Electronic Supplementary Material (ESI) for Chemical Communications

NHC-Catalyzed C-O or C-N Bond Formation: Efficient Approaches to α,β-Unsaturated Esters and Amides

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Supporting Information

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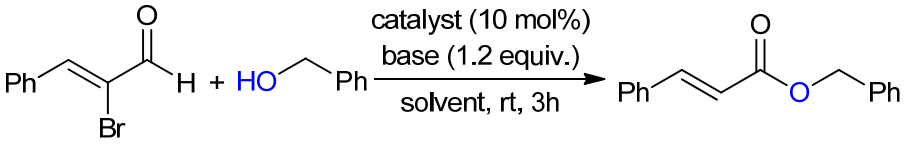
General Remarks

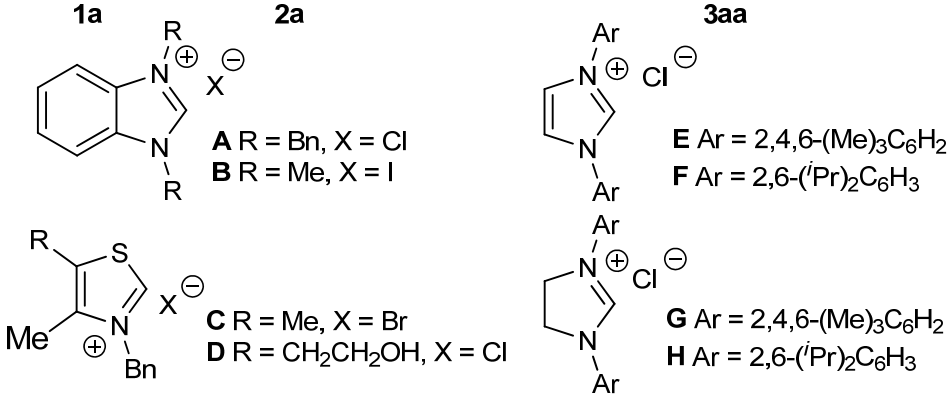
All manipulations were conducted with a standard Schlenk tube under Ar. ^{1}H-NMR spectra were recorded on Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were recorded by PE SCLEX QSTAR spectrometer. HR-MS were obtained using electrospray ionization (ESI) mass spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF, dioxane and toluene were distilled from sodium and benzophenone, DCM, CH_3CN and DMF was distilled from CaH_2. Bromoenal **1a** was purchased from Alfa Aesar. Bromoenals **1b**,[1] **1c**,[2] **1d**,[1] **1e**,[1] **1f**[2] were prepared according to reported methods. α,β-Dibromoaldehyde **6** were prepared according to reported methods.[3]

Reaction conditions screening

Table S1. Optimization of reaction conditions for NHC-catalyzed ester bond formation[a]



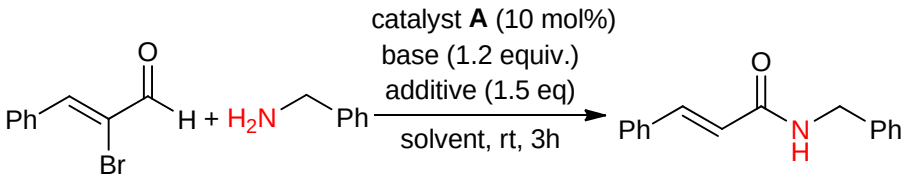
1a **2a** **3aa**



entry	catalyst	solvent	base	Yield (%)[b]
1	**A**	THF	Cs_2CO_3	78
2	**B**	THF	Cs_2CO_3	55
3	**C**	THF	Cs_2CO_3	45
4	**D**	THF	Cs_2CO_3	22
5	**E**	THF	Cs_2CO_3	64
6	**F**	THF	Cs_2CO_3	45
7	**G**	THF	Cs_2CO_3	58
8	**H**	THF	Cs_2CO_3	29
9	**A**	DCM	Cs_2CO_3	75
10	**A**	CH_3CN	Cs_2CO_3	24
11	**A**	DMF	Cs_2CO_3	trace
12	**A**	toluene	Cs_2CO_3	65
13	**A**	**dioxane**	**Cs_2CO_3**	**81**
14	**A**	dioxane	DBU	22
15	**A**	dioxane	Et_3N	72
16	**A**	dioxane	K_2CO_3	44
17	**A**	dioxane	KO^{t}Bu	36

[a] Reacion condition: **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (0.05 mmol), Cs_2CO_3 (0.6 mmol) in 2.5 mL THF at rt under Ar for 3 h. [b] Isolated yields.

Table S2. Optimization of reaction conditions for NHC-catalyzed amide bond formation.[a]

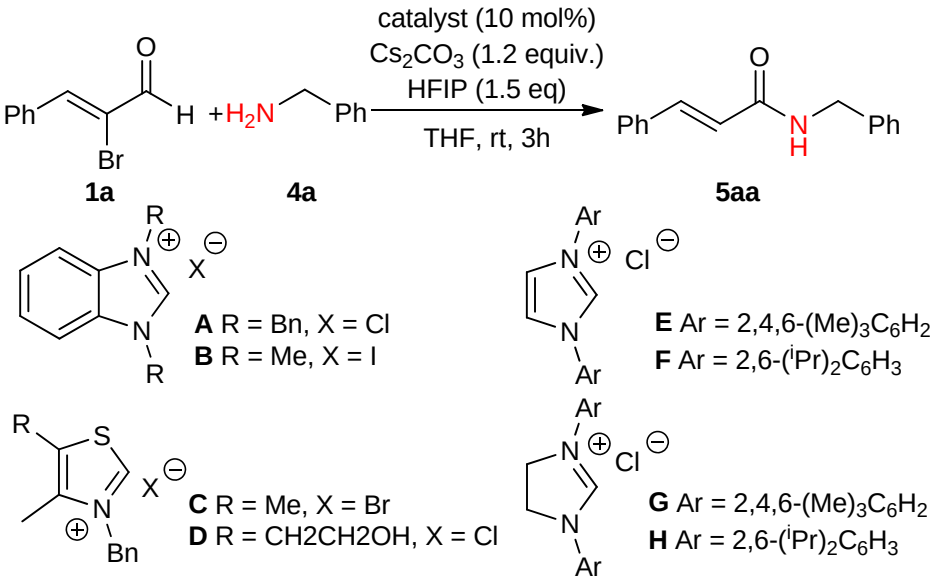


1a **4a** **5aa**

entry	additive	solvent	base	Yield (%)[b]
1	**---**	THF	Cs_2CO_3	nr
2	imidazole	THF	Cs_2CO_3	13
3	benzimidazole	THF	Cs_2CO_3	trace
4	DMAP	THF	Cs_2CO_3	nr
5	HOBt	THF	Cs_2CO_3	nr
6	HOAt	THF	Cs_2CO_3	nr
7	PFPOH	THF	Cs_2CO_3	trace
8	HFIP	THF	Cs_2CO_3	54
9[c]	HFIP	THF	Cs_2CO_3	trace
10	HFIP	dioxane	Cs_2CO_3	50
11	HFIP	toluene	Cs_2CO_3	trace
12	HFIP	DCM	Cs_2CO_3	nr
13	HFIP	THF	K_2CO_3	trace
14	HFIP	THF	DBU	49
15	HFIP	THF	Et_3N	nr
16[d]	**HFIP**	**THF**	**Cs_2CO_3**	**81**
17[e]	HFIP	THF	Cs_2CO_3	80
18[f]	HFIP	THF	Cs_2CO_3	10

[a] Reacion condition: **1a** (0.5 mmol), additive (0.75 mmol), catalyst **A** (0.05 mmol), base (0.6 mmol) in 2.5 mL solvent at rt under Ar for 30 min prior to addition of amine **4a** (0.6 mmol) at rt for 3h. [b] Isolated yields; nr = no reaction [c] 15 mol % of HFIP was used. [d] 2.0 equiv of **4a** was used. [e] 3.0 equiv of **4a** was used. [f] **2a** was added at the beginning of this reaction. DMAP = 4-dimethylamino-pyridine. HOBt = 1-hydroxybenzotriazole. HOAt = 1-hydroxy-7-azabenzotriazole. PFPOH = 2,2,3,3,3-pentafluoro-1-propanol. HFIP = 1.1.1.3.3.3-hexafluoro-2-propanol.

Table S3. Catalyst screening for NHC-catalyzed amide bond formation.[a]



entry	catalyst	Yield (%)[b]
1	**A**	54
2	**B**	41
3	**C**	16
4	**D**	35
5	**E**	trace
6	**F**	nr
7	**G**	trace
8	**H**	nr

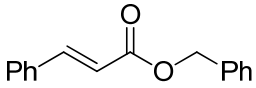
[a] Reacion condition: **1a** (0.5 mmol), HFIP (0.75 mmol), catalyst (0.05 mmol), Cs_2CO_3 (0.6 mmol) in 2.5 mL THF at rt under Ar for 30 min prior to addition of amine **4a** (0.6 mmol) at rt for 3h. [b] Isolated yields; nr = no reaction. HFIP = 1.1.1.3.3.3-hexafluoro-2-propanol.

Experimental section

1. Experimental procedures and characterization of products

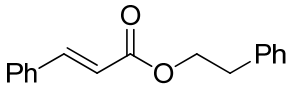
1.1 Experimental procedures and characterization of products for NHC-catalyzed ester bond formation

Benzyl cinnamate (3aa)[4]



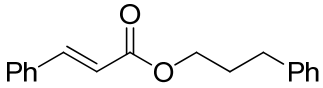
Typical procedure: (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol) and imidazolium salt **A** (16.9 mg, 0.05 mmol) were placed in a 25 mL dry Schlenk tube under Ar. Dioxane 2.5 mL were added, followed by the addition of phenylmethanol **2a** (65 μL, 0.6 mmol). After stirring for 2 min, Cs_2CO_3 (195.6 mg, 0.6 mmol) was added. The reaction mixture was stirred at room temperature for 3 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et_2O = 10/1) to afford 95.9 mg (81 % yield) of **3aa**. **3aa**: white solid; IR:(KBr) ν_{max} 3030, 2954, 1709, 1634, 1308, 1156, 766, 752, 694 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.50-7.36 (m, 10H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 145.1, 136.0, 134.3, 130.3, 128.8, 128.5, 128.2, 128.1, 117.9, 66.3; MS (70 eV): m/z (%): 238.1 (10) $[M]^+$, 91.0 (100).

phenethyl cinnamate (3ab)[5]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.5 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), 2-phenylethanol **2b** (72 μL, 0.6 mmol) and Cs_2CO_3 (196.5 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 88.0 mg (70 % yield) of **3ab**. **3ab**: white solid; IR:(KBr) ν_{max} 3029, 2951, 1710, 1637, 1313, 1173, 770, 701 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.51-7.50 (m, 2H), 7.37-7.24 (m, 8H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.42 (t, *J* = 7.0 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.9, 144.8, 137.8, 134.3, 130.3, 128.9, 128.8, 128.4, 128.0, 126.5, 118.0, 65.0, 35.1; MS (70 eV): m/z (%): 252.0 (1) $[M]^+$, 103.5 (100).

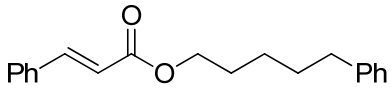
3-Phenylpropyl cinnamate (3ac)[6]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.5 mg, 0.5 mmol), imidazolium salt A (17.3 mg, 0.05 mmol), 3-phenylpropan-1-ol **2c** (85 μL, 0.6 mmol) and Cs_2CO_3 (196.8 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 87.4 mg (66 % yield) of **3ac**. **3ac**: colourless oil; IR:(KBr) ν_{max} 3027, 2952, 1710,

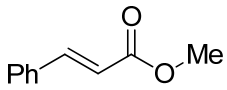
1638, 1311, 1169, 767, 700 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53-7.52 (m, 2H), 7.34-7.42 (m, 3H), 7.31-7.27 (m, 2H), 7.22-7.20 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.07-2.00 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.9, 144.7, 141.2, 134.4, 130.2, 128.8, 128.40, 128.38, 128.0, 126.0, 118.1, 66.8, 32.2, 30.2; MS (70 eV): m/z (%): 266.1 (1) $[M]^+$, 117.7 (100).

5-Phenylpentyl cinnamate (3ad)



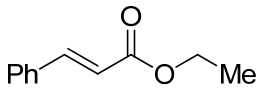
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), 5-phenylpentan-1-ol **2d** (101 μL, 0.6 mmol) and Cs_2CO_3 (196.5 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 91.9 mg (63 % yield) of **3ad**. **3ad**: colourless oil; IR:(KBr) ν_{max} 3027, 2935, 1712, 1638, 1452, 1311, 1279, 1170, 768, 700 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.52-7.51 (m, 2H), 7.34-7.42 (m, 3H), 7.29-7.24 (m, 2H), 7.19-7.17 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.77-1.64 (m, 4H), 1.49-1.41 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.0, 144.6, 142.4, 134.4, 130.2, 128.8, 128.4, 128.3, 128.0, 125.7, 118.2, 64.5, 35.8, 31.1, 28.5, 25.6; MS (70 eV): m/z (%): 294.2 (3) $[M]^+$, 146.1 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{22}NaO_2$ $[M+Na]^+$ 317.1512, Found: 317.1505.

Methyl cinnamate (3ae)[7]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (16.8 mg, 0.05 mmol), methanol **2e** (25 μL, 0.6 mmol) and Cs_2CO_3 (196.5 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 68.4 mg (84 % yield) of **3ae**. **3ae**: white solid; IR:(KBr) ν_{max} 3028, 2949, 1717, 1638, 1316, 1203, 1172, 769 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.51-7.50 (m, 2H), 7.34-7.40 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.3, 144.8, 134.3, 130.2, 128.8, 128.0, 117.7, 51.6; MS (70 eV): m/z (%): 162.3 (46) $[M]^+$, 131.0 (100).

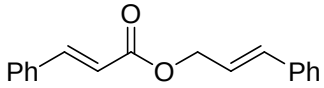
Ethyl cinnamate (3af)[7]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.3 mg, 0.05 mmol), ethanol **2f** (35 μL, 0.6 mmol) and Cs_2CO_3 (196.8 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 55.3 mg (63 % yield) of **3af**. **3af**: colourless oil; IR:(KBr) ν_{max} 2964, 2921, 1713, 1639, 1312, 1263,

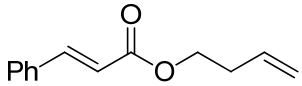
1187, 1207, 802, 686 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.48-7.56 (m, 2H), 7.34-7.42 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 6.6 Hz, 2H), 1.34 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.0, 144.5, 134.4, 130.2, 128.8, 128.0, 118.2, 60.4, 14.3; MS (70 eV): m/z (%): 176.2 (4) $[M]^+$, 57.0 (100).

Cinnamyl cinnamate (3ag)[4]



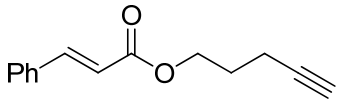
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), (*E*)-3-phenylprop-2-en-1-ol **2g** (82 mg, 0.6 mmol) and Cs_2CO_3 (196.4 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 93.9 mg (71 % yield) of **3ag**. **3ag**: colourless oil; IR:(KBr) ν_{max} 3060, 2942, 1712, 1637, 1310, 1165, 970, 768, 690 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 16.4 Hz, 1H), 7.514-7.508 (m, 2H), 7.41-7.23 (m, 8H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.39-6.31 (m, 1H), 4.86 (d, *J* = 6.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.6, 145.0, 136.2, 134.3, 134.2, 130.3, 128.8, 128.5, 128.05, 127.99, 126.6, 123.3, 117.9, 65.0; MS (70 eV): m/z (%): 264.2 (6) $[M]^+$, 131.1 (100).

But-3-en-1-yl cinnamate (3ah)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.2 mg, 0.5 mmol), imidazolium salt **A** (16.9 mg, 0.05 mmol), but-3-en-1-ol **2h** (52 μL, 0.6 mmol) and Cs_2CO_3 (196.2 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 66.1 mg (65 % yield) of **3ah**. **3ah**: colourless oil; IR:(KBr) ν_{max} 3063, 2956, 1715, 1639, 1312, 1170, 984, 768, 711, 685 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 15.6 Hz, 1H), 7.517-7.510 (m, 2H), 7.33-7.43 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.89-5.79 (m, 1H), 5.17-5.09 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 2.46 (d, *J* = 6.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.9, 144.7, 134.4, 134.0, 130.2, 128.8, 128.0, 118.1, 117.2, 63.5, 33.1; MS (70 eV): m/z (%): 202.2 (4) $[M]^+$, 131.1 (100); HRMS m/z (ESI): Calcd. for $C_{13}H_{15}O_2$ $[M+H]^+$ 203.1067, Found: 203.1065.

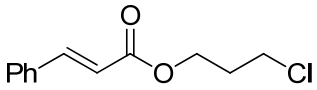
Pent-4-yn-1-yl cinnamate (3ai)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), pent-4-yn-1-ol **2i** (56 μL, 0.6 mmol) and Cs_2CO_3 (196.2 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 71.6 mg (67 % yield) of **3ai**. **3ai**: colourless oil; IR:(KBr) ν_{max} 3297, 2959, 2118, 1715,

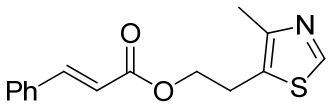
1638, 1310, 1271, 1169, 1035, 981, 768, 684, 641 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.53-7.52 (m, 2H), 7.35-7.42 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.32 (t, *J* = 6.0 Hz, 2H), 2.36-2.33 (m, 2H), 1.99-1.92 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.8, 144.8, 134.4, 130.3, 128.9, 128.0, 118.0, 83.0, 69.0, 63.0, 27.6, 15.2; HRMS m/z (ESI): Calcd. for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 215.1067, Found: 215.1065.

3-Chloropropyl cinnamate (3aj)



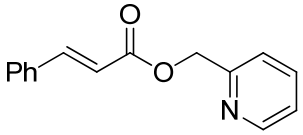
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), 3-chloropropan-1-ol **2j** (51 µL, 0.6 mmol) and Cs_2CO_3 (196.6 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 78.7 mg (70 % yield) of **3aj**. **3aj**: colourless oil; IR:(KBr) ν_{max} 3029, 2964, 1714, 1638, 1311, 1168, 768 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.48-7.58 (m, 2H), 7.32-7.44 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.36 (t, *J* = 5.0 Hz, 2H), 3.67 (t, *J* = 5.5 Hz, 2H), 2.17 (t, *J* = 5.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 145.0, 134.2, 130.3, 128.8, 128.0, 117.6, 61.1, 41.2, 31.6; MS (70 eV): m/z (%): 224.0 (25) $[M]^+$, 131.1 (100); HRMS m/z (ESI): Calcd. for $C_{12}H_{14}ClO_2$ $[M+H]^+$ 225.0677, Found: 225.0676.

2-(4-Methylthiazol-5-yl)ethyl cinnamate (3ak)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.4 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), 2-(4-methylthiazol-5-yl)ethanol **2k** (75 µL, 0.6 mmol) and Cs_2CO_3 (196.3 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 108.7 mg (80 % yield) of **3ak**. **3ak**: white solid; IR:(KBr) ν_{max} 3066, 2958, 1705, 1639, 1315, 1176, 768 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.60 (s, 1H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.48-7.58 (m, 2H), 7.34-7.44 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.5, 149.9, 149.8, 145.2, 134.1, 130.3, 128.8, 128.0, 126.7, 117.5, 64.0, 25.8, 14.8; MS (70 eV): m/z (%): 124.9 (100); HRMS m/z (ESI): Calcd. for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896, Found: 274.0891.

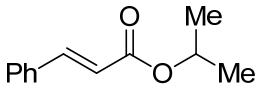
Pyridin-2-ylmethyl cinnamate (3al)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (16.9 mg, 0.05 mmol), pyridin-2-ylmethanol **2l** (58 µL, 0.6 mmol)

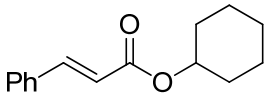
and Cs_2CO_3 (196.1 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 78.5 mg (66 % yield) of **3al**. **3al**: colourless oil; IR:(KBr) ν_{max} 3061, 2942, 1716, 1637, 1311, 1277, 1164, 981, 767 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.62 (d, *J* = 4.4 Hz, 1H), 7.78 (d, *J* = 15.8 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.50-7.58 (m, 2H), 7.42-7.39 (m, 4H), 7.27-7.22 (m, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 5.38 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.5, 155.9, 149.5, 145.5, 136.7, 134.2, 130.4, 128.9, 128.1, 122.8, 121.8, 117.5, 66.8; MS (70 eV): m/z (%): 239.2 (32) $[M]^+$, 102.9 (100); HRMS m/z (ESI): Calcd. for $C_{15}H_{14}NO_2$ $[M+H]^+$ 240.1019, Found: 240.1015.

Isopropyl cinnamate (3am)[7]



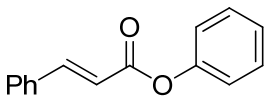
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), propan-2-ol **2m** (115 μL, 1.5 mmol) and Cs_2CO_3 (196.7 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 30.5 mg (32 % yield) of **3am**. **3am**: colourless oil; IR:(KBr) ν_{max} 2980, 1710, 1639, 1309, 1177, 1109, 986, 768 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.52-7.51 (m, 2H), 7.38-7.37 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.17-5.11 (m, 1H), 1.31 (d, *J* = 6.0 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.5, 144.3, 134.5, 130.1, 128.8, 128.0, 118.8, 67.8, 21.9; MS (70 eV): m/z (%): 190.0 (29) $[M]^+$, 130.9 (100).

Cyclohexyl cinnamate (3an)[7]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), cyclohexanol **2n** (160 μL, 1.5 mmol) and Cs_2CO_3 (196.4 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 59.8 mg (52 % yield) of **3an**. **3an**: colourless oil; IR:(KBr) ν_{max} 2936, 2859, 1709, 1639, 1450, 1307, 1279, 1174, 1040, 1017, 982, 767 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 15.8 Hz, 1H), 7.58-7.46 (m, 2H), 7.44-7.30 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.00-4.82 (m, 1H), 1.91-1.76 (m, 4H), 1.54-1.30 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.4, 144.2, 134.6, 130.0, 128.8, 128.0, 118.9, 72.7, 31.7, 25.4, 23.8; MS (70 eV): m/z (%): 230.2 (3) $[M]^+$, 131.1 (100).

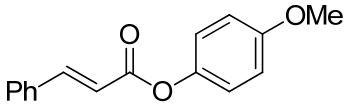
Phenyl cinnamate (3ao)[8]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), phenol **2o** (58 mg, 0.6 mmol) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 68.7 mg (61

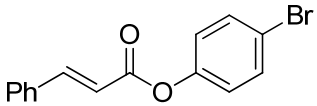
% yield) of **3ao**. **3ao**: white solid; IR:(KBr) ν_{max} 3059, 1728, 1636, 1308, 1202, 1144, 764, 705 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.62-7.54 (m, 2H), 7.42-7.38 (m, 5H), 7.26-7.23 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.3, 150.8, 146.5, 134.1, 130.7, 129.4, 129.0, 128.3, 125.7, 121.6, 117.3; MS (70 eV): m/z (%): 224.1 (4) $[M]^+$, 131.0 (100).

4-Methoxyphenyl cinnamate (3ap)[9]



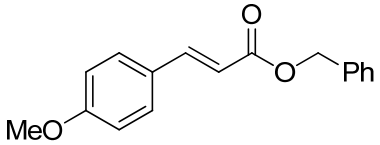
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.2 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), 4-methoxyphenol **2p** (75.1 mg, 0.6 mmol) and Cs_2CO_3 (196.6 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 95.8 mg (75 % yield) of **3ap**. **3ap**: white solid; IR:(KBr) ν_{max} 3062, 2958, 1724, 1636, 1503, 1312, 1205, 1152, 853, 766 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, *J* = 16.0 Hz, 1H), 7.54-7.62 (m, 2H), 7.37-7.46 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.8, 157.2, 146.3, 144.2, 134.2, 130.6, 128.9, 128.2, 122.3, 117.3, 114.4, 55.5; MS (70 eV): m/z (%): 254.1 (3) $[M]^+$, 131.0 (100).

4-Bromophenyl cinnamate (3aq)[8]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), 4-bromophenol **2q** (104.4 mg, 0.6 mmol) and Cs_2CO_3 (196.3 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 76.2 mg (50 % yield) of **3aq**. **3aq**: white solid; IR:(KBr) ν_{max} 1740, 1633, 1482, 1309, 1210, 1141, 1067, 998, 844, 764 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 15.8 Hz, 1H), 7.55-7.63 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38-7.46 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 15.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.0, 149.8, 147.0, 134.0, 132.4, 130.8, 129.0, 128.3, 123.4, 118.8, 116.8; MS (70 eV): m/z (%): 303.9 (4) $[M]^+$, 131.0 (100).

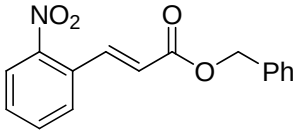
(*E*)-Benzyl 3-(4-methoxyphenyl)acrylate (3ba)[10]



The reaction of (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylaldehyde **1b** (121.0 mg, 0.5 mmol), imidazolium salt **A** (16.9 mg, 0.05 mmol), phenylmethanol **2a** (65 μL, 0.6 mmol) and Cs_2CO_3 (196.7 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 93.7 mg (70 % yield) of **3ba**. **3ba**: white solid; IR:(KBr) ν_{max} 3032, 2958,

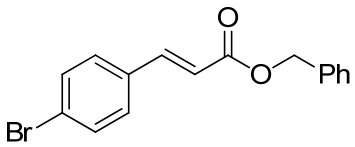
1706, 1632, 1602, 1511, 1250, 1160, 830 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, *J* = 15.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42-7.34 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.24 (s, 2H), 3.81 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.1, 161.4, 144.8, 136.2, 129.7, 128.5, 128.2, 128.1, 127.0, 115.3, 114.3, 66.1, 55.3; MS (70 eV): m/z (%): 268.1 (61) $[M]^+$, 91.0 (100).

(*E*)-Benzyl 3-(2-nitrophenyl)acrylate (3ca)



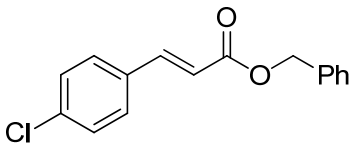
The reaction of (*Z*)-2-bromo-3-(2-nitrophenyl)acrylaldehyde **1c** (128.6 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), phenylmethanol **2a** (65 μL, 0.6 mmol) and Cs_2CO_3 (196.2 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 87.7 mg (62 % yield) of **3ca**. **3ca**: white solid; IR:(KBr) ν_{max} 3035, 2961, 1710, 1524, 1341, 1288, 1176, 755, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, *J* = 16.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.66-7.62 (m, 2H), 7.55-7.53 (m, 1H), 7.41-7.34 (m, 5H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.27 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 148.2, 140.4, 135.7, 133.5, 130.5, 130.3, 129.1, 128.6, 128.32, 128.27, 124.9, 122.9, 66.6; HRMS m/z (ESI): Calcd. for $C_{16}H_{13}NNaO_4$ $[M+Na]^+$ 306.0737, Found: 306.0739.

(*E*)-Benzyl 3-(4-bromophenyl)acrylate (3da)



The reaction of (*Z*)-2-bromo-3-(4-bromophenyl)acrylaldehyde **1d** (145.6 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), phenylmethanol **2a** (65 μL, 0.6 mmol) and Cs_2CO_3 (196.9 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 94.7 mg (60 % yield) of **3da**. **3da**: light yellow solid; IR:(KBr) ν_{max} 3032, 2956, 1708, 1635, 1485, 1309, 1165, 821, 694 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 7H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.24 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.4, 143.7, 135.9, 133.2, 132.1, 129.4, 128.6, 128.3, 124.6, 118.6, 66.4; MS (70 eV): m/z (%): 317.9 (4) $[M]^+$, 91.0 (100); HRMS m/z (ESI): Calcd. for $C_{16}H_{13}BrNaO_2$ $[M+Na]^+$ 338.9991, Found: 338.9992.

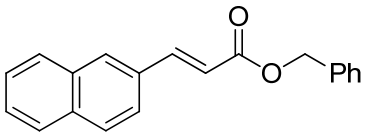
(*E*)-Benzyl 3-(4-chlorophenyl)acrylate (3ea)[10]



The reaction of (*Z*)-2-bromo-3-(4-chlorophenyl)acrylaldehyde **1e** (123.2 mg, 0.5

mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), phenylmethanol **2a** (65 μL, 0.6 mmol) and Cs_2CO_3 (197.4 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 95.4 mg (70 % yield) of **3ea**. **3ea**: light yellow solid; IR:(KBr) ν_{max} 3033, 2958, 1709, 1636, 1489, 1310, 1167, 824, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (d, *J* = 15.8 Hz, 1H), 7.42-7.35 (m, 9H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.25 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.5, 143.6, 136.2, 135.9, 132.8, 129.2, 129.1, 128.6, 128.3, 118.4, 66.4; MS (70 eV): m/z (%): 272.1 (6) $[M]^+$, 91.1 (100).

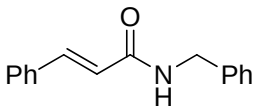
(*E*)-Benzyl 3-(naphthalen-2-yl)acrylate (3fa)



The reaction of (*Z*)-2-bromo-3-(naphthalen-2-yl)acrylaldehyde **1f** (130.6 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), phenylmethanol **2a** (65 μL, 0.6 mmol) and Cs_2CO_3 (197.1 mg, 0.6 mmol) in dioxane (2.5 mL) at rt under Ar for 3 h afforded 106.0 mg (74 % yield) of **3fa**. **3fa**: light yellow solid; IR:(KBr) ν_{max} 3058, 2959, 1709, 1634, 1308, 1260, 1164, 982, 820, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.89-7.81 (m, 5H), 7.64-7.62 (m, 1H), 7.49-7.39 (m, 7H), 6.58 (d, *J* = 16.0 Hz, 1H), 5.27 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.8, 145.1, 136.1, 134.2, 133.2, 131.8, 130.0, 128.65, 128.56, 128.5, 128.24, 128.20, 127.7, 127.2, 126.7, 123.4, 118.0, 66.3; MS (70 eV): m/z (%): 288.2 (28) $[M]^+$,91.1 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{16}NaO_2$ $[M+Na]^+$ 311.1043, Found: 311.1045.

1.2 Experimental procedures and characterization of products for NHC-catalyzed amide bond formation

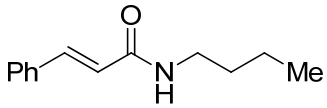
(*E*)-*N*-Benzylcinnamamide (5aa)[11]



Typical procedure: (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol) and imidazolium salt **A** (17.3 mg, 0.05 mmol) were placed in a 25 mL dry Schlenk tube under Ar. THF 2.5 mL were added, followed by the addition of HFIP (78 μL, 0.75 mmol). After stirring for 2 min, Cs_2CO_3 (197.2 mg, 0.6 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. Then, phenylmethanamine **4a** (110 μL, 1.0 mmol) was added and continuingly stirred at rt for additional 3 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et_2O = 1/1) to afford 95.8 mg (81 % yield) of **5aa**. **5aa**: white solid; IR:(KBr) ν_{max} 3265, 3029, 1652, 1615, 1541, 1220, 757, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 15.8 Hz, 1H), 7.54-7.46 (m, 2H), 7.36-7.28 (m, 8H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.26 (brs, 1H), 4.57 (d, *J* = 5.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.8, 141.3, 138.2, 134.7,

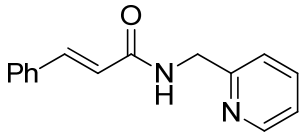
130.0, 128.8, 128.7, 127.9, 127.8, 127.5, 120.5, 43.8; MS (70 eV): m/z (%): 237.0 (36) $[M]^+$, 102.9 (100).

(*E*)-*N*-butylcinnamamide (5ab)[12]



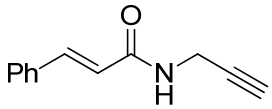
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.0 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (197.3 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with butan-1-amine **4b** (100 µL, 1.0 mmol) at rt for 3 h afforded 83.3 mg (82 % yield) of **5ab**. **5ab**: light yellow solid; IR:(KBr) ν_{max} 3289, 2956, 2931, 1655, 1617, 1559, 1342, 1224, 993, 768, 734, 673 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 15.6 Hz, 1H), 7.47-7.46 (m, 2H), 7.36-7.28 (m, 3H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.22 (brs, 1H), 3.41-3.36 (m, 2H), 1.59-1.52 (m, 2H), 1.42-1.33 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.0, 140.5, 134.9, 129.5, 128.7, 127.7, 121.0, 39.4, 31.7, 20.1, 13.7; MS (70 eV): m/z (%): 203.0 (15) $[M]^+$, 131.0 (100).

(*E*)-*N*-(Pyridin-2-ylmethyl)cinnamamide (5ac)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (197.0 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with pyridin-2-ylmethanamine **4c** (105 µL, 1.0 mmol) at rt for 3 h afforded 95.4 mg (80 % yield) of **5ac**. **5ac**: white solid; IR:(KBr) ν_{max} 3247, 3069, 2922, 1655, 1618, 1564, 1345, 1235, 1215, 987, 762, 682 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.55 (d, *J* = 3.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.50-7.49 (m, 2H), 7.35-7.30 (m, 4H), 7.22-7.19 (m, 2H), 6.55 (d, *J* = 15.6 Hz, 1H), 4.70 (d, *J* = 4.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.9, 156.3, 148.9, 141.0, 136.8, 134.8, 129.6, 128.7, 127.8, 122.4, 122.2, 120.6, 44.6; MS (70 eV): m/z (%): 238.0 (12) $[M]^+$, 149.0 (100); HRMS m/z (ESI): Calcd. for $C_{15}H_{15}N_2O$ $[M+H]^+$ 239.1179, Found: 239.1176.

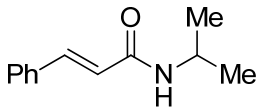
(*E*)-*N*-(Prop-2-yn-1-yl)cinnamamide (5ad)[13]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.2 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (197.4 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with prop-2-yn-1-amine **4d** (64 µL, 1.0 mmol) at rt for 3 h afforded 38.4 mg (42 % yield) of **5ad**. **5ad**: light yellow solid; IR:(KBr) ν_{max} 3280, 3047, 2926, 1658, 1619, 1544,

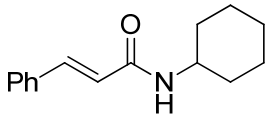
1331, 1226, 1041, 966, 734, 670, 653 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (d, *J* = 15.8 Hz, 1H), 7.54-7.44 (m, 2H), 7.39-7.30 (m, 3H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.36 (brs, 1H), 4.20 (d, *J* = 2.8 Hz, 2H), 2.25 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.7, 141.7, 134.6, 129.8, 128.8, 127.8, 119.9, 79.5, 71.6, 29.4; MS (70 eV): m/z (%): 185.2 (9) $[M]^+$, 102.9 (100).

(*E*)-*N*-Isopropylcinnamamide (5ae)[14]



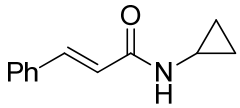
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.2 mg, 0.5 mmol), imidazolium salt **A** (16.9 mg, 0.05 mmol), HFIP (78 μL, 0.75 mmol) and Cs_2CO_3 (196.8 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with propan-2-amine **4e** (85 μL, 1.0 mmol) at rt for 6 h afforded 63.9 mg (68 % yield) of **5ae**. **5ae**: light yellow solid; IR:(KBr) ν_{max} 3268, 2957, 1655, 1616, 1549, 1225, 977, 725 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.61 (d, *J* = 15.2 Hz, 1H), 7.47-7.46 (m, 2H), 7.38-7.27 (m, 3H), 6.44 (d, *J* = 15.2 Hz, 1H), 5.99 (brs, 1H), 4.25-4.21 (m, 1H), 1.22 (d, *J* = 6.0 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.1, 140.5, 134.9, 129.4, 128.7, 127.6, 121.3, 41.5, 22.7; MS (70 eV): m/z (%): 189.0 (16) $[M]^+$, 131.0 (100).

(*E*)-*N*-Cyclohexylcinnamamide (5af)[14]



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.2 mg, 0.5 mmol), imidazolium salt **A** (17.3 mg, 0.05 mmol), HFIP (78 μL, 0.75 mmol) and Cs_2CO_3 (196.6 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with cyclohexanamine **4f** (115 μL, 1.0 mmol) at rt for 6 h afforded 80.0 mg (70 % yield) of **5af**. **5af**: light yellow solid; IR:(KBr) ν_{max} 3277, 2917, 2852, 1655, 1618, 1554, 1343, 1219, 993, 734 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.49-7.48 (m, 2H), 7.35-7.34 (m, 3H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.56 (brs, 1H), 3.95-3.88 (m, 1H), 2.01-1.98 (m, 2H), 1.75-1.72 (m, 2H), 1.65-1.62 (m, 1H), 1.45-1.36 (m, 2H), 1.26-1.15 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 164.9, 140.6, 135.0, 129.5, 128.8, 127.7, 121.2, 48.4, 32.2, 25.6, 24.8; MS (70 eV): m/z (%): 229.1 (27) $[M]^+$, 131.0 (100).

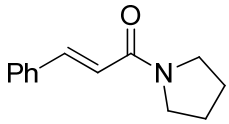
(*E*)-*N*-Cyclopropylcinnamamide (5ag)



The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), HFIP (78 μL, 0.75 mmol) and Cs_2CO_3 (196.8 mg, 0.6 mmol) in THF (2.5 mL) at 50℃ under Ar for 30 min. Treatment with

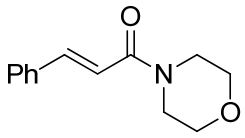
cyclopropanamine **4g** (70 μL, 1.0 mmol) at 50℃ for 6 h afforded 51.8 mg (55 % yield) of **5ag**. **5ag**: light yellow solid; IR:(KBr) ν_{max} 3220, 3030, 1654, 1613, 1547, 1337, 991, 736, 680 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 15.6 Hz, 1H), 7.52-7.43 (m, 2H), 7.40-7.28 (m, 3H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.20 (brs, 1H), 2.87-2.86 (m, 1H), 0.83-0.81 (m, 2H), 0.67-0.54 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.3, 140.8, 134.9, 129.6, 128.8, 127.7, 120.6, 22.9, 6.7; MS (70 eV): m/z (%): 187.0 (9) $[M]^+$, 131.0 (100); HRMS m/z (ESI): Calcd. for $C_{12}H_{13}NNaO$ $[M+Na]^+$ 210.0889, Found: 210.0887.

(*E*)-3-Phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one (5ah)[14]



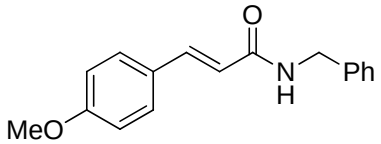
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.3 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), HFIP (78 μL, 0.75 mmol) and Cs_2CO_3 (196.6 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with pyrrolidine **4h** (84 μL, 1.0 mmol) at rt for 3 h afforded 88.1 mg (88 % yield) of **5ah**. **5ah**: light yellow solid; IR:(KBr) ν_{max} 2968, 2874, 1653, 1599, 1455, 987, 764, 706 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.70 (d, *J* = 15.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.36-7.34 (m, 3H), 6.73 (d, *J* = 15.6 Hz, 1H), 3.63-3.57 (m, 4H), 1.99 (t, *J* = 6.4 Hz, 2H), 1.88 (t, *J* = 6.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 164.5, 141.5, 135.3, 129.3, 128.6, 127.7, 118.8, 46.4, 45.9, 26.0, 24.2; MS (70 eV): m/z (%): 201.0 (7) $[M]^+$, 131.0 (100).

(*E*)-1-Morpholino-3-phenylprop-2-en-1-one (5ai)[15]



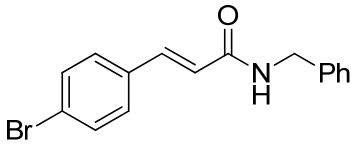
The reaction of (*Z*)-2-bromo-3-phenylacrylaldehyde **1a** (106.1 mg, 0.5 mmol), imidazolium salt **A** (17.0 mg, 0.05 mmol), HFIP (78 μL, 0.75 mmol) and Cs_2CO_3 (197.0 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with morpholine **4i** (86 μL, 1.0 mmol) at rt for 6 h afforded 71.8 mg (66 % yield) of **5ai**. **5ai**: light yellow solid; IR:(KBr) ν_{max} 2965, 2858, 1650, 1599, 1434, 1228, 1117, 973, 763, 702 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 15.6 Hz, 1H), 7.52-7.51 (m, 2H), 7.37-7.36 (m, 3H), 6.84 (d, *J* = 15.6 Hz, 1H), 3.72 (s, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 143.1, 135.1, 129.7, 128.8, 127.7, 116.6, 66.8; MS (70 eV): m/z (%): 217.0 (21) $[M]^+$, 131.0 (100).

(*E*)-*N*-Benzyl-3-(4-methoxyphenyl)acrylamide (5ba)[16]



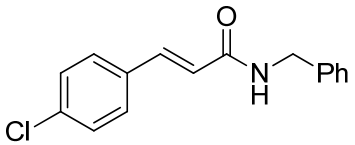
The reaction of (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylaldehyde **1b** (121.8 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (196.8 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with phenylmethanamine **4a** (110 µL, 1.0 mmol) at rt for 3 h afforded 93.0 mg (70 % yield) of **5ba 5ba**: white solid; IR:(KBr) ν_{max} 3284, 3028, 2836, 1644, 1604, 1528, 1254, 1216, 1029, 973, 827, 754, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29-7.25 (m, 5H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.35-6.31 (m, 2H), 4.51 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 166.2, 160.8, 140.8, 138.3, 129.3, 128.6, 127.8, 127.44, 127.39, 118.1, 114.1, 55.2, 43.7; MS (70 eV): m/z (%): 267.1 (52) $[M]^+$, 161.1 (100).

(*E*)-*N*-Benzyl-3-(4-bromophenyl)acrylamide (5da)[17]



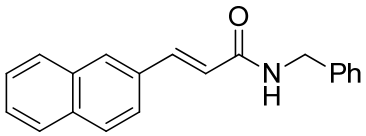
The reaction of (*Z*)-2-bromo-3-(4-bromophenyl)acrylaldehyde **1d** (145.4 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (197.2 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with phenylmethanamine **4a** (110 µL, 1.0 mmol) at rt for 3 h afforded 103.9 mg (66 % yield) of **5da 5da**: light yellow solid; IR:(KBr) ν_{max} 3289, 2924, 1654, 1621, 1548, 1334, 1223, 972, 819, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 15.4 Hz, 1H), 7.46-7.44 (m, 2H), 7.40-7.20 (m, 7H), 6.42 (d, *J* = 15.4 Hz, 1H), 6.25 (s, 1H), 4.53 (d, *J* = 2.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 140.0, 138.1, 133.7, 132.0, 129.2, 128.7, 127.8, 127.6, 123.8, 121.2, 43.8; MS (70 eV): m/z (%): 316.9 (42) $[M]^+$, 101.9 (100).

(*E*)-*N*-Benzyl-3-(4-chlorophenyl)acrylamide (5ea)[17]



The reaction of (*Z*)-2-bromo-3-(4-chlorophenyl)acrylaldehyde **1e** (123.1 mg, 0.5 mmol), imidazolium salt **A** (17.2 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (197.2 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with phenylmethanamine **4a** (110 µL, 1.0 mmol) at rt for 3 h afforded 97.3 mg (72 % yield) of **5ea 5ea**: light yellow solid; IR:(KBr) ν_{max} 3288, 3024, 1654, 1623, 1549, 1335, 1223, 972, 822, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.58 (d, *J* = 15.6 Hz, 1H), 7.35-7.30 (m, 9H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.33 (brs, 1H), 4.53 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.6, 139.9, 138.1, 135.5, 133.3, 129.0, 128.9, 128.7, 127.8, 127.5, 121.1, 43.8; MS (70 eV): m/z (%): 271.1 (83) $[M]^+$, 106.1 (100).

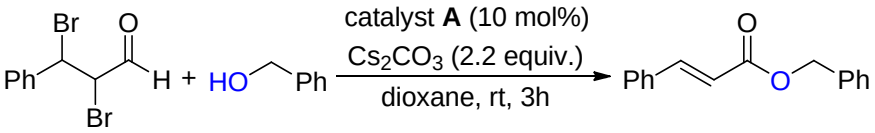
(*E*)-*N*-Benzyl-3-(naphthalen-2-yl)acrylamide (5fa)[18]



The reaction of (*Z*)-2-bromo-3-(naphthalen-2-yl)acrylaldehyde **1f** (131.0 mg, 0.5 mmol), imidazolium salt **A** (17.1 mg, 0.05 mmol), HFIP (78 µL, 0.75 mmol) and Cs_2CO_3 (196.7 mg, 0.6 mmol) in THF (2.5 mL) at rt under Ar for 30 min. Treatment with phenylmethanamine **4a** (110 µL, 1.0 mmol) at rt for 3 h afforded 100.3 mg (70 % yield) of **5fa 5fa**: light yellow solid; IR:(KBr) ν_{max} 3272, 3056, 2926, 1647, 1616, 1539, 1362, 1322, 1218, 970, 826, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.88-7.80 (m, 5H), 7.62-7.60 (m, 1H), 7.43-7.54 (m, 2H), 7.34-7.29 (m, 5H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.10 (brs, 1H), 4.59 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 165.8, 141.4, 138.2, 134.0, 133.4, 132.3, 129.4, 128.8, 128.6, 128.4, 127.9, 127.7, 127.6, 126.9, 126.6, 123.5, 120.7, 43.9; MS (70 eV): m/z (%): 287.1 (27) $[M]^+$, 151.9 (100).

2. Esterification and amidation from α,β-dibromoaldehyde by NHC catalysis

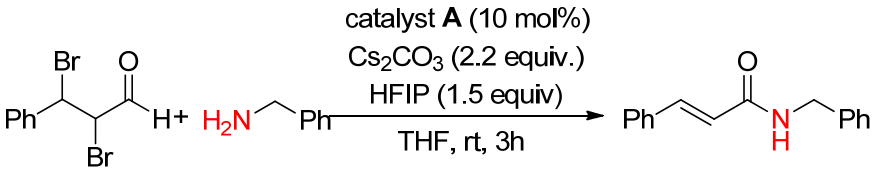
2.1 Esterification from α,β-dibromoaldehyde by NHC catalysis



6 **2a** **3aa** (78%)

2,3-Dibromo-3-phenylpropanal **6** (150.1 mg, 0.5 mmol) and imidazolium salt **A** (16.8 mg, 0.05 mmol) were placed in a 25 mL dry Schlenk tube under Ar. Dioxane 2.5 mL were added, followed by the addition of phenylmethanol **2a** (65 μL, 0.6 mmol). After stirring for 2 min, Cs_2CO_3 (359.0 mg, 1.1 mmol) was added. The reaction mixture was stirred at room temperature for 3 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et_2O = 10/1) to afford 92.6 mg (78 % yield) of **3aa**.

2.2 Amidation from α,β-dibromoaldehyde by NHC catalysis

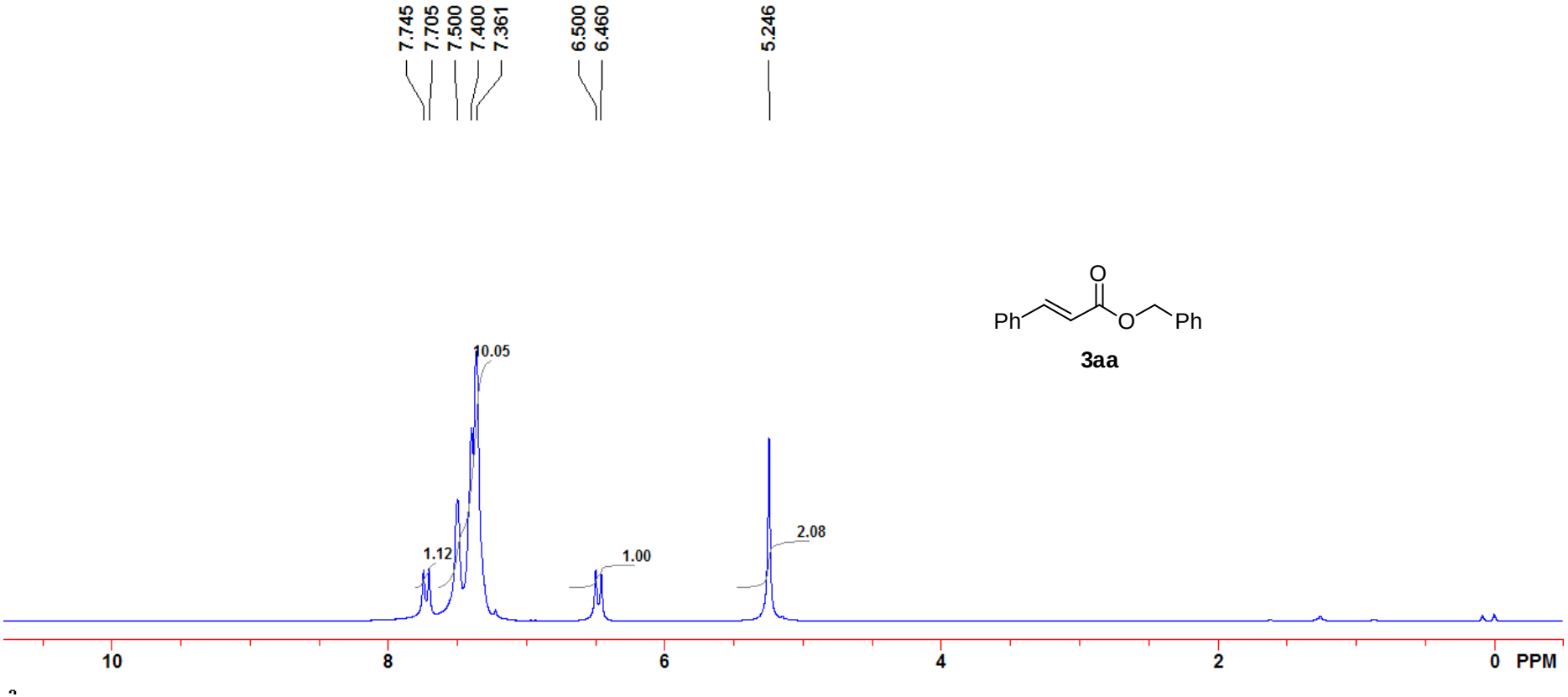


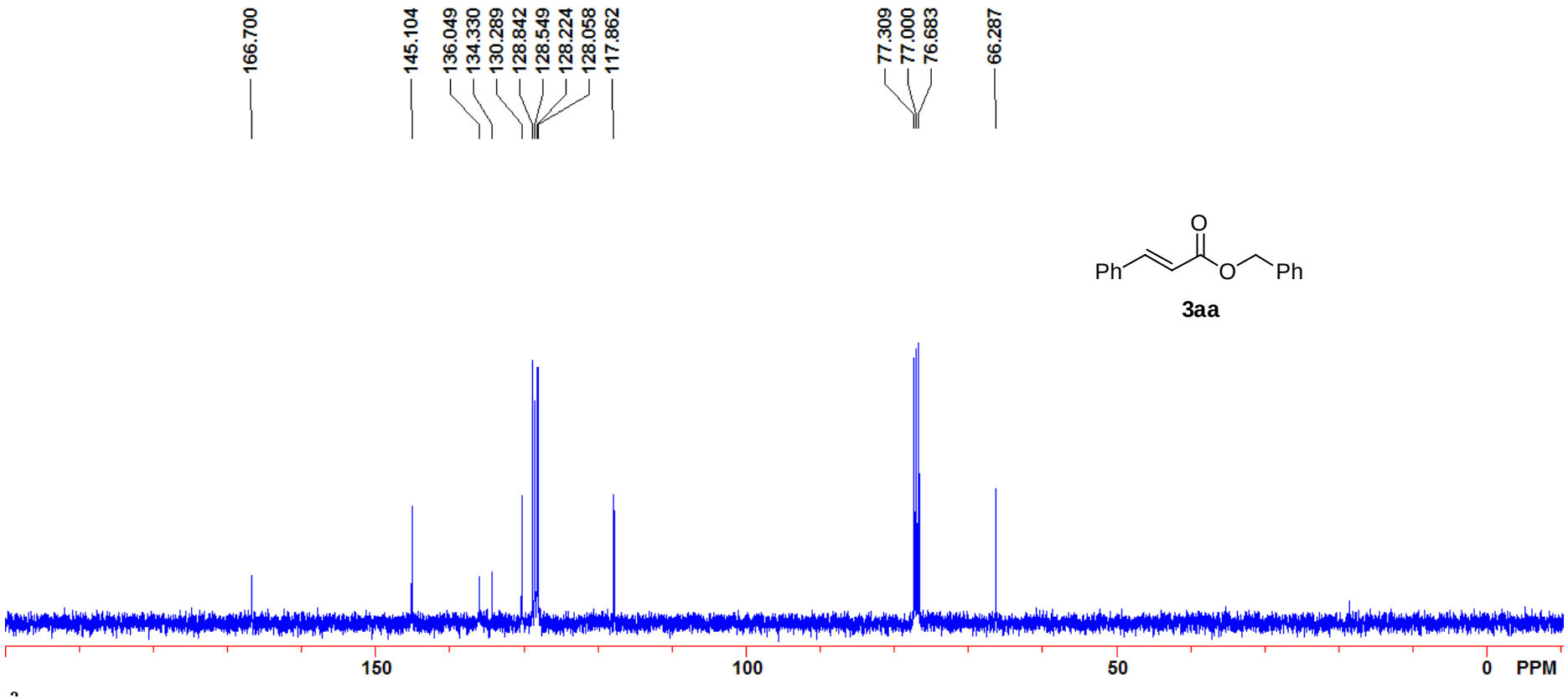
6 **4a** **5aa** (76%)

2,3-Dibromo-3-phenylpropanal **6** (150.3 mg, 0.5 mmol) and imidazolium salt **A** (17.2 mg, 0.05 mmol) were placed in a 25 mL dry Schlenk tube under Ar. THF 2.5 mL were added, followed by the addition of HFIP (78 μL, 0.75 mmol). After stirring for 2 min, Cs_2CO_3 (361.0 mg, 1.1 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. Then, phenylmethanamine **4a** (110 μL, 1.0 mmol) was added and continuingly stirred at rt for additional 3 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et_2O = 1/1) to afford 90.1 mg (76 % yield) of **5aa**.

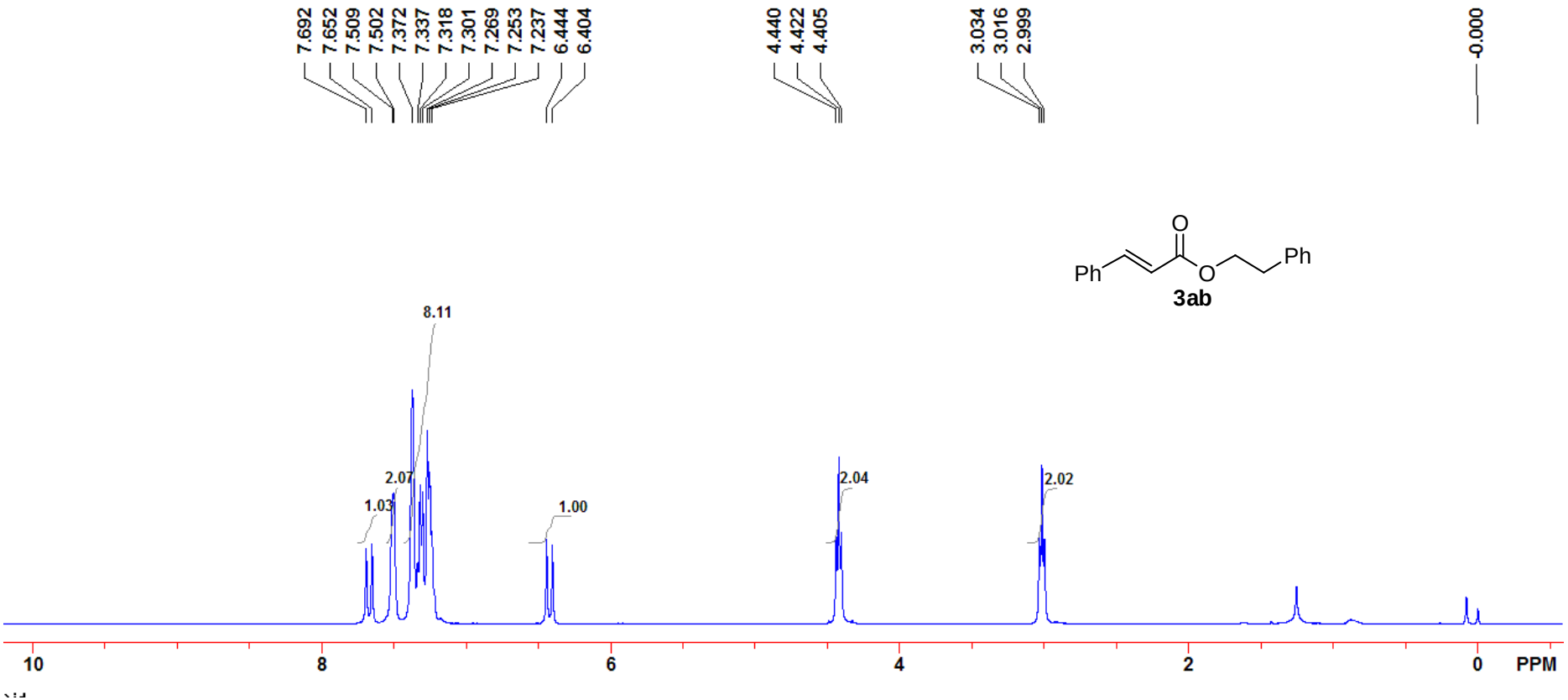
Reference:

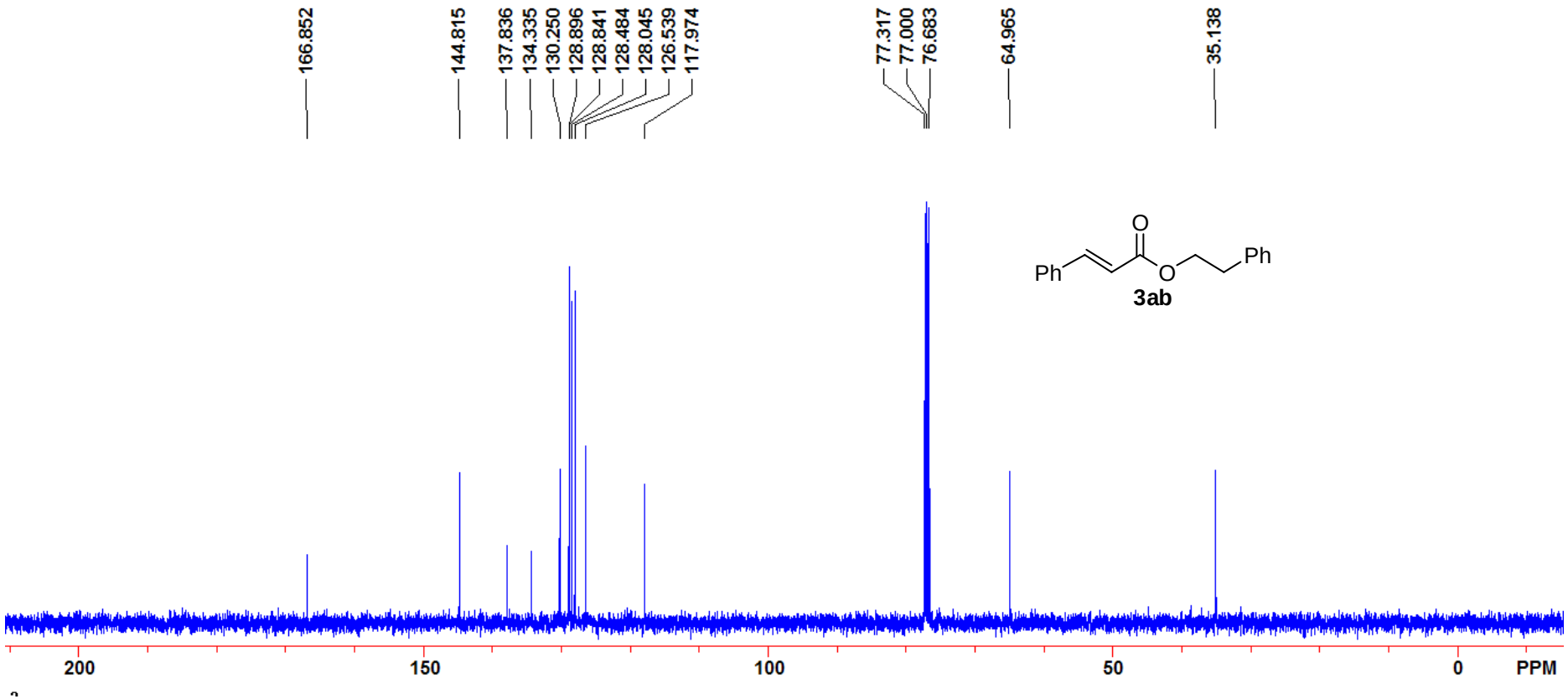
(1) Belil, et al. *Chem. Abstr.* **1962**, *57*, 16535.
(2) Shastin, et al. *Russ. Chem. B+* **2005**, *54*, 1733.
(3) Allen, C. F. H.; Edens, C. O. *Org. Synth.* **1945**, *25*, 92.
(4) Maji, B.; Vedachalan, S.; Ge, X.; Cai, S.; Liu, X.-W. *J. Org. Chem.* **2011**, *76*, 3016.
(5) Magens, S.; Ertelt, M.; Jatsch, A.; Plietker, B. *Org. Lett.* **2008**, *10*, 53.
(6) Sinha, A. K.; Sharma, A.; Swaroop, A.; Kumar, V. *Tetrahedron.* **2007**, *63*, 1000.
(7) Sarkar, S. D.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2010**, *132*, 1190.
(8) Reddy, R. S.; Rosa, J. N.; Veiros, L. F.; Caddick, S.; Gois, P. M. P. *Org. Biomol. Chem.* **2011**, *9*, 3126.
(9) Bentley, S. A.; Davies, S. G.; Lee, J. A.; Roberts, P. M.; Thomson, J. E. *Org. Lett.* **2011**, *13*, 2544.
(10) Batta-El, A.; Jiang, C.; Zhao, W.; Anness, R.; Cooksy, A. L.; Bergdahl, M. *J. Org. Chem.* **2007**, *72*, 5244.
(11) Lu, Z.; Peng, L.; Wu, W.; Wu, L. *Syn. Comm.* **2008**, *38*, 2357.
(12) Rolfe, A.; Loh, J. K.; Maity, P. K.; Hanson, P. R. *Org. Lett.* **2011**, *13*, 4.
(13) Wipf, P.; Hopkins, C. R. *J. Org. Chem.* **1999**, *64*, 6881.
(14) Sarkar, S. D.; Studer, A. *Org. Lett.* **2010**, *12*, 1992.
(15) Rao, Y.; Li, X.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2009**, *131*, 12924.
(16) Imashiro, R.; Seki, M. *J. Org. Chem.* **2004**, *69*, 4216.
(17) Chen, C.-C.; Ho, J.-C.; Chang, N.-C. *Tetrahedron.* **2008**, *64*, 10350.
(18) Gandon, V.; Bertus, P; Szymoniak, J. *Tetrahedron.* **2000**, *56*, 4467.

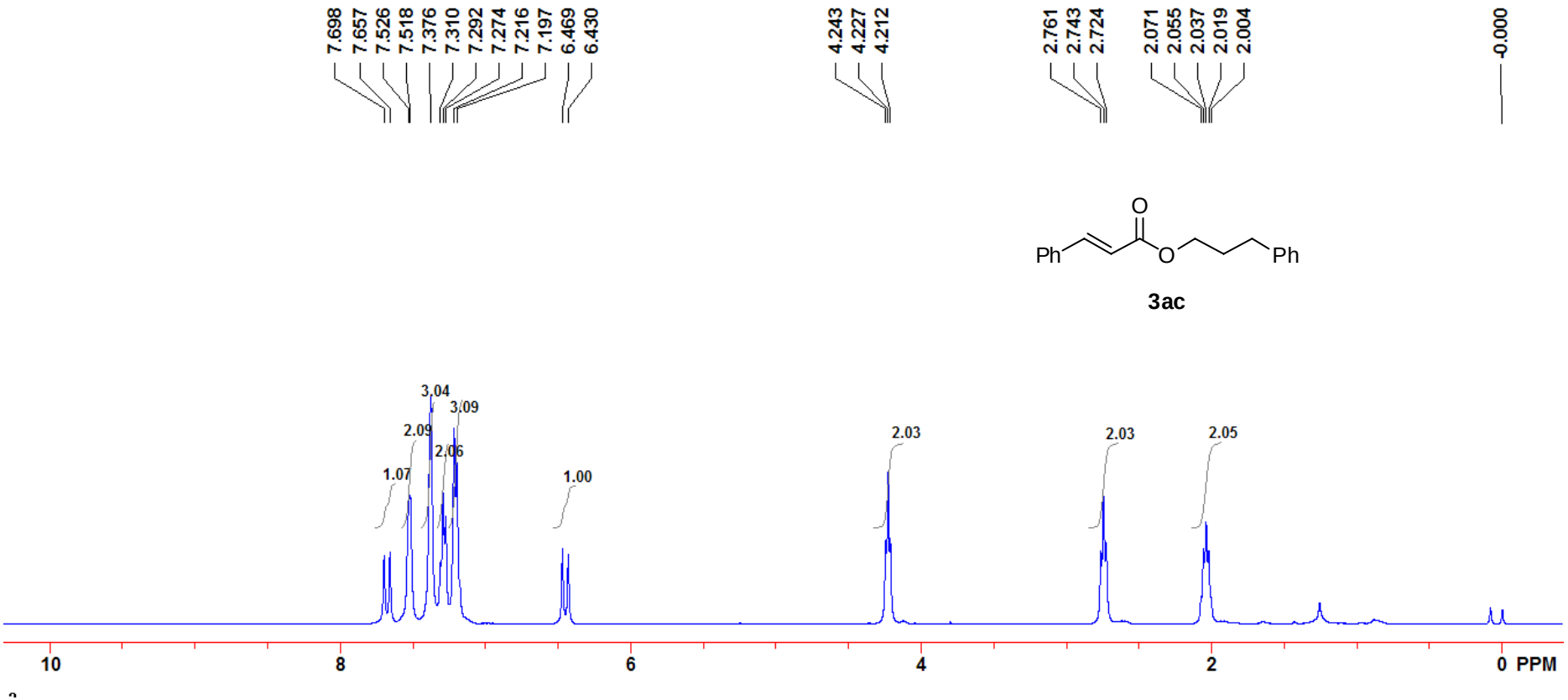


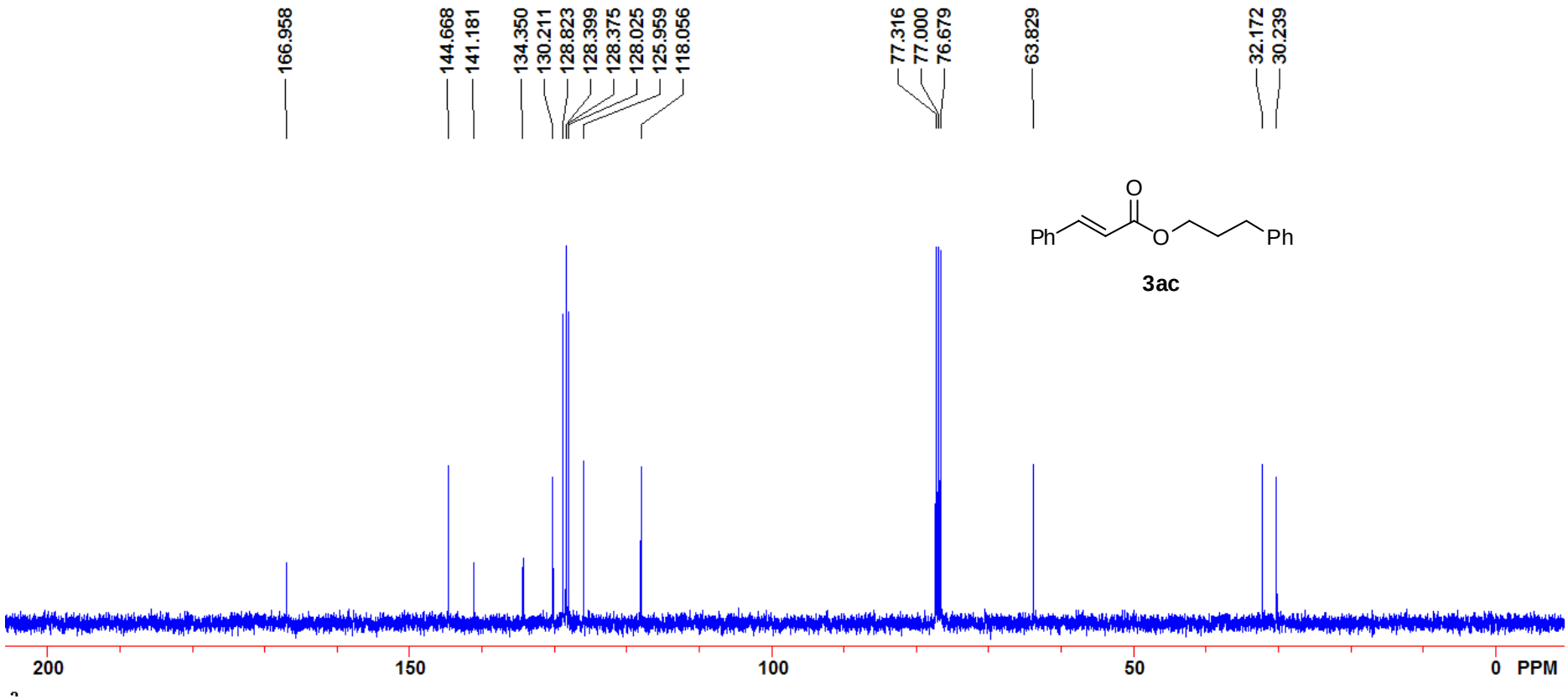


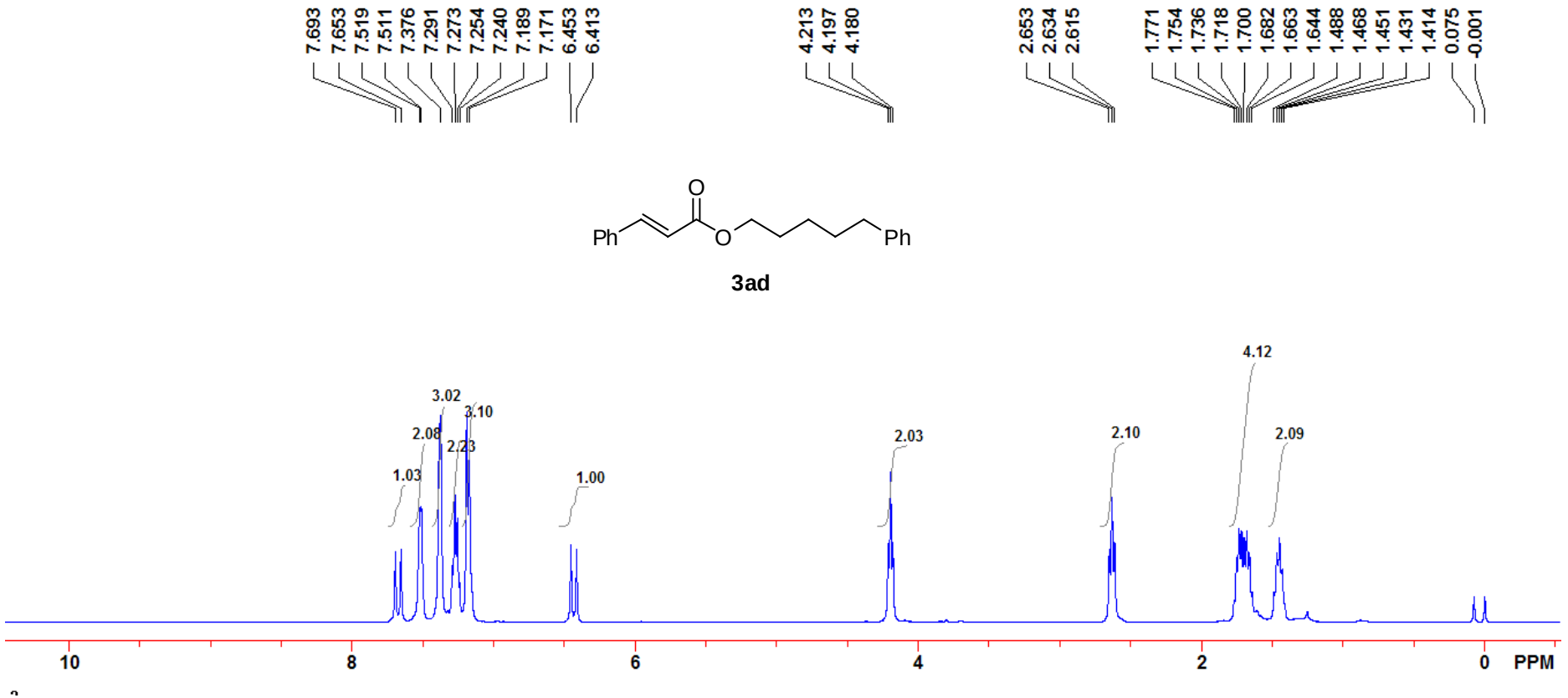
3aa

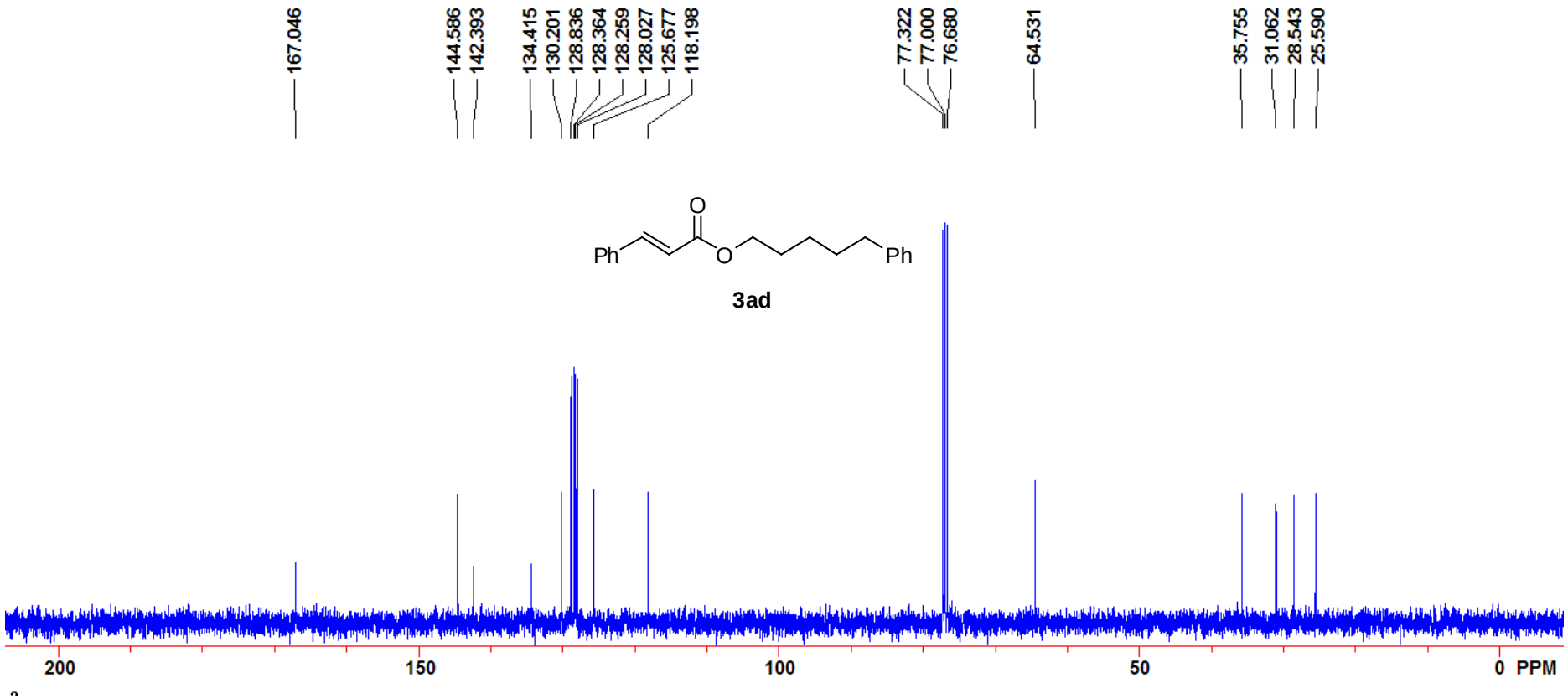


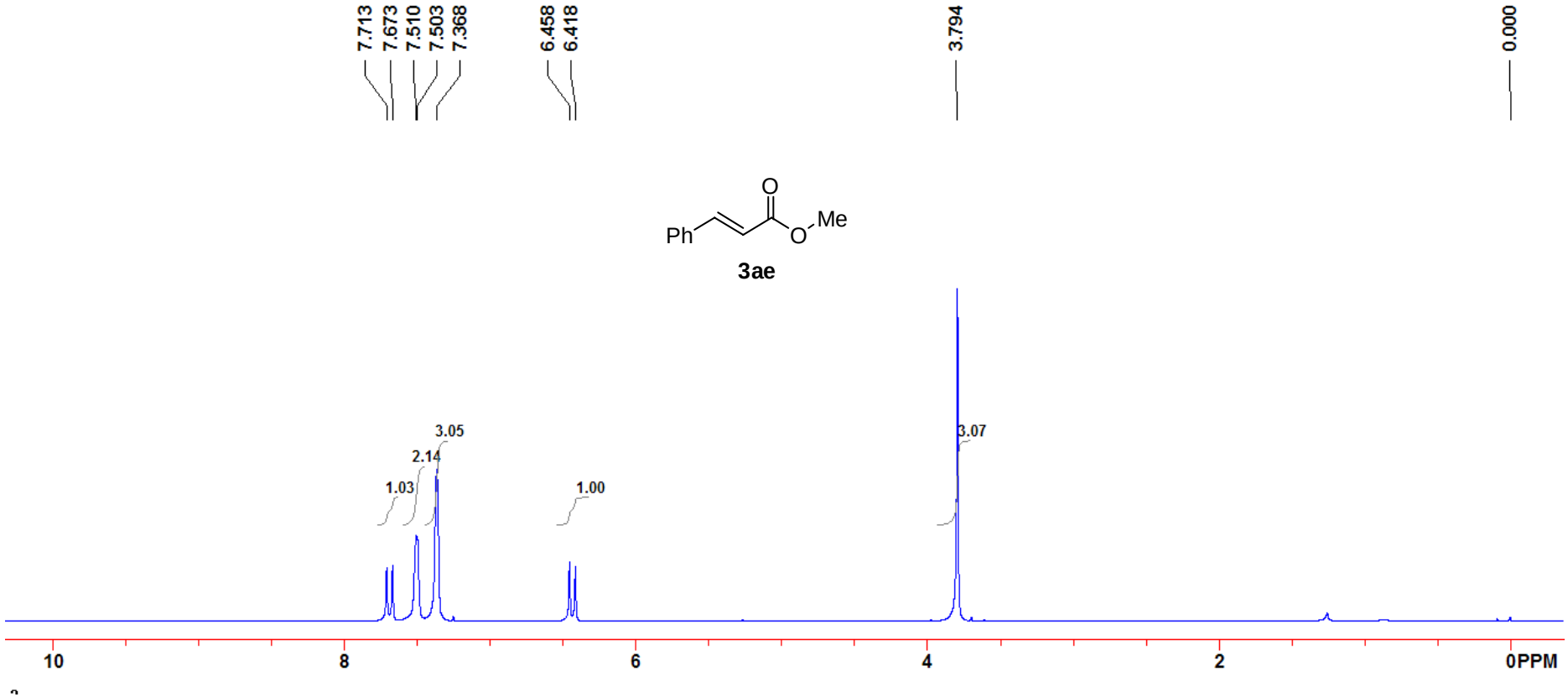


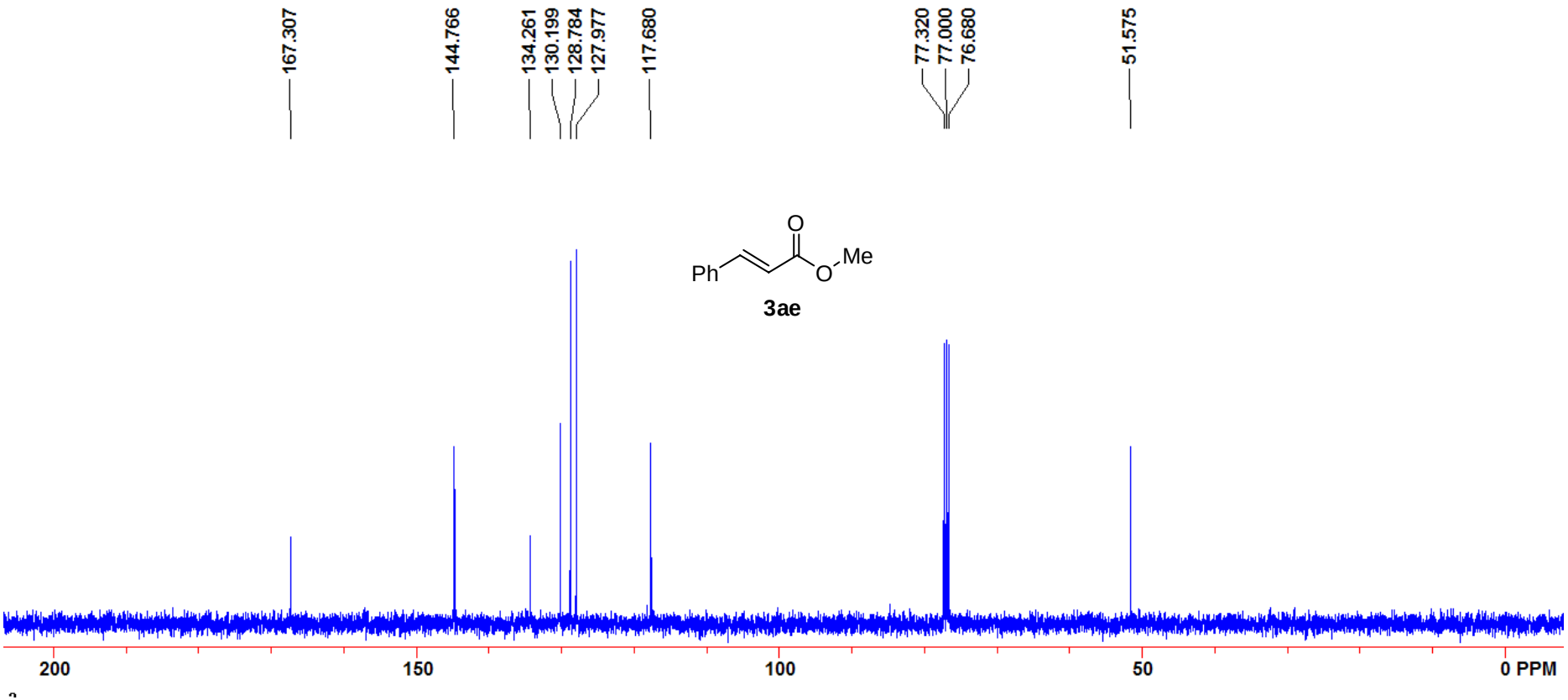












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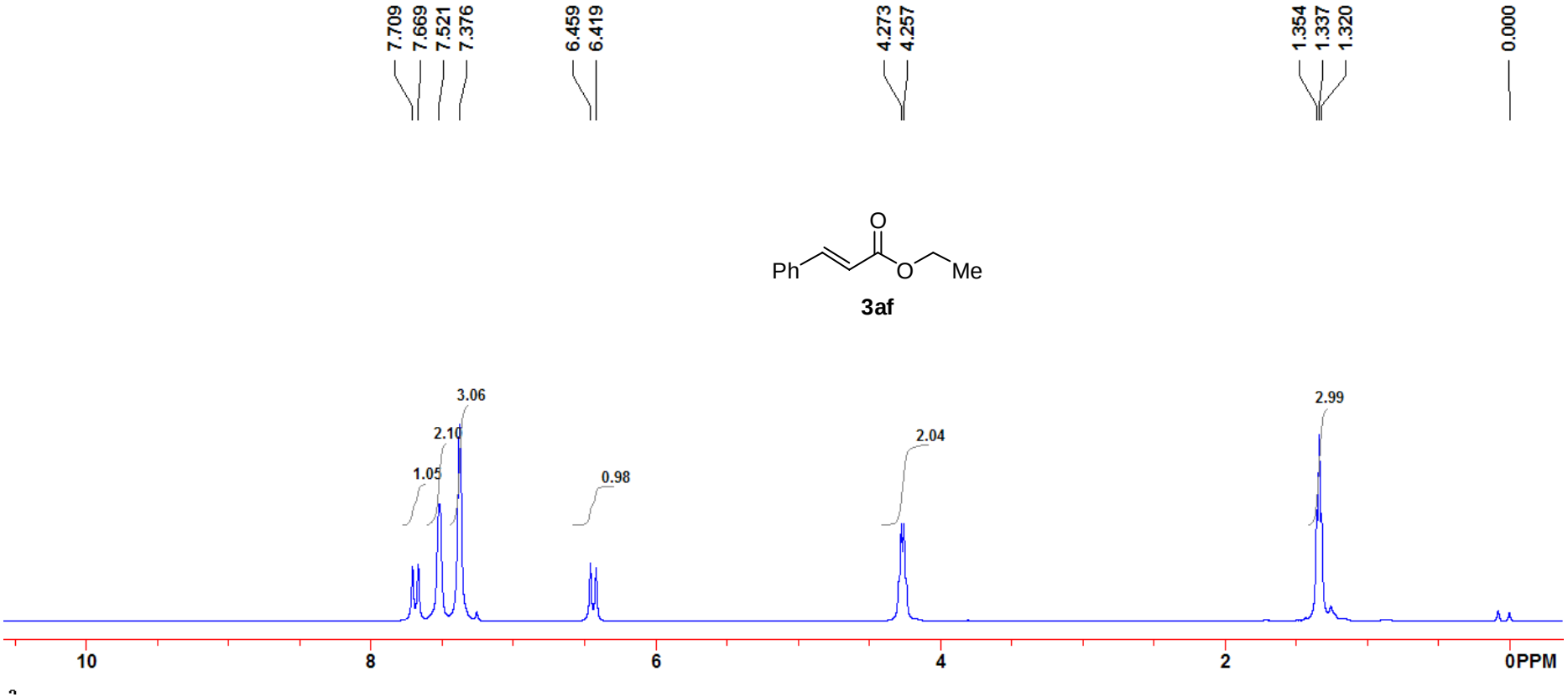

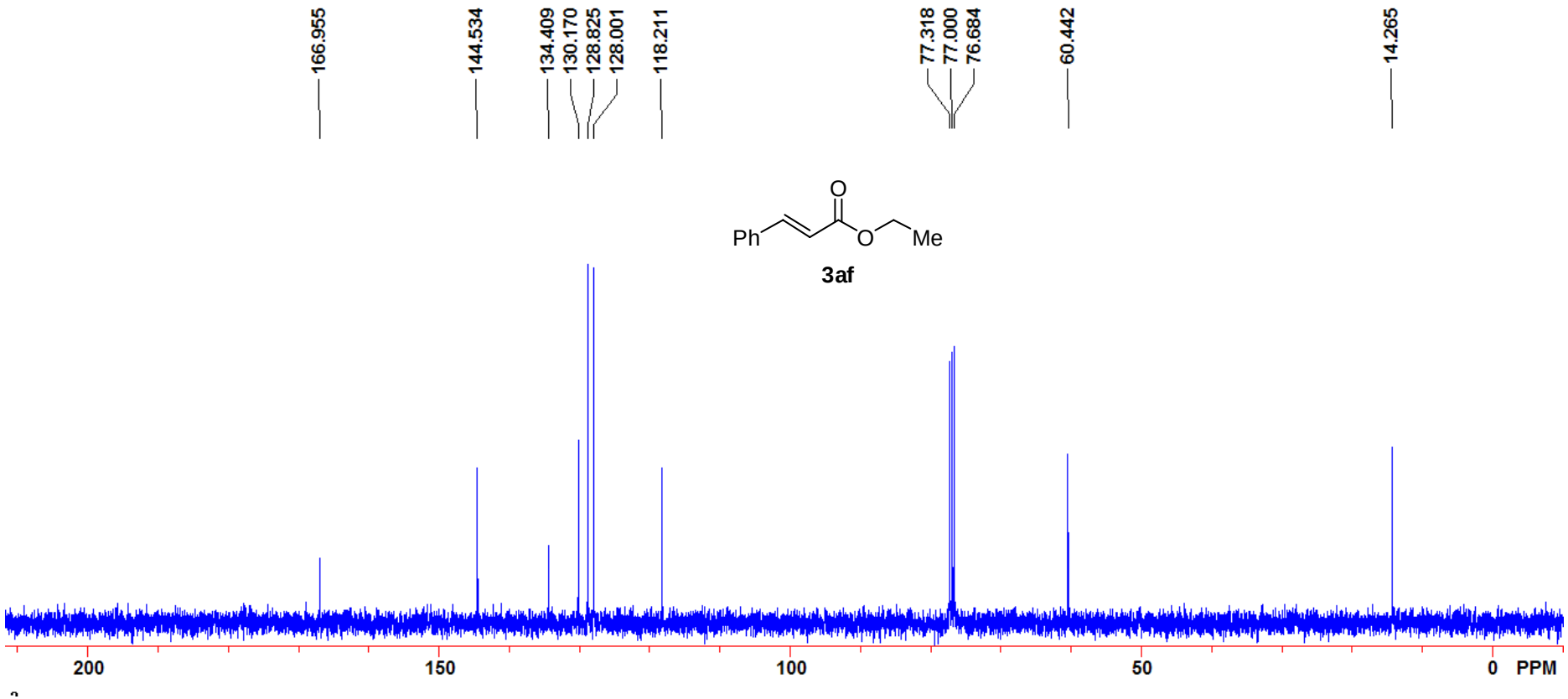

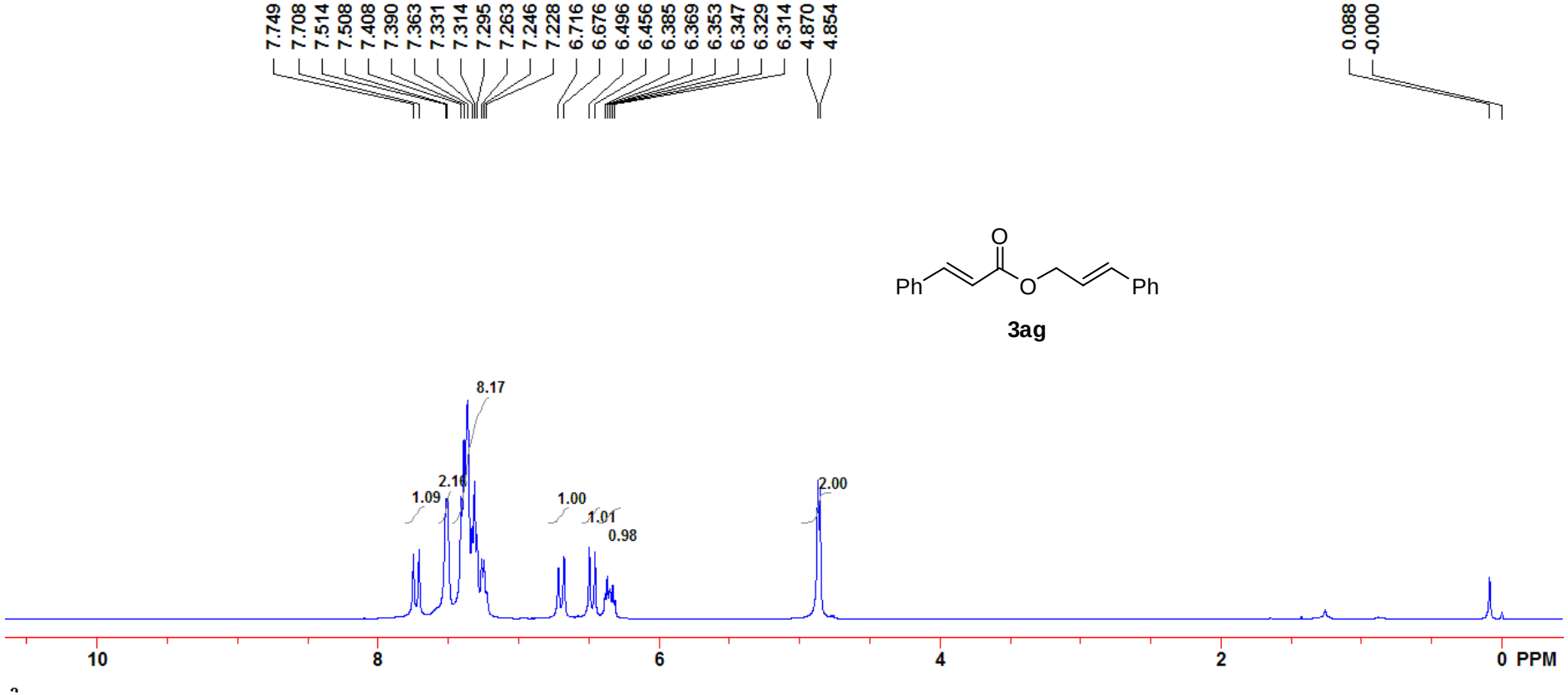

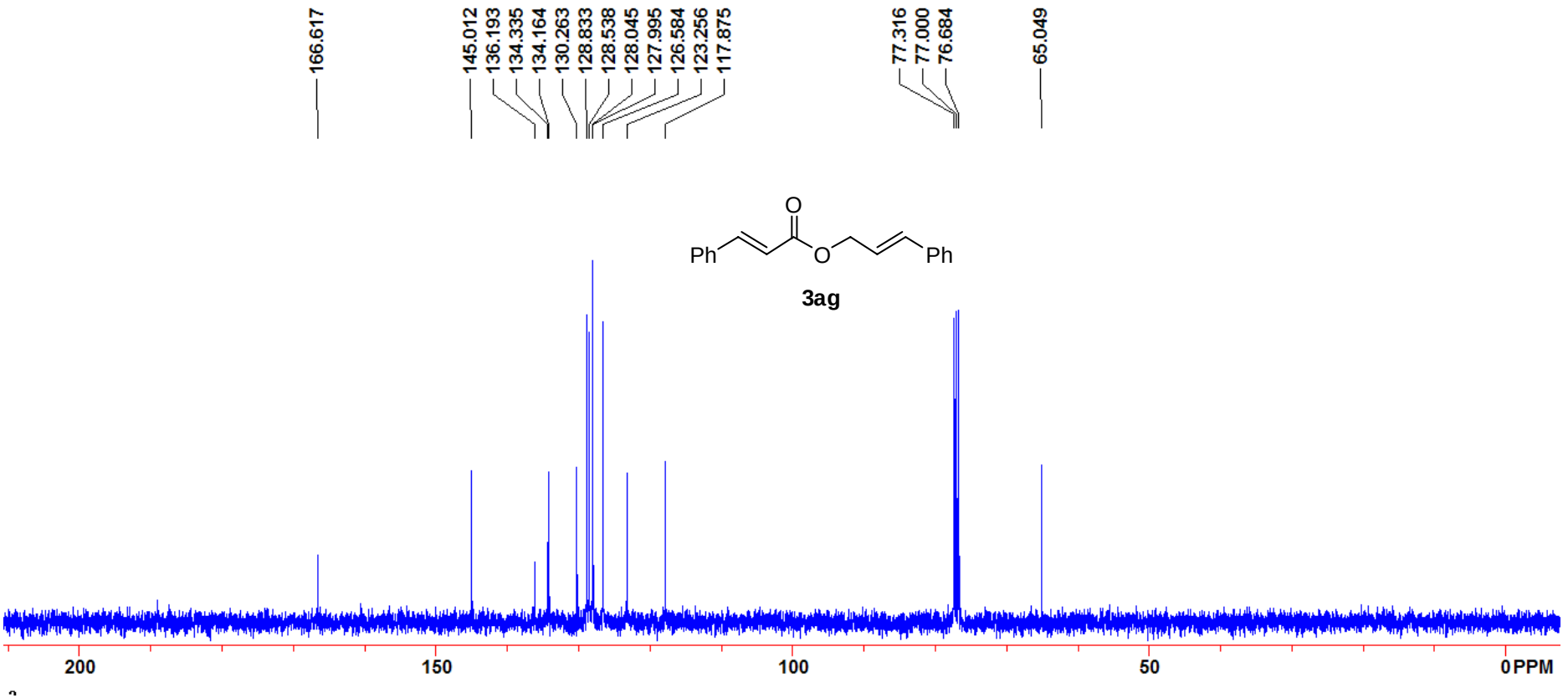

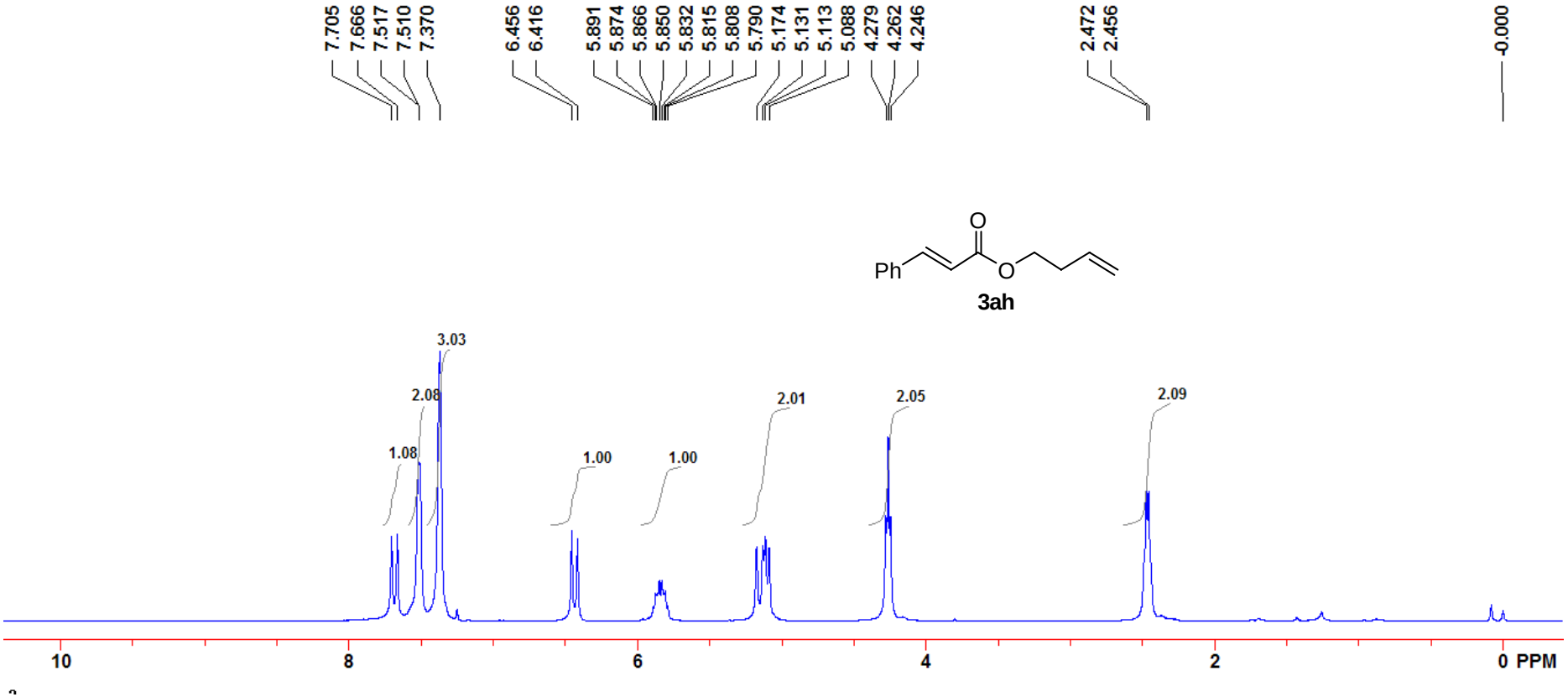

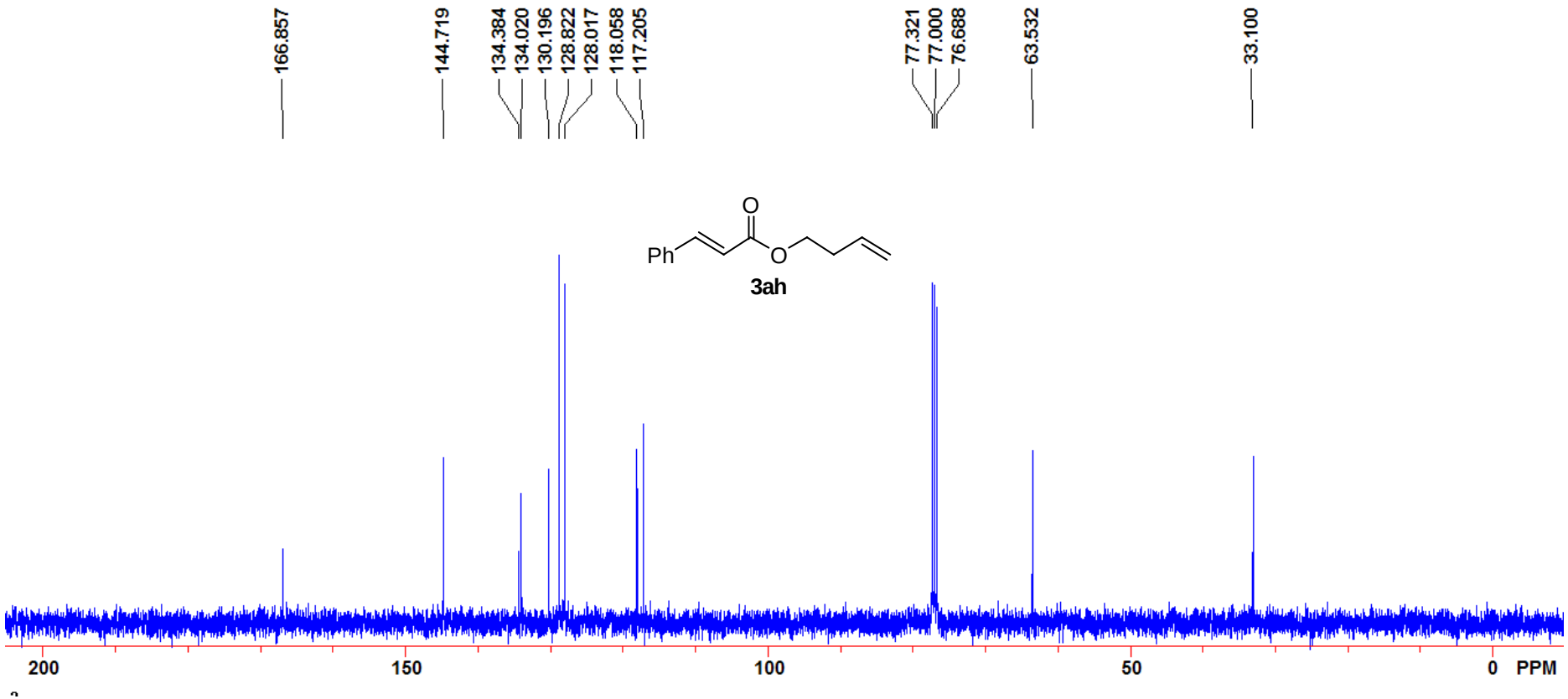

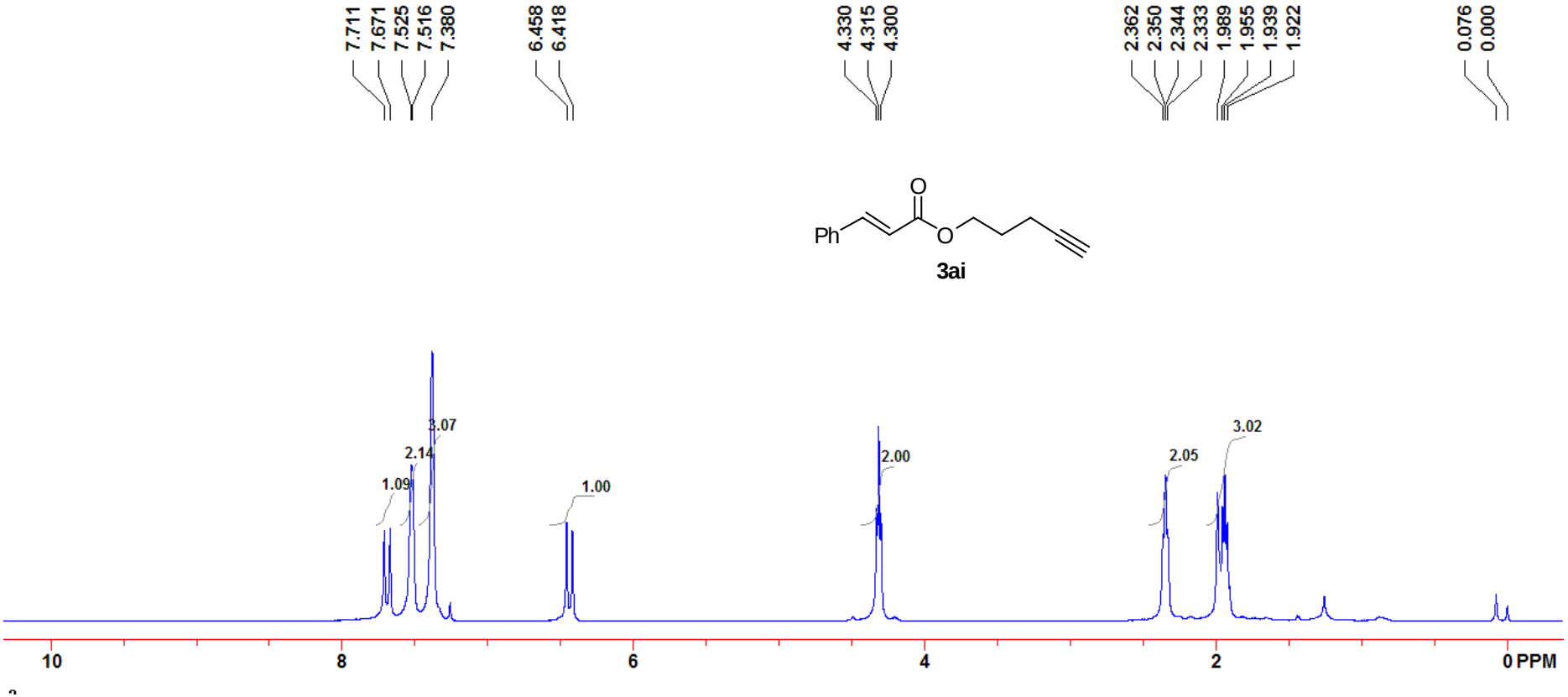

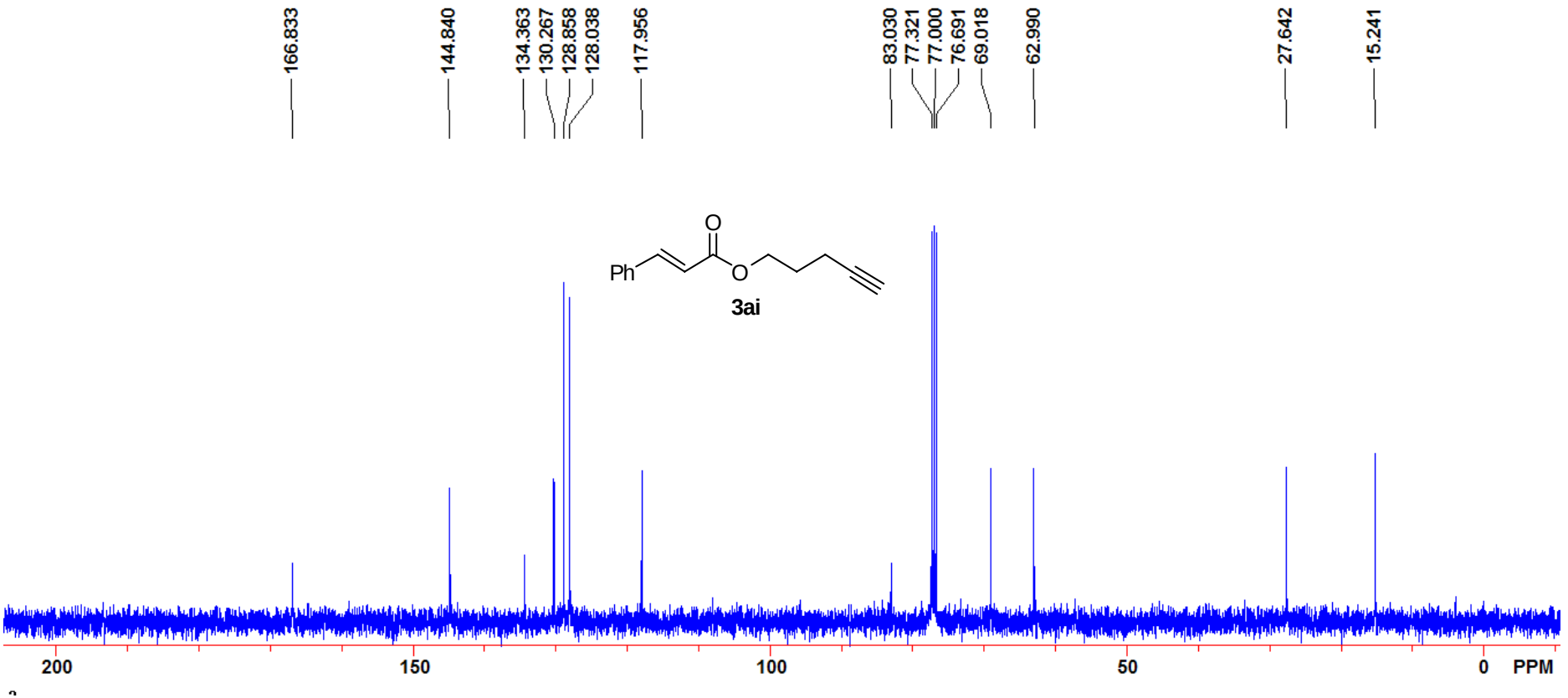

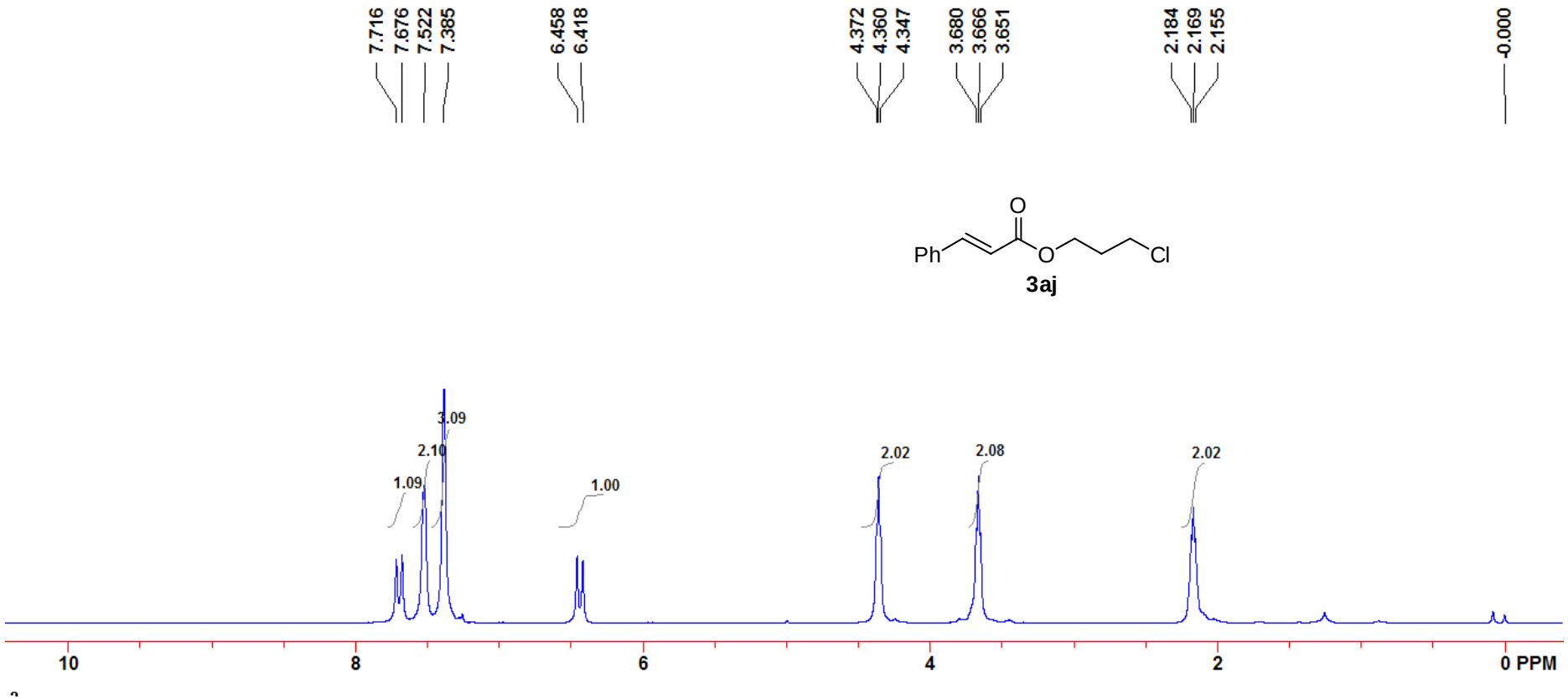

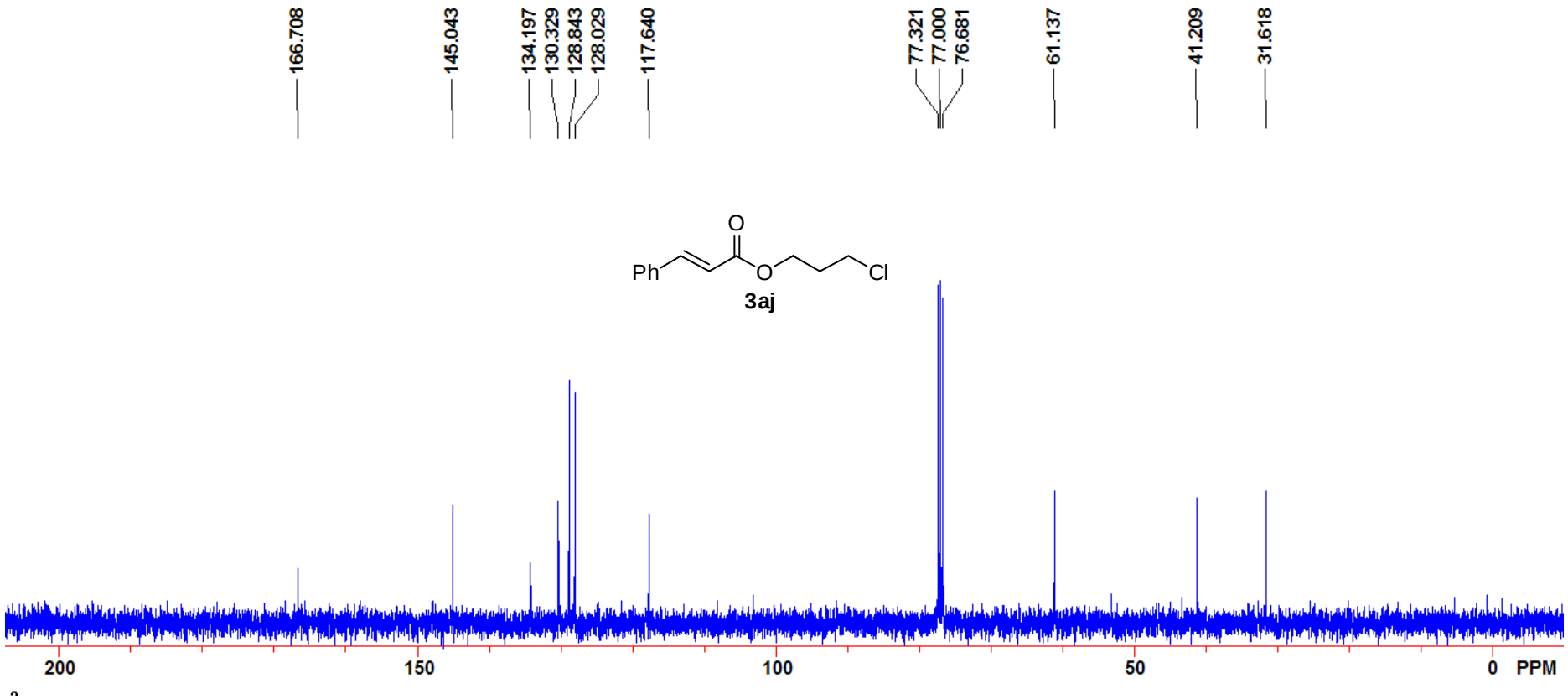

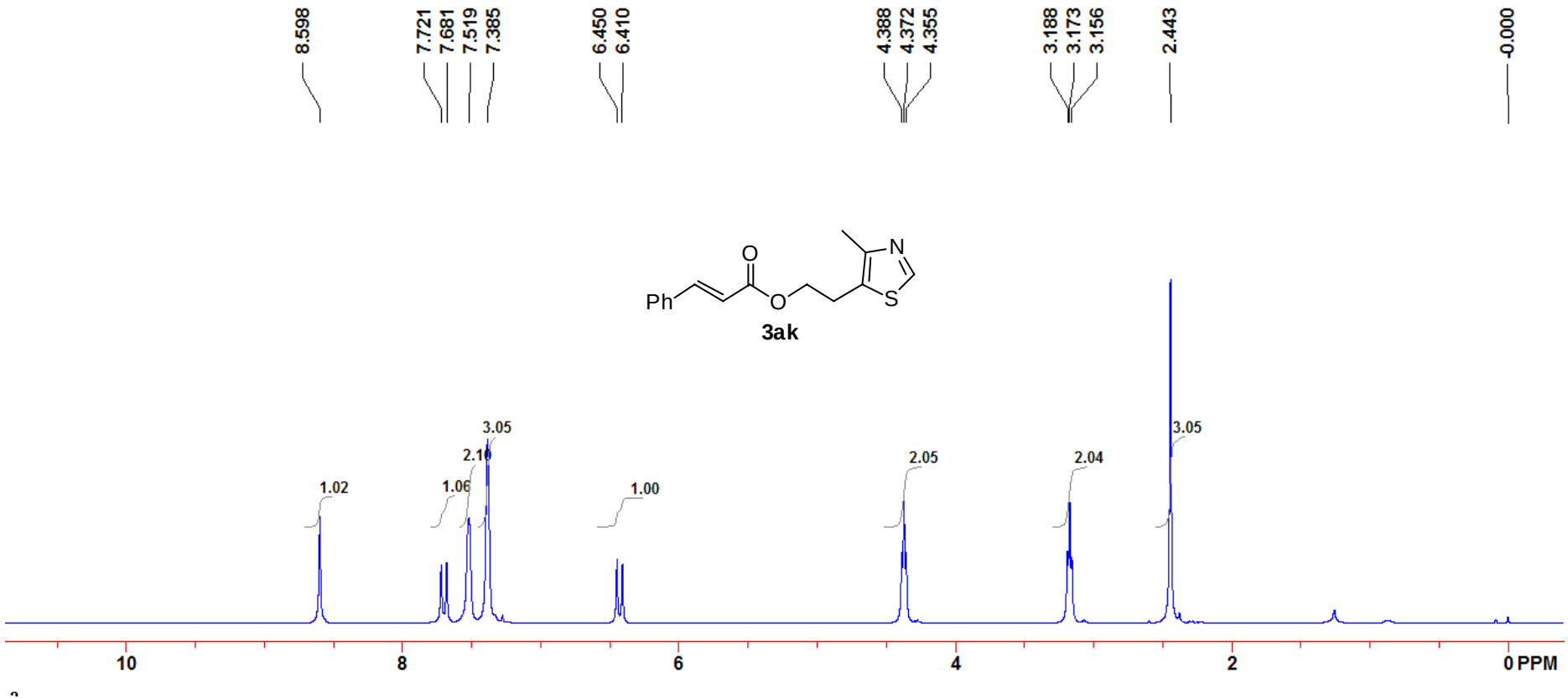

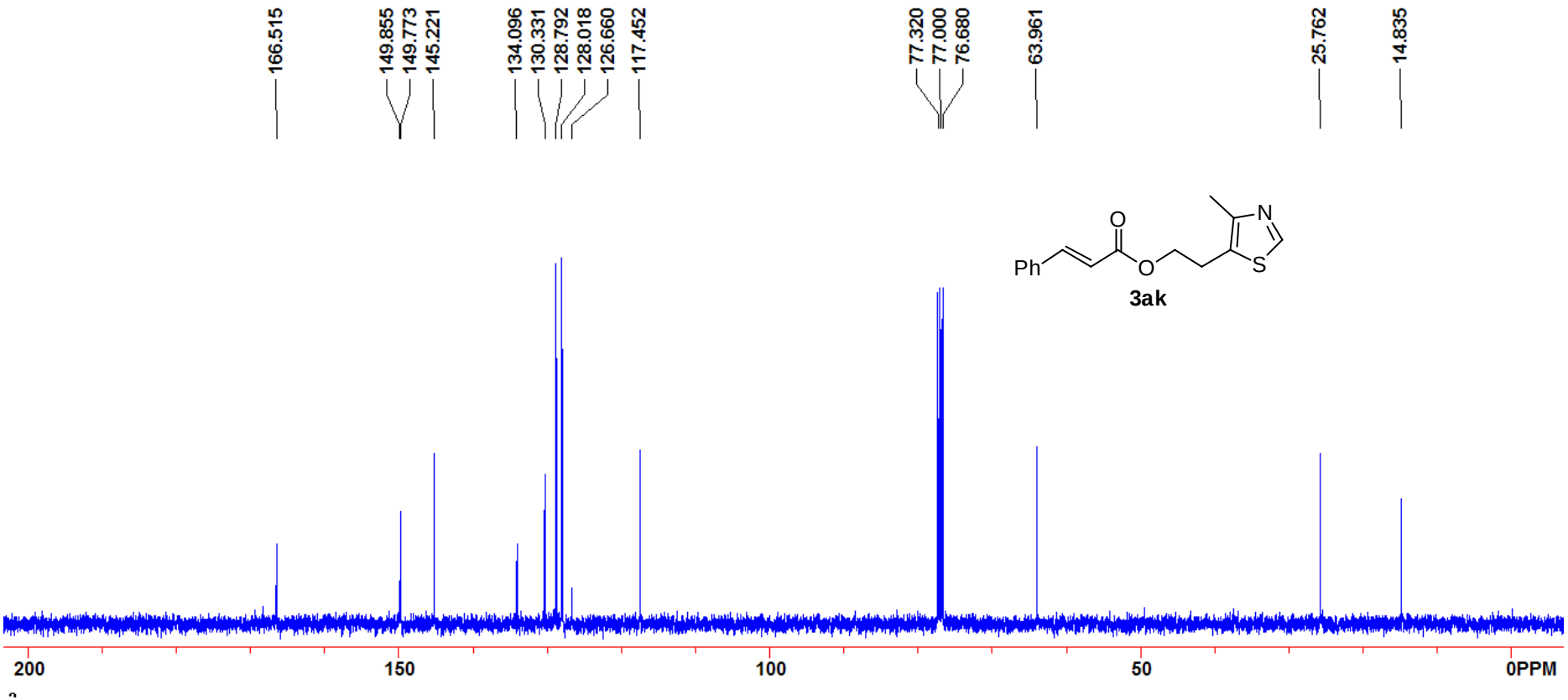

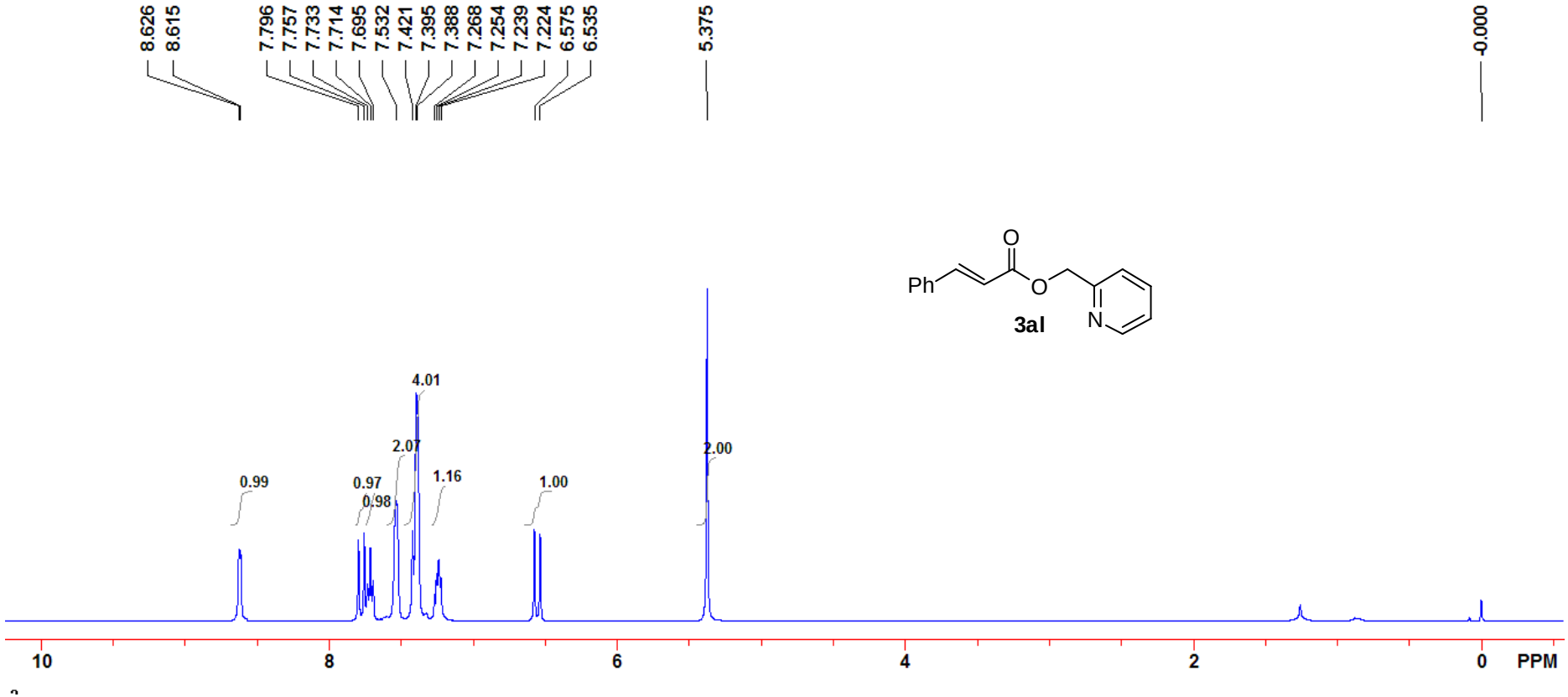

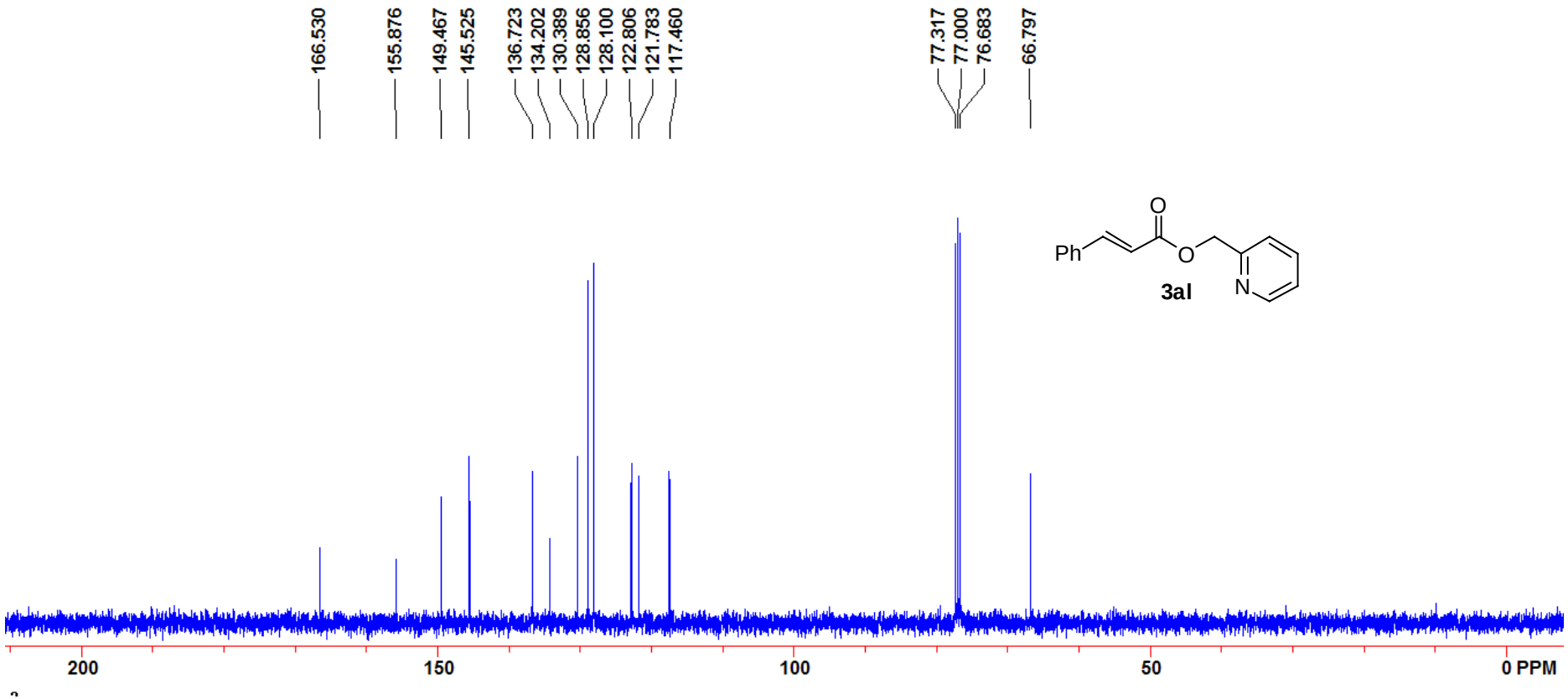

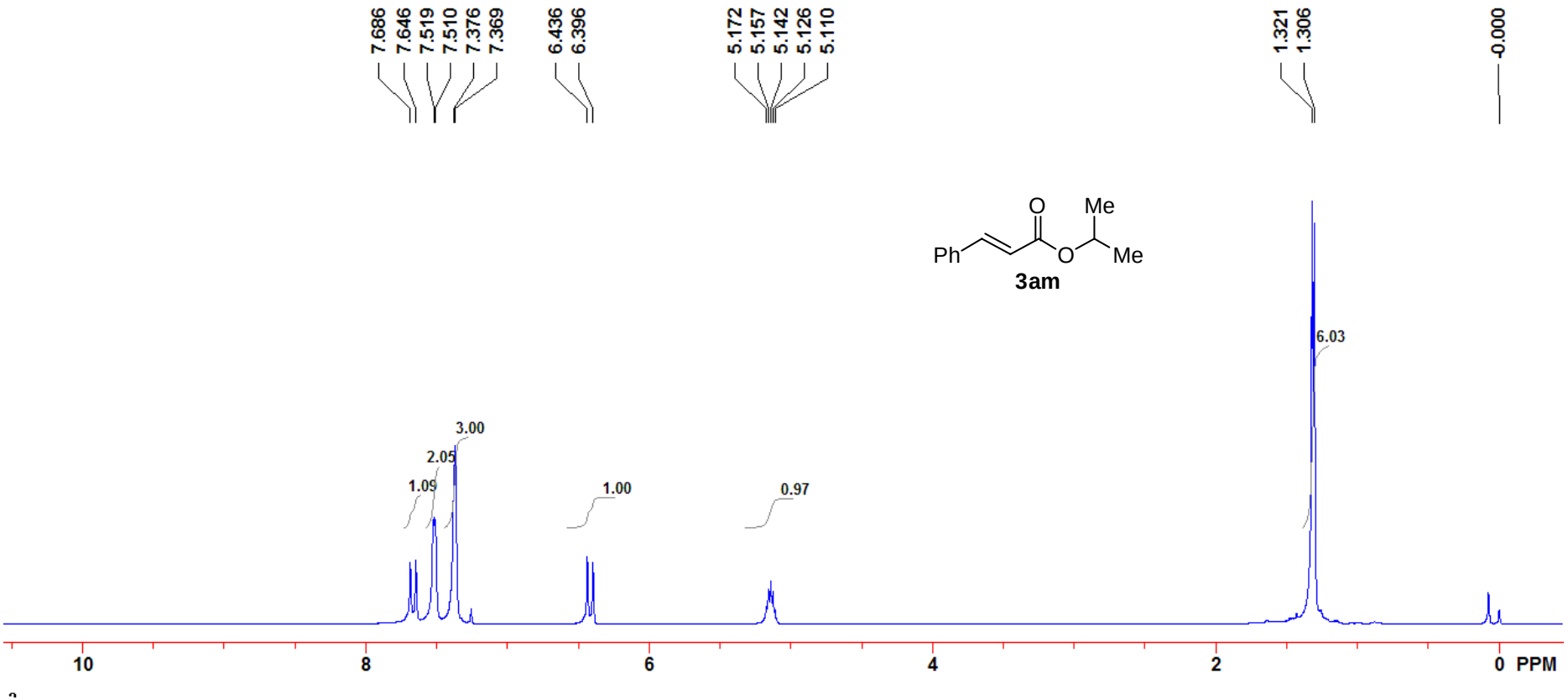

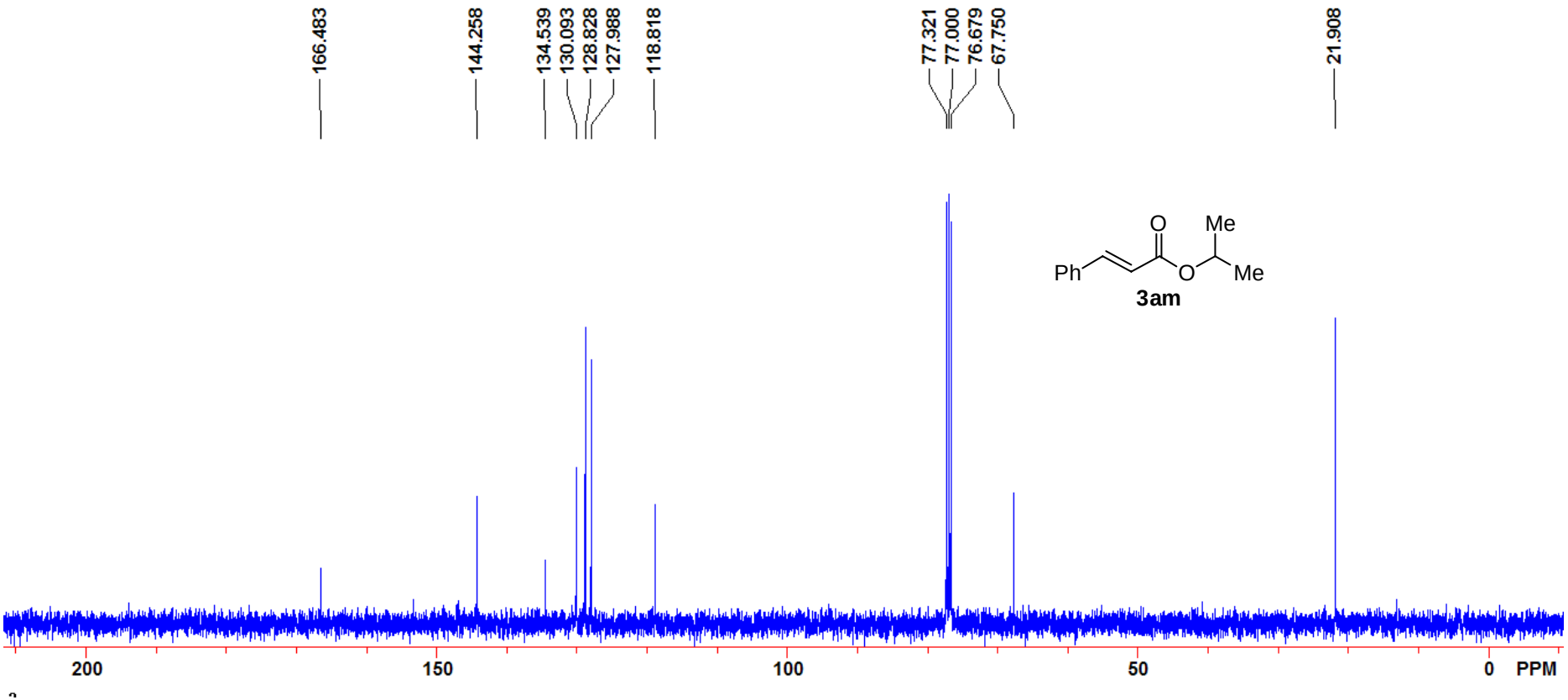

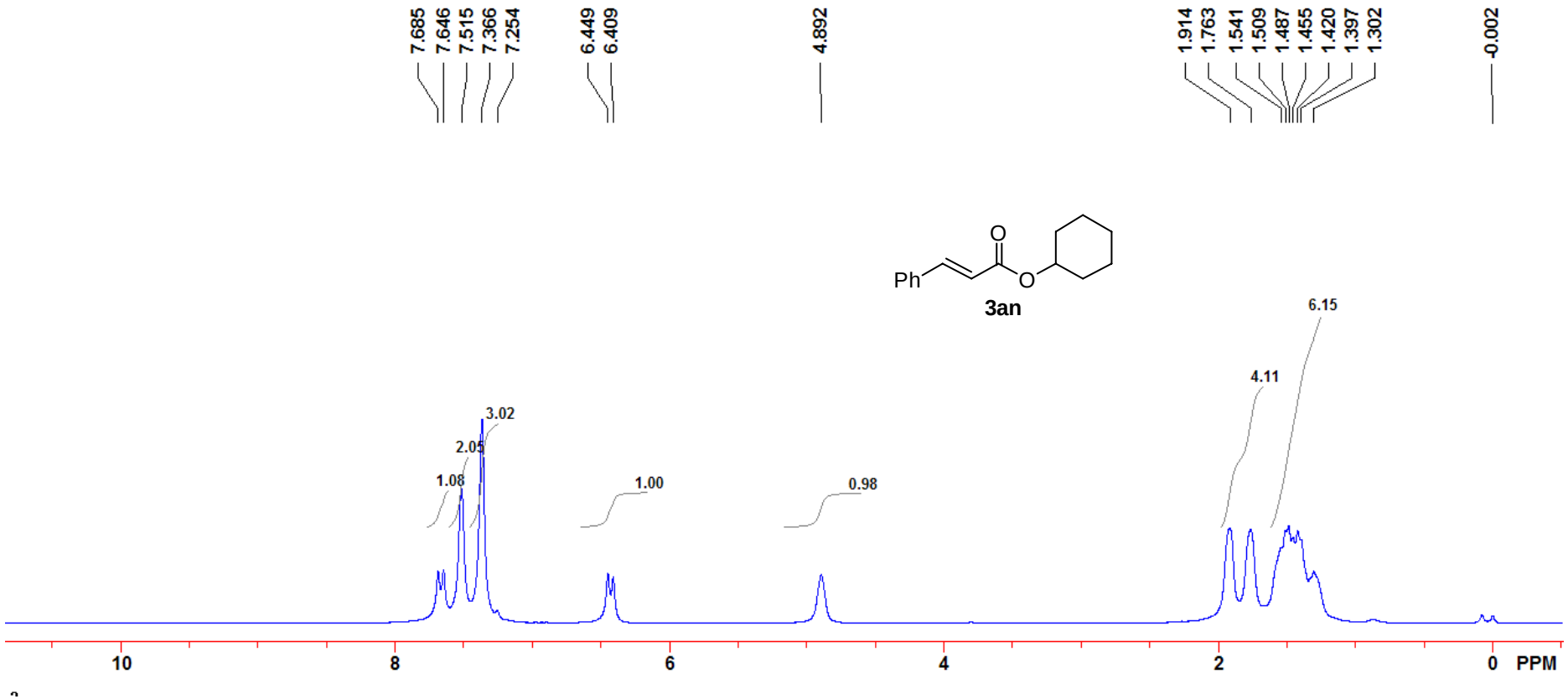

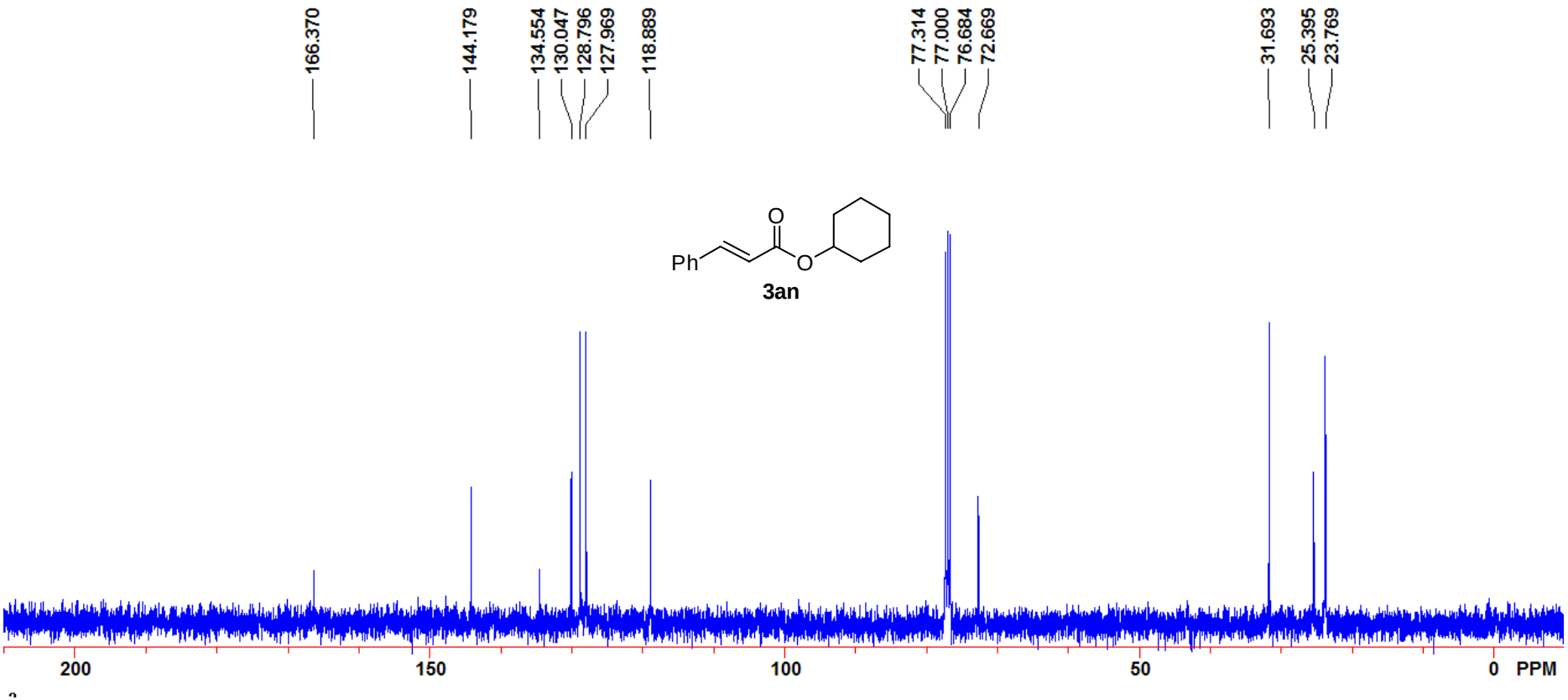

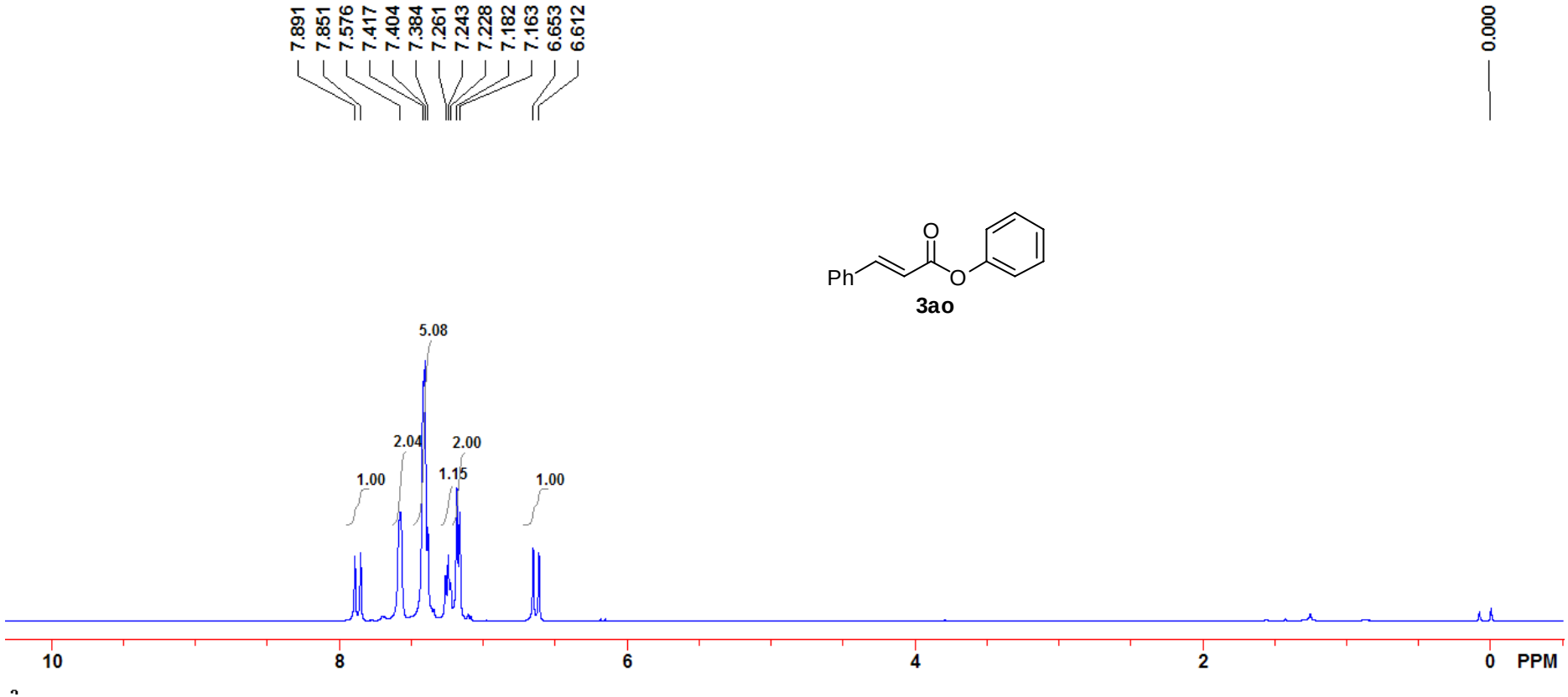

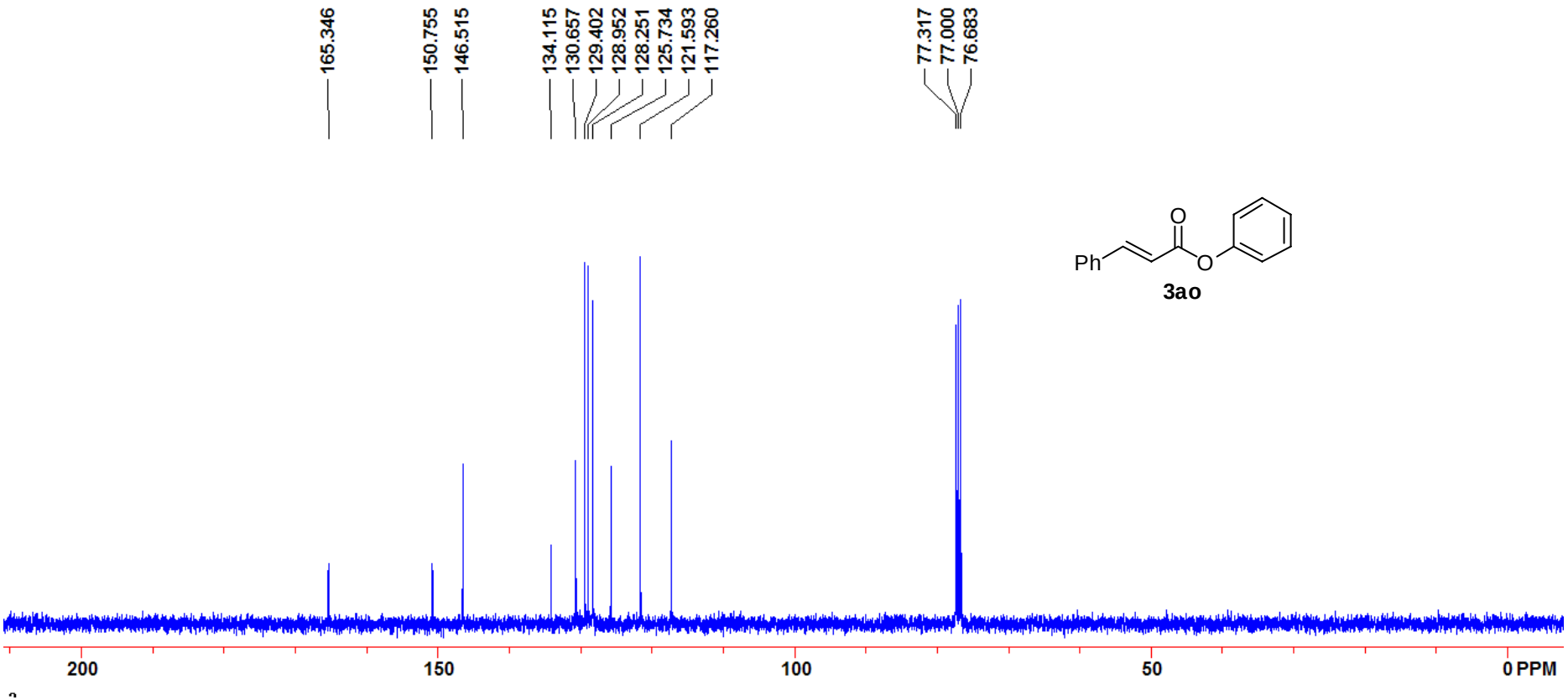

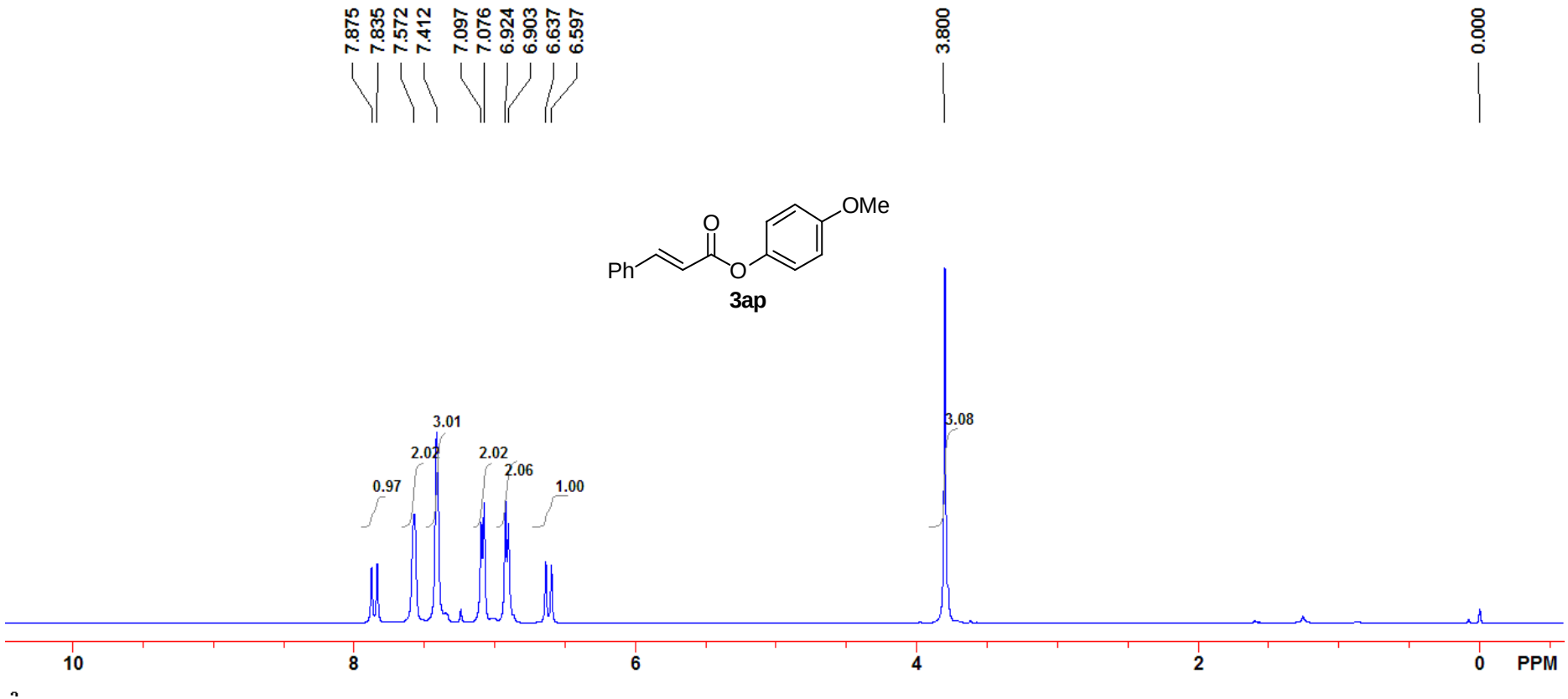

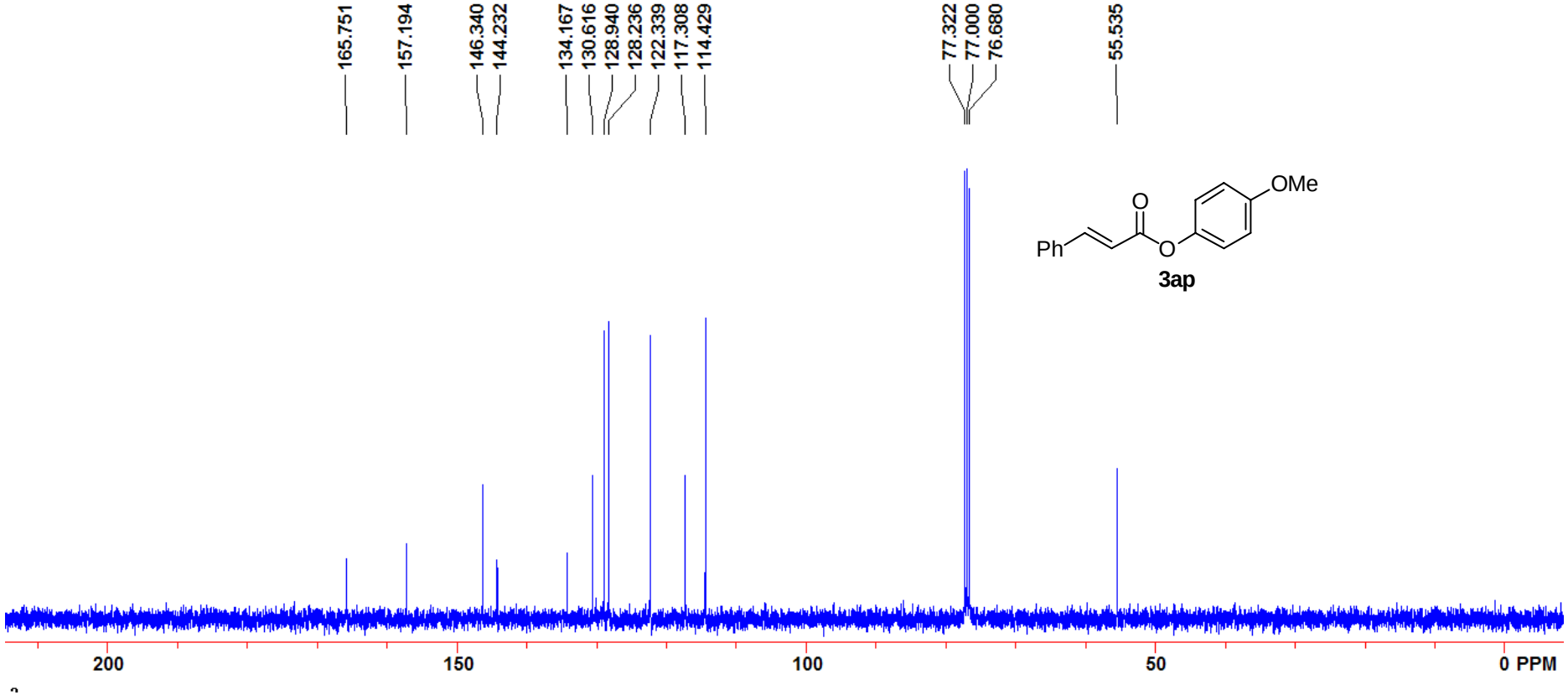

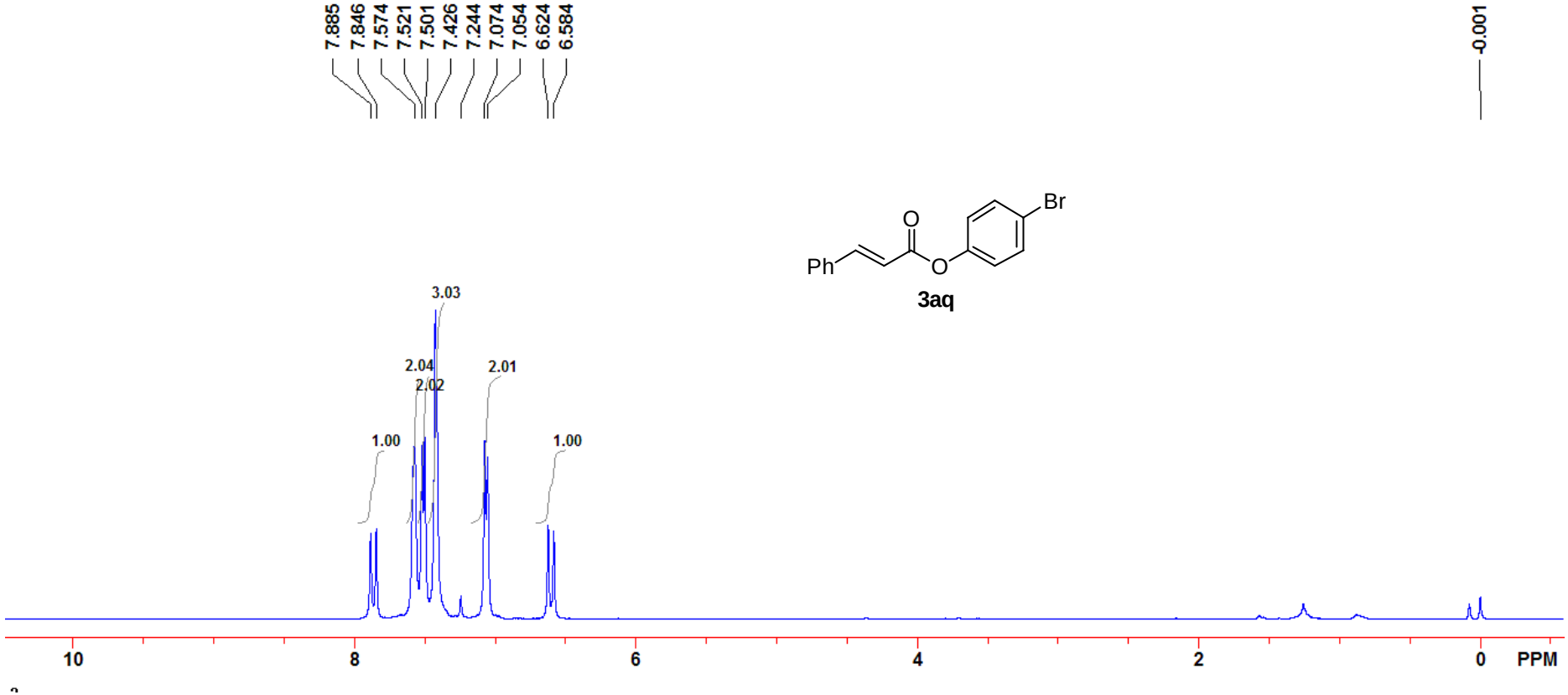

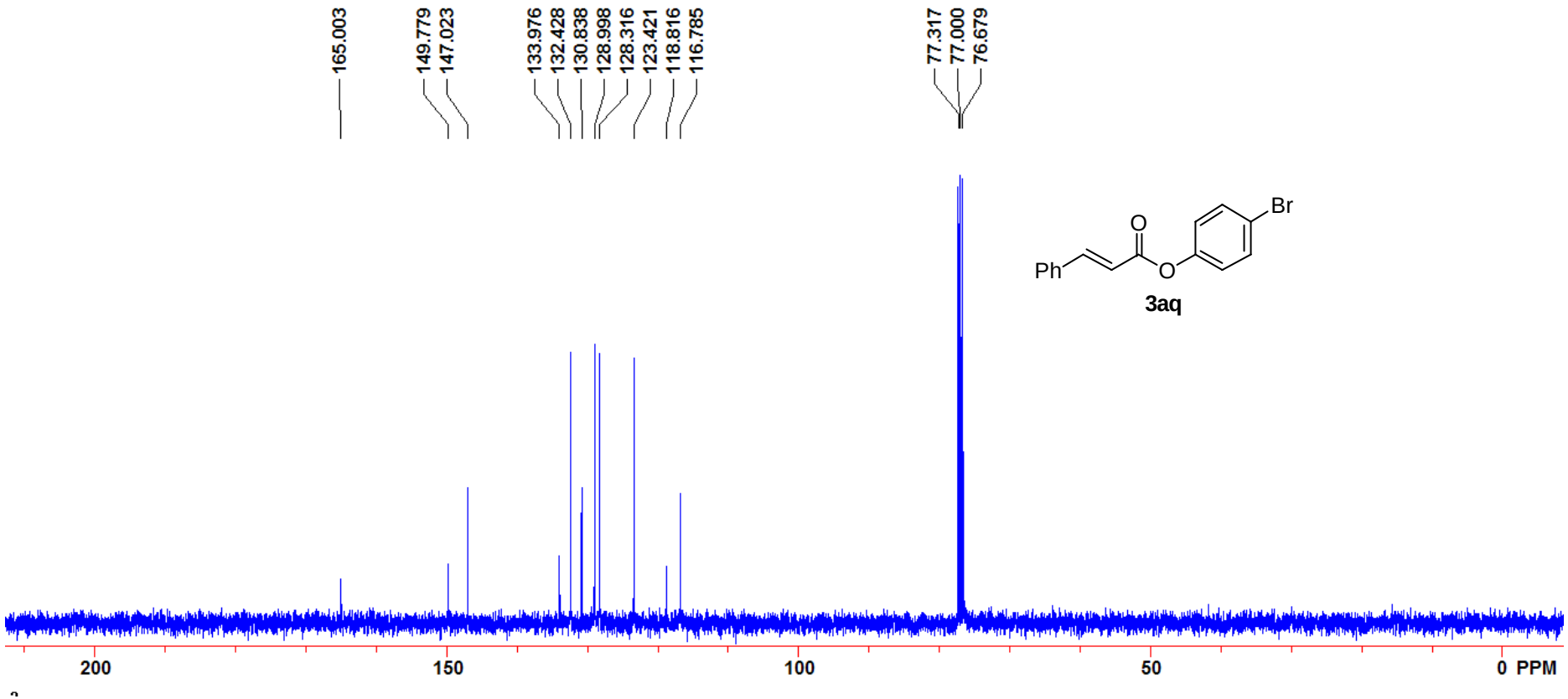

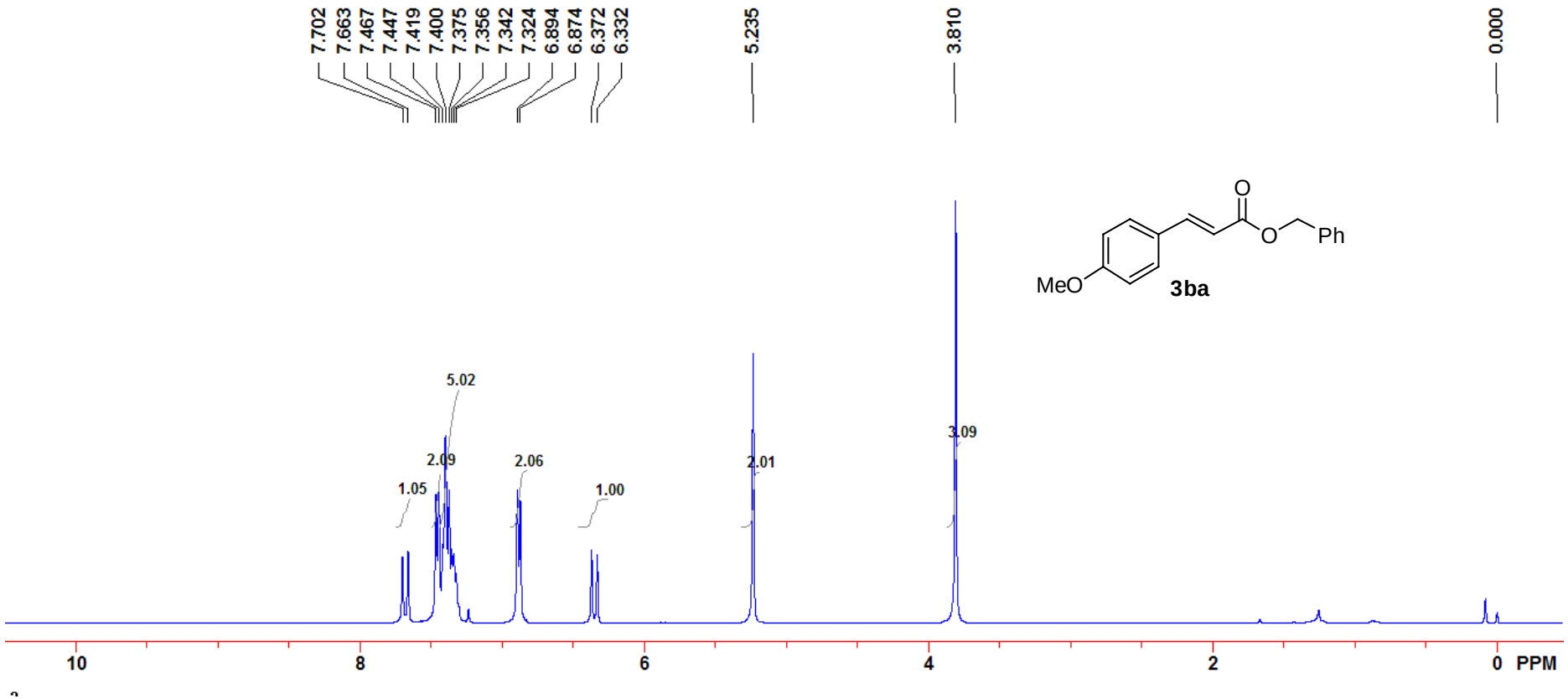

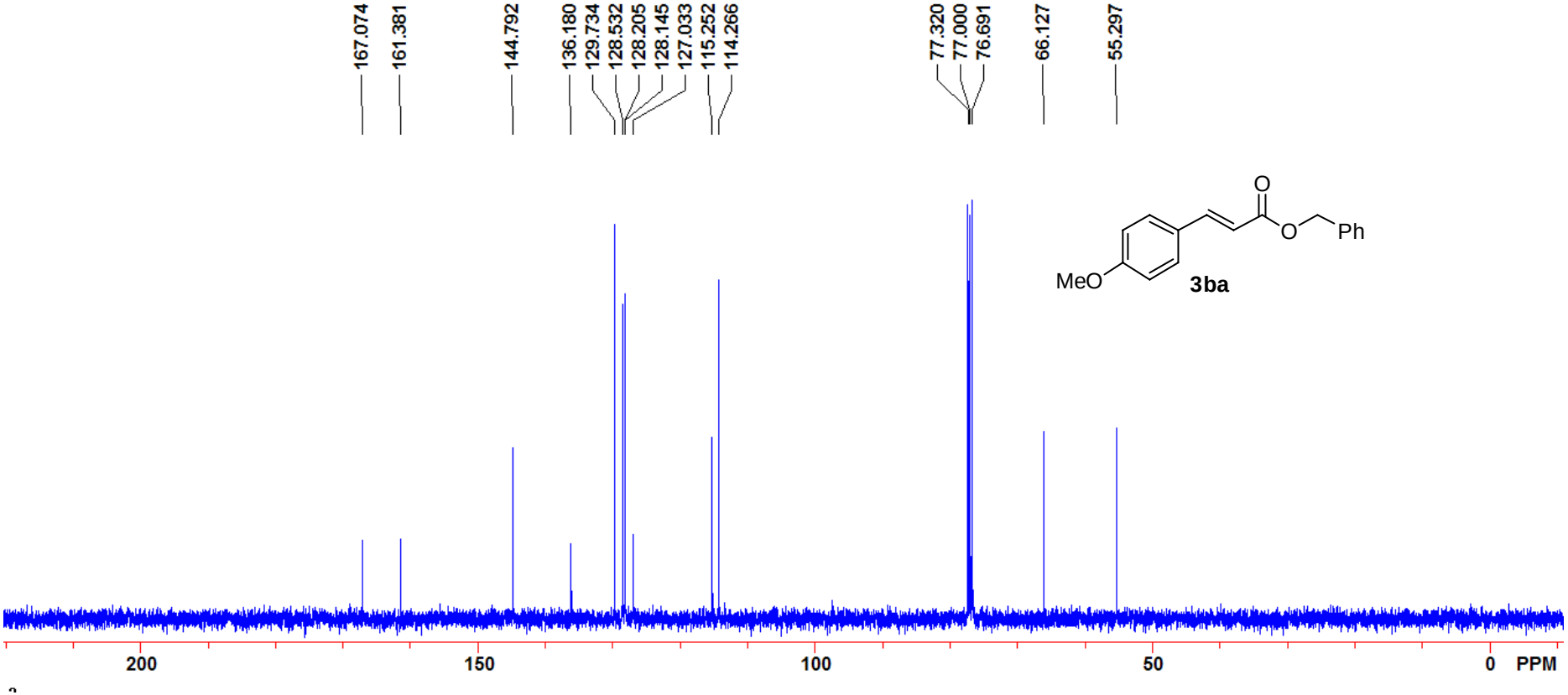

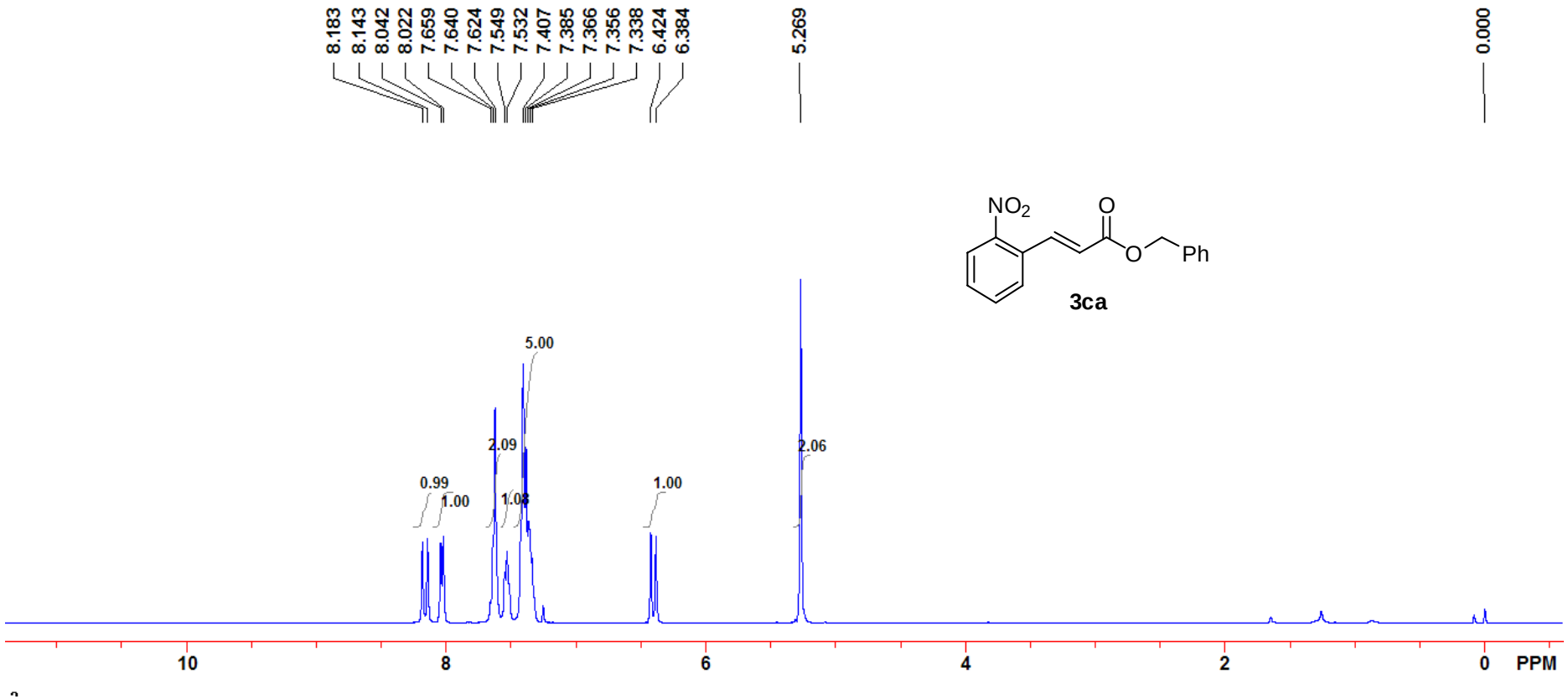

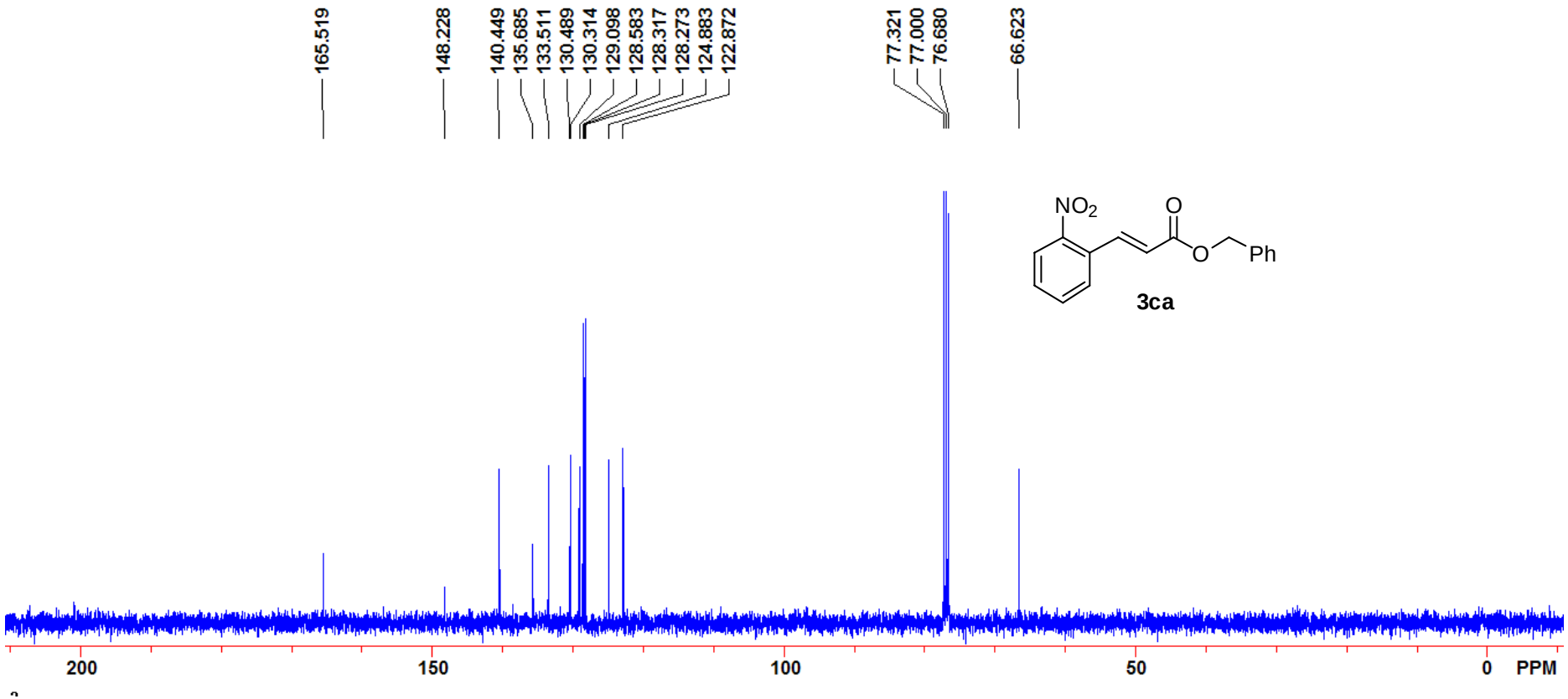

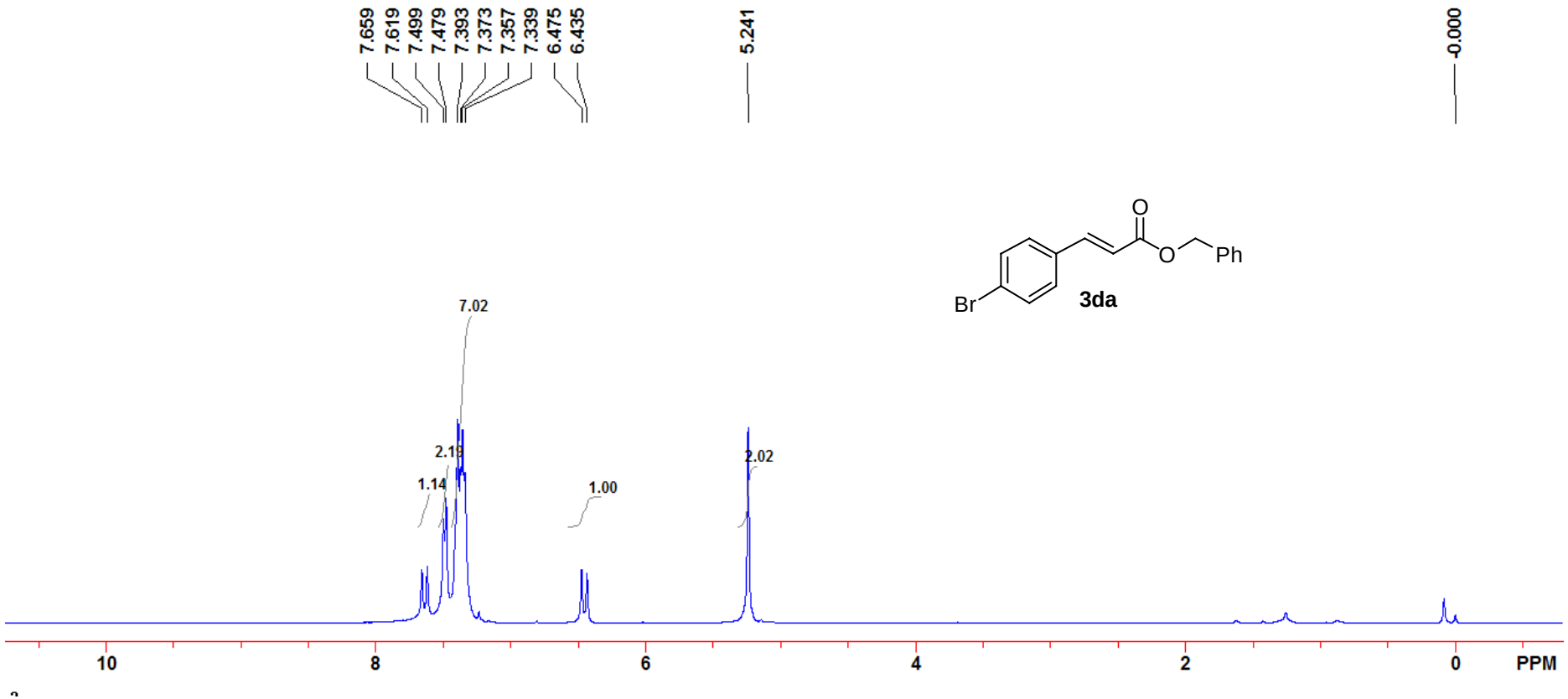

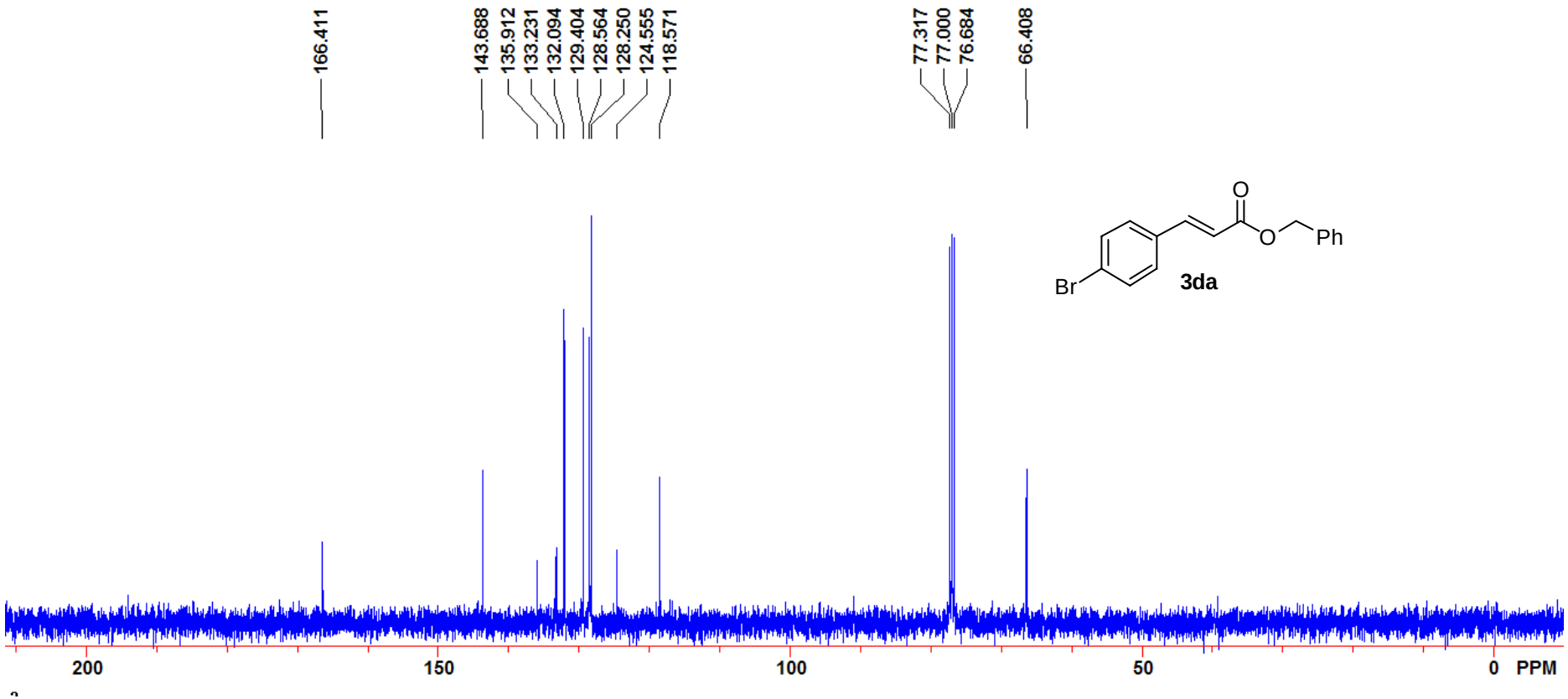

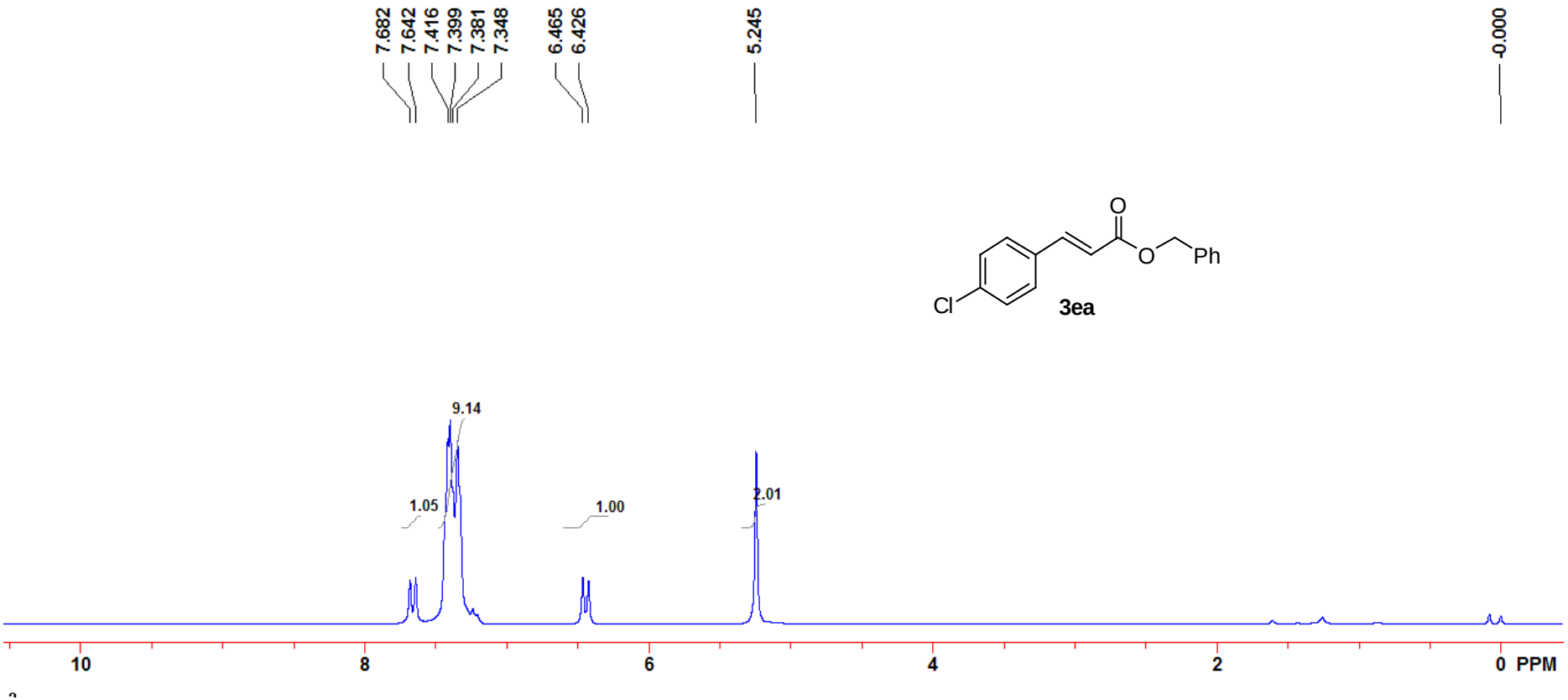

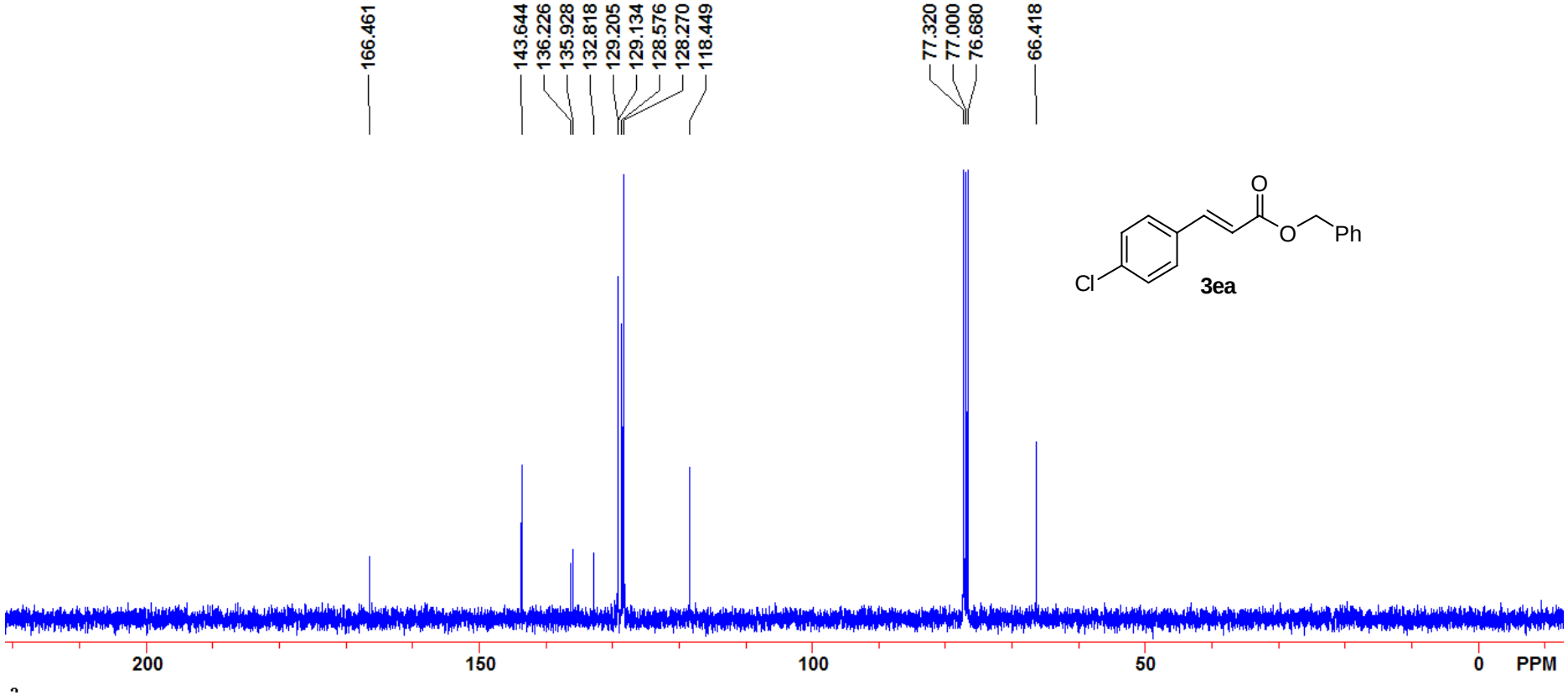

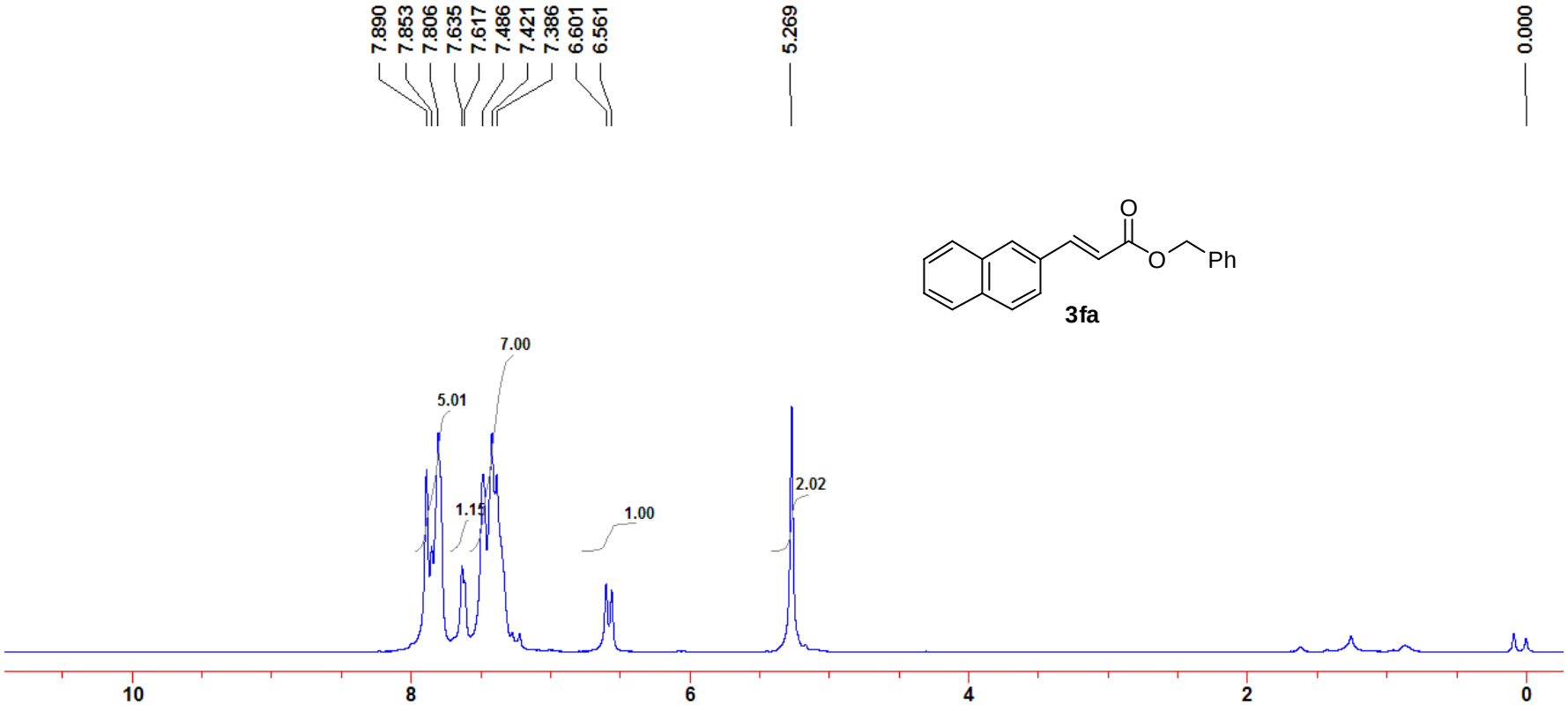

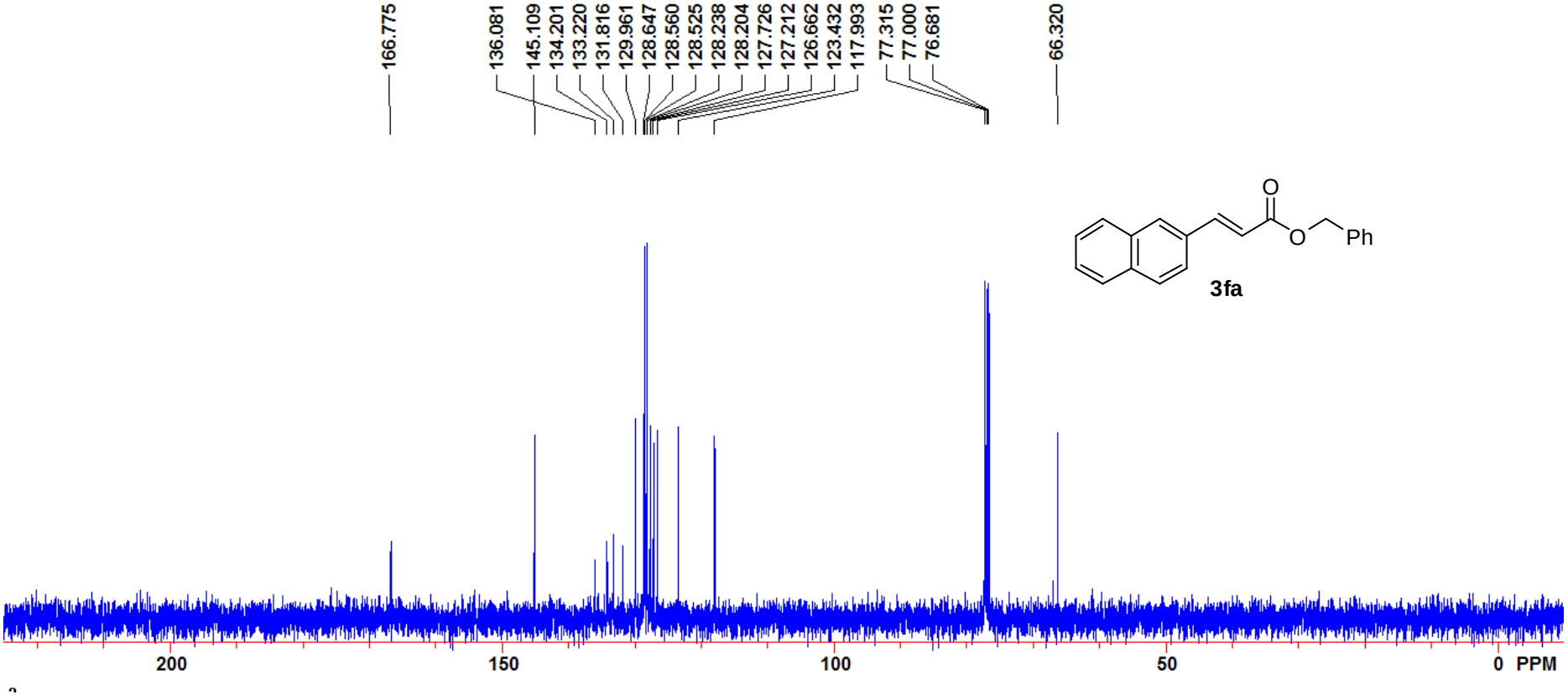

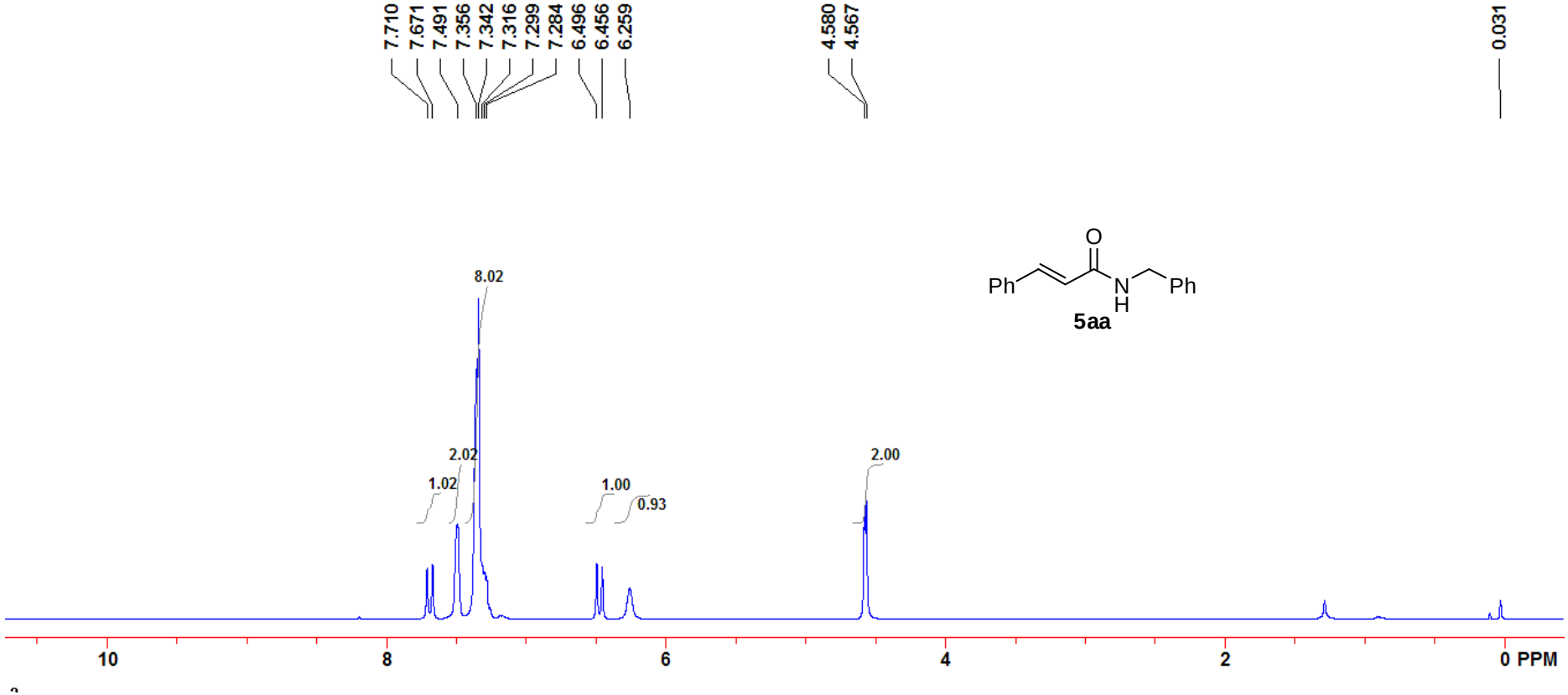

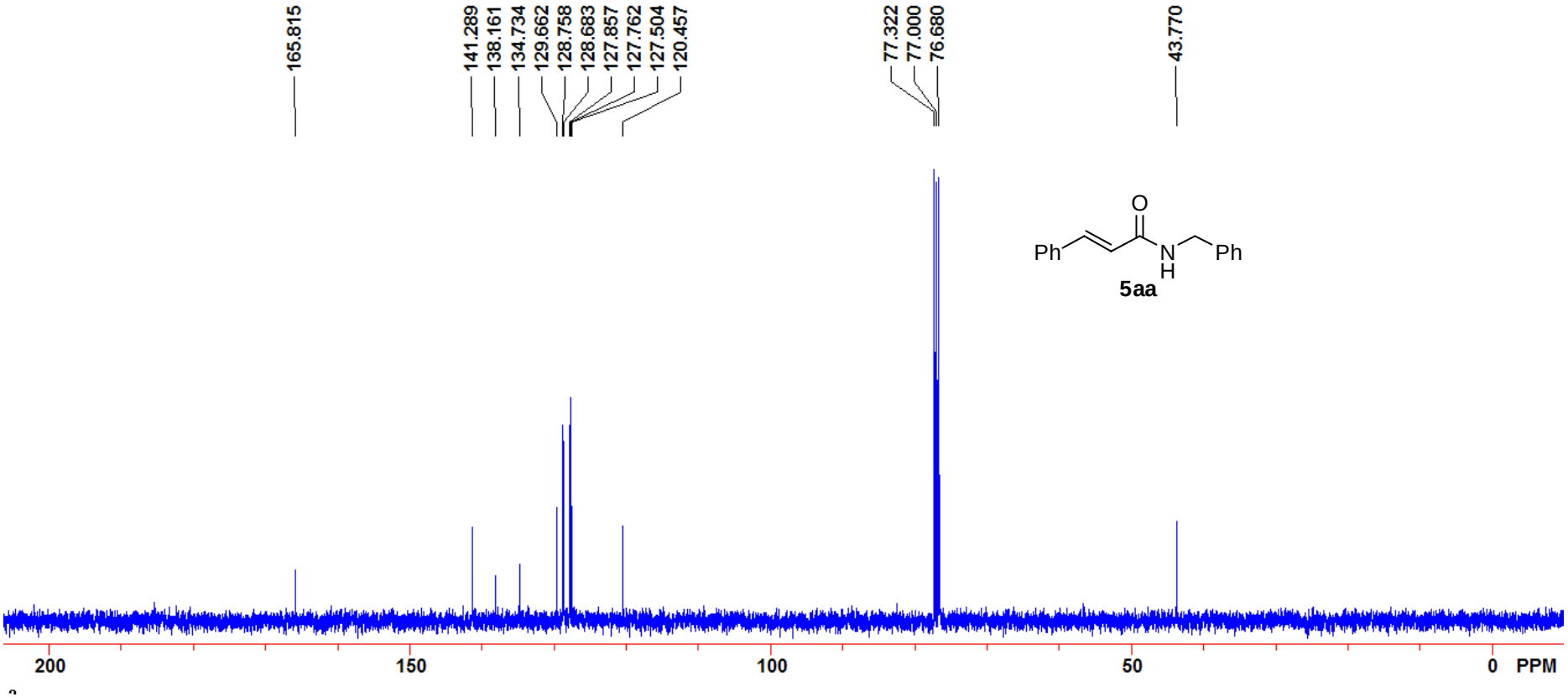

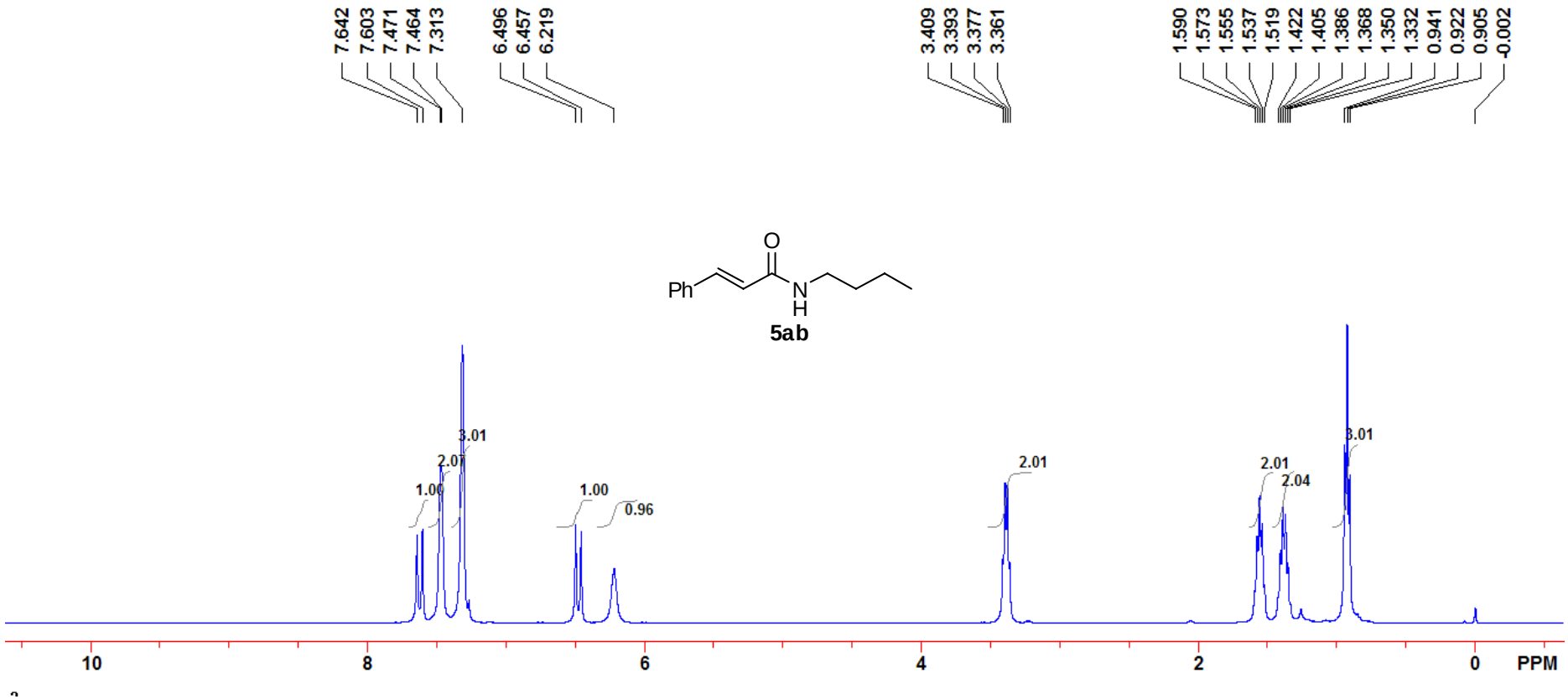

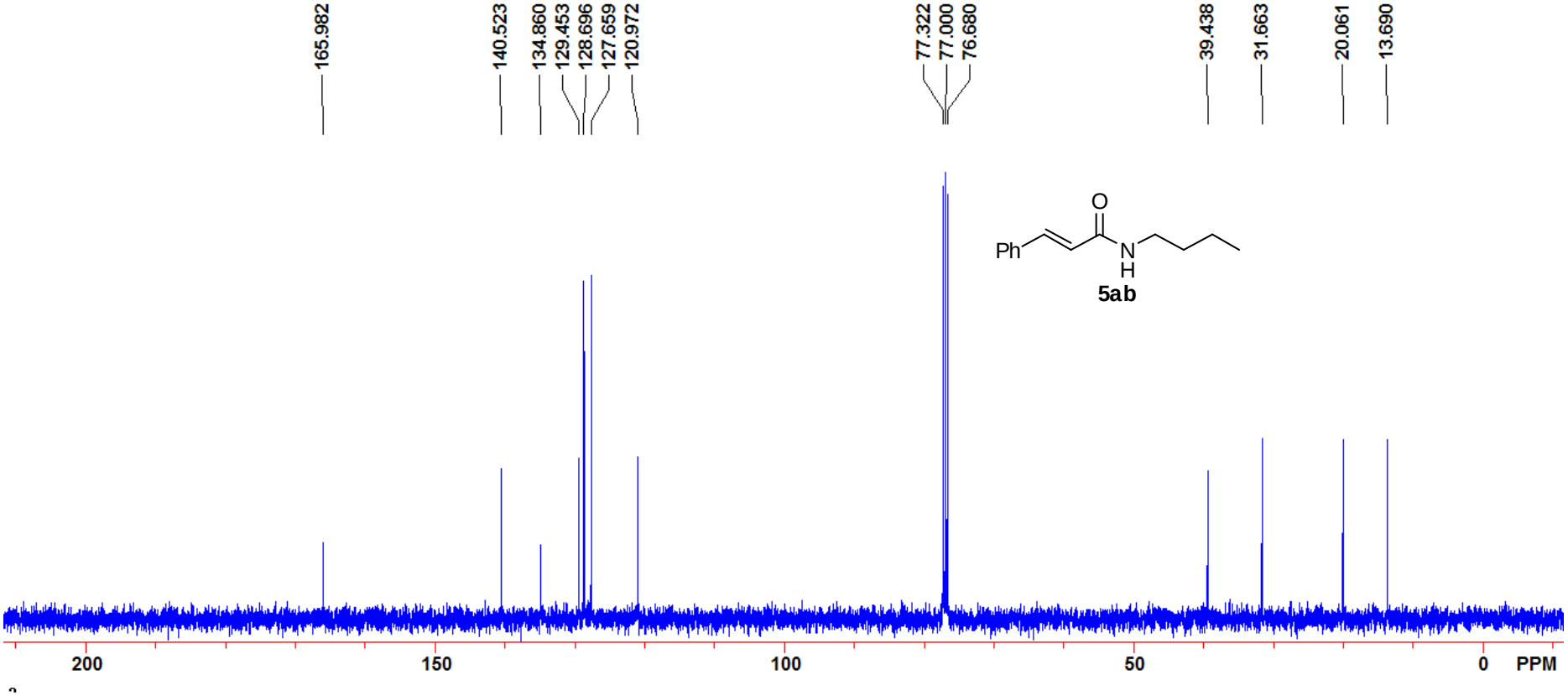

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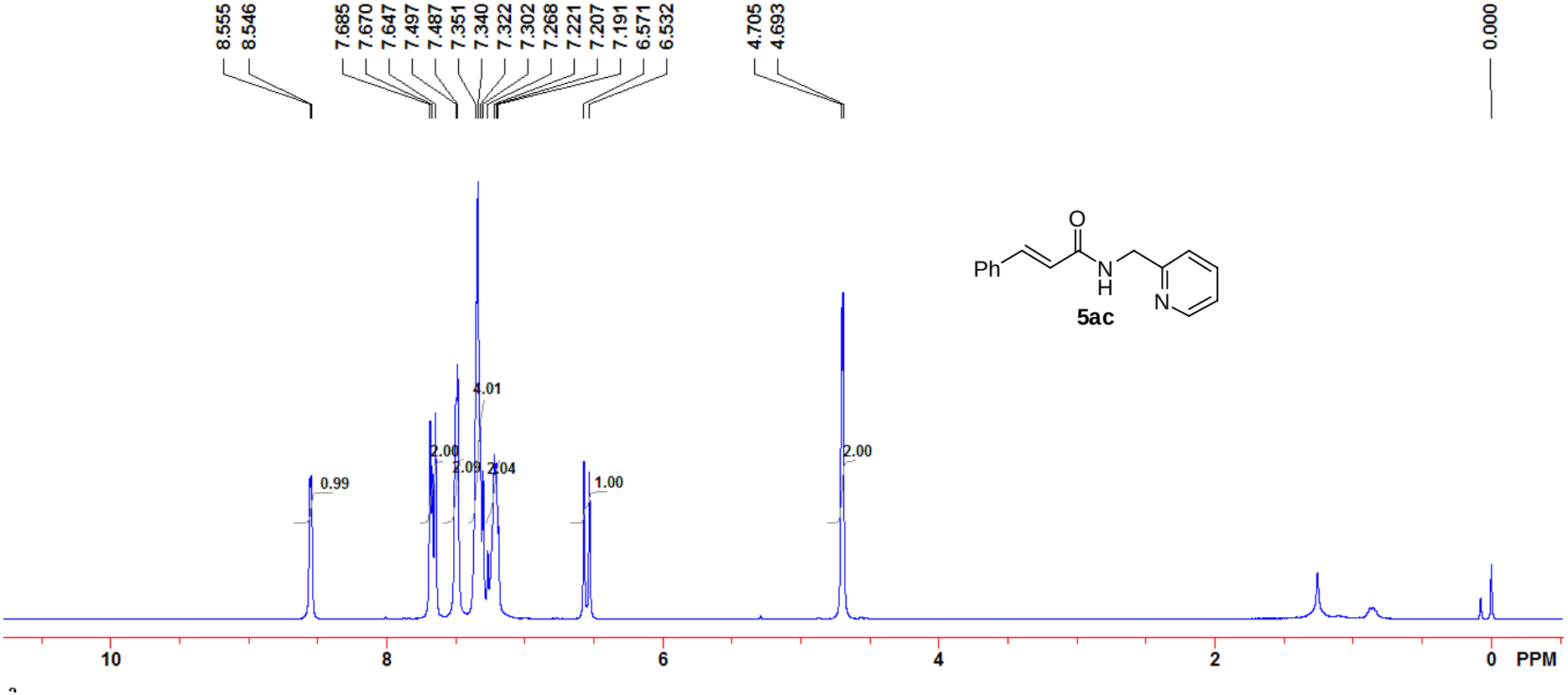

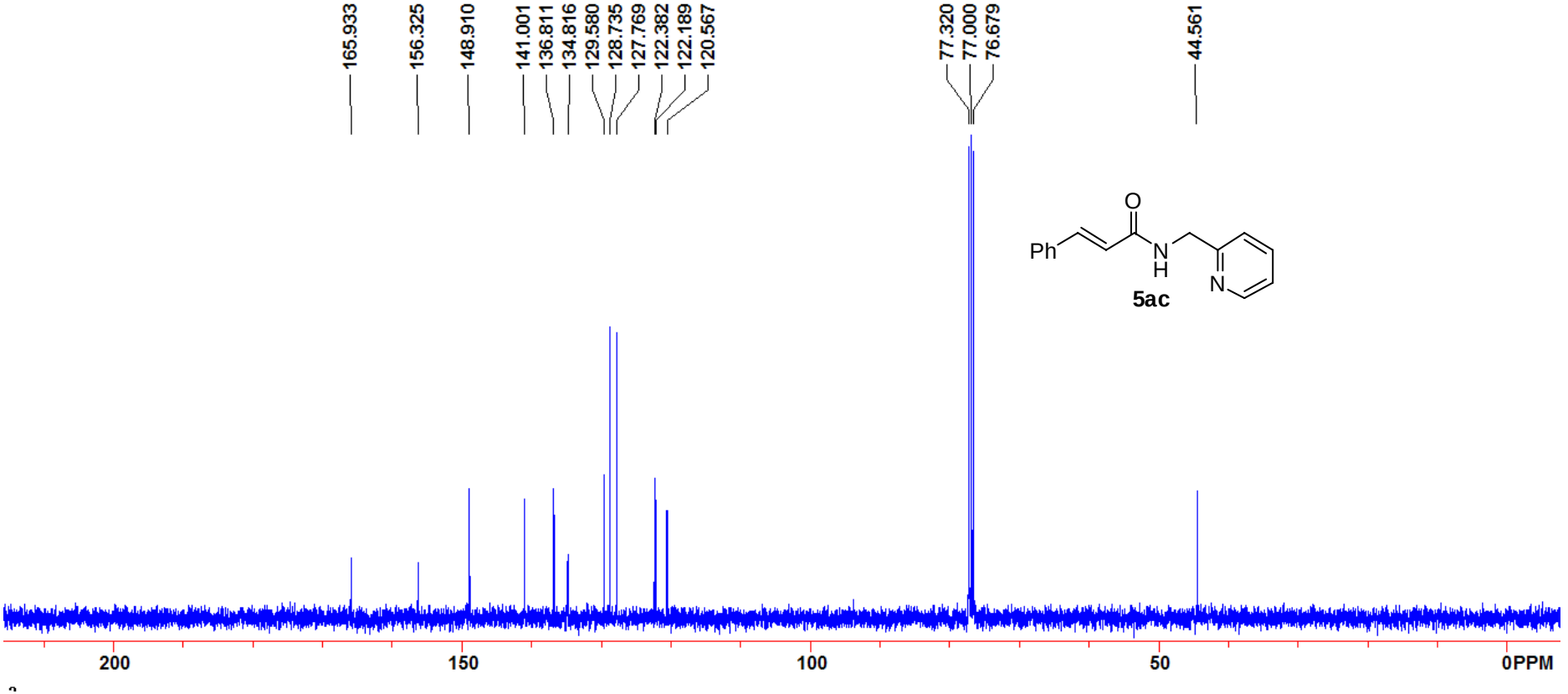

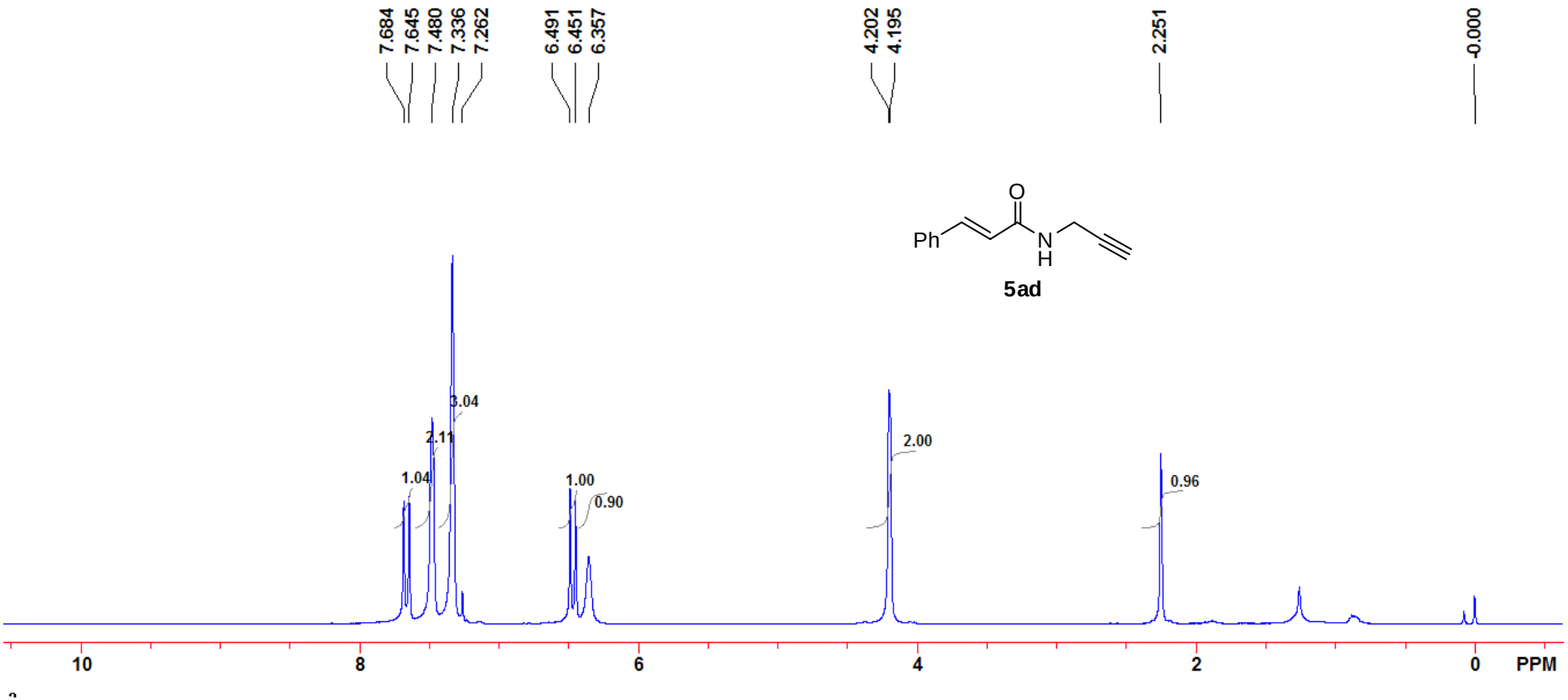

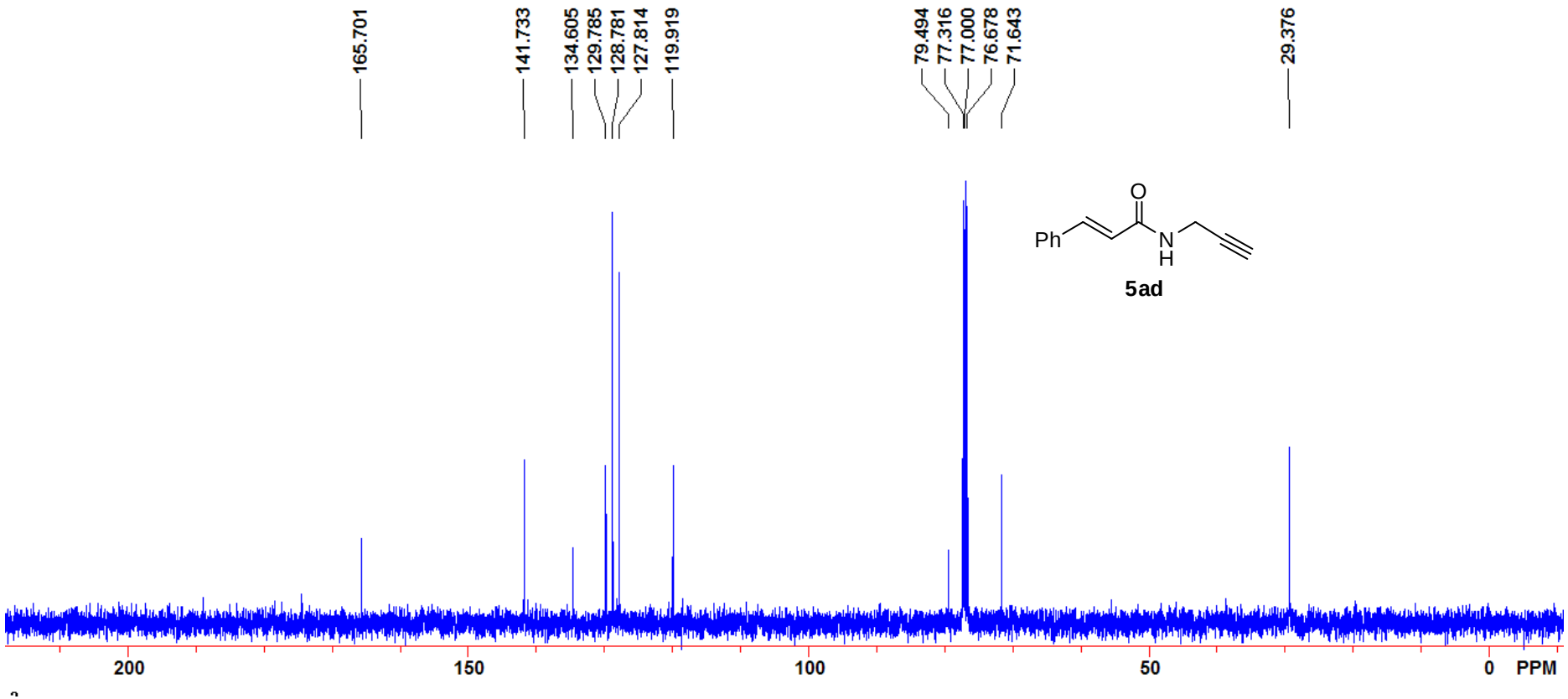

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