

Direct Carboxylation of Allylic Halides with Carbon Dioxide in the Presence of Indium

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Supporting Information

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General Information. All reactions were carried out in a 25 mL autoclave. Allylic bromides **1a-1e** and **1j-1o** were prepared from the corresponding alcohols according to the literature.^{1,2} Allylic bromides **1f** (from Adamas), **1g** (from Acros), **1h** (from TCI), **1i** (from Alfa-Aesar) were purchased from commercial sources. Indium powder (425 mesh) was purchased from Changsha Asian Light Economic Trade Co, Ltd and used without further purification. CsF was purchased from Alfa-Aesar. DMF and DCM were dried over CaH₂ before distillation. The purity of CO₂ is over 99.995% and used without purification. All the temperatures are referred to the bath temperature. NMR spectra were taken using TMS (¹H, δ = 0), CDCl₃ (¹³C CPD, δ = 77.0) and CFCI₃ (¹⁹F CPD, δ = 0) as the internal standards.

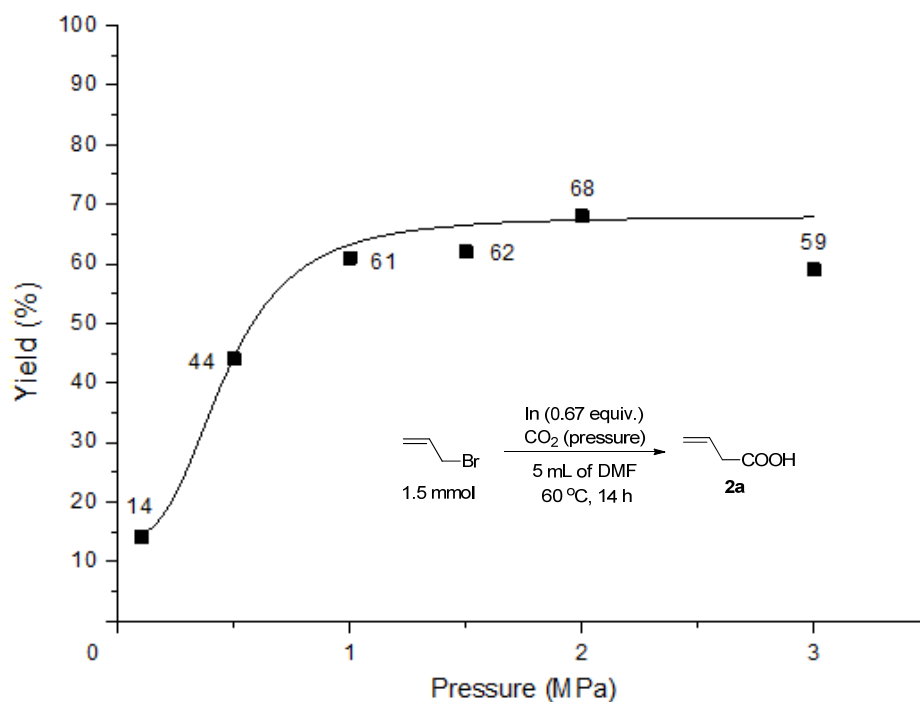
Table S1 Survey of Solvents for In-mediated Allylation of Carbon Dioxide.^a

$$\text{In} + \text{CH}_2=\text{CH}-\text{CH}_2\text{Br} \xrightarrow[\text{solvent, 60 } ^\circ\text{C, 14 h}]{\text{CO}_2 (3.0 \text{ MPa})} \text{CH}_2=\text{CH}-\text{CH}_2\text{COOH}$$

0.67 equiv. 1.0 equiv. **2a**

Entry	Solvent ^b	Yield of 2a (%) ^c
1	DMF	59
2	DMF ^d	51
3	DMA	17
4	DMI	39
5	NMP	23
6	DME	11
7	Dioxane	2
8	MTBE	1
9	THF	23
10	H ₂ O:THF=1:1	n.d.
11	NH ₄ Cl(aq.) :THF=1:1	n.d.
12	H ₂ O	n.d.
13	NH ₄ Cl (aq.)	n.d.
14	EtOH	n.d.
15	CH ₃ CN	n.d.
16	DCM	n.d.
17	Toluene	n.d.

^a The reaction was conducted with 1.5 mmol of allyl bromide, 1.0 mmol of Indium powder (425 mesh) under a 3 MPa CO₂ atmosphere in 5 mL of corresponding solvents at 60 °C. ^b DMF, DMA, DMI, NMP, CH₃CN and DCM were dried over CaH₂ before distillation. DME, dioxane, MTBE, THF and toluene were dried over sodium before distillation. EtOH was dried with magnesium before distillation. ^c Determined by ¹H NMR analysis using 17.5 μ L of CH₂Br₂ as the internal standard. ^d Purchased from Shanghai Chemical Reagent Co., Ltd. and was used without further drying.




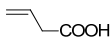
Scheme S1. The Effect of CO₂ Pressure on the Reaction.

Table S2. Survey of Temperature and Loading of Indium.^a

$\text{In } x \text{ equiv.} + \text{allyl bromide } 1.0 \text{ equiv.} \xrightarrow[\text{DMF, temp., 14 h}]{\text{CO}_2 (2 \text{ MPa})} \text{allyl carboxylic acid } 2a$			
Entry	Temp. (°C)	x	Yield of 2a ^b
1	60	0.67	68
2	45	0.67	32
3	19	0.67	6
4	60	0.77	62
5	60	0.91	53

^a The reaction was conducted with 1.5 mmol of allyl bromide, x mmol of In (powder, 425 mesh) under a 2 MPa CO₂ atmosphere in 5 ml of anhydrous DMF. ^b Determined by ¹H NMR analysis using CH₂Br₂ as the internal standard. ^c 14.5 h. ^d The reaction was conducted with 1.3 mmol of allyl bromide. ^e The reaction was conducted with 1.1 mmol of allylic bromide.

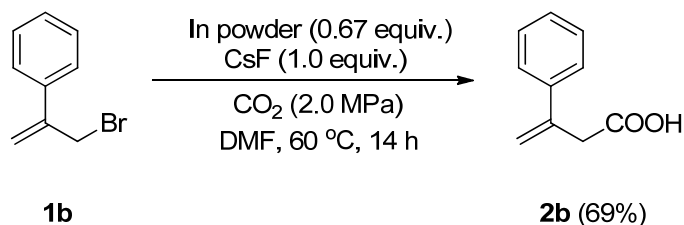
Table S3. Survey of Additives.^a

<div><div>In</div><div>+</div><div></div><div>0.67 equiv.</div></div> <div><div><div>CO₂ (2.0 MPa) additive (x equiv.)</div><div>DMF, 60 °C, 14 h</div></div><div>→</div></div> <div><div></div><div>2a</div></div>		
Entry	Additive (equiv.)	Yield of 2a ^b
1	-	68
2	LiI (1.0)	47
3	NaI (1.0)	57
4	LiCl (1.0)	61
5	CsF (1.0)	72
6	CsF(0.67)	69
7	CsF (0.1)	65

^a The reaction was conducted with 1.5 mmol of allyl bromide, 1.0 mmol of In (powder, 425 mesh) and corresponding additive under a 2 MPa CO₂ atmosphere in 5 mL of anhydrous DMF at 60 °C. ^b Determined by ¹H NMR analysis using CH₂Br₂ as the internal standard.

Synthesis of β,γ -unsaturated Carboxylic Acids by Carboxylation of Allylic Bromides with CO₂ (Table 5 and Table 6).

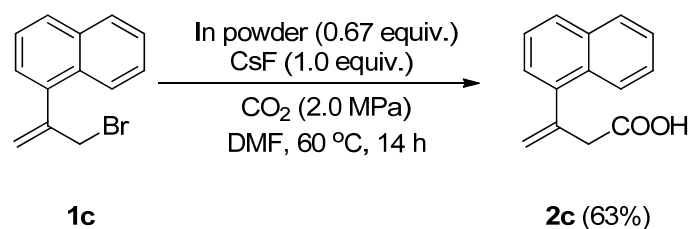
1. Synthesis of 3-Phenyl-3-butenic Acid (**2b**, mbky-7-094):



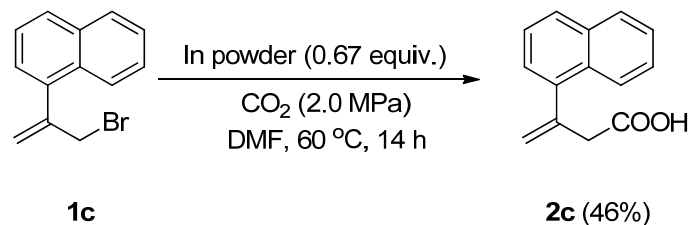
Typical procedure I: To a 25 mL autoclave equipped with a magnetic stirring bar was added CsF (227.9 mg, 1.50 mmol), which was stored in a glove box. Then indium powder (114.7 mg, 1.00 mmol), **1b** (295.6 mg, 1.50 mmol), and DMF (5 mL) were added in the open air. The autoclave was pressurized to 2 MPa with CO₂ and the resulting solution was stirred at 60 °C for 14 h. After slowly releasing the pressure, the resulting suspension was transferred into a 50 mL funnel flask with a glass dropper. The autoclave was washed with ethyl acetate (5 mL \times 2) and the mixture was quenched with 20 mL of 3 M HCl. The aqueous layer was extracted with ethyl acetate (10 mL \times 4) and the combined organic layer was washed with 30 mL of brine, dried over anhydrous Na₂SO₄, filtrated and concentrated. The crude product was purified by column chromatography on silica gel to afford 168.9 mg of **2b**³ (69%, eluent: petroleum ether/ethyl acetate = 5/1 \rightarrow dichloromethane / methanol = 80/1) as a yellow solid: m.p. 48-49 °C (petroleum ether/ ethyl acetate) (Lit.^{3d} m.p.: 45-46 °C, petroleum ether): ¹H NMR (300 MHz, CDCl₃) δ 11.07 (bs, 1 H, COOH), 7.50-7.16 (m, 5 H, ArH), 5.57 (s, 1 H, one proton of CH₂=), 5.24 (s, 1 H, one proton of CH₂=), 3.53 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.9, 140.0, 139.3, 128.4, 127.9, 125.7, 116.8, 40.9; MS (m/z) 162 (M⁺, 93.27), 115 (100); IR (neat, cm⁻¹) 2925, 2858, 1709, 1630, 1495, 1409, 1298, 1228, 1166, 1077, 1028.

The following compounds were prepared according to this **Typical Procedure I**.

2. Synthesis of 3-(1-Naphthyl)-3-butenic Acid (**2c**, mbky-7-120, mbky-8-079):

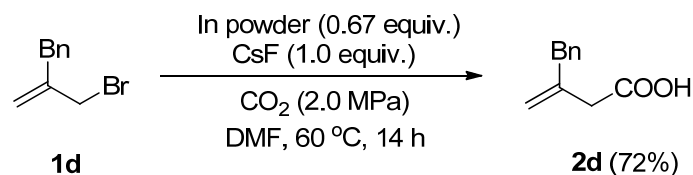


The reaction of **1c** (370.7 mg, 1.50 mmol), indium powder (114.9 mg, 1.00 mmol), CsF (228.0 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 201.1 mg of **2c**³ (63%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a white solid: m.p. 76-77 °C (petroleum ether/ ethyl acetate) (Lit.^{3a} m.p.: 74.5 °C): ¹H NMR (300 MHz, CDCl₃) δ 10.01 (bs, 1 H, COOH), 8.05-7.90 (m, 1 H, ArH) 7.85-7.70 (m, 2 H, ArH), 7.50-7.20 (m, 4 H, ArH), 5.59 (s, 1 H, one proton of CH₂=), 5.32 (s, 1 H, one proton of CH₂=), 3.53 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.4, 140.3, 139.4, 133.7, 130.8, 128.3, 127.8, 126.1, 125.7, 125.4, 125.3, 125.2, 120.3, 43.3; MS (m/z) 212 (M⁺, 4.90), 91 (100); IR (neat, cm⁻¹) 3039, 2929, 2851, 1708, 1440, 1411, 1320, 1297, 1269, 1168, 1129, 1005.



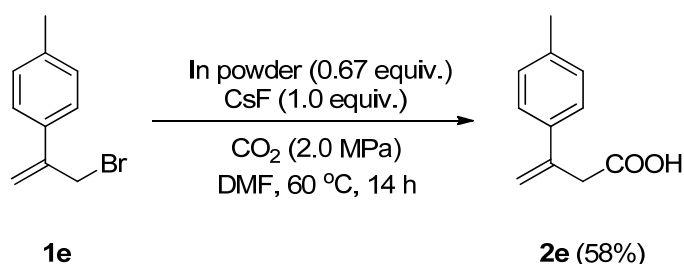
The reaction of **1c** (370.7 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol) and CO₂ in 5 mL of DMF afforded 147.8 mg of **2c**³ (46%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a white solid: m.p. 76-77 °C (petroleum ether/ ethyl acetate) (Lit.^{3a} m.p.: 74.5 °C): ¹H NMR (300 MHz, CDCl₃) δ 10.21 (bs, 1 H, COOH), 8.06-7.96 (m, 1 H, ArH) 7.88-7.72 (m, 2 H, ArH), 7.51-7.32 (m, 4 H, ArH), 5.61 (s, 1 H, one proton of CH₂=), 5.34 (s, 1 H, one proton of CH₂=), 3.55 (s, 2 H, CH₂).

3. Synthesis of 3-Benzyl-3-butenic Acid (**2d**, mbky-7-113):



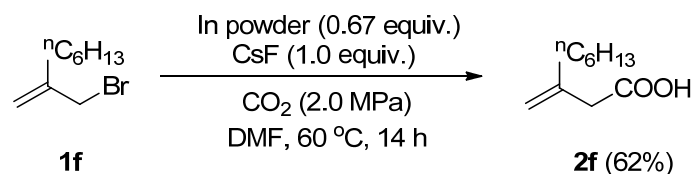
The reaction of **1d** (316.1 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), CsF (227.0 mg, 1.49 mmol) and CO₂ in 5 mL of DMF afforded 189.5 mg of **2d**³ (72%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 9.11 (bs, 1 H, COOH), 7.40-6.70 (m, 5 H, ArH), 5.04 (s, 1 H, one proton of CH₂=), 5.00 (s, 1 H, one proton of CH₂=), 3.48 (s, 2 H, CH₂Ph), 3.02 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.8, 141.2, 138.5, 129.1, 128.4, 126.4, 116.3, 42.6, 40.6; MS (m/z) 176 (M⁺, 85.22), 131 (100); IR (neat, cm⁻¹) 3085, 3063, 3029, 2922, 1707, 1650, 1603, 1495, 1454, 1432, 1415, 1332, 1290, 1255, 1226, 1178, 1075, 1030.

4. Synthesis of 3-(4-Tolyl)-3-butenic Acid (**2e**, mbky-8-096):

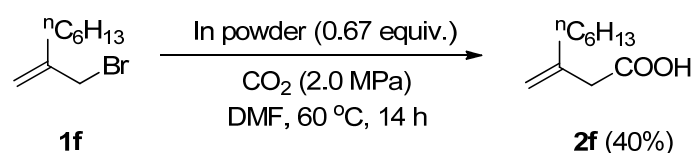


The reaction of **1e** (316.5 mg, 1.50 mmol), indium powder (114.9 mg, 1.00 mmol), CsF (227.3 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 153.5 mg of **2e**³ (58%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a white solid: sublimation observed at 99 °C, m.p. 112-113 °C (petroleum ether/ ethyl acetate) (Lit.^{3a} m.p.: 106-107 °C): ¹H NMR (300 MHz, CDCl₃) δ 10.27 (bs, 1 H, COOH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 7.13 (d, *J* = 8.1 Hz, 2 H, ArH), 5.54 (s, 1 H, one proton of CH₂=), 5.19 (s, 1 H, one proton of CH₂=), 3.51 (s, 2 H, CH₂), 2.33 (s, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 177.9, 139.9, 137.7, 136.4, 129.1, 125.5, 115.9, 40.9, 21.1; MS (m/z) 176 (M⁺, 47.58), 91 (100); IR (neat, cm⁻¹) 2986, 2971, 2919, 1689, 1631, 1513, 1418, 1346, 1305, 1228, 1053.

5. Synthesis of 3-Hexyl-3-butenic Acid (**2f**, mbky-7-121, mbky-8-125):

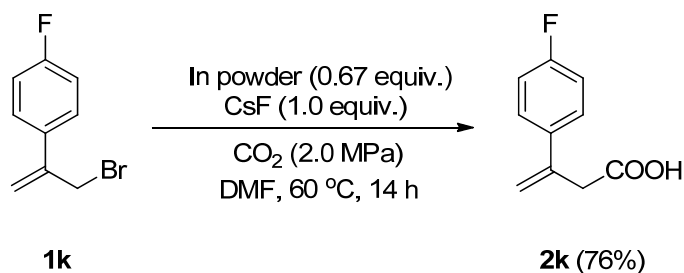


The reaction of **1f** (244.2 mg, 1.19 mmol), indium powder (91.1 mg, 0.79 mmol), CsF (180.9 mg, 1.19 mmol), and CO₂ in 4 mL of DMF afforded 126.4 mg of **2f** (62%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 11.29 (bs, 1 H, COOH), 4.96 (s, 1 H, one proton of CH₂=), 4.93 (s, 1 H, one proton of CH₂=), 3.08 (s, 2 H, CH₂CO), 2.12 (t, *J* = 7.5 Hz, 2 H, CH₂), 1.55-1.16 (m, 8 H, 4 × CH₂), 0.88 (t, *J* = 6.6 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 178.2, 142.0, 114.0, 41.6, 35.8, 31.7, 28.9, 27.3, 22.6, 14.1; MS (ESI) 169 [(M-H)⁻]; IR (neat, cm⁻¹) 2958, 2929, 2858, 1711, 1649, 1408, 1295, 1218, 1155; HRMS (ESI) calcd. for C₁₀H₁₈O₂ [(M-H)⁻]: 169.1234; Found: 169.1231.



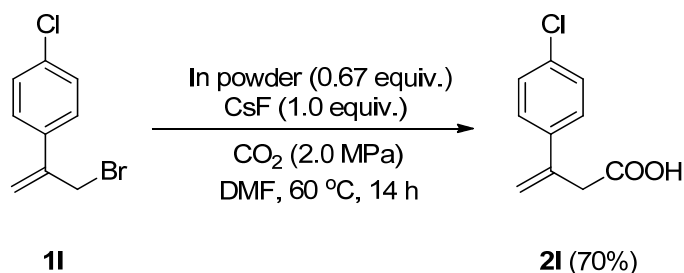
The reaction of **1f** (307.8 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), and CO₂ in 5 mL of DMF afforded 102.7 mg of **2f** (40%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 9.70 (bs, 1 H, COOH), 4.96 (s, 1 H, one proton of CH₂=), 4.95 (s, 1 H, one proton of CH₂=), 3.08 (s, 2 H, CH₂CO), 2.12 (t, *J* = 7.2 Hz, 2 H, CH₂), 1.52-1.20 (m, 8 H, 4 × CH₂), 0.88 (t, *J* = 6.8 Hz, 3 H, CH₃).

6. Synthesis of 3-(4-Fluorophenyl)-3-butenic Acid (**2k**, mbky-7-112):



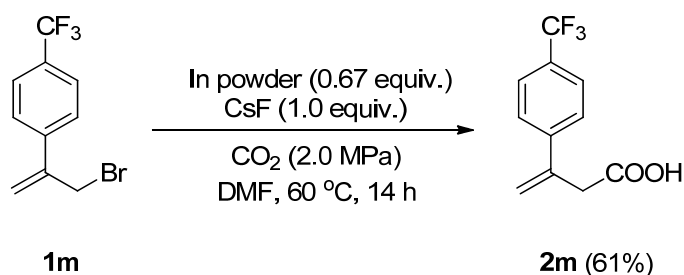
The reaction of **1k** (322.6 mg, 1.50 mmol), indium powder (114.9 mg, 1.00 mmol), CsF (227.6 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 204.8 mg of **2k**^{3c} (76%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 30/1) as a white solid: m.p. 66-68 °C (petroleum ether/ ethyl acetate) (Lit.^{3e} m.p.: 67 °C): ¹H NMR (300 MHz, CDCl₃) δ 10.80 (bs, 1 H, COOH), 7.50-7.30 (m, 2 H, ArH), 7.10-6.90 (m, 2 H, ArH), 5.51 (s, 1 H, one proton of CH₂=), 5.23 (s, 1 H, one proton of CH₂=), 3.51 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.8, 162.5 (d, *J* = 245.8 Hz), 139.1, 135.4 (d, *J* = 3.4 Hz), 127.4 (d, *J* = 8.0 Hz), 116.8, 115.3 (d, *J* = 21.4 Hz), 41.0; ¹⁹F NMR (282 MHz, CDCl₃) δ -114.8; MS (*m/z*) 180 (*M*⁺, 99.1), 109 (100); IR (neat, cm⁻¹) 3034, 2927, 2853, 1715, 1704, 1631, 1602, 1510, 1416, 1341, 1300, 1225, 1164, 1111, 1014.

7. Synthesis of 3-(4-Chlorophenyl)-3-butenic Acid (**2l**, mbky-9-011):



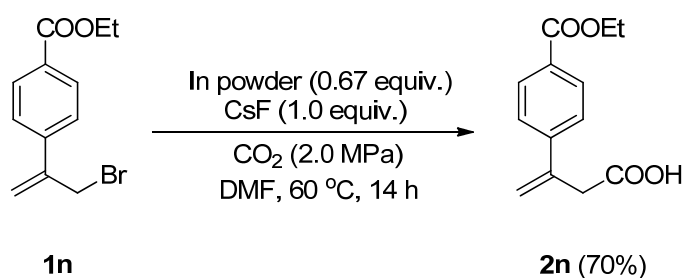
The reaction of **1l** (347.4 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), CsF (227.6 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 206.0 mg of **2l**^{3c} (70%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 80/1) as a white solid: m.p. 123-124 °C (petroleum ether/ ethyl acetate): ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.20 (m, 4 H, ArH), 5.56 (s, 1 H, one proton of CH₂=), 5.27 (s, 1 H, one proton of CH₂=), 3.52 (s, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 139.1, 137.8, 133.8, 128.6, 127.1, 117.5, 40.7; MS (*m/z*) 198 (³⁷Cl, *M*⁺, 16.7), 196 (³⁵Cl, *M*⁺, 50.1), 115 (100); IR (neat, cm⁻¹) 3056, 2919, 2851, 2744, 2620, 1691, 1633, 1492, 1420, 1349, 1311, 1229, 1104, 1089, 1012.

8. Synthesis of 3-(4-Trifluoromethylphenyl)-3-butenic Acid (**2m**, mbky-7-107):



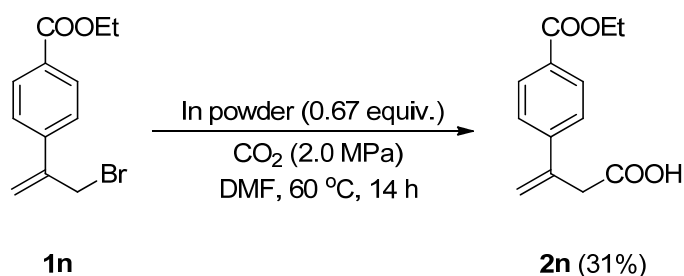
The reaction of **1m** (397.6 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), CsF (227.9 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 211.5 mg of **2m**^{3c} (61%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 30/1) as a white solid: sublimation observed at 100-101 °C, m.p. 105-106 °C (petroleum ether/ ethyl acetate): ¹H NMR (300 MHz, CDCl₃) δ 8.73 (bs, 1 H, COOH), 7.59 (d, *J* = 8.4 Hz, 2 H, ArH), 7.52 (d, *J* = 8.4 Hz, 2 H, ArH), 5.64 (s, 1 H, one proton of CH₂=), 5.36 (s, 1 H, one proton of CH₂=), 3.56 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.2, 142.9 (d, *J* = 1.3 Hz), 139.1, 129.9 (q, *J* = 33.7 Hz), 126.1, 125.4 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 270.1 Hz), 119.0, 40.7; ¹⁹F NMR (282 MHz, CDCl₃) δ -63.1; MS (*m/z*) 230 (*M*⁺, 45.19), 44 (100); IR (neat, cm⁻¹) 3663, 2985, 2972, 2902, 1694, 1407, 1323, 1227, 1168, 1120, 1102, 1066, 1016.

9. Synthesis of 3-[4-(Ethoxycarbonyl)phenyl]-3-butenic Acid (**2n**, mbky-7-135, 9-117):



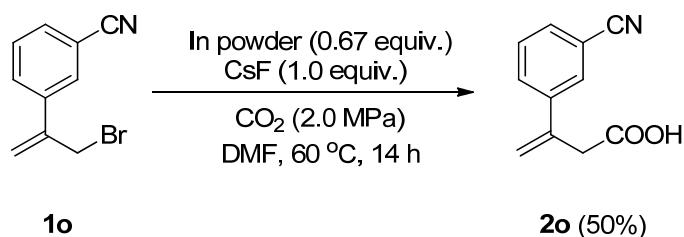
The reaction of **1n** (403.7 mg, 1.50 mmol), indium powder (114.9 mg, 1.00 mmol), CsF (226.9 mg, 1.49 mmol), and CO₂ in 5 mL of DMF afforded 247.2 mg of **2n** (70%, eluent: petroleum ether/ethyl acetate = 7/1 → dichloromethane / methanol = 30/1) as a white solid: m.p. 88-90 °C (petroleum ether/ ethyl acetate): ¹H NMR (300 MHz, CDCl₃) δ 8.05-7.94 (m, 2 H, ArH), 7.52-7.45 (m, 2 H ArH), 5.66 (s, 1 H, one proton of CH₂=), 5.36 (s, 1 H, one proton of CH₂=), 4.37 (q, *J* = 7.2 Hz, 2 H, OCH₂), 3.56 (s,

2 H, CH₂), 1.39 (t, $J = 7.1$ Hz, 3 H, CH₃); ¹H NMR (300 MHz, DMSO-*D*₆) δ 12.33 (bs, 1 H, -COOH), 7.96-7.88 (m, 2 H, ArH), 7.65-7.57 (m, 2 H ArH), 5.69 (s, 1 H, one proton of CH₂=), 5.35 (s, 1 H, one proton of CH₂=), 4.30 (q, $J = 7.2$ Hz, 2 H, OCH₂), 3.55 (s, 2 H, CH₂), 1.31 (t, $J = 6.9$ Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 177.2, 166.3, 143.7, 139.4, 129.8, 125.7, 118.8, 61.0, 40.6, 14.3; MS (m/z) 234 (M^+ , 39.68), 189 (100); ¹³C NMR (75 MHz, DMSO-*D*₆) δ 172.2, 165.5, 144.1, 140.4, 129.2, 128.9, 125.9, 118.2, 60.7, 40.3, 14.0 ; IR (neat, cm⁻¹) 2926, 2855, 1707, 1689, 1607, 1405, 1282, 1222, 1185, 1127, 1113, 1022; Anal. calcd for C₁₃H₁₄O₄: C 66.66, H 6.02; found: C 66.35, H 6.10.



The reaction of **1n** (404.2 mg, 1.50 mmol), indium powder (115.0 mg, 1.00 mmol), and CO₂ in 5 mL of DMF afforded 110.0 mg of **2n** (31%, eluent: petroleum ether/ethyl acetate = 7/1 → dichloromethane / methanol = 30/1) as a white solid: m.p. 88-90 °C (petroleum ether/ ethyl acetate): ¹H NMR (300 MHz, CDCl₃) δ 8.05-7.96 (m, 2 H, ArH), 7.52-7.45 (m, 2 H ArH), 5.67 (s, 1 H, one proton of CH₂=), 5.36 (s, 1 H, one proton of CH₂=), 4.37 (q, $J = 6.9$ Hz, 2 H, OCH₂), 3.57 (s, 2 H, CH₂), 1.39 (t, $J = 7.2$ Hz, 3 H, CH₃).

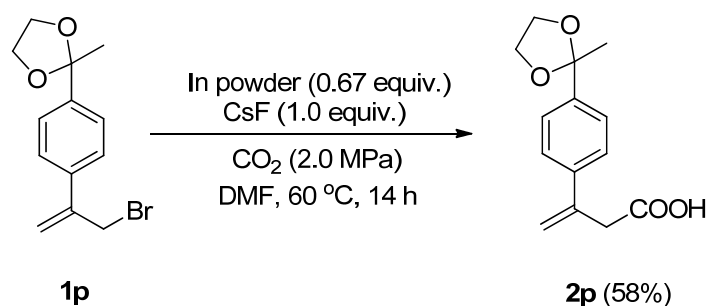
10. Synthesis of 3-(3-Cyanophenyl)-3-butenic Acid (**2o**, mbky-8-156):



The reaction of **1o** (333.3 mg, 1.50 mmol), indium powder (115.0 mg, 1.00 mmol), CsF (228.2 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded 139.8 mg of **2o** (50%,

eluent: petroleum ether/ethyl acetate = 5/1→ dichloromethane / methanol = 30/1) as a white solid: m.p. 81-82 °C (petroleum ether/ ethyl acetate); ^1H NMR (300 MHz, CDCl_3) δ 8.74 (bs, 1 H, COOH), 7.70 (s, 1 H, ArH), 7.65 (d, J = 8.1 Hz, 1 H, ArH), 7.58 (d, J = 7.8 Hz, 1 H, ArH), 7.45 (t, J = 7.8 Hz, 1 H, ArH), 5.62 (s, 1 H, one proton of $\text{CH}_2=$), 5.39 (s, 1 H, one proton of $\text{CH}_2=$), 3.55 (s, 2 H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 176.7, 140.8, 138.4, 131.3, 130.1, 129.5, 129.3, 119.3, 118.6, 112.7, 40.5; MS (m/z) 187 (M^+ , 54.85), 117 (100); IR (neat, cm^{-1}) 2922, 2852, 2230, 1698, 1635, 1487, 1416, 1399, 1341, 1311, 1296, 1277, 1225; HRMS calcd. for $\text{C}_{11}\text{H}_9\text{NO}_2$ (M^+): 187.0633; Found: 187.0632.

11. Synthesis of 3-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)-3-butenic Acid (**2p**, mbky-8-155):

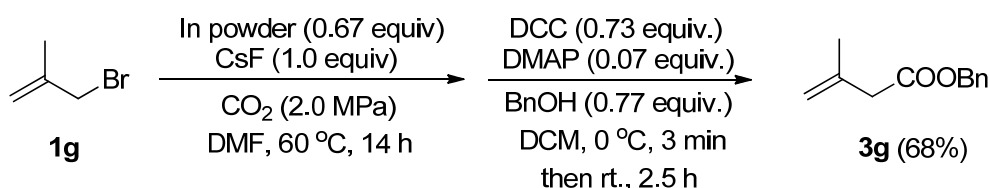


The reaction of **1p** (424.9 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), CsF (228.0 mg, 1.50 mmol), and CO_2 in 5 mL of DMF afforded 217.7 mg of **2p** (58%, eluent: petroleum ether/ethyl acetate = 6/1→ dichloromethane / methanol = 30/1) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.60 (bs, 1 H, COOH), 7.50-7.30 (m, 4 H, ArH), 5.59 (s, 1 H, one proton of $\text{CH}_2=$), 5.26 (s, 1 H, one proton of $\text{CH}_2=$), 4.10-3.90 (m, 2 H, OCH_2), 3.85-3.70 (m, 2 H, OCH_2), 3.54 (s, 2 H, CH_2CO), 1.64 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 177.3, 142.9, 139.7, 138.8, 125.5, 125.4, 116.9, 108.7, 64.4, 40.7, 27.43, 27.40; MS (m/z) 248 (M^+ , 3.31), 233 (100); IR (neat, cm^{-1}) 2995, 2855, 1697, 1628, 1450, 1423, 1373, 1291, 1255, 1235, 1194, 1175, 1101, 1078, 1040, 1015; HRMS calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_4$ (M^+): 248.1049; Found: 248.1051.

Carboxylation of Commercially Available Allylic Bromides with CO_2 Followed

by Benzyl Esterification (Scheme 3).

1. Synthesis of Benzyl 3-methylbut-3-enoate (**3g**, mbky-7-180):

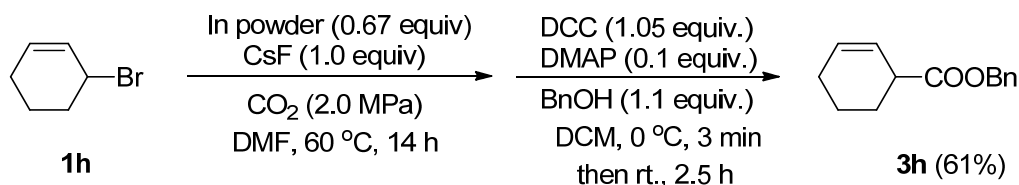


To a 25 mL autoclave equipped with a magnetic stirring bar was added CsF (228.2 mg, 1.50 mmol), which was stored in a glove box. Then indium powder (114.8 mg, 1.00 mmol), **1g** (Adamas, purity: 97%, 208.9 mg, 1.50 mmol), and DMF (5 mL) in the air were added. The autoclave was pressurized to 2 MPa with CO₂ and stirred at 60 °C for 14 h. After slowly releasing the pressure, the resulting suspension was transferred into a 50 mL funnel flask with a glass dropper. The autoclave was washed with ethyl acetate (5 mL × 2). The combined mixture was quenched with 20 mL of 3 M HCl. The aqueous layer was extracted with ethyl acetate (10 mL × 4). The combined organic layer was washed with 30 mL of brine, dried over anhydrous Na₂SO₄, filtrated, and concentrated to afford the crude product acid.

To a 25 mL Schlenk tube were added BnOH (0.12 mL, density: 1.049, 1.16 mmol), 1 mL of DCM, DMAP (13.0 mg, 0.11 mmol) and the crude product acid prepared above in 4 mL of DCM sequentially. The resulting solution was cooled with a bath of ice-water, which was followed by the addition of a solution of DCC (228.2 mg, 1.10 mmol) in 1 mL of DCM within 3 minutes. Then the resulting mixture was allowed to warm to room temperature and the esterification reaction completed after 2.5 h as monitored by TLC. DCM (30 mL) was added into the suspension and the resulting mixture was filtered through a short pad of silica gel (300-400 mesh) eluted with DCM (10 mL × 2) and concentrated. The crude product was purified by column chromatography on silica gel to afford 195.3 mg of **3g**^{4a} (68%, eluent: petroleum ether/diethyl ether = 80/1) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.27 (m, 5 H, ArH), 5.14 (s, 2 H, CH₂Ph), 4.94-4.88 (m, 1 H, one proton of CH₂=), 4.88-4.83 (m, 1 H, one proton of CH₂=), 3.09 (s, 2 H, =CCH₂), 1.80 (s, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.2, 138.4, 135.9, 128.5, 128.19, 128.16, 114.8, 66.4,

43.4, 22.5; MS (m/z) 190 (M^+ , 0.69), 91 (100); IR (neat, cm^{-1}) 1737, 1652, 1498, 1377, 1331, 1283, 1256, 1234, 1149, 1028.

2. Synthesis of Benzyl 2-Cyclohexene-1-carboxylate (**3h**, mbky-8-004):

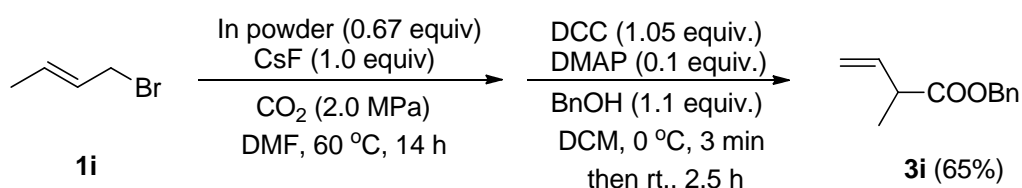


Typical procedure II: To a 25 mL autoclave equipped with a magnetic stirring bar was added CsF (228.1 mg, 1.50 mmol), which was stored in a glove box. Then indium powder (114.8 mg, 1.00 mmol), **1h** (Acros, purity: 95%, 254.3 mg, 1.50 mmol) and DMF (5 mL) were added in the air. The autoclave was pressurized to 2 MPa with CO₂ and stirred at 60 °C for 14 h. After slowly releasing the pressure, the resulting suspension was transferred into a 50 mL funnel flask with a glass dropper. The autoclave was washed with ethyl acetate (5 mL \times 2) and the combined mixture was quenched with 20 mL of 3 M aqueous HCl solution. The aqueous layer was extracted with ethyl acetate (10 mL \times 4). The combined organic layer was washed with 30 mL of brine, dried over anhydrous Na₂SO₄, filtrated and concentrated in a 100 mL flask to afford the crude product acid. DCM (5 mL), DMAP (18.5 mg, 0.15 mmol) and BnOH (0.17 mL, 1.65 mmol, density: 1.049) were added sequentially into this flask, which was followed by cooling with a bath of ice-water and the addition of a solution of DCC (228.2 mg, 1.10 mmol) in 1 mL of DCM dropwise within 3 minutes. Then the resulting mixture was allowed to warm to room temperature and the esterification reaction completed after 2.5 h as monitored by TLC. DCM (30 mL) was added into the suspension and the resulting mixture was filtered through a short pad of silica gel (300-400 mesh) eluted with DCM (10 mL \times 2) and concentrated. The crude product was purified by column chromatography on silica gel to afford 198.5 mg of **3h** (61%, eluent: petroleum ether/diethyl ether = 80/1) as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.27 (m, 5 H, ArH), 5.90-5.73 (m, 2 H, CH=CH), 5.14 (s, 2 H, CH₂Ph), 3.20-3.10 (m, 1 H, =CCHCO), 2.15-1.68 (m, 5 H, protons of cyclohexene), 1.68-1.49

(m, 1 H, proton of cyclohexene); ^{13}C NMR (75 MHz, CDCl_3) δ 174.3, 136.1, 129.7, 128.5, 128.1, 128.0, 124.1, 66.2, 41.1, 25.2, 24.6, 20.7; MS (m/z) 216 (M^+ , 1.72), 91 (100); IR (neat, cm^{-1}) 3033, 2937, 1734, 1498, 1455, 1376, 1308, 1212, 1167, 1092, 1022; HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_2$ [$(\text{M}+\text{H})^+$]: 217.1223; Found: 217.1223.

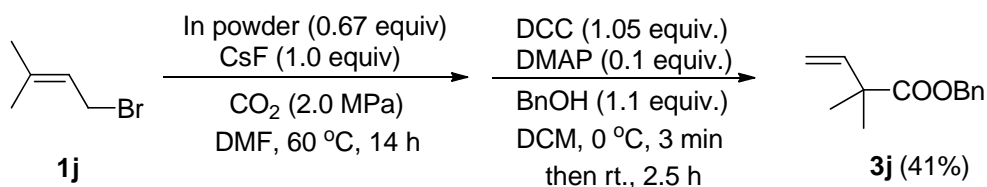
The following compounds were prepared according to this **Typical Procedure II**.

3. Synthesis of Benzyl 2-Methyl-3-butenolate (**3i**, mbky-9-137):



The reaction of allylic bromide **1i** (TCI, purity: 83%, 243.7 mg, 1.50 mmol), indium powder (114.6 mg, 1.00 mmol), CsF (228.3 mg, 1.50 mmol), and CO_2 in 5 mL of DMF afforded the crude product acid. The esterification reaction of the crude product acid, BnOH (0.17 mL, 1.65 mmol, density: 1.049), DMAP (18.3 mg, 0.15 mmol), and DCC (325.6 mg, 1.58 mmol) in 6 mL of DCM afforded 186.2 mg of **3i**^{4b} (65%, eluent: petroleum ether/diethyl ether = 100/1) as a faint yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.27 (m, 5 H, ArH), 5.94 (ddd, $J_1 = 17.4$ Hz, $J_2 = 9.9$ Hz, $J_3 = 7.5$ Hz, 1 H, =CH), 5.20-5.06 (m, 4 H, $\text{CH}_2\text{Ph} + \text{CH}_2=$), 3.27-3.10 (m, 1 H, CHCO), 1.29 (d, $J = 7.2$ Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 174.2, 137.0, 136.0, 128.5, 128.1, 128.0, 116.0, 66.3, 43.7, 16.7; MS (m/z) 190 (M^+ , 2.44), 91 (100); IR (neat, cm^{-1}) 3088, 3066, 3034, 2980, 2937, 1736, 1640, 1498, 1456, 1378, 1326, 1253, 1212, 1155, 1082, 1030.

4. Synthesis of Benzyl 2,2'-Dimethylbut-3-enoate (**3j**, mbky-8-001):

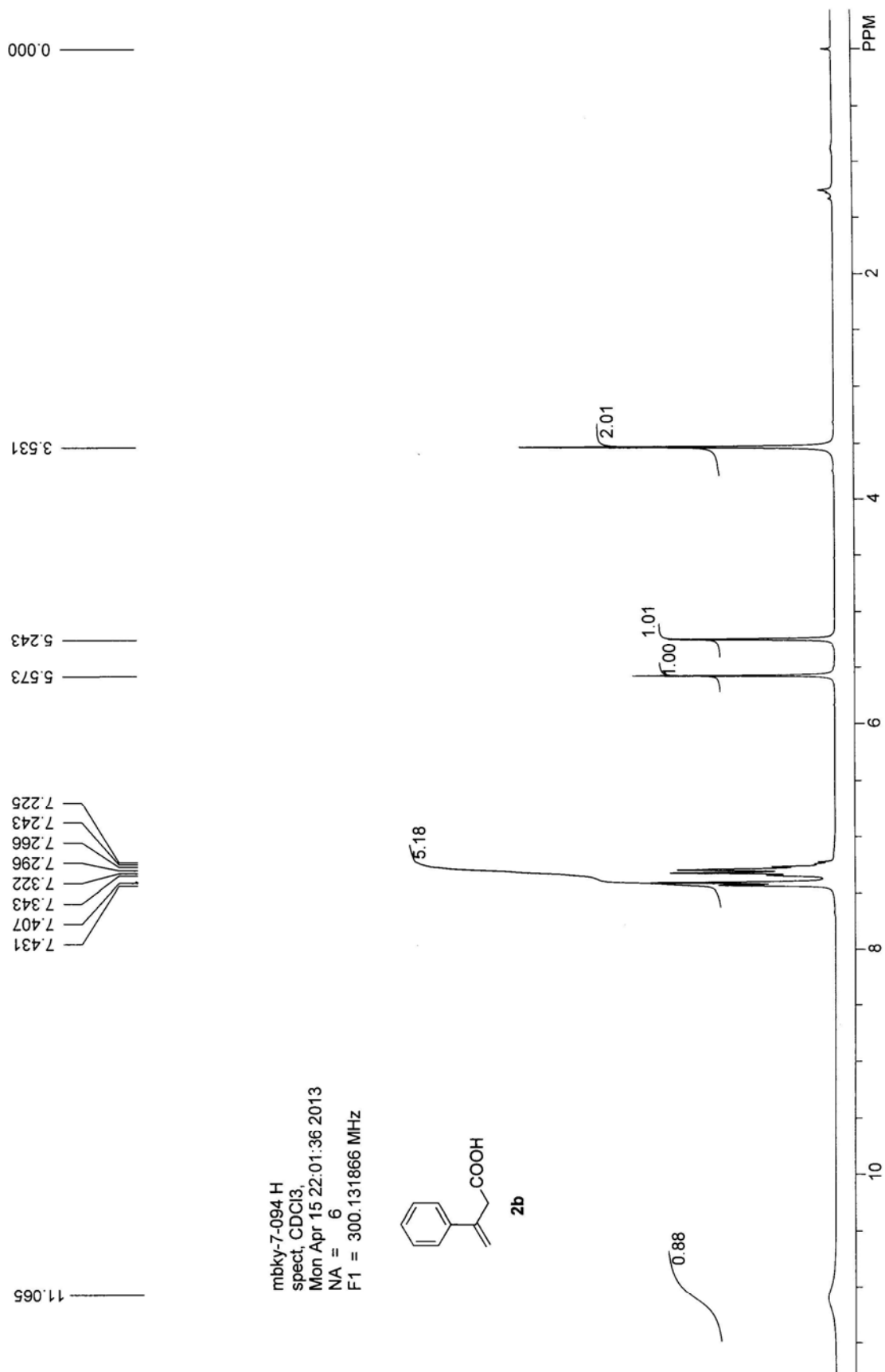
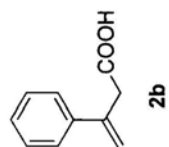


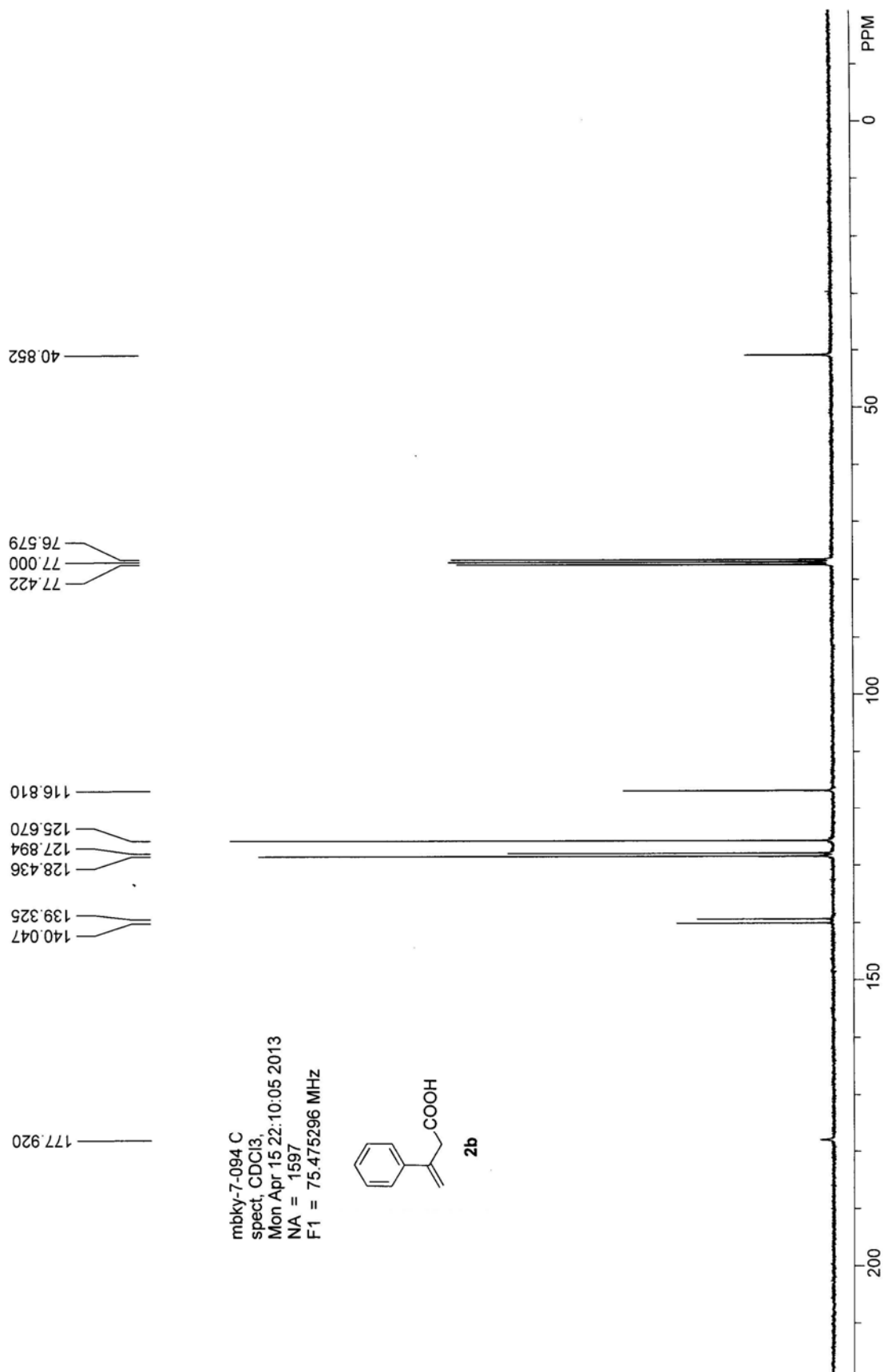
The reaction of **1j** (Alfa-Aesar, purity: 90%, 248.3 mg, 1.50 mmol), indium powder (114.8 mg, 1.00 mmol), CsF (227.9 mg, 1.50 mmol), and CO₂ in 5 mL of DMF afforded the crude acid. The esterification reaction of the crude product acid, BnOH (0.17 mL, 1.65 mmol, density: 1.049), DMAP (18.3 mg, 0.15 mmol), and DCC (325.6 mg, 1.58 mmol) in 6 mL of DCM afforded 126.6 mg of **3j** (41%, eluent: petroleum ether/diethyl ether = 80/1) as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.26 (m, 5 H, ArH), 6.05 (dd, *J*₁ = 17.4 Hz, *J*₂ = 10.5 Hz, 1 H, =CH), 5.15-5.03 (m, 4 H, CH₂Ph + CH₂=), 1.33 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 176.1, 142.4, 136.2, 128.5, 128.0, 127.7, 113.0, 66.3, 44.9, 24.6, 24.5; MS (ESI) 205 [(M+H)⁺]; IR (neat, cm⁻¹) 1732, 1640, 1498, 1461, 1415, 1376, 1261, 1224, 1136; HRMS (ESI) calcd. for C₁₃H₁₇O₂ [(M+H)⁺]: 205.1223; Found: 205.1221.

References

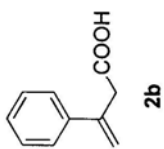
- (1) Liu, H.; Qiao, Z.; Jiang, X. *Org. Biomol. Chem.* **2012**, *10*, 7274.
- (2) Mo, J.; Xu, L.; Ruan, J.; Liu, S.; Xiao, J. *Chem. Commun.* **2006**, 42, 3591.
- (3) a) Itoh, K.; Harada, T.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3746. b) Yamamoto, K.; Ikeda, K.; Yin, L. *J. Organomet. Chem.* **1989**, *370*, 319. c) Sun, X.; Zhou, L.; Wang, C.; Zhang, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 2623. d) Luteri, G. F.; Ford, W. T. *J. Org. Chem.* **1977**, *42*, 820. e) Wiley, R. H.; Plus, V. D. *J. Chem. Eng. Data* **1965**, *10*, 72.
- (4) a) Molander, G. A.; Barcellos, T.; Traister, K. M. *Org. Lett.* **2013**, *15*, 3342. b) M. Taniguchi, M.; Koga, K. Yamada, S. *Chem. Pharm. Bull.* **1972**, *20*, 1438.

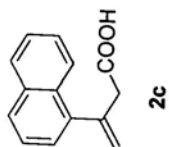
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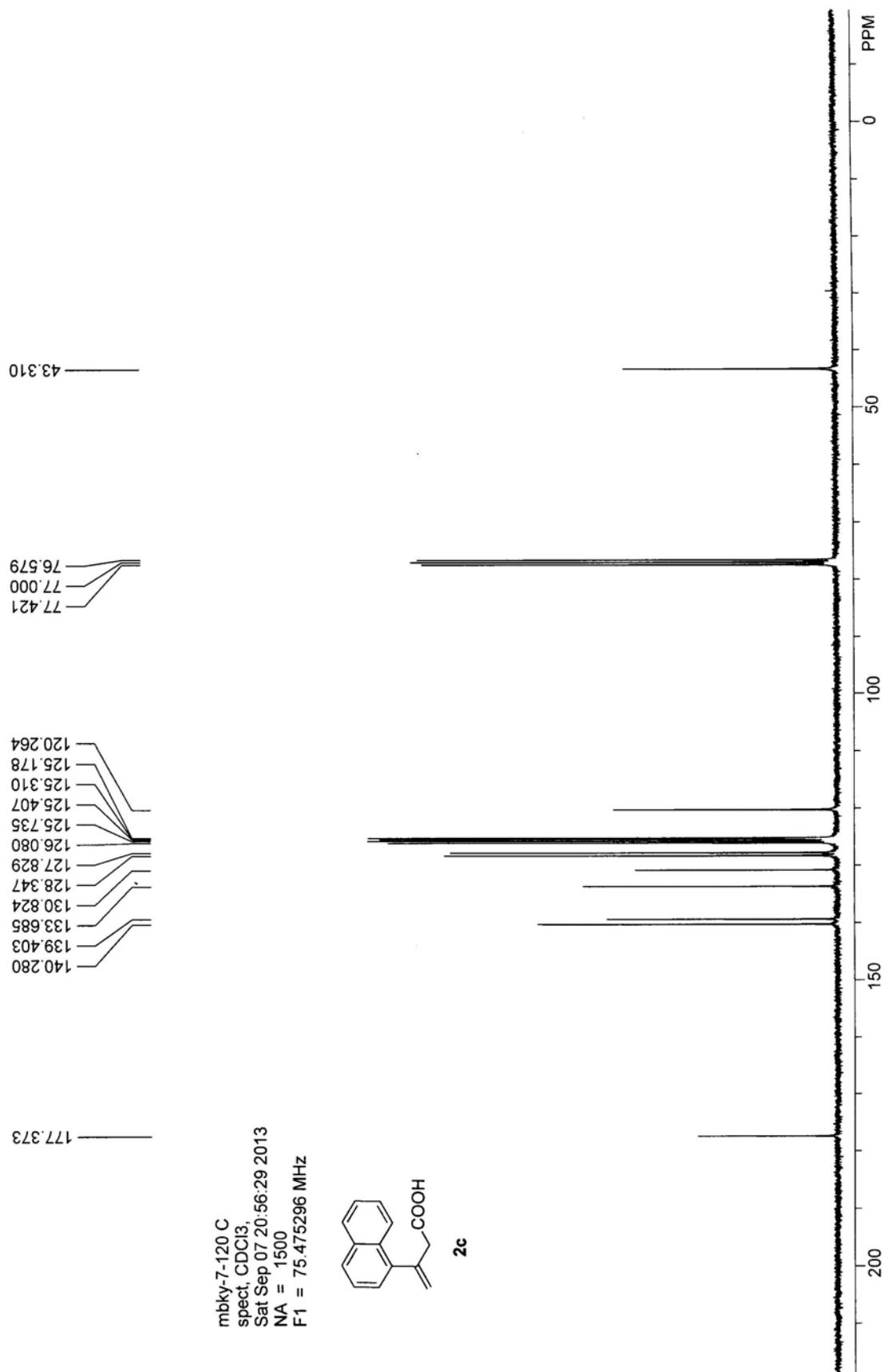


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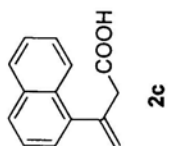


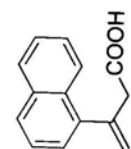


S19



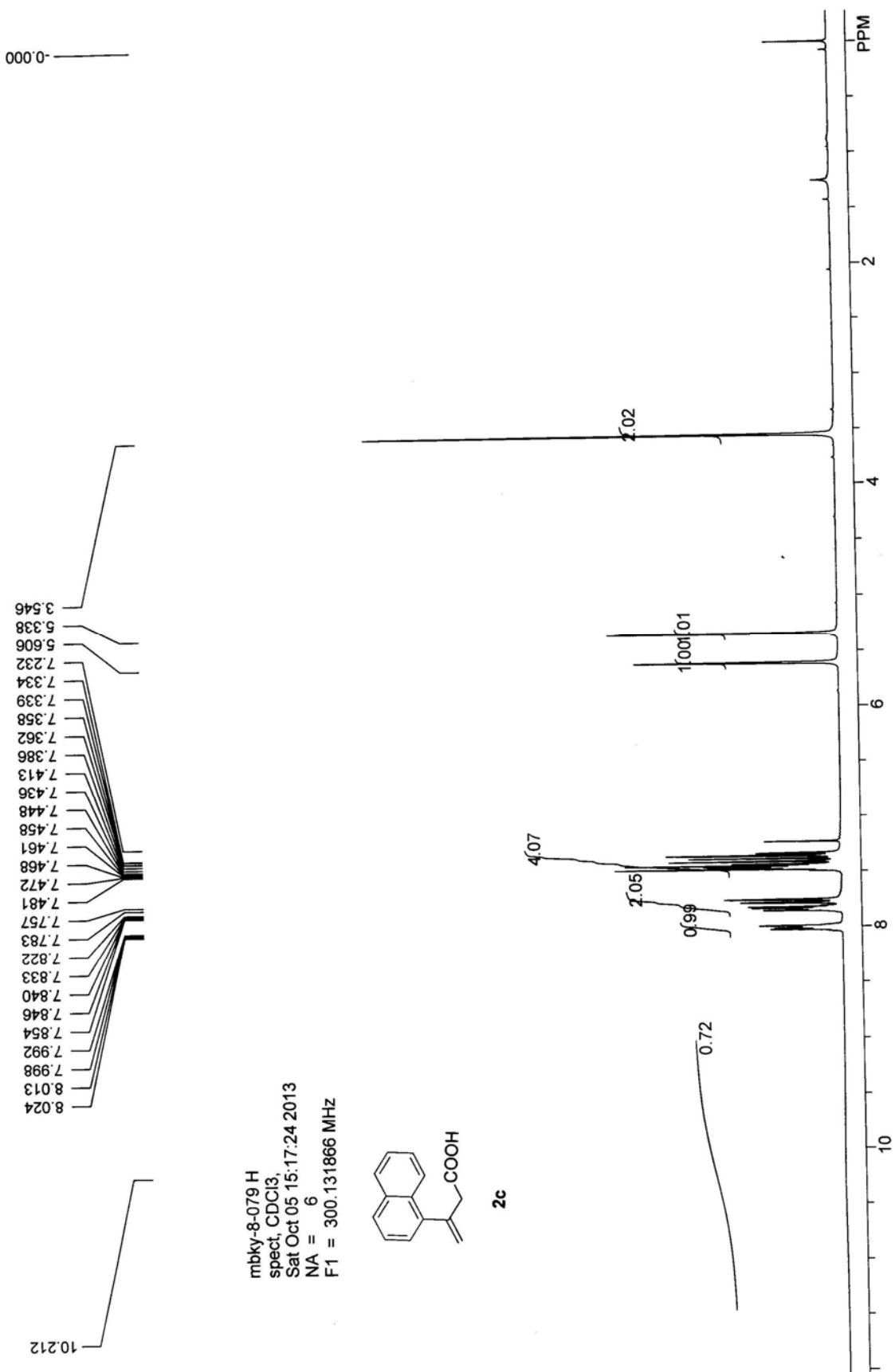
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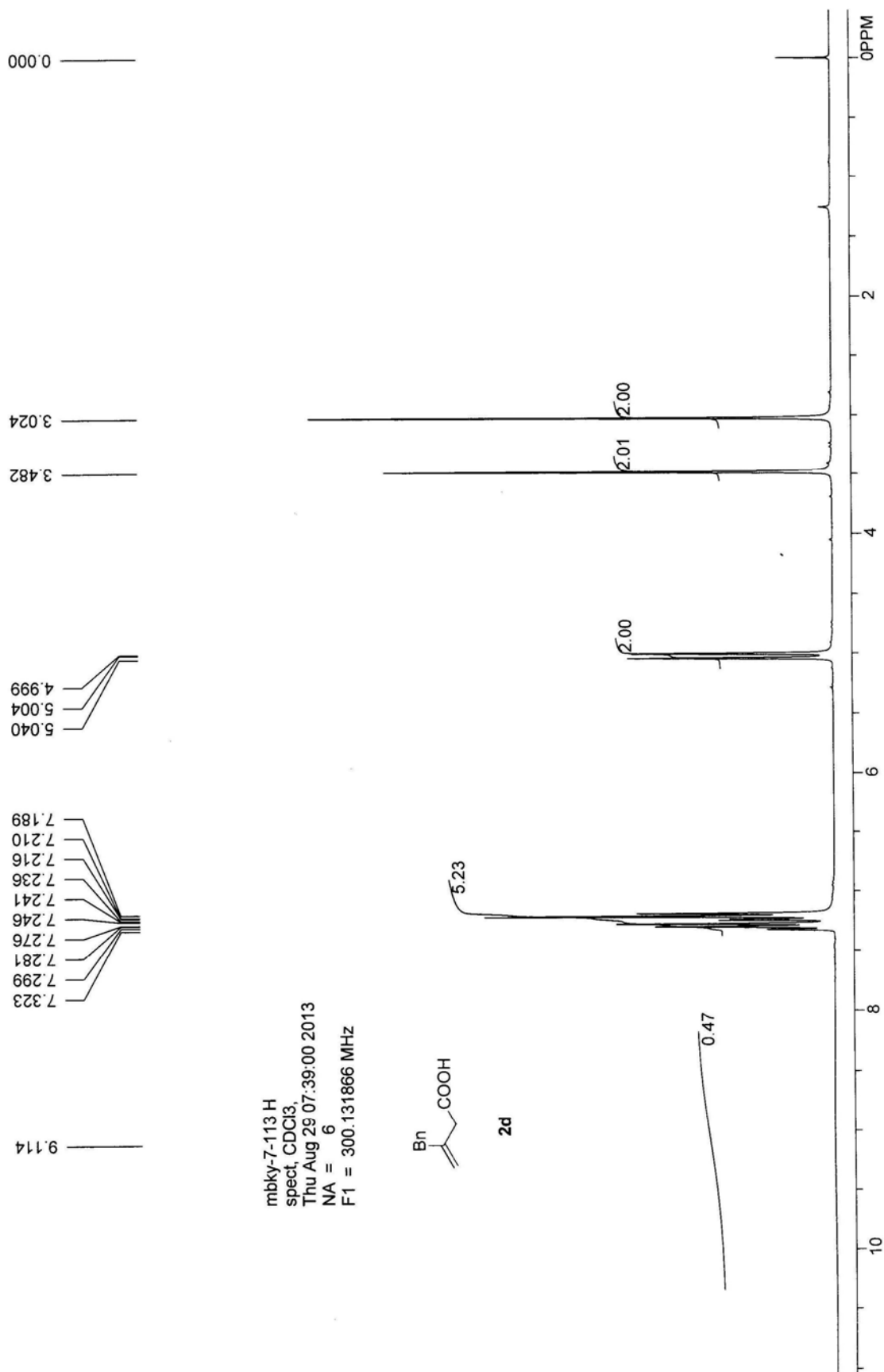




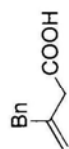
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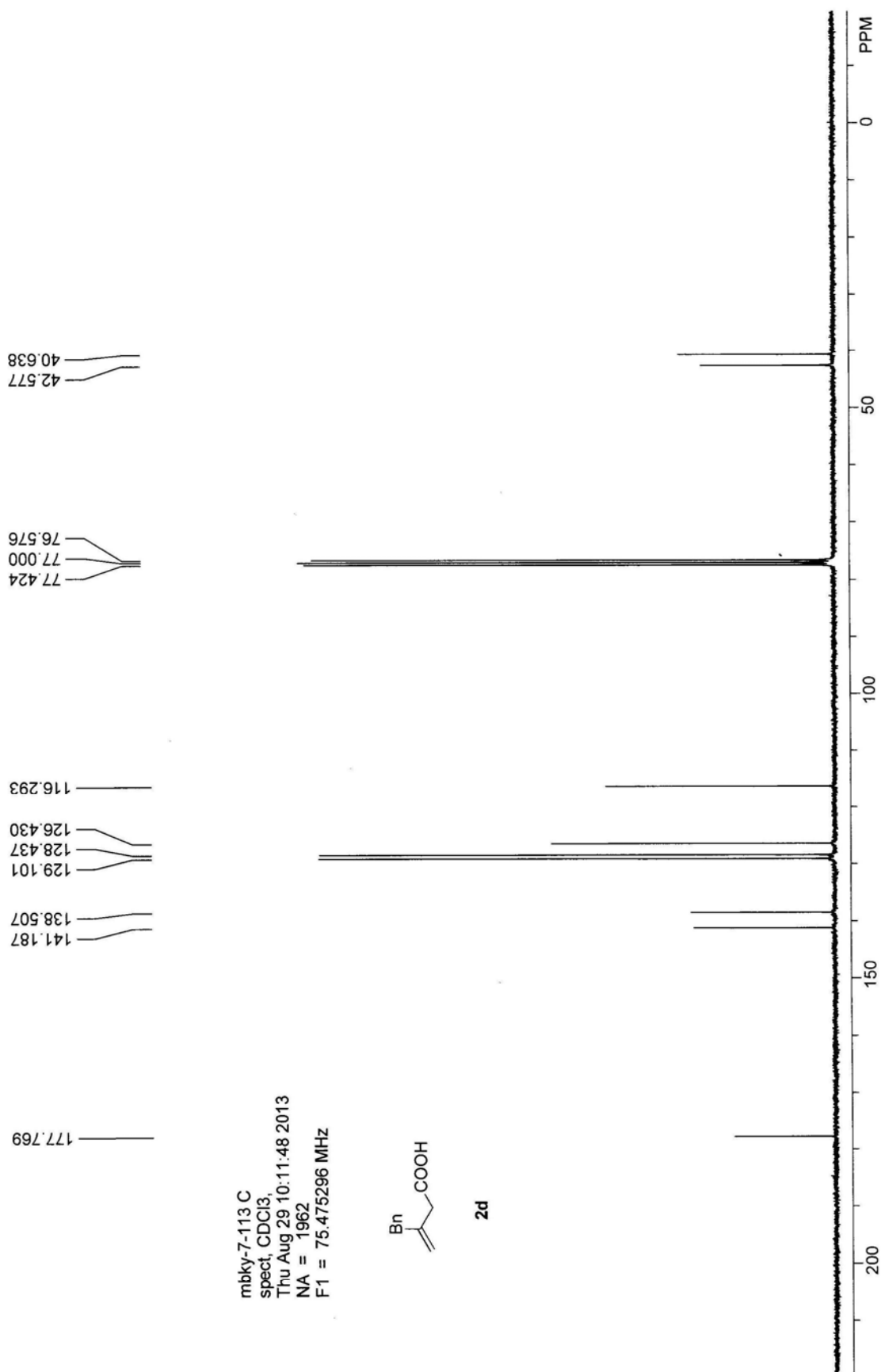




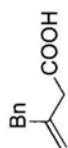
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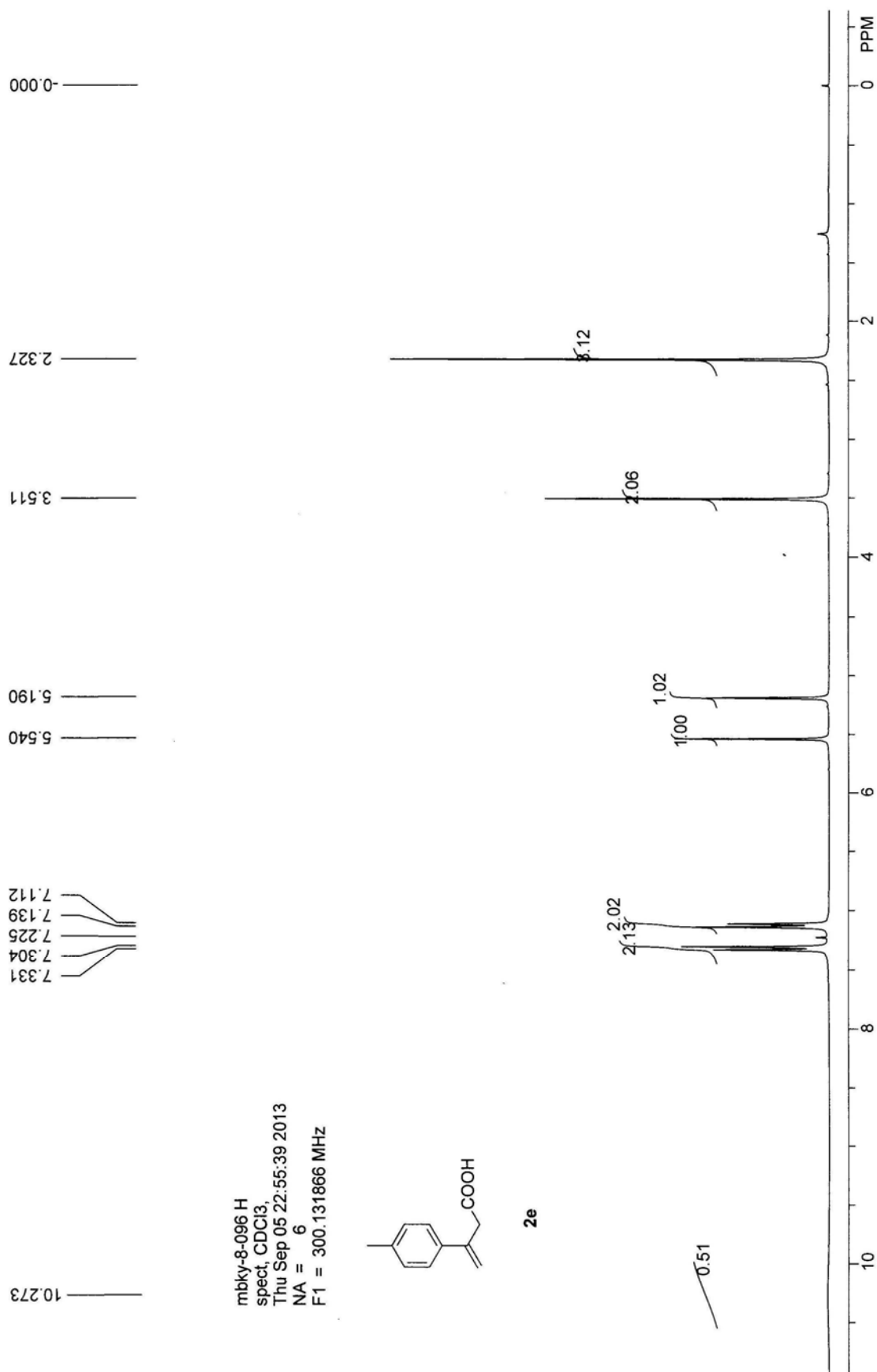
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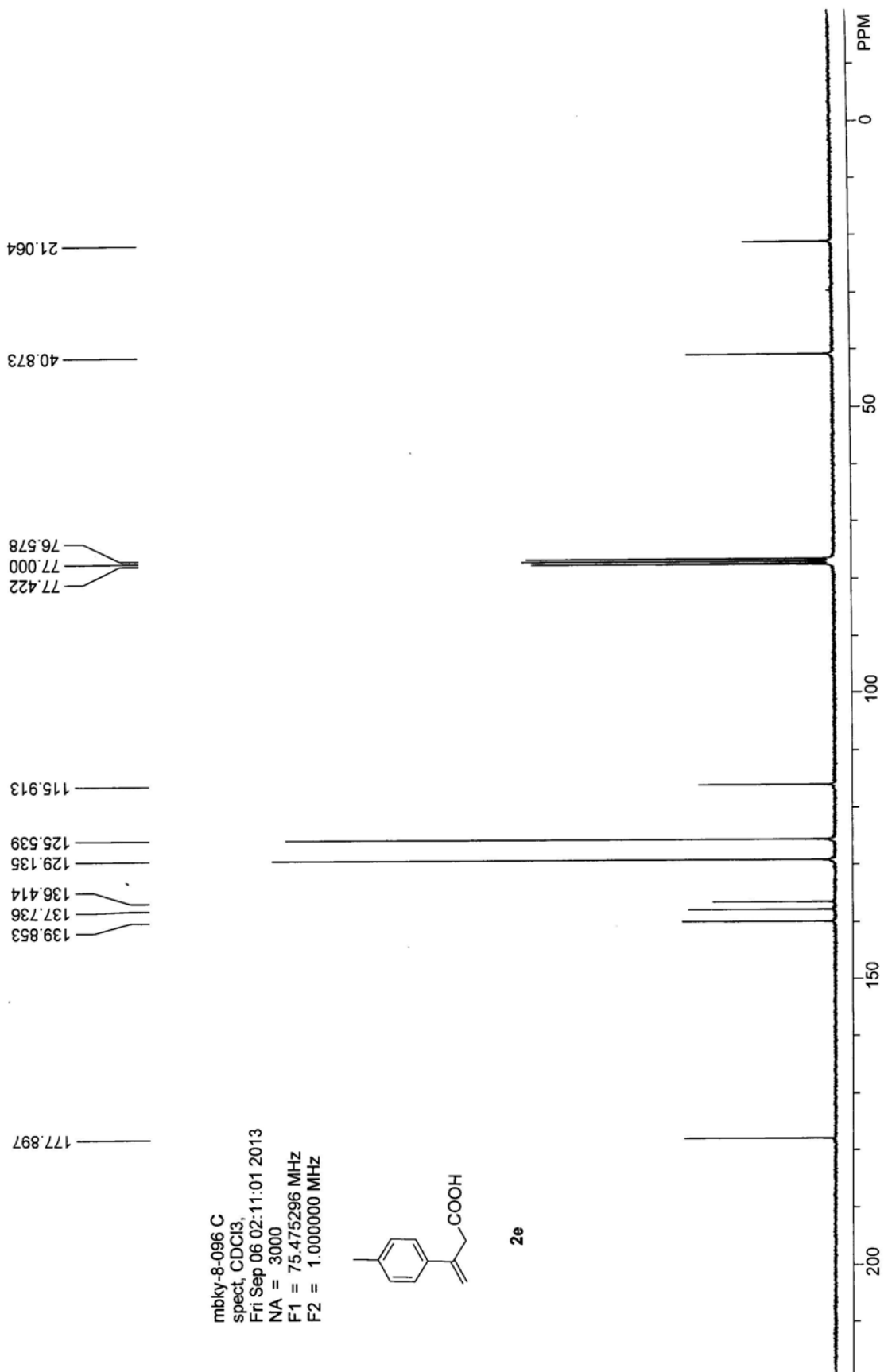


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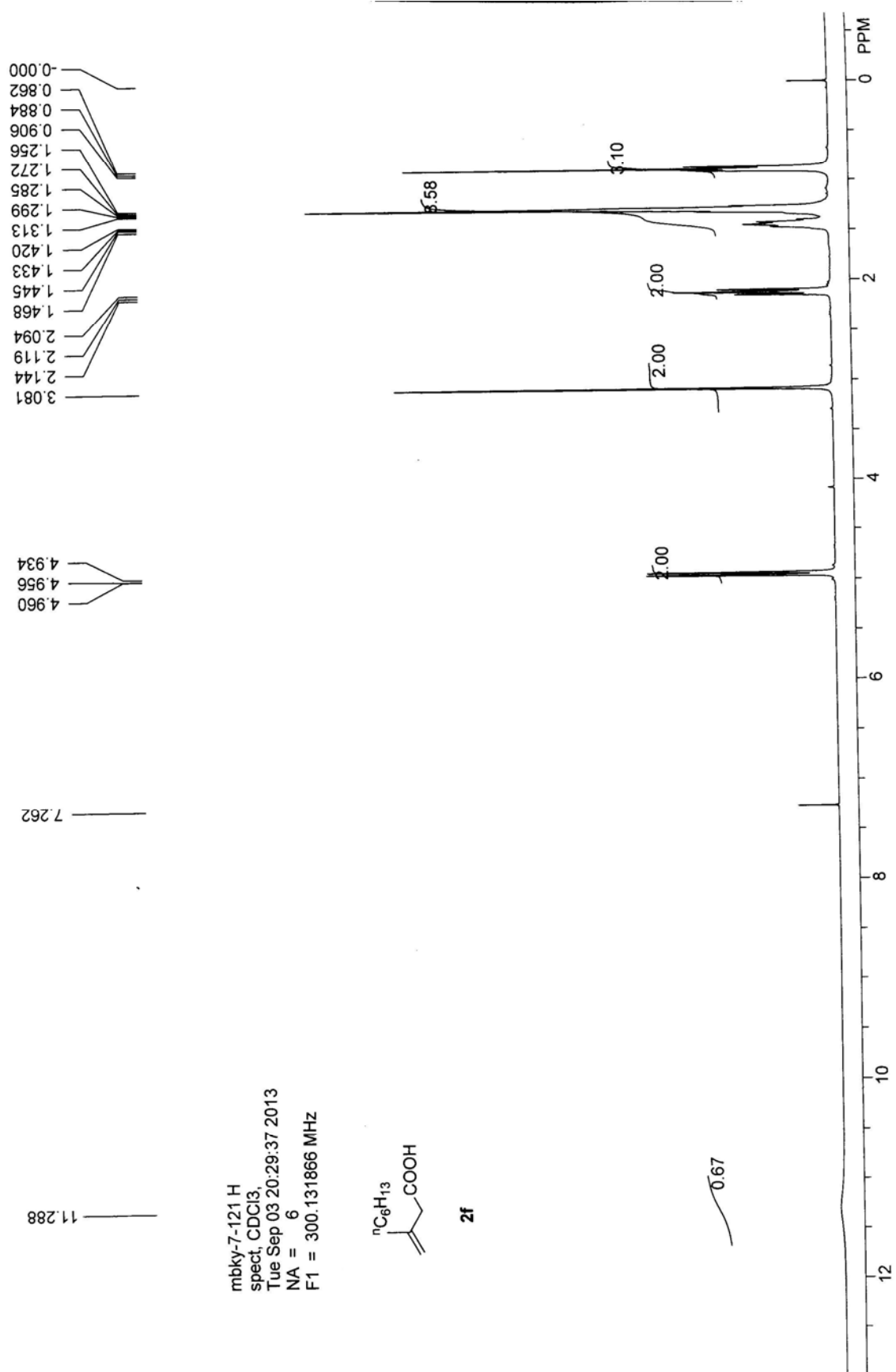


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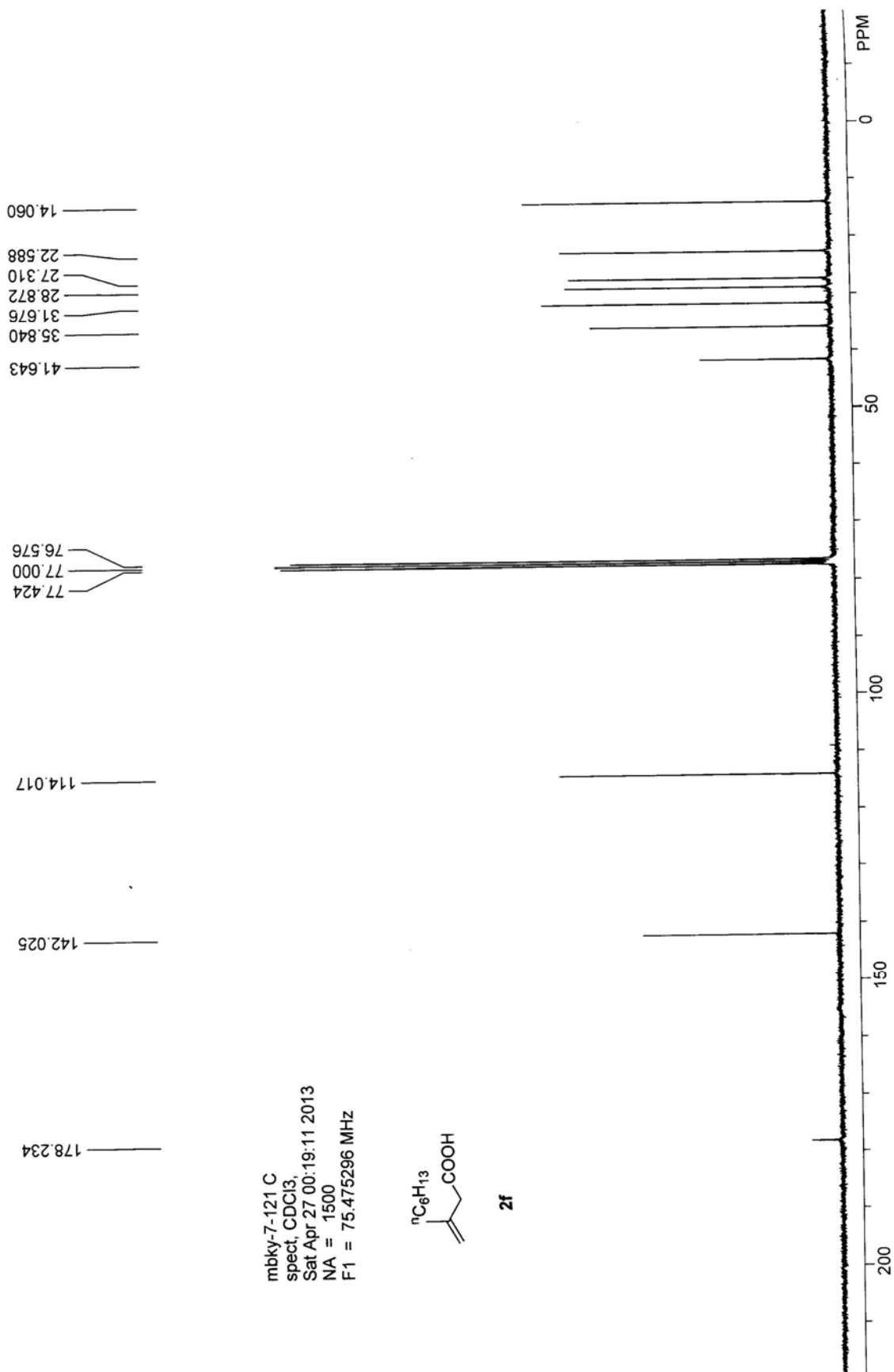
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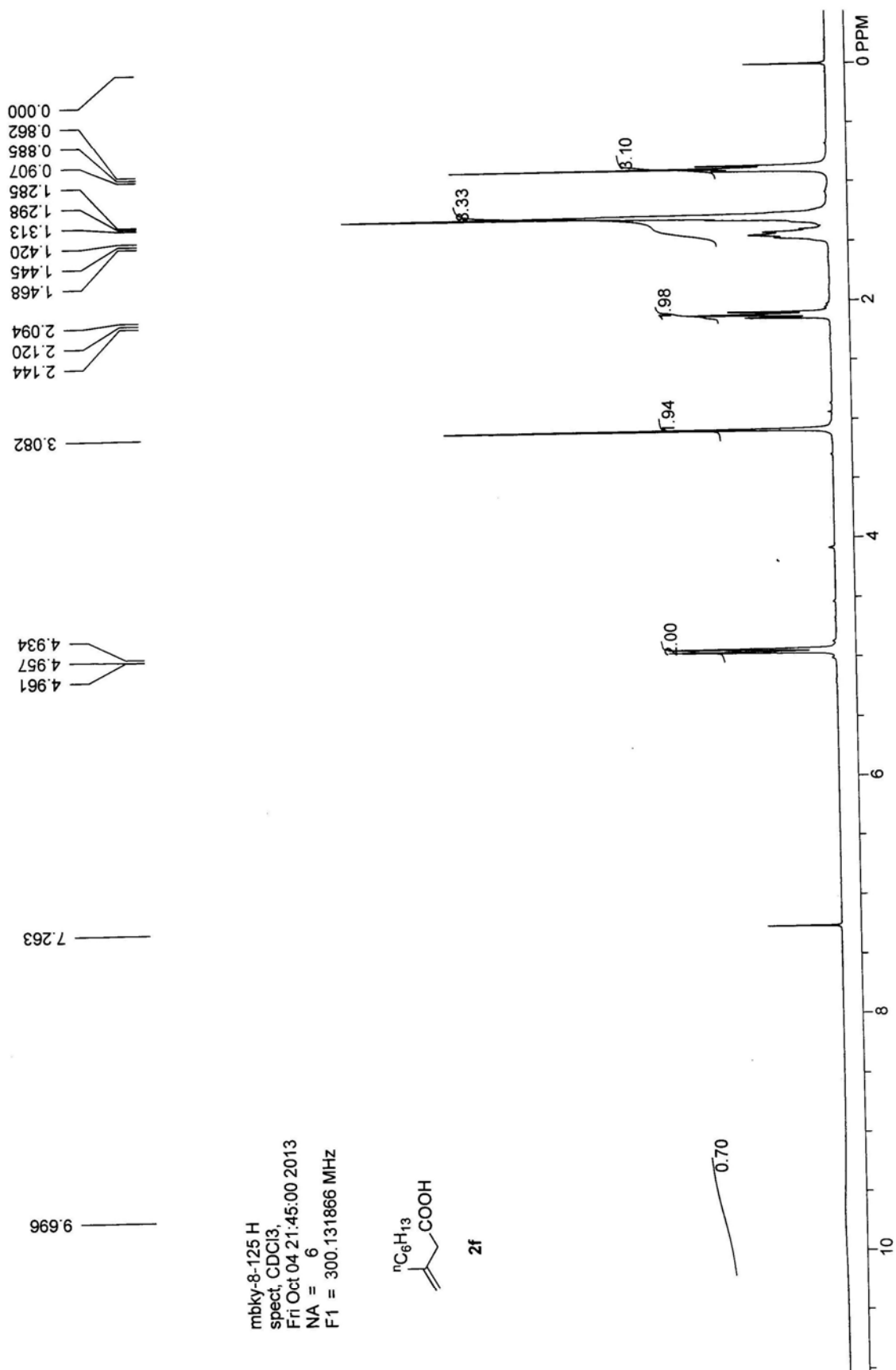
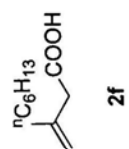
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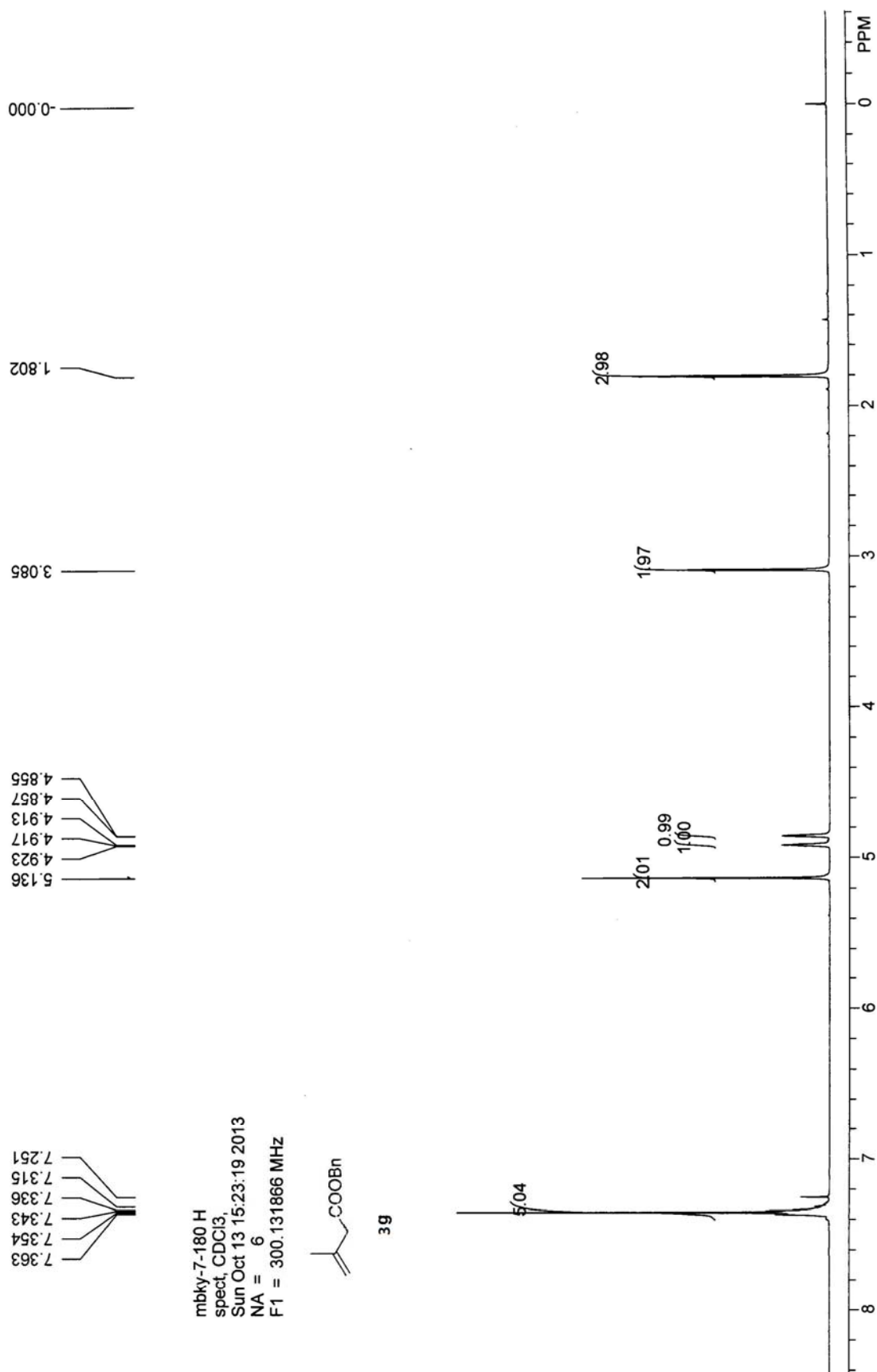


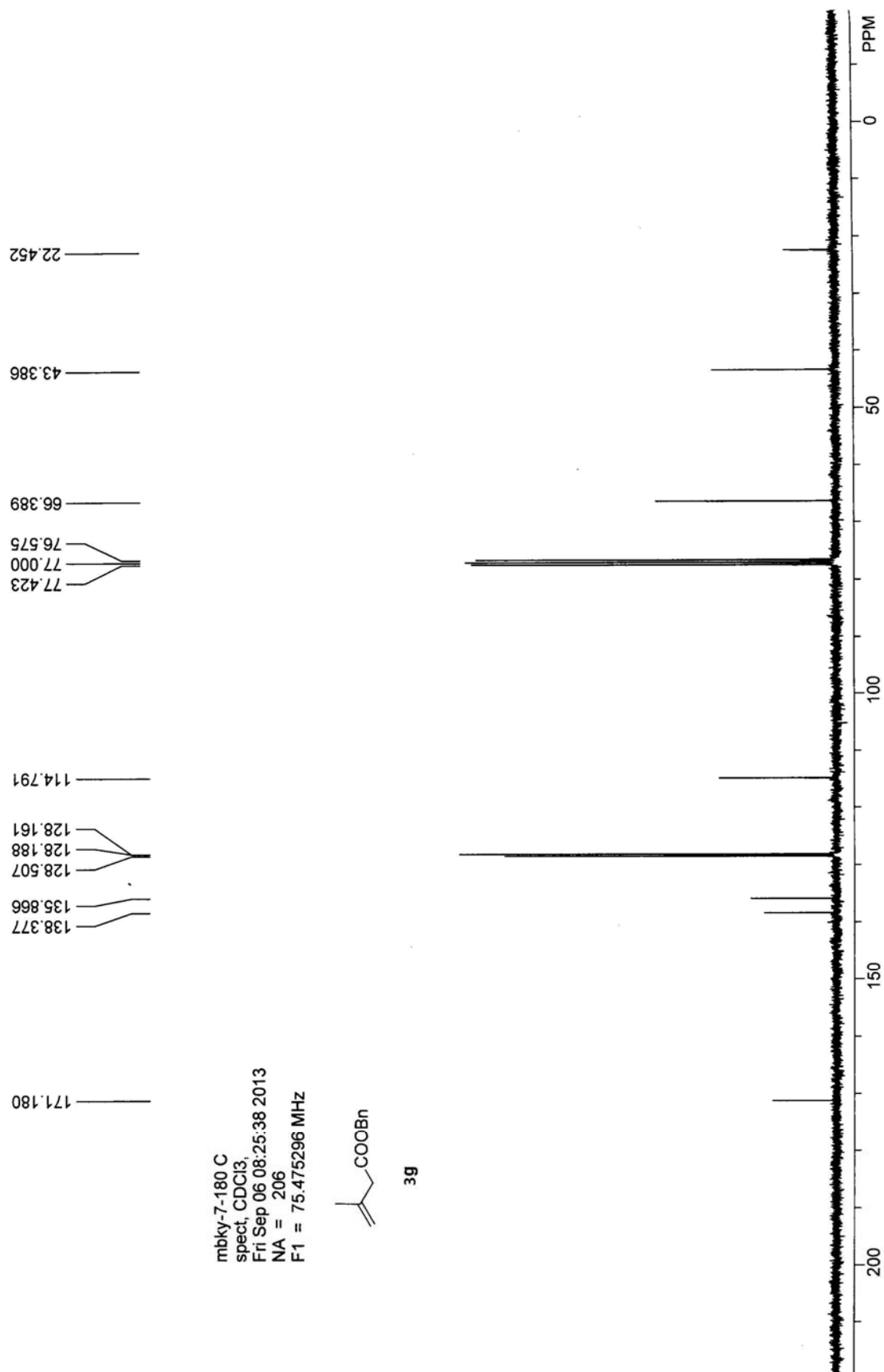
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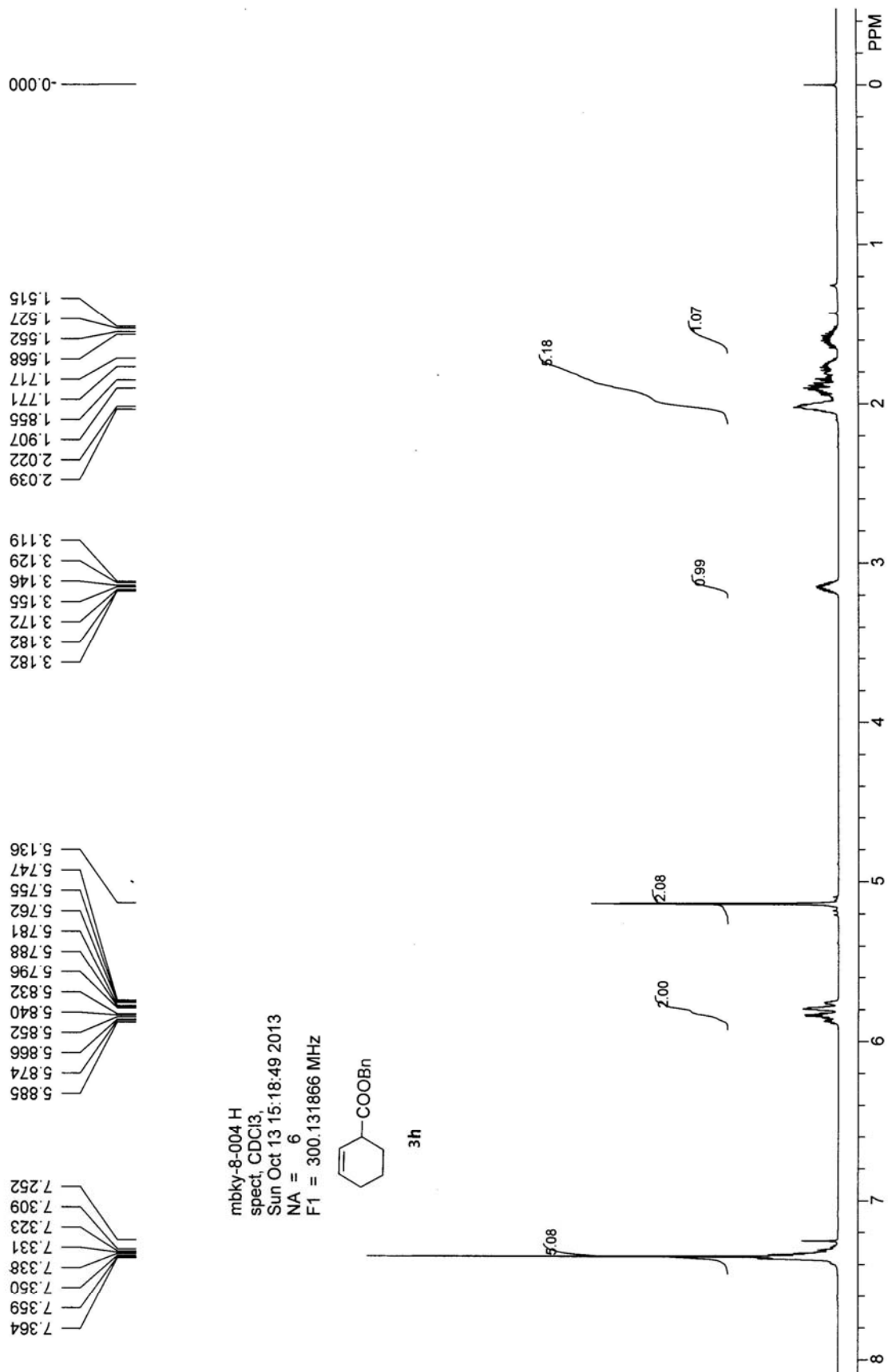




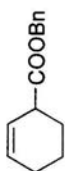
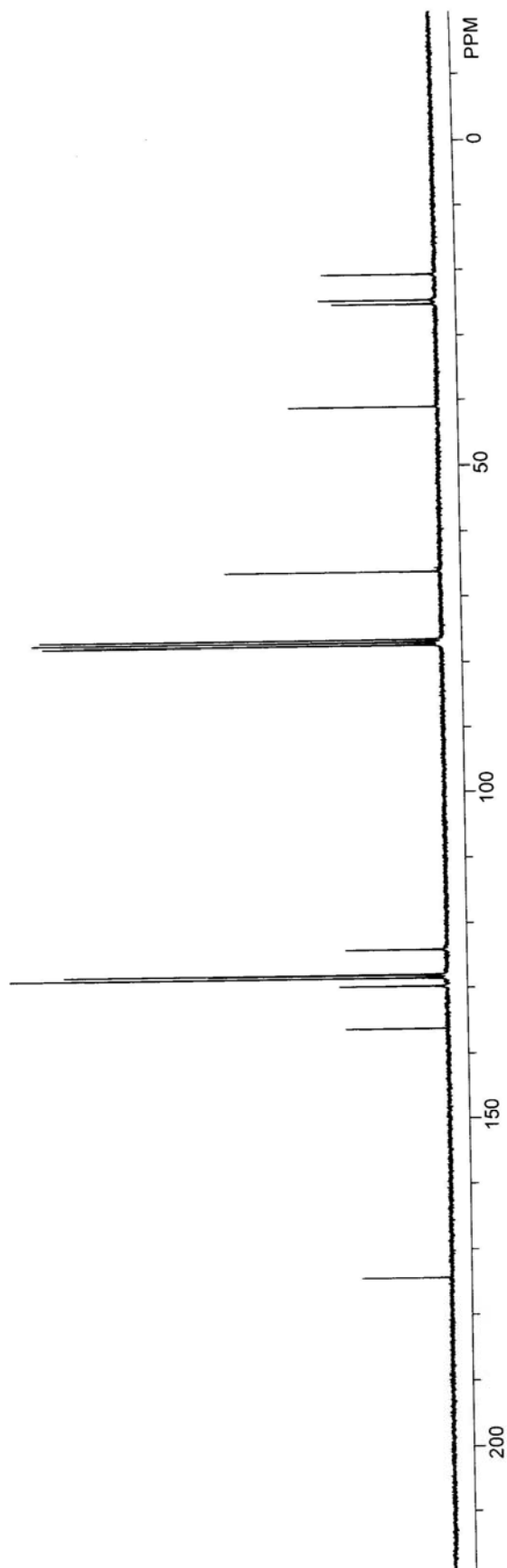
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3g



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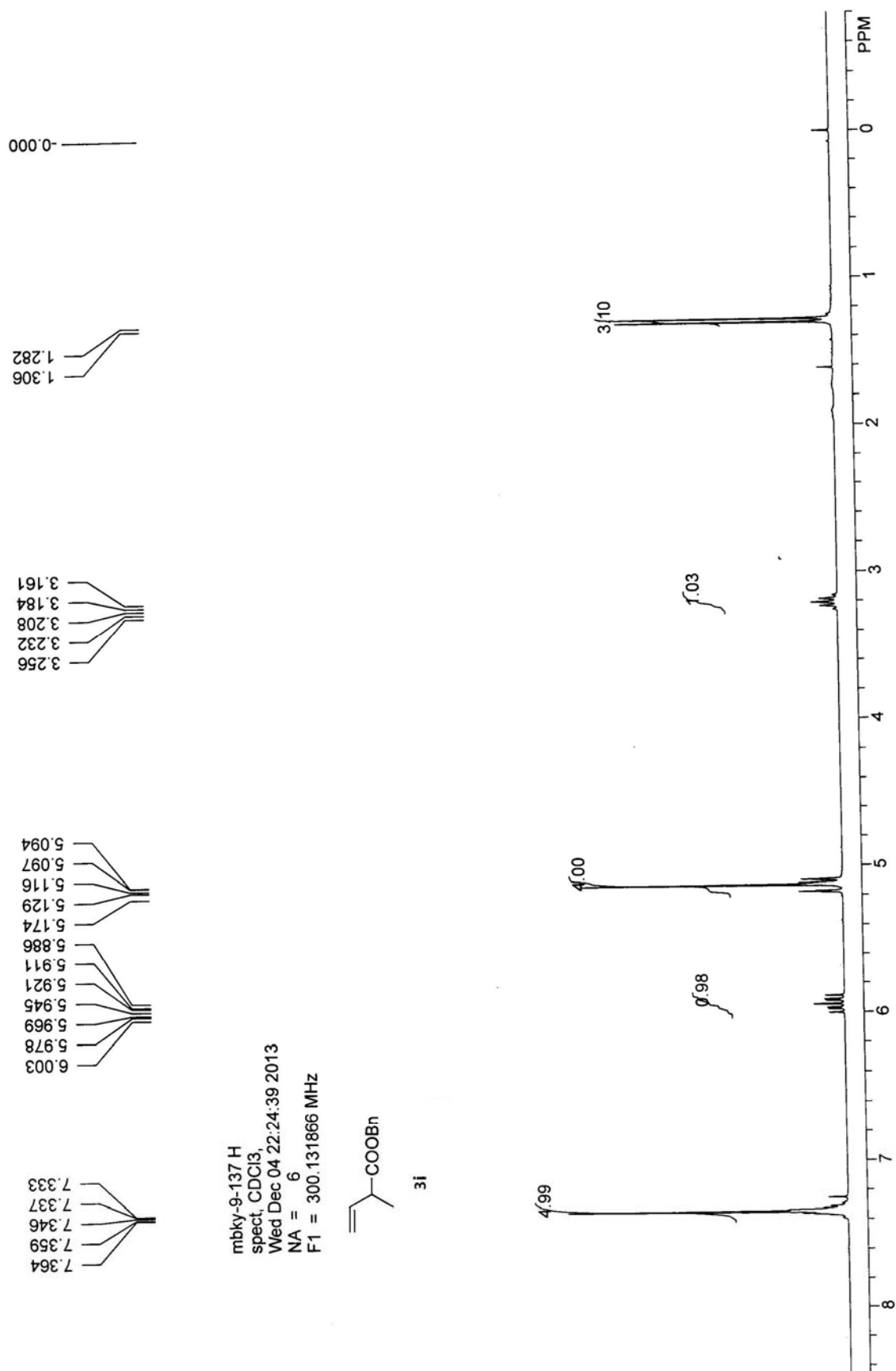
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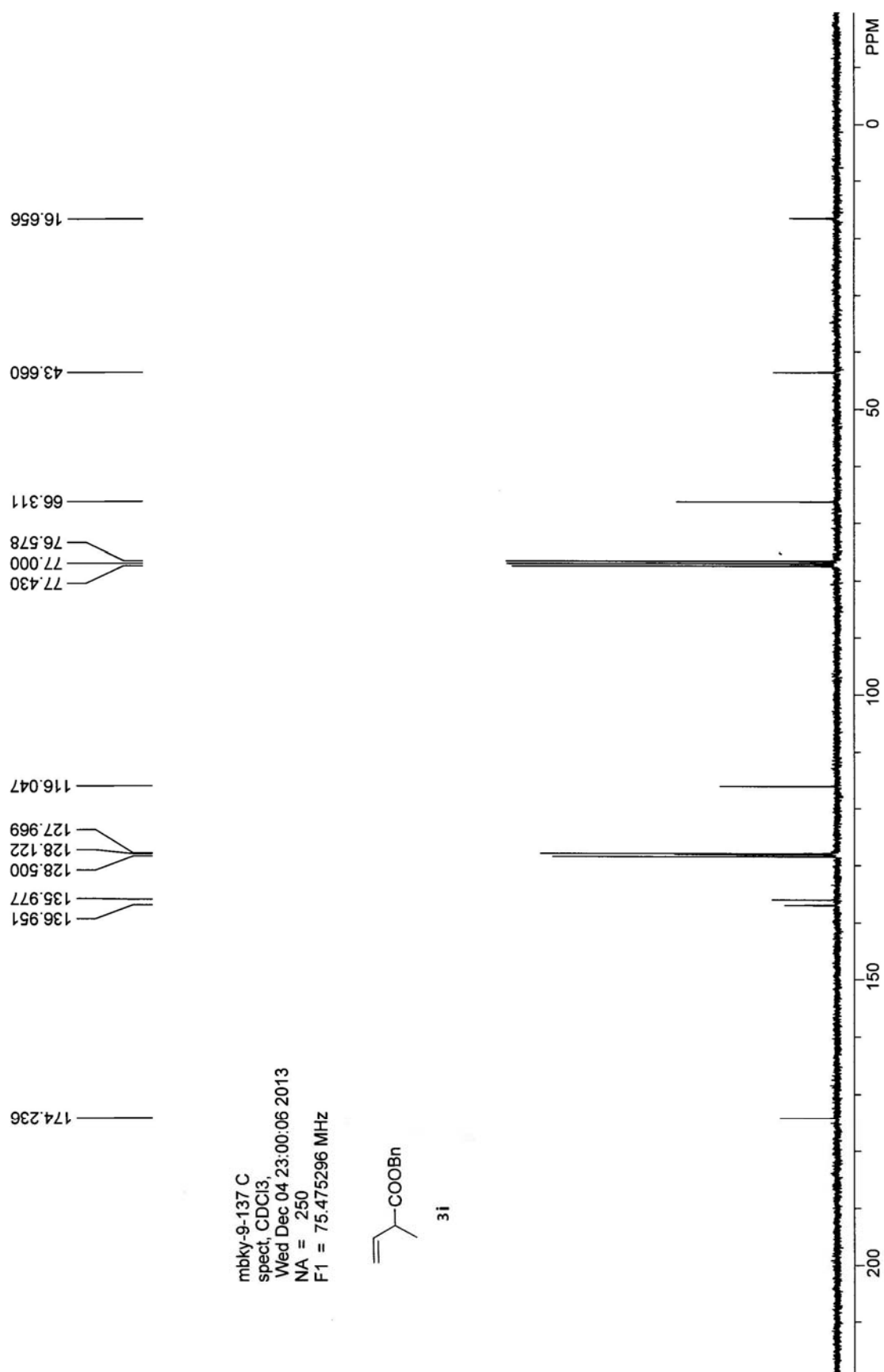
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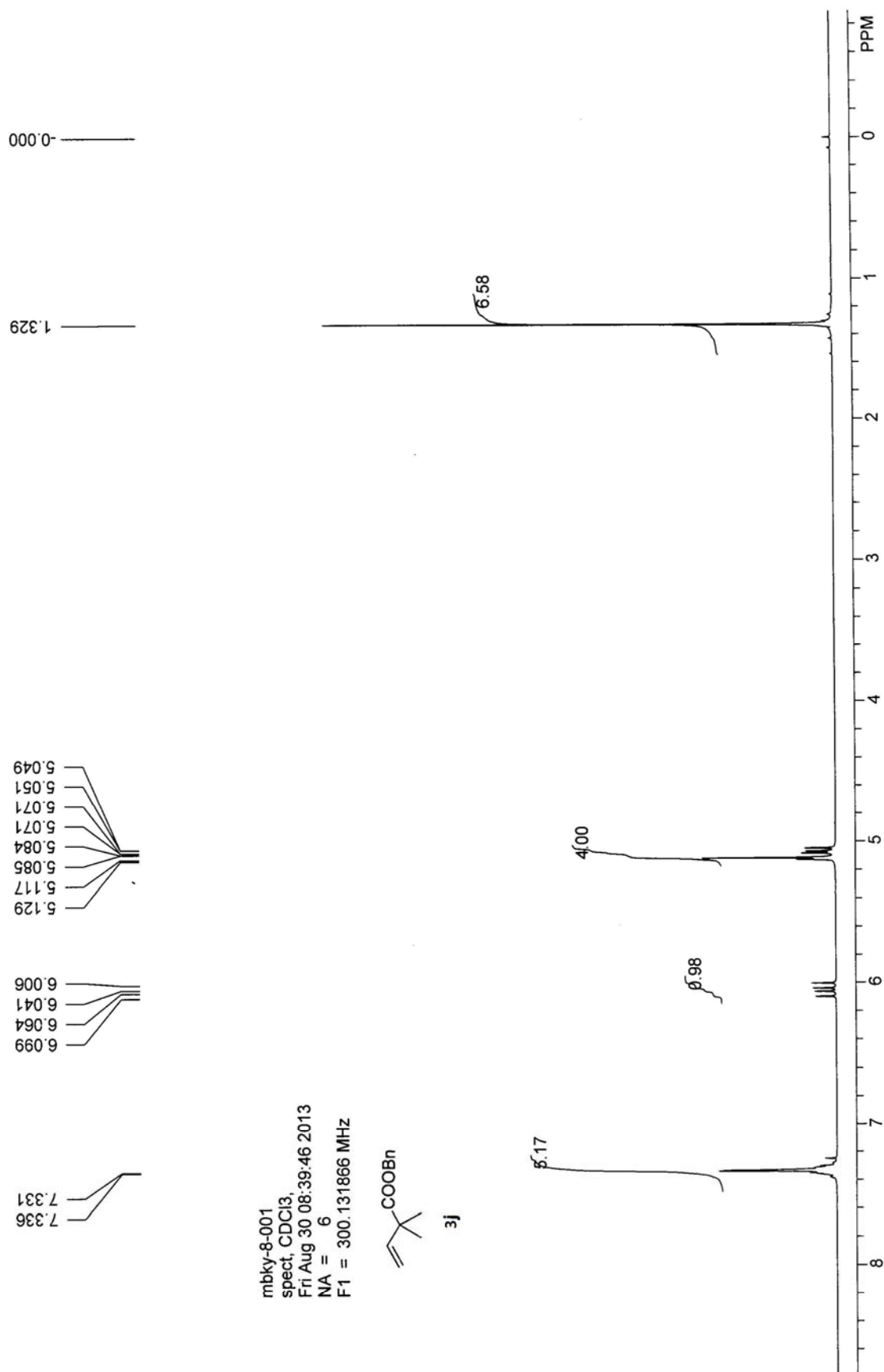
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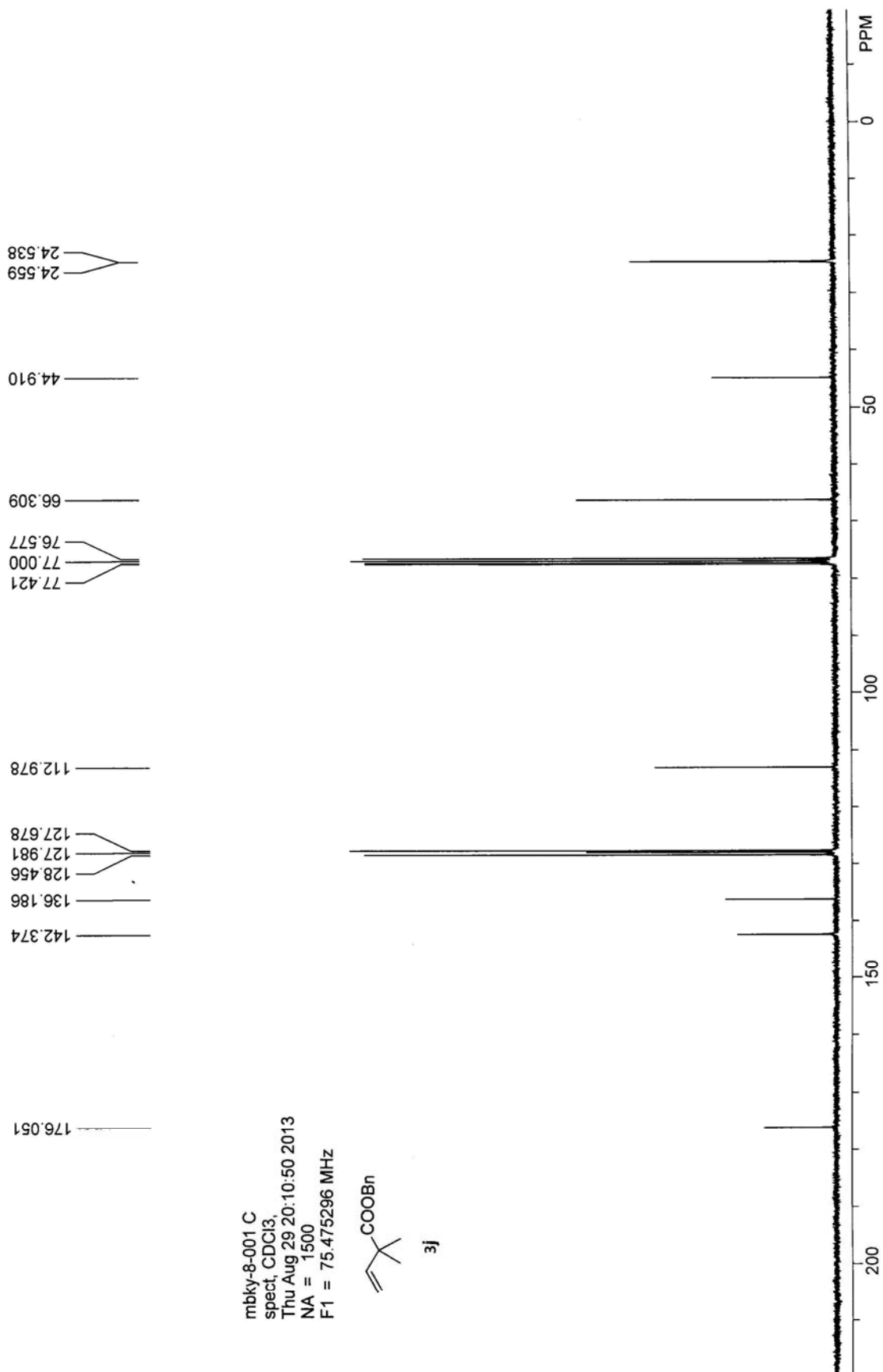
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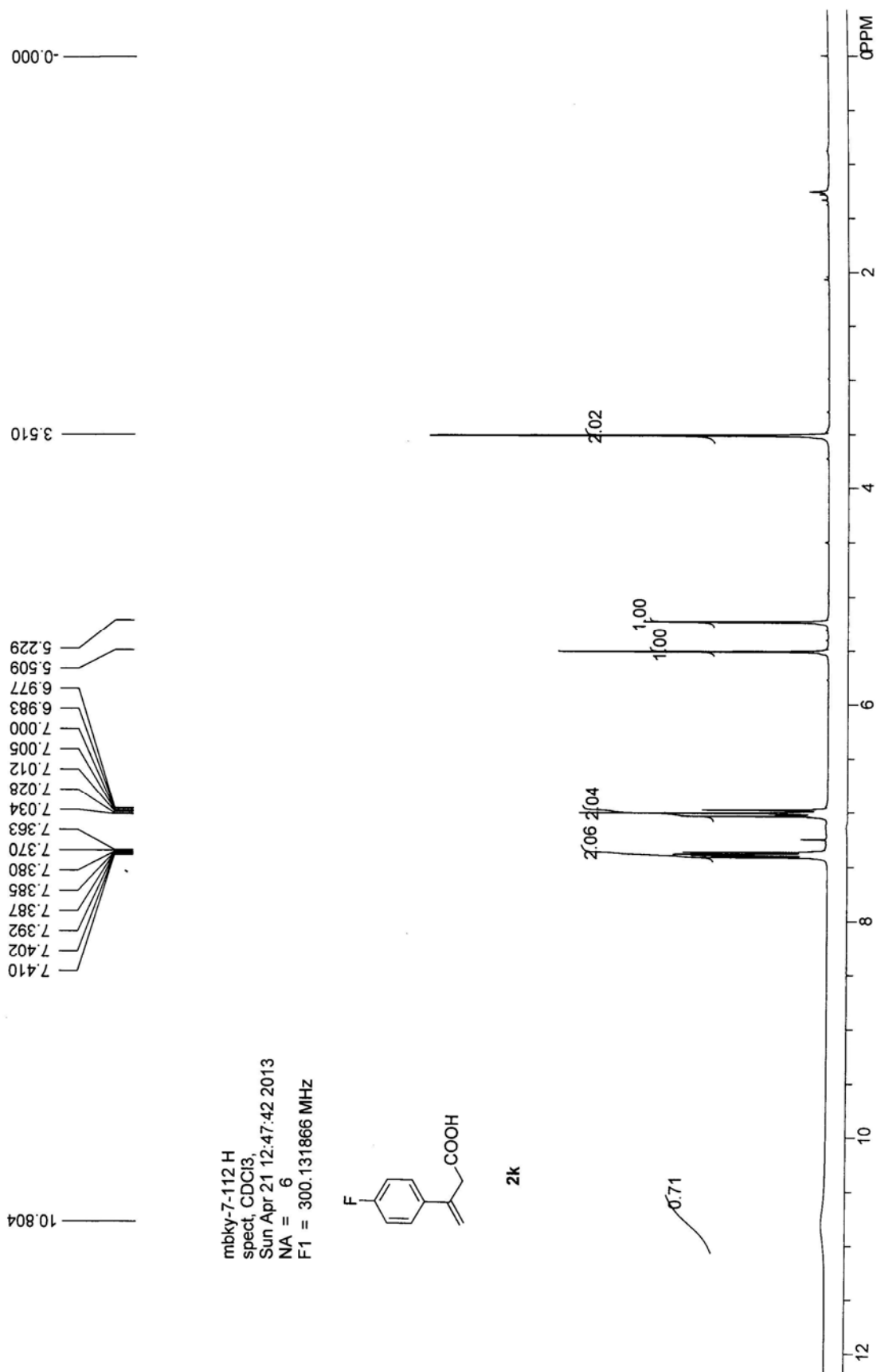


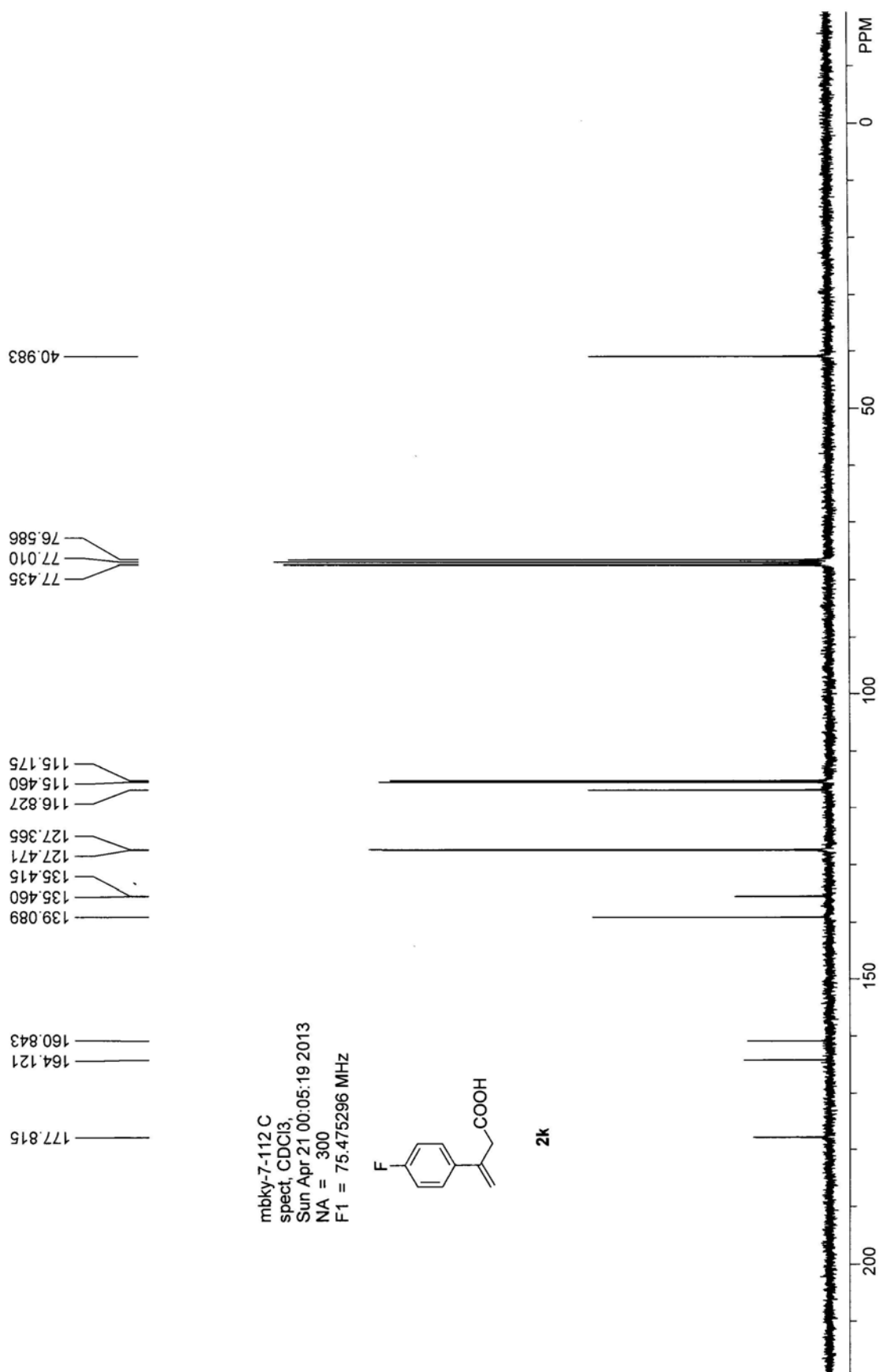




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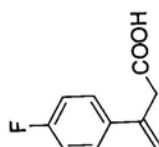


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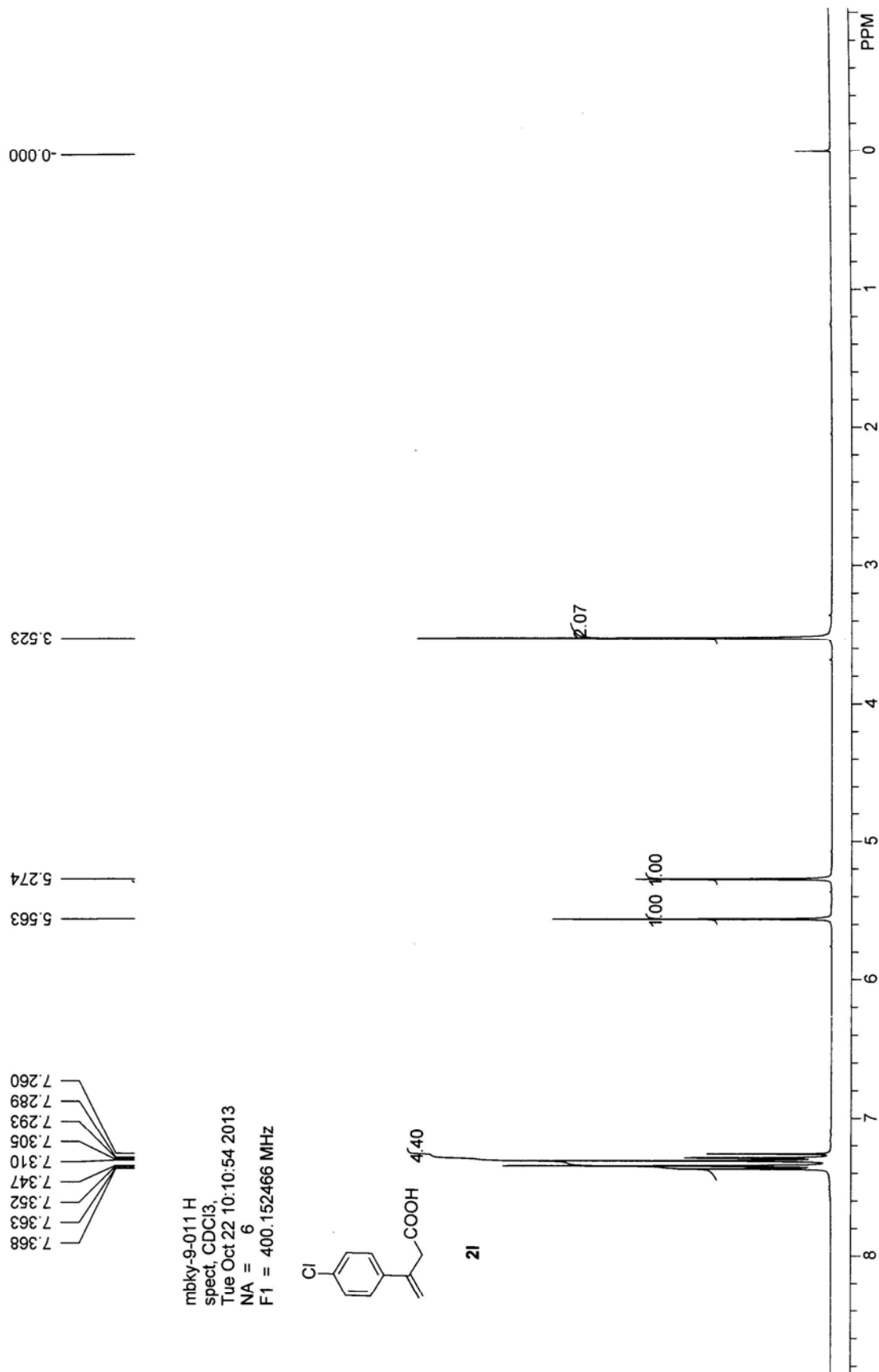
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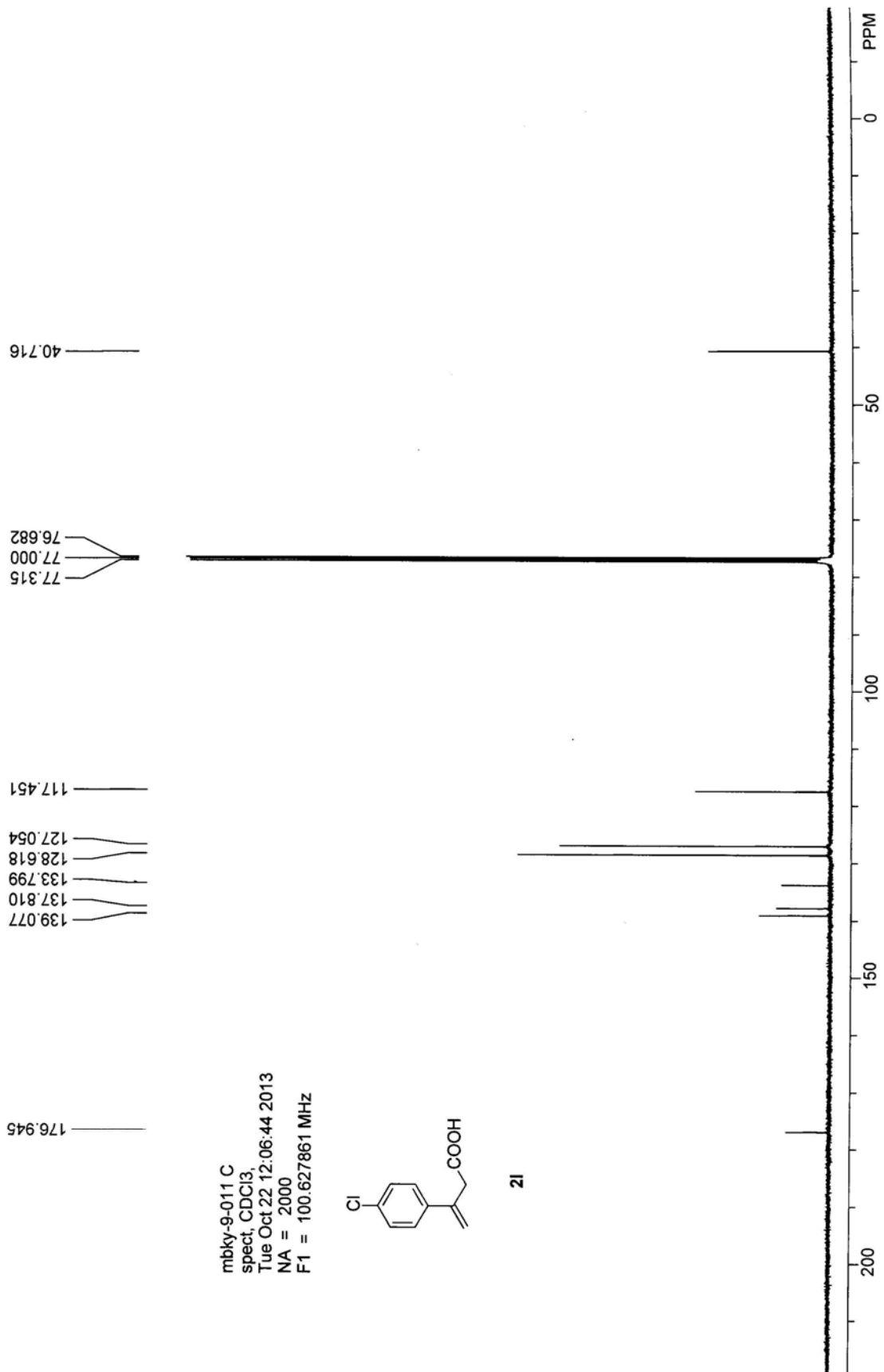
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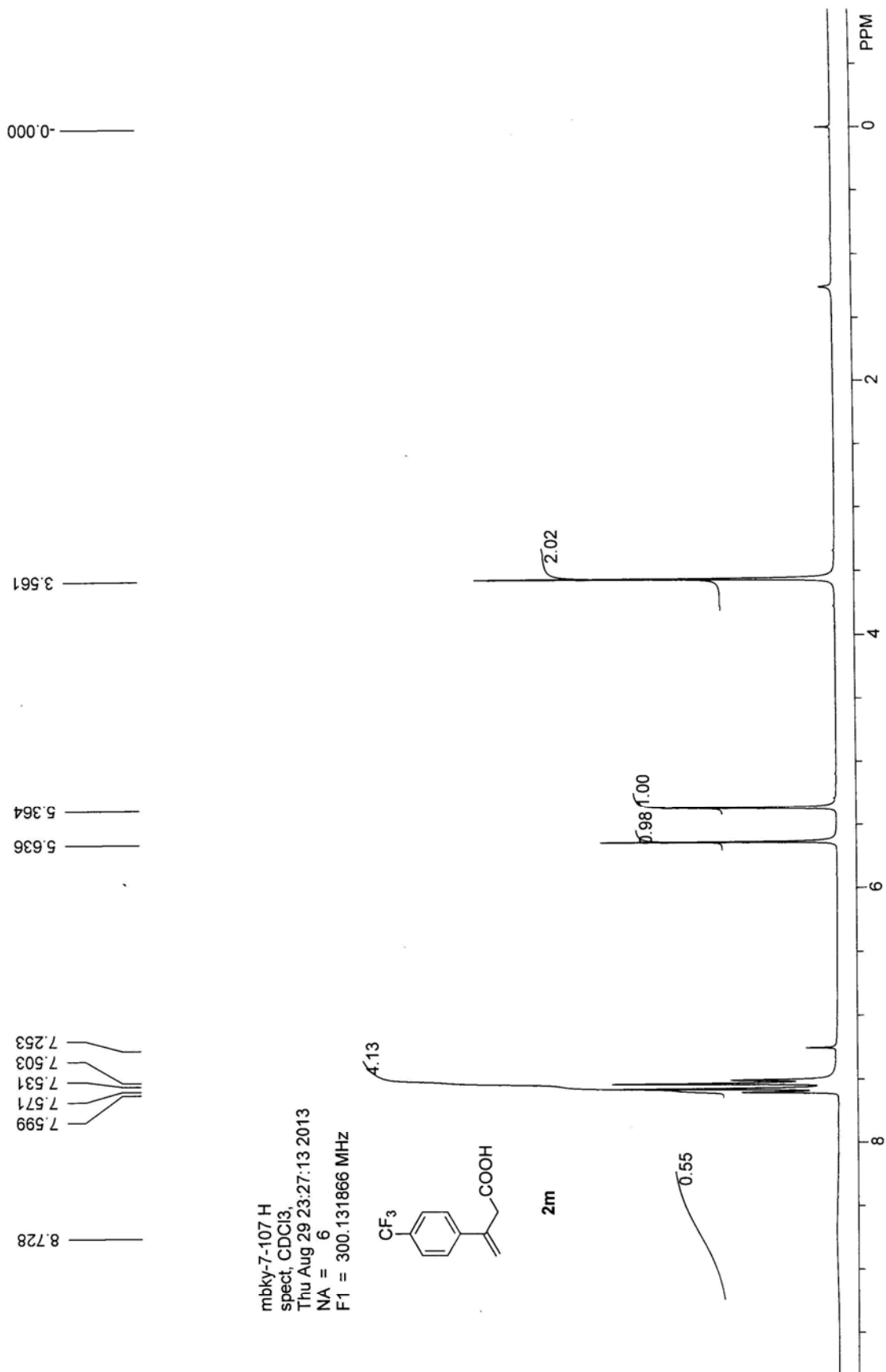
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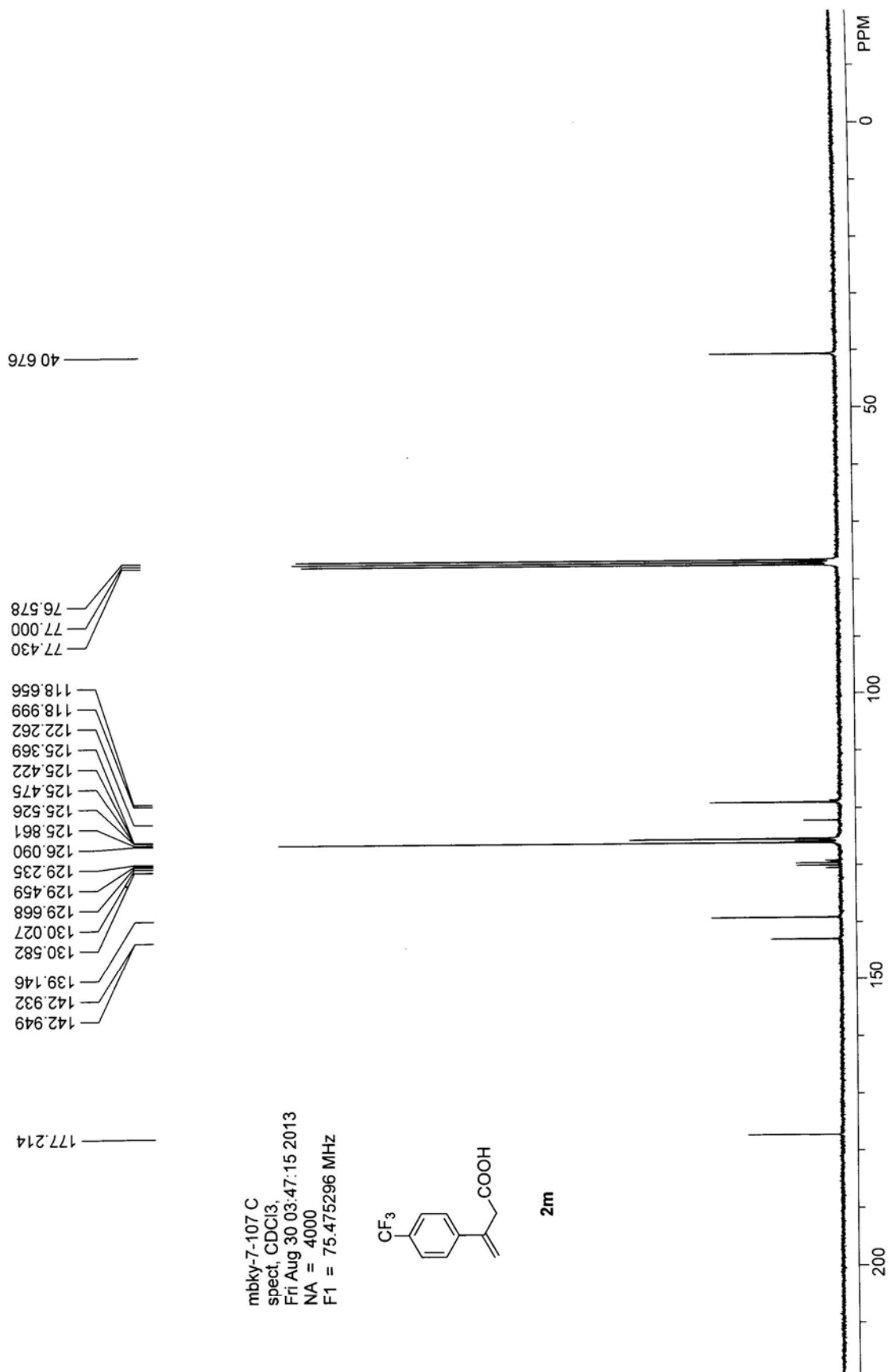
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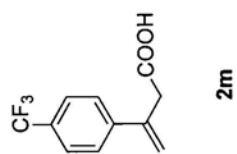


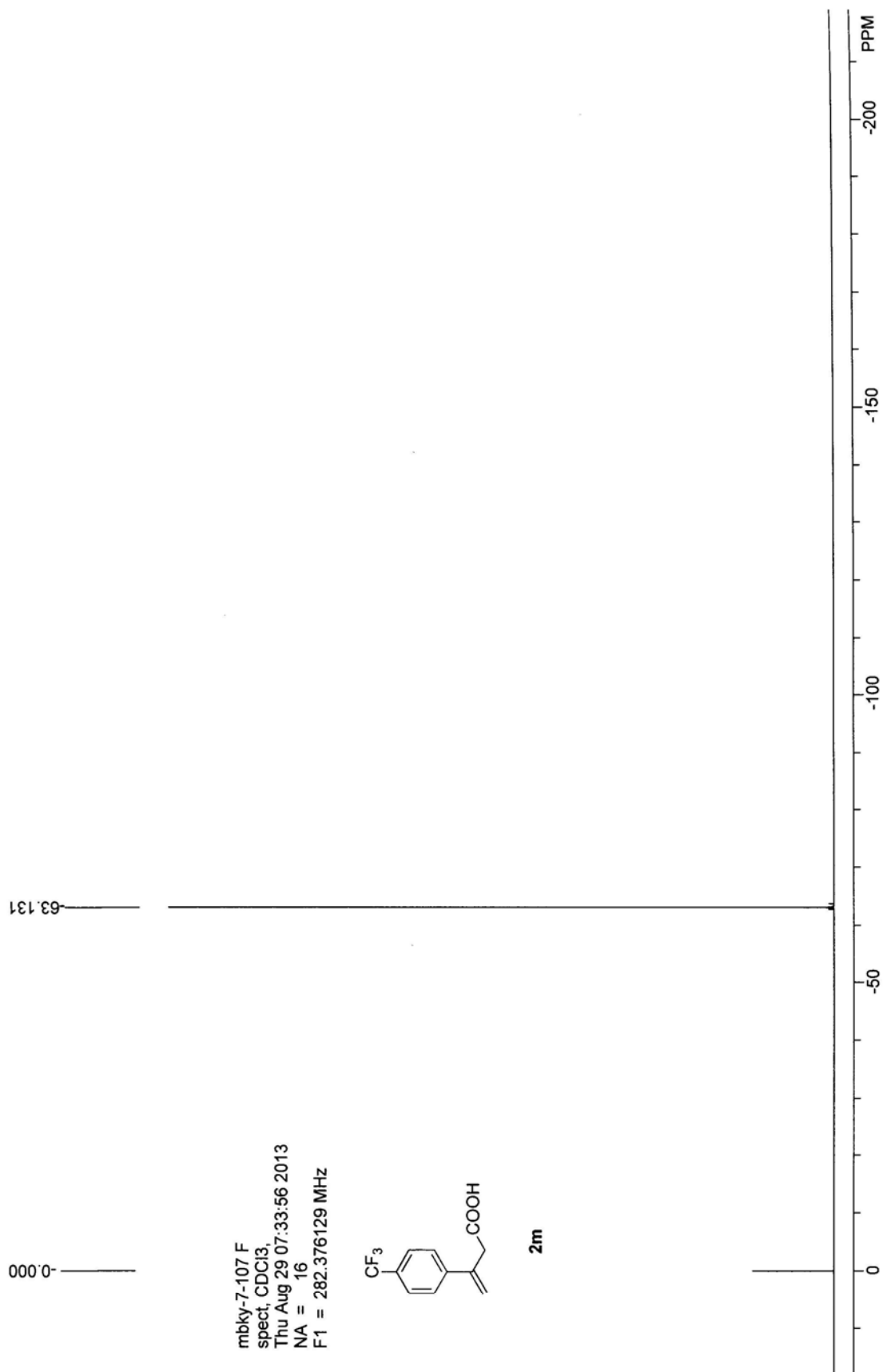
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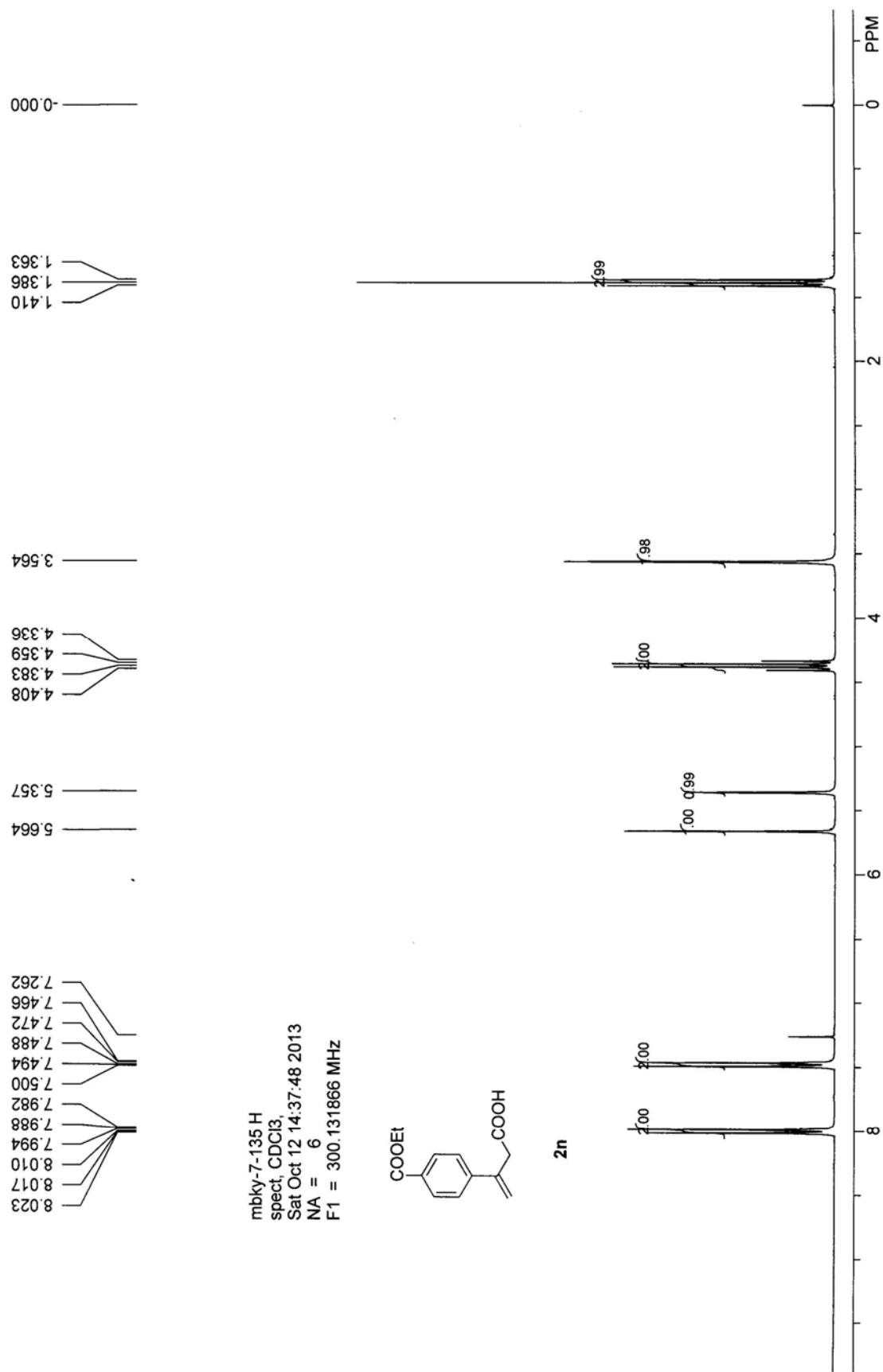




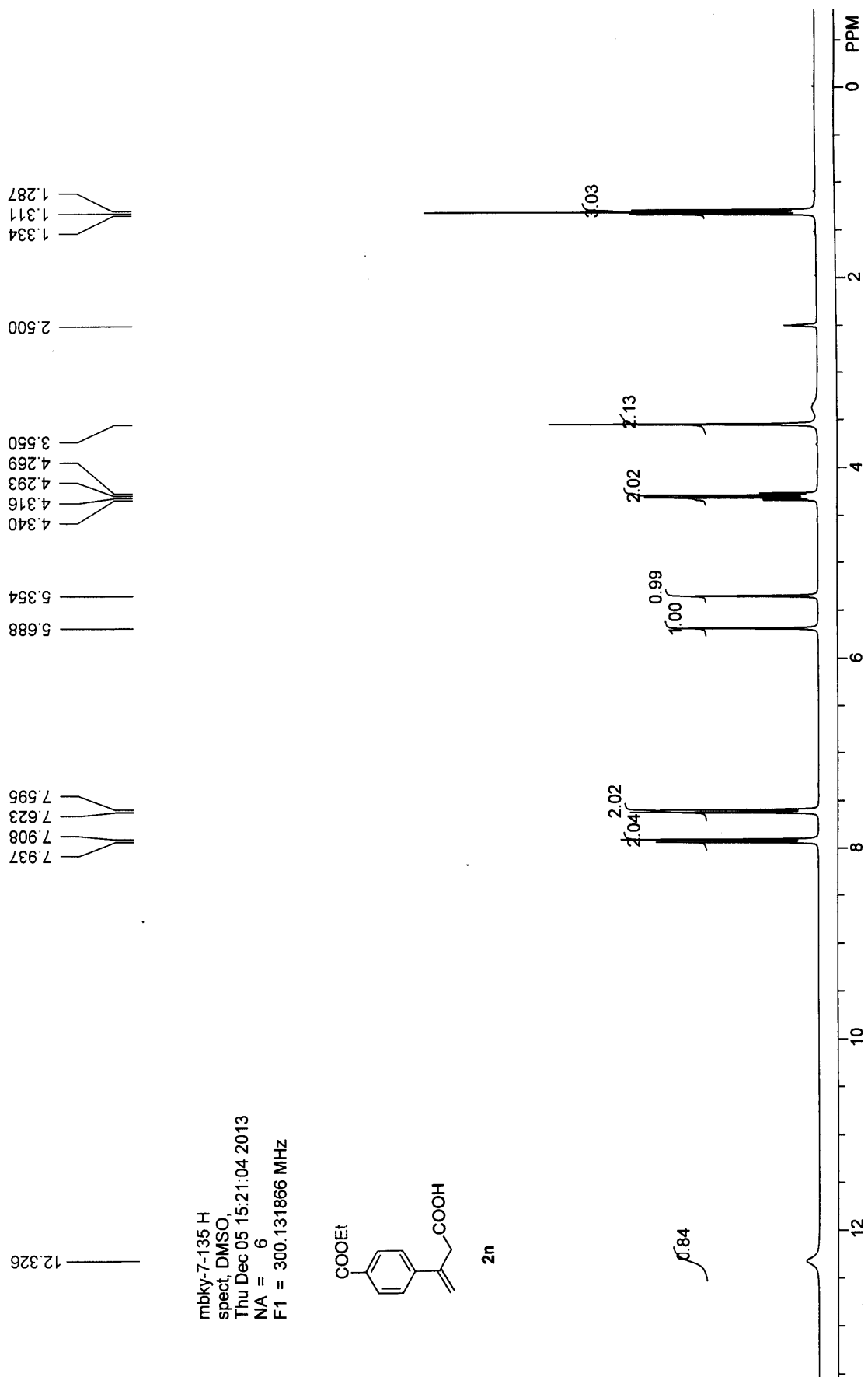
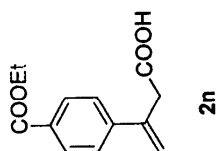
mbky-7-107 C
 spect, CDCl₃,
 Fri Aug 30 03:47:15 2013
 NA = 4000
 F1 = 75.475296 MHz

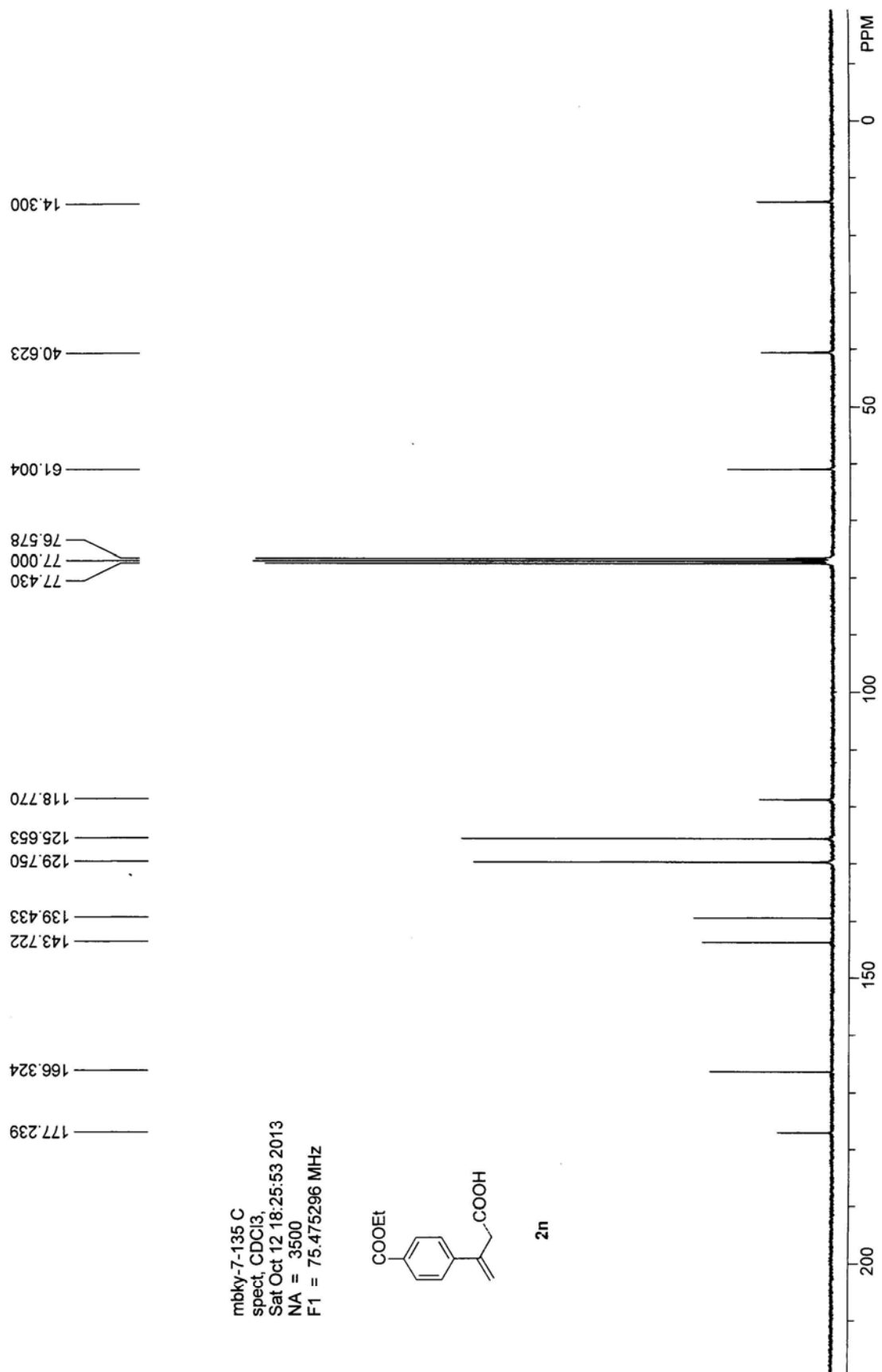


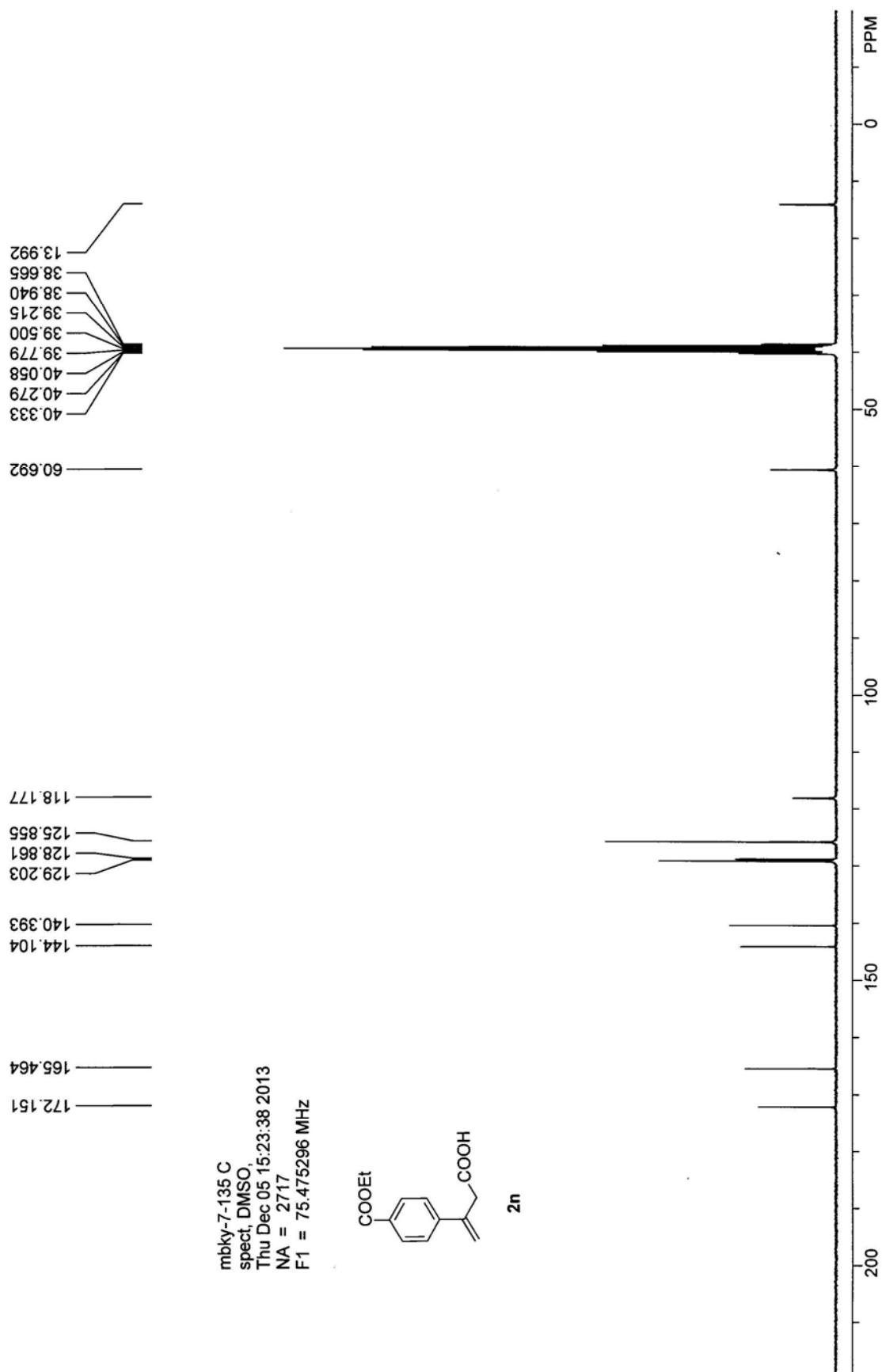




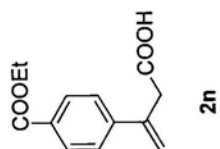
mbky-7-135 H
spect, DMSO,
Thu Dec 05 15:21:04 2013
NA = 6
F1 = 300.131866 MHz

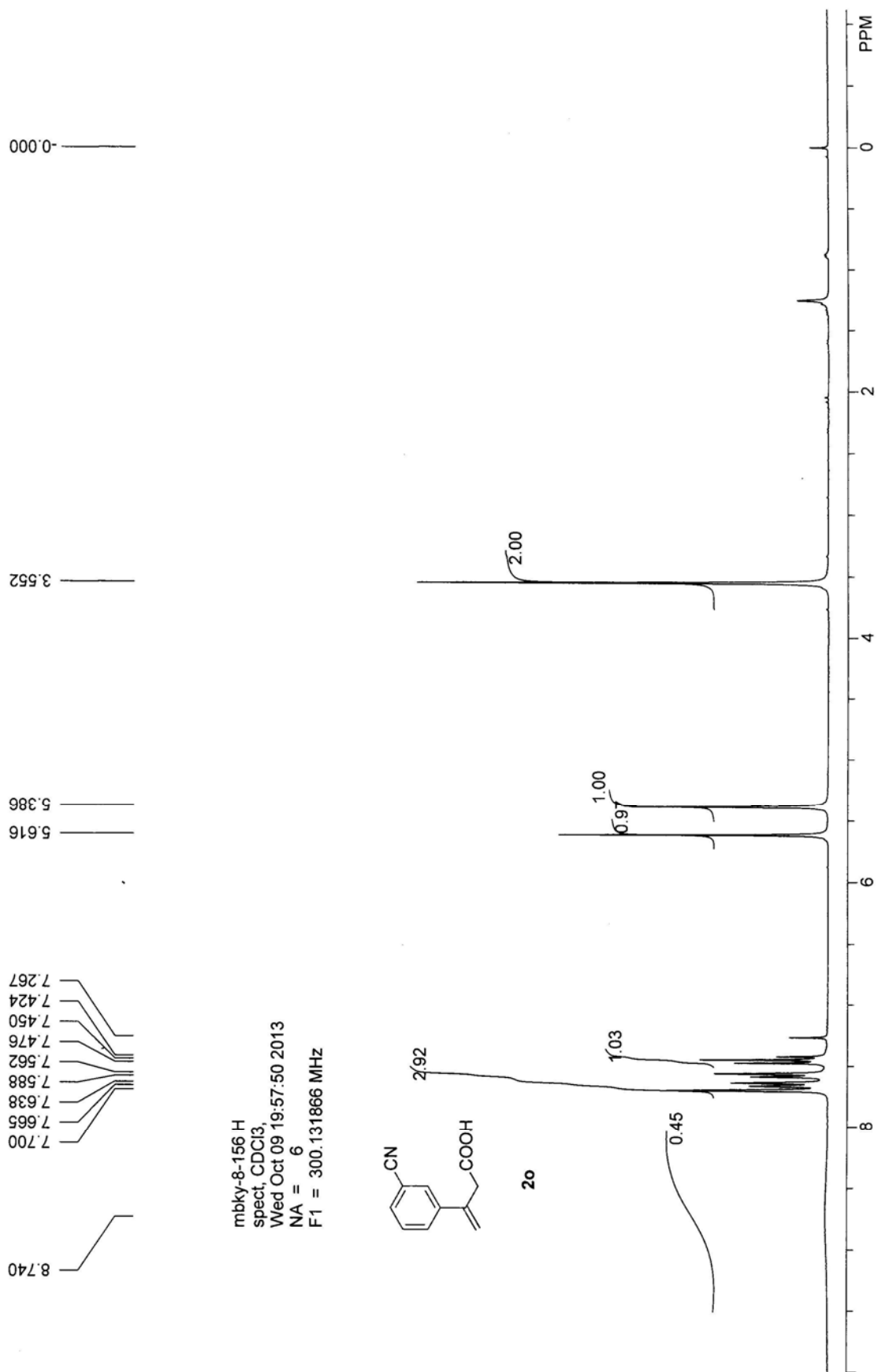




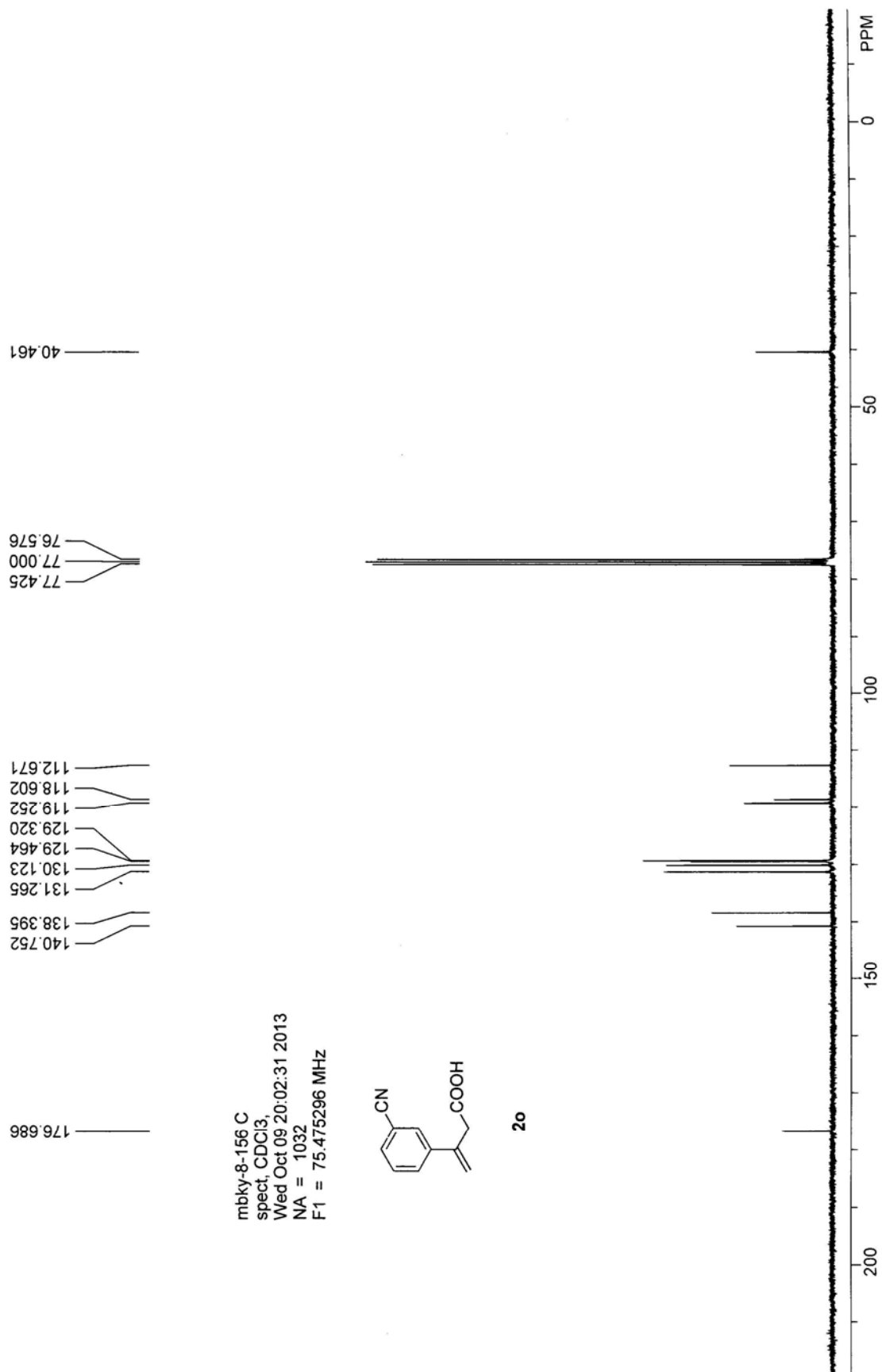


mbky-7-135 C
spect, DMSO,
Thu Dec 05 15:23:38 2013
NA = 2717
F1 = 75.475296 MHz

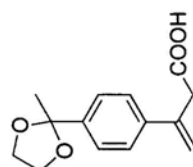




mbky-8-156 H
spect, CDCl₃,
Wed Oct 09 19:57:50 2013
NA = 6
F1 = 300.131866 MHz



mbky-8-155 H
 spect, CDCl₃,
 Wed Oct 09 21:14:53 2013
 NA = 6
 F1 = 300.131866 MHz



2p

