

Supporting Information

## **Chemoselective One-pot Cleavage and Oxidation of Silyl Ethers into Corresponding Carbonyl Compounds Using IBX and Acid Catalyst**

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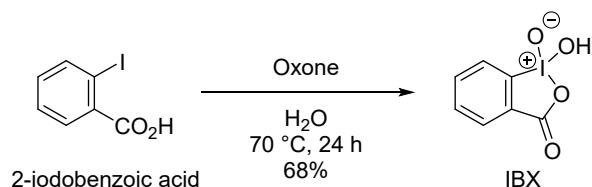
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All reactions were carried out under an argon atmosphere under anhydrous conditions, unless otherwise noted. Anhydrous solvents and reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Oil baths were used to heat reaction mixtures. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F<sub>254</sub>, 0.25 mm). Flash chromatography was performed using silica gel CHROMATOREX PSQ60B (neutral, 60 μm; Fuji Silysia Chemical LTD.). Preparative thin layer chromatography (PTLC) was performed on Merck precoated TLC plates (silica gel 60 F<sub>254</sub>, 1.0 mm). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on JEOL ECA-600 spectrometers. Chemical shift values are reported in δ (ppm) relative to residual solvent signals (CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H and 77.00 ppm for <sup>13</sup>C, DMSO-*d*<sub>6</sub>: 2.49 ppm for <sup>1</sup>H). NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, m: multiplet, br: broad signal), coupling constant, and integration. High-resolution mass spectra (ESI-TOF) were measured on JEOL JMS-T100LP.

## 2. Experimental Procedures

### Preparation of IBX



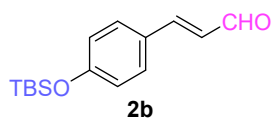
IBX was prepared according to the literature procedure by Wang and co-workers with slight modification<sup>1</sup>.

To a solution of Oxone (162.5 g, 264 mmol) in deionized H<sub>2</sub>O (130 mL) was added 2-iodoxybenzoic acid (15.0 g, 60.5 mmol) at rt. The suspension was stirred at 70 °C for 24 h, and then slowly cooled to 0 °C. The white crystalline precipitate was separated by filtration, and washed with cold deionized H<sub>2</sub>O (50 mL × 4) and acetone (50 mL × 4). After the white crystalline solid was dried at rt for overnight, IBX was obtained (11.52 g, 41.1 mmol, 68%, containing ~5% of 2-iodobenzoic acid). The structure of prepared IBX was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>1</sup>

<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 8.13 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.99 (dd, *J* = 7.2, 6.6 Hz, 1), 7.83 (dd, *J* = 7.8, 6.6 Hz, 1H). Residual 2-iodobenzoic acid was observed: 7.98 (overlapped), 7.70 (dd, *J* = 7.2, 1.2 Hz, 0.05H), 7.47 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 0.05H), 7.23 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 0.05H).

**General Procedures for one-pot cleavage and oxidation of silyl ethers.** To a solution of **1b–z** (1.0 equiv.) in anhydrous DMSO (0.15 M) were added IBX (1.5 equiv.) and TsOH·H<sub>2</sub>O (0.1 equiv.) at rt. The reaction mixture was stirred at 50 °C for the indicated time under an argon atmosphere. After the reaction mixture was cooled to rt, the reaction was quenched by the addition of H<sub>2</sub>O and diluted with EtOAc. The resultant mixture was extracted with EtOAc (two times). The combined organic solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography or preparative TLC to give **2b–z**.

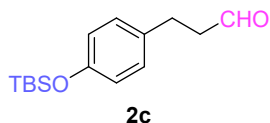
*(E)*-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)acrylaldehyde (**2b**).<sup>2</sup>



The titled compound was synthesized according to the general procedure using **1b** (30.1 mg, 79.5  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1) to give **2b** (19.4 mg, 73.9  $\mu\text{mol}$ , 93%) as a colorless oil. The structure of **2b** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>2</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.65 (d,  $J = 8.4$  Hz, 1H), 7.47 (dd,  $J = 7.2, 1.8$  Hz, 2H), 7.42 (d,  $J = 15.6$  Hz, 1H), 6.88 (dd,  $J = 7.2, 1.8$  Hz, 2H), 6.61 (dd,  $J = 15.6, 8.4$  Hz, 1H), 0.99 (s, 9H), 0.23 (s, 6H).

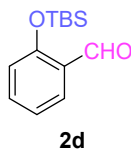
### 3-(4-(tert-butyldimethylsilyloxy)phenyl)propanal (**2c**).<sup>3</sup>



The titled compound was synthesized according to the general procedure using **1c** (30.2 mg, 79.3  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1) to give **2c** (18.3 mg, 69.2  $\mu\text{mol}$ , 88%) as a colorless oil. The structure of **2c** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>3</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.81 (t,  $J = 1.2$  Hz, 1H), 7.04 (d,  $J = 9.0$  Hz, 2H), 6.76 (d,  $J = 9.0$  Hz, 2H), 2.89 (t,  $J = 7.8$  Hz, 2H), 2.74 (td,  $J = 7.2, 1.2$  Hz, 2H), 0.97 (s, 9H), 0.18 (s, 6H).

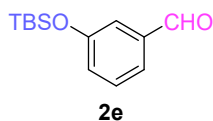
### 2-(tert-butyldimethylsilyloxy)benzaldehyde (**2d**).<sup>4</sup>



The titled compound was synthesized according to the general procedure using **1d** (75.2 mg, 213  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 99/1) to give **2d** (41.1 mg, 174  $\mu\text{mol}$ , 82%) as a colorless oil. The structure of **2d** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>4</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.47 (s, 1H), 7.81 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.48-7.45 (m, 1H), 7.04 (t,  $J = 7.2$  Hz, 1H), 6.89 (d,  $J = 7.2$  Hz, 1H), 1.02 (s, 9H), 0.28 (s, 6H).

### 3-(tert-butyldimethylsilyloxy)benzaldehyde (**2e**).<sup>5</sup>

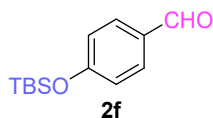


The titled compound was synthesized according to the general procedure using **1e** (75.2 mg, 213  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 99/1 to 97/1)

to give **2e** (44.3 mg, 187  $\mu$ mol, 88%) as a colorless oil. The structure of **2e** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>5</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.95 (s, 1H), 7.47 (ddd,  $J = 7.8, 1.8, 1.2$  Hz, 1H), 7.40 (dd,  $J = 7.8, 7.2$  Hz, 1H), 7.33 (dd,  $J = 1.8, 1.2$  Hz, 1H), 7.11 (ddd,  $J = 7.2, 1.8, 1.2$  Hz, 1H), 1.00 (s, 9H), 0.22 (s, 6H).

#### 4-((*tert*-butyldimethylsilyl)oxy)benzaldehyde (**2f**).<sup>6</sup>



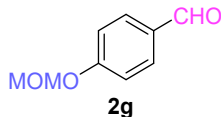
**Table 2:** The titled compound was synthesized according to the general procedure using **1f** (50.0 mg, 142  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 99/1 to 19/1) to give **2f** (29.3 mg, 124  $\mu$ mol, 87%) as a colorless oil.

**Table 2 (gram scale):** The titled compound was synthesized according to the general procedure using **1f** (1.00 g, 2.84 mmol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 49/1 to 19/1) to give **2f** (562.5 mg, 2.38 mmol, 84%) as a colorless oil.

The structure of **2f** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>6</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.89 (s, 1H), 7.79 (d,  $J = 9.0$  Hz, 2H), 6.95 (d,  $J = 9.0$  Hz, 2H), 0.99 (s, 9H), 0.25 (s, 6H).

#### 4-(methoxymethoxy)benzaldehyde (**2g**).<sup>7</sup>



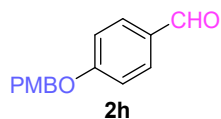
**Table 2:** The titled compound was synthesized according to the general procedure using **1g** (70.0 mg, 266  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 4/1) to give **2g** (40.6 mg, 244  $\mu$ mol, 92%) as a colorless oil.

**Table 2 (gram scale):** The titled compound was synthesized according to the general procedure using **1g** (1.00 g, 3.54 mmol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **2g** (496.2 mg, 2.99 mmol, 84%) as a colorless oil.

The structure of **2g** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>7</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (s, 1H), 7.84 (d,  $J = 9.0$  Hz, 2H), 7.15 (d,  $J = 9.0$  Hz, 2H), 5.26 (s, 2H), 3.49 (s, 3H).

#### 4-((4-methoxybenzyl)oxy)benzaldehyde (**2h**).<sup>8</sup>

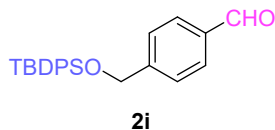


The titled compound was synthesized according to the general procedure using **1h** (75.4 mg, 210  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 3/2)

to give **2h** (47.7 mg, 197  $\mu\text{mol}$ , 94%) as a colorless oil. The structure of **2h** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>8</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.88 (s, 1H), 7.84 (d,  $J = 9.0$  Hz, 2H), 7.36 (d,  $J = 9.0$  Hz, 2H), 7.07 (d,  $J = 9.0$  Hz, 2H), 6.94 (d,  $J = 9.0$  Hz, 2H), 5.07 (s, 2H), 3.82 (s, 3H).

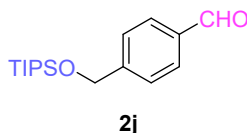
#### 4-(((tert-butyl)dimethylsilyloxy)methyl)benzaldehyde (**2i**).<sup>9</sup>



The titled compound was synthesized according to the general procedure using **1i** (50.0 mg, 102  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **2i** (28.9 mg, 77.2  $\mu\text{mol}$ , 76%) as a colorless oil. The structure of **2i** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>9</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.01 (s, 1H), 7.86 (d,  $J = 7.8$  Hz, 2H), 7.69 (d,  $J = 7.2$  Hz, 4H), 7.52 (d,  $J = 7.8$  Hz, 2H), 7.46-7.38 (m, 6H), 4.84 (s, 2H), 1.12 (s, 9H).

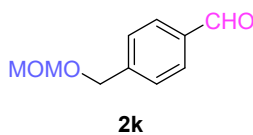
#### 4-(((triisopropyl)silyloxy)methyl)benzaldehyde (**2j**).<sup>9</sup>



The titled compound was synthesized according to the general procedure using **1j** (50.0 mg, 122  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 49/1 to 9/1) to give **2j** (21.2 mg, 72.5  $\mu\text{mol}$ , 59%) as a colorless oil. The structure of **2j** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>9</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.00 (s, 1H), 7.86 (d,  $J = 8.4$  Hz, 2H), 7.52 (d,  $J = 8.4$  Hz, 2H), 4.91 (s, 2H), 1.22-1.16 (m, 3H), 1.10 (d,  $J = 6.6$  Hz, 18H).

#### 4-(((triisopropyl)silyloxy)methyl)benzaldehyde (**2k**).<sup>10</sup>



**From 1k:** The titled compound was synthesized according to the general procedure using **1k** (75.0 mg, 253  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 4/1) to give **2k** (36.8 mg, 204  $\mu\text{mol}$ , 81%) as a colorless oil.

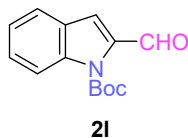
**From 1r:** The titled compound was synthesized according to the general procedure using **1r** (75.0 mg, 222  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 4/1) to give **2k** (31.5 mg, 174  $\mu\text{mol}$ , 79%) as a colorless oil.

**From 1s:** The titled compound was synthesized according to the general procedure using **1s** (75.0 mg, 178  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by preparative TLC (hexane/EtOAc = 17/3) to give **2k** (27.0 mg, 150  $\mu\text{mol}$ , 84%) as a colorless oil.

The structure of **2k** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>10</sup> HRMS were also measured since HRMS data of **2k** was not reported previously.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.01 (s, 1H), 7.87 (d,  $J = 6.6$  Hz, 2H), 7.52 (d,  $J = 6.6$  Hz, 2H), 4.74 (s, 2H), 4.68 (s, 2H), 3.42 (s, 3H).; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ) 181.0859, found 181.0867.

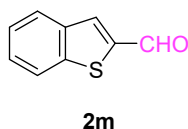
**tert-butyl 2-formyl-1H-indole-1-carboxylate (2l).**<sup>11</sup>



The titled compound was synthesized according to the general procedure using **1l** (75.3 mg, 208  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **2l** (44.5 mg, 181  $\mu\text{mol}$ , 87%) as a colorless oil. The structure of **2l** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>11</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.44 (s, 1H), 8.17 (d,  $J = 7.8$  Hz, 1H), 7.68 (d,  $J = 8.4$  Hz, 1H), 7.48 (ddd,  $J = 7.8, 7.2, 1.2$  Hz, 1H), 7.44 (br s, 1H), 7.30 (dd,  $J = 8.4, 7.2$  Hz, 1H), 1.72 (s, 9H).

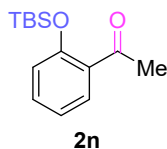
**benzo[b]thiophene-2-carbaldehyde (2m).**<sup>9</sup>



The titled compound was synthesized according to the general procedure using **1m** (76.0 mg, 273  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **2m** (38.6 mg, 238  $\mu\text{mol}$ , 87%) as a colorless oil. The structure of **2m** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>9</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.03 (s, 1H), 7.94 (d, 7.8 Hz, 1H), 7.90 (d,  $J = 8.4$  Hz, 1H), 7.51 (dd,  $J = 8.4, 7.8$  Hz, 1H), 7.44 (dd,  $J = 7.8, 7.8$  Hz, 1H).

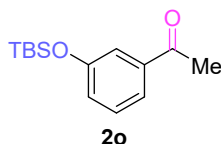
**1-(2-((tert-butyldimethylsilyloxy)phenyl)ethan-1-one (2n).**



The titled compound was synthesized according to the general procedure using **1n** (75.0 mg, 205  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 99/1 to 97/3) to give **2n** (23.6 mg, 94.2  $\mu\text{mol}$ , 46%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J = 7.8, 1.8$  Hz, 1H), 7.34 (ddd,  $J = 7.8, 7.2, 1.8$  Hz, 1H), 6.99 (dd,  $J = 7.8, 7.2$  Hz, 1H), 6.87 (d,  $J = 7.8$  Hz, 1H), 2.60 (s, 3H), 1.00 (s, 9H), 0.27 (s, 6H).;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  201.0, 154.7, 132.9, 131.4, 130.0, 121.2, 120.2, 31.3, 25.8 (3C), 18.4, -4.0.; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{23}\text{O}_2\text{Si}$  ( $[\text{M}+\text{H}]^+$ ) 251.1462, found 251.1473.

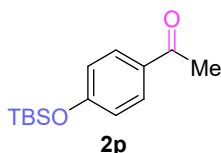
**1-(3-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one (2o).**



The titled compound was synthesized according to the general procedure using **1o** (75.0 mg, 205  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 99/1 to 97/3) to give **2o** (31.2 mg, 125  $\mu$ mol, 61%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (ddd,  $J = 7.2, 1.8, 1.2$  Hz, 1H), 7.41 (dd,  $J = 1.8, 1.8$  Hz, 1H), 7.32 (dd,  $J = 7.2, 8.4$  Hz, 1H), 7.04 (ddd,  $J = 8.4, 1.8, 1.2$  Hz, 1H), 2.56 (s, 3H), 0.99 (s, 9H), 0.22 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  197.9, 156.0, 138.6, 129.5, 124.9, 121.5, 119.5, 26.7, 25.6 (3C), 18.2, -4.4.; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{23}\text{O}_2\text{Si}$  ( $[\text{M}+\text{H}]^+$ ) 251.1462, found 251.1462.

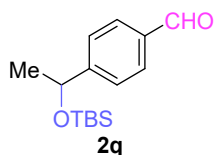
**1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one (2p).<sup>12</sup>**



The titled compound was synthesized according to the general procedure using **1p** (50.0 mg, 136  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 49/1 to 9/1) to give **2p** (16.2 mg, 64.7  $\mu$ mol, 48%) as a colorless oil. The structure of **2p** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>12</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.8$  Hz, 2H), 6.87 (d,  $J = 7.8$  Hz, 2H), 2.55 (s, 3H), 0.99 (s, 9H), 0.23 (s, 6H).

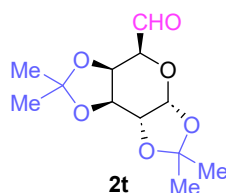
**4-(1-((tert-butyldimethylsilyl)oxy)ethyl)benzaldehyde (2q).**



The titled compound was synthesized according to the general procedure using **1q** (75.3 mg, 198  $\mu$ mol) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **2q** (32.9 mg, 124  $\mu$ mol, 63%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.99 (s, 1H), 7.84 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 8.4$  Hz, 2H), 4.93 (q,  $J = 7.2$  Hz, 1H), 1.42 (d,  $J = 7.2$  Hz, 3H), 0.91 (s, 9H), 0.07 (s, 3H), -0.02 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 154.0, 135.2, 129.8 (2C), 125.7 (2C), 70.5, 27.0, 25.8 (3C), 18.2, -4.86, -4.89; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{28}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{MeOH}+\text{Na}]^+$ ) 319.1700, found 319.1711 (Methanol adduct was only observed.).

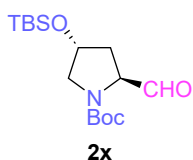
**(3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carbaldehyde (2t).<sup>13</sup>**



The titled compound was synthesized according to the general procedure using **1t** (30 mg, 80.1  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 1/1) to give **2t** (16.0 mg, 62.0  $\mu\text{mol}$ , 77%) as a colorless oil. The structure of **2t** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>13</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.62 (s, 1H), 5.67 (d,  $J = 4.8$  Hz, 1H), 4.65 (dd,  $J = 7.2, 2.4$  Hz, 1H), 4.60 (dd,  $J = 7.2, 3.0$  Hz, 1H), 4.39 (dd,  $J = 4.8, 3.0$  Hz, 1H), 4.20 (d,  $J = 2.4$  Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H).

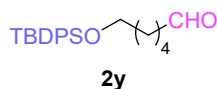
**tert-butyl (2S,4R)-4-((tert-butyl dimethylsilyl)oxy)-2-formylpyrrolidine-1-carboxylate (2x).**<sup>14</sup>



The titled compound was synthesized according to the general procedure using **1x** (30.0 mg, 67.3  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **2x** (11.2 mg, 34.0  $\mu\text{mol}$ , 51%) as a white solid. The structure of **2x** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>14</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ~2:1 mixture of rotamers)  $\delta$  9.56 (d,  $J = 3.0$  Hz, 0.35 H), 9.44 (d,  $J = 3.6$  Hz, 0.65 H), 4.38-4.19 (m, 2H), 3.55-3.35 (m, 2H), 2.06-1.89 (m, 2H), 1.48 and 1.43 (rotamers, s, 9H), 0.87 (s, 9H), 0.067 (s, 3H), 0.065 (s, 3H).

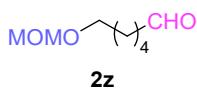
**6-((tert-butyl diphenylsilyl)oxy)hexanal (2y).**<sup>15</sup>



The titled compound was synthesized according to the general procedure using **1y** (75.0 mg, 159  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 97/3) to give **2y** (43.2 mg, 122  $\mu\text{mol}$ , 76%) as a colorless oil. The structure of **2y** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>15</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.75 (t,  $J = 1.8$  Hz, 1H), 7.67-7.65 (m, 4H), 7.44-7.36 (m, 6H), 3.66 (t,  $J = 6.0$  Hz, 2H), 2.40 (td,  $J = 6.6, 1.8$  Hz, 2H), 1.64-1.55 (m, 4H), 1.43-1.38 (m, 2H), 1.05 (s, 9H).

**6-(methoxymethoxy)hexanal (2z).**

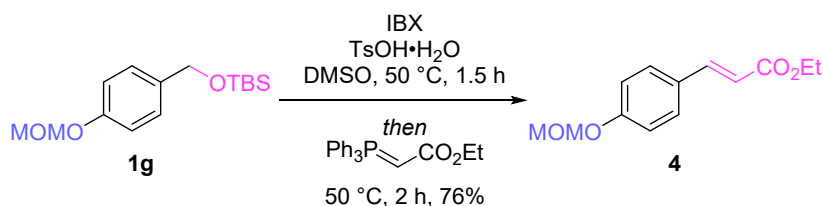




The titled compound was synthesized according to the general procedure using **1z** (75.0 mg, 272  $\mu\text{mol}$ ) as a substrate. The obtained crude material was purified by flash column chromatography (hexane/EtOAc = 9/1 to 7/3) to give **2z** (33.2 mg, 207  $\mu\text{mol}$ , 76%) as a pale yellow oil. The structure of **2z** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.76 (br s, 1H), 4.60 (s, 2H), 3.51 (t,  $J = 6.0$  Hz, 2H), 3.34 (s, 3H), 2.44 (t,  $J = 7.2$  Hz, 2H), 1.68-1.58 (m, 4H), 1.45-1.38 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 96.4, 67.4, 55.1, 43.8, 29.5, 25.8, 21.8; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_8\text{H}_{16}\text{O}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 183.0992, found 183.0997.

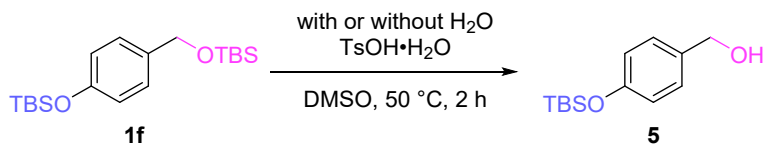
**ethyl (E)-3-(4-(methoxymethoxy)phenyl)acrylate (4).**



To a solution of **1g** (100.0 mg, 354  $\mu\text{mol}$ ) in anhydrous DMSO (2.4 mL) were added IBX (129.7 mg, 463  $\mu\text{mol}$ ) and  $\text{TsOH}\cdot\text{H}_2\text{O}$  (6.4 mg, 34  $\mu\text{mol}$ ) at rt. After the reaction was stirred at 50  $^\circ\text{C}$  for 1.5 h, (carbethoxymethylene)triphenylphosphorane (185.5 mg, 532  $\mu\text{mol}$ ) was added and the mixture was stirred for further 2 h at 50  $^\circ\text{C}$ . After the reaction mixture was cooled to rt, the reaction was quenched by the addition of  $\text{H}_2\text{O}$  and diluted with EtOAc. The resultant mixture was extracted with EtOAc (two times). The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) and by preparative TLC (hexane/EtOAc = 19/1) to give **4** (63.8 mg, 270  $\mu\text{mol}$ , 76%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 16.2$  Hz, 1H), 7.47 (d,  $J = 9.0$  Hz, 2H), 7.04 (d,  $J = 9.0$  Hz, 2H), 6.32 (d,  $J = 16.2$  Hz, 1H), 5.20 (s, 2H), 4.25 (q,  $J = 7.2$  Hz, 2H), 3.48 (s, 3H), 1.33 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 158.9, 144.1, 129.6 (2C), 128.2, 116.4 (2C), 116.3, 94.2, 60.4, 56.3, 14.3; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{17}\text{O}_4$  ( $[\text{M}+\text{H}]^+$ ) 237.1121, found 237.1125.

**(4-((tert-butyldimethylsilyl)oxy)phenyl)methanol (5).<sup>16</sup>**



**Without  $\text{H}_2\text{O}$ :** To a solution of **1f** (75.0 mg, 213  $\mu\text{mol}$ ) in anhydrous DMSO (1.4 mL) was added  $\text{TsOH}\cdot\text{H}_2\text{O}$  (4.1 mg, 22  $\mu\text{mol}$ ) at rt. The reaction was stirred at 50  $^\circ\text{C}$  for 2 h. After the reaction mixture was cooled to rt, the reaction was quenched by the addition of  $\text{H}_2\text{O}$  and diluted with EtOAc. The resultant mixture was extracted with EtOAc (two times). The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **5** (7.2 mg, 3  $\mu\text{mol}$ , 14%) as a colorless oil and **1f** (58.3 mg, 78%).

**With  $\text{H}_2\text{O}$ :** To a solution of **1f** (75.0 mg, 213  $\mu\text{mol}$ ) in anhydrous DMSO (1.4 mL) were added  $\text{TsOH}\cdot\text{H}_2\text{O}$  (4.1 mg, 22  $\mu\text{mol}$ ) and  $\text{H}_2\text{O}$  (5.7  $\mu\text{L}$ , 317  $\mu\text{mol}$ ) at rt. The reaction was stirred at 50  $^\circ\text{C}$  for 2 h. After the reaction mixture

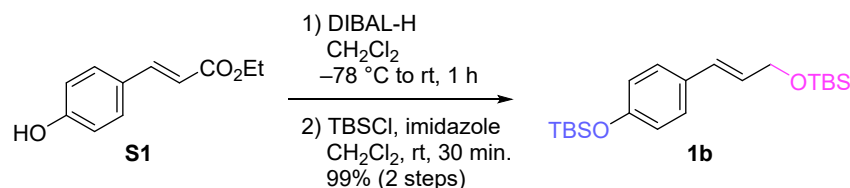
was cooled to rt, the reaction was quenched by the addition of H<sub>2</sub>O and diluted with EtOAc. The resultant mixture was extracted with EtOAc (two times). The combined organic solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **5** (43.1 mg, 181 μmol, 85%) as a colorless oil and **1f** (4.0 mg, 5%).

The structure of **5** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>16</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.23 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.61 (s, 2H), 0.98 (s, 9H), 0.19 (s, 6H).

### Preparation of substrates.

#### *(E)*-tert-butyl((3-(4-((tert-butyldimethylsilyl)oxy)phenyl)allyl)oxy)dimethylsilane (**1b**)

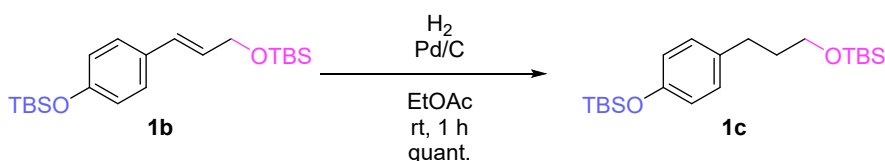


To a solution of known ethyl ester **S1**<sup>17</sup> (1.15 g, 5.98 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25.0 mL) was added a solution of DIBAL-H (1.02 M in hexane, 18.8 mL, 19.2 mmol) dropwise via syringe at -78 °C. After completion of addition of DIBAL-H, the resultant solution was allowed to warm to rt. After being stirred for 1 h, to the reaction mixture were added sat. NH<sub>4</sub>Cl aq. (5.3 mL) and Et<sub>2</sub>O (35 mL). The resultant suspension was stirred for further 1.5 h. MgSO<sub>4</sub> (25.0 g) was added to the mixture and the resultant suspension was filtrated, washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated to give crude alcohol.

To a suspension of crude alcohol (prepared above) in CH<sub>2</sub>Cl<sub>2</sub> (25.0 mL) were added imidazole (1.90 g, 27.9 mmol) and TBSCl (2.11 g, 14.0 mmol) at rt. The reaction mixture was stirred at rt for 30 min. The reaction was quenched by the addition of sat. NH<sub>4</sub>Cl aq. and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 49/1 to 14/1) to give **1b** (2.25 g, 5.94 mmol, 99%, *E*:*Z* = 10:1) as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.14 (dt, *J* = 15.6, 5.4 Hz, 1H), 4.32 (dd, *J* = 5.4, 1.2 Hz, 2H), 0.98 (s, 9H), 0.93 (s, 9H), 0.19 (s, 6H), 0.10 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ 155.1, 130.4, 129.2, 127.5 (2C), 127.1, 120.1 (2C), 64.1, 26.0 (3C), 25.7 (3C), 18.5, 18.2, -4.4 (2C), -5.1 (2C); HRMS (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>38</sub>O<sub>2</sub>Si<sub>2</sub>Na ([M+Na]<sup>+</sup>) 401.2303, found 401.2323.

#### *tert*-butyl(3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propoxy)dimethylsilane (**1c**)<sup>18</sup>

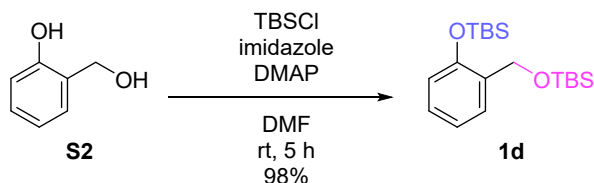


A suspension of **1b** (200.0 mg, 528 μmol) and Pd/C (5% on carbon, 20.3 mg) in EtOAc (5.3 mL) was stirred under an H<sub>2</sub> atmosphere at rt for 1 h. The reaction mixture was passed through a pad of Celite and filtrate was

concentrated to give **1c** (200.9 mg, 528  $\mu\text{mol}$ , quant.) as a colorless oil. The structure of **1c** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>18</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (d,  $J = 8.4$  Hz, 2H), 6.75 (d,  $J = 8.4$  Hz, 2H), 3.62 (t,  $J = 7.2$  Hz, 2H), 2.61 (t,  $J = 7.8$  Hz, 2H), 1.83-1.79 (m, 2H), 0.99 (s, 9H), 0.91 (s, 9H), 0.19 (s, 6H), 0.06 (s, 6H).

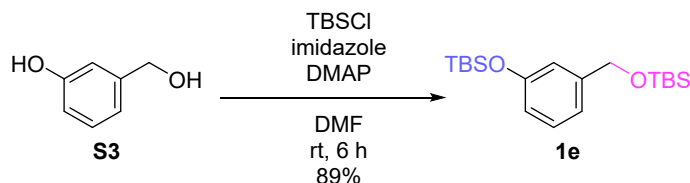
***tert-butyl((2-((tert-butyldimethylsilyl)oxy)benzyl)oxy)dimethylsilane (1d)***<sup>19</sup>



To a solution of 2-hydroxybenzyl alcohol (**S2**, 264.0 mg, 2.13 mmol) in DMF (4.3 mL) were added imidazole (608.5 mg, 8.94 mmol), DMAP (77.3 mg, 63.3  $\mu\text{mol}$ ), and TBSCl (674.2 mg, 4.47 mmol) at rt. The reaction mixture was stirred at rt for 5 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1) to give **1d** (735.8 mg, 2.09 mmol, 98%) as a colorless oil. The structure of **1d** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>19</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.11 (ddd,  $J = 8.4, 7.8, 1.2$  Hz, 1H), 6.97 (ddd,  $J = 7.8, 7.2, 1.2$  Hz, 1H), 6.74 (dd,  $J = 8.4, 1.2$  Hz, 1H), 4.76 (s, 2H), 1.00 (s, 9H), 0.95 (s, 9H), 0.21 (s, 6H), 0.10 (s, 6H).

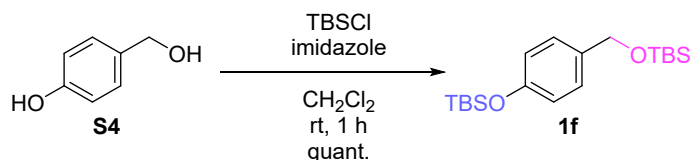
***tert-butyl((3-((tert-butyldimethylsilyl)oxy)benzyl)oxy)dimethylsilane (1e)***<sup>18</sup>



To a solution of 3-hydroxybenzyl alcohol (**S3**, 406.6 mg, 3.27 mmol) in DMF (6.6 mL) were added imidazole (938.1 mg, 13.8 mmol), DMAP (120.3 mg, 985  $\mu\text{mol}$ ), and TBSCl (1.03 g, 6.83 mmol) at rt. The reaction mixture was stirred at rt for 6 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1) to give **1e** (1.03 g, 2.92 mmol, 89%) as a colorless oil. The structure of **1e** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>18</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (dd,  $J = 8.4, 7.8$  Hz, 1H), 6.88 (d,  $J = 7.8$  Hz, 1H), 6.84 (br s, 1H), 6.71 (dd,  $J = 8.4, 1.8$  Hz, 1H), 4.69 (s, 2H), 0.98 (s, 9H), 0.94 (s, 9H), 0.19 (s, 6H), 0.09 (s, 6H).

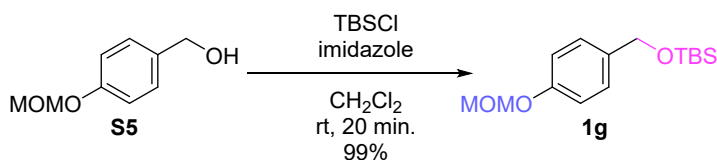
***tert-butyl((4-((tert-butyldimethylsilyl)oxy)benzyl)oxy)dimethylsilane (1f)***<sup>18</sup>



To a solution of 4-hydroxybenzyl alcohol (**S4**, 2.00 g, 16.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (35 mL) were added imidazole (4.71 g, 69.2 mmol) and TBSCl (5.20 g, 34.5 mmol) at rt. The reaction mixture was stirred at rt for 1 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1) to give **1f** (5.67 g, 16.1 mmol, quant.) as a colorless oil. The structure of **1e** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>18</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (d,  $J = 8.4$ , 2H), 6.80 (d,  $J = 8.4$  Hz, 2H), 4.67 (s, 2H), 0.98 (s, 9H), 0.93 (s, 9H), 0.18 (s, 6H), 0.08 (s, 6H).

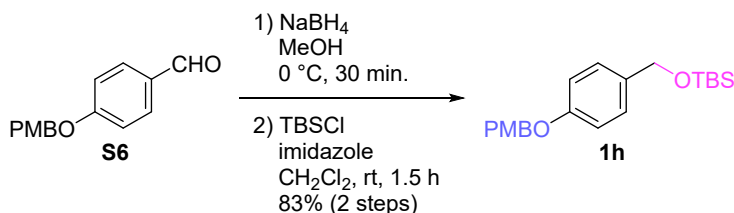
***tert-butyl((4-((tert-butyl dimethylsilyl)oxy)benzyl)oxy)dimethylsilane (1g)***



To a solution of known alcohol **S5**<sup>7</sup> (183.6 mg, 1.09 mmol) in  $\text{CH}_2\text{Cl}_2$  (5.5 mL) were added imidazole (186.2 mg, 2.74 mmol) and TBSCl (182.1 mg, 1.21 mmol) at rt. The reaction mixture was stirred at rt for 20 min. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **1g** (304.0 mg, 1.08 mmol, 99%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 9.0$  Hz, 2H), 7.01 (d,  $J = 9.0$  Hz, 2H), 5.17 (s, 2H), 4.68 (s, 2H), 3.48 (s, 3H), 0.94 (s, 9H), 0.10 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 134.9, 127.4 (2C), 116.0 (2C), 94.5, 64.6, 55.9, 25.9 (3C), 18.4,  $-5.2$  (2C); HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{26}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 305.1543, found 305.1529.

***tert-butyl((4-((4-methoxybenzyl)oxy)benzyl)oxy)dimethylsilane (1h)***

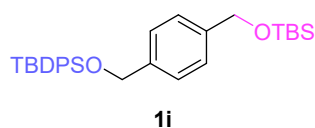


To a solution of known aldehyde **S6**<sup>20</sup> (200.0 mg, 826  $\mu\text{mol}$ ) in MeOH (5.5 mL) was added  $\text{NaBH}_4$  (38.1 mg, 2.74 mmol) at  $0^\circ\text{C}$ . The reaction mixture was stirred at  $0^\circ\text{C}$  for 30 min. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a crude benzyl alcohol.

To a solution of crude benzyl alcohol (prepared above) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) were added imidazole (142.1 mg, 2.09 mmol) and TBSCl (138.1 mg, 916 μmol) at rt. The reaction mixture was stirred at rt for 1.5 h. The reaction was quenched by the addition of 1 M HCl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **1h** (244.3 mg, 681 μmol, 83%) as a colorless oil.

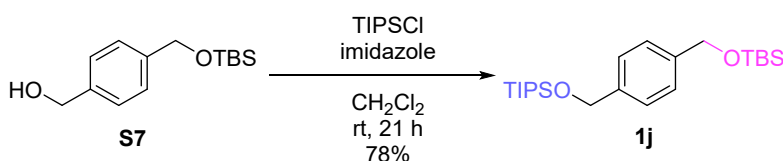
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.99 (s, 2H), 4.69 (s, 2H), 3.82 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); <sup>13</sup>C {<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ 159.4, 157.9, 133.7, 129.2 (2C), 129.1, 127.5 (2C), 114.6 (2C), 113.9 (2C), 69.8, 64.7, 55.3, 26.0 (3C), 18.4, -5.2 (2C); HRMS (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>SiNa ([M+Na]<sup>+</sup>) 381.1856, found 381.1839.

***tert*-butyl((4-(((*tert*-butyldimethylsilyl)oxy)methyl)benzyl)oxy)diphenylsilane (**1i**)**<sup>9</sup>



Compound **1i** was prepared according to literature procedure and the structure of prepared **1i** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>9</sup>

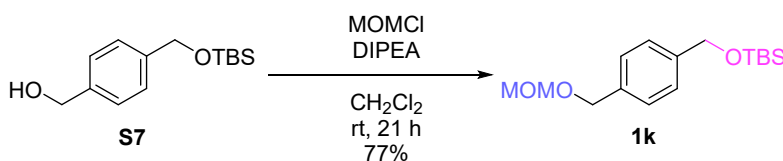
***tert*-butyldimethyl((4-(((*triisopropylsilyl*)oxy)methyl)benzyl)oxy)silane (**1j**)**



To a solution of known alcohol **S7**<sup>19</sup> (150.0 mg, 594 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) were added imidazole (89.9 mg, 1.32 mmol) and TIPSCl (139 μL, 656 μmol) at rt. The reaction mixture was stirred at rt for 21 h. The reaction was quenched by the addition of sat. NH<sub>4</sub>Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 49/1 to 9/1) to give **1j** (188.7 mg, 462 μmol, 78%) as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 2H), 4.73 (s, 2H), 1.20-1.14 (m, 3H), 1.09 (d, *J* = 6.6 Hz, 18H), 0.94 (s, 9H), 0.09 (s, 6H); <sup>13</sup>C {<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>) δ 140.3, 139.9, 125.9 (2C), 125.6 (2C), 64.9 (2C), 26.0 (3C), 18.4, 18.0 (6C), 12.0 (3C), -5.2 (2C); HRMS (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>44</sub>O<sub>2</sub>Si<sub>2</sub>Na ([M+Na]<sup>+</sup>) 431.2772, found 431.2792.

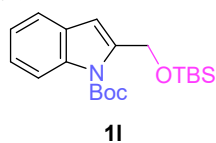
***tert*-butyl((4-((methoxymethoxy)methyl)benzyl)oxy)dimethylsilane (**1k**)**



To a solution of known alcohol **S7**<sup>21</sup> (200.0 mg, 792  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (1.6 mL) were added DIPEA (404  $\mu\text{L}$ , 2.38 mmol) and MOMCl (139  $\mu\text{L}$ , 1.06 mmol) at rt. The reaction mixture was stirred at rt for 21 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **1k** (179.7 mg, 606  $\mu\text{mol}$ , 77%) as a colorless oil.

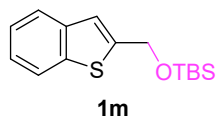
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J$  = 9.0 Hz, 2H), 7.31 (d,  $J$  = 9.0 Hz, 2H), 4.74 (s, 2H), 4.70 (s, 2H), 4.58 (s, 2H), 3.41 (s, 3H), 0.94 (s, 9H), 0.09 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 136.4, 127.9 (2C), 126.1 (2C), 95.6, 69.0, 64.8, 55.3, 25.9, 18.4, -5.2 (2C); HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{28}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 319.1700, found 319.1713.

**tert-butyl 2-(((tert-butyl dimethylsilyl)oxy)methyl)-1H-indole-1-carboxylate (1l)**<sup>22</sup>



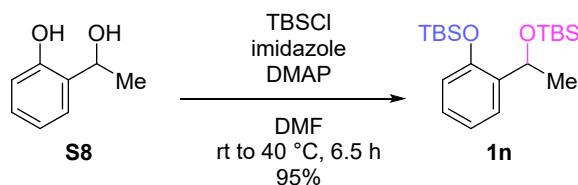
Compound **1l** was prepared according to literature procedure and the structure of prepared **1l** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>22</sup>

**(benzo[b]thiophen-2-ylmethoxy)(tert-butyl)dimethylsilane (1m)**<sup>9</sup>



Compound **1m** was prepared according to literature procedure and the structure of prepared **1m** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>9</sup>

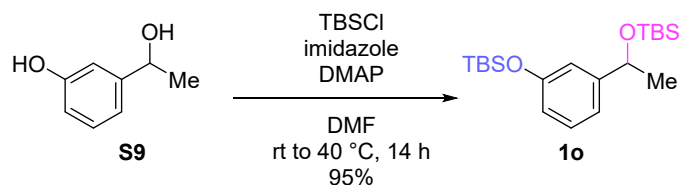
**tert-butyl(2-(1-(((tert-butyl dimethylsilyl)oxy)ethyl)phenoxy)dimethylsilane (1n)**<sup>23</sup>



To a solution of known compound **S8**<sup>24</sup> (390.0 mg, 2.82 mmol) in DMF (5.6 mL) were added imidazole (809.2 mg, 11.9 mmol), DMAP (102.4 mg, 838  $\mu\text{mol}$ ), and TBSCl (893.6 mg, 5.93 mmol) at rt. The reaction mixture was stirred at 40  $^\circ\text{C}$  for 6.5 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1) to give **1n** (984.3 mg, 2.68 mmol, 95%) as a colorless oil. The structure of **1n** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>23</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (dd,  $J$  = 7.8, 1.2 Hz, 1H), 7.09 (ddd,  $J$  = 7.8, 7.2, 1.2 Hz, 1H), 6.96 (dd,  $J$  = 7.8, 7.2 Hz, 1H), 6.74 (d,  $J$  = 7.8 Hz, 1H), 5.22 (q,  $J$  = 6.6 Hz, 1H), 1.36 (d,  $J$  = 6.6 Hz, 3H), 1.03 (s, 9H), 0.91 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H), 0.04 (s, 3H), -0.01 (s, 3H).

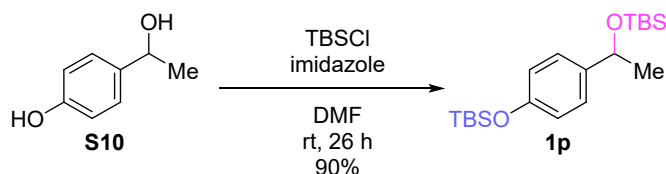
***tert-butyl(3-(1-((tert-butyldimethylsilyl)oxy)ethyl)phenoxy)dimethylsilane (1o)***



To a solution of 3-hydroxy- $\alpha$ -methylbenzyl alcohol (**S9**, 300.0 mg, 2.17 mmol) in DMF (4.3 mL) were added imidazole (620.9 mg, 9.12 mmol), DMAP (81.2 mg, 66.5  $\mu$ mol), and TBSCl (689.1 mg, 4.57 mmol) at rt. The reaction mixture was stirred at 40 °C for 14 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1) to give **1o** (760.1 mg, 2.07 mmol, 95%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (dd,  $J$  = 8.4, 7.8 Hz, 1H), 6.88 (d,  $J$  = 7.8 Hz, 1H), 6.85 (d,  $J$  = 1.2 Hz, 1H), 6.69 (ddd,  $J$  = 8.4, 1.2, 1.2 Hz, 1H), 4.81 (q,  $J$  = 6.6 Hz, 1H), 1.38 (d,  $J$  = 6.6 Hz, 3H), 0.98 (s, 9H), 0.90 (s, 9H), 0.19 (s, 6H), 0.05 (s, 3H), -0.02 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 148.6, 128.9, 118.4, 118.2, 116.9, 70.6, 27.2, 25.9 (3C), 25.7 (3C), 18.25, 18.20, -4.4 (2C), -4.8, -4.9; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{38}\text{O}_2\text{Si}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 389.2303, found 389.2297.

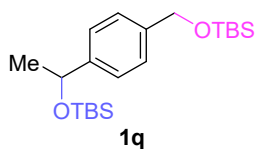
***tert-butyl(4-(1-((tert-butyldimethylsilyl)oxy)ethyl)phenoxy)dimethylsilane (1p)***



To a solution of 4-(1-hydroxyethyl)phenol (**S10**, 100.3 mg, 726  $\mu$ mol) in DMF (2.5 mL) were added imidazole (207.8 mg, 3.05 mmol) and TBSCl (232.1 mg, 1.54 mmol) at rt. The reaction mixture was stirred at rt for 20 h. To the mixture were added imidazole (100.9 mg, 1.48 mmol) and TBSCl (55.4 mg, 369  $\mu$ mol) at rt and resulting mixture was stirred for further 6h. The reaction was quenched by the addition of 1 M HCl aq. and diluted with EtOAc and water. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 1/0 to 49/1) to give **1p** (237.8 mg, 649  $\mu$ mol, 90%) as a colorless oil.

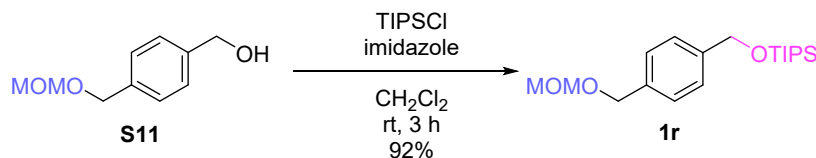
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (d,  $J$  = 9.0 Hz, 2H), 6.76 (d,  $J$  = 9.0 Hz, 2H), 4.80 (q,  $J$  = 6.6 Hz, 1H), 1.38 (d,  $J$  = 6.6 Hz, 3H), 0.97 (s, 9H), 0.88 (s, 9H), 0.18 (s, 6H), 0.02 (s, 3H), -0.06 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  154.3, 139.7, 126.3 (2C), 119.5 (2C), 70.5, 27.2, 25.9 (3C), 25.7 (3C), 18.25, 18.18, -4.4 (2C), -4.79, -4.84; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{38}\text{O}_2\text{Si}_2\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ) 389.2303, found 389.2319.

***tert-butyl((4-(1-((tert-butyldimethylsilyl)oxy)ethyl)benzyl)oxy)dimethylsilane (1q)<sup>25</sup>***



Compound **1q** was prepared according to literature procedure and the structure of prepared **1q** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>25</sup>

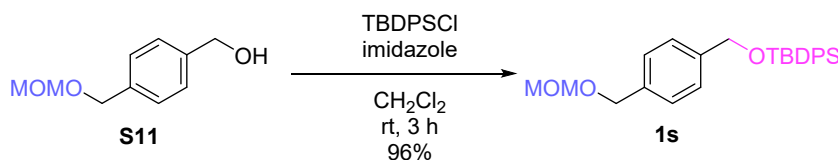
**triisopropyl((4-((methoxymethoxy)methyl)benzyl)oxy)silane (1r)**



To a solution of known benzyl alcohol **S11**<sup>26</sup> (200.0 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL) were added imidazole (165.4 mg, 2.43 mmol) and TIPSCl (139  $\mu\text{L}$ , 1.21 mmol) at rt. The reaction mixture was stirred at rt for 3 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1) to give **1r** (343.5 mg, 1.01 mmol, 92%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J$  = 8.4 Hz, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 4.84 (s, 2H), 4.71 (s, 2H), 4.59 (s, 2H), 3.42 (s, 3H), 1.22-1.15 (m, 3H), 1.09 (d,  $J$  = 7.2 Hz, 18H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 136.2, 127.9 (2C), 125.8 (2C), 95.6, 69.0, 64.8, 55.3, 18.0 (6C), 12.0 (3C); HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{34}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 361.2169, found 361.2178.

**tert-butyl((4-((methoxymethoxy)methyl)benzyl)oxy)diphenylsilane (1s)**

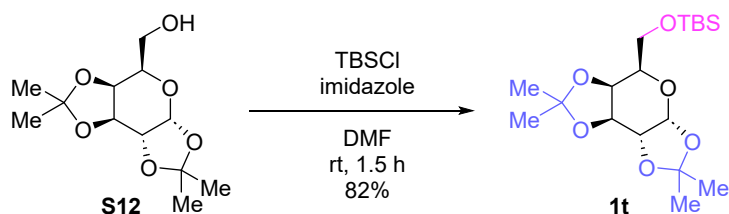


To a solution of known benzyl alcohol **S11**<sup>26</sup> (200.0 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL) were added imidazole (166.1 mg, 2.44 mmol) and TBDPSCI (310  $\mu\text{L}$ , 1.21 mmol) at rt. The reaction mixture was stirred at rt for 3 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 9/1) to give **1s** (444.2 mg, 1.06 mmol, 96%) as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71-7.69 (m, 4H), 7.45-7.33 (m, 10H), 4.78 (s, 2H), 4.72 (s, 2H), 4.60 (s, 2H), 3.43 (s, 3H), 1.10 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 136.4, 135.6 (4C), 133.5 (2C), 129.7 (2C), 127.9 (2C), 127.7 (4C), 126.1 (2C), 95.6, 69.0, 65.3, 55.3, 26.8 (3C), 19.3; HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{32}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 443.2032, found 443.1995.

**tert-butyl dimethyl(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)silane (1t)**<sup>27</sup>

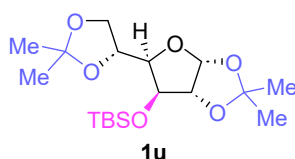




To a solution of 1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranose (**S12**, 770.0 mg, 2.96 mmol) in DMF (6.0 mL) were added imidazole (443.5 mg, 6.51 mmol) and TBSCl (467.8 mg, 3.10 mmol) at rt. The reaction mixture was stirred at rt for 1.5 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 97/3 to 19:1) to give **1t** (912.3 mg, 2.44 mmol, 82%) as a colorless oil. The structure of **1t** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>27</sup>

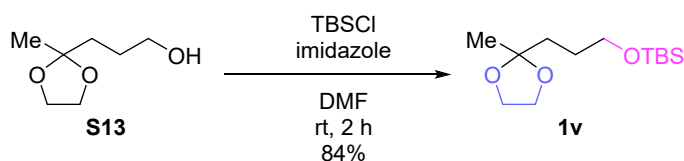
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.52 (d,  $J = 4.8$  Hz, 1H), 4.59 (dd,  $J = 7.8, 2.4$  Hz, 1H), 4.31-4.28 (m, 2H), 3.85-3.78 (m, 2H), 3.73 (dd,  $J = 9.6, 3.6$  Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H).

*tert*-butyl(((3*aR*,5*R*,6*S*,6*aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)dimethylsilane (**1u**)<sup>28</sup>



Compound **1u** was prepared according to literature procedure and the structure of prepared **1u** was confirmed by comparison of its  $^1\text{H}$  NMR spectrum with that reported.<sup>28</sup>

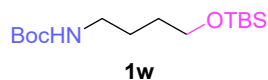
*tert*-butyldimethyl(3-(2-methyl-1,3-dioxolan-2-yl)propoxy)silane (**1v**)



To a solution of **S13**<sup>29</sup> (200.3 mg, 1.37 mmol) in DMF (2.7 mL) were added imidazole (205.5 mg, 3.02 mmol) and TBSCl (226.9 mg, 1.51 mmol) at rt. The reaction mixture was stirred at rt for 2 h. The reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 97/3) to give **1v** (299.8 mg, 1.15 mmol, 84%) as a colorless oil.

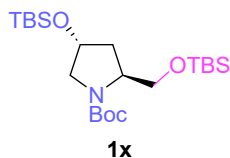
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.96-3.90 (m, 4H), 3.61 (t,  $J = 6.6$  Hz, 2H), 1.69-1.58 (m, 4H), 1.32 (s, 3H), 0.89 (s, 9H), 0.04 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  110.1, 64.6 (2C), 63.2, 35.4, 27.6, 25.9 (3C), 23.8, 18.3, -5.3 (2C); HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{28}\text{O}_3\text{SiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 283.1700, found 283.1714.

*tert*-butyl (4-((*tert*-butyldimethylsilyl)oxy)butyl)carbamate (**1w**)<sup>30</sup>



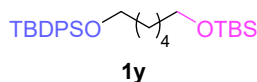
Compound **1w** was prepared according to literature procedure and the structure of prepared **1w** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>30</sup>

*tert*-butyl (2*S*,4*R*)-4-((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)pyrrolidine-1-carboxylate (**1x**)<sup>31</sup>



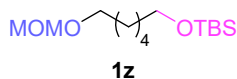
Compound **1x** was prepared according to literature procedure and the structure of prepared **1x** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>31</sup>

2,2,3,3,13,13-hexamethyl-12,12-diphenyl-4,11-dioxo-3,12-disilatetradecane (**1y**)<sup>32</sup>



Compound **1y** was prepared according to literature procedure and the structure of prepared **1y** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>32</sup>

12,12,13,13-tetramethyl-2,4,11-trioxa-12-silatetradecane (**1z**)<sup>32</sup>



Compound **1z** was prepared according to literature procedure and the structure of prepared **1z** was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that reported.<sup>32</sup>

### 3. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data

Figure S1. <sup>1</sup>H NMR spectrum (600 MHz, DMSO-*d*<sub>6</sub>) of IBX (containing ~5% of 2-iodobenzoic acid).

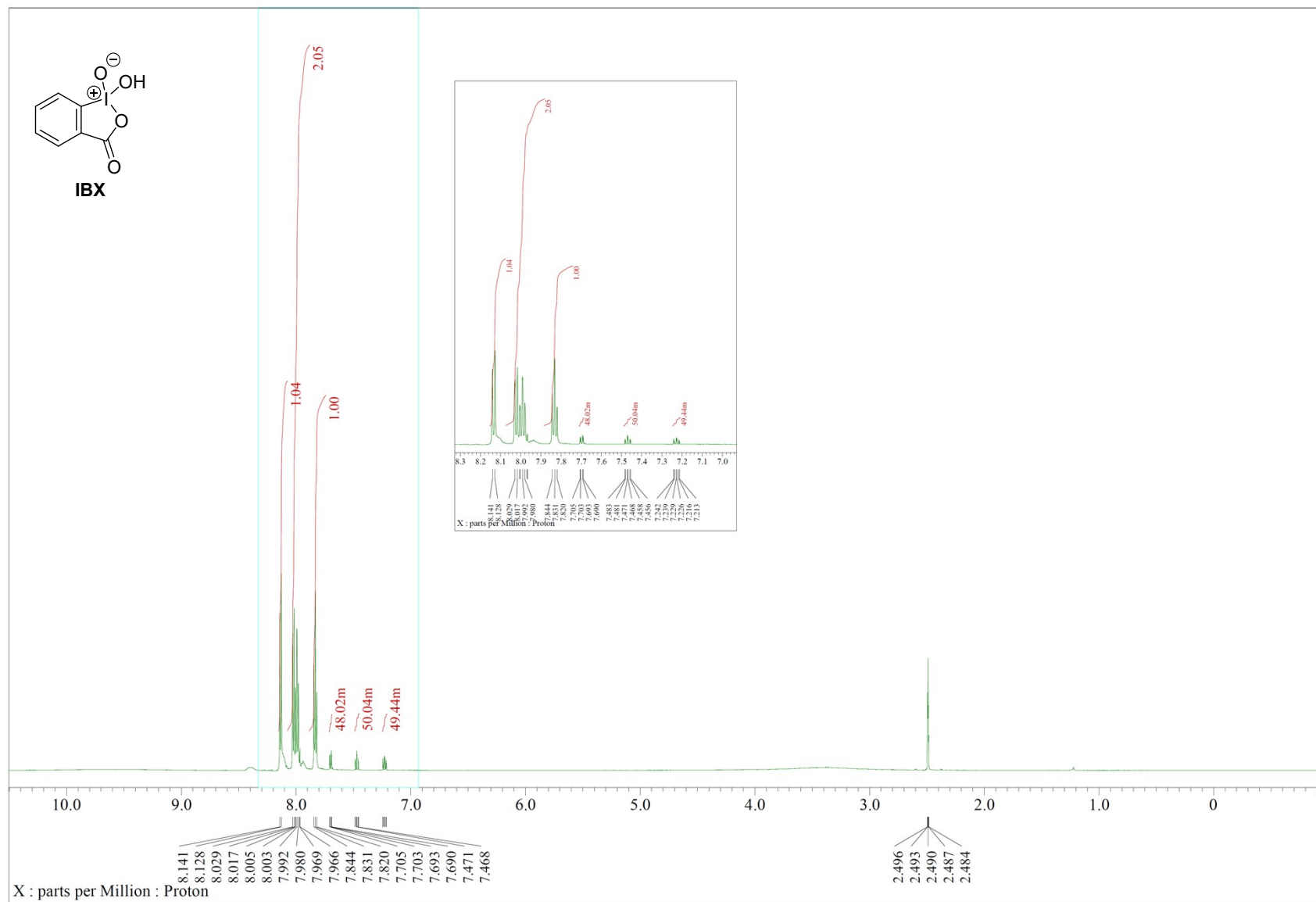


Figure S2. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2b.

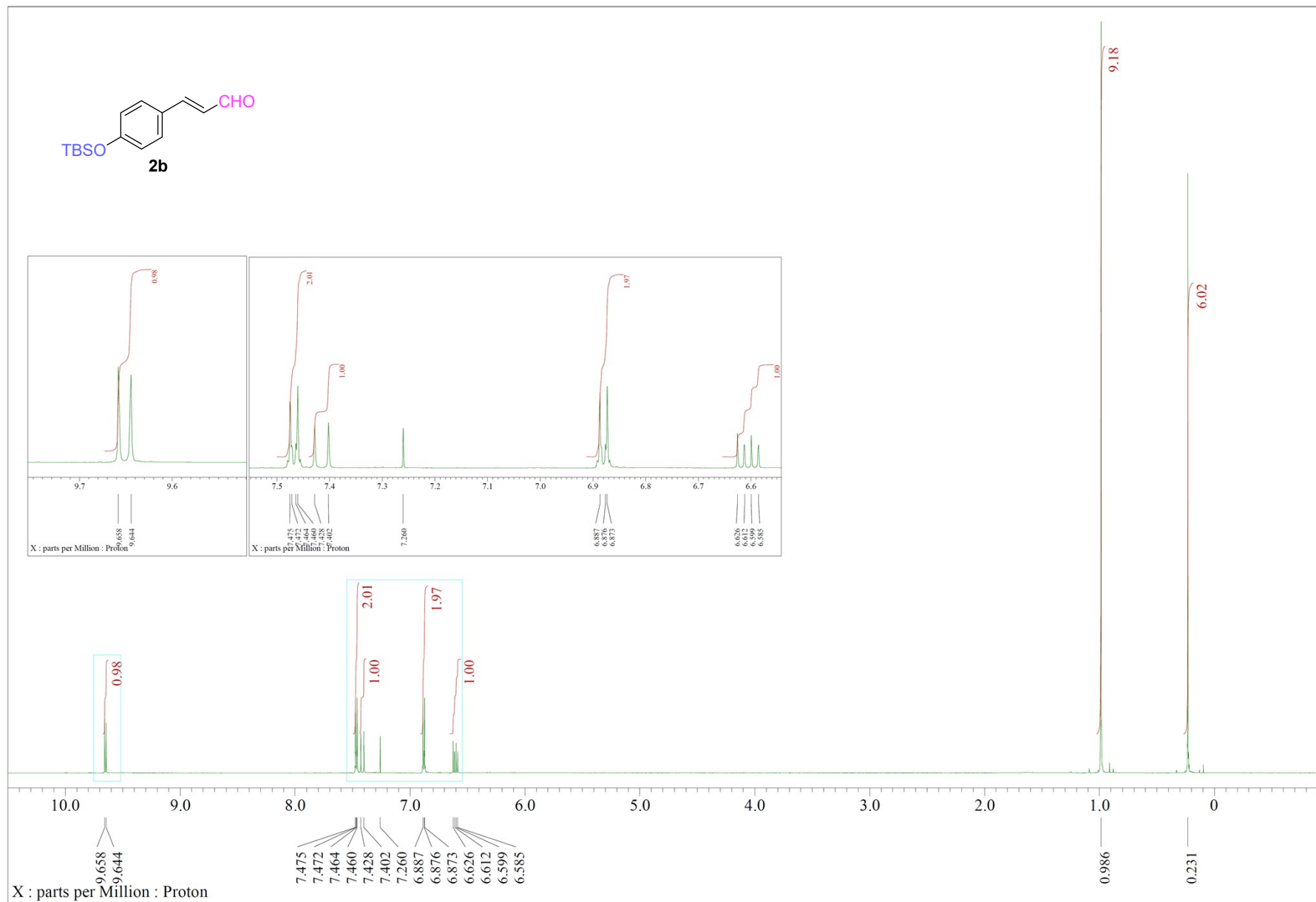


Figure S3. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2c.

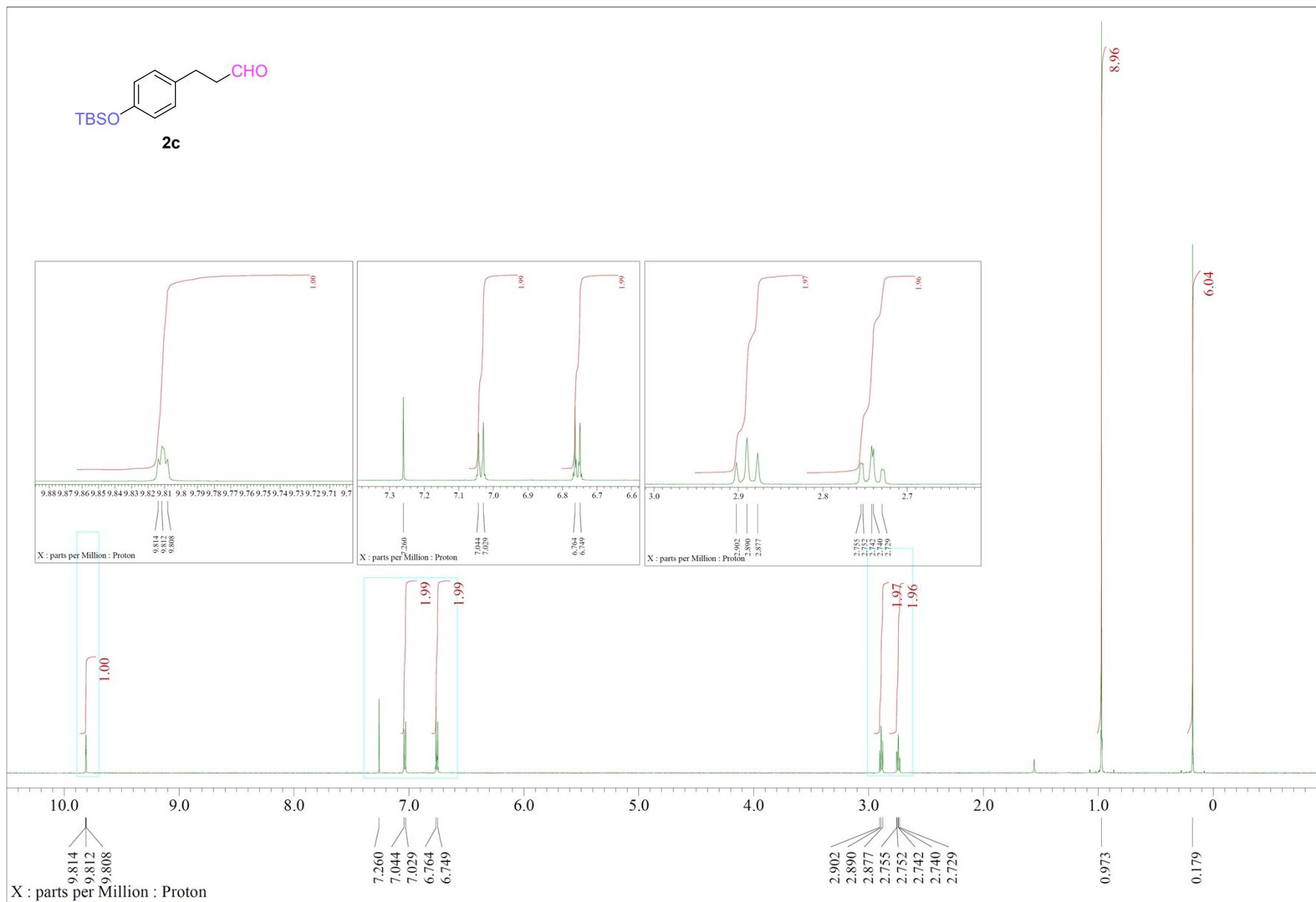


Figure S4. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2d.

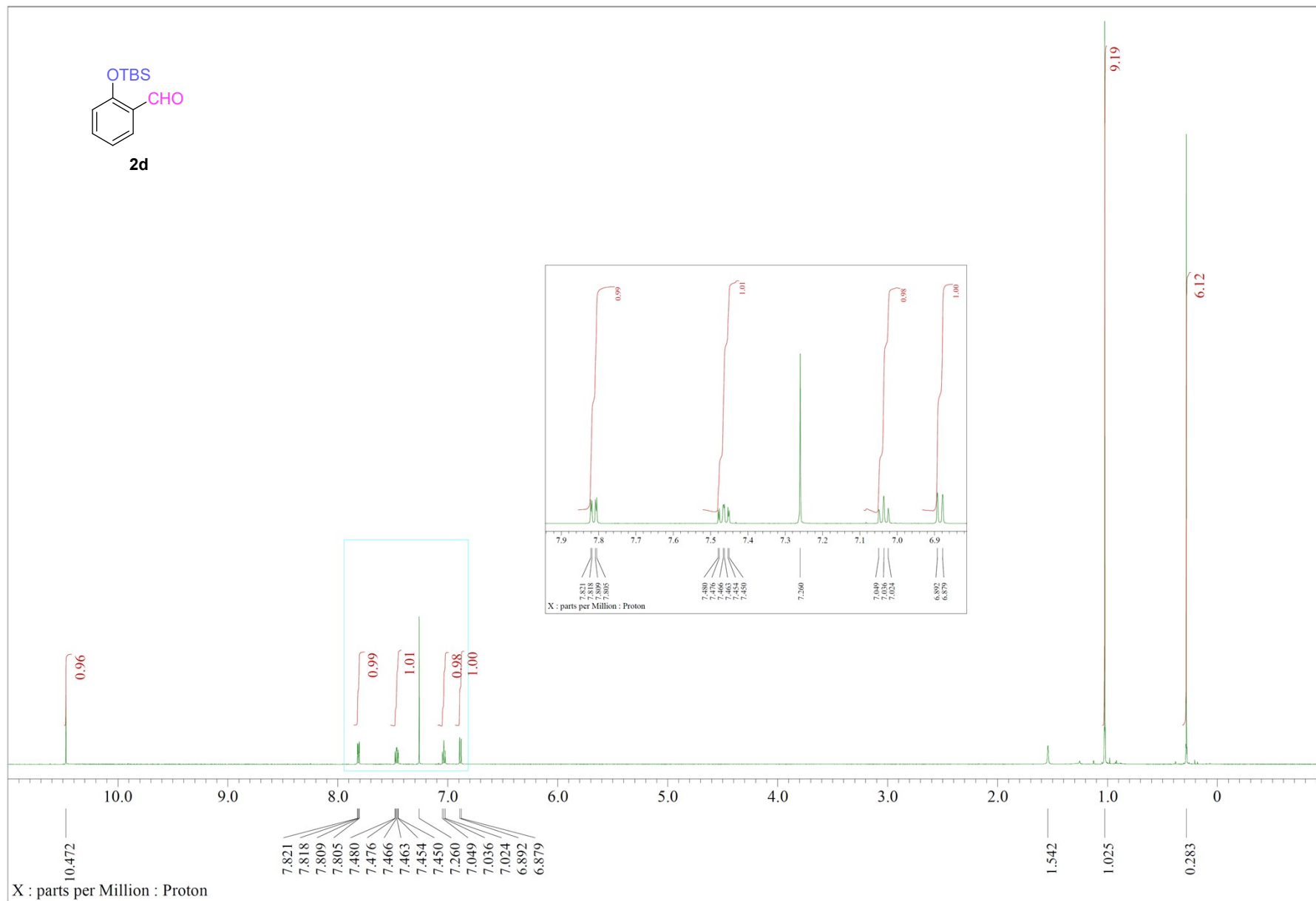


Figure S5. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2e.

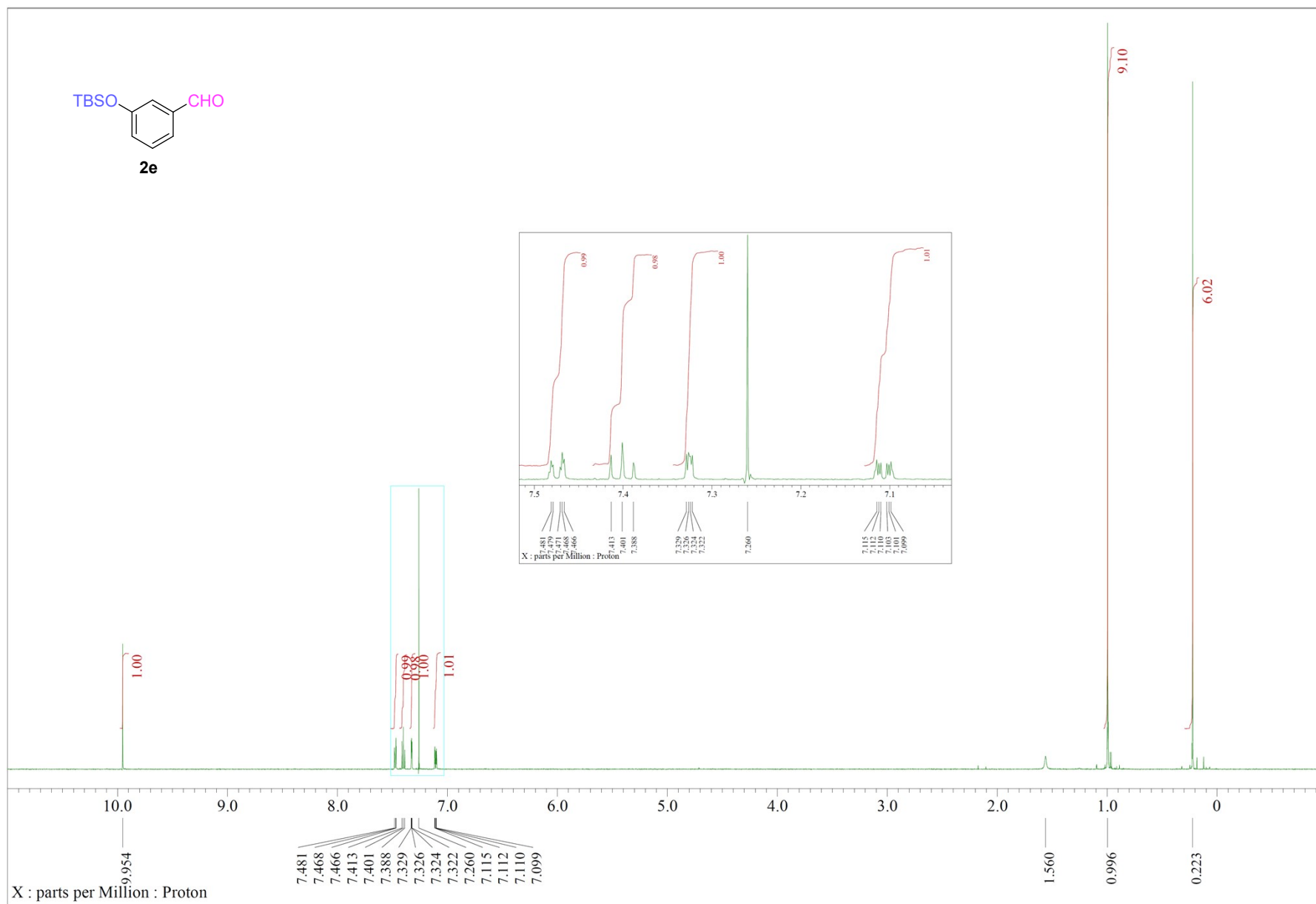


Figure S6. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2f.

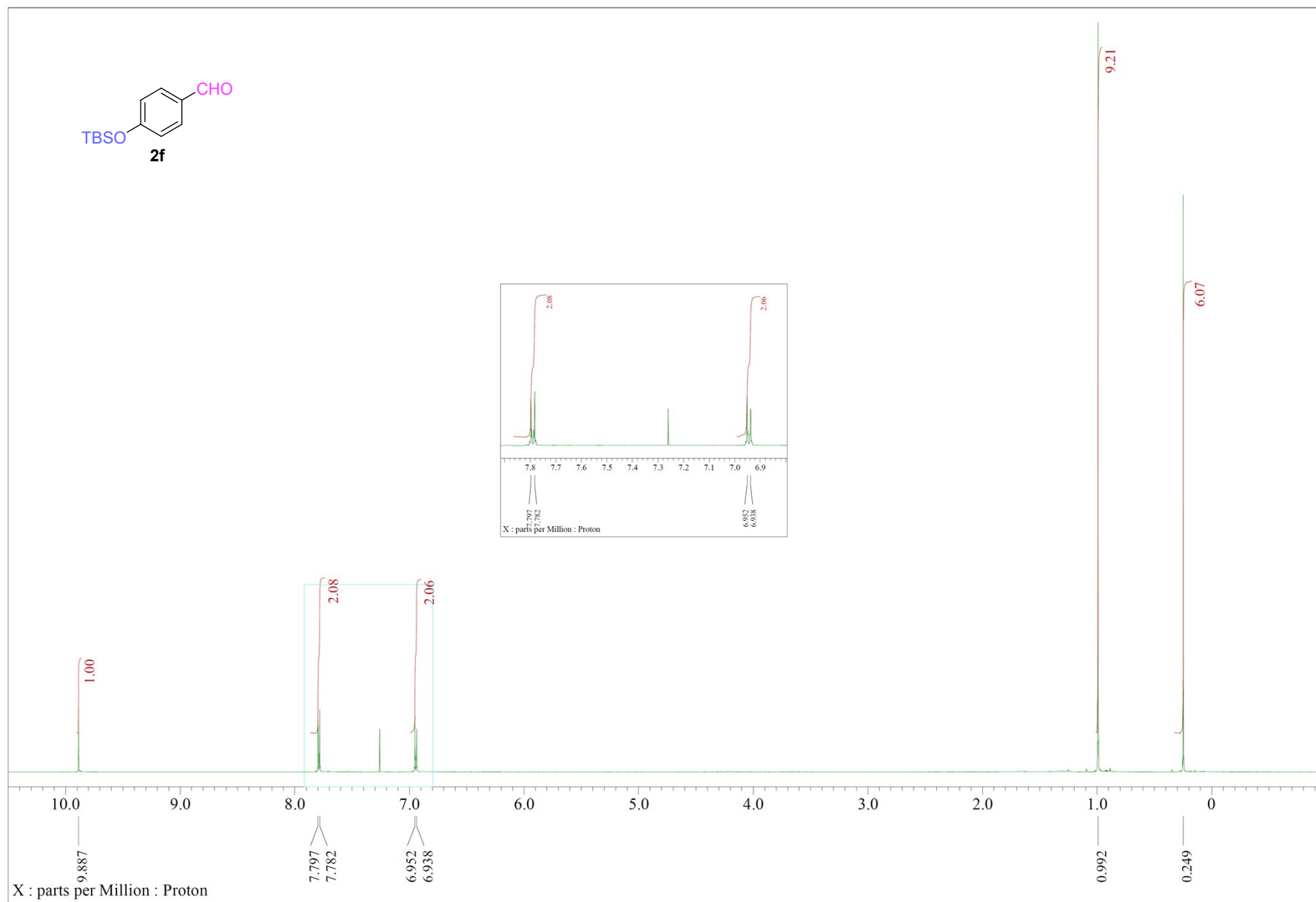




Figure S7. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2g.

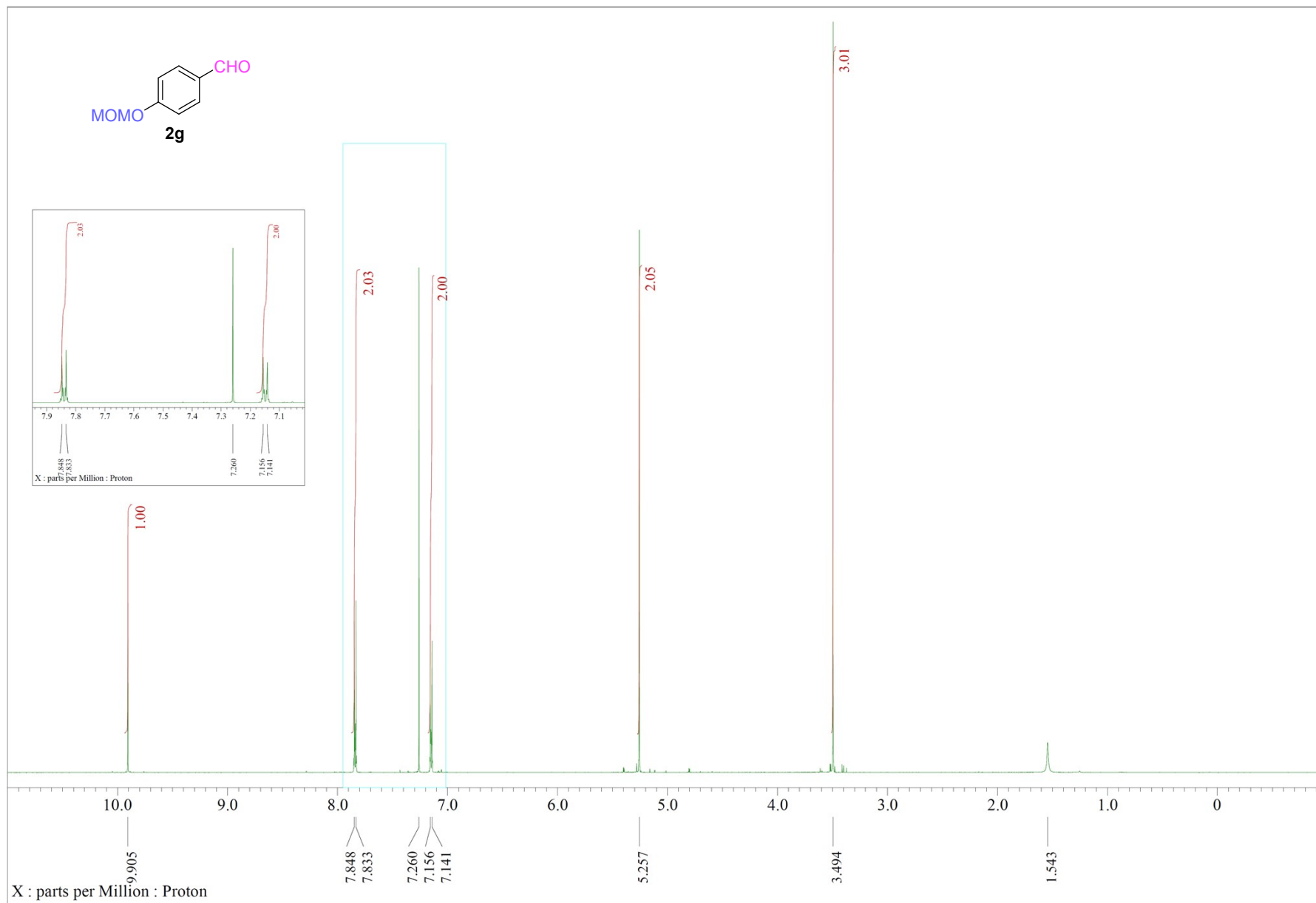


Figure S8. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2h.

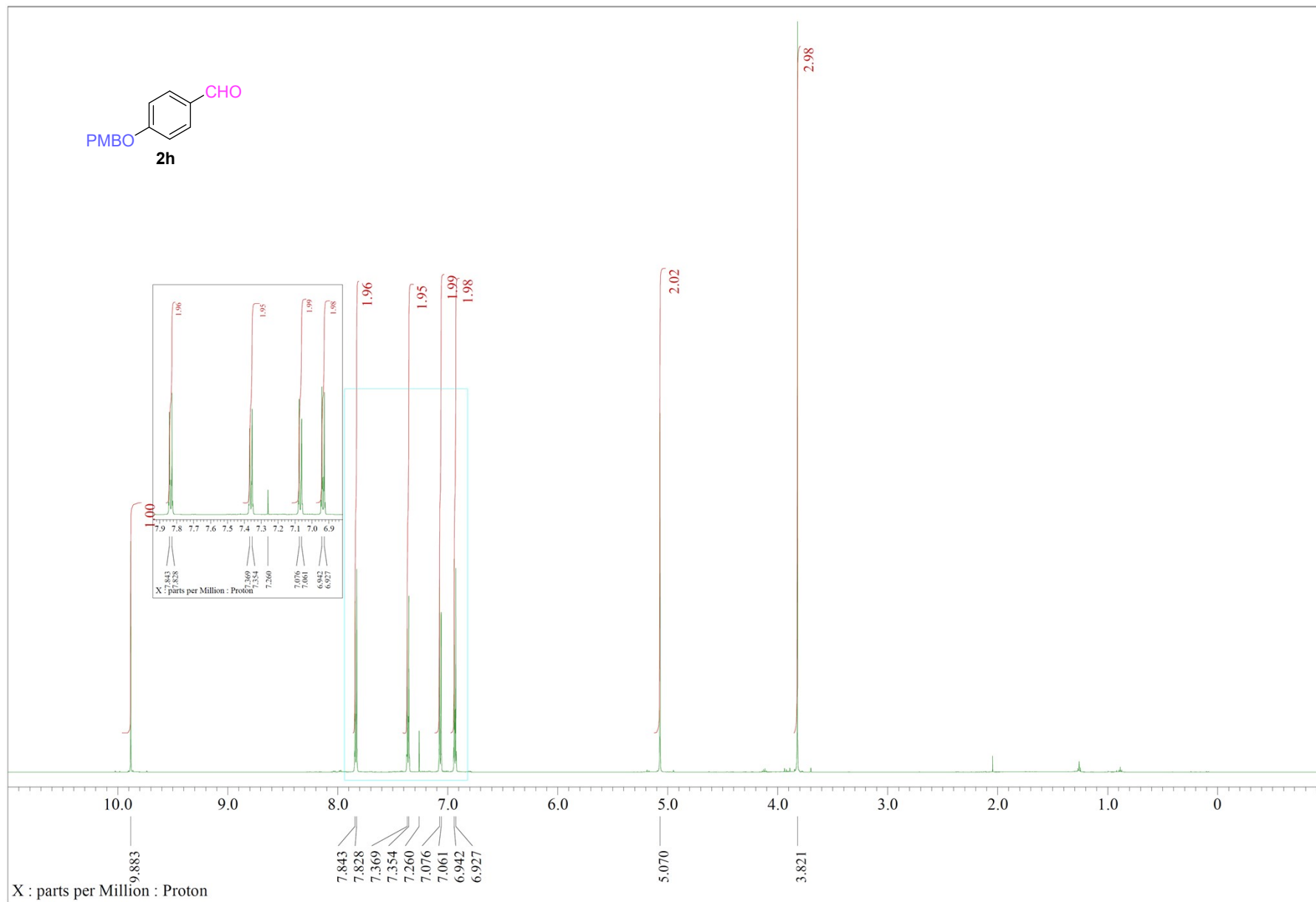






Figure S11. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2k.

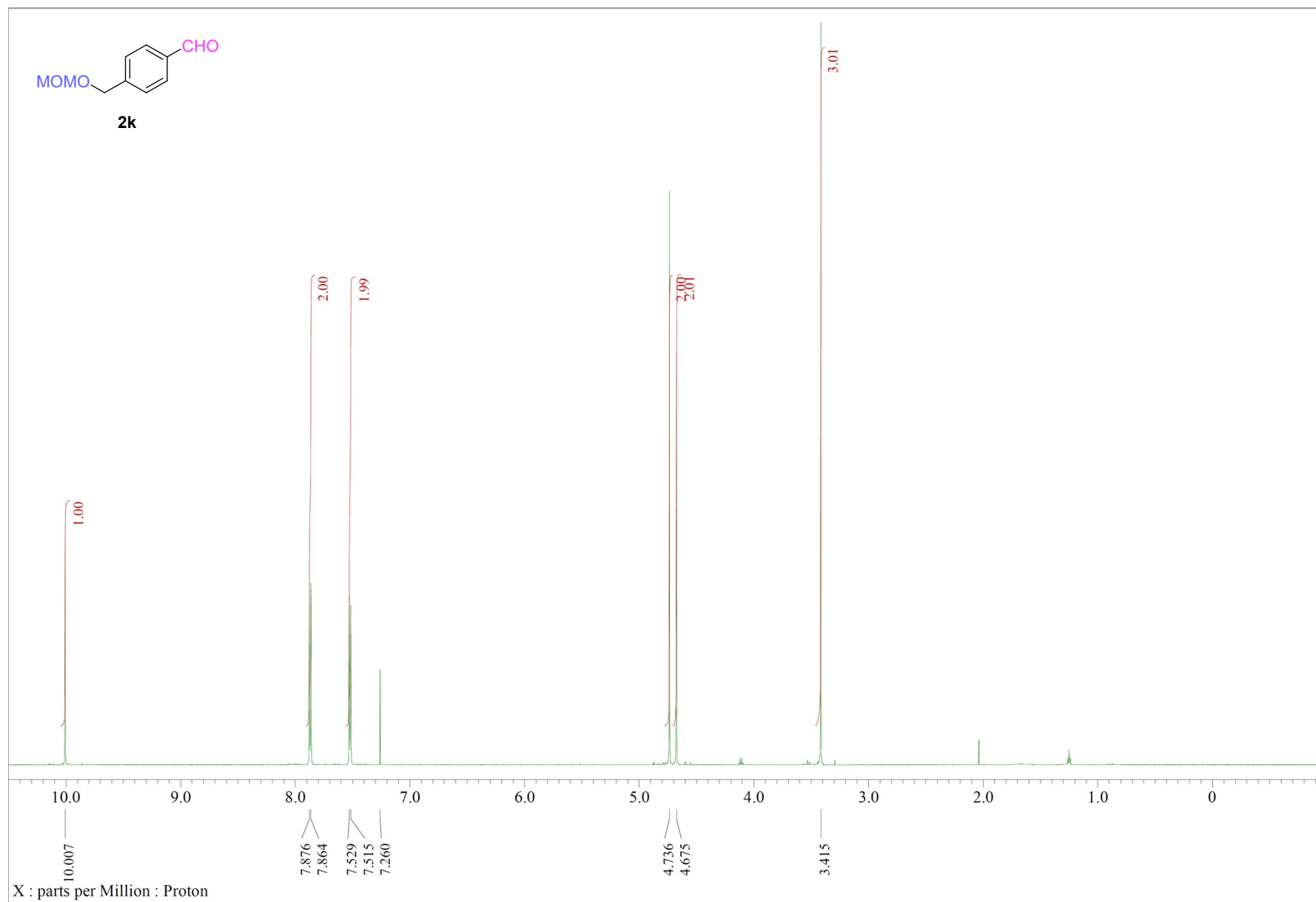


Figure S12. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2l.

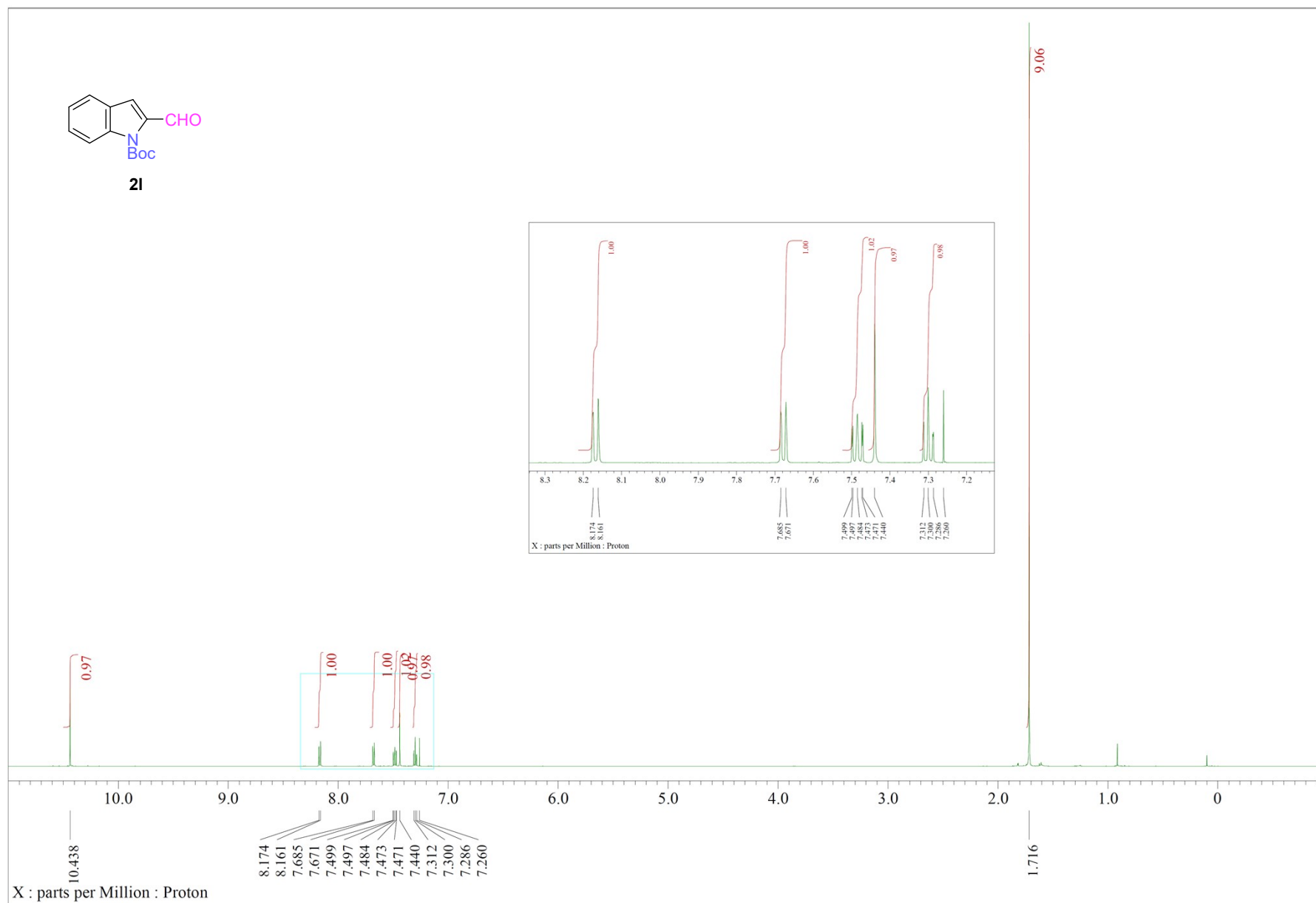


Figure S13. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2m.

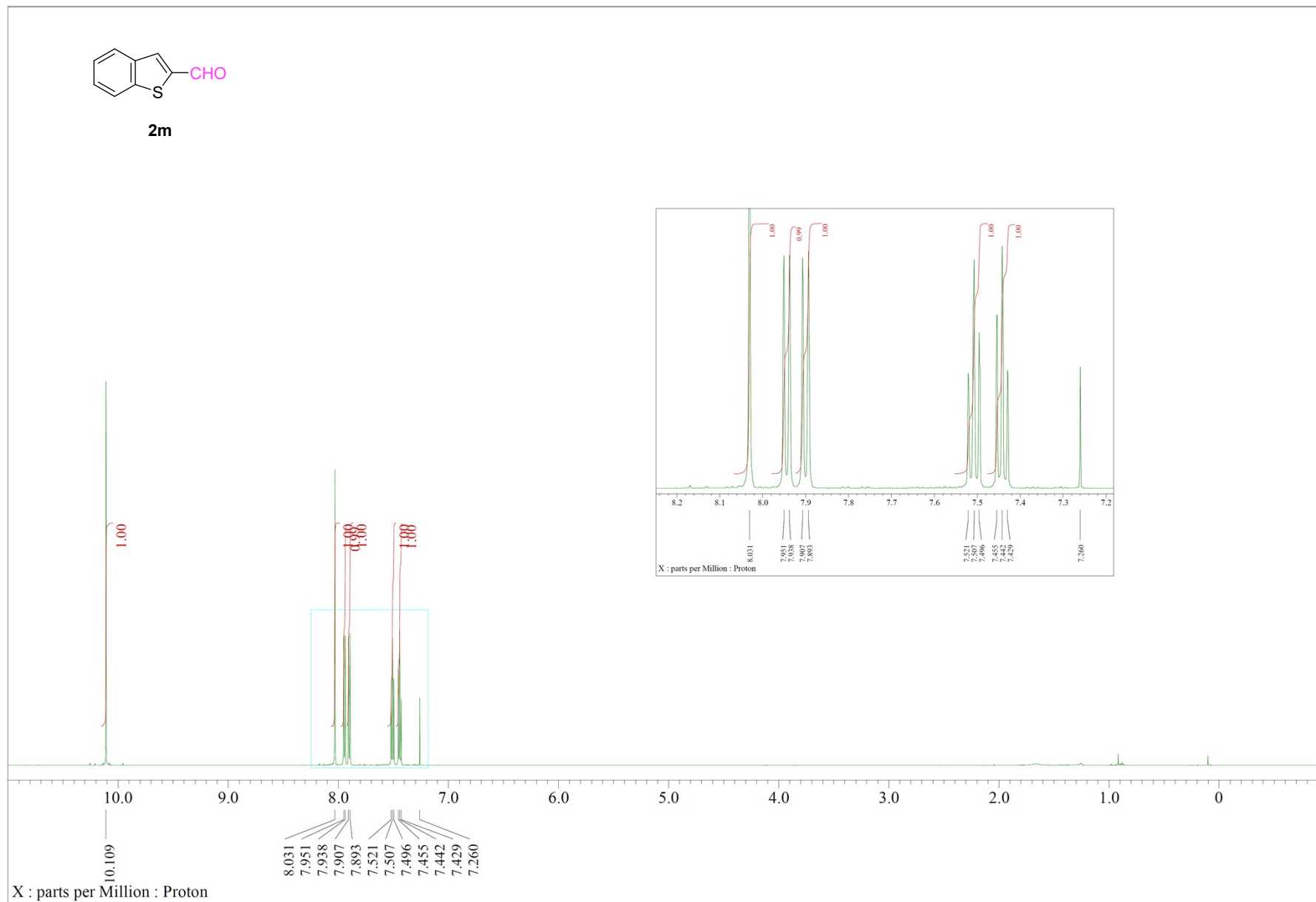


Figure S14. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2n.

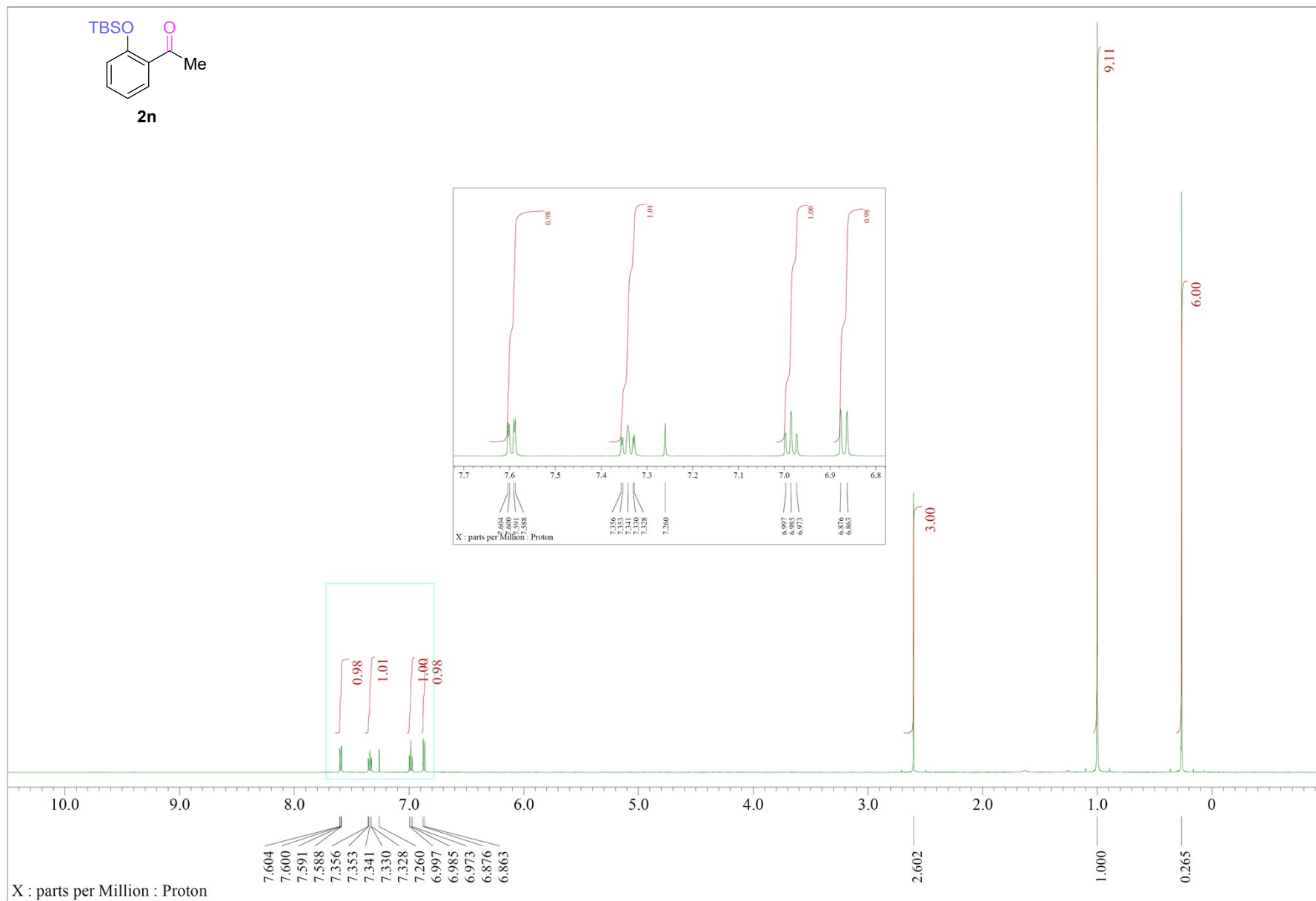




Figure S15.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound 2n.

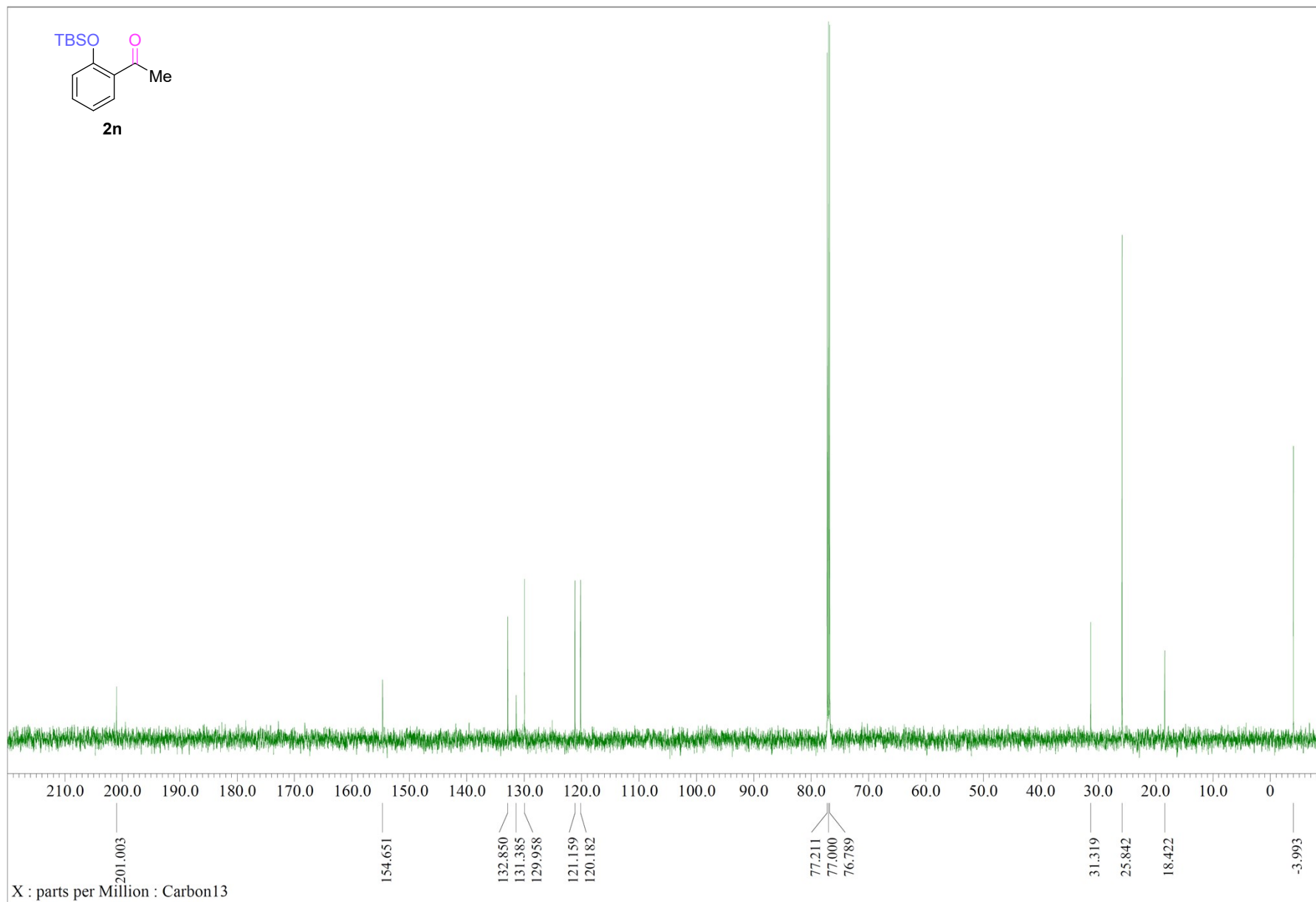


Figure S16. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2o.

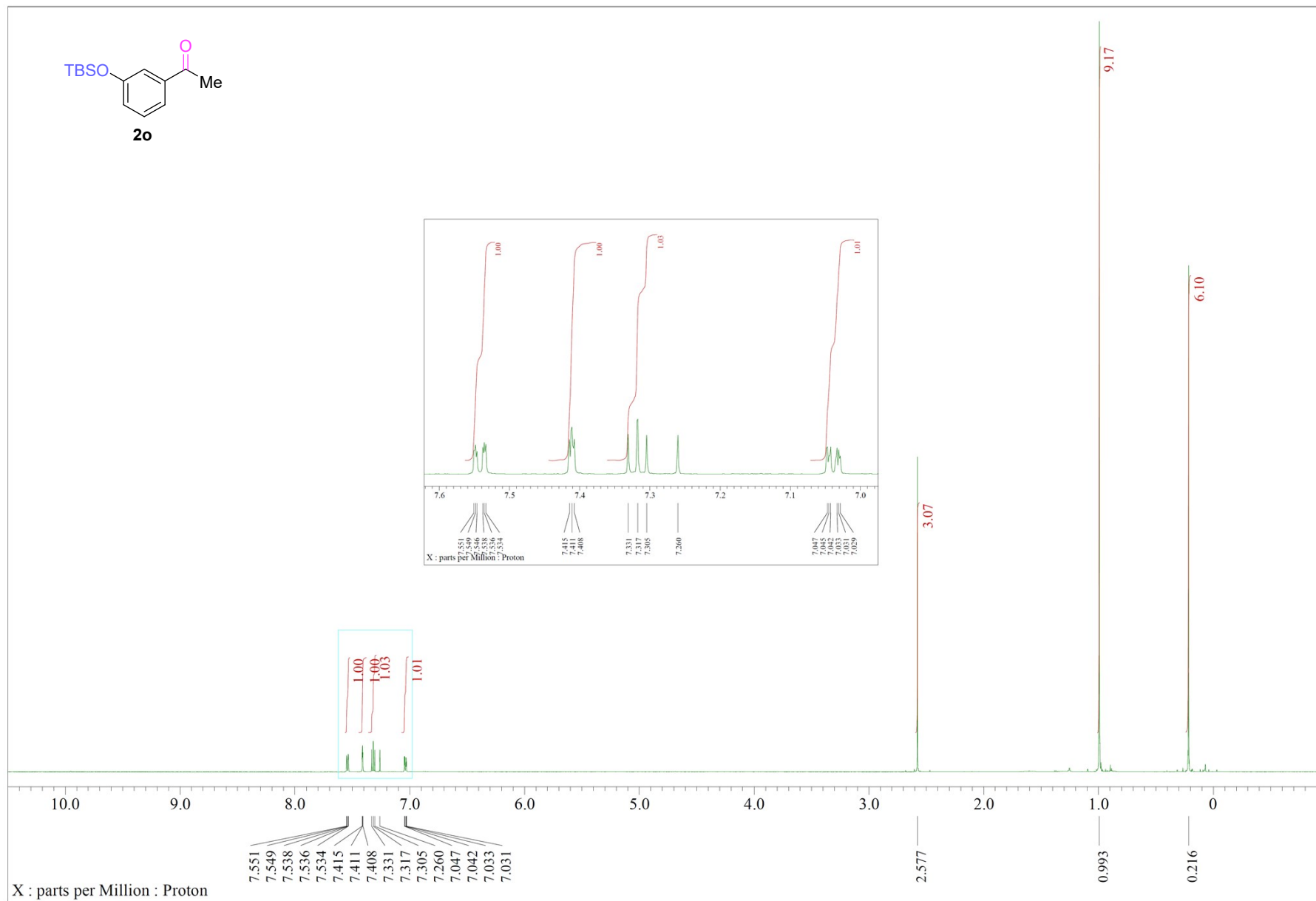


Figure S17.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **2o**.

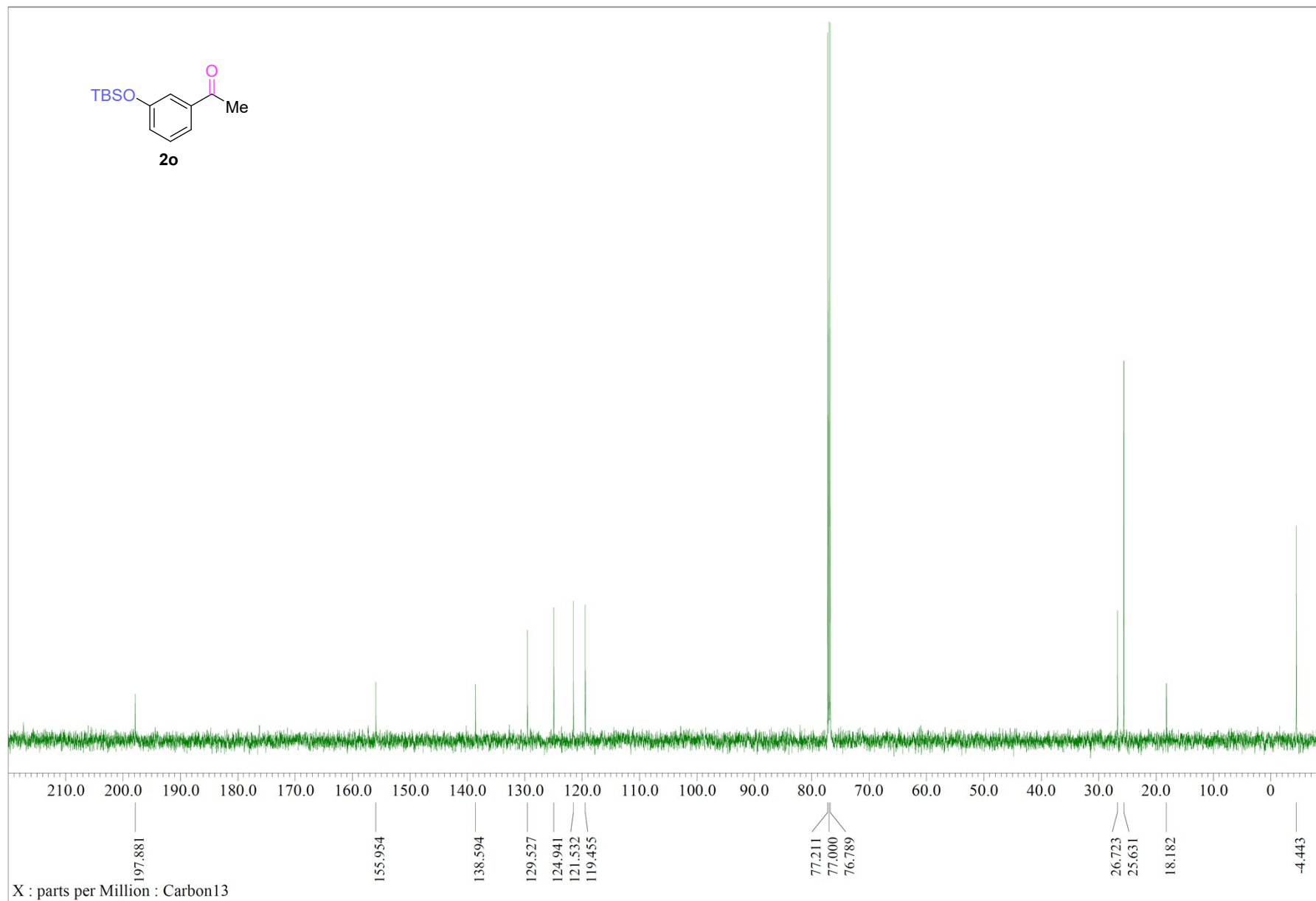


Figure S18. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2p.

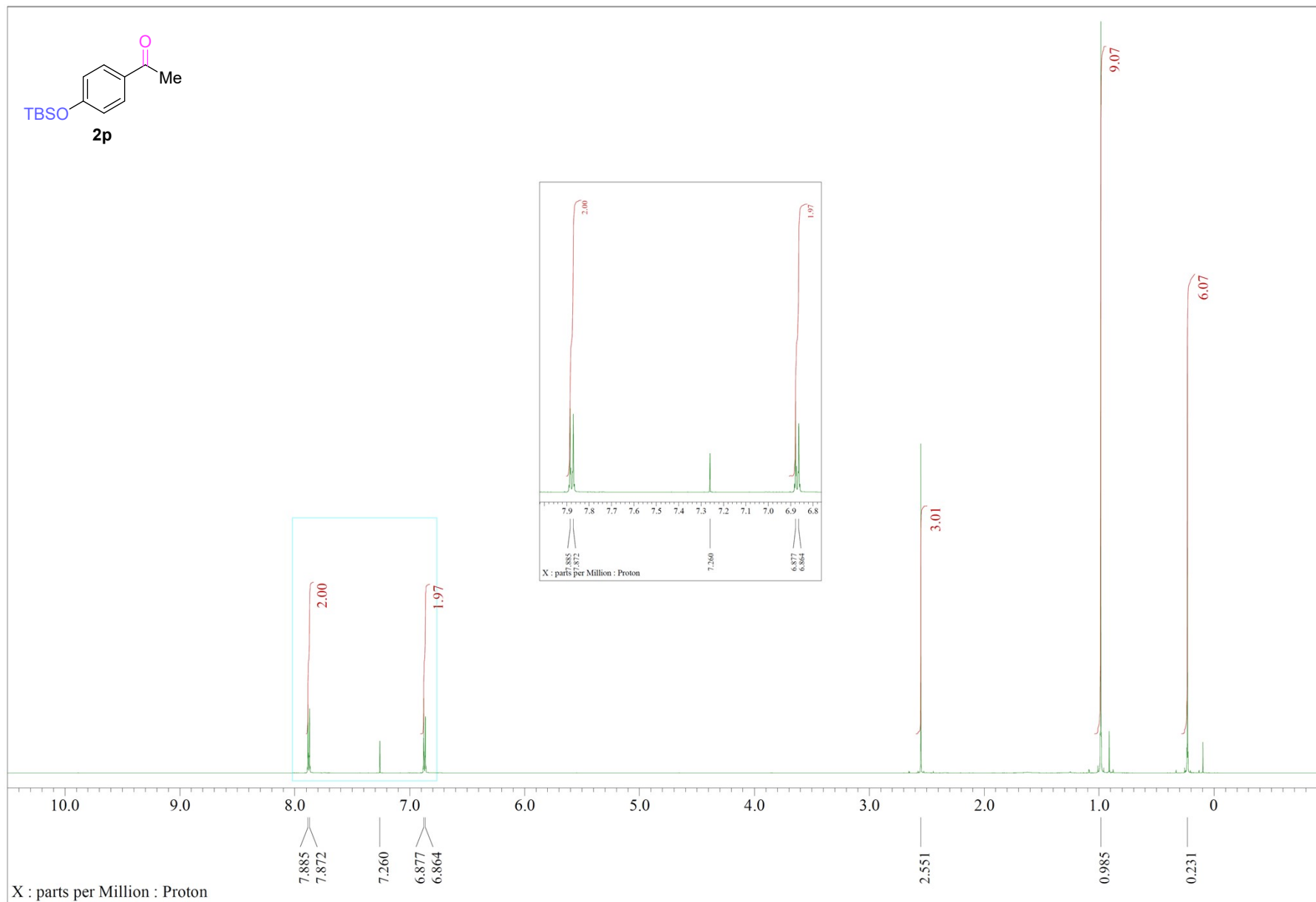




Figure S20.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound 2q.

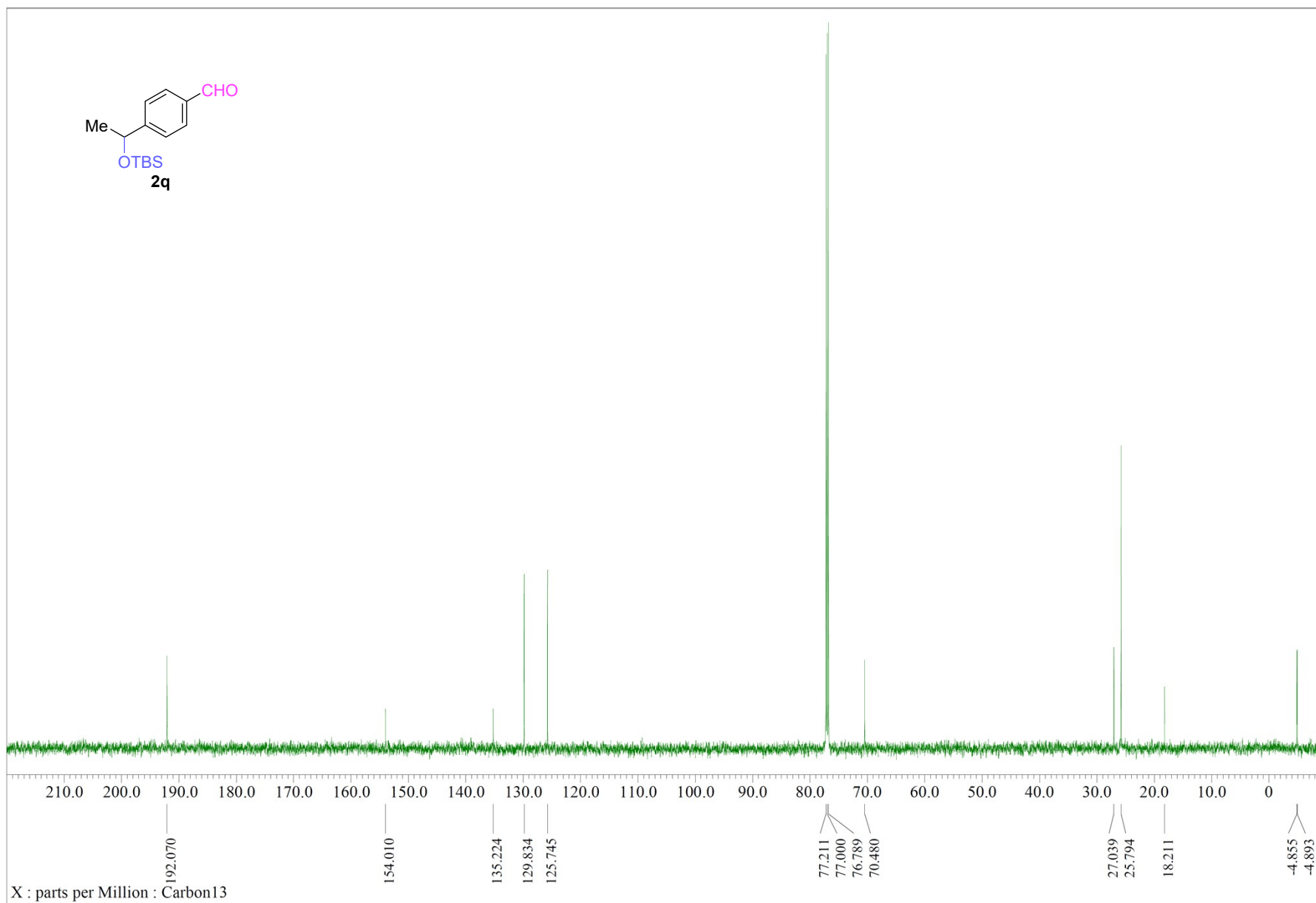


Figure S21. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2t.

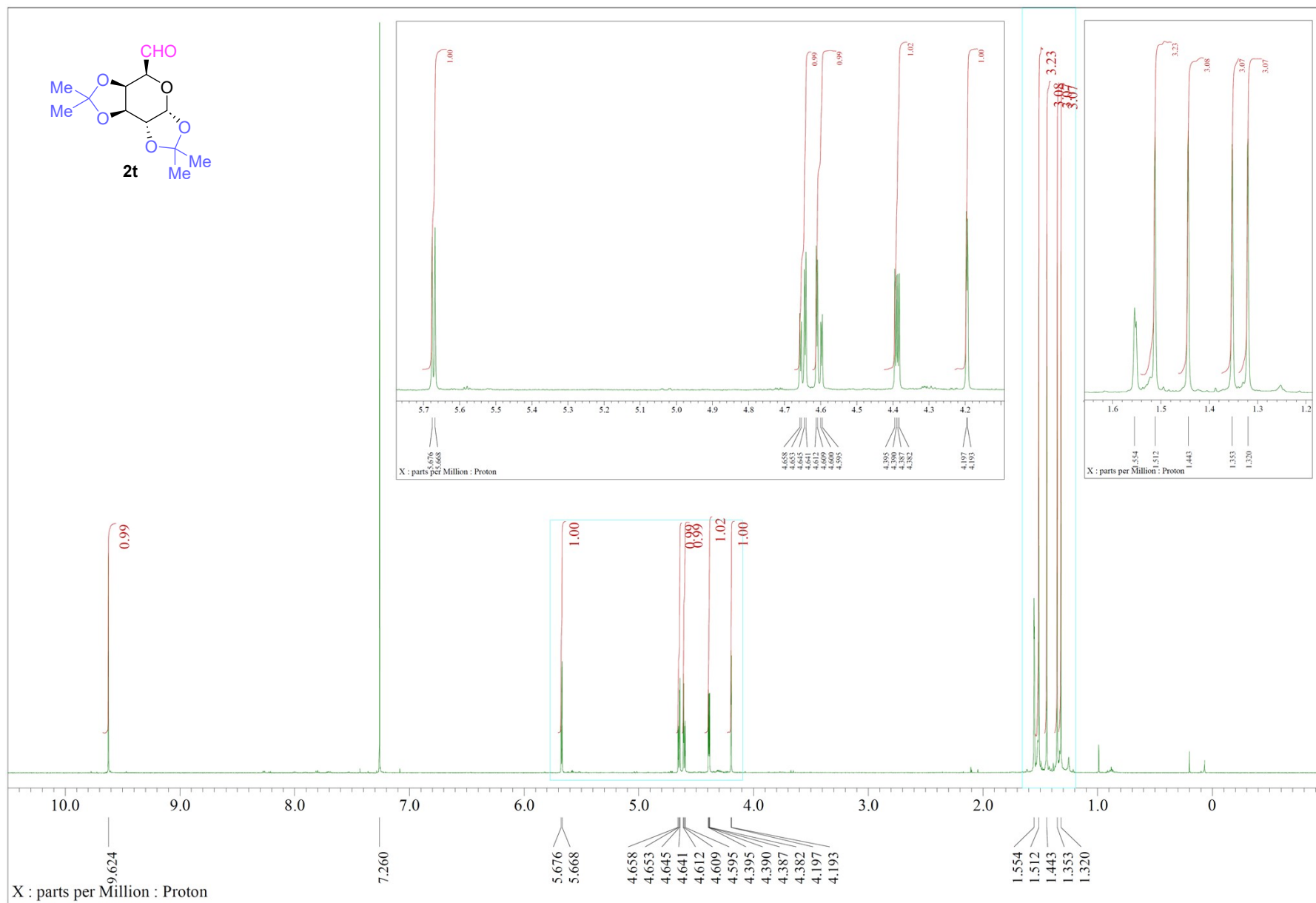


Figure S22. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, ~1:2 mixture of rotamer) of compound 2x.

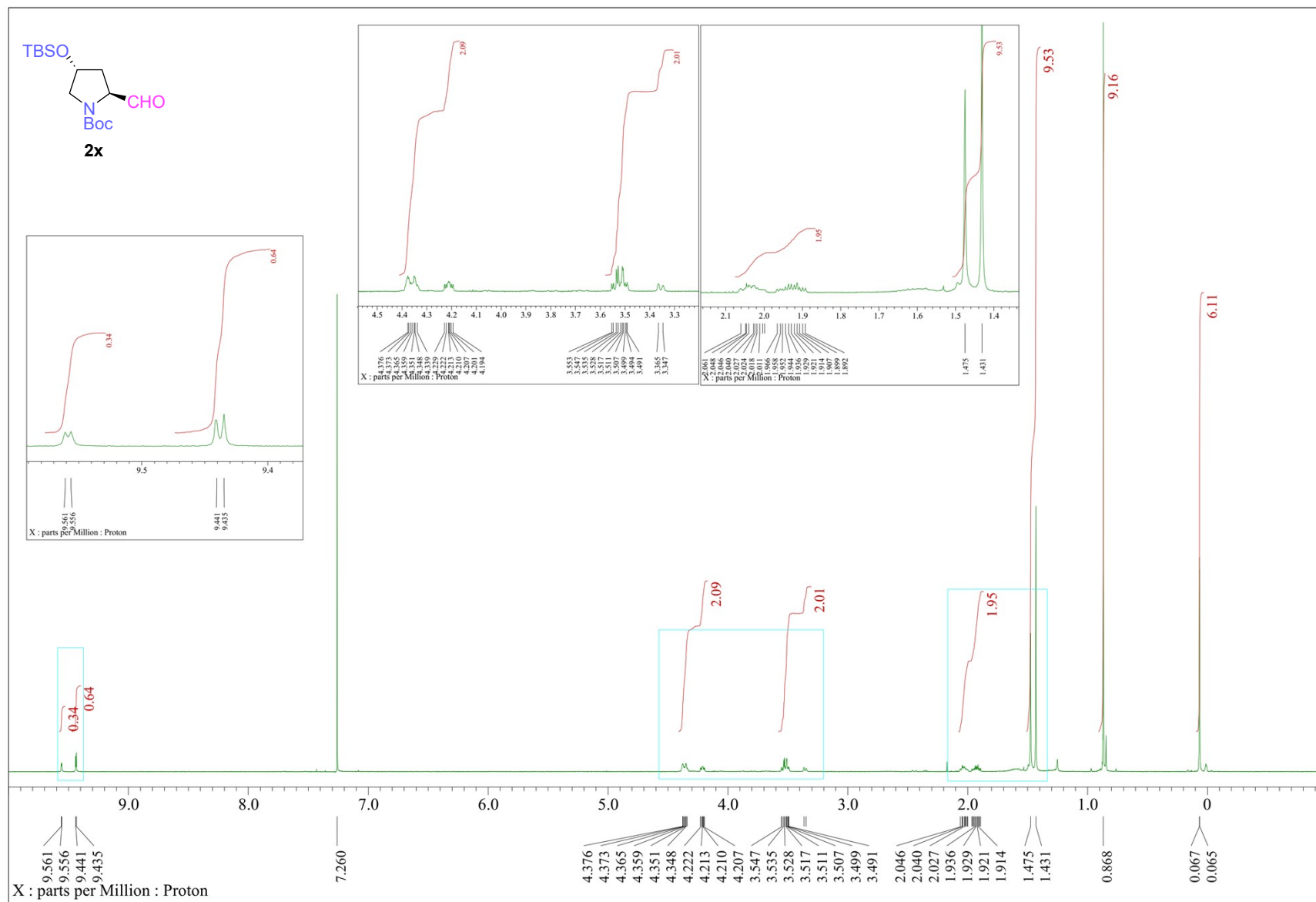






Figure S24. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 2z.

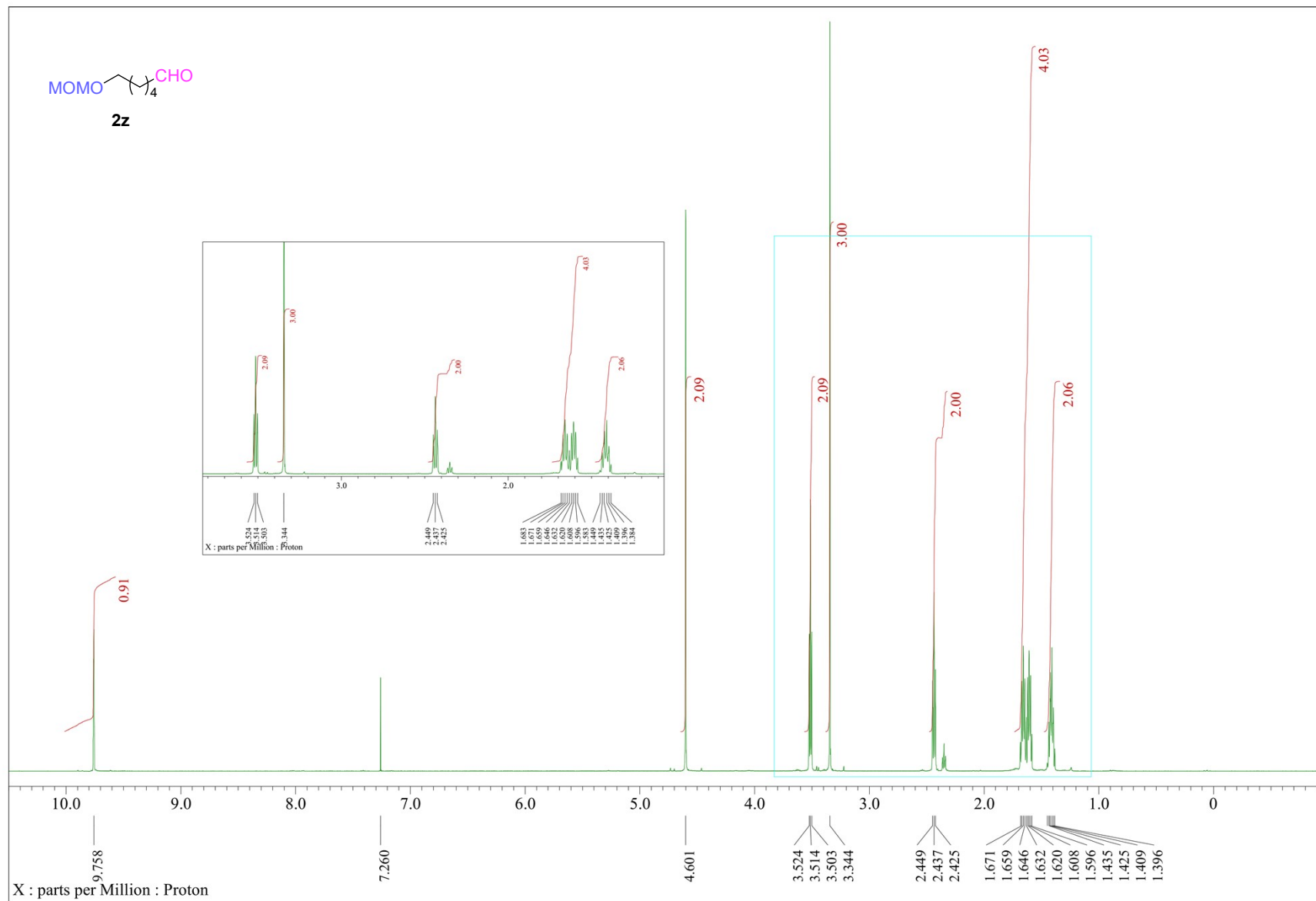


Figure S25.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **2z**.

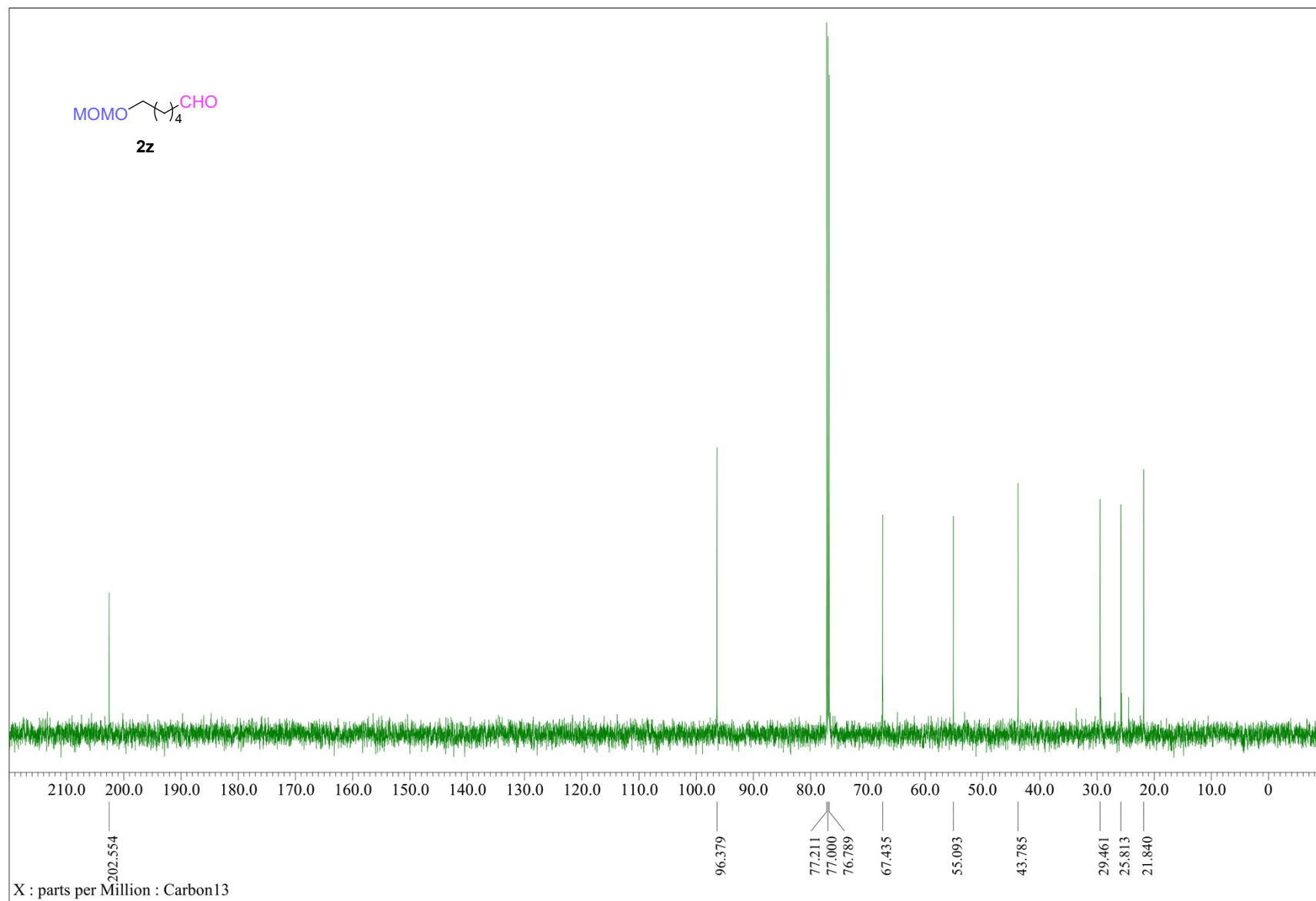


Figure S26. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 4.

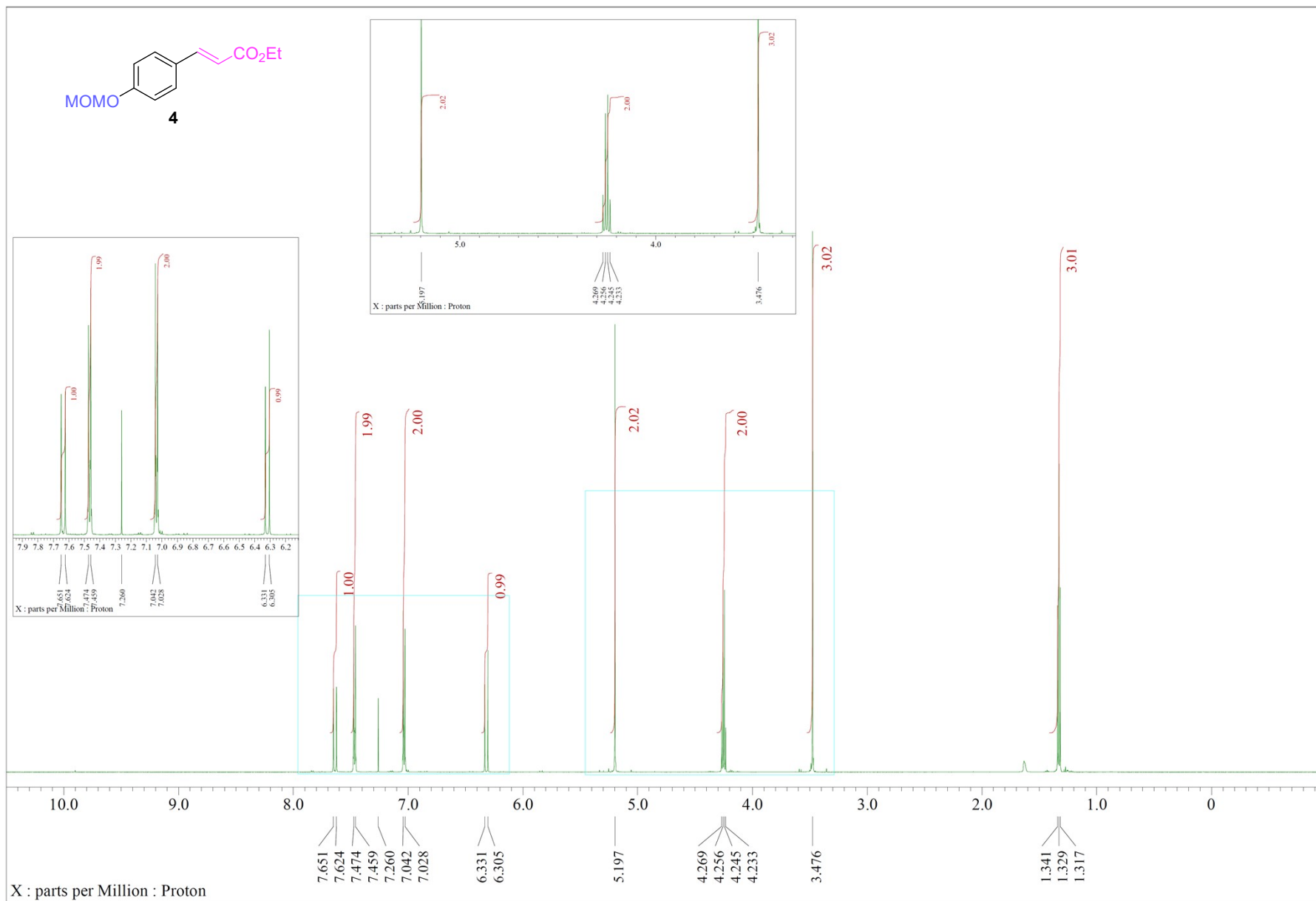


Figure S27.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound 4.

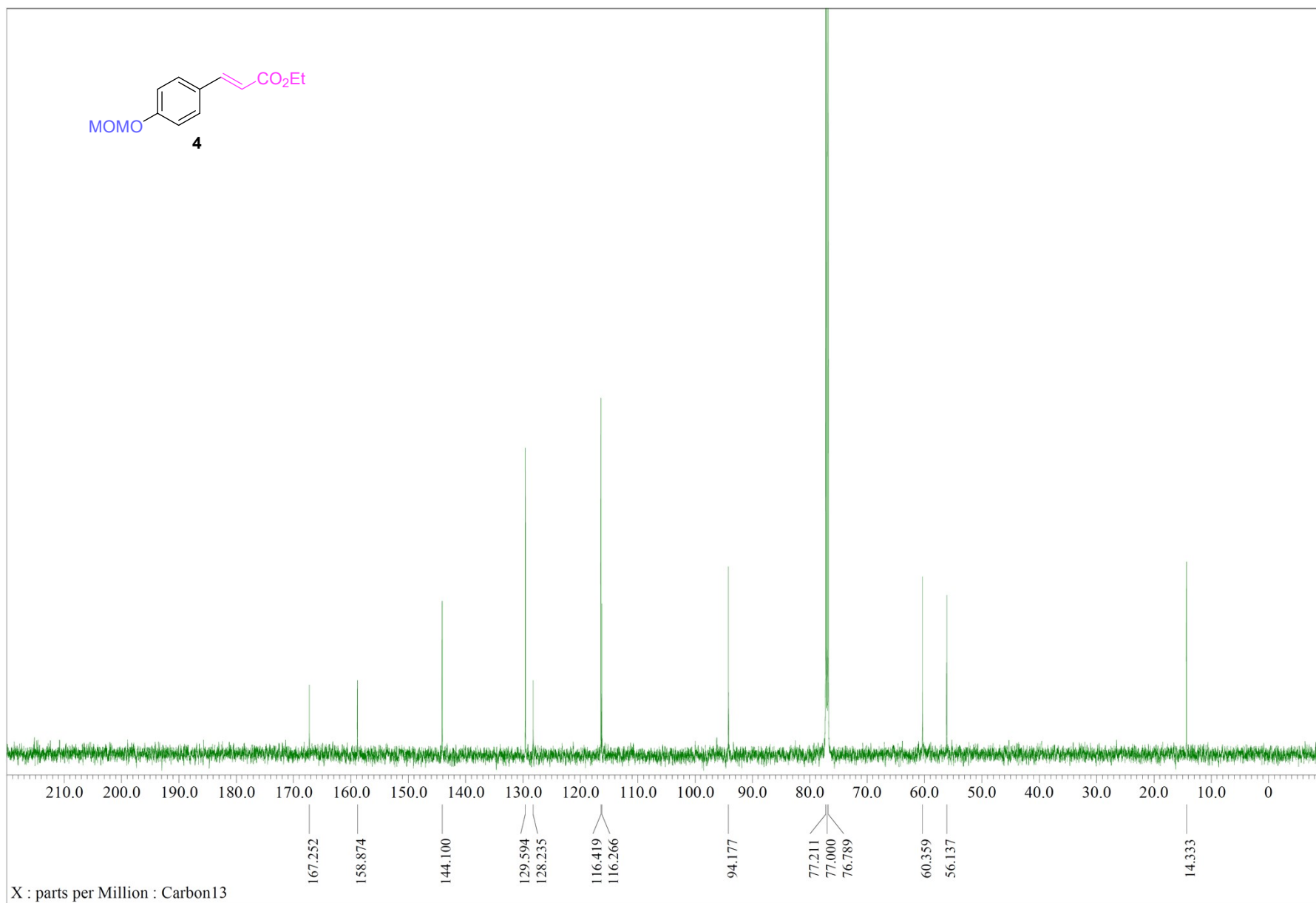


Figure S28. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 5.

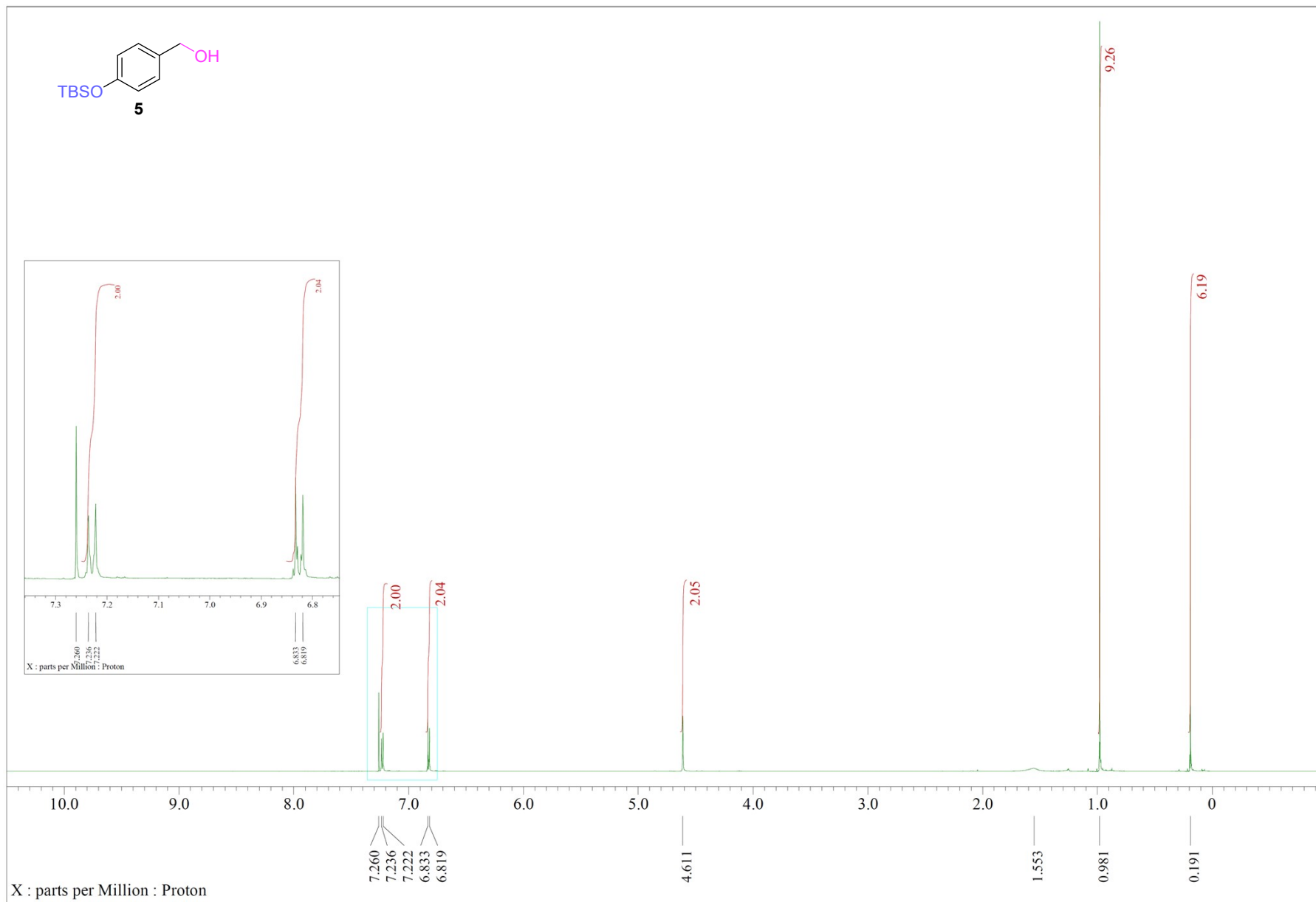


Figure S29. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1b (*E/Z* = 10:1).

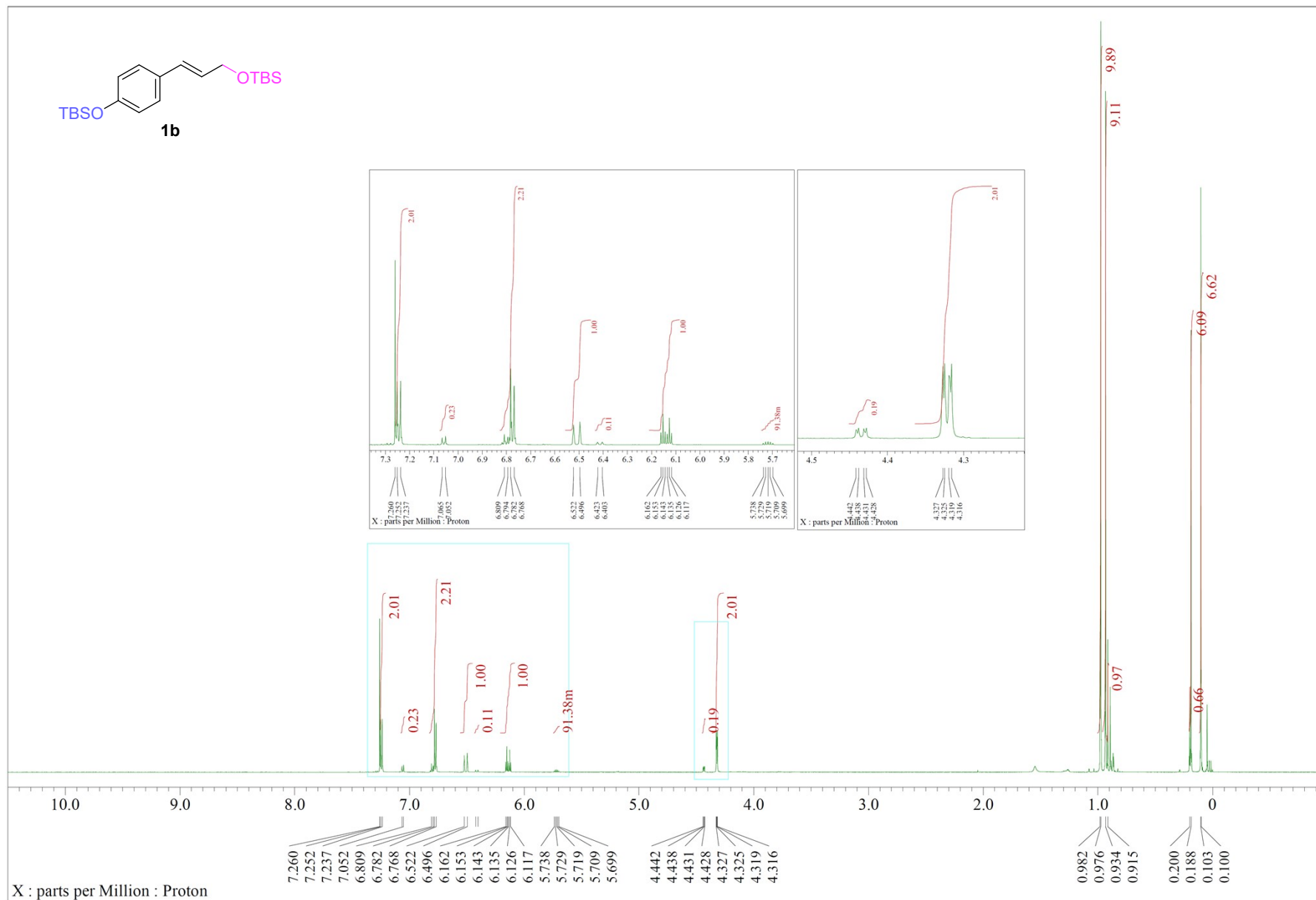


Figure S30.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1b** ( $E/Z = 10:1$ ).

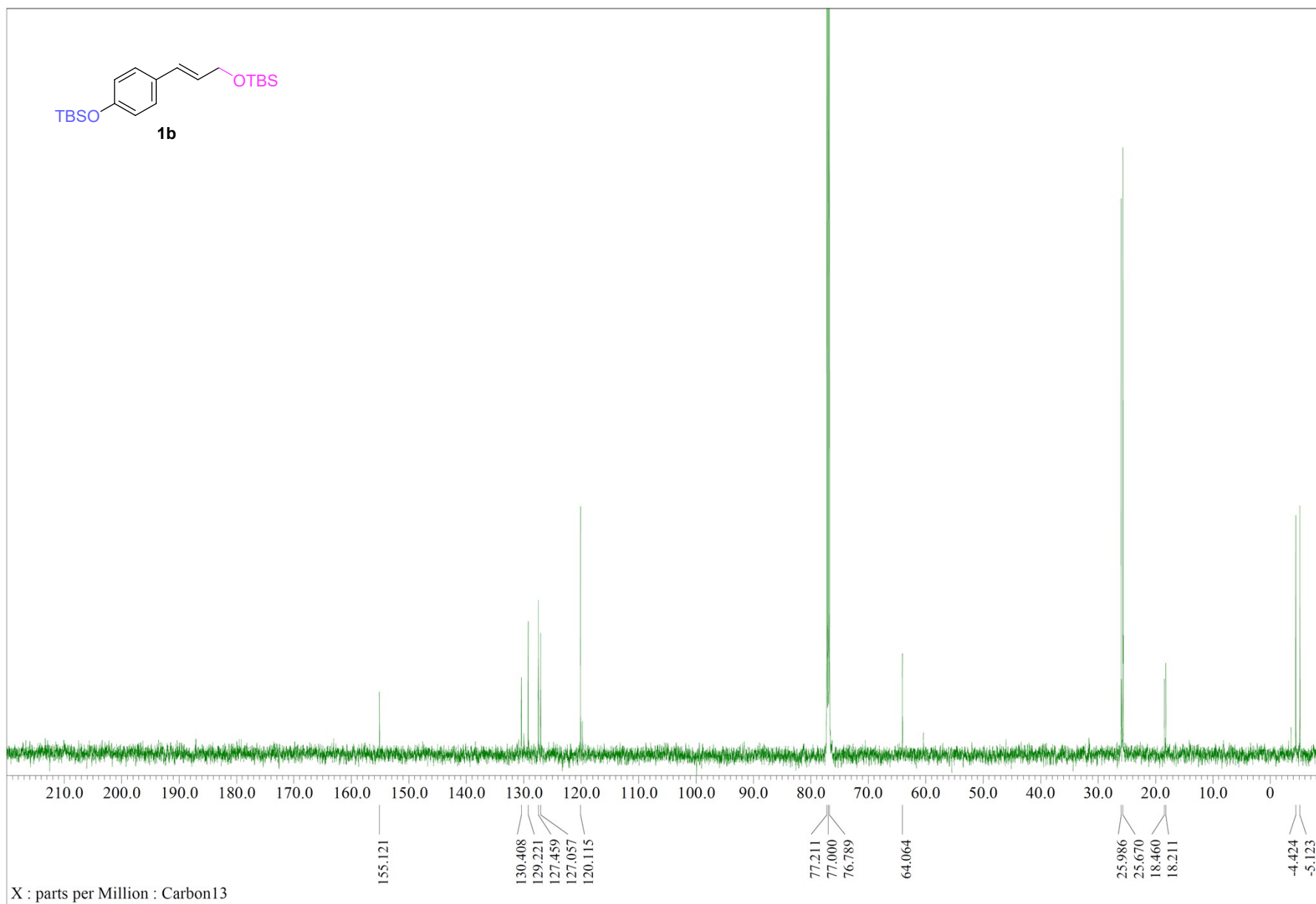




Figure S31. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1c.

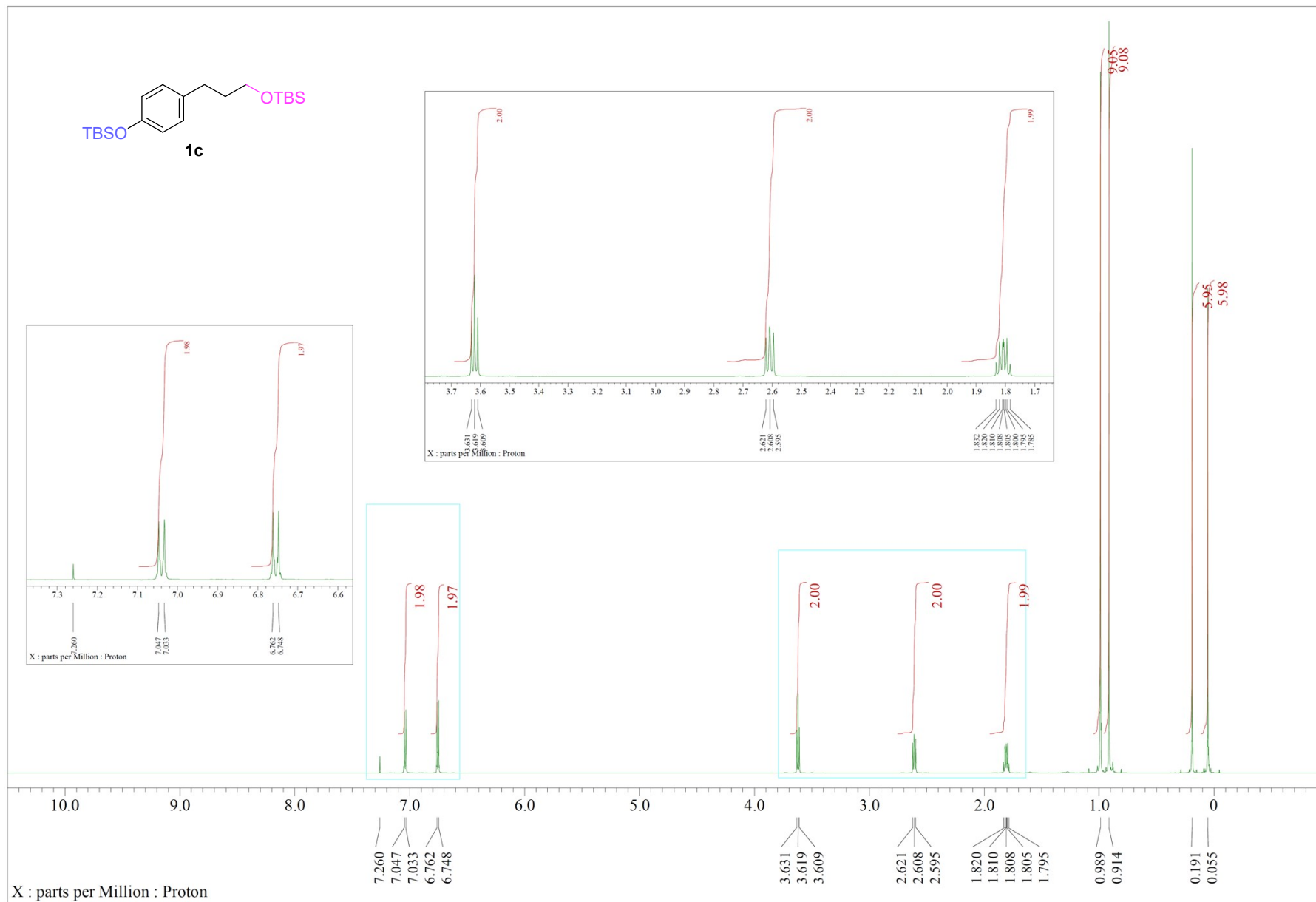


Figure S32. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1d.

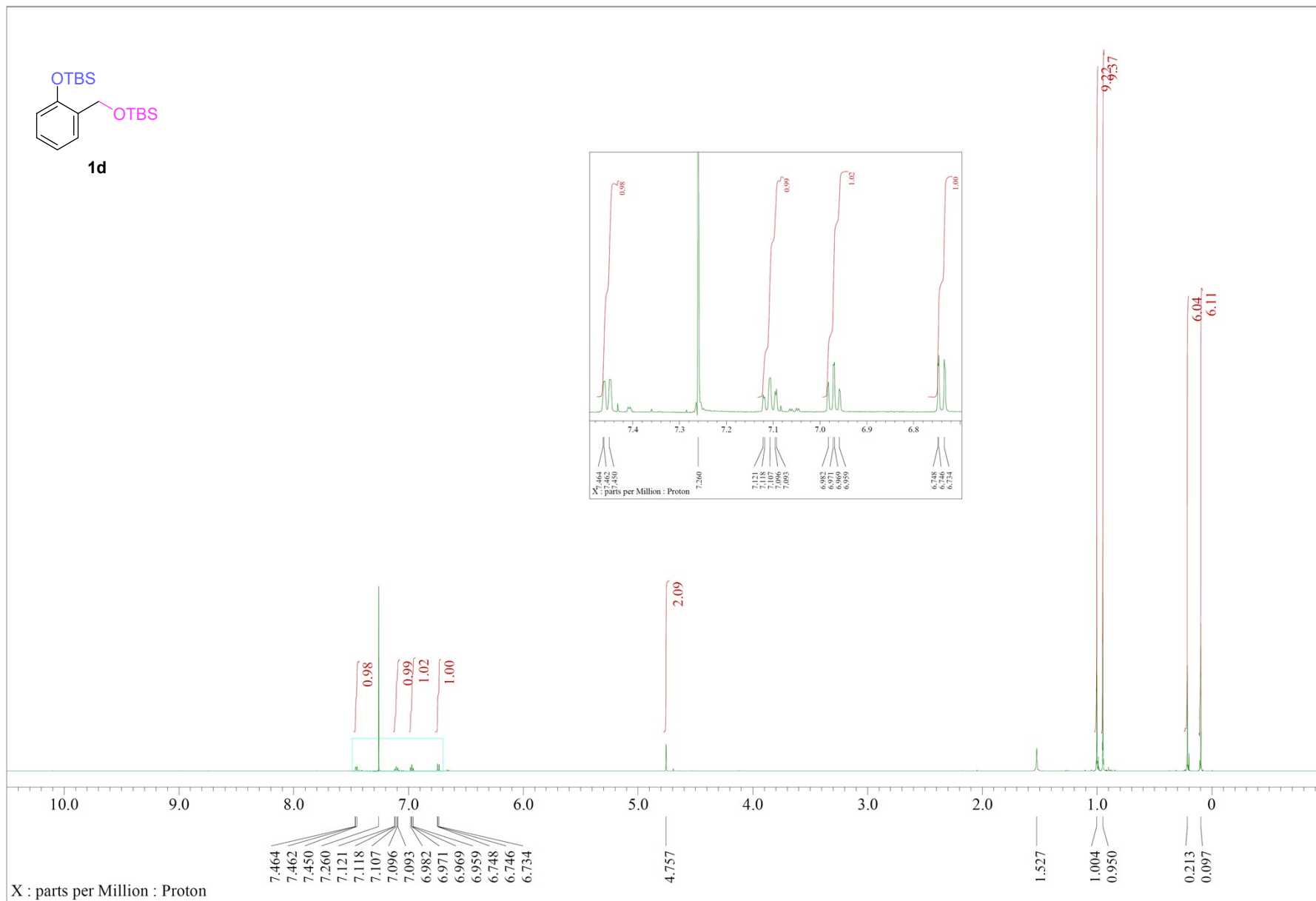


Figure S33. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1e.

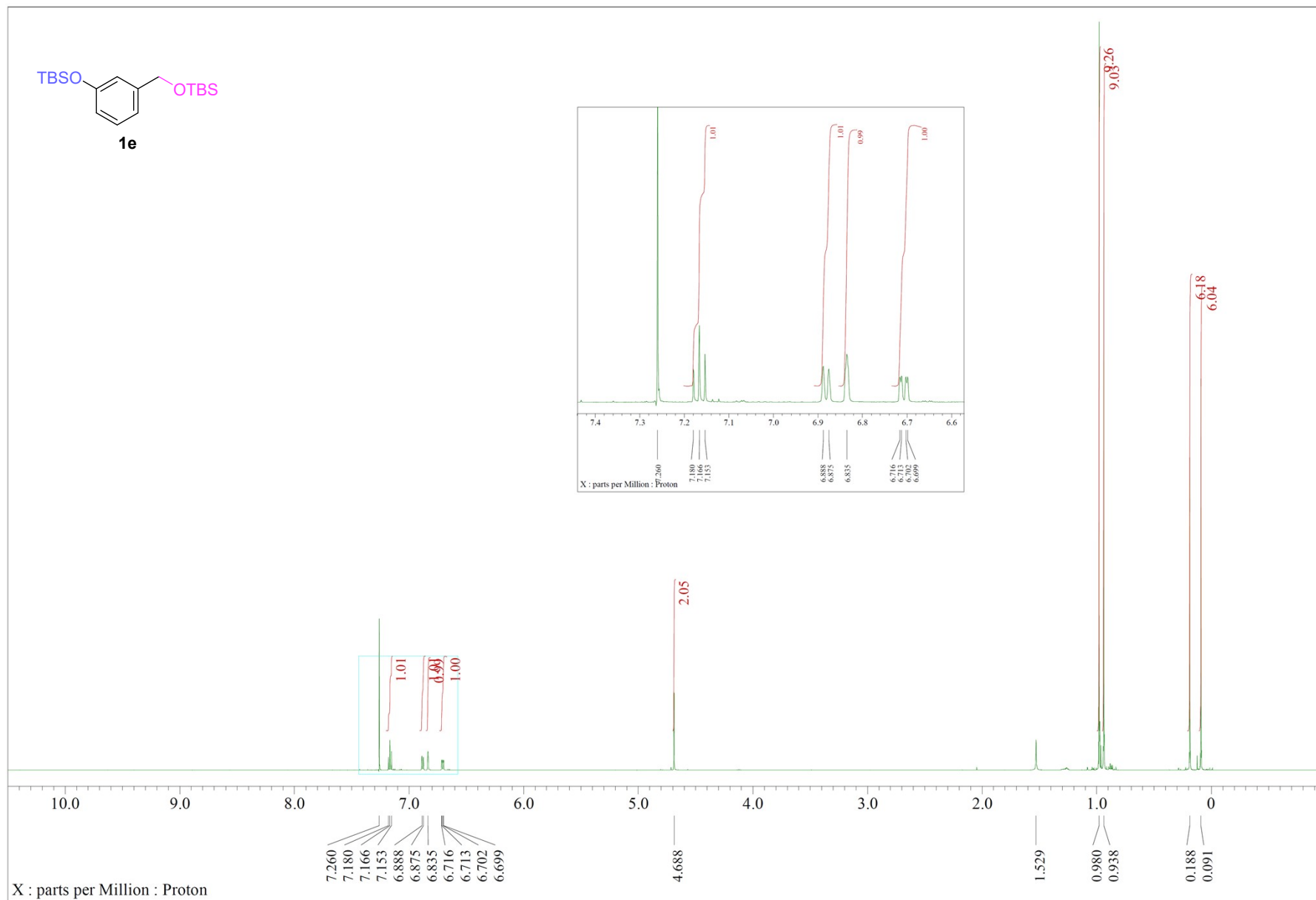


Figure S34. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1f.

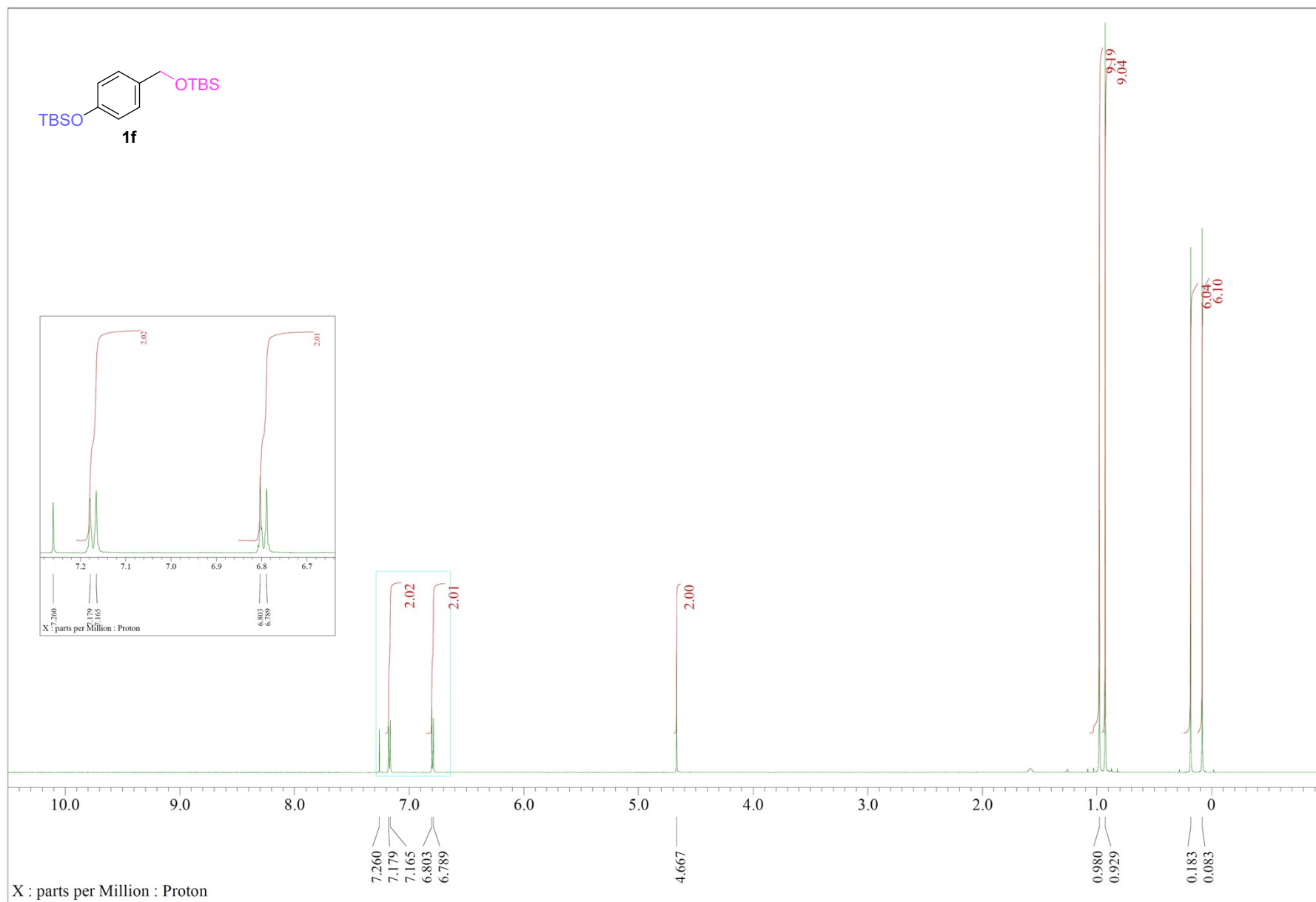


Figure S35. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1g.

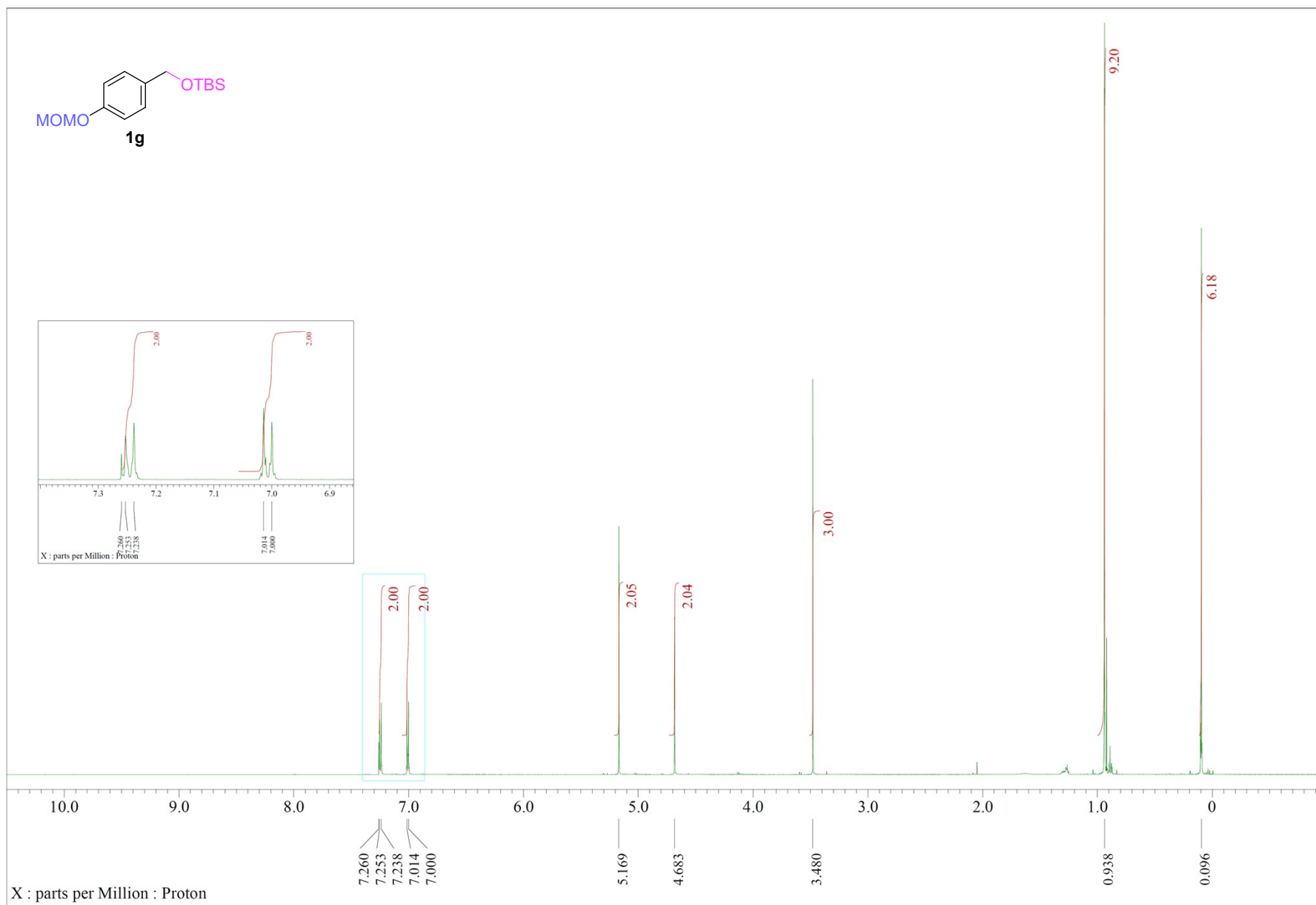


Figure S36.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1g**.

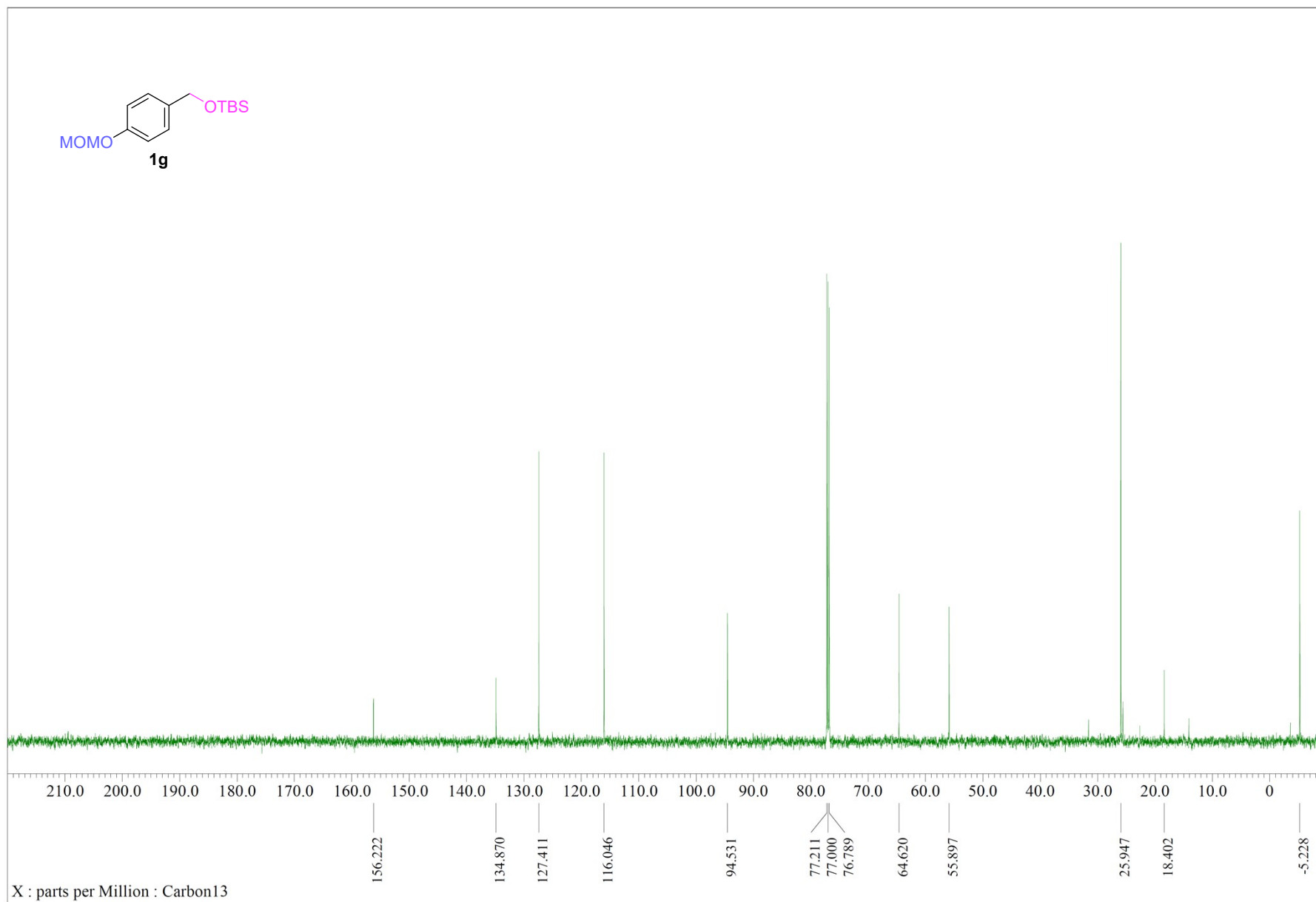


Figure S37. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1h.

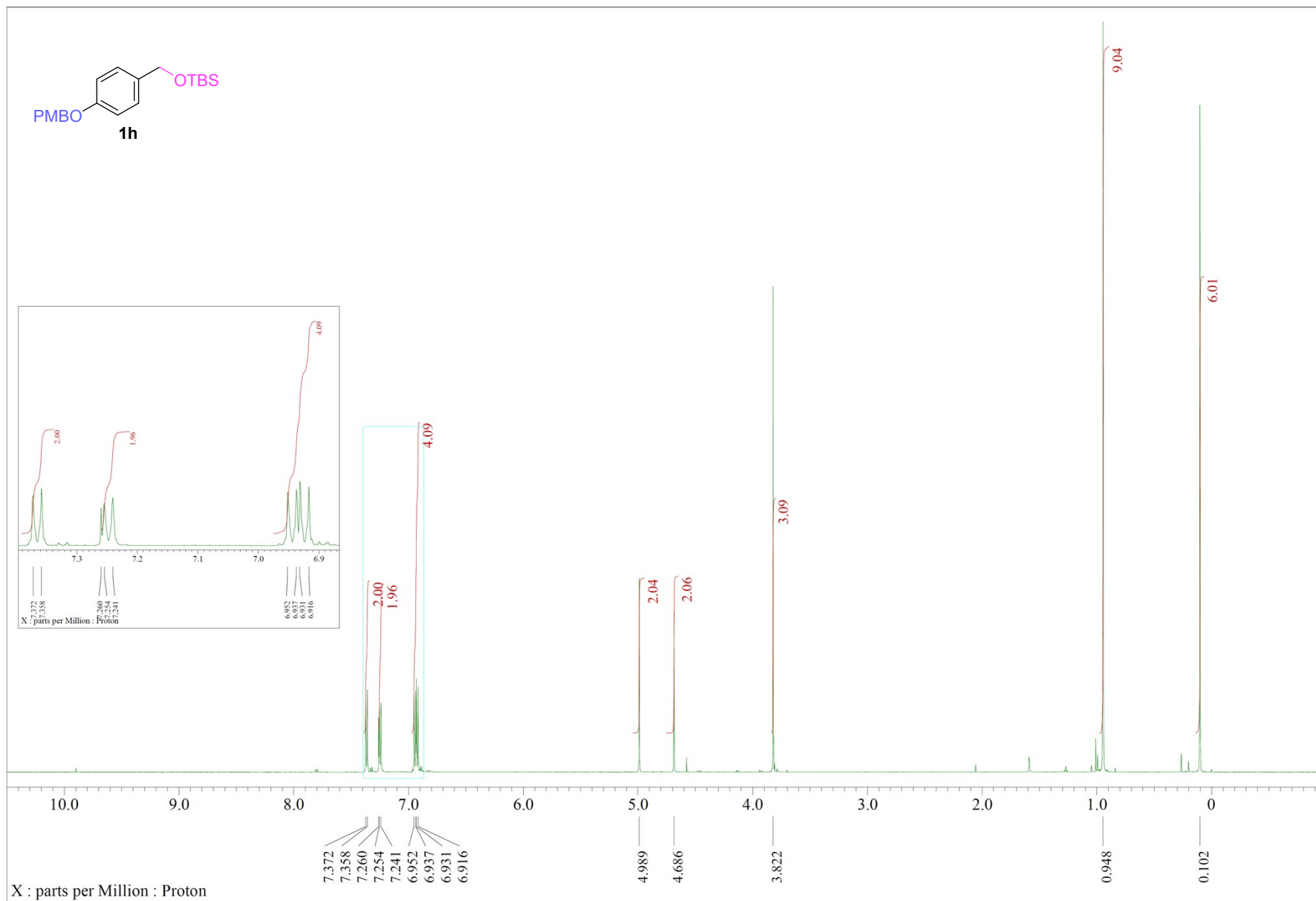


Figure S38.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1h**.

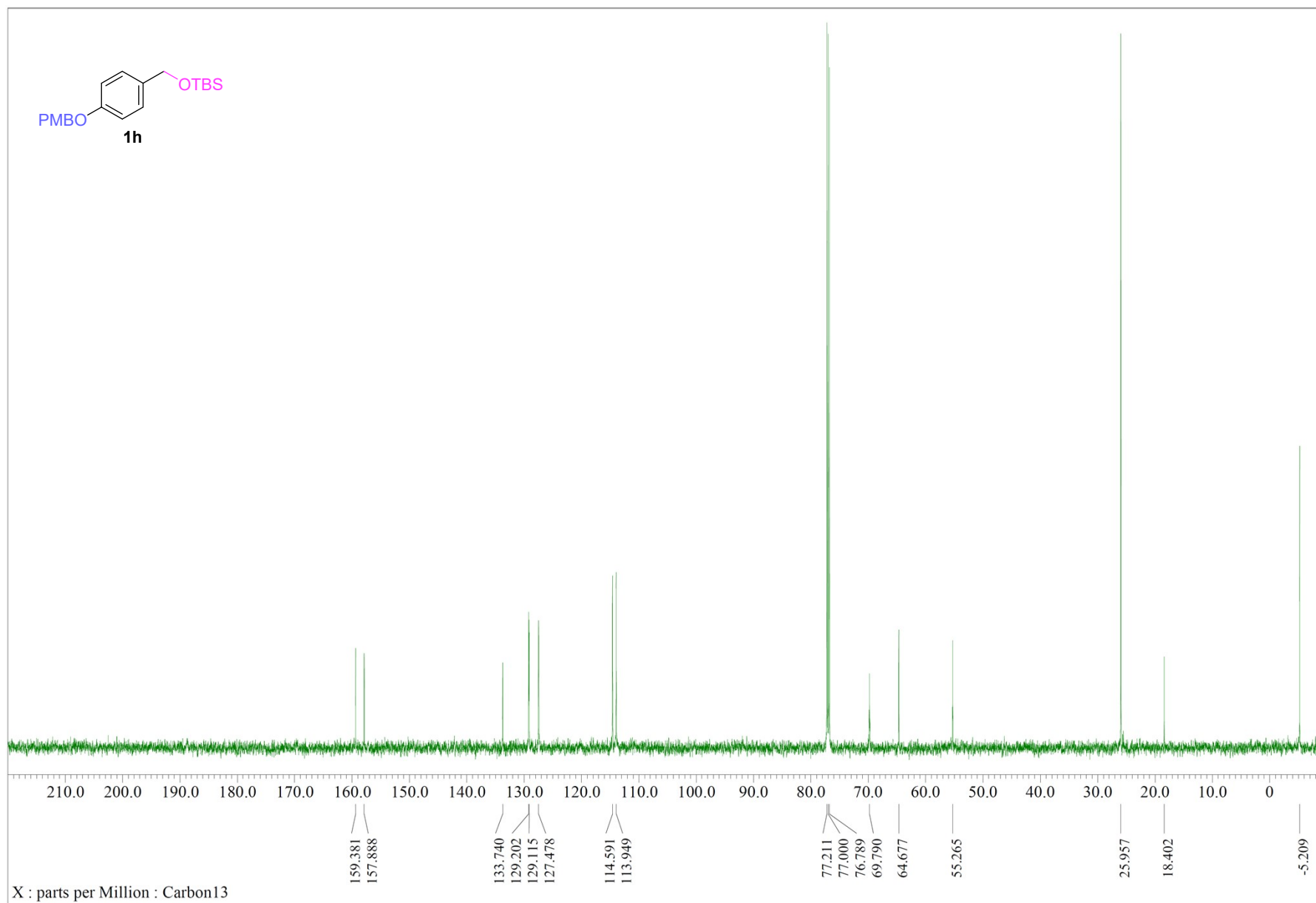




Figure S39. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1i.

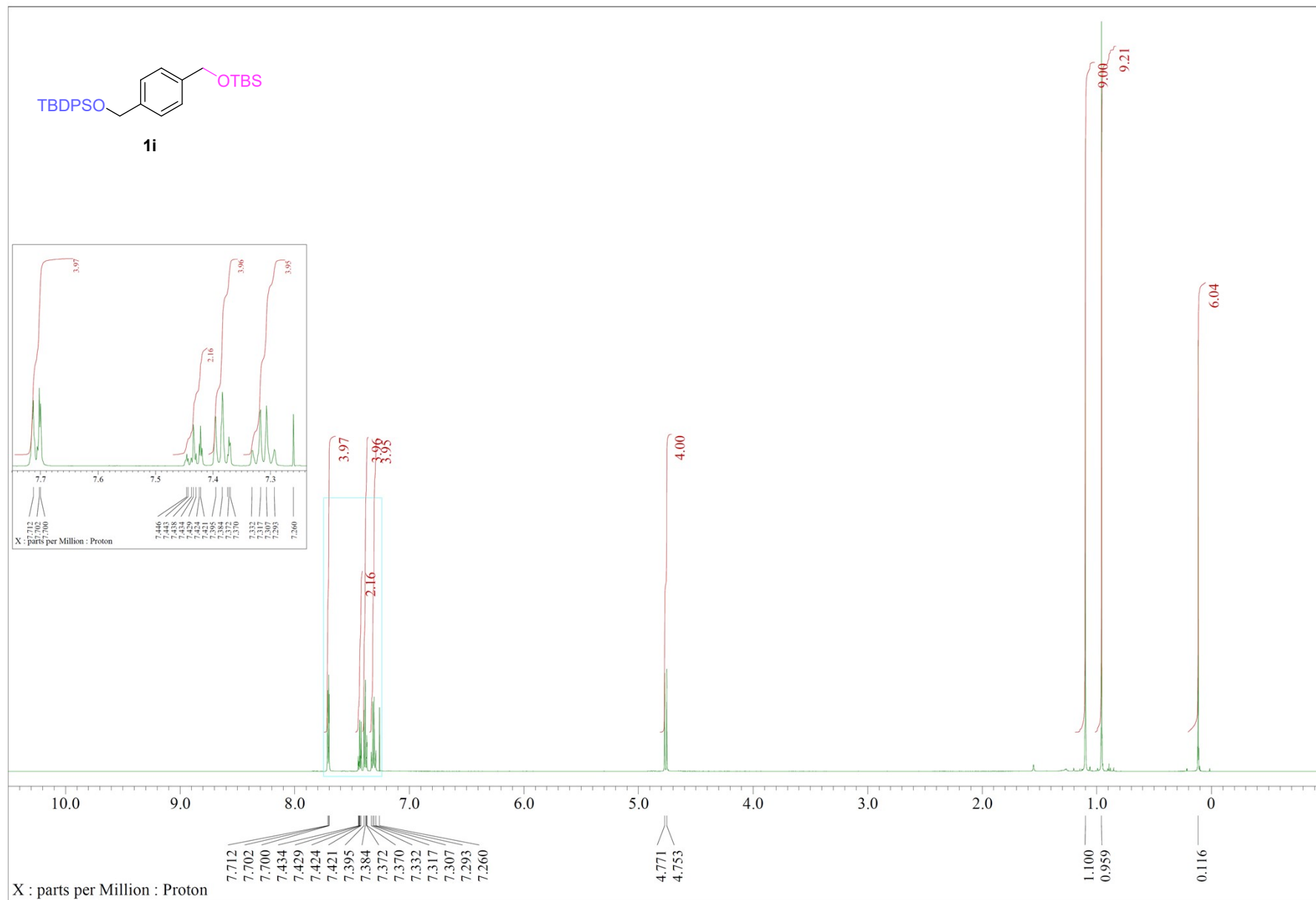


Figure S40. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1j.

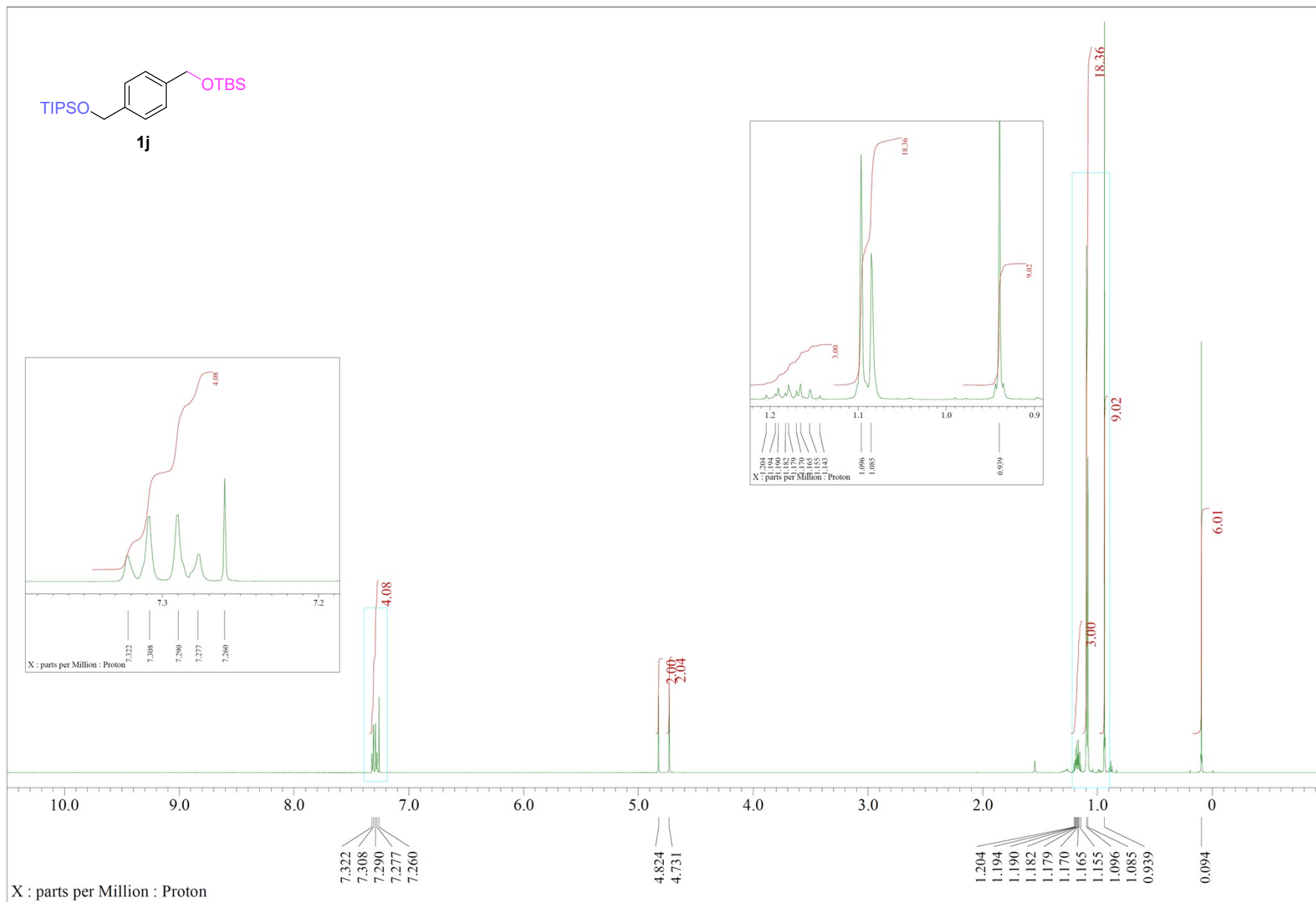


Figure S41.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound 1j.

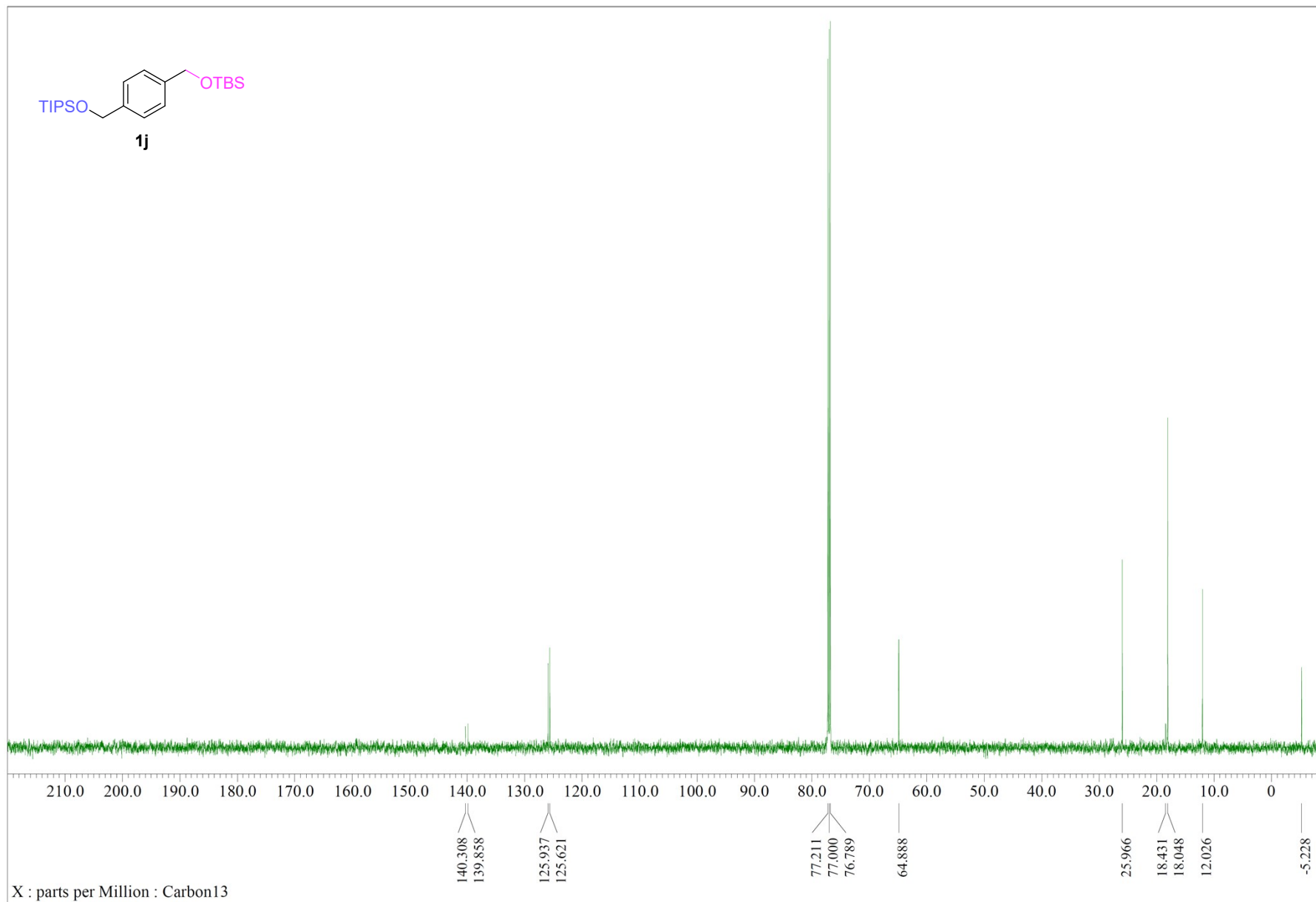


Figure S42. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1k.

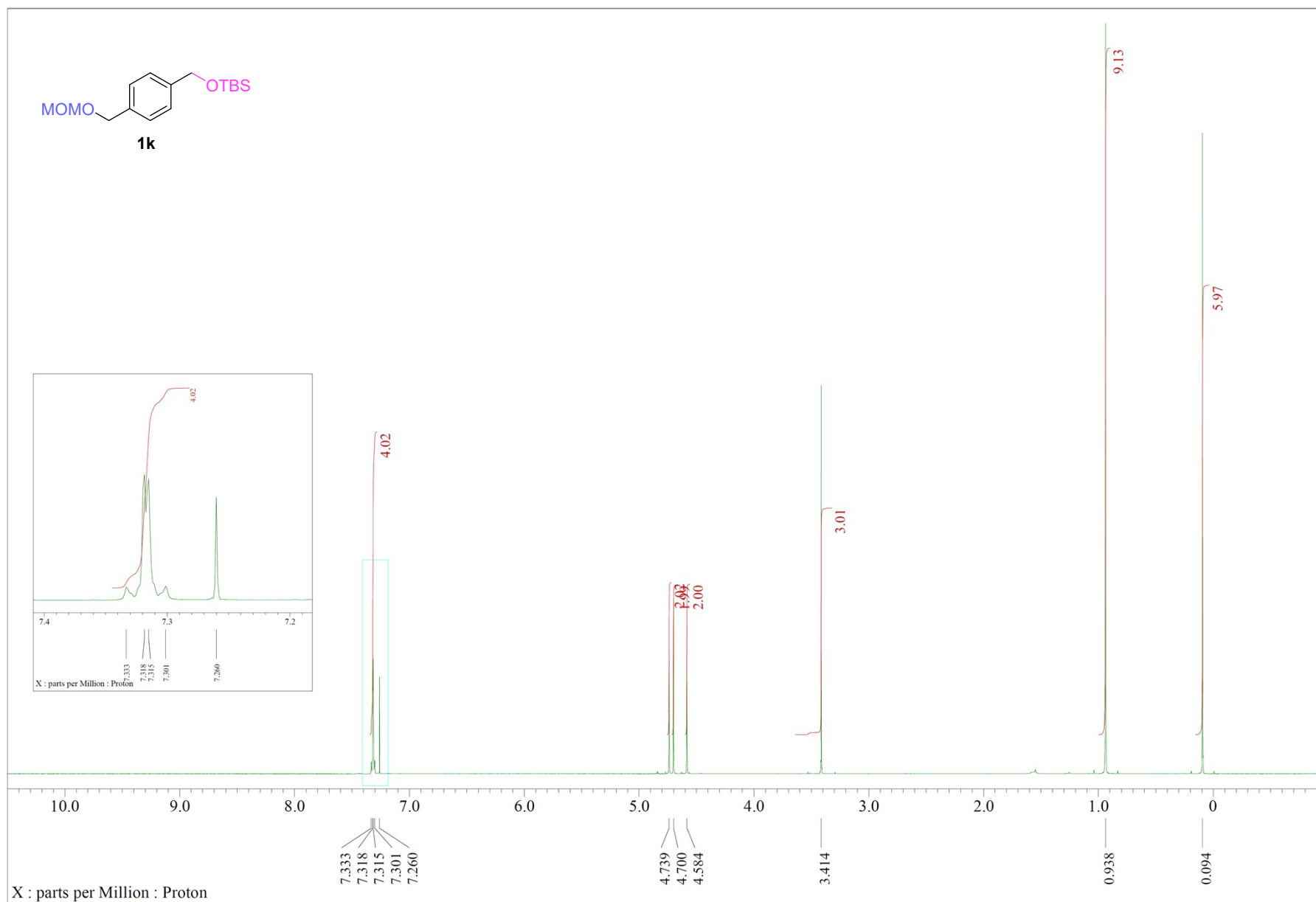


Figure S43.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1k**.

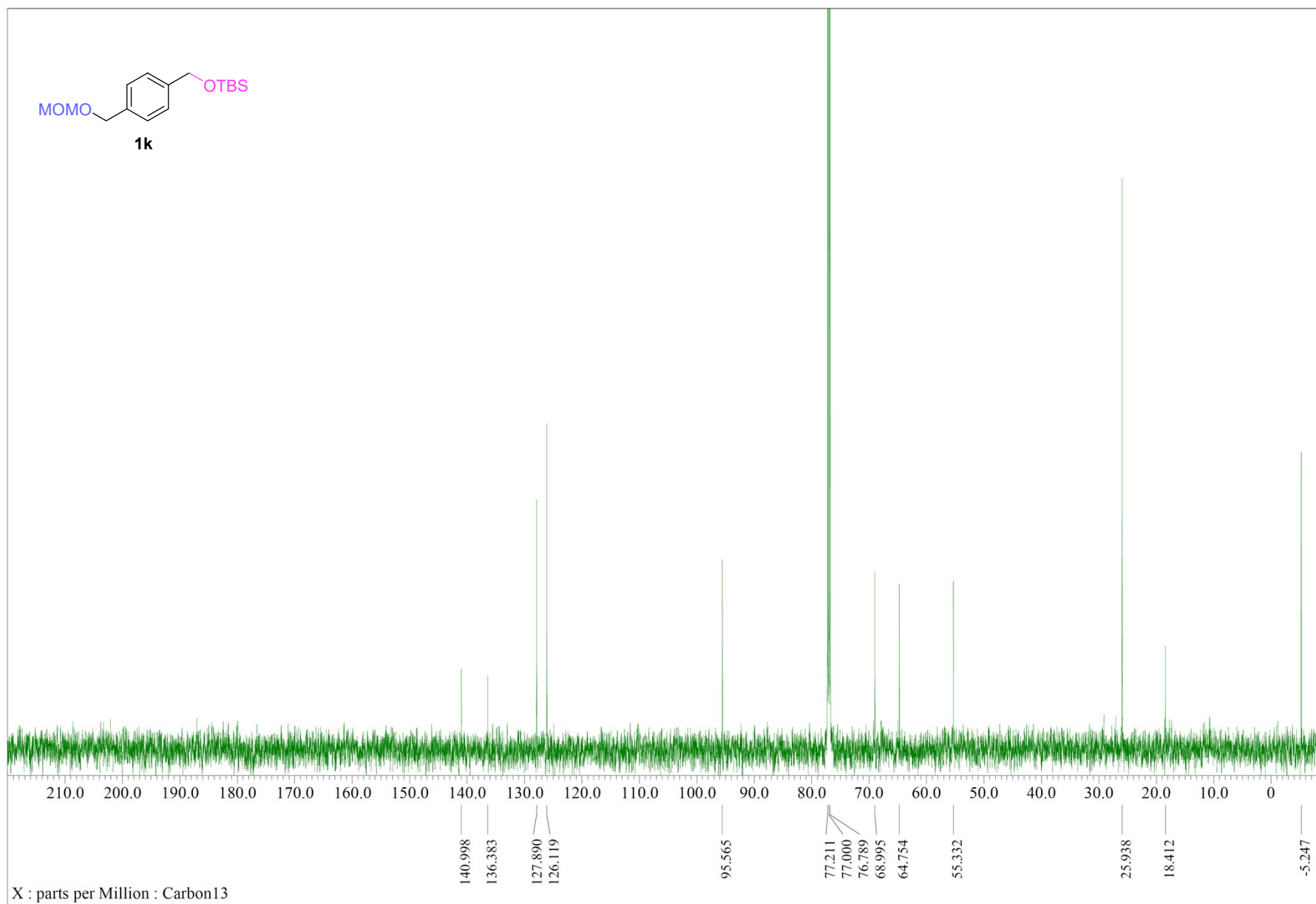


Figure S44. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 11.

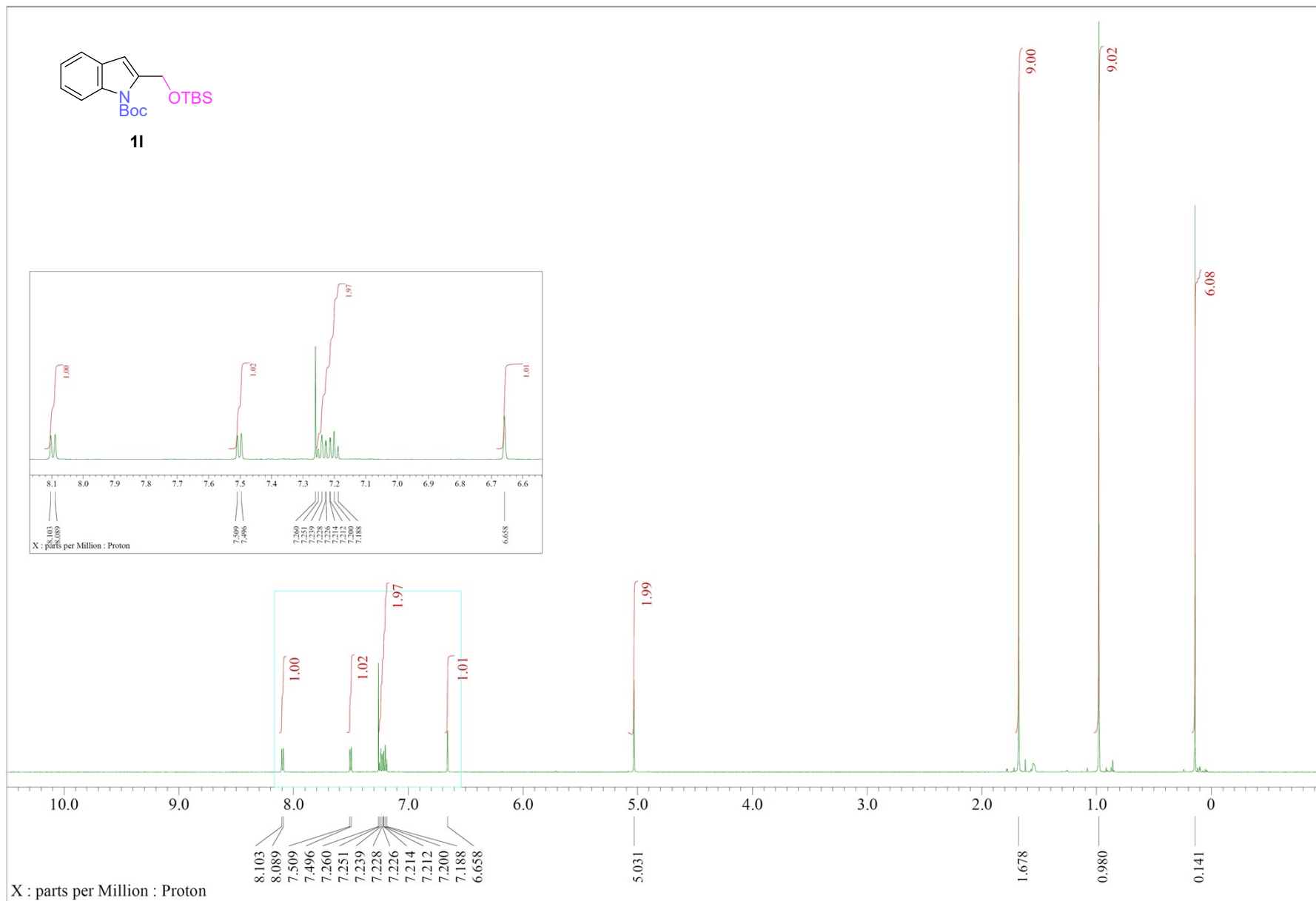


Figure S45. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1m.

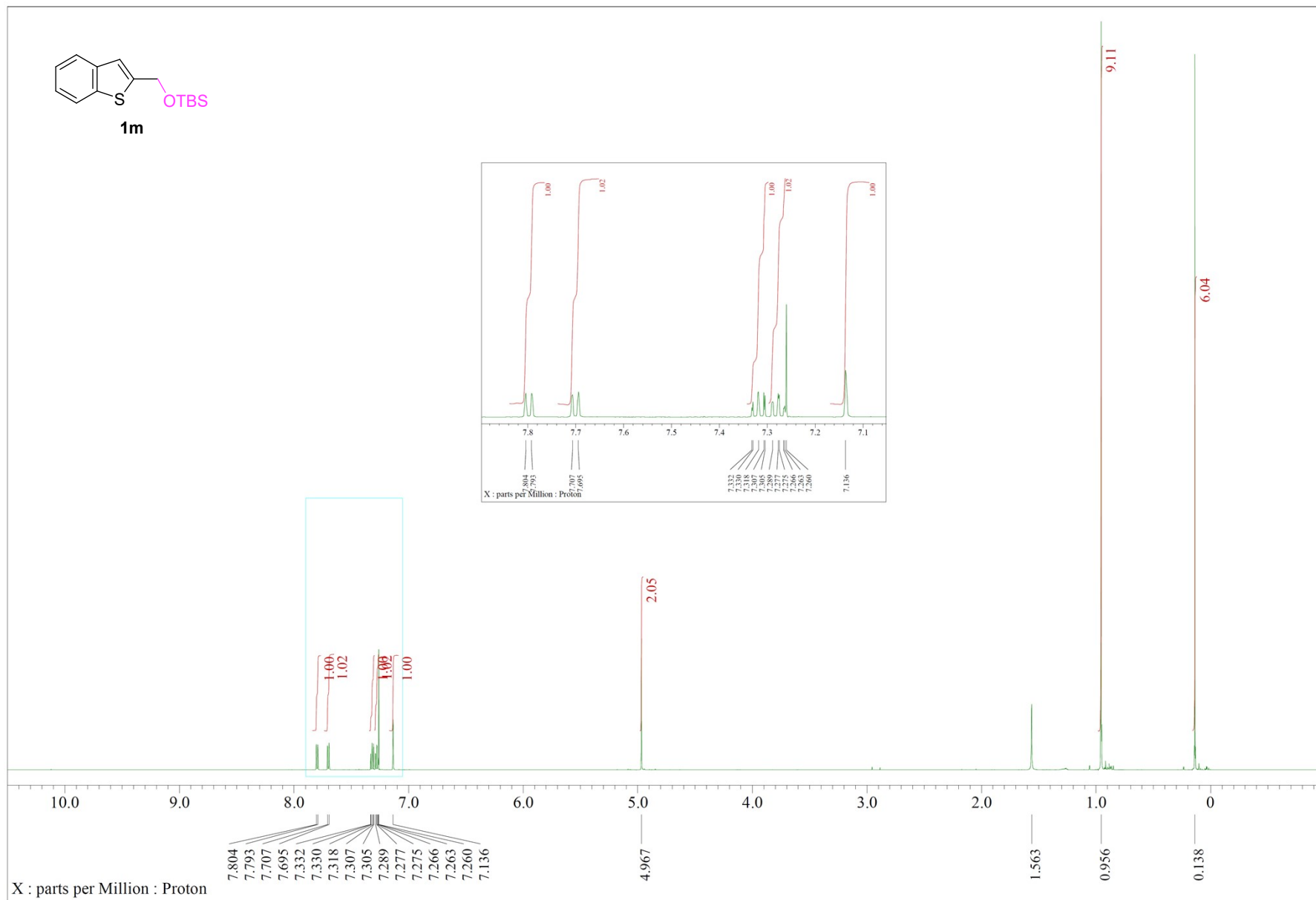


Figure S46. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1n.

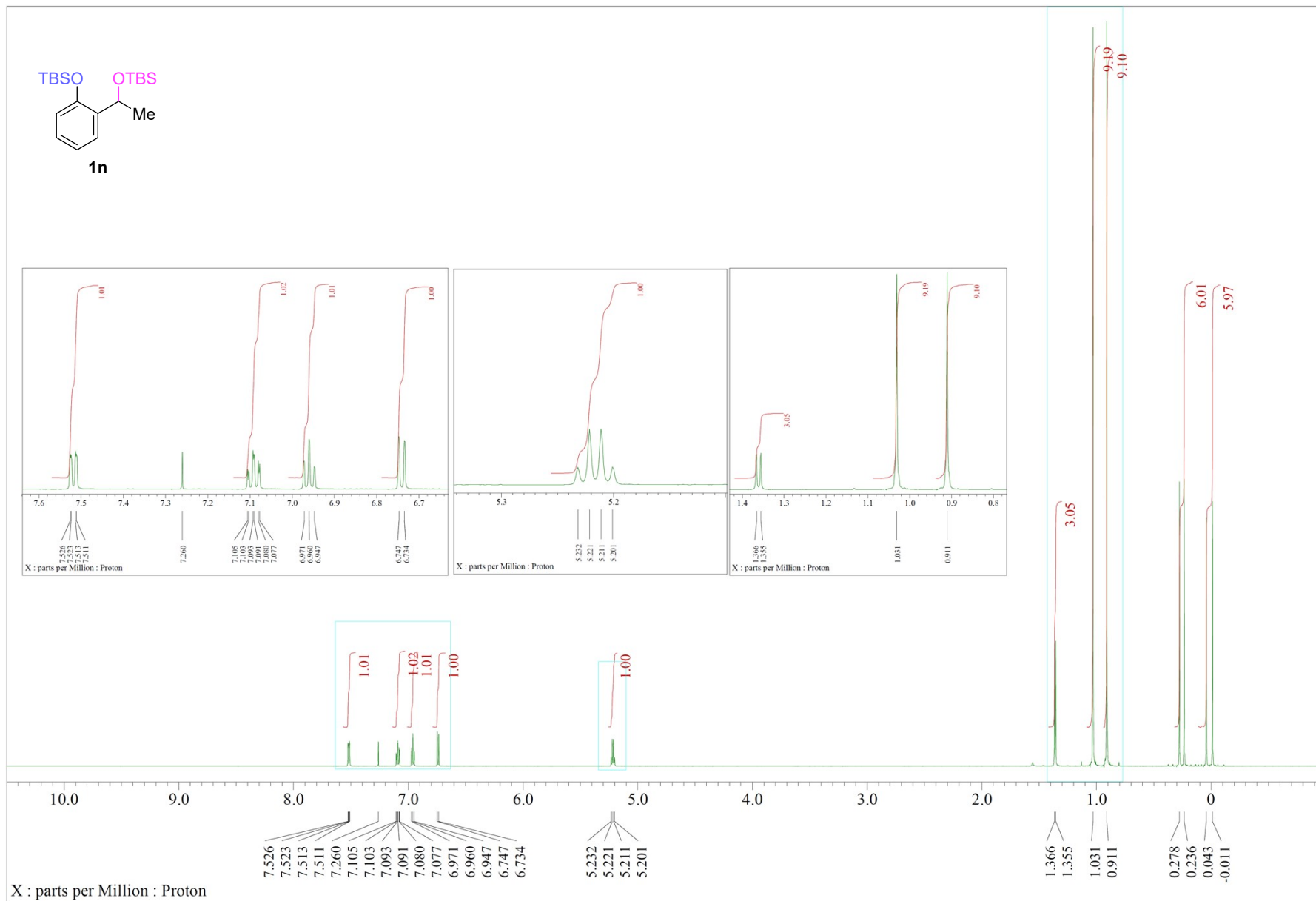




Figure S47. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1o.

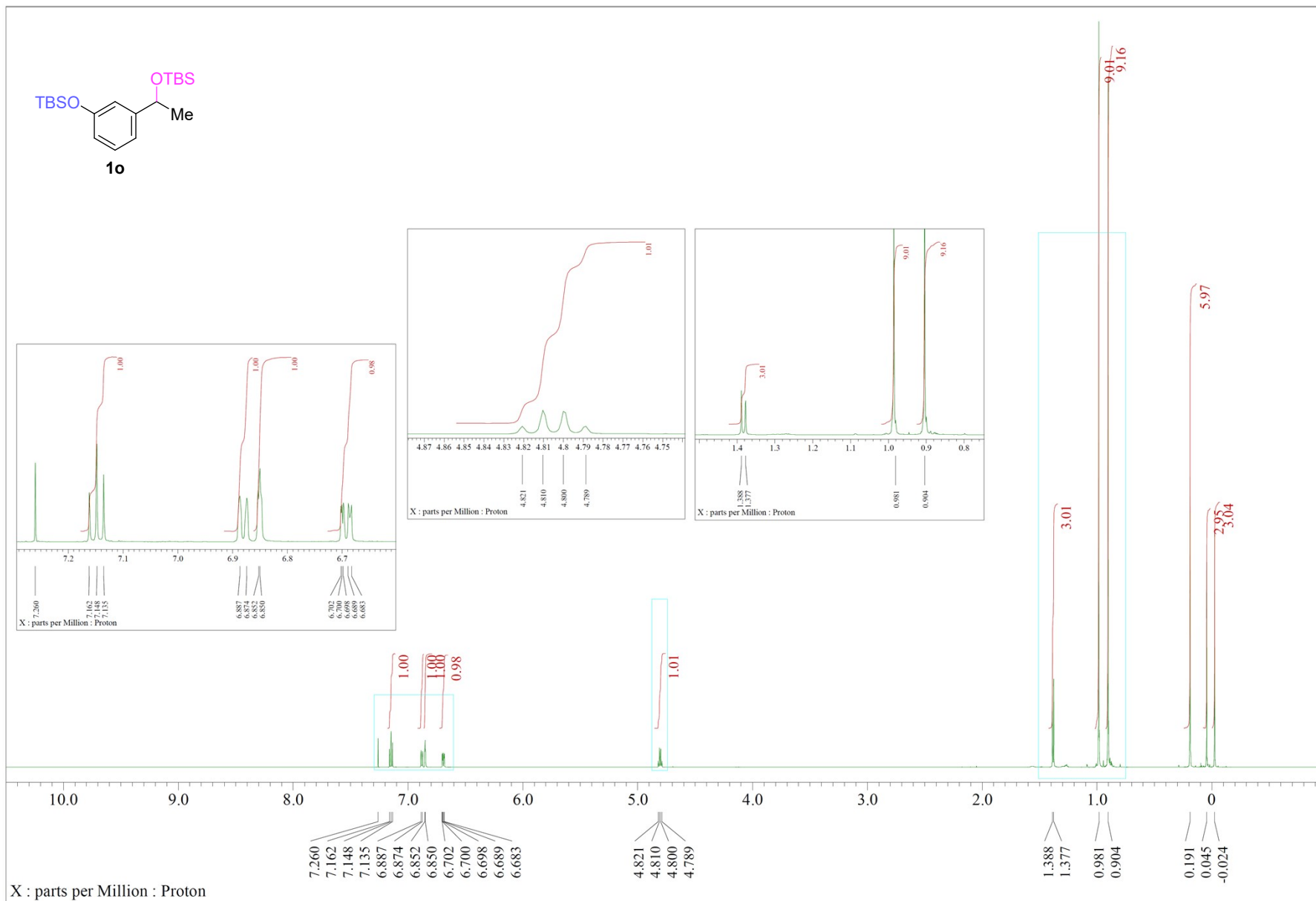


Figure S48.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1o**.

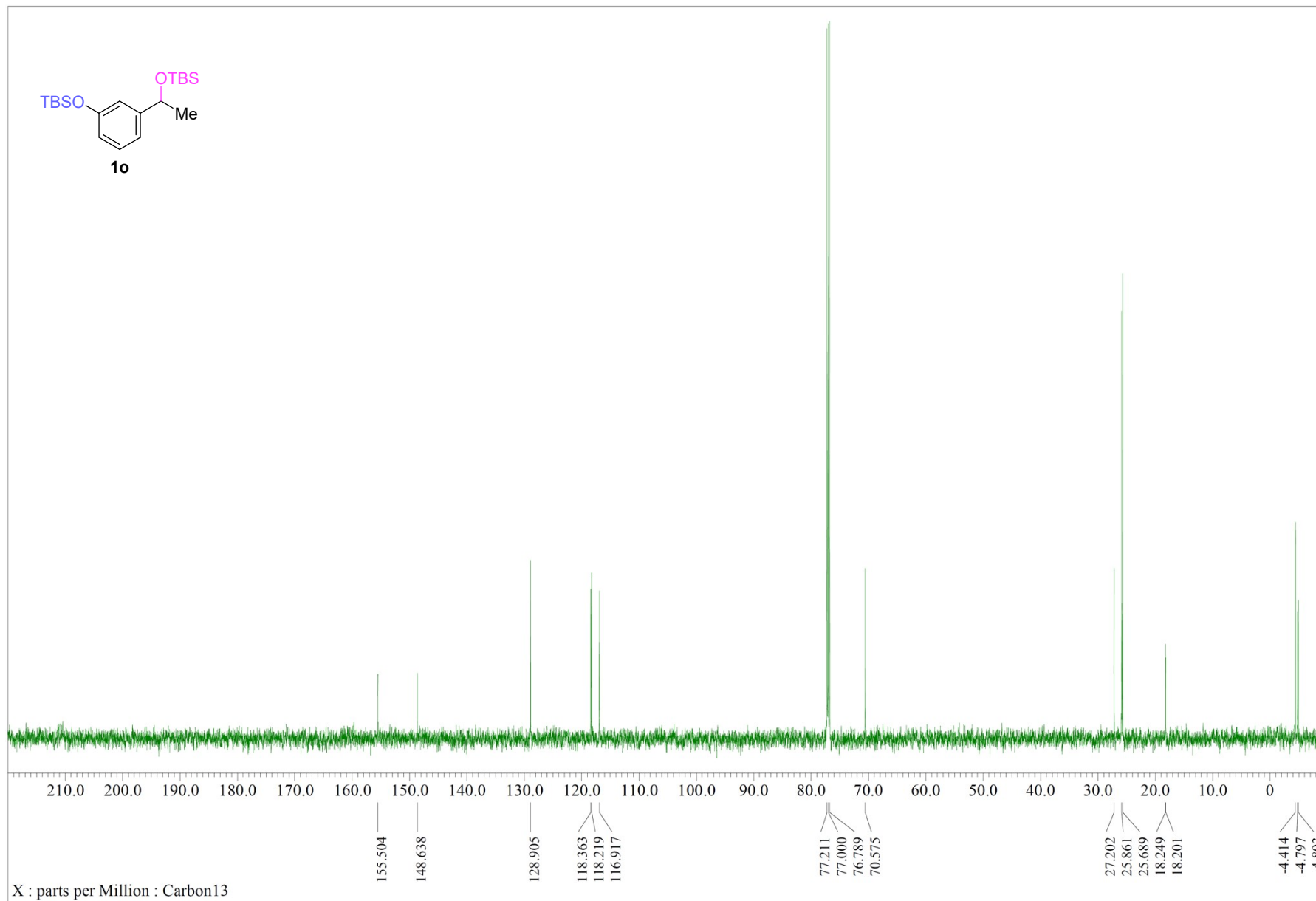


Figure S49. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1p.

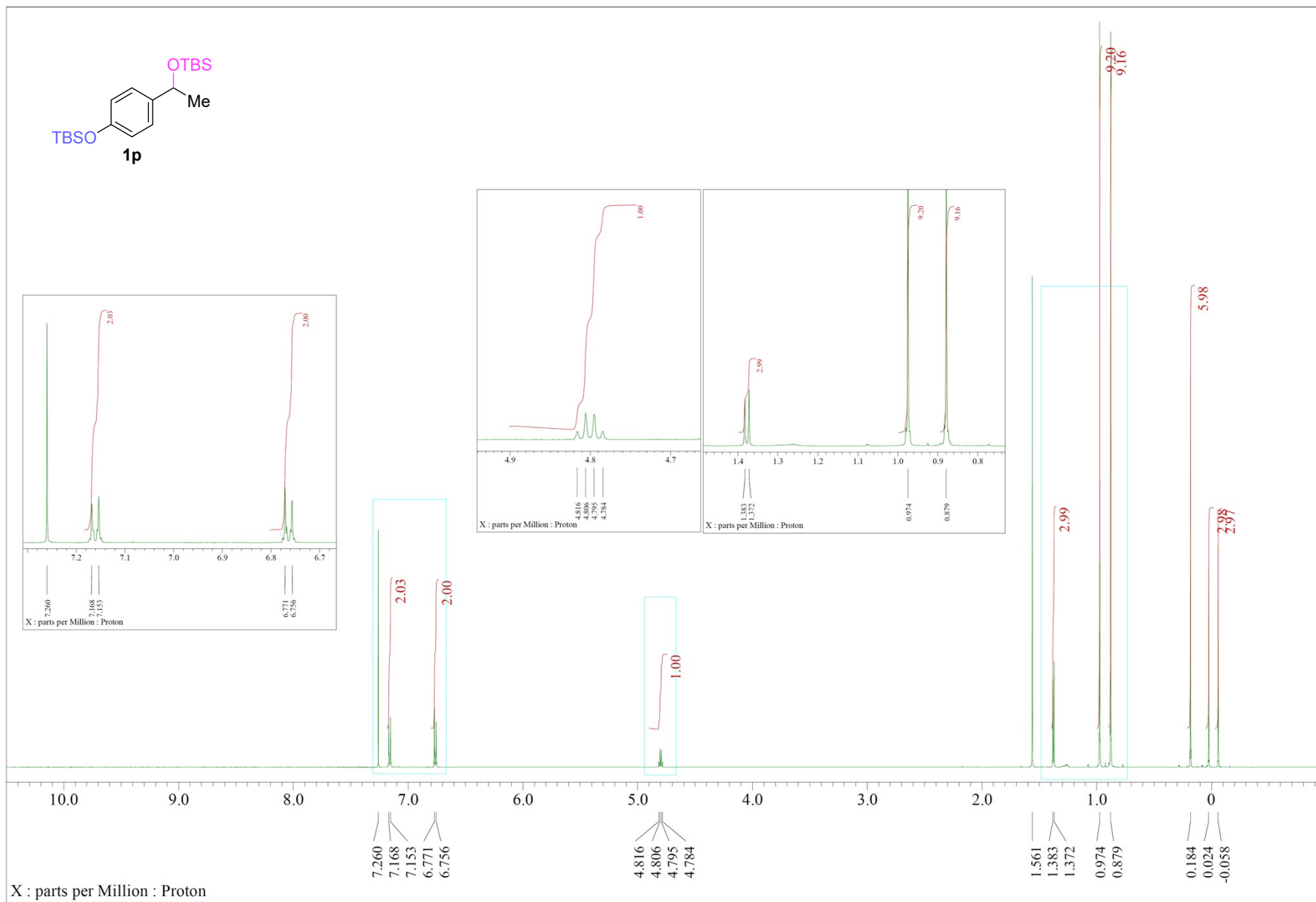


Figure S50.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound 1p.

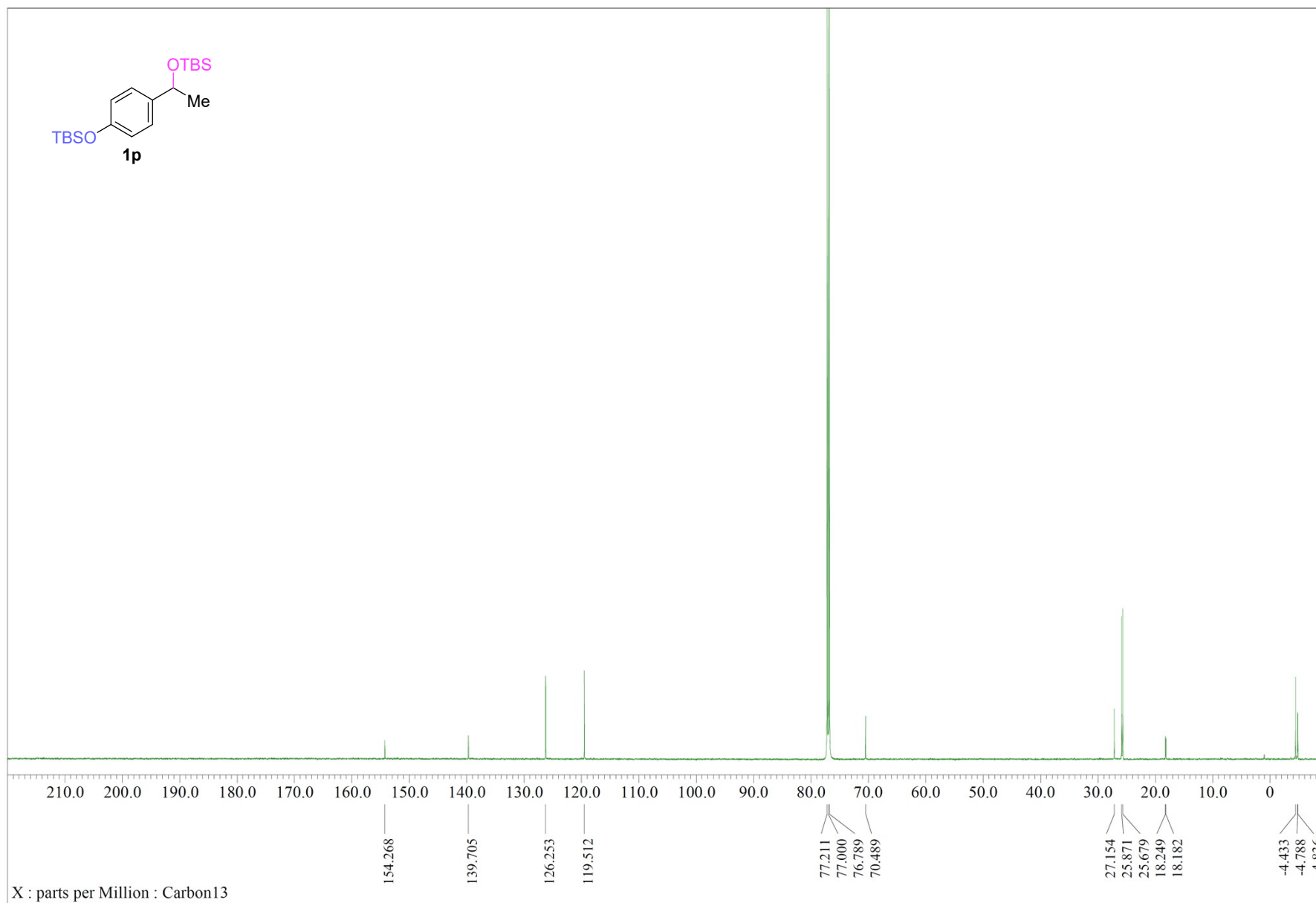


Figure S51. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1q.

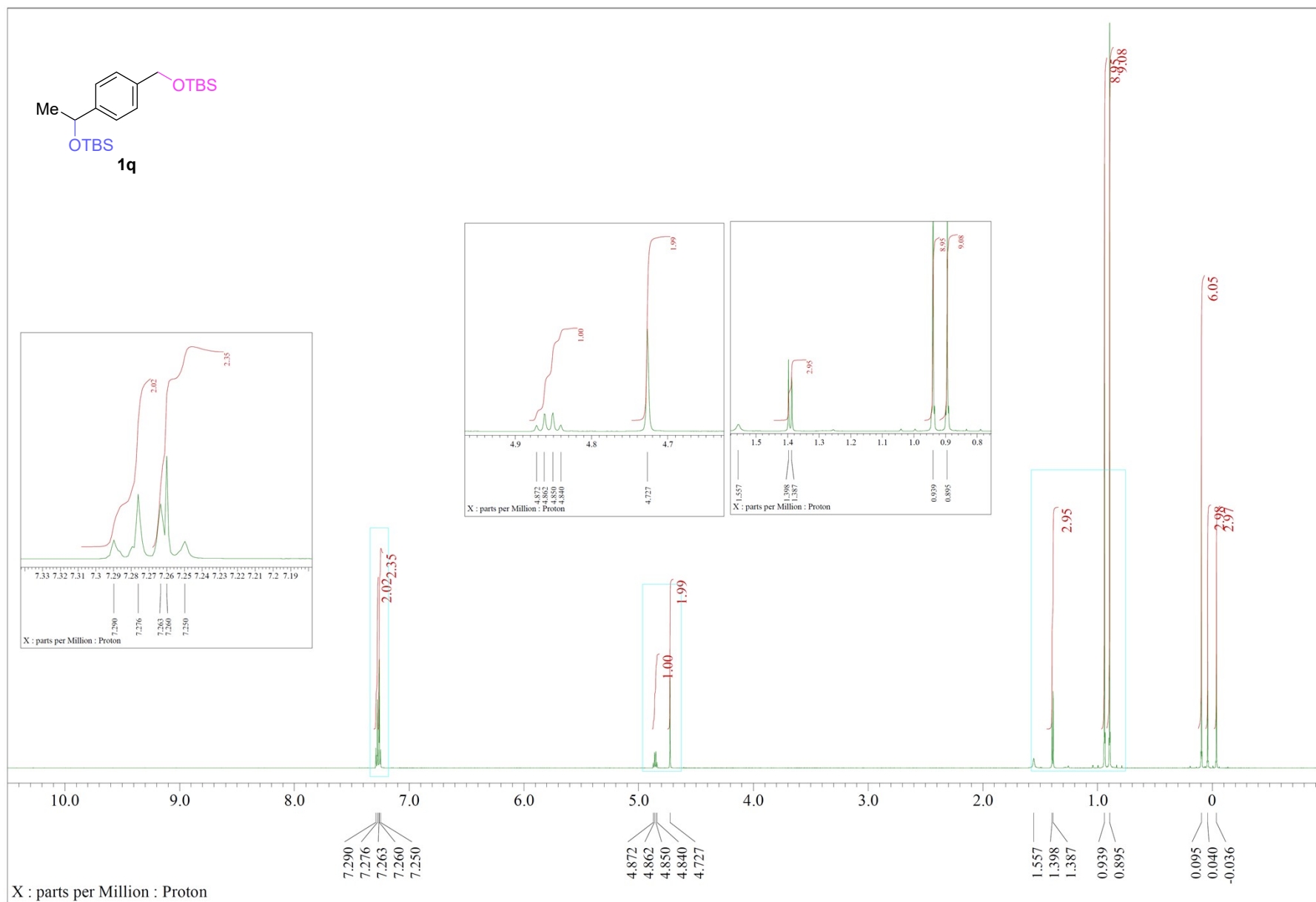


Figure S52. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1r.

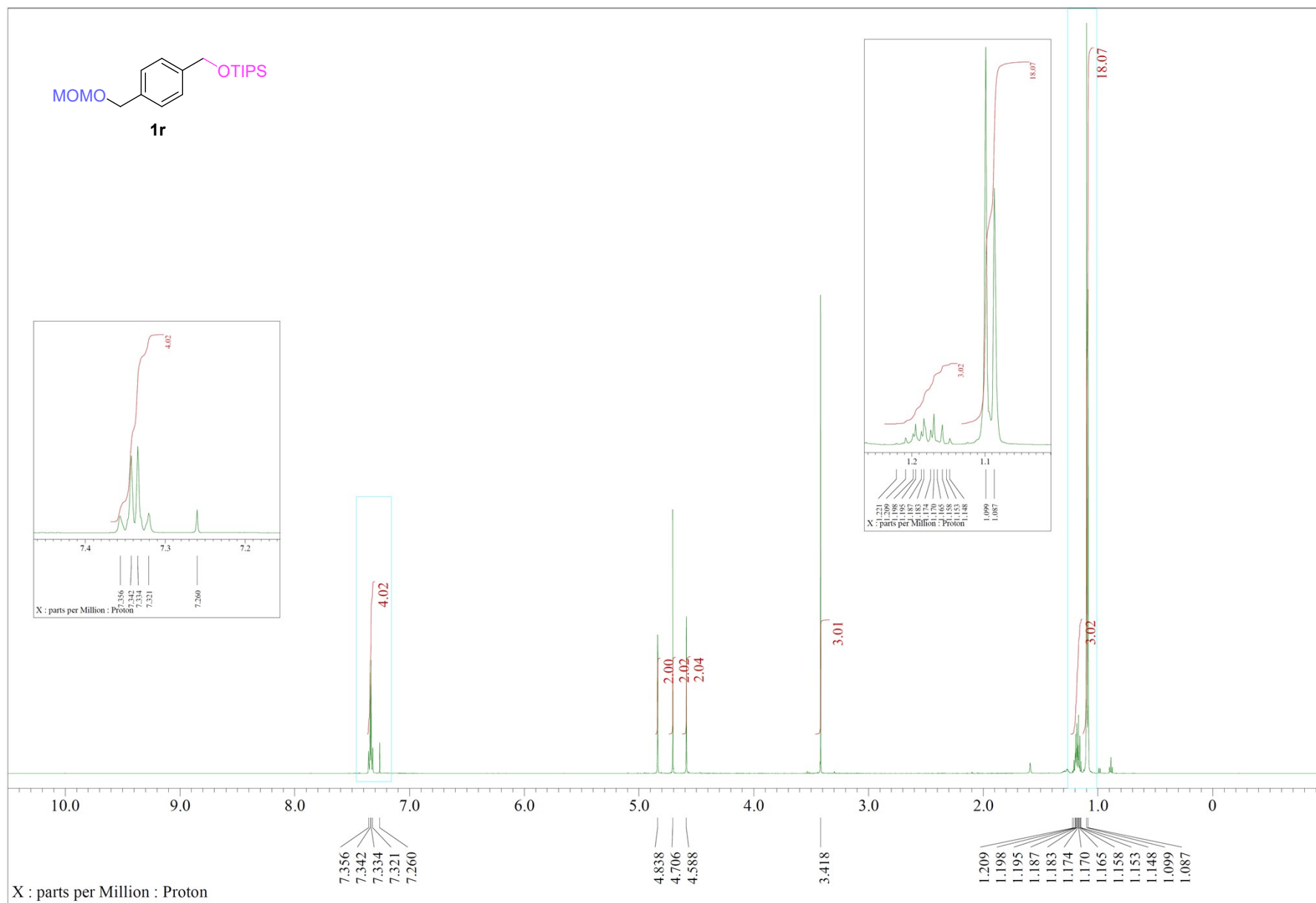


Figure S53.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **1r**.

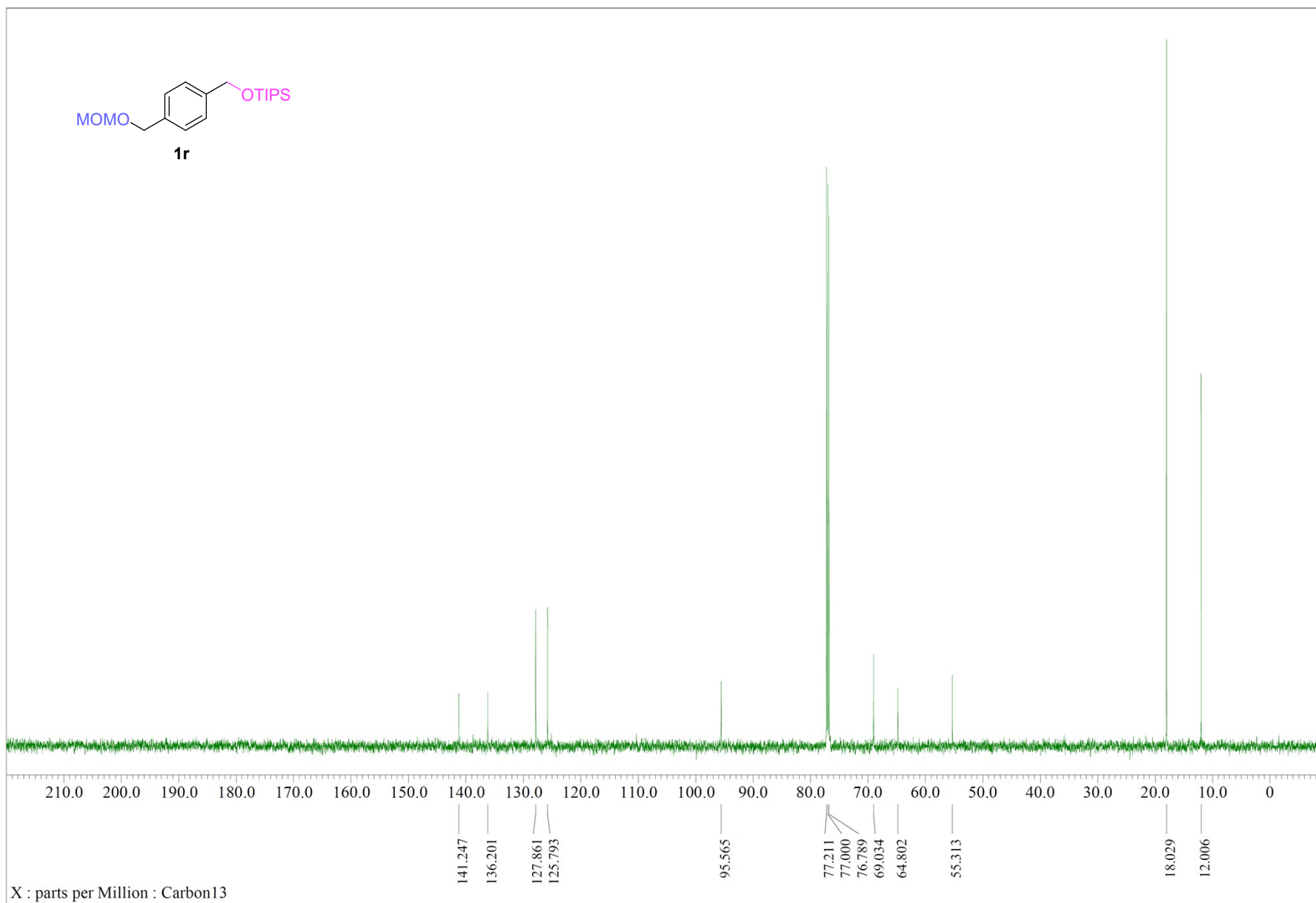






Figure S55.  $^{13}\text{C}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of compound **1s**.

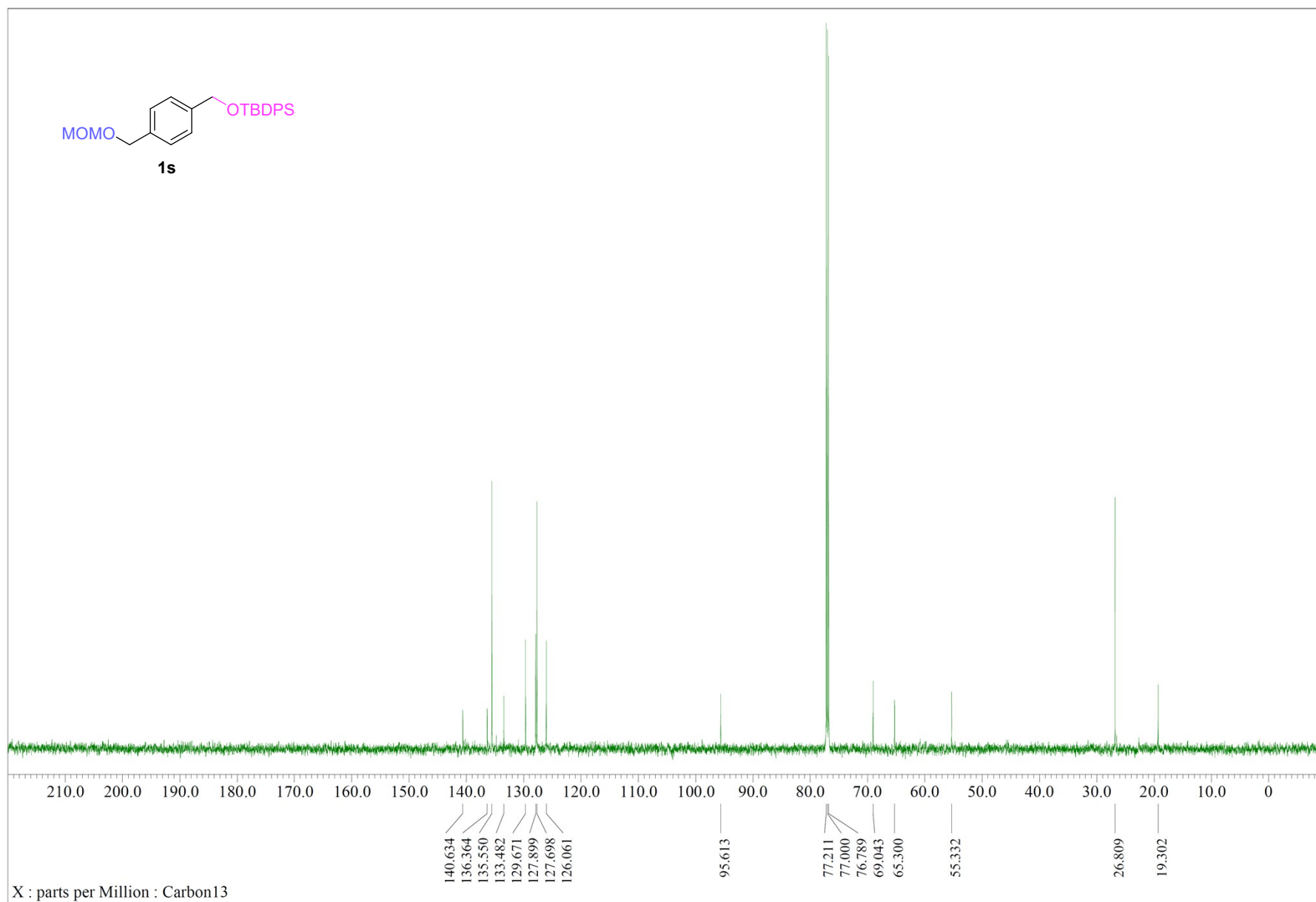




Figure S57. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of compound 1v.

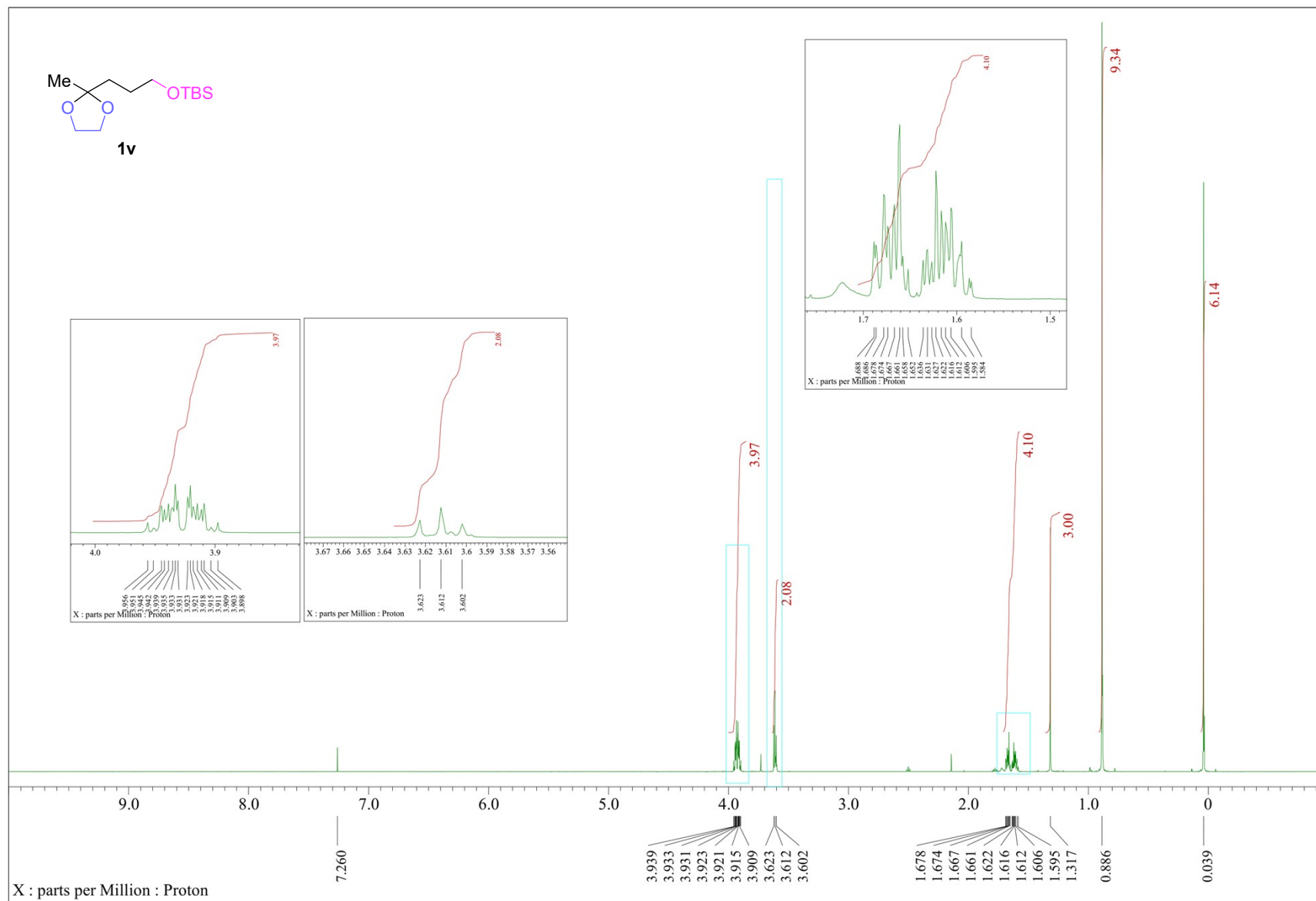
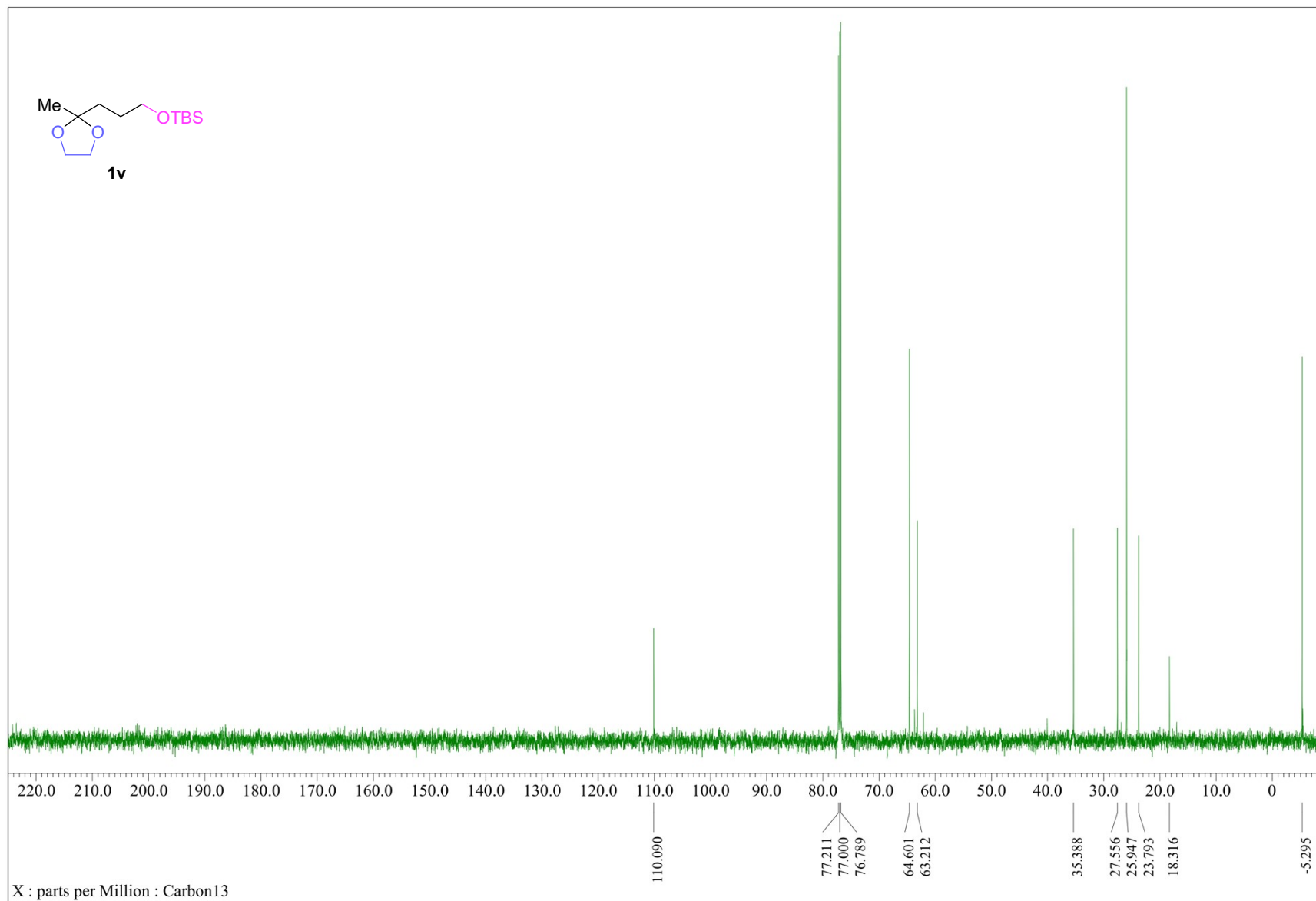


Figure S58.  $^{13}\text{C}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of compound **1v**.



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