Supporting Information for:

Silver-Catalyzed Olefination of Acetals and Ketals with Diazoesters to β-Alkoxyacrylates

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1. General experiment details and materials

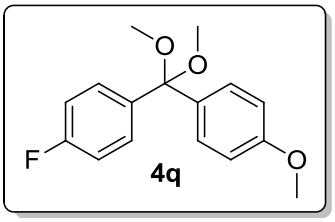
All non-aqueous reactions and manipulations were used by standard Schlenk techniques. All solvents before used were dried and degassed by standard methods and stored under argon atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avance III (400 MHz) spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI). GC analysis were performed on Agilent 7890 with OV-225 column or Hp-5 column. GS-MS analysis were performed with Agilent 7890A/5975C GC-MS system. Acetals and ketals used here were known compounds and synthesized according to the reported references.[1] Methyl diazoacetate was synthesized according to the reported reference.[2] *t*-butyl diazoacetate was synthesized according to the reported reference.[3] **3r** and **3r'** were synthesized according to the reported reference.[4]

2. General procedure for the synthesis of acetal and ketal

Acetals and ketals were synthesized according the below proceduer.

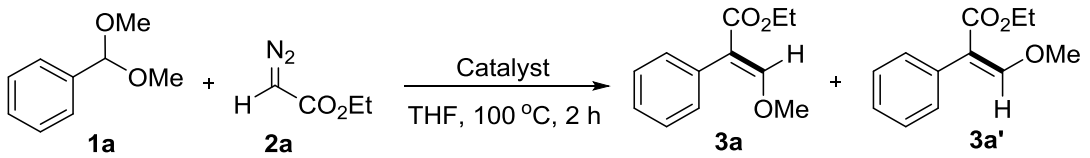
(4-fluorophenyl)(4-methoxyphenyl)methanone (11.5 g, 50 mmol), methyl orthoformate (6.4 g, 60 mmol) and MeOH (30 mL) were added to a 250 mL flask under nitrogen at 25 °C. Then H_2SO_4 (98%, 100 uL) was added into the mixture and the mixture was stirred at 25 °C for 24 hours. After the reaction finished NaOH (30% aq, 5 mL) was added. The solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on neutral aluminium oxide and eluted with EtOAc/hexane (1/100 – 1/20) to afford the desired product 1-(dimethoxy(4-methoxyphenyl)methyl)-4-fluorobenzene as a with solid 12.7 g (92%).

1-(dimethoxy(4-methoxyphenyl)methyl)-4-fluorobenzene (4q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 6H), 3.78 (s, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.94-6.99 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.43-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.2, 55.2, 102.4, 113.3, 114.8 (d, *J* = 85.2 Hz), 128.1, 128.7 (d, *J* = 32.4 Hz), 134.5, 138.6, 158.9, 160.8, 163.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5; HRMS (ESI) calcd. for $C_{16}H_{17}FNaO_3$ [M+Na]: 299.1054, found: 299.1044.



3. Optimization of reaction conditions

Table S1: Screening of catalysts[a]

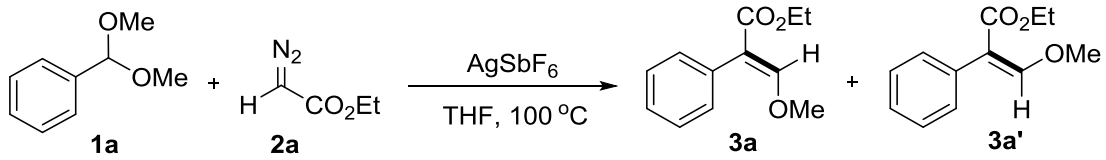


entry	catalyst	yield (%)[b]	**3a**/**3a'** (*E*/*Z*)[c]
1	BPh_3	0	-
2	$BF_3{\cdot}Et_2O$	16	3:1
3	$Yb(OTf)_3{\cdot}xH_2O$	9	4:1
4	$Bi(OTf)_3{\cdot}xH_2O$	7	2:1
5	$Eu(OTf)_3{\cdot}xH_2O$	6	3:1
6	$Sc(OTf)_3$	2	-
7	$ZnCl_2$	0	-
8	$SnCl_2$	0	-
9	$AlCl_3$	0	-
10	Ag_2WO_4	0	-
11	Ag_2SO_4	0	-

12	Ag_2SO_3	0	-
13	$AgBrO_3$	0	-
14	$AgNO_3$	0	-
15	AgF	0	-
16	AgNCO	0	-
17	Silver steearate	0	-
18	Ag_2O	0	-
19	Ag_2CrO_4	0	-
20	AgTFA	0	-
21	PhCOOAg	0	-
22	Ag_3PO_4	0	-
23	Ag_2CO_3	0	-
24	$AgBF_4$	0	-
25	$AgClO_4$	0	-
26	$AgPF_6$	22	2:1
27	$AgSbF_6$	69	> 20:1
28	HOTf	0	-
29	TsOH	0	-
30	$NaSbF_6$	0	-
31	-	0	-

[a] Reaction conditions: **1a** (76.0 mg, 0.5 mmol), **2a** (68.4 mg, 0.6 mmol), catalyst (1.0 mol %), THF (1.0 mL) at 100 °C for 2 hours. [b] Yield was determined by GC using *n*-tetradecane as the internal standard. [c] Ratios (*E*/*Z*) were determined by GC-MS and GC analysis of the crude reaction mixture.

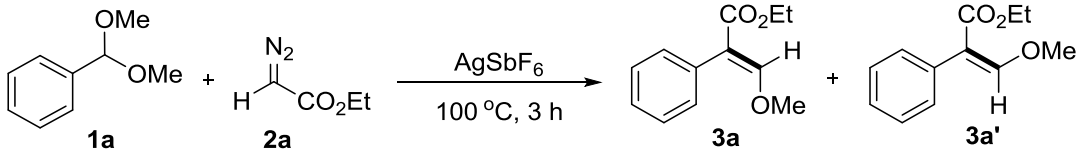
Table S2: Screening of reaction time[a]



entry	time (h)	yield (%)[b]	*E*/*Z* ratio[c]
1	1	24	2:1
2	2	69	>20:1
3	3	73	>20:1
4	4	70	>20:1

[a] Reaction conditions: **1a** (76.0 mg, 0.5 mmol), **2a** (68.4 mg, 0.6 mmol), $AgSbF_6$ (1.0 mol %), THF (1.0 mL) at 100 °C. [b] Yield was determined by GC using *n*-tetradecane as the internal standard. [c] Ratios (*E*/*Z*) were determined by GC-MS and GC analysis of the crude reaction mixture.

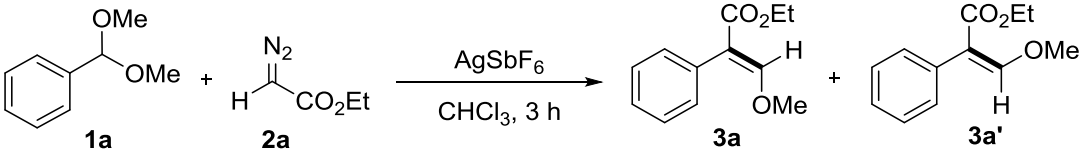
Table S3: Screening of solvent[a]



entry	solvent	yield (%)[b]	*E*/*Z* ratio[c]
1	CH_3CN	0	-
2	toluene	0	-
3	DMF	0	-
4	DMSO	0	-
5	2-PrOH	0	-
6	DCM	76	> 20:1
7	1,4-dioxane	0	-
8	NMP	0	-
9	ether	0	-
10	$CHCl_3$	91	> 20:1
11	CCl_4	4	> 20:1
12	$ClCH_2CH_2Cl$	68	> 20:1
13	$Cl_2CHCHCl_2$	82	> 20:1
14	$Br_2CHCHBr_2$	61	10:1
15	$CH_3CH_2CH_2CH_2Br$	15	4:1
16	C_6H_5Br	0	-

[a] Reaction conditions: **1a** (76.0 mg, 0.5 mmol), **2a** (68.4 mg, 0.6 mmol), $AgSbF_6$ (1.0 mol %), solvent (1.0 mL) at 100 °C for 3 hours. [b] Yield was determined by GC using *n*-tetradecane as the internal standard. [c] Ratios (*E*/*Z*) were determined by GC-MS and GC analysis of the crude reaction mixture.

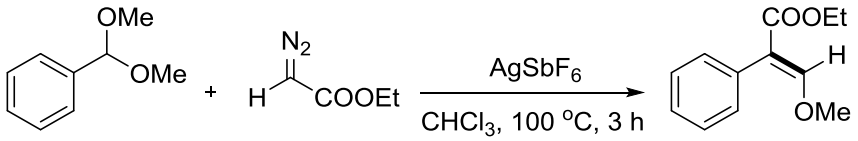
Table S4: Screening of temperature[a]



entry	temp. (°C)	yield (%)[b]	*E*/*Z* ratio[c]
1	25	23	> 20:1
2	80	31	> 20:1
3	100	91	> 20:1
4	120	78	8:1

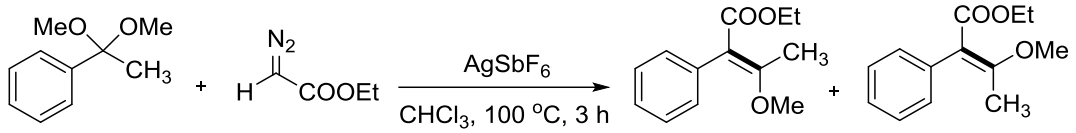
[a] Reaction conditions: **1a** (76.0 mg, 0.5 mmol), **2a** (68.4 mg, 0.6 mmol); $AgSbF_6$ (1.0 mol %), $CHCl_3$ (1.0 mL) for 3 hours. [b] Yield was determined by GC using *n*-tetradecane as the internal standard. [c] Ratios (*E*/*Z*) were determined by GC-MS and GC analysis of the crude reaction mixture.

4. General procedure for the olefination of acetals/ketals with diazoesters



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

$AgSbF_6$ (1.7 mg, 0.005 mmol) was added into a 25 mL flame-dried Young-type tube in a glove box. Then acetal **1a** (76.0 mg, 0.5 mmol), $CHCl_3$ (1.0 mL) and ethyl diazoacetate **2a** (68.4 mg, 0.6 mmol) were added into the tube under argon atmosphere. The mixture was stirred at 100 °C for 3 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/50 – 1/10) to afford the desired product **3a**.

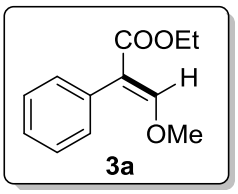


4a **2a** **5a** **5a'**

$AgSbF_6$ (1.7 mg, 0.005 mmol) was added into a 25 mL flame-dried Young-type tube in a glove box. Then ketal **4a** (83.0 mg, 0.5 mmol), $CHCl_3$ (1.0 mL) and ethyl diazoacetate **2a** (114 mg, 1.0 mmol) were added into the tube under argon atmosphere. The mixture was stirred at 100 °C for 3 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/50 – 1/5) to afford the desired product **5a** and **5a'**.

5. Experimental characterization data for products

(*E*)-ethyl 3-methoxy-2-phenylacrylate (3a): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 83.4 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 3.84 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.23-7.29 (m, 1H), 7.34-7.35 (m, 4H), 7.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 60.3, 61.9, 111.9, 127.1, 127.7, 130.2, 132.6, 159.4, 167.7; HRMS (ESI) calcd. for $C_{12}H_{14}NaO_3$ [M+Na]: 229.0835, found: 229.0837.



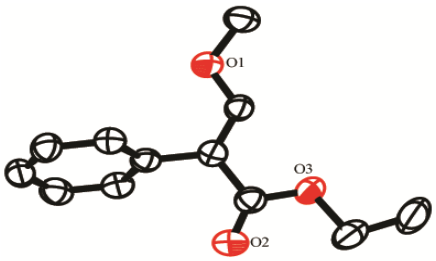
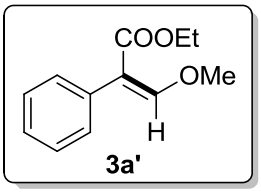
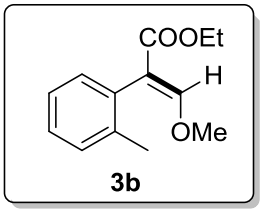


Figure S1. ORTEP drawing of product **3a**

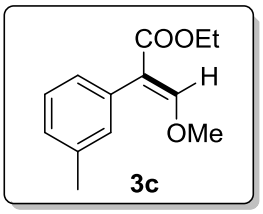
(*Z*)-ethyl 3-methoxy-2-phenylacrylate (3a'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 3H), 3.82 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 7.16-7.25 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.4, 62.3, 112.7, 127.0, 128.2, 128.9, 135.7, 157.6, 166.0; HRMS (ESI) calcd. for $C_{12}H_{14}NaO_3$ [M+Na]: 229.0835, found: 229.0834.



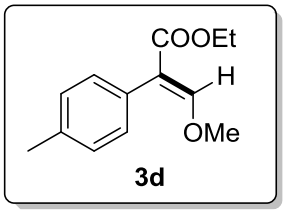
(*E*)-ethyl 3-methoxy-2-(*o*-tolyl)acrylate (3b): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 97.8 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 6.8 Hz, 3H), 2.19 (s, 3H), 3.82 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.10-7.11 (m, 1H), 7.16-7.26 (m, 3H), 7.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 19.7, 60.2, 61.8, 111.6, 125.4, 127.7, 129.8, 130.7, 132.4, 137.2, 159.4, 167.7; HRMS (ESI) calcd. for $C_{13}H_{16}NaO_3$ [M+Na]: 243.0992, found: 243.1000.



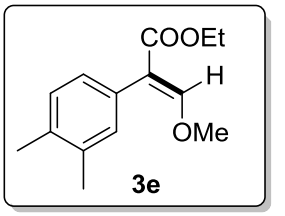
(*E*)-ethyl 3-methoxy-2-(*m*-tolyl)acrylate (3c): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 94.0 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.81 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 7.06-7.14 (m, 3H), 7.21-7.25 (m, 1H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.5, 60.3, 61.9, 112.0, 127.3, 127.7, 128.0, 130.9, 132.5, 137.2, 159.3, 167.8; HRMS (ESI) calcd. for $C_{13}H_{16}NaO_3$ [M+Na]: 243.0992, found: 243.0999.



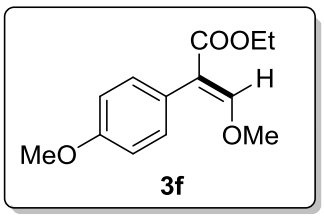
(*E*)-ethyl 3-methoxy-2-(*p*-tolyl)acrylate (3d): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 101.2 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.84 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.22-7.24 (m, 2H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.3, 60.3, 61.9, 111.8, 128.6, 129.6, 130.1, 136.8, 159.2, 167.8; HRMS (ESI) calcd. for $C_{13}H_{16}NaO_3$ [M+Na]: 243.0992, found: 243.1002.



(*E*)-ethyl 2-(3,4-dimethylphenyl)-3-methoxyacrylate (3e): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 86.3 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 6.8 Hz, 3H), 2.24-2.25 (m, 6H), 3.82 (s, 3H), 4.24 (q, *J* = 6.8 Hz, 2H), 7.05-7.12 (m, 3H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 19.6, 19.9, 60.3, 61.9, 112.0, 127.6, 129.2, 130.0, 131.3, 135.6, 135.9, 159.1, 167.9; HRMS (ESI) calcd. for $C_{14}H_{18}NaO_3$ [M+Na]: 257.1148, found: 257.1147.

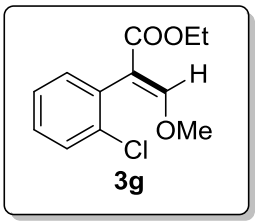


(*E*)-ethyl 3-methoxy-2-(4-methoxyphenyl)acrylate (3f): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 98.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 3.83 (s, 3H),



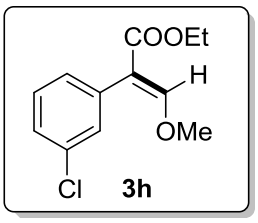
4.24 (q, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 55.2, 60.3, 61.9, 111.4, 113.3, 124.9, 131.3, 158.5, 159.0, 167.9; HRMS (ESI) calcd. for $C_{13}H_{16}NaO_4$ [M+Na]: 259.0941, found: 259.0953.

(*E*)-ethyl 2-(2-chlorophenyl)-3-methoxyacrylate (3g): The title compound was



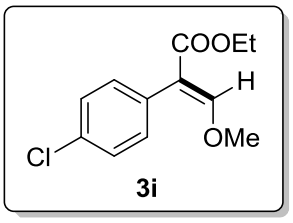
prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 57.5 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.84 (s, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 7.21-7.27 (m, 3H), 7.40-7.42 (m, 1H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.4, 62.0, 110.2, 126.3, 128.9, 129.3, 132.1, 132.3, 134.5, 160.1, 167.0; HRMS (ESI) calcd. for $C_{12}H_{13}ClNaO_3$ [M+Na]: 263.0445, found: 263.0456.

(*E*)-ethyl 2-(3-chlorophenyl)-3-methoxyacrylate (3h): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 81.6 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.21-7.29 (m, 3H), 7.35 (s, 1H), 7.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 60.5, 62.1, 110.6, 127.1, 128.4, 128.9, 130.3, 133.5, 134.4, 159.9, 167.2; HRMS (ESI) calcd. for $C_{12}H_{13}ClNaO_3$ [M+Na]: 263.0445, found: 263.0453.

(*E*)-ethyl 2-(4-chlorophenyl)-3-methoxyacrylate (3i): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel to give the white solid, 82.0 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 6.8 Hz, 3H), 3.86 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.26-7.32 (m, 4H), 7.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 60.4, 62.1, 110.8, 127.9, 131.0, 131.6, 132.8, 159.7, 167.3; HRMS (ESI) calcd. for $C_{12}H_{13}ClNaO_3$ [M+Na]: 263.0445, found: 263.0452.

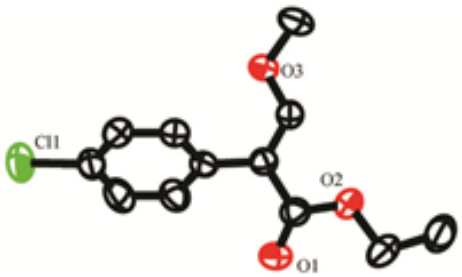
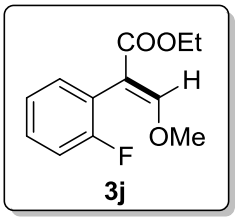


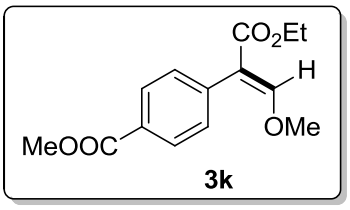
Figure S2. ORTEP drawing of product **3i**

(*E*)-ethyl 2-(2-fluorophenyl)-3-methoxyacrylate (3j): The title compound was



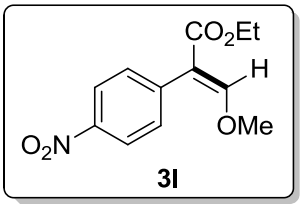
prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 36.0 mg, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 7.04-7.14 (m, 2H), 7.23-7.31 (m, 2H), 7.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.4, 62.0, 106.2, 115.5 (d, *J* = 22.0 Hz), 120.6 (d, *J* = 16.1 Hz), 123.5 (d, *J* = 3.5 Hz), 129.3 (d, *J* = 8.2 Hz), 132.3 (d, *J* = 3.5 Hz), 160.4, 161.4 (d, *J* = 246.1 Hz), 167.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5; HRMS (ESI) calcd. for $C_{12}H_{13}FNaO_3$ [M+Na]: 247.0741, found: 247.0729.

(*E*)-methyl 4-(3-ethoxy-1-methoxy-3-oxoprop-1-en-2-yl)benzoate (3k): The title



compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 34.2 mg, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 6.8 Hz, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 52.1, 60.5, 62.2, 111.0, 128.5, 129.0, 130.3, 137.7, 160.2, 167.1, 167.2; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_5$ [M+Na]: 287.0890, found: 287.0900.

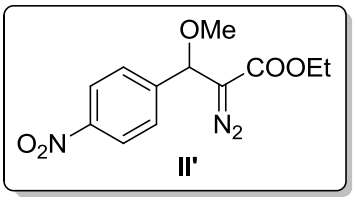
(*E*)-ethyl 3-methoxy-2-(4-nitrophenyl)acrylate (3l): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 4.2 mg, 3% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 6.8 Hz, 3H), 3.93 (s, 3H), 4.27 (q, *J* = 7.2 Hz,

2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.65 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.7, 62.5, 110.0, 122.9, 131.1, 139.8, 146.5, 160.9, 166.6; HRMS (ESI) calcd. for $C_{12}H_{13}NNaO_5$ [M+Na]: 274.0686, found: 274.0693.

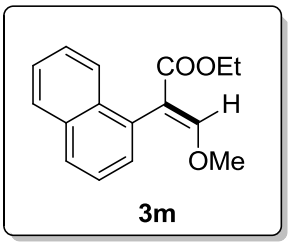
Ethyl 2-diazo-3-methoxy-3-(4-nitrophenyl)propanoate (II'): The title compound



II'

was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the yellow oil, 8.5 mg, 7% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.48 (s, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 5.46 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 56.9, 61.4, 76.1, 124.0, 126.8, 145.7, 147.7, 165.5; HRMS (ESI) calcd. for $C_{12}H_{13}N_3NaO_5$ [M+Na]: 302.0747, found: 302.0749.

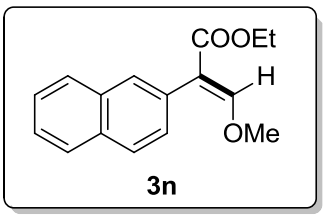
(*E*)-ethyl 3-methoxy-2-(naphthalen-1-yl)acrylate (3m): The title compound was



3m

prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 107.5 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 3.76 (s, 3H), 4.18 (q, *J* = 6.8 Hz, 2H), 7.33-7.34 (m, 1H), 7.41-7.49 (m, 3H), 7.73-7.75 (m, 2H), 7.80-7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 60.3, 61.9, 110.4, 125.3, 125.5, 125.6, 125.8, 128.1, 128.3, 128.4, 130.7, 132.1, 133.6, 160.4, 168.0; HRMS (ESI) calcd. for $C_{16}H_{16}NaO_3$ [M+Na]: 279.0992, found: 279.1003.

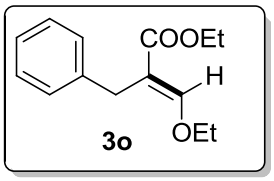
(*E*)-ethyl 3-methoxy-2-(naphthalen-2-yl)acrylate (3n): The title compound was



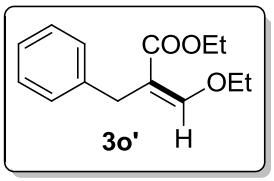
3n

prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 85.0 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 3.85 (s, 3H), 4.27 (q, *J* = 6.8 Hz, 2H), 7.42-7.46 (m, 3H), 7.62 (s, 1H), 7.79-7.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 60.4, 62.0, 111.9, 125.7, 125.8, 127.1, 127.6, 128.1, 128.3, 129.3, 130.2, 132.5, 133.1, 159.7, 167.8; HRMS (ESI) calcd. for $C_{16}H_{16}NaO_3$ [M+Na]: 279.0992, found: 279.0993.

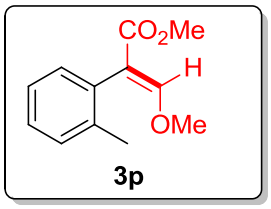
(*E*)-ethyl 2-benzyl-3-ethoxyacrylate (3o): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 39.8 mg, 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 3.59 (s, 2H), 4.10 (q, *J* = 3.6 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 7.13-7.28 (m, 5H), 7.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.5, 29.8, 59.9, 70.1, 110.3, 125.7, 128.1, 128.6, 141.0, 157.8, 168.3; HRMS (ESI) calcd. for $C_{14}H_{18}NaO_3$ [M+Na]: 257.1148, found: 257.1145.



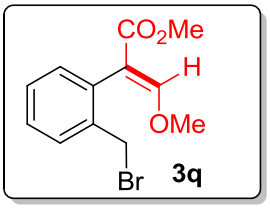
(*Z*)-ethyl 2-benzyl-3-ethoxyacrylate (3o'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 3.31 (s, 2H), 3.93 (q, *J* = 6.8 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 5.79 (s, 1H), 7.16-7.22 (m, 3H), 7.26-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.5, 37.7, 60.9, 63.1, 102.9, 125.8, 128.3, 128.7, 137.0, 152.0, 170.6; HRMS (ESI) calcd. for $C_{14}H_{18}NaO_3$ [M+Na]: 257.1148, found: 257.1138.



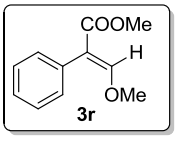
(*E*)-methyl 3-methoxy-2-(o-tolyl)acrylate (3p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 3.69 (s, 3H), 3.81 (s, 3H), 7.10-7.11 (m, 1H), 7.16-7.23 (m, 3H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 51.6, 61.8, 111.3, 125.4, 127.8, 129.8, 130.6, 132.3, 137.2, 159.6, 168.3.



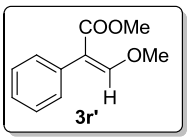
(*E*)-methyl 2-(2-(bromomethyl)phenyl)-3-methoxyacrylate (3q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.83 (s, 3H), 4.41 (s, 2H), 7.11-7.16 (m, 1H), 7.28-7.34 (m, 2H), 7.45-7.49 (m, 1H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 51.7, 62.0, 109.8, 128.5, 130.3, 131.5, 132.6, 136.6, 160.5, 167.8.



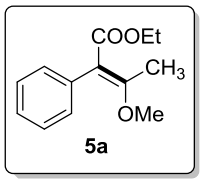
(*E*)-methyl 3-methoxy-2-phenylacrylate (3r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.84 (s, 3H), 7.25-7.29 (m, 1H), 7.31-7.37 (m, 4H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 62.0, 111.6, 127.2, 127.8, 130.2, 132.5, 159.7, 168.2.



(*Z*)-methyl 3-methoxy-2-phenylacrylate (3r'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.91 (s, 3H), 6.66 (s, 1H), 7.25-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 62.4, 112.2, 127.1, 128.2, 129.0, 135.6, 158.1, 166.4.



(*E*)-ethyl 3-methoxy-2-phenylbut-2-enoate (5a): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5a**+**5a'**) 90.3 mg, 82% yield, *E*/*Z* = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 2.49 (s, 3H), 3.61 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 7.16-7.29 (m, 3H), 7.29-7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 55.3, 60.1, 112.9, 126.3, 127.6, 130.3, 136.2, 165.1, 169.0; HRMS (ESI) calcd. for $C_{13}H_{16}O_3Na$ [M+Na]: 243.0992, found: 243.0990.



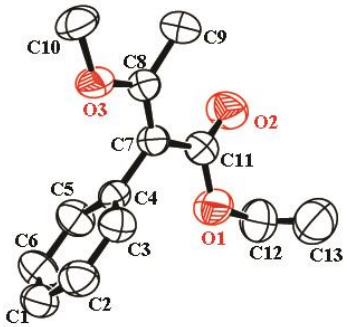
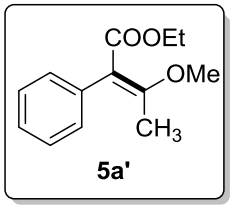
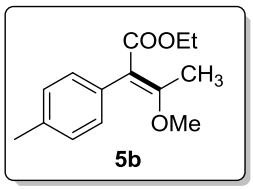


Figure S3. ORTEP drawing of product **5a**

(*Z*)-ethyl 3-methoxy-2-phenylbut-2-enoate (5a'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 3H), 1.89 (s, 3H), 3.79 (s, 3H), 4.18 (q, *J* = 6.8 Hz, 2H), 7.20-7.28 (m, 3H), 7.31-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.5, 56.1, 60.2, 113.6, 126.9, 128.2, 130.3, 136.9, 160.8, 167.4; HRMS (ESI) calcd. for $C_{13}H_{16}O_3Na$ [M+Na]: 243.0992, found: 243.0990.

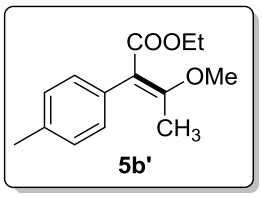


(*E*)-ethyl 3-methoxy-2-(p-tolyl)but-2-enoate (5b): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5b**+**5b'**) 105.6 mg, 90% yield, *E*/*Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 6.8 Hz, 3H), 2.34 (s, 3H), 2.47 (s, 3H), 3.61 (s, 3H),



4.15 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.3, 21.3, 55.3, 60.1, 112.7, 128.5, 130.1, 133.1, 135.9, 164.9, 169.2; HRMS (ESI) calcd. for $C_{14}H_{18}O_3Na$ [M+Na]: 257.1148, found: 257.1145.

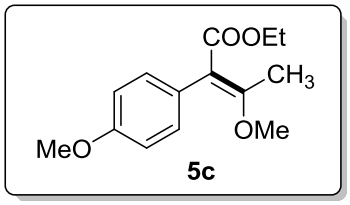
(*Z*)-ethyl 3-methoxy-2-(p-tolyl)but-2-enoate (5b'): ^{1}H NMR (400 MHz, $CDCl_3$) δ



5b'

1.22 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 2.34 (s, 3H), 3.77 (s, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.4, 21.2, 56.1, 60.2, 113.6, 128.9, 130.0, 133.8, 136.5, 160.3, 167.6; HRMS (ESI) calcd. for $C_{14}H_{18}O_3Na$ [M+Na]: 257.1148, found: 257.1148.

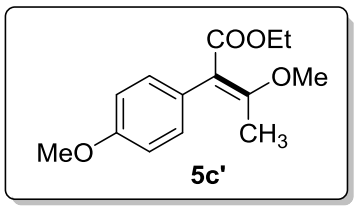
(*E*)-ethyl 3-methoxy-2-(4-methoxyphenyl)but-2-enoate (5c): The title compound



5c

was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5c**+**5c'**) 95.8 mg, 77% yield, *E*/*Z* = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 6.8 Hz, 3H), 2.46 (s, 3H), 3.62 (s, 3H), 3.81 (s, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.3, 55.1, 55.3, 60.1, 112.4, 113.1, 128.4, 131.3, 158.0, 164.7, 169.3; HRMS (ESI) calcd. for $C_{14}H_{18}O_4Na$ [M+Na]: 273.1097, found: 273.1096.

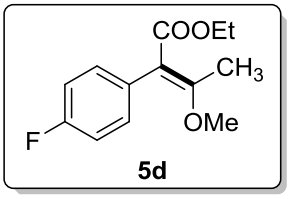
(*Z*)-ethyl 3-methoxy-2-(4-methoxyphenyl)but-2-enoate (5c'): ^{1}H NMR (400 MHz,



5c'

$CDCl_3$) δ 1.23 (t, *J* = 6.8 Hz, 3H), 1.88 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 4.18 (q, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.4, 55.2, 56.1, 60.2, 113.2, 113.6, 129.1, 131.3, 158.5, 160.4, 167.7; HRMS (ESI) calcd. for $C_{14}H_{18}O_4Na$ [M+Na]: 273.1097, found: 273.1094.

(*E*)-ethyl 2-(4-fluorophenyl)-3-methoxybut-2-enoate (5d): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5d**+**5d'**) 90.6 mg, 76% yield, *E*/*Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 6.8 Hz, 3H), 2.49 (s, 3H), 3.62 (s, 3H), 4.14 (q, *J* = 6.8 Hz, 2H), 6.97-7.01 (m, 2H), 7.11-7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.1, 55.2, 60.1, 111.7, 114.6 (d, *J* = 21.0 Hz), 131.9 (d, *J* = 7.9 Hz), 132.1 (d, *J* = 3.5 Hz), 162.6 (d, *J* = 243.1 Hz), 165.7, 168.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5; HRMS (ESI) calcd. for $C_{13}H_{15}FO_3Na$ [M+Na]: 261.0897, found: 261.0891.

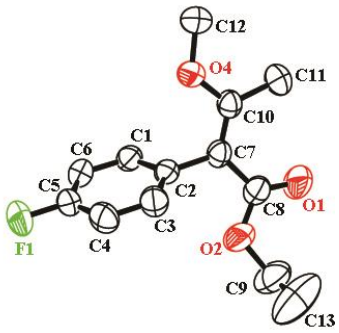
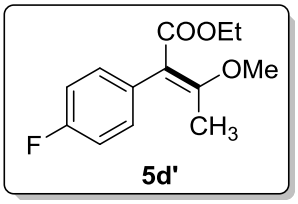


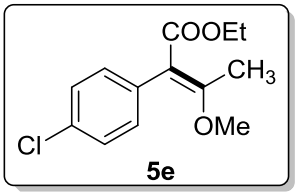
Figure S4. ORTEP drawing of product **5d**

(*Z*)-ethyl 2-(4-fluorophenyl)-3-methoxybut-2-enoate (5d'): δ 1.22 (t, *J* = 7.2 Hz, 3H),



1.87 (s, 3H), 3.80 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.98-7.04 (m, 2H), 7.14-7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.6, 56.2, 60.2, 112.3, 115.2 (d, *J* = 21.2 Hz), 132.0 (d, *J* = 7.9 Hz), 132.9 (d, *J* = 3.5 Hz), 161.4, 163.1 (d, *J* = 244.2 Hz), 167.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6; HRMS (ESI) calcd. for $C_{13}H_{15}FO_3Na$ [M+Na]: 261.0897, found: 261.0892.

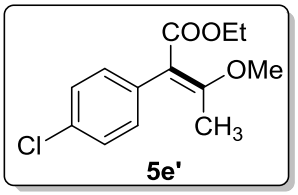
(*E*)-ethyl 2-(4-chlorophenyl)-3-methoxybut-2-enoate (5e): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5e**+**5e'**) 97.7 mg, 77% yield, *E*/*Z* = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 2.50 (s,

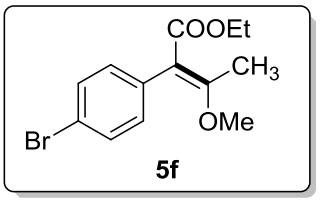
3H), 3.63 (s, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.1, 55.2, 60.1, 111.5, 127.9, 131.8, 132.1, 134.7, 165.9, 168.5; HRMS (ESI) calcd. for $C_{13}H_{15}ClO_3Na$ [M+Na]: 277.0602, found: 277.0595.

(*Z*)-ethyl 2-(4-chlorophenyl)-3-methoxybut-2-enoate (5e'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 3.80 (s, 3H), 4.17 (q, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.6, 56.2, 60.2, 112.2, 128.4, 131.7, 132.9, 135.5, 161.7, 166.9; HRMS (ESI) calcd. for $C_{13}H_{16}ClO_3$ [M+H]: 255.0782, found: 255.0790.



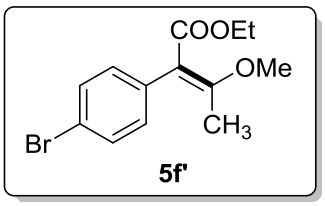
5e'

(*E*)-ethyl 2-(4-bromophenyl)-3-methoxybut-2-enoate (5f): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5f**+**5f'**) 101.6 mg, 68% yield, *E*/*Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 6.8 Hz, 3H), 2.49 (s, 3H), 3.62 (s, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.1, 55.2, 60.1, 111.5, 120.3, 130.8, 132.2, 135.3, 165.9, 168.4; HRMS (ESI) calcd. for $C_{13}H_{15}BrO_3Na$ [M+Na]: 321.0097, found: 321.0087.



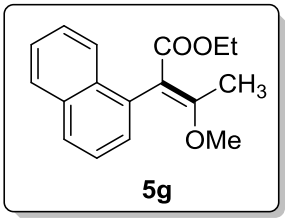
5f

(*Z*)-ethyl 2-(4-bromophenyl)-3-methoxybut-2-enoate (5f'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 3.80 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.7, 56.2, 60.3, 112.1, 121.0, 131.4, 132.1, 136.0, 161.7, 166.8; HRMS (ESI) calcd. for $C_{13}H_{15}BrO_3Na$ [M+Na]: 321.0097, found: 321.0085.



5f'

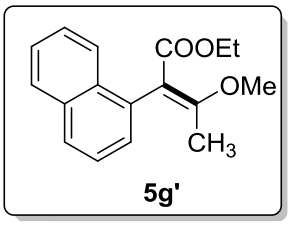
(*E*)-ethyl 3-methoxy-2-(naphthalen-1-yl)but-2-enoate (5g): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5g**+**5g'**) 54.2 mg, 40% yield, *E*/*Z* = 2:1. ^{1}H



5g

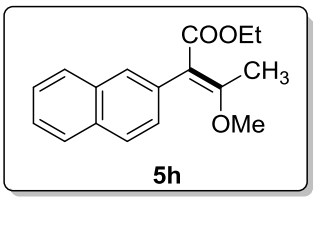
NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.2 Hz, 3H), 2.65 (s, 3H), 3.49 (s, 3H), 4.04 (q, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.27-7.47 (m, 3H), 7.73-7.78 (m, 2H), 7.82-7.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.2, 55.3, 59.9, 110.1, 125.3, 125.4, 125.4, 125.5, 127.1, 127.9, 128.2, 132.7, 133.6, 134.4, 167.3, 168.9; HRMS (ESI) calcd. for $C_{17}H_{18}O_3Na$ [M+Na]: 293.1148, found: 293.1145.

(*Z*)-ethyl 3-methoxy-2-(naphthalen-1-yl)but-2-enoate (5g'): ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.72 (s, 3H), 3.89 (s, 3H), 4.08 (q, *J* = 6.8 Hz, 2H), 7.33-7.35 (m, 1H), 7.43-7.49 (m, 3H), 7.79-7.87 (m, 2H), 7.91-7.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 16.0, 56.3, 59.9, 110.0, 125.5, 125.5, 125.7, 126.1, 127.8, 128.3, 128.5, 133.0, 133.8, 134.9, 163.6, 166.9; HRMS (ESI) calcd. for $C_{17}H_{18}O_3Na$ [M+Na]: 293.1148, found: 293.1150.



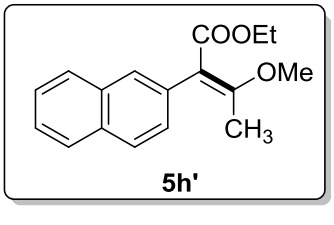
5g'

(*E*)-ethyl 3-methoxy-2-(naphthalen-2-yl)but-2-enoate (5h): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5h**+**5h'**) 110.8 mg, 82% yield, *E*/*Z* = 3:1. ^1H NMR (400 MHz, $CDCl_3$) δ 1.12-1.16 (m, 3H), 2.52 (s, 3H), 3.58 (s, 3H), 4.09-4.15 (m, 2H), 7.30-7.32 (m, 1H), 7.41-7.43 (m, 2H), 7.65 (s, 1H), 7.76-7.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.3, 55.4, 60.1, 112.7, 125.5, 125.6, 126.9, 127.6, 128.0, 129.0, 129.1, 132.2, 133.3, 133.9, 165.8, 169.0; HRMS (ESI) calcd. for $C_{17}H_{18}O_3Na$ [M+Na]: 293.1148, found: 293.1144.



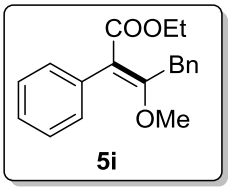
5h

(*Z*)-ethyl 3-methoxy-2-(naphthalen-2-yl)but-2-enoate (5h'): ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.93 (s, 3H), 3.83 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.33-7.36 (m, 1H), 7.44-7.49 (m, 2H), 7.67 (m, 1H), 7.79-7.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.7, 56.2, 60.2, 113.4, 125.9, 126.0, 127.6, 127.7, 127.9, 128.6, 129.0, 132.3, 133.3, 134.5, 161.4, 167.4; HRMS (ESI) calcd. for $C_{17}H_{18}O_3Na$ [M+Na]: 293.1148, found: 293.1145.



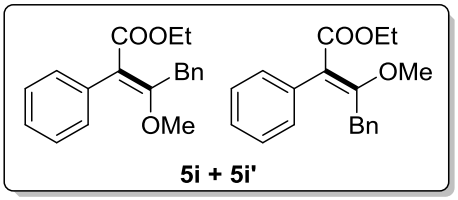
5h'

(*E*)-ethyl 3-methoxy-2,4-diphenylbut-2-enoate (5i): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5i**+**5i'**) 77.6 mg, 52% yield, *E*/*Z* = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.72 (s, 3H), 4.13-4.26 (m, 2H), 4.92 (s, 1H), 5.84 (s, 1H), 7.17-7.25 (m, 3H), 7.26-7.33 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 52.4, 55.2, 61.2, 102.3, 126.1, 127.2, 128.3, 128.4, 129.1, 129.1, 136.6, 136.8, 155.5, 171.1; HRMS (ESI) calcd. for $C_{19}H_{20}O_3Na$ [M+Na]: 319.1305, found: 319.1296.



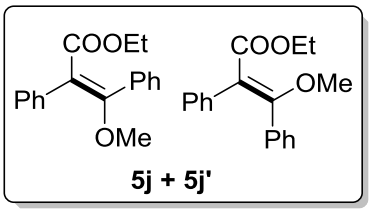
5i

Ethyl 3-methoxy-2,4-diphenylbut-2-enoate (5i+5i'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.29 (m, 3H), 3.58 (s, 1.1H), 3.72 (s, 1.9H), 4.12-4.29 (m, 2H), 4.66 (s, 0.4H), 4.92 (s, 0.6H), 5.61 (s, 0.4H), 5.83 (s, 0.6H), 7.14-7.50 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.2, 52.4, 55.2, 56.0, 58.0, 61.2, 61.4, 102.3, 112.8, 126.1, 126.6, 127.2, 127.8, 128.2, 128.3, 128.4, 128.7, 128.7, 129.1, 129.1, 135.3, 135.9, 136.6, 136.8, 154.9, 155.5, 171.1, 171.2; HRMS (ESI) calcd. for $C_{19}H_{20}O_3Na$ [M+Na]: 319.1305, found: 319.1299.



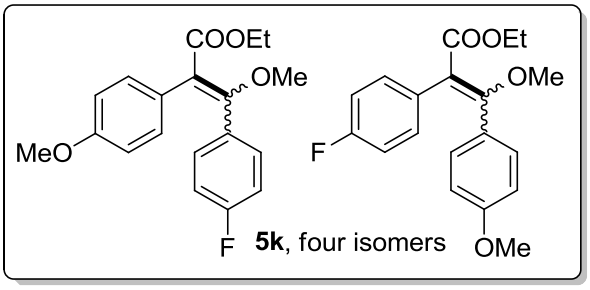
5i + 5i'

Ethyl 3-methoxy-2,3-diphenylacrylate (5j+5j'): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5j**+**5j'**) 95.5 mg, 68% yield, *E*/*Z* = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 1.7H), 1.32 (t, *J* = 7.2 Hz, 1.3H), 3.39 (s, 1.8H), 3.52 (s, 1.2H), 3.93 (q, *J* = 6.8 Hz, 1.1H), 4.32 (q, *J* = 7.2 Hz, 0.8H), 7.02-7.04 (m, 0.8H), 7.04-7.13 (m, 1.2H), 7.21-7.30 (m, 3H), 7.35-7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.3, 57.8, 58.2, 60.4, 60.8, 116.6, 118.9, 126.8, 127.0, 128.0, 128.0, 128.2, 128.3, 128.9, 129.1, 129.3, 129.6, 130.1, 130.1, 132.8, 134.6, 135.3, 135.4, 159.0, 162.2, 168.6, 169.1; HRMS (ESI) calcd. for $C_{18}H_{18}O_3Na$ [M+Na]: 305.1148, found: 305.1142.

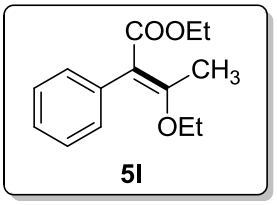


5j + 5j'

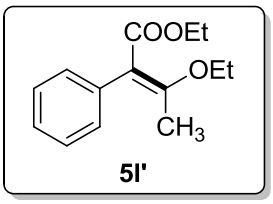
Ethyl 3-(4-fluorophenyl)-3-methoxy-2-(4-methoxyphenyl)acrylate/ethyl 2-(4-fluorophenyl)-3-methoxy-3-(4-methoxyphenyl)acrylate (5k): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 103.0 mg, 62% yield, *isomer ratio* = 2:2:1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91-0.95 (m, 1.8H), 1.28-1.33 (m, 1.2H), 3.39 (s, 0.8H), 3.39 (s, 0.8H), 3.51 (s, 0.5H), 3.53 (s, 0.5H), 3.74 (s, 0.5H), 3.77 (s, 0.5H), 3.82 (s, 0.9H), 3.85 (s, 1H), 3.96 (q, *J* = 7.2 Hz, 1.2H), 4.25-4.32 (m, 0.7H), 6.68-7.42 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.8, 14.3, 55.1, 55.2, 55.2, 55.3, 57.7, 57.9, 58.3, 58.3, 60.4, 60.5, 60.8, 60.9, 113.6, 113.7, 113.7, 113.8, 114.8, 114.9, 115.0, 115.2, 115.3, 115.5, 115.5, 116.7, 116.8, 119.0, 124.7, 126.5, 127.3, 127.5, 129.0, 130.3, 130.7, 130.8, 130.8, 131.1, 131.3, 131.3, 131.6, 131.8, 131.9, 131.9, 132.0, 132.0, 157.0, 158.6, 158.6, 160.0, 160.2, 160.5, 160.5, 161.6, 162.0, 162.6, 162.8, 162.9, 164.1, 164.5, 168.6, 168.8, 169.1, 169.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4, -115.4, -111.3, -111.2; HRMS (ESI) calcd. for $C_{19}H_{19}FNaO_4$ [M+Na]: 353.1160, found: 353.1156.



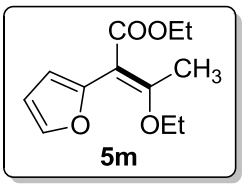
(*E*)-ethyl 3-ethoxy-2-phenylbut-2-enoate (5l): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5l**+**5l'**) 104.3 mg, 89% yield, *E*/*Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, *J* = 6.8 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 2.45 (s, 3H), 3.92 (q, *J* = 6.8 Hz, 2H), 4.15 (q, *J* = 6.8 Hz, 2H), 7.18-7.23 (m, 3H), 7.27-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.1, 15.9, 60.0, 63.6, 113.5, 126.2, 127.5, 130.3, 136.4, 164.5, 169.2; HRMS (ESI) calcd. for $C_{14}H_{19}O_3$ [M+H]: 235.1329, found: 235.1318.



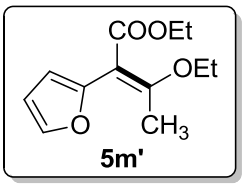
(*Z*)-ethyl 3-ethoxy-2-phenylbut-2-enoate (5l'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 6.8 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 4.06 (q, *J* = 6.8 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 7.22-7.27 (m, 3H), 7.31-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.3, 15.9, 60.2, 64.4, 114.5, 126.9, 128.2, 130.2, 136.8, 159.6, 167.7; HRMS (ESI) calcd. for $C_{14}H_{19}O_3$ [M+H]: 235.1329, found: 235.1328.



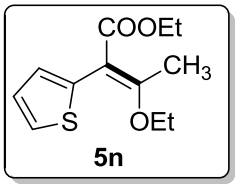
(*E*)-ethyl 2-(furan-2-yl)-3-methoxybut-2-enoate (5m): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5m**+**5m'**) 74.9 mg, 67% yield, *E*/*Z* = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 6.8 Hz, 3H), 2.35 (s, 3H), 4.03 (q, *J* = 6.8 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.38-6.40 (m, 2H), 7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 16.0, 60.5, 64.0, 104.7, 109.3, 110.5, 140.4, 148.6, 163.6, 168.1; HRMS (ESI) calcd. for $C_{12}H_{16}O_4Na$ [M+Na]: 247.0941, found: 247.0938.



(*Z*)-ethyl 2-(furan-2-yl)-3-methoxybut-2-enoate (5m'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 6.8 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 2.07 (s, 3H), 4.07 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.17-6.18 (m, 1H), 6.37-6.39 (m, 1H), 7.38-7.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 15.8, 60.8, 64.1, 109.0, 124. 3, 125.2, 125.7, 136.5, 158.2, 168.8; HRMS (ESI) calcd. for $C_{12}H_{16}O_4Na$ [M+Na]: 247.0941, found: 247.0934.

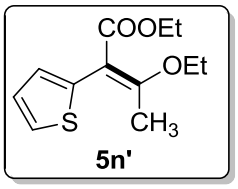


(*Z*)-ethyl 3-methoxy-2-(thiophen-2-yl)but-2-enoate (5n): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5n**+**5n'**) 87.6 mg, 73% yield, *E*/*Z* = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 4.10 (q, *J* = 6.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.94-6.98 (m, 2H), 7.19-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 15.8, 60.8, 64.1, 109.0, 124.3,



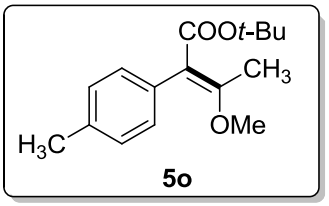
125.2, 125.7, 136.5, 158.2, 168.8; HRMS (ESI) calcd. for $C_{12}H_{16}O_3SNa$ [M+Na]: 263.0712, found: 263.0714.

(*E*)-ethyl 3-methoxy-2-(thiophen-2-yl)but-2-enoate (5n'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 6.8 Hz, 3H), 2.01 (s, 3H), 4.07 (q, *J* = 6.8 Hz, 2H), 4.22 (q, *J* = 6.8 Hz, 2H), 6.84-6.85 (m, 1H), 6.96-6.99 (m, 1H), 7.26-7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.2, 16.1, 60.4, 64.6, 107.0, 125.7, 126.7, 127.7, 138.1, 161.6, 167.1; HRMS (ESI) calcd. for $C_{12}H_{16}O_3SNa$ [M+Na]: 263.0712, found: 263.0705.



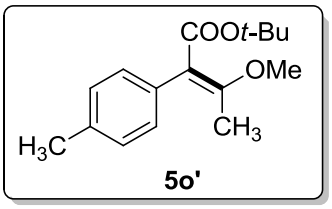
5n'

(*E*)-*tert*-butyl 3-methoxy-2-(p-tolyl)but-2-enoate (5o): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, (**5o**+**5o'**) 85.1 mg, 65% yield, *E*/*Z* = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.33 (s, 3H), 2.39 (s, 3H), 3.58 (s, 3H), 7.09 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 21.2, 28.2, 55.3, 80.0, 114.7, 128.3, 129.9, 133.5, 135.6, 162.4, 168.8; HRMS (ESI) calcd. for $C_{16}H_{22}O_3Na$ [M+Na]: 285.1461, found: 285.1451.



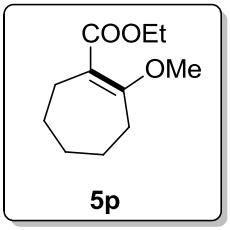
5o

(*Z*)-*tert*-butyl 3-methoxy-2-(p-tolyl)but-2-enoate (5o'): ^{1}H NMR (400 MHz, $CDCl_3$) δ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 1.80 (s, 3H), 2.26 (s, 3H), 3.68 (s, 3H), 7.01-7.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 21.2, 28.2, 56.1, 80.1, 115.9, 128.8, 129.8, 134.0, 136.3, 158.3, 167.3; HRMS (ESI) calcd. for $C_{16}H_{22}O_3Na$ [M+Na]: 285.1461, found: 285.1449.



5o'

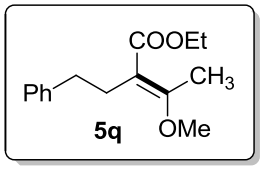
Ethyl 2-methoxycyclohept-1-enecarboxylate (5p): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 46.1 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.53-1.62 (m, 4H), 1.72-1.78 (m, 2H), 2.37-2.40 (m, 2H), 2.42-2.45 (m, 2H), 3.63 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.8, 26.8, 27.7, 30.7, 31.8, 56.9, 60.0, 115.3, 167.3,



5p

168.8; HRMS (ESI) calcd. for $C_{11}H_{19}O_3$ [M+H]: 199.1329, found: 199.1324.

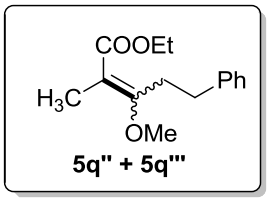
(*E*)-ethyl 3-methoxy-2-phenethylbut-2-enoate (5q): The title compound was



5q

prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 45.6 mg, 37% yield ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 2.58-2.68 (m, 4H), 3.60 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.14-7.21 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 14.6, 28.2, 35.6, 54.7, 59.6, 110.3, 125.5, 128.1, 128.6, 142.9, 165.2, 169.4; HRMS (ESI) calcd. for $C_{15}H_{20}NaO_3$ [M+Na]: 271.1305, found: 271.1305.

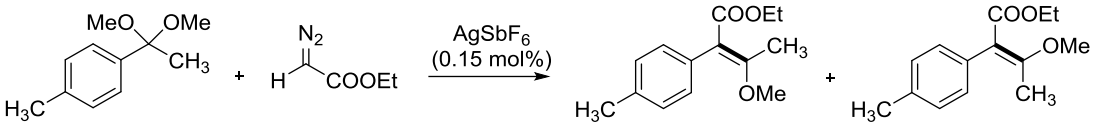
Ethyl 3-methoxy-2-methyl-5-phenylpent-2-enoate (5q'' + 5q'''): The title compound



5q'' + 5q'''

was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the colorless oil, 24.0 mg, 19% yield, *isomer ratio* = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.83 (s, 2.4H), 1.84 (s, 0.6H), 2.80-2.84 (m, 2H), 3.02-3.08 (m, 2H), 3.71 (s, 2.4H), 3.98 (q, *J* = 6.8 Hz, 0.4H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.18-7.22 (m, 1H), 7.25-7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 12.1, 14.4, 15.5, 29.9, 30.6, 34.4, 55.1, 59.8, 63.2, 107.7, 108.4, 126.1, 126.1, 128.4, 128.4, 128.4, 141.4, 141.5, 166.4, 166.9, 169.2, 169.3; HRMS (ESI) calcd. for $C_{15}H_{20}NaO_3$ [M+Na]: 271.1305, found: 271.1304.

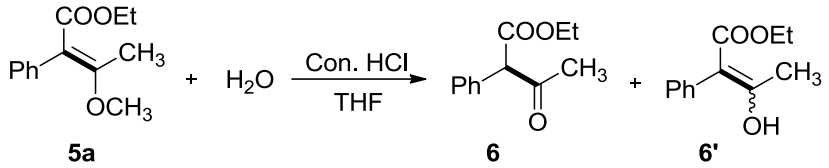
6. Gram-scale reaction



4b **2a** **5b** **5b'**

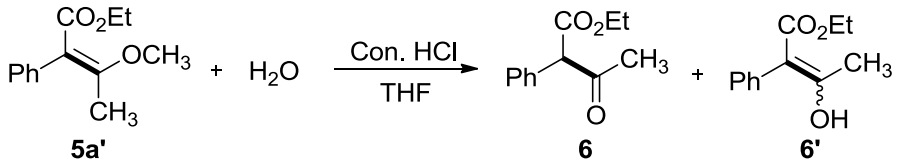
$AgSbF_6$ (5.2 mg, 0.015 mmol) was added into a 100 mL flame-dried Young-type tube in a glove box. Then ketal **4b** (1.8 g, 10 mmol), $CHCl_3$ (10 mL) and diazo acetate **2a** (2.3 g, 20 mmol) were added into the tube under argon atmosphere. The mixture was degassed by the freeze-thaw method. Then the mixture was stirred at 100 ^oC for 24 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/50 – 1/5) to afford the desired product **5b** and **5b'** (1.4 g, 60% yield, *E*/*Z*= 3:1).

7. Hydrolysis of alkenyl ether



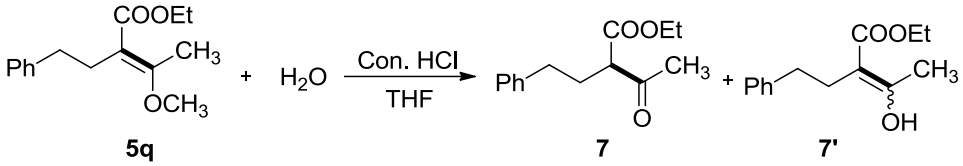
5a **6** **6'**

Alkenyl ether **5a** (110 mg, 0.5 mmol), H_2O (9.0 μL, 0.5 mmol), THF (1.0 mL) and Con. HCl (5.0 μL) were added into a 25 mL Young-type tube. The mixture was stirred at 25 °C for 12 hours. Then the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/100 – 1/50) to afford the desired product **6** and **6'** (97.6 mg, 95% yield, **6**/**6'** = 1:1).



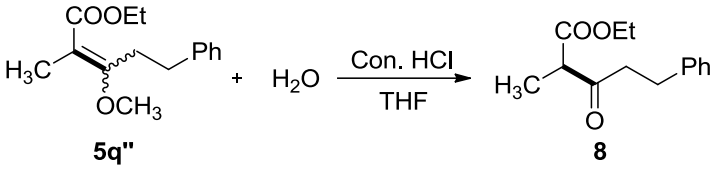
5a' **6** **6'**

Alkenyl ether **5a'** (110 mg, 0.5 mmol), H_2O (9.0 μL, 0.5 mmol), THF (1.0 mL) and Con. HCl (5.0 μL) were added into a 25 mL Young-type tube. The mixture was stirred at 25 °C for 12 hours. Then the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/100 – 1/50) to afford the desired product **6** and **6'** (84.9 mg, 82% yield, **6**/**6'** = 1:1).



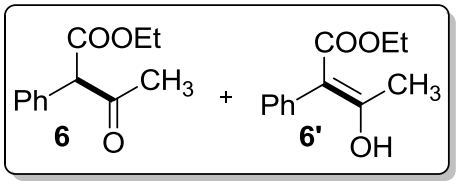
5q **7** **7'**

Alkenyl ether **5q** (248 mg, 1.0 mmol), H_2O (18 μL, 1.0 mmol), THF (2.0 mL) and Con. HCl (10 μL) were added into a 25 mL Young-type tube. The mixture was stirred at 25 °C for 12 hours. Then the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/100 – 1/50) to afford the desired product **7** and **7'** (198 mg, 85% yield, **7**/**7'** = 9:1).

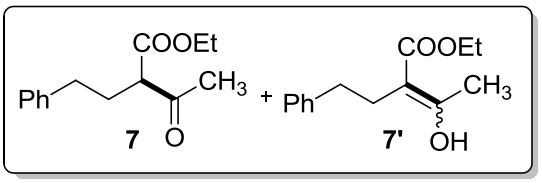


Alkenyl ether **5q''** (248 mg, 1.0 mmol), H_2O (18 μL, 1.0 mmol), THF (2.0 mL) and Con. HCl (10 μL) were added into a 25 mL Young-type tube. The mixture was stirred at 25 °C for 12 hours. Then the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/100 – 1/50) to afford the desired product **8** (192 mg, 82% yield).

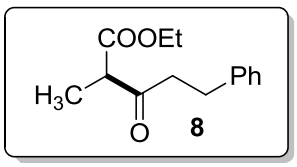
Hydrolysis products (6+6'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 6.8 Hz, 1.3H), 1.29 (t, *J* = 7.2 Hz, 1.8H), 1.85 (s, 1.3H), 2.18 (s, 1.7H), 4.14-4.26 (m, 2H), 4.69 (s, 0.5H), 7.14-7.40 (m, 5H), 13.14 (s, 0.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 19.9, 28.8, 60.6, 61.6, 65.8, 104.4, 126.9, 128.0, 128.3, 128.9, 129.3, 131.2, 132.7, 135.2, 168.5, 172.6, 173.9, 201.6.



Hydrolysis products (7+7'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.83 (s, 0.3H), 2.10-2.24 (m, 4.6H), 2.44-2.48 (m, 0.2H), 2.55-2.69 (m, 2H), 3.44 (t, *J* = 7.2 Hz, 0.9H), 4.22 (q, *J* = 7.2 Hz, 2H), 7.15-7.22 (m, 3H), 7.26-7.31 (m, 2H), 12.81 (s, 0.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.3, 18.4, 28.5, 28.9, 29.6, 33.3, 36.2, 58.9, 60.3, 61.4, 125.9, 126.3, 128.3, 128.5, 128.6, 140.7, 169.7, 203.0; HRMS (ESI) calcd. for $C_{14}H_{18}NaO_3$ [M+Na]: 257.1148, found: 257.1151.

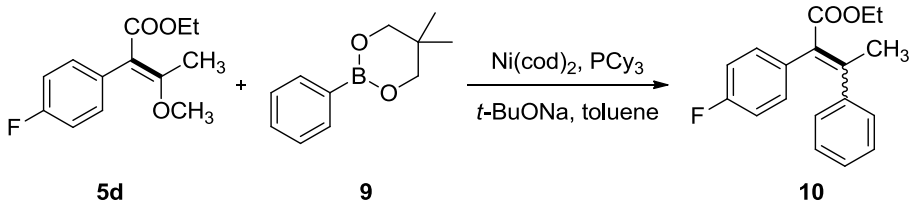


Hydrolysis product (8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 7.2 Hz, 3H), 2.76-2.96 (m, 4H), 3.51 (q, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.17-7.22 (m, 3H), 7.26-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 14.1, 29.6, 43.0, 53.0, 61.4, 126.2, 128.3, 128.5, 140.8, 170.4, 205.0; HRMS (ESI) calcd. for



$C_{14}H_{18}NaO_3$ [M+Na]: 257.1148, found: 257.1154.

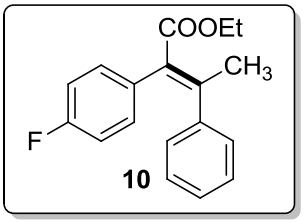
8. Procedure for the Ni-catalyzed Suzuki coupling reaction[5]



5d **9** **10**

Reactions were carried out in 25 mL Young-type tube and chemicals were manipulated in a glove box filled with argon. $Ni(cod)_2$ (13.8 mg, 0.05 mmol), PCy_3 (56.0 mg, 0.2 mmol), *t*-BuONa (24.0 mg, 0.25 mmol), **5d** (119 mg, 0.5 mmol) and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (142.5 mg, 0.75 mmol) were added into toluene (2.0 mL) at room temperature. Then the mixture was proceeded at 120 ^oC for 12 hours. After cooling to room temperature, the crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 20/1) to give **10** as the colorless oil (120.4 mg, 85% yield, *E/Z* = 1:1).

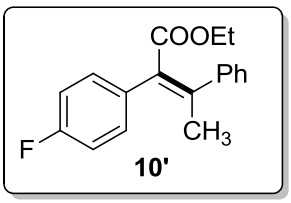
(*E*)-ethyl 2-(4-fluorophenyl)-3-phenylbut-2-enoate (10): ^1H NMR (400 MHz, $CDCl_3$)



10

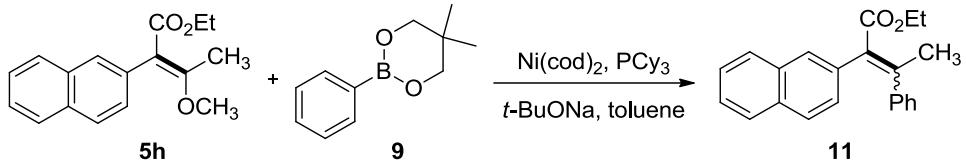
δ 1.31 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 6.77-6.81 (m, 2H), 6.96-7.02 (m, 4H), 7.11-7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.1, 61.0, 114.9 (d, *J* = 21.4 Hz), 127.1, 128.0, 128.4, 131.0, 131.6 (d, *J* = 8.0 Hz), 133.2 (d, *J* = 3.5 Hz), 141.8, 144.2, 162.8 (d, *J* = 244.8 Hz), 169.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2; HRMS (ESI) calcd. for $C_{18}H_{17}FO_2Na$ [M+Na]: 307.1105, found: 307.1109.

(*Z*)-ethyl 2-(4-fluorophenyl)-3-phenylbut-2-enoate (10'): ^1H NMR (400 MHz,



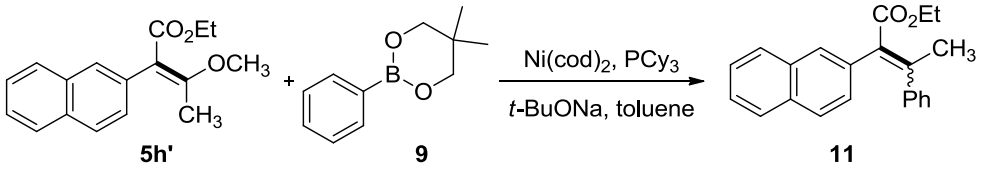
10'

$CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 3H), 2.04 (s, 3H), 3.91 (q, *J* = 7.2 Hz, 2H), 7.07-7.11 (m, 2H), 7.30-7.36 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 22.4, 60.6, 115.4 (d, *J* = 21.3 Hz), 127.0, 127.6, 128.2, 131.1 (d, *J* = 8.0 Hz), 131.9, 133.1 (d, *J* = 3.4 Hz), 142.9, 144.1, 163.4 (d, *J* = 245.3 Hz), 169.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4; HRMS (ESI) calcd. for $C_{18}H_{17}FO_2Na$ [M+Na]: 307.1105, found: 307.1113.



5h **9** **11**

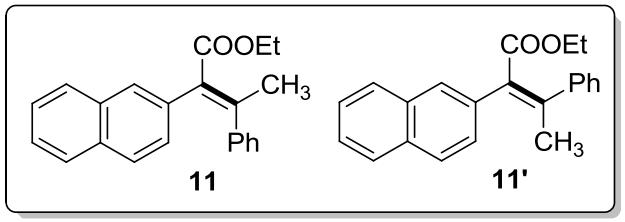
Reactions were carried out in 25 mL Young-type tube and chemicals were manipulated in a glove box filled with argon. $Ni(cod)_2$ (13.8 mg, 0.05 mmol), PCy_3 (56.0 mg, 0.2 mmol), *t*-BuONa (24.0 mg, 0.25 mmol), **5h** (135 mg, 0.5 mmol) and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (142.5 mg, 0.75 mmol) were added into toluene (2.0 mL) at room temperature. Then the mixture was proceeded at 120 ^oC for 12 hours. After cooling to room temperature, the crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 20/1) to give **11** as the colorless oil (129.6 mg, 82% yield, *E/Z* = 1:1).



5h' **9** **11**

Reactions were carried out in 25 mL Young-type tube and chemicals were manipulated in a glove box filled with argon. $Ni(cod)_2$ (13.8 mg, 0.05 mmol), PCy_3 (56.0 mg, 0.2 mmol), *t*-BuONa (24.0 mg, 0.25 mmol), **5h'** (135 mg, 0.5 mmol) and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (142.5 mg, 0.75 mmol) were added into toluene (2.0 mL) at room temperature. Then the mixture was proceeded at 120 ^oC for 12 hours. After cooling to room temperature, the crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 20/1) to give **11** as the colorless oil (119.3 mg, 75% yield, *E/Z* = 1:1).

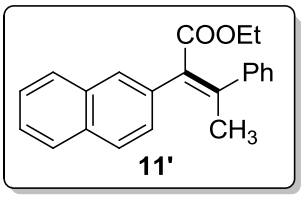
Ethyl 2-(naphthalen-2-yl)-3-phenylbut-2-enoate (11+11'): ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 1.8H), 1.22 (t, *J* = 7.2 Hz, 1.3H), 2.02 (s, 1.7H), 2.31 (s, 1.3H), 3.86 (q, *J* = 6.8 Hz, 1.1H), 4.24 (q, *J* = 7.2 Hz, 0.8H), 6.98-7.04 (m, 2.5H), 7.22-7.31 (m, 3.8H), 7.38-7.47 (m, 2.6H), 7.54-7.62 (m, 1H), 7.74-7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 14.3, 22.5, 23.2, 60.7,



11 **11'**

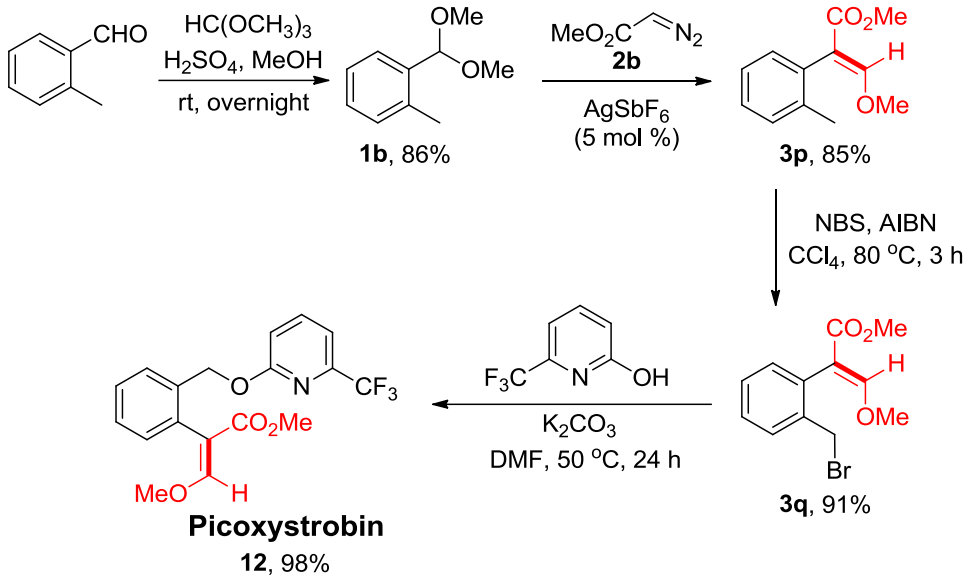
61.0, 125.9, 125.9, 126.2, 127.2, 127.2, 127.3, 127.5, 127.6, 127.7, 128.0, 128.1, 128.1, 128.1, 128.3, 128.4, 128.6, 128.7, 132.0, 132.2, 132.7, 133.0, 133.1, 133.3, 134.6, 134.7, 141.7, 143.1, 143.3, 143.9, 169.5, 169.8; HRMS (ESI) calcd. for $C_{22}H_{20}O_2Na$ [M+Na]: 339.1356, found: 339.1369.

(*Z*)-ethyl 2-(naphthalen-2-yl)-3-phenylbut-2-enoate (11'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3H), 2.02 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 2H), 7.21-7.31 (m, 5H), 7.40-7.43 (m, 3H), 7.72-7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.5, 60.7, 126.2, 127.1, 127.3, 127.6, 127.7, 128.0, 128.1, 128.3, 128.4, 132.7, 133.0, 133.3, 134.7, 143.1, 143.9, 169.5; HRMS (ESI) calcd. for $C_{22}H_{20}O_2Na$ [M+Na]: 339.1356, found: 339.1363.



11'

9. Procedure for the synthesis of picoxystrobin



The procedure for the synthesis of 1b[1]: The aldehyde (30 mmol) and trimethyl orthoformate (1.0 equiv) were mixed in a flask containing MeOH (15 mL). Then H_2SO_4 (50 uL) was added and the mixture was stirred at room temperature for 24 hours. 30% NaOH aqueous (3.0 mL) was added and the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on nuetral alumina and eluted with *n*-hexane to afford the desired product **1b** (4.3 g, 86% yield).

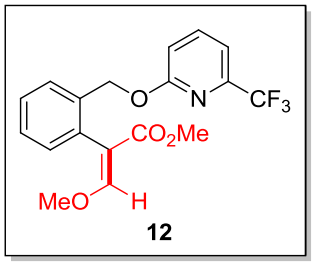
The procedure for the synthesis of 3p: $AgSbF_6$ (8.5 mg, 0.025 mmol) was added into a 25 mL flame-dried Young-type tube in a glove box. Then acetal **1b** (83.0 mg, 0.5 mmol), $CHCl_3$ (1.0 mL) and methyl diazoacetate (60.0 mg, 0.6 mmol) were added into the tube under argon atmosphere. The mixture was stirred at 100 °C for 3 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/50 – 1/10) to afford the desired product **3p** (87.7 mg, 85% yield, *E*/*Z* > 20:1).

The procedure for the synthesis of 3q[6]: To a solution of Alkenyl ether **3p** (206 mg, 1.0 mmol) in carbon tetrachloride (2.0 mL), azaisobutyronitrile (AIBN, 0.1 mmol) and *N*-bromosuccinamade (NBS, 1.2 mmol) was added under argon atmosphere. The

mixture was stirred at 80 °C for 3 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/50 – 1/10) to afford the desired product **3q** (258.4 mg, 91% yield).

The procedure for the synthesis of picoxystrobin 12[7]: Alkenyl ether **3q** (285 mg, 1.0 mmol), 6-(trifluoromethyl)pyridin-2-ol (212 mg, 1.3 mmol), K_2CO_3 (259 mg, 2.0 mmol) and DMF (5.0 mL) were added into a 50 mL Young-type tube under argon atmosphere. The mixture was stirred at 50 °C for 24 hours. Then the reaction mixture was cooled to room temperature. Water (20 mL) and EtOAc (20 mL) were subsequently added to the mixture. The aqueous layer was extracted with EtOAc (20 mL × 3) after separation. The combined organic layer was concentrated after washing with brine (20 mL × 3) and dried with anhydrous Na_2SO_4. The crude product was puratrified by flash column chromatography on silica gel and eluted with EtOAc/hexane (1/20 – 1/10) to afford the desired product **12** (359.7 mg, 98% yield).

Picoxystrobin 12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.81 (s, 3H), 5.33 (s, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.18-7.24 (m, 2H), 7.32-7.36 (m, 2H), 7.55-7.59 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 61.9, 66.3, 110.2, 113.3 (d, *J* = 3.3 Hz), 114.7, 122.8 (d, *J* = 271.9 Hz), 127.9 (d, *J* = 4.7 Hz), 128.9, 131.1, 132.3, 135.7, 139.4, 145.9 (q, *J* = 34.4 Hz), 160.0, 163.6, 168.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.4.



12

10. References

1. a) Ladépêche, A.; Tam, E.; Ancel, J.-E.; Ghosez, L. *Synthesis* **2004**, *9*, 1375; b) Ortholand, J.-Y.; Vicart, N.; Greiner, A. *J. Org. Chem.* **1995**, *60*, 1880.
2. a) Mao, H.; Lin, A.; Shi, Y.; Mao, Z.; Zhu, X.; Li, W.; Hu, H.; Cheng, Y.; Zhu, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 6288.
3. Bew, S. P.; Ashford, P.-A.; Bachera, D. U. *Synthesis* **2013**, *45*, 903.
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5. Shindo, M.; Sato, Y.; Yoshikawa, T.; Koretsune, R.; Shishido, K. *J. Org. Chem.* **2004**, *69*, 3912.
6. Chaudhary, P. M.; Tupe, S. G.; Jorwekar, S. U.; Sant, D. G.; Deshpande, S. R.; Maybhate, S. P.; Likhite, A. P.; Deshpande, M. V. *India J. Chem.* **2015**, *54B*, 908.
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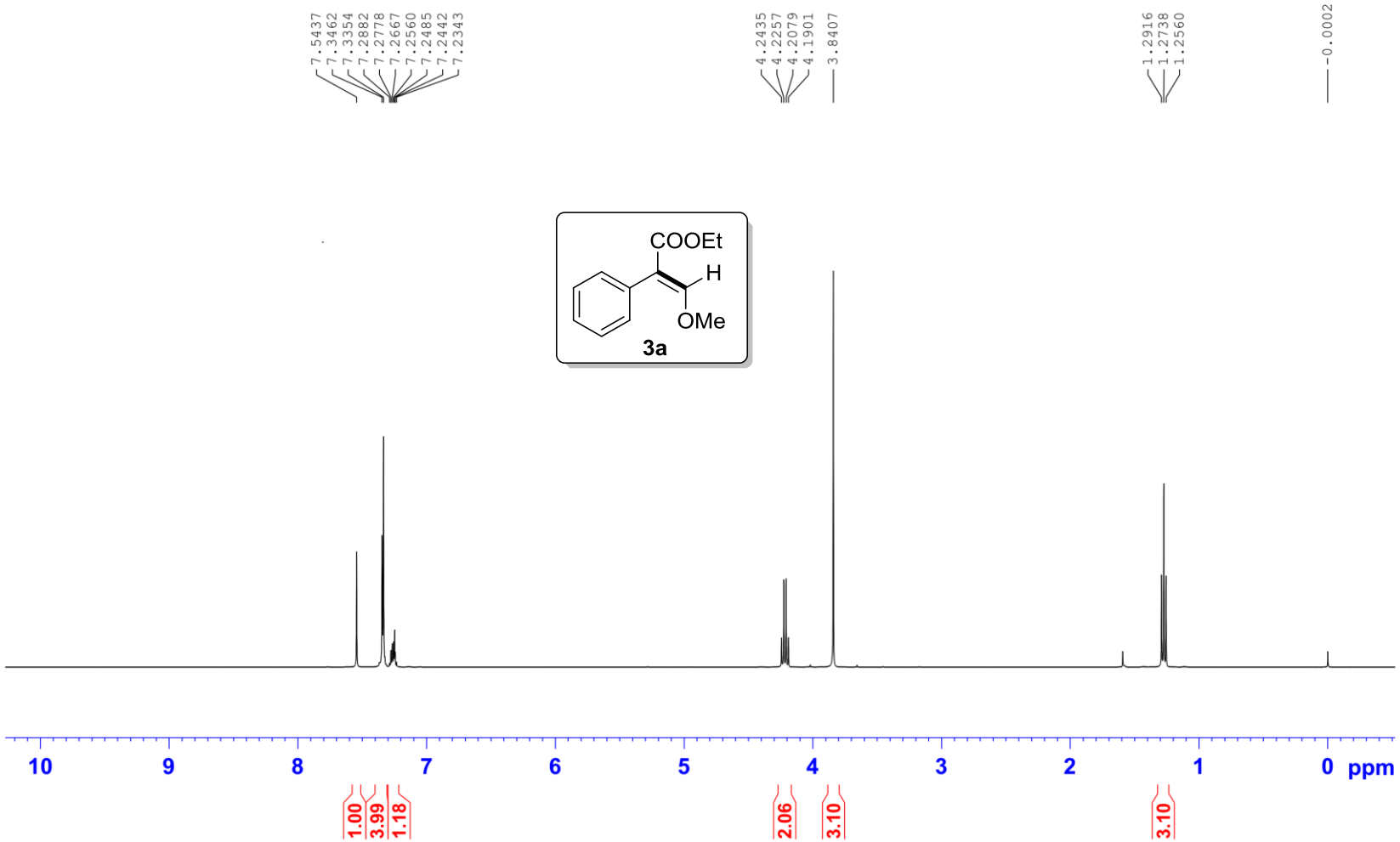
11. Copies for NMR of products

LJW-X160419-2-HNMR(3)



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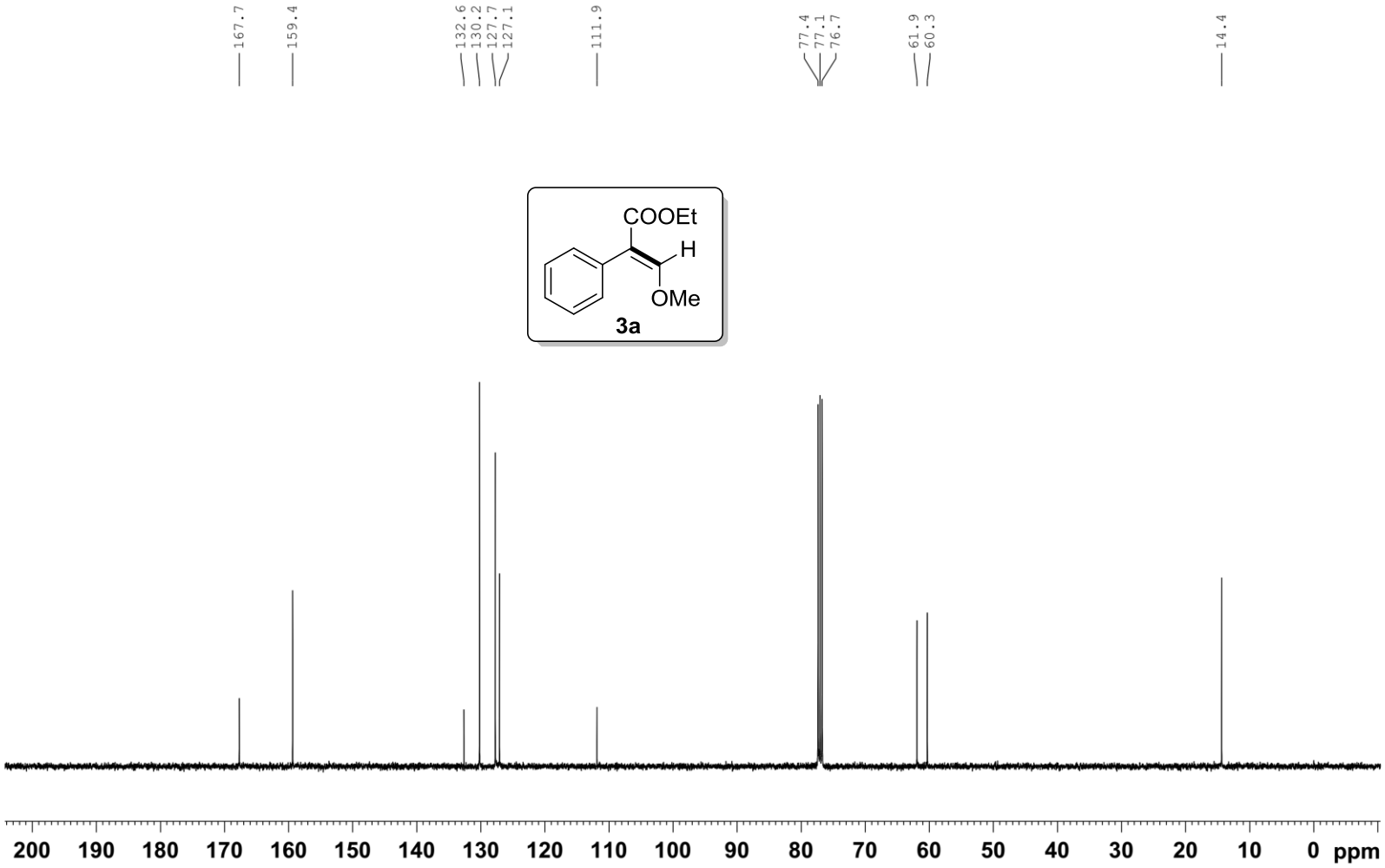
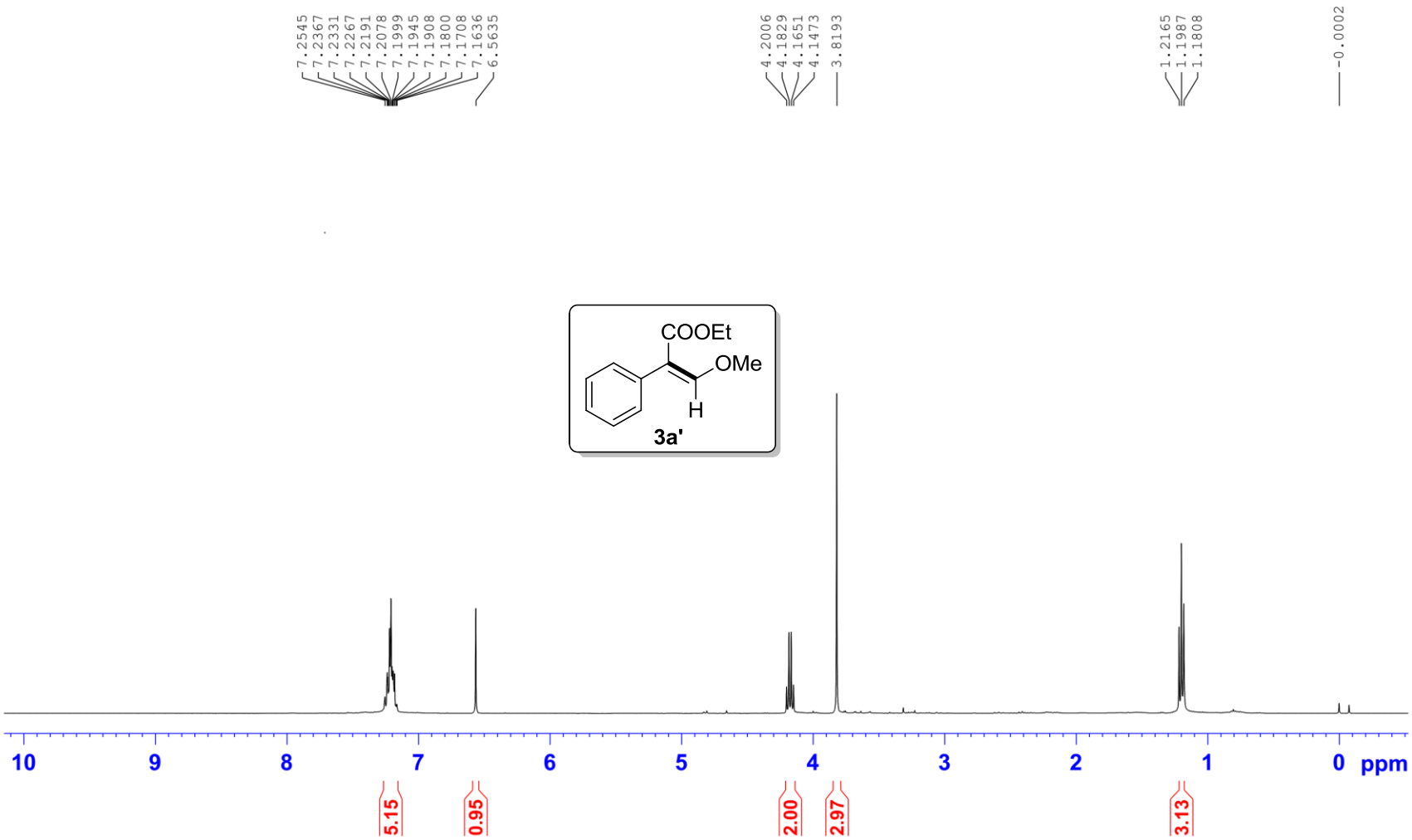


LJW-X180907-1-HNMR



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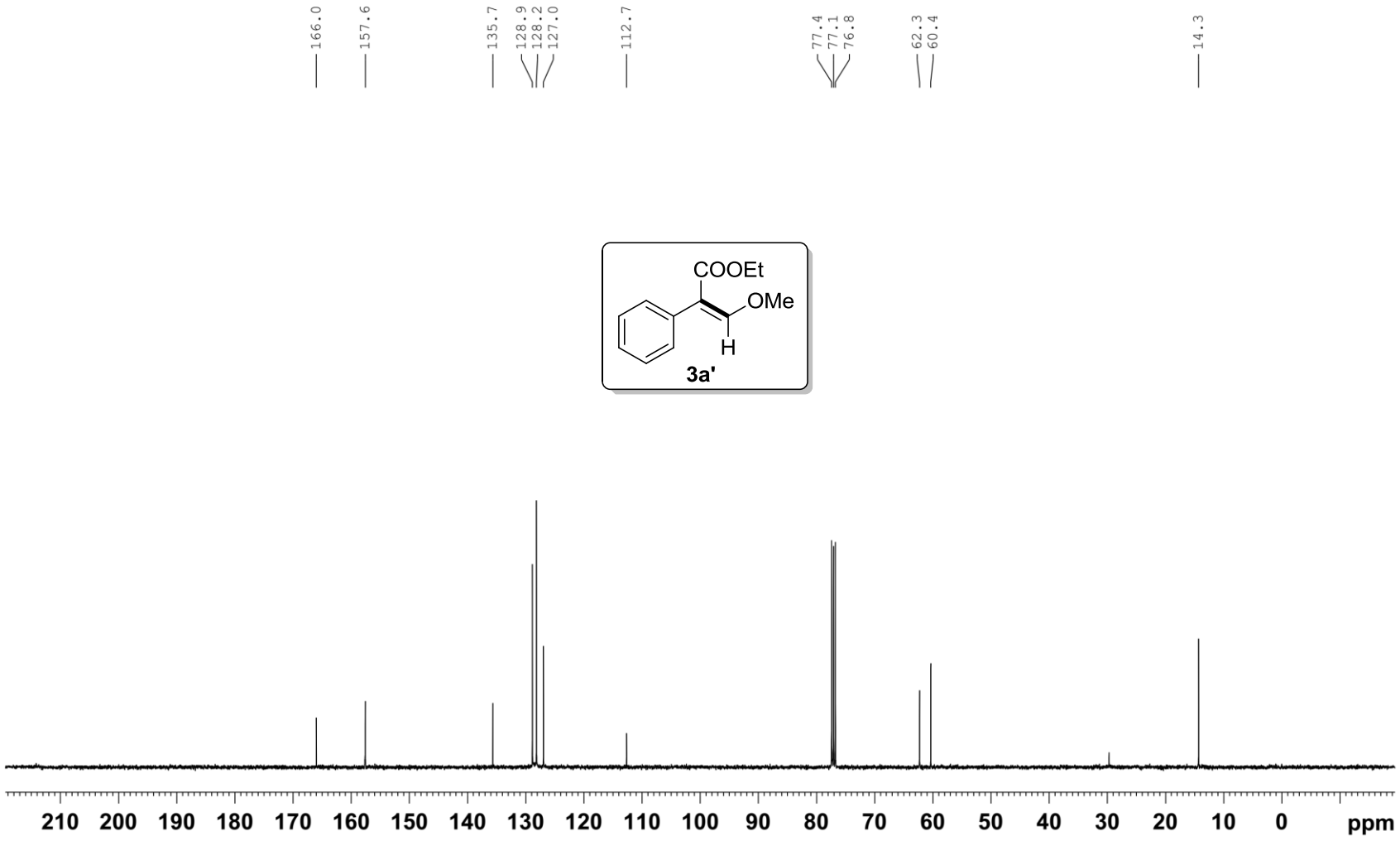

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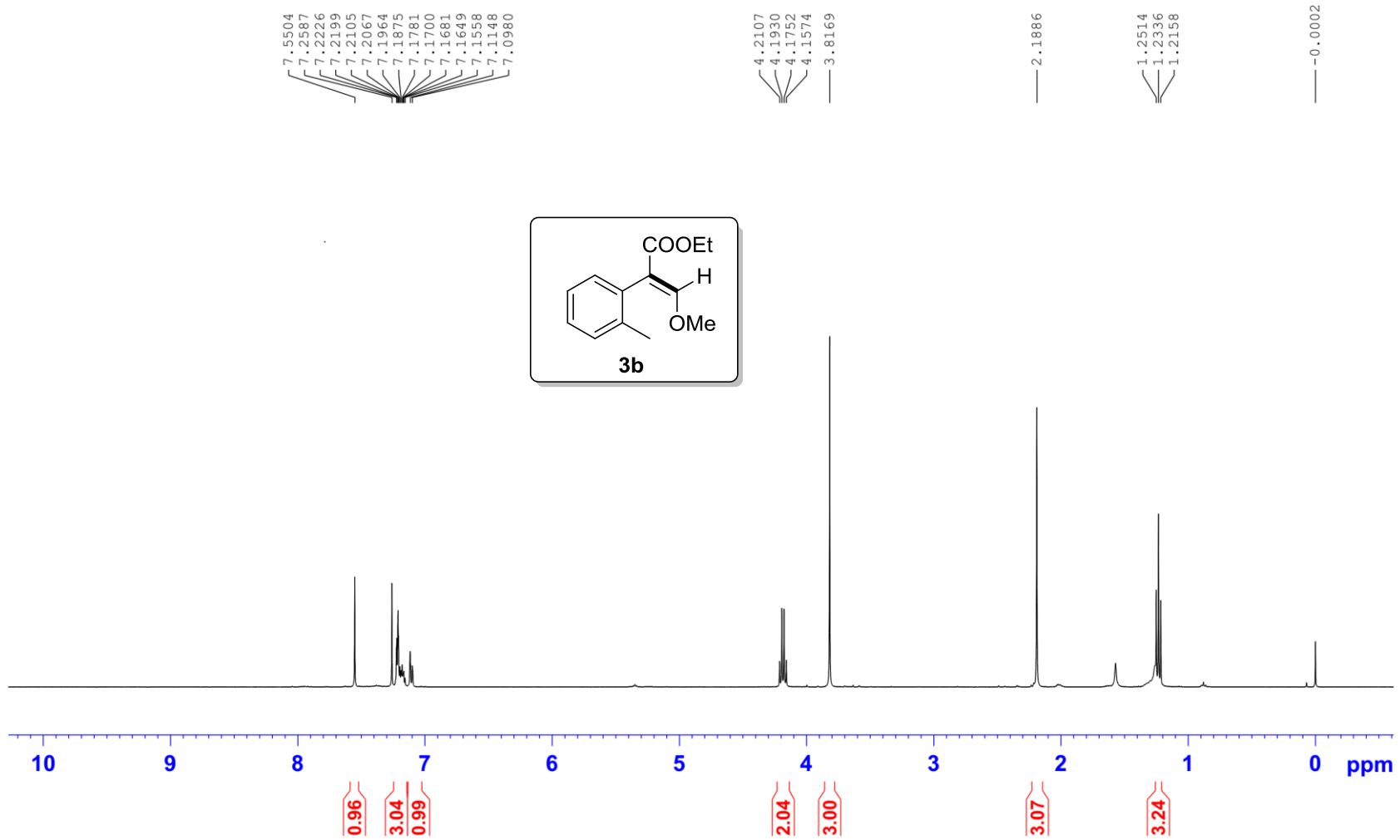
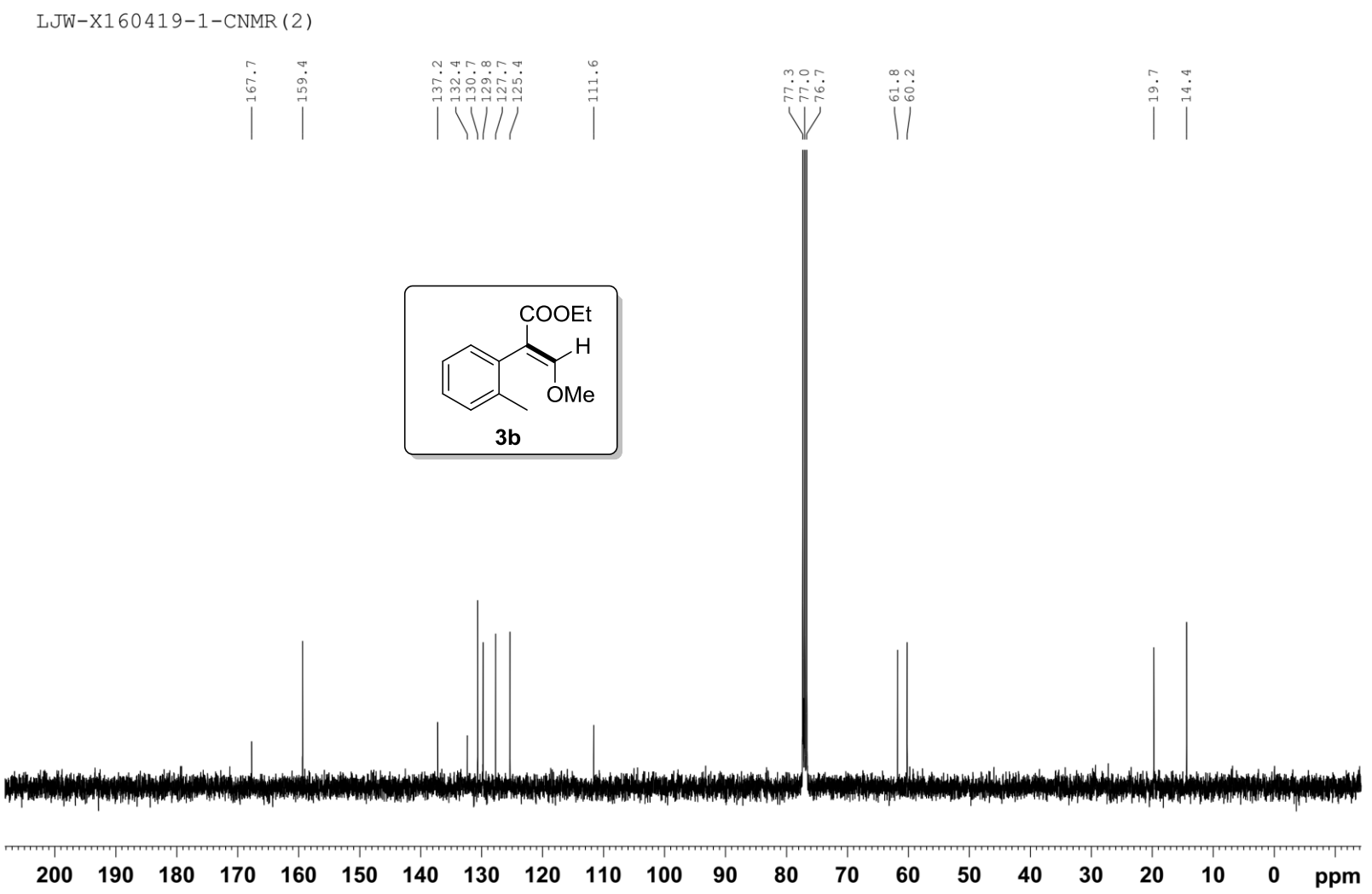
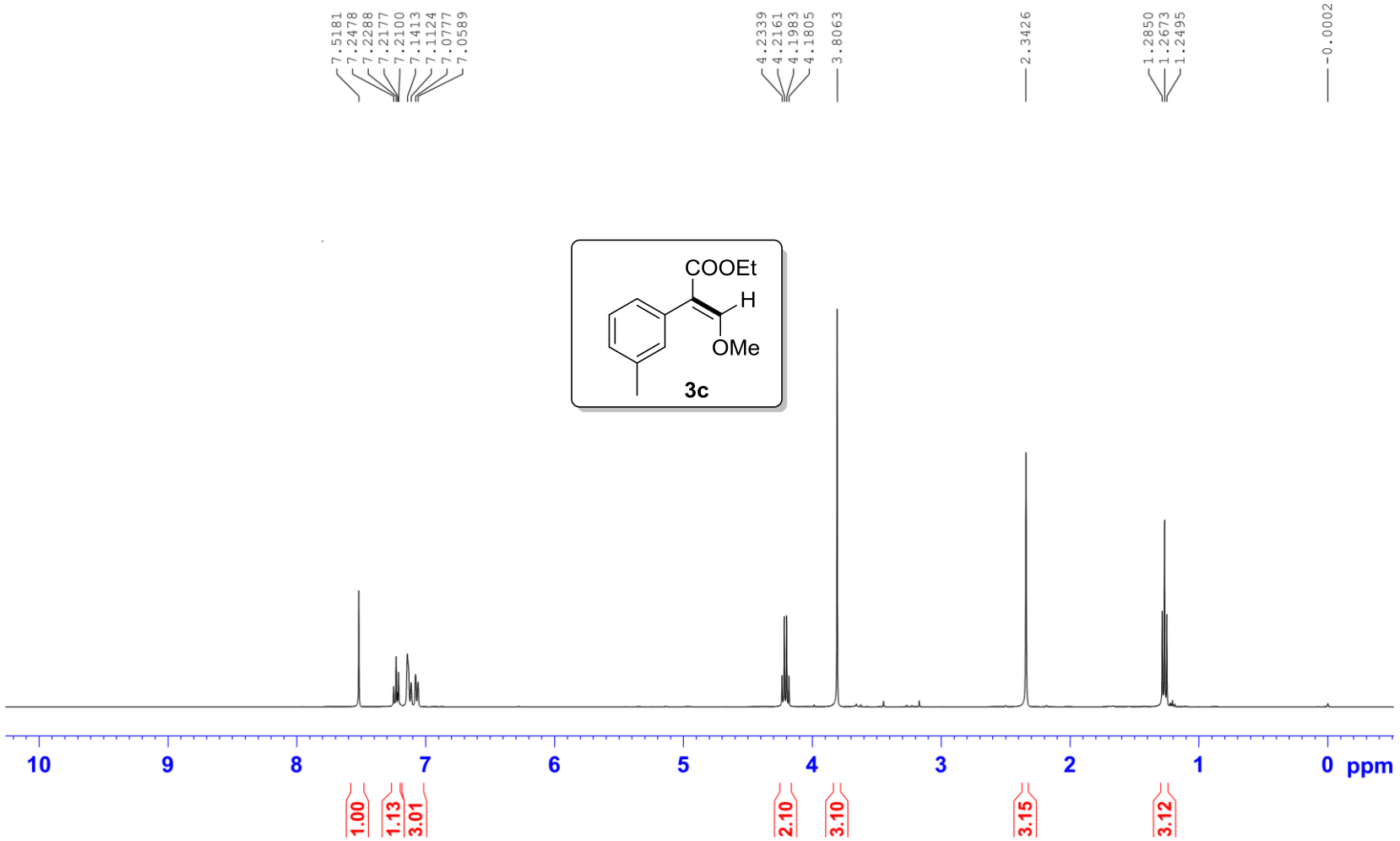



LJW-X160419-1-CNMR(2)
167.7
159.4
137.2
132.4
130.7
129.8
127.7
125.4
111.6
77.3
77.0
76.7
61.8
60.2
19.7
14.4
COOEt
H
OMe
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X160511-2-HNMR(2)



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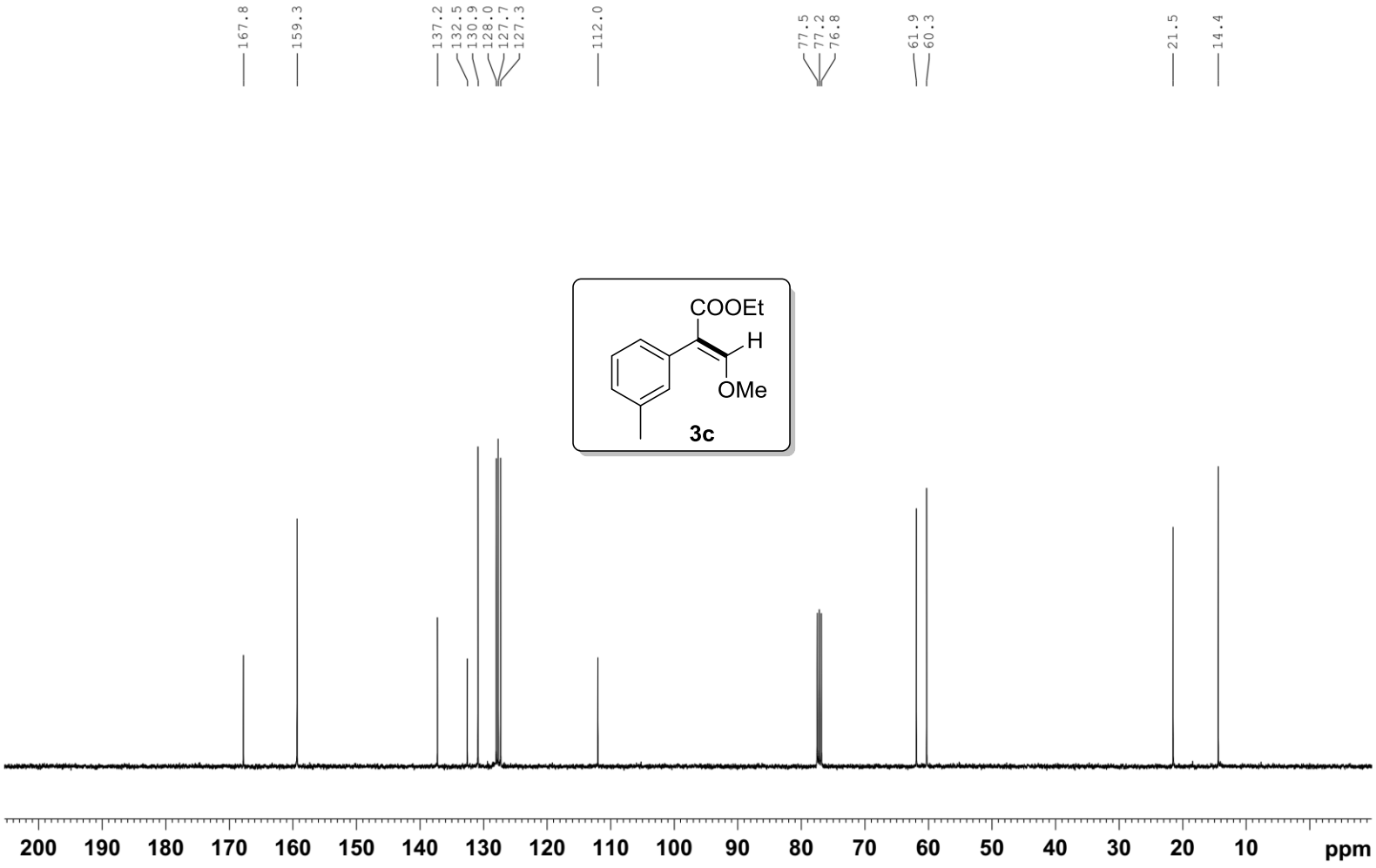

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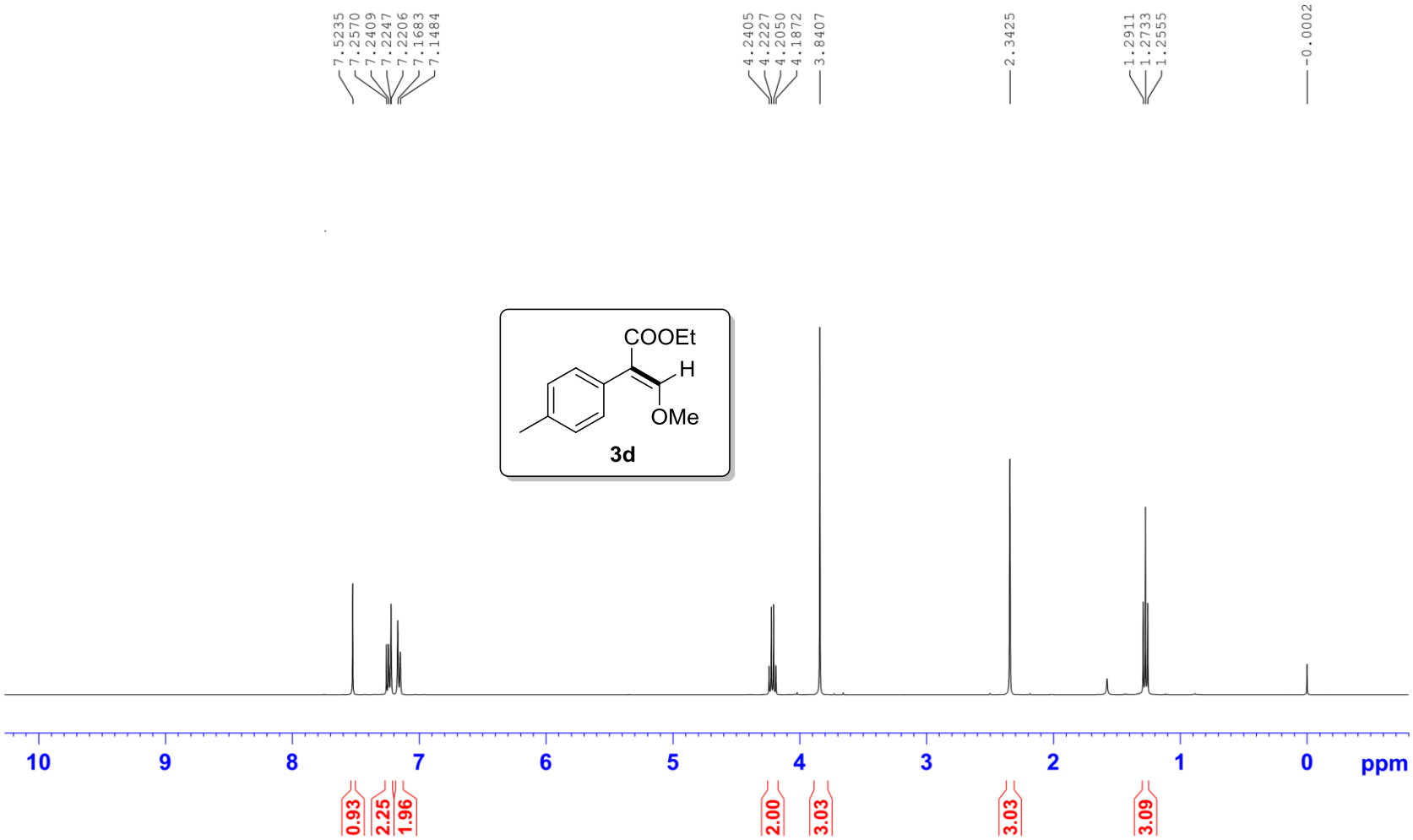
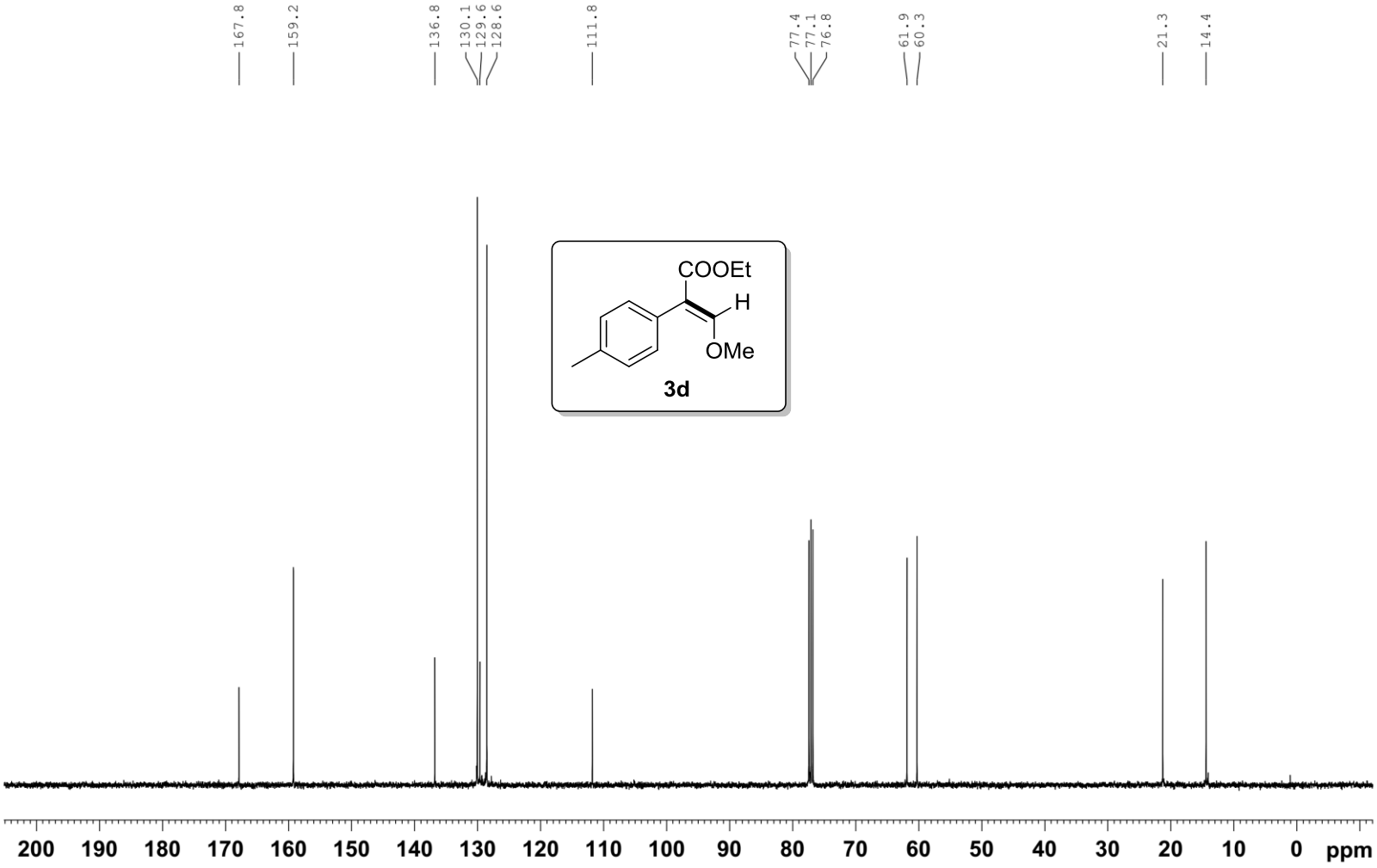


LJW-X160602-2-CNMR(22)



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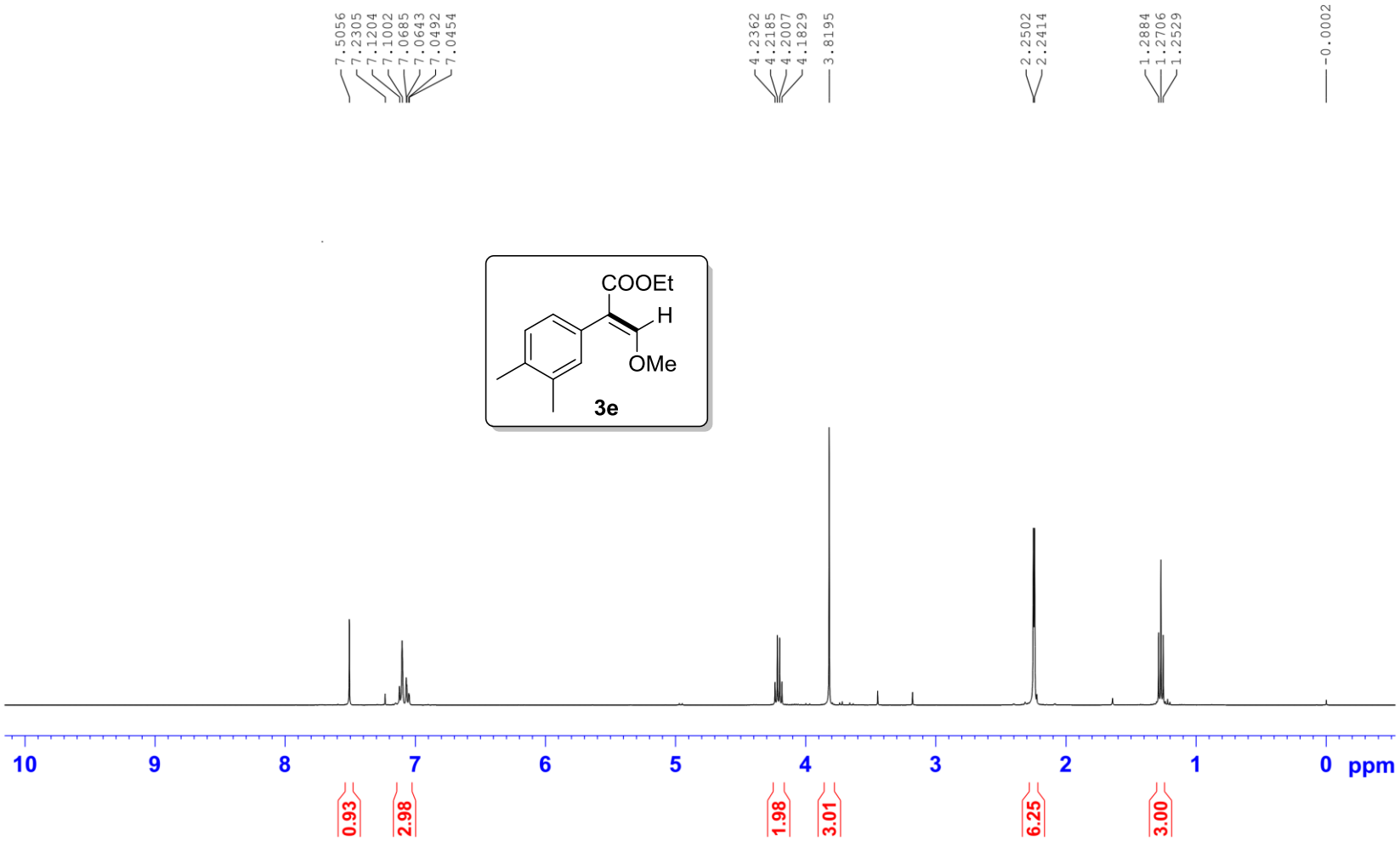

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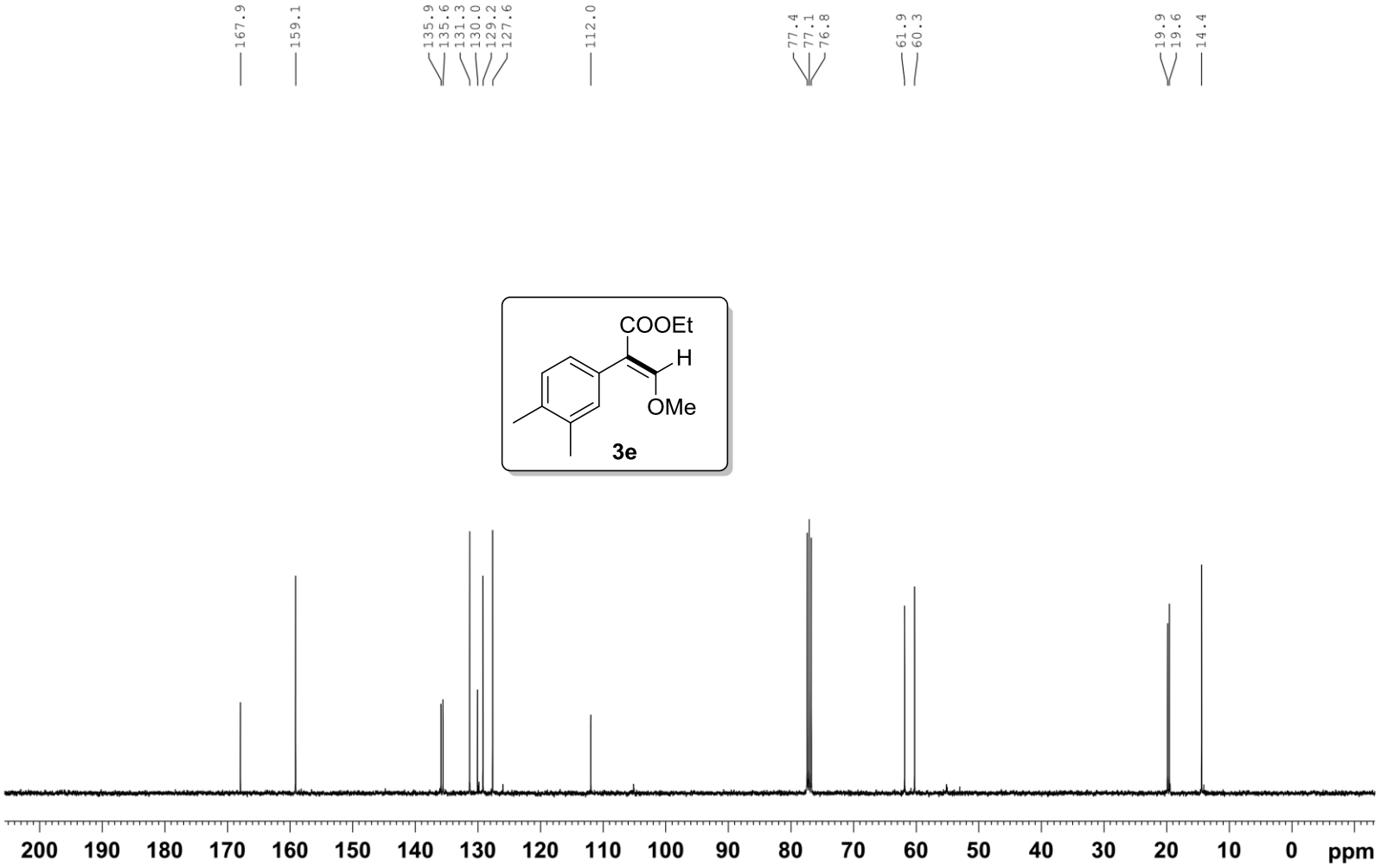

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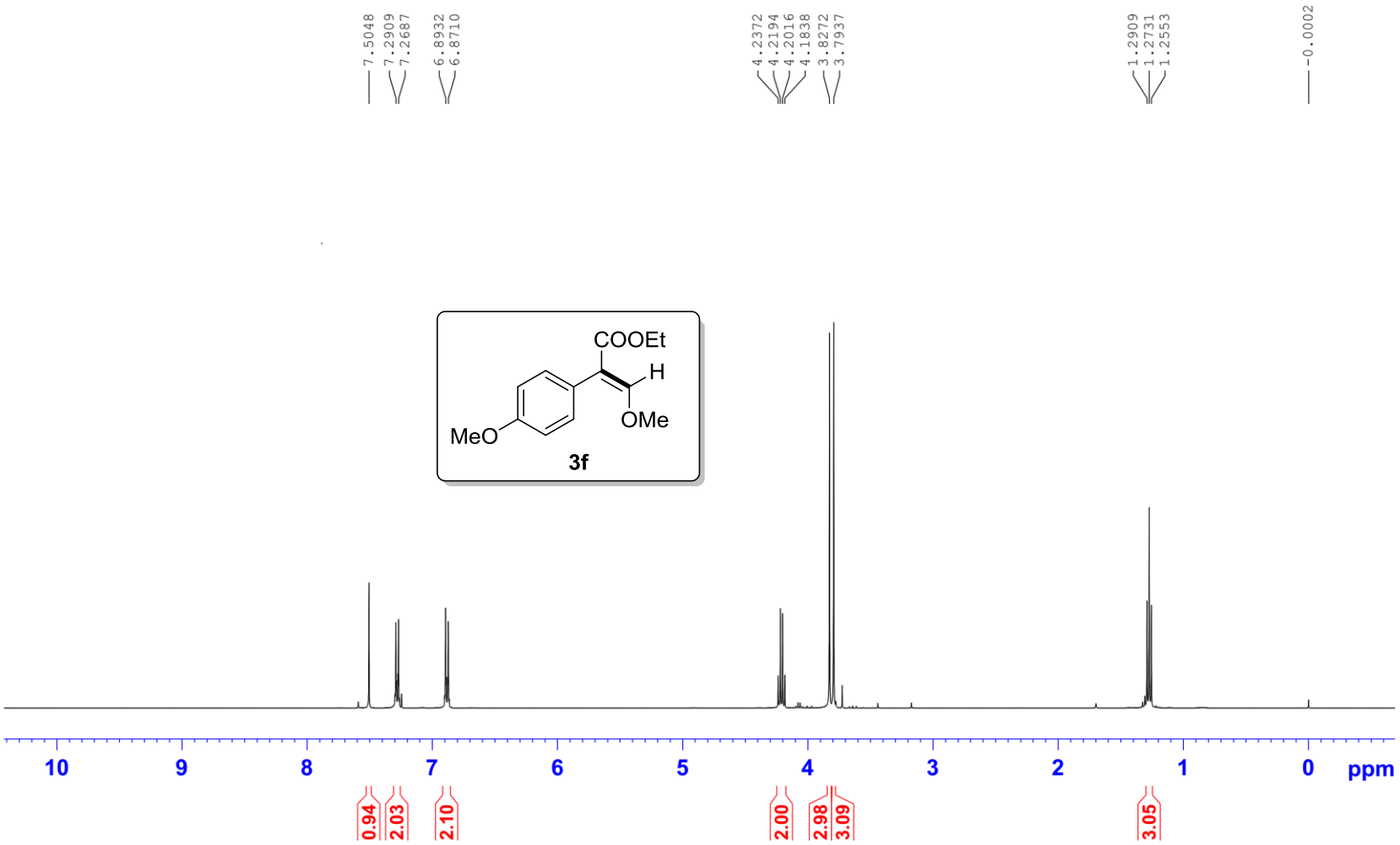

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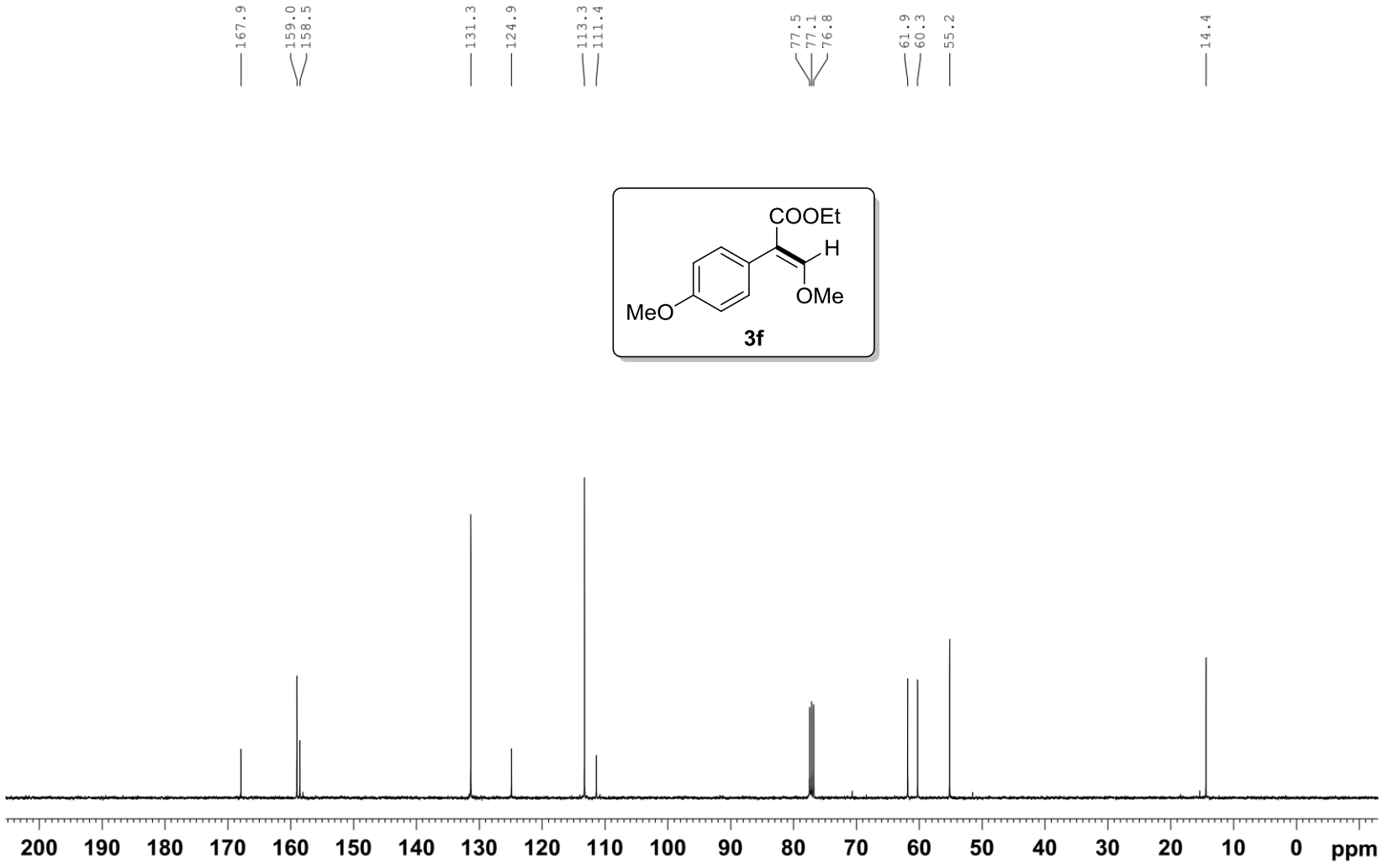

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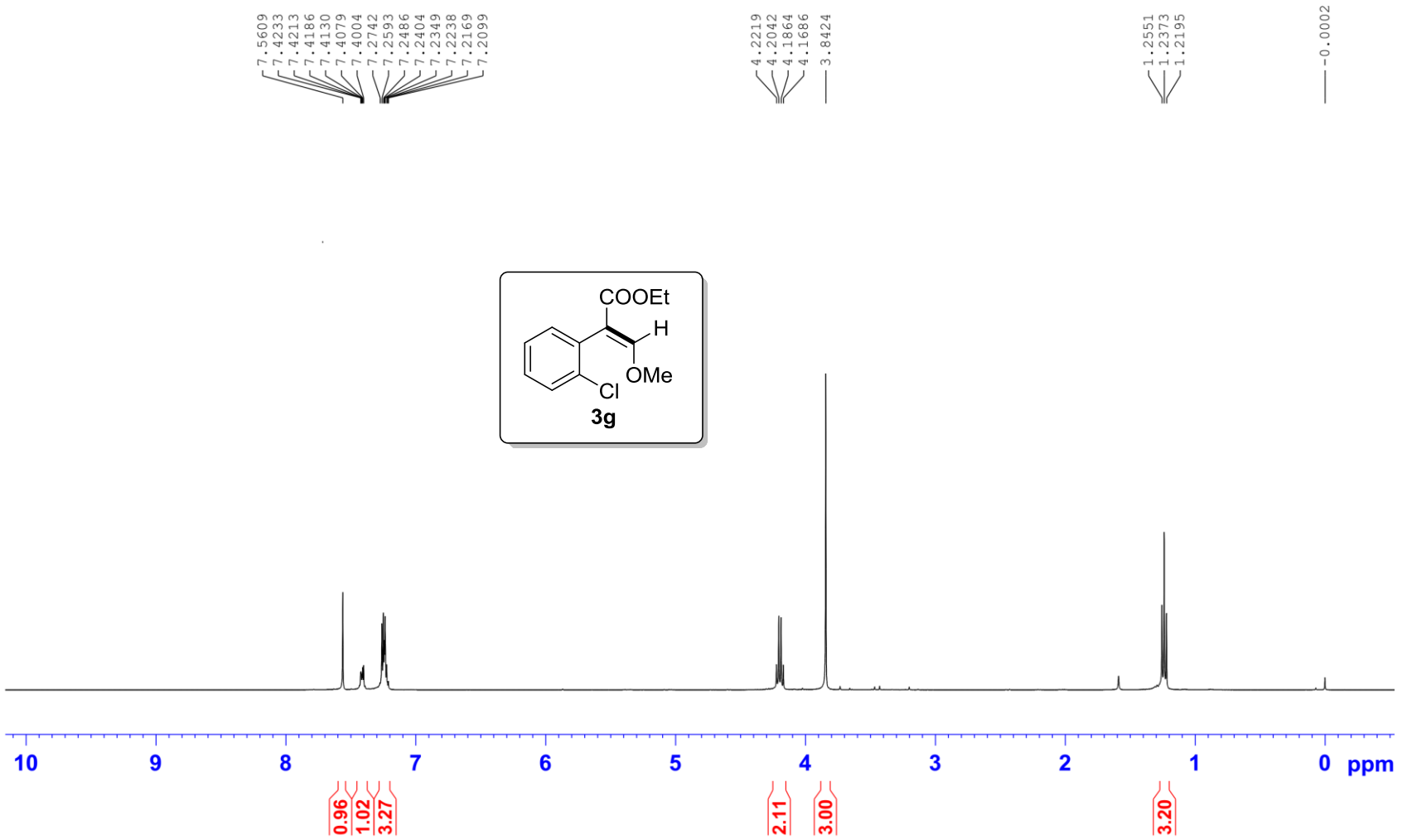

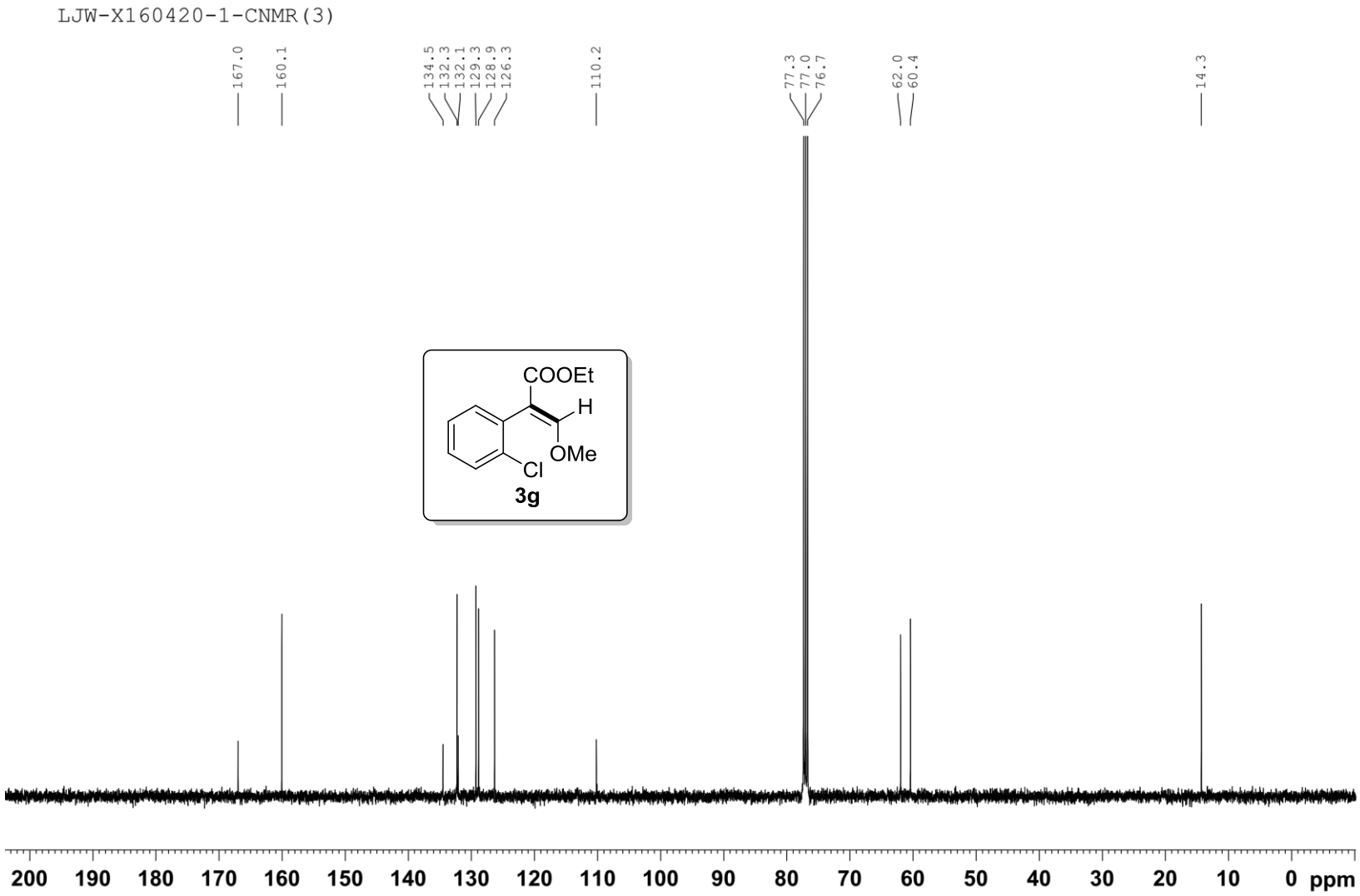
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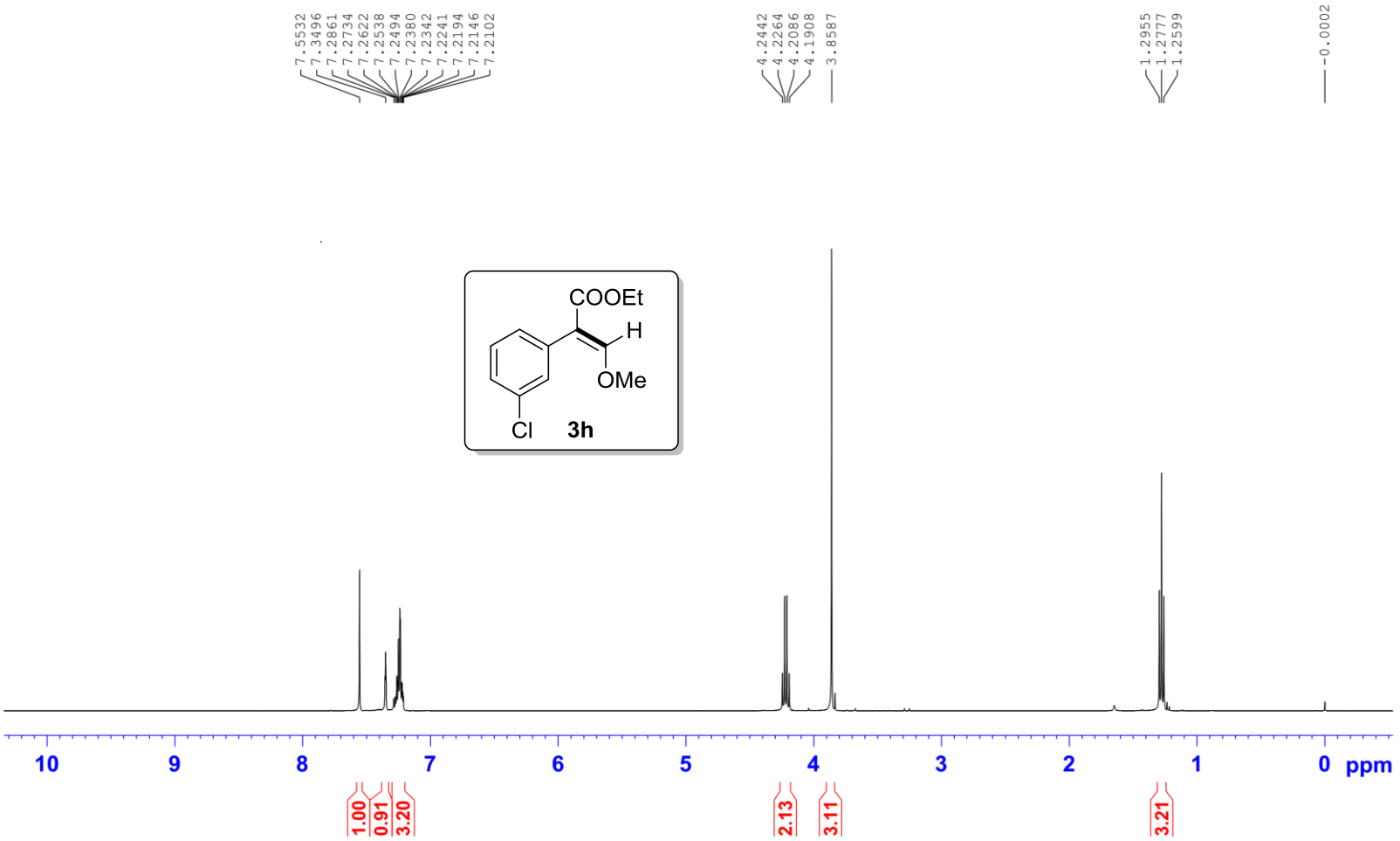
167.0
160.1
134.5
132.3
132.1
129.3
128.9
126.3
110.2
77.3
77.0
76.7
62.0
60.4
14.3
COOEt
H
OMe
Cl
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X160608-6-HNMR



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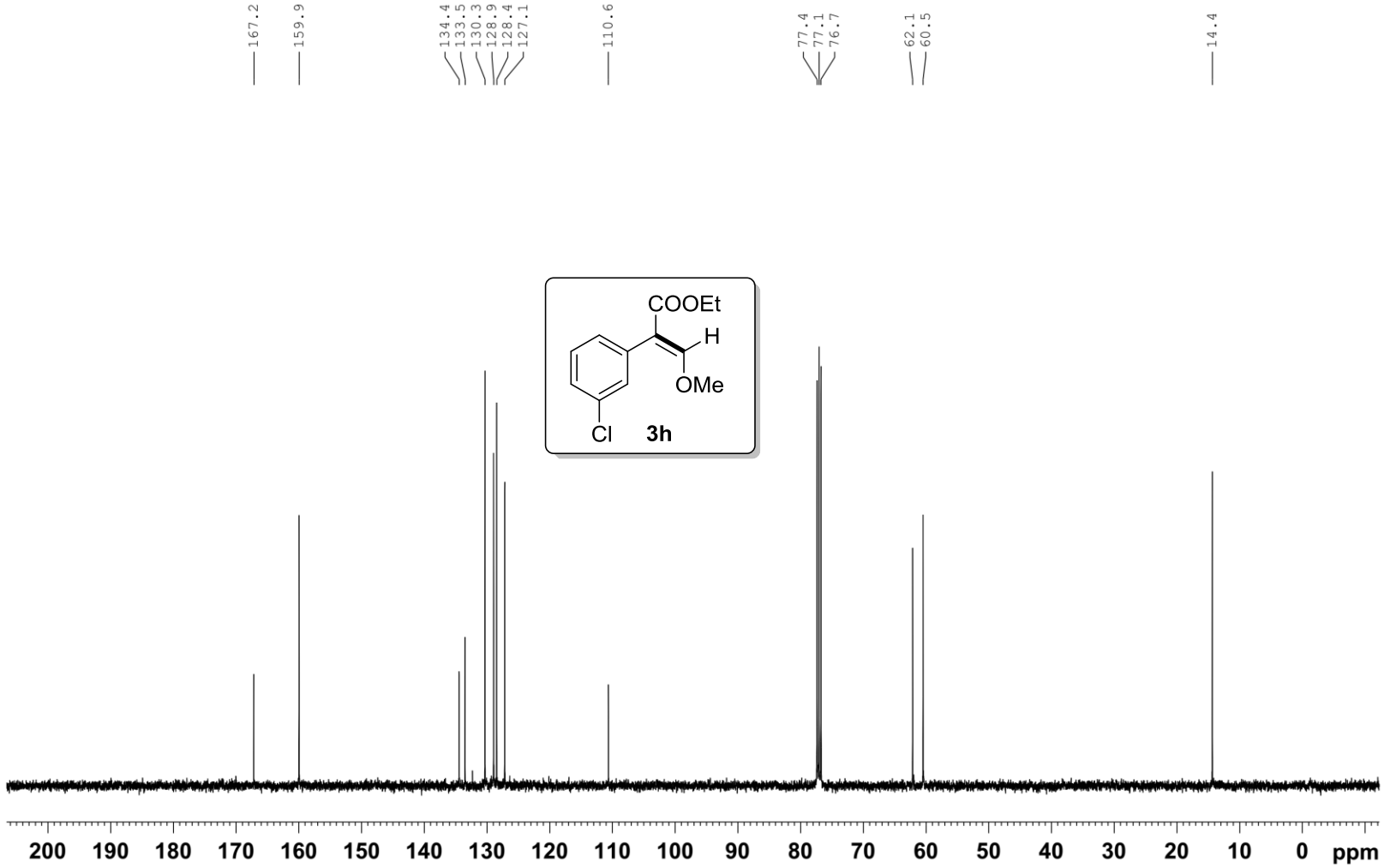

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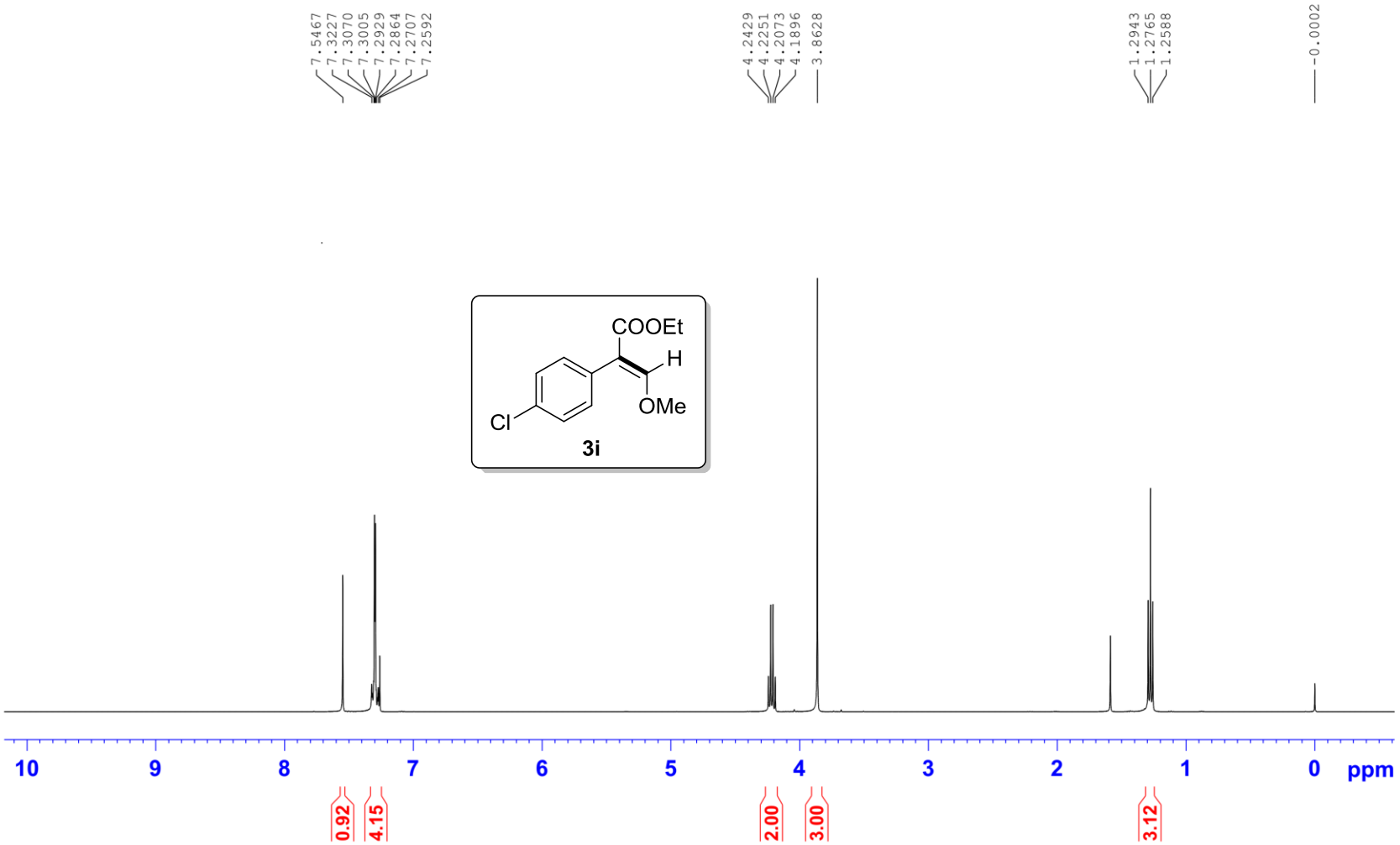

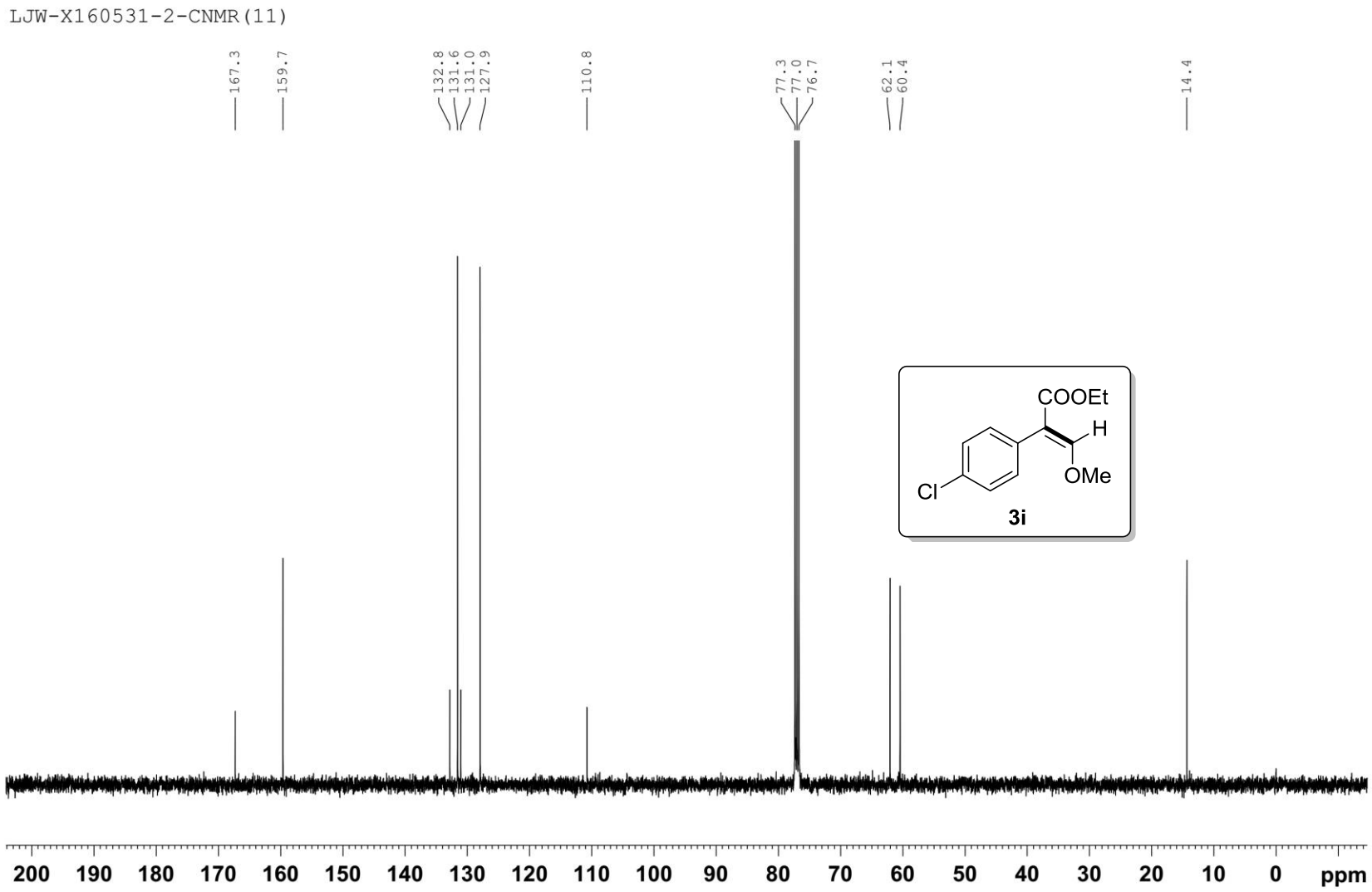
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132.8
131.6
131.0
127.9
110.8
77.3
77.0
76.7
62.1
60.4
14.4
COOEt
H
OMe
Cl
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

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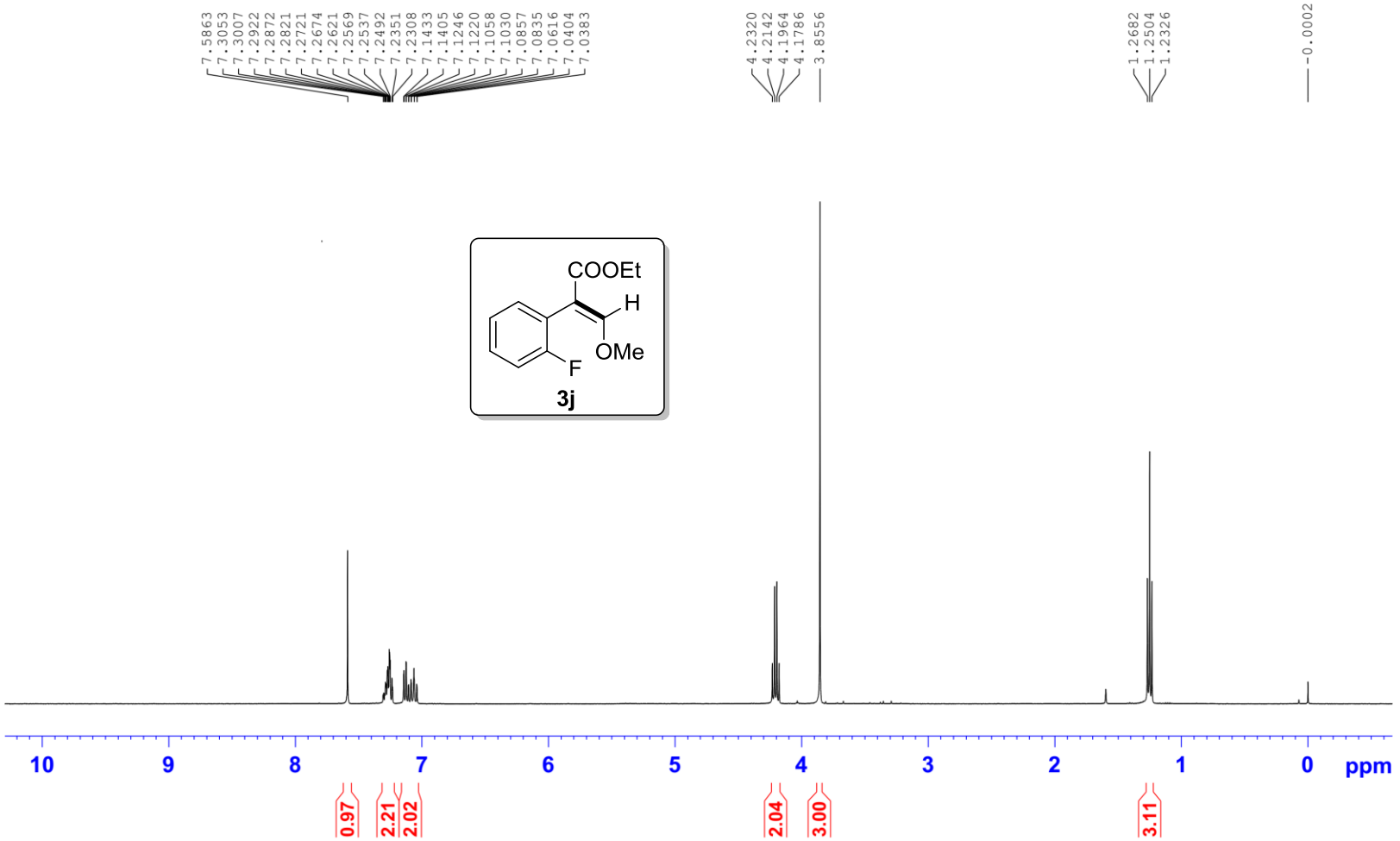

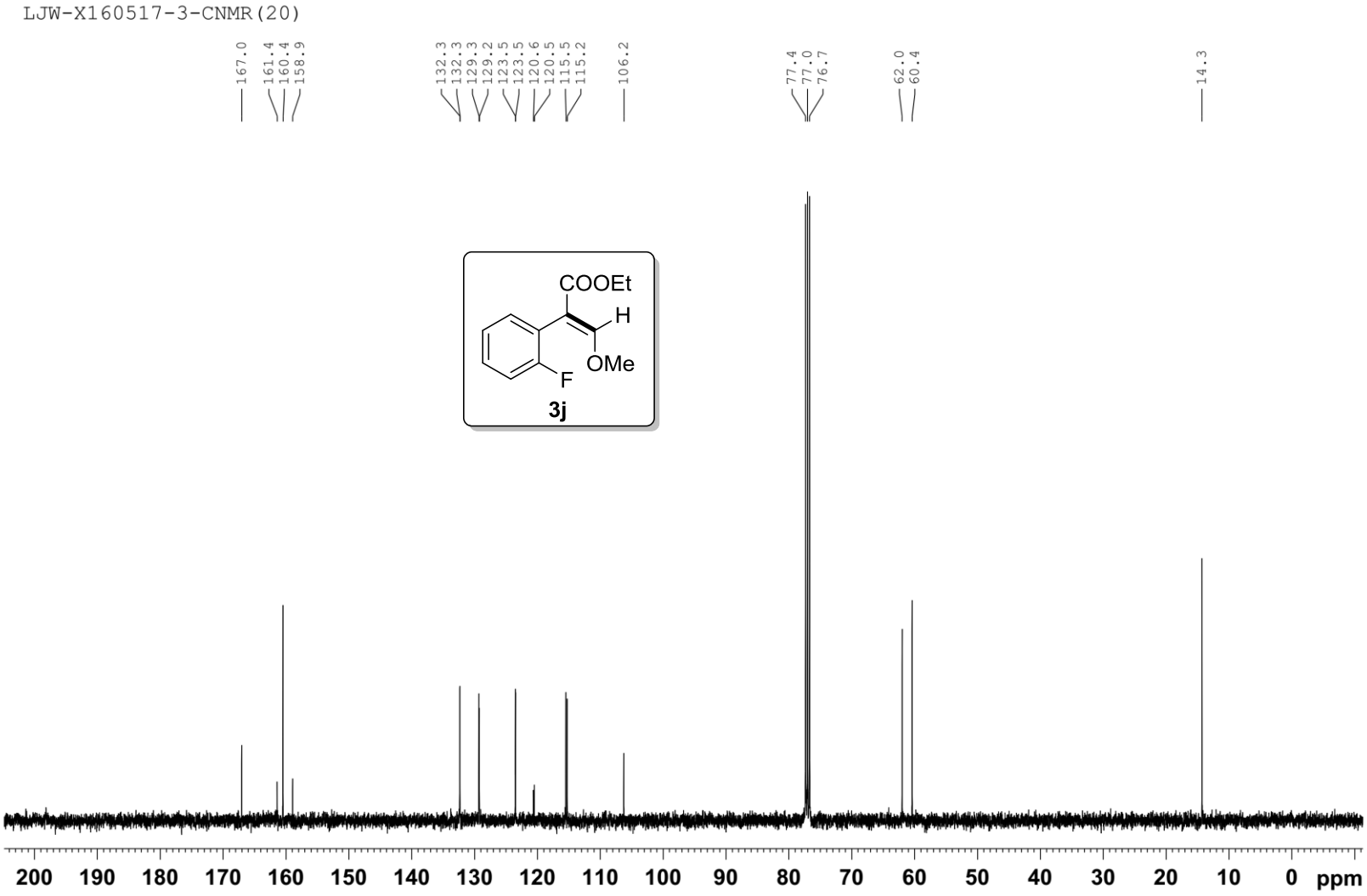
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160.4
158.9
132.3
132.3
129.3
129.2
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123.5
120.6
120.5
115.5
115.2
106.2
77.4
77.0
76.7
62.0
60.4
14.3
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H
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F
3j
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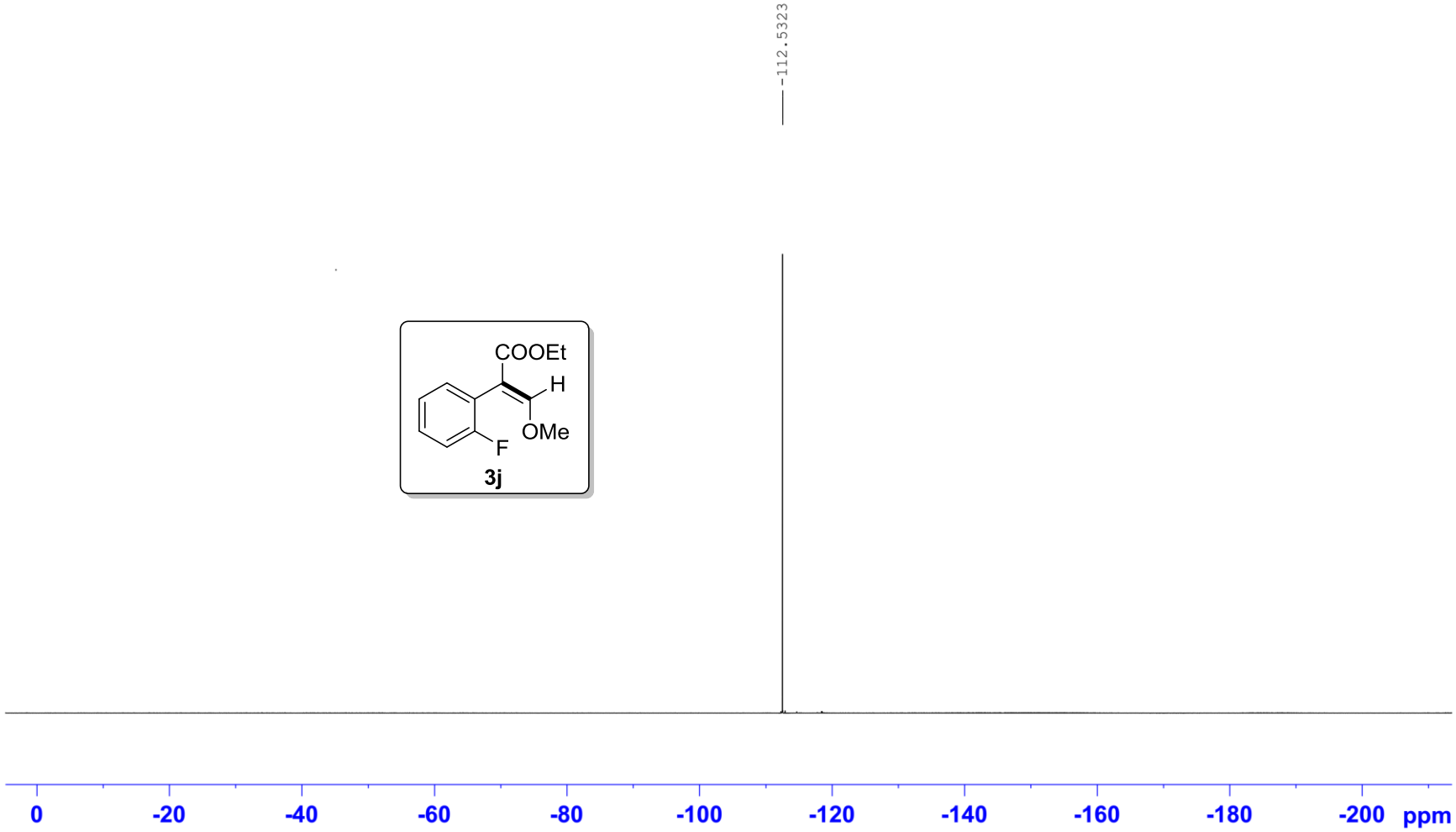
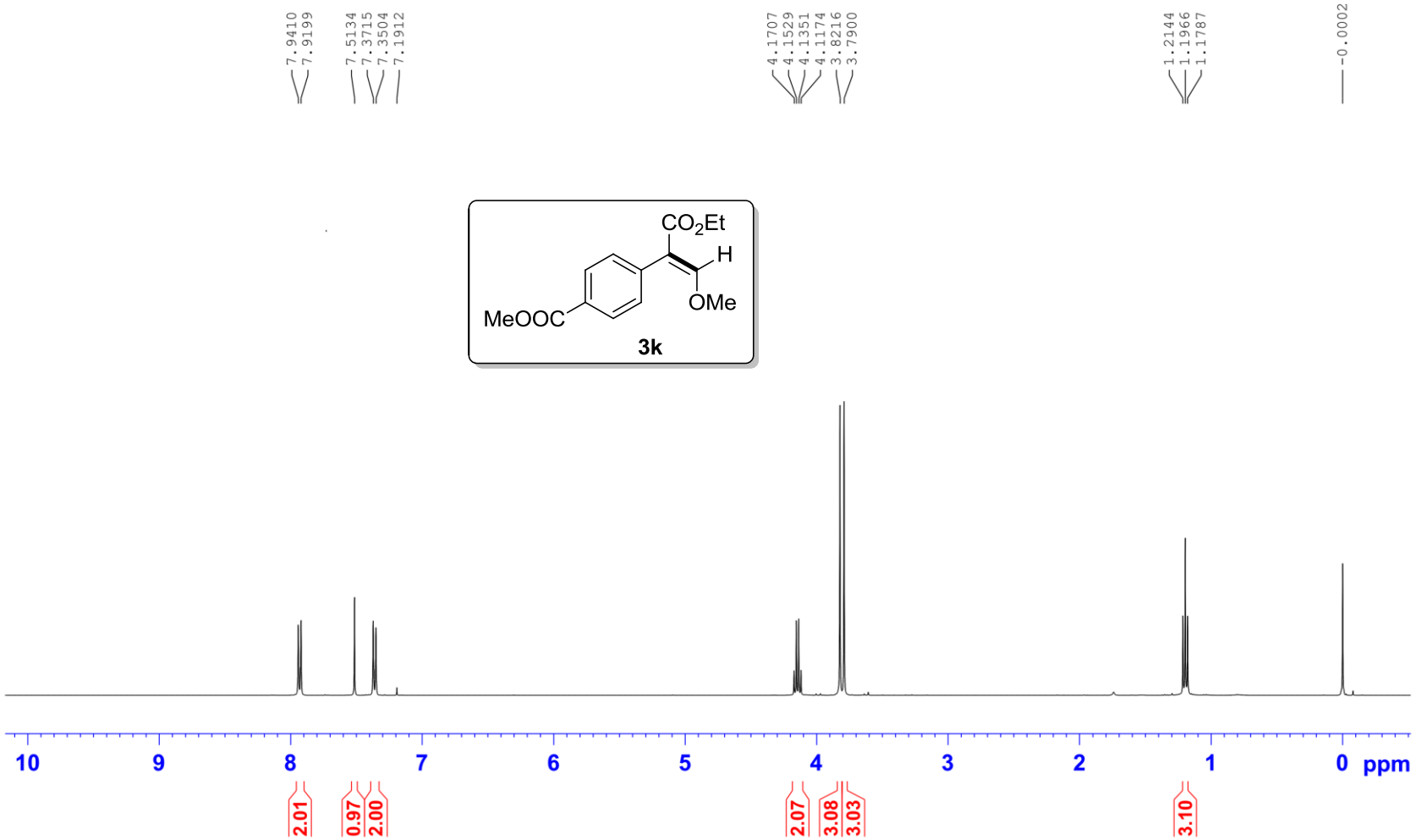
LJW-X160516-4-FNMR(31)



LJW-X180914-1-HNMR



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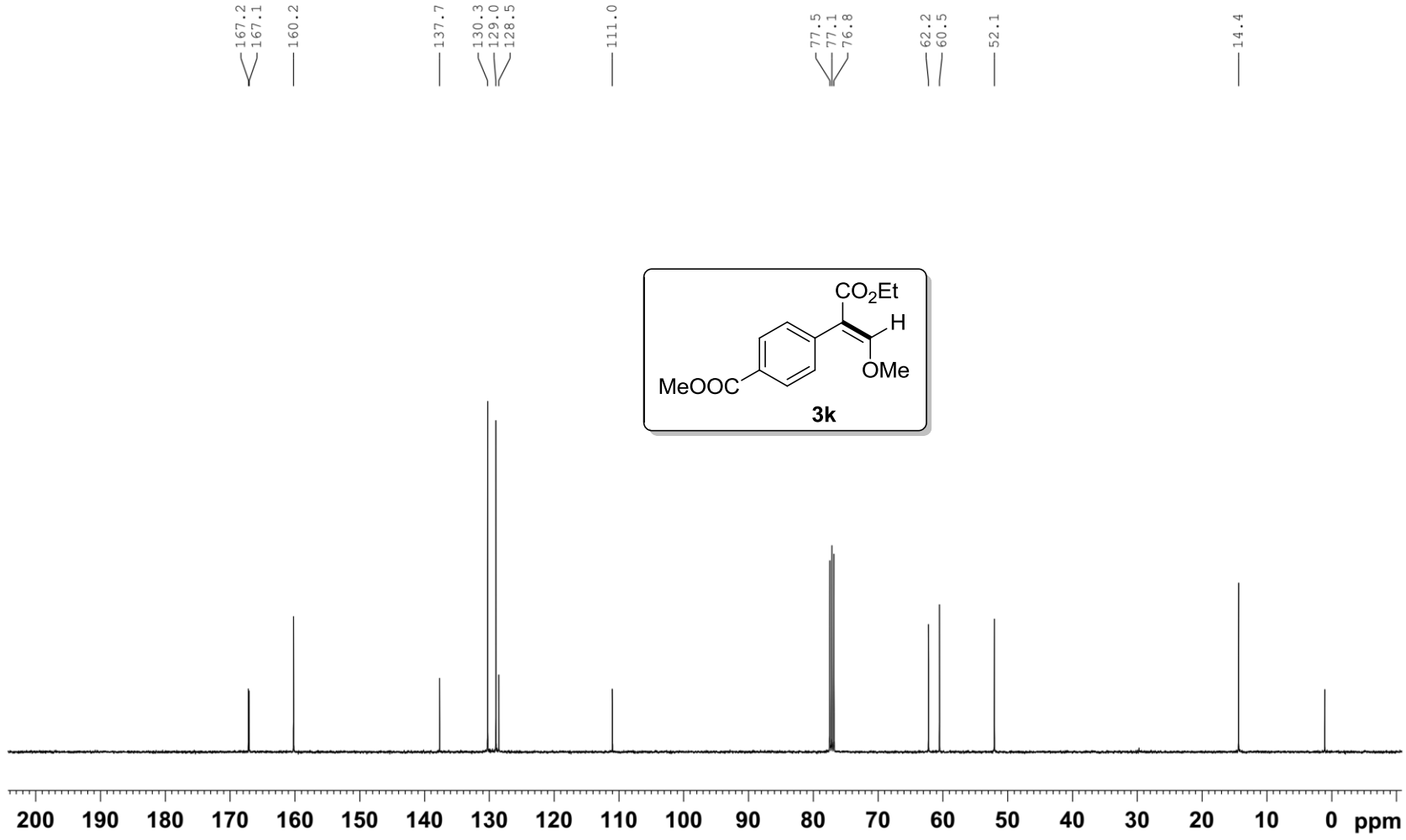

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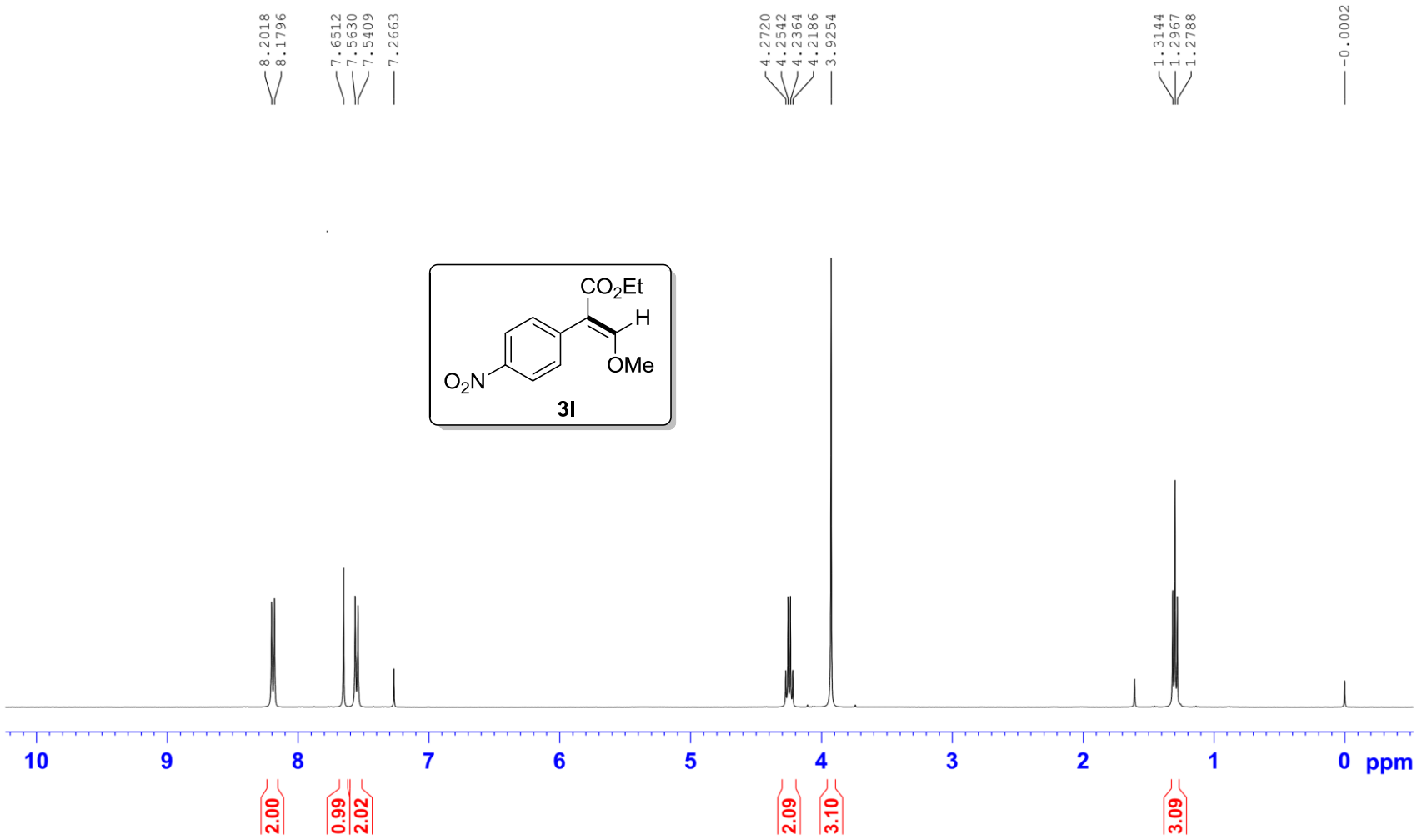

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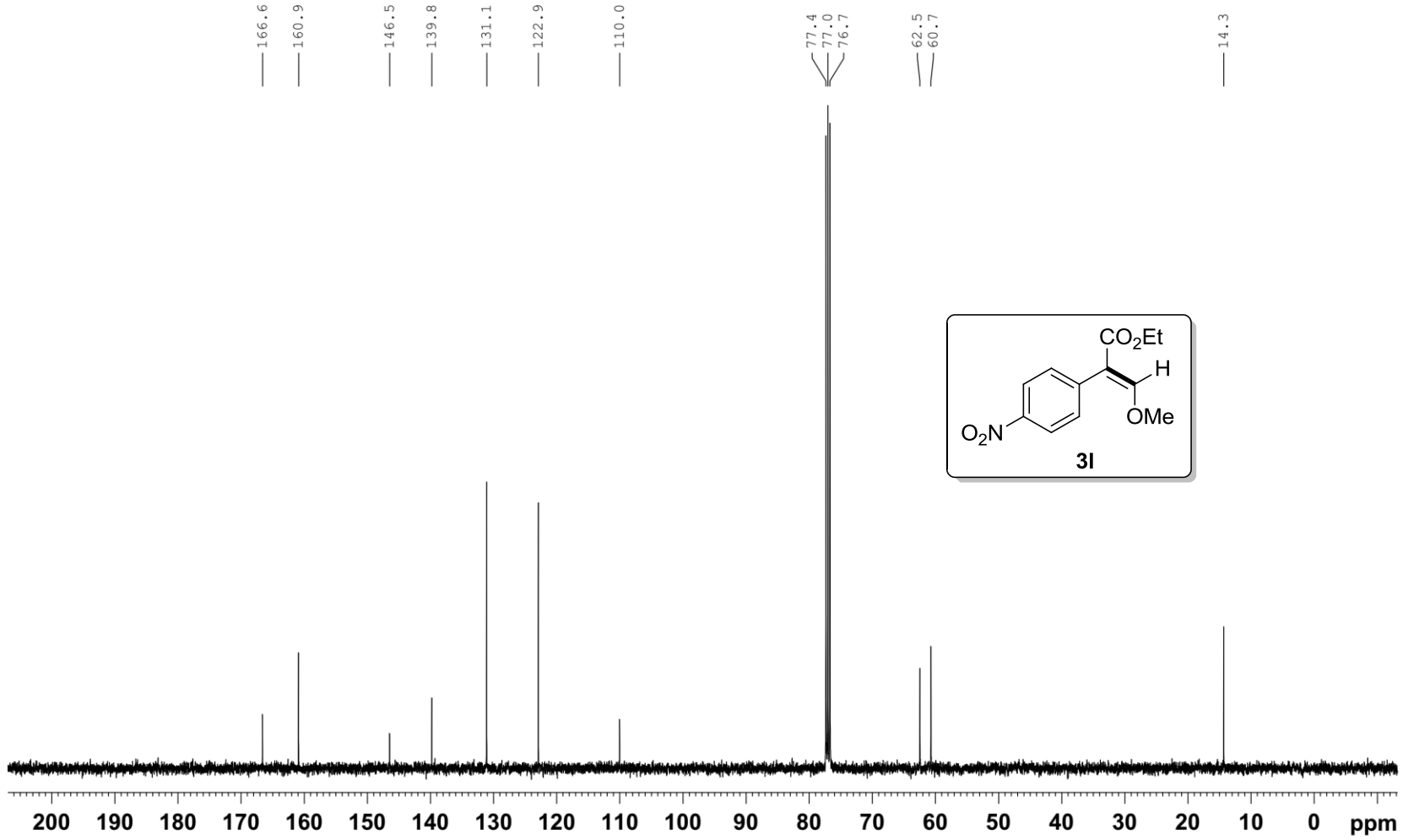

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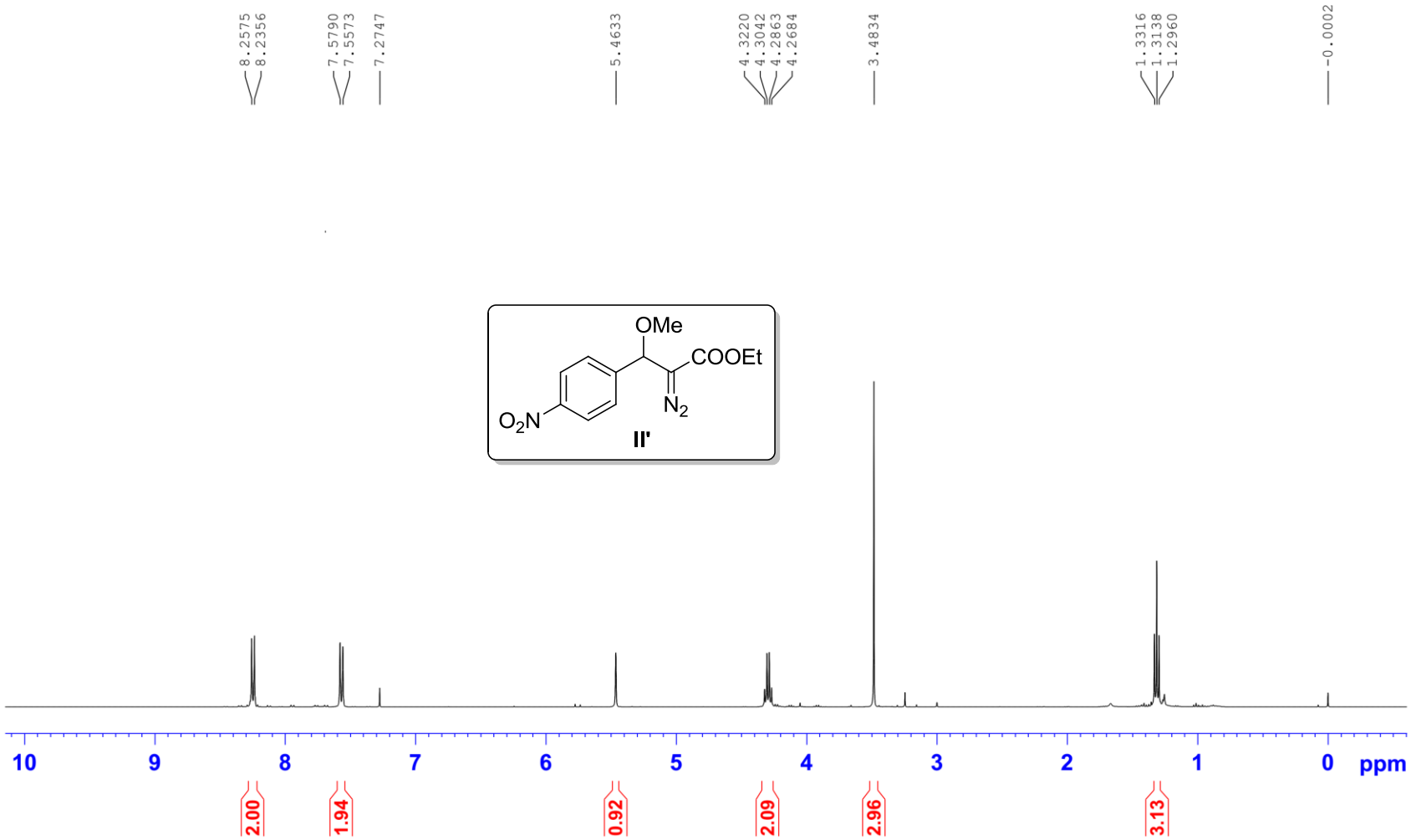

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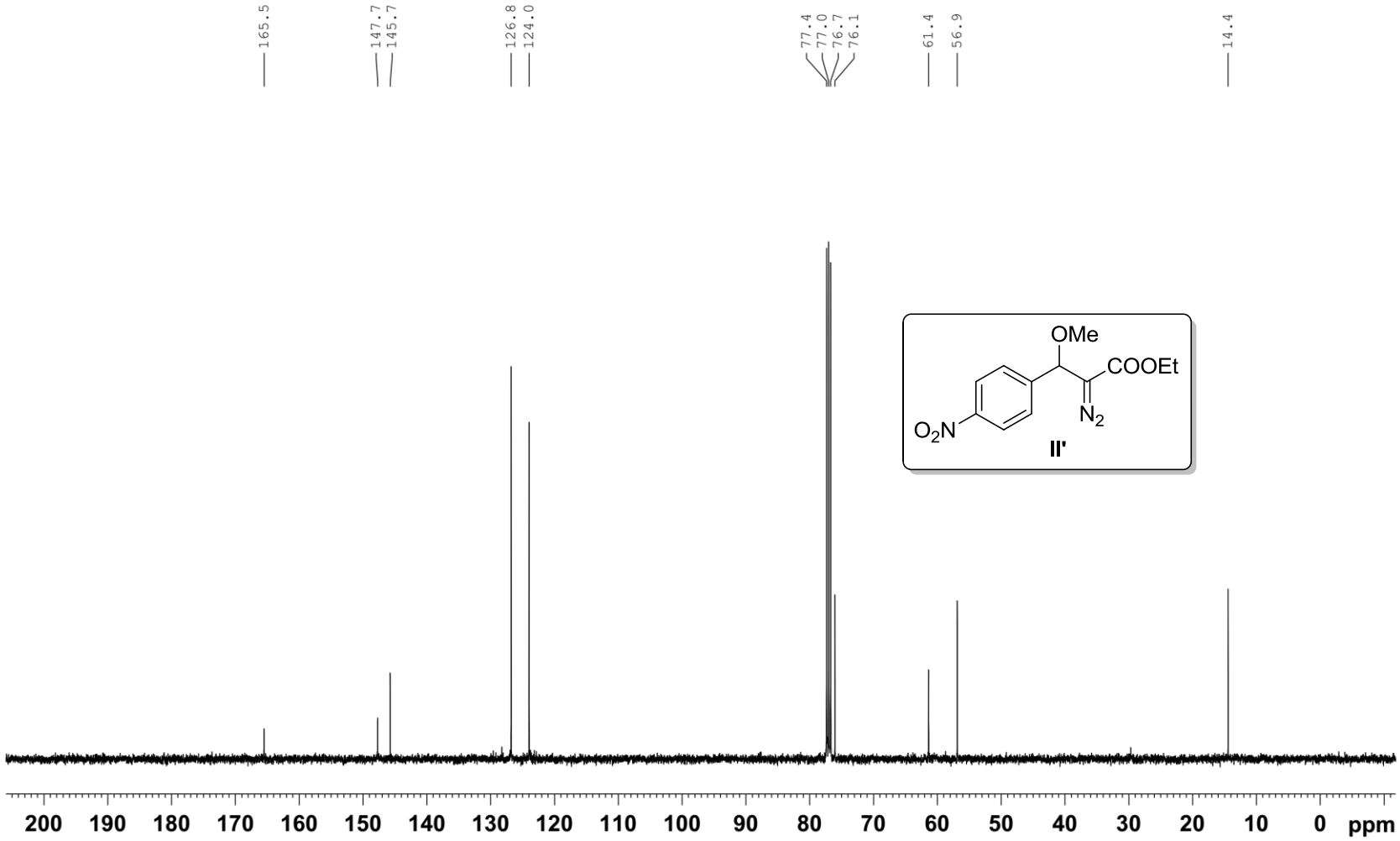

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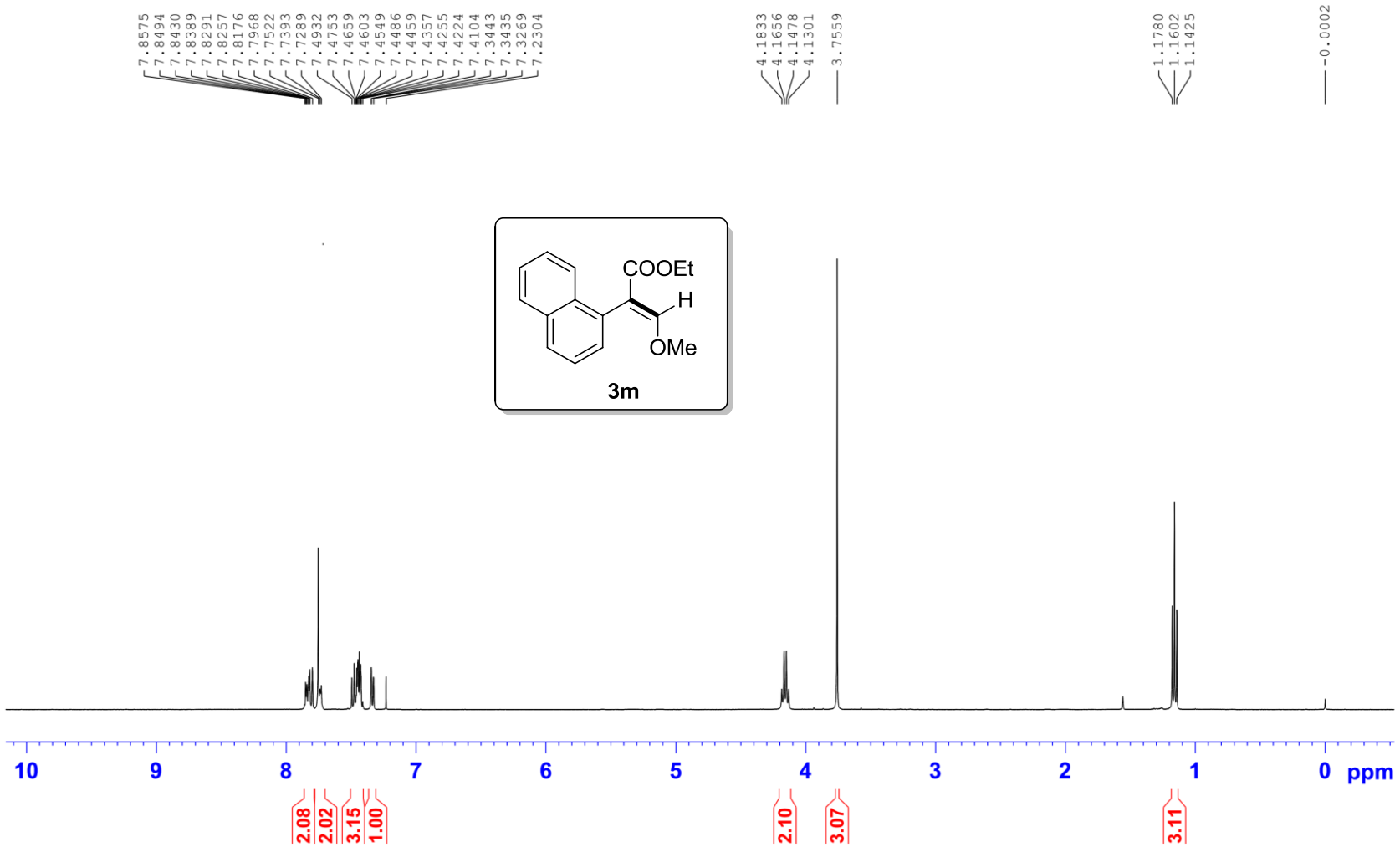

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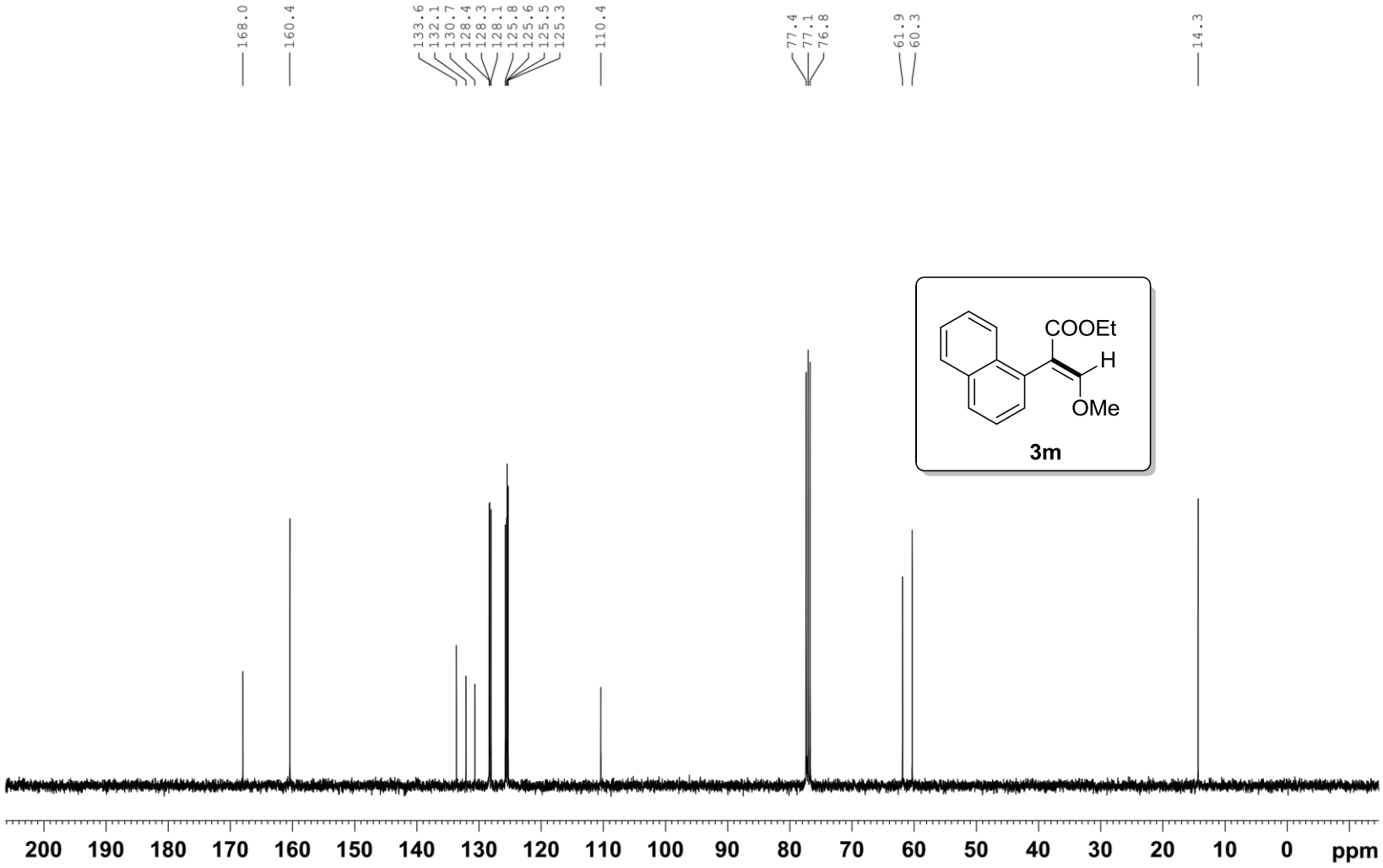

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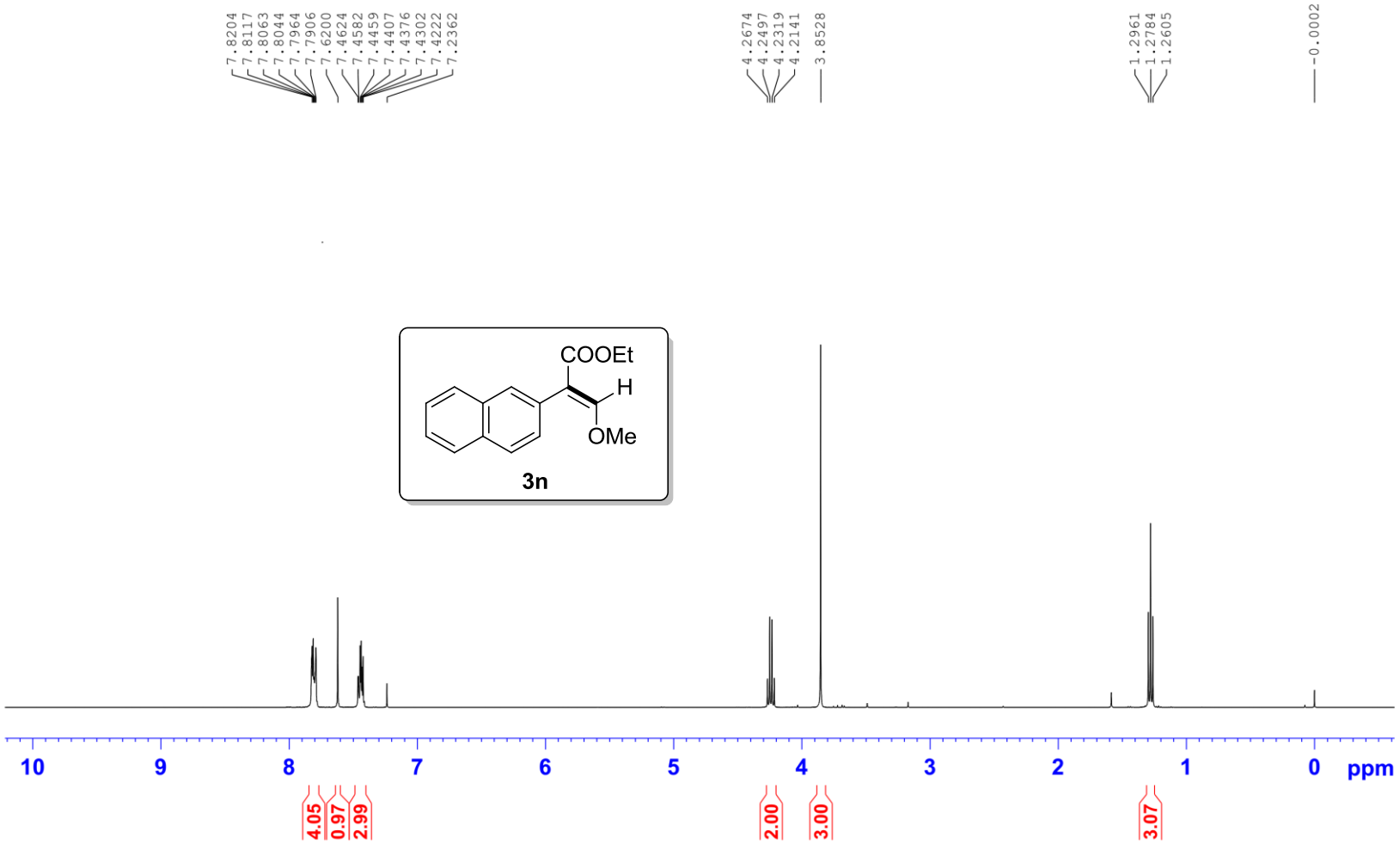

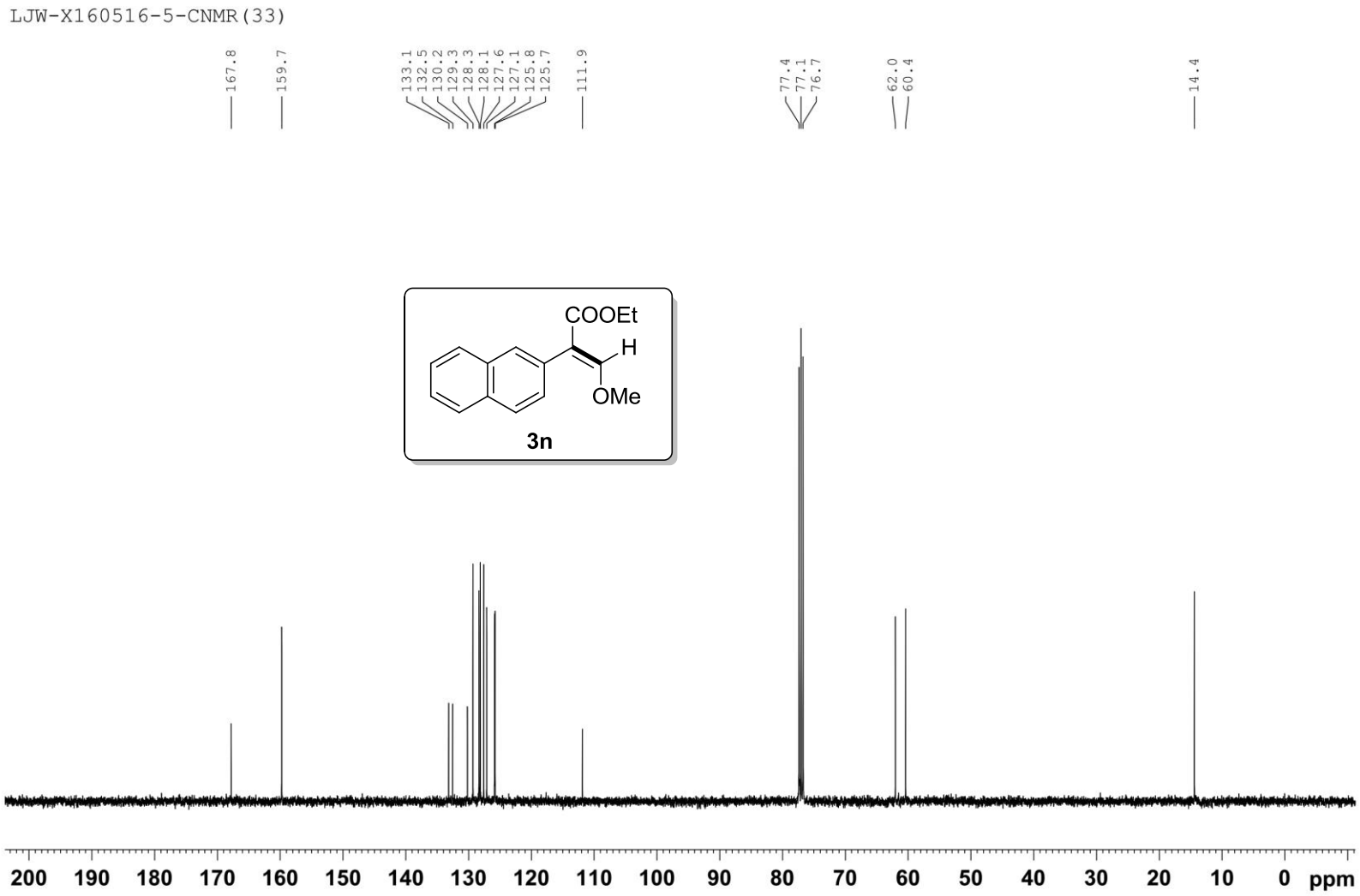
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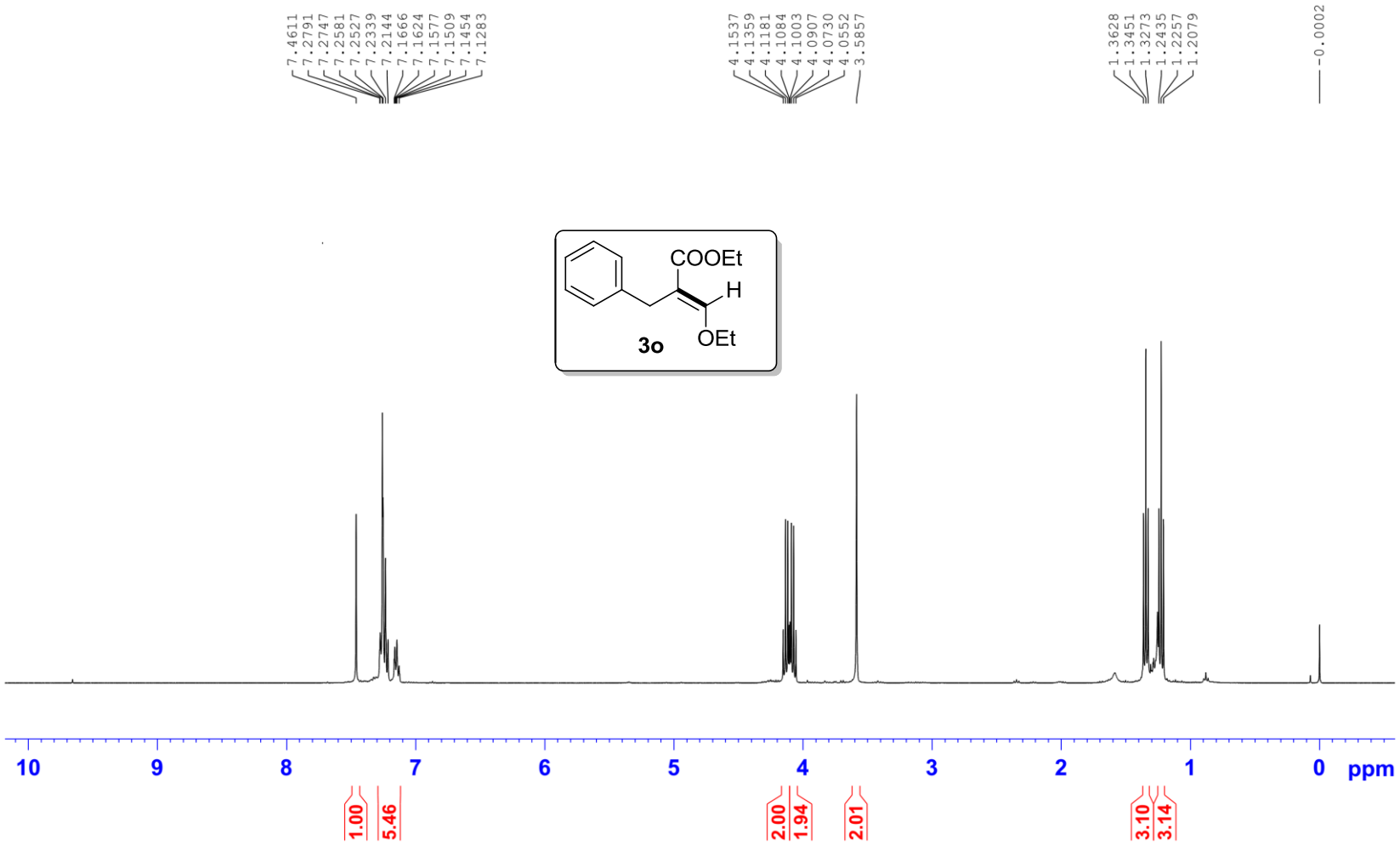
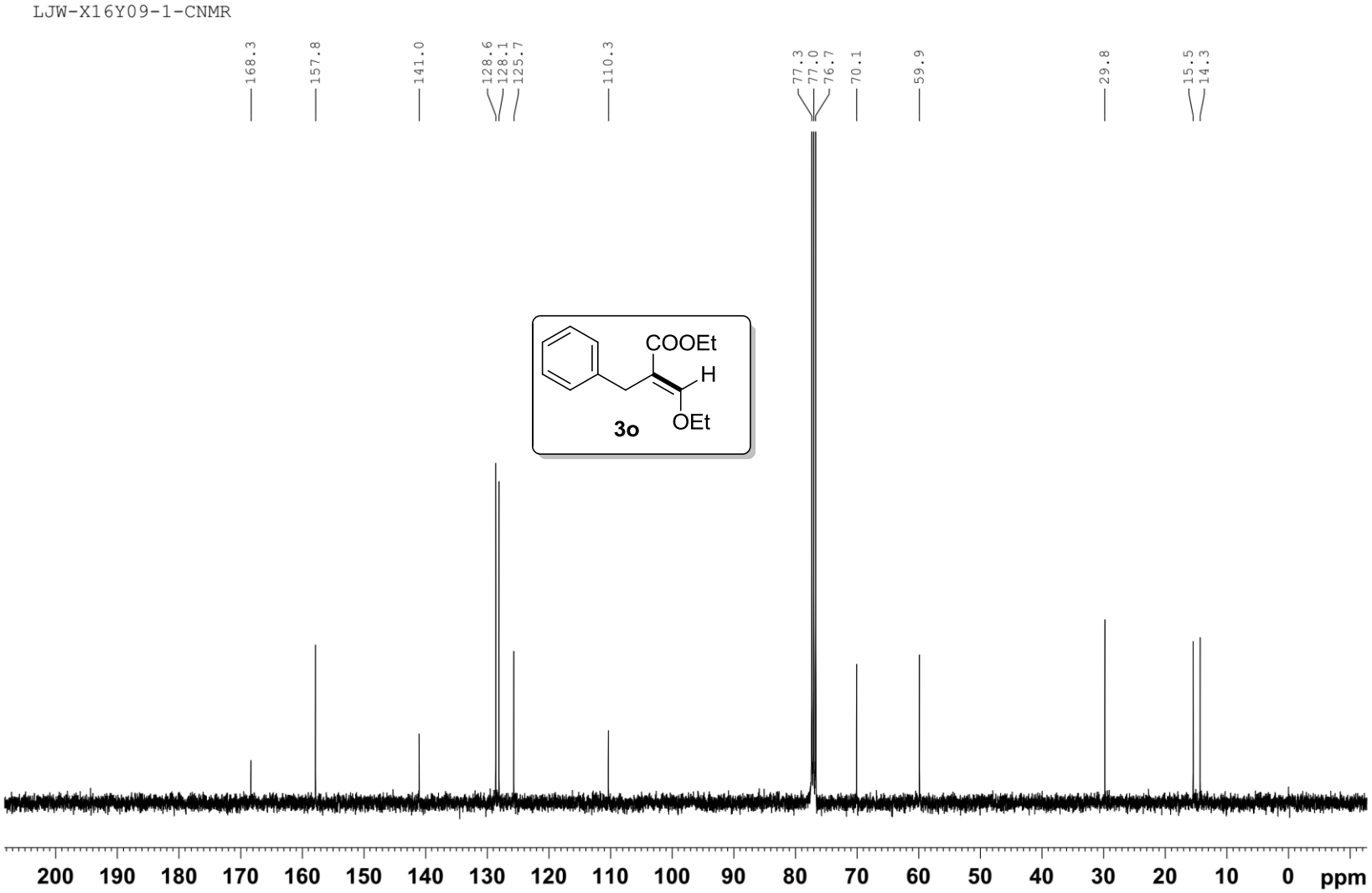
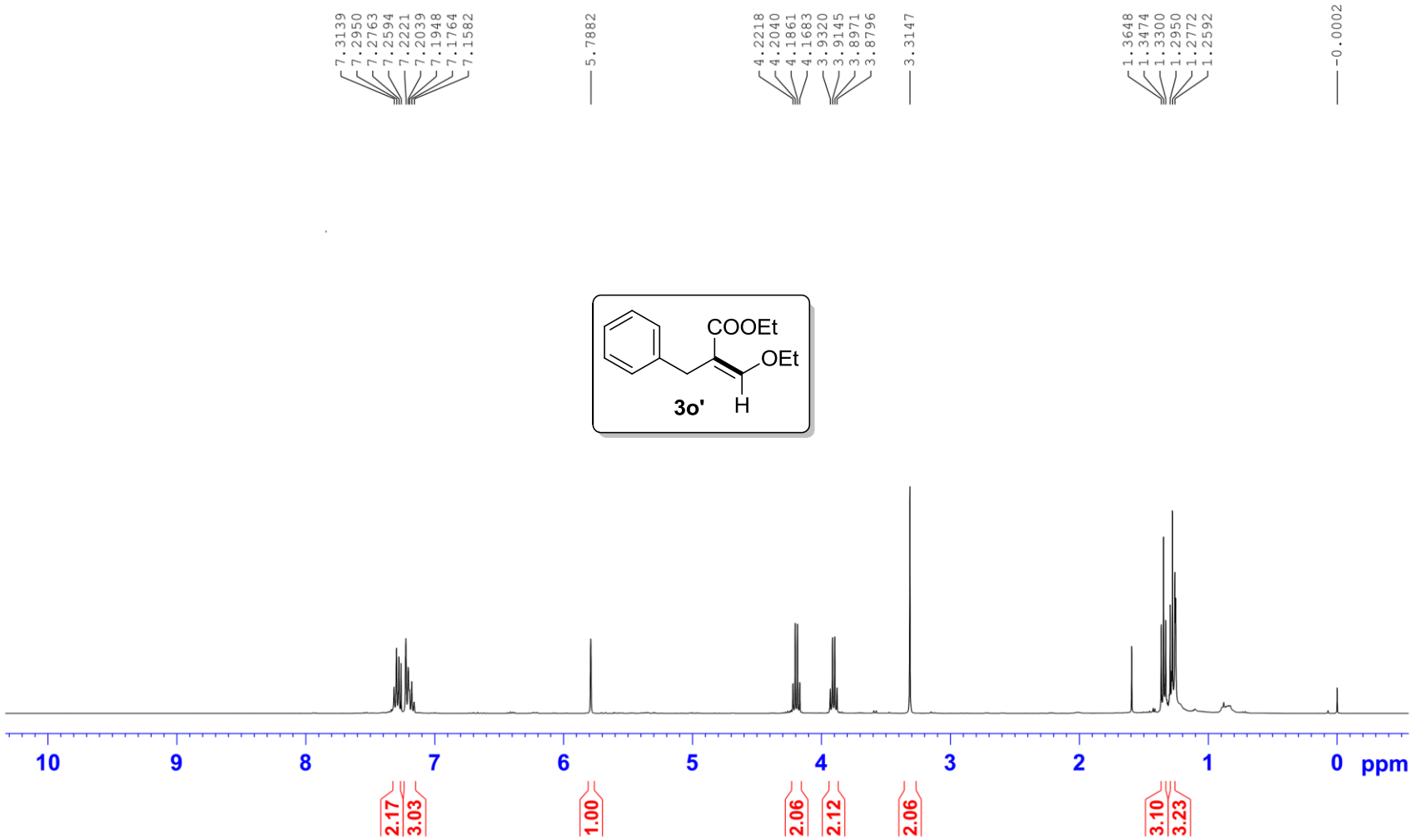
130.2
129.3
128.3
128.1
127.6
127.1
125.8
125.7
111.9
77.4
77.1
76.7
62.0
60.4
14.4
COOEt
H
OMe
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X16Y09-1-HNMR

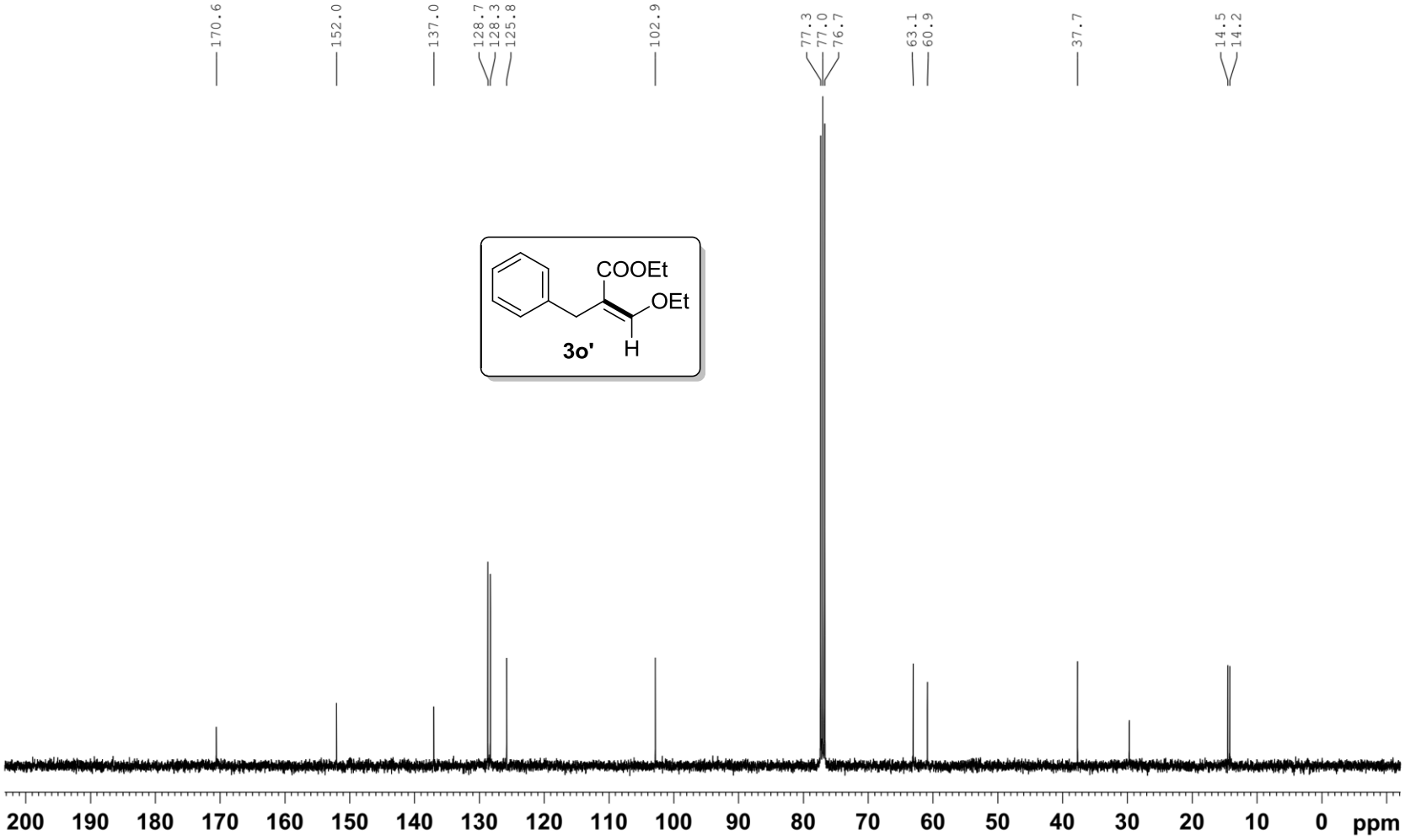



LJW-X16Y09-1-CNMR
168.3
157.8
141.0
128.6
128.1
125.7
110.3
77.3
77.0
76.7
70.1
59.9
29.8
15.5
14.3
COOEt
H
OEt
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

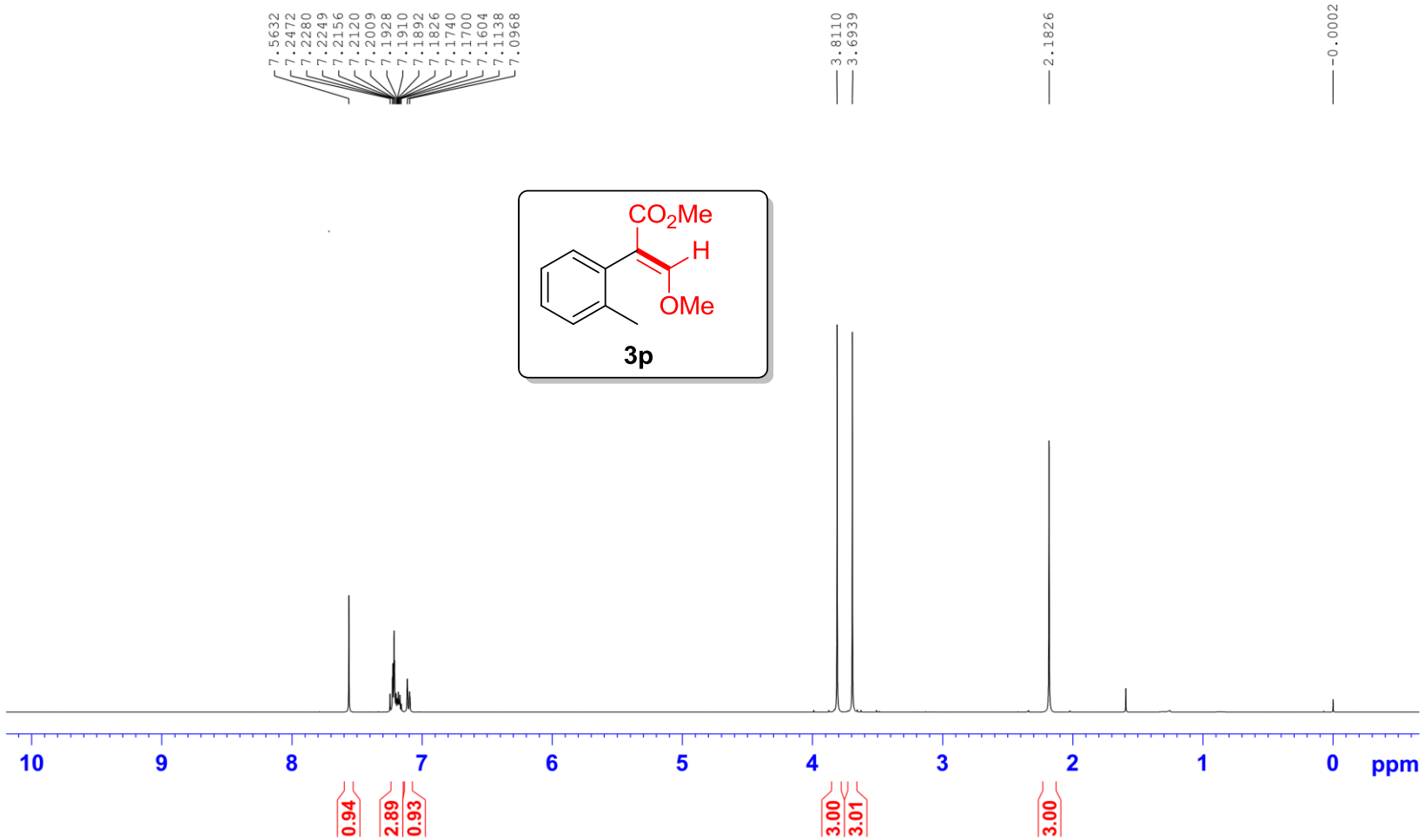
LJW-X180917-8-HNMR

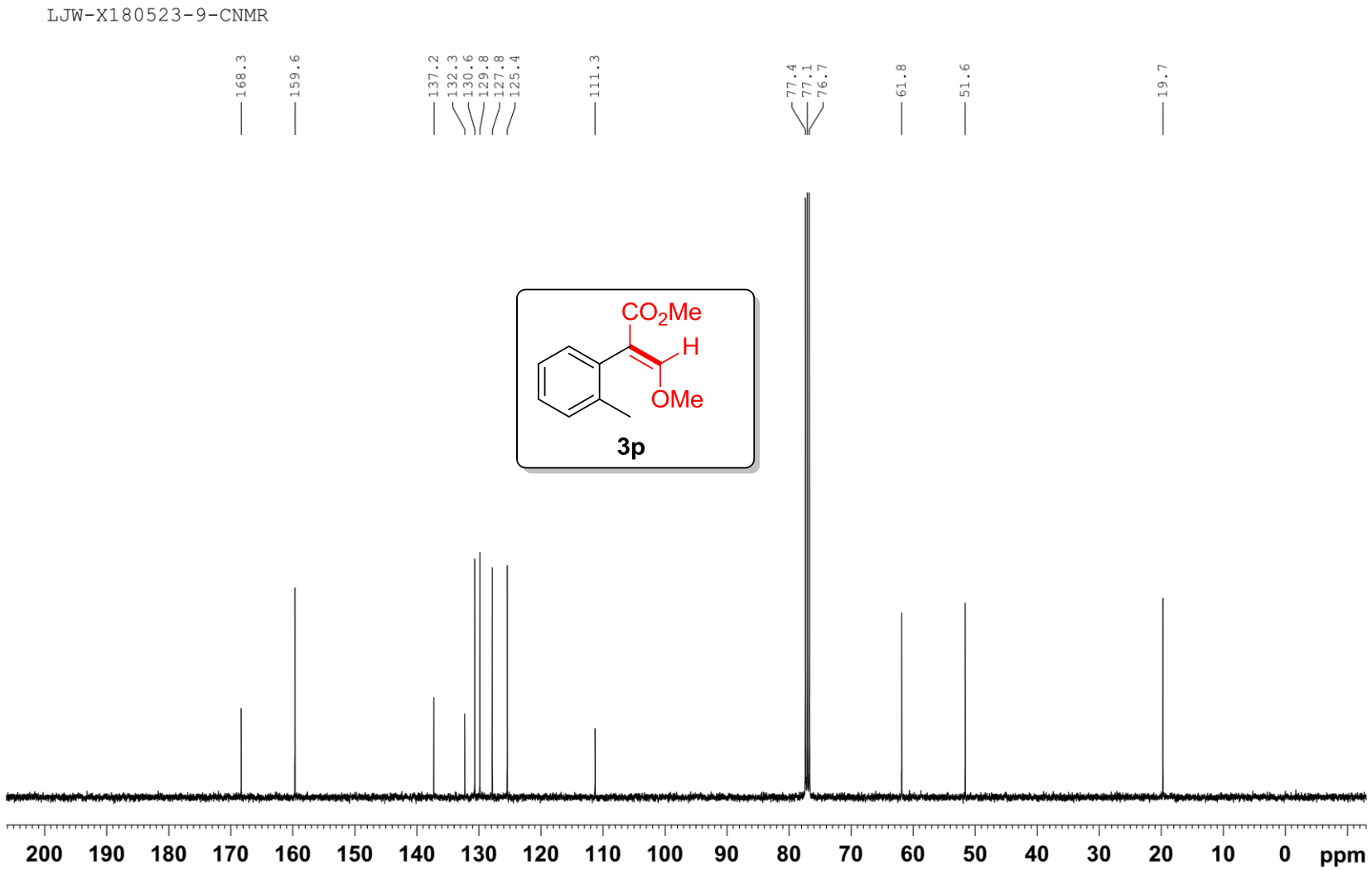


LJW-X180917-8-CNMR

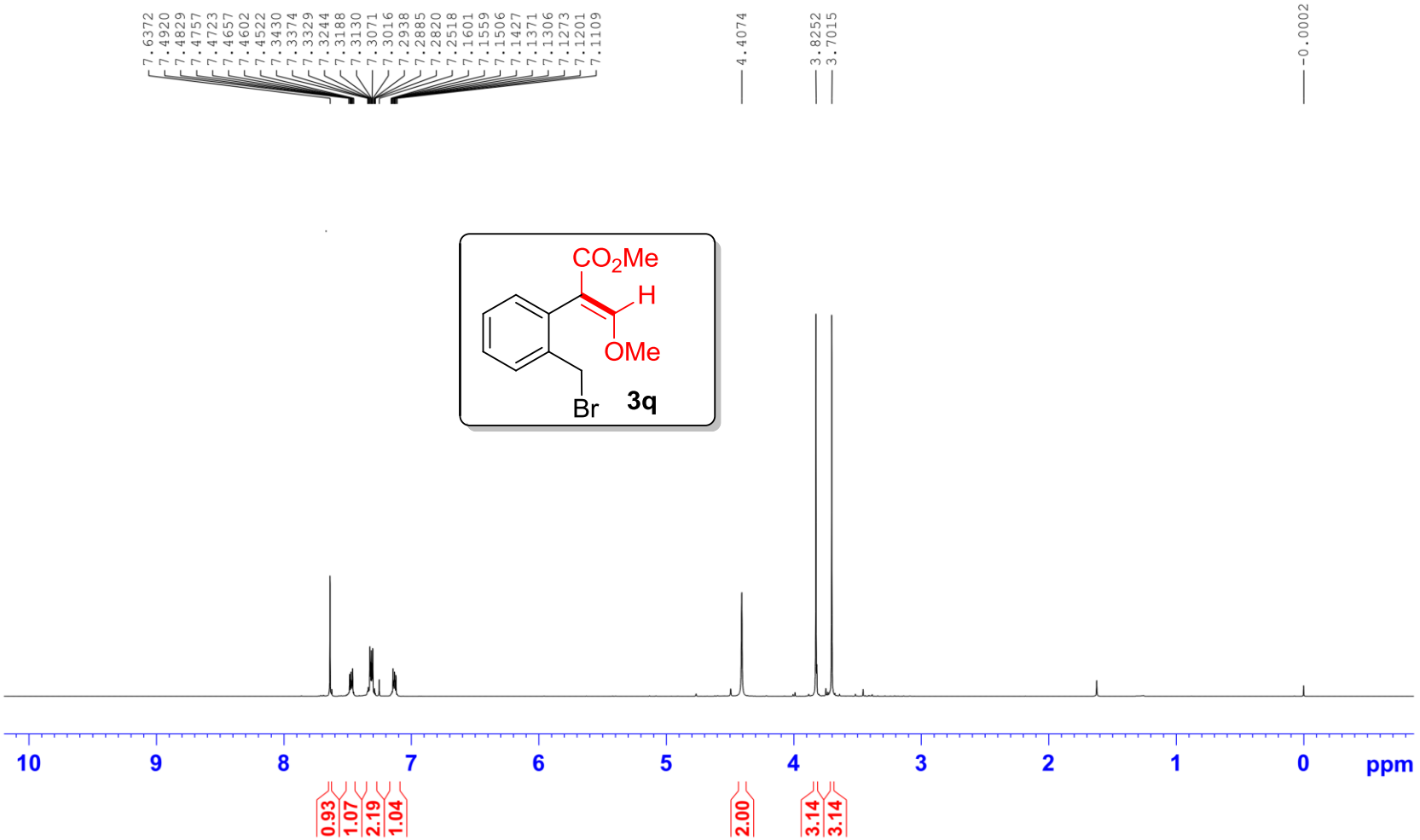


LJW-X180523-9-HNMR




LJW-X180523-9-CNMR
168.3
159.6
137.2
132.3
130.6
129.8
127.8
125.4
111.3
77.4
77.1
76.7
61.8
51.6
19.7
CO2Me
H
OMe
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X180507-1-HNMR



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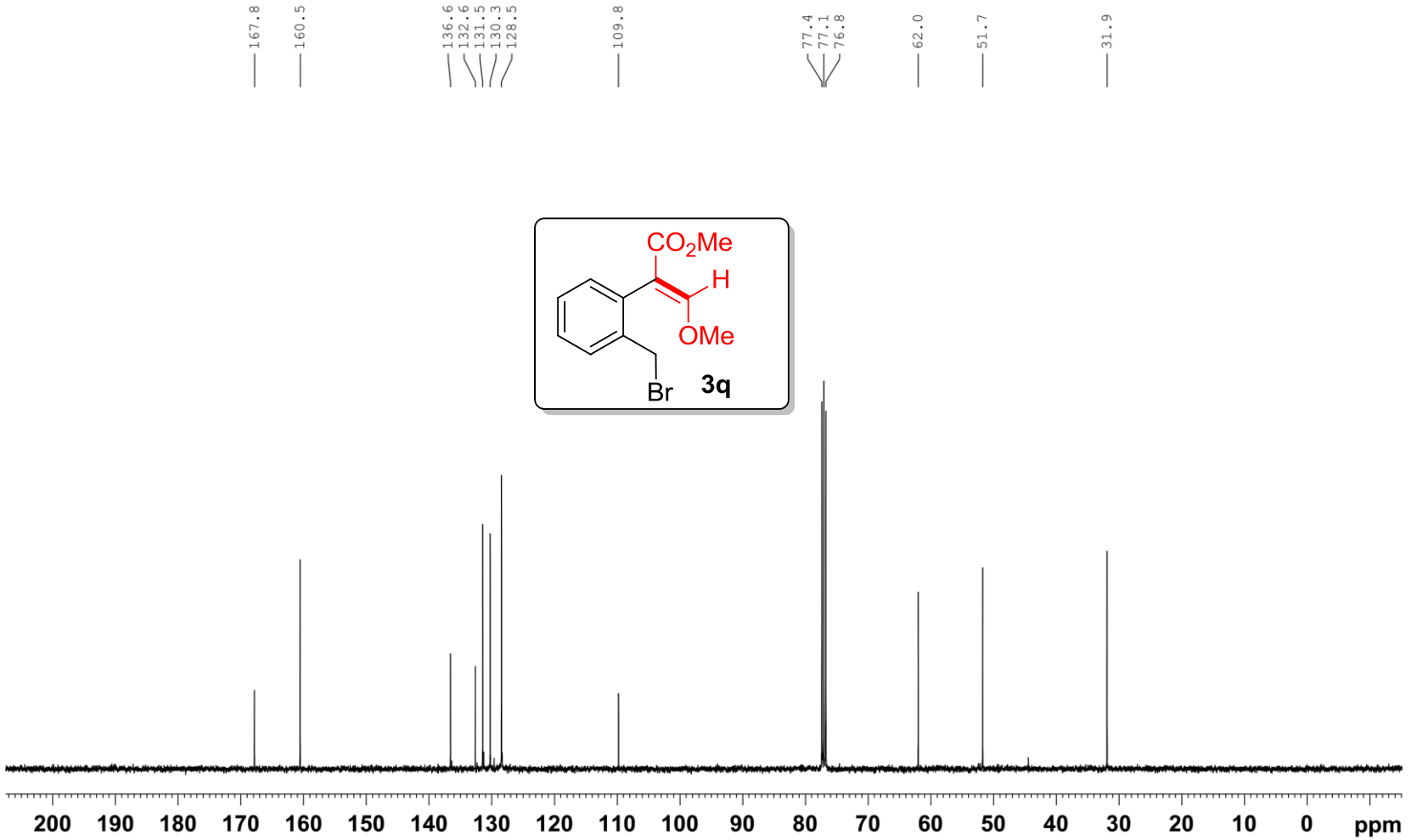

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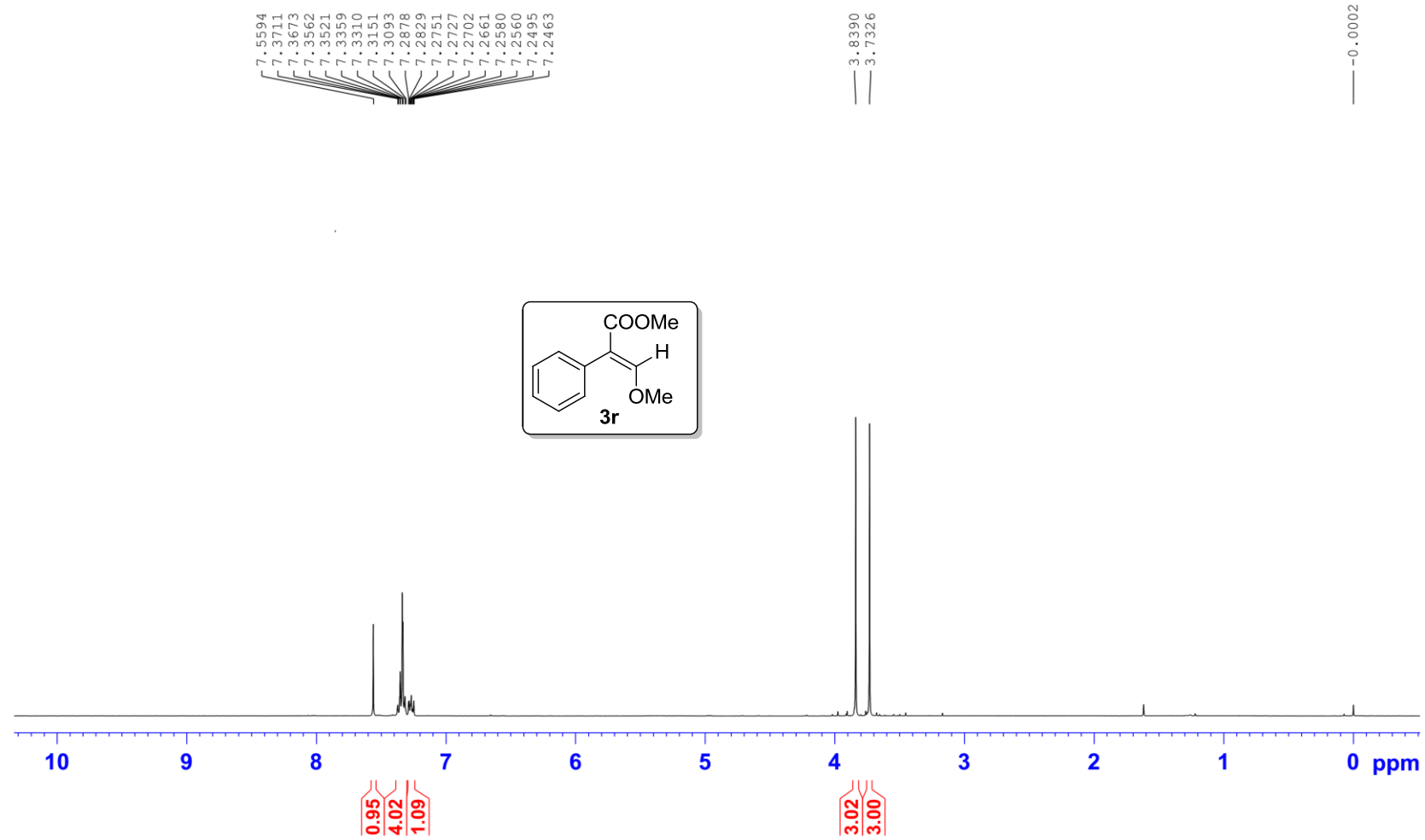

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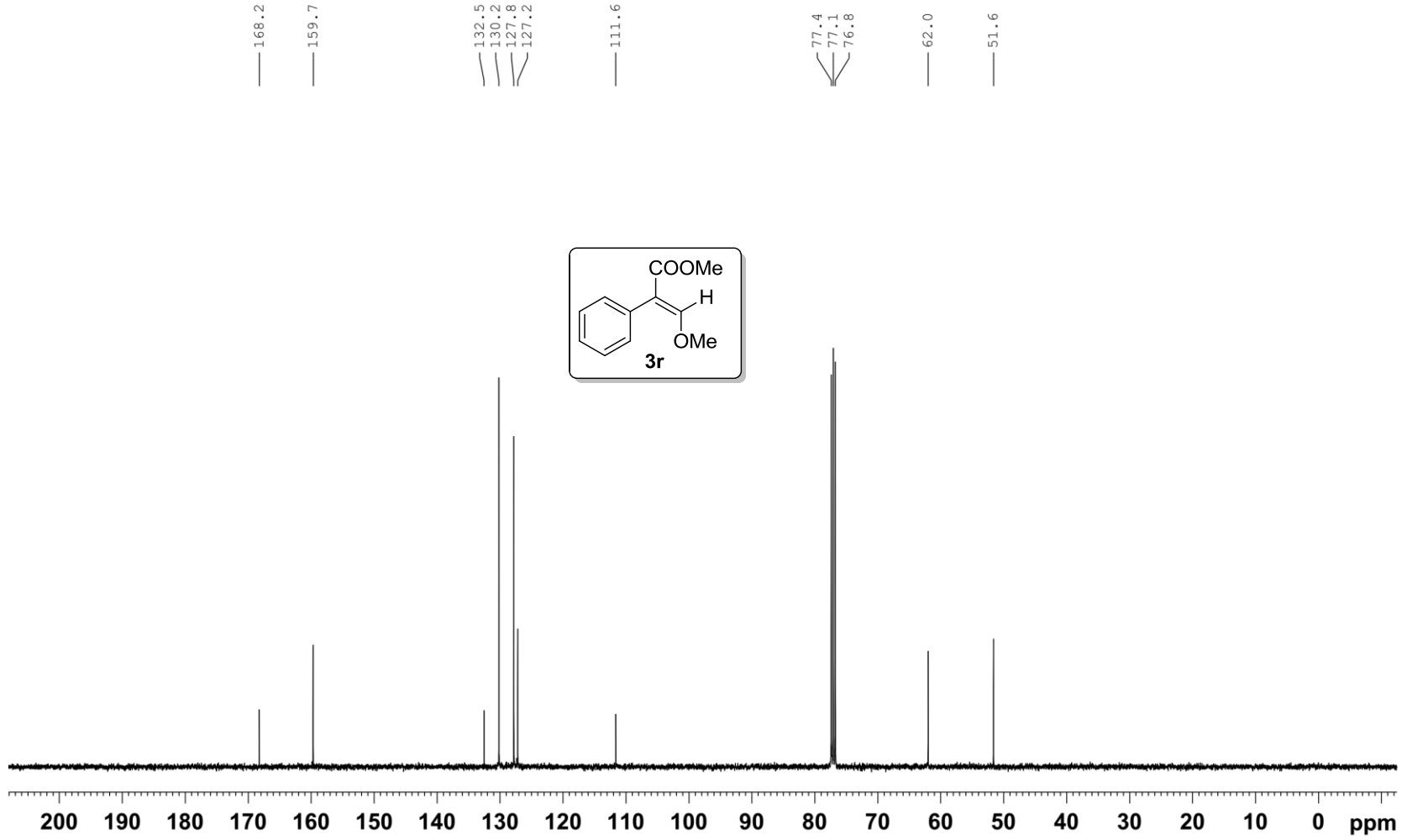
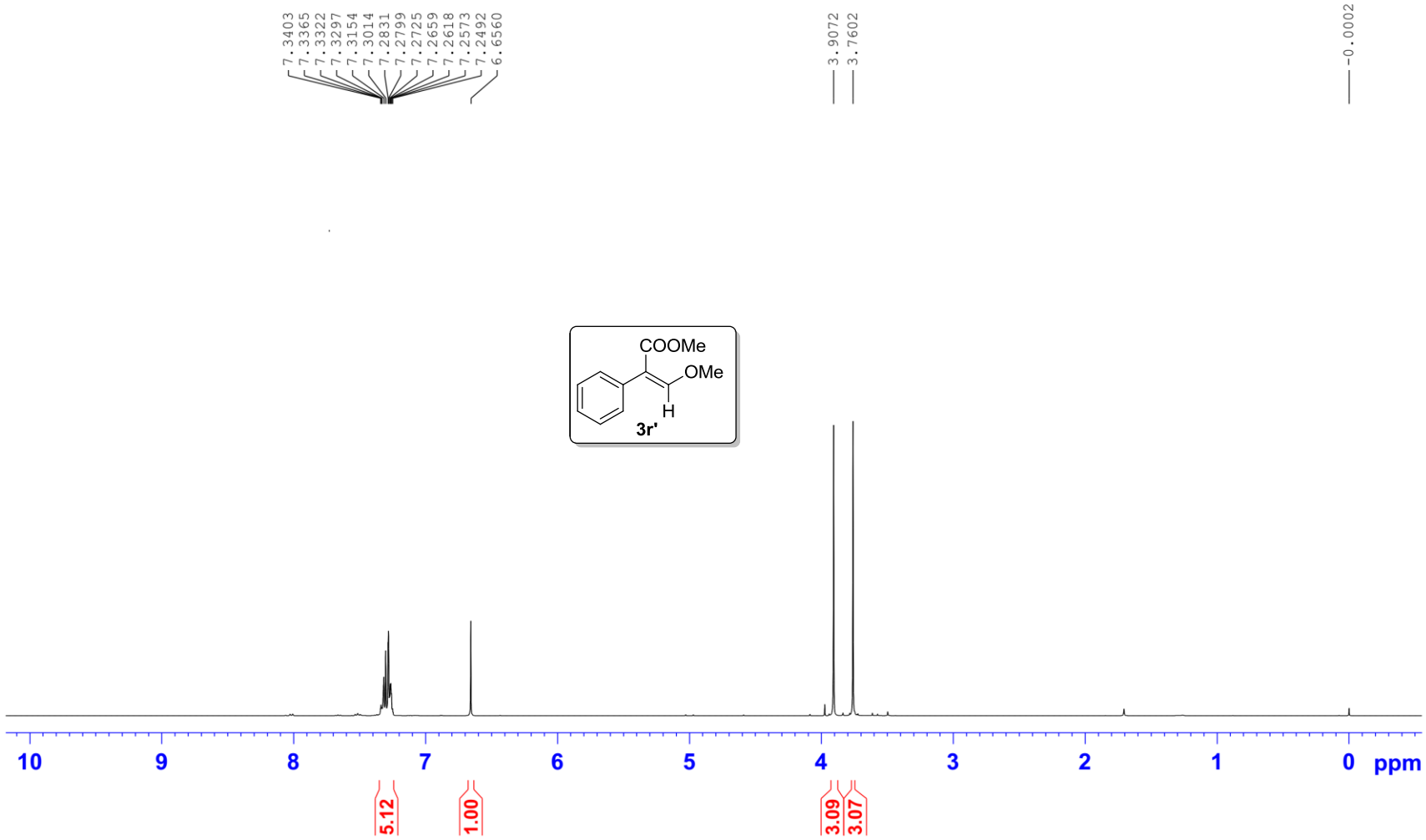


LJW-X180923-2-HNMR



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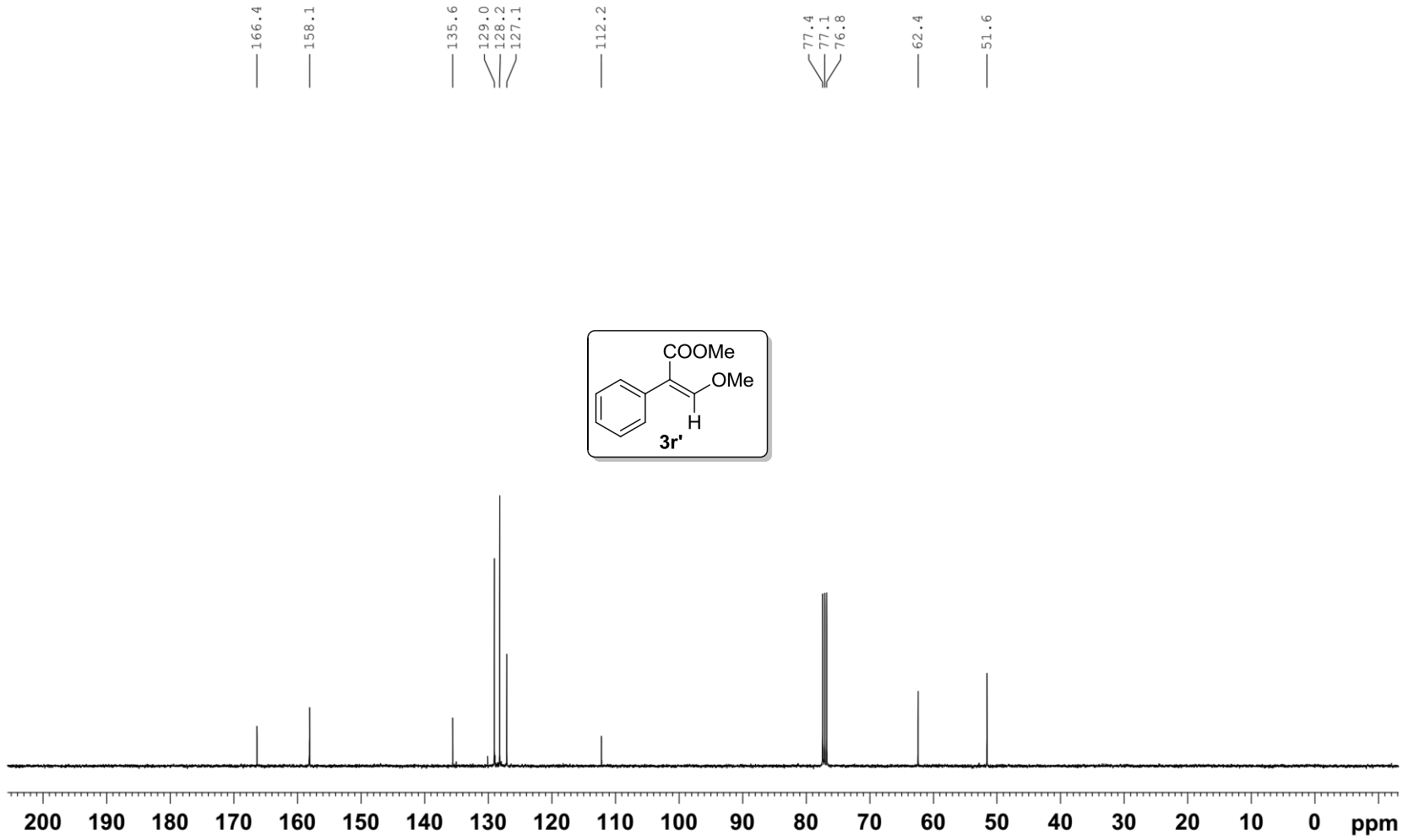
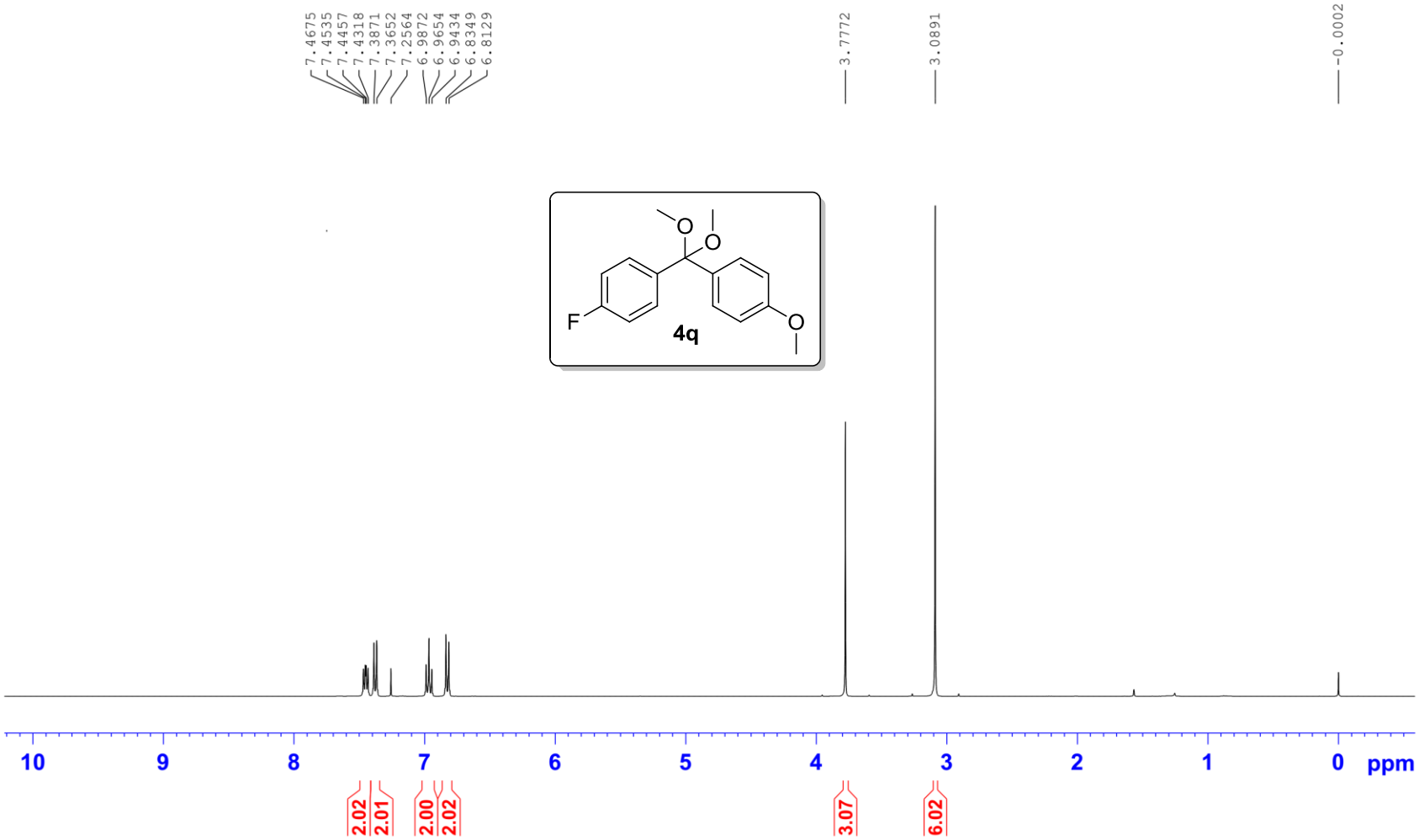


LJW-X180910-2HNMR



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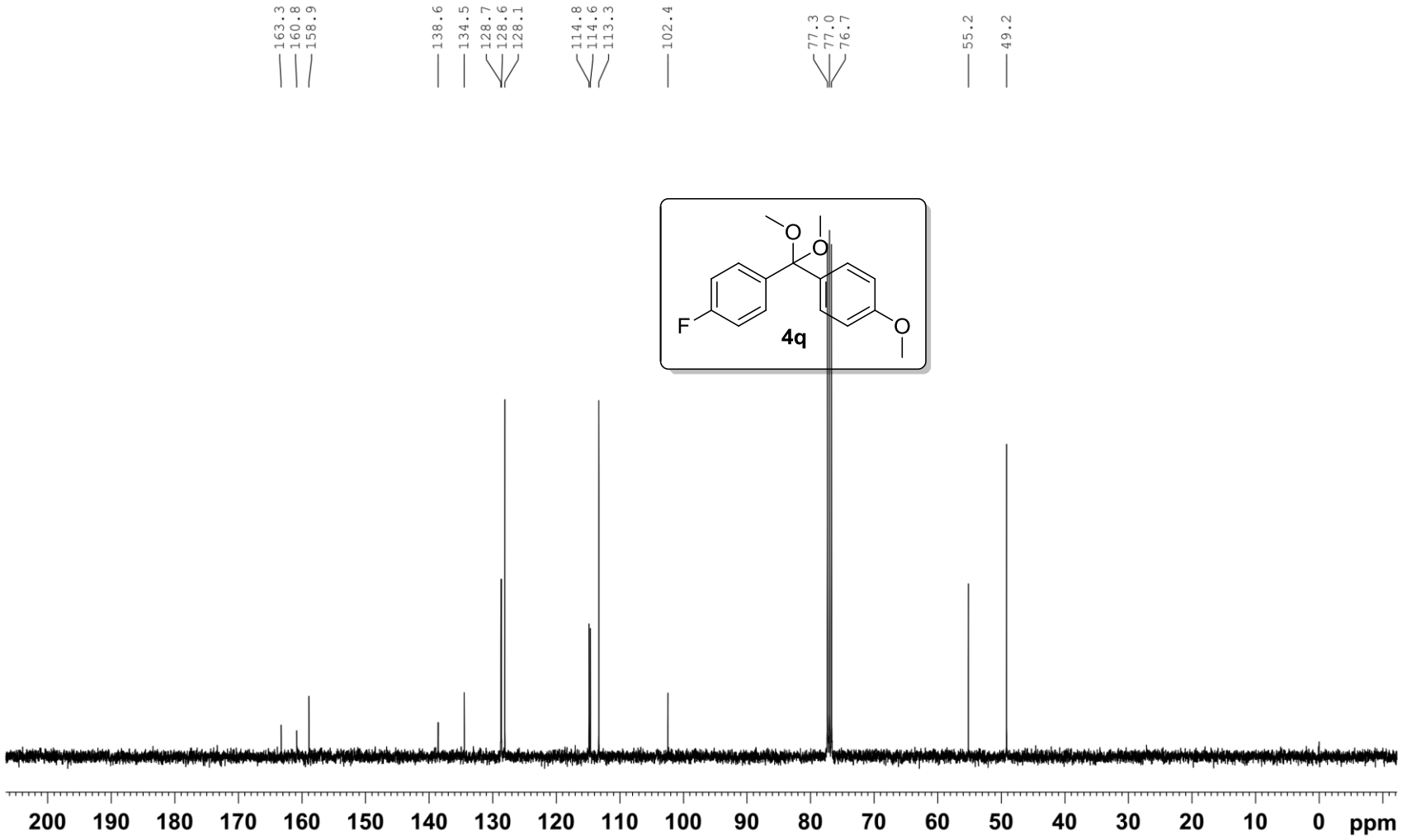

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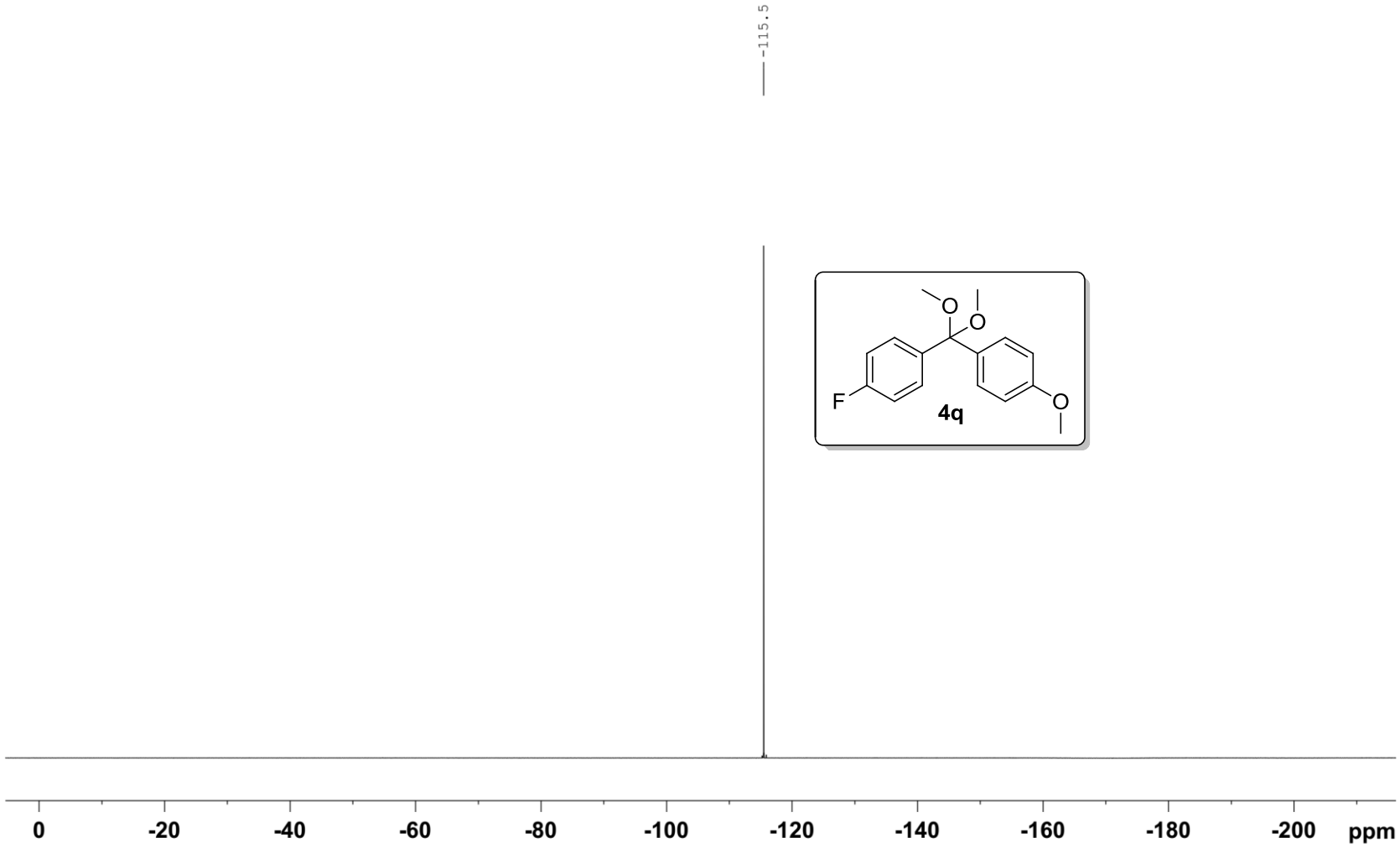
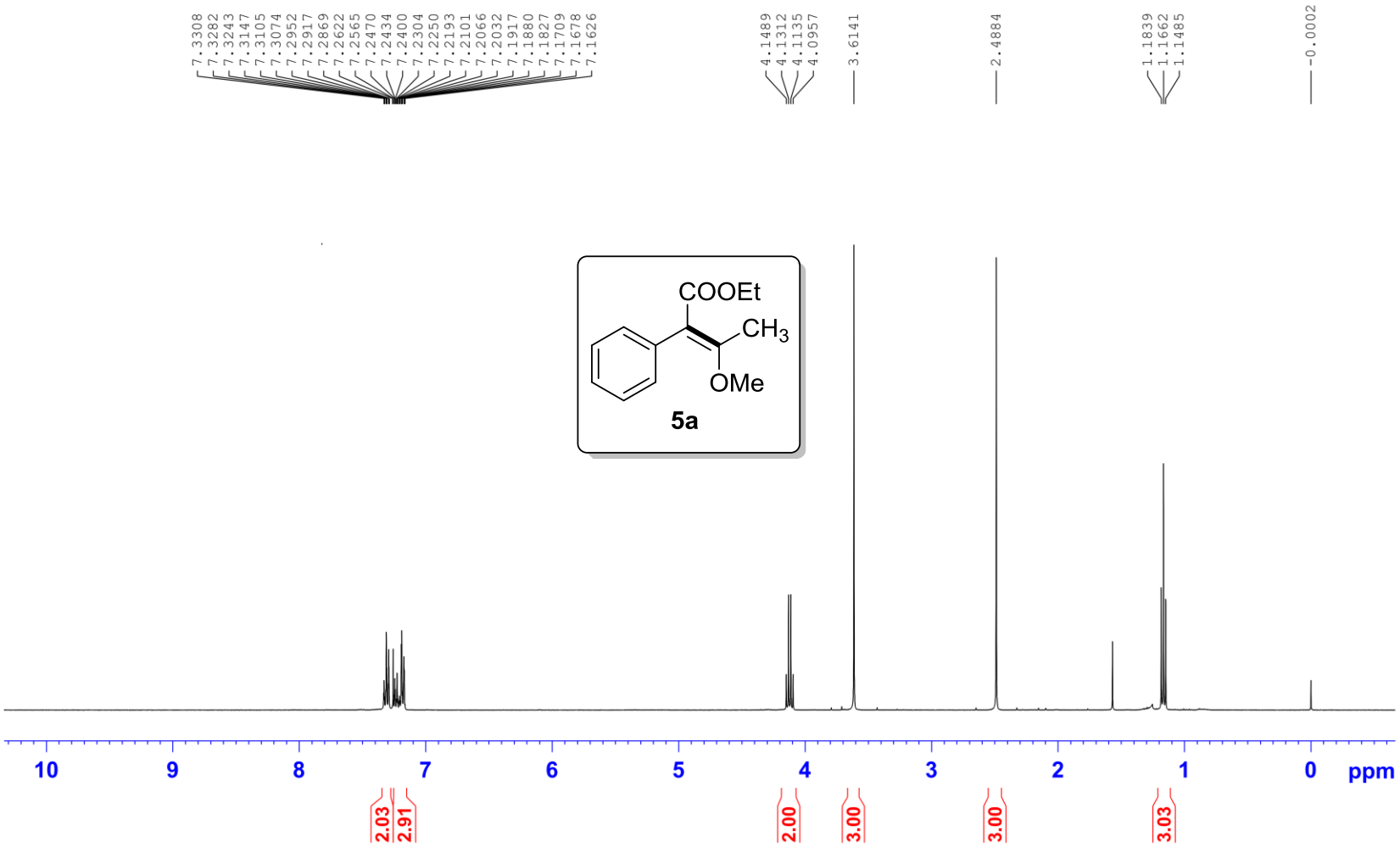


LJW-X170522-8-HNMR



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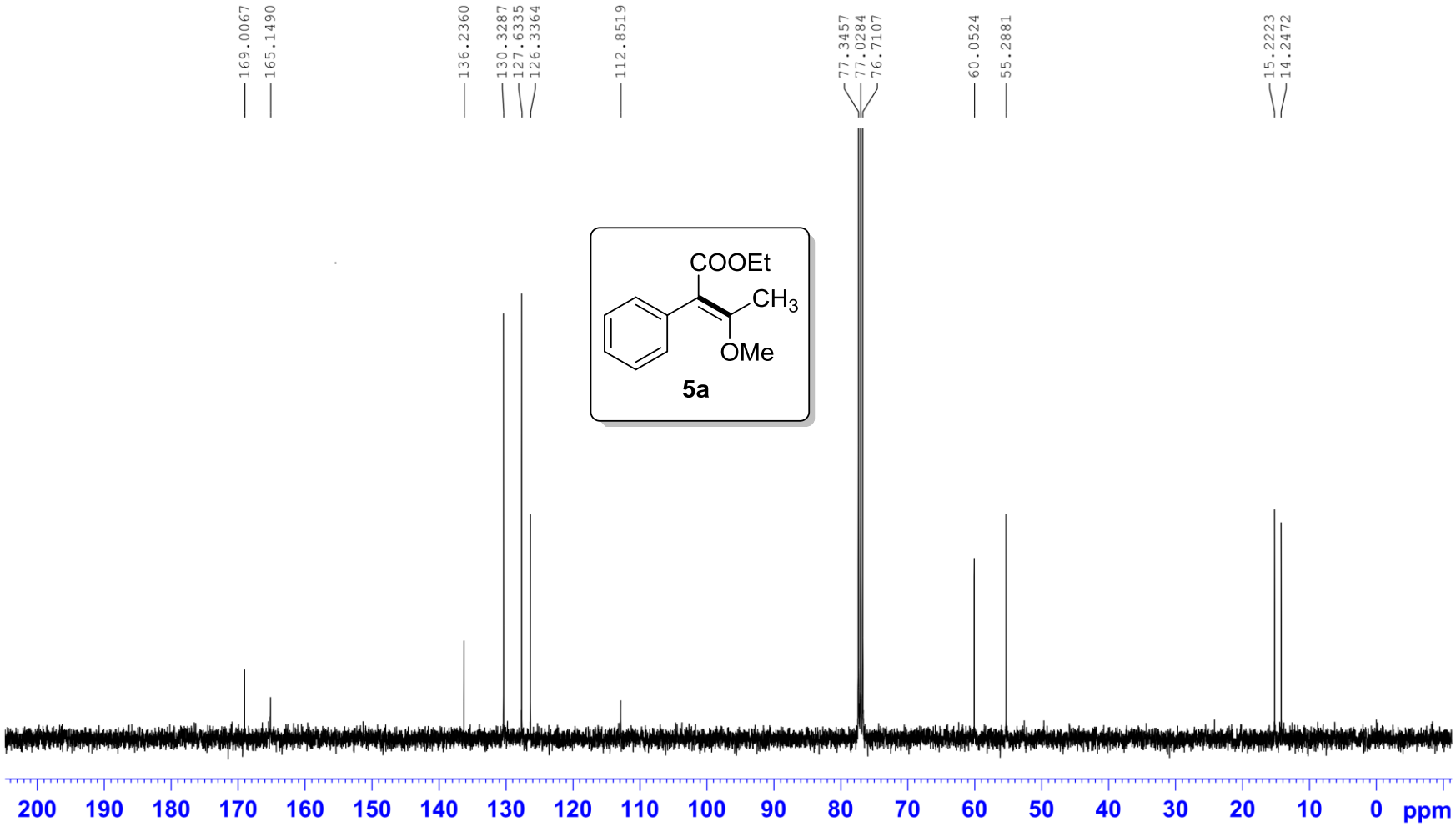
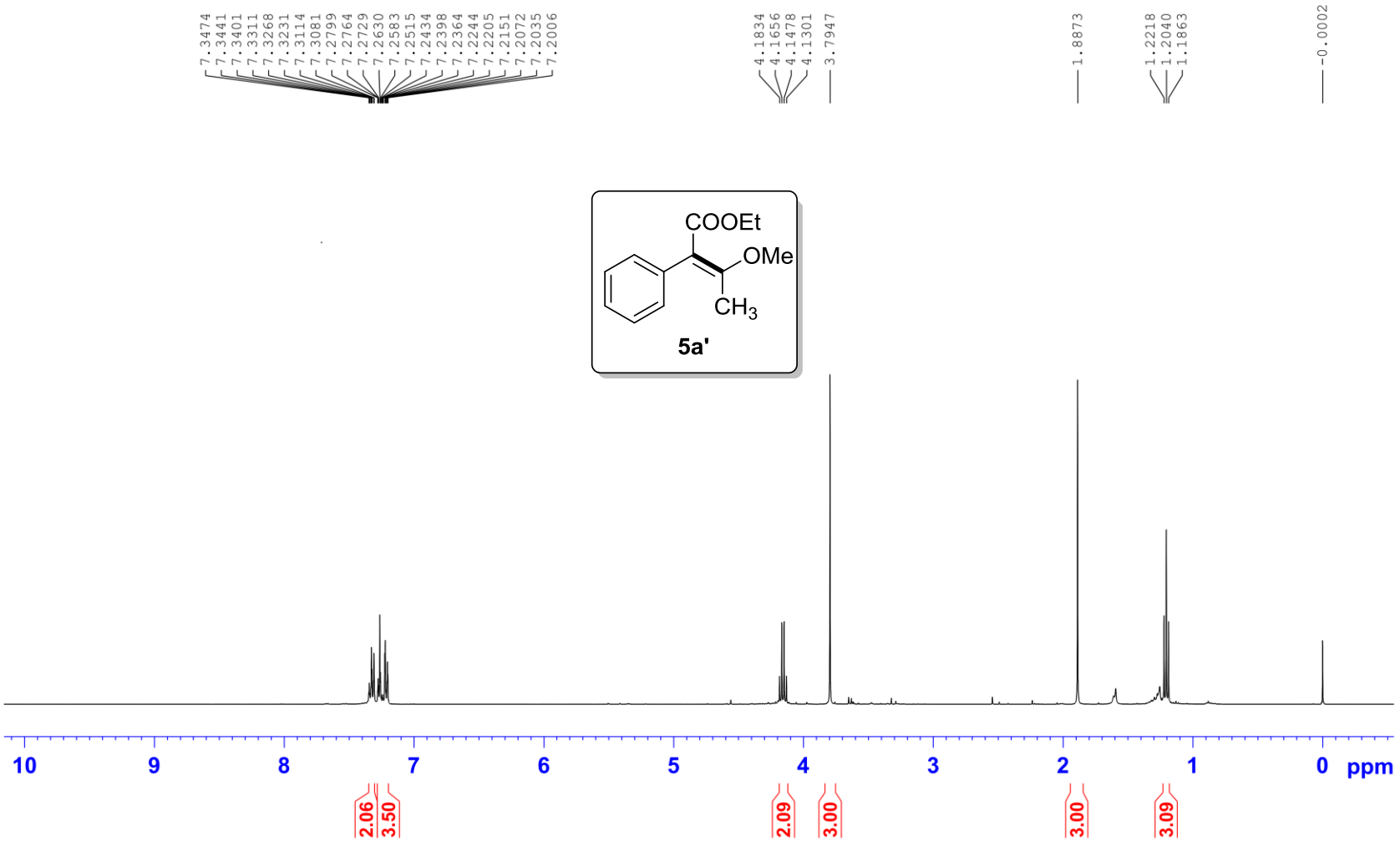


LJW-X170703-9-HNMR



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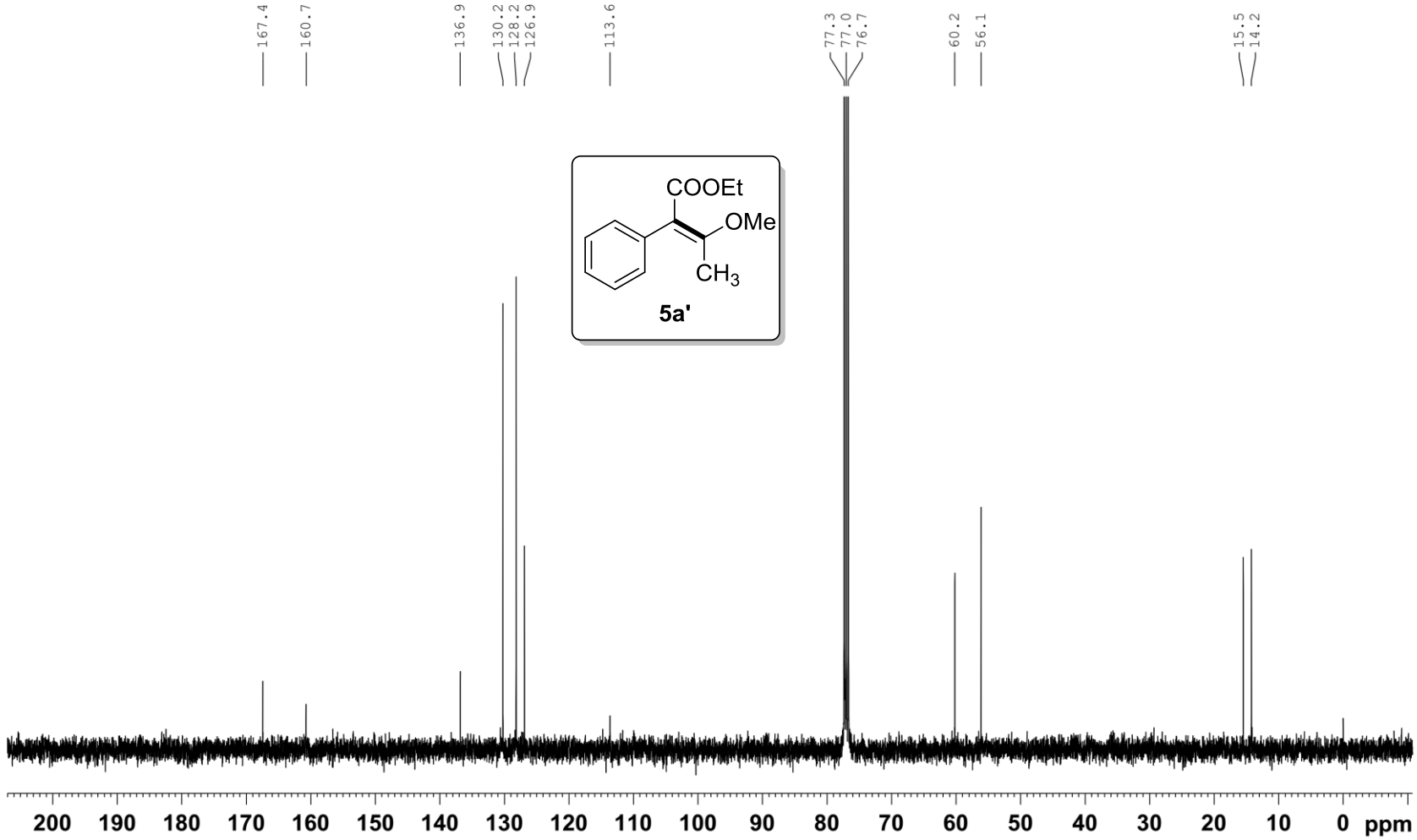
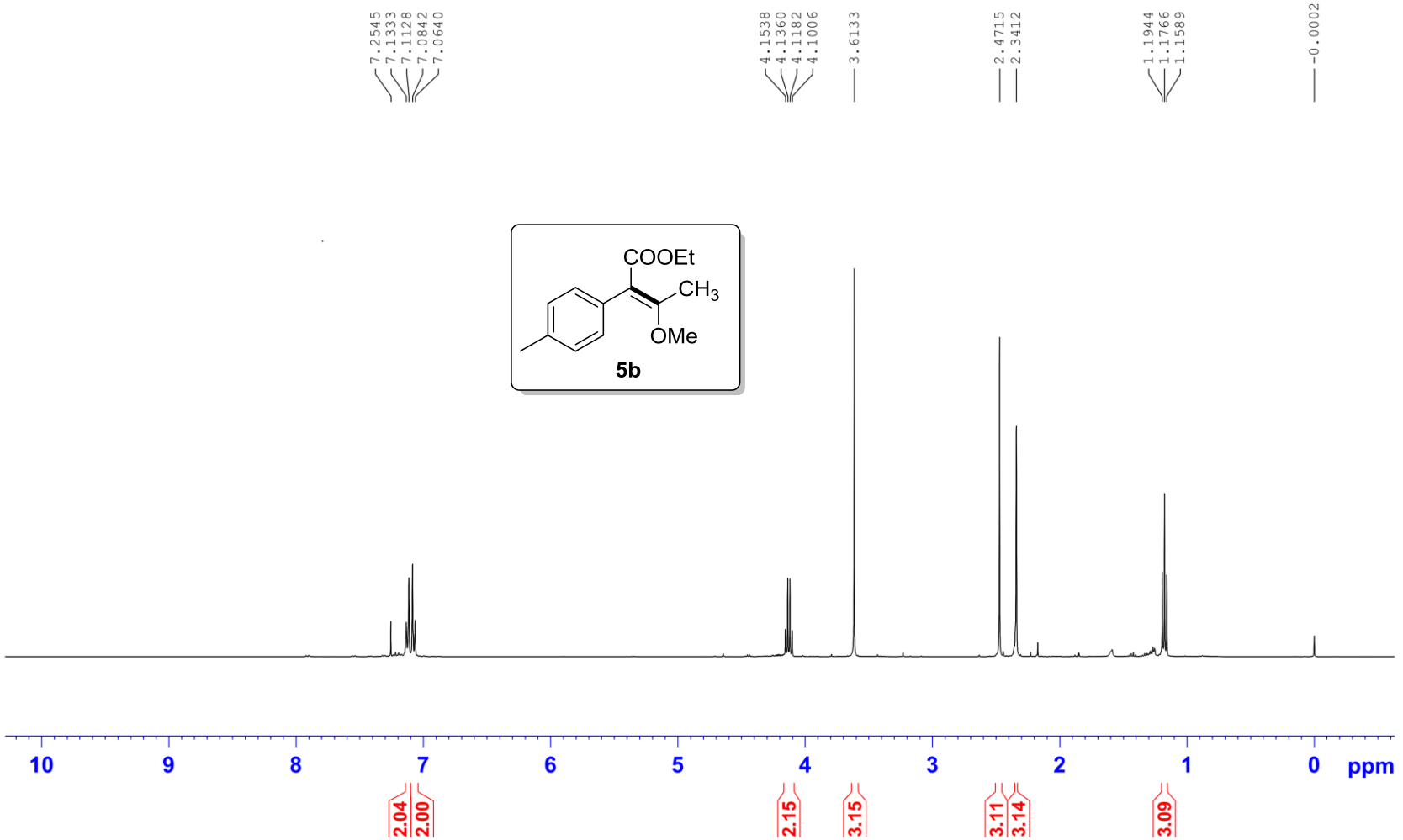


LJW-X170703-10-HNMR



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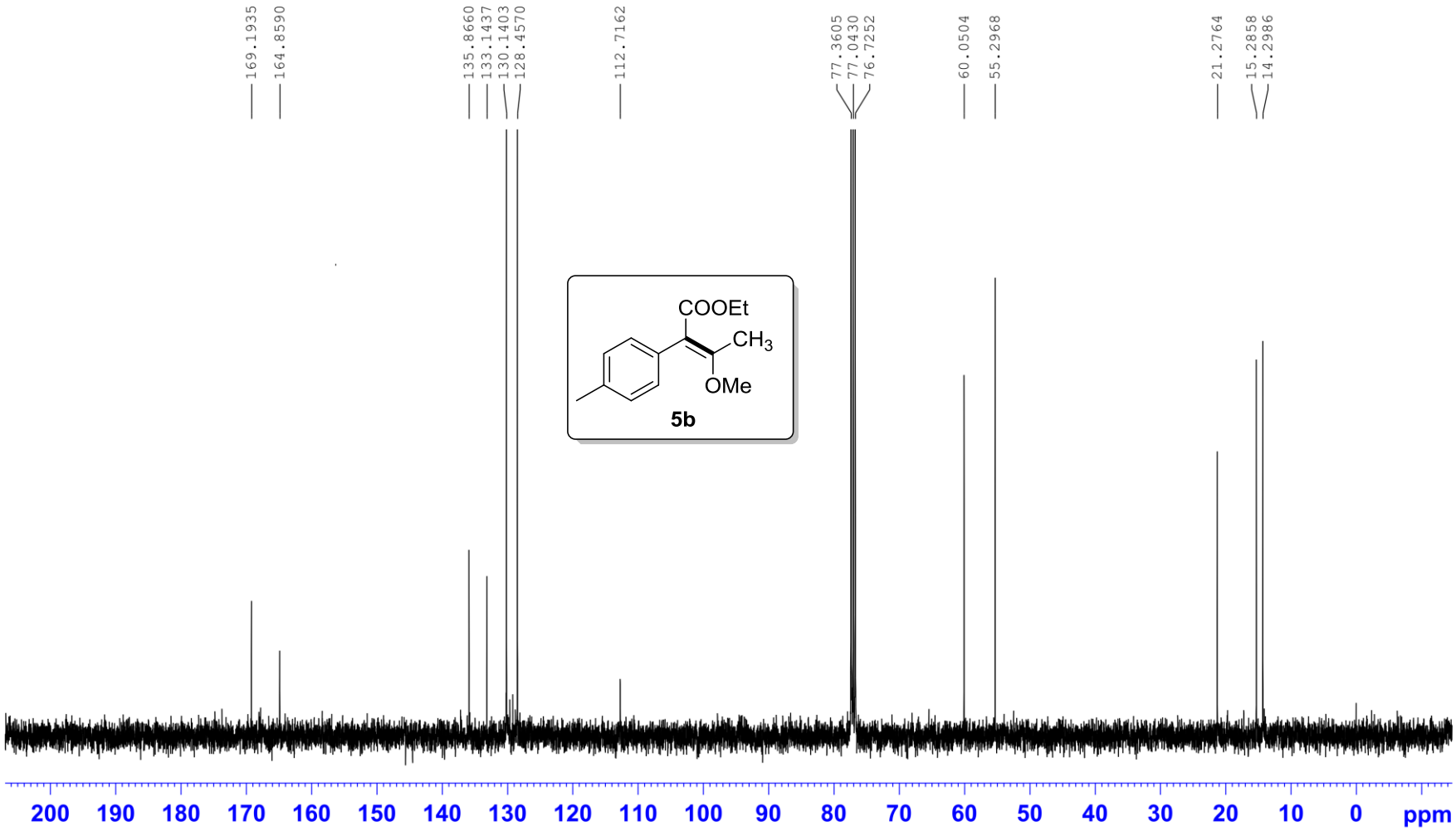
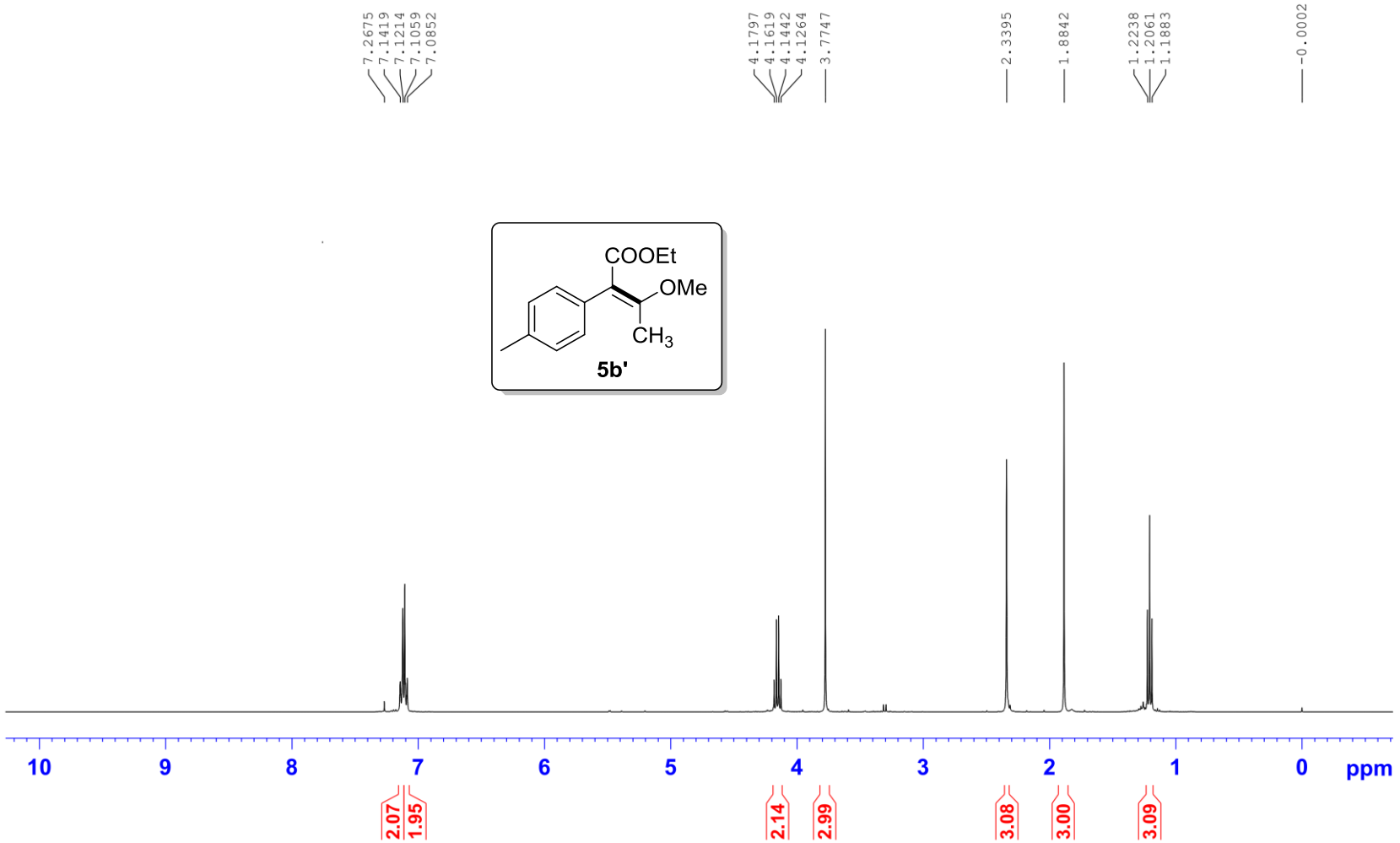


LJW-X170705-2-HNMR



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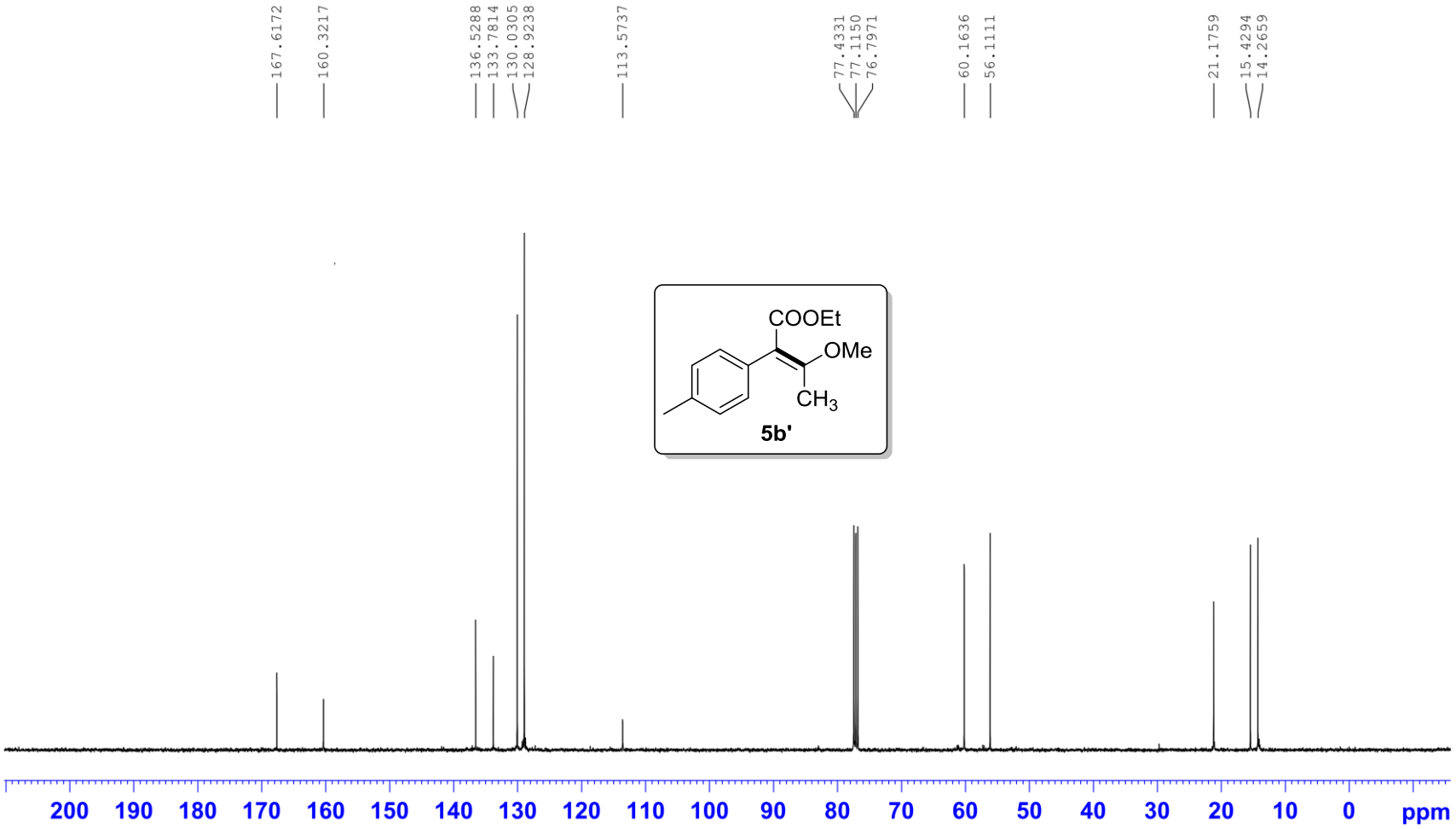
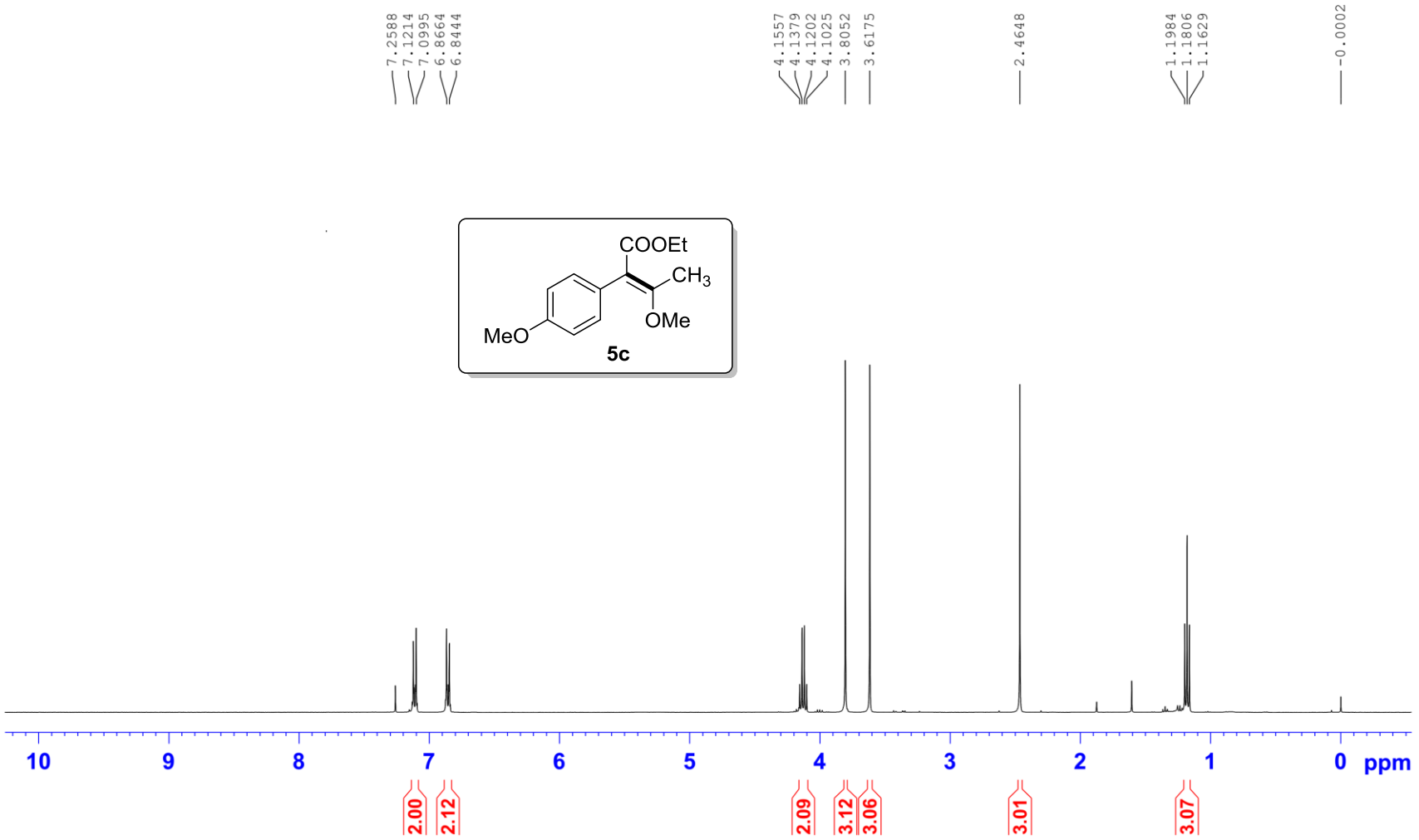


LJW-X180531-4-HNMR



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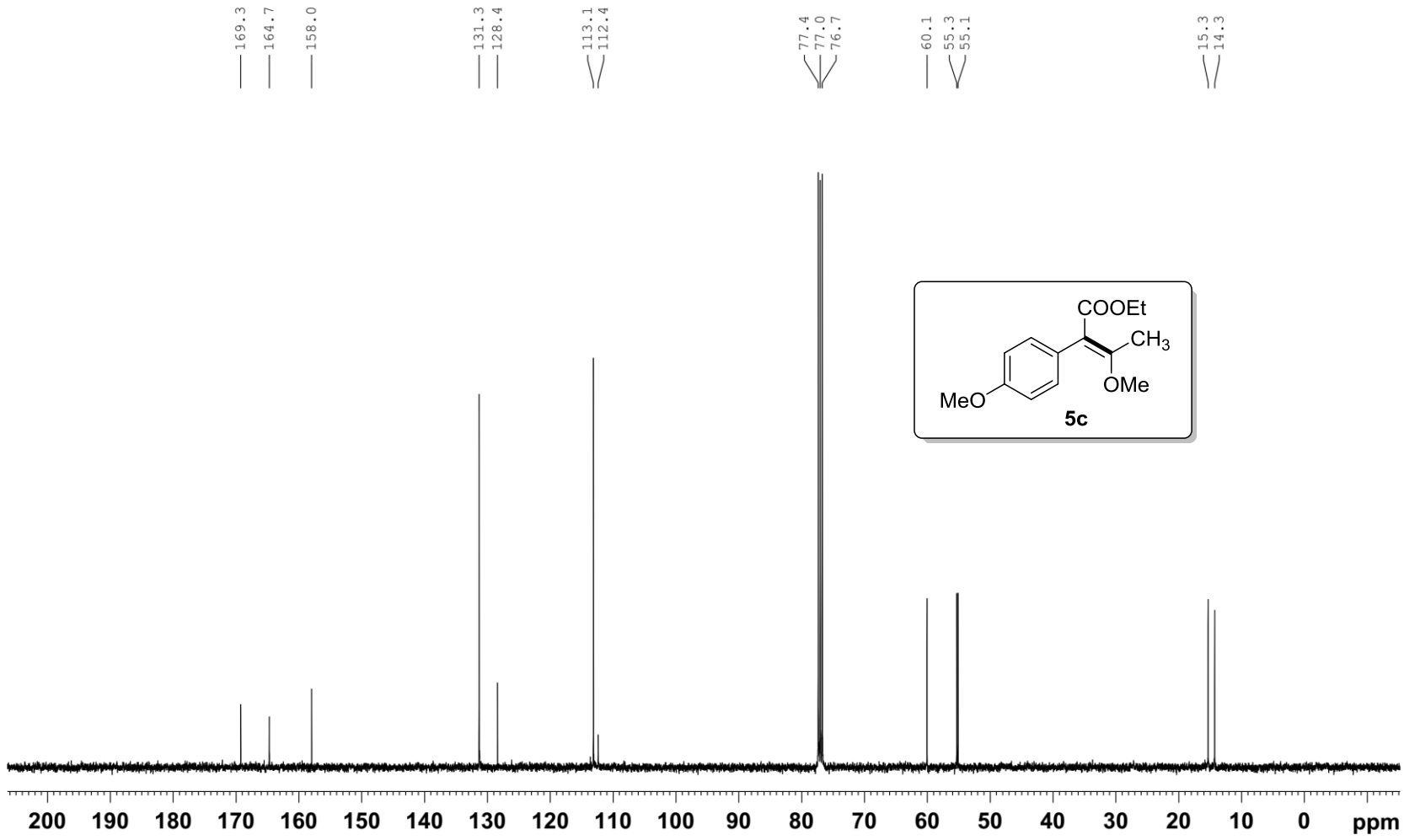
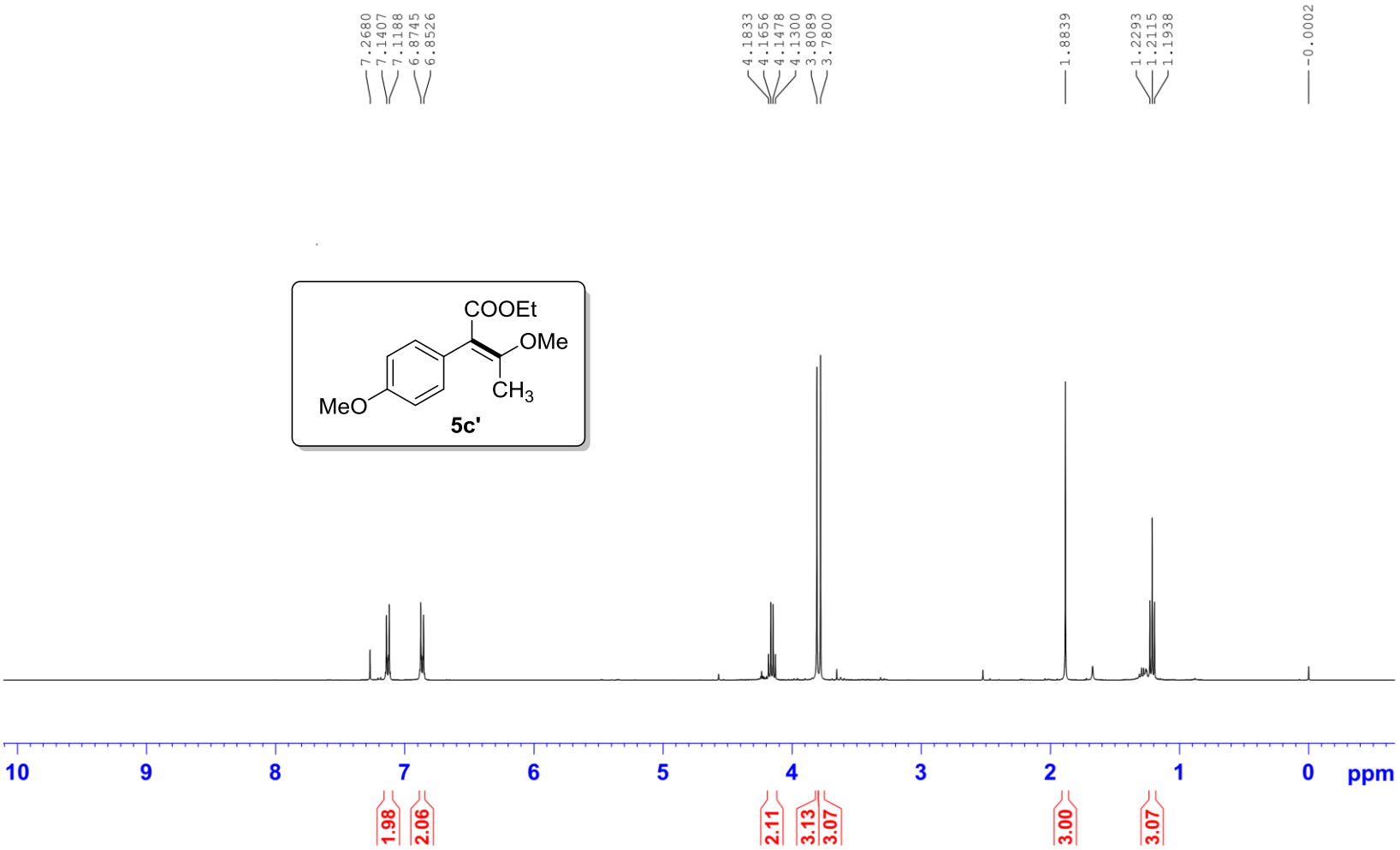


LJW-X170704-5-HNMR



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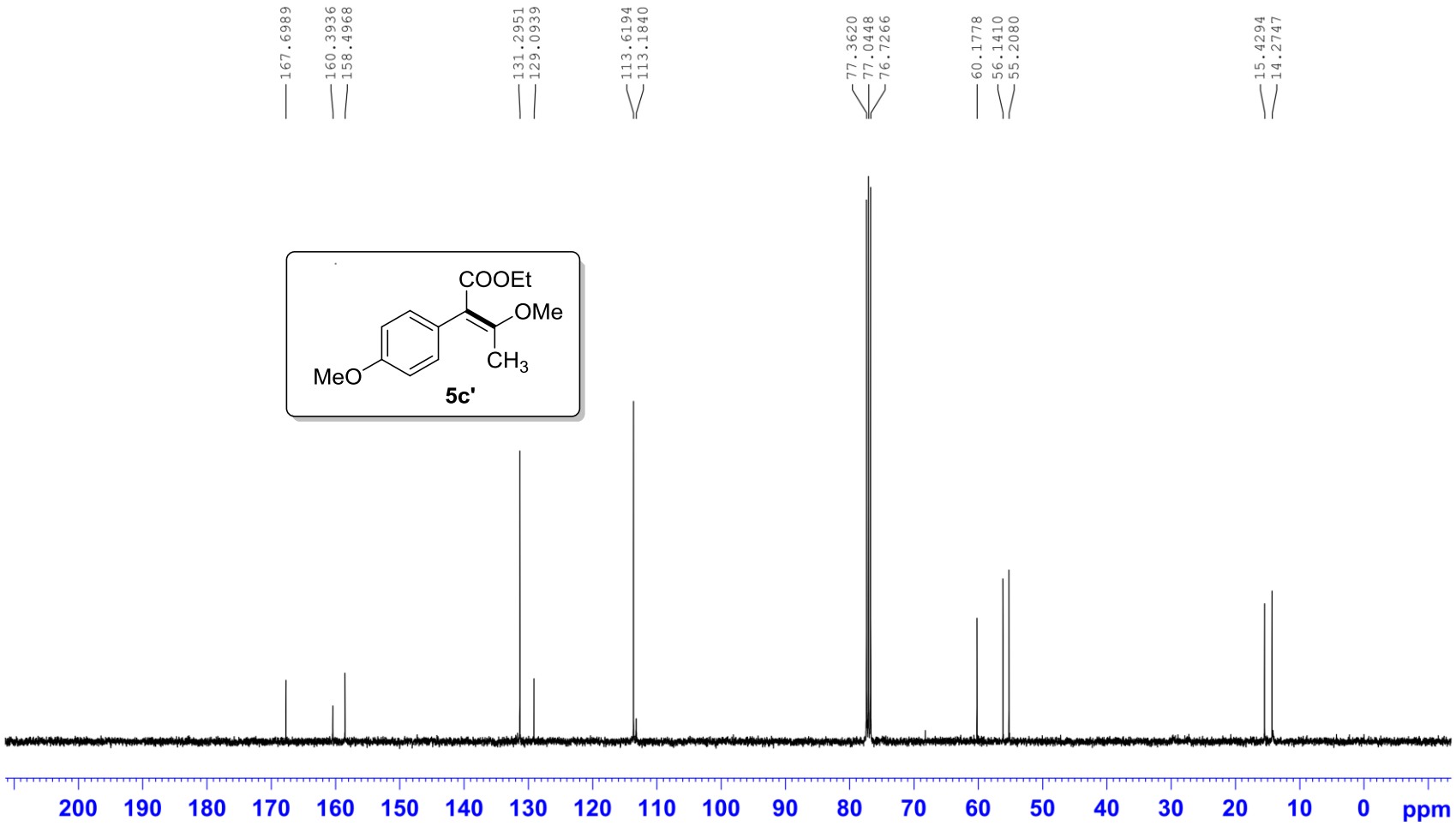
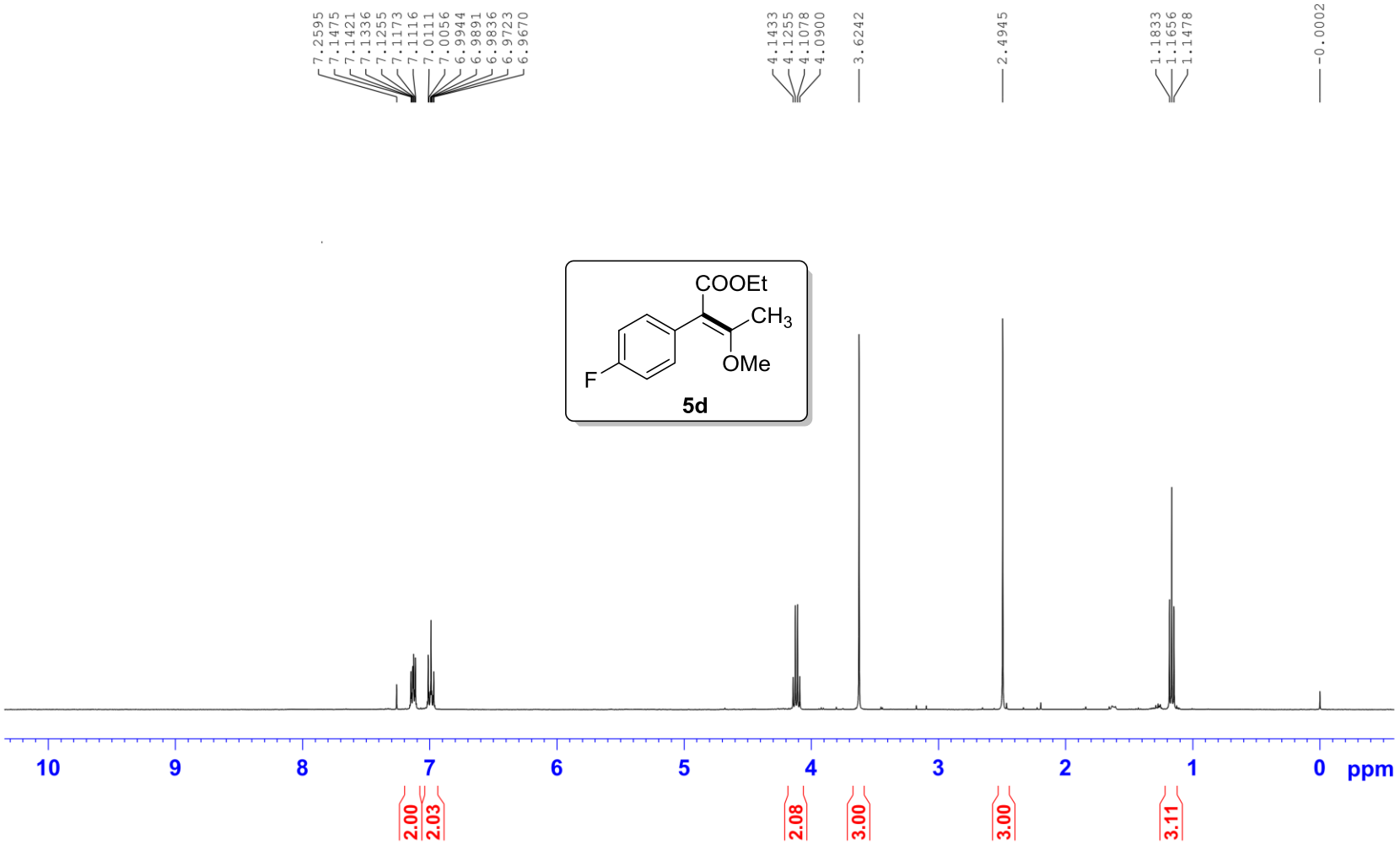


LJW-X170703-14-HNMR



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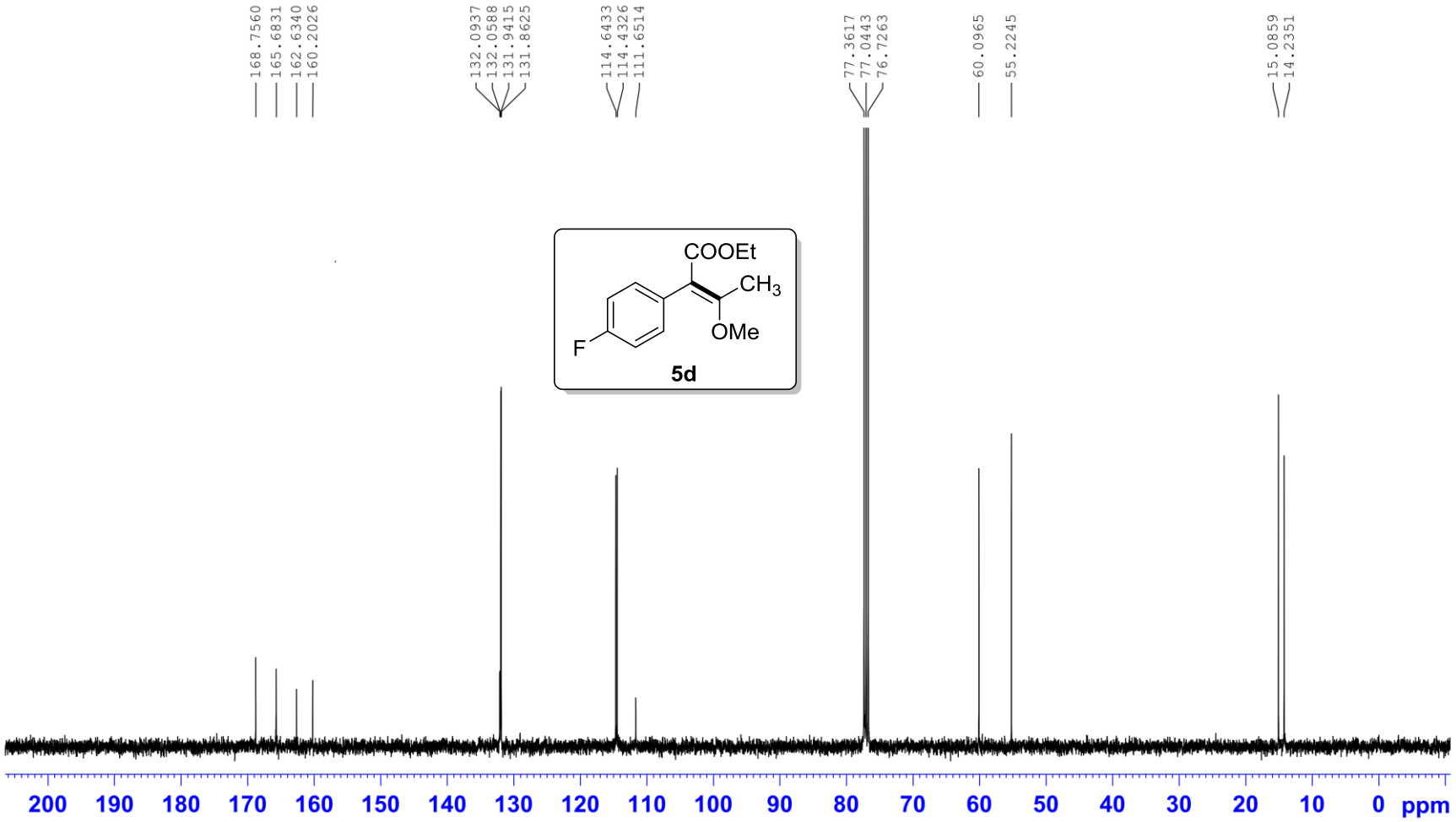

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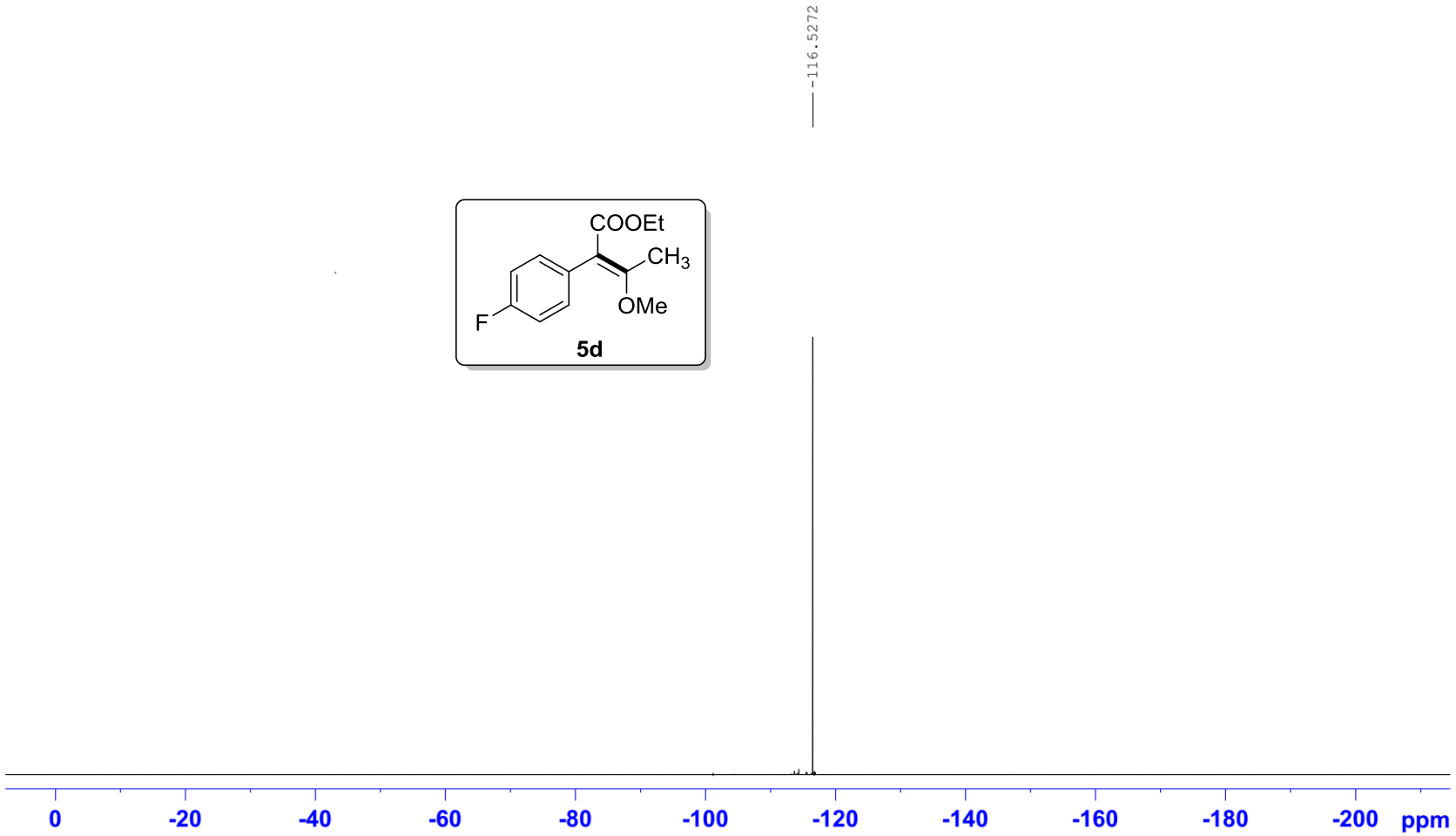

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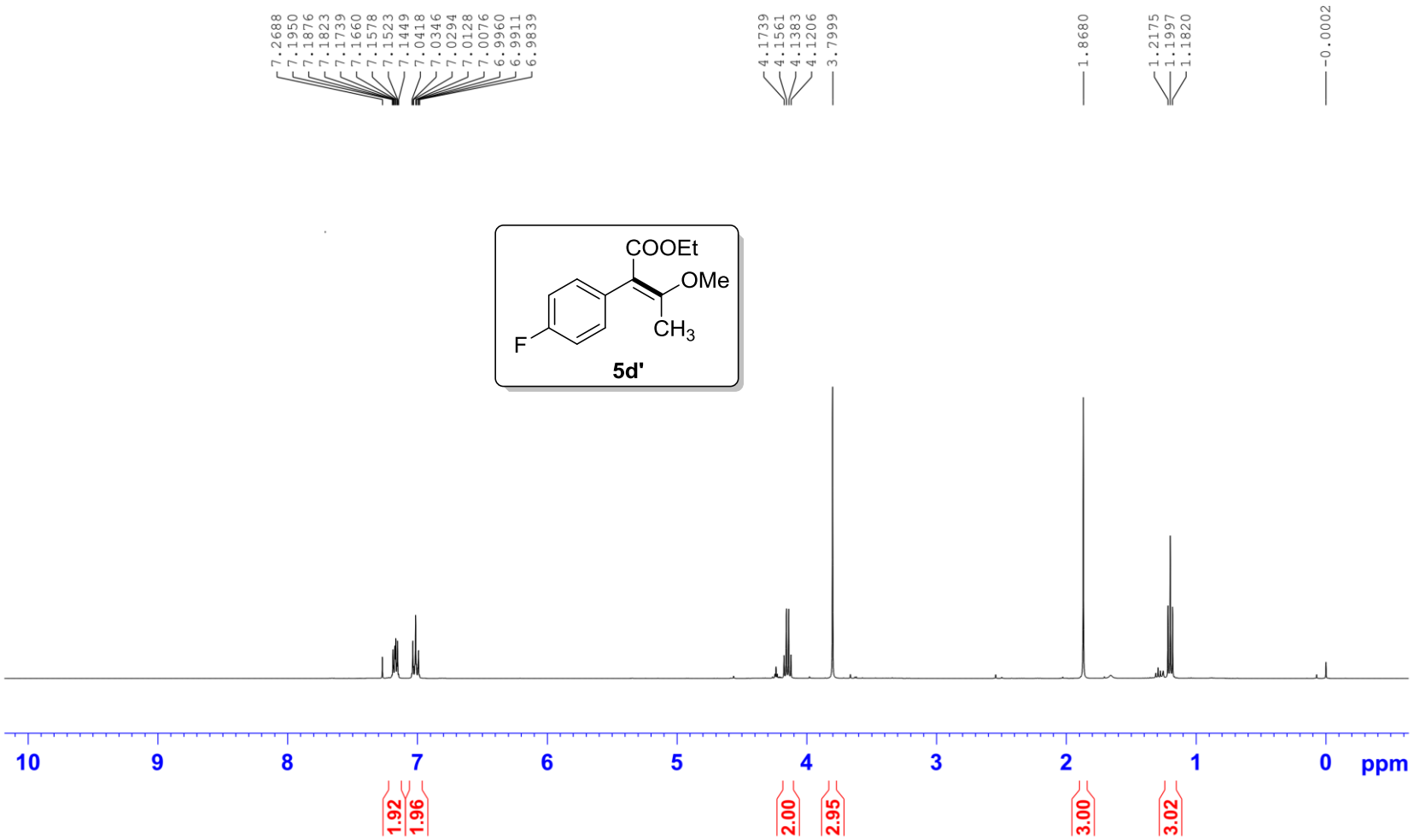

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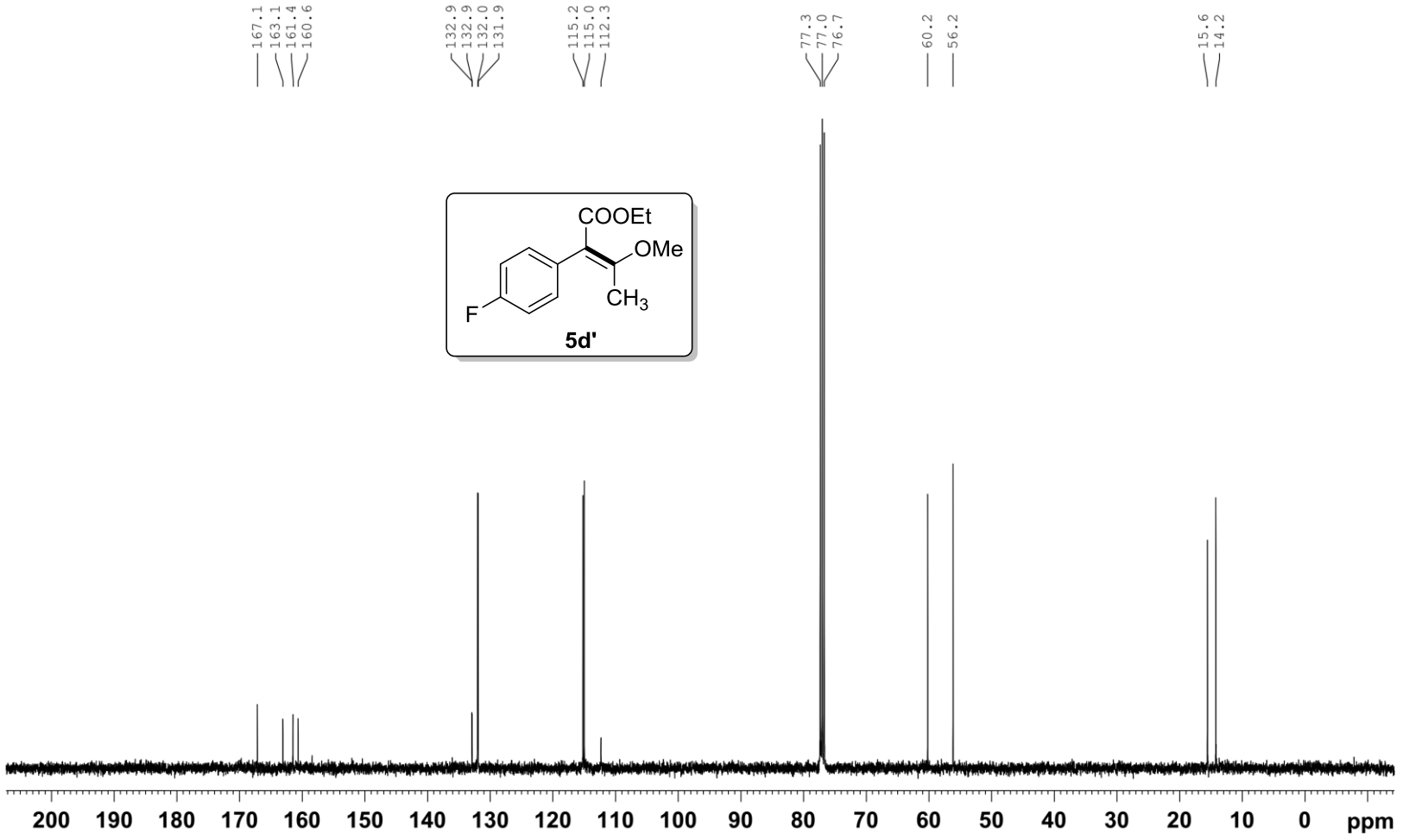

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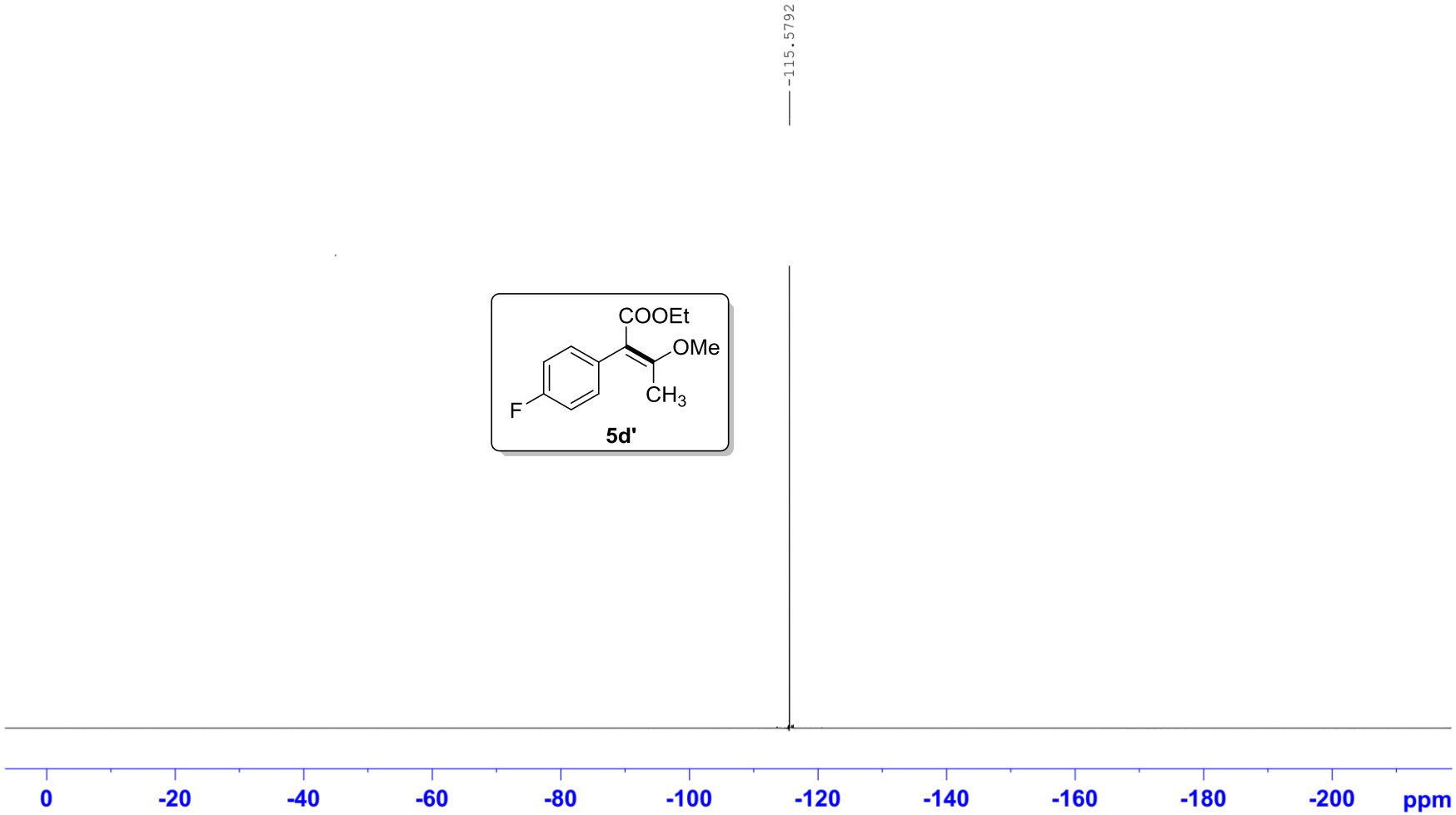
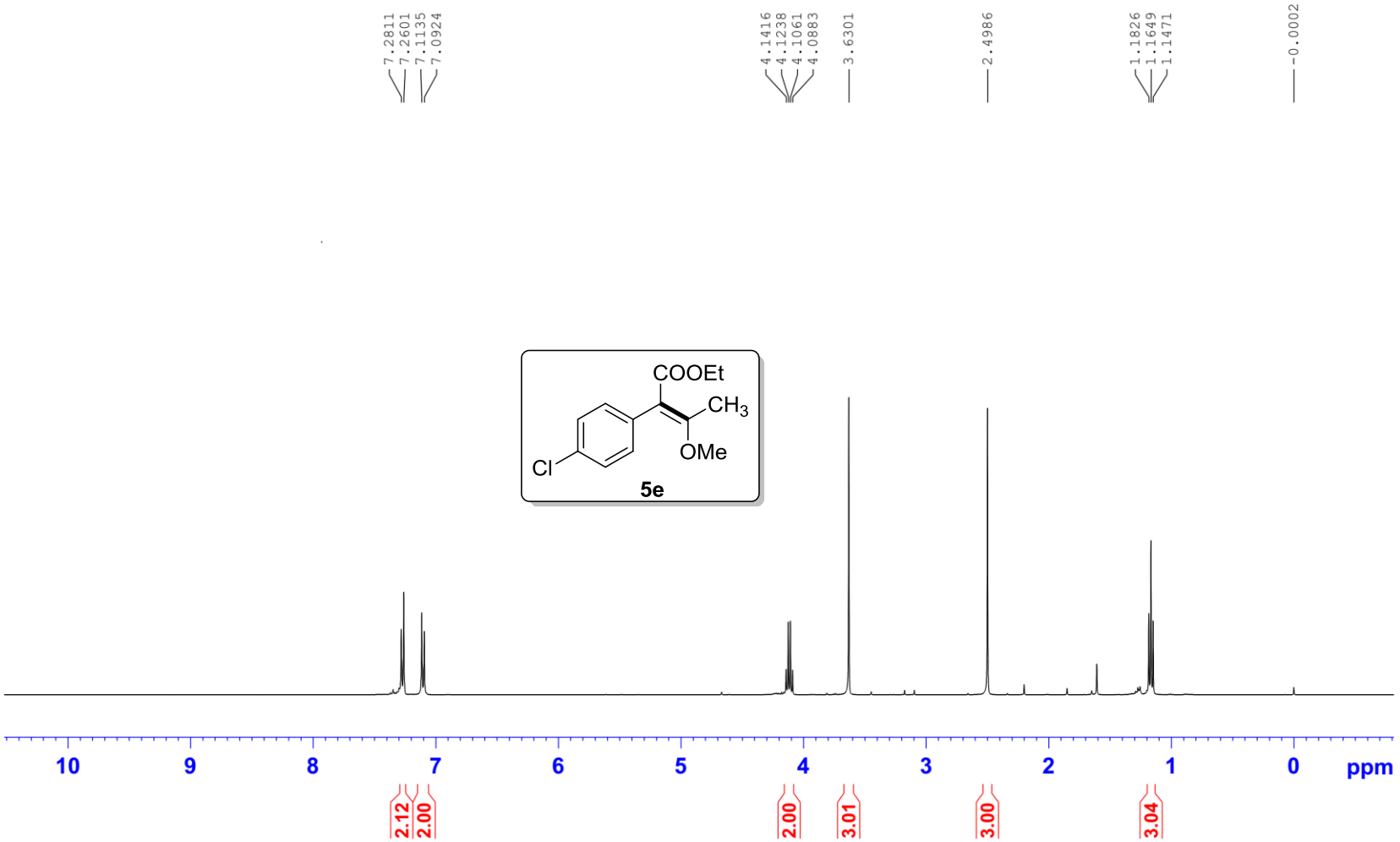


LJW-X170705-6-HNMR



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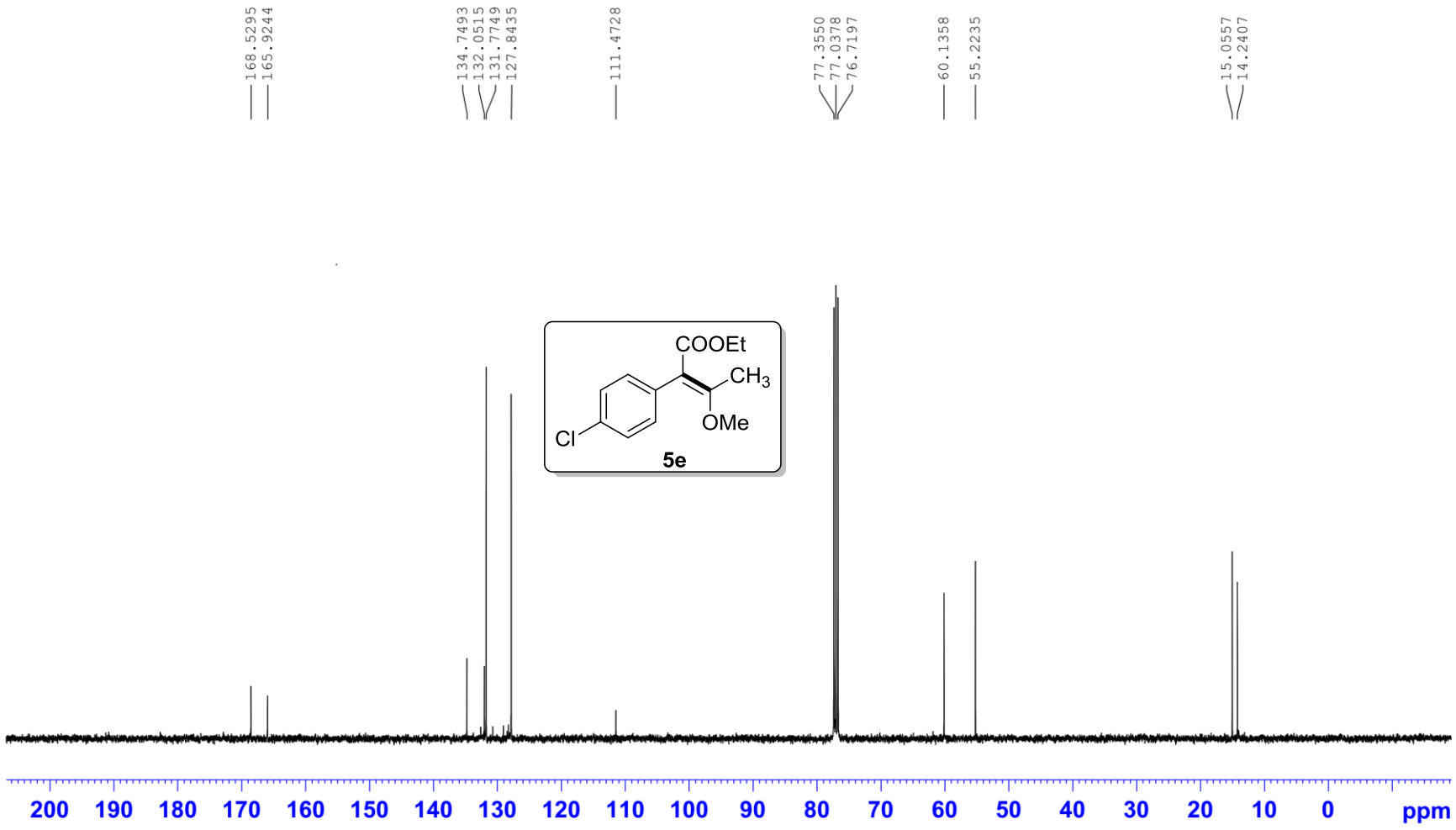
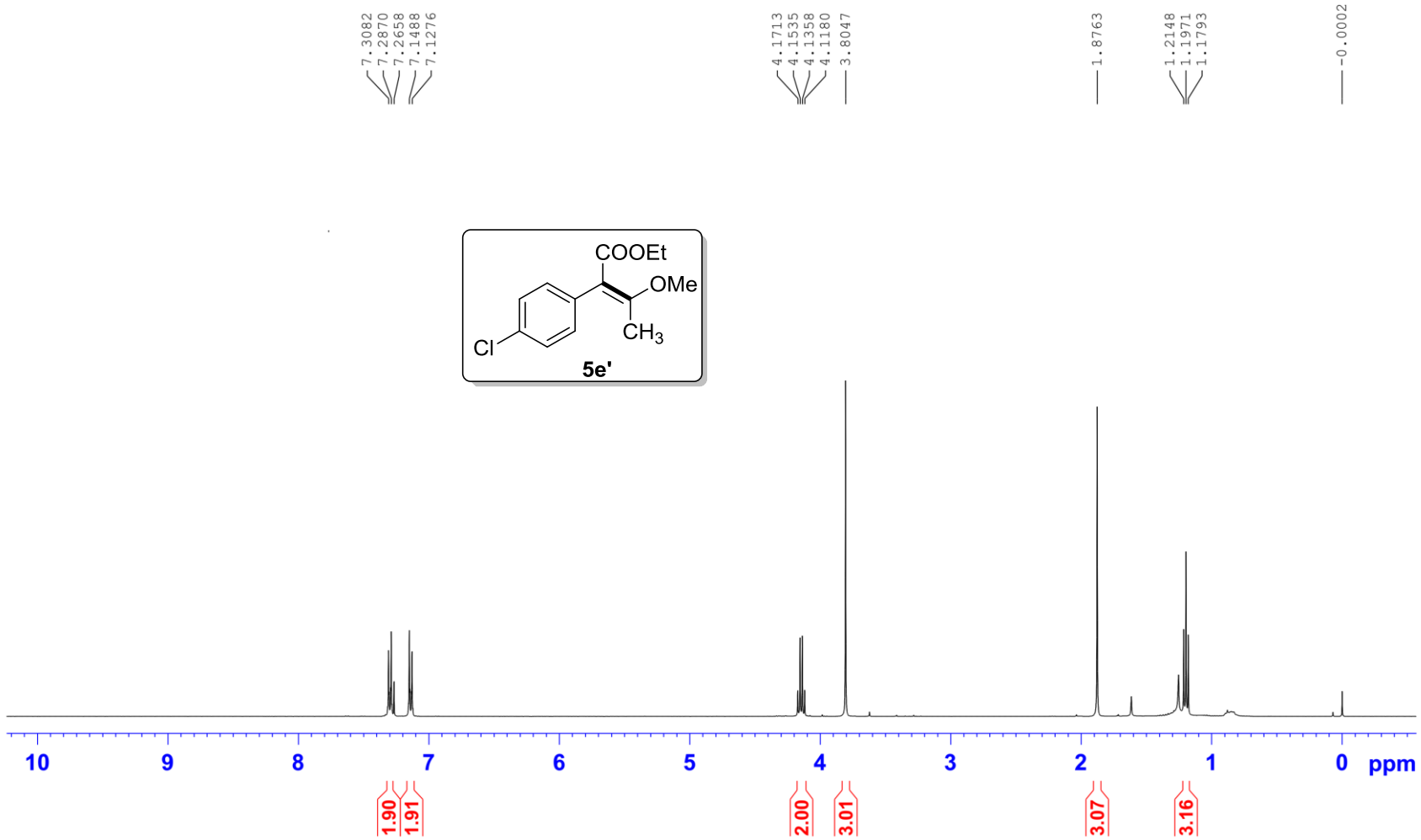
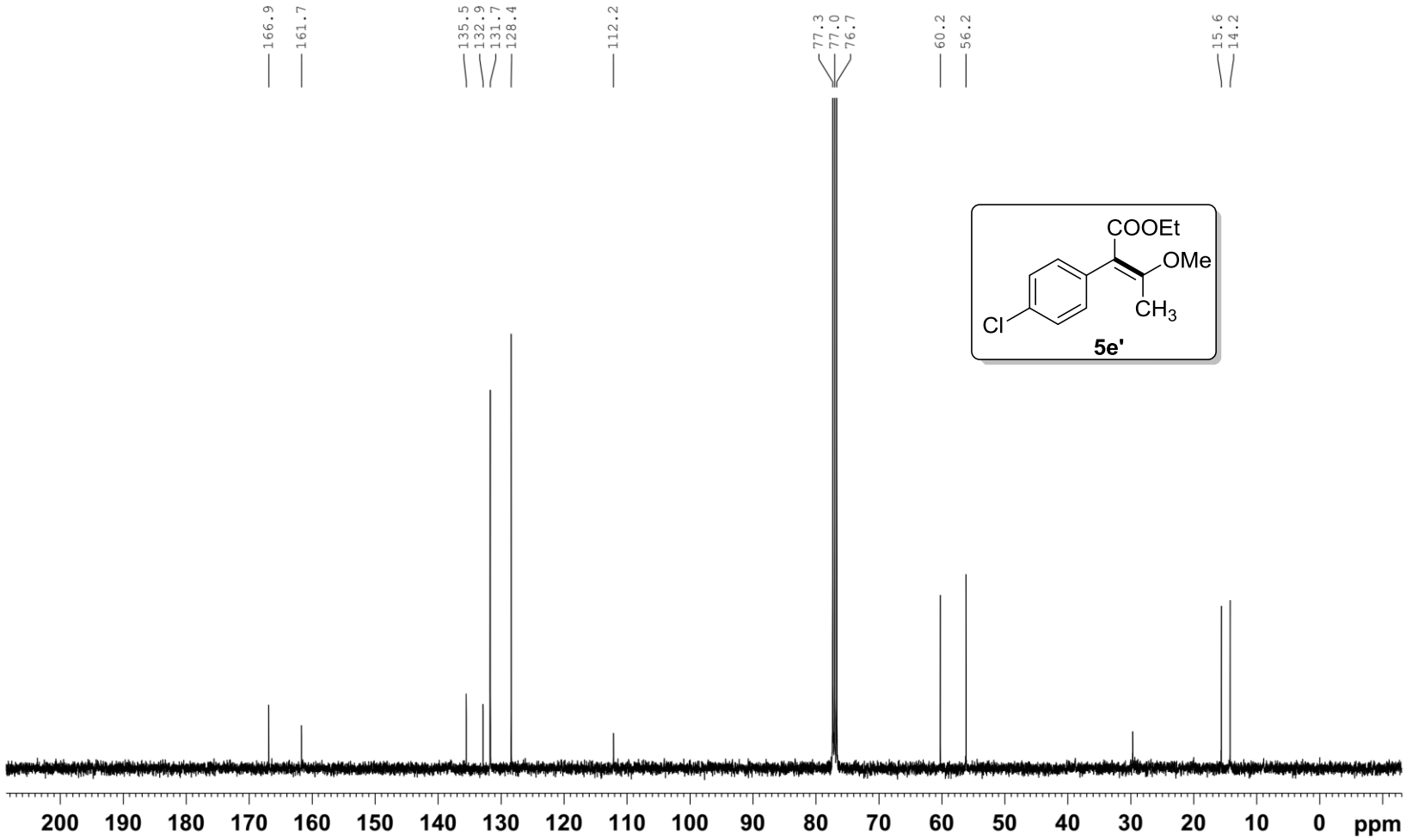


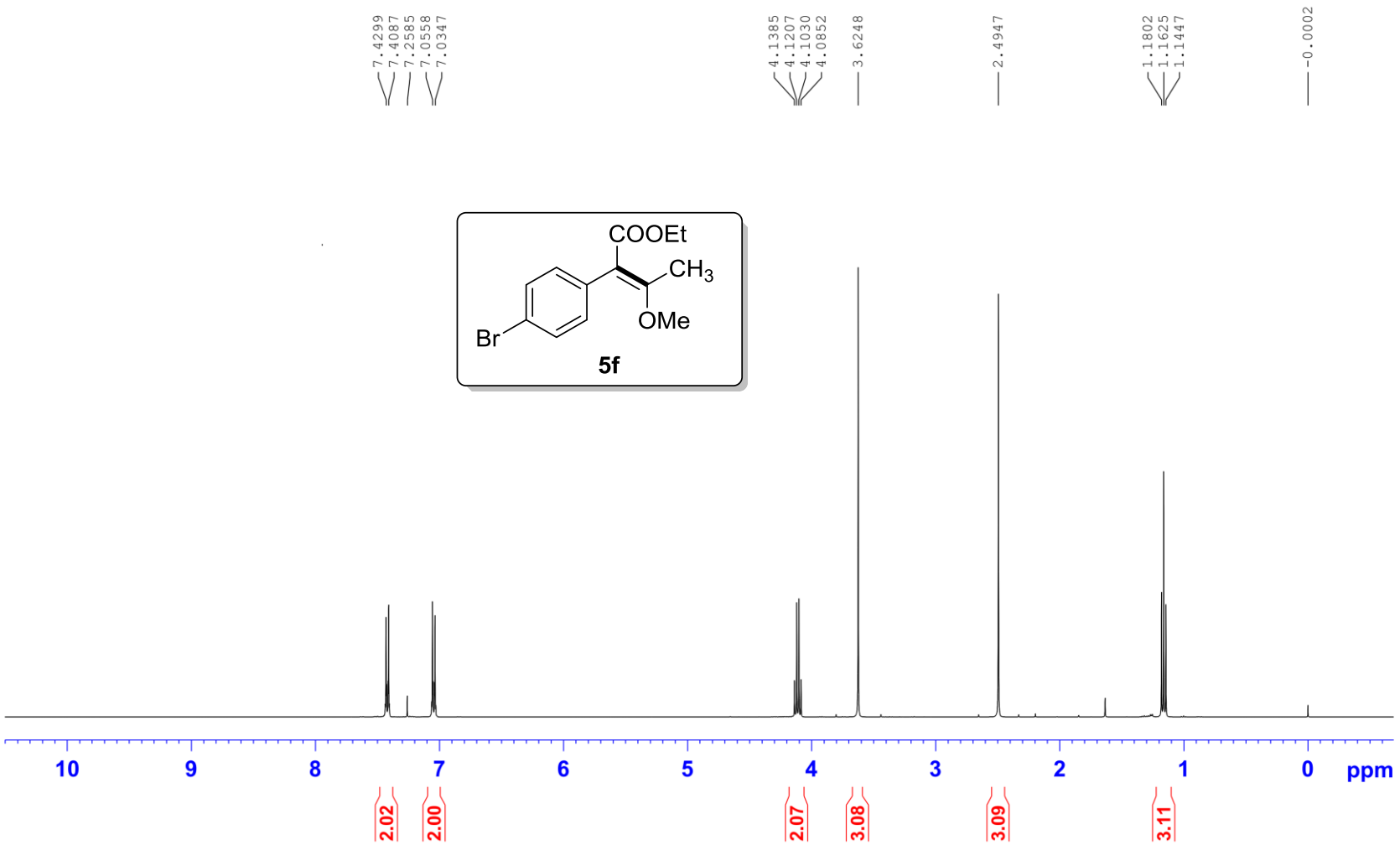
LJW-X180531-6-HNMR



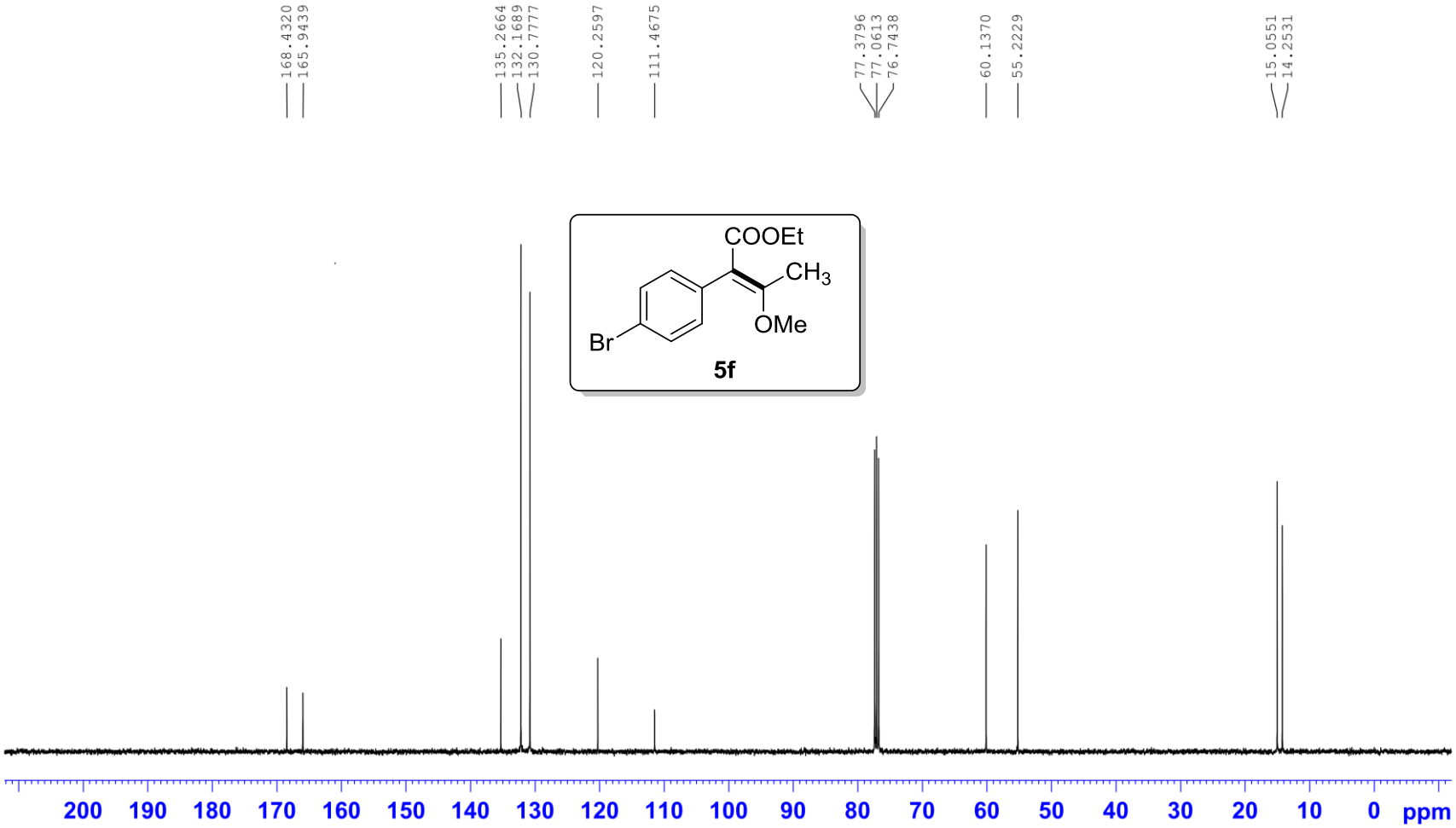
LJW-X180531-6-CNMR



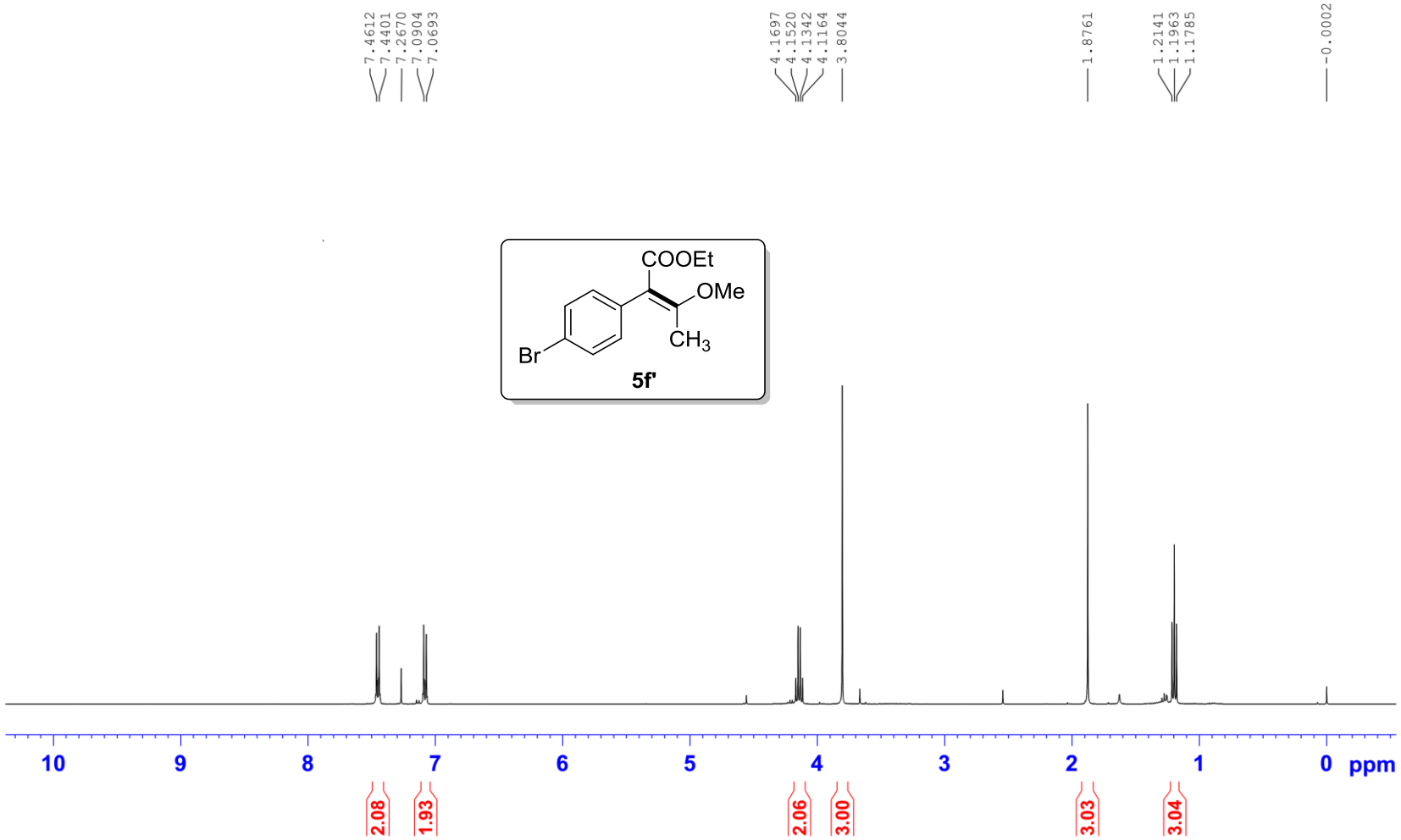
LJW-X170708-2-HNMR

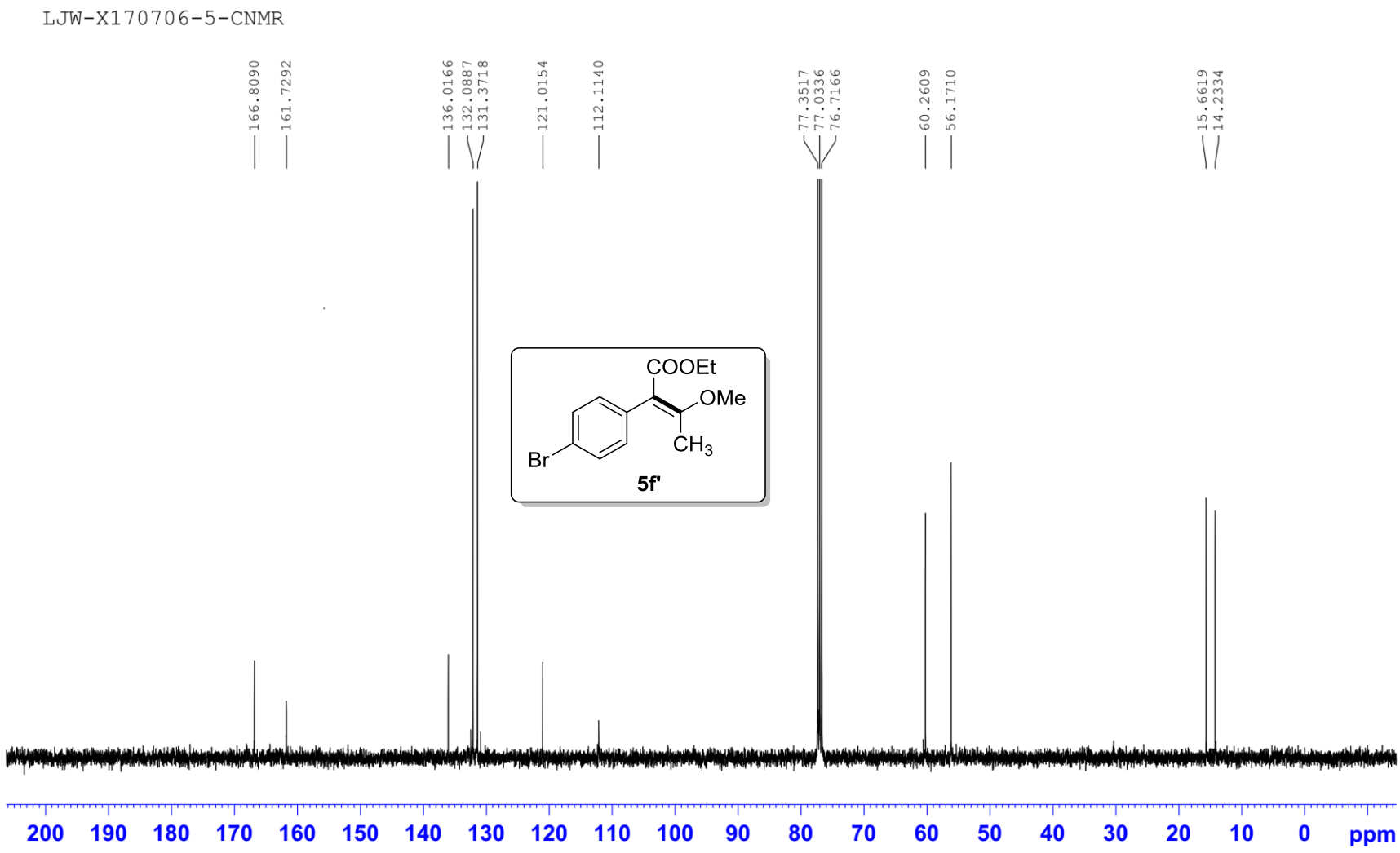


LJW-X170708-2-CNMR



LJW-X170706-5-HNMR

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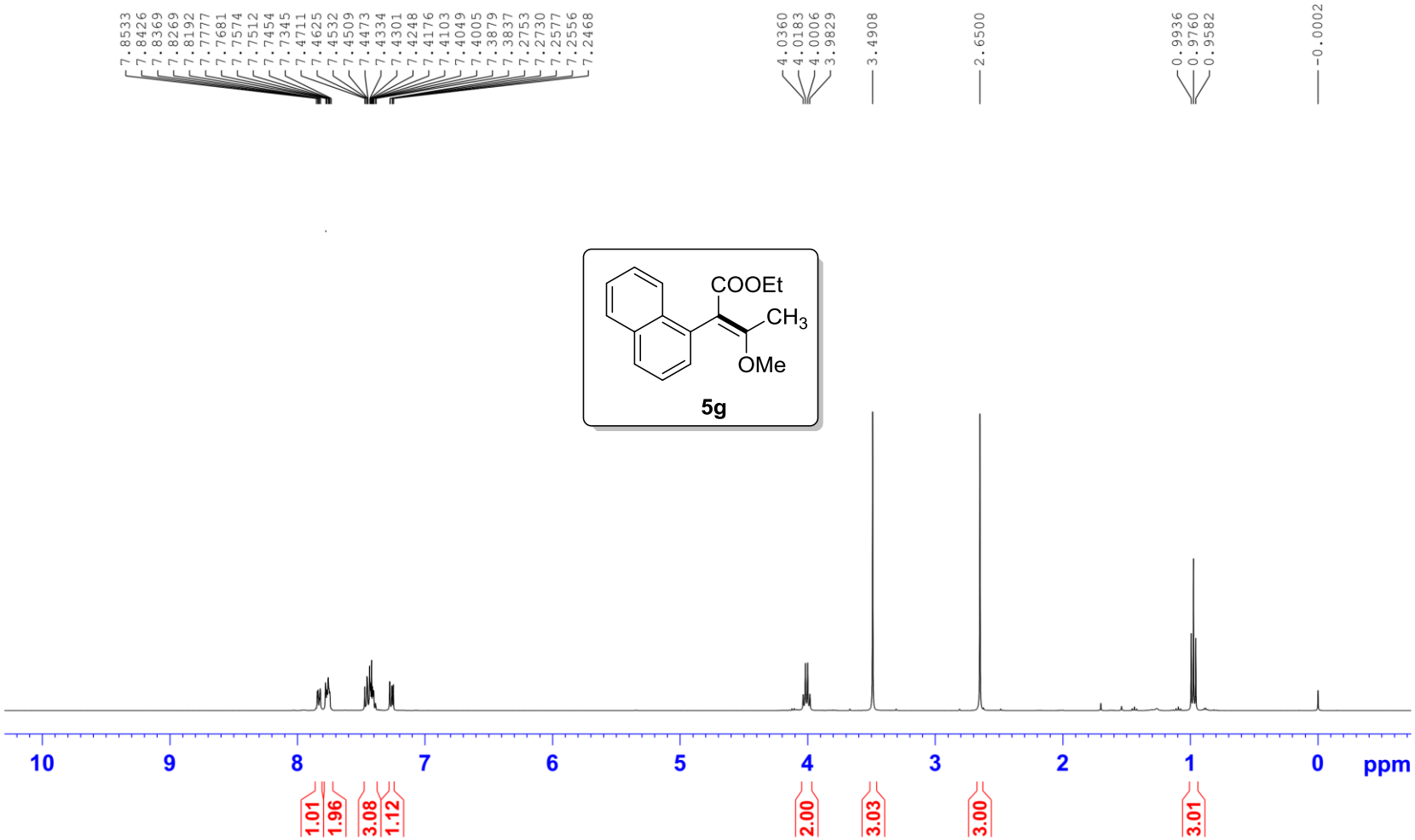
161.7292
136.0166
132.0887
131.3718
121.0154
112.1140
77.3517
77.0336
76.7166
60.2609
56.1710
15.6619
14.2334
COOEt
OMe
CH3
Br
5f'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X180606-8-HNMR



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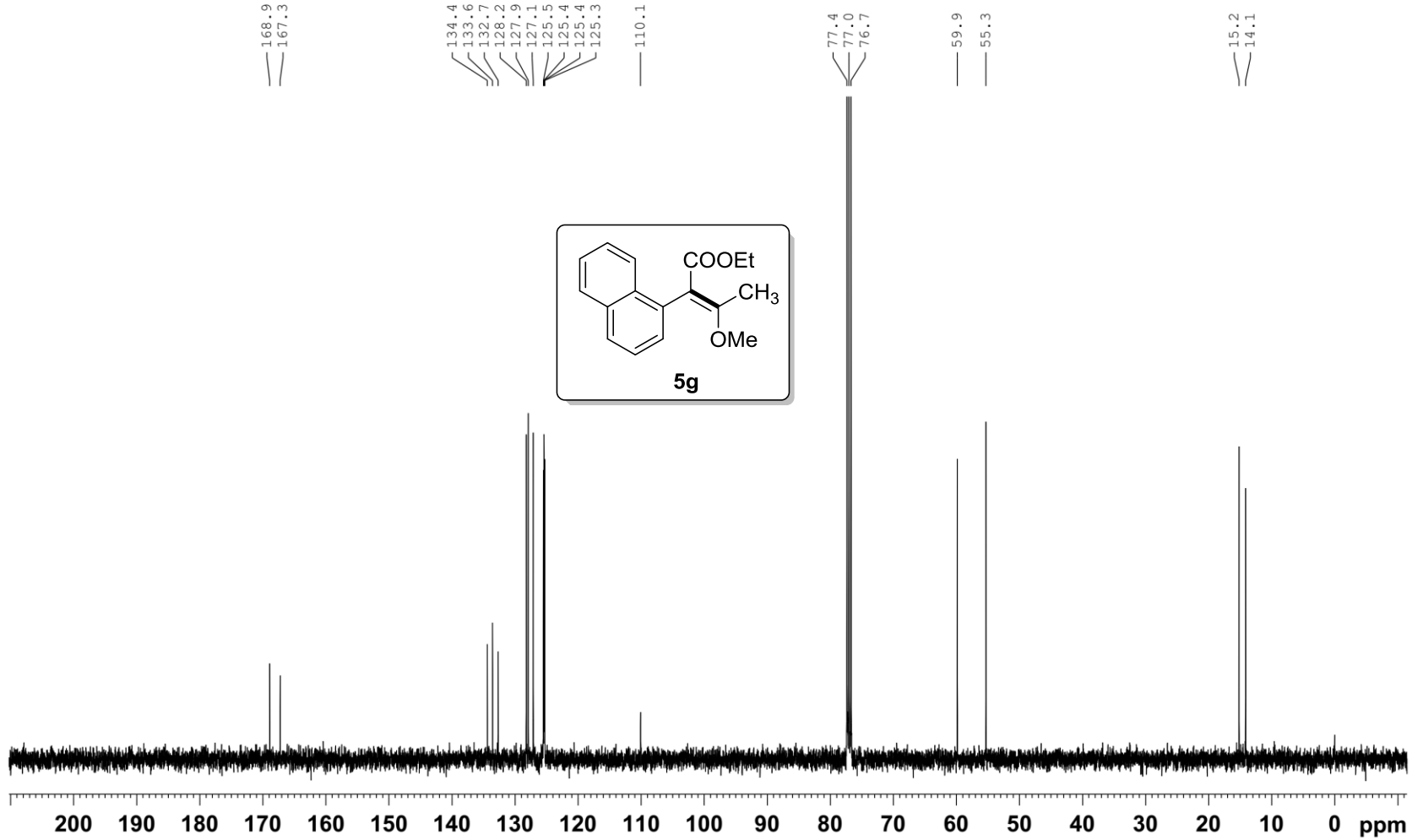
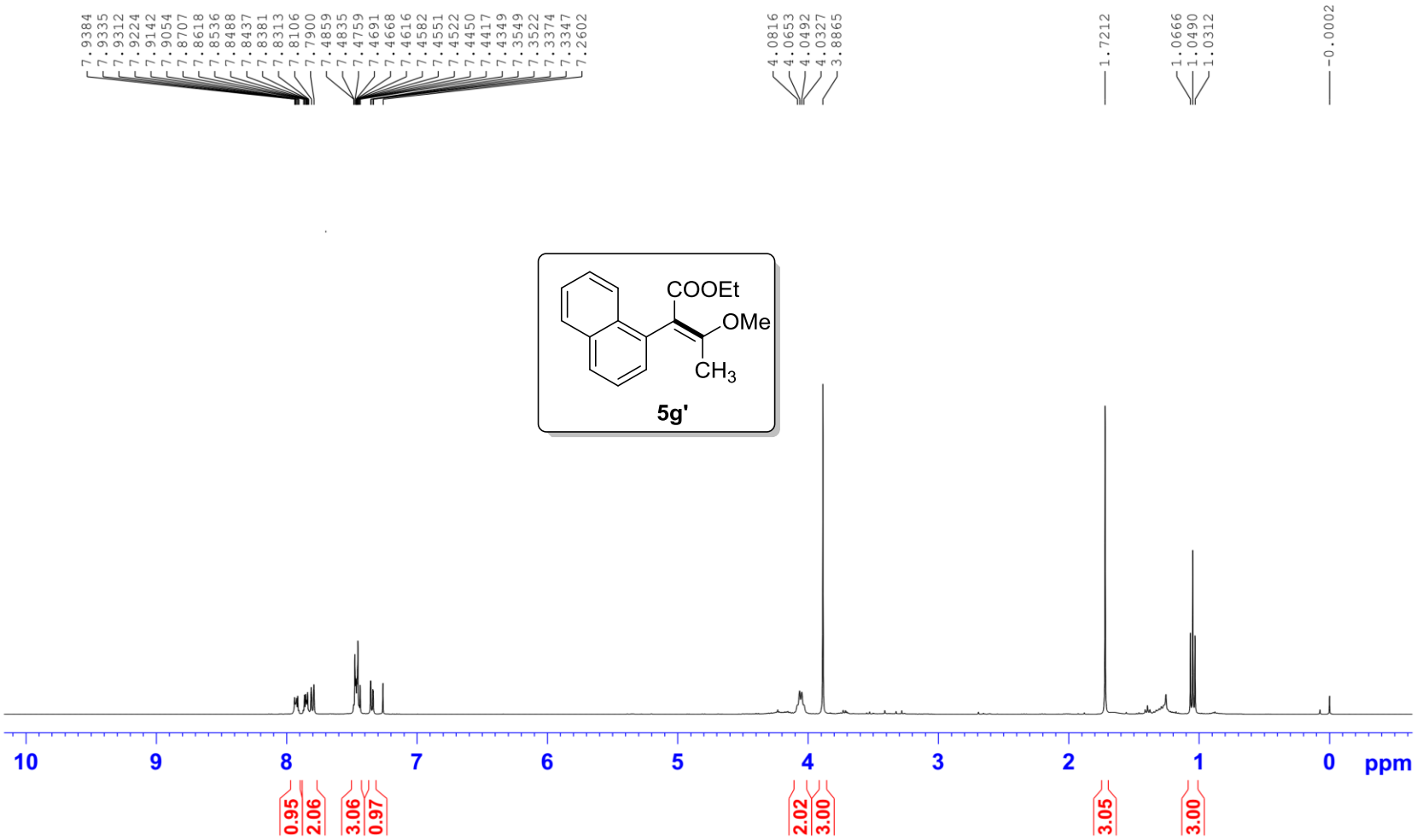


LJW-X180606-15-HNMR



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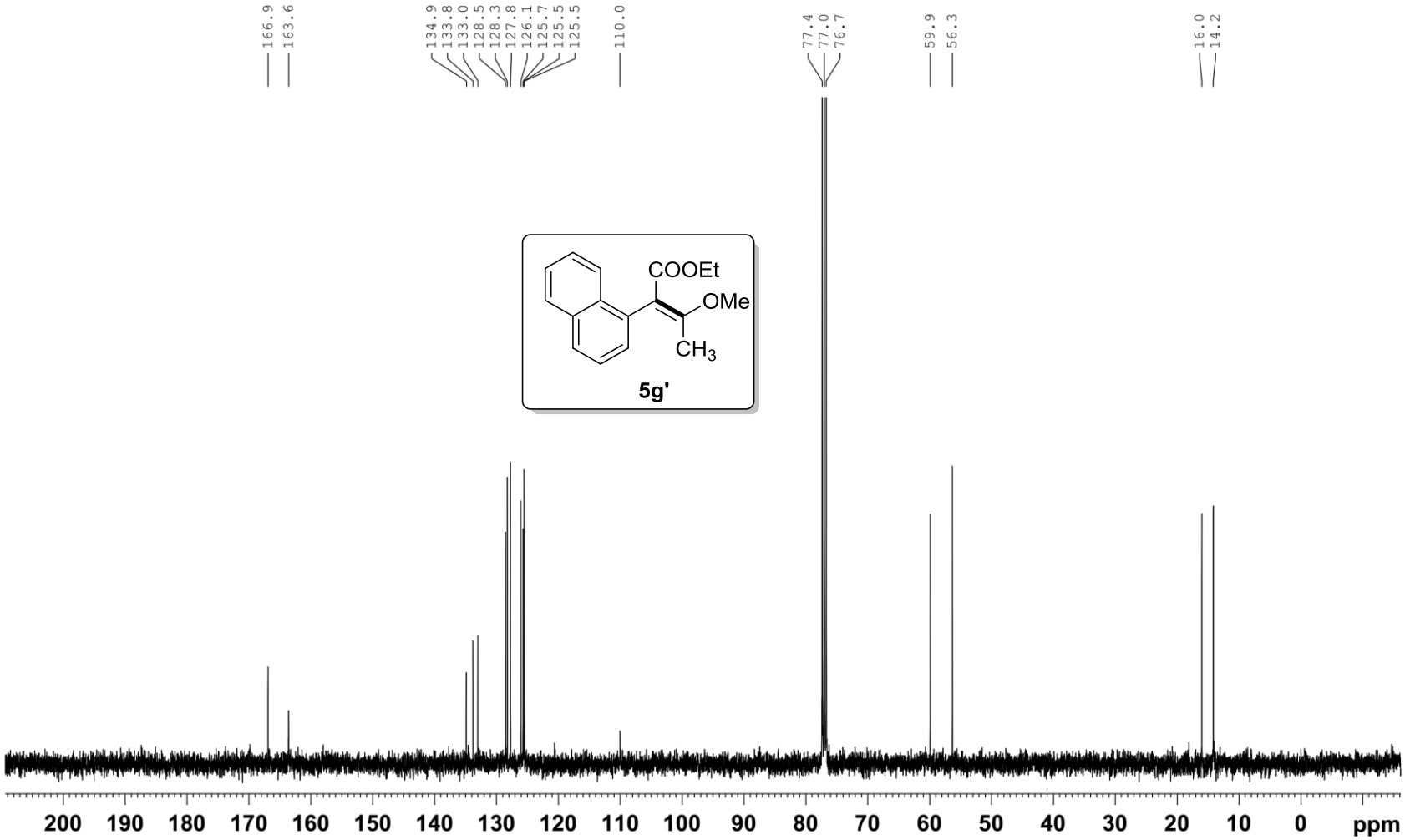

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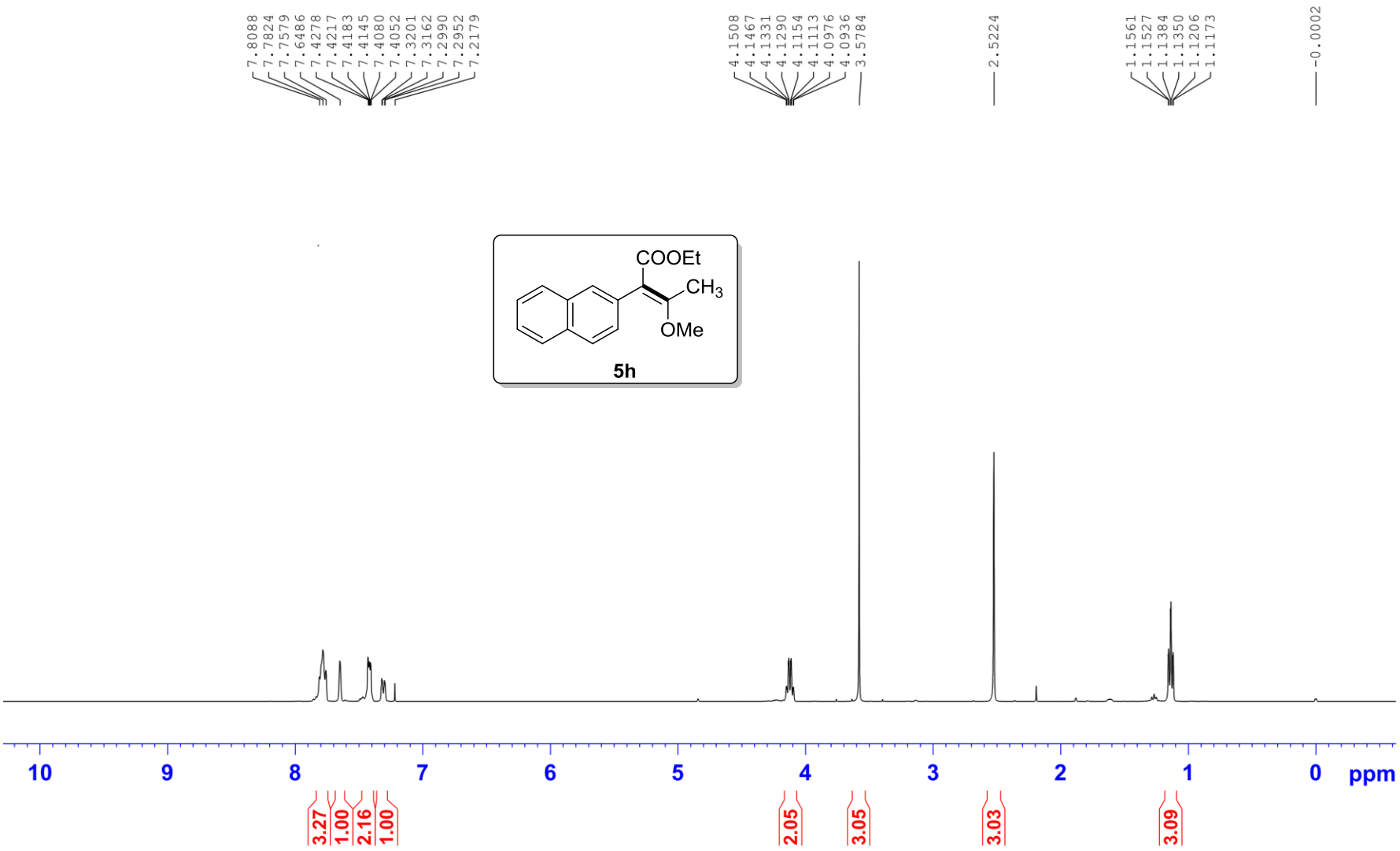

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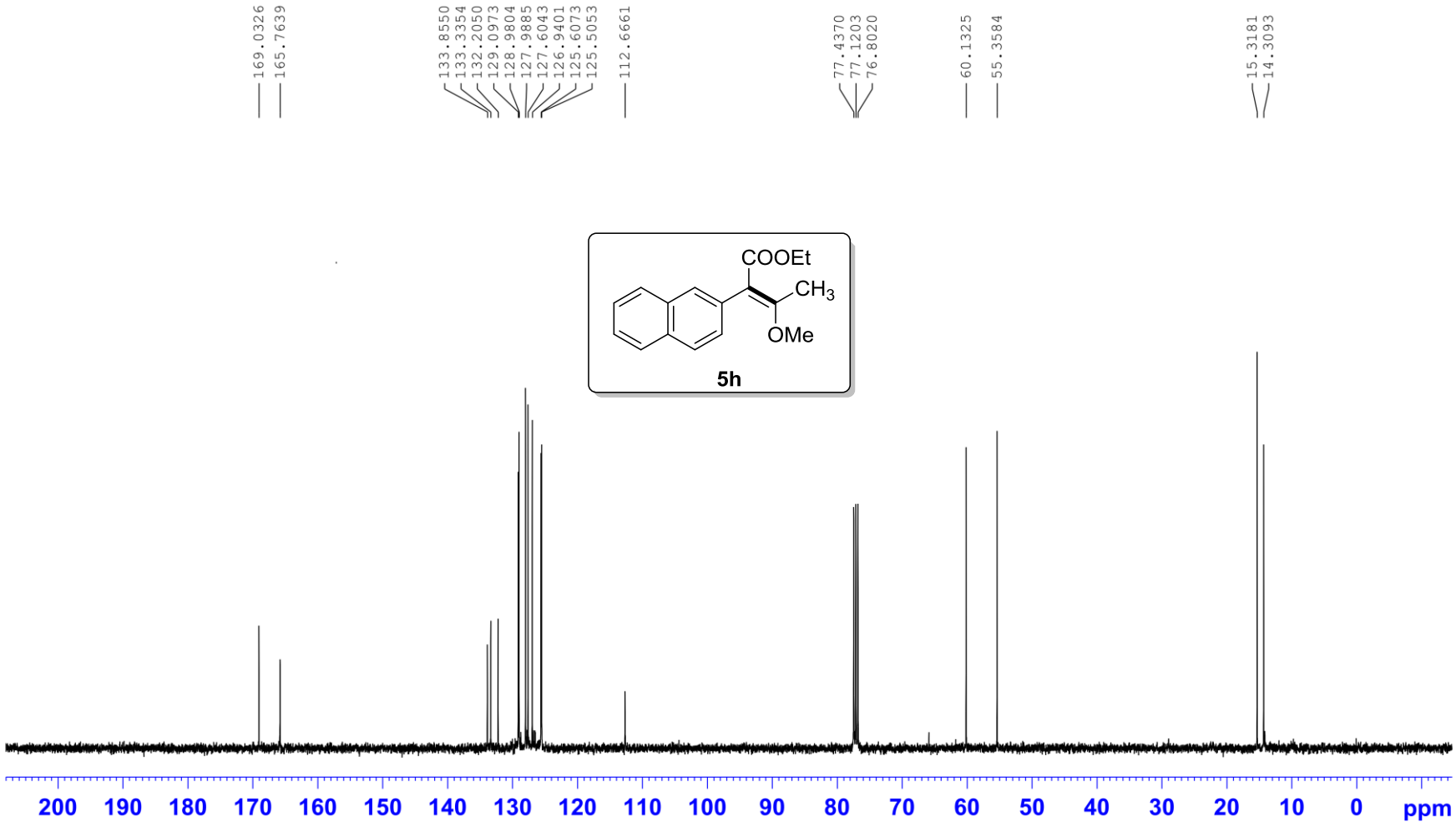
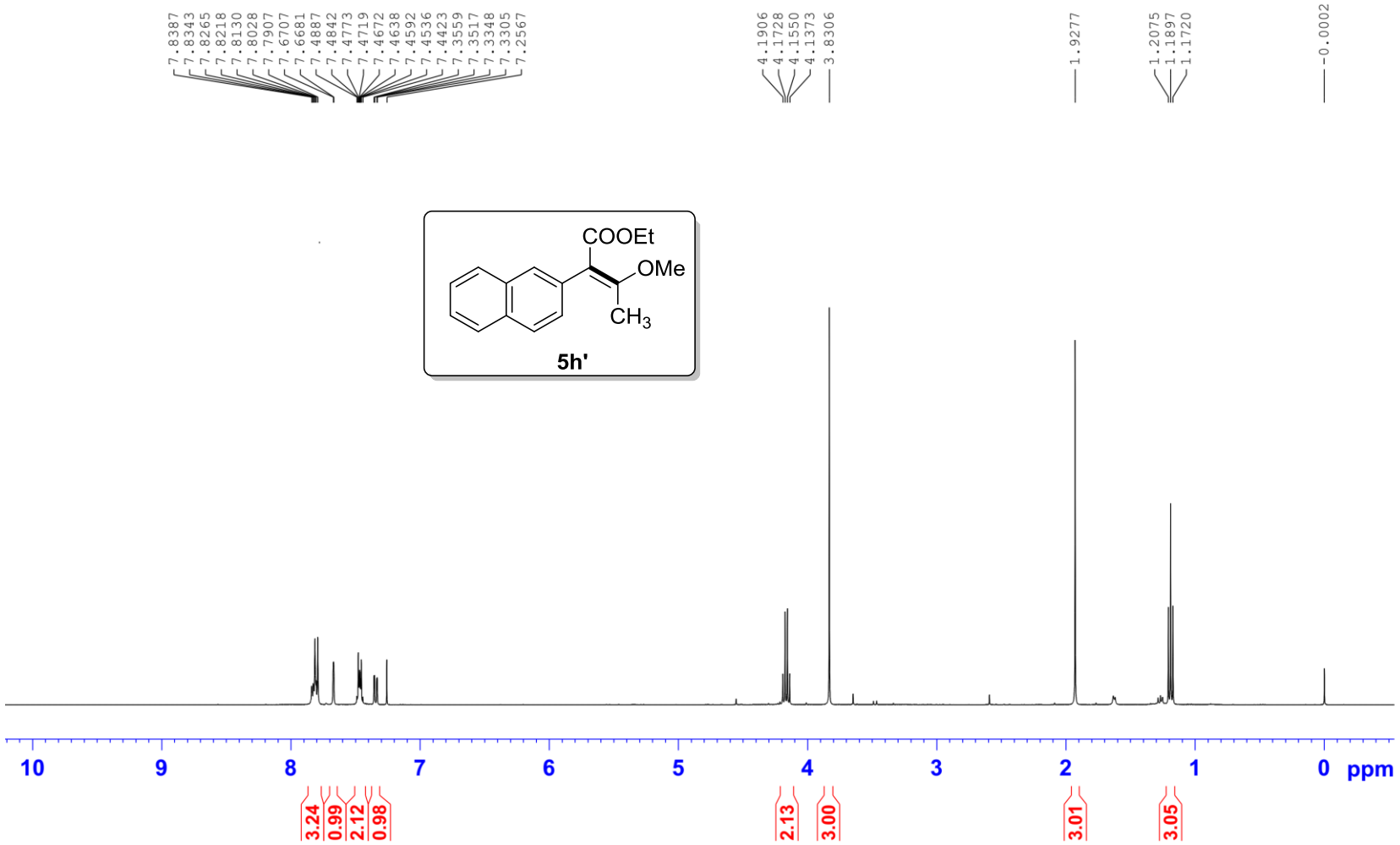
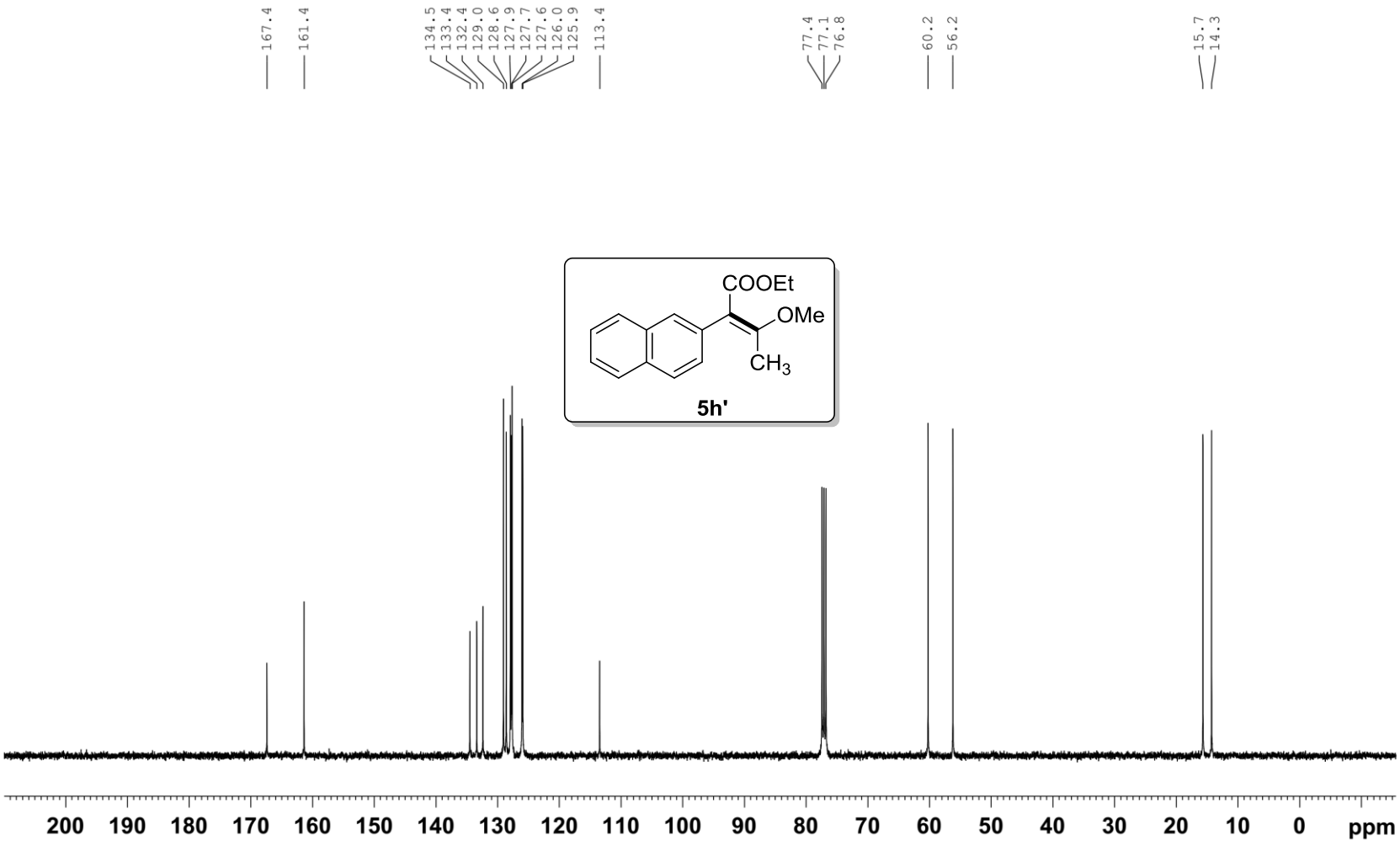


LJW-X170703-23-HNMR



LJW-X180319-5-CNMR



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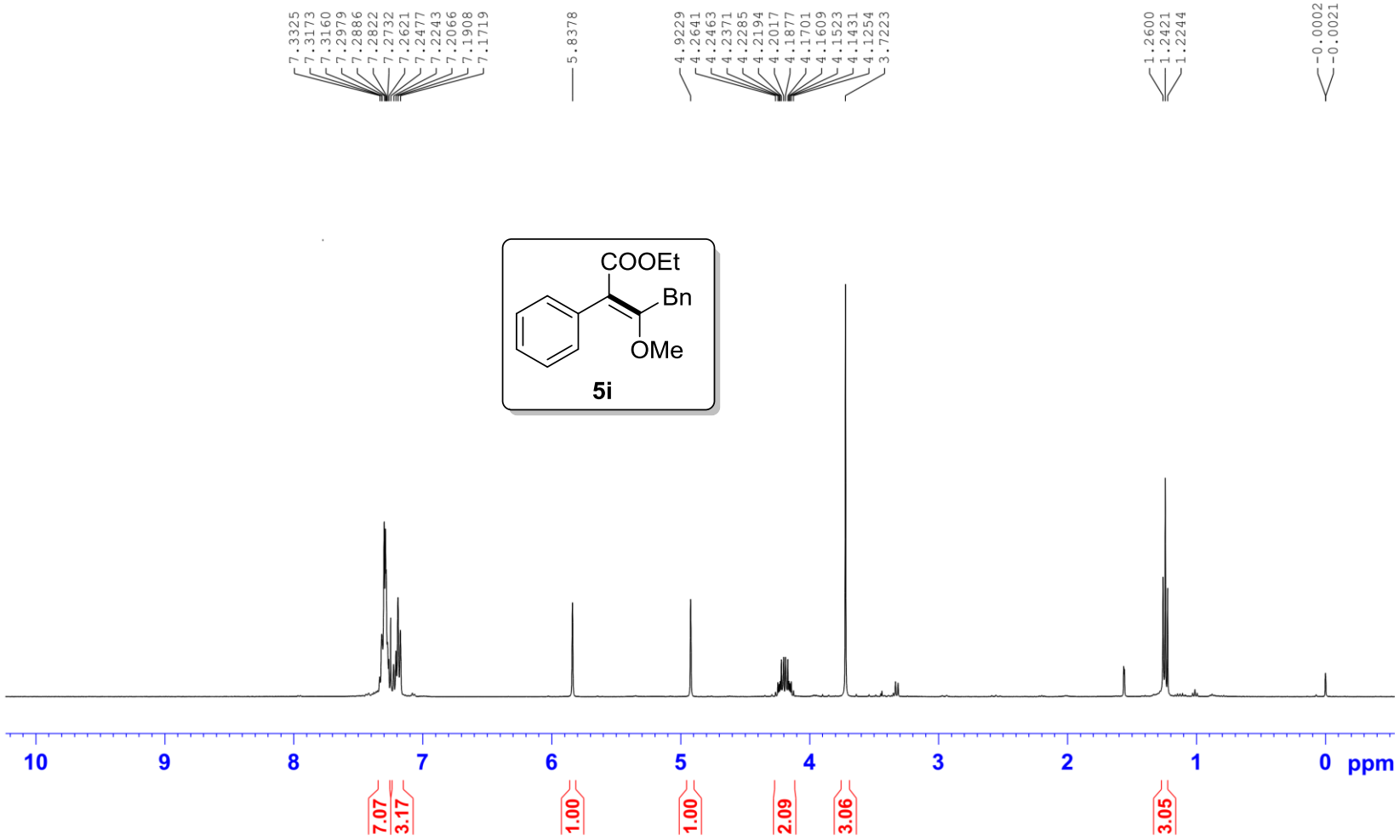
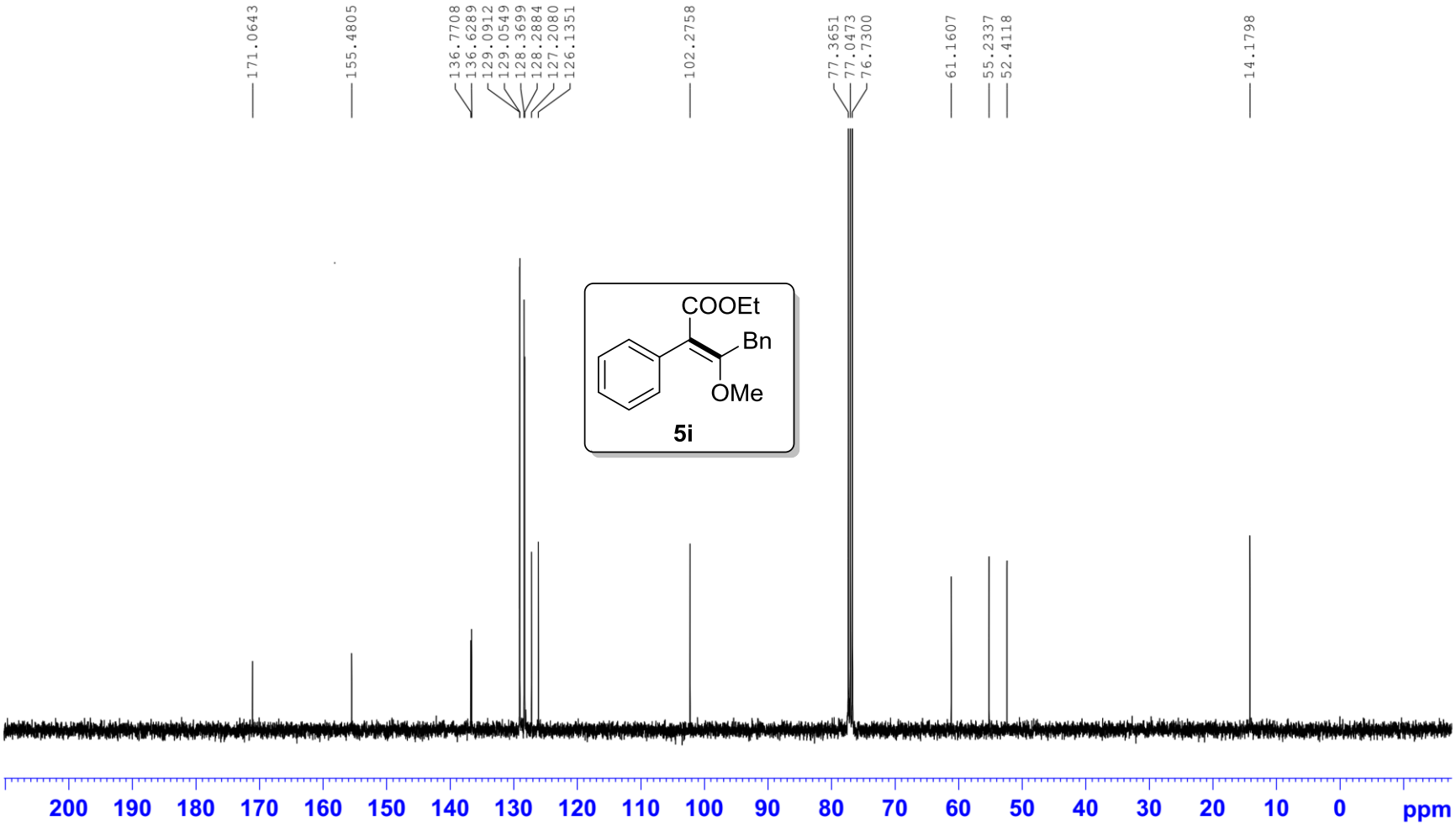
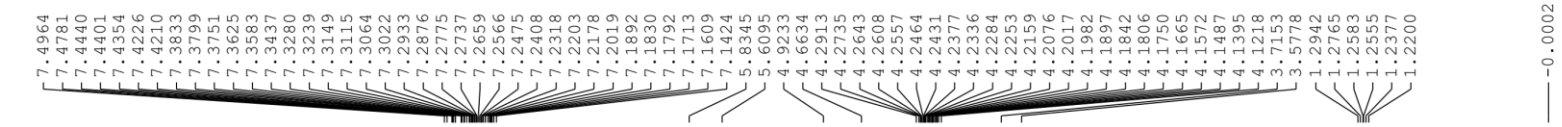
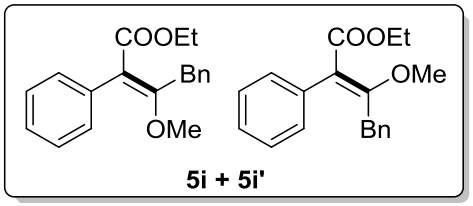


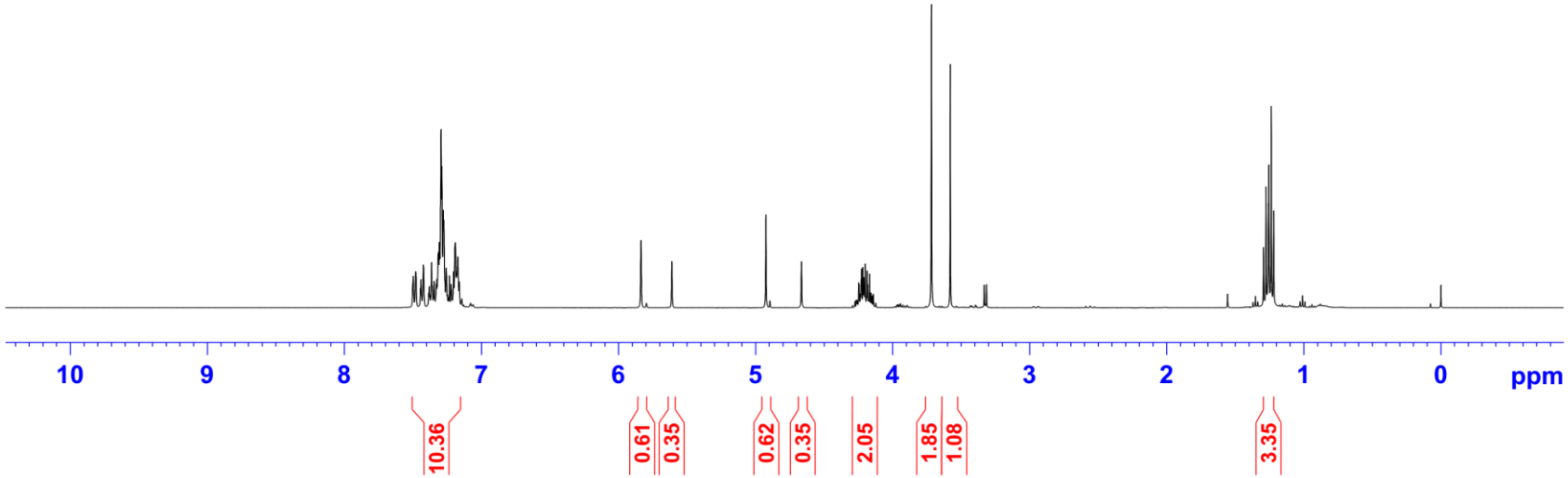
LJW-X170703-24-CNMR



LJW-X180608-2-HNMR







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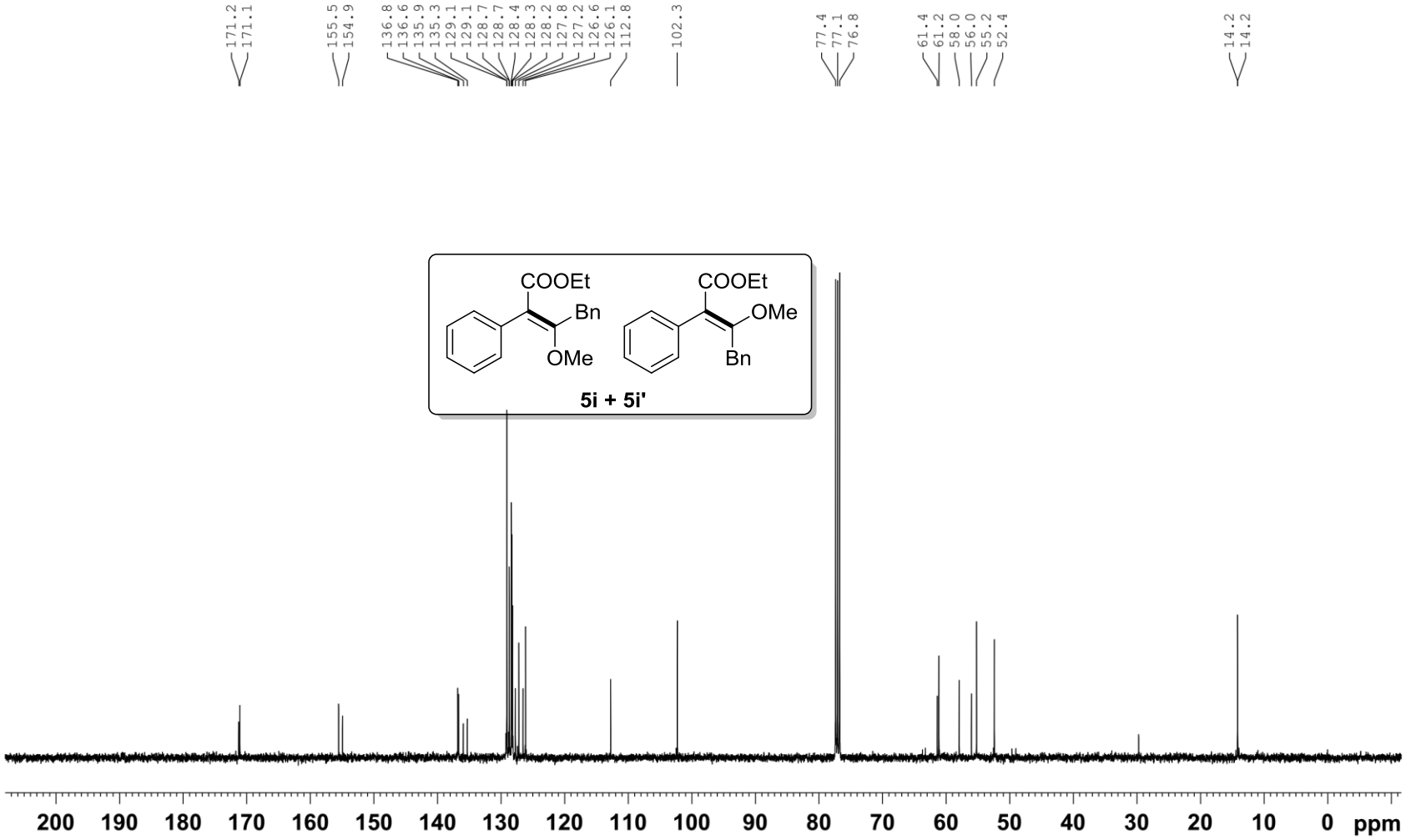
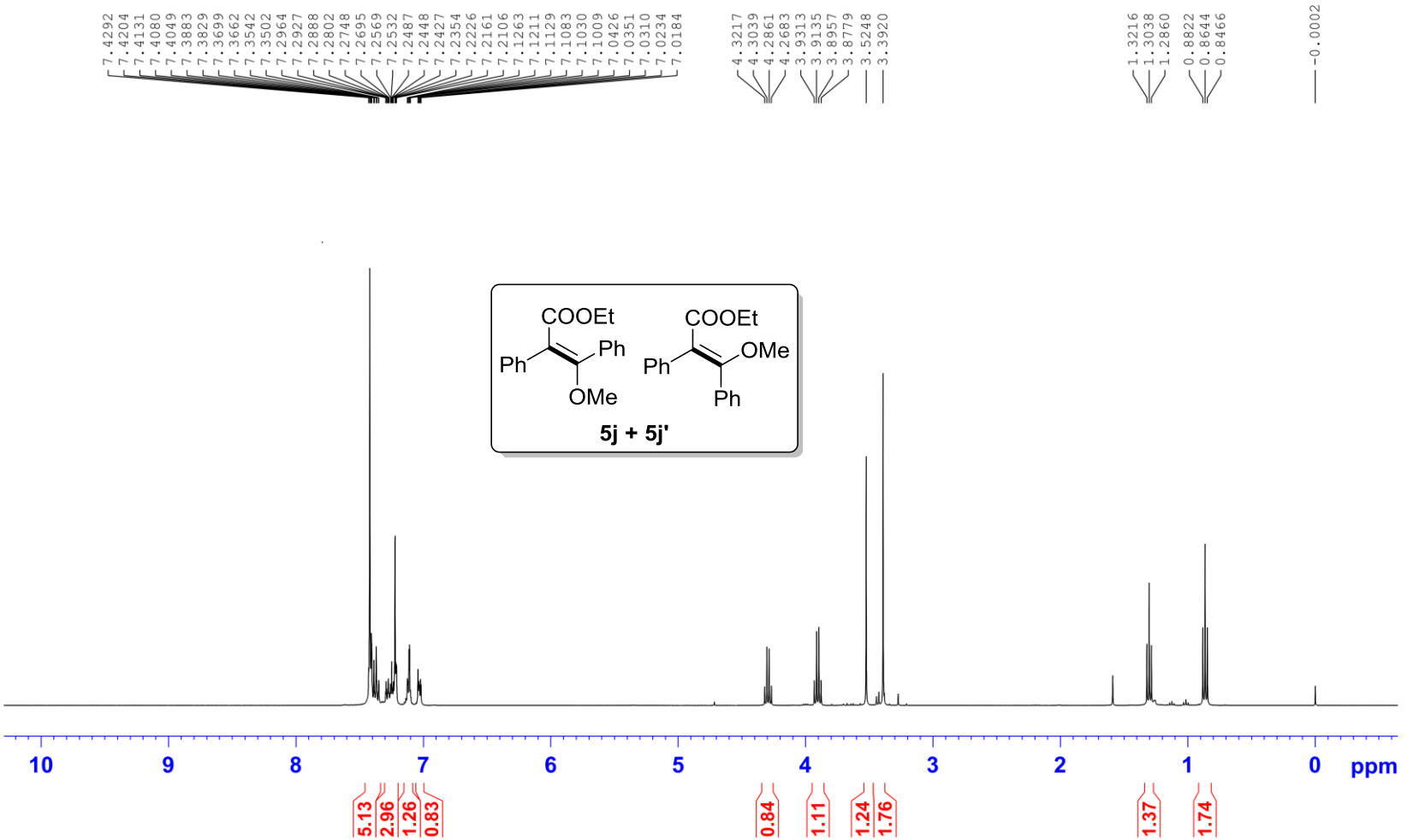
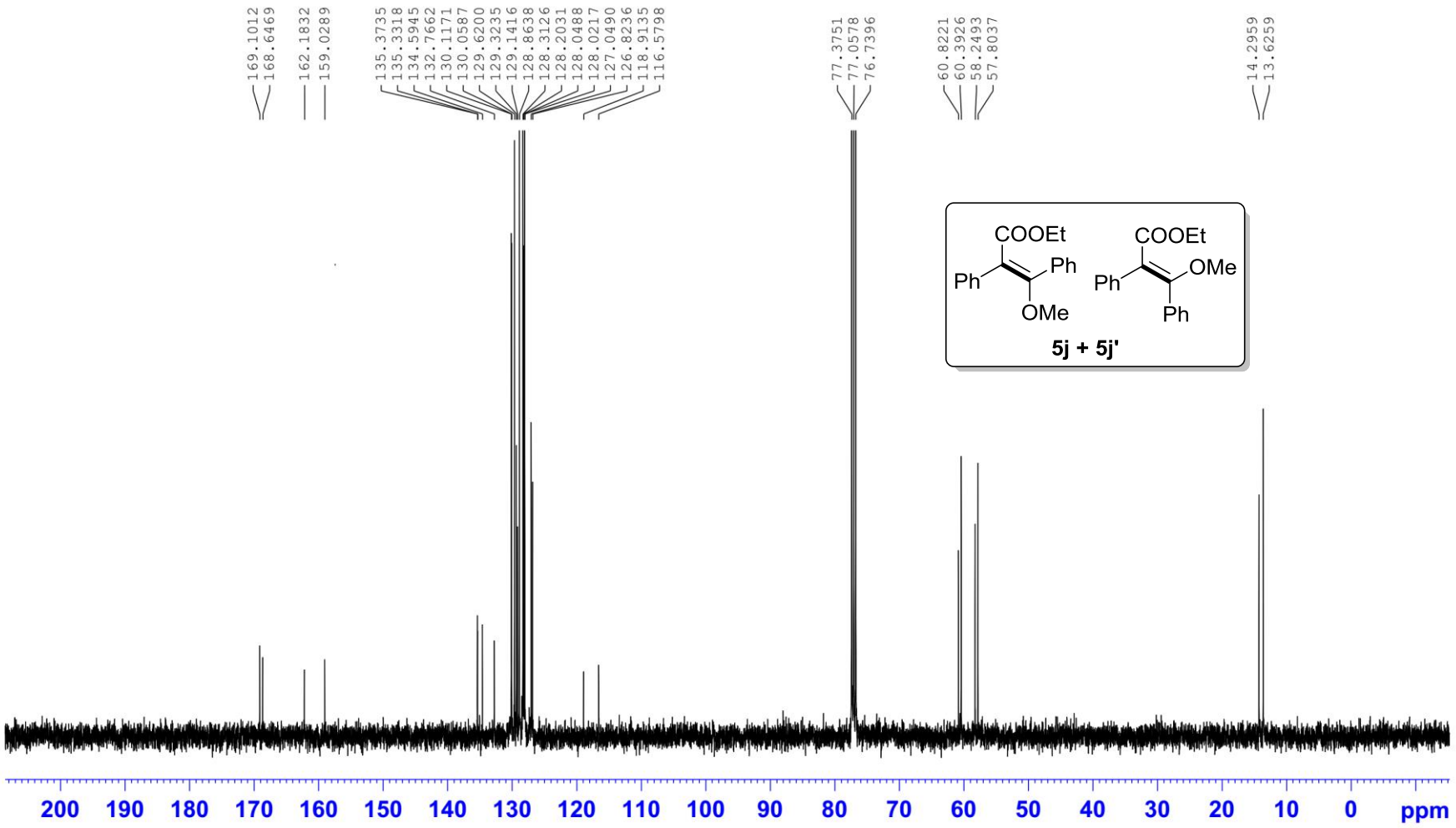


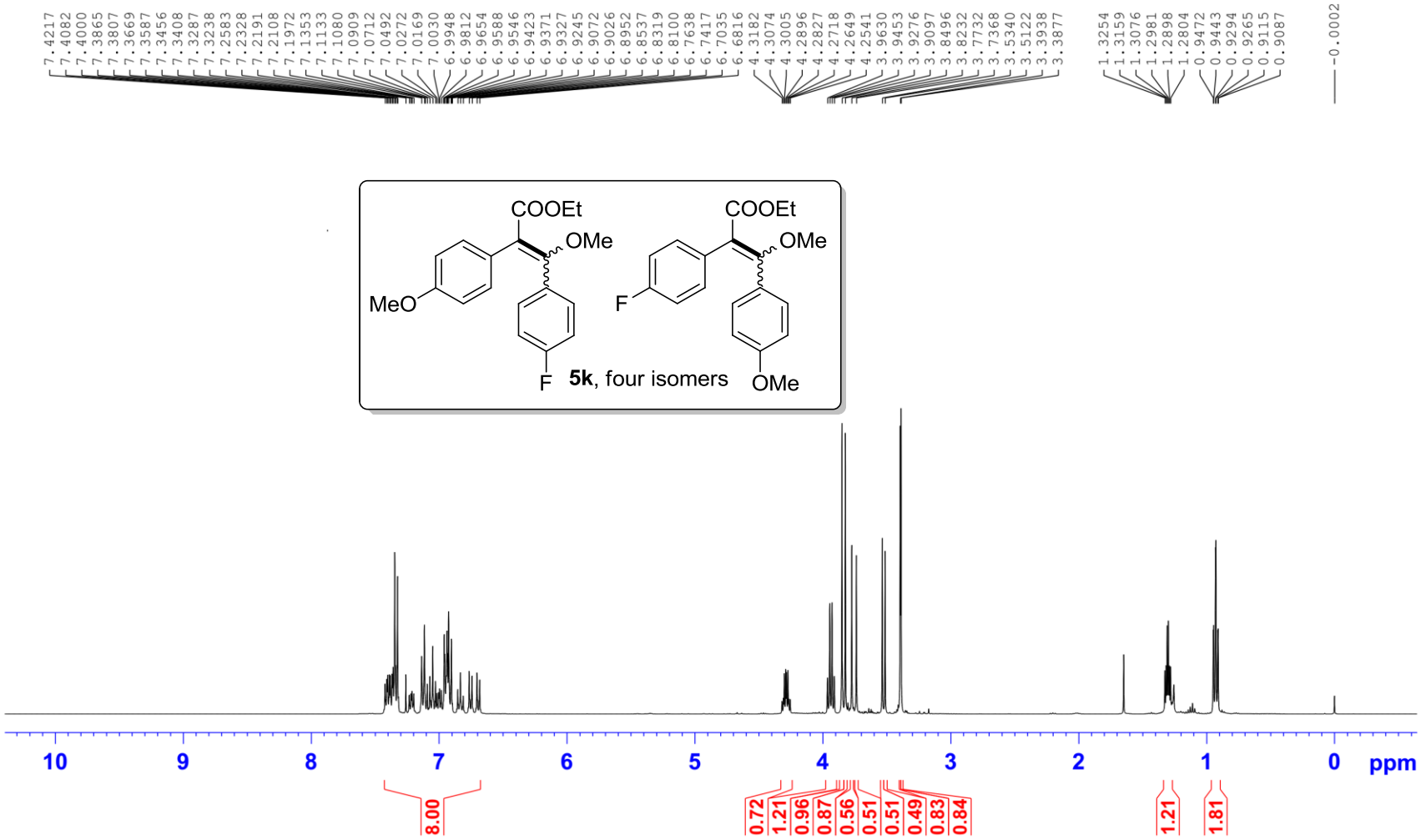
LJW-X170531-1-HNMR



LJW-X170531-1-CNMR



LJW-X180911-3-HNMR



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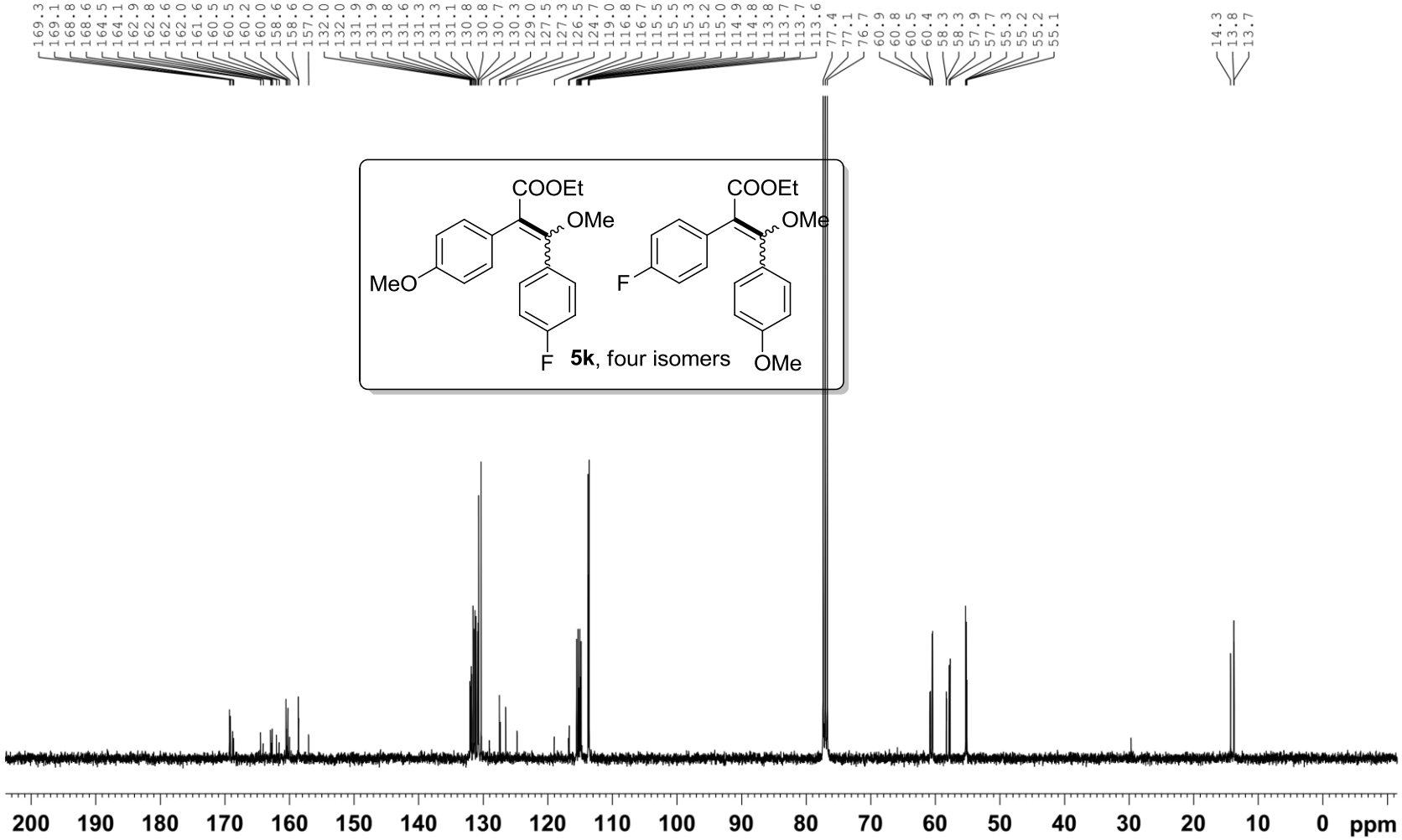

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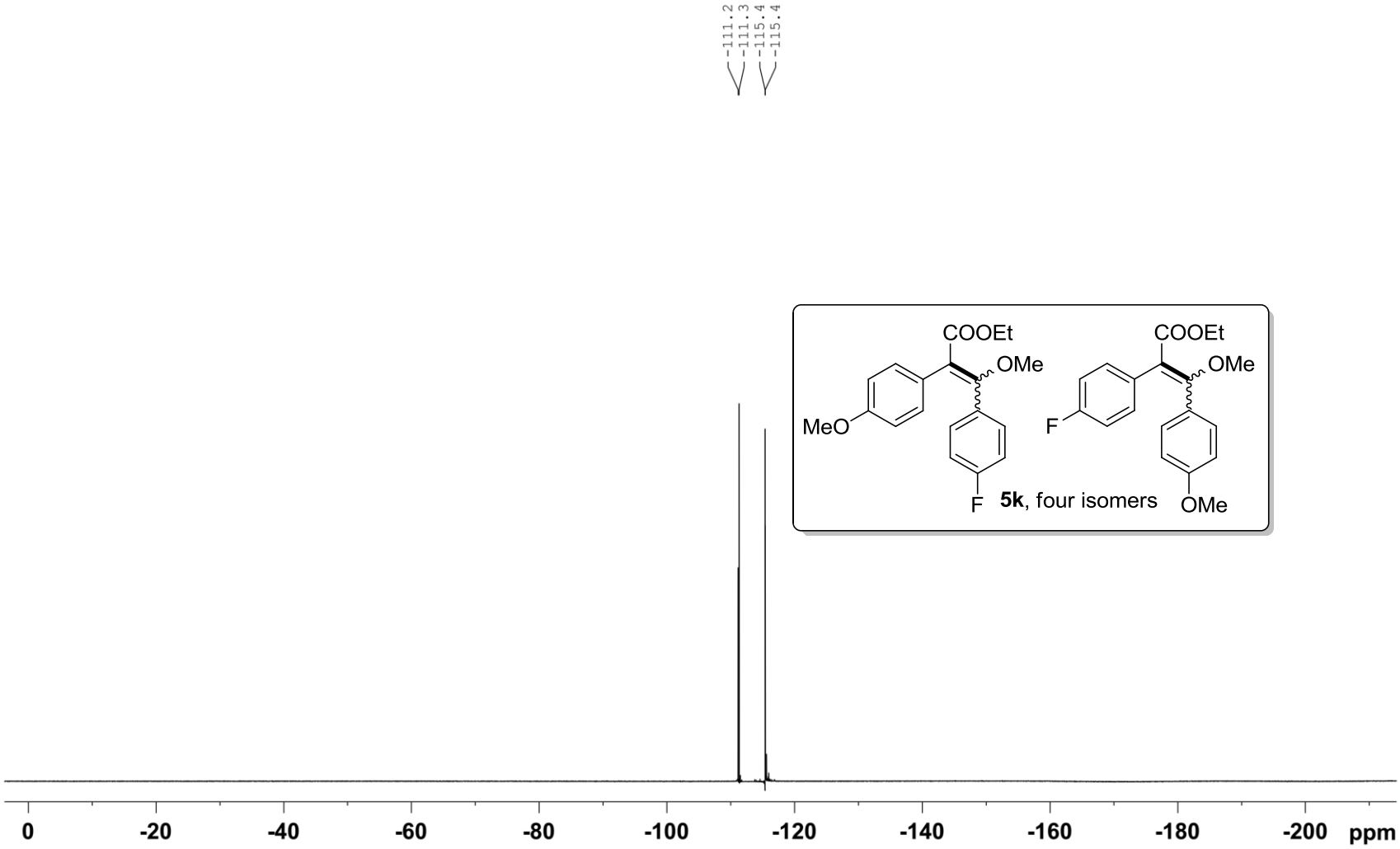
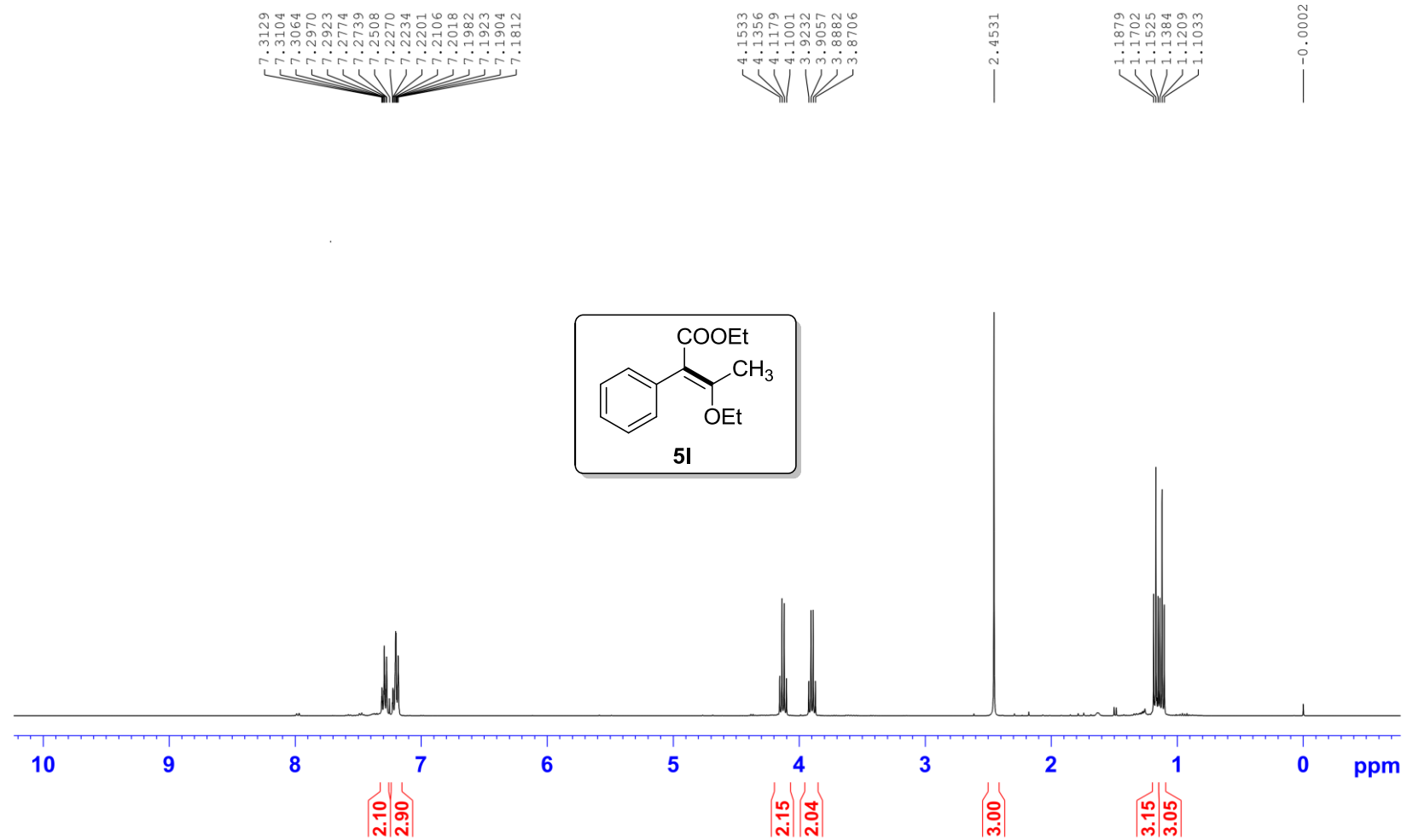
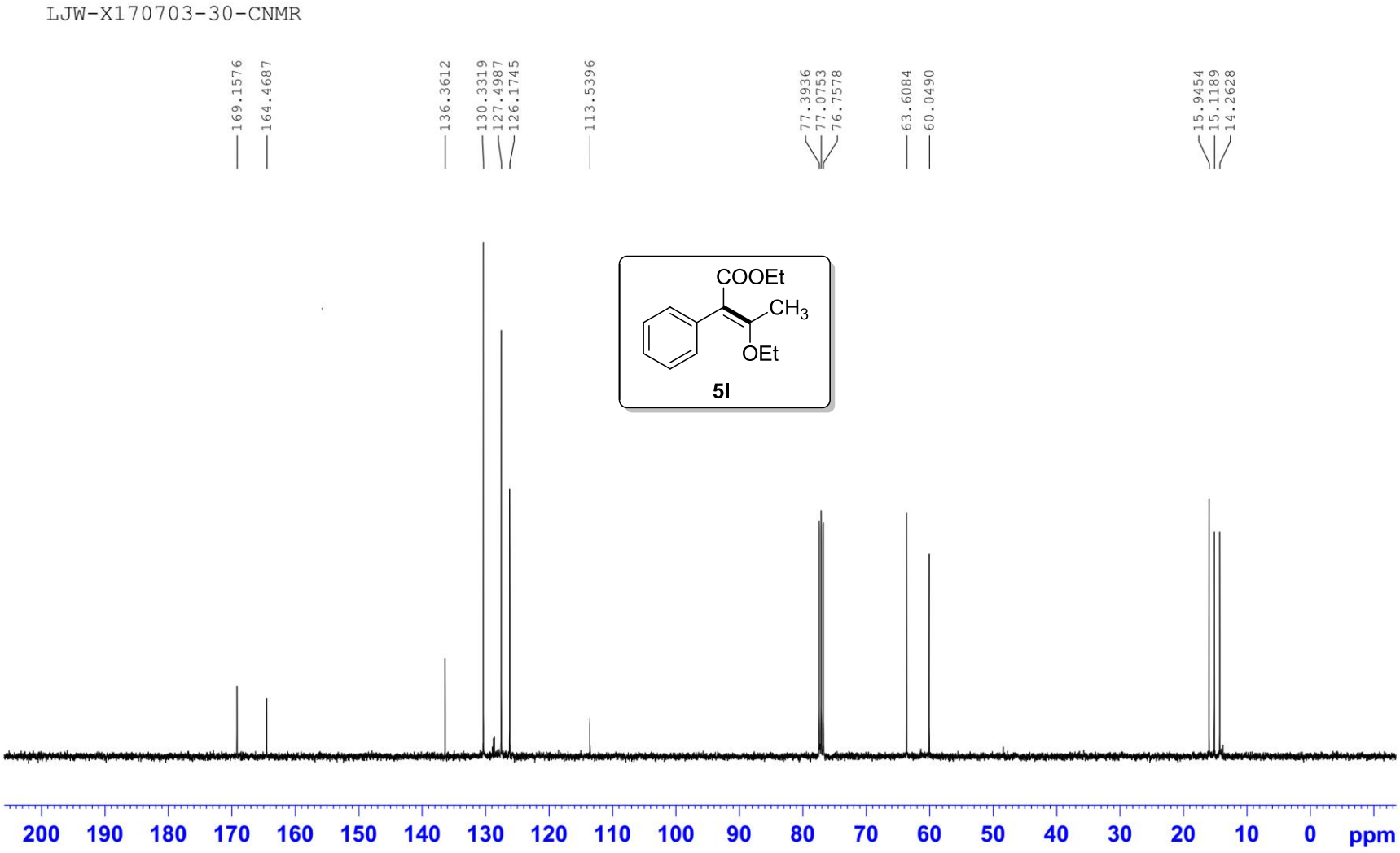


LJW-X170703-30-HNMR

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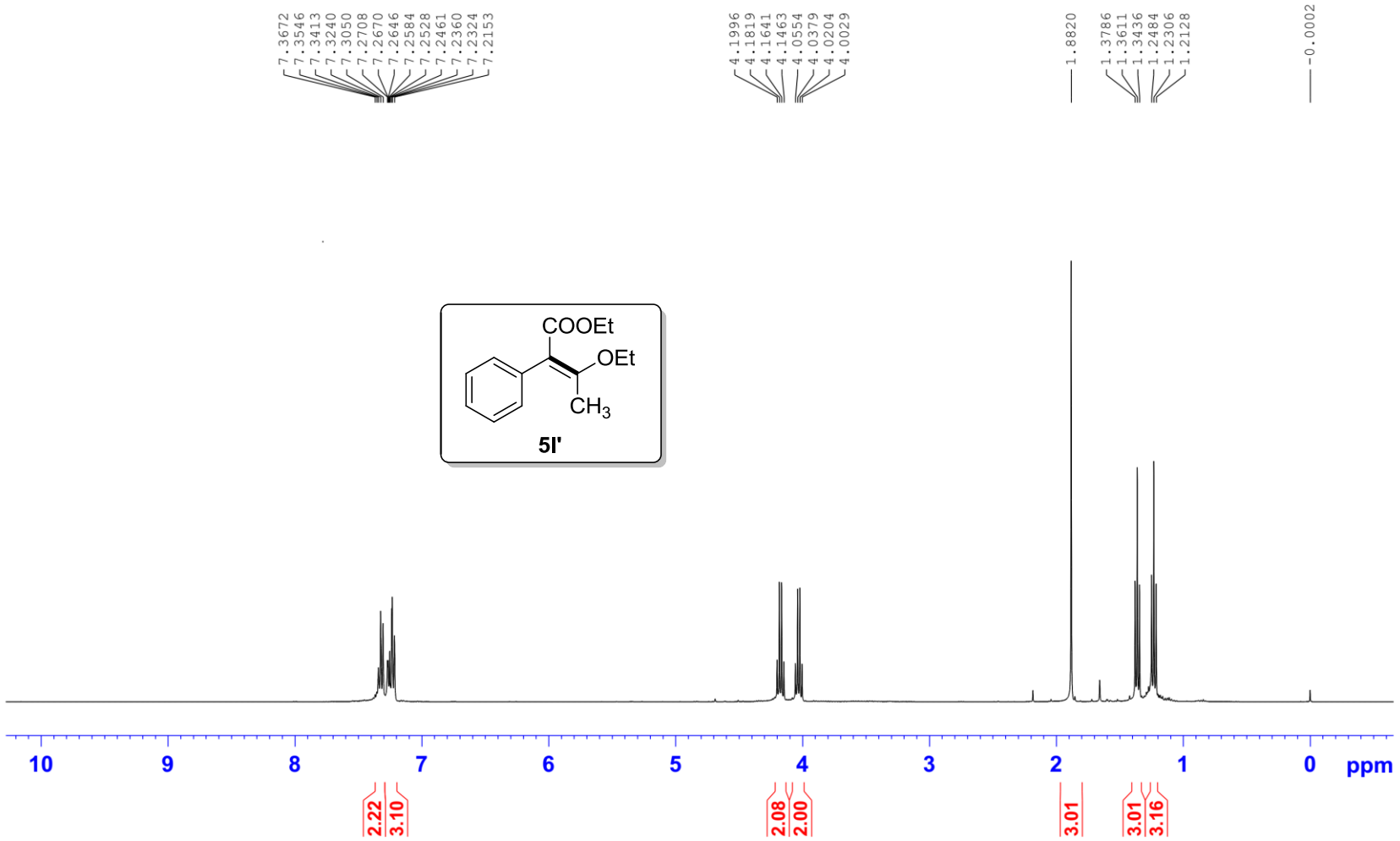
169.1576
164.4687
136.3612
130.3319
127.4987
126.1745
113.5396
77.3936
77.0753
76.7578
63.6084
60.0490
15.9454
15.1189
14.2628
COOEt
CH3
OEt
5l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LJW-X170706-2-HNMR



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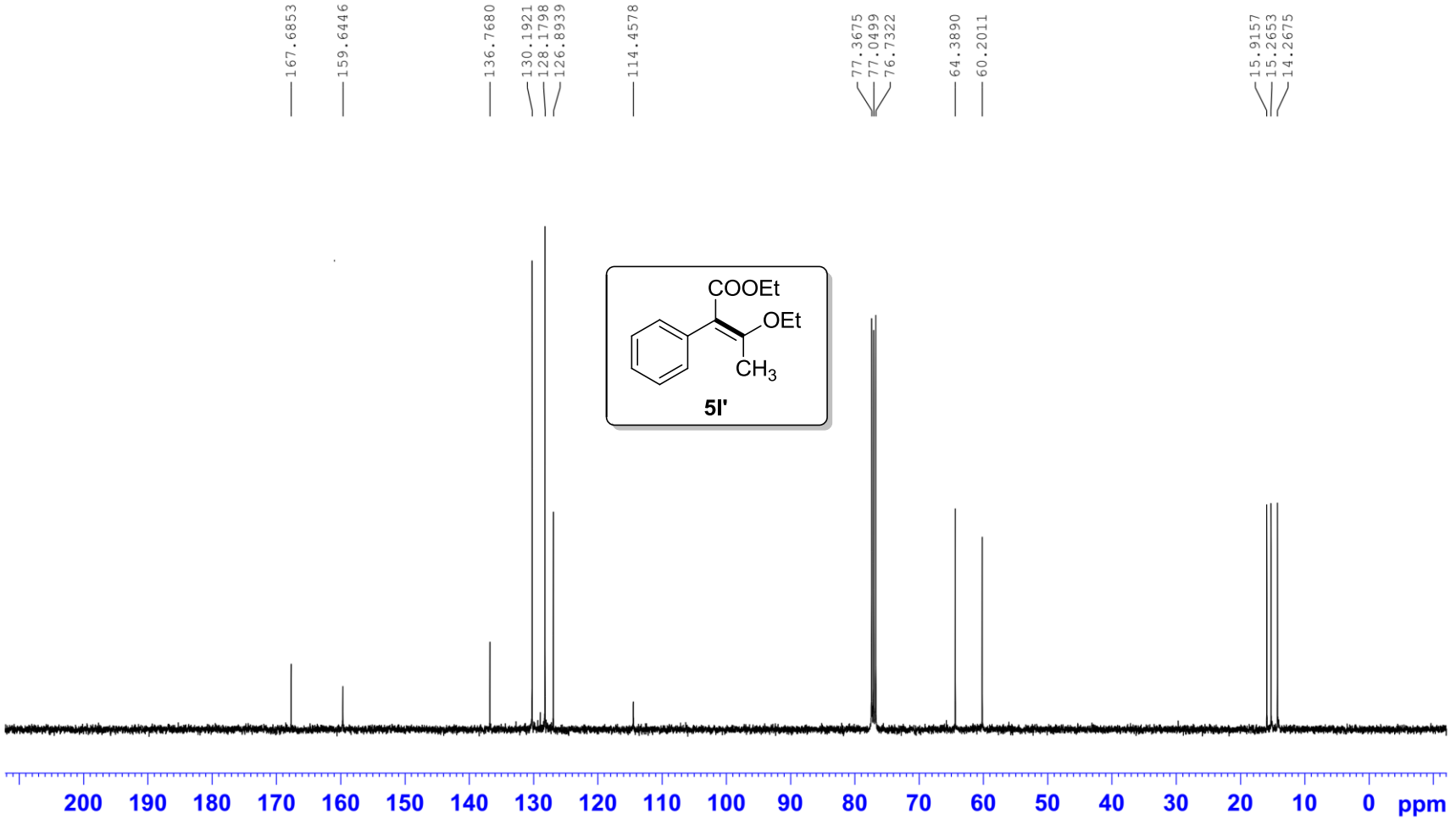
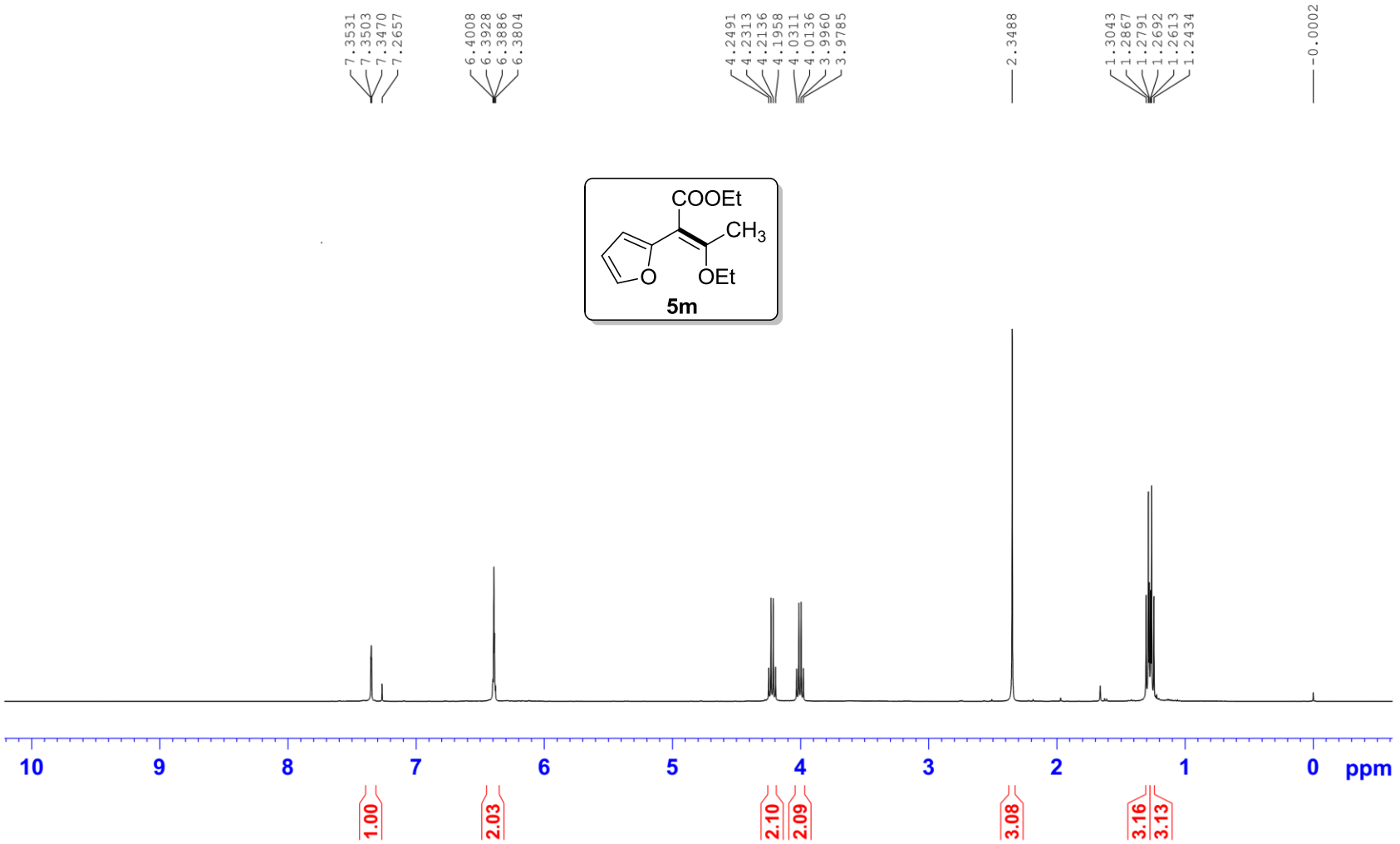


LJW-X170703-36-HNMR



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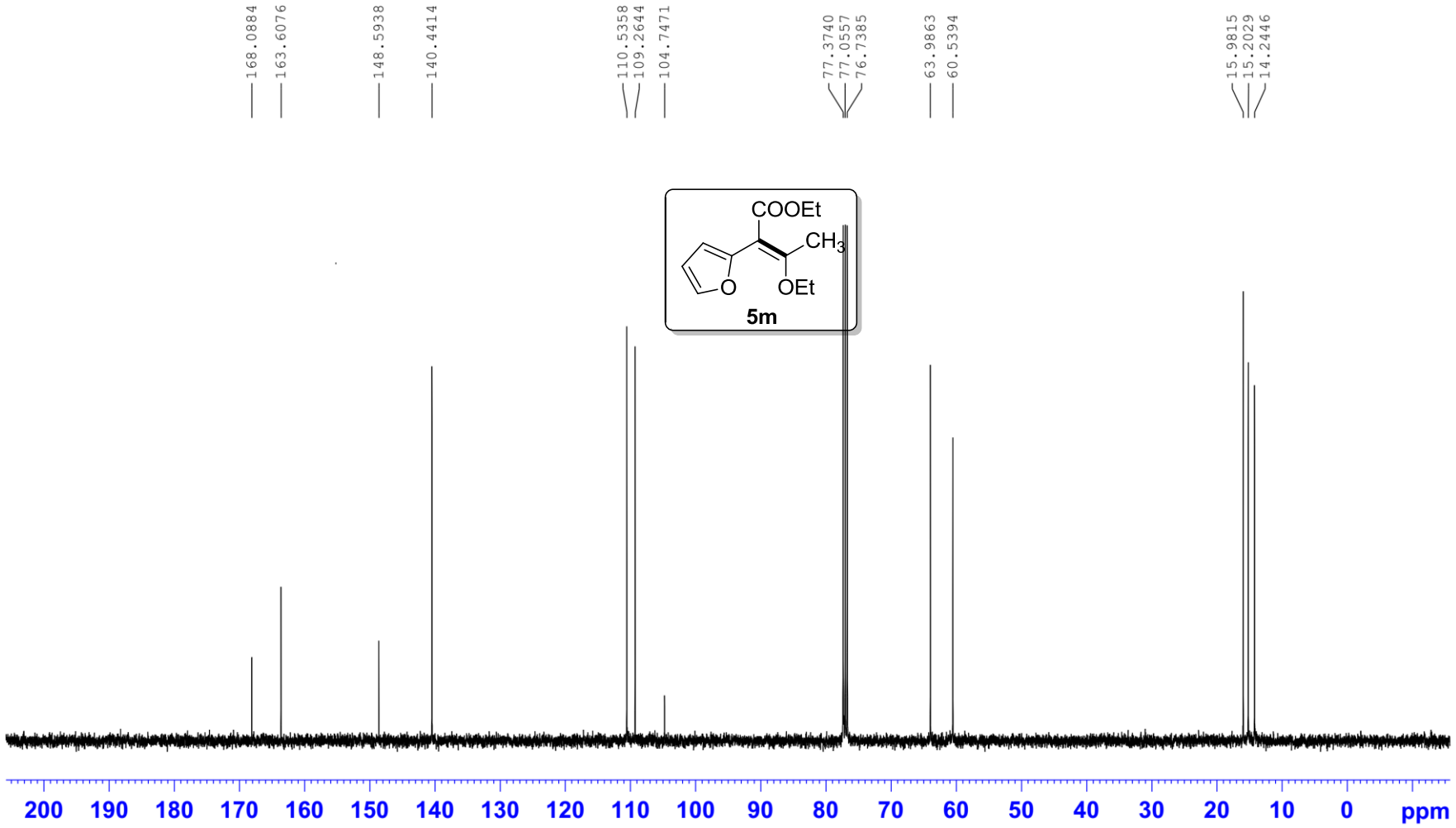
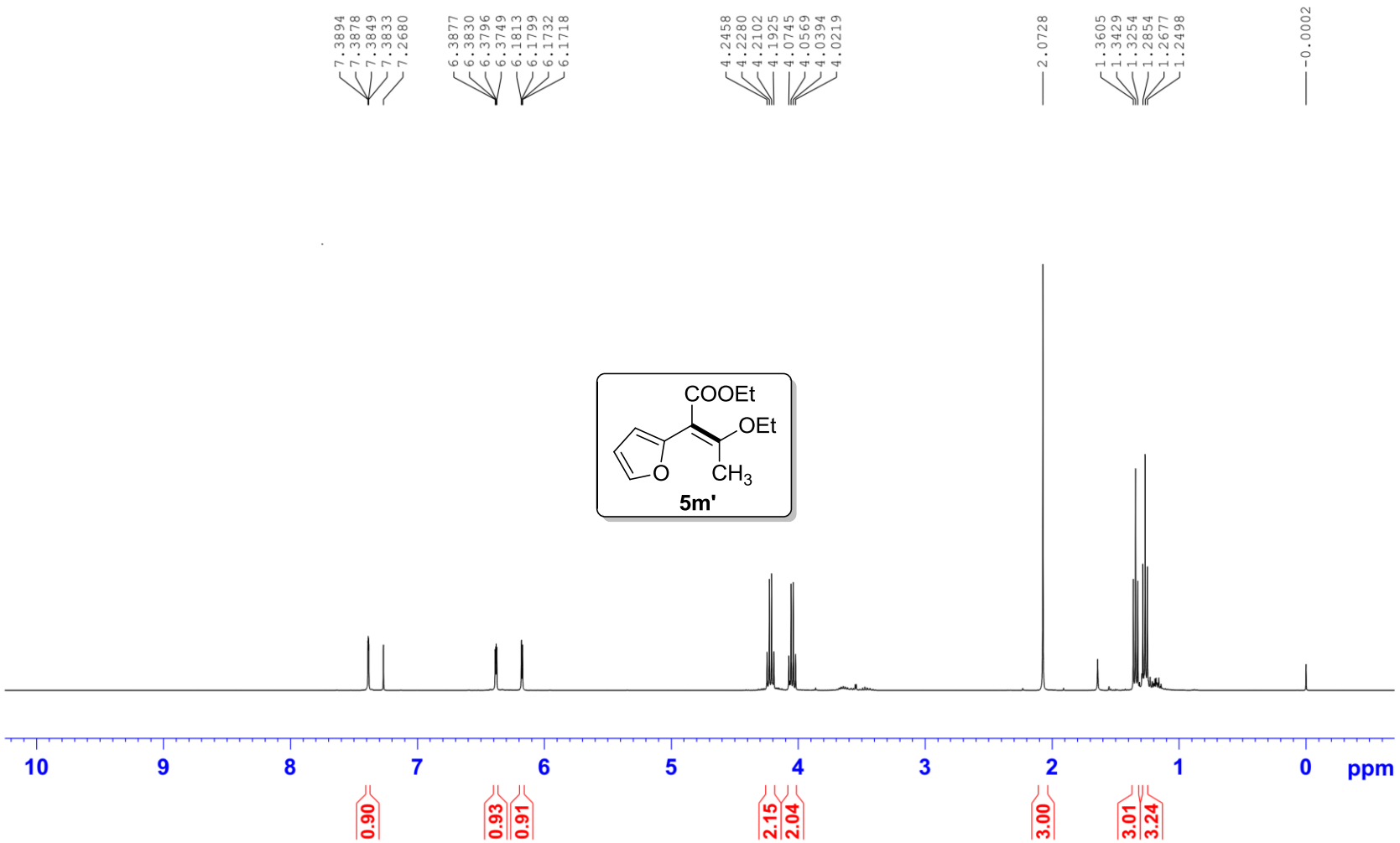


LJW-X170703-37-HNMR



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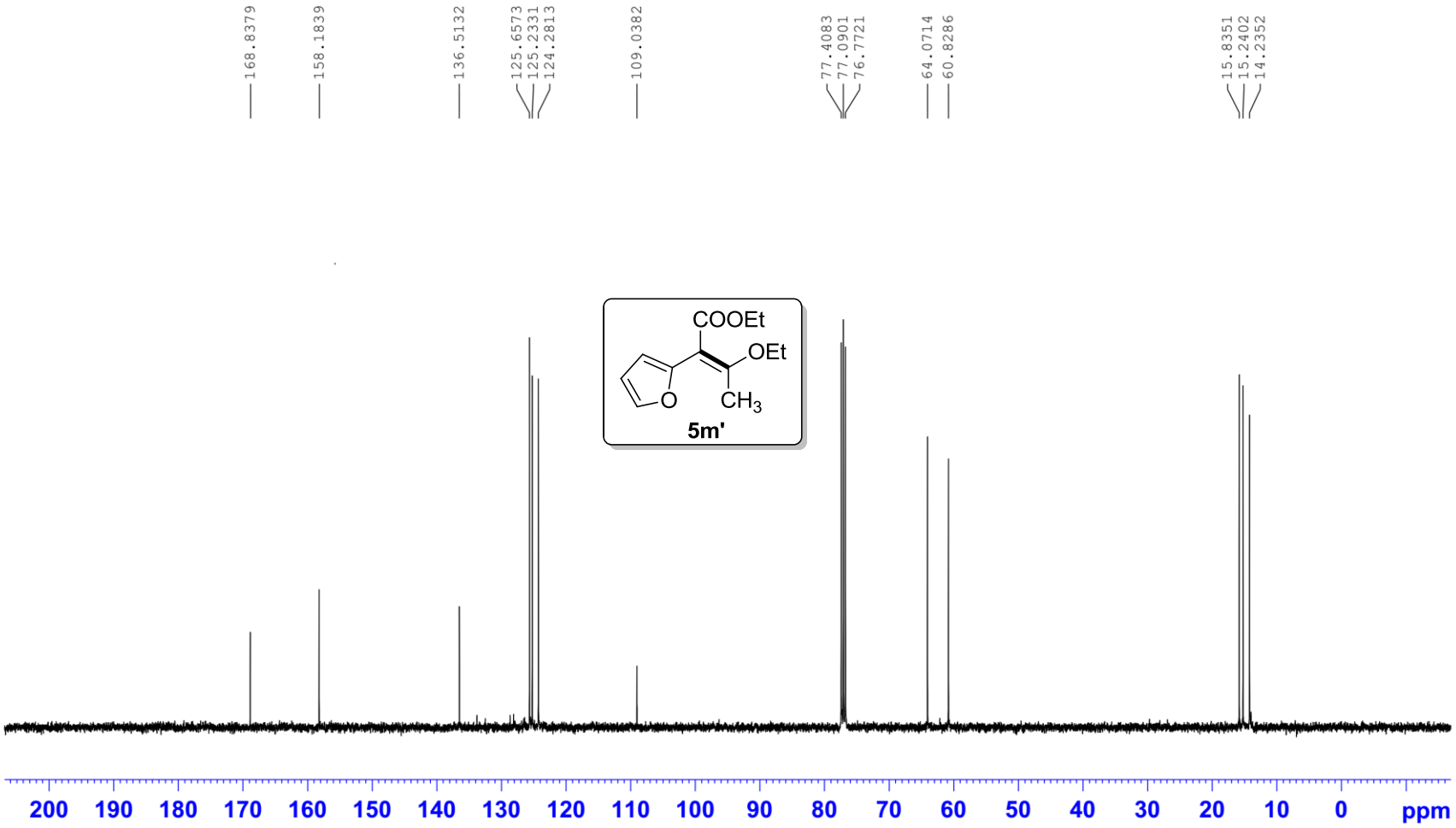

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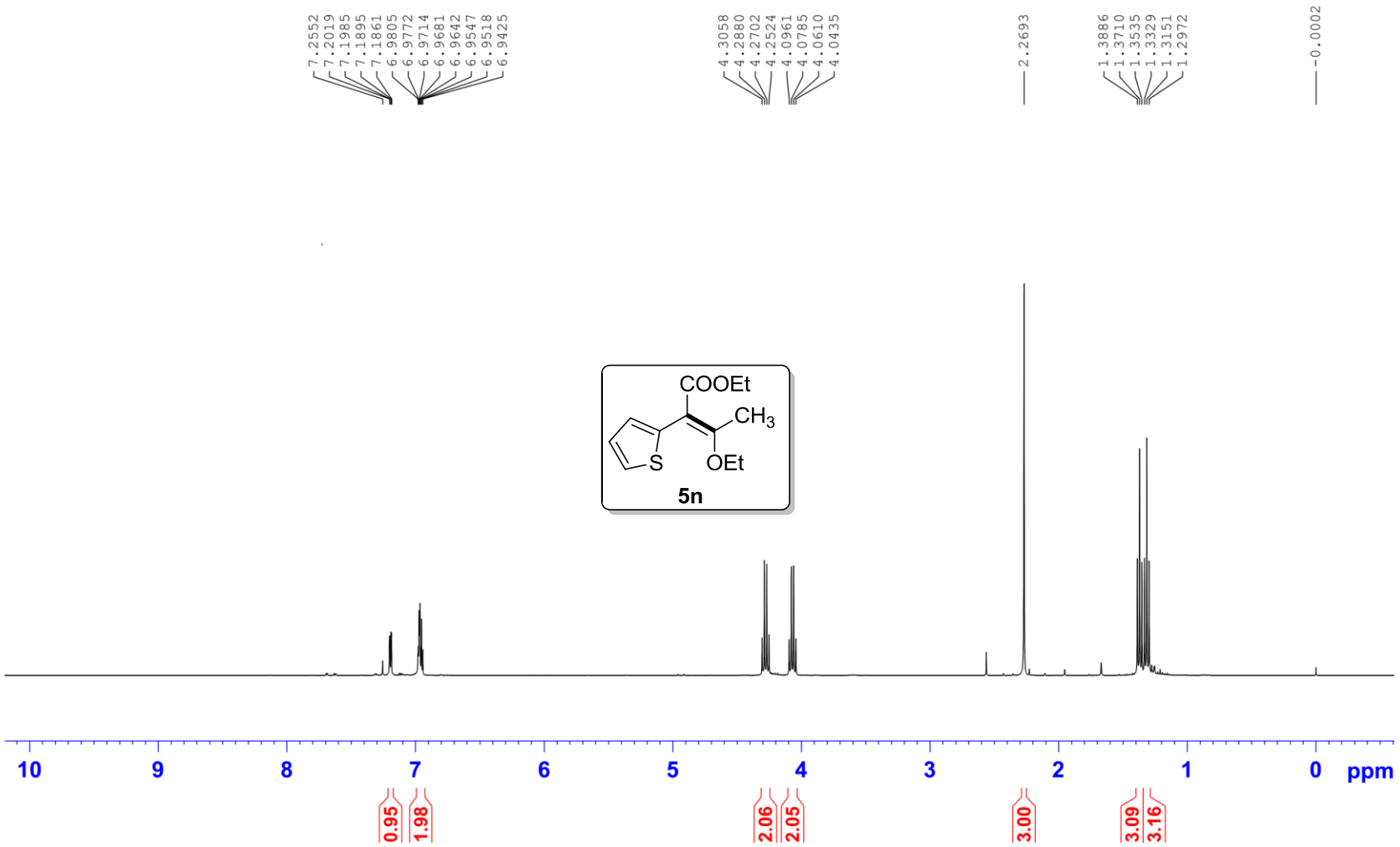

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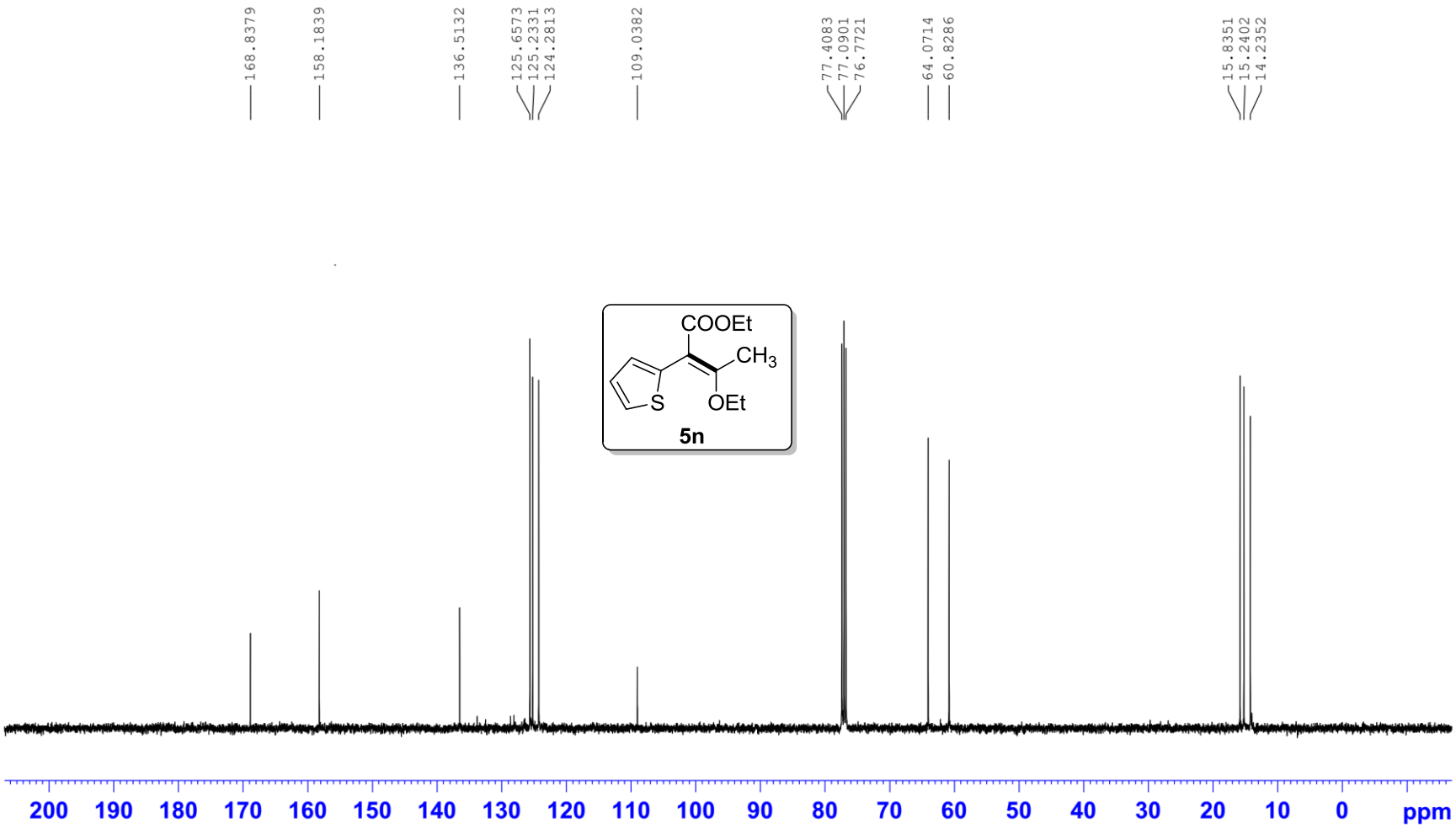
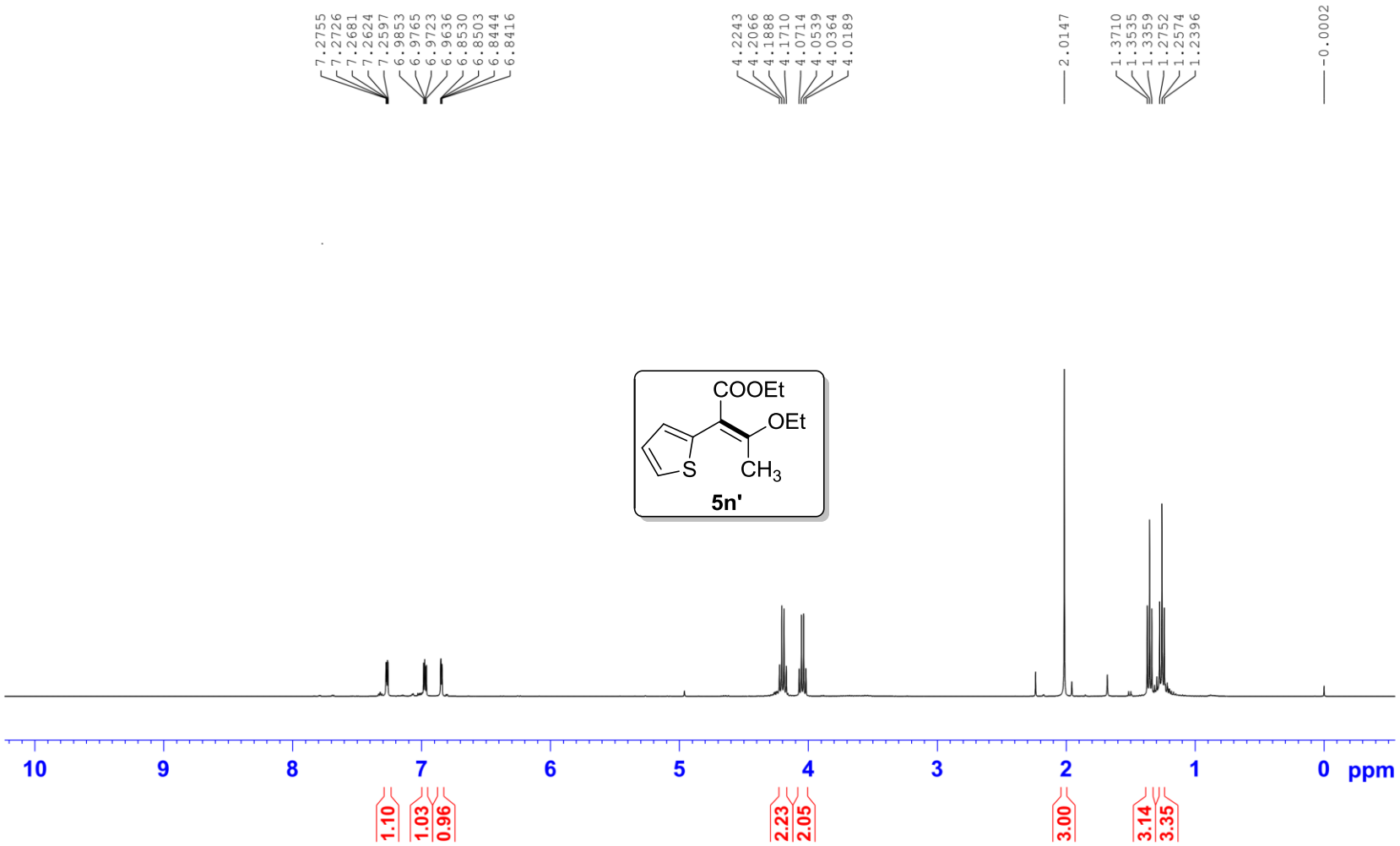


LJW-X170703-39-HNMR



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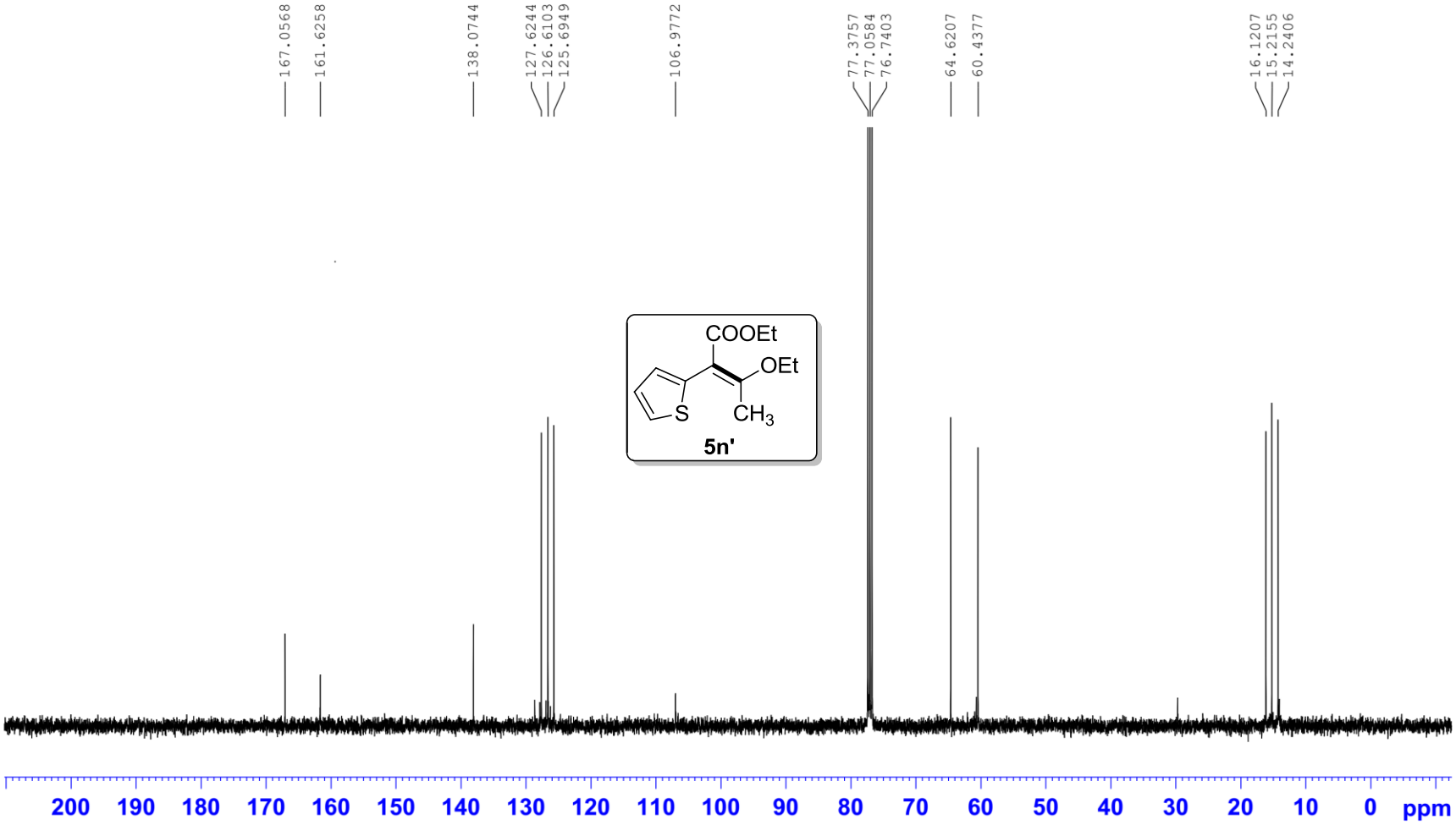
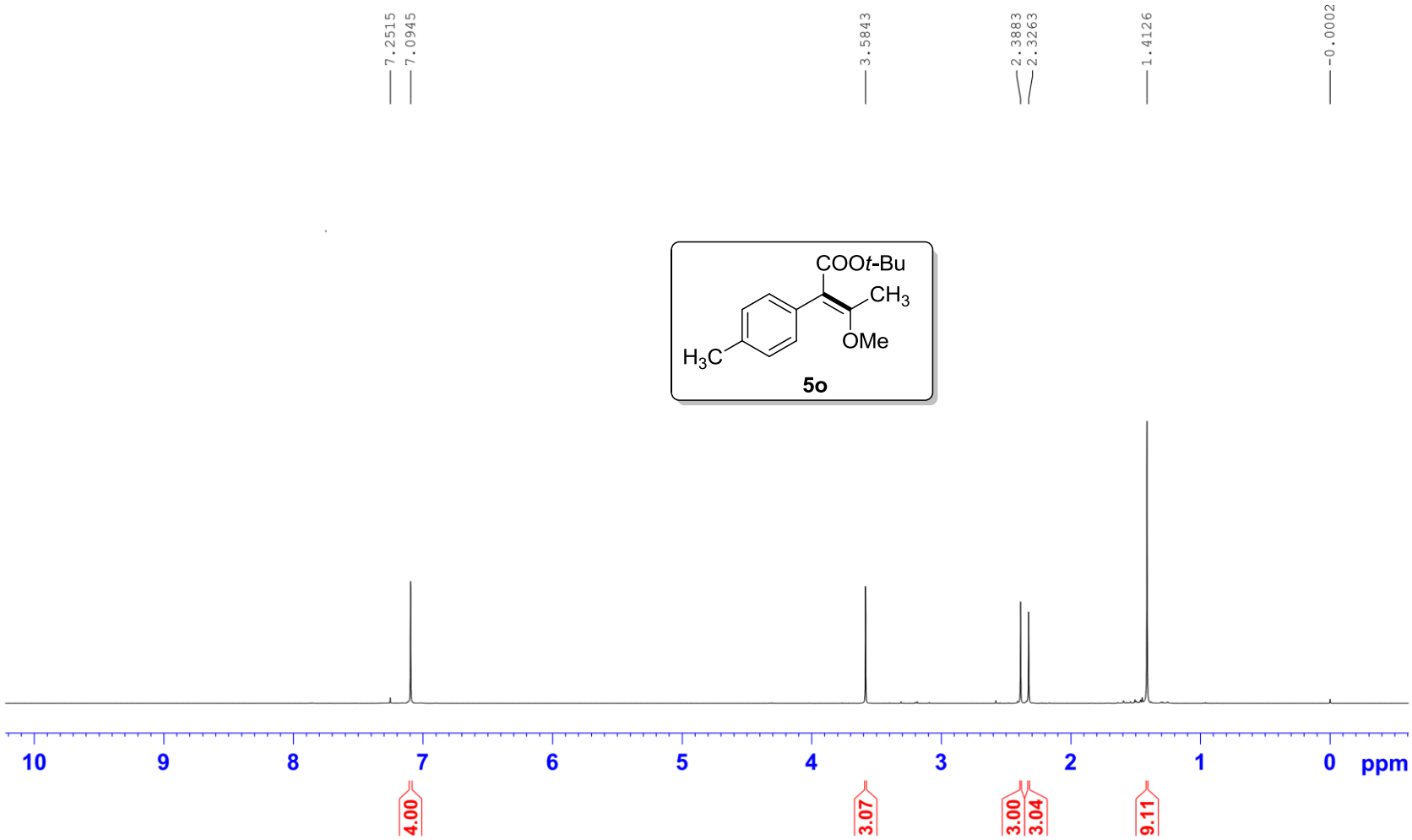
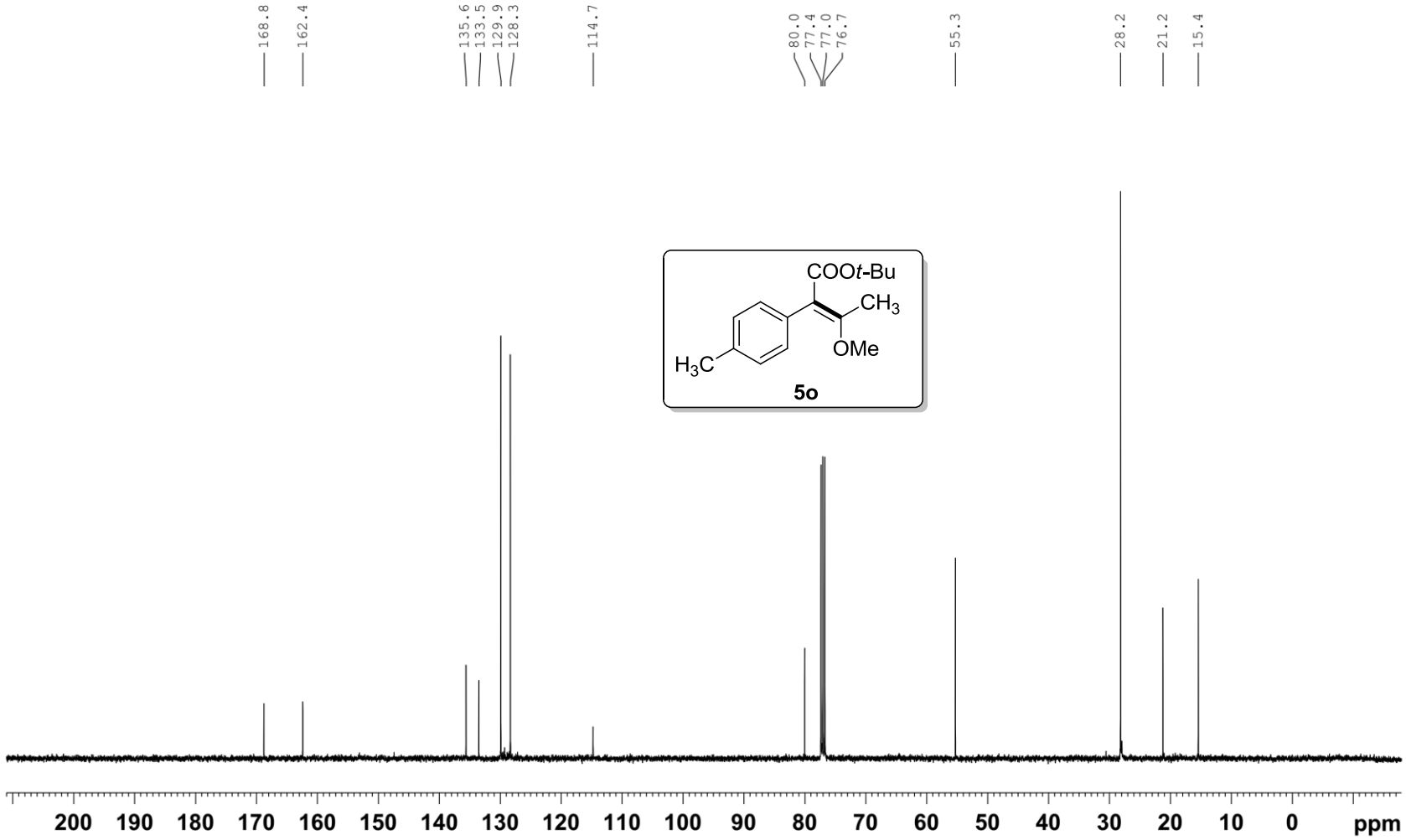


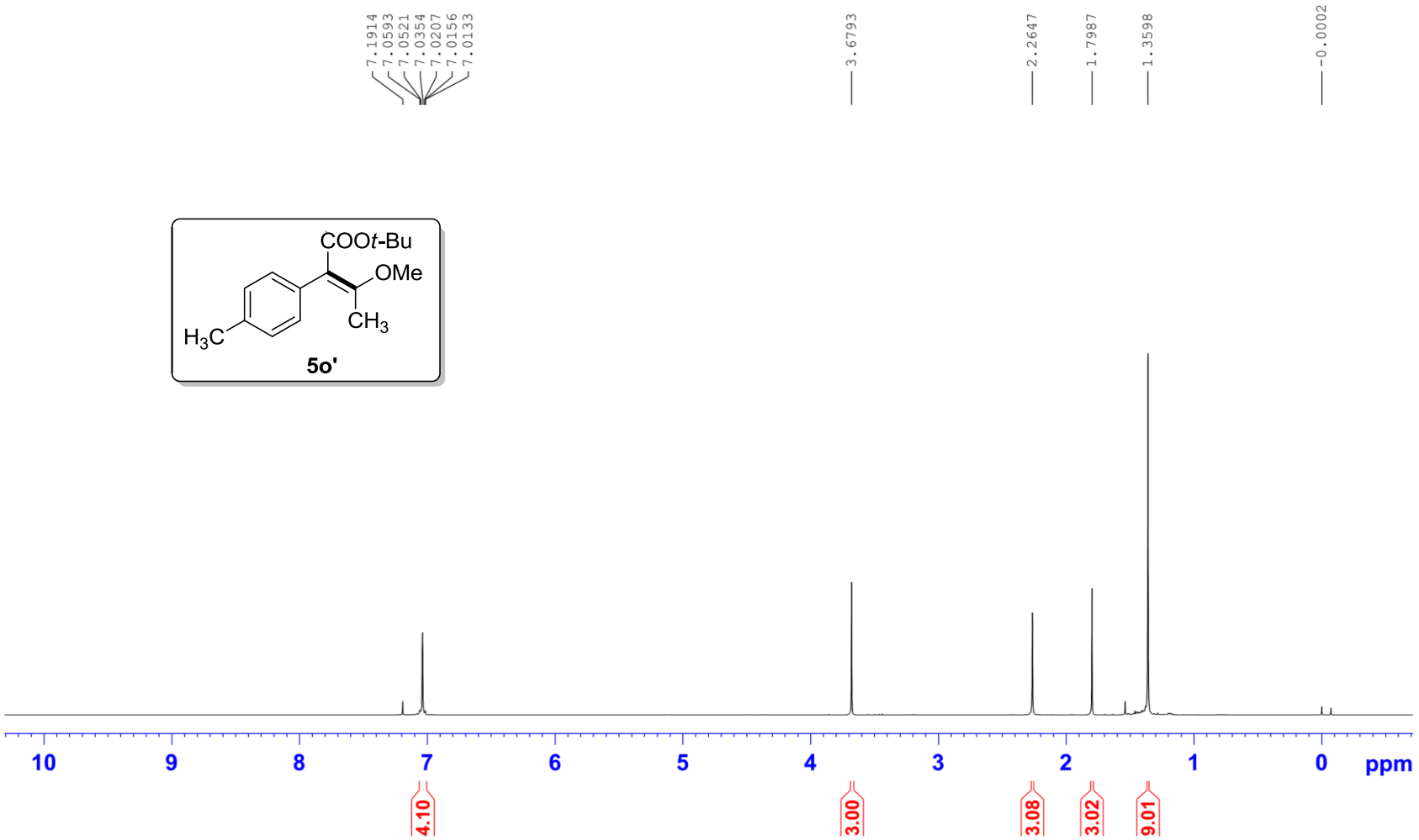
LJW-X180531-7-HNMR



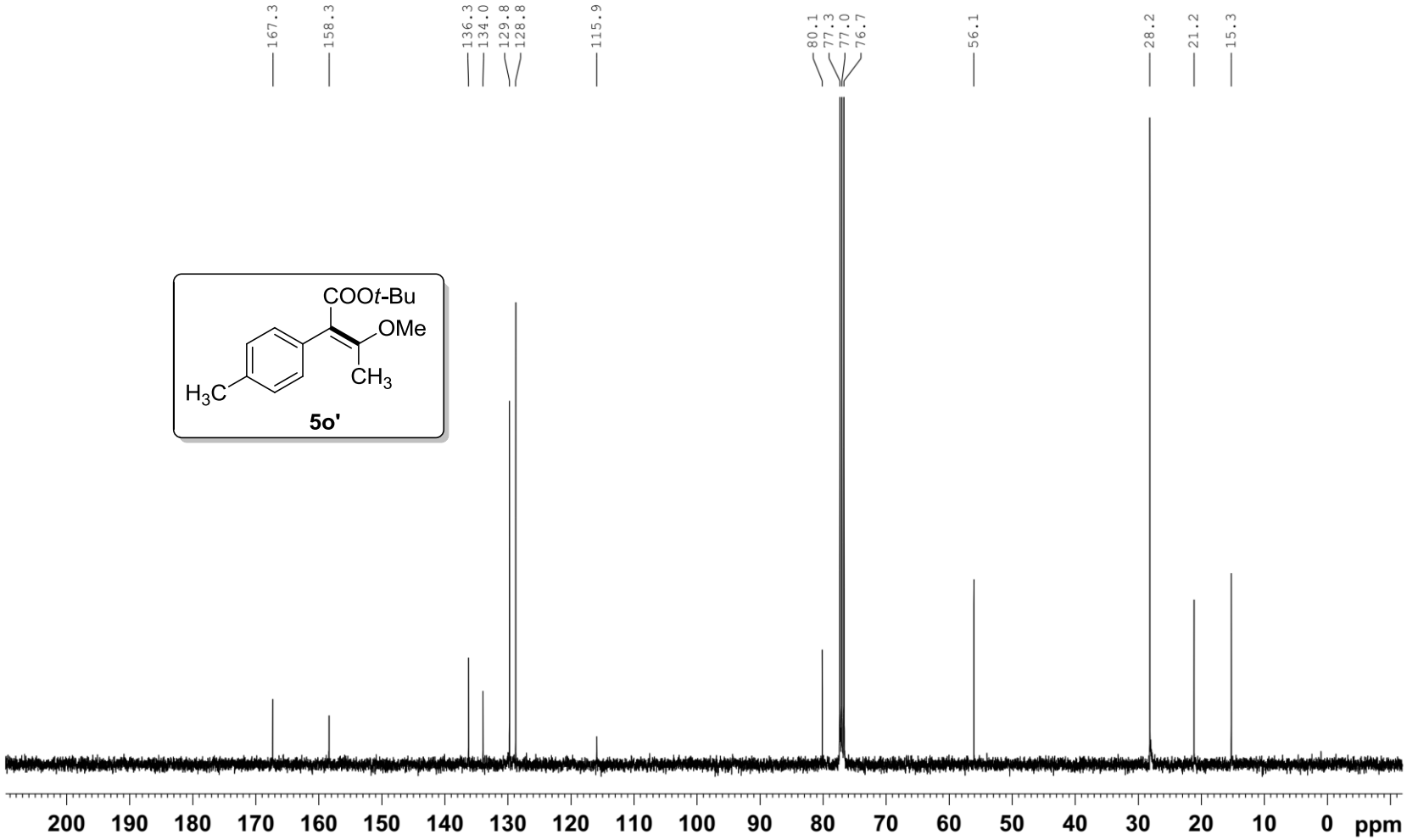
LJW-X180531-7-CNMR



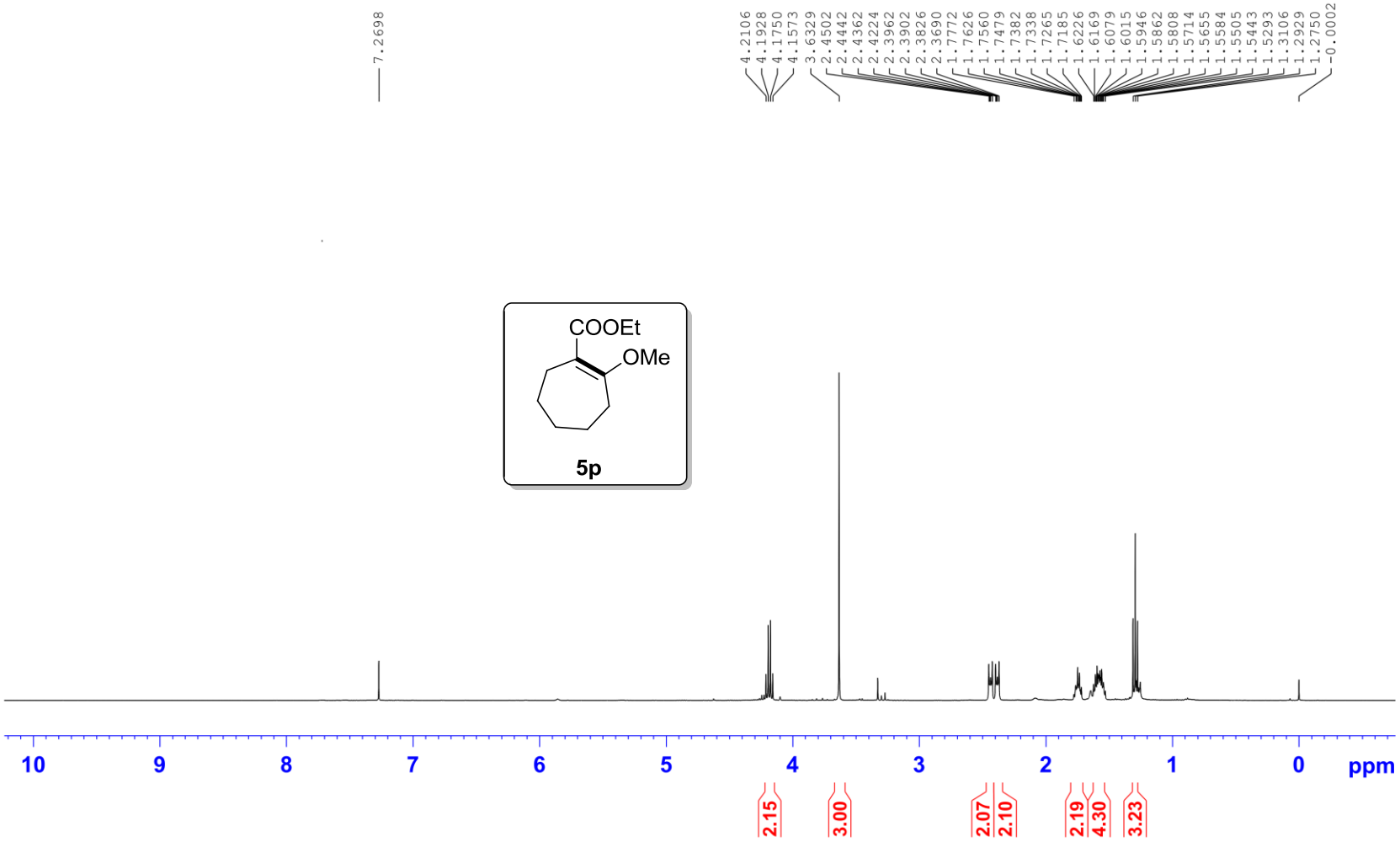
LJW-X180531-8-HNMR



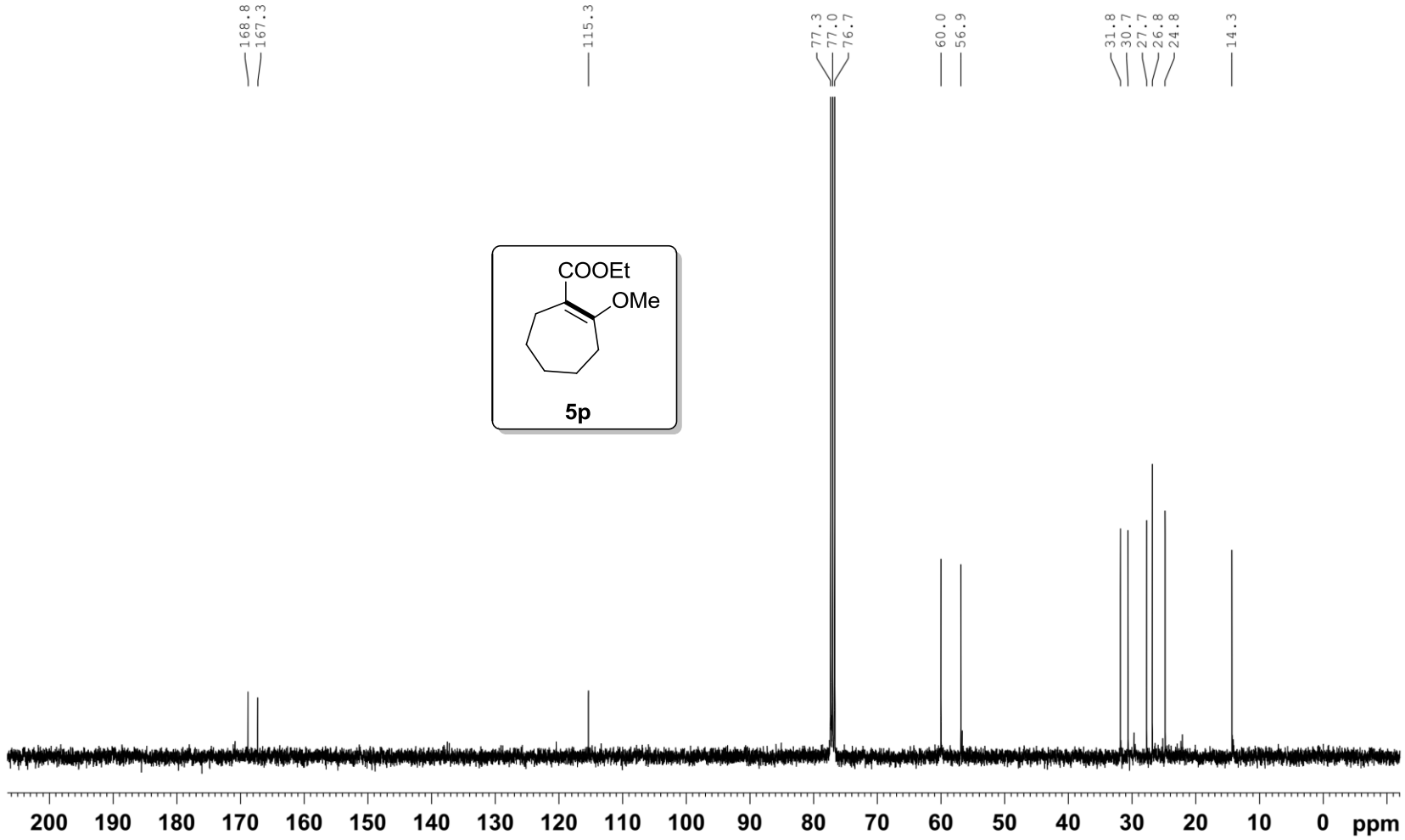
LJW-X180531-8-CNMR



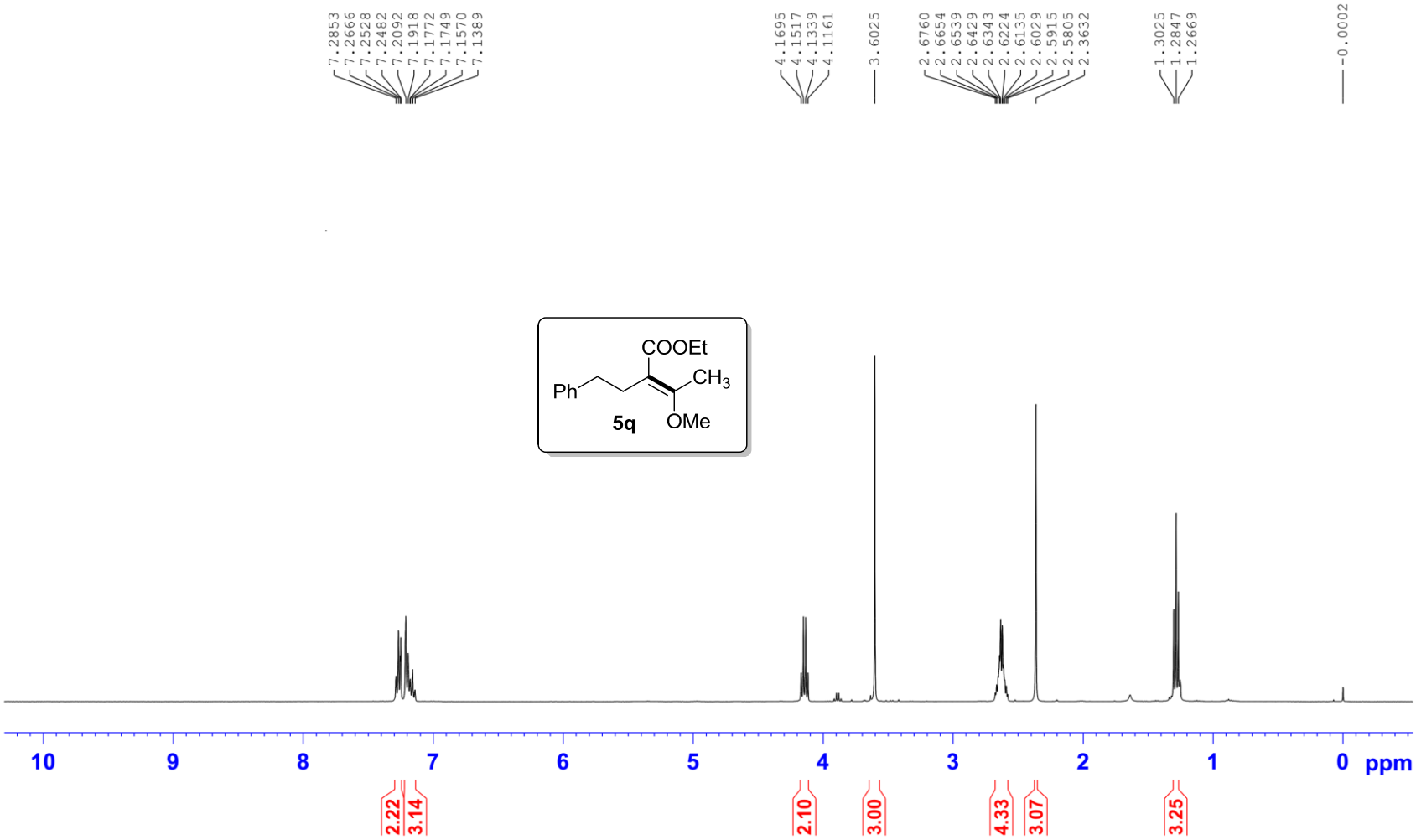
LJW-X170717-2-HNMR



LJW-X170717-2-CNMR



LJW-X180917-3-HNMR



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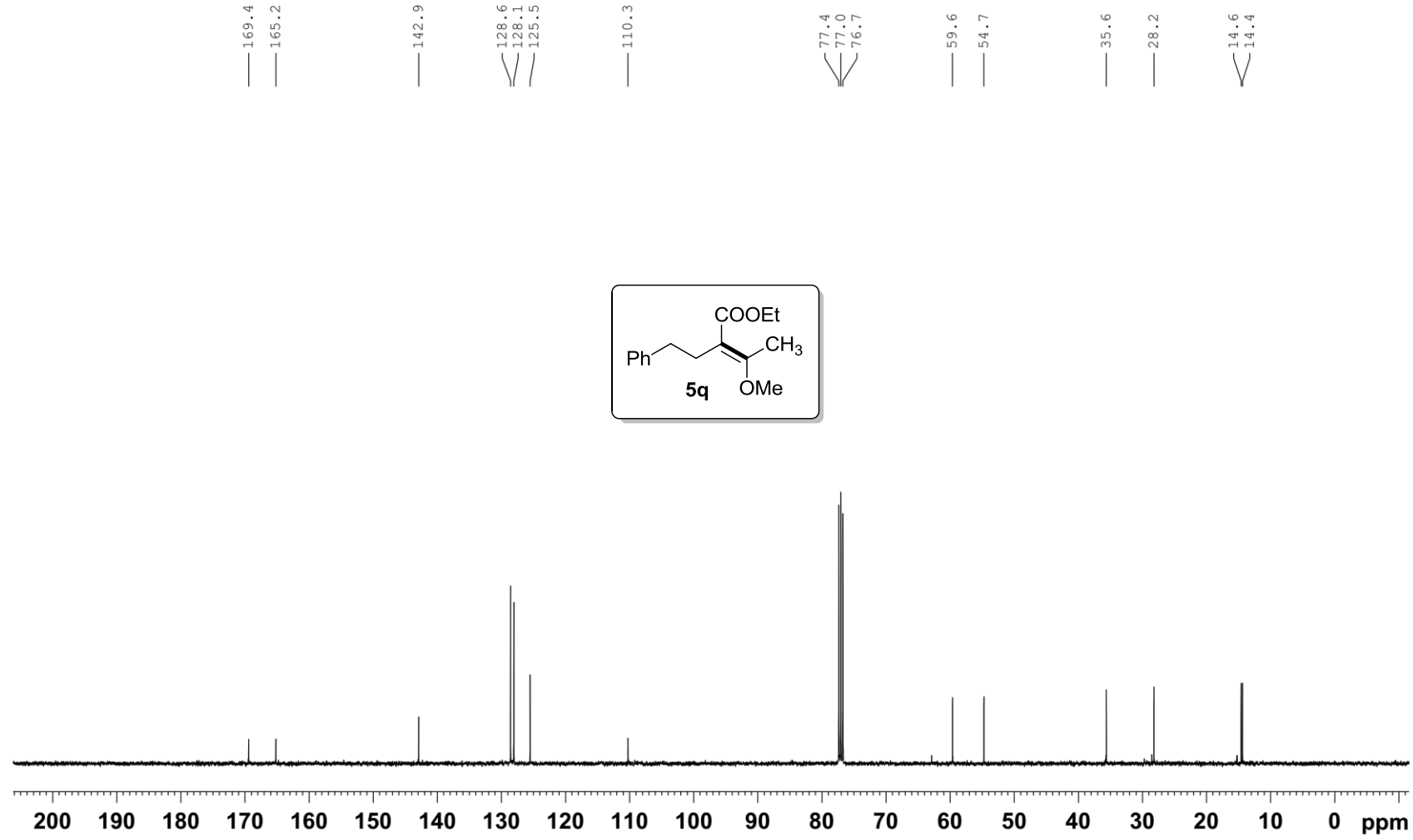

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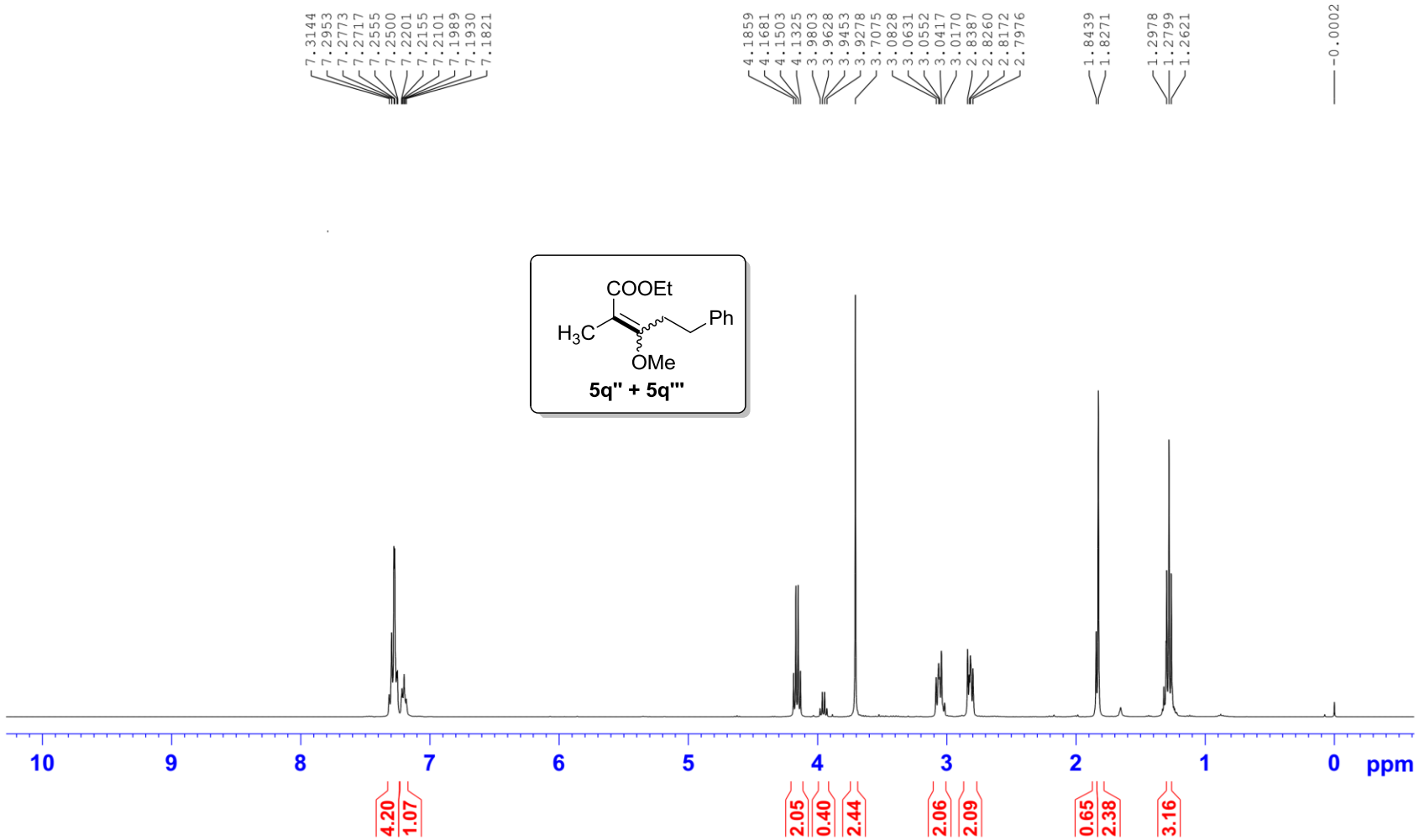

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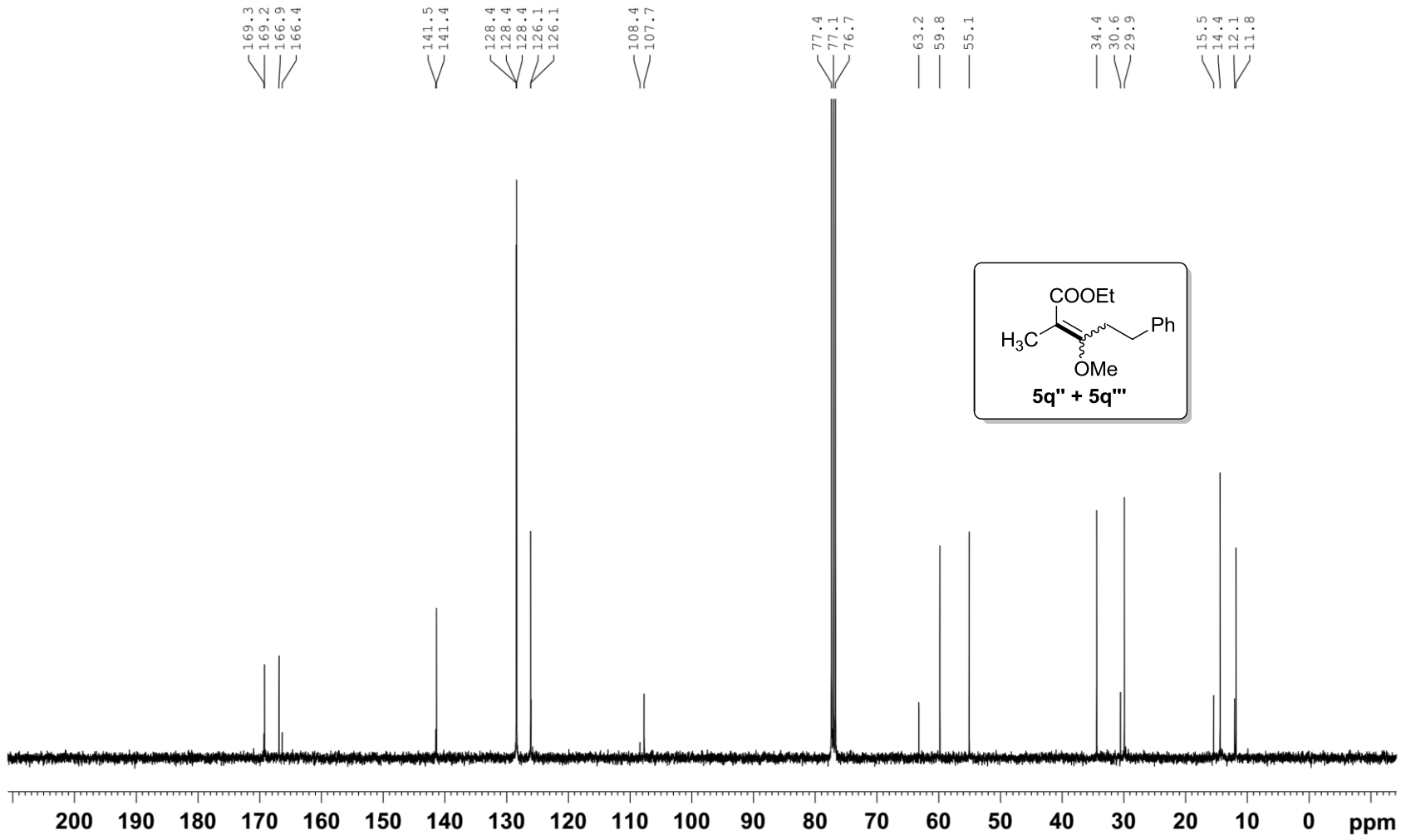
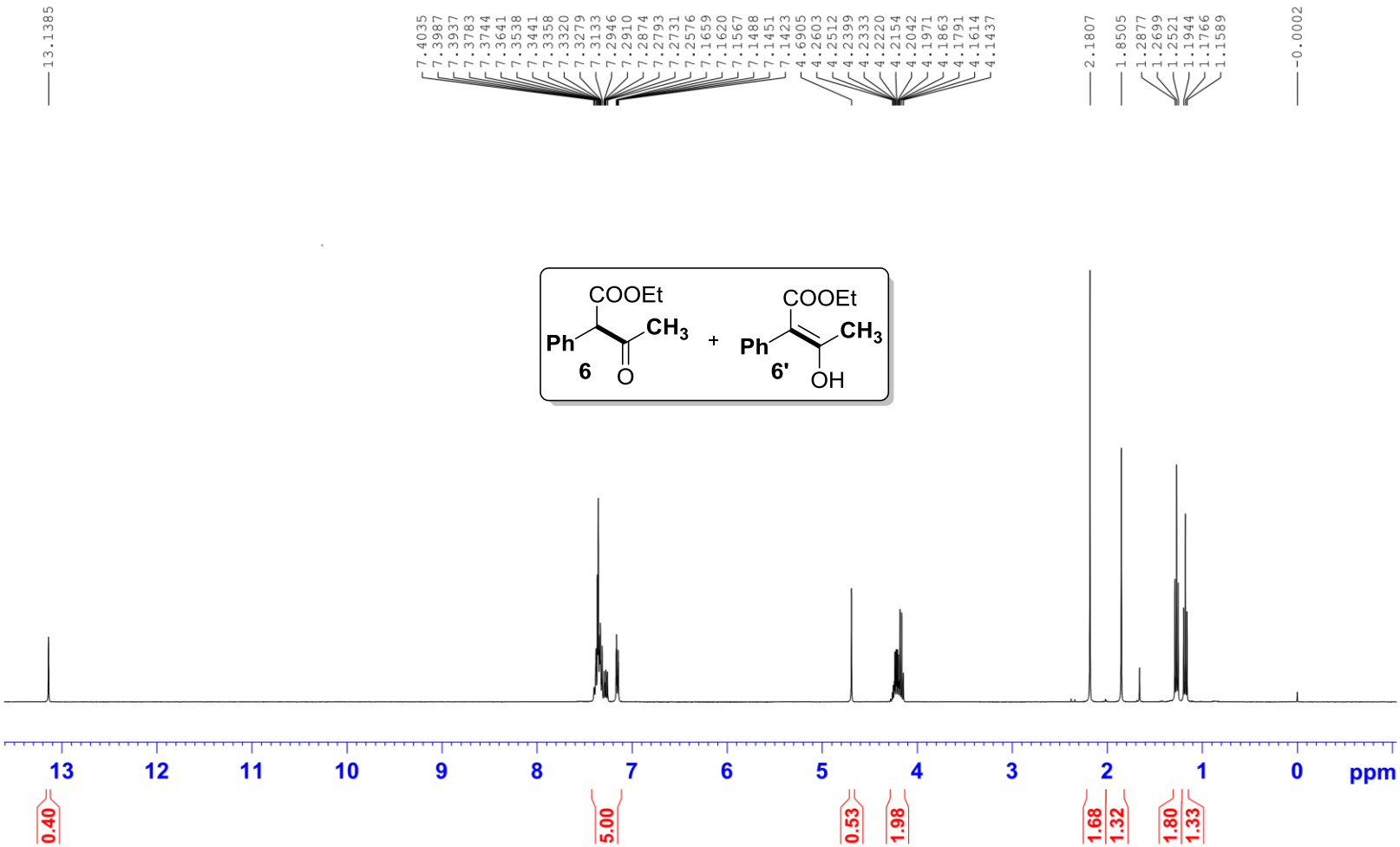


LJW-X170904-1-HNMR



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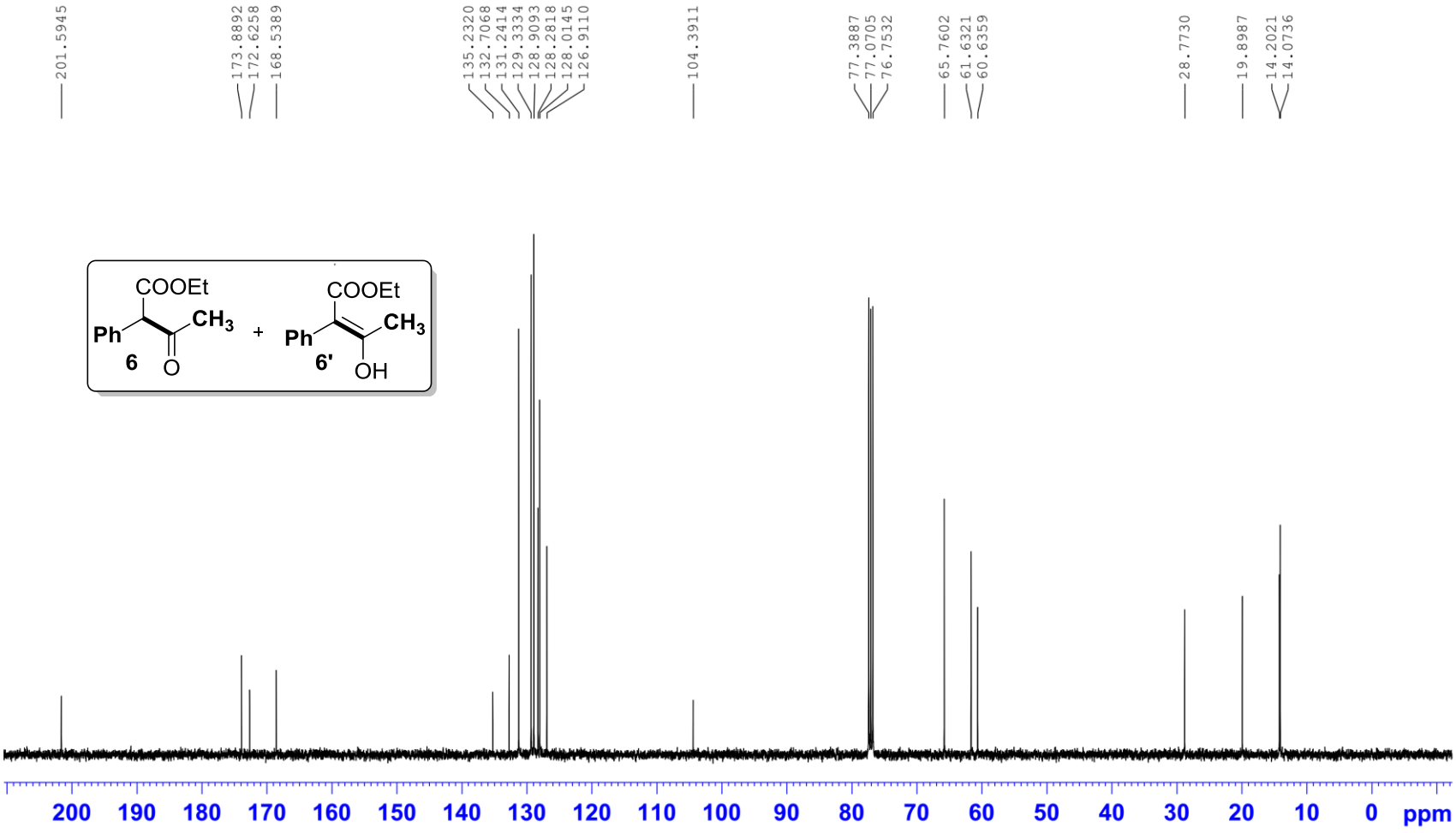
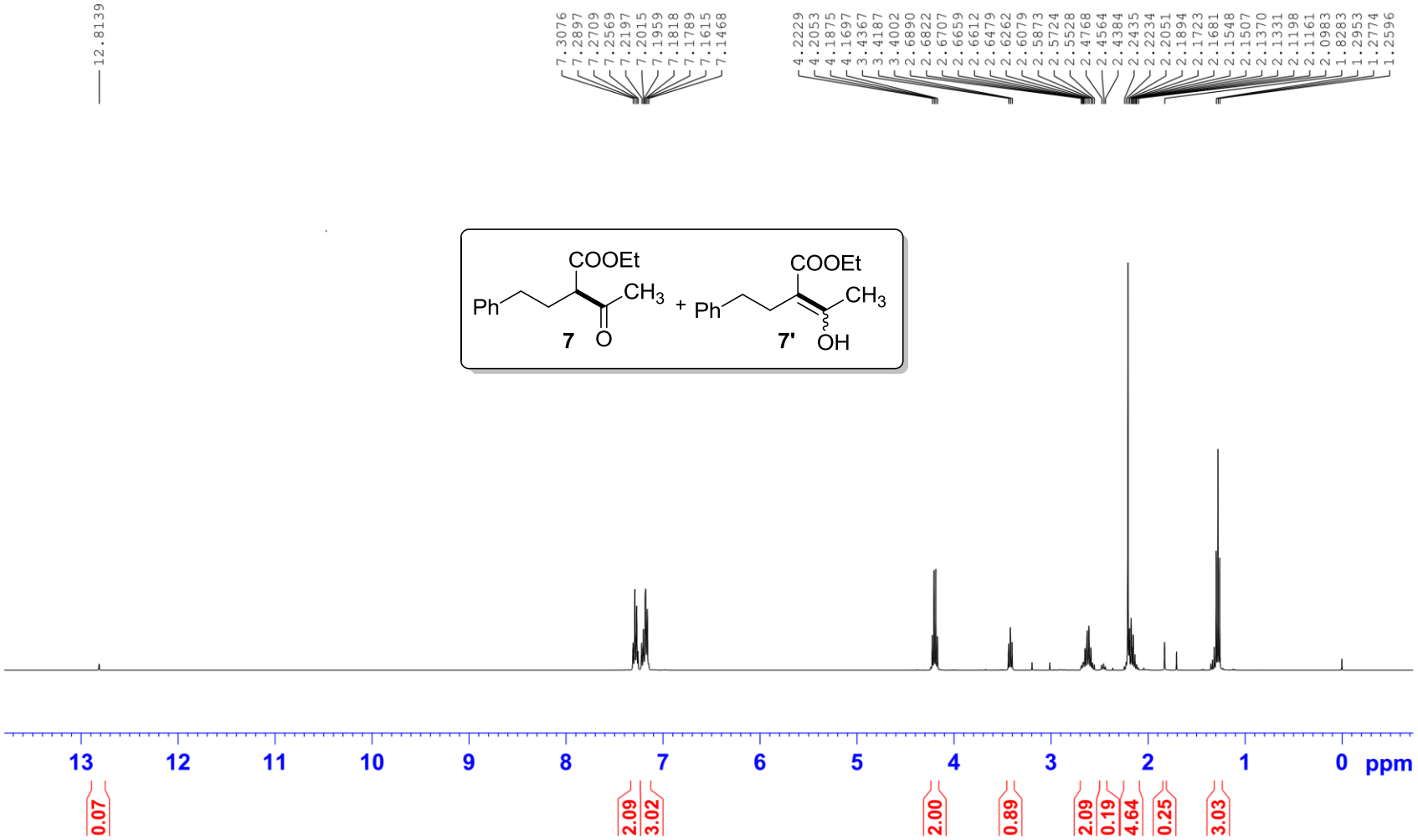


LJW-X180920-2-HNMR



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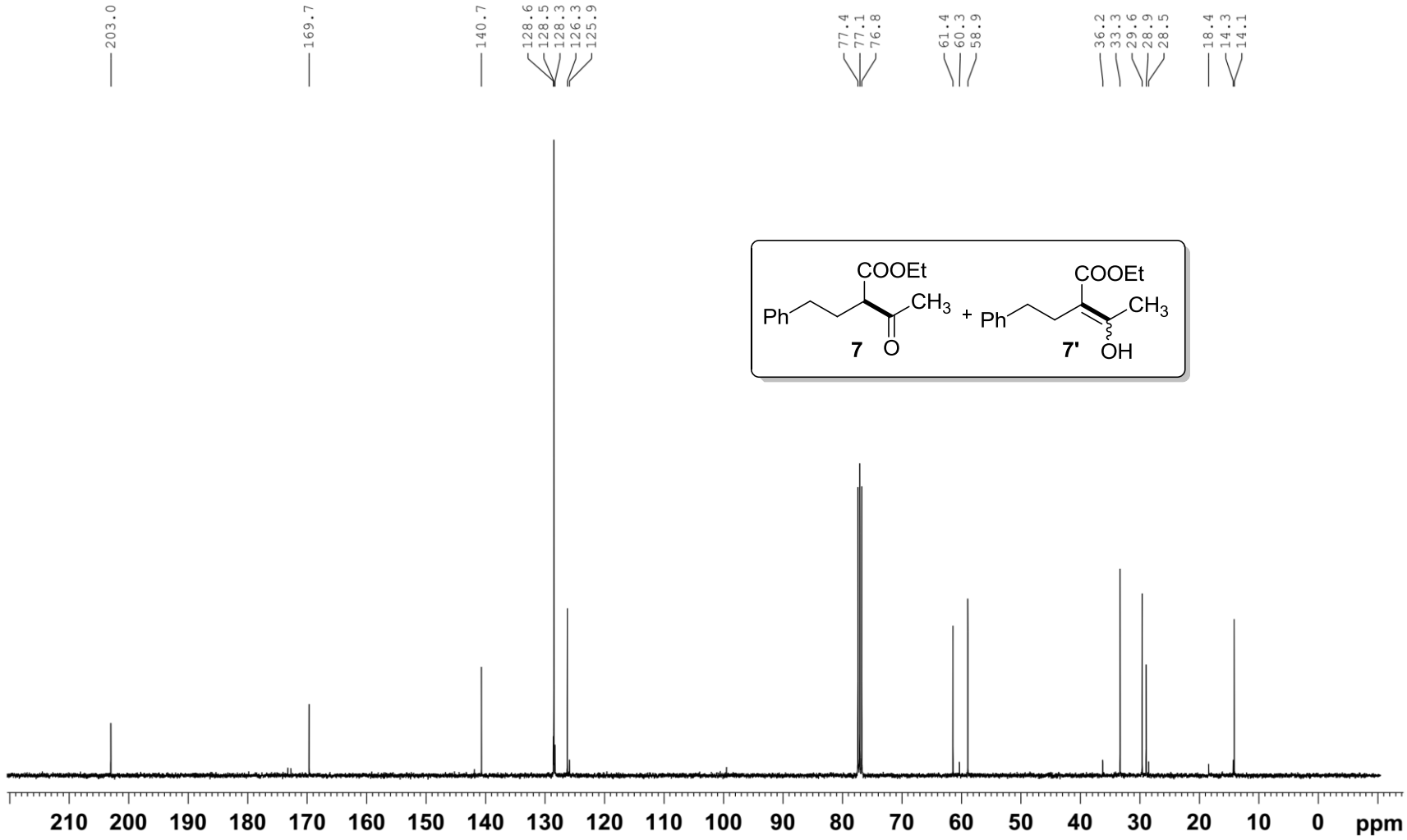

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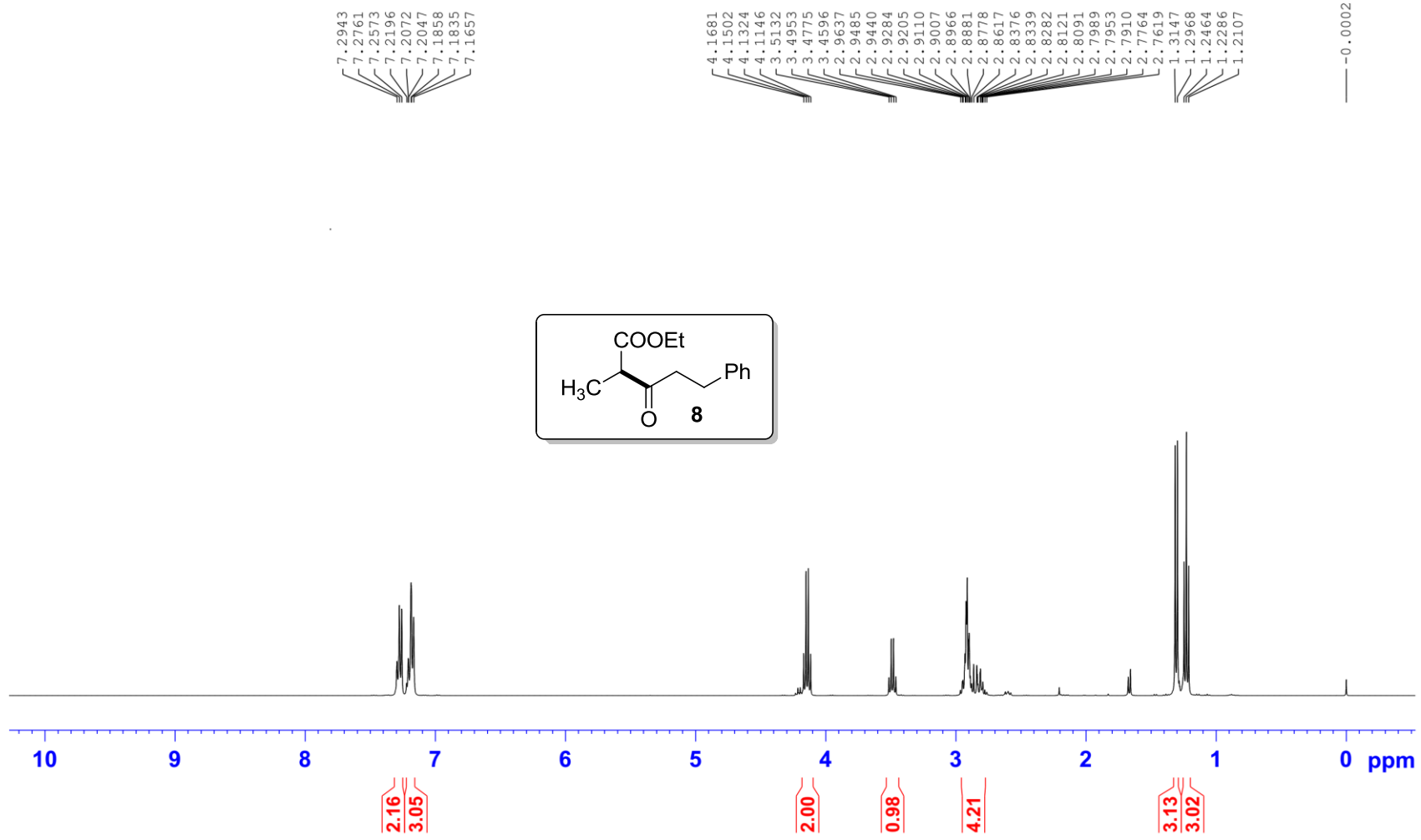

LJW-X180920-1-CNMR

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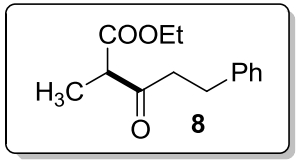
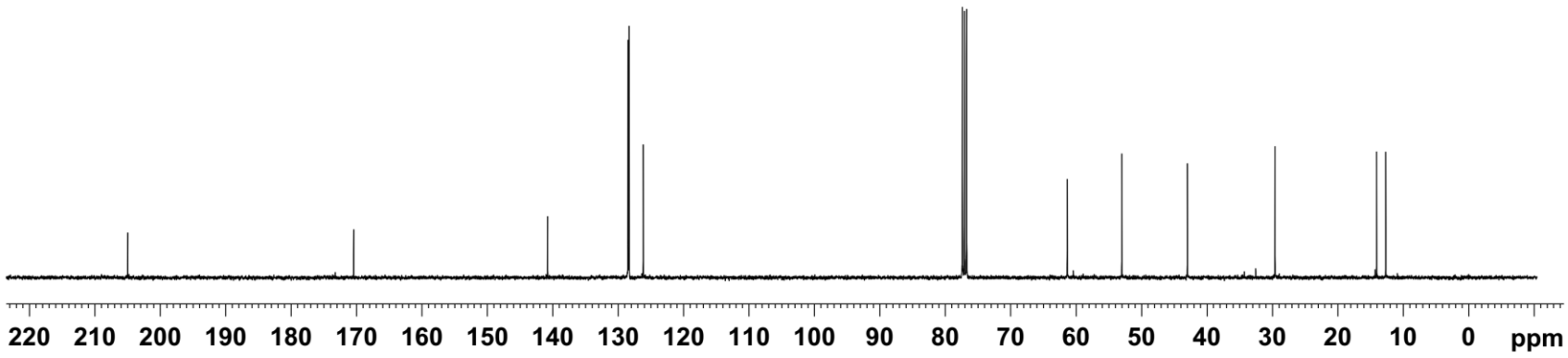
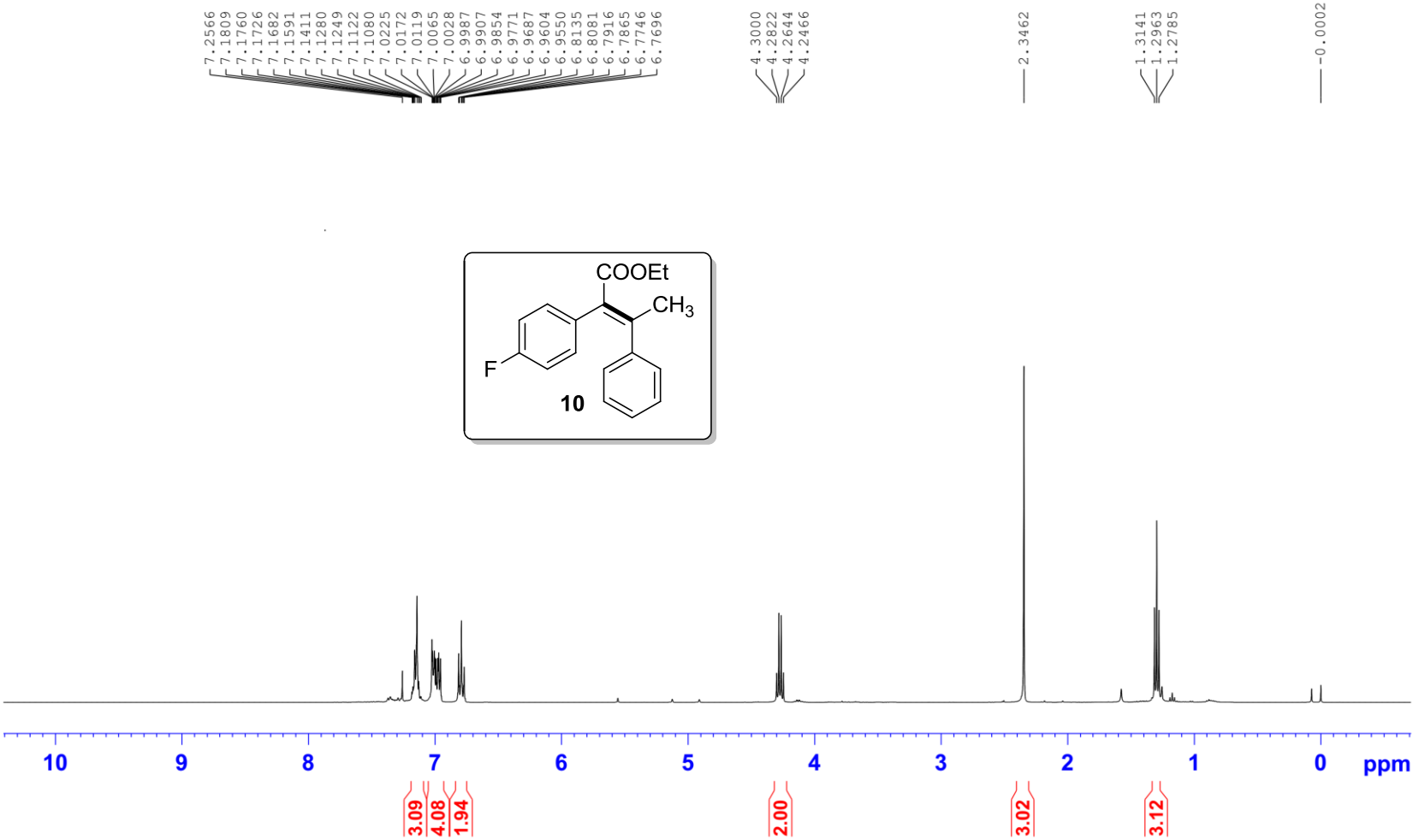


8



LJW-X180528-8-HNMR



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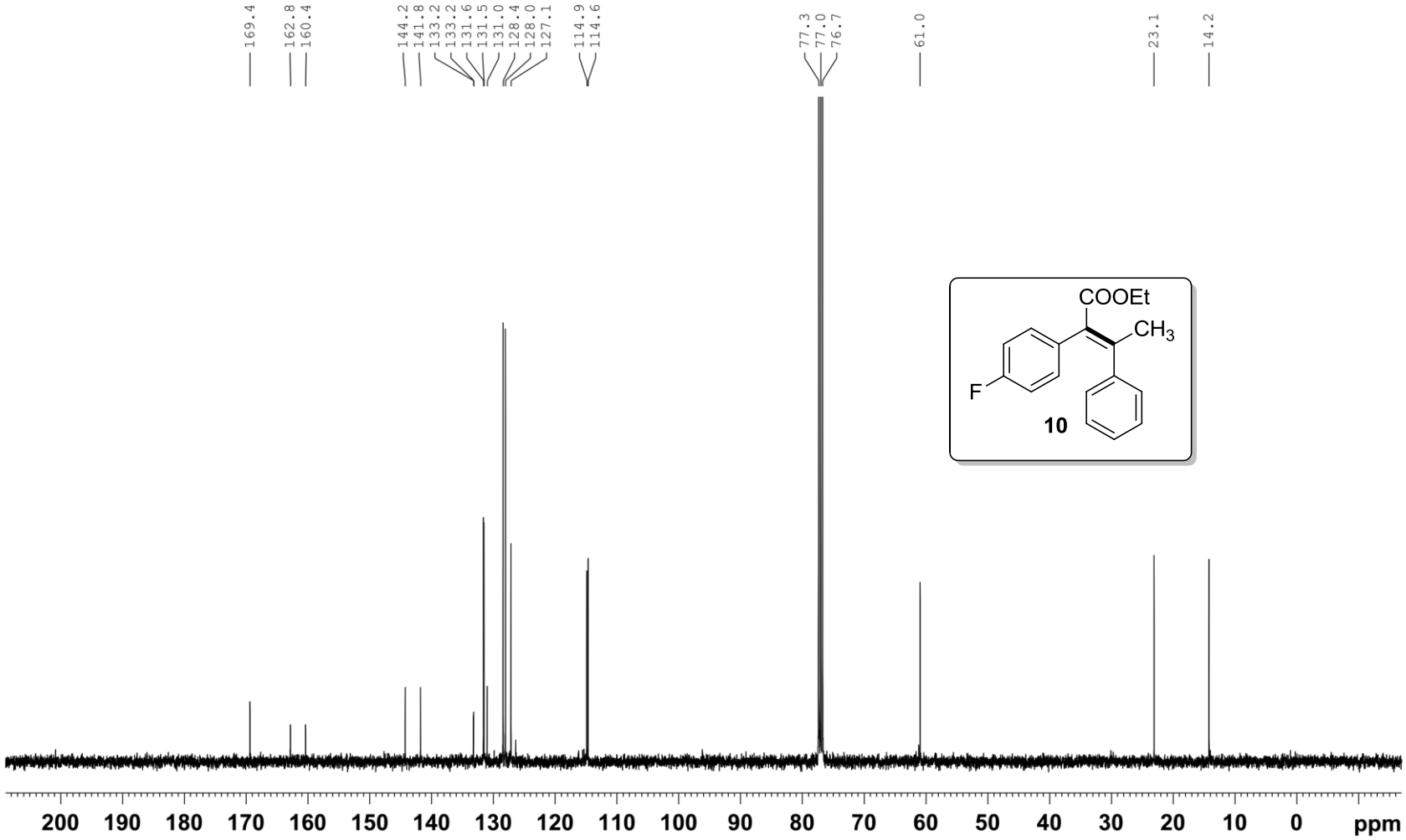

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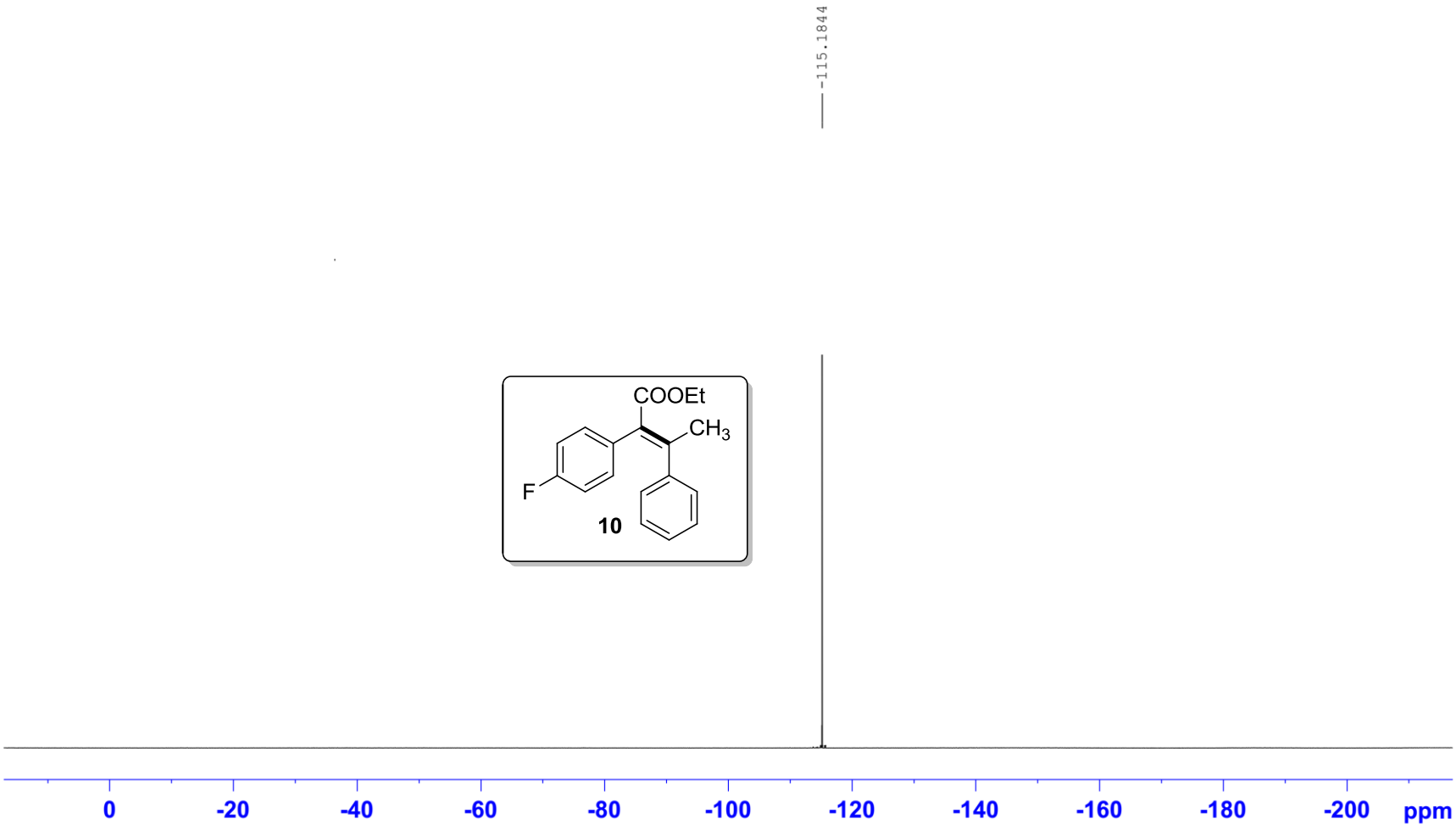

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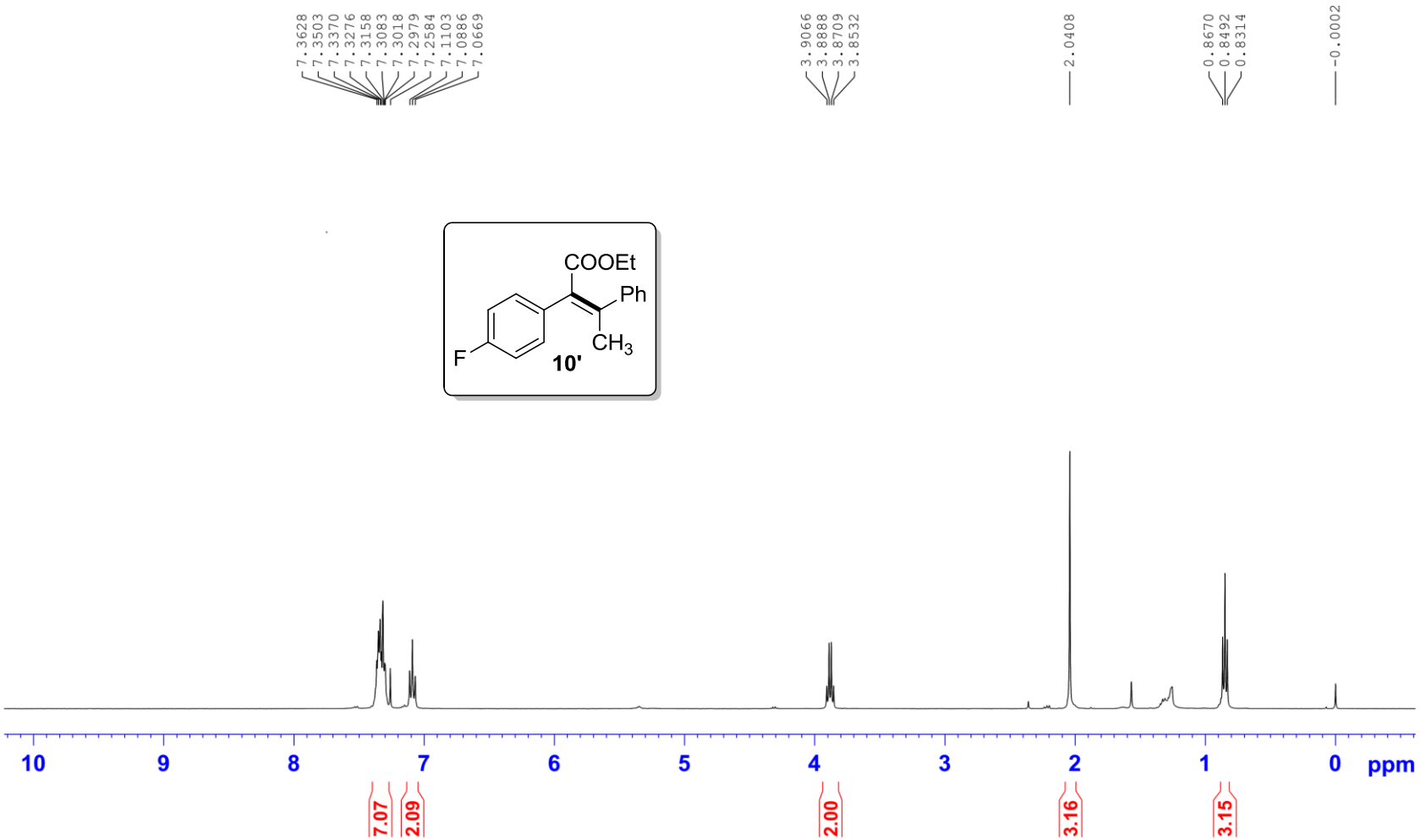

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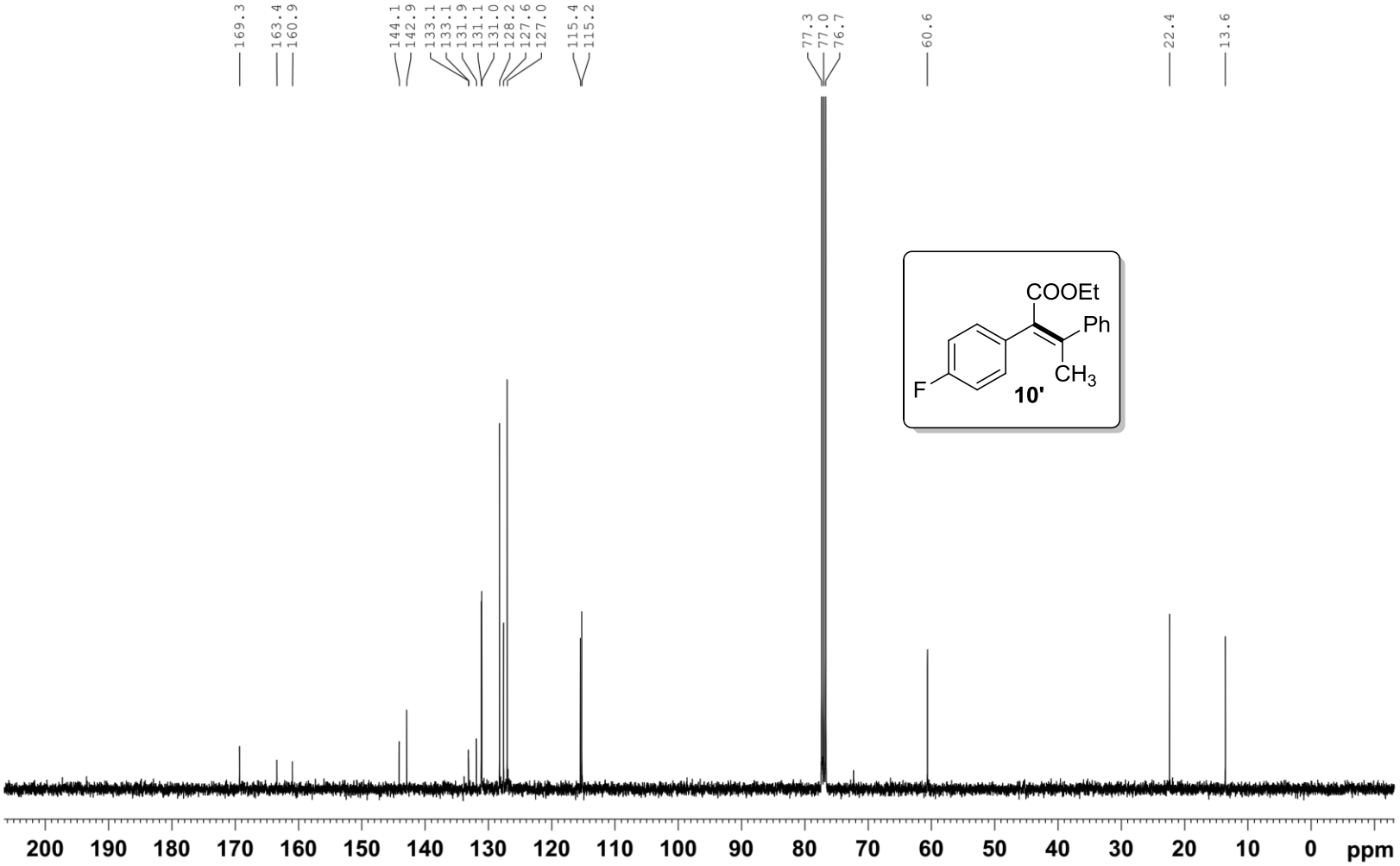

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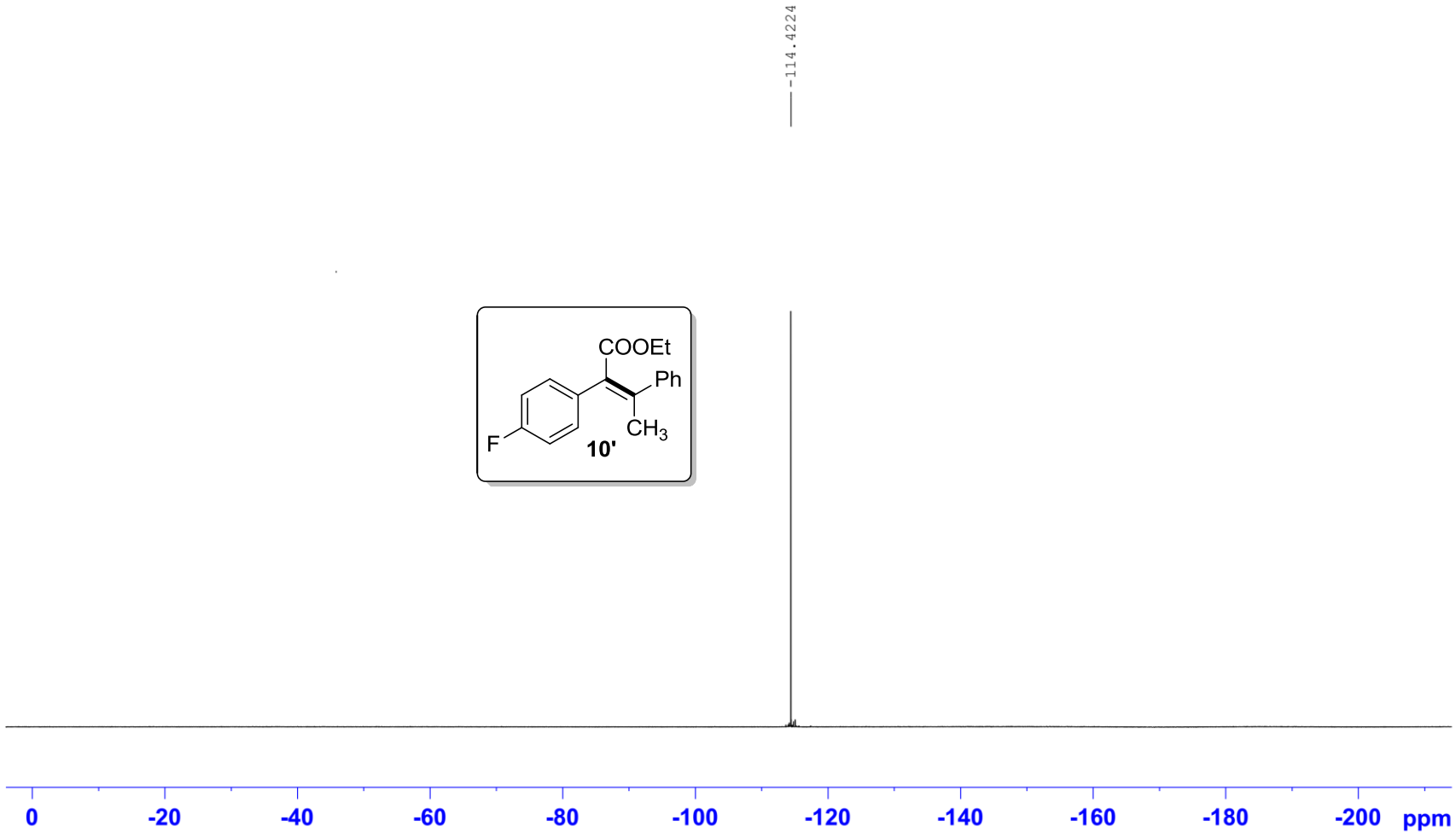

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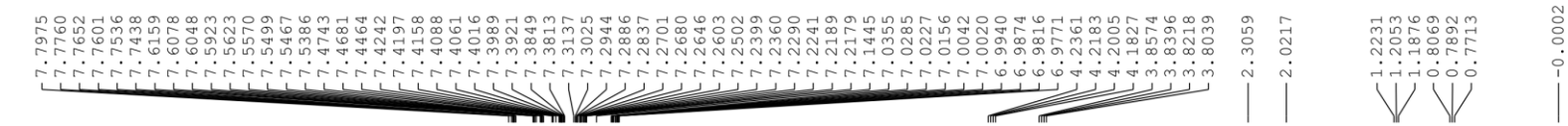

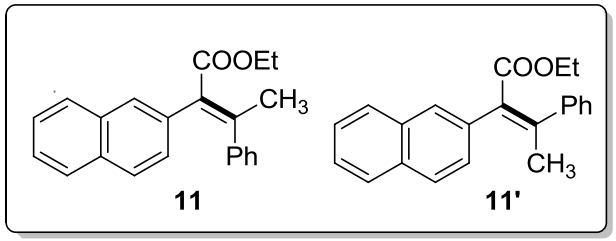

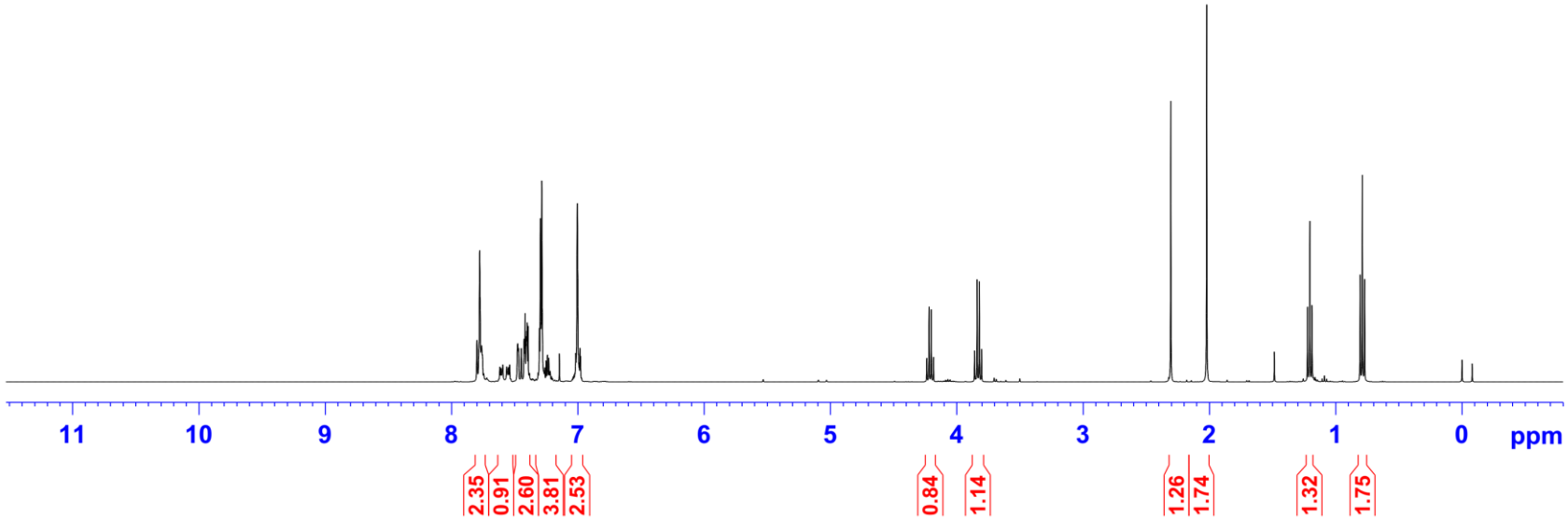

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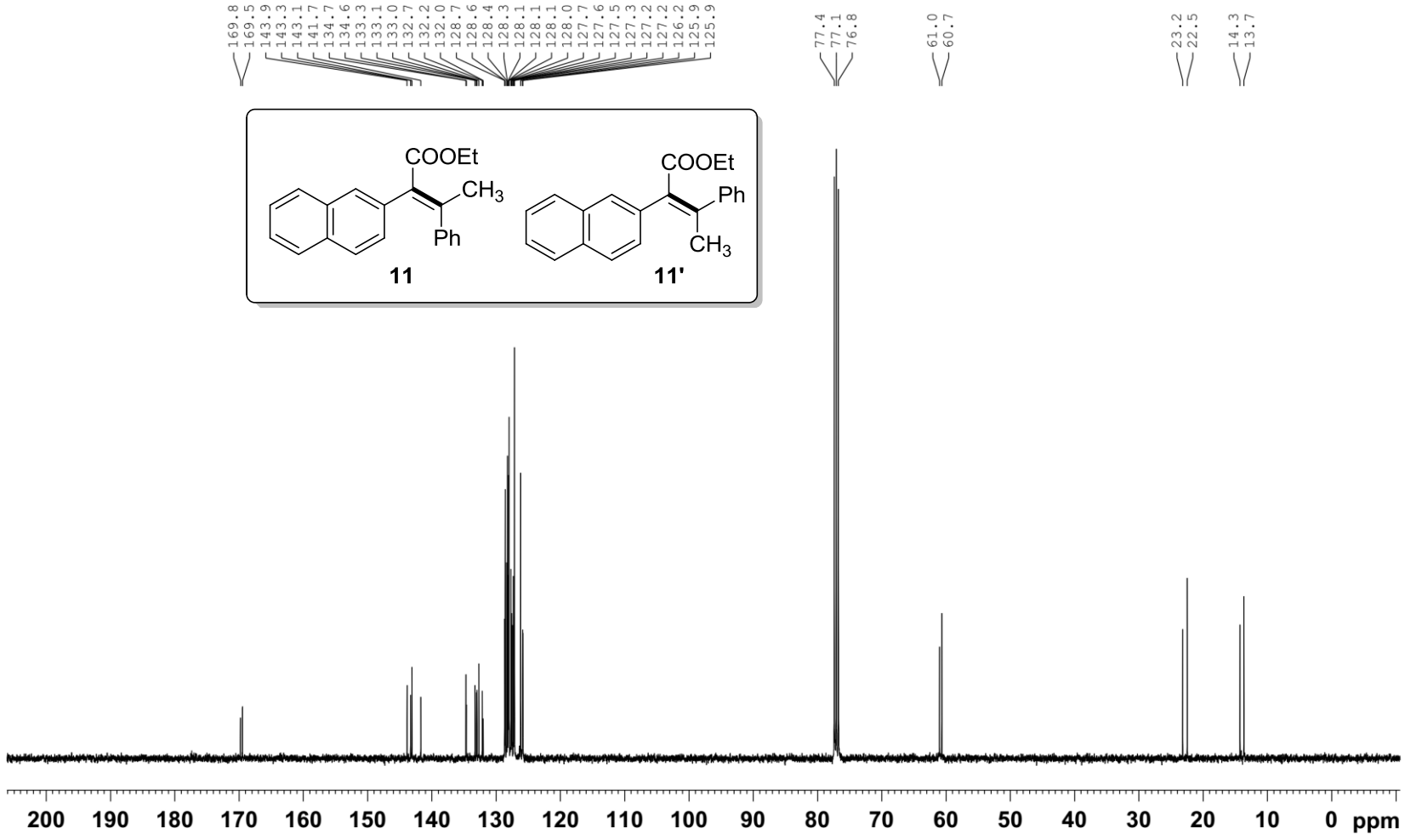

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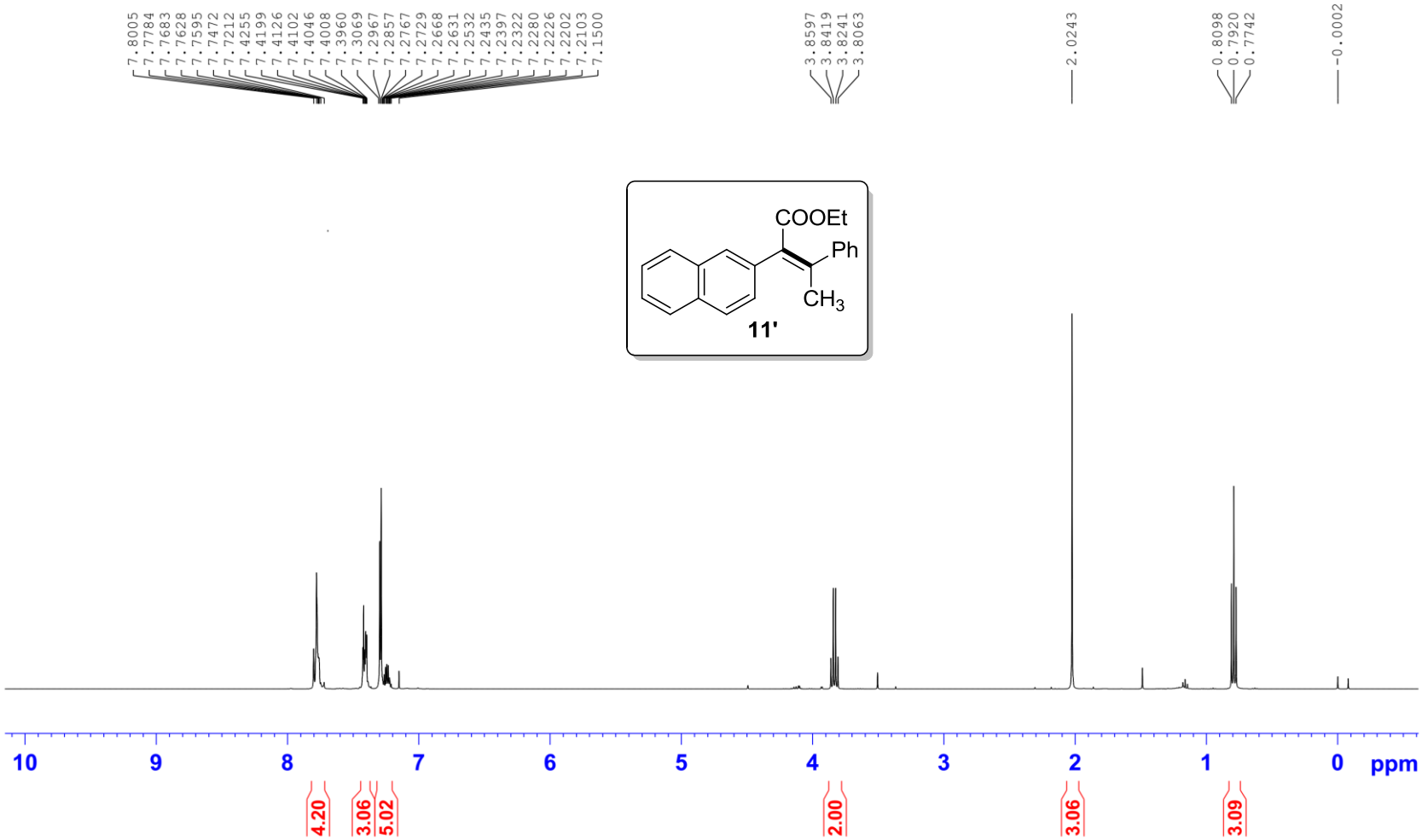

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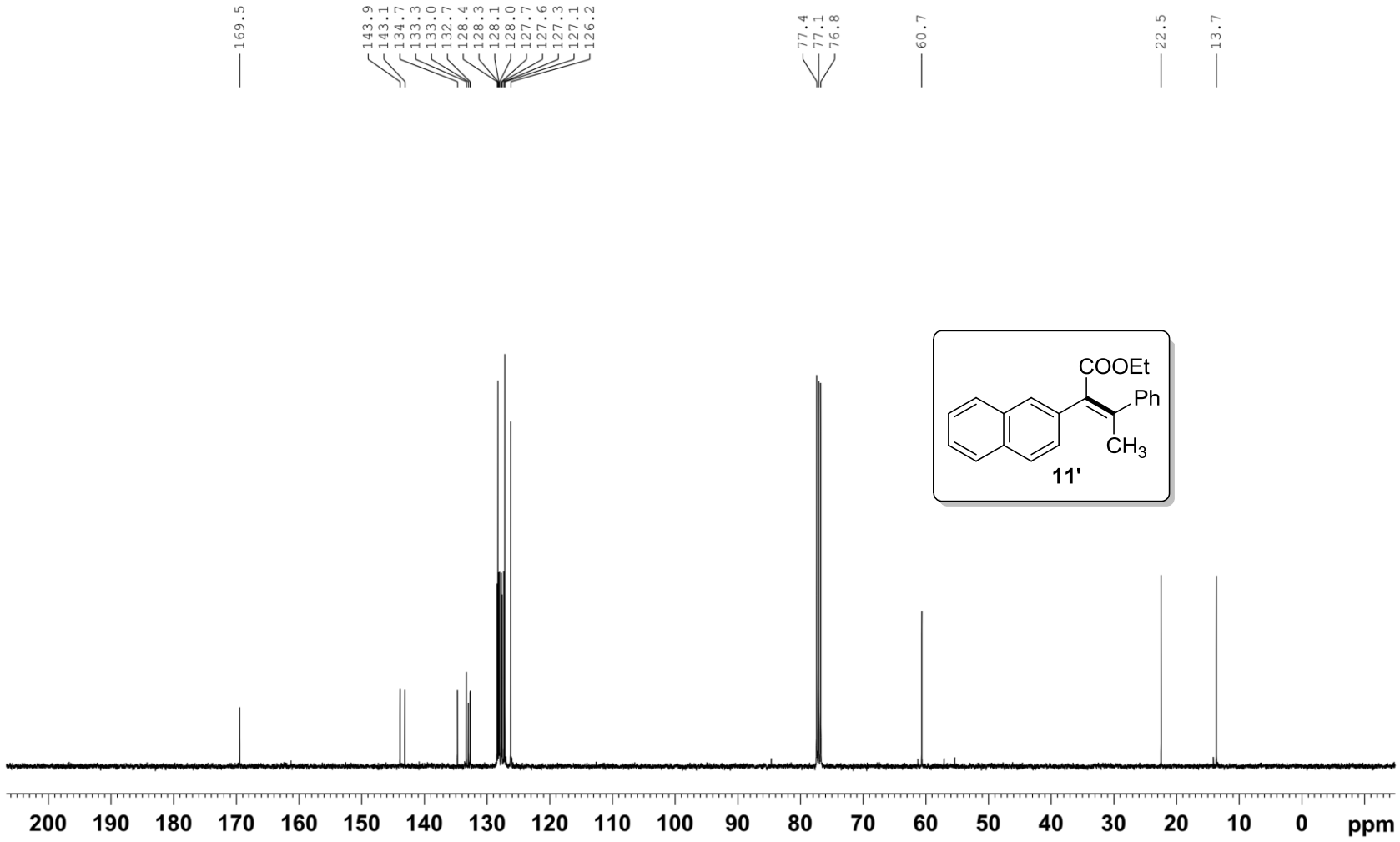

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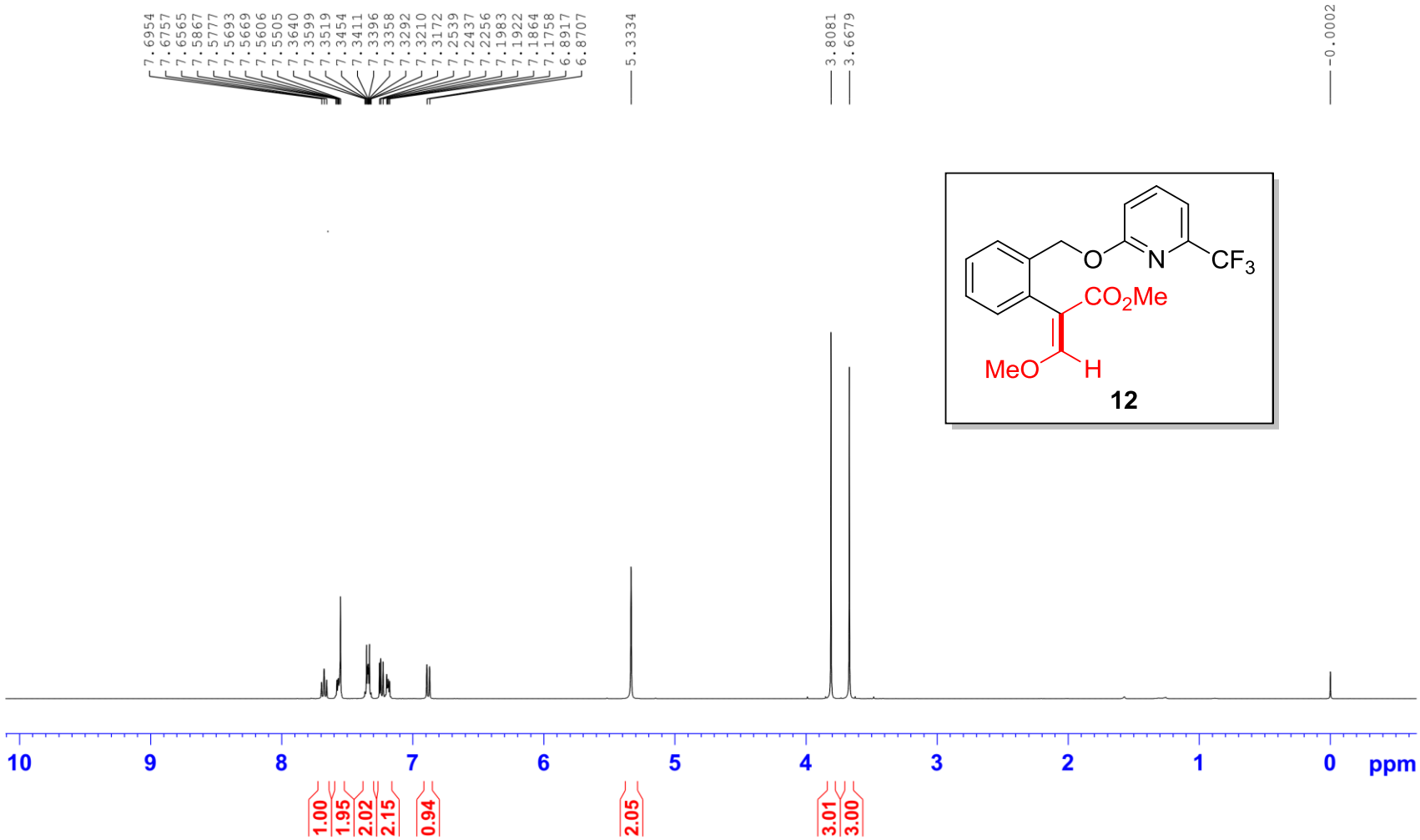

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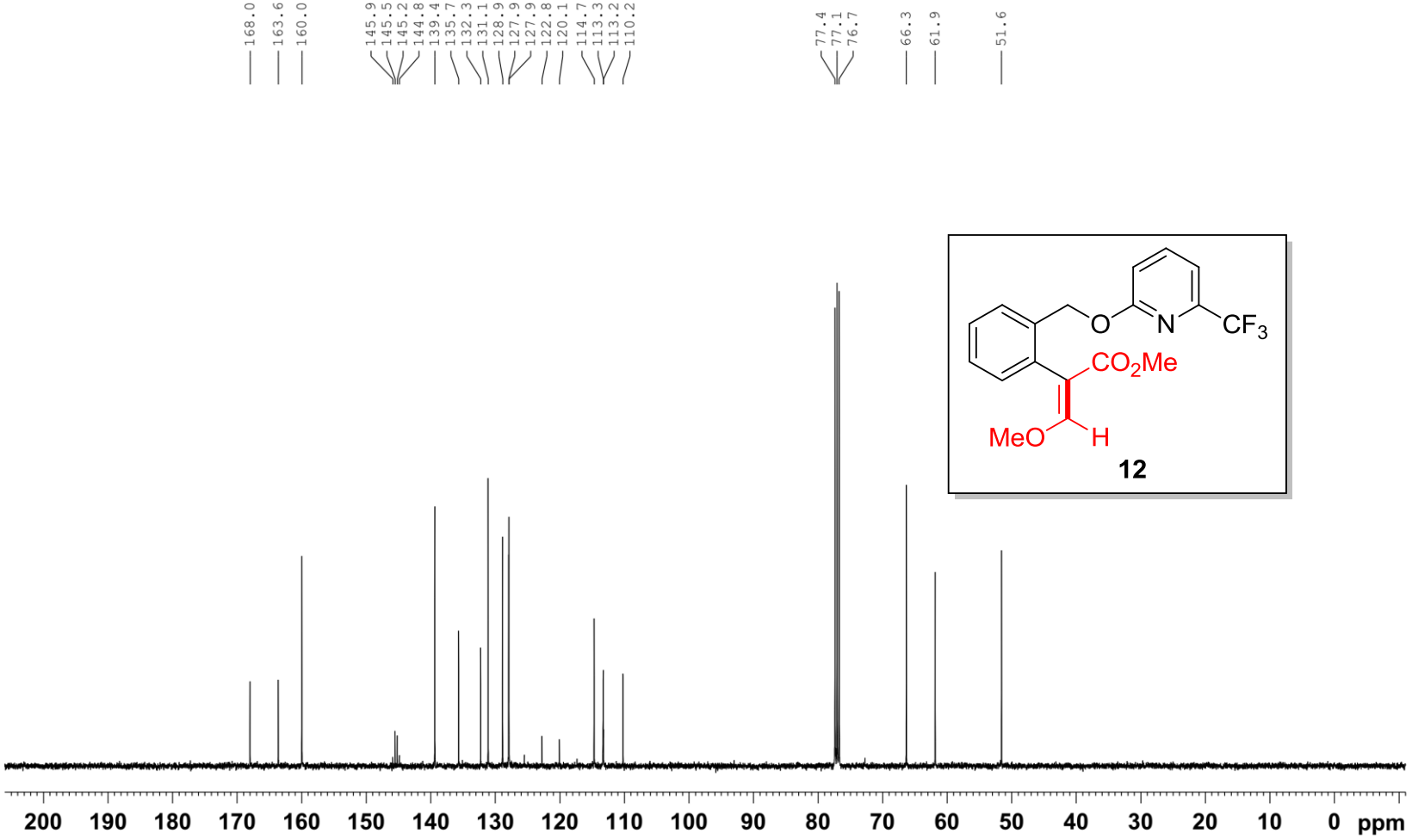

LJW-X180606-6-FNMR