Nucleophilic addition of tertiary propargylic amines to arynes followed by a [2,3]-sigmatropic rearrangement

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Supporting information

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General information

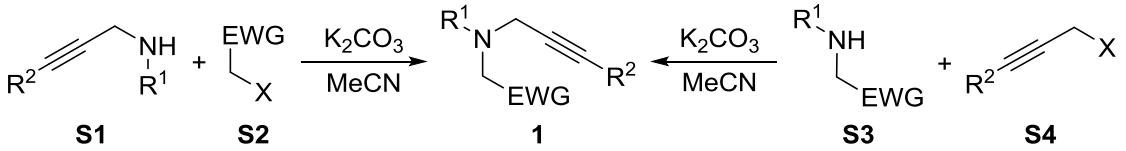
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump, using a Daicel Chiralpak column (OJ, AD) with isopropanol/hexane as mobile phase, and the UV detection was monitored at 254 nm. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\ ℃}$ (c = g/100 mL, solvent). Melting points are uncorrected.

2-(Trimethylsilyl)aryl triflates **2d-f**,[1] compounds **6**[2] and **S1b**[3] were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

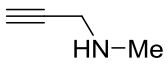
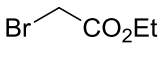
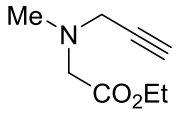
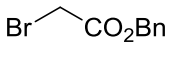
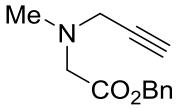
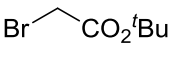
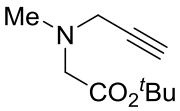
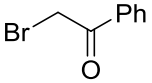
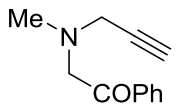
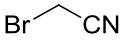
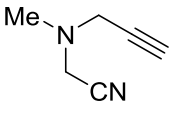
Abbreviations: Bn = benzyl, DMF = *N*,*N*-dimethylformamide, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMS = trimethylsilyl.

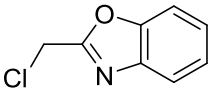
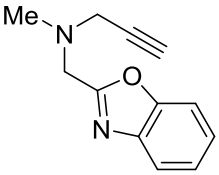
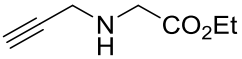
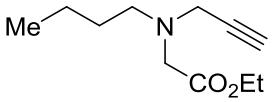
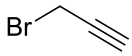
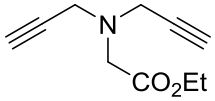
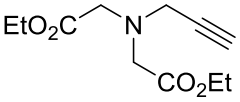
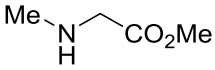
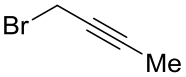
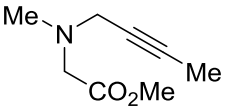
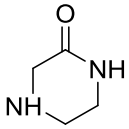
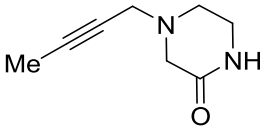
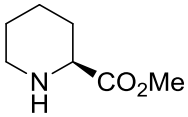
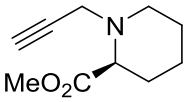
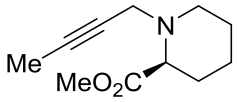
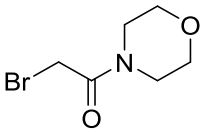
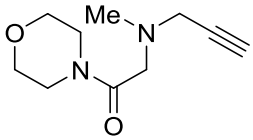
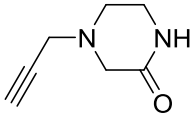
Preparation of tertiary propargylic amines

(1) Method A

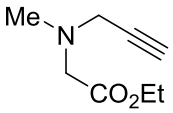


S1 **S2** **1** **S3** **S4**

Entry	Amine	Alkyl halide	Temp. (°C)	Time (h)	**1**
1	 **S1a**	 **S2a**	25	4	 **1a**
2	**S1a**	 **S2b**	25	4	 **1b**
3	**S1a**	 **S2c**	25	4	 **1c**
4	**S1a**	 **S2d**	25	4	 **1d**
5	**S1a**	 **S2e**	25	4	 **1e**

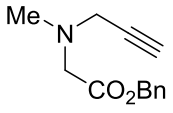
6	**S1a**	 **S2f**	25	4	 **1f**
7	 **S1b**	$Me(CH_2)_3Br$ **S2g**	80	16	 **1g**
8	**S1b**	 **S2h**	25	4	 **1h**
9	**S1b**	**S2a**	25	4	 **1i**
10	 **S3a**	 **S4a**	25	4	 **1s**
11	 **S3b**	**S4a**	50	10	 **1u**
12	 **S3c**	**S2h**	25	4	 **1v**
13	**S3c**	**S4a**	25	4	 **1w**
14	**S1a**	 **S2i**	25	4	 **1x**
15	**S3b**	**S2h**	25	4	 **1y**

To a mixture of amine **S1** (or **S3**, 5.0 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) in acetonitrile (10 mL) was added alkyl halide **S2** (or **S4**, 5.0 mmol). The mixture was stirred at 25-80 °C for 4-16 h (as specified in the above table), filtered, and concentrated. The residue was purified by silica gel chromatography (petroleum/ethyl acetate = 10:1 to 5:1) to give amine **1**.



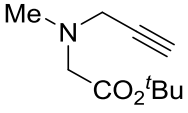
1a

Ethyl *N*-methyl-*N*-(prop-2-yn-1-yl)glycinate (**1a**). Pale yellow oil (712 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 2H), 3.51 (s, 2H), 3.32 (s, 2H), 2.43 (s, 3H), 2.27 (t, J = 2.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 78.0, 73.8, 60.8, 56.6, 45.6, 42.0, 14.3; HRMS (ESI) calcd for $C_8H_{14}NO_2^+$ $(M+H)^+$ 156.1019, found 156.1017.



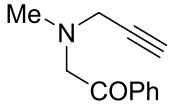
1b

Benzyl *N*-methyl-*N*-(prop-2-yn-1-yl)glycinate (**1b)**. Pale yellow oil (542 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 5.17 (s, 2H), 3.51 (d, J = 2.4 Hz, 2H), 3.38 (s, 2H), 2.43 (s, 3H), 2.25 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 135.7, 128.7, 128.5, 78.0, 73.9, 66.6, 56.5, 45.6, 42.0; HRMS (ESI) calcd for $C_{13}H_{16}NO_2^+$ $(M+H)^+$ 218.1176, found 218.1171.



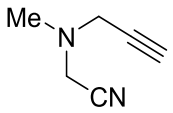
1c

tert-Butyl *N*-methyl-*N*-(prop-2-yn-1-yl)glycinate (**1c**). Pale yellow oil (642 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (d, J = 2.4 Hz, 2H), 3.22 (s, 2H), 2.42 (s, 3H), 2.25 (t, J = 2.4 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 81.3, 78.3, 73.6, 57.2, 45.6, 41.9, 28.2; HRMS (ESI) calcd for $C_{10}H_{18}NO_2^+$ $(M+H)^+$ 184.1332, found 184.1331.



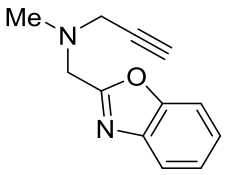
1d

2-(Methyl(prop-2-yn-1-yl)amino)-1-phenylethan-1-one (**1d)**. Yellow oil (801 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.97 (m, 2H), 7.61-7.55 (m, 1H), 7.50-7.44 (m, 2H), 3.97 (s, 2H), 3.57 (d, J = 2.4 Hz, 2H), 2.47 (s, 3H), 2.29 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 136.0, 133.5, 128.8, 128.2, 78.1, 74.1, 61.3, 46.0, 42.4; HRMS (ESI) calcd for $C_{12}H_{14}NO^+$ $(M+H)^+$ 188.1070, found 188.1067.



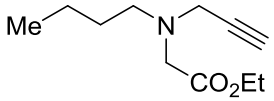
1e

2-(Methyl(prop-2-yn-1-yl)amino)acetonitrile (**1e**). Pale yellow oil (303 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 2H), 3.36 (d, J = 2.4 Hz, 2H), 2.45 (s, 3H), 2.34 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.9, 77.7, 74.4, 45.1, 43.8, 41.7; HRMS (ESI) calcd for $C_6H_9N_2^+$ $(M+H)^+$ 109.0760, found 109.0758.



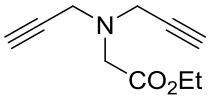
1f

N-(Benzo[*d*]oxazol-2-ylmethyl)-*N*-methylprop-2-yn-1-amine (**1f**). Pale yellow oil (670 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.70 (m, 1H), 7.56-7.51 (m, 1H), 7.37-7.31 (m, 2H), 3.97 (s, 2H), 3.54 (d, J = 2.4 Hz, 2H), 2.49 (s, 3H), 2.31 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 151.0, 141.0, 125.2, 124.5, 120.2, 110.8, 77.7, 74.2, 52.7, 45.8, 42.0; HRMS (ESI) calcd for $C_{12}H_{13}N_2O^+$ $(M+H)^+$ 201.1022, found 201.1022.



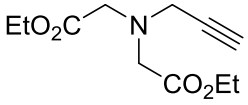
1g

Ethyl *N*-butyl-*N*-(prop-2-yn-1-yl)glycinate (**1g**). Pale yellow oil (594 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, J = 7.2 Hz, 2H), 3.56 (s, 2H), 3.37 (s, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.22 (s, 1H), 1.52-1.42 (m, 2H), 1.39-1.30 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 78.4, 73.4, 60.7, 54.9, 53.6, 42.7, 29.8, 20.6, 14.3, 14.1; HRMS (ESI) calcd for $C_{11}H_{20}NO_2^+$ $(M+H)^+$ 198.1489, found 198.1486.



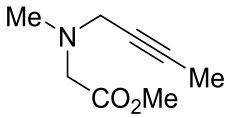
1h

Ethyl di(prop-2-yn-1-yl)glycinate (**1h**). Pale yellow oil (701 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 2H), 3.57 (d, J = 2.4 Hz, 4H), 3.46 (s, 2H), 2.28 (t, J = 2.4 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 78.3, 73.8, 60.9, 53.6, 42.7, 14.3; HRMS (ESI) calcd for $C_{10}H_{14}NO_2^+$ $(M+H)^+$ 180.1019, found 180.1017.



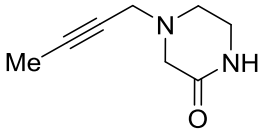
1i

Diethyl 2,2'-(prop-2-yn-1-ylazanediyl)diacetate (**1i**). Pale yellow oil (980 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, J = 7.2 Hz, 4H), 3.68 (d, J = 2.4 Hz, 2H), 3.55 (s, 4H), 2.28 (t, J = 2.4 Hz, 1H), 1.28 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 78.3, 73.9, 60.9, 54.4, 43.4, 14.3; HRMS (ESI) calcd for $C_{11}H_{18}NO_4^+$ $(M+H)^+$ 228.1230, found 228.1227.



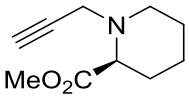
1s

Methyl *N*-(but-2-yn-1-yl)-*N*-methylglycinate (**1s**). Pale yellow oil (151 mg, 20% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.41 (q, J = 2.4 Hz, 2H), 3.33 (s, 2H), 2.40 (s, 3H), 1.84 (t, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 81.5, 73.3, 56.7, 51.9, 46.2, 42.1, 3.6; HRMS (ESI) calcd for $C_8H_{14}NO_2^+$ $(M+H)^+$ 156.1019, found 156.1021.



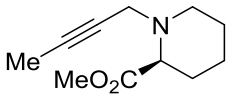
1u

4-(But-2-yn-1-yl)piperazin-2-one (**1u**). Pale yellow solid (612 mg, 80% yield). m.p. 85-86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (br, s, 1H), 3.41-3.37 (m, 2H), 3.35-3.27 (m, 2H), 3.25 (s, 2H), 2.73 (t, J = 5.6 Hz, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 82.1, 72.6, 55.3, 48.0, 46.3, 41.3, 3.5; HRMS (ESI) calcd for $C_8H_{13}N_2O^+$ $(M+H)^+$ 153.1022, found 153.1025.



1v

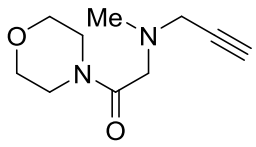
Methyl (*S*)-1-(prop-2-yn-1-yl)piperidine-2-carboxylate (**1v**). Pale yellow oil (791 mg, 88% yield); $[\alpha]_D^{20}$ = -134.1 (c = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.55 (dd, J = 17.2, 2.4 Hz, 1H), 3.39 (dd, J = 17.2, 2.4 Hz, 1H), 3.27 (dd, J = 10.4, 3.2 Hz, 1H), 2.93-2.86 (m, 1H), 2.58-2.50 (m, 1H), 2.26 (t, J = 2.4 Hz, 1H), 1.95-1.88 (m, 1H), 1.77-1.62 (m, 4H), 1.39-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 77.9, 74.0, 63.1, 52.1, 51.3, 44.6, 30.1, 25.3, 23.1; HRMS (ESI) calcd for $C_{10}H_{16}NO_2^+$ $(M+H)^+$ 182.1176, found 182.1177.



1w

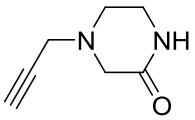
Methyl (*S*)-1-(but-2-yn-1-yl)piperidine-2-carboxylate (**1w**). Pale yellow oil (803 mg, 82% yield). $[\alpha]_D^{20}$ = -131.6 (c = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.44-3.28 (m, 2H), 3.24 (dd, J = 10.0, 3.2 Hz, 1H), 2.97-2.90 (m, 1H), 2.52-2.43 (m, 1H), 1.93-1.86 (m, 1H), 1.83 (t, J = 2.4 Hz, 3H), 1.75-1.62 (m, 4H), 1.38-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 81.6, 73.2,

63.4, 52.0, 51.3, 45.1, 30.0, 25.3, 23.0, 3.7; HRMS (ESI) calcd for $C_{11}H_{18}NO_2^+$ $(M+H)^+$ 196.1332, found 196.1337.



1x

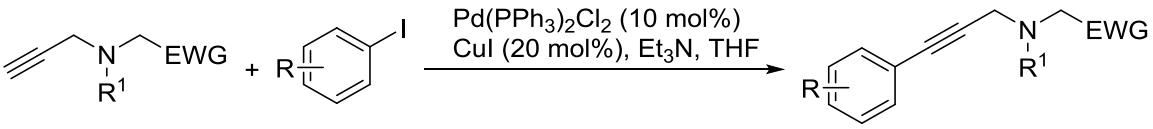
2-(Methyl(prop-2-yn-1-yl)amino)-1-morpholinoethan-1-one (**1x**). Pale yellow oil (731 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68-3.65 (m, 4H), 3.62-3.59 (m, 4H), 3.40 (s, 2H), 3.29 (s, 2H), 2.37 (s, 3H), 2.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 78.2, 73.8, 67.0, 58.0, 46.1, 45.9, 42.2, 42.1; HRMS (ESI) calcd for $C_{10}H_{17}N_2O_2^+$ $(M+H)^+$ 197.1285, found 197.1280.



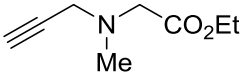
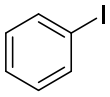
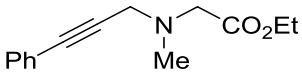
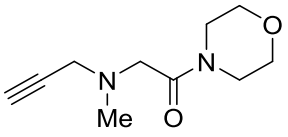
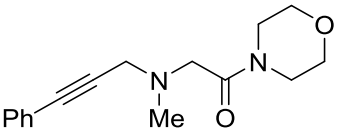
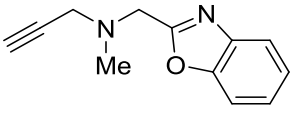
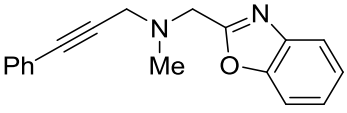
1y

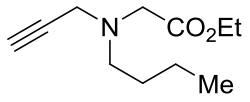
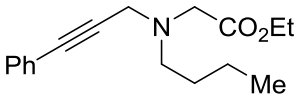
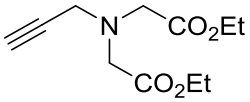
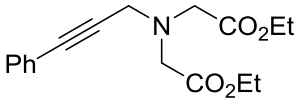
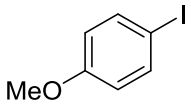
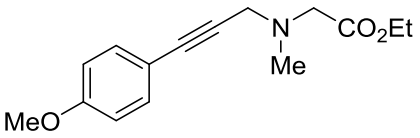
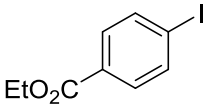
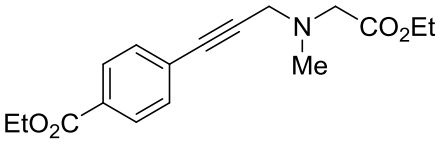
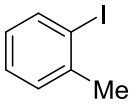
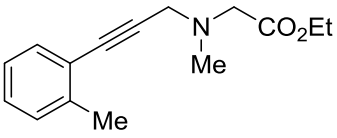
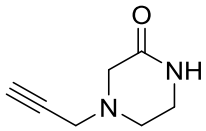
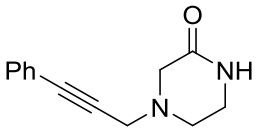
4-(Prop-2-yn-1-yl)piperazin-2-one (**1y**). White solid (472 mg, 69% yield); m. p. 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (br, s, 1H), 3.43-3.38 (m, 4H), 3.28 (s, 2H), 2.77 (t, J = 5.6 Hz, 2H), 2.31 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 74.4, 55.2, 47.8, 45.8, 41.4; HRMS (ESI) calcd for $C_7H_{11}N_2O^+$ $(M+H)^+$ 139.0866, found 139.0863.

(2) Method B

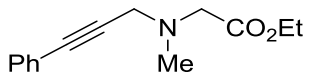


terminal propargylic amine **S5** internal propargylic amine

Entry	Terminal propargylic amine	Aryl iodide	Internal propargylic amine
1	 **1a**	 **S5a**	 **1j**
2	 **1x**	**S5a**	 **1k**
3	 **1f**	**S5a**	 **1l**

4	 **1g**	**S5a**	 **1m**
5	 **1i**	**S5a**	 **1o**
6	**1a**	 **S5b**	 **1p**
7	**1a**	 **S5c**	 **1q**
8	**1a**	 **S5d**	 **1r**
9	 **1y**	**S5a**	 **1t**

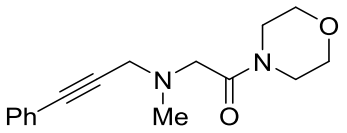
To a solution of CuI (38.1 mg, 0.20 mmol), Pd $(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol), and aryl iodide **S5** (1.1 mmol) in THF/Et_3N (1:1, 5.0 mL) under nitrogen was added a terminal propargylic amine (1.0 mmol). The mixture was stirred at 50 ^oC for 5 h, and then cooled to room temperature. Saturated aqueous NH_4Cl solution (10 mL) was added to the mixture, and then extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum/ethyl acetate = 10:1 to 5:1) to give the corresponding internal propargylic amine.



1j

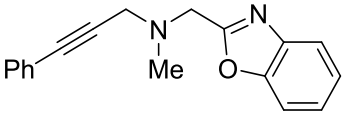
Ethyl *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)glycinate (**1j**). Pale yellow oil (191 mg, 82% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.32-7.28 (m, 3H), 4.21 (q, J = 7.2 Hz, 2H), 3.71 (s, 2H), 3.39 (s, 2H), 2.49 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7,

131.8, 128.4, 128.3, 123.1, 85.9, 83.8, 60.8, 56.9, 46.6, 42.2, 14.3; HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ $(M+H)^+$ 232.1332, found 232.1330.



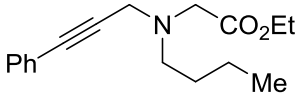
1k

2-(Methyl(3-phenylprop-2-yn-1-yl)amino)-1-morpholinoethan-1-one (**1k**). Yellow oil (202 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.33-7.29 (m, 3H), 3.69-3.59 (m, 10H), 3.36 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 131.8, 128.4, 123.0, 86.0, 84.0, 67.1, 67.0, 58.3, 46.9, 46.2, 42.3; HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2^+$ $(M+H)^+$ 273.1598, found 273.1593.



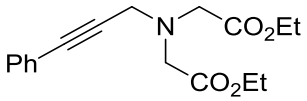
1l

N-(Benzo[d]oxazol-2-ylmethyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (**1l**). Yellow oil (241 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.69 (m, 1H), 7.56-7.50 (m, 1H), 7.43-7.38 (m, 2H), 7.35-7.27 (m, 5H), 4.03 (s, 2H), 3.76 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 151.1, 141.1, 131.8, 128.3, 125.2, 124.4, 122.9, 120.2, 110.8, 86.3, 83.4, 53.0, 46.8, 42.2; HRMS (ESI) calcd for $C_{18}H_{17}N_2O^+$ $(M+H)^+$ 277.1335, found 277.1337.



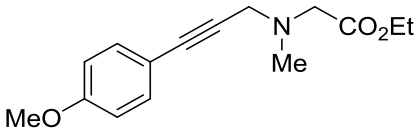
1m

Ethyl *N*-butyl-*N*-(3-phenylprop-2-yn-1-yl)glycinate (**1m**). Yellow oil (230 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.32-7.29 (m, 3H), 4.20 (q, J = 7.2 Hz, 2H), 3.78 (s, 2H), 3.45 (s, 2H), 2.65 (t, J = 7.6 Hz, 2H), 1.58-1.48 (m, 2H), 1.42-1.31 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 131.8, 128.4, 128.2, 123.2, 85.7, 84.1, 60.8, 55.2, 53.8, 43.7, 29.8, 20.6, 14.4, 14.1; HRMS (ESI) calcd for $C_{17}H_{24}NO_2^+$ $(M+H)^+$ 274.1802, found 274.1806



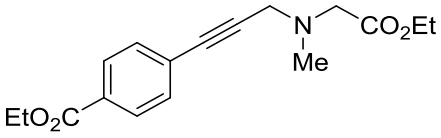
1o

Diethyl 2,2'-((3-phenylprop-2-yn-1-yl)azanediyl)diacetate (**1o**). Yellow oil (251 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.32-7.28 (m, 3H), 4.19 (q, J = 7.2 Hz, 4H), 3.89 (s, 2H), 3.63 (s, 4H), 1.28 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 131.9, 128.4, 122.9, 85.9, 83.9, 60.9, 54.6, 44.4, 14.3; HRMS (ESI) calcd for $C_{17}H_{22}NO_4^+$ $(M+H)^+$ 304.1543, found 304.1548.



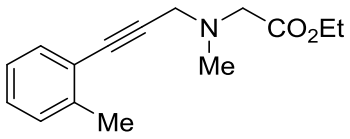
1p

Ethyl *N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-*N*-methylglycinate (**1p**). Yellow soild (244 mg, 92% yield). m.p. 45-46 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.69 (s, 2H), 3.38 (s, 2H), 2.48 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.6, 133.2, 115.2, 114.0, 85.8, 82.2, 60.8, 57.0, 55.4, 46.7, 42.2, 14.4; HRMS (ESI) calcd for $C_{15}H_{20}NO_3^+$ $(M+H)^+$ 262.1438, found 262.1441.



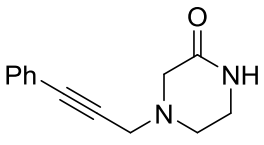
1q

Ethyl 4-(3-((2-ethoxy-2-oxoethyl)(methyl)amino)prop-1-yn-1-yl)benzoate (**1q**). Yellow oil (272 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.74 (s, 2H), 3.39 (s, 2H), 2.50 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 166.1, 131.7, 130.0, 129.5, 127.6, 87.0, 85.4, 61.3, 60.9, 56.9, 46.6, 42.3, 14.4; HRMS (ESI) calcd for $C_{17}H_{22}NO_4^+$ $(M+H)^+$ 304.1543, found 304.1549.



1r

Ethyl *N*-methyl-*N*-(3-(*o*-tolyl)prop-2-yn-1-yl)glycinate (**1r**). Yellow oil (203 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 7.24-7.17 (m, 2H), 7.16-7.10 (m, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.77 (s, 2H), 3.41 (s, 2H), 2.51 (s, 3H), 2.44 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 140.2, 132.2, 129.5, 128.3, 125.6, 122.9, 87.4, 85.0, 60.9, 56.9, 46.7, 42.3, 21.0, 14.4; HRMS (ESI) calcd for $C_{15}H_{20}NO_2^+$ $(M+H)^+$ 246.1489, found 246.1490.

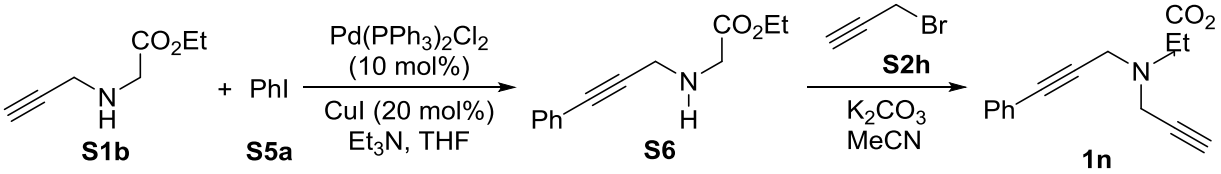


1t

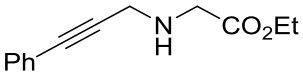
4-(3-Phenylprop-2-yn-1-yl)piperazin-2-one (**1t**). White solid (181 mg, 84% yield). m.p. 123-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.33-7.29 (m, 3H), 6.75 (br, s, 1H), 3.64 (s, 2H), 3.45-3.41 (m, 2H), 3.36 (s, 2H), 2.84 (t, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7,

131.9, 128.5, 128.4, 122.6, 86.5, 82.6, 55.4, 48.0, 46.7, 41.3; HRMS (ESI) calcd for $C_{13}H_{15}N_2O^+$ $(M+H)^+$ 215.1179, found 215.1181.

(3) Method C

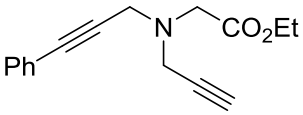


Amines **S6** and **1n** were prepared according to methods B and A, respectively.



S6

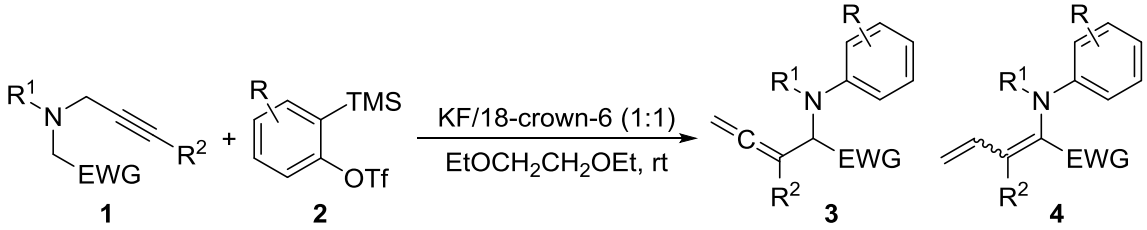
Ethyl (3-phenylprop-2-yn-1-yl)glycinate (**S6**). Yellow oil (279 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.31-7.28 (m, 3H), 4.20 (q, J = 7.2 Hz, 2H), 3.72 (s, 2H), 3.57 (s, 2H), 1.89 (br, s, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 131.8, 128.4, 128.3, 123.0, 86.8, 84.2, 61.0, 49.5, 38.5, 14.3; HRMS (ESI) calcd for $C_{13}H_{16}NO_2^+$ $(M+H)^+$ 218.1176, found 218.1178.



1n

Ethyl *N*-(3-phenylprop-2-yn-1-yl)-*N*-(prop-2-yn-1-yl)glycinate (**1n**). Pale yellow oil (161 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.32-7.29 (m, 3H), 4.21 (q, J = 7.2 Hz, 2H), 3.77 (s, 2H), 3.65 (d, J = 2.4 Hz, 2H), 3.53 (s, 2H), 2.29 (t, J = 2.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 131.9, 128.4, 123.0, 85.7, 84.0, 78.5, 73.9, 61.0, 53.8, 43.8, 43.0, 14.3; HRMS (ESI) calcd for $C_{16}H_{18}NO_2^+$ $(M+H)^+$ 256.1332, found 256.1334.

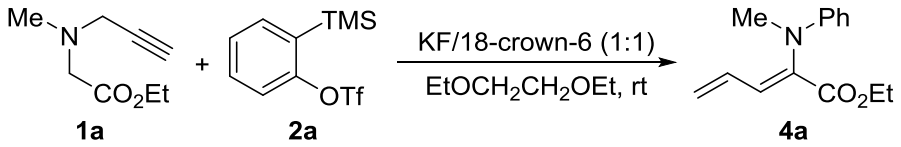
General procedure for the aryne-mediated [2,3]-sigmatropic rearrangement of tertiary propargylic amines



To a mixture of amine **1** (0.20 mmol), KF (23.2 mg, 0.40 mmol), and 18-crown-6 (106 mg, 0.40 mmol) in ethylene glycol diethyl ether (1.0 mL) was added 2-(trimethylsilyl)aryl triflate **2** (0.24 mmol). The mixture was stirred at room temperature for 6 h, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum/ethyl acetate = 40:1 to 2:1) to give allene **3** or conjugated diene **4**.

The two stereoisomers of diene **4e** are separable on silica gel chromatography, and the rest of conjugated diene products were obtained as a mixture of (*Z*)- and (*E*)-isomers. Except the (*E*)-isomer of conjugated diene **4e** (**4eE**),[4] the rest of conjugated diene products are unknown compounds and their *Z/E* ratios were determined by ^{1}H NMR spectroscopic analysis of their crude samples. The configuration of conjugated diene **4a** was assigned by 2D NOESY analysis and that of the rest of new conjugated diene products was assigned by analogy. The structure of allene **3c** was confirmed by single crystal X-ray analysis (CCDC 1534313, see below).

A gram-scale reaction

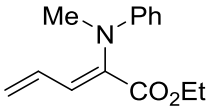


1a **2a** **4a**

To a mixture of amine **1a** (1.80 g, 11.6 mmol), KF (1.35 g, 23.2 mmol), and 18-crown-6 (6.13 g, 23.2 mmol) in ethylene glycol diethyl ether (50 mL) was added 2-(trimethylsilyl)phenyl triflate (**2a**) (4.15 g, 13.9 mmol) dropwise. The mixture was stirred at room temperature for 6 h, and concentrated under reduced pressure. The residue was filtered through a short silica gel column (5 cm), eluting with petroleum/ethyl acetate = 20:1(100 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum/ethyl acetate = 20:1) to give diene **4a** (1.55g, 58% yield).

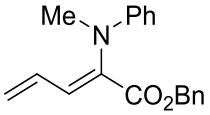
Analytical data for the products

(1) Table 2



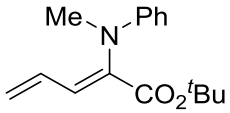
4a

Ethyl (*Z*)-2-(methyl(phenyl)amino)penta-2,4-dienoate (**4a**). Yellow oil (30.0 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 3H), 6.79-6.74 (m, 1H), 6.67-6.64 (m, 2H), 6.64-6.53 (m, 1H), 5.65 (d, J = 18.0 Hz, 1H), 5.44 (d, J = 11.2 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.12 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 148.4, 137.6, 136.1, 131.8, 129.2, 125.3, 118.1, 113.1, 61.0, 39.1, 14.3; HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ $(M+H)^+$ 232.1332, found 232.1336.



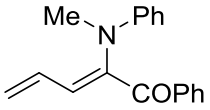
4b

Benzyl (*Z*)-2-(methyl(phenyl)amino)penta-2,4-dienoate (**4b**). Yellow oil (35.8 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.19 (m, 6H), 7.11-7.09 (m, 2H), 6.82-6.77 (m, 1H), 6.68-6.65 (m, 2H), 6.64-6.55 (m, 1H), 5.66 (d, J = 17.2 Hz, 1H), 5.46 (d, J = 10.0 Hz, 1H), 5.11 (s, 2H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 148.4, 138.3, 135.9, 131.7, 129.3, 128.5, 128.1, 127.9, 125.6, 118.2, 113.2, 66.8, 39.2; HRMS (ESI) calcd for $C_{19}H_{20}NO_2^+$ $(M+H)^+$ 294.1489, found 294.1490.



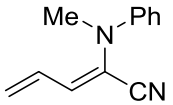
4c

tert-Butyl (*Z*)-2-(methyl(phenyl)amino)penta-2,4-dienoate (**4c**). Yellow oil (32.1 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 2H), 7.10-7.05 (m, 1H), 6.79-6.74 (m, 1H), 6.68-6.55 (m, 3H), 5.62 (d, J = 16.0 Hz, 1H), 5.41 (d, J = 11.2 Hz, 1H), 3.10 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 148.8, 137.8, 136.2, 131.9, 129.1, 124.5, 118.1, 113.3, 81.2, 39.3, 28.0; HRMS (ESI) calcd for $C_{16}H_{22}NO_2^+$ $(M+H)^+$ 260.1645, found 260.1648.



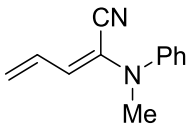
4d

(*Z*)-2-(Methyl(phenyl)amino)-1-phenylpenta-2,4-dien-1-one (**4d**). Yellow oil (31.6 mg, 60% yield); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.77-7.73 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.17-7.11 (m, 2H), 6.82-6.63 (m, 5H), 5.70 (d, J = 16.8 Hz, 1H), 5.50 (d, J = 10.0 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 195.7, 149.1, 144.4, 139.4, 138.0, 133.1, 133.0, 129.9, 129.7, 129.3, 125.5, 119.0, 114.4, 40.4; HRMS (ESI) calcd for $C_{18}H_{18}NO^+$ $(M+H)^+$ 264.1383, found 264.1385.



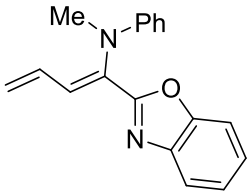
4eZ

(*Z*)-2-(Methyl(phenyl)amino)penta-2,4-dienenitrile (**4eZ**) was separated from the corresponding (*E*)-isomer (**4eE**) by silica gel chromatography. Yellow oil (13.3 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 6.95-6.90 (m, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.63-6.48 (m, 2H), 5.59 (d, J = 16.8 Hz, 1H), 5.43 (d, J = 9.2 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 139.0, 130.2, 129.5, 125.3, 120.6, 118.7, 116.8, 115.3, 39.1; HRMS (ESI) calcd for $C_{12}H_{13}N_2^+$ $(M+H)^+$ 185.1073, found 185.1075.



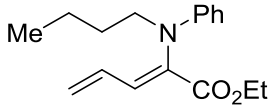
4eE

(*E*)-2-(Methyl(phenyl)amino)penta-2,4-dienenitrile (**4eE**).[4] Yellow oil (5.9 mg, 16% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.09-7.02 (m, 3H), 6.73-6.62 (m, 1H), 6.06 (d, J = 11.2 Hz, 1H), 5.24 (d, J = 16.8 Hz, 1H), 5.14 (d, J = 10.0 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 132.6, 129.5, 124.7, 123.3, 123.0, 122.1, 118.6, 114.5, 40.4.



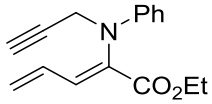
4f

(*Z*)-*N*-(1-(Benzo[*d*]oxazol-2-yl)buta-1,3-dien-1-yl)-*N*-methylaniline (**4f**). Yellow oil (27.1 mg, 49% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 1H), 7.47-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.18 (m, 2H), 6.79-6.73 (m, 3H), 6.69-6.58 (m, 1H), 5.67 (d, J = 16.8 Hz, 1H), 5.42 (d, J = 10.0 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 150.8, 148.0, 142.1, 134.9, 132.7, 131.8, 129.3, 125.4, 124.6, 124.2, 120.4, 118.1, 113.1, 110.6, 39.0; HRMS (ESI) calcd for $C_{18}H_{17}N_2O^+$ $(M+H)^+$ 277.1335, found 277.1337.



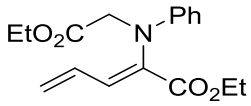
4g

Ethyl (*Z*)-2-(butyl(phenyl)amino)penta-2,4-dienoate (**4g**). Yellow oil (38.3 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 1H), 7.21-7.15 (m, 2H), 6.75-6.70 (m, 1H), 6.67-6.63 (m, 2H), 6.61-6.50 (m, 1H), 5.64 (d, J = 17.2 Hz, 1H), 5.42 (d, J = 10.0 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 8.0 Hz, 2H), 1.68-1.59 (m, 2H), 1.43-1.30 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 148.0, 138.6, 134.7, 132.1, 129.2, 125.3, 117.8 , 113.3, 61.1, 51.5, 30.1, 20.5, 14.3, 14.1; HRMS (ESI) calcd for $C_{17}H_{24}NO_2^+$ $(M+H)^+$ 274.1802, found 274.1807.



4h

Ethyl (*Z*)-2-(phenyl(prop-2-yn-1-yl)amino)penta-2,4-dienoate (**4h**) was obtained as a 95:5 mixture of *Z*/*E* isomers. Yellow oil (31.6 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 1H), 7.20-7.13 (m, 2H), 6.77-6.68 (m, 3H), 6.66-6.54 (m, 1H), 5.60 (d, J = 16.8 Hz, 1H), 5.39 (d, J = 10.0 Hz, 1H), 4.14-4.05 (m, 4H), 2.21 (s, 1H), 1.11 (t, J = 7.2 Hz, 3H); Partial ^{1}H NMR (400 MHz, $CDCl_3$) for the minor (*E*)-isomer: δ 6.92-6.87 (m, 2H), 6.37-6.33 (m, 1H), 5.31 (d, J = 16.8 Hz, 1H), 5.18 (d, J = 10.4 Hz, 1H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 146.9, 139.5, 134.2, 132.0, 129.2, 126.1, 118.9, 113.8, 79.9, 72.8, 61.2, 41.2, 14.3; HRMS (ESI) calcd for $C_{16}H_{18}NO_2^+$ $(M+H)^+$ 256.1332, found 256.1335.

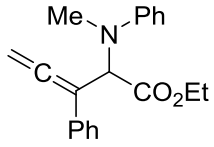


4i

Ethyl (*Z*)-2-((2-ethoxy-2-oxoethyl)(phenyl)amino)penta-2,4-dienoate (**4i**) was obtained as a 96:4 mixture of *Z*/*E* isomers. Yellow oil (26.1 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 1H), 7.15-7.09 (m, 2H), 6.87-6.76 (m, 1H), 6.74-6.69 (m, 1H), 6.56-6.52 (m, 2H), 5.56 (d, J =

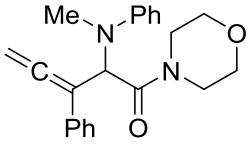
17.2 Hz, 1H), 5.36 (d, *J* = 10.0 Hz, 1H), 4.18-4.06 (m, 6H), 1.25-1.11(m, 6H); Partial ^{1}H NMR (400 MHz, $CDCl_3$) for the minor (*E*)-isomer: δ 6.25 (d, *J* = 11.2 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.24 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 165.7, 147.3, 139.3, 133.6, 132.4, 129.2, 125.9, 118.9, 113.3, 61.3, 61.2, 53.6, 14.3; HRMS (ESI) calcd for $C_{17}H_{22}NO_4^+$ $(M+H)^+$ 304.1543, found 304.1548.

(2) Table 3



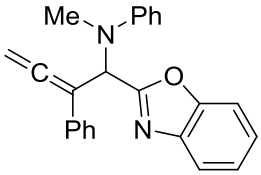
3b

Ethyl 2-(methyl(phenyl)amino)-3-phenylpenta-3,4-dienoate (**3b**). Pale yellow solid (43.0 mg, 70% yield); m.p. 80-81 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 7H), 6.85-6.78 (m, 3H), 5.50-5.48 (m, 1H), 5.34-5.25 (m, 2H), 4.26-4.15 (m, 2H), 2.97 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 171.5, 149.2, 134.0, 129.5, 128.7, 127.5, 126.1, 117.8, 113.0, 103.0, 81.0, 62.6, 61.1, 33.4, 14.5; HRMS (ESI) calcd for $C_{20}H_{22}NO_2^+$ $(M+H)^+$ 308.1645, found 308.1648.



3c

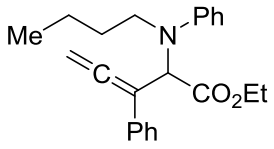
2-(Methyl(phenyl)amino)-1-morpholino-3-phenylpenta-3,4-dien-1-one (**3c**). Pale yellow solid (43.2 mg, 62% yield); m.p. 178-179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (m, 7H), 6.80-6.73 (m, 3H), 5.52 (s, 1H), 5.35-5.25 (m, 2H), 3.77-3.60 (m, 6H), 3.53-3.46 (m, 1H), 3.44-3.36 (m, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 169.0, 149.1, 133.9, 129.5, 128.9, 127.7, 126.0, 117.6, 112.6, 102.6, 81.2, 67.3, 66.7, 60.3, 46.1, 42.3, 34.4; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_2^+$ $(M+H)^+$ 349.1911, found 349.1914.



3d

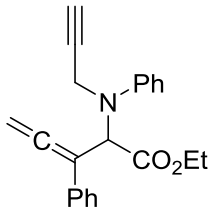
N-(1-(Benzo[*d*]oxazol-2-yl)-2-phenylbuta-2,3-dien-1-yl)-*N*-methylaniline (**3d**). Pale yellow solid (33.1 mg, 47% yield); m.p. 115-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 1H), 7.52-7.48 (m, 1H), 7.39-7.19 (m, 9H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.80-6.75 (m, 1H), 6.33 (s, 1H), 5.08 (dd, *J* = 12.8, 3.2 Hz, 1H), 4.99 (dd, *J* = 12.8, 3.2 Hz, 1H), 3.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 164.9, 150.8, 148.8, 140.9, 133.8, 129.5, 128.8, 127.6, 126.1, 125.1, 124.4, 120.4, 117.9, 113.1, 110.8, 104.9, 81.1, 58.4, 33.6; HRMS (ESI) calcd for $C_{24}H_{21}N_2O^+$ $(M+H)^+$ 353.1648, found

353.1653.



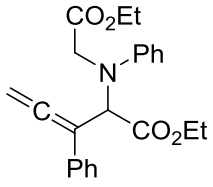
3e

Ethyl 2-(butyl(phenyl)amino)-3-phenylpenta-3,4-dienoate (**3e**). Pale yellow solid (52.4 mg, 75% yield); m.p. 66-67 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.30-7.25 (m, 4H), 7.23-7.17 (m, 1H), 6.83-6.76 (m, 3H), 5.44 (s, 1H), 5.29-5.27 (m, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.52-3.42 (m, 1H), 3.38-3.29 (m, 1H), 1.62-1.50 (m, 1H), 1.29-1.16 (m, 6H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 171.5, 148.4, 134.3, 129.5, 128.7, 127.5, 126.1, 117.8, 113.5, 103.0, 80.9, 62.9, 61.1, 47.3, 30.5, 20.4, 14.5, 13.9; HRMS (ESI) calcd for $C_{23}H_{28}NO_2^+$ $(M+H)^+$ 350.2115, found 350.2118.



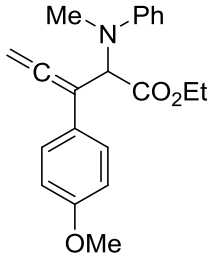
3f

Ethyl 3-phenyl-2-(phenyl(prop-2-yn-1-yl)amino)penta-3,4-dienoate (**3f**). Pale yellow solid (42.4 mg, 64% yield); m.p. 125-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 6H), 7.23-7.17 (m, 1H), 6.98-6.94 (m, 2H), 6.89-6.84 (m, 1H), 5.47 (s, 1H), 5.38-5.27 (m, 2H), 4.35 (d, J = 18.4 Hz, 1H), 4.21 (q, J = 7.2, 2H), 4.12 (d, J = 18.4 Hz, 1H), 1.95 (s, 1H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 171.2, 147.7, 133.9, 129.5, 128.6, 127.5, 126.3, 118.9, 113.9, 103.0, 81.2, 81.0, 71.4, 62.4, 61.4, 37.0, 14.5; HRMS (ESI) calcd for $C_{22}H_{22}NO_2^+$ $(M+H)^+$ 332.1645, found 332.1652.



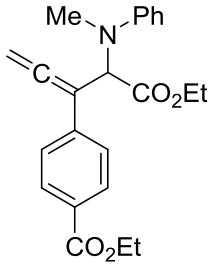
3g

Ethyl 2-((2-ethoxy-2-oxoethyl)(phenyl)amino)-3-phenylpenta-3,4-dienoate (**3g**). Pale yellow solid (47.8 mg, 63% yield); m.p. 90-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.31-7.24 (m, 4H), 7.22-7.16 (m, 1H), 6.88-6.83 (m, 1H), 6.81-6.77 (m, 2H), 5.52 (s, 1H), 5.34-5.25 (m, 2H), 4.40 (d, J = 18.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 4.12 (d, J = 18.4 Hz, 1H), 3.97-3.87 (m, 1H), 3.80-3.71 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 171.4, 171.0, 148.6, 133.8, 129.5, 128.5, 127.5, 126.4, 119.0, 113.8, 103.0, 81.2, 62.1, 61.4, 60.8, 50.4, 14.5, 14.0; HRMS (ESI) calcd for $C_{23}H_{26}NO_4^+$ $(M+H)^+$ 380.1856, found 380.1862.



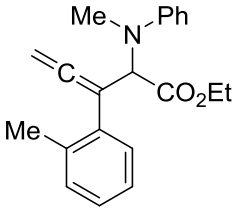
3h

Ethyl 3-(4-methoxyphenyl)-2-(methyl(phenyl)amino)penta-3,4-dienoate (**3h**). Pale yellow oil (50.6 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4H), 6.85-6.78 (m, 5H), 5.45 (s, 1H), 5.30-5.21 (m, 2H), 4.20-4.17 (m, 2H), 3.76 (s, 3H), 2.96 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 171.5, 159.1, 149.2, 129.5, 127.3, 126.1, 117.8, 114.2, 112.9, 102.5, 80.9, 62.8, 61.1, 55.4, 33.3, 14.5; HRMS (ESI) calcd for $C_{21}H_{24}NO_3^+$ $(M+H)^+$ 338.1751, found 338.1755.



3i

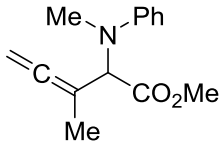
Ethyl 4-(5-ethoxy-4-(methyl(phenyl)amino)-5-oxopenta-1,2-dien-3-yl)benzoate (**3i**). Pale yellow oil (54.6 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.32-7.26 (m, 2H), 6.84-6.80 (m, 3H), 5.50 (s, 1H), 5.39-5.31 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.25-4.15 (m, 2H), 2.94 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.2, 166.4, 149.0, 138.7, 129.9, 129.5, 129.3, 125.9, 118.0, 113.0, 102.7, 81.5, 62.4, 61.2, 61.0, 33.4, 14.5, 14.4; HRMS (ESI) calcd for $C_{23}H_{26}NO_4^+$ $(M+H)^+$ 380.1856, found 380.1862.



3j

Ethyl 2-(methyl(phenyl)amino)-3-(*o*-tolyl)penta-3,4-dienoate (**3j**). Pale yellow oil (45.0 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.07 (m, 6H), 6.77-6.71 (m, 3H), 5.37 (s, 1H), 5.05-4.97 (m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.04 (s, 3H), 2.42 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 171.0, 149.6, 136.5, 134.3, 130.9, 129.3, 127.8, 127.7, 126.2, 117.9, 113.4, 101.1, 78.3, 65.1, 61.0, 34.2, 20.5, 14.5; HRMS (ESI) calcd for $C_{21}H_{24}NO_2^+$ $(M+H)^+$ 322.1802,

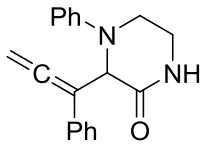
found 322.1805.



3k

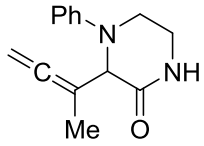
Methyl 3-methyl-2-(methyl(phenyl)amino)penta-3,4-dienoate (**3k**). Yellow oil (19.9 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 6.82-6.74 (m, 3H), 4.91 (s, 1H), 4.83-4.80 (m, 2H), 3.68 (s, 3H), 3.01 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 171.7, 149.7, 129.4, 117.9, 113.2, 96.3, 77.0, 65.6, 51.8, 33.6, 17.3; HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ $(M+H)^+$ 232.1332, found 232.1336.

(3) Scheme 2



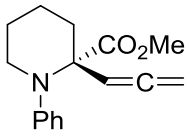
3l

4-Phenyl-3-(1-phenylpropa-1,2-dien-1-yl)piperazin-2-one (**3l**). Pale yellow solid (42.4 mg, 73% yield); m.p. 155-156 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.24-7.11 (m, 5H), 6.84-6.79 (m 3H), 6.37 (br, s, 1H), 5.16-5.07 (m, 3H), 3.66-3.59 (m, 1H), 3.53-3.45 (m, 1H), 3.42-3.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 169.6, 148.1, 134.4, 129.5, 128.5, 127.3, 127.2, 120.1, 116.2, 105.1, 80.4, 62.5, 43.2, 39.6; HRMS (ESI) calcd for $C_{19}H_{19}N_2O^+$ $(M+H)^+$ 291.1492, found 291.1497.



3m

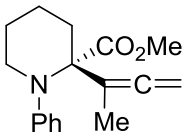
3-(Buta-2,3-dien-2-yl)-4-phenylpiperazin-2-one (**3m**). Pale yellow solid (38.4 mg, 84% yield); m.p. 125-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 6.86-6.77 (m, 3H), 4.75-4.72 (m, 2H), 4.55 (s, 1H), 3.59-3.46 (m, 4H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 170.0, 148.1, 129.3, 118.9, 114.4, 97.9, 77.3, 64.6, 43.0, 39.6, 16.5; HRMS (ESI) calcd for $C_{14}H_{17}N_2O^+$ $(M+H)^+$ 229.1335, found 229.1338.



3n

Methyl (*S*)-1-phenyl-2-(propa-1,2-dien-1-yl)piperidine-2-carboxylate (**3n**). Yellow oil (21.6 mg,

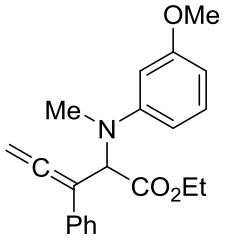
42% yield); $[\alpha]_D^{20}$ = -48.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 7.06-7.02 (m, 2H), 6.94-6.89 (m, 1H), 5.42 (t, *J* = 6.8 Hz, 1H), 4.84-4.74 (m, 2H), 3.64 (s, 3H), 3.54-3.47 (m, 1H), 3.37-3.29 (m, 1H), 2.25-2.17 (m, 1H), 1.94-1.87 (m, 1H), 1.76-1.73 (m, 3H), 1.65-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 174.5, 150.2, 128.3, 122.8, 121.7, 92.4, 78.0, 66.4, 52.2, 49.8, 35.8, 25.9, 20.9; HRMS (ESI) calcd for $C_{16}H_{20}NO_2^+$ $(M+H)^+$ 258.1489, found 258.1494. The ee was determined to be 72% by HPLC analysis (Chiralpak OJ column, λ = 254 nm, hexane/isopropanol = 80/20, flow rate = 1.0 mL/min): t_R(major) = 11.7 min, t_R(minor) = 21.8 min.



3o

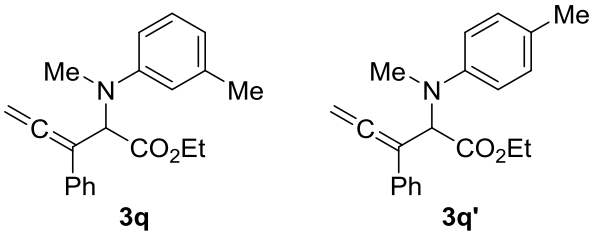
Methyl (*S*)-2-(buta-2,3-dien-2-yl)-1-phenylpiperidine-2-carboxylate (**3o**). Colorless oil (40.1 mg, 74% yield); $[\alpha]_D^{20}$ = +136.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.12 (m, 4H), 6.93-6.88 (m, 1H), 4.70-4.59 (m, 2H), 3.69 (s, 3H), 3.47-3.38 (m, 2H), 2.28-2.20 (m, 1H), 2.02-1.92 (m, 1H), 1.83-1.75 (m, 1H), 1.66-1.61 (m, 2H), 1.52-1.48 (m, 3H), 1.47-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 173.6, 150.8, 127.9, 124.5, 121.7, 100.5, 76.1, 70.5, 51.8, 33.8, 25.6, 22.3, 15.4; HRMS (ESI) calcd for $C_{17}H_{22}NO_2^+$ $(M+H)^+$ 272.1645, found 272.1646. The ee was determined to be 73% by HPLC analysis (Chiralpak AD column, λ = 254 nm, hexane/isopropanol = 99/1, flow rate = 0.6 mL/min): t_R(minor) = 8.0 min, t_R(major) = 8.9 min.

(4) Table 4



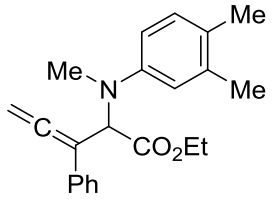
3p

Ethyl 2-((3-methoxyphenyl)(methyl)amino)-3-phenylpenta-3,4-dienoate (**3p**). Pale yellow oil (41.8 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 4H), 7.23-7.16 (m, 2H), 6.46-6.42 (m, 1H), 6.39-6.35 (m, 2H), 5.47 (t, *J* = 3.2 Hz, 1H), 5.34-5.24 (m, 2H), 4.25-4.14 (m, 2H), 3.80 (s, 3H), 2.95 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 171.4, 160.9, 150.6, 133.9, 130.2, 128.7, 127.5, 126.0, 105.8, 102.9, 102.5, 99.6, 81.0, 62.6, 61.1, 55.3, 33.4, 14.5; HRMS (ESI) calcd for $C_{21}H_{24}NO_3^+$ $(M+H)^+$ 338.1751, found 338.1756.



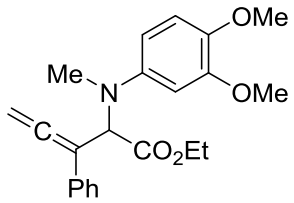
3q **3q'**

A 56:44 mixture of ethyl 2-(methyl(*m*-tolyl)amino)-3-phenylpenta-3,4-dienoate (**3q**) and ethyl 2-(methyl(*p*-tolyl)amino)-3-phenylpenta-3,4-dienoate (**3q'**). Yellow oil (30.2 mg, 47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 3H), 7.29-7.23 (m, 2H), 7.22-7.14 (m, 2H), 6.64-6.61 (m, 2H), 5.49-5.47 (m, 1H), 5.32-5.24 (m, 2H), 4.24-4.14 (m, 2H), 2.95 (s, 3H), 2.33 (s, 3H), 1.29-1.23 (m, 3H); Partial ^{1}H NMR (400 MHz, $CDCl_3$) for the minor isomer **3q'**: δ 7.09 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 5.46-5.44 (m, 1H), 2.27 (s, 3H); HRMS (ESI) calcd for $C_{21}H_{24}NO_2^+$ $(M+H)^+$ 322.1802, found 322.1804.



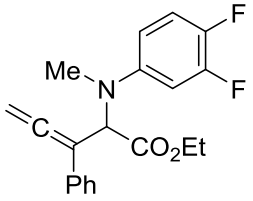
3r

Ethyl 2-((3,4-dimethylphenyl)(methyl)amino)-3-phenylpenta-3,4-dienoate (**3r**). Pale yellow oil (28.2 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.29-7.24 (m, 2H), 7.22-7.17 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.66 (s, 1H), 6.61 (d, J = 9.6 Hz, 1H), 5.45 (s, 1H), 5.33-5.24 (m, 2H), 4.26-4.11 (m, 2H), 2.95 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 171.7, 147.5, 137.5, 134.1, 130.5, 128.7, 127.4, 126.1, 125.8, 114.6, 110.4, 103.0, 80.9, 62.6, 61.0, 53.6, 33.4, 20.6, 18.8, 14.5; HRMS (ESI) calcd for $C_{22}H_{26}NO_2^+$ $(M+H)^+$ 336.1958, found 336.1962.



3s

Ethyl 2-((3,4-dimethoxyphenyl)(methyl)amino)-3-phenylpenta-3,4-dienoate (**3s**). Pale yellow oil (41.8 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.31-7.25 (m, 2H), 7.24-7.18 (m, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.45 (s, 1H), 6.35 (d, J = 8.8 Hz, 1H), 5.39 (s, 1H), 5.33-5.24 (m, 2H), 4.24-4.14 (m, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 2.96 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 171.6, 149.9, 144.5, 141.8, 134.1, 128.7, 127.5, 126.1, 113.1, 104.7, 102.9, 99.2, 80.9, 63.5, 61.0, 56.6, 55.9, 53.6, 33.9, 14.5; HRMS (ESI) calcd for $C_{22}H_{26}NO_4^+$ $(M+H)^+$ 368.1856, found 368.1861.

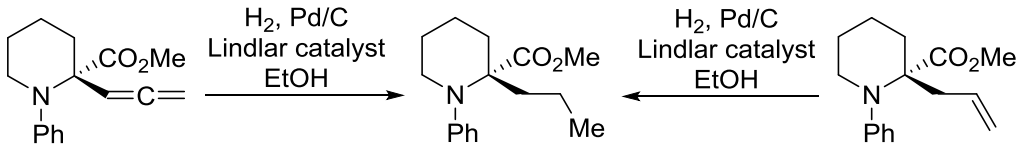


3t

Ethyl 2-((3,4-difluorophenyl)(methyl)amino)-3-phenylpenta-3,4-dienoate (**3t**). Pale yellow solid (31.0 mg, 45% yield); m.p. 54-55^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 4H), 7.25-7.19 (m,

1H), 7.05 (q, *J* = 9.6 Hz, 1H), 6.63-6.55 (m, 1H), 6.47-6.43 (m, 1H), 5.35 (t, *J* = 2.8 Hz, 1H), 5.31-5.28 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.91 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 171.1, 150.9 (dd, *J* = 229.8, 13.3 Hz), 146.4 (dd, *J* = 8.0, 1.3 Hz), 143.3 (dd, *J* = 236.3, 12.8 Hz), 133.7, 128.8, 127.7, 126.0, 117.6 (dd, *J* = 17.6, 1.9 Hz), 108.0 (dd, *J* = 5.3, 3.0 Hz), 102.7, 102.1 (d, *J* = 21.3 Hz), 81.2, 63.0, 61.3, 33.8, 14.5; HRMS (ESI) calcd for $C_{20}H_{20}F_2NO_2^+$ $(M+H)^+$ 344.1457, found 344.1461.

Synthesis of compound 5

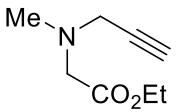


3n (72% ee) **5** **6** (92% ee)

Compound **3n** or **6** (0.10 mmol) was dissolved in ethanol (1.0 mL). Then Pd/C (10% Pd, 5.3 mg) and Lindlar catalyst (5% Pd, 5.3 mg) were added to the above solution. The mixture was stirred under hydrogen atmosphere at room temperature for 6 h, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum/ethyl acetate = 20:1) to give methyl (*R*)-1-phenyl-2-propylpiperidine-2-carboxylate (**5**) as a colorless oil (From **3n**: 22.2 mg, 85% yield, 72% ee; From **6**: 25.8 mg, 99% yield, 92% ee). $[\alpha]_D^{20}$ = +17.1 (*c* = 0.4, $CHCl_3$) for a sample with 72% ee; $[\alpha]_D^{20}$ = +37.2 (*c* = 1.2, $CHCl_3$) for a sample with 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.14-7.10 (m, 2H), 7.05-6.99 (m, 1H), 3.68 (s, 3H), 3.40-3.33 (m, 1H), 3.20-3.15 (m, 1H), 2.15-2.11 (m, 1H), 1.79-1.56 (m, 7H), 1.26-1.14 (m, 1H), 1.10-0.98 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 150.7, 128.1, 126.8, 123.4, 66.5, 51.6, 51.2, 39.8, 34.5, 26.5, 21.8, 17.2, 14.6; HRMS (ESI) calcd for $C_{16}H_{24}NO_2^+$ $(M+H)^+$ 262.1802, found 262.1805. The ee was determined by HPLC analysis (Chiralpak OJ column, λ = 254 nm, hexane/isopropanol = 90/10, flow rate = 1.0 mL/min): t_R(major) = 6.5 min, t_R(minor) = 10.7 min.

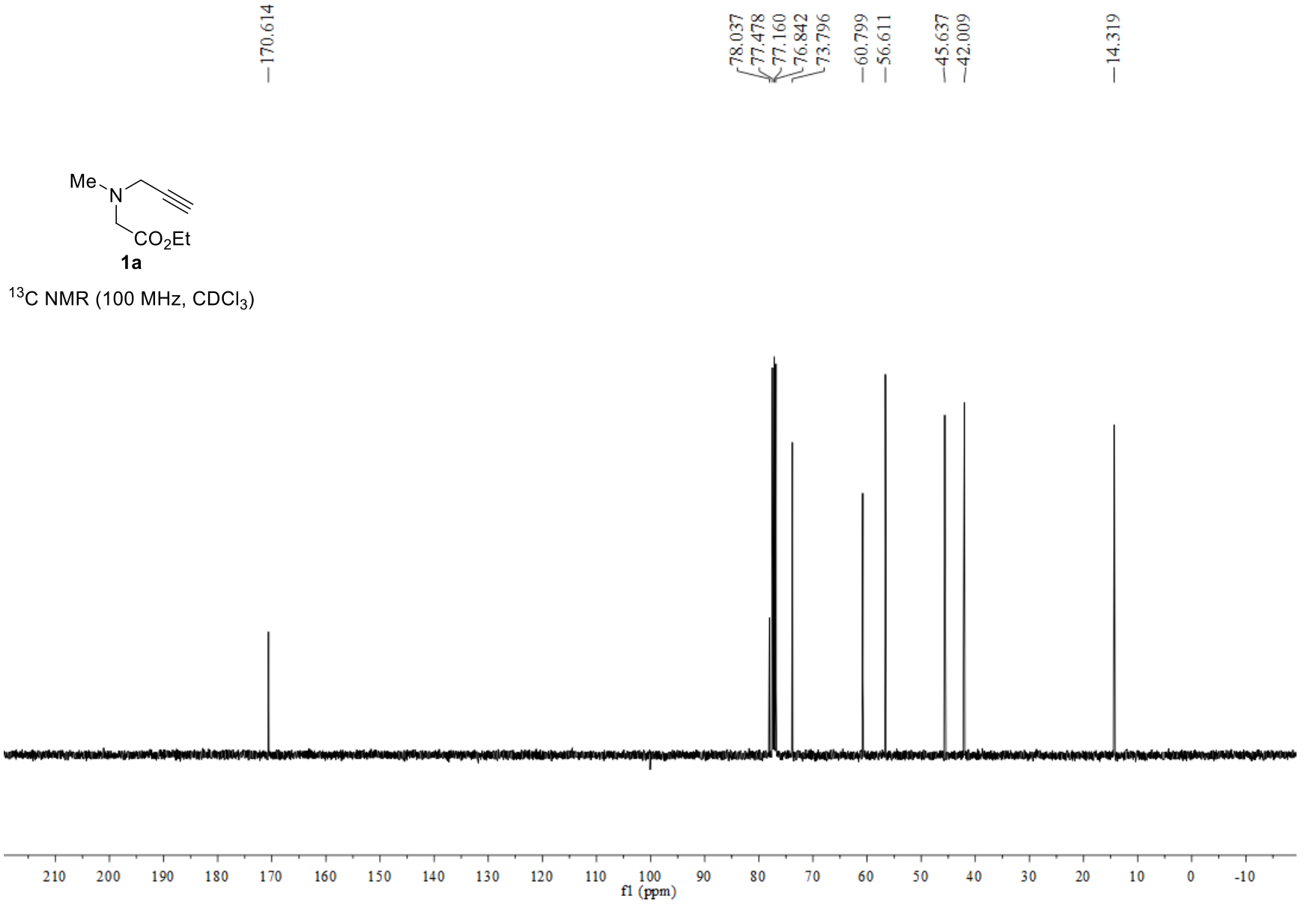
References

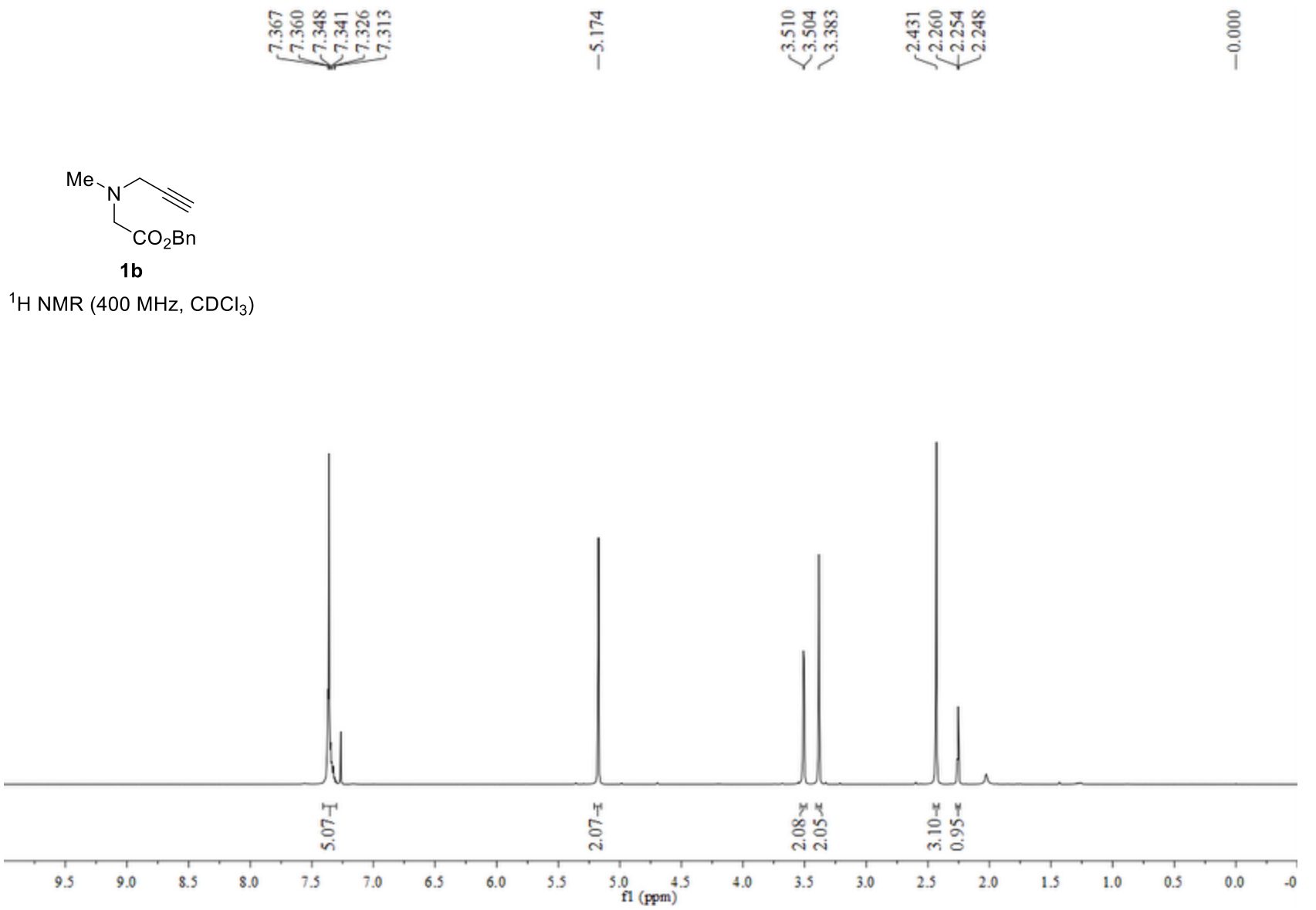
(1) B. S. Shaibu, R. K. Kawade and R.-S. Liu, *Org. Biomol. Chem.*, 2012, **10**, 6834.
(2) J. Zhang, Z.-X. Chen, T. Du, B. Li, Y. Gu and S.-K. Tian, *Org. Lett.*, 2016, **18**, 4872.
(3) A. S. Norgren, C. Budke, Z. Majer, C. Heggemann, T. Koop and N. Sewald, *Synthesis*, 2009, 488.
(4) C.-C. Chen, S.-T. Chen, T.-H. Chuang and J.-M. Fang, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2217.



1a

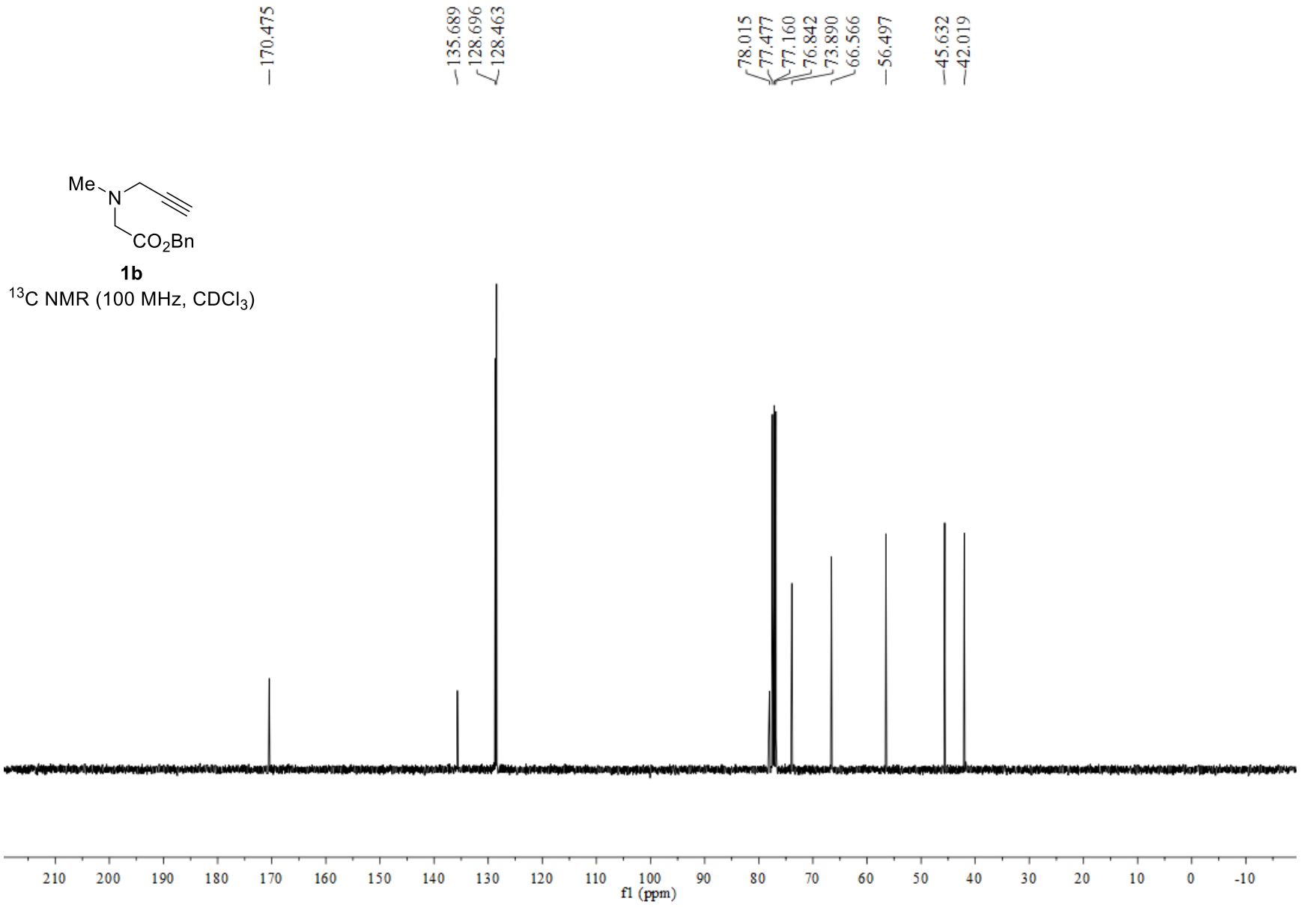
^{1}H NMR (400 MHz, $CDCl_3$)


170.614
78.037
77.478
77.160
76.842
73.796
60.799
56.611
45.637
42.009
14.319
Me
N
CO2Et
1a
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1b

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


170.475
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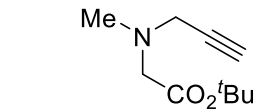
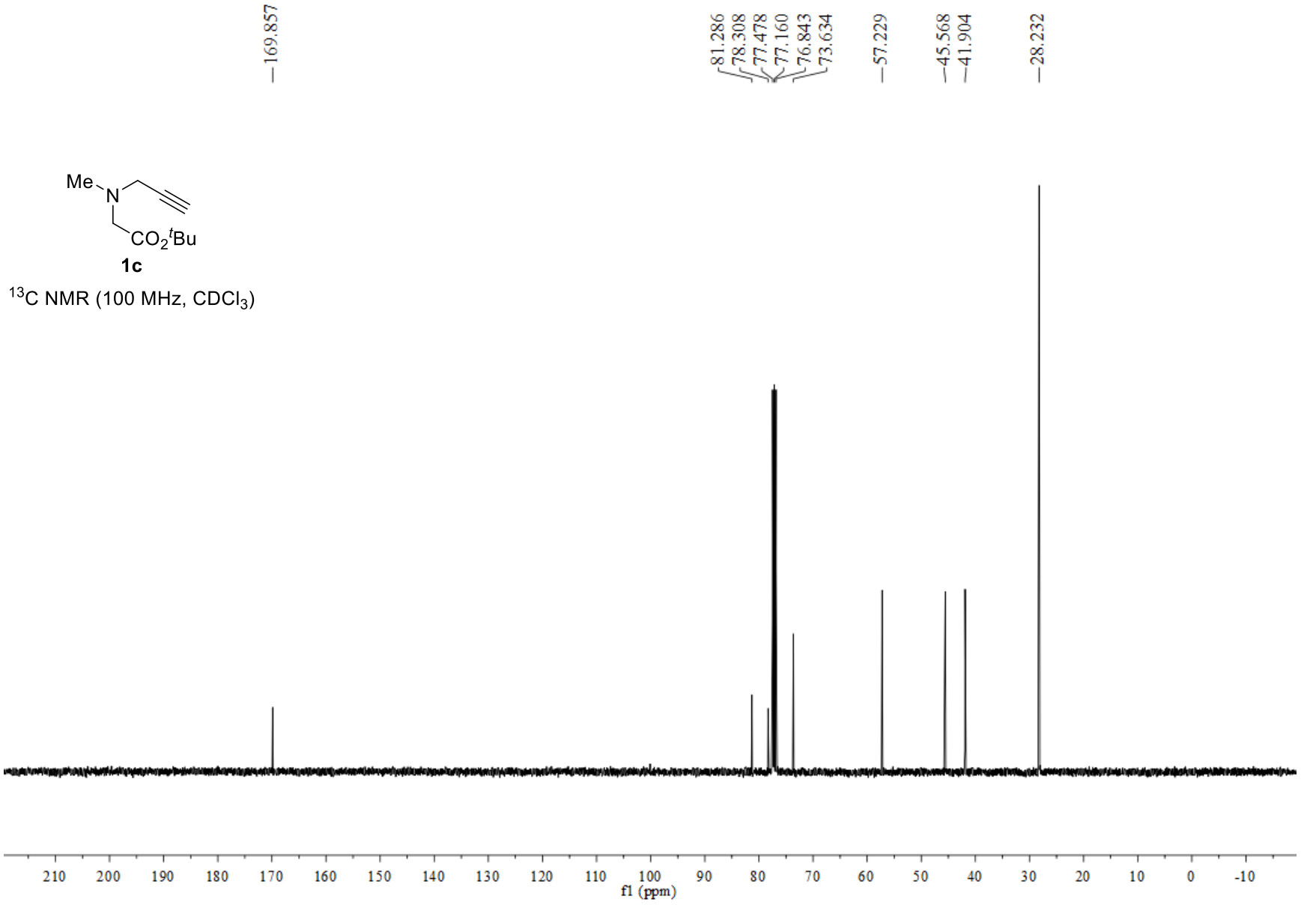
128.696
128.463
78.015
77.477
77.160
76.842
73.890
66.566
56.497
45.632
42.019
Me
N
CO2Bn
1b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1c

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


169.857
81.286
78.308
77.478
77.160
76.843
73.634
57.229
45.568
41.904
28.232
Me
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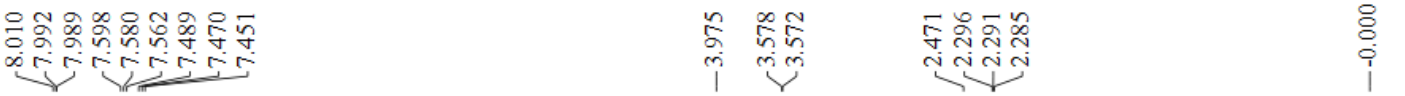
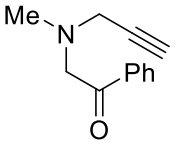
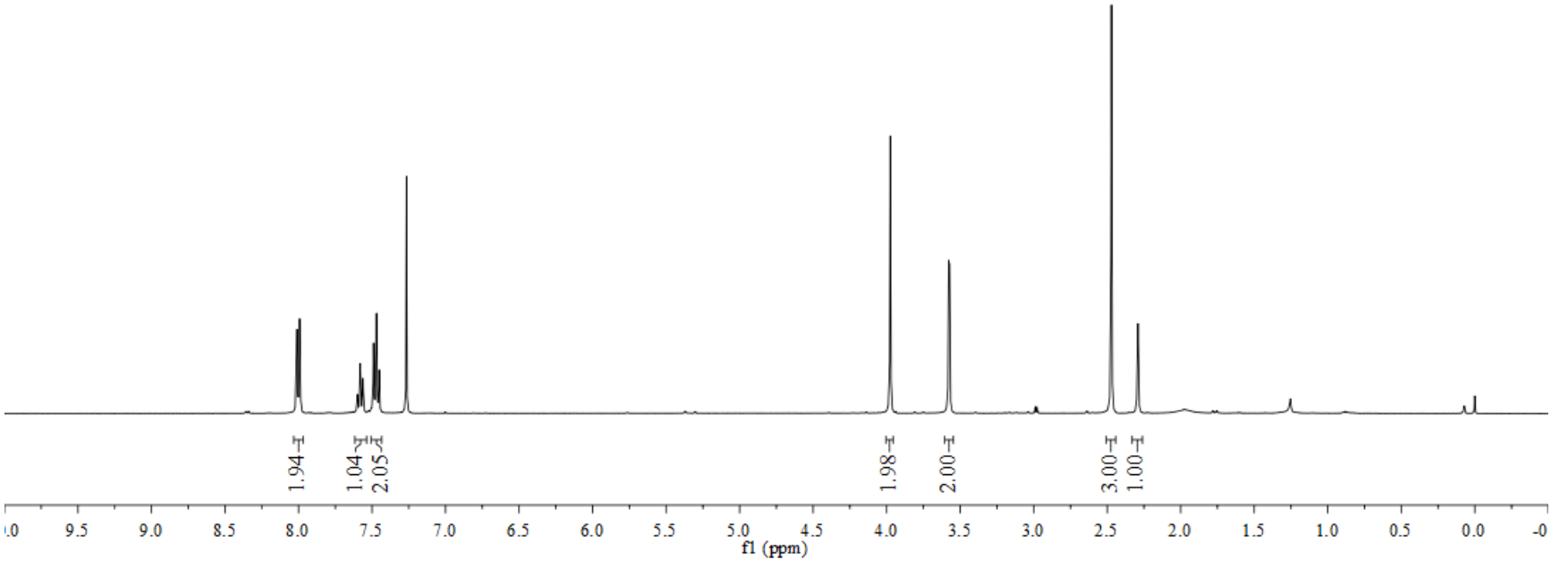
1c
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

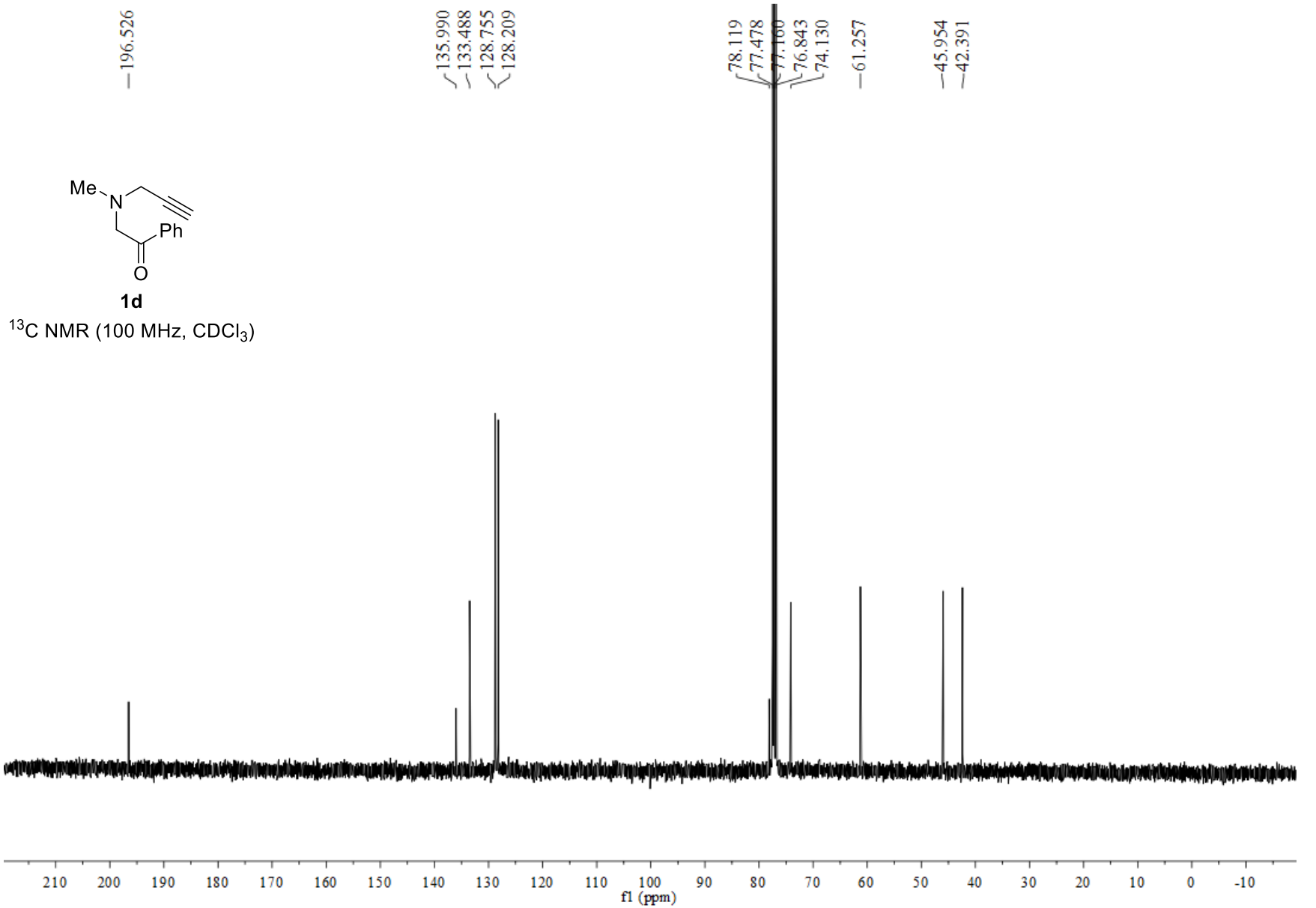




1d

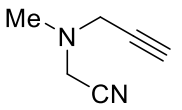
^{1}H NMR (400 MHz, $CDCl_3$)





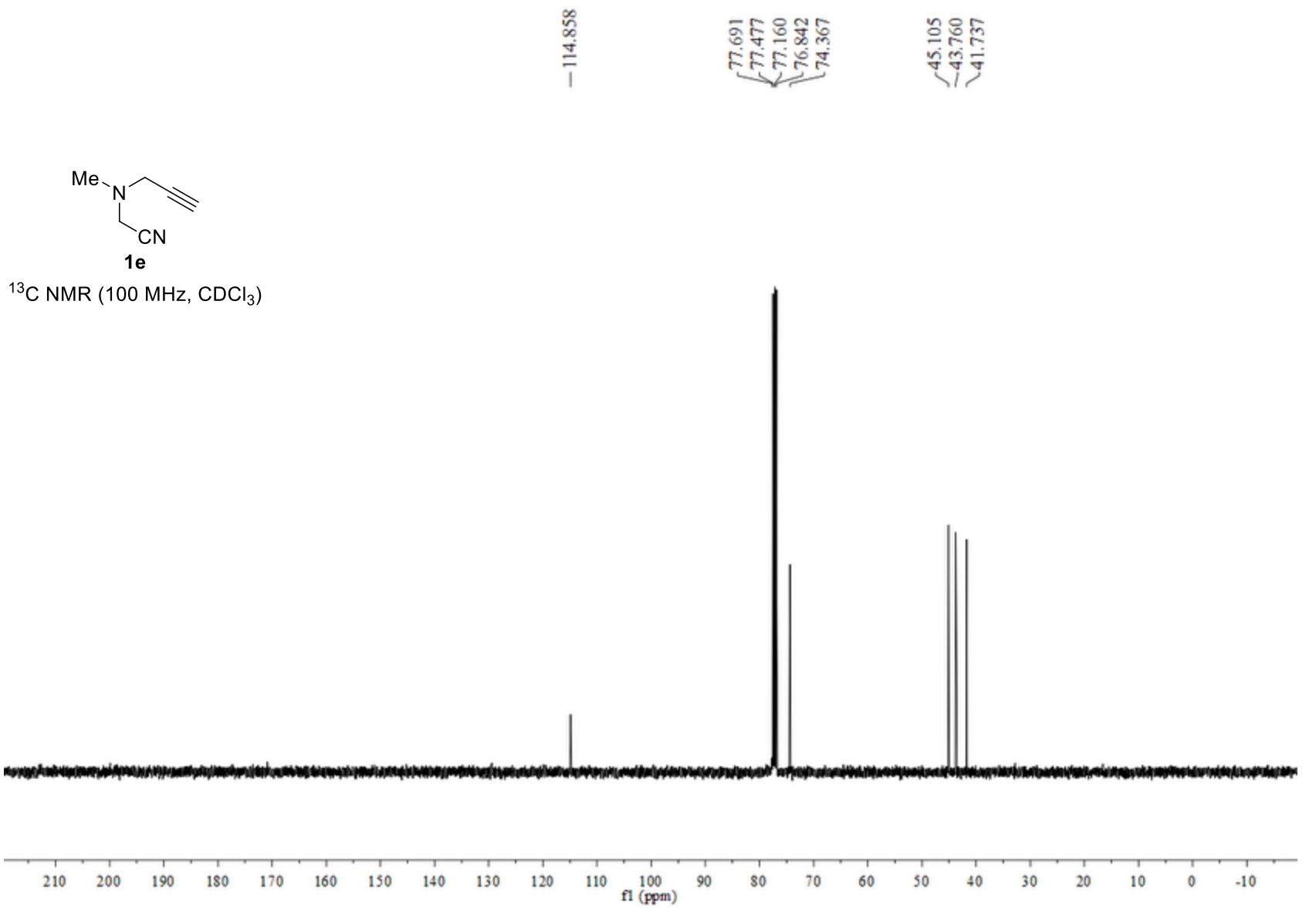
1d

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



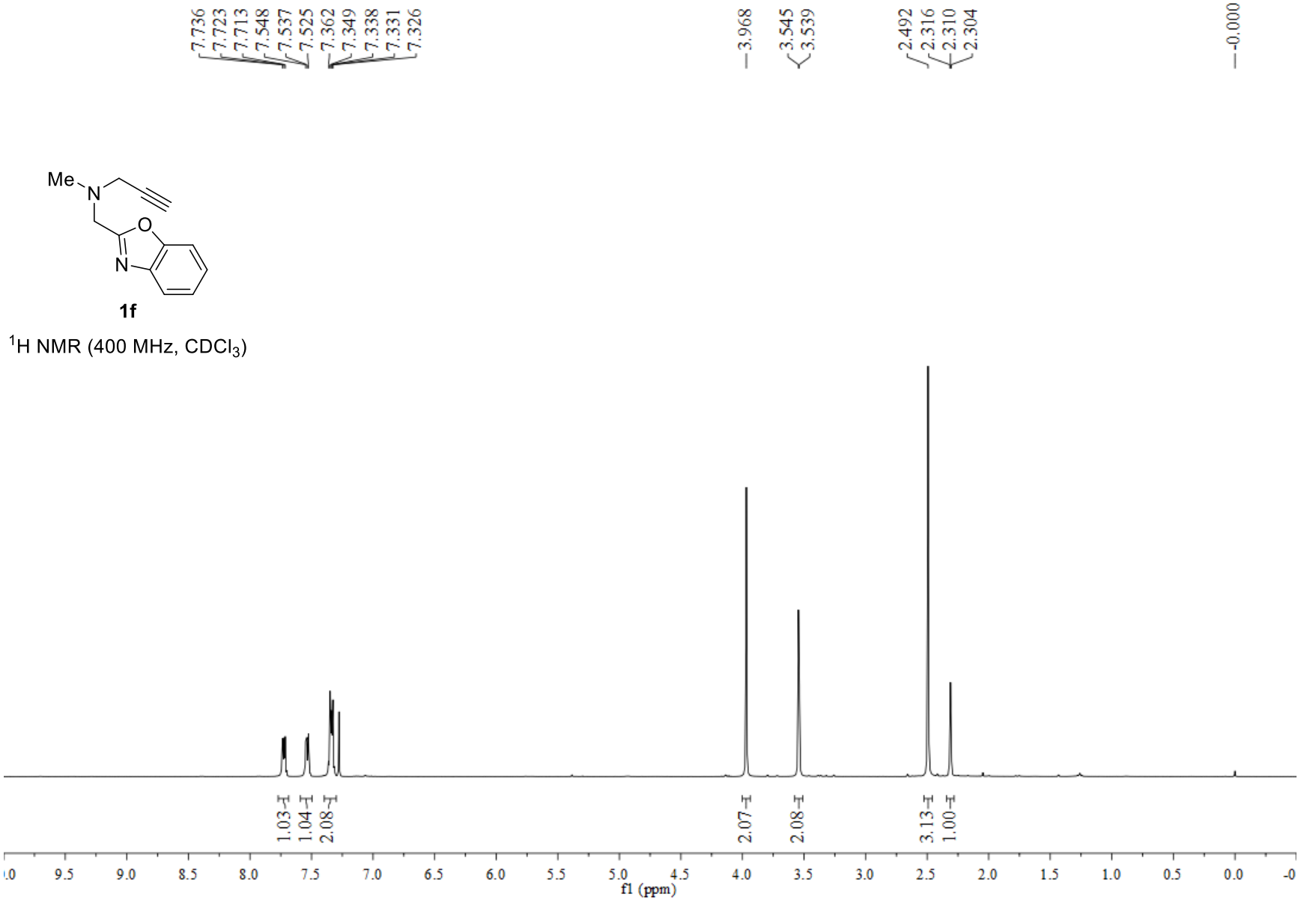
1e

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



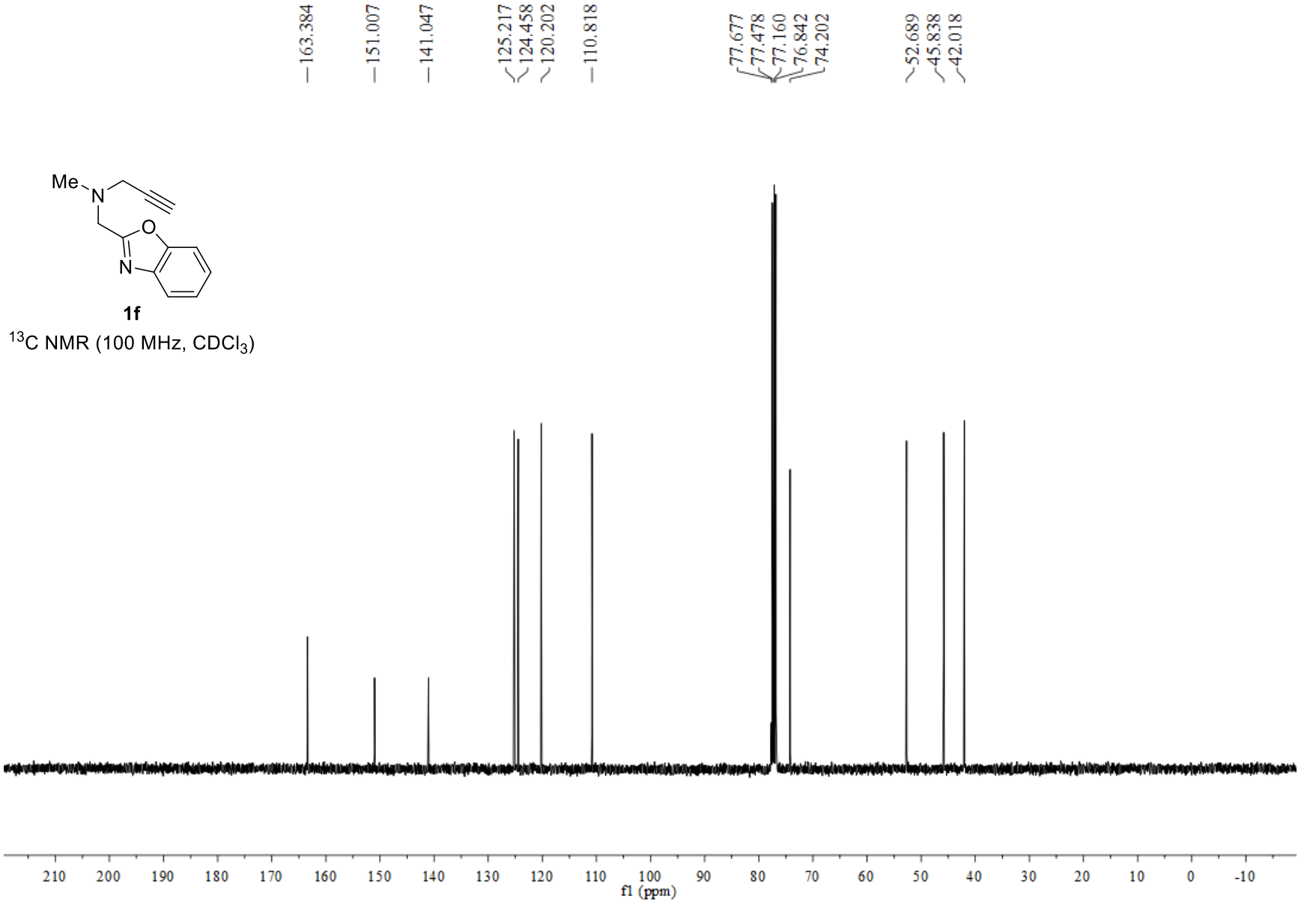
1e

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



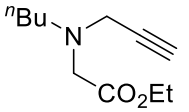
1f

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



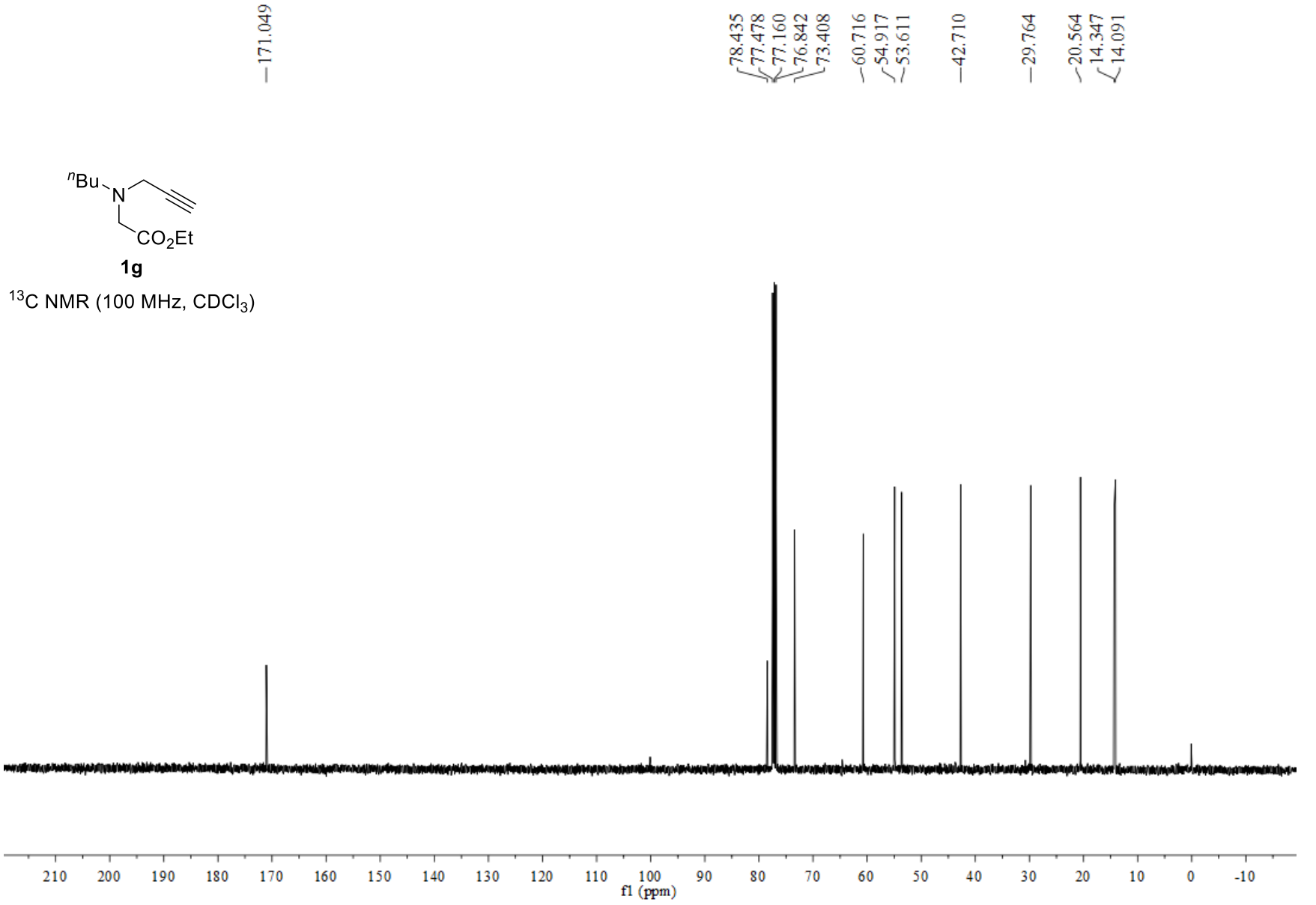
1f

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



1g

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


171.049
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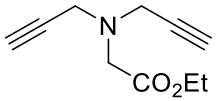
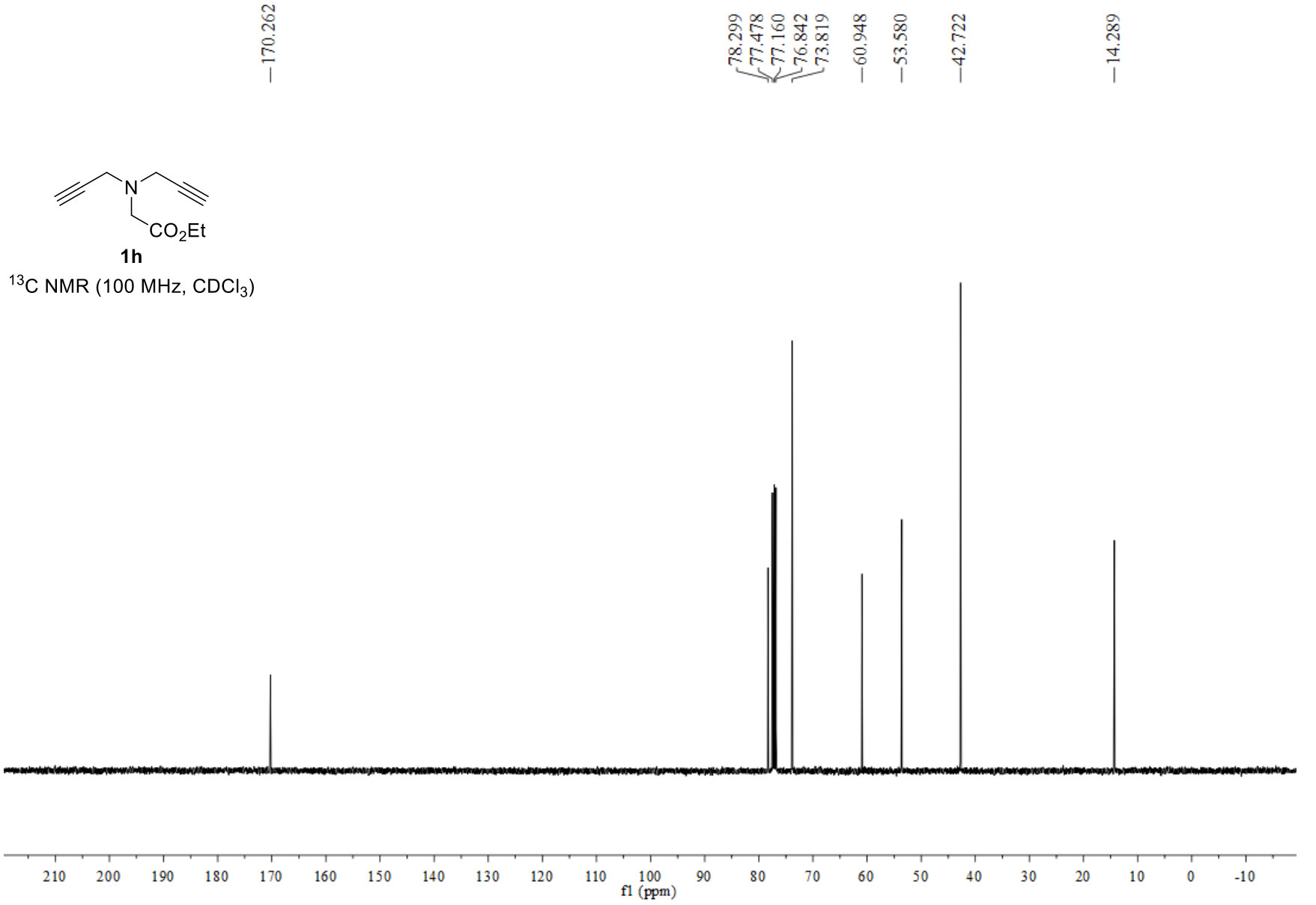
76.842
73.408
60.716
54.917
53.611
42.710
29.764
20.564
14.347
14.091
nBu
N
CO2Et
1g
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1h

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



1h

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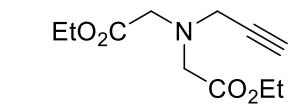
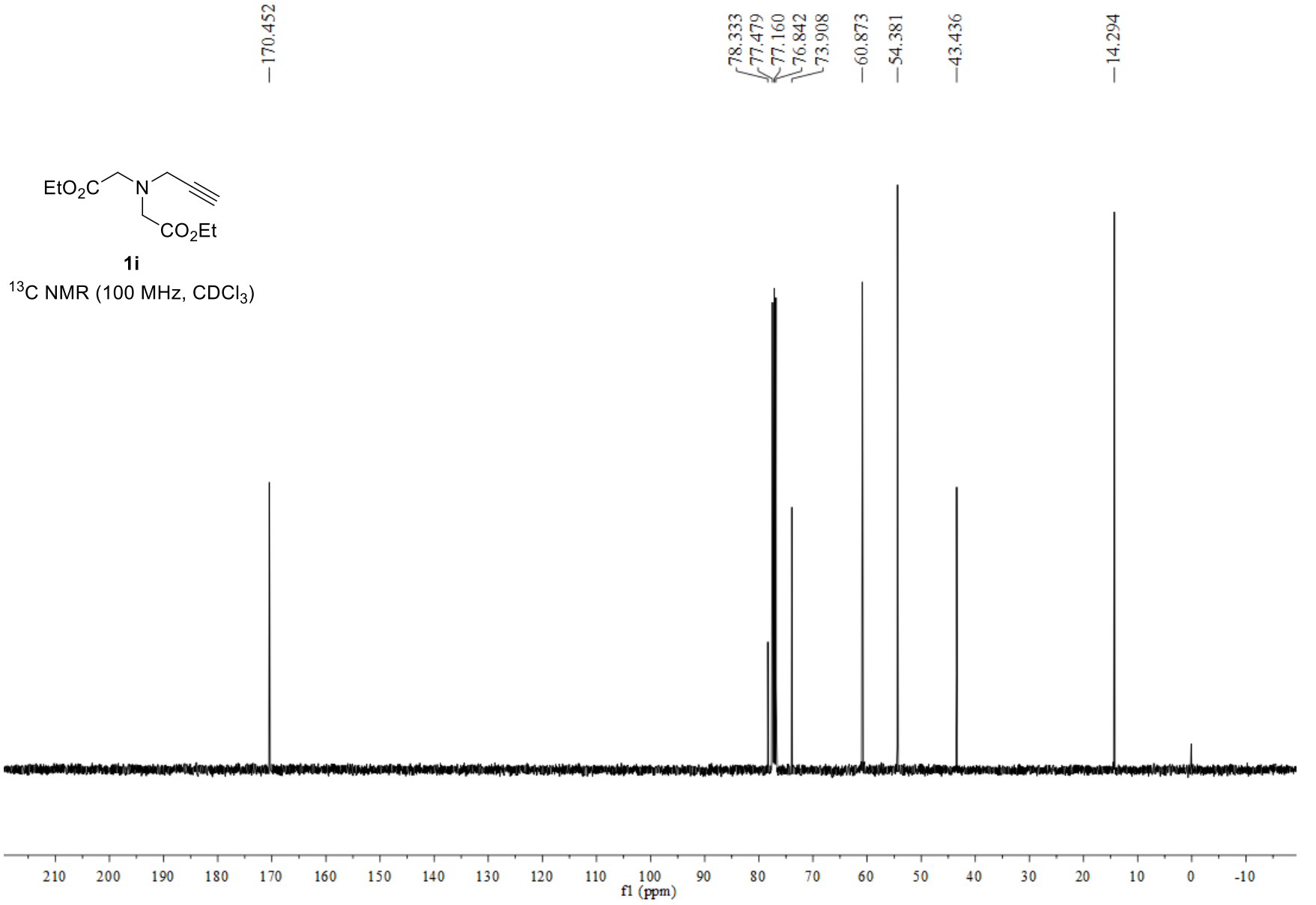


1i

^{1}H NMR (400 MHz, $CDCl_3$)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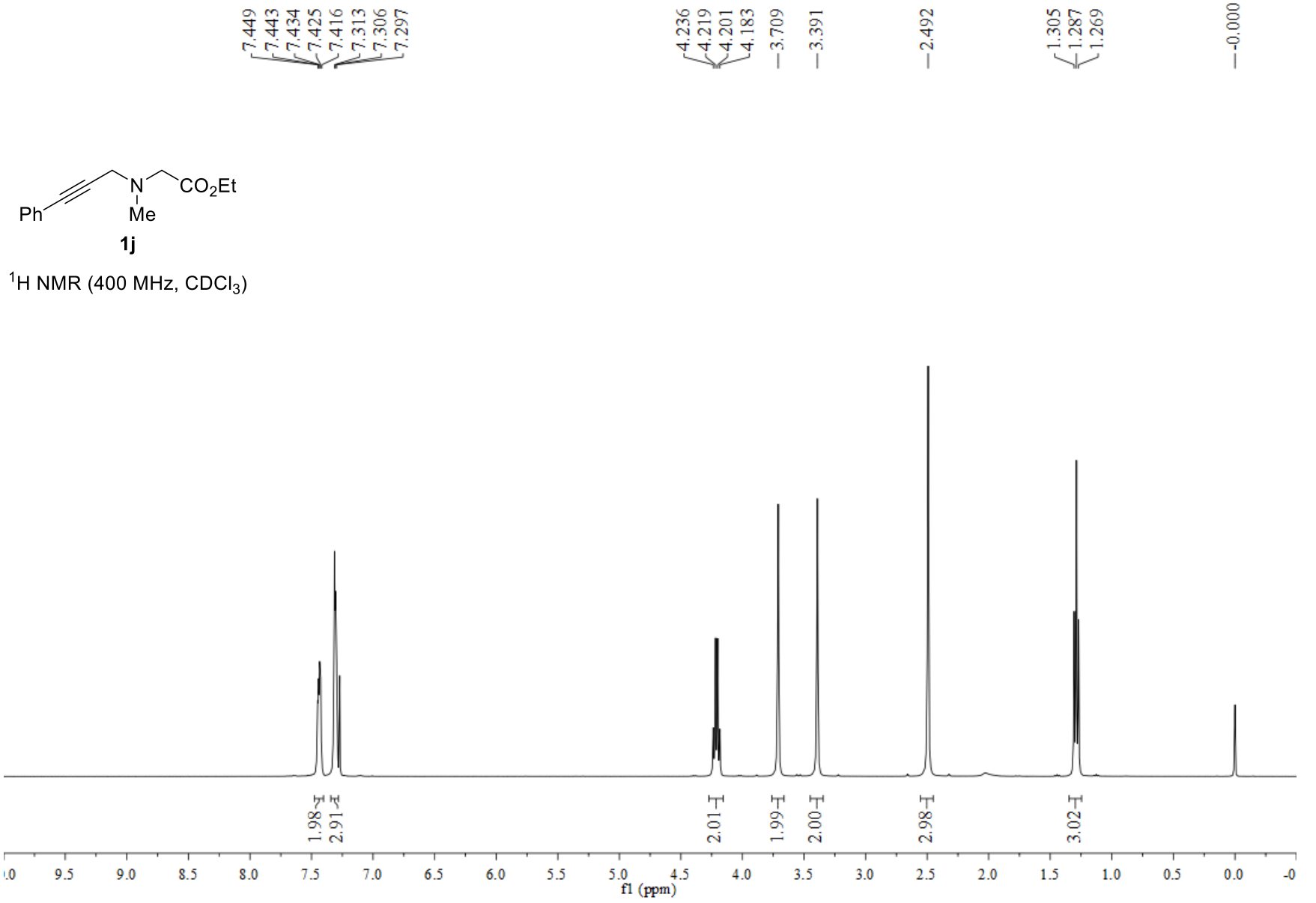
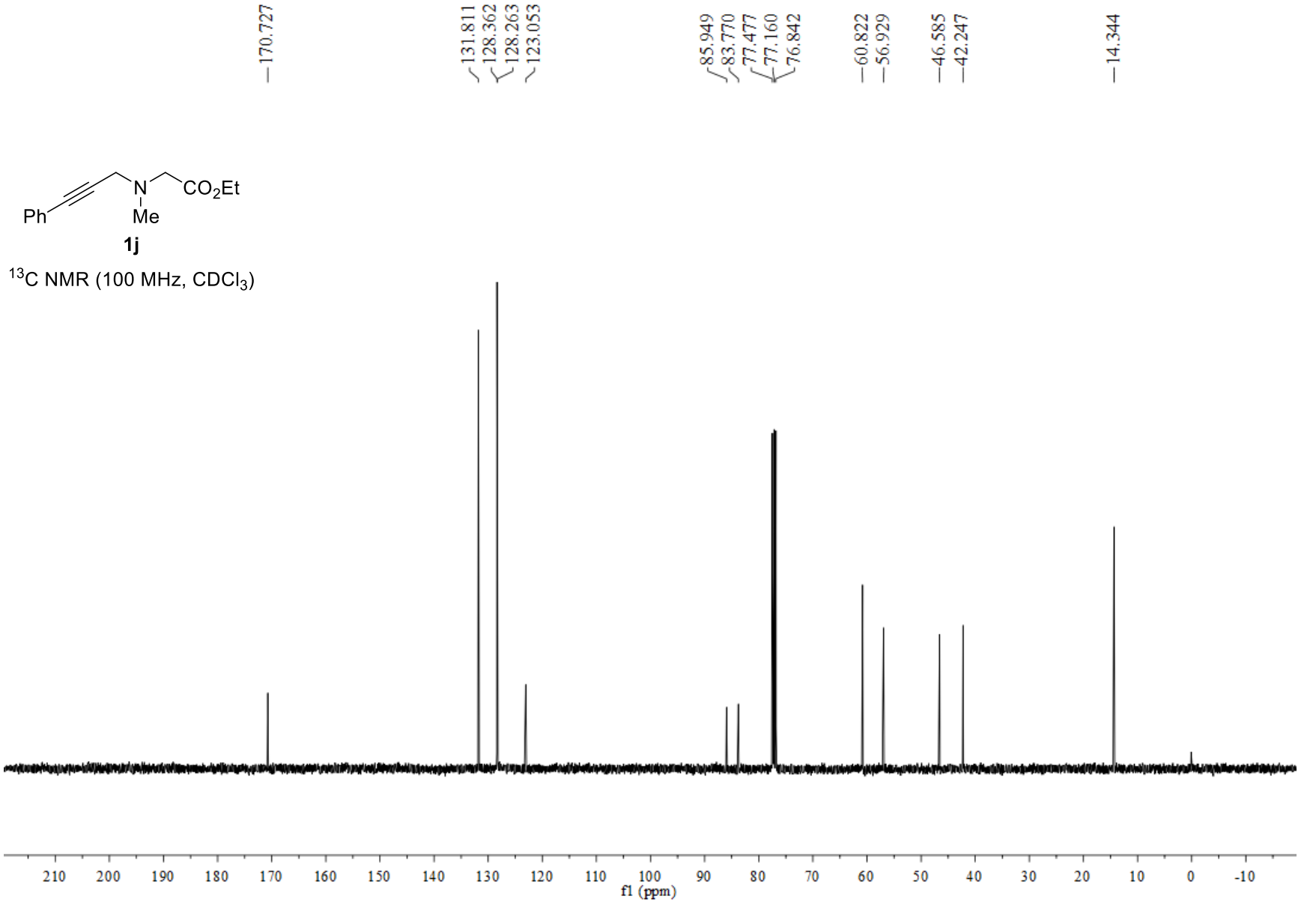
76.842
73.908
60.873
54.381
43.436
14.294
EtO2C
N
CO2Et
1i
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1j

^{1}H NMR (400 MHz, $CDCl_3$)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77.477
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76.842
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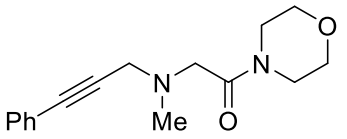
56.929
46.585
42.247
14.344
Ph
N
Me
CO2Et
1j
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1k

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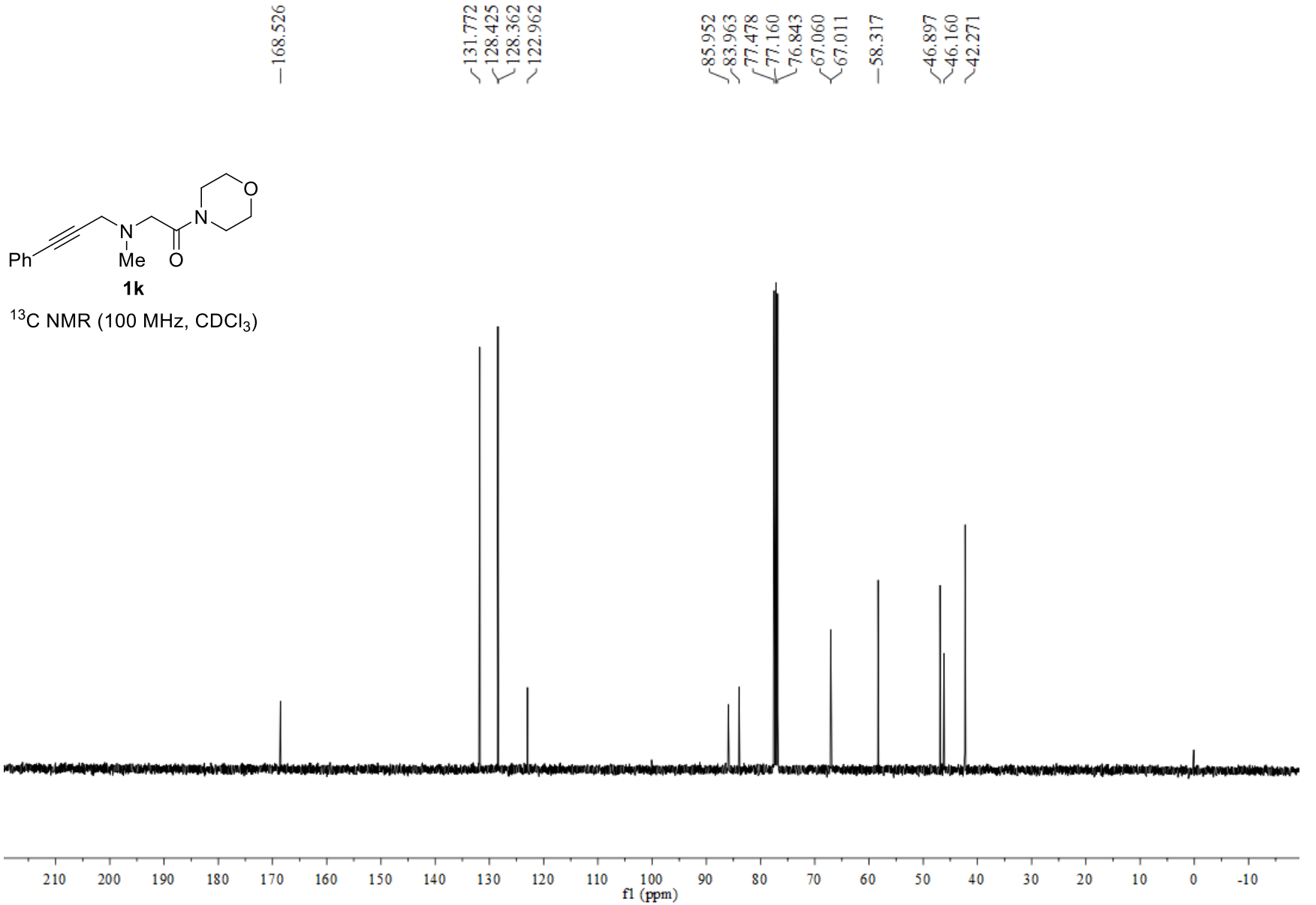
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46.160
42.271
Ph
N
Me
O
N
O
1k
13C NMR (100 MHz, CDCl3)
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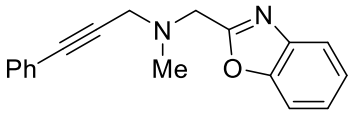
f1 (ppm)



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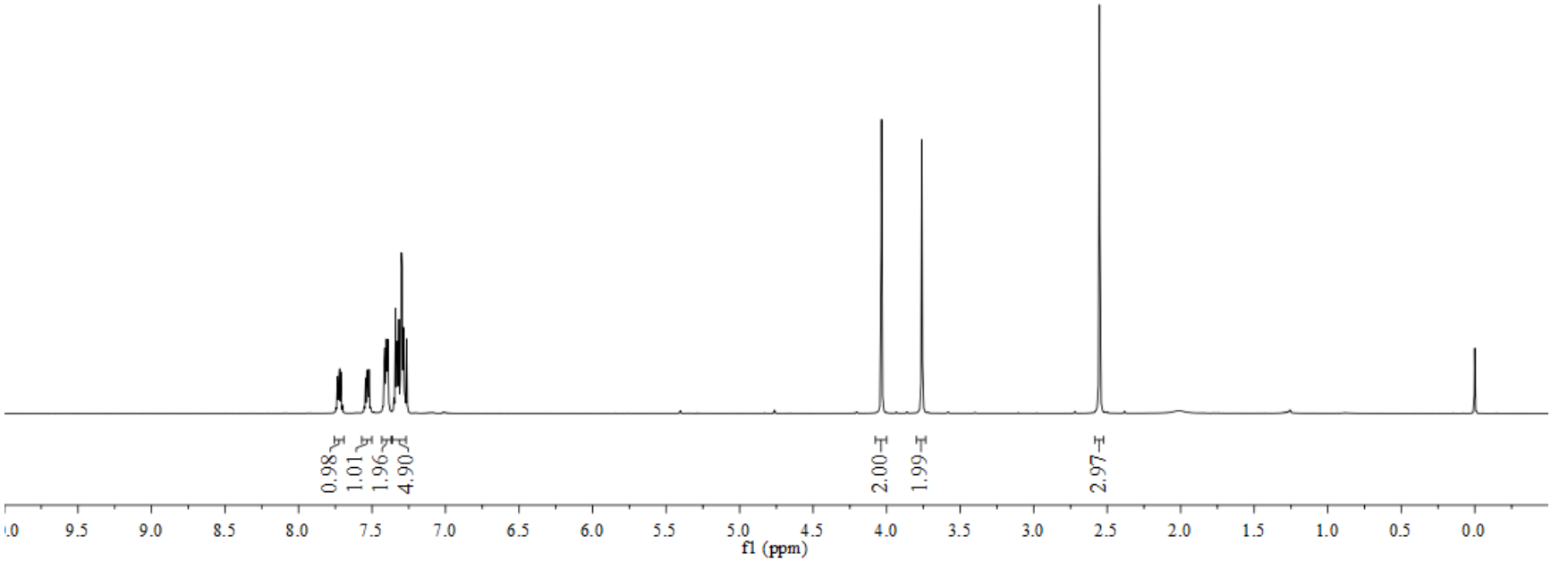
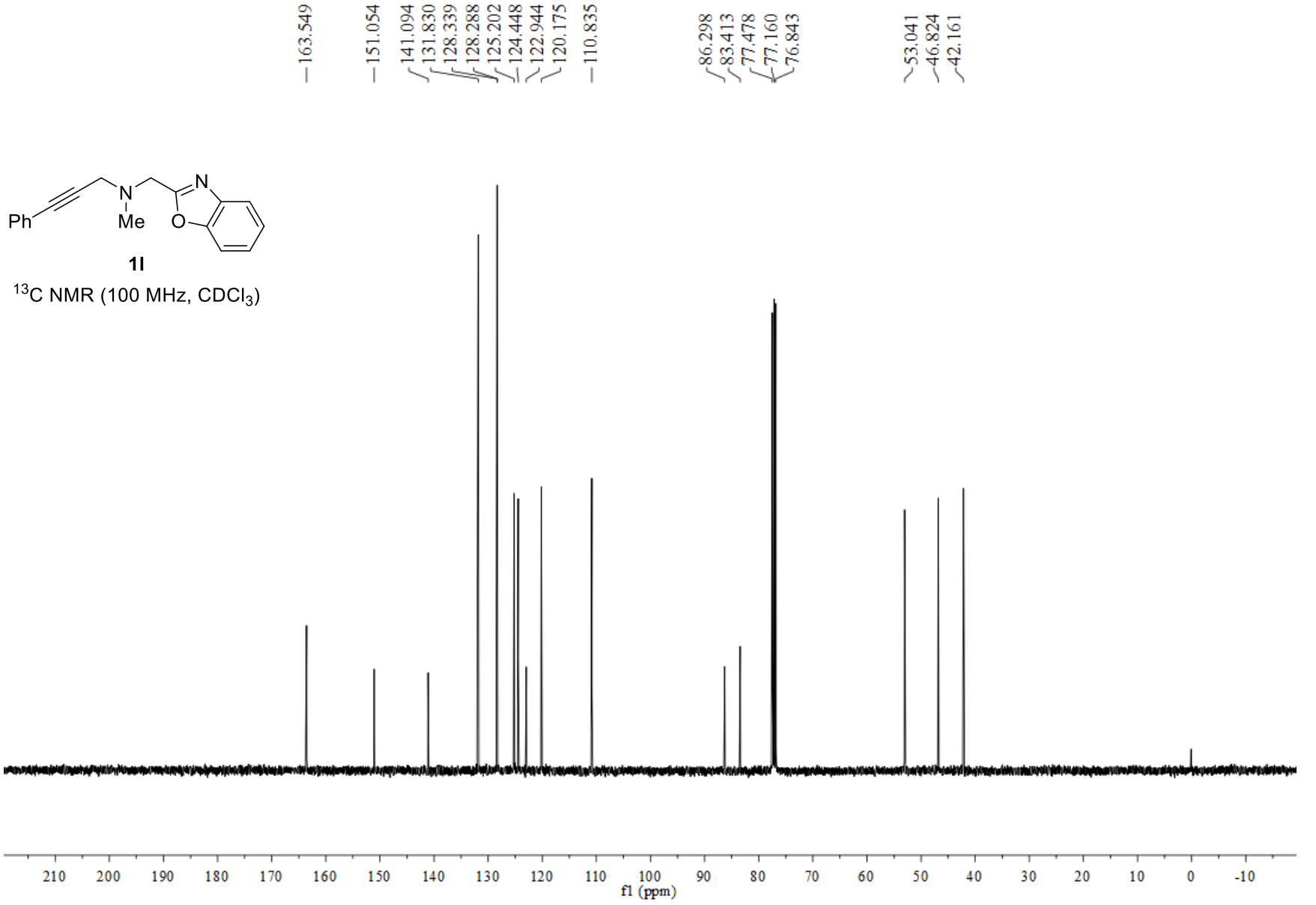
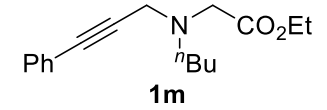
^{1}H NMR (400 MHz, $CDCl_3$)





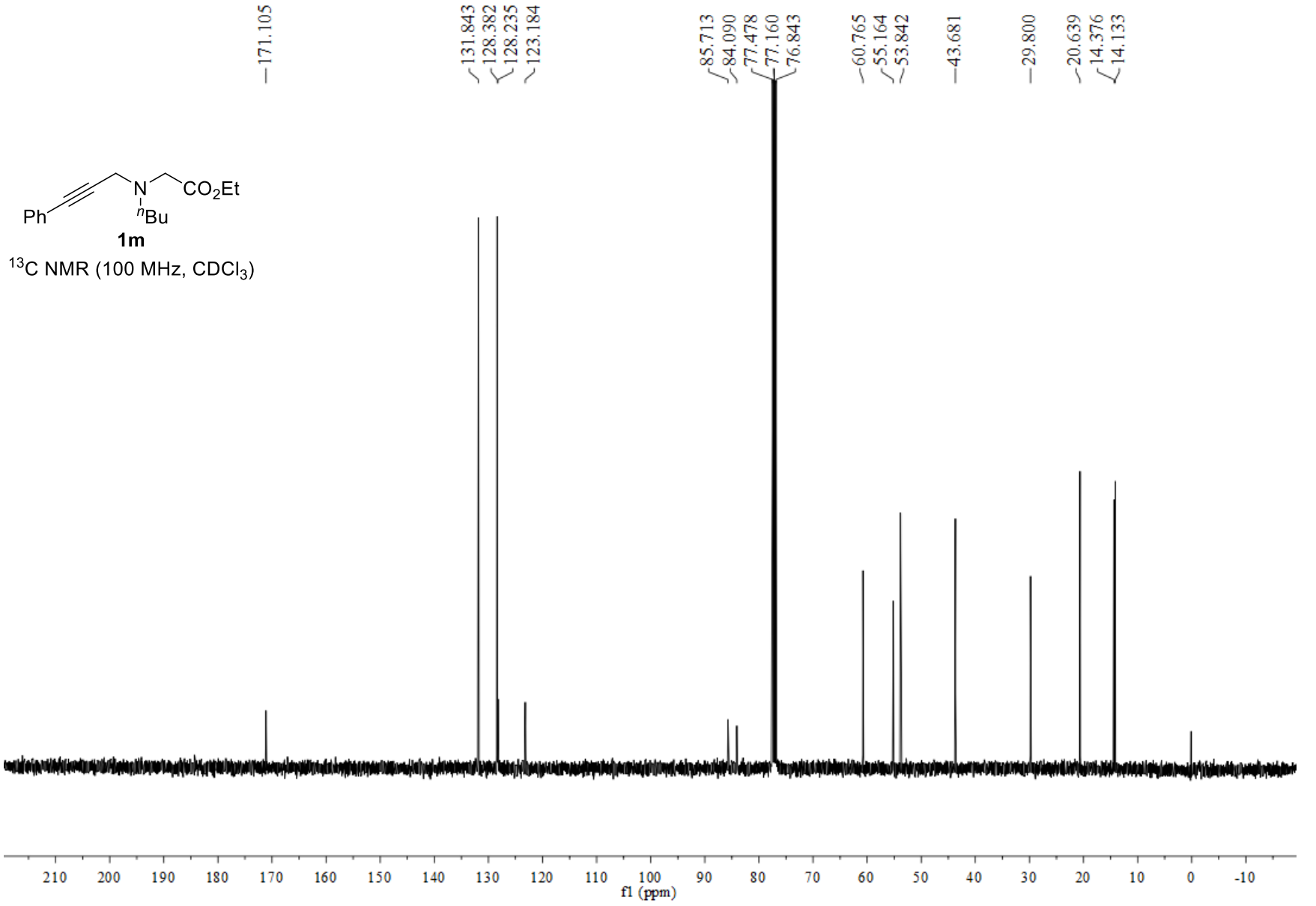
1l

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



1m

^{1}H NMR (400 MHz, $CDCl_3$)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128.382
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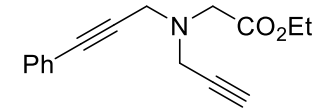
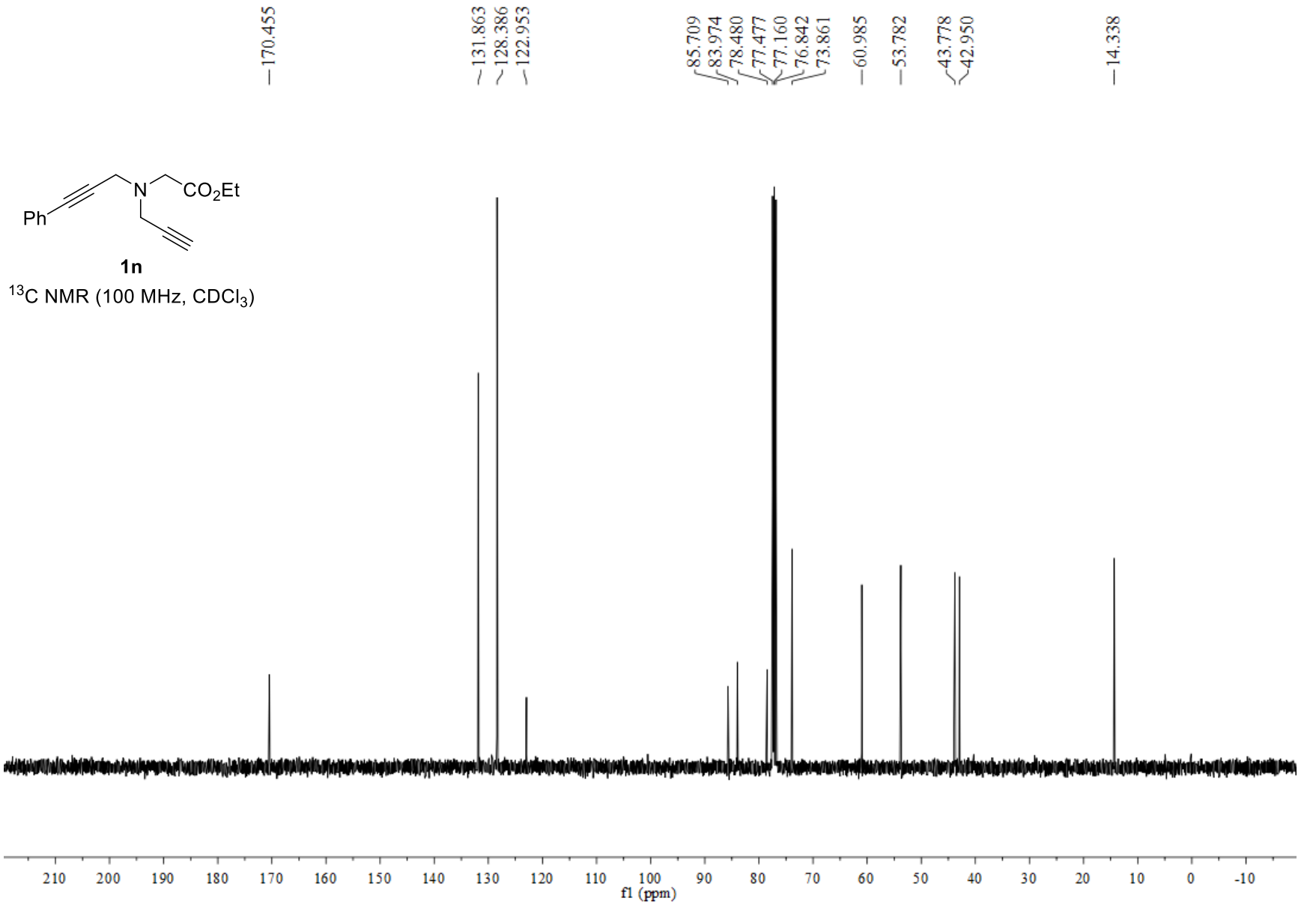
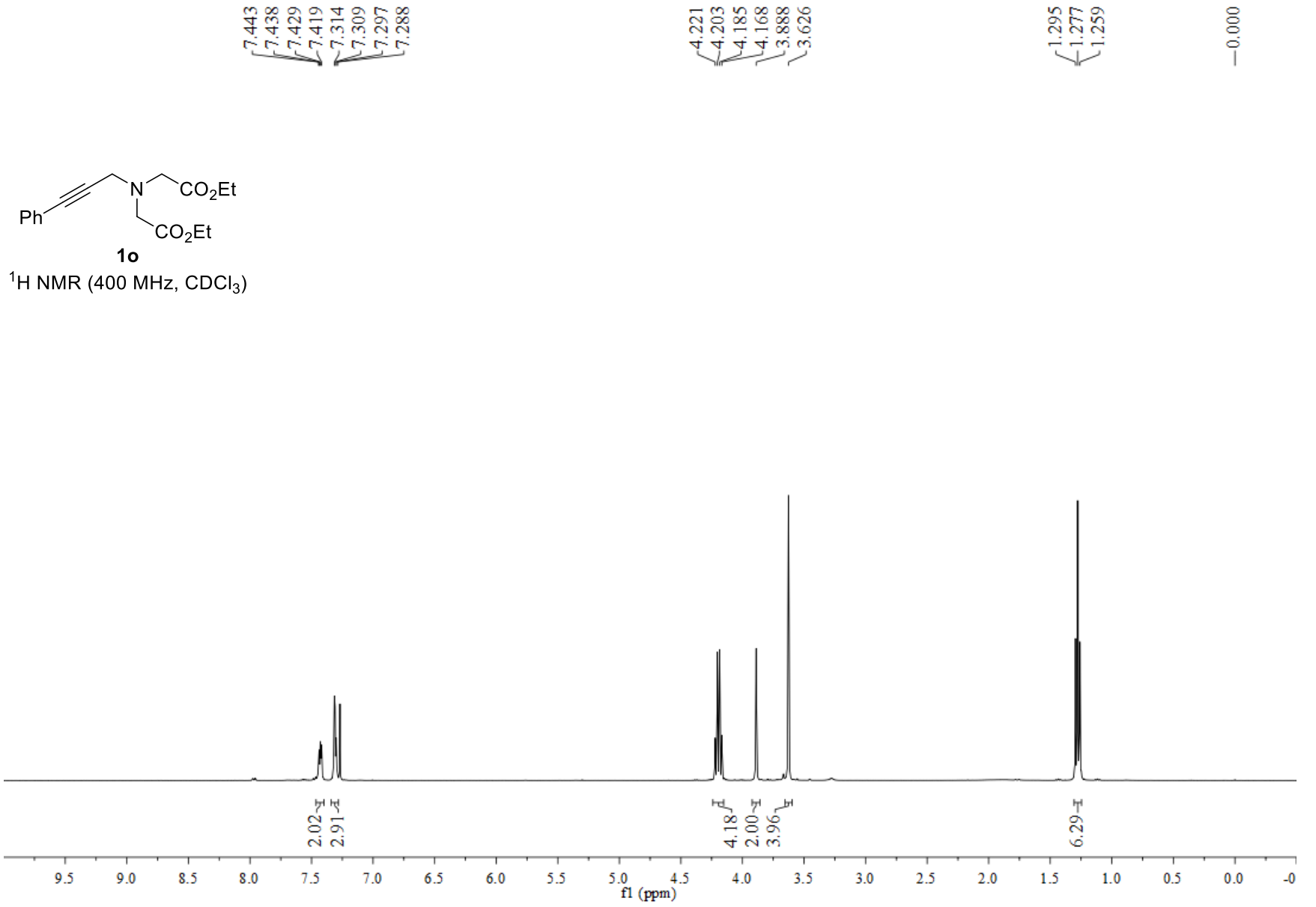
84.090
77.478
77.160
76.843
60.765
55.164
53.842
43.681
29.800
20.639
14.376
14.133
Ph
N
CO2Et
nBu
1m
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1n

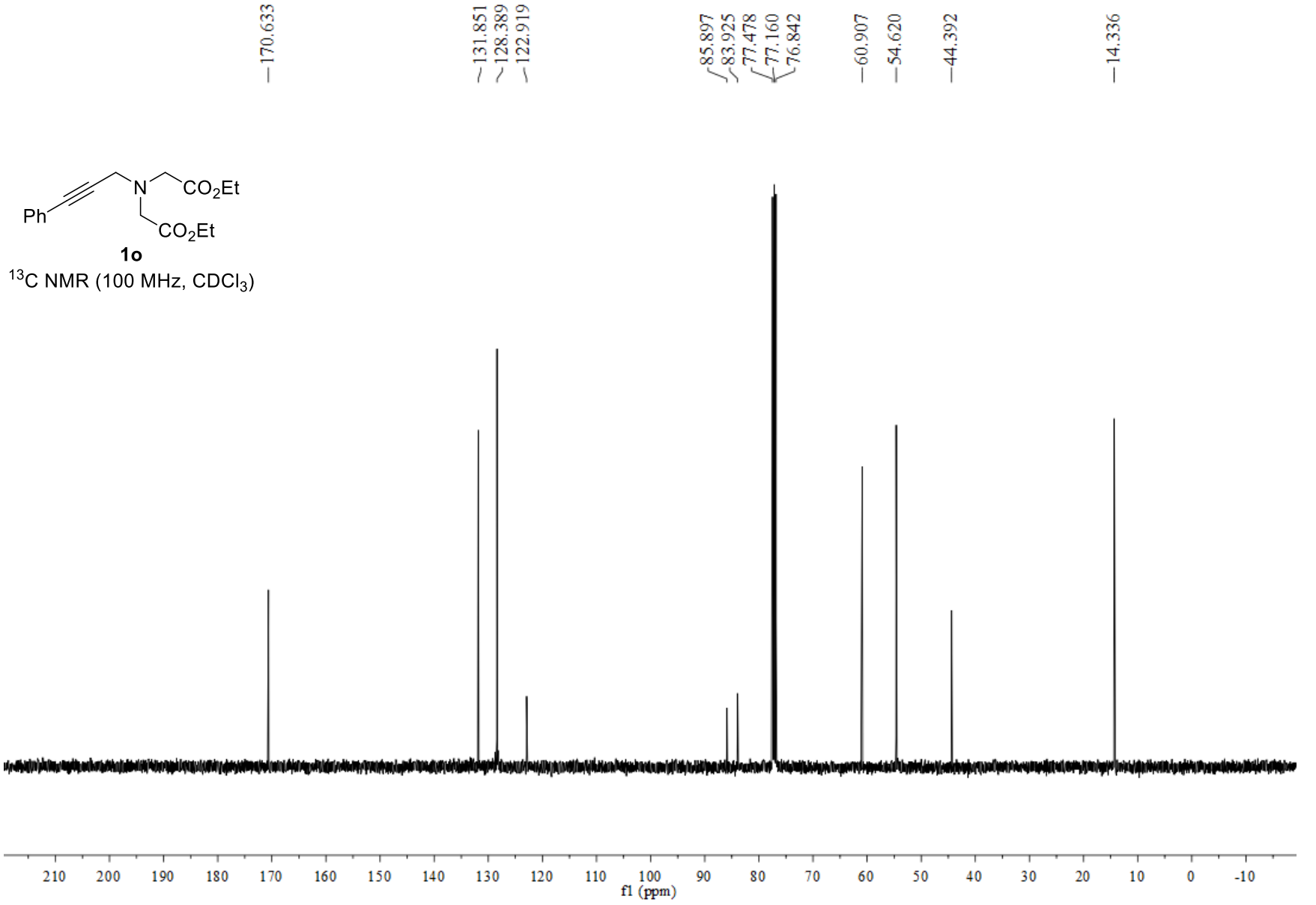
^{1}H NMR (400 MHz, $CDCl_3$)


170.455
131.863
128.386
122.953
85.709
83.974
78.480
77.477
77.160
76.842
73.861
60.985
53.782
43.778
42.950
14.338
Ph
N
CO2Et
1n
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



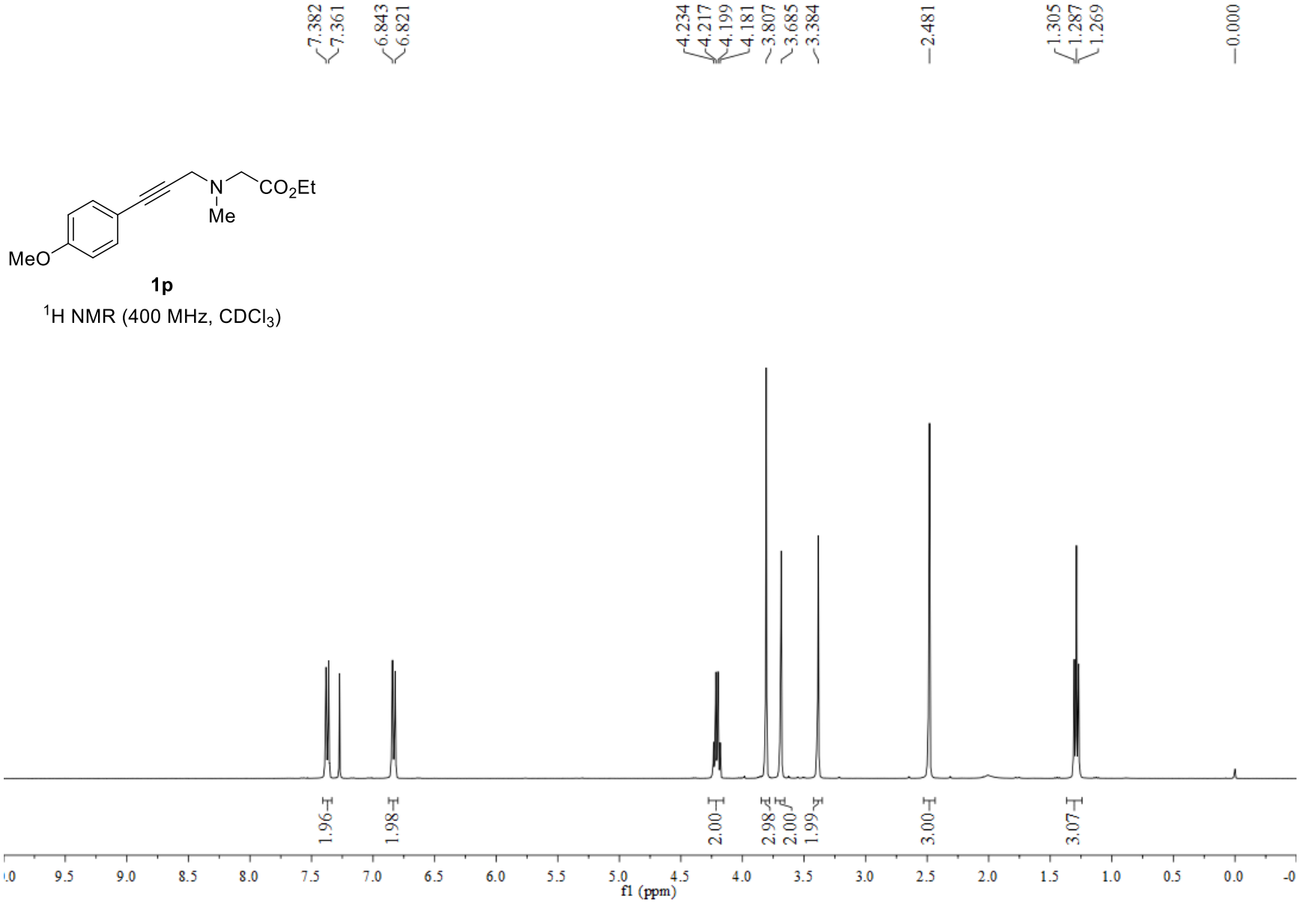
1o

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



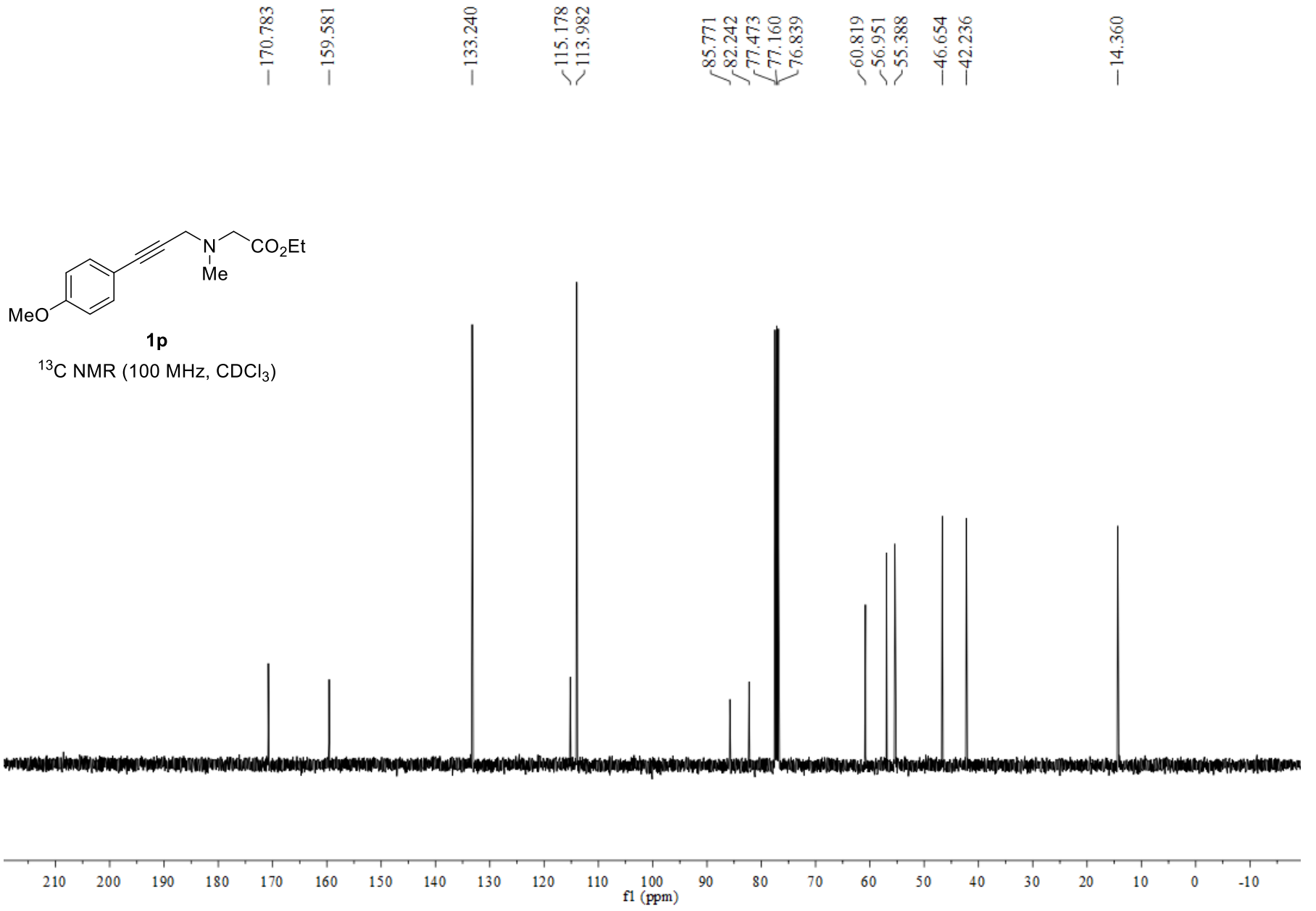
1o

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



1p

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


170.783
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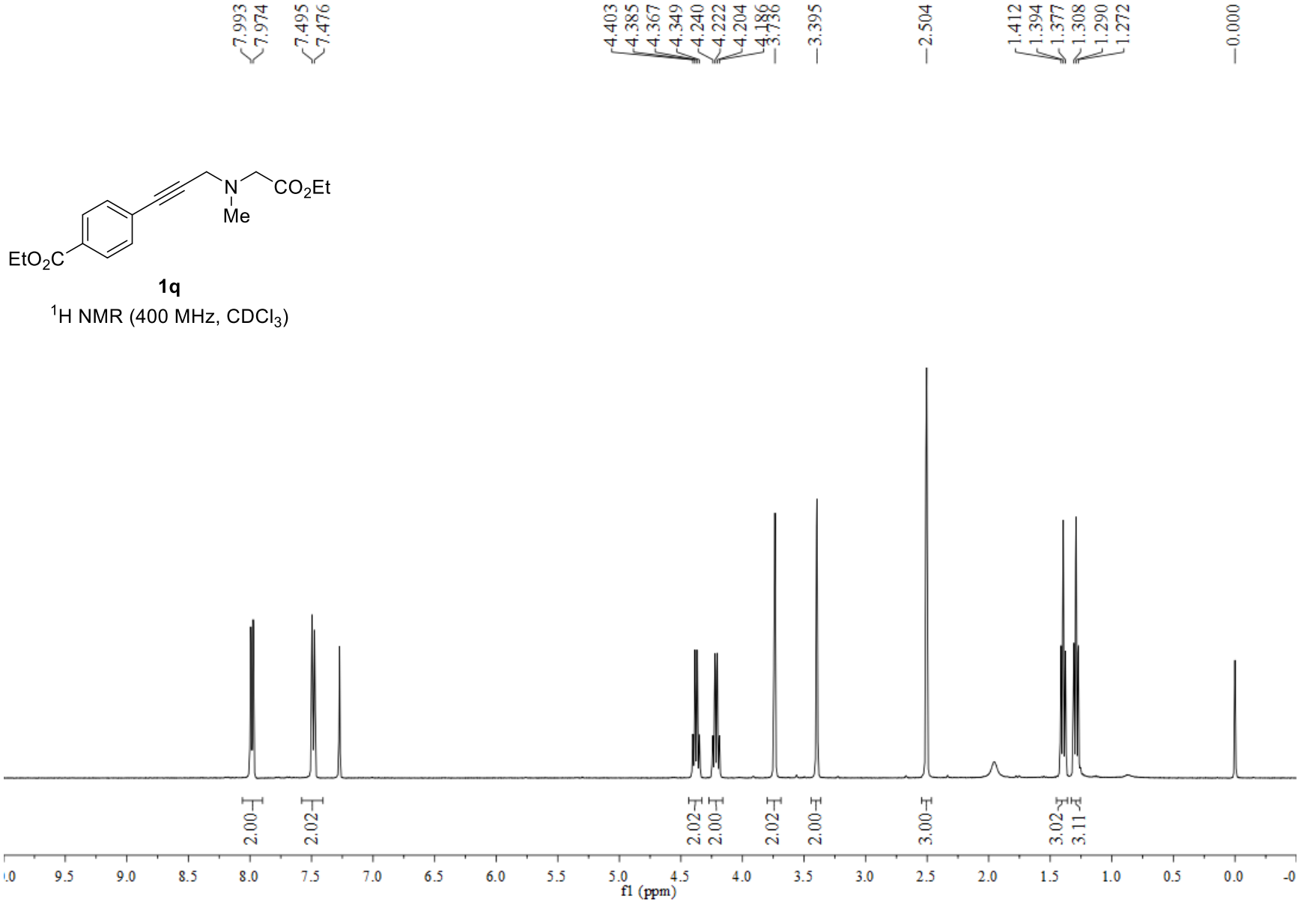
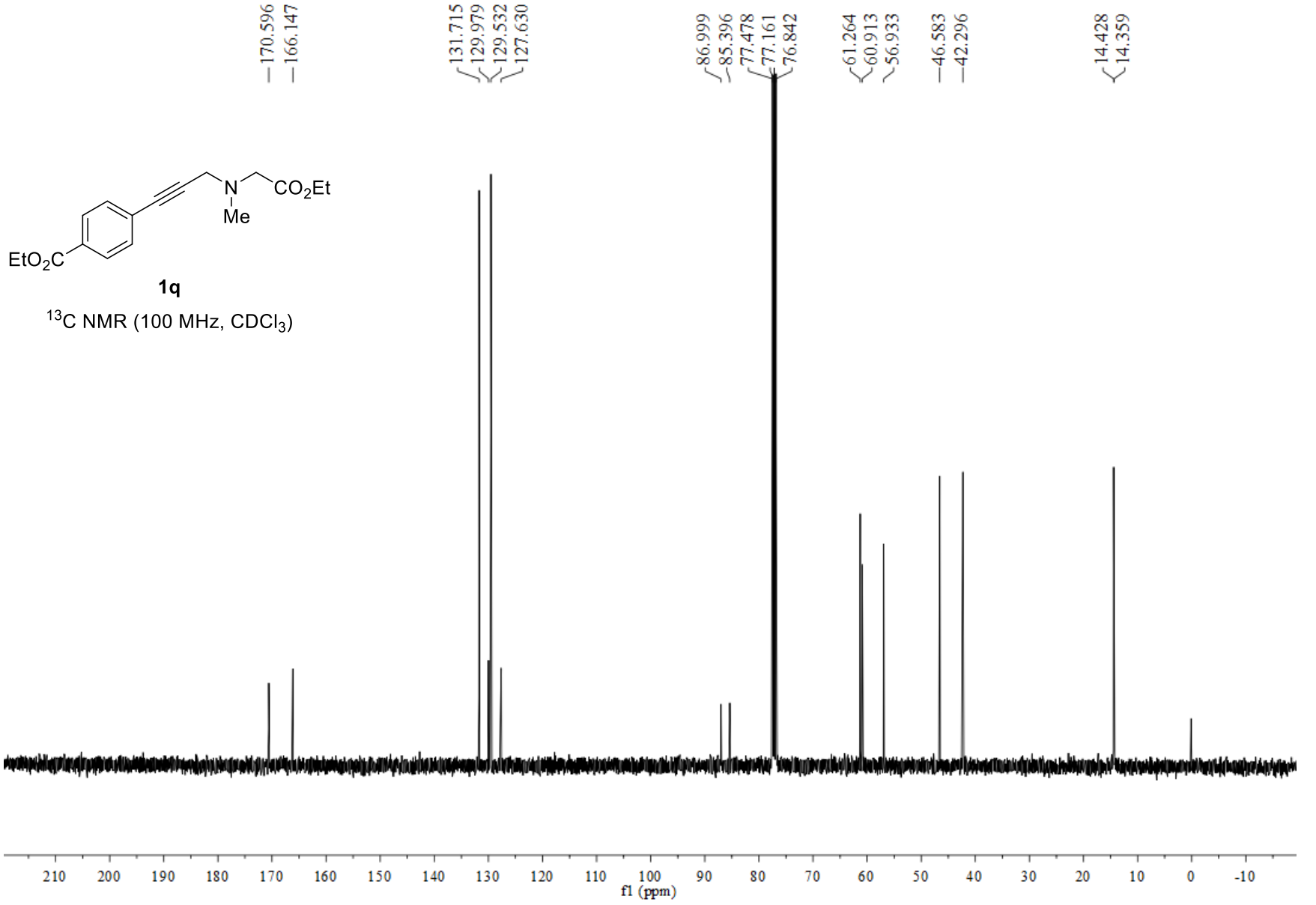
133.240
115.178
113.982
85.771
82.242
77.473
77.160
76.839
60.819
56.951
55.388
46.654
42.236
14.360
N
CO2Et
Me
MeO
1p
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



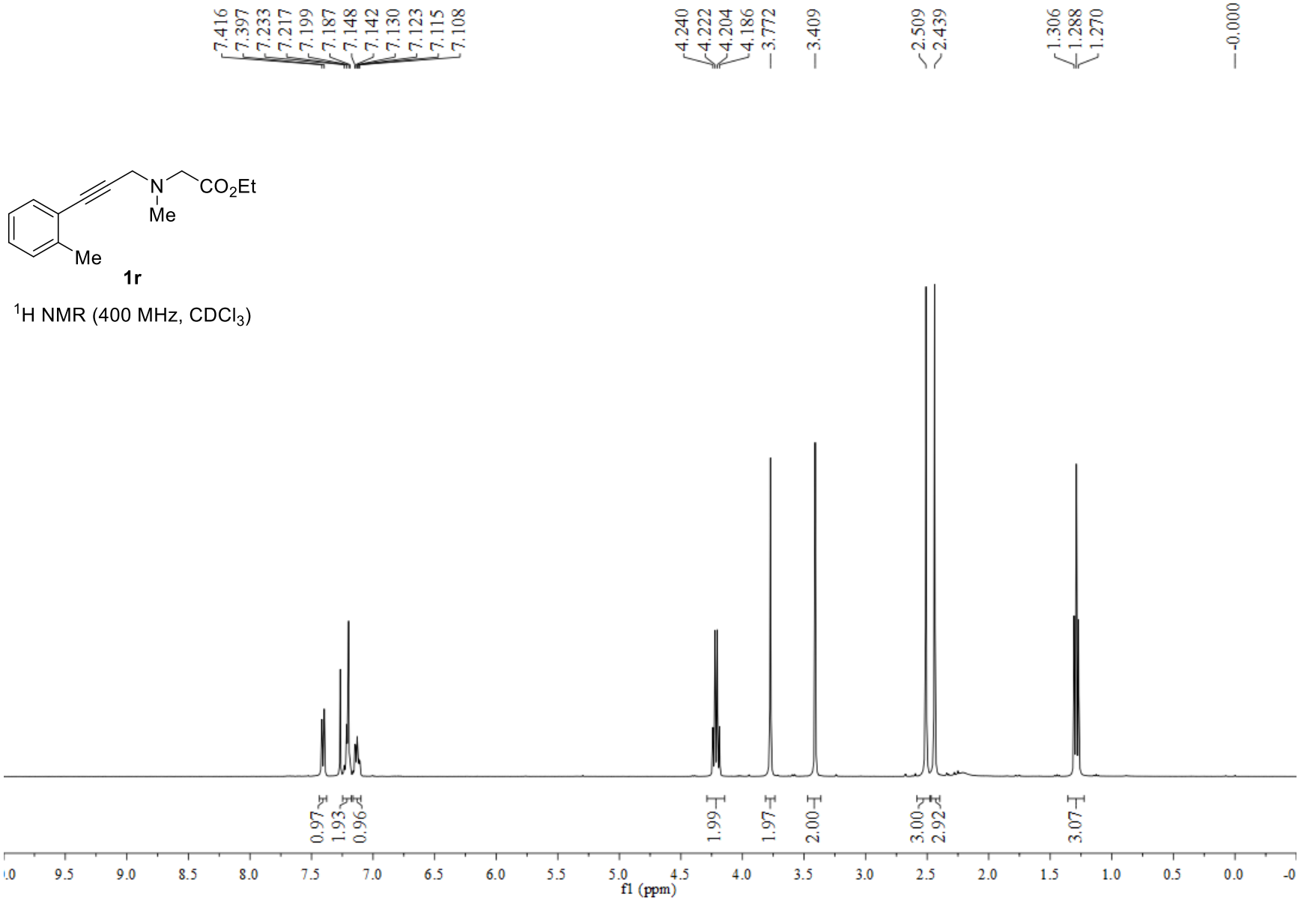
1q

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



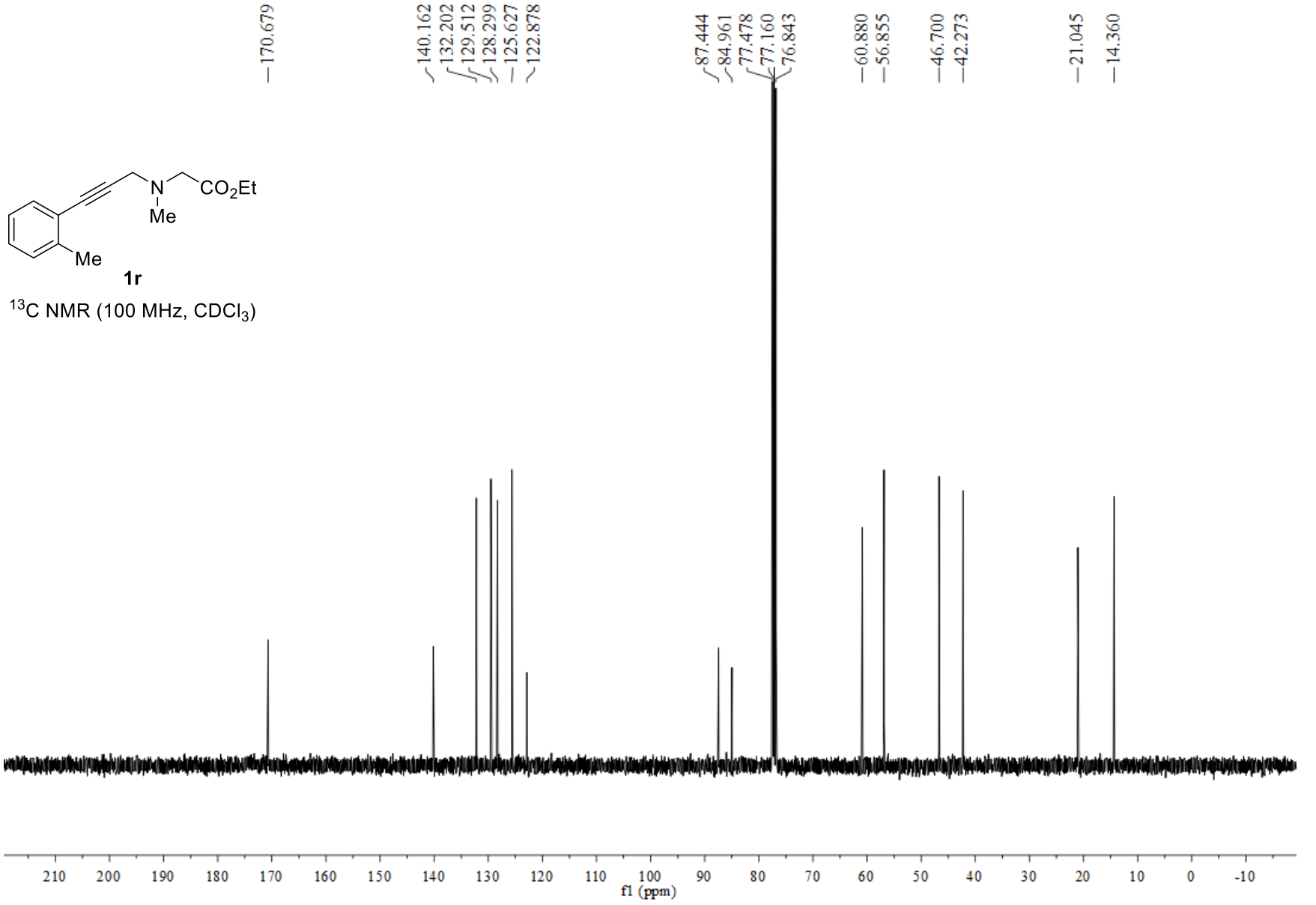
1q

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



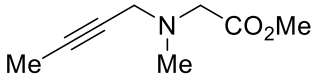
1r

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



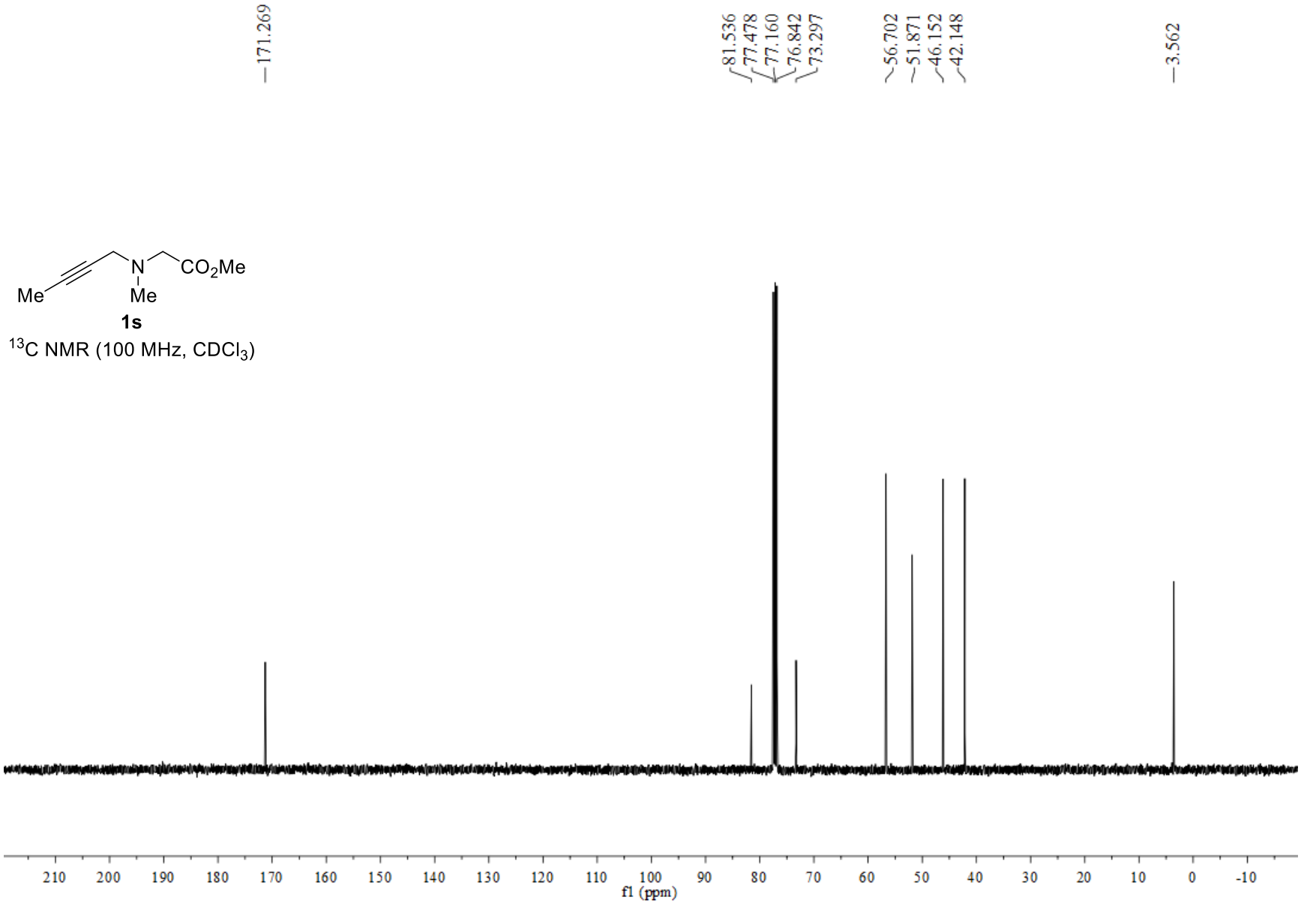
1r

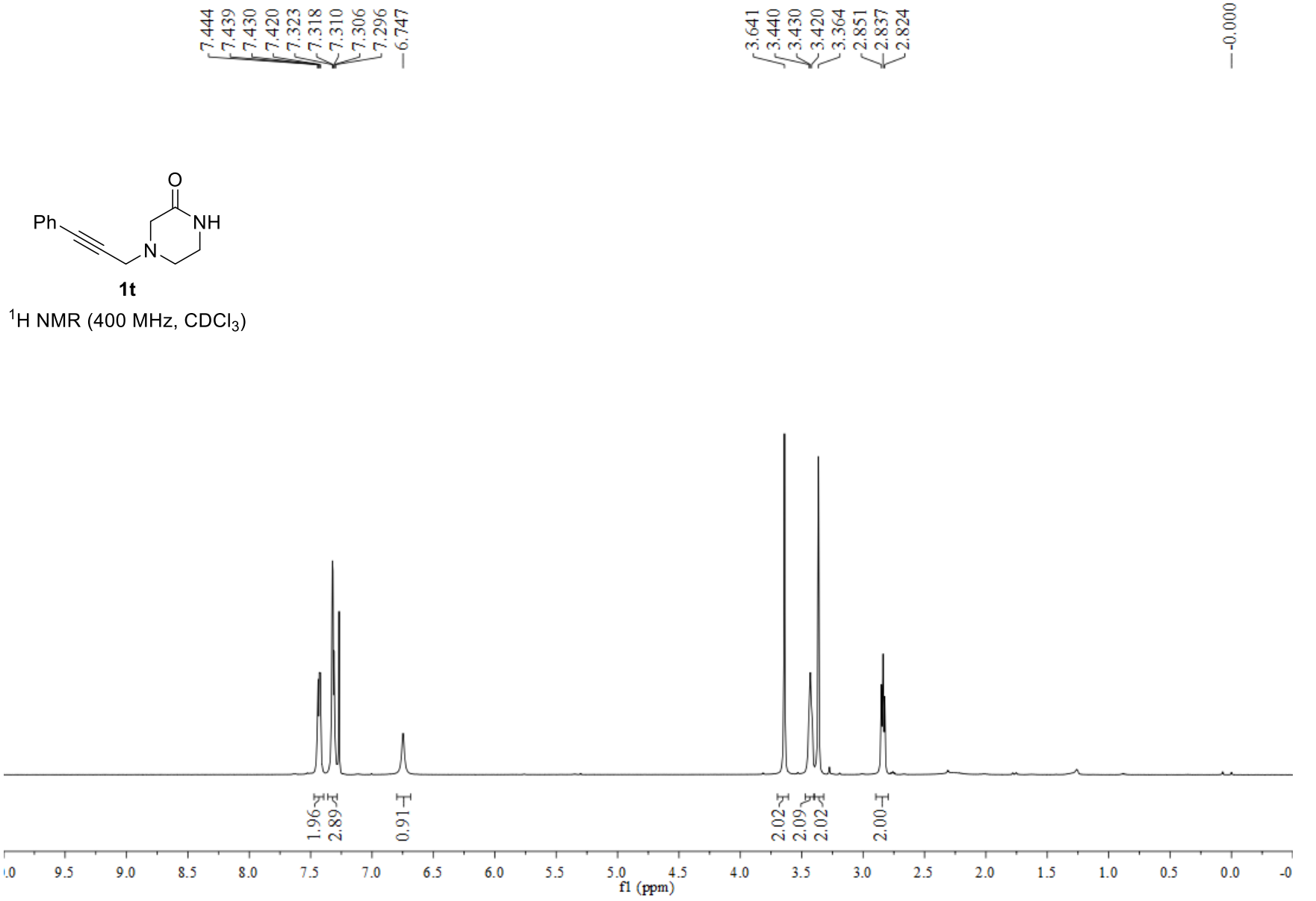
^{13}C NMR (100 MHz, $CDCl_3$)



1s

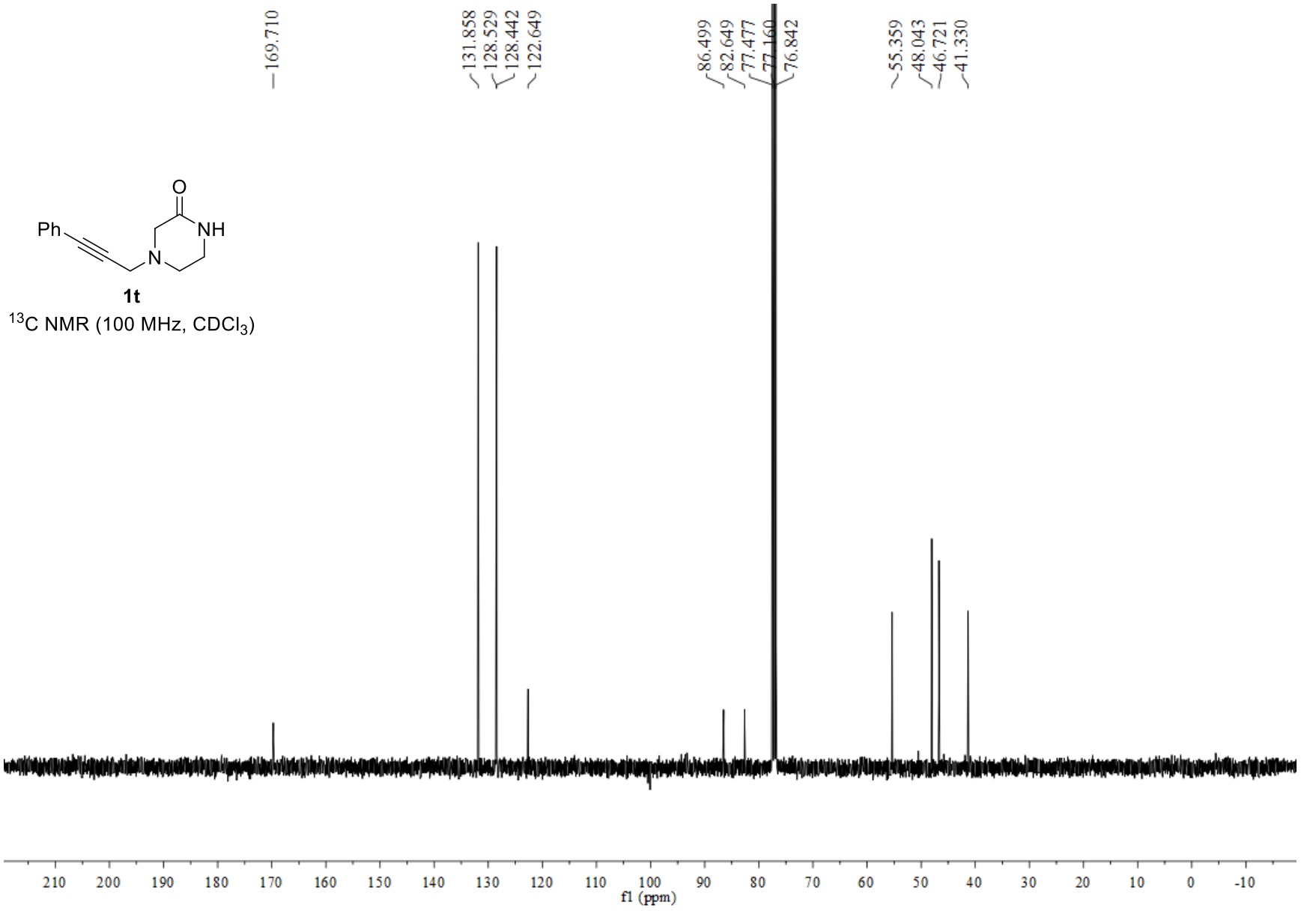
^{1}H NMR (400 MHz, $CDCl_3$)

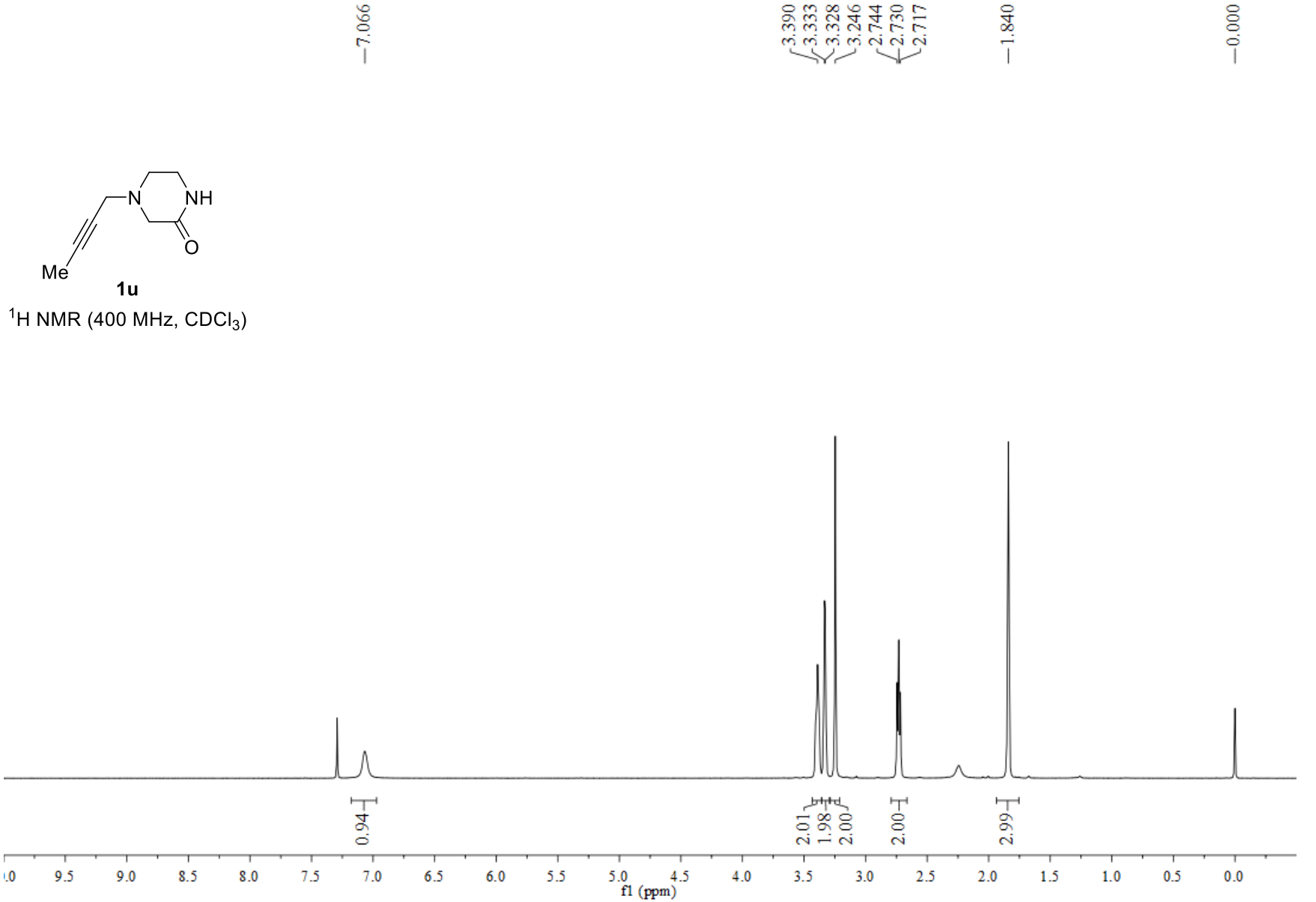

171.269
81.536
77.478
77.160
76.842
73.297
56.702
51.871
46.152
42.148
3.562
Me
N
CO2Me
Me
1s
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1t

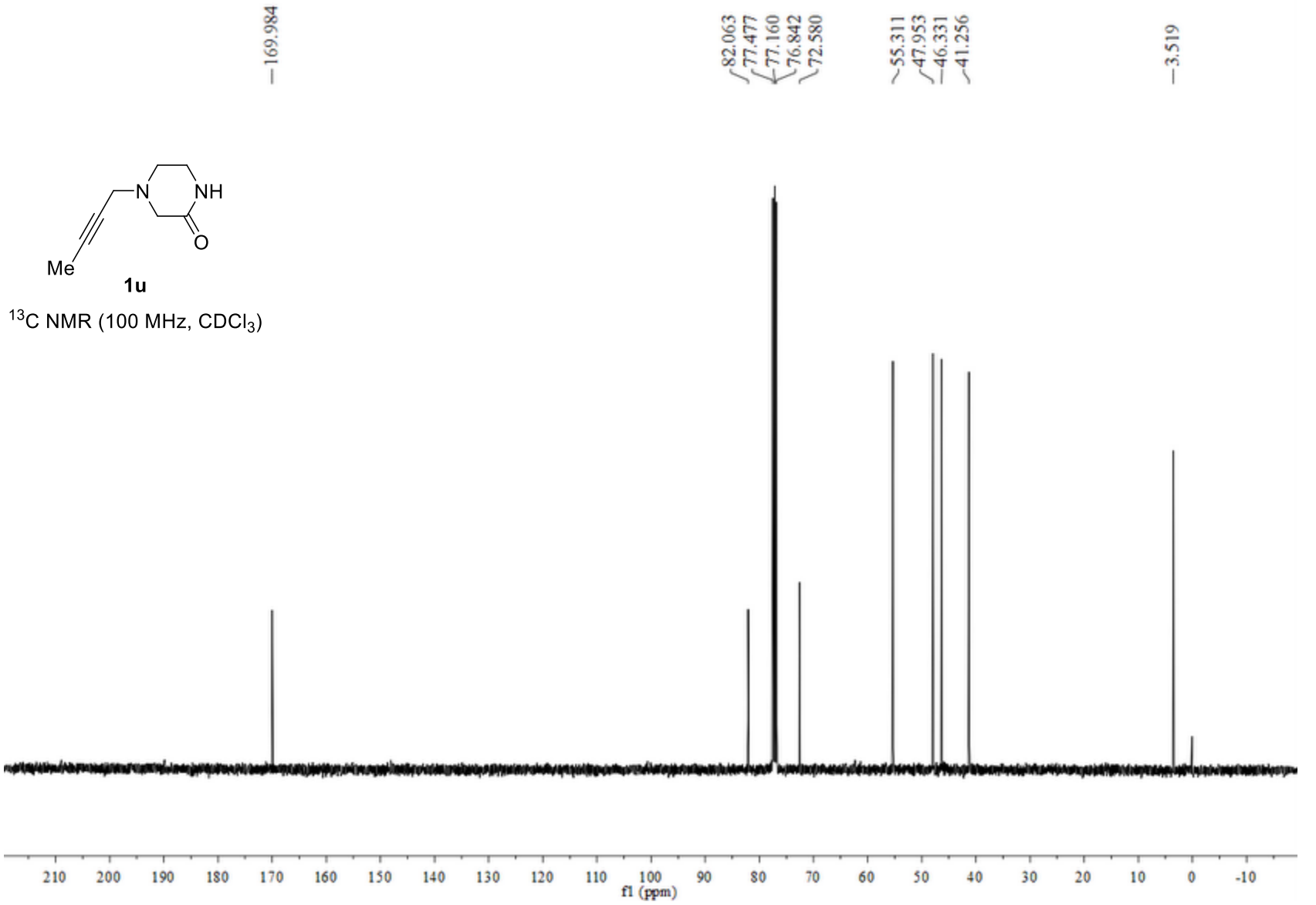
^{1}H NMR (400 MHz, $CDCl_3$)


169.710
131.858
128.529
128.442
122.649
86.499
82.649
77.477
77.160
76.842
55.359
48.043
46.721
41.330
O
NH
Ph
N
1t
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



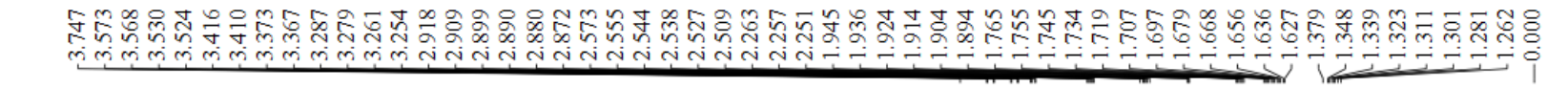
1u

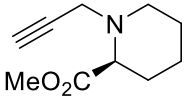
^{1}H NMR (400 MHz, $CDCl_3$)



1u

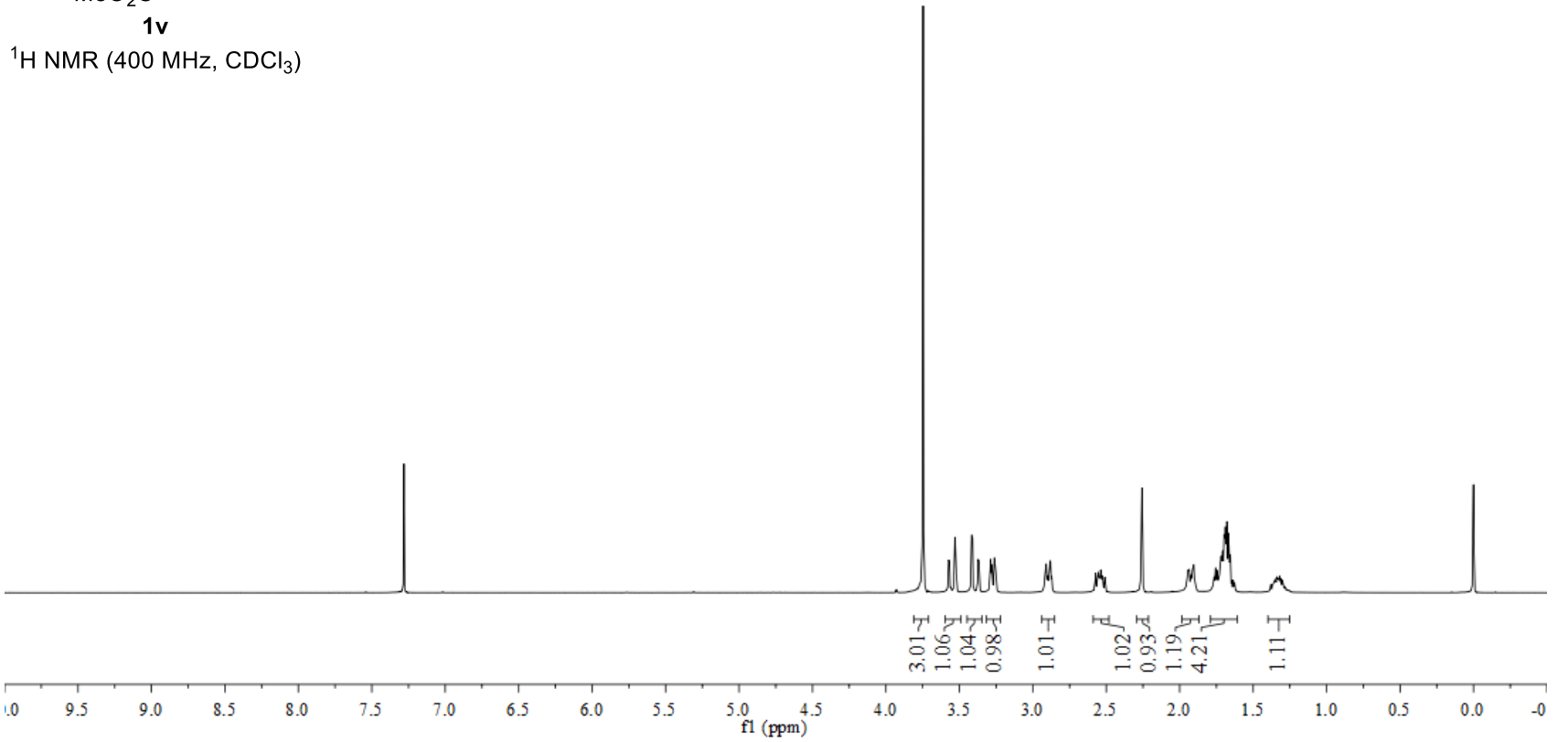
^{13}C NMR (100 MHz, $CDCl_3$)

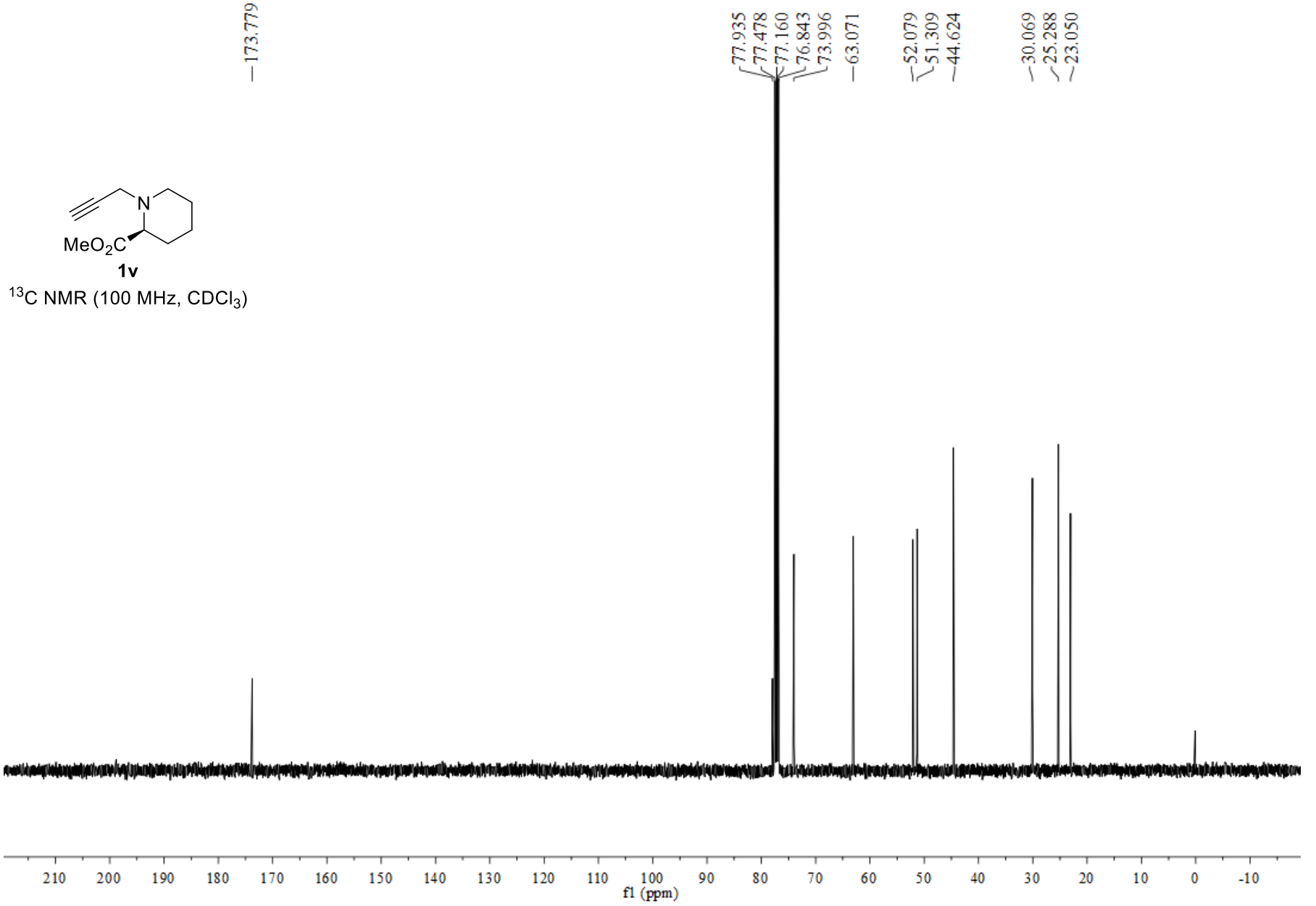


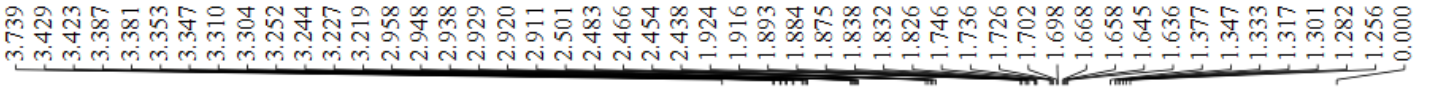


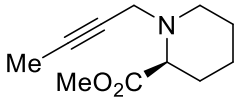
1v

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



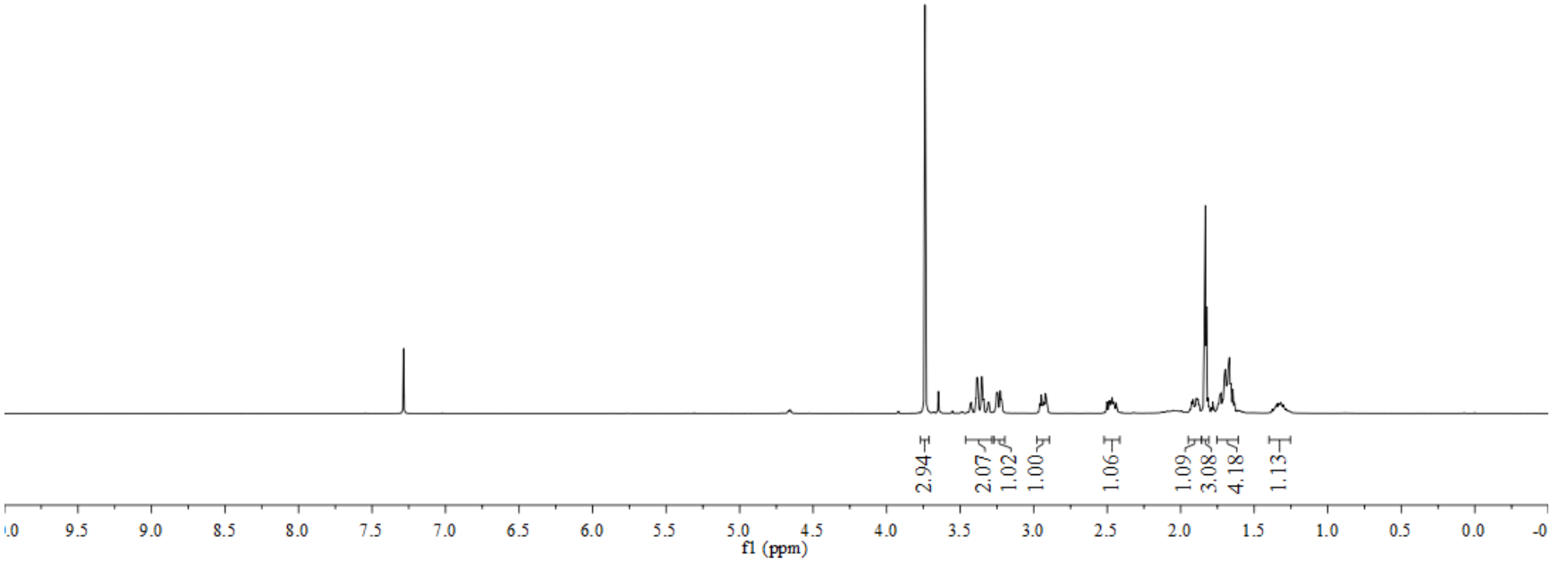

173.779
77.935
77.478
77.160
76.843
73.996
63.071
52.079
51.309
44.624
30.069
25.288
23.050
N
MeO2C
1v
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

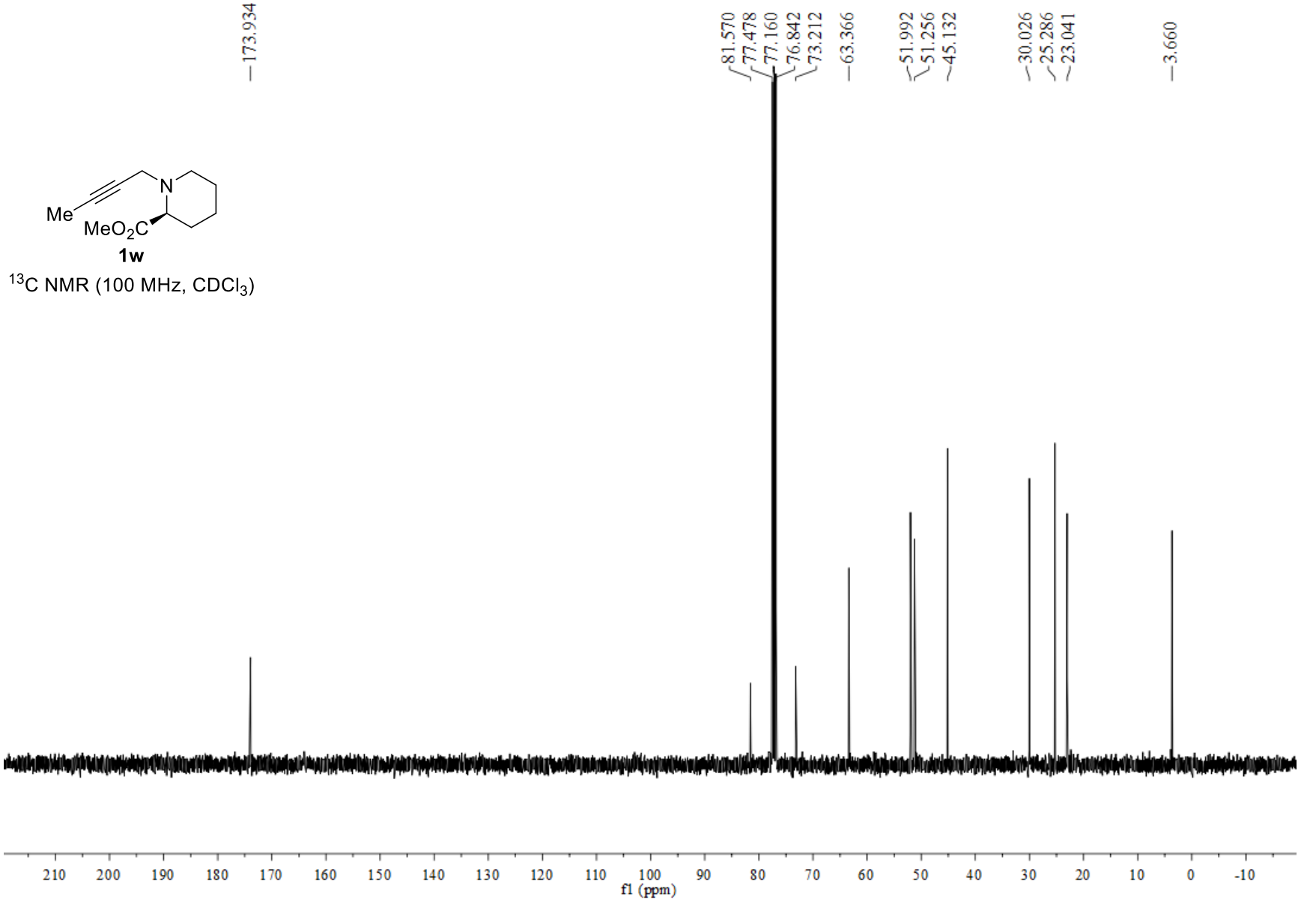




1w

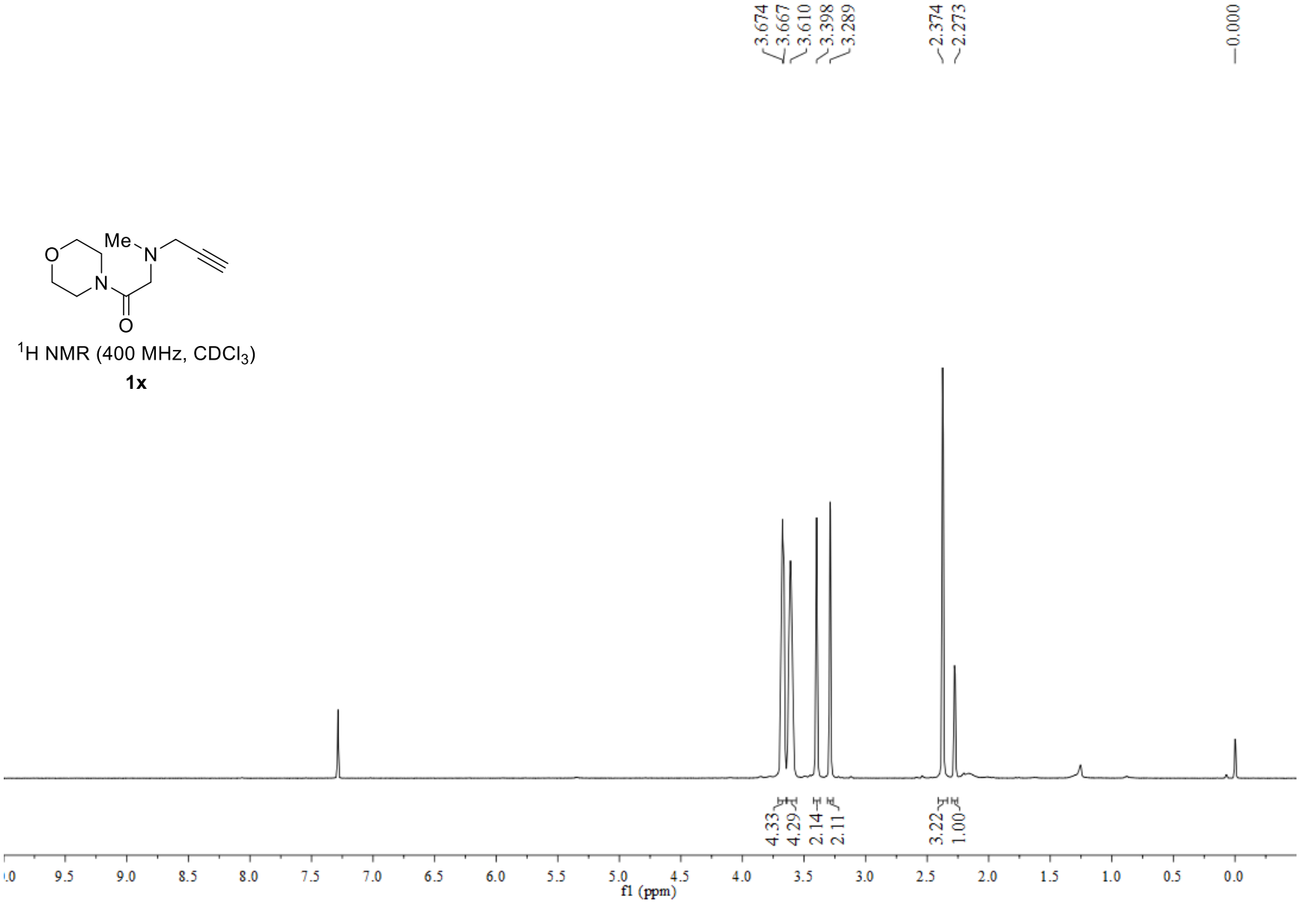
^{1}H NMR (400 MHz, $CDCl_3$)





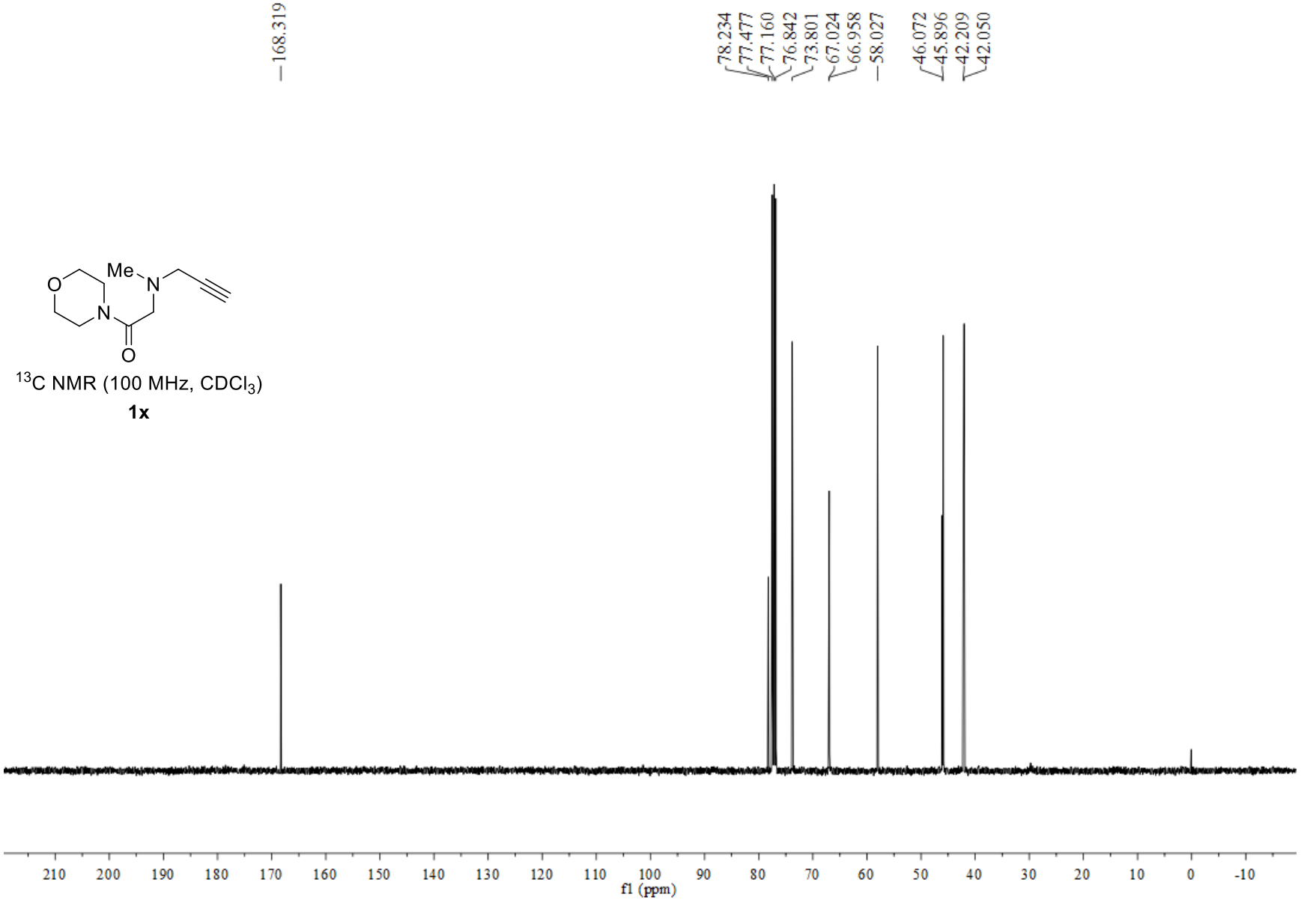
1w

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



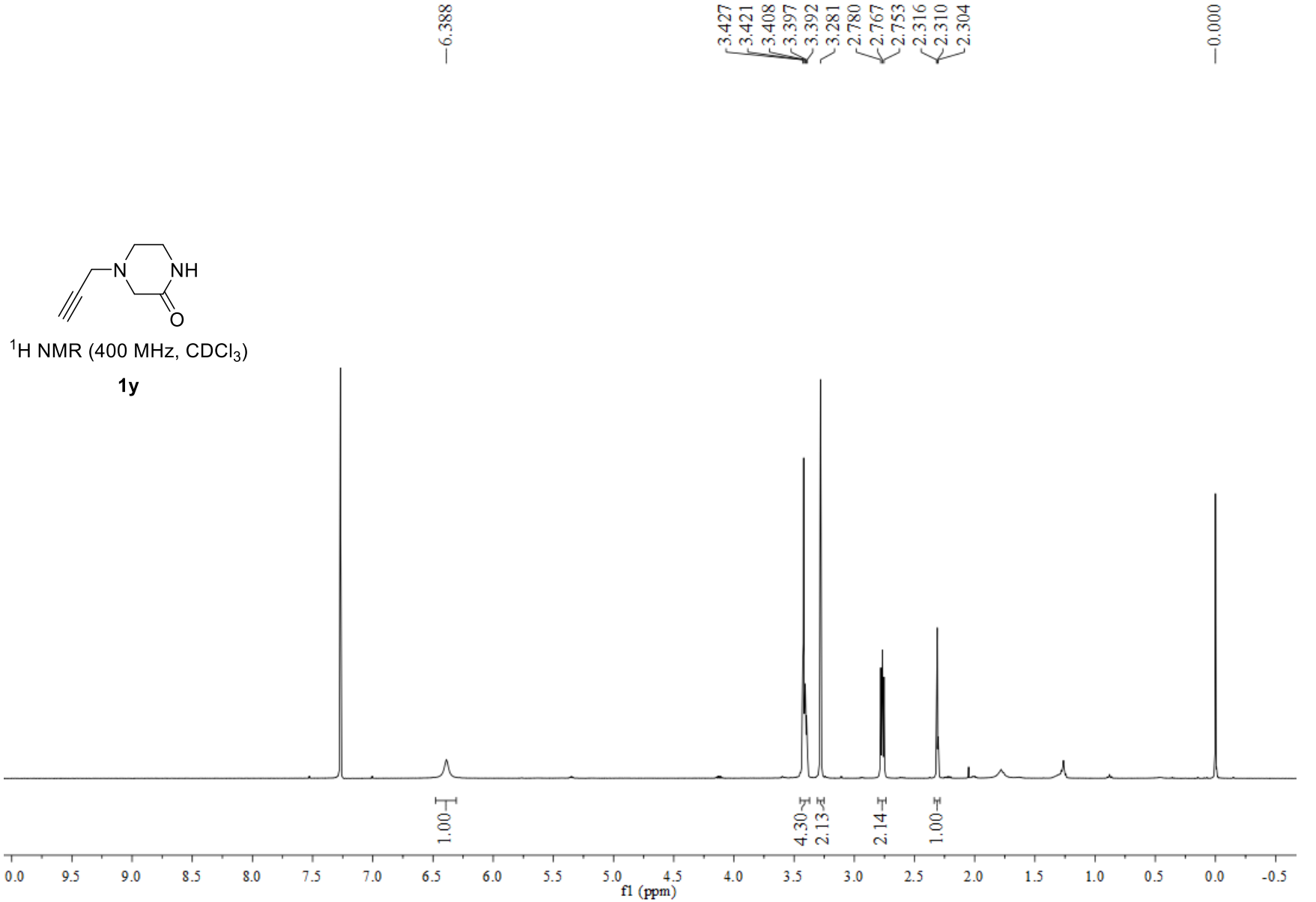
^{1}H NMR (400 MHz, $CDCl_3$)

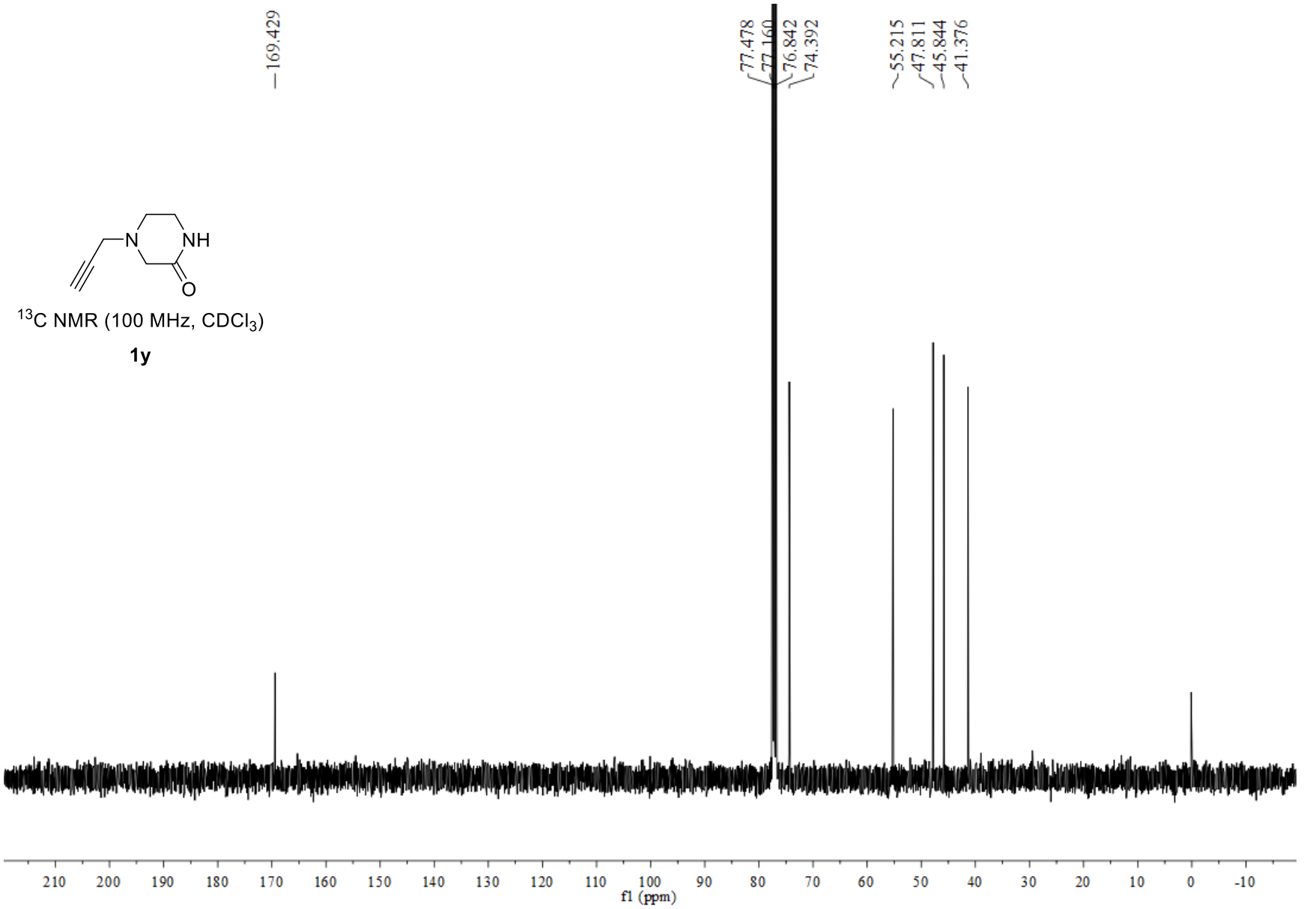
1x



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

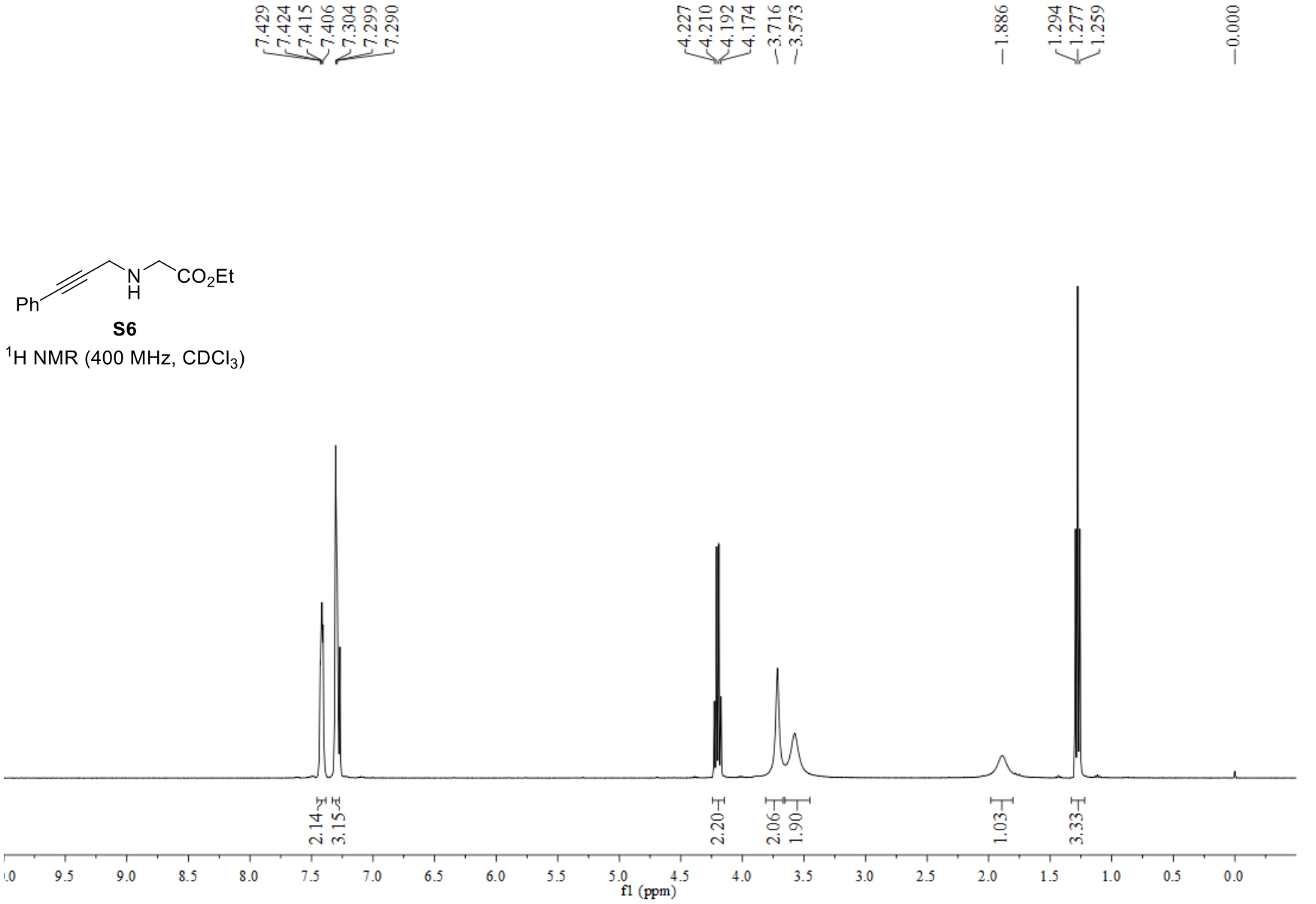
1x


6.388
3.427
3.421
3.408
3.397
3.392
3.281
2.780
2.767
2.753
2.316
2.310
2.304
0.000
N
NH
O
1H NMR (400 MHz, CDCl3)
1y
1.00
4.30
2.13
2.14
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



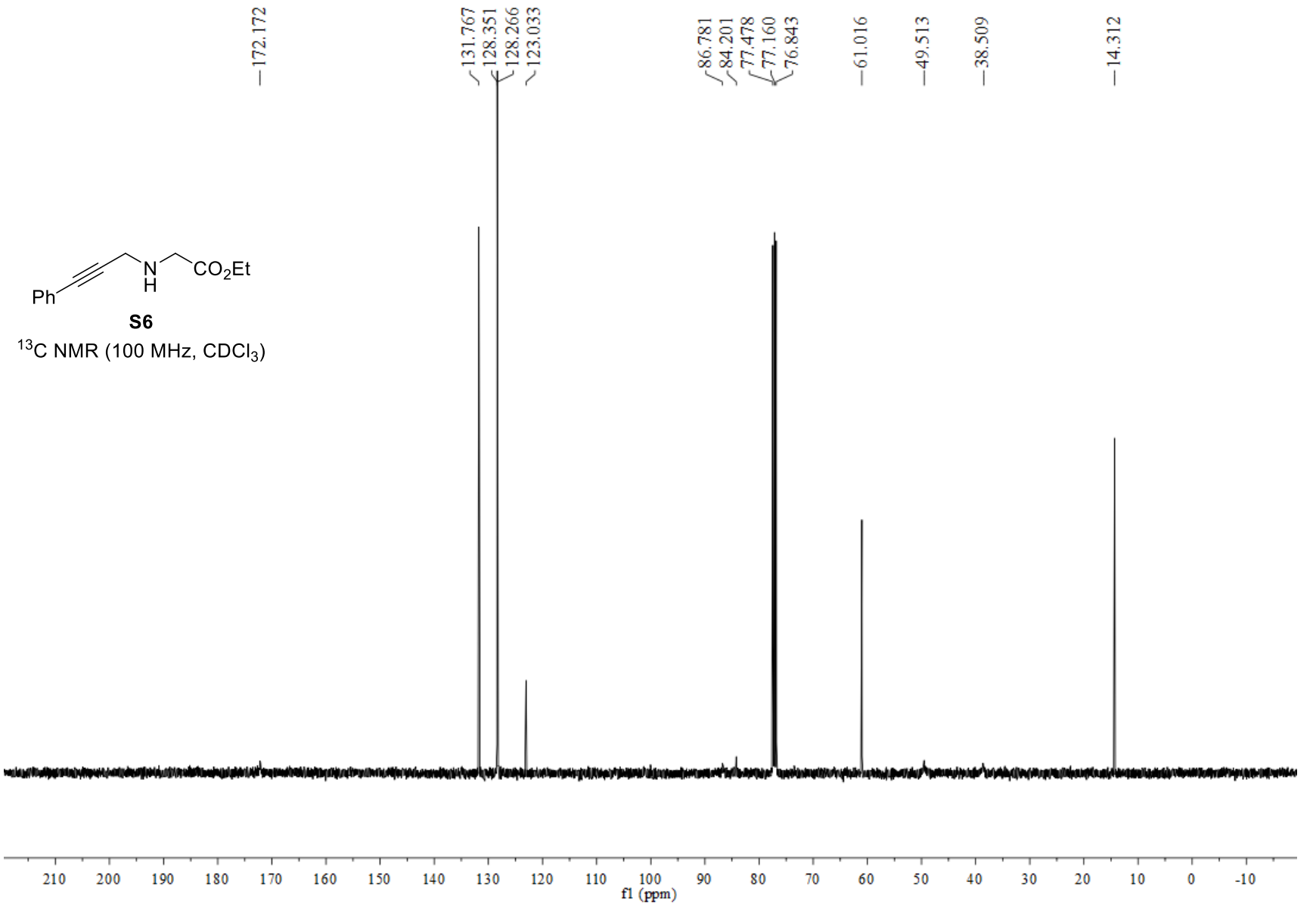
^{13}C NMR (100 MHz, $CDCl_3$)

1y



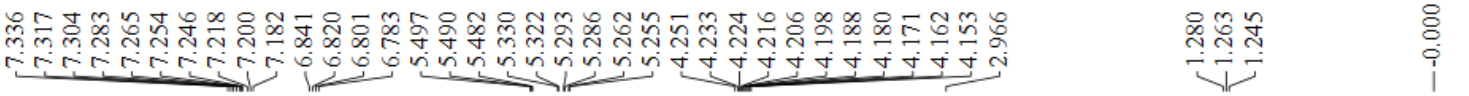
S6

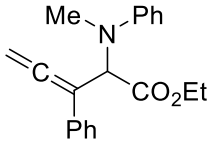
^{1}H NMR (400 MHz, $CDCl_3$)



S6

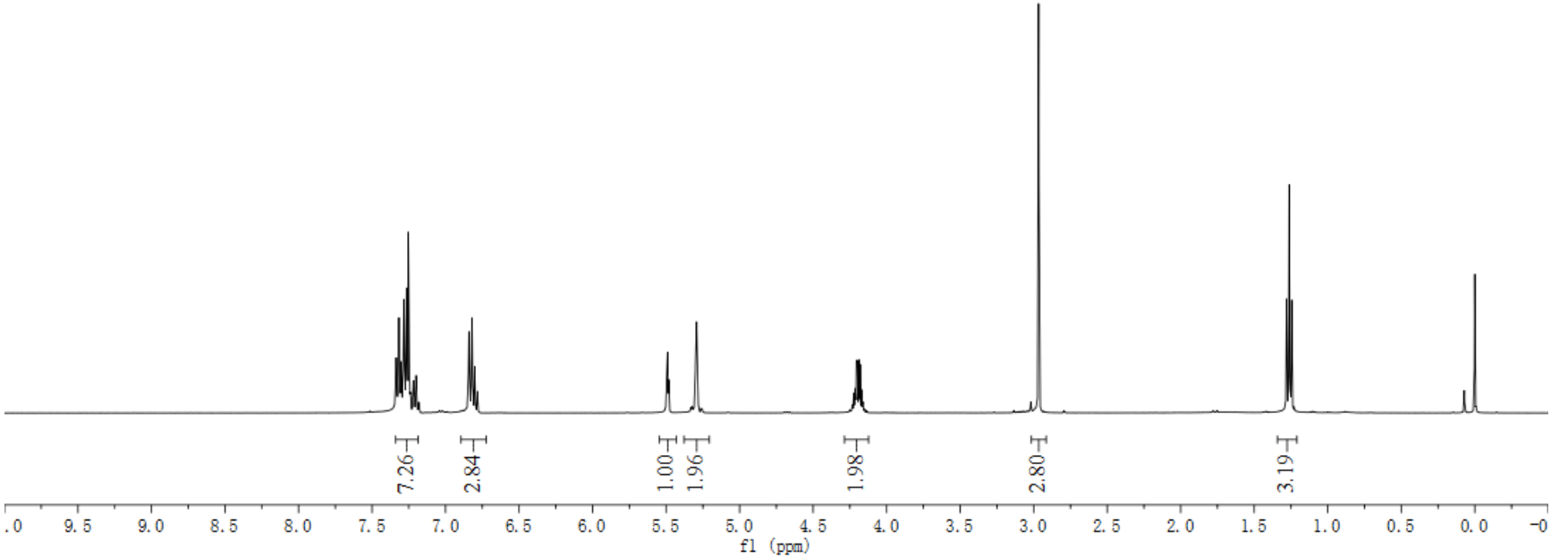
^{13}C NMR (100 MHz, $CDCl_3$)

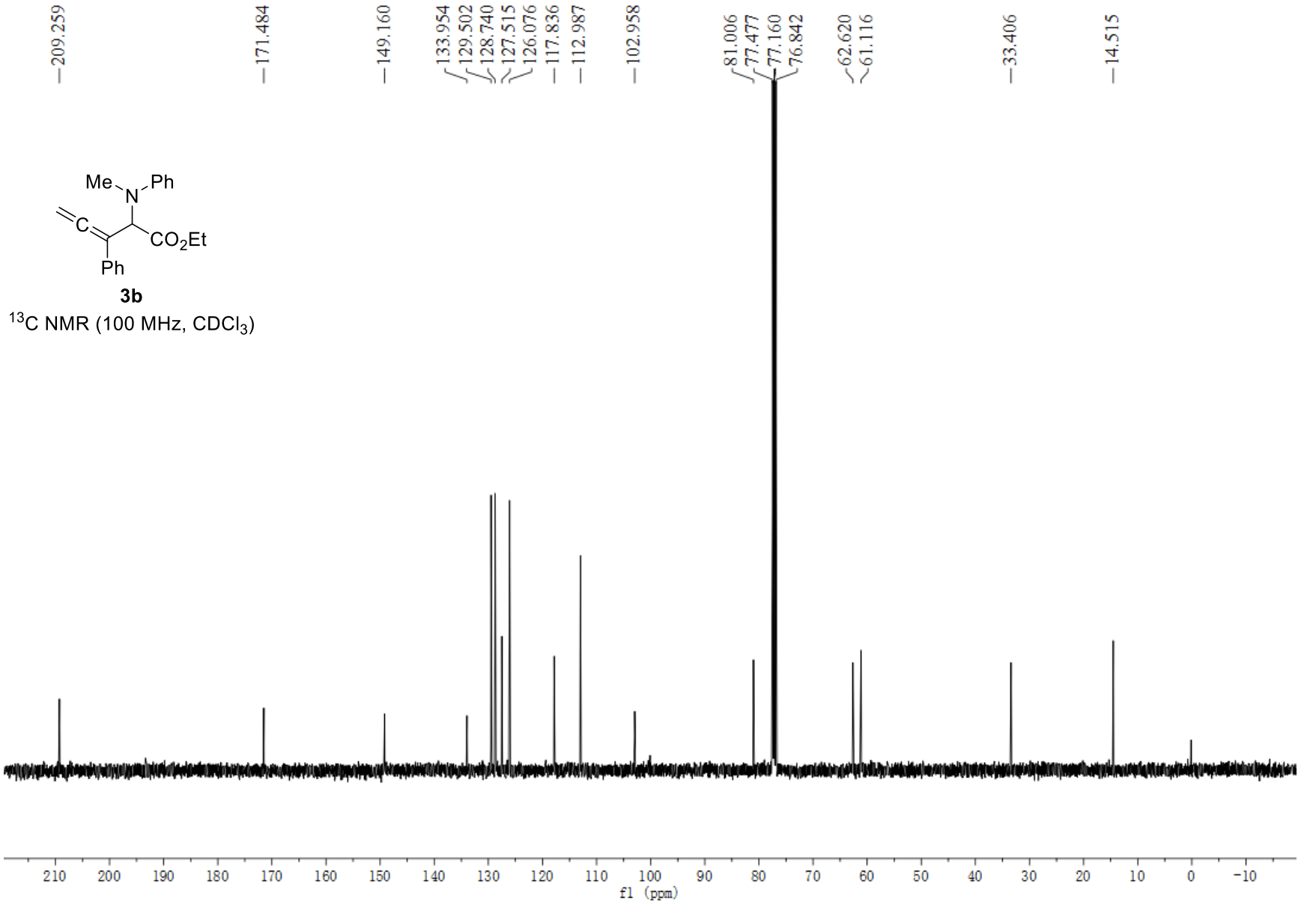




3b

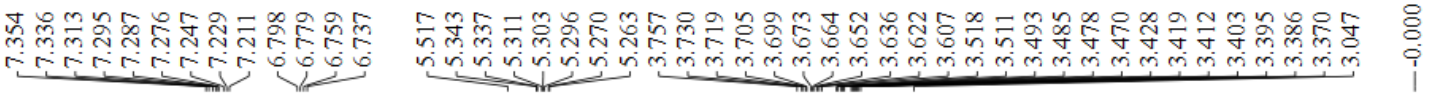
^{1}H NMR (400 MHz, $CDCl_3$)

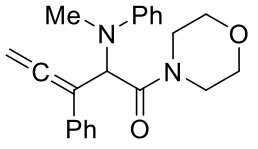




3b

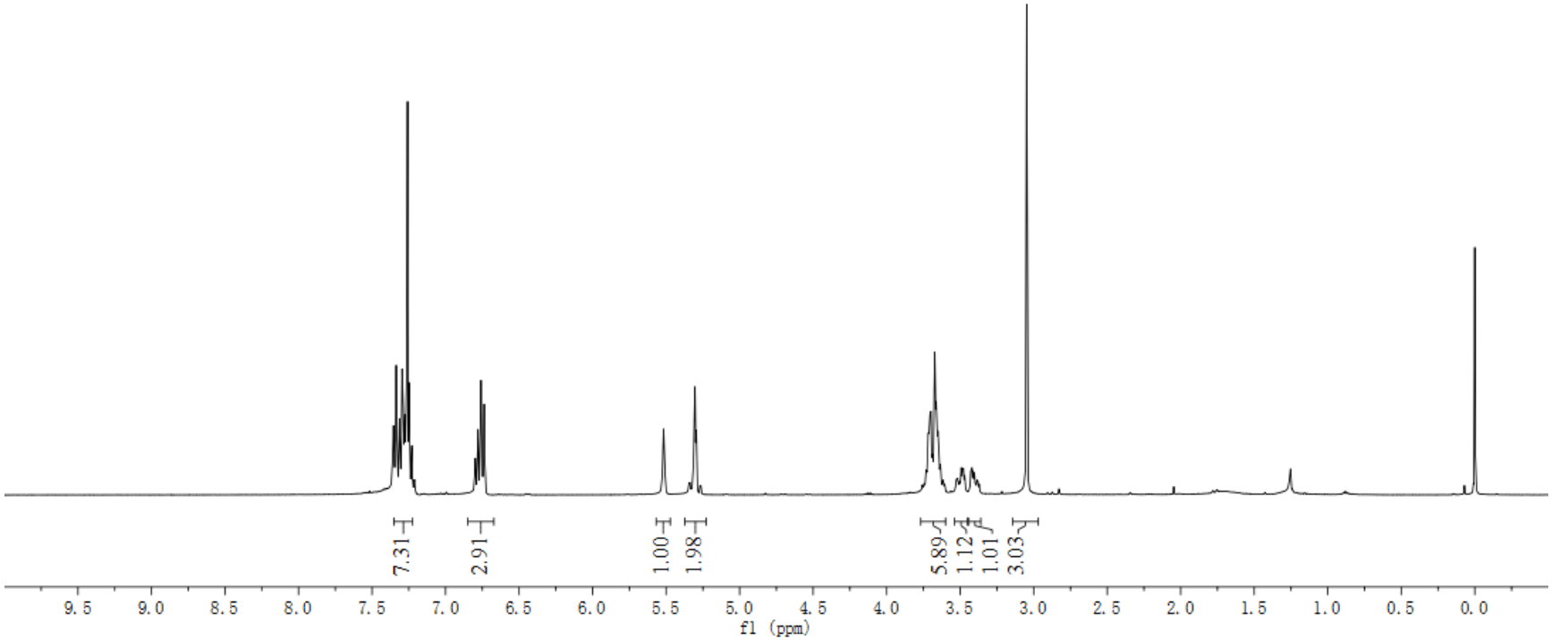
^{13}C NMR (100 MHz, $CDCl_3$)

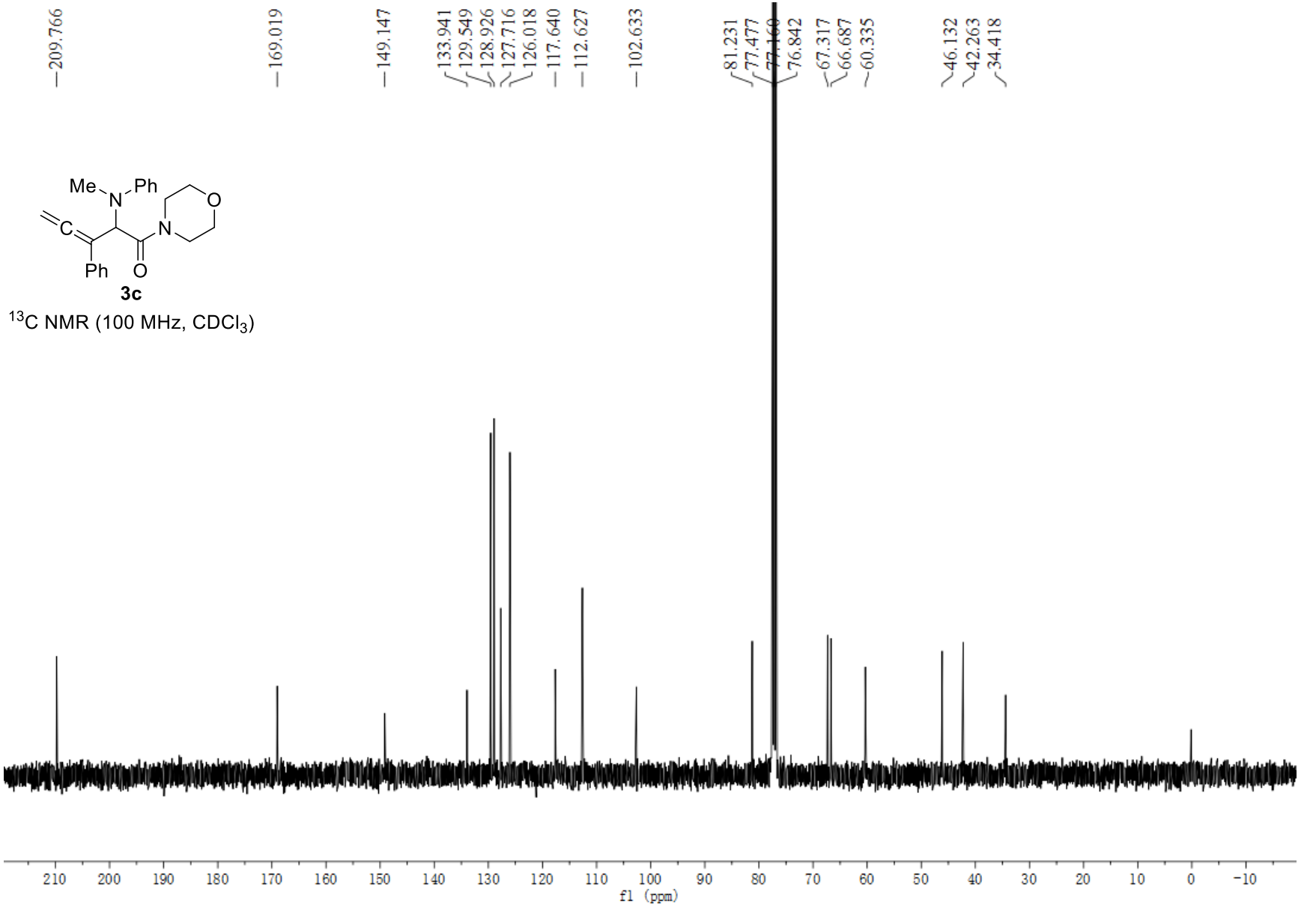




3c

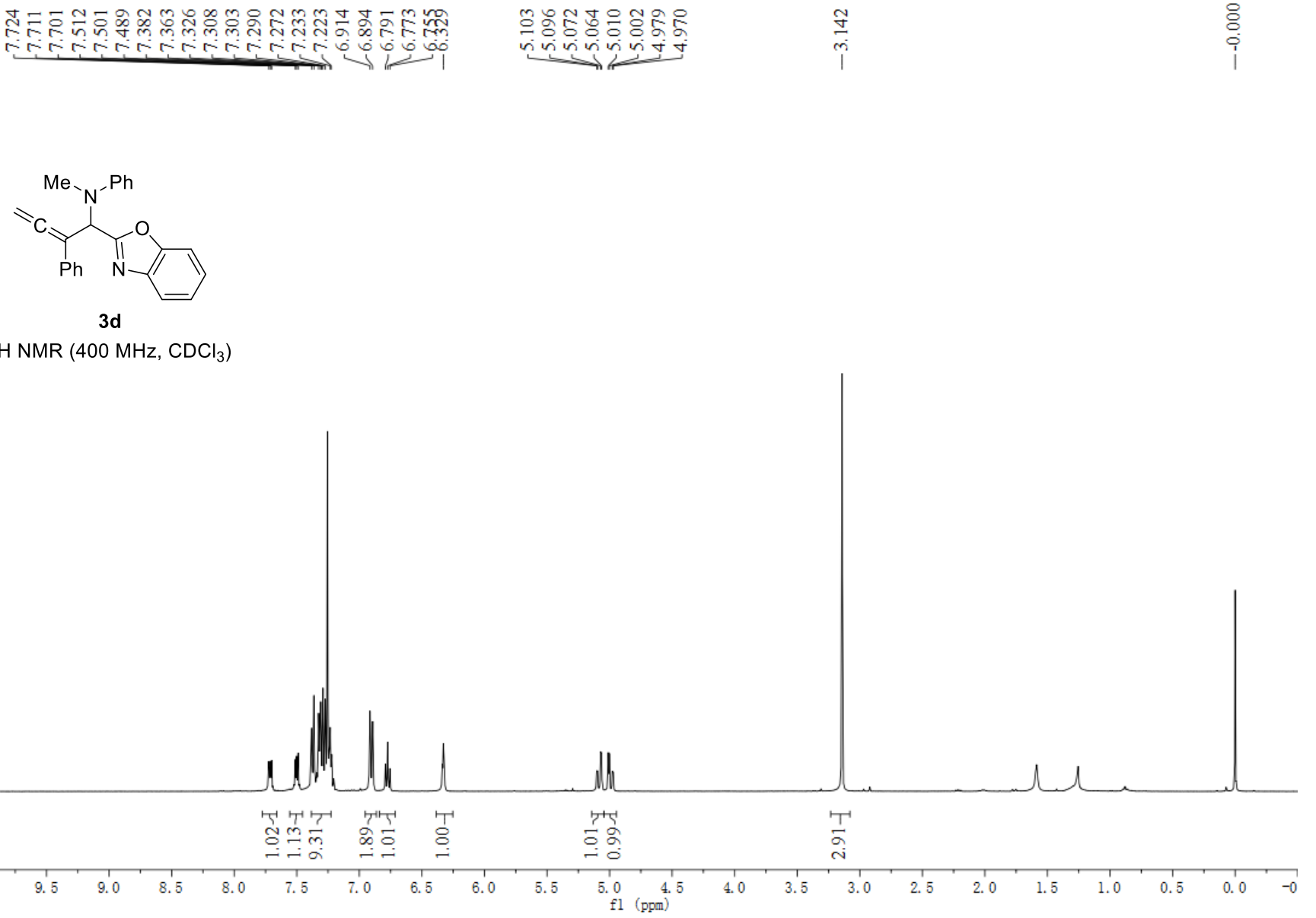
^{1}H NMR (400 MHz, $CDCl_3$)





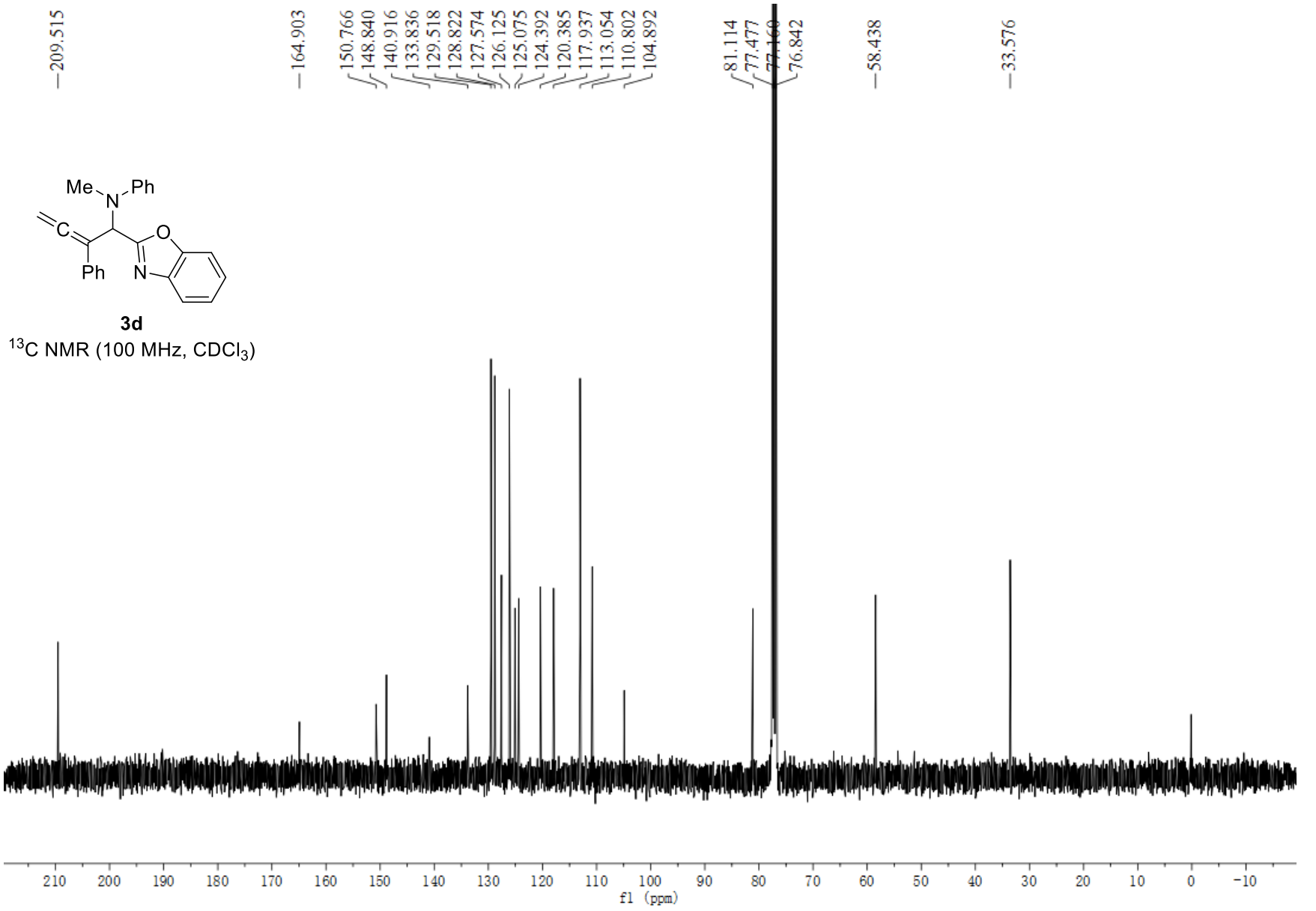
3c

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



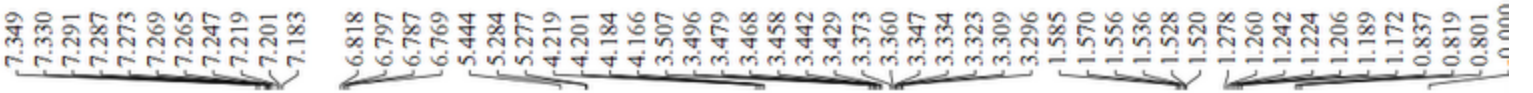
3d

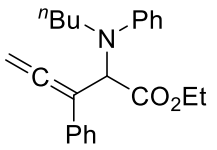
^{1}H NMR (400 MHz, $CDCl_3$)



3d

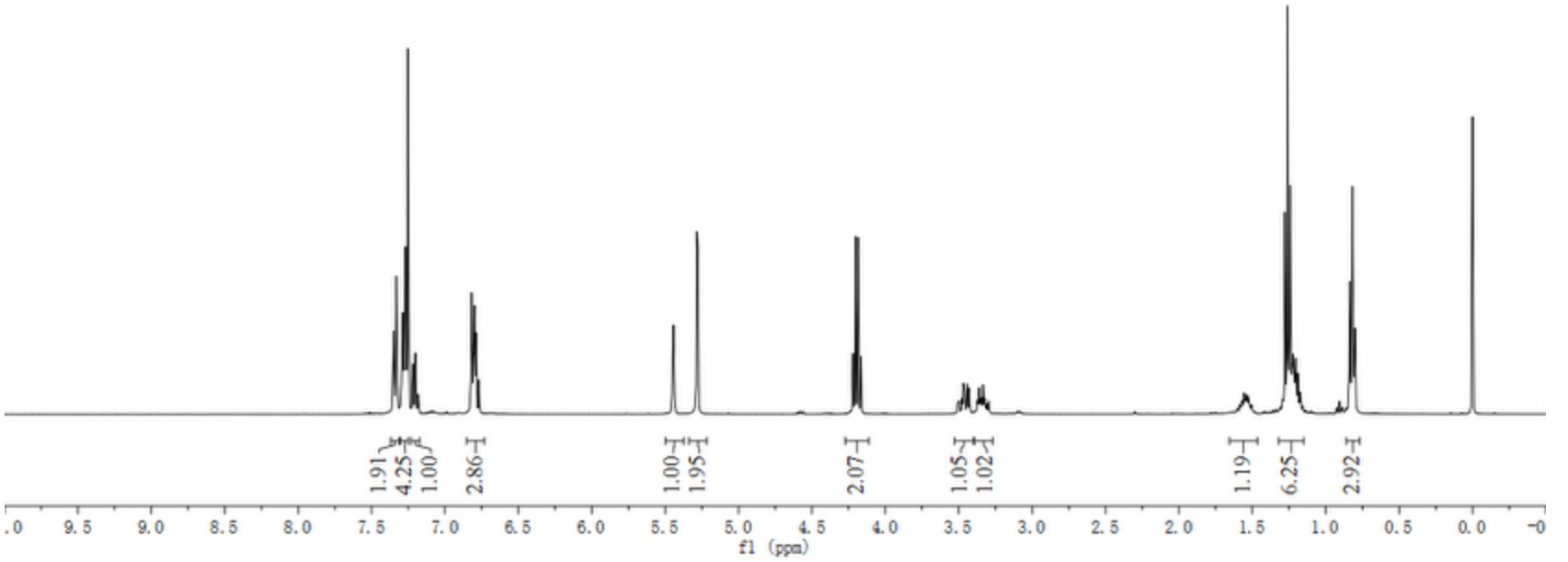
^{13}C NMR (100 MHz, $CDCl_3$)

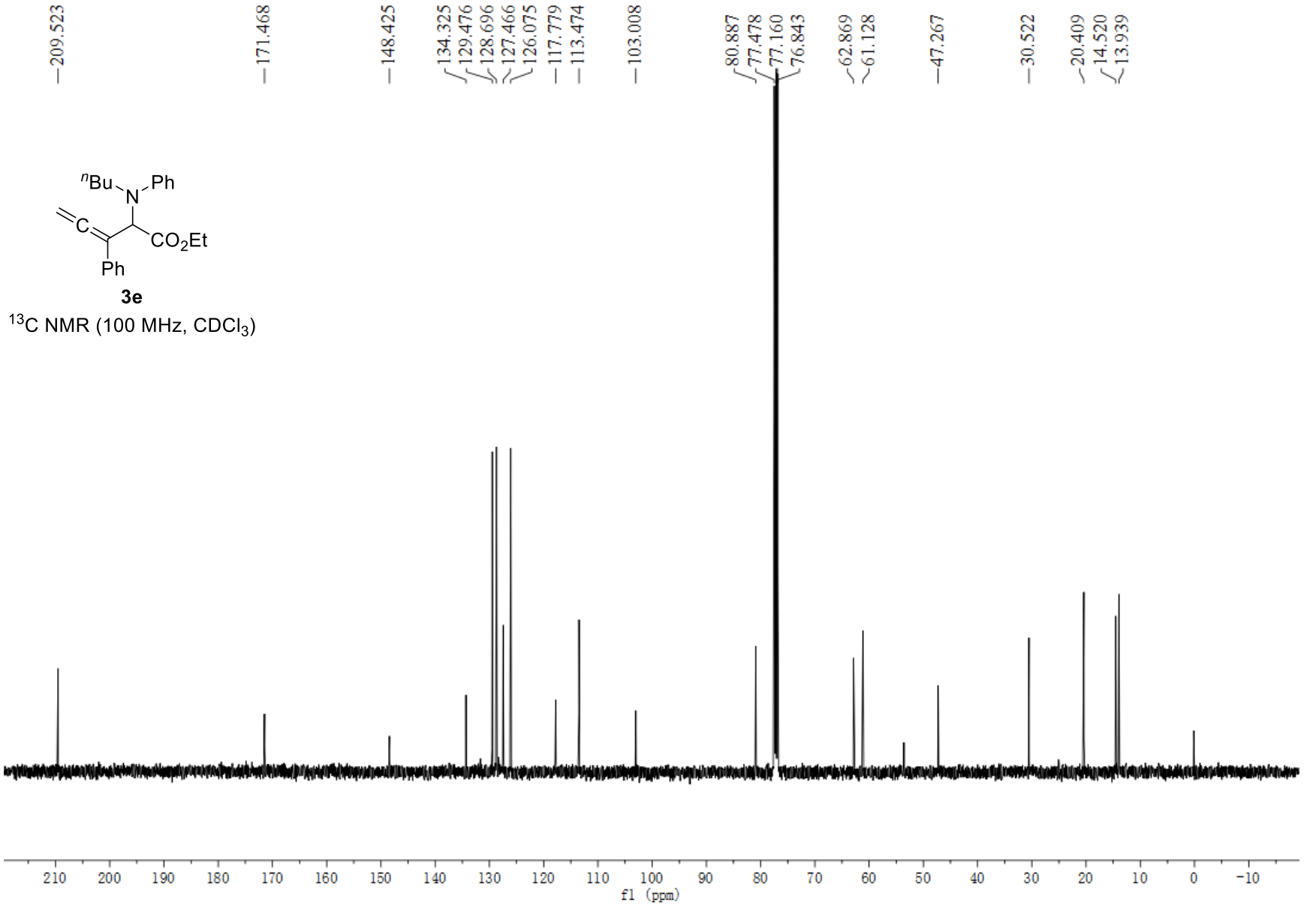




3e

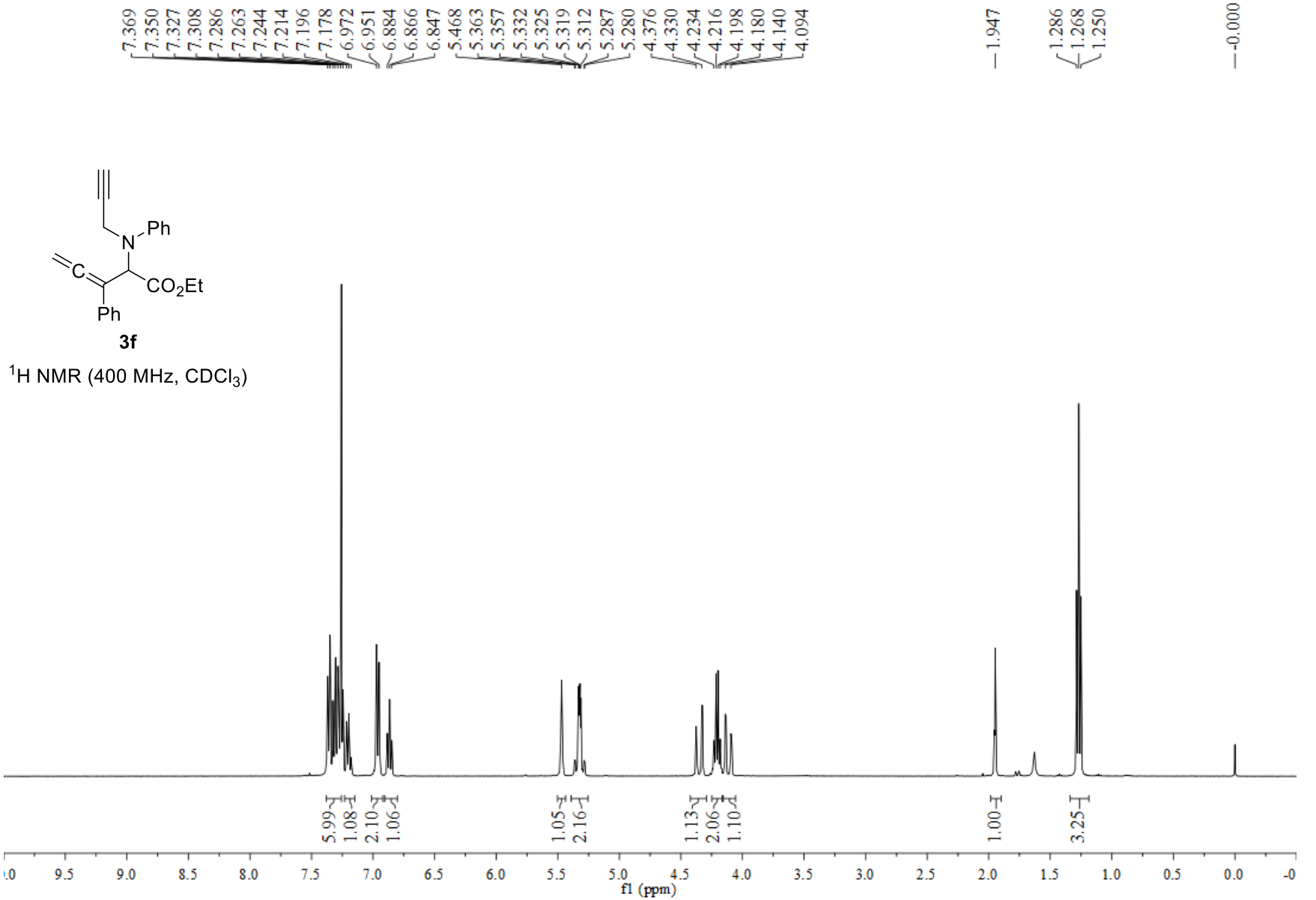
^{1}H NMR (400 MHz, $CDCl_3$)

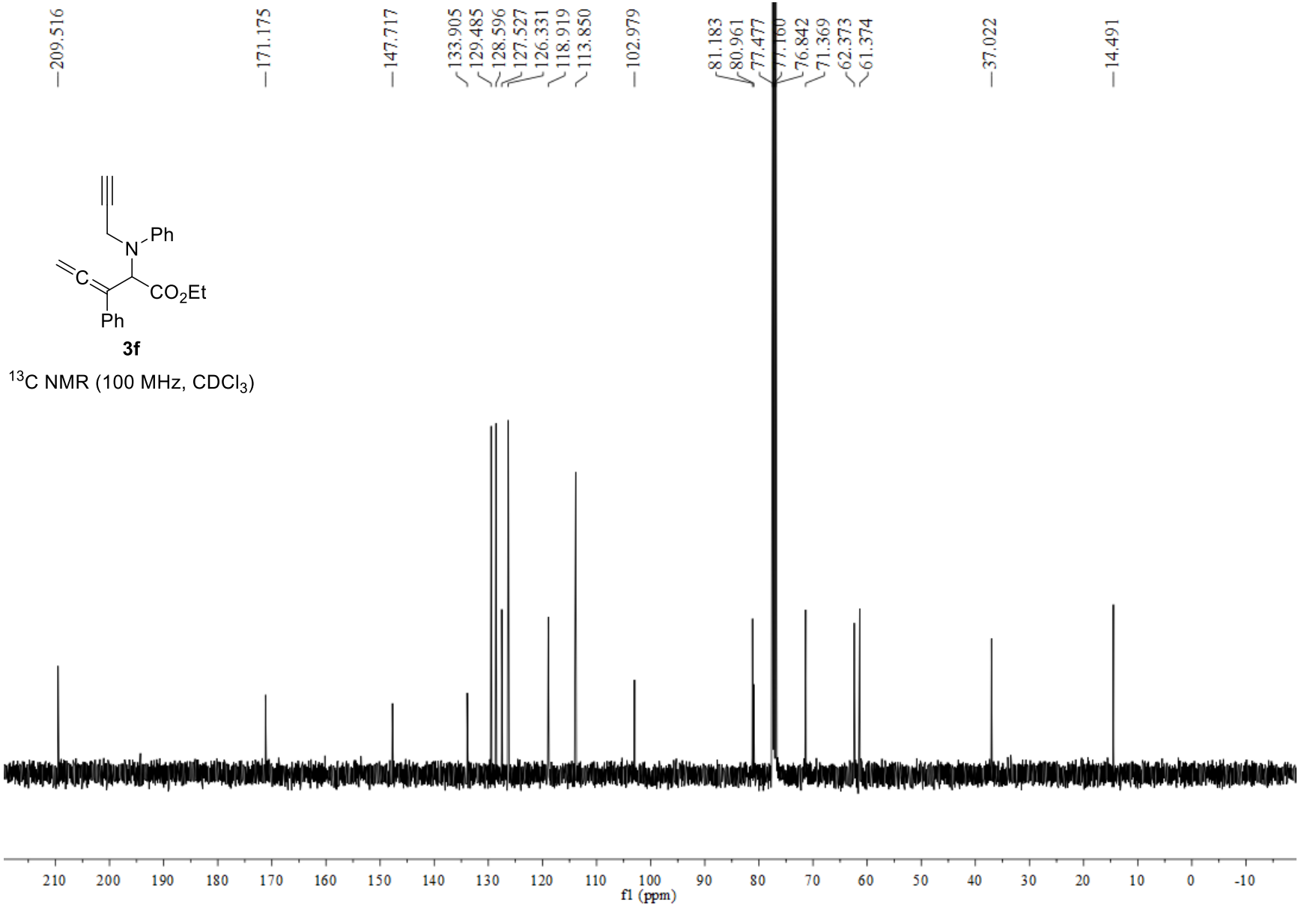




3e

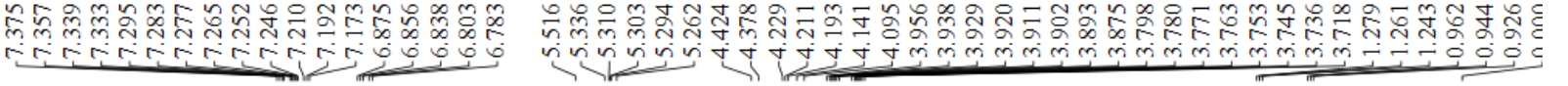
^{13}C NMR (100 MHz, $CDCl_3$)

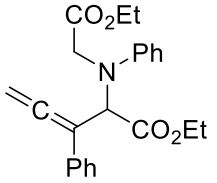

7.369
7.350
7.327
7.308
7.286
7.263
7.244
7.214
7.196
7.178
6.972
6.951
6.884
6.866
6.847
5.468
5.363
5.357
5.332
5.325
5.319
5.312
5.287
5.280
4.376
4.330
4.234
4.216
4.198
4.180
4.140
4.094
1.947
1.286
1.268
1.250
-0.000
Ph
N
C
CO2Et
Ph
3f
1H NMR (400 MHz, CDCl3)
5.99
1.08
2.10
1.06
1.05
2.16
1.13
2.06
1.10
1.00
3.25
f1 (ppm)



3f

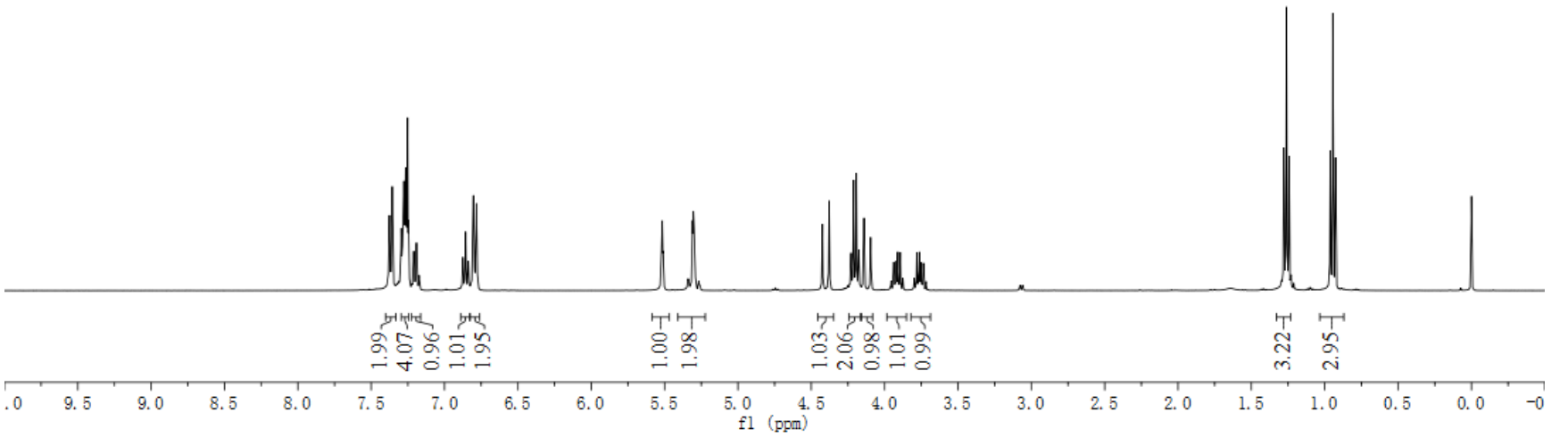
^{13}C NMR (100 MHz, $CDCl_3$)

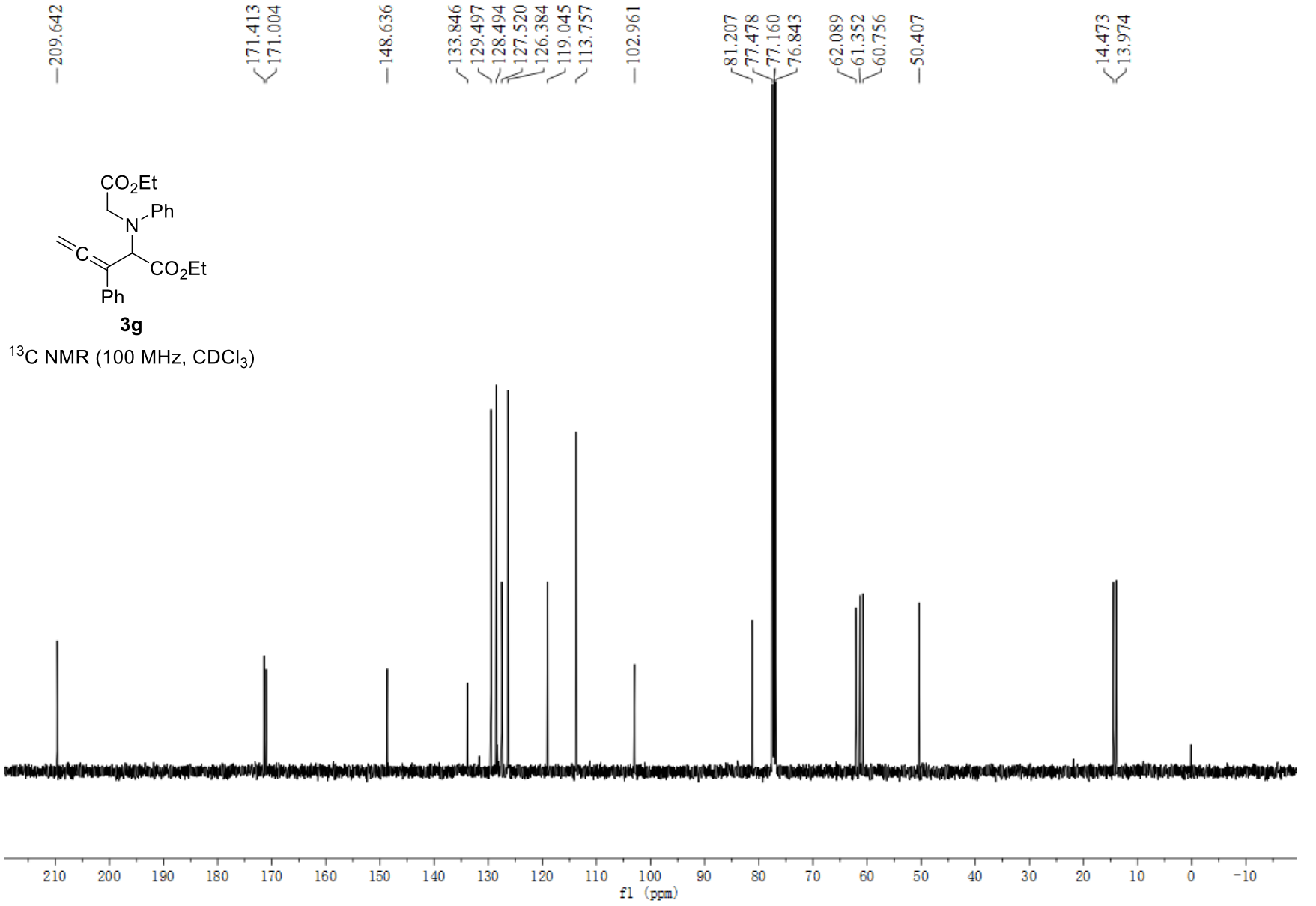


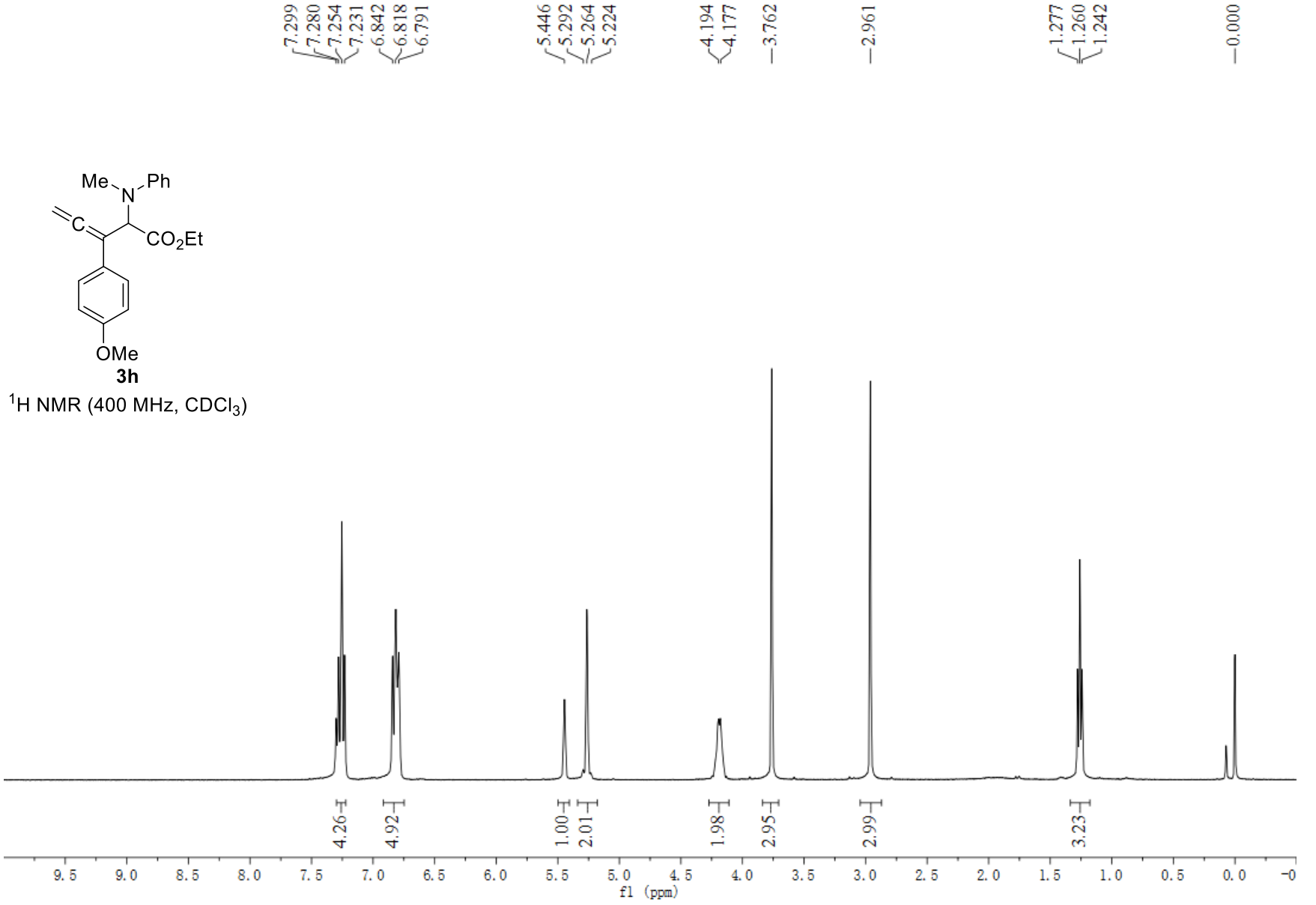


3g

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

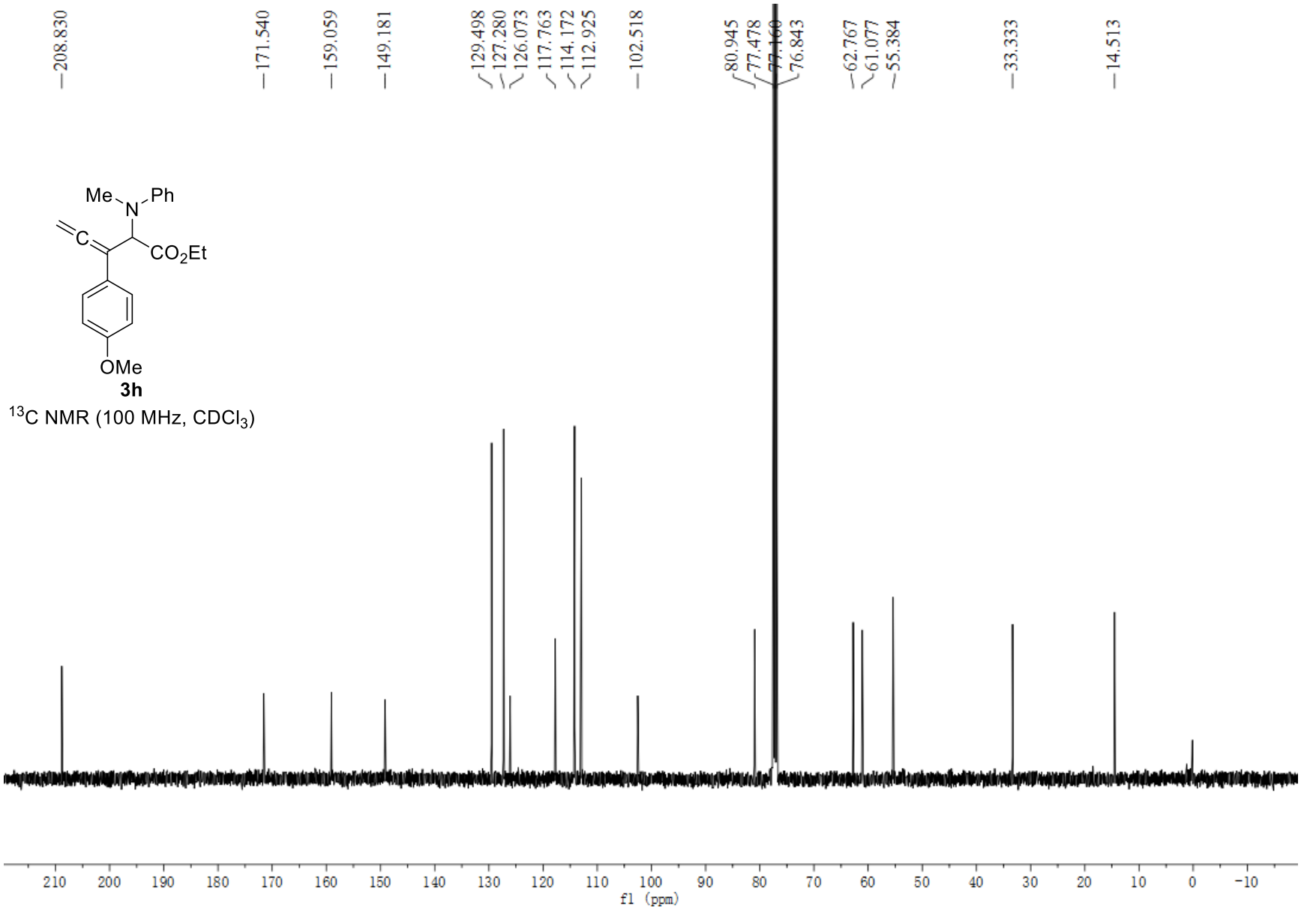



209.642
171.413
171.004
148.636
133.846
129.497
128.494
127.520
126.384
119.045
113.757
102.961
81.207
77.478
77.160
76.843
62.089
61.352
60.756
50.407
14.473
13.974
CO2Et
N
Ph
C
CO2Et
Ph
3g
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



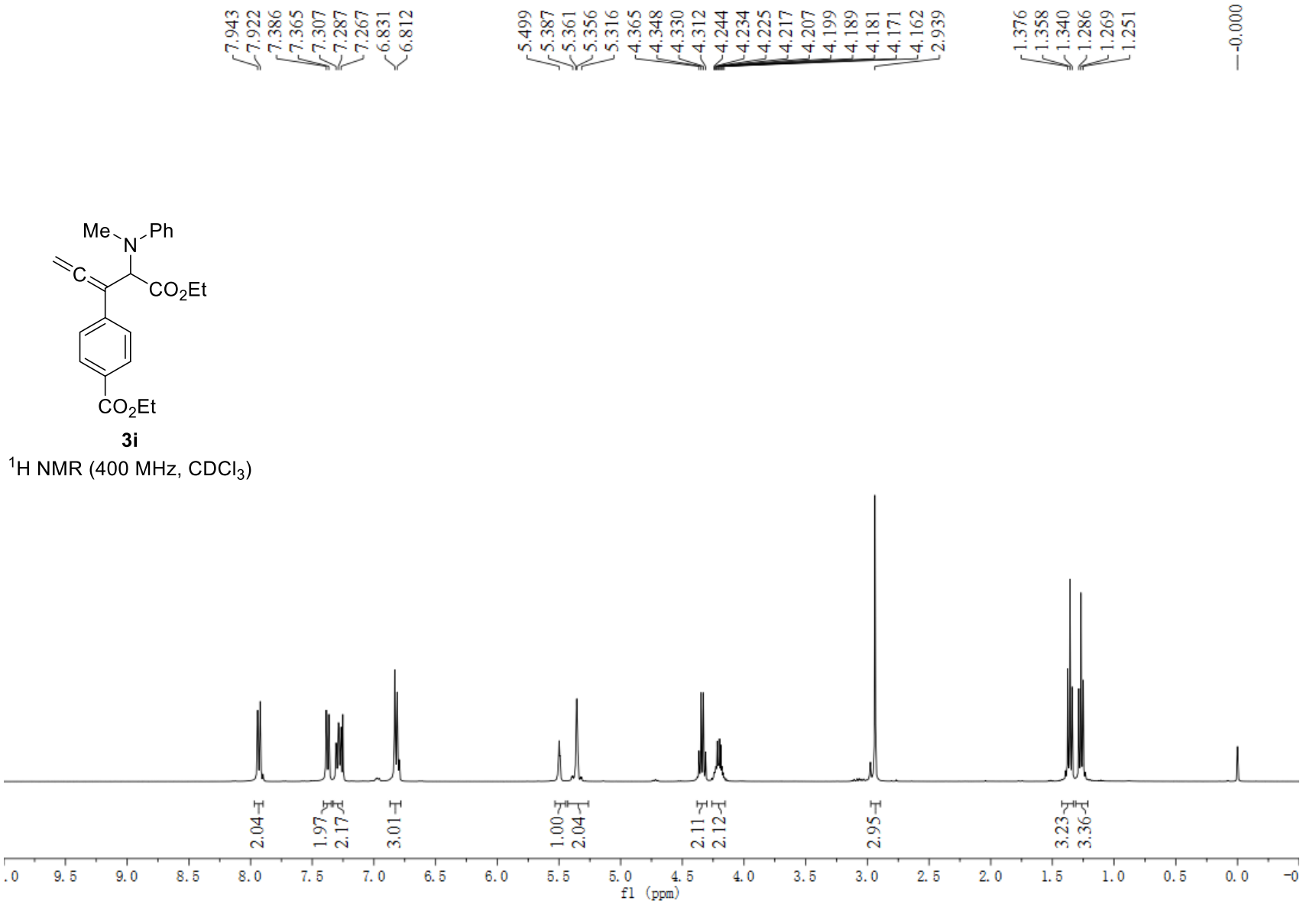
3h

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



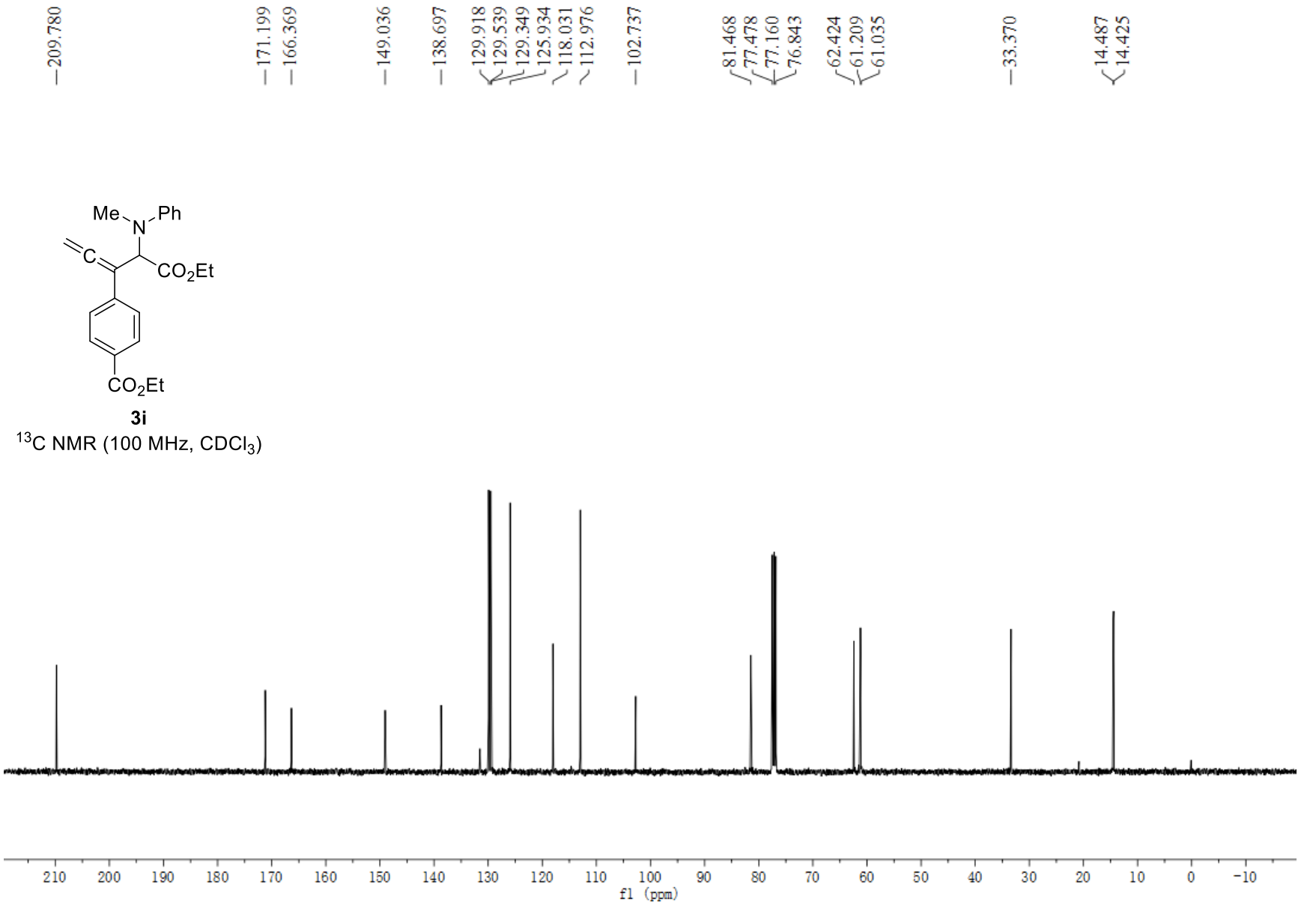
3h

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



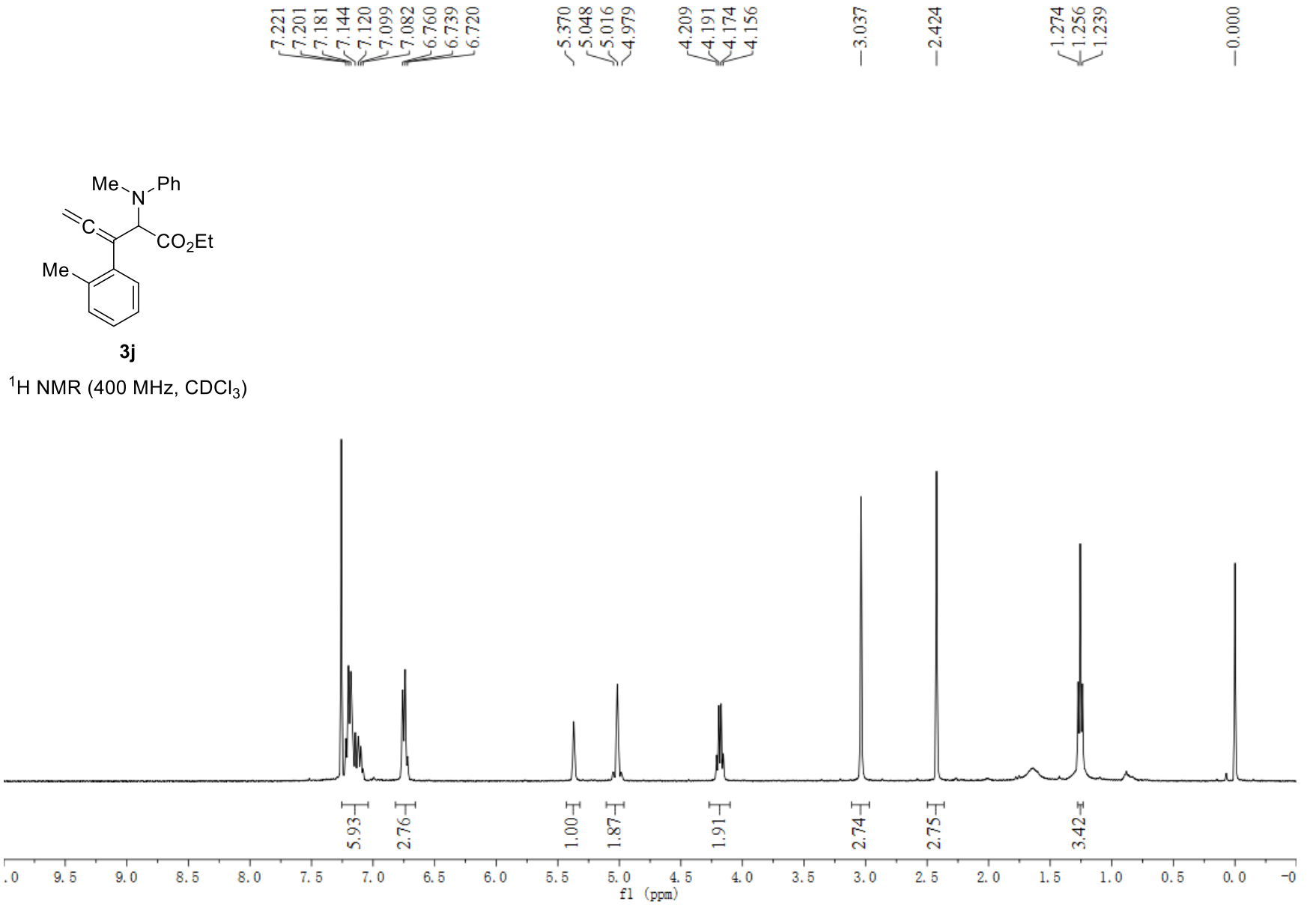
3i

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



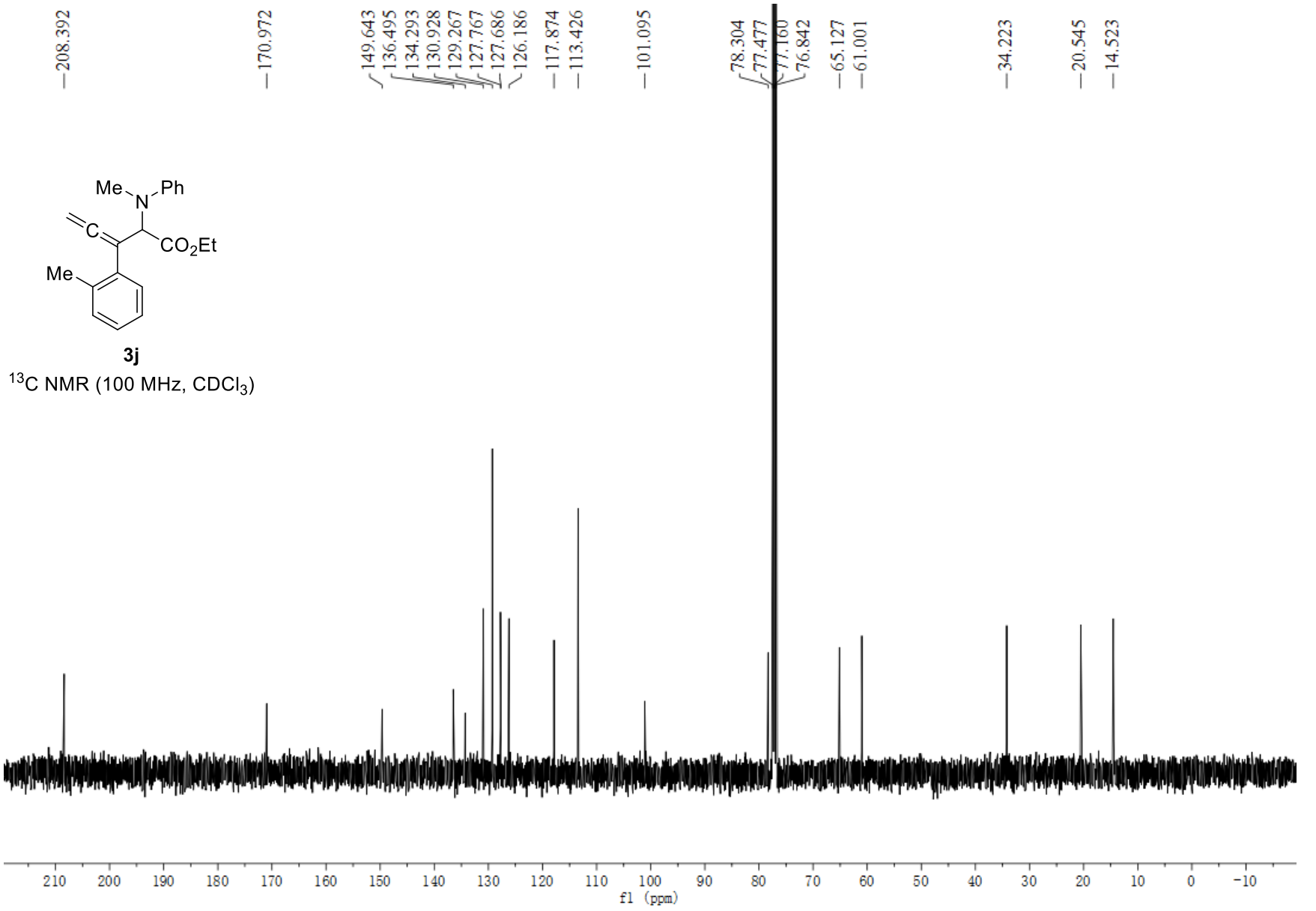
3i

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



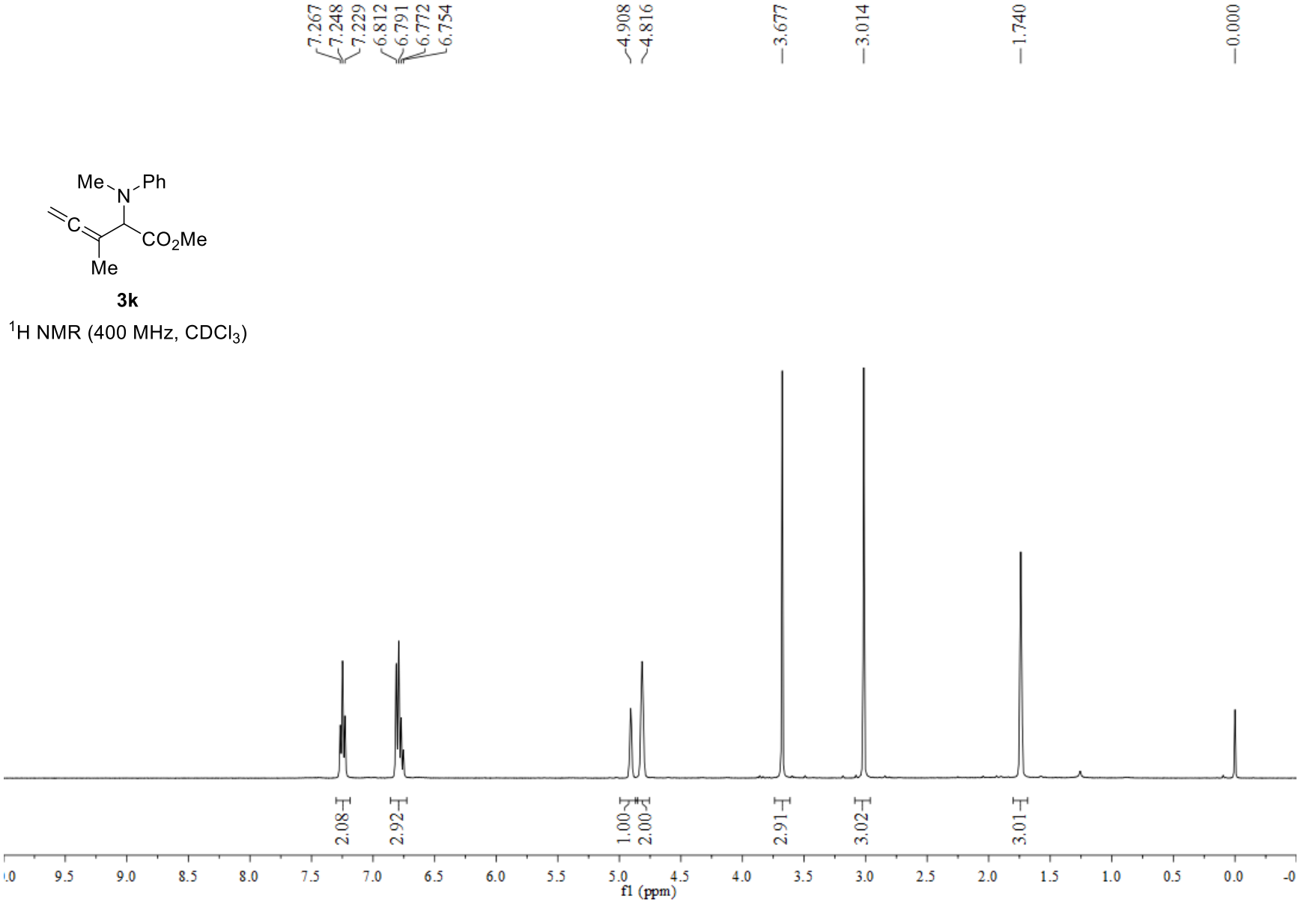
3j

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



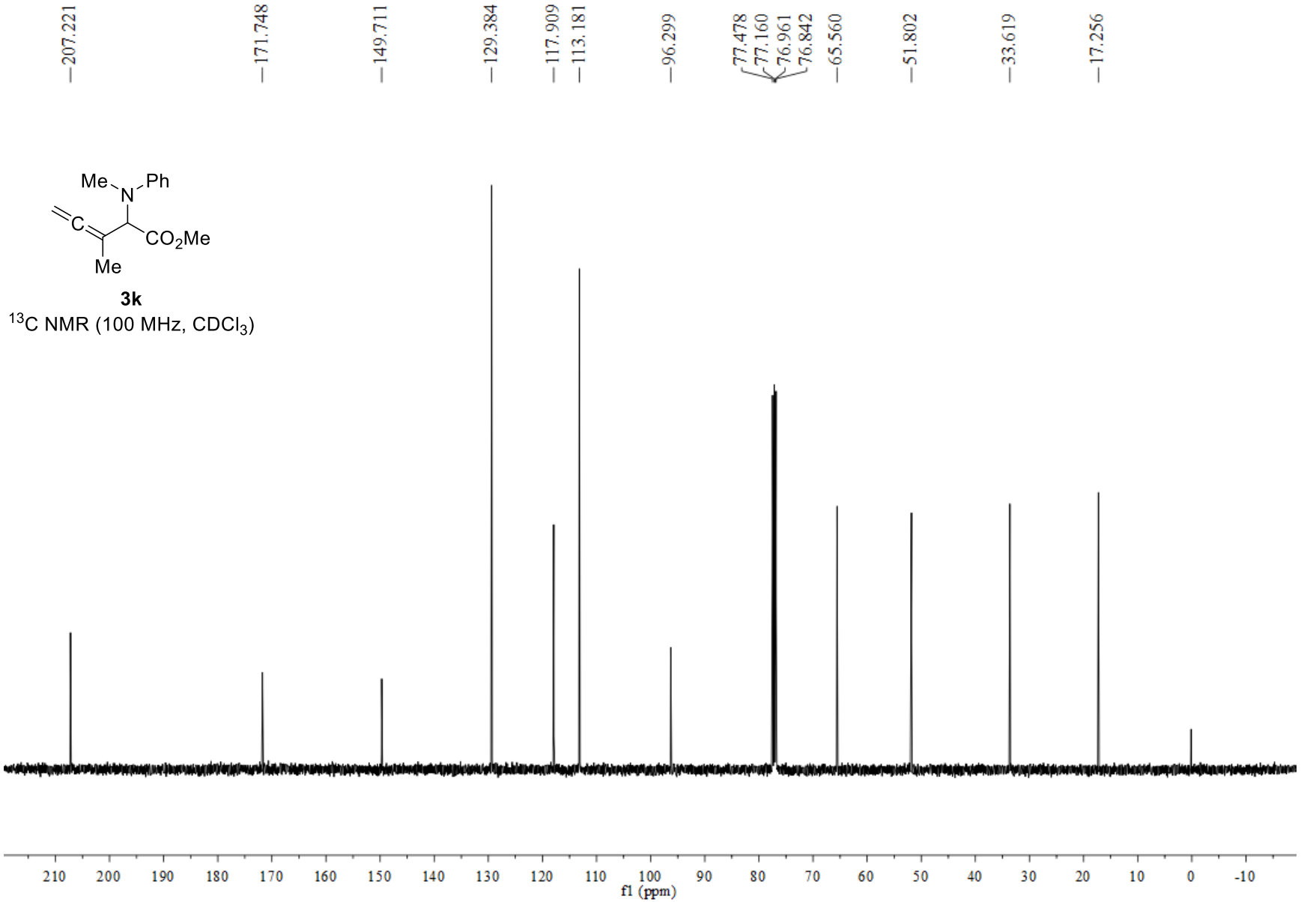
3j

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



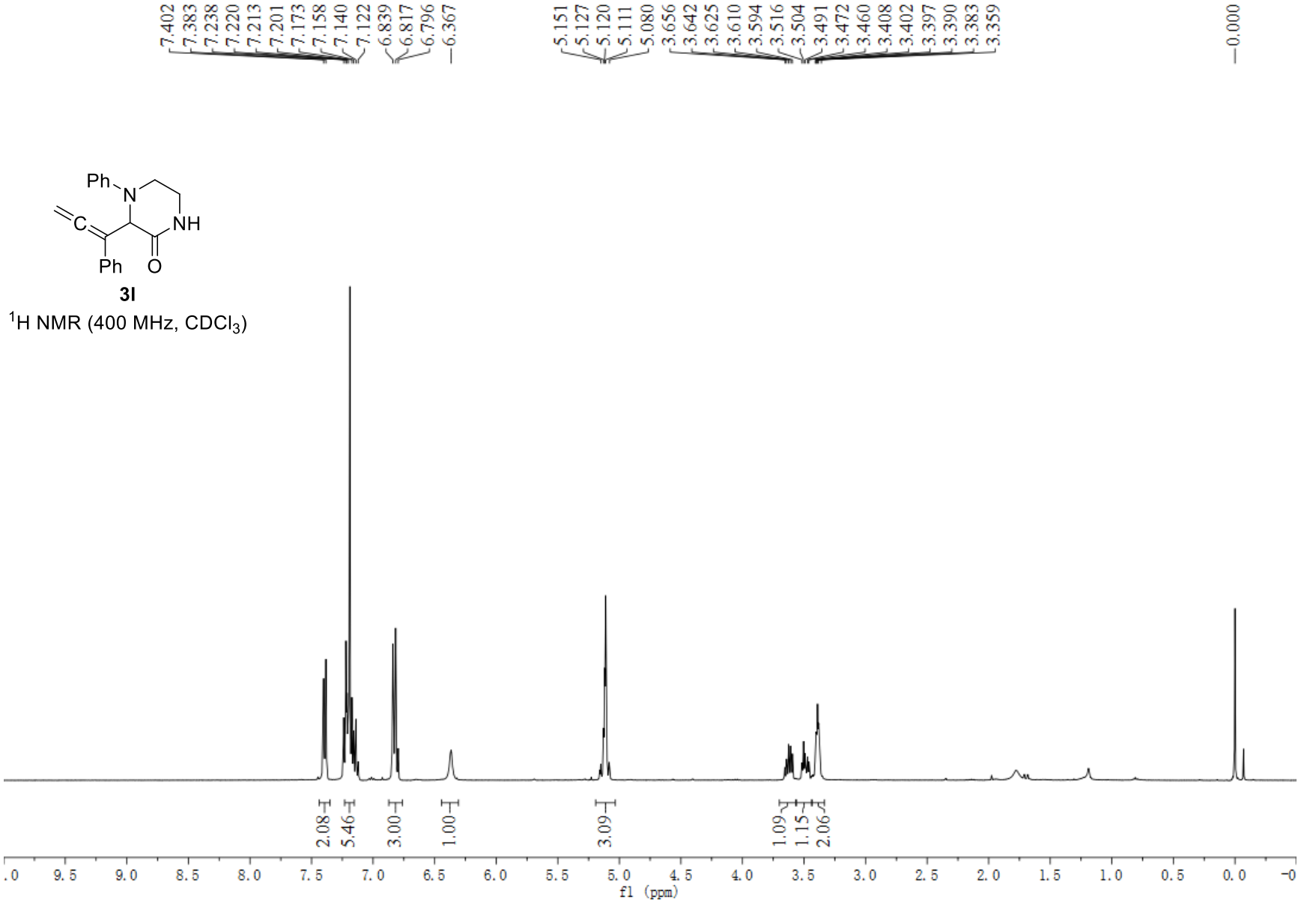
3k

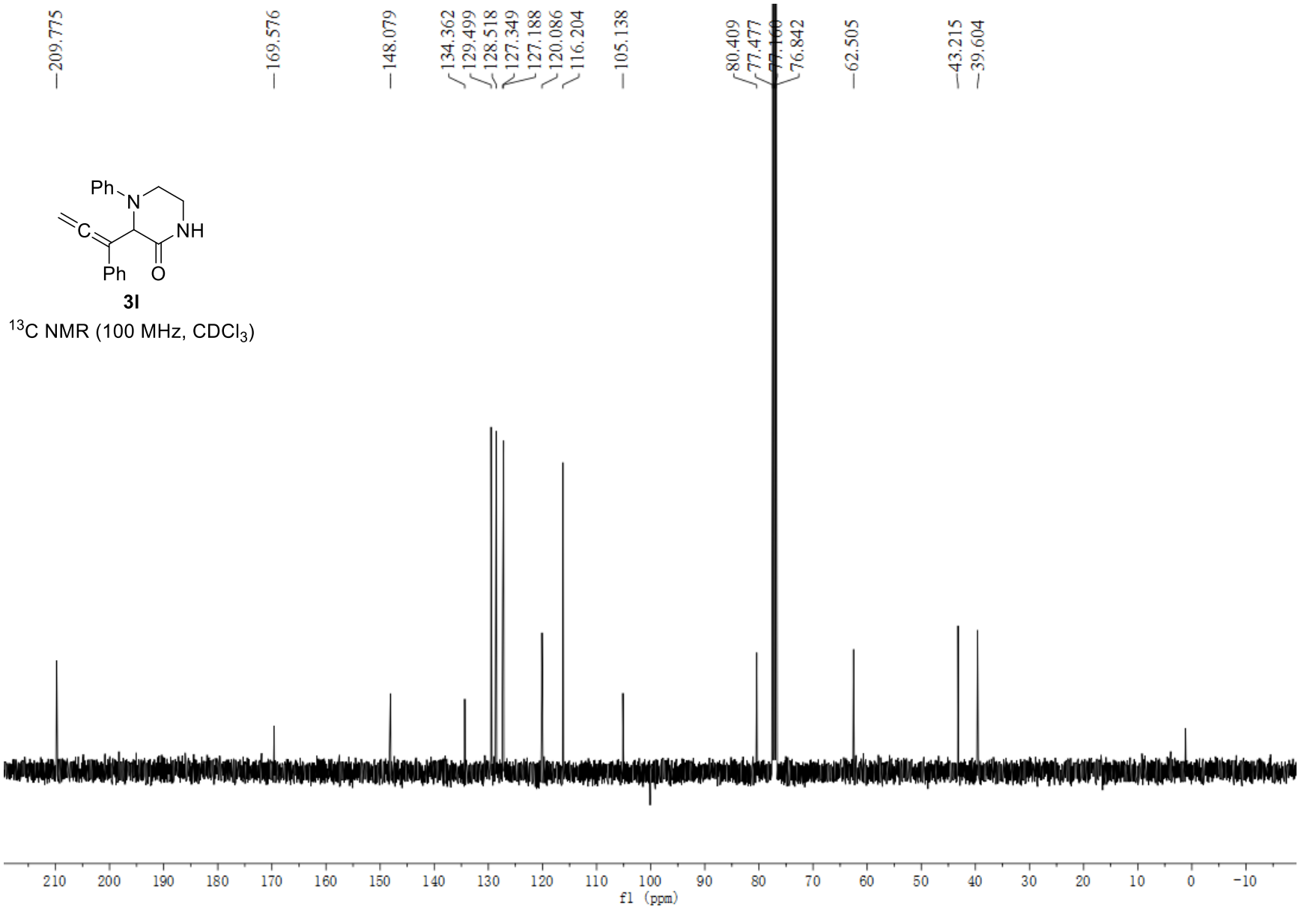
^{1}H NMR (400 MHz, $CDCl_3$)



3k

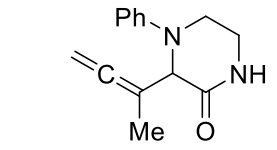
^{13}C NMR (100 MHz, $CDCl_3$)


7.402
7.383
7.238
7.220
7.213
7.201
7.173
7.158
7.140
7.122
6.839
6.817
6.796
6.367
5.151
5.127
5.120
5.111
5.080
3.656
3.642
3.625
3.610
3.594
3.516
3.504
3.491
3.472
3.460
3.408
3.402
3.397
3.390
3.383
3.359
0.000
Ph
N
NH
C
Ph
O
3l
1H NMR (400 MHz, CDCl3)
2.08
5.46
3.00
1.00
3.09
1.09
1.15
2.06
f1 (ppm)



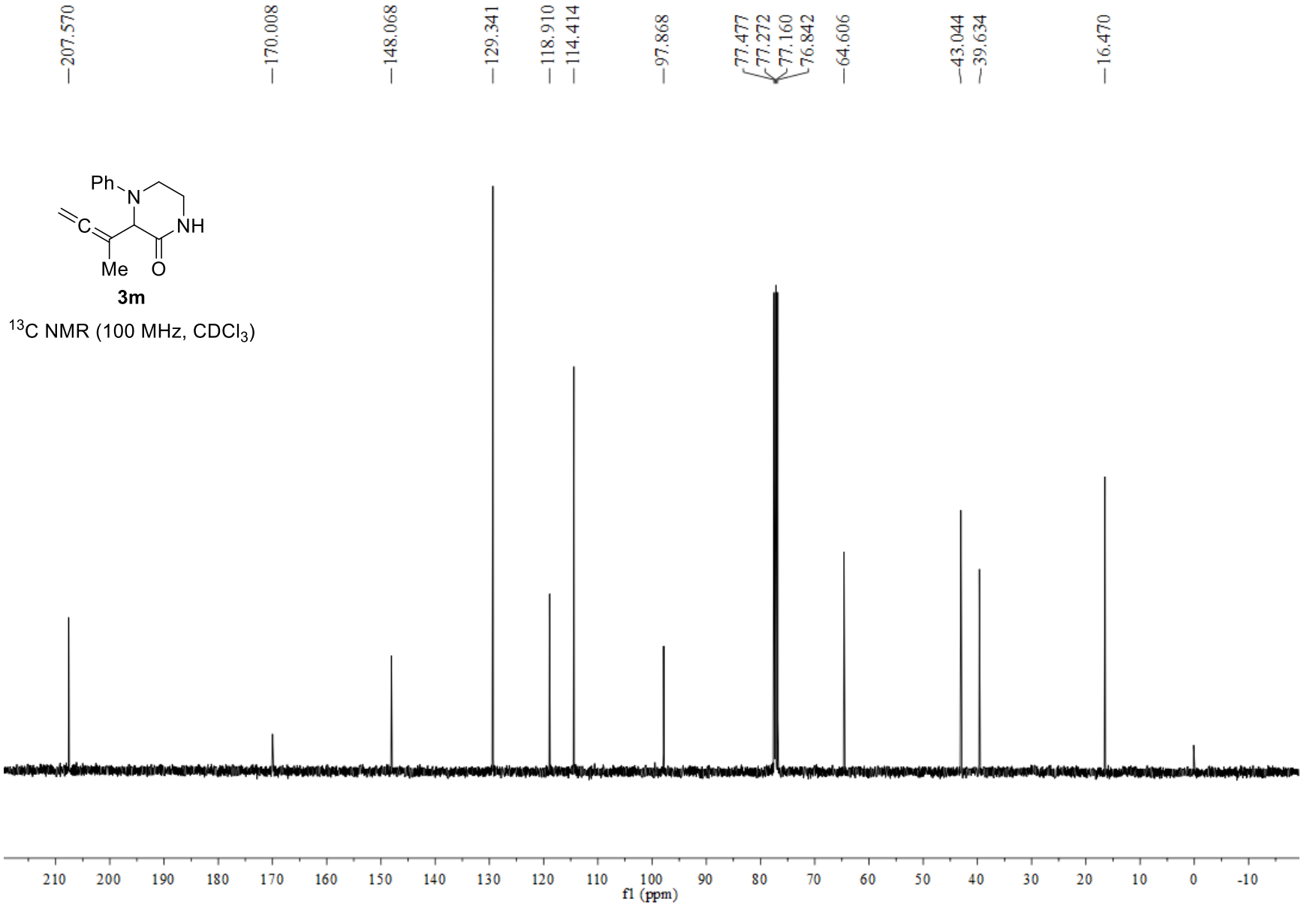
3l

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

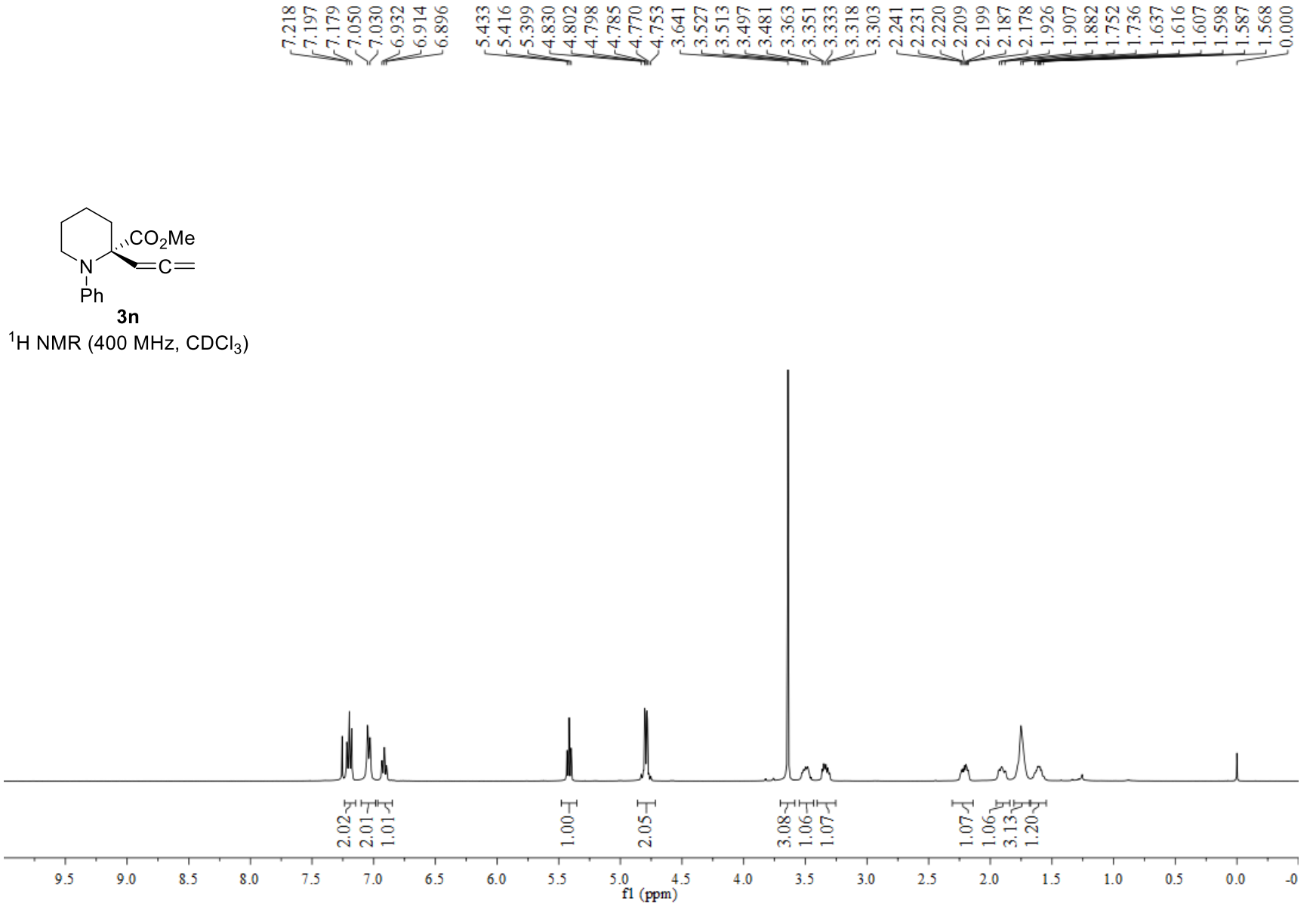


3m

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

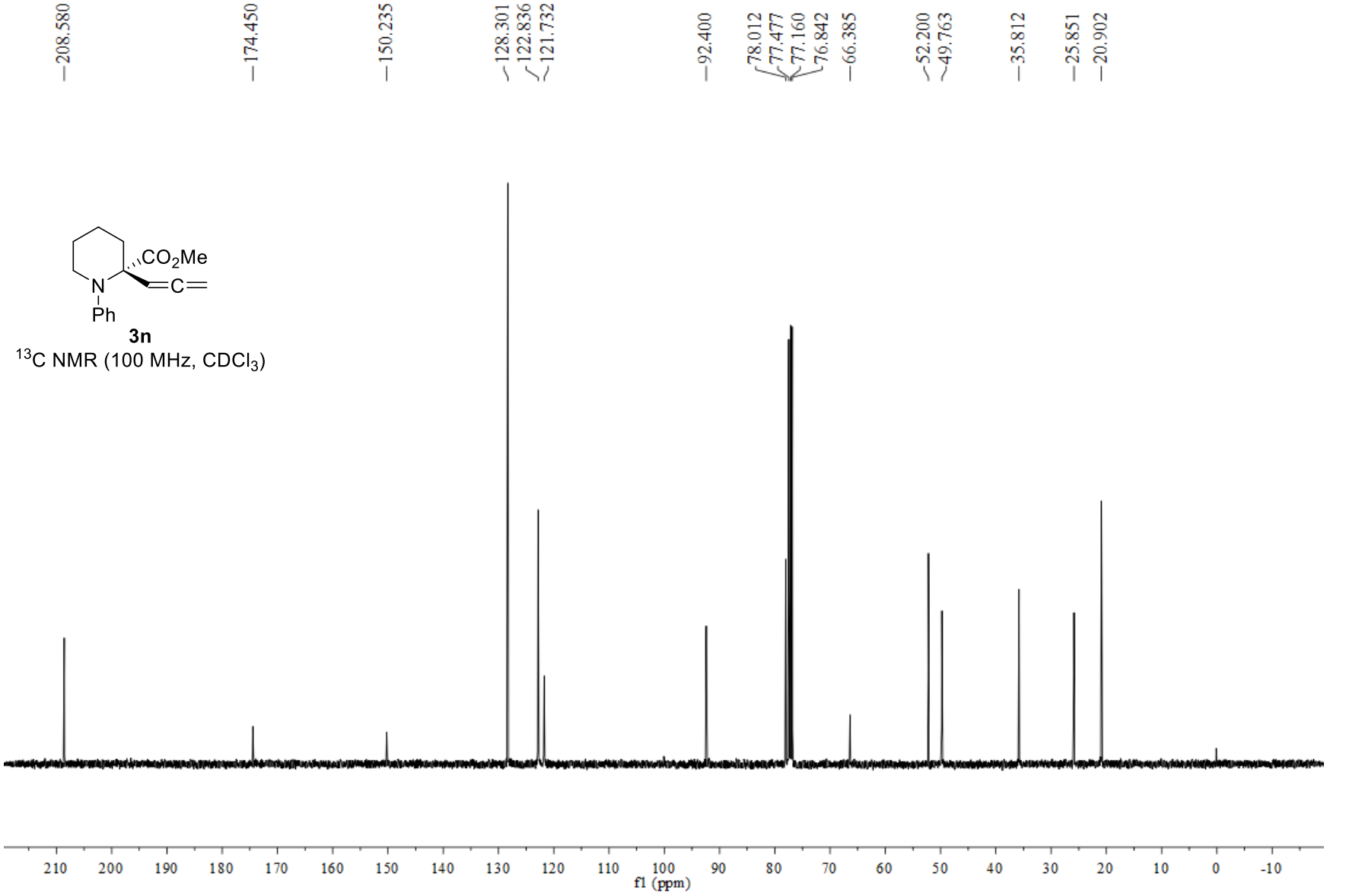


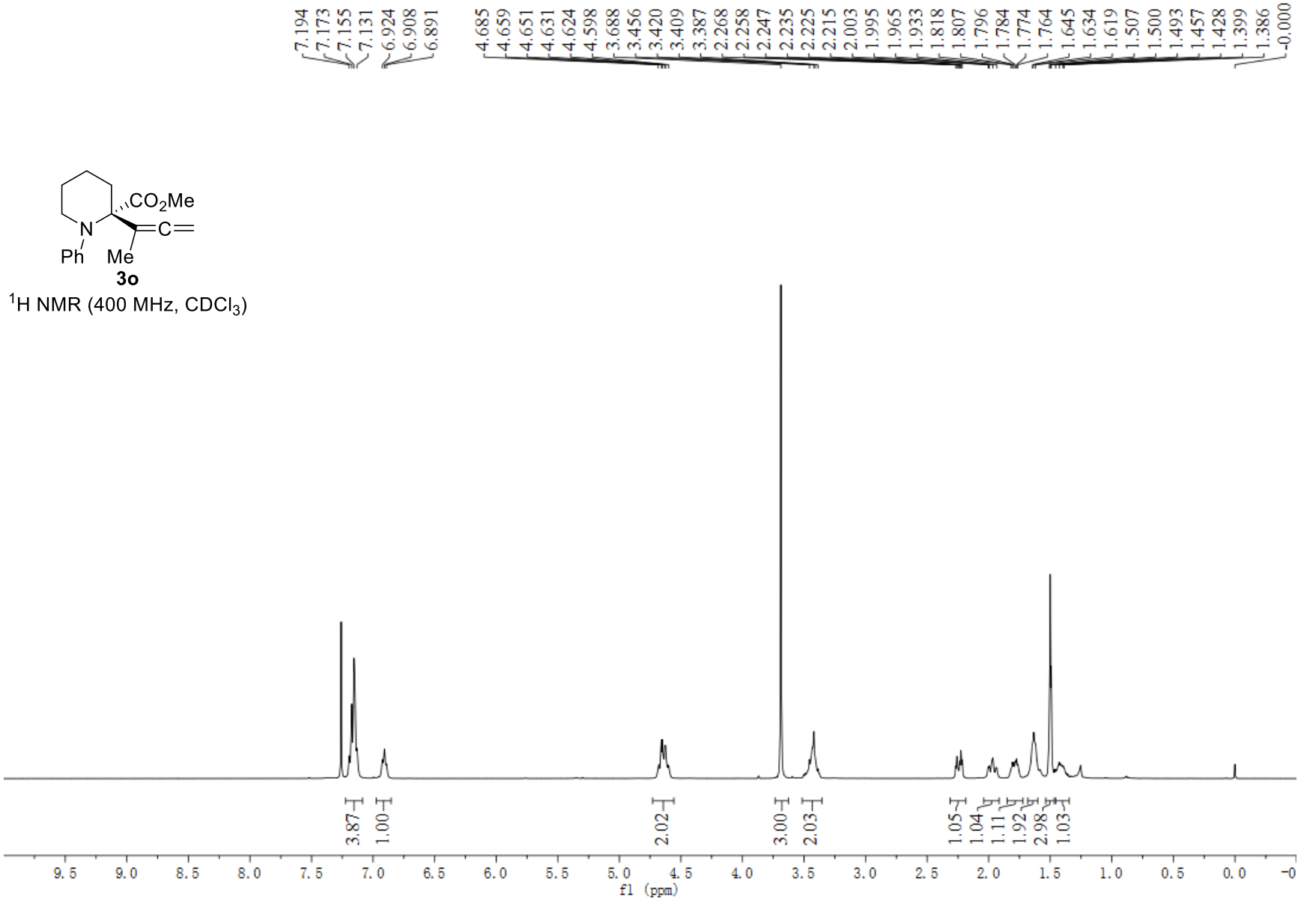
^{13}C NMR (100 MHz, $CDCl_3$)

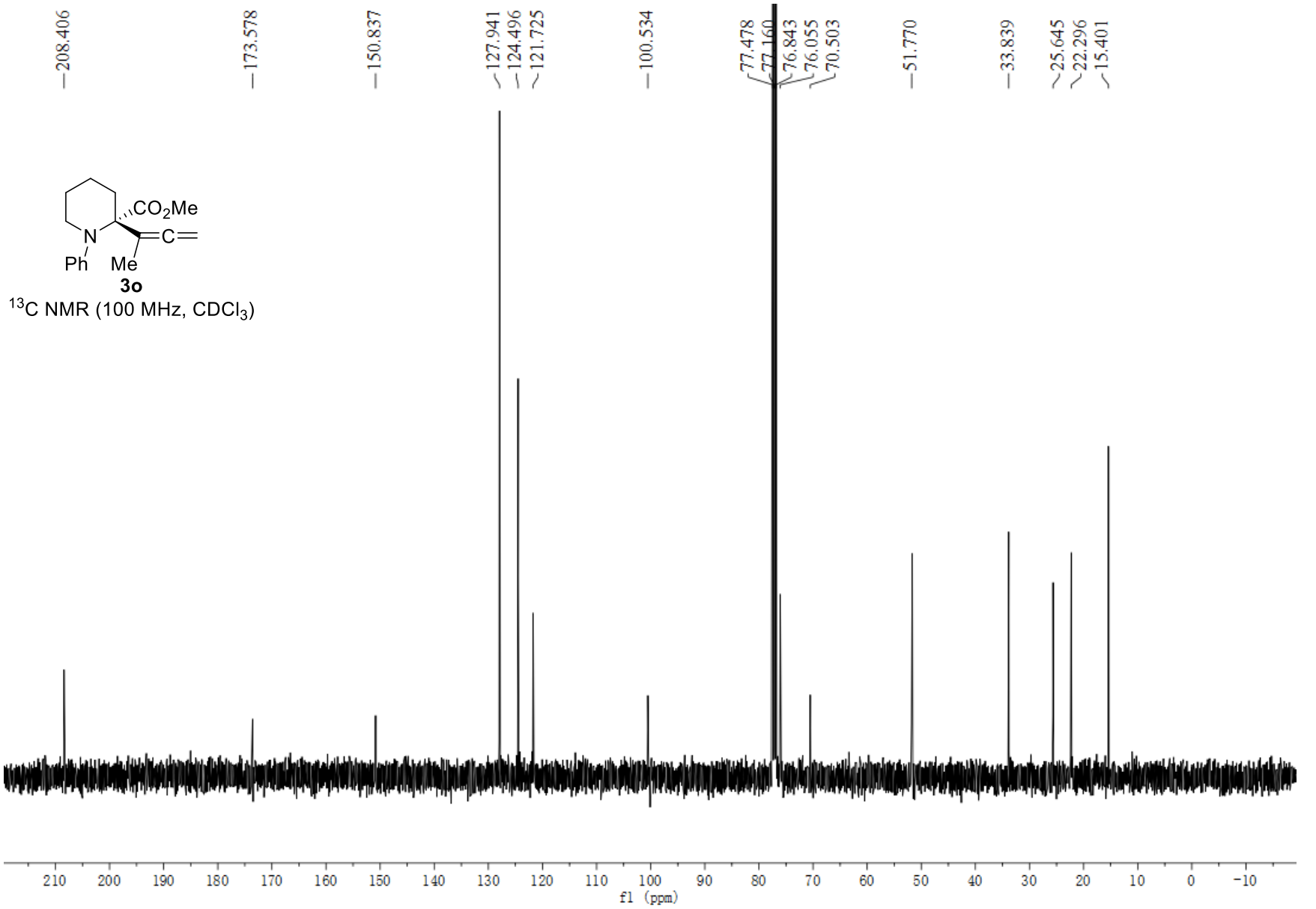


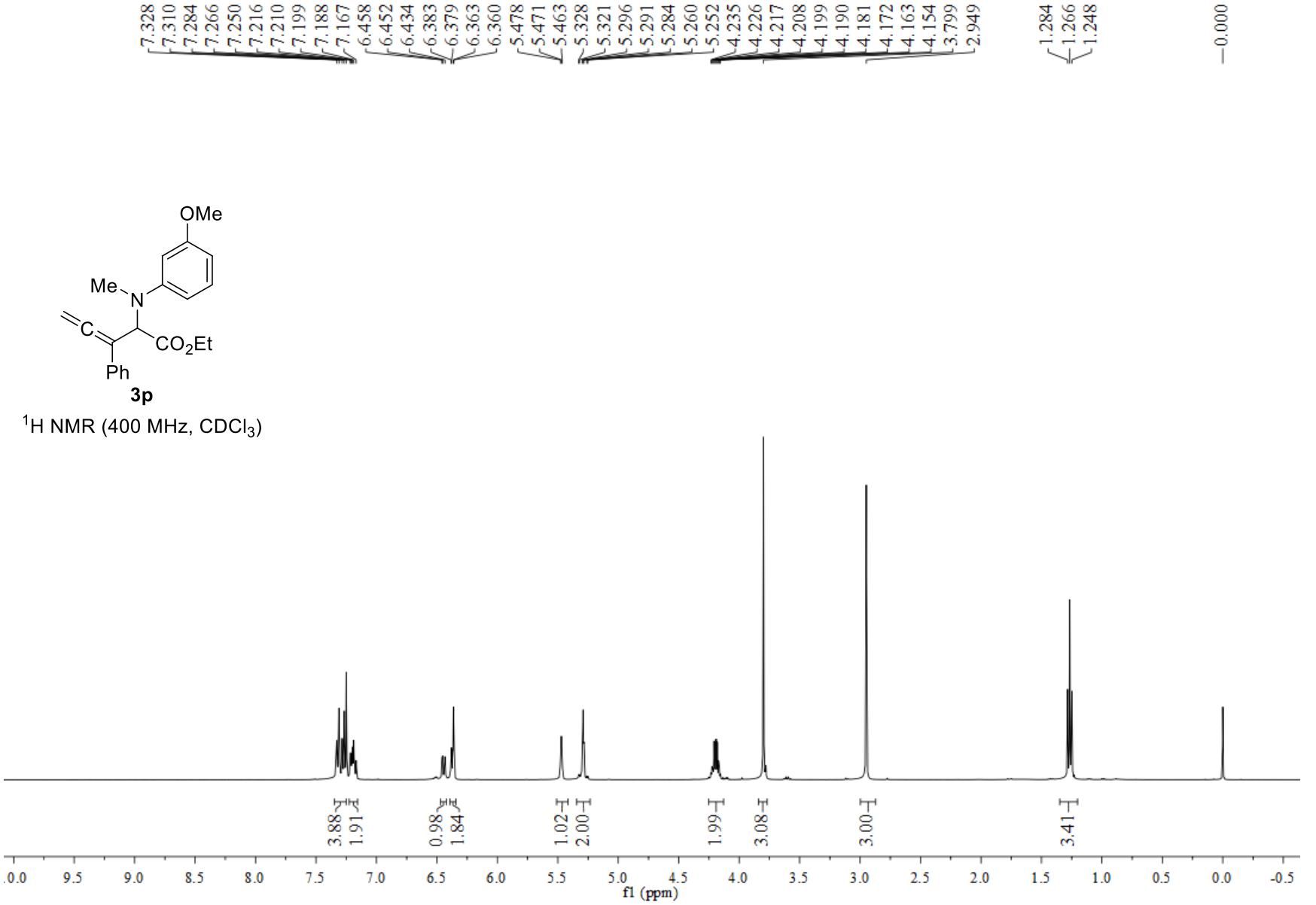
3n

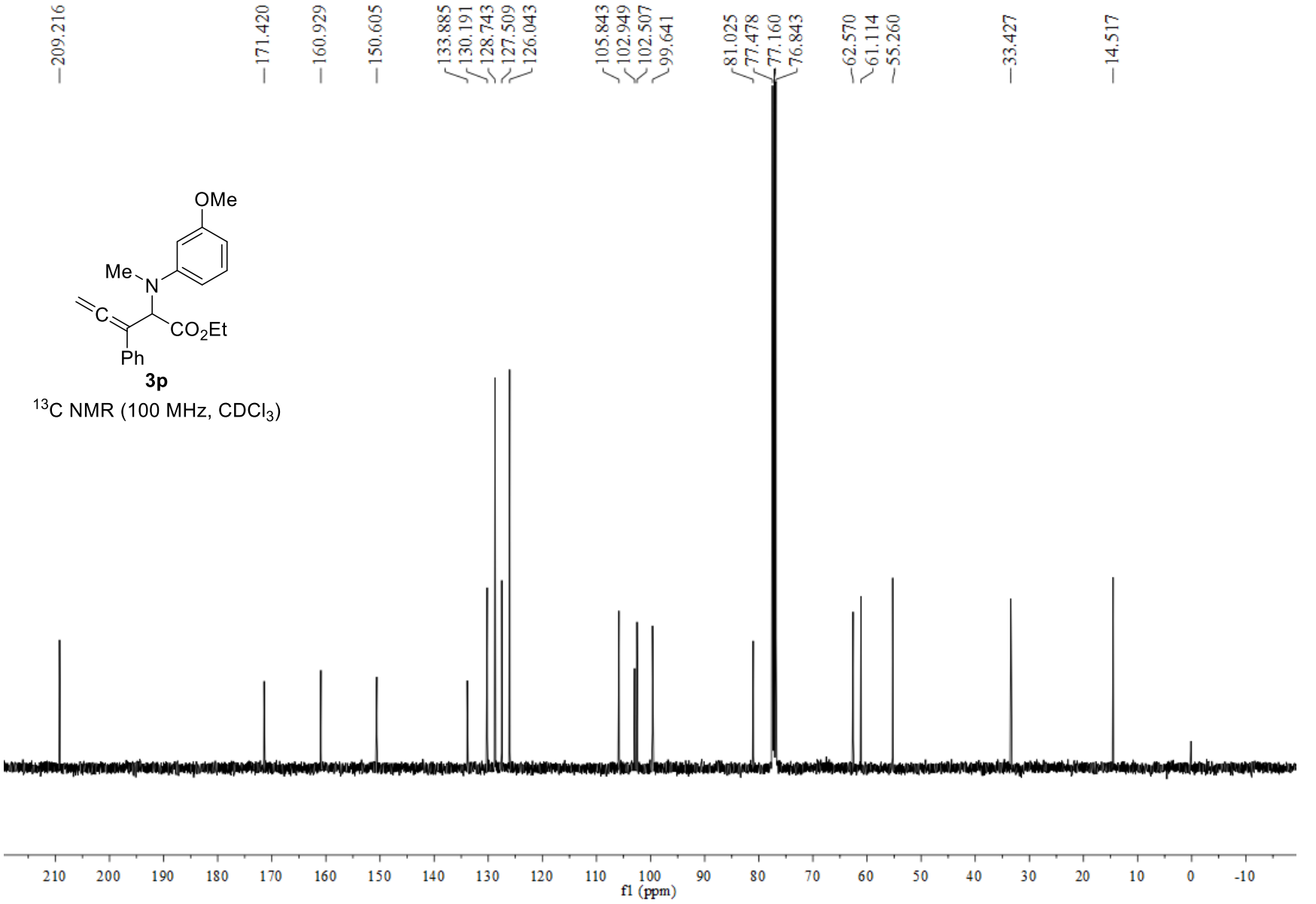
^{1}H NMR (400 MHz, $CDCl_3$)


208.580
174.450
150.235
128.301
122.836
121.732
92.400
78.012
77.477
77.160
76.842
66.385
52.200
49.763
35.812
25.851
20.902
CO2Me
N
Ph
C
3n
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.194
7.173
7.155
7.131
6.924
6.908
6.891
4.685
4.659
4.651
4.631
4.624
4.598
3.688
3.456
3.420
3.409
3.387
2.268
2.258
2.247
2.235
2.225
2.215
2.003
1.995
1.965
1.933
1.818
1.807
1.796
1.784
1.774
1.764
1.645
1.634
1.619
1.507
1.500
1.493
1.457
1.428
1.399
1.386
-0.000
CO2Me
N
C
Ph
Me
3o
1H NMR (400 MHz, CDCl3)
3.87
1.00
2.02
3.00
2.03
1.05
1.04
1.11
1.92
2.98
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

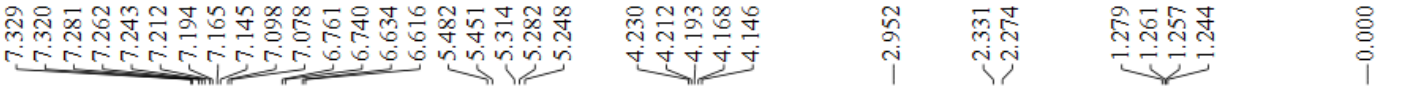

208.406
173.578
150.837
127.941
124.496
121.725
100.534
77.478
77.160
76.843
76.055
70.503
51.770
33.839
25.645
22.296
15.401
CO2Me
N
C
Ph
Me
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)

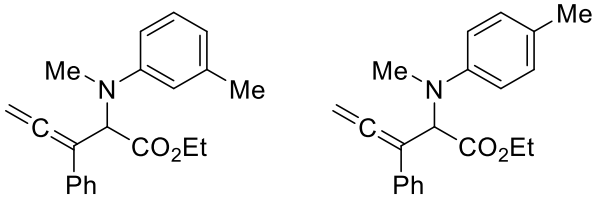

7.328
7.310
7.284
7.266
7.250
7.216
7.210
7.199
7.188
7.167
6.458
6.452
6.434
6.383
6.379
6.363
6.360
5.478
5.471
5.463
5.328
5.321
5.296
5.291
5.284
5.260
5.252
4.235
4.226
4.217
4.208
4.199
4.190
4.181
4.172
4.163
4.154
3.799
2.949
1.284
1.266
1.248
0.000
OMe
Me
N
C
CO2Et
Ph
3p
1H NMR (400 MHz, CDCl3)
3.88
1.91
0.98
1.84
1.02
2.00
1.99
3.08
3.00
3.41
f1 (ppm)



3p

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

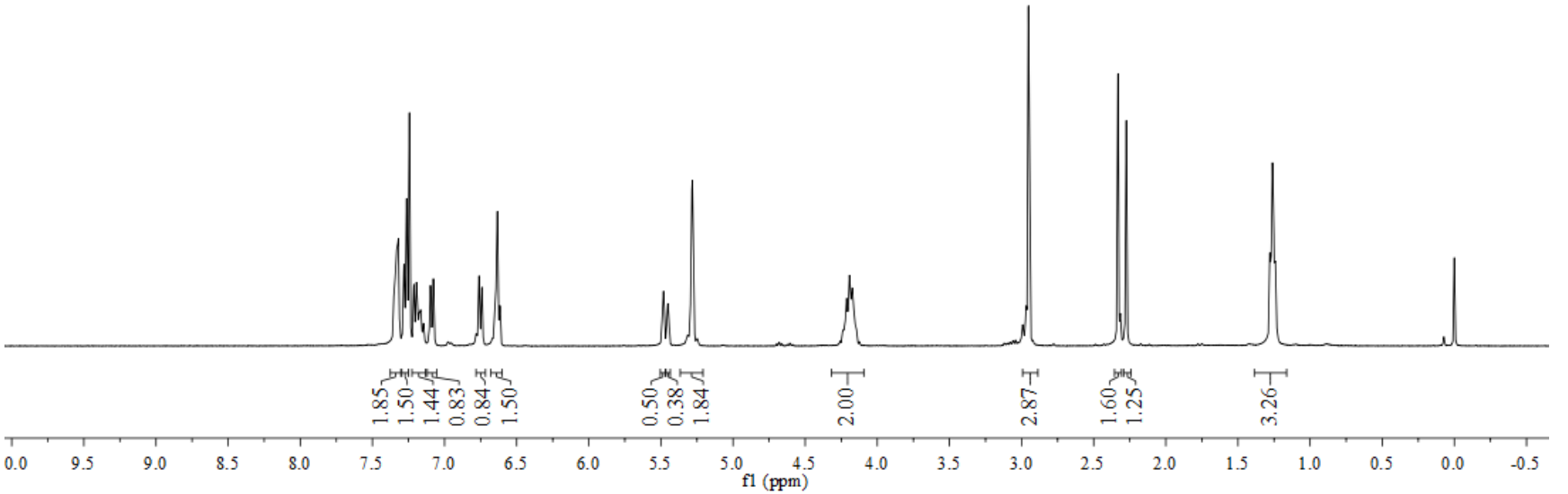


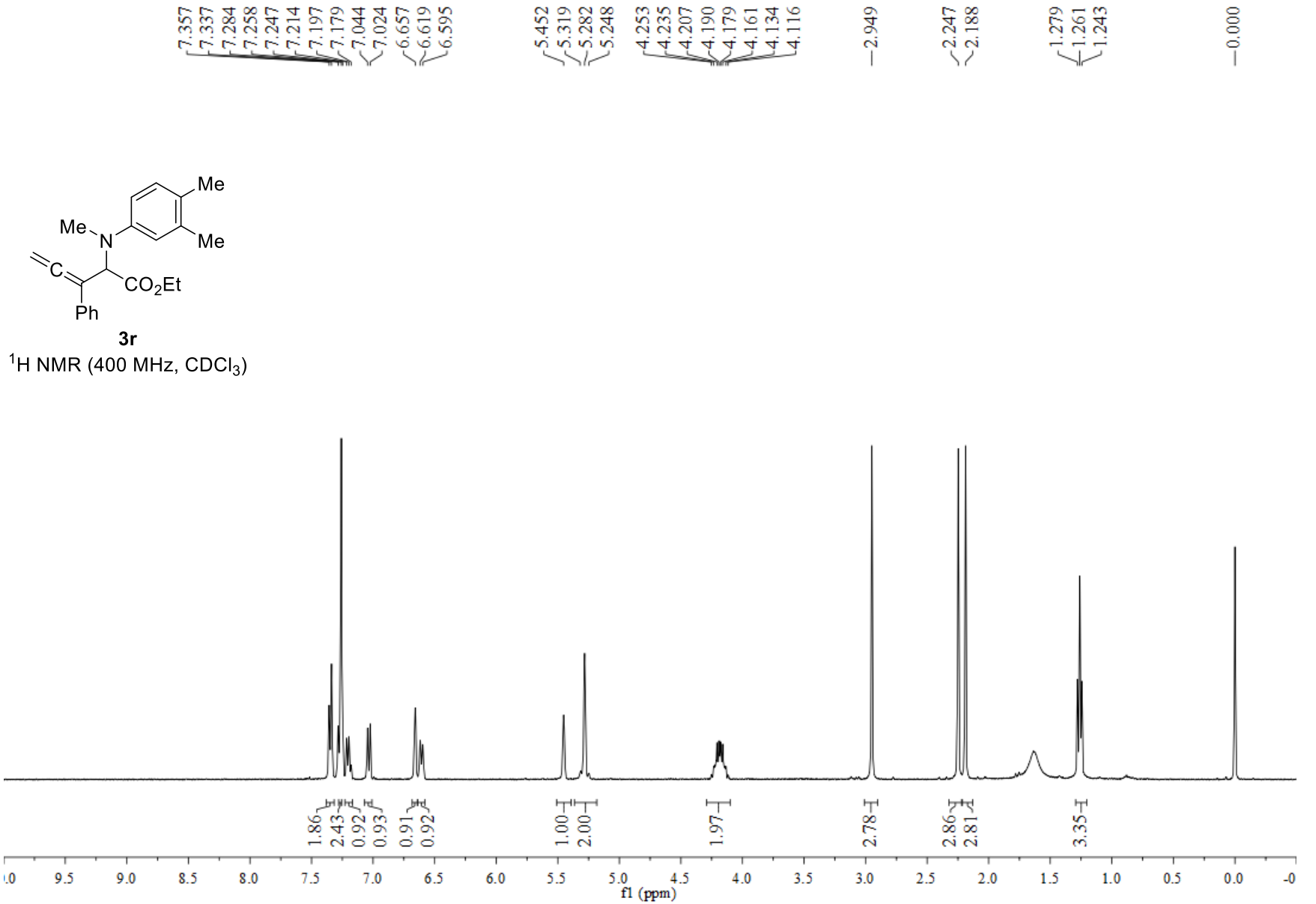


3q

3q'

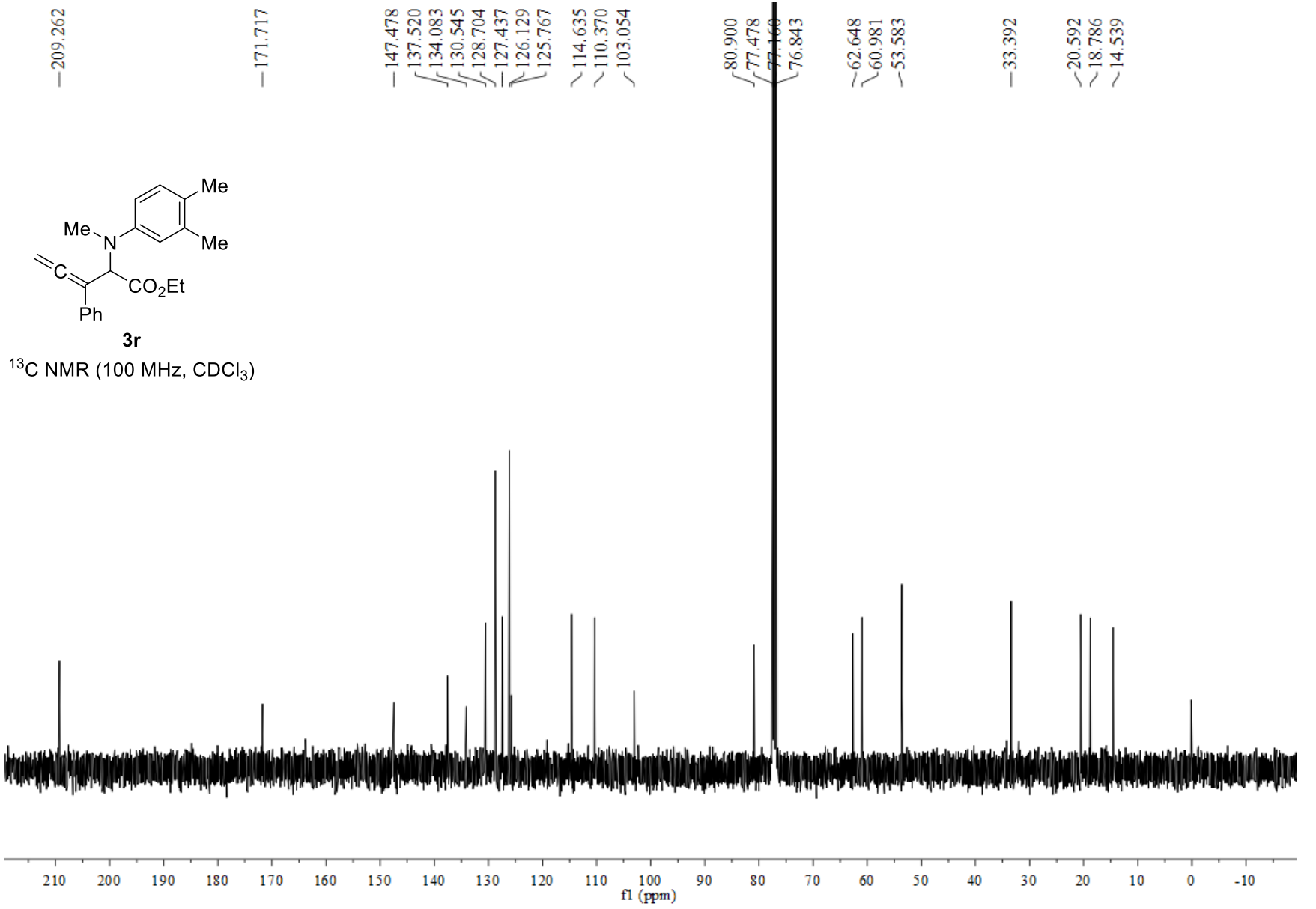
^{1}H NMR (400 MHz, $CDCl_3$)





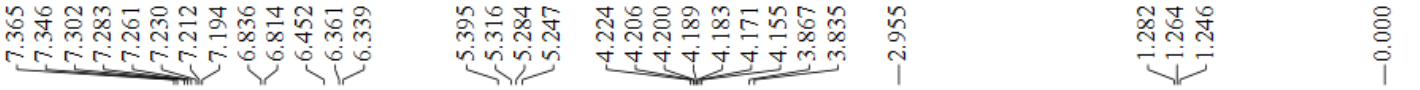
3r

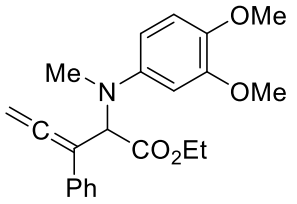
^{1}H NMR (400 MHz, $CDCl_3$)



3r

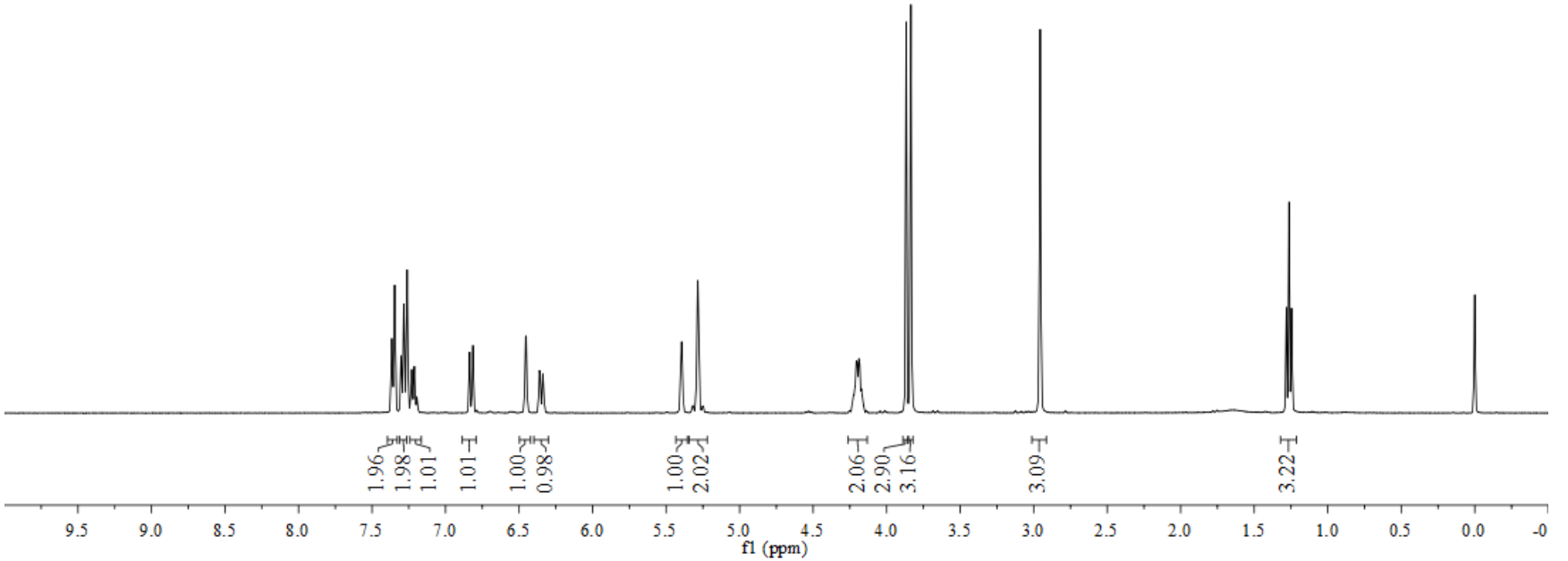
^{13}C NMR (100 MHz, $CDCl_3$)

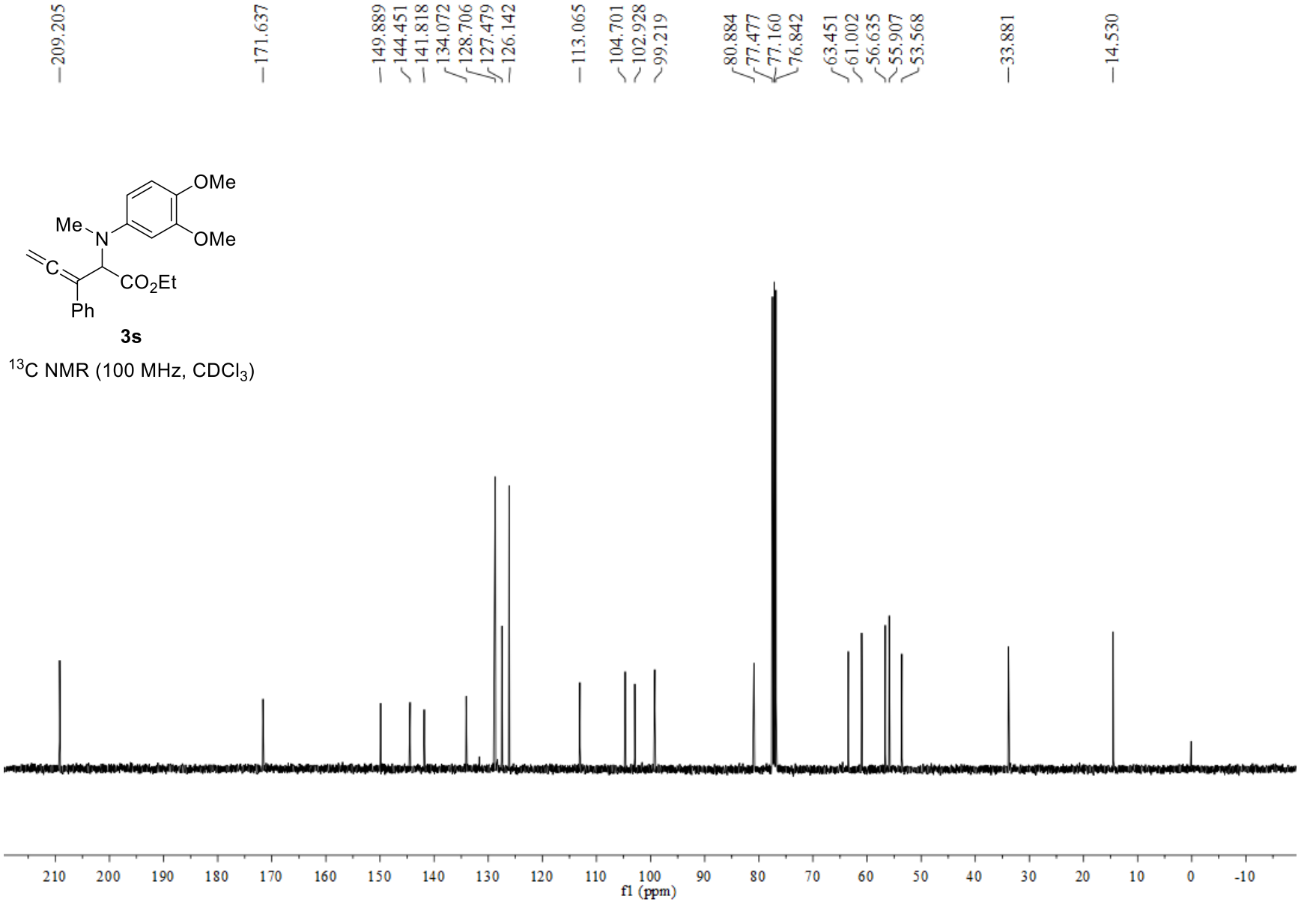




3s

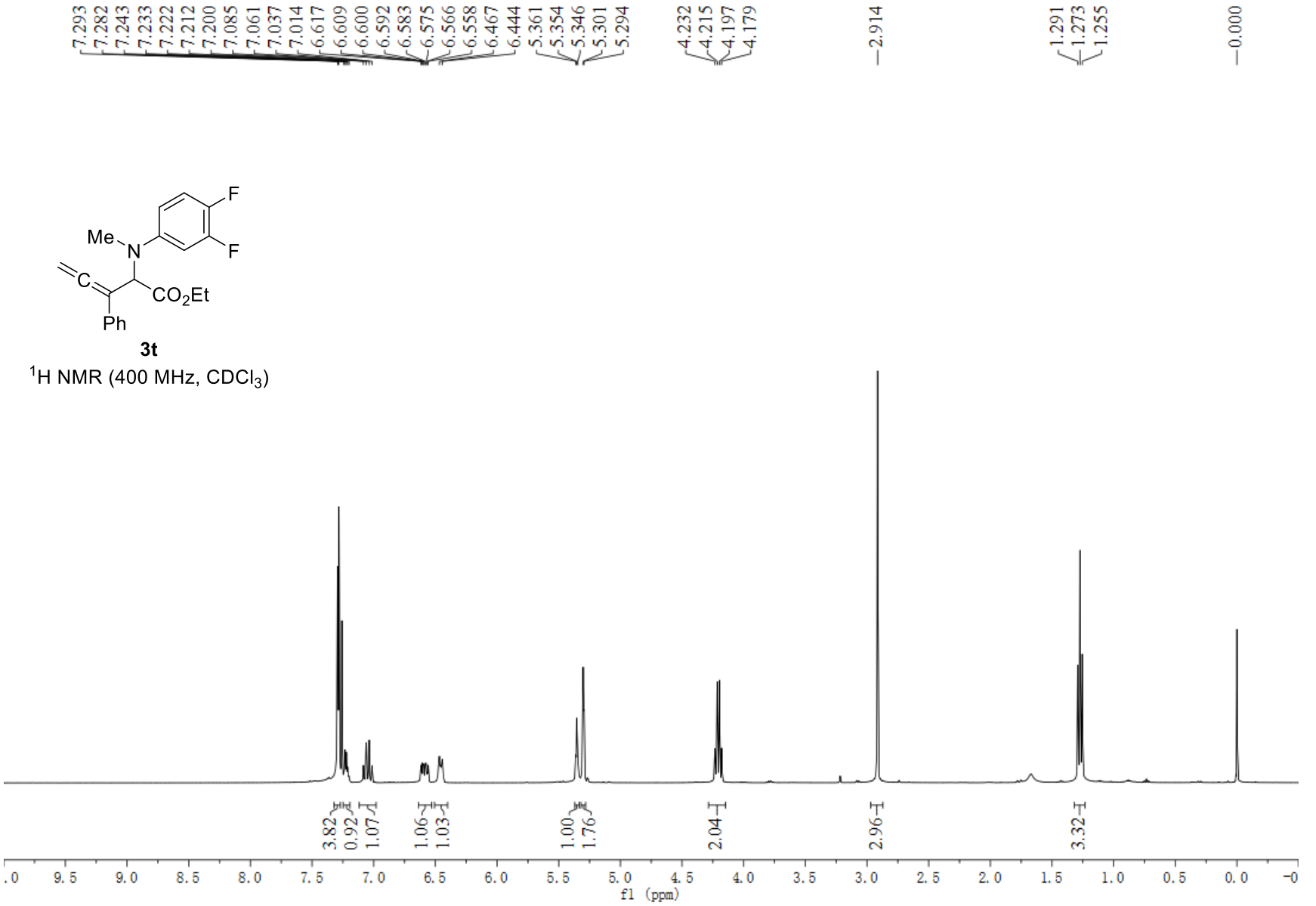
^{1}H NMR (400 MHz, $CDCl_3$)





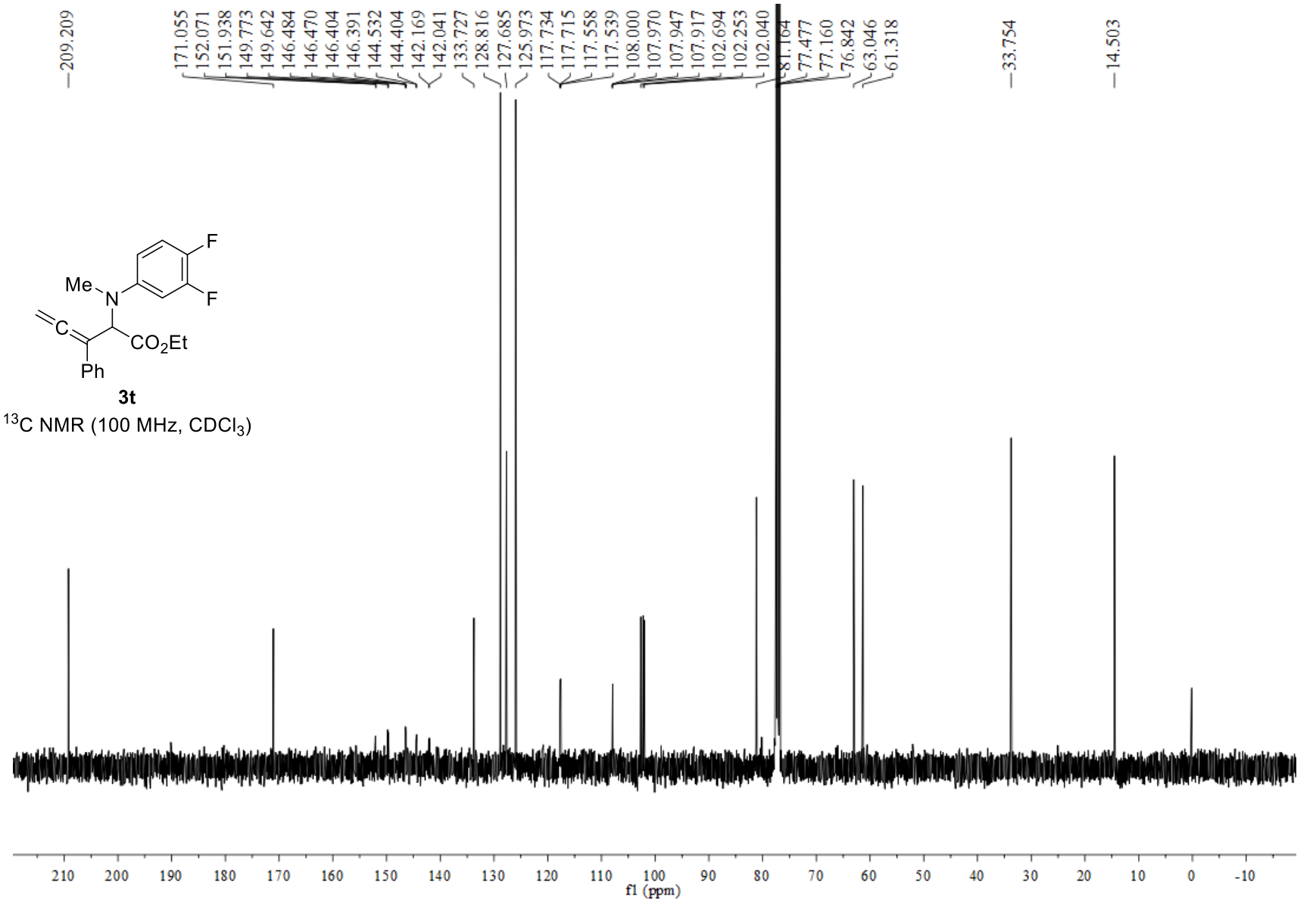
3s

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



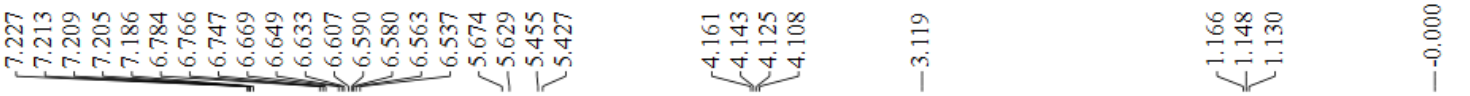
3t

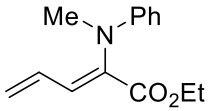
^{1}H NMR (400 MHz, $CDCl_3$)



3t

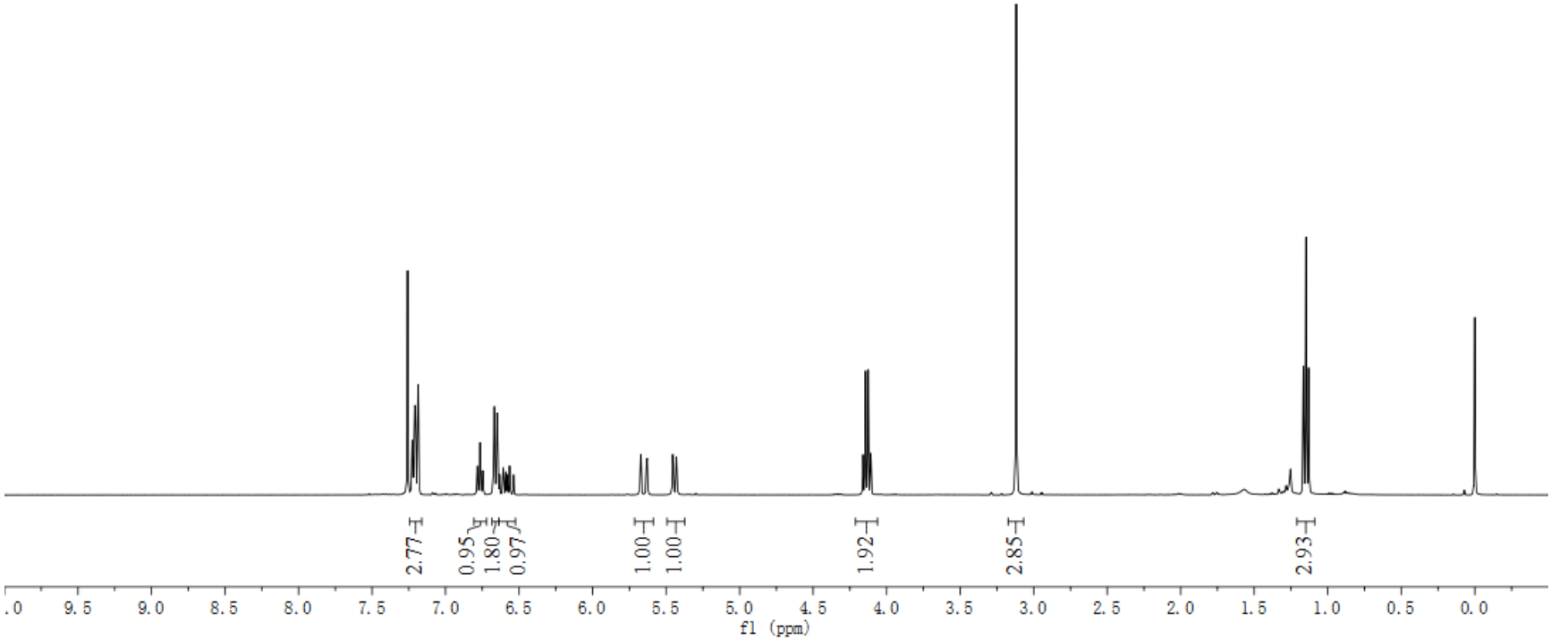
^{13}C NMR (100 MHz, $CDCl_3$)

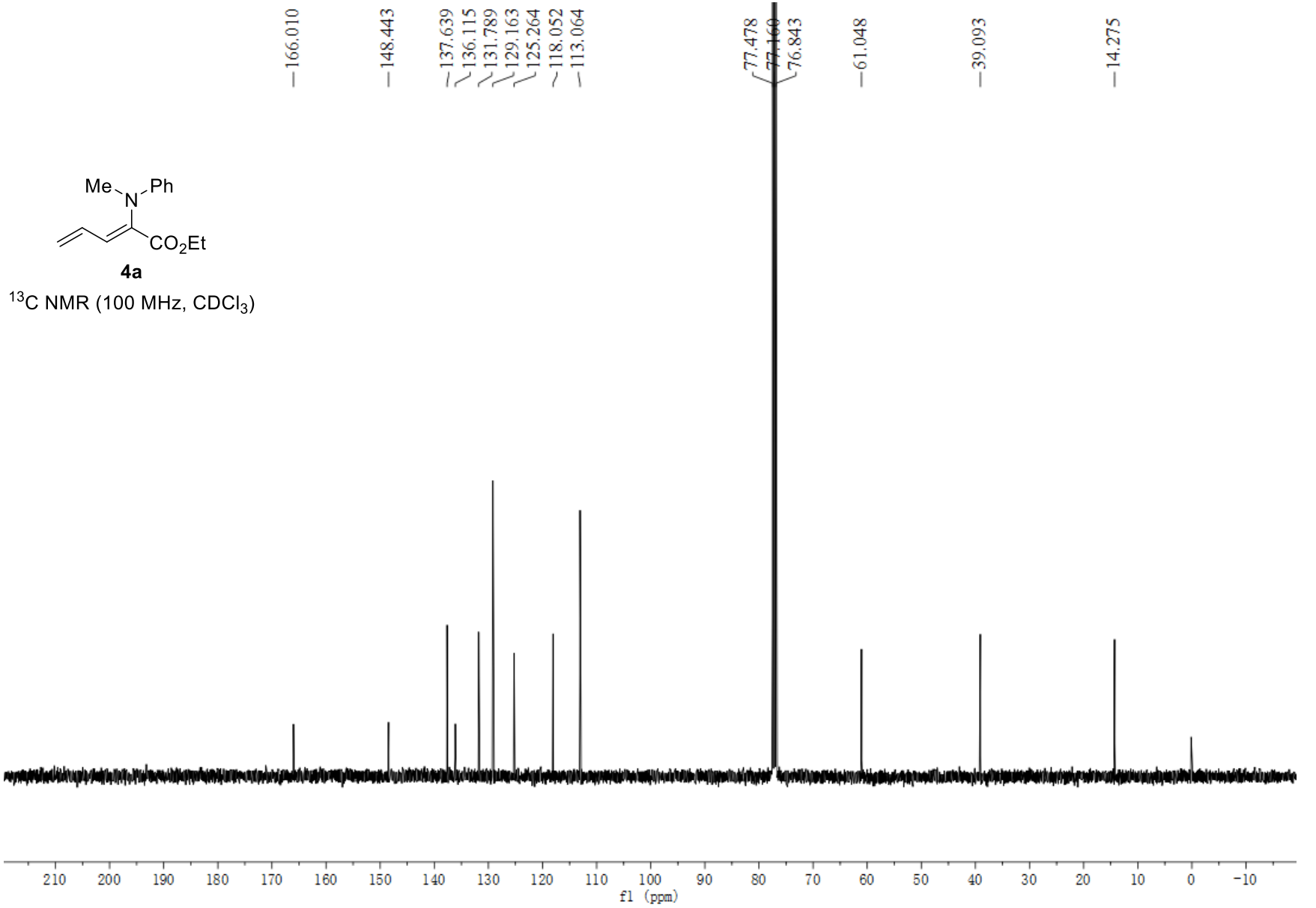


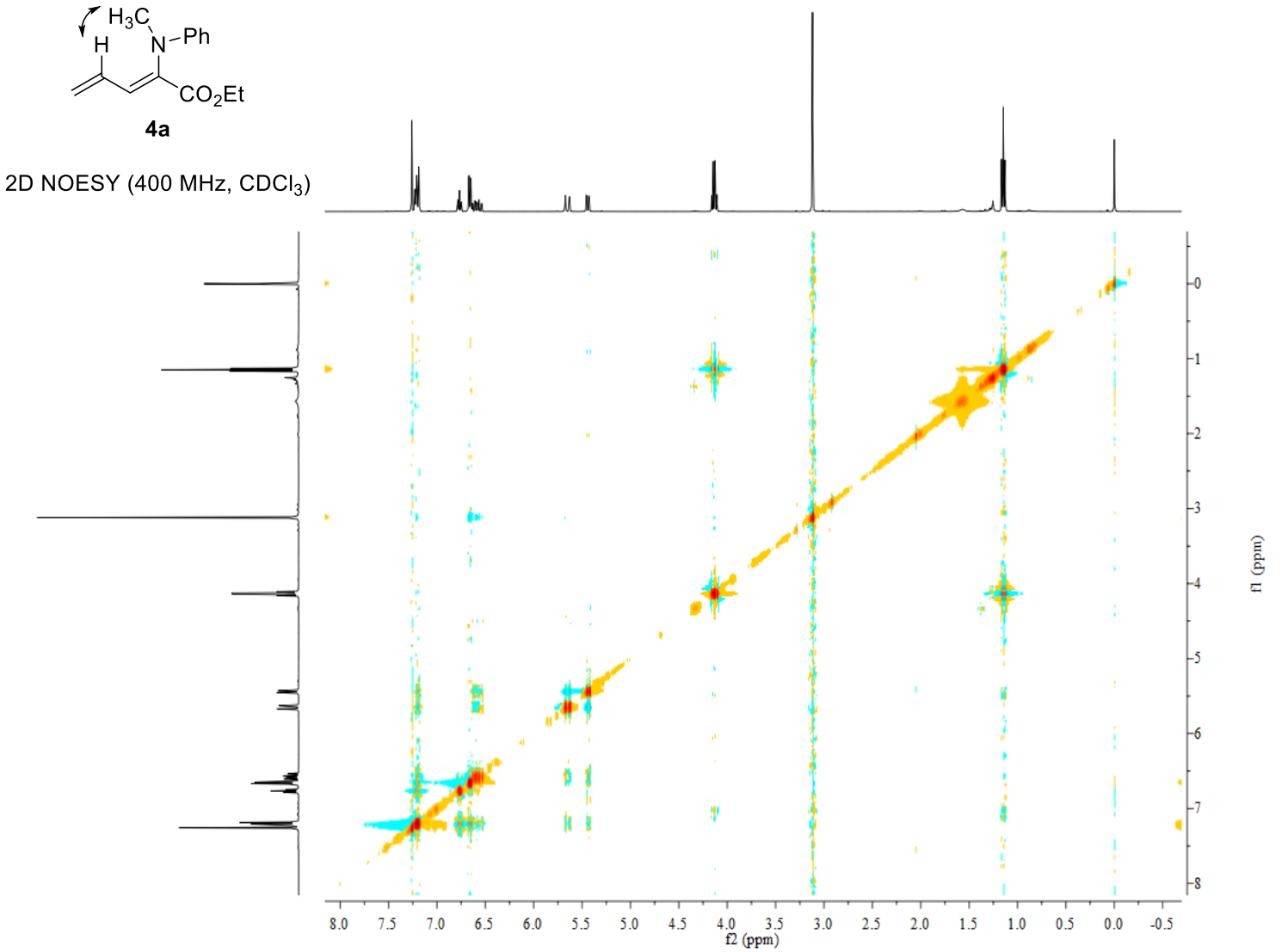


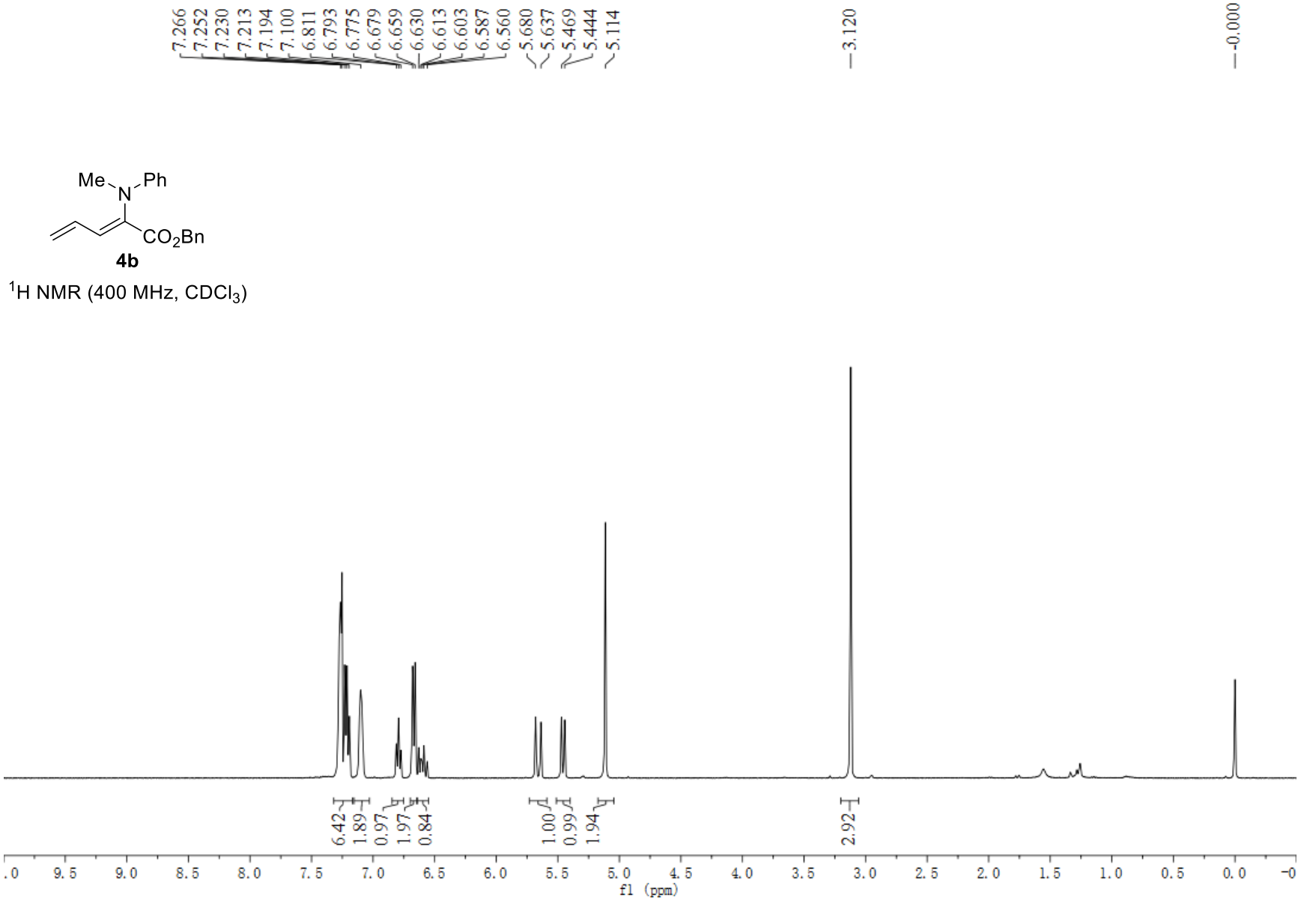
4a

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



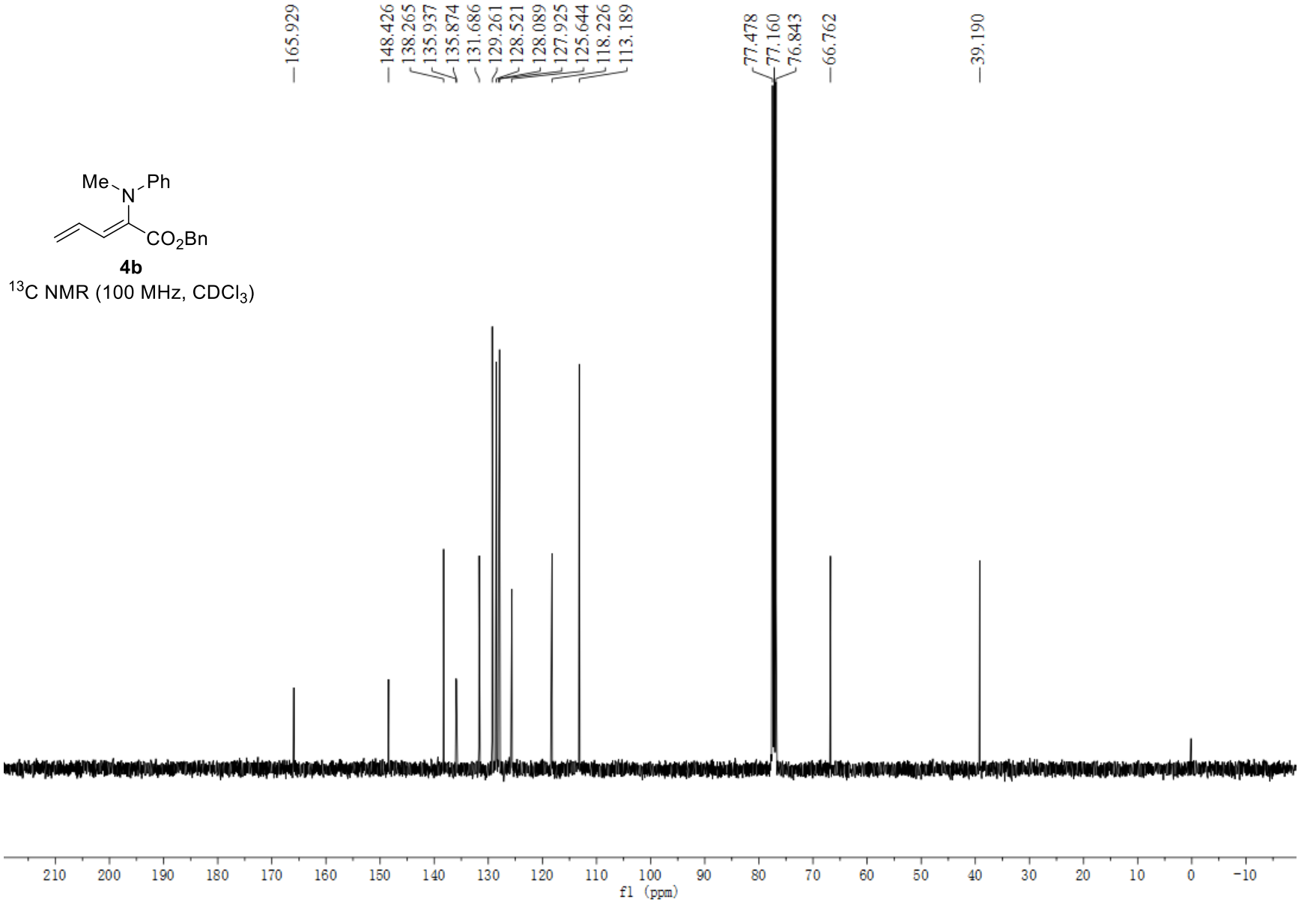

166.010
148.443
137.639
136.115
131.789
129.163
125.264
118.052
113.064
77.478
77.160
76.843
61.048
39.093
14.275
Me
N
Ph
CO2Et
4a
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

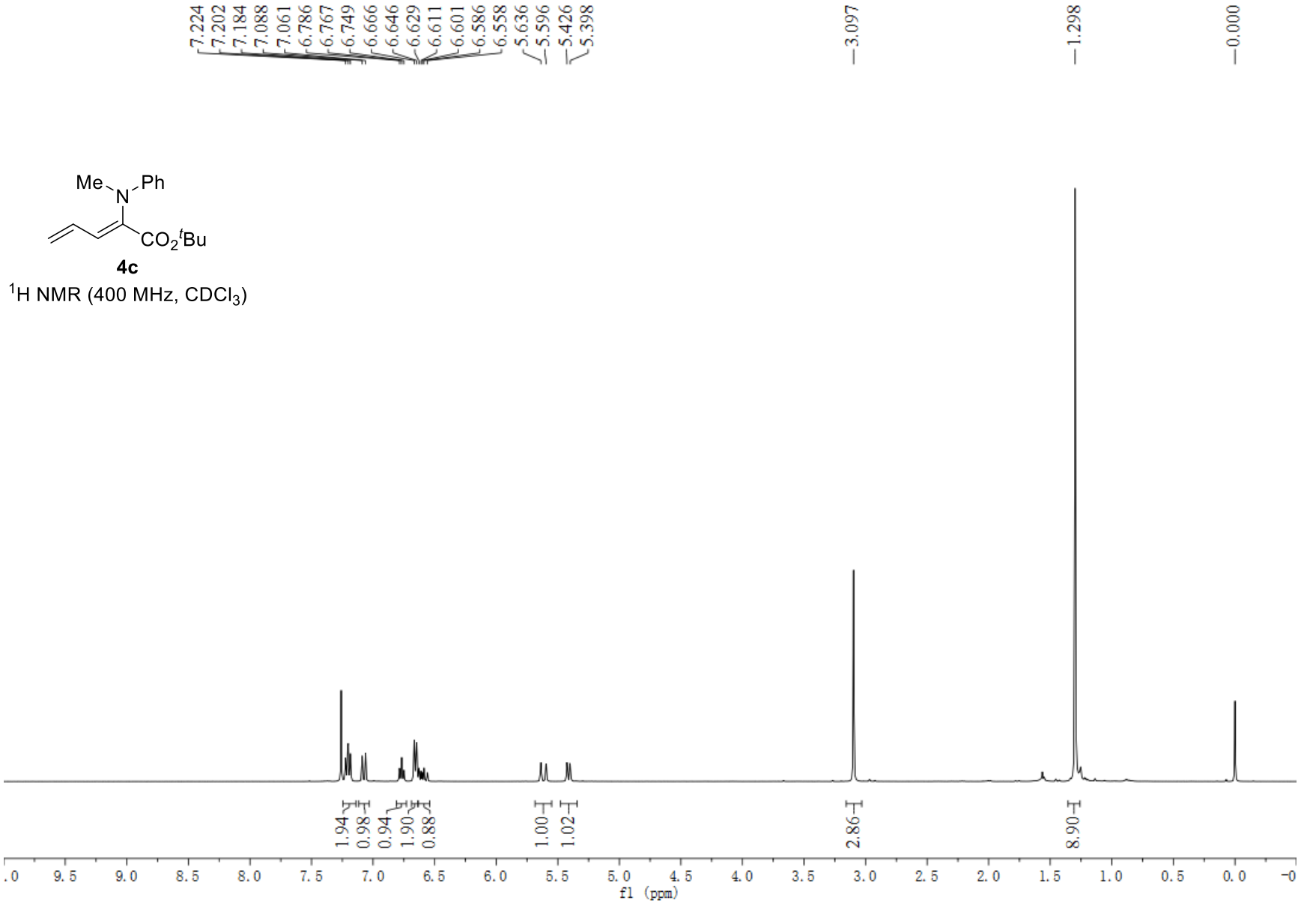

H3C
H
N
Ph
CO2Et
4a
2D NOESY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

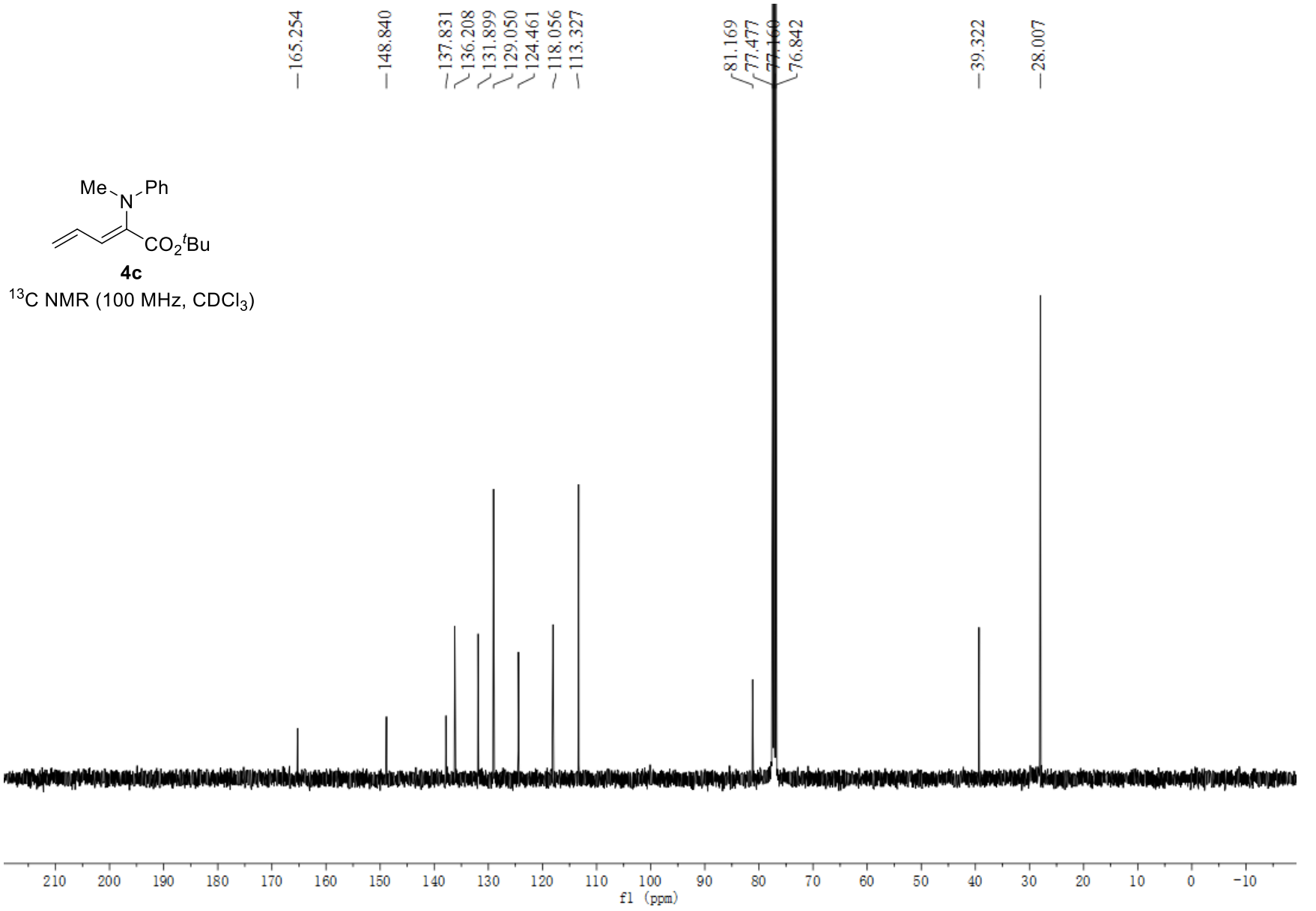


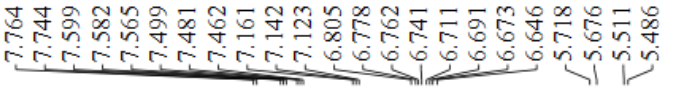
4b

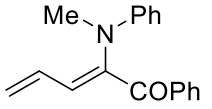
^{1}H NMR (400 MHz, $CDCl_3$)


165.929
148.426
138.265
135.937
135.874
131.686
129.261
128.521
128.089
127.925
125.644
118.226
113.189
77.478
77.160
76.843
66.762
39.190
Me
N
Ph
CO2Bn
4b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.224
7.202
7.184
7.088
7.061
6.786
6.767
6.749
6.666
6.646
6.629
6.611
6.601
6.586
6.558
5.636
5.596
5.426
5.398
3.097
1.298
0.000
Me
N
Ph
CO2tBu
4c
1H NMR (400 MHz, CDCl3)
1.94
0.98
0.94
1.90
0.88
1.00
1.02
2.86
8.90
f1 (ppm)

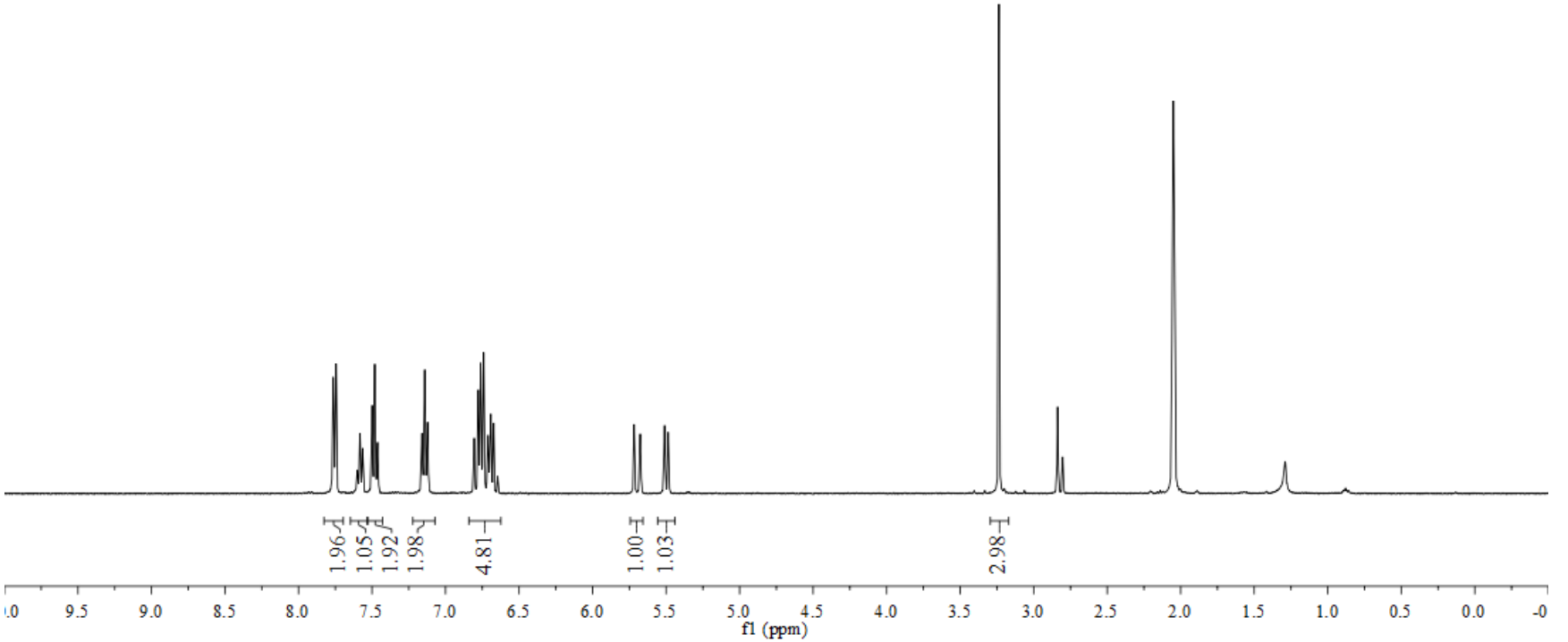

165.254
148.840
137.831
136.208
131.899
129.050
124.461
118.056
113.327
81.169
77.477
77.160
76.842
39.322
28.007
Me
N
Ph
CO2tBu
4c
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

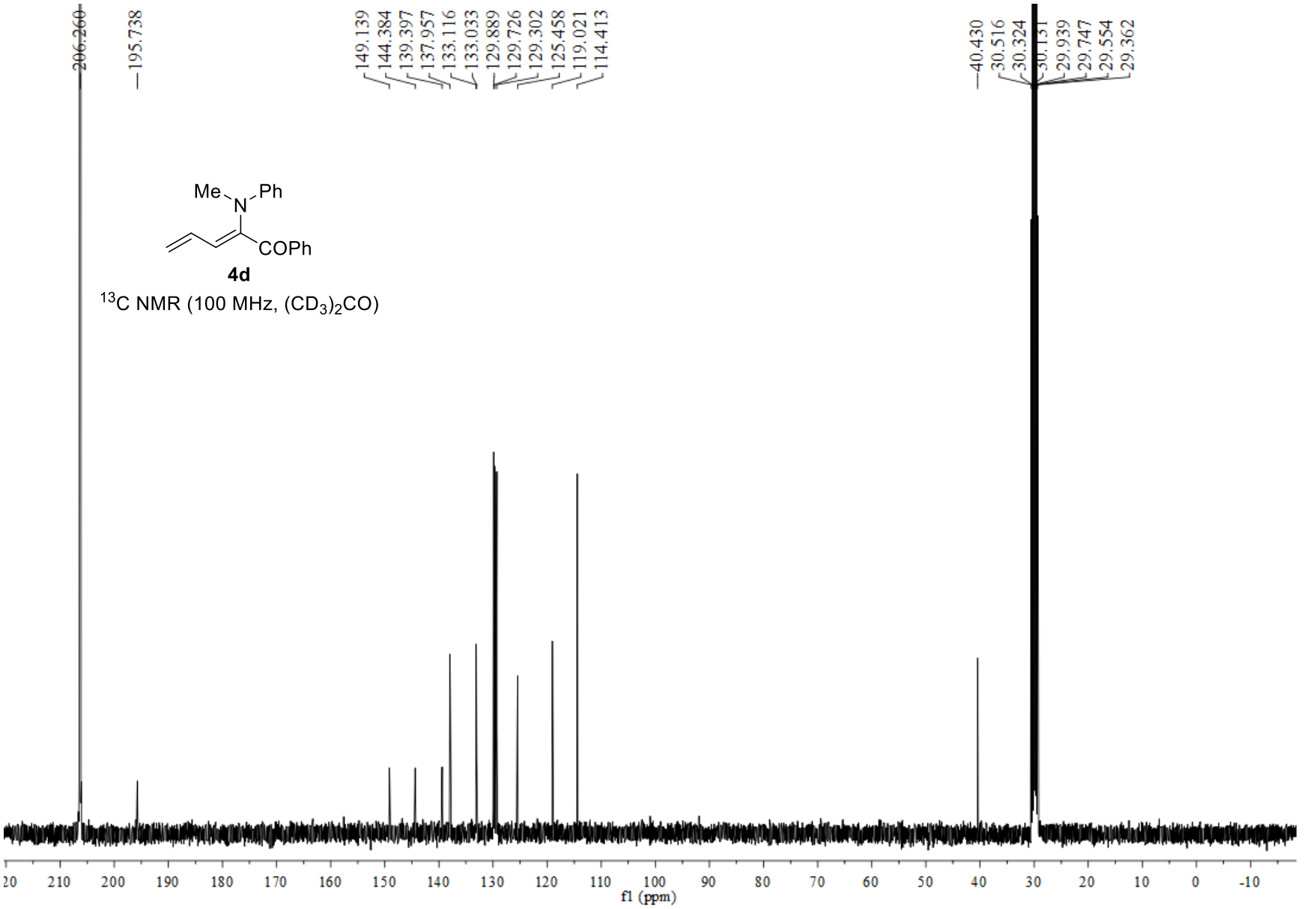


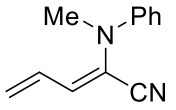


4d

^{1}H NMR (400 MHz, $(CD_3)_2CO$)

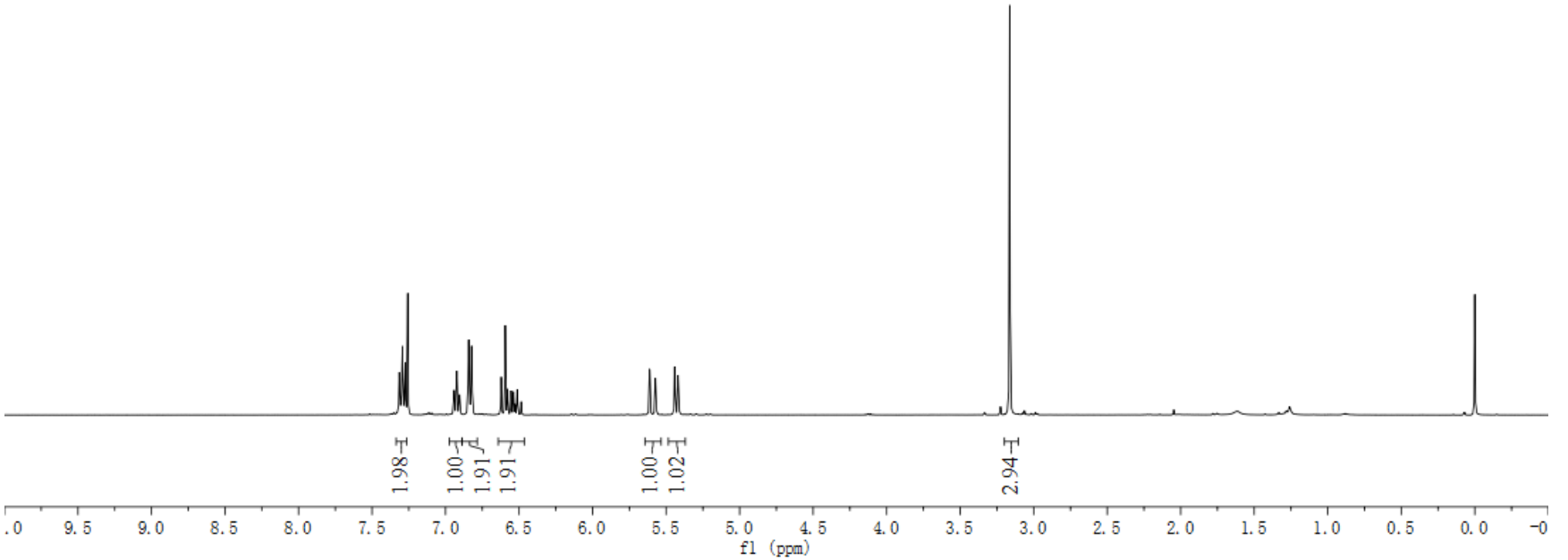


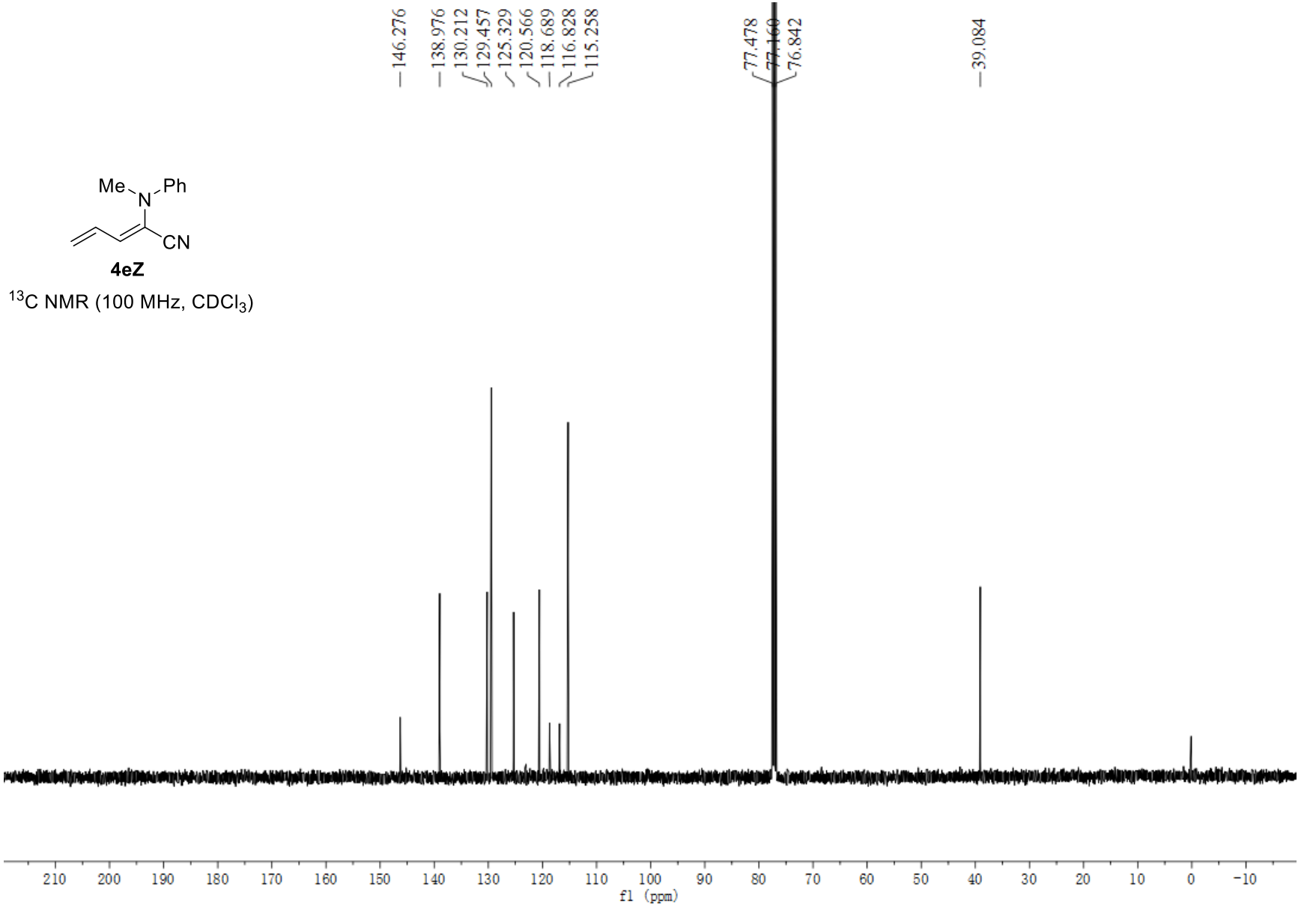

206.260
195.738
149.139
144.384
139.397
137.957
133.116
133.033
129.889
129.726
129.302
125.458
119.021
114.413
40.430
30.516
30.324
30.131
29.939
29.747
29.554
29.362
Me
N
Ph
COPh
4d
13C NMR (100 MHz, (CD3)2CO)
f1 (ppm)



4eZ

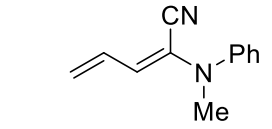
^{1}H NMR (400 MHz, $CDCl_3$)





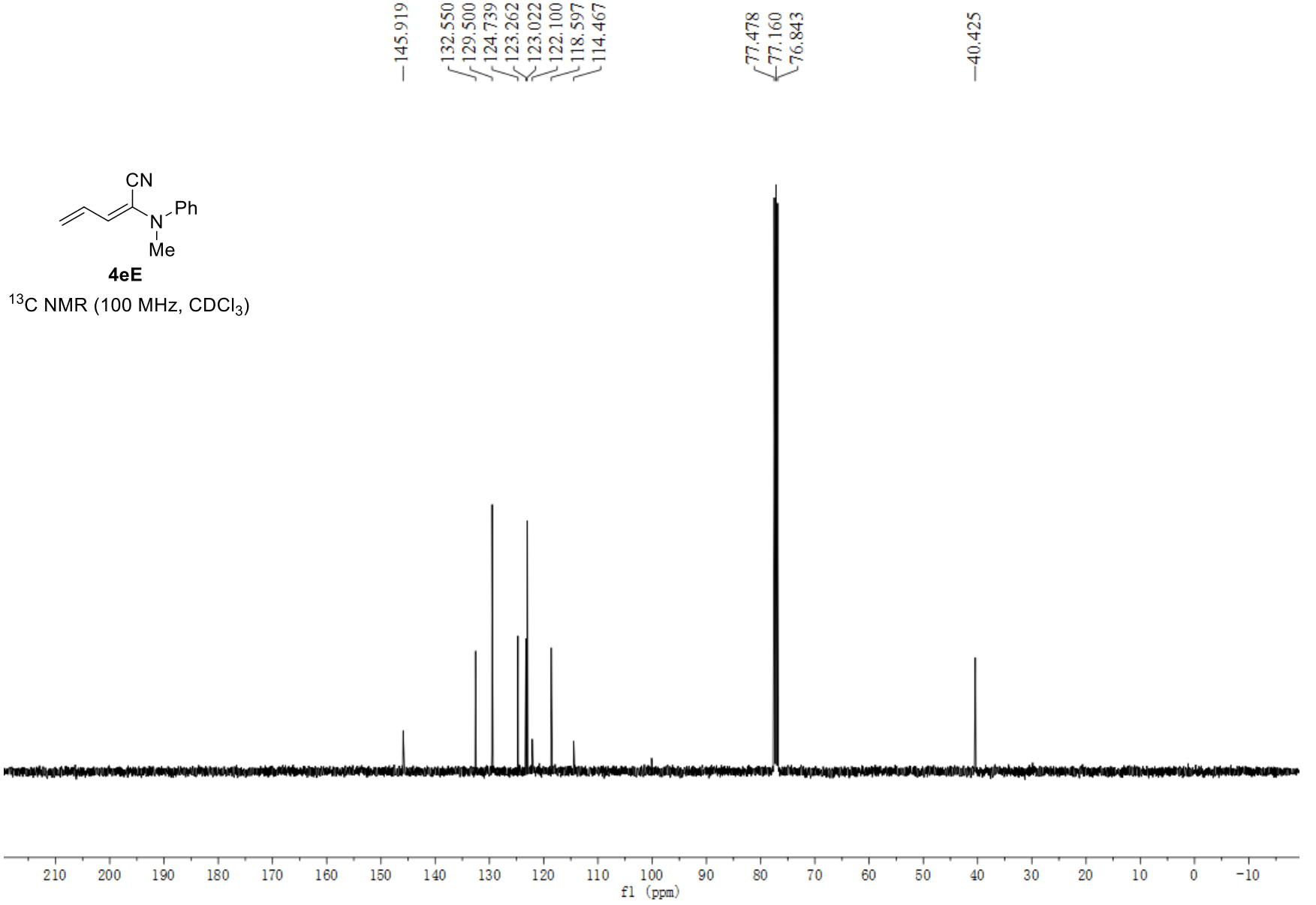
4eZ

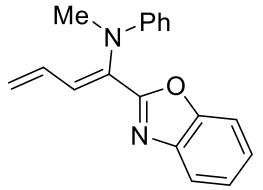
^{13}C NMR (100 MHz, $CDCl_3$)



4eE

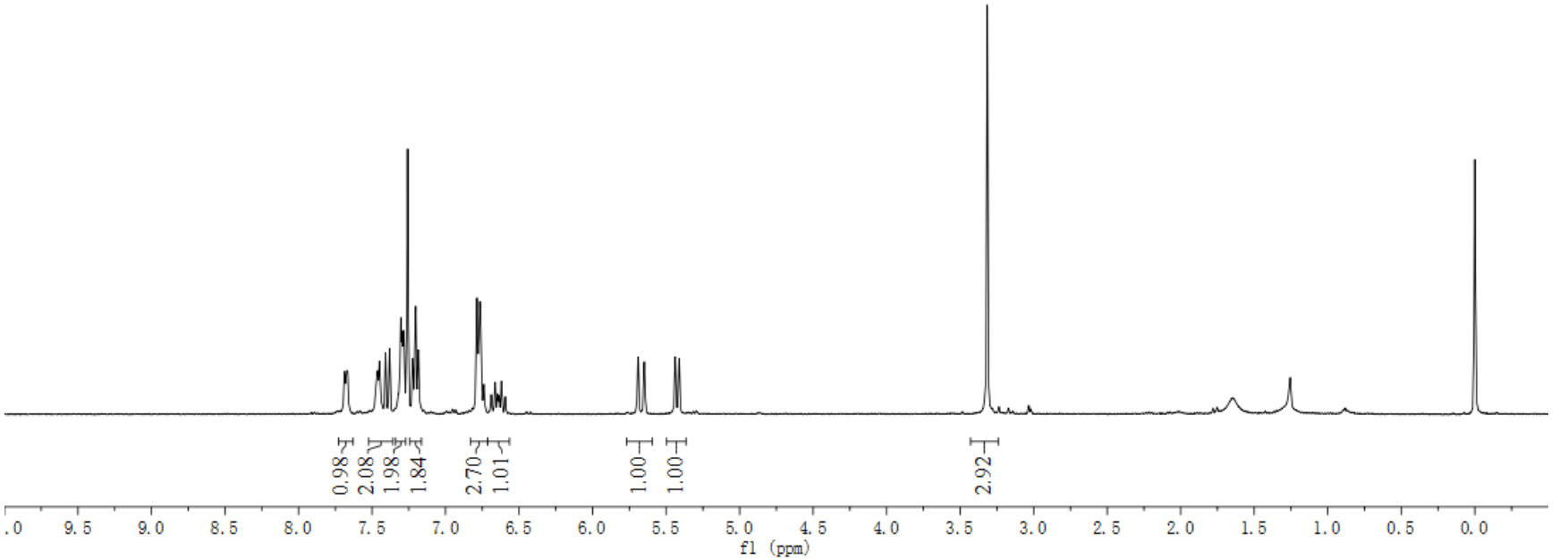
^{1}H NMR (400 MHz, $CDCl_3$)

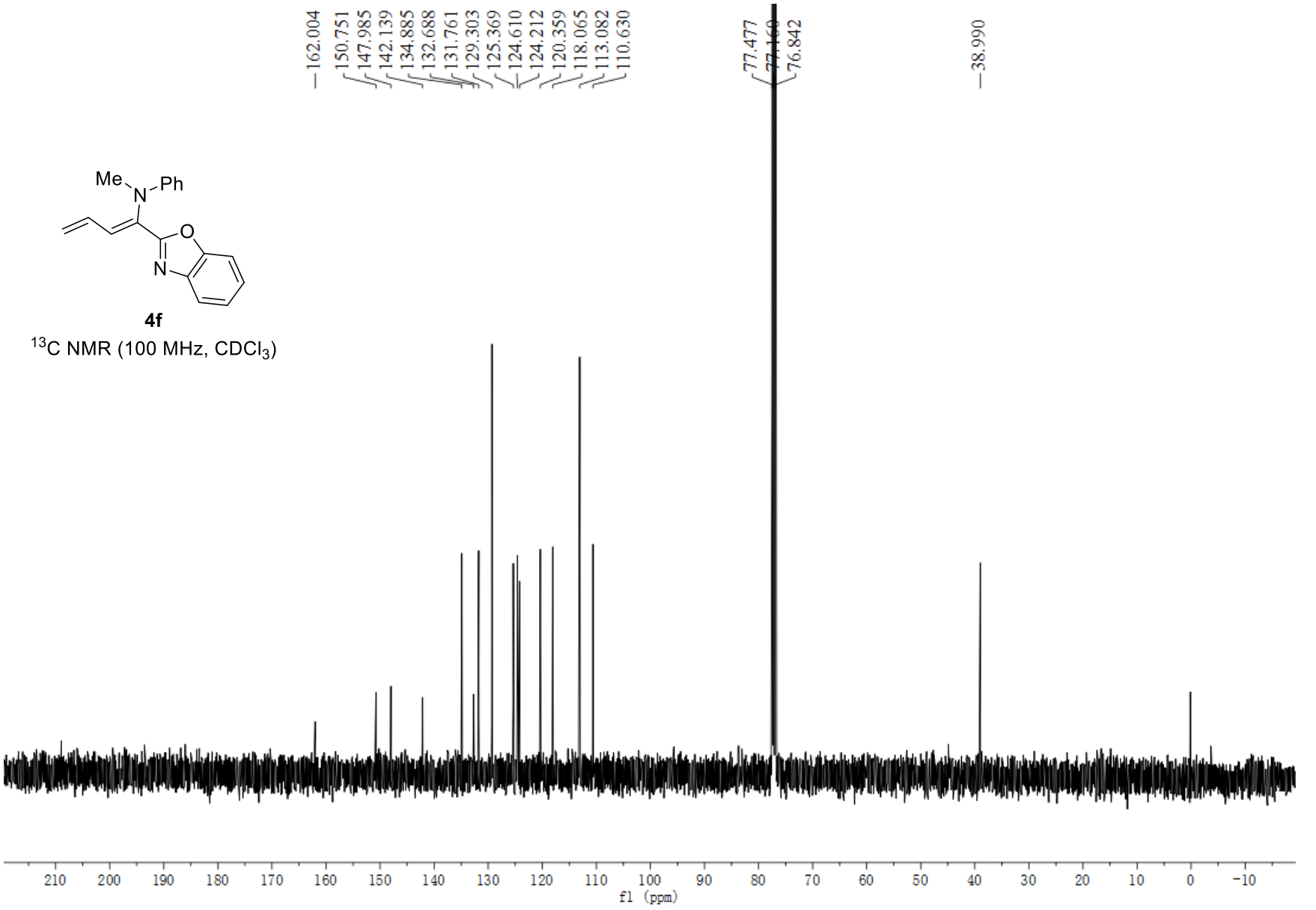

145.919
132.550
129.500
124.739
123.262
123.022
122.100
118.597
114.467
77.478
77.160
76.843
40.425
CN
Ph
N
Me
4eE
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

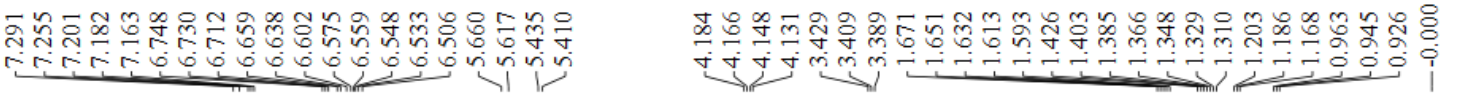


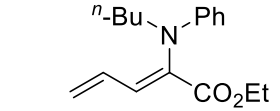
4f

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



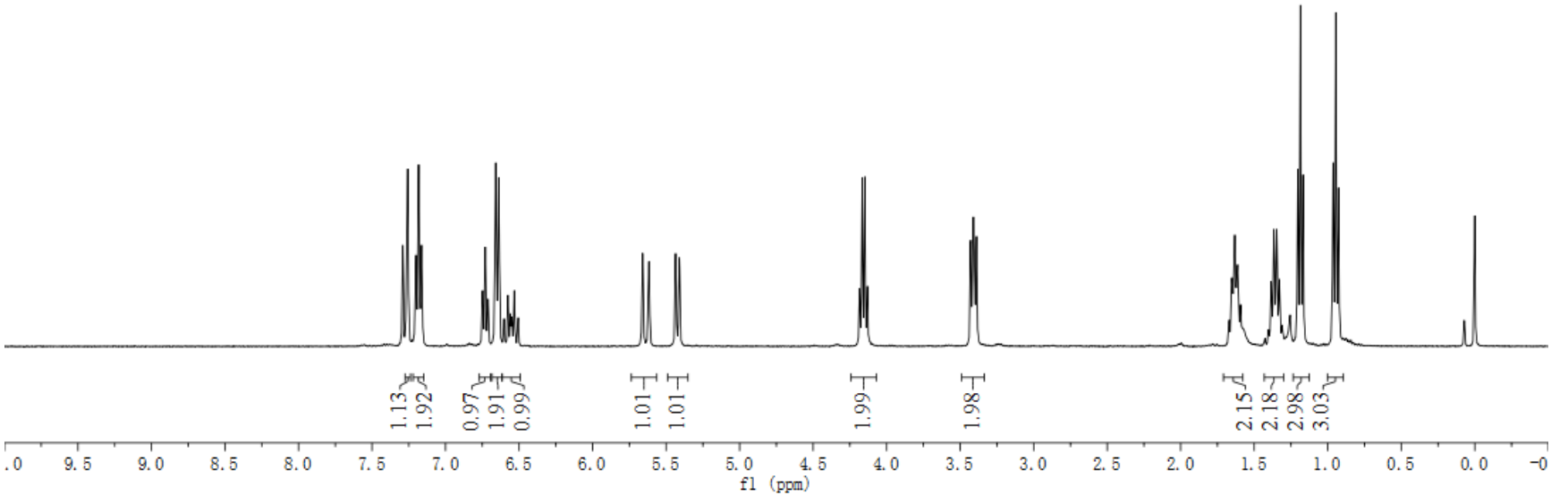

162.004
150.751
147.985
142.139
134.885
132.688
131.761
129.303
125.369
124.610
124.212
120.359
118.065
113.082
110.630
77.477
77.160
76.842
38.990
Me
N
Ph
O
N
4f
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

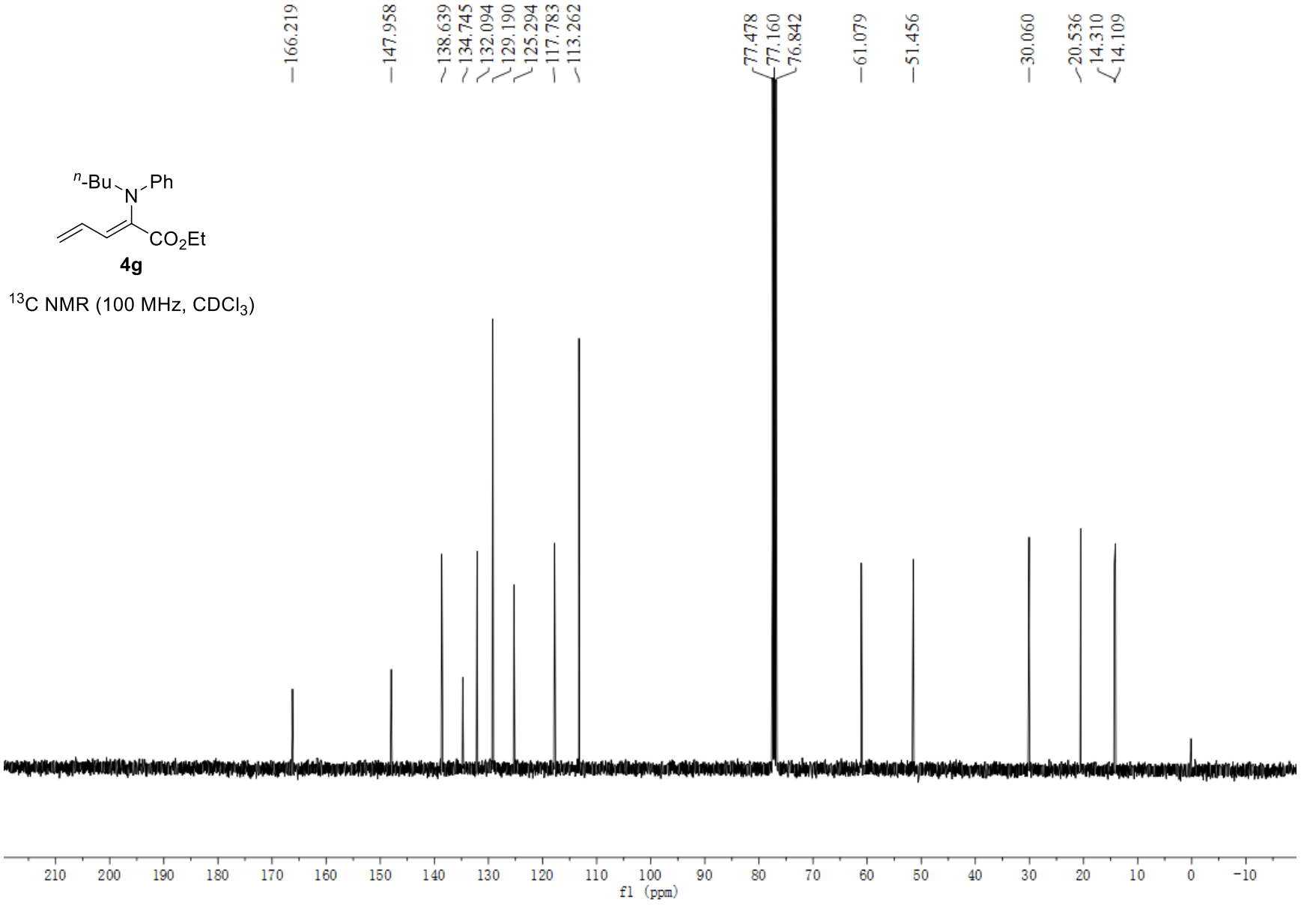


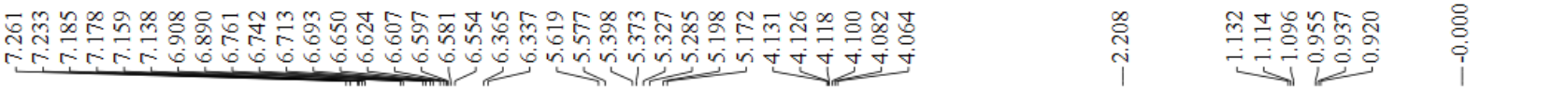


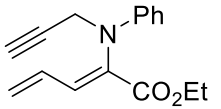
4g

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



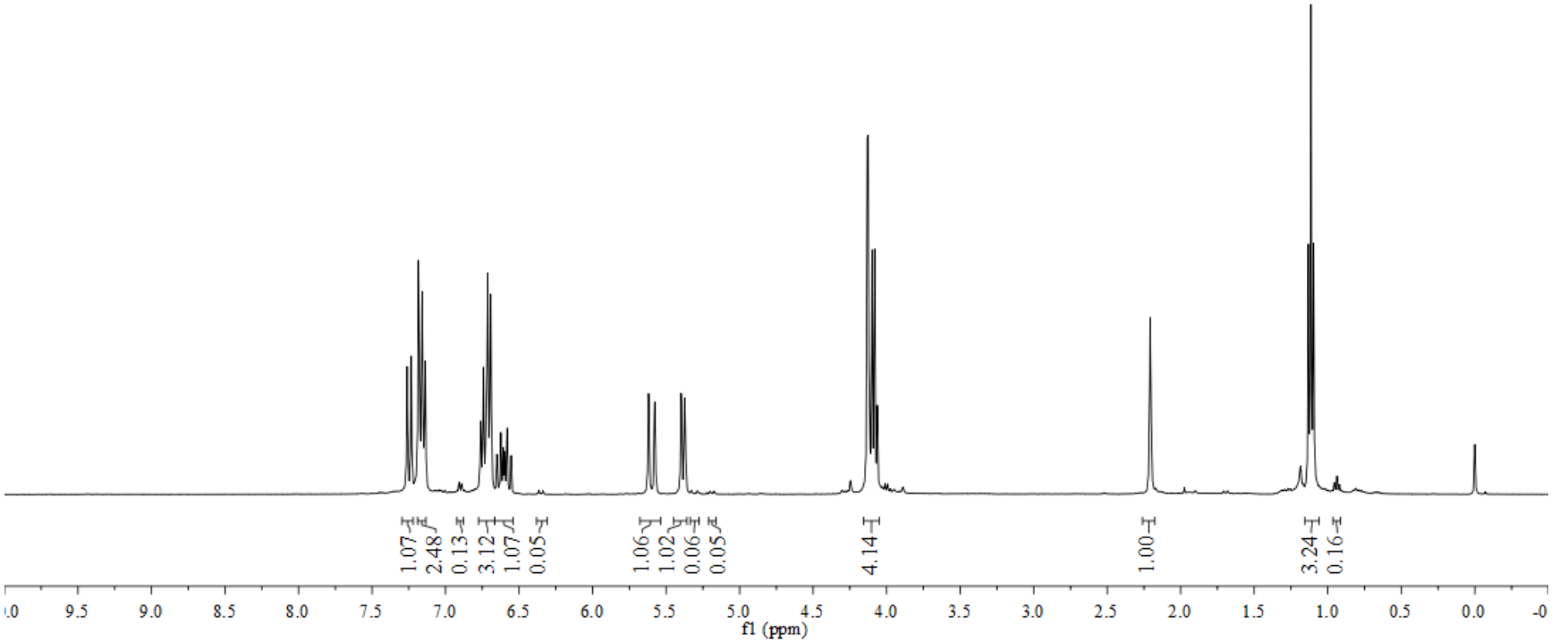

166.219
147.958
138.639
134.745
132.094
129.190
125.294
117.783
113.262
77.478
77.160
76.842
61.079
51.456
30.060
20.536
14.310
14.109
n-Bu
N
Ph
CO2Et
4g
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

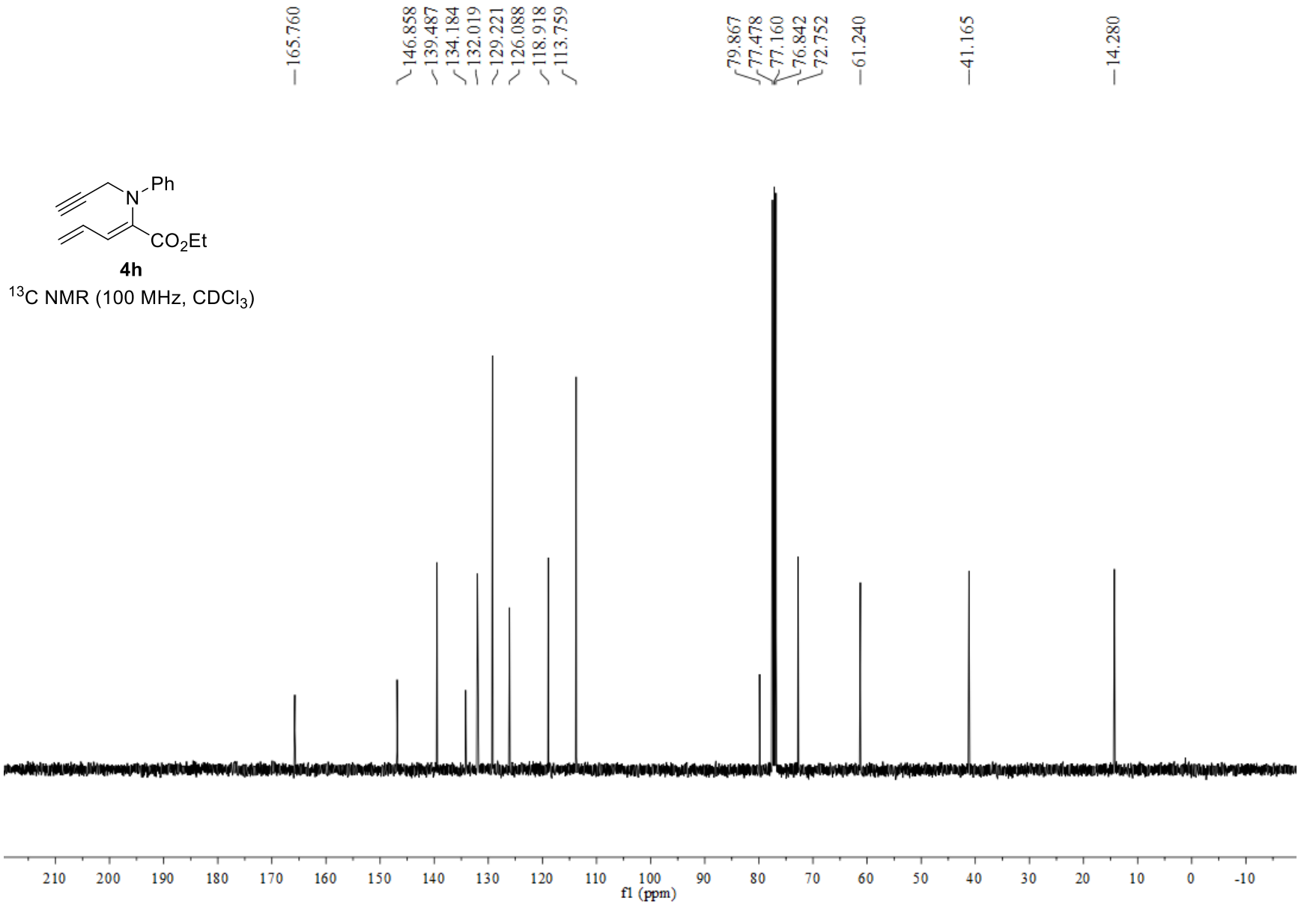




4h

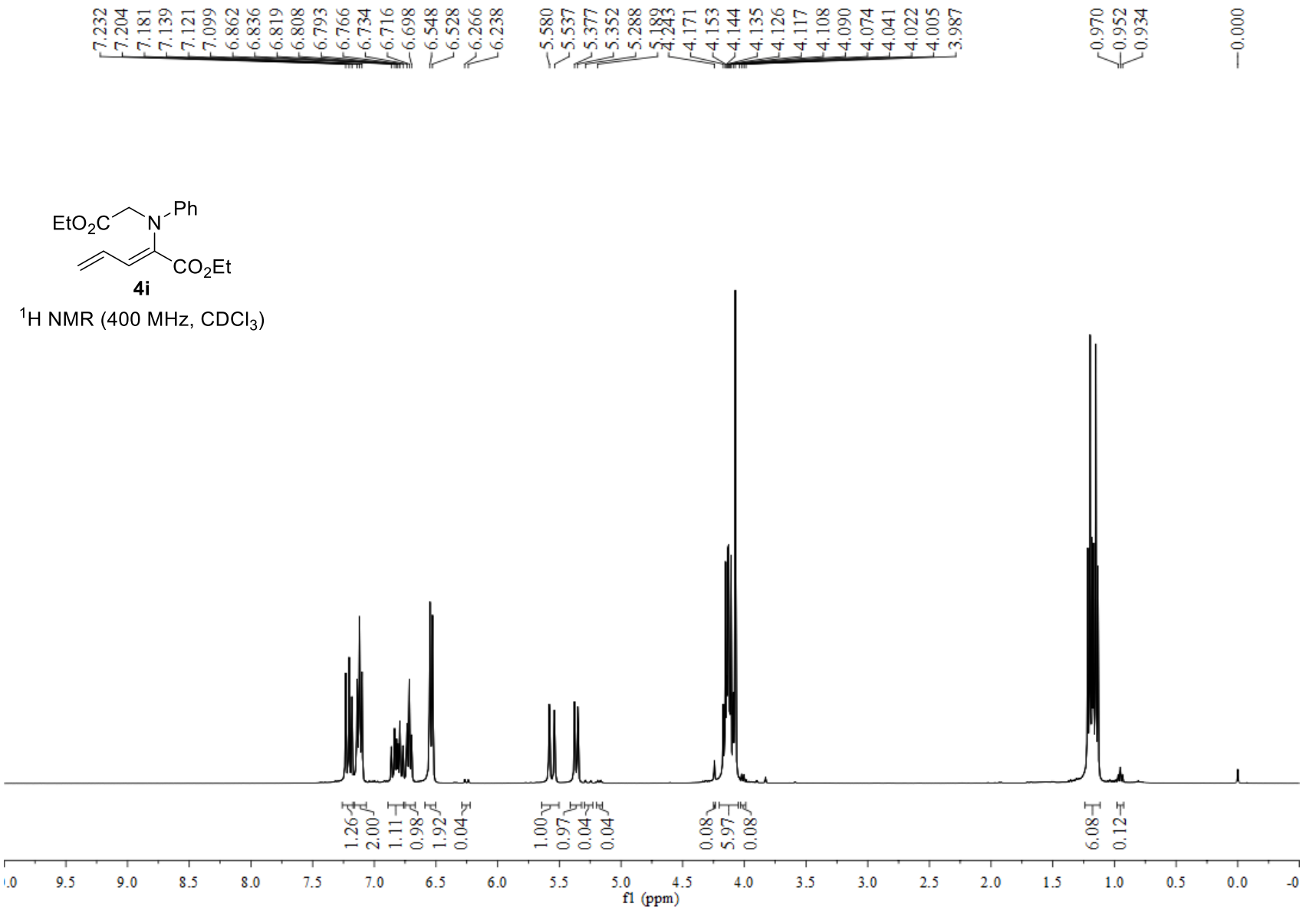
^{1}H NMR (400 MHz, $CDCl_3$)

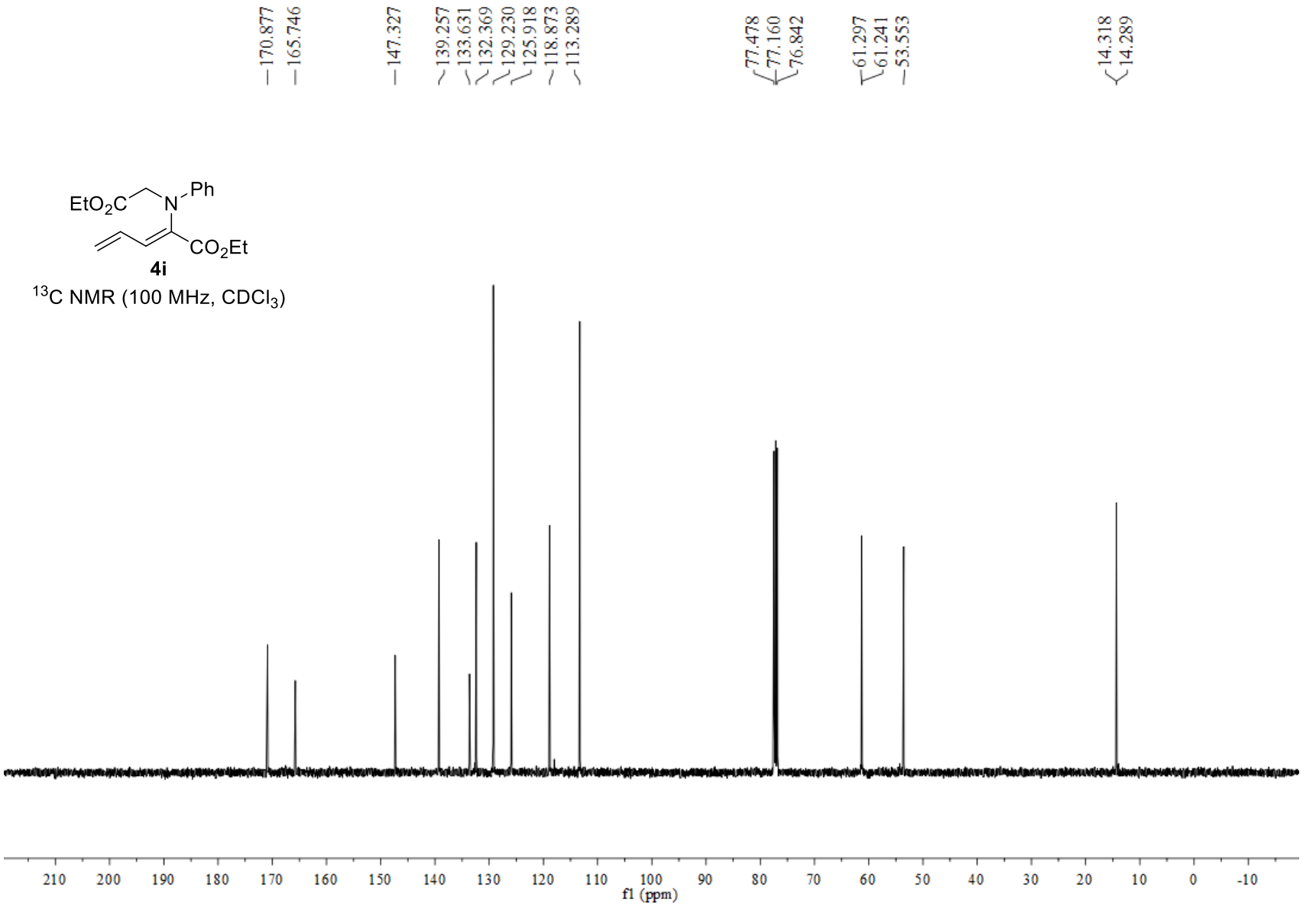


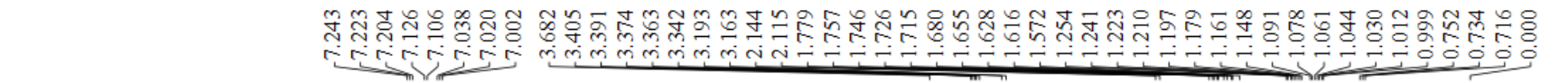


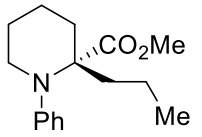
4h

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


7.232
7.204
7.181
7.139
7.121
7.099
6.862
6.836
6.819
6.808
6.793
6.766
6.734
6.716
6.698
6.548
6.528
6.266
6.238
5.580
5.537
5.377
5.352
5.288
4.171
4.153
4.144
4.135
4.126
4.117
4.108
4.090
4.074
4.041
4.022
4.005
3.987
0.970
0.952
0.934
0.000
EtO2C
N
Ph
CO2Et
4i
1H NMR (400 MHz, CDCl3)
1.26
2.00
1.11
0.98
1.92
0.04
1.00
0.97
0.04
0.04
0.08
5.97
0.08
6.08
0.12
f1 (ppm)

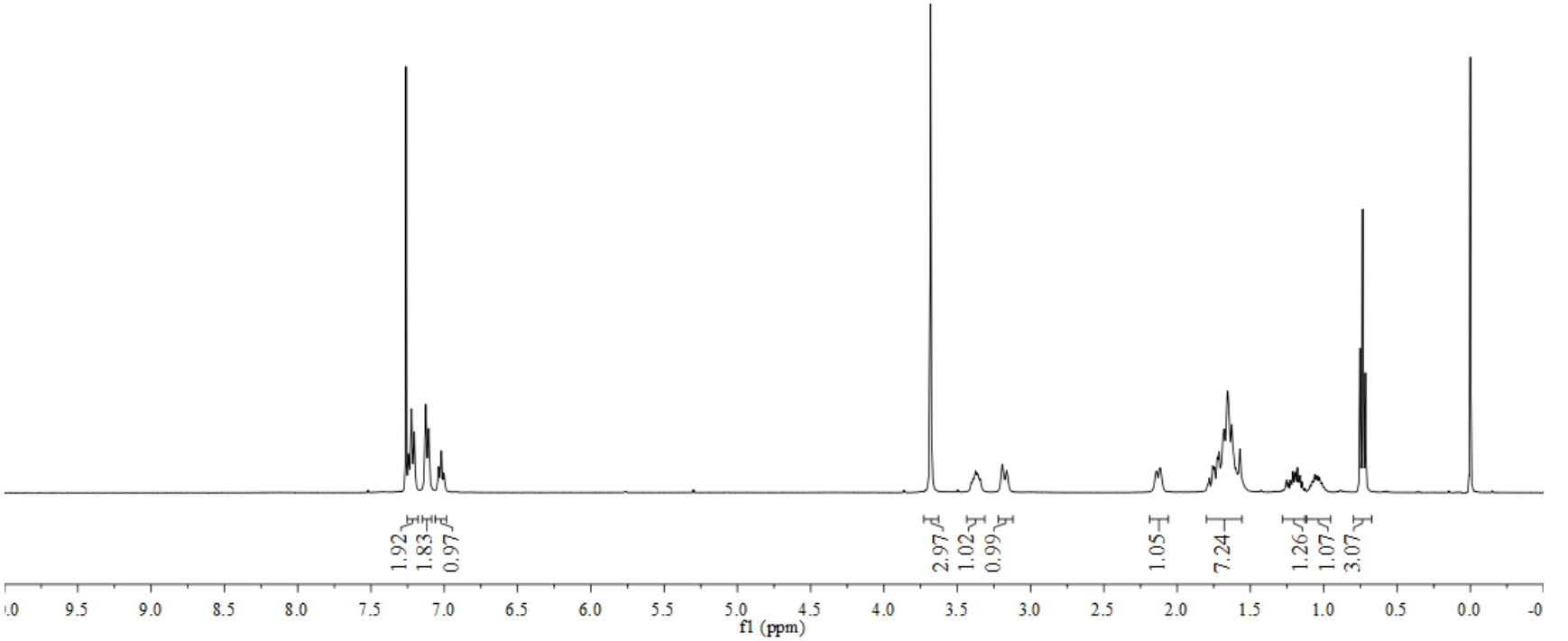

170.877
165.746
147.327
139.257
133.631
132.369
129.230
125.918
118.873
113.289
77.478
77.160
76.842
61.297
61.241
53.553
14.318
14.289
EtO2C
N
Ph
CO2Et
4i
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

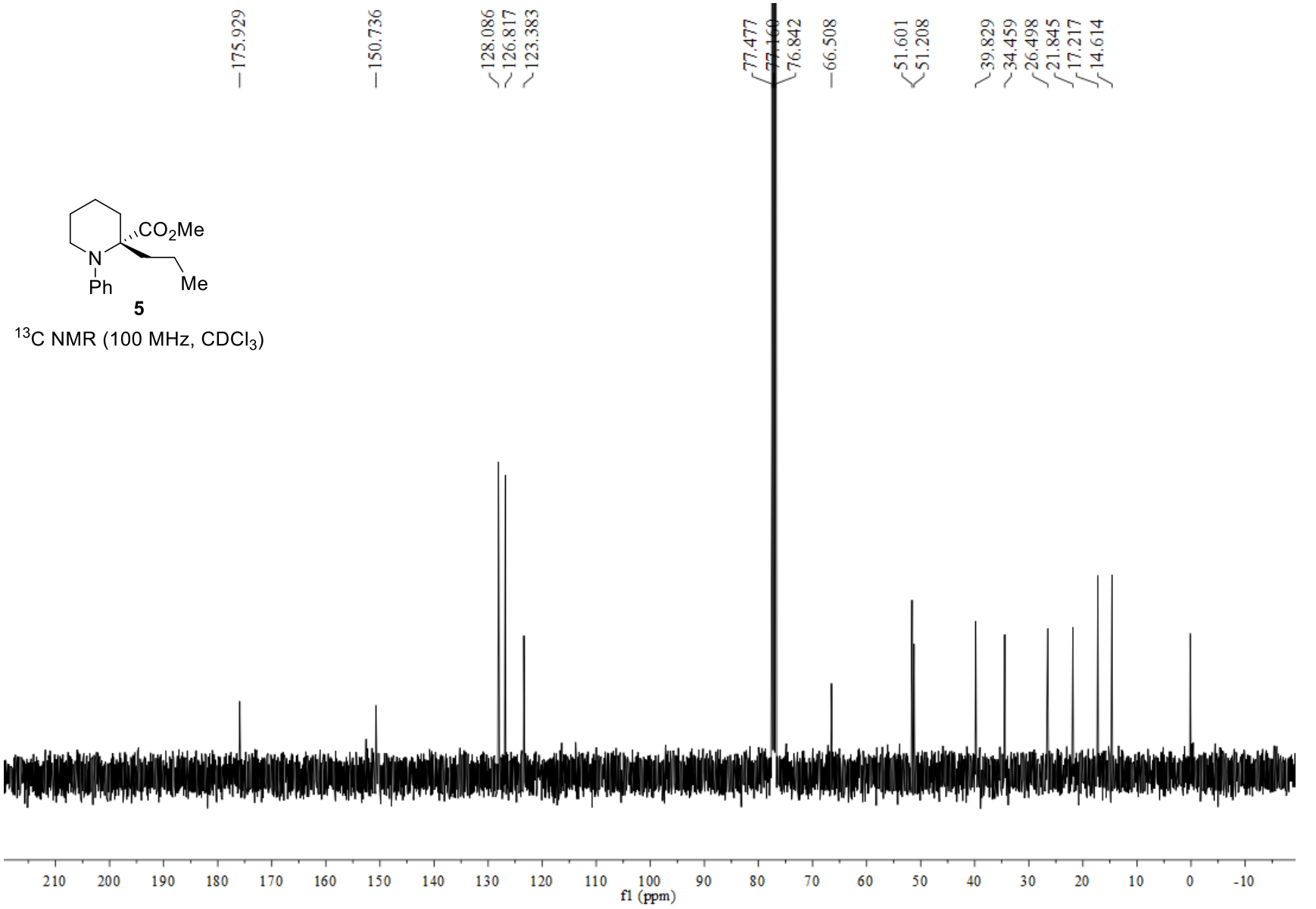




5

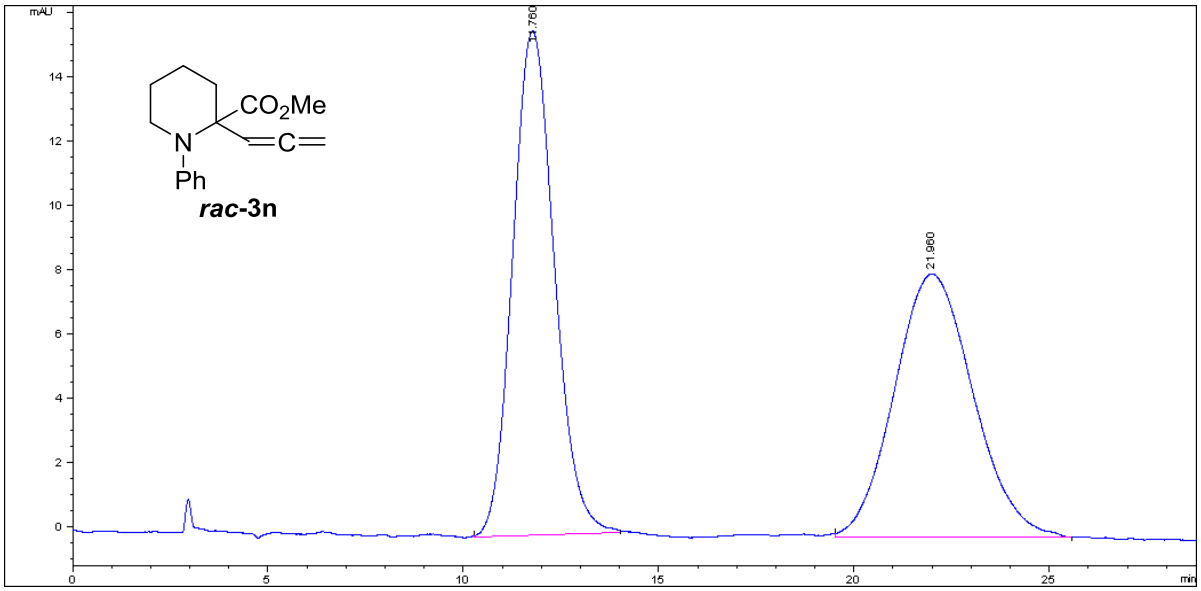
^{1}H NMR (400 MHz, $CDCl_3$)



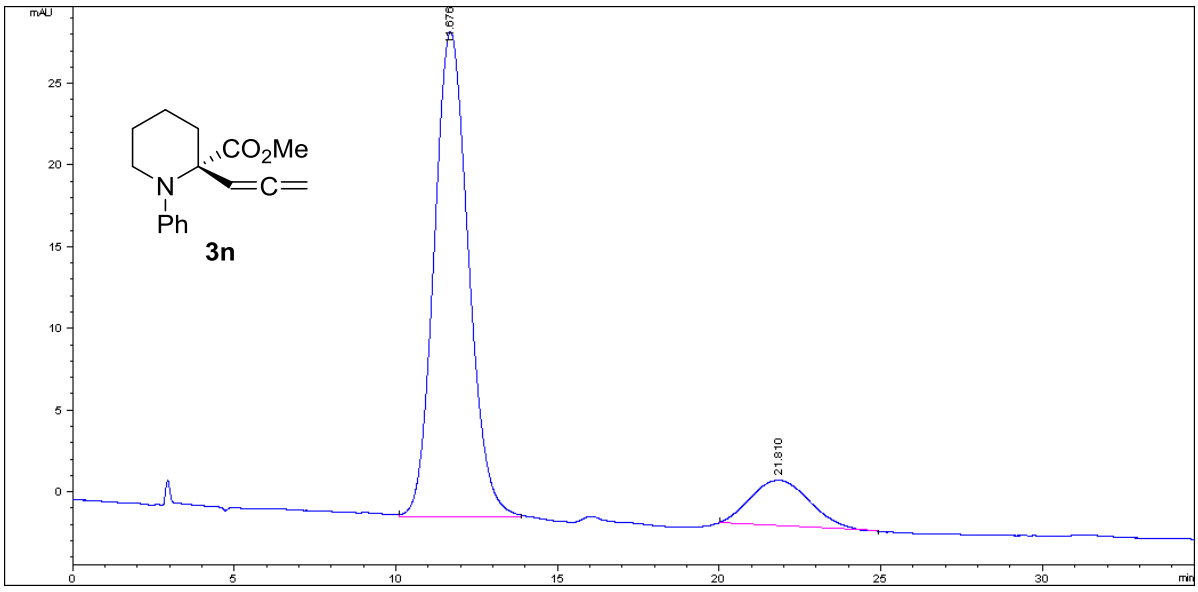


5

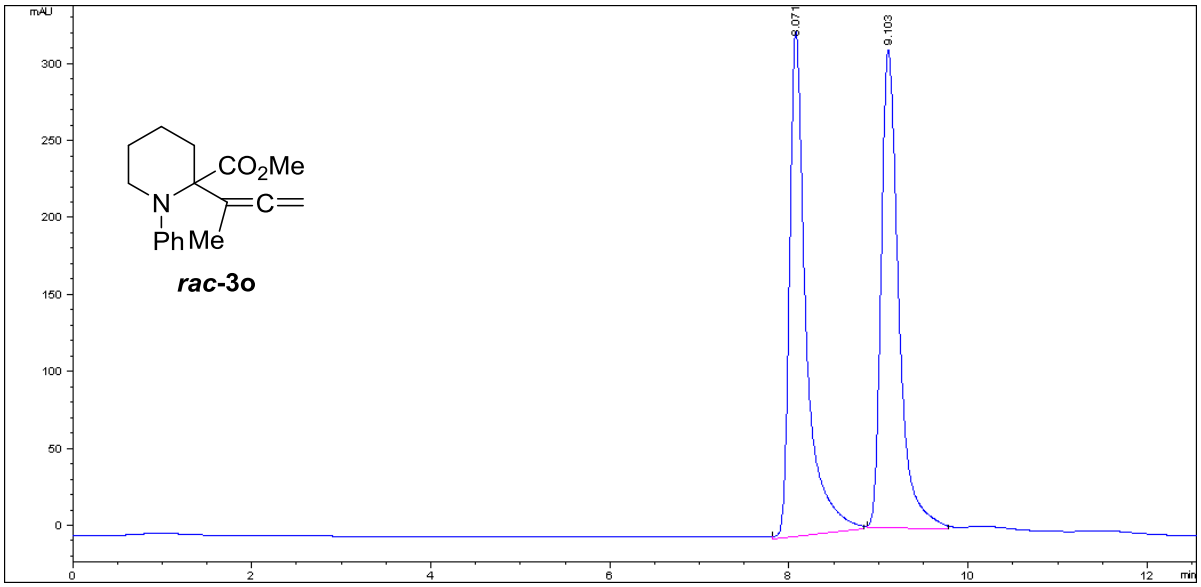
^{13}C NMR (100 MHz, $CDCl_3$)



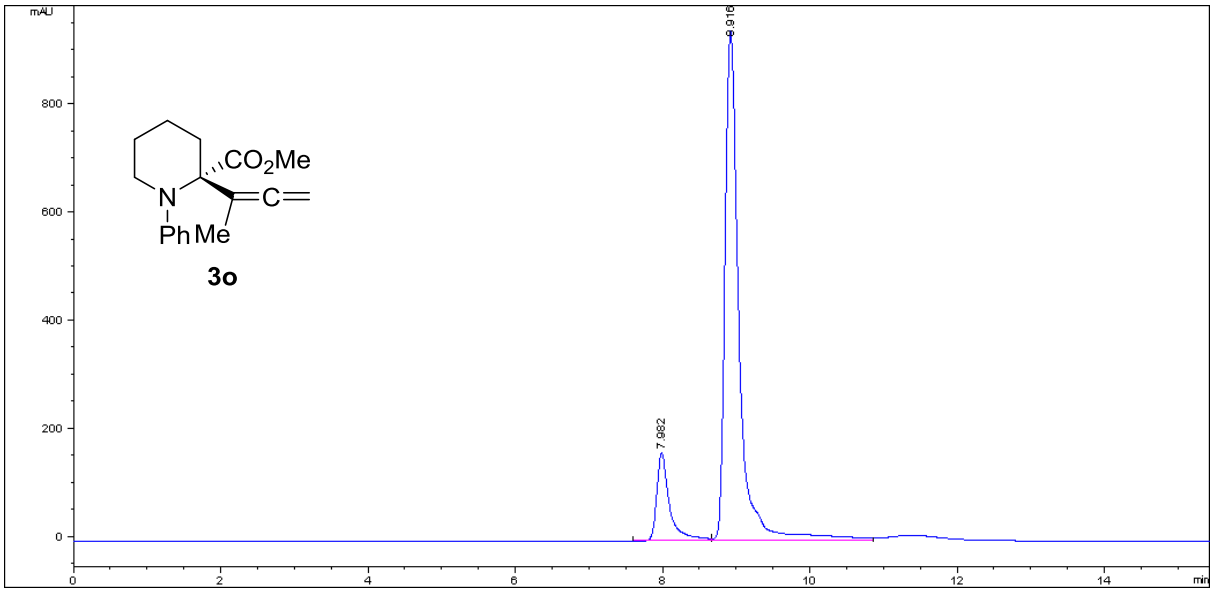
Number	Time(min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area(%)
1	11.76	1165	15.7	1.2386	0.876	50.284
2	21.96	1151.9	8.2	2.3391	0	49.716



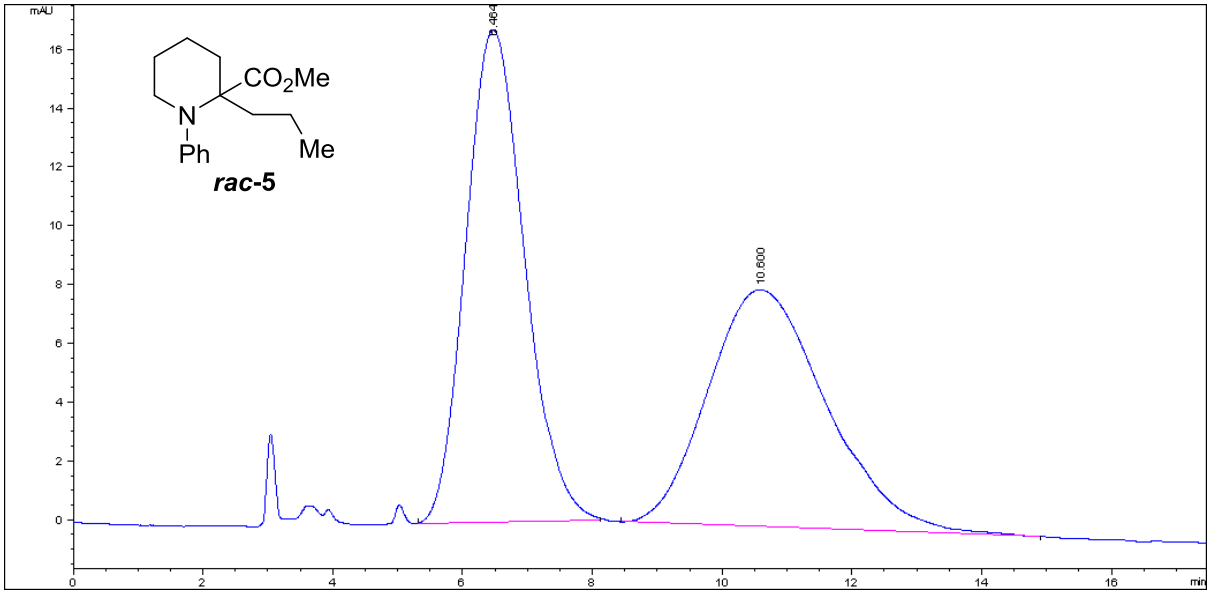
Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	11.676	2194.4	29.7	1.2316	0.878	85.979
2	21.81	357.9	2.8	1.4947	0.83	14.021



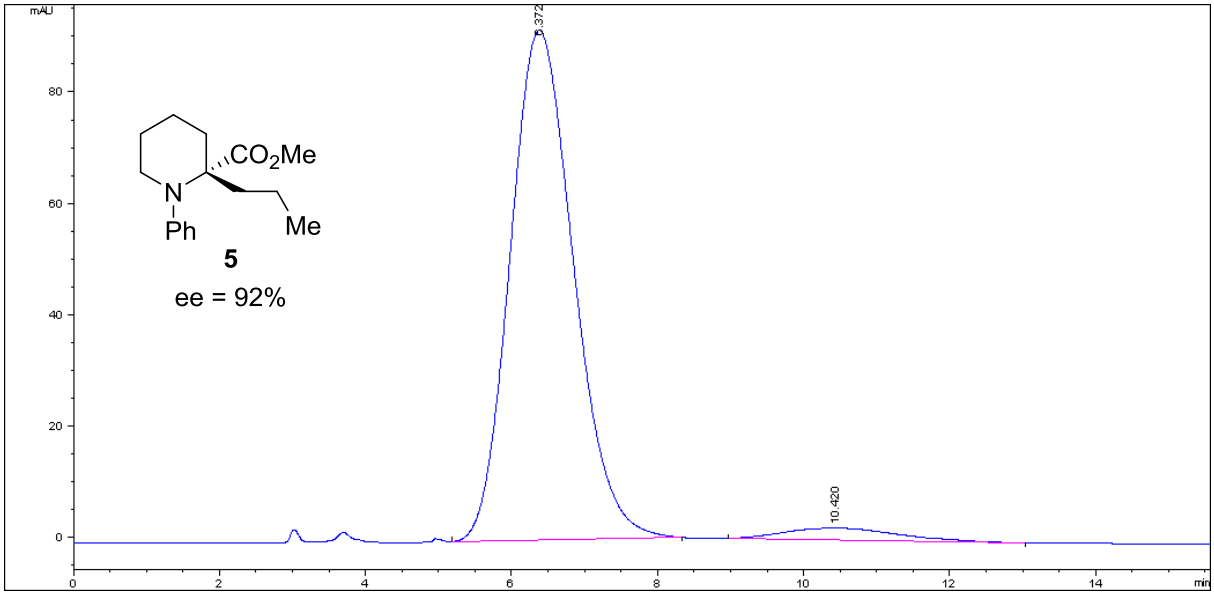
Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	8.071	4232.8	328.6	0.2147	0.578	49.854
2	9.103	4257.6	310.9	0.2282	0.649	50.146



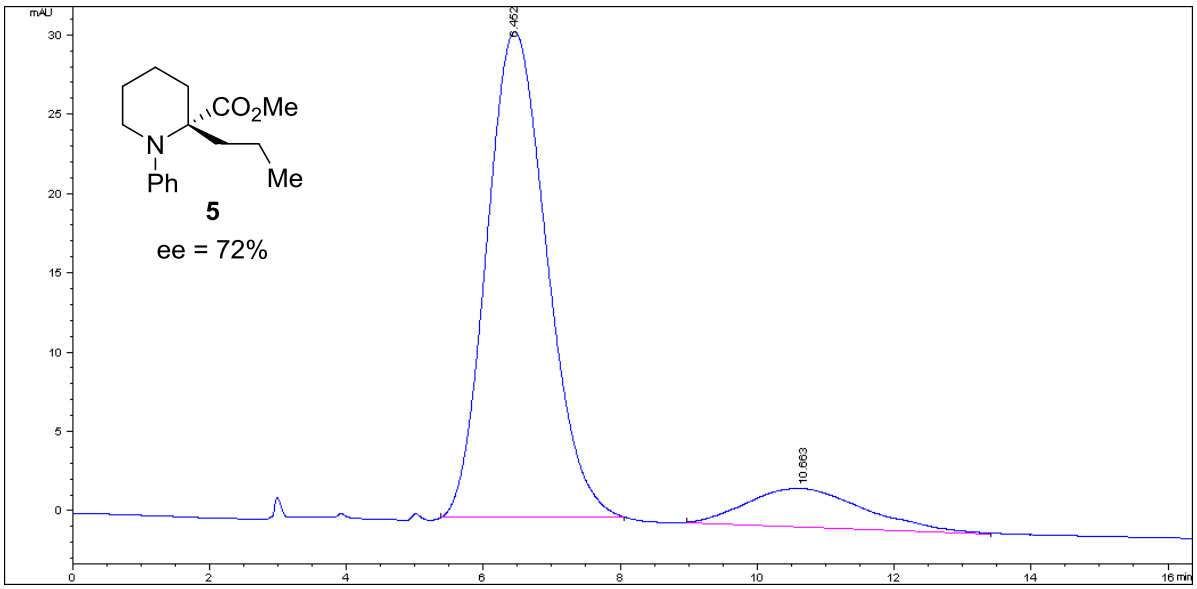
Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	7.982	2005.4	162.4	0.1804	0.545	13.582
2	8.916	12759.9	943.1	0.203	0.543	86.418



Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	6.464	1053.4	16.7	0.9585	0.825	50.661
2	10.6	1025.9	8.1	2.1203	0.729	49.339

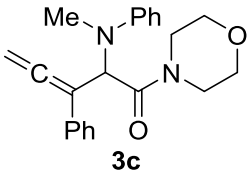


Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	6.372	5539.5	91.8	0.9402	0.804	95.900
2	10.42	236.8	2.2	1.2815	0.742	4.100



Number	Time (min)	Area(mAU s)	Height(mAU)	Width(min)	Symmetry factor	Area (%)
1	6.452	1862.8	30.6	1.0138	0.838	86.153
2	10.663	299.4	2.4	2.0374	0.673	13.847

The crystal of compound **3c** was obtained by leaving alone its solution in hexane and ether at room temperature in the open air for seven days. The crystal data of compound **3c** have been deposited in CCDC with number 1534313.



3c

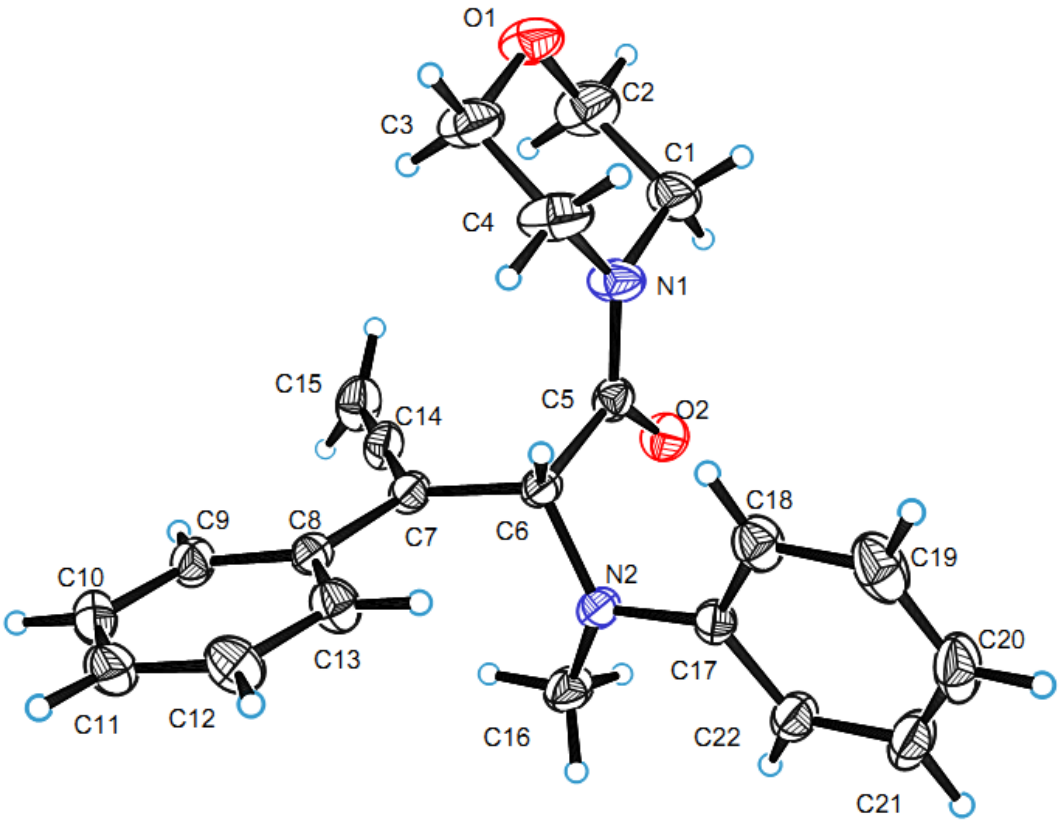


Table 1 Crystal data and structure refinement for zmg-08-07.

Identification code	zmg-08-07
Empirical formula	$C_{22}H_{24}N_2O_2$
Formula weight	348.43
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.8982(2)
b/Å	5.94960(10)
c/Å	21.2447(3)

α/°	90
β/°	97.1390(10)
γ/°	90
Volume/Å^3	1868.50(5)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.631
F(000)	744.0
Crystal size/mm^3	0.320 × 0.310 × 0.250
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.388 to 142.53
Index ranges	-14 ≤ h ≤ 18, -7 ≤ k ≤ 4, -19 ≤ l ≤ 25
Reflections collected	6476
Independent reflections	3508 [R_{int} = 0.0143, R_{sigma} = 0.0184]
Data/restraints/parameters	3508/1/236
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1837
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1895
Largest diff. peak/hole / e Å^{-3}	0.66/-0.37

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for zmg-08-07. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	6517.2(11)	6749(3)	4749.0(8)	57.3(4)
N2	8066.0(11)	4226(3)	5110.5(7)	42.7(4)
O1	4566.4(12)	2914(4)	3134.1(9)	74.4(6)
N1	5835.3(13)	3848(3)	4199.1(10)	58.1(5)
C17	7808.2(13)	3377(3)	5674.3(9)	41.1(5)
C6	7489.9(12)	3726(3)	4521.4(8)	38.8(4)
C7	7940.4(13)	4315(3)	3936.1(9)	41.2(4)
C8	8739.2(13)	2962(3)	3797.1(9)	40.7(4)
C5	6568.8(13)	4920(3)	4495.9(9)	42.6(5)
C14	7624.1(15)	5948(4)	3562(1)	49.5(5)
C9	9182.1(15)	3491(4)	3276.7(10)	53.1(5)
C13	9056.9(15)	1150(4)	4170.9(11)	52.8(5)
C22	8107.5(16)	4405(4)	6252.5(10)	55.0(6)
C16	8616.3(17)	6237(4)	5142.3(11)	57.3(6)
C18	7283.7(16)	1439(4)	5693.1(12)	56.6(6)
C11	10197.3(16)	397(5)	3498.0(12)	61.1(6)

C12	9783.2(16)	-120(4)	4021.6(13)	60.7(6)
C10	9904.3(16)	2220(5)	3132.4(11)	62.3(7)
C15	7324.3(19)	7587(5)	3191.9(11)	64.4(7)
C21	7913(2)	3480(6)	6821.1(11)	73.5(9)
C19	7107(2)	563(5)	6275.0(16)	75.1(8)
C20	7420(2)	1569(6)	6835.7(13)	78.3(9)
C1	4950.1(16)	4934(6)	4120.0(14)	71.7(8)
C3	5434(2)	1905(6)	3210.8(15)	79.2(9)
C4	5807(2)	1657(5)	3882.3(16)	78.9(9)
C2	4611(2)	5069(6)	3438.1(16)	85.3(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for zmg-08-07. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	59.1(9)	50.1(9)	62.9(10)	-18.9(7)	8.5(7)	4.8(7)
N2	45.4(9)	48.0(9)	33.8(8)	-0.6(7)	2.2(6)	-8.1(7)
O1	61(1)	83.3(12)	71.8(12)	-5.5(10)	-19.8(9)	5.7(9)
N1	44.4(9)	54.8(11)	71.9(13)	-16.4(10)	-5.9(8)	8.8(8)
C17	38.4(9)	46.9(11)	38.3(10)	4.8(8)	5.3(7)	10.0(8)
C6	39.6(9)	42(1)	34.1(9)	-3.7(8)	1.2(7)	0.6(8)
C7	42.7(10)	45.5(11)	34.8(9)	-2.4(8)	2.1(7)	6.1(8)
C8	39.9(9)	44.9(11)	36.6(9)	-4.0(8)	1.8(7)	2.2(8)
C5	46.4(10)	42.4(11)	39.4(10)	-5.5(8)	6.4(8)	3.5(8)
C14	54.9(12)	55.9(13)	38.3(10)	-0.9(9)	8.5(8)	13.6(10)
C9	52.8(12)	67.0(14)	39.8(10)	4.7(10)	6.6(9)	10.5(10)
C13	50.0(11)	51.7(12)	58.1(13)	9.3(10)	12.2(9)	7.3(9)
C22	56.5(12)	66.7(14)	41.1(11)	0.6(10)	3.8(9)	11.9(11)
C16	64.6(14)	60.4(14)	45.5(11)	-0.1(10)	1.1(10)	-21.3(11)
C18	57.9(13)	55.4(13)	58.1(13)	9.6(11)	12.9(10)	-2(1)
C11	46.0(11)	68.1(15)	69.5(15)	-12.4(13)	8.1(10)	11.5(11)
C12	51.0(12)	52.6(13)	78.6(16)	7.6(12)	8.4(11)	12.2(10)
C10	53.2(12)	87.8(18)	47.7(12)	-4.0(12)	13.8(10)	9.7(12)
C15	74.3(15)	68.6(16)	51.3(13)	11.3(12)	11.3(11)	22.9(13)
C21	73.7(16)	110(2)	37.4(12)	8.3(13)	7.9(11)	32.5(17)
C19	66.8(15)	73.9(18)	90(2)	33.1(16)	29.6(14)	8.8(14)
C20	74.7(17)	108(2)	56.6(16)	36.4(16)	25.4(13)	32.3(17)
C1	45.7(12)	87.2(19)	81.6(18)	-18.1(15)	5.7(11)	14.0(13)
C3	68.6(16)	79.3(19)	83.5(19)	-31.6(16)	-14.9(14)	10.6(14)
C4	69.6(16)	58.1(15)	100(2)	-19.4(15)	-25.8(15)	8.9(13)
C2	73.7(18)	86.0(18)	90(2)	-5.0(16)	-13.1(15)	28.0(16)

Table 4 Bond Lengths for zmg-08-07.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C5	1.221(2)	C7	C8	1.496(3)
N2	C17	1.397(3)	C8	C13	1.387(3)
N2	C16	1.448(3)	C8	C9	1.392(3)
N2	C6	1.457(2)	C14	C15	1.296(3)
O1	C3	1.417(3)	C9	C10	1.380(3)
O1	C2	1.433(4)	C13	C12	1.389(3)
N1	C5	1.352(3)	C22	C21	1.391(4)
N1	C1	1.459(3)	C18	C19	1.396(4)
N1	C4	1.465(3)	C11	C12	1.372(4)
C17	C22	1.395(3)	C11	C10	1.373(4)
C17	C18	1.396(3)	C21	C20	1.356(5)
C6	C7	1.525(3)	C19	C20	1.362(5)
C6	C5	1.540(3)	C1	C2	1.476(4)
C7	C14	1.306(3)	C3	C4	1.472(4)

Table 5 Bond Angles for zmg-08-07.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	N2	C16	118.25(17)	O2	C5	N1	122.33(19)
C17	N2	C6	117.85(16)	O2	C5	C6	120.03(18)
C16	N2	C6	118.59(16)	N1	C5	C6	117.63(17)
C3	O1	C2	109.7(2)	C15	C14	C7	179.0(3)
C5	N1	C1	120.7(2)	C10	C9	C8	120.8(2)
C5	N1	C4	127.6(2)	C8	C13	C12	120.8(2)
C1	N1	C4	111.5(2)	C21	C22	C17	120.9(3)
C22	C17	C18	117.1(2)	C19	C18	C17	120.1(3)
C22	C17	N2	120.3(2)	C12	C11	C10	119.5(2)
C18	C17	N2	122.51(19)	C11	C12	C13	120.3(2)
N2	C6	C7	112.41(15)	C11	C10	C9	120.6(2)
N2	C6	C5	111.29(15)	C20	C21	C22	121.6(3)
C7	C6	C5	110.22(15)	C20	C19	C18	121.9(3)
C14	C7	C8	121.06(18)	C21	C20	C19	118.4(2)
C14	C7	C6	120.35(18)	N1	C1	C2	109.3(2)
C8	C7	C6	118.59(17)	O1	C3	C4	112.5(3)
C13	C8	C9	117.96(19)	N1	C4	C3	110.0(2)
C13	C8	C7	121.90(18)	O1	C2	C1	112.6(3)
C9	C8	C7	120.14(18)				

Table 6 Torsion Angles for zmg-08-07.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	N2	C17	C22	-2.5(3)	C13	C8	C9	C10	1.2(3)
C6	N2	C17	C22	-156.41(18)	C7	C8	C9	C10	-178.2(2)
C16	N2	C17	C18	-179.5(2)	C9	C8	C13	C12	-1.3(3)
C6	N2	C17	C18	26.6(3)	C7	C8	C13	C12	178.1(2)
C17	N2	C6	C7	-168.02(17)	C18	C17	C22	C21	2.1(3)
C16	N2	C6	C7	38.2(2)	N2	C17	C22	C21	-175.1(2)
C17	N2	C6	C5	67.8(2)	C22	C17	C18	C19	-2.3(3)
C16	N2	C6	C5	-86.0(2)	N2	C17	C18	C19	174.8(2)
N2	C6	C7	C14	-112.7(2)	C10	C11	C12	C13	1.8(4)
C5	C6	C7	C14	12.1(3)	C8	C13	C12	C11	-0.2(4)
N2	C6	C7	C8	68.2(2)	C12	C11	C10	C9	-1.9(4)
C5	C6	C7	C8	-167.01(17)	C8	C9	C10	C11	0.4(4)
C14	C7	C8	C13	-176.7(2)	C17	C22	C21	C20	-0.7(4)
C6	C7	C8	C13	2.4(3)	C17	C18	C19	C20	1.2(4)
C14	C7	C8	C9	2.6(3)	C22	C21	C20	C19	-0.5(4)
C6	C7	C8	C9	-178.26(19)	C18	C19	C20	C21	0.3(4)
C1	N1	C5	O2	5.4(4)	C5	N1	C1	C2	121.3(3)
C4	N1	C5	O2	-179.6(3)	C4	N1	C1	C2	-54.4(4)
C1	N1	C5	C6	-176.0(2)	C2	O1	C3	C4	57.5(4)
C4	N1	C5	C6	-1.1(4)	C5	N1	C4	C3	-120.8(3)
N2	C6	C5	O2	32.6(3)	C1	N1	C4	C3	54.5(4)
C7	C6	C5	O2	-92.8(2)	O1	C3	C4	N1	-56.3(4)
N2	C6	C5	N1	-145.96(19)	C3	O1	C2	C1	-57.9(4)
C7	C6	C5	N1	88.6(2)	N1	C1	C2	O1	56.5(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for zmg-08-07.

Atom	*x*	*y*	*z*	U(eq)
H6	7375	2103	4512	47
H9	8989	4716	3023	64
H13	8780	782	4526	63
H22	8442	5727	6258	66
H16A	8277	7478	5280	86
H16B	8786	6557	4730	86
H16C	9150	6011	5438	86
H18	7052	730	5318	68

H11	10673	-480	3392	73
H12	9990	-1328	4278	73
H10	10195	2602	2785	75
H15A	7710	8747	3108	77
H15B	6723	7601	3011	77
H21	8126	4188	7201	88
H19	6767	-744	6280	90
H20	7298	960	7219	94
H1A	4999	6432	4301	86
H1B	4531	4078	4340	86
H3A	5844	2814	2997	95
H3B	5395	435	3012	95
H4A	5433	629	4091	95
H4B	6412	1034	3912	95
H2A	4013	5737	3389	102
H2B	5005	6044	3230	102