Supplementary Information (SI)

One-pot synthesis of a highly active single-atom Pd catalyst for Heck reaction

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I. General information

Materials. Pure graphene, N,N-dimethylformamide (DMF), distilled water, anhydrous ethanol, 2-methylimidazole, palladium acetate, acrylates and their derivatives, acrolein, aryl iodides, anhydrous potassium carbonate, sodium carbonate, sodium bicarbonate, potassium hydroxide, triethylamine, DBU, pure ethyl acetate, petroleum ether, methanol, hexane, silica gel (200-300 mesh), etc. Unless otherwise stated, all reagents are pure. Unless otherwise stated, all reagents are more than 99% pure, and the reagents are used directly without further purification. All solutions are prepared with ultrapure water. Graphene was purchased from Hunan Fenghua Materials Development Co., Ltd. in China, and other reagents were purchased from McLean, Anegi, and Aladdin.

Physical characterizations. Physical Characterizations. TEM and SAED images were acquired using a JEM-2100 equipped with an X-Max80 at 200 kV. XPS analysis was performed on a Thermo Fisher Scientific K-Alpha+ to investigate the surface chemical state of Pd in the catalyst samples. XRD measurements were carried out using a PANalytical Empyrean (Netherlands) with a scan rate of 0.1° min^{-1}. Raman spectroscopy was conducted on a Renishaw inVia (UK). HRTEM and elemental mapping images were obtained using a JEOL JEM-F200 (Japan) at 200 kV. Elemental mapping was also performed on a Thermo Fisher Spectra 200 (Czech Republic) with an accelerating voltage of 200 kV. Metal loading analysis by ICP was conducted using a Horiba Ultima Expert and an Agilent 5800. The X-ray absorption fine structure (XAFS) data were collected at the BL14W1 beamline in Shanghai Synchrotron Radiation Facility (SSRF).

Structure characterization of product 3. The NMR structure of **compound 3** was analyzed using an AVANCE NEO 400 MHz NMR instrument (Bruker, Switzerland), including ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. ^{13}C NMR chemical shifts were recorded relative to solvent resonance. The NMR spectra of the product were compared with literature data and found to be consistent with the reported structural patterns.[S1]

II. Sythesis of Pd catalysts

Preparation of Pd SACs/NG. Pd SACs/NG were synthesized using an anchored-in situ pyrolysis method. Briefly, 15.5 mg of 2-methylimidazole was dissolved in 40 mL of DMF, followed by the addition of 10.5 mg of palladium acetate and 1000 mg of graphene. The mixture was stirred for 12 h at room temperature. During this process, the graphene interacted with 2-methylimidazole, and the ligand was uniformly dispersed on the surface of the graphene via π-π stacking interactions. The 2-methylimidazole molecules then coordinated with Pd^{2+} and anchored the palladium ions onto the graphene. Afterward, the graphene with anchored Pd^{2+} was separated, and the DMF solvent was removed by centrifugation (due to the high boiling point of DMF). The resulting samples were calcined in a tube furnace under a 10% H_2/N_2 atmosphere at a heating rate of 5℃/min to 800 ℃, and maintained at that temperature for 2 h. After natural cooling, the Pd SACs/NG samples were obtained. During the calcination, 2-methylimidazole acted as a nitrogen source, decomposing at high temperatures due to its thermal instability and forming Pd-N-C bonds with graphene and Pd^{2+}.[S2] The resulting catalyst samples could be used directly without additional milling or post-treatment steps.

Preparation of Pd NPs/NG. The key difference between the preparation of Pd NPs/NG and Pd SACs/NG lies in the fact that N-doped graphene is formed prior to the addition of palladium acetate, which serves as the palladium source. The detailed procedure is as follows: First, 154.3 mg of 2-methylimidazole was dissolved in 40 mL of ethanol,

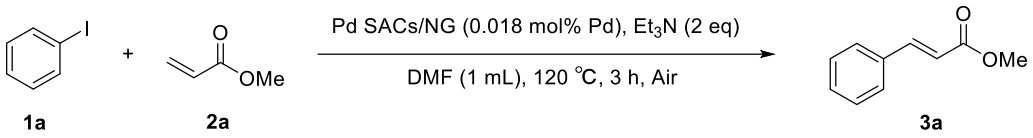
and 1000 mg of graphene was added to the solution and stirred at room temperature for 12 h. The ethanol solvent was then removed by rotary evaporation. Second, the graphene-2-methylimidazole mixture was calcined by heating at a rate of 5℃/min to 800 ℃, where it was maintained for 2 h. N-doped graphene was obtained by natural cooling. Third, 105.5 mg of palladium acetate was dissolved in 40 mL of DMF, and 1000 mg of N-doped graphene was added to this solution. The mixture was stirred at room temperature for 12 h, during which the palladium acetate molecules were uniformly dispersed and anchored onto the N-doped graphene. The DMF solvent was then removed by centrifugation. Finally, the samples were calcined in a tube furnace under a 10% H_2/N_2 atmosphere at a heating rate of 5℃/min up to 800 ℃ and maintained at this temperature for 2 h. The Pd NPs/NG samples were obtained after natural cooling. These catalyst samples can be used directly without further grinding or post-treatment.

III. General procedure for the Pd SACs/NG in Heck reaction

Catalytic reactions. Catalytic Reactions. Pd SACs/NG (2 mg, 0.018 mol% Pd) and triethylamine (Et_3N, 140 μL, 1 mmol) were added to a 10 mL Schlenk tube. At room temperature, aryl iodide (0.5 mmol) and olefin (2.0 mmol) were introduced, followed by the addition of DMF solvent using a 1000 μL pipette. The Heck coupling reaction was then carried out at 120℃ for 3 h. After the reaction, the products were extracted with ethyl acetate (30 mL) and water (30 mL). The aqueous layer was further extracted with ethyl acetate (10 mL × 3) to minimize product loss. The organic solvents were removed under reduced pressure using a rotary evaporator. The product was purified by column chromatography, using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent.

IV. Conditioning screening of Pd SACs/NG in Heck reaction

For the screening of conditions of Pd SACs/NG in Heck reaction, we can see the **Table S1**. In the solvent screening, THF and H_2O resulted in minimal product formation (entries 2 and 4). However, yields of 78% and 40% were obtained with DMSO and CH_3OH (entries 3 and 5), respectively. For base screening, KOH, Na_2CO_3, and K_2CO_3 led to satisfactory yields (entries 6-8). The use of triethylenediamine (DABCO) (entry 9) resulted in poor performance, likely due to the strong basic nature of DABCO, which may decompose at high temperatures and interact with the DMF solvent, inhibiting the reaction. In the temperature optimization, a certain temperature range (entries 10-12) provided favorable results. However, due to the tendency of methyl acrylate to polymerize at high temperatures, increasing the temperature did not improve the yield. At 150 ℃, the yield decreased to only 55% (entry 13). The yield at 1 h was 49% (entry 14), and at 5 h, it did not increase significantly, remaining at 93% (entry 15).



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

Table S1. Conditioning screening of Heck reaction.

Entry	Variation from the standard conditions	Yield (%)
1	None	94
2	THF instead of DMF	＜5
3	DMSO instead of DMF	78
4	H_2O instead of DMF	＜5
5	CH_3OH instead of DMF	40
6	KOH instead of Et_3N	76
7	Na_2CO_3 instead of Et_3N	63
8	K_2CO_3 instead of Et_3N	83
9	DABCO instead of Et_3N	＜5
10	90℃ instead of 120℃	37
11	100℃ instead of 120℃	52
12	110℃ instead of 120℃	81
13	150℃ instead of 120 ℃	55
14	1 h instead of 3 h	49
15	5 h instead of 3 h	93

[a]Standard conditions: 0.5 mmol of **1a**, 2.0 mmol of **2a**, 0.018 mol% of Pd SACs/NG in DMF (1 mL) at 120 ℃ for 3 h.
[b]Isolated yields.

Ⅴ. Gram-scale reaction, hot filtration test, stability test and steps of recycling catalysts

Gram-scale reaction:

In a round-bottomed flask, iodobenzene (12 mmol, 1.343 mL) and methyl acrylate (44 mmol, 3.97 mL) were mixed sequentially. Pd SACs/NG (2 mg, 0.0007 mol%), triethylamine (Et_3N, 24 mmol), and 30 mL of DMF were then added. The mixture was subjected to reflux at 120 ℃ for 4.5 hours. After the reaction was completed, the system was cooled to room temperature. The product was extracted using ethyl acetate (150 mL) and distilled water (200 mL). The combined organic phase was partitioned with saturated saline, and sodium sulfate was added to remove any

residual water. The volatile solvents were removed under reduced pressure using a rotary evaporator. The product was purified by column chromatography, using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE : EA = 50 : 1). The desired product (**3a**) was obtained as a light-yellow solid (1.87 g) with a yield of 96%. The TON value was 133,256, and the TOF value was 29,612 h^{-1}.

Hot filtration test:

Pd SACs/NG (2 mg, 0.018 mol% Pd), triethylamine (Et_3N, 140 µL, 1 mmol), iodobenzene (0.5 mmol) and methyl acrylate (2.0 mmol) were added to a 10 mL Schlenk tube, followed by the addition of DMF solvent using a 1000 µL pipette. The Heck coupling reaction was then carried out at 120 ℃ for 1 h. The reaction was then directly filtered through a preheated (120 ℃) pad of Celite into a fresh vial, and was then analyzed by HPLC prior to heating for an additional 2 h at 120 ℃. Subsequent analysis showed that the reaction yield did not increase after the hot filtration.

The catalyst recycling experiment in Heck reaction:

Recycle performance of 0.018 mol% Pd SACs/NG in Heck reaction. We selected iodobenzene and methyl acrylate as model reactants for the study. The reaction using Pd SACs/NG showed a high yield of over 80% even after 15 cycles (**Figure S1**). After 15 reaction cycles of iodobenzene with methyl acrylate, the used Pd SACs/NG catalysts were further characterized by TEM and AC-HAADF-STEM (**Figure S15**).

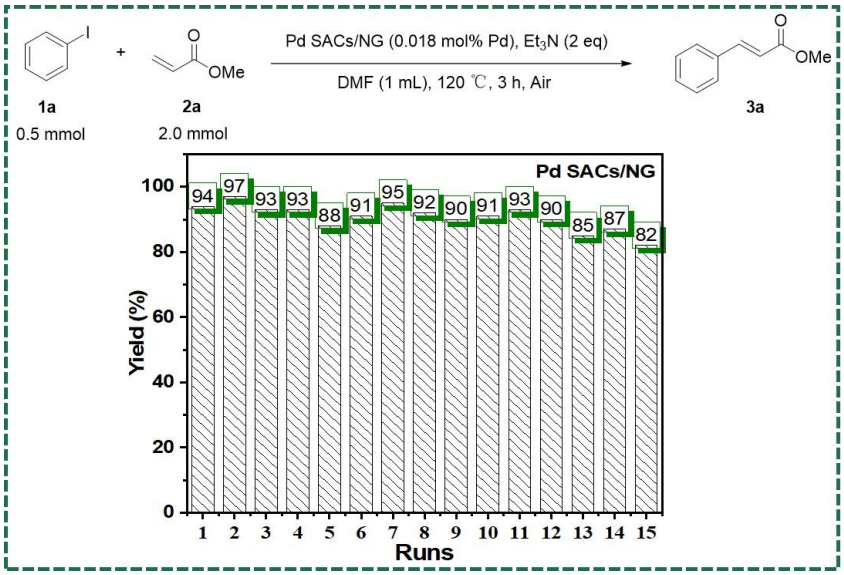


Figure S1. Recycle performance of 0.018 mol% Pd SACs/NG in the Heck reaction (0.5 mmol scale).

The cyclic reaction was carried out as follows (Figure S2): Pd SACs/NG (0.018 mol%), triethylamine (Et_3N), iodobenzene and methyl acrylate were mixed together in the heat-resistant centrifuge tube, followed by the addition of DMF solvent using a 1000 µL pipette. The Heck coupling reaction was then carried out at 120 ℃ for 3 h. At the end of the reaction, deionized water and ethyl acetate (EA) were added to the reaction mixture for centrifugal separation to isolate the catalyst. Due to the miscibility of DMF with water, additional DMF was introduced into the heat-resistant centrifuge tube to remove residual H_2O through phase transfer. After this step, only the catalyst and residual DMF remained in the heat-resistant centrifuge tube. Fresh DMF (1 mL) was then introduced as the reaction solvent. The supernatant obtained from two consecutive centrifugation steps was subjected to liquid-liquid extraction to eliminate residual DMF and H_2O, followed by final purification of the product via column chromatography and the desired product was obtained. In the next cycle, iodobenzene, methyl acrylate,

Et_3N were added again into the heat-resistant centrifuge tube which was remained catalyst and DMF, and the reaction was carried out at 120 ℃ for 3 h. These steps were repeated in subsequent cycles.

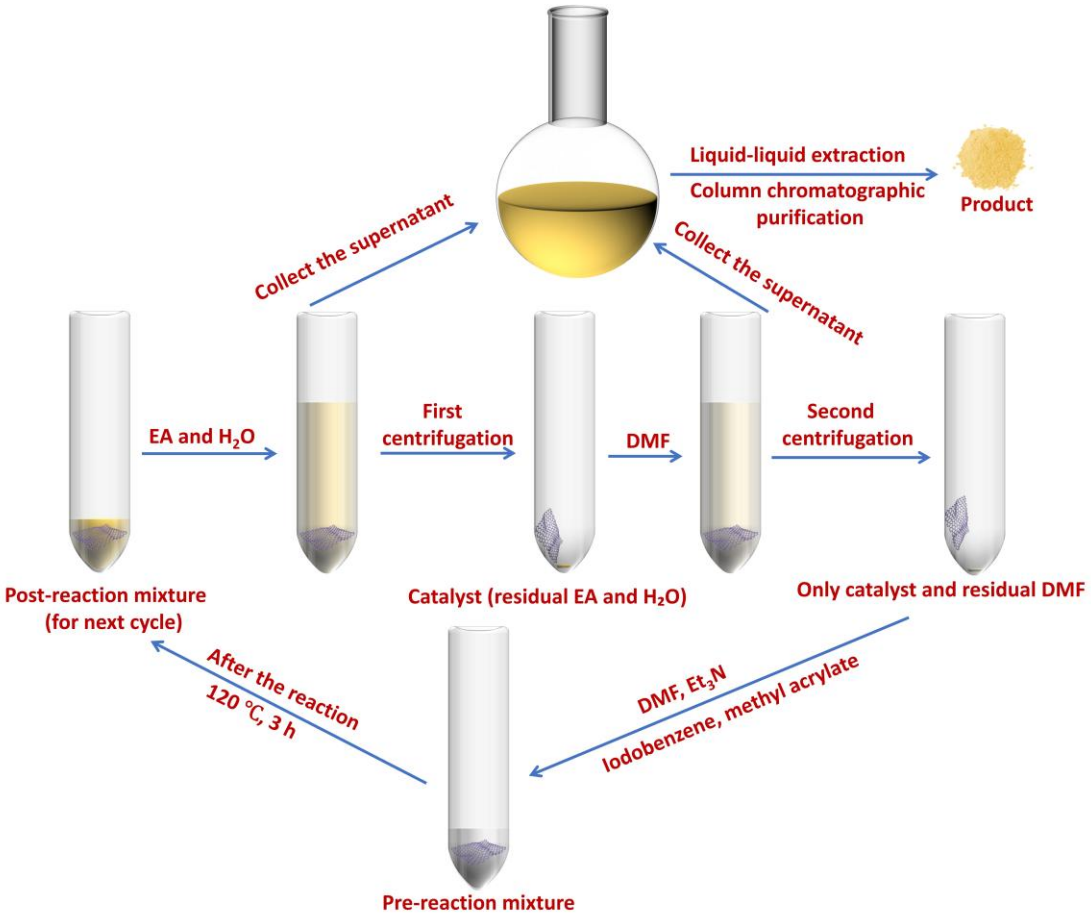


Figure S2. Catalyst recycling process of 0.018 mol% Pd SACs/NG in the Heck reaction (0.5 mmol scale).

The gram-scale cyclic reaction was carried out as follows (Figure S3): Pd SACs/NG (0.0007 mol%), triethylamine (Et_3N), iodobenzene and methyl acrylate were mixed together in the round bottom flask, followed by the addition of DMF solvent. The Heck coupling reaction was then carried out at 120 ℃ for 4.5 h. At the end of the reaction, the reaction mixture was transferred into a high-resistant centrifuge tube for the first centrifugation. After collecting the supernatant, ethyl acetate (EA) and H_2O were sequentially added to the same tube for second centrifugation, the upper organic layer was removed, followed by the addition of DMF for third centrifugation to eliminate residual H_2O via phase transfer. Ultimately, only the catalyst and residual DMF remained in the heat-resistant centrifuge tube. And then fresh DMF was then introduced to quantitatively transfer the residual catalyst to a new round-bottom flask. The supernatant obtained from three times centrifugation steps was subjected to liquid-liquid extraction to eliminate the DMF and H_2O, followed by final purification of the product via column chromatography and the desired product was obtained. In the next cycle, iodobenzene, methyl acrylate, Et_3N were added again into the round-bottom flask which was remained catalyst and DMF, and the reaction was carried out at 120 ℃ for 4.5 h. These steps were repeated in subsequent cycles. (The catalyst was maintained in the solvent DMF until it was transferred from the heat-resistant centrifuge tube to prevent any loss of catalyst.)

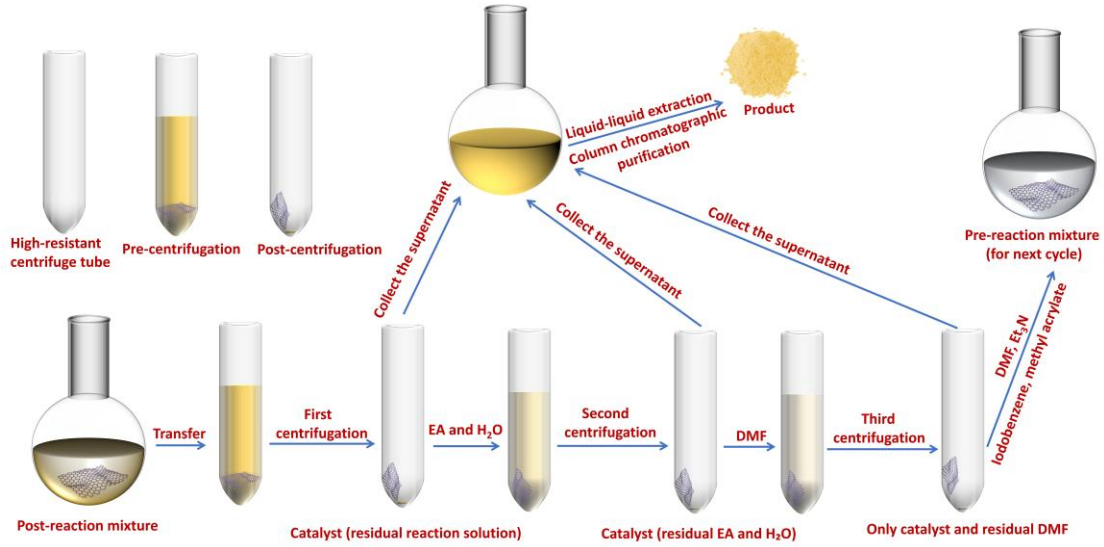


Figure S3. Catalyst recycling process of 0.0007 mol% Pd SACs/NG in the gram-scale Heck reaction.

VI. Characterization of graphene and Pd catalysts

By EXAFS fitting analyzed (**Figure 2a-d**), it was determined that the isolated Pd atoms in the Pd SACs/NG were tetragonally coordinated (Pd-N_4, with a coordination number of 4), with an average Pd-N bond length of 2.18 Å (**Table S2**). To further validate the coordination environment of Pd in Pd SACs/NG, its Pd K-edge EXAFS data were analyzed by wavelet transform (WT), which has high resolution in both k-space and R-space. Unlike the Pd foils and PdO (**Figure S4a-c**), the WT contour plots of the Pd SACs/NG (**Figure S4a**) showed only an intensity maximum at ~5 $Å^{-1}$ attributed to Pd-N coordination, while no Pd-Pd contribution was observed.

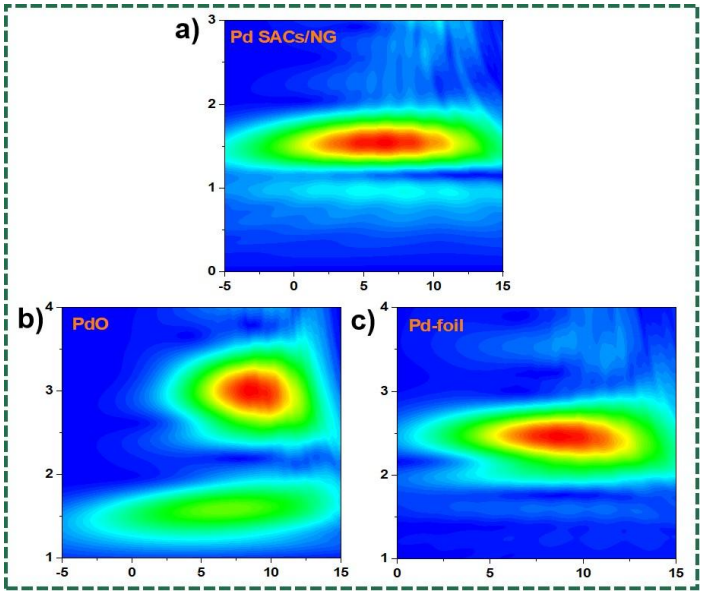


Figure S4. a-b) Wavelet transforms for the Pd K-edge EXAFS signals of a) Pd SACs/NG, b) PdO and c) Pd foil.

The surface properties of the Pd SACs/NG catalysts were investigated using X-ray photoelectron spectroscopy (XPS). The full XPS spectrum (**Figure S7a**) clearly shows the presence of C, O, N, and Pd elements in the catalysts, with no

impurity peaks observed. In the Pd 3d spectra (**Figure S7b**), the characteristic peaks of palladium are sharp and symmetric, corresponding to the $Pd_{5/2}$ and $Pd_{3/2}$ orbitals. The binding energies of these peaks are observed at 337.13 eV and 342.48 eV, respectively, indicating that Pd SACs/NG predominantly exists in the Pd^{2+} chemical state.[S3] Transmission electron microscopy (TEM) images of Pd SACs/NG are shown in **Figure S7c**. For comparison, the TEM image of pristine graphene (**Figure S6a**) reveals that the wrinkled structure of the carrier is preserved, with no visible particles observed. Palladium atoms are uniformly distributed on the graphene surface. The energy-dispersive X-ray spectroscopy (EDS) pattern of Pd SACs/NG (**Figure S7d–g**) shows uniform dispersion of Pd, N, and C on the graphene, confirming that nitrogen-doped graphene was formed during calcination and serves as a support for palladium.

For comparison, we prepared graphene-loaded palladium nanoparticle catalysts (Pd NPs/NG) by two-step formation of Pd-N-C, obvious Pd nano-particles can be observed on graphene as shown in **Figure S8a** and **Figure S8c**, it can be seen in its SAED that the Pd crystalline phase is present (insert in **Figure S8c**). The surface properties of the Pd NPs/NG catalysts were analyzed using XPS. The complete XPS full-spectrum mapping (**Figure S8b**) revealed the presence of C, O, N, and Pd elements in the catalysts without any detectable impurity peaks. In the Pd 3d spectra **(Figure S8d**), two distinct Pd signals were observed. The binding energies of the two peaks at the Pd 3d5/2 orbital were 335.12 eV and 337.18 eV, corresponding to Pd^0 and Pd^{2+}, respectively, with a ratio of 2:3.[S4] After fitting the C 1s fine spectra of Pd SACs/NG and Pd NPs/NG (**Figure S9**), it was found that the C element primarily existed in the form of graphitized carbon (C-C), C-N bonds, and C-O bonds. Similarly, fitting the N 1s fine spectra (**Figure S10**) revealed that the N element was predominantly present as pyridine nitrogen, pyrrole nitrogen, and graphitized nitrogen, indicating successful nitrogen doping in the graphene structure.[S5]

XRD analysis of pristine graphene, Pd SACs/NG, and Pd NPs/NG **(Figure S11**) showed no diffraction peaks corresponding to Pd for Pd SACs/NG, suggesting that Pd is highly dispersed on the carbon support. In contrast, the XRD spectrum of Pd NPs/NG exhibited characteristic peaks for Pd nanoparticles, with distinct diffraction peaks at 40.2°, 46.8°, and 68.3° corresponding to the Pd (111), (200), and (220) planes, confirming the crystalline nature and structure of the Pd nanoparticles. Raman spectroscopy of pristine graphene, Pd SACs/NG, and Pd NPs/NG (**Figure S12**) showed high intensity ratios of the D-band (~1327 cm^{-1}) to the G-band (~1588 cm^{-1}), which reflects the defect density in the graphene. The ID/IG ratio clearly indicated that the nitrogen-doped graphene-supported single-atom catalysts exhibited the highest degree of defects, likely due to the highly dispersed nature of the single-atom catalysts and their strong interaction with the nitrogen-doped graphene substrate. Additionally, the Pd content in Pd SACs/NG and Pd NPs/NG was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), yielding values of 0.46 wt% and 4.2 wt%, respectively.

Sample	shell	CN[a]	R[b](Å)	σ²[c](Å²)	ΔE$_0$[d](eV)	R factor
Pd-foil	Pd-Pd	12.00	2.73±0.03	0.0046	6.8	0.002
Pd SACs	Pd-N	3.95±0.5	2.18±0.08	0.0059	2.9	0.017
PdO	Pd-O	4	2.00±0.02	0.0011	3.59	0.010
	Pd-Pd$_1$	4	3.04±0.01	0.0029		
	Pd-Pd$_2$	8	3.44±0.01	0.0069		

Table S2. EXAFS fitting parameters at the Pd K-edge for various samples（S_0^2=0.9）. [a]*CN*: coordination numbers; [b]*R*: bond distance; [c]σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. R factor: goodness of fit. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as CN±20%; R ± 1%; σ² ± 20%.

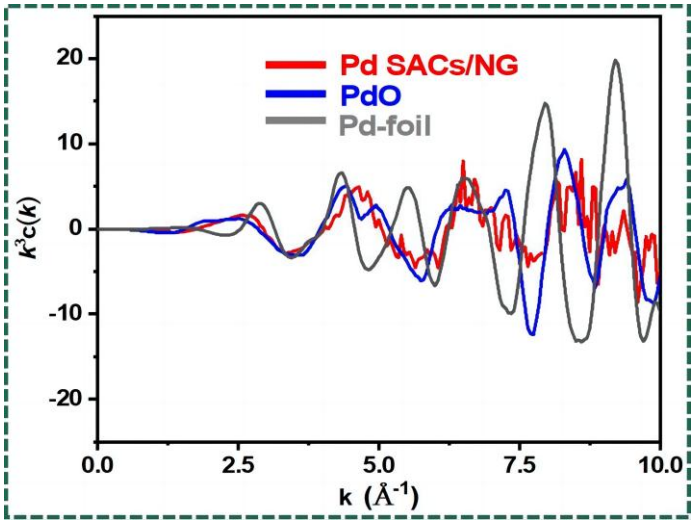


Figure S5. The EXAFS spectra of Pd SACs/NG, PdO and Pd foil at k space.

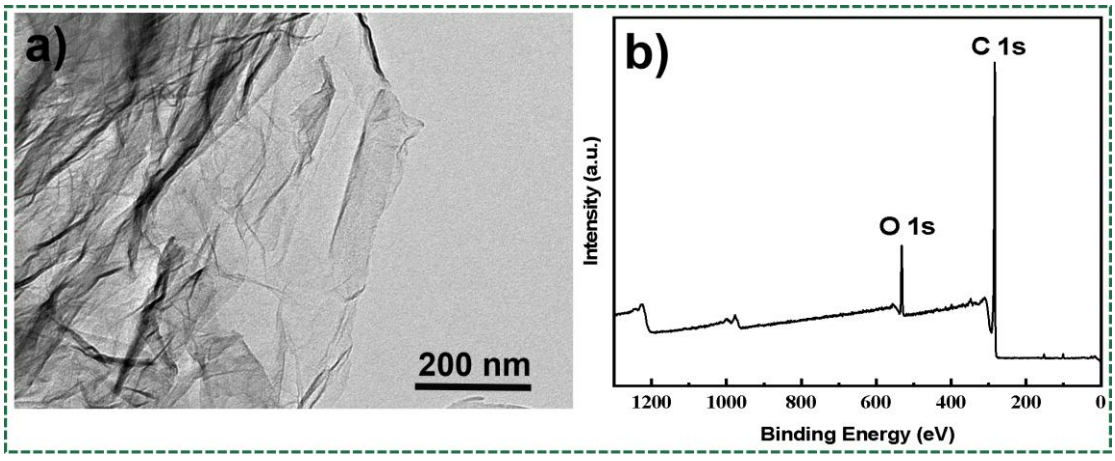


Figure S6. a) TEM image of raw graphene and b) XPS survey of raw graphene.

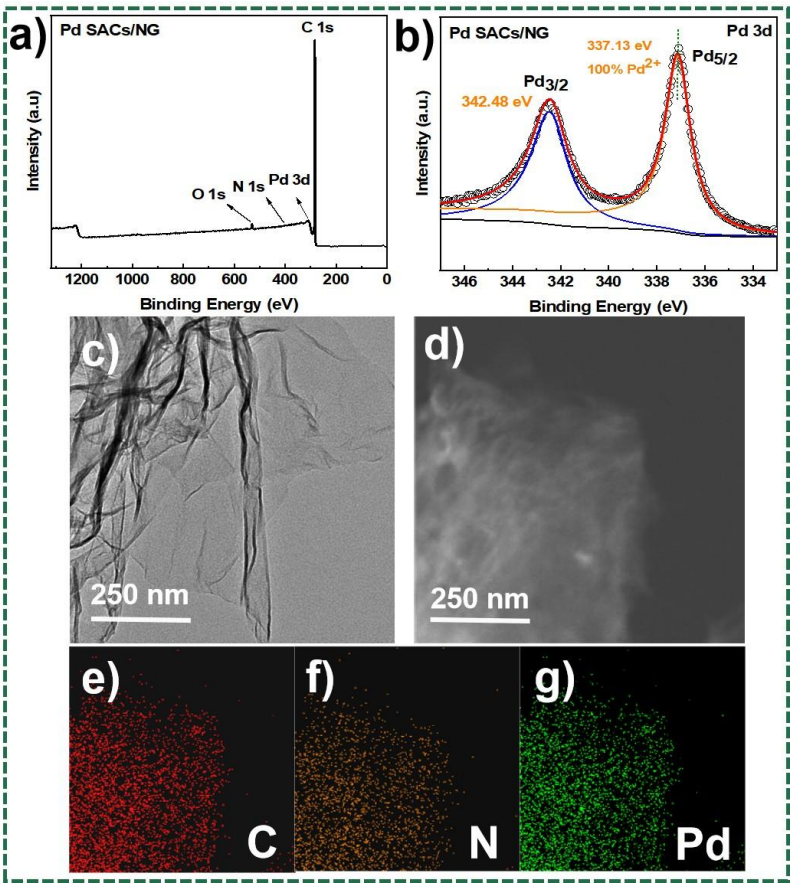


Figure S7. characterization of Pd SACs/NG. a) XPS spectra of Pd 3d spectrum and b) XPS survey; c) TEM image of Pd SACs/NG, d~g) EDS mapping of Pd SACs/NG.

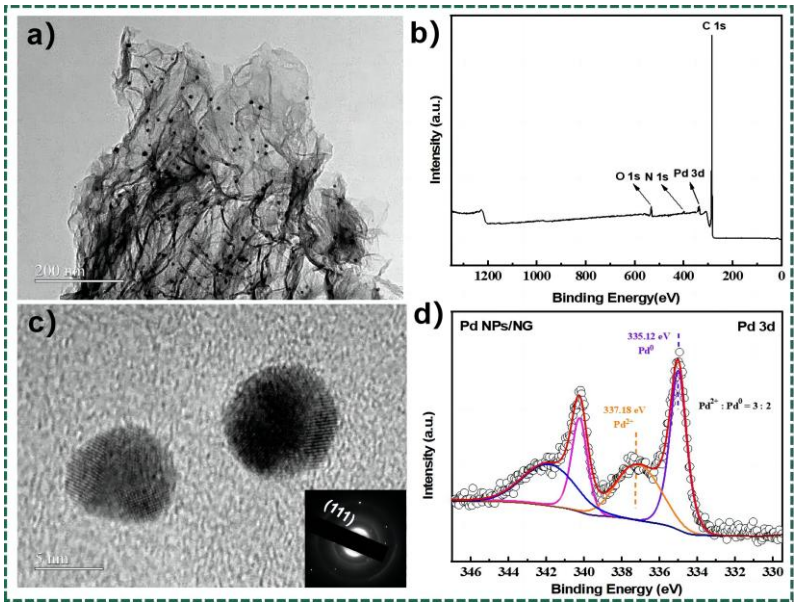


Figure S8. a) TEM image of Pd NPs/NG, c) HRTEM image and corresponding SEAD mode, b) XPS full spectrum image of Pd NPs/NG, d) XPS Pd 3d image of Pd NPs/NG.

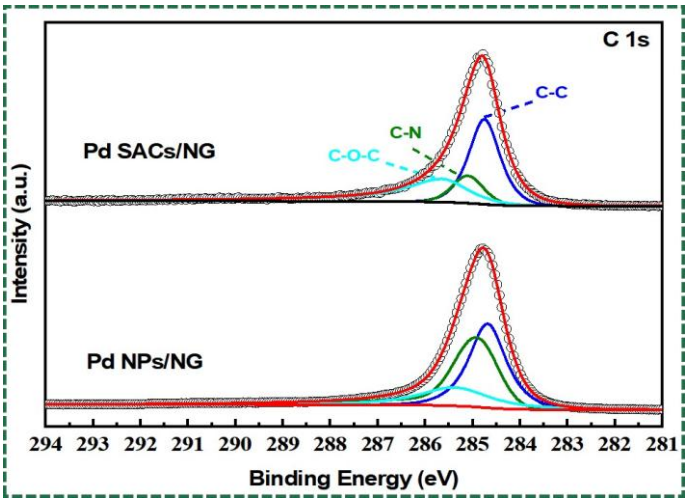


Figure S9. XPS C1s spectra of Pd SACs/NG and Pd NPs/NG.

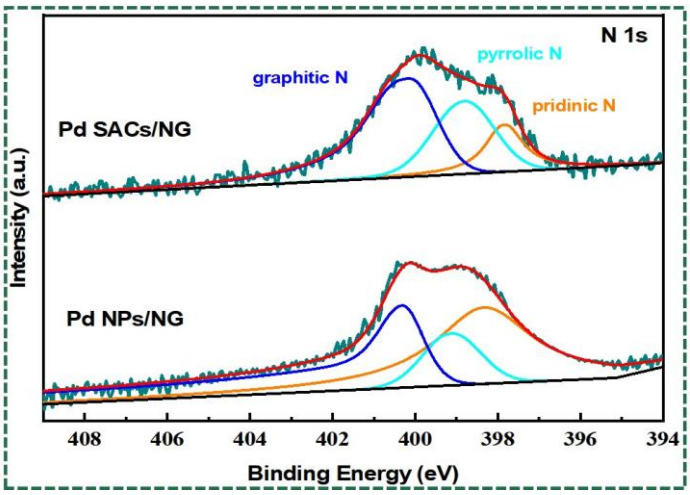


Figure S10. XPS N1s spectra of Pd SACs/NG and Pd NPs/NG.

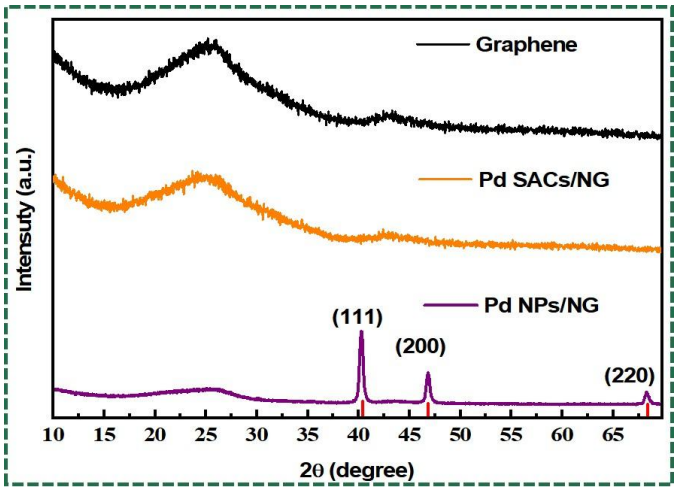


Figure S11. XRD patterns of raw graphene, Pd SACs/NG and Pd NPs/NG.

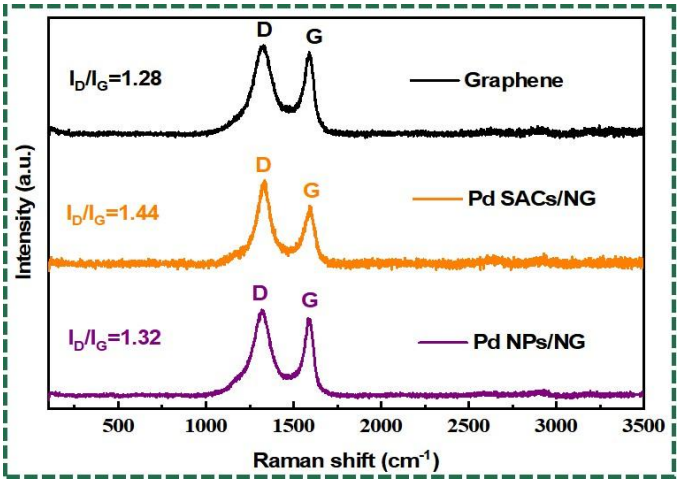


Figure S12. Raman patterns of raw graphene, Pd SACs/NG and Pd NPs/NG.

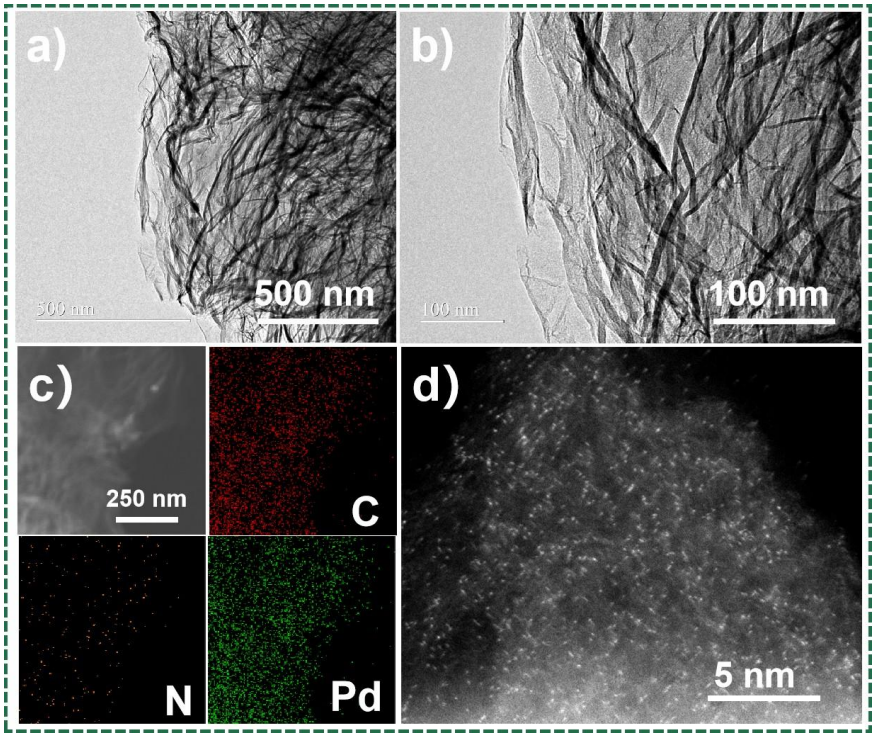


Figure S13. a) and b) TEM image, c) EDS mapping spectra, d) AC-HAADF-STEM image were obtained after Pd SACs/NG participated in the reaction.

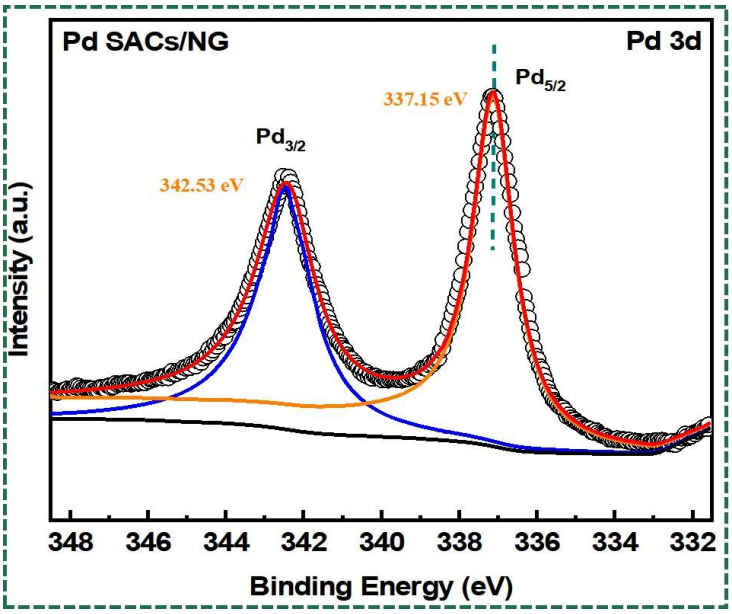


Figure S14. Pd 3d XPS spectra of Pd SACs/NG after the reaction.

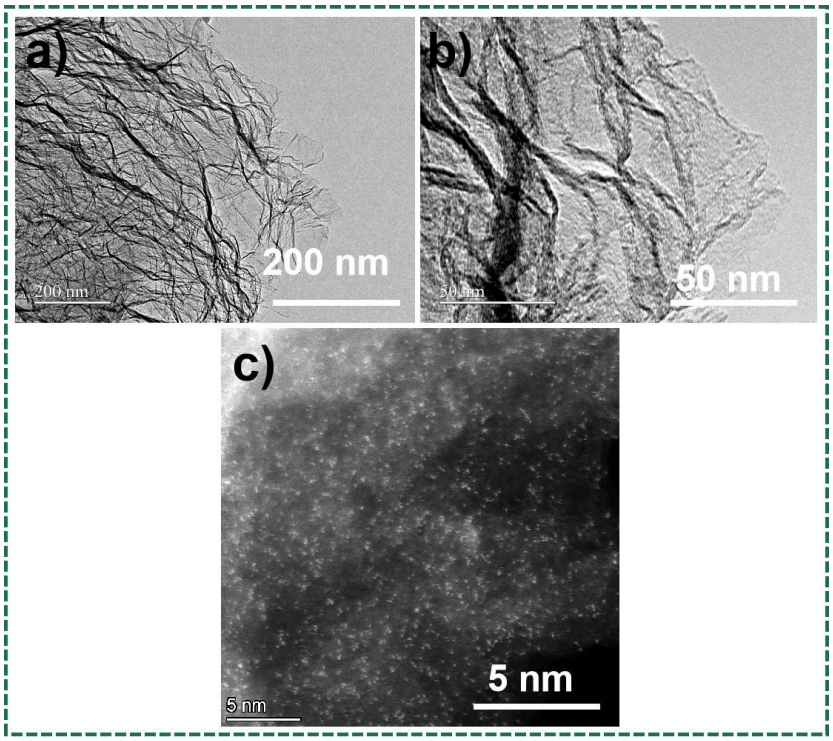
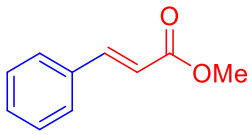


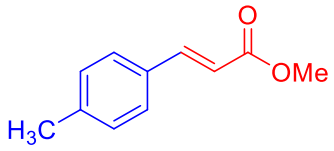
Figure S15. a) and b) TEM images and c) AC-HAADF-STEM image after 15 cycles of reaction tests of Pd SACs/NG.

VII. The characterization of product 3.



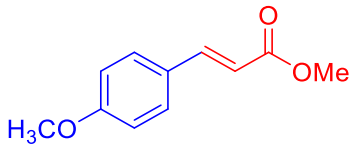
3a, 94%

Methyl-cinnamate (3a, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 76.2 mg in 94% yield as a yellow solid, m.p.: 260 - 262 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.34 – 7.27 (m, 3H), 6.41 (d, *J* = 16.1 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 144.72, 134.34, 130.22, 128.82, 128.05, 117.78, 51.48.



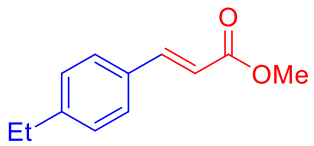
3b, 95%

Methyl-4-methylcinnamate (3b, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 83.7 mg in 95% yield as light yellow solid, m.p.: 273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 143.81, 139.62, 130.62, 128.56, 127.02, 50.51, 20.37.



3c, 89%

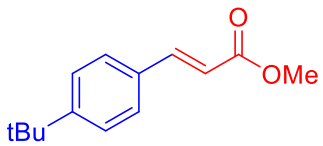
Methyl-p-methoxycinnamate (3c, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 85.5 mg in 89% yield as light yellow solid, m.p.: 311 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.73, 161.40, 144.51, 129.72, 127.10, 115.24, 114.32, 55.32, 51.53.



3d, 95%

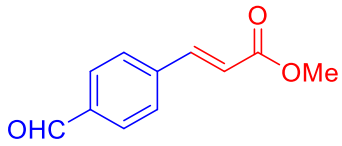
Methyl-3-(4-ethylphenyl)-2-propenoate (3d, known compound).[S1b] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 90.4 mg in 95% yield as light yellow solid, m.p.: 288.2 ± 9°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.0 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H),

6.29 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).



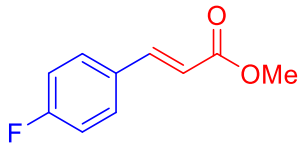
3e, 99%

Methyl-3-(4-tert-butylphenyl) prop-2-enoate (3e, known compound).[S1n] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 108.1 mg in 99% yield as light yellow solid, m.p.: 300±11 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 153.82, 144.78, 131.67, 127.97, 125.87, 116.91, 51.58, 34.87, 31.16.



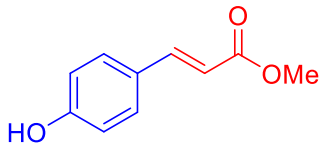
3f, 87%

4-Formylcinnamic acid methyl ester (3f, known compound).[S1i] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 82.7 mg in 87% yield as light yellow solid, m.p.: 334.1±25.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.63 (m, 3H), 6.54 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.39, 166.71, 143.05, 139.96, 137.17, 130.11, 128.49, 120.93, 51.89.



3g, 88%

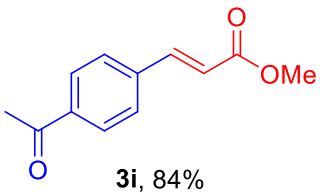
Methyl-3-(4-fluorophenyl) acrylate (3g, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 79.3 mg in 88% yield as light yellow liquid, m.p.: 130-133 ℃ (Press: 15 Torr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.1 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.10 – 7.02 (m, 2H), 6.35 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.62 (tt, *J* = 8.3, 5.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.22, 165.12, 162.62, 143.48, 130.63, 130.60, 129.96, 129.88, 117.54, 117.51, 116.10, 115.88, 51.65.



3h, 91%

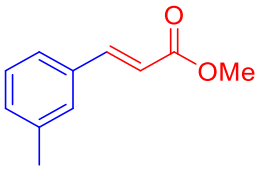
Methyl-4-hydroxycinnamate (3h, known compound).[S1m] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 81.1 mg in 91% yield as light yellow liquid, m.p.: 306.6±17 ℃. ^{1}H NMR (400 MHz, DMSO) δ 10.04 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 3.71 (s,

3H). ^{13}C NMR (101 MHz, DMSO) δ 167.51, 160.33, 145.20, 130.75, 125.54, 116.24, 114.37, 51.65.



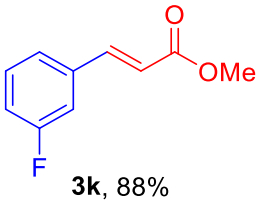
3i, 84%

2-Propenoic acid, 3-(4-acetylphenyl)-, methyl ester (3i, known compound).[S1h] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 85.8 mg in 84% yield as Off-white to beige soliid, m.p.: 347,4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 3.73 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.27, 166.88, 143.26, 138.66, 138.00, 128.84, 128.13, 120.30, 51.87, 26.65.



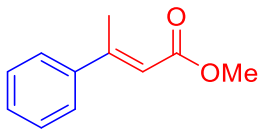
3j, 95%

Methyl-3-methylcinnamate (3j, known compound).[S1i] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 83.7 mg in 95% yield as light yellow solid, m.p.: 271±9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.9 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.24 (d, *J* = 17.0 Hz, 1H), 3.69 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.44, 142.52, 137.65, 133.35, 130.80, 130.05, 126.40, 126.36, 118.82, 51.65, 19.75.



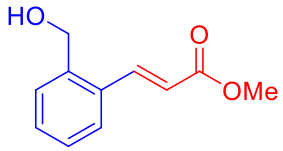
3k, 88%

Methyl-3-(3-fluorophenyl) acrylate (3k, known compound).[S1l] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 79.3 mg in 88% yield as clear liquid, m.p.: 133 ℃/17 mm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 16.0 Hz, 1H), 7.26 (m, *J* = 7.9, 5.7 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.09 (m, 1H), 7.03 – 6.95 (m, 1H), 6.34 (d, *J* = 16.0 Hz, 1H).^{19}F NMR (377 MHz, $CDCl_3$) δ -112.51 (td, *J* = 9.0, 5.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 164.22, 161.77, 143.42, 136.58, 130.40, 124.08, 119.20, 117.24, 117.03, 114.39, 114.18, 51.79.



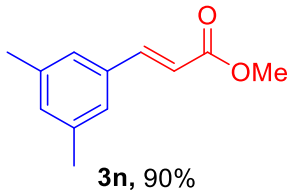
3l, 93%

2-Butenoic acid, 3-phenyl-, methyl ester (3l, known compound).[S1e] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 81.9 mg in 93% yield as light yellow liquid, m.p.: 250-300 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.28 (dd, *J* = 5.1, 2.3 Hz, 3H), 6.06 (d, *J* = 1.4 Hz, 1H), 3.66 (s, 3H), 2.50 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 155.91, 142.17, 129.06, 128.53, 126.32, 116.71, 51.12, 17.99.



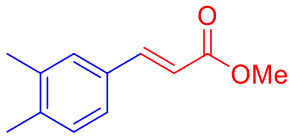
3m, 88%

2-Propenoic acid, 3-[2-(hydroxymethyl) phenyl], methyl ester (3m, known compound).[S1i] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 84.6 mg in 88% yield as light yellow solid, m.p.: 335±22 ℃ . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 15.9 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.25 (m, *J* = 14.9, 9.1, 7.4 Hz, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 4.68 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 141.83, 139.75, 132.95, 130.22, 128.76, 128.15, 126.74, 119.52, 62.66, 51.81.



3n, 90%

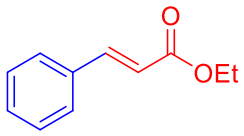
Methyl-3,5-dimethylcinnamate (3n, known compound).[S1c] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 79.3 mg in 90% yield as light yellow solid, m.p.: 371℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 16.0 Hz, 1H), 7.01 (s, 2H), 6.89 (s, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 3.68 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 144.14, 137.30, 133.25, 131.03, 124.91, 116.25, 50.51, 20.09.



3o, 86%

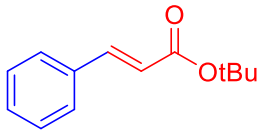
Methyl-3,4-dimethylcinnamate (3o, known compound).[S1a] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 75.8 mg in 86% yield as light yellow solid, m.p.: 371℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.0 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 3.65 (s, 3H), 2.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 145.04, 139.40, 137.04, 132.07, 130.15, 129.31,

125.70, 116.45, 51.49, 19.72.



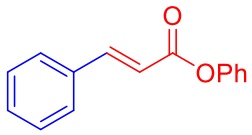
3p, 95%

Ethyl-cinnamate (3p, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 83.7 mg in 95% yield as light yellow liquid, m.p.: 271 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, *J* = 15.3, 11.7, 4.8 Hz, 1H), 7.51 – 7.34 (m, 2H), 7.33 – 7.17 (m, 3H), 6.44 – 6.29 (m, 1H), 4.27 – 4.10 (m, 2H), 1.36 – 1.14 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.62, 144.37, 134.40, 130.10, 128.77, 127.97, 118.23, 60.26, 14.24.



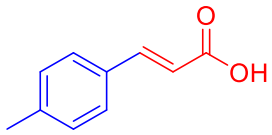
3q, 97%

Tert-butyl cinnamate (3q, known compound).[S1j] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 99.1 mg in 97% yield as light yellow liquid, m.p.: 85℃/0.12 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.36 (m, *J* = 5.1, 1.9 Hz, 3H), 6.37 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.35, 143.55, 134.69, 129.96, 128.83, 127.96, 120.21, 80.51, 28.22.



3r, 97%

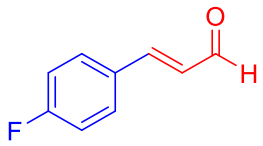
2-Propenoic acid, 3-phenyl-, phenyl ester (3r, known compound).[S1g] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 108.8 mg in 97% yield as white to light yellow solid, m.p.: 325.66℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.1 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.29 – 7.21 (m, 5H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.04 (dd, *J* = 8.7, 1.2 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.23, 149.74, 145.44, 133.04, 129.59, 128.34, 127.88, 127.21, 124.67, 120.57, 116.20.



3s, 90%

3-(4-methylphenyl) acrylic acid (3s, known compound).[S1m] The residue was purified by flash chromatography (eluent: PE : EA = 10 : 1) to give the desired product 73 mg in 90% yield as white solid, m.p.: 300±11 ℃ . ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.34 (s, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.5 Hz,

1H), 6.43 (d, *J* = 15.9 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.86, 147.32, 138.66, 134.04, 131.64, 129.08, 128.88, 125.64, 117.17, 21.34.



3t, 51%

4-Fluorocinnamalaehyde (3t, known compound).[S1f] The residue was purified by flash chromatography (eluent: PE : EA = 50 : 1) to give the desired product 38.3 mg in 51% yield as white solid, m.p.: 246±15 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.65 (dd, *J* = 16.1, 7.7 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -107.73 – -107.85 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.50, 165.63, 163.12, 151.39, 130.57, 130.49, 130.35, 130.32, 128.29, 128.27, 116.40, 116.18.

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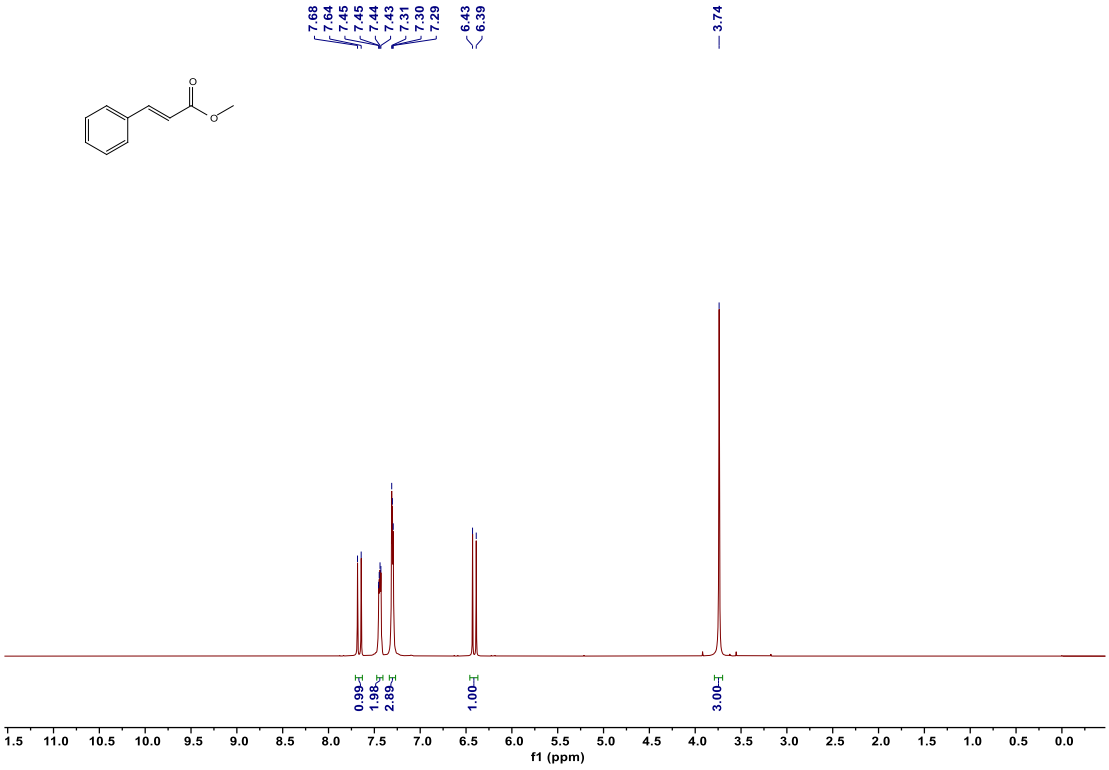
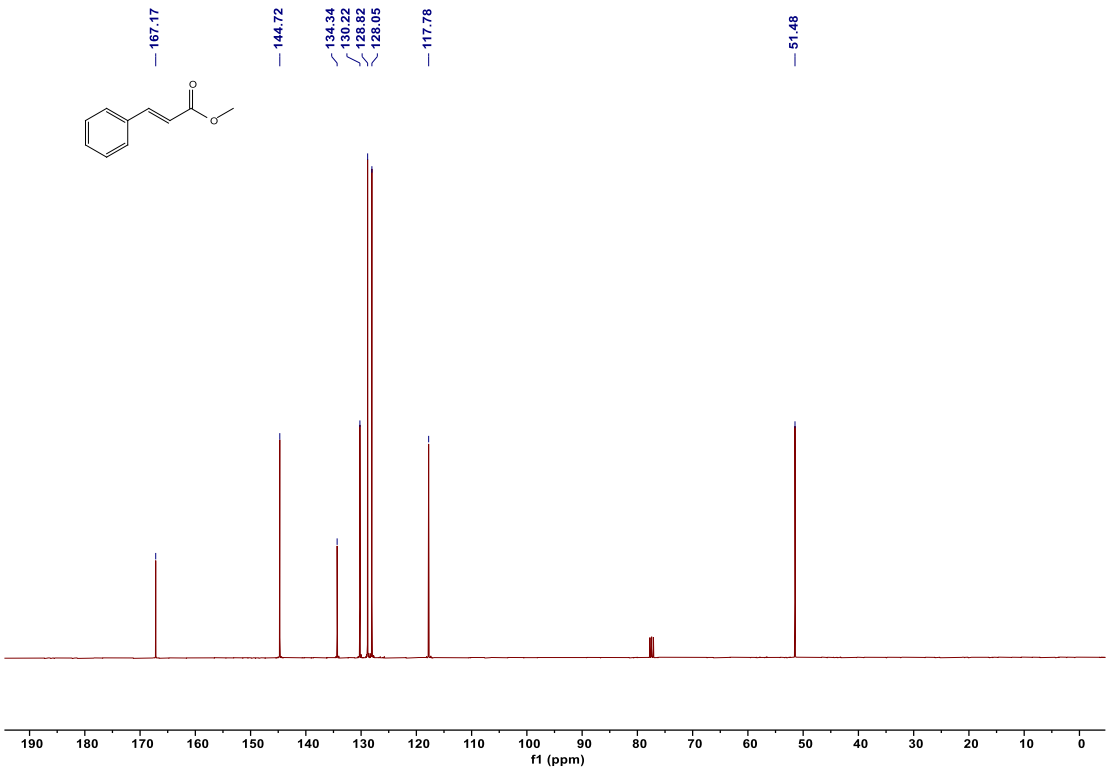
IX. ^{1}H, ^{13}C and ^{19}F NMR spectra of product 3.

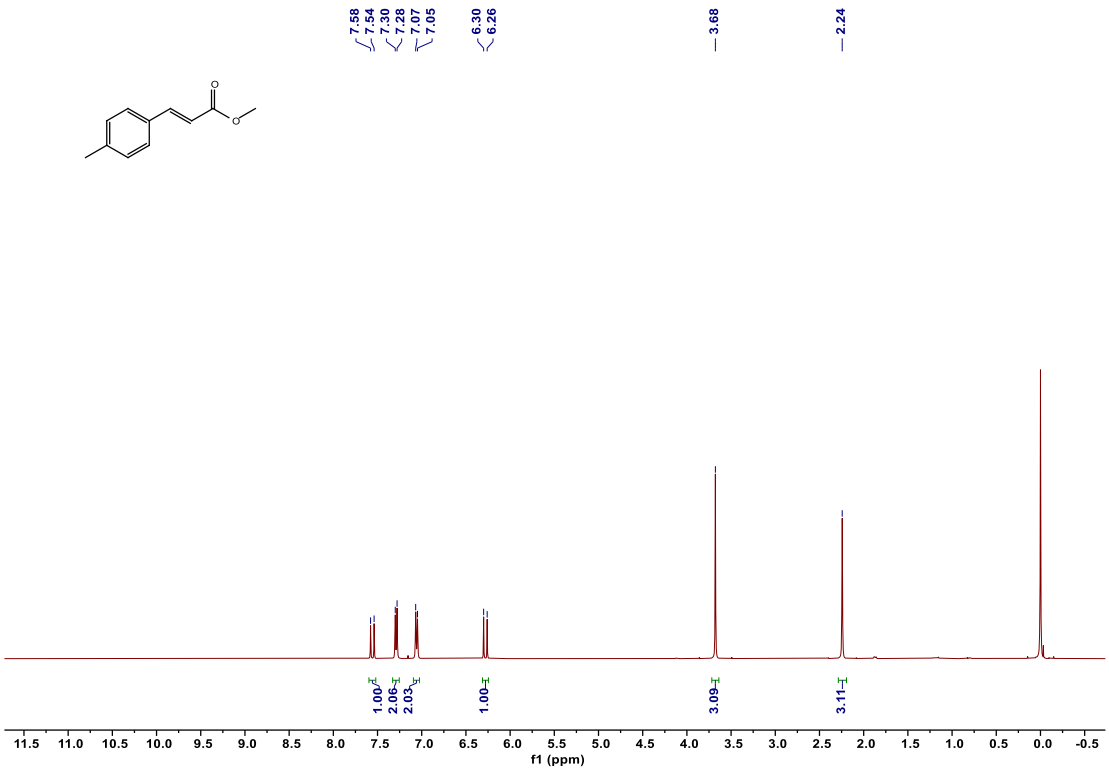
^{1}H NMR (400MHz, $CDCl_3$)



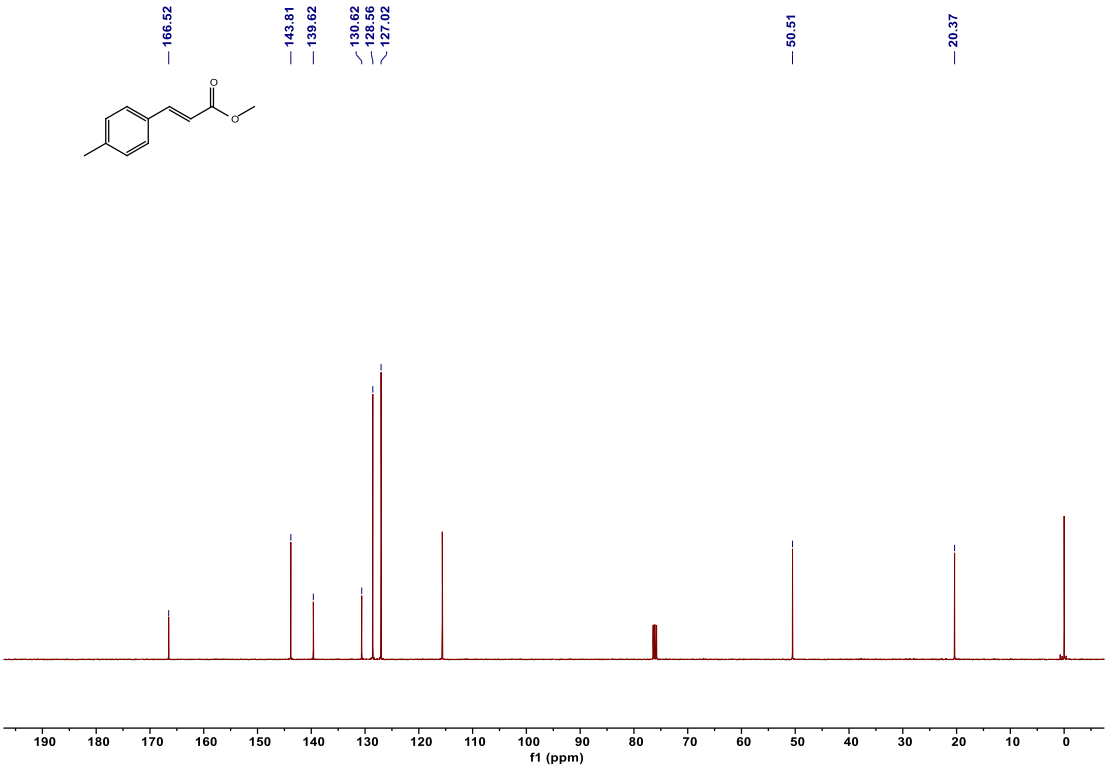
^{13}C NMR (101 MHz, $CDCl_3$)



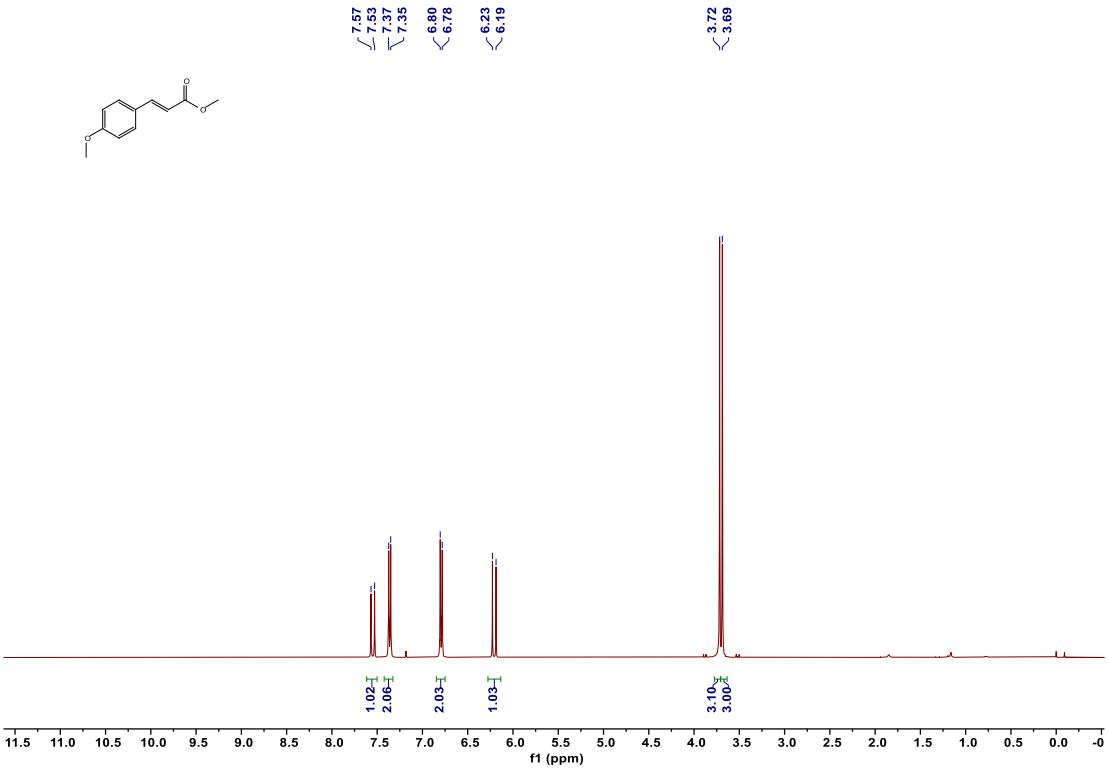
^{1}H NMR (400MHz, $CDCl_3$)



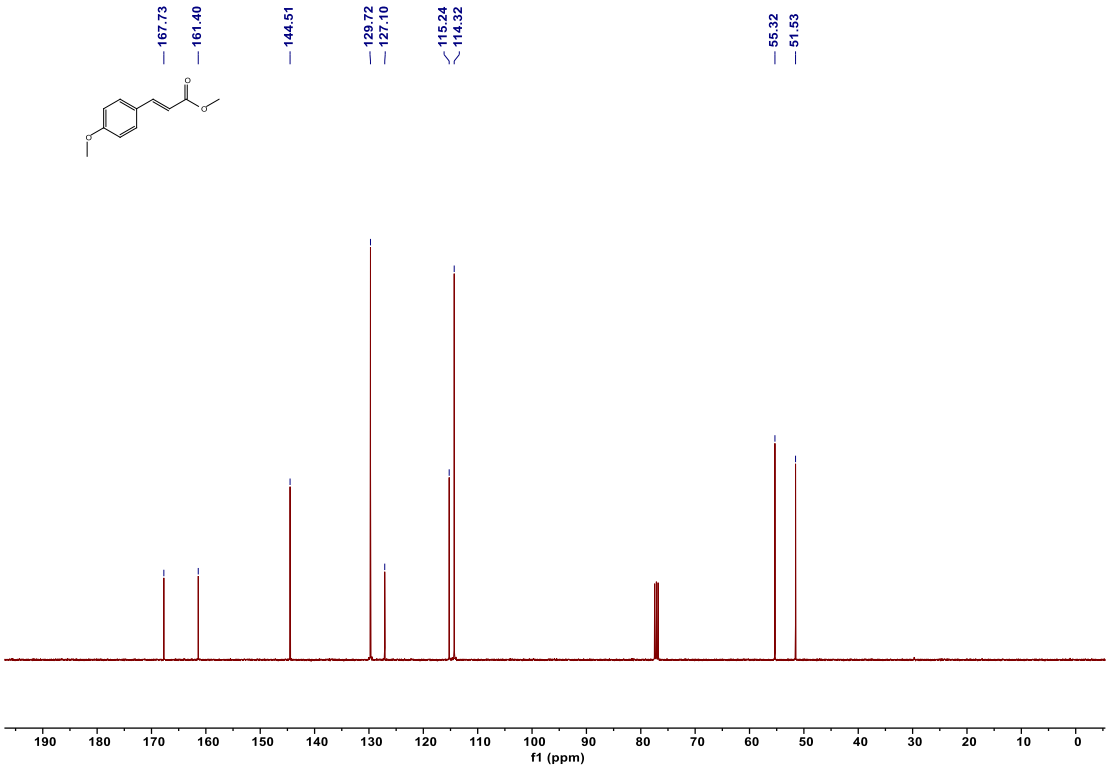
^{13}C NMR (101 MHz, $CDCl_3$)



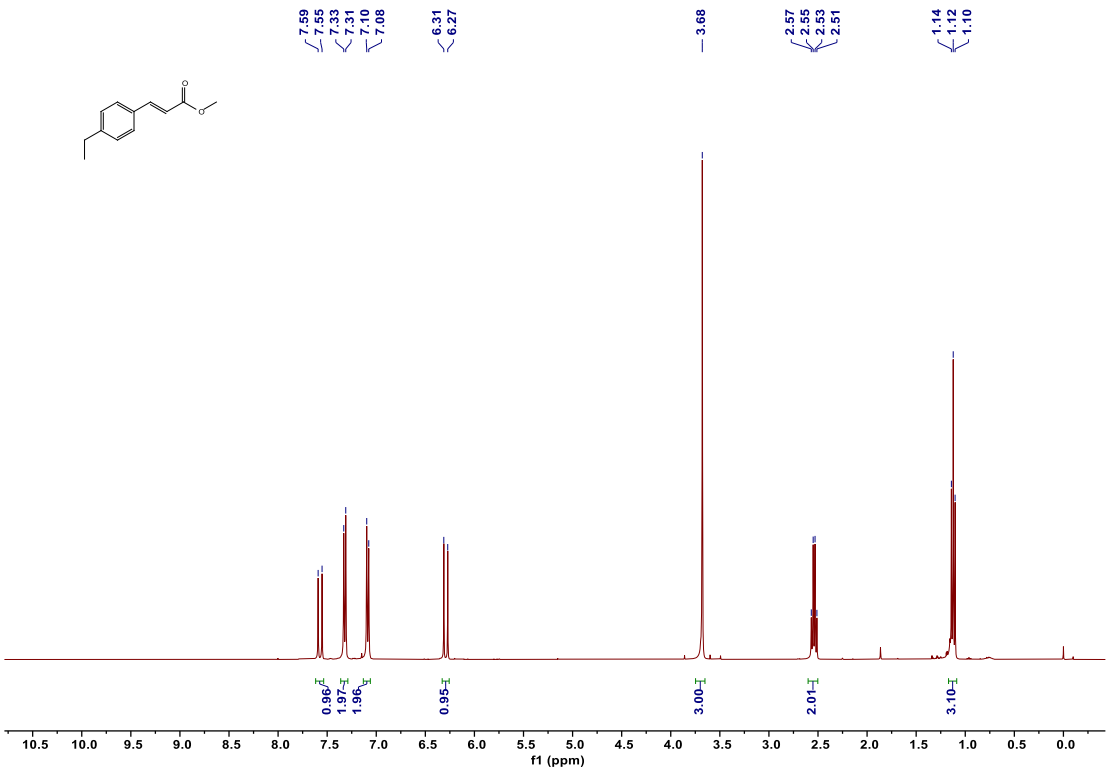
^{1}H NMR (400MHz, $CDCl_3$)



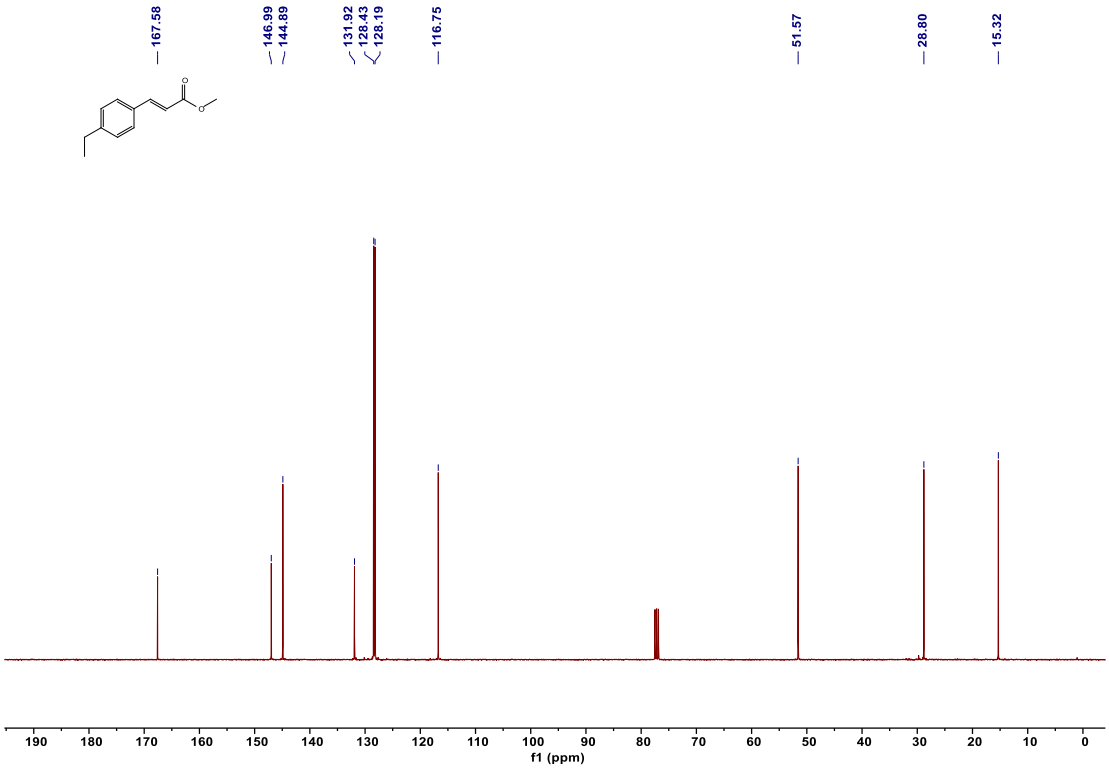
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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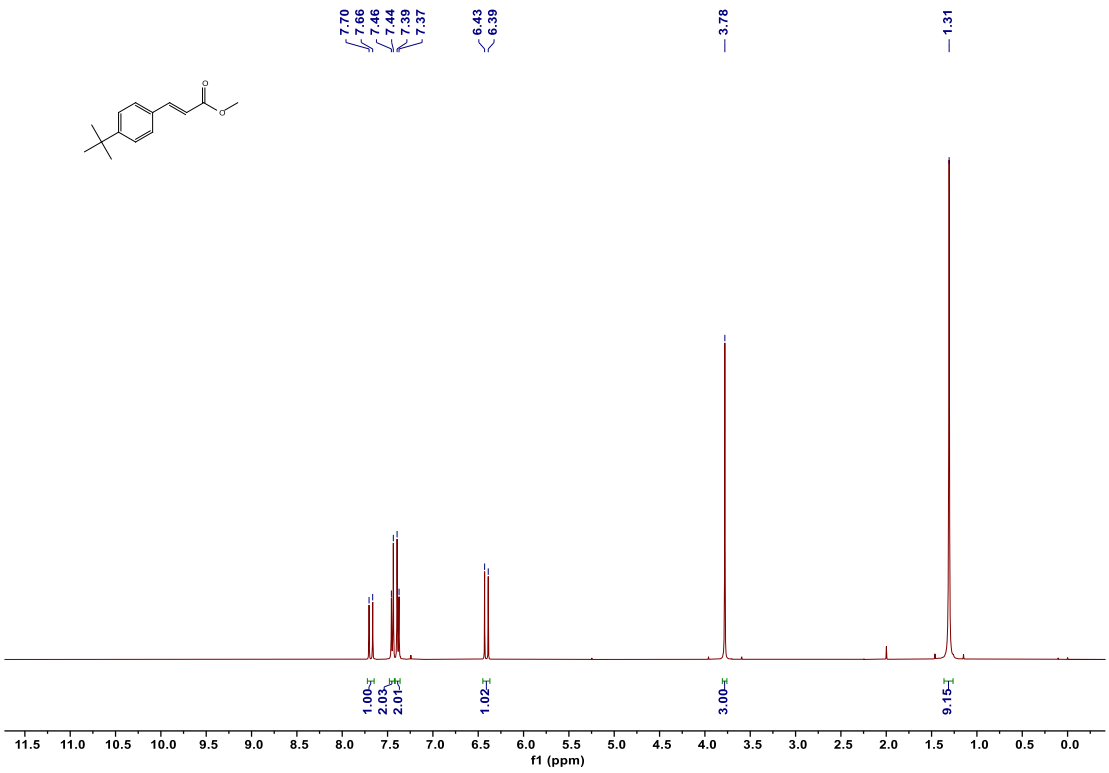

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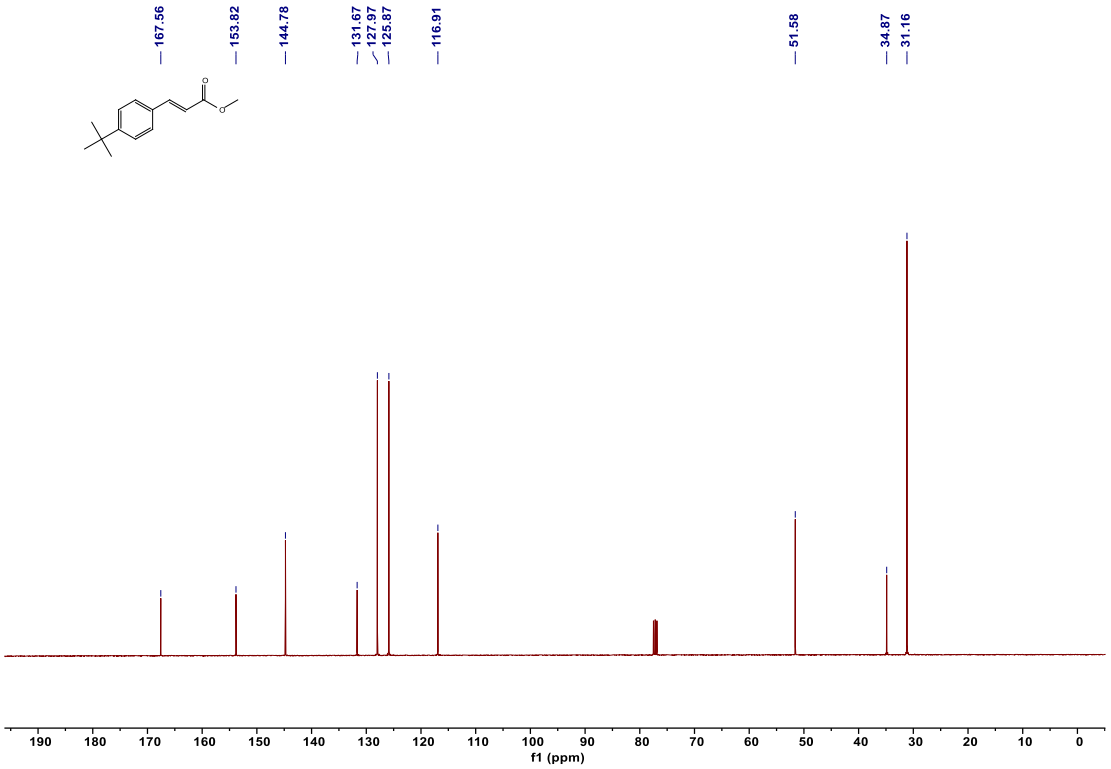

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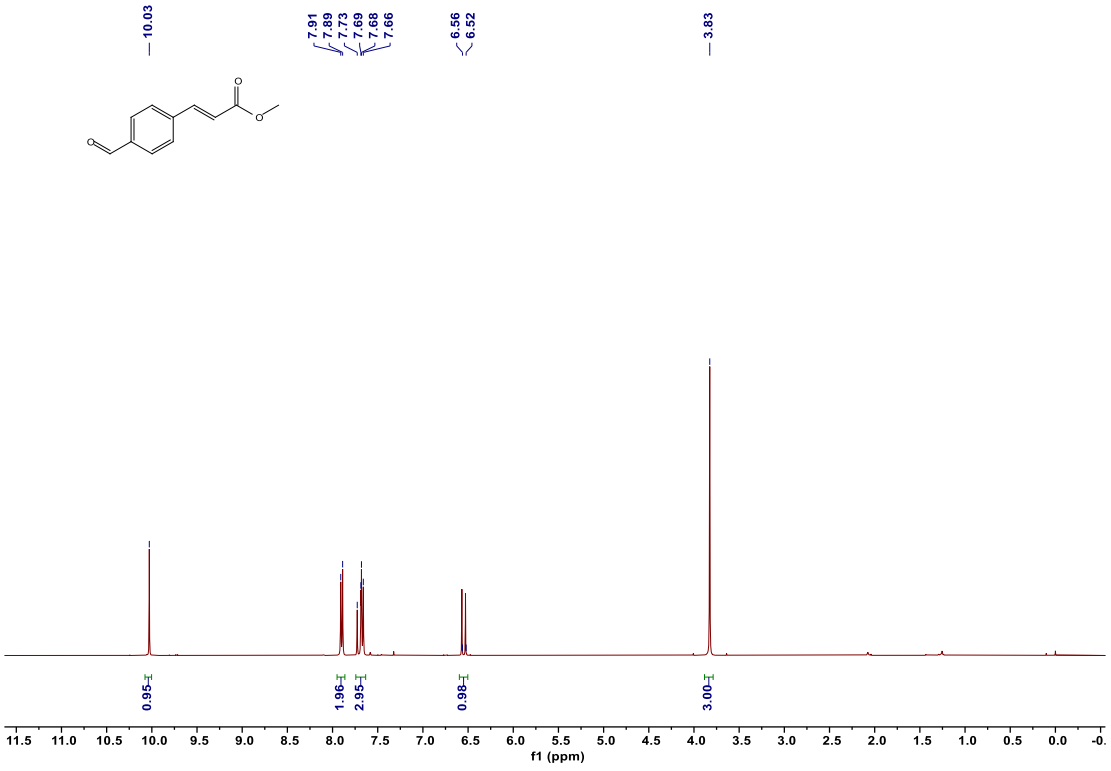
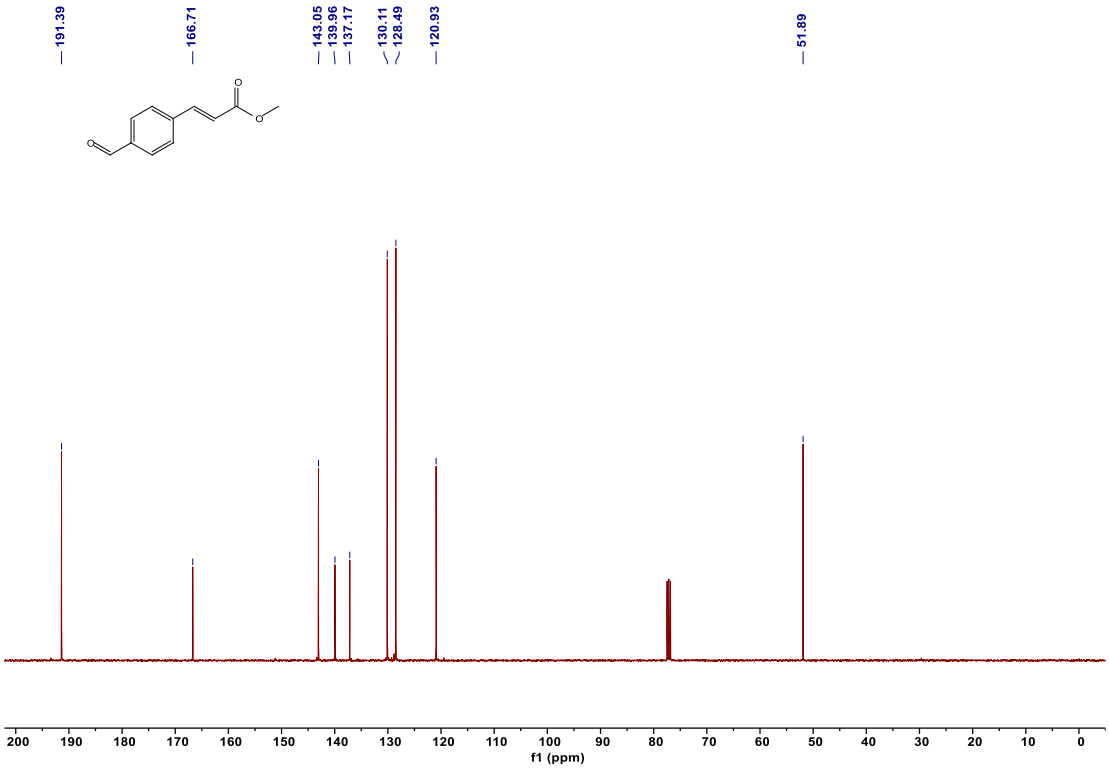
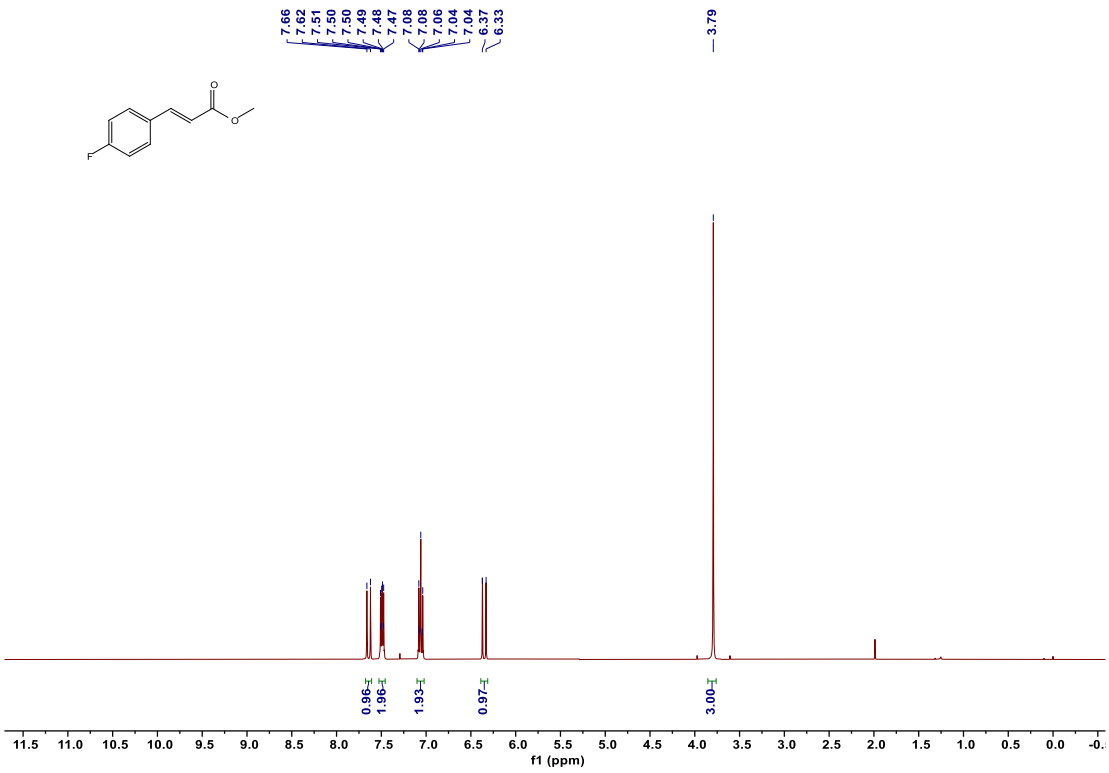


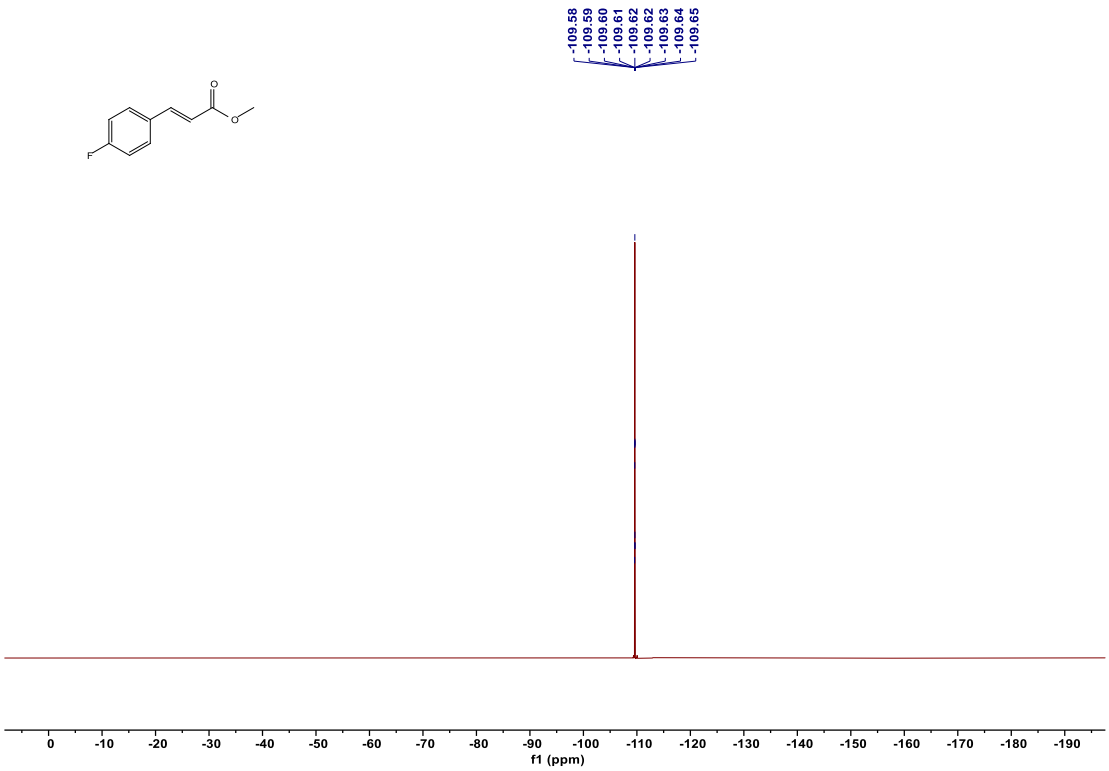
^{13}C NMR (101 MHz, $CDCl_3$)



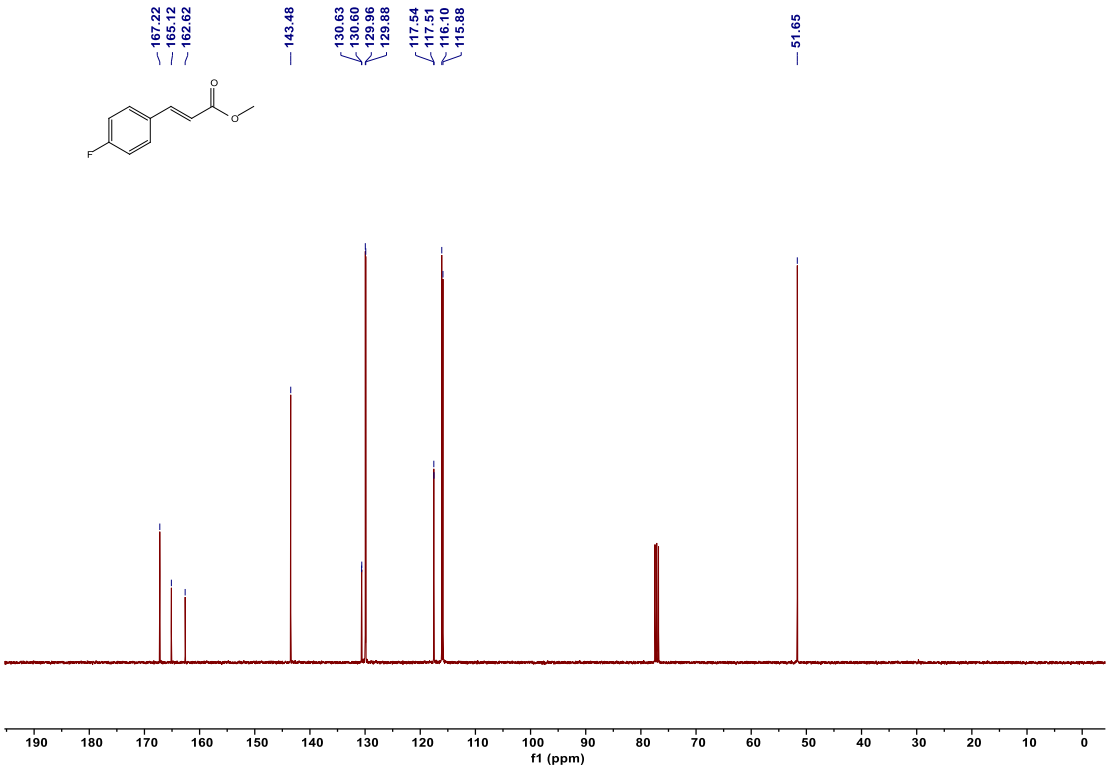
^{1}H NMR (400MHz, $CDCl_3$)



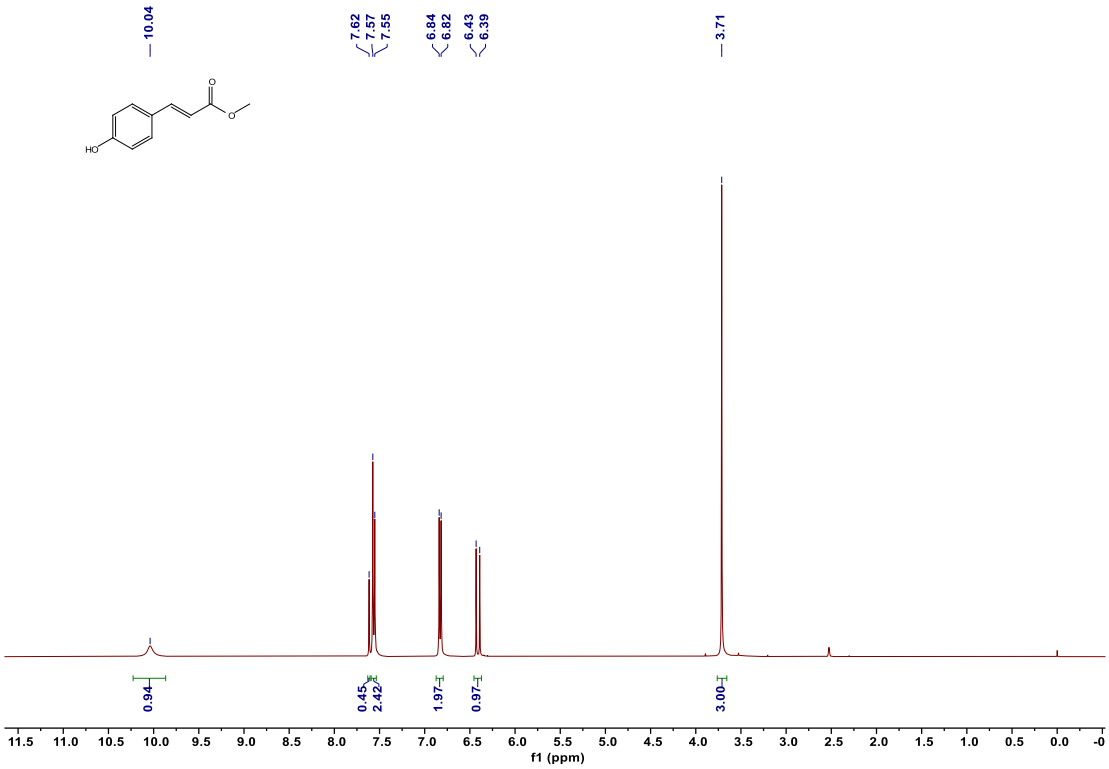
^{19}F NMR (377 MHz, $CDCl_3$)



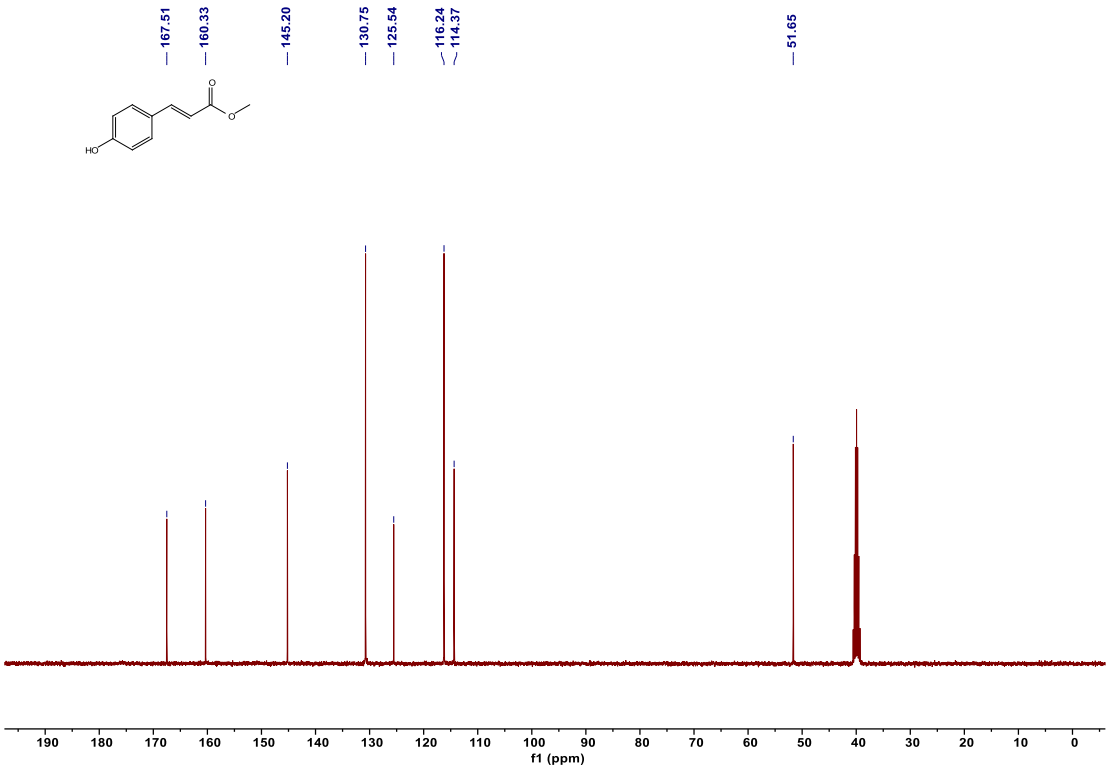
^{13}C NMR (101 MHz, $CDCl_3$)



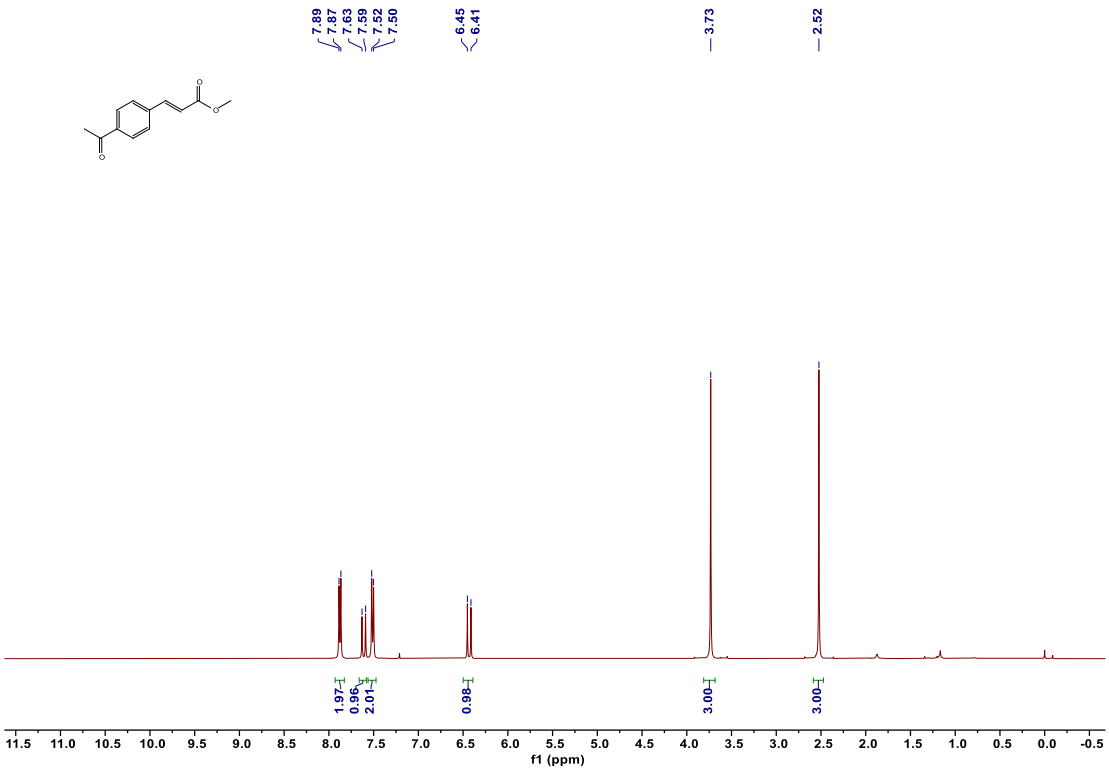
^{1}H NMR (400MHz, DMSO)



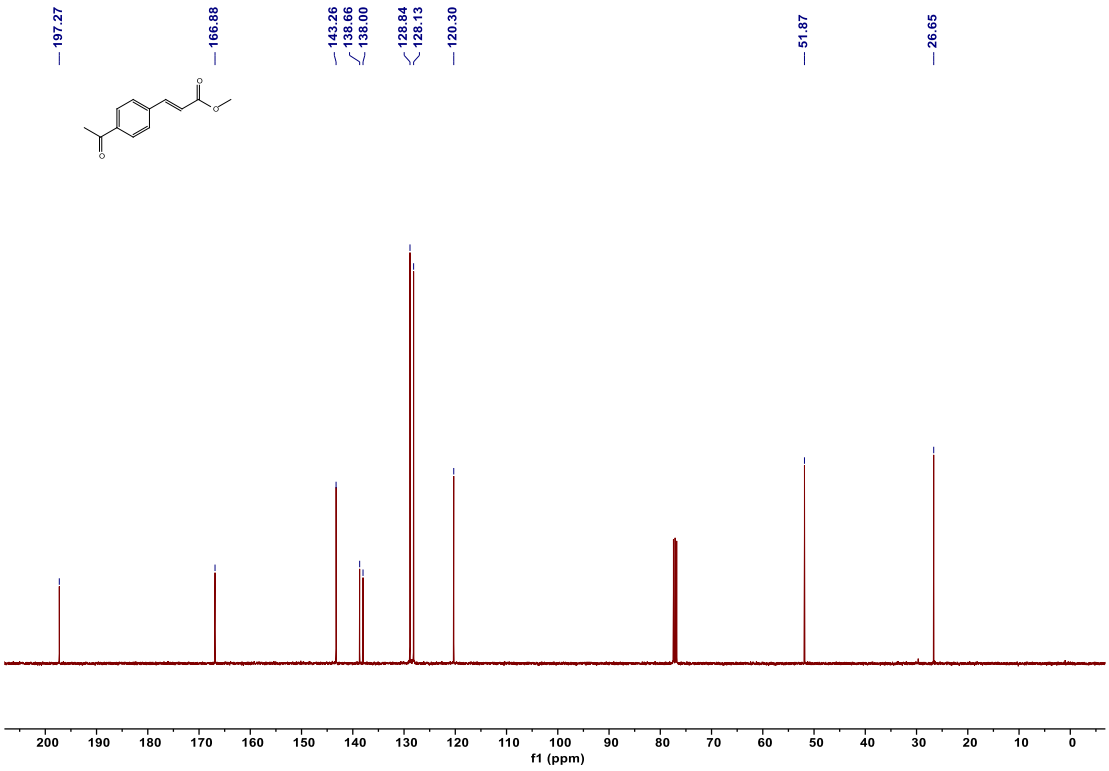
^{13}C NMR (101 MHz, DMSO)



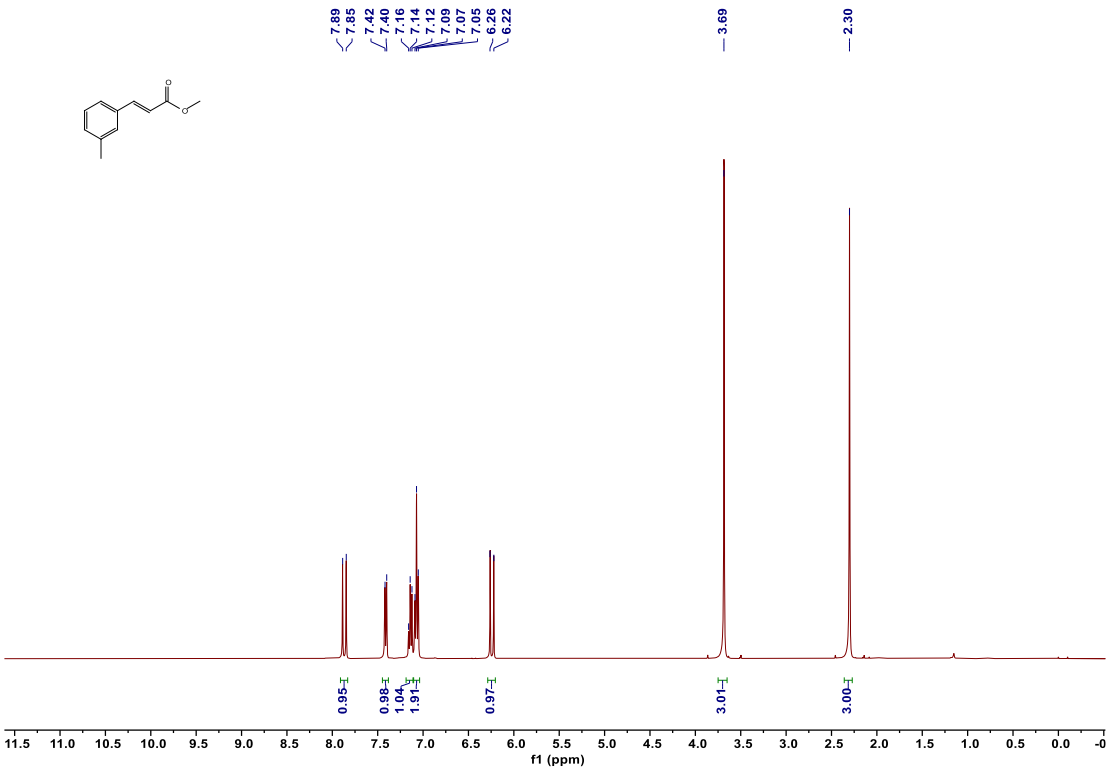
^{1}H NMR (400MHz, $CDCl_3$)



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



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



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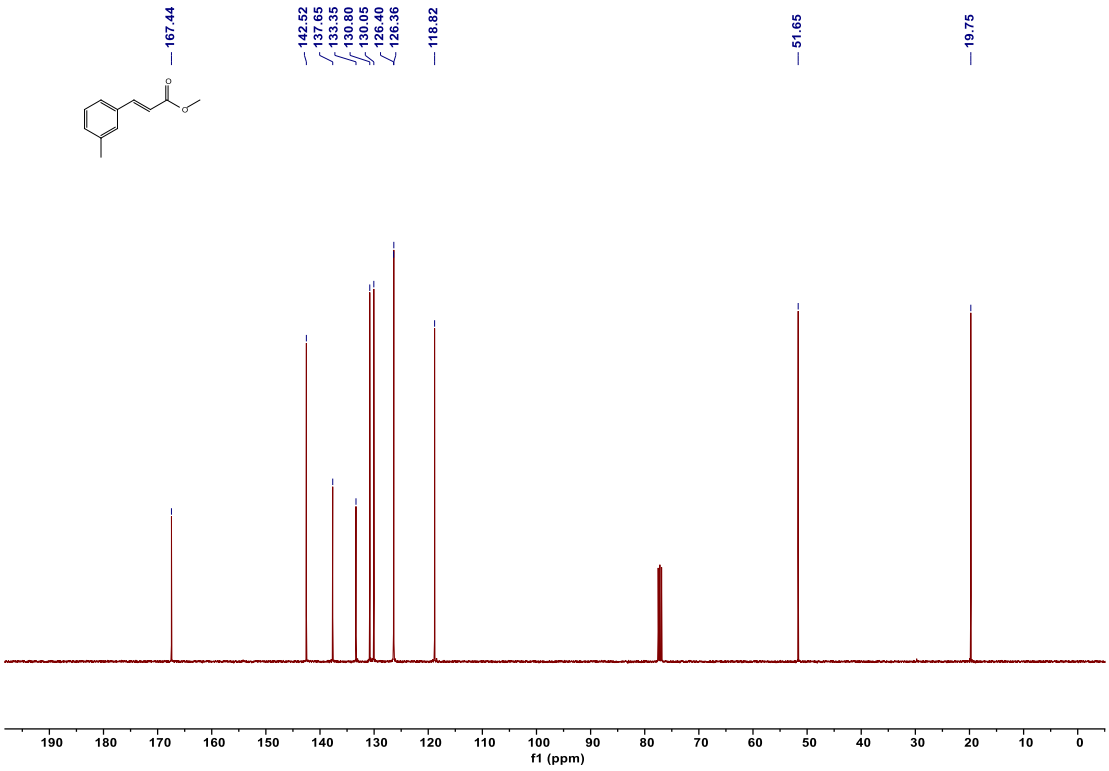
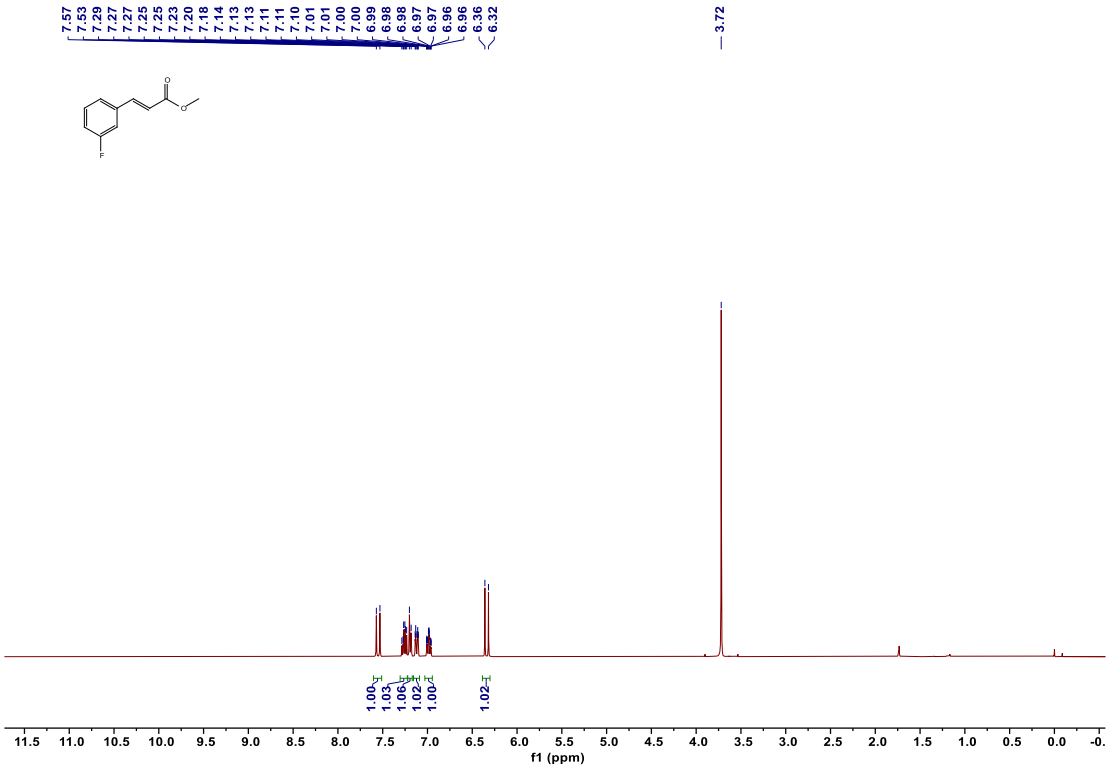
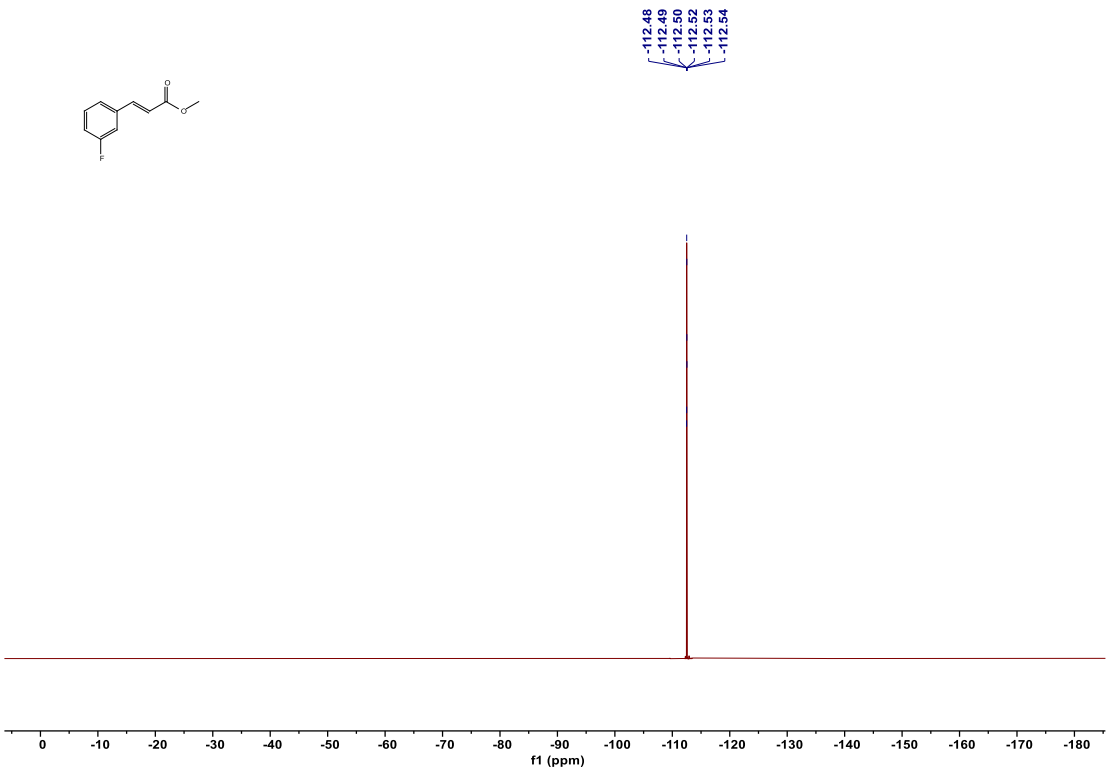


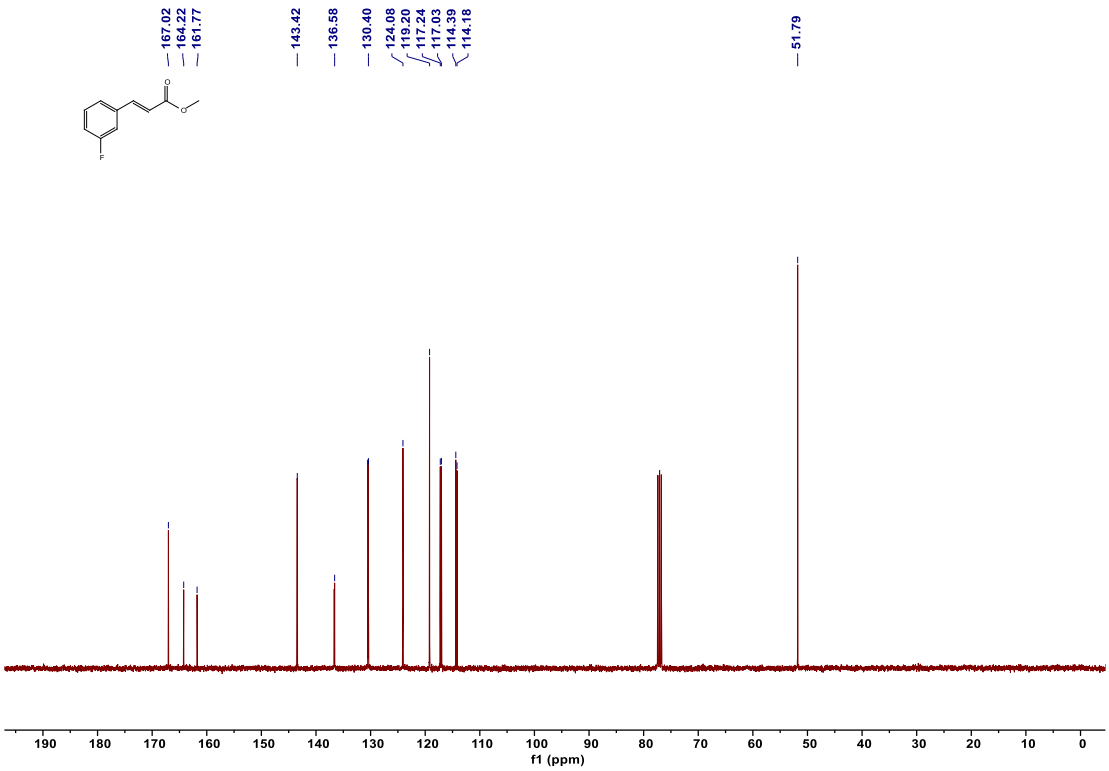
^{1}H NMR (400MHz, $CDCl_3$)



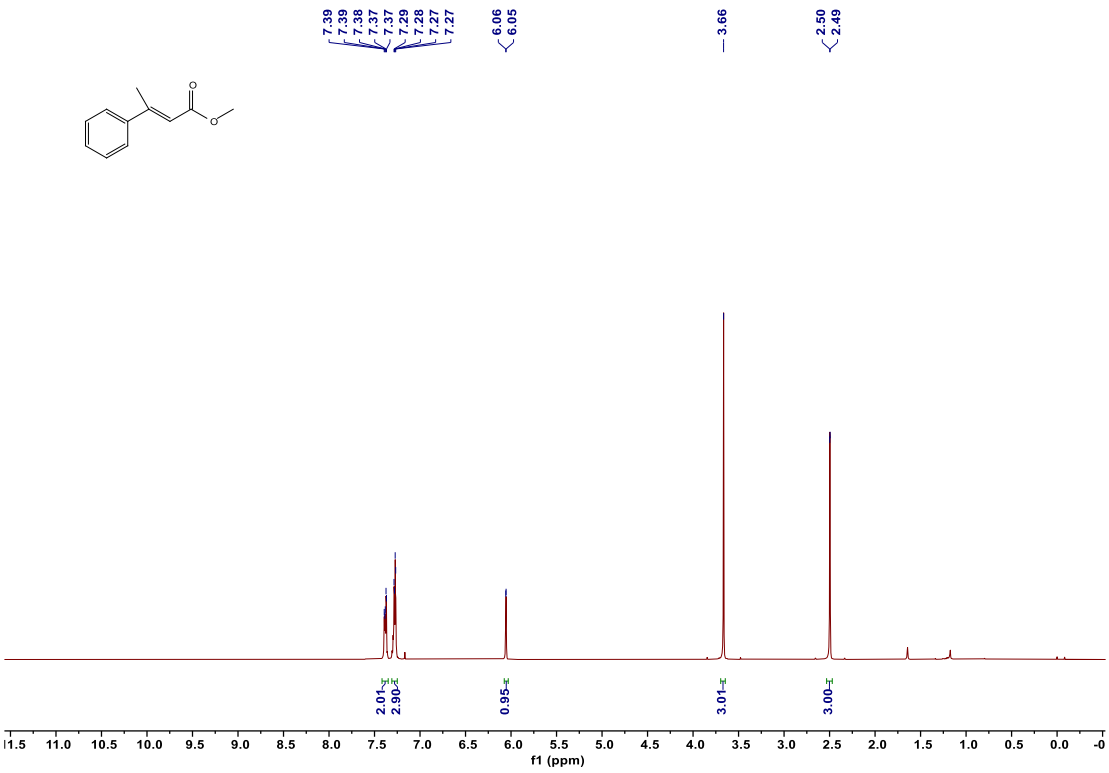
^{19}F NMR (377 MHz, $CDCl_3$)



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



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



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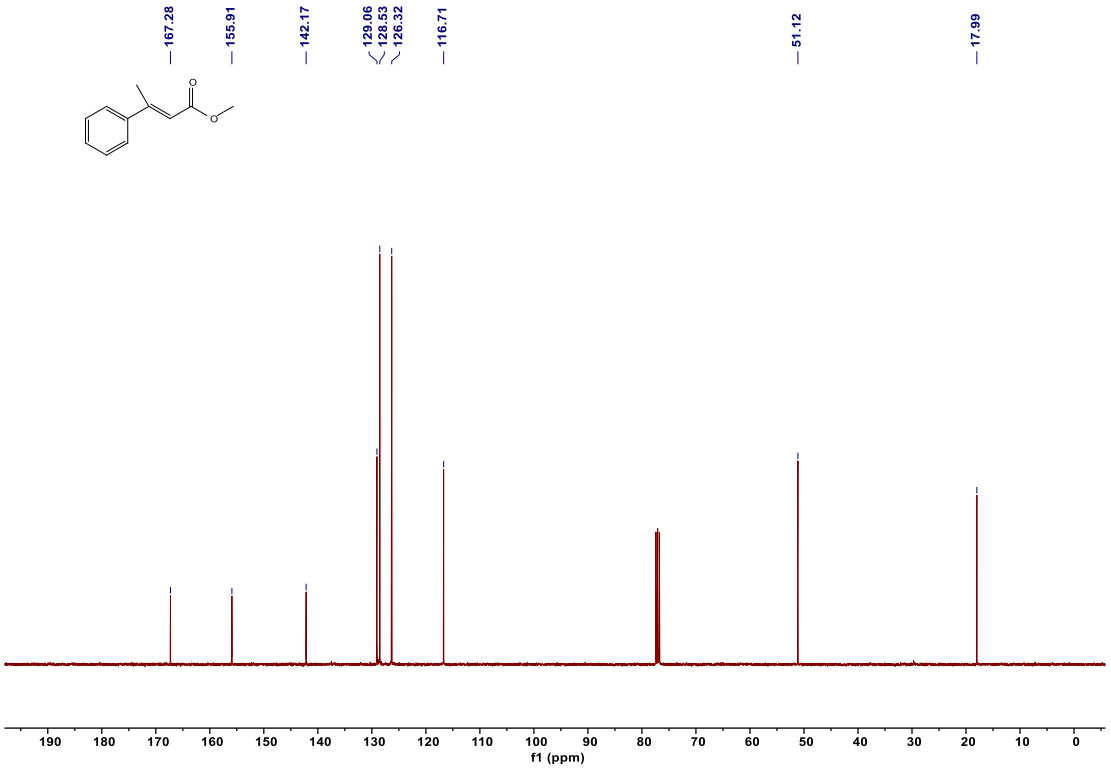
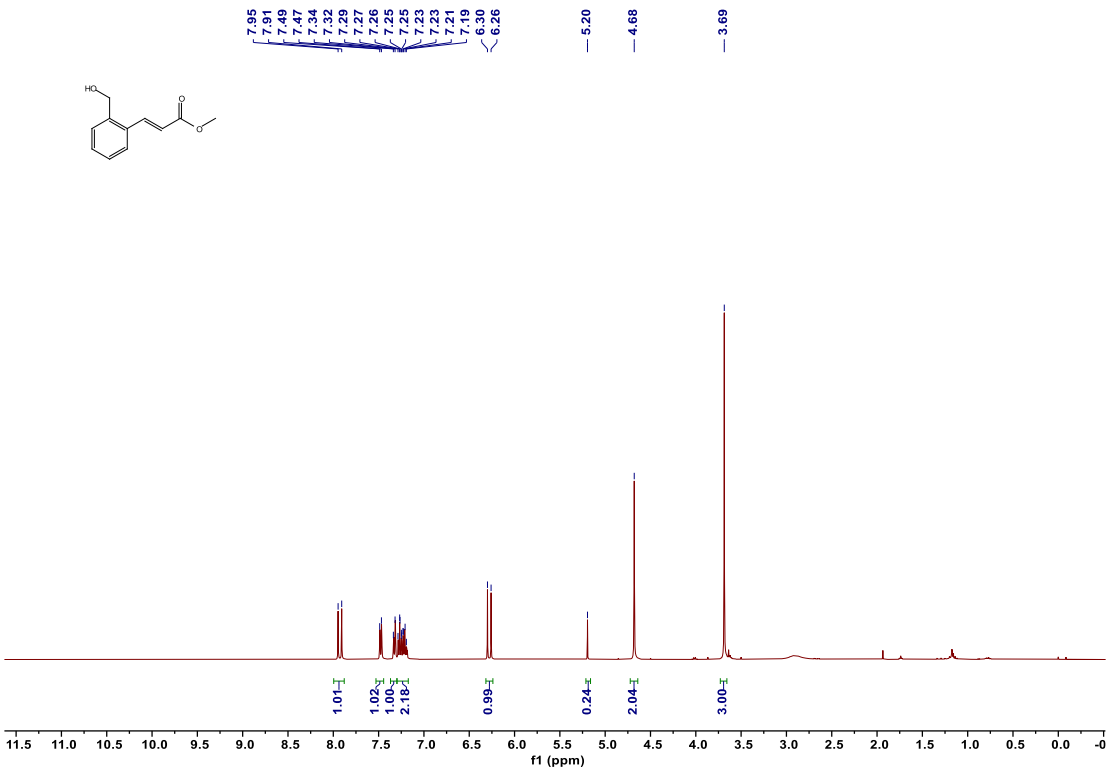


^{1}H NMR (400MHz, $CDCl_3$)



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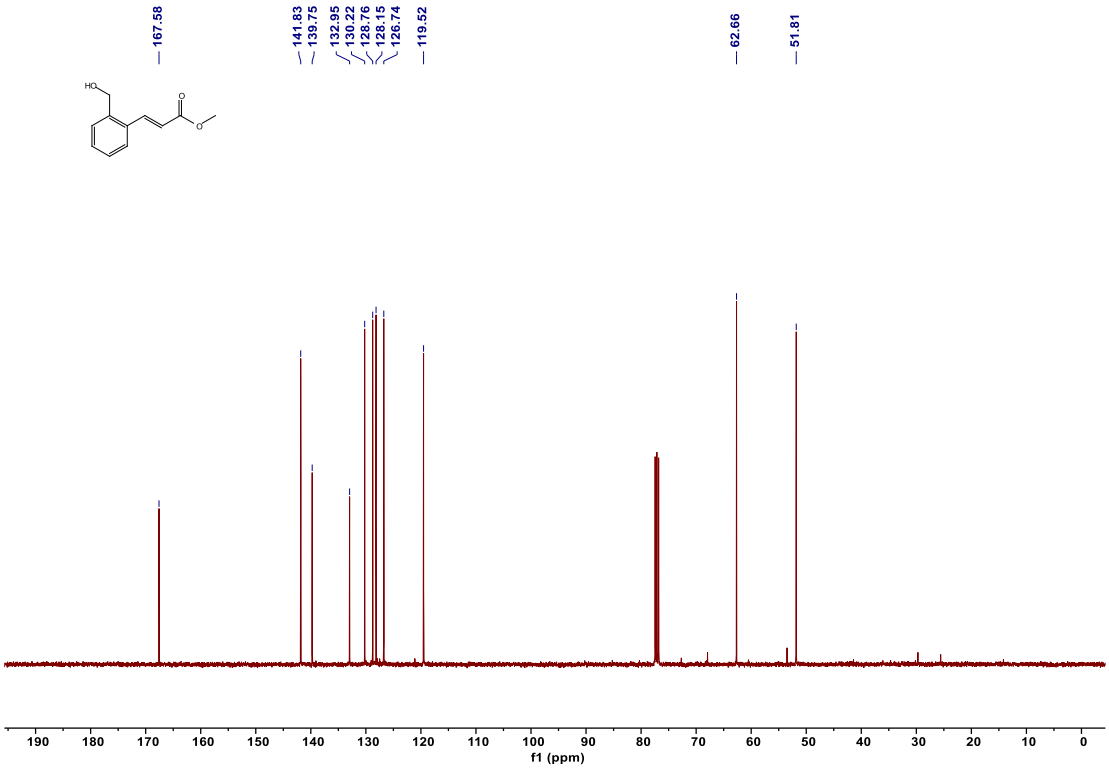

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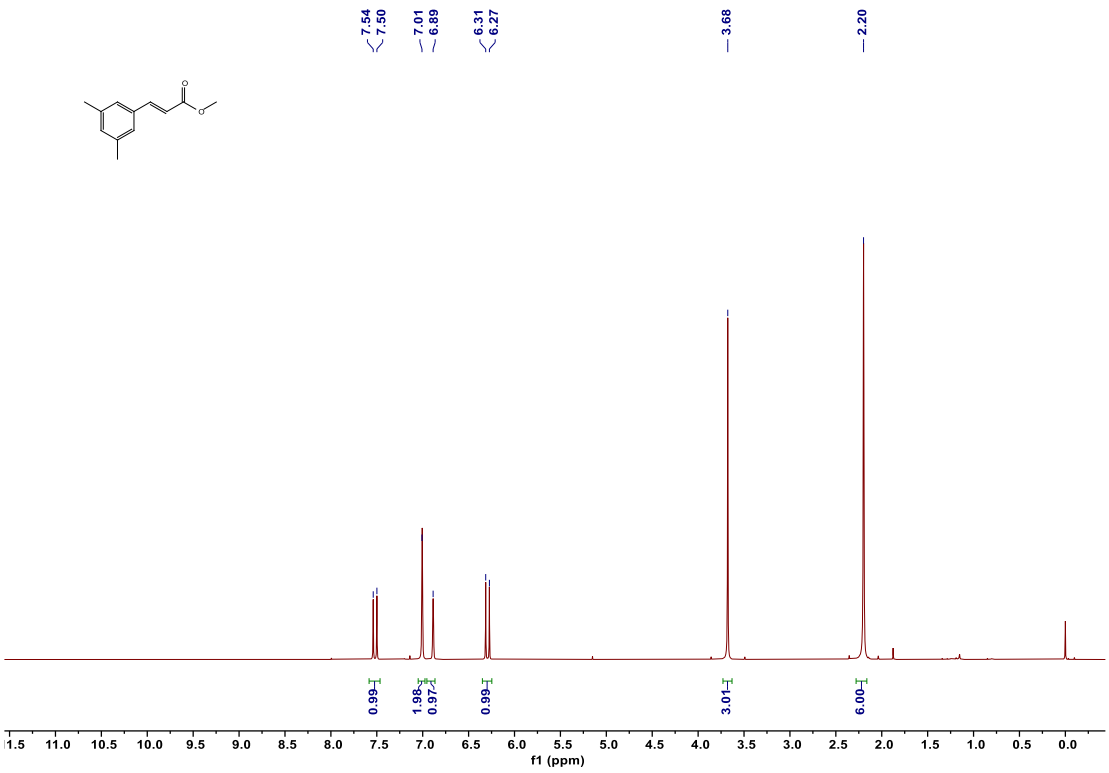

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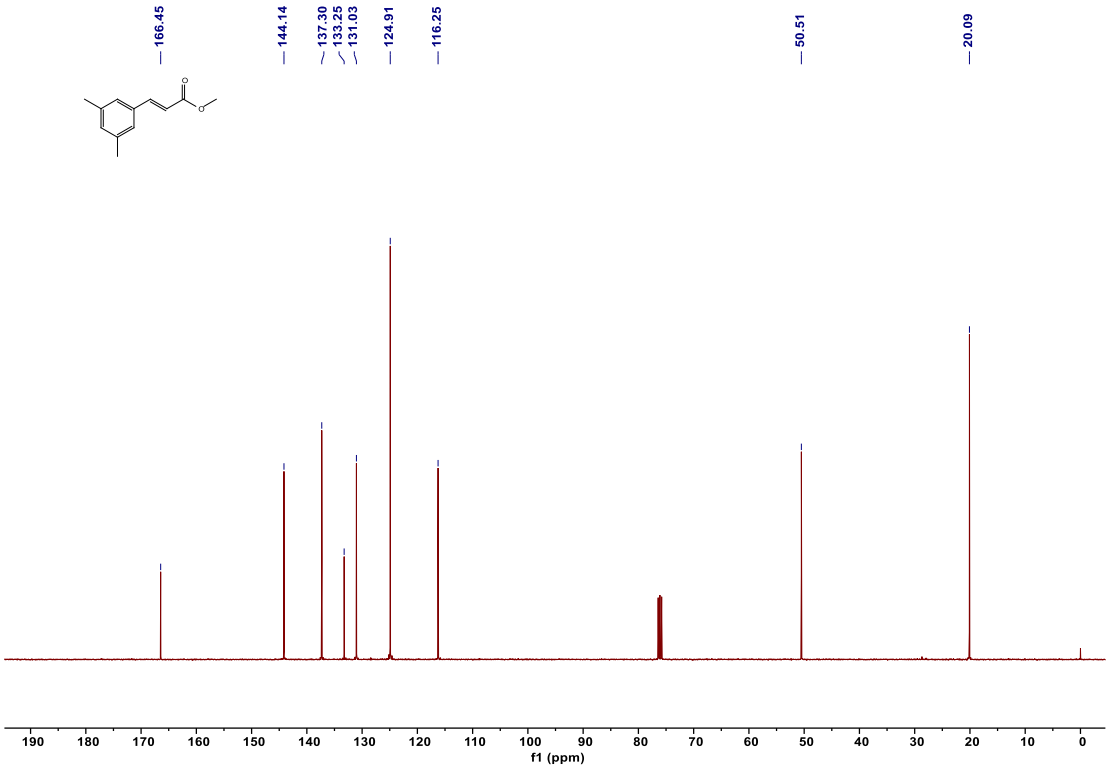

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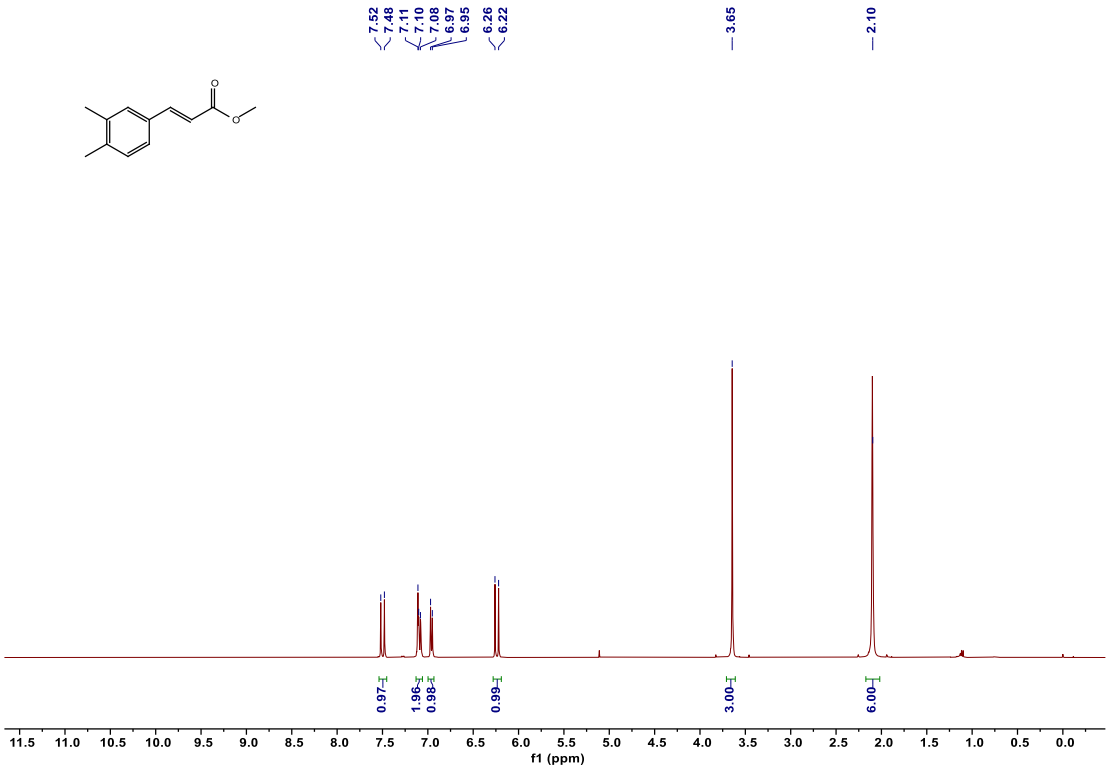

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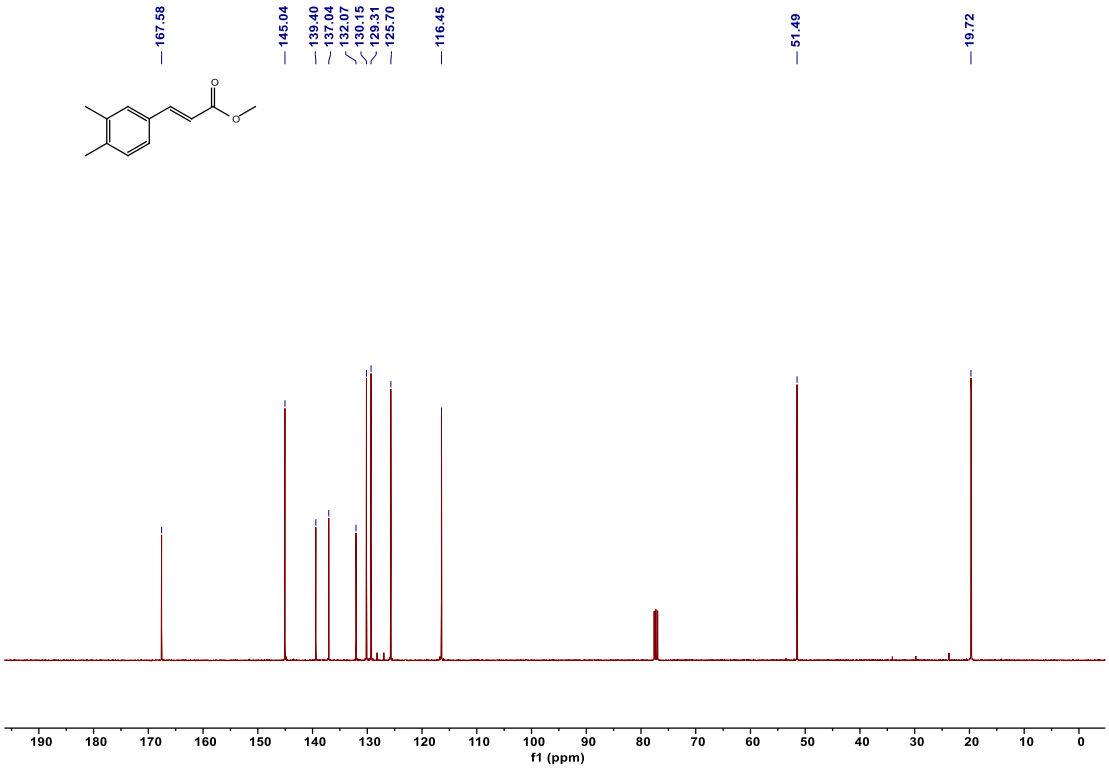

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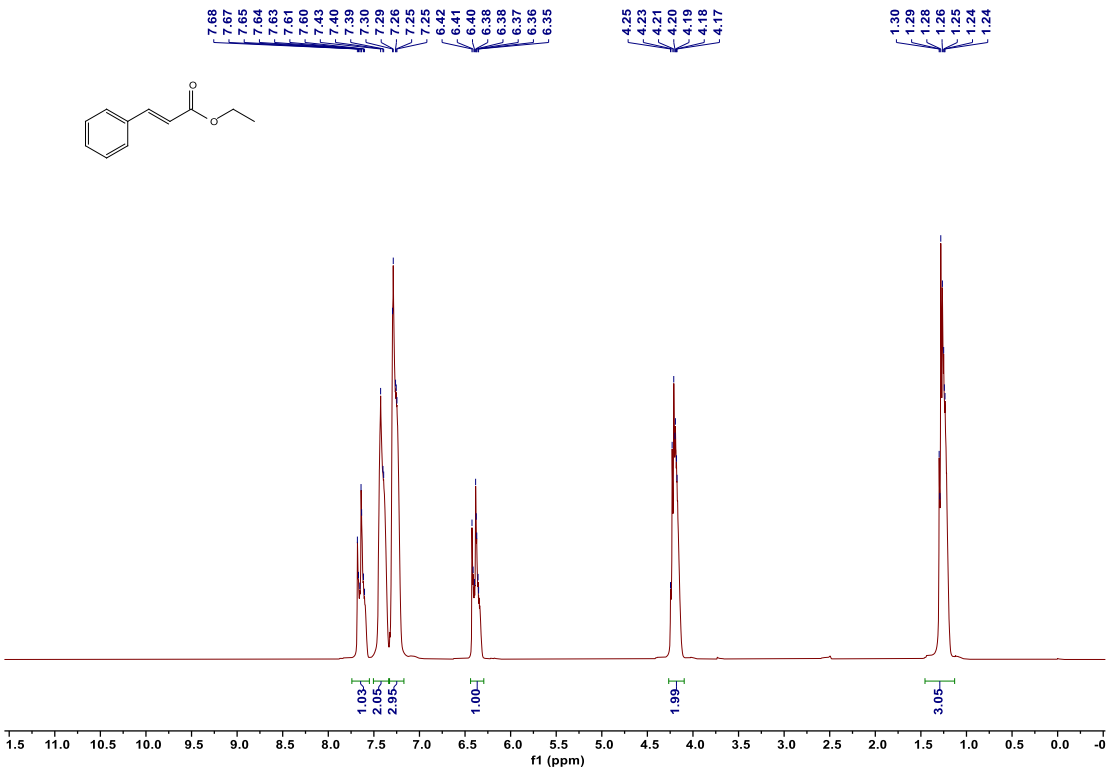

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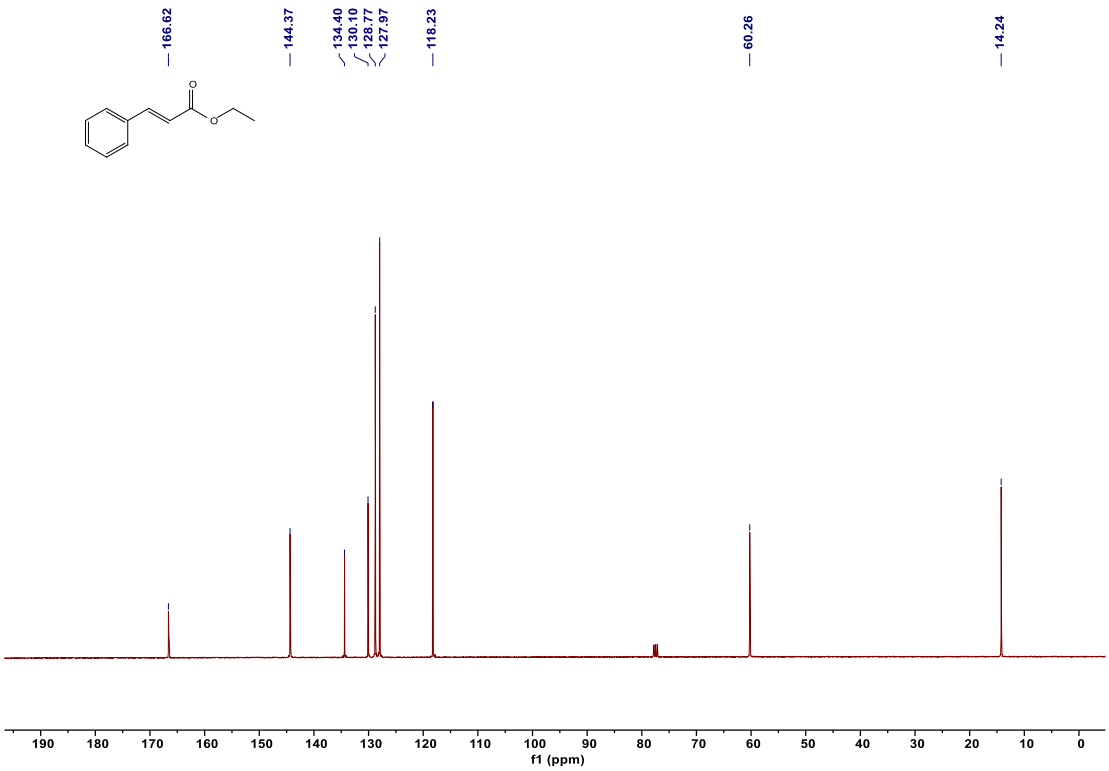

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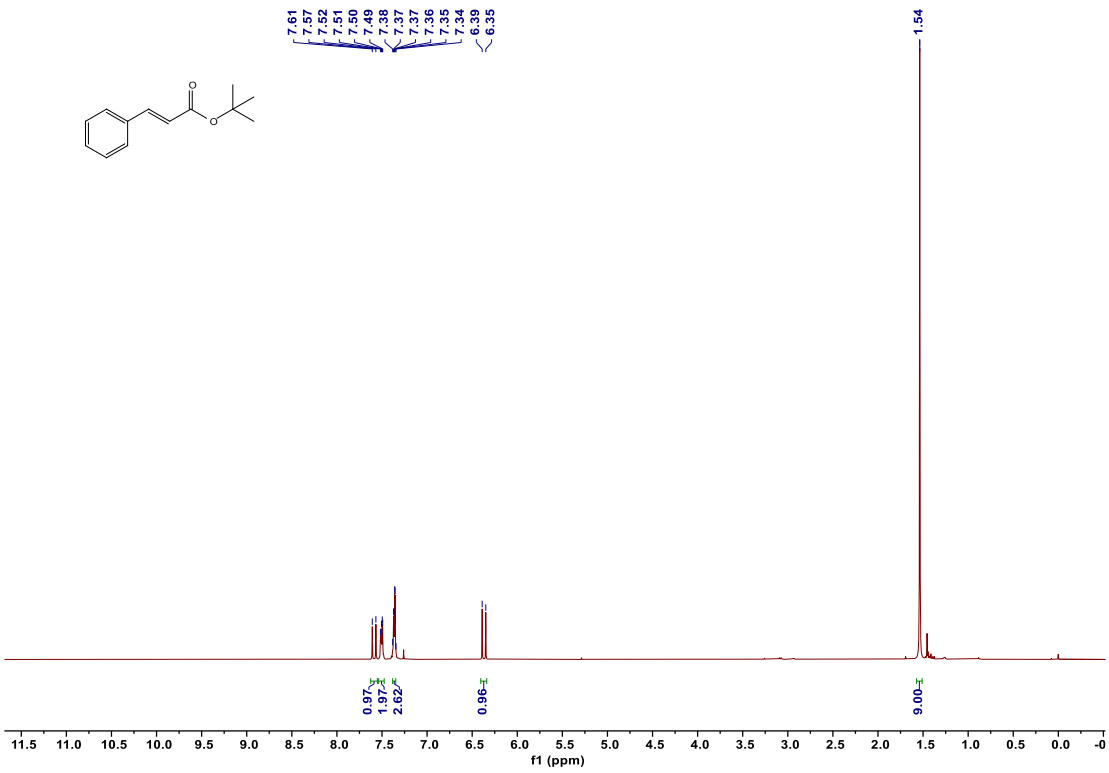

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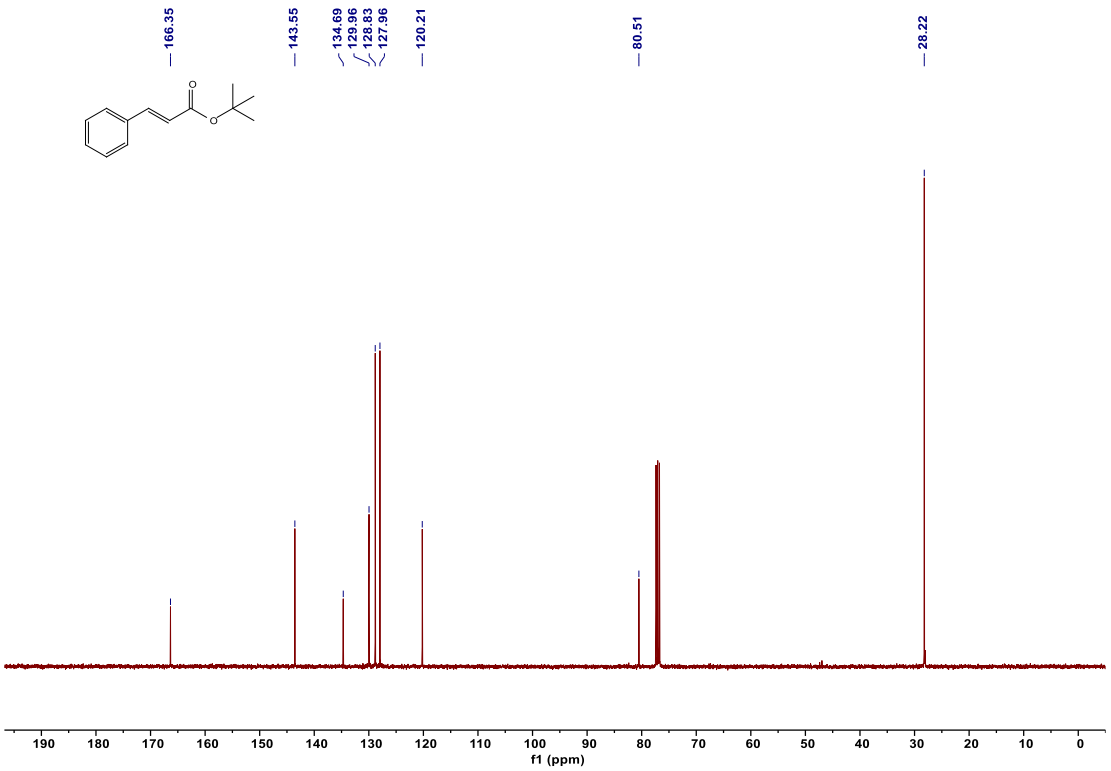

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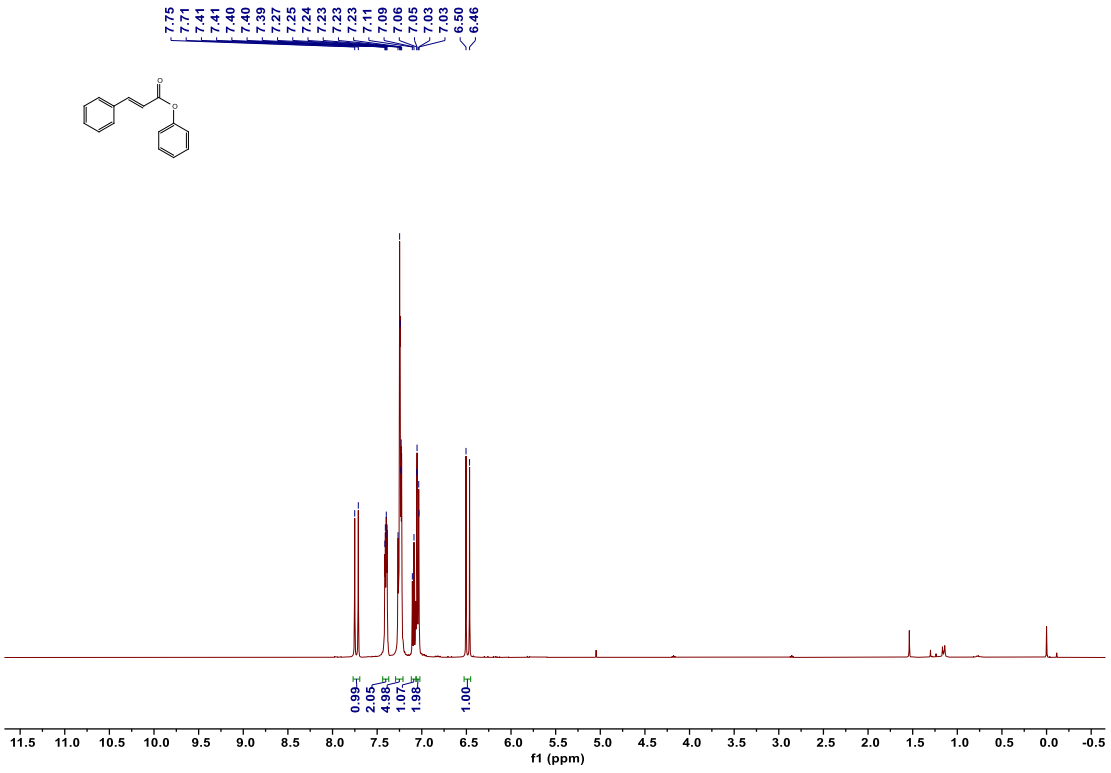

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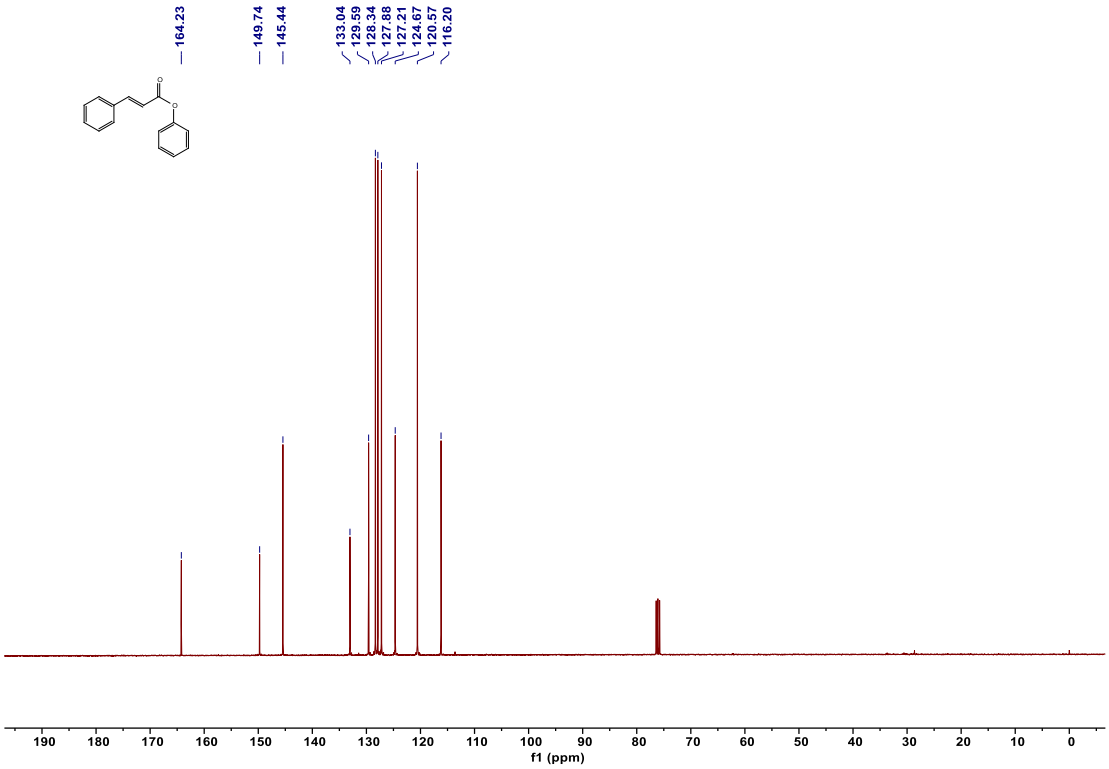

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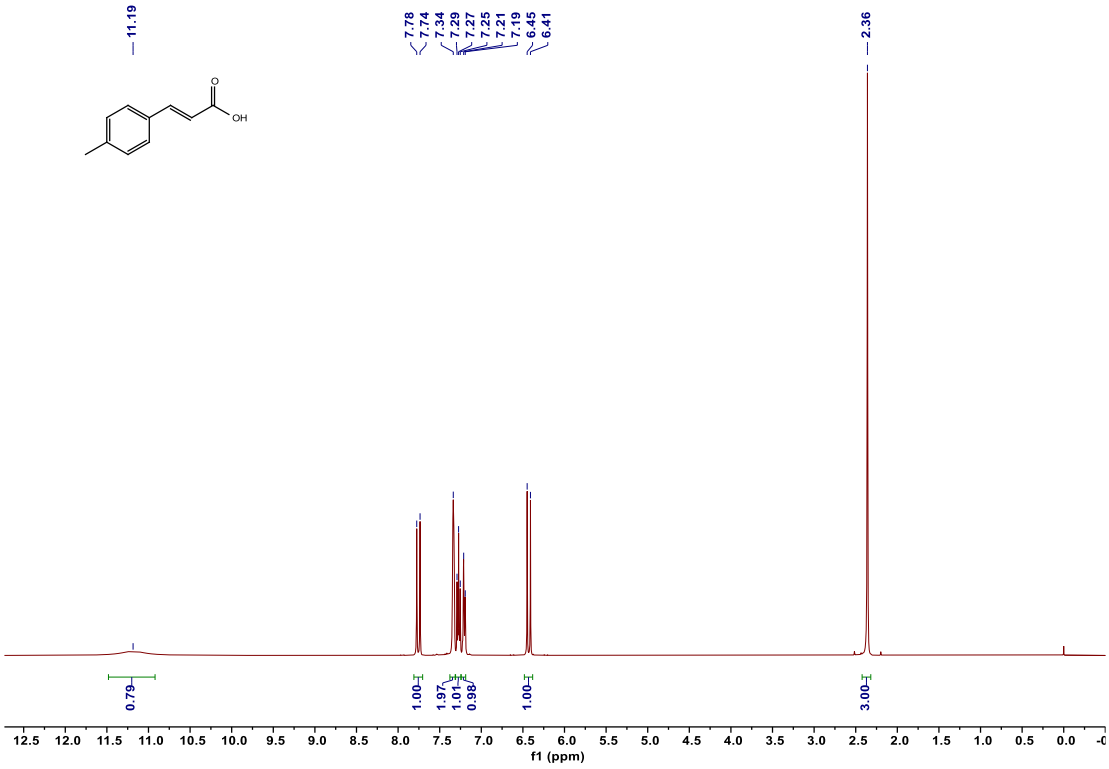

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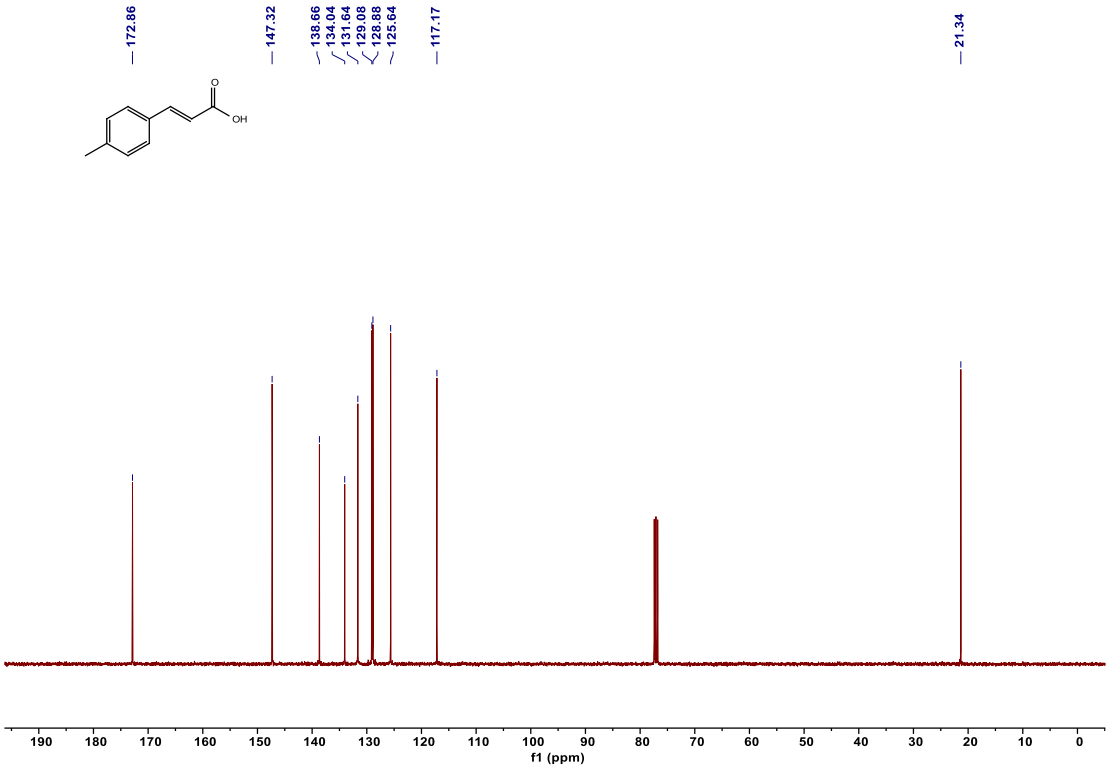

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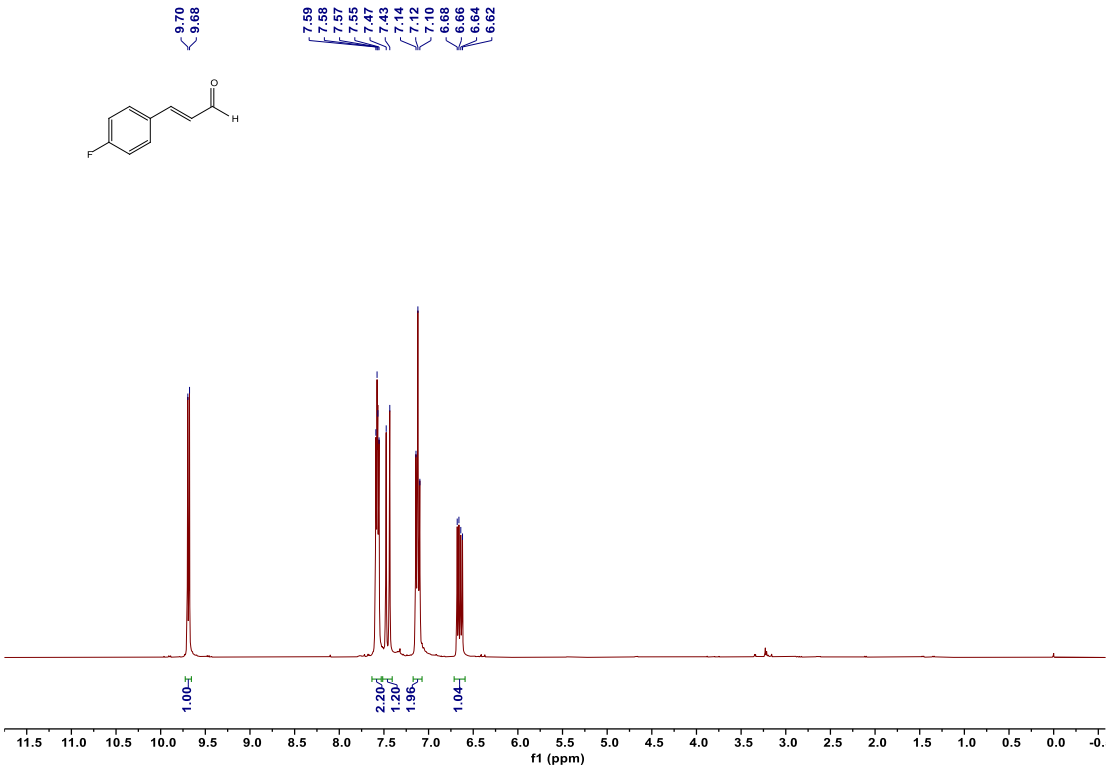

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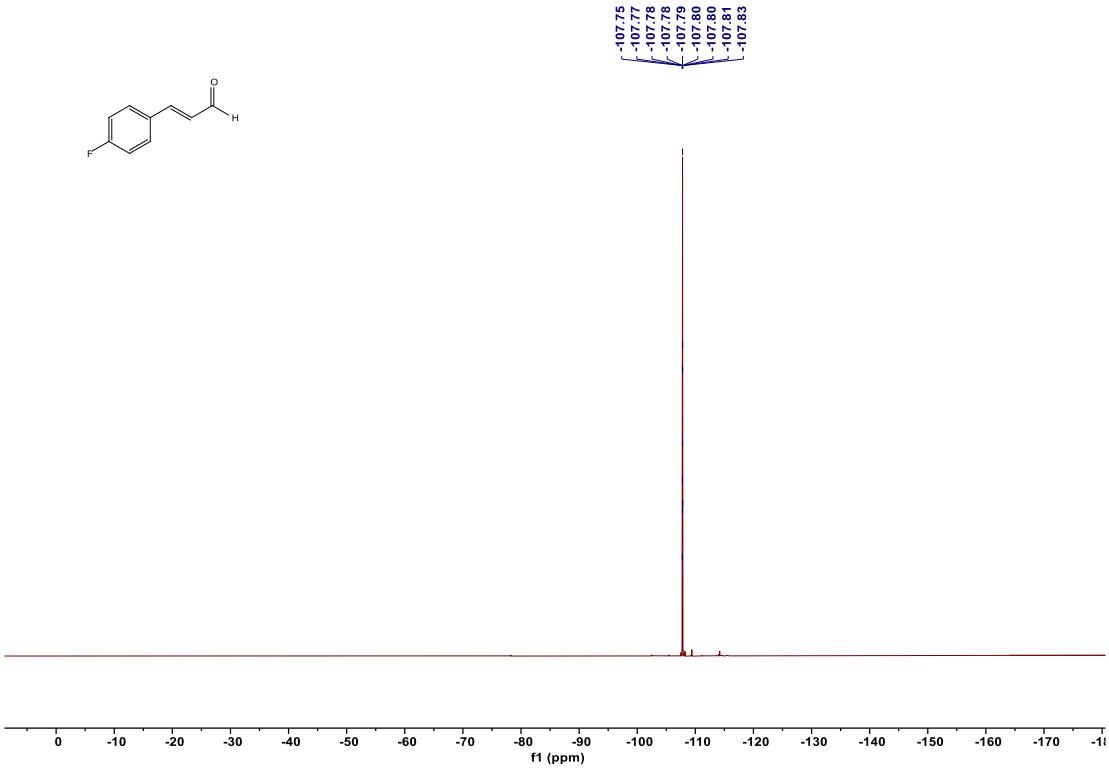

^{13}C NMR (101 MHz, $CDCl_3$)