

**Weakly Coordinating Aldehyde as a Traceless Directing Group for
Rhodium-Catalyzed Regioselective C–H Alkenylation of
Benzaldehydes**

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1. General experimental details

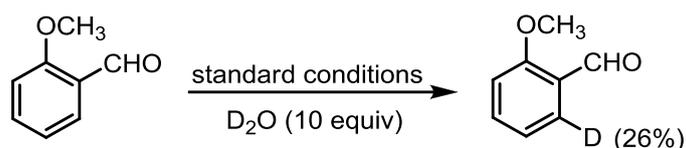
All reagents were obtained from commercial suppliers and utilized without further purification. All work-up and purification procedures were carried out with analytical reagent solvents. ^1H NMR spectra and ^{13}C NMR spectra were measured on a 400 MHz or 600 MHz spectrometer with tetramethylsilane (TMS) as internal standard at room temperature. Chemical shifts are given in δ relative to TMS, with the coupling constants J given in Hz. High-resolution mass spectra (HRMS) were detected by a Bruker Compass-Maxis instrument (APCI or ESI). MALDI-FT-ICR-MS analysis of intermediates were obtained from a Bruker Fourier-transform Ion Cyclotron Resonance Mass Spectrometry (solariX XR).

2. General procedure for synthesizing products

A 10 mL glass tube charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (4.6 mg, 0.0075 mmol), AgNTf_2 (11.6 mg, 0.03 mmol), AgNO_3 (8.5 mg, 0.05 mmol), $\text{NaOPiv}\cdot\text{H}_2\text{O}$ (25.2 mg, 0.175 mmol), DCE (0.6 mL), benzaldehydes (0.1 mmol) and acrylates (0.2 mmol), was sealed in nitrogen. The mixture was stirred at 140 °C (oil bath) for 18 hours. The residue after removing the solvent was then purified by silica gel column chromatography (PE/EA=50/1) to afford the desired products.

3. Mechanism studies

3.1 H/D exchange experiment



$[\text{Cp}^*\text{RhCl}_2]_2$ (4.6 mg, 0.0075 mmol), AgNTf_2 (11.6 mg, 0.03 mmol), AgNO_3 (8.5 mg, 0.05 mmol), $\text{NaOPiv}\cdot\text{H}_2\text{O}$ (25.2 mg, 0.175 mmol), 2-methoxybenzaldehyde (0.1 mmol, 12.3 μL) and DCE (0.6 mL) were successively added to a reaction vessel. The vessel was sealed under N_2 and heated at 140 °C (oil bath temperature) for 18 h. The resulting mixture was cooled to room temperature, filtered through a short column of silica gel. The solvent was removed under reduced pressure and the amount of D_1 -2-methoxybenzaldehyde was determined by integral area in ^1H NMR of crude reaction mixture (Figure S1).

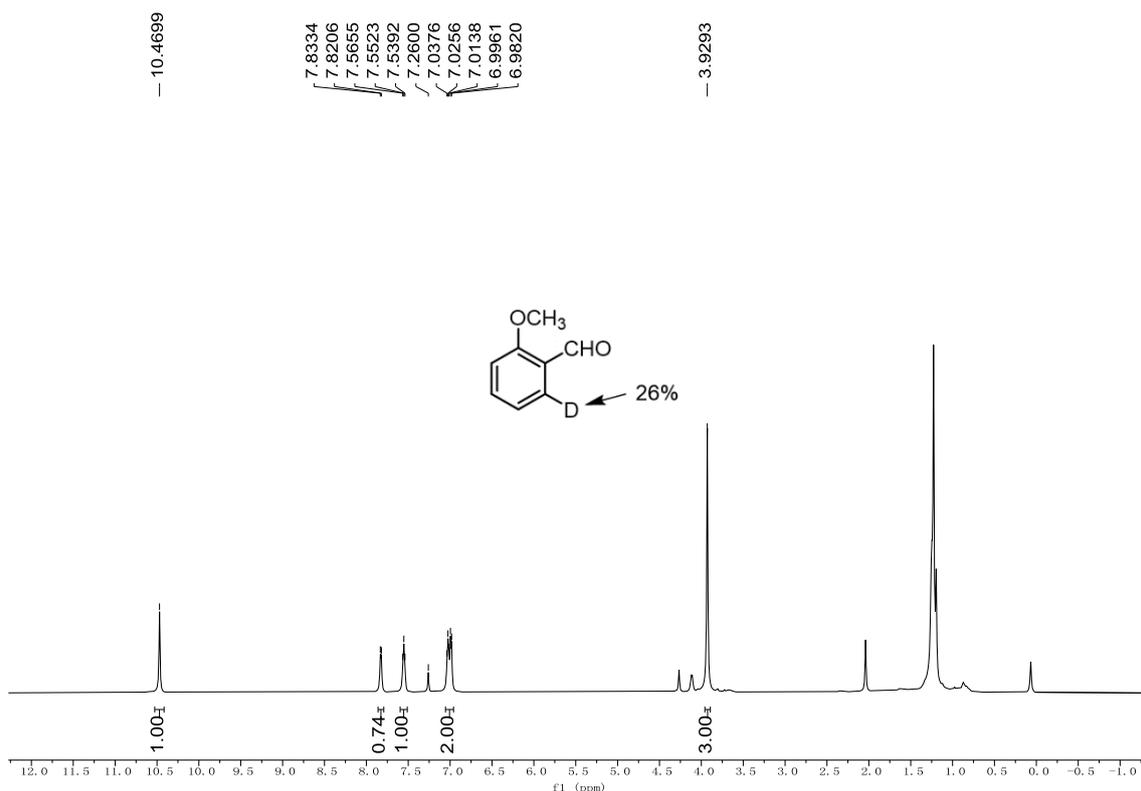
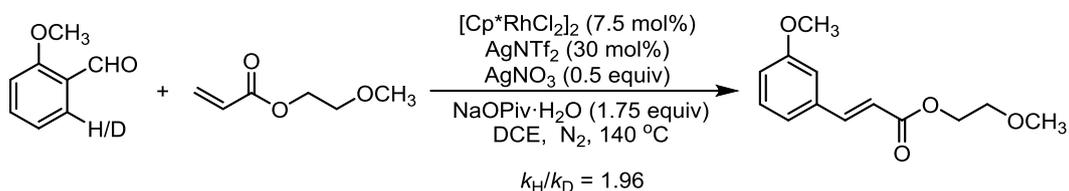


Figure S1. The ^1H NMR spectrum of H/D₁-2-methoxybenzaldehyde

3.2 KIE experiment



[Cp*RhCl₂]₂ (4.6 mg, 0.0075 mmol), AgNTf₂ (11.6 mg, 0.03 mmol), AgNO₃ (8.5 mg, 0.05 mmol), NaOPiv·H₂O (25.2 mg, 0.175 mmol), 2-methoxybenzaldehyde (0.1 mmol, 12.3 μL) and DCE (0.6 mL) were successively added to a reaction vessel. In another reaction vessel, 2-methoxybenzaldehyde was replaced by D₁-2-methoxybenzaldehyde (0.1 mmol, 12.3 μL). The vessel was sealed under air. The two reactions were stirred at 140 $^{\circ}\text{C}$ for 0.5 h, 1 h, 1.5 h, 2 h, and 2.5 h respectively. Then the two reaction mixtures were cooled to temperature and filtered through a short column of silica gel. The solvent was then removed. The yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Table S1. The yields using 2-methoxybenzaldehyde and D₁-2-methoxybenzaldehyde

Entry	Time / h	Yield using 2-methoxybenzaldehyde / %	Yield using D ₁ -2-methoxybenzaldehyde / %
1	0.5	4.26	1.14
2	1	5.74	1.88
3	1.5	7.42	2.63
4	2	8.70	3.20
5	2.5	9.90	4.11

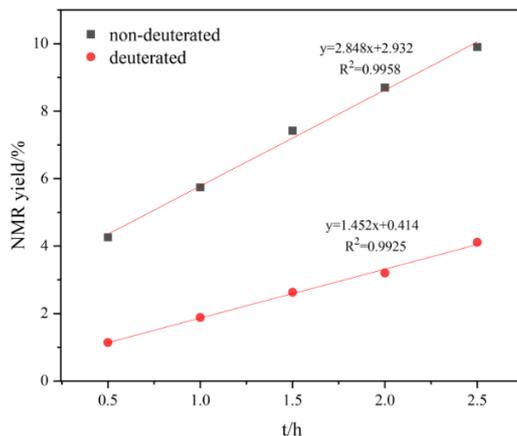


Figure S2. The Pseudo-First Order Plots for the reaction using 2-methylbenzaldehyde and D₁-2-methoxybenzaldehyde

3.3 The analysis of reaction using 2,4-dimethoxybenzaldehyde and benzyl acrylate as substrates

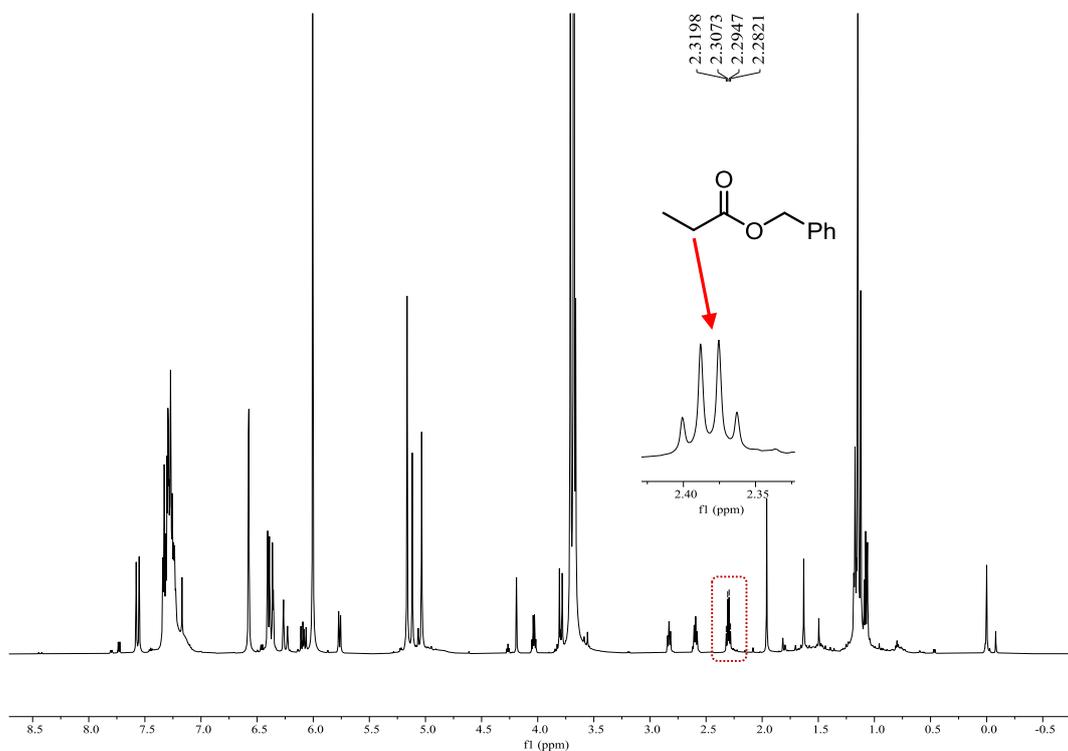


Figure S3. ¹H NMR spectrum of the crude reaction mixture using 2,4-dimethoxybenzaldehyde and benzyl acrylate

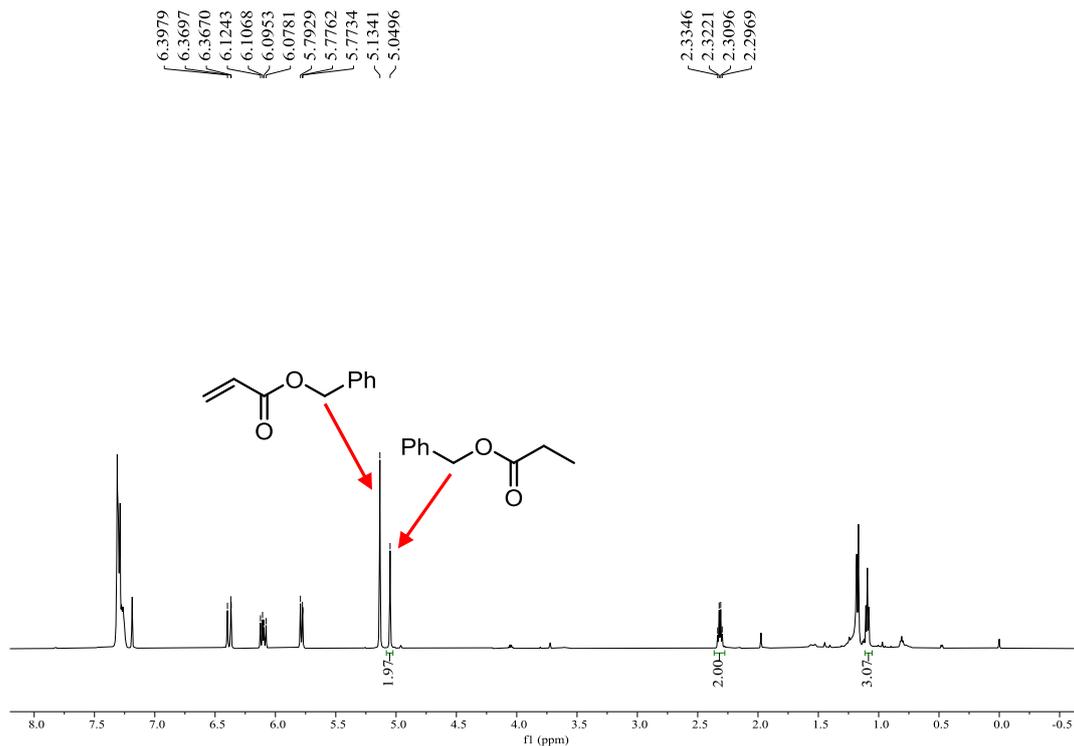


Figure S4. ^1H NMR spectrum of the isolated mixture of benzyl acrylate and benzyl propionate from crude mixture using 2,4-dimethoxybenzaldehyde and benzyl acrylate (hexane/EtOAc = 50/1)

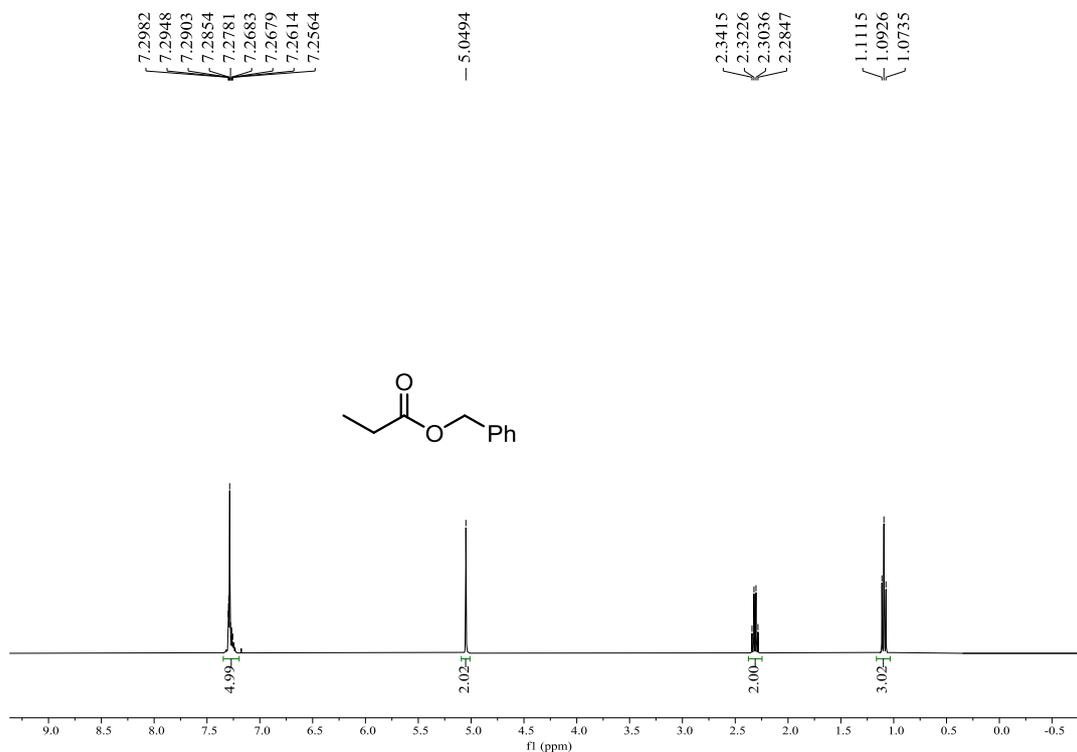


Figure S5. ^1H NMR spectrum of benzyl propionate

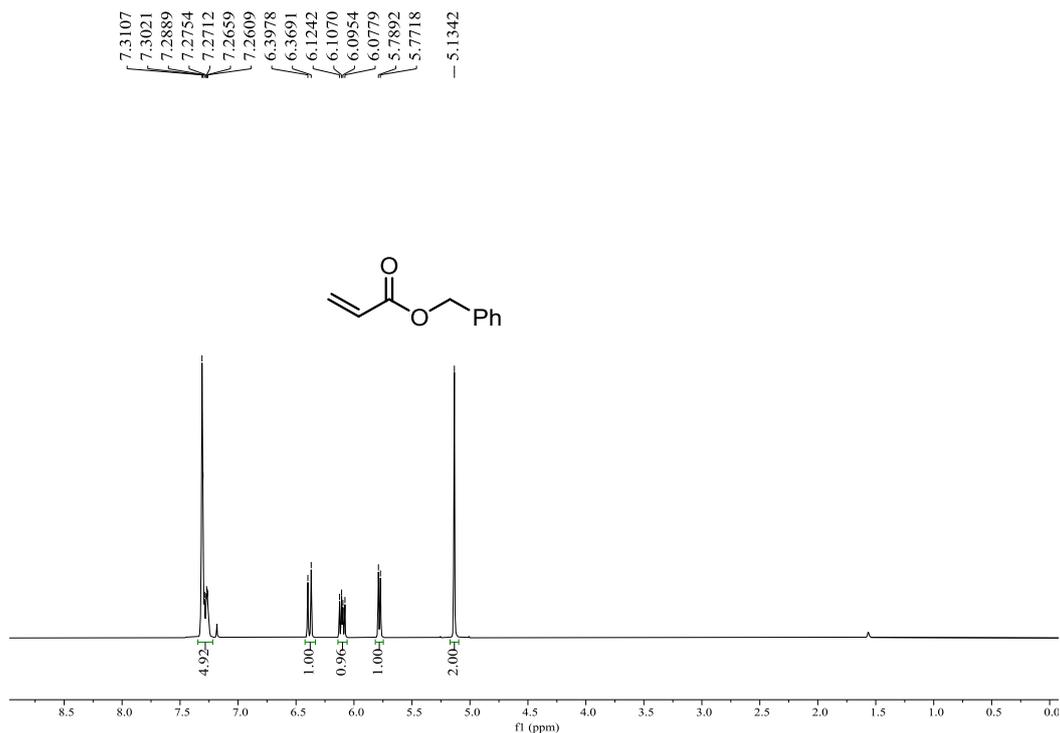


Figure S6. ¹H NMR spectrum of benzyl acrylate

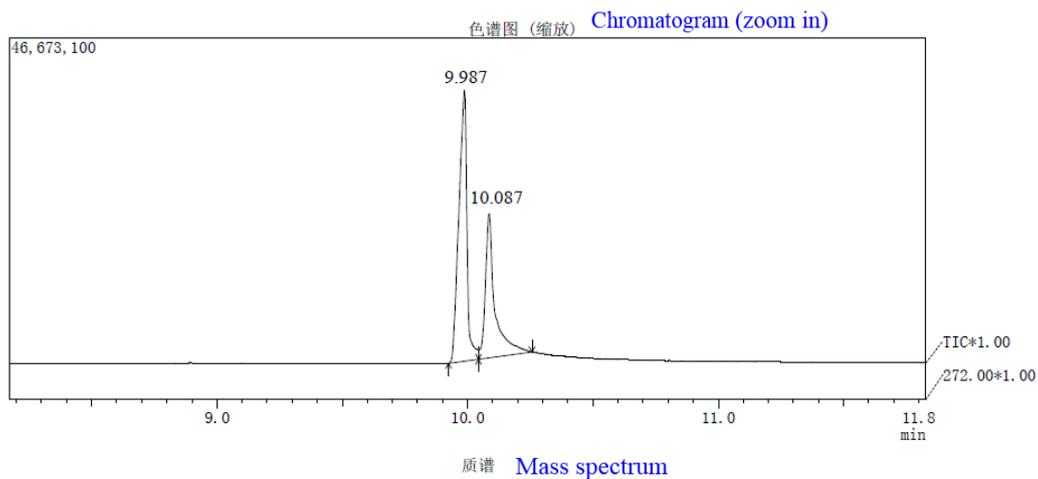
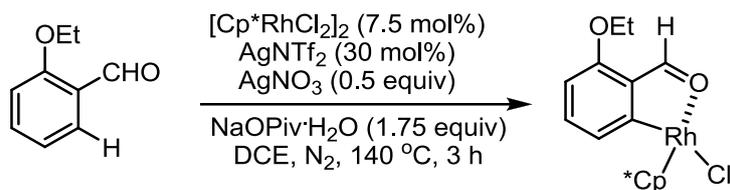


Figure S7. GC-MS spectrum of the isolated mixture using 2,4-dimethoxybenzaldehyde and benzyl acrylate as substrate (hexane/EtOAc = 50/1)

3.4 MALDI-FT-ICR-MS analysis of intermediate C



$[\text{Cp}^*\text{RhCl}_2]_2$ (4.63 mg, 0.0075 mmol), AgNTf_2 (11.6 mg, 0.03 mmol), AgNO_3 (8.5 mg, 0.05 mmol), $\text{NaOPiv}\cdot\text{H}_2\text{O}$ (25.2 mg, 0.175 mmol), *o*-ethoxybenzaldehyde (14 μL , 0.1 mmol) and DCE (0.6 mL) were successively added to a reaction vessel equipped with a stir bar. The vessel was sealed under N_2 and stirred at 140 $^\circ\text{C}$ for 3 h. After being cooled to room temperature, the mixture was detected by the MALDI-FT-ICR-MS. FT-ICR-MS (MALDI) m/z (intermediate C): calculated for $\text{C}_{19}\text{H}_{25}\text{ClO}_2\text{Rh}$ $[\text{M}+\text{H}]^+$: 423.05926; found: 423.05985.

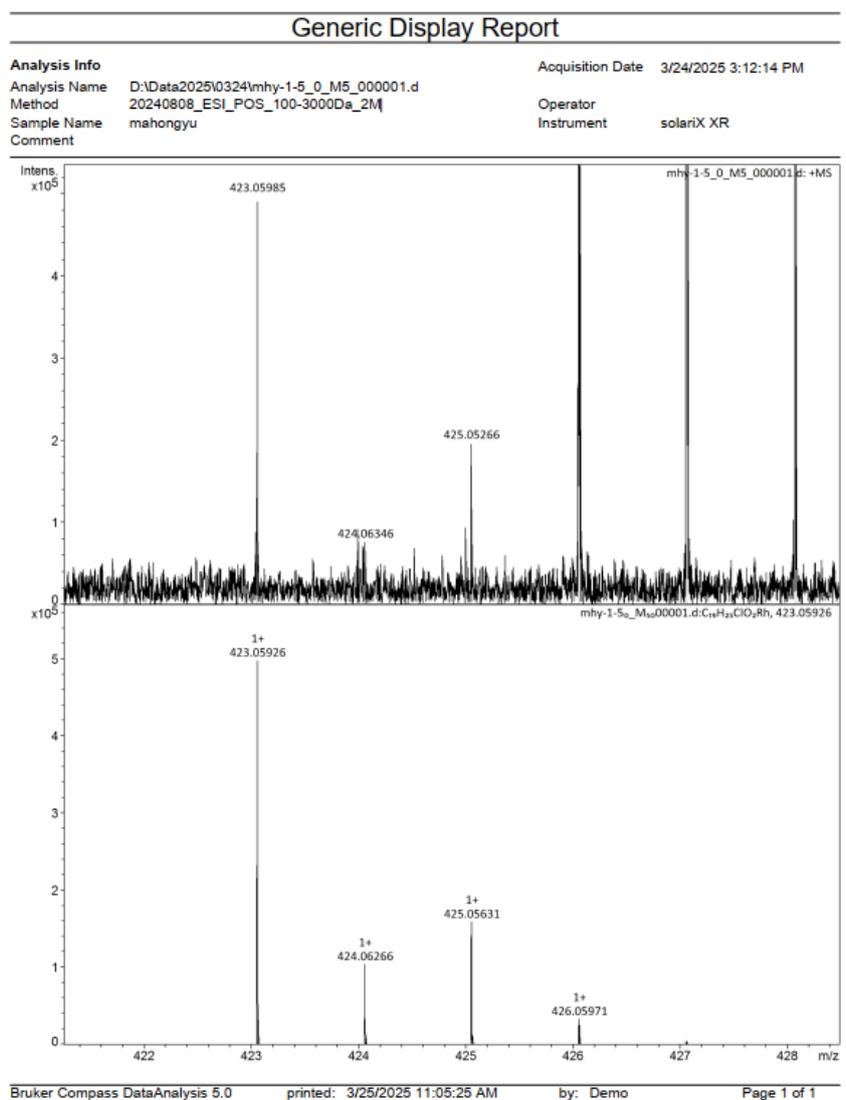


Figure S8. MALDI-FT-ICR-MS of intermediate C

4. The yields of several propionates

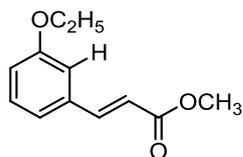
Table S2 The yields of several propionate^a

R	PhCH ₂	PhCH ₂ CH ₂	3,5,5-trimethylhexyl	2-ethylhexyl	Ph
Propionate yield(%)	27	9	15	18	19
R	PhOCH ₂ CH ₂		CH ₃ OCH ₂ CH ₂	C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ CH ₂	
Propionate yield(%)	17	16	8	16	

^aDetermined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

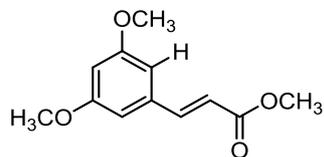
5. Experimental characterization data for compounds

methyl (*E*)-3-(3-ethoxyphenyl)acrylate (**3a**)¹



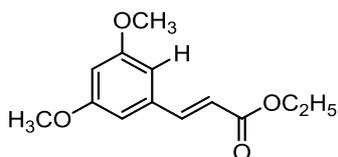
12.4 mg, 60% (isolated yield), colourless oil; $R_f=0.14$ (hexane/EtOAc = 50/1). ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.65 (d, J = 16.0 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.04 – 7.02 (m, 1H), 6.92 (dd, J = 8.3, 2.6 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 4.05 (q, J = 6.9 Hz, 2H), 3.81 (s, 3H), 1.43 (t, J = 6.9 Hz, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ [ppm] = 167.4, 159.3, 144.9, 135.7, 129.9, 120.7, 118.0, 116.7, 113.6, 63.5, 51.7, 14.8. HRMS (ESI-Q-TOF) m/z calculated for C₁₂H₁₄O₃Na [M+Na]⁺: 229.0835; found: 229.0836.

methyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3b**)²



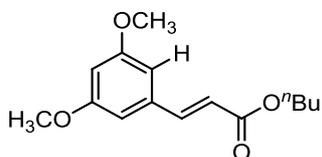
13.5 mg, 61% (isolated yield), colourless oil; $R_f=0.16$ (hexane/EtOAc = 50/1). ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.61 (d, J = 16.0 Hz, 1H), 6.66 (d, J = 2.2 Hz, 2H), 6.49 (s, 1H), 6.41 (d, J = 16.0 Hz, 1H), 3.81 (s, 6H), 3.81 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ [ppm] = 167.3, 161.0, 144.9, 136.3, 118.3, 106.0, 102.6, 55.4, 51.7. HRMS (ESI-Q-TOF) m/z calculated for C₁₂H₁₄O₄Na [M+Na]⁺: 245.0784; found: 245.0782.

ethyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3c)³



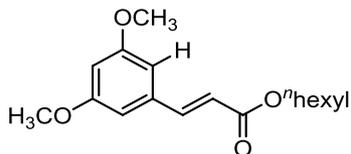
15.5 mg, 66% (isolated yield), colourless oil; $R_f=0.33$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.60 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.41 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.81 (s, 6H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.9, 161.0, 144.6, 136.4, 118.8, 105.9, 102.5, 60.5, 55.4, 14.3. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{13}\text{H}_{17}\text{O}_4$ $[\text{M}+\text{H}]^+$: 237.1121; found: 237.1121.

butyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3d)⁴



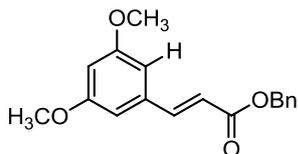
12.7 mg, 48% (isolated yield), colourless oil; $R_f=0.37$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.60 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 4.21 (t, $J = 6.7$ Hz, 2H), 3.81 (s, 6H), 1.71 – 1.67 (m, 2H), 1.47 – 1.40 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.0, 161.0, 144.5, 136.4, 118.8, 105.9, 102.6, 64.5, 55.4, 30.8, 19.2, 13.7. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 287.1254; found: 287.1252.

hexyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3e)



15.2 mg, 52% (isolated yield), colourless oil; $R_f=0.43$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.60 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 4.20 (t, $J = 6.8$ Hz, 2H), 3.81 (s, 6H), 1.72 – 1.68 (m, 2H), 1.43 – 1.38 (m, 2H), 1.34 – 1.32 (m, 4H), 0.90 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.0, 161.0, 144.5, 136.4, 118.8, 105.9, 102.5, 64.8, 55.4, 31.5, 28.7, 25.7, 22.6, 14.0. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 315.1567; found: 315.1564.

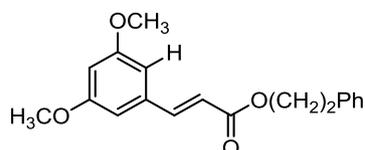
benzyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3f)⁵



20.8 mg, 70% (isolated yield), colourless oil; $R_f=0.31$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.65 (d, $J = 15.9$ Hz, 1H), 7.43 – 7.41 (m, 2H), 7.39 (td, $J = 7.8, 1.3$ Hz, 2H), 7.38 – 7.35 (m,

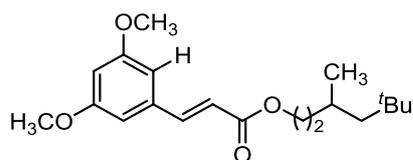
1H), 6.66 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.46 (d, $J = 15.9$ Hz, 1H), 5.25 (s, 2H), 3.80 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.7, 161.0, 145.2, 136.2, 136.0, 128.6, 128.3, 128.3, 118.4, 106.0, 102.7, 66.4, 55.4. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 321.1097; found: 321.1089.

phenethyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3g**)⁶



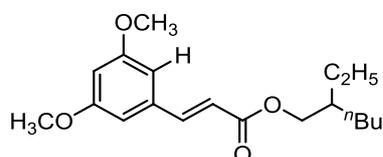
20.3 mg, 65% (isolated yield), colourless oil; $R_f=0.21$ (hexane/EtOAc = 20/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.59 (d, $J = 16.0$ Hz, 1H), 7.34 – 7.31 (m, 2H), 7.27 – 7.24 (m, 3H), 6.65 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 4.43 (t, $J = 7.1$ Hz, 2H), 3.81 (s, 6H), 3.02 (t, $J = 7.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 161.0, 144.9, 137.9, 136.3, 128.9, 128.5, 126.6, 118.6, 106.0, 102.6, 65.1, 55.4, 35.2. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 335.1254; found: 335.1248.

3,6-dimethylheptyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3h**)



29.4 mg, 58% (isolated yield), colourless oil; $R_f=0.37$ (hexane/EtOAc = 20/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.59 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 4.22 (td, $J = 6.9, 2.6$ Hz, 2H), 3.81 (s, 6H), 1.72 – 1.65 (m, 2H), 1.57 – 1.53 (m, 1H), 1.28 (d, $J = 3.6$ Hz, 1H), 1.11 (dd, $J = 14.0, 6.1$ Hz, 1H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.91 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.0, 161.0, 144.6, 136.4, 118.8, 106.0, 102.5, 63.2, 55.4, 51.0, 37.9, 31.1, 30.0, 26.3, 22.6. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 357.2036; found: 357.2033.

2-ethylhexyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3i**)



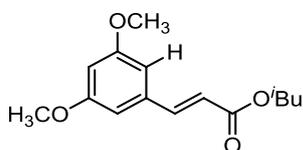
18.6 mg, 58% (isolated yield), colourless oil; $R_f=0.46$ (hexane/EtOAc = 20/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.59 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.2$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 4.15 – 4.09 (m, 2H), 3.82 (s, 6H), 1.65 (dt, $J = 12.3, 6.1$ Hz, 1H), 1.46 – 1.38 (m, 2H), 1.38 – 1.28 (m, 6H), 0.92 (dt, $J = 11.1, 7.1$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.1, 161.0, 144.5, 136.4, 118.9, 106.0, 102.6, 67.1, 55.4, 38.9, 30.5, 29.0, 23.9, 23.0, 14.1, 11.0. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{19}\text{H}_{28}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 343.1880; found: 343.1879.

phenyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3j**)⁷



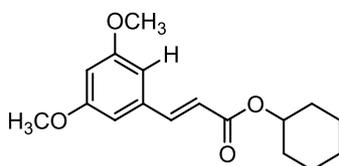
17.1 mg, 61% (isolated yield), colourless oil; $R_f=0.36$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.79 (d, $J = 15.9$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.26 (d, $J = 3.3$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 6.73 (t, $J = 2.2$ Hz, 2H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.54 (d, $J = 2.3$ Hz, 1H), 3.84 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 165.3, 161.1, 150.8, 146.6, 136.1, 129.5, 125.8, 121.6, 117.9, 106.2, 103.0, 55.5. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 307.0941; found: 307.0940.

isopropyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3k**)



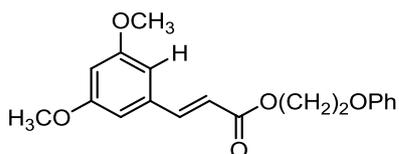
15.8 mg, 60% (isolated yield), colourless oil; $R_f=0.45$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.60 (d, $J = 15.9$ Hz, 1H), 6.67 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 3.99 (d, $J = 6.7$ Hz, 2H), 3.81 (s, 6H), 2.05 – 1.98 (m, 1H), 0.99 (s, 3H), 0.98 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.0, 161.0, 144.6, 136.4, 118.8, 105.9, 102.6, 70.7, 55.4, 27.8, 19.2. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 287.1254; found: 287.1250.

cyclohexyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3l**)



15.9 mg, 55% (isolated yield), colourless oil; $R_f=0.42$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.58 (d, $J = 15.9$ Hz, 1H), 6.67 (s, 2H), 6.48 (d, $J = 2.3$ Hz, 1H), 6.40 (d, $J = 15.9$ Hz, 1H), 4.91 – 4.87 (m, 1H), 3.81 (s, 6H), 1.94 – 1.91 (m, 2H), 1.78 – 1.75 (m, 2H), 1.59 – 1.57 (m, 1H), 1.49 (dd, $J = 21.3, 10.8$ Hz, 2H), 1.41 (dd, $J = 23.1, 11.4$ Hz, 2H), 1.33 – 1.26 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.3, 161.0, 144.3, 136.5, 119.4, 105.9, 102.5, 72.8, 55.4, 31.8, 25.4, 23.8. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{17}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 313.1410; found: 313.1411.

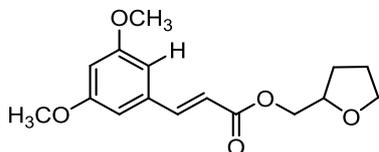
2-phenoxyethyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (**3m**)



22.9 mg, 69% (isolated yield), colourless oil; $R_f=0.33$ (hexane/EtOAc = 5/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.63 (d, $J = 15.9$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.01 – 6.93 (m, 3H), 6.66 (s, 2H), 6.50 (d, $J = 2.4$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 4.56 (t, $J = 4.9$ Hz, 2H), 4.26 (t, $J = 4.8$ Hz, 2H), 3.81 (s, 6H).

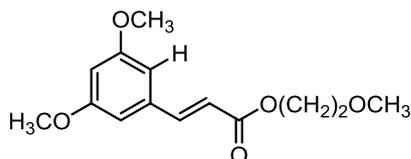
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 161.0, 158.5, 145.4, 136.2, 129.5, 121.2, 118.2, 114.7, 106.0, 102.8, 66.0, 63.0, 55.4. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 351.1203; found: 351.1199.

(tetrahydrofuran-2-yl)methyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3n)



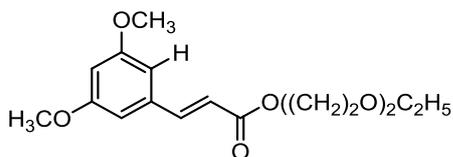
20.4 mg, 70% (isolated yield), colourless oil; $R_f=0.11$ (hexane/EtOAc = 10/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.63 (d, $J = 16.0$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 2H), 6.49 (t, $J = 2.2$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 4.31 (dd, $J = 11.4, 3.4$ Hz, 1H), 4.20 (qd, $J = 7.1, 3.4$ Hz, 1H), 4.12 (dd, $J = 11.4, 7.1$ Hz, 1H), 3.96 – 3.90 (m, 1H), 3.86 – 3.82 (m, 1H), 3.81 (s, 6H), 2.08 – 2.01 (m, 1H), 1.99 – 1.88 (m, 2H), 1.70 – 1.61 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 161.0, 145.1, 136.3, 118.4, 106.0, 102.7, 68.5, 66.6, 55.4, 28.0, 25.7. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 315.1203; found: 315.1200.

2-methoxyethyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3o)

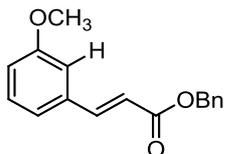


14.6 mg, 55% (isolated yield), colourless oil; $R_f=0.2$ (hexane/EtOAc = 5/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.63 (d, $J = 16.0$ Hz, 1H), 6.66 (t, $J = 2.0$ Hz, 2H), 6.48 (q, $J = 2.3$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 4.38 – 4.34 (m, 2H), 3.80 (s, 6H), 3.66 (td, $J = 4.7, 1.6$ Hz, 2H), 3.42 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ [ppm] = 167.0, 161.1, 145.3, 136.4, 118.5, 106.1, 102.8, 70.7, 63.7, 59.2, 55.5. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 289.1046; found: 289.1048.

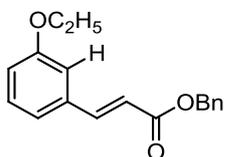
2-(2-ethoxyethoxy)ethyl (*E*)-3-(3,5-dimethoxyphenyl)acrylate (3p)



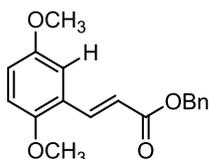
21.1 mg, 65% (isolated yield), colourless oil; $R_f=0.12$ (hexane/EtOAc = 5/1). ^1H NMR (600 MHz, CDCl_3): δ [ppm] = 7.62 (d, $J = 15.9$ Hz, 1H), 6.66 (d, $J = 2.3$ Hz, 2H), 6.49 (t, $J = 2.3$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 4.40 – 4.35 (m, 2H), 3.81 (s, 6H), 3.80 – 3.77 (m, 2H), 3.68 (dd, $J = 5.8, 3.7$ Hz, 2H), 3.61 (dd, $J = 5.8, 3.8$ Hz, 2H), 3.54 (q, $J = 7.0$ Hz, 2H), 1.22 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 161.0, 145.0, 136.3, 118.5, 106.0, 102.7, 70.7, 69.8, 69.3, 66.7, 63.7, 55.4, 15.2. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{17}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 347.1465; found: 347.1462.

benzyl (*E*)-3-(3-methoxyphenyl)acrylate (3q)⁵

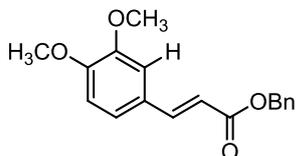
12.0 mg, 45% (isolated yield), colourless oil; $R_f=0.26$ (hexane/EtOAc = 20/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.70 (d, $J = 16.0$ Hz, 1H), 7.42 (d, $J = 7.3$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.37 – 7.33 (m, 1H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.12 (d, $J = 8.7$ Hz, 1H), 7.04 (t, $J = 2.1$ Hz, 1H), 6.94 (dd, $J = 8.3, 2.6$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 5.26 (s, 2H), 3.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 159.9, 145.1, 136.0, 135.7, 129.9, 128.6, 128.3, 128.3, 120.8, 118.2, 116.3, 112.9, 66.4, 55.3. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 291.0992; found: 291.0991.

benzyl (*E*)-3-(3-ethoxyphenyl)acrylate (3r)⁵

15.4 mg, 52% (isolated yield), colourless oil; $R_f=0.15$ (hexane/EtOAc = 50/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.69 (d, $J = 15.9$ Hz, 1H), 7.44 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 7.28 (t, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 2.0$ Hz, 1H), 6.92 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 5.25 (s, 2H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 159.3, 145.2, 136.1, 135.7, 129.9, 128.6, 128.3, 128.3, 120.7, 118.1, 116.8, 113.5, 66.4, 63.5, 14.8. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 305.1148; found: 305.1143.

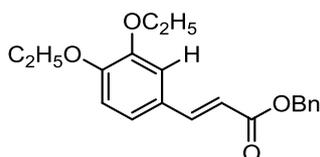
benzyl (*E*)-3-(2,5-dimethoxyphenyl)acrylate (3s)⁵

13.4 mg, 45% (isolated yield), colourless oil; $R_f=0.35$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 8.01 (d, $J = 16.1$ Hz, 1H), 7.45 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.04 (d, $J = 3.1$ Hz, 1H), 6.91 (dd, $J = 9.0, 3.1$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 1H), 6.56 (d, $J = 16.1$ Hz, 1H), 5.26 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.2, 153.5, 152.9, 140.5, 136.2, 128.6, 128.3, 128.2, 123.9, 118.6, 117.3, 113.3, 112.5, 66.3, 56.1, 55.8. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 321.1097; found: 321.1092.

benzyl (*E*)-3-(2,5-dimethoxyphenyl)acrylate (3t)⁵

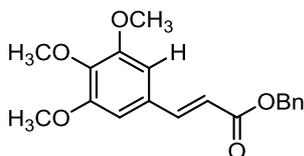
14.9 mg, 50% (isolated yield), colourless oil; $R_f=0.25$ (hexane/EtOAc = 5/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.67 (d, $J = 15.9$ Hz, 1H), 7.44 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 7.10 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.05 (d, $J = 2.0$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 5.25 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.2, 151.3, 149.3, 145.2, 136.3, 128.7, 128.4, 128.4, 127.5, 122.8, 115.7, 111.1, 109.7, 66.4, 56.1, 56.0. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 321.1097; found: 321.1098.

benzyl (*E*)-3-(3,4-diethoxyphenyl)acrylate (**3u**)



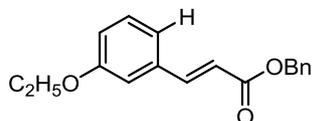
22.8 mg, 70% (isolated yield), colourless oil; $R_f=0.32$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.66 (d, $J = 15.9$ Hz, 1H), 7.43 – 7.41 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.09 – 7.04 (m, 2H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.34 (d, $J = 15.9$ Hz, 1H), 5.24 (s, 2H), 4.11 (dq, $J = 10.0, 7.0$ Hz, 4H), 1.46 (td, $J = 7.0, 2.0$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.1, 151.0, 148.8, 145.2, 136.2, 128.6, 128.3, 128.2, 127.2, 122.7, 115.3, 112.7, 111.9, 66.2, 64.6, 64.5, 14.8, 14.7. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 349.1406; found: 349.1410.

benzyl (*E*)-3-(3,4-diethoxyphenyl)acrylate (**3v**)⁸



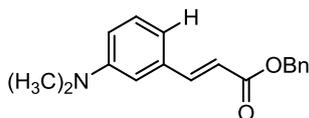
20.2 mg, 62% (isolated yield), colourless oil; $R_f=0.23$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.64 (d, $J = 15.9$ Hz, 1H), 7.44 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 6.75 (s, 2H), 6.40 (d, $J = 15.9$ Hz, 1H), 5.25 (s, 2H), 3.88 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.8, 153.4, 145.1, 140.2, 136.0, 129.9, 128.6, 128.3, 128.3, 117.1, 105.2, 66.4, 61.0, 56.2. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 351.1203; found: 351.1205.

benzyl (*E*)-3-(3-ethoxyphenyl)acrylate (**3w**)⁵



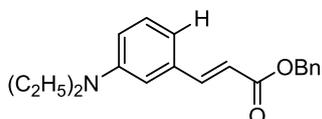
12.7 mg, 45% (isolated yield), colourless oil; $R_f=0.25$ (hexane/EtOAc = 30/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.69 (d, $J = 16.0$ Hz, 1H), 7.43 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 7.28 (t, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 7.03 (t, $J = 2.0$ Hz, 1H), 6.92 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 5.25 (s, 2H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.9, 159.4, 145.3, 136.2, 135.8, 130.0, 128.7, 128.4, 128.4, 120.8, 118.2, 117.0, 113.7, 66.5, 63.7, 14.9. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 305.1148; found: 305.1148.

benzyl (*E*)-3-(3-(dimethylamino)phenyl)acrylate (**3x**)



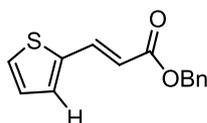
16.9 mg, 60% (isolated yield), yellow oil; $R_f=0.26$ (hexane/EtOAc = 20/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.72 (d, $J = 16.0$ Hz, 1H), 7.43 (d, $J = 6.9$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.36 – 7.33 (m, 1H), 7.24 (d, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 6.84 (s, 1H), 6.77 (dd, $J = 8.3, 2.7$ Hz, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 5.26 (s, 2H), 2.97 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.0, 150.8, 146.4, 136.2, 135.0, 129.5, 128.6, 128.3, 128.3, 117.3, 116.4, 114.6, 111.9, 66.3, 40.5. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 304.1308; found: 304.1302.

benzyl (*E*)-3-(3-(diethylamino)phenyl)acrylate (**3y**)



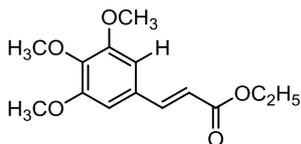
19.0 mg, 61% (isolated yield), yellow oil; $R_f=0.39$ (hexane/EtOAc = 20/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.71 (d, $J = 16.0$ Hz, 1H), 7.44 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.1$ Hz, 1H), 7.22 (t, $J = 7.9$ Hz, 1H), 6.83 (d, $J = 7.4$ Hz, 1H), 6.79 (s, 1H), 6.72 (dd, $J = 8.4, 2.7$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 5.26 (s, 2H), 3.37 (q, $J = 7.1$ Hz, 4H), 1.17 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.1, 148.0, 146.7, 136.2, 135.2, 129.7, 128.6, 128.4, 128.3, 117.1, 115.2, 113.9, 111.3, 66.3, 44.4, 12.5. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 332.1621; found: 332.1612.

benzyl (*E*)-3-(thiophen-2-yl)acrylate (**3z**)⁹



7.3 mg, 30% (isolated yield), colourless oil; $R_f=0.53$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.83 (d, $J = 15.7$ Hz, 1H), 7.43 – 7.35 (m, 6H), 7.26 (d, $J = 3.8$ Hz, 1H), 7.05 (t, $J = 4.5$ Hz, 1H), 6.29 (d, $J = 15.8$ Hz, 1H), 5.24 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 166.7, 139.5, 137.6, 136.1, 131.1, 128.6, 128.6, 128.3, 128.3, 128.1, 116.6, 66.4. HRMS (ESI-Q-TOF) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{SO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 267.0450; found: 267.0447.

ethyl (*E*)-3-(3,4,5-trimethoxyphenyl)acrylate (**3aa**)⁸



14.6 mg, 55% (isolated yield), colourless oil; $R_f=0.16$ (hexane/EtOAc = 10/1). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ [ppm] = 7.59 (d, $J = 15.9$ Hz, 1H), 6.75 (s, 2H), 6.34 (d, $J = 15.8$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.88 (s, 6H), 3.87 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ [ppm] = 167.1, 153.5,

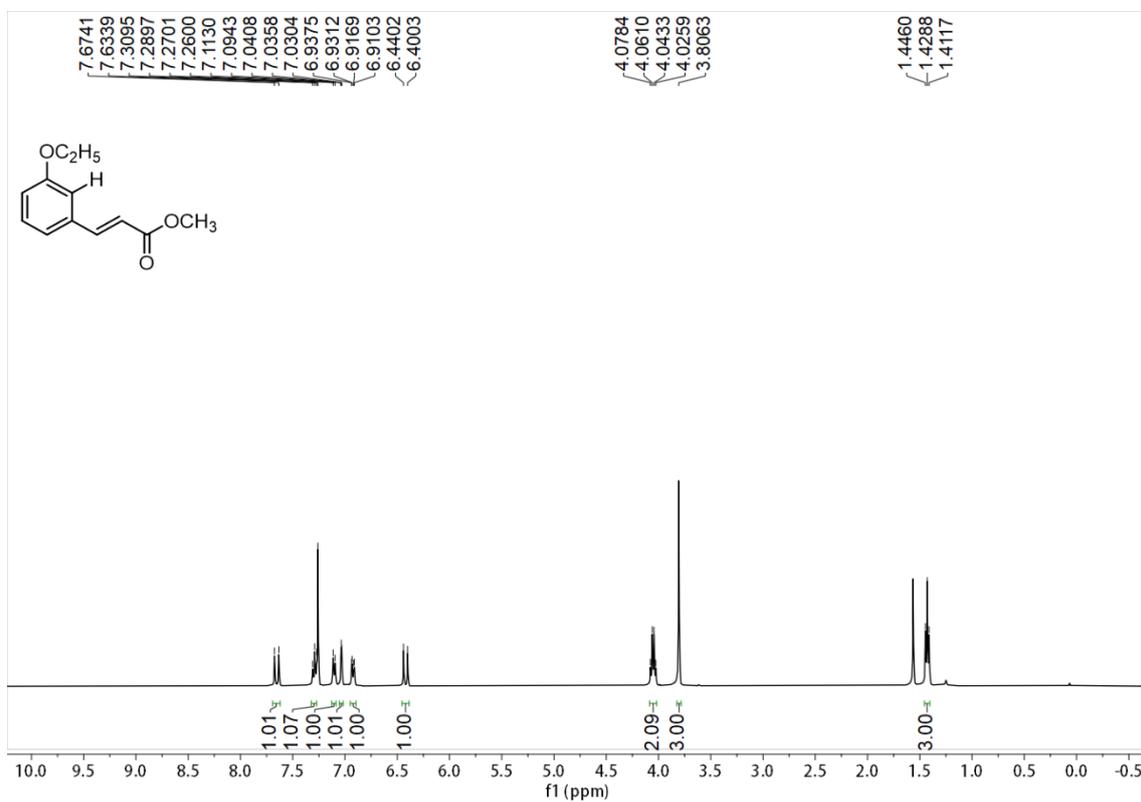
144.7, 140.2, 130.1, 117.6, 105.3, 61.1, 60.6, 56.3, 14.5. HRMS (ESI-Q-TOF) m/z calculated for C₁₄H₁₈O₅Na [M+Na]⁺: 289.1046; found: 289.1040.

6. References

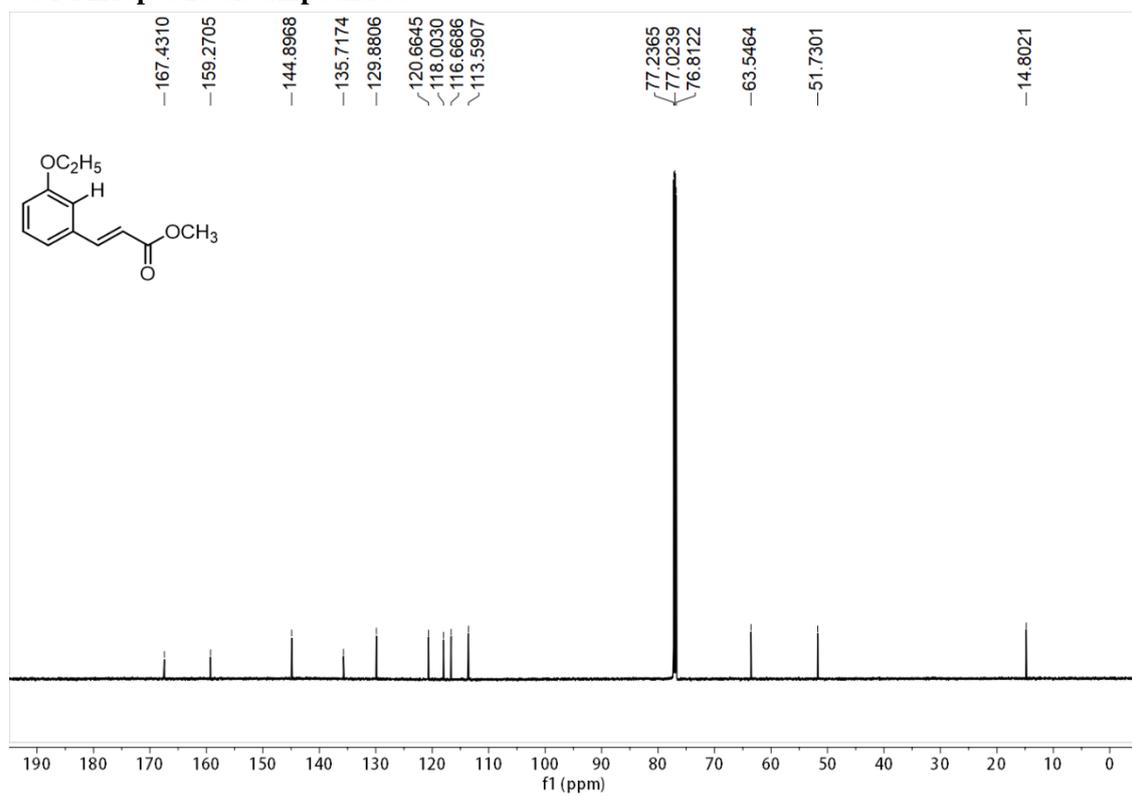
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7. The ^1H NMR and ^{13}C NMR spectra of compounds

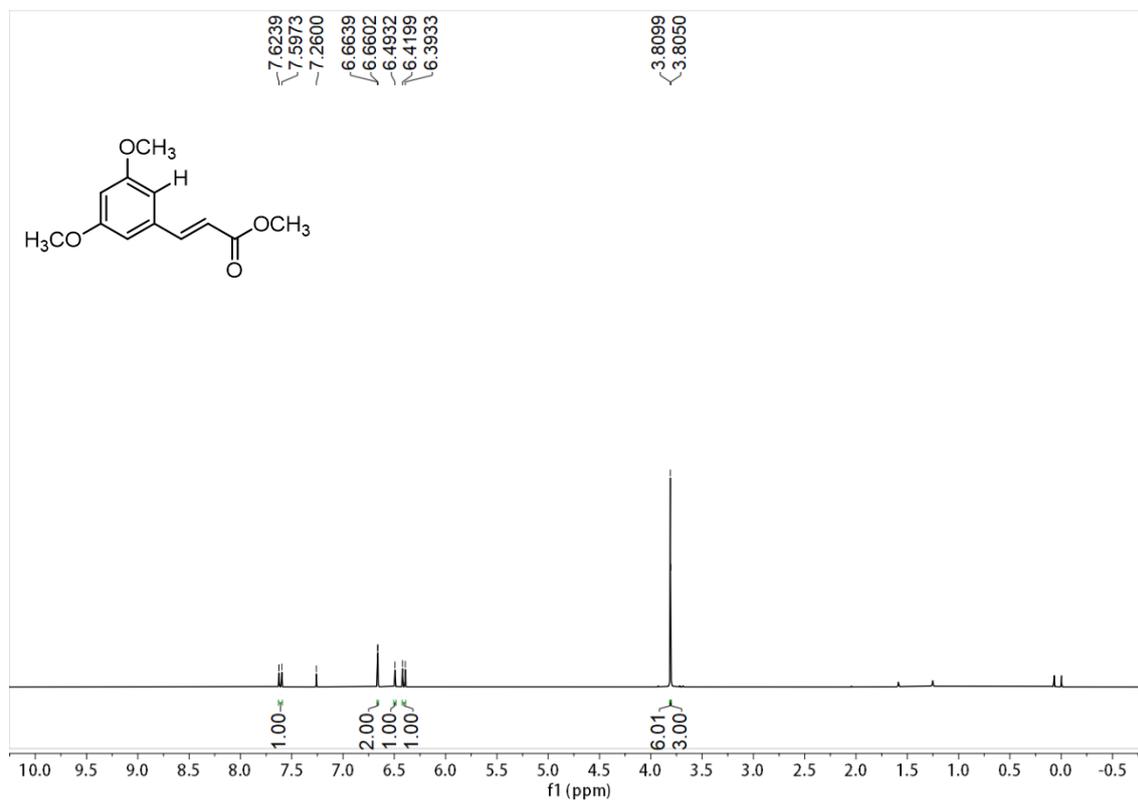
^1H NMR spectra of compound 3a



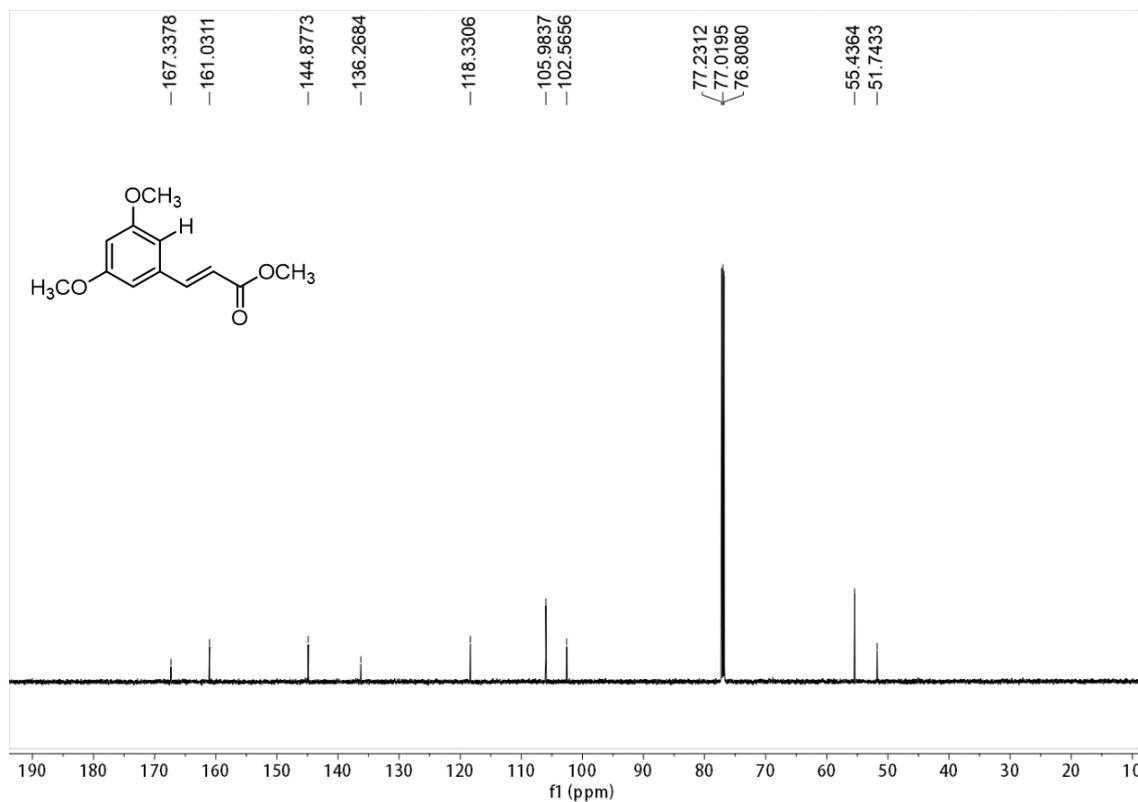
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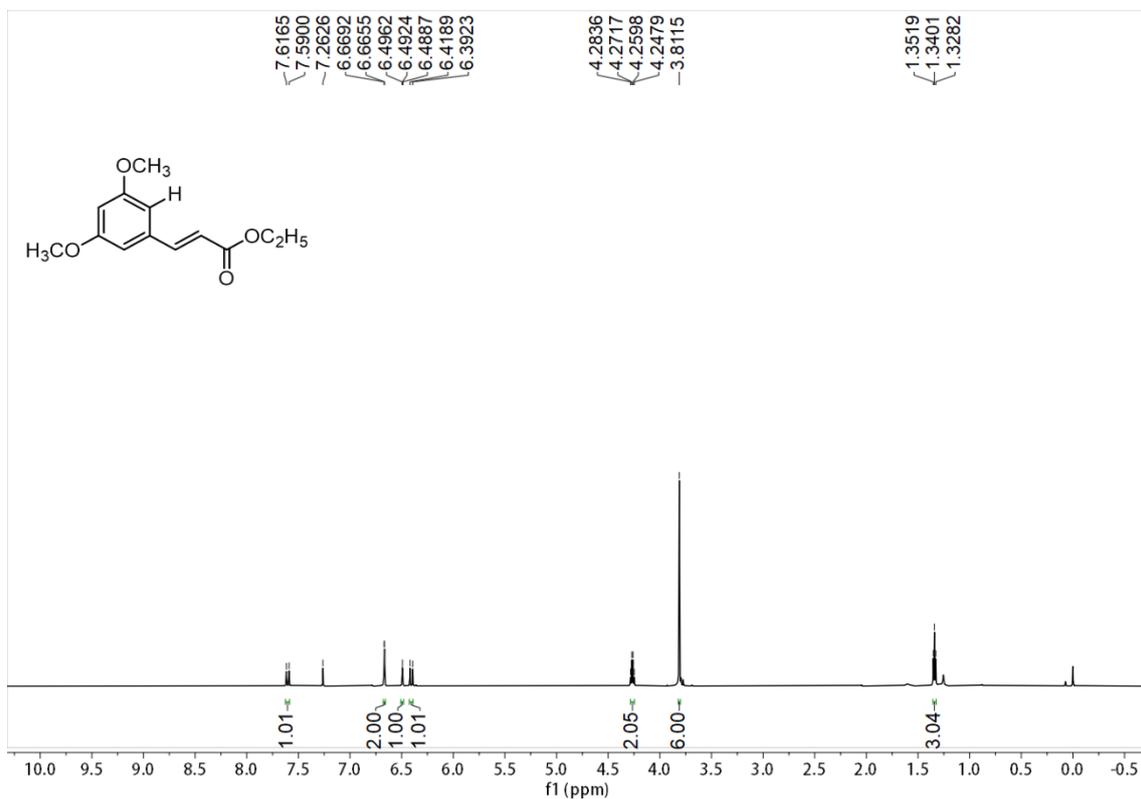
¹H NMR spectra of compound 3b



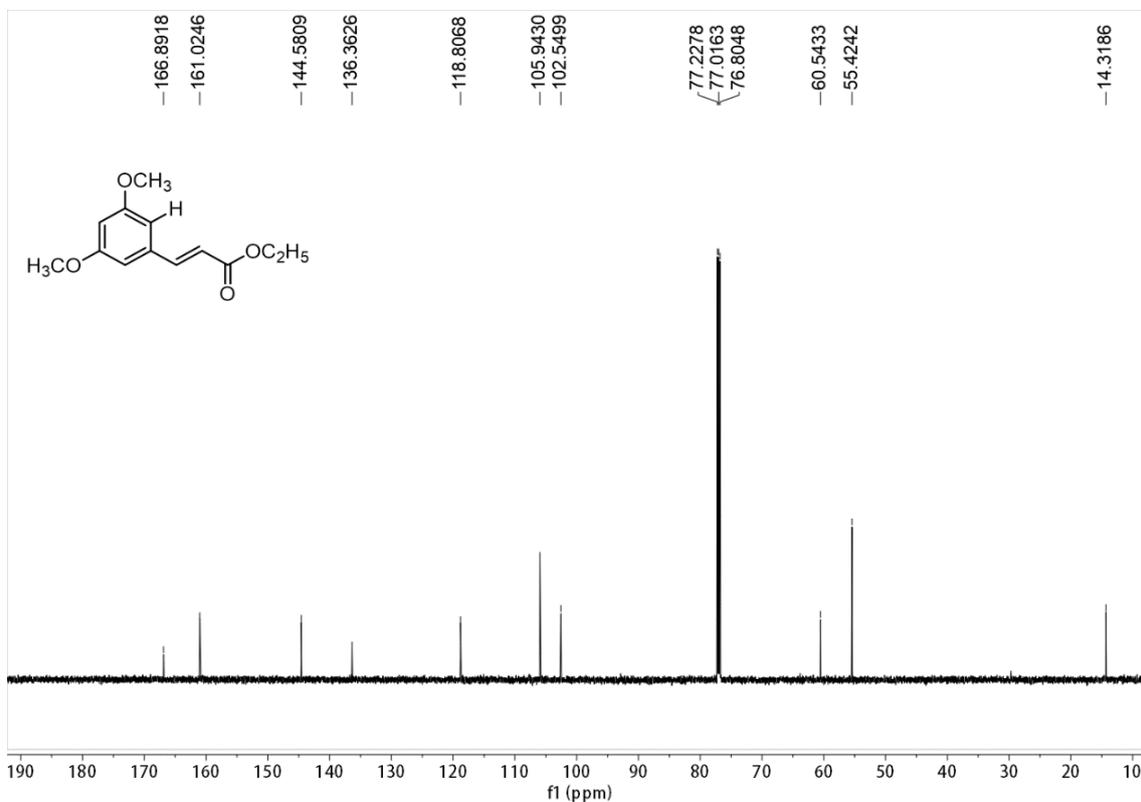
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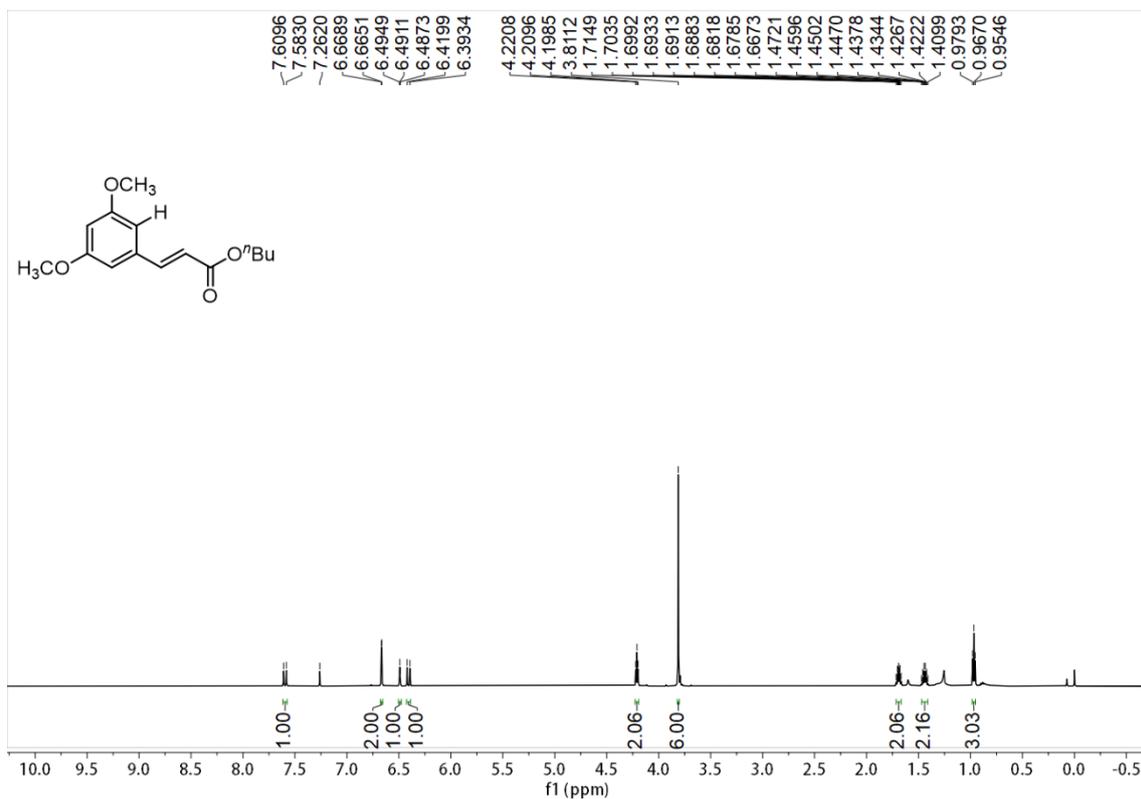
¹H NMR spectra of compound 3c



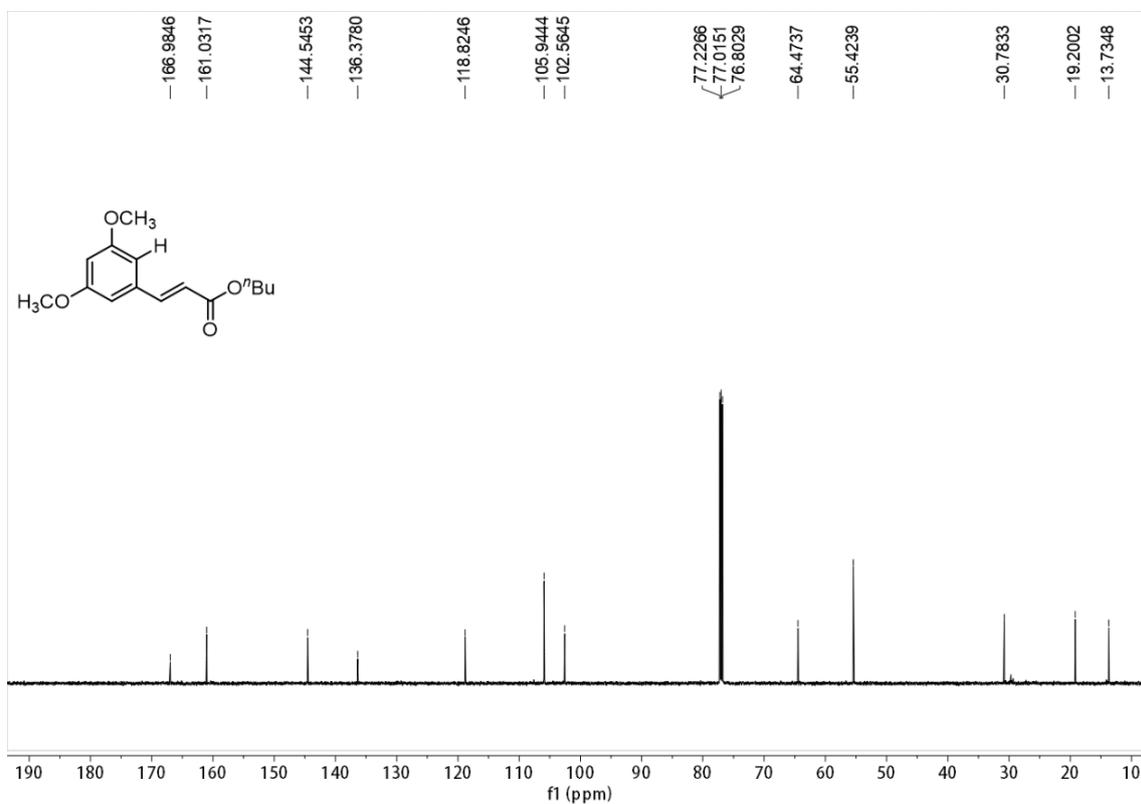
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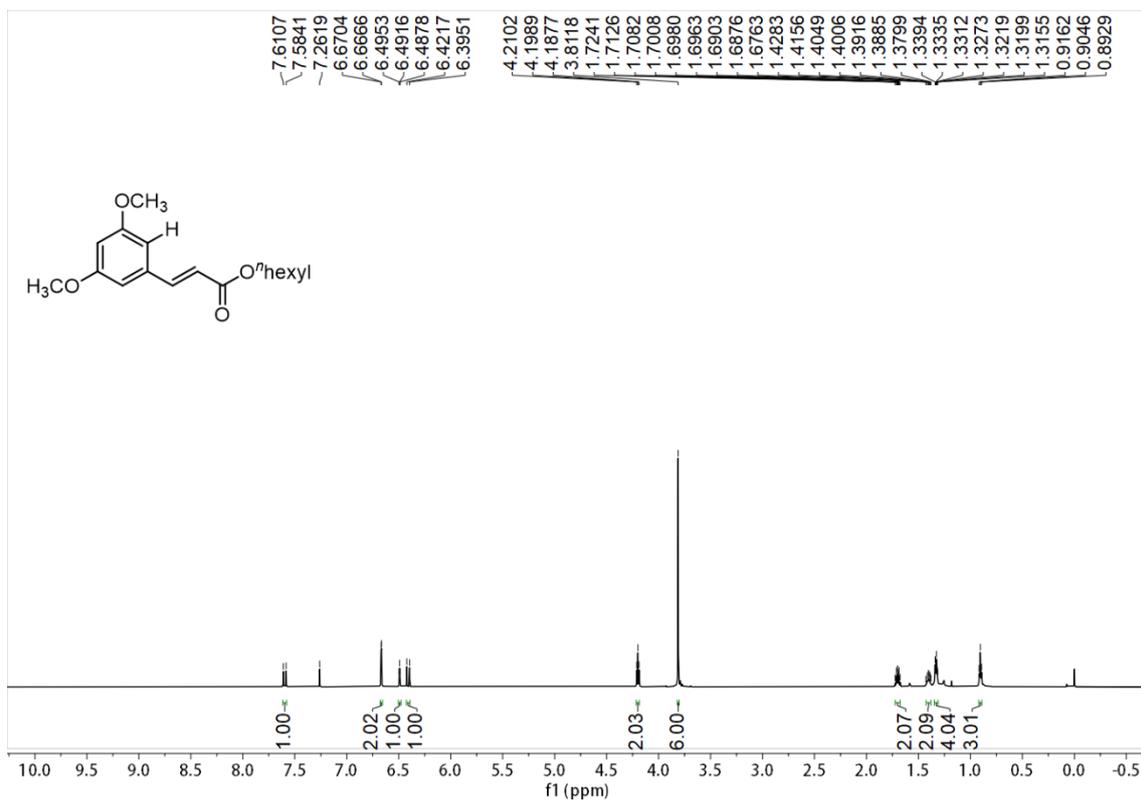
¹H NMR spectra of compound 3d



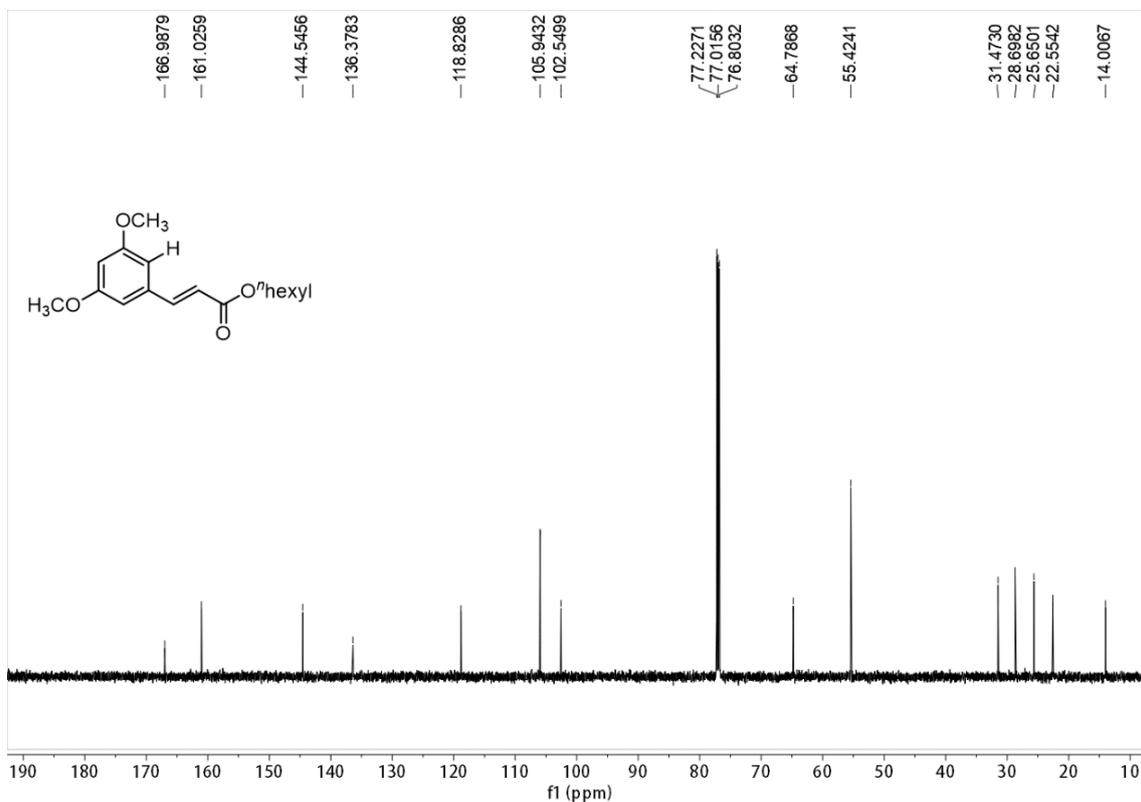
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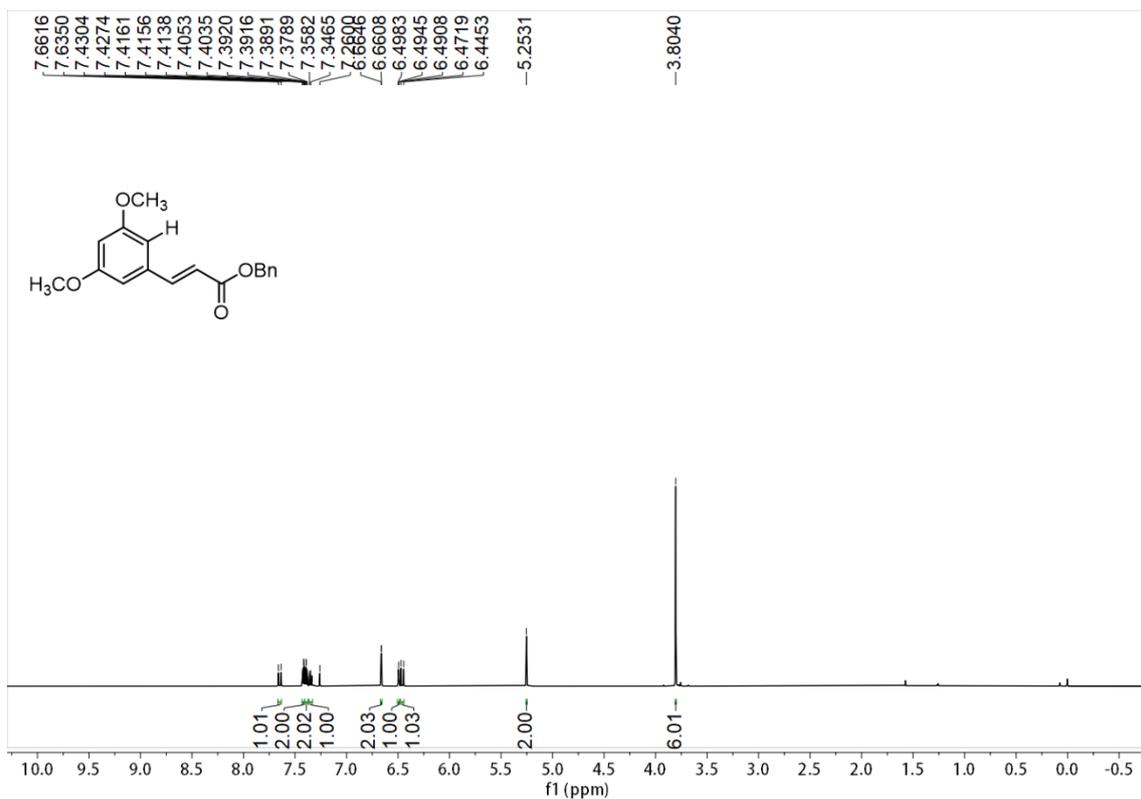
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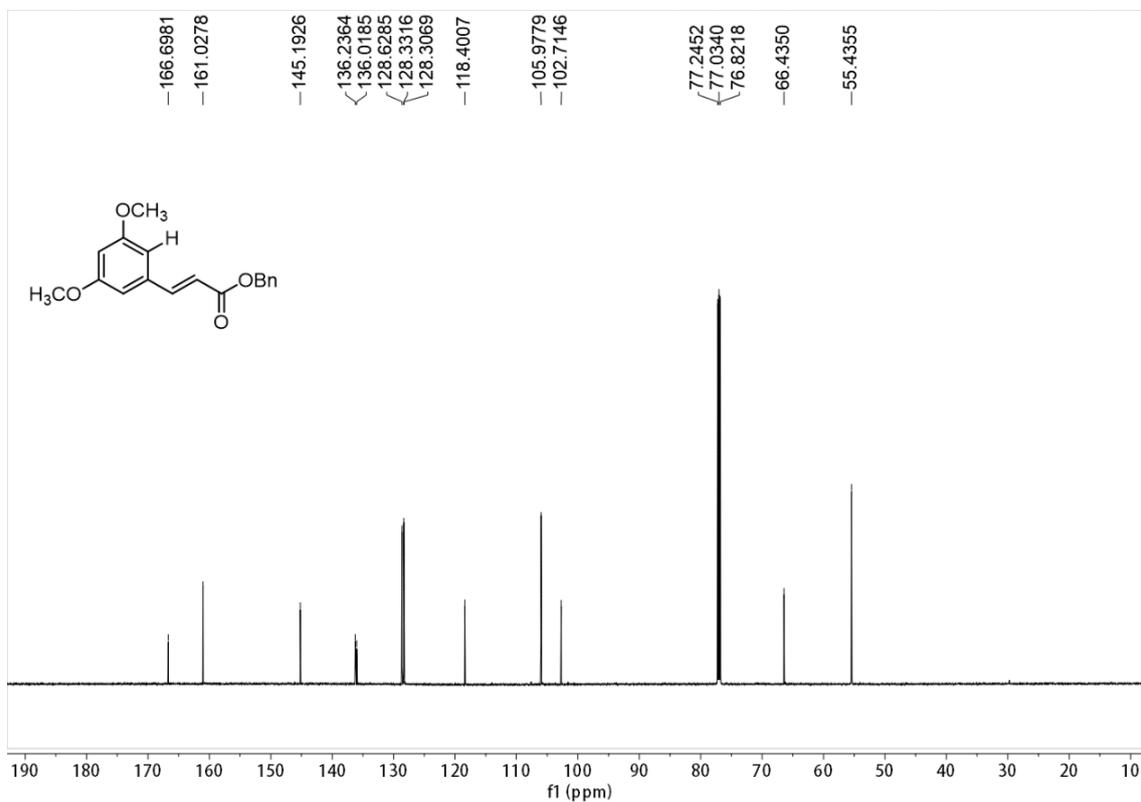
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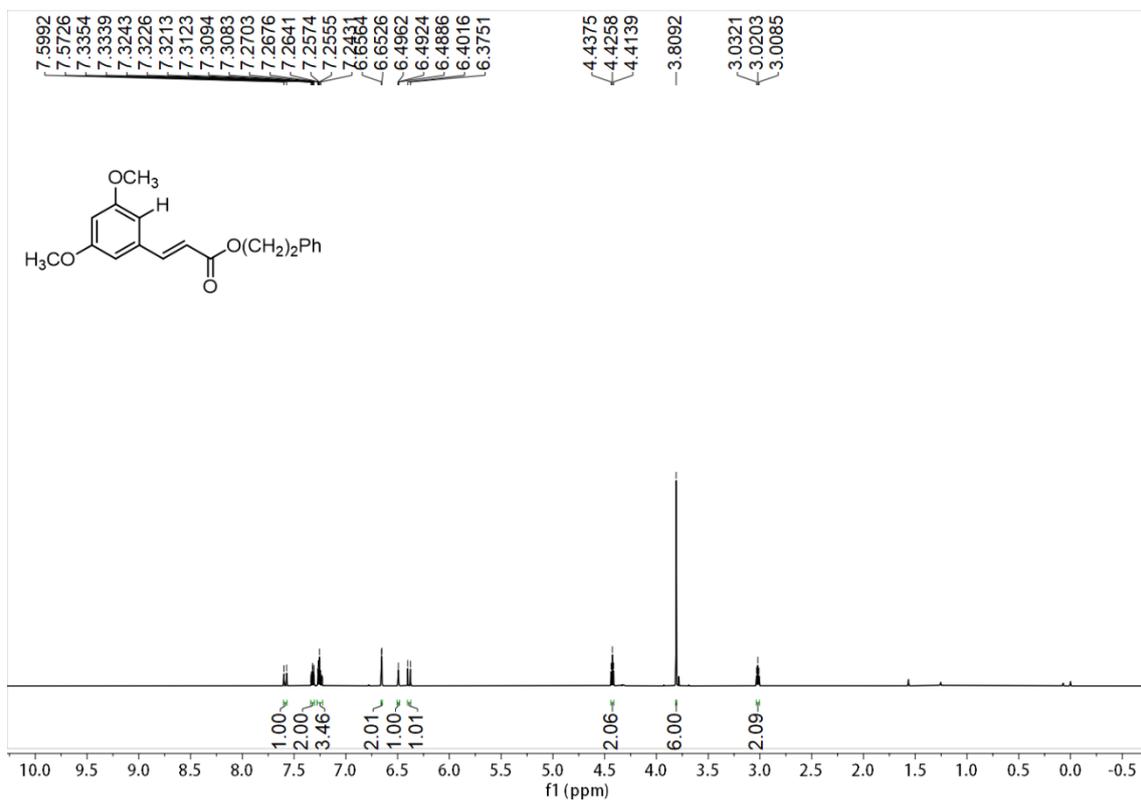
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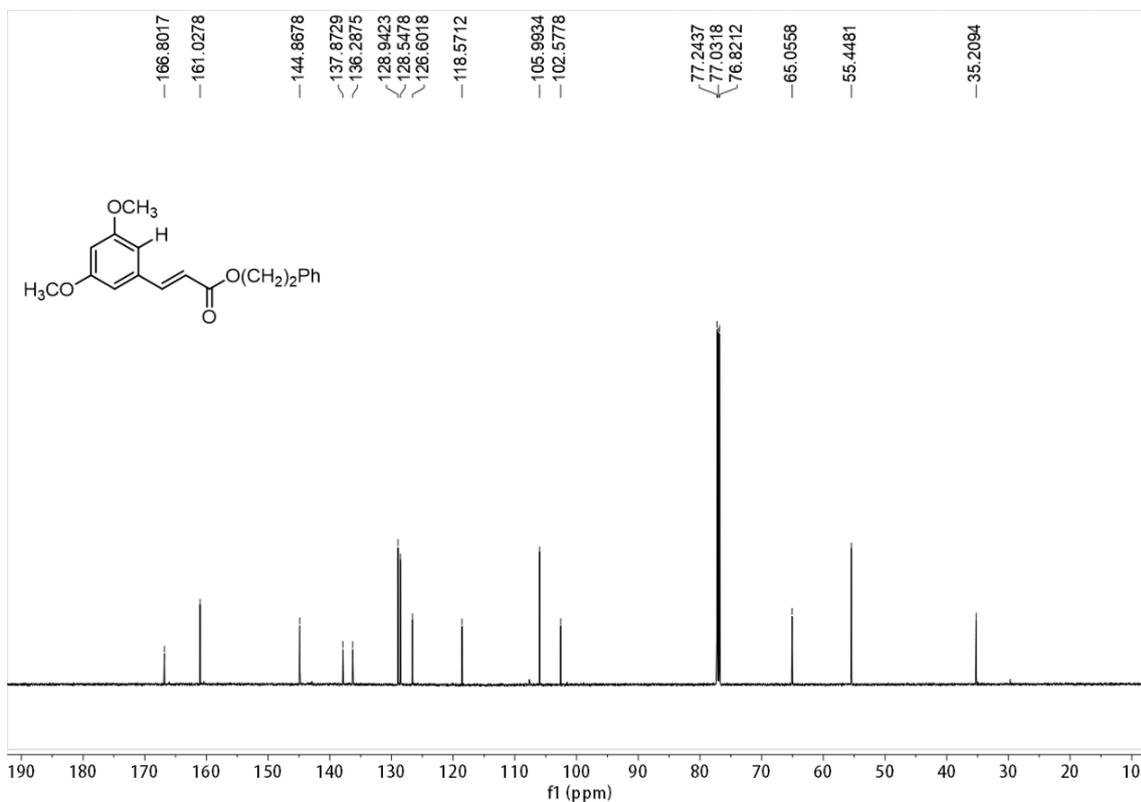
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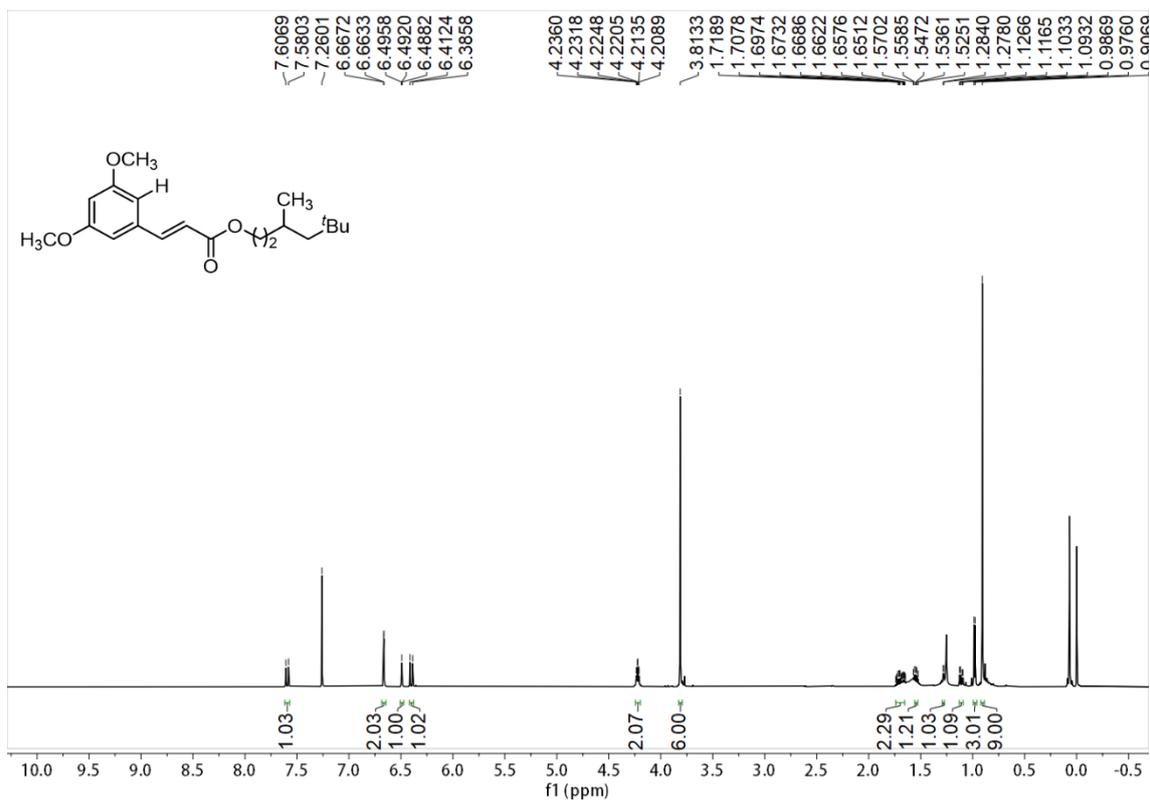
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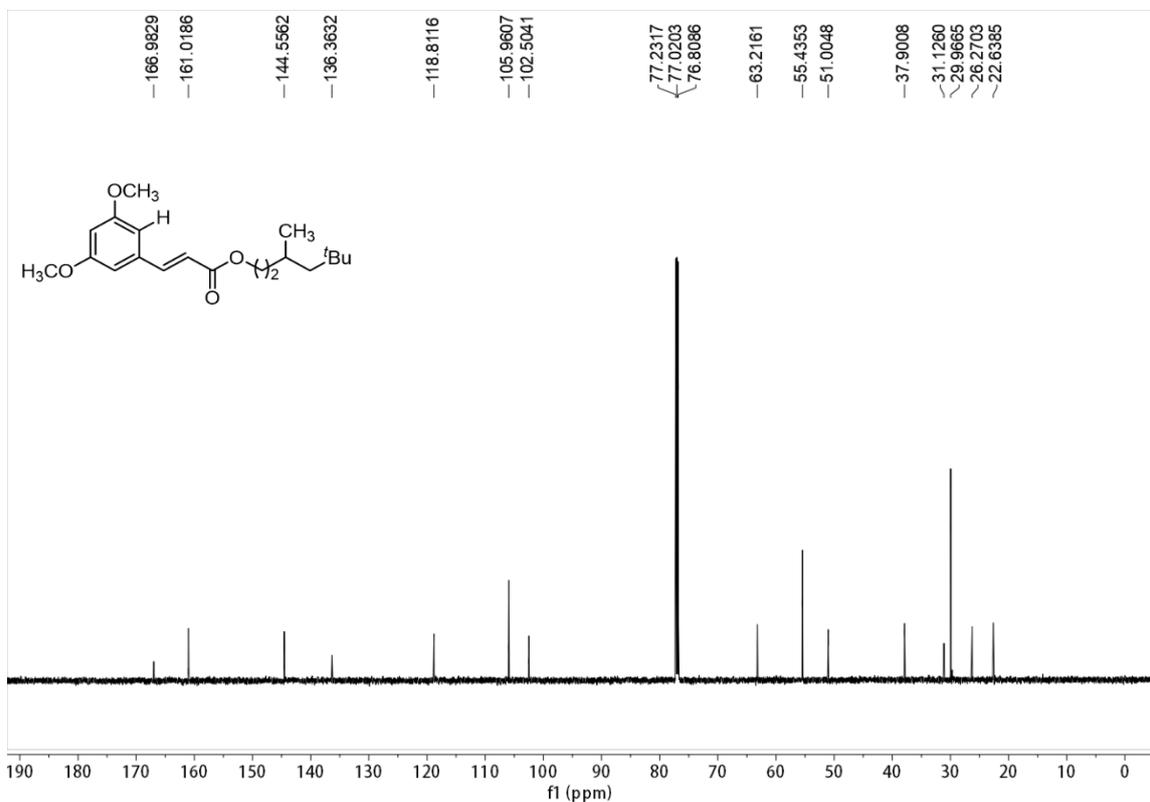
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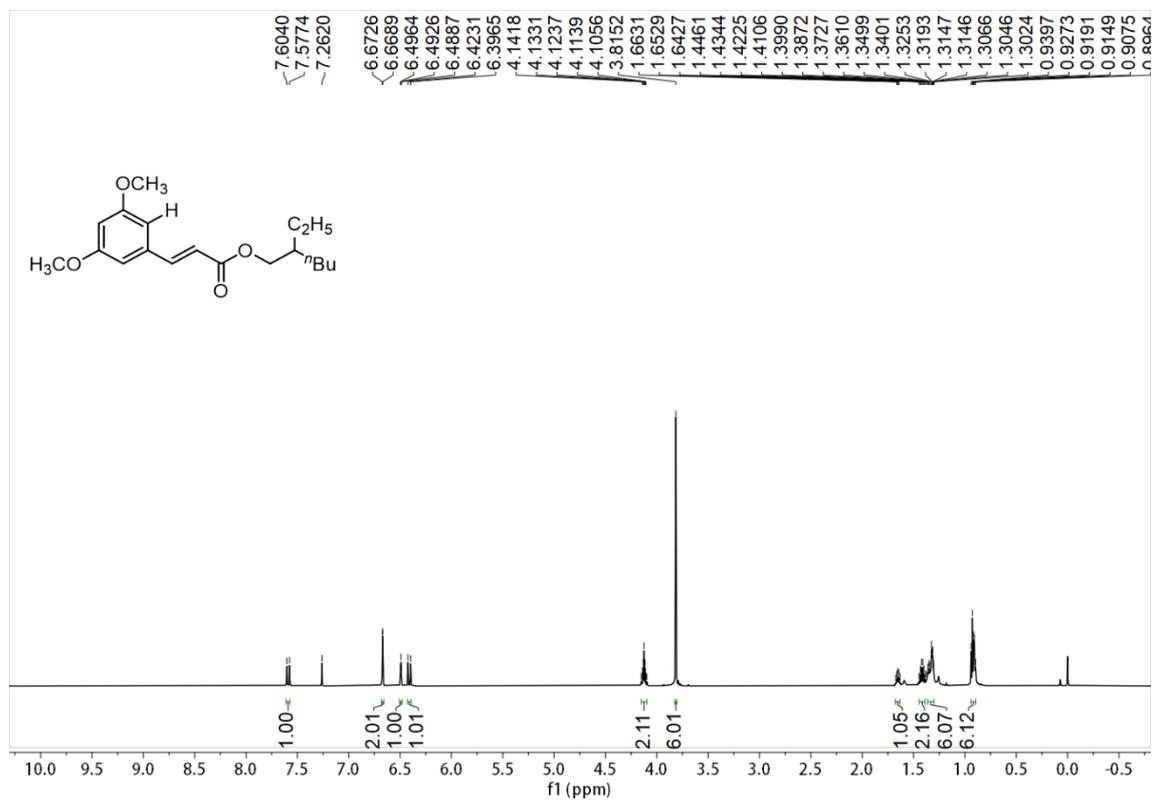
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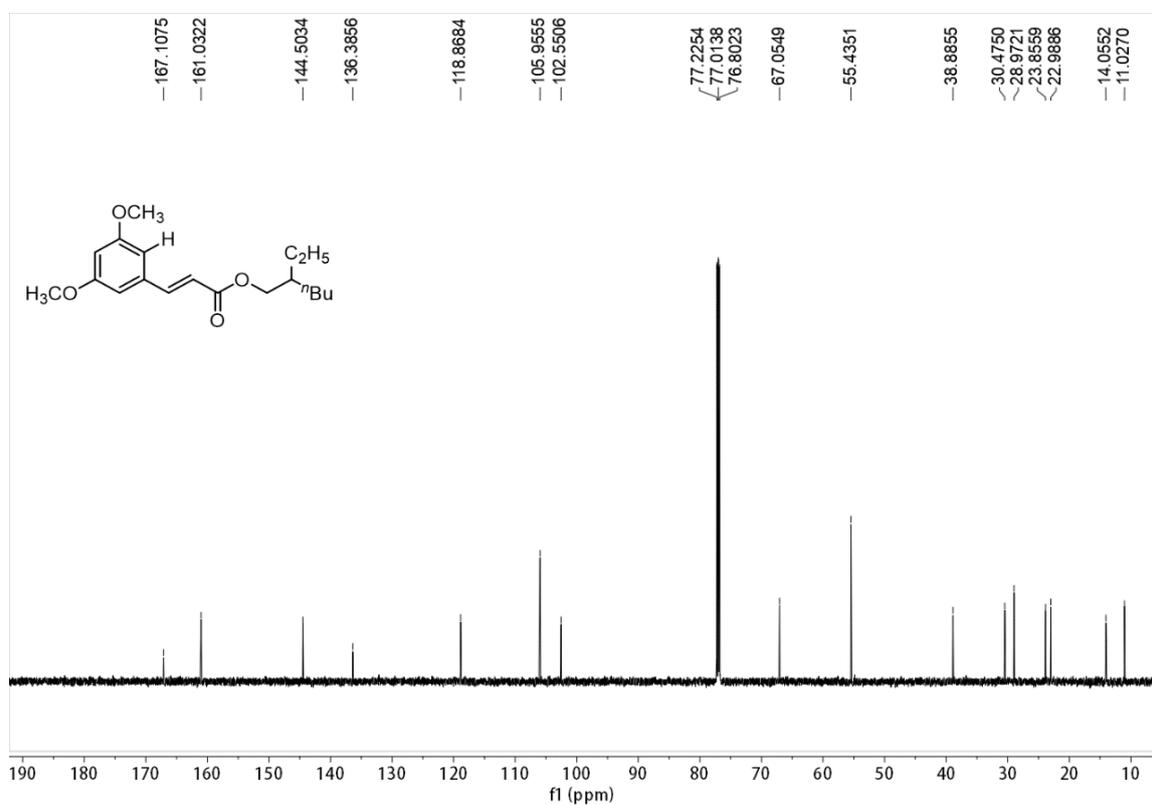
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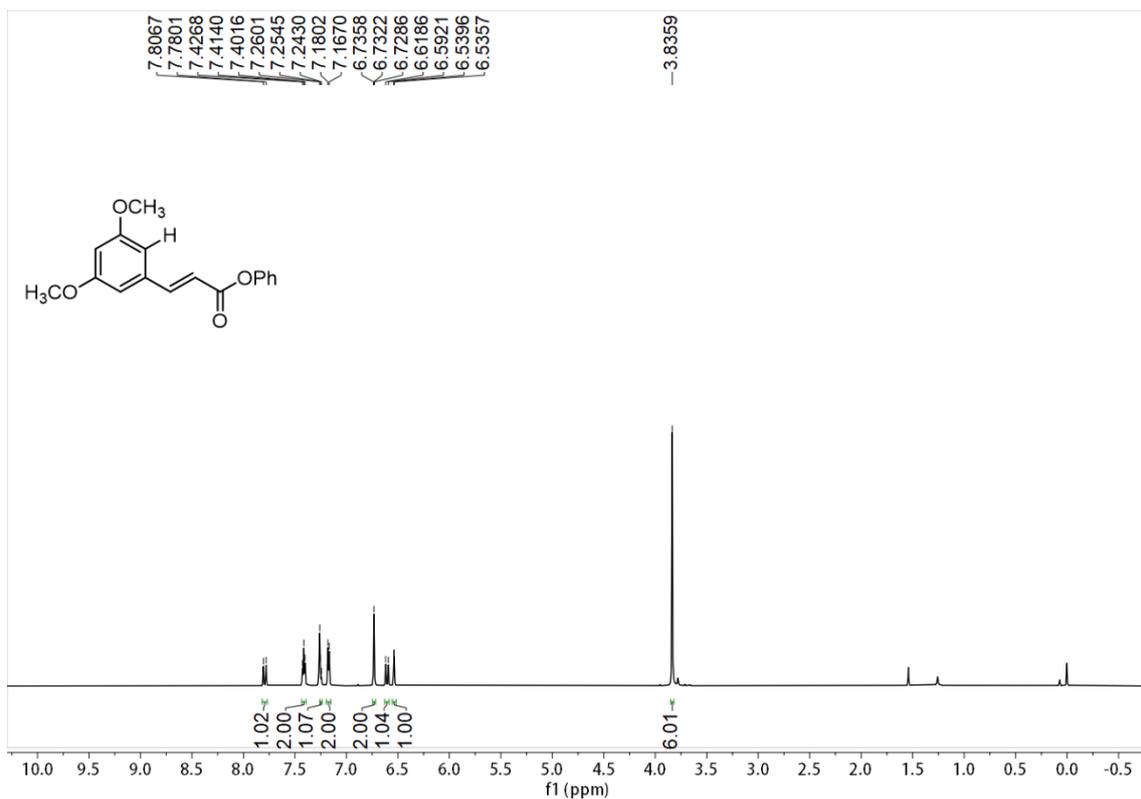
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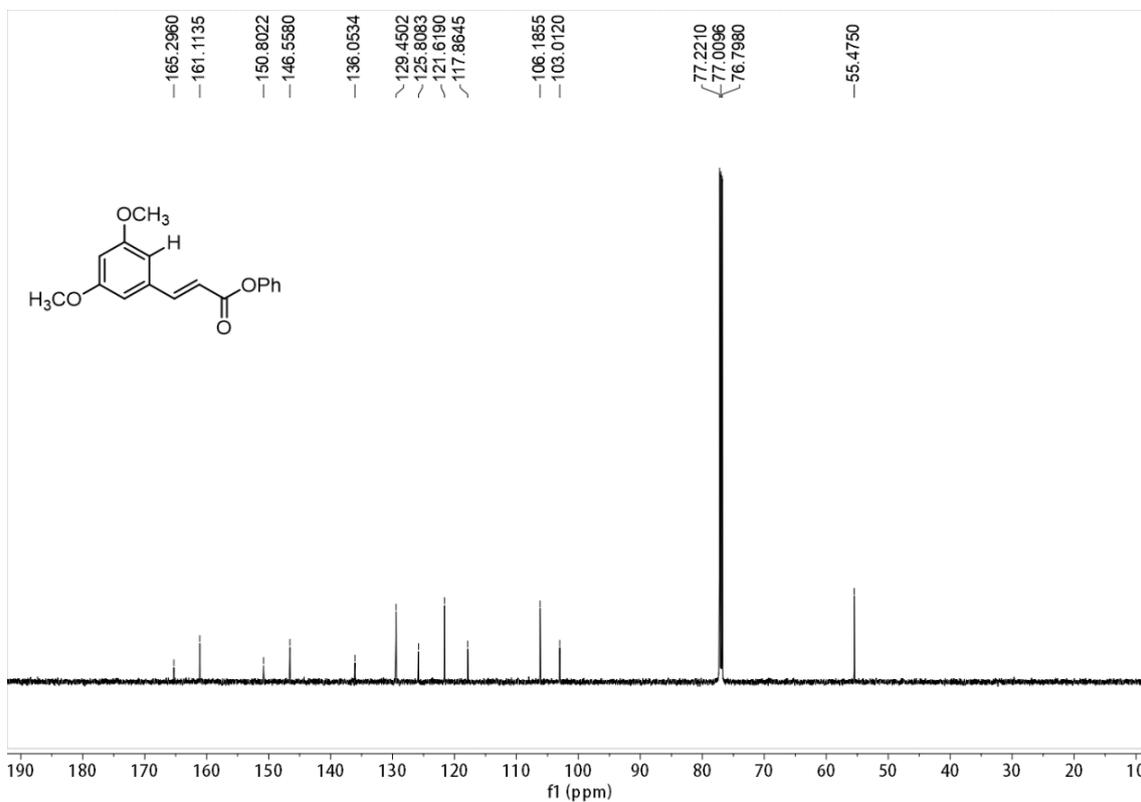
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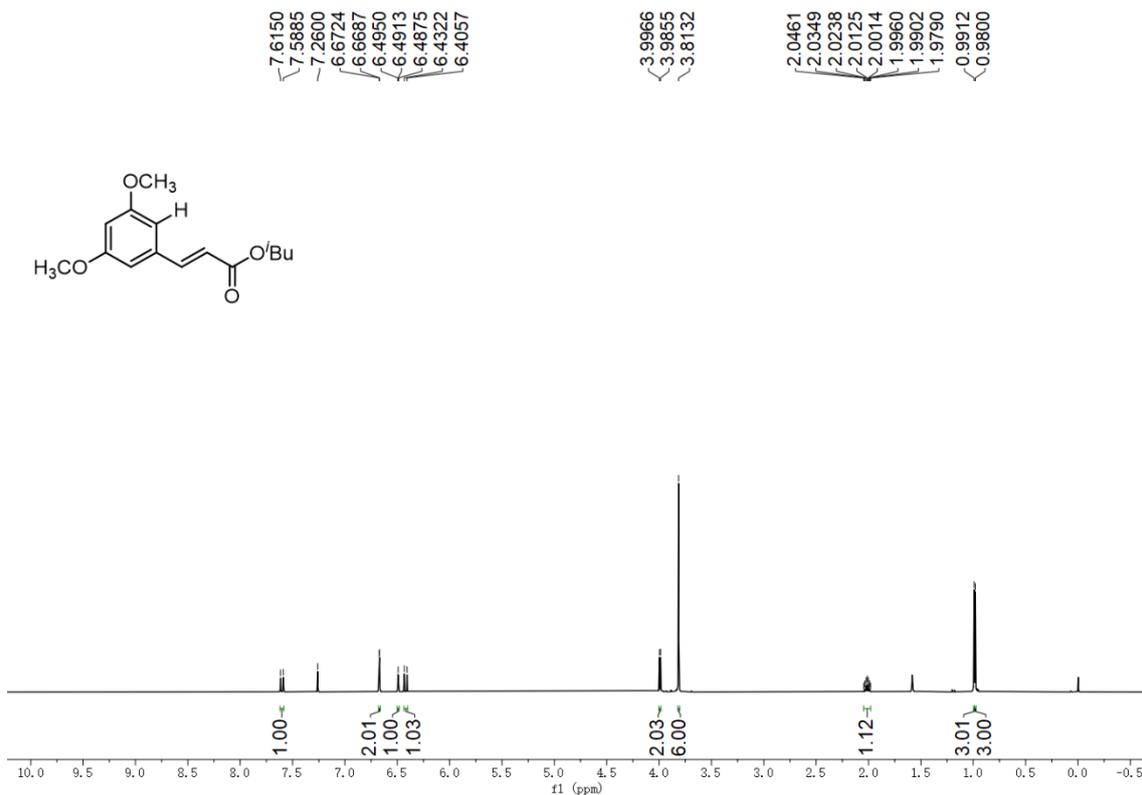
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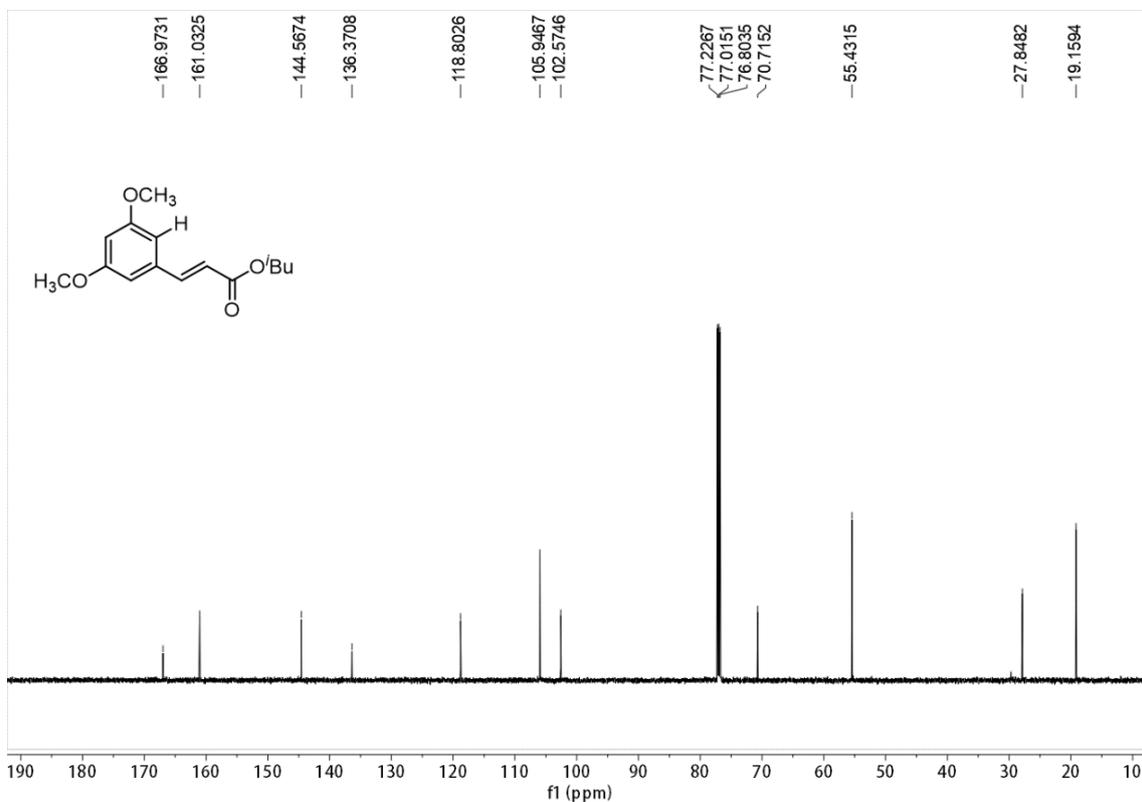
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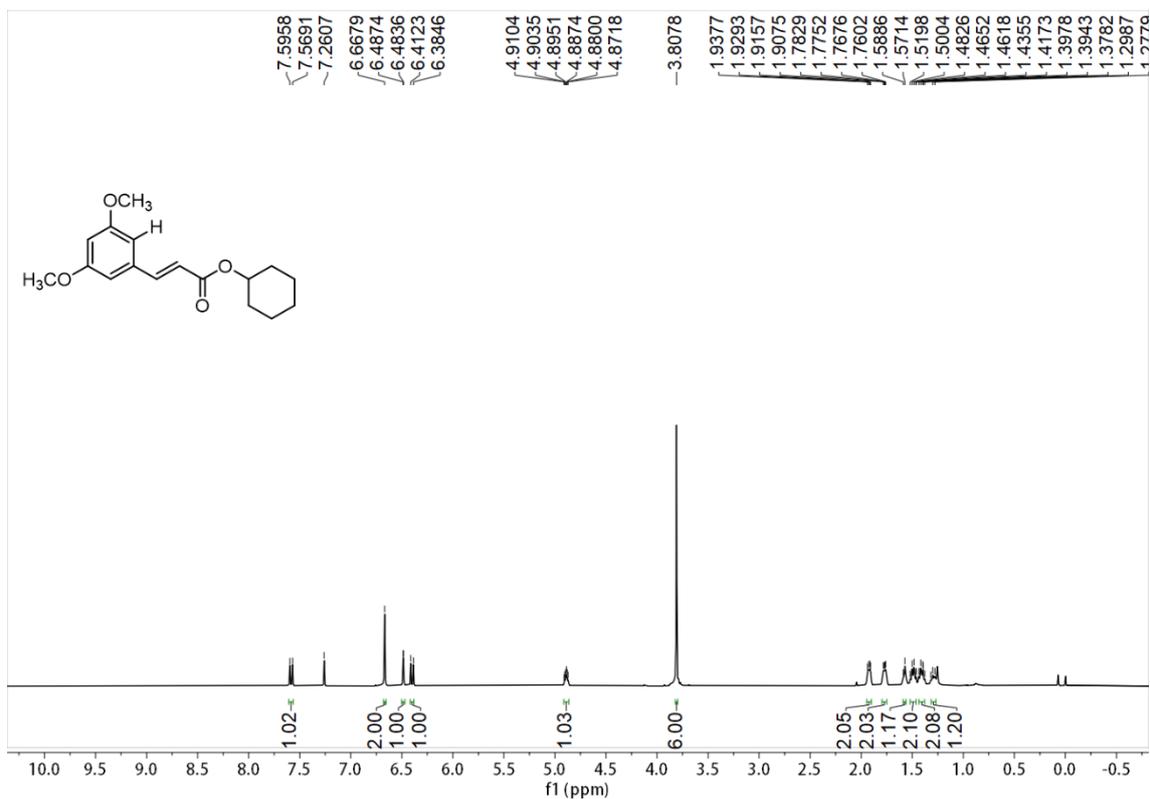
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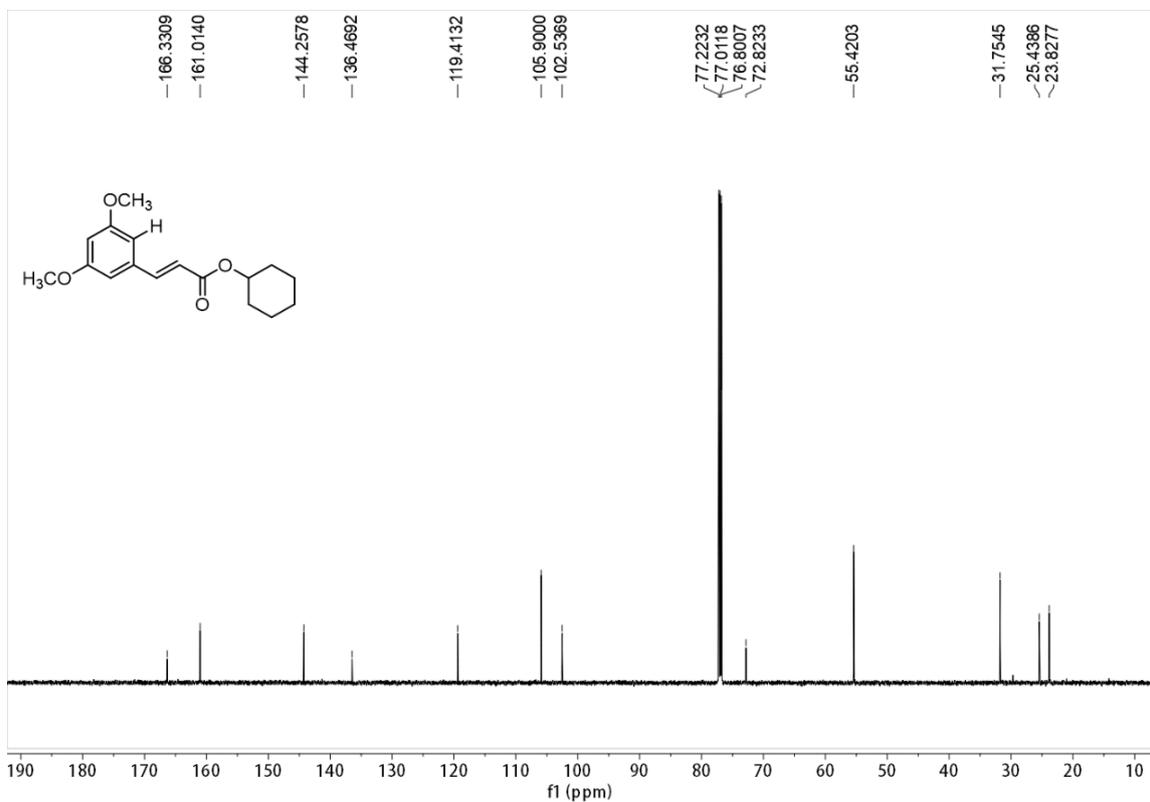
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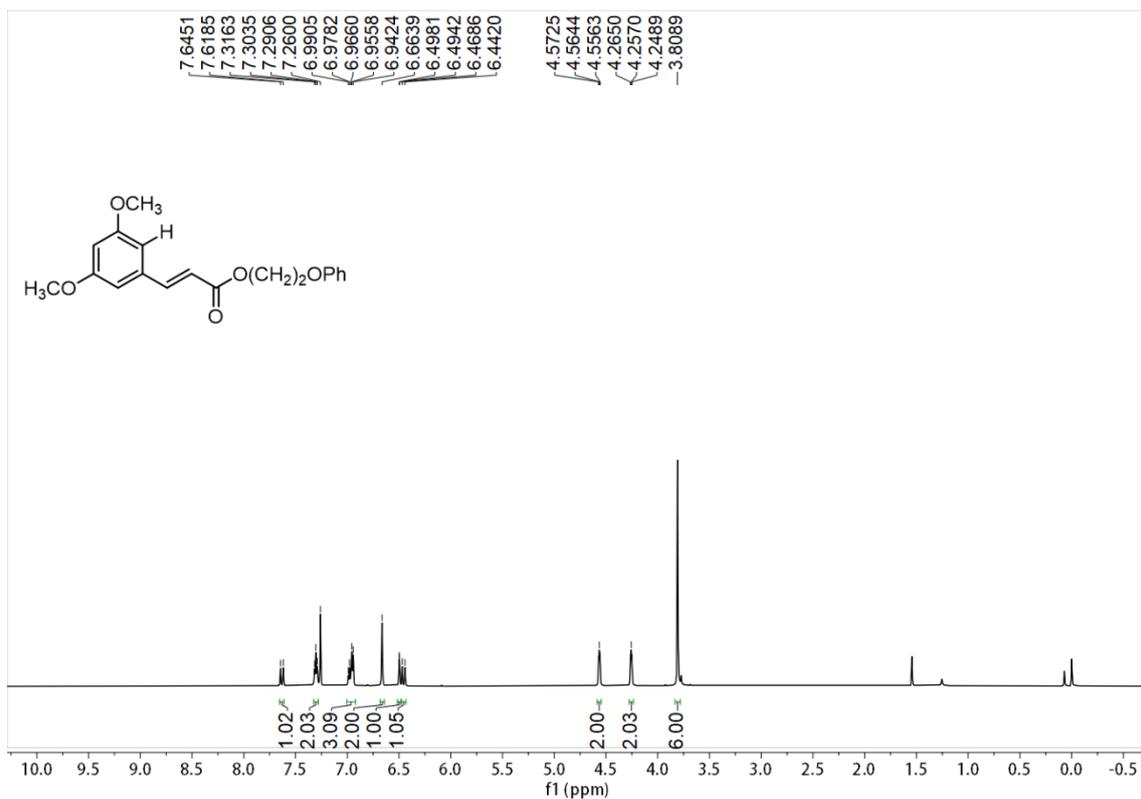
¹H NMR spectra of compound 31



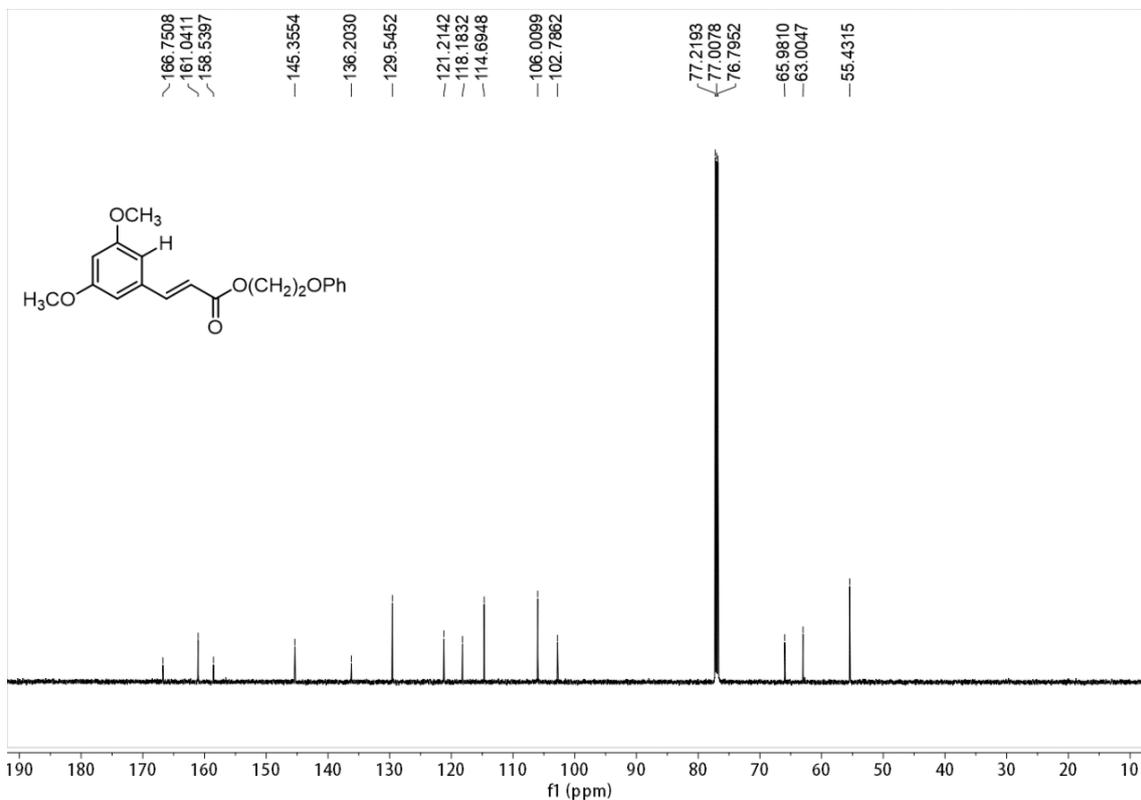
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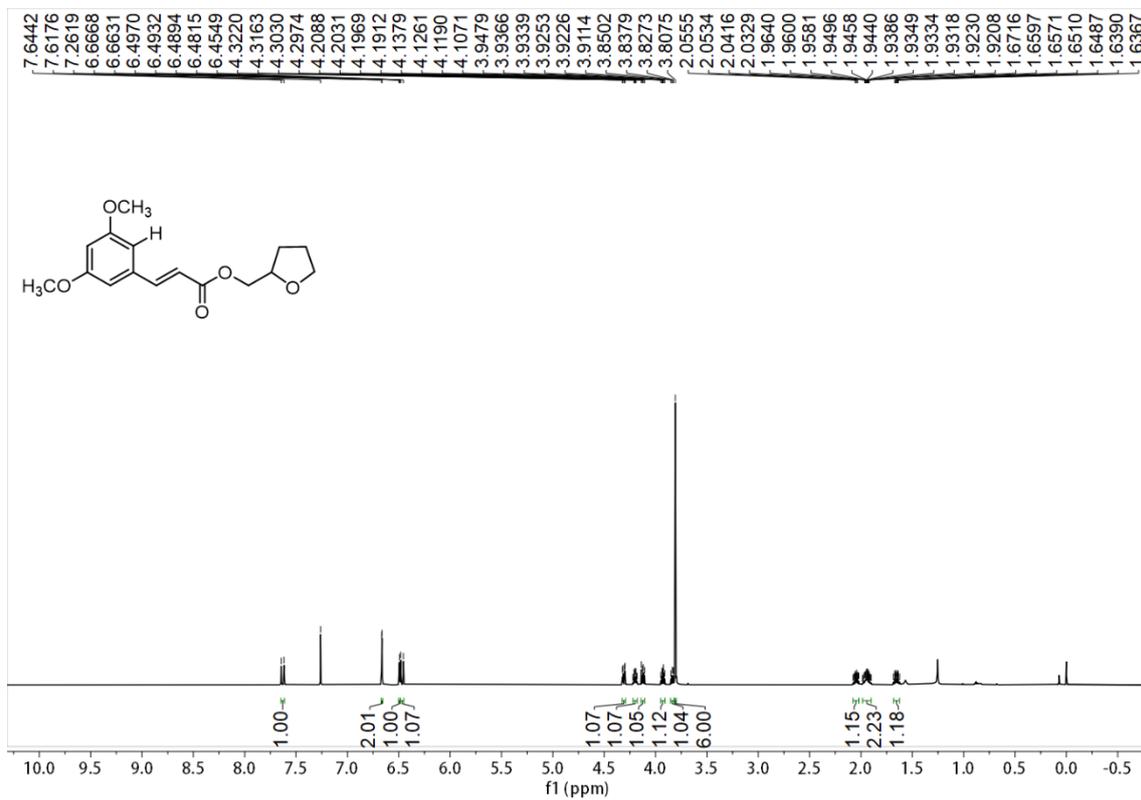
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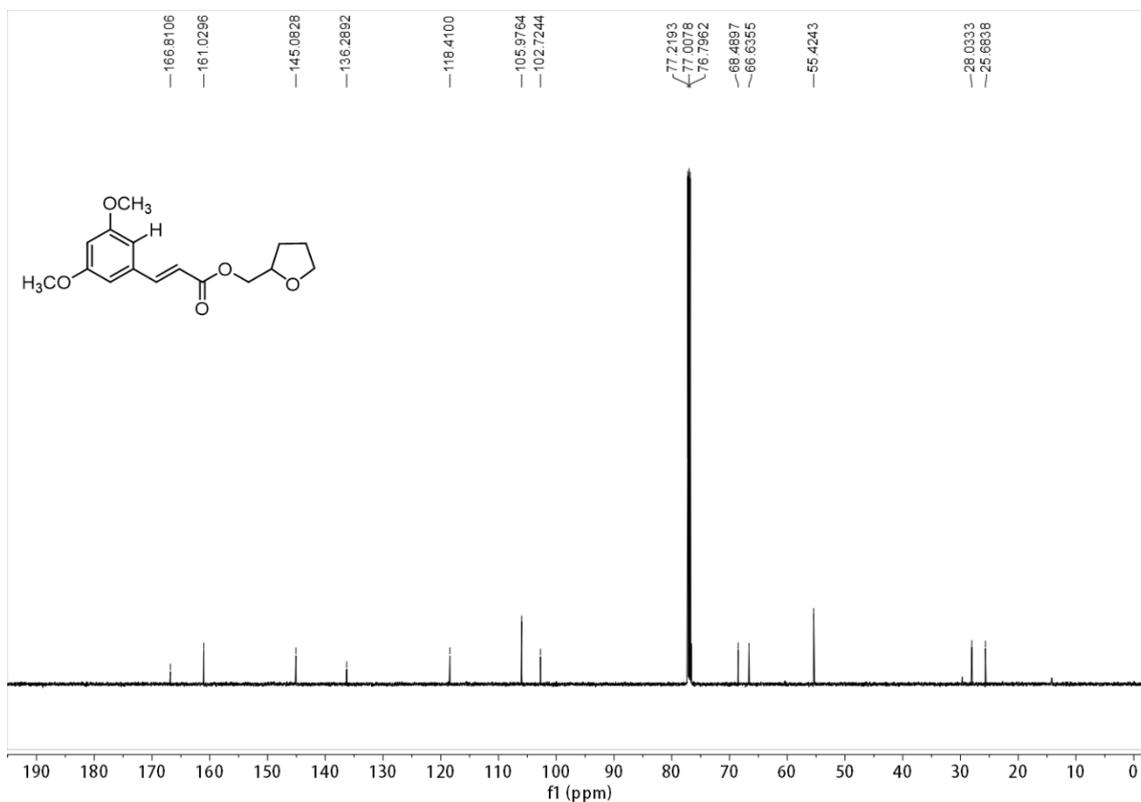
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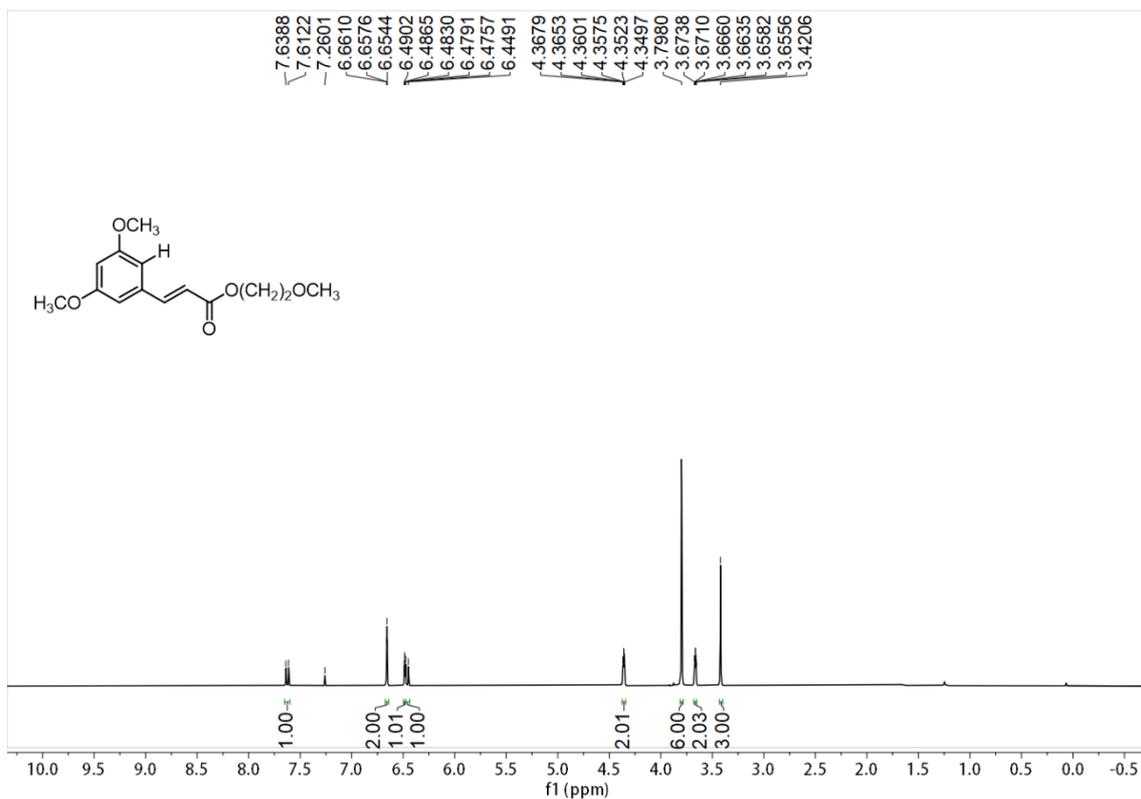
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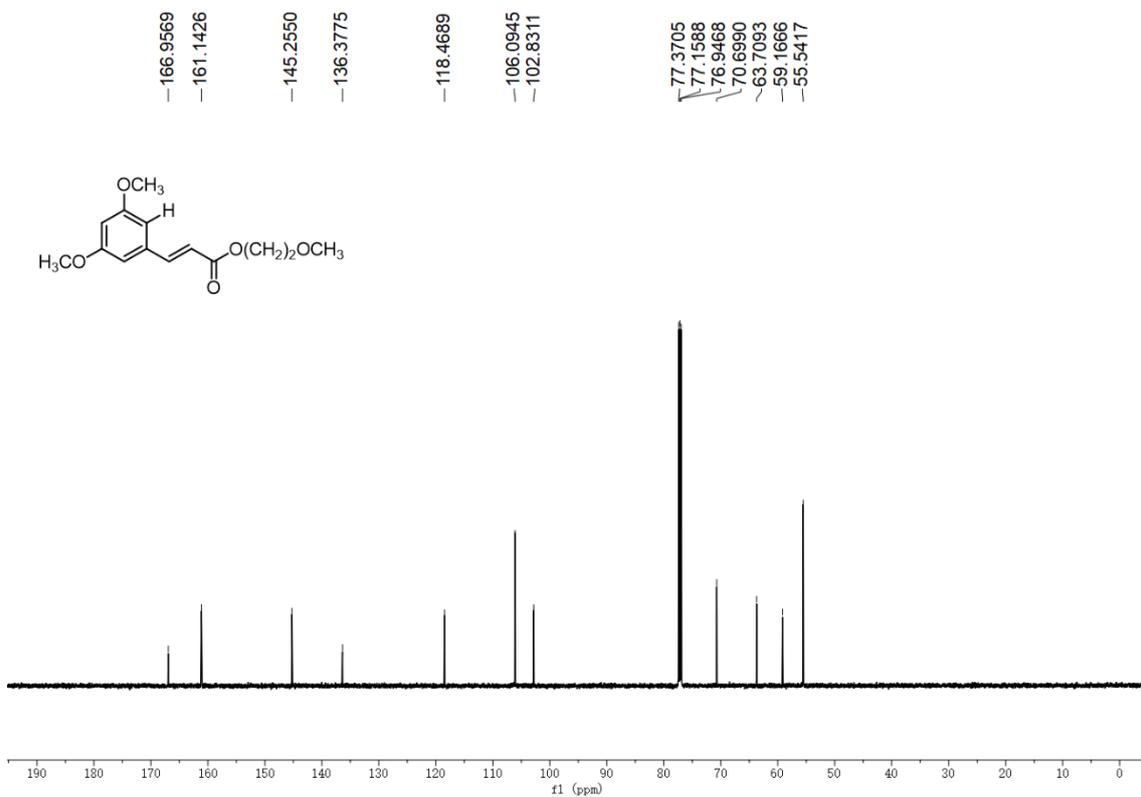
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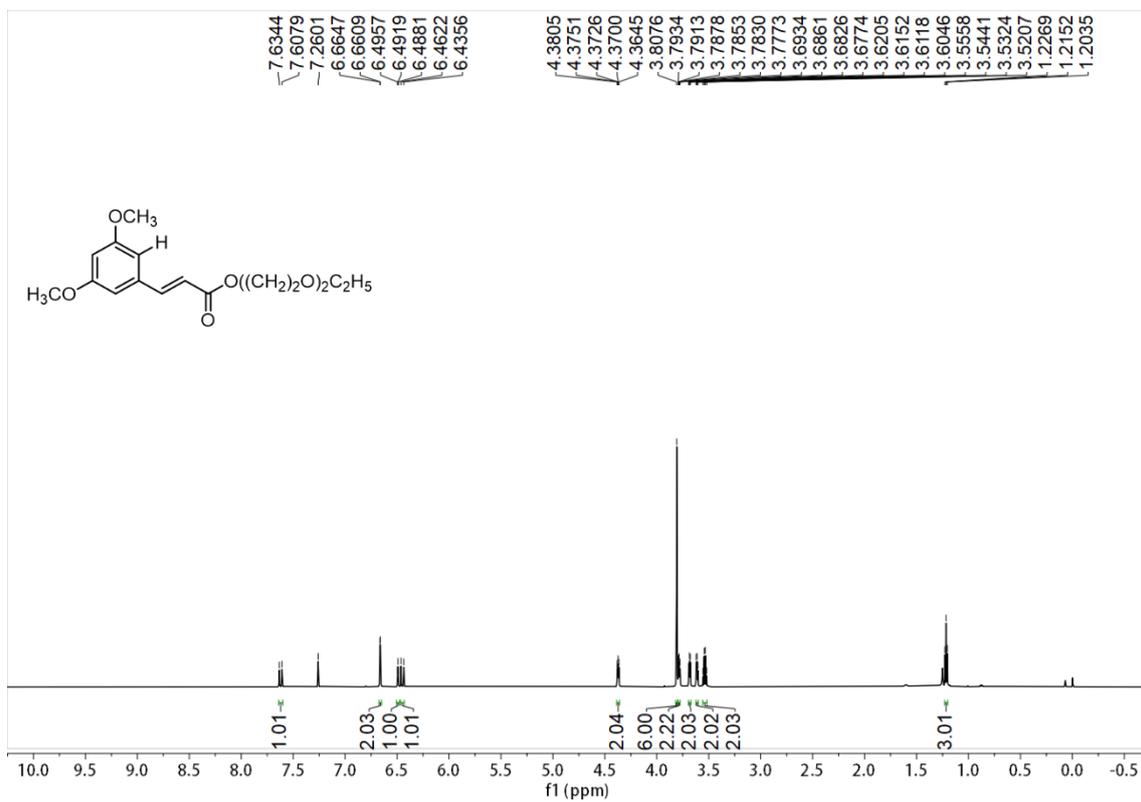
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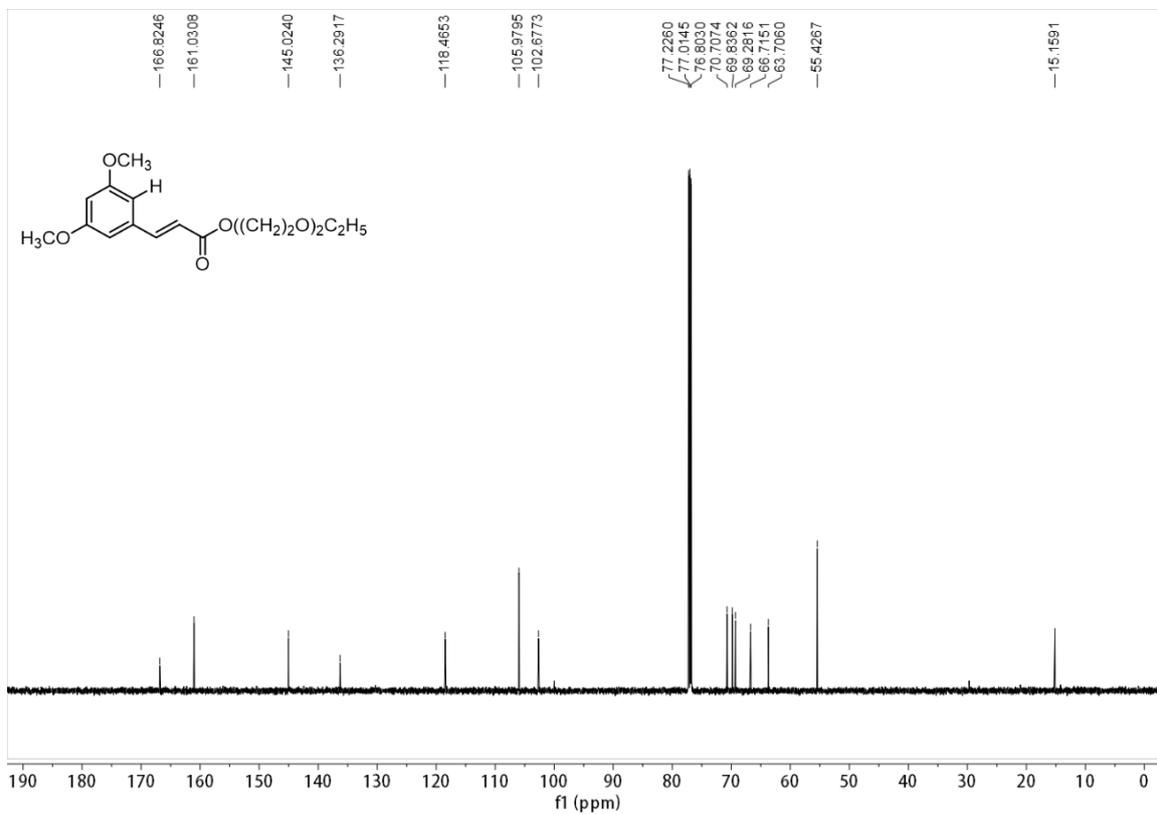
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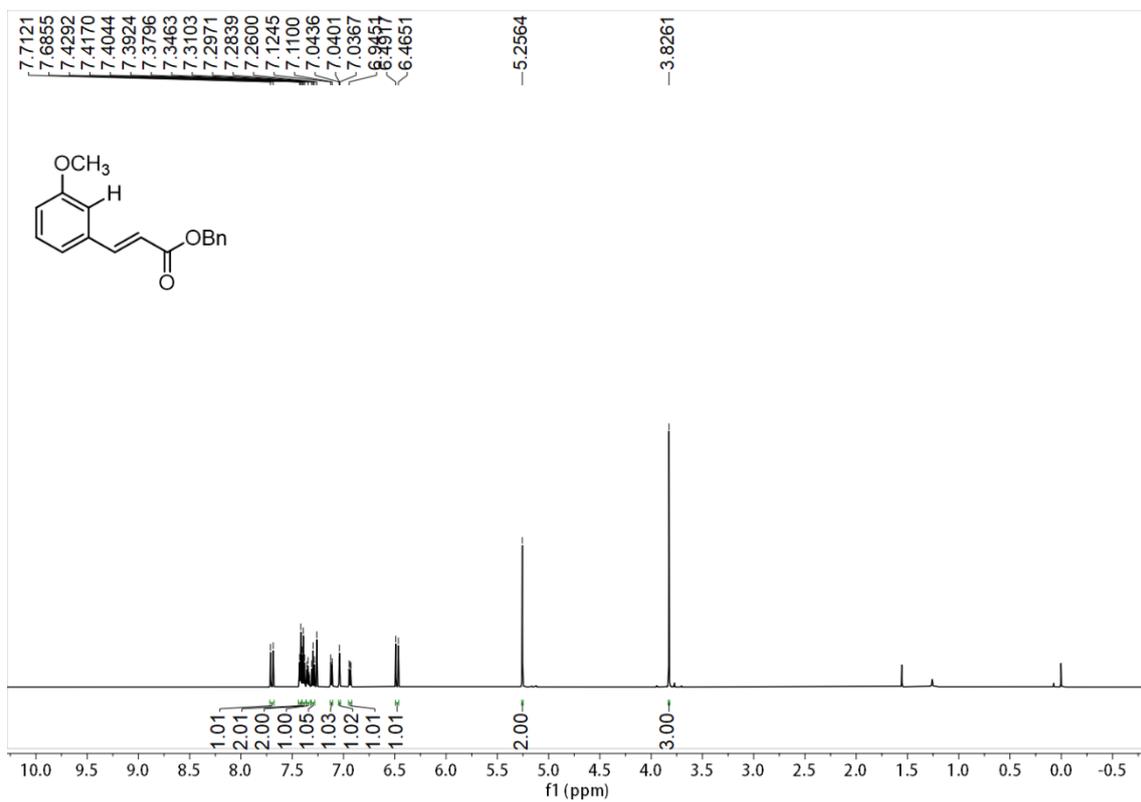
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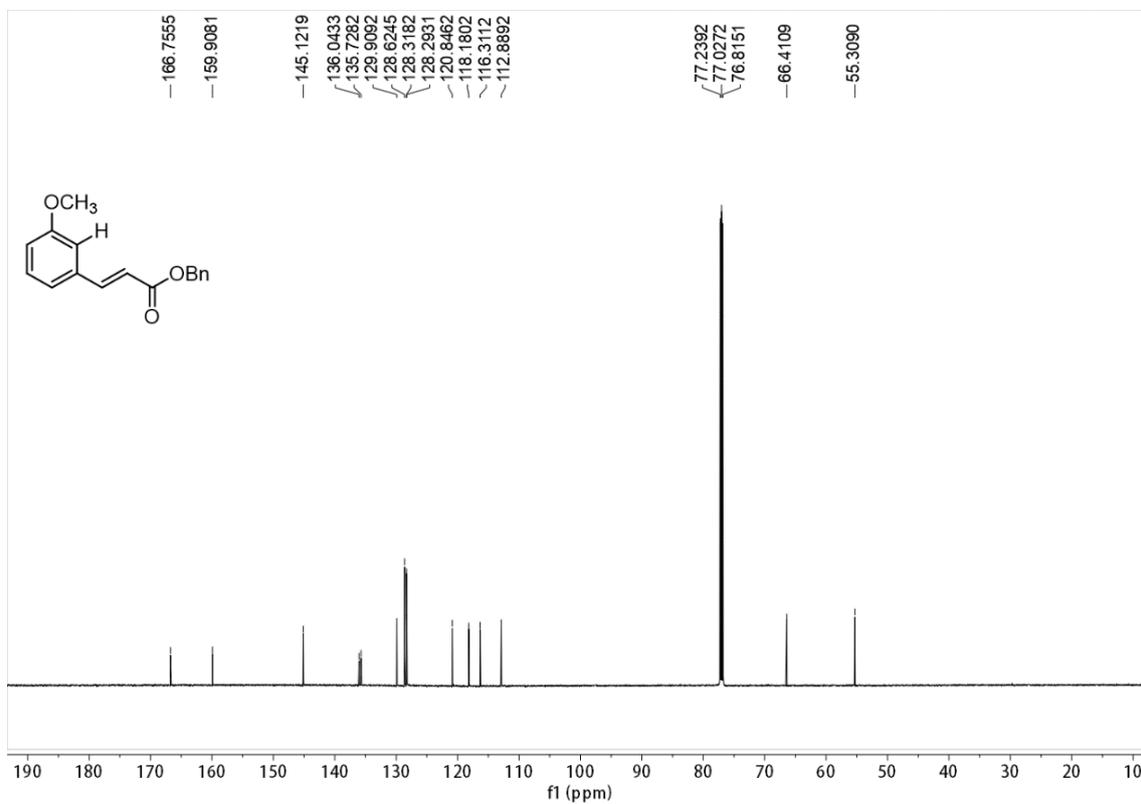
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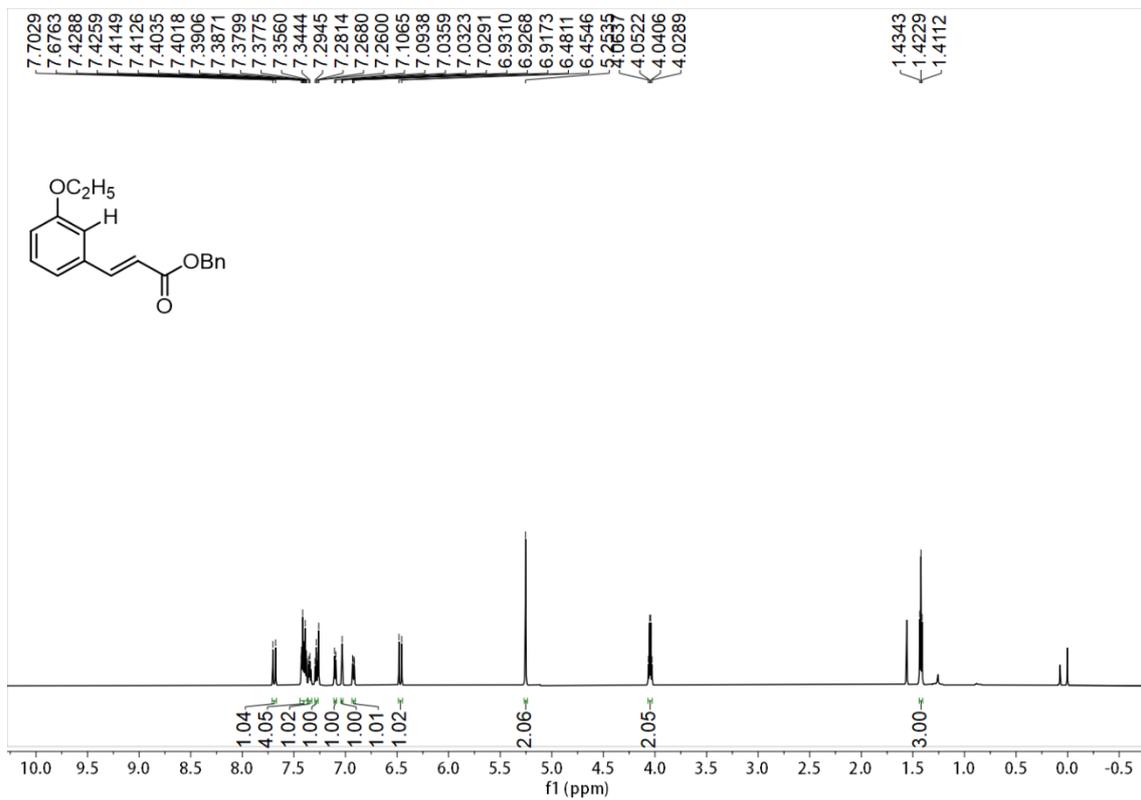
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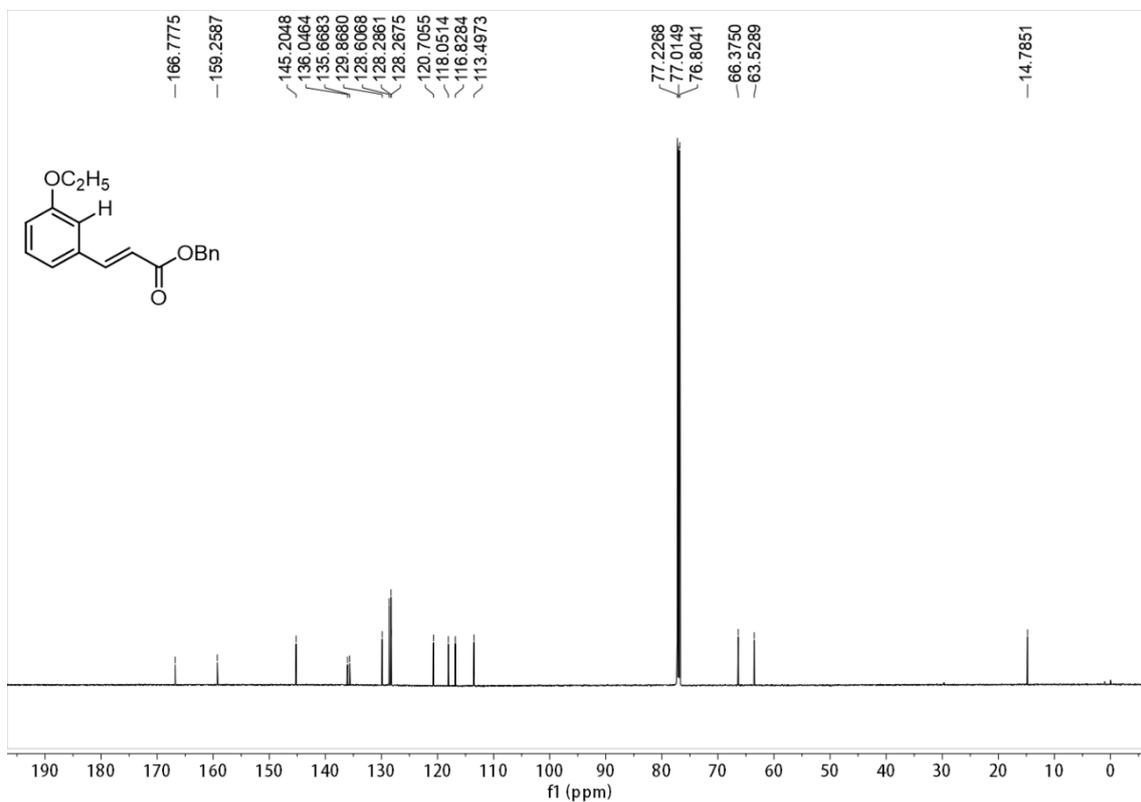
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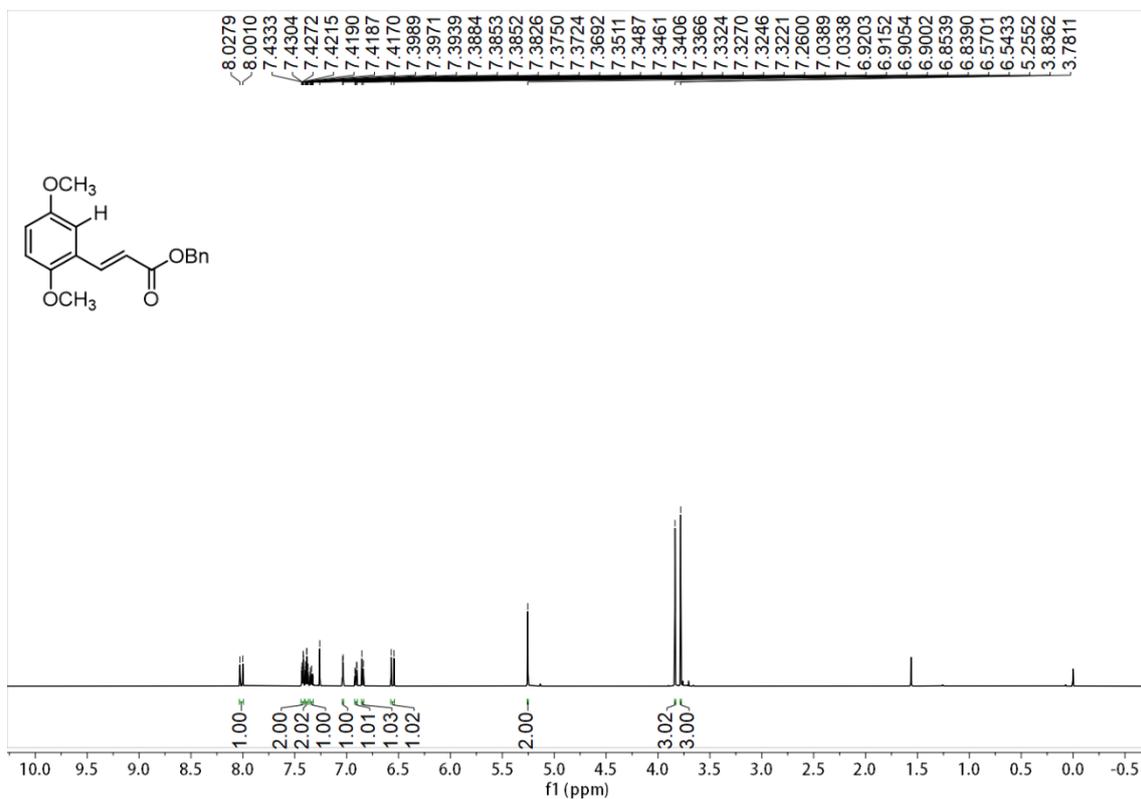
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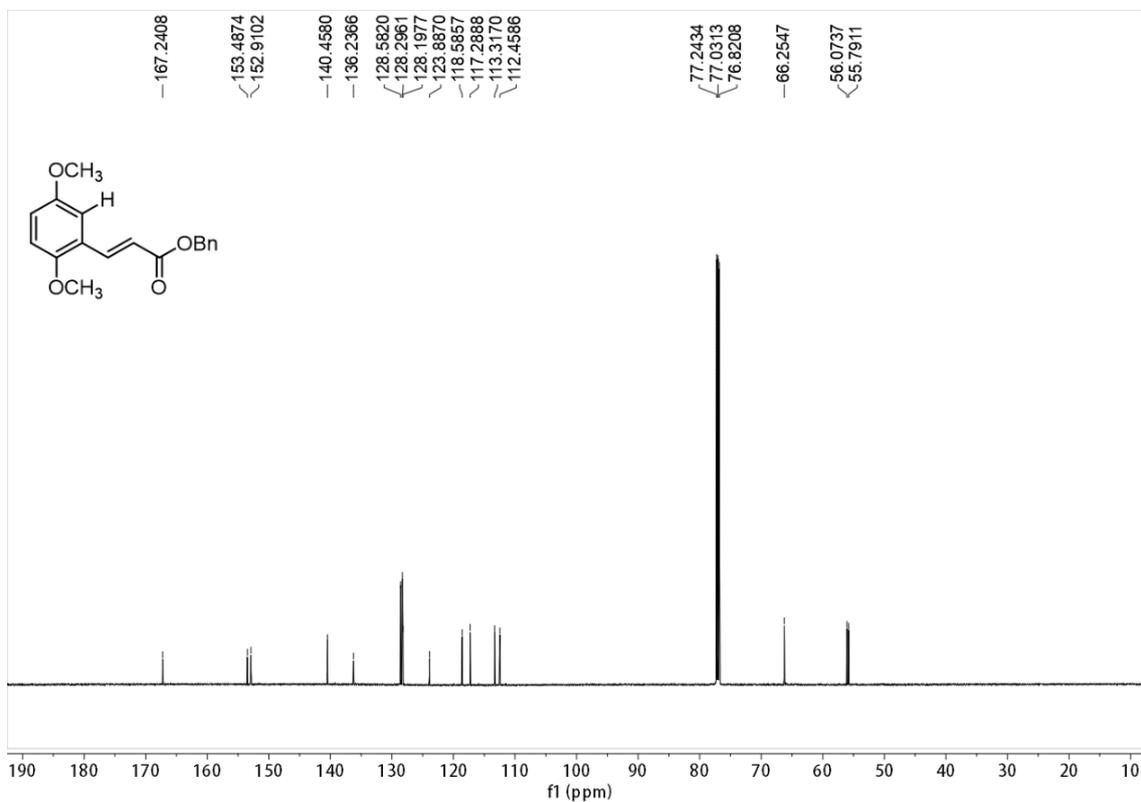
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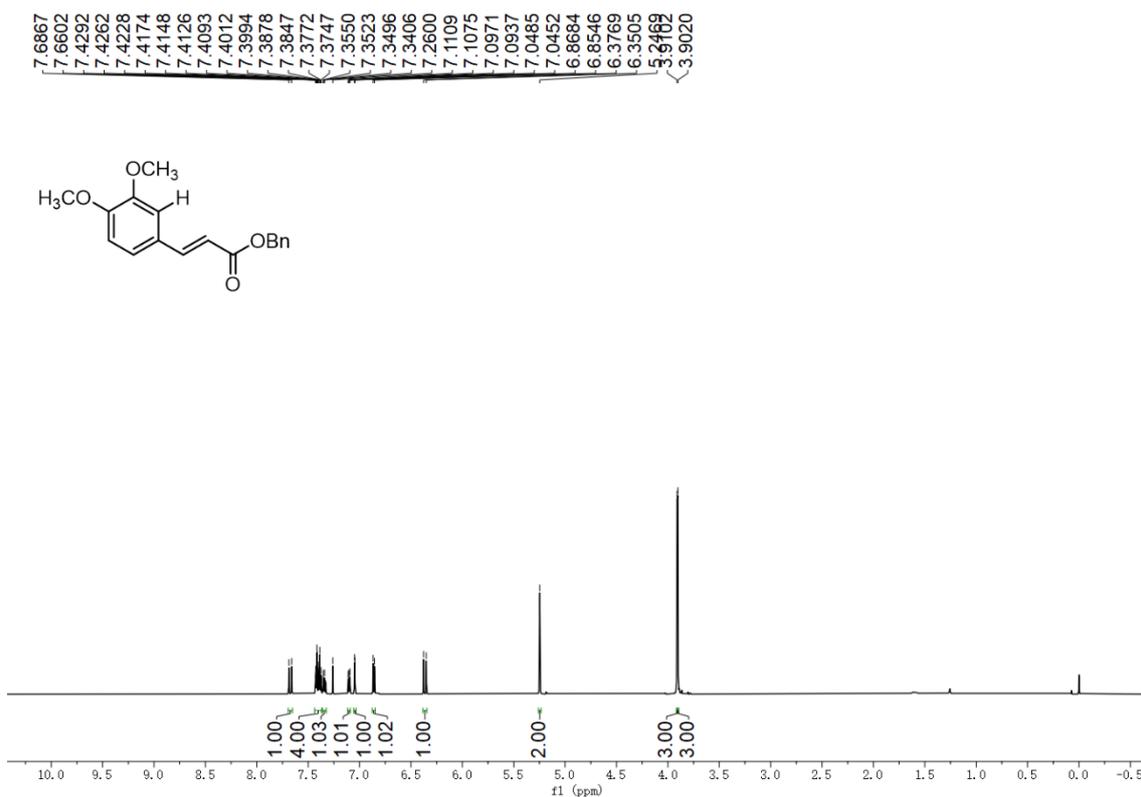
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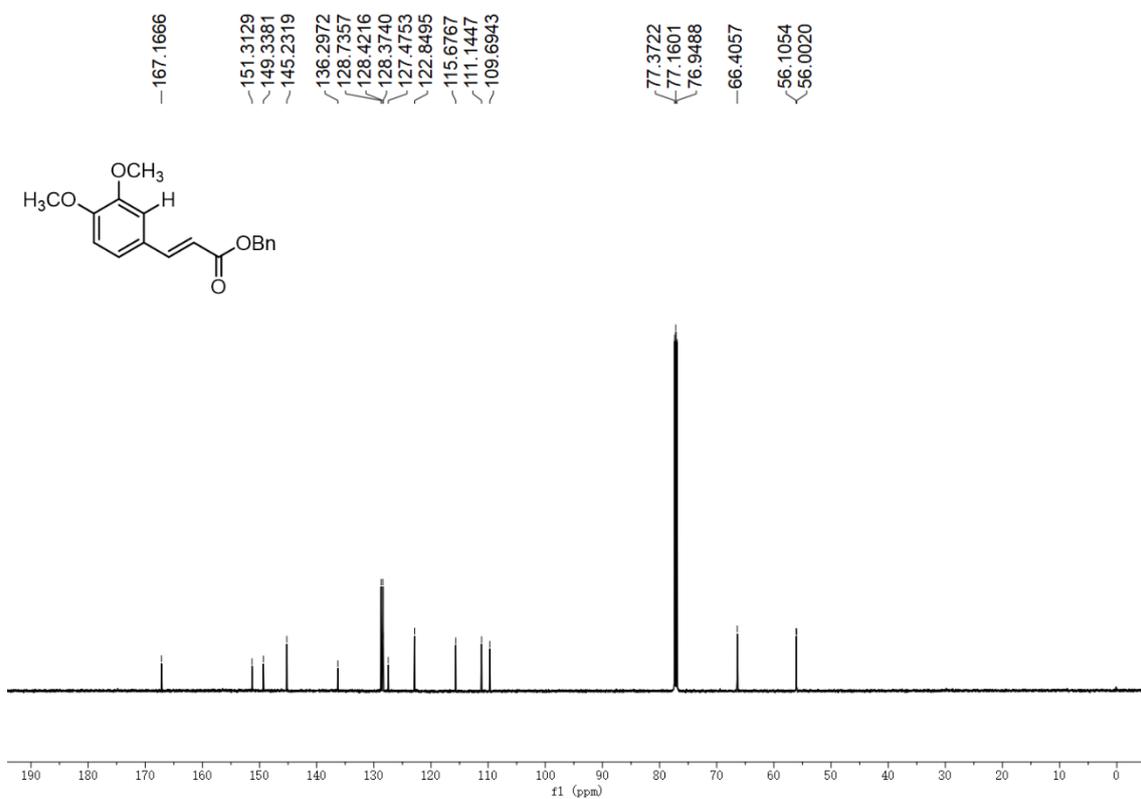
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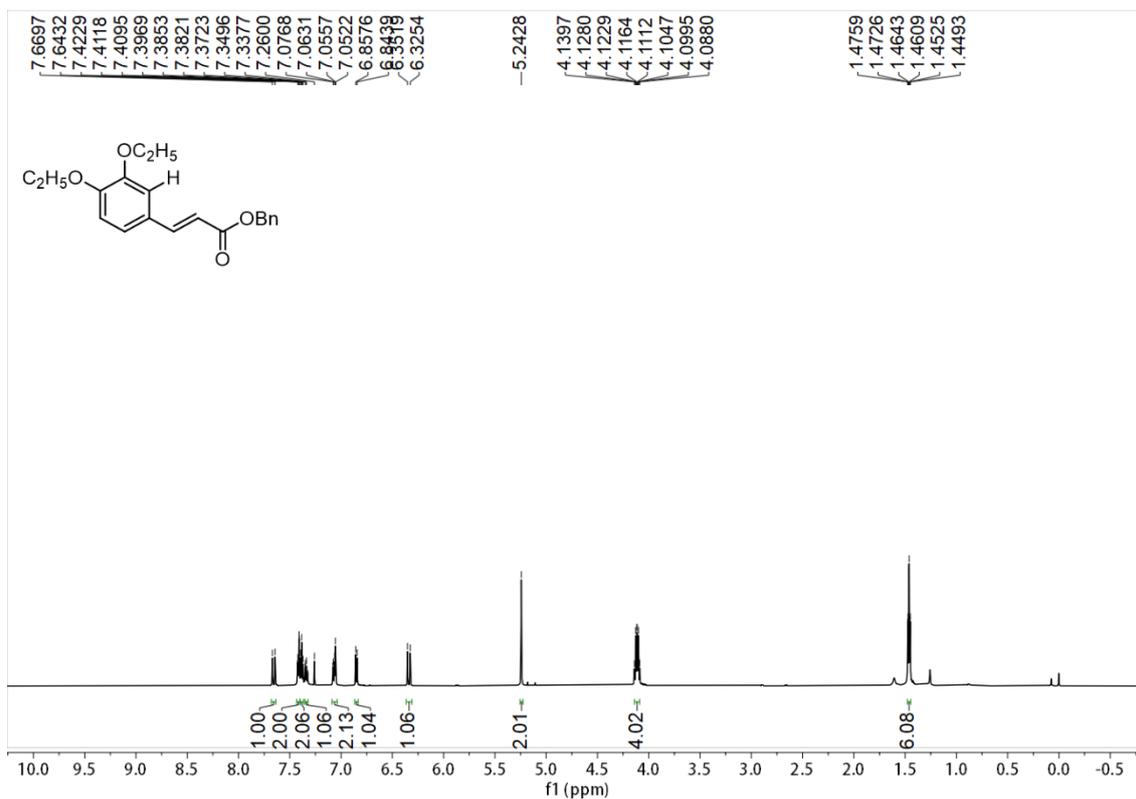
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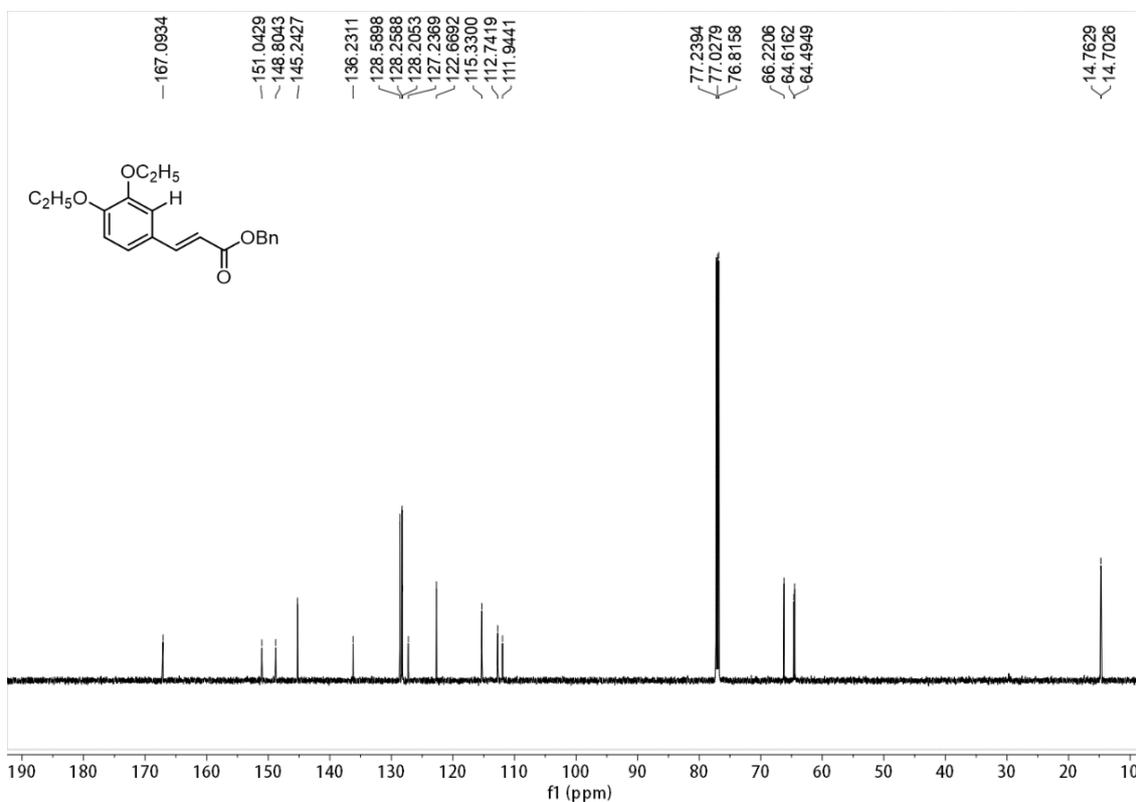
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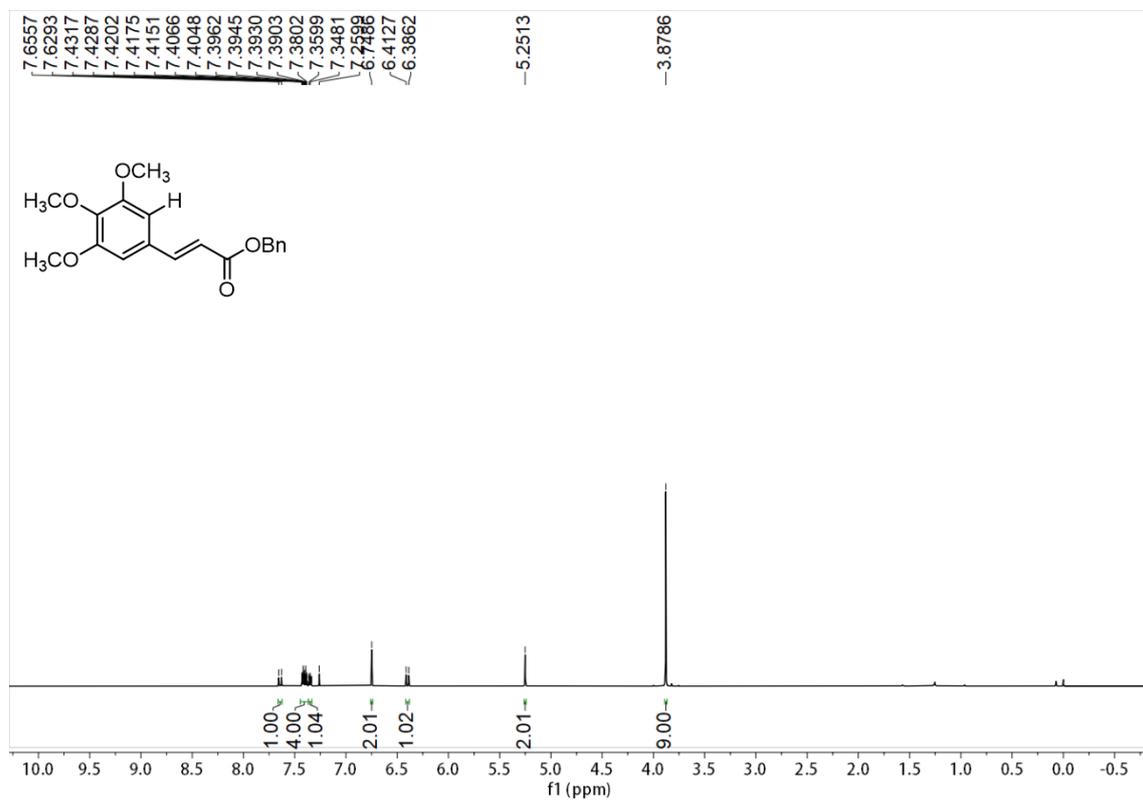
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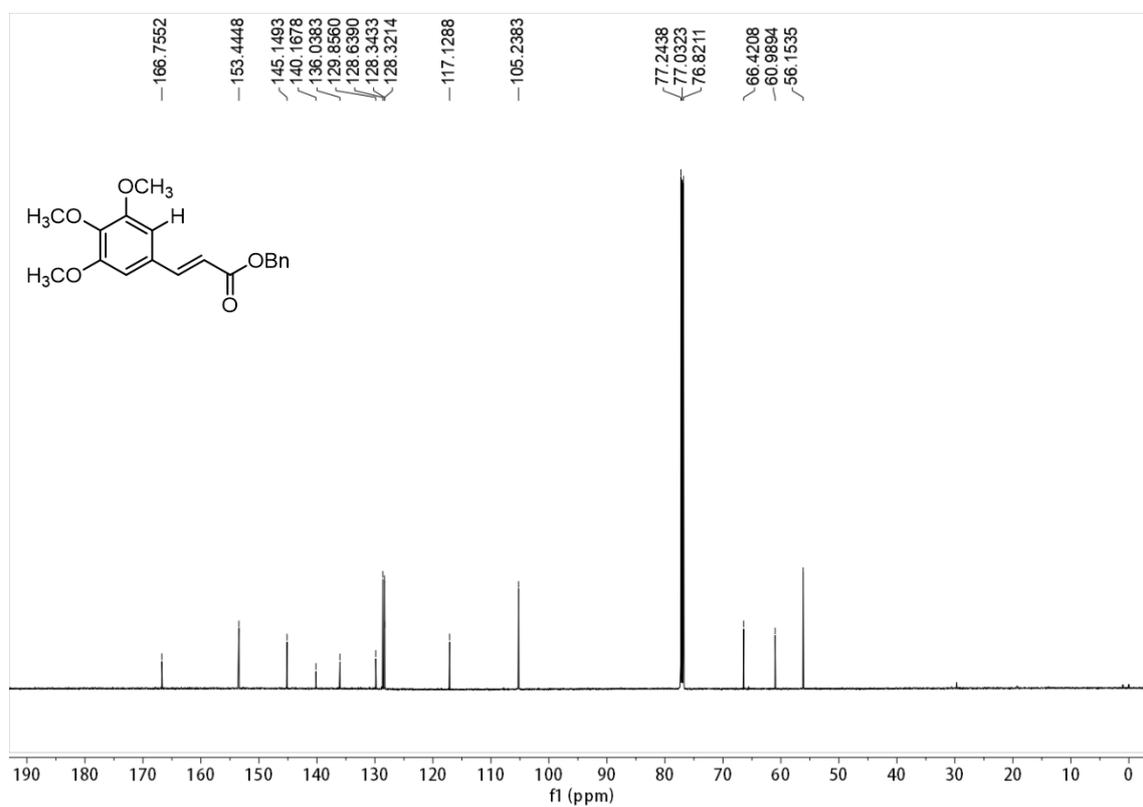
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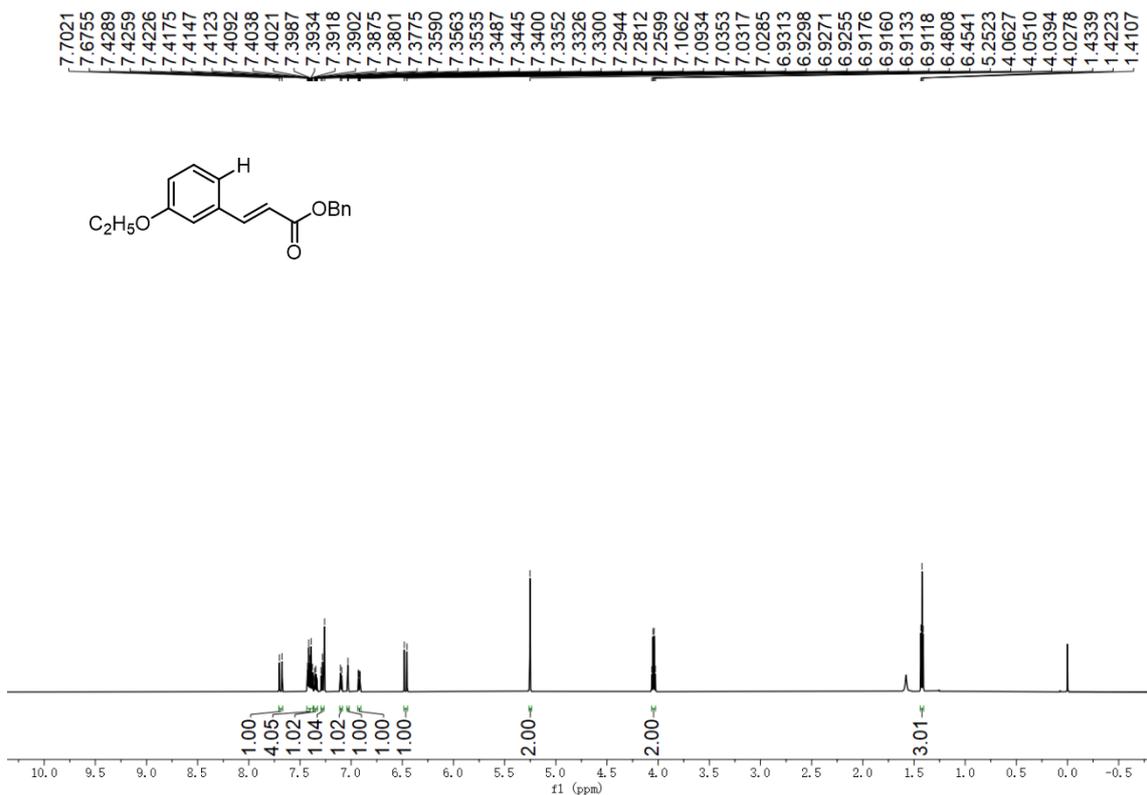
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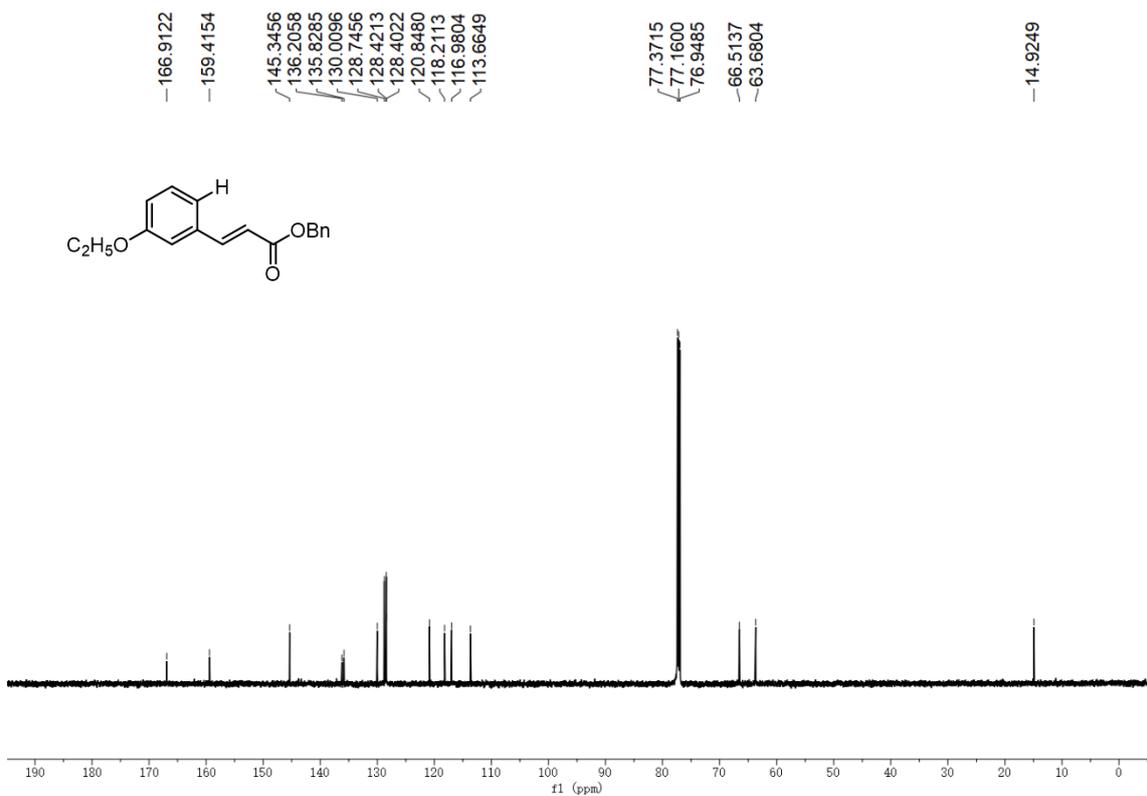
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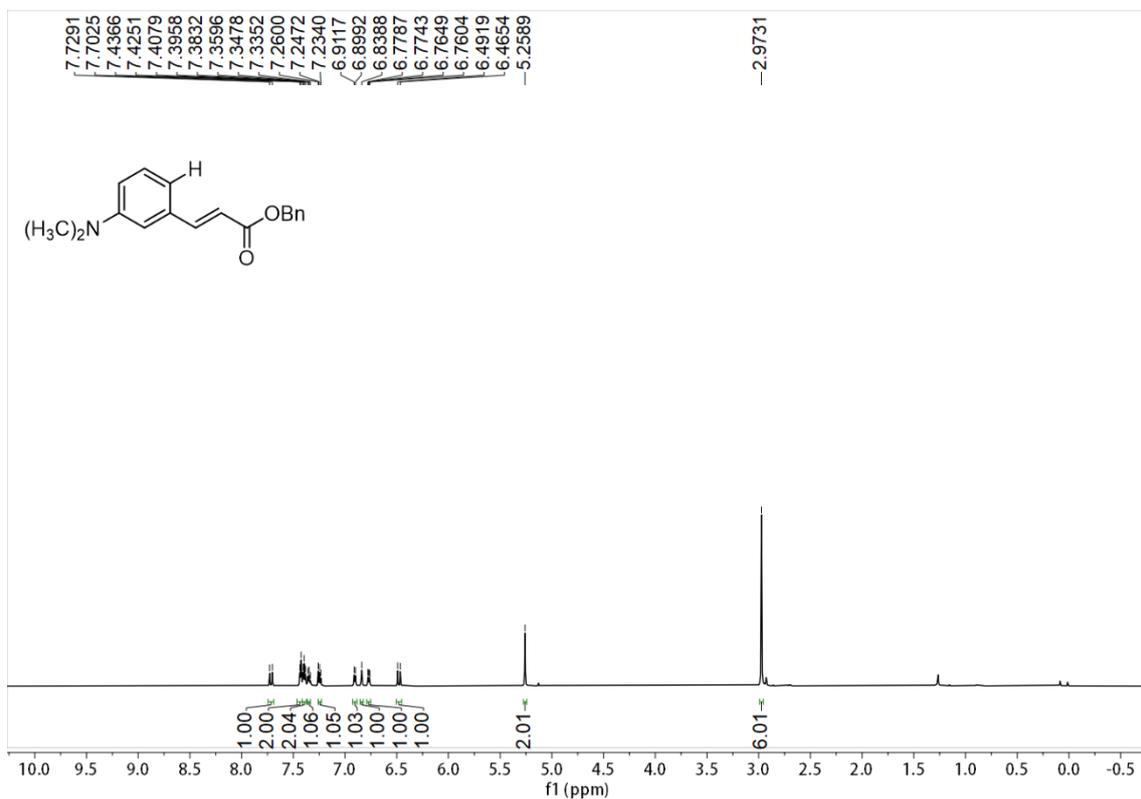
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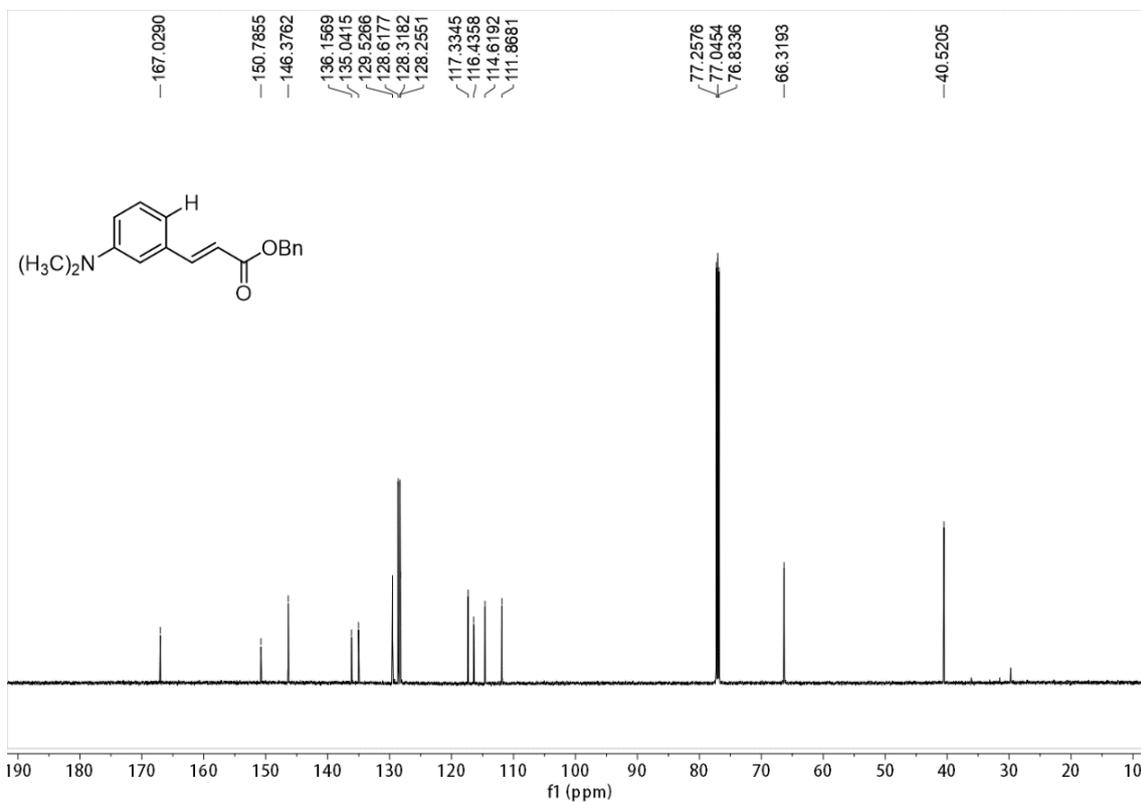
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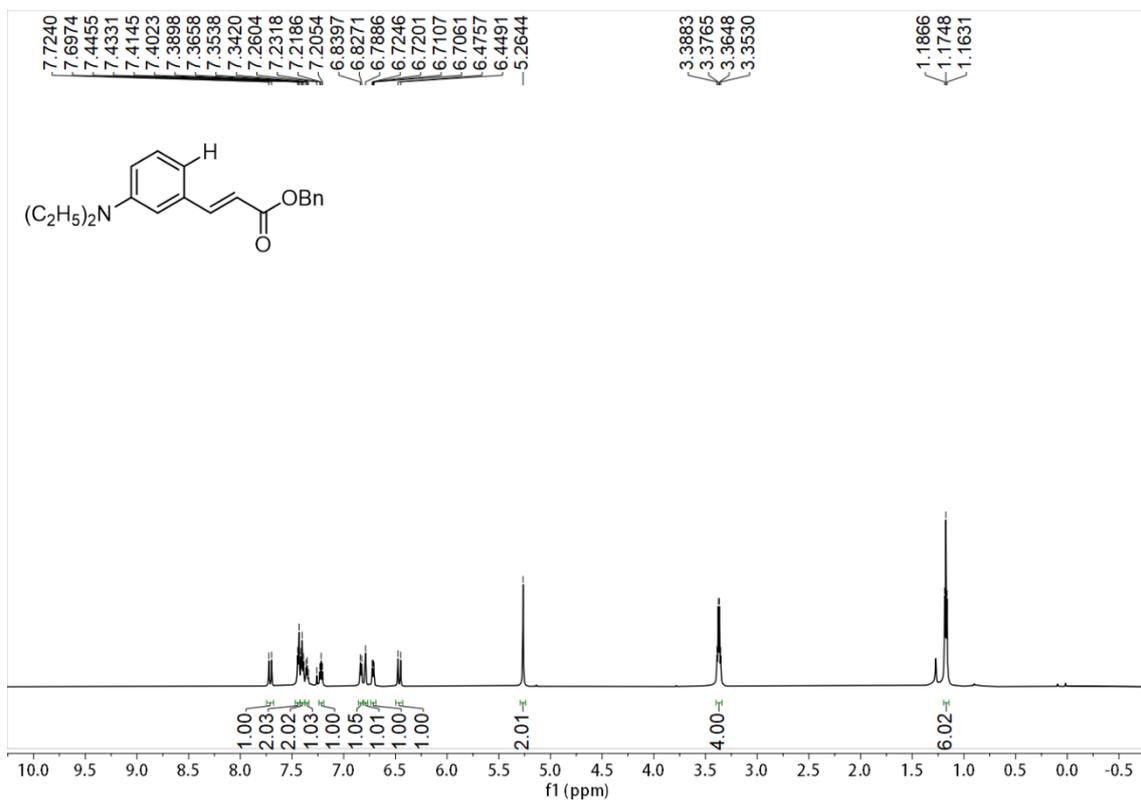
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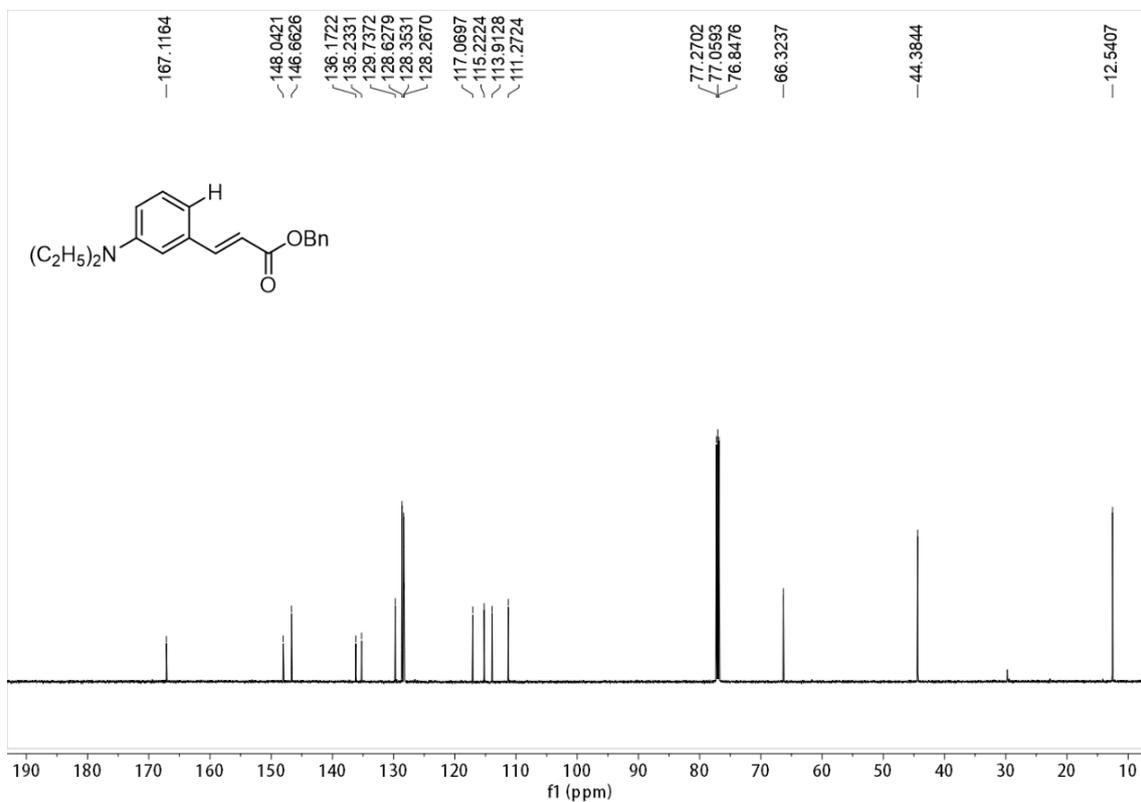
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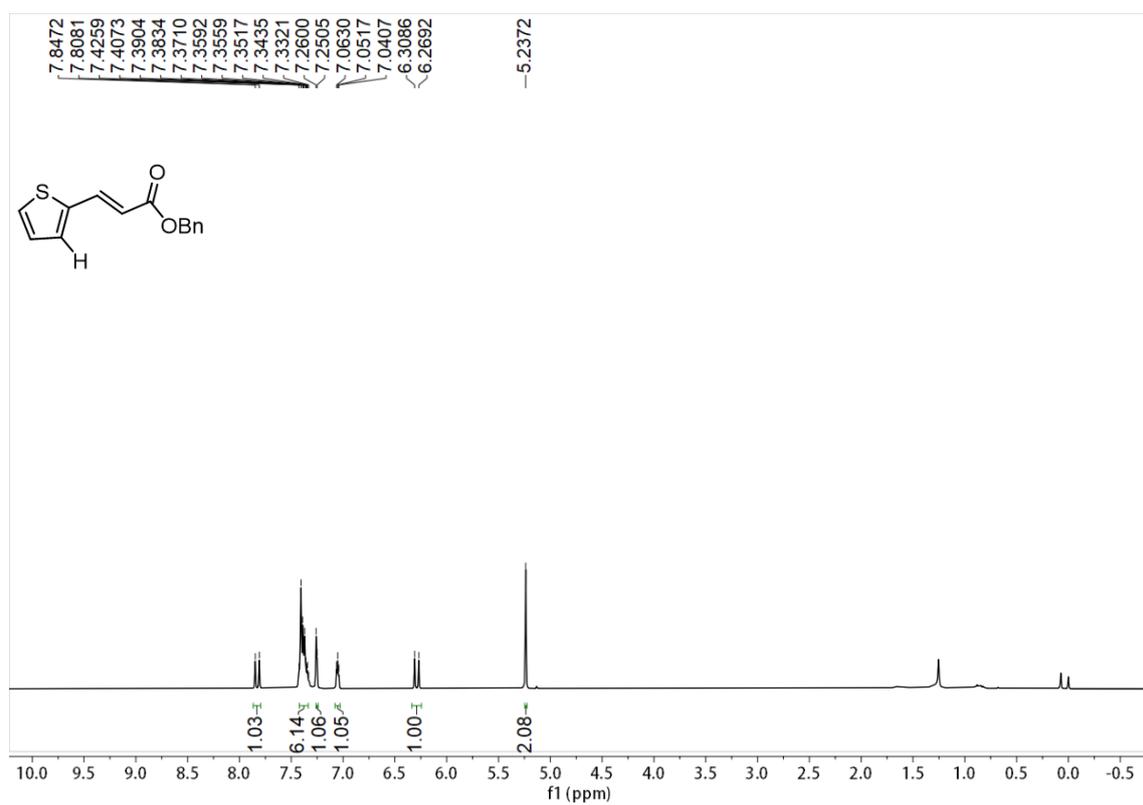
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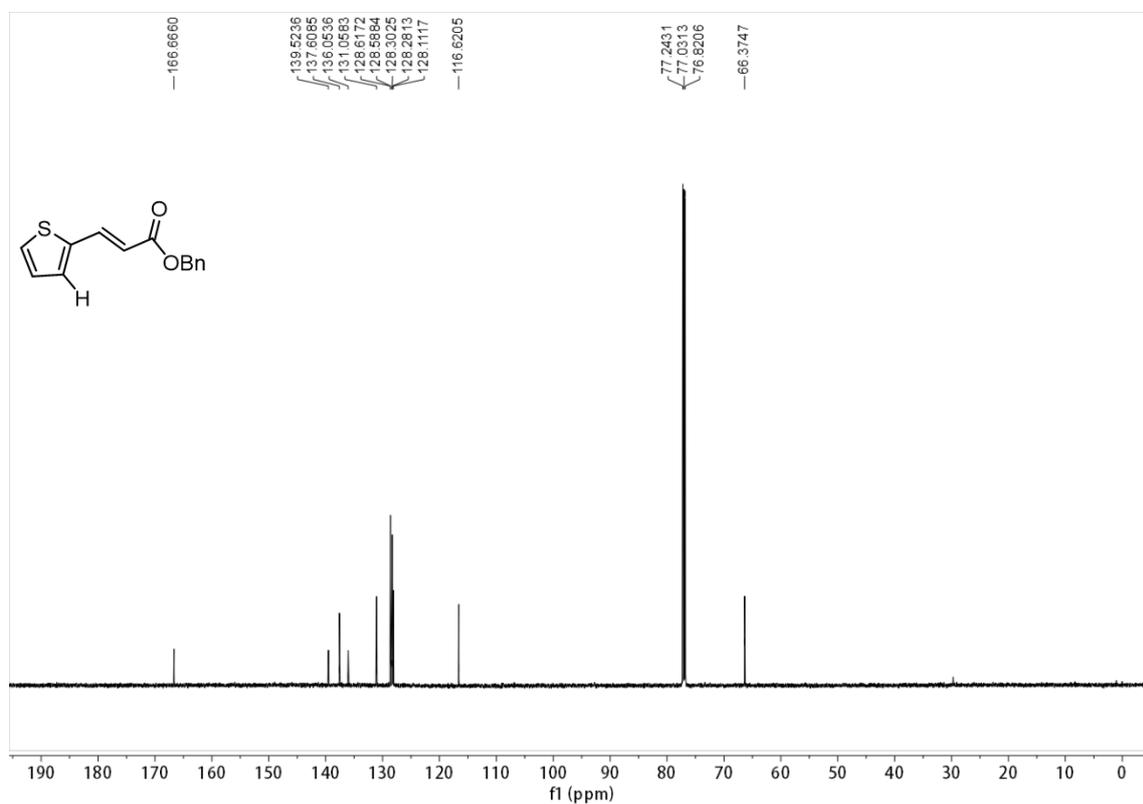
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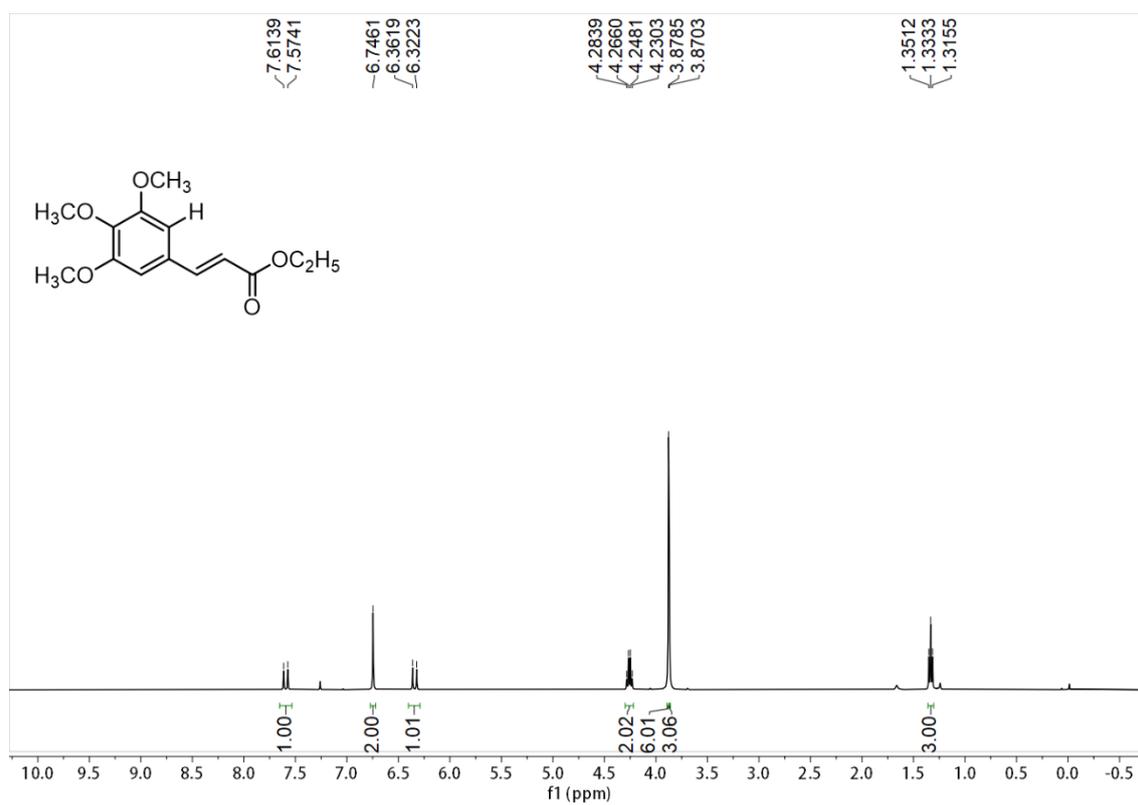
¹H NMR spectra of compound 3z



¹³C NMR spectra of compound 3z



¹H NMR spectra of compound 3aa



¹³C NMR spectra of compound 3aa

