Supporting Information

Bifunctional Organocatalyst for Activation of Carbon Dioxide and Epoxide to Produce Cyclic Carbonate: Betaine as a New Catalytic Motif

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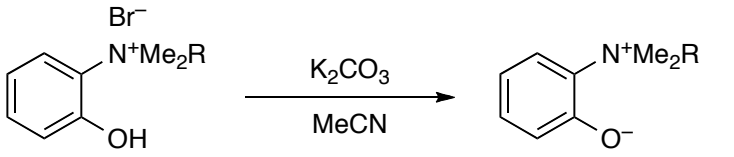
[1] Synthetic Procedures for Catalysts.

(1-A) Synthetic Procedure for Catalyst 1.

Allyldimethyl(2-hydroxyphenyl)ammonium bromide (**11**) was prepared according to the literature.[1]



11: R = $CH_2CH{=}CH_2$
12: R = CH_2Ph

1: R = $CH_2CH{=}CH_2$
2: R = CH_2Ph

2-(Allyldimethylammonio)phenolate (1).[2] A mixture of **11** (800 mg, 3.10 mmol) and K_2CO_3 (514 mg, 3.72 mmol) in dry MeCN (15 mL) under N_2 was stirred at room temperature for 16 h. After filtration, the filtrate was concentrated. The product was washed with Et_2O to give **1** as a light brown powder (521 mg, 95%): mp 75–80 ºC (lit.[2] mp 80–83 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 6H), 5.00 (d, J = 7.2 Hz, 2H), 5.43–5.51 (m, 2H), 5.59–5.68 (m, 1H), 6.24 (t, J = 8.4 Hz, 1H), 6.84 (dd, J = 1.2, 8.4 Hz, 1H), 6.97 (dd, J = 1.2, 8.4 Hz, 1H), 7.11–7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 65.7, 108.7, 119.0, 124.9, 126.3, 126.9, 130.0, 131.2, 163.2; IR (KBr) 3006, 1645, 1591, 1479, 1451, 1402, 1310, 1134, 1076, 1042, 959, 891, 829, 749, 700 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{11}H_{16}NO$ 178.1232, found 178.1244 (M + H).

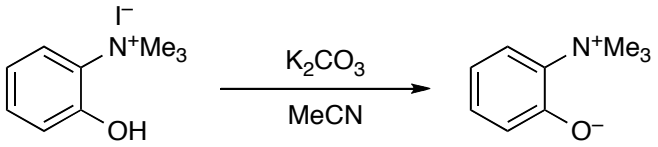
(1-B) Synthetic Procedure for Catalyst 2.

Benzyldimethyl(2-hydroxyphenyl)ammonium bromide (**12**) was prepared according to the literature.[1]

2-(Benzyldimethylammonio)phenolate (2).[2] A mixture of **12** (308 mg, 1.00 mmol) and K_2CO_3 (166 mg, 1.20 mmol) in dry MeCN (5 mL) under N_2 was stirred at room temperature for 16 h. After filtration, the filtrate was concentrated. The product was washed with Et_2O to give **2** as a white foamy solid (226 mg, 99%): mp 95–97 ºC (lit.[2] mp 95–97 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 6H), 5.60 (s, 2H), 6.29 (t, J = 7.6 Hz, 1H), 6.75 (dd, J = 1.6, 8.4 Hz, 1H), 7.07 (dd, J = 1.6, 8.4 Hz, 1H), 7.17–7.27 (m, 5H), 7.32–7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 65.3, 110.8, 119.8, 122.8, 127.9, 128.8, 129.4, 129.5, 130.9, 132.0, 160.7; IR (KBr) 3030, 2949, 2849, 2802, 1589, 1493, 1452, 1366, 1252, 1090, 1028, 937, 831, 731, 696 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{15}H_{18}NO$ 228.1388, found 228.1405 (M + H).

(1-C) Synthetic Procedure for Catalyst 3.

(2-Hydroxyphenyl)trimethylammonium iodide (**13**) was prepared according to the literature.[3]

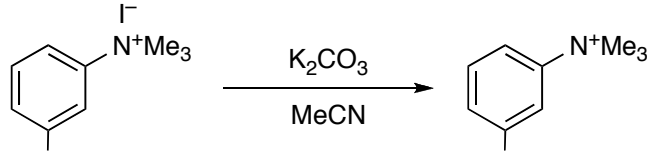


13 **3**

2-(Trimethylammonio)phenolate (3).[4] A mixture of **13** (884 mg, 3.17 mmol) and K_2CO_3 (525 mg, 3.80 mmol) in dry MeCN (16 mL) under N_2 was stirred at room temperature for 16 h. After filtration, the filtrate was concentrated. The product was washed with Et_2O to give **3** as a white powder (314 mg, 66%): mp 122 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.57 (s, 9H), 5.96 (t, J = 8.0 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 8.4 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 53.3, 107.5, 119.6, 123.5, 130.3, 133.6, 162.9; IR (KBr) 3055, 3032, 1591, 1485, 1462, 1435, 1406, 1337, 1234, 1138, 1042, 845, 820 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_9H_{14}NO$ 152.1075, found 152.1085 (M + H).

(1-D) Synthetic Procedure for Catalyst 4.

(3-Hydroxyphenyl)trimethylammonium iodide (**14**) was prepared according to the literature.[5]

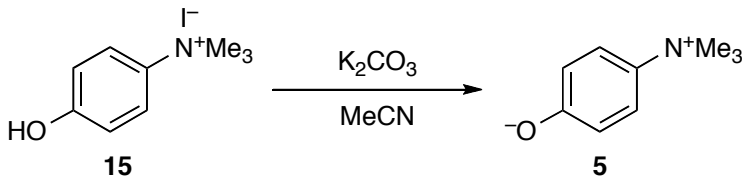


14 **4**

3-(Trimethylammonio)phenolate (4).[6] A mixture of **14** (350 mg, 1.25 mmol) and K_2CO_3 (207 mg, 1.50 mmol) in dry MeCN (6 mL) under N_2 was stirred at room temperature for 17 h. After filtration, the filtrate was concentrated. The product was washed with Et_2O and CH_2Cl_2 to give **4** as a white powder (139 mg, 73%): mp 135–137 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.39 (s, 9H), 6.09 (dd, J = 1.8, 8.4 Hz, 1H), 6.16 (dd, J = 2.7, 8.4 Hz, 1H), 6.32 (t, J = 2.4 Hz, 1H), 6.80 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.4, 104.4, 108.2, 118.3, 130.1, 148.7, 165.8; IR (KBr) 3082, 2889, 1601, 1531, 1492, 1342, 1300, 1138, 945, 833, 745 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_9H_{14}NO$ 152.1075, found 152.1076 (M + H).

(1-E) Synthetic Procedure for Catalyst 5.

(4-Hydroxyphenyl)trimethylammonium iodide (**15**) was prepared according to the literature.[3]

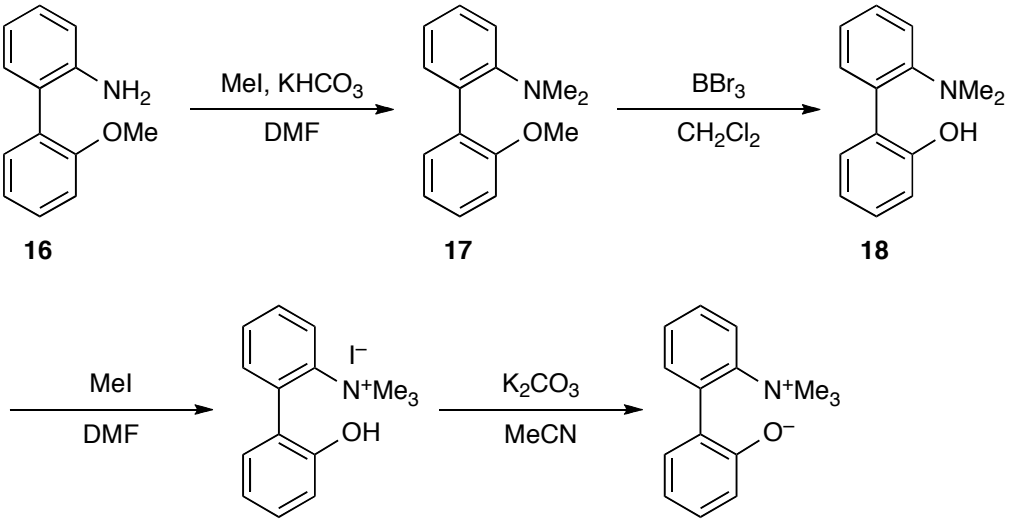


15 **5**

4-(Trimethylammonio)phenolate (5).[7] A mixture of **15** (350 mg, 1.25 mmol) and K_2CO_3 (207 mg, 1.50 mmol) in dry MeCN (6 mL) under N_2 was stirred at room temperature for 16 h. After filtration, the filtrate was concentrated. The product was washed with Et_2O to give **5** as a white powder (115 mg, 61%): mp 210 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.47 (s, 9H), 6.61 (d, J = 9.3 Hz, 2H), 7.51 (d, J = 9.3 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.8, 116.7, 121.1, 134.8, 164.5; IR (KBr) 3190, 3012, 1597, 1516, 1489, 1416, 1215, 1146, 961, 833, 644 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_9H_{14}NO$ 152.1075, found 152.1082 (M + H).

(1-F) Synthetic Procedure for Catalyst 6.

2-Amino-2'-methoxybiphenyl (**16**) was prepared according to the literature.[8]



16 **17** **18**

19 **6**

2-(*N*,*N*-Dimethylamino)-2'-methoxybiphenyl (17). A mixture of **16** (6.71 g, 33.7 mmol), $KHCO_3$ (7.09 g, 70.8 mmol), and MeI (5.3 mL, 84 mmol) in DMF (50 mL) under N_2 was stirred at room temperature for 5 h. After addition of H_2O (10 mL), the product was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over $MgSO_4$, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc (5:1)) gave **17** as a colorless oil (6.92 g, 90%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (s, 6H), 3.79 (s, 3H), 6.97–7.01 (m, 3H), 7.05 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 1.8, 7.8 Hz, 1H), 7.26–7.29 (m, 2H), 7.31 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.2, 55.5, 111.2, 117.7, 120.5, 120.7, 127.9, 128.0, 130.7, 131.0, 131.1, 132.2, 151.8, 156.4; IR (neat) 3046, 2938, 2831, 2778,

1590, 1502, 1482, 1459, 1428, 1320, 1258, 1232, 1122, 1052, 1029, 1004, 947, 755, 736 cm^{-1}; Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.36; H, 7.60; N, 5.82.

2-(*N*,*N*-Dimethylamino)-2'-hydroxybiphenyl (18). A solution of BBr_3 in dry CH_2Cl_2 (1.0 M, 36 mL, 36 mmol) was added dropwise to a solution of **17** (6.92 g, 30.4 mmol) in dry CH_2Cl_2 (90 mL) under N_2 in an ice bath over 5 min. The mixture was stirred at room temperature for 22 h. After addition of H_2O (10 mL) and adjustment to pH 7 by using 10% NaOH, the product was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried over $MgSO_4$, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc (5:1)) gave **18** as a white solid (6.21 g, 96%): mp 53–55 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.72 (s, 6H), 7.00 (dt, J = 1.2, 7.8 Hz, 1H), 7.04 (dd, J = 1.2, 7.8 Hz, 1H), 7.21–7.24 (m, 2H), 7.30 (ddd, J = 1.8, 7.2, 7.8 Hz, 1H), 7.37–7.41 (m, 2H), 7.44 (dd, J = 1.8, 7.8 Hz, 1H), 10.89 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.5, 118.1, 118.8, 120.4, 124.6, 128.1, 128.4, 129.0, 130.7, 133.5, 134.6, 148.2, 155.2; IR (KBr) 3018, 2953, 2845, 2783, 1599, 1493, 1474, 1460, 1429, 1296, 1267, 1236, 1153, 1042, 932, 764, 729 cm^{-1}; Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.68; H, 7.15; N, 6.19.

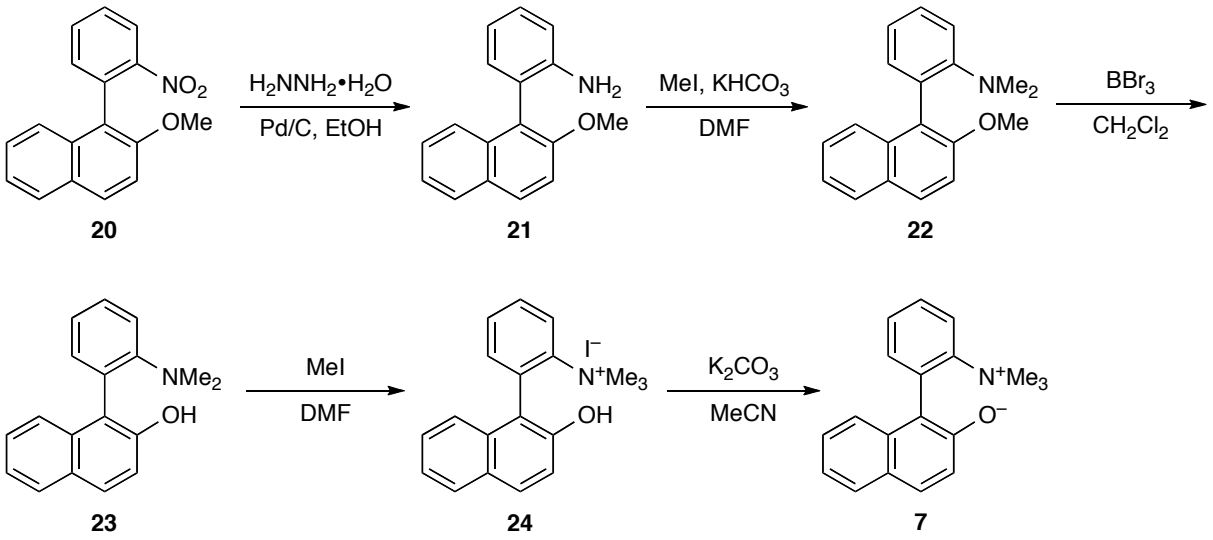
2-(2-Hydroxyphenyl)phenyltrimethylammonium iodide (19). A mixture of **18** (6.34 g, 29.7 mmol) and MeI (5.7 mL, 91 mmol) in dry DMF (30 mL) under N_2 was stirred at 40 ºC for 3 d. After removal of DMF, recrystallization from MeOH/Et_2O gave **19** as colorless crystals (7.84 g, 74%): mp 186–187 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.50 (s, 9H), 6.95 (dt, J = 1.2, 7.2 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 7.17 (dd, J = 1.8, 7.8 Hz, 1H), 7.24 (dd, J = 1.8, 7.2 Hz, 1H), 7.32–7.35 (m, 1H), 7.58 (dt, J = 1.2, 7.2 Hz, 1H), 7.63 (ddd, J = 1.8, 7.2, 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 10.02 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 57.3, 116.2, 119.5, 121.8, 127.0, 129.5, 130.1, 130.5, 131.3, 132.5, 135.7, 144.9, 154.1; IR (KBr) 3204, 3063, 3032, 1587, 1487, 1447, 1269, 1198, 1111, 1088, 847, 772 cm^{-1}; Anal. Calcd for $C_{15}H_{18}NOI$: C, 50.72; H, 5.11; N, 3.94. Found: C, 51.09; H, 5.14; N, 3.55.

2-(2-Trimethylammoniophenyl)phenolate (6). A mixture of **19** (945 mg, 2.66 mmol) and K_2CO_3 (393 mg, 2.84 mmol) in dry MeCN (13 mL) under N_2 was stirred at room temperature overnight. After filtration and concentration, the product was washed with Et_2O to give **6** as a white powder (567 mg, 94%): mp 150 ºC (dec); ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.55 (s, 9H), 6.51 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.98 (dd, J = 1.8, 7.8 Hz, 1H), 7.03–7.05 (m, 1H), 7.12 (dd, J = 2.4, 7.2 Hz, 1H), 7.50–7.55 (m, 2H), 7.96 (dd, J = 1.2, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, methanol-d_4) δ 58.6, 117.6, 119.6, 122.0, 129.2, 130.3, 131.2, 131.4, 132.1, 136.0, 137.6, 146.4, 160.6; IR (KBr) 3063, 3026, 1622, 1593, 1483, 1306, 1150, 1049, 1003, 941, 851, 768, 613, 563 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for

$C_{15}H_{18}NO$ 228.1383, found 228.1390 (M + H).

(1-G) Synthetic Procedure for Catalyst 7.

2-Methoxy-1-(2-nitrophenyl)naphthalene (**20**) was prepared according to the literature.[9]



1-(2-Aminophenyl)-2-methoxynaphthalene (21).[9] Hydrazine monohydrate (80%, 12.5 mL) was added dropwise to a mixture of **20** (5.59 g, 20.0 mmol) and Pd/C (10% (w/w), 2.76 g) in EtOH (60 mL) at 50 ºC over 25 min. The mixture was heated at reflux for 12 h. After filtration and concentration, the product was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc (7:1)–(2:1)) gave **21** as white crystals (4.18 g, 84%): mp 84.5–86 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.34 (br s, 2H), 3.88 (s, 3H), 6.88 (d, J = 7.8 Hz, 1H), 6.92 (dt, J = 1.2, 7.2 Hz, 1H), 7.11 (dd, J = 1.2, 7.2 Hz, 1H), 7.27 (dt, J = 1.2, 7.8 Hz, 1H), 7.35–7.38 (m, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.44–7.47 (m, 1H), 7.83–7.85 (m, 1H), 7.92 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 56.7, 113.9, 115.4, 118.4, 121.3, 121.8, 123.7, 125.0, 126.6, 127.9, 128.6, 129.2, 129.5, 131.7, 133.3, 144.7, 154.4; IR (KBr) 3450, 3364, 3017, 2937, 2829, 1618, 1591, 1506, 1495, 1454, 1273, 1252, 1065, 810, 748 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{17}H_{16}NO$ 250.1232, found 250.1243 (M + H).

1-[2-(*N*,*N*-Dimethylamino)phenyl]-2-methoxynaphthalene (22). A mixture of **21** (3.73 g, 15.0 mmol), $KHCO_3$ (3.30 g, 33.0 mmol), and MeI (2.3 mL, 38 mmol) in dry DMF (30 mL) under N_2 was stirred at room temperature for 4 h. After addition of H_2O (20 mL), the product was extracted with hexane/EtOAc (1:1) (40 mL × 3), and the combined organic layers were washed with H_2O (30 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc (10:1)) gave **22** as a white solid (3.65 g, 88%): mp 78–79 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.46 (s, 6H), 3.89 (s, 3H), 7.06 (t, J = 6.6 Hz, 1H), 7.13–7.16 (m, 2H), 7.30–7.34 (m, 2H), 7.38–7.40 (m, 3H), 7.81 (dd, J = 1.8, 7.2 Hz, 1H),

7.88 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.2, 56.6, 113.9, 117.8, 121.0, 123.4, 125.3, 125.7, 126.0, 127.7, 128.2, 128.7, 129.0, 129.1, 133.0, 133.0, 152.8, 153.6; IR (KBr) 3047, 2937, 2822, 2768, 1618, 1591, 1508, 1493, 1464, 1448, 1431, 1331, 1313, 1269, 1256, 1144, 1069, 1049, 941, 806, 770, 758 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{19}H_{20}NO$ 278.1545, found 278.1557 (M + H).

1-[2-(*N*,*N*-Dimethylamino)phenyl]-2-hydroxynaphthalene (23). A solution of BBr_3 in dry CH_2Cl_2 (1.0 M, 12 mL, 12 mmol) was added to a solution of **22** (2.77 g, 10.0 mmol) in dry CH_2Cl_2 (20 mL) under N_2 in an ice bath. The mixture was stirred at room temperature for 9 h. After adjustment to pH 7 by using 10% NaOH, the product was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc (10:1)) gave **23** as a white solid (2.33 g, 89%): mp 123.5–124.5 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 (s, 6H), 7.16 (dt, J = 1.2, 7.2 Hz, 1H), 7.28 (dd, J = 1.2, 8.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.34 (ddd, J = 1.2, 6.6, 8.4 Hz, 1H), 7.37 (ddd, J = 1.2, 6.6, 8.4 Hz, 1H), 7.41–7.43 (m, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.83 (dd, J = 1.8, 7.8 Hz, 1H), 10.01 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.5, 118.1, 120.6, 121.0, 122.9, 123.1, 125.3, 126.0, 128.1, 128.4, 129.3, 129.9, 130.6, 133.3, 135.3, 149.9, 152.0; IR (KBr) 3017, 2953, 2883, 2837, 1618, 1591, 1489, 1466, 1456, 1333, 1238, 1178, 1153, 1096, 988, 924, 820, 770, 756, 673 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{18}H_{18}NO$ 264.1388, found 264.1376 (M + H).

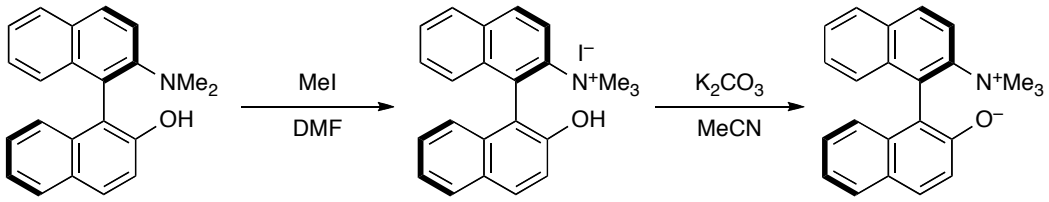
2-(2-Hydroxy-1-naphthyl)phenyltrimethylammonium iodide (24). A mixture of **23** (1.84 g, 7.00 mmol) and MeI (1.3 mL, 21 mmol) in dry DMF (7 mL) under N_2 was stirred at 40 ºC for 3 d. After removal of DMF, recrystallization from MeOH/Et_2O gave **24** as a white solid (2.49 g, 88%): mp 192–193 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.45 (s, 9H), 6.98 (d, J = 7.8 Hz, 1H), 7.15 (dd, J = 1.8, 7.8 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.35 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.40 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.65 (dt, J = 1.2, 7.2 Hz, 1H), 7.72 (ddd, J = 1.8, 7.2, 9.0 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 10.39 (br s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 56.8, 118.5, 118.6, 122.4, 123.4, 124.4, 127.6, 128.1, 128.5, 129.9, 130.3, 130.8, 131.1, 133.5, 136.4, 146.0, 152.1; IR (KBr) 3179, 3063, 3011, 1622, 1506, 1489, 1429, 1340, 1273, 984, 947, 820, 760, 745 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{19}H_{20}NO$ 278.1545, found 278.1558 (M – I).

1-(2-Trimethylammoniophenyl)-2-naphtholate (7). A mixture of **24** (405 mg, 1.00 mmol) and K_2CO_3 (166 mg, 1.20 mmol) in dry MeCN (7 mL) under N_2 was stirred at room temperature overnight. After filtration and concentration, the product was washed with Et_2O to give **7** as a yellow powder (238 mg, 86%): mp 123–125 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.60 (s, 9H), 6.76 (d, J = 8.4 Hz, 1H), 7.16 (dt, J = 1.2, 7.2 Hz, 1H), 7.22–7.23 (m, 2H), 7.28

(d, J = 9.0 Hz, 1H), 7.47 (dt, J = 1.2, 7.2 Hz, 1H), 7.51 (ddd, J = 1.8, 7.2, 9.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 57.5, 117.6, 120.8, 121.2, 122.1, 122.9, 126.6, 128.2, 129.2, 130.5, 130.8, 133.4, 134.3, 137.7, 145.9, 158.5; IR (KBr) 3055, 1616, 1587, 1489, 1421, 1366, 1340, 1275, 1234, 988, 951, 826, 756 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{19}H_{20}NO$ 278.1545, found 278.1554 (M + H).

(1-H) Synthetic Procedure for Catalyst 8.

(*R*)-2-(*N*,*N*-Dimethylamino)-2'-hydroxy-1,1'-binaphthyl (**25**) was prepared according to the literature.[10]

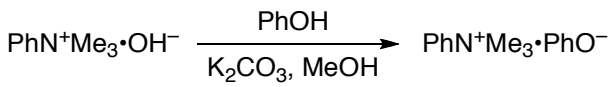


25 **26** **8**

(*R*)-1-(2-Hydroxy-1-naphthyl)-2-naphthyltrimethylammonium iodide (26). A mixture of **25** (627 mg, 2.00 mmol) and MeI (0.37 mL, 6.0 mmol) in dry DMF (2 mL) under N_2 was stirred at 40 ºC for 3 d. After removal of DMF, purification by silica gel column chromatography (CH_2Cl_2/MeOH (1:0)–(10:1)) gave **26** as a pale yellow solid (573 mg, 63%): mp 117–118 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.48 (s, 9H), 6.68 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.22–7.25 (m, 2H), 7.33 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.80–7.90 (m, 4H), 8.03 (d, J = 9.6 Hz, 1H), 8.06 (d, J = 9.5 Hz, 1H), 8.43 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 58.3, 114.5, 118.3, 119.1, 123.9, 127.2, 127.9, 127.9, 127.9, 128.3, 128.4, 128.6, 128.8, 131.4, 131.7, 133.2, 133.7, 133.8, 142.6, 152.5; IR (KBr) 3398, 3153, 3067, 3018, 1622, 1508, 1494, 1477, 1433, 1342, 1271, 974, 935, 916, 893, 820, 751 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{23}H_{22}NO$ 328.1701, found 328.1703 (M – I).

(*R*)-1-(2-Trimethylammonio-1-naphthyl)-2-naphtholate (8). A mixture of **26** (455 mg, 1.00 mmol) and K_2CO_3 (166 mg, 1.20 mmol) in dry MeCN (5 mL) under N_2 was stirred at room temperature for 5 h. After filtration and concentration, the product was washed with Et_2O to give **8** as a yellow powder (304 mg, 93%): mp 124–125.5 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.39 (s, 9H), 6.41 (d, J = 8.4 Hz, 1H), 7.07 (ddd, J = 1.2, 6.6, 7.8 Hz, 1H), 7.10–7.15 (m, 3H), 7.24 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.52 (ddd, J = 1.2, 6.6, 7.8 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.93–7.94 (m, 2H), 8.07 (d, J = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 57.8, 113.2, 117.7, 121.2, 122.0, 122.9, 126.4, 126.8, 127.7, 128.1, 128.2, 130.2, 130.9, 131.6, 133.4, 134.5, 134.8, 142.6, 159.7; IR (KBr) 3423, 3049, 2955, 1612, 1589, 1495, 1421, 1346, 1273, 1236, 1211, 980, 939, 891, 808, 748 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{23}H_{22}NO$ 328.1701, found 328.1718 (M + H).

(1-I) Synthetic Procedure for Phenyltrimethylammonium Phenoxide.[11]



A mixture of phenyltrimethylammonium hydroxide (153 mg, 1.00 mmol), phenol (94 mg, 1.00 mmol), K_2CO_3 (152 mg, 1.10 mmol), and molecular sieves 3A (5 pieces) in MeOH (1 mL) was stirred at room temperature for 24 h. After filtration, repeated evaporation with toluene and Et_2O gave the product as a brown viscous solid (216 mg, 94%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 9H), 6.61 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 7.2 Hz, 2H), 7.06–7.09 (m, 2H), 7.48–7.54 (m, 3H), 7.73 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 57.0, 116.0, 117.0, 119.5, 129.3, 130.4, 130.6, 146.7, 161.8; IR (KBr) 3013, 1664, 1593, 1474, 1416, 1248, 1165, 949, 849, 762, 694 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_9H_{14}N$ 136.1126, found 136.1129 (M – PhO).

[2] Coupling Reaction of CO_2 with Epoxide.

General Procedure for Coupling Reaction of CO_2 with Epoxide.

A stainless autoclave was charged with epoxide (10 mmol), catalyst (a catalytic amount), and then CO_2 (initial pressure 1 MPa at room temperature). The mixture was heated with stirring at a constant temperature for a reaction time. The reactor was cooled in an ice bath for 30 min, and excess CO_2 was released carefully. The crude product was dissolved in Et_2O, and the solution was concentrated. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard. The product was purified by distillation or silica gel column chromatography.

4-*n*-Butyl-1,3-dioxolan-2-one (10a).[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 1.33–1.52 (m, 4H), 1.66–1.72 (m, 1H), 1.79–1.85 (m, 1H), 4.07 (dd, J = 7.2, 8.4 Hz, 1H), 4.52 (t, J = 8.4 Hz, 1H), 4.68–4.72 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 22.1, 26.3, 33.4, 69.3, 77.0, 155.0; IR (neat) 2953, 2934, 2874, 1794, 1553,1483, 1468, 1387, 1175, 1124, 1067, 775, 718 cm^{-1}.

4-Methyl-1,3-dioxolan-2-one (10b).[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 (d, J = 6.6 Hz, 3H), 4.03 (dd, J = 7.2, 8.4 Hz, 1H), 4.55 (dd, J = 7.8, 8.4 Hz, 1H), 4.83–4.88 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.3, 70.6, 73.5, 155.0; IR (neat) 2990, 2924, 1790, 1556, 1485, 1456, 1387, 1354, 1182, 1120, 1051, 851, 777, 712 cm^{-1}.

4-*n*-Octyl-1,3-dioxolan-2-one (10c).[13] ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 1.26–1.39 (m, 11H), 1.45–1.50 (m, 1H), 1.65–1.71 (m, 1H), 1.78–1.83 (m, 1H), 4.07 (dd, J =

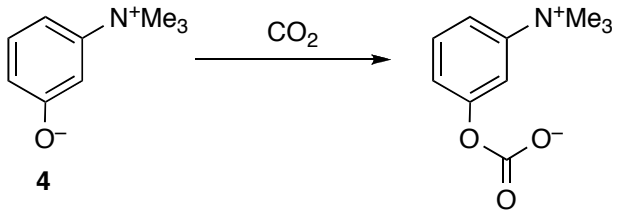
7.2, 8.4 Hz, 1H), 4.52 (dd, J = 7.8, 8.4 Hz, 1H), 4.70 (dq, J = 5.4, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 22.6, 24.3, 29.0, 29.1, 29.2, 31.7, 33.8, 69.4, 77.0, 155.1; IR (neat) 2928, 2855, 1801, 1466, 1385, 1169, 1065, 775, 721 cm^{-1}.

4-Methoxymethyl-1,3-dioxolan-2-one (10d).[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.42 (s, 3H), 3.57 (dd, J = 3.6, 10.8 Hz, 1H), 3.64 (dd, J = 3.6, 10.8 Hz, 1H), 4.38 (dd, J = 6.0, 8.4 Hz, 1H), 4.49 (t, J = 8.4 Hz, 1H), 4.78–4.82 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 59.4, 66.0, 71.3, 75.0, 154.9; IR (neat) 2991, 2934, 2897, 2822, 1794, 1481, 1398, 1175, 1132, 1103, 1084, 1074, 1047, 775, 714 cm^{-1}.

4-Phenyl-1,3-dioxolan-2-one (10e).[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.35 (t, J = 8.4 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 5.68 (t, J = 8.4 Hz, 1H), 7.36–7.38 (m, 2H), 7.43–7.47 (m. 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 71.1, 77.9, 125.8, 129.1, 129.6, 135.7, 154.8; IR (KBr) 2976, 2922, 1778, 1460, 1358, 1327, 1169, 1055, 760, 700 cm^{-1}.

4-Chloromethyl-1,3-dioxolan-2-one (10f).[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.70–3.78 (m, 2H), 4.42 (dd, J = 6.0, 9.0 Hz, 1H), 4.59 (dd, J = 8.4, 9.0 Hz, 1H), 4.94–4.98 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.8, 66.8, 74.3, 154.3; IR (neat) 3221, 2984, 2968, 1794, 1481, 1431, 1396, 1356, 1335, 1167, 1072, 1045, 768, 718, 664 cm^{-1}.

[3] Synthesis of Betaine–CO_2 Adduct and Subsequent Reaction with Epoxide.



A 30-mL stainless autoclave was charged with **4** (151 mg, 1.00 mmol) and CO_2 (initial pressure 1 MPa). The mixture was stirred at a constant temperature for 24 h. Excess CO_2 was released carefully to give a **4**–CO_2 adduct as a white powder: ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.48 (s, 9H), 6.71 (d, J = 8.2 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.99 (s, 1H), 7.18 (t, J = 8.2 Hz, 1H); ^{13}C NMR (150 MHz, methanol-d_4) δ 57.9, 108.7, 109.8, 119.2, 132.1, 149.6, 161.2, 162.7; IR (KBr) 3013, 1655, 1609, 1497, 1470, 1412, 1219, 945, 918, 837 cm^{-1}.

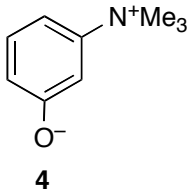
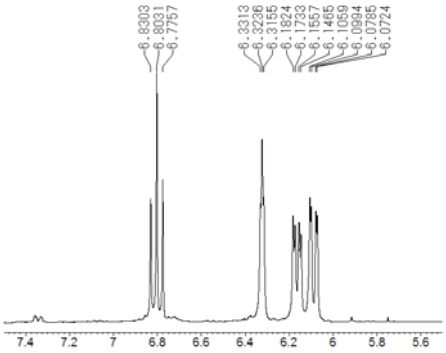
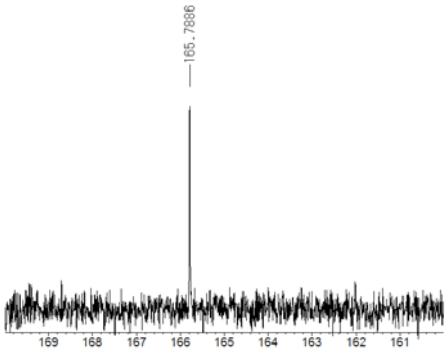
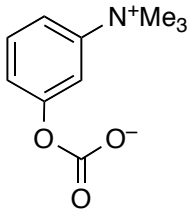
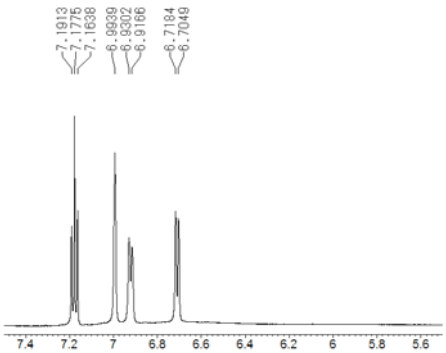
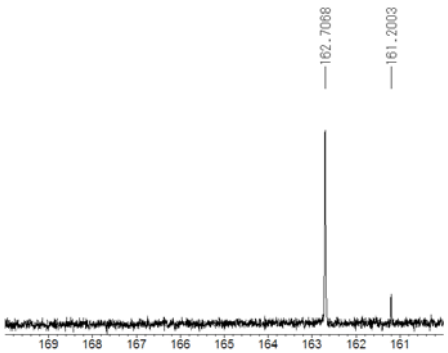
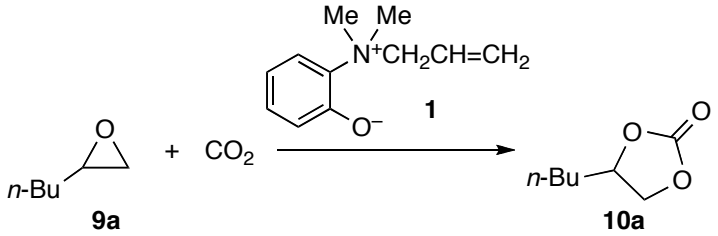
structure	^{1}H NMR	^{13}C NMR
		
		

Figure S1. Selected Regions of ^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C NMR (150 MHz, methanol-d_4) Spectra of **4** and its CO_2-adduct.

The **4**–CO_2 adduct was allowed to react with **9a** (1.21 mL, 10.0 mmol) under Ar in an autoclave at 120 ºC for 24 h. The reactor was then cooled in an ice bath for 30 min. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard. The results are summarized in Figure 3 in the text.

[4] Optimization of Reaction Conditions Using Catalyst 1.



9a **10a**

A 50-mL stainless autoclave was charged with epoxide **9a** (10 mmol), catalyst (indicated in Table S1), and then CO_2 (pressure indicated in Table S1). The mixture was heated with stirring at the indicated temperature for the reaction time indicated. The reactor was cooled in an ice bath for 30 min, and excess CO_2 was released carefully. The crude product was dissolved in Et_2O, and the solution was concentrated. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard.

The yield showed signs of leveling off at 0.5–2.0 MPa CO_2 (entries 1–4), while the yield increased with an increase in the amount of catalyst (entries 3 and 5–8). Next we changed the temperature using 3 mol % of catalyst at 1.0 MPa CO_2 to find that the yield reached a plateau at 130 ºC (entries 3 and 9–12). When the progress of the reaction was then monitored under the optimal conditions (5 mol % of catalyst, 1.0 MPa CO_2, and 130 ºC), the reaction reached 99% in 48 h (entries 13–16).

Table S1. Optimization of Reaction Conditions Using Catalyst **1**.

entry	CO_2 (MPa)	loading (mol %)	temp (ºC)	time (h)	yield (%)
1	0.1	3	120	48	54
2	0.5	3	120	48	76
3	1.0	3	120	48	76
4	2.0	3	120	48	75
5	1.0	1	120	48	18
6	1.0	2	120	48	60
7	1.0	4	120	48	85
8	1.0	5	120	48	99
9	1.0	3	100	48	63
10	1.0	3	110	48	77
11	1.0	3	130	48	79
12	1.0	3	140	48	79
13	1.0	5	130	6	19
14	1.0	5	130	12	65
15	1.0	5	130	24	73
16	1.0	5	130	48	99

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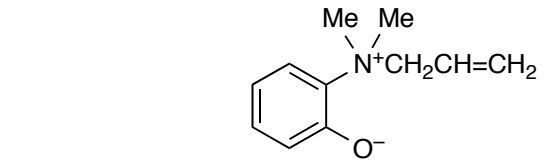
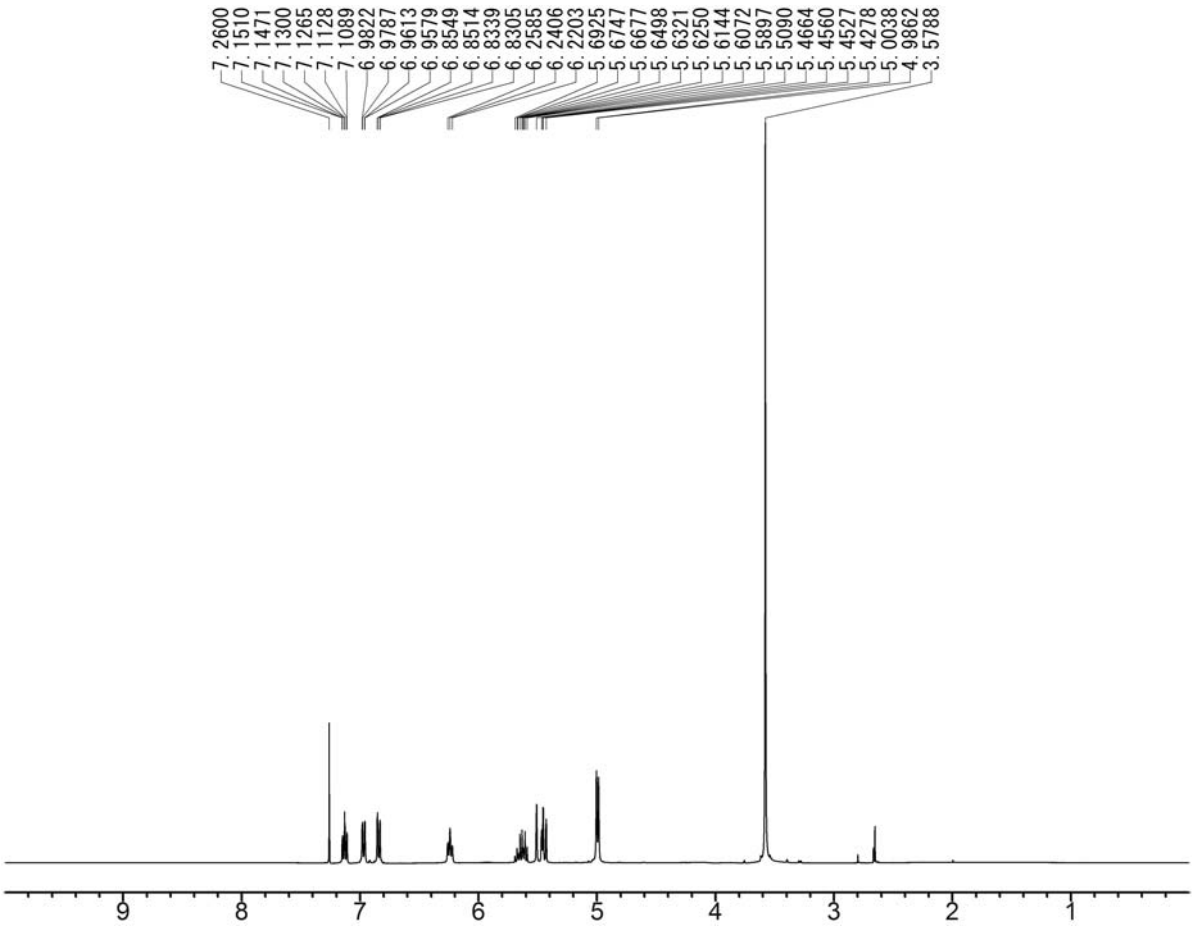
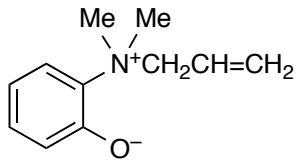
[5] ^{1}H and ^{13}C NMR Spectra.



1



400 MHz ^{1}H NMR of **1** in $CDCl_3$.



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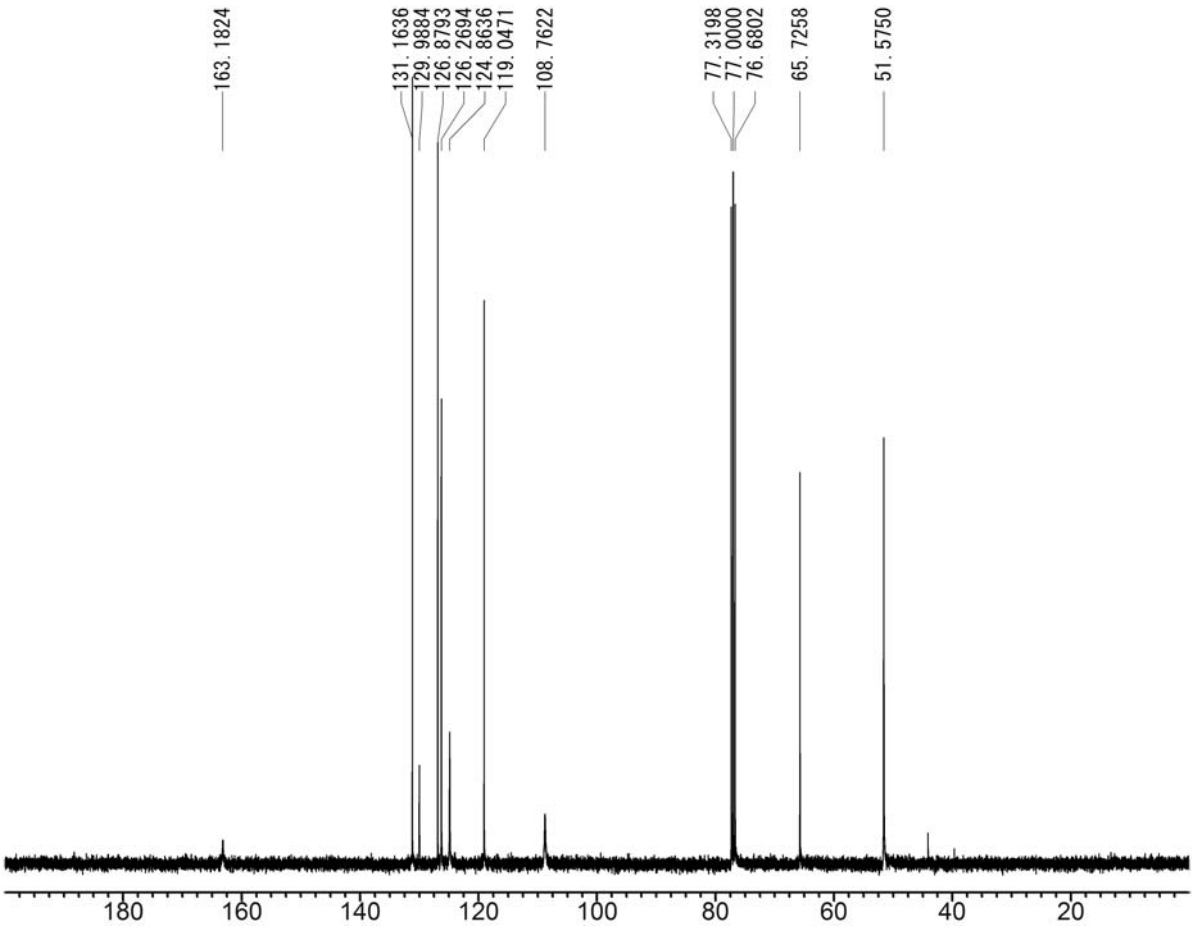
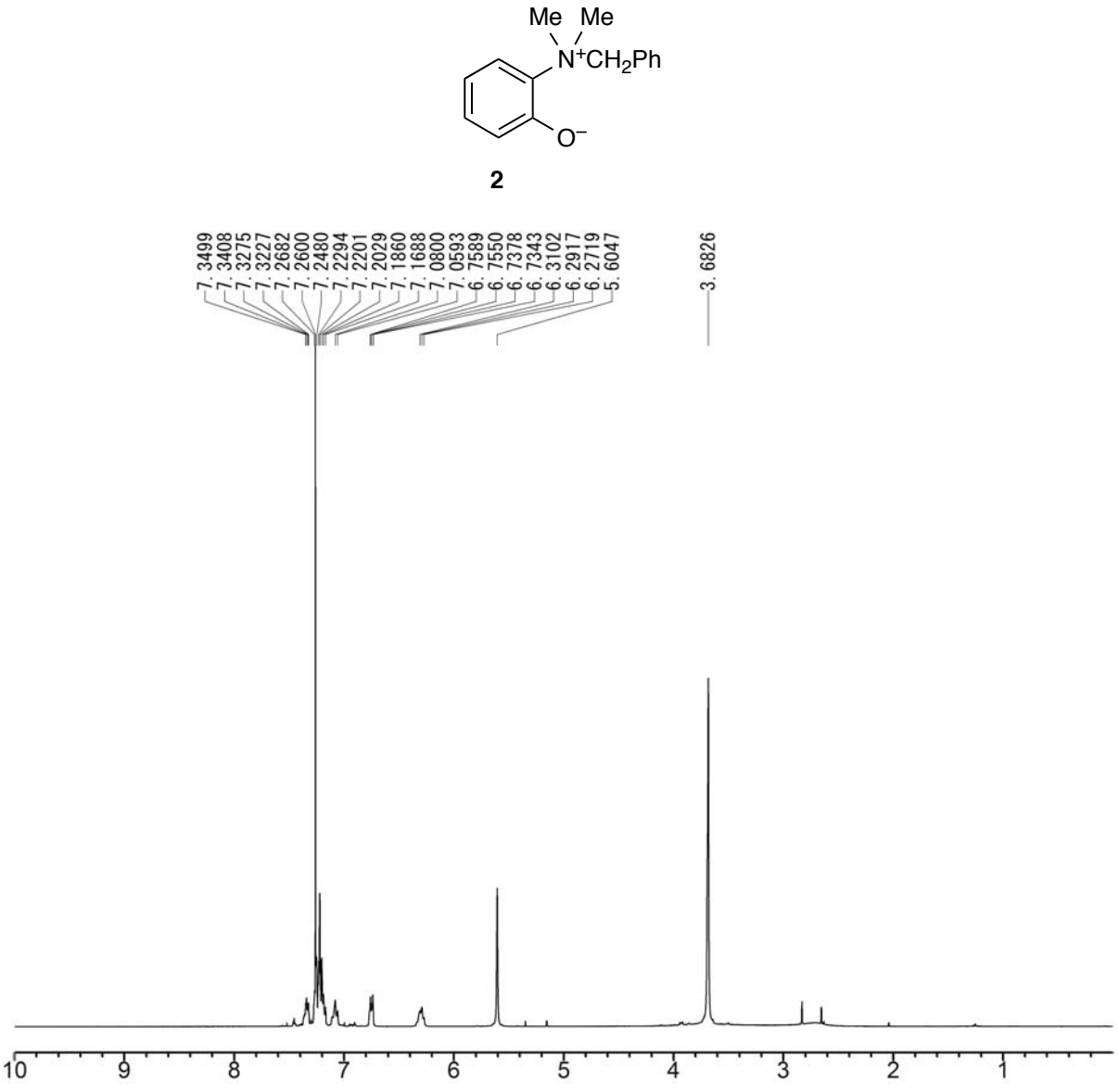
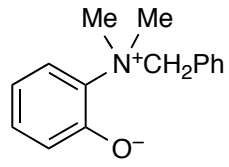


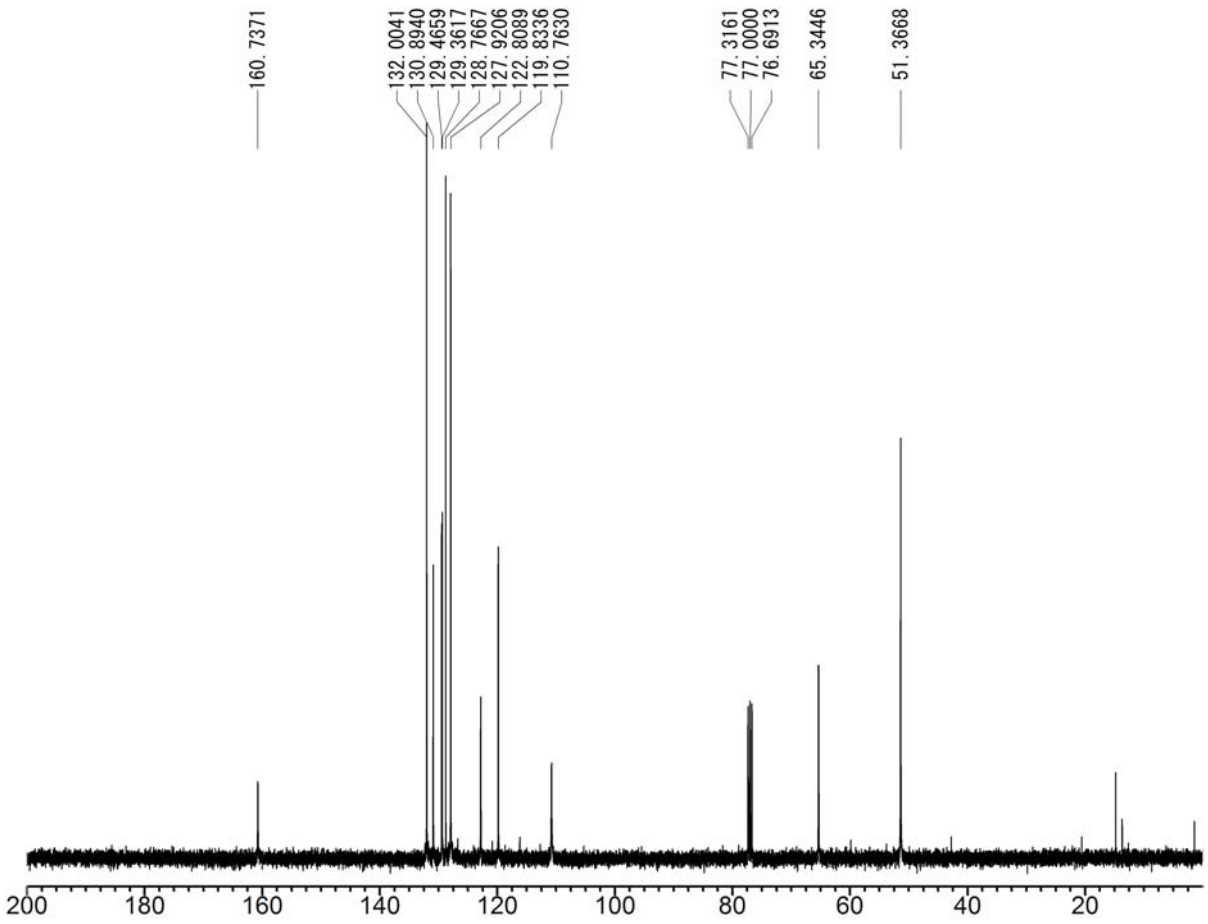
100 MHz ^{13}C NMR of **1** in $CDCl_3$.



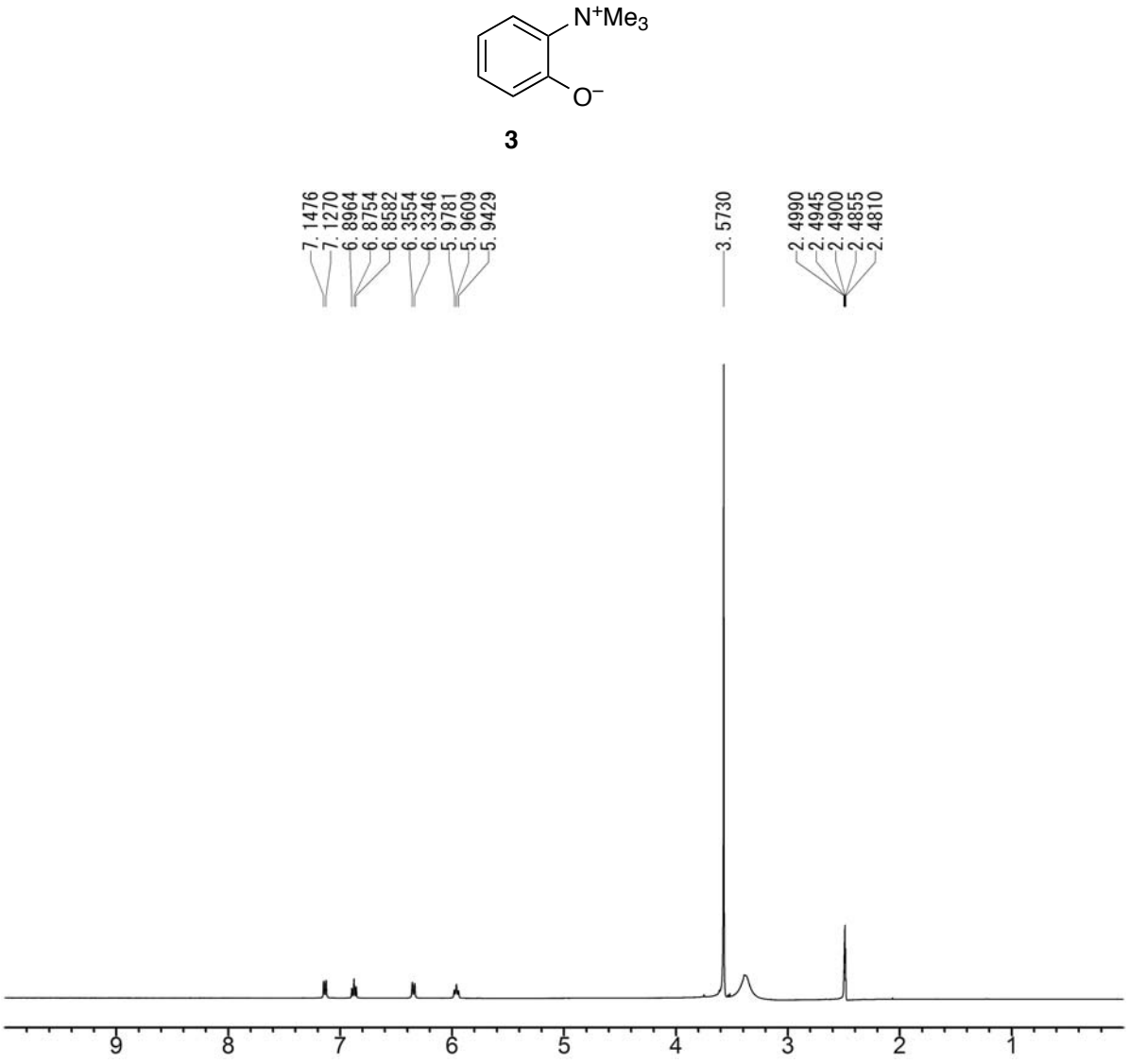
400 MHz ^{1}H NMR of **2** in $CDCl_3$.



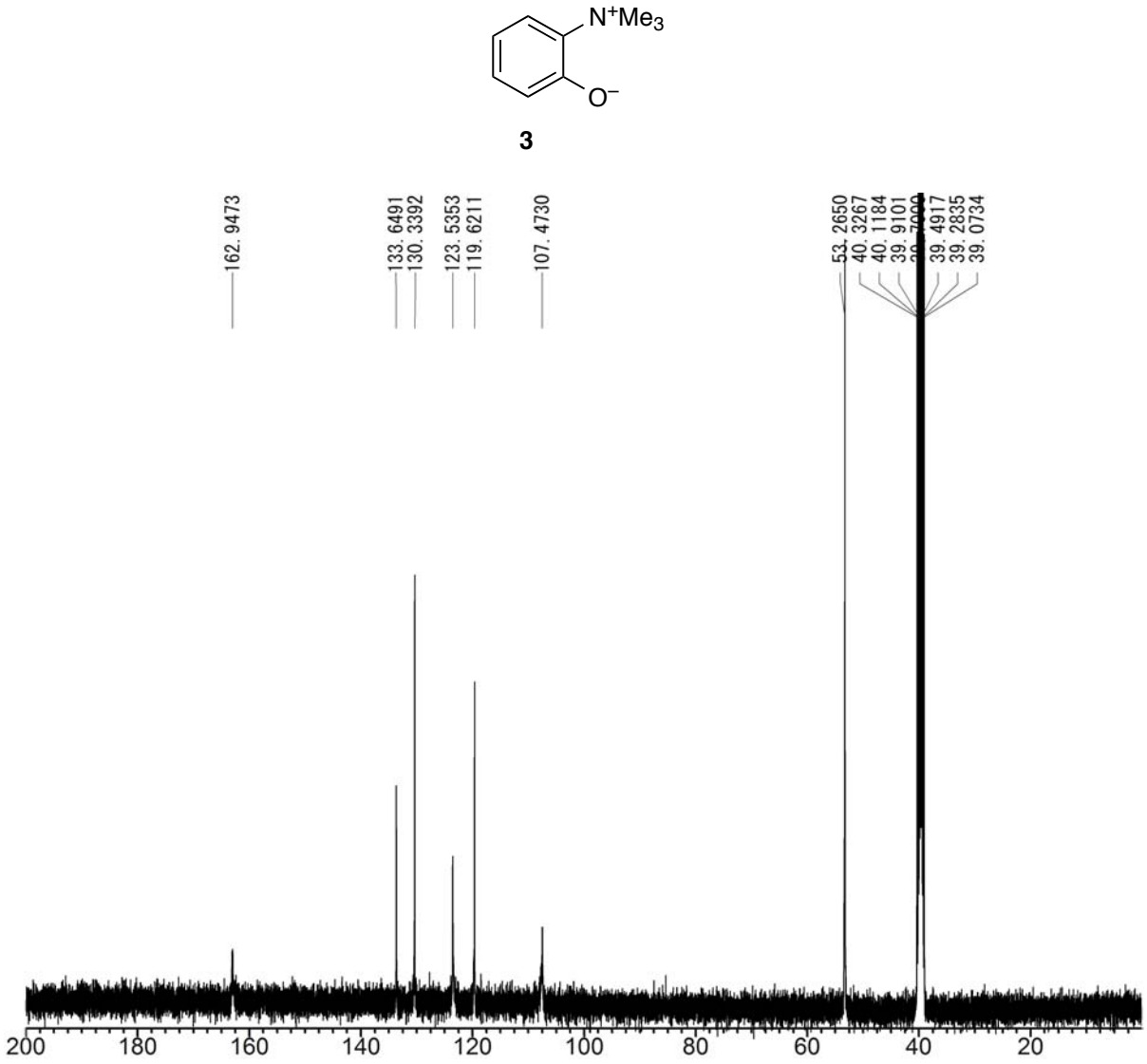
2



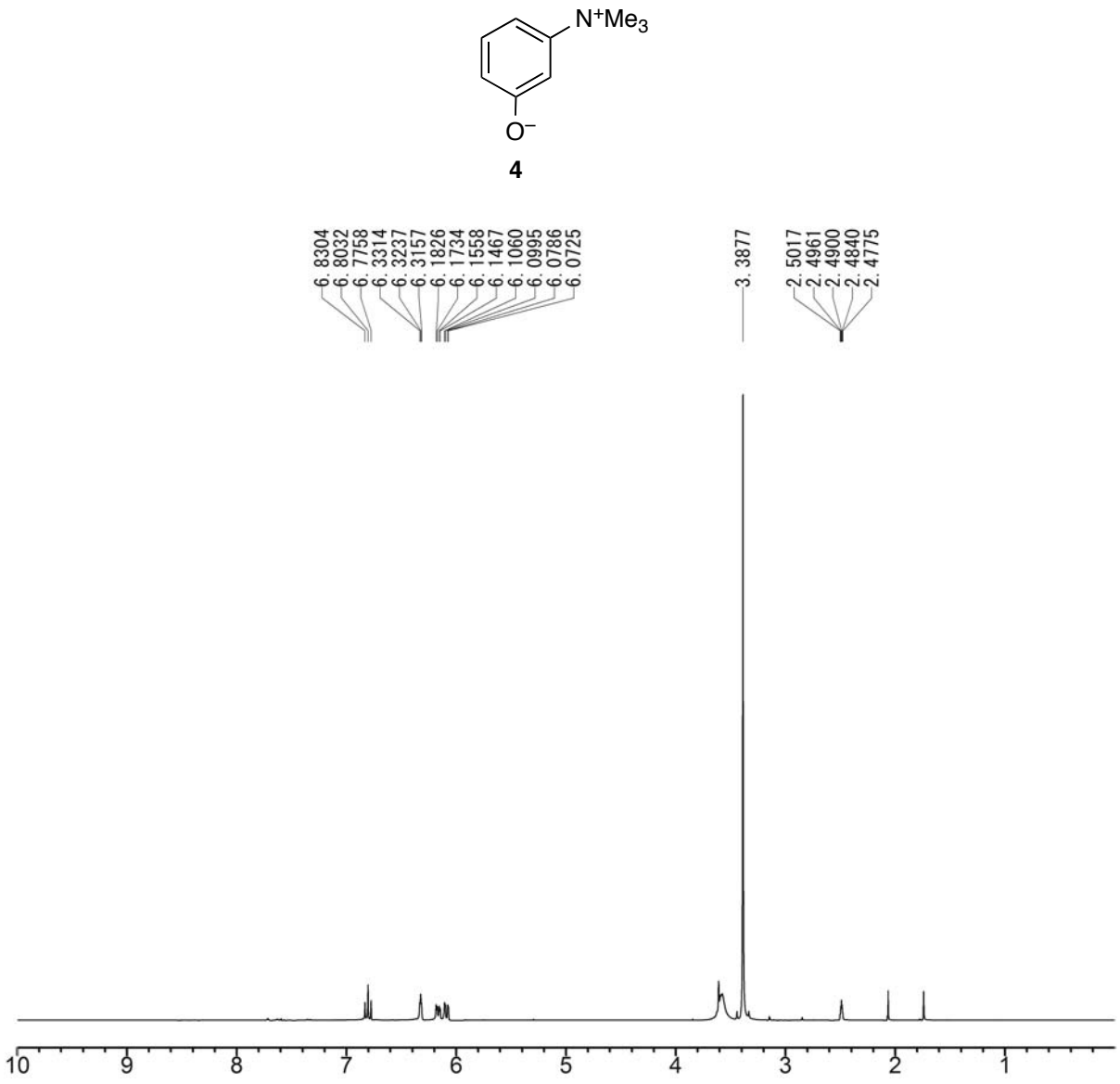
100 MHz ^{13}C NMR of **2** in $CDCl_3$.



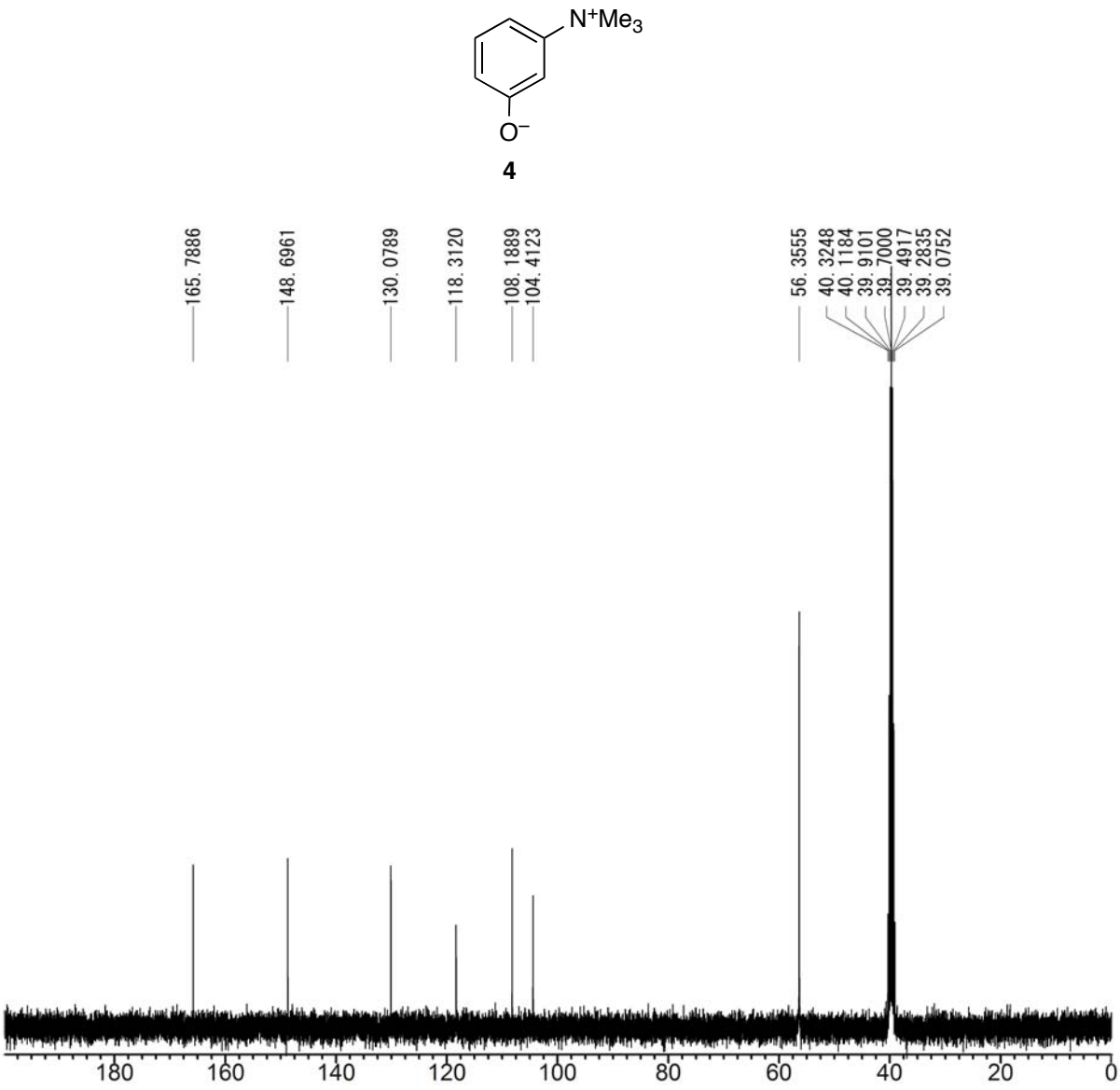
400 MHz ^{1}H NMR of **3** in DMSO-d_6.



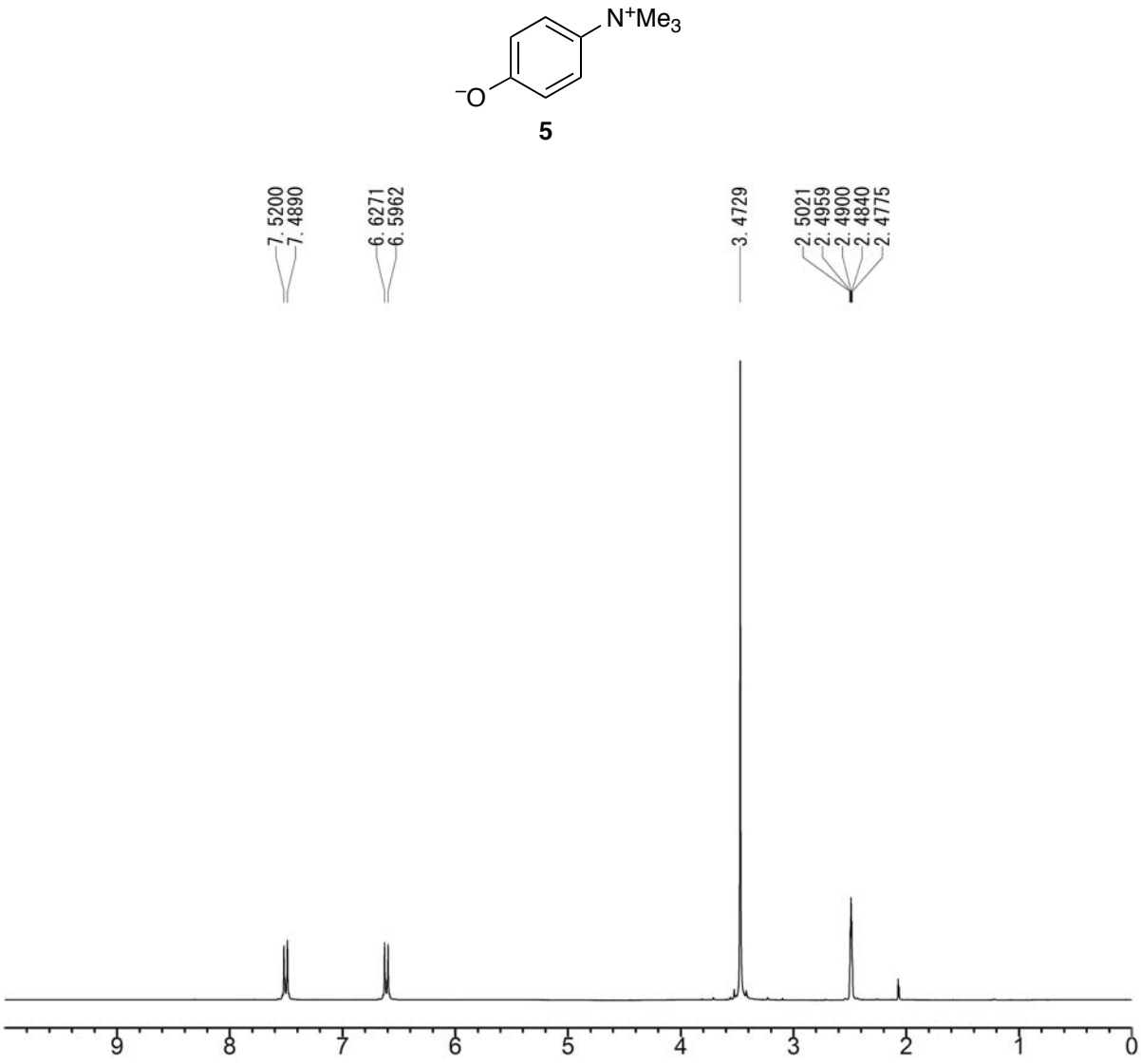
100 MHz ^{13}C NMR of **3** in DMSO-d_6.



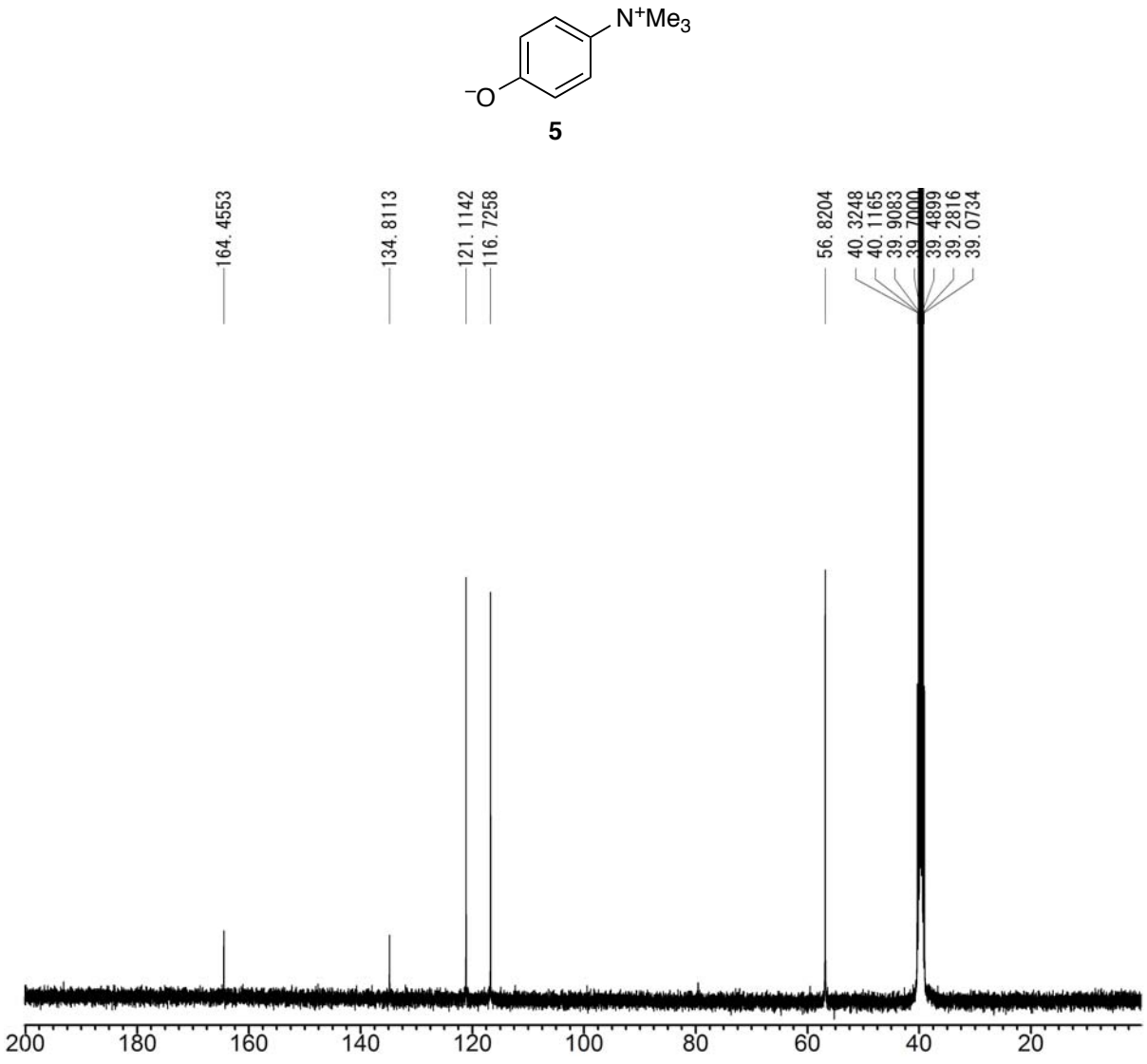
300 MHz ^{1}H NMR of **4** in DMSO-d_6.



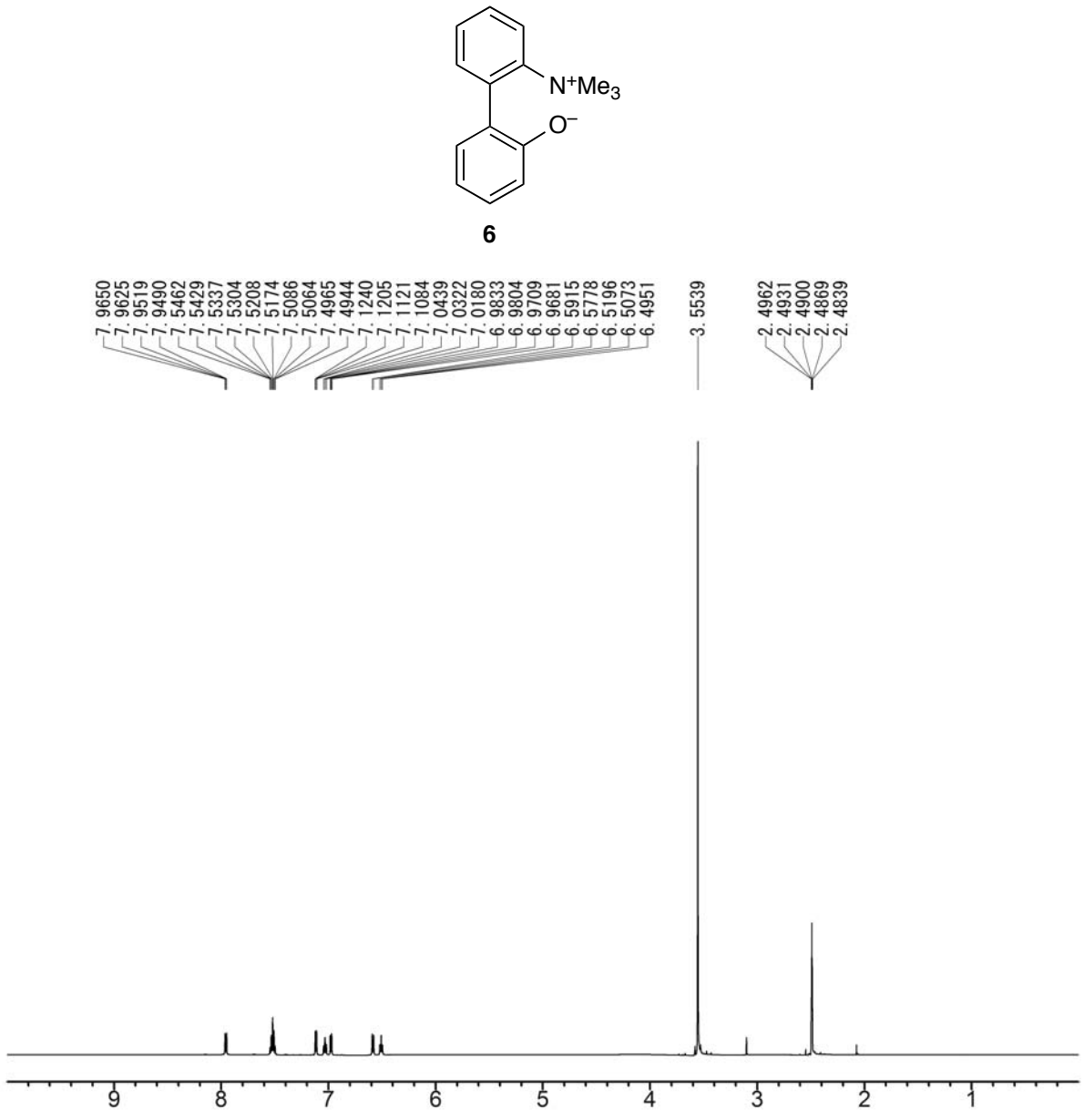
100 MHz ^{13}C NMR of **4** in DMSO-d_6.



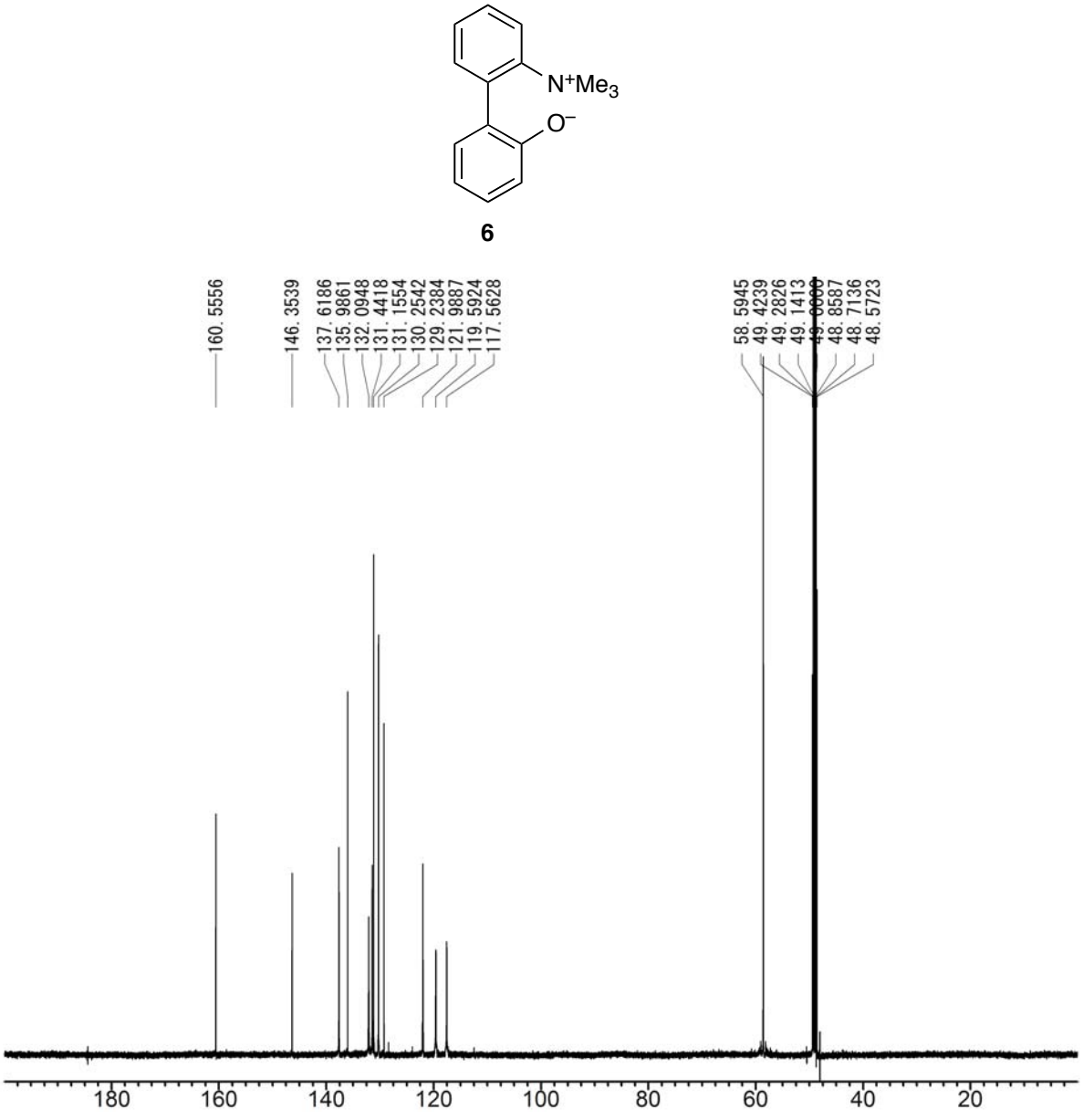
300 MHz ^{1}H NMR of **5** in DMSO-d_6.



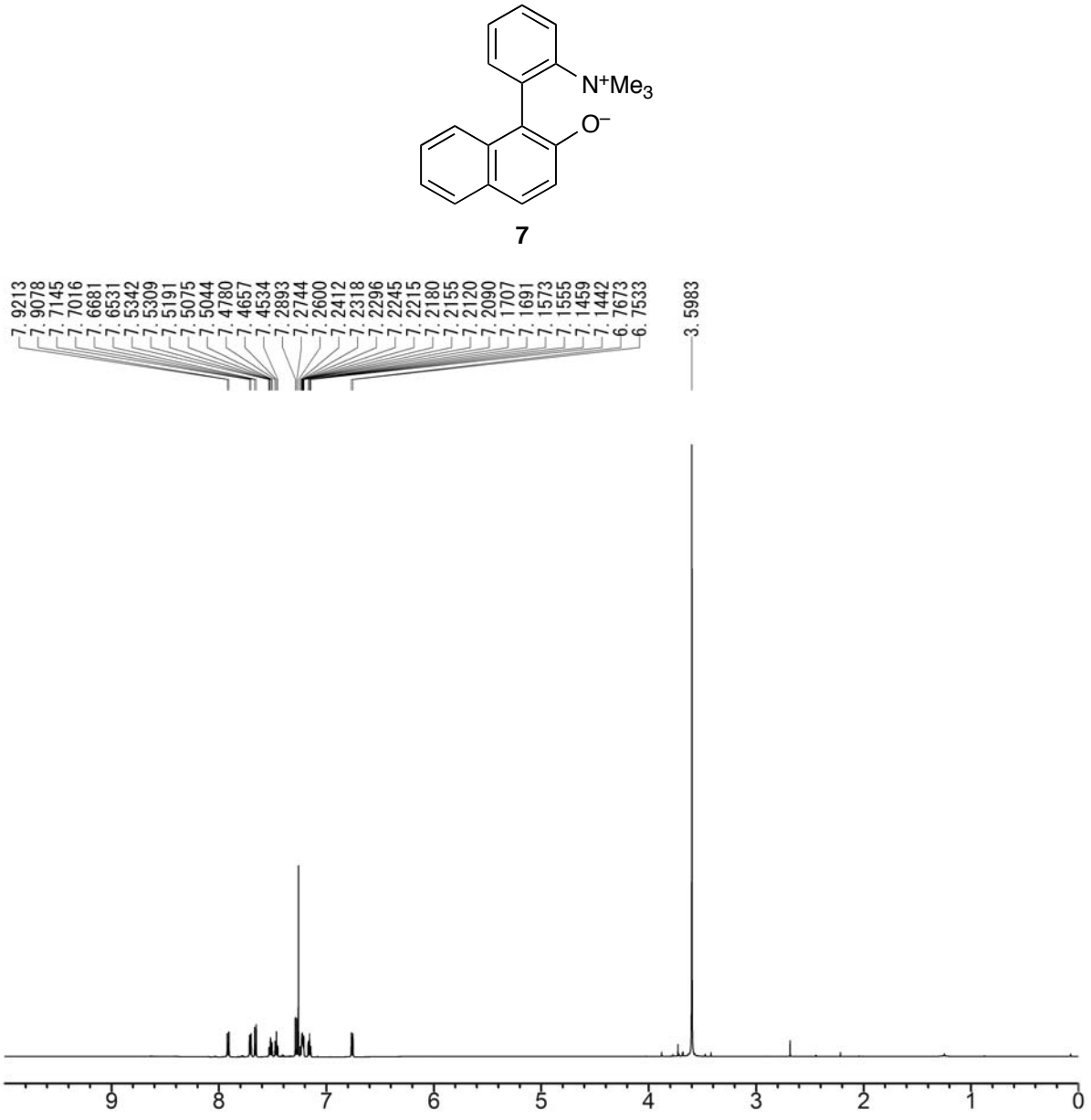
100 MHz ^{13}C NMR of **5** in DMSO-d_6.



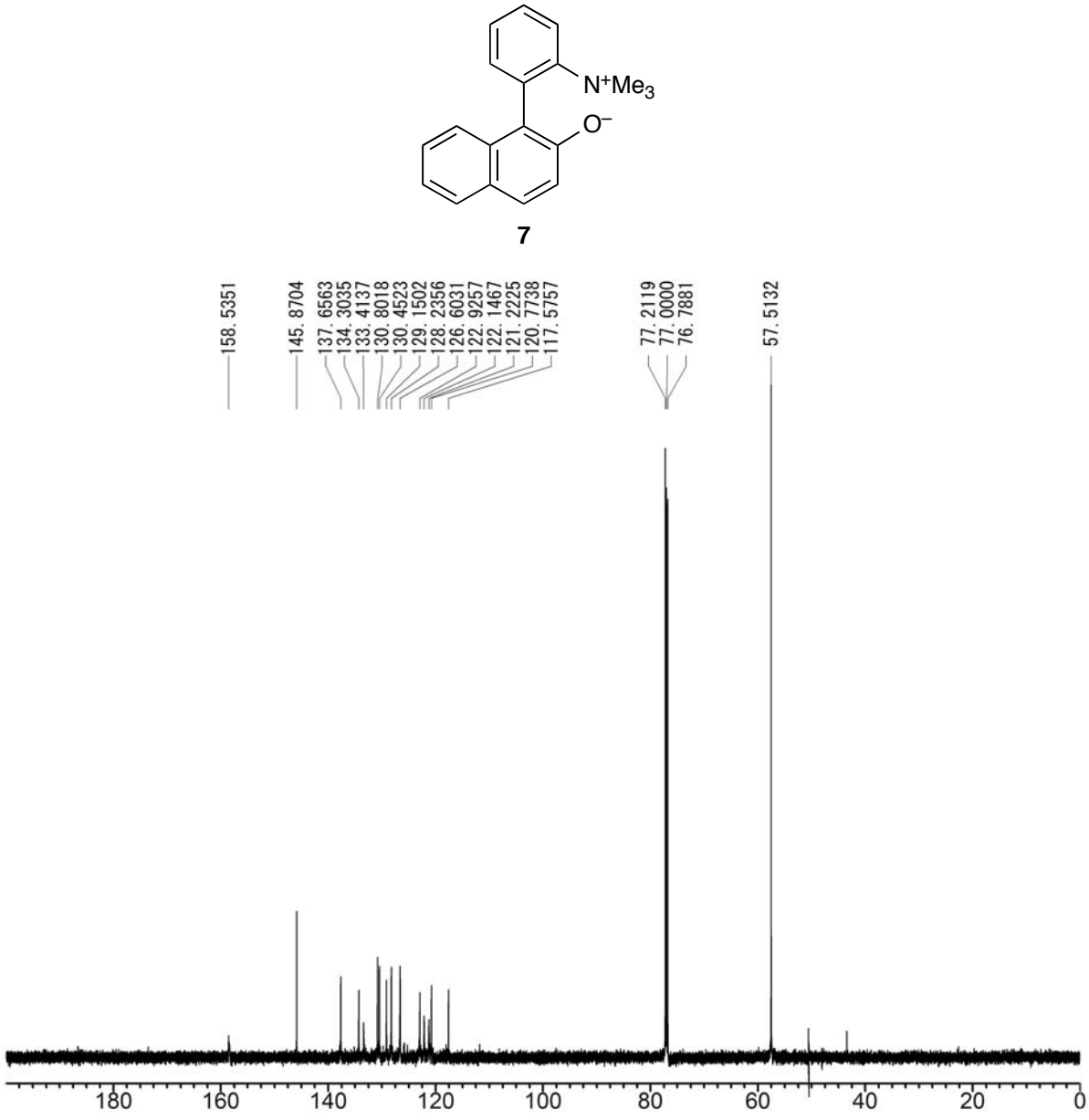
600 MHz ^{1}H NMR of **6** in DMSO-d_6.



150 MHz ^{13}C NMR of **6** in methanol-d_4.

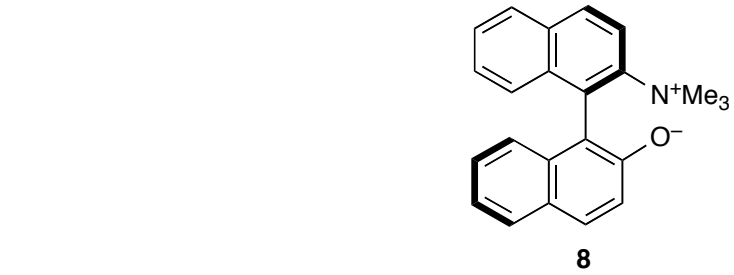


600 MHz ^{1}H NMR of **7** in $CDCl_3$.



7

150 MHz ^{13}C NMR of **7** in $CDCl_3$.



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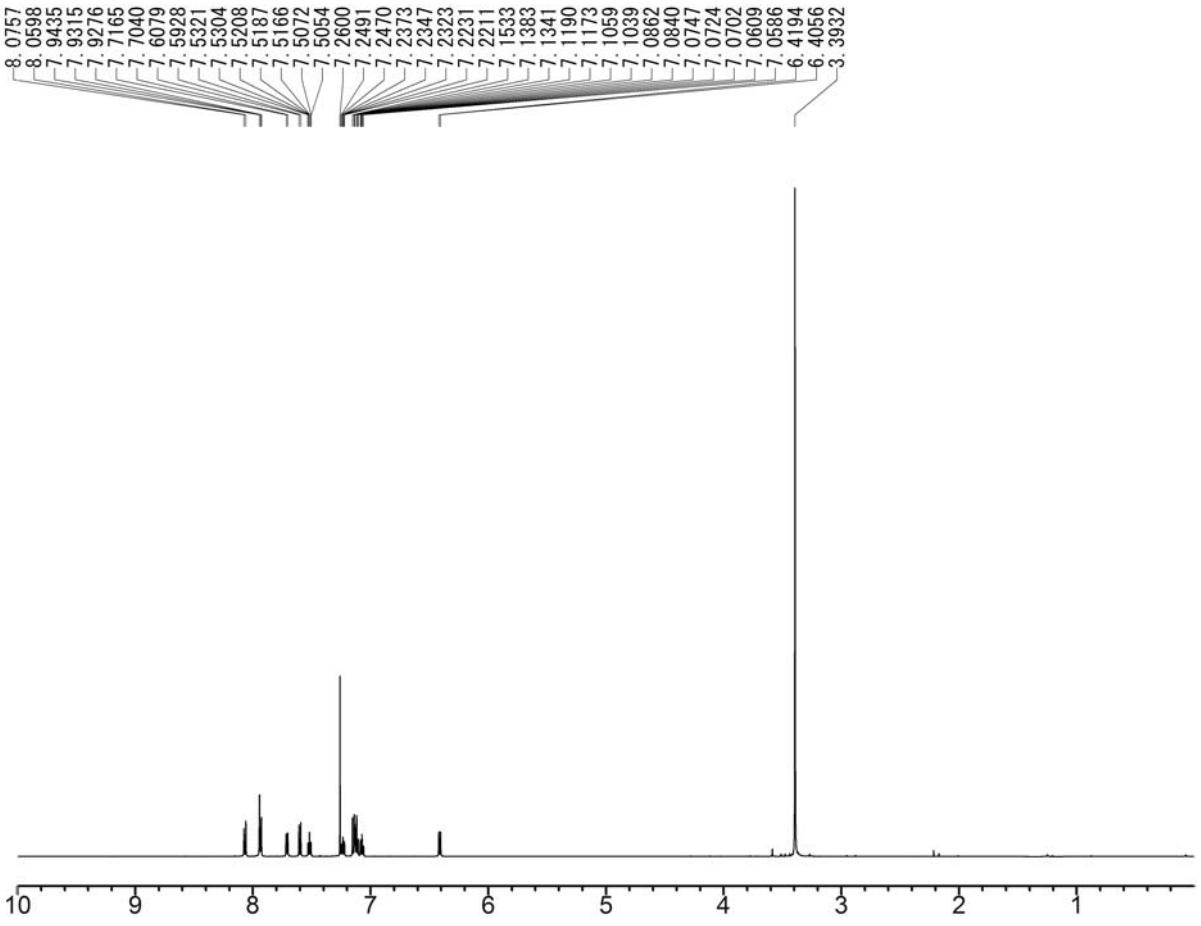
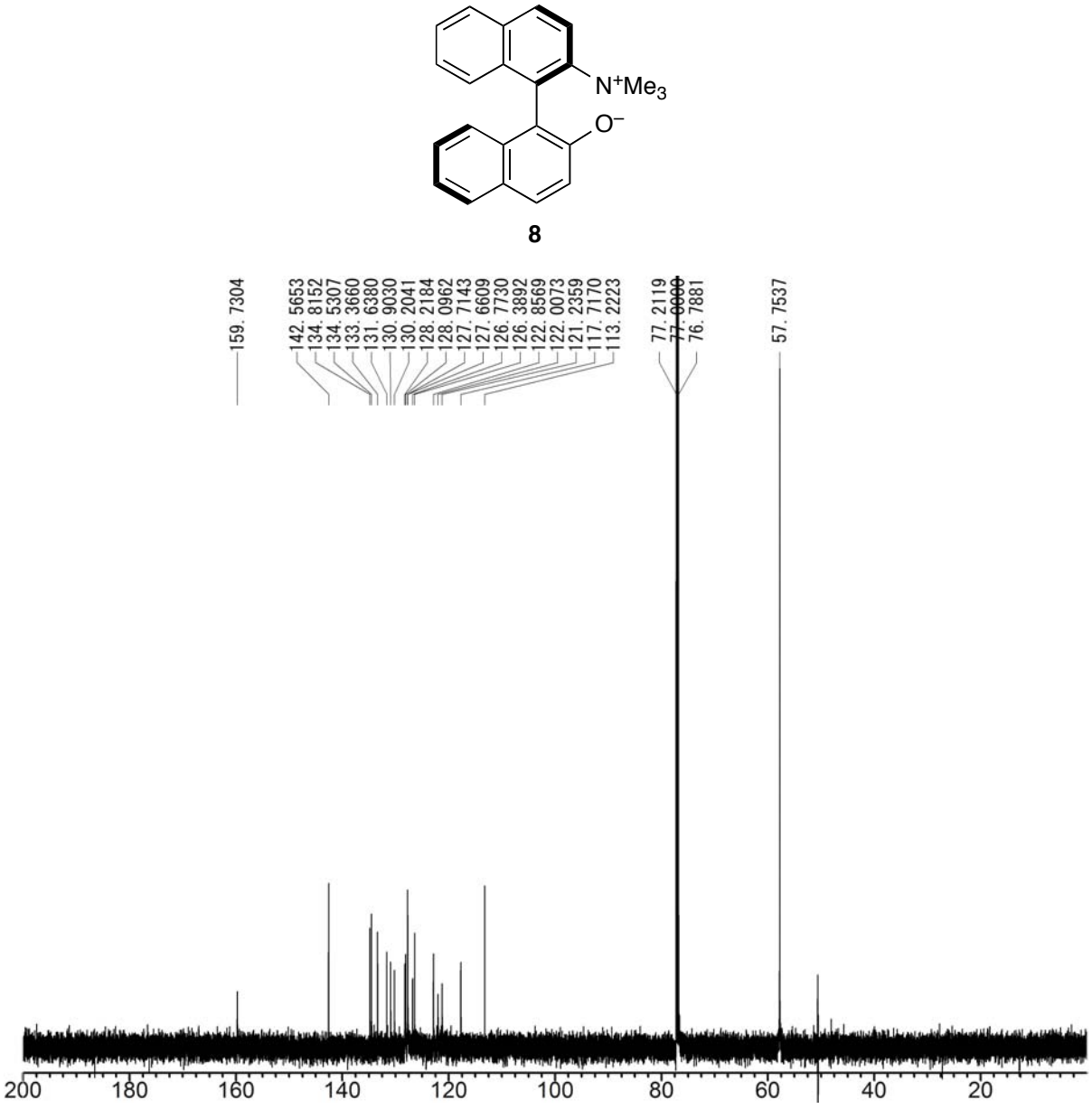
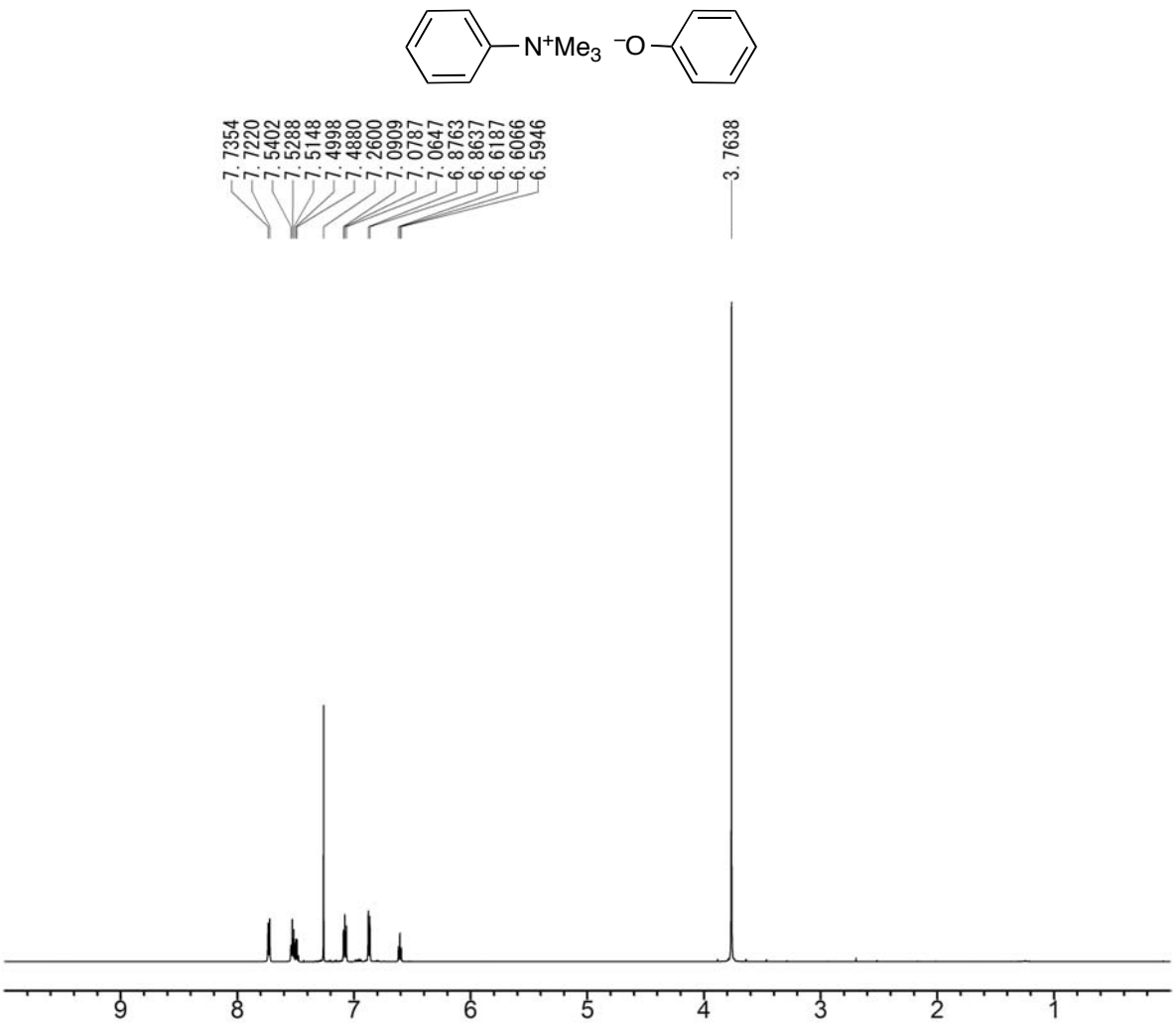


600 MHz ^{1}H NMR of **8** in $CDCl_3$.

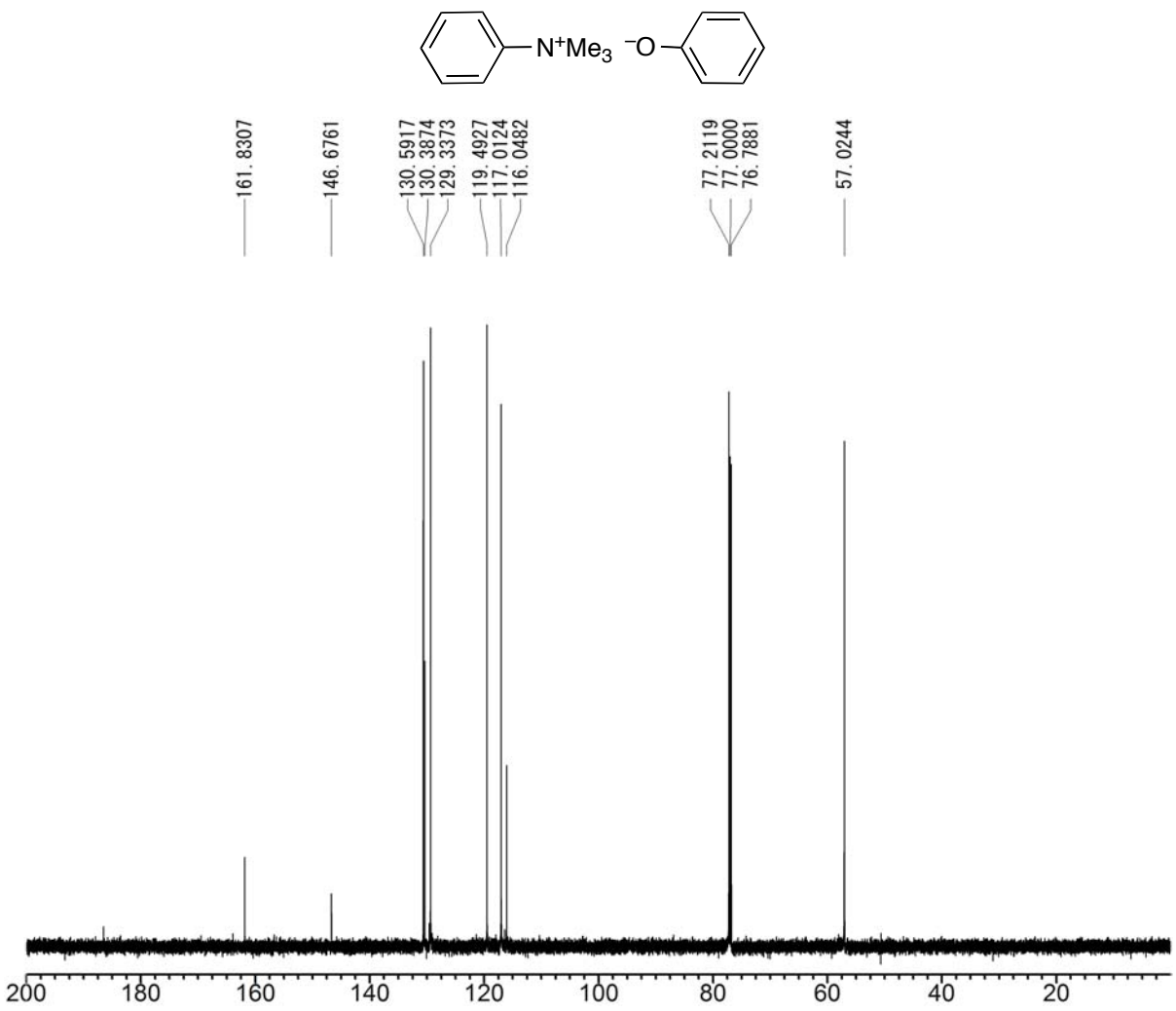


8

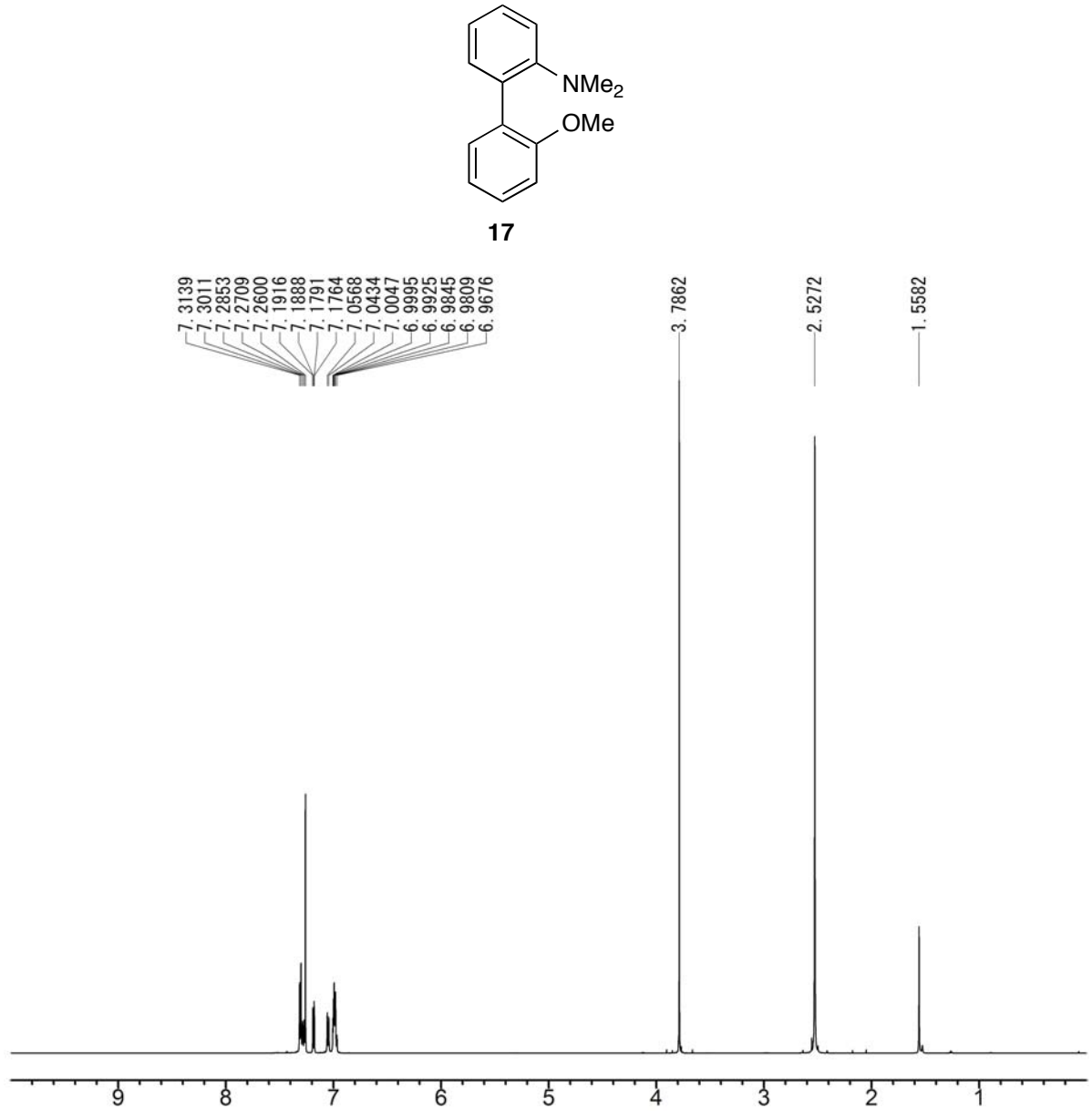
150 MHz ^{13}C NMR of **8** in $CDCl_3$.



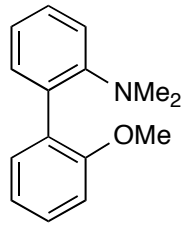
600 MHz ^{1}H NMR of phenyltrimethylammonium phenoxide in $CDCl_3$.



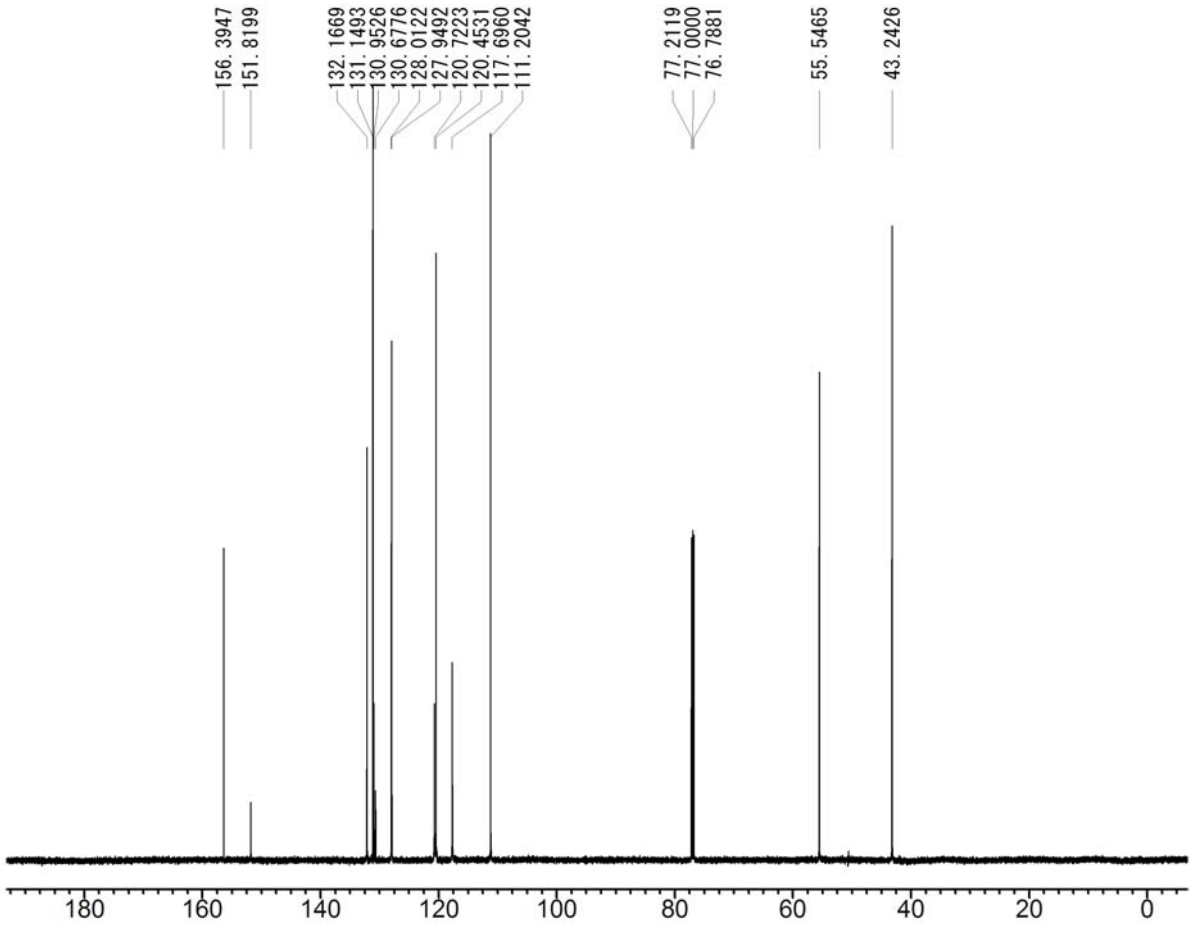
150 MHz ^{13}C NMR of phenyltrimethylammonium phenoxide in $CDCl_3$.



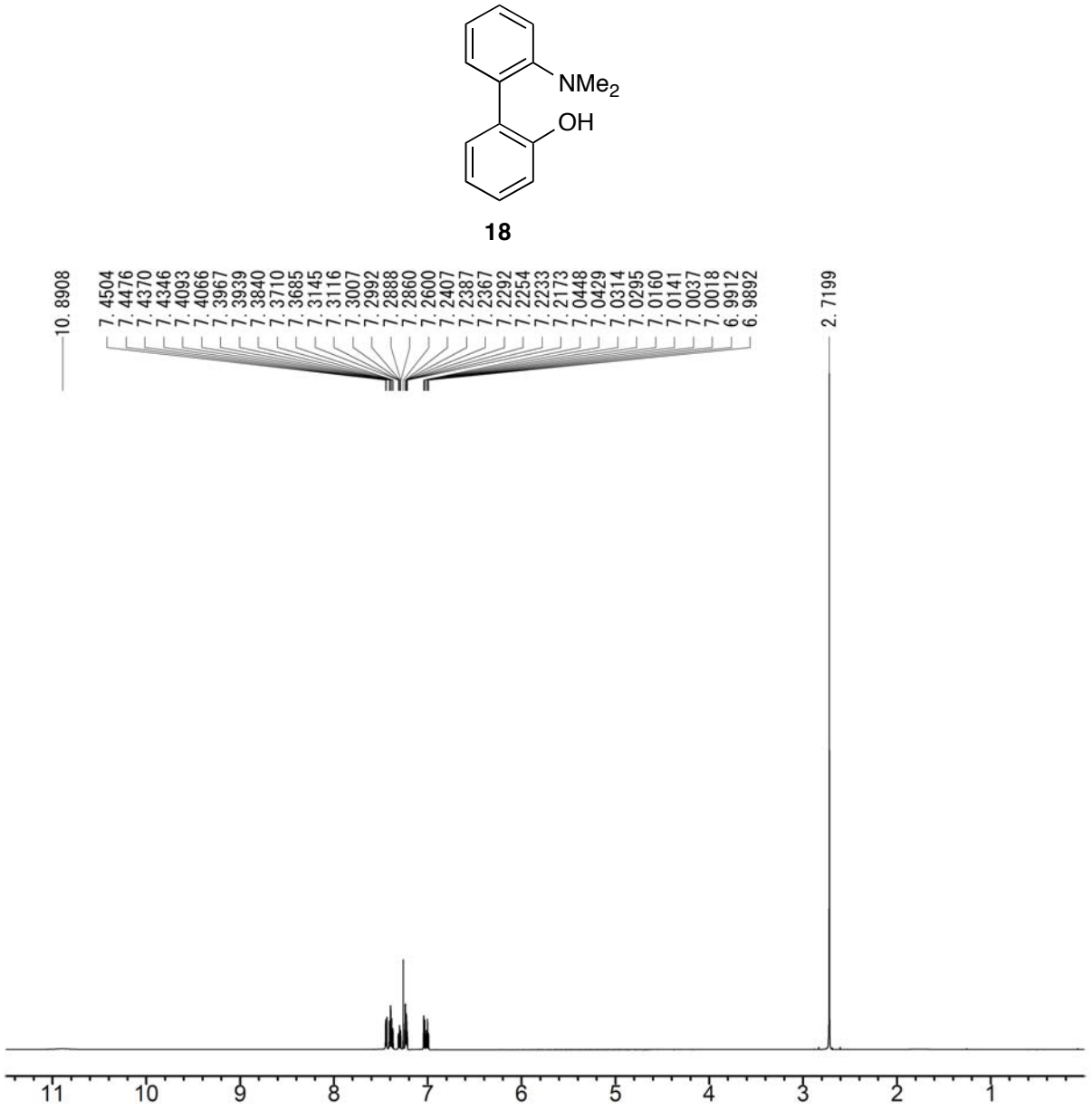
600 MHz ^{1}H NMR of **17** in $CDCl_3$.



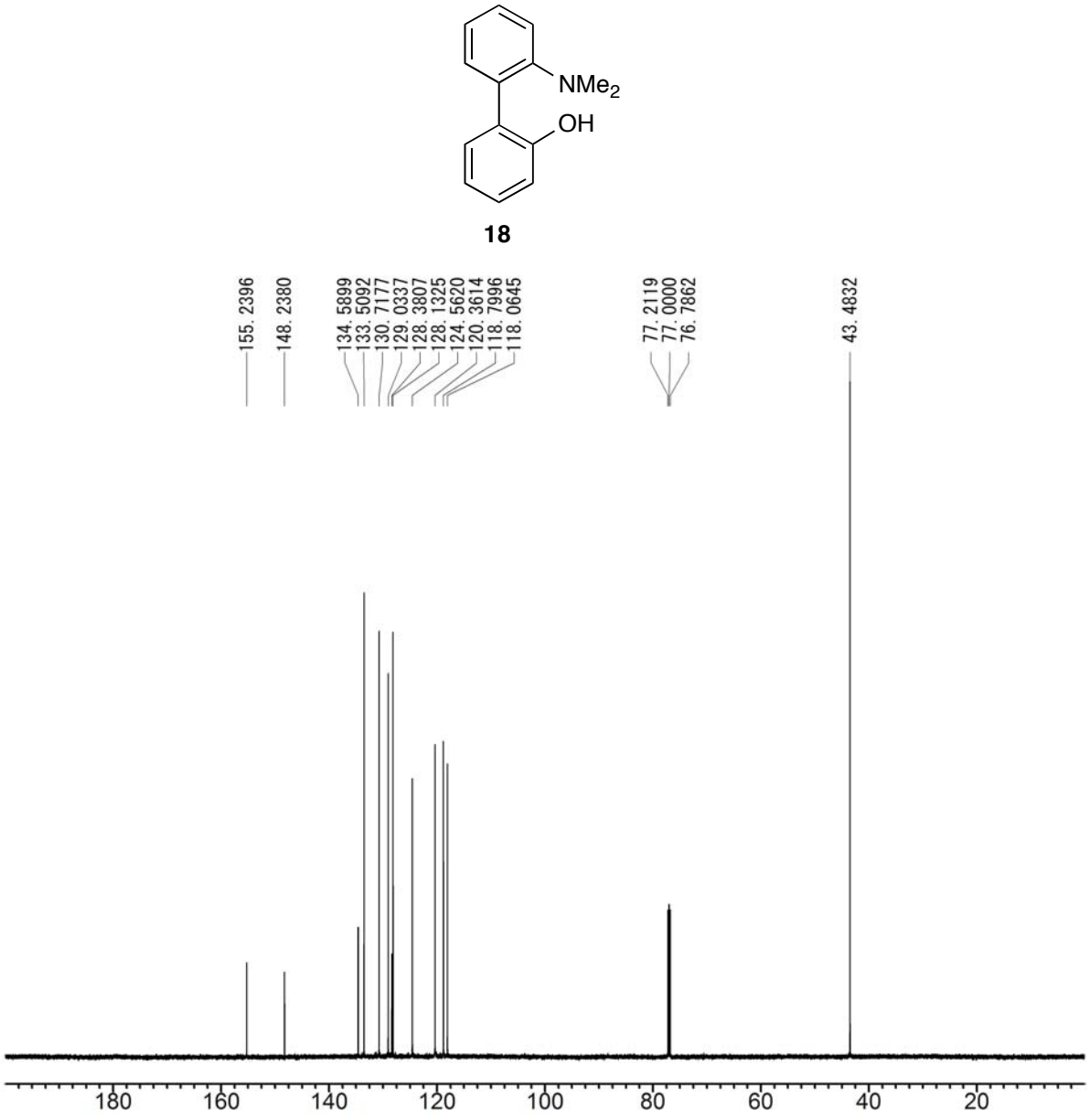
17



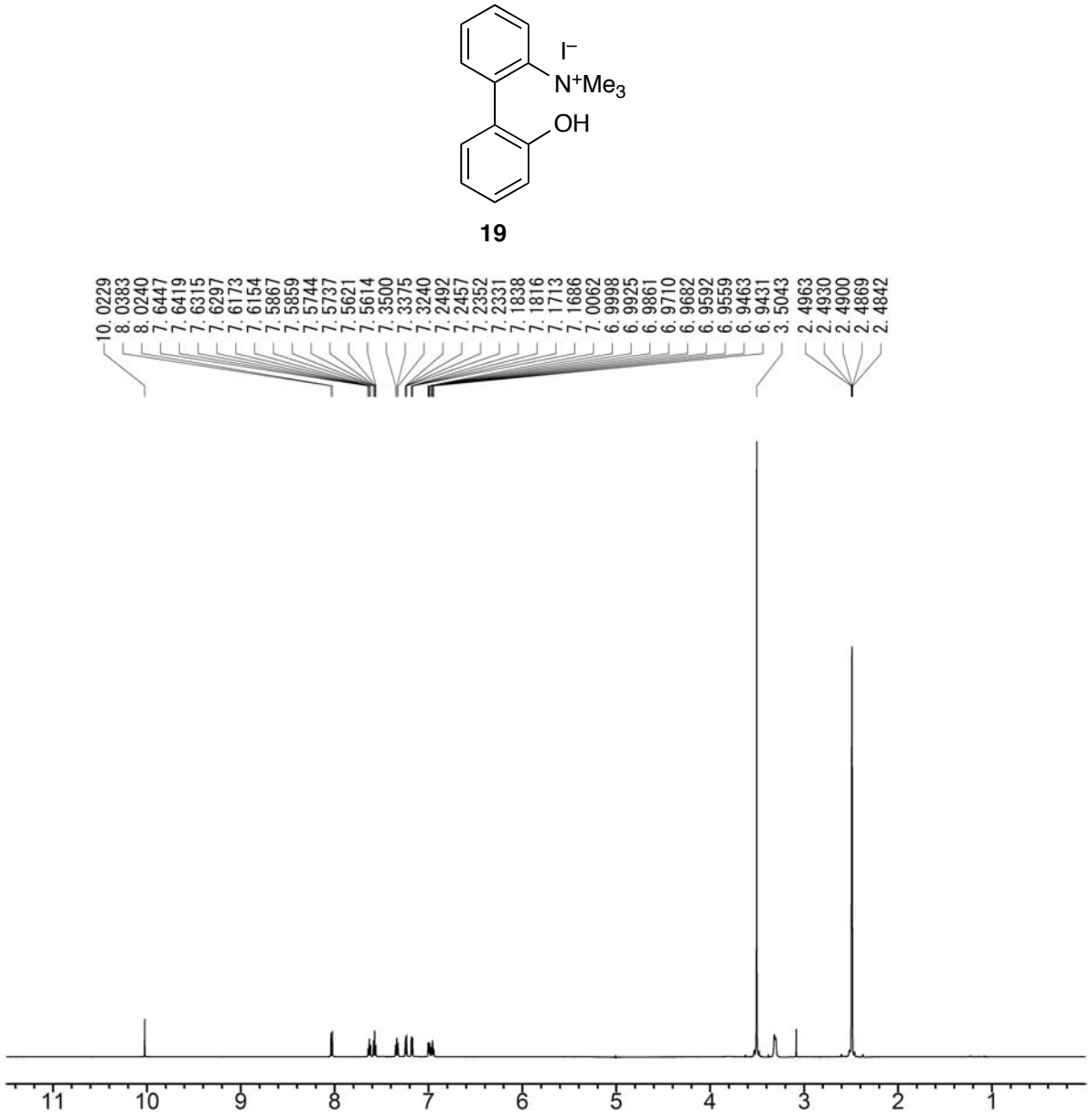
150 MHz ^{13}C NMR of **17** in $CDCl_3$.



600 MHz ^{1}H NMR of **18** in $CDCl_3$.

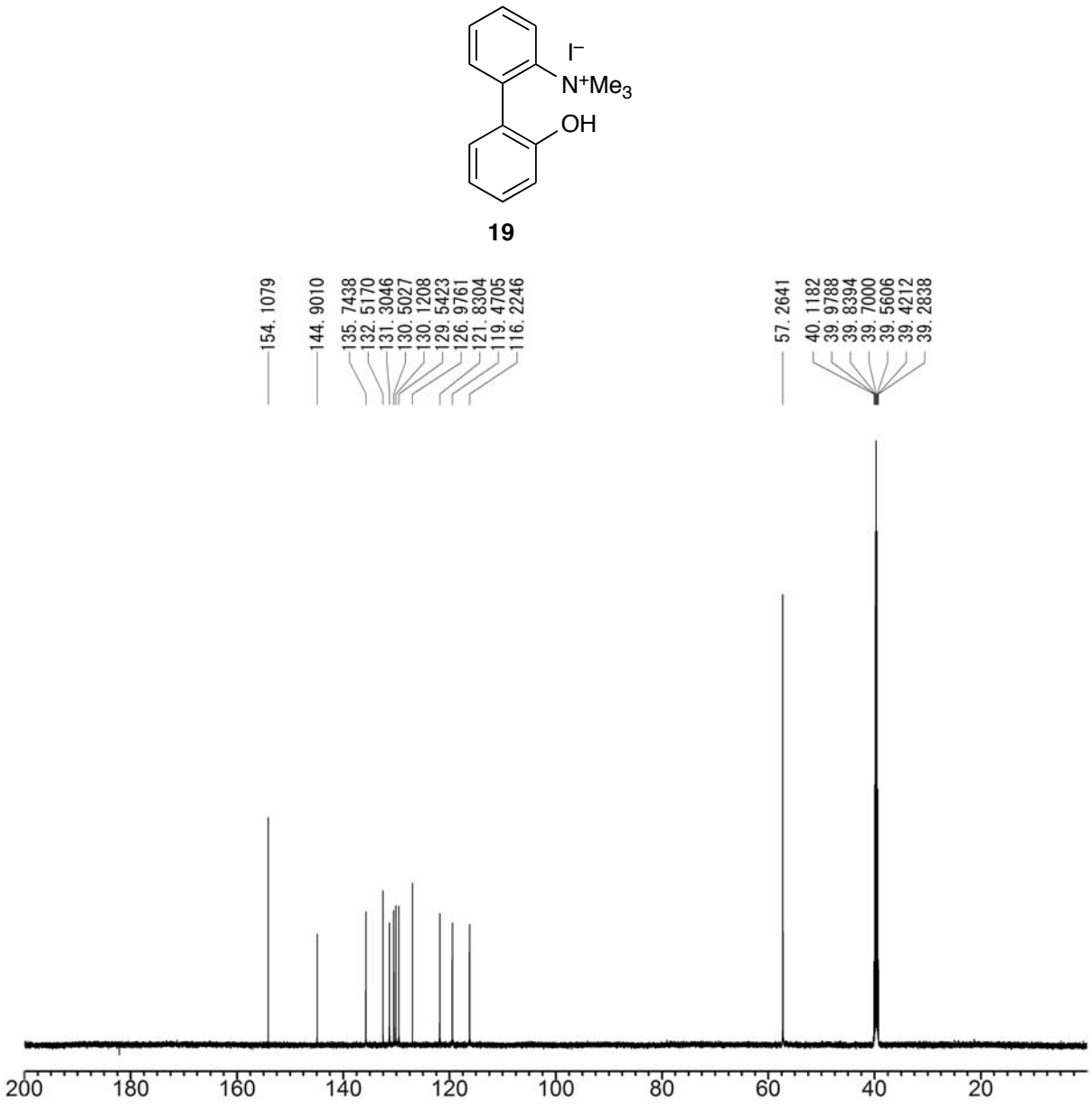


150 MHz ^{13}C NMR of **18** in $CDCl_3$.



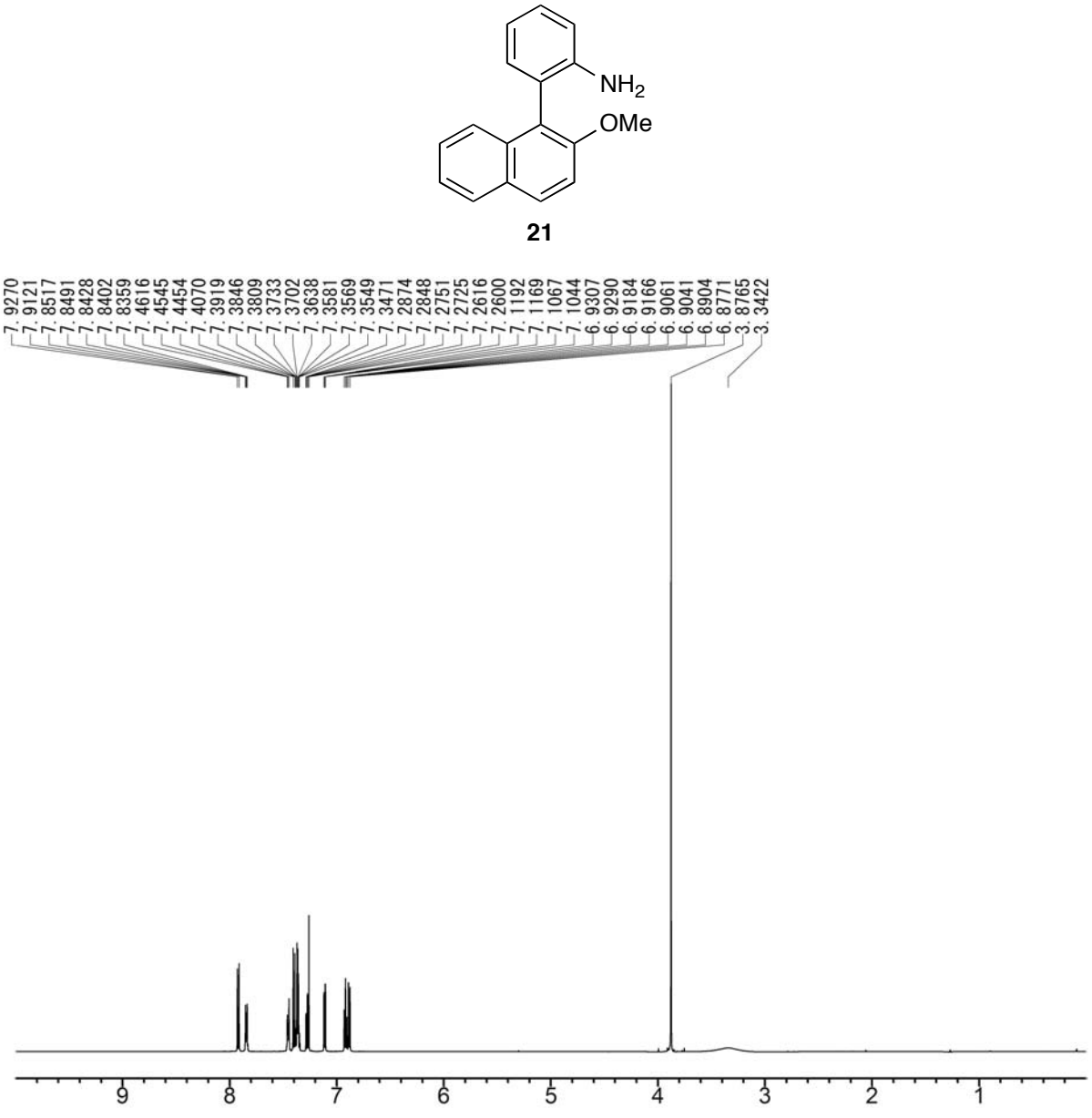
19

600 MHz ^{1}H NMR of **19** in DMSO-d_6.

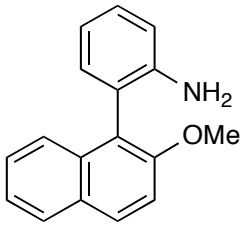


19

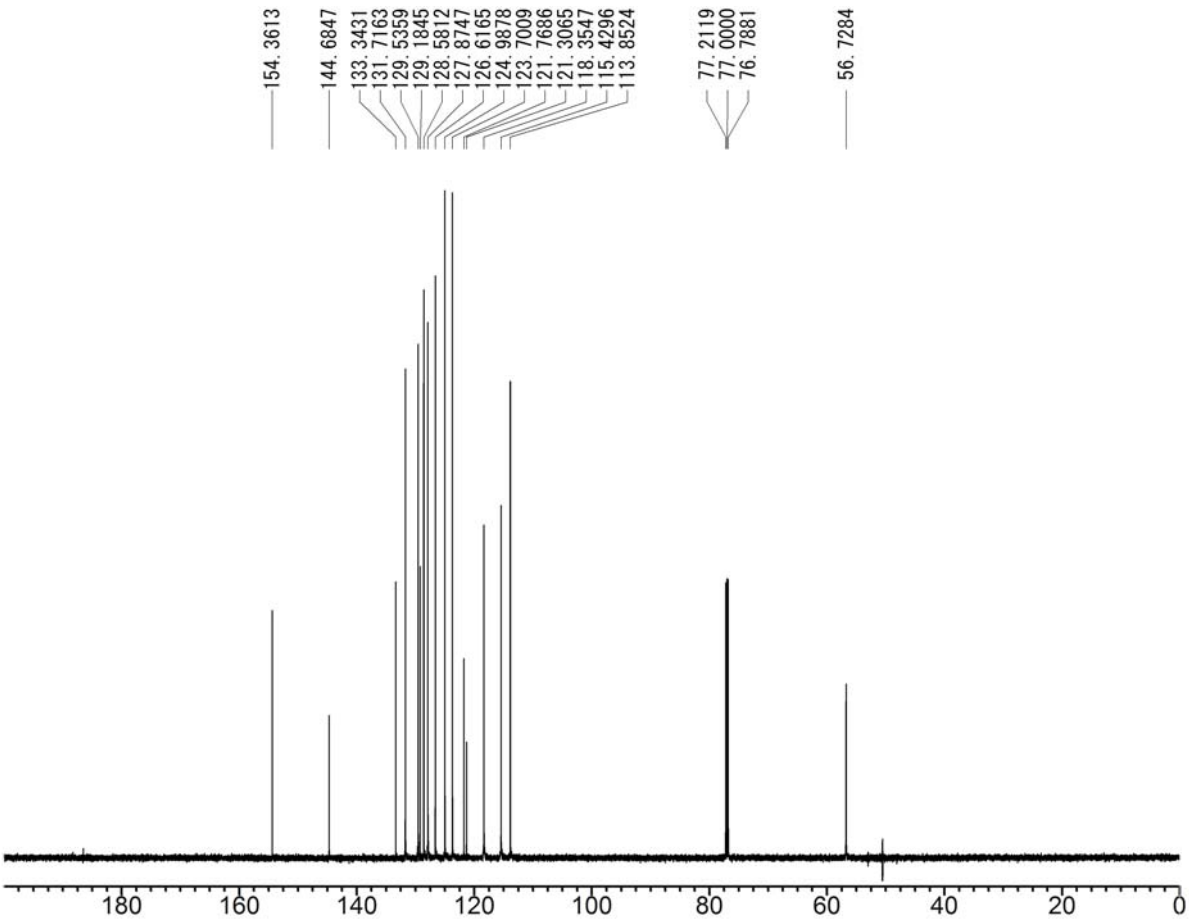
150 MHz ^{13}C NMR of **19** in DMSO-d_6.



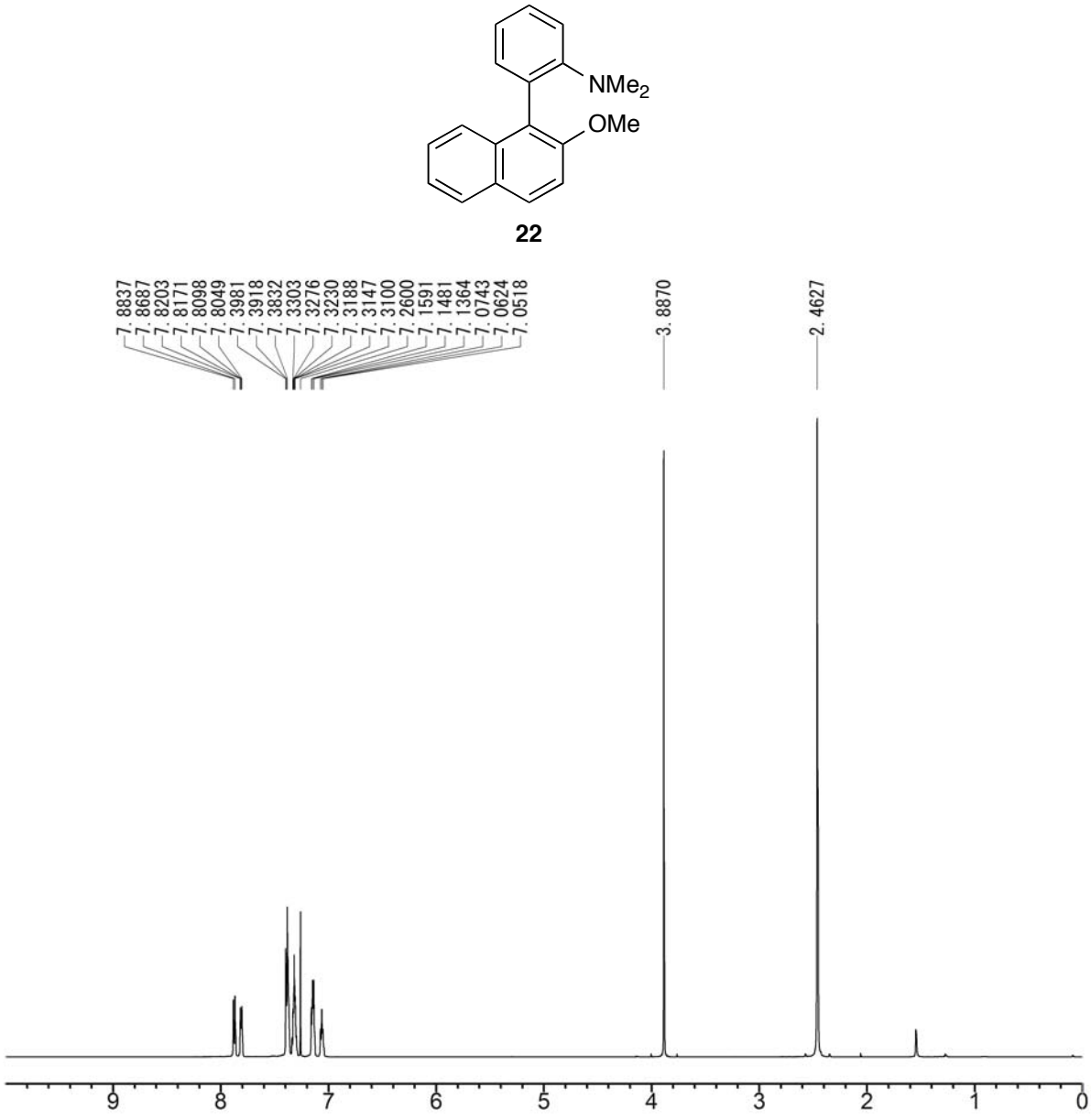
600 MHz ^{1}H NMR of **21** in $CDCl_3$.



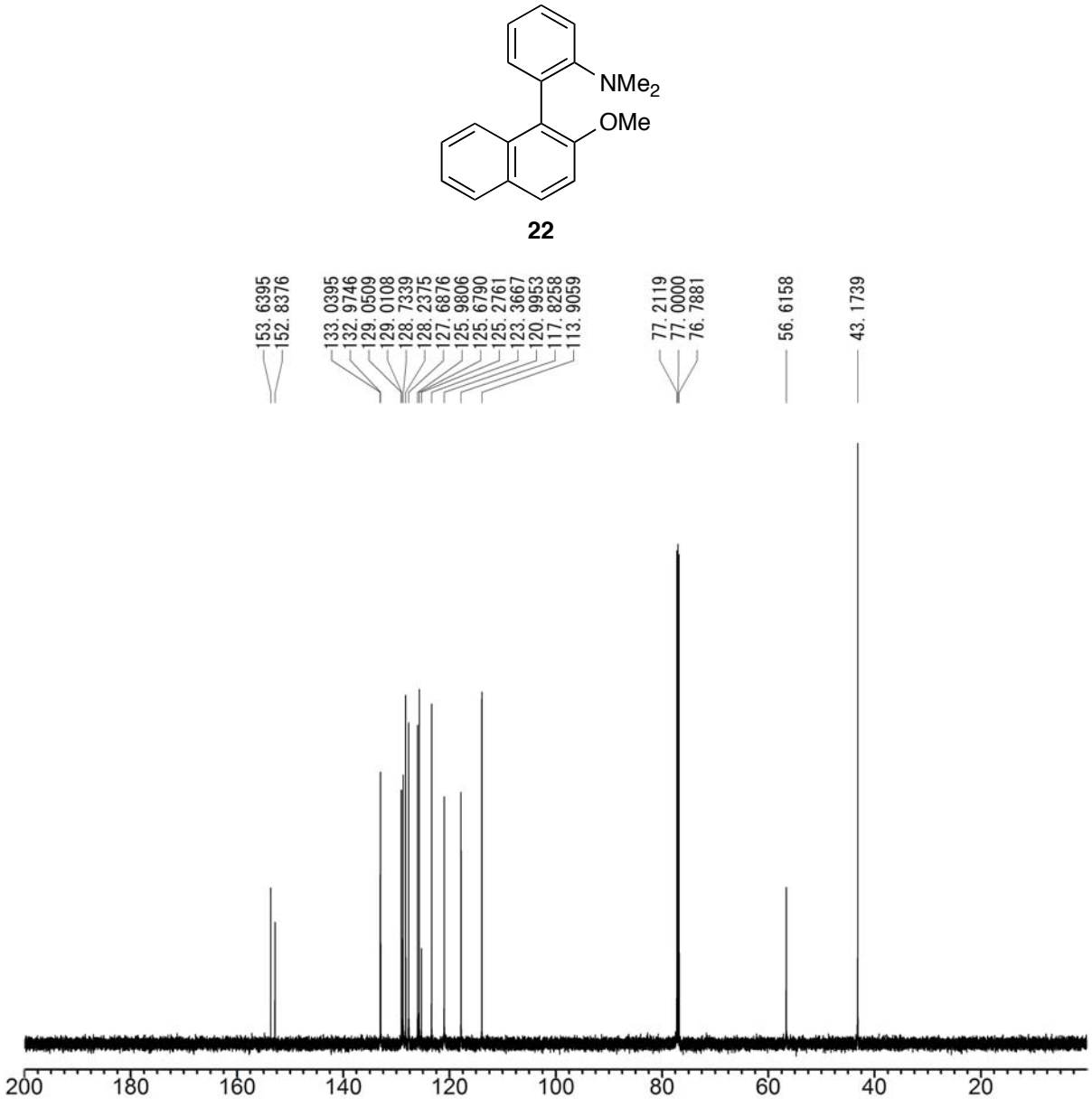
21



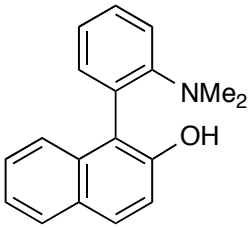
150 MHz ^{13}C NMR of **21** in $CDCl_3$.



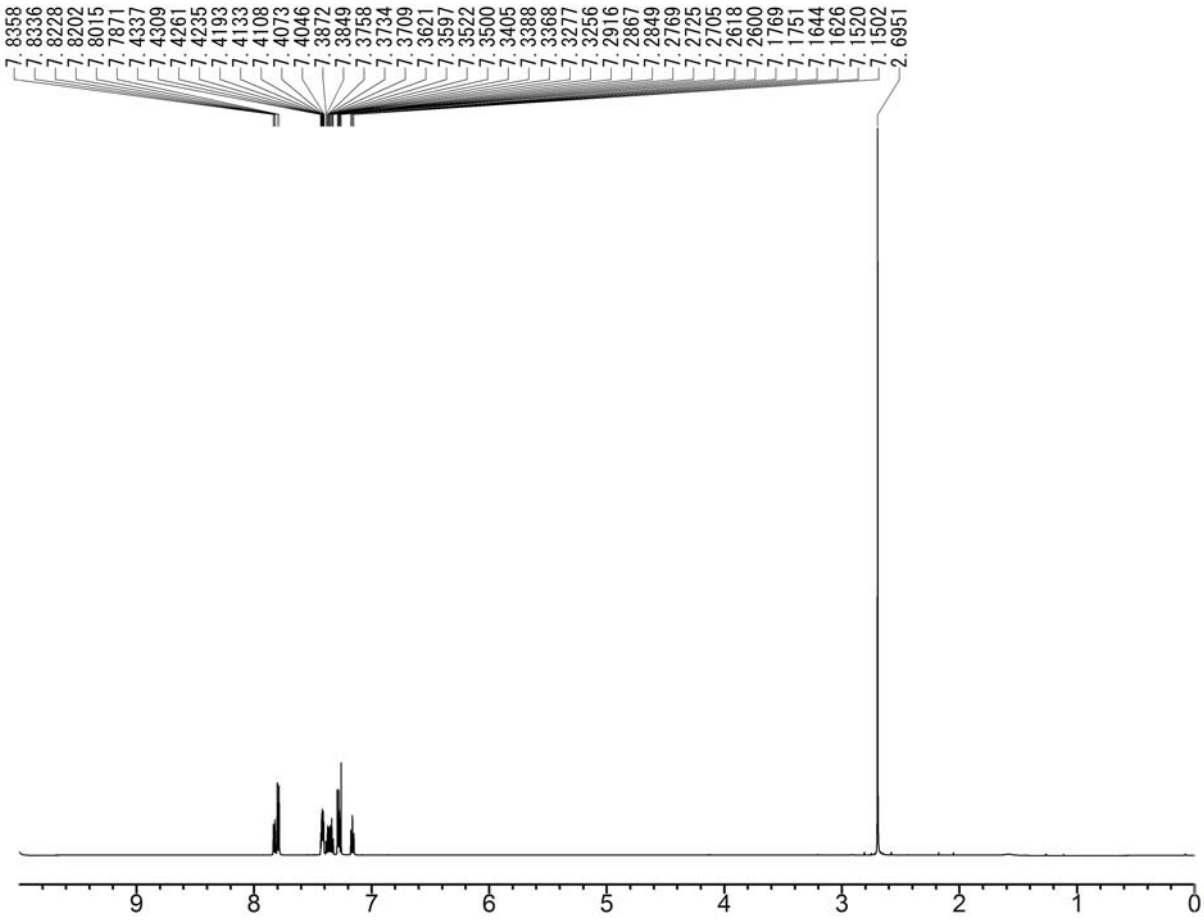
600 MHz ^{1}H NMR of **22** in $CDCl_3$.



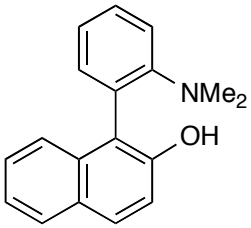
150 MHz ^{13}C NMR of **22** in $CDCl_3$.



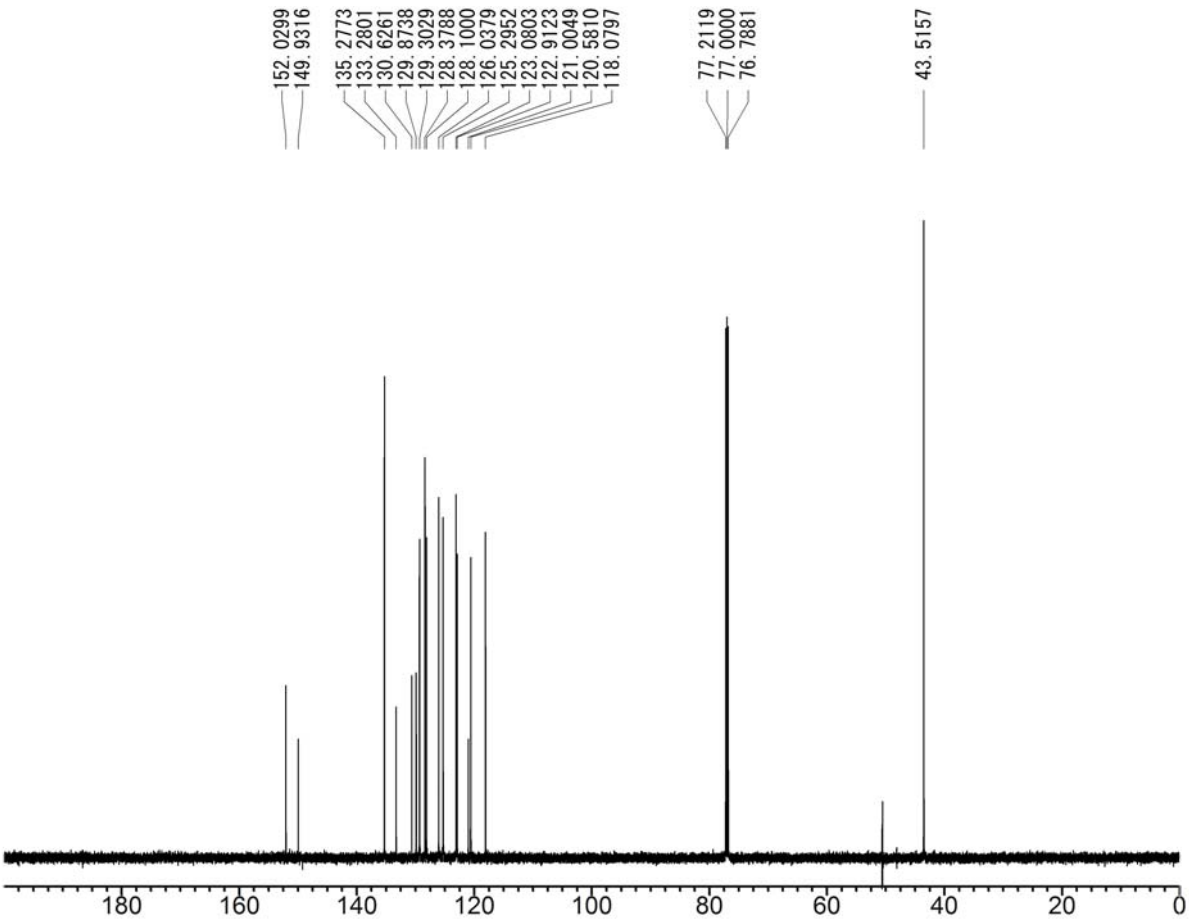
23



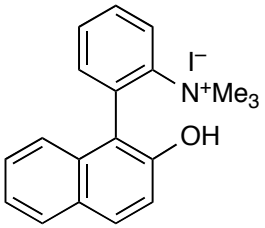
600 MHz ^{1}H NMR of **23** in $CDCl_3$.



23



150 MHz ^{13}C NMR of **23** in $CDCl_3$.



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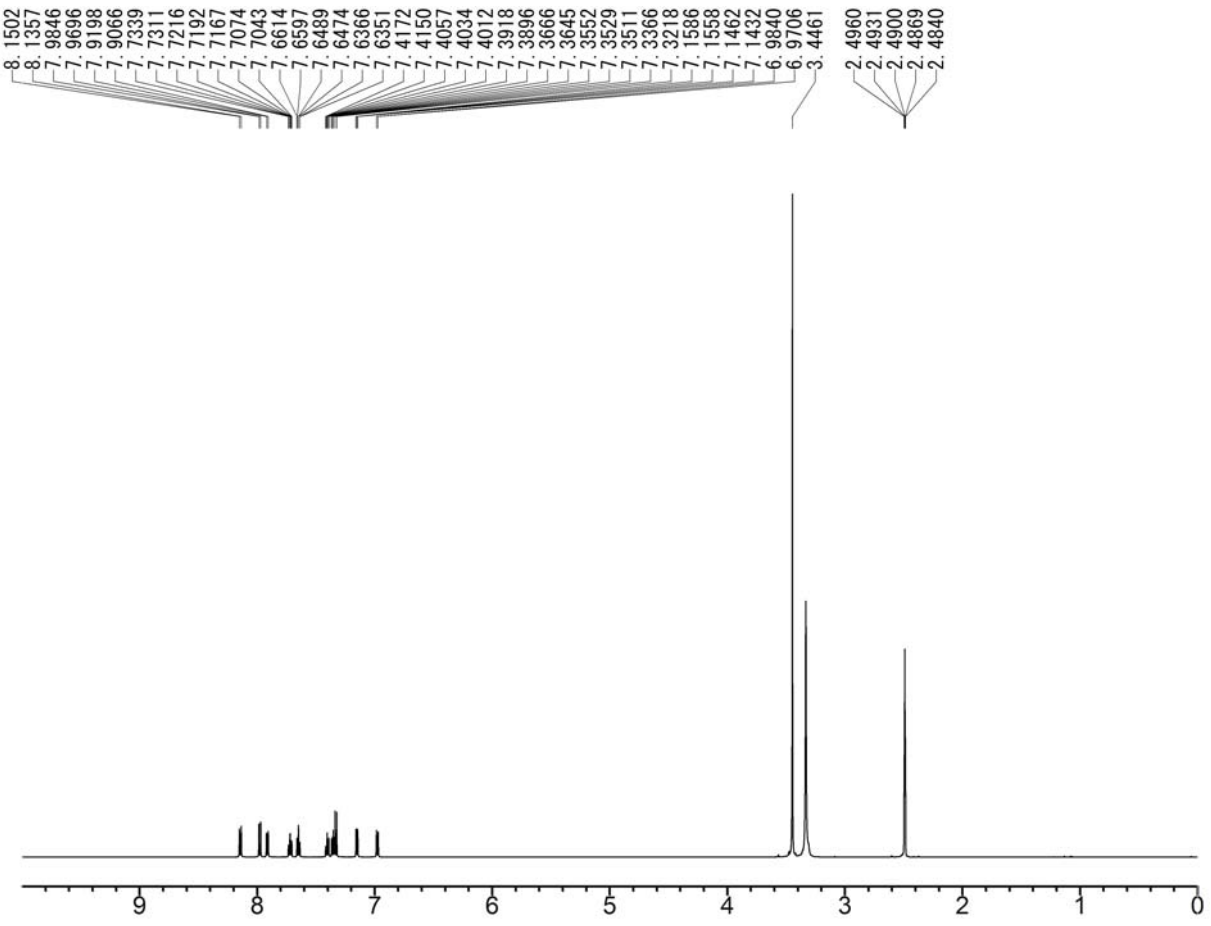
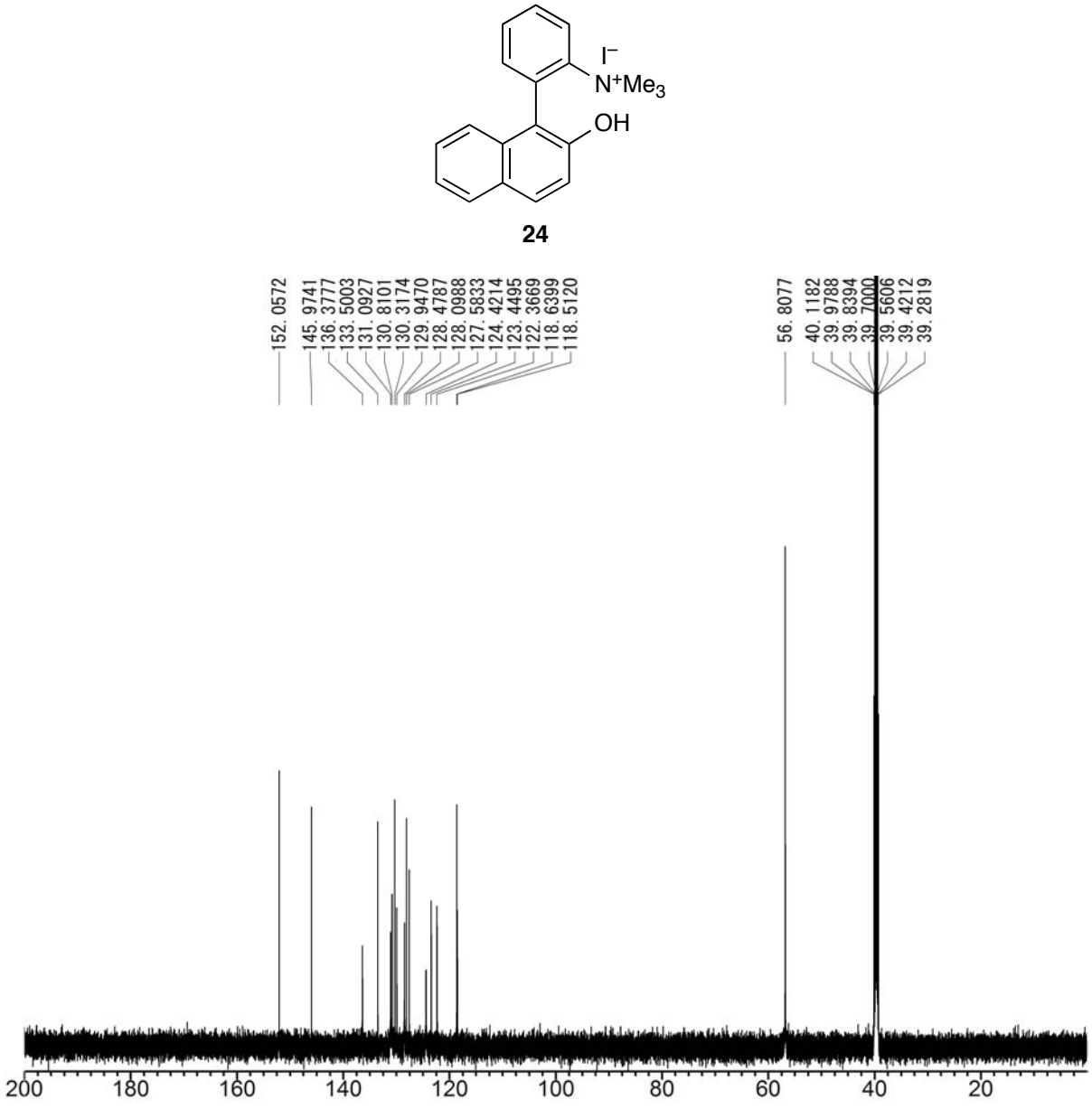
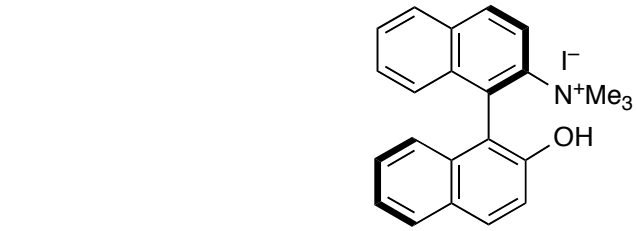


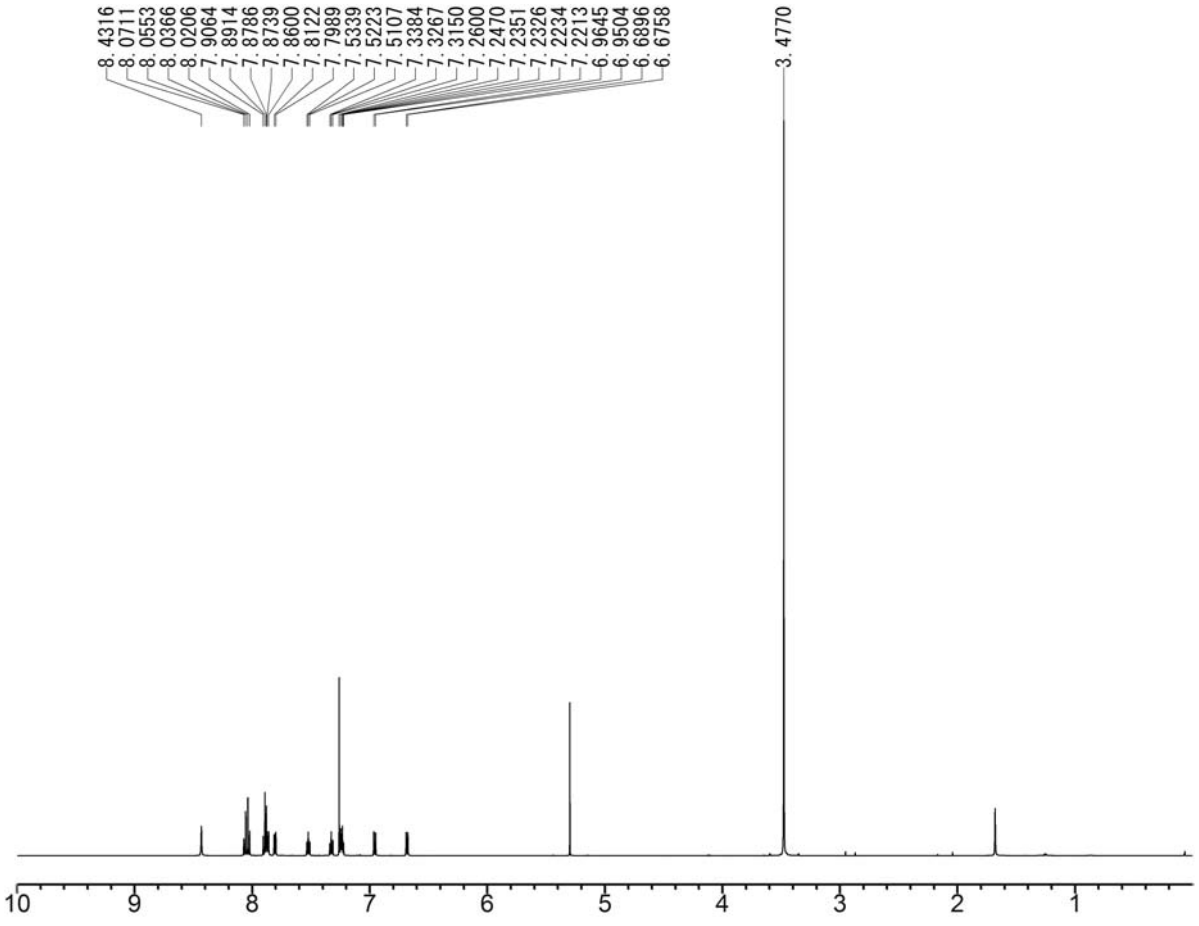
600 MHz ^{1}H NMR of **24** in DMSO-d_6.



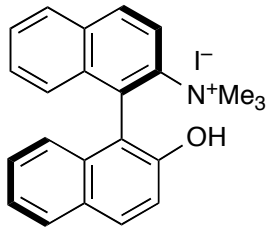
150 MHz ^{13}C NMR of **24** in DMSO-d_6.



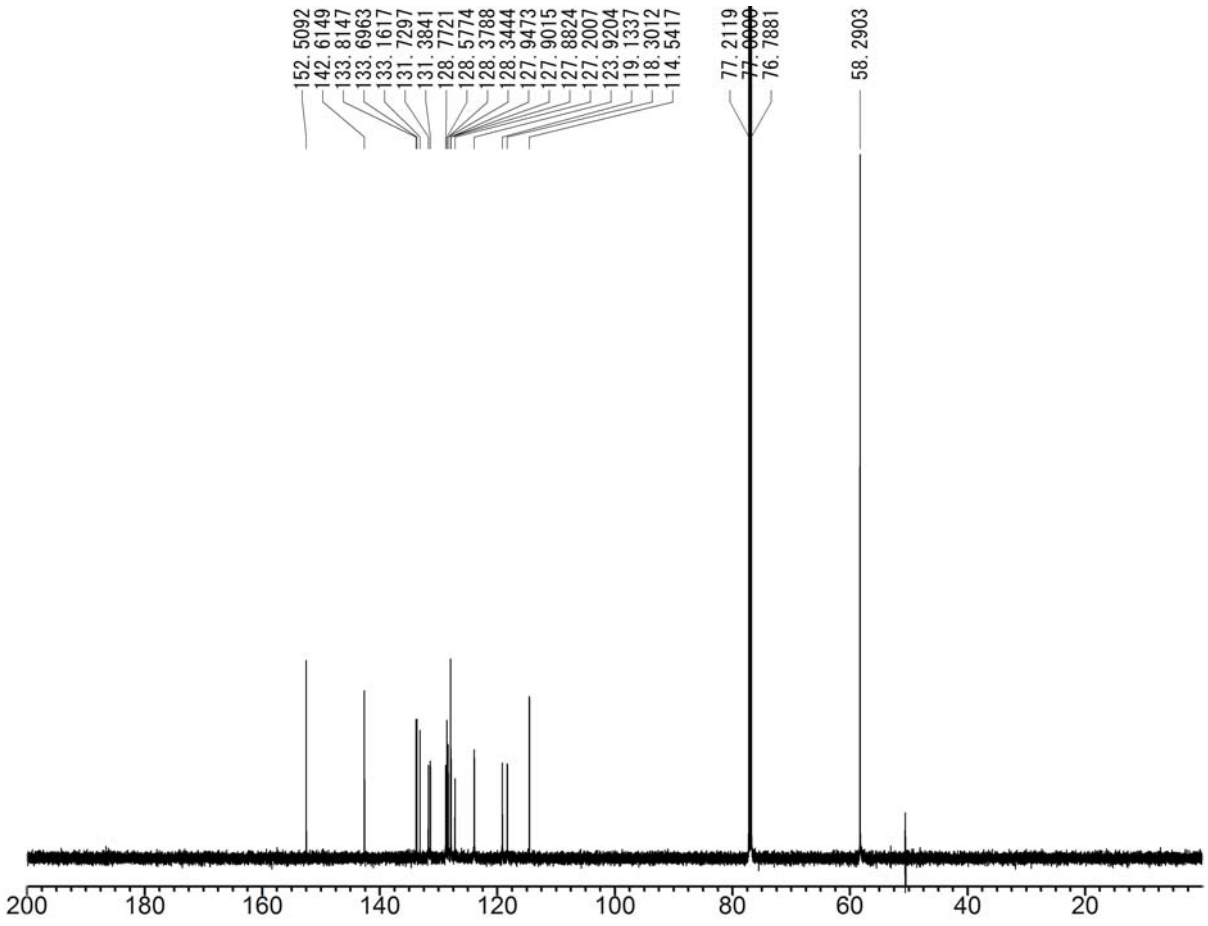
26



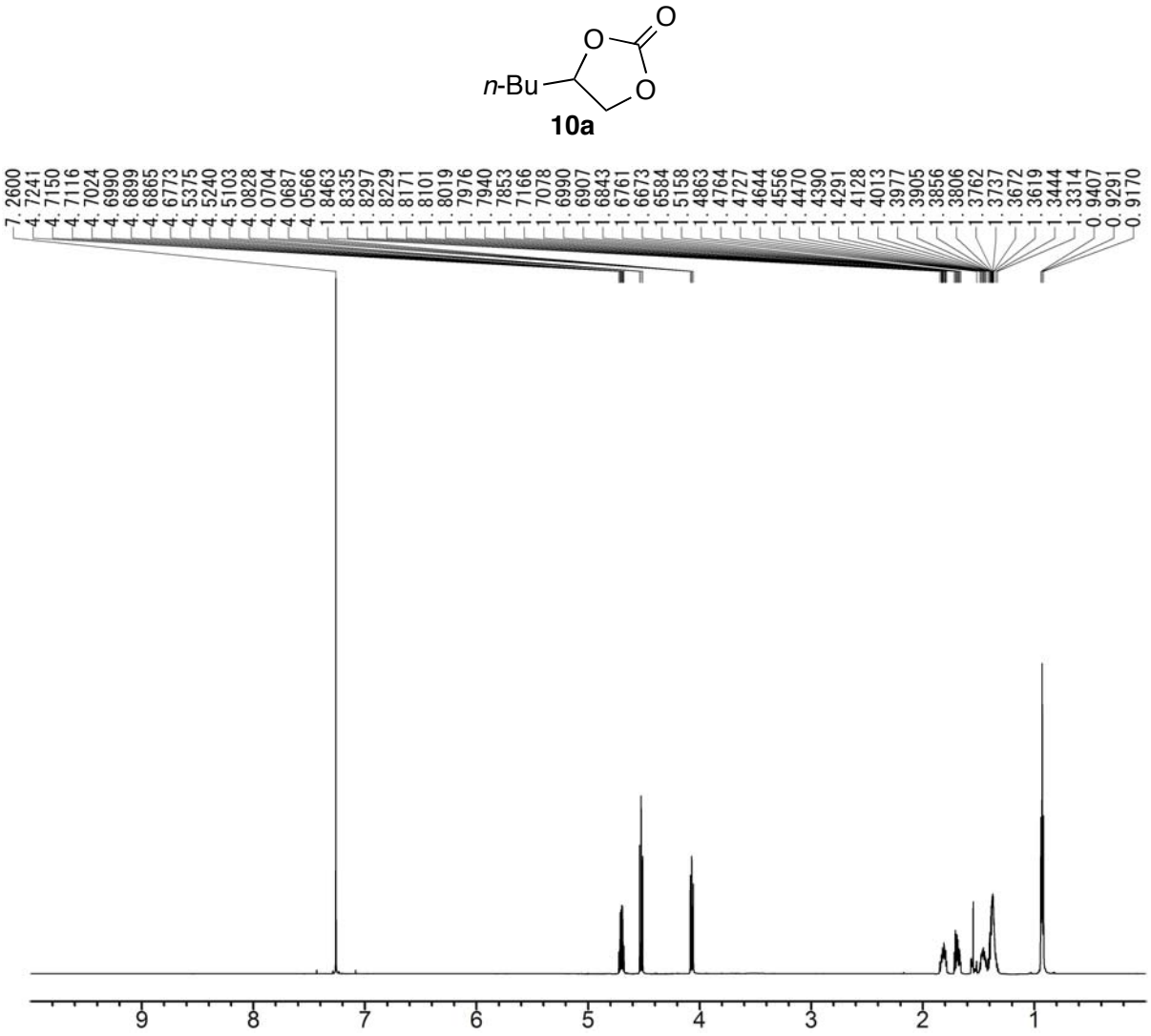
600 MHz ^{1}H NMR of **26** in $CDCl_3$.



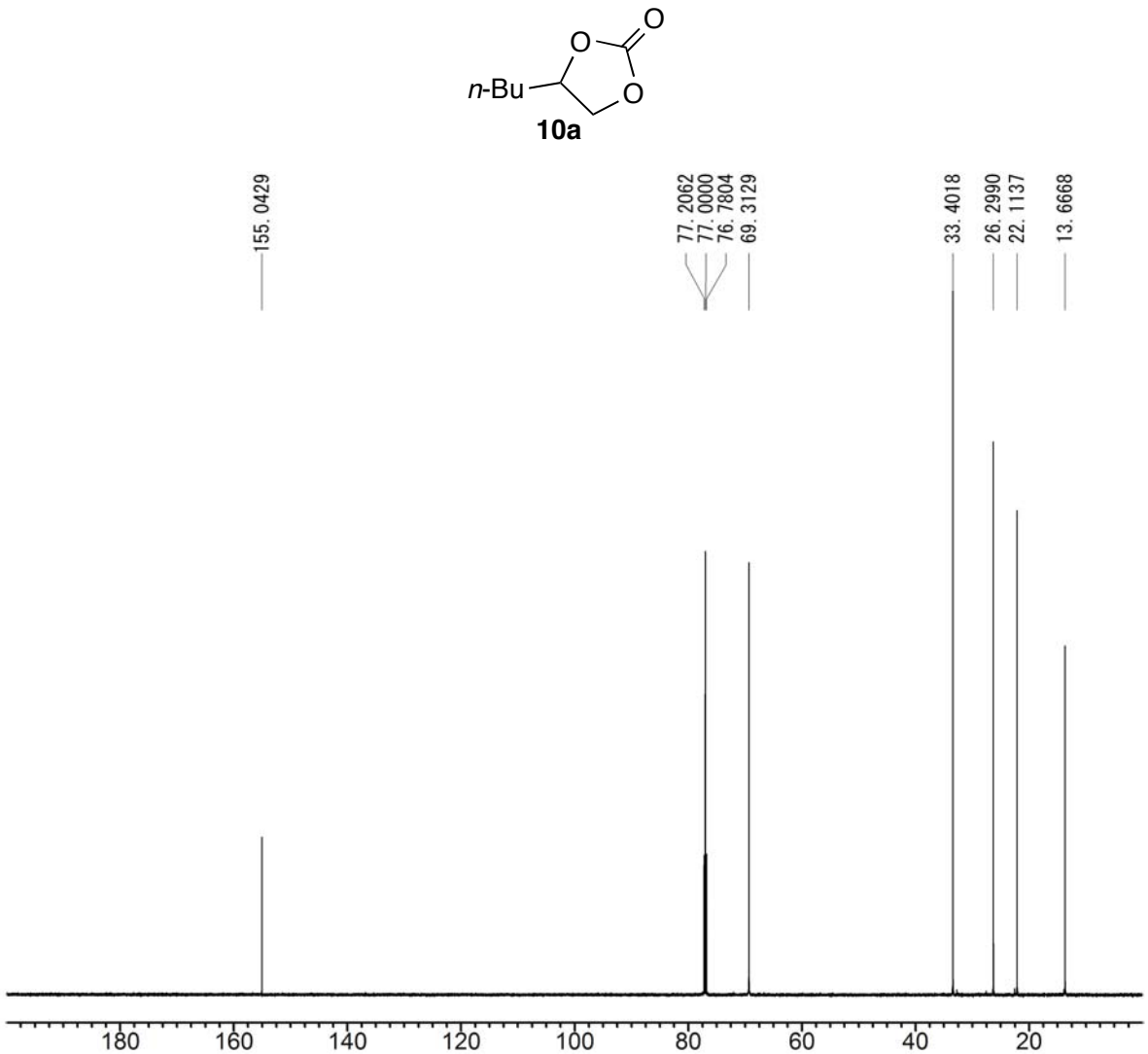
26



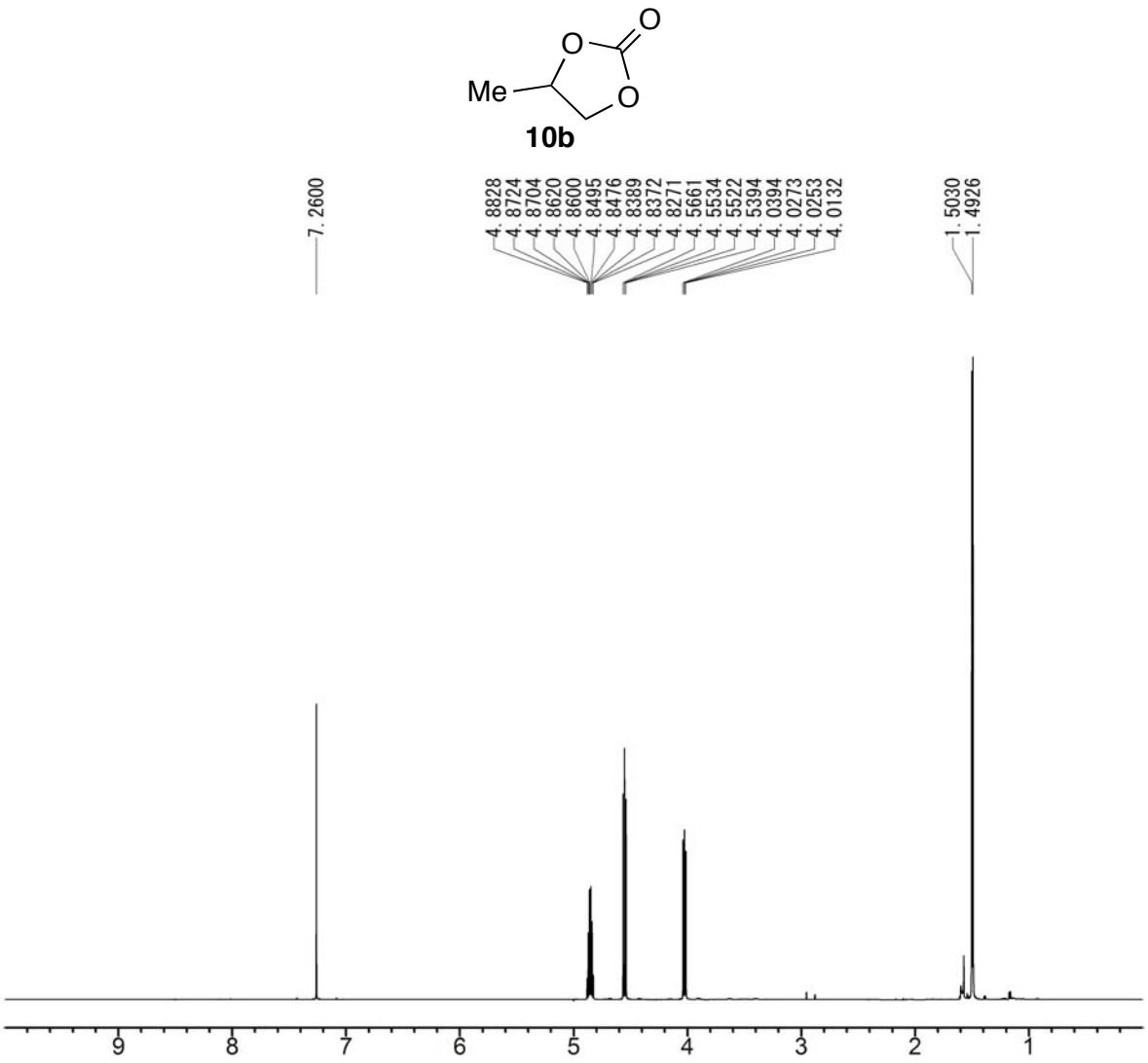
150 MHz ^{13}C NMR of **26** in $CDCl_3$.



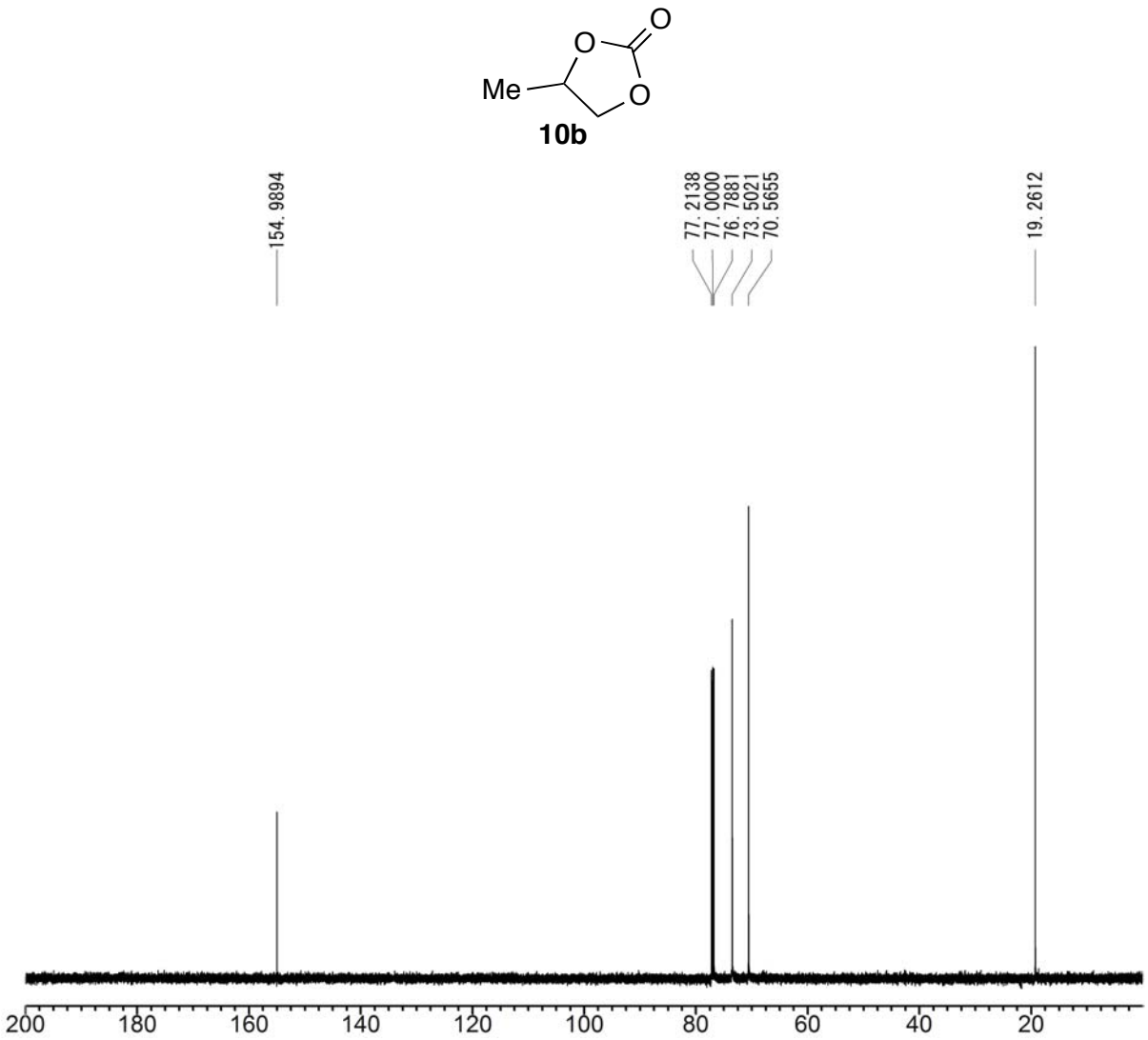
600 MHz ^{1}H NMR of **10a** in $CDCl_3$.



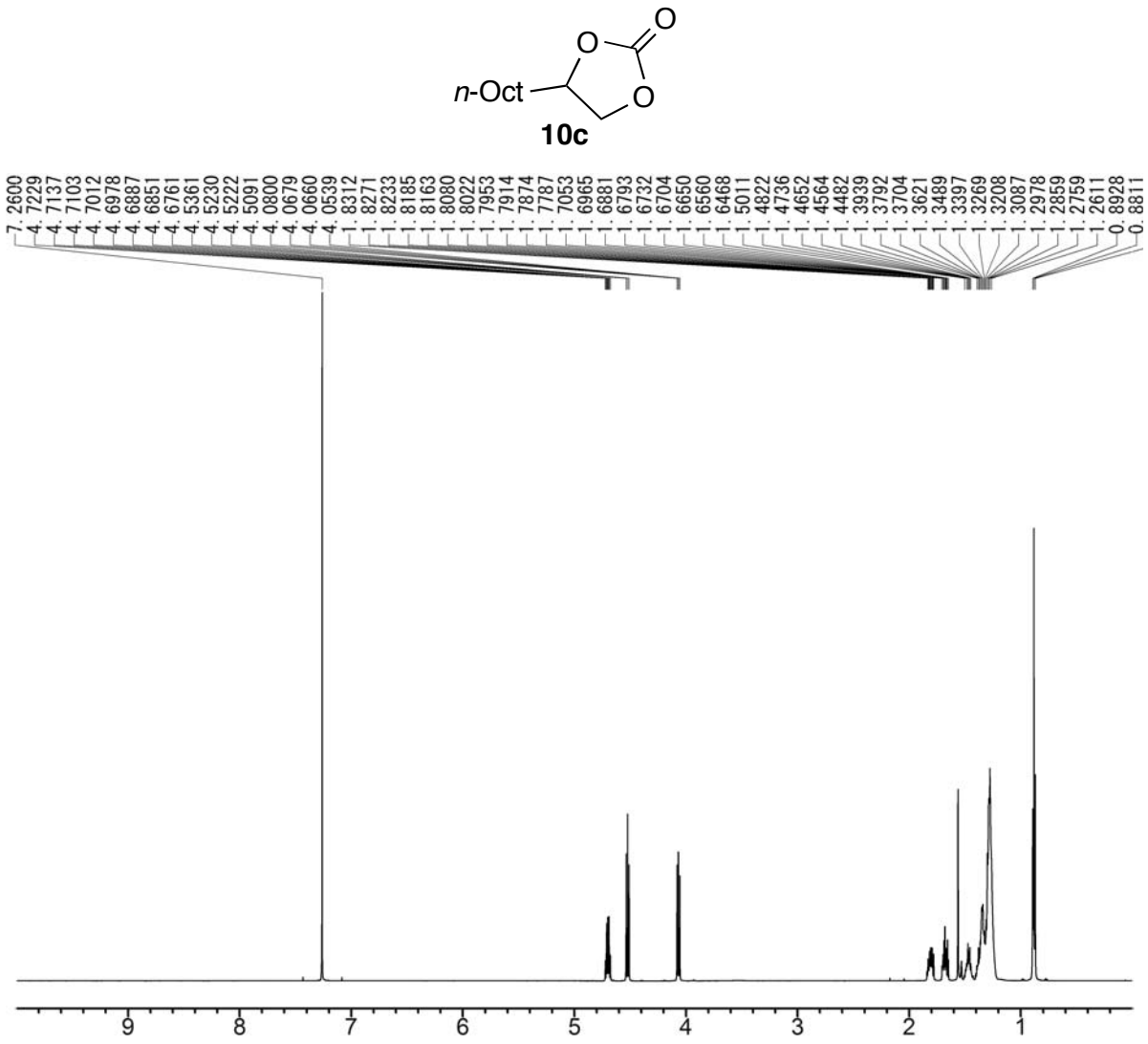
150 MHz ^{13}C NMR of **10a** in $CDCl_3$.



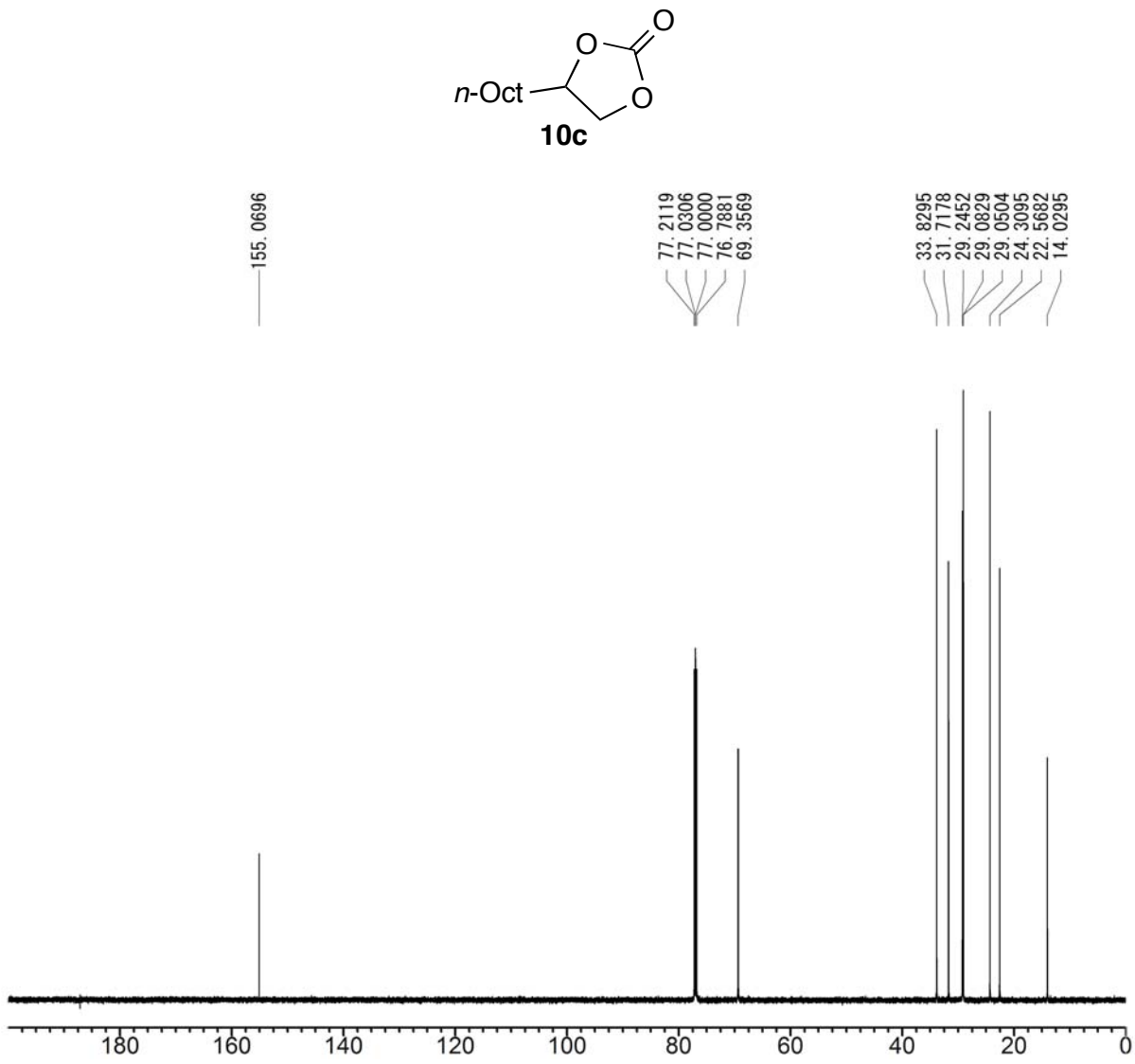
600 MHz ^{1}H NMR of **10b** in $CDCl_3$.



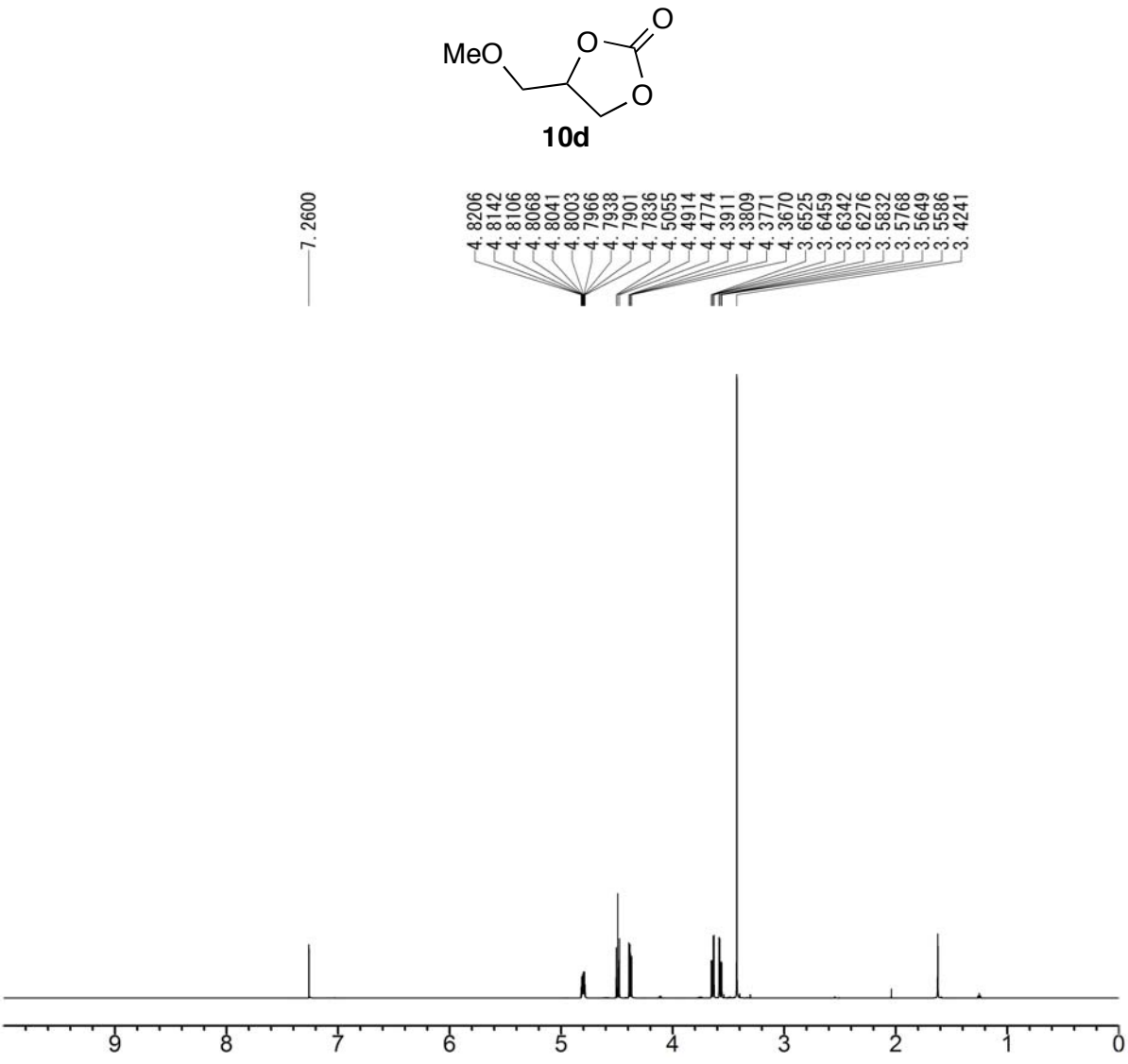
150 MHz ^{13}C NMR of **10b** in $CDCl_3$.



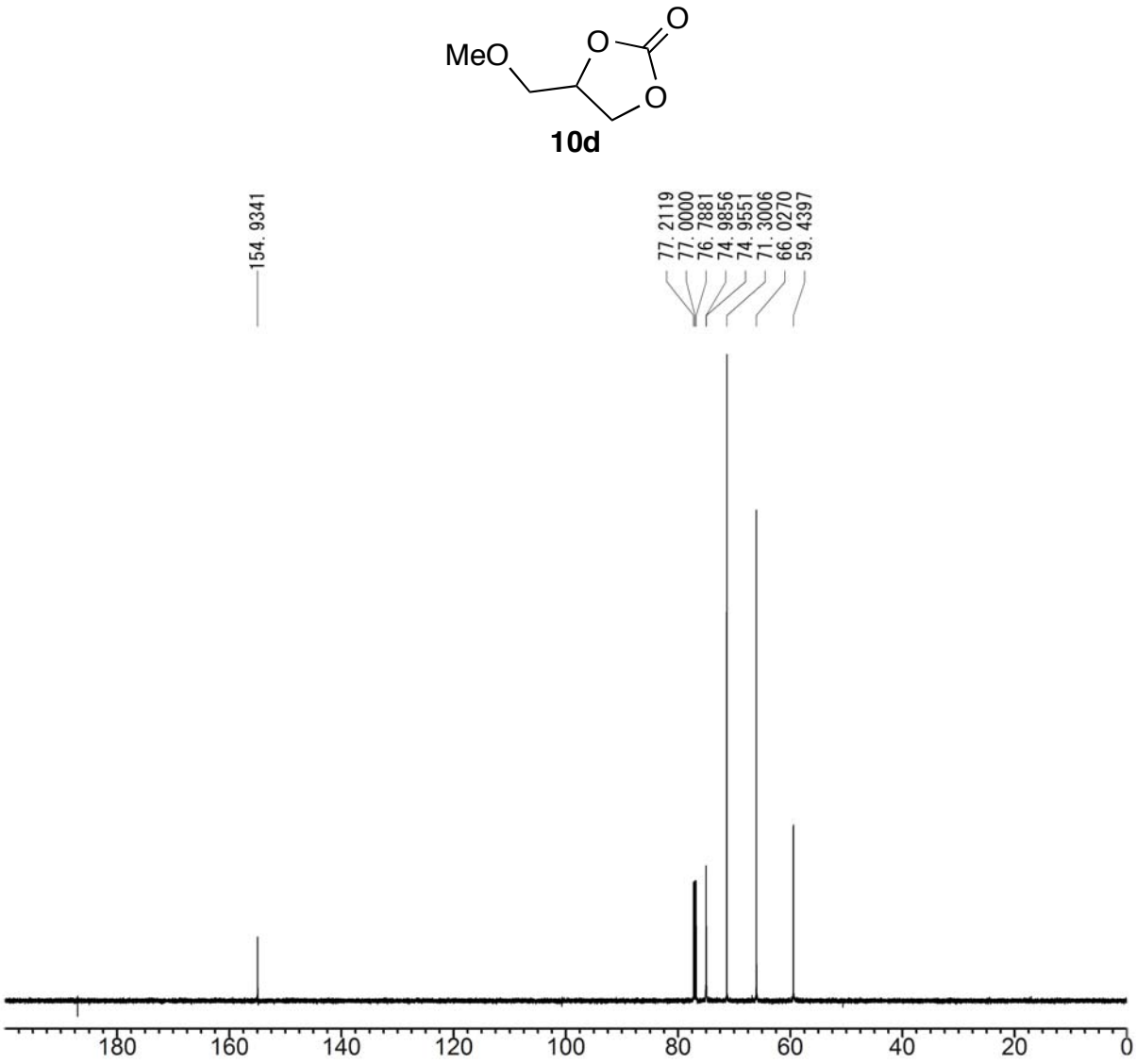
600 MHz ^{1}H NMR of **10c** in $CDCl_3$.



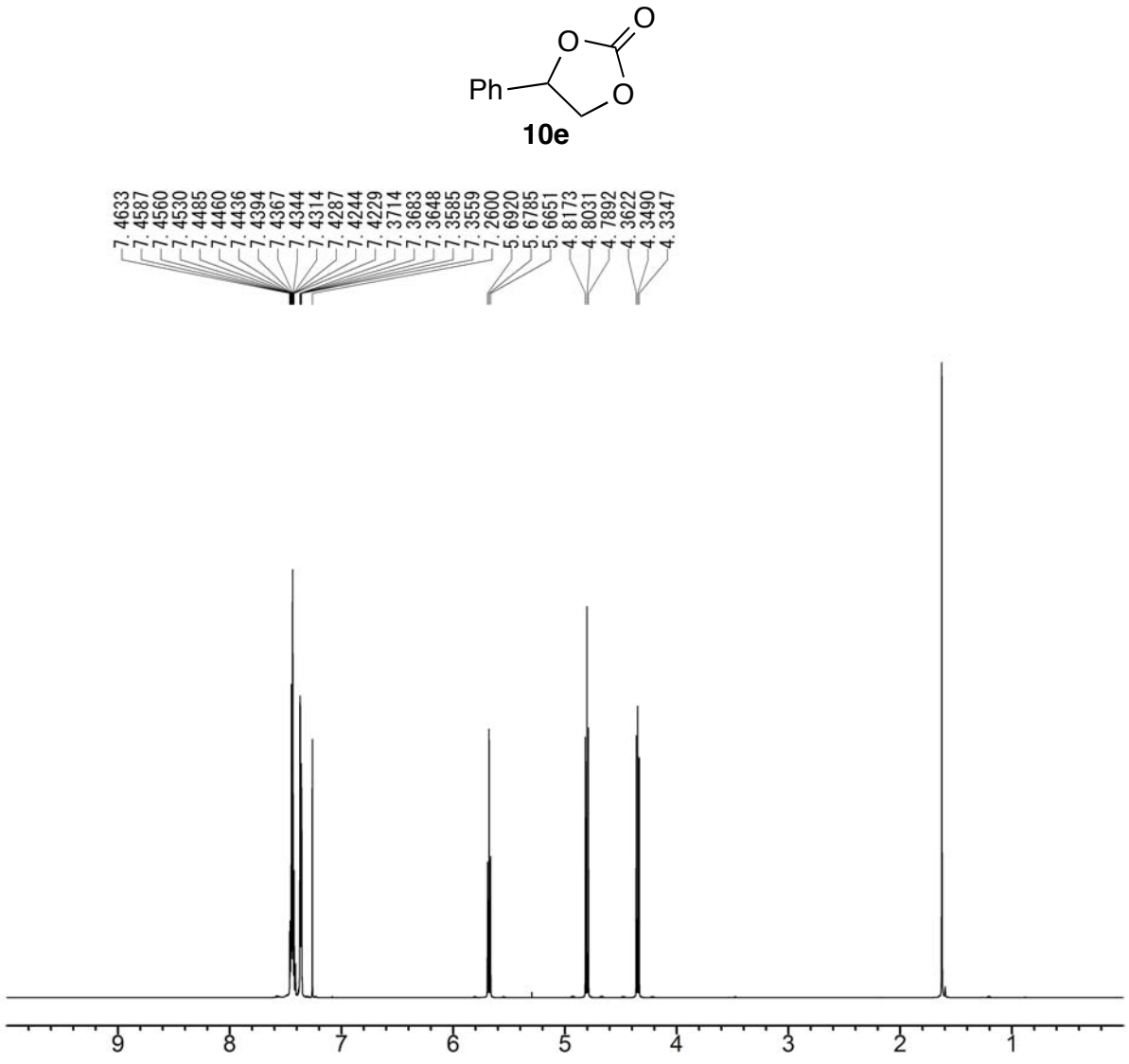
150 MHz ^{13}C NMR of **10c** in $CDCl_3$.



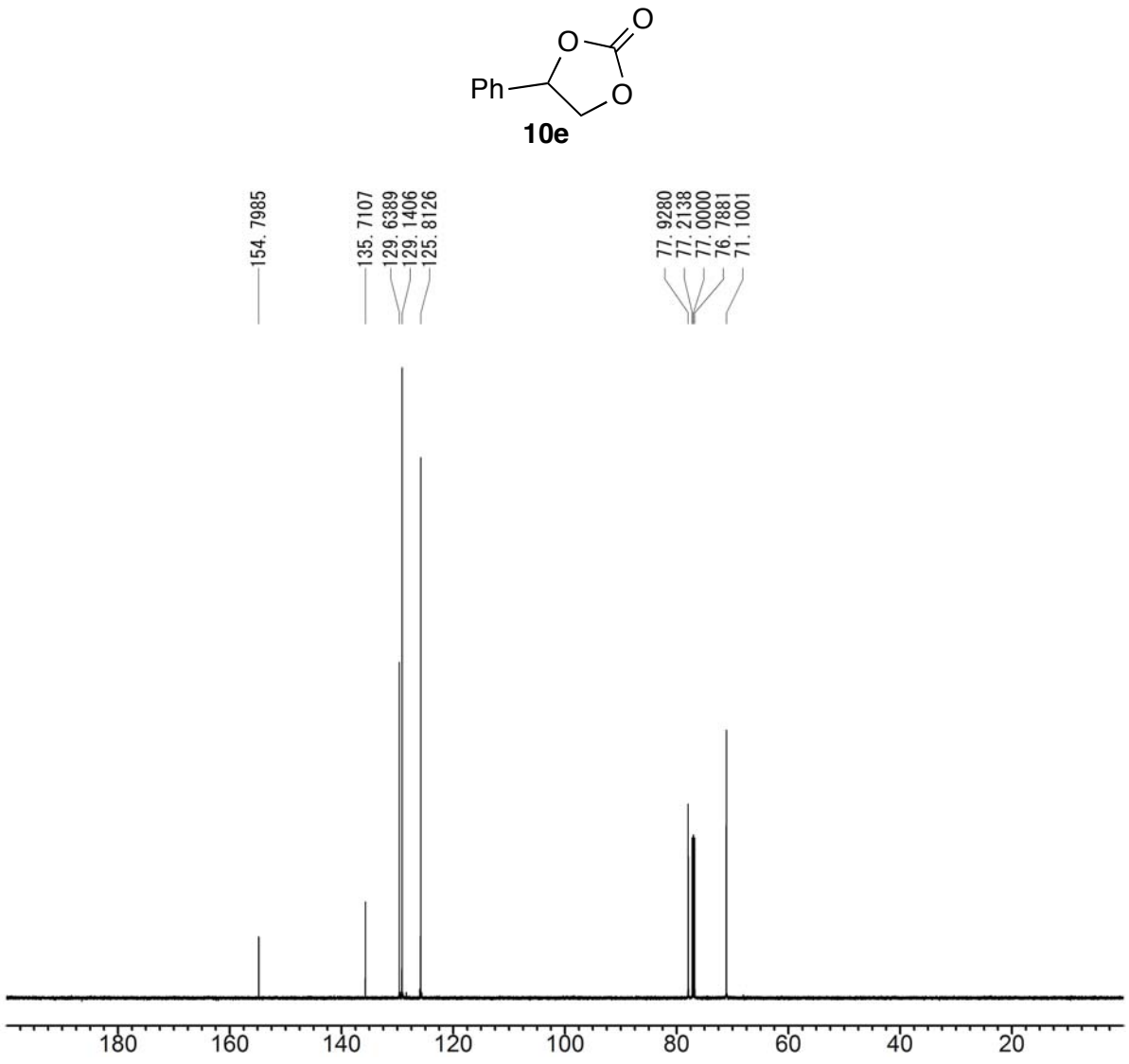
600 MHz ^{1}H NMR of **10d** in $CDCl_3$.



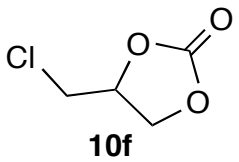
150 MHz ^{13}C NMR of **10d** in $CDCl_3$.



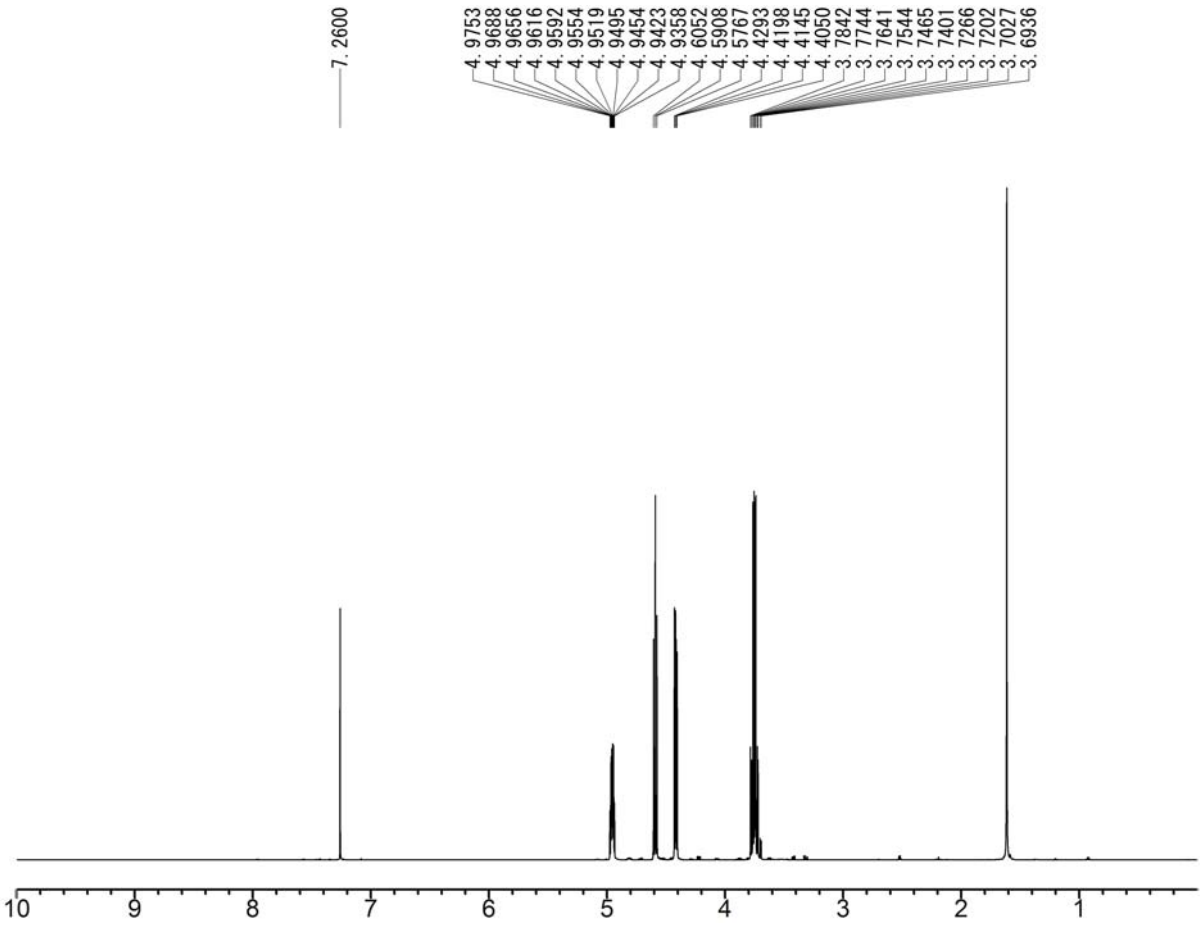
600 MHz ^{1}H NMR of **10e** in $CDCl_3$.



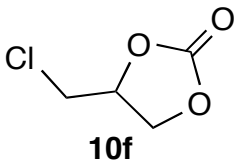
150 MHz ^{13}C NMR of **10e** in $CDCl_3$.



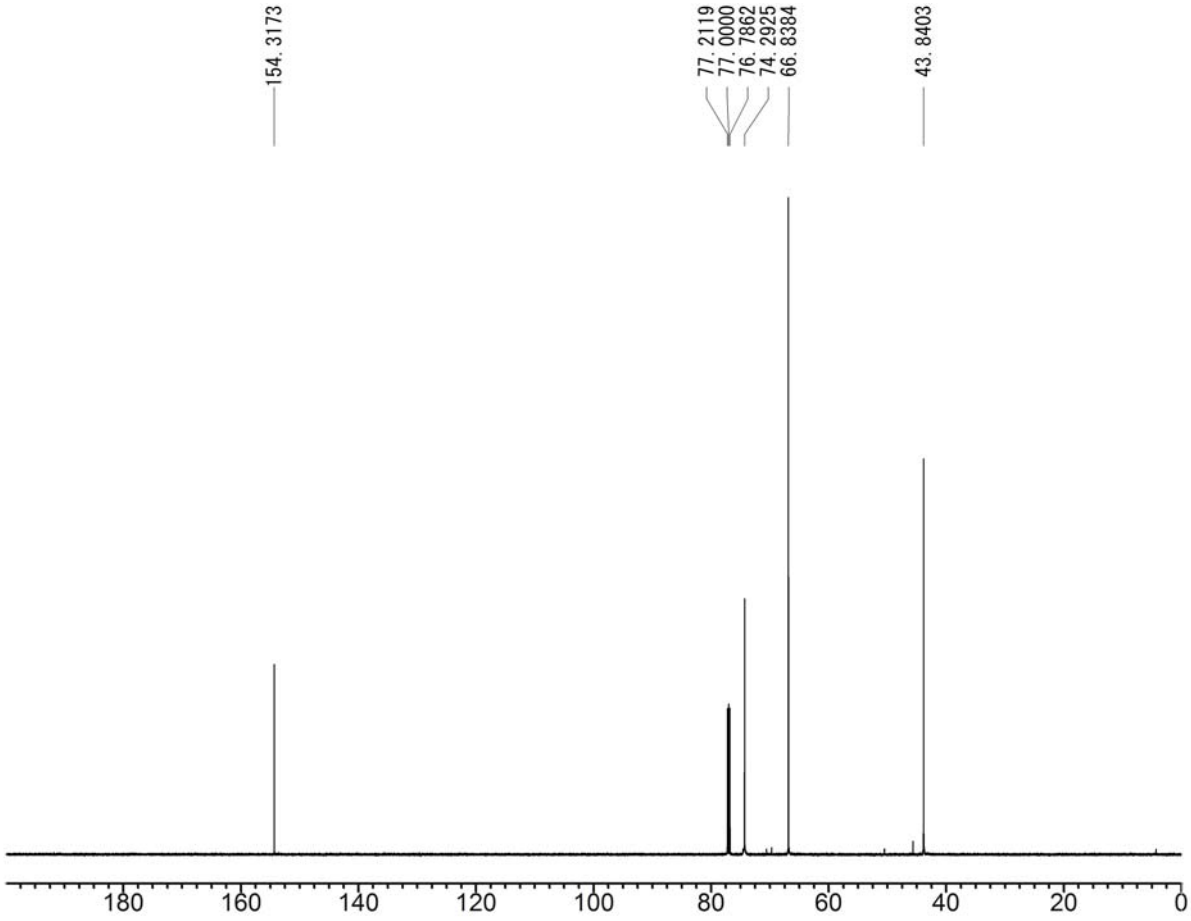
10f



600 MHz ^{1}H NMR of **10f** in $CDCl_3$.



10f



150 MHz ^{13}C NMR of **10f** in $CDCl_3$.