Oxidative alkoxycarbonylation of terminal alkenes with carbazates

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Supporting information

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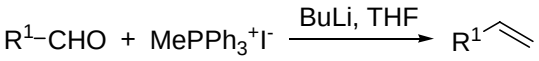
General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electron spray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Melting points were uncorrected.

Alkenes **1d**, **1h**, **1j**, **1k**, **1l**, and **1n** were prepared according to literature procedures.[1] The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

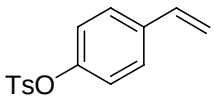
Abbreviations: Ac = acetyl, DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, ms = molecular sieves, THF = tetrahydrofuran, Ts = *p*-toluenesulfonyl.

Preparation of alkenes



1

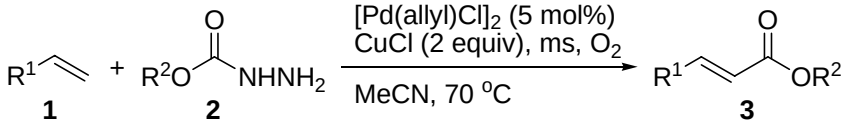
BuLi (1.6 M in hexanes, 3.40 mL, 5.5 mmol) was added to a suspension of methyltriphenylphosphonium iodide (2.42 g, 6.0 mmol) in tetrahydrofuran (20 mL) under nitrogen at -78 °C. After stirring for 1 h, the corresponding aldehyde (5.0 mmol) was added. The reaction was warmed to 23 °C overnight, quenched with water (60 mL), and extracted with ethyl acetate (3 x 60 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether / ethyl acetate, 50:1) to give alkene **1**.



1d

Alkene **1d** was obtained in 42% yield as a white solid. m.p. 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 6.8, 1.6 Hz, 2H), 7.32-7.27 (m, 4H), 6.93 (dd, J = 6.8, 2.0 Hz, 2H), 6.64 (dd, J = 17.6, 10.8 Hz, 1H), 5.68 (dd, J = 17.6, 0.8 Hz, 1H), 5.25 (dd, J = 10.8, 0.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 145.4, 136.6, 135.5, 132.4, 129.8, 128.5, 127.3, 122.5, 114.9, 21.7; HRMS (EI) calcd for $C_{15}H_{14}O_3S$ (M) 274.0664, found 274.0648.

General procedure for the oxidative alkoxycarbonylation of terminal alkenes with carbazates

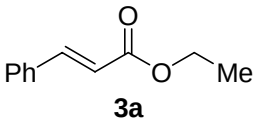


1 **2** **3**

A Schlenk tube was charged with alkene **1** (0.30 mmol), CuCl (59.4 mg, 0.60 mmol), $[Pd(allyl)Cl]_2$ (5.5 mg, 0.015 mmol, 5 mol %), 5 Å molecular sieves (160 mg), and acetonitrile (0.30 mL). To the stirred mixture under oxygen atmosphere at 70 °C was added dropwise via syringe a solution of carbazate **2** (0.60 mmol) in acetonitrile (1.0 mL) for 5 h. The mixture was cooled to room temperature, and purified by silica gel chromatography, eluting with petroleum ether / acetone (100:1 to 40:1), to give α,β-unsaturated ester **3**.

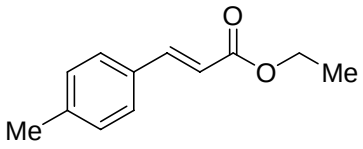
The *E/Z* ratios of the products were determined by integrating the vinyl proton signals in the ^{1}H NMR spectra.

Analytical data for the products



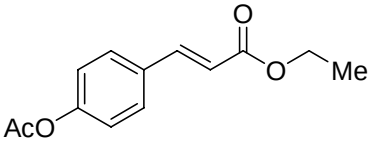
3a

3a,[2] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.39–7.35 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3.



3b

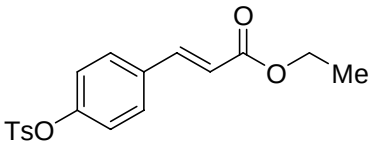
3b,[3] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 16.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.5, 140.6, 131.7, 129.6, 128.0, 117.2, 60.3, 21.4, 14.3.



3c

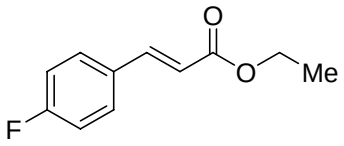
3c,[4] white solid, m.p. 40–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 16.0 Hz, 1H), 7.53 (dd, J = 6.8, 2.0 Hz, 2H), 7.12 (dd, J = 6.8, 2.0 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 169.1, 166.9, 152.1, 143.4, 132.2, 129.2, 122.1, 118.5, 60.6, 21.1, 14.3.



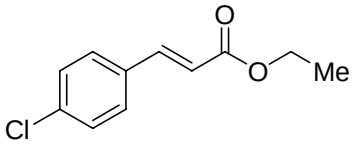
3d

3d,[5] white solid, m.p. 75–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 16.0 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.7, 145.6, 142.9, 133.4, 132.3, 129.9, 129.3, 128.5, 122.9, 119.3, 60.6, 21.7, 14.3.



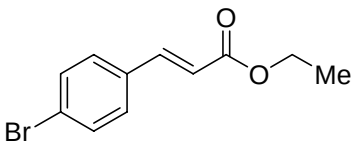
3e

3e,[6] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 16.0 Hz, 1H), 7.53–7.47 (m, 2H), 7.10–7.02 (m, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 163.9 (d, $J_{C\text{-}F}$ = 249.6 Hz), 143.3, 130.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8.4 Hz), 118.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.7 Hz), 60.6, 14.3.



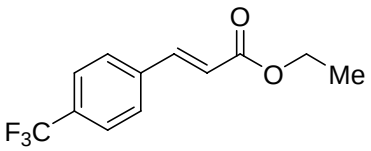
3f

3f,[2] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 16.0 Hz, 1H), 7.46–7.42 (m, 2H), 7.37–7.33 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 143.2, 136.2, 133.1, 129.3, 119.0, 60.7, 14.4.



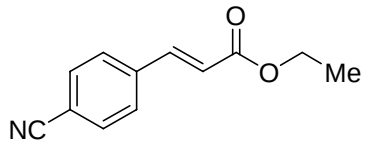
3g

3g,[3] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 16.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.40–7.35 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 143.1, 133.4, 132.1, 129.4, 124.4, 119.0, 60.6, 14.3.



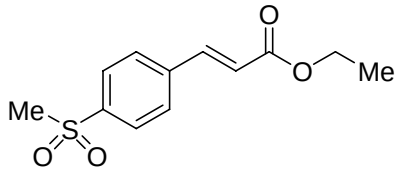
3h

3h,[3] light yellow solid, m.p. 31–33 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.68–7.59 (m, 4H), 6.51 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 142.7, 137.9, 131.9, 131.6, 128.1, 125.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.2, 122.5, 120.9, 60.8, 14.3.



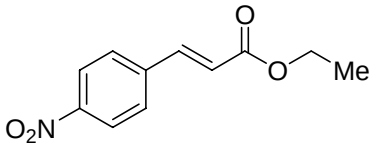
3i

3i,[2] white solid, m.p. 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.58 (m, 5H), 6.52 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.1, 138.8, 132.6, 128.4, 121.9, 118.4, 113.4, 60.9, 14.3.



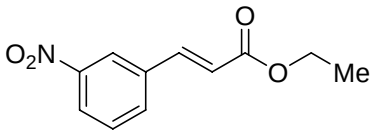
3j

3j,[2] white solid, m.p. 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.95 (m, 2H), 7.73–7.68 (m, 3H), 6.55 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.07 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 142.0, 141.5, 139.8, 128.7, 128.1, 122.2, 61.0, 44.5, 14.3.



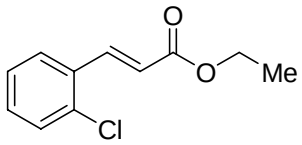
3k

3k,[2] white solid, m.p. 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.23 (m, 2H), 7.74–7.65 (m, 3H), 6.56 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 148.9, 142.0, 141.0, 129.0, 124.6, 123.0, 61.4, 14.6.



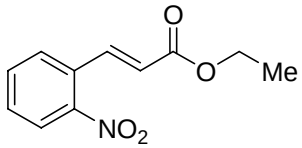
3l

3l,[3] obtained as a 97:3 mixture of *E*/*Z* isomers, white solid, m.p. 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.25–8.22 (m, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.62-7.57 (m, 1H), 6.56 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); Partial ^{1}H NMR for the minor *Z*-isomer: δ 7.00 (d, J = 12.4 Hz, 1H), 6.11 (d, J = 12.4 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 148.7, 141.6, 136.2, 133.6, 129.9, 124.5, 122.4, 121.5, 60.9, 14.3.



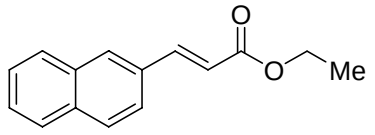
3m

3m,[3] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 16.0 Hz, 1H), 7.62–7.59 (m, 1H), 7.42–7.39 (m, 1H), 7.33–7.24 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.3, 134.9, 132.8, 131.0, 130.2, 127.6, 127.1, 121.0, 60.7, 14.3.



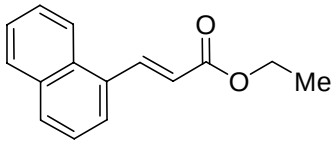
3n

3n,[3] light yellow solid, m.p. 42–44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 15.6 Hz, 1H), 8.05–8.02 (m, 1H), 7.65–7.62 (m, 2H), 7.57–7.52 (m, 1H), 6.36 (d, J = 15.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.4, 139.8, 133.5, 130.7, 130.2, 129.1, 124.9, 123.4, 60.9, 14.3.



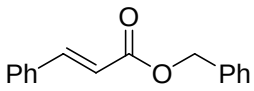
3o

3o,[7] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.88–7.80 (m, 4H), 7.68–7.64 (m, 1H), 7.53–7.47 (m, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.6, 134.2, 133.3, 132.0, 129.9, 128.7, 128.6, 127.8, 127.2, 126.7, 123.5, 118.5, 60.5, 14.4.



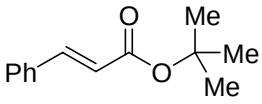
3p

3p,[3] obtained as a 97:3 mixture of *E*/*Z* isomers, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 16.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.89–7.84 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.58–7.46 (m, 3H), 6.52 (d, J = 16.0 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); Partial ^{1}H NMR for the minor *Z*-isomer: δ 6.24 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 141.8, 133.9, 132.0, 131.6, 130.6, 128.9, 127.0, 126.4, 125.6, 125.2, 123.6, 121.1, 60.8, 14.5.



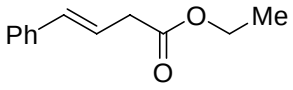
3q

3q,[2] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.43–7.30 (m, 8H), 6.48 (d, J = 16.0 Hz, 1H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.2, 136.1, 134.4, 130.3, 128.9, 128.6, 128.3, 128.2, 128.1, 117.9, 66.4.



3r

3r,[2] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1H), 7.52–7.48 (m, 2H), 7.38–7.34 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.5, 134.7, 129.9, 128.8, 128.0, 120.2, 80.5, 28.2.



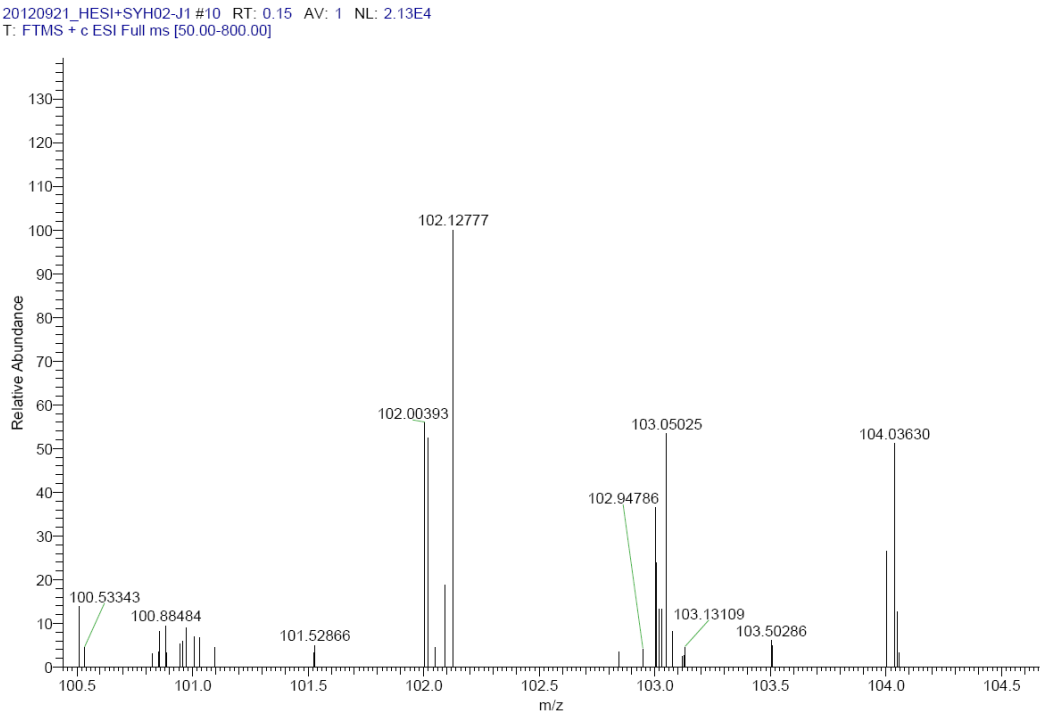
4

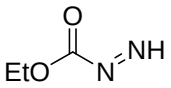
4,[8] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.18 (m, 5H), 6.48 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 7.2 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.23 (dd, J = 7.2, 1.6 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 136.9, 133.4, 128.5, 127.5, 126.3, 121.9, 60.8, 38.5, 14.2.

ESI-MS Analysis of the Reaction Mixture

A 1:1 mixture of ethyl carbazate (**1a**) (1.0 mg, 0.01 mmol) and $[Pd(allyl)Cl]_2$ (3.6 mg, 0.01 mmol) in acetonitrile (0.50 mL) was heated at 70 °C under oxygen atmosphere for 5 min, and cooled to room temperature. The resulting mixture was subjected to ESI-MS (positive mode) spectrometric analysis. Copied below is the ESI-MS spectrum we obtained. The following species were tentatively assigned

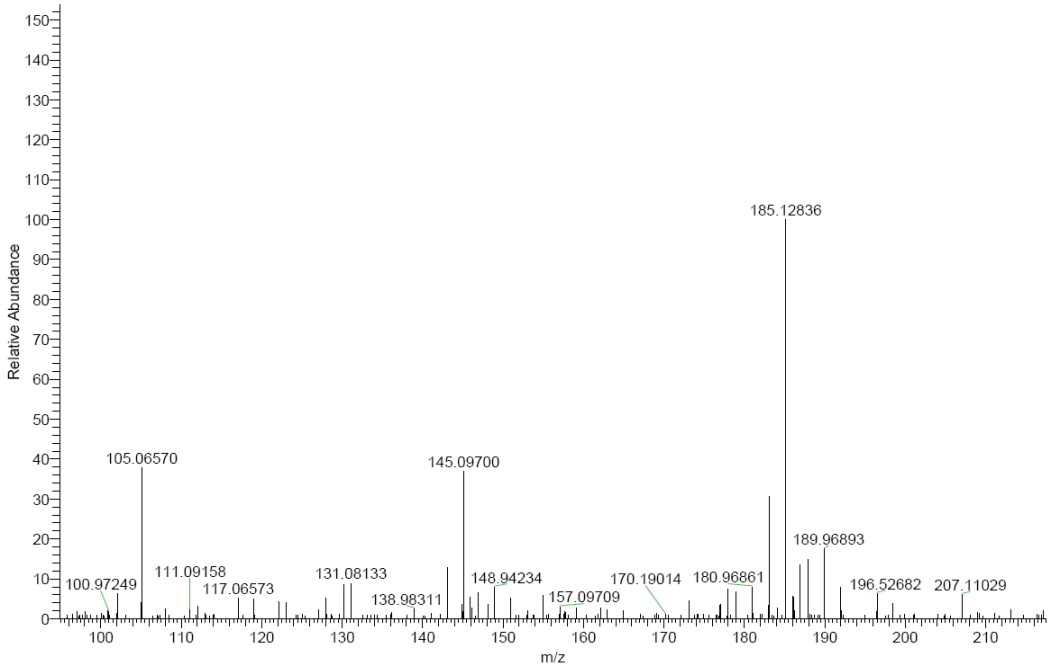
according to the high resolution mass data.

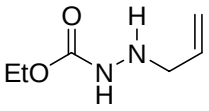




9a

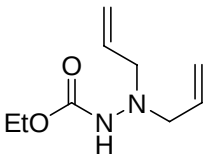
Diazene **9a**: HRMS (ESI) calcd for $C_3H_7O_2N_2^+$ (**9a** + H)$^+$ 103.05020, found 103.05025.





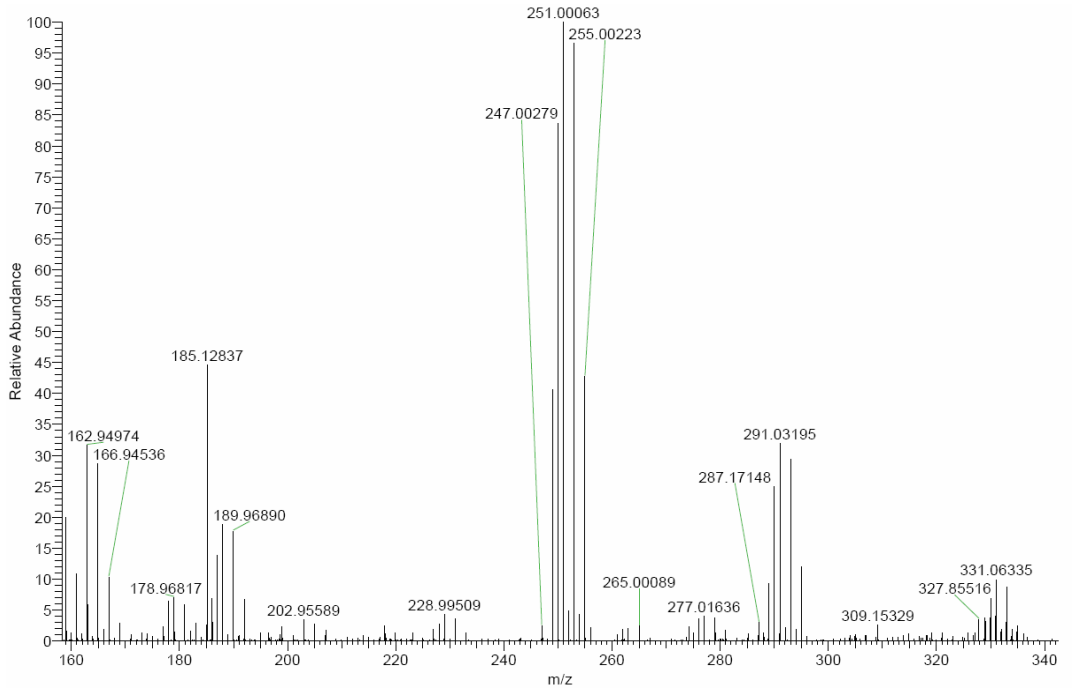
10a

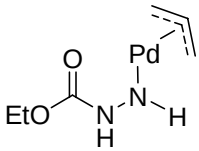
Carbazate **10a**: HRMS (ESI) calcd for $C_6H_{13}O_2N_2^+$ (**10a** + H)$^+$ 145.09715, found 145.09700.



11a

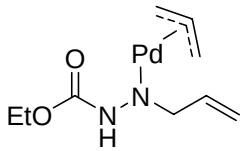
Carbazate **11a**: HRMS (ESI) calcd for $C_9H_{17}O_2N_2^+$ (**11a** + H)$^+$ 185.12845, found 185.12836.





12a

Carbazate-Pd(II) complex **12a**: HRMS (ESI) calcd for $C_6H_{13}O_2N_2Pd^+$ (**12a** + H)$^+$ 251.00064, found 251.00063.



13a

Carbazate-Pd(II) complexe **13a:** HRMS (ESI) calcd for $C_9H_{17}O_2N_2Pd^+$ (**13a** + $H)^+$ 291.03194, found 291.03195.

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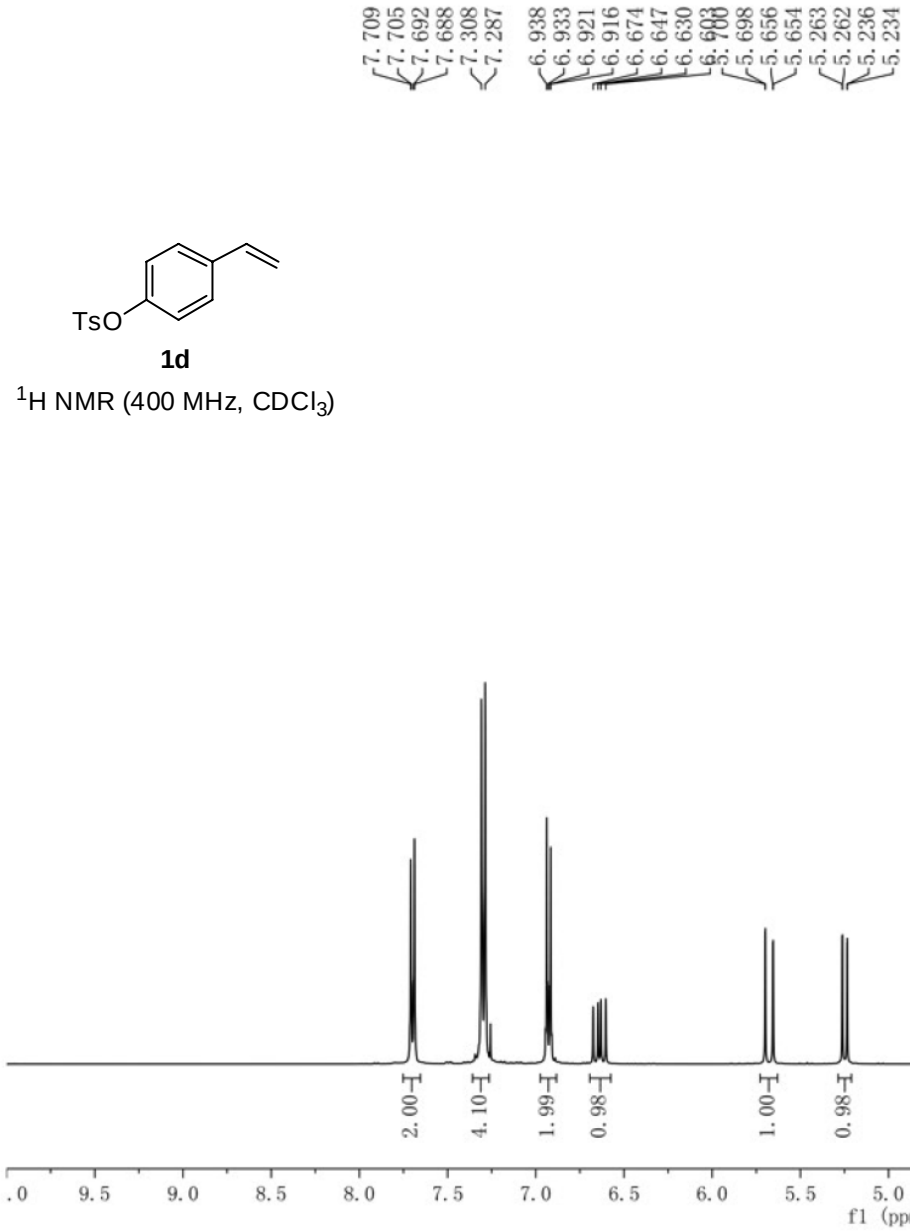
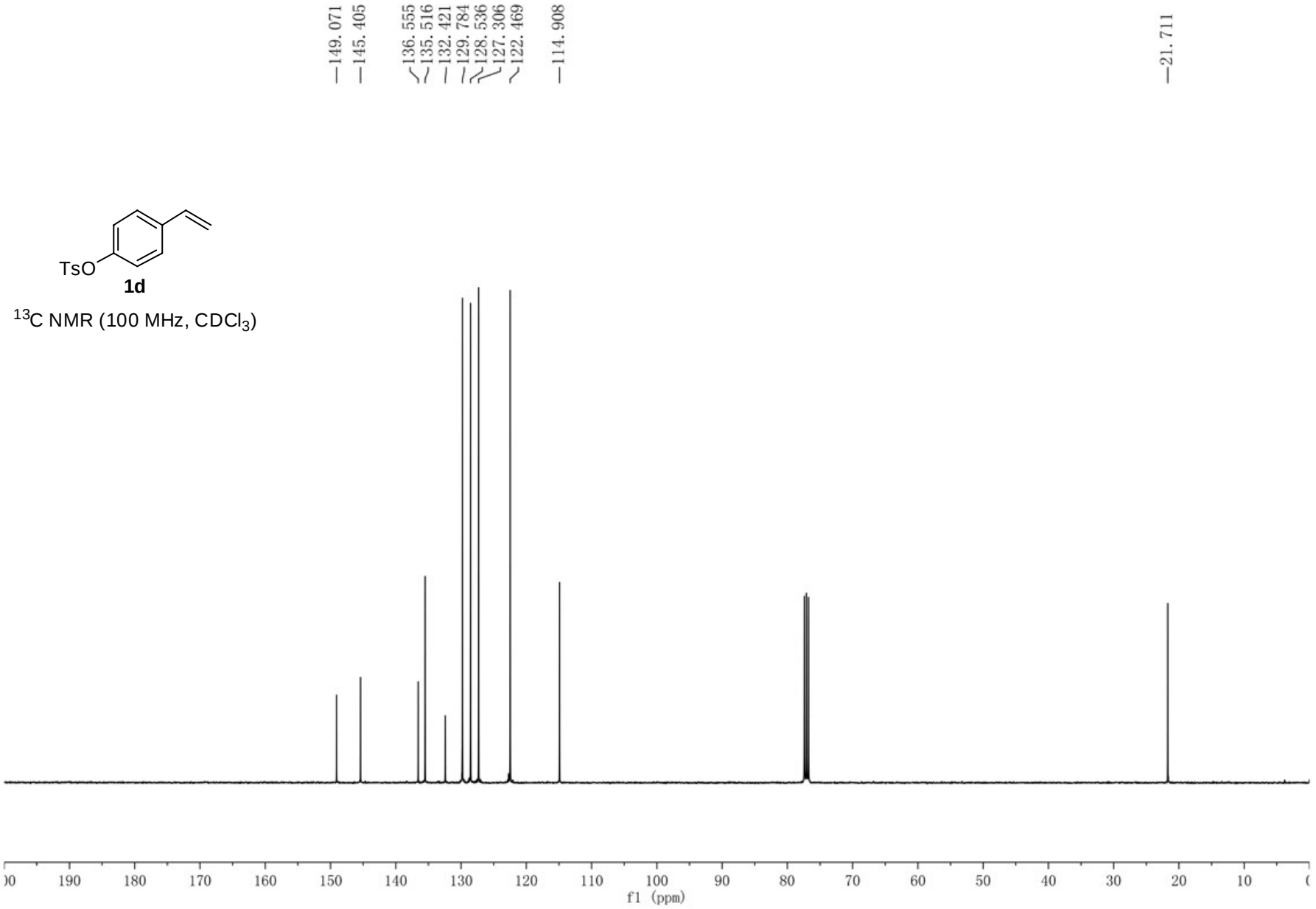
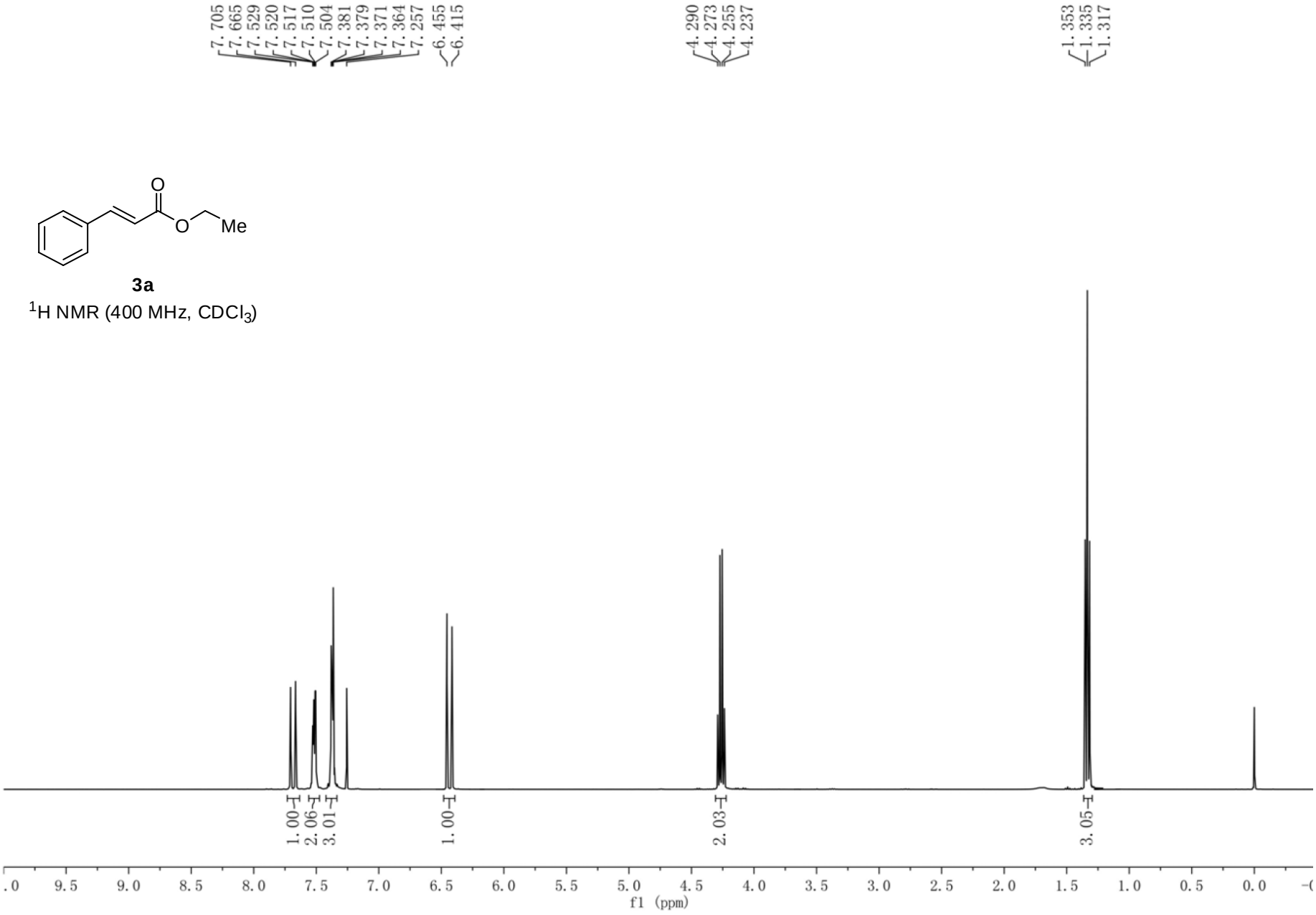


1d

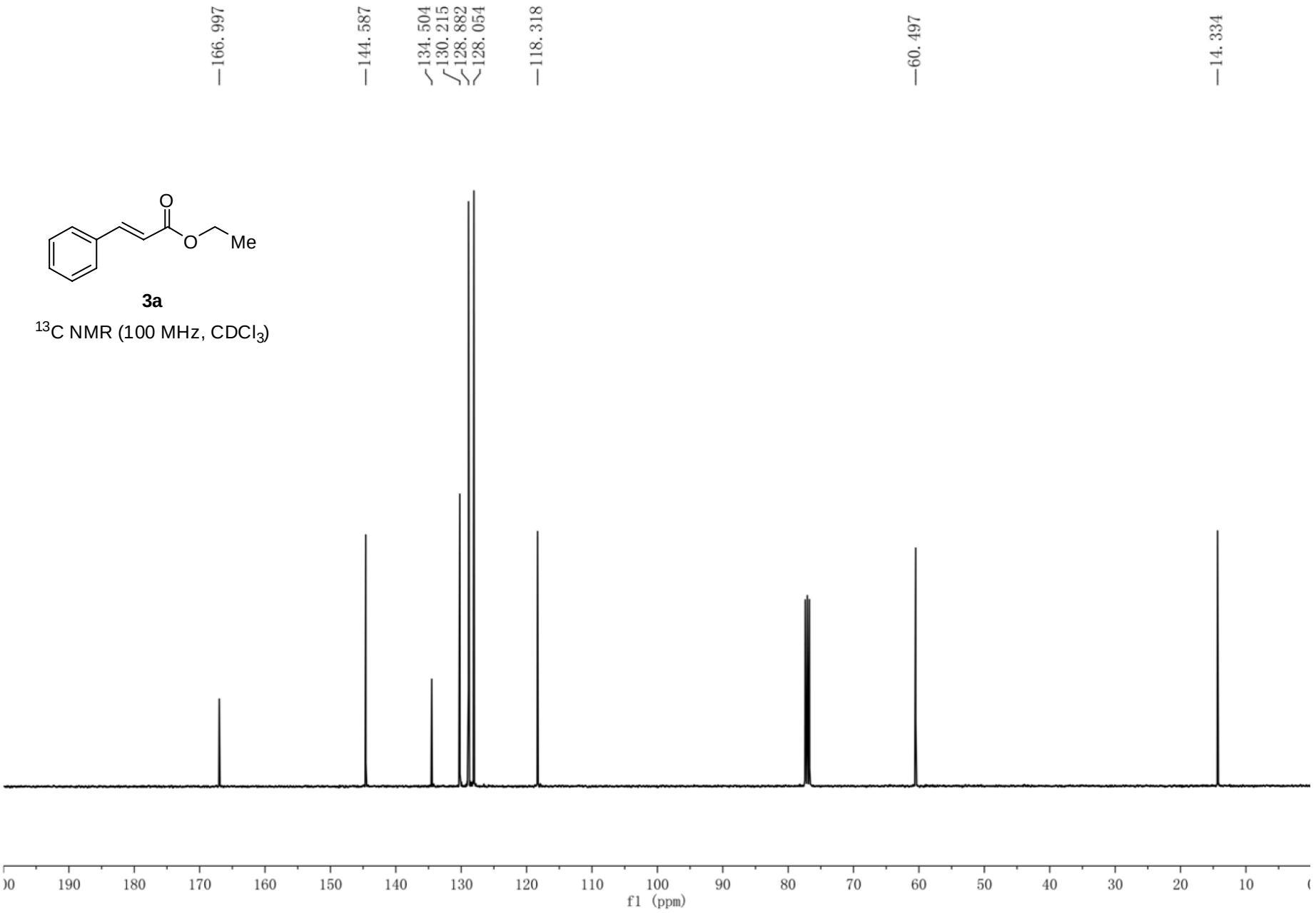
^{1}H NMR (400 MHz, $CDCl_3$)

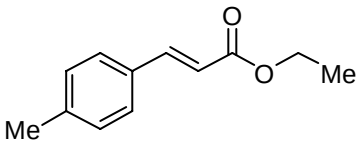




3a

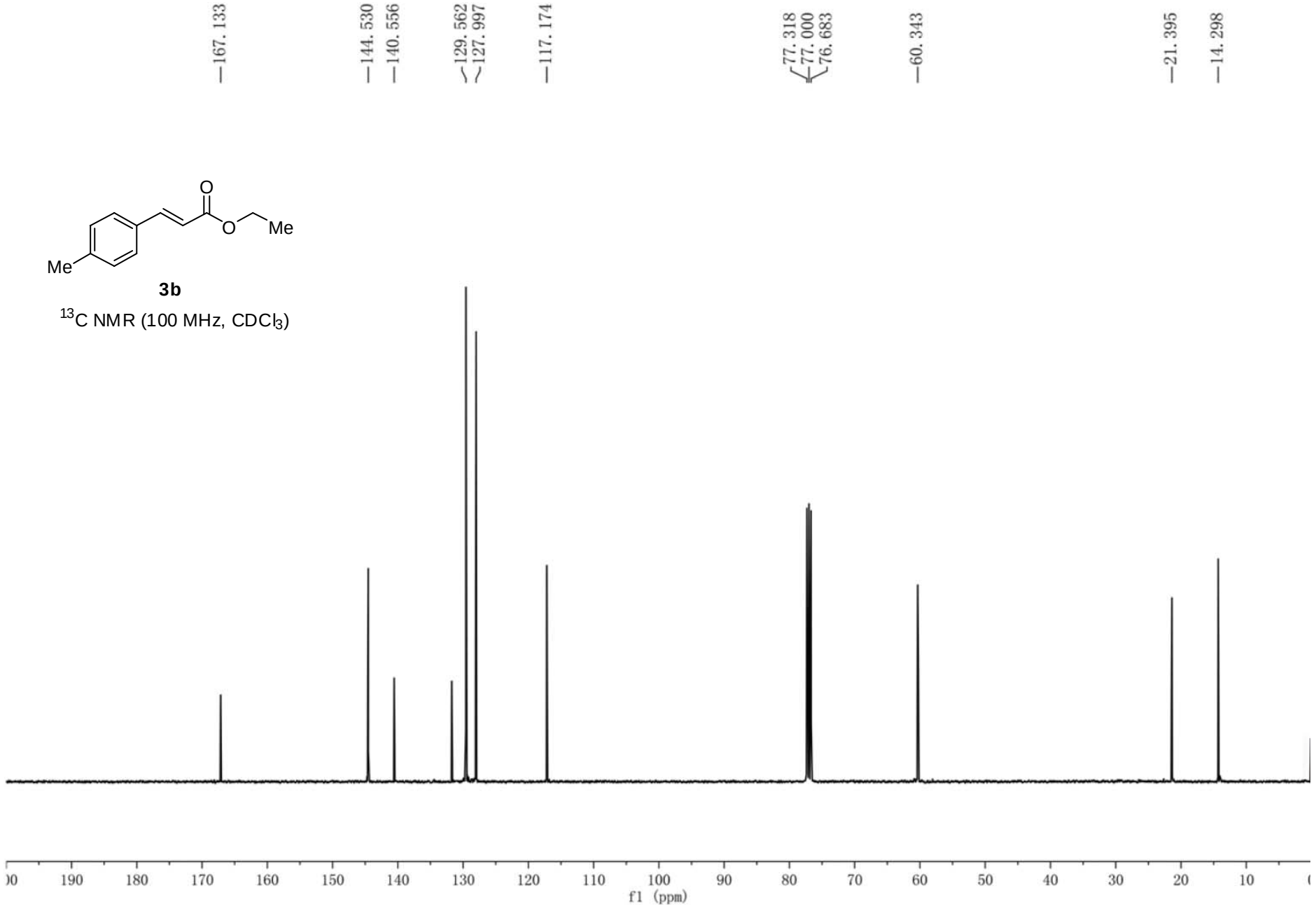
^{1}H NMR (400 MHz, $CDCl_3$)


166. 997
144. 587
134. 504
130. 215
128. 882
128. 054
118. 318
60. 497
14. 334
O
O
Me
3a
13C NMR (100 MHz, CDCl3)
f1 (ppm)



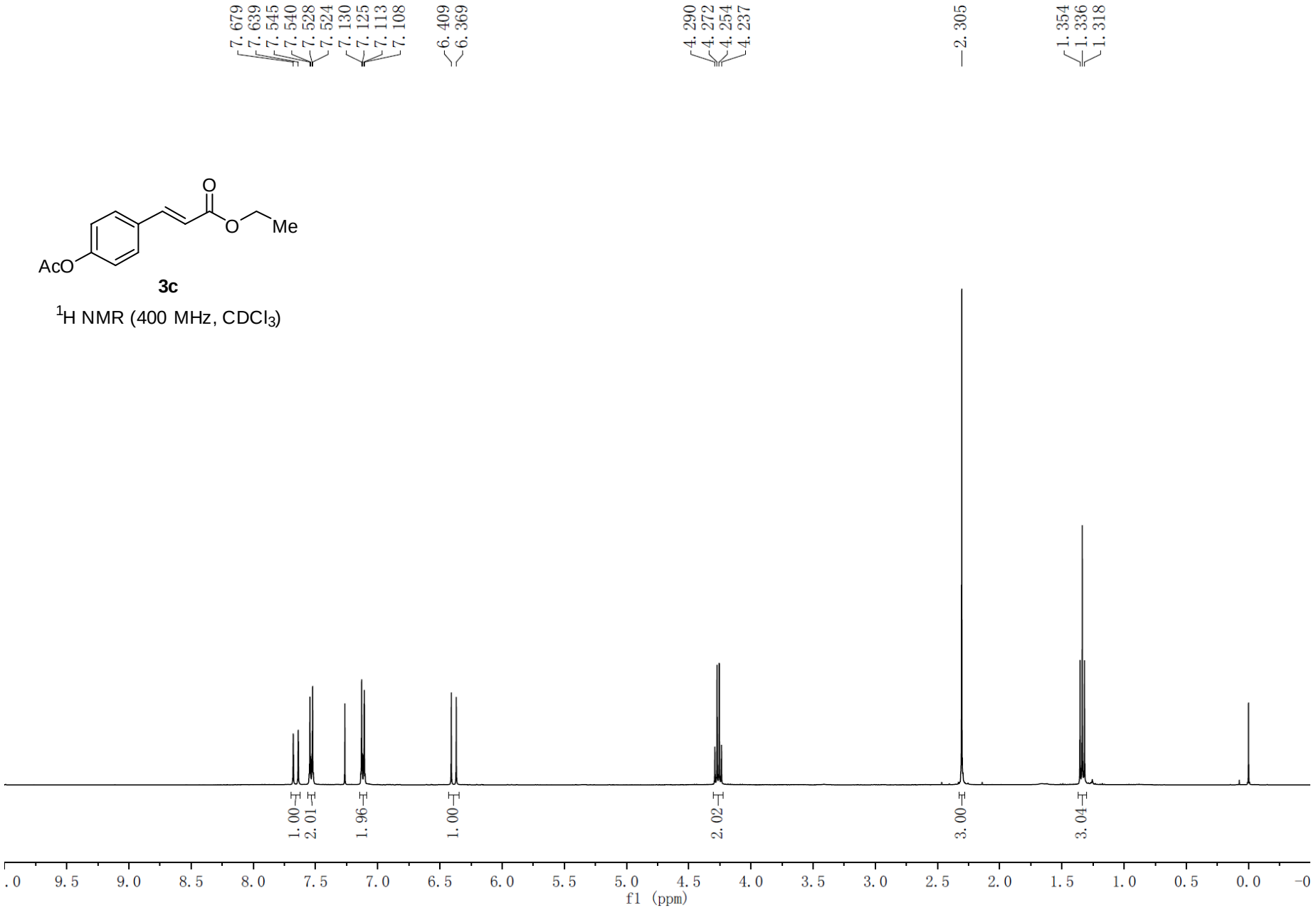
3b

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



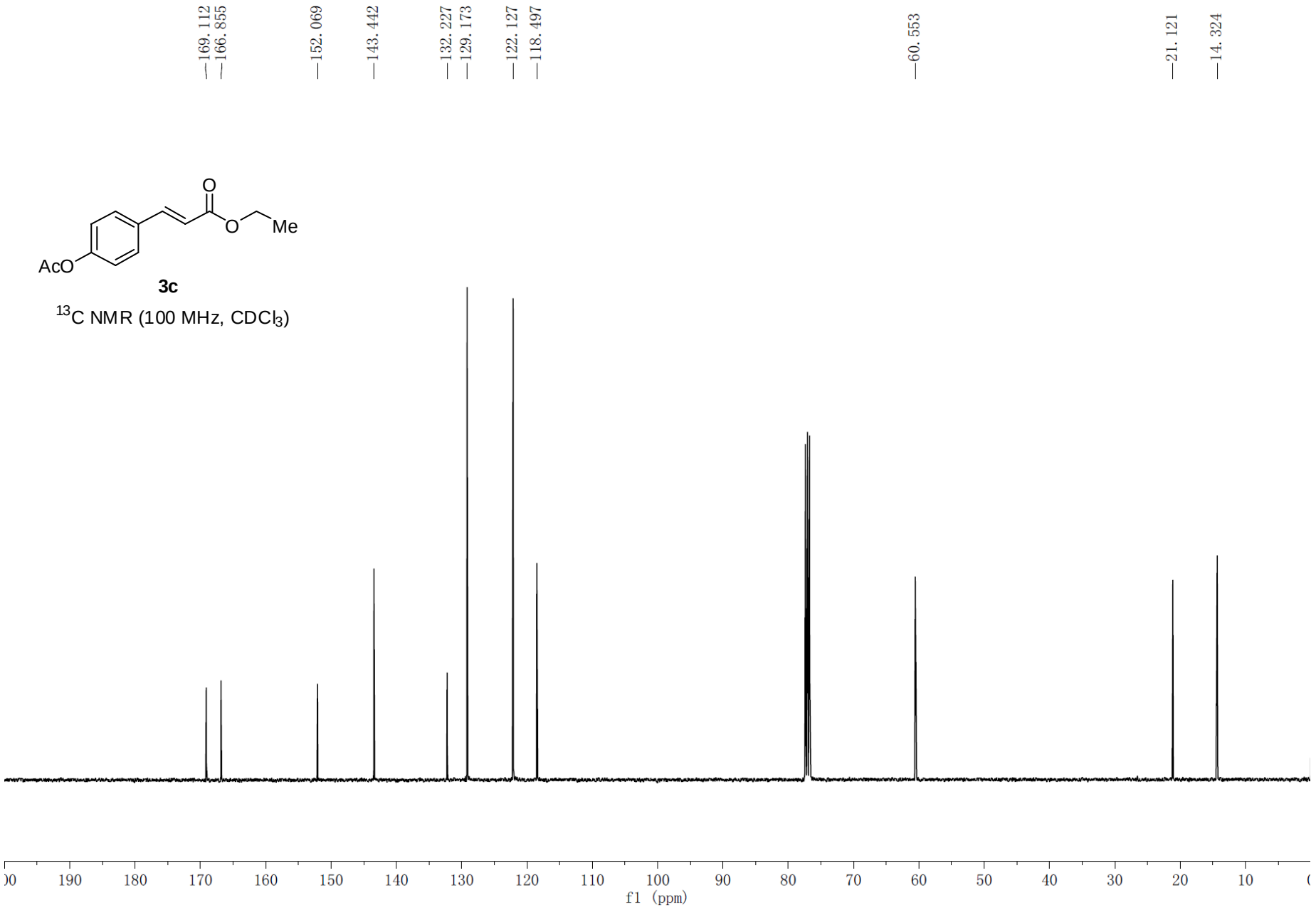
3b

^{13}C NMR (100 MHz, $CDCl_3$)



3c

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



3c

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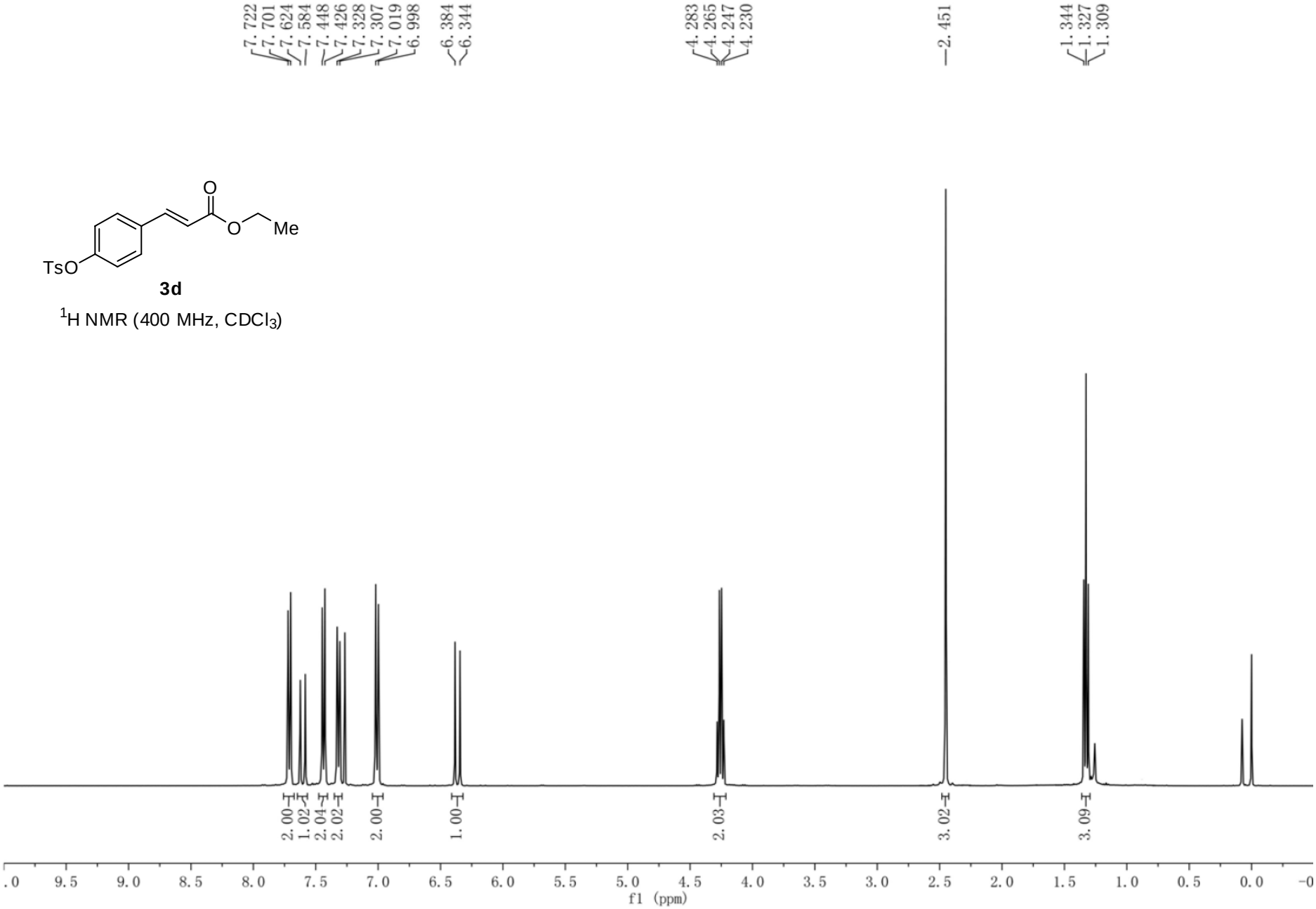
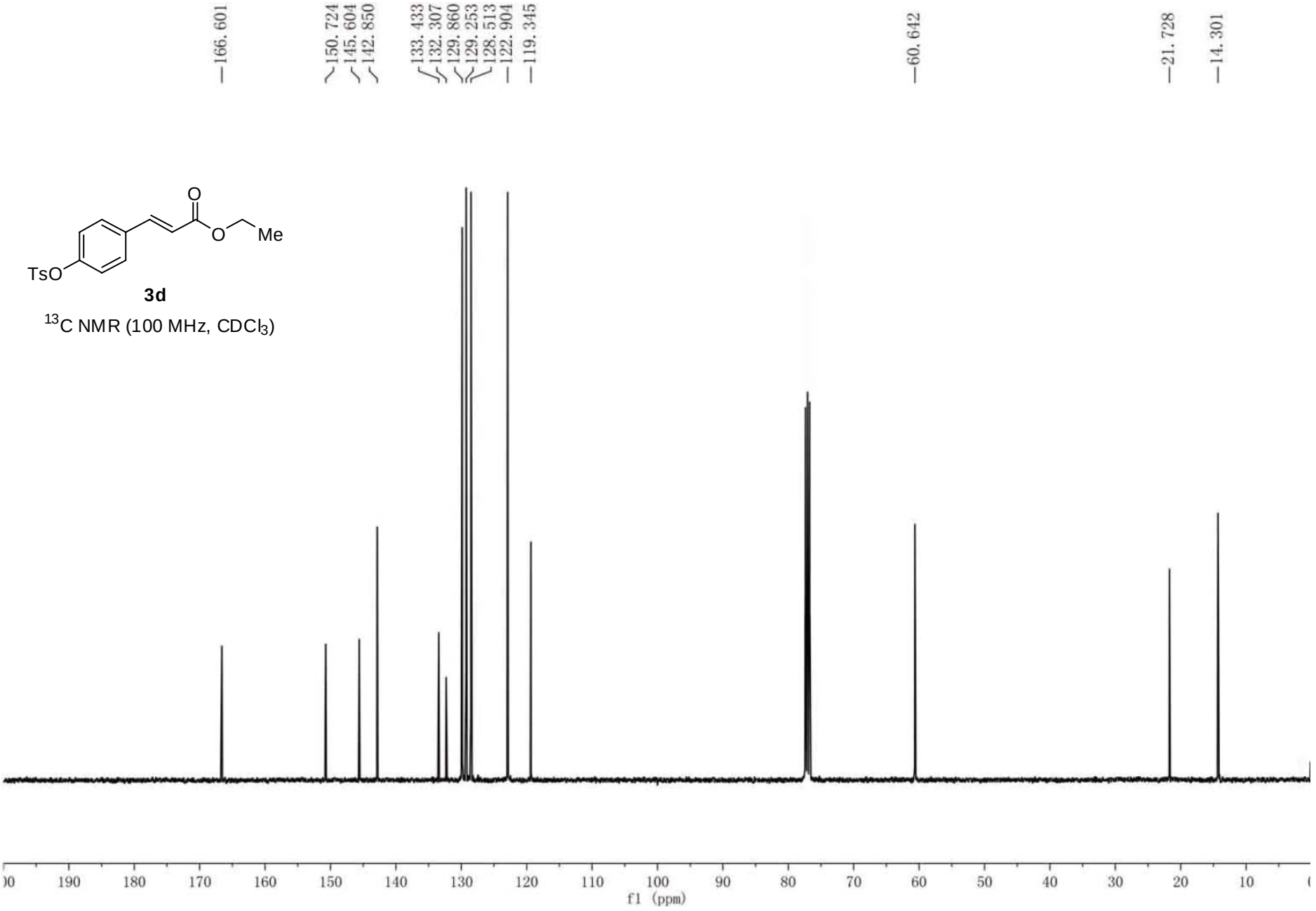


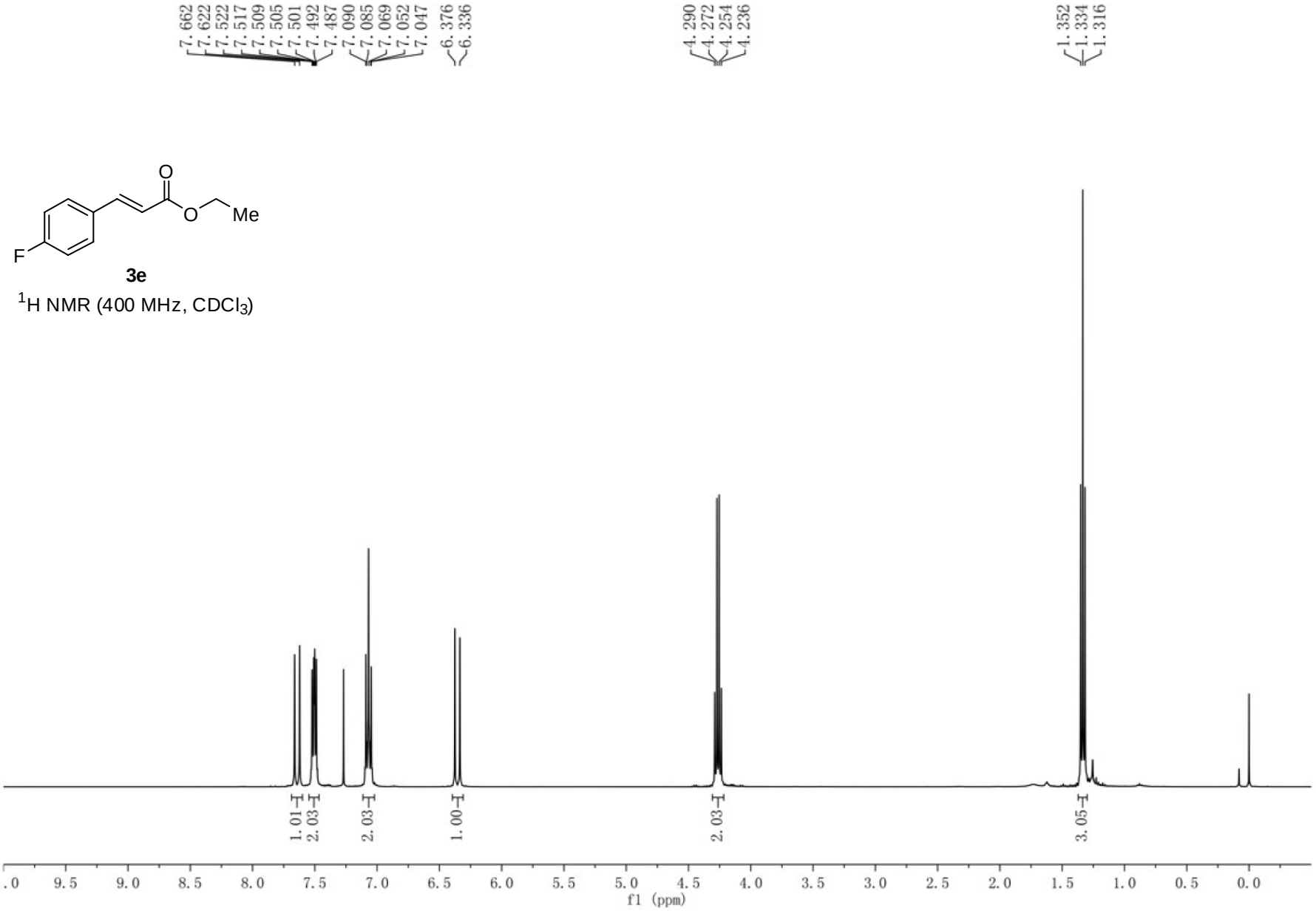
3d

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



3d

^{13}C NMR (100 MHz, $CDCl_3$)



3e

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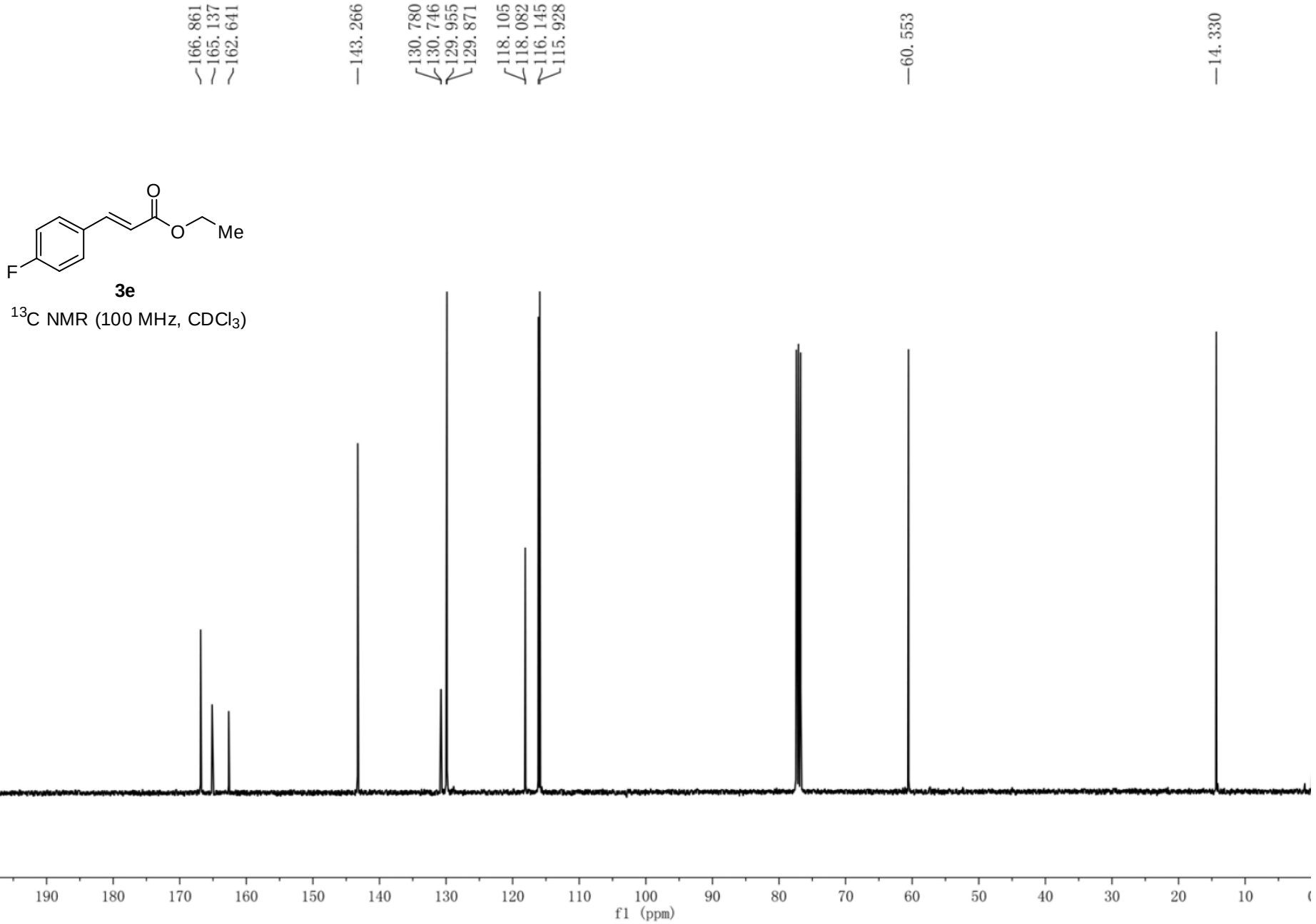
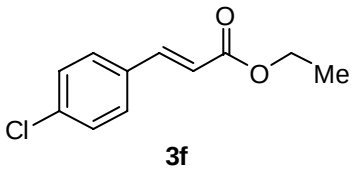


3e

^{13}C NMR (100 MHz, $CDCl_3$)



3f

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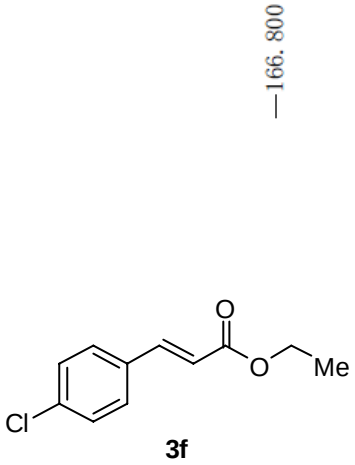
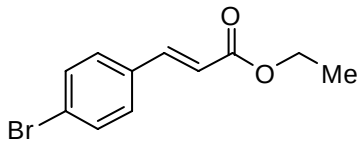


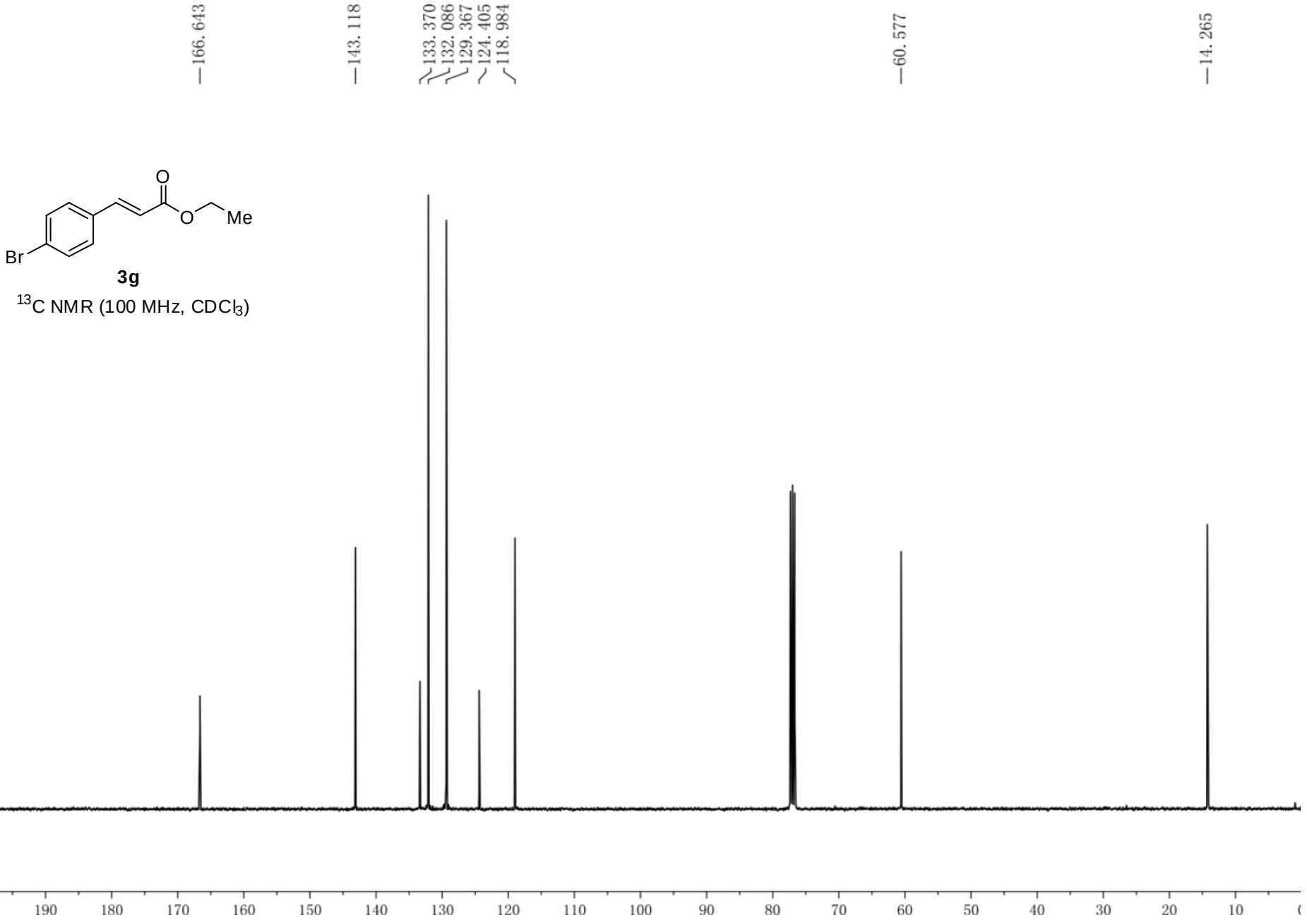
3f

^{13}C NMR (100 MHz, $CDCl_3$)



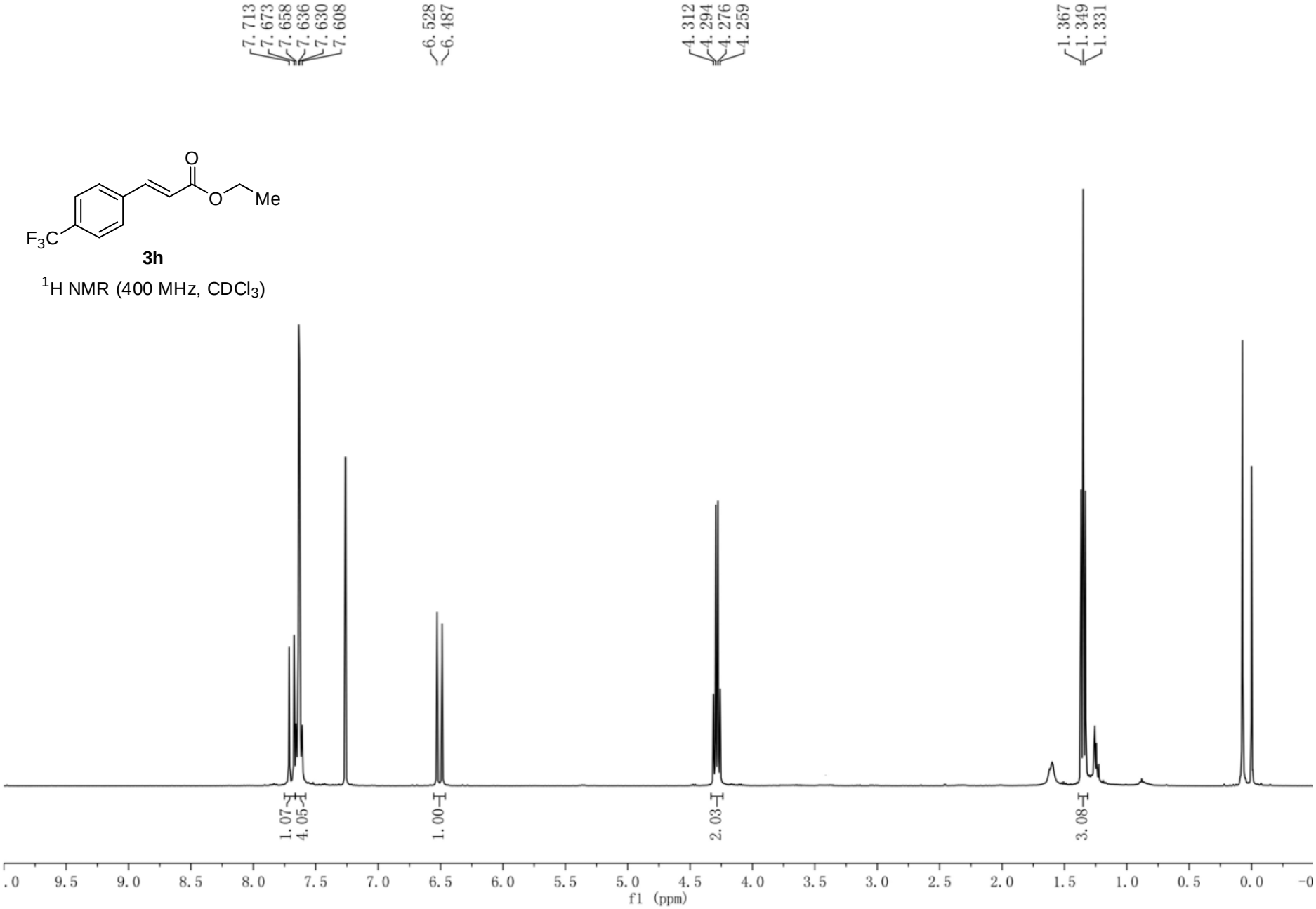
3g

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



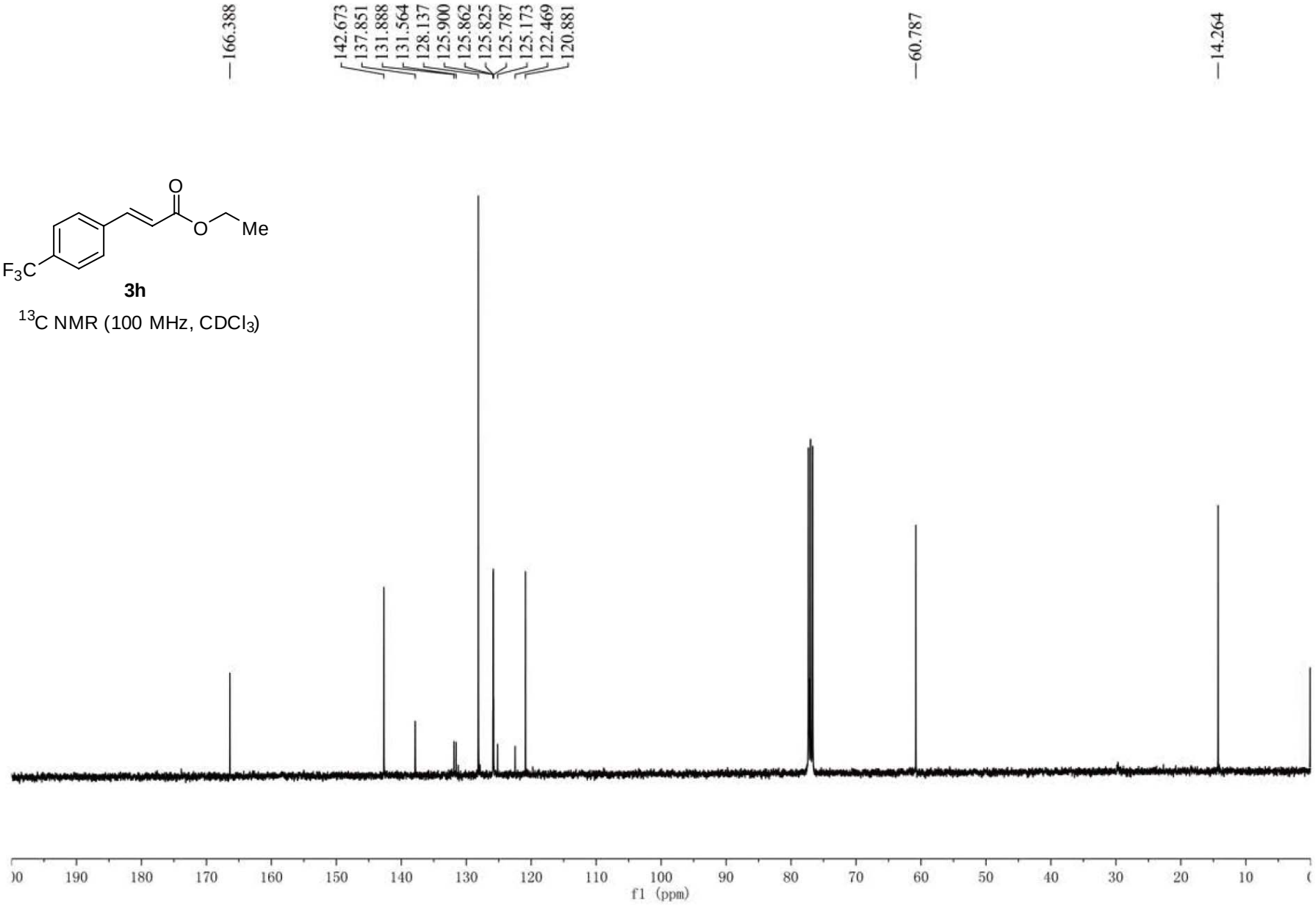
3g

^{13}C NMR (100 MHz, $CDCl_3$)



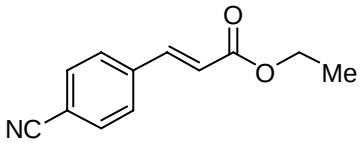
3h

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



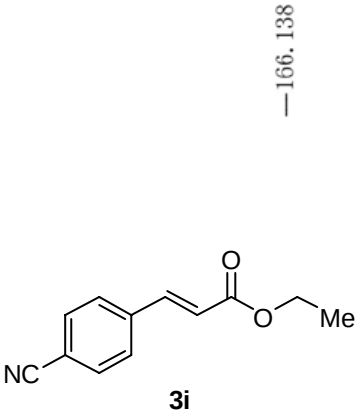
3h

^{13}C NMR (100 MHz, $CDCl_3$)



3i

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



3i

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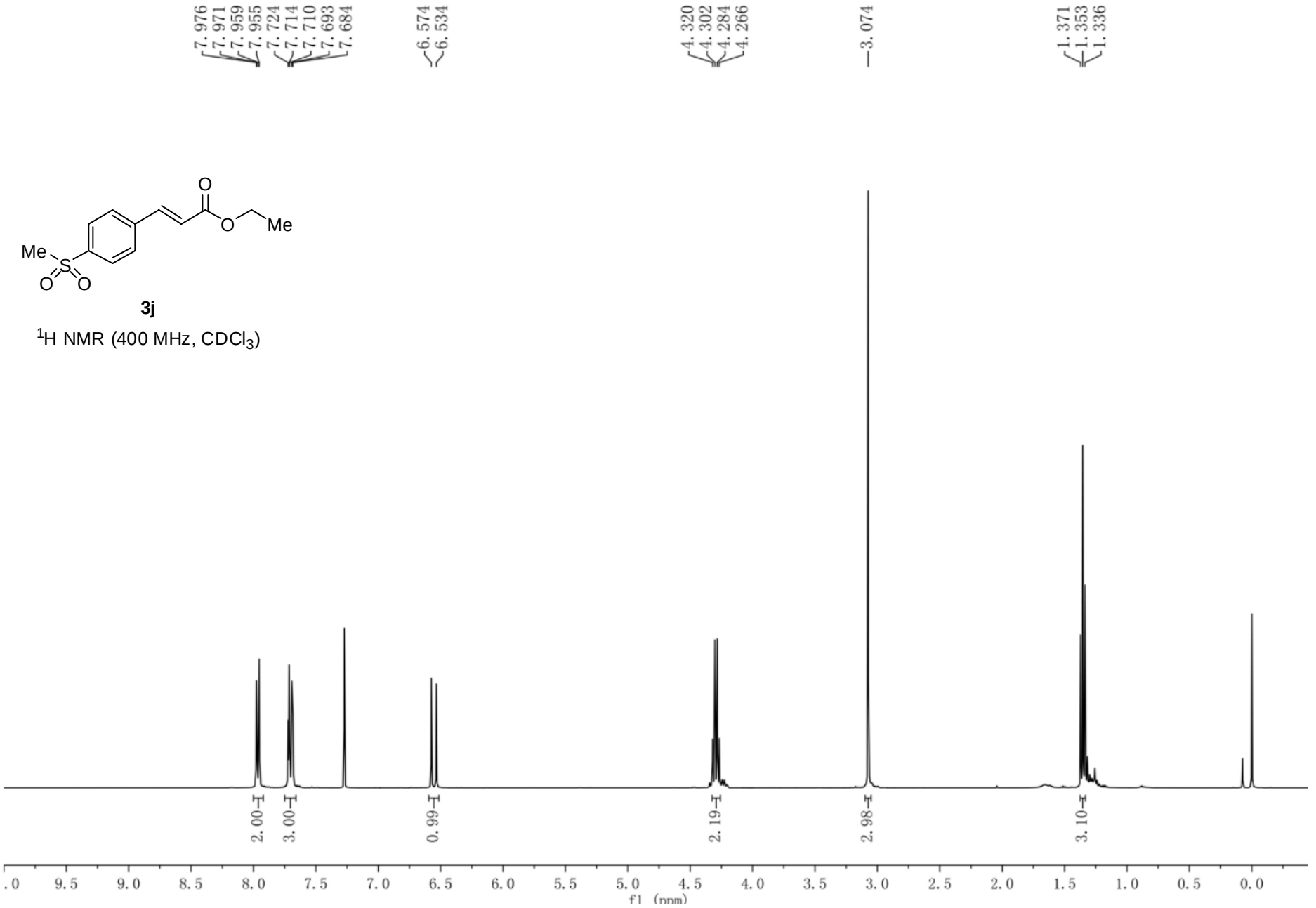

3j

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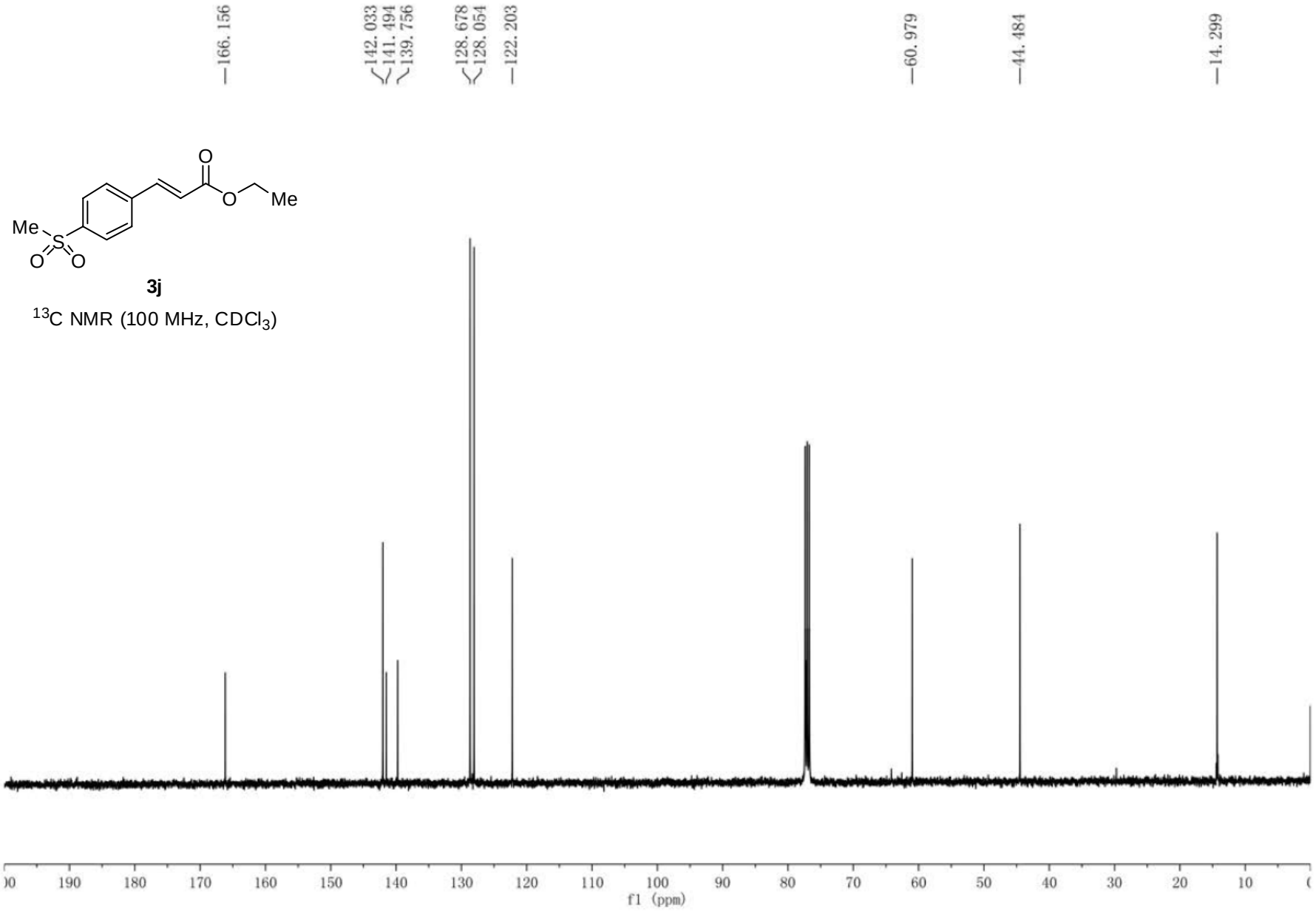

3j

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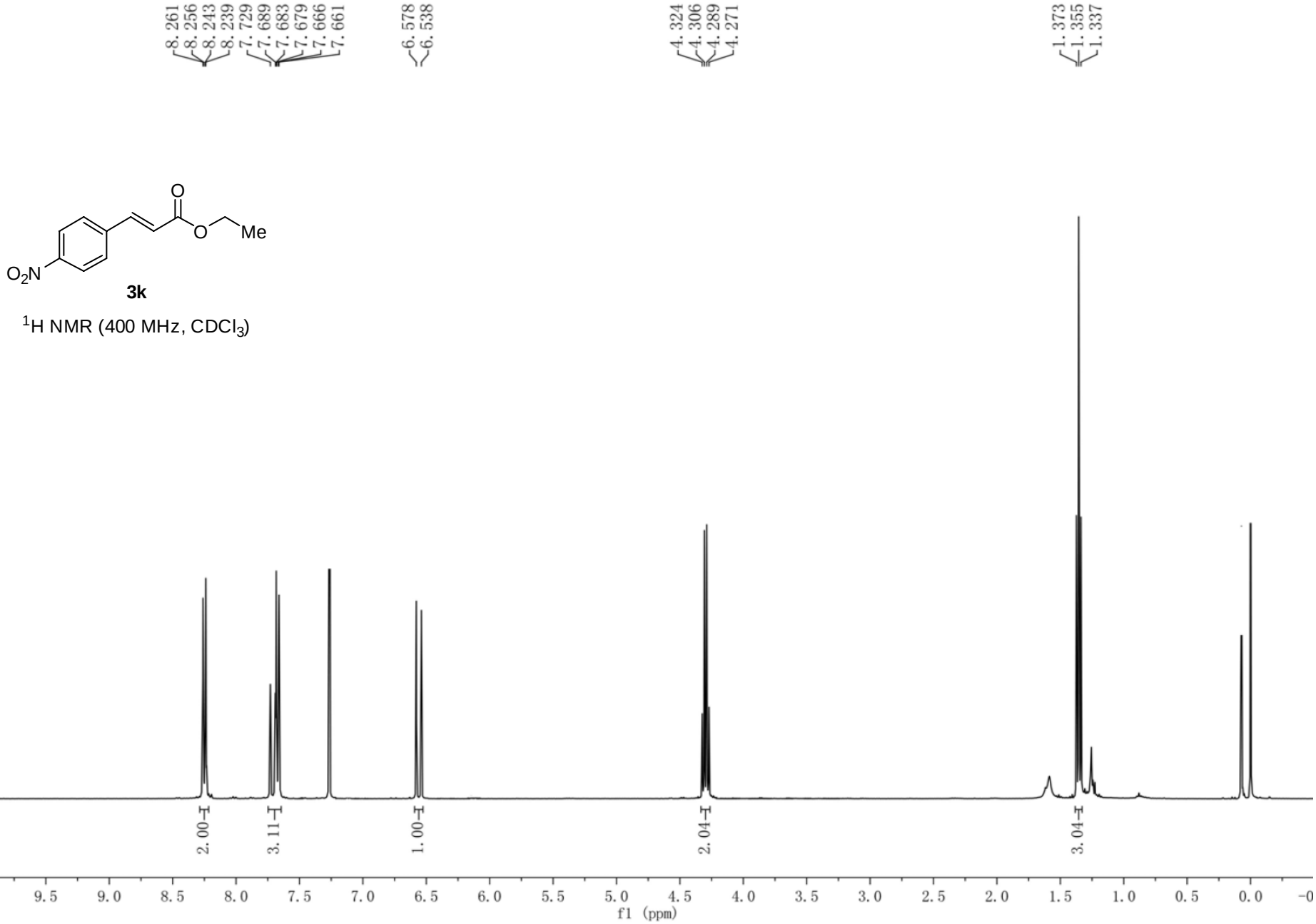

3k

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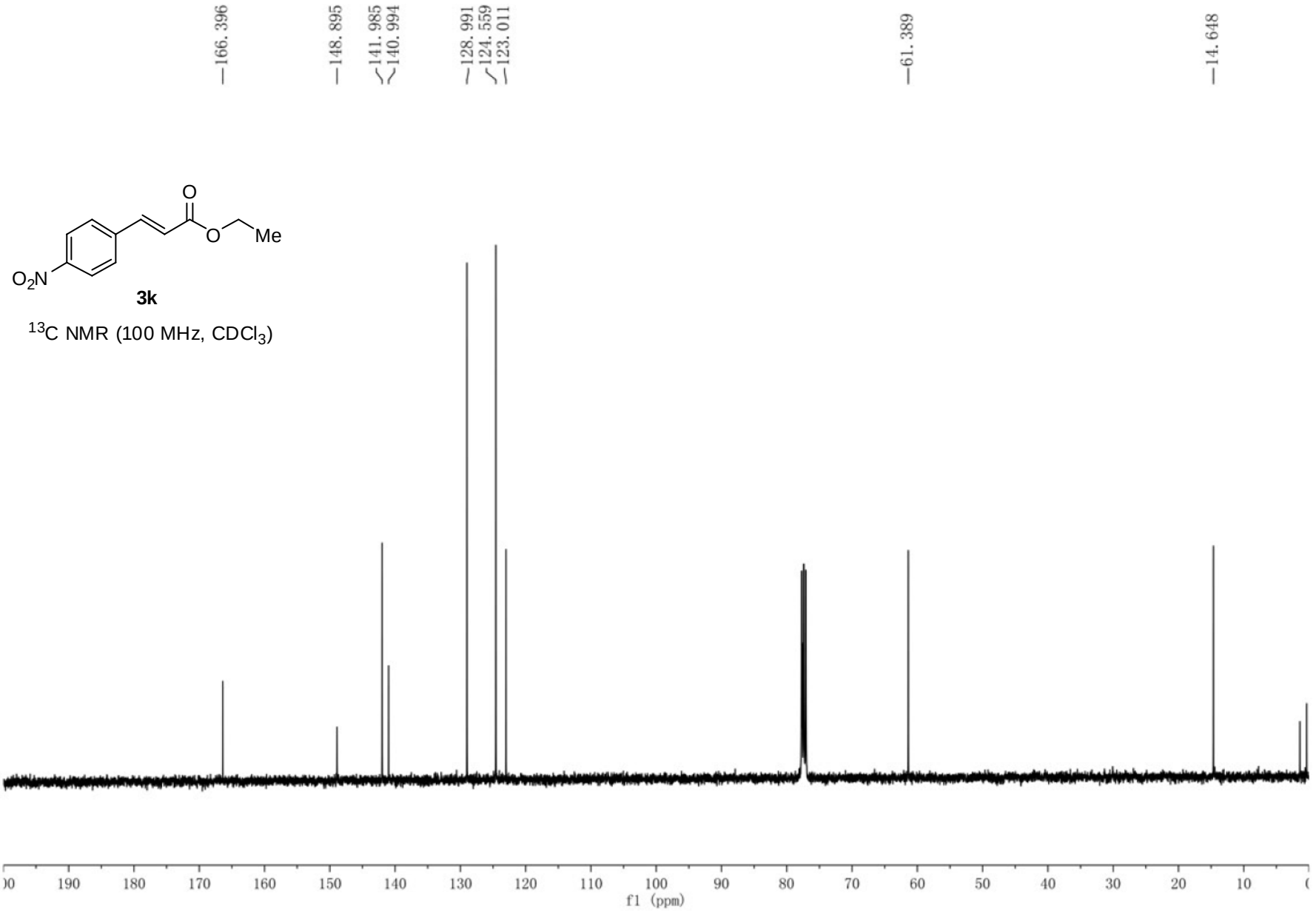

3k

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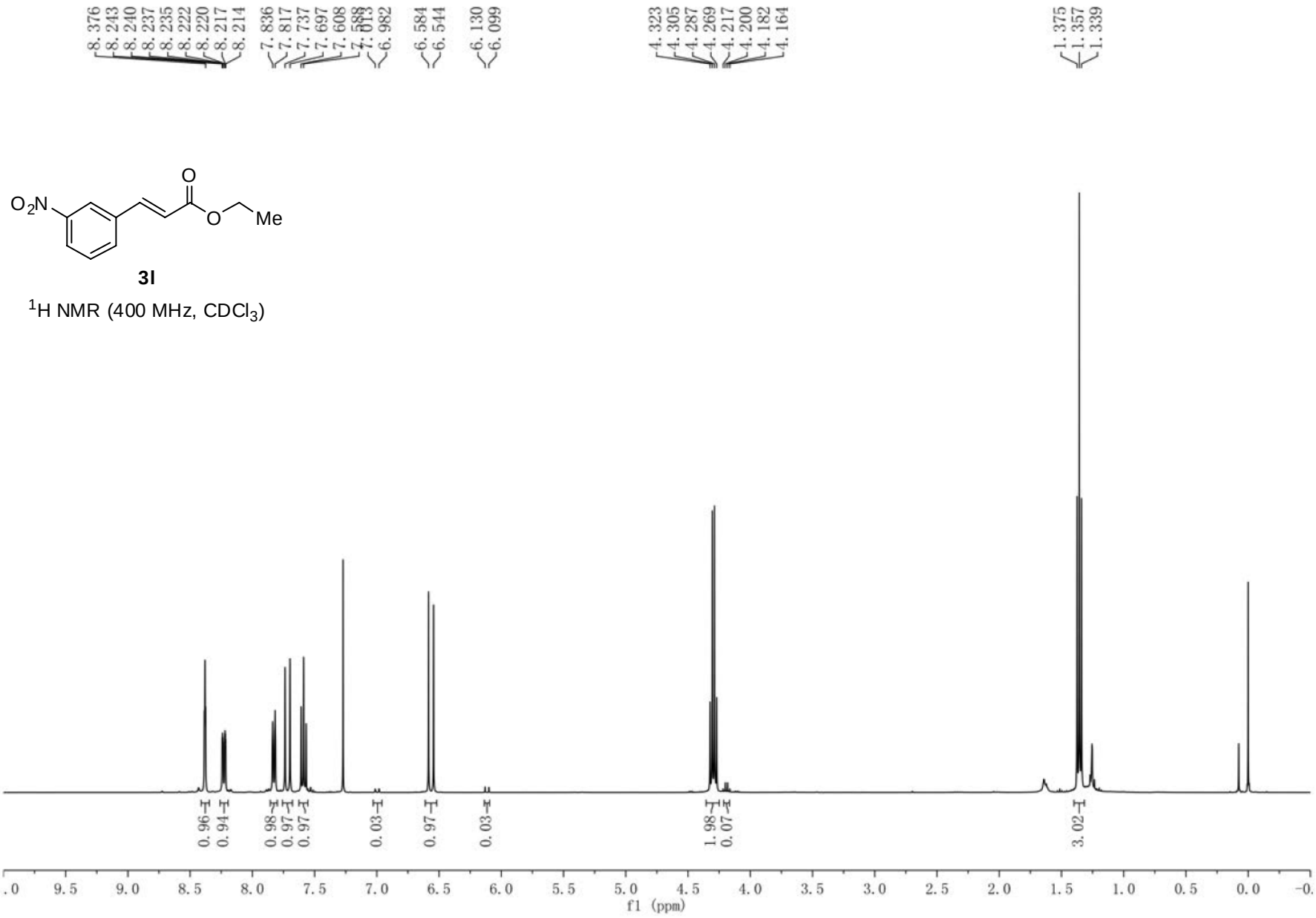

3l

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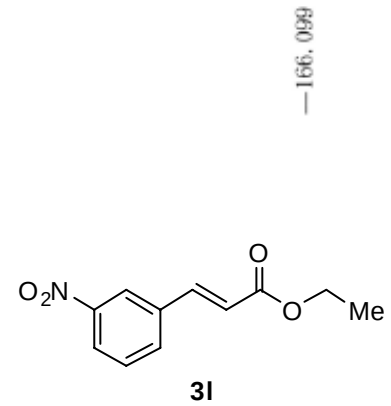

3l

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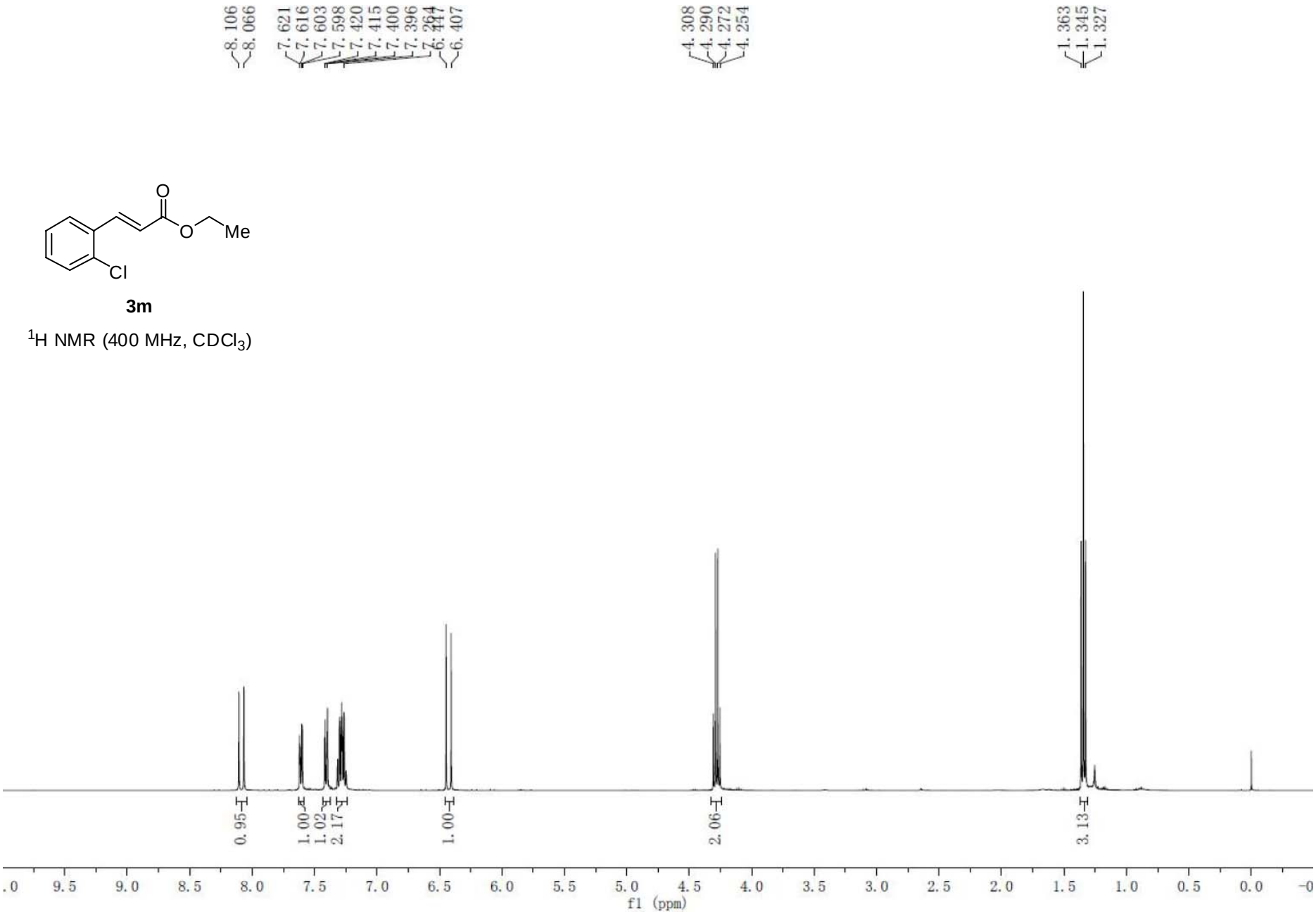
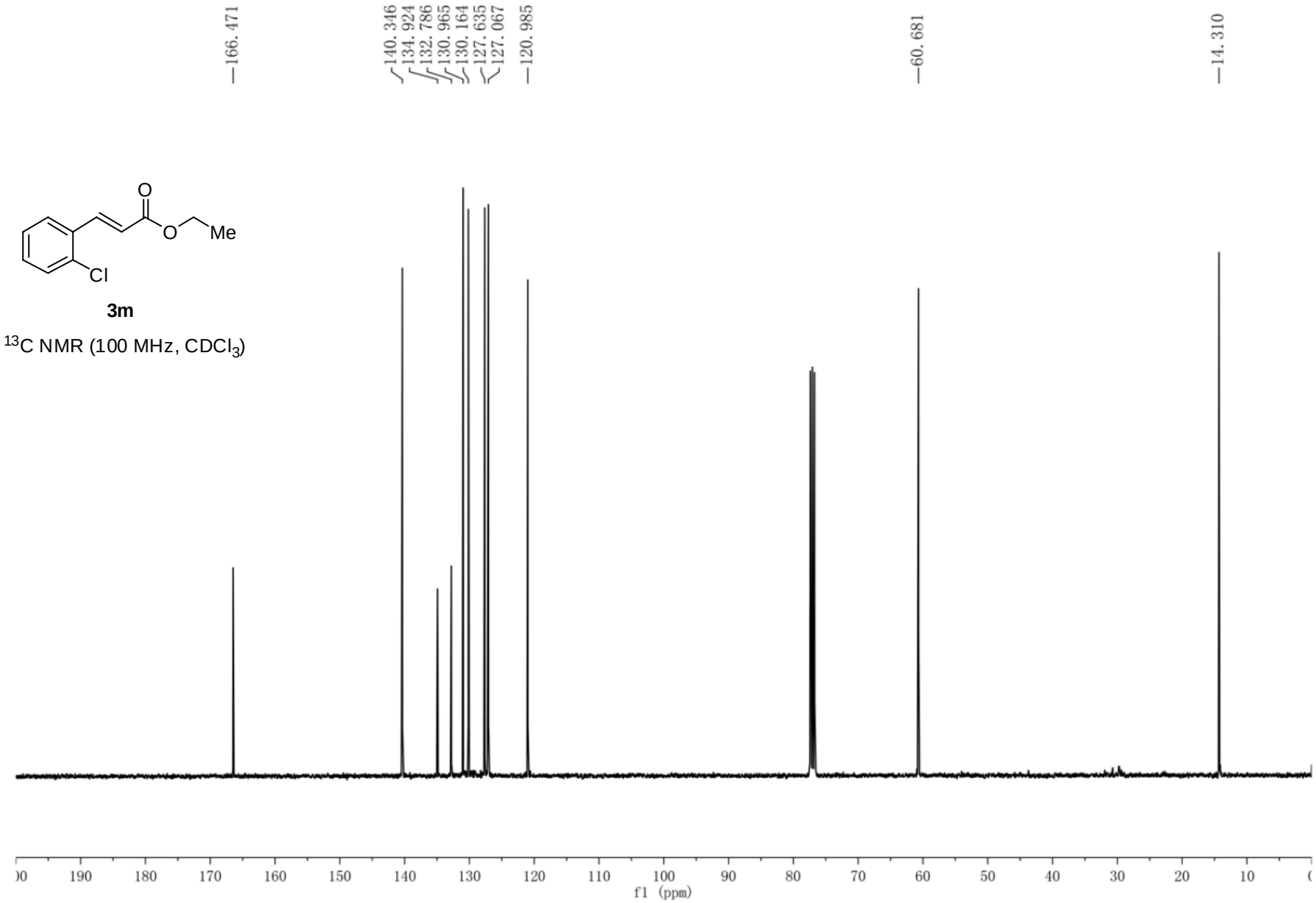


3m

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



3m

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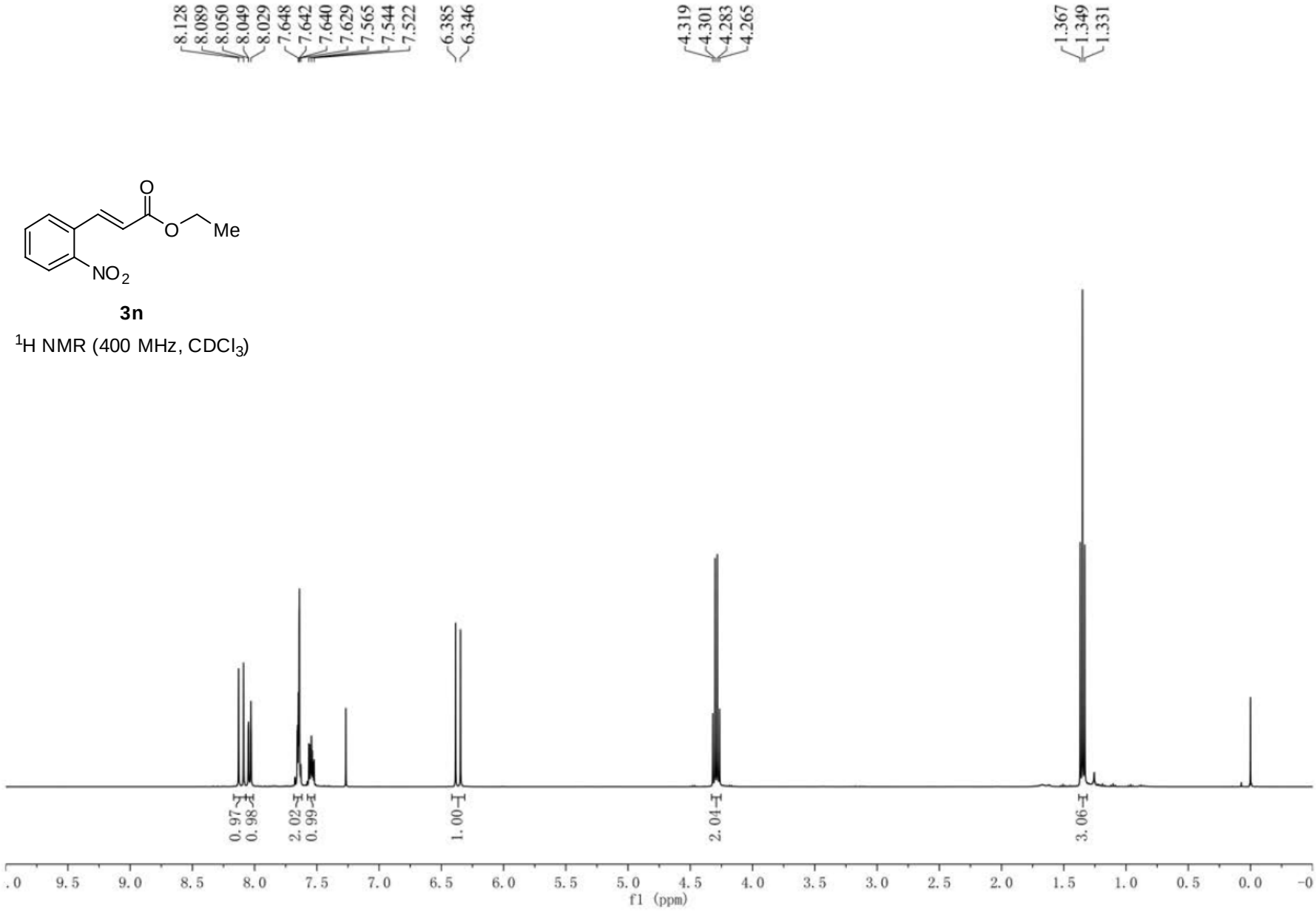

3n

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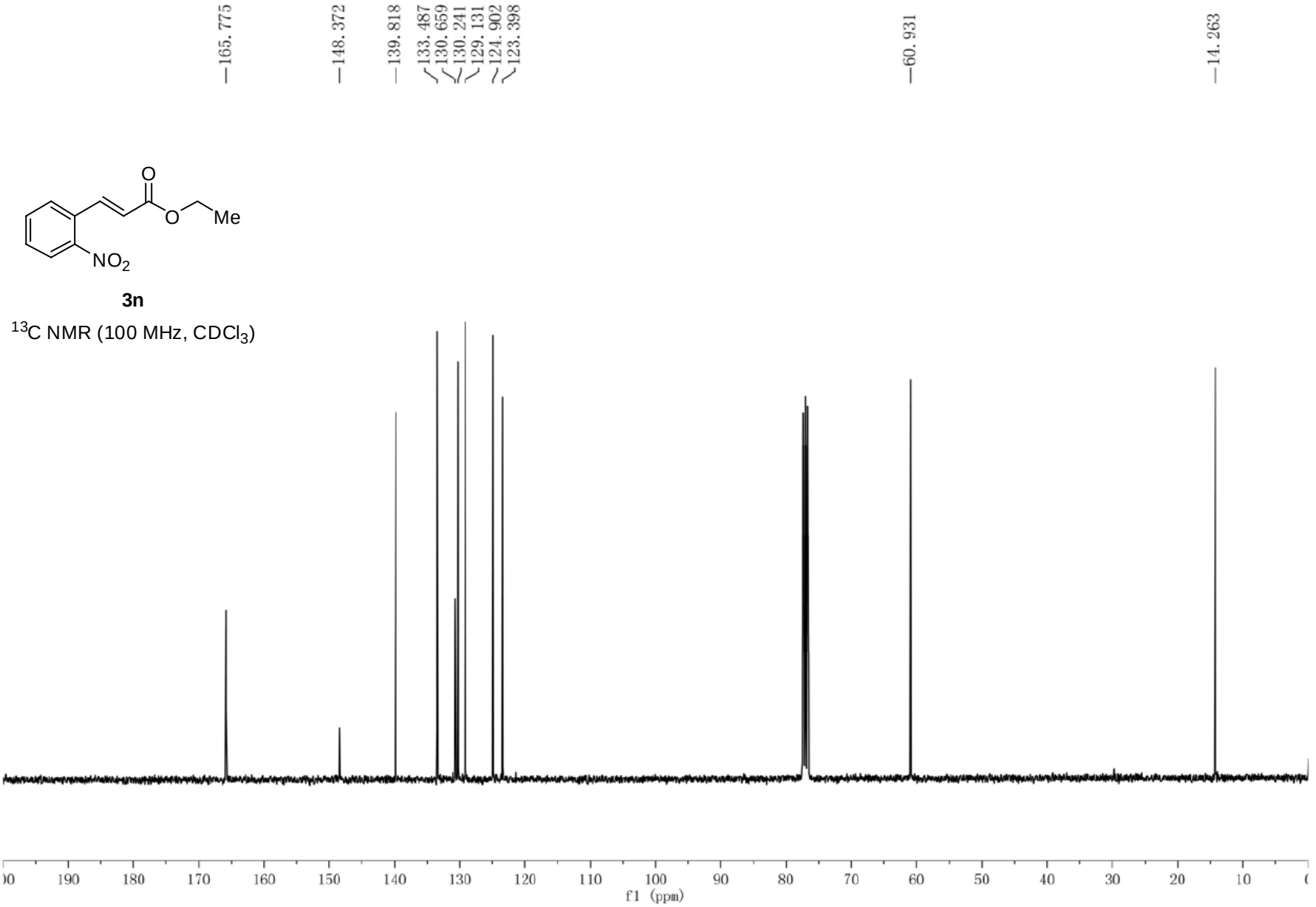

3n

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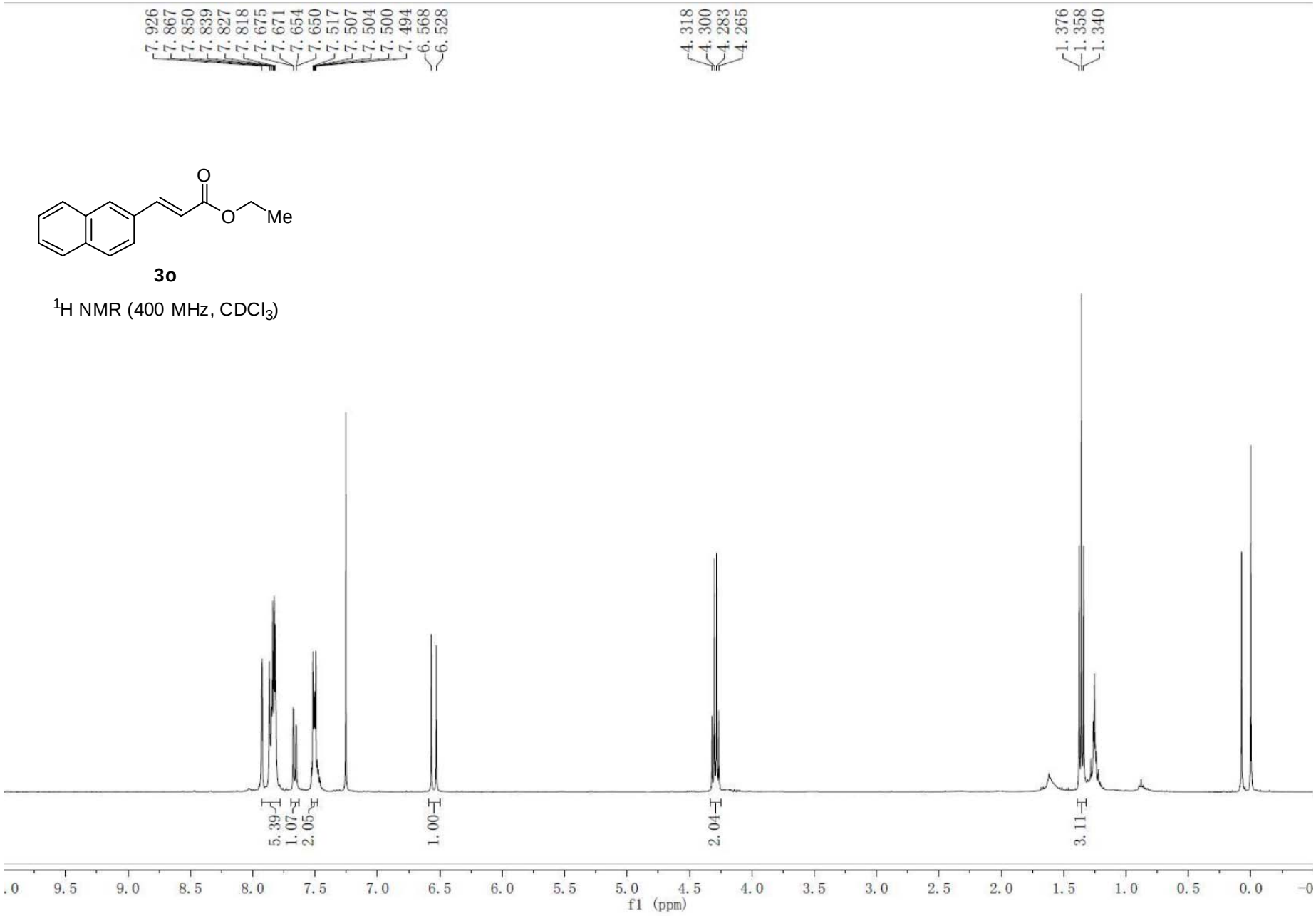

3o

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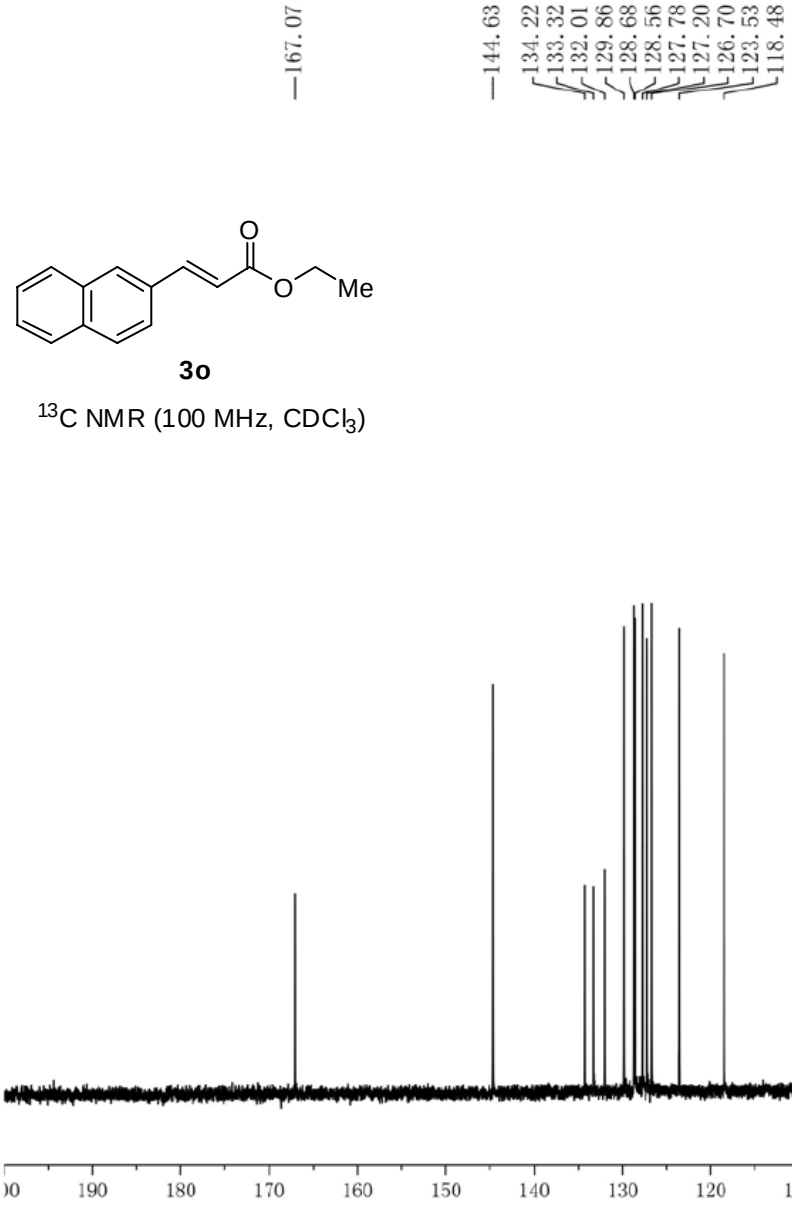

3o

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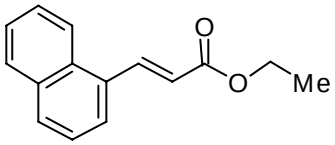

3p

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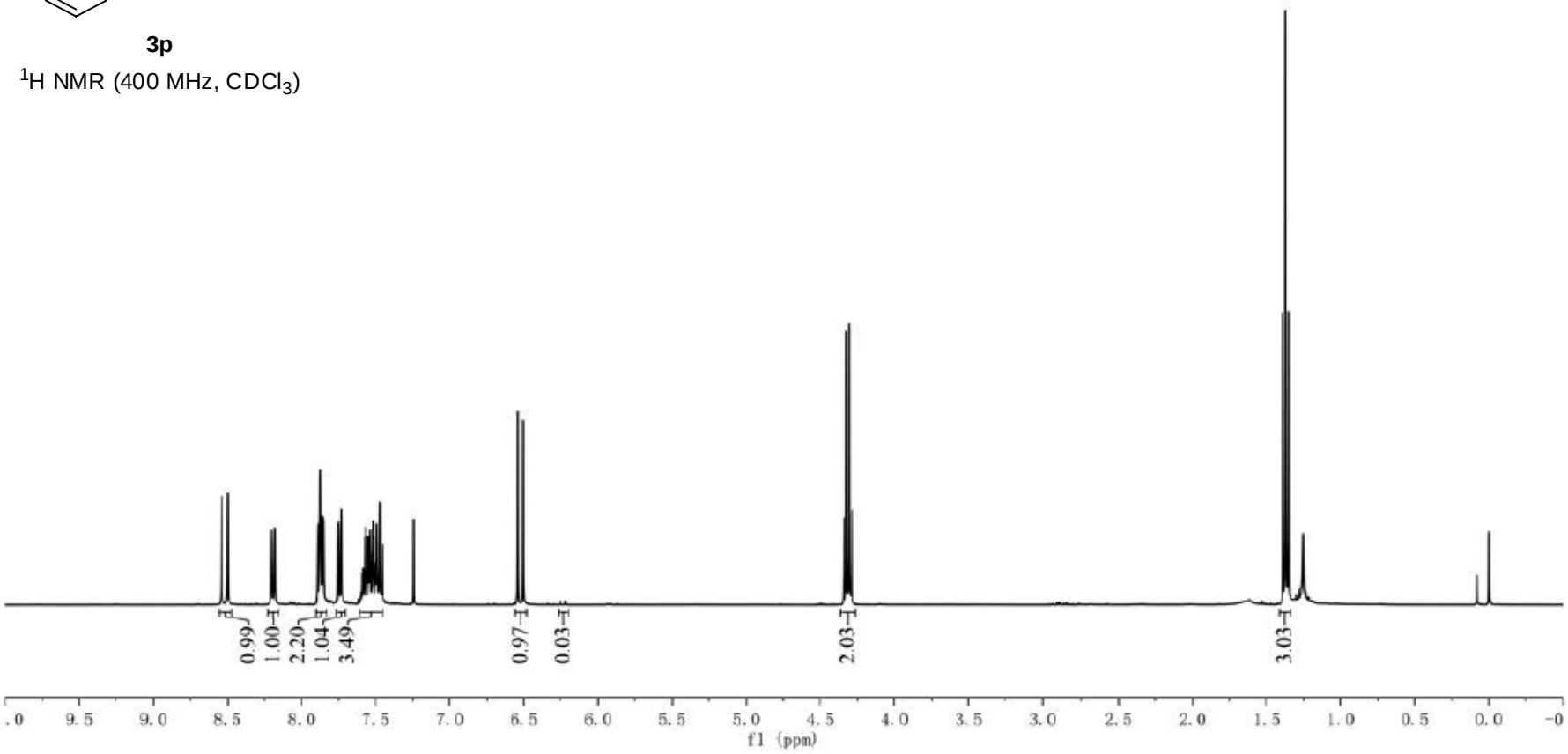

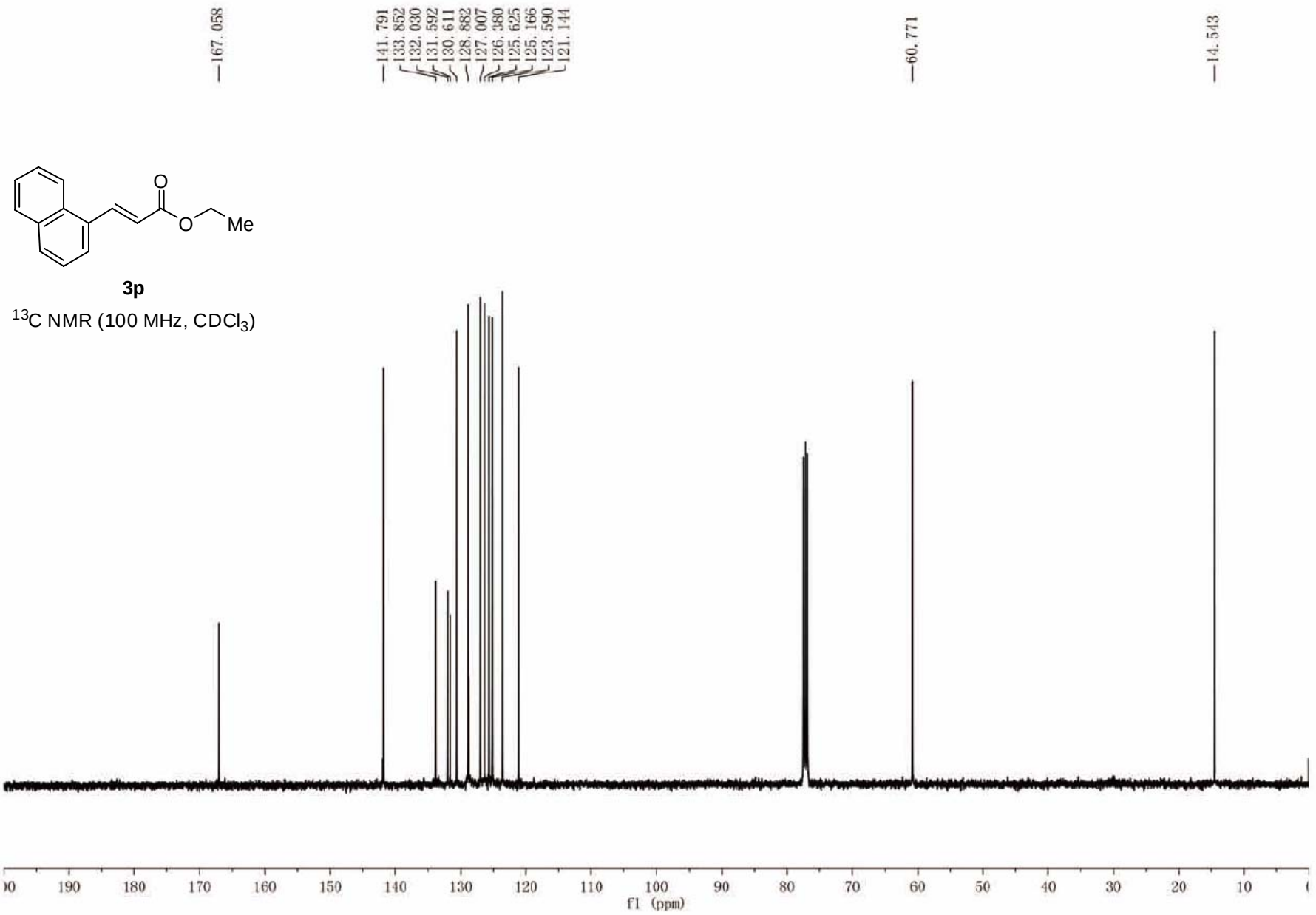

3p

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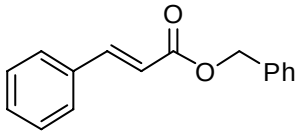

3q

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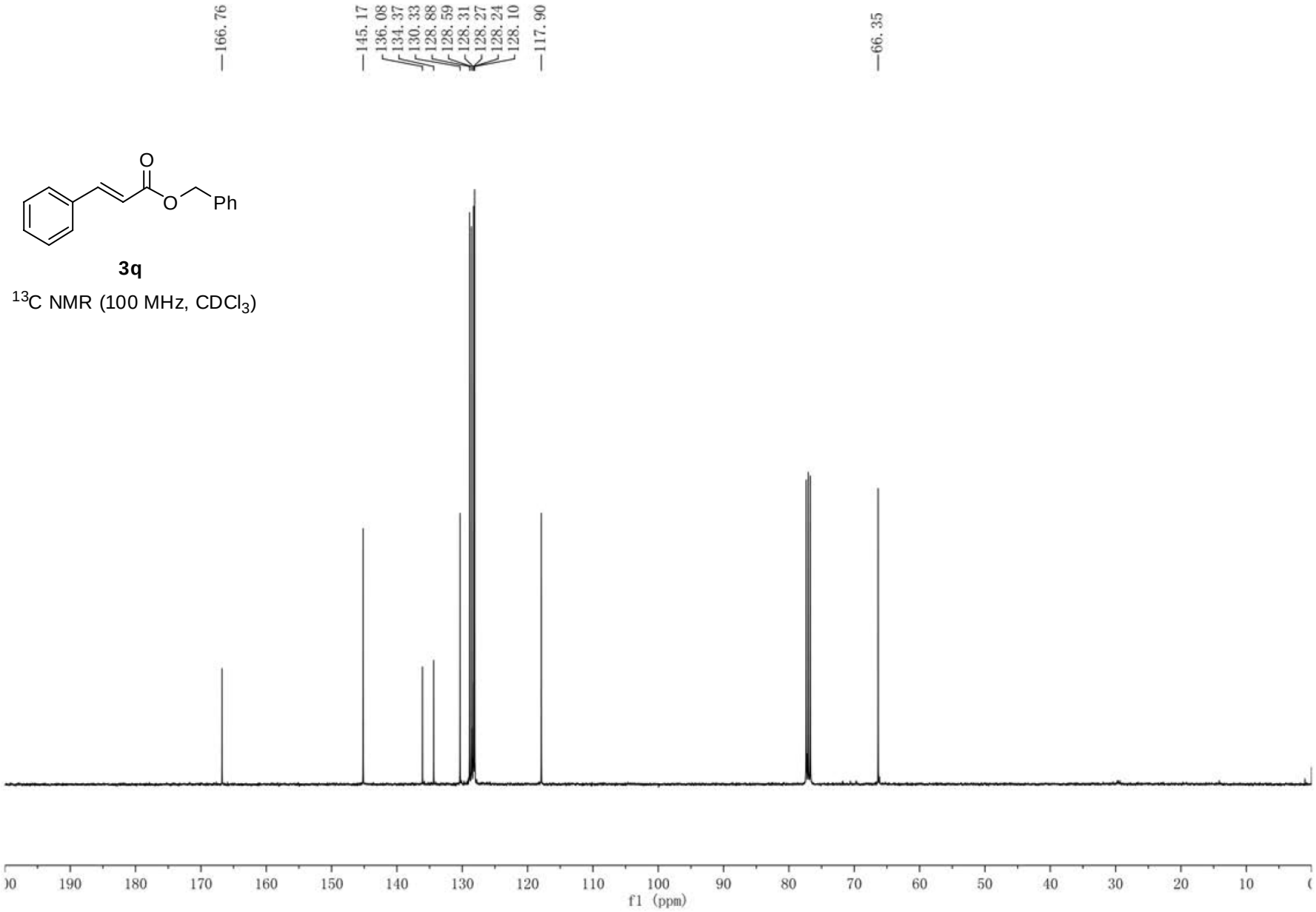

3q

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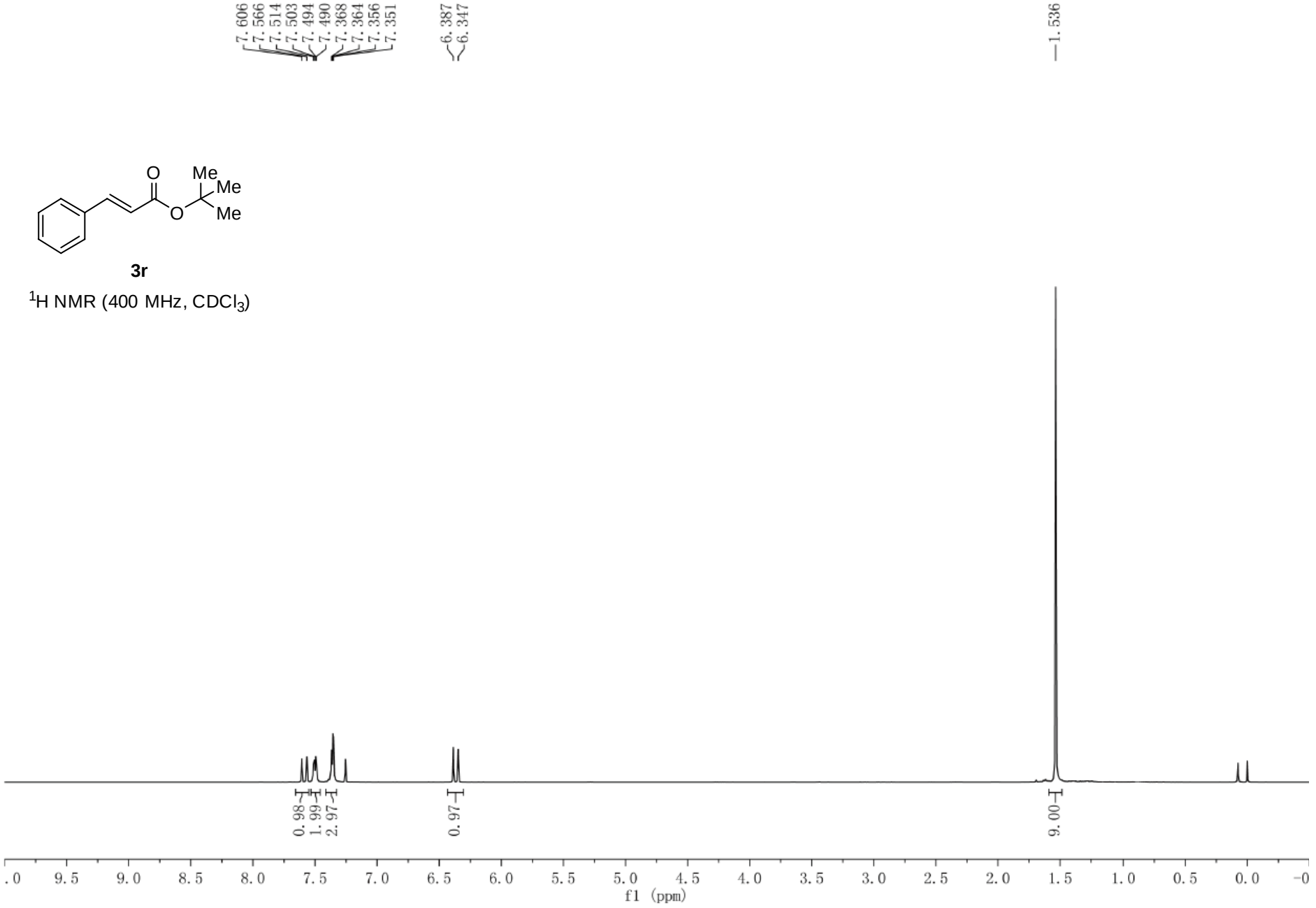

3r

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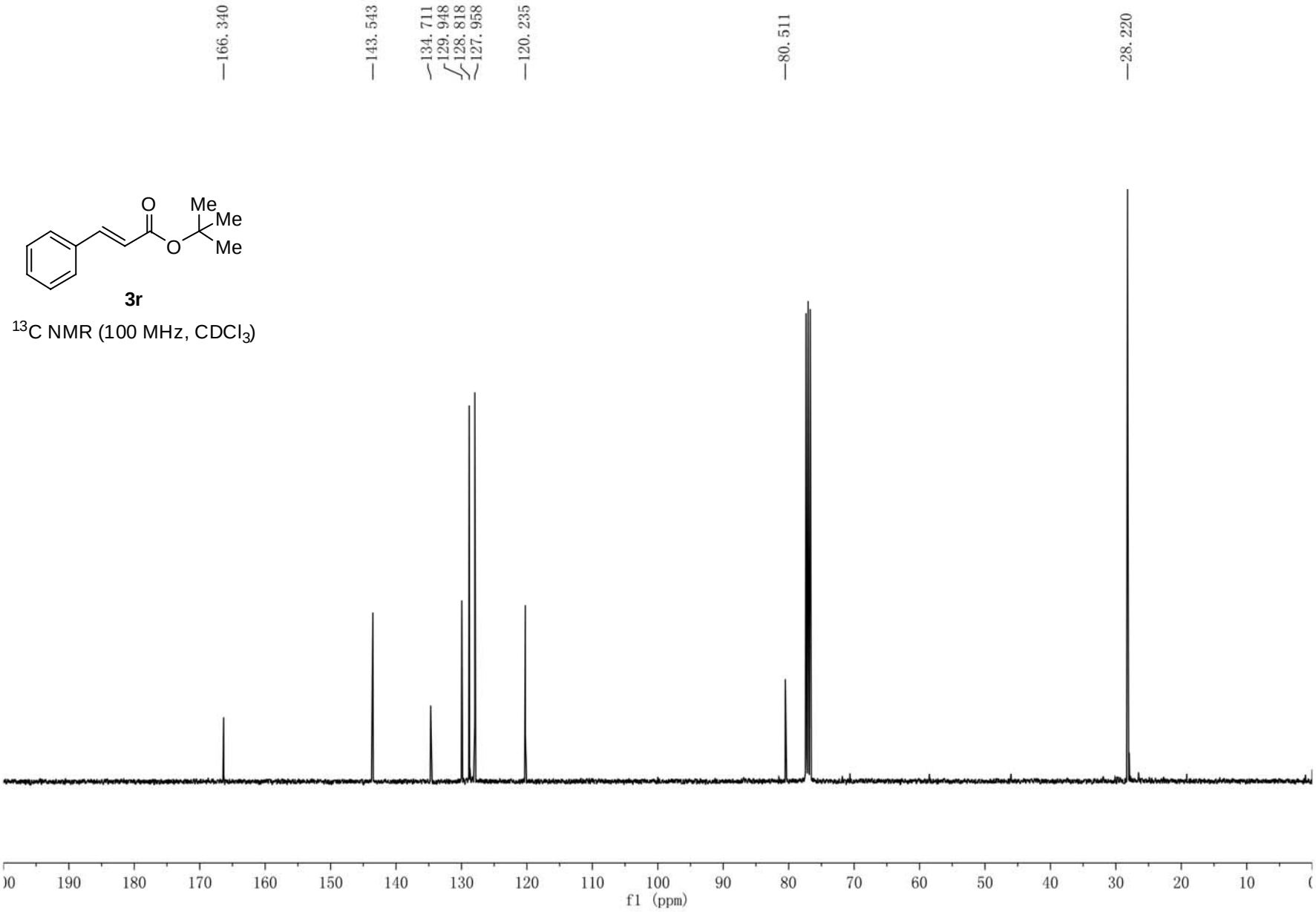
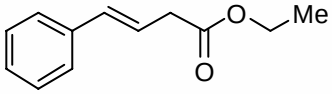


3r

^{13}C NMR (100 MHz, $CDCl_3$)



4

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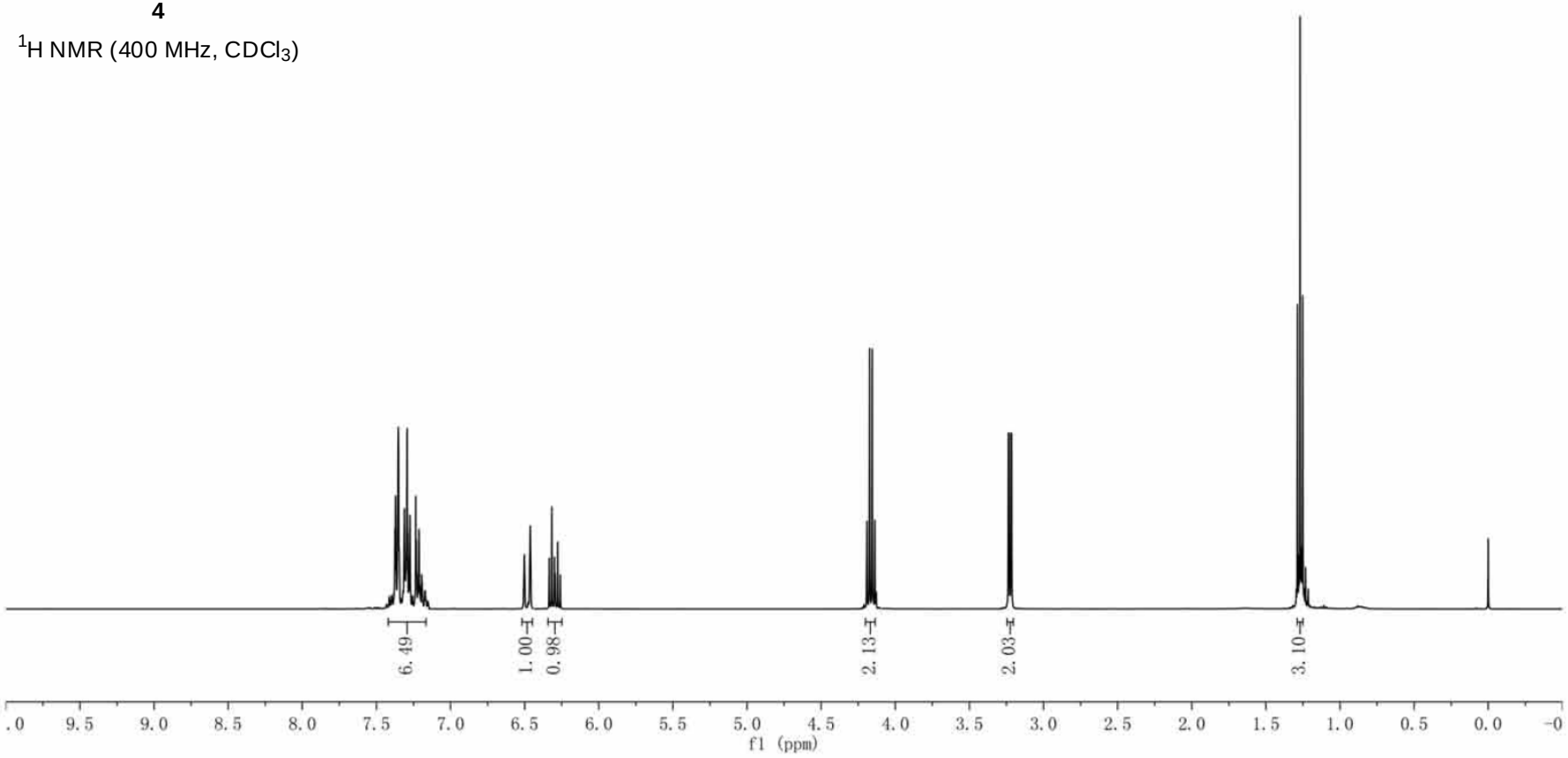

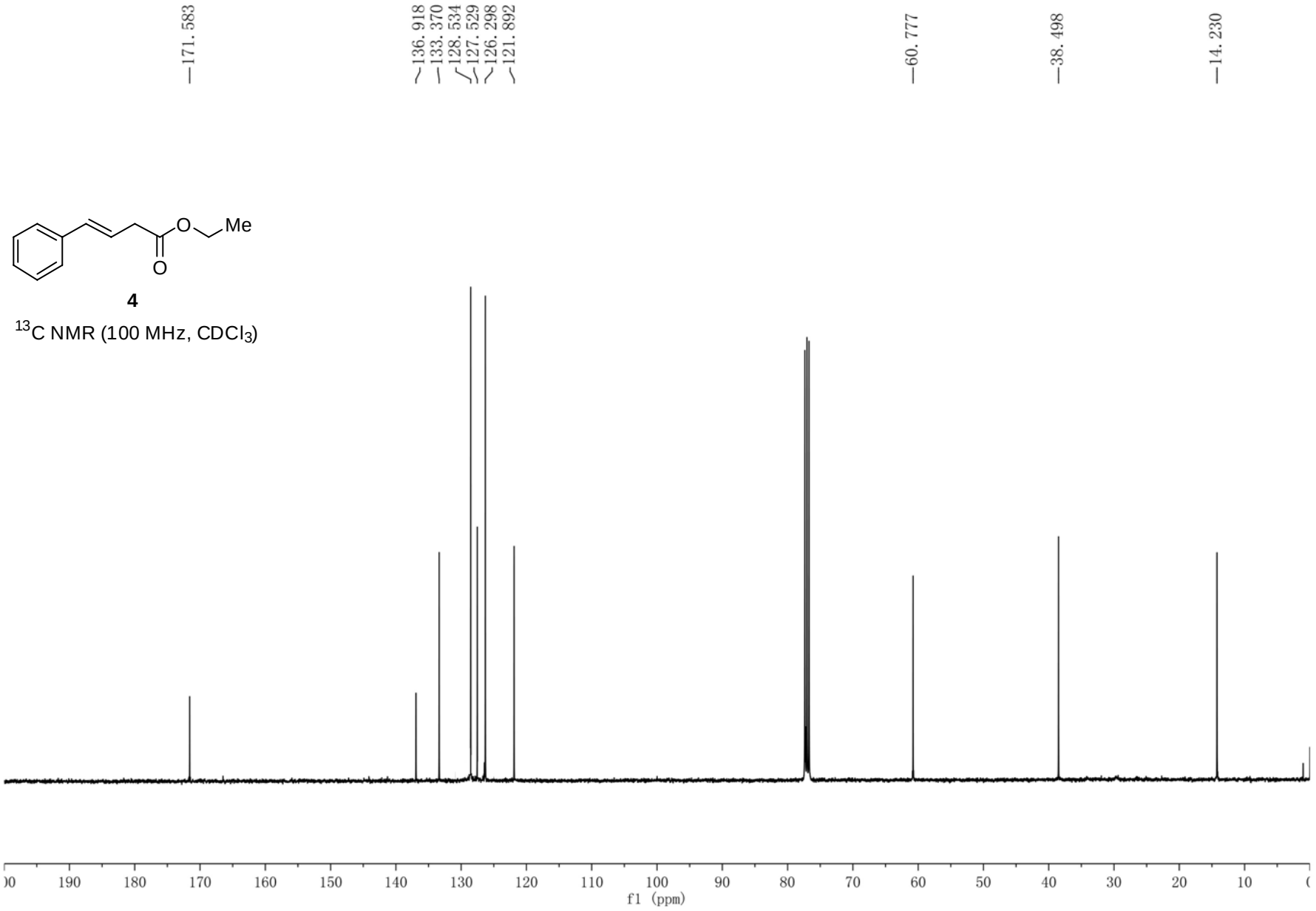

4

^{13}C NMR (100 MHz, $CDCl_3$)