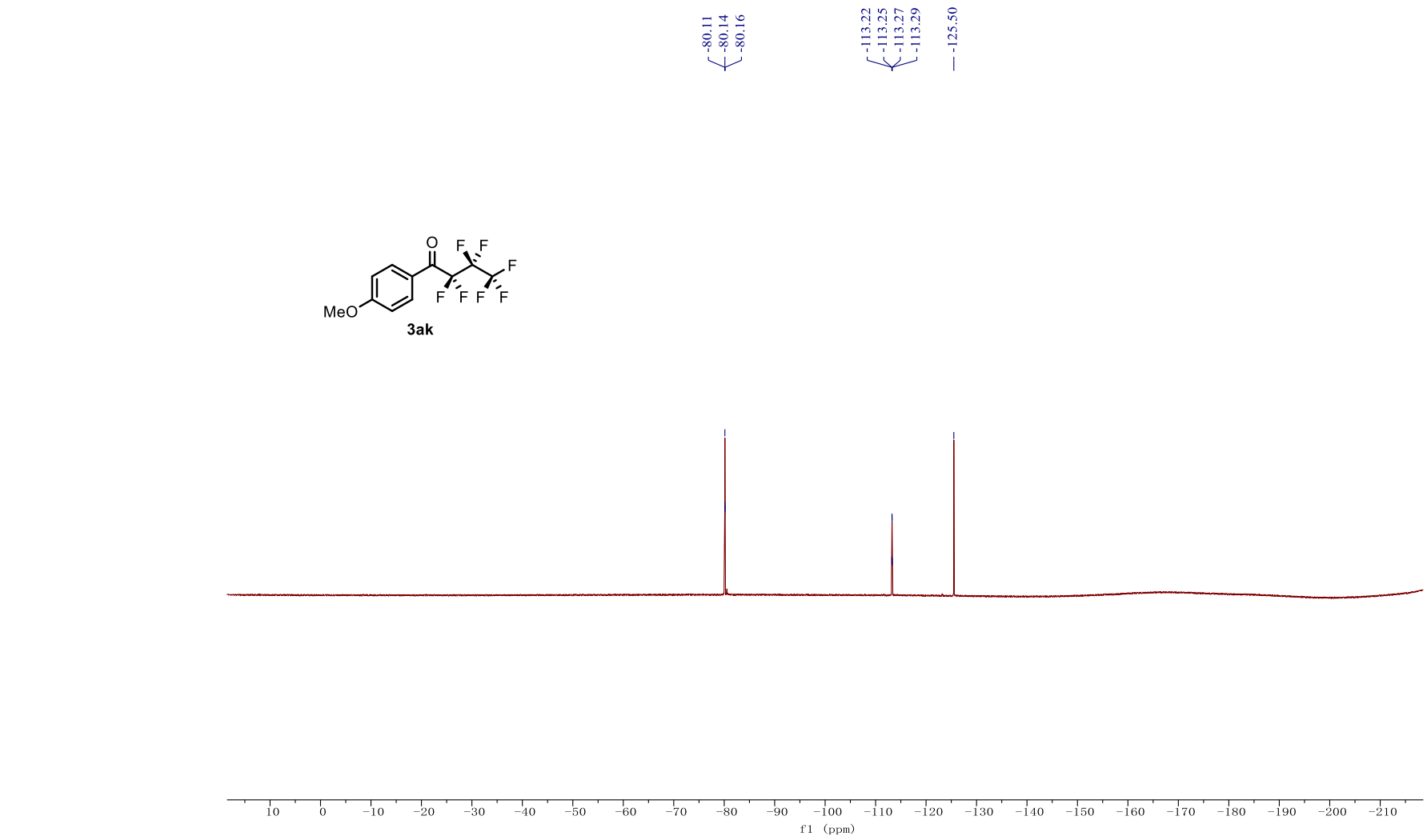

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of methyl cinnamate **(3al)**.

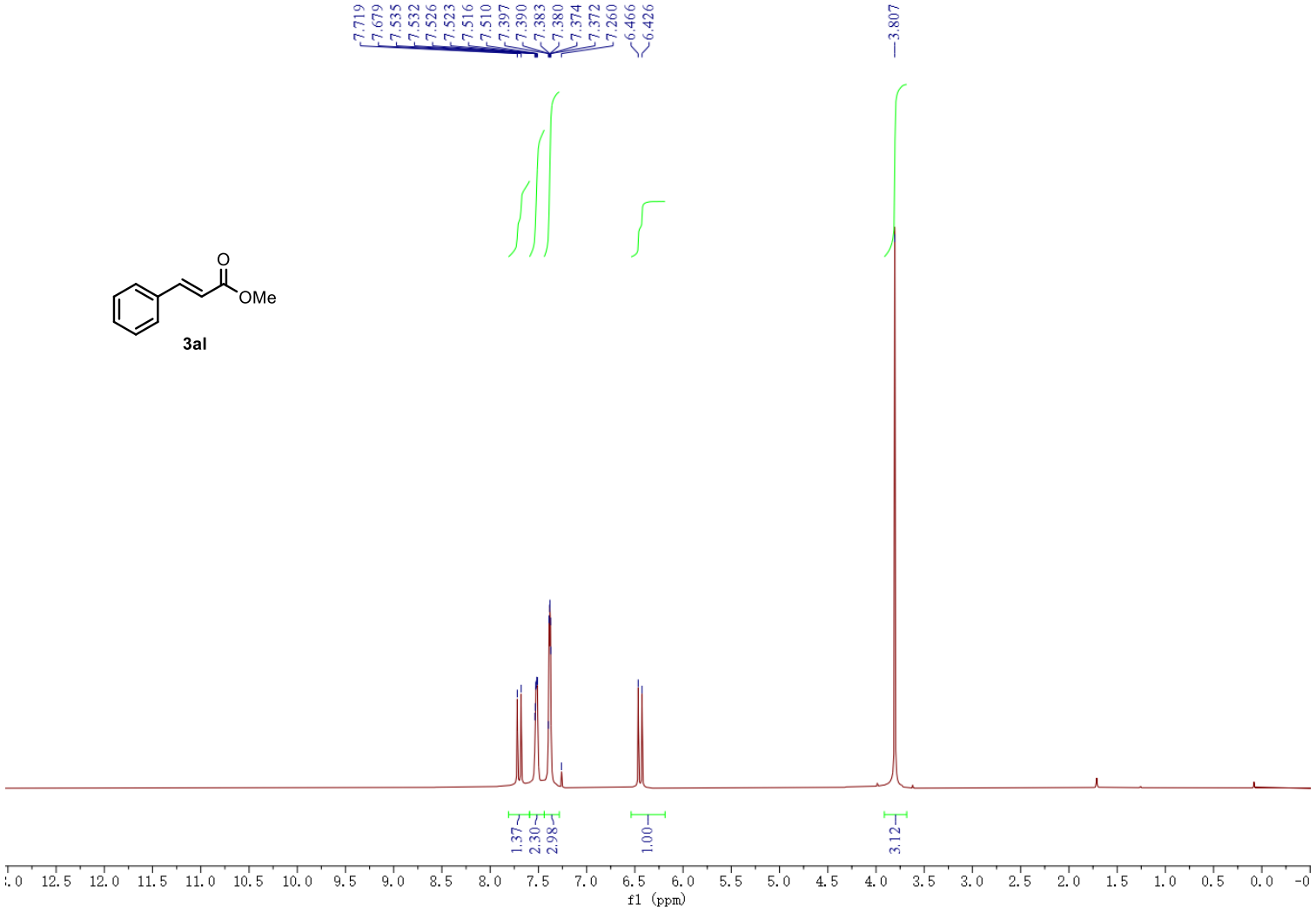

Figure S84. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of methyl cinnamate **(3al)**.

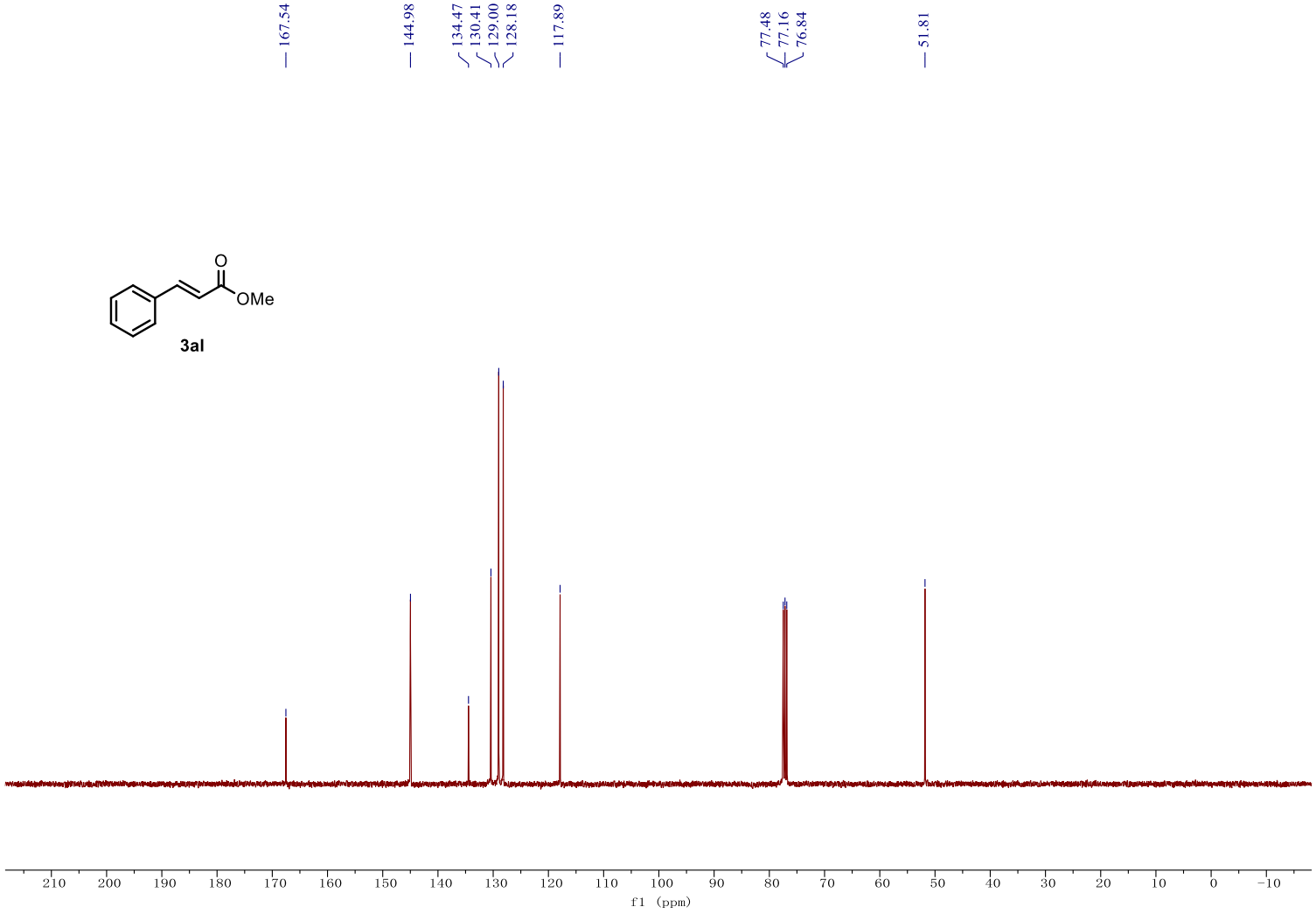

Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of Propyl cinnamate **(3am)**.

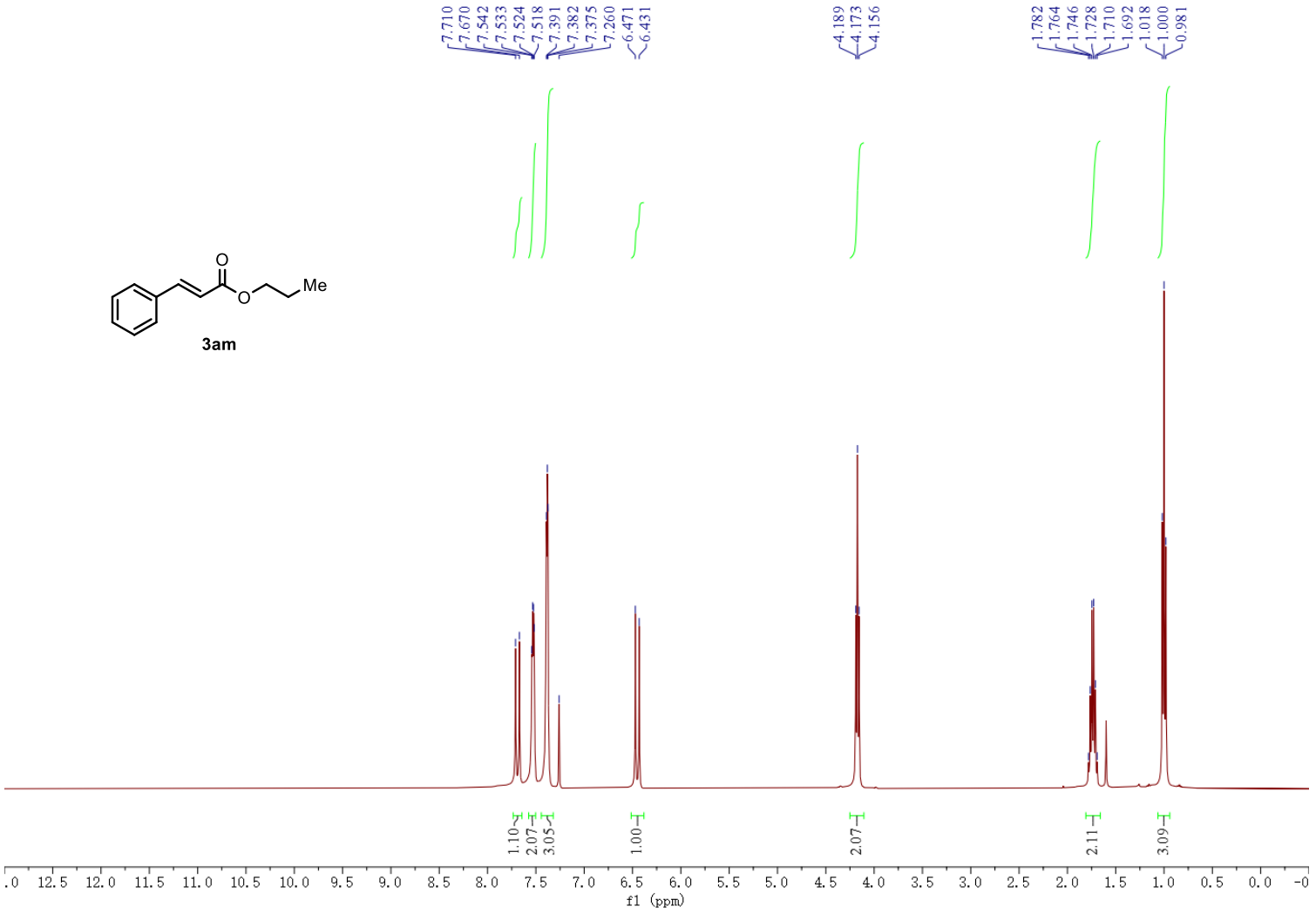

Figure S86. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of Propyl cinnamate **(3am)**.

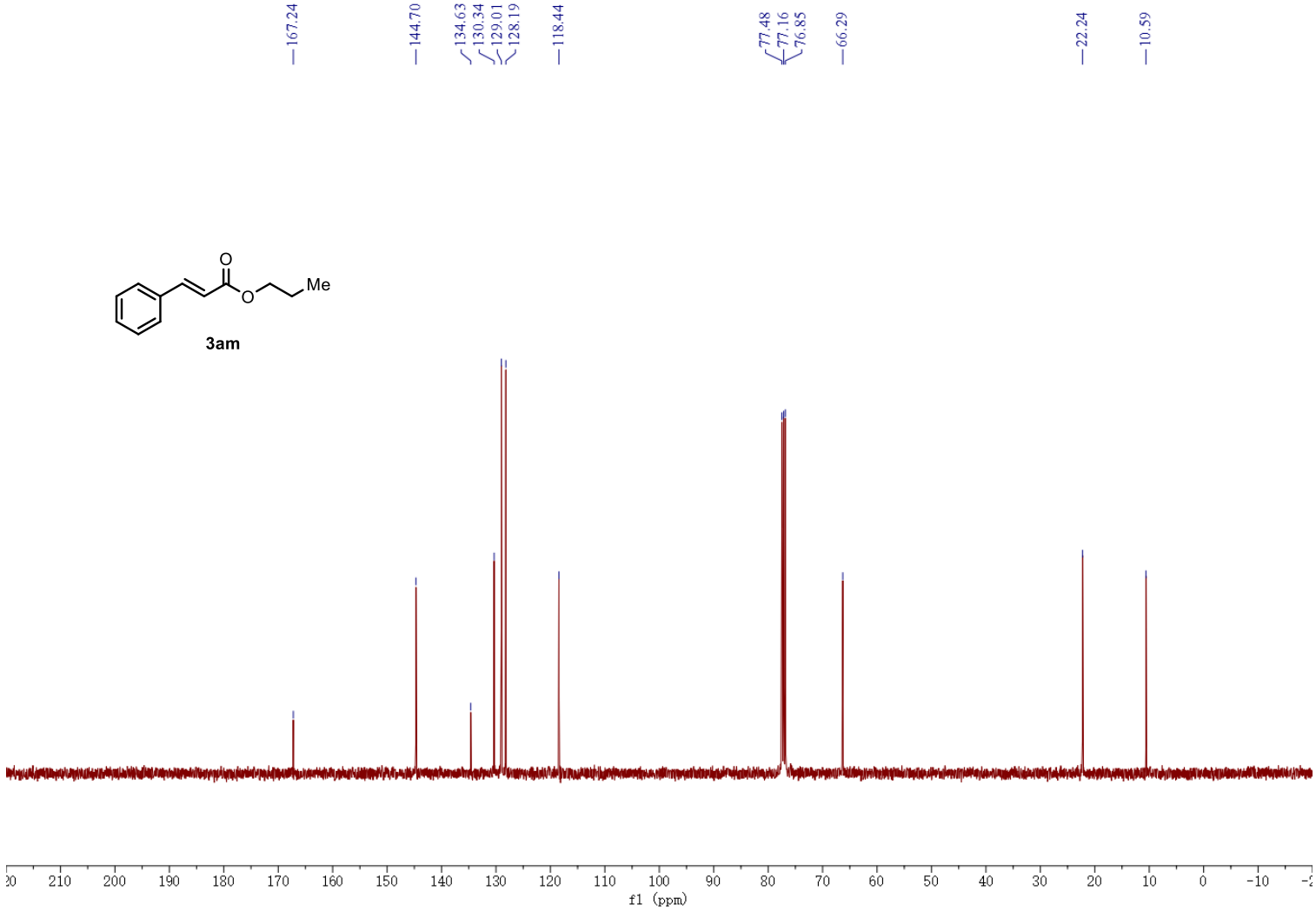

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of *(E)*-isopropyl cinnamate **(3an)**.

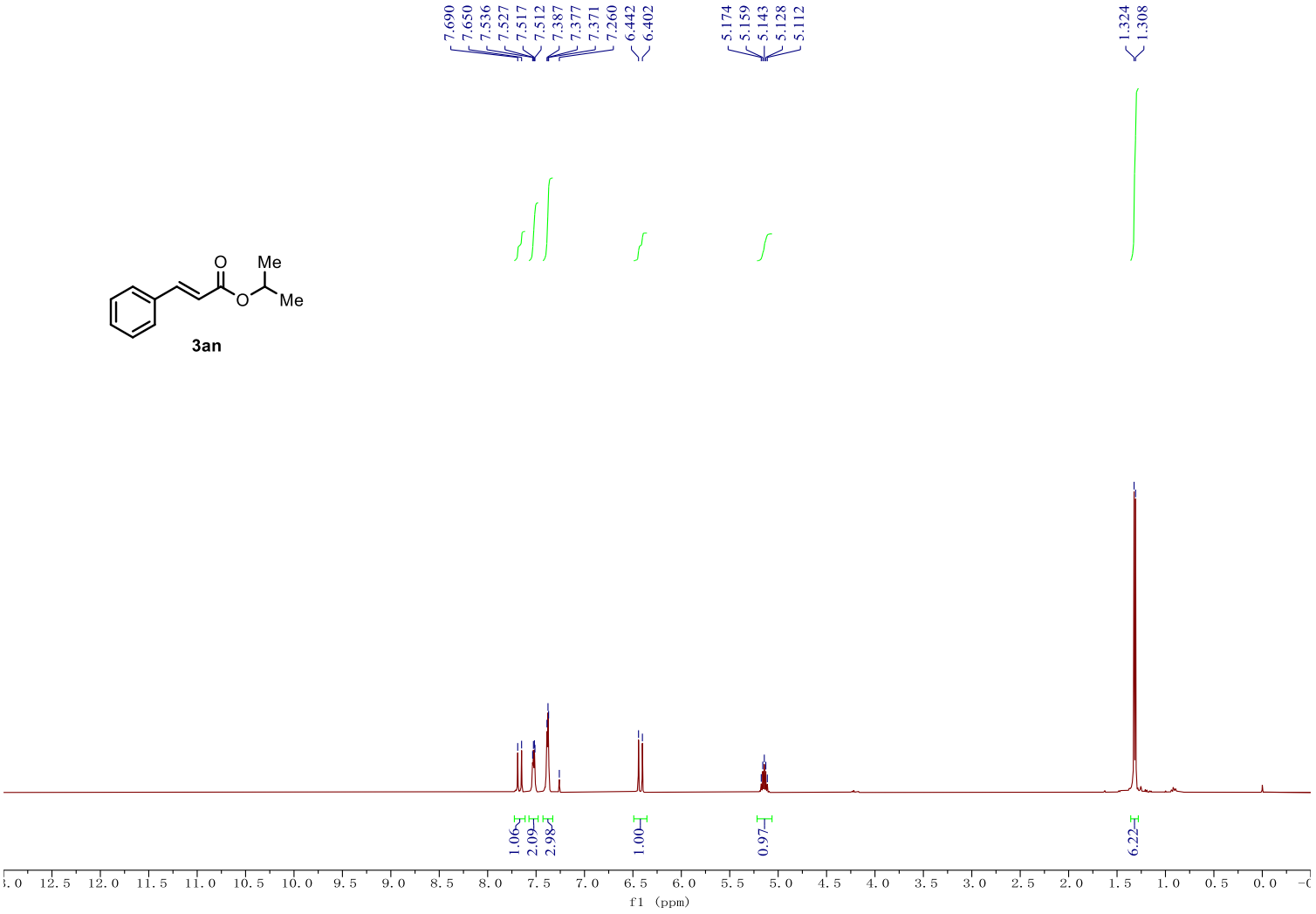

Figure S88. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of *(E)*-isopropyl cinnamate **(3an)**.

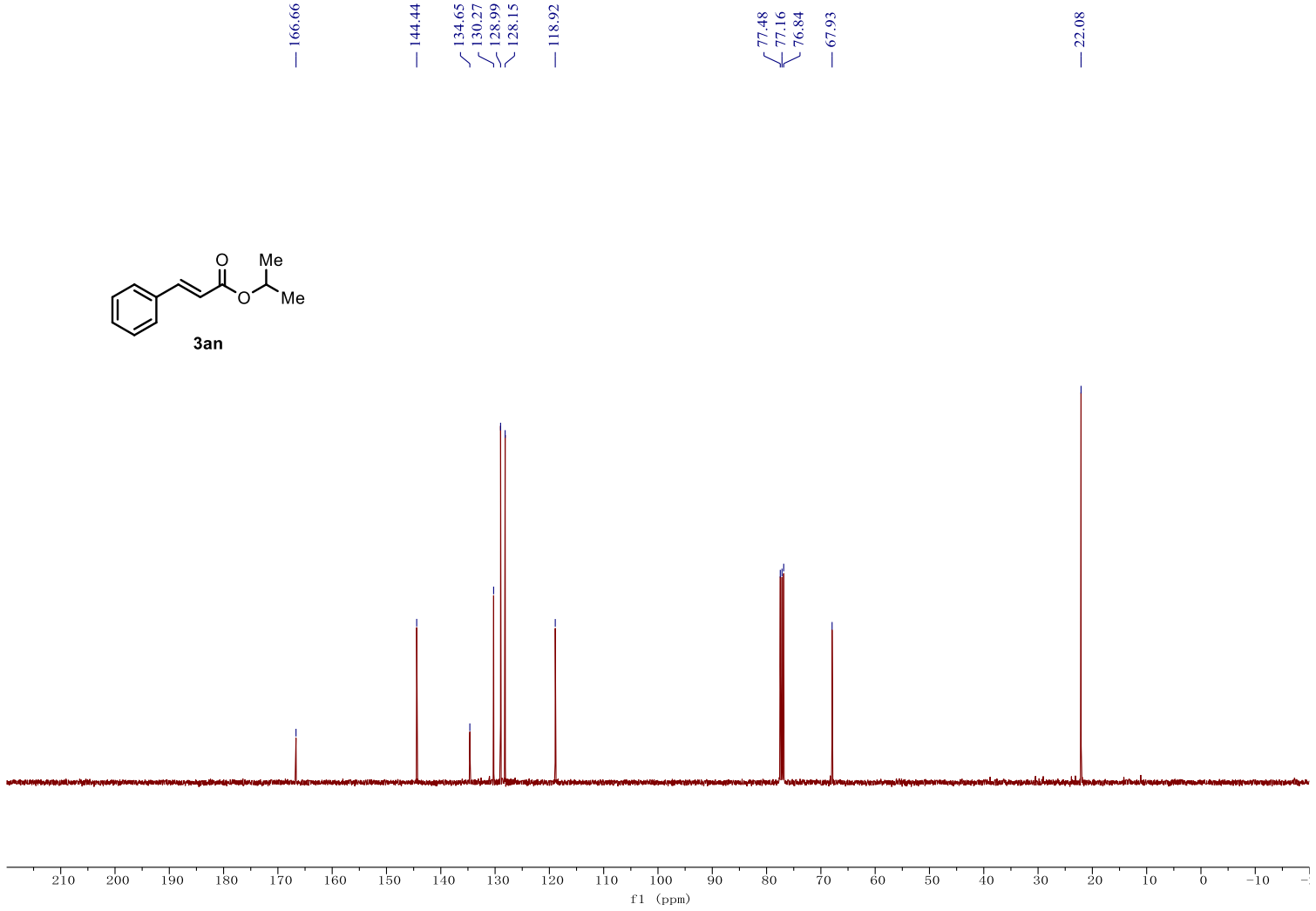

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of ^{2}*(E)*-3-(phenyl)acrylic acid butyl ester **(3ao)**.

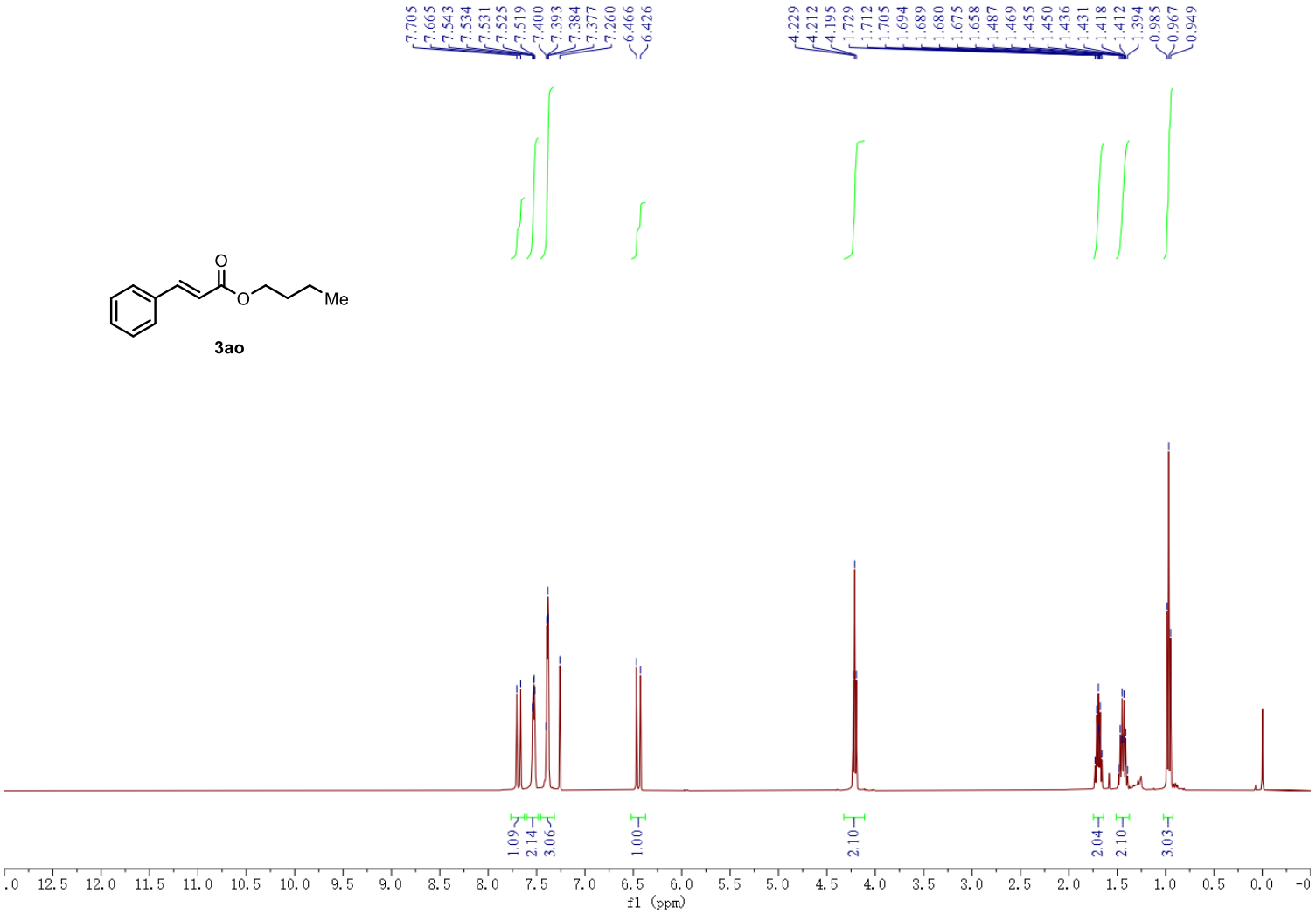

Figure S90. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of *(E)*-3-(phenyl)acrylic acid butyl ester **(3ao)**.

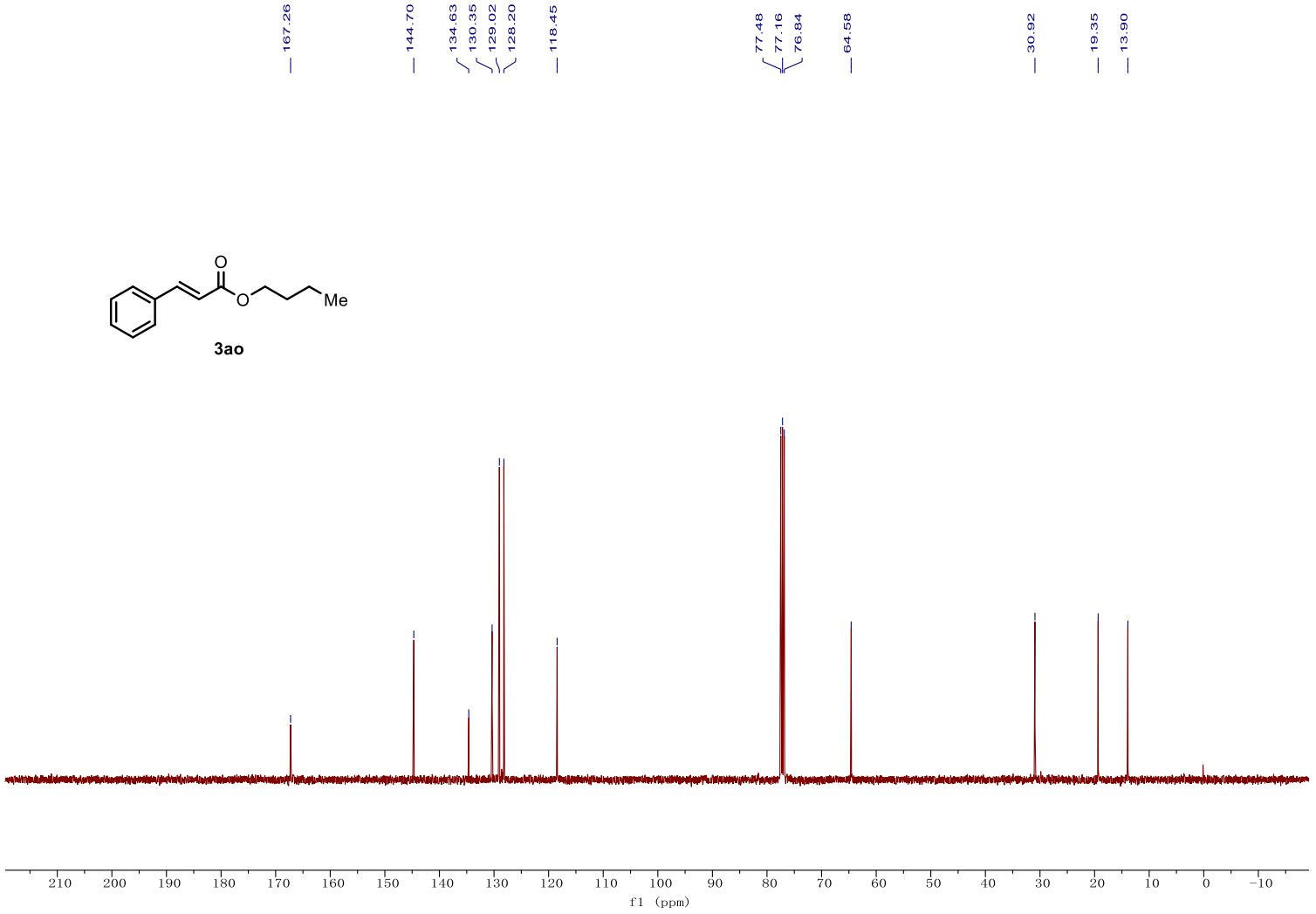

Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of Hexyl cinnamate **(3ap)**.

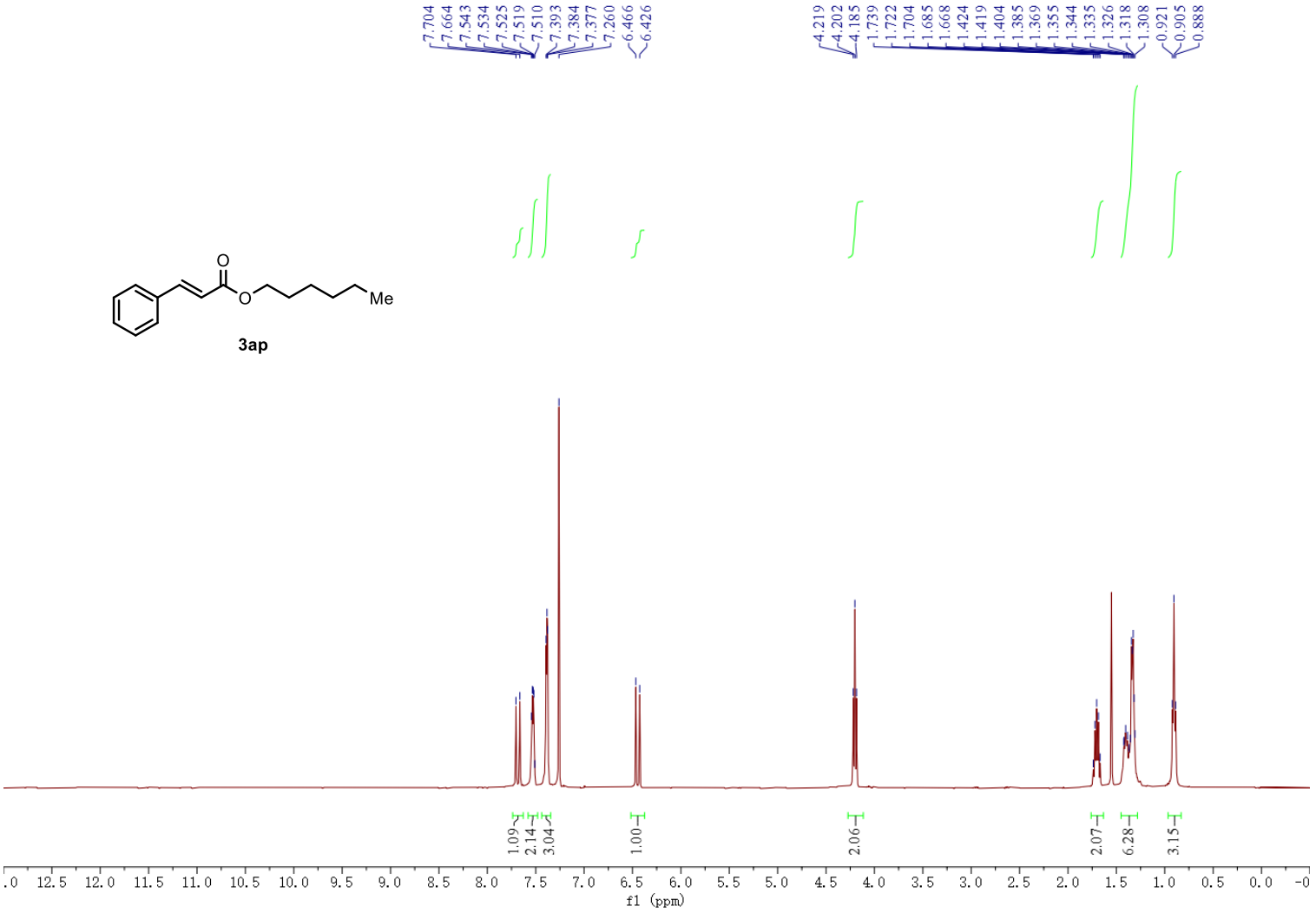

Figure S92. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of Hexyl cinnamate **(3ap)**.

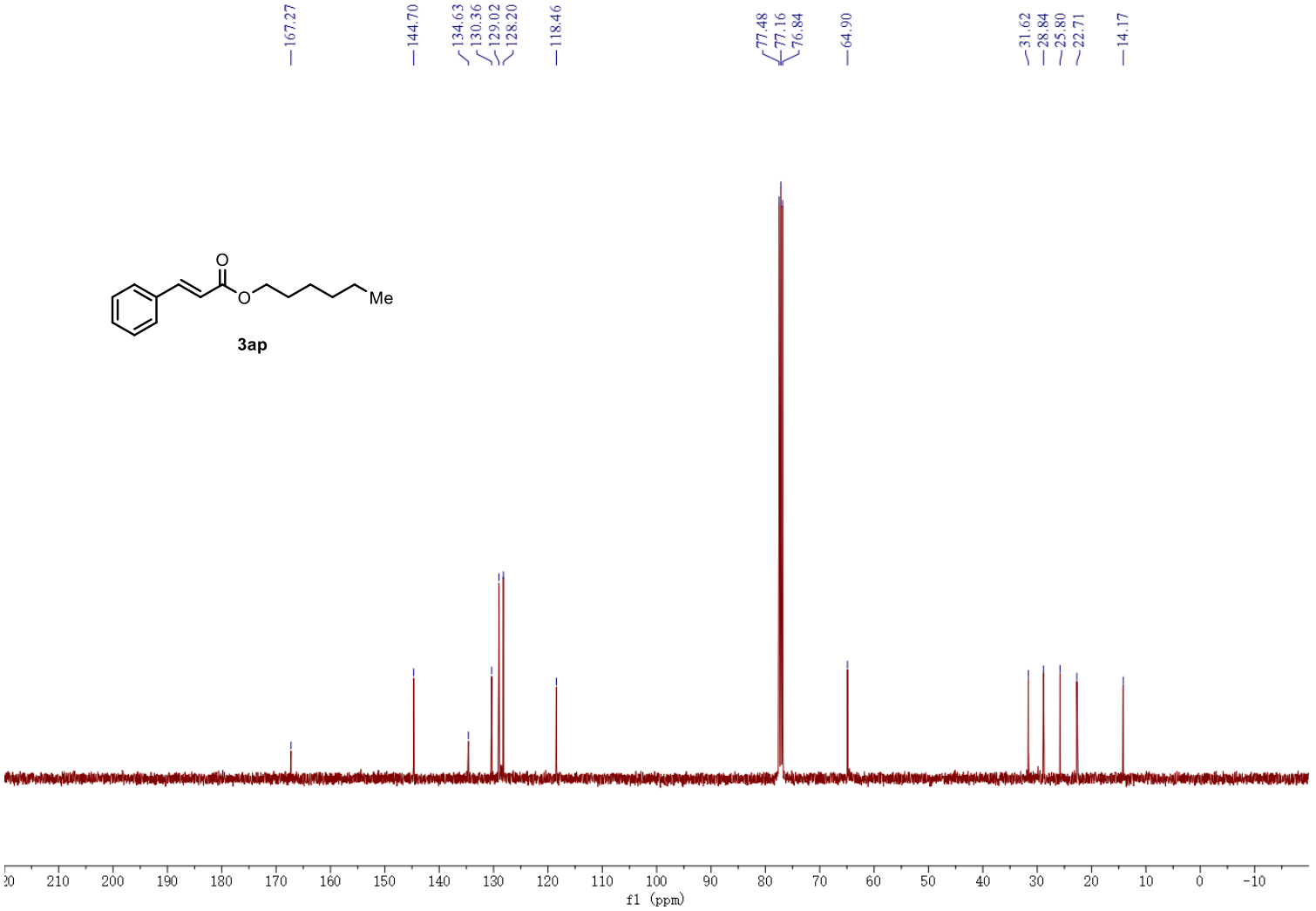

Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of Hexyl cinnamate **(3aq)**.

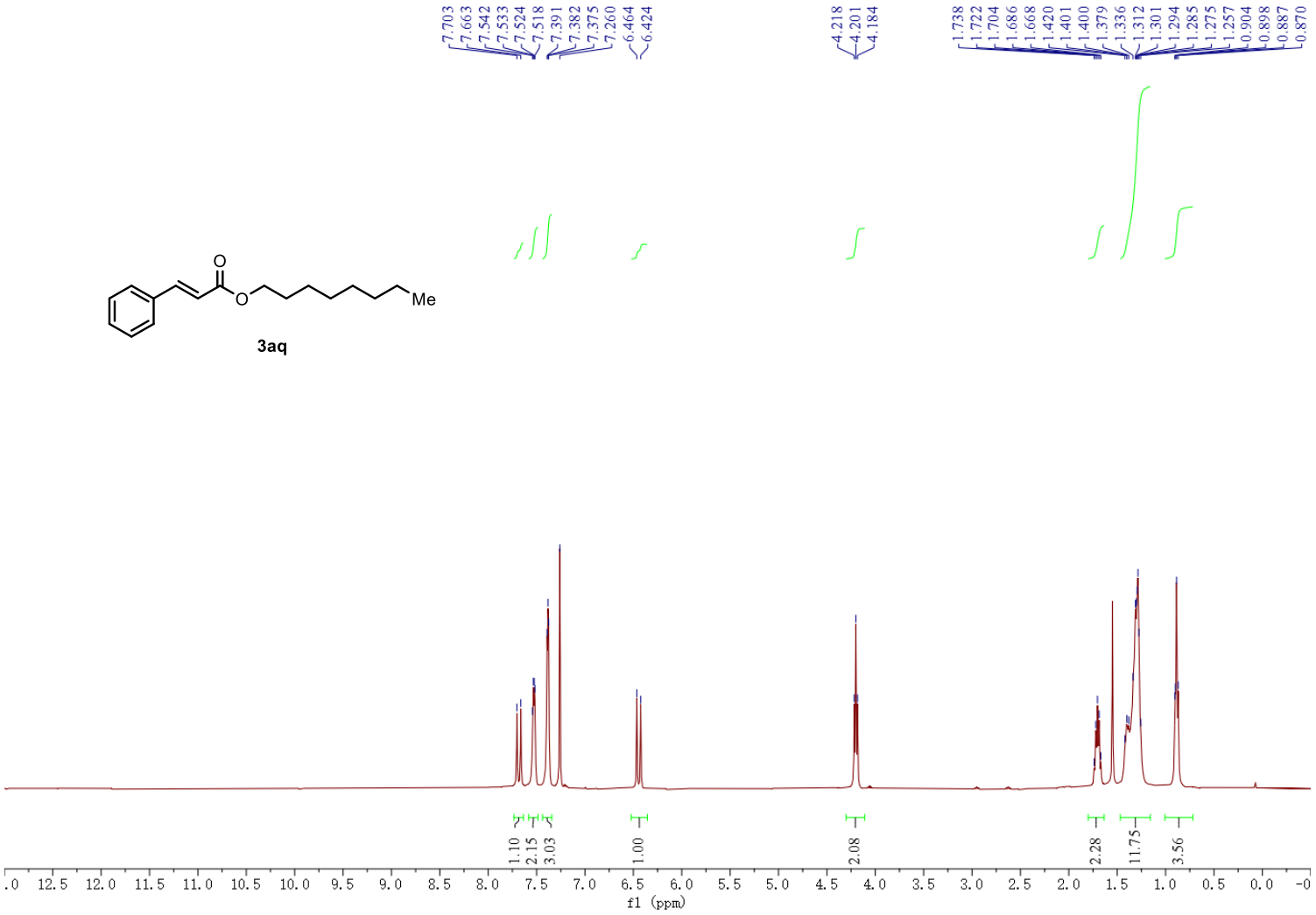

Figure S94. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of Hexyl cinnamate **(3aq)**.

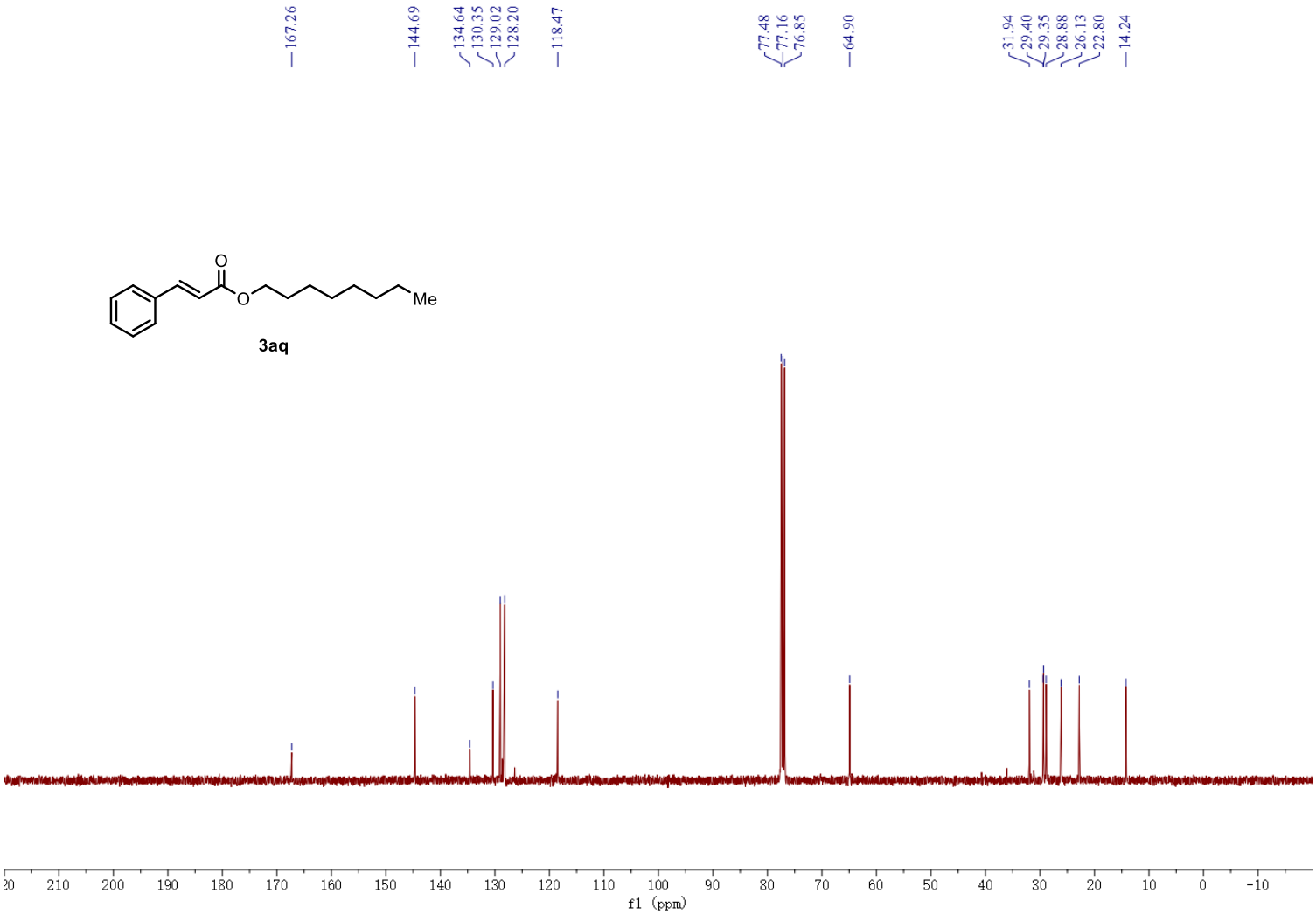

Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 2-bromoethyl cinnamate **(3ar)**.

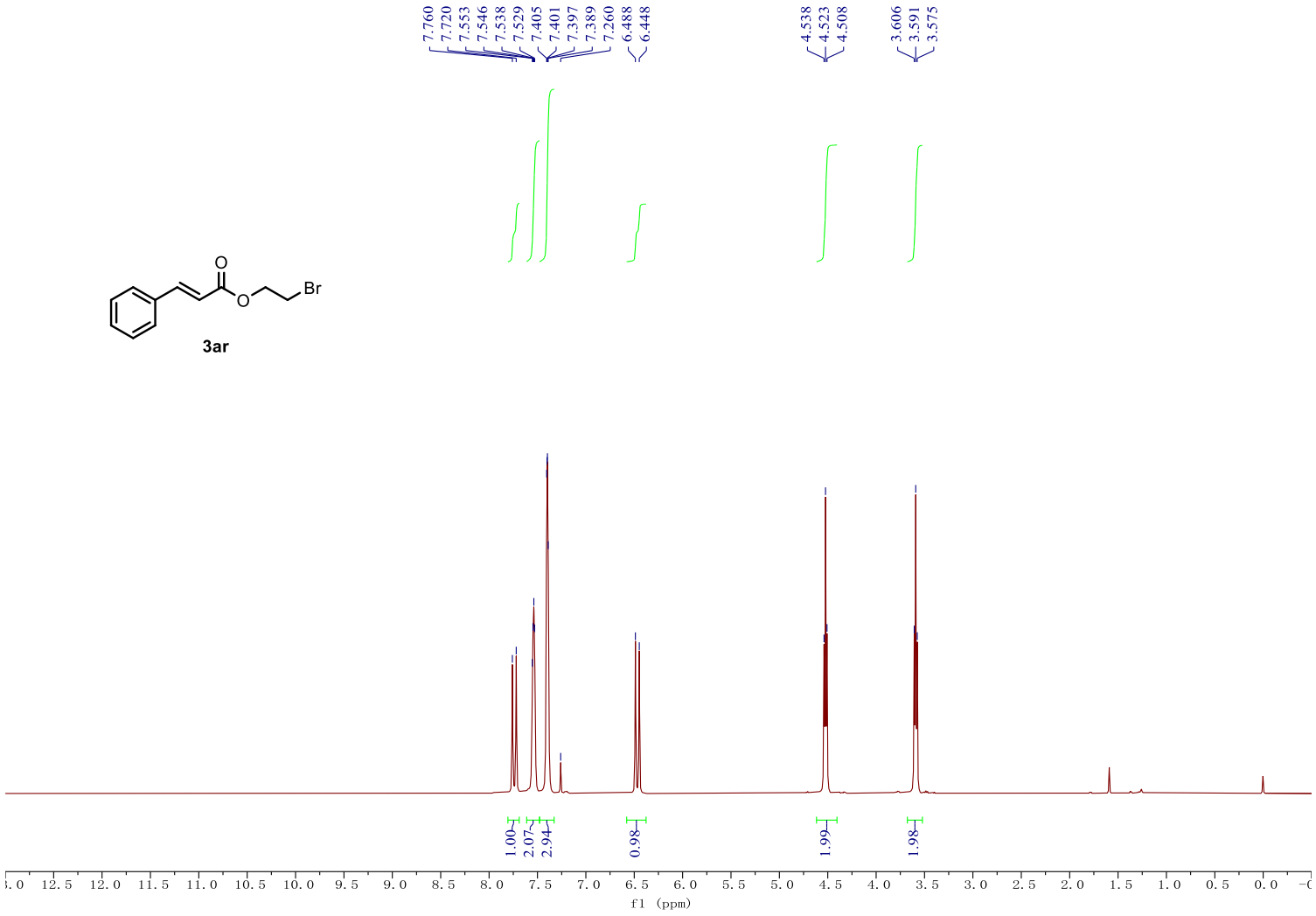

Figure S96. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 2-bromoethyl cinnamate **(3ar)**.

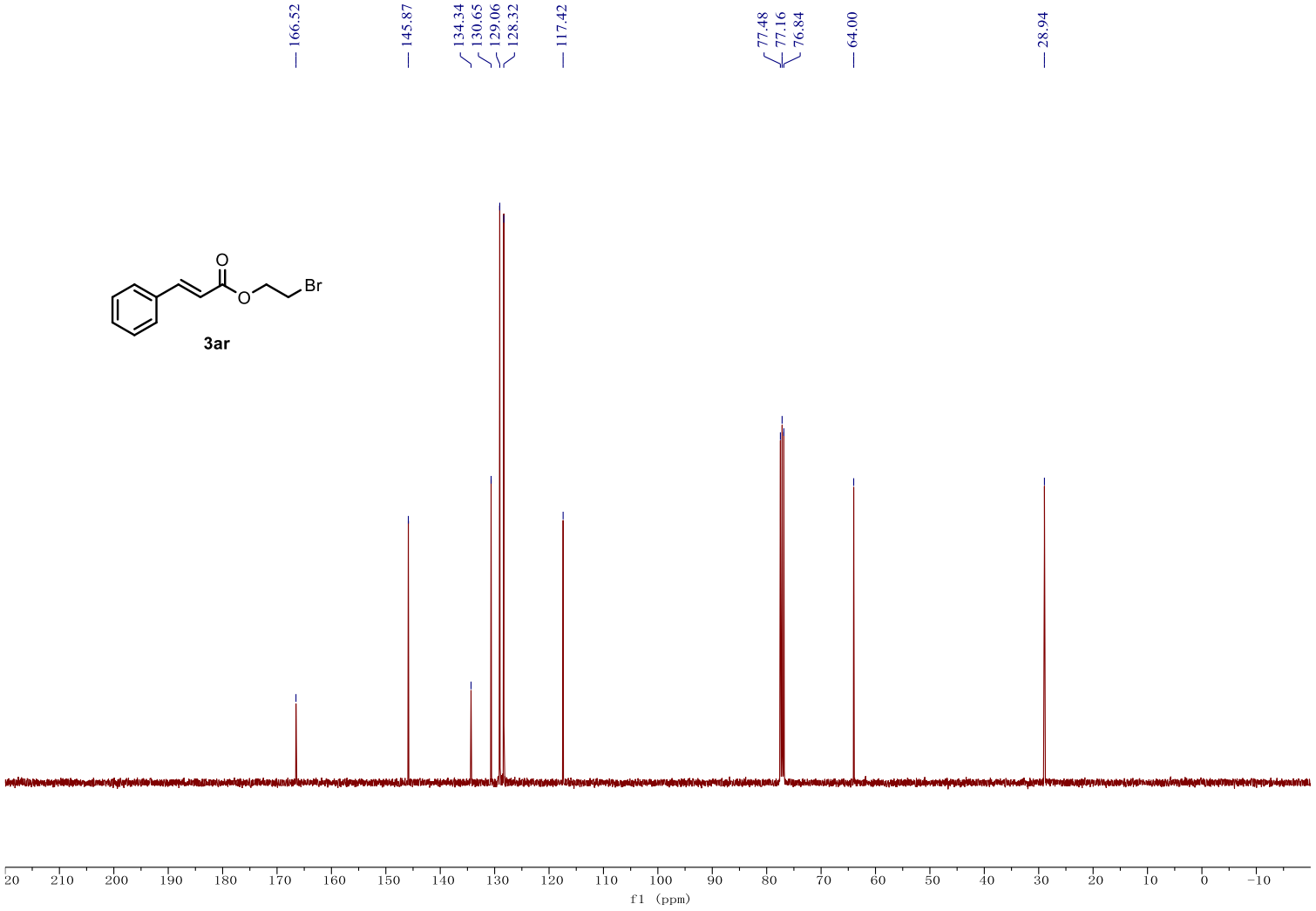

Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3-bromopropyl cinnamate **(3as)**.

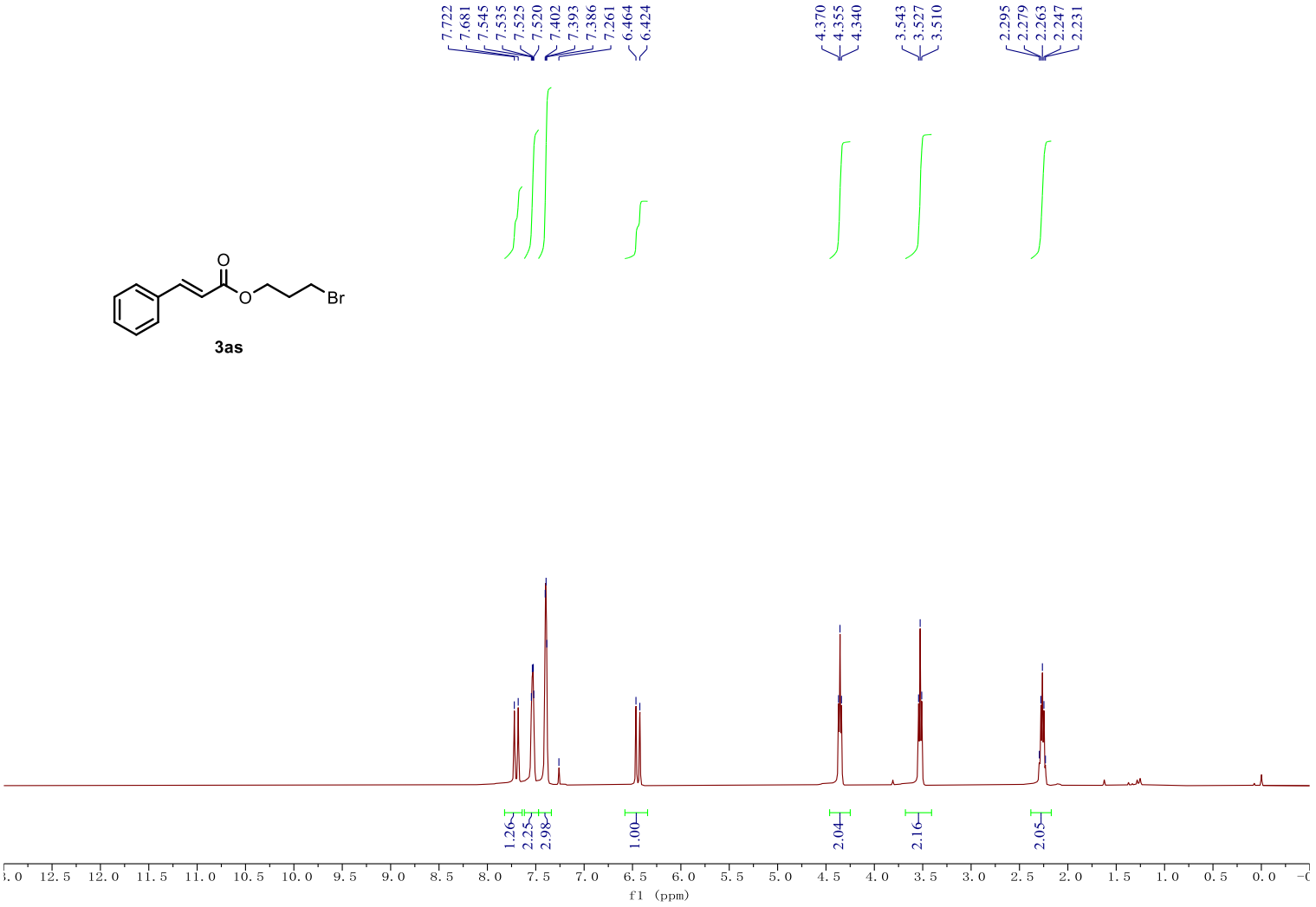

Figure S98. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 3-bromopropyl cinnamate **(3as)**.

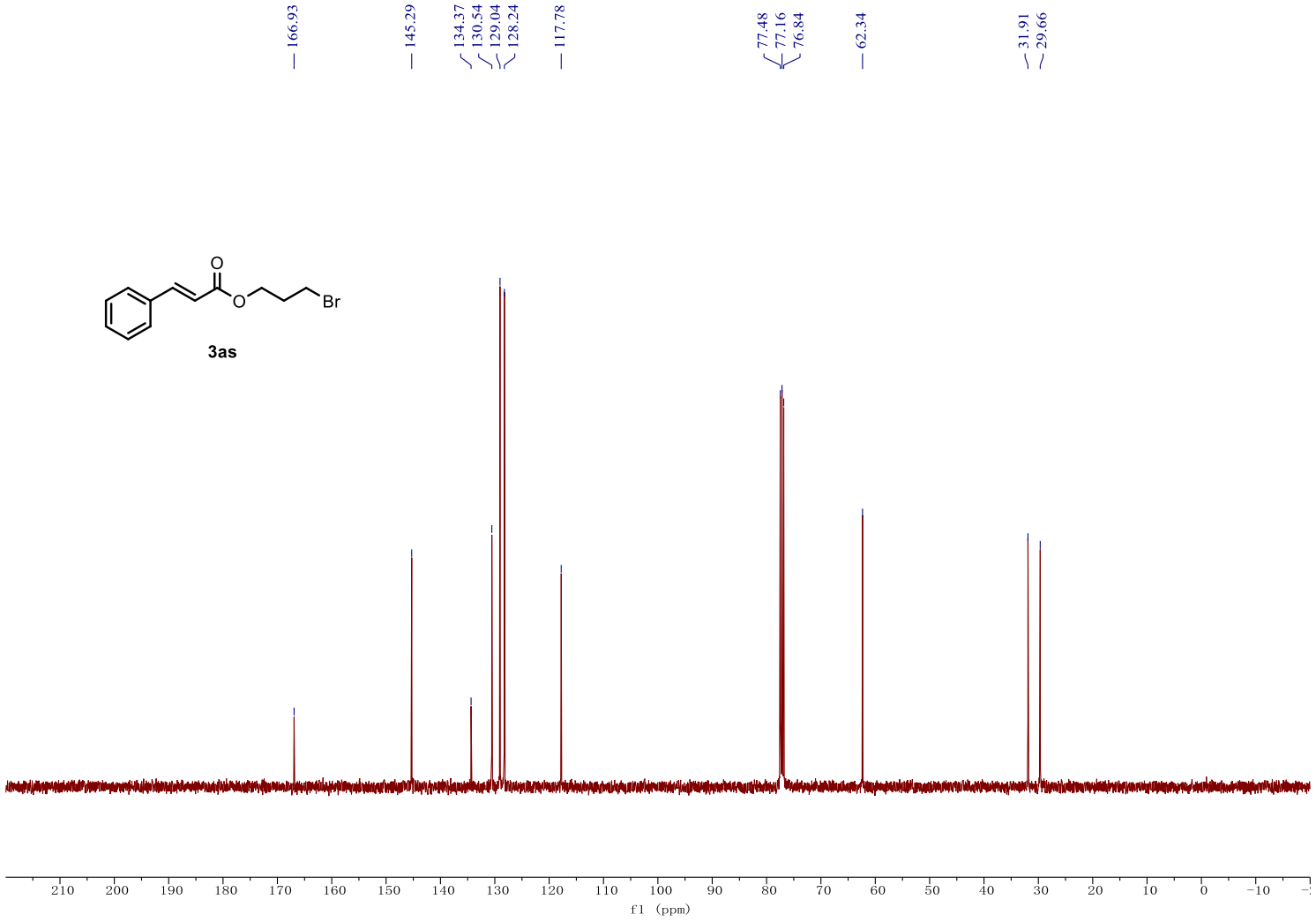

Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 4-bromobutyl cinnamate **(3at)**.

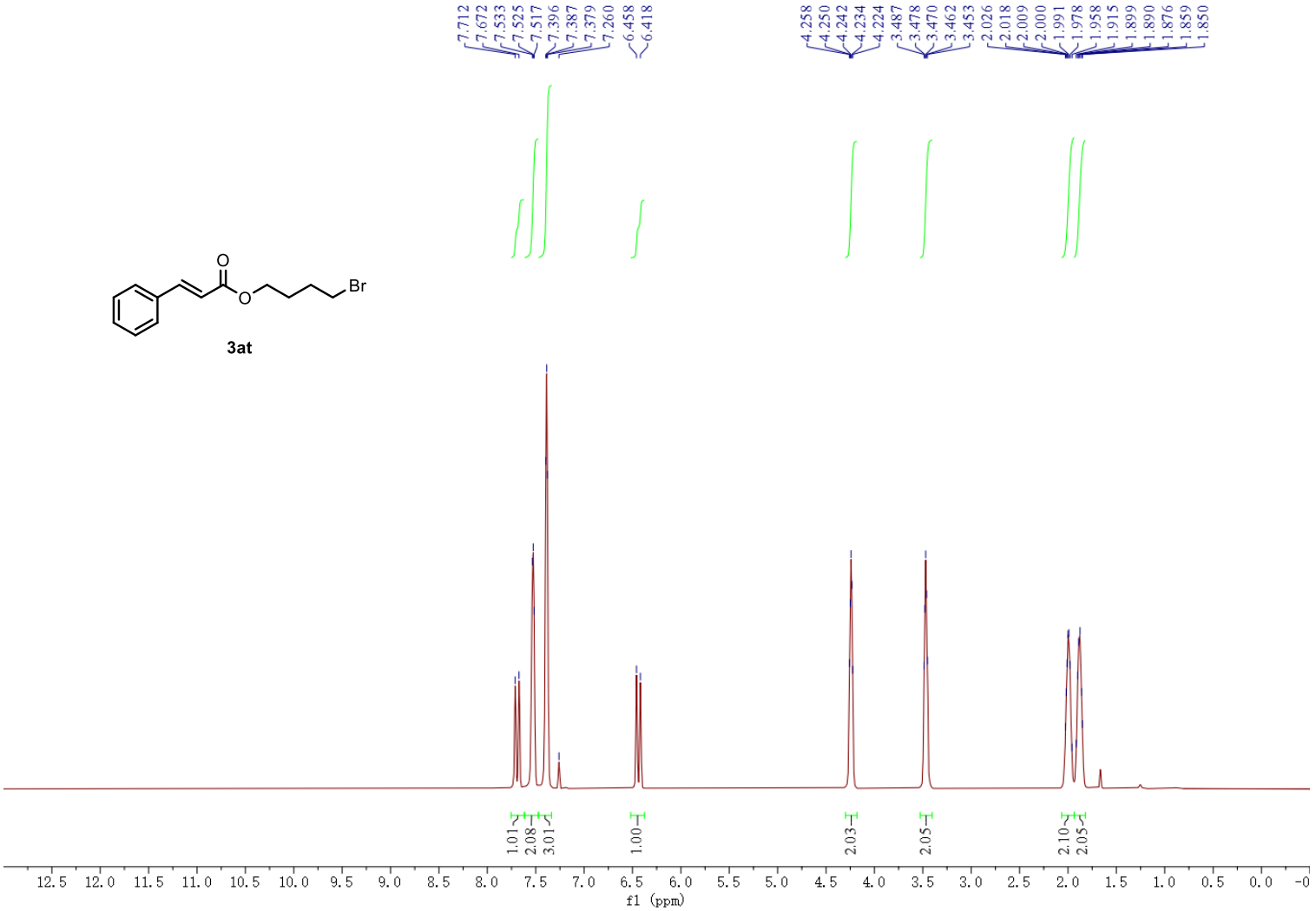

Figure S100. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 4-bromobutyl cinnamate **(3at)**.

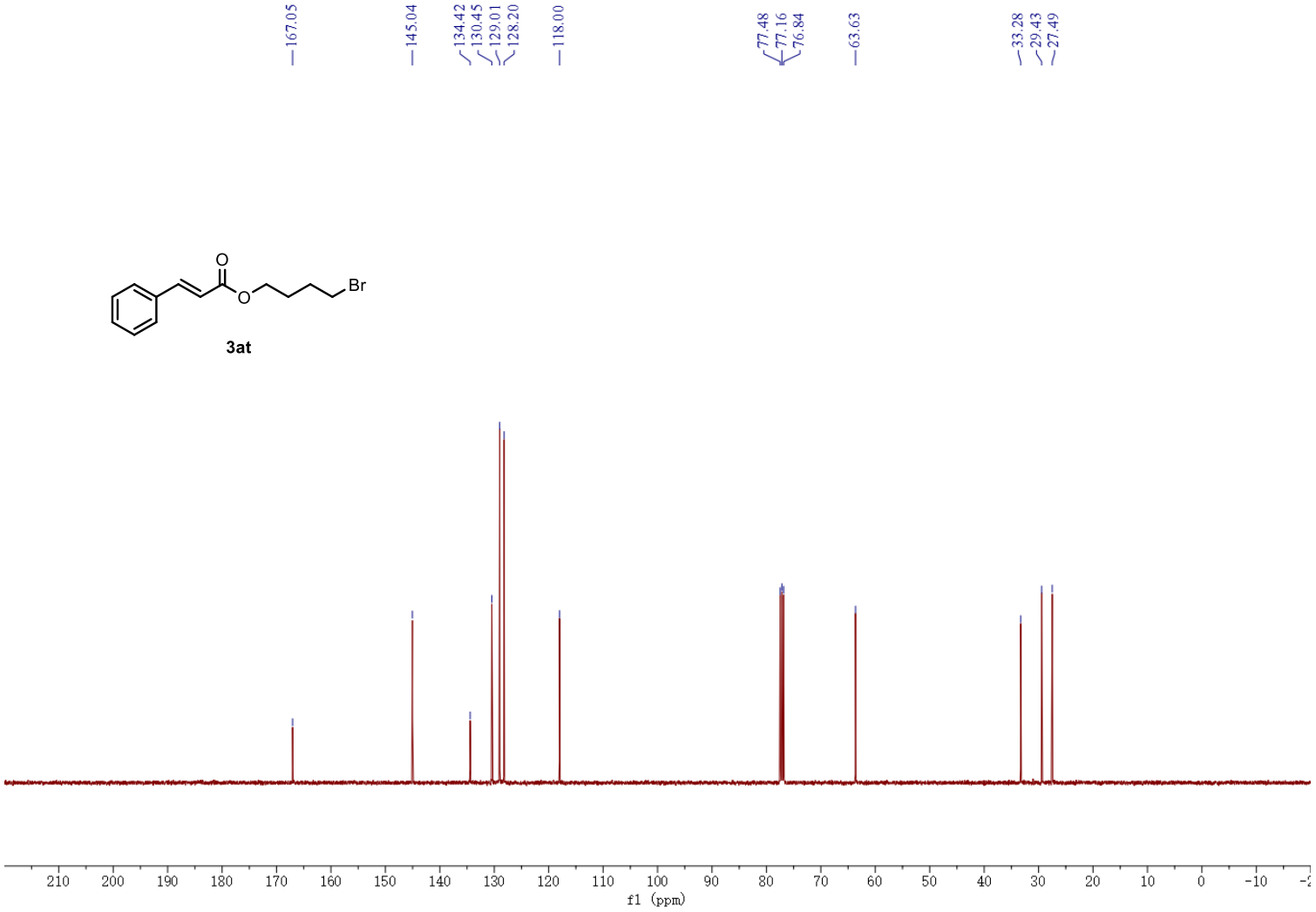

Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 2-chloroethyl cinnamate **(3au)**.

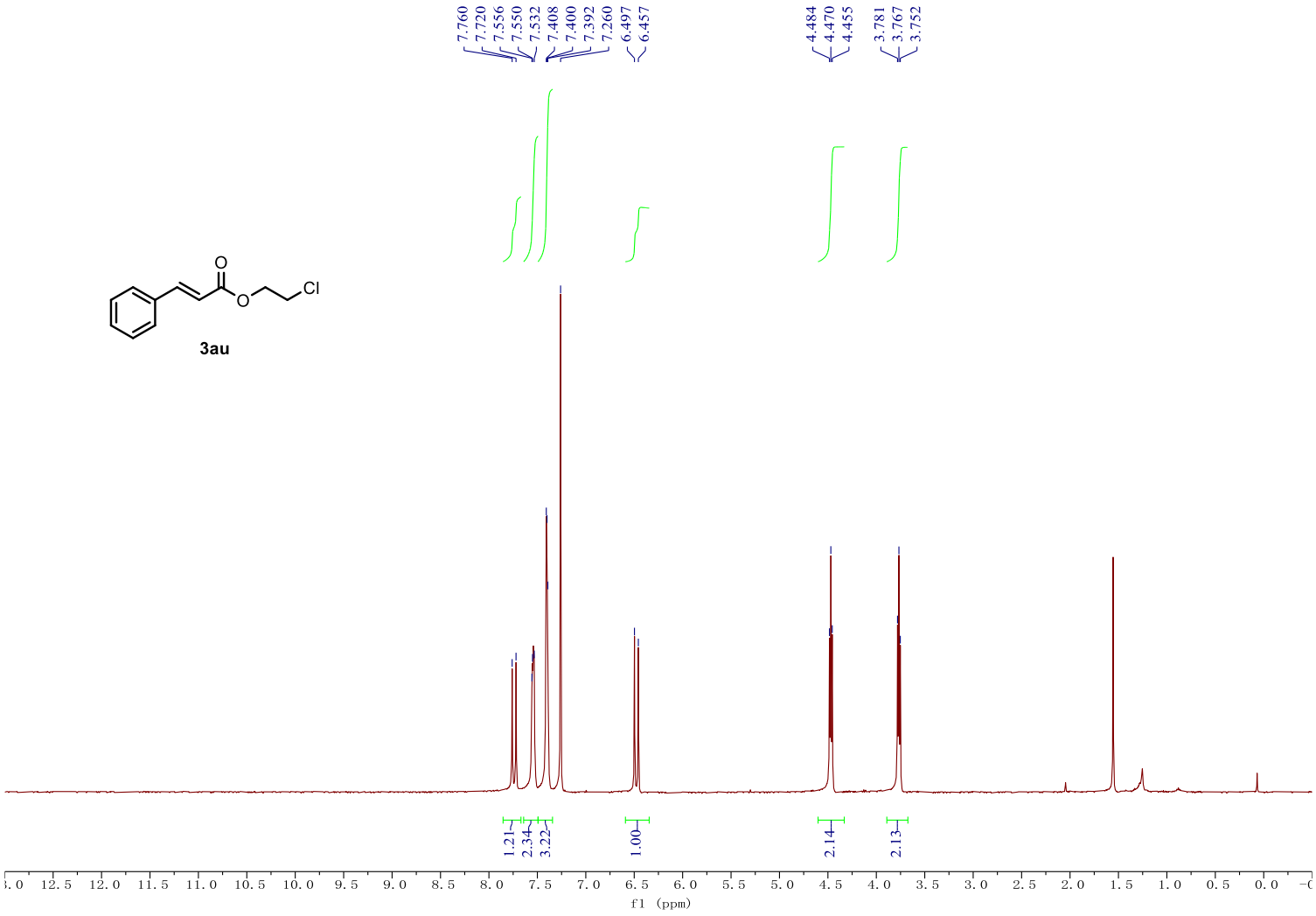

Figure S102. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 2-chloroethyl cinnamate **(3au)**.

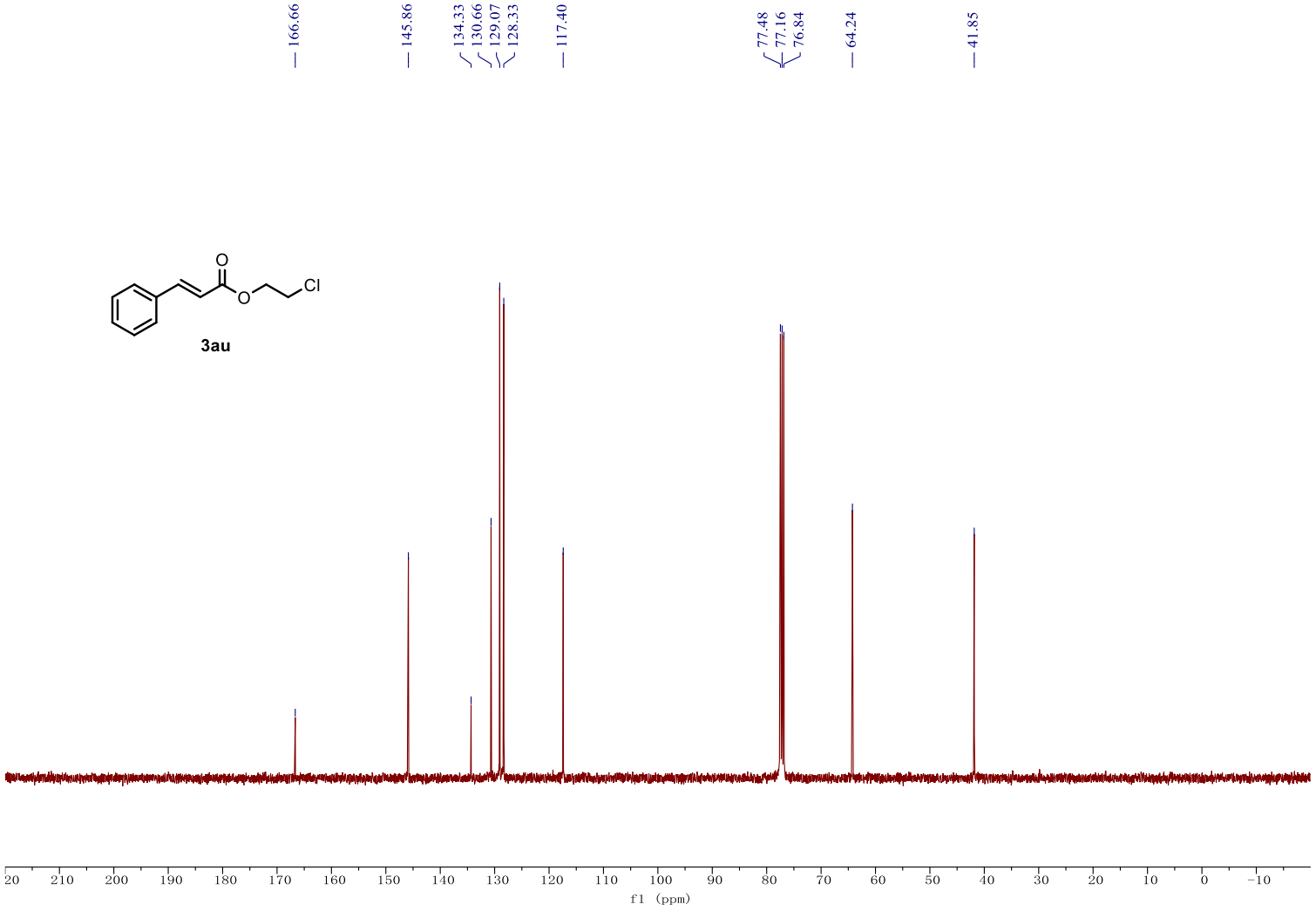

Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3-chloropropyl cinnamate **(3av)**.

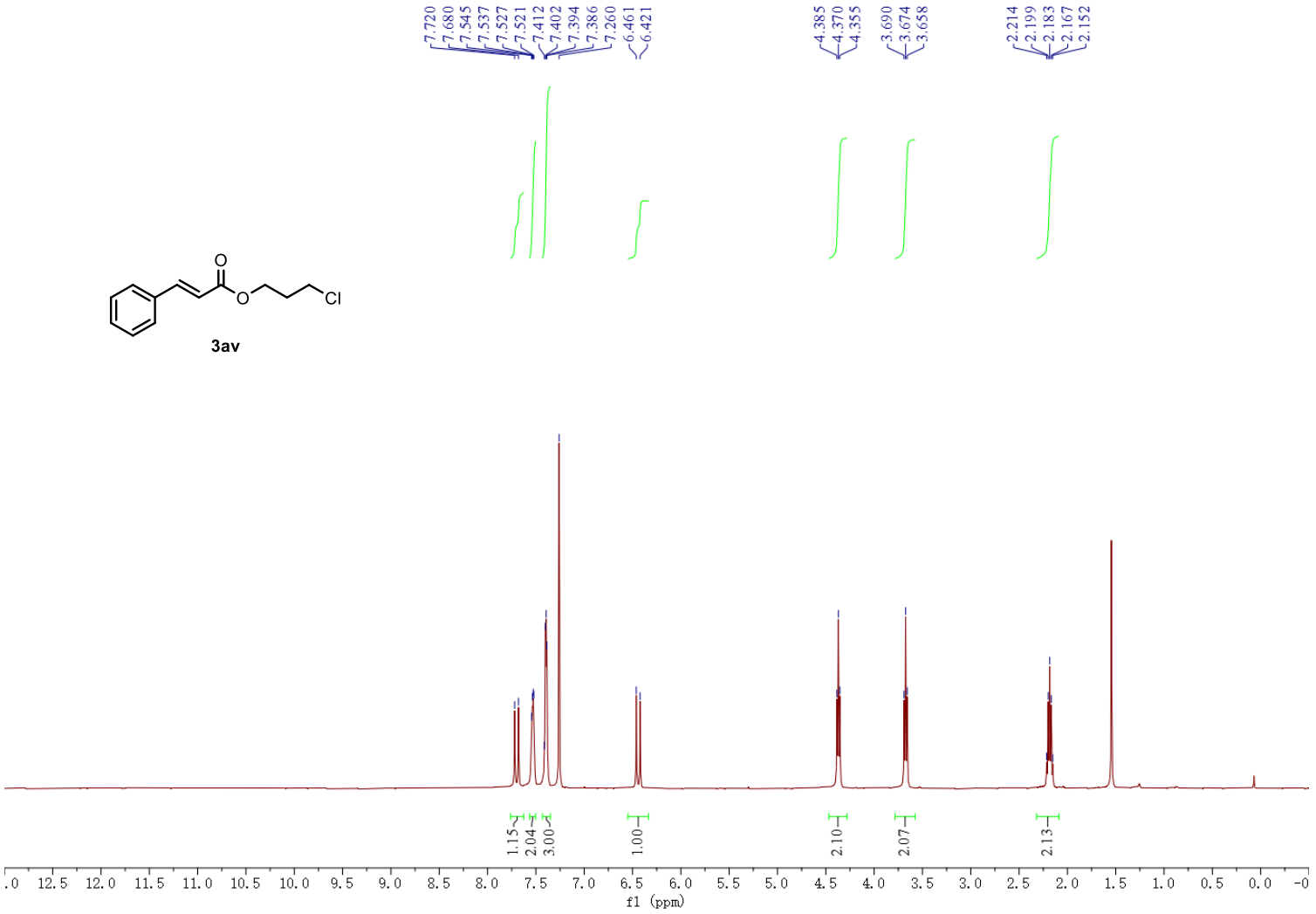

Figure S104. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 3-chloropropyl cinnamate **(3av)**.

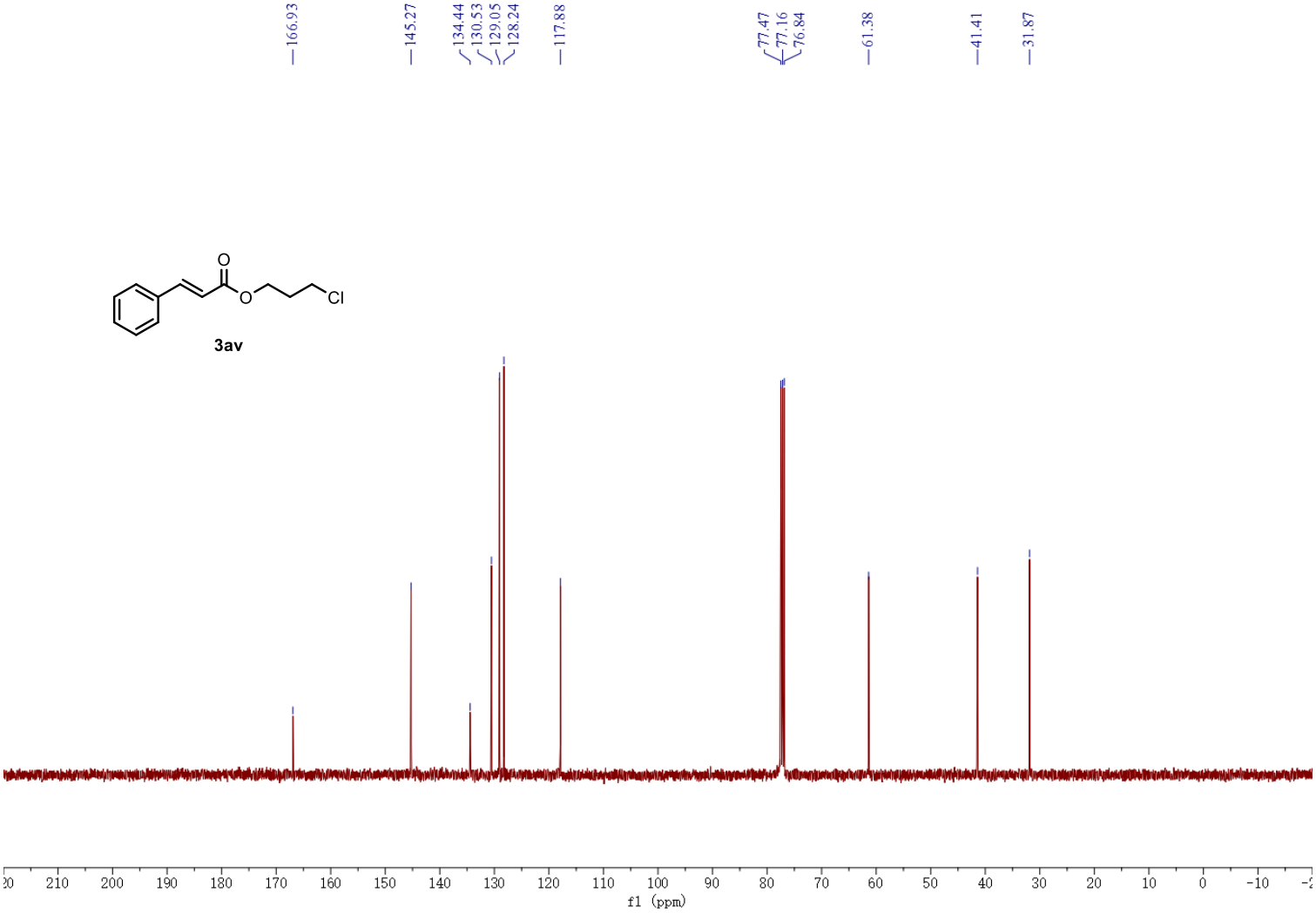

Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 4-chlorobutyl cinnamate **(3aw)**.

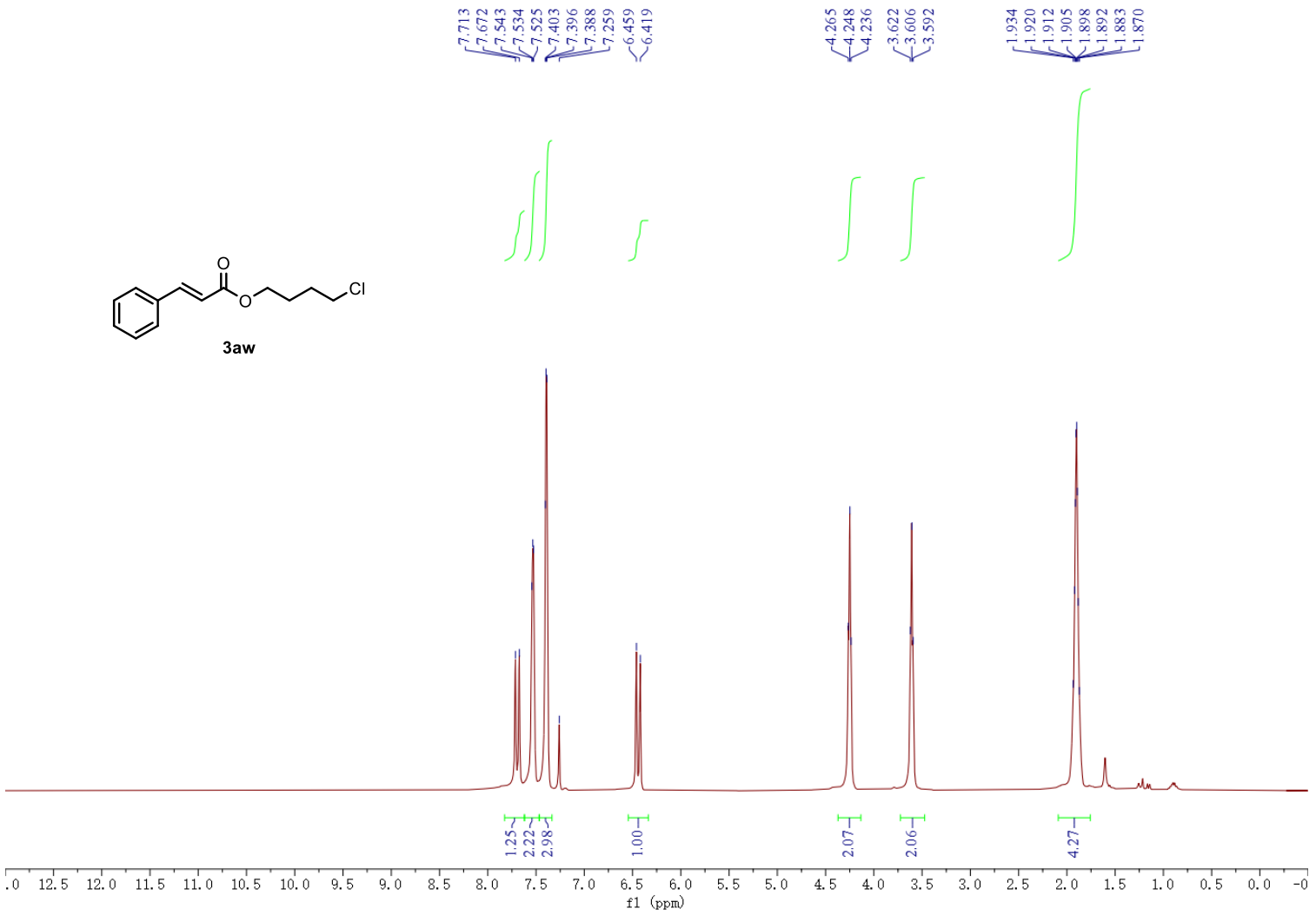

Figure S106. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 4-chlorobutyl cinnamate**(3aw)**.

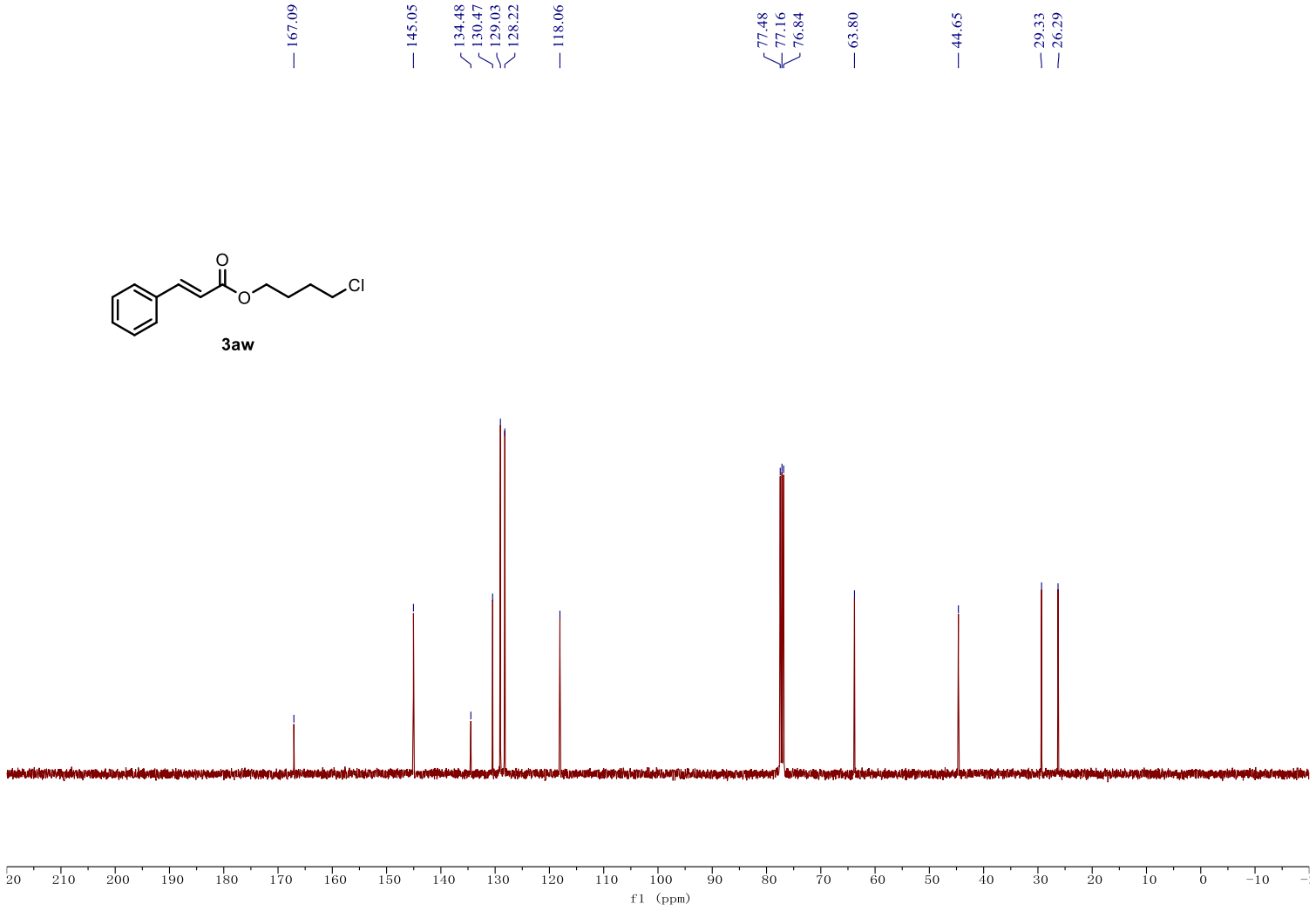

Figure S107. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 2-methoxyethyl 3-(phenyl)-2-propenoate **(3ax)**.

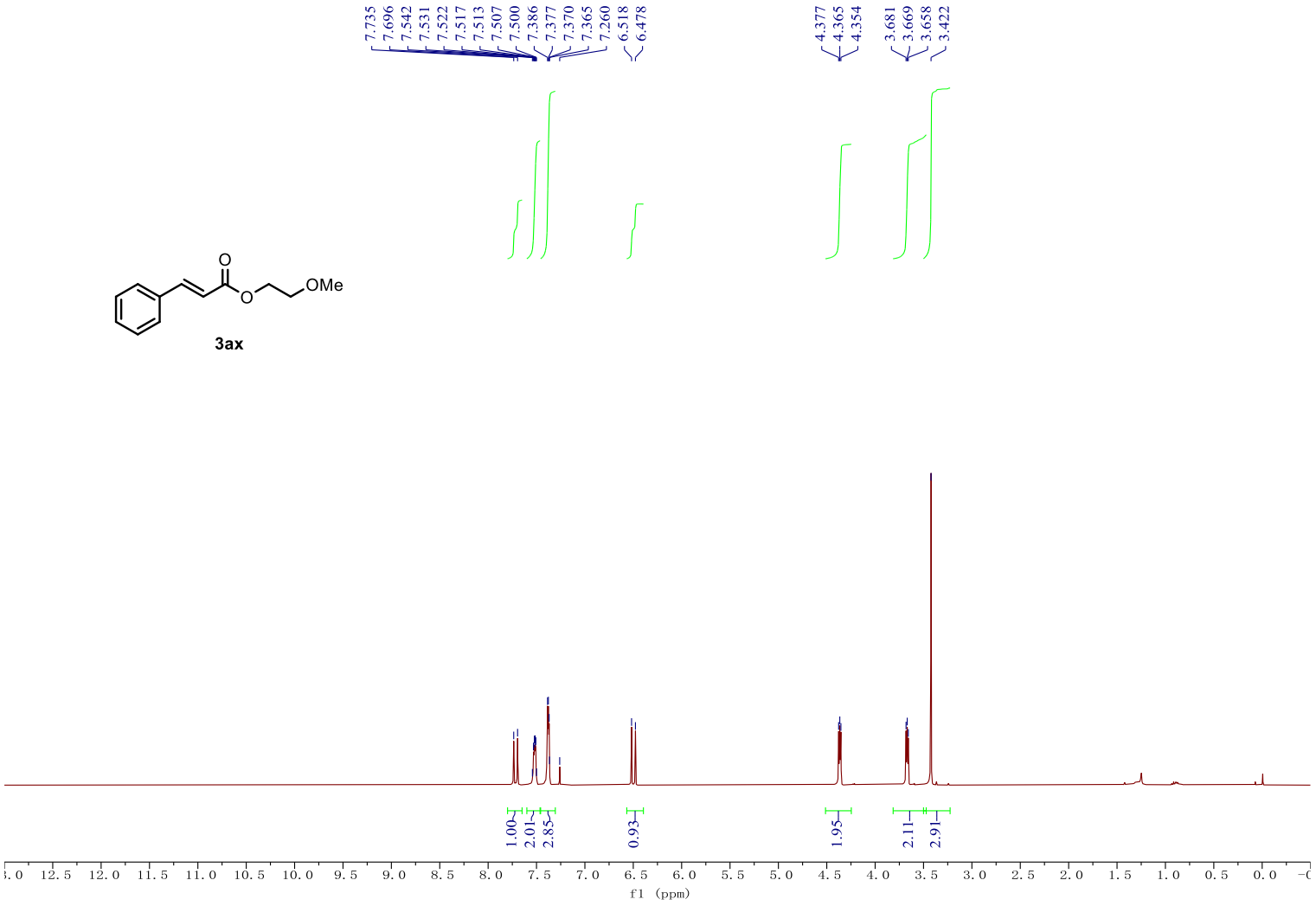

Figure S108. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) of 2-methoxyethyl 3-(phenyl)-2-propenoate **(3ax)**.