

# Electronic Supplementary Information

## A Facile Chemoselective Deprotection of Aryl Silyl Ethers using Sodium Hydride/DMF and *in situ* Protection of Phenol with Various Groups

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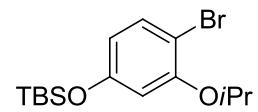
## General information

Solvents were dried by standard procedures. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with KMnO<sub>4</sub> or by using a UV lamp. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on Bruker Avance III 400 or 500 spectrometers and the chemical shifts are based on TMS peak at  $\delta = 0.00$  ppm for proton NMR and CDCl<sub>3</sub> peak at  $\delta = 77.00$  ppm (t) in carbon NMR. IR spectra were obtained on Perkin Elmer Spectrum One FT-IR spectrometer. Optical rotations were measured with Jasco P-2000 polarimeter using Sodium D line (589 nm). HRMS were recorded using Micromass: Q-Tof micro (YA-105) spectrometer.

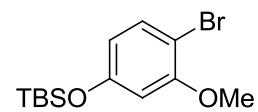
Silyl ethers were prepared from phenols\alcohols using the standard procedure (TBDMS chloride, TBDPS chloride or TES chloride, imidazole, DCM or THF). Silyl ether **4b** synthesis is reported by us.<sup>1</sup> Similarly, **4a** and **4b** were prepared. Silyl ethers **4d-p** were prepared from commercially available phenols or known compounds.<sup>2</sup> Bis-silyl ethers **6a**<sup>3</sup>, **6b**<sup>4</sup>, **6c**<sup>5</sup>, **6e**<sup>6</sup>, **6f**<sup>7</sup> **9a**<sup>8</sup> and **9b**<sup>2a</sup> are known compounds. Silyl ether **6d**<sup>9</sup> and **6i**<sup>10</sup> were prepared from known phenols. Silyl ethers **6g** and **6j** were prepared from **4c** through Dötz benzannulation reaction similar to **1** and **6h**.<sup>1</sup> The characterization data for all are given.

## Characterization data of aryl silyl ethers **4a-p**

### (4-Bromo-3-isopropoxyphenoxy)-*tert*-butyldimethylsilane (**4a**):

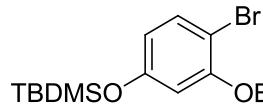
 Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta = 0.19$  (s, 6H), 1.00 (s, 9H), 1.37 (d,  $J = 6.1$  Hz, 6H), 4.45–4.51 (m, 1H), 6.34 (dd,  $J = 8.6, 2.6$  Hz, 1H), 6.42 (d,  $J = 2.6$  Hz, 1H), 7.33 (d,  $J = 8.6$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = -4.5, 18.2, 22.0, 25.6, 72.0, 105.2, 108.5, 113.7, 133.1, 155.0, 155.9$ ; HRMS *m/z* calcd for [C<sub>15</sub>H<sub>25</sub>O<sub>2</sub>SiBr + Na]<sup>+</sup> 367.0699, found 369.0682; IR (CHCl<sub>3</sub>)  $\nu = 2956, 2931, 2897, 2859, 1583, 1473, 1412, 1386, 1297, 1255, 1195, 1172, 1123, 1109, 1040, 1005, 938, 866, 838, 781, 714, 670$  cm<sup>-1</sup>.

### (4-Bromo-3-methoxyphenoxy)-*tert*-butyldimethylsilane (**4b**):

 Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta = 0.20$  (s, 6H), 0.98 (s, 9H), 3.85 (s, 3H), 6.34 (dd,  $J = 8.5, 2.6$  Hz, 1H), 6.41 (d,  $J = 2.6$  Hz, 1H), 7.33 (d,  $J = 8.5$  Hz,

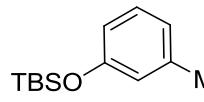
1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.5, 18.2, 25.6, 56.1, 103.0, 105.0, 113.2, 133.0, 156.2, 156.4$ ; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{21}\text{BrO}_2\text{Si} + \text{H}]^+$  317.0567, found 317.0565; IR ( $\text{CHCl}_3$ )  $\nu = 2956, 2930, 2858, 1589, 1486, 1448, 1404, 1302, 1257, 1205, 1170, 1121, 1053, 1026, 979, 841, 781, 705, 670 \text{ cm}^{-1}$ .

**3-(Benzyl)-4-bromophenoxy-*tert*-butyldimethylsilane (4c):**



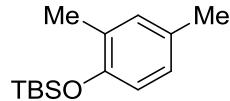
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 0.12$  (s, 6H), 0.94 (s, 9H), 5.12 (s, 2H), 6.35 (dd,  $J = 8.6, 2.6 \text{ Hz}$ , 1H), 6.42 (d,  $J = 2.6 \text{ Hz}$ , 1H), 7.29–7.47 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.6, 18.2, 25.6, 70.7, 103.8, 106.9, 113.7, 126.9, 127.9, 128.6, 133.1, 136.4, 155.4, 156.0$ ; HRMS  $m/z$  calcd for  $[\text{C}_{19}\text{H}_{25}\text{BrO}_2\text{Si} + \text{Na}]^+$  415.0699, found 415.0698; IR ( $\text{CHCl}_3$ )  $\nu = 2956, 2931, 2886, 2859, 1583, 1484, 1471, 1414, 1380, 1300, 1256, 1182, 1121, 1048, 1018, 989, 908, 842, 782, 736 \text{ cm}^{-1}$ .

***tert*-Butyldimethyl(*m*-tolyloxy)silane (4d):**



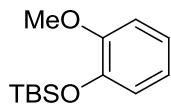
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 0.22$  (s, 6H), 1.02 (s, 9H), 2.32 (s, 3H), 6.67–6.69 (m, 2H), 6.79 (d,  $J = 7.5 \text{ Hz}$ , 1H), 7.13 (t,  $J = 7.7 \text{ Hz}$ , 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.4, 18.2, 21.4, 25.7, 117.0, 120.9, 122.1, 129.0, 139.4, 155.5$ ; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{22}\text{OSi} + \text{H}]^+$  223.1513, found 223.1513; IR ( $\text{CHCl}_3$ )  $\nu = 2951, 2934, 2851, 2837, 1658, 1607, 1585, 1487, 1465, 1280, 1253, 1159, 1024, 956, 840, 776, 691 \text{ cm}^{-1}$ .

***tert*-Butyl(2,4-dimethylphenoxy)dimethylsilane (4e):**



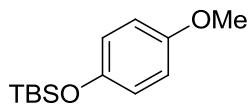
Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 0.21$  (s, 6H), 1.02 (s, 9H), 2.18 (s, 3H), 2.26 (s, 3H), 6.67 (d,  $J = 8.1 \text{ Hz}$ , 1H), 6.86 (d,  $J = 8.1 \text{ Hz}$ , 1H), 6.95 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = -4.3, 16.8, 18.2, 20.5, 25.8, 118.3, 126.9, 128.5, 130.1, 131.6, 151.5$ ; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{24}\text{Osi} + \text{H}]^+$  237.1669, found 237.1669; IR ( $\text{CHCl}_3$ ):  $\nu = 2958, 2930, 2896, 2859, 1614, 1504, 1473, 1269, 1228, 1150, 1130, 944, 897, 840, 799, 779, 691 \text{ cm}^{-1}$ .

***tert*-Butyl(2-methoxyphenoxy)dimethylsilane (4f):**



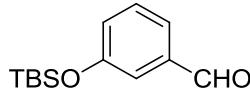
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.17 (s, 6H), 1.01 (s, 9H), 3.81 (s, 3H), 6.81–6.94 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.7, 18.4, 25.7, 55.4, 112.1, 120.9, 121.0, 121.7, 145.0, 151.0; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si} + \text{Na}]^+$  261.1281, found 261.1288; IR ( $\text{CHCl}_3$ )  $\nu$  = 3065, 3040, 2954, 2930, 2896, 2858, 1593, 1504, 1471, 1456, 1439, 1281, 1266, 1225, 1179, 1114, 1045, 1034, 922, 838, 826, 811, 783, 745, 702, 660  $\text{cm}^{-1}$ .

***tert*-Butyl(4-methoxyphenoxy)dimethylsilane (4g):**



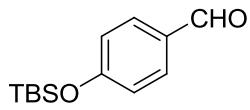
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.18 (s, 6H), 1.0 (s, 9H), 3.76 (s, 3H), 6.77 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.5, 18.2, 25.7, 55.6, 114.4, 120.6, 149.3, 154.0; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si} + \text{K}]^+$  277.1021, found 277.1024; IR ( $\text{CHCl}_3$ )  $\nu$  = 3043, 2997, 2922, 2931, 2897, 2859, 2834, 1507, 1471, 1442, 1255, 1235, 1180, 1099, 1041, 1007, 932, 830, 812, 780, 689  $\text{cm}^{-1}$ .

**3-(*tert*-Butyldimethylsilyloxy)benzaldehyde (4h):**



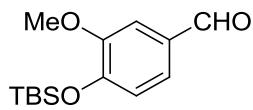
Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta$  = 0.23 (s, 6H), 1.00 (s, 9H), 7.10–7.12 (m, 1H), 7.33 (dd,  $J$  = 2.4, 1.5 Hz, 1H), 7.40 (t,  $J$  = 7.8 Hz, 1H), 7.48 (dt,  $J$  = 7.1, 1.3 Hz, 1H), 9.95 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = −4.5, 18.2, 25.6, 119.9, 123.5, 126.5, 130.1, 137.9, 156.4, 192.1; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si} + \text{Na}]^+$  259.1125, found 259.1123; IR ( $\text{CHCl}_3$ )  $\nu$  = 3003, 2943, 2862, 1696, 1637, 1599, 1443, 1376, 1274, 1158, 1039, 918, 846, 705  $\text{cm}^{-1}$ .

**4-(*tert*-Butyldimethylsilyloxy)benzaldehyde (4i):**



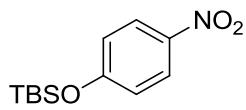
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.25 (s, 6H), 0.99 (s, 9H), 6.94 (d,  $J$  = 8.6 Hz, 2H), 7.79 (d,  $J$  = 8.6 Hz, 2H), 9.88 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.4, 18.2, 25.5, 120.5, 130.4, 131.9, 161.5, 190.9; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si} + \text{Na}]^+$  259.1125, found 259.1126; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2931, 2857, 1702, 1600, 1509, 1471, 1276, 1157, 1046, 1021, 910, 840, 702, 670  $\text{cm}^{-1}$ .

**4-(*tert*-Butyldimethylsilyloxy)-3-methoxybenzaldehyde (**4j**):**



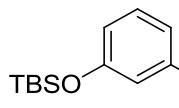
Colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.19 (s, 6H), 0.99 (s, 9H), 3.87 (s, 3H), 6.96 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 7.36 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 7.40 (d,  $J$  = 1.9 Hz, 1H), 9.83 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.6, 18.5, 25.6, 55.4, 110.0, 120.7, 126.3, 130.9, 151.3, 151.6, 190.1; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{22}\text{O}_3\text{Si} + \text{Na}]^+$  289.1230, found 289.1229; IR ( $\text{CHCl}_3$ )  $\nu$  = 3069, 3002, 2932, 2886, 2858, 2737, 1699, 1594, 1509, 1465, 1422, 1391, 1292, 1257, 1236, 1152, 1123, 1034, 1007, 960, 937, 901, 869, 841, 824, 809, 784, 730, 707, 667  $\text{cm}^{-1}$ .

***tert*-Butyldimethyl(4-nitrophenoxy)silane (**4k**):**



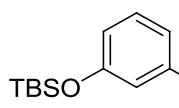
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.26 (s, 6H), 0.99 (s, 9H), 6.89 (dd,  $J$  = 7.0, 2.1 Hz, 2H), 8.15 (dd,  $J$  = 7.1, 2.1 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.4, 18.2, 25.5, 120.1, 125.8, 141.9, 161.7; HRMS  $m/z$  calcd for  $[\text{C}_{12}\text{H}_{19}\text{O}_2\text{NSi} + \text{K}]^+$  276.0817, found 276.0814; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2932, 2887, 2860, 1603, 1591, 1514, 1496, 1472, 1343, 1283, 1164, 1111, 1006, 908, 854, 841, 822, 805, 784, 724, 692, 674  $\text{cm}^{-1}$ .

**3-(*tert*-Butyldimethylsilyloxy)phenyl acetate (**4l**)<sup>2a</sup>:**



Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.20 (s, 6H), 0.98 (s, 9H), 2.27 (s, 3H), 6.58 (t,  $J$  = 2.2 Hz, 1H), 6.59–6.71 (m, 2H), 7.20 (t,  $J$  = 8.2 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.5, 18.1, 21.1, 25.6, 113.7, 114.4, 117.5, 129.6, 151.4, 156.5, 169.2; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{22}\text{O}_3\text{Si} + \text{Na}]^+$  289.1230, found 289.1227; IR ( $\text{CHCl}_3$ )  $\nu$  = 2957, 2932, 2898, 2859, 1769, 1603, 1588, 1486, 1473, 1443, 1369, 1283, 1258, 1209, 1161, 1136, 1005, 980, 911, 865, 837, 782  $\text{cm}^{-1}$ .

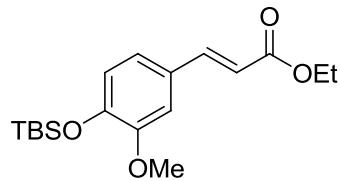
***tert*-butyl[3-(methoxymethoxy)phenoxy]dimethylsilane (**4m**)<sup>2b</sup>:**



Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.20 (s, 6H), 0.98 (s, 9H), 3.47 (s, 3H), 5.14 (s, 2H), 6.50 (dd,  $J$  = 8.1, 2.6 Hz, 1H), 6.55 (t,  $J$  = 2.3 Hz, 1H), 6.65 (ddd,  $J$  = 8.3, 2.3, 0.7 Hz, 1H), 7.11 (t,  $J$  = 8.2 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.5, 18.2, 25.7, 55.9, 94.4, 108.6, 109.0, 113.7, 129.7, 156.7, 158.3; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si}]^+$

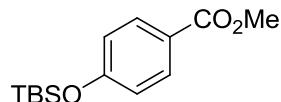
$\text{Na}^+$  291.1387, found 291.1380; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2931, 2858, 1646, 1599, 1487, 1472, 1281, 1266, 1144, 1075, 1020, 841, 740  $\text{cm}^{-1}$ .

**(E)-Ethyl 3-[4-(tert-butyldimethylsilyloxy)-3-methoxyphenyl]acrylate (4n)<sup>2c</sup>:**



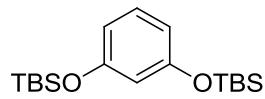
Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.17 (s, 6H), 1.00 (s, 9H), 1.34 (t,  $J$  = 7.1 Hz, 3H), 3.83 (s, 3H), 4.25 (q,  $J$  = 7.1 Hz, 2H), 6.30 (d,  $J$  = 15.9 Hz, 1H), 6.84 (d,  $J$  = 8.7 Hz, 1H), 7.01–7.02 (m, 2H), 7.61 (d,  $J$  = 15.9 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.6, 14.3, 18.5, 25.6, 55.4, 60.3, 110.7, 115.9, 121.0, 122.2, 128.3, 144.7, 147.4, 151.1, 167.3; HRMS  $m/z$  calcd for  $[\text{C}_{18}\text{H}_{28}\text{O}_4\text{Si} + \text{Na}]^+$  359.1649, found 359.1646; IR ( $\text{CHCl}_3$ )  $\nu$  = 2955, 2930, 2898, 1713, 1635, 1597, 1512, 1465, 1419, 1367, 1285, 1264, 1175, 1160, 1127, 1039, 908, 842, 822, 784, 691  $\text{cm}^{-1}$ .

**Methyl 4-(tert-butyldimethylsilyloxy)benzoate (4o)<sup>2d</sup>:**



Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.22 (s, 6H), 0.98 (s, 9H), 3.88 (s, 3H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 7.94 (d,  $J$  = 8.8 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.4, 18.2, 25.6, 51.8, 119.8, 123.2, 131.5, 160.0, 166.9; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{22}\text{O}_3\text{Si} + \text{Na}]^+$  289.1230, found 289.1233; IR ( $\text{CHCl}_3$ )  $\nu$  = 2955, 2931, 2860, 1723, 1604, 1509, 1464, 1435, 1272, 1217, 1163, 1113, 1098, 1014, 911, 857, 839, 803, 774, 699  $\text{cm}^{-1}$ .

**1,3-Bis(tert-butyldimethylsilyloxy)benzene (4p):**

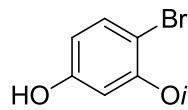


Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.20 (s, 12H), 1.0 (s, 18H), 6.35 (t,  $J$  = 2.2 Hz, 1H), 6.47 (dd,  $J$  = 8.1, 2.2 Hz, 2H), 7.07 (t,  $J$  = 8.1 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.4, 18.2, 25.7, 112.3, 113.4, 129.5, 156.6; HRMS  $m/z$  calcd for  $[\text{C}_{18}\text{H}_{34}\text{O}_2\text{Si}_2 + \text{Na}]^+$  361.1990, found 361.1991; IR ( $\text{CHCl}_3$ )  $\nu$  = 2957, 2931, 2896, 2859, 1587, 1479, 1438, 1298, 1259, 1175, 1146, 995, 901, 832, 781, 689, 668  $\text{cm}^{-1}$ .

**General Procedure for aryl silyl ether deprotection:** To a stirred solution of aryl silyl ether **4/6/9a/9b** (0.1 mmol, 1.0 equiv) in dry DMF (3 mL) was added sodium hydride

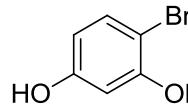
(0.15 mmol, 1.5 equiv) at room temperature and stirred for specified time. After completion of reaction (monitored by TLC) it was quenched with water (1 mL) and diluted with EtOAc (10 mL). The organic layer was separated, washed with water ( $3 \times 5$  mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as eluent to give the phenol **5/7/10a/10c**.

**4-Bromo-3-*iso*-propoxyphenol (5a):**



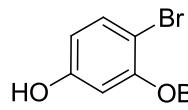
Colorless oil; yield 100%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 1.36 (d,  $J$  = 6.1 Hz, 6H), 4.45–4.50 (m, 1H), 5.30 (s, 1H, *OH*), 6.32 (dd,  $J$  = 8.9, 2.7 Hz, 1H), 6.45 (d,  $J$  = 2.7 Hz, 1H), 7.33 (d,  $J$  = 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 22.0, 72.3, 103.7, 104.2, 108.9, 133.4, 155.3, 155.9; HRMS  $m/z$  calcd for  $[\text{C}_9\text{H}_{11}\text{O}_2\text{Br} + \text{Na}]^+$  252.9835 found 252.9837; IR ( $\text{CHCl}_3$ )  $\nu$  = 3390, 2979, 2930, 1585, 1483, 1454, 1385, 1374, 1294, 1265, 1189, 1130, 1107, 1037, 998, 919, 834, 799, 623  $\text{cm}^{-1}$ .

**4-Bromo-3-methoxyphenol (5b):**



White solid; yield 93%; mp = 74–76 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 3.84 (s, 3H), 5.68 (s, 1H, *OH*), 6.34 (dd,  $J$  = 8.5, 2.7 Hz, 1H), 6.45 (d,  $J$  = 2.7 Hz, 1H), 7.33 (d,  $J$  = 8.5 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 56.1, 100.5, 102.1, 108.6, 133.3, 156.1, 156.6; HRMS  $m/z$  calcd for  $[\text{C}_7\text{H}_7\text{BrO}_2 + \text{Na}]^+$  224.9522, found 224.9523; IR ( $\text{CHCl}_3$ )  $\nu$  = 3462, 3010, 2943, 1607, 1590, 1487, 1468, 1450, 1430, 1297, 1267, 1199, 1168, 1128, 1047, 1024, 951, 830, 797, 625  $\text{cm}^{-1}$ .

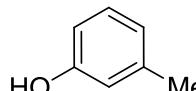
**3-(Benzylxy)-4-bromophenol (5c):**



Colorless oil; yield 92%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 5.06 (s, 2H), 5.54 (s, 1H, *OH*), 6.32 (dd,  $J$  = 8.5, 2.7 Hz, 1H), 6.45 (d,  $J$  = 2.7 Hz, 1H), 7.28–7.45 (m, 5H), 7.37 (d,  $J$  = 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 70.7, 102.2, 102.9, 109.0, 126.9, 127.9, 128.6, 133.4, 136.2, 155.7, 156.0; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{11}\text{O}_2\text{Br} + \text{Na}]^+$  300.9835,

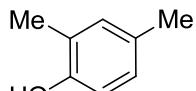
found 300.9835; IR ( $\text{CHCl}_3$ ):  $\nu = 3400, 3060, 3033, 2927, 1605, 1586, 1486, 1447, 1381, 1295, 1265, 1176, 1128, 1042, 1025, 971, 829, 738, 696 \text{ cm}^{-1}$ .

**m-Cresol (5d):**



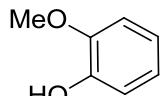
Colorless oil; yield 91%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 2.31$  (s, 3H), 4.98 (s, 1H, *OH*), 6.63-6.67 (m, 2H), 6.76 (d,  $J = 7.5 \text{ Hz}$ , 1H), 7.13 (t,  $J = 7.7 \text{ Hz}$ , 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 21.3, 112.3, 116.0, 121.6, 129.4, 139.8, 155.3$ .

**2,4-Dimethylphenol (5e):**



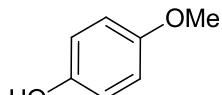
Pale yellow oil; yield 83%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 2.23$  (s, 3H), 2.26 (s, 3H), 4.69 (s, 1H, *OH*), 6.67 (d,  $J = 8.0 \text{ Hz}$ , 1H), 6.88 (dd,  $J = 8.0, 1.5 \text{ Hz}$ , 1H), 6.94 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 15.7, 20.4, 114.7, 127.4, 129.9, 131.6, 151.4$ .

**2-Methoxyphenol (5f):**



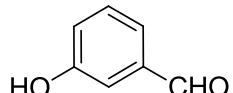
Colorless oil; yield 88%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 3.88$  (s, 3H), 5.65 (s, 1H, *OH*), 6.84-6.94 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 55.8, 110.7, 114.5, 120.1, 121.4, 145.6, 146.5$ .

**4-Methoxyphenol (5g):**



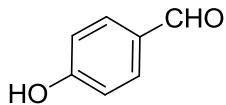
White solid; yield 85%; mp = 54–55 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 3.77$  (s, 3H), 5.13 (brs, 1H, *OH*), 6.75-6.81 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 55.8, 114.9, 116.1, 149.5, 153.5$ .

**3-Hydroxybenzaldehyde (5h):**



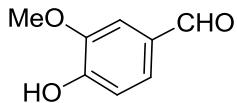
White solid; yield 97%; mp = 100–102 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 6.31$  (s, 1H, *OH*), 7.16-7.18 (m, 1H), 7.40-7.46 (m, 3H), 9.95 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 144.8, 122.5, 123.5, 130.4, 137.5, 156.7, 193.3$ .

**4-Hydroxybenzaldehyde (5i):**



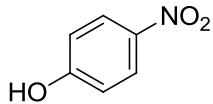
White solid; yield 93%; mp = 109–111 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/TMS) δ = 7.00 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 9.85 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 116.3, 129.6, 132.6, 161.9, 191.4.

**4-Hydroxy-3-methoxybenzaldehyde (5j):**



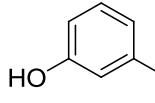
White solid; yield 91%; mp = 80–81 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 3.96 (s, 3H), 6.28 (brs, 1H, OH), 7.04 (d, *J* = 8.5 Hz, 1H), 7.42–7.43 (m, 2H), 9.82 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 56.1, 108.7, 114.4, 127.5, 129.9, 147.1, 151.7, 190.9.

**4-Nitrophenol (5k):**



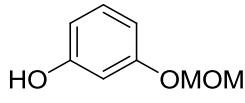
Pale yellow solid; yield 100%; mp = 108–110 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 6.51 (s, 1H, OH), 6.94 (d, *J* = 9.2 Hz, 2H), 8.17 (d, *J* = 9.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 115.8, 126.3, 141.4, 161.7.

**3-Hydroxyphenyl acetate (5l):**



Colorless oil; yield 70%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 2.30 (s, 3H), 6.35 (s, 1H, OH), 6.54 (t, *J* = 2.2 Hz, 1H), 6.61–6.66 (m, 2H), 7.19 (t, *J* = 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 21.2, 109.1, 113.3, 113.33, 130.1, 151.3, 156.8, 170.3 ; HRMS *m/z* calcd for [C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> + Na]<sup>+</sup> 175.0366, found 175.0362; IR (CHCl<sub>3</sub>) ν = 3419, 3020, 2933, 2857, 1736, 1603, 1486, 1462, 1372, 1306, 1272, 1232, 1135, 1018, 1001, 964, 908, 872, 758, 687, 671 cm<sup>-1</sup>.

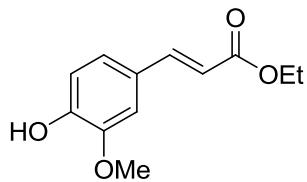
**3-(Methoxymethoxy)phenol (5m):**



Colorless oil; yield 100%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 3.48 (s, 3H), 5.15 (s, 2H), 6.23 (brs, 1H, OH), 6.49–6.52 (m, 1H), 6.56–6.61 (m, 2H), 7.12 (t, *J* = 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 56.0, 94.3, 103.8, 108.2, 109.1, 130.1, 157.1, 158.4; HRMS *m/z* calcd for [C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> + Na]<sup>+</sup> 177.0522, found 177.0521; IR (CHCl<sub>3</sub>) ν = 3365, 2930,

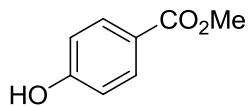
2852, 1661, 1596, 1490, 1463, 1388, 1283, 1215, 1144, 1076, 1019, 995, 942, 925, 848, 769 cm<sup>-1</sup>.

**(E)-Ethyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (5n):**



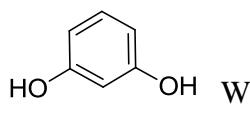
Colorless oil; yield 97%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 1.33 (t, *J* = 7.1 Hz, 3H), 3.92 (s, 3H), 4.25 (q, *J* = 7.1 Hz, 2H), 5.88 (s, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 1.9 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.61 (d, *J* = 15.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 14.3, 55.9, 60.3, 109.3, 114.7, 115.6, 123.0, 127.0, 144.7, 146.7, 147.9, 167.3; HRMS *m/z* calcd for [C<sub>12</sub>H<sub>14</sub>O<sub>4</sub> + Na]<sup>+</sup> 245.0784, found 245.0778; IR (CHCl<sub>3</sub>) ν = 3393, 2981, 2938, 1704, 1698, 1633, 1603, 1592, 1515, 1465, 1430, 1369, 1269, 1210, 1178, 1159, 1124, 1034, 981, 846, 818 cm<sup>-1</sup>.

**Methyl 4-hydroxybenzoate (5o):**



White solid, yield 97%; mp = 124–127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS) δ = 3.80 (s, 3H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 52.1, 115.3, 122.0, 131.9, 160.5, 167.6; HRMS *m/z* calcd for [C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> + Na]<sup>+</sup> 175.0366, found 175.0374; IR (CHCl<sub>3</sub>) ν = 3353, 3025, 2998, 2954, 2848, 1693, 1609, 1591, 1516, 1437, 1313, 1283, 1235, 1195, 1167, 1118, 1101, 1023, 965, 912, 853, 773, 735, 700 cm<sup>-1</sup>.

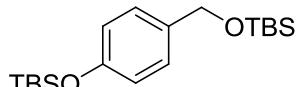
**Resorcinol (5p):**



White solid, yield 100%; mp = 106–108 °C; <sup>1</sup>H NMR (500 MHz, acetone D<sup>6</sup>) δ = 3.41 (s, 1H, OH), 6.30–6.35 (m, 3H), 6.97 (t, *J* = 8.0 Hz, 1H), 8.32 (s, 1H, OH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 103.2, 107.2, 130.5, 159.3.

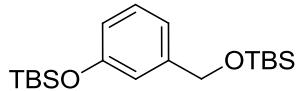
**Characterization data for bis-silyl ethers 6a-j and 1:**

***tert*-Butyl[4-(*tert*-butyldimethylsilyloxy)benzyloxy]dimethylsilane (6a):**



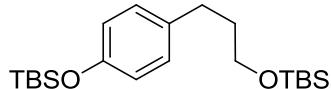
Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.08 (s, 6H), 0.18 (s, 6H), 0.92 (s, 9H), 0.98 (s, 9H), 4.66 (s, 2H), 6.97 (d,  $J$  = 8.4 Hz, 2H), 7.17 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.2, -4.5, 18.2, 18.4, 25.7, 26.0, 64.8, 119.8, 127.4, 134.1, 154.6; HRMS  $m/z$  calcd for  $[\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}_2 + \text{Na}]^+$  375.2146, found 375.2154; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2930, 2886, 2858, 1610, 1583, 1510, 1472, 1463, 1389, 1375, 1362, 1256, 1164, 1106, 1087, 1006, 916, 839, 778, 692  $\text{cm}^{-1}$ .

***tert*-Butyl[3-(*tert*-butyldimethylsilyloxy)benzyloxy]dimethylsilane (6b):**



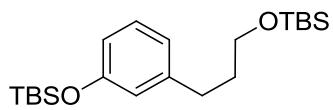
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.09 (s, 6H), 0.19 (s, 6H), 0.94 (s, 9H), 0.98 (s, 9H), 4.69 (s, 2H), 6.71 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 6.84 (d,  $J$  = 1.8 Hz, 1H), 6.89 (dd,  $J$  = 7.6, 0.7 Hz, 1H), 7.17 (t,  $J$  = 7.8 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, -4.4, 18.2, 18.4, 25.7, 25.9, 64.7, 117.6, 118.6, 118.8, 129.1, 143.1, 155.7; HRMS  $m/z$  calcd for  $[\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}_2 + \text{Na}]^+$  375.2146, found 375.2136; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2930, 2886, 2858, 1605, 1589, 1486, 1472, 1459, 1442, 1362, 1279, 1257, 1167, 1153, 1103, 1072, 1004, 965, 939, 839, 779, 691  $\text{cm}^{-1}$ .

***tert*-Butyl[3-(4-(*tert*-butyldimethylsilyloxyphenyl)propoxy]dimethylsilane (6c):**



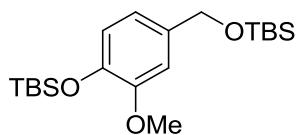
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.04 (s, 6H), 0.18 (s, 6H), 0.90 (s, 9H), 0.98 (s, 9H), 1.76–1.83 (m, 2H), 2.60 (t,  $J$  = 7.7 Hz, 2H), 3.61 (t,  $J$  = 6.4 Hz, 2H), 6.74 (d,  $J$  = 8.4 Hz, 2H), 7.03 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, -4.5, 18.2, 18.3, 25.7, 26.0, 31.2, 34.5, 62.4, 119.8, 129.2, 134.8, 153.5; HRMS  $m/z$  calcd for  $[\text{C}_{21}\text{H}_{40}\text{O}_2\text{Si}_2 + \text{Na}]^+$  403.2459, found 403.2458; IR ( $\text{CHCl}_3$ )  $\nu$  = 2950, 2930, 2857, 1607, 1510, 1470, 1388, 1256, 1168, 1101, 960, 918, 838, 777, 685  $\text{cm}^{-1}$ .

***tert*-Butyl[3-(*tert*-butyldimethylsilyloxyphenyl)propoxy]dimethylsilane (6d):**



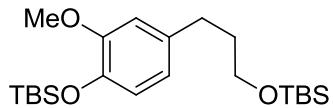
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.19 (s, 6H), 0.91 (s, 9H), 0.98 (s, 9H), 1.79–1.84 (m, 2H), 2.61 (t,  $J$  = 7.7 Hz, 2H), 3.62 (t,  $J$  = 6.4 Hz, 2H), 6.64–6.68 (m, 2H), 6.78 (d,  $J$  = 7.5 Hz, 1H), 7.12 (t,  $J$  = 7.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, -4.4, 18.2, 18.3, 25.7, 26.0, 31.9, 34.3, 62.3, 117.3, 120.3, 121.5, 129.1, 143.8, 155.6; HRMS  $m/z$  calcd for  $[\text{C}_{21}\text{H}_{40}\text{O}_2\text{Si}_2 + \text{H}]^+$  381.2640, found 381.2637; IR ( $\text{CHCl}_3$ )  $\nu$  = 2955, 2931, 2888, 2858, 1603, 1585, 1485, 1472, 1277, 1256, 1158, 1103, 1004, 838, 777, 667  $\text{cm}^{-1}$ .

***tert*-Butyl[4-(*tert*-butyldimethylsilyloxy)-3-methoxybenzyloxy]dimethylsilane (6e):**



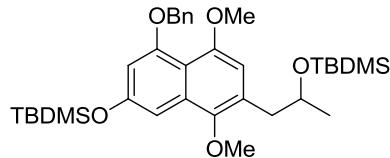
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.08 (s, 6H), 0.14 (s, 6H), 0.93 (s, 9H), 0.99 (s, 9H), 3.80 (s, 3H), 4.67 (s, 2H), 6.73 (dd,  $J$  = 8.1, 2.0, Hz, 1H), 6.79 (d,  $J$  = 8.1 Hz, 1H), 6.87 (d,  $J$  = 2.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.2, -4.7, 18.4, 18.4, 25.7, 26.0, 55.4, 64.9, 110.3, 118.3, 120.5, 134.9, 143.8, 150.8; HRMS  $m/z$  calcd for  $[\text{C}_{20}\text{H}_{38}\text{O}_3\text{Si}_2 + \text{Na}]^+$  405.2252, found 405.2250; IR ( $\text{CHCl}_3$ )  $\nu$  = 2955, 2931, 2886, 2858, 1606, 1513, 1446, 1418, 1285, 1256, 1157, 1090, 1040, 937, 902, 839, 780, 698  $\text{cm}^{-1}$ .

***tert*-Butyl [3-(4-*tert*-butyldimethylsilyloxy-3-methoxyphenyl)propoxy]dimethylsilane (6f):**



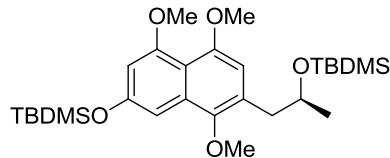
Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.04 (s, 6H); 0.14 (s, 6H), 0.90 (s, 9H), 0.99 (s, 9H), 1.78–1.84 (m, 2H), 2.60 (t,  $J$  = 7.7 Hz, 2H), 3.61 (t,  $J$  = 6.4 Hz, 2H), 3.78 (s, 3H), 6.62 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 6.68 (d,  $J$  = 1.9 Hz, 1H), 6.74 (d,  $J$  = 8 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, -4.7, 18.35, 18.4, 25.8, 26.0, 31.7, 34.5, 55.5, 62.4, 112.6, 120.5, 120.6, 135.7, 142.9, 150.6; HRMS  $m/z$  calcd for  $[\text{C}_{22}\text{H}_{42}\text{O}_3\text{Si}_2 + \text{Na}]^+$  433.2565, found 433.2568; IR ( $\text{CHCl}_3$ )  $\nu$  = 3005, 2942, 2859, 1637, 1513, 1439, 1376, 1256, 1234, 1155, 1098, 1039, 918, 839, 779, 667  $\text{cm}^{-1}$ .

**1-[5-Benzyl-7-*tert*-butyldimethylsilyloxy-1,4-dimethoxynaphthalen-2-yl]propan-2-yloxy]tert-butyldimethylsilane (**6g**):**



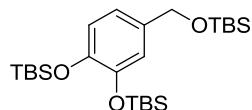
Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = -0.13$  (s, 3H),  $-0.03$  (s, 3H),  $0.24$  (s, 6H),  $0.84$  (s, 9H),  $1.00$  (s, 9H),  $1.19$  (d,  $J = 6.0$  Hz, 3H),  $2.77$  (dd,  $J = 13.1, 6.0$  Hz, 1H),  $2.92$  (dd,  $J = 13.1, 6.9$  Hz, 1H),  $3.81$  (s, 3H),  $3.89$  (s, 3H),  $4.17$ – $4.22$  (m, 1H),  $5.17$  (s, 2H),  $6.50$  (d,  $J = 2.2$  Hz, 1H),  $6.54$  (s, 1H),  $7.02$  (d,  $J = 2.2$  Hz, 1H),  $7.30$ – $7.48$  (m, 3H),  $7.58$  (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.93, -4.91, -4.46, -4.32, 18.1, 18.3, 23.9, 25.6, 25.7, 40.7, 56.4, 61.2, 69.2, 71.2, 102.7, 104.4, 107.4, 113.3, 113.8, 126.9, 127.5, 128.3, 131.9, 137.4, 146.7, 153.1, 154.2, 157.5$ ; HRMS  $m/z$  calcd for  $[\text{C}_{34}\text{H}_{52}\text{O}_5\text{Si}_2 + \text{H}]^+$  597.3426, found 597.3417. IR ( $\text{CHCl}_3$ ):  $\nu = 2955, 2931, 2858, 1621, 1603, 1583, 1507, 1463, 1409, 1374, 1255, 1178, 1154, 1126, 1091, 1046, 998, 939, 867, 837, 778, 735 \text{ cm}^{-1}$ .

**(S)-*tert*-Butyl-1-[(7-*tert*-butyldimethylsilyloxy-1,4,5-trimethoxynaphthalen-2-yl)propan-2-yloxy]dimethylsilane (**6h**):**



Colorless oil;  $[\alpha]_D^{25} = +15.4$  ( $c = 0.65$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = -0.16$  (s, 3H),  $-0.05$  (s, 3H),  $0.28$  (s, 6H),  $0.83$  (s, 9H),  $1.02$  (s, 9H),  $1.19$  (d,  $J = 6.1$  Hz, 3H),  $2.77$  (dd,  $J = 13.1, 5.8$  Hz, 1H),  $2.90$  (dd,  $J = 13.1, 7.1$  Hz, 1H),  $3.80$  (s, 3H),  $3.91$  (s, 3H),  $3.93$  (s, 3H),  $4.15$ – $4.21$  (m, 1H),  $6.42$  (d,  $J = 2.2$  Hz, 1H),  $6.53$  (s, 1H),  $6.99$  (d,  $J = 2.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.94, -4.90, -4.26, 18.1, 18.3, 23.9, 25.8, 25.9, 40.7, 56.3, 56.6, 61.2, 69.2, 102.1, 107.4, 113.2, 128.4, 131.9, 146.8, 153.0, 154.3, 158.6$ ; HRMS  $m/z$  calcd for  $[\text{C}_{28}\text{H}_{48}\text{O}_5\text{Si}_2 + \text{K}]^+$  559.2677, found 559.2670; IR ( $\text{CHCl}_3$ ):  $\nu = 2956, 2931, 2858, 1603, 1586, 1507, 1471, 1464, 1455, 1404, 1379, 1255, 1192, 1154, 1124, 1085, 1045, 998, 981, 939, 859, 838, 777, 667 \text{ cm}^{-1}$ .

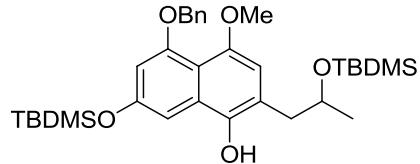
***tert*-Butyldimethyl-(3,4-bis-*tert*-butyldimethylsilyloxy)benzyloxysilane (**6i**):**



Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 0.08$  (s, 6H),  $0.18$  (s, 6H),  $0.20$  (s, 6H),  $0.93$  (s, 9H),  $0.98$  (s, 9H),  $0.99$  (s, 9H),  $4.61$  (s, 2H),  $6.72$  (dd,  $J = 8.1, 2.1$  Hz,

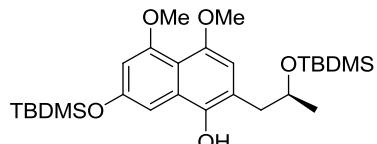
1H), 6.77 (d,  $J$  = 8.1 Hz, 1H), 6.84 (d,  $J$  = 2.1 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.0, -3.94, -3.9, 18.6, 18.64, 26.2, 64.8, 119.1, 119.3, 120.9, 134.8, 145.8, 146.9; HRMS  $m/z$  calcd for  $[\text{C}_{25}\text{H}_{50}\text{O}_3\text{Si}_3 + \text{Na}]^+$  505.2960, found 505.2963; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2930, 2686, 2858, 1606, 1579, 1510, 1472, 1423, 1390, 1362, 1299, 1255, 1228, 1162, 1122, 1093, 1005, 974, 908, 779, 697, 667  $\text{cm}^{-1}$ .

**(S)-5-Benzylxyloxy-7-*tert*-butyldimethylsilyloxy-2-(2-*tert*-butyldimethylsilyloxy)propyl-4-methoxynaphthalen-1-ol (6j):**



Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = -0.09 (s, 3H), 0.05 (s, 3H), 0.23 (s, 3H), 0.24 (s, 3H), 0.89 (s, 9H), 1.00 (s, 9H), 1.24 (d,  $J$  = 6.0 Hz, 3H), 2.89 (d,  $J$  = 5.2 Hz, 2H), 3.86 (s, 3H), 4.23–4.30 (m, 1H), 5.17 (s, 2H), 6.41 (s, 1H), 6.52 (d,  $J$  = 2.4 Hz, 1H), 7.30 (d,  $J$  = 2.2 Hz, 1H), 7.32 (d,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.60 (d,  $J$  = 7.5 Hz, 2H), 8.06 (s, 1H, OH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.2, -4.8, -4.4, -4.3, 18.0, 18.3, 23.2, 25.7, 25.8, 41.8, 57.4, 71.1, 71.8, 103.3, 104.5, 109.0, 114.0, 118.9, 127.0, 127.4, 128.3, 129.7, 137.5, 144.2, 150.3, 153.4, 156.6; HRMS  $m/z$  calcd for  $[\text{C}_{33}\text{H}_{50}\text{O}_5\text{Si}_2 + \text{K}]^+$  621.2828, found 621.2815; IR ( $\text{CHCl}_3$ )  $\nu$  = 3273, 2955, 2930, 2858, 1605, 1508, 1464, 1390, 1375, 1327, 1258, 1187, 1158, 1124, 1089, 1067, 1035, 969, 839, 782, 696  $\text{cm}^{-1}$ .

**(S)-7-*tert*-Butyldimethylsilyloxy-2-(2-*tert*-butyldimethylsilyloxypropyl)-4,5-dimethoxy-naphthalen-1-ol (1)<sup>1</sup>:**

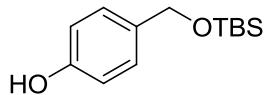


Pale yellow semisolid;  $[\alpha]_D^{25} = -10.6$  ( $c$  = 1.2,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = -0.12 (s, 3H), 0.04 (s, 3H), 0.26 (s, 6H), 0.88 (s, 9H), 1.01 (s, 9H), 1.23 (d,  $J$  = 6.1 Hz, 3H), 2.88 (d,  $J$  = 5.2 Hz, 2H), 3.88 (s, 3H), 3.93 (s, 3H), 4.21–4.28 (m, 1H), 6.39 (s, 1H), 6.44 (d,  $J$  = 2.4 Hz, 1H), 7.26 (d,  $J$  = 2.4 Hz, 1H), 8.4 (s, 1H, OH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, -4.9, -4.44, -4.4, 17.9, 18.3, 23.1, 25.7, 25.8, 41.7, 56.1, 57.4, 71.7, 102.2, 102.6, 108.8, 113.4, 118.9, 129.6, 144.1, 150.2, 153.5, 157.7; HRMS  $m/z$  calcd for  $[\text{C}_{27}\text{H}_{46}\text{O}_5\text{Si}_2 + \text{H}]^+$  507.2962, found 507.2955; IR ( $\text{CHCl}_3$ )  $\nu$  = 3434, 2956, 2927, 2856, 1653, 1605, 1592, 1512, 1464, 1378, 1328, 1258, 1159, 1125, 1090, 1036, 985, 939, 838, 780  $\text{cm}^{-1}$ .

### Chemoselective deprotection of aryl silyl ethers **6a-i**

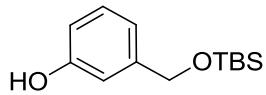
The procedure for chemoselective deprotection of silyl ethers **6a-i** is same as described earlier.

#### **4-(*tert*-Butyldimethylsilyloxy)methylphenol (**7a**):**



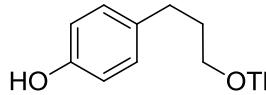
Colorless oil; yield 95%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.09 (s, 6H), 0.93 (s, 9H), 4.66 (s, 2H), 4.85 (s, 1H, *OH*), 6.78 (d,  $J$  = 8.5 Hz, 2H), 7.19 (d,  $J$  = 8.6 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.2, 18.4, 26.0, 64.7, 115.0, 127.8, 133.7, 154.5; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si} + \text{Na}]^+$  261.1281, found 261.1286; IR ( $\text{CHCl}_3$ )  $\nu$  = 3368, 2954, 2930, 2884, 2858, 1615, 1599, 1516, 1471, 1376, 1362, 1254, 1168, 1106, 1085, 1006, 938, 909, 838, 778, 668  $\text{cm}^{-1}$ .

#### **3-(*tert*-Butyldimethylsilyloxy)methylphenol (**7b**):**



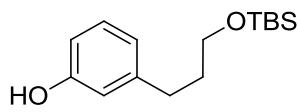
Colorless oil; yield 92%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.11 (s, 6H), 0.95 (s, 9H), 4.70 (s, 2H), 6.70 (dd,  $J$  = 7.8, 2.2 Hz, 1H), 6.83–647 (m, 2H), 7.18 (t,  $J$  = 7.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, 18.4, 25.9, 64.7, 112.9, 113.8, 118.3, 129.4, 143.3, 155.6; HRMS  $m/z$  calcd for  $[\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si} + \text{Na}]^+$  261.1281, found 261.1288; IR ( $\text{CHCl}_3$ )  $\nu$  = 3378, 2955, 2930, 2885, 2857, 1592, 1484, 1461, 1380, 1362, 1257, 1153, 1102, 1073, 1005, 930, 838, 778, 691, 669  $\text{cm}^{-1}$ .

#### **4-(3-*tert*-Butyldimethylsilyloxypropyl)phenol (**7c**):**



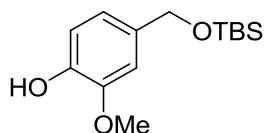
Colorless oil; yield 97%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.06 (s, 6H), 0.90 (s, 9H), 1.77–1.84 (m, 2H), 2.60 (t,  $J$  = 7.7 Hz, 2H), 3.64 (t,  $J$  = 6.4 Hz, 2H), 5.18 (brs, 1H, *OH*), 6.75 (d,  $J$  = 8.5 Hz, 2H), 7.05 (d,  $J$  = 8.5 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, 18.3, 26.0, 31.1, 34.6, 62.5, 115.1, 129.5, 134.3, 153.5; HRMS  $m/z$  calcd for  $[\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si} + \text{Na}]^+$  289.1594, found 289.1590; IR ( $\text{CHCl}_3$ )  $\nu$  = 3357, 2953, 2930, 2885, 2857, 1614, 1597, 1515, 1471, 1463, 1387, 1361, 1255, 1172, 1100, 1066, 963, 836, 777, 712, 662  $\text{cm}^{-1}$ .

**3-(3-*tert*-Butyldimethylsilyloxypropyl)phenol (7d):**



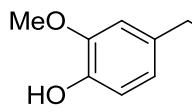
Colorless oil; yield 100%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.07 (s, 6H), 0.92 (s, 9H), 1.80–1.87 (m, 2H), 2.63 (t,  $J$  = 7.8 Hz, 2H), 3.65 (t,  $J$  = 6.4 Hz, 2H), 5.42 (s, 1H, *OH*), 6.64–6.68 (m, 2H), 6.76 (d,  $J$  = 7.5 Hz, 1H), 7.13 (t,  $J$  = 7.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −5.3, 18.3, 26.0, 31.9, 34.1, 62.6, 112.7, 115.4, 120.8, 129.4, 144.1, 155.6; HRMS  $m/z$  calcd for  $[\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si} + \text{H}]^+$  267.1775, found 267.1777; IR ( $\text{CHCl}_3$ )  $\nu$  = 3391, 2953, 2931, 2858, 1599, 1590, 1460, 1389, 1256, 1156, 1104, 969, 940, 836, 780, 695  $\text{cm}^{-1}$ .

**4-(*tert*-Butyldimethylsilyloxymethyl)-2-methoxyphenol (7e):**



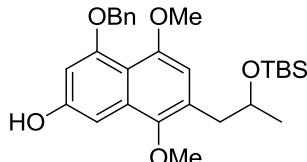
Colorless oil; yield 91%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.10 (s, 6H), 0.94 (s, 9H), 3.87 (s, 3H), 4.67 (s, 2H), 5.59 (s, 1H, *OH*), 6.79 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 6.87 (d,  $J$  = 8.0 Hz, 1H), 6.90 (d,  $J$  = 1.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −5.2, 18.4, 25.9, 55.8, 64.9, 109.0, 114.0, 119.0, 133.4, 144.5, 146.4; HRMS  $m/z$  calcd for  $[\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si} + \text{Na}]^+$  291.1387, found 291.1373; IR ( $\text{CHCl}_3$ )  $\nu$  = 3550, 2929, 2856, 1612, 1515, 1464, 1432, 1362, 1258, 1206, 1185, 1153, 1081, 1036, 1006, 938, 920, 838, 777, 668, 558  $\text{cm}^{-1}$ .

**4-(3-*tert*-Butyldimethylsilyloxypropyl)-2-methoxyphenol (7f):**



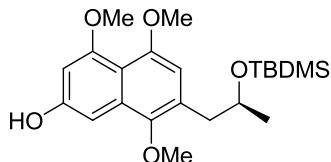
Colorless oil, yield 100%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.91 (s, 9H), 1.77–1.84 (m, 2H), 2.61 (t,  $J$  = 7.7 Hz, 2H), 3.63 (t,  $J$  = 6.3 Hz, 2H), 3.87 (s, 3H), 5.48 (s, 1H, *OH*), 6.68 (dd,  $J$  = 7.9, 2.0 Hz, 1H), 6.70 (d,  $J$  = 1.6 Hz, 1H), 6.83 (d,  $J$  = 7.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −5.3, 18.3, 25.9, 31.7, 34.7, 55.8, 62.3, 111.0, 114.1, 120.9, 134.1, 143.5, 146.3; HRMS  $m/z$  calcd for  $[\text{C}_{16}\text{H}_{28}\text{O}_3\text{Si} + \text{Na}]^+$  319.1700, found 319.1686; IR ( $\text{CHCl}_3$ )  $\nu$  = 3548, 2950, 2830, 2857, 1614, 1516, 1464, 1431, 1362, 1270, 1152, 1101, 1037, 967, 837  $\text{cm}^{-1}$ .

**4-Benzylxyloxy-7-(2-*tert*-butyldimethylsilyloxypropyl)-5,8-dimethoxynaphthalen-2-ol (7g):**



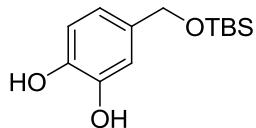
Pale yellow oil; yield 92%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = -0.12$  (s, 3H), 0.02 (s, 3H), 0.85 (s, 9H), 1.20 (d,  $J = 6.1$  Hz, 3H), 2.07 (s, 1H, *OH*), 2.79 (dd,  $J = 13.2, 5.9$  Hz, 1H), 2.95 (dd,  $J = 13.2, 7.0$  Hz, 1H), 3.78 (s, 3H), 3.89 (s, 3H), 4.19–4.23 (m, 1H), 5.07 (s, 2H), 6.53 (d,  $J = 2.1$  Hz, 1H), 6.54 (s, 1H), 7.05 (d,  $J = 2.1$  Hz, 1H), 7.30–7.4 (m, 3H), 7.55 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = -4.9, -4.8, 18.1, 23.9, 25.9, 40.6, 56.5, 61.3, 69.3, 71.1, 97.4, 100.1, 107.1, 113.3, 127.0, 127.6, 128.4, 128.9, 132.2, 137.2, 146.3, 153.4, 154.8, 158.0$ ; HRMS  $m/z$  calcd for  $[\text{C}_{28}\text{H}_{38}\text{O}_5\text{Si} + \text{Na}]^+$  505.2381, found 505.2388; IR ( $\text{CHCl}_3$ )  $\nu = 3371, 2955, 2930, 2857, 1622, 1607, 1593, 1463, 1412, 1374, 1256, 1177, 1150, 1123, 1088, 1038, 998, 910, 835, 775, 735, 697 \text{ cm}^{-1}$ .

**(S)-7-(2-*tert*-Butyldimethylsilyloxypropyl)-4,5,8-trimethoxynaphthalen-2-ol (7h):**



Colorless oil; yield 85%;  $[\alpha]_D^{25} = +18.7$  ( $c = 0.7, \text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = -0.16$  (s, 3H),  $-0.04$  (s, 3H), 0.83 (s, 9H), 1.19 (d,  $J = 6.0$  Hz, 3H), 2.77 (dd,  $J = 13.1, 5.7$  Hz, 1H), 2.90 (dd,  $J = 13.1, 7.2$  Hz, 1H), 3.79 (s, 3H), 3.91 (s, 6H), 4.16–4.21 (m, 1H), 6.47 (d,  $J = 2.3$  Hz, 1H), 6.52 (s, 1H), 6.97 (d,  $J = 2.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -5.0, -4.9, 18.1, 23.9, 25.8, 40.5, 56.1, 56.6, 61.1, 69.2, 96.8, 98.1, 107.0, 112.5, 128.8, 132.1, 146.3, 153.0, 154.9, 158.8$ ; HRMS  $m/z$  calcd for  $[\text{C}_{22}\text{H}_{34}\text{O}_5\text{Si} + \text{H}]^+$  407.2254, found 407.2249; IR ( $\text{CHCl}_3$ )  $\nu = 3409, 2956, 2931, 2857, 1622, 1607, 1594, 1515, 1464, 1454, 1409, 1381, 1361, 1269, 1256, 1192, 1178, 1150, 1120, 1082, 1038, 1001, 971, 871, 836, 776 \text{ cm}^{-1}$ .

**4-(*tert*-Butyldimethylsilyloxyethyl)benzene-1,2-diol (7i):**



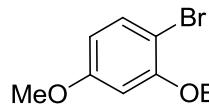
Colorless oil; yield 93%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta = 0.10$  (s, 6H), 0.94 (s, 9H), 4.62 (s, 2H), 6.71 (d,  $J = 7.4$  Hz, 1H), 6.77 (d,  $J = 6.9$  Hz, 1H), 6.83 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -5.2, 18.5, 26.0, 65.0, 113.9, 115.1, 119.0, 133.8, 142.8, 143.5$ ;

HRMS  $m/z$  calcd for  $[C_{13}H_{22}O_3Si + Na]^+$  277.1230, found 277.1233; IR ( $CHCl_3$ )  $\nu = 3392, 2954, 2929, 2885, 2856, 1492, 1471, 1463, 1439, 1410, 1388, 1362, 1287, 1255, 1153, 1096, 1007, 939, 877, 835, 773, 666\text{ cm}^{-1}$ .

**General procedure for one pot chemoselective aryl silyl deprotection/reprotection with other protecting groups:**

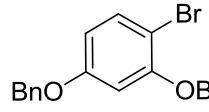
To a stirred solution of aryl silyl ether **1**, **4** or **6** (0.1 mmol, 1.0 equiv) in dry DMF (3 mL) was added sodium hydride (0.15 mmol, 1.5 equiv) at room temperature and subsequently the alkyl halide or acetyl chloride (0.1 mmol, 1.0 equiv) was added. After completion of reaction (monitored by TLC) it was quenched with water (1 mL) and diluted with EtOAc (10 mL). The organic layer was separated, washed with water ( $3 \times 5$  mL), dried ( $Na_2SO_4$ ) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as eluent to give differently protected product **2** or **8**.

**2-Benzylxy-1-bromo-4-methoxybenzene (8a):**



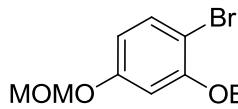
Colorless oil; yield (91%);  $^1H$  NMR (400 MHz,  $CDCl_3/TMS$ )  $\delta = 3.76$  (s, 3H), 5.13 (s, 2H), 6.41 (dd,  $J = 8.7, 2.7$  Hz, 1H), 6.53 (d,  $J = 2.7$  Hz, 1H), 7.30–7.49 (m, 5H), 7.42 (d,  $J = 8.7$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta = 55.5, 70.7, 101.6, 103.2, 106.5, 127.0, 127.9, 128.5, 133.2, 136.4, 155.6, 160.0$ ; HRMS  $m/z$  calcd for  $[C_{14}H_{13}O_2Br + Na]^+$  314.9991, found 314.9955; IR ( $CHCl_3$ )  $\nu = 3031, 2937, 2835, 1595, 1487, 1459, 1418, 1381, 1306, 1282, 1256, 1200, 1168, 1061, 1025, 907, 832, 789, 735, 696, 630, 599\text{ cm}^{-1}$ .

**4-Bromo-1,3-dibenzylxybenzene (8b):**



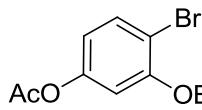
Colorless oil; yield 72%;  $^1H$  NMR (400 MHz,  $CDCl_3/TMS$ )  $\delta = 4.99$  (s, 2H), 5.09 (s, 2H), 6.47 (dd,  $J = 8.7, 2.7$  Hz, 1H), 6.60 (d,  $J = 2.7$  Hz, 1H), 7.24–7.46 (m, 11H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta = 70.3, 70.6, 102.4, 103.4, 107.4, 126.9, 127.5, 127.9, 128.1, 128.5, 128.6, 133.1, 136.3, 136.4, 155.6, 159.1$ ; HRMS  $m/z$  calcd for  $[C_{20}H_{17}O_2Br + Na]^+$  391.0304, found 391.0303; IR ( $CHCl_3$ ):  $\nu = 3088, 3064, 3031, 2927, 2860, 1581, 1485, 1454, 1425, 1379, 1304, 1281, 1256, 1181, 1054, 1022, 907, 833, 786, 737, 696\text{ cm}^{-1}$ .

**2-Benzylxyloxy-1-bromo-4-(methoxymethoxy)benzene (8c):**



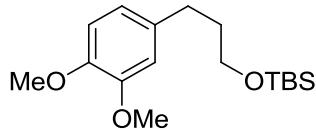
Colorless oil; yield 80%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 3.45 (s, 3H), 5.12 (s, 2H), 5.13 (s, 2H), 6.57 (dd,  $J$  = 8.7, 2.6 Hz, 1H), 6.68 (d,  $J$  = 2.6 Hz, 1H), 7.30–7.49 (m, 5H), 7.40 (d,  $J$  = 8.7 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 56.0, 70.8, 94.7, 103.3, 104.5, 109.5, 127.1, 127.9, 128.6, 133.3, 136.4, 155.6, 157.7; HRMS  $m/z$  calcd for  $[\text{C}_{15}\text{H}_{15}\text{O}_3\text{Br} + \text{Na}]^+$  345.0097, found 345.0096; IR ( $\text{CHCl}_3$ ):  $\nu$  = 2927, 2862, 1586, 1483, 1456, 1421, 1381, 1279, 1152, 1079, 1046, 1015, 921, 836, 754, 734, 696  $\text{cm}^{-1}$ .

**3-Benzylxyloxy-4-bromophenyl acetate (8d):**



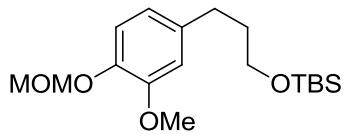
Colorless oil; yield 83%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 2.29 (s, 3H), 5.12 (s, 2H), 6.64 (dd,  $J$  = 8.6, 2.4 Hz, 1H), 6.73 (d,  $J$  = 2.4 Hz, 1H), 7.34 (t,  $J$  = 7.2 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.47 (d,  $J$  = 7.3 Hz, 2H), 7.55 (d,  $J$  = 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.1, 70.9, 107.8, 109.1, 115.1, 127.0, 128.1, 128.6, 133.3, 136.0, 150.6, 155.6, 169.1; HRMS  $m/z$  calcd for  $[\text{C}_{15}\text{H}_{13}\text{O}_3\text{Br} + \text{Na}]^+$  342.9940, found 342.9936; IR ( $\text{CHCl}_3$ ):  $\nu$  = 3019, 2918, 2850, 1762, 1596, 1497, 1481, 1416, 1370, 1278, 1156, 1122, 1044, 1018, 970, 897, 838, 696, 668  $\text{cm}^{-1}$ .

**tert-Butyl-3-(3,4-dimethoxyphenyl)propoxydimethylsilane (8e):**



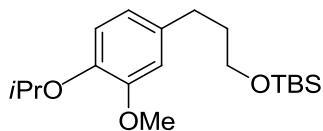
Colorless oil; yield 81%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.91 (s, 9H), 1.79–1.84 (m, 2H), 2.62 (t,  $J$  = 7.8 Hz, 2H), 3.63 (t,  $J$  = 6.3 Hz, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 6.71–6.74 (m, 2H), 6.79 (d,  $J$  = 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, 18.3, 25.9, 31.6, 34.6, 55.7, 55.9, 62.3, 111.1, 111.7, 120.2, 134.8, 147.0, 148.7; HRMS  $m/z$  calcd for  $[\text{C}_{17}\text{H}_{30}\text{O}_3\text{Si} + \text{Na}]^+$  333.1856 found: 333.1856 IR ( $\text{CHCl}_3$ ):  $\nu$  = 2953, 2933, 2857, 1591, 1516, 1464, 1417, 1388, 1259, 1156, 1140, 1101, 1031, 968, 912, 837, 809, 775, 734, 665  $\text{cm}^{-1}$ .

***tert*-Butyl-[3-(3-methoxy-4-(methoxymethoxy)phenyl)propoxy]dimethylsilane (8f):**



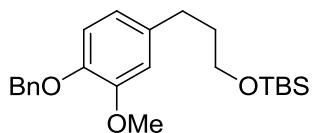
Colorless oil; yield 89%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.90 (s, 9H), 1.78–1.85 (m, 2H), 2.62 (t,  $J$  = 7.8 Hz, 2H), 3.51 (s, 3H), 3.63 (t,  $J$  = 6.3 Hz, 2H), 3.86 (s, 3H), 5.19 (s, 2H), 6.70 (dd,  $J$  = 8.1, 1.9 Hz, 1H), 6.74 (d,  $J$  = 1.9 Hz, 1H), 7.05 (d,  $J$  = 8.1 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, 18.3, 25.9, 31.7, 34.5, 55.8, 56.1, 62.3, 95.6, 112.2, 116.5, 120.4, 136.7, 144.4, 149.5; HRMS  $m/z$  calcd for  $[\text{C}_{18}\text{H}_{32}\text{O}_4\text{Si} + \text{Na}]^+$  363.1962, found 363.1967; IR ( $\text{CHCl}_3$ )  $\nu$  = 2952, 2930, 2896, 2857, 1591, 1514, 1464, 1418, 1388, 1360, 1262, 1227, 1200, 1156, 1134, 1101, 1079, 1038, 1006, 924, 837, 814, 775, 665  $\text{cm}^{-1}$ .

***tert*-Butyl-[3-(4-isopropoxy-3-methoxyphenyl)propoxy]dimethylsilane (8g):**



Colorless oil; yield 85%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.91 (s, 9H), 1.35 (d,  $J$  = 6.1 Hz, 6H), 1.78–1.85 (m, 2H), 2.61 (t,  $J$  = 7.7 Hz, 2H), 3.63 (t,  $J$  = 6.4 Hz, 2H), 3.84 (s, 3H), 4.43–4.49 (m, 1H), 6.69 (dd,  $J$  = 8.1, 2.0 Hz, 1H), 6.72 (d,  $J$  = 2.0 Hz, 1H), 6.81 (d,  $J$  = 8.1 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.1, 18.5, 22.4, 26.2, 31.9, 34.7, 56.1, 62.6, 71.8, 112.7, 116.4, 120.4, 135.7, 145.4, 150.5; HRMS  $m/z$  calcd for  $[\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si} + \text{Na}]^+$  361.2169, found 361.2170; IR ( $\text{CHCl}_3$ )  $\nu$  = 2930, 2858, 1607, 1587, 1511, 1464, 1417, 1382, 1258, 1223, 1157, 1105, 1039, 958, 836, 775, 658  $\text{cm}^{-1}$ .

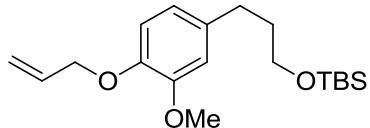
**3-(4-Benzylxy-3-methoxyphenyl)propoxy-*tert*-butyldimethylsilane (8h):**



Colorless oil; yield 94%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.05 (s, 6H), 0.91 (s, 9H), 1.78–1.83 (m, 2H), 2.61 (t,  $J$  = 7.7 Hz, 2H), 3.62 (t,  $J$  = 6.3 Hz, 2H), 3.87 (s, 3H), 5.12 (s, 2H), 6.65 (dd,  $J$  = 8.1, 1.9 Hz, 1H), 6.74 (d,  $J$  = 1.9 Hz, 1H), 6.79 (d,  $J$  = 8.1 Hz, 1H), 7.29 (t,  $J$  = 7.3 Hz, 1H), 7.35 (t,  $J$  = 7.4 Hz, 2H), 7.43 (d,  $J$  = 7.1 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.3, 18.3, 25.9, 31.6, 34.5, 55.9, 62.3, 71.2, 112.4, 114.2, 120.2, 127.3, 127.7, 127.8, 128.4, 128.5, 135.6, 135.6, 137.4, 146.2, 149.5; HRMS  $m/z$  calcd for  $[\text{C}_{23}\text{H}_{34}\text{O}_3\text{Si} + \text{Na}]^+$

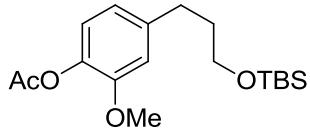
409.2169 found 409.2180; IR (CHCl<sub>3</sub>)  $\nu$  = 2950, 2930, 2857, 1590, 1514, 1464, 1418, 1385, 1259, 1229, 1160, 1140, 1101, 1036, 969, 911, 837, 775, 738, 696 cm<sup>-1</sup>.

**3-(4-Allyloxy-3-methoxyphenyl)propoxy-*tert*-butyldimethylsilane (8i):**



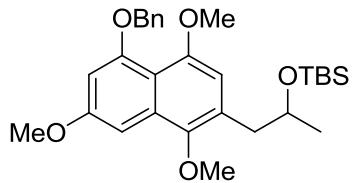
Colorless oil; yield 94%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  = 0.05 (s, 6H), 0.91 (s, 9H), 1.78–1.85 (m, 2H), 2.62 (t,  $J$  = 7.7 Hz, 2H), 3.63 (t,  $J$  = 6.3 Hz, 2H), 3.86 (s, 3H), 4.59 (dt,  $J$  = 5.4, 1.4 Hz, 2H), 5.27 (dq,  $J$  = 12.0, 1.3 Hz, 1H), 5.39 (dq,  $J$  = 17.2, 1.5 Hz, 1H), 6.04–6.13 (m, 1H), 6.69 (dd,  $J$  = 8.1, 1.9 Hz, 1H), 6.73 (d,  $J$  = 1.9 Hz, 1H), 6.80 (d,  $J$  = 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -5.3, 18.3, 25.9, 31.6, 34.5, 55.8, 62.3, 70.0, 112.1, 113.5, 117.8, 120.1, 133.6, 135.3, 146.0, 149.2; HRMS *m/z* calcd for [C<sub>19</sub>H<sub>32</sub>O<sub>3</sub>Si + Na]<sup>+</sup> 359.2013 found 359.2016; IR (CHCl<sub>3</sub>)  $\nu$  = 2952, 2930, 2858, 1590, 1514, 1464, 1419, 1388, 1361, 1258, 1231, 1158, 1141, 1101, 1079, 1038, 926, 837, 811, 775, 663 cm<sup>-1</sup>.

**4-[3-(Tert-butyldimethylsilyloxy)propyl]-2-methoxyphenyl acetate (8j):**



Colorless oil; yield 92%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  = 0.06 (s, 6H), 0.91 (s, 9H), 1.79–1.87 (m, 2H), 2.30 (s, 3H), 2.66 (t,  $J$  = 7.8 Hz, 2H), 3.64 (t,  $J$  = 6.3 Hz, 2H), 3.82 (s, 3H), 6.76 (dd,  $J$  = 8.0, 1.8 Hz, 1H), 6.80 (d,  $J$  = 1.8 Hz, 1H), 6.92 (d,  $J$  = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -5.3, 18.3, 20.7, 25.9, 32.0, 34.3, 55.8, 62.2, 112.6, 120.5, 122.3, 137.6, 141.3, 150.7, 169.3; HRMS *m/z* calcd for [C<sub>18</sub>H<sub>30</sub>O<sub>4</sub>Si + Na]<sup>+</sup> 361.1806 found 361.1801; IR (CHCl<sub>3</sub>)  $\nu$  = 2950, 2930, 2857, 1768, 1604, 1511, 1465, 1369, 1279, 1199, 1152, 1101, 1034, 836, 776, 663 cm<sup>-1</sup>.

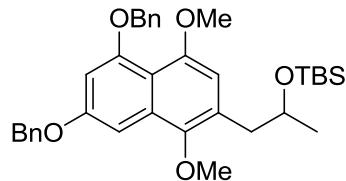
**1-[5-Benzyl-1,4,7-trimethoxynaphthalen-2-yl]propan-2-yloxy-*tert*-butyldimethylsilane (8k) from 6g:**



White solid; yield 90%, mp = 68–69 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  = -0.09 (s, 3H), 0.01 (s, 3H), 0.88 (s, 9H), 1.21 (d,  $J$  = 6.0 Hz, 3H), 2.81 (dd,  $J$  = 13.1, 6.2 Hz, 1H), 2.97 (dd,  $J$  = 13.1, 6.8 Hz, 1H), 3.86 (s, 3H), 3.91 (s, 3H), 3.94 (s, 3H),

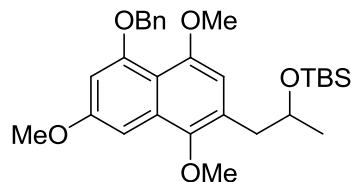
4.21–4.26 (m, 1H), 5.19 (s, 2H), 6.58 (s, 1H), 6.60 (d,  $J$  = 2.0 Hz, 1H), 7.01 (d,  $J$  = 1.9 Hz, 1H), 7.33 (t,  $J$  = 7.2 Hz, 1H), 7.42 (t,  $J$  = 7.6 Hz, 2H), 7.61 (d,  $J$  = 7.7 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.9, −4.86, 18.1, 23.8, 25.9, 40.8, 55.2, 56.5, 61.0, 69.2, 71.0, 93.5, 100.3, 107.5, 113.5, 126.9, 127.5, 128.3, 128.7, 132.0, 137.3, 146.9, 153.2, 157.6, 158.3; HRMS  $m/z$  calcd for  $[\text{C}_{29}\text{H}_{40}\text{O}_5\text{Si} + \text{Na}]^+$  519.2537, found 519.2529; IR ( $\text{CHCl}_3$ )  $\nu$  = 2955, 2930, 2857, 1621, 1606, 1511, 1499, 1456, 1406, 1375, 1354, 1244, 1158, 1126, 1088, 1062, 1003, 872, 834, 775, 757, 697  $\text{cm}^{-1}$ .

**1-[(5,7-Bis-benzyloxy)-1,4-dimethoxynaphthalen-2-yl-propan-2-yloxy]-*tert*-butyldimethylsilane (8l):**



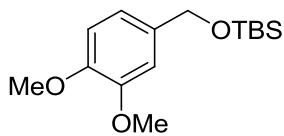
Pale yellow oil; yield 70%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = −0.09 (s, 3H), 0.01 (s, 3H), 0.88 (s, 9H), 1.20 (d,  $J$  = 6.0 Hz, 3H), 2.80 (dd,  $J$  = 13.1, 6.2 Hz, 1H), 2.97 (dd,  $J$  = 13.1, 6.8 Hz, 1H), 3.77 (s, 3H), 3.91 (s, 3H), 4.20–4.24 (m, 1H), 5.19 (s, 2H), 5.21 (s, 2H), 6.58 (s, 1H), 6.69 (d,  $J$  = 2.3 Hz, 1H), 7.07 (d,  $J$  = 2.3 Hz, 1H), 7.30–7.44 (m, 6H), 7.51 (d,  $J$  = 7.2 Hz, 2H), 7.60 (d,  $J$  = 7.2 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.9, −4.8, 18.1, 23.8, 25.9, 40.8, 56.5, 61.0, 69.2, 70.0, 71.0, 94.8, 100.6, 107.6, 113.6, 126.9, 127.5, 127.7, 128.0, 128.3, 128.6, 128.8, 131.9, 136.9, 137.3, 146.9, 153.2, 157.4, 157.7; HRMS  $m/z$  calcd for  $[\text{C}_{35}\text{H}_{44}\text{O}_5\text{Si} + \text{Na}]^+$  595.2850, found 595.2837; IR ( $\text{CHCl}_3$ )  $\nu$  = 3032, 2950, 2929, 2857, 1618, 1603, 1495, 1454, 1412, 1375, 1352, 1255, 1176, 1154, 1124, 1083, 1056, 998, 901, 834, 773, 735, 694  $\text{cm}^{-1}$ .

**1-[(5-Benzyl-1,4,7-trimethoxynaphthalen-2-yl)propan-2-yloxy]-*tert*-butyldimethylsilane (8k) from 6j:**



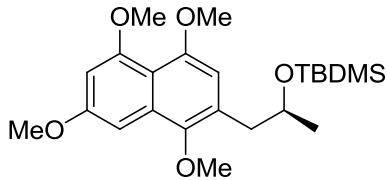
White solid; yield 68%, mp = 68–69 °C. Other data were same as earlier.

**tert-Butyl-(3,4-dimethoxybenzyloxy)dimethylsilane (8m):**



Colorless oil; yield 82%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.09 (s, 6H), 0.94 (s, 9H), 3.87 (s, 3H), 3.88 (s, 3H), 4.68 (s, 2H), 6.83 (s, 2H), 6.90 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.2, 18.4, 25.9, 55.7, 55.9, 64.8, 109.6, 110.8, 118.1, 134.1, 147.9, 148.8; HRMS ( $m/z$ ) calcd for  $[\text{C}_{15}\text{H}_{26}\text{O}_3\text{Si} + \text{Na}]^+$  305.1543, found 305.1540; IR ( $\text{CHCl}_3$ )  $\nu$  = 2950, 2931, 2856, 1593, 1516, 1464, 1418, 1376, 1258, 1234, 1157, 1137, 1091, 1031, 927, 838, 812, 777, 668  $\text{cm}^{-1}$ .

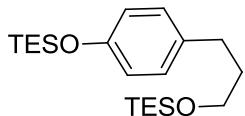
**(S)-tert-Butyldimethyl[1-(1,4,5,7-tetramethoxynaphthalen-2-yl)propan-2-yloxy]silane (2)<sup>1</sup>:**



Colorless oil; yield 70%;  $[\alpha]_D^{25} = +24.6$  ( $c = 0.25$ ,  $\text{CHCl}_3$ )  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = -0.14 (s, 3H), -0.03 (s, 3H), 0.84 (s, 9H), 1.19 (d,  $J$  = 6.0 Hz, 3H), 2.78 (dd,  $J$  = 13.1, 5.9 Hz, 1H), 2.92 (dd,  $J$  = 13.1, 7.0 Hz, 1H), 3.84 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 4.15–4.23 (m, 1H), 6.49 (d,  $J$  = 2.4 Hz, 1H), 6.54 (s, 1H), 6.96 (d,  $J$  = 2.4 Hz, 1H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.0, -4.9, 18.1, 23.8, 25.8, 40.8, 55.2, 56.2, 56.6, 61.0, 69.2, 92.9, 98.3, 107.5, 113.0, 128.8, 132.0, 146.9, 153.0, 158.4, 158.6; HRMS  $m/z$  calcd for  $[\text{C}_{23}\text{H}_{36}\text{O}_5\text{Si} + \text{H}]^+$  421.2410, found 421.2398; IR ( $\text{CHCl}_3$ )  $\nu$  = 2956, 2930, 2856, 1676, 1621, 1606, 1468, 1404, 1380, 1246, 1155, 1124, 1083, 1061, 1006, 833  $\text{cm}^{-1}$ .

**Characterisation data of TES and TBDPS bis-silyl ethers 9a and 9b**

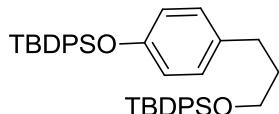
**Triethyl-[3-(4-triethylsilyloxyphenyl)propoxy]silane (9a):**



Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.6 (q,  $J$  = 7.9 Hz, 6H), 0.75 (q,  $J$  = 7.9 Hz, 6H), 0.91–1.01 (m, 18H), 1.79–1.86 (m, 2H), 2.61 (t,  $J$  = 7.7 Hz, 2H), 3.61 (t,  $J$  = 6.5 Hz, 2H), 6.76 (d,  $J$  = 8.5 Hz, 2H), 7.03 (d,  $J$  = 8.5 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 4.4, 5.0, 6.4, 6.6, 31.3, 34.6, 62.2, 68.9, 119.7, 129.2, 134.8, 153.5; HRMS  $m/z$  calcd

for  $[C_{21}H_{40}O_2Si_2 + H]^+$  381.2640 found 381.2644; IR ( $CHCl_3$ )  $\nu = 2955, 2912, 2877, 1610, 1509, 1458, 1415, 1261, 1239, 1169, 1096, 1074, 1015, 1005, 975, 911, 742\text{ cm}^{-1}$ .

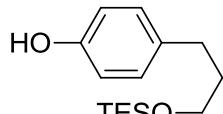
**tert-Butyl-[3-(4-*tert*-butyldiphenylsilyloxy)phenyl]propoxy]diphenylsilane (9b):**



Colorless oil;  $^1H$  NMR (500 MHz,  $CDCl_3/TMS$ )  $\delta = 1.03$  (s, 9H), 1.09 (s, 9H), 1.76–1.79 (m, 2H), 2.57 (t,  $J = 7.7\text{ Hz}$ , 2H), 3.62 (t,  $J = 6.3\text{ Hz}$ , 2H), 6.65 (d,  $J = 8.5\text{ Hz}$ , 2H), 6.86 (d,  $J = 8.5\text{ Hz}$ , 2H), 7.33–7.43 (m, 12H), 7.64 (dd,  $J = 8.0, 1.4\text{ Hz}$ , 4H), 7.71 (dd,  $J = 8.0, 1.4\text{ Hz}$ , 4H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta = 19.2, 19.5, 26.5, 26.9, 31.1, 34.2, 63.0, 119.3, 127.6, 127.7, 129.1, 129.5, 129.8, 133.1, 134.0, 134.5, 135.5, 135.54, 153.5$ ; HRMS  $m/z$  calcd for  $[C_{41}H_{48}O_2Si_2 + Na]^+$  651.3085 found 651.3070; IR ( $CHCl_3$ )  $\nu = 3072, 2959, 2934, 2899, 2860, 1590, 1509, 1474, 1428, 1392, 1363, 1257, 1189, 1113, 1068, 921, 838, 828, 740, 702, 611\text{ cm}^{-1}$ .

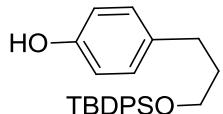
**Procedure for selective deprotection of aryl TES or TBDPS silyl ethers:** The procedure is same as described earlier.

**4-[3-(triethylsilyloxy)propyl]phenol (10a):**



Colorless oil; yield 96%;  $^1H$  NMR (500 MHz,  $CDCl_3/TMS$ )  $\delta = 0.61$  (q,  $J = 8.0\text{ Hz}$ , 6H), 0.97 (t,  $J = 8.0\text{ Hz}$ , 9H), 1.80–1.85 (m, 2H), 2.60 (t,  $J = 7.8\text{ Hz}$ , 2H), 3.64 (t,  $J = 6.5\text{ Hz}$ , 2H), 5.26 (brs, 1H), 6.75 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.04 (d,  $J = 8.4\text{ Hz}$ , 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta = 4.6, 7.0, 31.4, 34.8, 62.4, 115.3, 129.6, 134.4, 153.8$ ; HRMS  $m/z$  calcd for  $[C_{15}H_{26}O_2Si + H]^+$  267.1775 found 267.1771; IR ( $CHCl_3$ )  $\nu = 3357, 2954, 2878, 1614, 1515, 1458, 1238, 1172, 1096, 1014, 804, 668, 553\text{ cm}^{-1}$ .

**4-[3-(*tert*-Butyldiphenylsilyloxy)propyl]phenol (10c):**

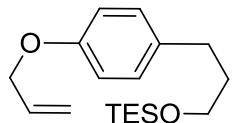


Colorless oil; yield 88%;  $^1H$  NMR (400 MHz,  $CDCl_3/TMS$ ):  $\delta = 1.06$  (s, 9H), 1.81–1.85 (m, 2H), 2.65 (t,  $J = 7.7\text{ Hz}$ , 2H), 3.63 (t,  $J = 6.2\text{ Hz}$ , 2H), 4.68 (s, 1H, *OH*), 6.73 (d,  $J = 8.5\text{ Hz}$ , 2H), 7.03 (d,  $J = 8.5\text{ Hz}$ , 2H), 7.35–7.44 (m, 6H), 7.67 (dd,  $J = 7.9, 1.5\text{ Hz}$ , 4H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta = 19.2, 26.9, 31.1, 34.4, 63.0, 115.1, 127.6, 129.5, 134.0$ .

134.4, 134.8, 135.6, 153.5; HRMS  $m/z$  calcd for [C<sub>25</sub>H<sub>30</sub>O<sub>2</sub>Si + H]<sup>+</sup> 391.2088 found 391.2083; IR (CHCl<sub>3</sub>)  $\nu$  = 3412, 2955, 2934, 2858, 1614, 1514, 1473, 1362, 1234, 1112, 822, 751, 742, 702, 610, 506 cm<sup>-1</sup>.

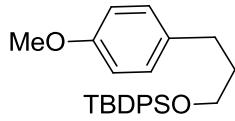
**Procedure for one-pot chemoselective aryl TES or TBDPS silyl deprotection/reprotection with other protecting groups:** The procedure is same as described earlier for aryl TBS silyl ether.

**3-[(4-Allyloxyphenyl)propoxy]triethylsilane (10b):**



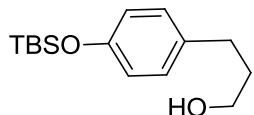
Colorless oil; yield 91%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  = 0.06 (q,  $J$  = 8.0 Hz, 6H), 0.91 (t,  $J$  = 8.0 Hz, 9H), 1.78–1.85 (m, 2H), 2.62 (t,  $J$  = 7.8 Hz, 2H), 3.63 (t,  $J$  = 6.3 Hz, 2H), 4.52 (dt,  $J$  = 5.3, 1.5 Hz, 2H), 5.28 (dq,  $J$  = 12.3, 1.6 Hz, 1H), 5.39 (dq,  $J$  = 17.2, 1.6 Hz, 1H), 6.01–6.10 (m, 1H), 6.84 (d,  $J$  = 8.7 Hz, 2H), 7.10 (d,  $J$  = 8.7 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 4.4, 6.8, 31.2, 34.7, 62.1, 68.9, 114.6, 117.5, 129.3, 133.5, 134.5, 156.7; HRMS  $m/z$  calcd for [C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>Si + H]<sup>+</sup> 307.2088, found 307.2080; IR (CHCl<sub>3</sub>)  $\nu$  = 2954, 2913, 2877, 1648, 1612, 1584, 1511, 1458, 1415, 1381, 1297, 1241, 1176, 1098, 1075, 1016, 1004, 961, 923, 806, 742 cm<sup>-1</sup>.

**tert-Butyl-[3-(4-methoxyphenyl)propoxy]diphenylsilane (10d):**



Colorless oil; yield 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  = 1.09 (s, 9H), 1.83–1.90 (m, 2H), 2.69 (t,  $J$  = 7.7 Hz, 2H), 3.71 (t,  $J$  = 6.2 Hz, 2H), 3.80 (s, 3H), 6.83 (d,  $J$  = 8.6 Hz, 2H), 7.10 (d,  $J$  = 8.6 Hz, 2H), 7.37–7.44 (m, 6H), 7.70 (dd,  $J$  = 7.9, 1.5 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 19.2, 26.9, 31.1, 34.4, 55.2, 63.0, 113.7, 127.6, 129.3, 129.5, 134.0, 134.3, 135.6, 157.7; HRMS  $m/z$  calcd for [C<sub>26</sub>H<sub>32</sub>O<sub>2</sub>Si + Na]<sup>+</sup> 427.2064 found 427.2060; IR (CHCl<sub>3</sub>)  $\nu$  = 3070, 2998, 2932, 2858, 1612, 1512, 1472, 1428, 1389, 1300, 1246, 1177, 1111, 1064, 1040, 965, 910, 823, 740, 702, 687 cm<sup>-1</sup>.

**3-(4-*tert*-Butyldimethylsilyloxyphenyl)propan-1-ol (14):<sup>11</sup>**



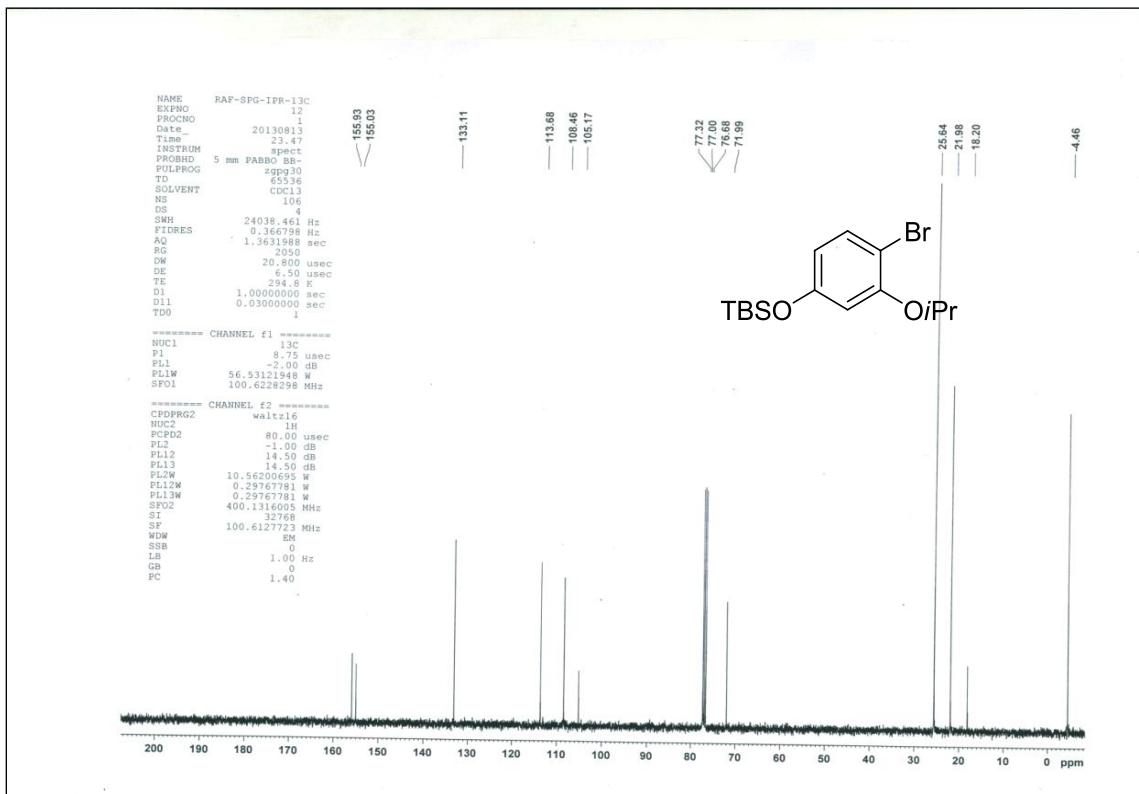
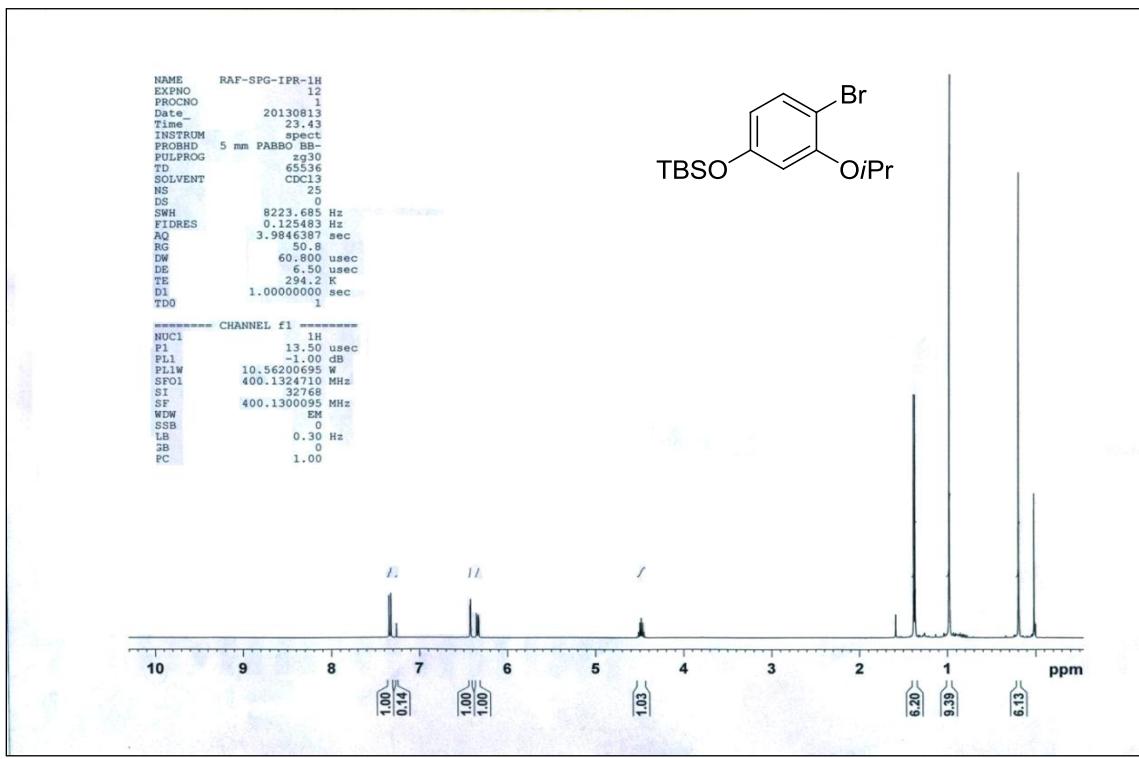
Colorless oil; yield 59%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  = 0.18 (s, 6H), 0.98 (s, 9H), 1.82–1.89 (m, 2H), 2.63 (t,  $J$  = 7.7 Hz, 2H), 3.66 (t,  $J$  = 6.4 Hz, 2H), 6.76 (d,  $J$  = 8.4 Hz, 2H), 7.04 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = −4.5, 18.2, 25.7, 31.2, 34.3, 62.3, 119.9, 129.2, 134.4, 153.7.

**References:**

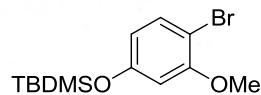
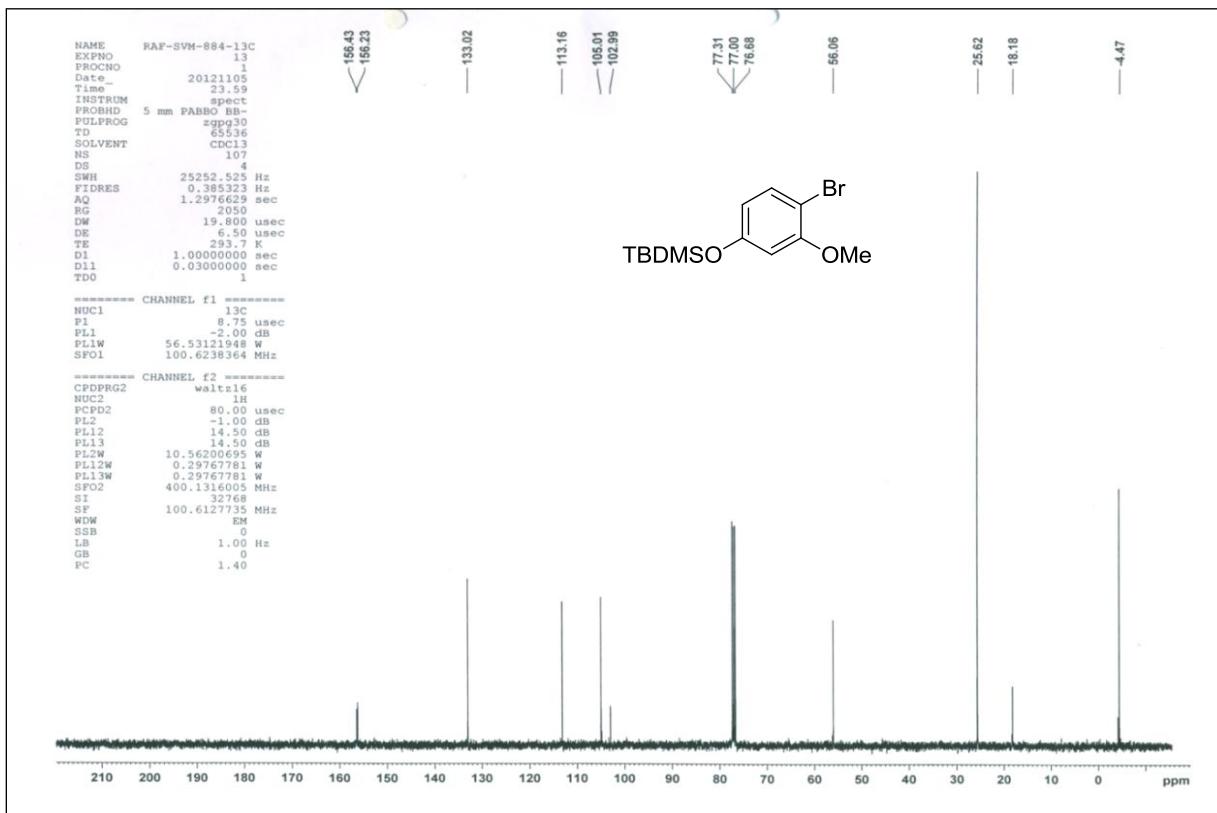
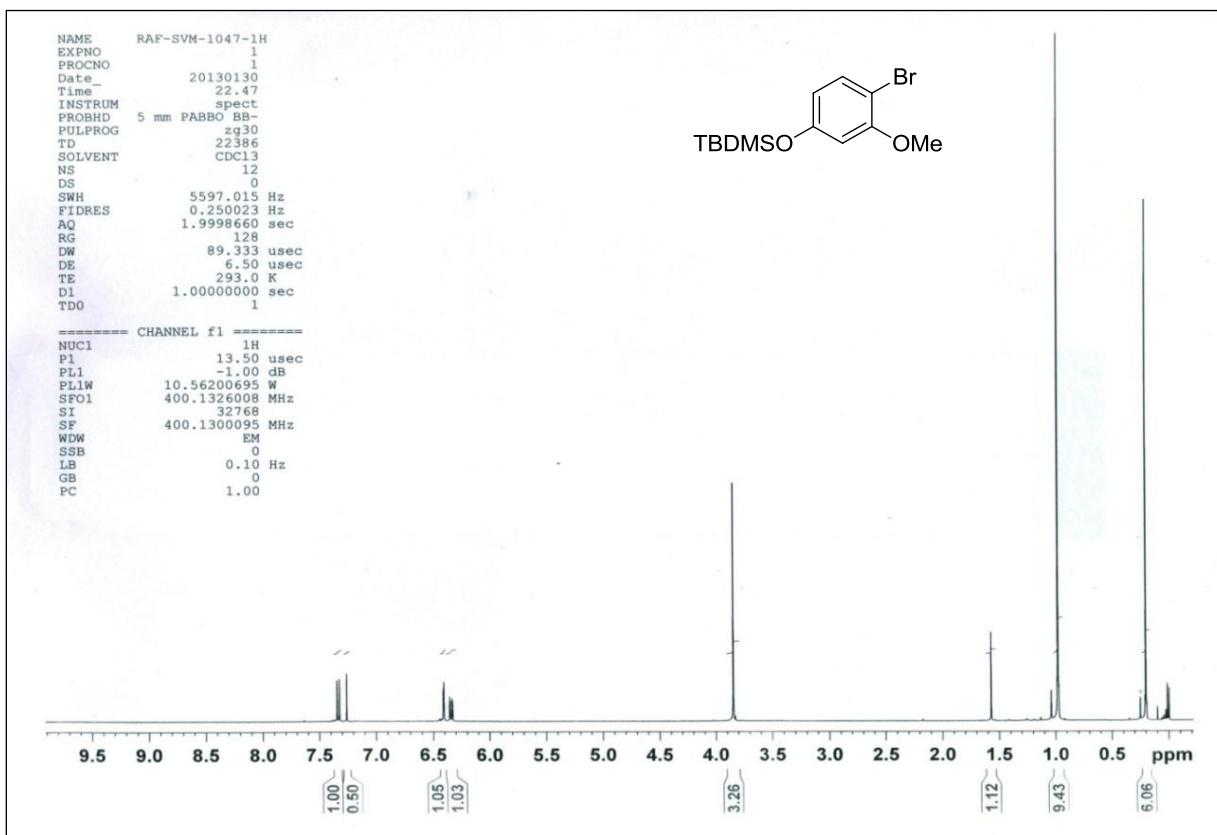
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## NMR Spectra:

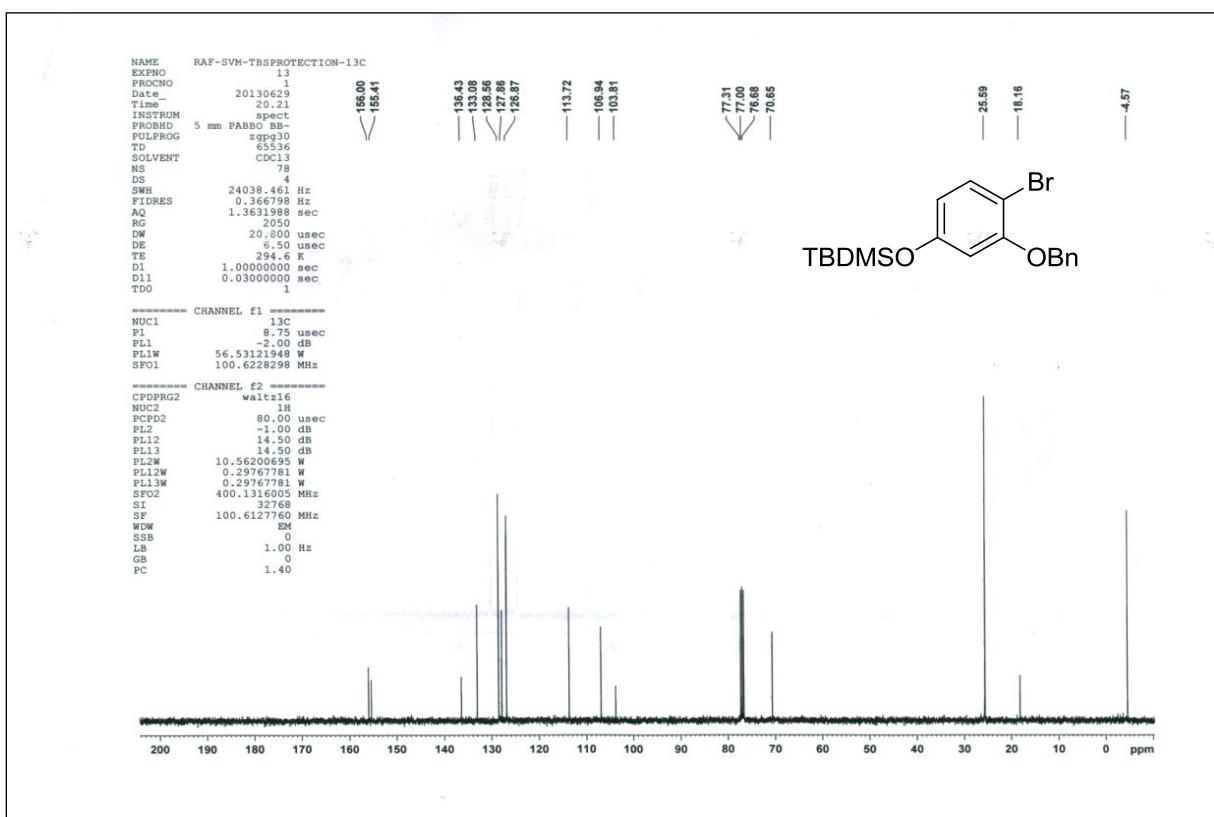
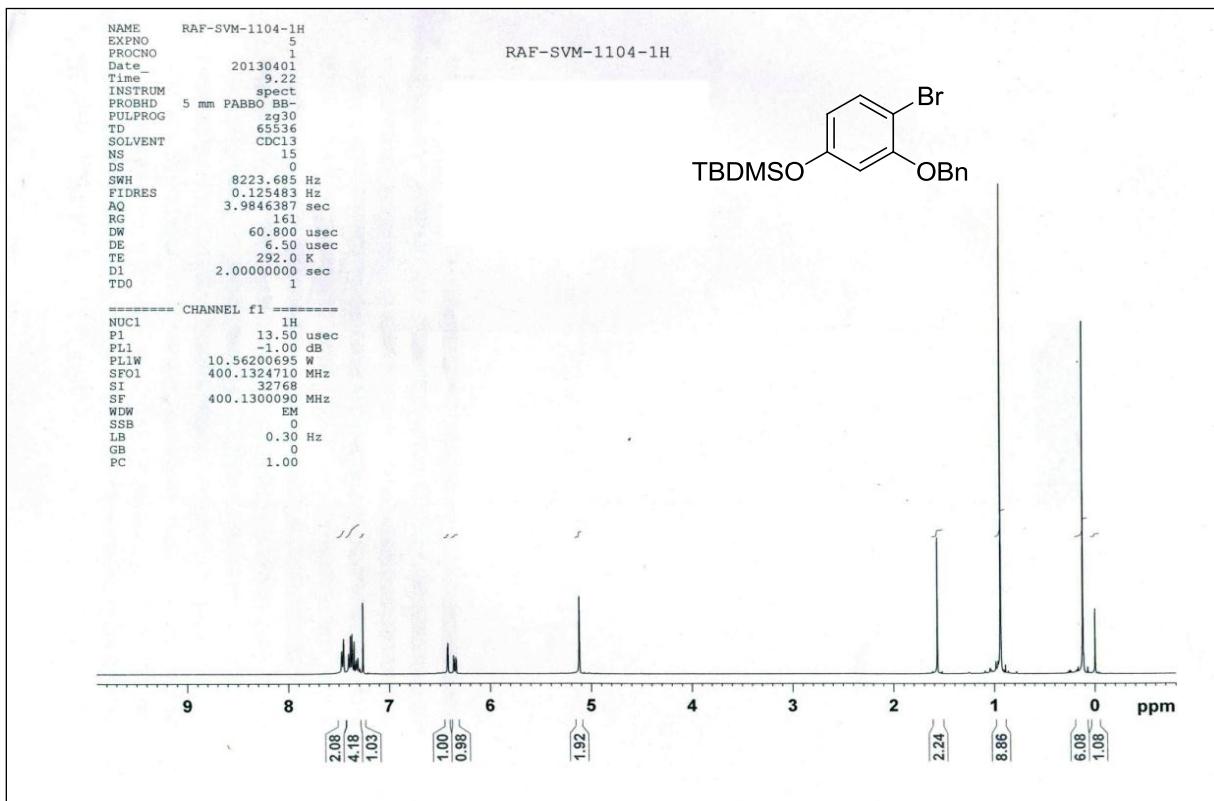
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4a**



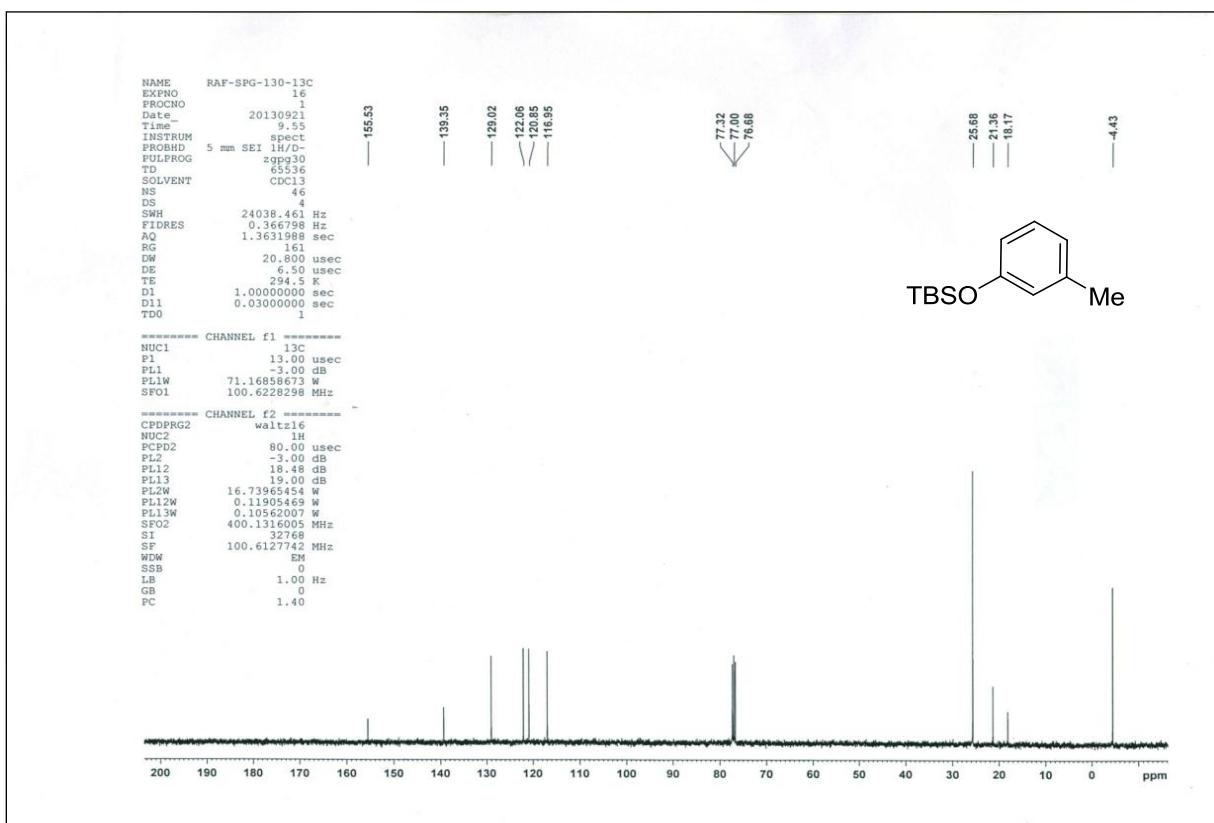
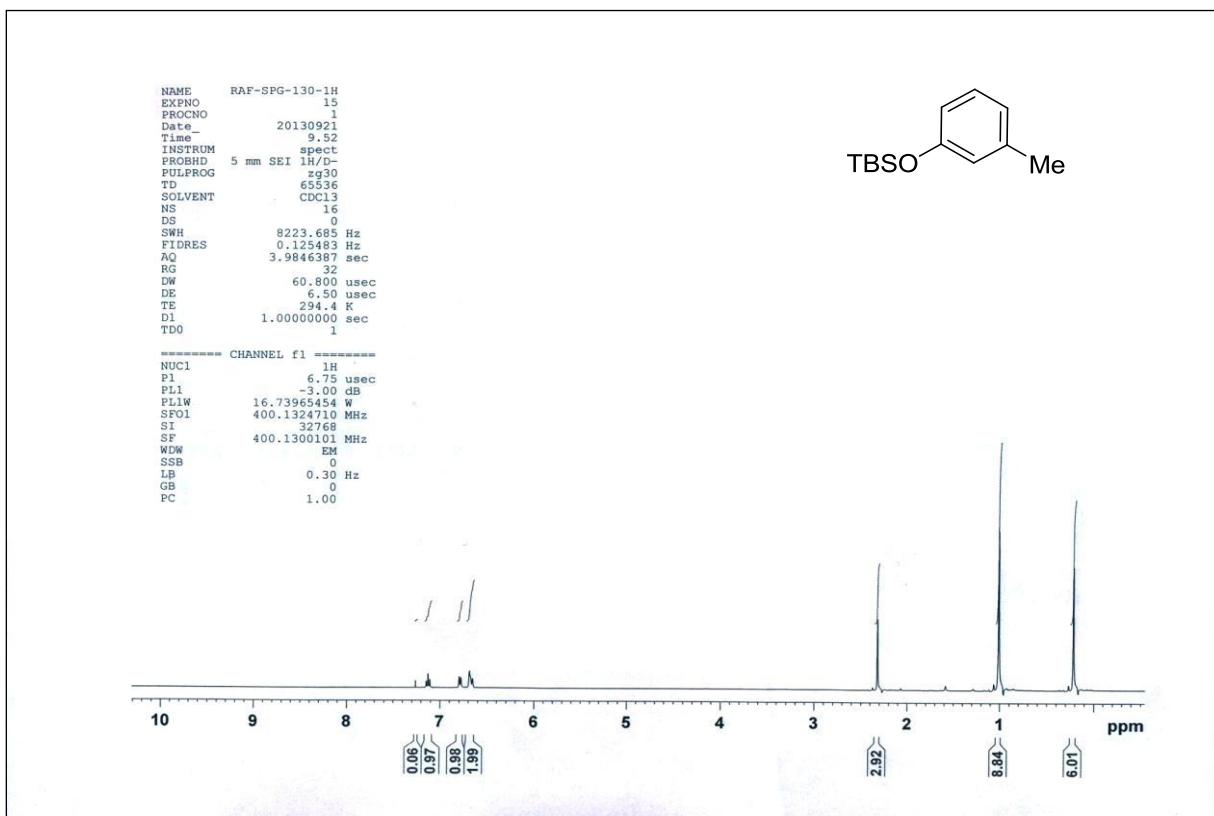
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4b**



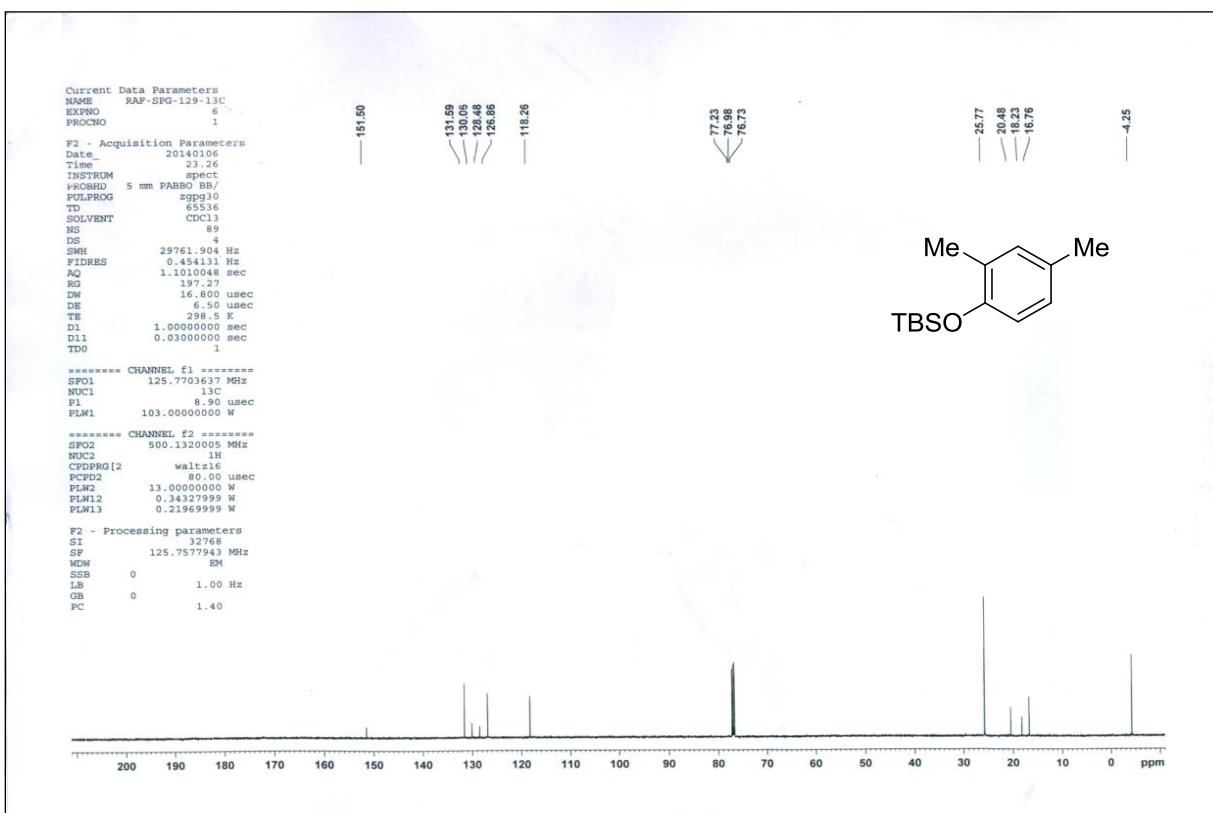
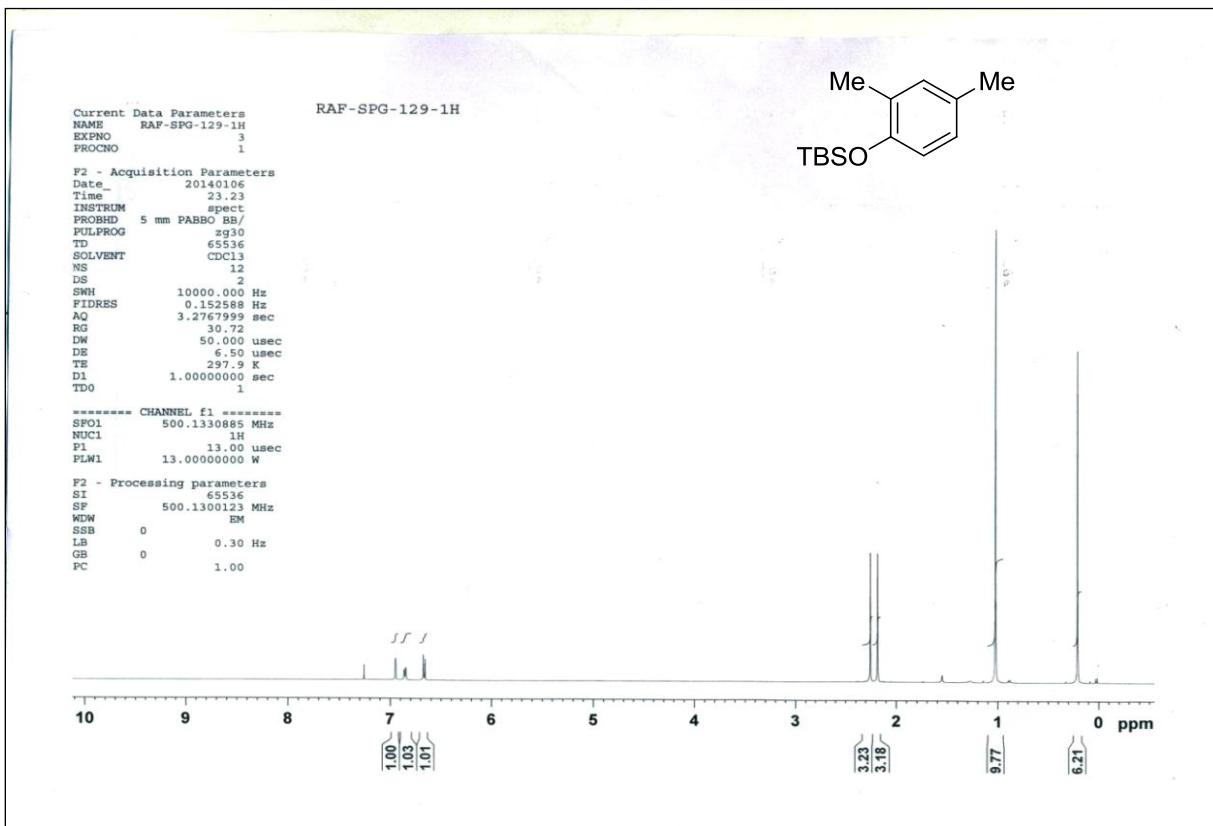
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4c**



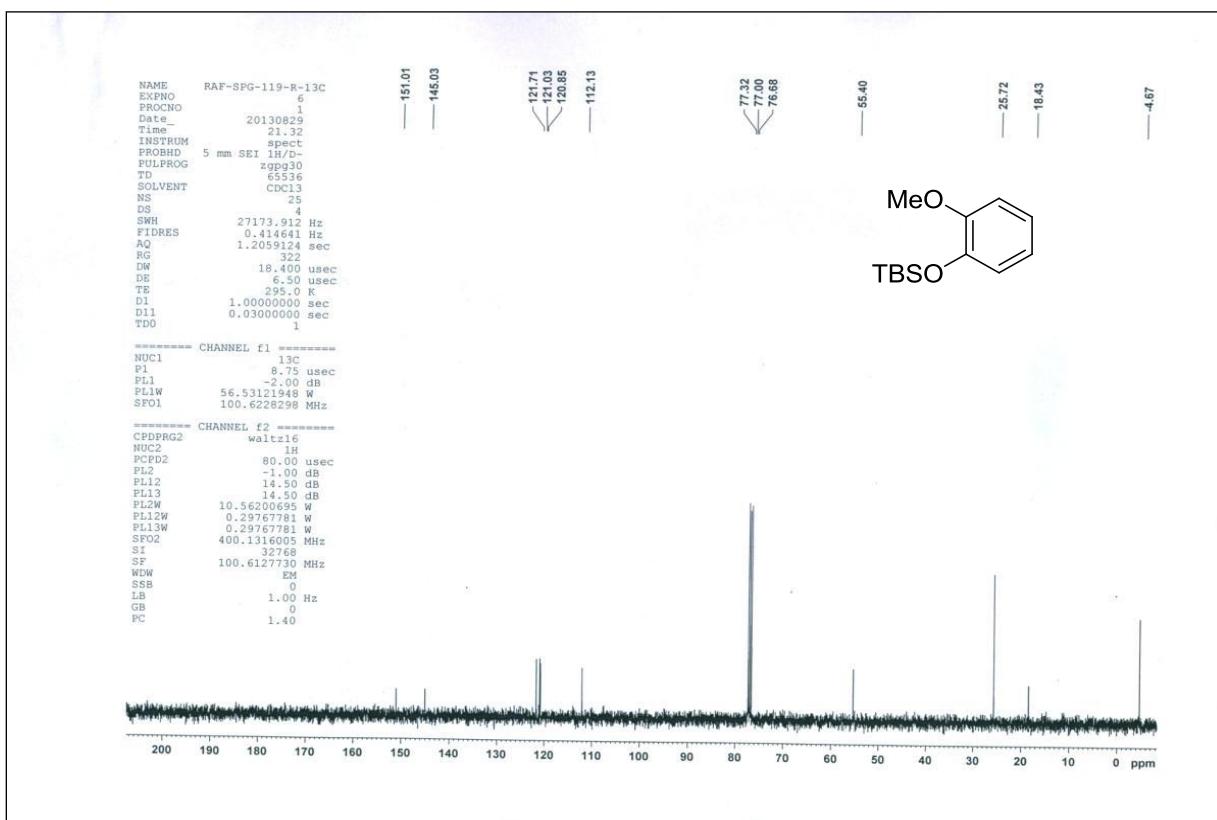
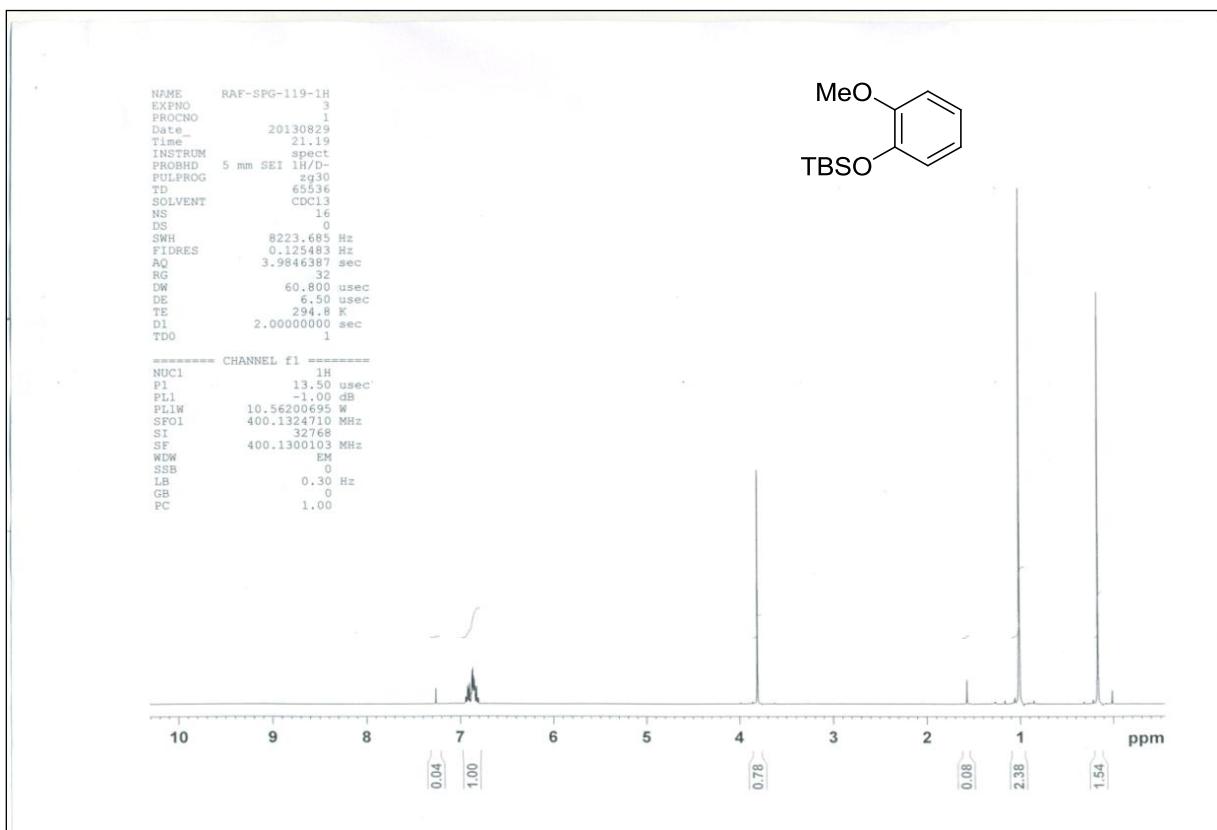
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4d**



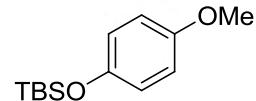
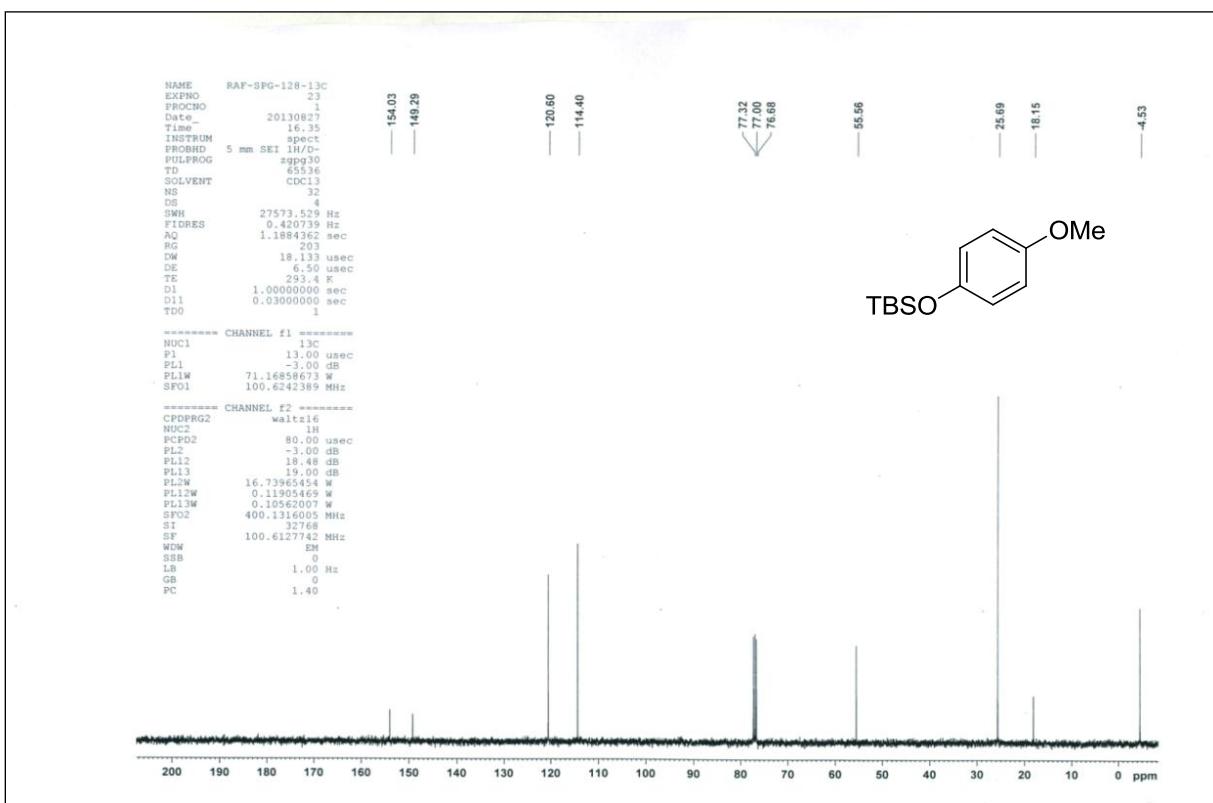
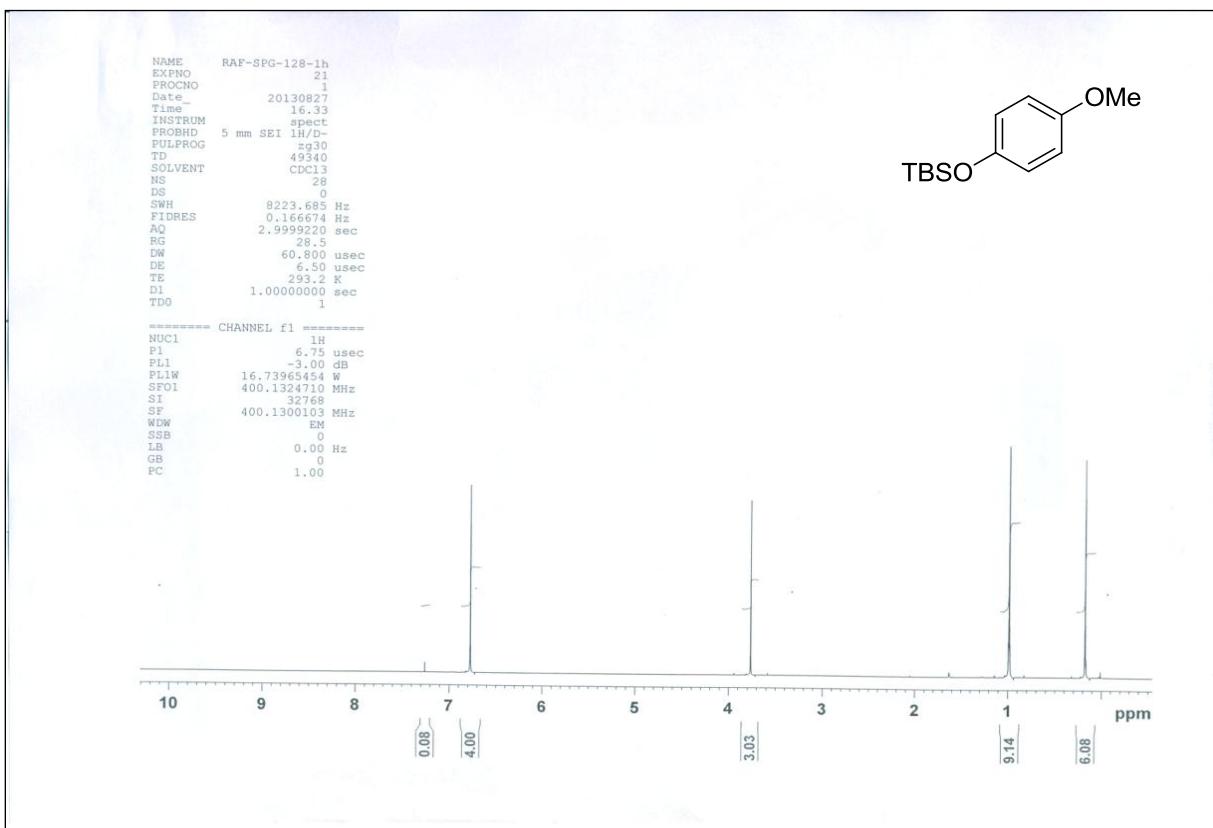
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **4e**



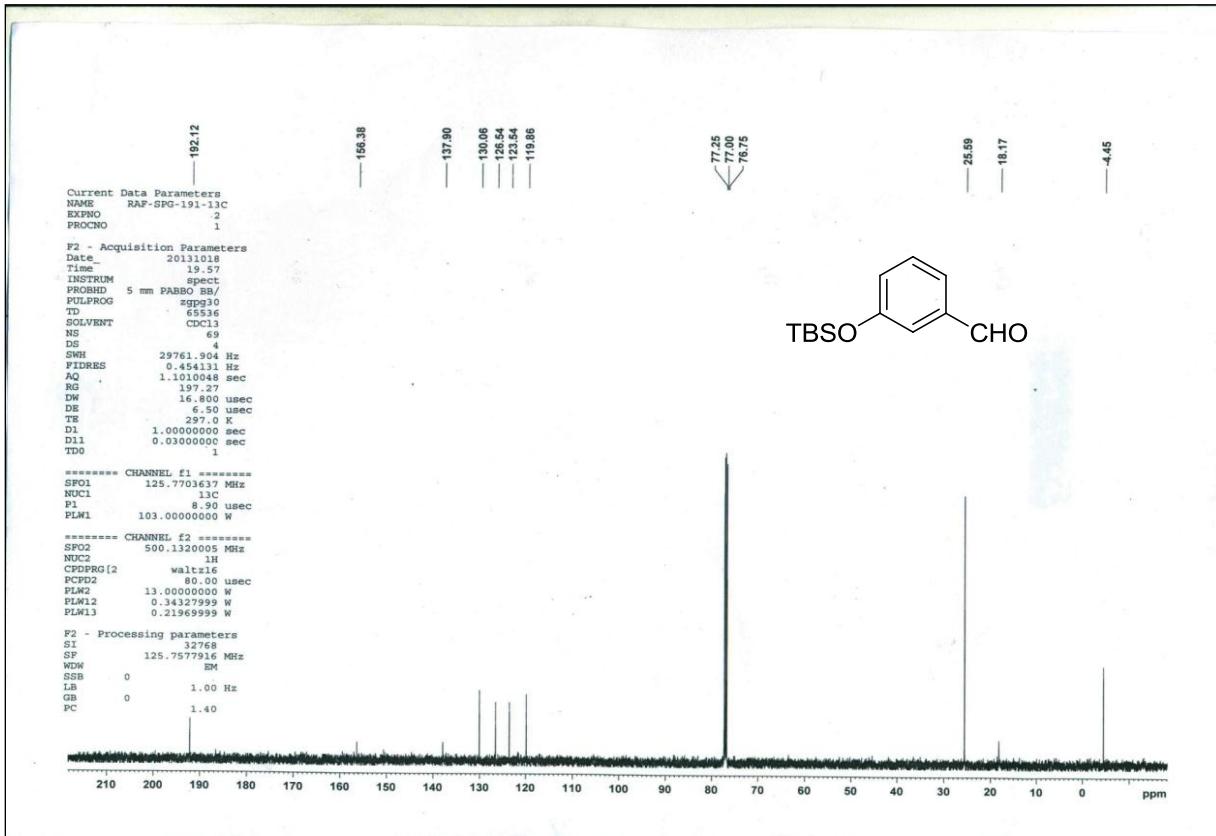
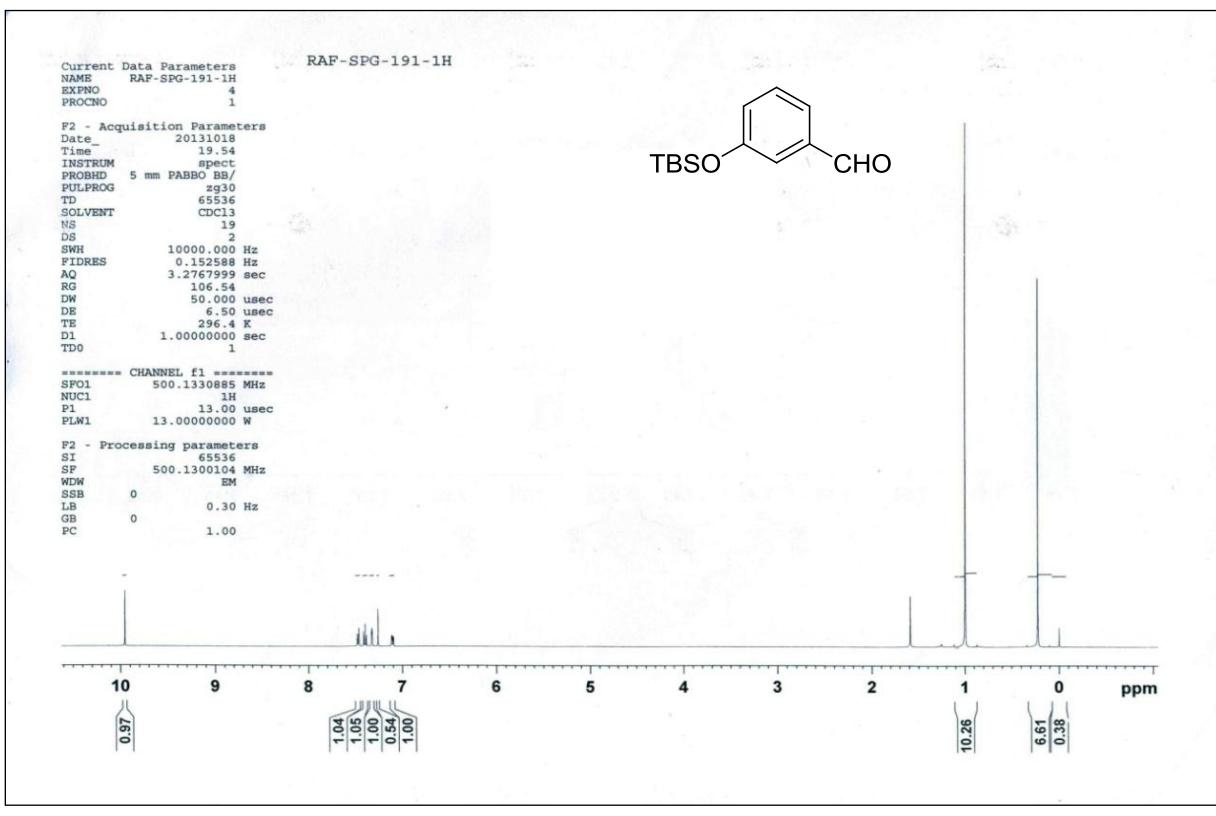
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 4f



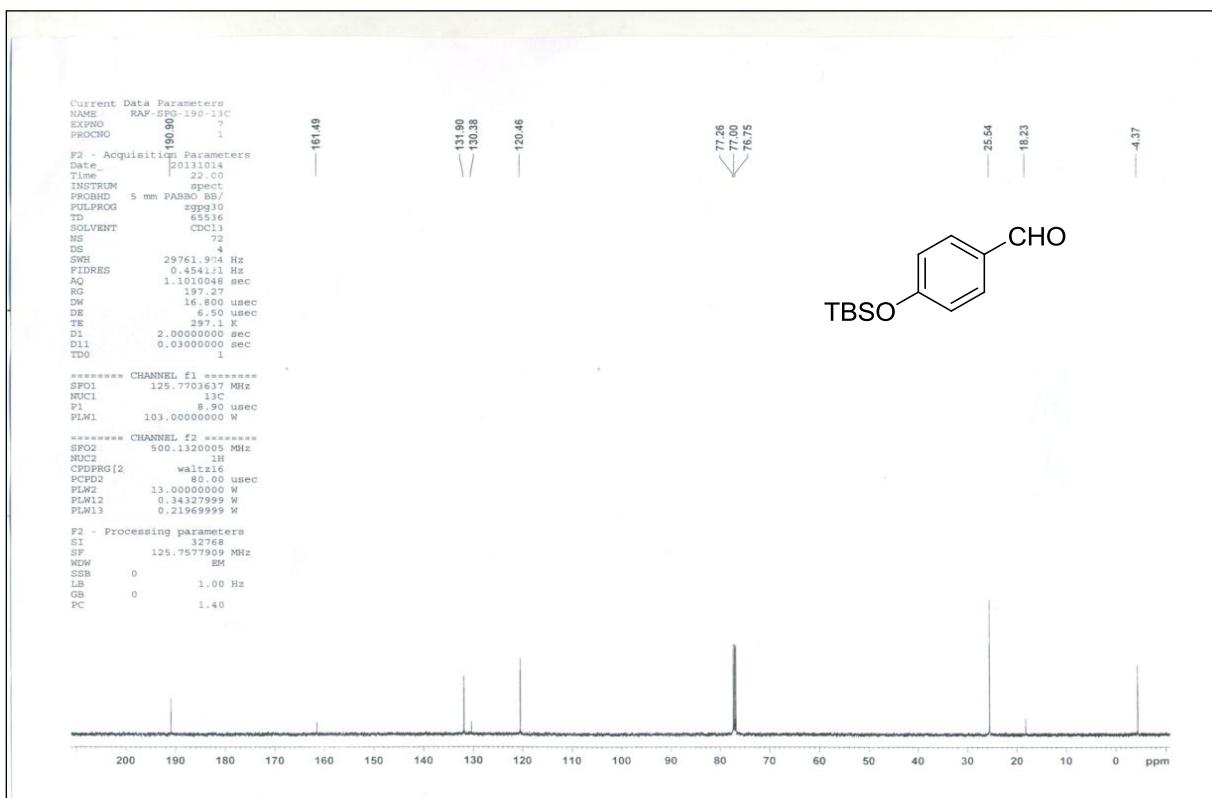
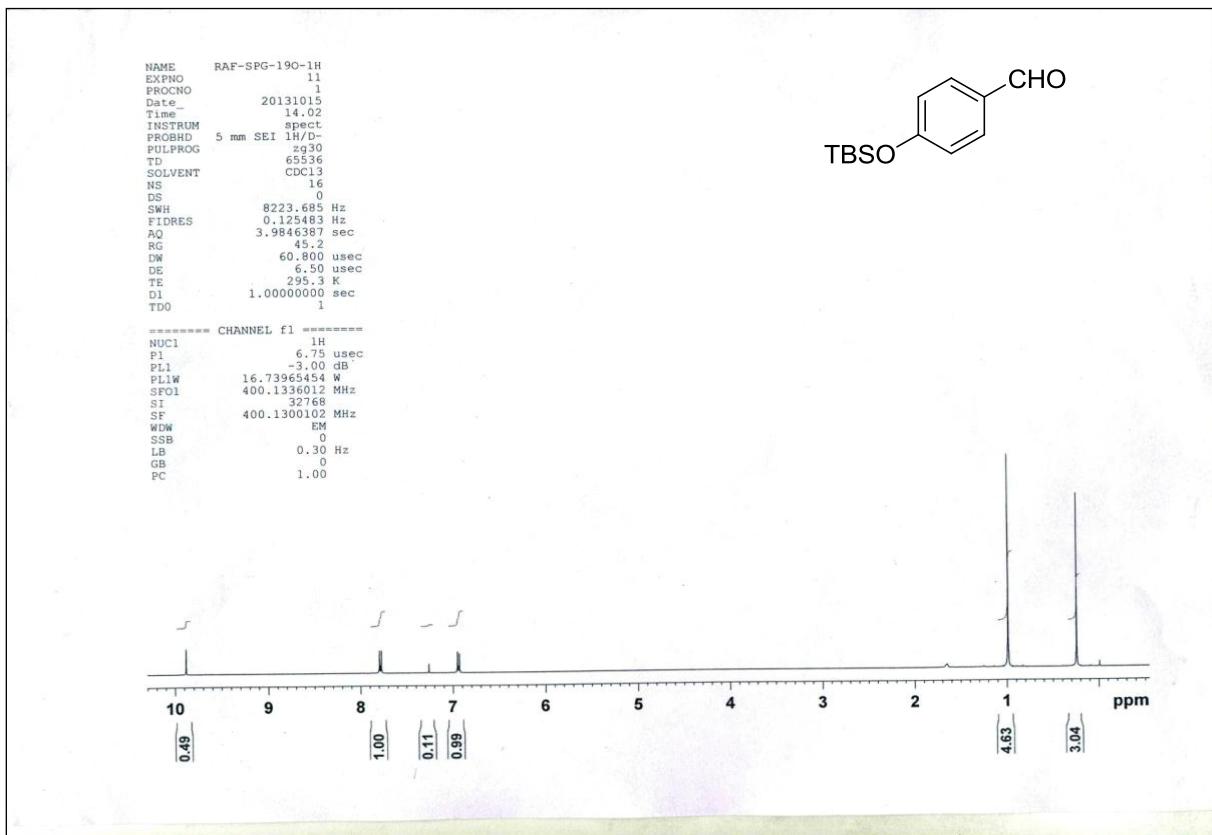
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 4g



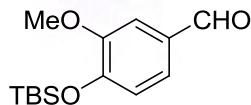
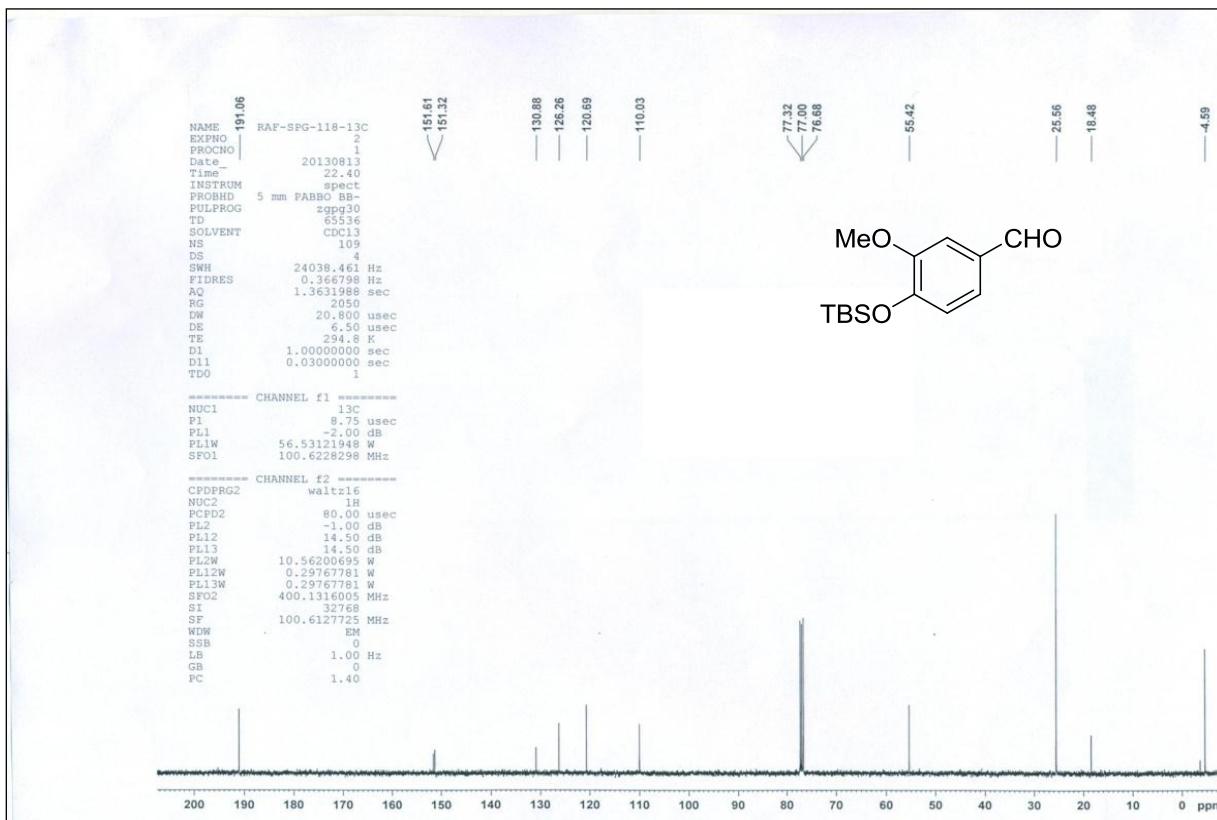
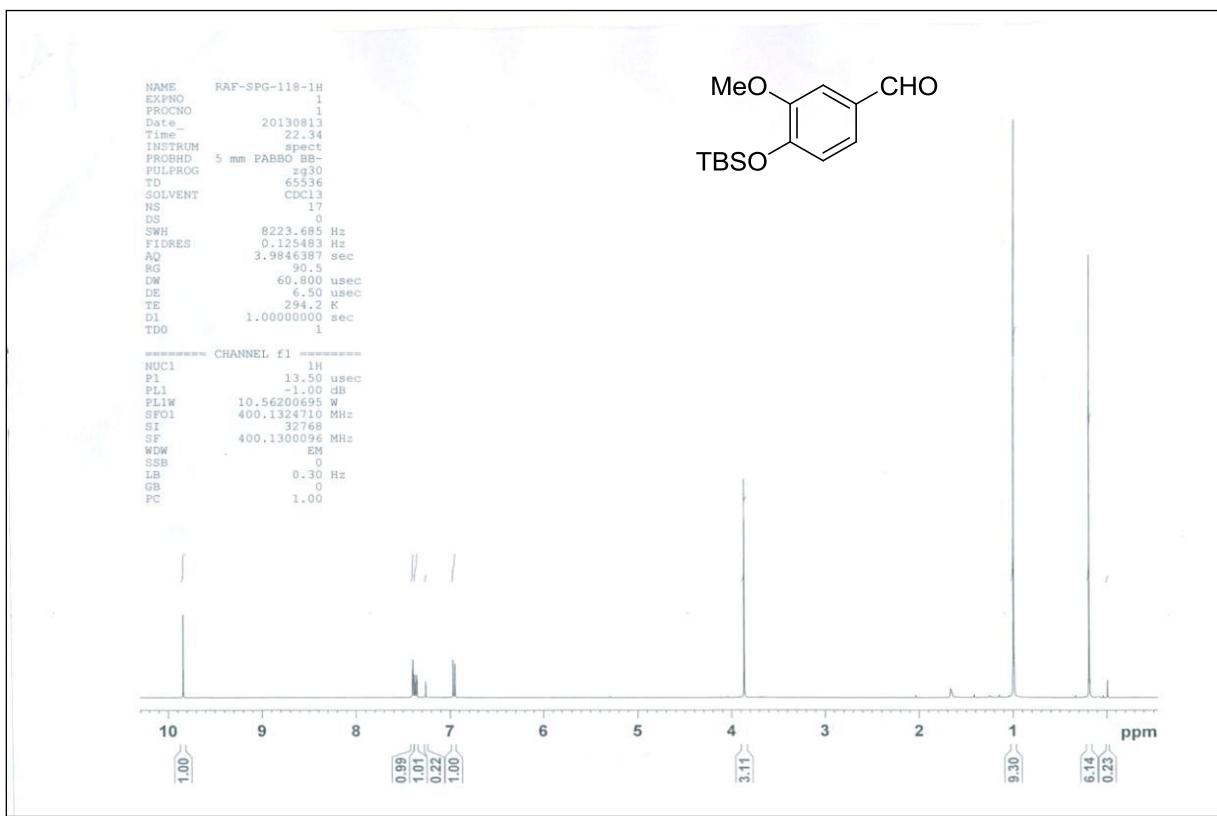
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **4h**



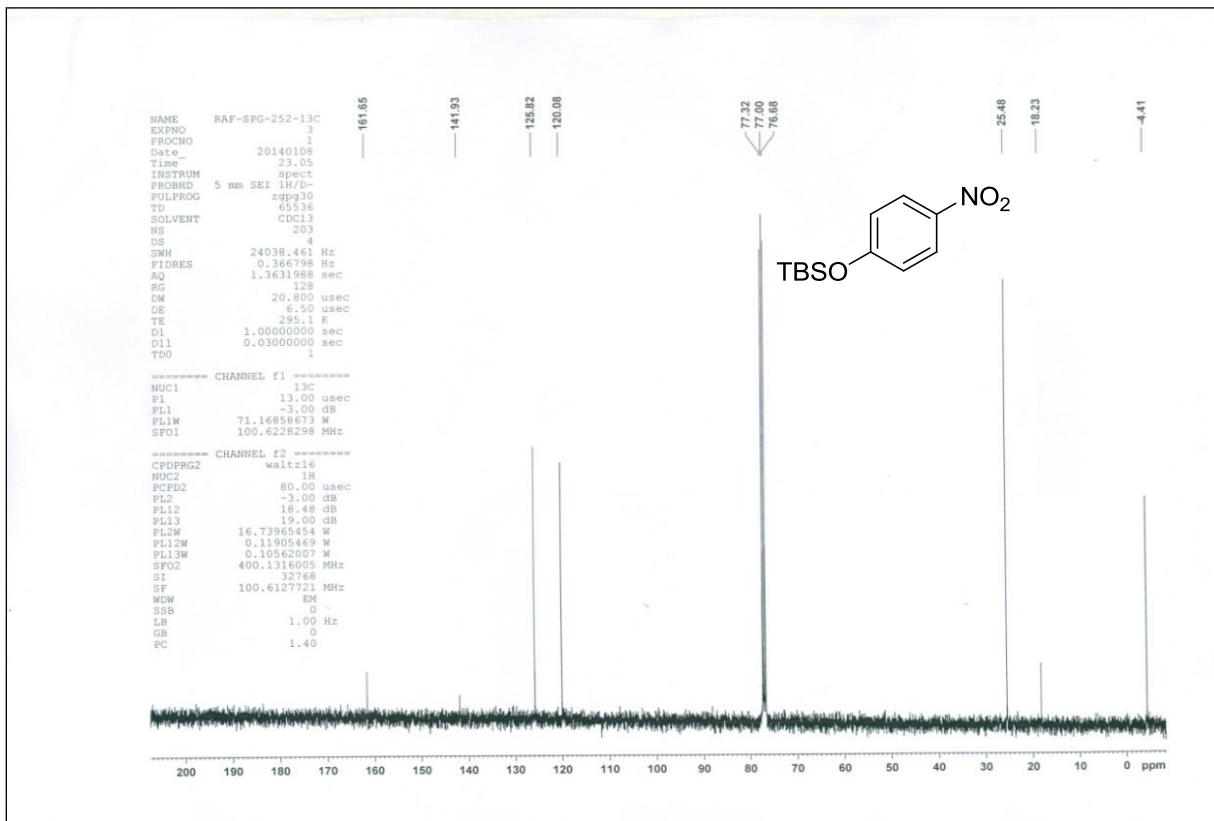
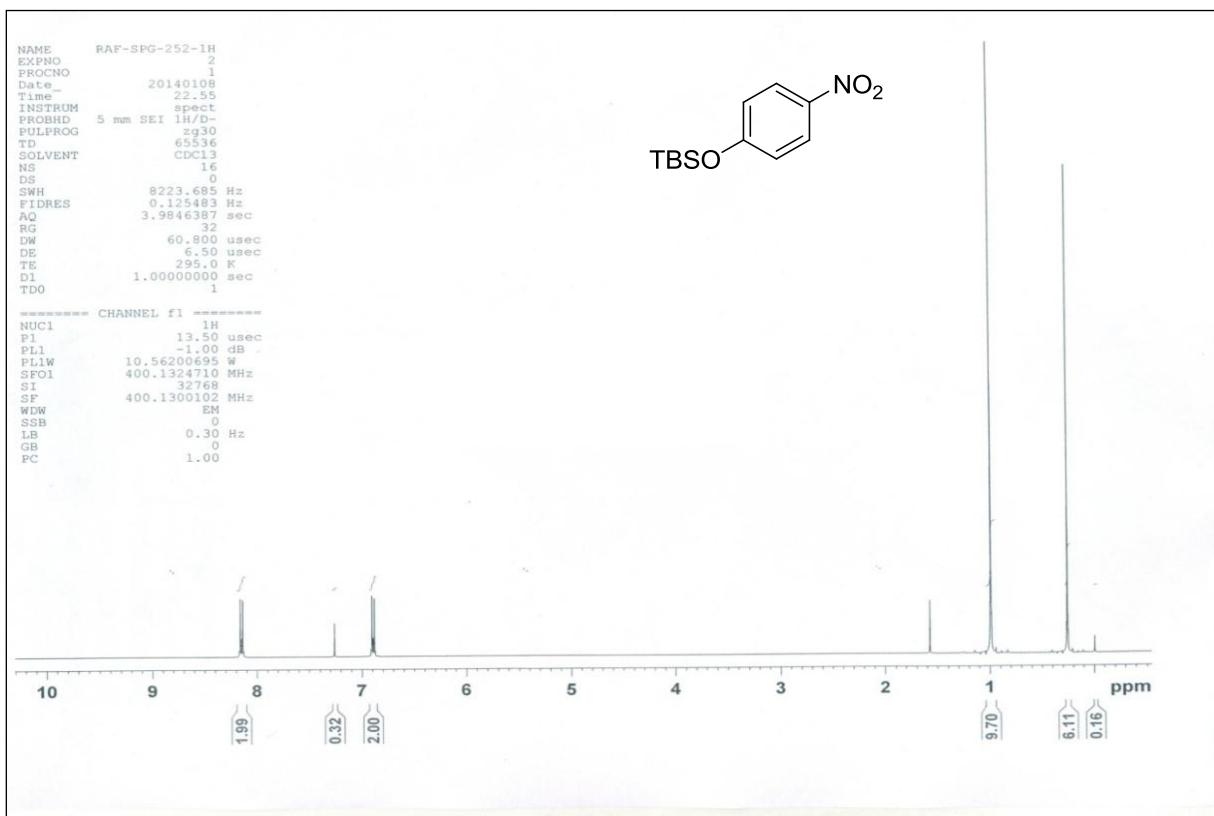
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **4i**



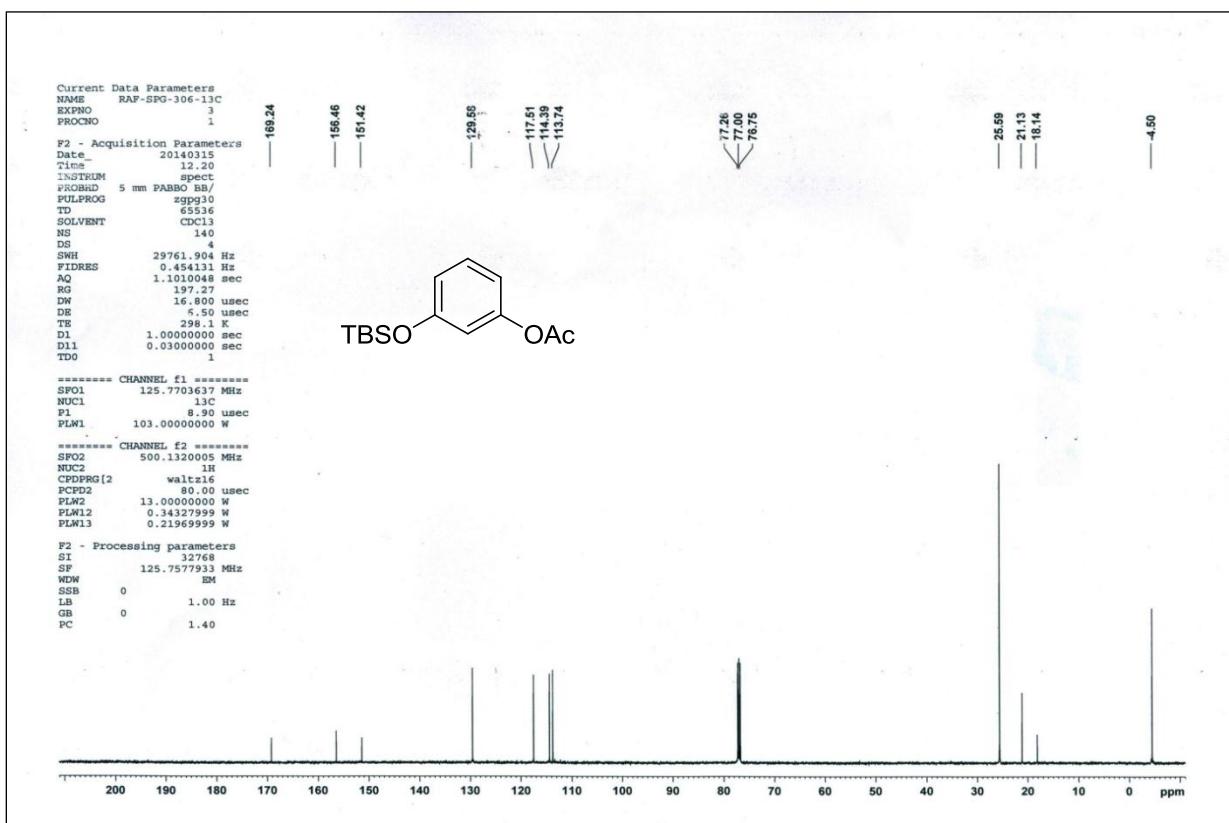
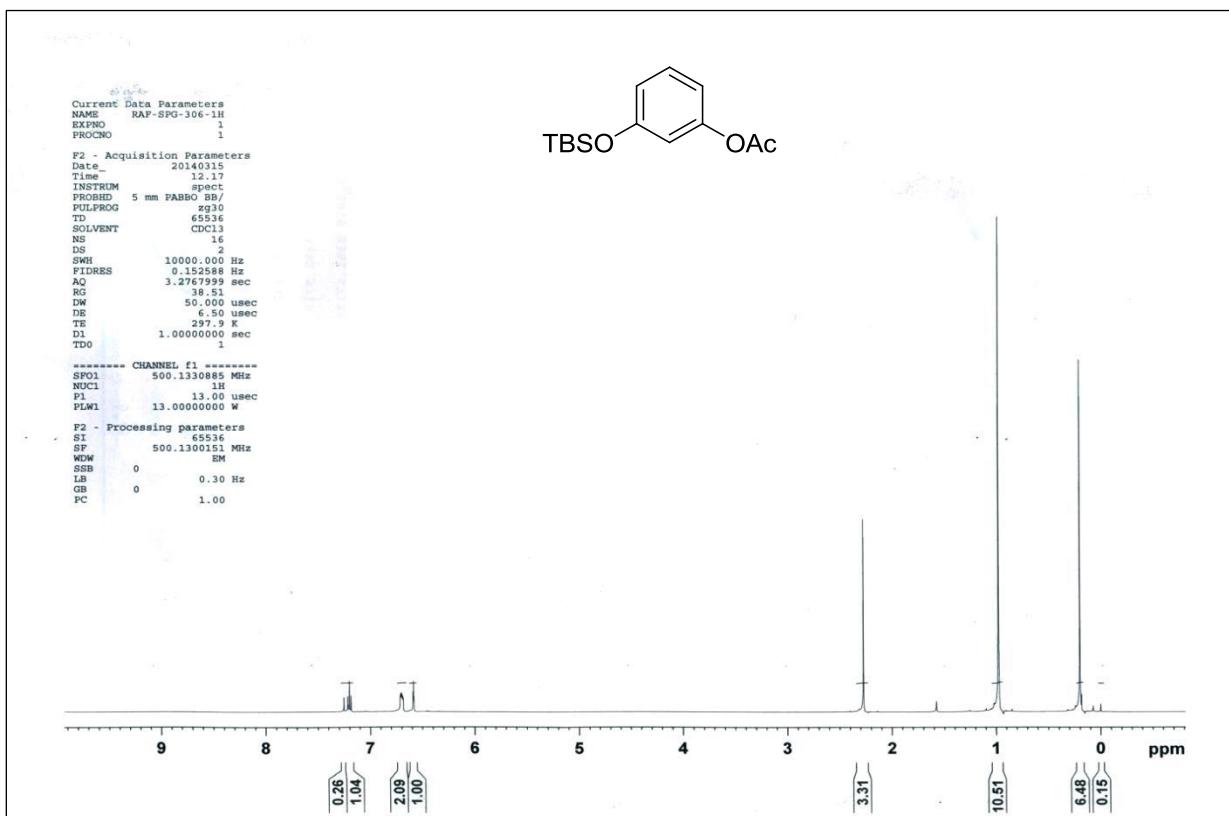
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4j**



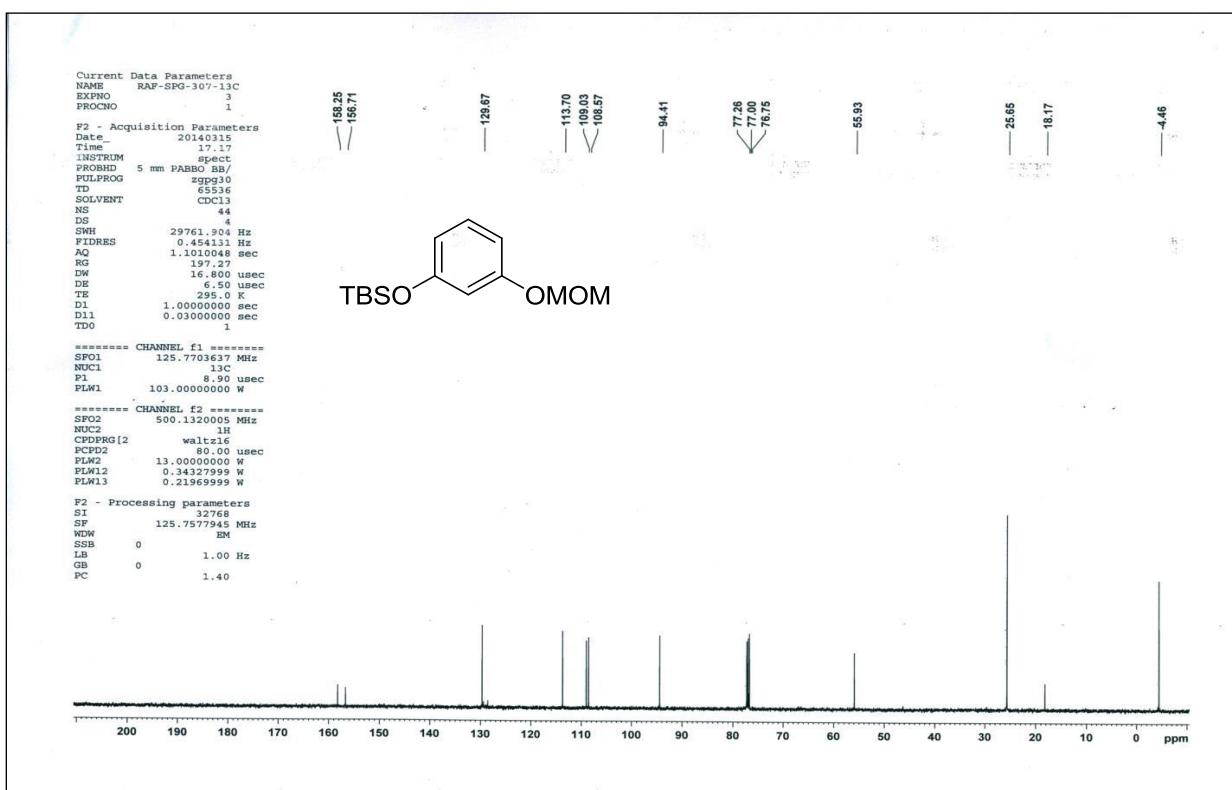
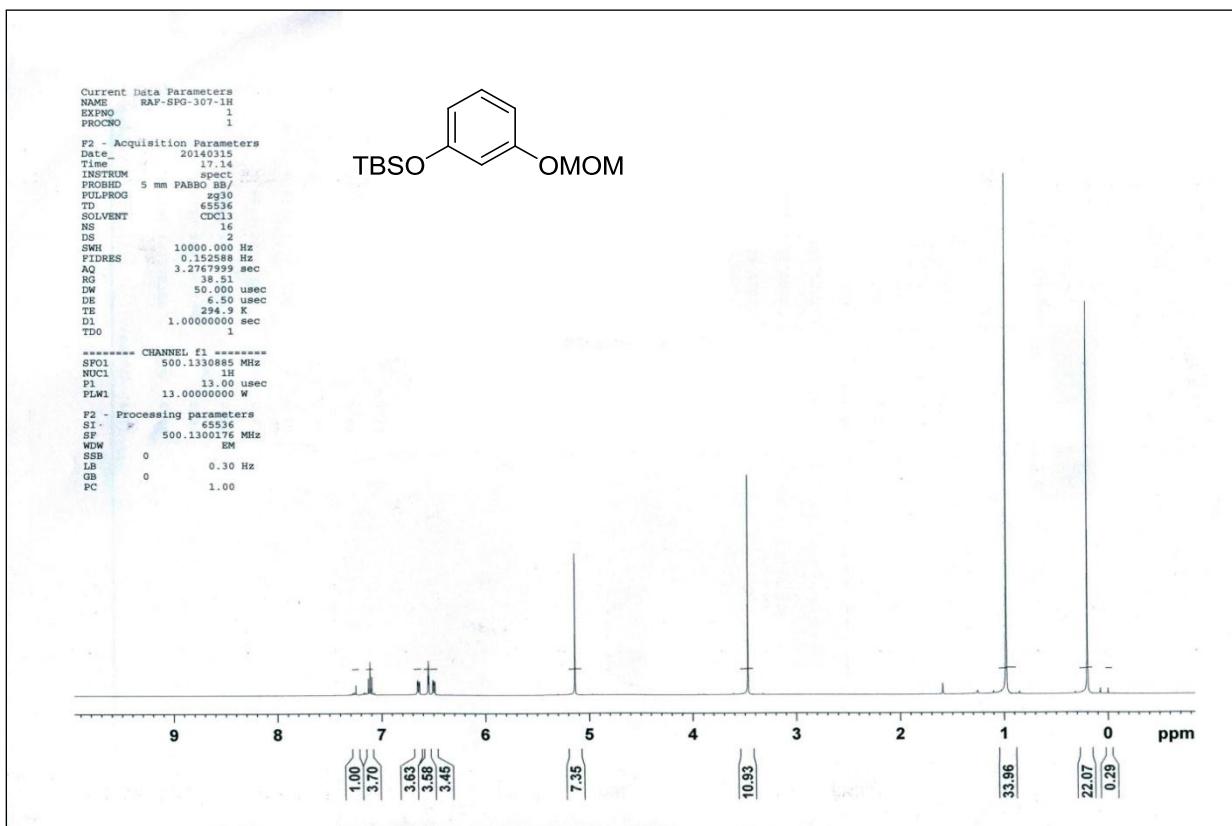
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4k**



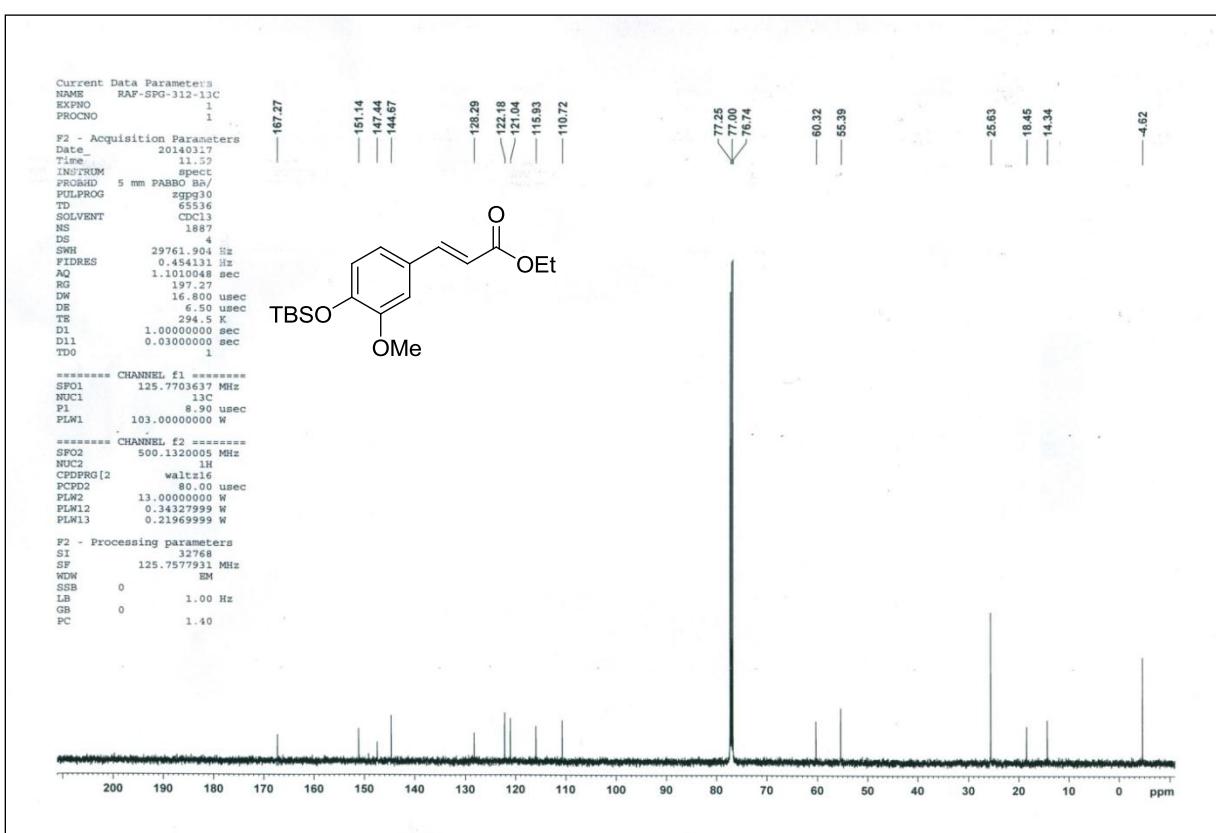
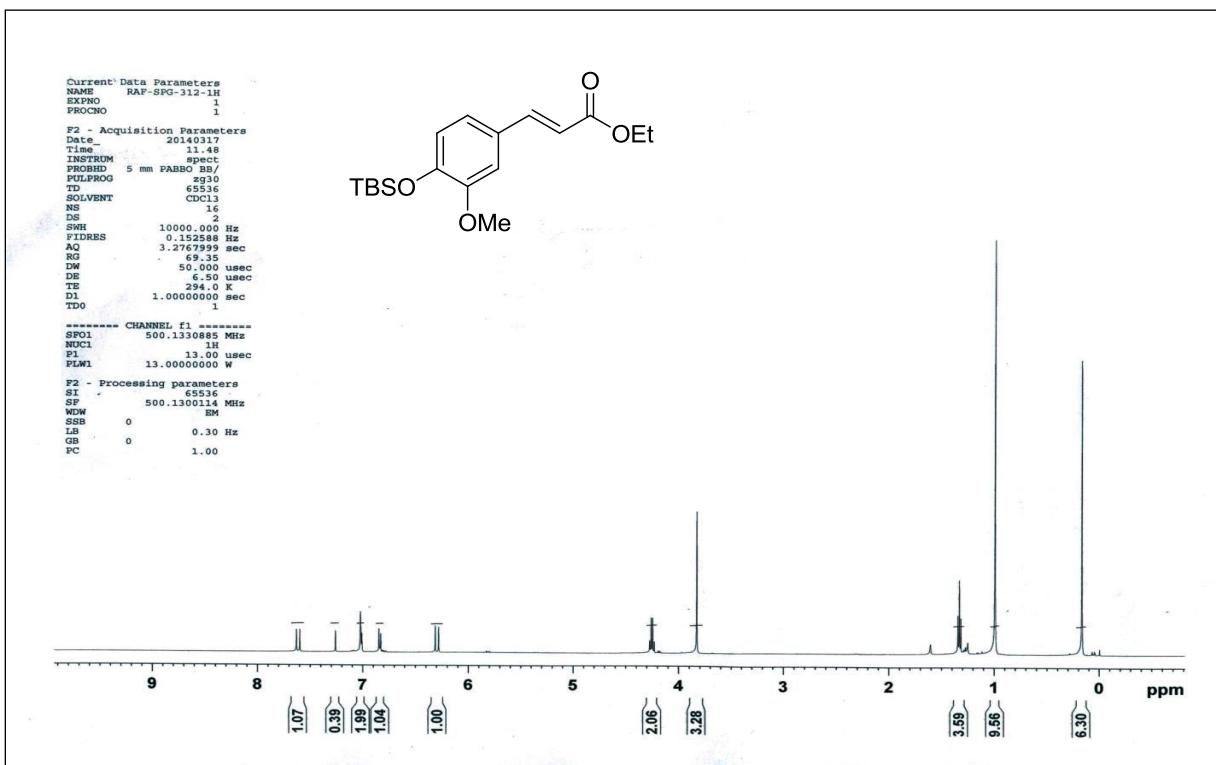
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound 4l



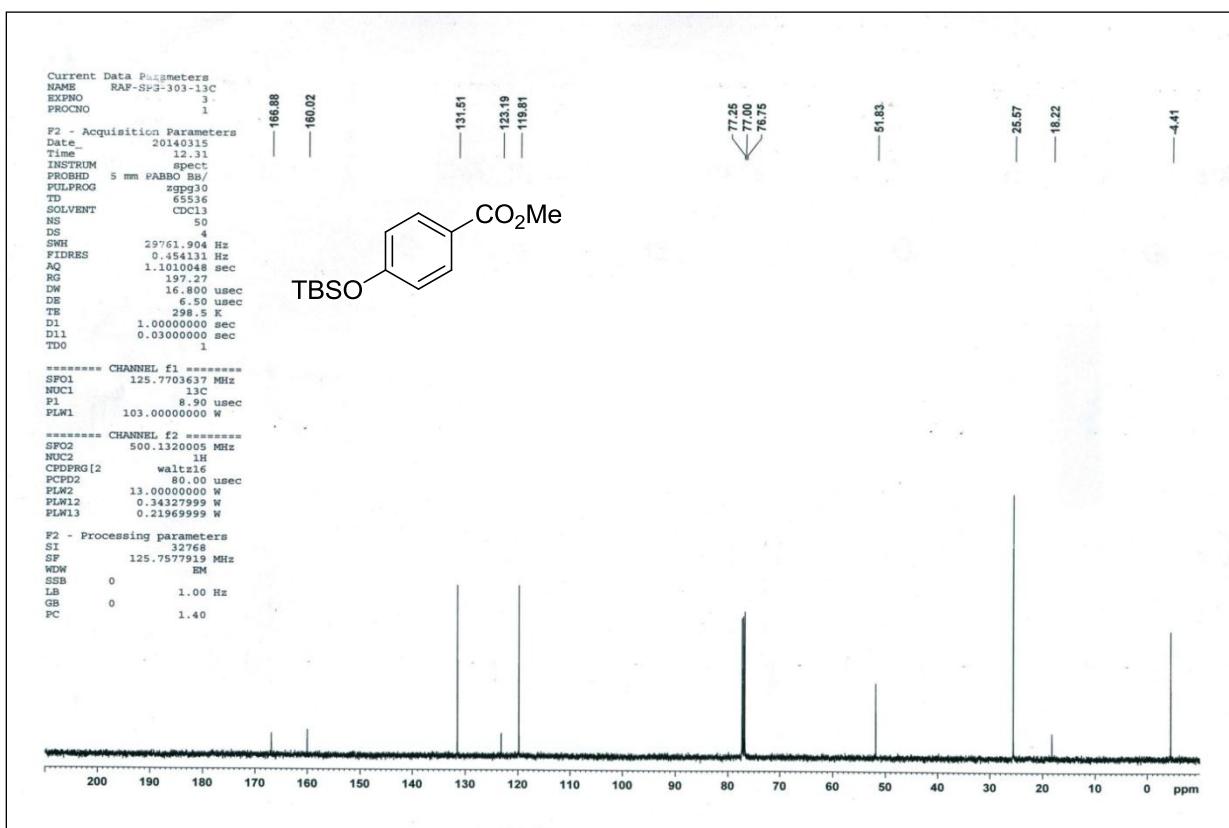
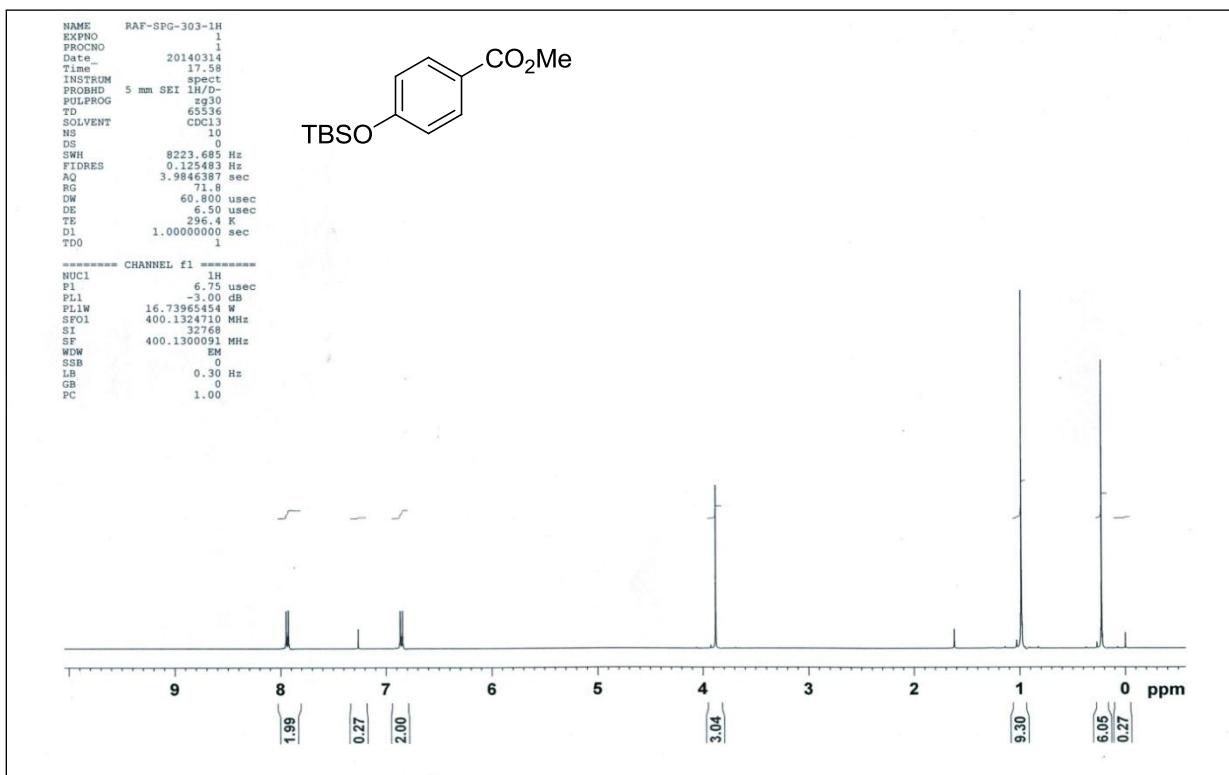
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **4m**



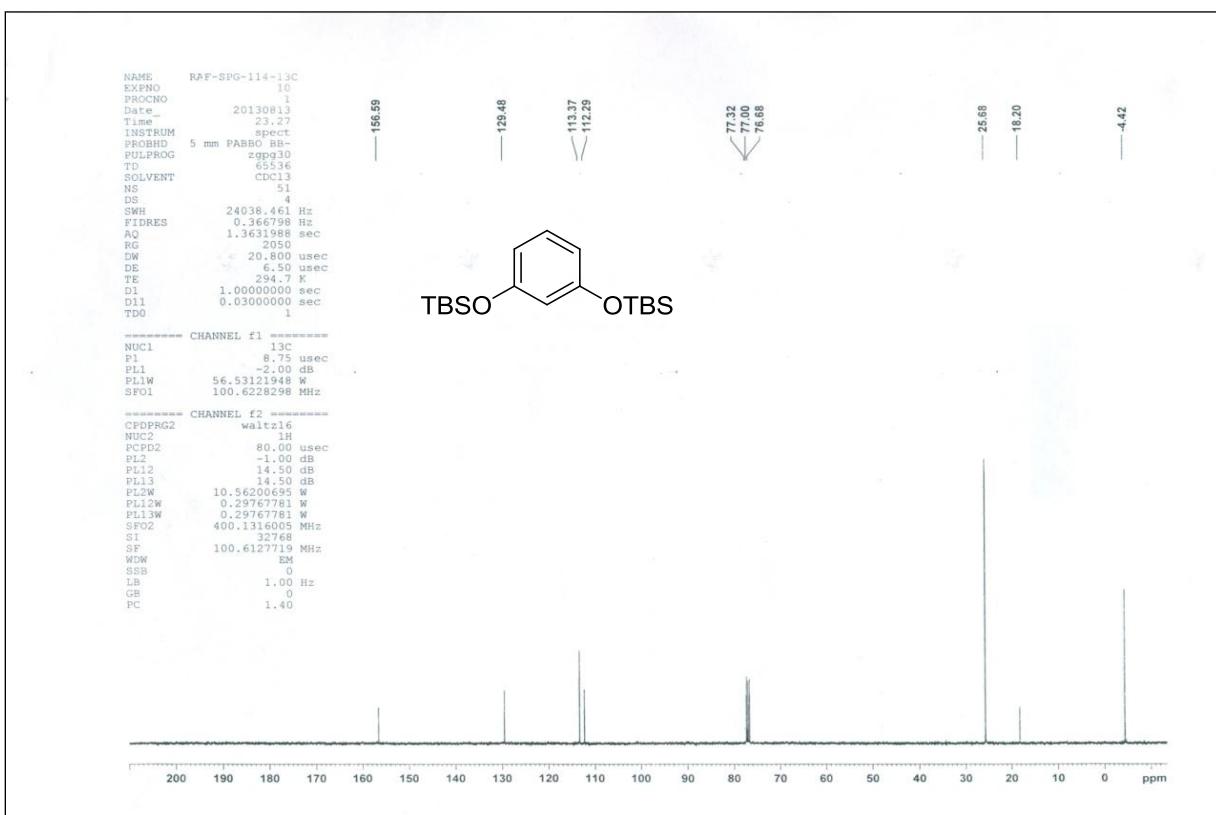
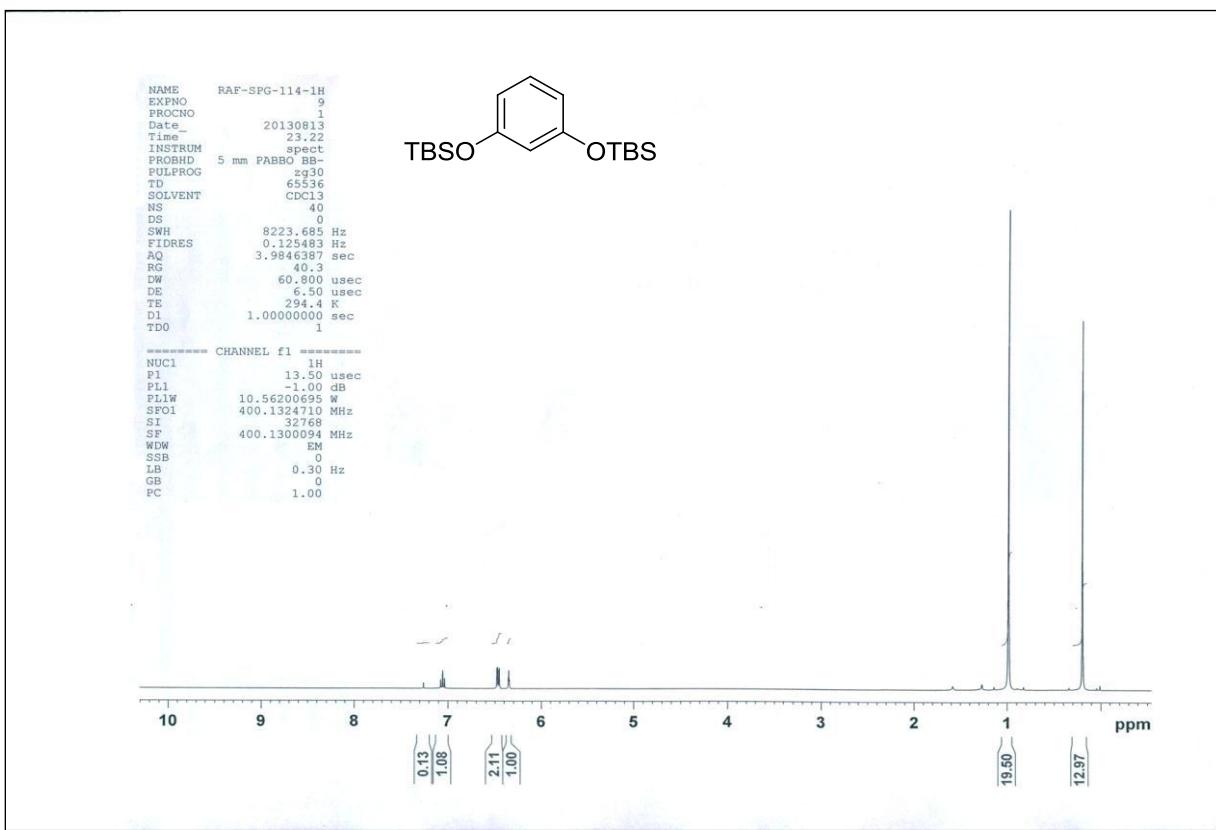
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound 4n



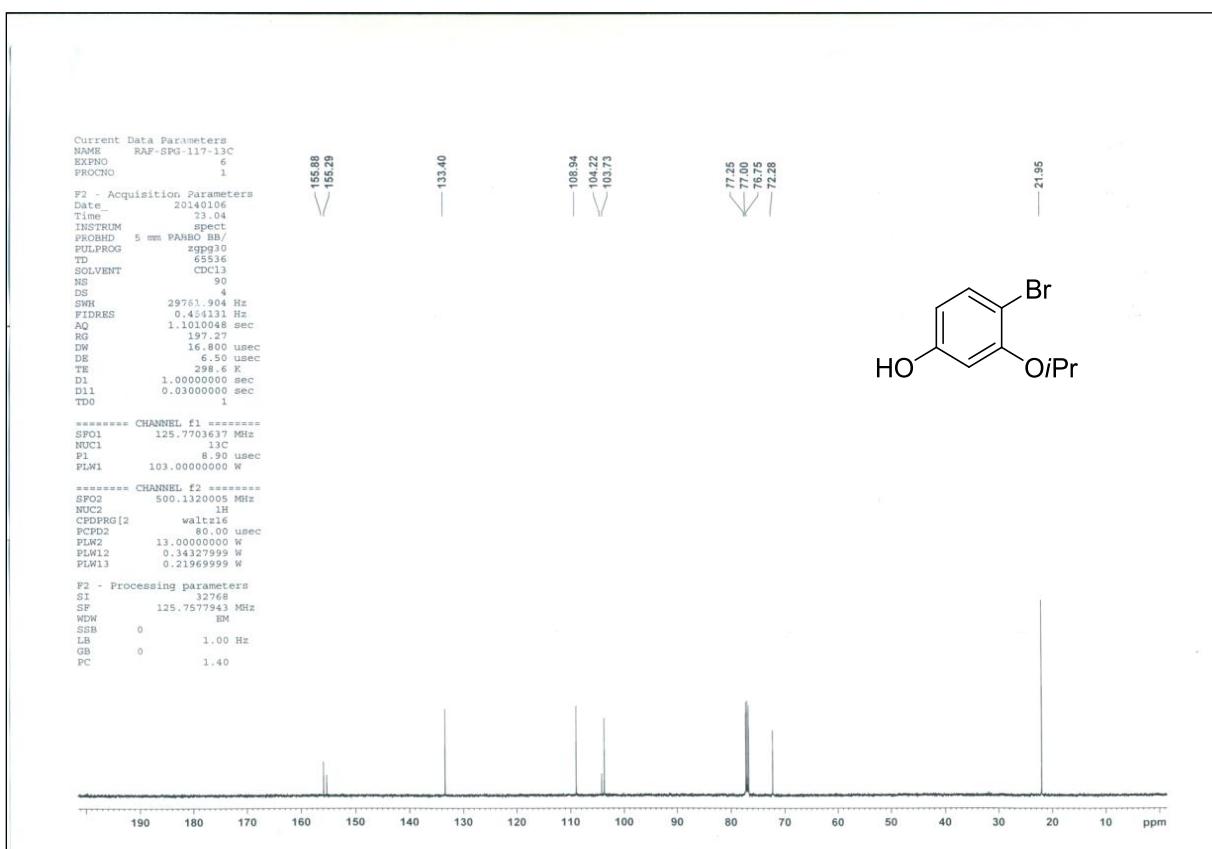
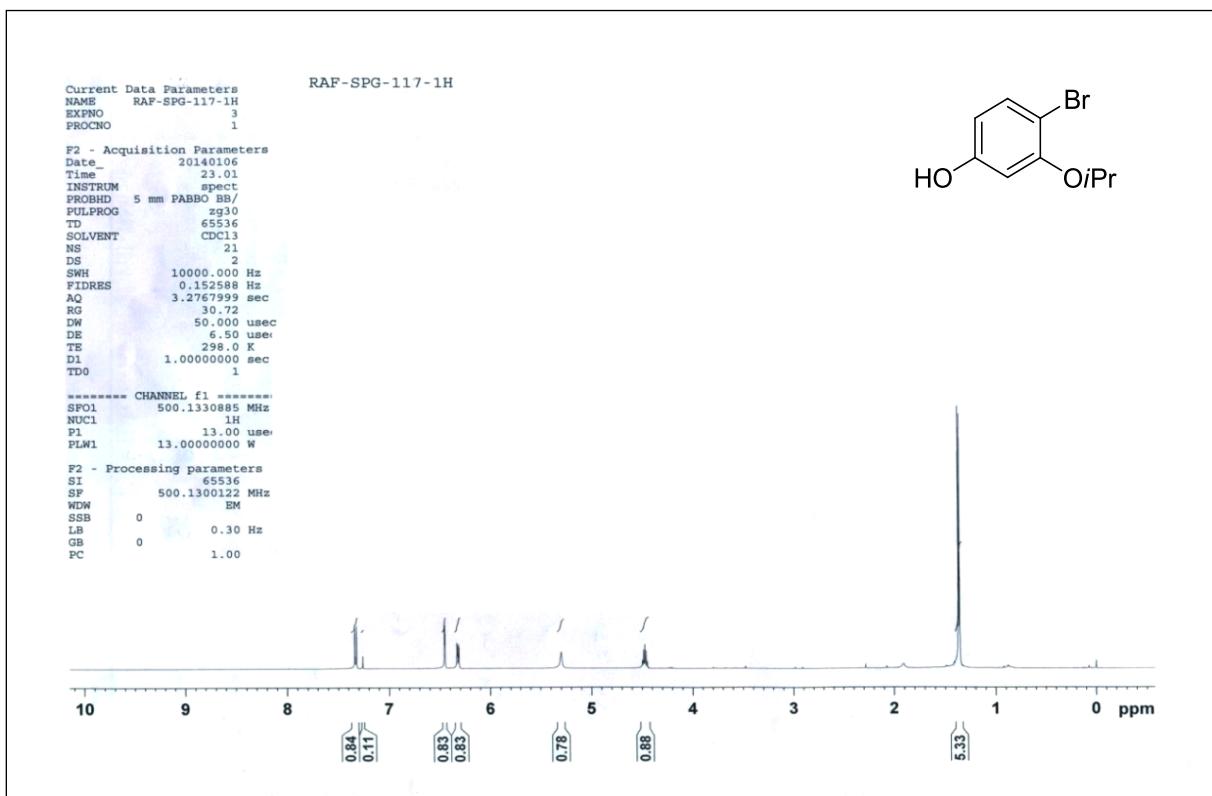
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **4o**



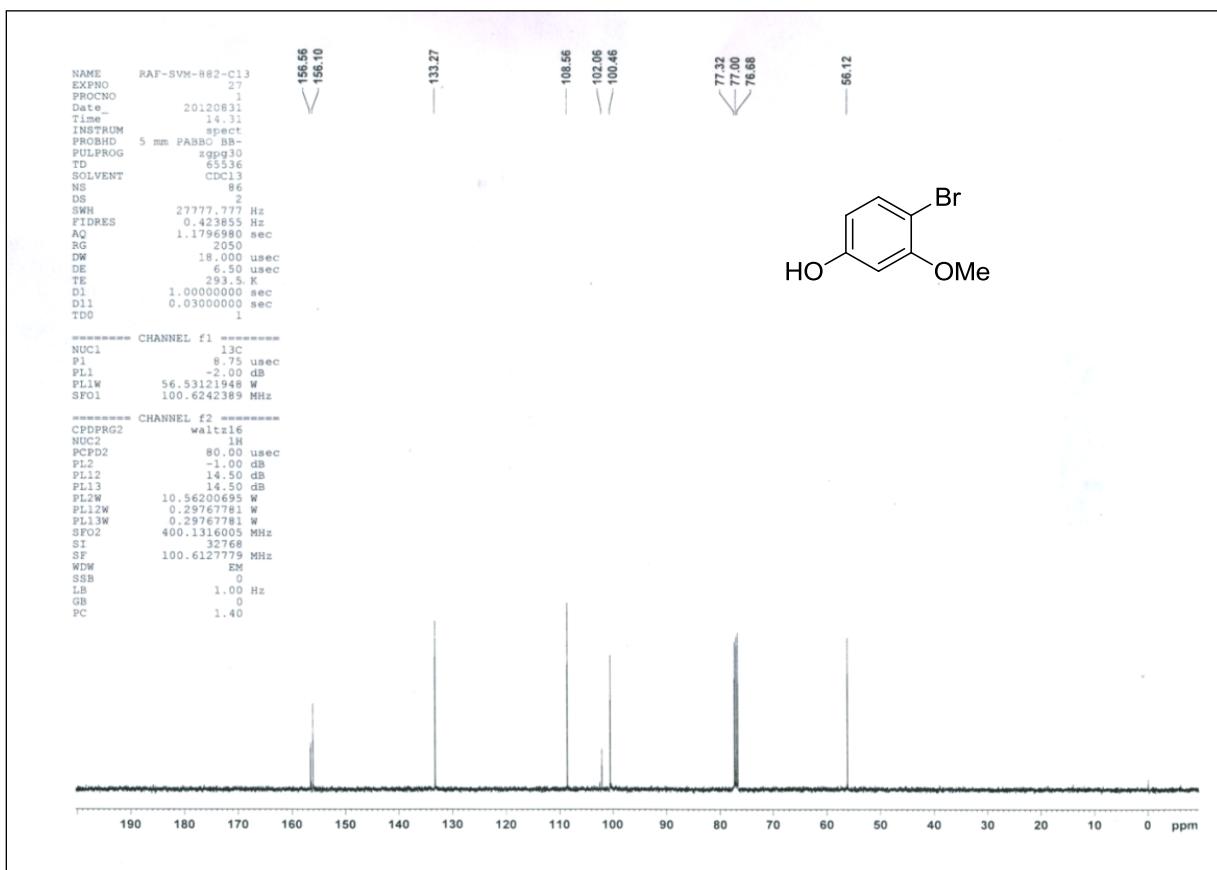
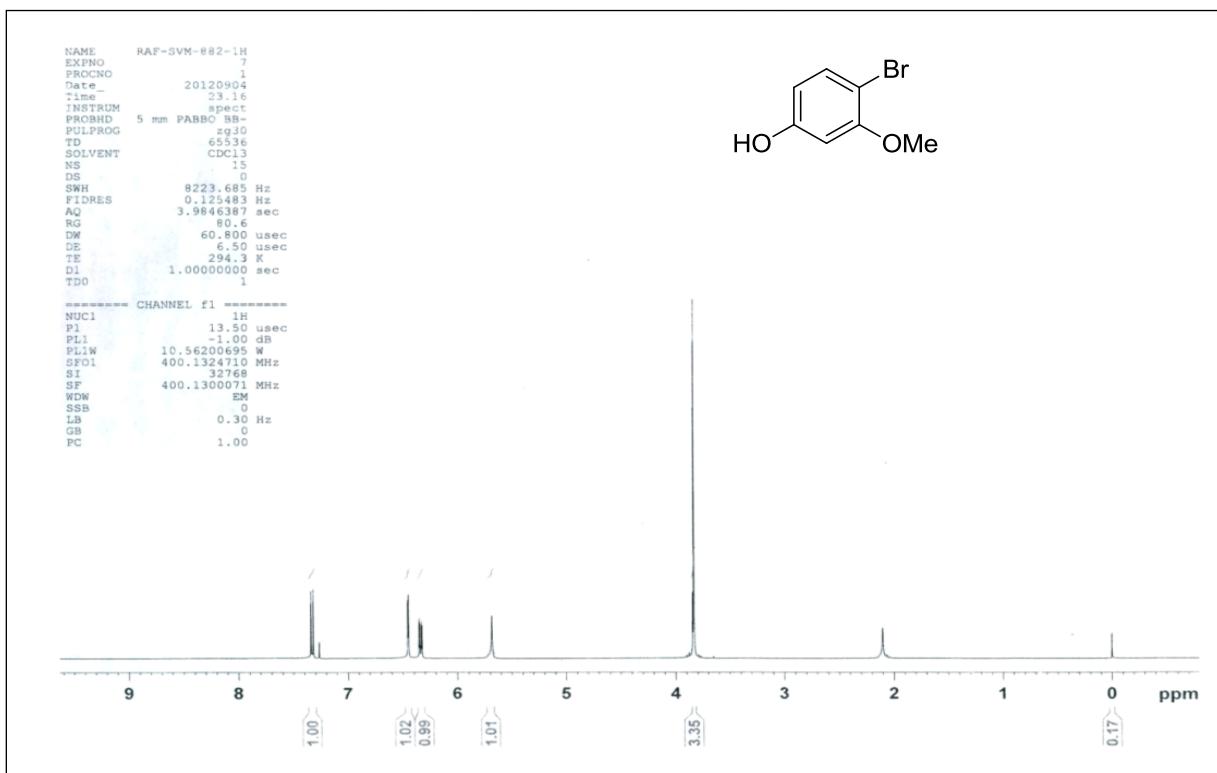
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **4p**



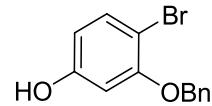
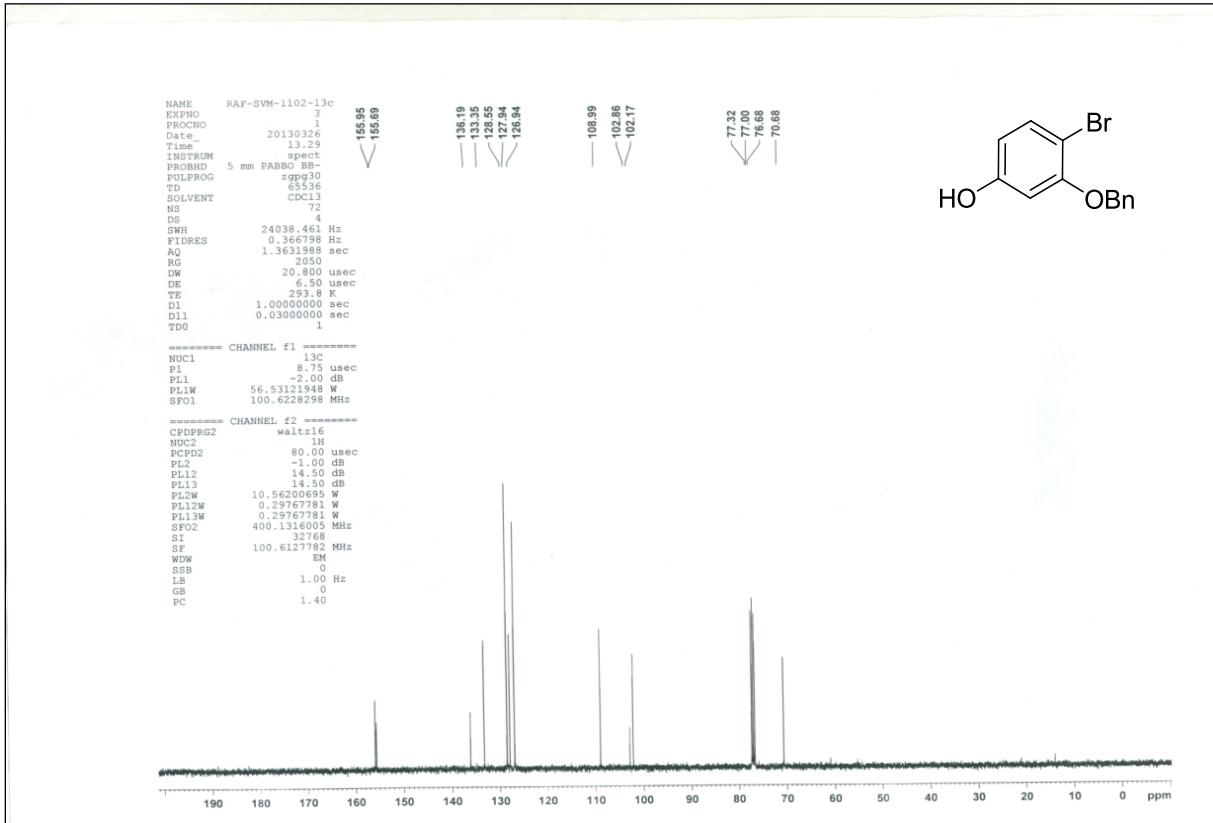
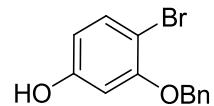
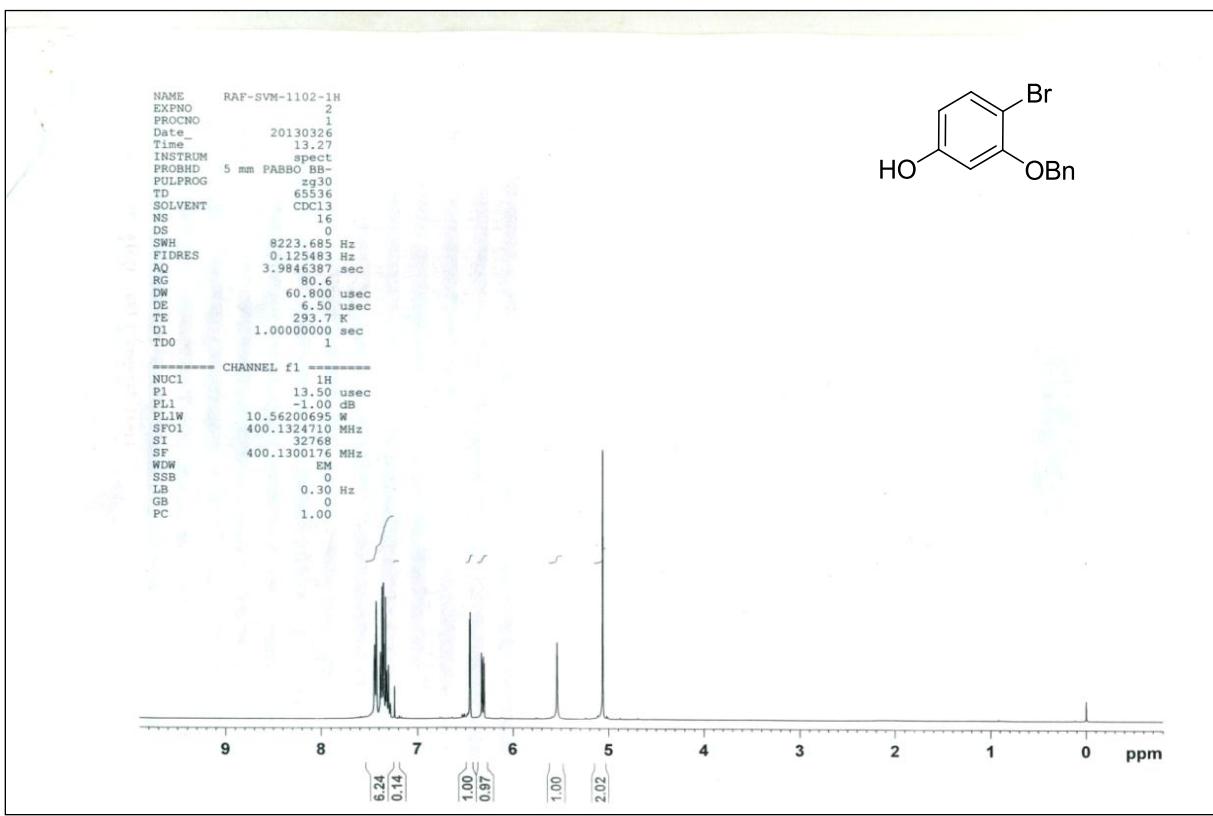
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5a**



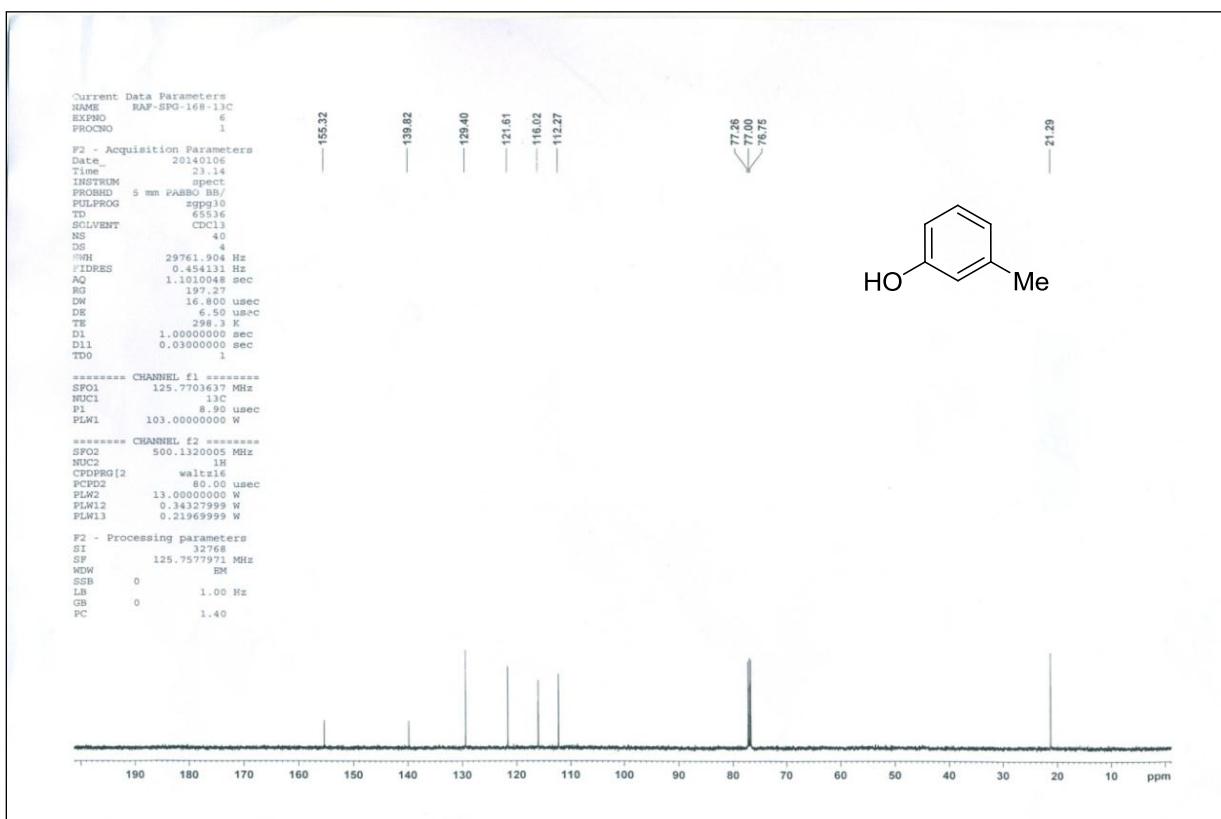
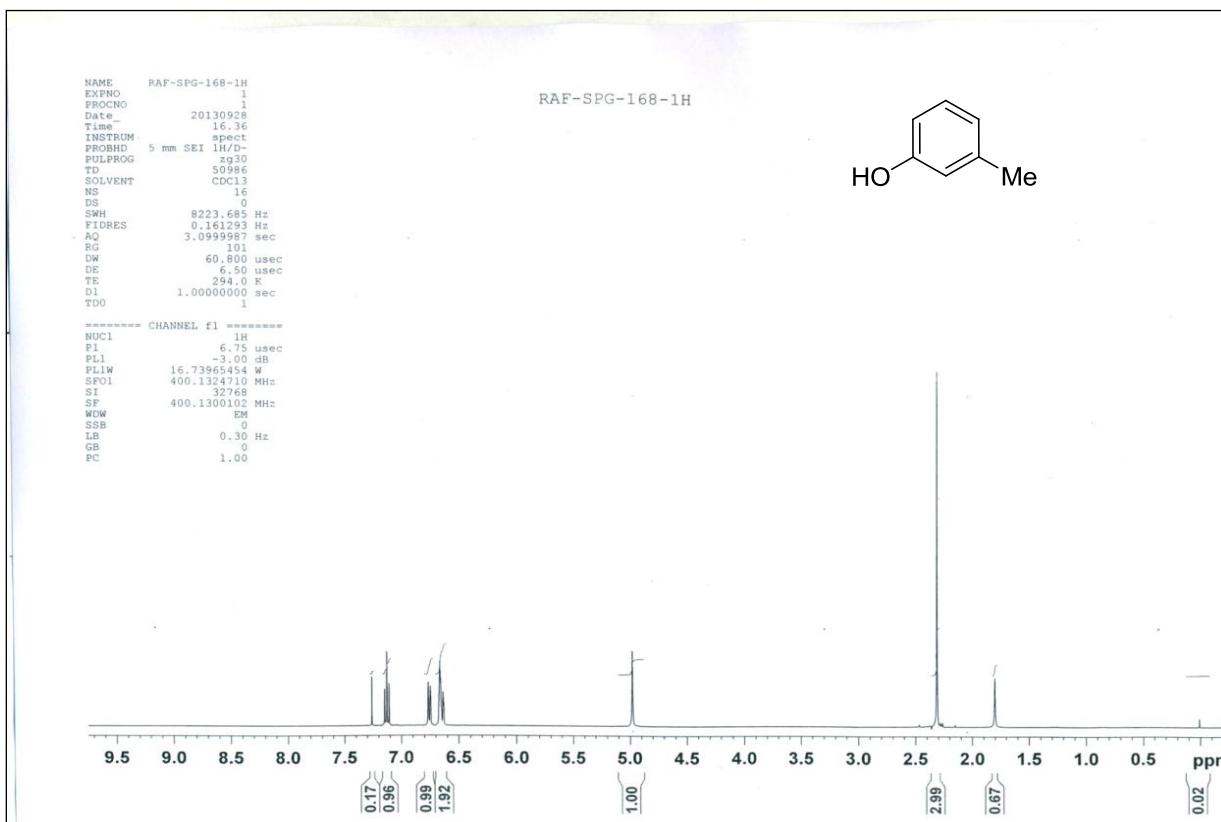
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5b**



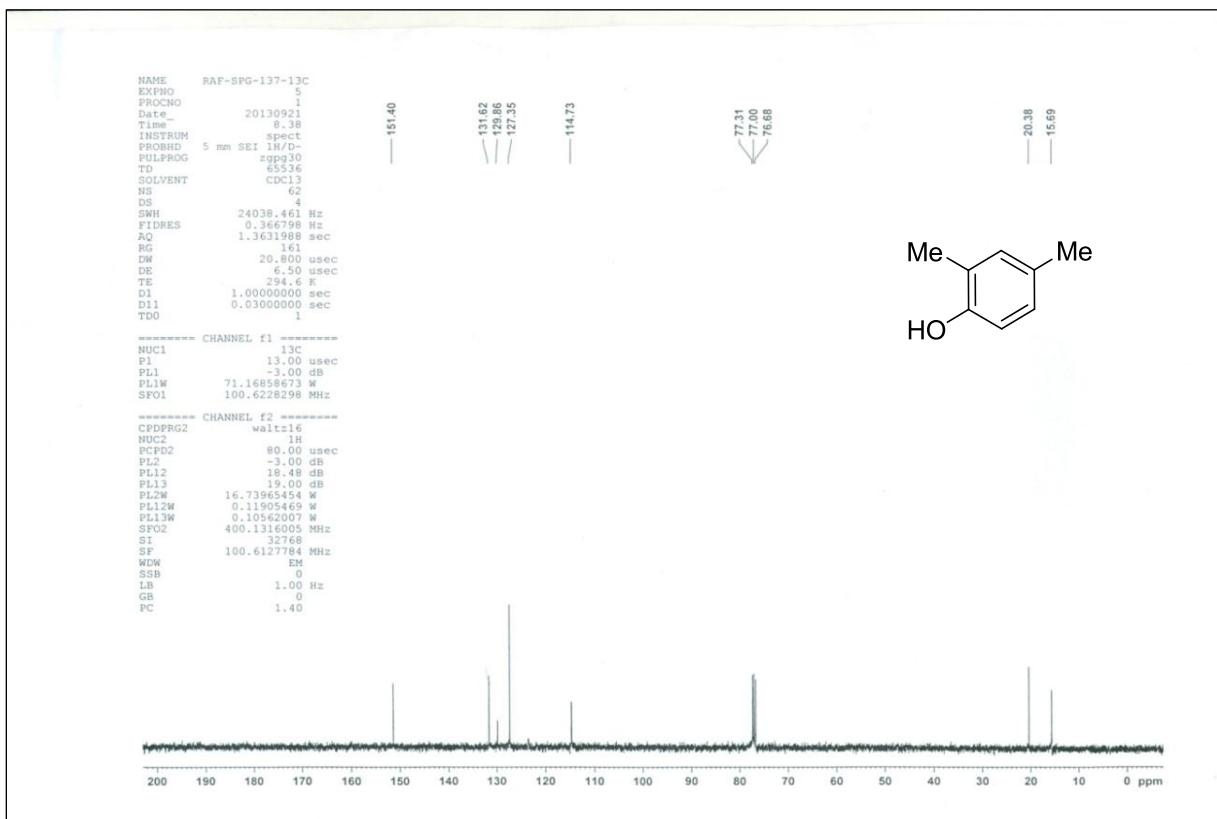
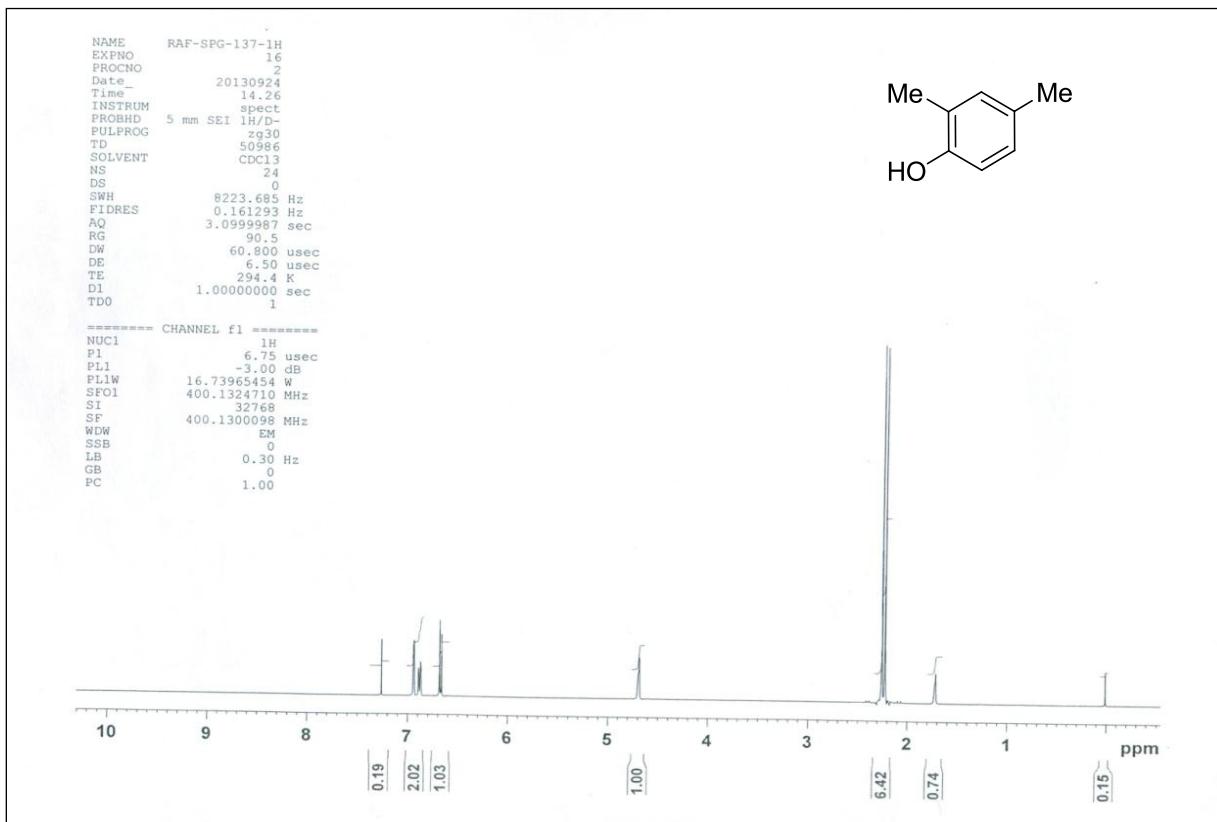
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5c**



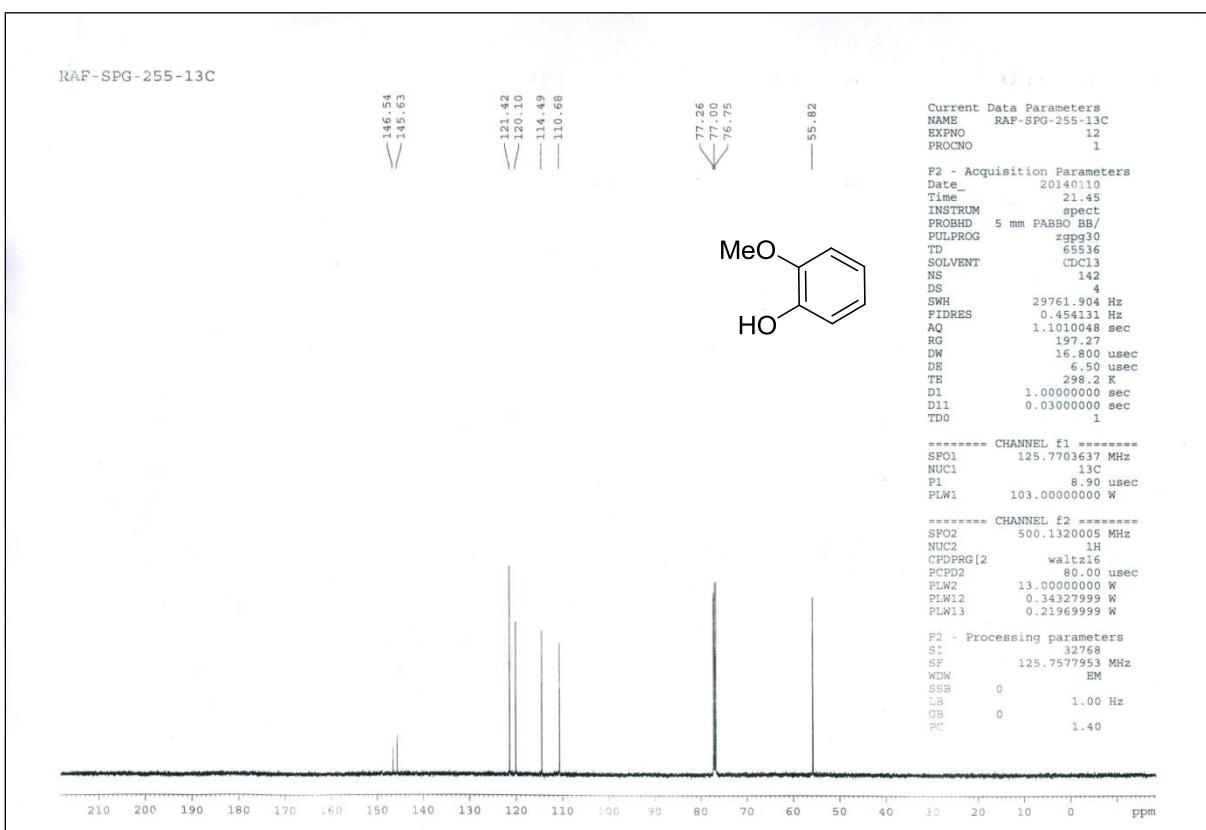
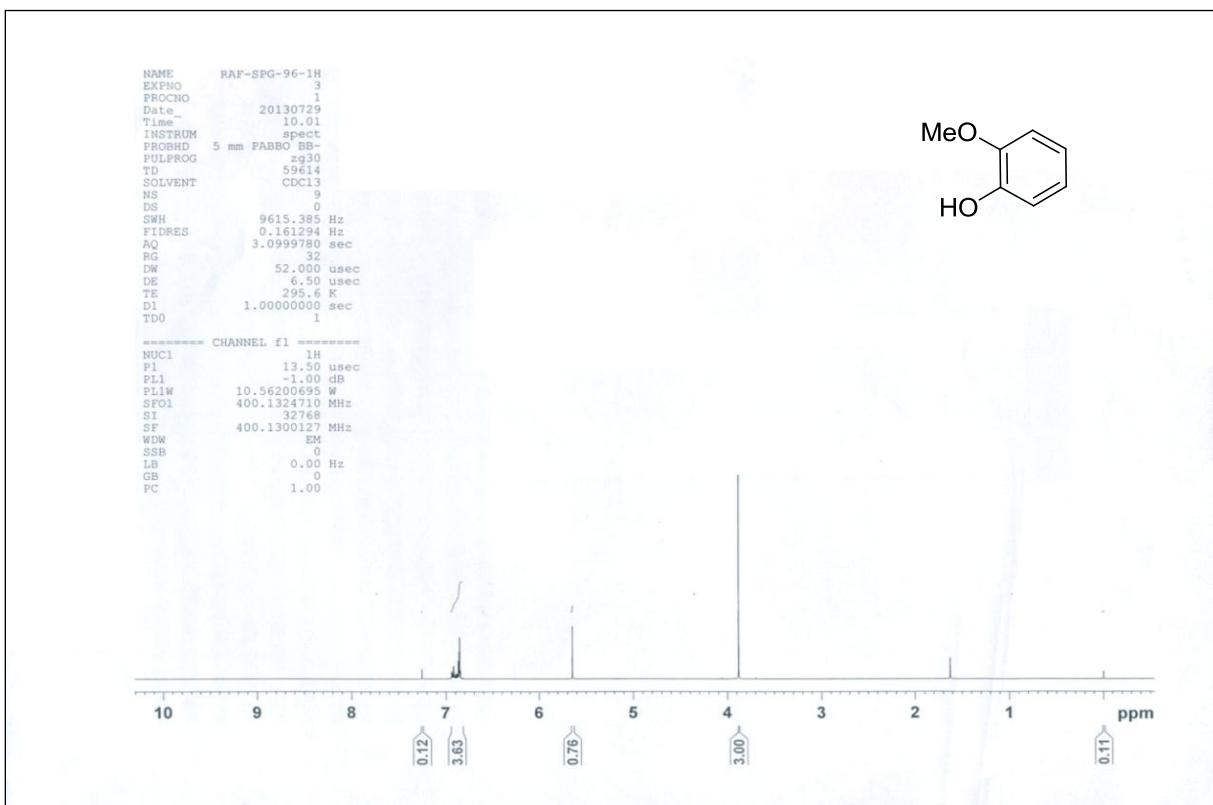
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5d**



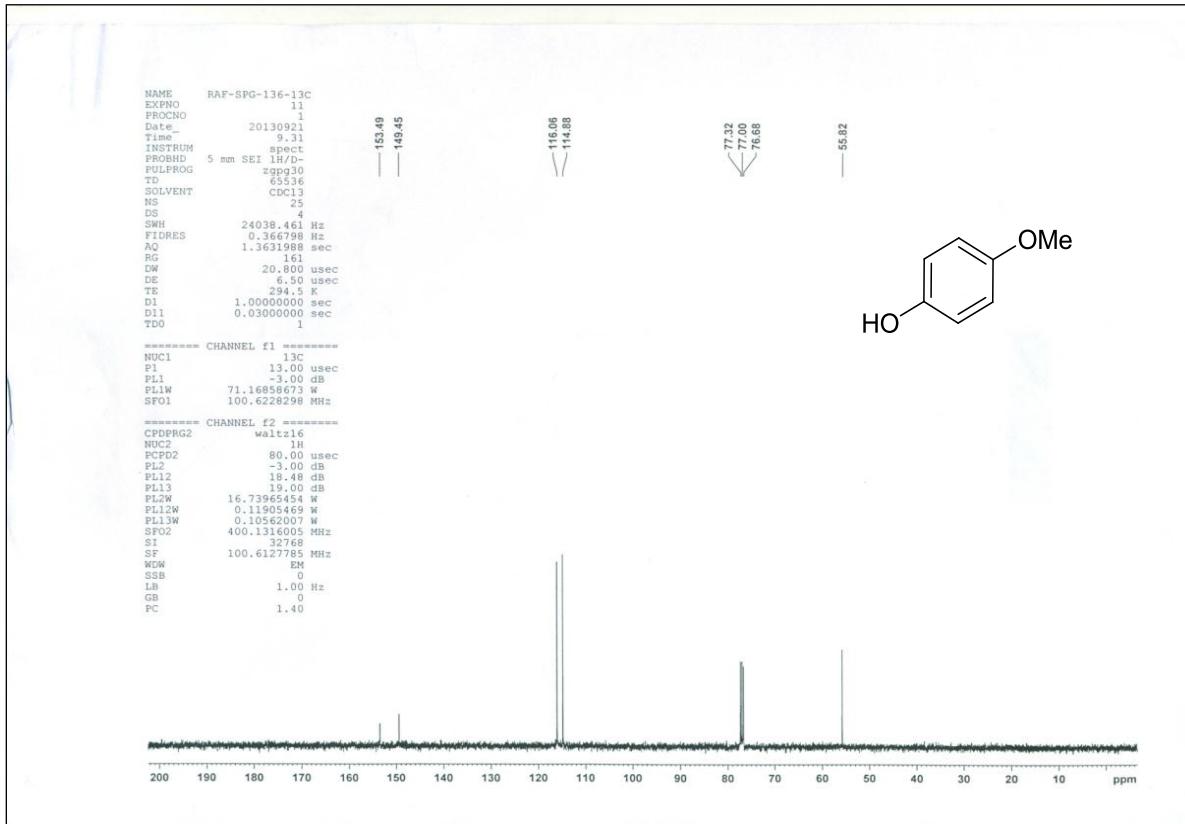
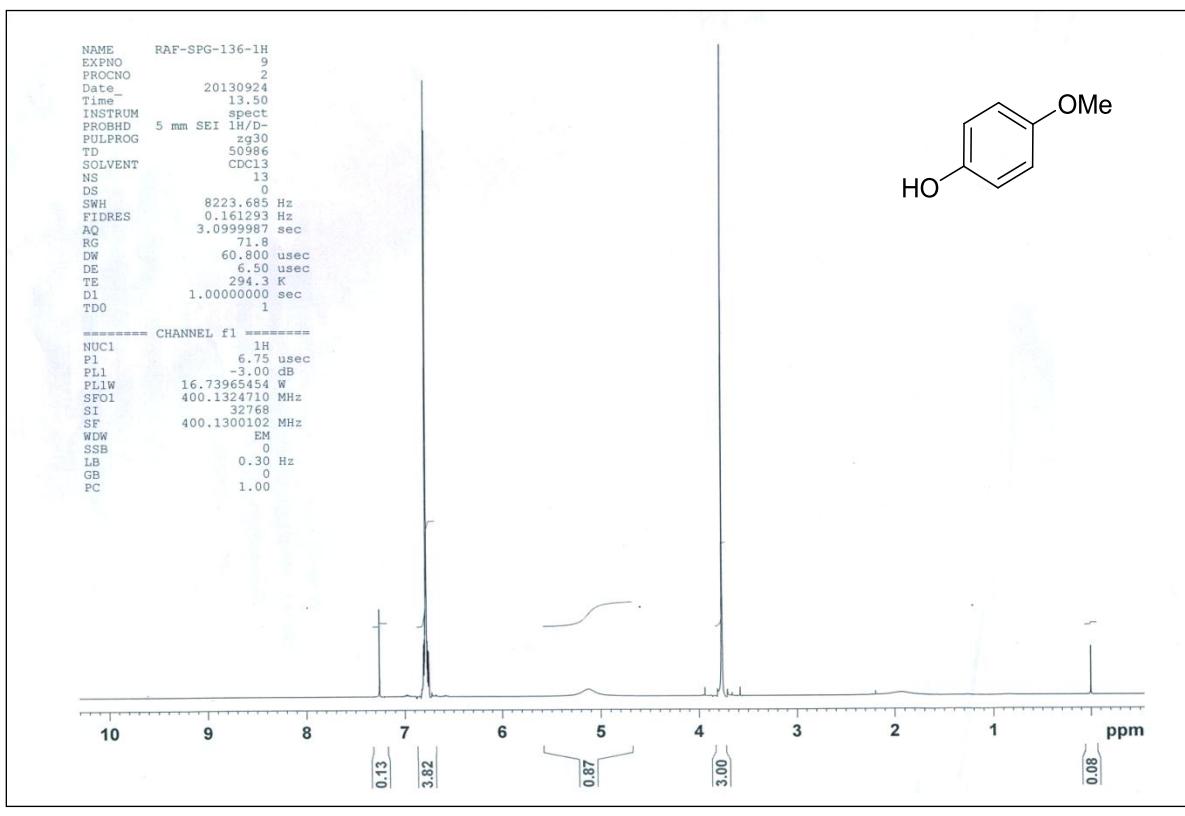
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5e**



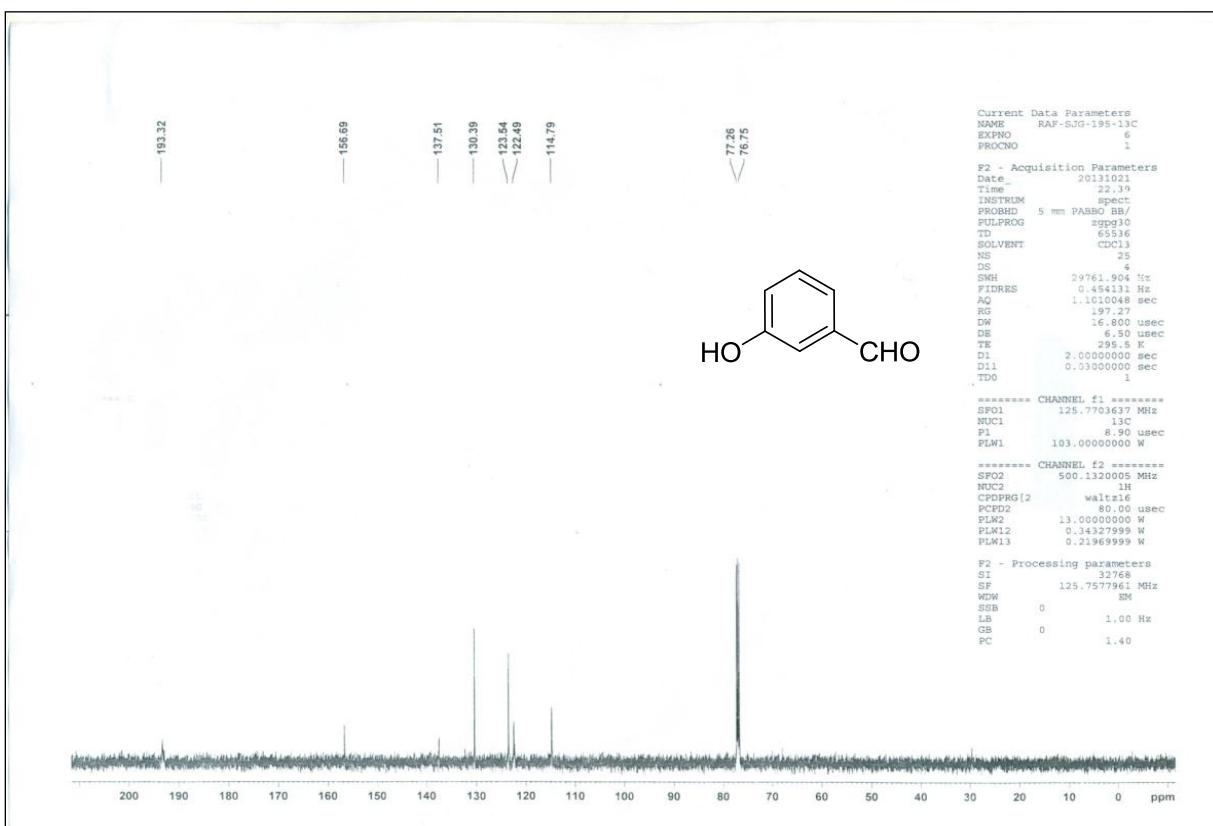
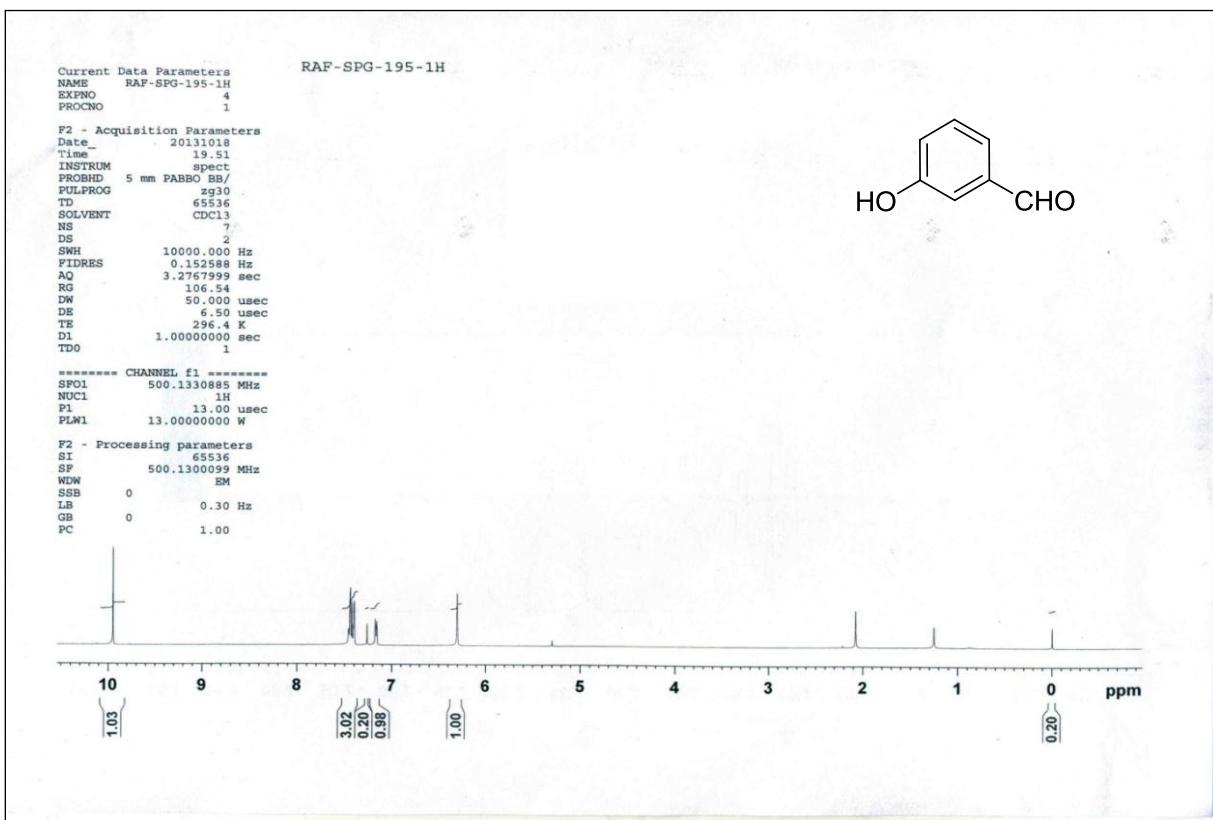
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5f**



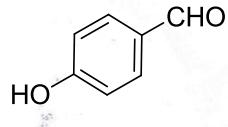
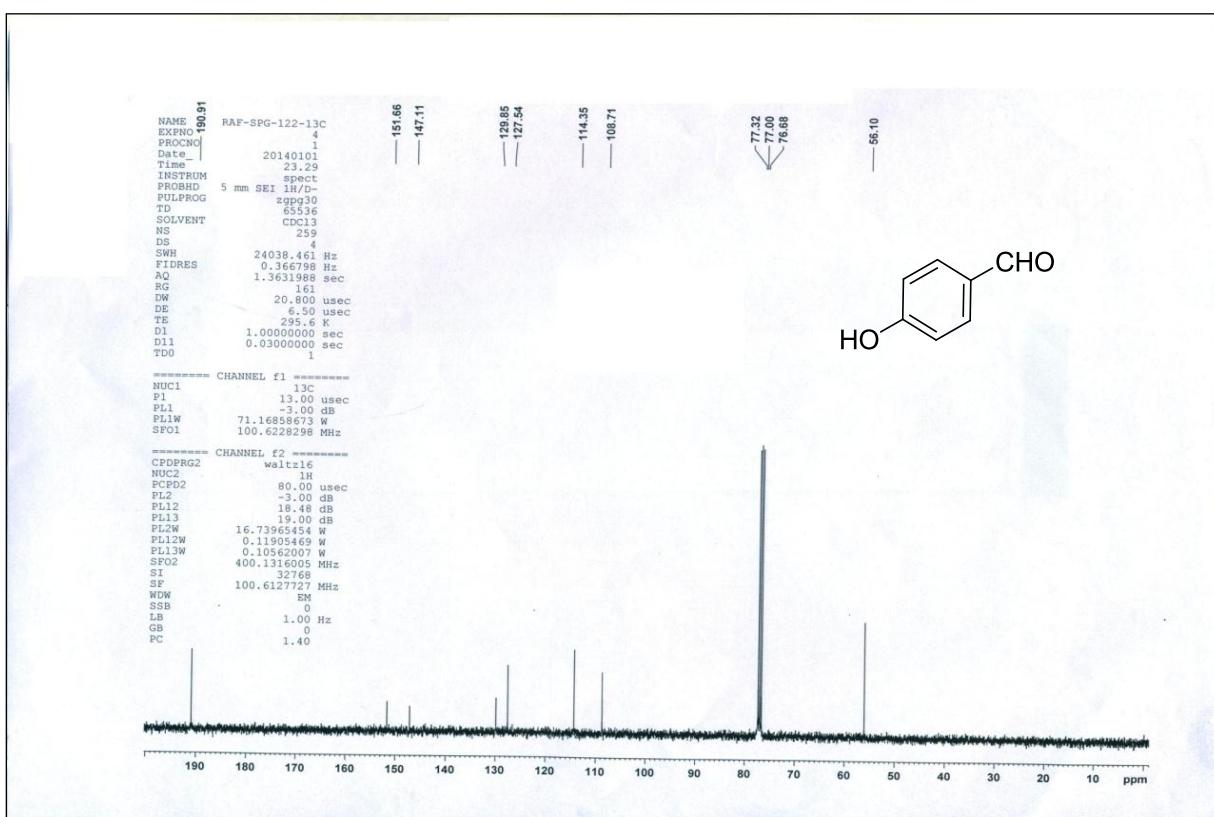
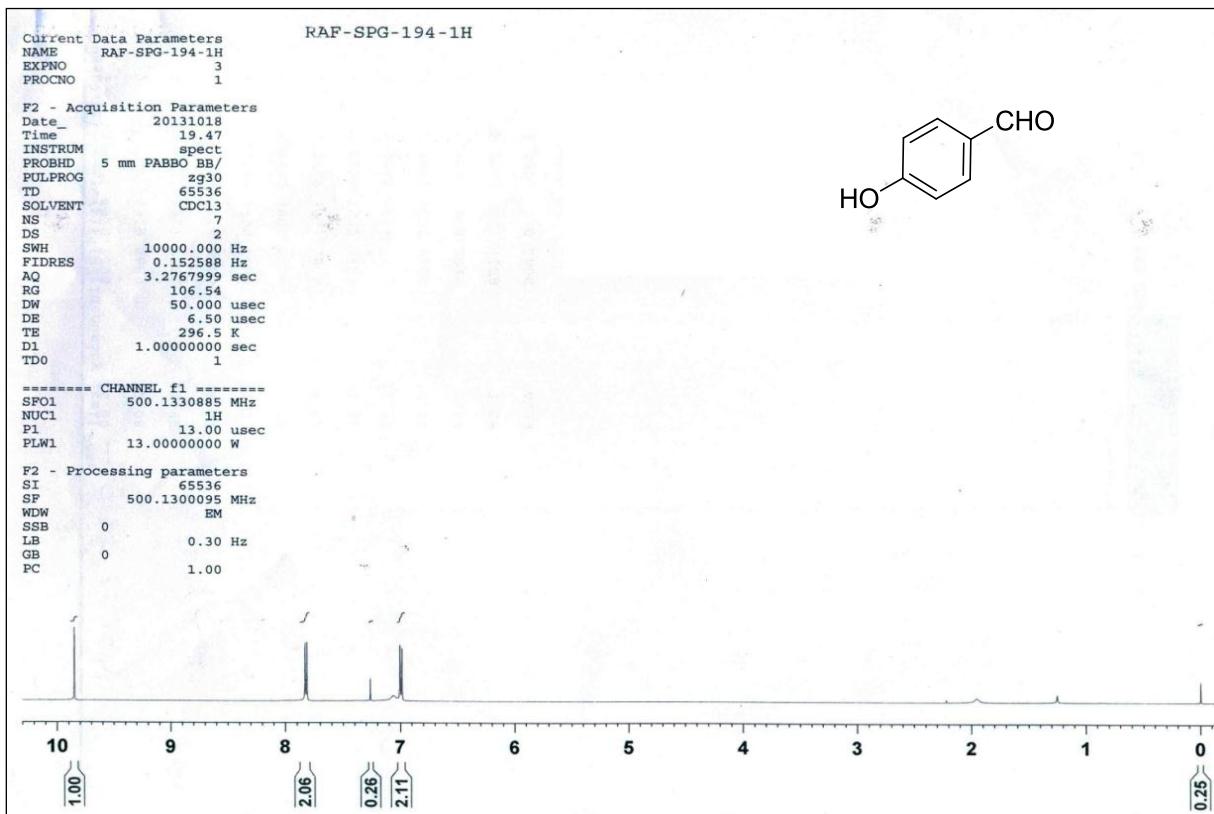
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 5g



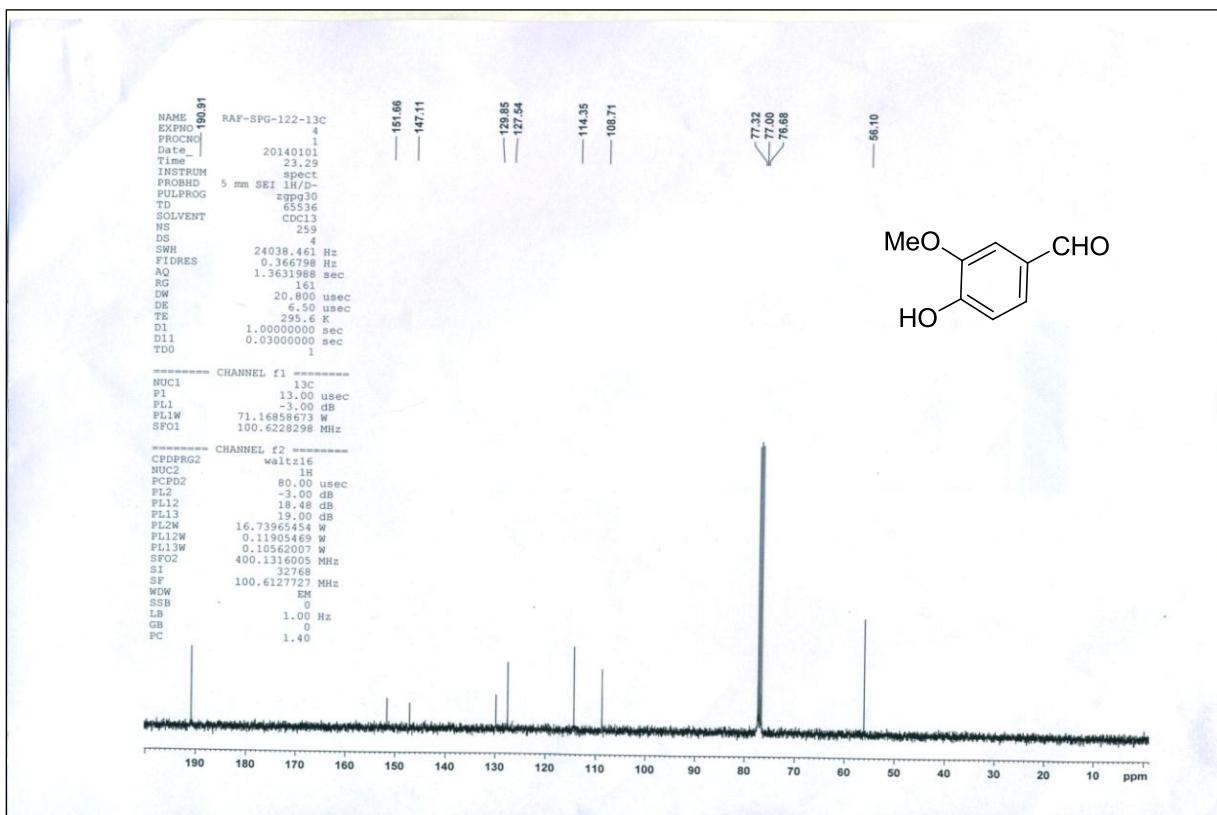
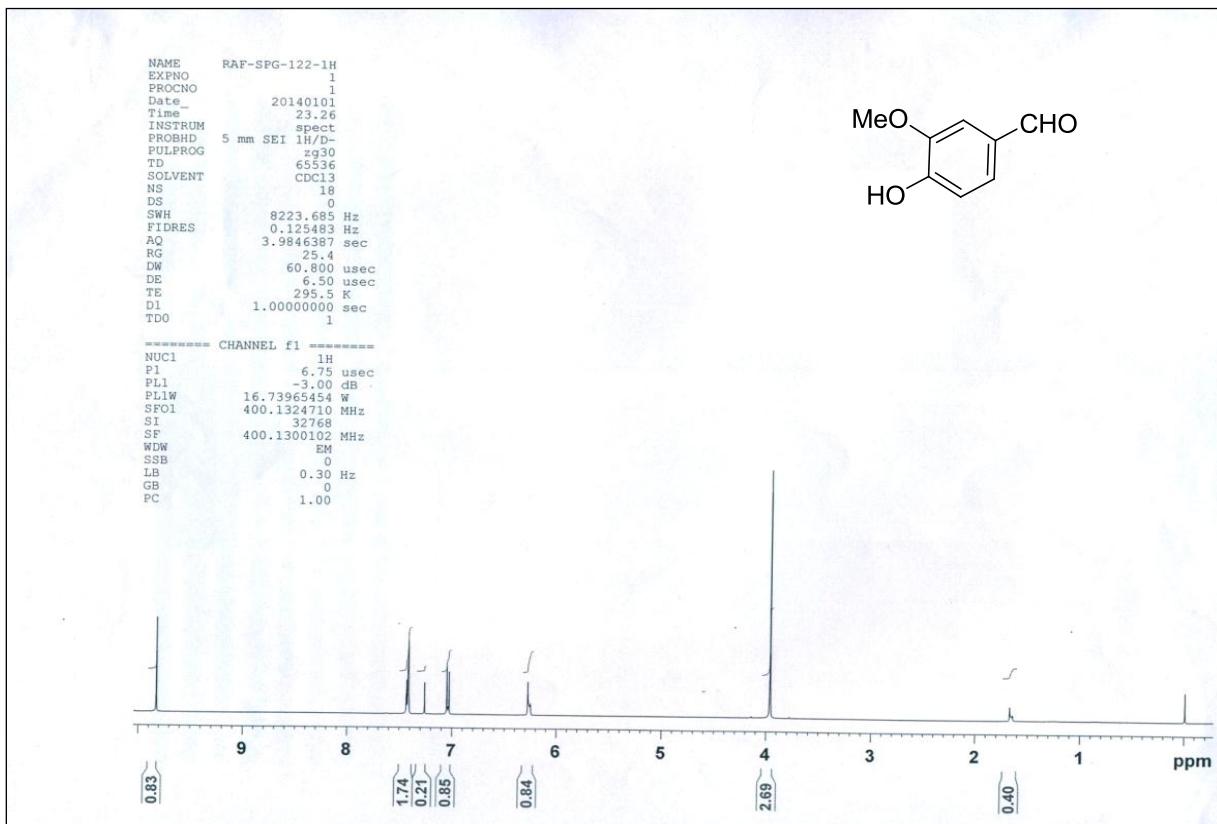
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5h**



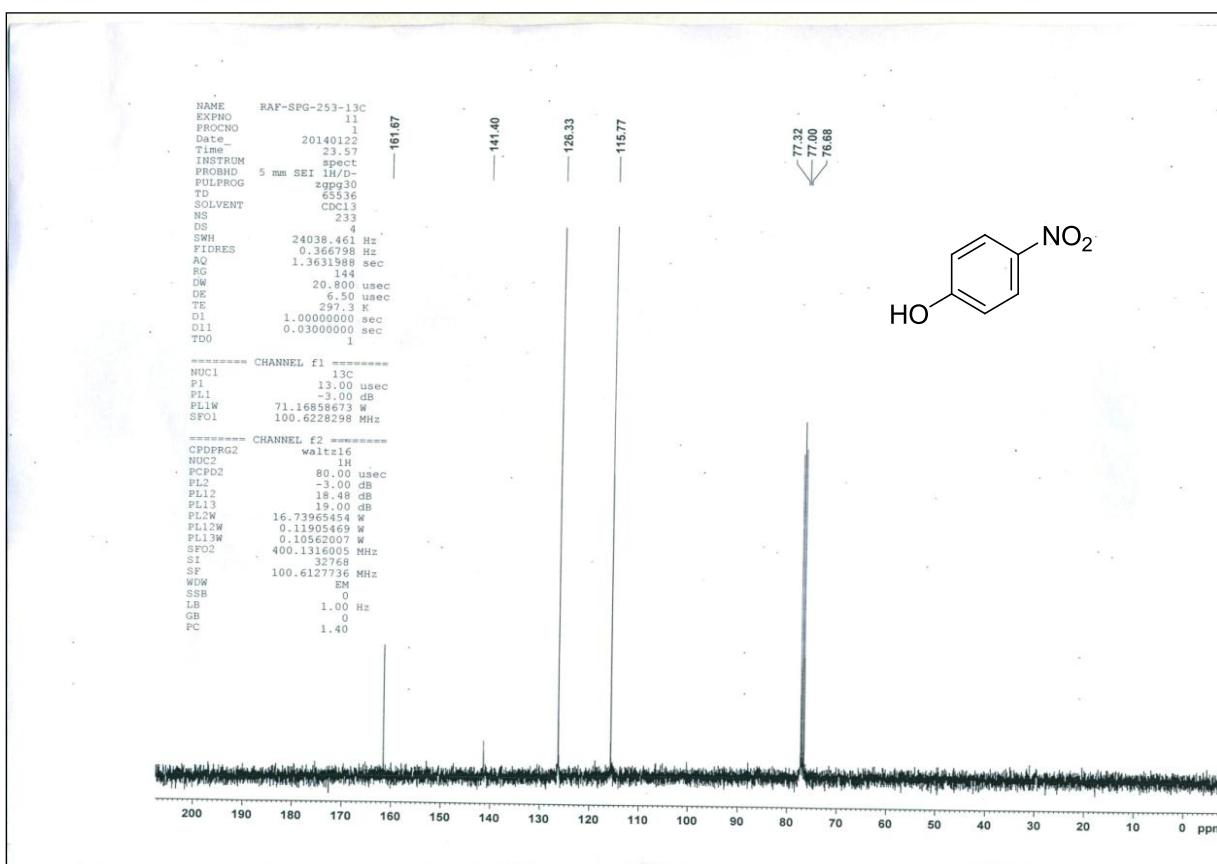
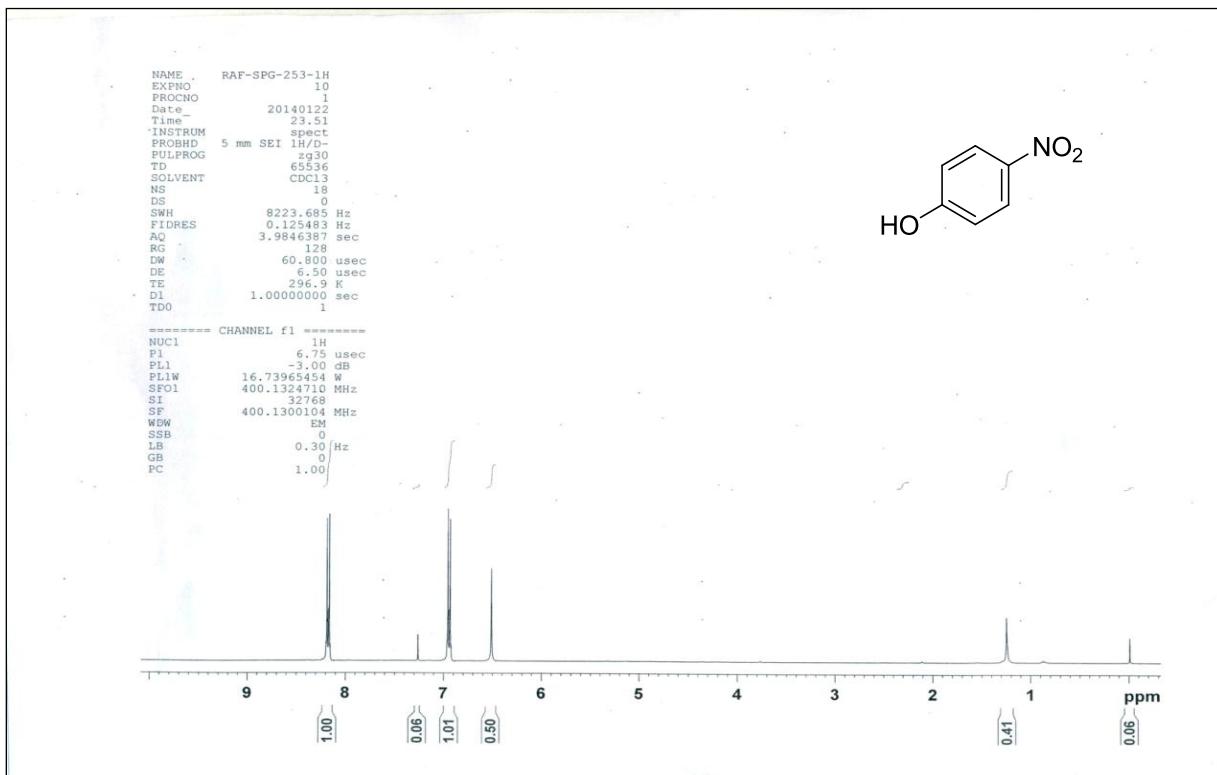
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5i**



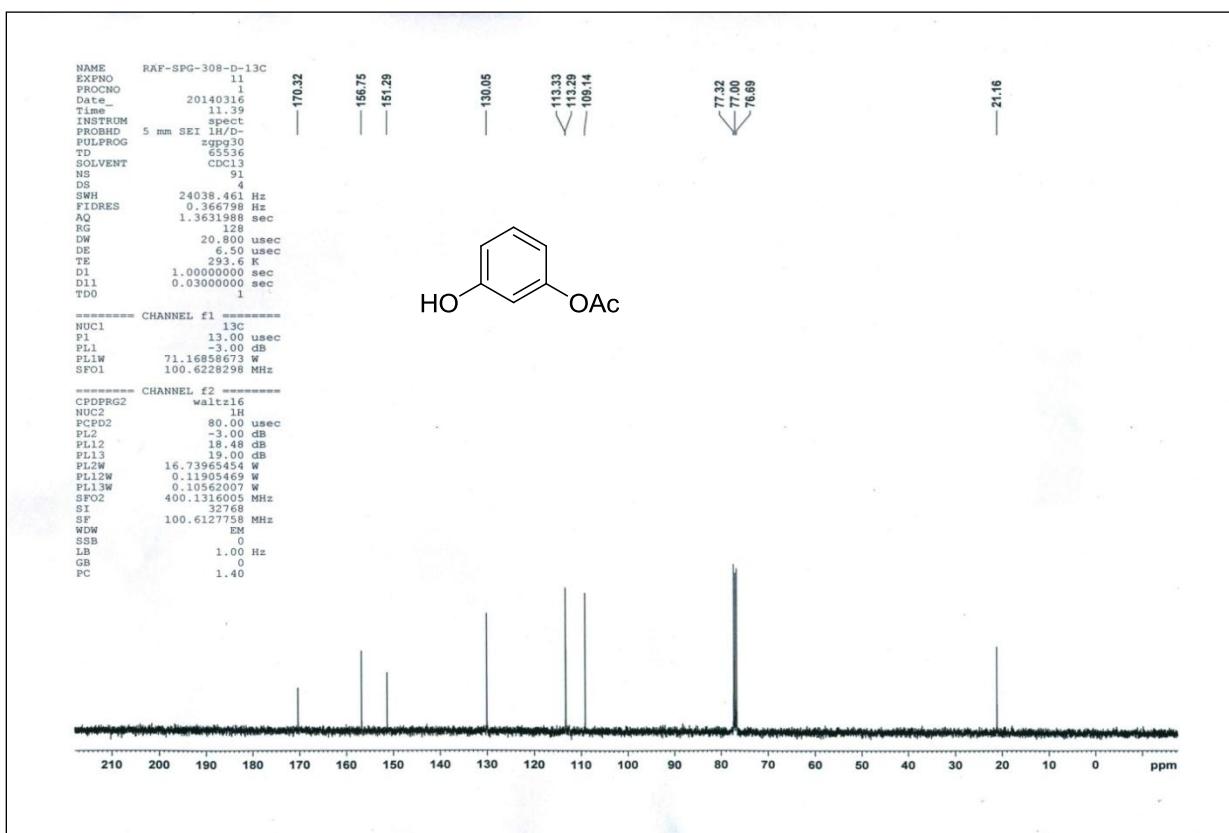
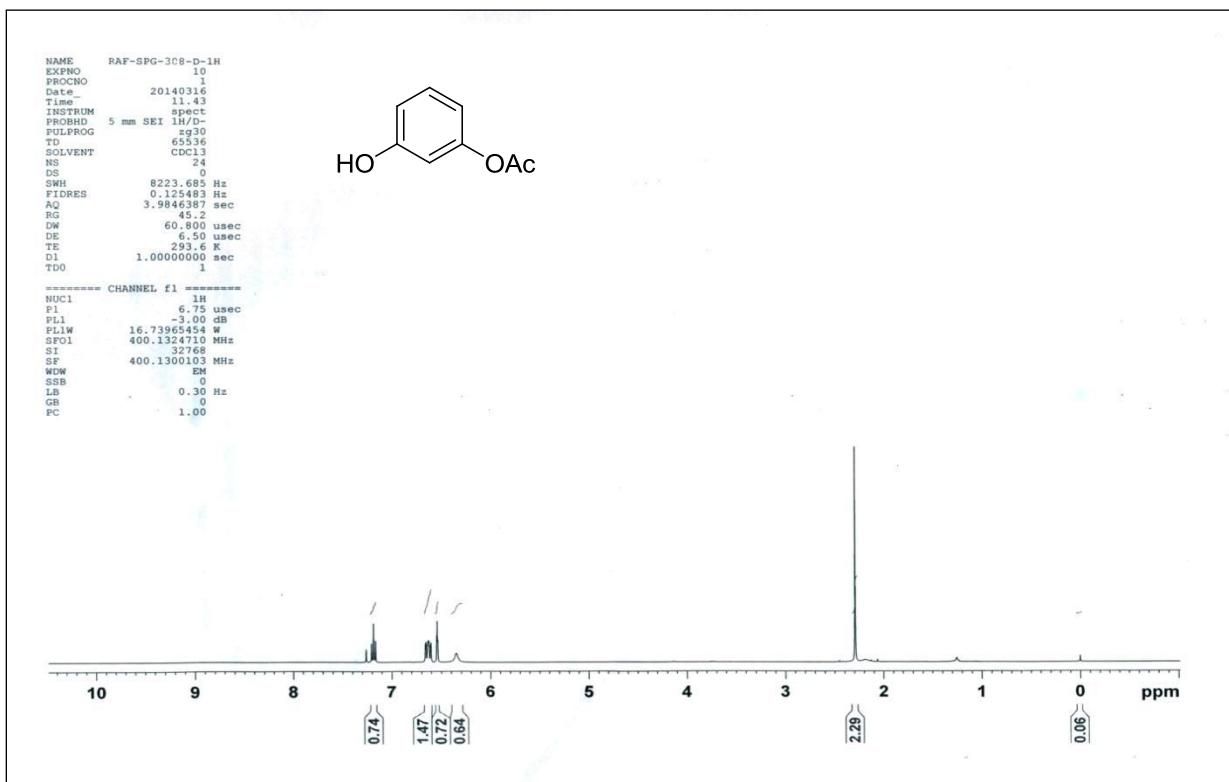
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 5j



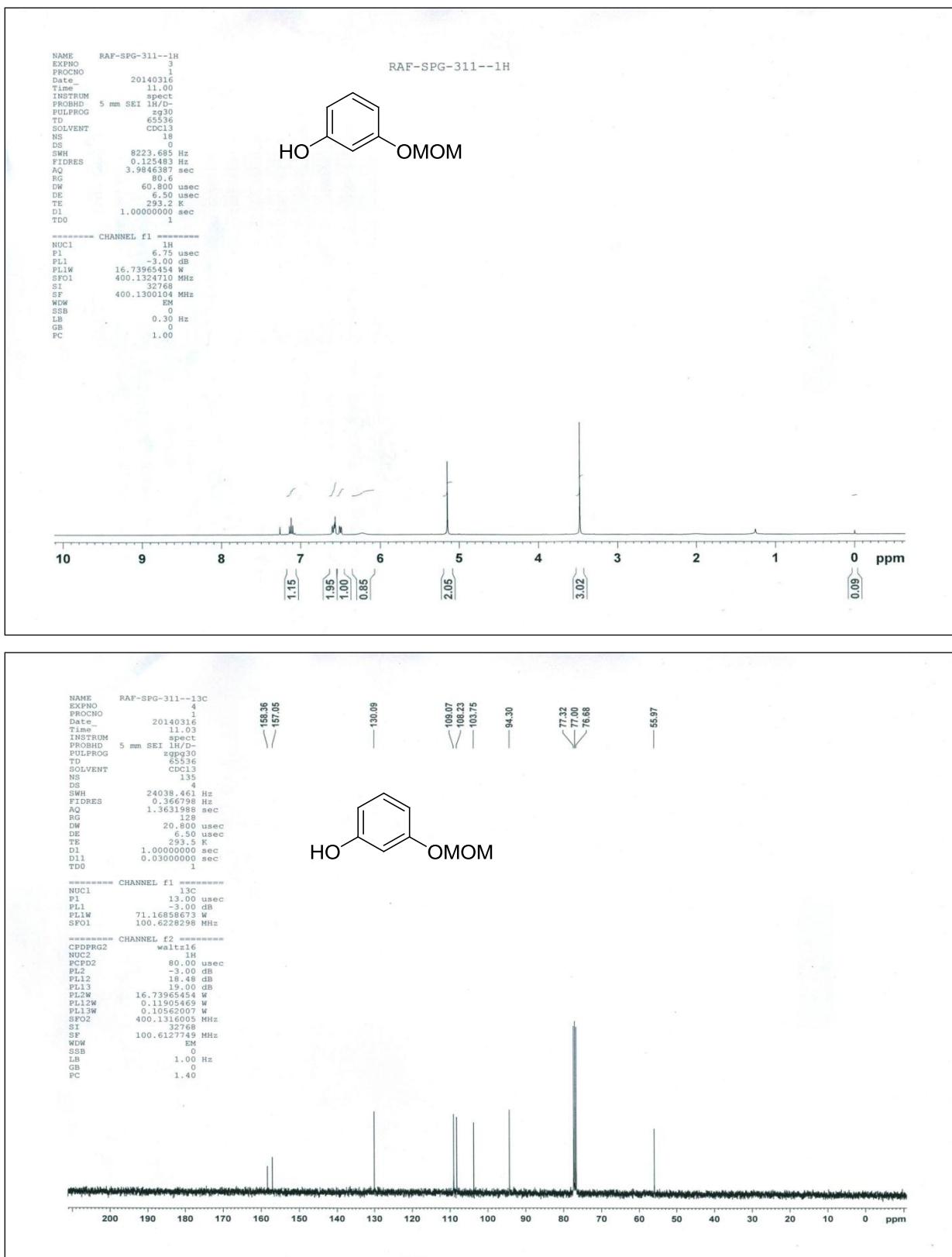
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5k**



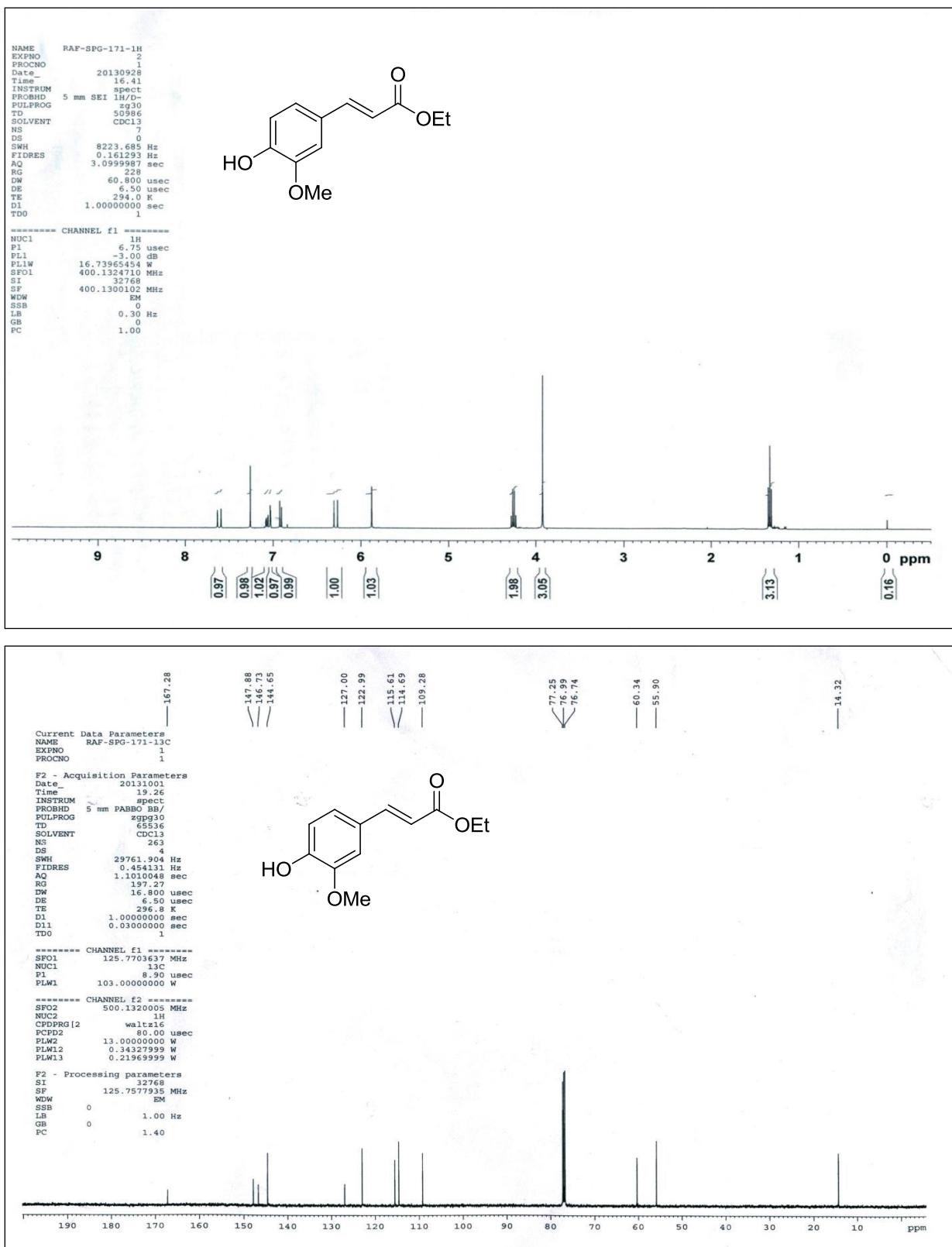
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 5I



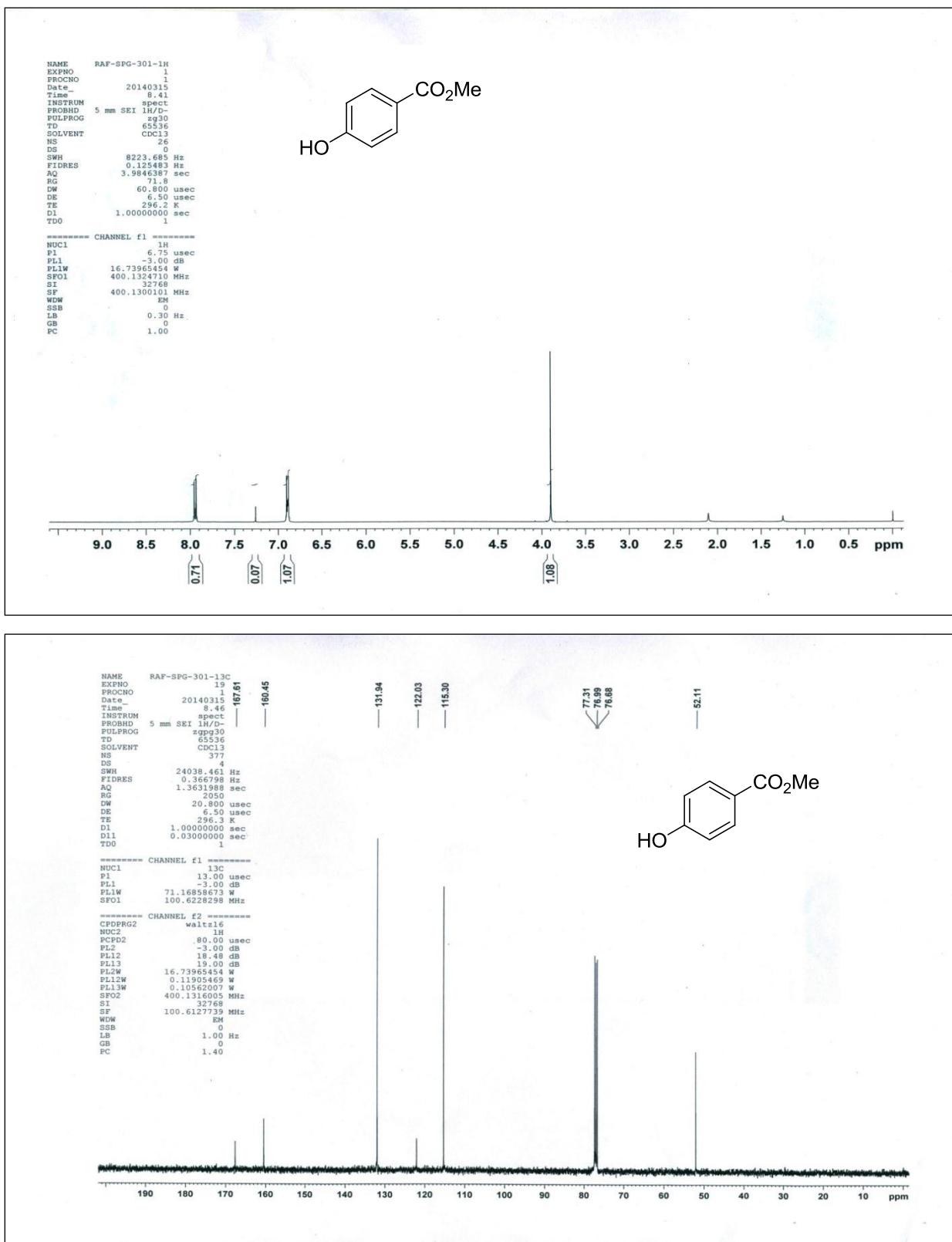
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5m**



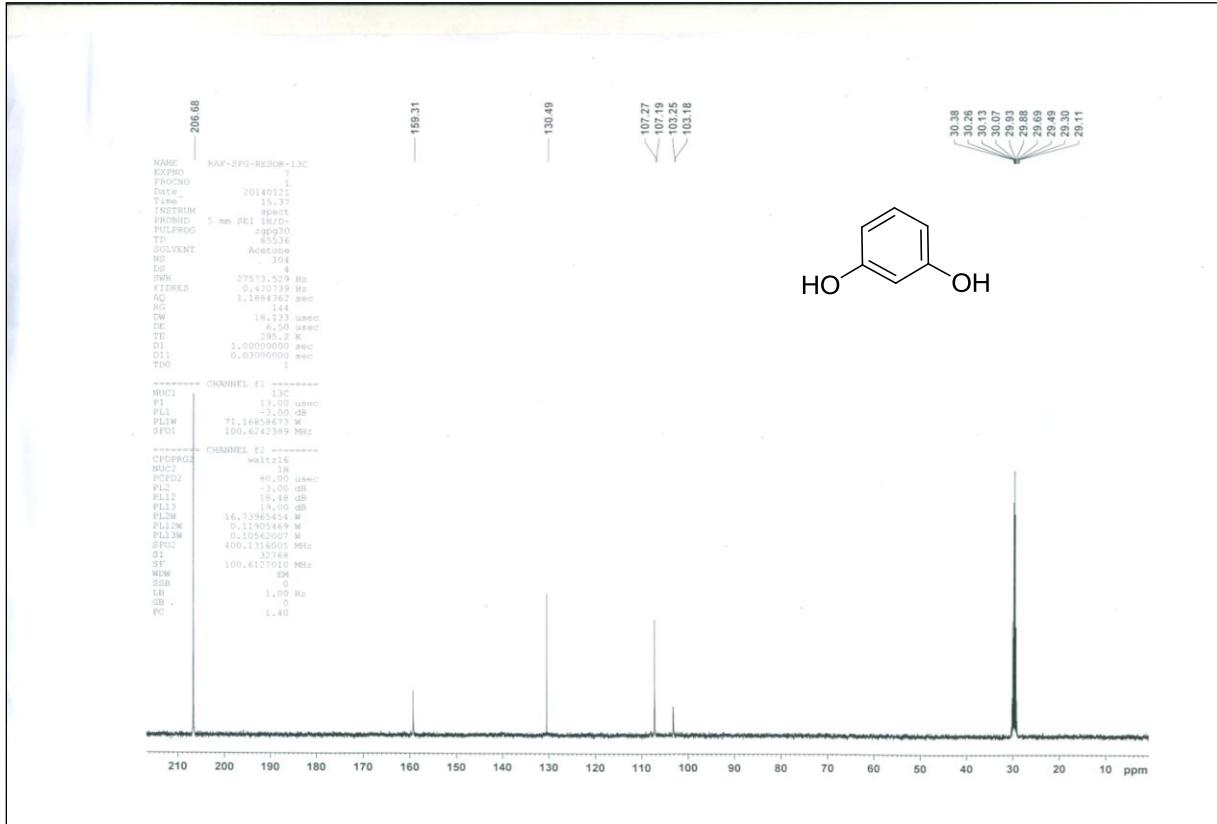
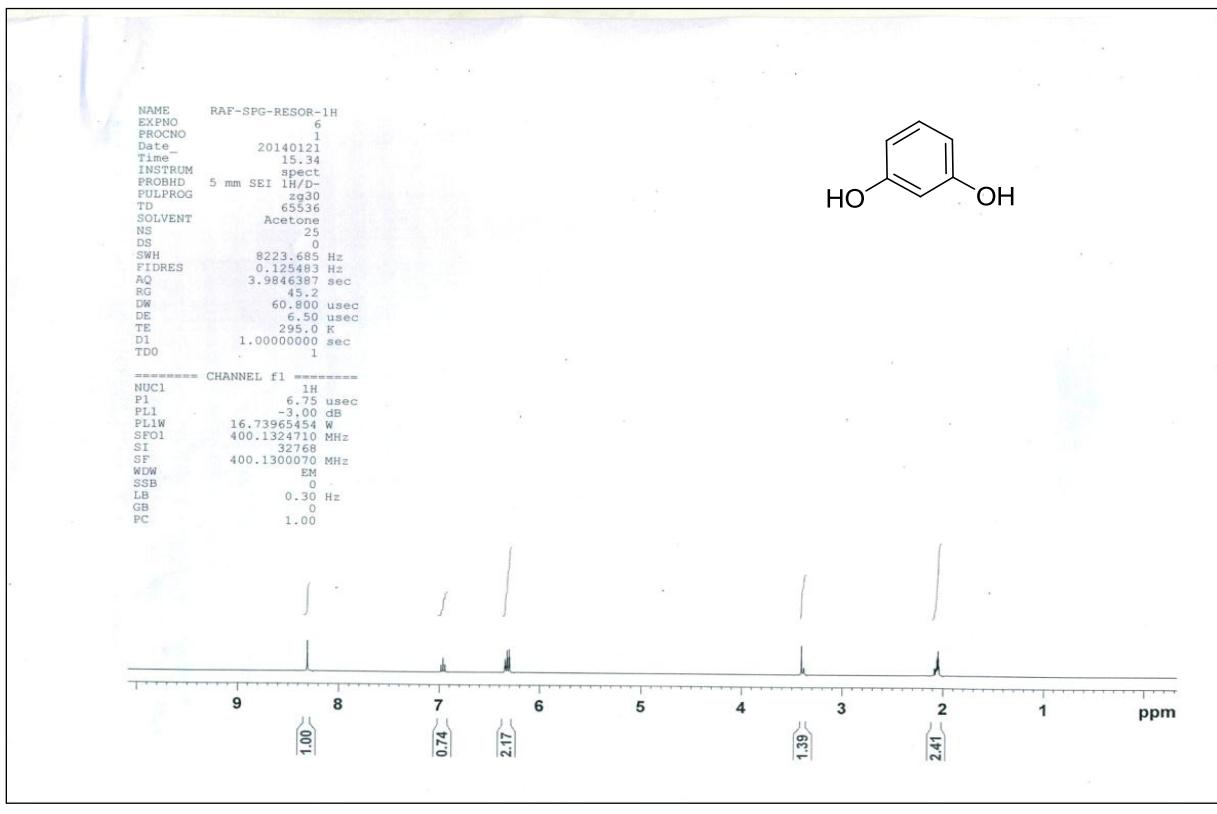
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **5n**



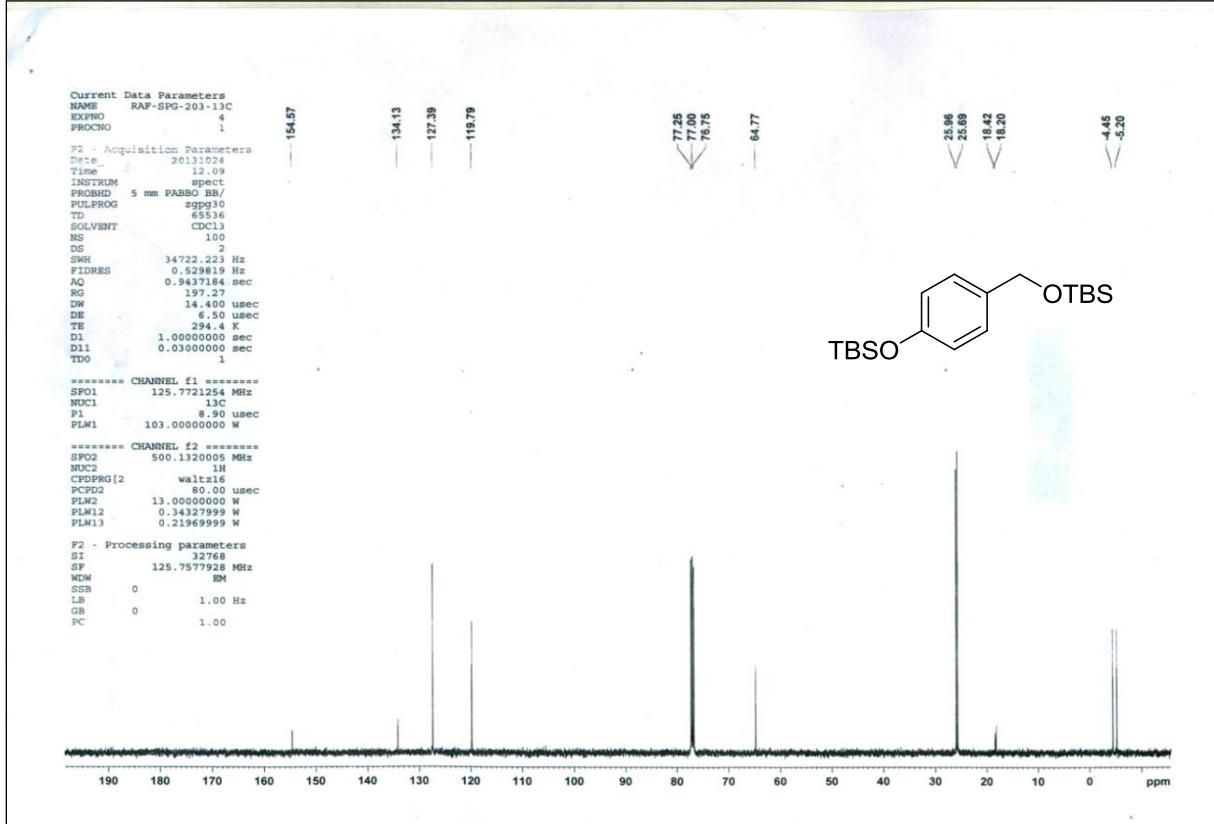
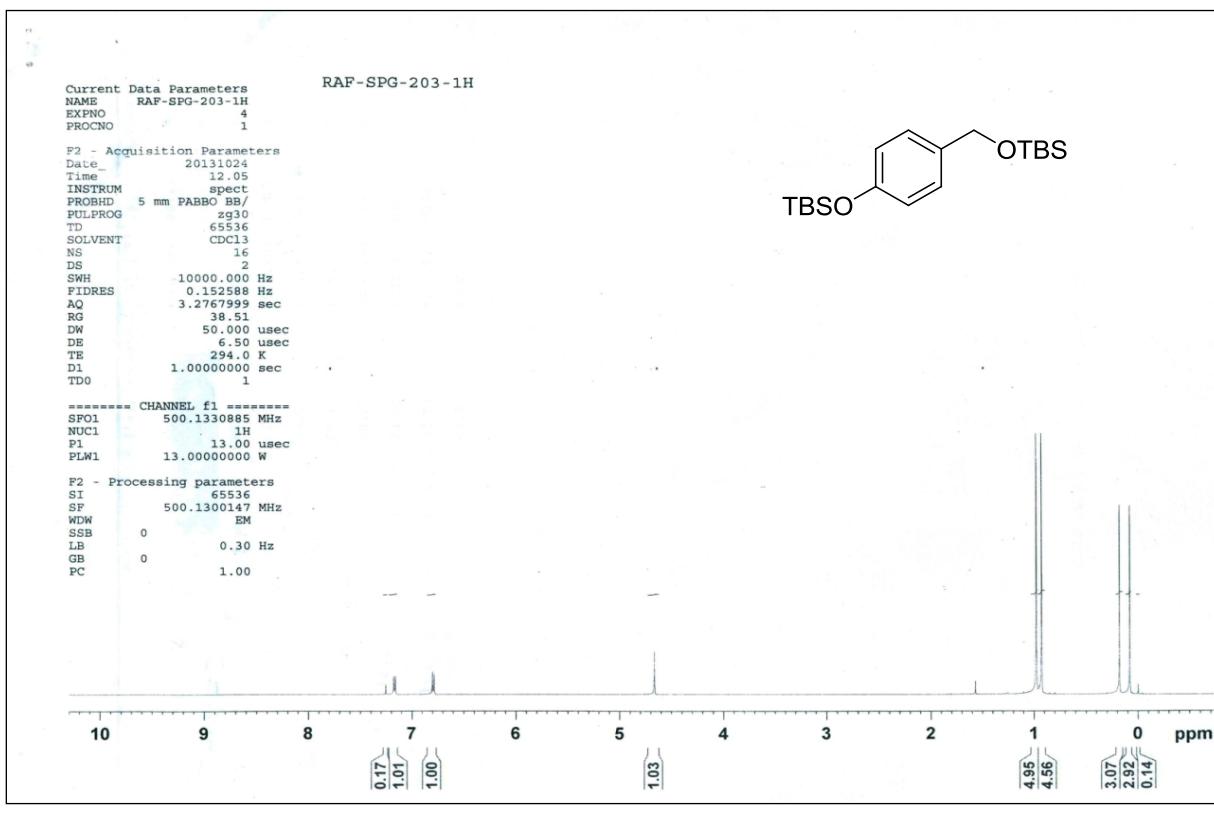
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **5o**



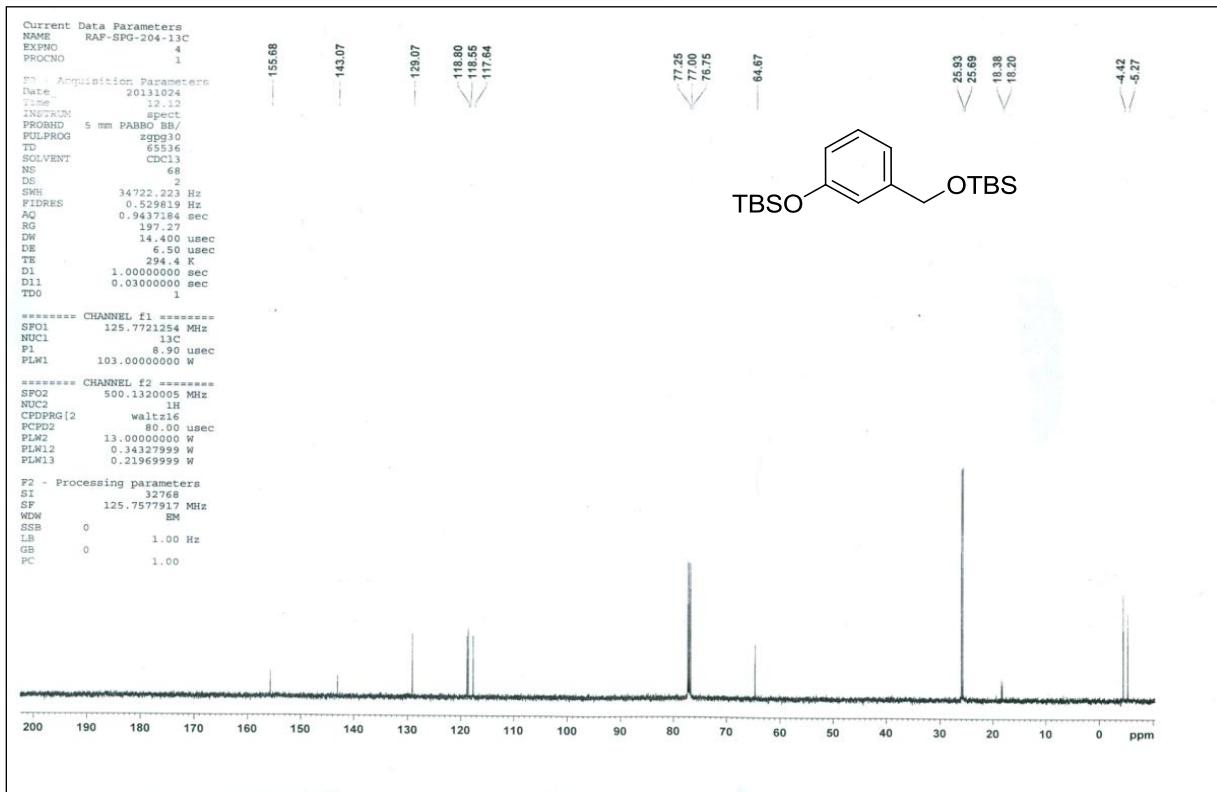
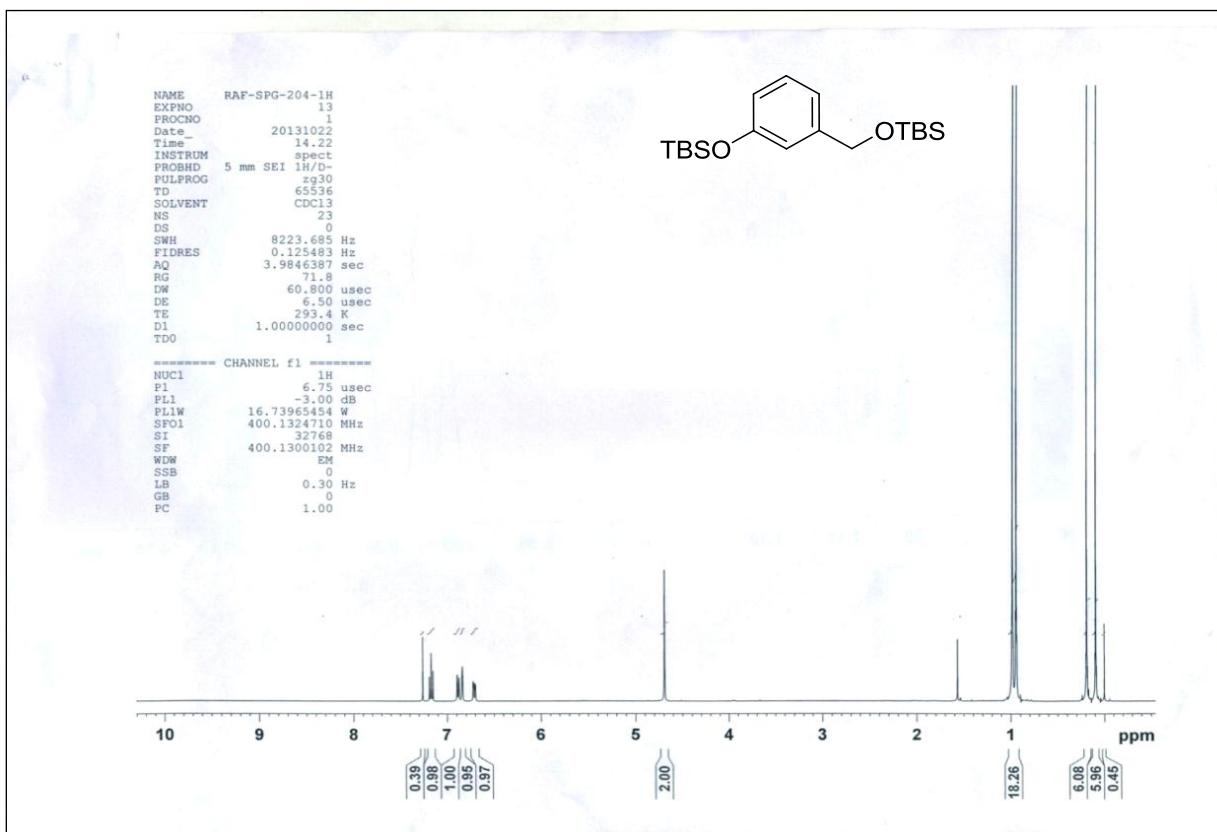
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, acetone d<sup>6</sup>) of compound 5p



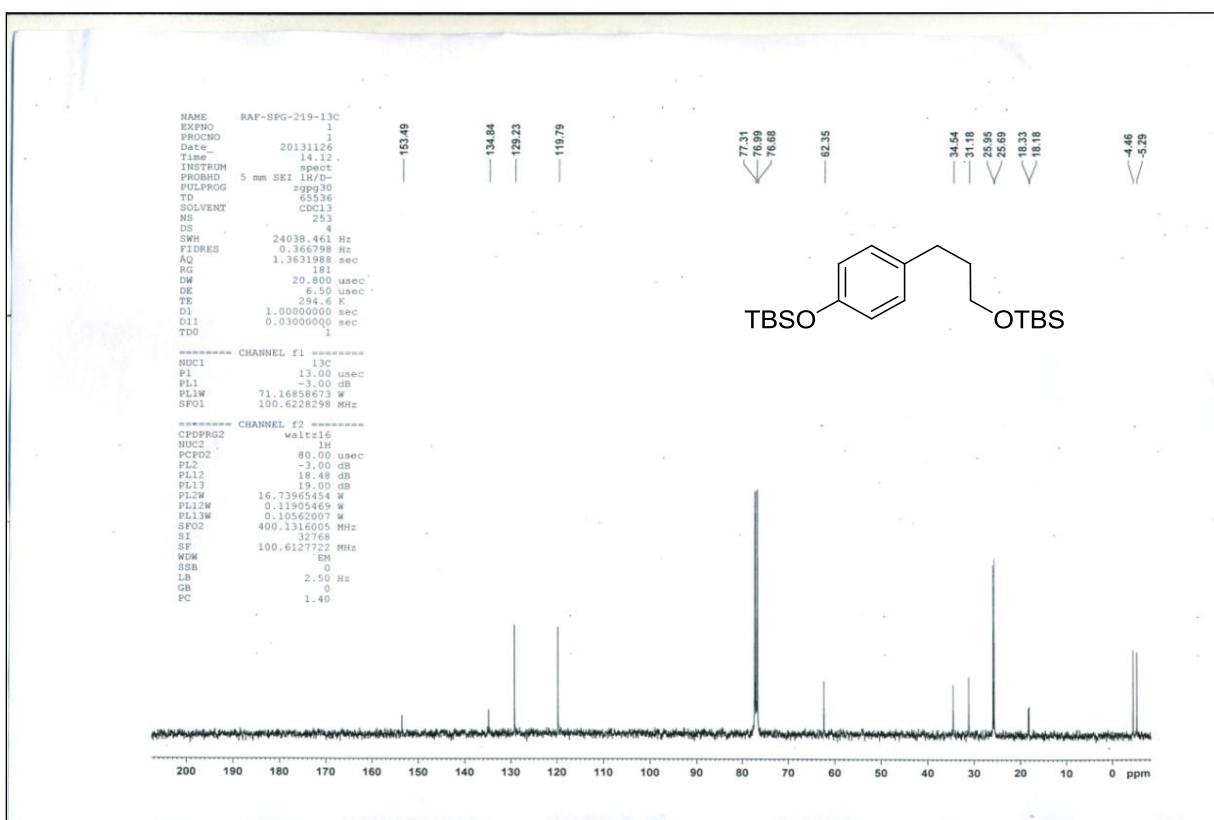
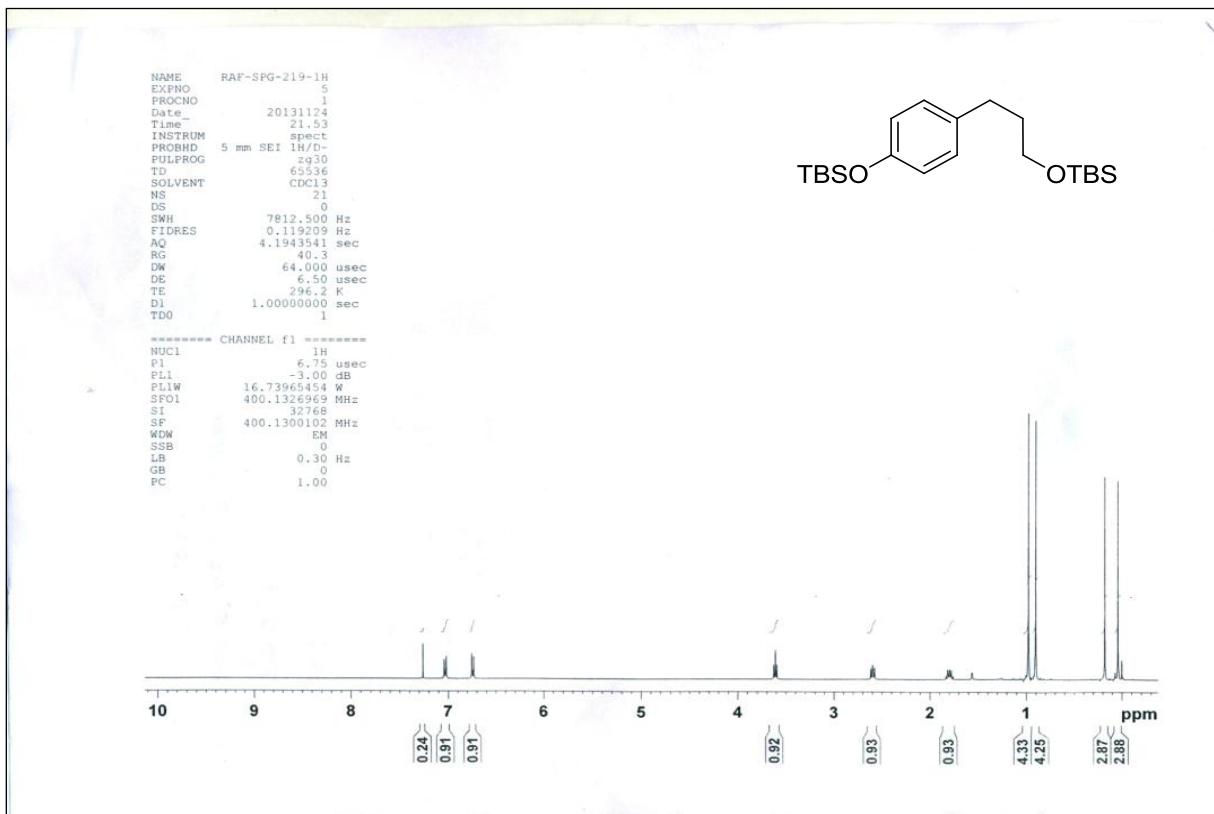
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **6a**



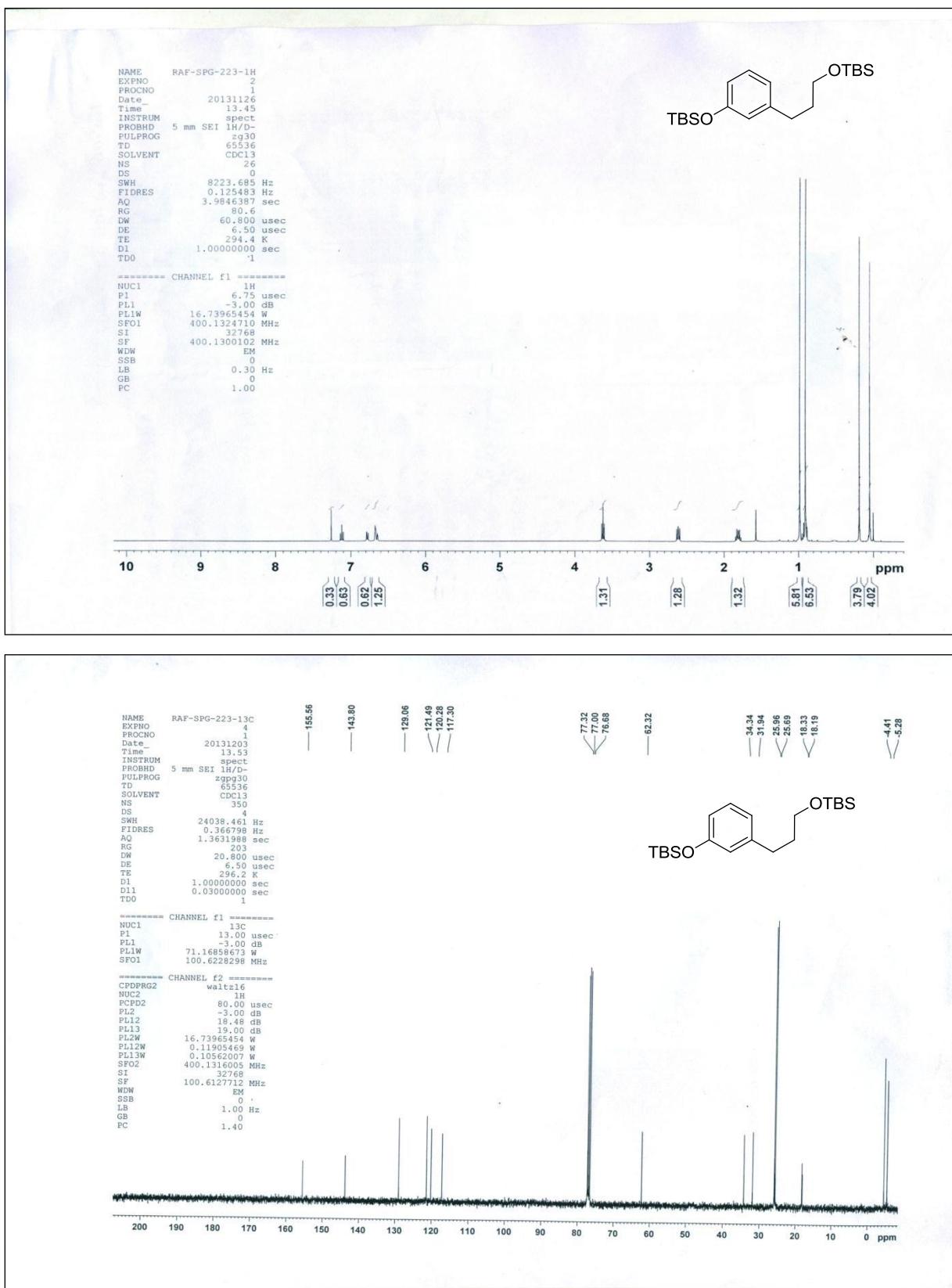
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **6b**



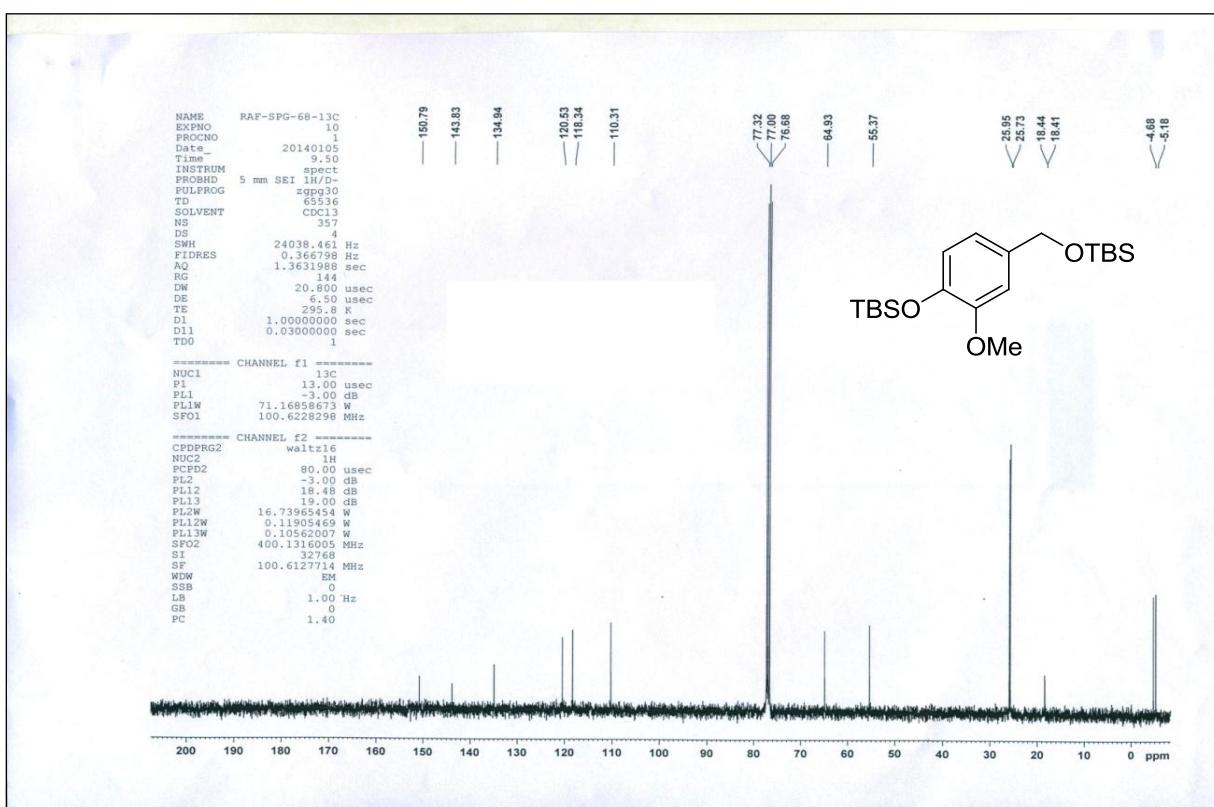
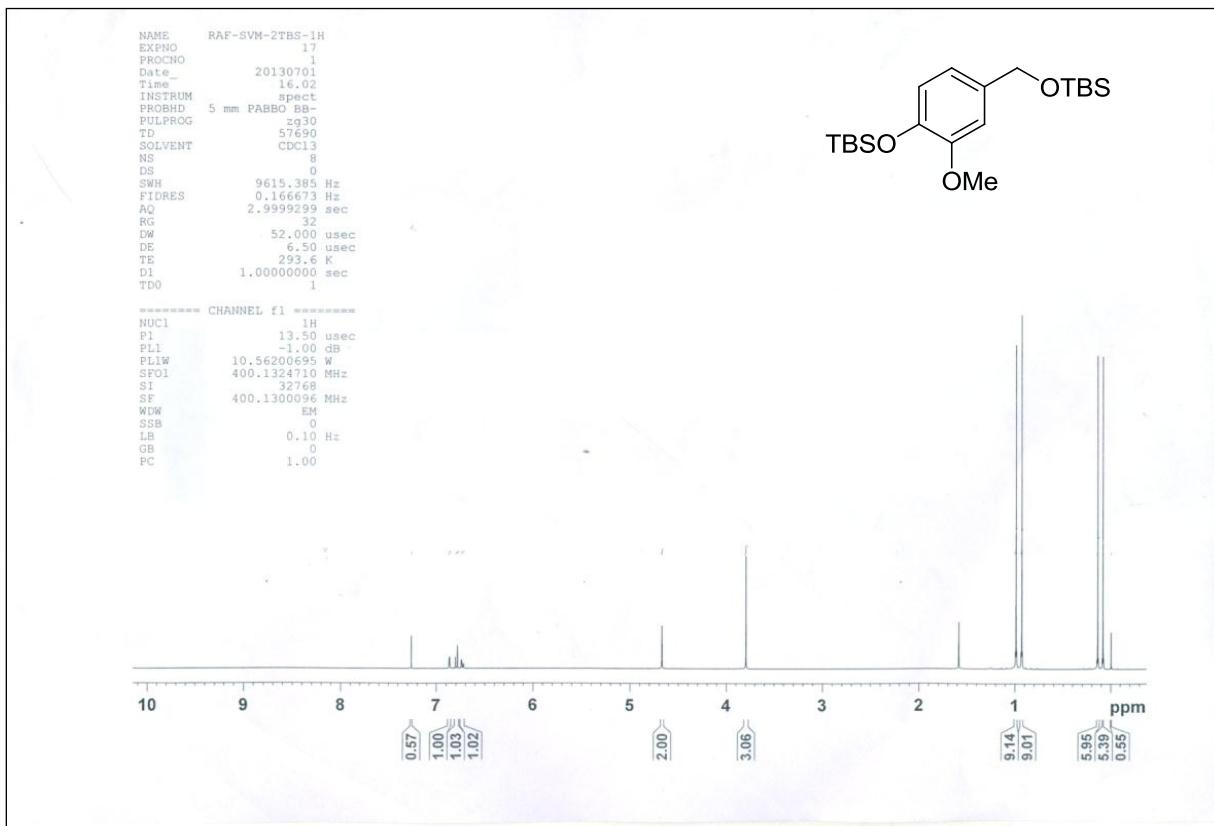
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6c**



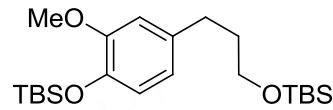
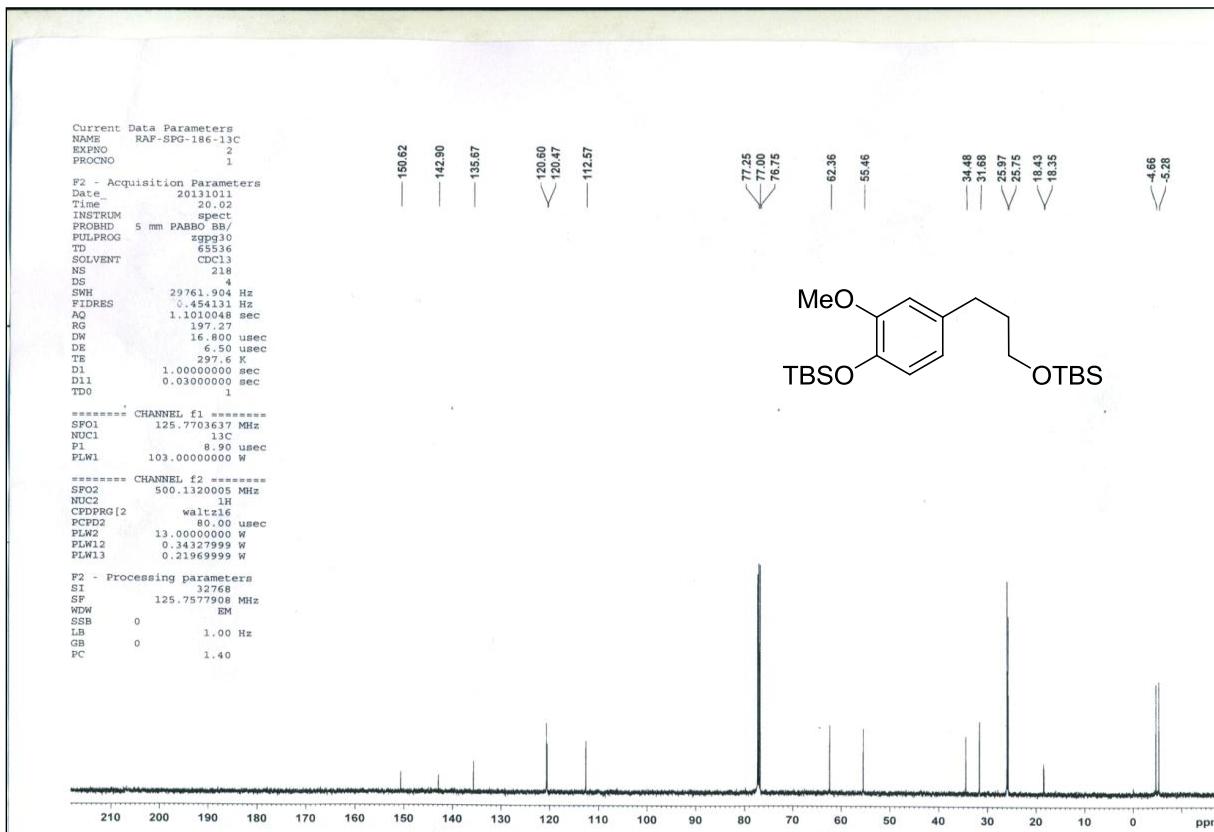
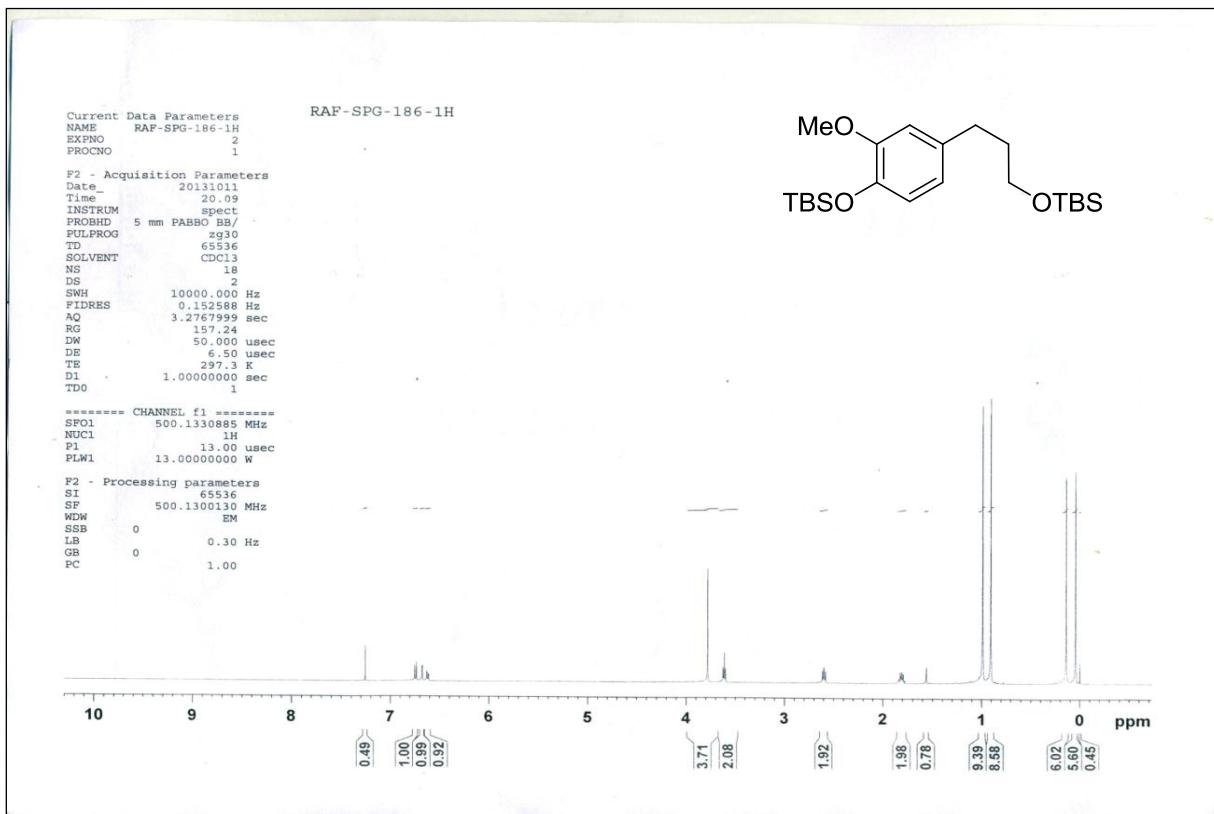
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6d**



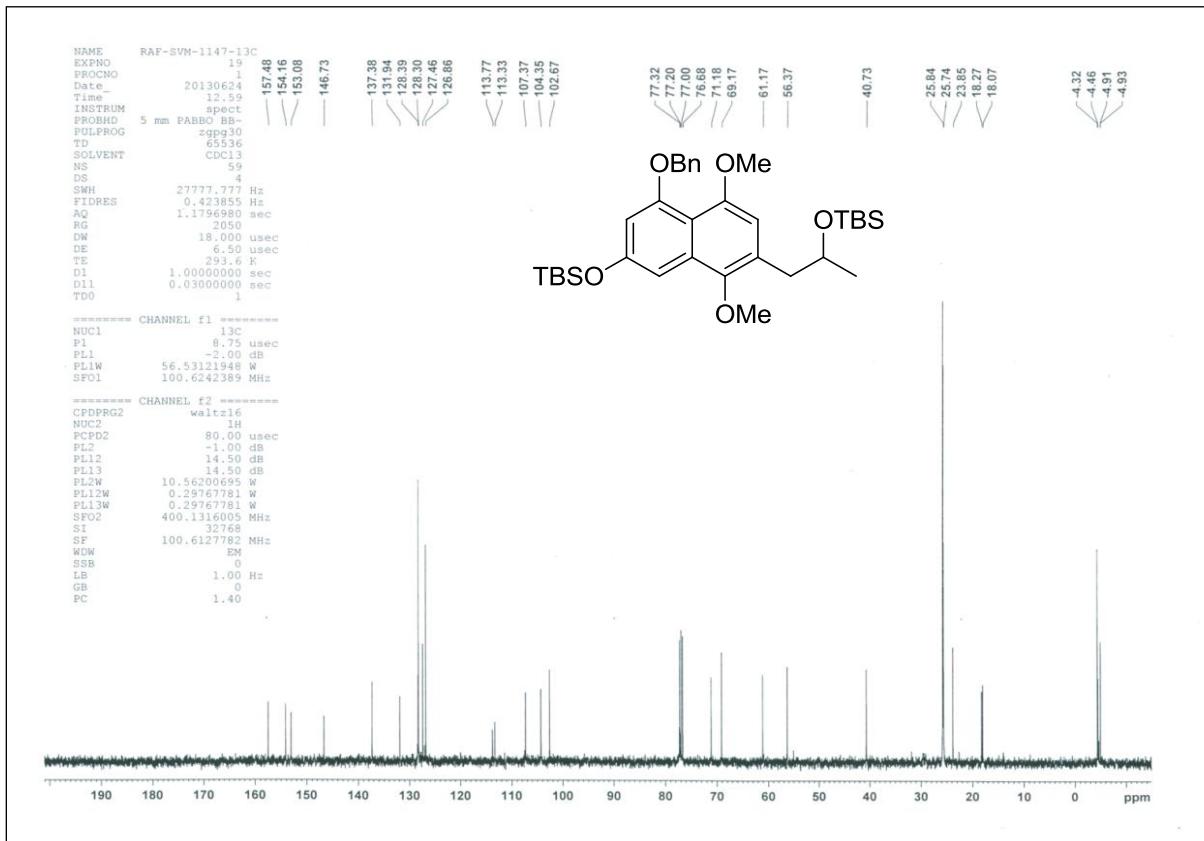
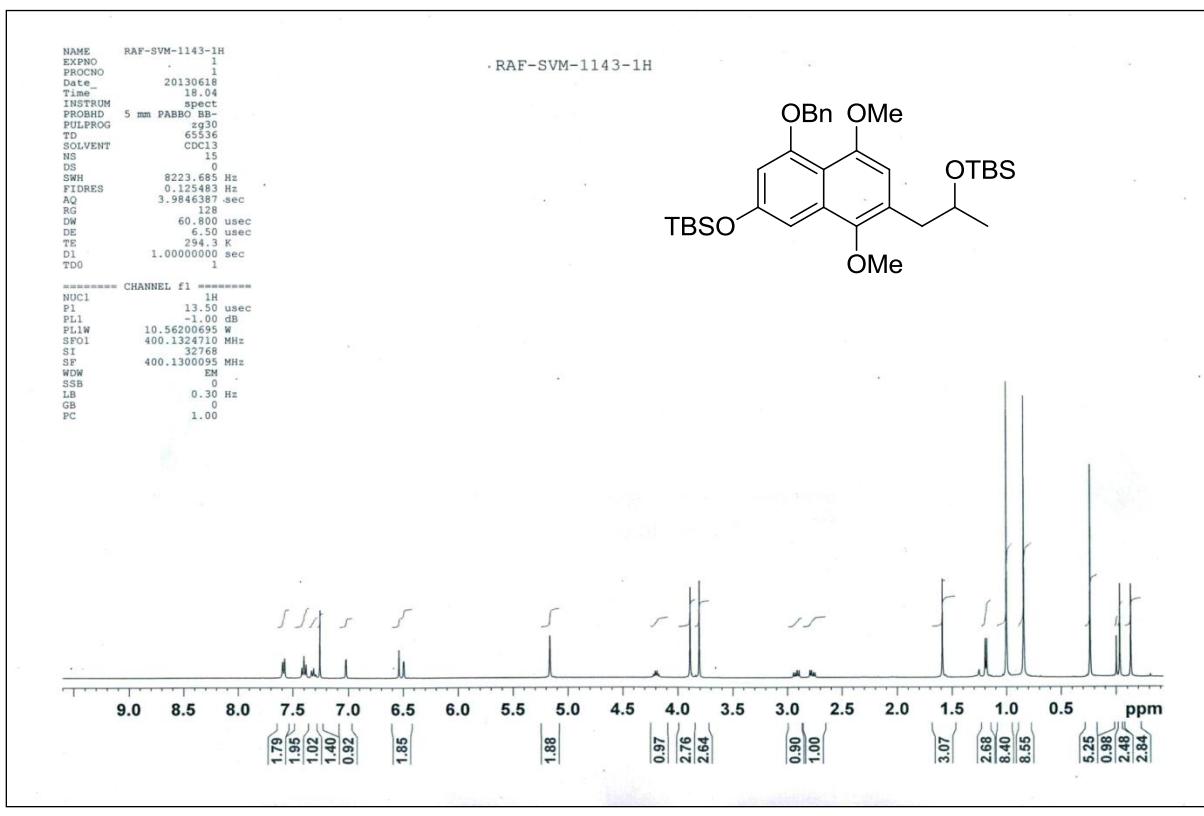
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6e**



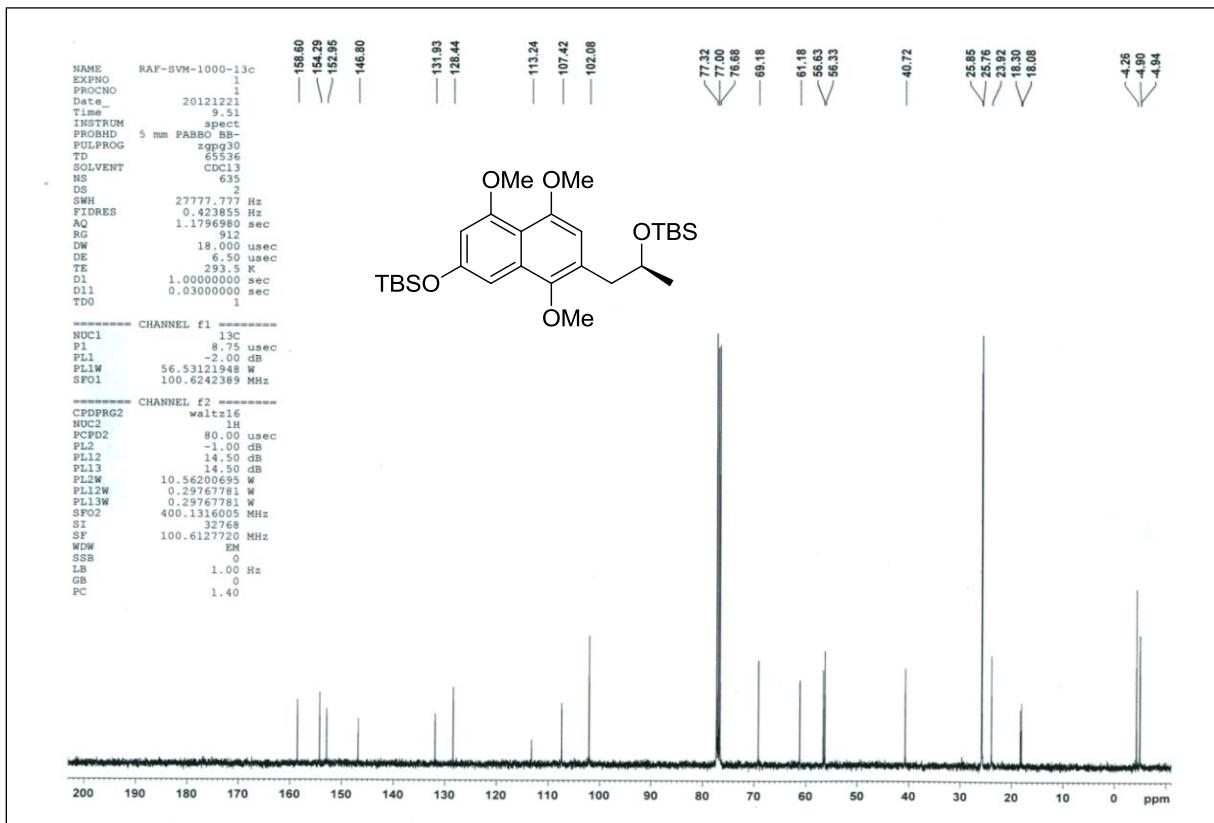
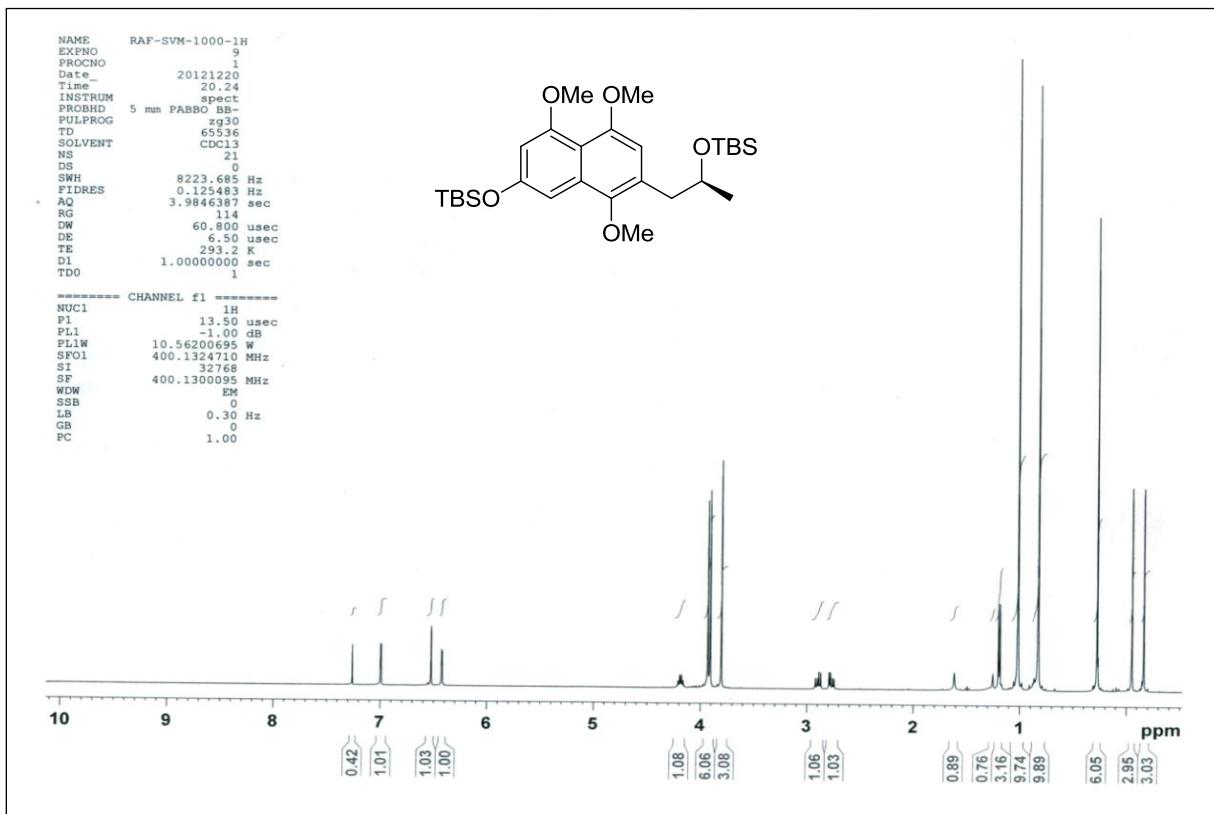
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **6f**



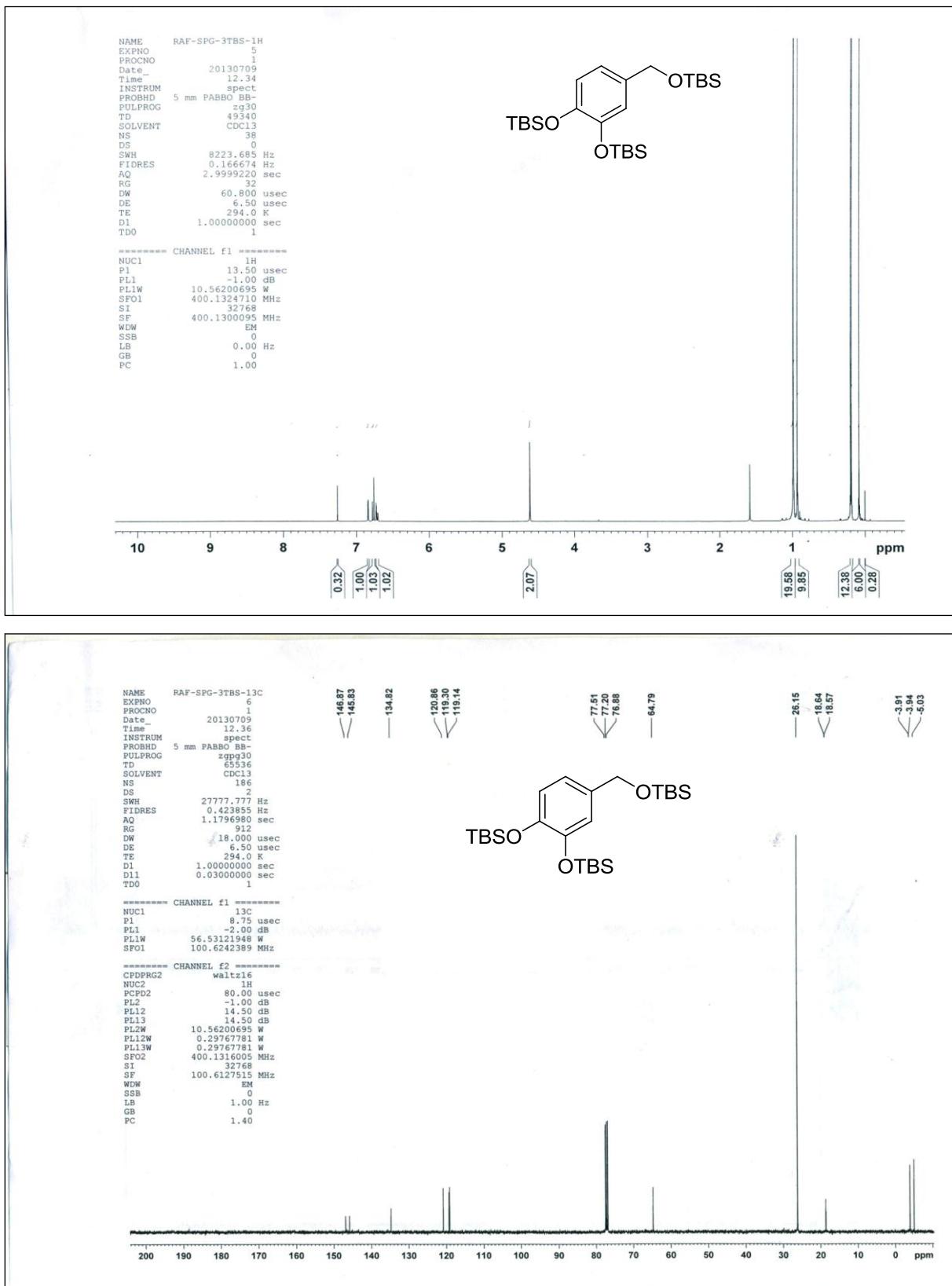
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6g**



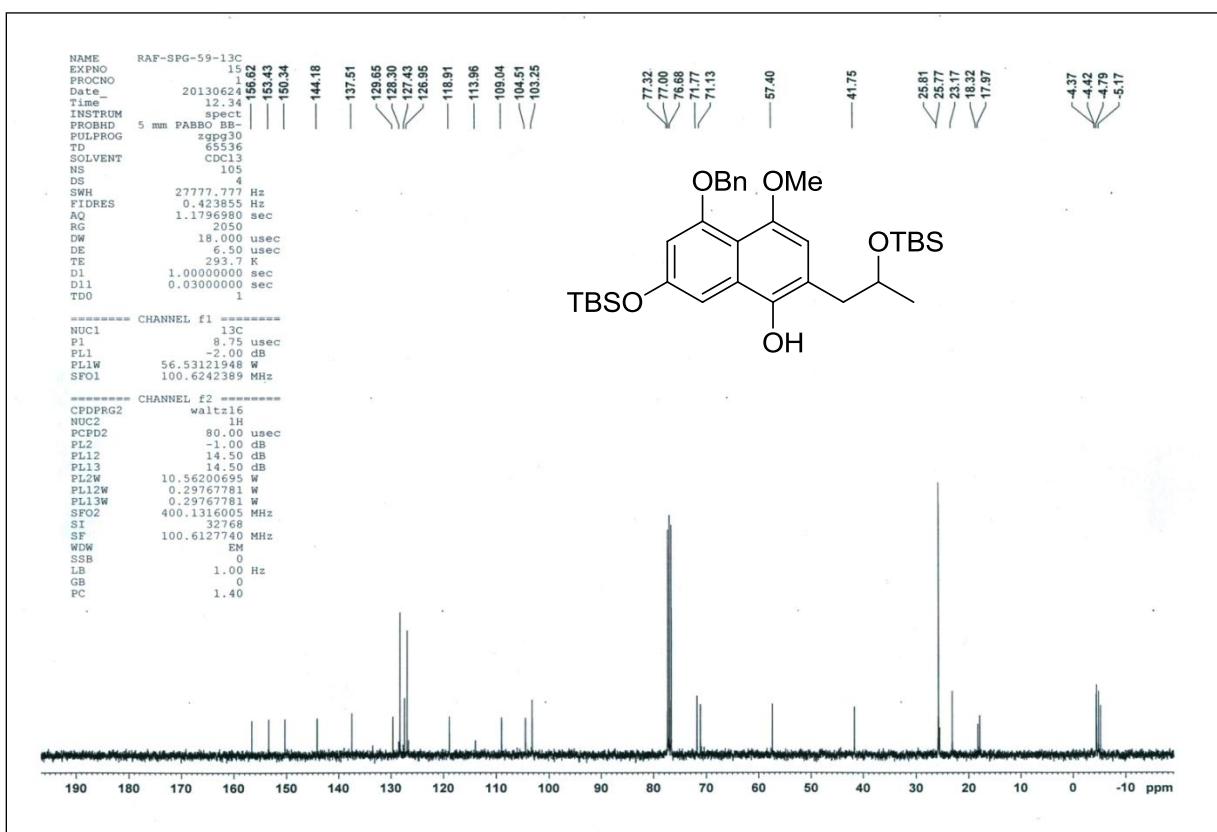
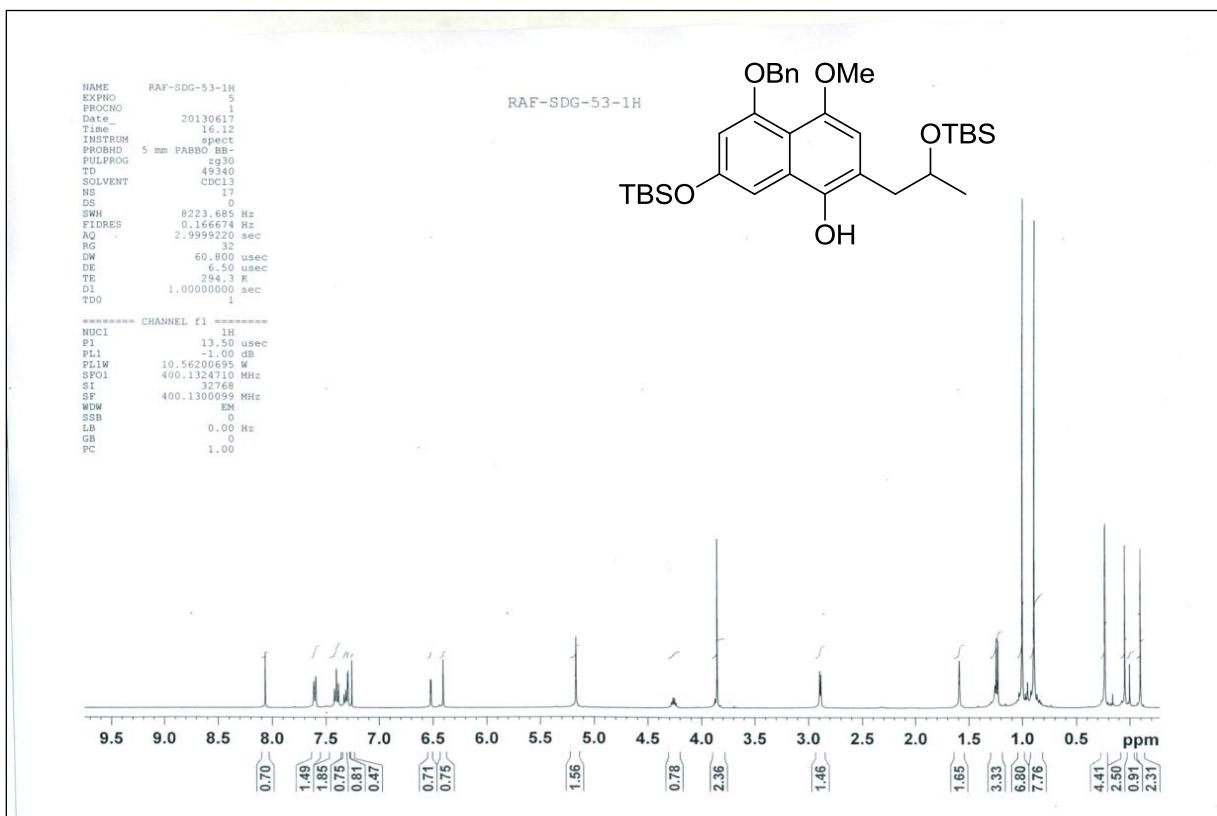
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6h**



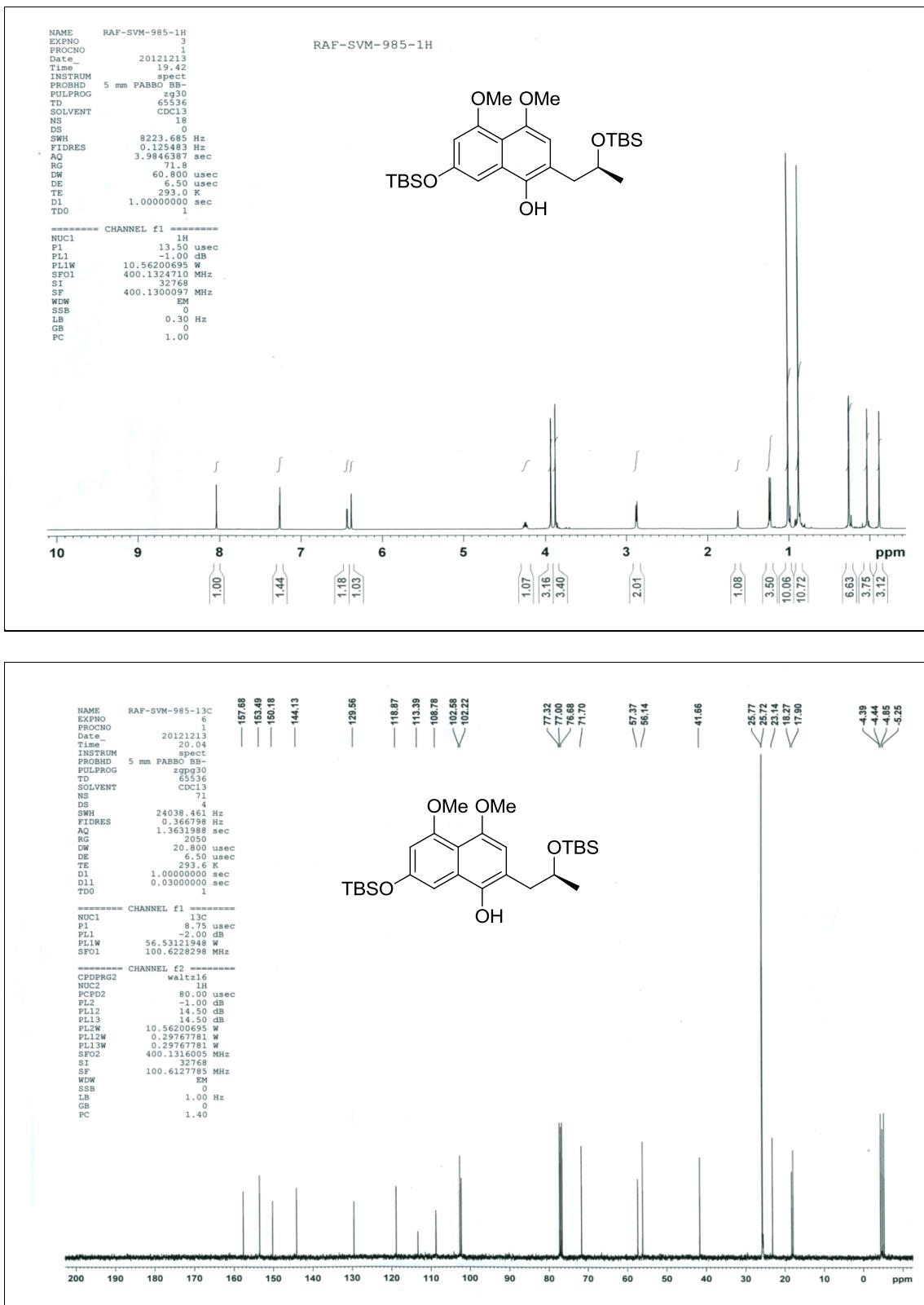
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6i**



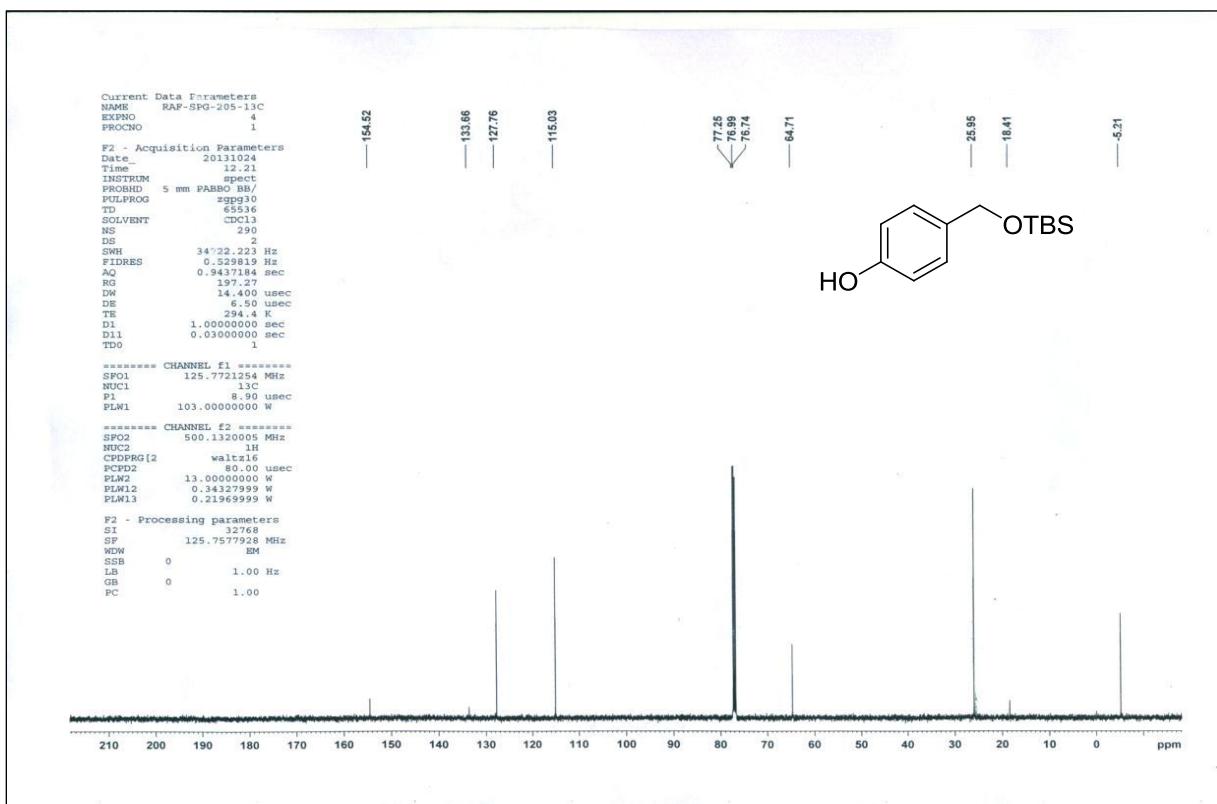
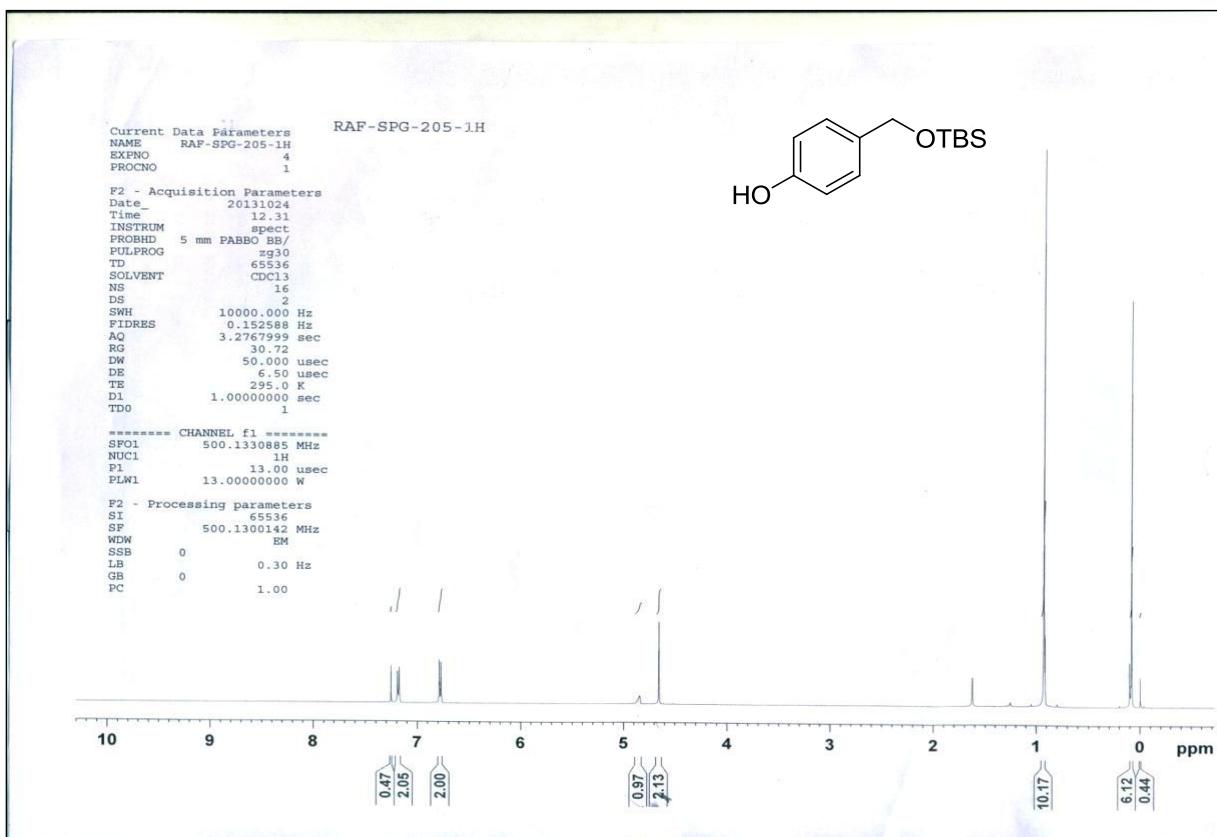
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **6j**



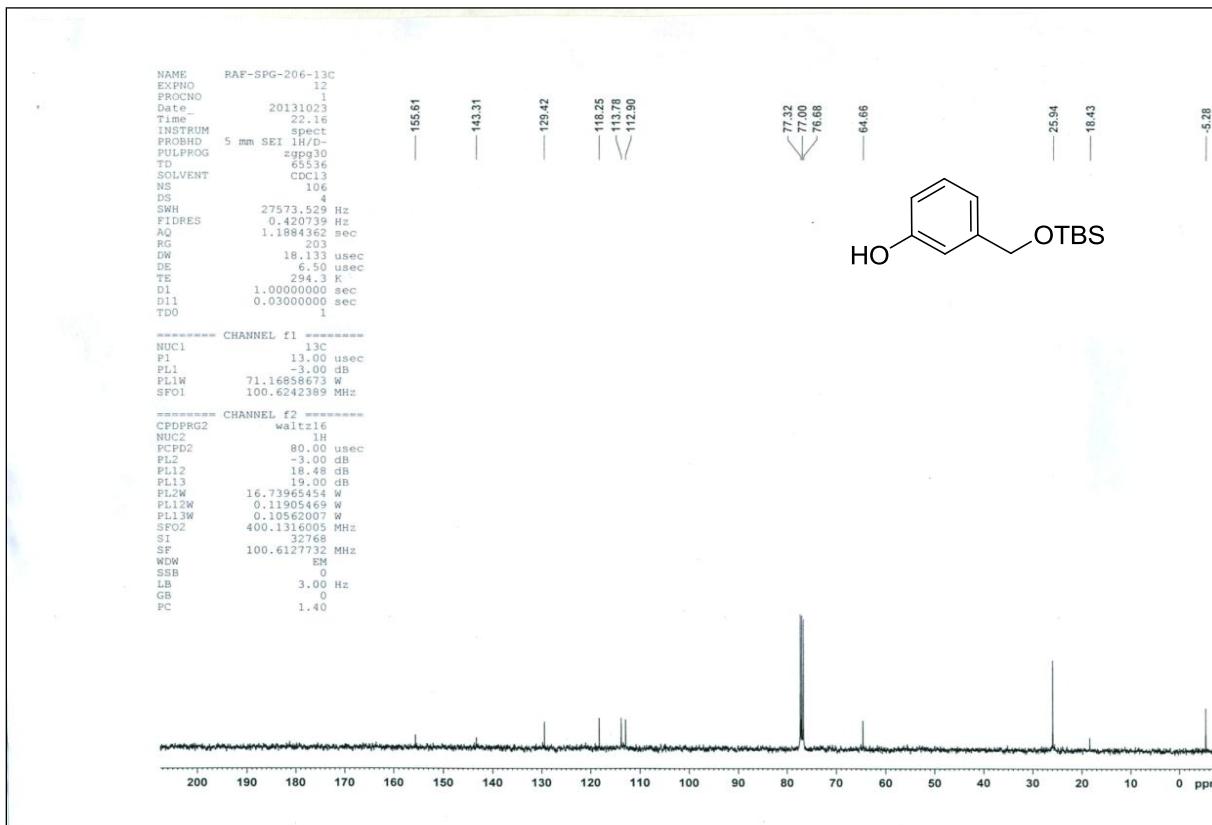
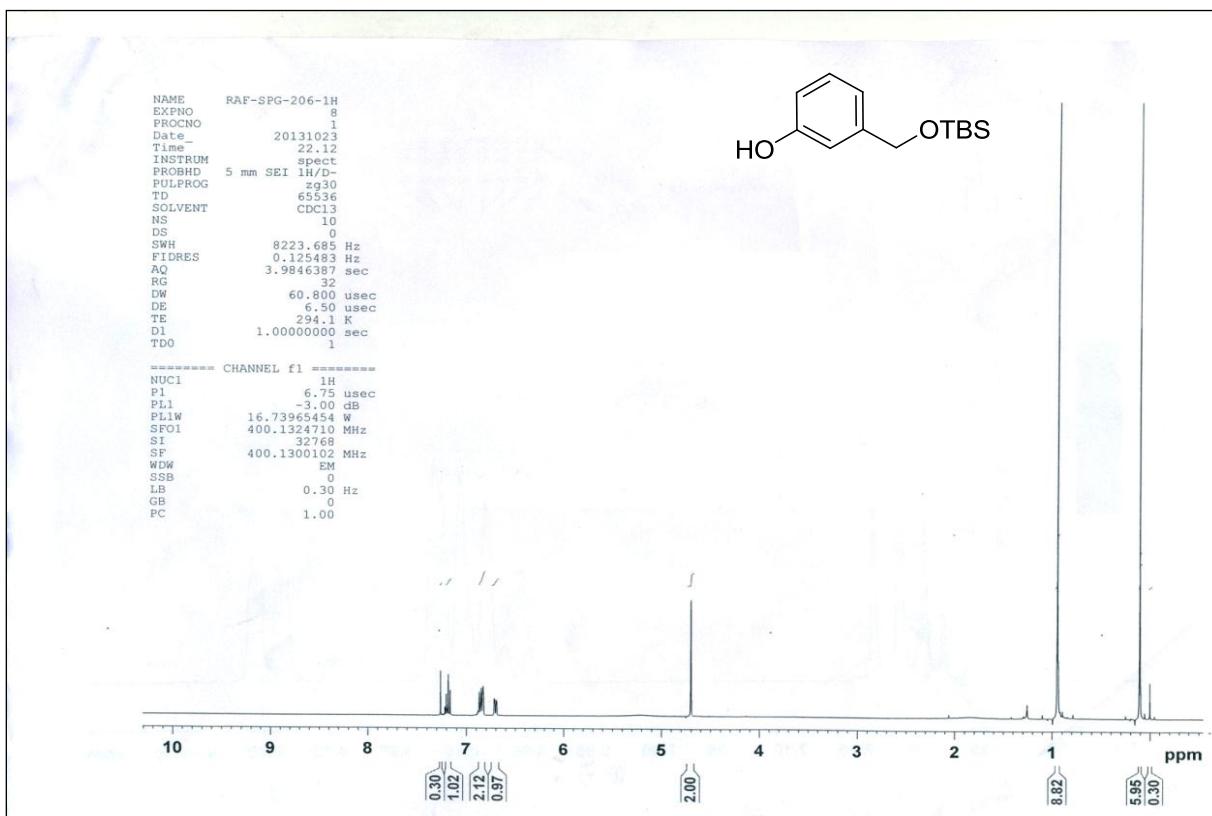
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **1**



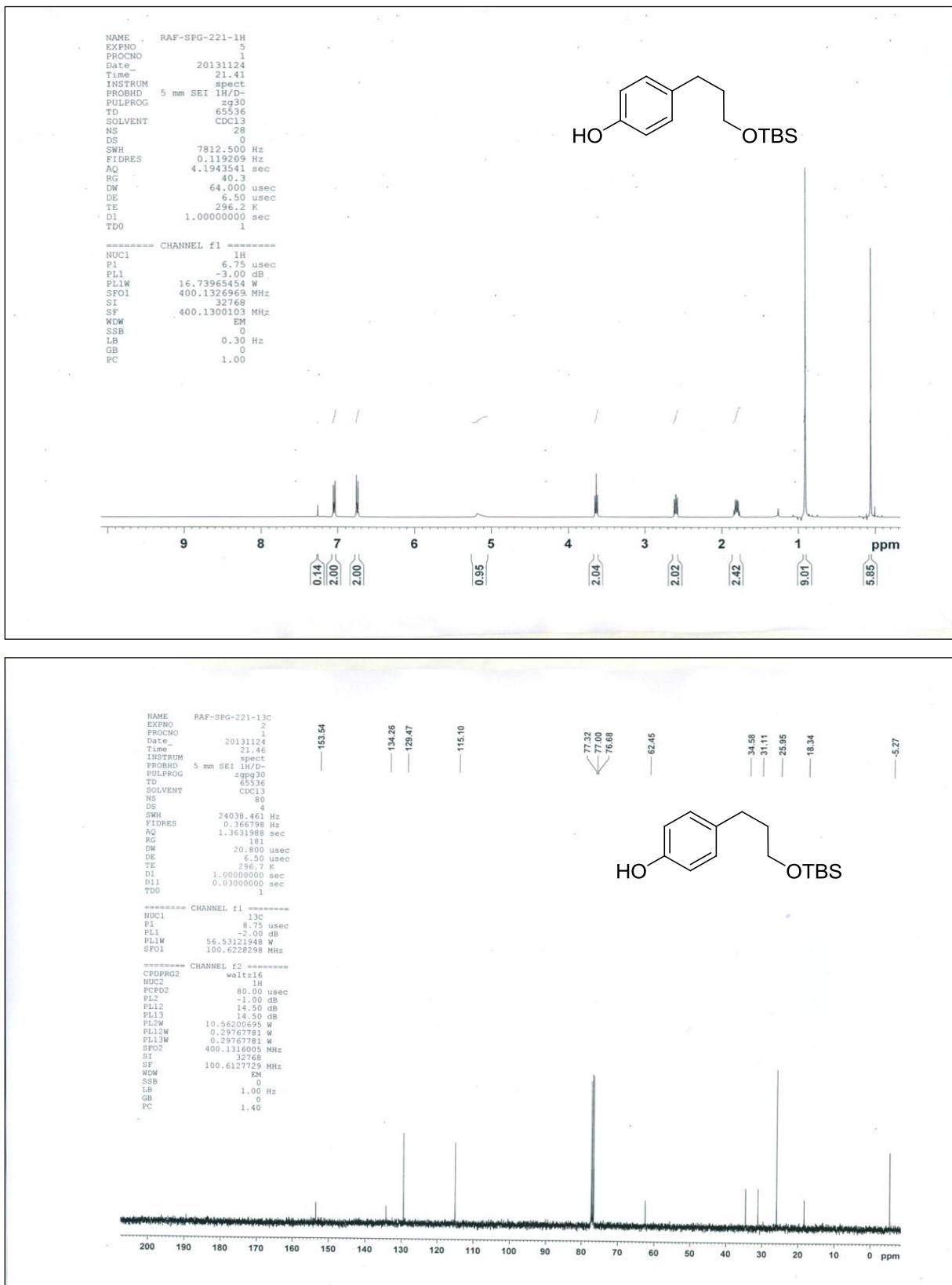
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) of compound 7a



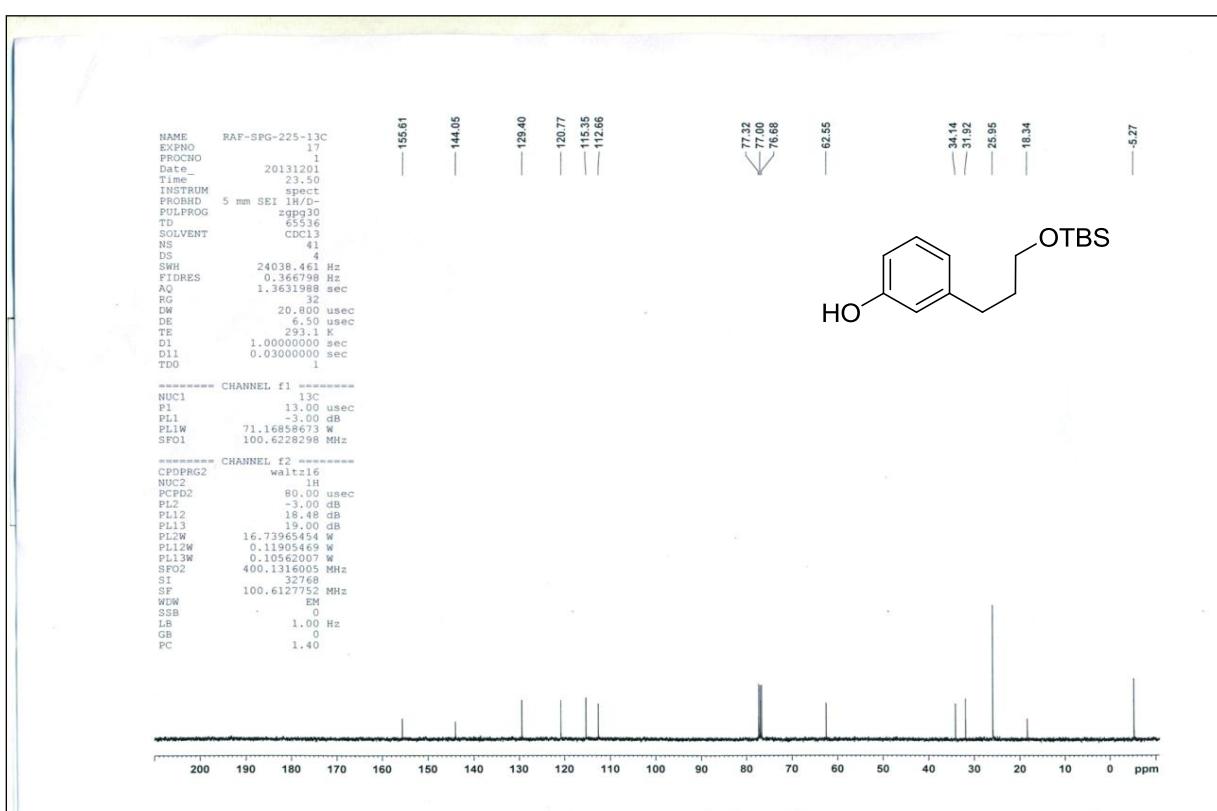
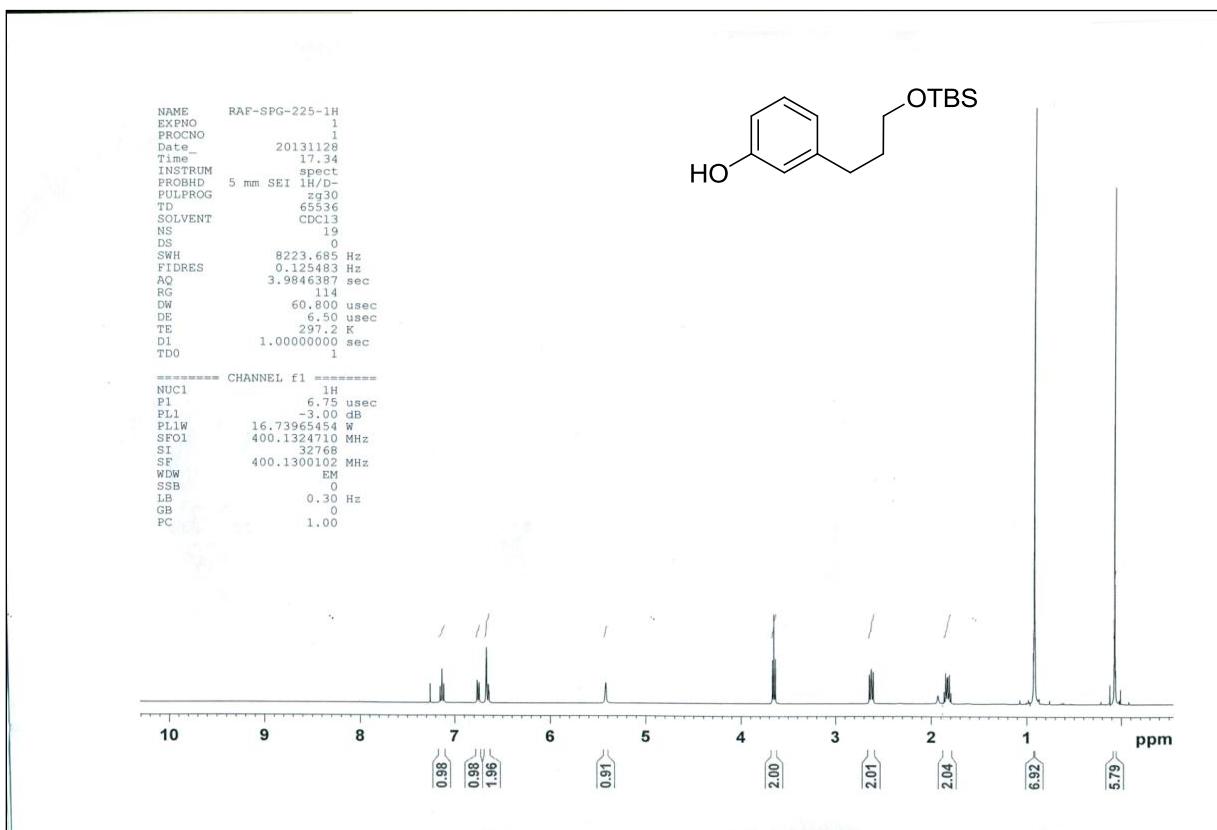
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7b



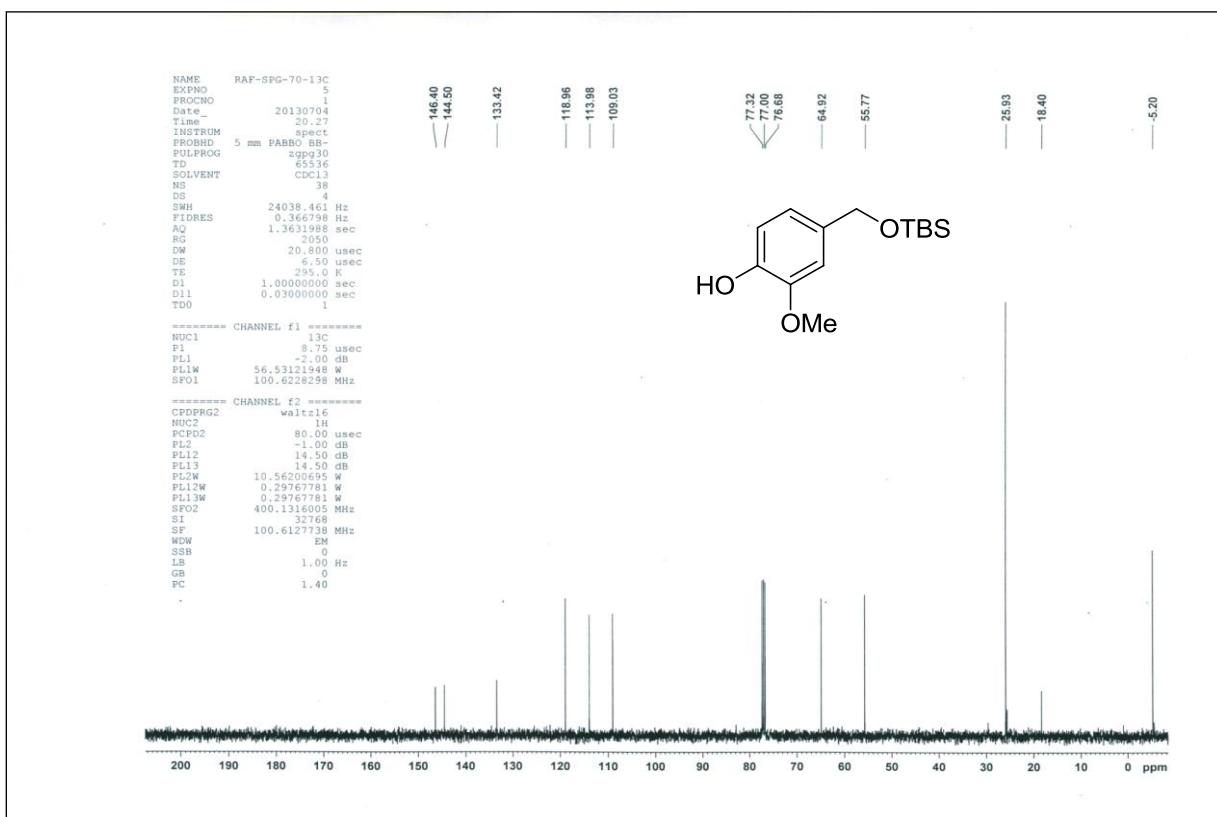
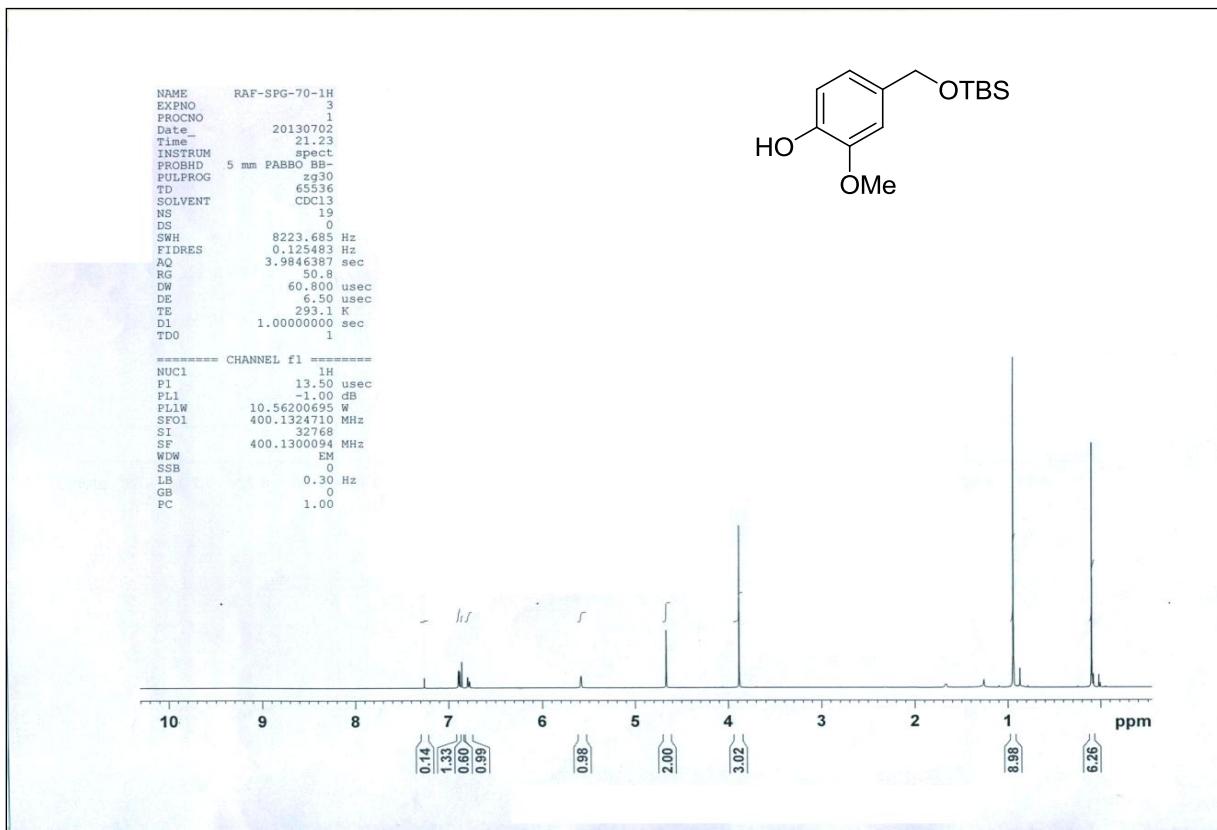
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7c



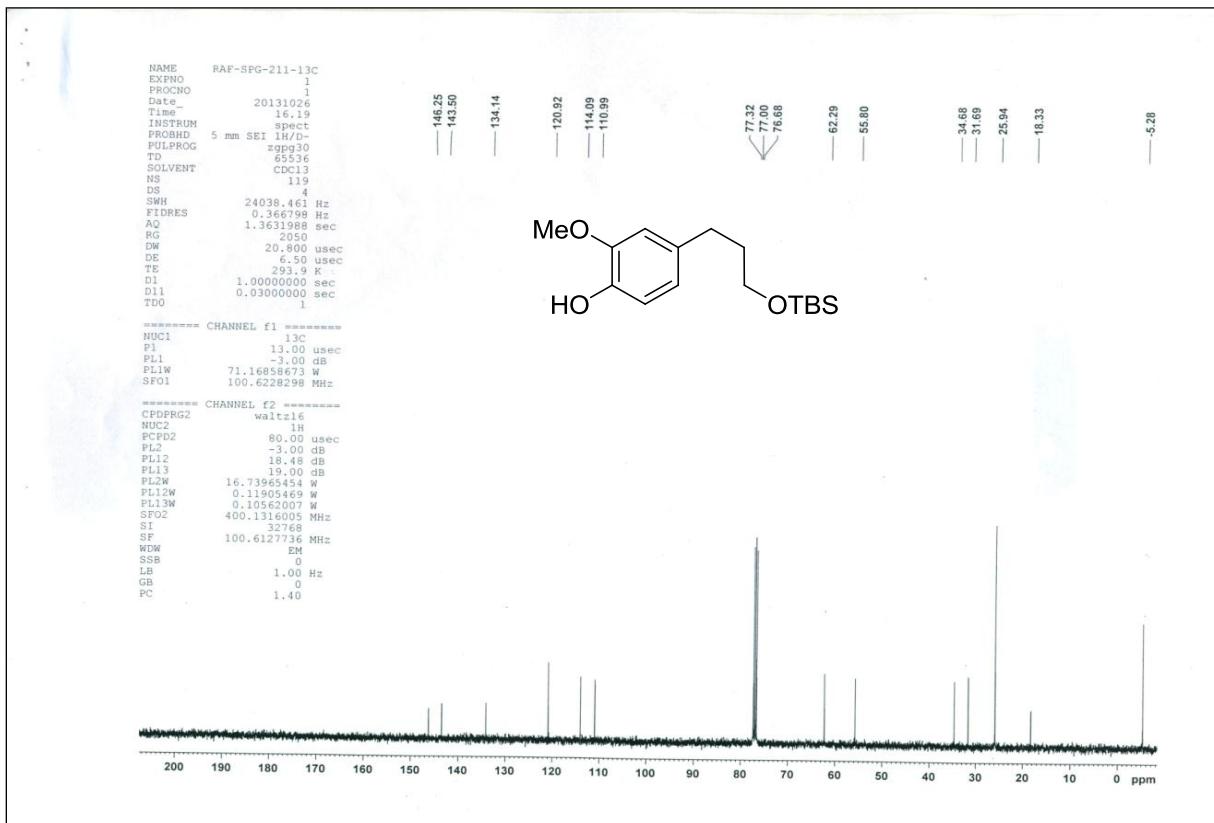
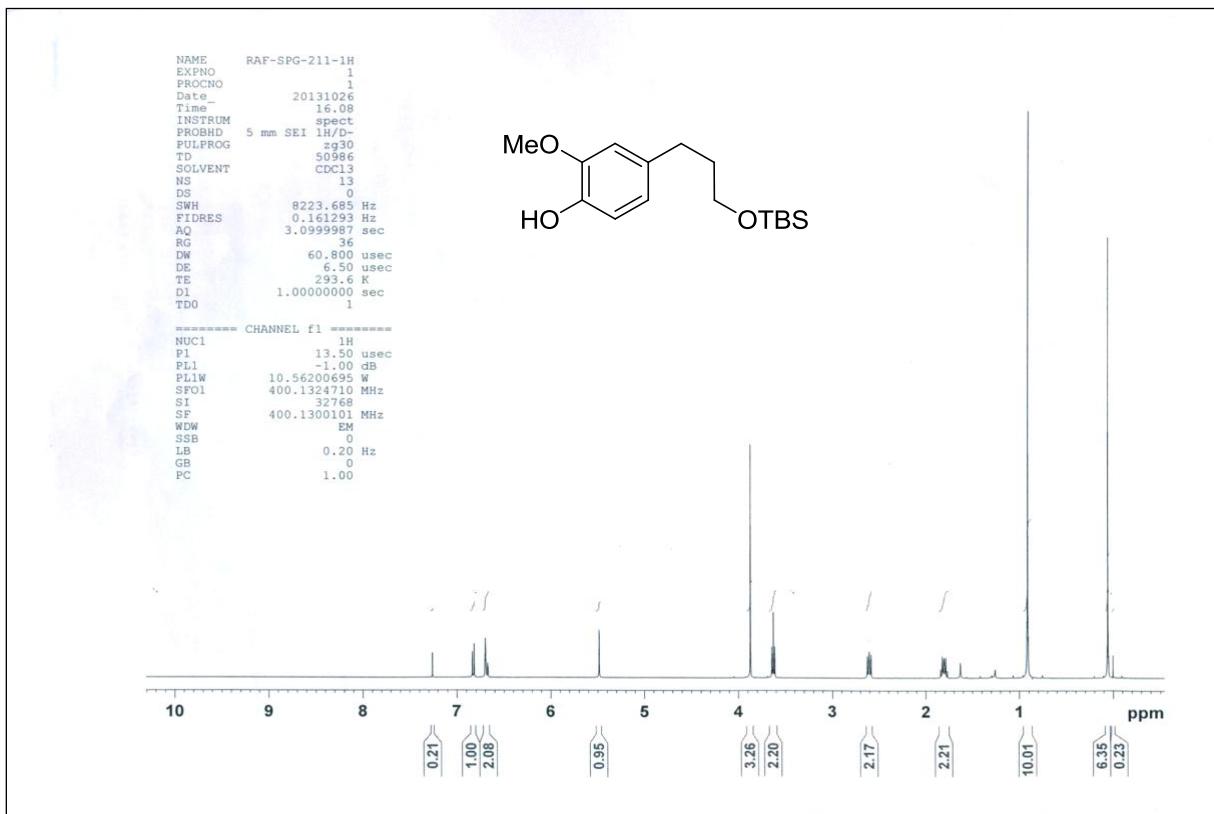
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7d



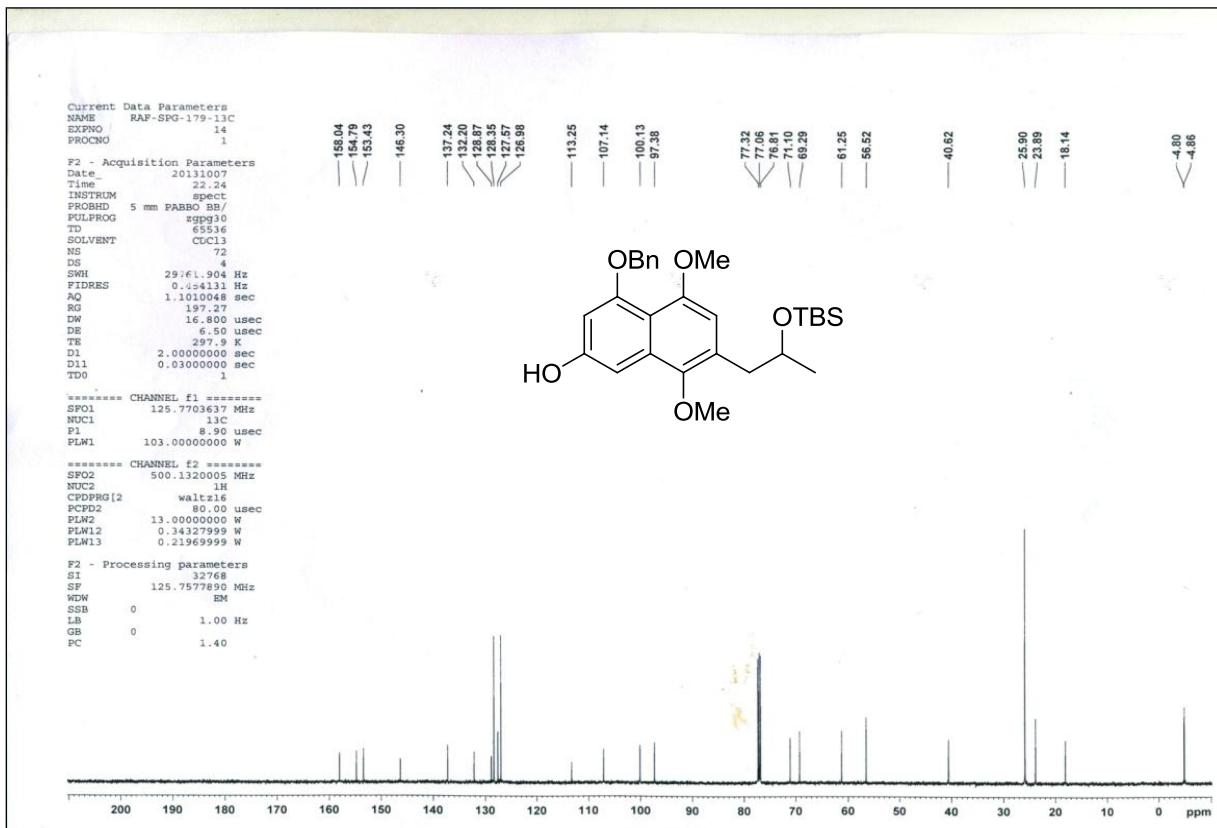
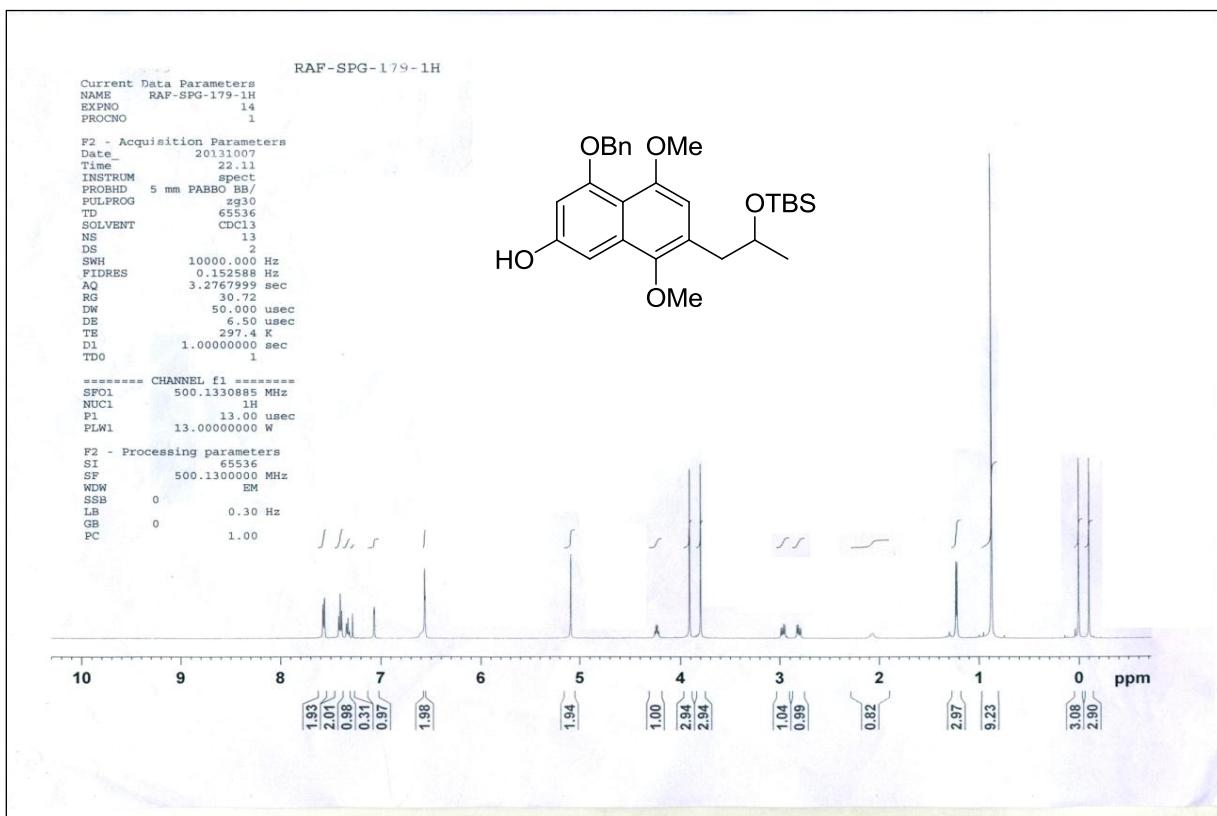
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7e



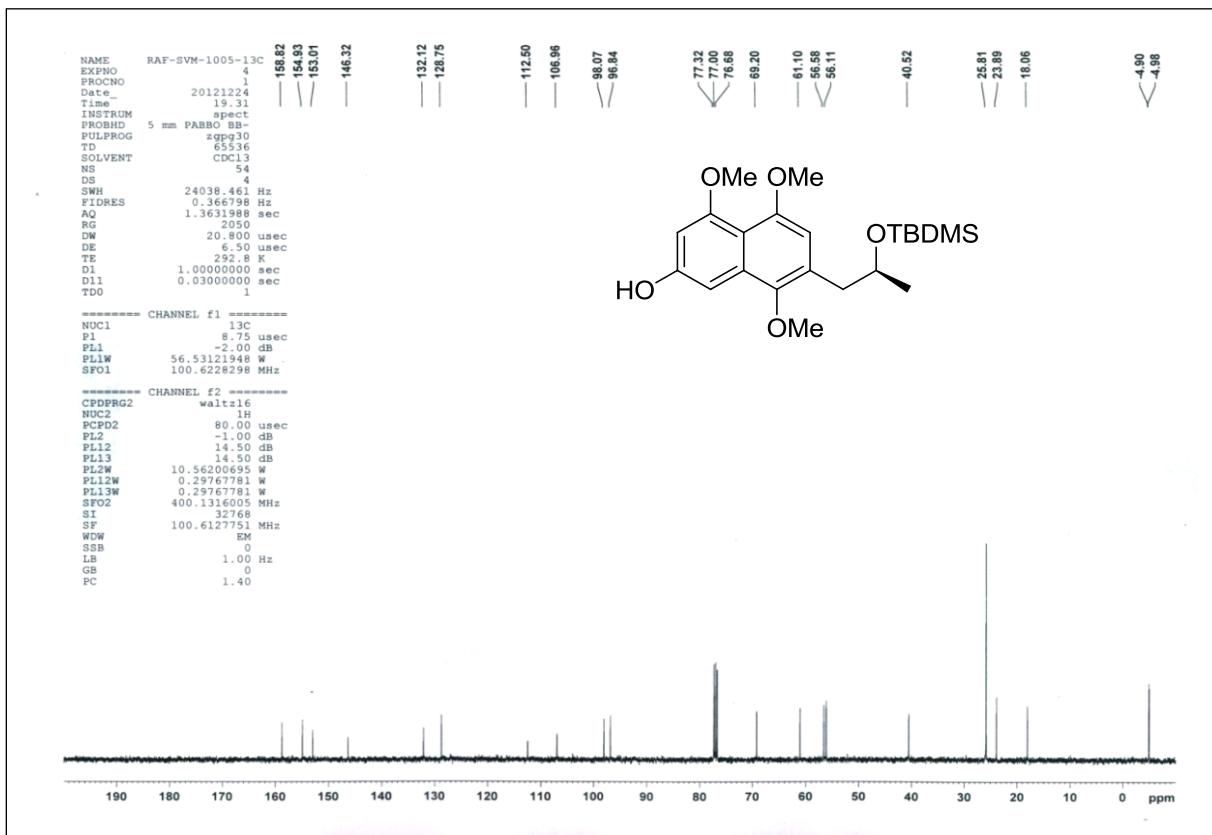
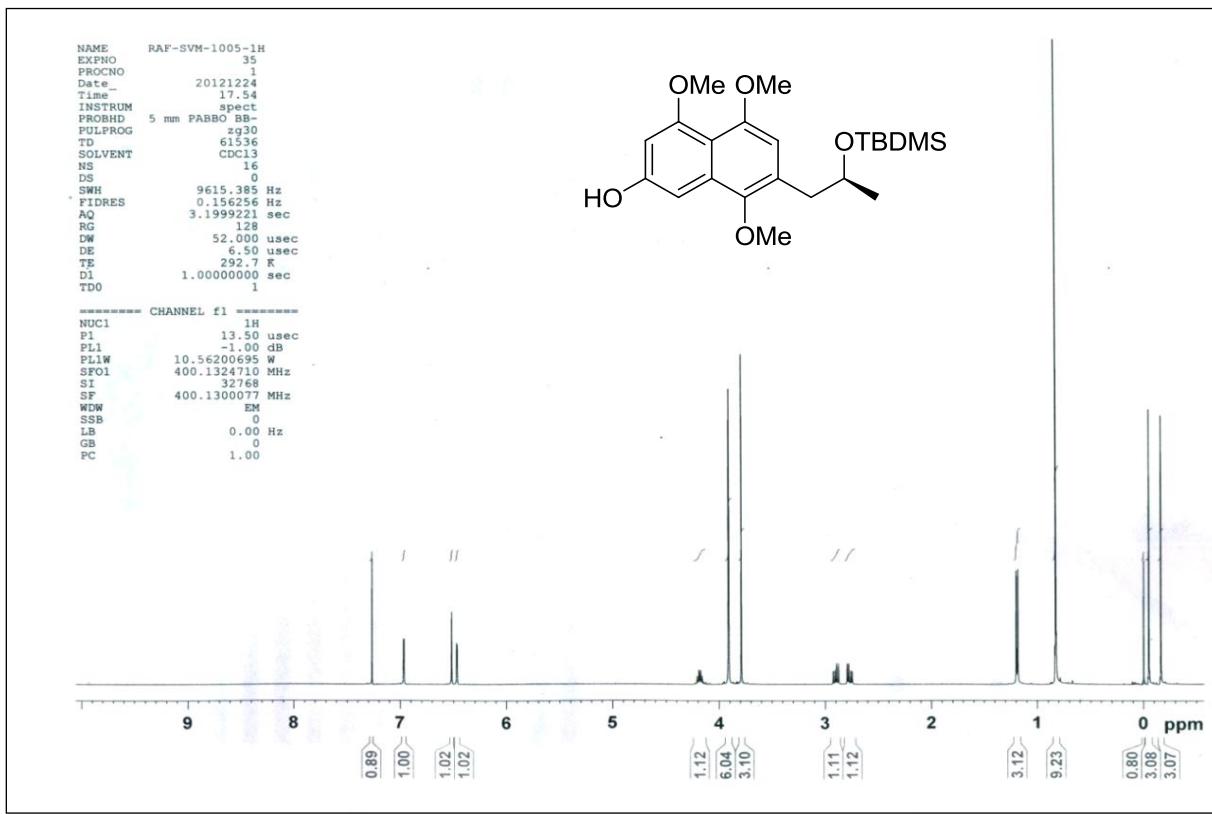
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7f



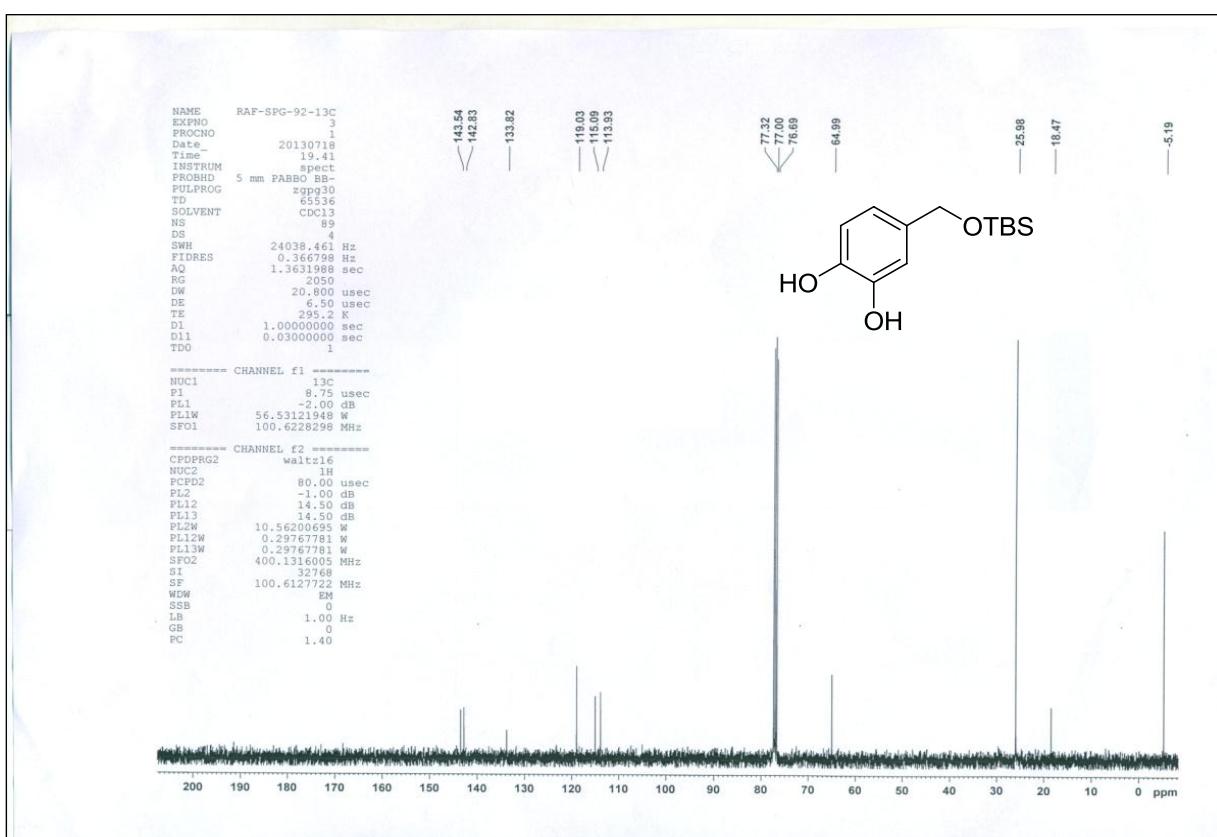
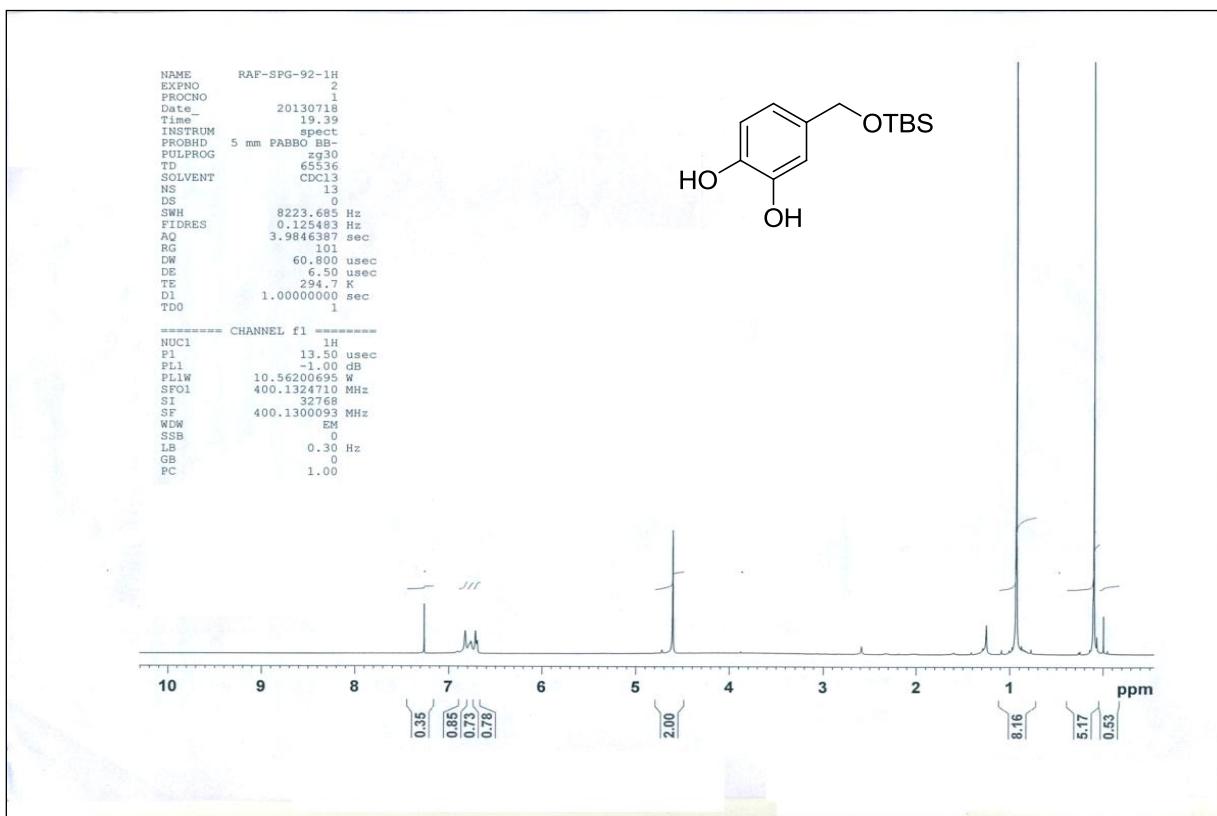
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) of compound 7g



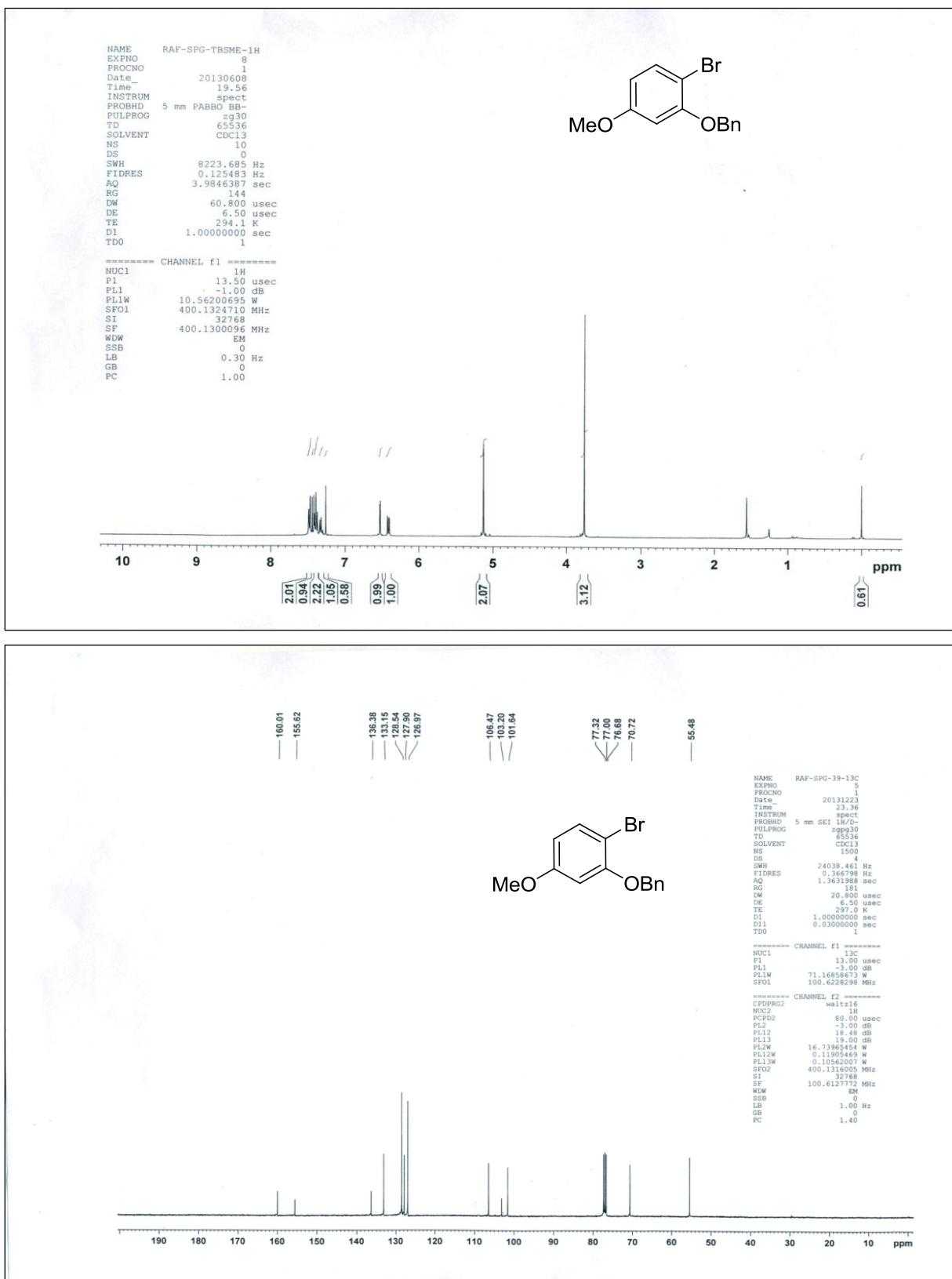
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7h



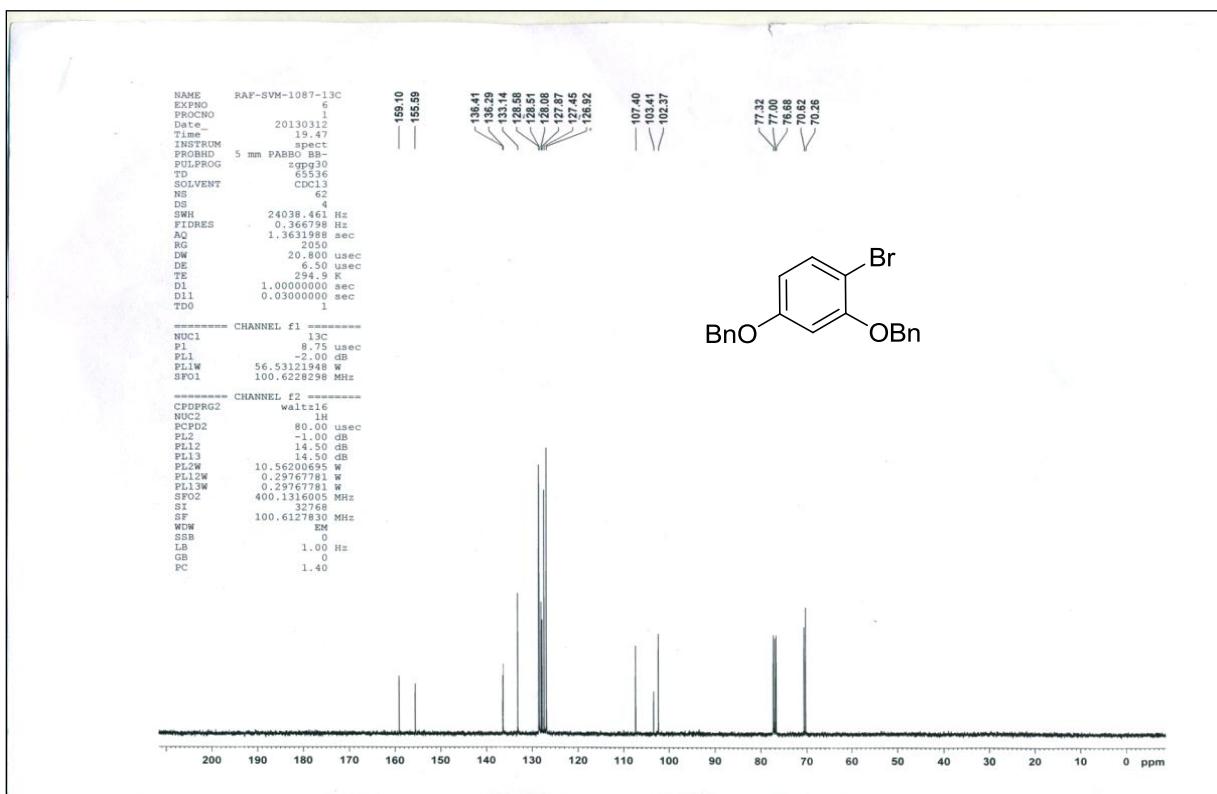
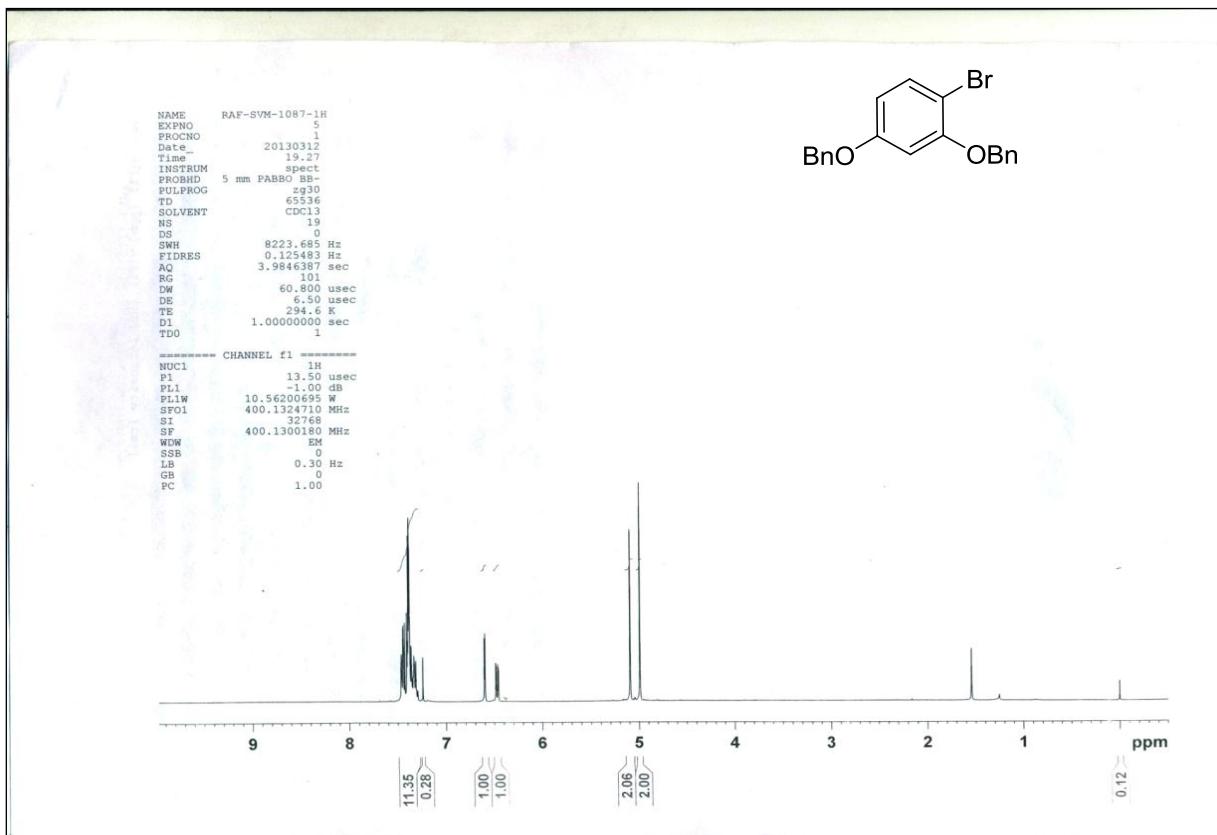
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7i



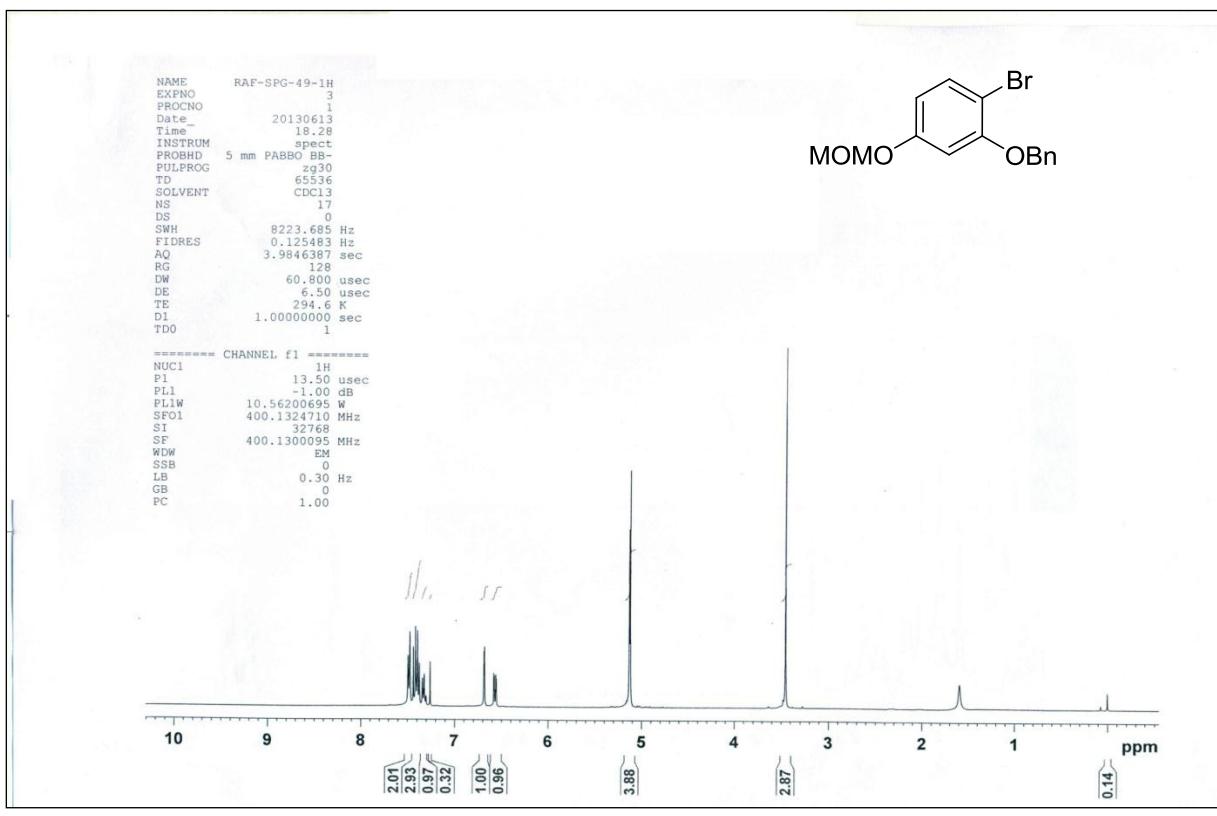
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8a**



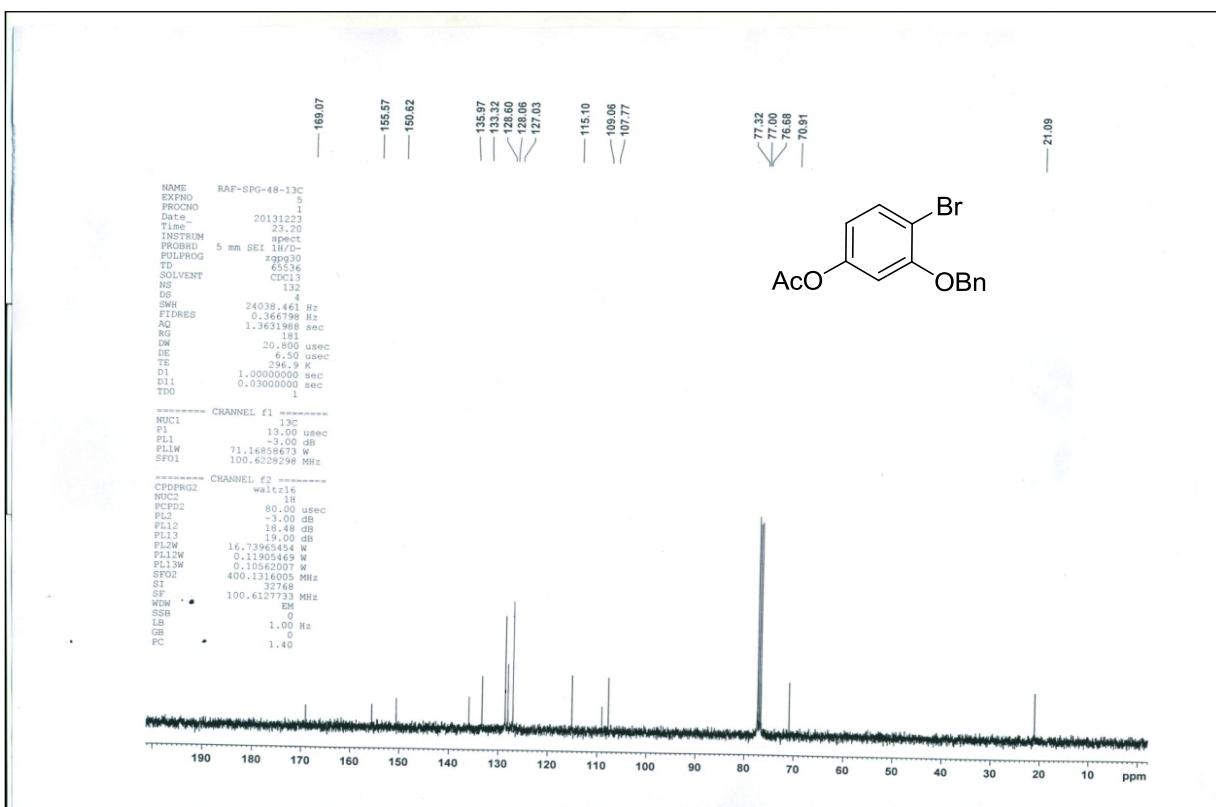
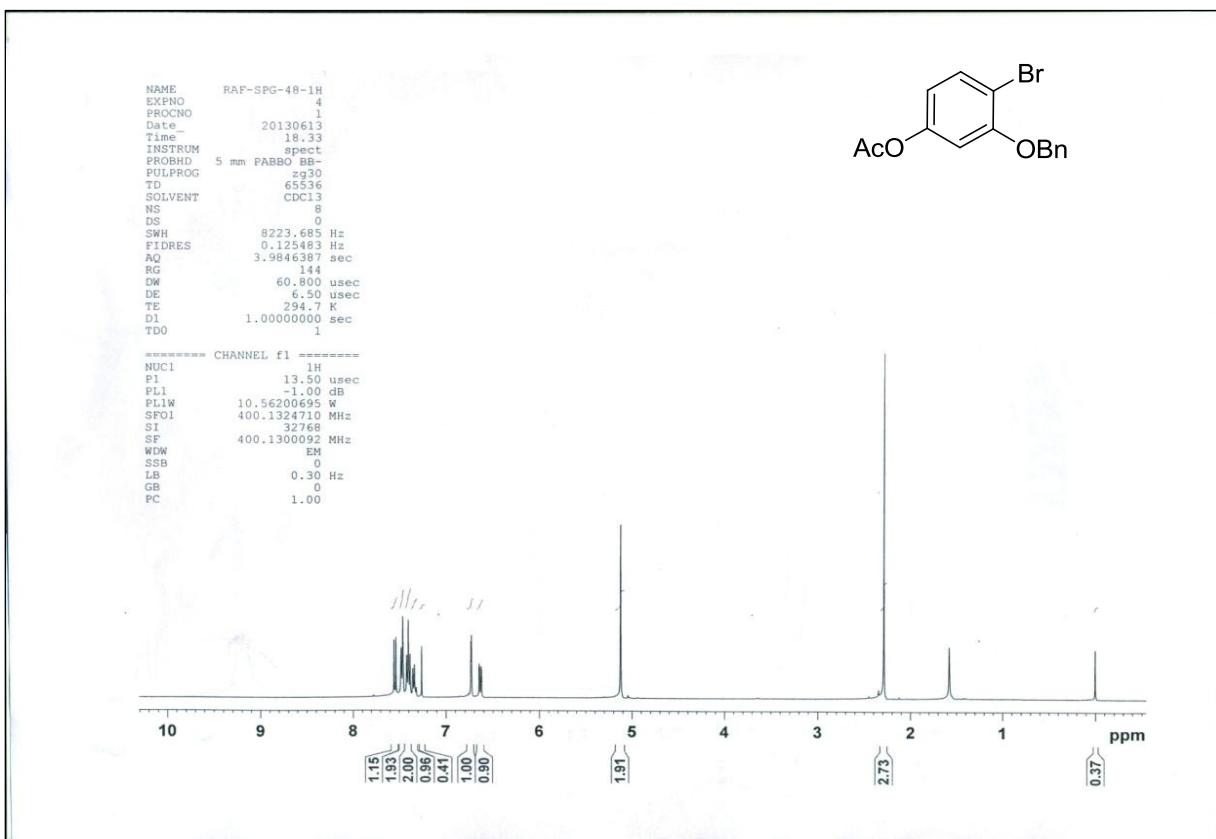
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8b**



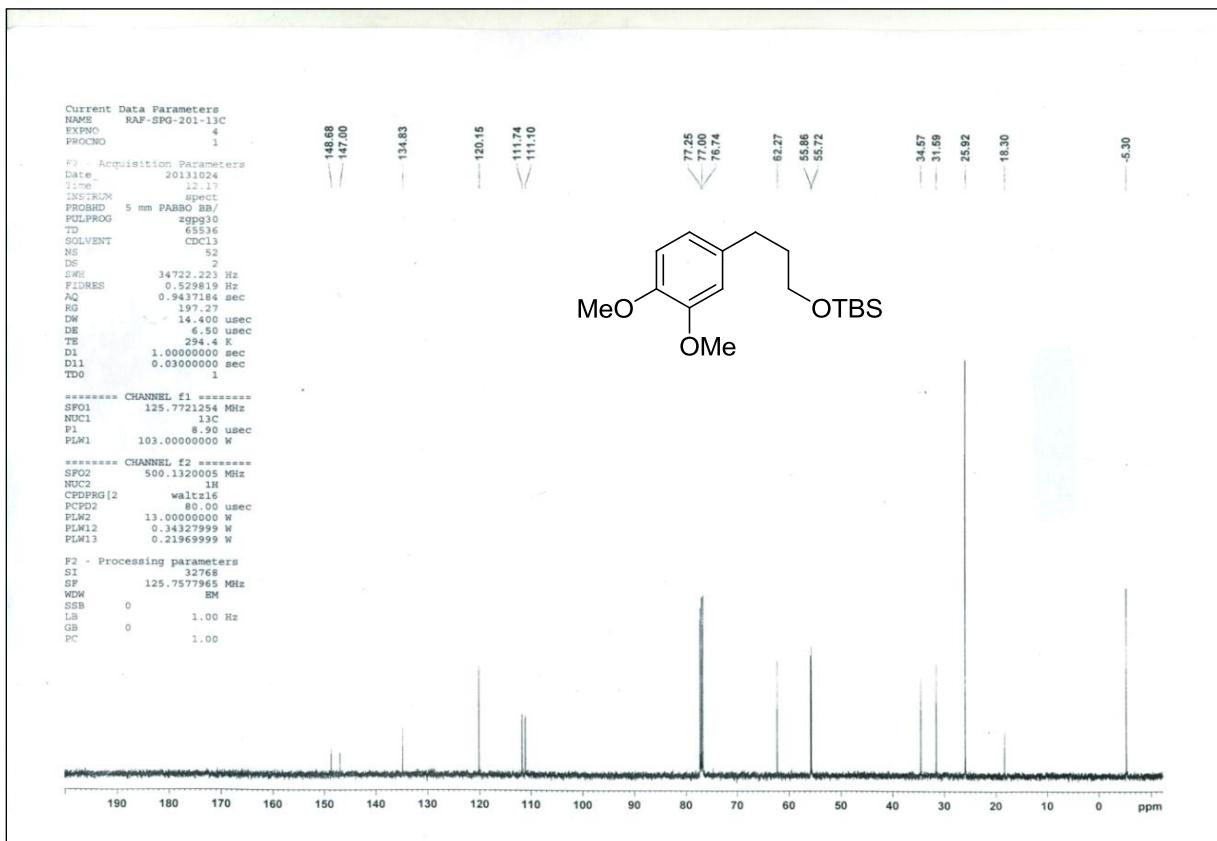
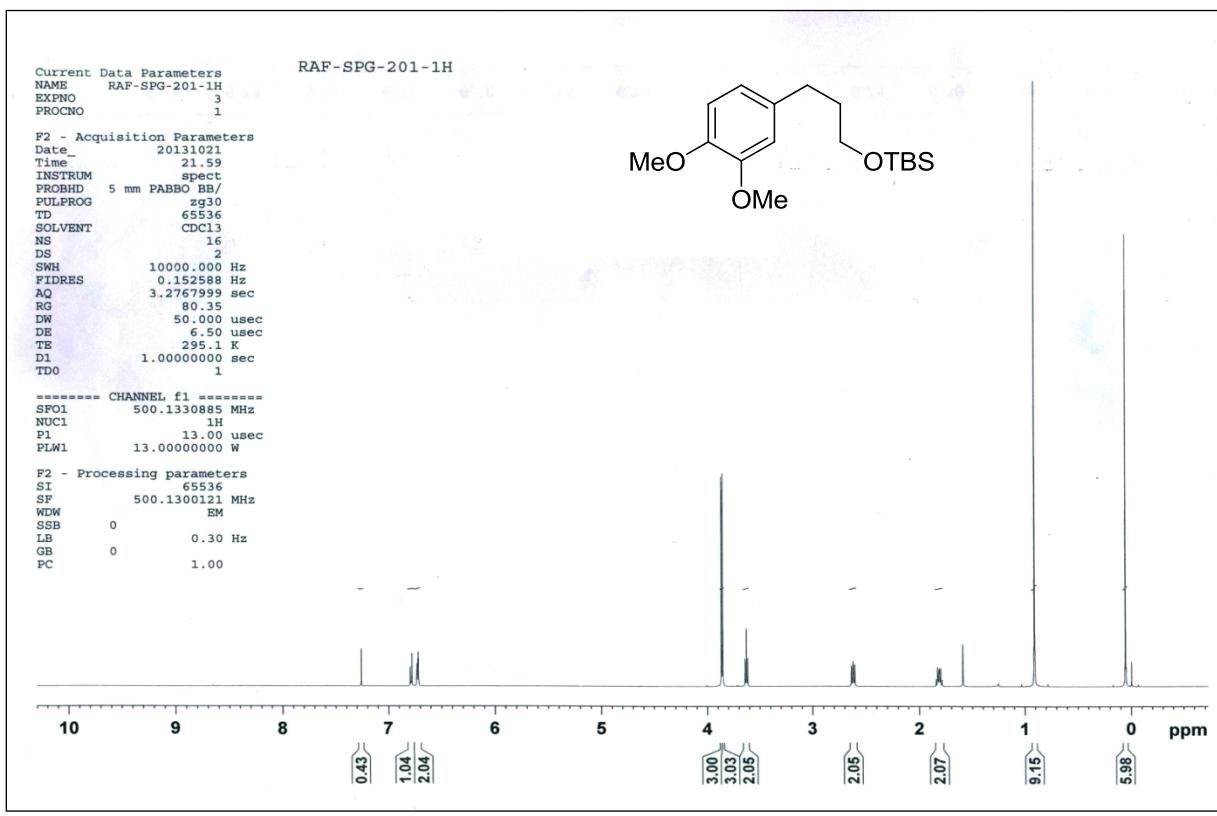
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **8c**



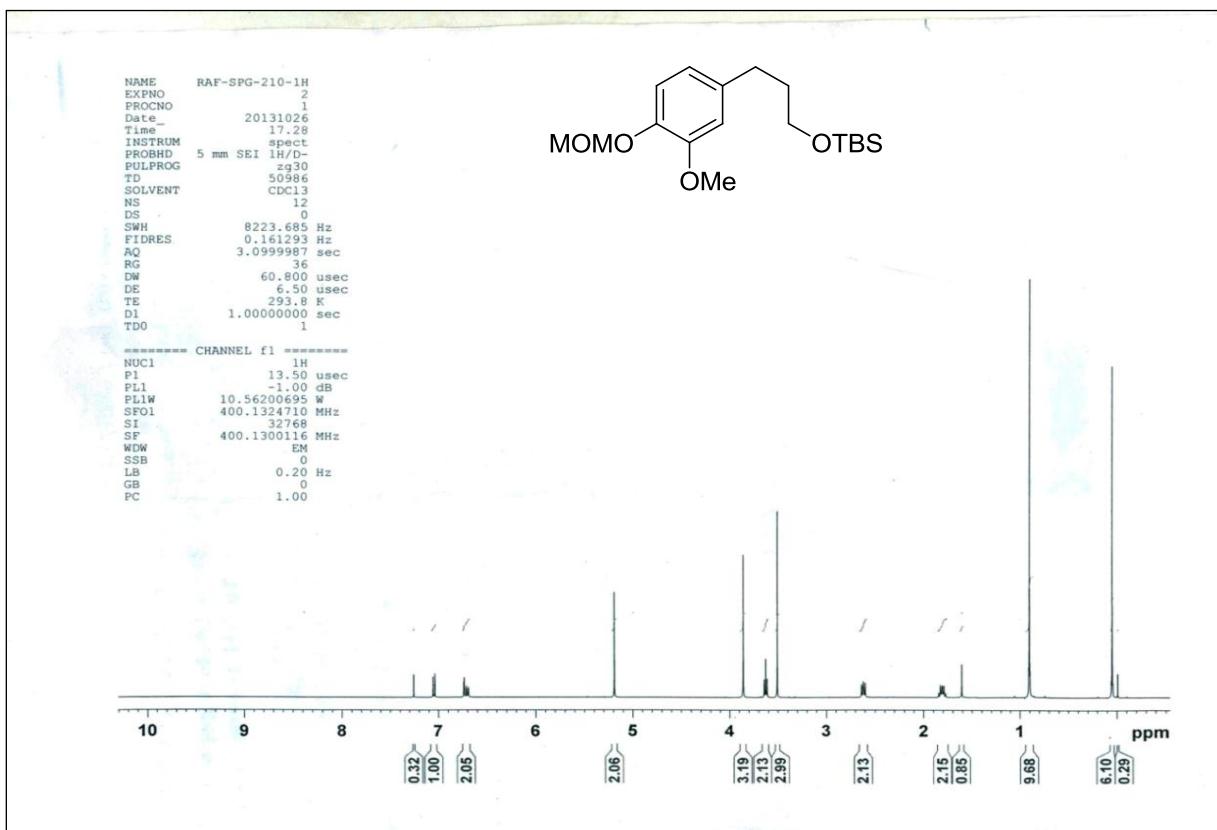
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8d**



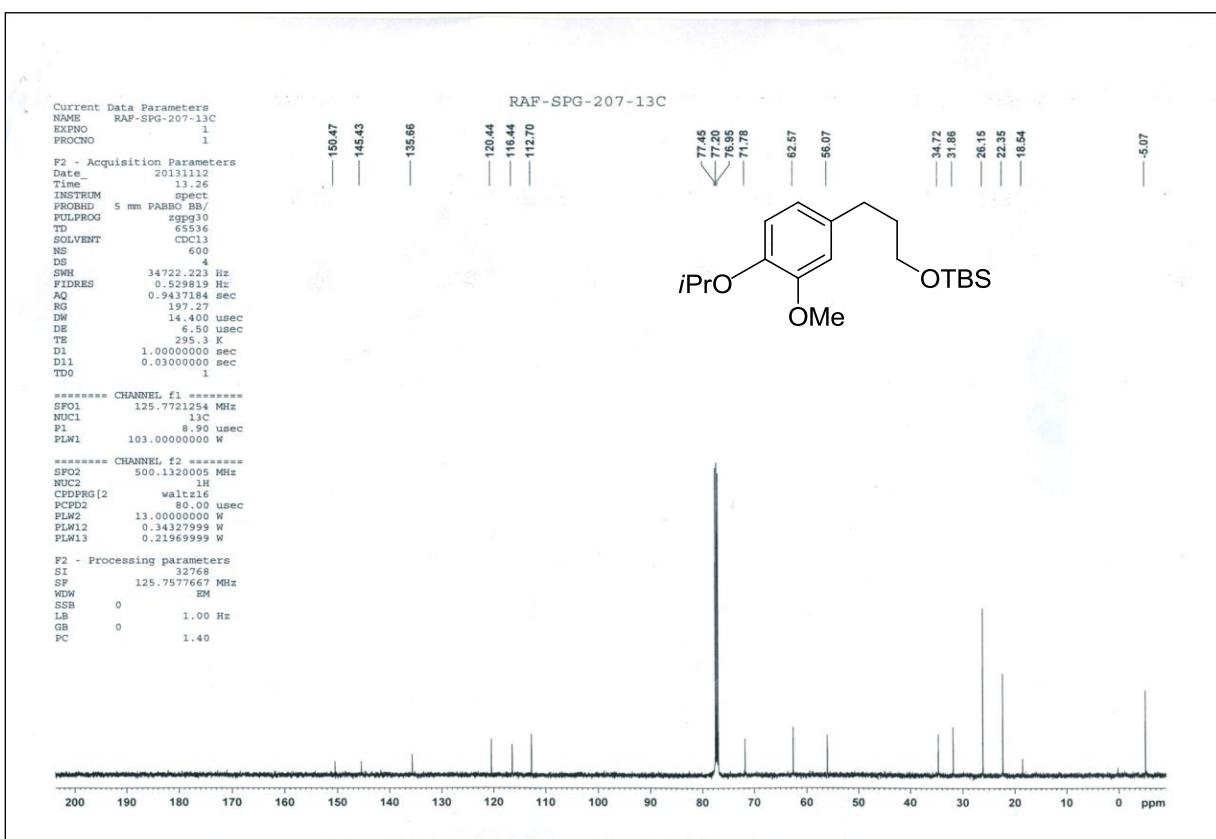
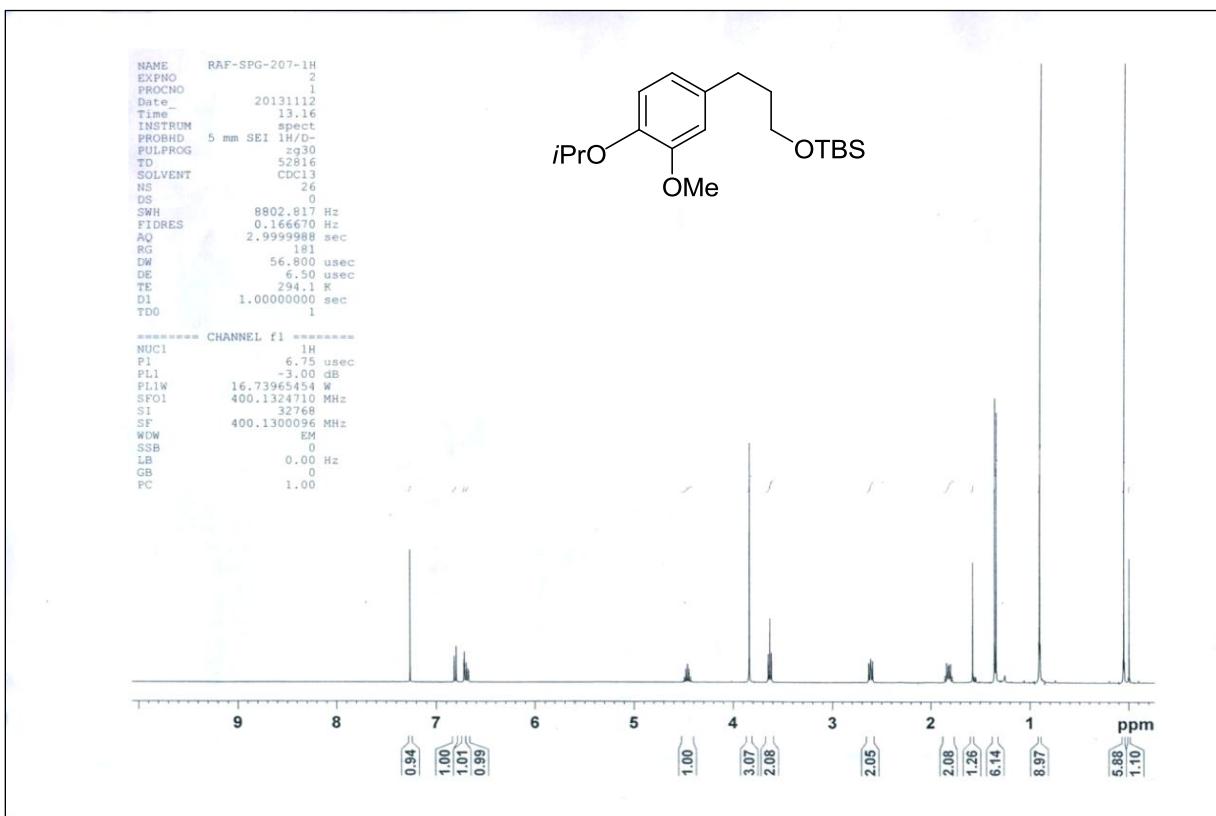
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound 8e



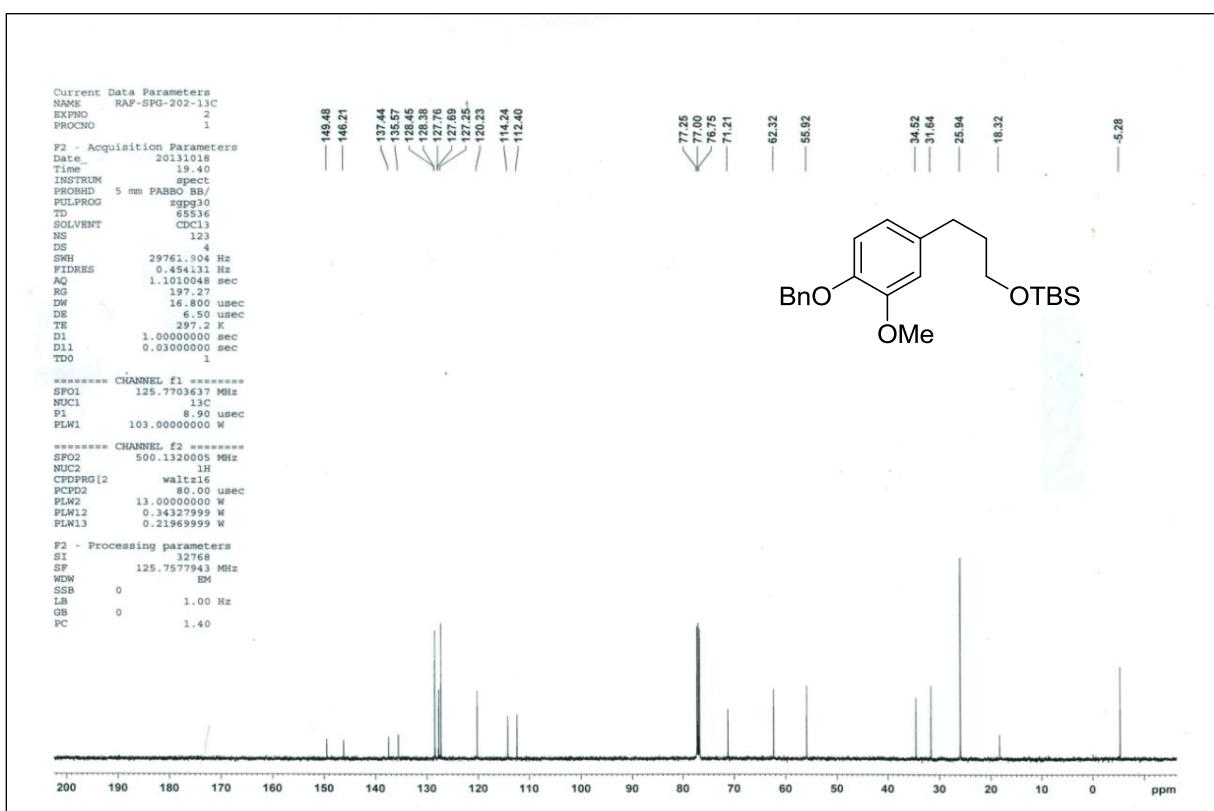
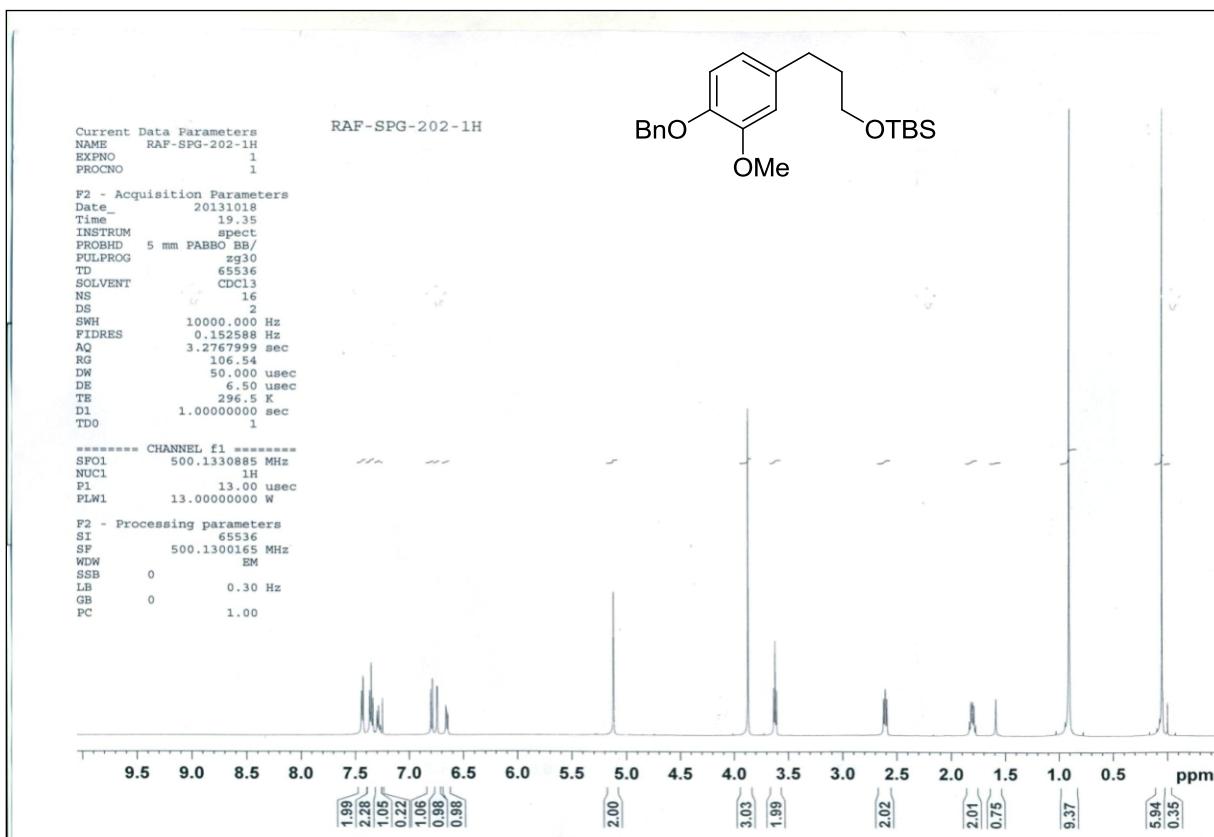
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8f**



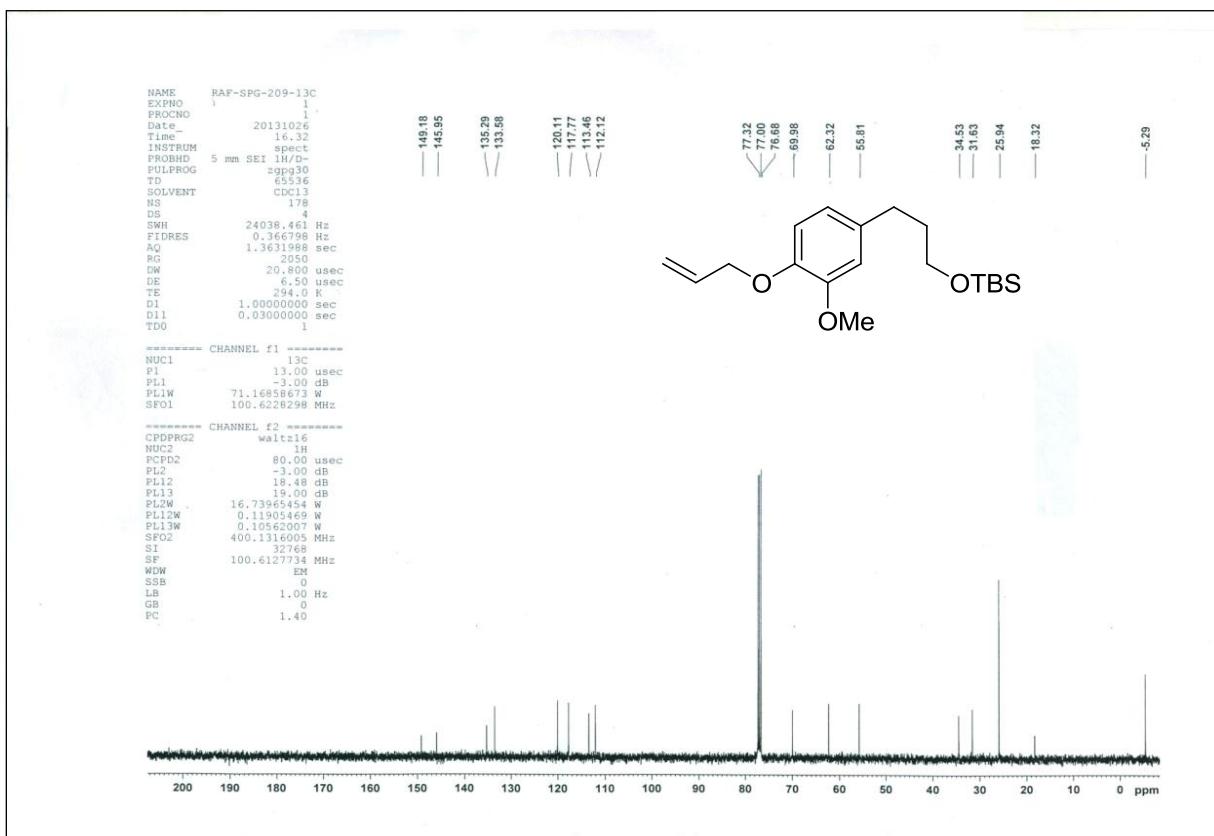
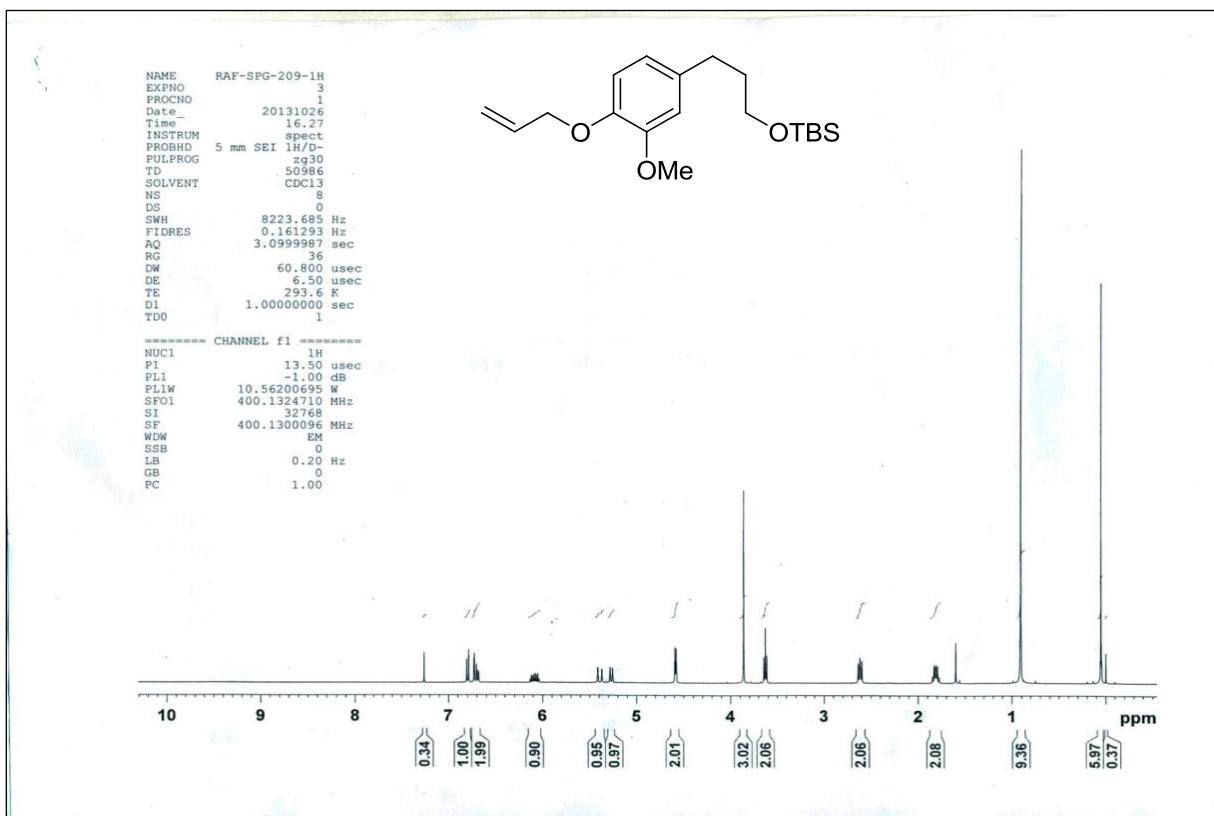
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound 8g



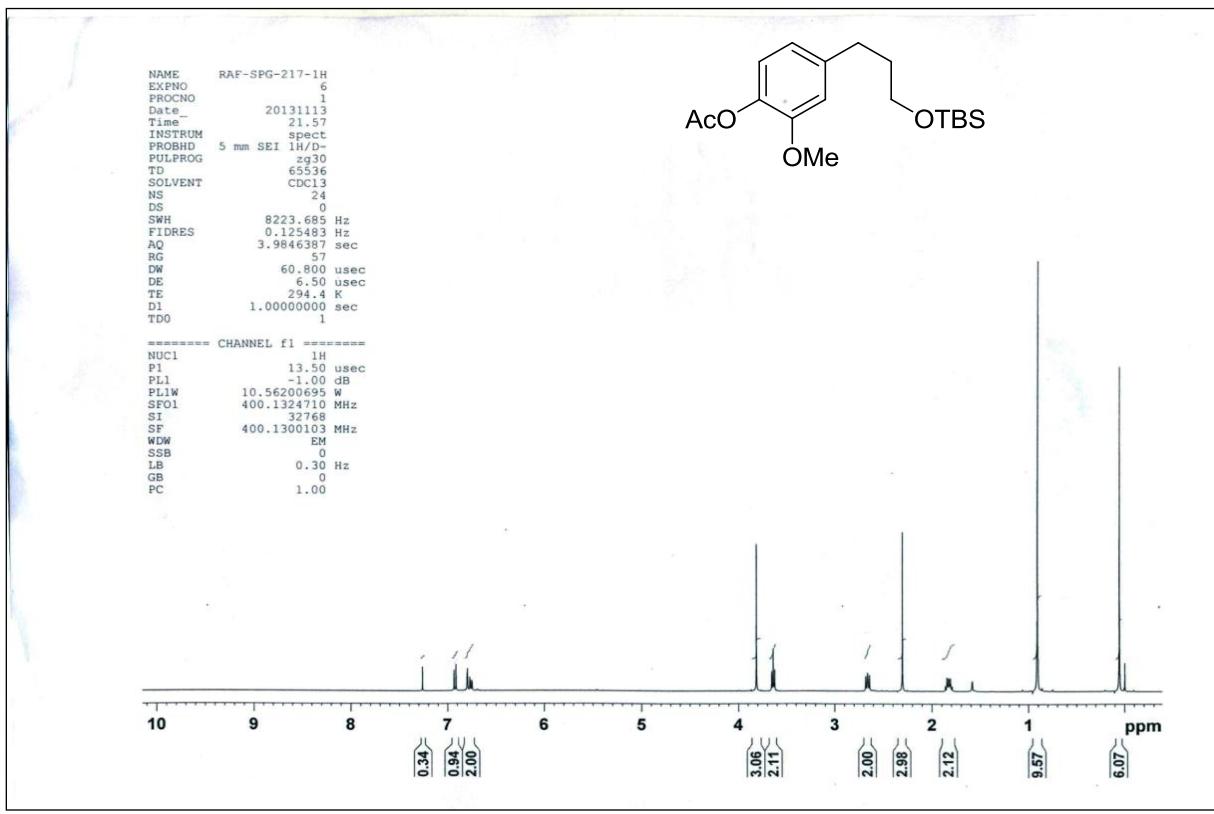
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **8h**



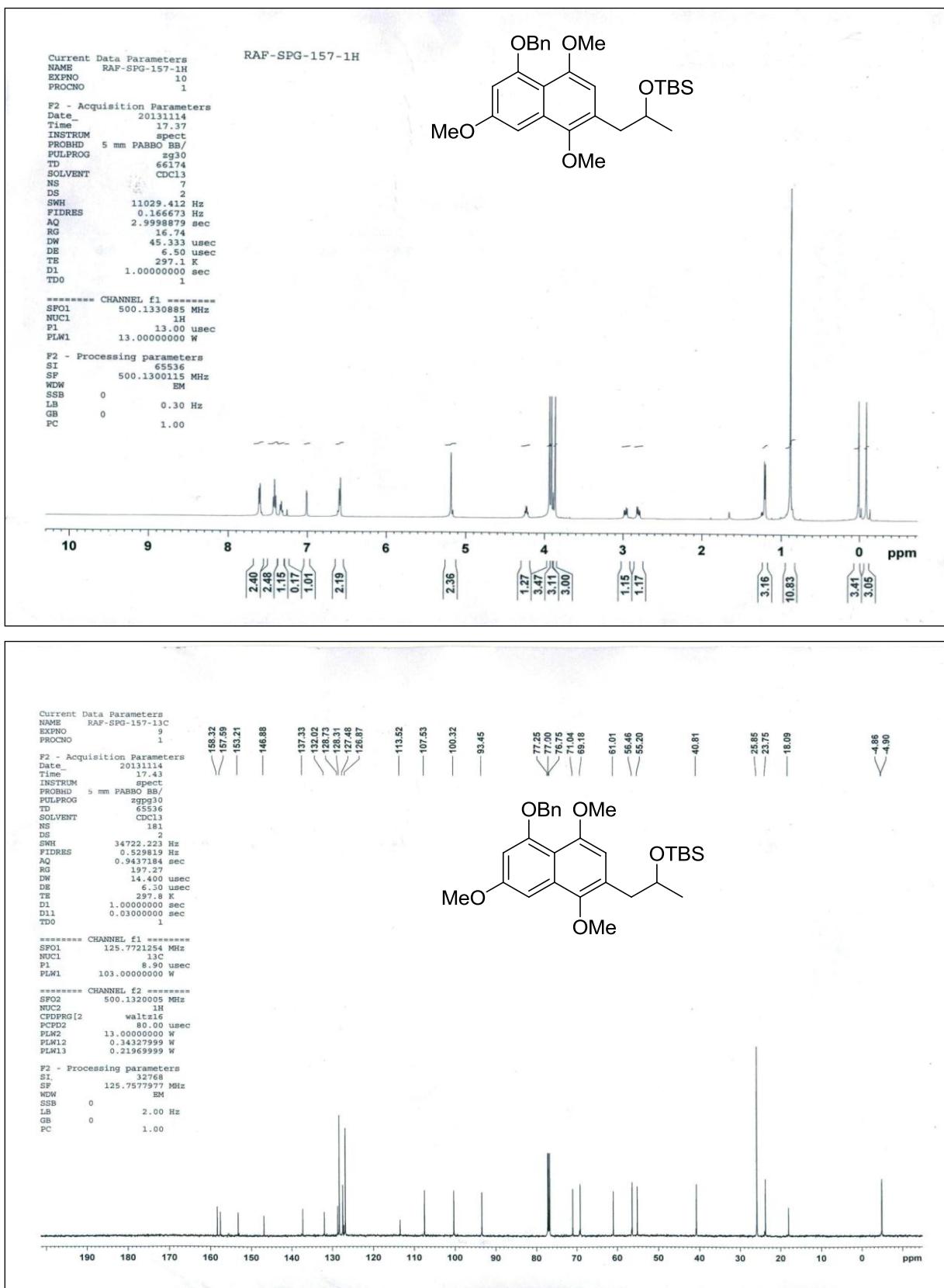
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8i**



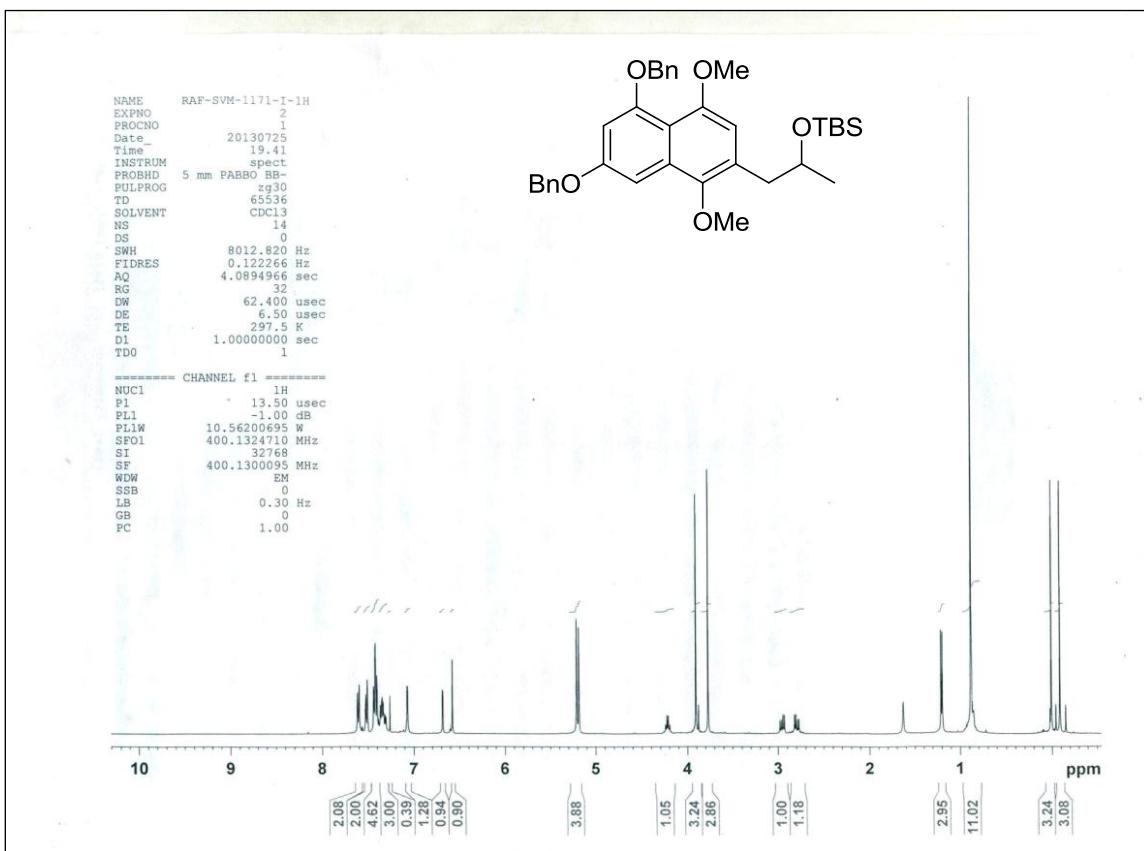
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8j**



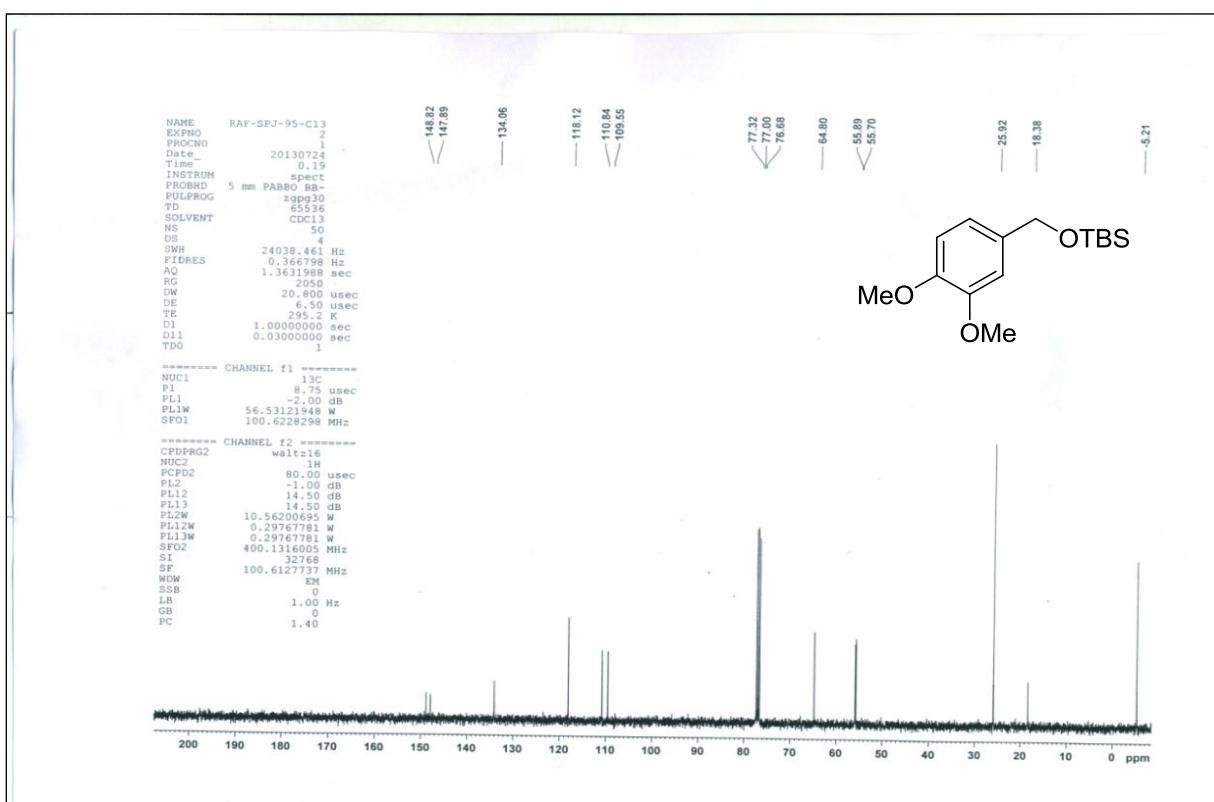
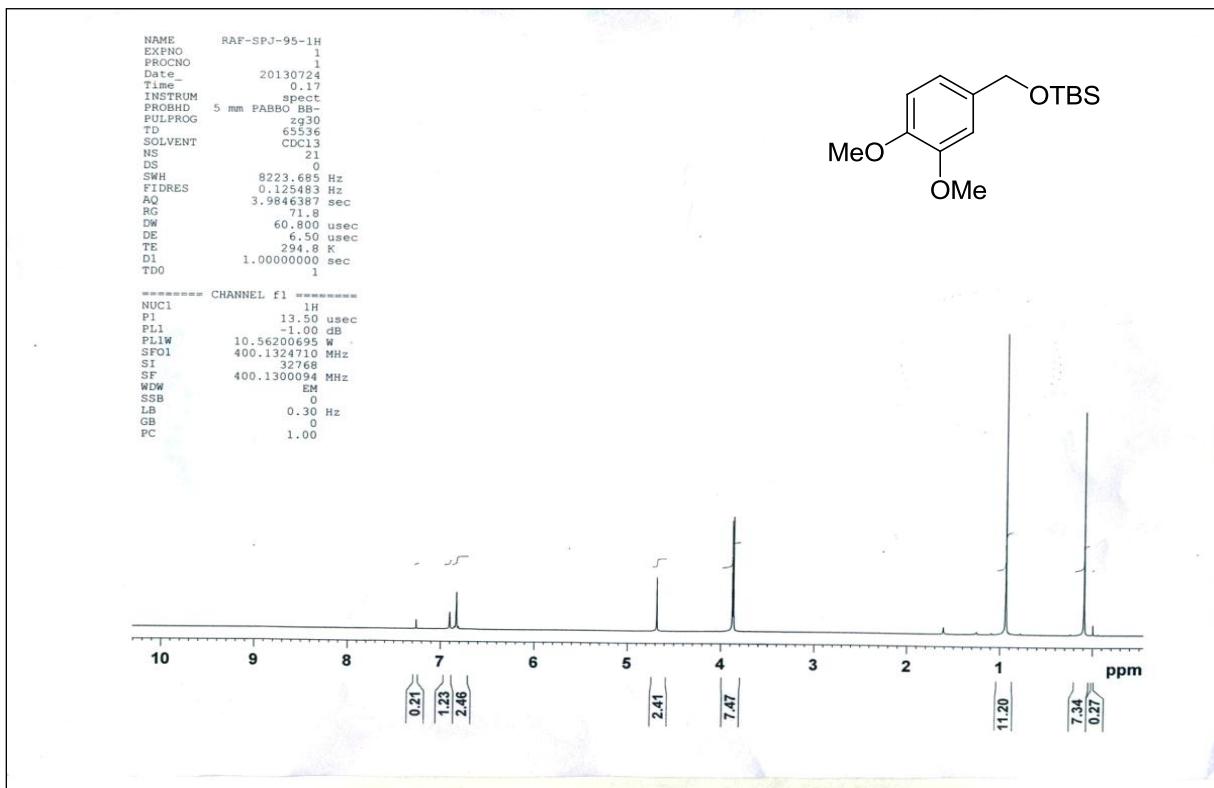
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **8k**



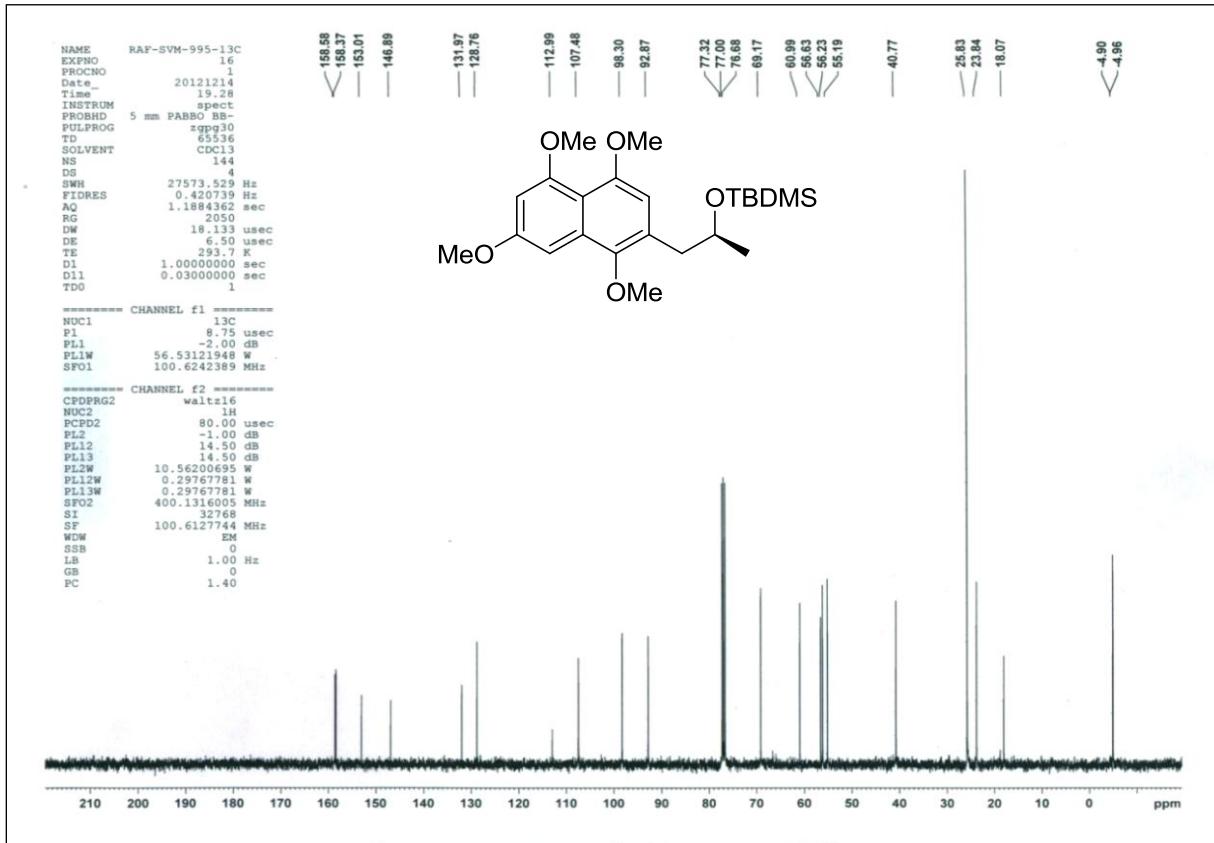
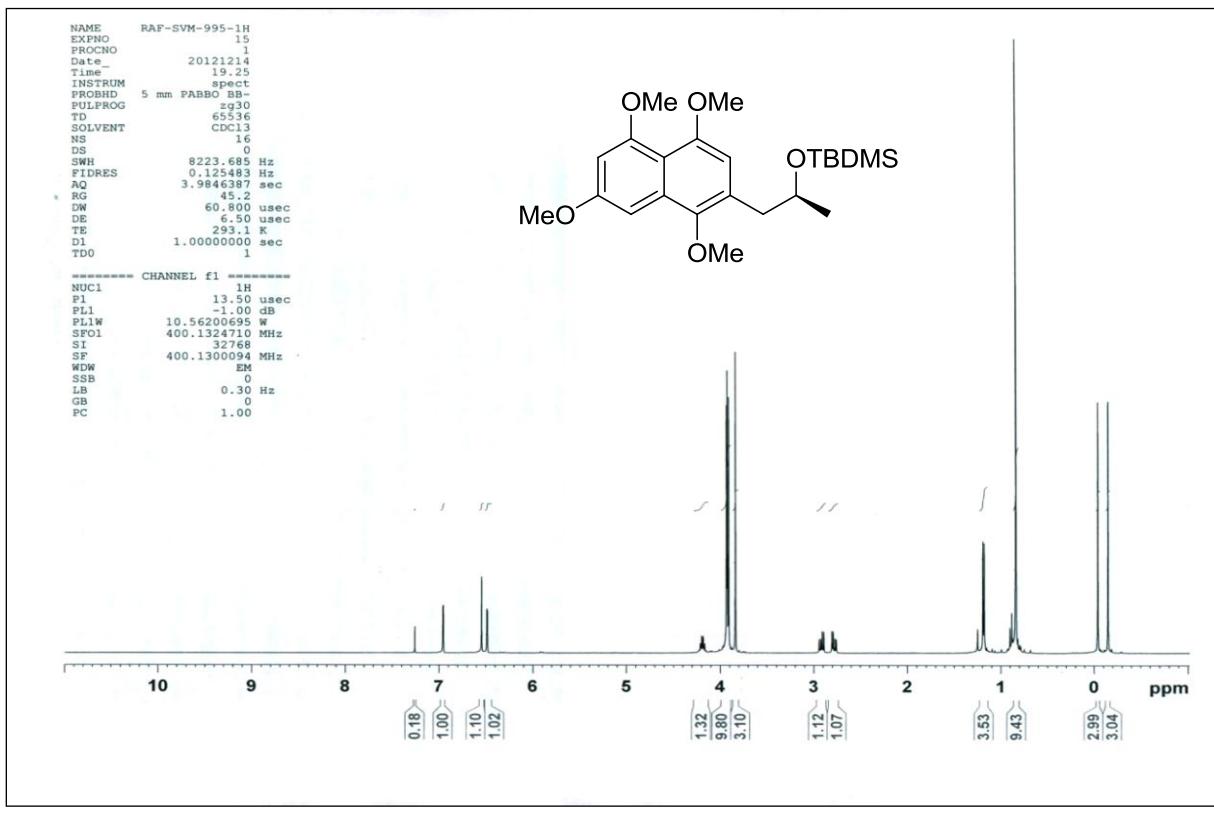
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8I**



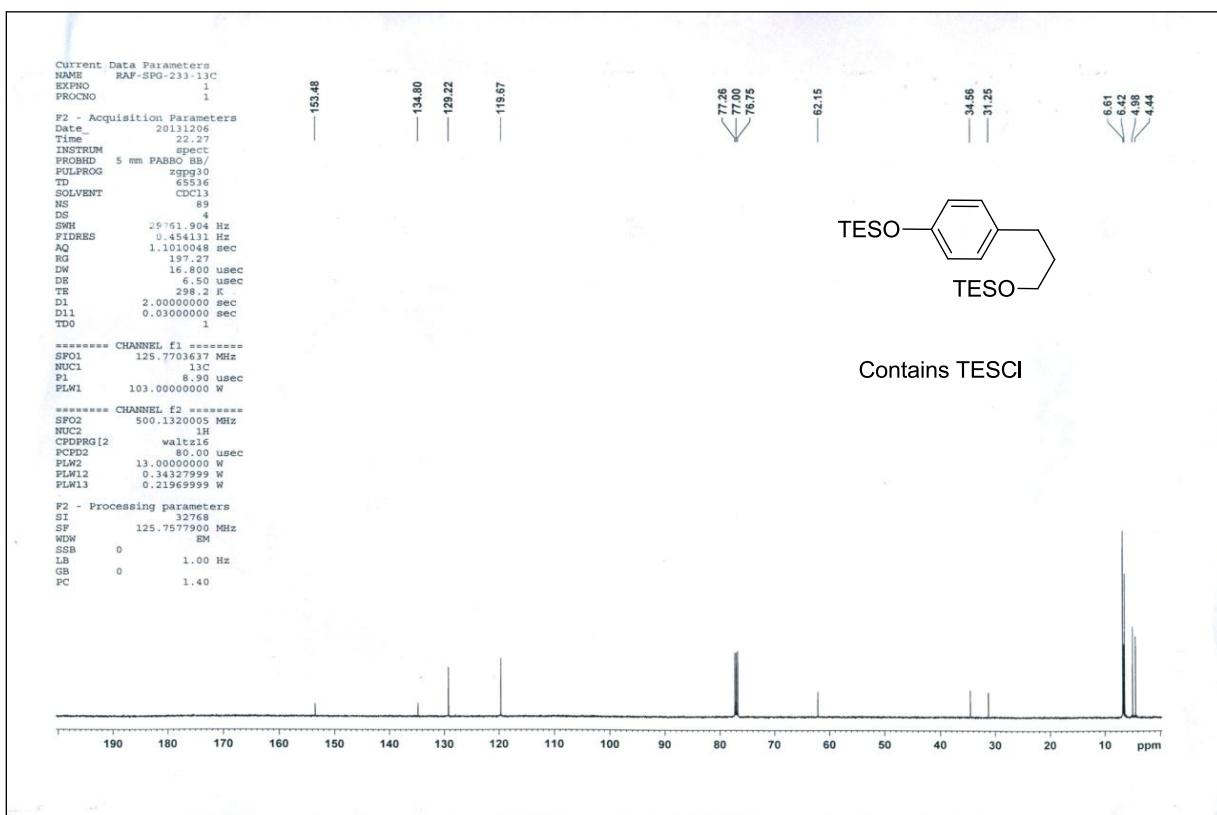
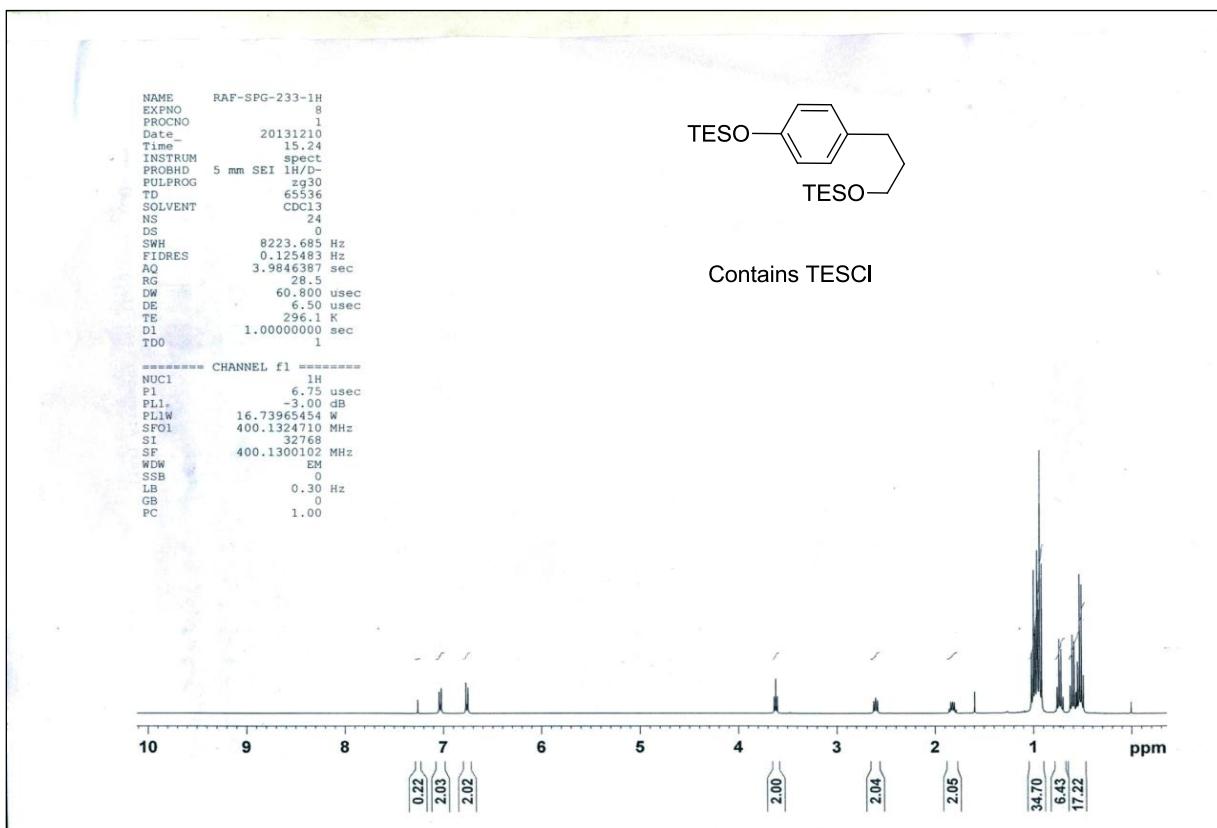
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **8m**



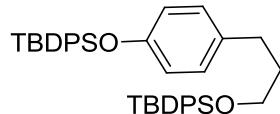
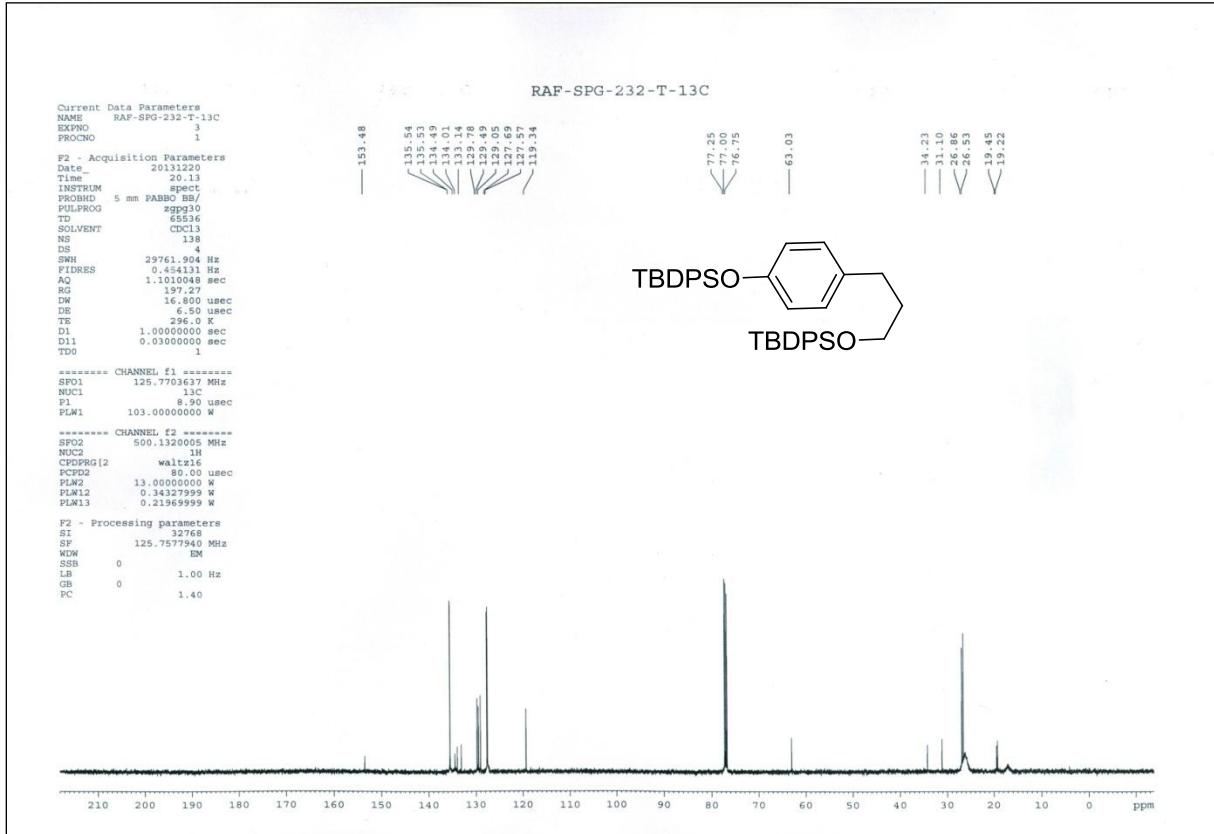
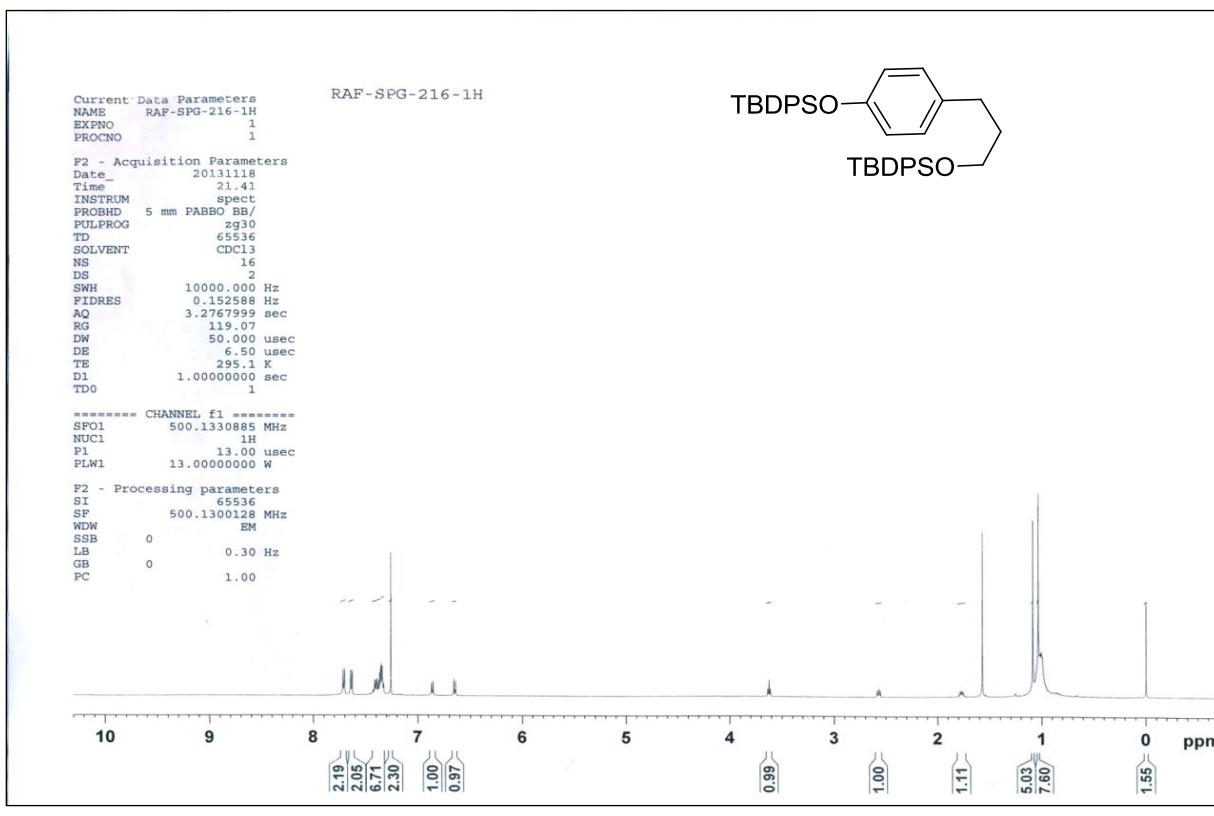
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 2



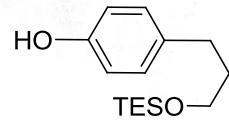
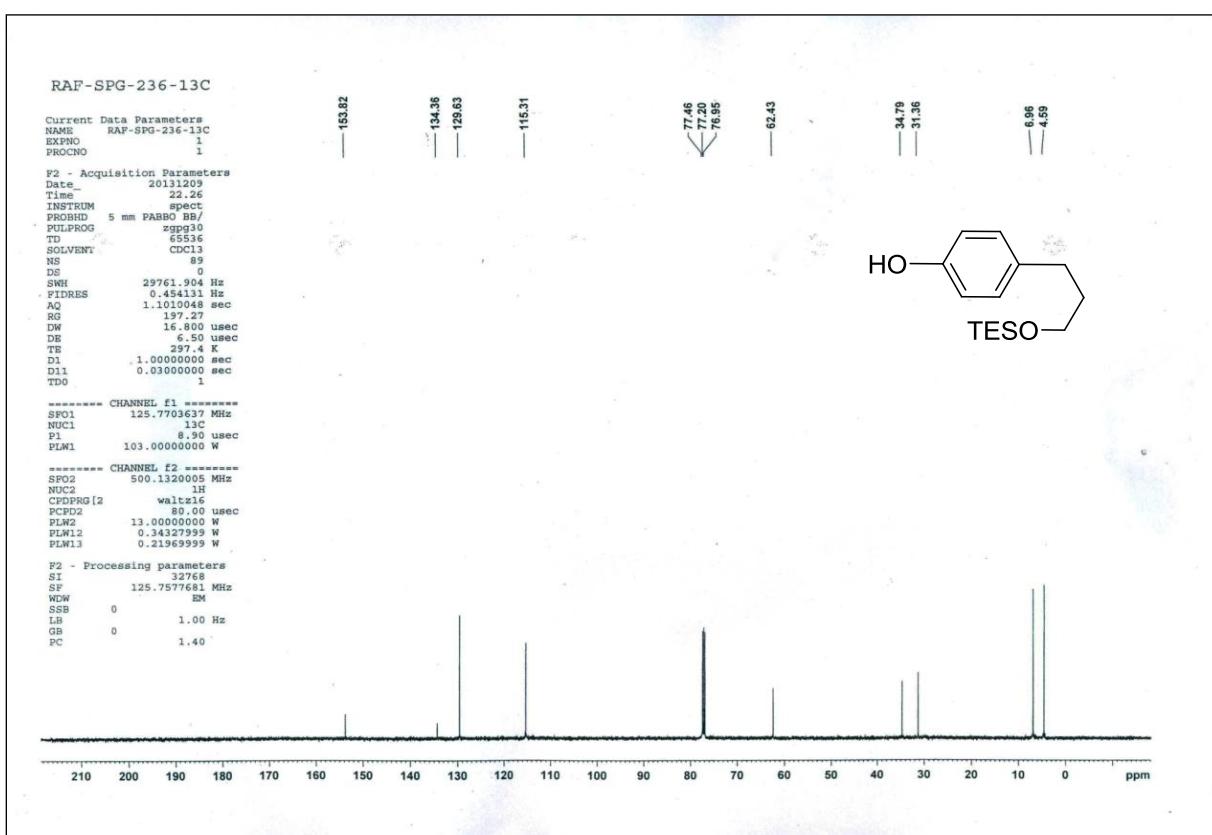
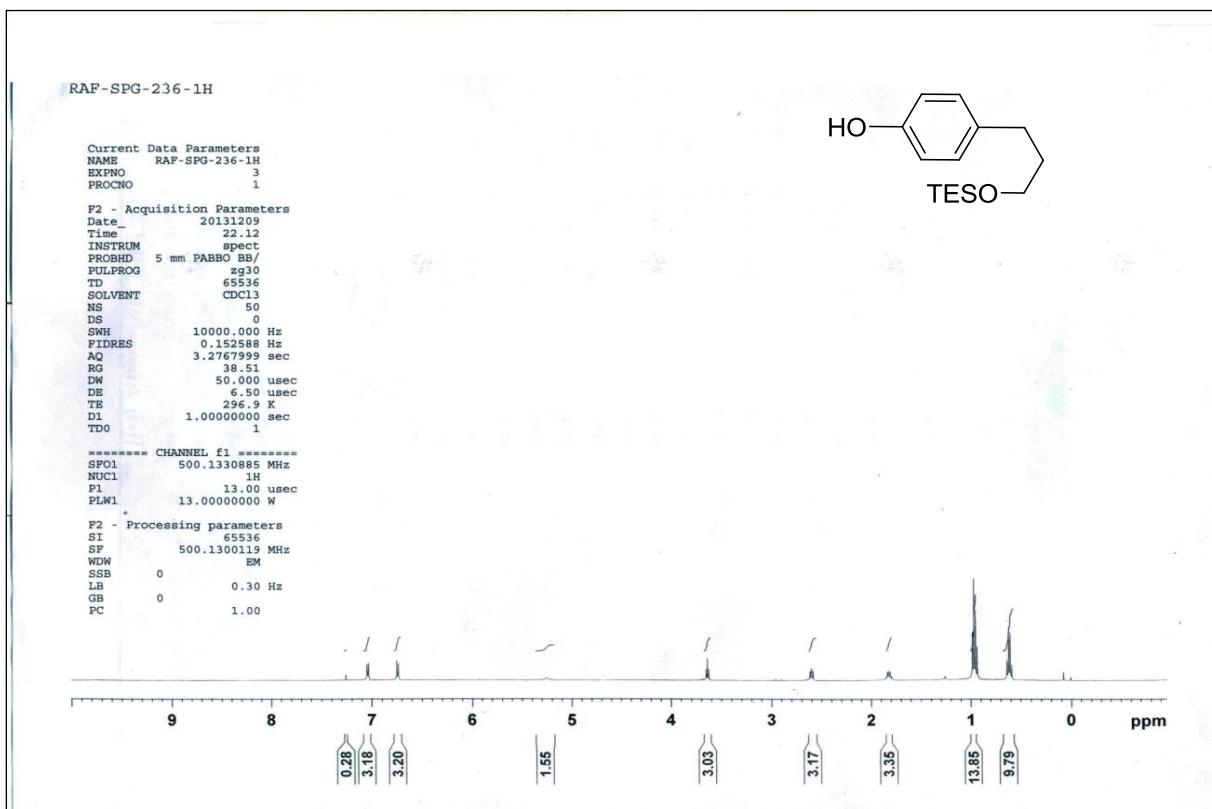
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **9a**



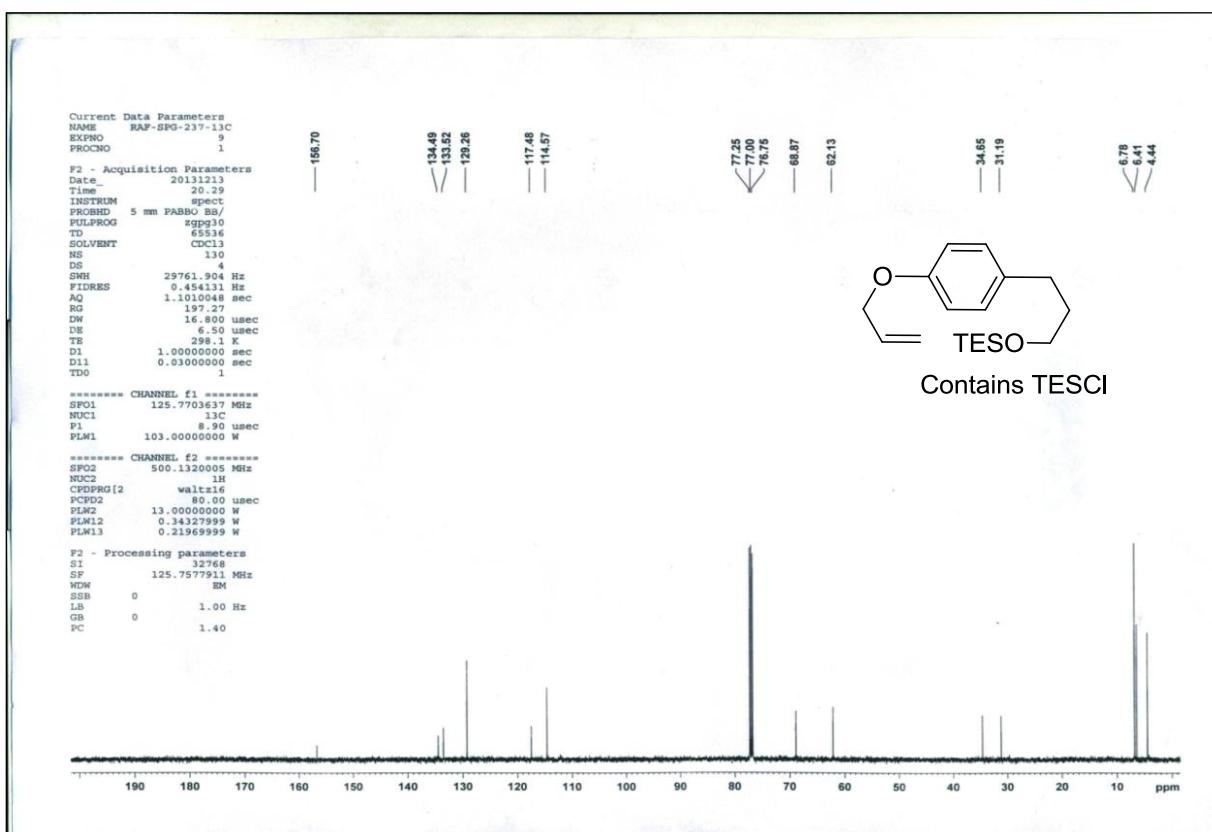
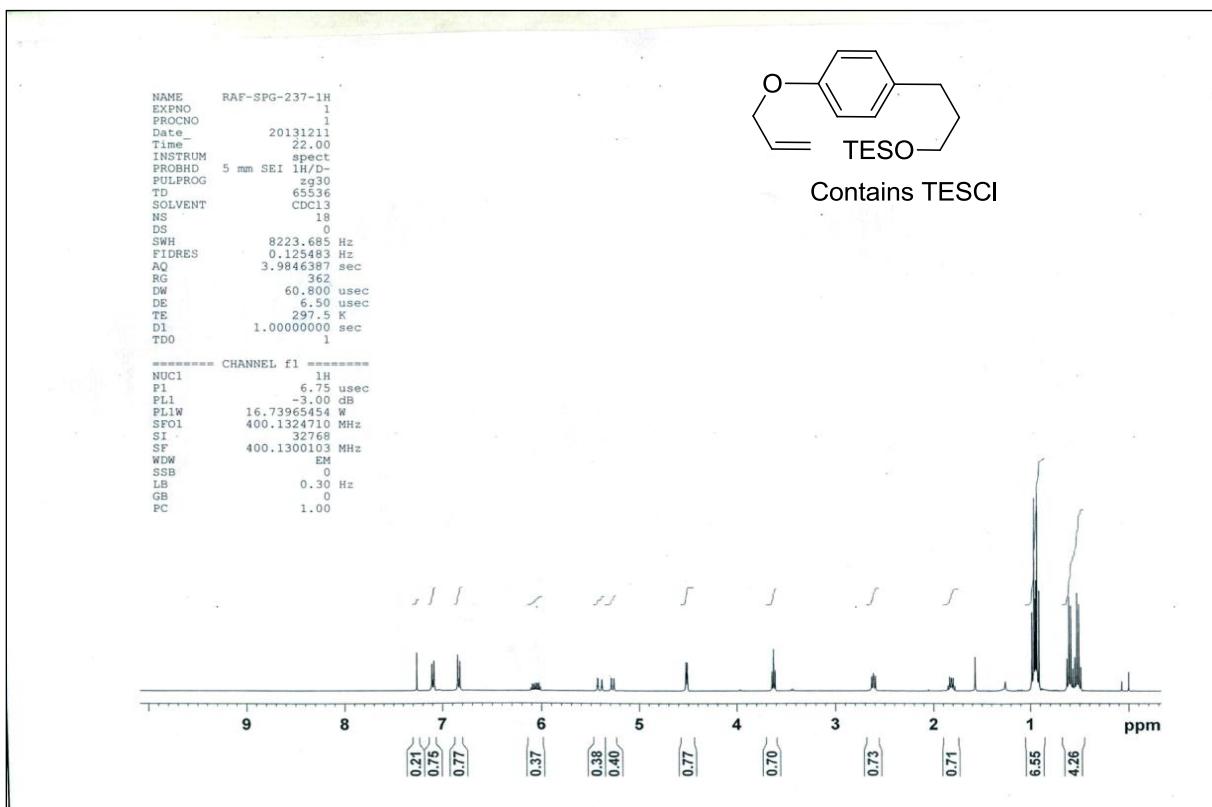
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **9b**



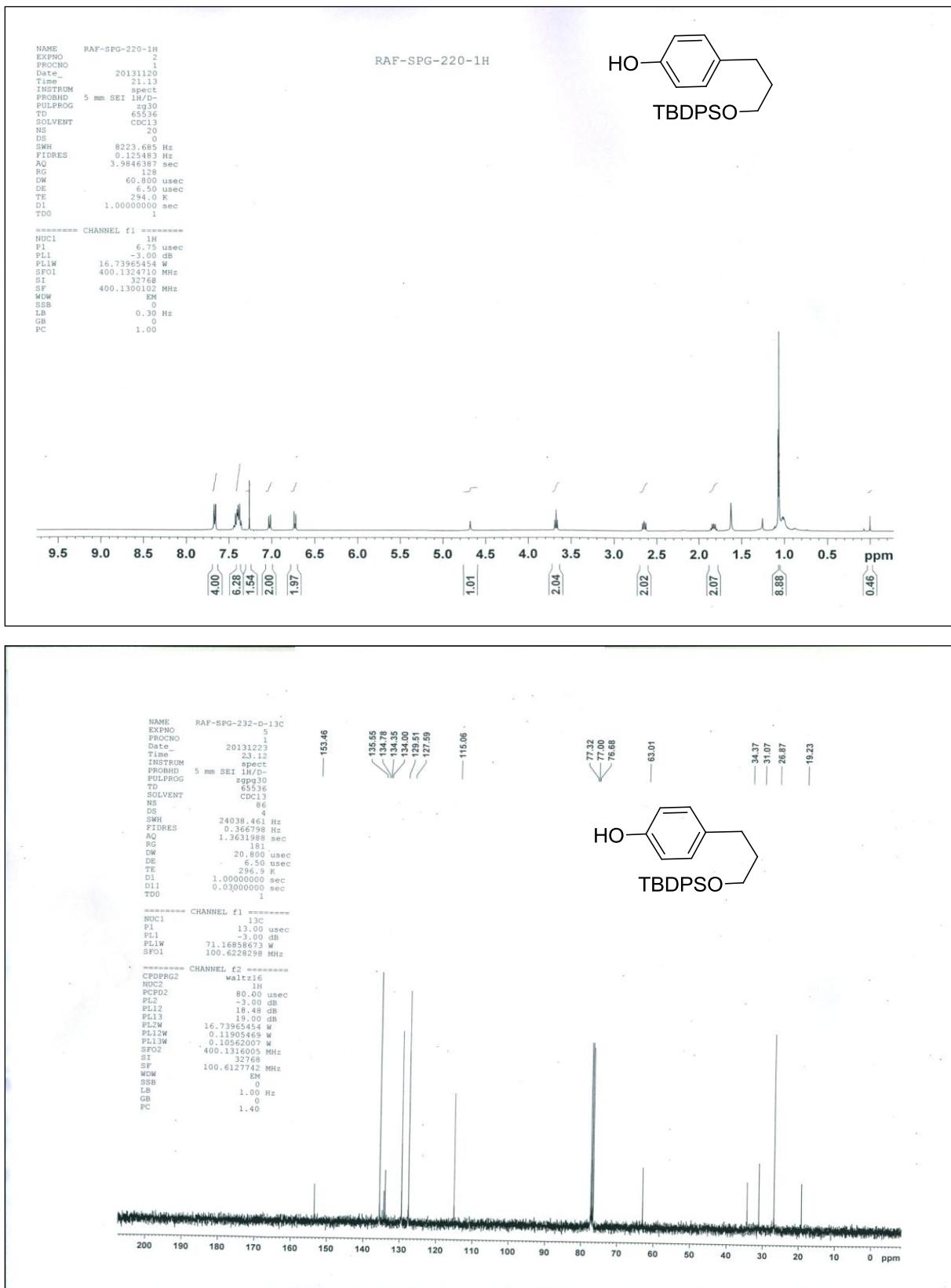
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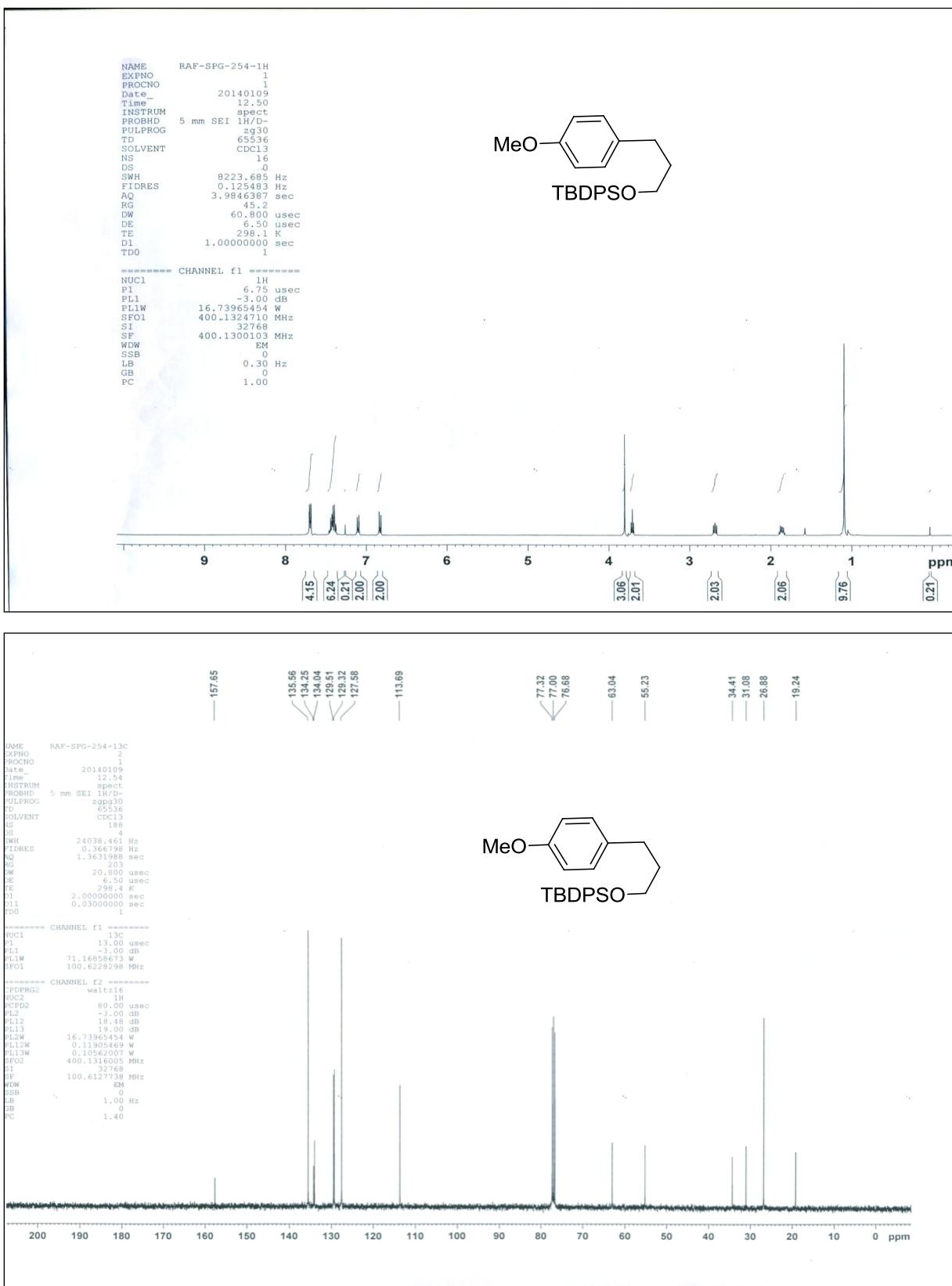
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound **10b**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **10c**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound **10d**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 14

