

SUPPORTING INFORMATION

**Gold-catalyzed *para*-selective C-H bond alkylation of
benzene derivatives with donor/acceptor-substituted diazo
compounds**

Ben Ma, Jiaojiao Wu, Lu Liu and Junliang Zhang**

*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and
Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai
200062, P. R. China.*

Fax: (+86)-021-6223-3213; E-mail : lliu@chem.ecnu.edu.cn, jlzhang@chem.ecnu.edu.cn

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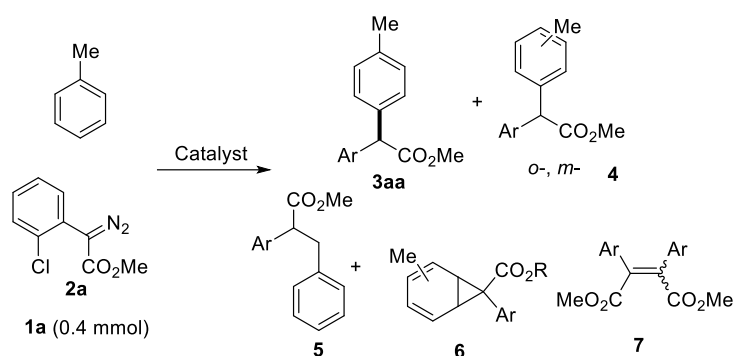
1. General Information:

Unless otherwise noted, all reactions were carried out in standard Schlenk techniques with magnetic stirring bar under air. Materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra were recorded on a BRUKER 500 (500 MHz), BRUKER 400 (400 MHz) spectrometer or a Bruker 300 MHz spectrometer in CDCl_3 . Chemical shifts are reported in ppm with tetramethylsilane (TMS: 0 ppm) with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a BRUKER 500 (125 MHz), BRUKER 400 (100 MHz) spectrometer and a Bruker 300 (75.0 MHz) spectrometer in CDCl_3 with complete proton decoupling. Chemical shifts are reported in ppm with the deuterium solvent as the internal standard (e.g. CDCl_3 : 77.0 ppm).

Anhydrous tetrahydrofuran (THF), toluene, dioxane, 1,2-Dimethoxyethane (DME) and diethyl ether (Et_2O) were distilled from sodium and benzophenone to use; AgOTf , AgSbF_6 , AgNTf_2 , AgBF_4 , and AgPF_6 were purchased from Alfa-Aesar Company and used directly .

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with hexane/ethyl acetate or hexane/ CH_2Cl_2 .

2. **Table S1.** Optimization of Reaction Conditions. ^a



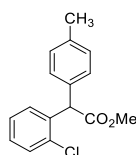
Entry	Catalyst	Condition	Time	Conv. (%)	Yield (%) ^b 3/4/5/6/7
1	Cu(CH ₃ CN) ₄ BF ₄	110 °C	24 h	75	0/0/0/0/70
2	Cu(CH ₃ CN) ₄ ClO ₄	110 °C	24 h	78	0/0/0/0/75
3	Cu(CH ₃ CN) ₄ PF ₆	110 °C	24 h	85	0/0/0/0/76
4	CuOTf	110 °C	24 h	100	0/0/0/0/86
5	Pd(PPh ₃) ₄	rt	48 h	100	0/0/0/0/(72)
6	PPh ₃ Ru(SbF ₆) ₂	110 °C	8 h	87	0/0/0/0/56
7	Ir(COD) ₂ (SbF ₆) ₂	110 °C	8 h	55	0/0/0/0/27
8	Ni(COD) ₂	110 °C	12 h	10	-
9	Rh(OAc) ₂	rt	5 min	100	0/0/57/0/18
10	Fe(OTf) ₂	110 °C	3 h	100	15/4/9/43/0
11	In(OTf) ₃	110 °C	3 h	100	36/20/12/0/23
12	Sc(OTf) ₃	110 °C	3 h	100	36/30/17/0/16
13	Mn(OTf) ₂	110 °C	2 h	100	0/0/0/16/74
14	AuCl ₃	110 °C	24 h	-	-
15	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuOTf	rt	3 min	100	(44)/0/0/0/(46)
16	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAu(PhCN)OTf	rt	3 min	100	(56)/0/0/0/(40)
17	IPrAuOTf	rt	5 min	100	3/0/0/0/90
18	PPh ₃ AuOTf	rt	3 min	100	(98)/0/0/0/1
19	JohnPhosAuOTf	rt	10 min	100	5/0/0/0/89
20	AgOTf	rt	24 h	100	0/0/0/(56)/34
21	PPh ₃ AuSbF ₆	rt	10 min	100	(40)/0/0/0/50
22	PPh ₃ AuNTf ₂	rt	24 h	20	(20)/0/0/0/73
23	PPh ₃ AuClO ₄	rt	24 h	5	-
24	PPh ₃ AuBF ₄	rt	24 h	-	-
25	PPh ₃ AuPF ₆	rt	24 h	-	-
26 ^c	PPh ₃ AuOTf	rt	3 min	100	(76)/0/0/0/(10)

^a Reaction conditions: **1a** (0.4 mmol), catalyst (5 mol%) in toluene (0.5 mL) at room temperature under Ar. ^b Determined by NMR of crude products (¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.). ^c Toluene (2 equiv.) was used in DCM (1 mL). The numbers in parenthesis are isolate yields.

3. General procedure for the synthesis of 3.

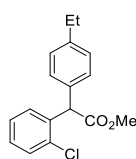
In a dried glass tube, a solution of Ph_3PAuCl (10.97 mg, 0.022 mmol, 5.5 mol%), AgOTf (5.13 mg, 5 mol%) in DCM (2 mL) was stirred at room temperature for 15 mins. After solvent was removed under reduced pressure, arenes 0.2 mL was added to the reaction mixture at room temperature. Then a solution of methyl 2-(2-chlorophenyl)-2-diazoacetate **1a** (84 mg, 0.4 mmol) dissolved in 0.8 mL arenes was introduced into the reaction mixture by a syringe in 1 mins. The resulting mixture was continually stirred at room temperature for 3 min and **1a** was consumed completely determined by TLC analysis. After being filtrated through celite and concentrated, the residue was purified by column chromatography on silica gel to afford the desired product.

1) Methyl 2-(2-chlorophenyl)-2-(p-tolyl)acetate (**3aa**)



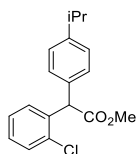
The general procedure was followed using **2a** (0.4 mmol) and use toluene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3aa** (110 mg, 98%) was obtained as a white solid, m.p. 60-61°C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32-7.28 (m, 1H), 7.17-7.07 (m, 7H), 5.36 (s, 1H), 3.67 (s, 3H), 2.26 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.5, 137.3, 136.7, 134.1, 133.9, 130.0, 129.5, 129.4, 128.7, 128.5, 126.9, 53.4, 52.5, 21.1; **MS** (EI): m/z (%): 274 (M^+ , 20.50), 276 ($[\text{M}+2]^+$, 6.85), 215 (100); **HRMS** (EI) calculated for $[\text{C}_{16}\text{H}_{15}\text{O}_2\text{Cl}]$: 274.0761, found: 274.0764.

2) Methyl 2-(2-chlorophenyl)-2-(4-ethylphenyl)acetate (**3ba**)



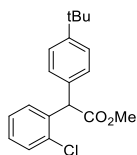
The general procedure was followed using **2a** (0.4 mmol) and use ethylbenzene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ba** (113 mg, 98%) was obtained as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30-7.28 (m, 1H), 7.16-7.08 (m, 7H), 5.37 (s, 1H), 3.66 (s, 3H), 2.55 (dd, J = 15.2, 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.5, 143.5, 136.7, 134.1, 130.0, 129.5, 128.8, 128.5, 128.2, 126.9, 53.4, 52.4, 28.4, 15.3; **MS** (EI): m/z (%): 288 (M^+ , 17.05), 290 ($[\text{M}+2]^+$, 5.54), 229 (100); **HRMS** (EI) calculated for $[\text{C}_{17}\text{H}_{17}\text{O}_2\text{Cl}]$: 288.0917, found: 288.0914.

3) Methyl 2-(2-fluorophenyl)-2-(4-isopropylphenyl)acetate (3ca)



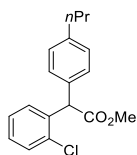
The general procedure was followed using **2a** (0.4 mmol) and cumene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ca** (111 mg, 92%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.38-7.35 (m, 1H), 7.26-7.06 (m, 7H), 5.46 (s, 1H), 3.73 (s, 3H), 2.92-2.85 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 148.1, 136.8, 134.3, 134.2, 130.1, 129.5, 128.7, 128.5, 126.9, 126.8, 53.3, 52.4, 33.7, 23.9; **MS** (EI): *m/z* (%): 302 (*M*⁺, 3.22), 304 ([*M*+2]⁺, 13.56), 184 (100); **HRMS** (ESI) calculated for [C₁₈H₁₉O₂ClNa][*M*+Na]⁺: 325.0966, found: 325.0968.

4) Methyl 2-(4-(*tert*-butyl)phenyl)-2-(2-chlorophenyl)acetate (3da)



The general procedure was followed using **2a** (0.4 mmol) and *tert*-butylbenzene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3da** (96 mg, 76%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.32-7.28 (m, 3H), 7.18-7.11 (m, 5H), 5.38 (s, 1H), 3.67 (s, 3H), 1.23 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.6, 150.3, 136.7, 134.1, 133.9, 130.1, 129.5, 128.5, 128.4, 126.9, 125.7, 53.2, 52.4, 34.5, 32.3; **MS** (EI): *m/z* (%): 316 (*M*⁺, 20.11), 318 ([*M*+2]⁺, 7.48), 257 (100); **HRMS** (EI) calculated for [C₁₉H₂₁O₂Cl]: 316.1227, found: 316.1230.

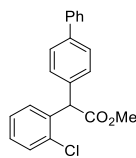
5) Methyl 2-(2-chlorophenyl)-2-(4-propylphenyl)acetate (3ea)



The general procedure was followed using **2a** (0.4 mmol) and propylbenzene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ea** (101 mg, 83%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.30-7.27 (m, 1H), 7.16-7.06 (m, 7H), 5.37 (s, 1H), 3.66 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.60-1.49 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 142.0, 136.8, 134.2, 134.1, 130.0, 129.5, 128.8, 128.7, 128.5, 126.9, 53.4, 52.4, 37.6, 24.4, 13.9; **MS** (EI): *m/z* (%): 302 (*M*⁺, 18.43), 244 (100); **HRMS** (EI)

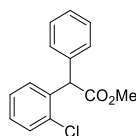
calculated for [C₁₈H₁₉ClO₂]: 302.1074, found: 302.1076.

6) Methyl 2-([1,1'-biphenyl]-4-yl)-2-(2-chlorophenyl)acetate (3fa)



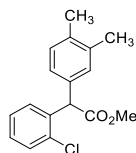
The general procedure was followed using **2a** (0.4 mmol), 1,1'-biphenyl (0.8 mmol, 124 mg, 2 equiv) and use DCM as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3fa** (97 mg, 72%) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.0 Hz, 4H), 7.45-7.29 (m, 4H), 7.24-7.21 (m, 2H), 5.53 (s, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 140.5, 140.4, 136.4, 136.0, 134.2, 130.0, 129.6, 129.3, 128.8, 128.7, 127.5, 127.4, 127.1, 127.0, 53.4, 52.6; MS (EI): *m/z* (%): 336 (M⁺, 16.69), 249 (100); HRMS (EI) calculated for [C₂₁H₁₇ClO₂]: 336.0917, found: 336.0915.

7) Methyl 2-(2-chlorophenyl)-2-phenylacetate (3ga)



The general procedure was followed using **2a** (0.4 mmol). After purification by column chromatography (PE/EtOAc 30 :1), **3bh** (76 mg, 73%) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.29 (m, 3H), 7.28-7.20 (m, 3H), 7.16-7.11 (m, 3H), 5.41 (s, 1H), 3.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 137.0, 136.5, 134.2, 130.0, 129.6, 128.9, 128.7, 128.6, 127.5, 126.9, 53.7, 52.5; MS (EI): *m/z* (%): 260 (M⁺, 15.00), 202 (100); HRMS (EI) calculated for [C₁₅H₁₃ClO₂]: 260.0604, found: 260.0603.

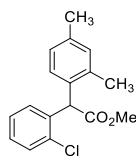
8) Methyl 2-(2-chlorophenyl)-2-(3,4-dimethylphenyl)acetate (3ha)



The general procedure was followed using **2a** (0.4 mmol) and use o-xylene (1 mL) as a solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ha** (113 mg, 98%) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 2.8 Hz, 1H), 7.28-7.09 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97-6.92 (m, 2H), 5.33 (s, 1H), 3.65 (s, 3H), 2.16 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 137.0, 136.7, 136.0, 134.2, 134.1, 130.1, 130.0, 129.9, 129.4, 128.4, 126.8, 126.2, 53.4, 52.4, 19.8, 19.4; MS (EI): *m/z* (%): 288 (M⁺, 21.67), 290 ([M+2]⁺, 7.38), 229

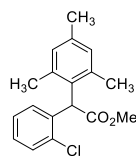
(100),; **HRMS** (EI) calculated for [C₁₇H₁₇O₂Cl]: 288.0915, found: 288.0917.

9) Methyl 2-(2-chlorophenyl)-2-(2,4-dimethylphenyl)acetate (3ia)



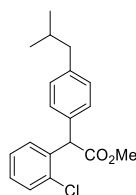
The general procedure was followed using **2a** (0.4 mmol) and use *m*-xylene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ia** (103 mg, 89%) was obtained as a white solid, m.p. 67-68 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.17-7.07 (m, 2H), 6.95-6.92 (m, 4H), 5.46 (s, 1H), 3.68 (s, 3H), 2.24 (s, 3H), 2.09 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.8, 137.3, 136.5, 136.0, 134.4, 132.5, 131.7, 130.1, 129.4, 128.5, 127.9, 126.9, 126.8, 52.5, 50.8, 21.0, 19.4; **MS** (EI): *m/z* (%): 288 (M⁺, 22.01), 290 ([M+2]⁺, 7.45), 229 (100),; **HRMS** (EI) calculated for [C₁₇H₁₇O₂Cl]: 288.0917, found: 288.0918.

10) Methyl 2-(2-chlorophenyl)-2-mesitylacetate (3ja)



The general procedure was followed using **2a** (0.4 mmol) and use mesitylene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ja** (111 mg, 92%) was obtained as a white solid, m.p. 109-110 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.24 (ddd, *J* = 1.6 Hz, 1H), 7.15 (ddd, *J* = 1.2 Hz, 1H), 6.96 (s, 2H), 6.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.64 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.22 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.7, 137.3, 137.1, 135.5, 134.4, 131.8, 130.0, 129.5, 129.4, 128.5, 126.8, 52.4, 49.6, 20.9, 20.6; **MS** (EI): *m/z* (%): 302 (M⁺, 35.99), 290 ([M+2]⁺, 11.37), 243 (100),; **HRMS** (EI) calculated for [C₁₈H₁₉O₂Cl]: 302.1074, found: 302.1072.

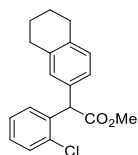
11) Methyl 2-(2-chlorophenyl)-2-(4-propylphenyl)acetate (3ka)



The general procedure was followed using **2a** (0.4 mmol) and use isobutylbenzene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3ka** (110 mg, 87%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.31-7.28 (m, 1H), 7.16-7.10 (m,

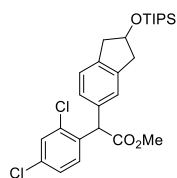
5H), 7.05-7.03 (m, 2H), 5.38 (s, 1H), 3.67 (s, 3H), 2.38 (d, $J = 7.2$ Hz, 2H), 1.90-1.69 (m, 1H), 0.82 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 141.0, 136.8, 134.2, 134.1, 130.1, 129.5, 129.4, 128.6, 128.5, 126.9, 53.4, 52.4, 45.0, 30.1, 22.4; **MS** (EI): m/z (%): 316 (M^+ , 11.33), 258 (100); **HRMS** (EI) calculated for $[\text{C}_{19}\text{H}_{21}\text{ClO}_2]$: 316.1230, found: 316.1228.

12) Methyl 2-(2-chlorophenyl)-2-(5,6,7,8-tetrahydronaphthalen-2-yl)acetate (3la)



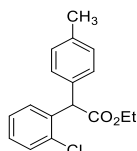
The general procedure was followed using **2a** (0.4 mmol) use 1,2,3,4-tetrahydronaphthalene (1 mL) as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3la** (110 mg, 87%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.41 (m, 1H), 7.31-7.22 (m, 3H), 7.10-7.04 (m, 3H), 5.46 (s, 1H), 3.79 (s, 3H), 2.79 (s, 4H), 1.83 (d, $J = 1.2$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 137.6, 136.8, 136.5, 134.1, 133.8, 130.1, 129.5, 129.46, 129.43, 128.41, 126.8, 125.8, 53.4, 52.4, 29.4, 29.0, 23.1, 23.0; **MS** (EI): m/z (%): 314 (M^+ , 22.43), 316 ($[\text{M}+2]^+$, 7.46), 255 (100); **HRMS** (EI) calculated for $[\text{C}_{19}\text{H}_{19}\text{O}_2\text{Cl}]$: 314.1074, found: 314.1070.

13) Methyl 2-([1,1'-biphenyl]-4-yl)-2-(2-chlorophenyl)acetate (3mm)



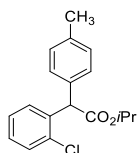
The general procedure was followed using **2g** (0.4 mmol), **1l** (1.2 mmol, 348 mg, 3 equiv) and use DCM as solvent. After purification by column chromatography (PE/EtOAc 30 :1), **3mm** (158 mg, 78%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.20-7.17 (m, 3H), 7.10-7.05 (m, 2H), 5.40 (s, 1H), 4.85-4.76 (m, 1H), 3.78 (s, 3H), 3.19 (dd, $J = 21.2, 9.2$ Hz, 2H), 2.94 (dd, $J = 21.2, 8.0$ Hz, 2H), 1.11 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 142.2, 141.2, 141.0, 135.5, 134.7, 133.7, 131.1, 129.3, 127.2, 127.0, 126.4, 124.5, 73.9, 53.1, 52.6, 42.9, 42.6, 18.0, 12.1; **MS** (EI): m/z (%): 506 (M^+ , 17.19), 334 (100); **HRMS** (EI) calculated for $[\text{C}_{27}\text{H}_{36}\text{O}_2\text{Cl}_2\text{Si}]$: 507.1811, found: 507.1813.

14) Ethyl 2-(2-chlorophenyl)-2-(p-tolyl)acetate (3ab)



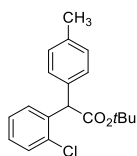
The general procedure was followed using **2b** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ab** (106 mg, 92%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.29-7.27 (m, 1H), 7.13-7.08 (m, 7H), 5.33 (s, 1H), 4.12 (dd, *J* = 9.6, 7.2 Hz, 2H), 2.24 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.0, 137.1, 136.9, 134.2, 134.1, 130.0, 129.5, 129.4, 128.8, 128.4, 126.8, 61.3, 53.5, 21.0, 14.1; **MS** (EI): *m/z* (%): 288 (*M*⁺, 21.25), 249 (100); **HRMS** (EI) calculated for [C₁₇H₁₇O₂Cl]: 288.0917, found: 288.0915.

15) Isopropyl 2-(2-chlorophenyl)-2-(p-tolyl)acetate (**3ac**)



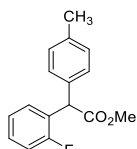
The general procedure was followed using **2c** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ac** (92 mg, 76%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.29-7.26 (m, 1H), 7.14-7.05 (m, 7H), 5.29 (s, 1H), 5.04-4.98 (m, 1H), 2.24 (s, 3H), 1.13 (dd, *J* = 15.2, 6.0 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.5, 137.1, 137.0, 134.2, 130.0, 129.4, 129.3, 128.7, 128.3, 126.7, 68.7, 53.7, 21.6, 21.5, 21.0; **MS** (EI): *m/z* (%): 302 (*M*⁺, 33.65), 268 (100); **HRMS** (EI) calculated for [C₁₈H₁₉O₂Cl]: 302.1074, found: 302.1076.

16) Tert-butyl 2-(2-chlorophenyl)-2-(p-tolyl)acetate (**3ad**)



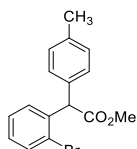
The general procedure was followed using **2d** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ad** (96 mg, 76%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.29-7.26 (m, 1H), 7.10-7.05 (m, 7H), 5.23 (s, 1H), 2.25 (s, 3H), 1.36 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.2, 137.4, 136.9, 134.5, 134.2, 130.0, 129.4, 129.3, 128.8, 128.2, 126.7, 81.4, 54.5, 27.9, 21.0; **MS** (EI): *m/z* (%): 316 (*M*⁺, 17.21), 282 (100); **HRMS** (EI) calculated for [C₁₉H₂₁O₂Cl]: 316.1230, found: 316.1232.

17) Methyl 2-(2-fluorophenyl)-2-(p-tolyl)acetate (**3ae**)



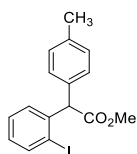
The general procedure was followed using **2e** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ae** (92 mg, 89%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.18-7.11 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.01-6.93 (m, 2H), 5.18 (s, 1H), 3.65 (s, 3H), 2.25 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 160.4 (d, *J* = 245 Hz), 137.2, 134.0, 129.8 (d, *J* = 4 Hz), 129.4, 128.9 (d, *J* = 8 Hz), 128.6, 126.3 (d, *J* = 14 Hz), 124.1 (d, *J* = 4 Hz), 115.3 (d, *J* = 22 Hz), 52.4, 49.4, 21.0; **MS** (EI): *m/z* (%): 258 (*M*⁺, 17.50), 199 (100); **HRMS** (EI) calculated for [C₁₆H₁₅O₂F]: 258.1056, found: 258.1055.

18) Methyl 2-(2-bromophenyl)-2-(p-tolyl)acetate (**3af**)



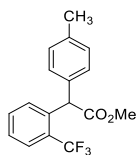
The general procedure was followed using **2f** (0.4 mmol) and toluene (1mL). After purification by column chromatography (PE/EtOAc 30 :1), **3af** (115 mg, 90%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.17-7.15 (m, 1H), 7.11-7.01 (m, 6H), 5.37 (s, 1H), 3.66 (s, 3H), 2.25 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 138.3, 137.2, 134.1, 132.9, 130.2, 129.5, 128.8, 128.7, 127.5, 125.0, 55.9, 52.5, 21.1; **MS** (EI): *m/z* (%): 318 (*M*⁺, 6.80), 320 ([*M*+2]⁺, 7.18), 165 (100); **HRMS** (EI) calculated for [C₁₆H₁₅O₂Br]: 318.0255, found: 318.0259.

19) Methyl 2-(2-iodophenyl)-2-(p-tolyl)acetate (**3ag**)



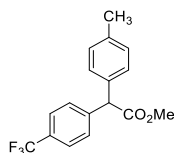
The general procedure was followed using **2g** (0.4 mmol). After purification by column chromatography (PE/EtOAc 30 :1), **3bd** (133 mg, 91%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.78 (d, *J* = 0.8 Hz, 1H), 7.77-7.15 (m, 2H), 7.10-7.05 (m, 4H), 6.88-6.83 (m, 1H), 5.29 (s, 1H), 3.66 (s, 3H), 2.25 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 141.4, 139.7, 137.1, 134.4, 129.7, 129.4, 128.9, 128.7, 128.3, 101.6, 60.6, 52.4, 21.0; **MS** (EI): *m/z* (%): 366 (*M*⁺, 10.57), 165 (100); **HRMS** (EI) calculated for [C₁₆H₁₅O₂I]: 366.0117, found: 366.0115.

20) Methyl 2-(p-tolyl)-2-(2-(trifluoromethyl)phenyl)acetate (**3ah**)



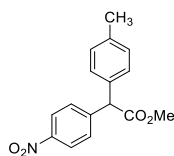
The general procedure was followed using **2h** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ah** (101 mg, 82%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.48-7.47 (m, 2H), 7.36-7.32 (m, 1H), 7.14 (s, 4H), 5.49 (s, 1H), 3.73 (s, 3H), 2.32 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.5, 137.2, 137.1, 135.0, 131.9, 131.5, 129.5, 128.3, 128.4 (q, *J* = 29 Hz), 127.2, 125.7 (q, *J* = 6 Hz), 124.4 (q, *J* = 272 Hz), 52.5, 51.7, 21.0; **MS** (EI): *m/z* (%): 308 (*M*⁺, 16.50), 218 (100); **HRMS** (EI) calculated for [C₁₇H₁₅O₂F₃]: 308.1024, found: 308.1026.

21) Methyl 2-(p-tolyl)-2-(4-(trifluoromethyl)phenyl)acetate (**3ai**)



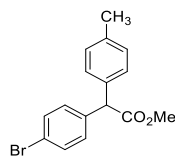
The general procedure was followed using **2i** (0.4 mmol) and 5 mol% catalyst. After purification by column chromatography (PE/EtOAc 30 :1), **3ai** (107 mg, 87%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 19.2, 8.0 Hz, 4H), 4.94 (s, 1H), 3.63 (s, 3H), 2.21 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.4, 142.8, 137.4, 134.8, 129.4 (q, *J* = 32 Hz), 129.5, 128.9, 128.3, 125.4 (q, *J* = 4 Hz), 125.1 (q, *J* = 271 Hz), 56.3, 52.4, 20.9; **MS** (EI): *m/z* (%): 308 (*M*⁺, 17.22), 249 (100); **HRMS** (EI) calculated for [C₁₇H₁₅O₂F₃]: 308.1024, found: 308.1023.

22) Ethyl 2-(4-nitrophenyl)-2-(p-tolyl)acetate (**3aj**)



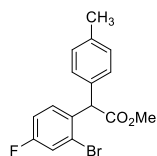
The general procedure was followed using **3j** (0.4 mmol) and 10 mol% catalyst. After purification by column chromatography (PE/EtOAc 10 :1), **3aj** (94 mg, 82%) was obtained as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.17-8.14 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 10.8, 8.4 Hz, 4H), 5.08 (s, 1H), 3.76 (s, 3H), 2.33 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.9, 147.1, 146.1, 137.7, 134.2, 129.6, 129.5, 128.3, 123.6, 56.2, 52.6, 21.0; **HRMS** (ESI) calculated for [C₁₆H₁₅NO₄Na][*M*+Na]⁺: 308.0899, found: 308.0893.

23) Methyl 2-(4-bromophenyl)-2-(p-tolyl)acetate (**3bi**)



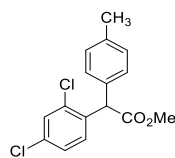
The general procedure was followed using **2k** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3ak** (57 mg, 45%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.13-7.02 (m, 6H), 4.85 (s, 1H), 3.63 (s, 3H), 2.22 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.6, 137.8, 137.2, 135.0, 131.6, 130.2, 129.4, 128.2, 121.2, 55.9, 52.3, 21.0; **MS** (EI): *m/z* (%): 318 (*M*⁺, 8.65), 320 ([*M*+2]⁺, 15.1), 259 (100); **HRMS** (EI) calculated for [C₁₆H₁₅O₂Br]: 318.0255, found: 318.0253.

24) Methyl 2-(2-bromo-4-fluorophenyl)-2-(p-tolyl)acetate (**3al**)



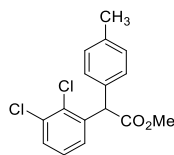
The general procedure was followed using **2l** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3al** (103 mg, 76%) was obtained as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.36 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.35-7.17 (m, 5H), 7.02-6.98 (m, 1H), 5.43 (s, 1H), 3.78 (s, 3H), 2.37 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 172.4, 161.0 (d, *J* = 248.75 Hz), 137.4, 134.4 (d, *J* = 3.75 Hz), 134.1, 131.2 (d, *J* = 7.5 Hz), 129.6, 128.6, 124.8 (d, *J* = 8.75 Hz), 120.0 (d, *J* = 25 Hz), 114.6 (d, *J* = 21.25 Hz), 55.1, 52.5, 21.1; **¹⁹F NMR** (282 MHz, CDCl₃) δ -113.187; **MS** (EI): *m/z* (%): 336 (*M*⁺, 8.65), 338 ([*M*+2]⁺, 9.00), 183 (100); **HRMS** (EI) calculated for [C₁₆H₁₄O₂FBr]: 336.0161, found: 336.0158.

25) Methyl 2-(2,4-dichlorophenyl)-2-(p-tolyl)acetate (**3am**)



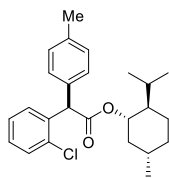
The general procedure was followed using **2m** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3am** (107 mg, 87%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (d, *J* = 1.6 Hz, 1H), 7.26-7.13 (m, 6H), 5.37 (s, 1H), 3.75 (s, 3H), 2.34 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.1, 137.4, 135.4, 134.7, 133.6, 133.5, 130.9, 129.6, 129.2, 128.6, 127.1, 52.8, 52.5, 21.0; **MS** (EI): *m/z* (%): 308 (*M*⁺, 18.95), 249 (100); **HRMS** (EI) calculated for [C₁₆H₁₄O₂Cl₂]: 308.0371, found: 308.0369.

26) Methyl 2-(2,3-dichlorophenyl)-2-(p-tolyl)acetate (**3an**)



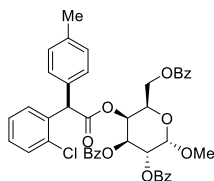
The general procedure was followed using **2n** (0.4 mmol) and toluene (1 mL). After purification by column chromatography (PE/EtOAc 30 :1), **3an** (116 mg, 94%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35-7.08 (m, 6H), 5.45 (s, 1H), 3.75 (s, 3H), 2.34 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.1, 139.1, 137.5, 133.5, 133.2, 132.5, 129.5, 129.3, 128.7, 128.2, 127.1, 54.2, 52.5, 21.0; **MS** (EI): *m/z* (%): 308 (*M*⁺, 18.95), 249 (100); **HRMS** (EI) calculated for [C₁₆H₁₄O₂Cl₂]: 308.0371, found: 308.0369.

27) (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl (R)-2-(2-chlorophenyl)-2-(p-tolyl)acetate (3ao)



The general procedure was followed using **2o** (0.4 mmol) and toluene as solvent (2 mL). After purification by column chromatography (PE/EtOAc 30:1), **3ai** (142 mg, 89%, 1.12:1 dr) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.27-7.25 (m, 2H), 7.12-7.04 (m, 16H), 5.33 (s, 1H), 5.28 (s, 1H), 4.68-4.61 (m, 2H), 2.23 (s, 6H), 2.00-1.91 (m, 3H), 1.76-1.72 (m, 1H), 1.56-1.22 (m, 12H), 0.95-0.83 (m, 5H), 0.79 (t, *J* = 6.4 Hz, 6H), 0.73 (d, *J* = 7.2 Hz, 4H), 0.63 (t, *J* = 7.2 Hz, 6H), 0.55 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.5 (171.4), 137.1 (137.0), 134.3 (134.2), 134.1 (134.0), 129.4, 129.3, 129.2, 128.8 (128.7), 128.3 (128.2), 75.21 (75.20), 54.1 (54.0), 53.73 (53.70), 46.9 (46.8), 34.2 (34.1), 31.4 (31.3), 25.8 (25.7), 23.3 (23.2), 22.0, 21.0, 20.6 (20.5), 16.0; **HRMS** (ESI) calculated for [C₂₅H₃₂ClO₂][*M*+*H*]⁺: 399.2082, found: 399.2085.

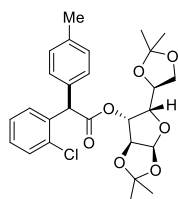
28) (2S,3R,4S,5S,6R)-6-((benzyloxy)methyl)-5-((R)-2-(2-chlorophenyl)-2-(p-tolyl)acetoxy)-2-methoxytetrahydro-2H-pyran-3,4-diyl dibenzoate (3ap)



The general procedure was followed using **2p** (0.4 mmol) and toluene as solvent (2 mL). After purification by column chromatography (PE/EtOAc 30:1), **3ai** (267 mg, 89%, 1.78:1 dr) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.00-7.97 (m, 3H),

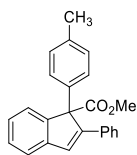
7.78-7.76 (m, 4H), 7.57-7.34 (m, 16H), 7.30-7.13 (m, 10H), 7.10-6.98 (m, 8H), 5.90-5.85 (m, 4H), 5.64-5.57 (m, 3H), 5.49 (dd, $J = 10.0, 3.6$ Hz, 1H), 5.19 (dd, $J = 10.0, 3.6$ Hz, 2H), 4.48-4.43 (m, 3H), 4.35 (dd, $J = 10.8, 6.8$ Hz, 1H), 4.11-4.05 (m, 1H), 3.94 (dd, $J = 10.8, 6.8$ Hz, 1H), 3.42 (d, $J = 2.8$ Hz, 6H), 2.29 (d, $J = 3.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.23 (170.96), 165.88 (165.80), 165.72 (165.69), 137.46 (137.00), 136.12 (135.89), 134.16 (134.05), 133.60 (133.48), 133.28 (133.18), 133.03 (132.96), 130.24 (129.39), 129.85 (129.82), 129.78, 129.76 (129.67), 129.57 (129.30), 129.53 (129.49), 129.22 (129.19), 128.74 (128.60), 128.71, 128.45 (128.39), 128.24 (128.16), 126.97 (126.89), 97.53, 69.53 (69.46), 68.98 (68.89), 68.46, 66.62 (66.57), 62.07 (61.79), 55.63, 53.56 (53.17), 21.05; HRMS (ESI) calculated for $[\text{C}_{43}\text{H}_{37}\text{ClNaO}_{10}][\text{M}+\text{Na}]^+$: 771.1973, found: 771.1967.

29) (3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (R)-2-(2-chlorophenyl)-2-(p-tolyl)acetate



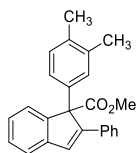
The general procedure was followed using **2q** (0.4 mmol) and toluene as solvent (1 mL). After purification by column chromatography (PE/EtOAc 30:1), **3ai** (171 mg, 85%, 1.37:1 dr) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.37 (m, 2H), 7.22-7.14 (m, 16H), 5.84 (d, $J = 3.6$ Hz, 1H), 5.72 (d, $J = 3.6$ Hz, 1H), 5.42 (d, $J = 4.4$ Hz, 2H), 5.36 (d, $J = 2.8$ Hz, 2H), 4.50 (d, $J = 3.6$ Hz, 1H), 4.44 (d, $J = 3.6$ Hz, 1H), 4.20-4.17 (m, 2H), 3.98-3.80 (m, 7H), 2.25 (s, 3H), 2.34 (s, 4H), 1.50 (d, $J = 2.0$ Hz, 7H), 1.38 (d, $J = 8.0$ Hz, 7H), 1.29 (m, 10H), 1.18 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6 (170.5), 137.44 (137.39), 136.36 (136.35), 134.1 (134.0), 133.4 (133.2), 130.1 (130.0), 129.5 (128.8), 129.5 (128.8), 129.4 (128.7), 127.0 (126.9), 112.4, 109.2 (109.1), 105.1 (105.0), 83.1 (82.9), 80.0, 76.6 (76.5), 72.1 (72.0), 67.2 (66.9), 53.7 (53.6), 26.7 (26.6), 26.2, 25.1 (24.9), 21.0; MS (EI): m/z (%): 502 (M^+ , 39.41), 249 (100); HRMS (EI) calculated for $[\text{C}_{27}\text{H}_{31}\text{ClO}_7]$: 502.1758, found: 502.1756.

30) Methyl 2-phenyl-1-(p-tolyl)-1H-indene-1-carboxylate (9a)



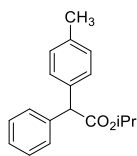
The general procedure was followed using **8** (0.4 mmol) and 10 mol% catalyst was used. After purification by column chromatography (PE/EtOAc 10 :1), **3aa** (98.0 mg, 72%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.47-7.41 (m, 5H), 7.33-7.17 (m, 7H), 7.05 (d, *J* = 6.8 Hz, 2H), 3.64 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.4, 150.3, 149.1, 142.7, 136.8, 135.5, 134.3, 129.5, 129.1, 128.2, 127.9, 127.6, 127.4, 127.2, 126.3, 123.9, 121.5, 68.5, 52.6, 21.0; **MS** (EI): *m/z* (%): 340 (*M*⁺, 12.66), 282 (100); **HRMS** (EI) calculated for [C₂₄H₂₀O₂]: 340.1463, found: 340.1466.

31) Methyl 1-(3, 4-dimethylphenyl)-2-phenyl-1H-indene-1-carboxylate (9h)



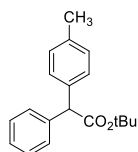
The general procedure was followed using **8** (0.4 mmol) and 10 mol% catalyst was used. After purification by column chromatography (PE/EtOAc 10:1), **3ai** (84.7 mg, 60%) was obtained as a white solid, m.p. 99-100 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.44-7.36 (m, 5H), 7.27-7.06 (m, 7H), 6.96 (d, *J* = 7.6 Hz, 1H), 3.58 (d, *J* = 2.8 Hz, 3H), 2.14 (d, *J* = 4.8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.4, 150.2, 149.2, 142.6, 136.4, 135.8, 135.5, 134.4, 129.6, 129.5, 128.5, 128.1, 127.8, 127.5, 127.2, 126.2, 124.9, 123.9, 121.4, 68.6, 52.6, 20.0, 19.3; **MS** (EI): *m/z* (%): 354 (*M*⁺, 39.49), 295 (100); **HRMS** (EI) calculated for [C₂₅H₂₂O₂]: 354.1620, found: 354.1616.

32) Isopropyl 2-phenyl-2-(p-tolyl)acetate



The general procedure was followed using **1a** (0.4 mmol). After purification by column chromatography (PE/EtOAc 30 :1), **3al** (32 mg, 30%) was obtained as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.37 (t, *J* = 3.5 Hz, 4H), 7.32-7.26 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 5.15 (m, 1H), 5.01 (s, 1H), 2.38 (s, 3H), 1.29 (d, *J* = 6.0 Hz, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 172.1, 139.1, 136.7, 135.9, 129.2, 128.5, 128.42, 128.40, 127.0, 68.4, 56.9, 21.6, 21.0; **MS** (EI): *m/z* (%): 268 (*M*⁺, 5.88), 181 (100); **HRMS** (EI) calculated for [C₁₈H₂₀O₂]: 268.1463, found: 268.1460.

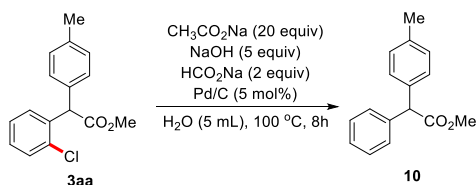
33) Tert-butyl 2-phenyl-2-(p-tolyl)acetate



The general procedure was followed using **2m** (0.4 mmol). After purification by column chromatography (PE/EtOAc 30 :1), **3am** (48 mg, 43%) was obtained as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.37-7.35 (m, 4H), 7.32-7.26 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 1H), 2.38 (s, 3H), 1.51 (s, 9H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.8, 139.4, 136.5, 136.2, 129.1, 128.5, 128.4, 128.3, 126.8, 81.1, 57.6, 27.9, 21.0; **MS** (EI): *m/z* (%): 282 (*M*⁺, 0.67), 181 (100); **HRMS** (ESI) calculated for [C₁₉H₂₂O₂Na][*M*+Na]⁺: 305.1512, found: 305.1522.

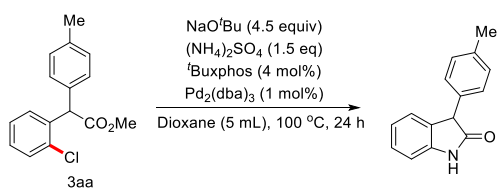
4. Synthetic Application

1) Methyl 2-phenyl-2-(p-tolyl)acetate (**10**)^[1]



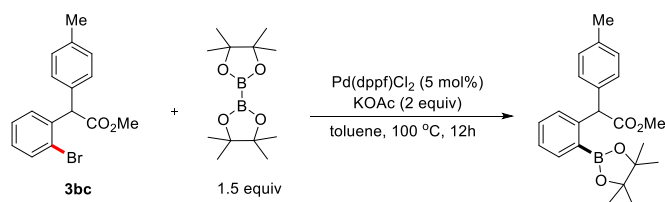
In a Schlenk tube, CH₃CO₂Na (1.7 g, 20 mmol) was firstly dissolved in water (5 ml) at 100 °C in an oil bath equipped with magnetic stirring and reflux concentration. Then, HCO₂Na (136 mg, 2 mmol), sodium hydroxide (200 mg, 5 mmol), Pd/C (5 wt%, 10 mg), and **3aa** (1 mmol, 274 mg) were added in the salts solutions. After the reaction was completed, filtered, extraction with additional CH₂Cl₂, and evaporated in vacuo, purified by column chromatography on silica gel to give the desired product as a colorless oil (182 mg, 76%). **¹H NMR** (500 MHz, CDCl₃) δ 7.35-7.17 (m, 9H), 5.05 (s, 1H), 3.78 (s, 3H), 2.36 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 173.1, 138.8, 137.0, 135.6, 129.3, 128.6, 128.5, 128.4, 127.2, 56.6, 52.3, 21.0; **MS** (EI): *m/z* (%): 240 (*M*⁺, 17.01), 181 (100); **HRMS** (EI) calculated for [C₁₆H₁₆O₂]: 240.1150, found: 240.1154.

2) 3-(p-Tolyl)indolin-2-one (**11**)^[2]



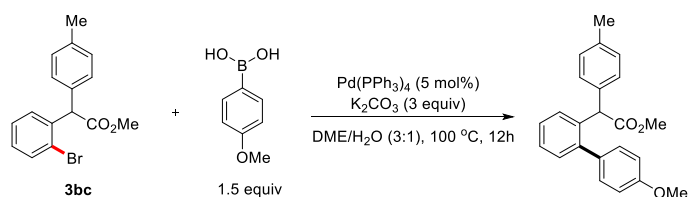
In a dried seal tube, **3aa** (274 mg, 1 mmol), NaO^tBu (432 mg, 4.5 mmol, 4.5 equiv), (NH₄)₂SO₄ (198 mg, 1.5 mmol, 1.5 equiv), ^tBuXphos (16.98 mg, 0.04 mmol) and Pd₂(dba)₃ (10.4 mg, 0.01 mmol) dissolved in dried 1,4-dioxane (5 mL), the resulting mixture was heated to 100 °C for 24 h. After cooling, filtered, evaporated the solvent in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 5:1) to give the desired product as a white solid (174 mg, 78%). **¹H NMR** (400 MHz, CDCl₃) δ 9.40 (br, 1H), 7.22-7.08 (m, 6H), 7.02-6.98 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 2H), 4.59 (s, 1H), 2.32 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 179.5, 141.7, 137.3, 133.4, 129.8, 129.6, 128.3, 125.1, 122.6, 110.1, 52.4, 21.0; **MS** (EI): *m/z* (%): 223 (M⁺, 29.36), 194 (100).

3) Methyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-(p-tolyl)acetate (**12**) ^[3]



In a dried Schlenk tube, to a solution of **3bc** (318 mg, 1 mmol), Pd(dppf)Cl₂ (40.8 mg, 5 mol%), bis(pinacolato)diboron (381 mg, 1.5 mmol, 1.5 equiv) in toluene (5 mL) was added KOAc (196 mg, 2 mmol, 2 equiv) at 100 °C and the reaction maintained 12 hours, filtered. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica chromatography (PE/EtOAc 20:1), **9a** (264 mg, 72%) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.38-7.34 (m, 1H), 7.27-7.16 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 3.69 (s, 3H), 2.30 (s, 3H), 1.30 (d, *J* = 2.4 Hz, 12H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.4, 145.0, 136.6, 136.3, 136.2, 131.0, 129.0, 128.3, 128.8, 126.2, 83.7, 54.3, 51.9, 24.8, 21.0; **MS** (EI): *m/z* (%): 334 (M⁺, 33.46), 252 (100); **HRMS** (EI) calculated for [C₂₂H₂₇BO₄]: 366.2002, found: 366.1998.

4) Methyl 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)acetate (**13**) ^[4]

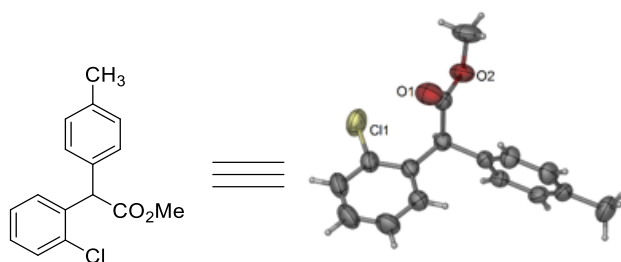


3bc (318 mg, 1.0 mmol) and $\text{Pd(PPh}_3)_4$ (57 mg, 0.05 mmol) were dissolved in DME (5 mL; dimethoxyethane) in a dried 25 mL Schlenk tube. K_2CO_3 (413 mg, 3.0 mmol, 3.0 equiv) in distilled water (3 mL) was added to the stirred solution. After 5 min, the corresponding boronic acid (1.5 mmol, 1.5 equiv) in 5 mL of DME was added, and the resulting mixture was heated to 100 °C for 12 h. After cooling, DME was partially evaporated under reduced pressure and the mixture was poured into water followed by an extraction with additional CH_2Cl_2 (20 mL). The combined organic layers were dried over MgSO_4 , filtered, evaporated in vacuo, and the residue was purified by column chromatography on silica gel to give the desired product as a colorless oil (332 mg, 96%). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.38 (d, J = 1.2 Hz, 1H), 7.36-7.11 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 5.07 (s, 1H), 3.71 (s, 3H), 3.52 (s, 3H), 2.18 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.5, 158.8, 142.0, 136.5, 136.3, 136.0, 133.3, 130.4, 129.1, 128.7, 128.4, 127.3, 126.9, 113.5, 55.1, 52.8, 52.0, 20.9; **MS** (EI): m/z (%): 346 (M^+ , 33.46), 195 (100); **HRMS** (EI) calculated for $[\text{C}_{23}\text{H}_{22}\text{O}_3]$: 346.1569, found: 346.1572.

5 Reference

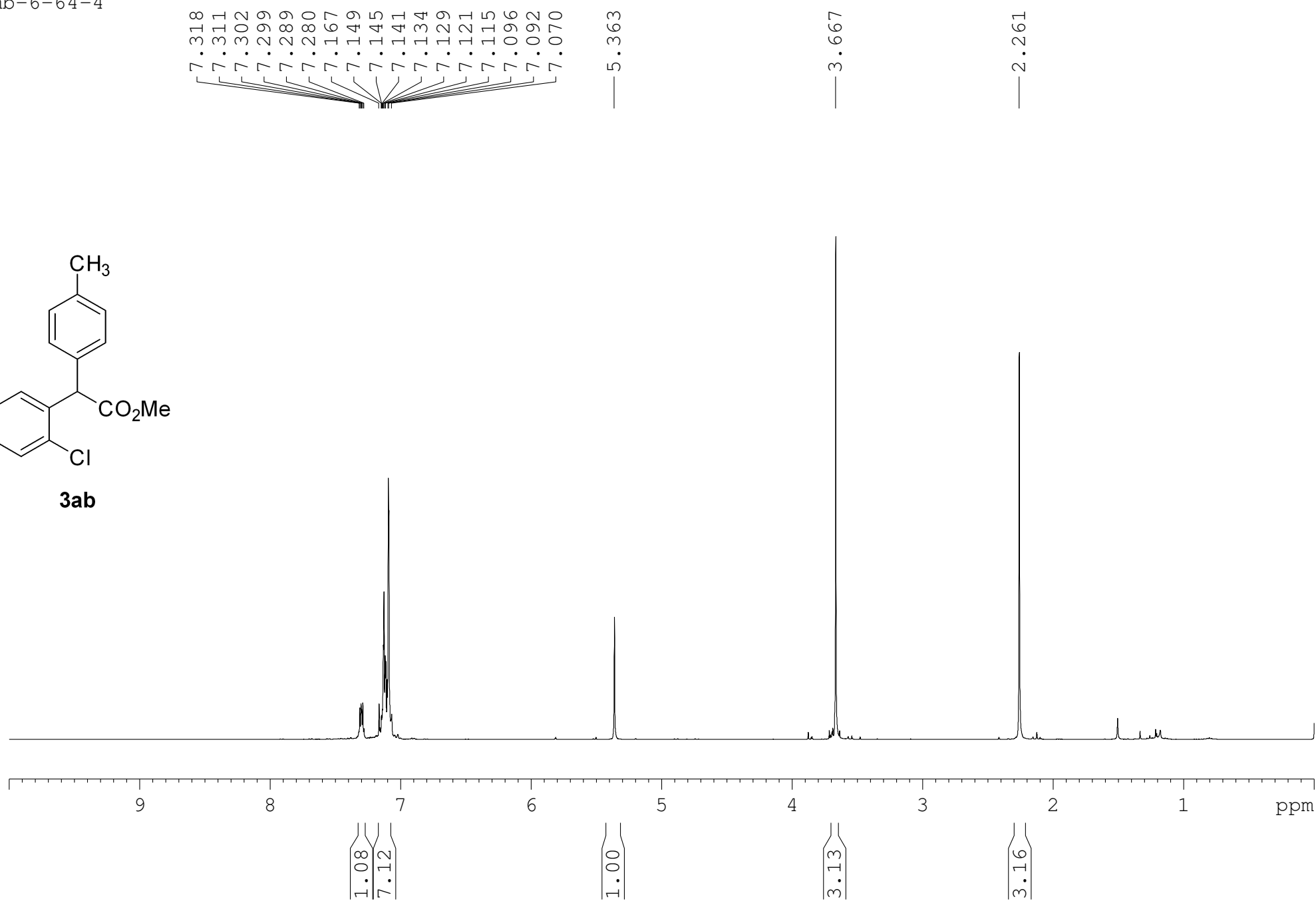
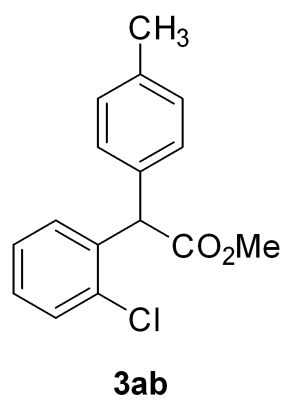
- [1] Z. Xue, X. Zhao, J. Wang, T. Mu. *RSC Adv.*, 2016, **6**, 102193;
- [2] C. W. Cheung, D.S. Surry, S. L. Buchwald, *Org. Lett.*, 2013, **15**, 3734;
- [3] L. Wang, J. Li, X. Cui, Y. Wu, Z. Zhu, Y. Wu, *Adv. Synth. Catal.*, 2010, **352**, 2002;
- [4] J. Kim, Y. Ohk, S. H. Park, Y. Jung, S. Chang. *Chem. Asian J.* 2011, **6**, 2040.

6 X-ray crystal structure of 3aa



7 NMR spectra of new compounds

mb-6-64-4



mb-6-64-4 C
mb-6-64-4 C

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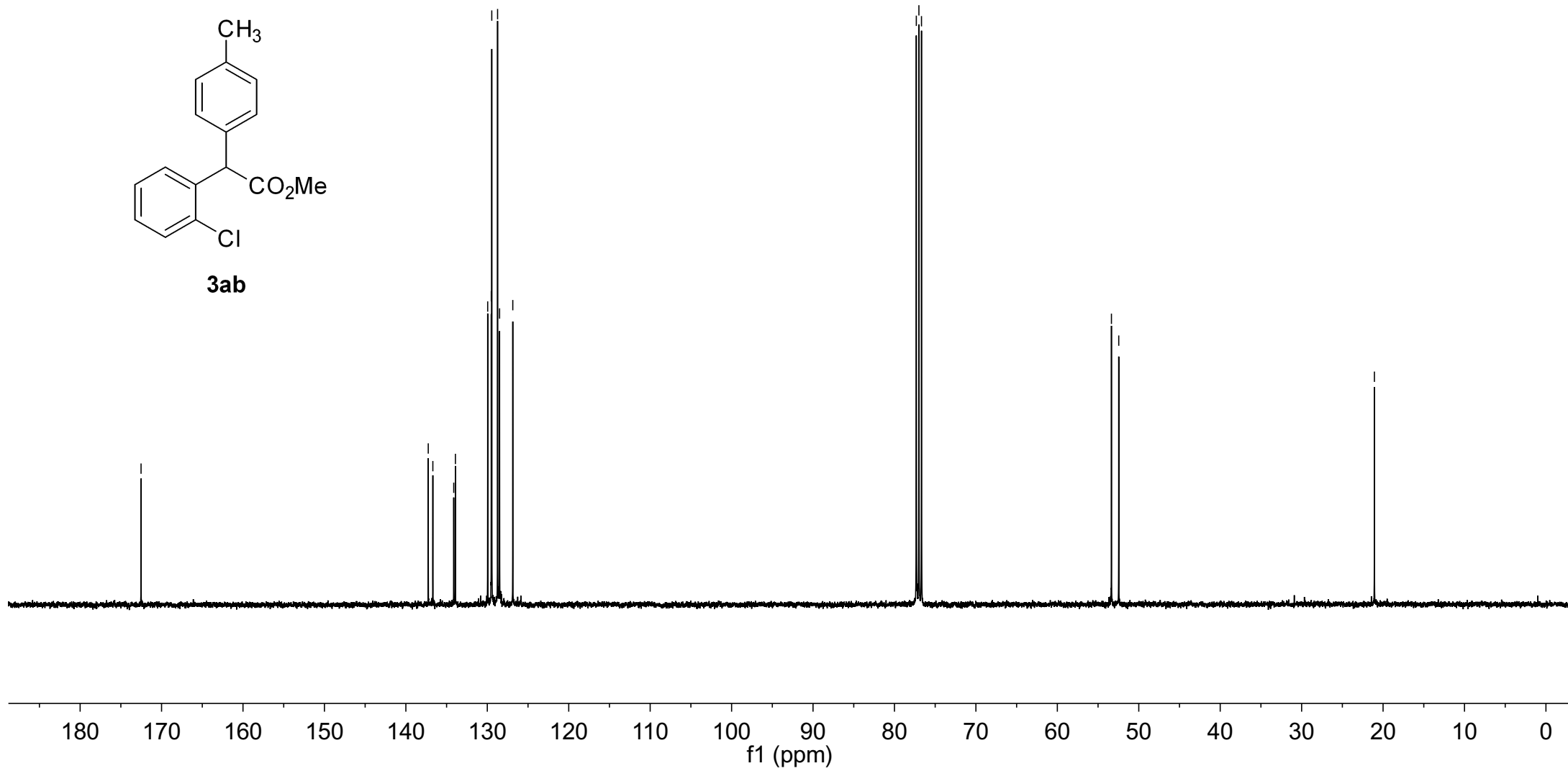
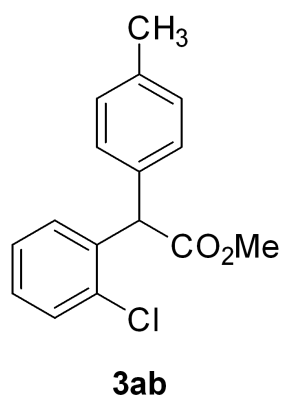
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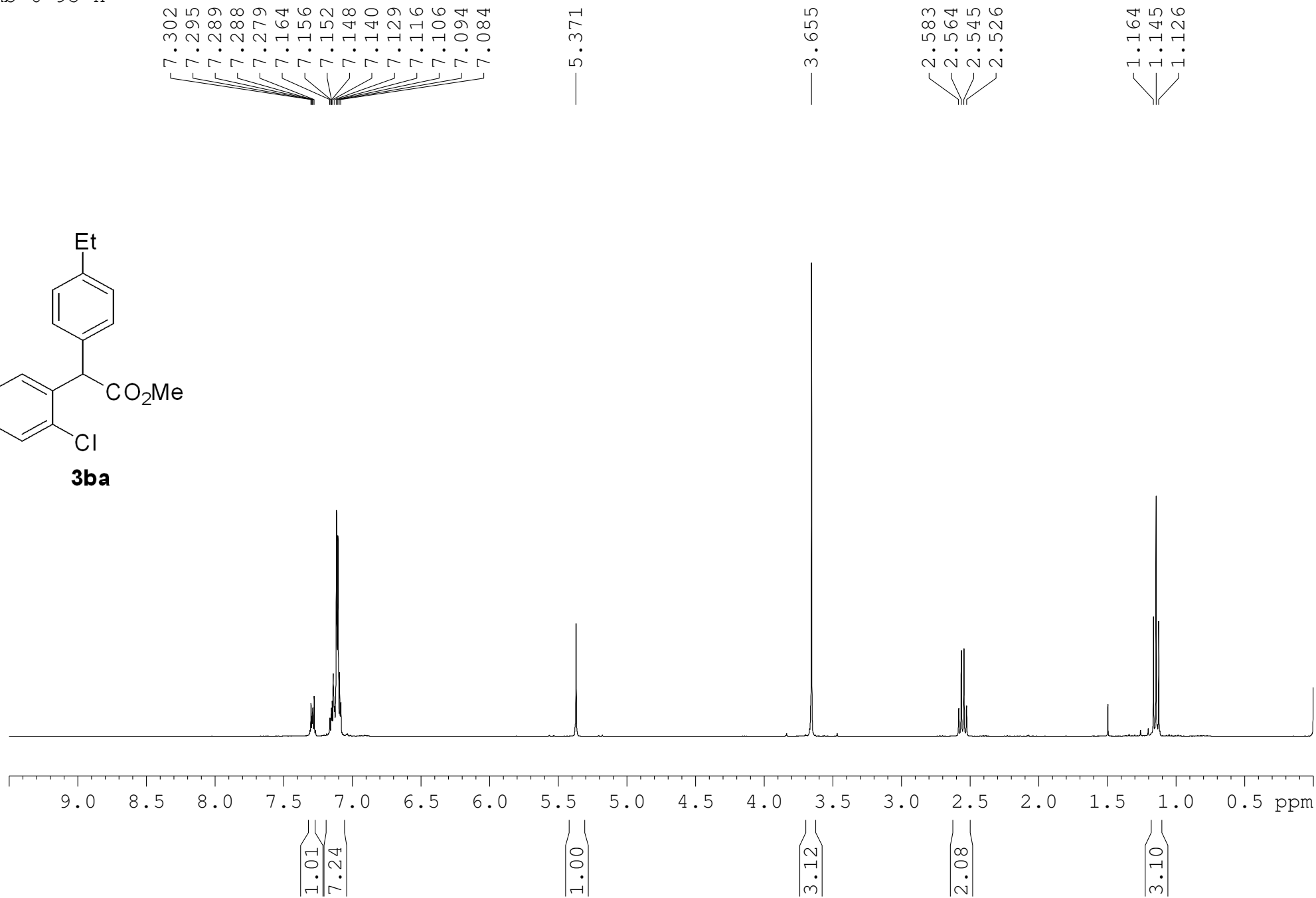
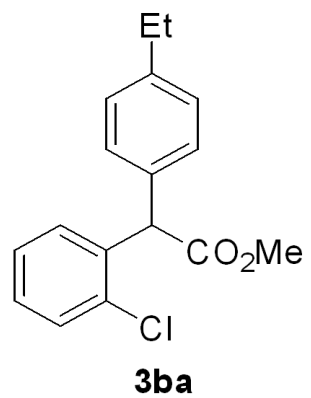
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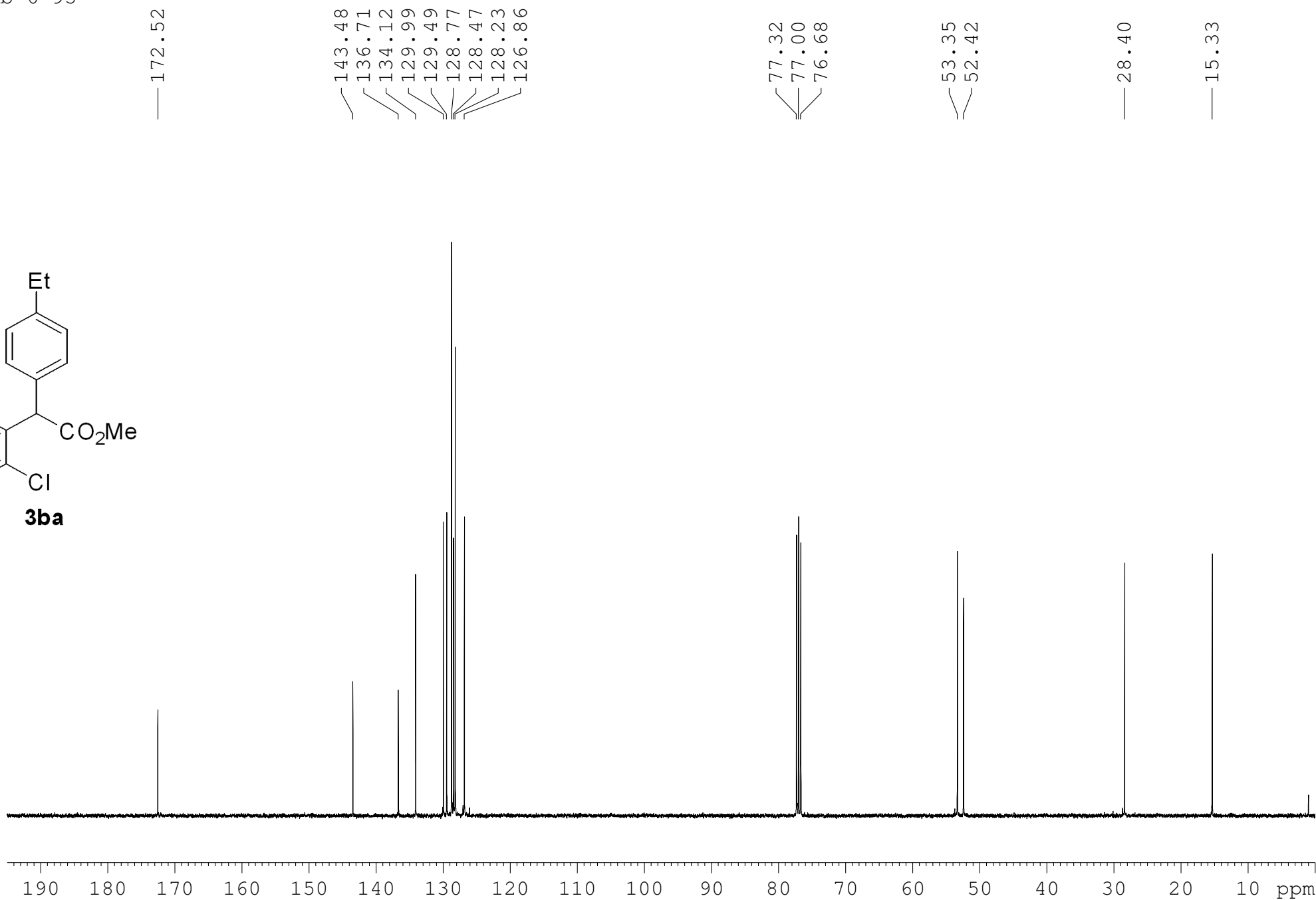
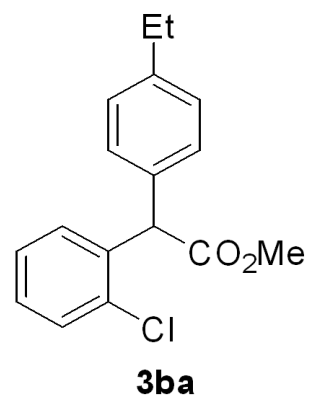
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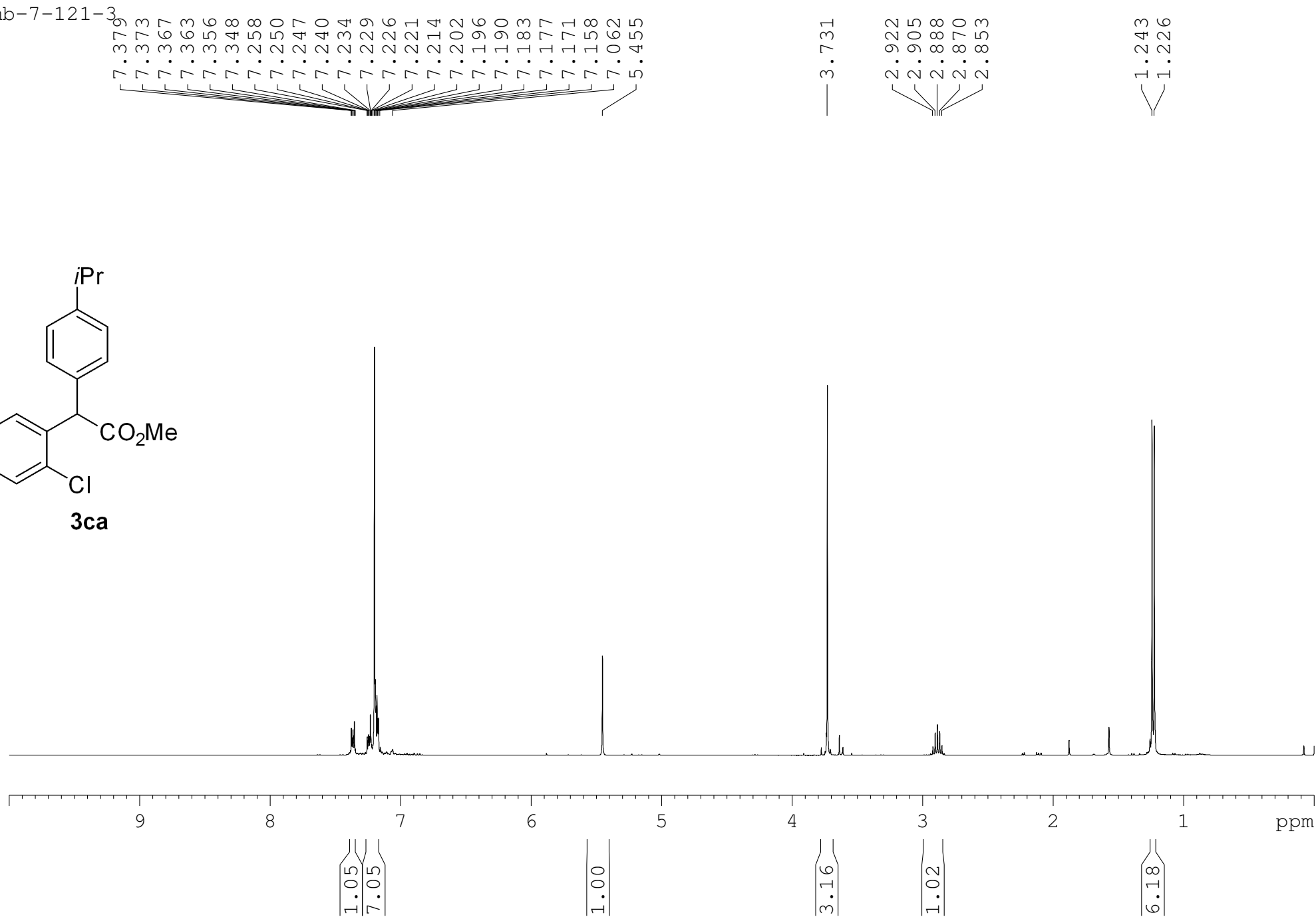
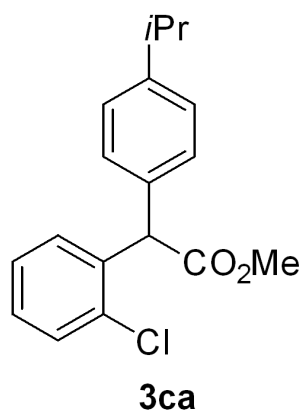


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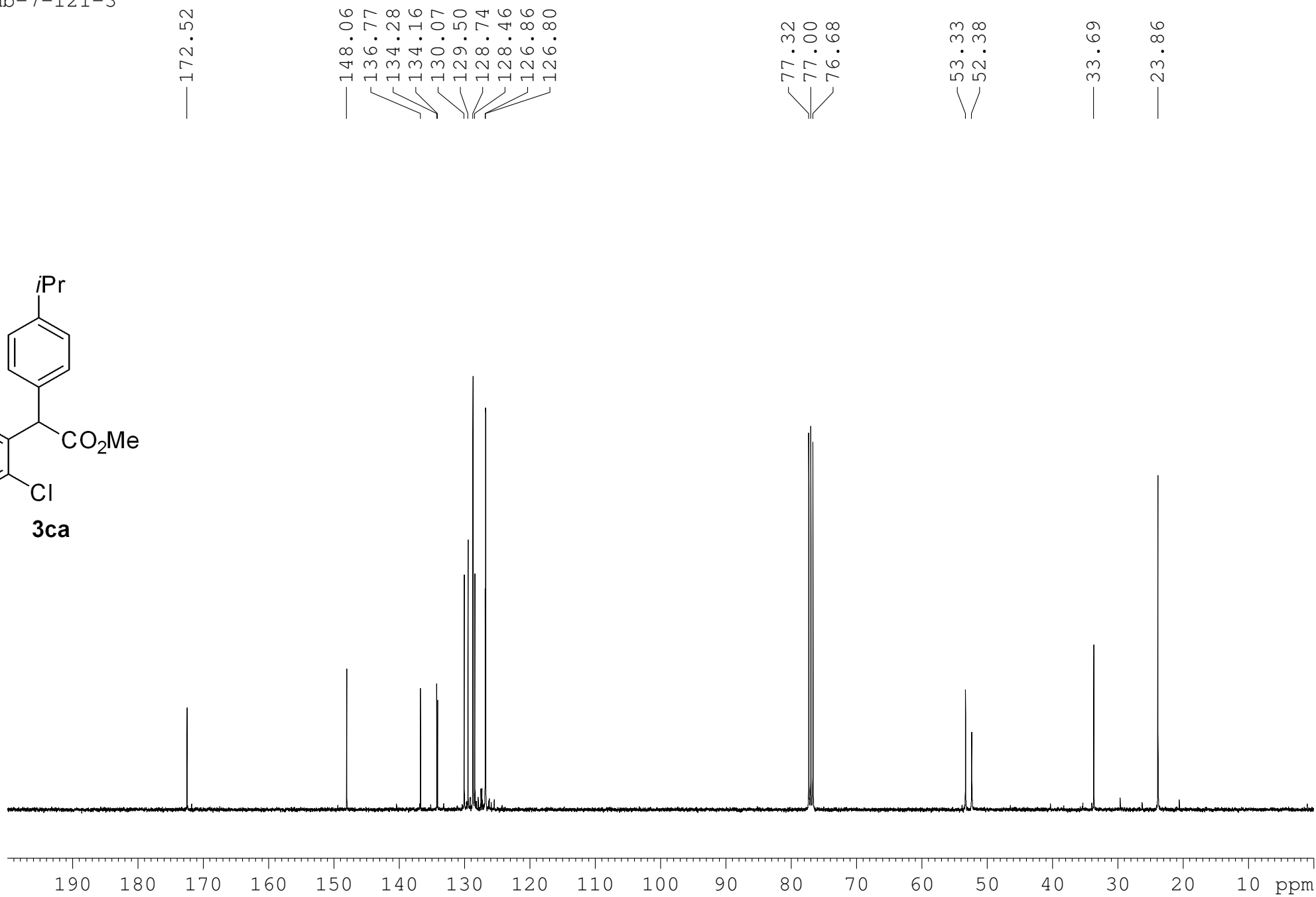
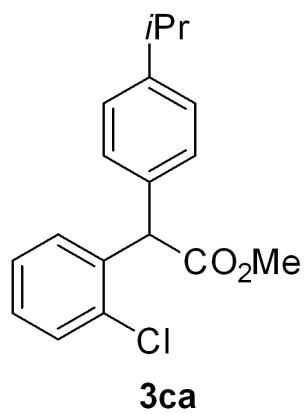


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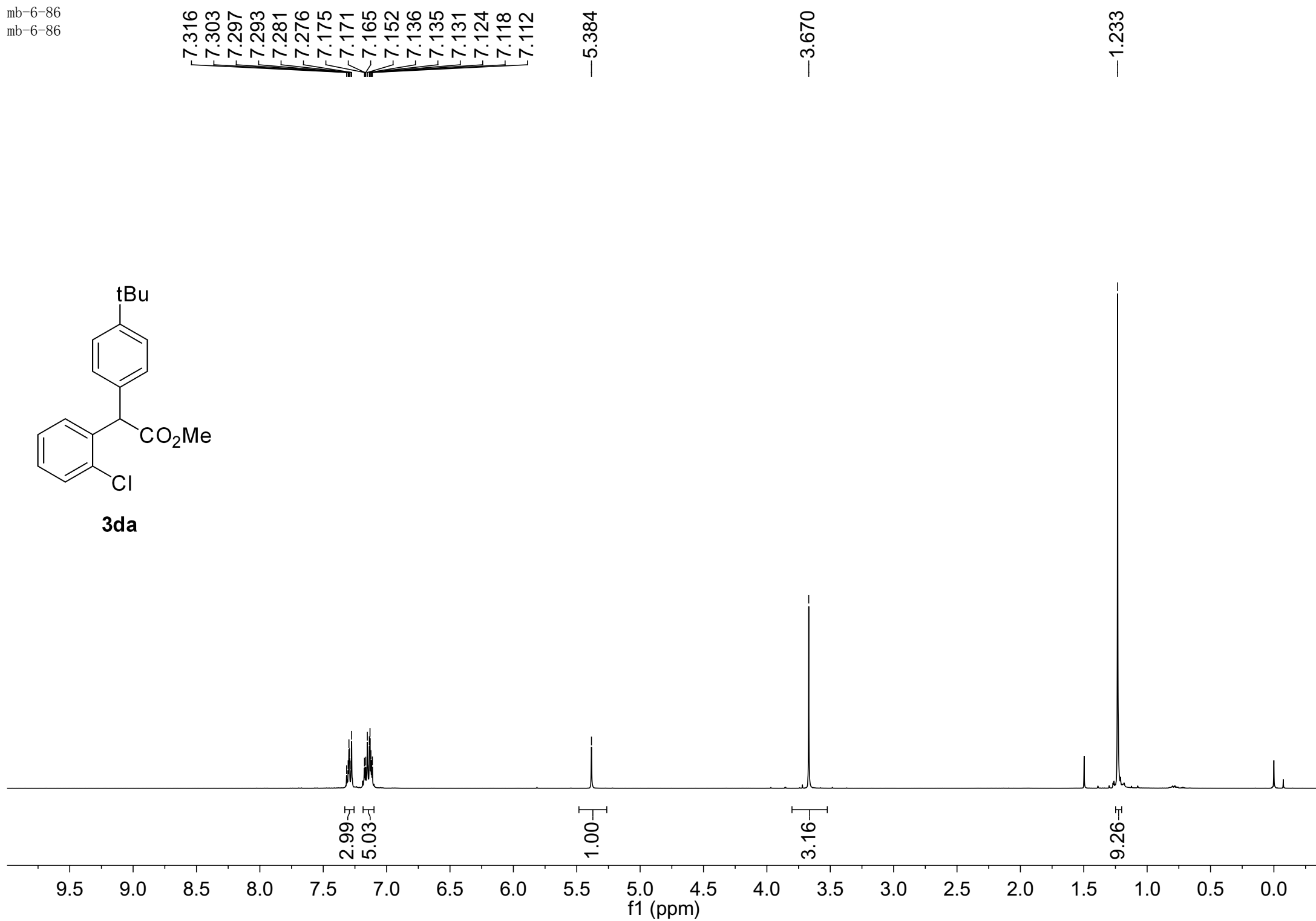
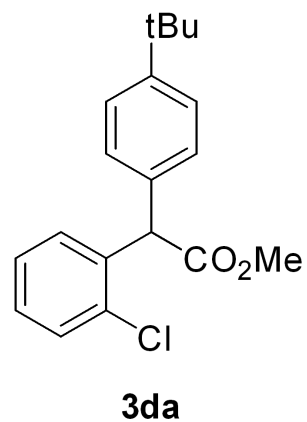




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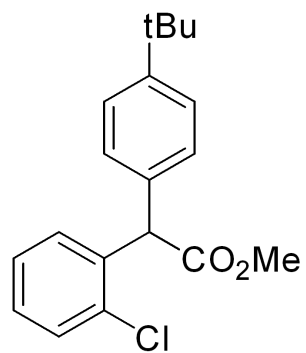
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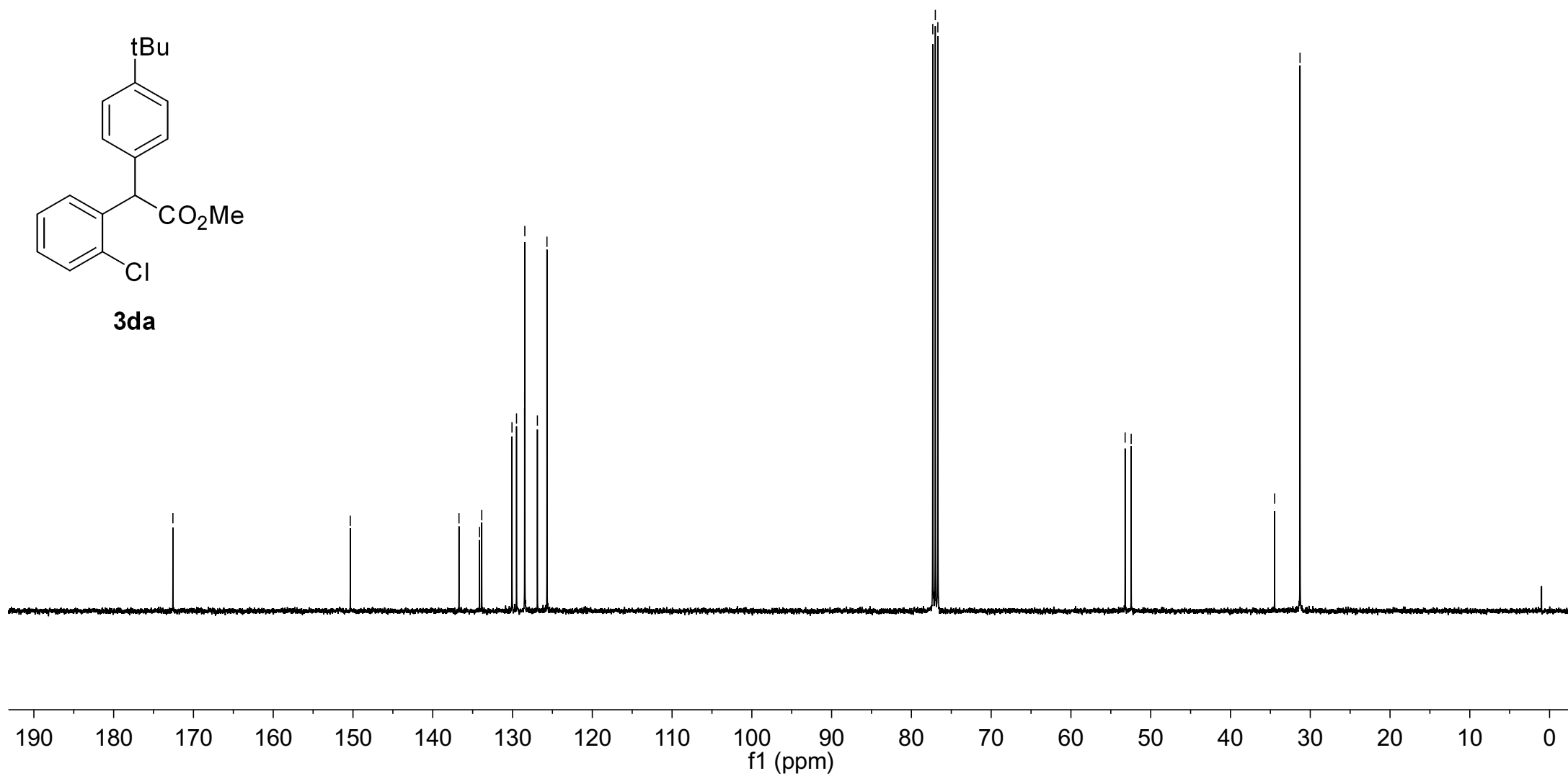
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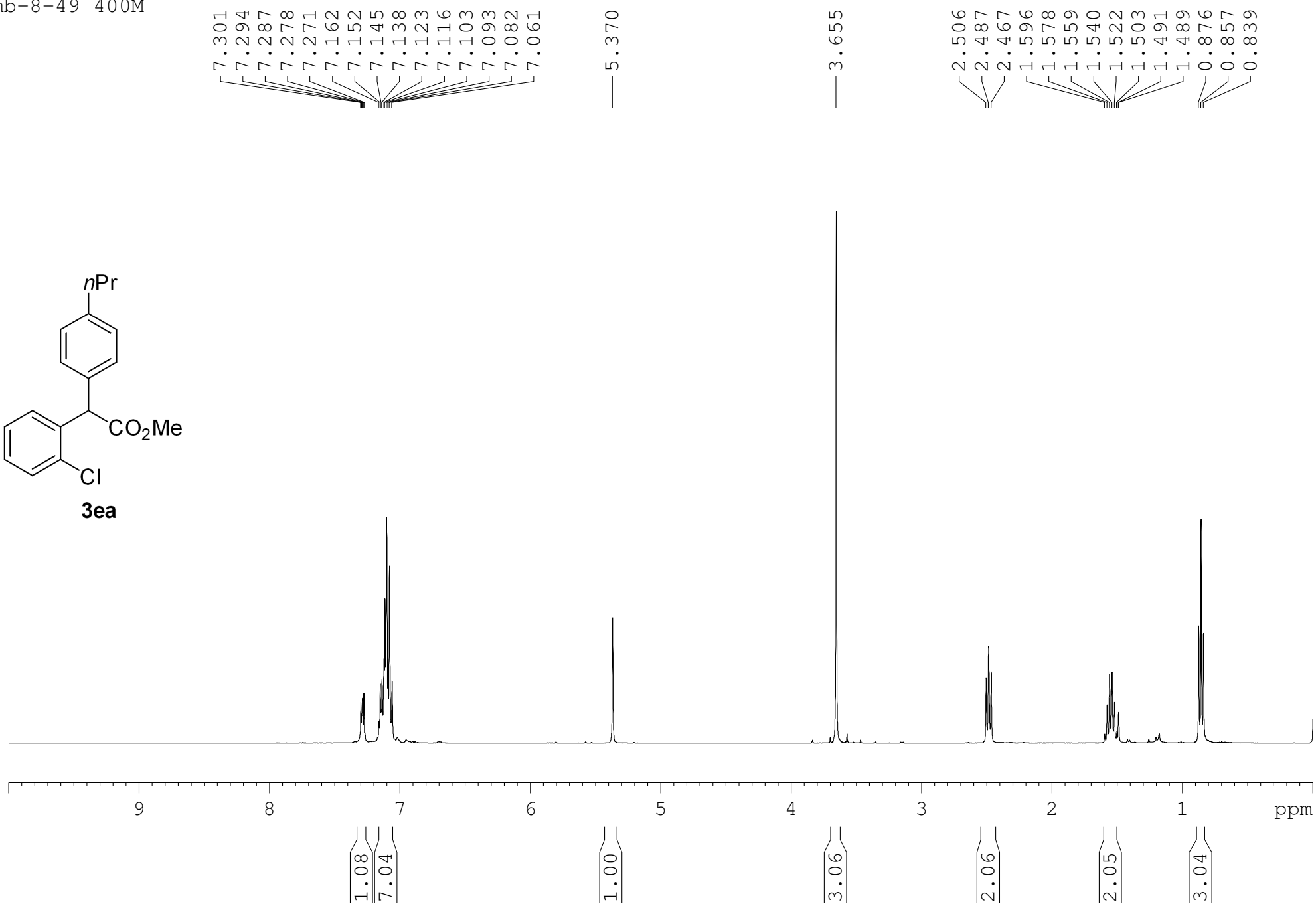
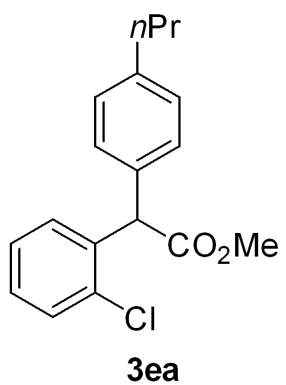
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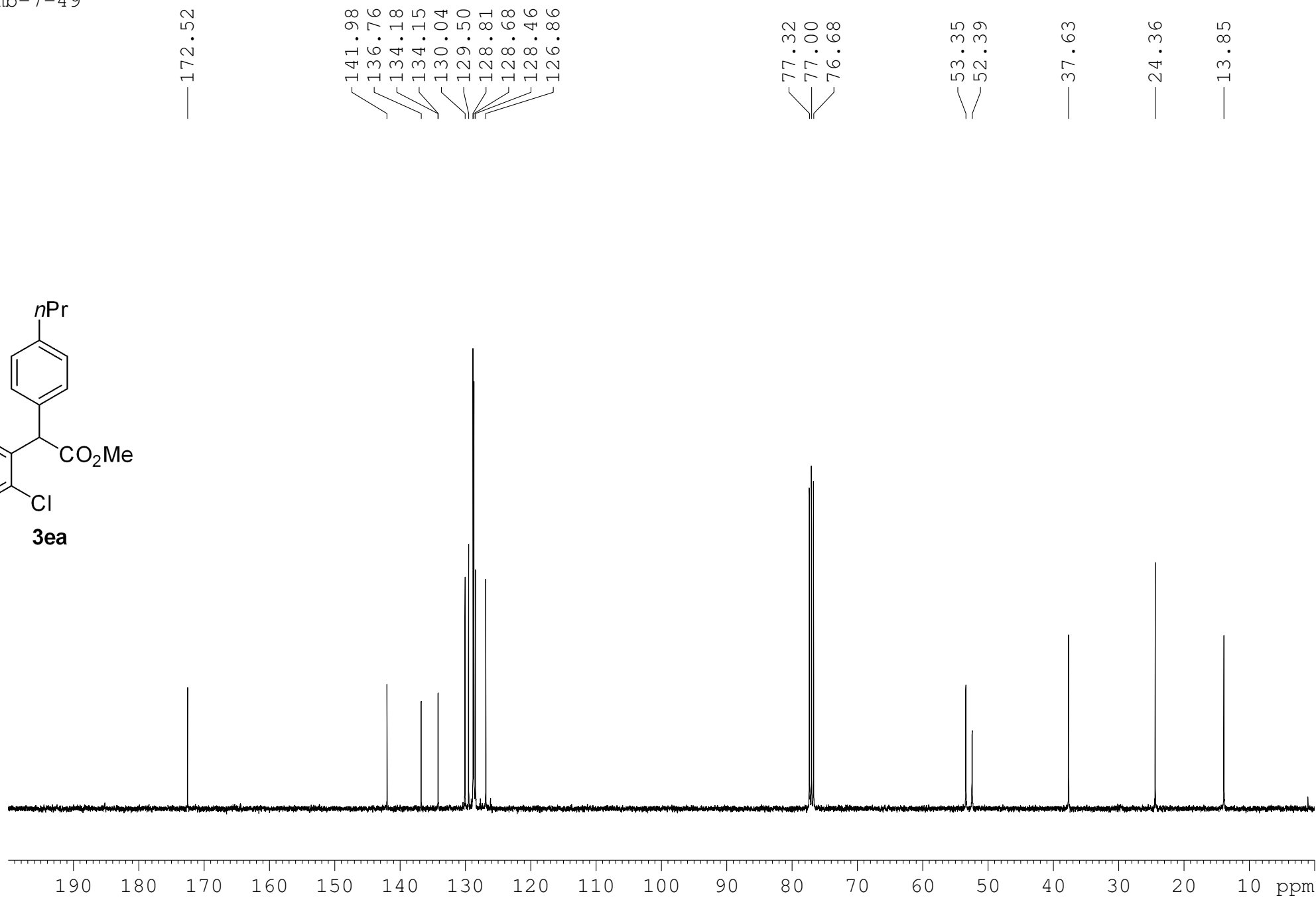
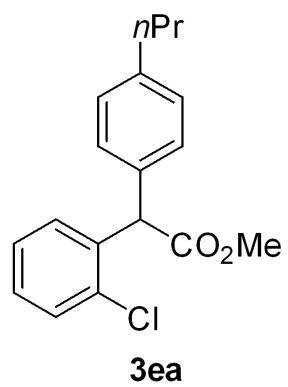
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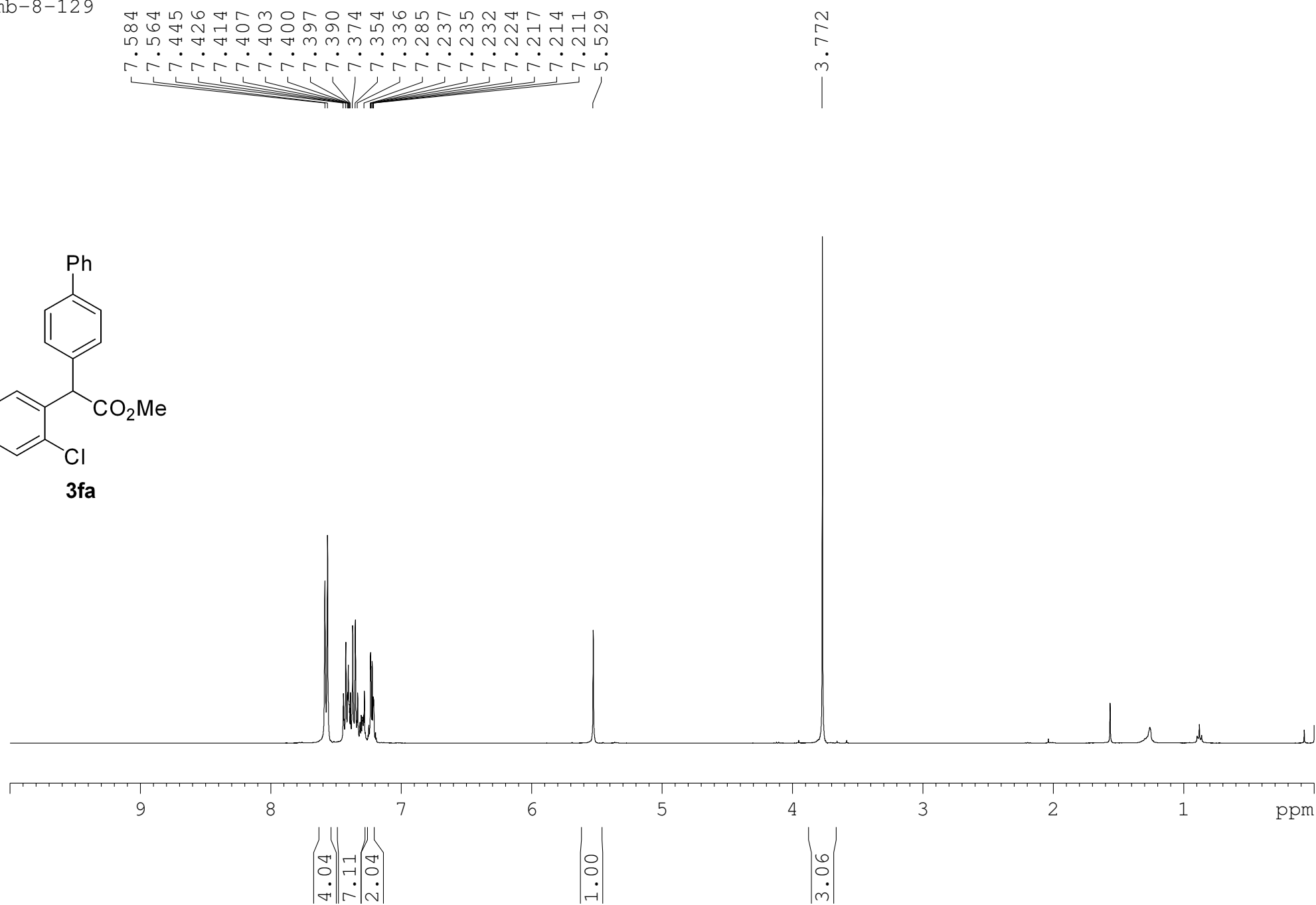
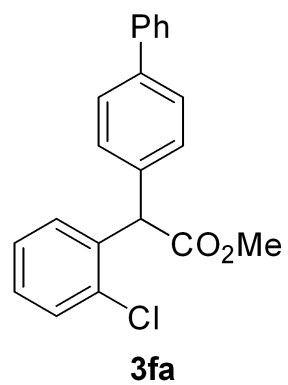
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mb-7-49



mb-8-129



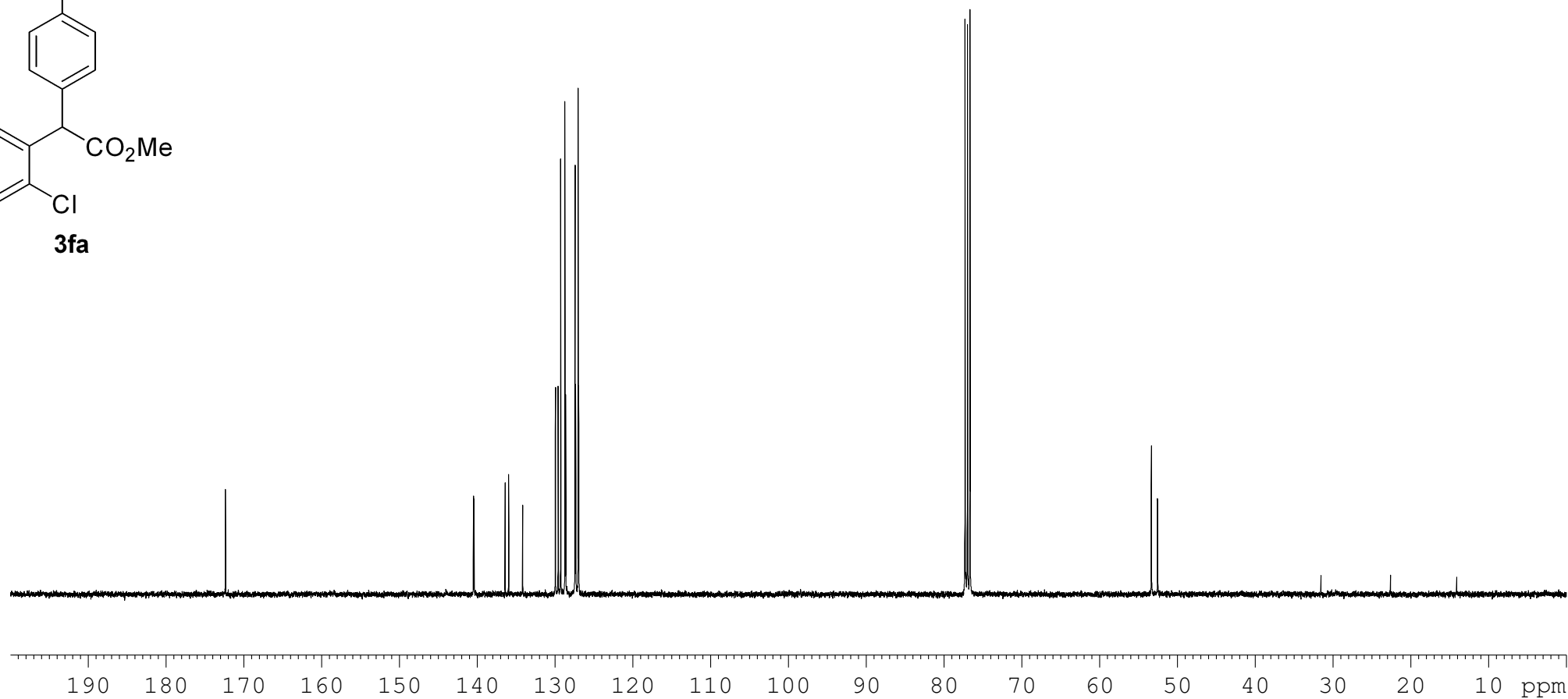
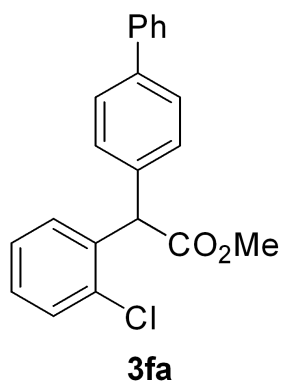
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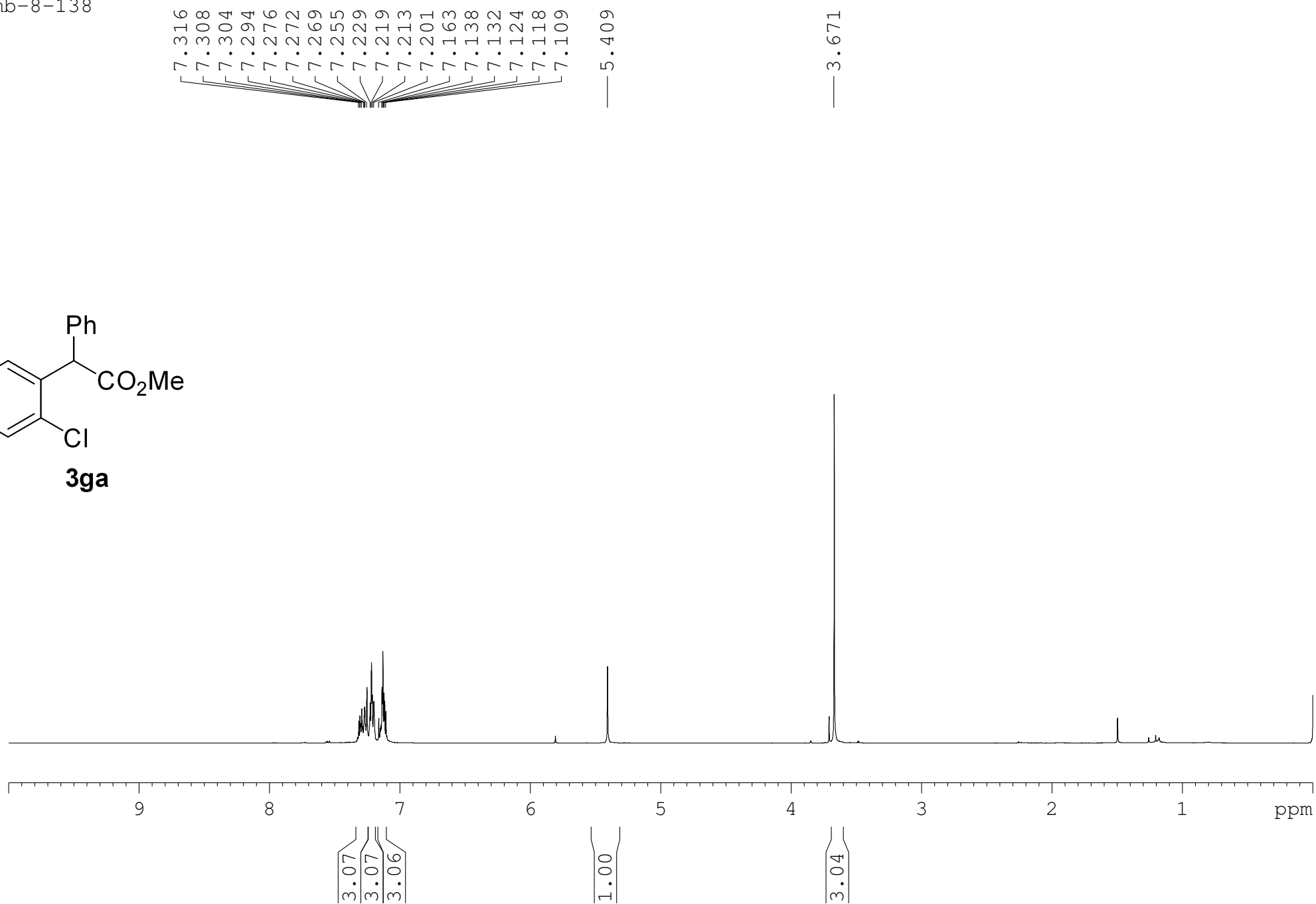
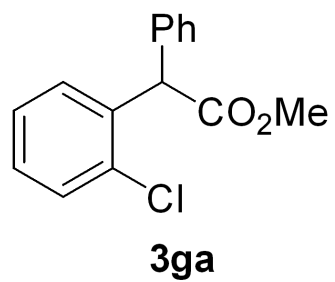
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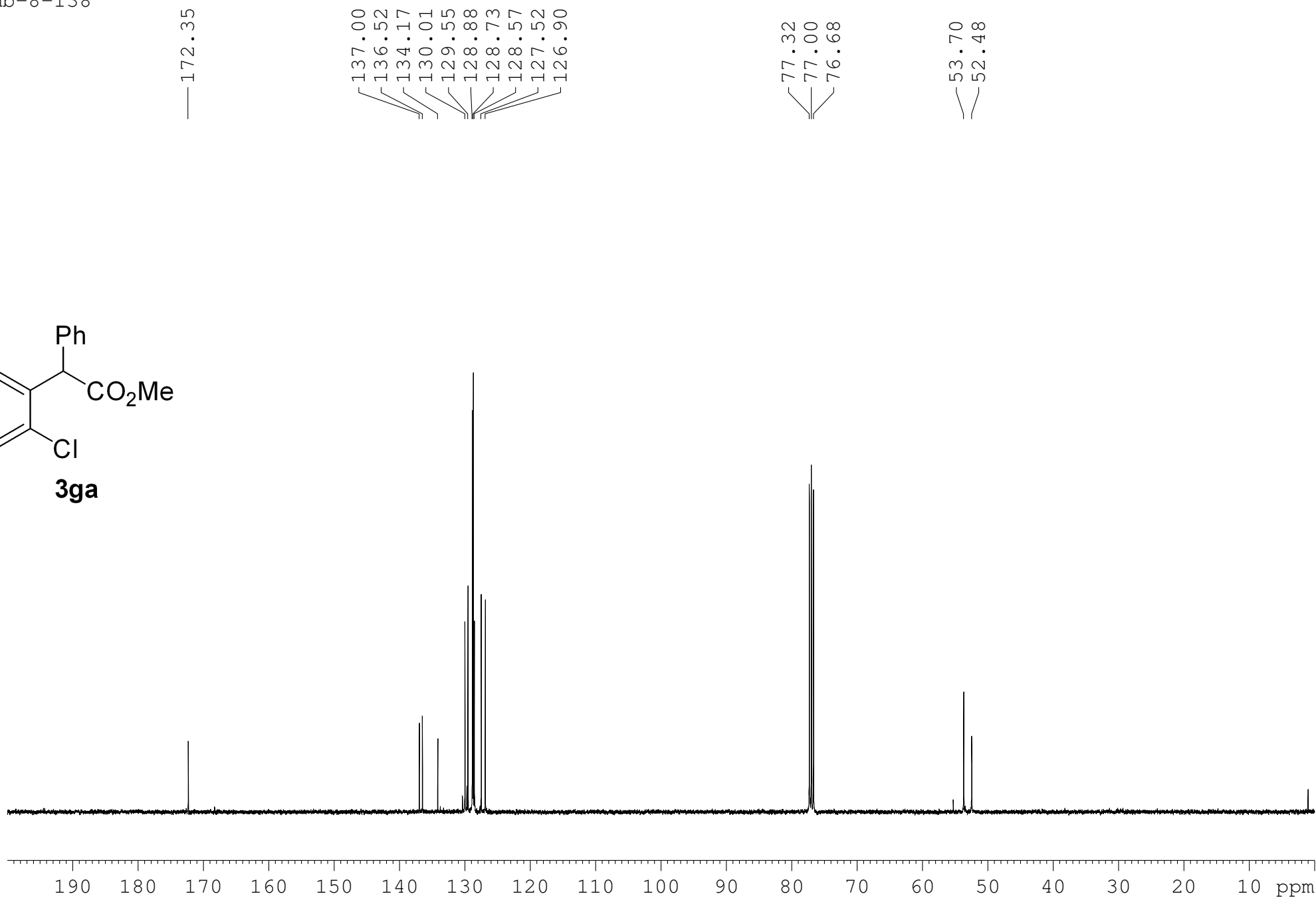
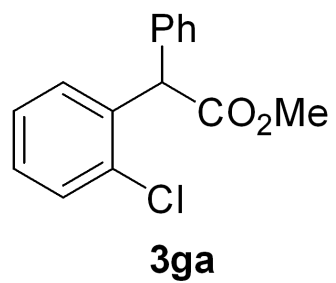
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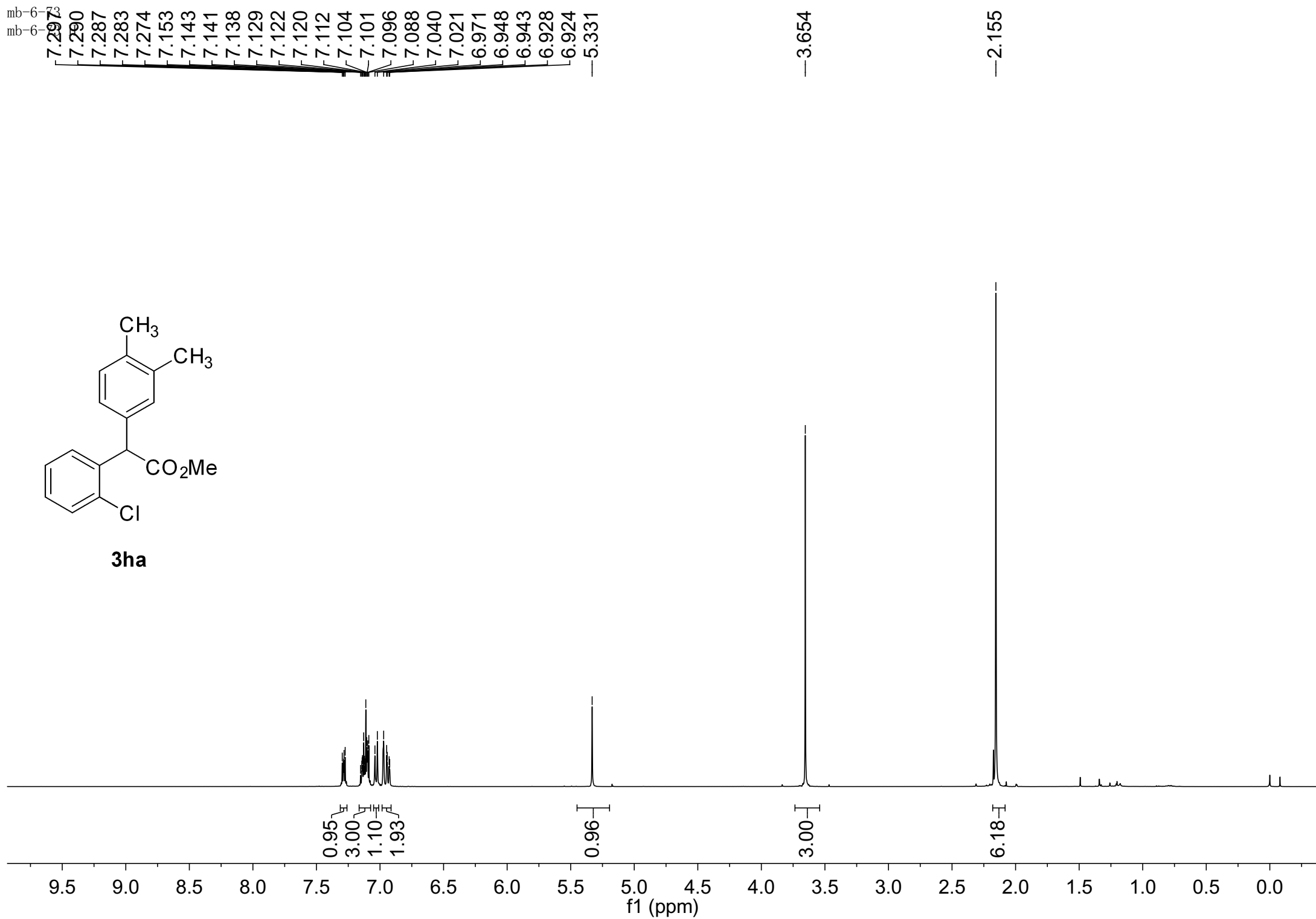


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mb-8-138





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mb-6-73 H

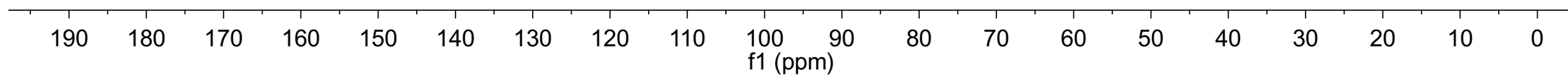
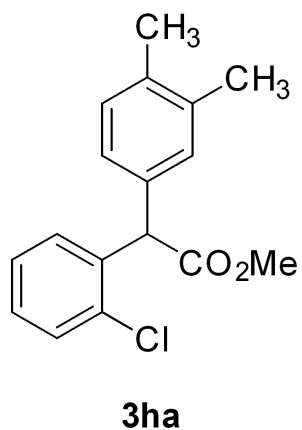
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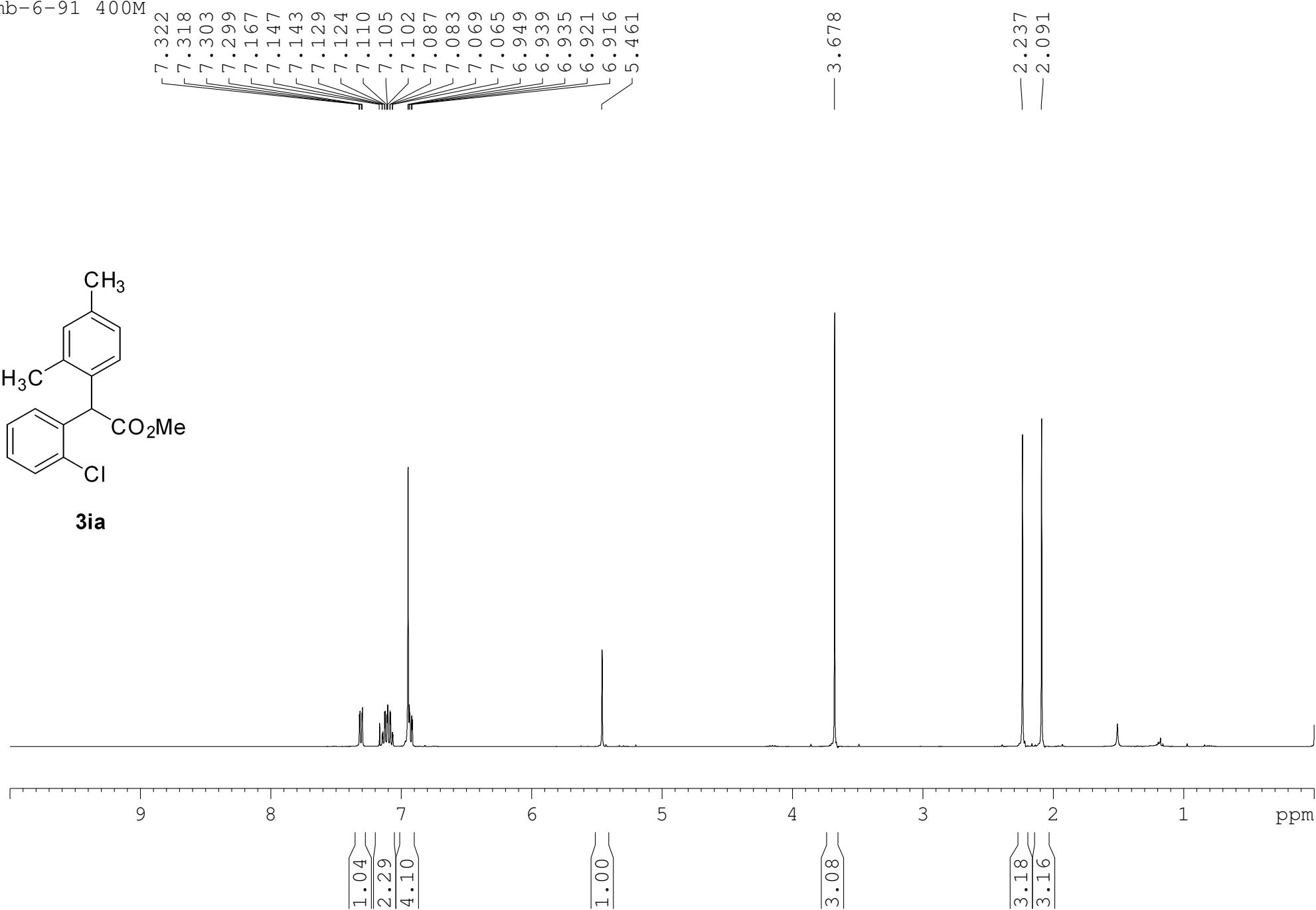
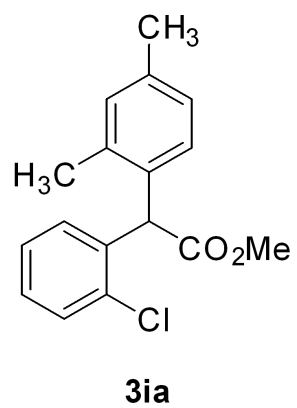
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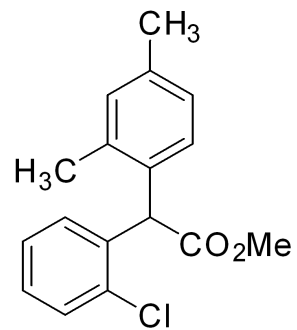
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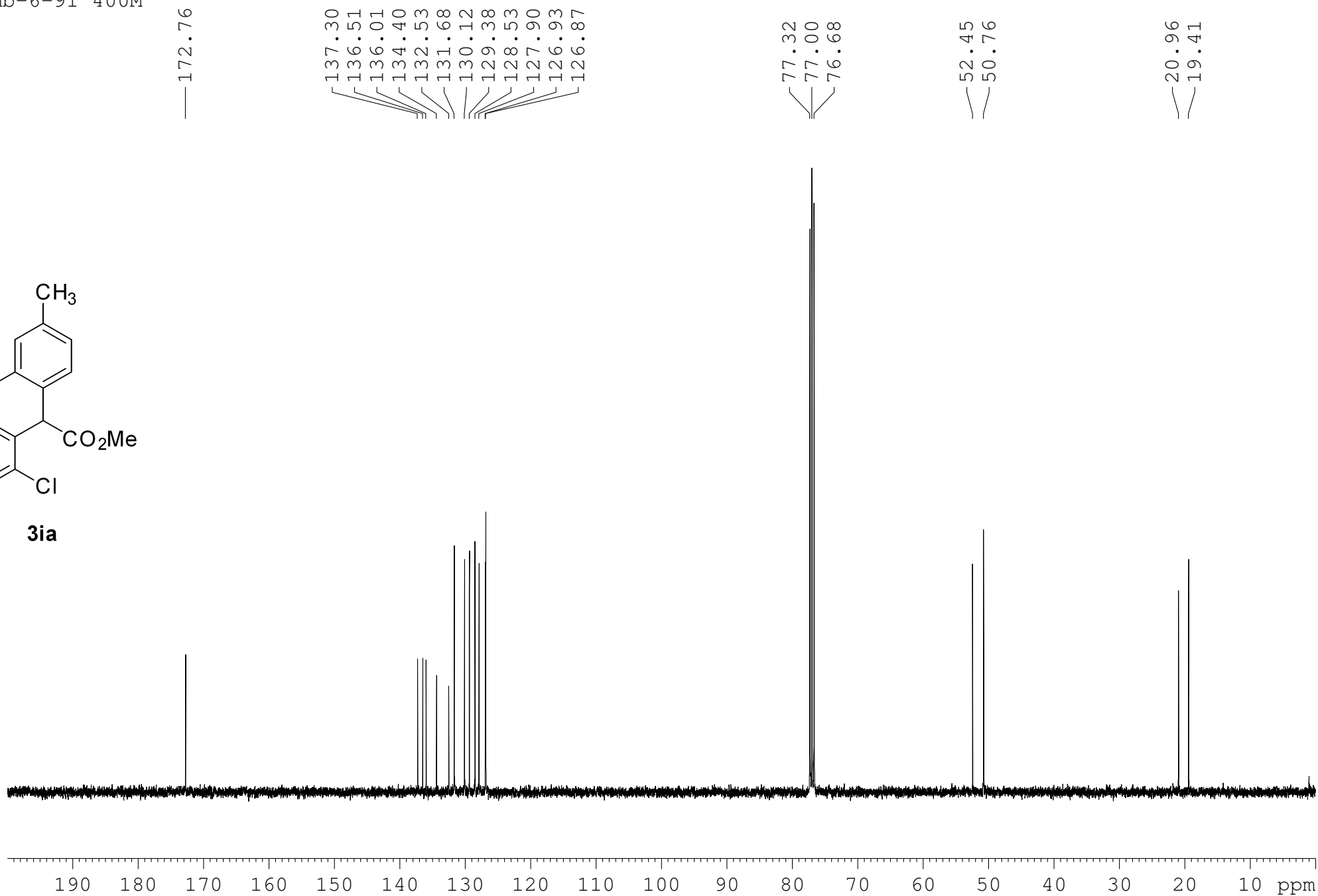
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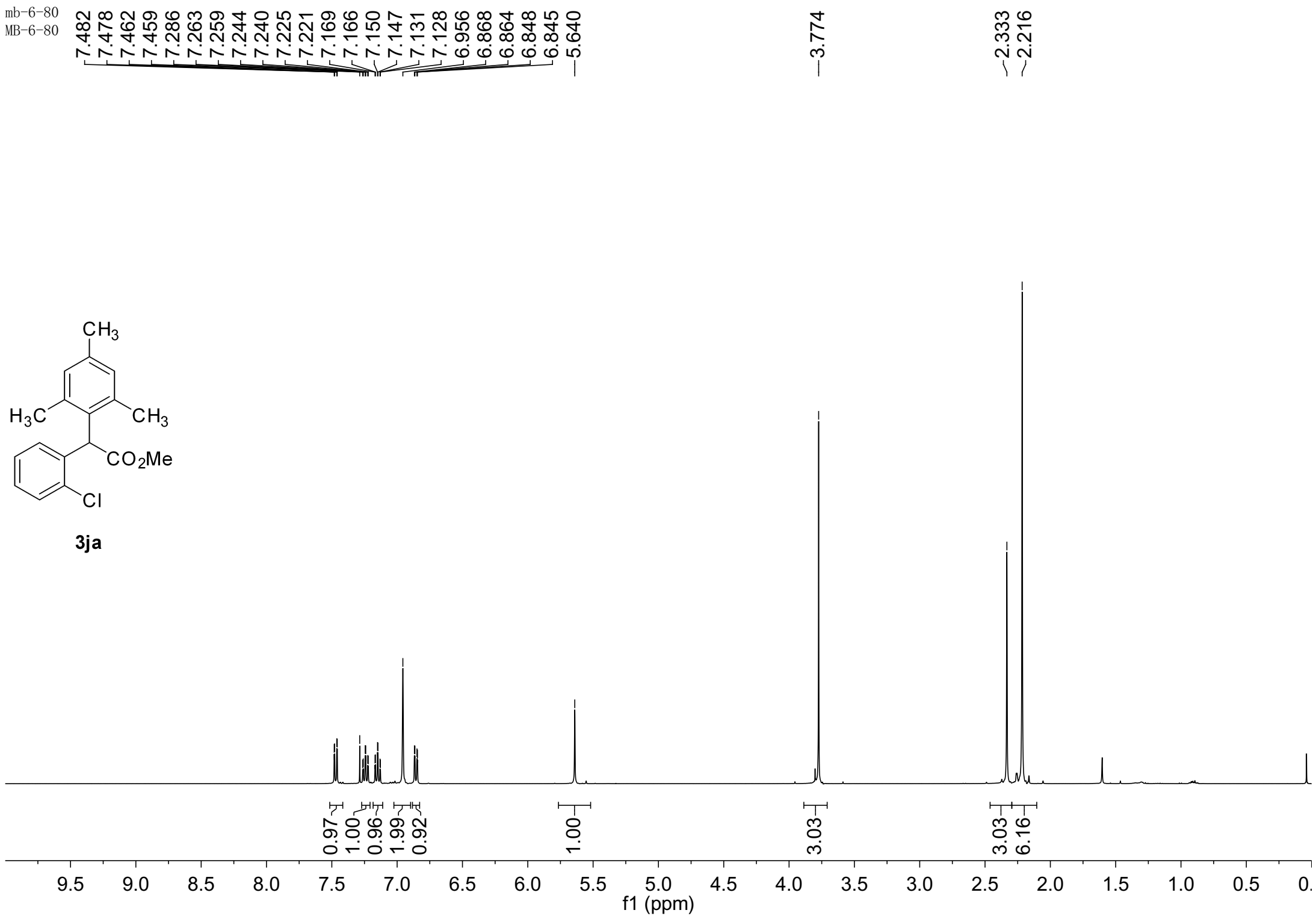
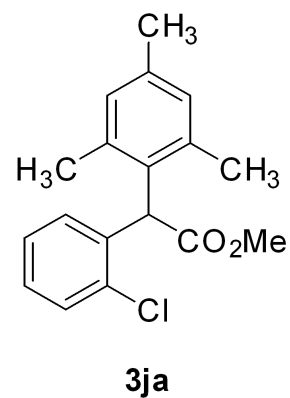
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MB-6-80



mb-6-80
MB-6-80

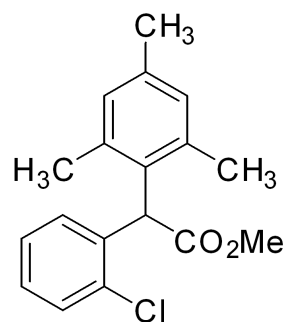
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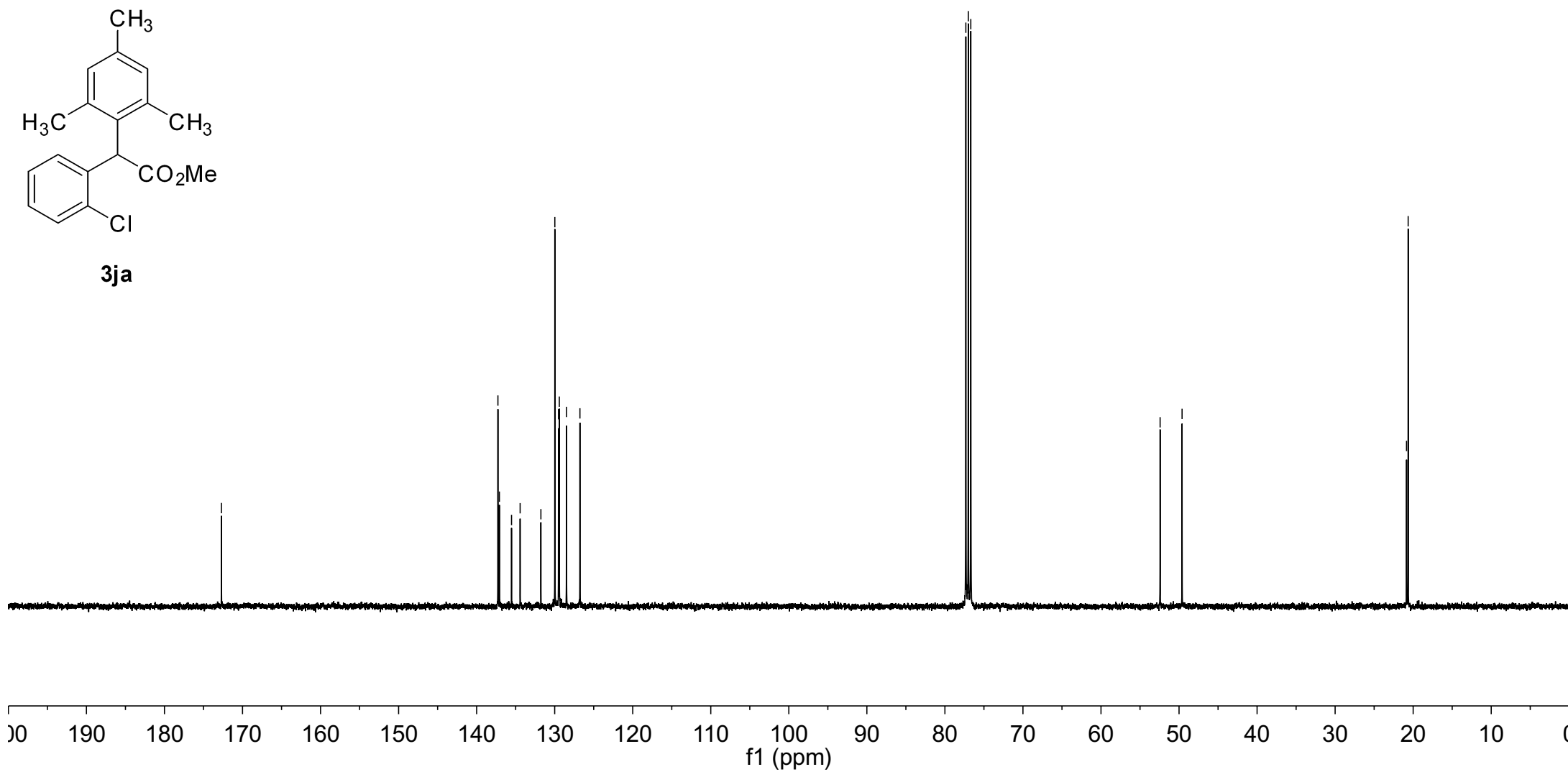
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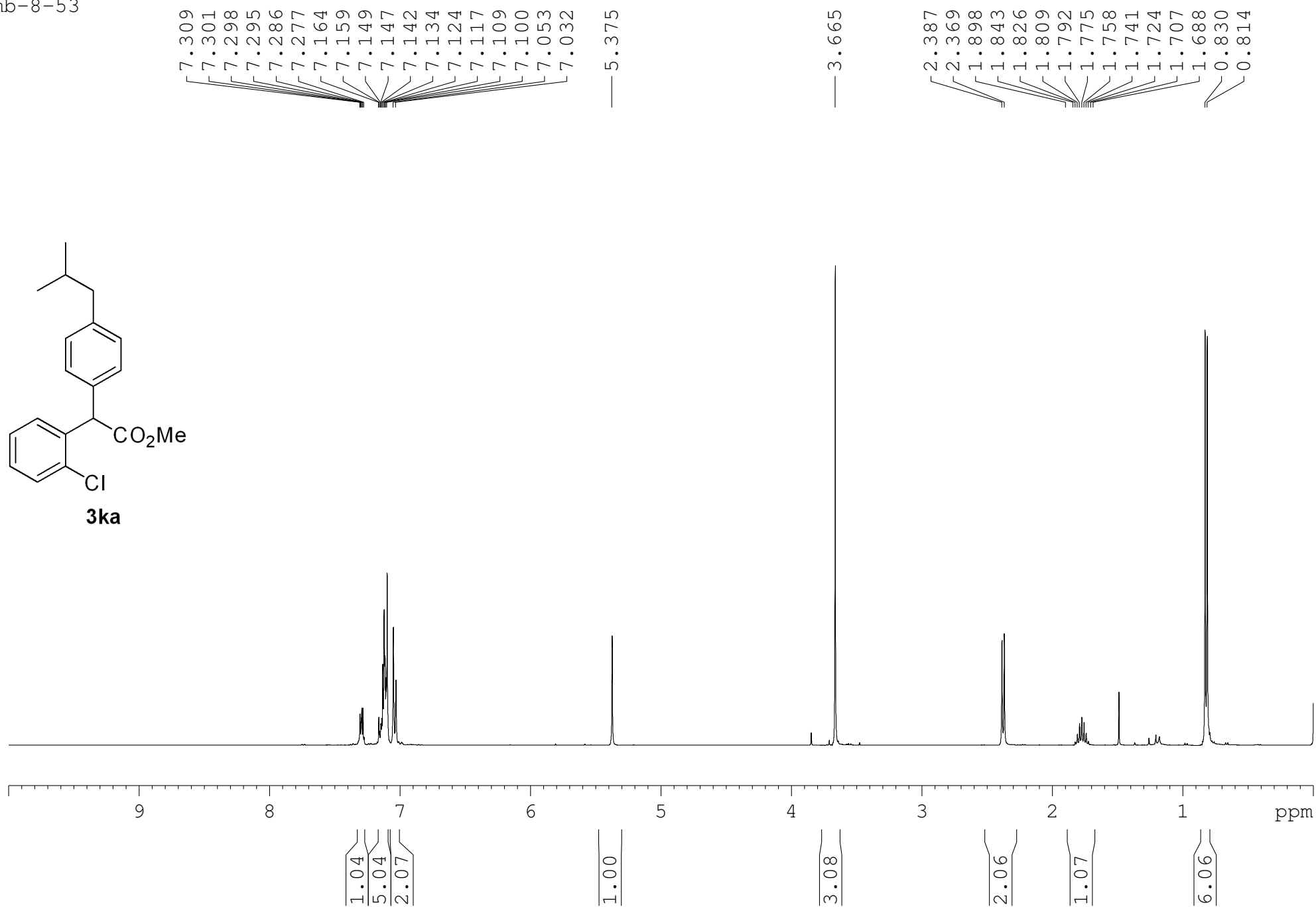
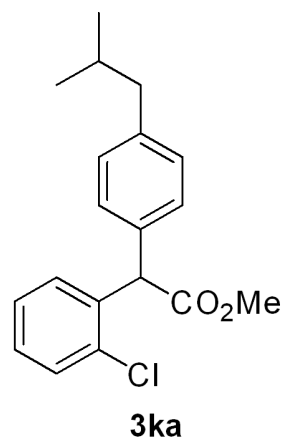
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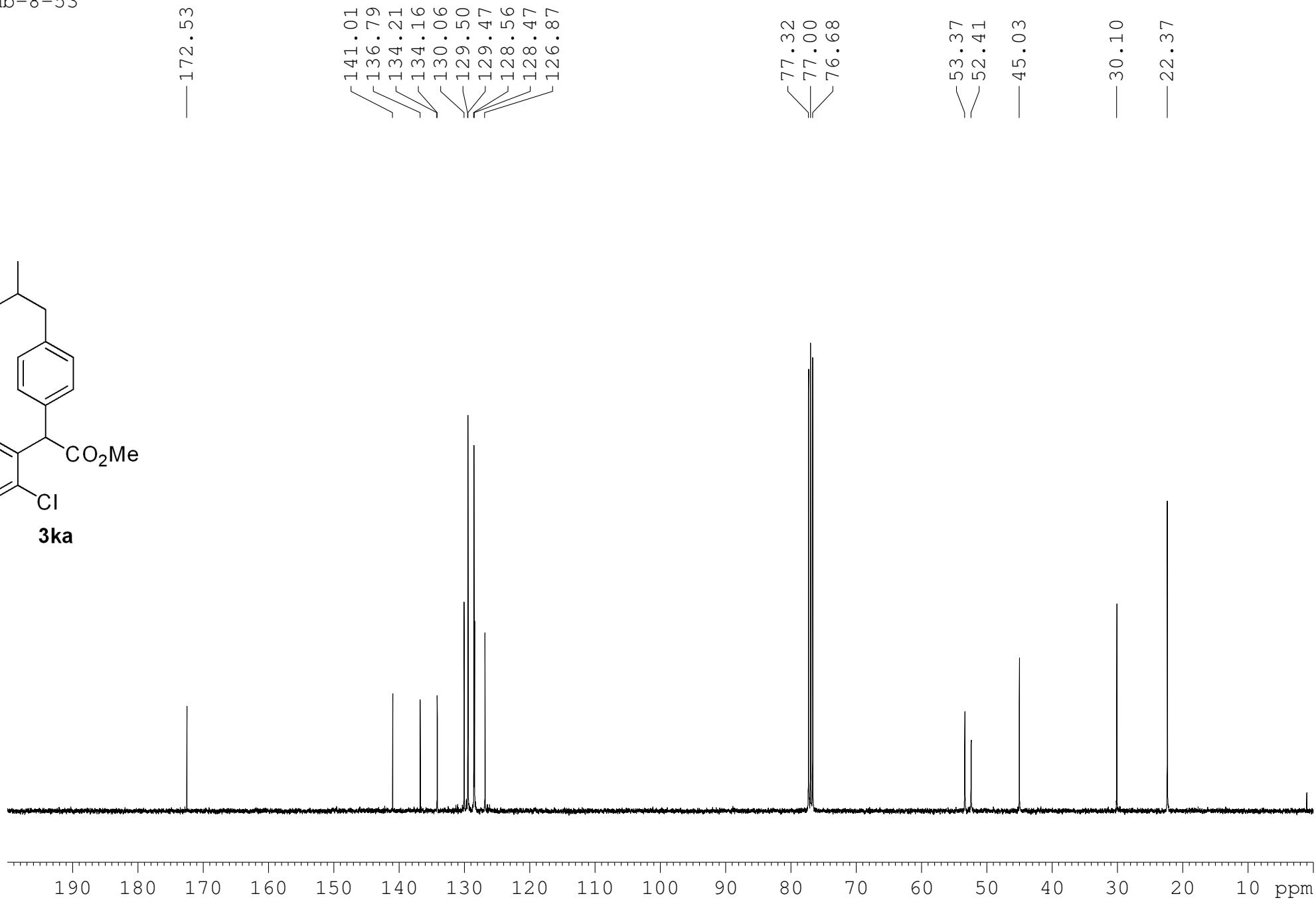
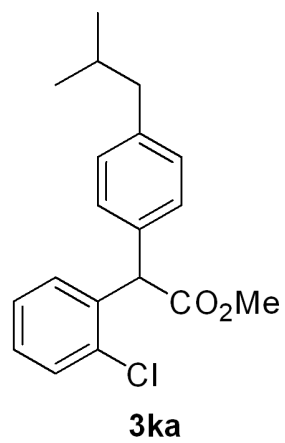
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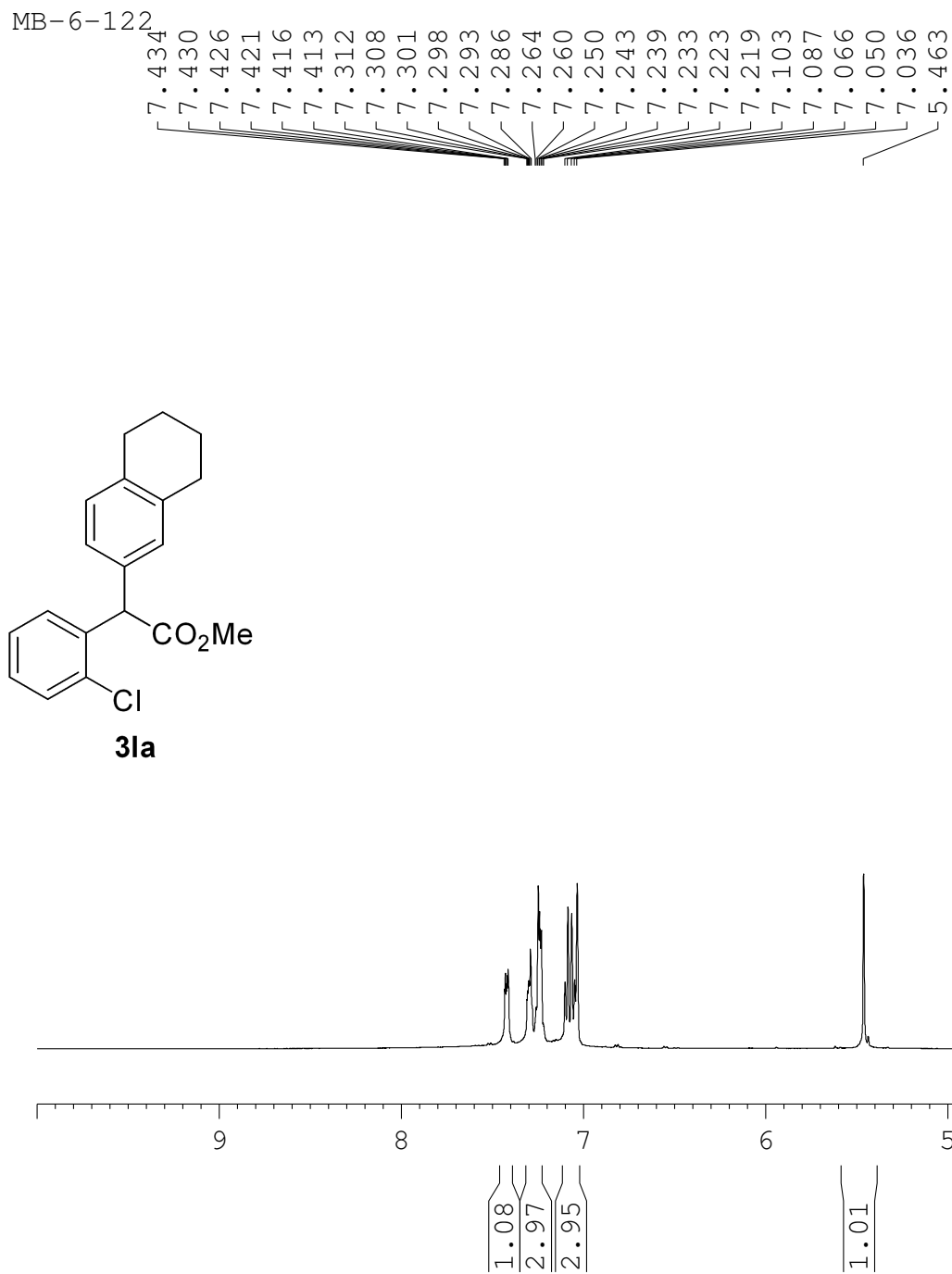
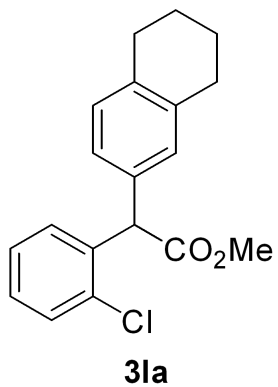


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mb-8-53



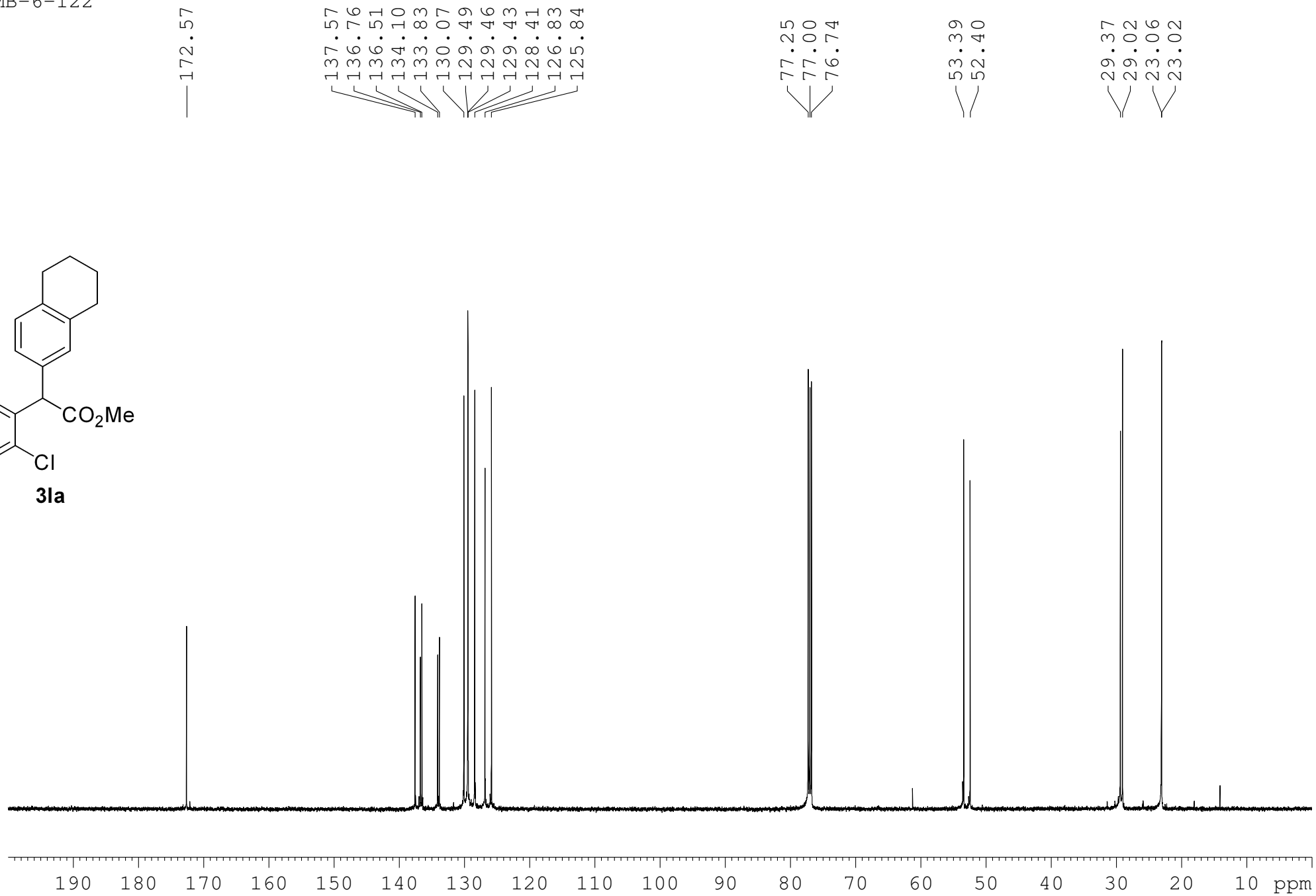
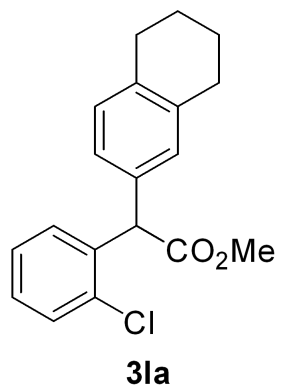


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— 2.793

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MB-6-122



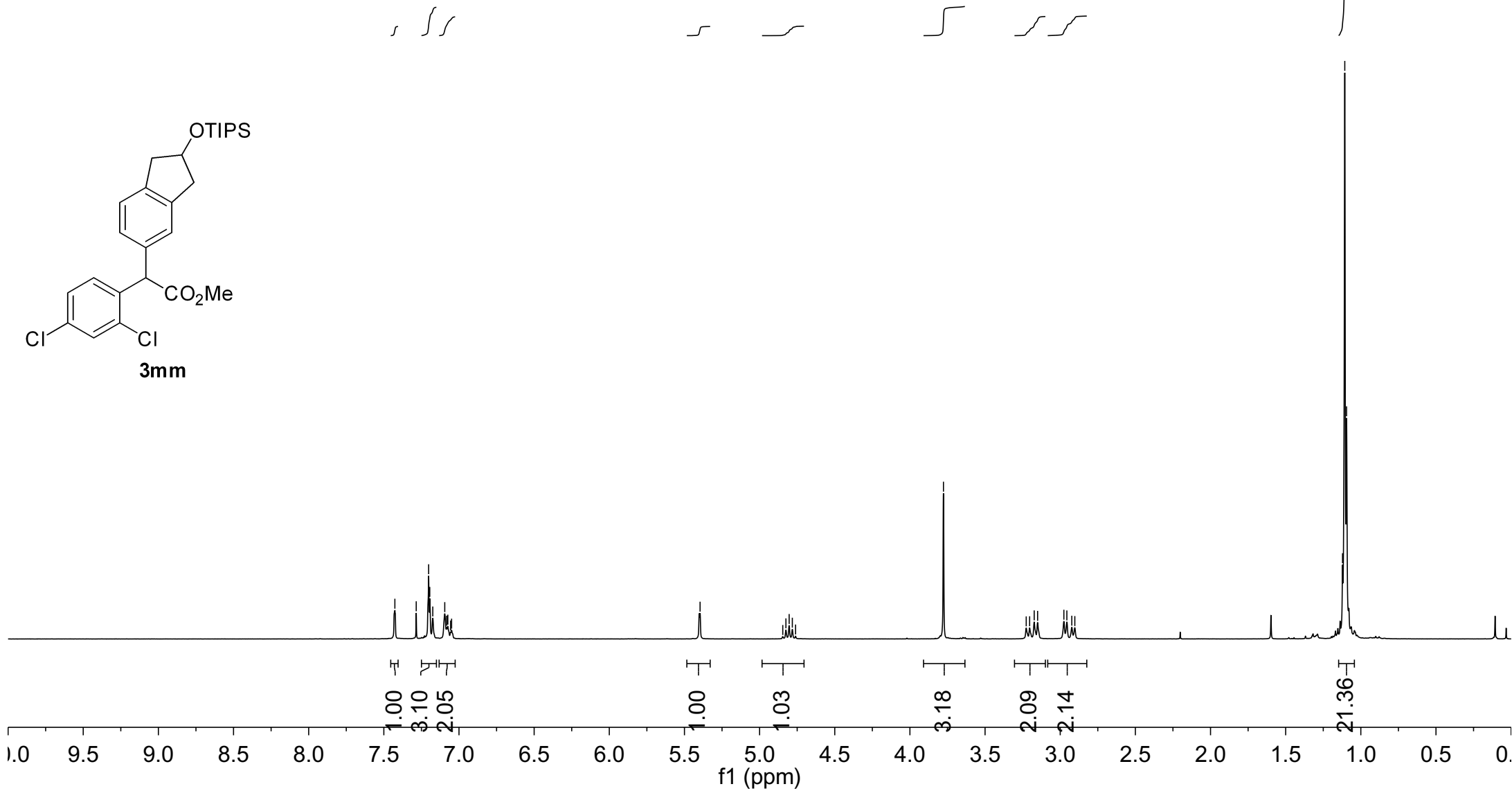
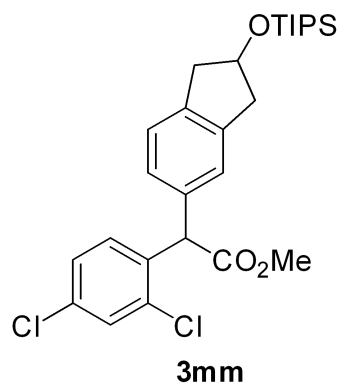
MB-9-85 (2)
MB-9-85 (2)

7.427
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7.202
7.194
7.174
7.095
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7.056
7.049

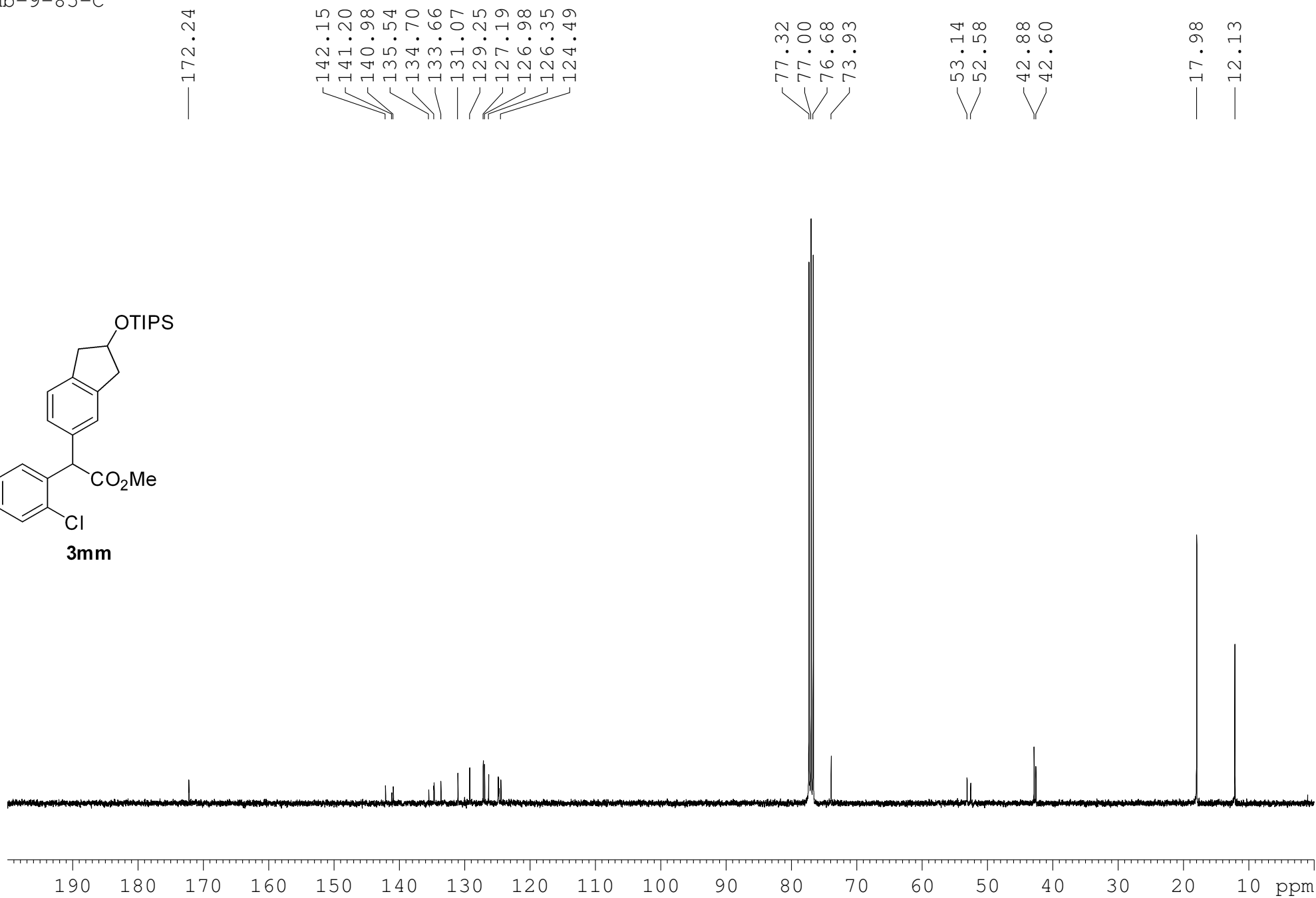
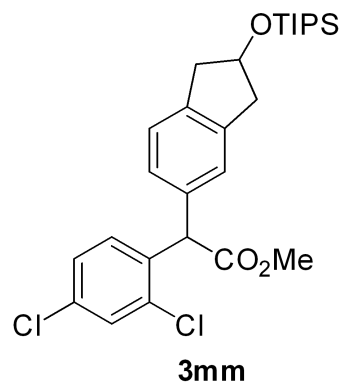
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4.825
4.803
4.782
4.761

3.777
3.226
3.203
3.173
3.150
2.976
2.956
2.923
2.903

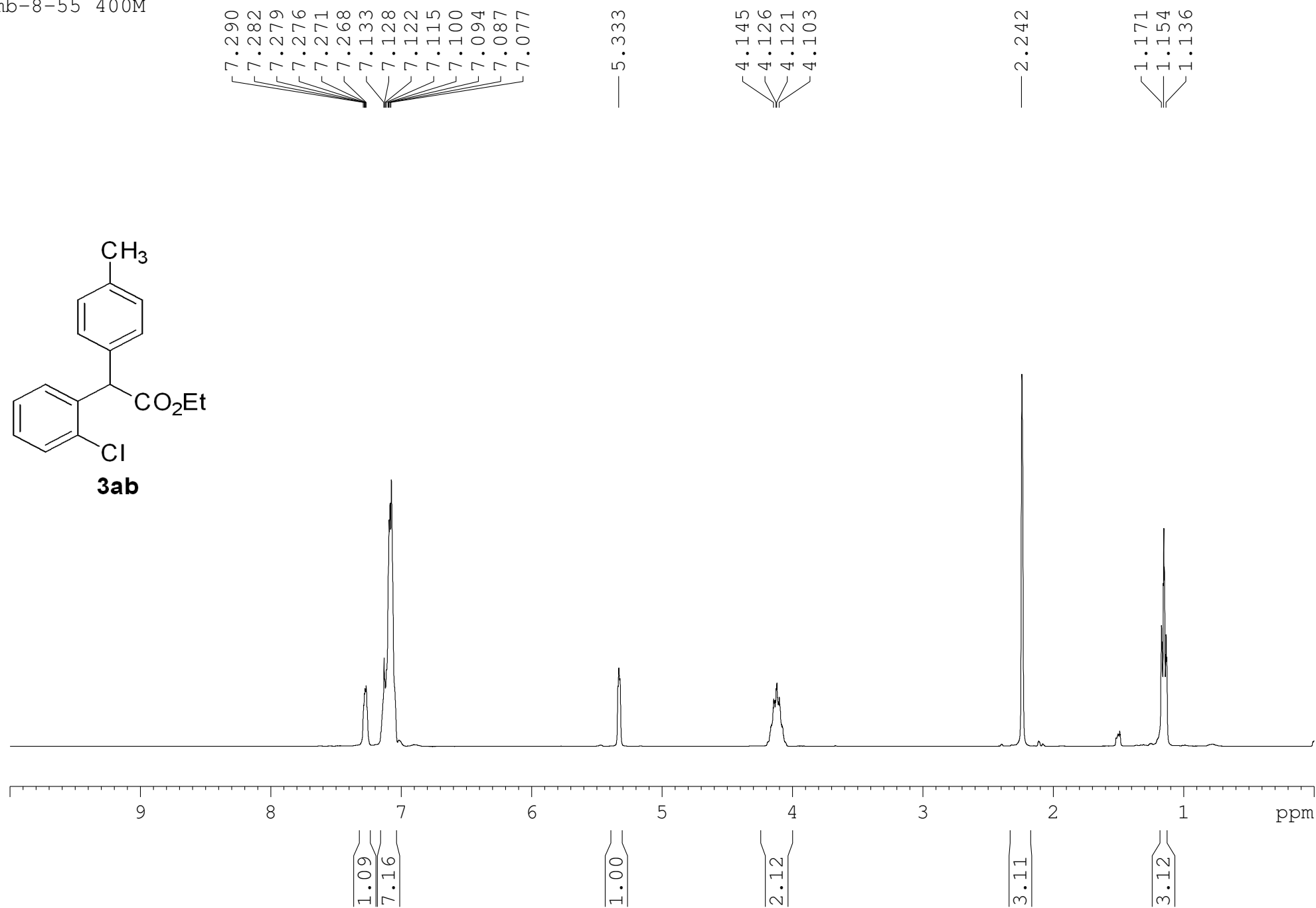
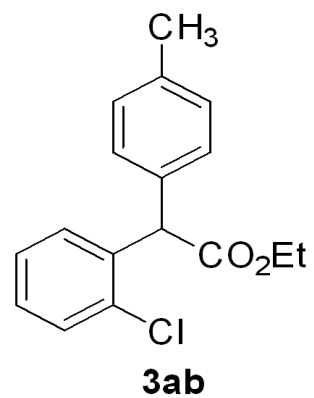
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1.107
1.095



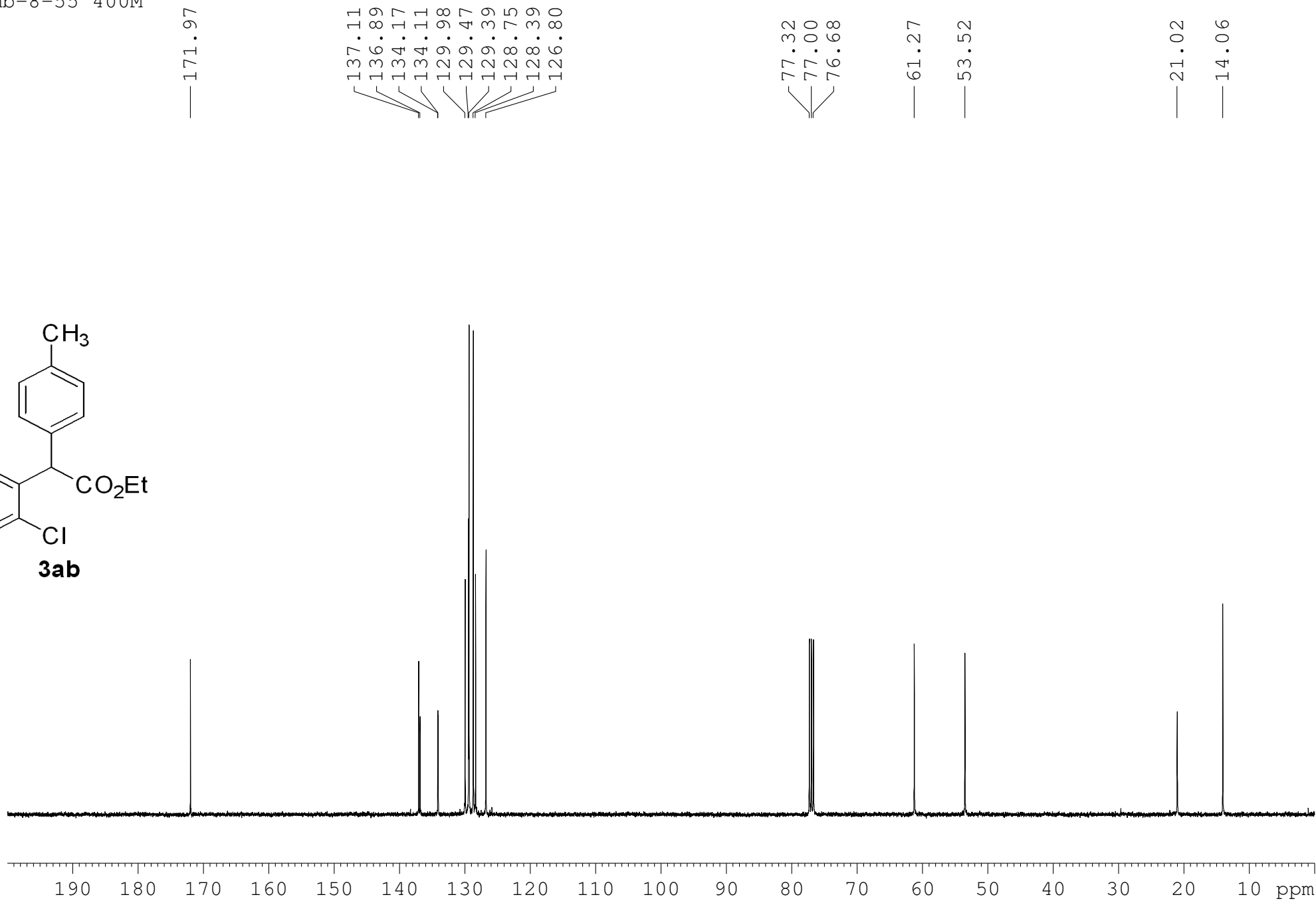
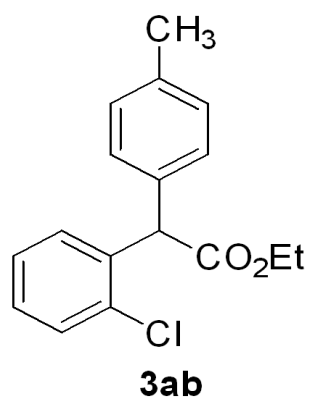
mb-9-85-C



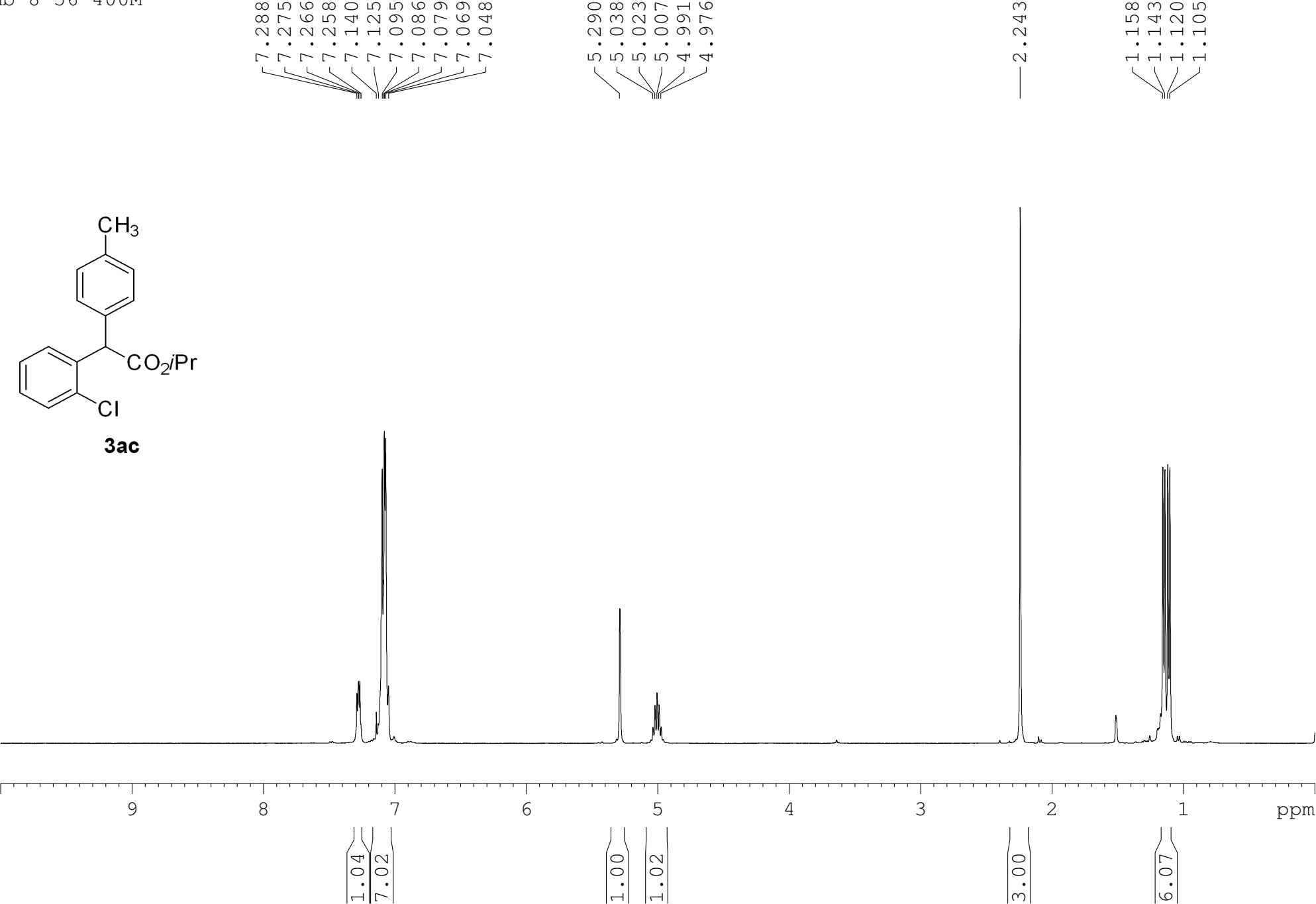
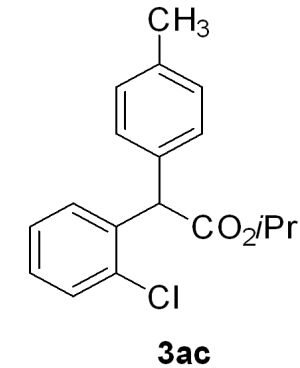
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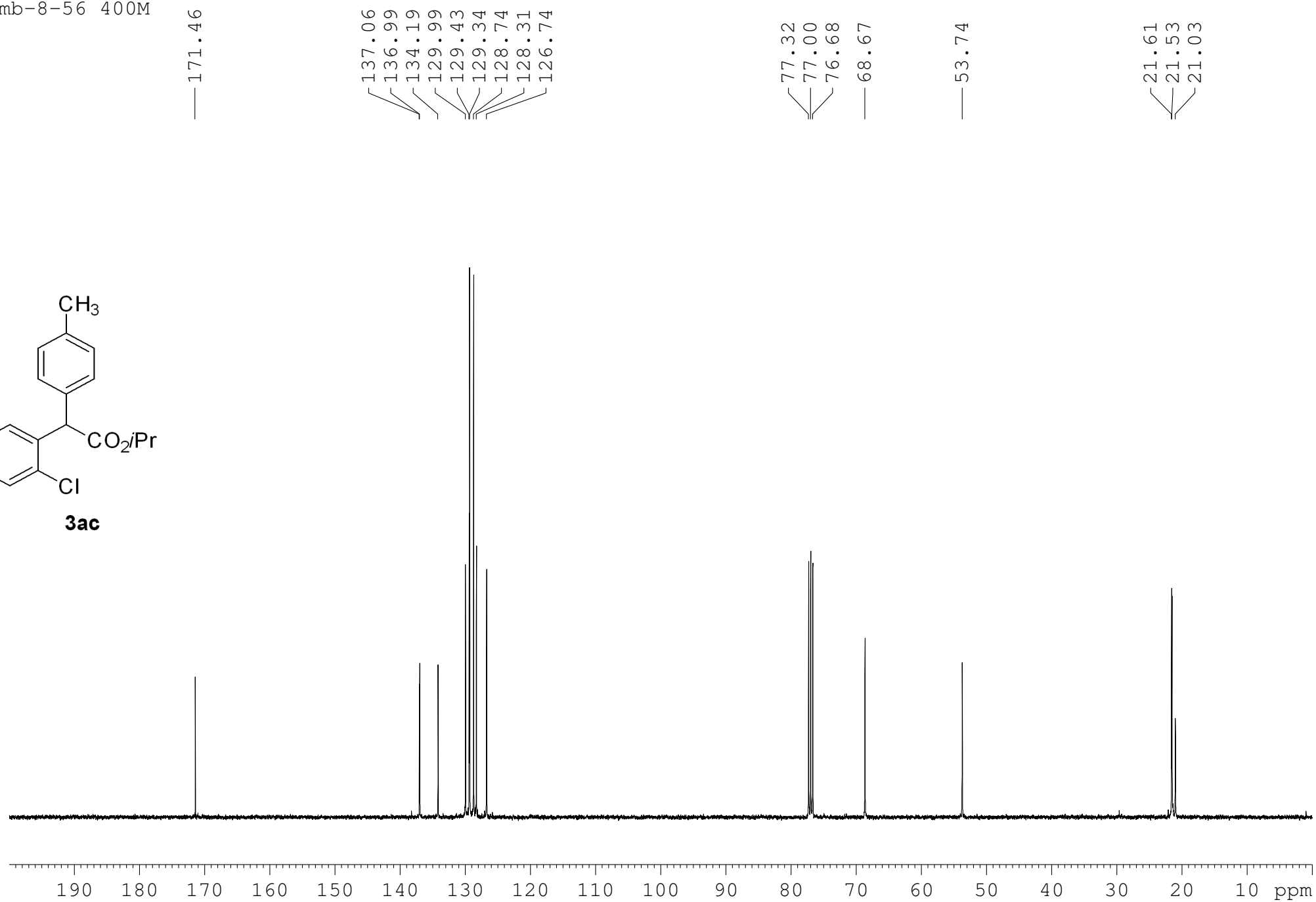
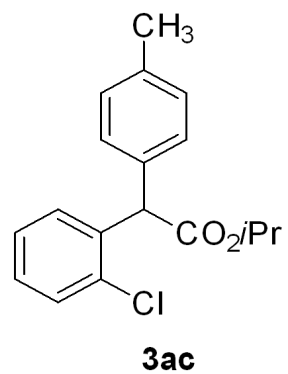
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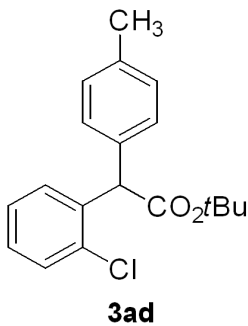
mb-8-56 400M



mb-8-56 400M



mb-8-57 400M

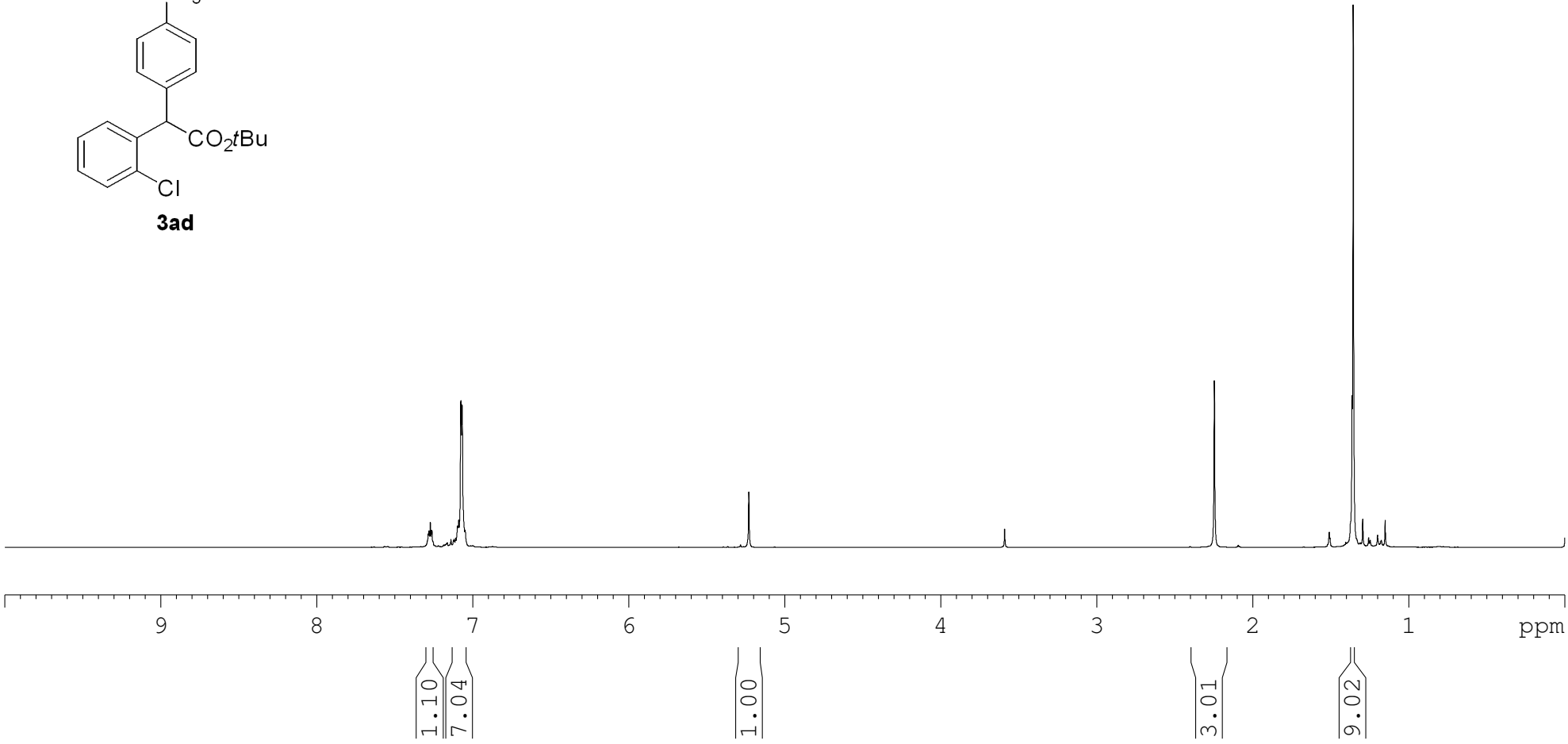


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7.263
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7.092
7.078
7.071
7.069
7.050

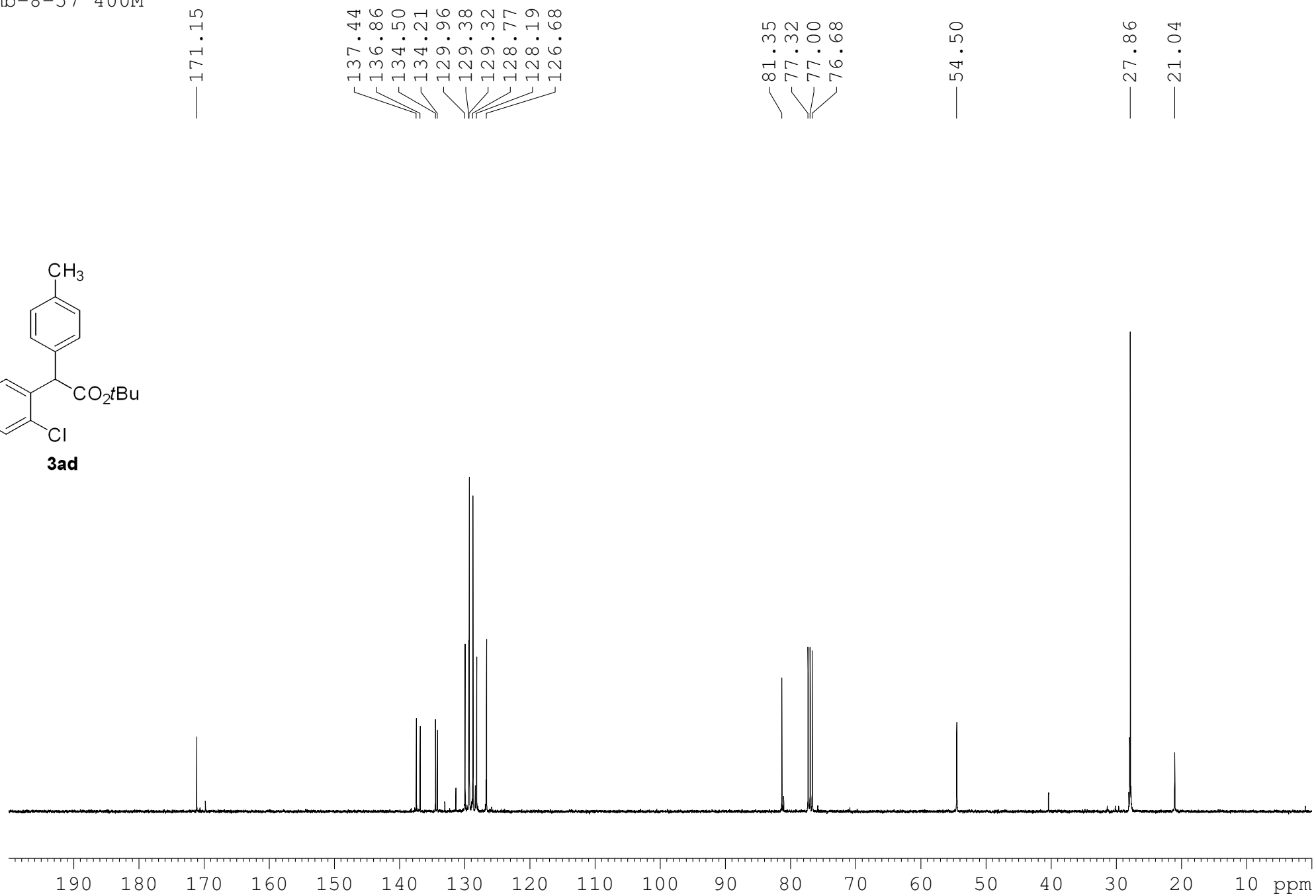
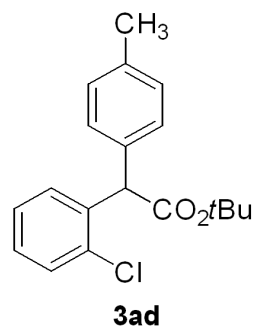
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2.247

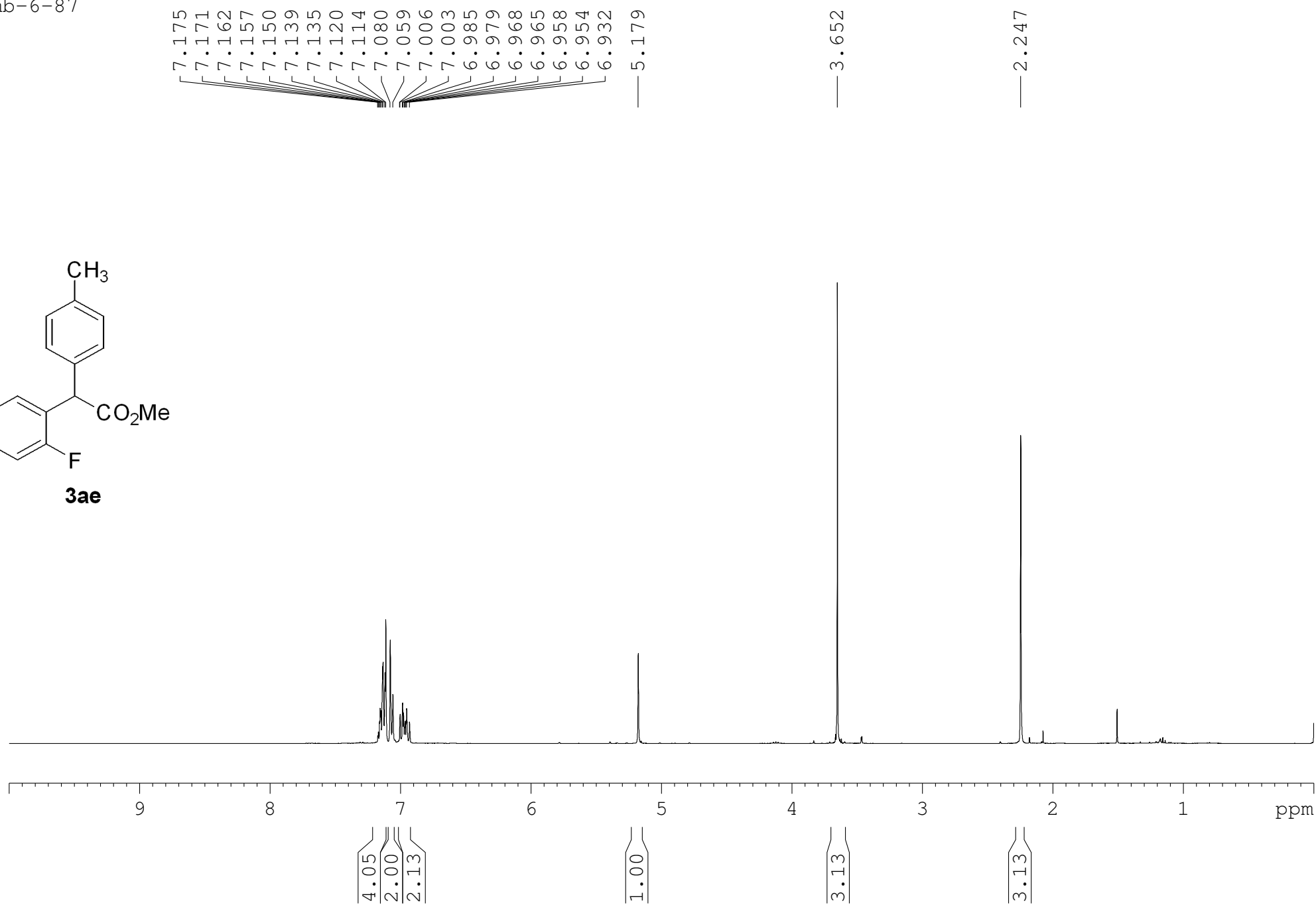
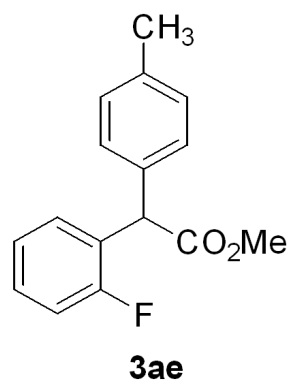
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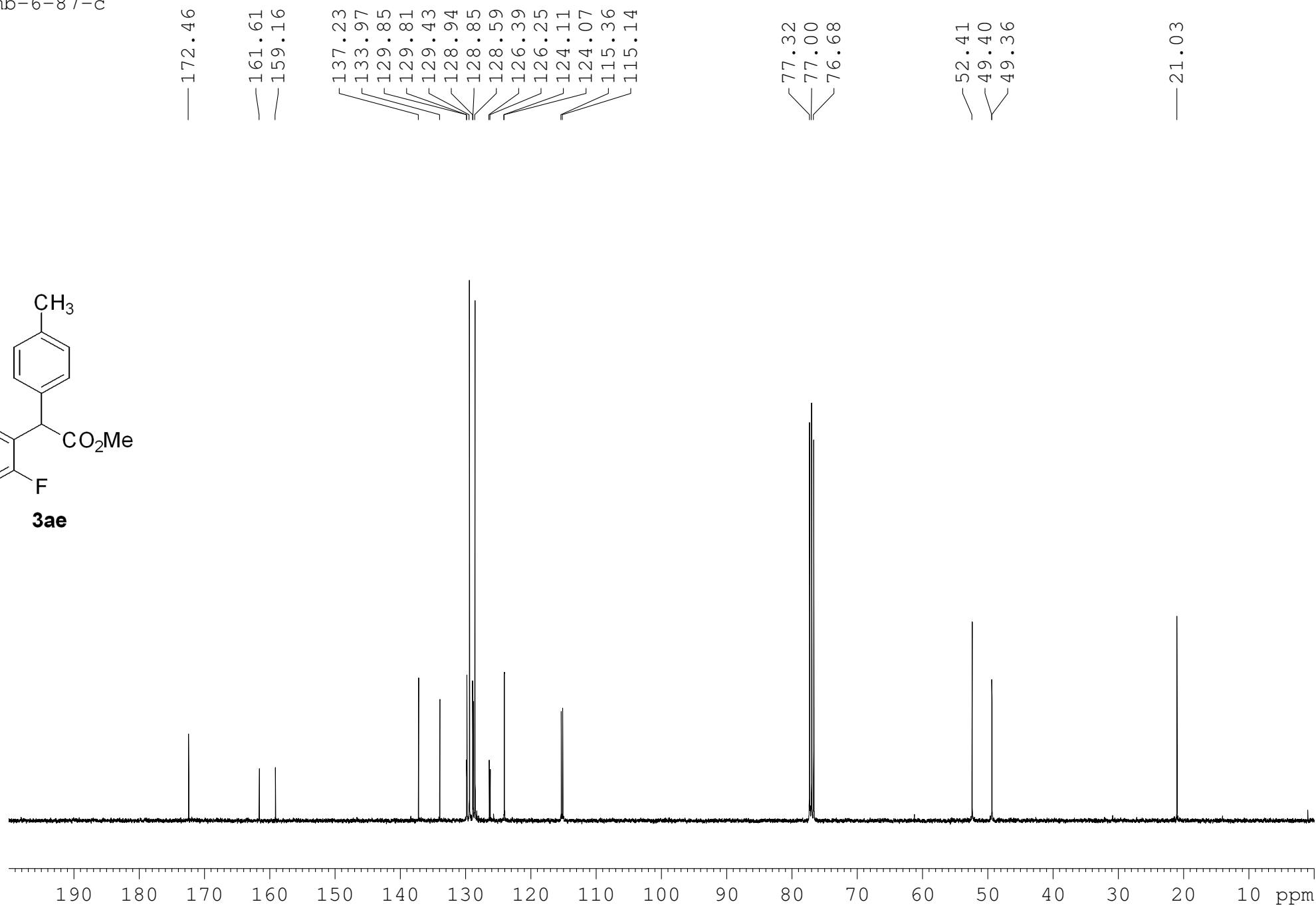
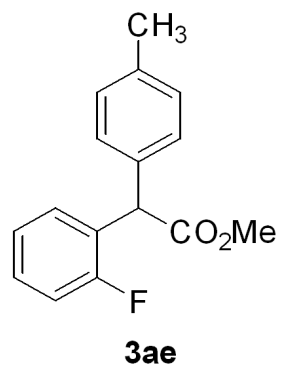
mb-8-57 400M



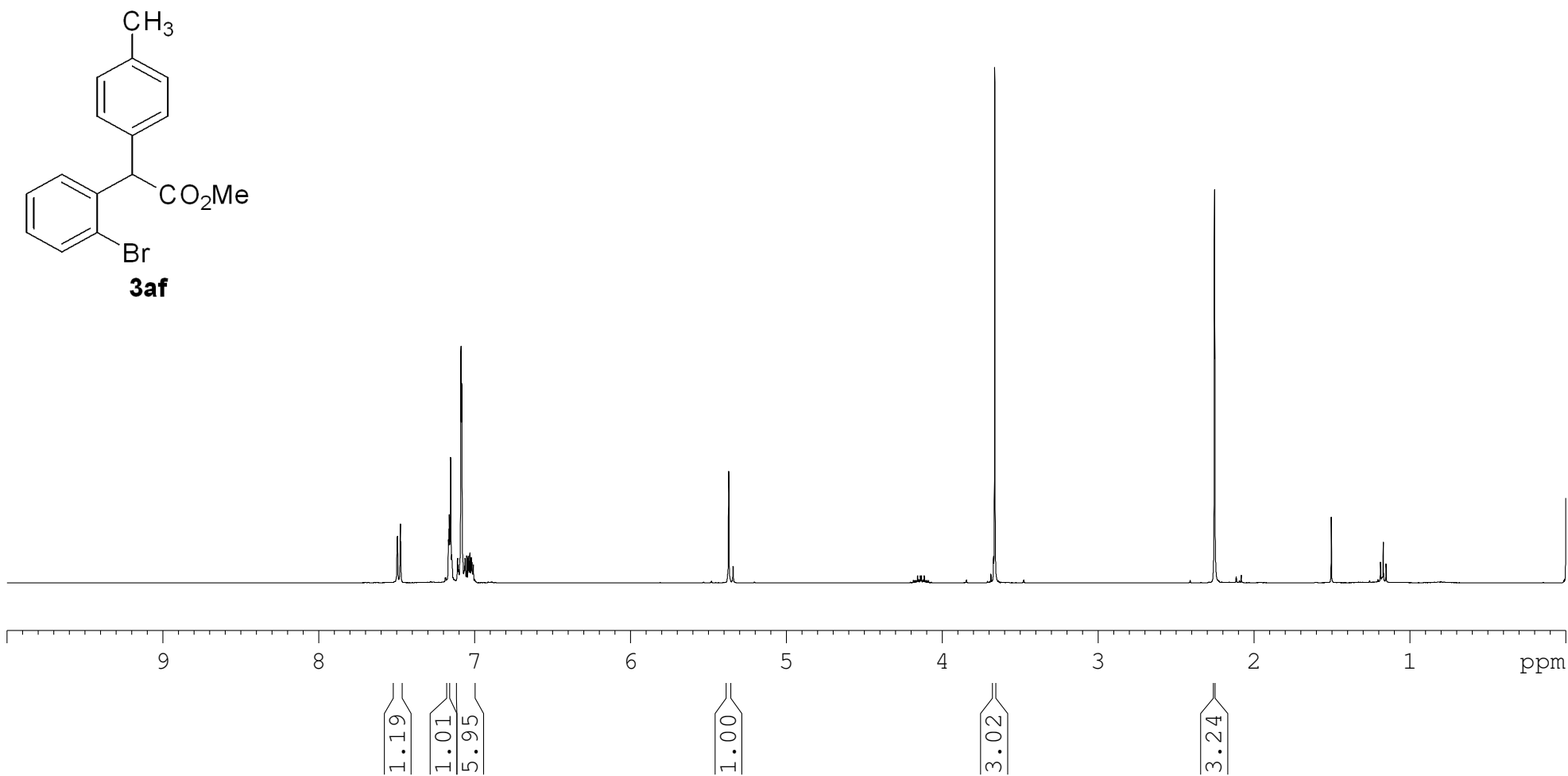
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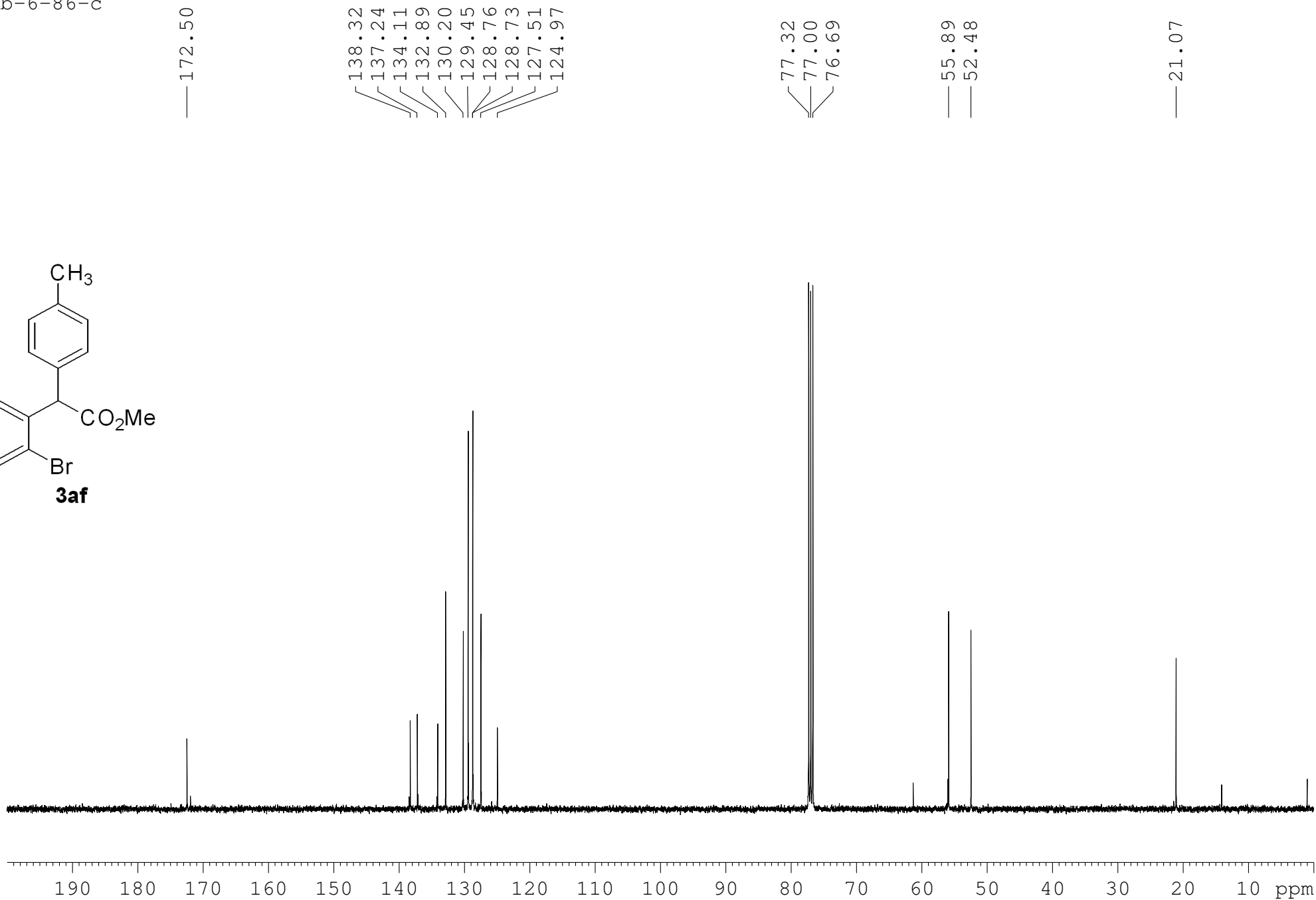
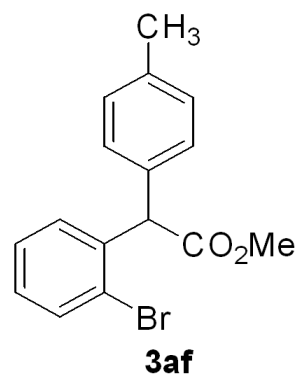
mb-6-87-c



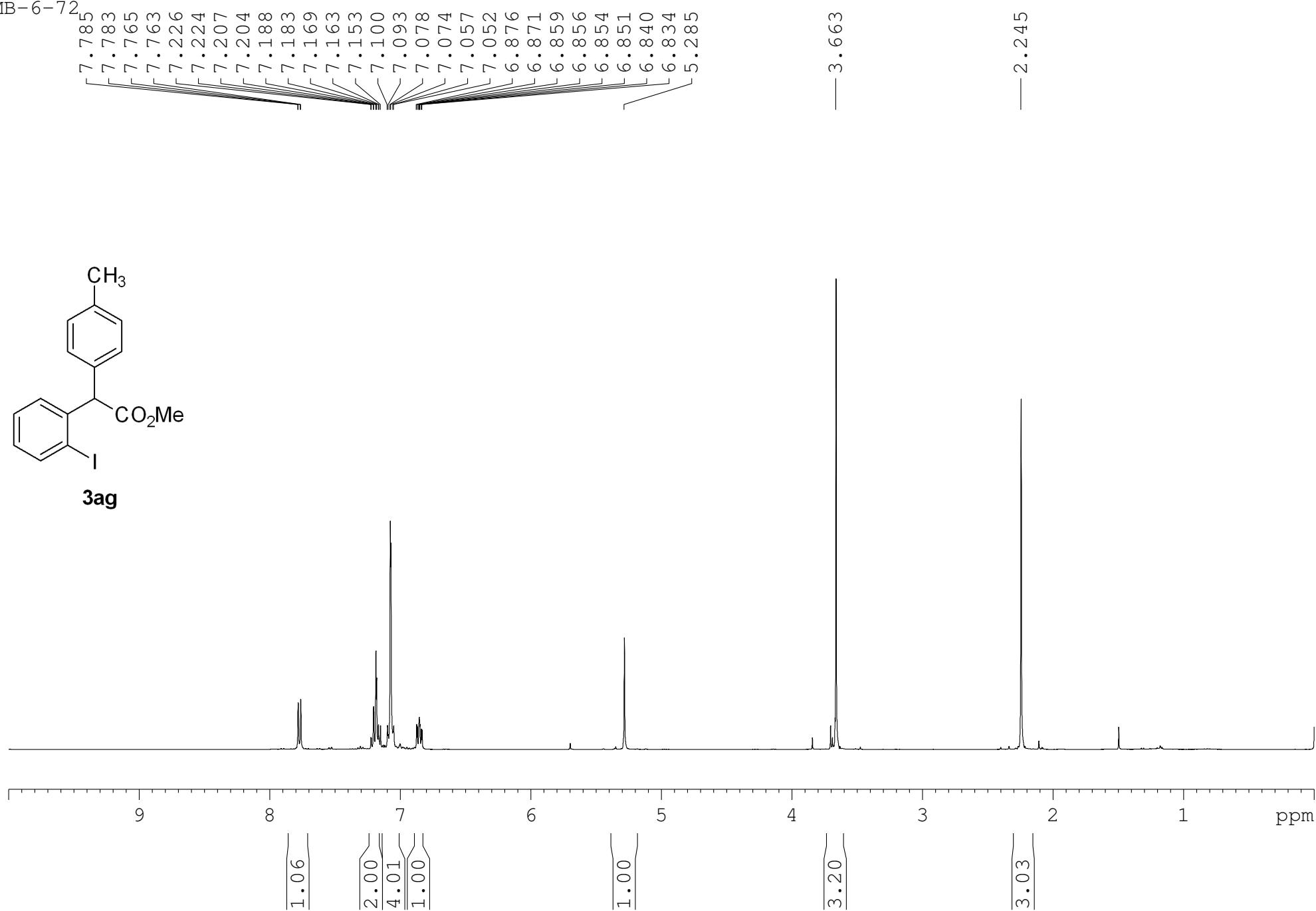
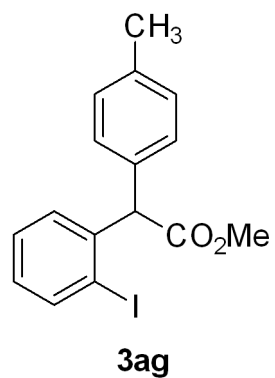
mb-6-85 H



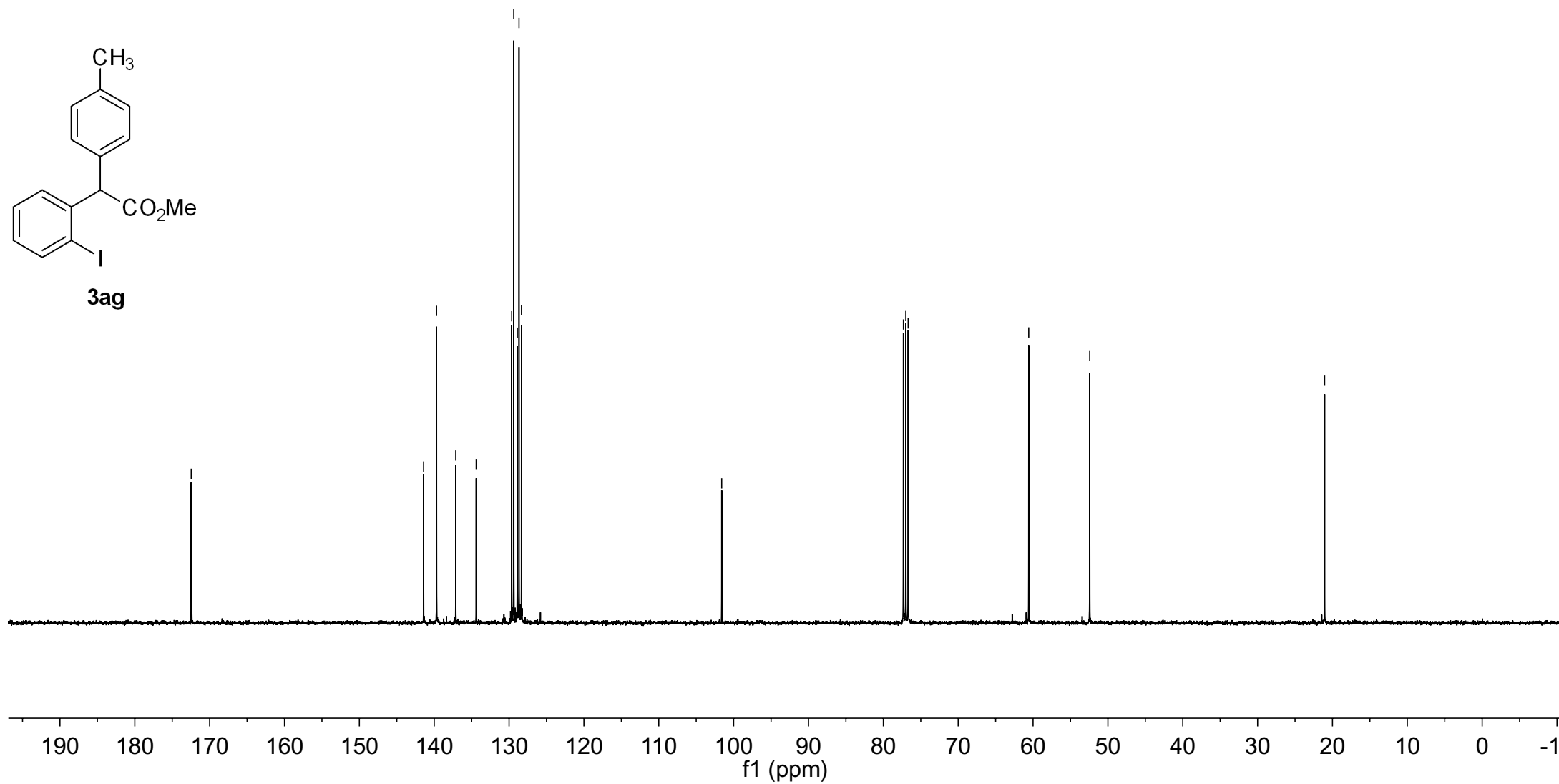
mb-6-86-c



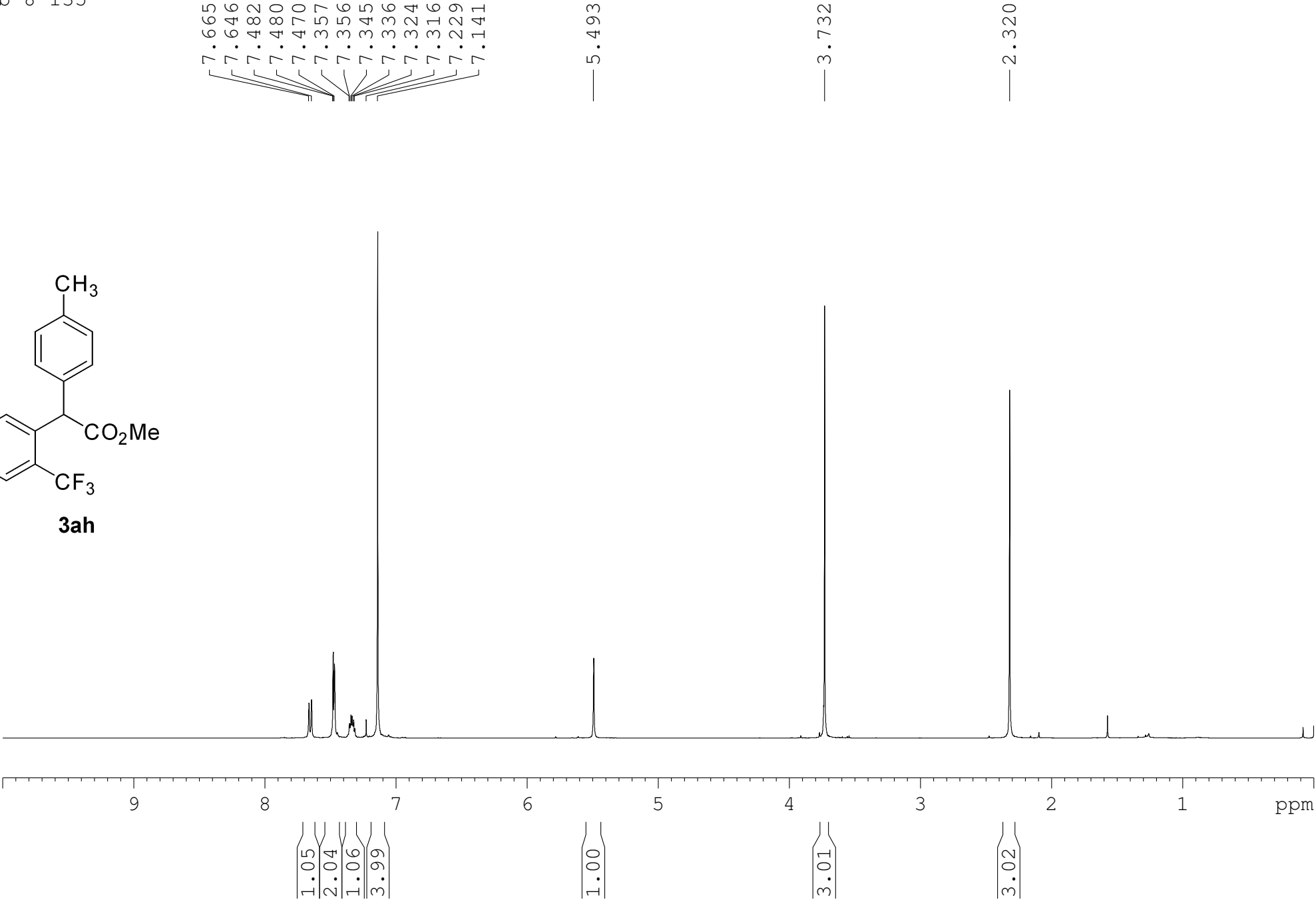
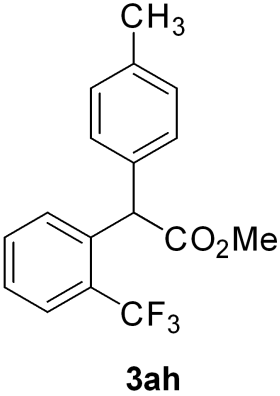
MB-6-72



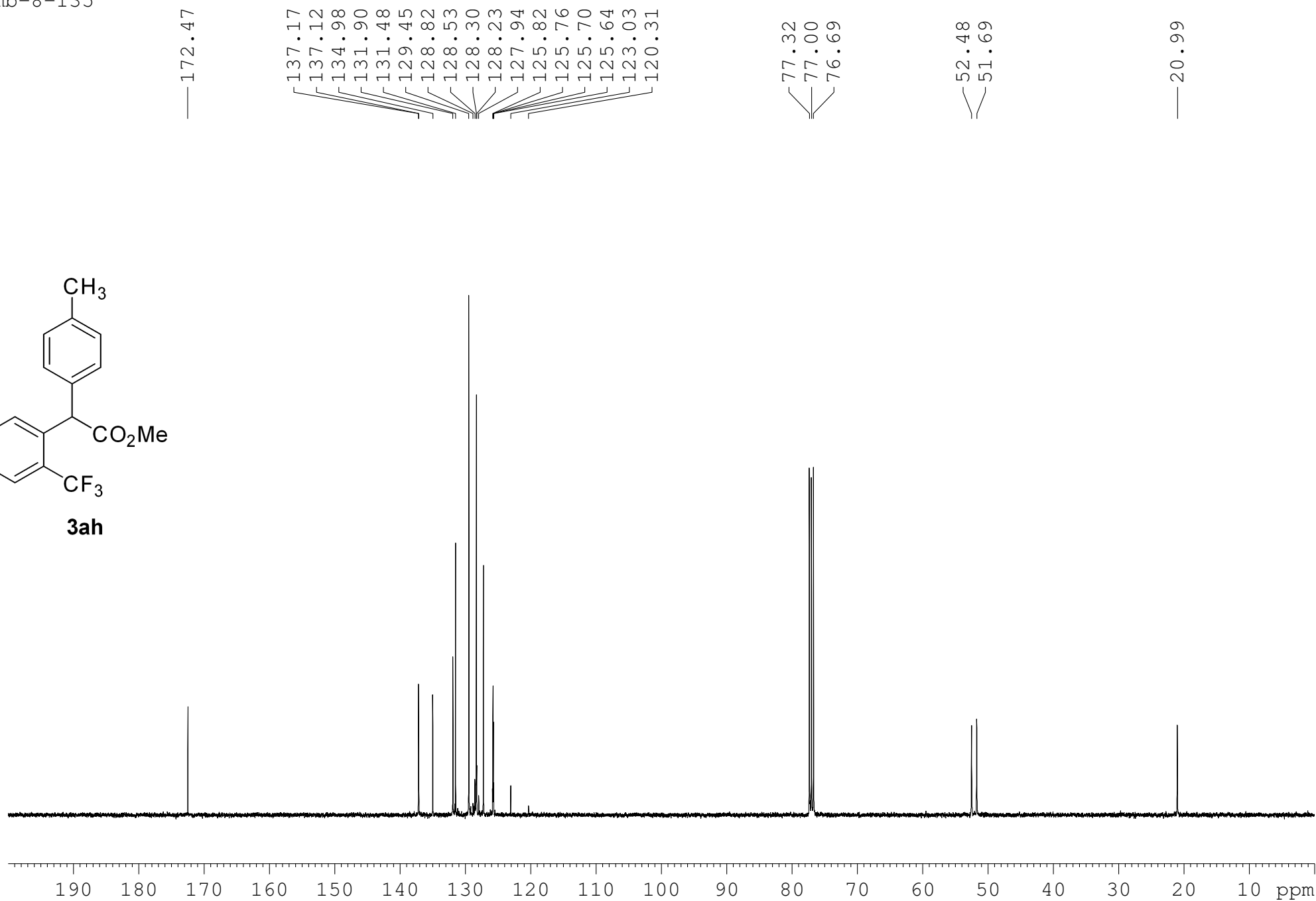
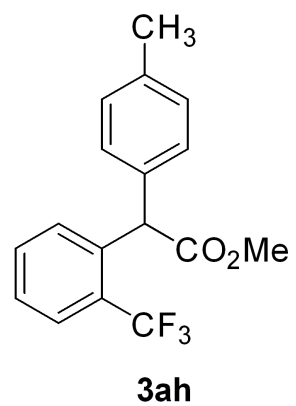
MB-6-72
MB-6-72



mb-8-135

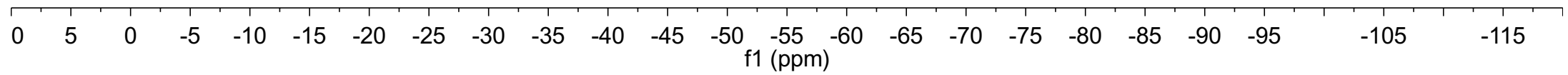
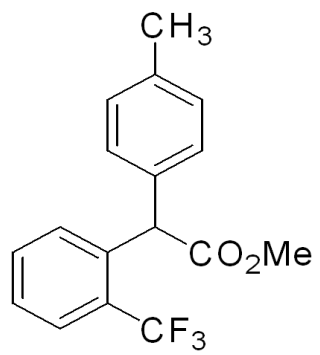


mb-8-135

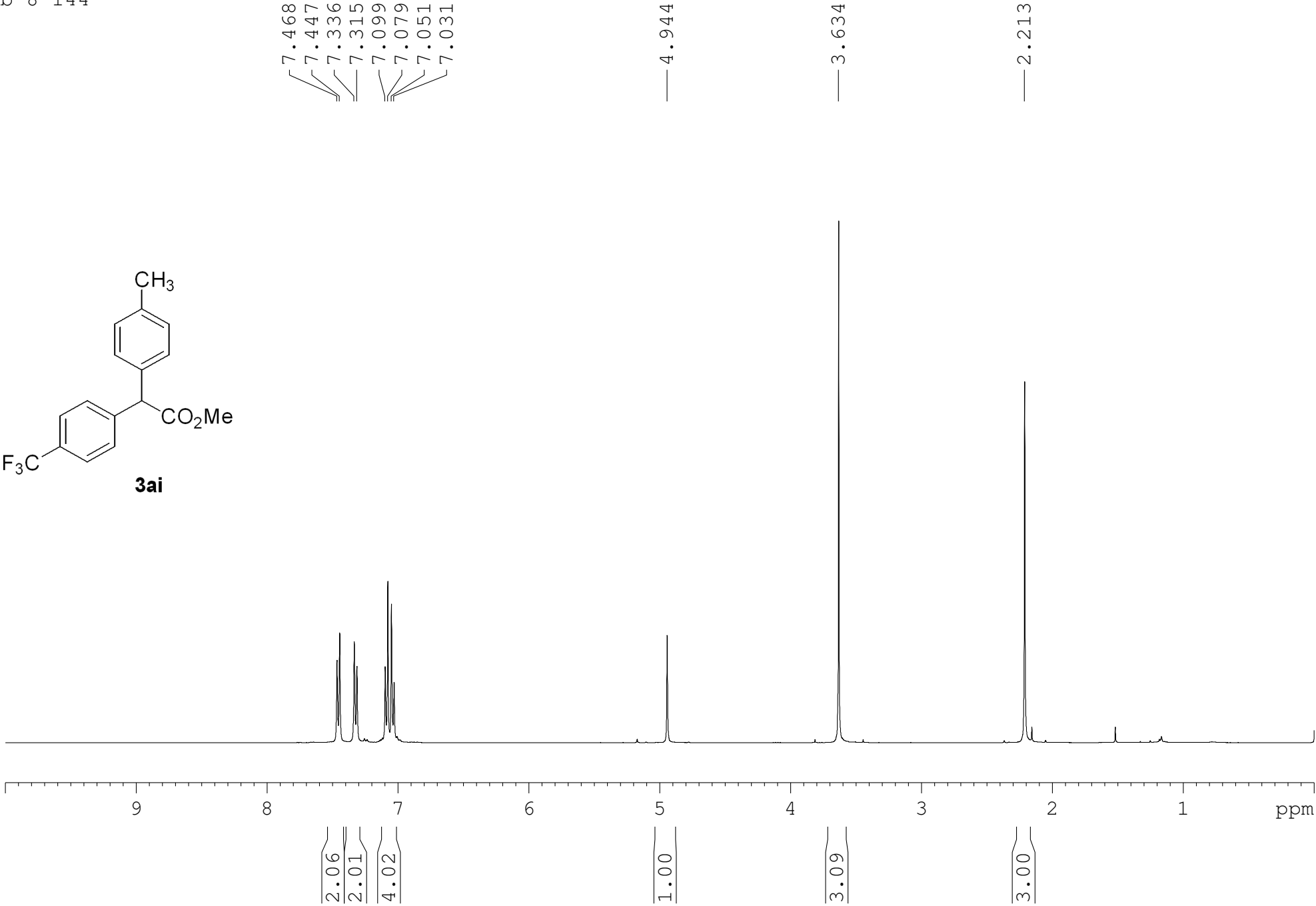
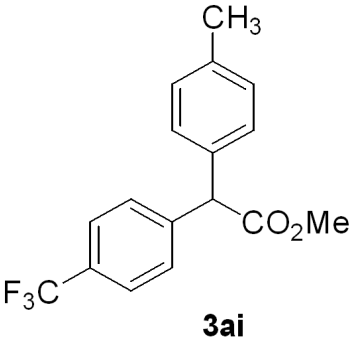


mb-8-135
mb-8-135

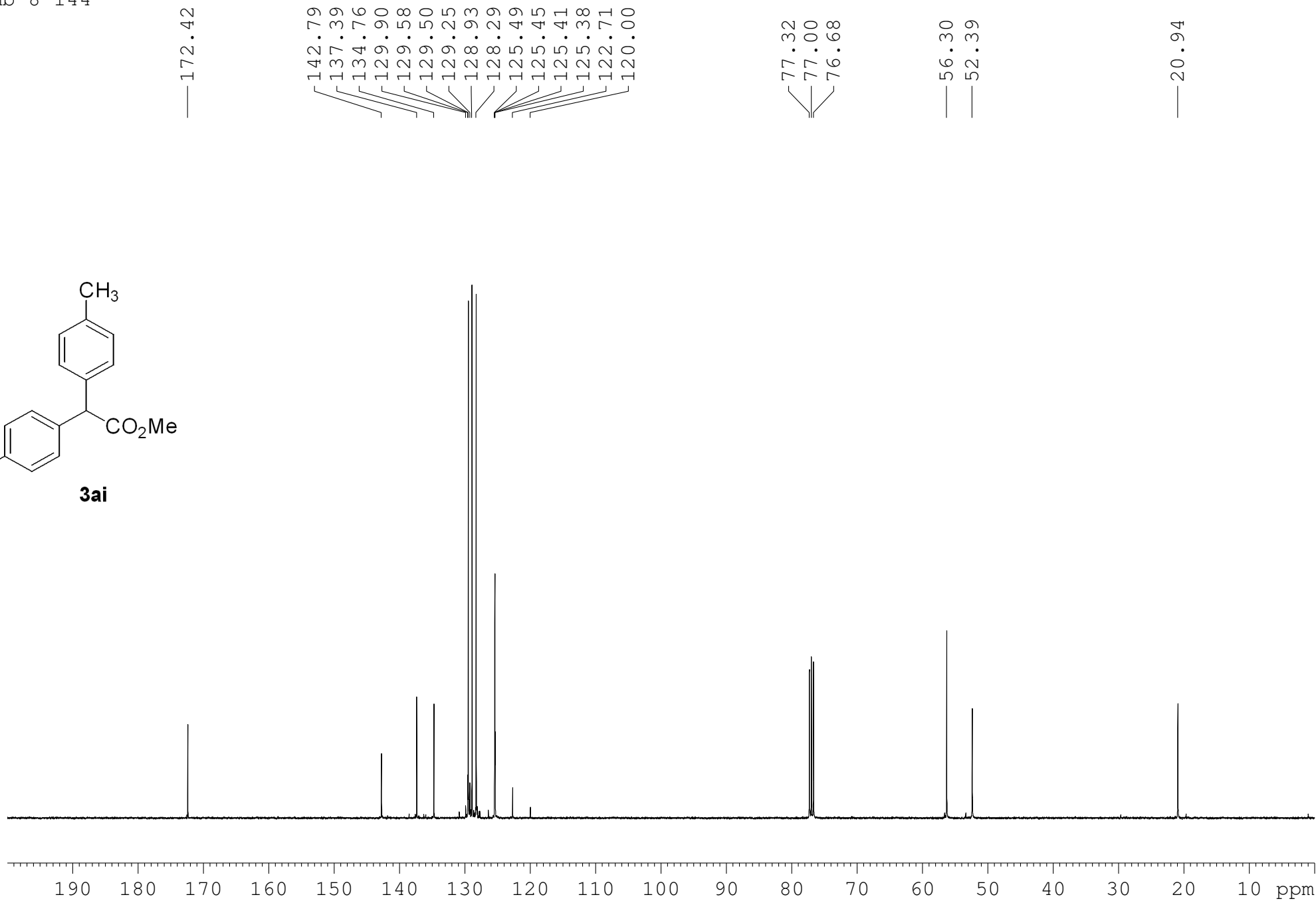
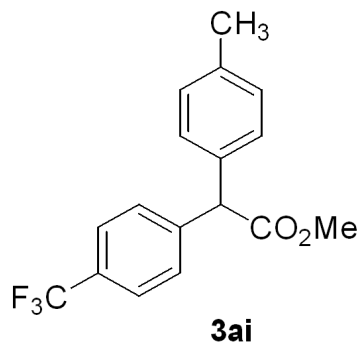
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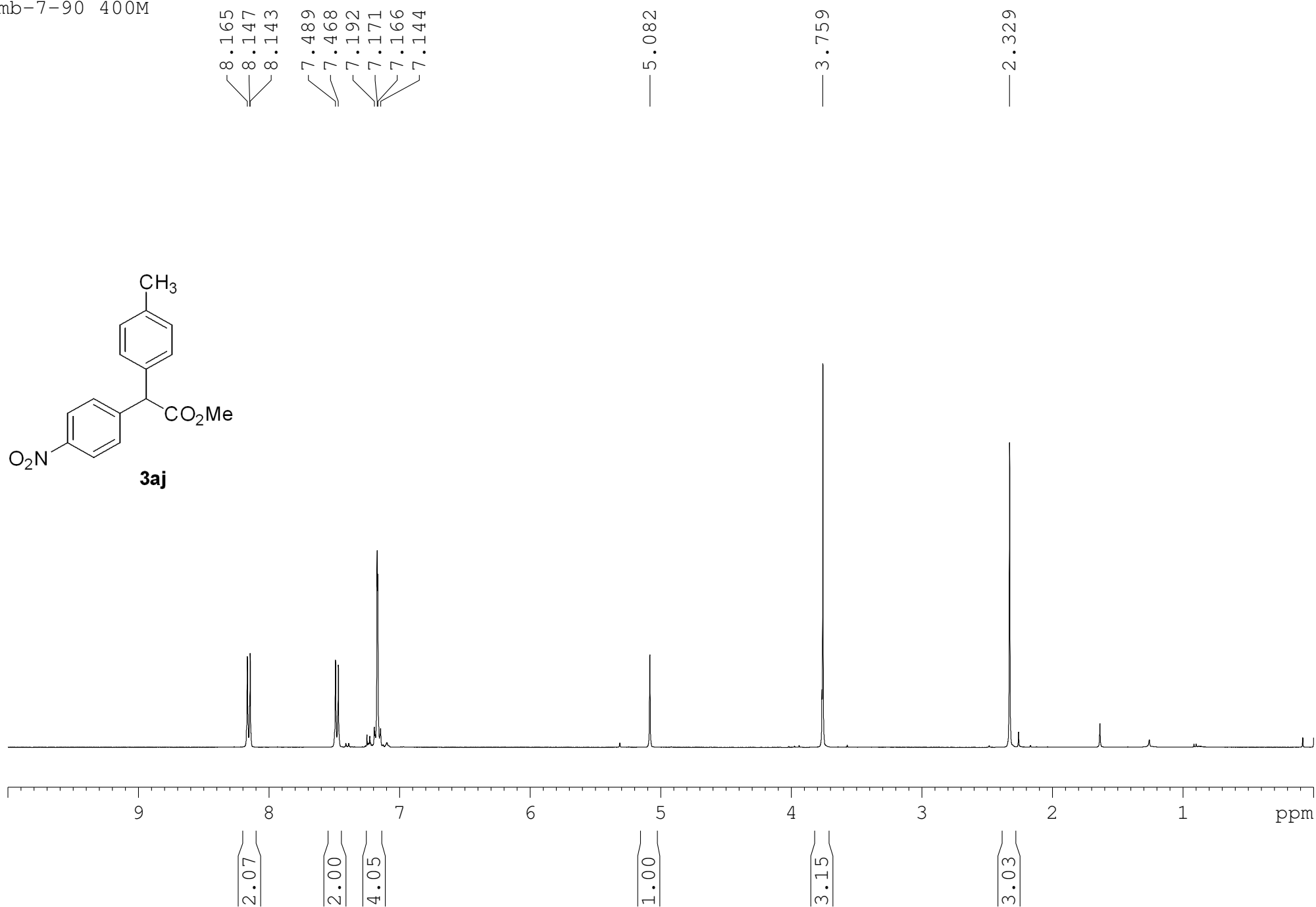
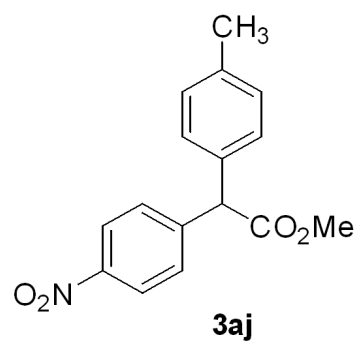
mb-8-144



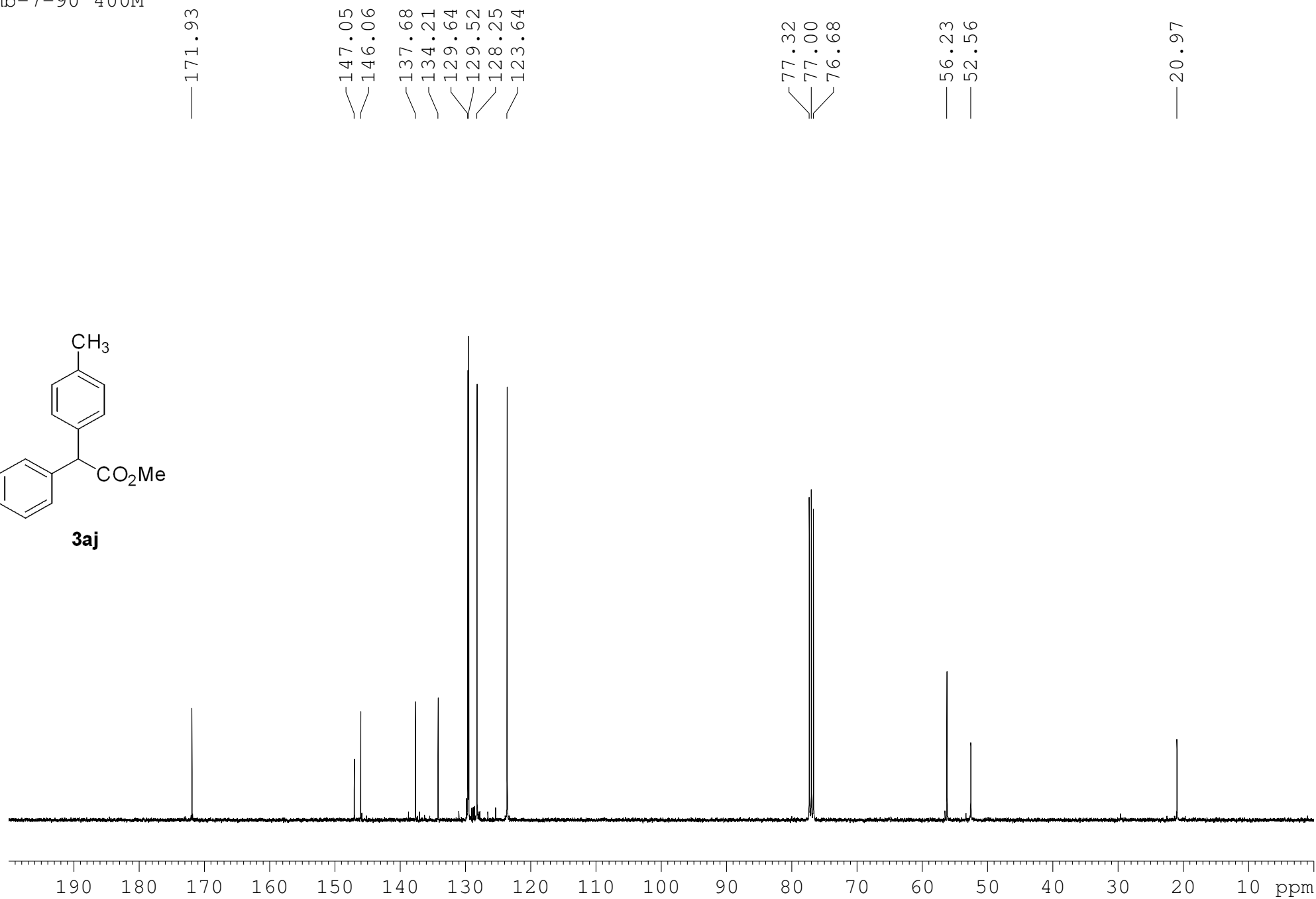
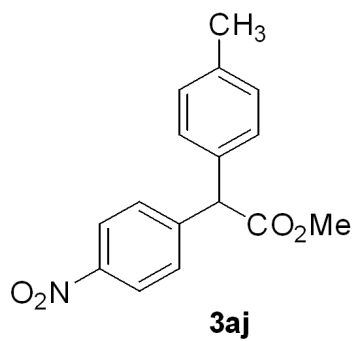
mb-8-144



mb-7-90 400M



mb-7-90 400M



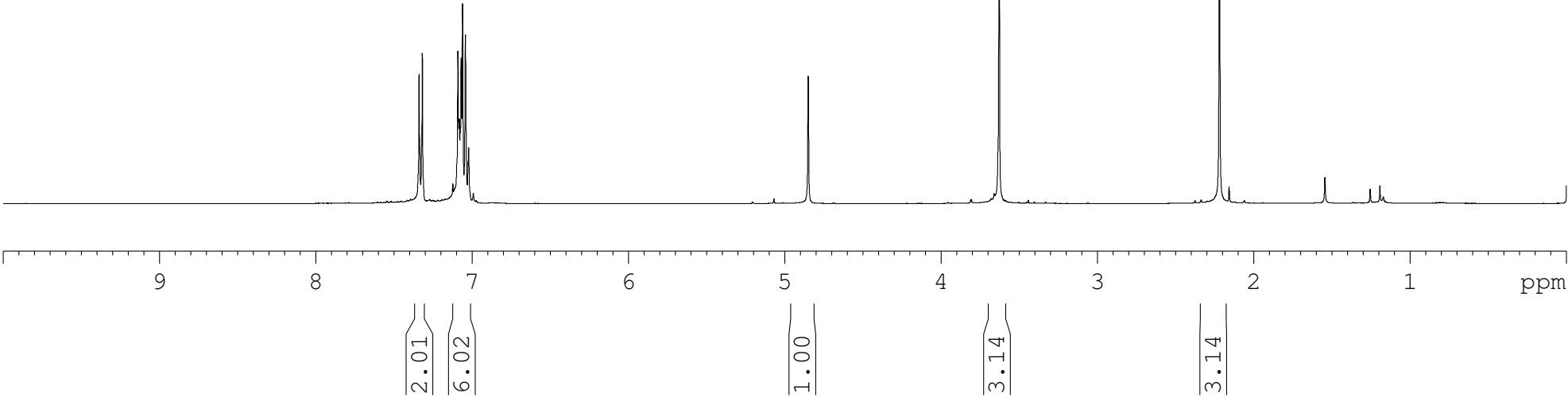
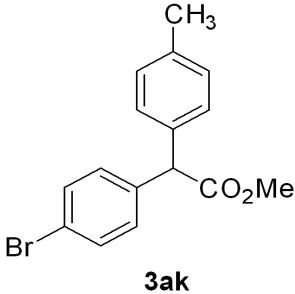
MB-6-74-H

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7.093
7.084
7.077
7.072
7.063
7.044
7.024

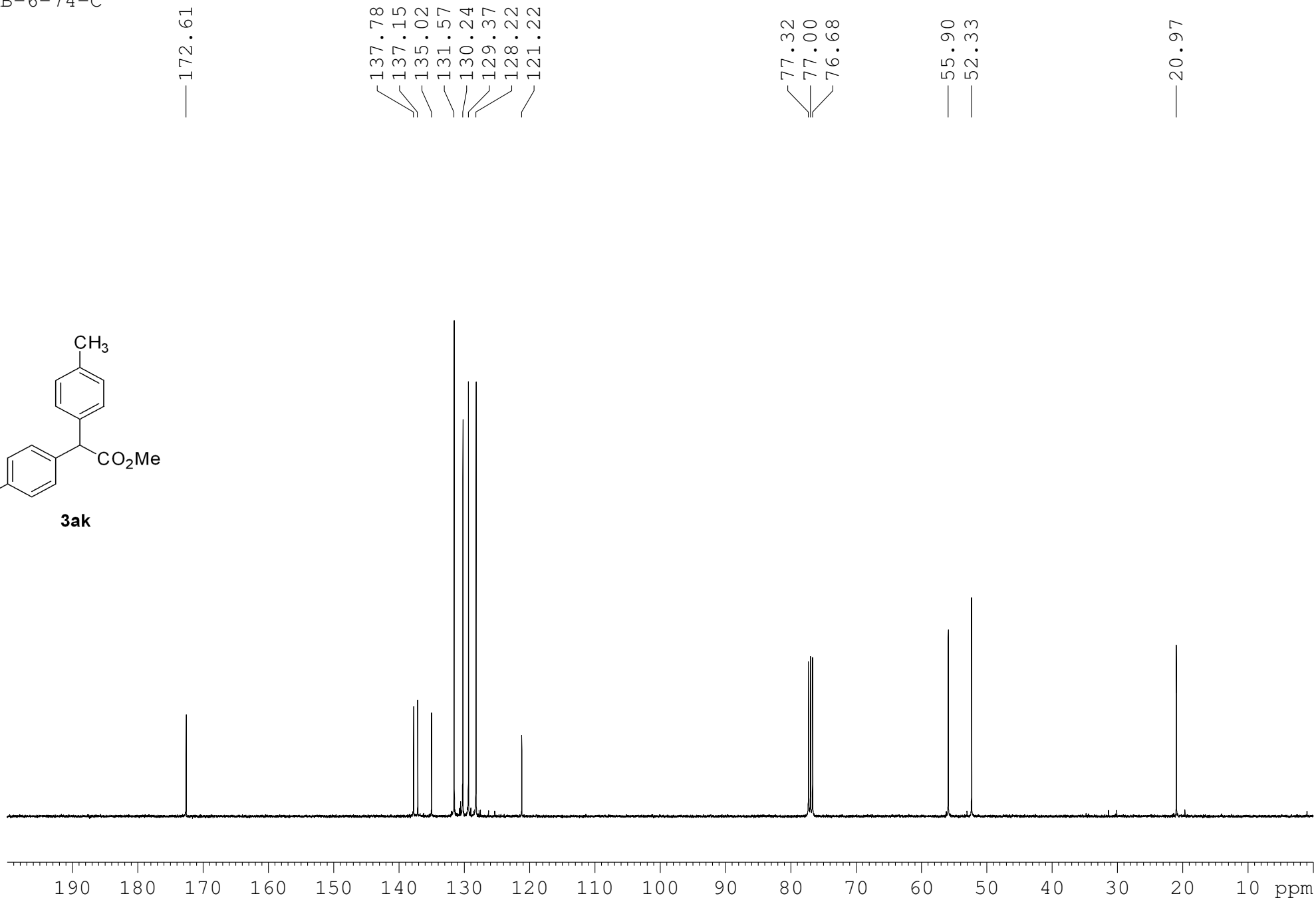
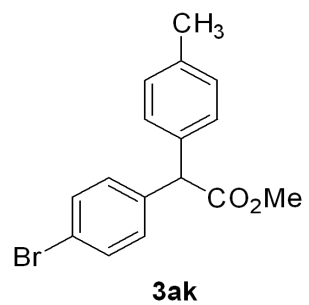
4.851

3.630

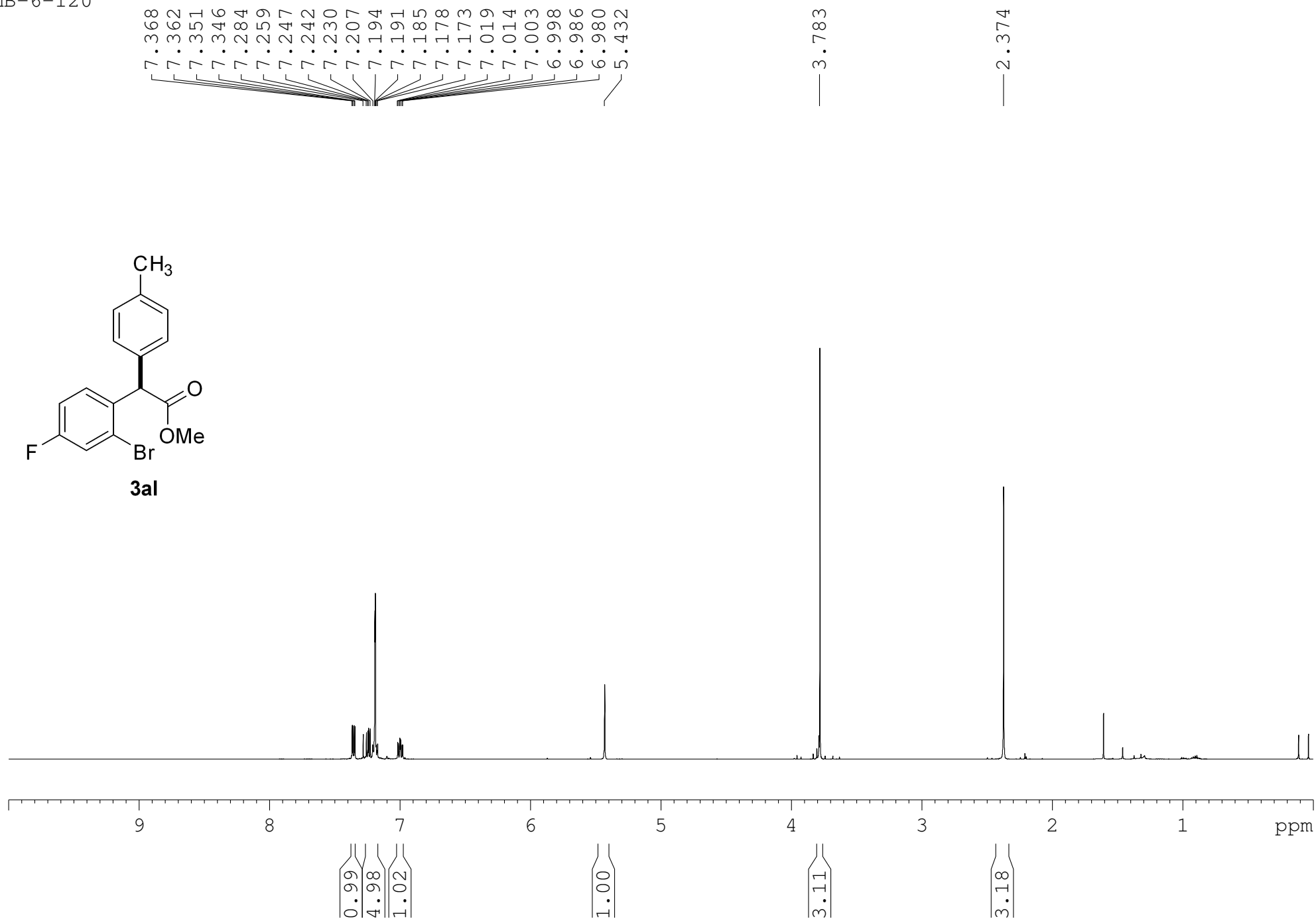
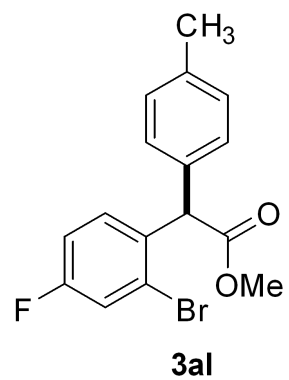
2.220



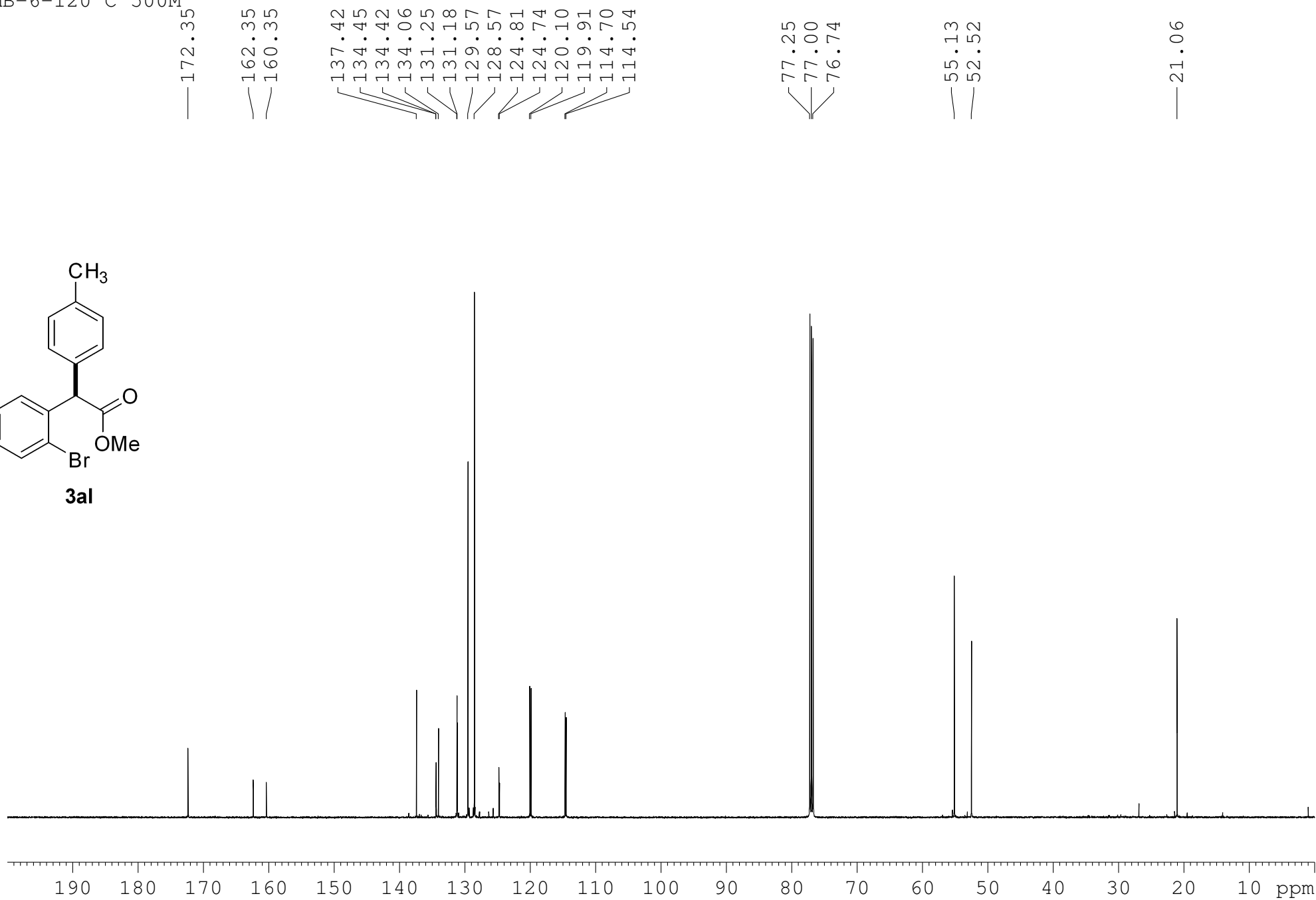
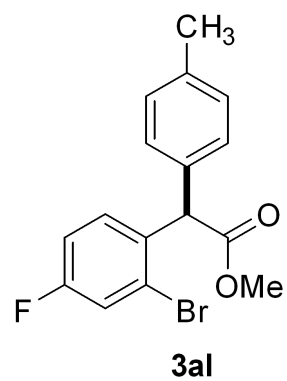
MB-6-74-C



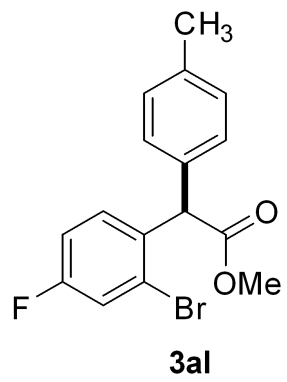
MB-6-120



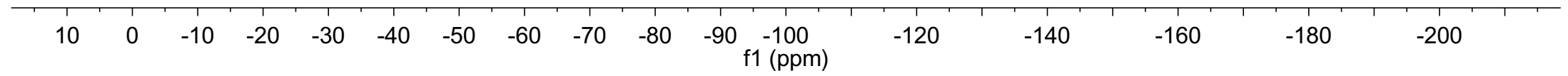
MB-6-120 C 500M



mb-6-120 F
mb-6-120 F



113.187



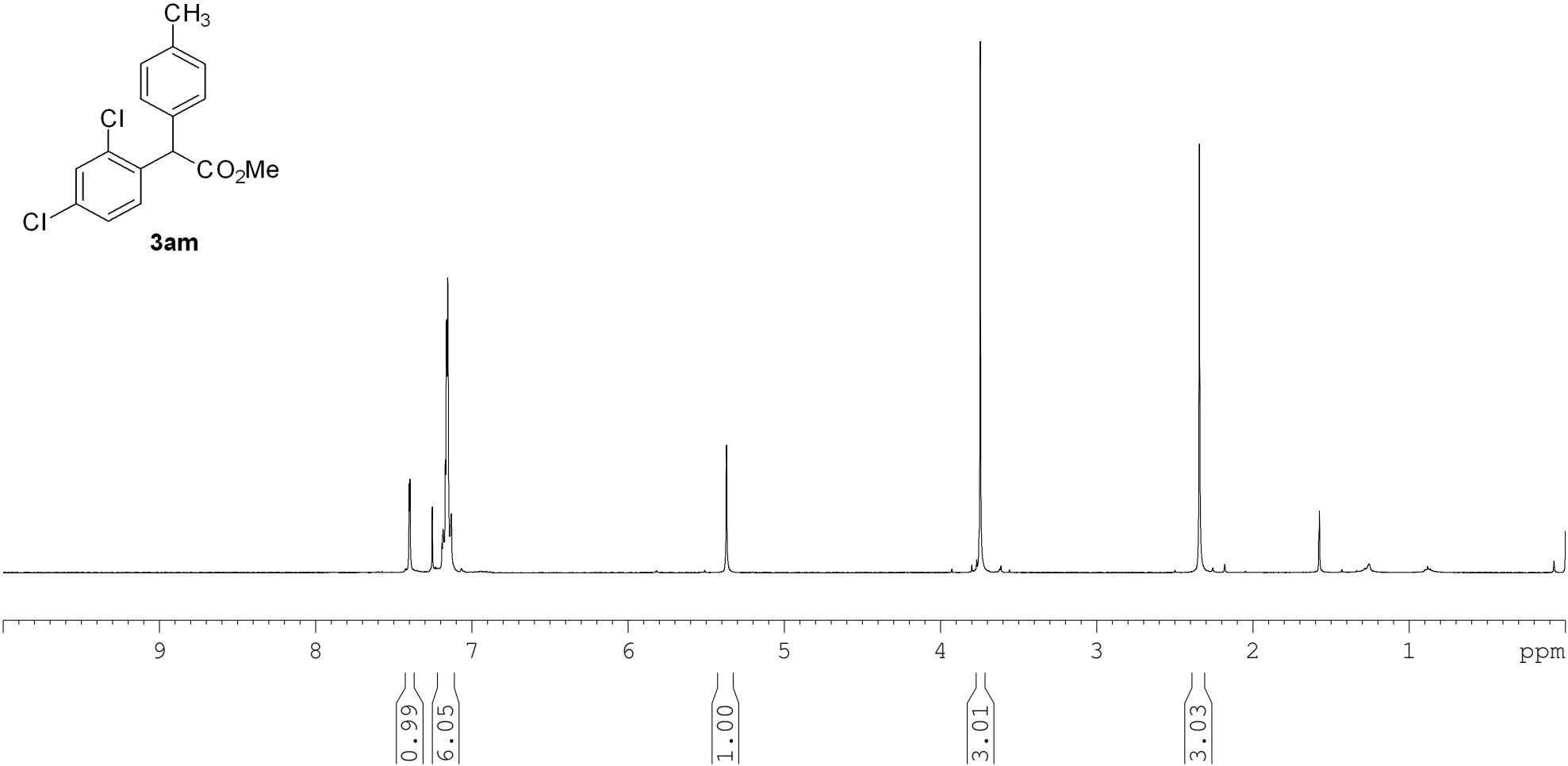
mb-8-143

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7.398
7.255
7.192
7.186
7.171
7.163
7.156
7.142
7.133

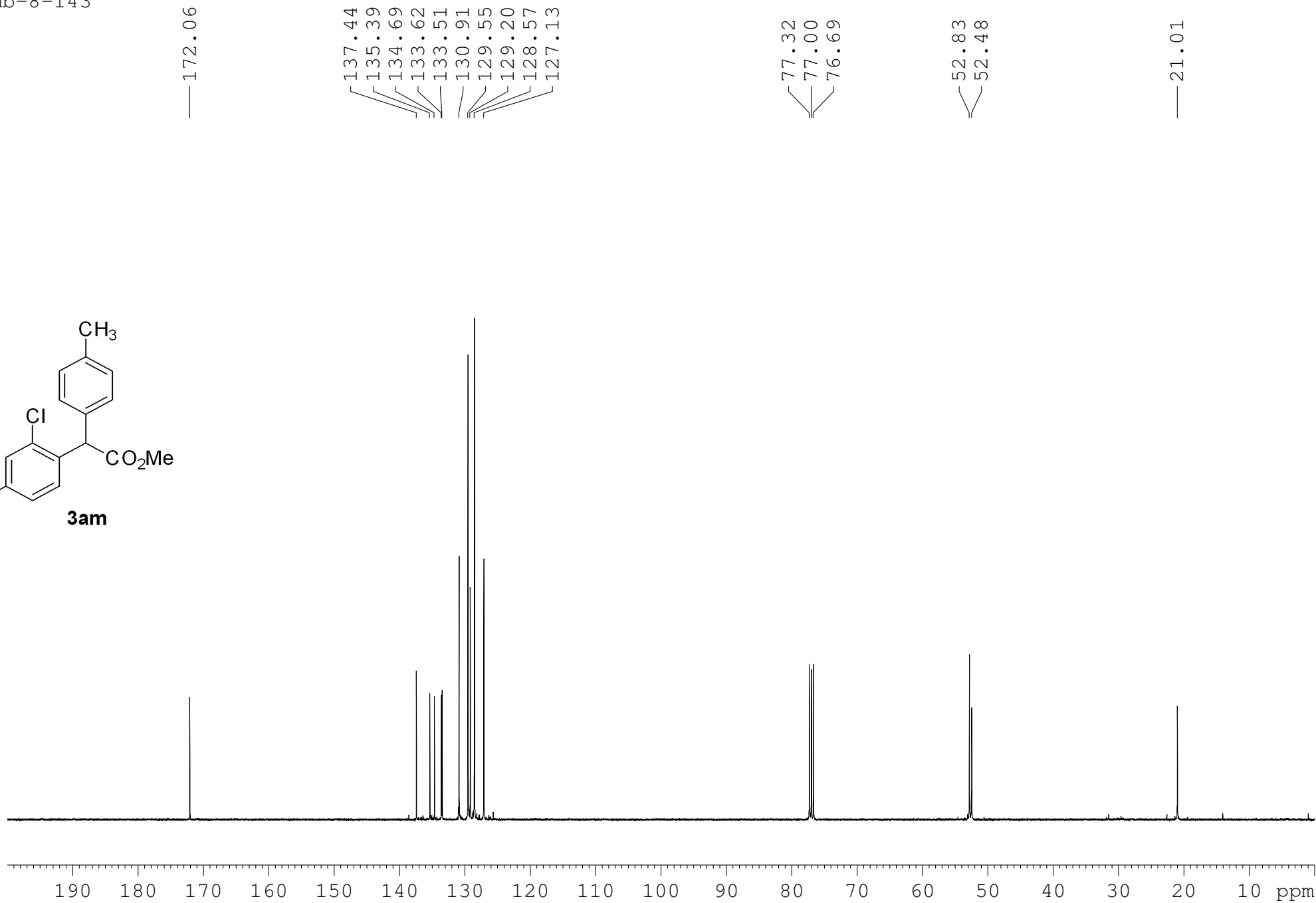
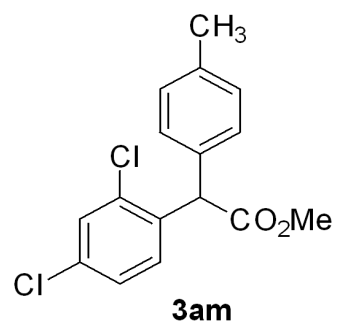
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3.747

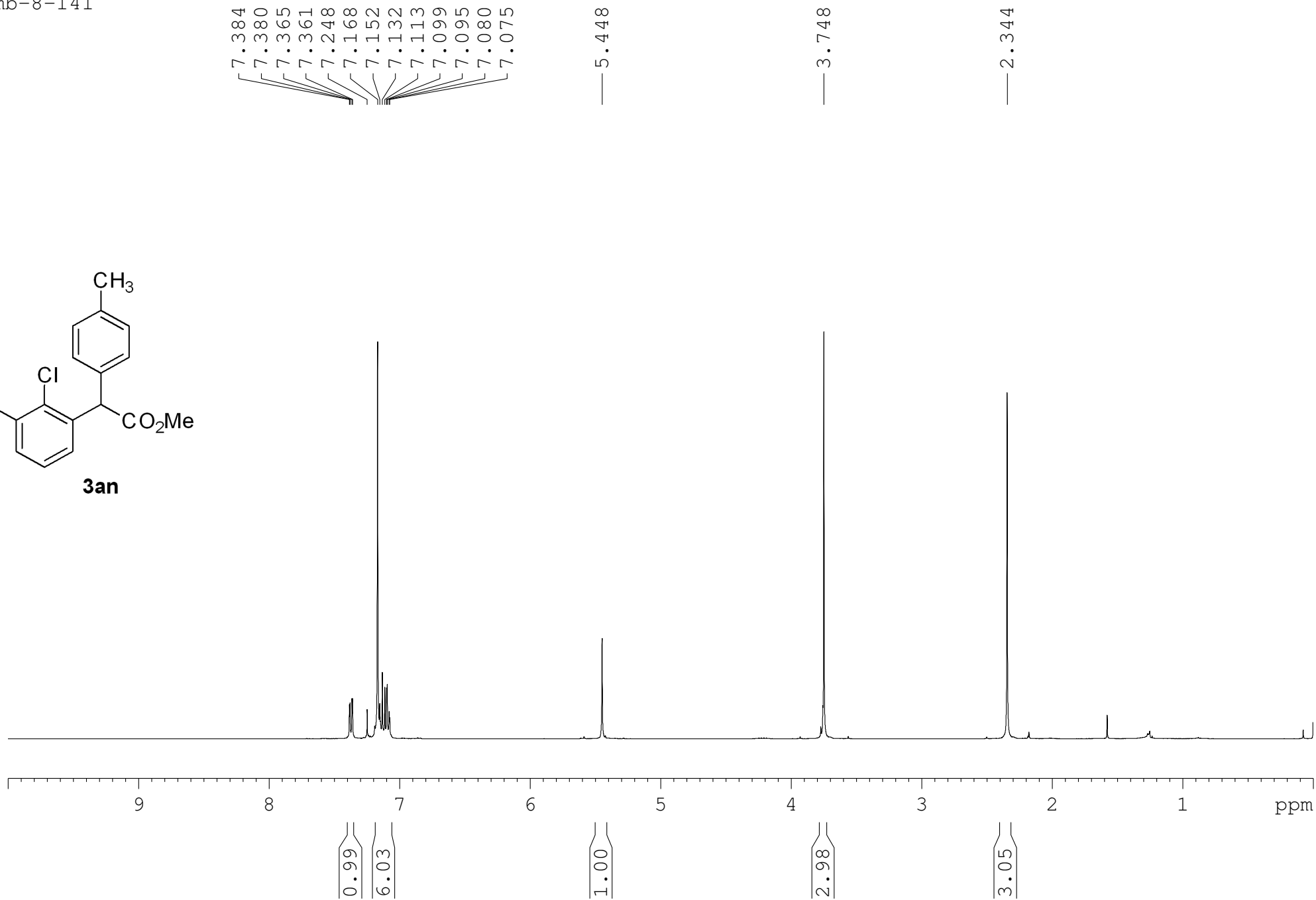
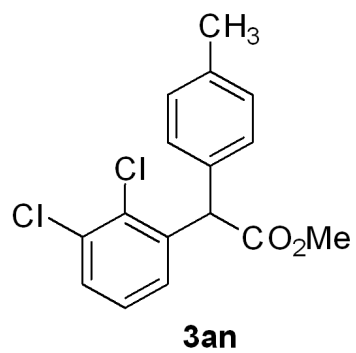
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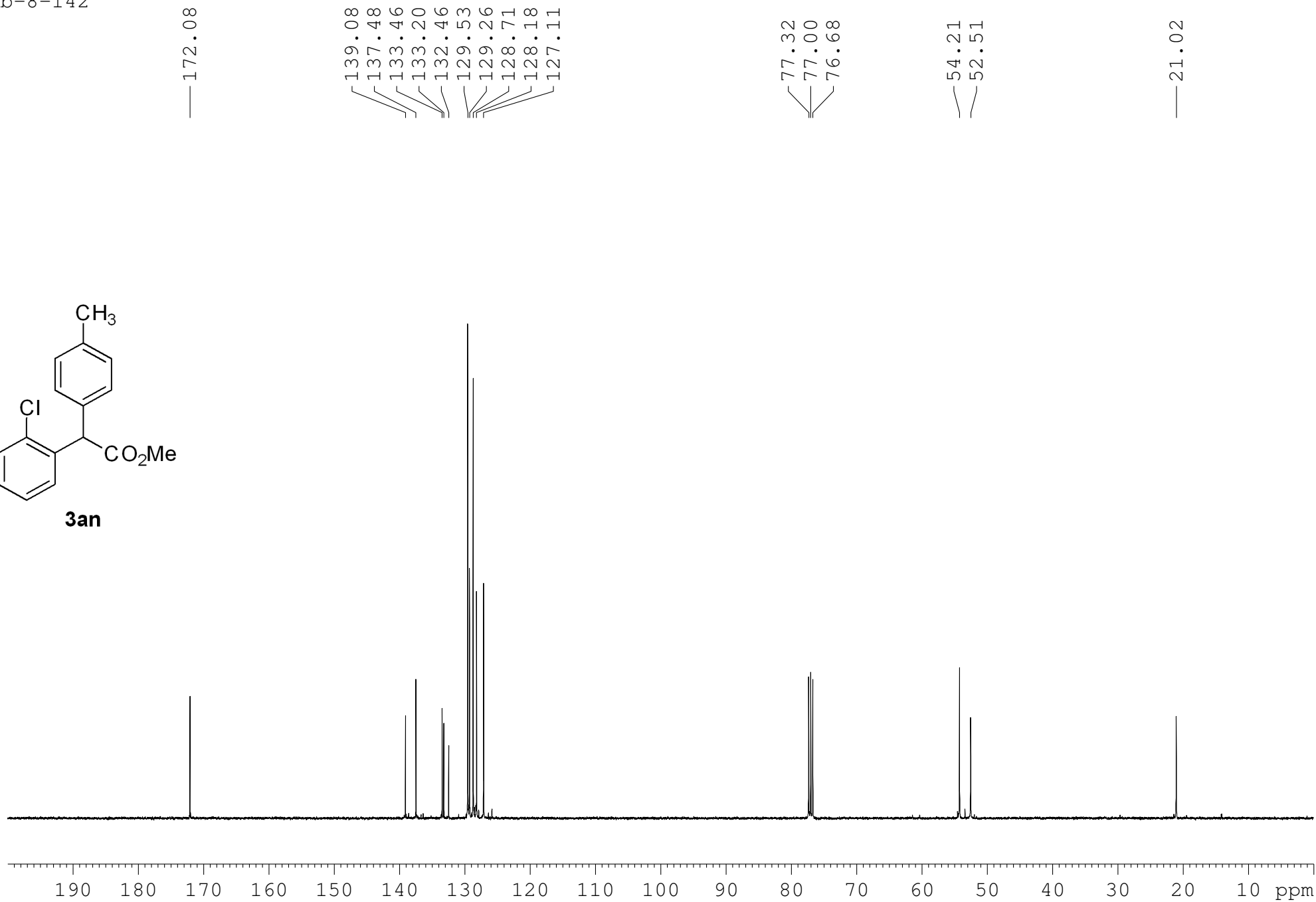
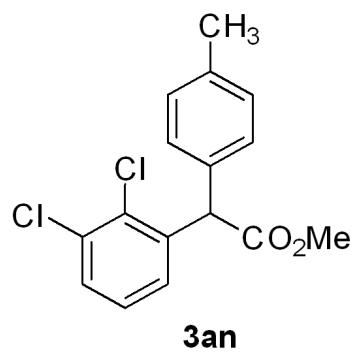
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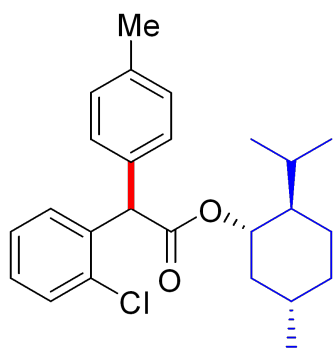


mb-8-141

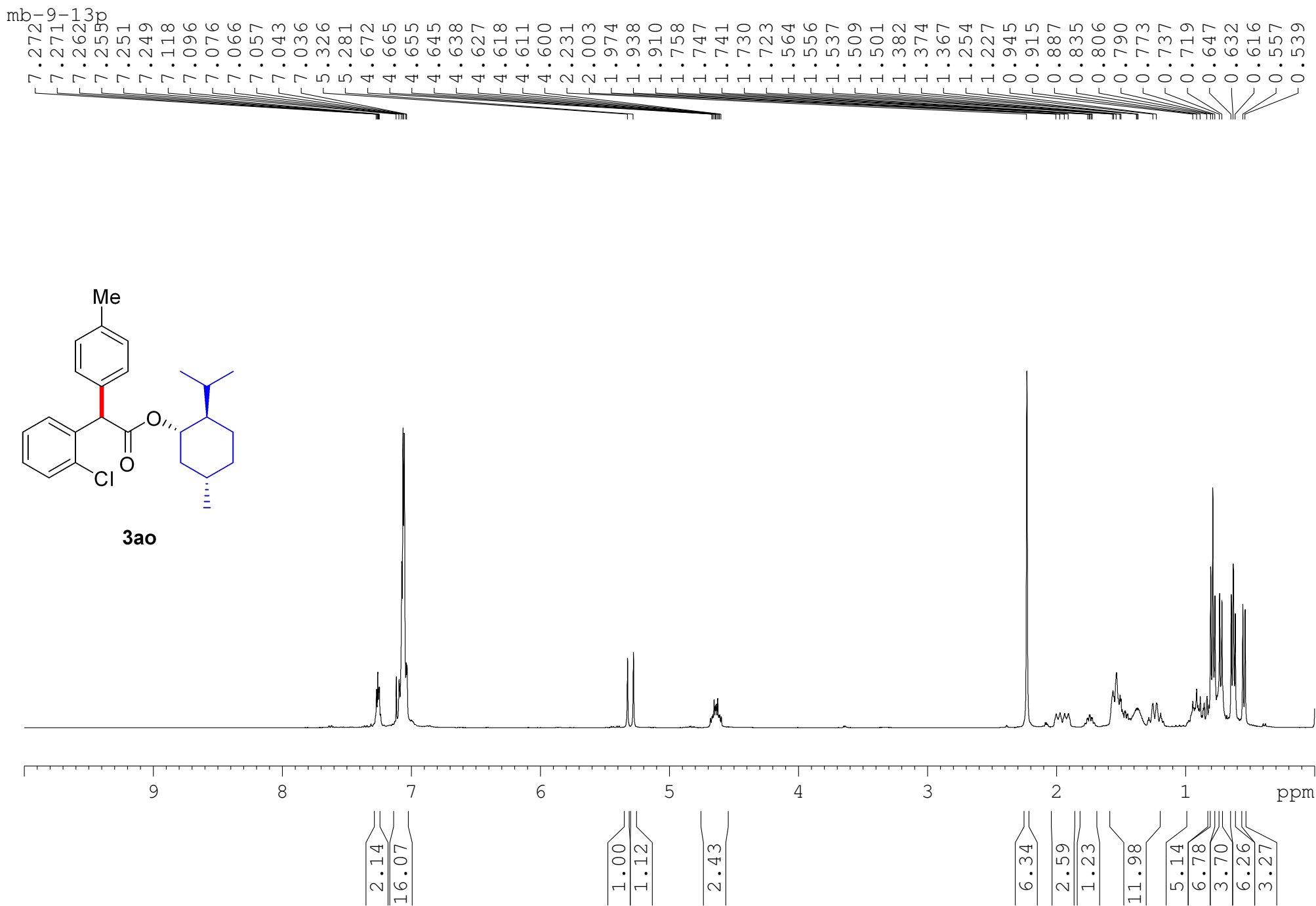


mb-8-142





3ao

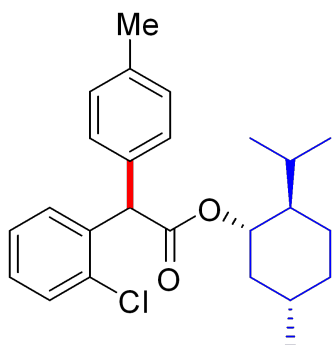


mb-9-13p

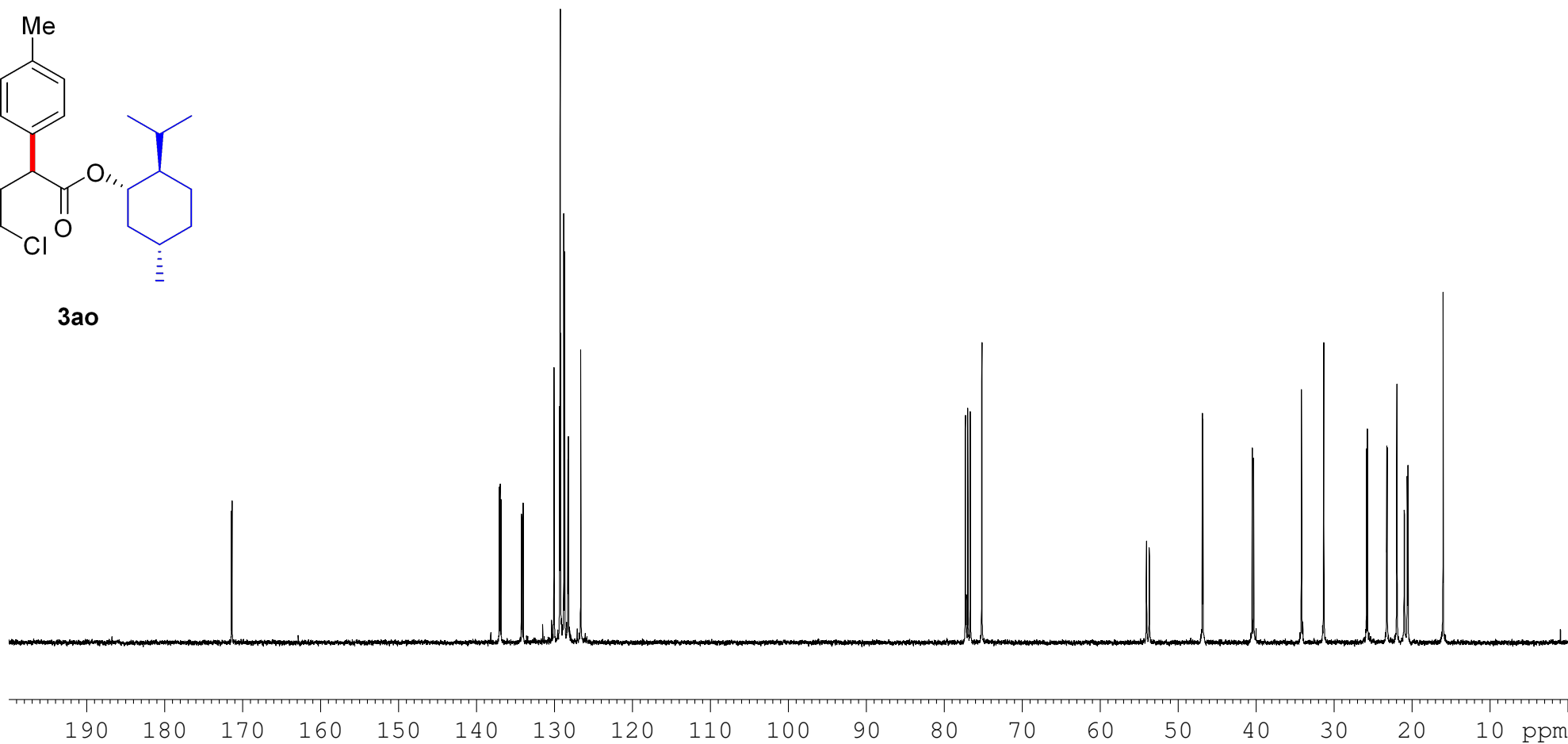
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171.39

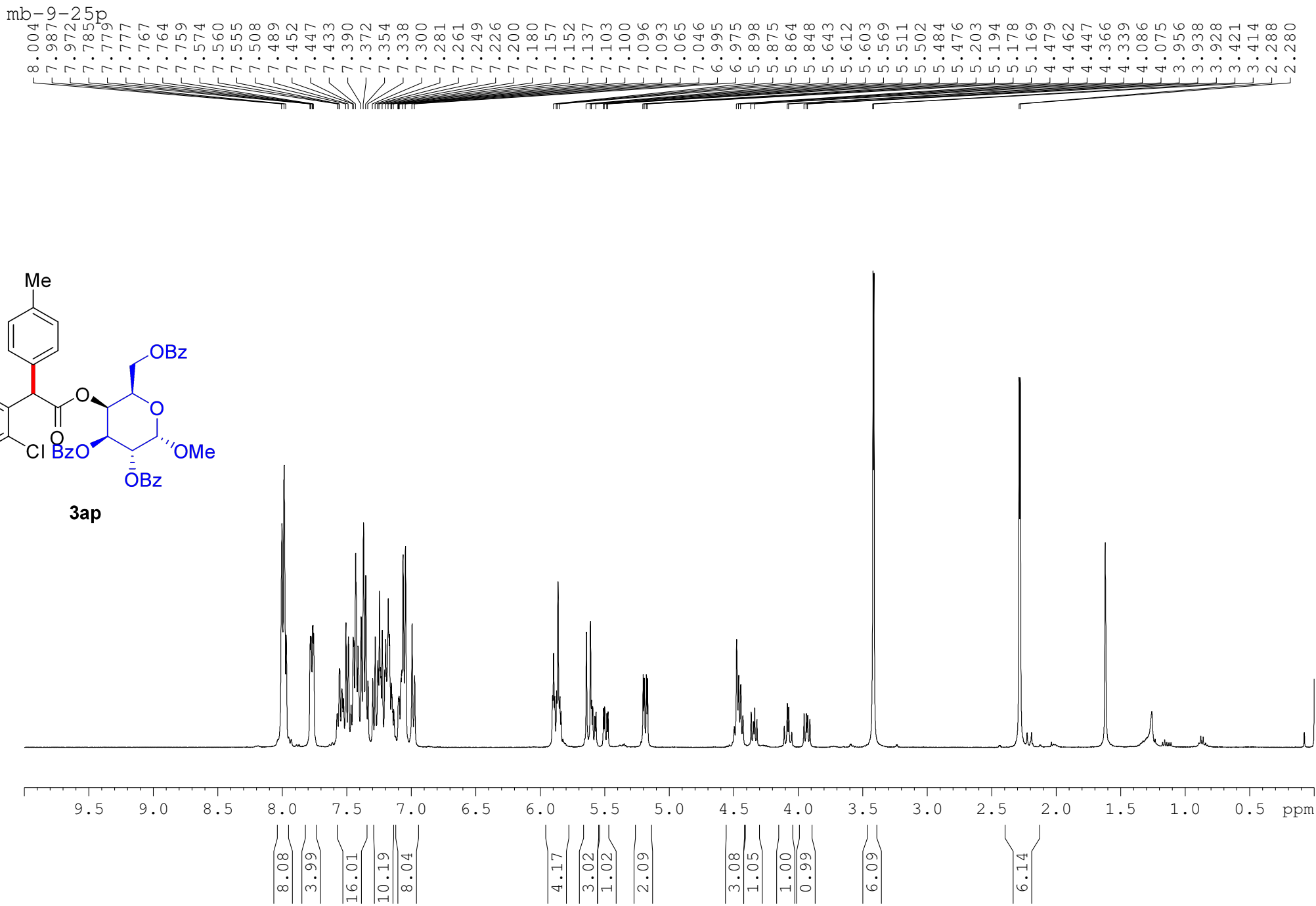
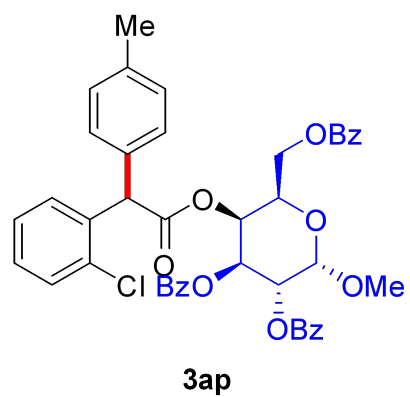
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137.03
136.98
136.88
134.27
134.23
134.16
134.03
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129.29
129.25
128.83
128.72
128.30
128.24
126.65

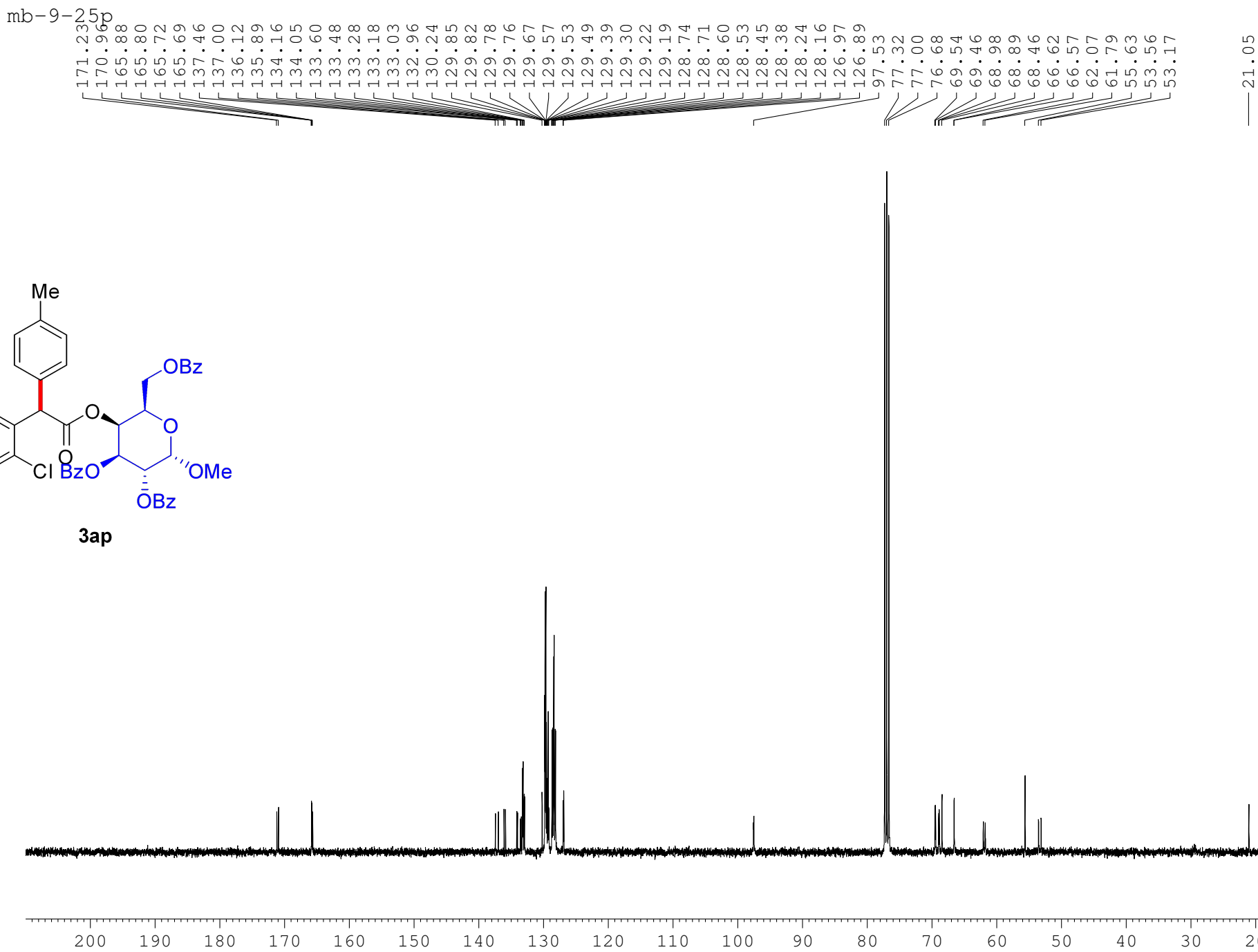
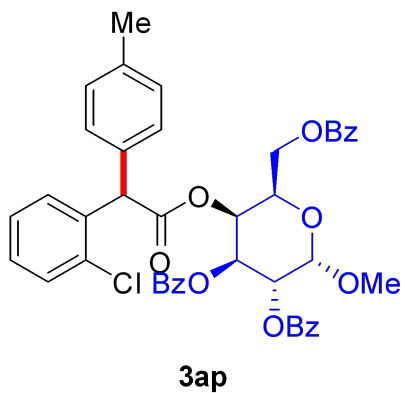
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77.00
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75.20
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54.06
53.73
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46.91
46.84
40.51
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23.21
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21.01
20.62

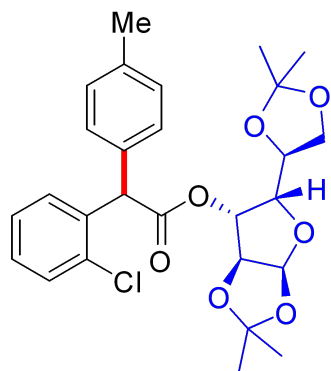


3ao

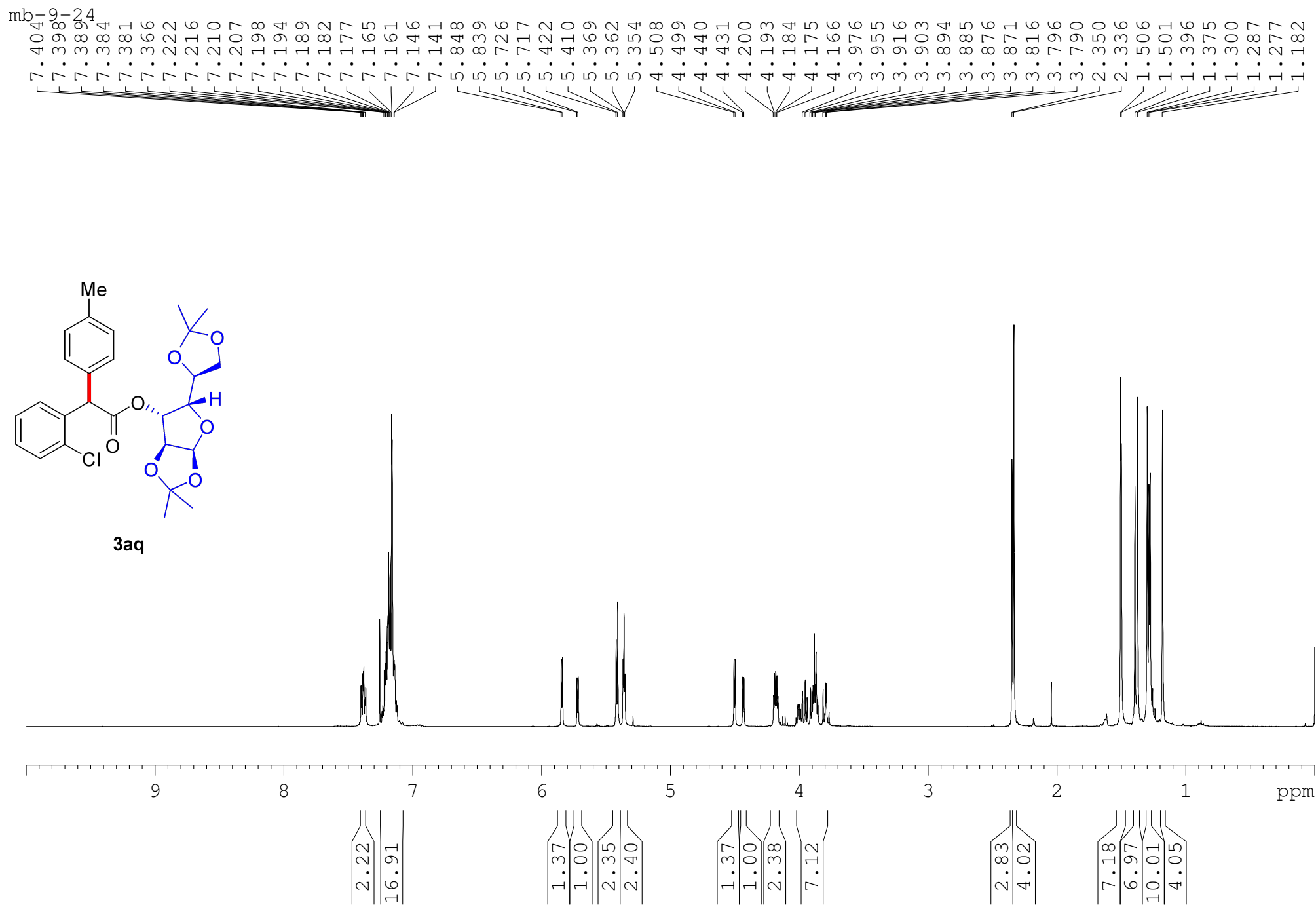




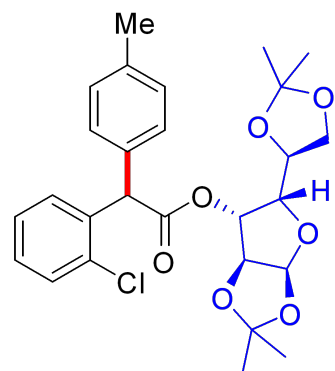




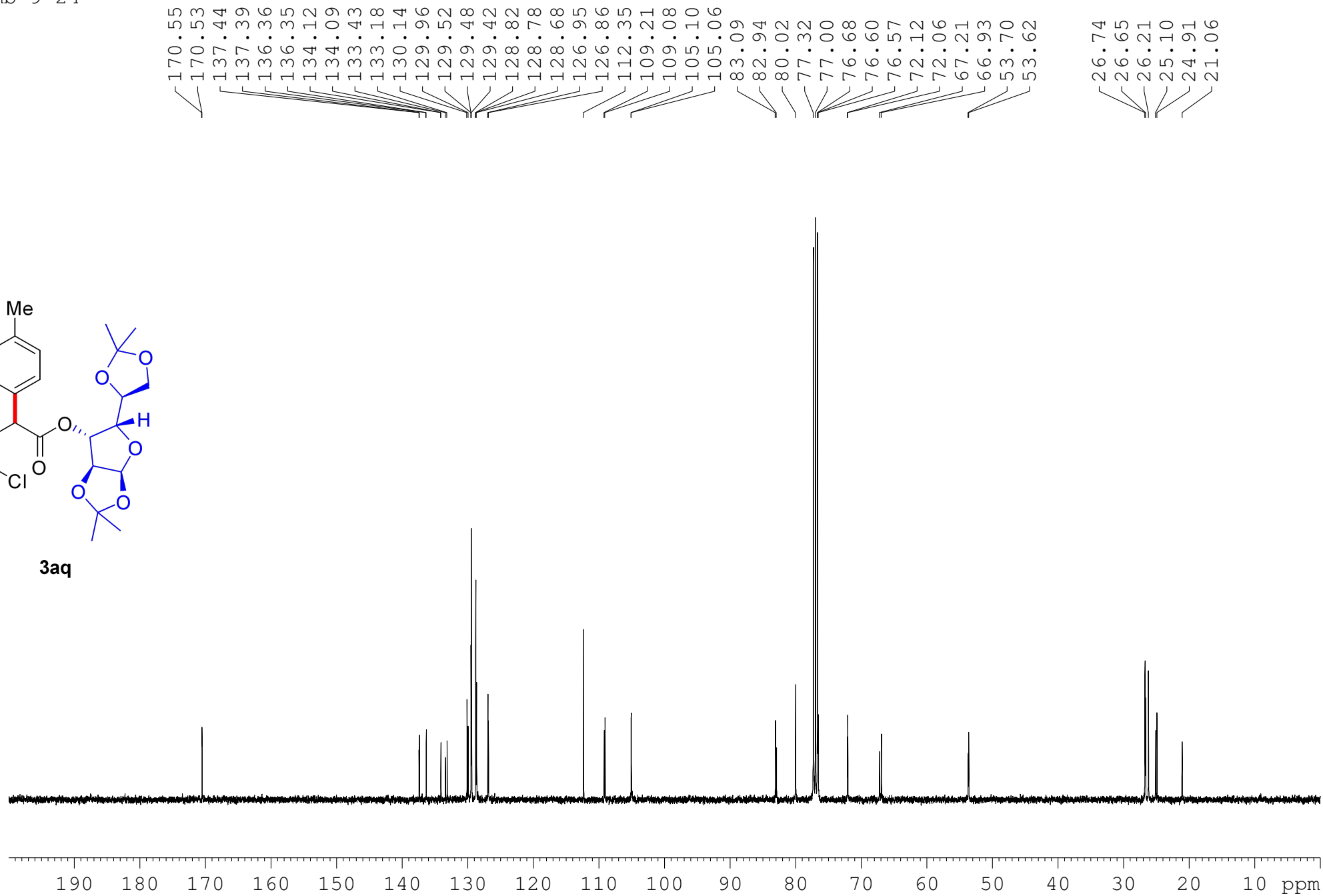
3aq

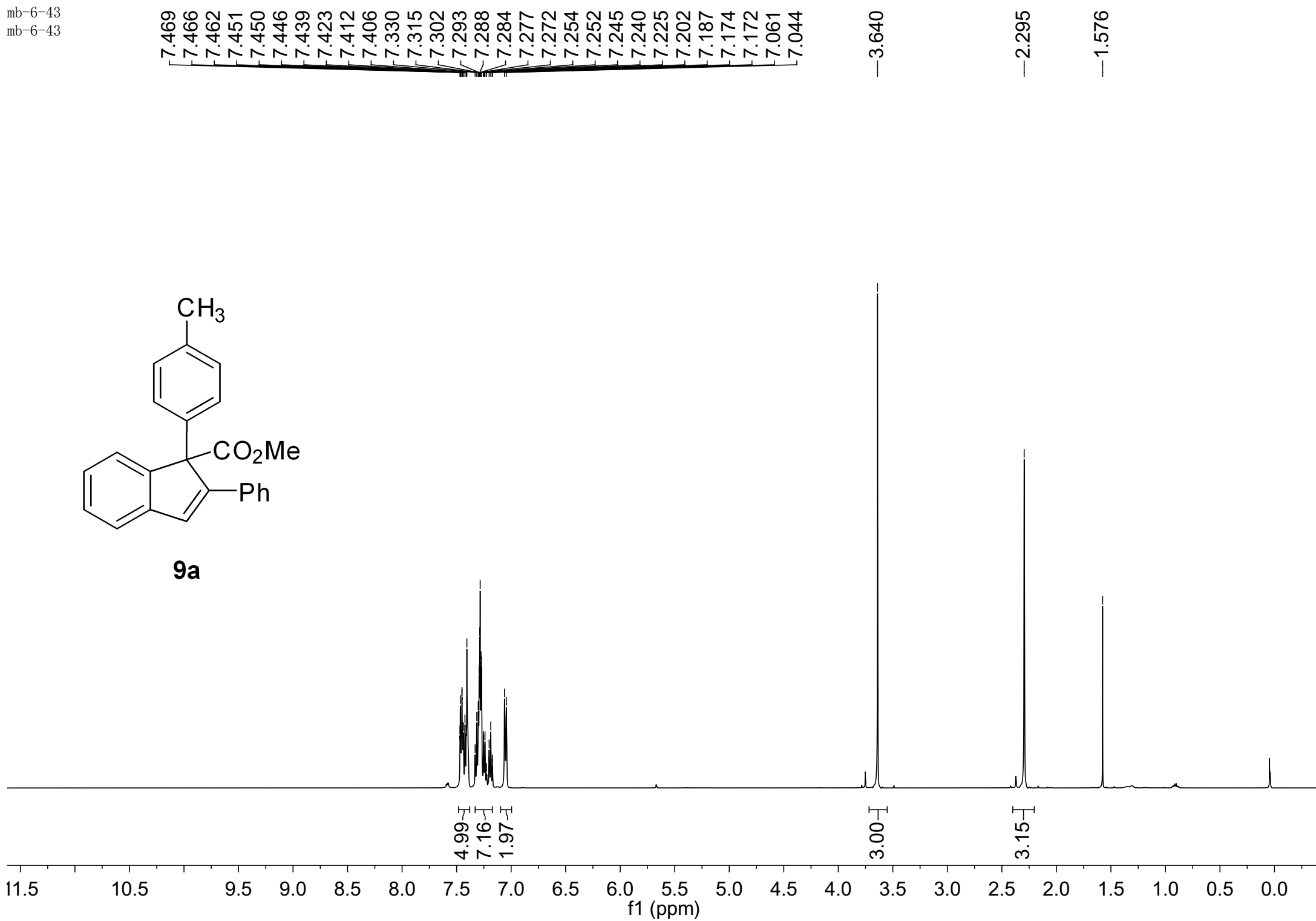


mb-9-24

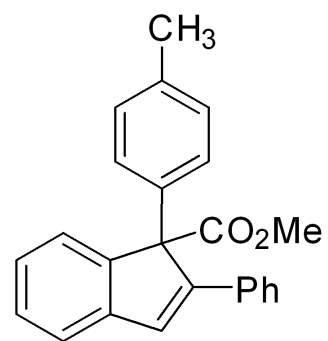


3aq

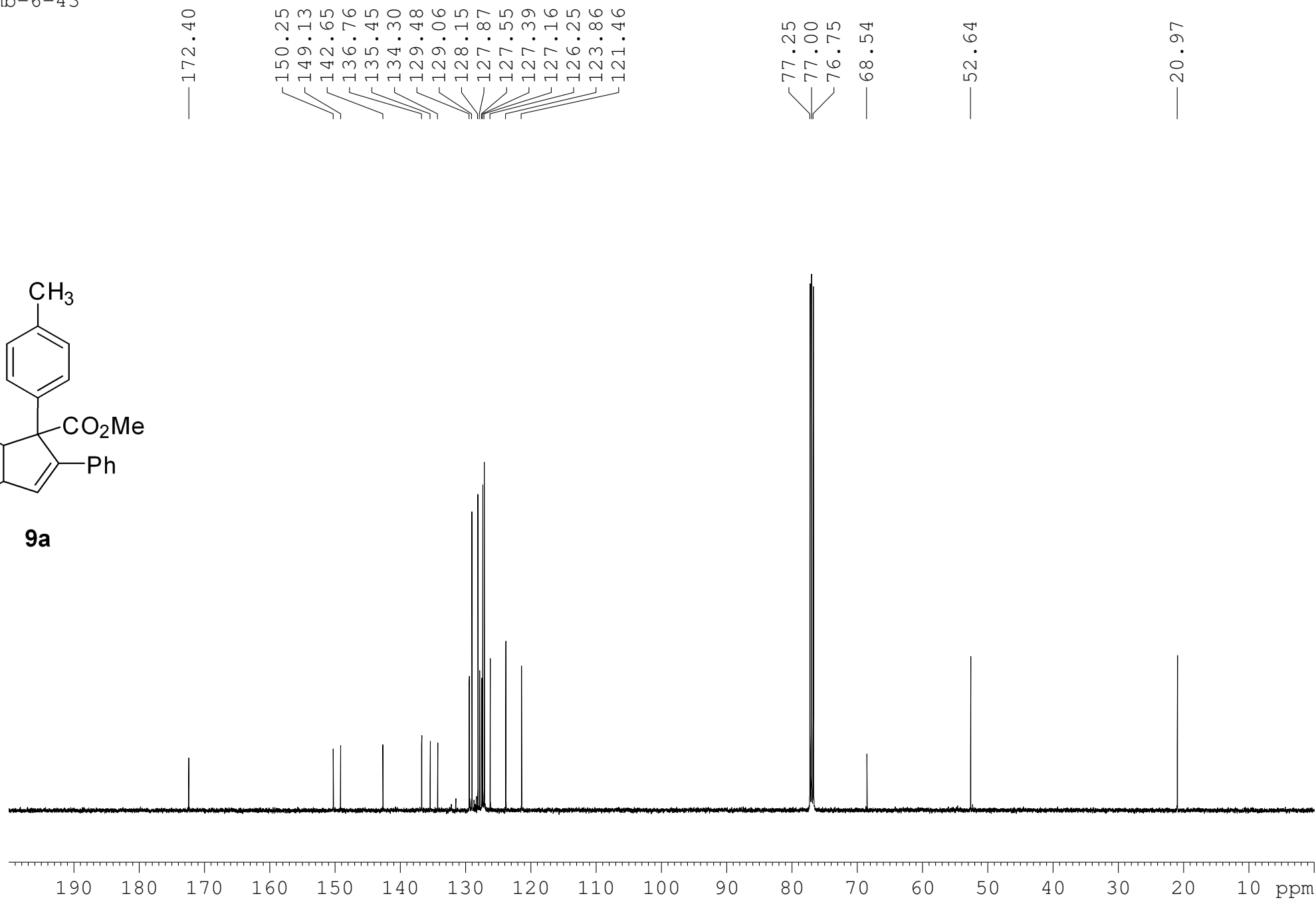




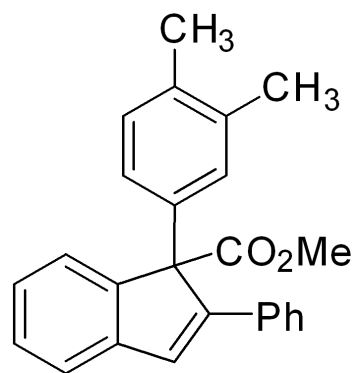
mb-6-43



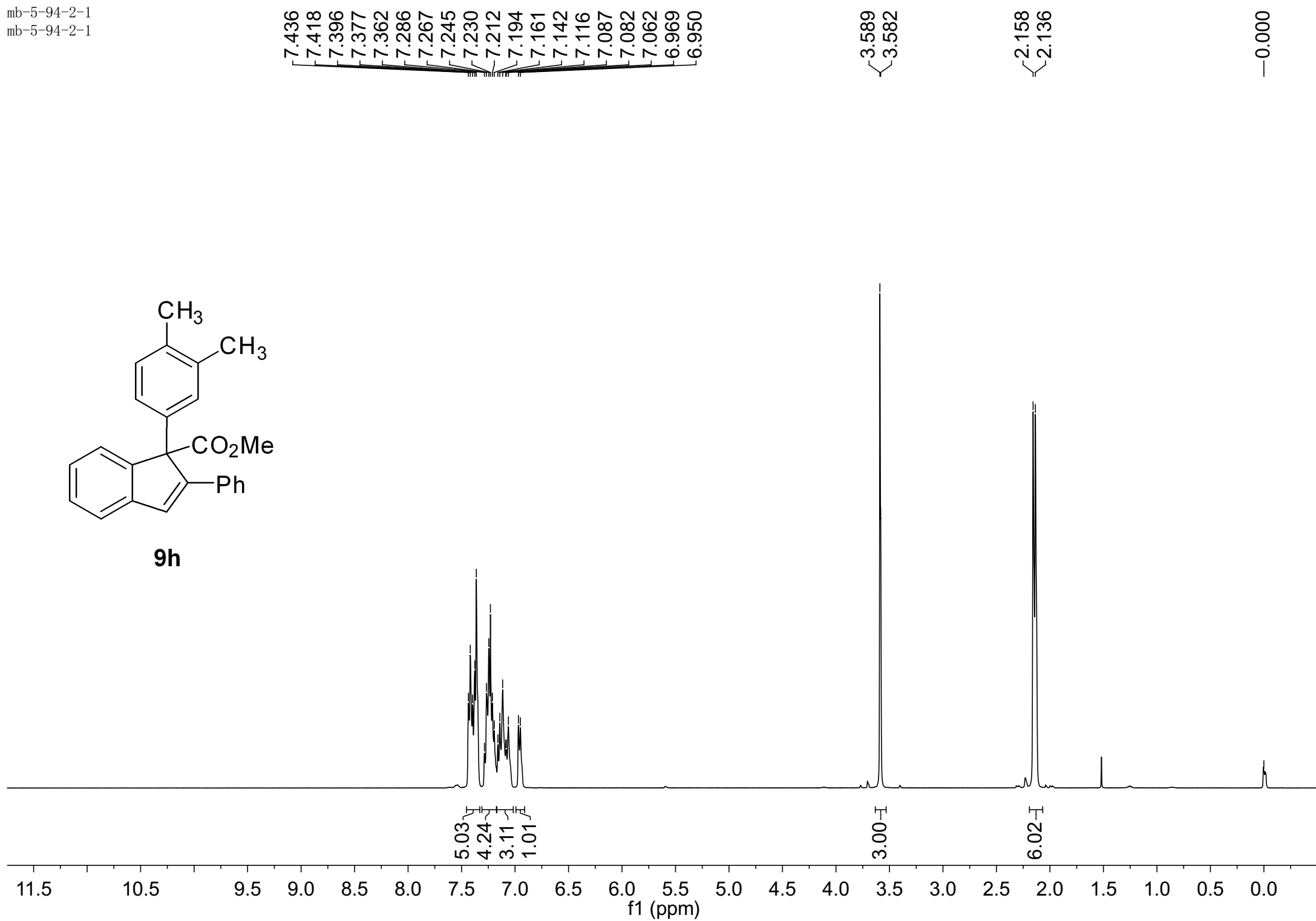
9a



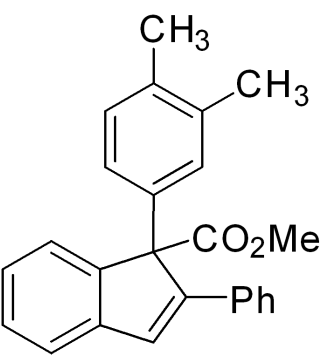
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mb-5-94-2-1



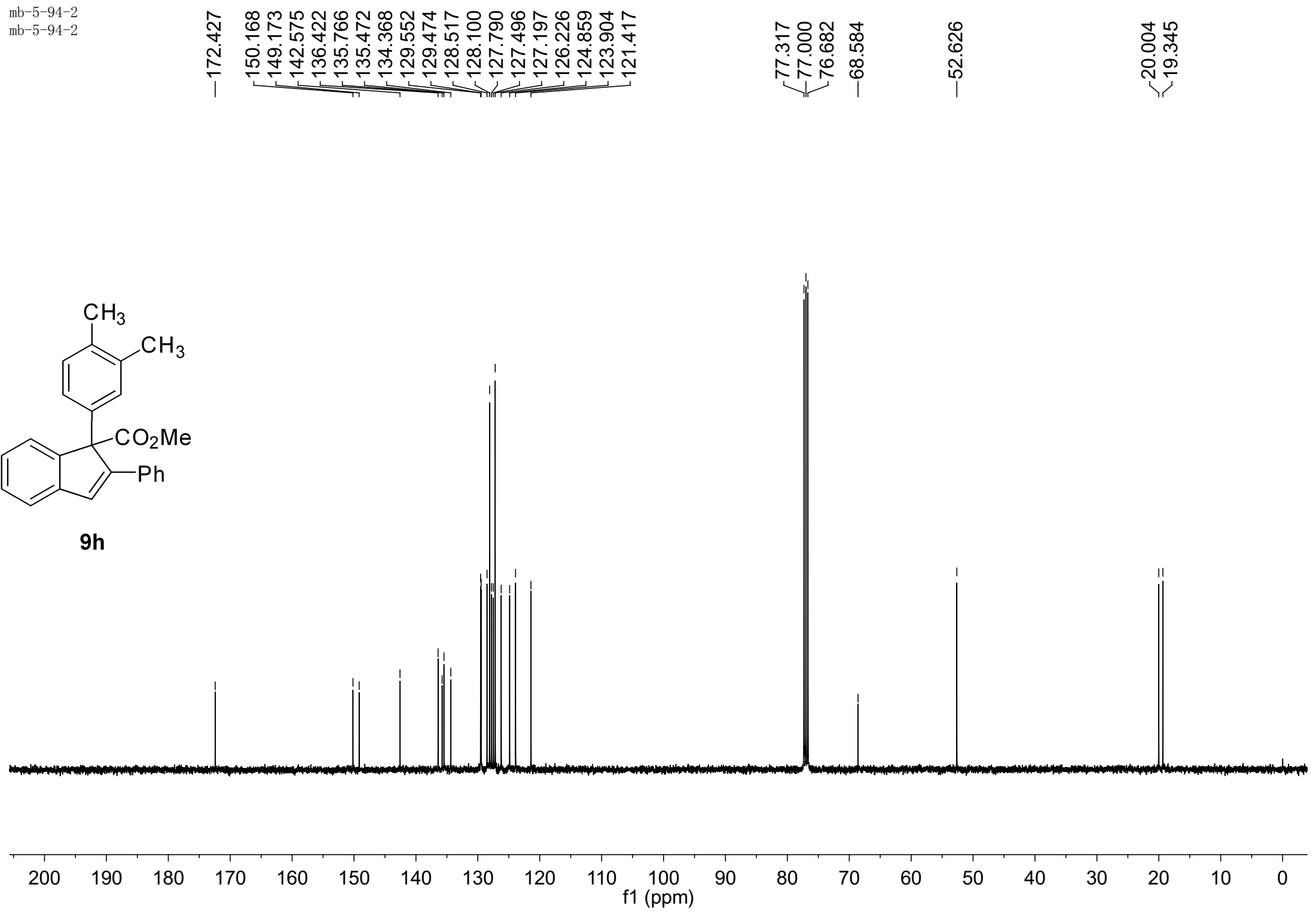
9h



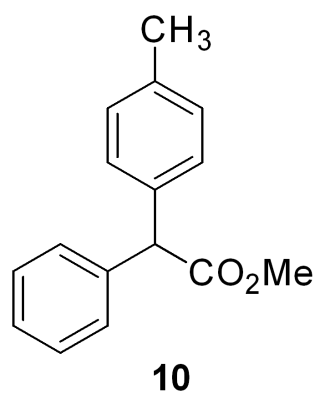
mb-5-94-2
mb-5-94-2



9h



mb-6-141-2

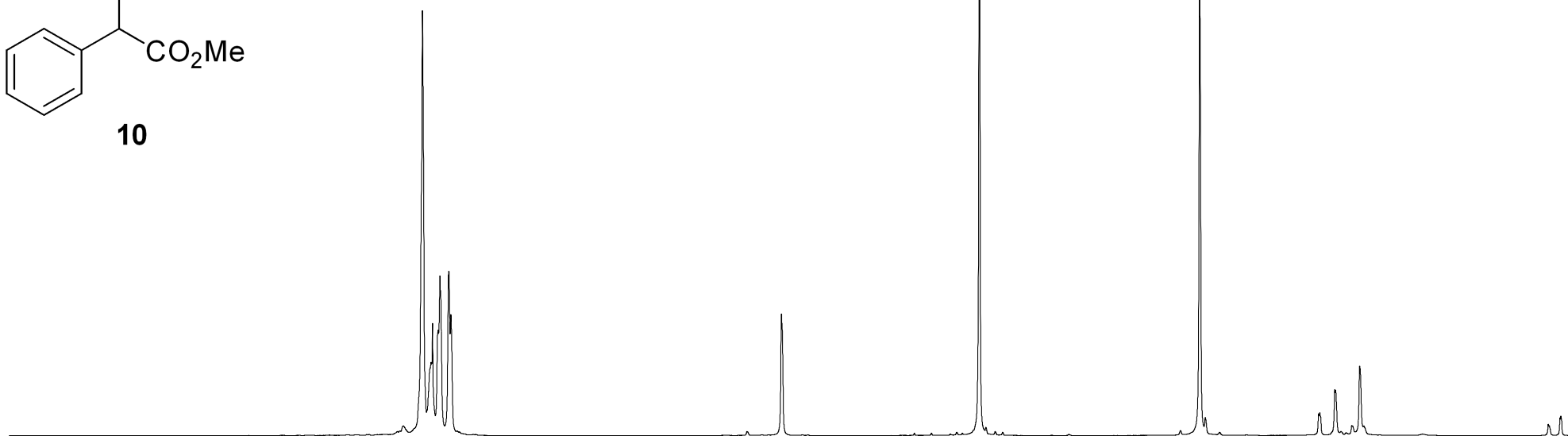


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7.290
7.284
7.248
7.237
7.180
7.167

— 5.046

— 3.778

— 2.364



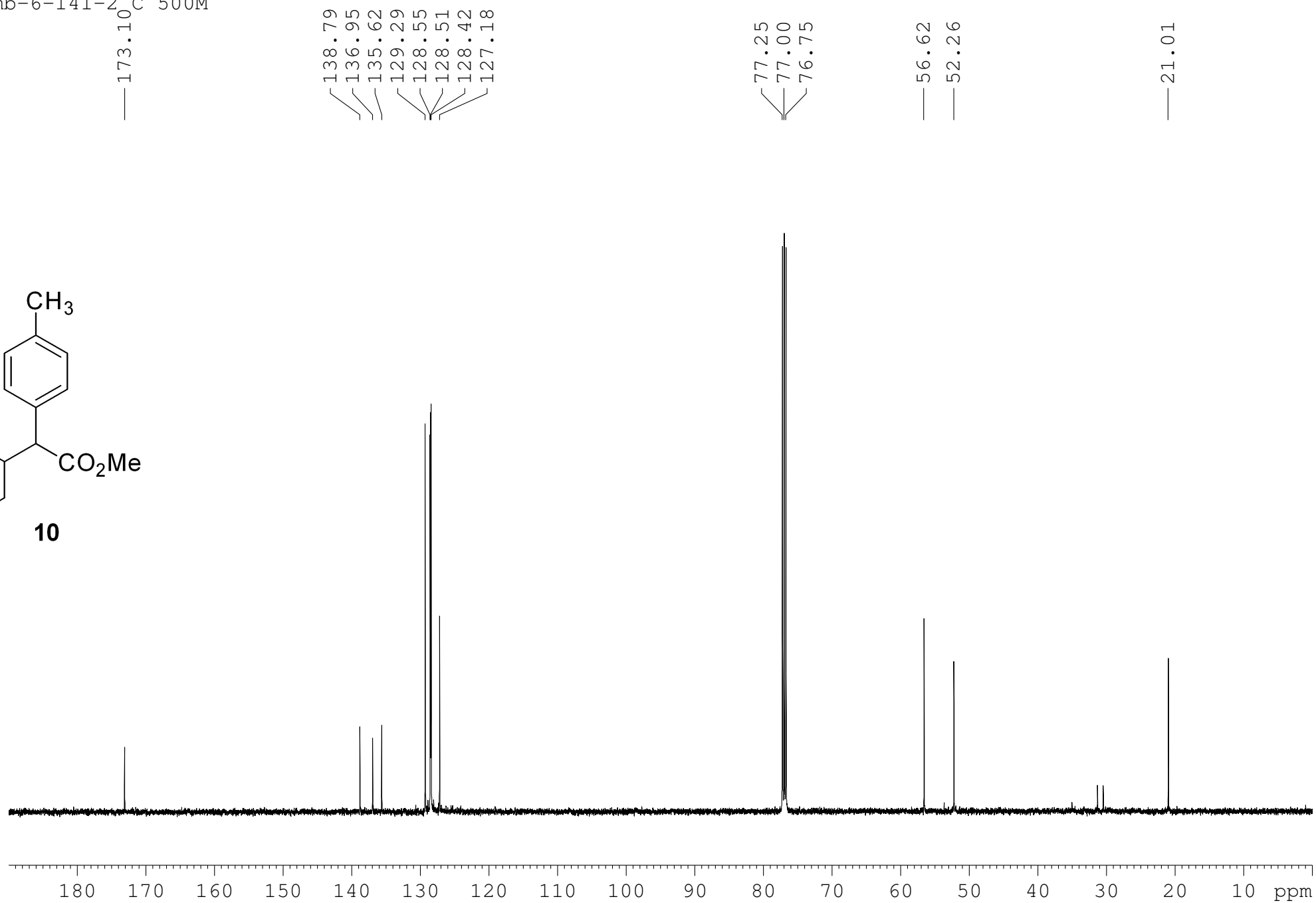
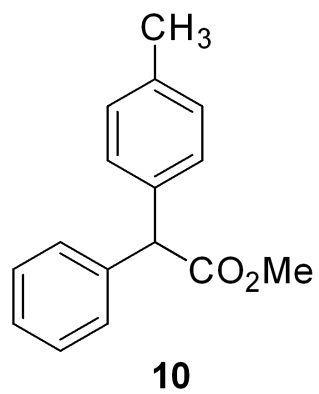
9.13

1.00

3.15

3.17

mb-6-141-2 C 500M



MB-9-146
MB-9-146

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7.203

7.184

7.150

7.130

7.103

7.083

7.015

6.997

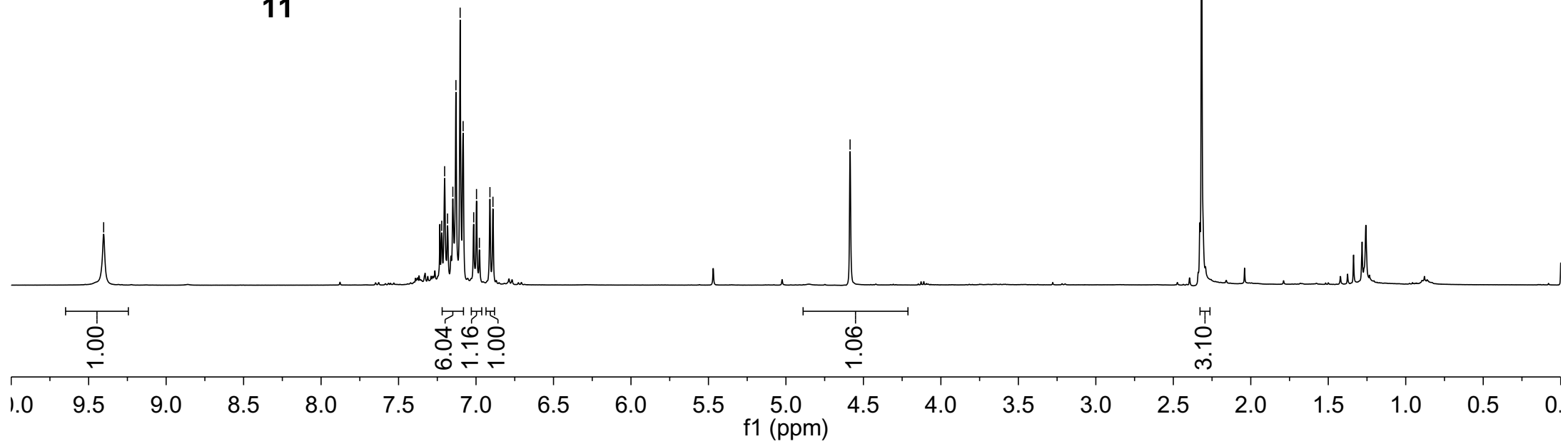
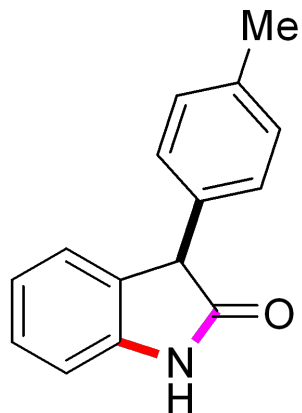
6.978

6.910

6.891

—4.586

—2.318



MB-9-146
MB-9-146

—179.453

141.726

137.332

133.358

129.817

129.608

128.309

128.249

125.082

122.637

—110.124

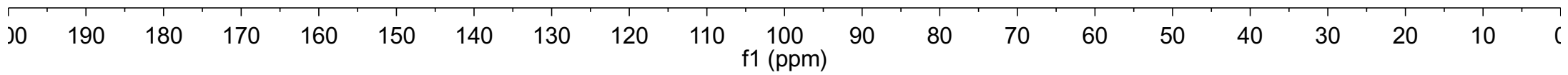
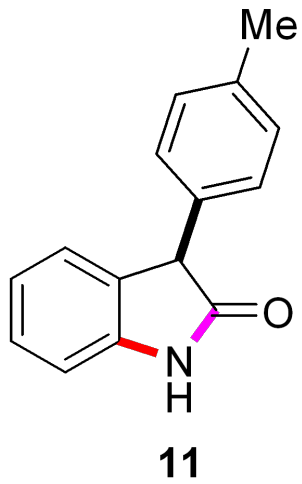
77.317

77.000

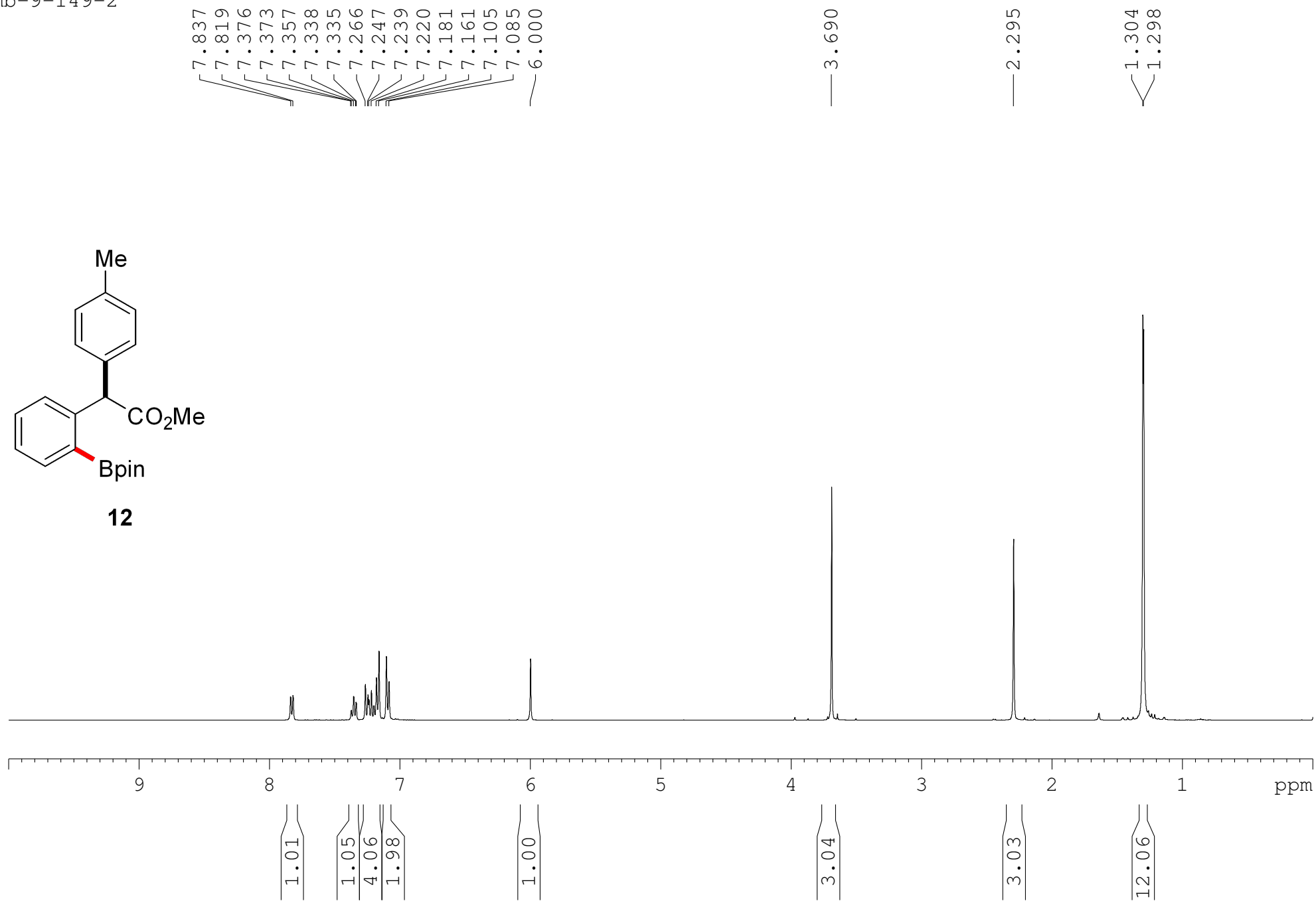
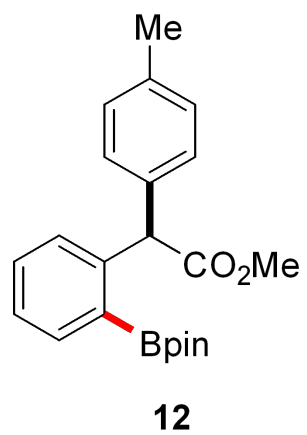
76.682

—52.420

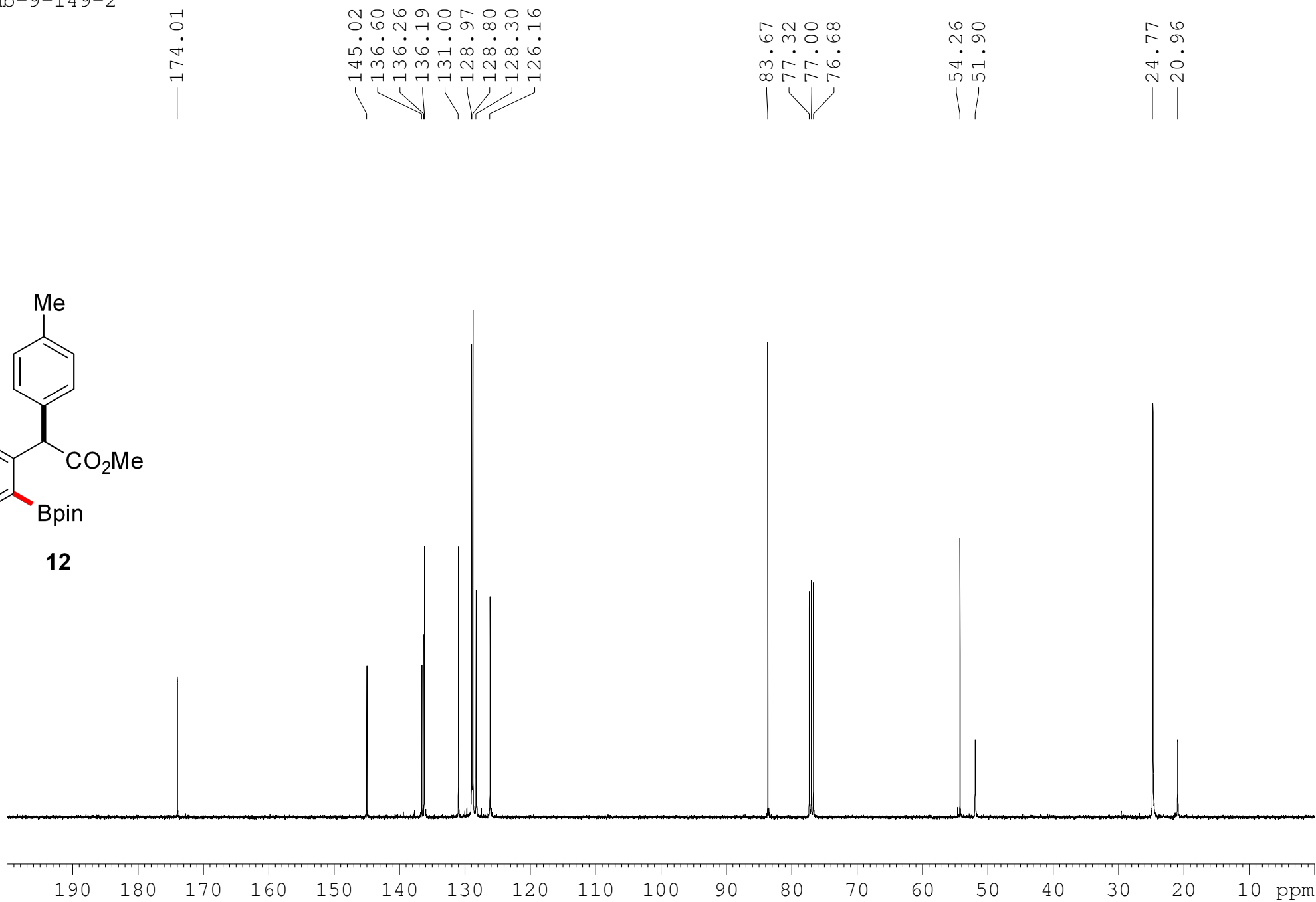
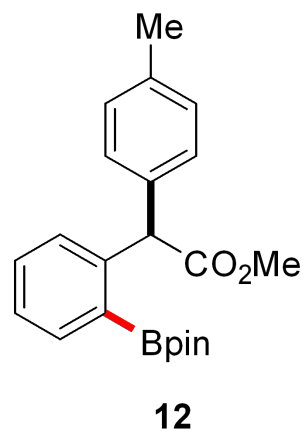
—21.046



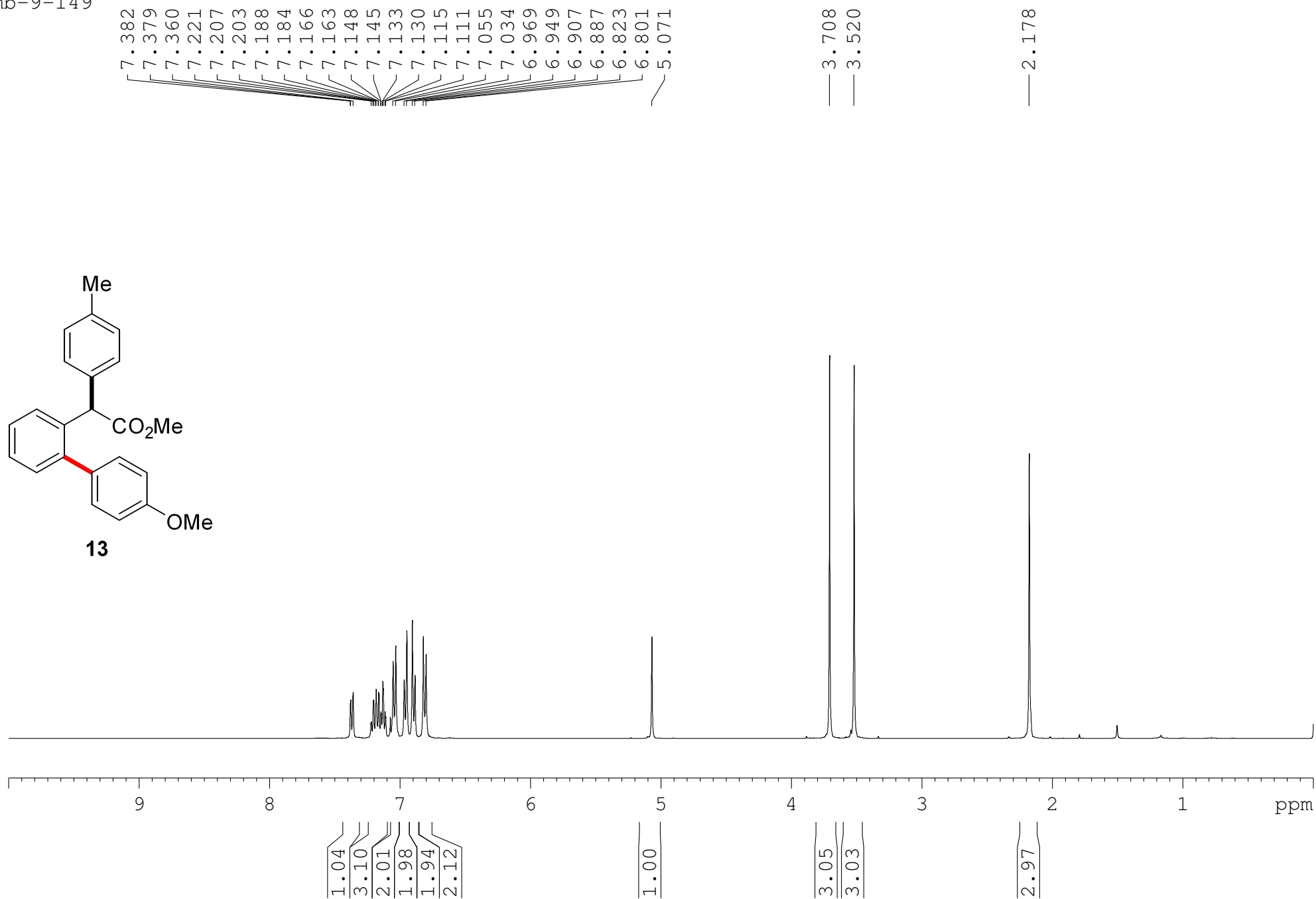
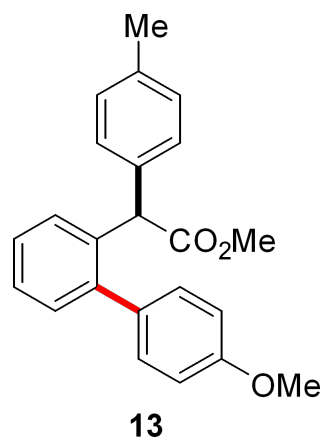
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mb-9-149-2



mb-9-149



mb-9-149

—173.46

—158.79

141.98

136.49

136.34

135.95

133.30

130.37

129.07

128.70

128.41

127.34

126.92

113.52

77.32

77.00

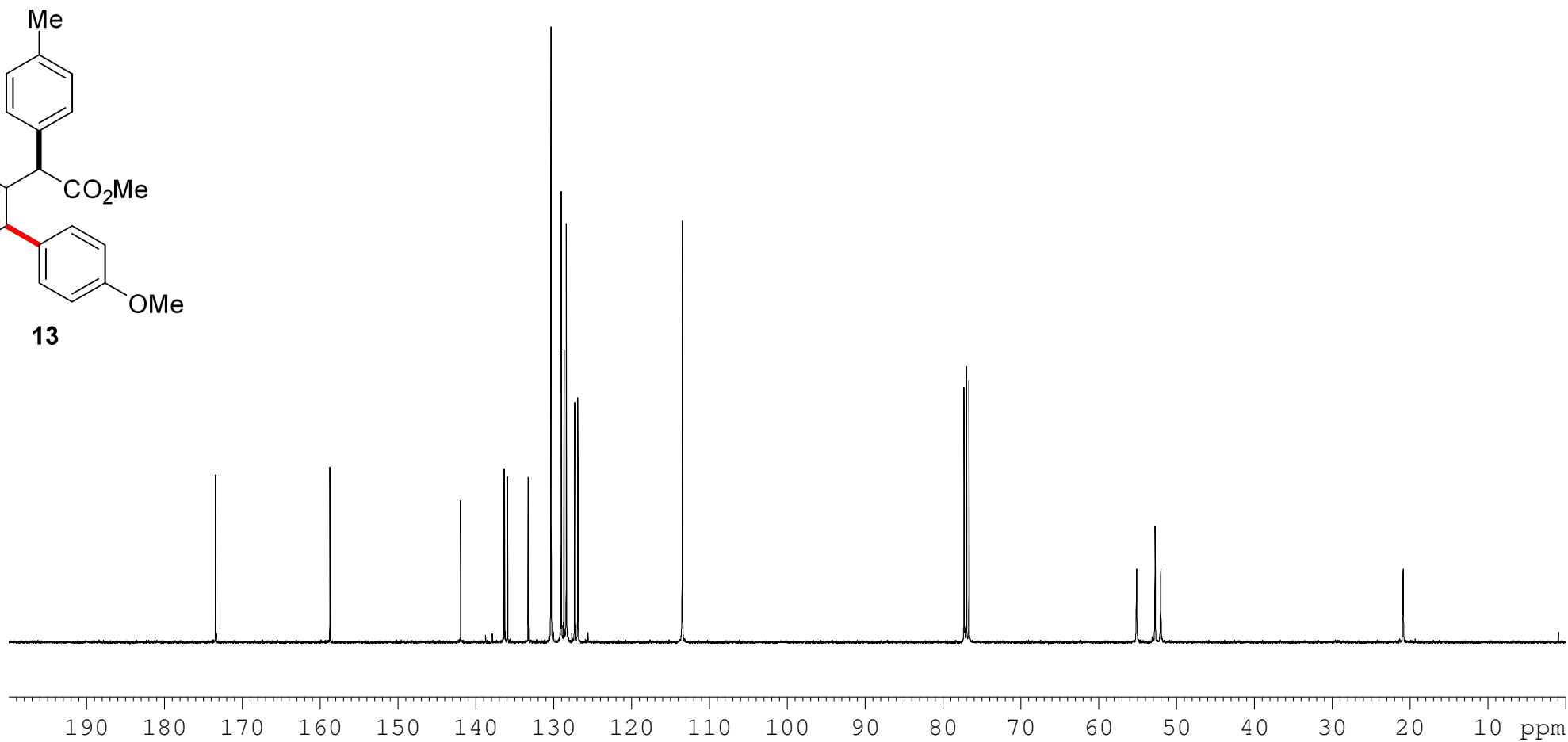
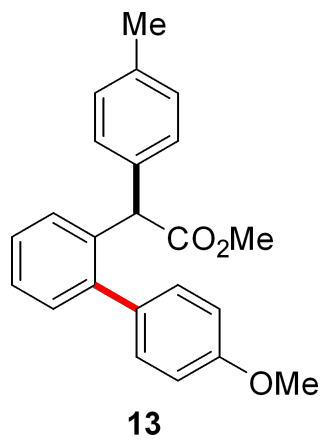
76.68

55.13

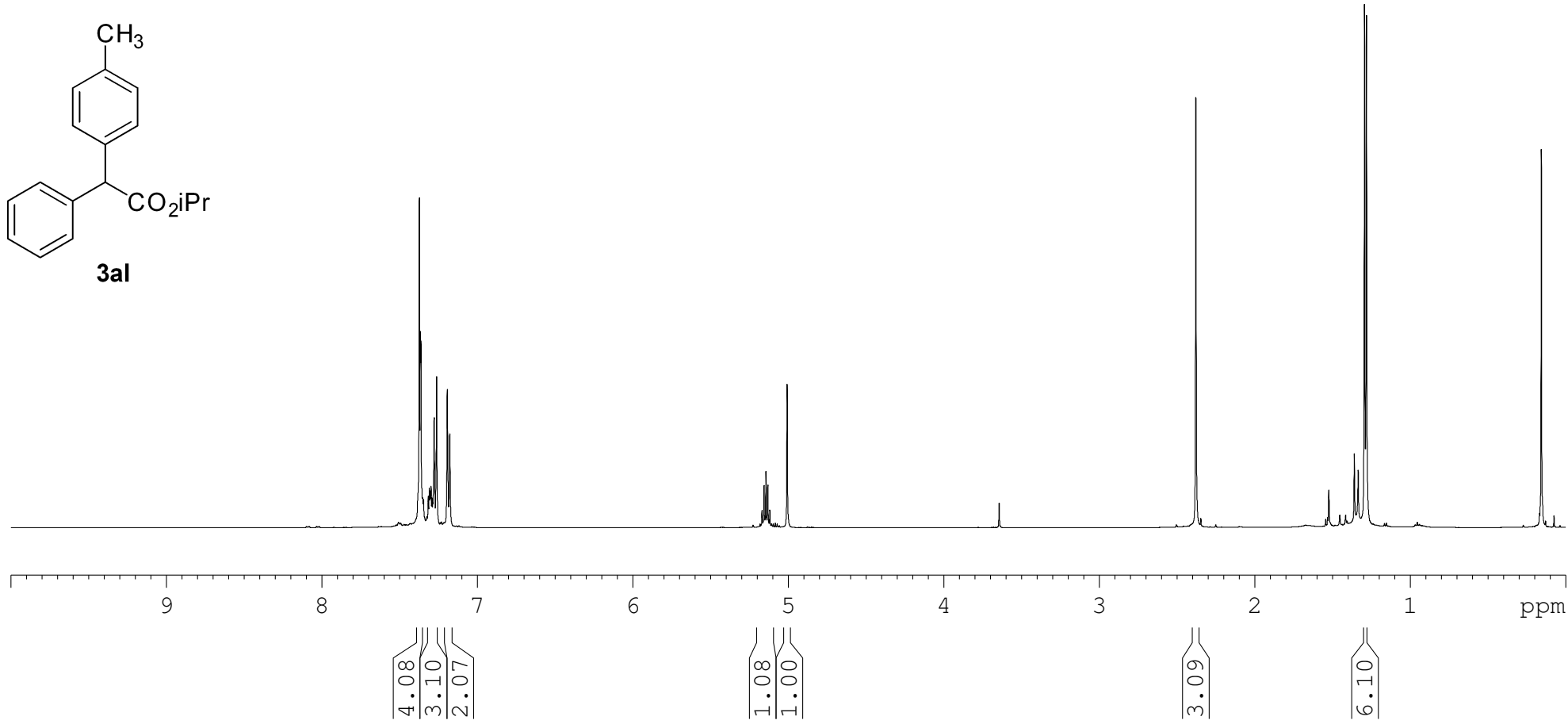
52.79

52.04

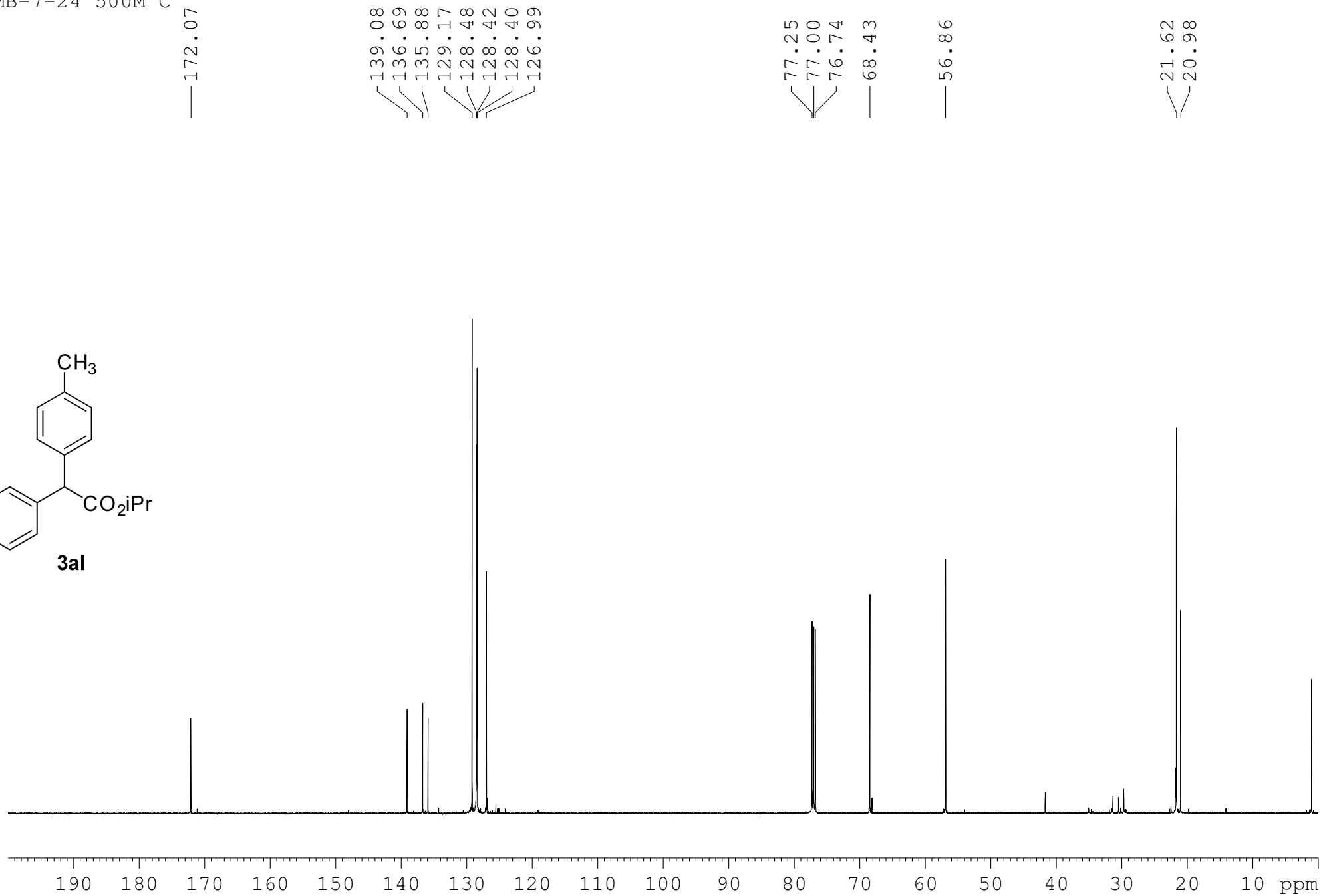
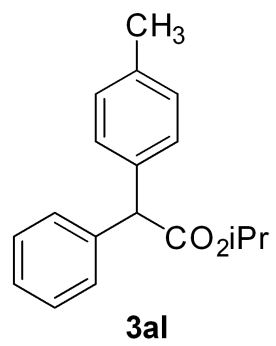
—20.90



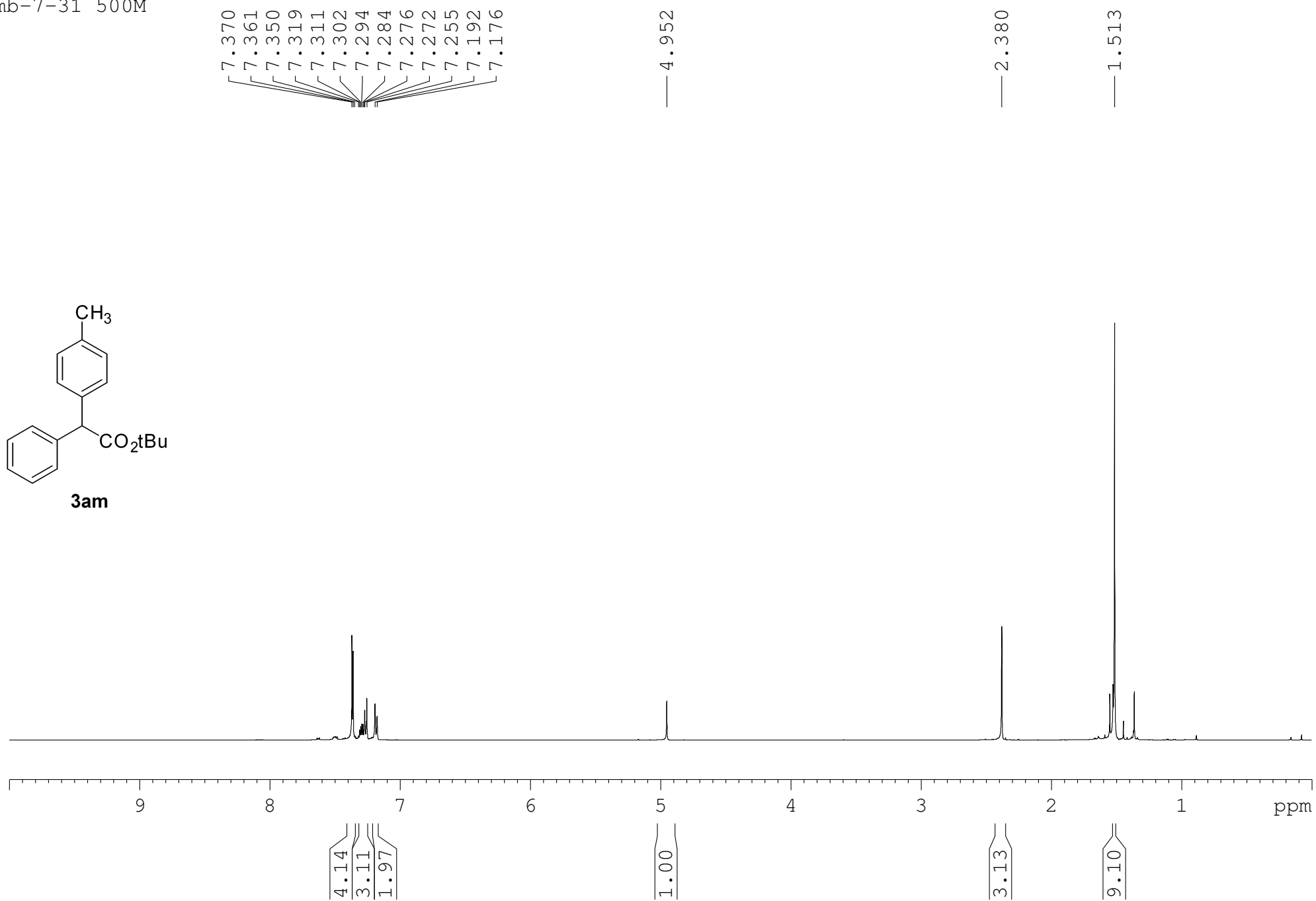
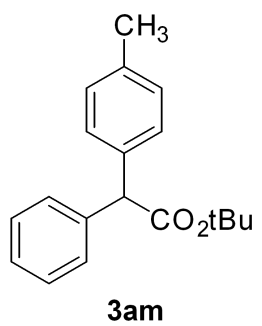
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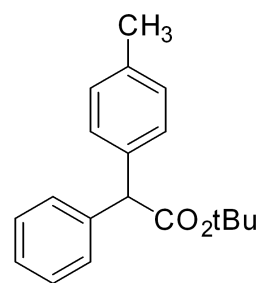
MB-7-24 500M C



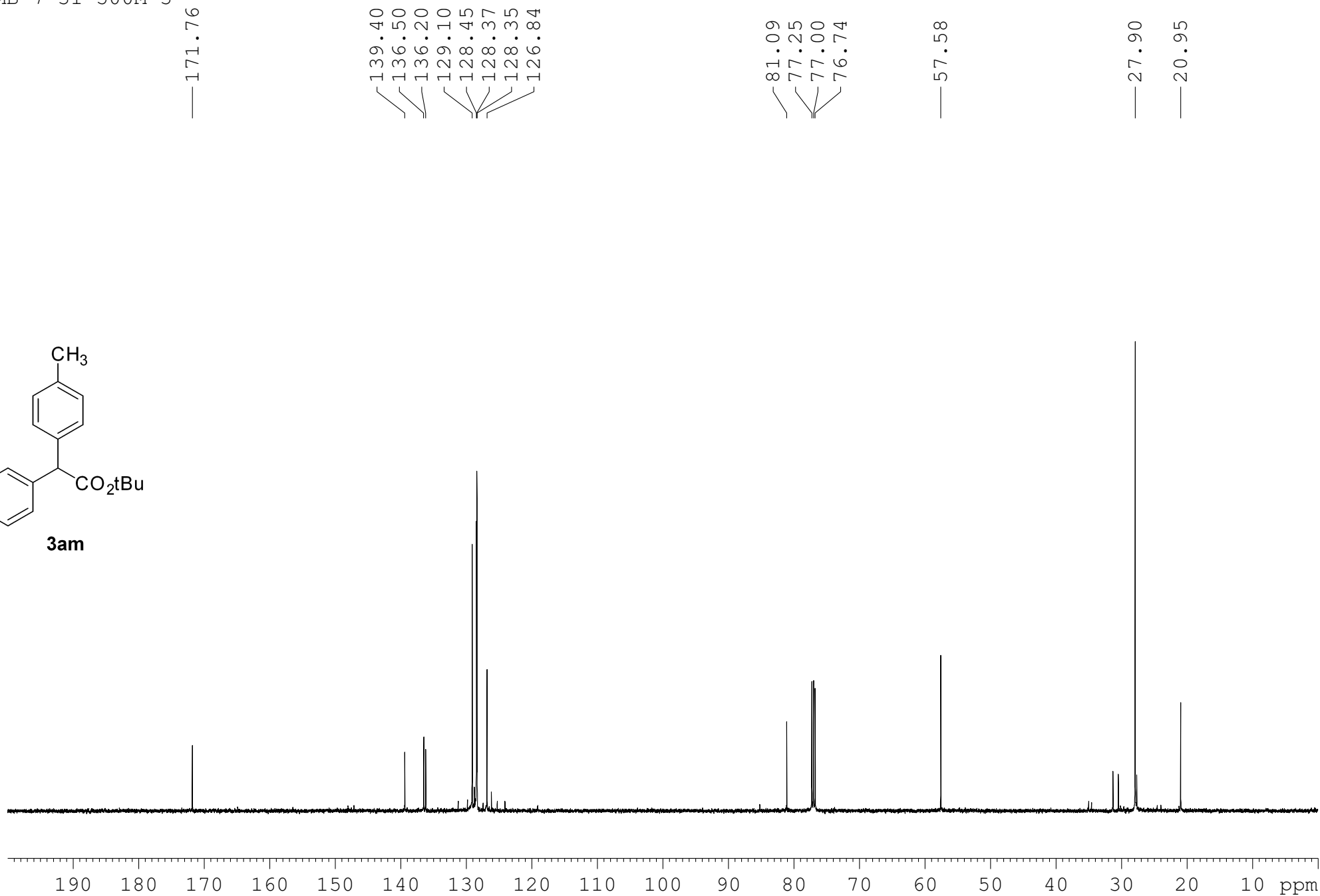
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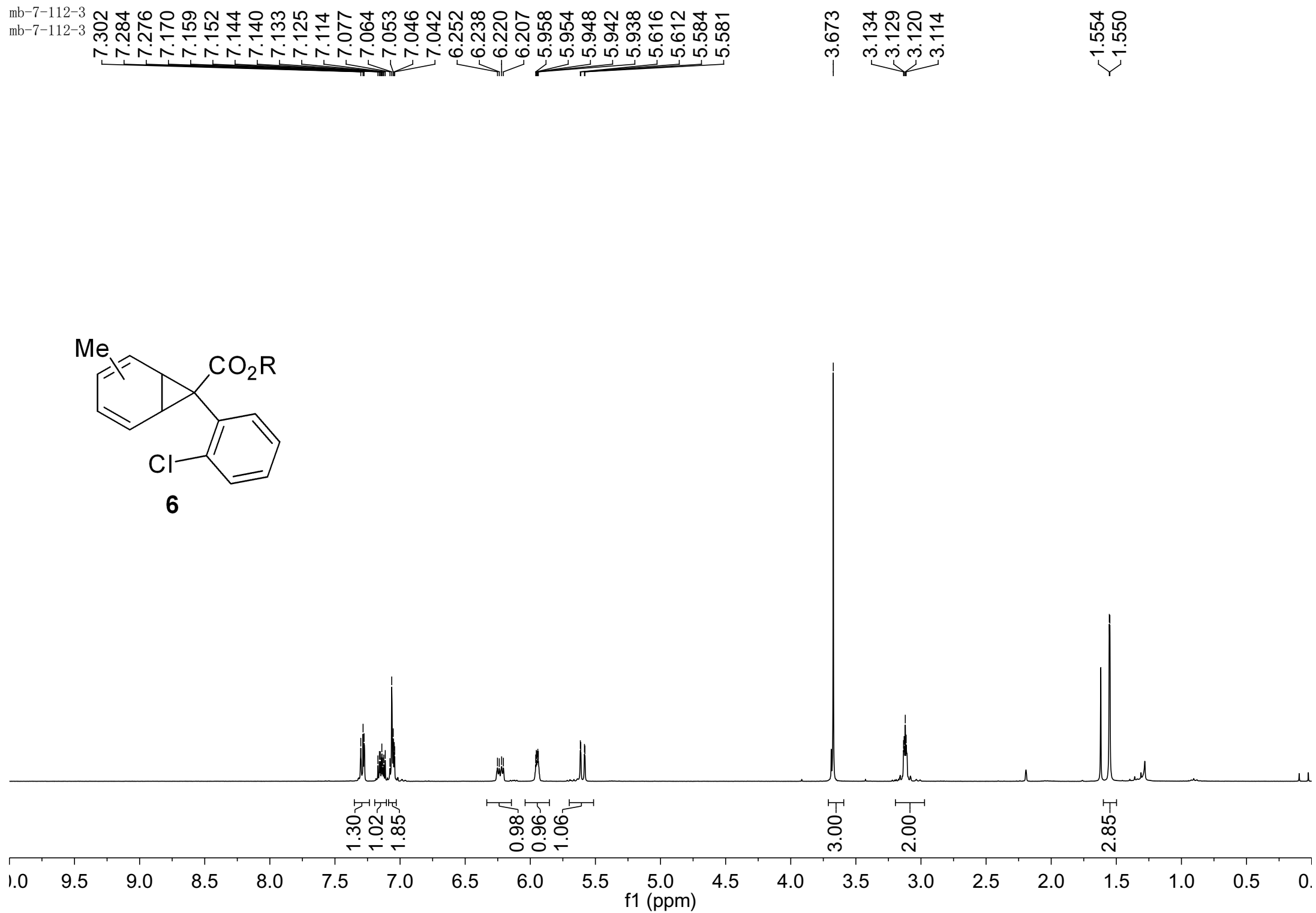
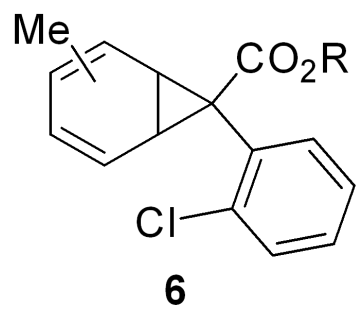
MB-7-31 500M-3



3am



mb-7-112-3
mb-7-112-3



mb-7-122-3
mb-7-122-3

—176.210

136.892
135.333
133.171
130.816
129.363
128.597
128.248
124.794
124.296
119.028

77.318
77.000
76.683

—52.855

37.637
36.728

—24.263
—21.084

