Water-Compatible Highly Active Reusable PEG-Coated Mesoporous Silica Supported Palladium Complex and Its Application in Organic Synthesis

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Supporting Information:

Analytical data	SI-1
^{1}H / ^{13}C / ^{19}F NMR Spectra	SI-11

Preparation of alcohol 2:[1] To a mixture of KOH (28.0 g, 0.50 mol) and tetra(ethylene glycol) **1** (89.0 g, 0.46 mol) in a three-necked flash was added allyl bromide (60.5 g, 0.50 mol) at 0 ^{o}C. The mixture was stirred at 60 °C for 3 h. After the reaction was complete as monitored by TLC (eluent: petroleum ether/ethyl acetate = 1/1), it was extracted with ether. Drying over $MgSO_4$, rotary evaporation, and flash chromatography on silica gel (eluent: petroleum ether/ether acetate = 1/1) afforded **2** as a yellow oil (38.2 g, 36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.98-5.82 (m, 1 H),

5.32-5.13 (m, 2 H), 4.02-3.98 (m, 2 H), 3.73-3.56 (m, 16 H), 2.73 (br, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.5, 117.2, 72.6, 72.2, 70.53, 70.47, 70.44, 70.1, 69.3, 61.62, 61.60. IR (neat): 3416, 3082, 2872, 1647, 1458, 1350, 1107 cm^{-1}. MS (EI) *m/z* (relative intensity) 235 (M^++1, 0.88), 45 (100).

Preparation of 3: To a solution of KOH (17.9 g, 0.32 mol) and **2** (38 g, 0.16 mol) in THF (100 mL) was added EtBr (26.6 g, 0.24 mol) at 0 ^{o}C. The mixture was then stirred at 60 °C for 3 h. After the reaction was complete as monitored by TLC (eluent: petroleum ether/ether acetate = 1/1), it was extracted with ether. Drying over $MgSO_4$, rotary evaporation, and flash chromatography on silica gel (eluent: petroleum ether/ether acetate = 1/1) afforded **3** as a yellow oil (38.6 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.96-5.82 (m, 1 H), 5.29-5.12 (m, 2 H), 4.02-3.98 (m, 2H), 3.64-3.54 (m, 16 H), 3.50 (q, *J* = 7.0 Hz, 2 H), 1.18 (q, *J* = 7.0 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.7, 117.0, 72.2, 70.61, 70.58, 70.54, 69.8, 69.4, 66.6, 15.1. IR (neat): 2896, 1349, 1114, 927 cm^{-1}. MS (EI) *m/z* (relative intensity) 263 (M^++1, 1.85), 45 (100). HRMS calcd for $C_{13}H_{26}O_5Na$ [M^++Na]: 285.1673, found: 285.1681.

Preparation of Organosilane 4: $H_2PtCl_6{\cdot}6H_2O$ (150 mg, 0.29 mmol) was dried under vacuum (3 h, 200 °C) in a 250 mL round bottom flask, followed by addition of **3**(38.5 g, 0.15 mol) and triethoxysilane (241 g, 1.46 mol) at rt under nitrogen. After stirring at ambient temperature for 24 h, the unreacted triethylsilane was removed in vacuo, and the residue was distilled to give product as a colorless oil (48.2 g, 77 %), b.p. 148-154 ºC/0.1 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (q, *J* = 7.3 Hz, 6 H), 3.66-3.47 (m, 18 H), 3.42 (t, *J* = 7.1 Hz, 2 H), 1.74-1.62 (m, 2 H), 1.24-1.16 (m, 12 H),

0.61 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 73.6, 70.6, 70.5, 69.9, 69.8, 66.6, 58.3, 22.8, 18.2, 15.1, 6.3. IR (neat): 3399, 2973, 2871, 1455, 1350, 1112, 954, 775 cm^{-1}. MS (ESI) 444 [M + NH_4^+]. Anal. Calcd for $C_{19}H_{42}O_8Si$: C, 53.49; H, 9.92; Found: C, 53.07; H, 9.51.

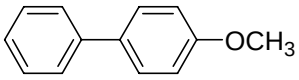
Preparation of SBA-15:[2] In a typical synthesis, pluronic P123(4.0 g) was dissolved in a mixture of water (30 mL) and 2 M HCl (120 mL). Tetraethoxysilane (8.5 g) was as added to this solution with vigorous stirring for 20 h at 40 ºC in a beaker. Then the mixture was poured into an autoclave and heated at 100 ºC for 2 days. The resultant solid was filtered off and then the surfactant template was removed by solvent extraction in refluxing ethanol with stirring for 2 days.

Preparation of coated SBA-15: To 13 g of template removed SBA-15 dried under vacuum at 120 ºC for 3 h was added 60 mL of dry toluene and 9.3 g of organosilane **4**. The resulting mixture was refluxed under N_2 for 6 h and then filtered. The solid obtained was washed repeatedly with toluene to afford the coated SBA-15.

Preparation of SBA-Si-PEG-Pd(PPh_3)$_n$ 6: Coated SBA-15 **5** (2.0 g) was dispersed in dry THF (20 ml) and then a solution of Pd(PPh_3)$_4$ (0.21 g, 1.8 mmol) in dry THF (20 mL) was added slowly. After stirring for 10 h at rt, the solid was filtered, washed with THF, and dried in vacuo. The Pd % in this supported catalyst is 0.050 mmol/g as determined by ICP, and the P % in this supported catalyst is 0.017 mmol/g as determined by HPIC.

Representative procedure for Suzuki coupling reaction catalyzed by SBA-Si-PEG--Pd(PPh$_3$)$_n$* 6 *(Table 3, entry 7): A mixture of *o*-iodophenol (4.40 g, 20 mmol), phenyl boronic acid (2.93 g, 24 mmol), $K_3PO_4 \cdot 3H_2O$ (10.4 g, 40 mmol), SBA-Si-PEG-Pd(PPh$_3$)$_n$ (0.001 mol%), and H_2O (40 mL) was stirred at 50 ºC for 24 h. After being cooled down to rt, the reaction mixture was extracted with Et_2O (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/Et_2O = 3:1) to yield 2-phenylphenol (**9i**)[1] as a white solid (3.322 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.38 (m, 5 H), 7.33-7.26 (m, 2 H), 7.07-7.00 (m, 2 H), 5.32 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.3, 137.0, 130.2, 129.2, 129.1, 129.0, 128.1, 127.8, 120.8, 115.8. IR (neat): 3565, 3528, 1584, 1484, 1434, 1101, 757, 699 cm^{-1}. MS (EI) *m/z* (relative intensity) 170 (M^+, 100).

(1) 4-Methoxybiphenyl (9a) (Table 2, entry 1): [2]

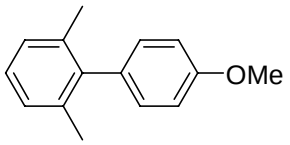


9a

The reaction of **6** (1.0 mol%), aryl iodide **7a** (61 mg, 0.30 mmol), *p*-methoxyphenyl boronic acid **8a** (55 mg, 0.36 mmol) and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9a** (50 mg, 90 %). *Condition B*: The reaction of **6** (0.5 mol%), phenyl bromide **7b** (316 mg, 2.0 mmol), phenylboronic acid **8a** (151 mg, 1.0 mmol), and $K_3PO_4 \cdot 3H_2O$ (532 mg, 2.0 mmol) in H_2O (3 mL) at 90 °C for 10 h afforded **9a** (160 mg, 87 %). *Condition C*: The reaction of **6** (0.5 mol%), phenyl chloride **7c** (229 mg, 2.0 mmol), benzeneboronic acid **8a** (152 mg, 1.0 mmol), SPhos (4 mg, 1 mol%), and $K_3PO_4 \cdot 3H_2O$ (532 mg, 0. 60 mmol) in H_2O (3 mL) at 60 °C for 10 h afforded **9a** (154

mg, 84 %). *Condition D*: The reaction of **6** (1.0 mol%), aryl iodide **7f** (70 mg, 0.30 mmol), phenylboronic acid **8b** (44 mg, 0.36 mmol), and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9a** (48 mg, 89 %). *Condition E*: The reaction of **6** (0.1 mol%), aryl iodide **7f** (72 mg, 0.30 mmol), benzeneboronic acid **8b** (44 mg, 0.36 mmol)**,** and $K_3PO_4 \cdot 3H_2O$ (160 g, 0. 60 mmol) in H_2O (3 mL) afforded **9a** (45 mg, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.58 (m, 4 H), 7.55-7.45 (m, 2 H), 7.41-7.34 (m, 1 H), 7.08-7.03 (m, 2 H), 3.90 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 140.7, 133.6, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2. IR (neat): 2962, 1607, 1488,1251, 834, 761 cm^{-1}. MS (EI) *m/z* (relative intensity) 184 (M^+, 66.94), 44 (100).

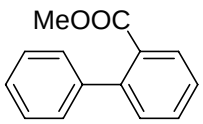
(2) 4-Methoxy-2',6'-dimethylbiphenyl (9b) (Table 2, entry 4): [3]



9b

The reaction of **6** (1.0 mol %), PPh_3 (2.0 mol %), aryl iodide (2,6-$Me_2C_6H_3I$, 67 mg, 0.29 mmol), *p*-methoxyphenyl boronic acid **8a (**55 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9b** (52 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23-7.09 (m, 5 H), 7.04-6.97 (m, 2 H), 3.89 (s, 3 H), 2.09 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 141.5, 136.5, 133.2, 130.0, 127.2, 126.8, 113.7, 55.1, 20.9. IR (neat): 2953, 1609, 1517, 1467, 1285, 1238, 837 cm^{-1}. MS (EI) *m/z* (relative intensity) 212 (M^+, 100).

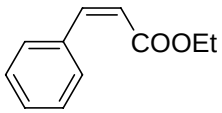
(3) 2-Methoxycarbonylbiphenyl (9c) (Table 2, entry 6):[4]



9c

The reaction of **6** (0.1 mol%), aryl iodide (*o*-$MeO_2CC_6H_4I$, 78 mg, 0.30 mmol), phenyl boronic acid **8b (**44 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 g, 0.60 mmol) in H_2O (3 mL) afforded **9c** (60 mg, 93 %). The special data were in accordance with those reported in the literature.[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.5 Hz, 1H), 7.58-7.52 (m, 1 H), 7.47-7.32 (m, 7 H), 3.66 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1, 142.4, 141.2, 131.2, 130.7, 130.6, 129.7, 128.2, 128.0, 127.15, 127.08, 51.9. IR (neat): 1731, 1289, 1126, 746, 700 cm^{-1}. MS (EI) *m/z* (relative intensity) 212 (M^+, 50.77), 181 (100).

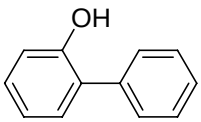
(4) (*Z*)3-phenyl-acrylic acid ethyl ester (9d) (Table 2, entry 7):[5]



9d

The reaction of **6** (0.1 mol%), iodide *(Z)*-$EtO_2CC_2H_2I$ **7g** (63 mg, 0.28 mmol), phenyl boronic acid **8b** (44 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9d** (44 mg, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62-7.56 (m, 2 H), 7.40-7.28 (m, 3 H), 6.96 (d, J = 12.6 Hz, 1 H), 5.96 (d, J = 12.6 Hz, 1 H), 4.18 (q, J = 7.2 Hz, 2 H), 1.25 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 143.0, 134.8, 129.6, 128.9, 127.9, 119.8, 60.3, 14.0. IR (neat): 2981, 1721, 1629, 1181, 1029 cm^{-1}. MS (EI) *m/z* (relative intensity) 176 (M^+, 24.19), 131 (100).

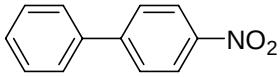
(5) 2-Phenylphenol (9e) (Table 2, entry 8) :[1]



9e

The reaction of **6** (0.1 mol%), aryl iodide (*o*-HOC_6H_4I, 64 mg, 0.29 mmol),phenyl boronic acid **8b (**44 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9e** (48 mg, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.59-7.38 (m, 5 H), 7.33-7.26 (m, 2 H), 7.07-7.00 (m, 2 H), 5.32 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.3, 137.0, 130.2, 129.2, 129.1, 129.0, 128.1, 127.8, 120.8, 115.8. IR (neat): 3565, 3528, 1584, 1484, 1434, 1101, 757 cm^{-1}. MS (EI) *m/z* (relative intensity) 170 (M^+, 100).

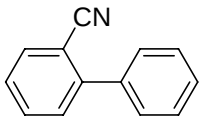
(6) 4-Nitrodiphenyl (9f) (Table 2, entry 9):[6]



9f

The reaction of **6** (0.1 mol%), aryl bromide (1-bromo-2-nitro benzene, 60 mg, 0.30 mmol), phenyl boronic acid **8b (**44 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9f** (48 mg, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.66-7.60 (m, 2 H), 7.55-7.42 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.5, 146.9, 138.6, 129.1, 128.9, 127.7, 127.3, 124.0. IR (neat): 1596, 1514, 1345, 853, 740 cm^{-1}. MS (EI) *m/z* (relative intensity) 199 (M^+, 86.93), 152 (100).

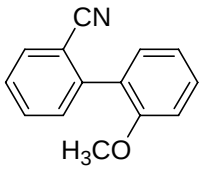
(7) 2-Cyanobiphenyl (9g) (Table 2, entry 10): [7]



9g

The reaction of **6** (0.1 mol%), aryl bromide (*o*-NCC_6H_4Br, 54 mg, 0.30 mmol), phenyl boronic acid **8b (**44 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9g** (44 mg, 83 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.73 (m, 1 H), 7.70-7.60 (m, 1 H), 7.60-7.41 (m, 7 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.3, 138.0, 133.6, 132.8, 130.0, 128.7, 128.63, 128.61, 127.5, 118.7, 111.1. IR (neat): 3064, 2224, 1595, 1477, 759, 700 cm^{-1}. MS (EI) *m/z* (relative intensity) 179 (M^+, 100).

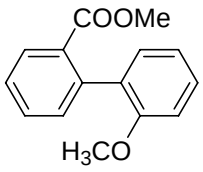
(8) 2-Methoxy-2-cyanobiphenyl (9h) (Table 2, entry 11): [8]



9h

The reaction of **6** (0.1 mol%), aryl bromide (*o*-NCC_6H_4Br, 182 mg, 1.0 mmol), *o*-methoxyphenyl boronic acid **8c (**182 mg, 1.2 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (532 mg, 2.0 mmol) in H_2O (3 mL) afforded **9h** (185 mg, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77-7.72 (m, 1 H), 7.60-7.67 (m, 1 H), 7.50-7.39 (m, 3 H), 7.31-7.26 (m, 1 H), 7.15-7.02 (m, 2 H), 3.85 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 142.4, 132.6, 132.3, 130.78, 130.75, 130.2, 127.2, 127.1, 120.6, 118.6, 113.2, 111.2, 55.3. IR (neat): 3066, 2226, 1602, 1500, 1255, 1026 cm^{-1}. MS (EI) *m/z* (relative intensity) 209 (M^+, 100).

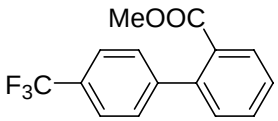
(9) 2-Methoxy-2'-(methoxycarbonyl)biphenyl (9i) (Table 2, entry 12): [9]



9i

The reaction of **6** (0.1 mol%), aryl iodide (*o*-$MeO_2CC_6H_4I$, 78 mg, 0.30 mmol), *o*-methoxyphenyl boronic acid **8c (**55 mg, 0.36 mmol**)** and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.60 mmol) in H_2O (3 mL) afforded **9i** (64 mg, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.4 Hz, 1 H), 7.60-7.53 (m, 1 H), 7.45-7.27 (m, 4 H), 7.11-7.03 (m, 1 H), 6.93 (d, J = 7.8 Hz, 1 H), 3.74 (s, 3 H), 3.68 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 155.9, 138.6, 131.5, 131.2, 130.4, 129.8, 129.2, 128.8, 127.0, 120.7, 110.0, 55.1, 51.6. IR (neat): 2951, 1732, 1598, 1293 cm^{-1}. MS (EI) *m/z* (relative intensity) 242 (M^+, 36.22), 211 (100).

(10) 4-(Trifluoromethyl)-2'-(methoxycarbonyl)biphenyl (9j) (Table 2, entry 13): [10]



9j

The reaction of **6** (0.1 mol%), aryl iodide (*o*-$MeO_2CC_6H_4I$, 262 mg, 1.0 mmol), 4-(Trifluoromethyl)-phenylboronic acid **8d** (228 mg, 1.2 mmol**)** and $K_3PO_4 \cdot 3H_2O$ were (532 mg, 2.0 mmol) in H_2O (3 mL) afforded **9j** (240 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, J_1 = 6.3 Hz, J_2 = 1.2 Hz, 1 H), 7.67 (d, J = 8.1 Hz, 2 H), 7.60-7.53 (m, 1 H), 7.50-7.46 (m, 1 H), 7.43(d, J = 8.1 Hz, 2 H), 7.37-1.32 (m, 1 H), 3.67 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3, 145.1, 141.4, 131.6, 130.7, 130.3, 130.2, 129.3 (q, $^2J_{CF}$ = 32.0 Hz), 128.7, 127.9, 124.9 (q, $^3J_{CF}$ = 3.6 Hz), 124.2 (q, $^1J_{CF}$ = 270.5 Hz), 52.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ = 62.8. IR (neat): 2949,

1730, 1326, 1255, 1126, 1069 cm^{-1}. MS (EI) *m/z* (relative intensity) 280 (M^+, 100).

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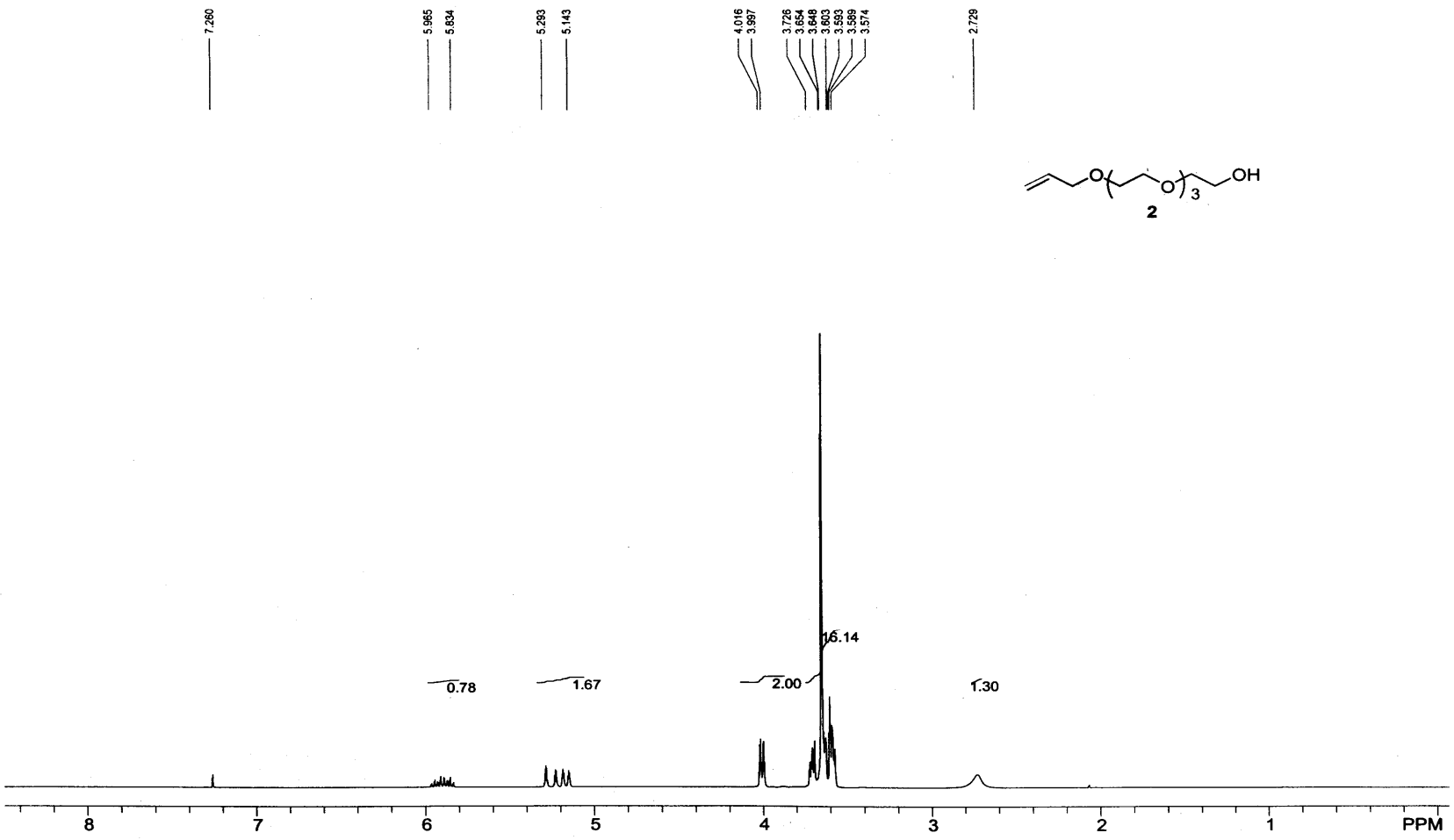
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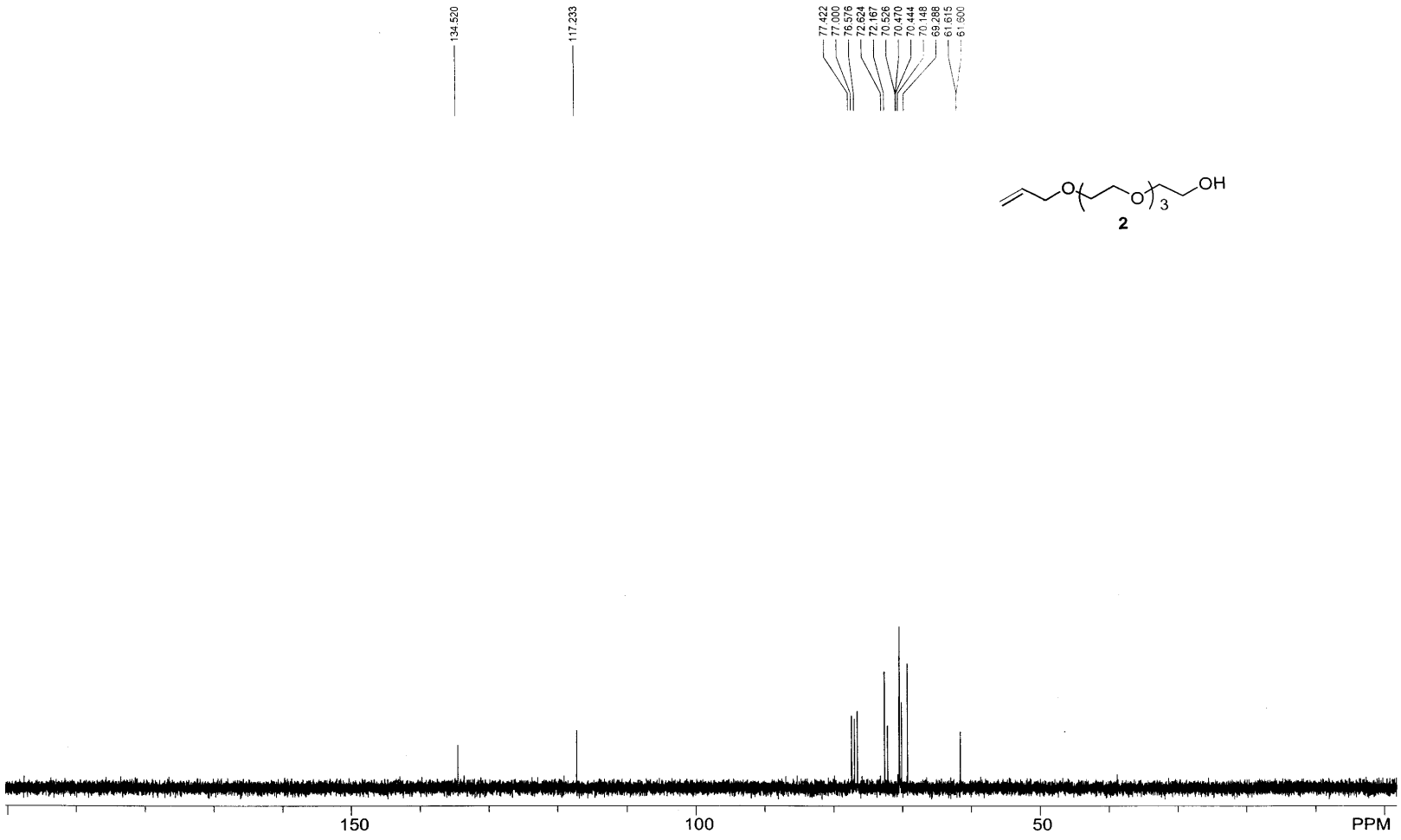
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O
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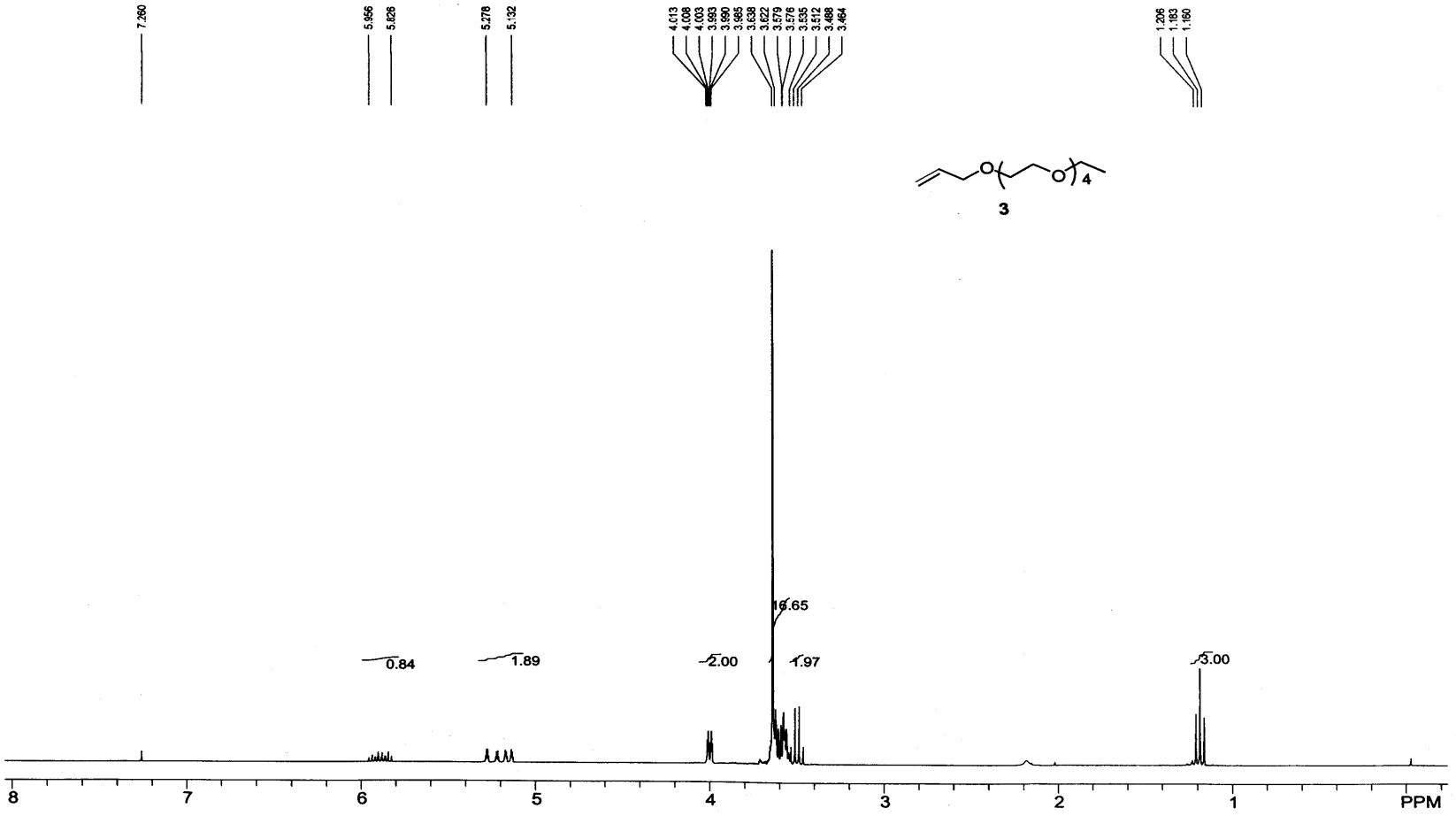
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3.638
3.622
3.579
3.576
3.535
3.512
3.488
3.464
1.206
1.183
1.160
O
O
4
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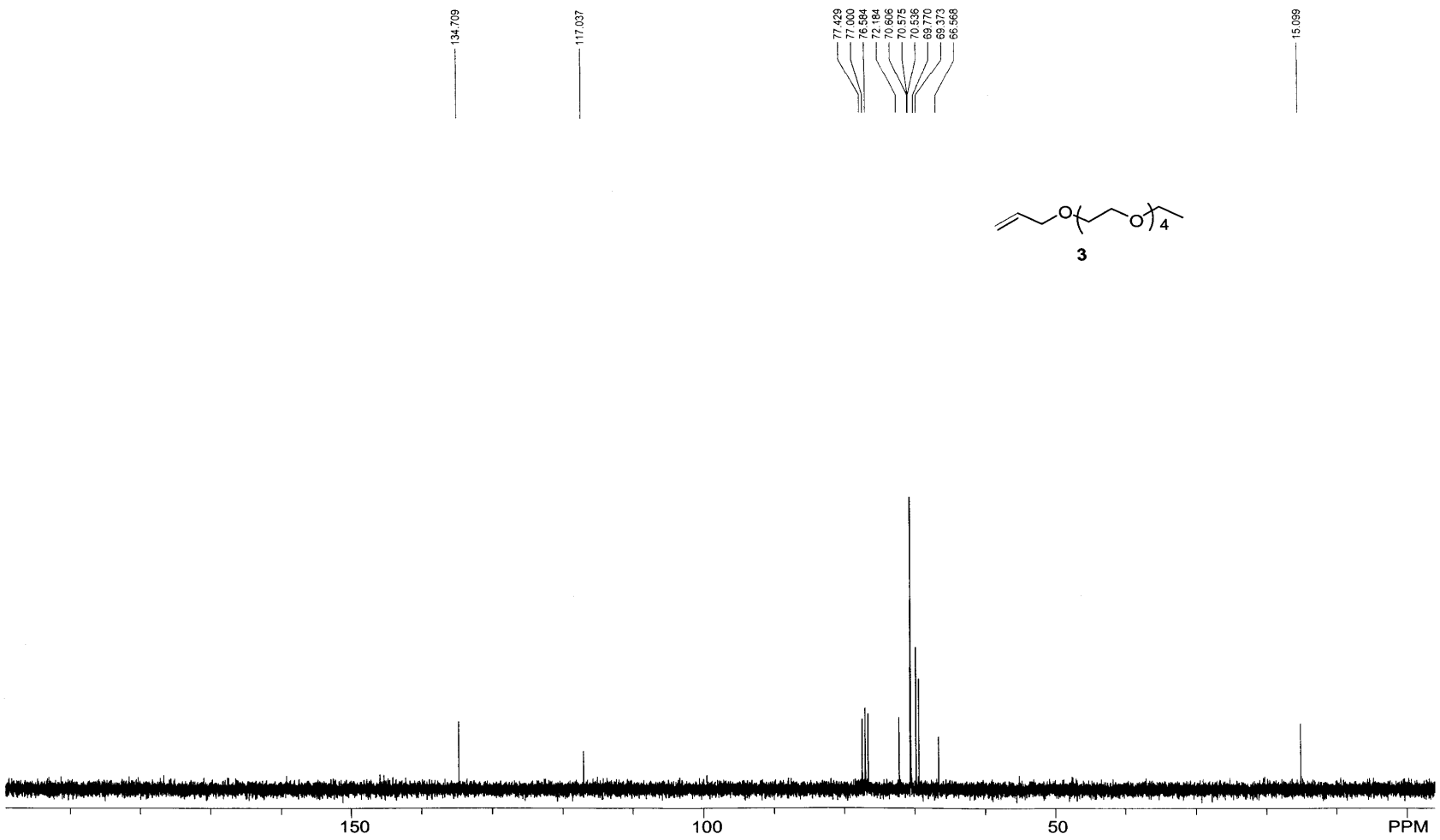
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O
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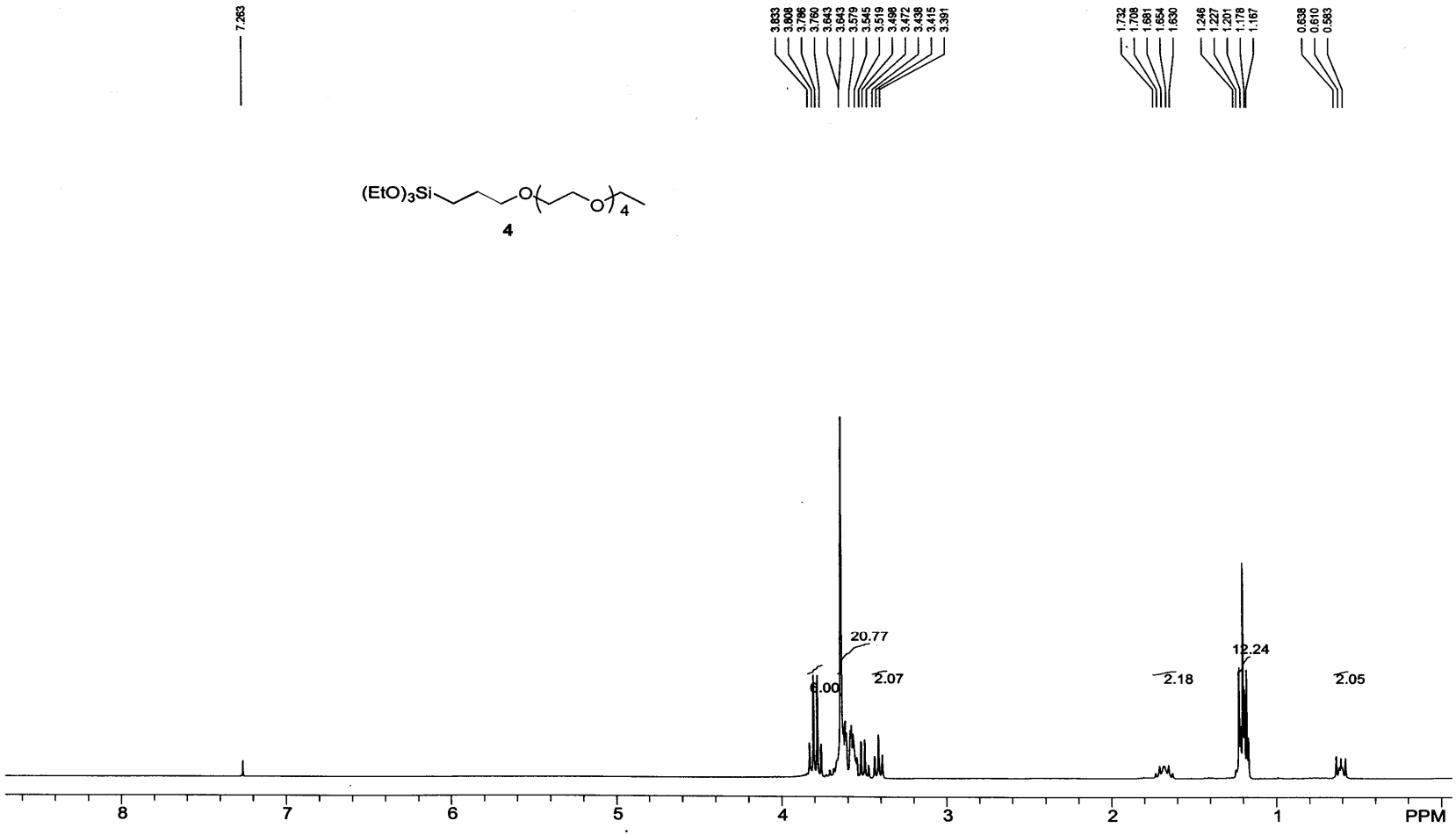
PPM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3.833
3.808
3.786
3.760
3.643
3.543
3.579
3.545
3.519
3.498
3.472
3.438
3.415
3.391
1.732
1.708
1.681
1.654
1.630
1.246
1.227
1.201
1.178
1.167
0.638
0.610
0.583
(EtO)3Si
O
O
4
4
20.77
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2.07
2.18
12.24
2.05
8
7
6
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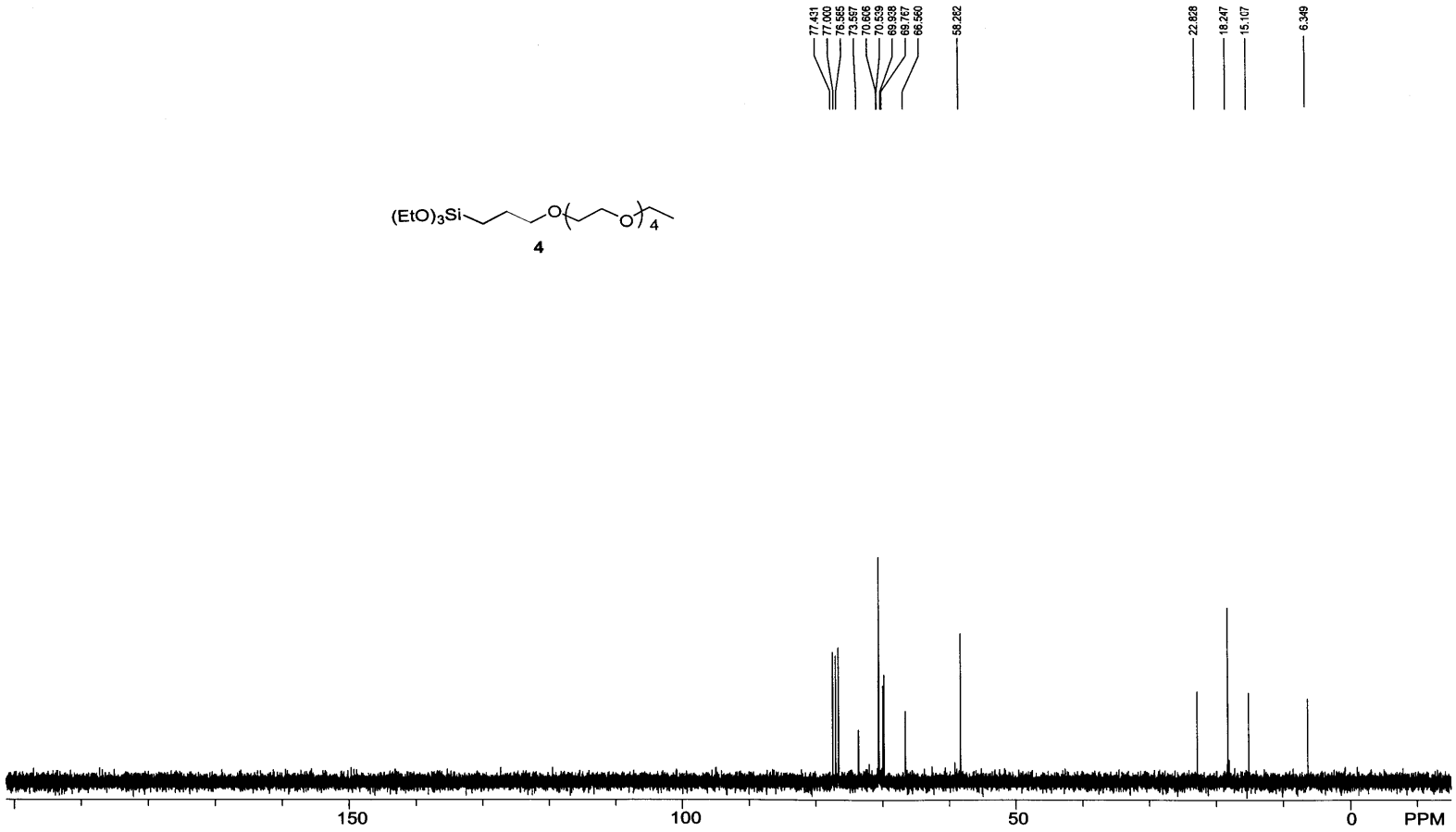
1
PPM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77.000
76.585
73.567
70.606
70.539
69.938
69.767
66.560
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18.247
15.107
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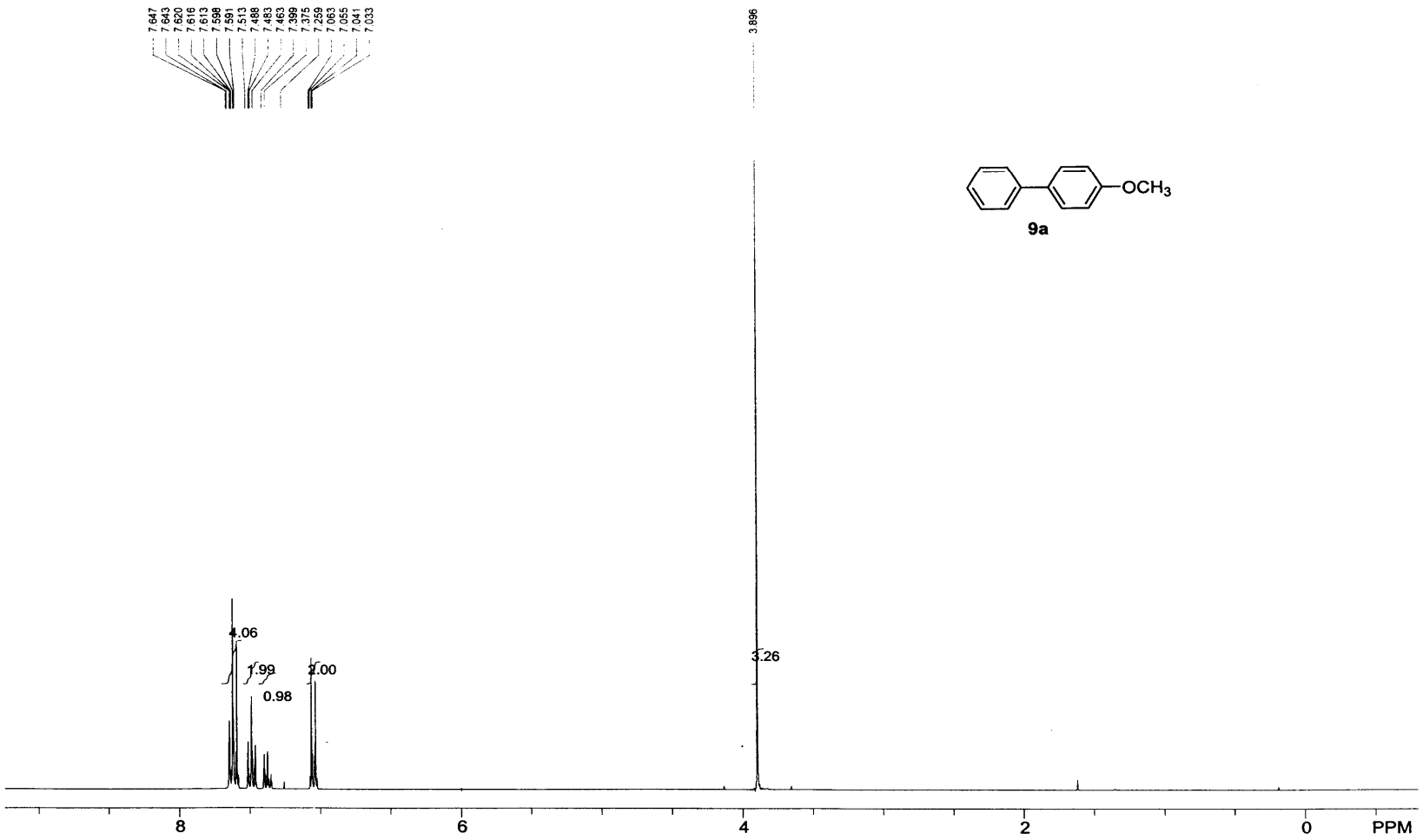
(EtO)3Si
O
O
4
4
150
100
50
0
PPM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7.643
7.620
7.616
7.613
7.598
7.591
7.513
7.488
7.483
7.463
7.399
7.375
7.259
7.063
7.055
7.041
7.033
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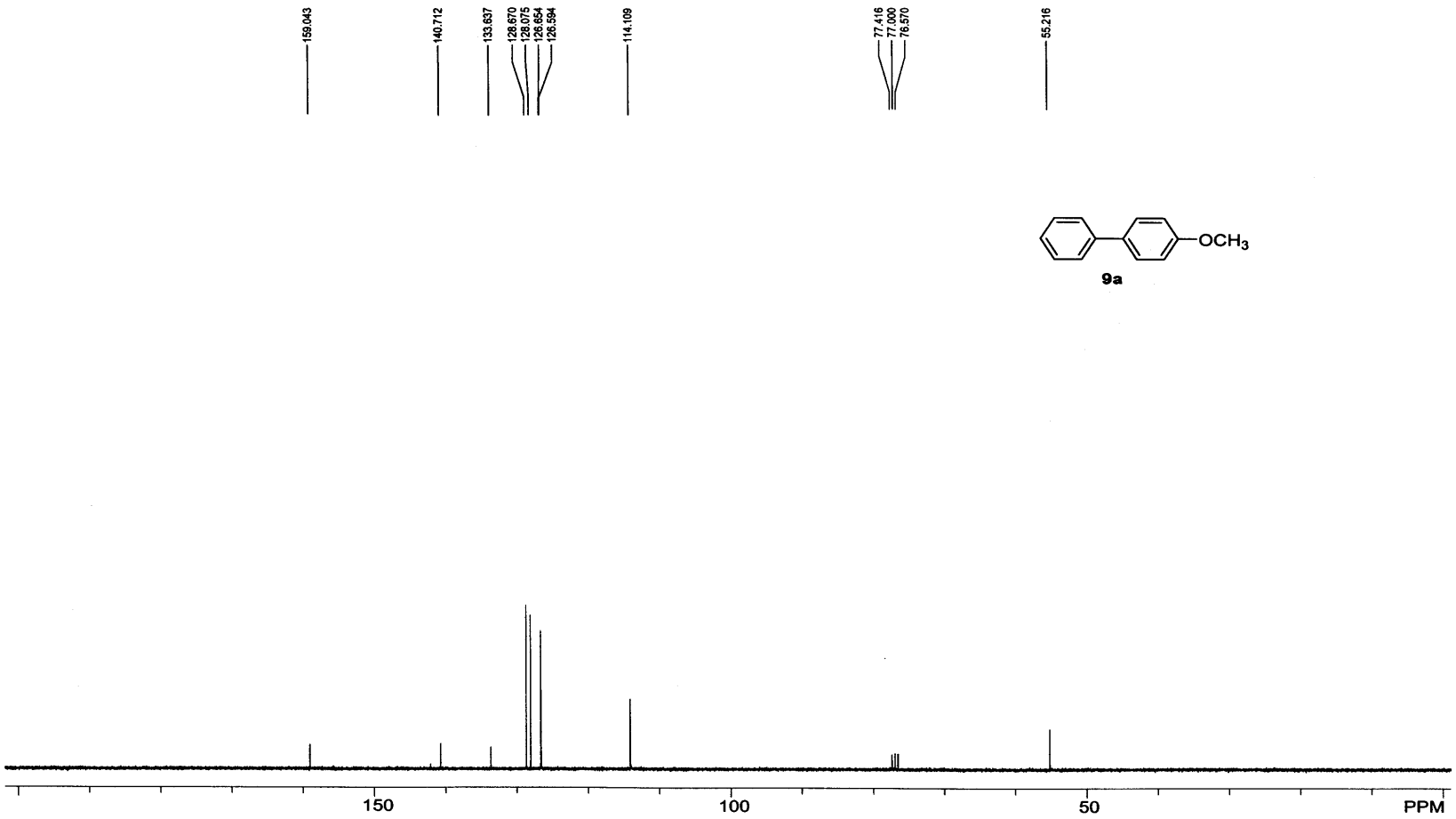
4.06
1.99
0.98
2.00
3.26
8
6
4
2
0
PPM

OCH3

9a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140.712
133.637
128.870
128.075
126.654
126.594
114.109
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77.000
76.570
55.216
OCH3
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150
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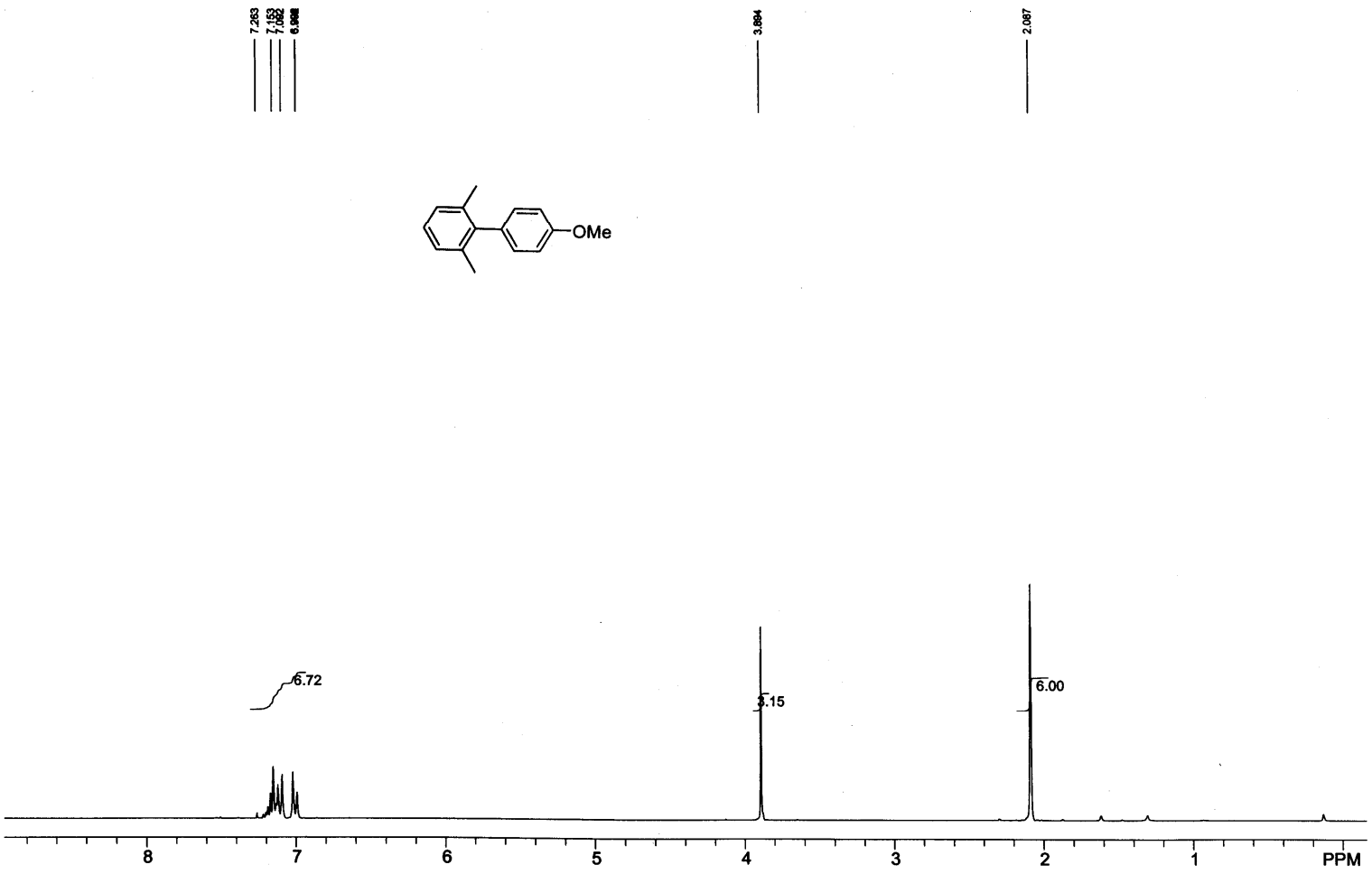
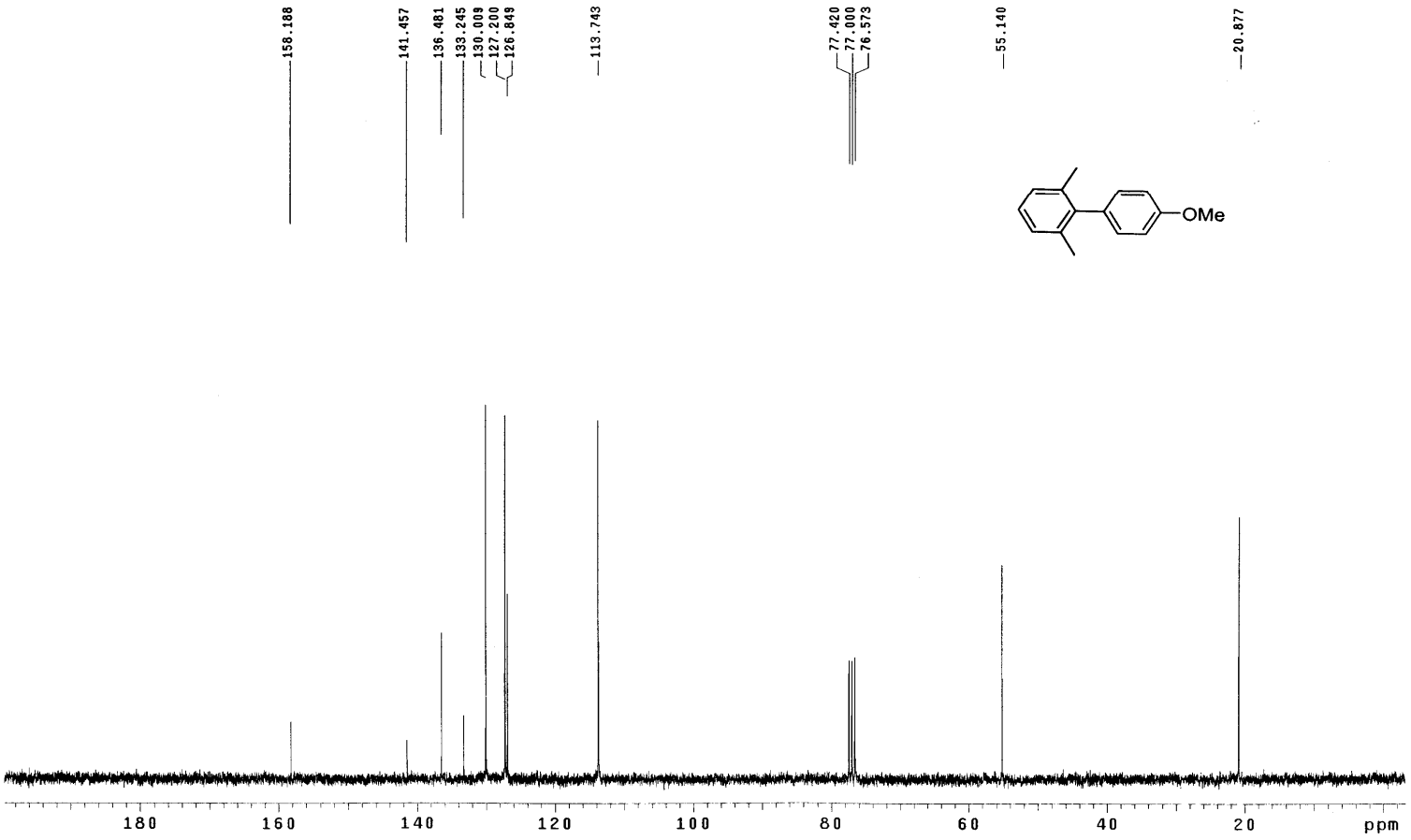
50
PPM


7.263
7.153
7.062
6.998
3.894
2.067
OMe
6.72
3.15
6.00
8
7
6
5
4
3
2
1
PPM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136.481
133.245
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127.200
126.849
113.743
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OMe
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140
120
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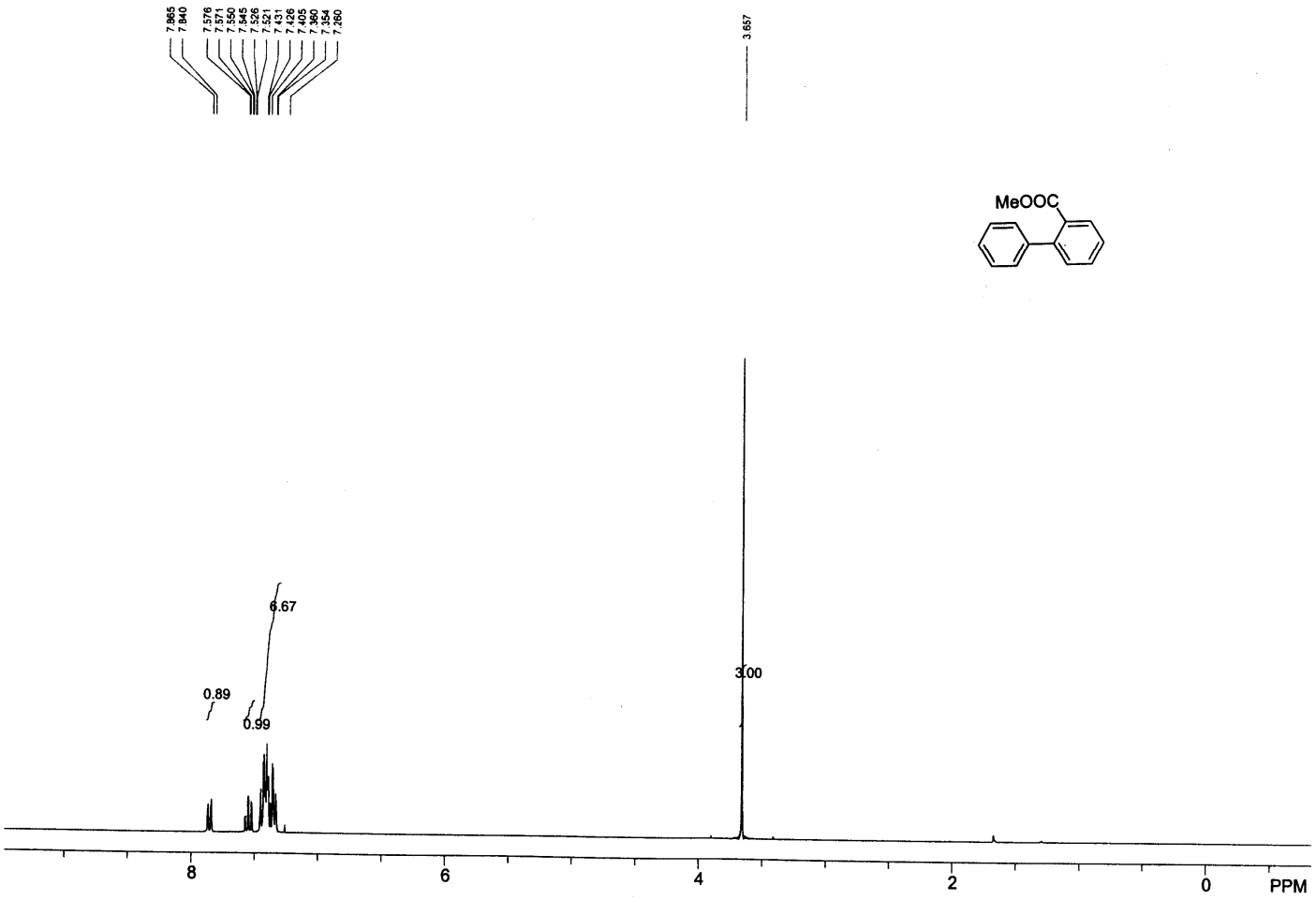
80
60
40
20
ppm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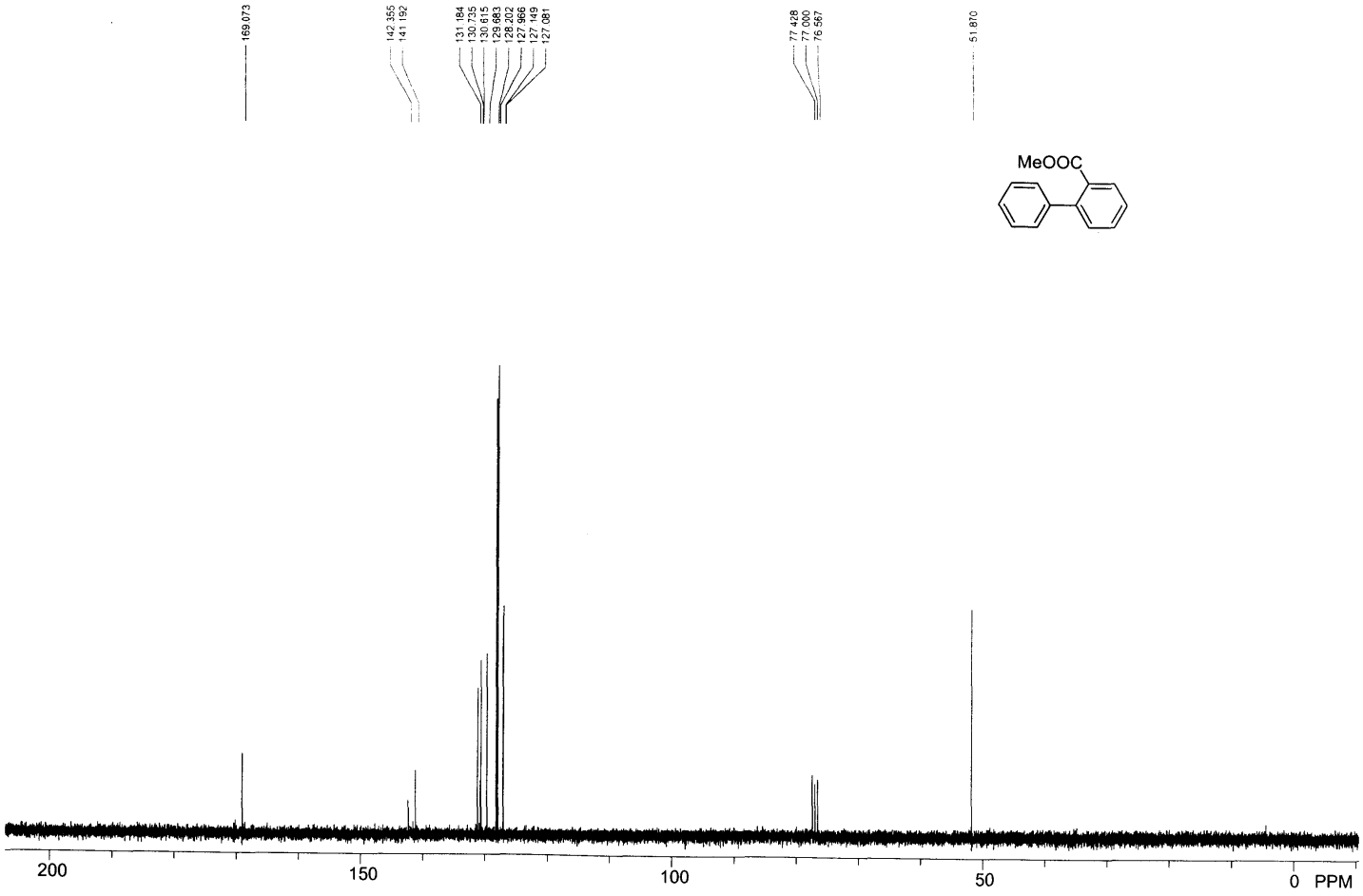
7.576
7.571
7.550
7.545
7.526
7.521
7.431
7.426
7.405
7.360
7.354
7.260
3.657
MeOOC
6.67
0.89
0.99
3.00
8
6
4
2
0
PPM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130.615
129.883
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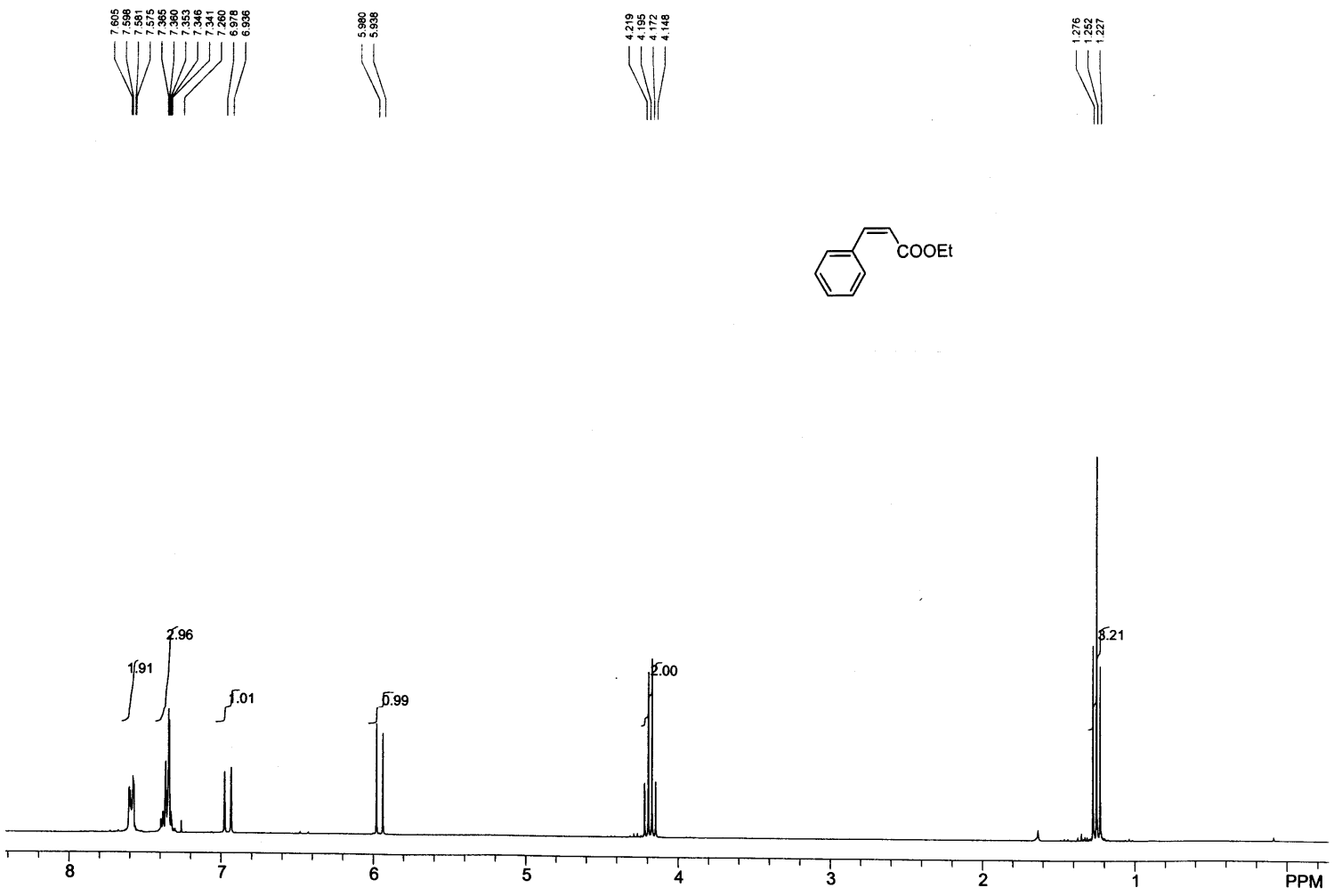
127.081
77.428
77.000
76.567
51.870
MeOOC
200
150
100
50
0 PPM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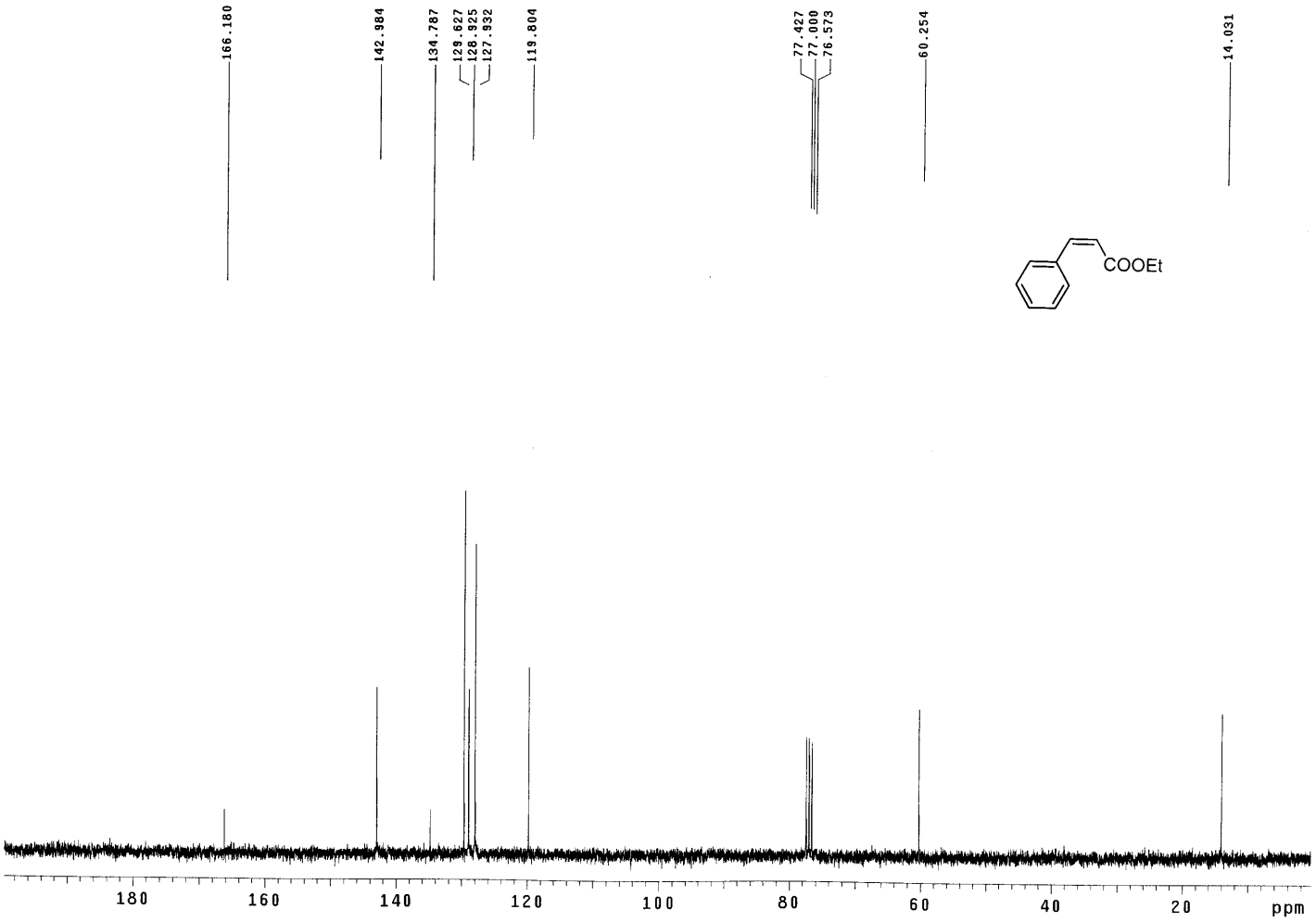
7.598
7.581
7.575
7.365
7.360
7.353
7.346
7.341
7.260
6.978
6.936
5.980
5.938
4.219
4.195
4.172
4.148
1.276
1.252
1.227
COOEt
1.91
2.96
1.01
0.99
2.00
3.21
8
7
6
5
4
3
2
1
PPM


166.180
142.984
134.787
129.627
128.925
127.932
119.804
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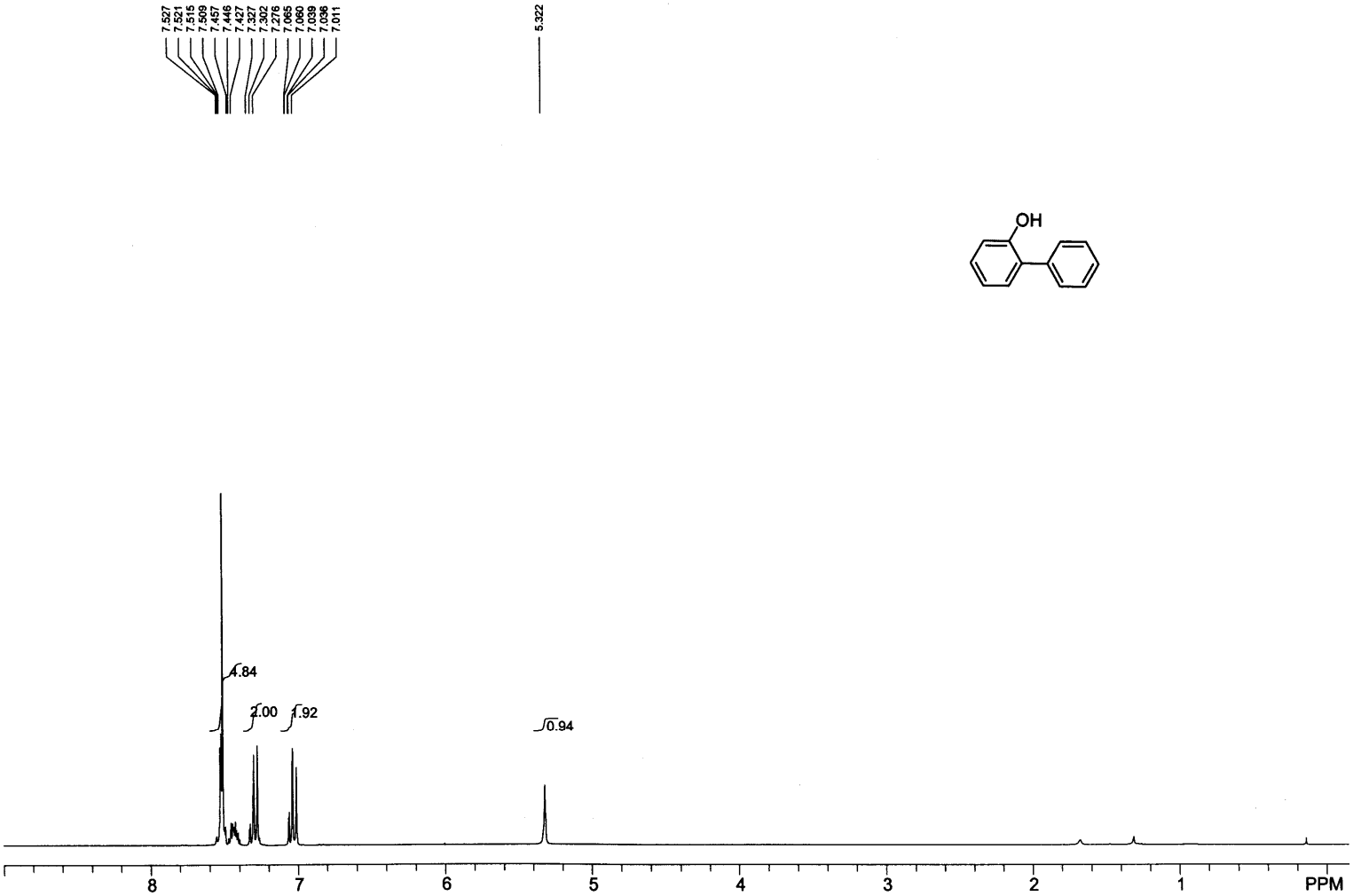
77.000
76.573
60.254
14.031
COOEt
180
160
140
120
100
80
60
40
20
ppm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7.521
7.515
7.509
7.457
7.446
7.427
7.327
7.302
7.276
7.065
7.060
7.039
7.036
7.011
5.322
OH
4.84
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1.92
0.94
8
7
6
5
4
3
2
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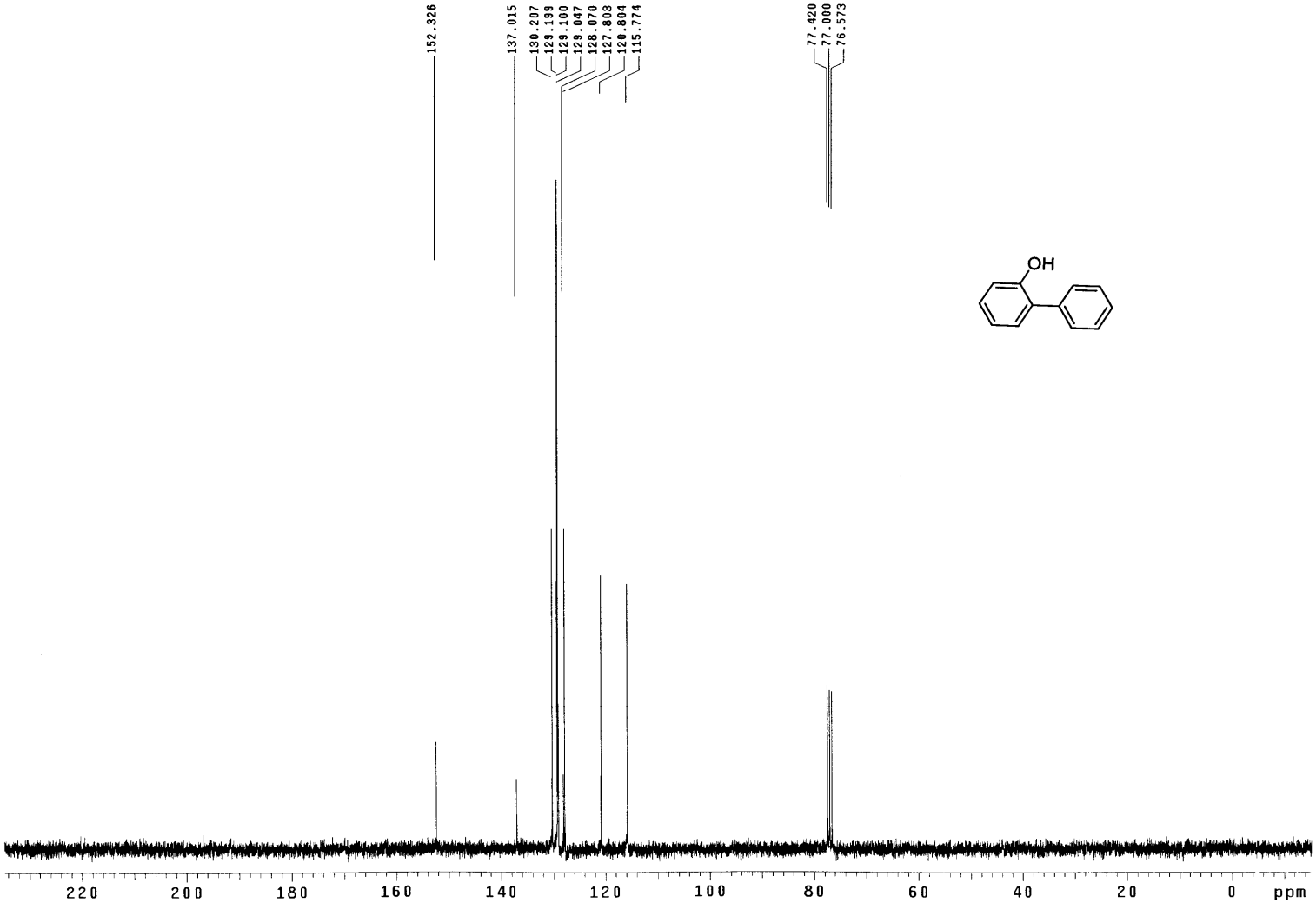
PPM


152.326
137.015
130.207
129.199
129.100
129.047
128.070
127.803
120.804
115.774
77.420
77.000
76.573
OH
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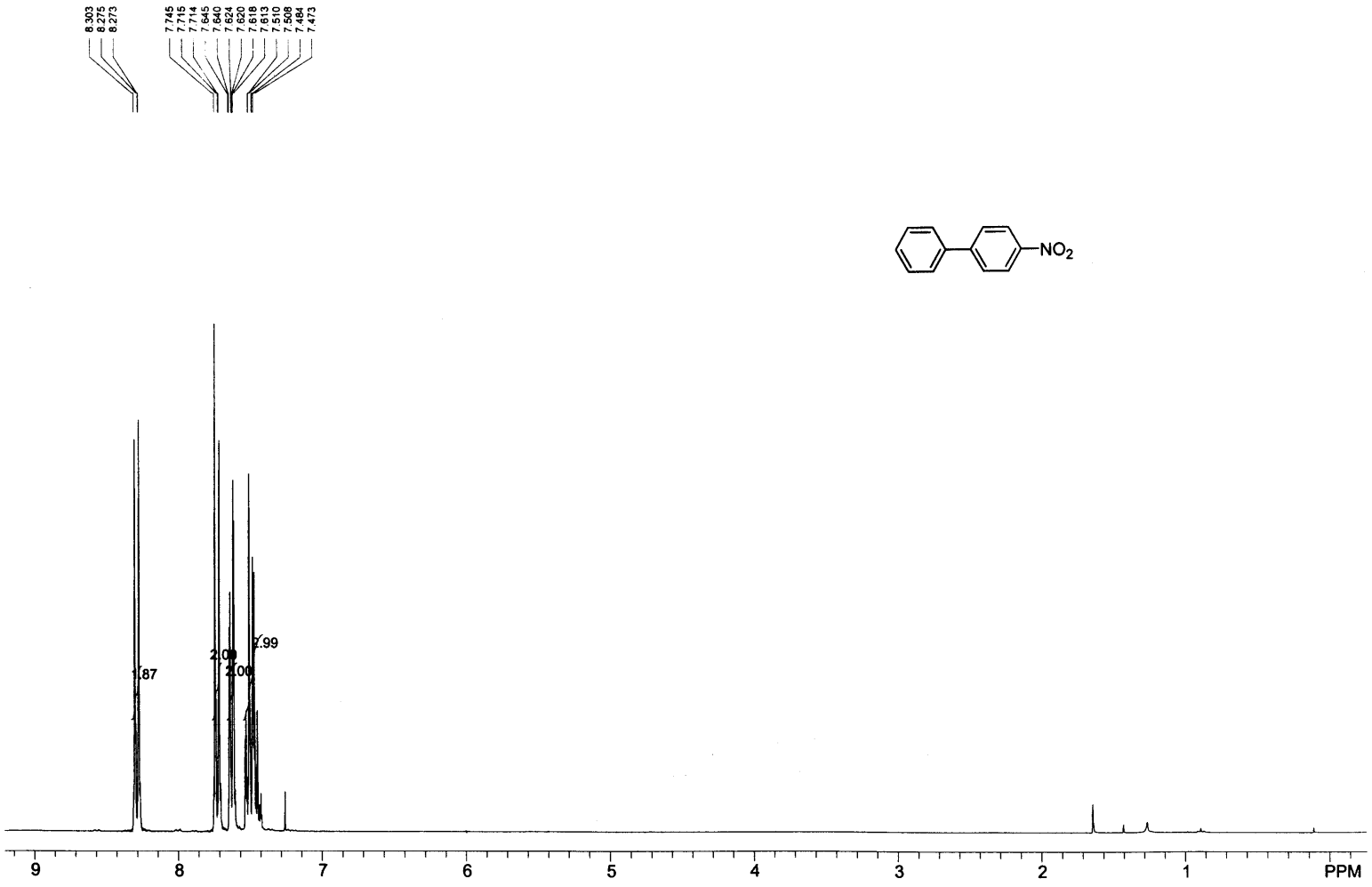
200
180
160
140
120
100
80
60
40
20
0
ppm


8.303
8.275
8.273
7.745
7.715
7.714
7.645
7.640
7.624
7.620
7.618
7.613
7.510
7.508
7.484
7.473
NO2
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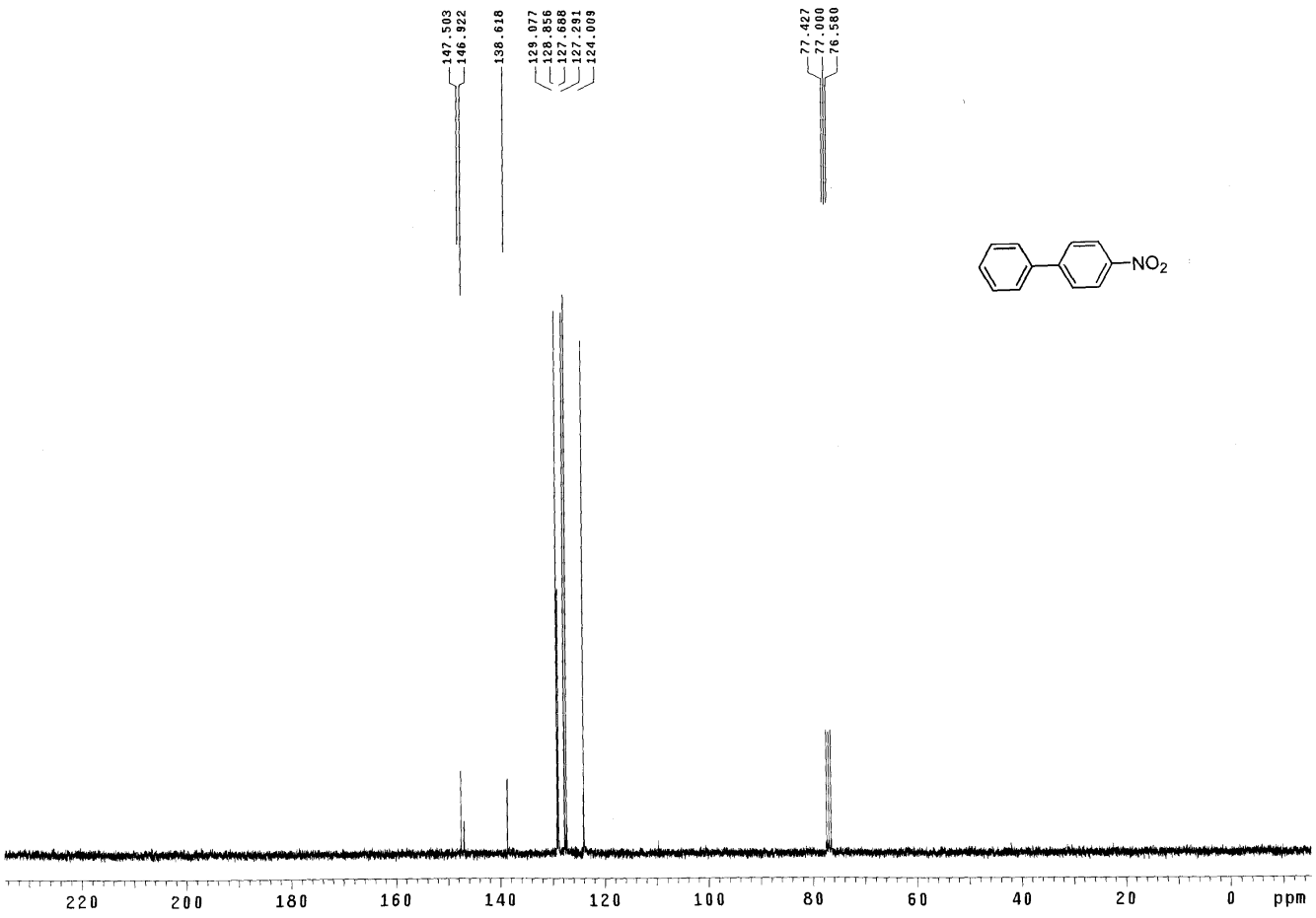
2.00
2.00
2.99
9
8
7
6
5
4
3
2
1
PPM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146.922
138.618
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128.856
127.688
127.291
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76.580
NO2
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140
120
100
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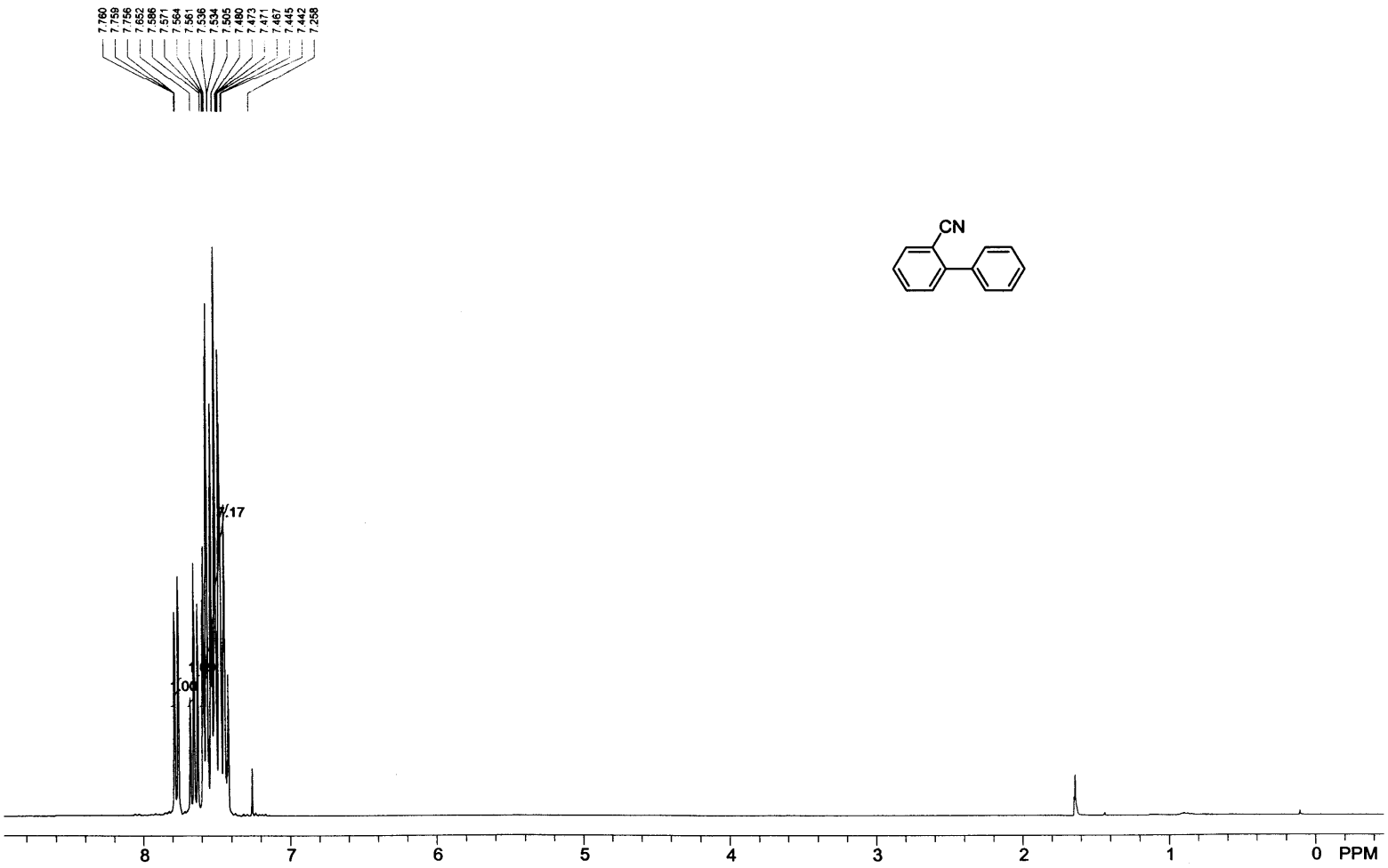
60
40
20
0
ppm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7.534
7.505
7.480
7.473
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7.442
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CN
17
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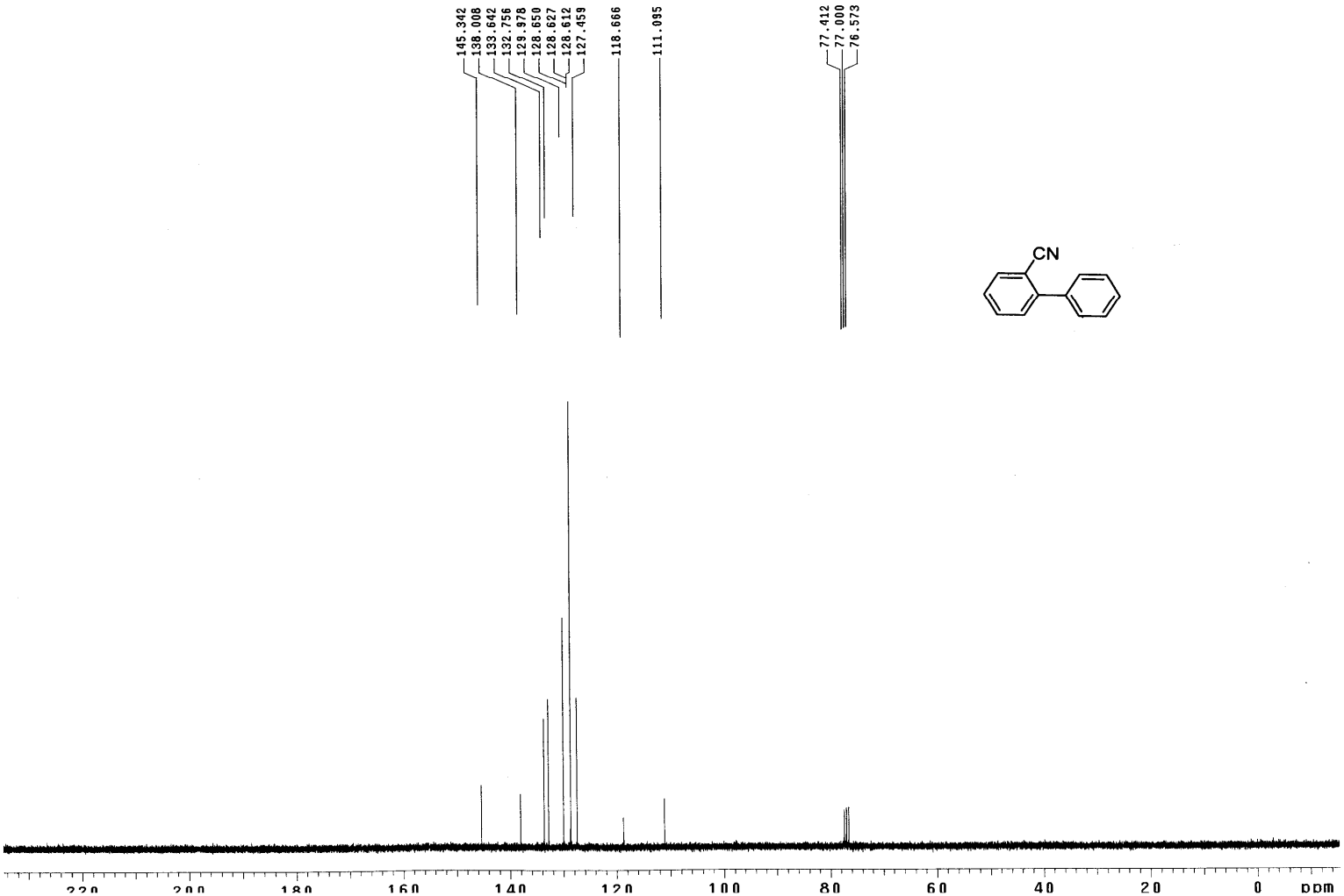
7
6
5
4
3
2
1
0
PPM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128.612
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120
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60
40
20
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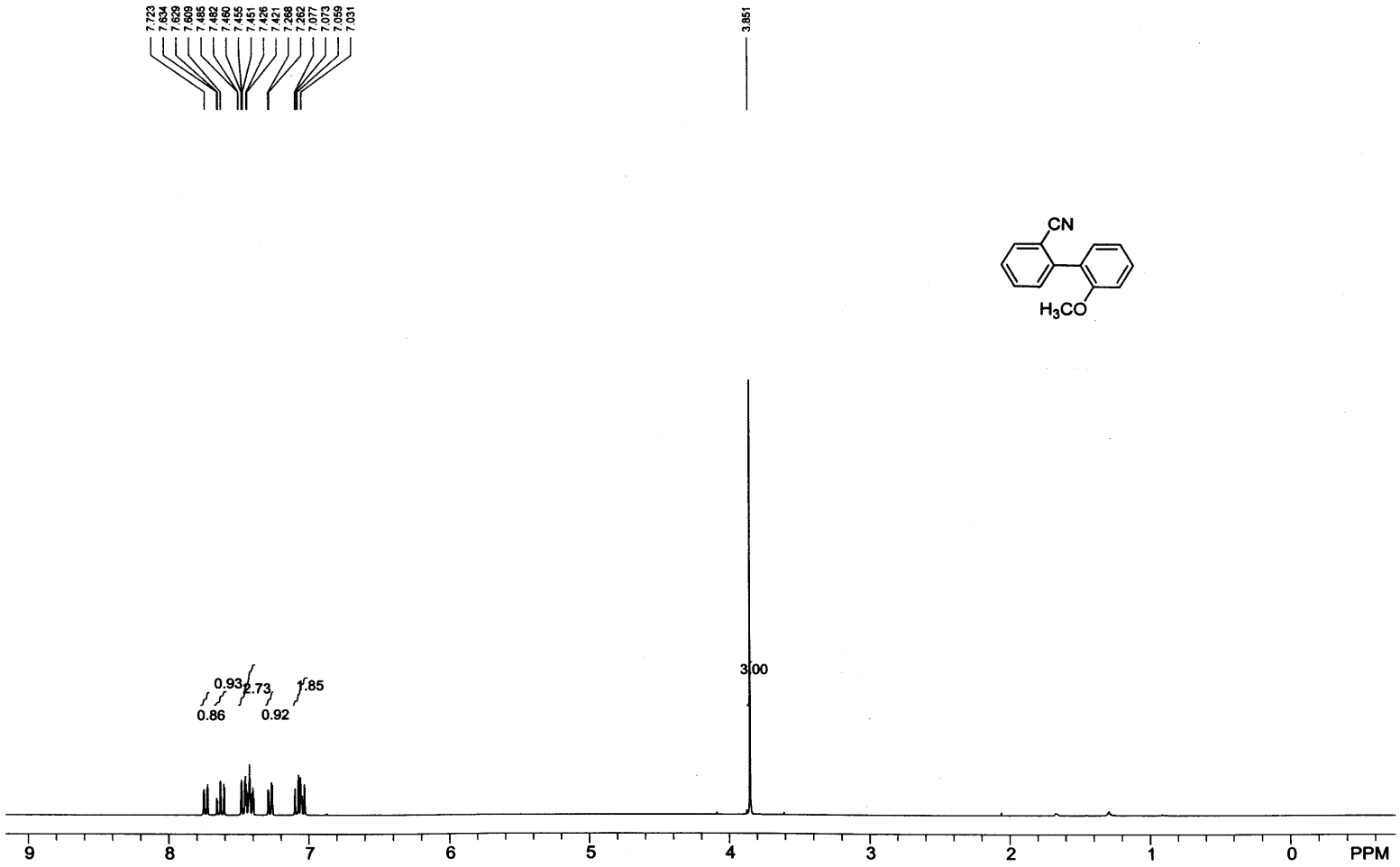
ppm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7.455
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7.426
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7.262
7.077
7.073
7.059
7.031
3.851
CN
H3CO
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0.92
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6
5
4
3
2
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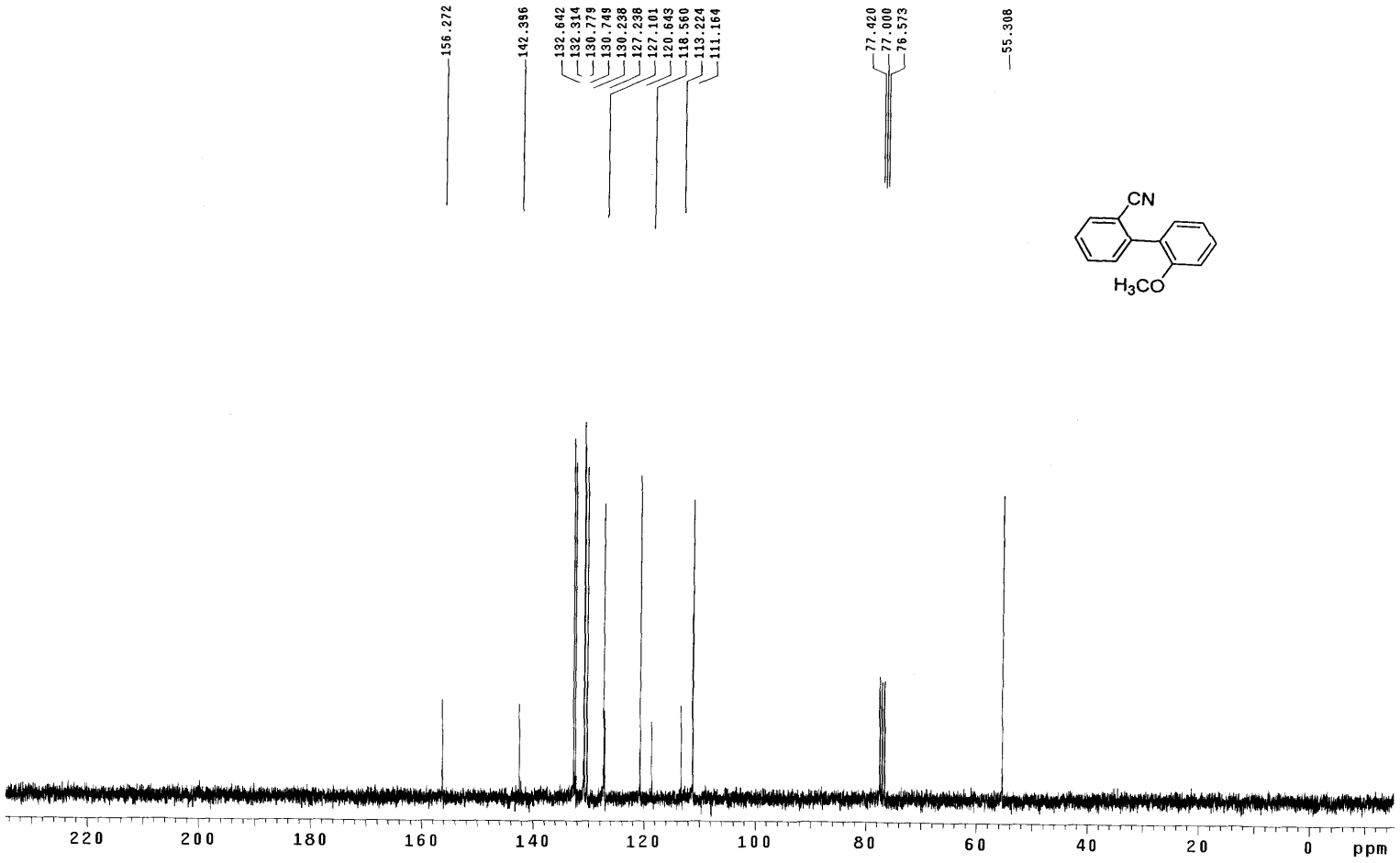
PPM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127.238
127.101
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113.224
111.164
77.420
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H3CO
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120
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40
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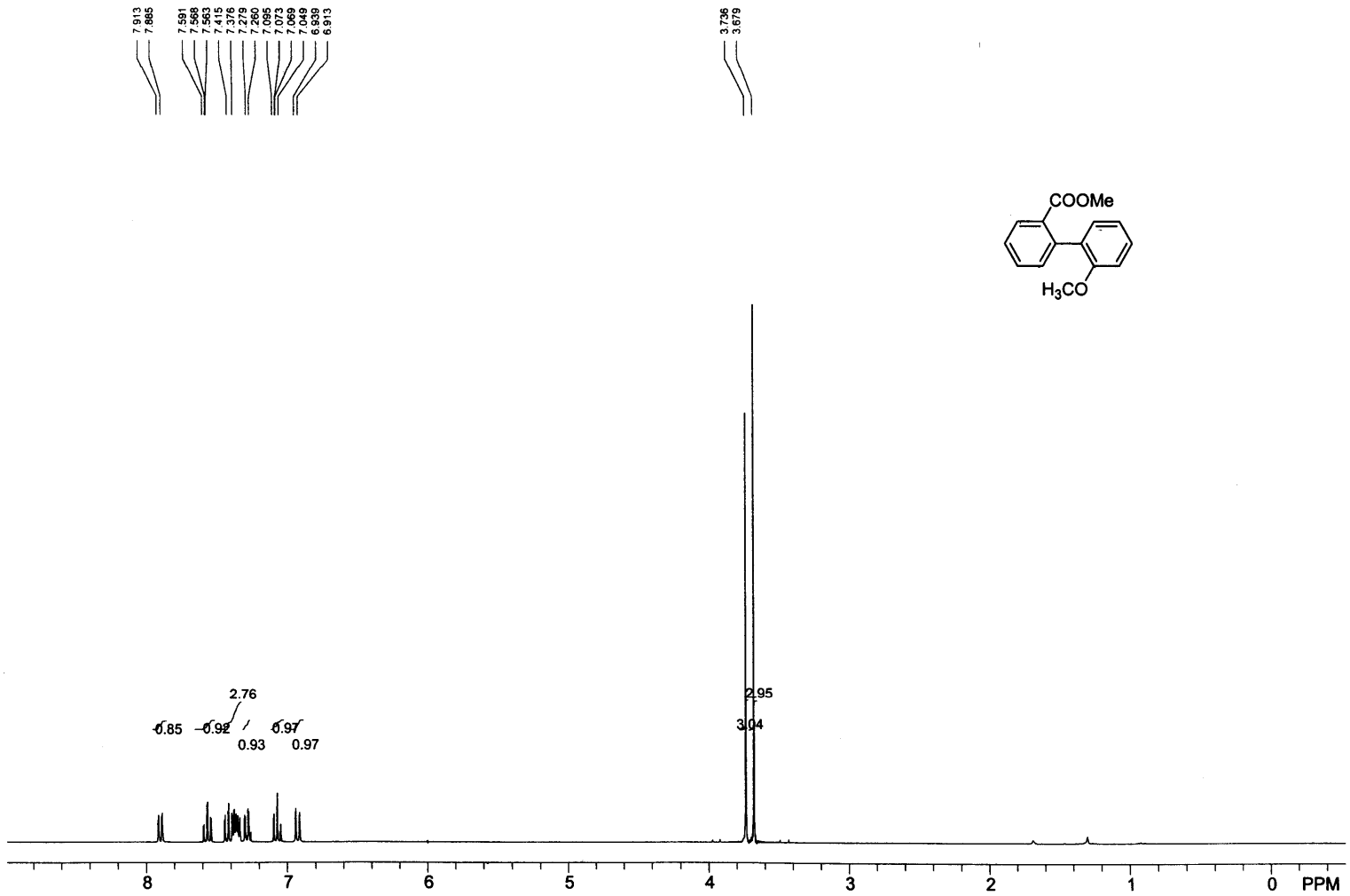
ppm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7.376
7.279
7.260
7.095
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7.069
7.049
6.939
6.913
3.736
3.679
COOMe
H3CO
2.76
0.85
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8
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5
4
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2
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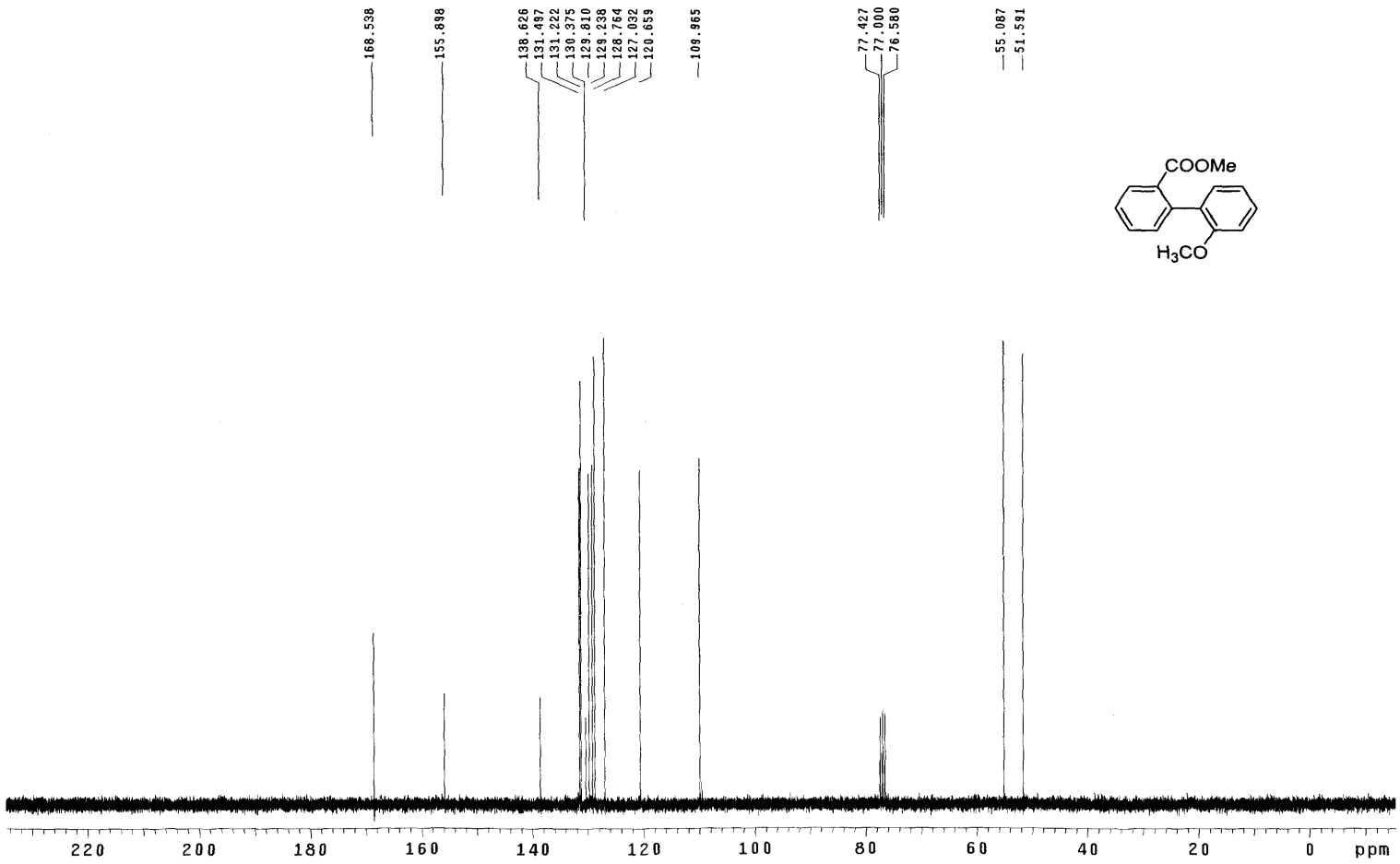
PPM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127.032
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77.000
76.580
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51.591
COOMe
H3CO
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200
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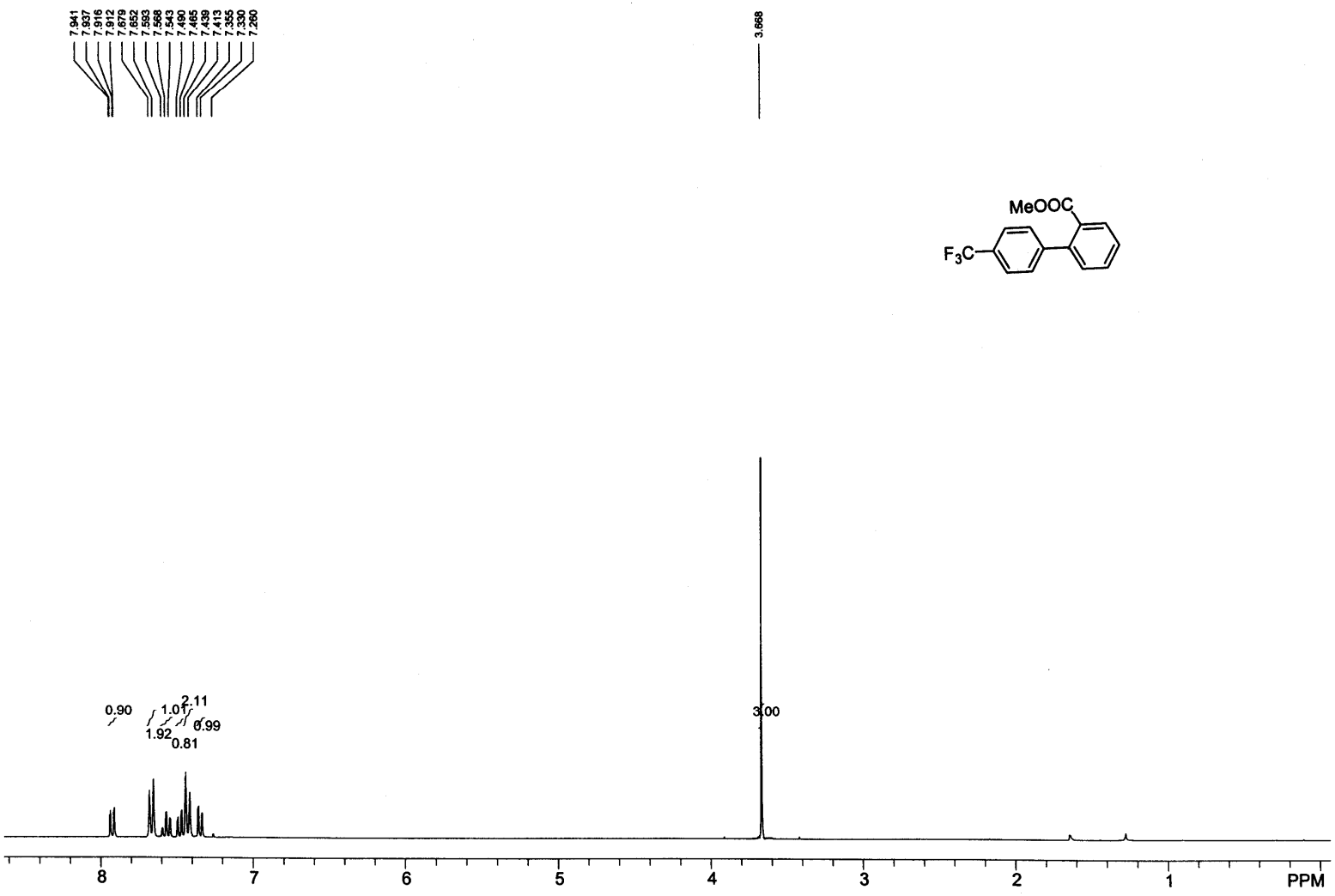
120
100
80
60
40
20
0
ppm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7.593
7.543
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7.465
7.439
7.413
7.355
7.330
7.280
3.668
MeOOC
F3C
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0.81
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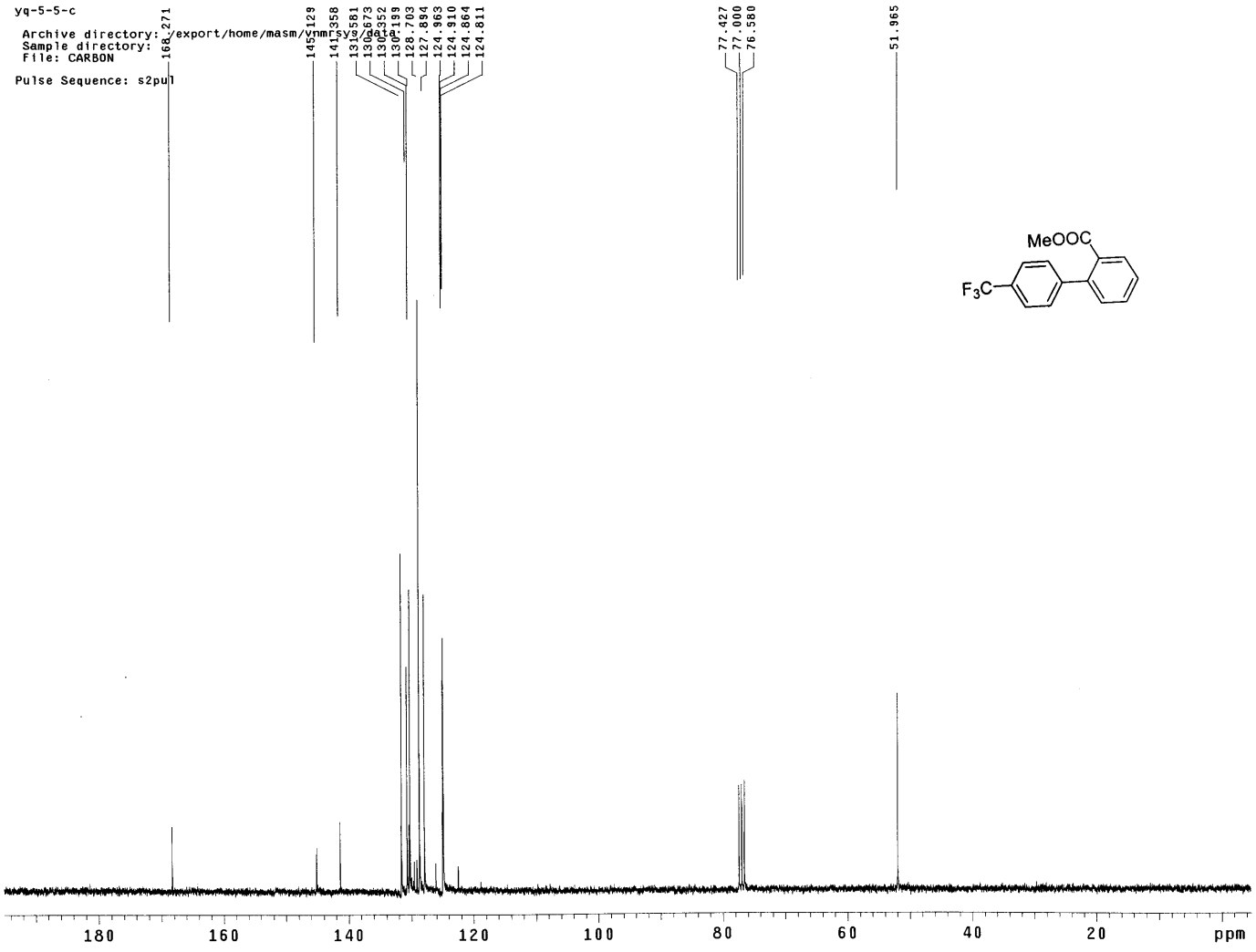
7
6
5
4
3
2
1
PPM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Sample directory:
File: CARBON
Pulse Sequence: s2pul
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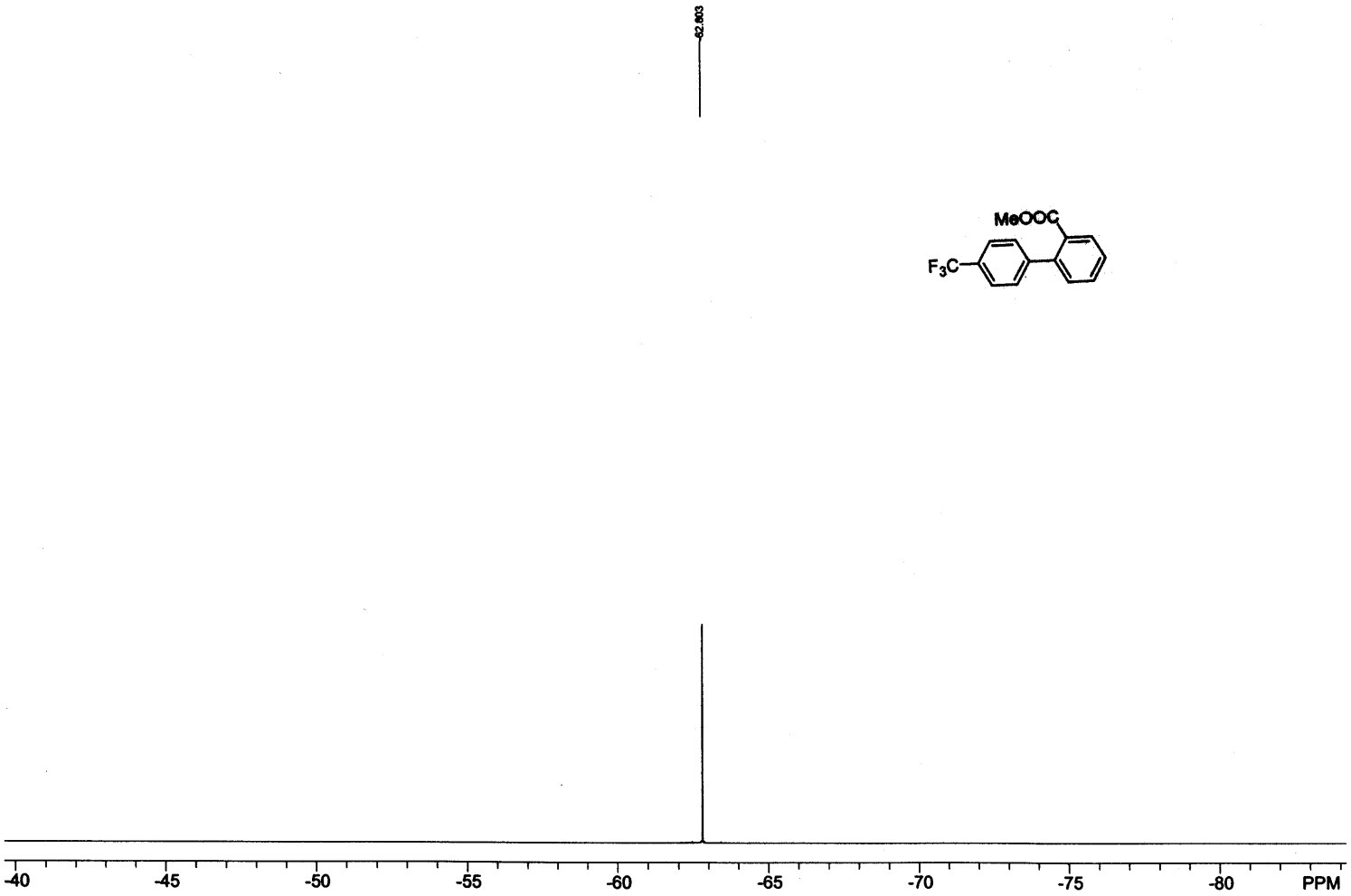
124.910
124.864
124.811
77.427
77.000
76.580
51.965
MeOOC
F3C
180
160
140
120
100
80
60
40
20
ppm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