

## Supporting Information

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### Formation and Reactivity of New Nicholas-Ferrier Pyranosidic Cations: Novel Access to Oxepanes via a 1,6-Hydride Shift/Cyclization Sequence

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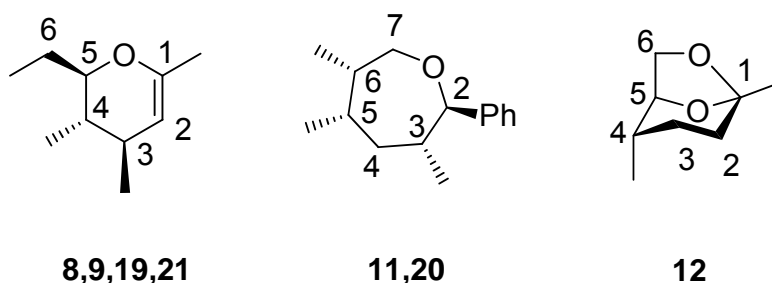
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## 1. General Methods.

All solvents and reagents were obtained commercially and used as received unless stated otherwise. Residual water was removed from starting compounds by repeated coevaporation. Reactions were executed at ambient temperatures unless stated otherwise. All moisture-sensitive reactions were performed in dry flasks fitted with glass stoppers or rubber septa under a positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred by syringe or stainless steel cannula. Anhydrous MgSO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> were used to dry organic solutions during workup, and evaporation of the solvents was performed under reduced pressure using a rotary evaporator. Flash column chromatography was performed using 230–400 mesh silica gel. Thin-layer chromatography was

conducted on Kieselgel 60 F254 (Merck). Spots were observed first under UV irradiation (254 nm) then by charring with a solution of 20 % aqueous H<sub>2</sub>SO<sub>4</sub> (200 mL) in AcOH (800 mL). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 300 and 75 or 100 MHz, respectively. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl<sub>3</sub>: δ 7.25 ppm). Coupling constants (*J*) are given in Hz. Where indicated, NMR peak assignments were made by using COSY and HSQC experiments. All presented <sup>13</sup>C spectra are proton-decoupled. The numbering pattern used for the <sup>1</sup>H NMR is illustrated below.



Mass spectra were recorded by direct injection with a mass spectrometer *Agilent 6250 Accurate Mass Q-TOF LC/MS* equipped with an electrospray ion source in positive mode. Optical rotations [ $\alpha$ ]<sub>D</sub> were measured for solutions in chloroform with a *Perkin-Elmer 241 MC* polarimeter (sodium D-line,  $\lambda$  = 589 nm).

Starting glycals **6a**<sup>11</sup>, **6b**<sup>12</sup> and lactone **7a**<sup>13</sup> were prepared according to described procedures.

## 2. Preparation and spectroscopic characterization data of compounds

*3,4-Di-O-benzyl-6-O-Triisopropyl-2-deoxy-D-arabino-hexono-1,5-lactone* **7b**. A solution of D-glucal **6b** (3.8 g, 8 mmol) in 1,2 dichloroethane (100 mL) under argon and in the presence of 4A molecular sieves was treated with PCC (3.4 g, 16 mmol). The ensuing suspension was heated to 80°C and stirred for 6 h. The mixture was then allowed to cool, diluted with Et<sub>2</sub>O and filtered through a small path of celite. The organic layer was concentrated and the residue purified by flash chromatography (Hexane/EtOAc 9:1) to give lactone **7b** (1.51 g, 44%) as a colorless oil. For **7b**:  $[\alpha]_D^{25} +30.7$  (c 1.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.32-7.16 (m, 10 H), 4.63 (d, *J* = 11.3 Hz, CH<sub>2</sub>Ph), 4.56 (d, *J* = 11.7 Hz, CH<sub>2</sub>Ph), 4.55 (d, *J* = 11.4 Hz, CH<sub>2</sub>Ph), 4.47 (d, *J* = 11.8 Hz, CH<sub>2</sub>Ph), 4.16 (td, *J* = 6.6, 3.8 Hz, 1 H, H-5), 3.97-3.84 (m, 3 H, H-4, H-6), 2.81 (dd, *J* = 16.6, 4.4 Hz, 1 H, H-2), 2.64 (dd, *J* = 16.5, 5.7 Hz, 1 H, H-2), 1.01-0.96 (m, 21 H, TIPS); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) δ 169.7, 138.0, 137.8, 128.9, 128.4, 128.4, 128.3, 128.1, 81.3, 75.1, 74.8, 73.5, 71.6, 62.9, 34.3, 18.4, 18.3, 12.3. HRMS (ESI<sup>+</sup>): found 499.2876 (M + H)<sup>+</sup>; calcd. for [C<sub>29</sub>H<sub>42</sub>O<sub>5</sub>Si + H]<sup>+</sup> 499,2874.

**General Procedure A. Transformation of Lactones 7 into Enynes 8.** A flame-dried 25 mL round bottom flask equipped with a stir bar and argon inlet was charged with a solution of phenylacetylene (3 equiv) in dry THF (2 mL/mmol). The reaction was cooled to -78 °C, and then treated with n-butyllithium (3.05 equiv). After 30 minutes at -78 °C a solution of the corresponding 2-deoxy-D-gluconolactone in dry THF ( 4 mL/mmol) was added and the reaction mixture was kept at that temperature for 2 hours after which time phosphorous oxychloride (4 equiv) was added. After warming to room temperature, the mixture was stirred for 20 minutes, then treated with pyridine (40 equiv) and left overnight. Aqueous work up and chromatography afforded the corresponding alkynylglucal **8**.

*1-(2-Phenyl-ethynyl)-3,4,6-Tris-O-benzyl-D-glucal* **8a**. This compound was prepared according to the general procedure from lactone **7a** (2.10 g, 4.86 mmol). Silica gel chromatography (hexane/Ethyl acetate 95:5) provided pure **8a** (1.32 g, 53%) as a white solid. For **8a**: m.p. 96-98 °C;  $[\alpha]_D^{25}$  -3.6 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.43-7.14 (m, 20 H), 5.36 (d, *J* = 3.0 Hz, 1 H, H-2), 4.77 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ph), 4.60 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ph), 4.59 (d, *J* = 11.1 Hz, 1 H, CH<sub>2</sub>Ph), 4.57 (d, *J* = 12.1 Hz, 1 H, CH<sub>2</sub>Ph), 4.52 (s, 2 H, CH<sub>2</sub>Ph), 4.46 (d, *J* = 14.8 Hz, 1 H, CH<sub>2</sub>Ph) 4.22 (dd, *J* = 6.2, 3.1 Hz, 1 H, H-3), 4.09 (dt, *J* = 8.7, 3.2 Hz, 1 H, H-5), 3.88 (dd, *J* = 8.8, 6.3 Hz, 1 H, H-4), 3.80 (dd, *J* = 11.1, 4.4 Hz, 1 H, H-6), 3.75 (dd, *J* = 11.1, 3.0 Hz, 1 H, H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) δ 138.3, 138.2, 138.1, 131.8 (x 2), 128.9, 128.5 (x 2), 128.4 (x 3), 128.4 (x 2), 128.4 (x 2), 128.2, 128.1 127.9 (x 2), 127.8 (x 2), 127.8 (x 2), 127.6, 122.0, 107.0, 88.8, 83.7, 77.8, 76.3, 73.8 (x 2), 73.5, 70.6, 68.2. HRMS (ESI<sup>+</sup>): found: 539.2193 (M+Na)<sup>+</sup>, calcd. for [C<sub>35</sub>H<sub>32</sub>O<sub>4</sub> + Na]<sup>+</sup> 539.2198.

*1-(2-Phenyl-ethynyl)-3,4-di-O-Benzyl-6-O-Triisopropyl-D-glucal* **8b**. This compound was prepared according to the general procedure from lactone **7b** (1.00 g, 2.00 mmol). Silica gel chromatography (hexane/Ethyl acetate 95:5) provided pure **8b** (854 mg, 74%) as a colorless oil. For **8b**:  $[\alpha]_D^{28}$  -17.4 (c 1.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.58 - 7.32 (m, 15 H), 5.46 (d, *J* = 3.0 Hz, 1 H, H-2), 4.93 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ph), 4.85 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ph), 4.74 (d, *J* = 11.7 Hz, 1 H, CH<sub>2</sub>Ph), 4.67 (d, *J* = 11.7 Hz, 1 H, CH<sub>2</sub>Ph), 4.38-4.33 (m, 1 H, H-5), 4.21-4.05 (m, 3 H, H-4, H-6), 1.31-1.07 (m, 21 H, TIPS); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 138.8, 138.6, 138.6, 132.1 (x 2), 129.2 (x 3), 128.8 (x 2), 128.7 (x 2), 128.4 (x 2), 128.2 (x 2), 128.1, 128.1, 122.6, 106.7, 88.7, 84.2, 79.1, 76.4, 74.3, 73.8, 71.2, 62.1, 18.4 (x 6), 12.5 (x 3). HRMS (ESI<sup>+</sup>): found: 605.3054 (M+Na)<sup>+</sup>, calcd. for [C<sub>37</sub>H<sub>46</sub>O<sub>4</sub>Si + Na]<sup>+</sup> 605.3063.

**General Procedure B. Transformation of 8b into the enyne precursors of differently substituted glycals, 19a-f.** 1-(2-Phenyl-ethynyl)-3,4-di-O-Benzyl-6-O-Triisopropyl-D-glucal **8b** (1.20 g, 2 mmol) was dissolved in THF (30 mL) and then

treated with tetrabutylammonium fluoride trihydrate (TBAF) (1.07 g, 4 mmol) and acetic acid (0.1 mL, 2 mmol). The reaction mixture was stirred for 24 h and subsequently diluted with EtOAc, poured into satd. aq. NaHCO<sub>3</sub> and extracted with EtOAc. The combined organic layers were dried and concentrated. The residue was purified by silica column chromatography (hexane/Ethyl acetate 6:4) to afford **desilylated-8b** (550 mg, 64%) as a white solid. m. p. 98-100°C;  $[\alpha]_D^{29} -16.4$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.65 – 6.97 (m, 15 H), 5.35 (d, *J* = 3.0 Hz, 1 H, H-2), 4.79 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ph), 4.66 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ph), 4.61 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ph), 4.50 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ph), 4.24 (dd, *J* = 6.5, 3.0 Hz, 1 H, H-3), 4.05 – 3.60 (m, 4 H, H-4, H-5, 2 x H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) δ 138.2, 138.1 (x 2), 131.9 (x 2), 129.1, 128.6 (x 4), 128.5 (x 2), 128.2 (x 2), 128.0, 127.9 (x 3), 121.9, 107.3, 89.1, 83.4, 78.5, 76.5, 74.1 (x 2), 70.9, 61.6; HRMS (ESI<sup>+</sup>): found: 427.1894 (M+H)<sup>+</sup>; 465.1468 (M+K)<sup>+</sup>, calcd. for [C<sub>28</sub>H<sub>26</sub>O<sub>4</sub> + H]<sup>+</sup> 427,1904.

Next, a solution of **desilylated-8b** (100 mg, 0.23 mmol) in dry THF (5 mL) was cooled to 0 °C and treated under argon atmosphere with NaH (60% dispersion in mineral oil, 14 mg, 0.34 mmol). After stirring at 0 °C for 30 min, the corresponding benzyl halide (1.2 eq) and tetrabutylammonium iodide (5% mol) were added. The reaction mixture was then allowed to reach room temperature and stirred overnight. The reaction was diluted with water (10 mL) and extracted with diethyl ether (3 x 15 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated *in vacuo*, and then purified by flash column chromatography (hexane/Ethyl acetate 95:5).

**Enyne precursor of 19a.** Following the general procedure, **desilylated-8b** was treated with *p*-methoxybenzyl chloride (42 mg, 0.28 mmol) to produce **enyne precursor of 19a** (65 mg, 54%) as a yellow oil.  $[\alpha]_D^{25} +6.71^\circ$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.73 – 6.74 (m, 19 H), 5.44 (d, *J* = 3.0 Hz, 1 H, H-2), 4.84 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ar), 4.68 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.66 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ar), 4.60 (d, *J* = 11.7 Hz, 1 H, CH<sub>2</sub>Ar), 4.59 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.51

(d,  $J = 11.7$  Hz, 1 H, CH<sub>2</sub>Ar), 4.31 (dd,  $J = 6.4, 3.0$  Hz, 1 H, H-3), 4.16 (ddd,  $J = 8.7, 4.3, 3.0$  Hz, 1 H, H-5), 3.95 (dd,  $J = 8.7, 6.4$  Hz, 1 H, H-4), 3.91 – 3.66 (m, 2 H, 2 x H-6), 3.79 (s, 3 H, CH<sub>3</sub>O); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz)  $\delta$  159.6, 138.7, 138.6 (x 2), 132.2 (x 2), 130.5, 129.9 (x 2), 129.3, 128.9 (x 2), 128.8 (x 2), 128.7 (x 2), 128.3 (x 2), 128.2 (x 2), 128.2, 128.1, 122.4, 114.2 (x 2), 107.4, 89.1, 84.1, 78.2, 76.7, 74.2 (x 2), 73.6, 71.0, 68.3, 55.7; HRMS (ESI+): found: 547.2468 (M+H)<sup>+</sup>; 569.2394 (M+Na)<sup>+</sup>, calcd. for [C<sub>36</sub>H<sub>34</sub>O<sub>5</sub> + H]<sup>+</sup> 547.2489.

**Enyne precursor of 19b.** Following the general procedure, **desilylated-8b** was treated with *p*-methylbenzyl bromide (54 mg, 0.28 mmol) to produce **enyne precursor of 19b** (92 mg, 72%) as a colorless oil.  $[\alpha]_D^{25} +7.8$  (c 0.9, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.01 – 6.94 (m, 19 H), 5.49 (d,  $J = 3.1$  Hz, 1 H, H-2), 4.88 (d,  $J = 11.1$  Hz, 1 H, CH<sub>2</sub>Ar), 4.77 – 4.62 (m, 4 H, CH<sub>2</sub>Ar), 4.59 (d,  $J = 12.5$  Hz, 1 H, CH<sub>2</sub>Ar), 4.35 (dd,  $J = 6.5, 3.1$  Hz, 1 H, H-3), 4.20 (dt,  $J = 8.9, 4.8$  Hz, 1 H, H-5), 4.00 (dd,  $J = 8.9, 6.5$  Hz, 1 H, H-4), 3.93 – 3.84 (m, 2 H, H-6), 2.39 (s, 3 H, Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz)  $\delta$  138.5, 138.3 (x 2), 137.5, 135.1, 131.9 (x 2), 129.2 (x 2), 129.0, 128.6 (x 2), 128.5 (x 2), 128.4 (x 2), 128.2 (x 2), 128.0 (x 2), 127.9 (x 2), 127.8 (x 2), 122.2, 107.1, 88.8, 83.8, 77.9, 76.4, 73.9 (x 2), 73.6, 70.7, 68.1, 21.3; HRMS (ESI+): found: 531.2541 (M+H)<sup>+</sup>; 553.2368 (M+Na)<sup>+</sup>, calcd. for [C<sub>36</sub>H<sub>34</sub>O<sub>5</sub> + H]<sup>+</sup> 531.2535.

**Enyne precursor of 19c.** Following the general procedure, **desilylated-8b** was treated with 2-naphthylmethyl bromide (58 mg, 0.28 mmol) to produce **enyne precursor of 19c** (60 mg, 48%) as a white solid. m. p. 97-100°C;  $[\alpha]_D^{25} -6.9$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.99 – 7.07 (m, 22 H), 5.45 (d,  $J = 3.0$  Hz, 1 H, H-2), 4.84 (d,  $J = 11.2$  Hz, 1 H, CH<sub>2</sub>Ar), 4.82 (d,  $J = 12.3$  Hz, 1 H, CH<sub>2</sub>Ar), 4.74 (d,  $J = 12.3$  Hz, 1 H, CH<sub>2</sub>Ar), 4.68 (d,  $J = 11.6$  Hz, 1 H, CH<sub>2</sub>Ar), 4.66 (d,  $J = 11.2$  Hz, 1 H, CH<sub>2</sub>Ar), 4.58 (d,  $J = 11.6$  Hz, 1 H, CH<sub>2</sub>Ar), 4.31 (dd,  $J = 6.3, 3.0$  Hz, 1 H, H-3), 4.19 (ddd,  $J = 8.6, 4.3, 2.9$  Hz, 1 H, H-5), 3.97 (dd,  $J = 8.6, 6.3$  Hz, 1 H, H-4), 3.92 (dd,  $J = 10.9, 4.3$  Hz, 1 H, H-6), 3.87 (dd,  $J = 10.9, 2.9$  Hz, 1 H, H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz)  $\delta$  138.4, 138.2, 138.1, 135.6, 133.3, 133.1, 131.8 (x 2), 128.9, 128.5 (x 2), 128.4 (x 3), 128.2, 128.0, 127.9, 127.9 (x 2), 127.8, 127.8 (x 2), 127.8 (x 2), 126.6,

126.1, 125.9 (x 2), 122.0, 107.0, 88.8, 83.8, 77.8, 76.3, 73.9, 73.8, 73.6, 70.6, 68.3; HRMS (ESI+): found: 567.2539 (M+H)<sup>+</sup>; 1150.5274 (2M+NH<sub>4</sub>)<sup>+</sup>, calcd. for [C<sub>39</sub>H<sub>34</sub>O<sub>4</sub> + H]<sup>+</sup> 567.2535.

**Enyne precursor of 19d.** Following the general procedure, **desilylated-8b** was treated with *p*-iodobenzyl bromide (83 mg, 0.28 mmol) to produce **enyne precursor of 19d** (96 mg, 78%) as a yellow solid. m. p. 63-65 °C, [α]<sub>D</sub><sup>25</sup> +1.7 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.56 (d, *J* = 8.1 Hz, 2 H, *o* I-C<sub>6</sub>H<sub>4</sub>), 7.45 – 7.11 (m, 15 H), 7.00 (d, *J* = 8.1 Hz, 2 H, *m* I-C<sub>6</sub>H<sub>4</sub>), 5.36 (d, *J* = 3.1 Hz, 1 H, H-2), 4.76 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ar), 4.59 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.57 (d, *J* = 11.4 Hz, 1 H, CH<sub>2</sub>Ar), 4.49 (d, *J* = 11.7 Hz, 1 H, CH<sub>2</sub>Ar), 4.48 (d, *J* = 12.0 Hz, 1 H, CH<sub>2</sub>Ar), 4.41 (d, *J* = 12.0 Hz, 1 H, CH<sub>2</sub>Ar), 4.21 (dd, *J* = 6.2, 3.1 Hz, 1 H, H-3), 4.07 (ddd, *J* = 8.8, 4.6, 2.9 Hz, 1 H, H-5), 3.84 (dd, *J* = 8.8, 6.2 Hz, 1 H, H-4), 3.77 (dd, *J* = 10.8, 4.6 Hz, 1 H, H-6), 3.71 (dd, *J* = 10.8, 2.9 Hz, 1 H, H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 138.4, 138.2 (x 2), 138.0, 137.6 (x 3), 131.9 (x 2), 129.7 (x 2), 129.0, 128.6 (x 2), 128.6 (x 2), 128.5 (x 2), 128.0 (x 2), 127.9, 127.9 (x 2), 122.1, 107.1, 93.2, 88.9, 83.7, 77.8, 76.4, 73.9 (x 2), 72.9, 70.8, 68.5; HRMS (ESI+): found: 643.1347 (M+H)<sup>+</sup>; 1302.2869 (2M+NH<sub>4</sub>)<sup>+</sup>, calcd. for [C<sub>35</sub>H<sub>31</sub>IO<sub>4</sub> + H]<sup>+</sup> 643.1345.

**Enyne precursor of 19e.** Following the general procedure, **desilylated-8b** was treated with *p*-bromobenzyl bromide (70 mg, 0.28 mmol) to produce **enyne precursor of 19e** (138 mg, 85%) as a yellow solid. m. p. 51-54 °C; [α]<sub>D</sub><sup>25</sup> -0.3 (c 1.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.57 – 7.06 (m, 19 H), 5.46 (d, *J* = 3.1 Hz, 1 H, H-2), 4.86 (d, *J* = 11.2 Hz, 1 H, CH<sub>2</sub>Ar), 4.69 (d, *J* = 11.5 Hz, 1 H, CH<sub>2</sub>Ar), 4.67 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ar), 4.64 – 4.47 (m, 3 H, CH<sub>2</sub>Ar), 4.31 (dd, *J* = 6.3, 3.1 Hz, 1 H, H-3), 4.17 (ddd, *J* = 8.9, 5.2, 3.1 Hz, 1 H, H-5), 3.94 (dd, *J* = 8.9, 6.3 Hz, 1 H, H-4), 3.87 (dd, *J* = 10.9, 5.2 Hz, 1 H, H-6), 3.80 (dd, *J* = 10.9, 3.1 Hz, 1 H, H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) δ 138.3, 138.1 (x 2), 137.2, 131.9 (x 2), 131.5 (x 2), 129.8, 129.5 (x 2), 129.1, 129.0, 128.5 (x 2), 128.5 (x 2), 128.4 (x 2), 127.9 (x 2), 127.9 (x 2), 122.0, 121.6, 107.0, 88.9, 83.6, 77.7, 76.2, 73.8 (x 2), 72.8, 70.7, 68.4; HRMS (ESI+): found: 595.1478 (M+H)<sup>+</sup>, calcd. for [C<sub>35</sub>H<sub>31</sub>BrO<sub>4</sub> + H]<sup>+</sup> 595.1484.



**Enyne precursor of 19f.** Following the general procedure, **desilylated-8b** was treated with *p*-fluorobenzyl bromide (60 mg, 0.28 mmol) to produce **enyne precursor of 19f** (108 mg, 78%) as a yellow solid. m. p. 82-86°C;  $[\alpha]_D^{25}$  -3.60 (c 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.48 – 6.79 (m, 19 H), 5.34 (d, *J* = 3.0 Hz, 1 H, H-2), 4.75 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ar), 4.57 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.56 (d, *J* = 11.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.49 (d, *J* = 5.6 Hz, 1 H, CH<sub>2</sub>Ar), 4.45 (d, *J* = 5.3 Hz, 1 H, CH<sub>2</sub>Ar), 4.41 (d, *J* = 12.2 Hz, 1 H, CH<sub>2</sub>Ar), 4.20 (dd, *J* = 6.2, 3.0 Hz, 1 H, H-3), 4.06 (ddd, *J* = 8.5, 4.6, 3.0 Hz, 1H, H-5), 3.83 (dd, *J* = 8.5, 6.2 Hz, 1H, H-4), 3.75 (dd, *J* = 10.9, 4.6 Hz, 1H, H-6), 3.69 (dd, *J* = 10.9, 3.0 Hz, 1H, H-6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 162.4 (<sup>1</sup>*J*<sub>C,F</sub> = 245.5 Hz), 138.3 (x 2), 138.2 (x 2), 133.9 (<sup>4</sup>*J*<sub>C,F</sub> = 3.1 Hz), 131.9 (x 2), 129.6 (<sup>3</sup>*J*<sub>C,F</sub> = 8.1 Hz) (x 2), 129.0, 128.5 (x 2), 128.5 (x 2), 128.4 (x 2), 127.9 (x 2), 127.9 (x 3), 122.0, 115.3 (<sup>2</sup>*J*<sub>C,F</sub> = 21.4 Hz) (x 2), 107.0, 88.8, 83.7, 77.8, 76.3, 73.9, 73.8, 72.8, 70.7, 68.3; HRMS (ESI<sup>+</sup>): found: 535.2285 (M+H)<sup>+</sup>, calcd. for [C<sub>35</sub>H<sub>31</sub>FO<sub>4</sub> + H]<sup>+</sup> 535.2285.

**General Procedure C. Preparation of cobalt-complexed enynes 9 and 19.** A solution of Co<sub>2</sub>(CO)<sub>8</sub> (1.2 eq) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1 ml/mmol) was added to a solution of the corresponding enyne in CH<sub>2</sub>Cl<sub>2</sub> (10 ml/mmol). The dark solution was stirred at room temperature until TLC showed complete formation of the complex (ca. 2 h). The solvent of the resulting reaction mixture was then removed under vacuum, and the residue was purified by flash chromatography. Dicobalt hexacarbonyl complexed enynes **19a-f** were used after chromatography without further characterization (For **19a**: 80%; **19b**: 98%; **19c**: 83%; **19d**: 90%; **19e**: 70%; **19f**: 76%).

**Dicobalt hexacarbonyl complex 9a.** Following the general procedure, complex **9a** was prepared from 1-(2-Phenyl-ethynyl)-3,4,6-tris-O-Benzyl-D-glucal **8a** (2.6 g, 5.0 mmol) and Co<sub>2</sub>(CO)<sub>8</sub> (2 g, 6 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 95:5) to give a brownish oil (3.45 g, 86 %); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.75 – 7.19 (m, 20 H), 5.45 (d, *J* = 3.0 Hz, 1 H, H-2), 4.91 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ph), 4.78 (d, *J* = 11.3 Hz, 1 H, CH<sub>2</sub>Ph), 4.66 (s, 2 H, CH<sub>2</sub>Ph), 4.63 (d, *J* = 12.0 Hz, 1 H, CH<sub>2</sub>Ph), 4.56 (d, *J* = 12.0 Hz, 1 H, CH<sub>2</sub>Ph),

4.37 (dd,  $J = 6.3, 3.0$  Hz, 1 H, H-3), 4.26 (ddd,  $J = 9.0, 4.1, 2.5$  Hz, 1 H, H-5), 4.10 (dd,  $J = 9.0, 6.3$  Hz, 1 H, H-4), 3.97 (dd,  $J = 10.9, 4.1$  Hz, 1 H, H-6), 3.84 (dd,  $J = 10.9, 2.5$  Hz, 1 H, H-6);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1 (x 6), 152.3, 138.5, 138.5, 138.4, 137.9, 129.8 (x 2), 128.9 (x 2), 128.6 (x 2), 128.5 (x 2), 128.4 (x 2), 128.0, 128.0 (x 2), 127.9 (x 2), 127.8 (x 2), 127.6, 127.6 (x 2), 101.2, 91.5, 84.4, 78.2, 77.6, 74.6, 74.0, 73.7, 70.9, 68.8.

**Dicobalt hexacarbonyl complex 9b.** Following the general procedure, complex **9b** was prepared from 1-(2-Phenyl-ethynyl)-3,4-di-O-Benzyl-6-O-Triisopropyl-D-glucal **8b** (854 mg, 1.46 mmol) and  $\text{Co}_2(\text{CO})_8$  (600 mg, 1.76 mmol) in dry  $\text{CH}_2\text{Cl}_2$ . The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 98:2) to give a brownish oil (1.10 g, 87 %);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.61 – 7.14 (m, 15 H), 5.35 (d,  $J = 3.1$  Hz, 1 H, H-2), 4.87 (d,  $J = 11.4$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.73 (d,  $J = 11.4$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.55 (s, 2 H,  $\text{CH}_2\text{Ph}$ ), 4.31 – 4.25 (m, 1 H, H-5), 4.07 – 3.99 (m, 4 H, H-3, H-4, 2 x H-6), 1.09 – 0.82 (m, 21 H, TIPS);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1 (x 6), 153.1, 138.8, 138.5, 138.0, 129.8 (x 2), 128.9 (x 2), 128.6 (x 2), 128.5 (x 2), 128.1 (x 2), 128.0, 127.9, 127.8 (x 2), 127.7, 101.7, 91.9, 84.9, 80.1, 77.9, 74.2, 73.6, 70.9, 62.2, 18.2 (x 6), 12.1 (x 3).

**General Procedure D. Preparation of oxepanes 11 and 20 from cobalt-complexed enynes.** A solution of the corresponding cobalt complex (1 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (100 mL/mmol) under an argon atmosphere and in the presence of 4Å molecular sieves was cooled to  $-20^\circ\text{C}$ , and treated with  $\text{BF}_3\cdot\text{OEt}_2$  (1.2 equiv). The mixture was kept at that temperature until no further progress was revealed by TLC analysis, and then quenched with saturated aqueous  $\text{NaHCO}_3$ . The cooling bath was removed and the layers were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography.

Oxepane **11**. Dicobalt hexacarbonyl complex **9a** (80 mg, 0.10 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (14 mg, 23%) followed by oxepane **11** (43 mg, 61%). For **11**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.37-7.23 (m, 15 H), 5.02 (d,  $J$  = 10.2 Hz, 1 H, H-2), 4.53 (d,  $J$  = 11.4 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.42 (d,  $J$  = 11.3 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.37-4.28 (m, 2 H, H-6, H-7), 3.90 (d,  $J$  = 10.7 Hz, 1 H, H-5), 3.68 (dd,  $J$  = 15.3, 8.8 Hz, 1 H, H-7), 3.47 (dt,  $J$  = 10.5, 3.3 Hz, 1 H, H-3), 2.65 (td,  $J$  = 13.9, 10.8 Hz, 1 H, H-4<sub>ax</sub>), 2.49 (d,  $J$  = 2.2 Hz, 1 H, OH), 2.14 (d,  $J$  = 14.6 Hz, 1 H, H-4<sub>eq</sub>);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.0, 198.0 (x 6), 141.3, 137.7, 136.4, 129.4 (x 2), 129.0 (x 2), 128.6 (x 3), 128.5, 128.0 (x 2), 127.8 (x 2), 127.5, 127.0 (x 2), 93.5, 86.1, 85.8, 79.4, 72.5, 71.3, 70.7, 59.1, 31.3. The stereochemistries at C-2 and C-3 were assigned on the basis of a  $J_{2,3}$  = 10.2 Hz coupling constant, and observed NOEs between H-2, H-7<sub>ax</sub>, H-4<sub>ax</sub> and OH.

For **12**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J$  = 7.6, 1.7 Hz, 2 H), 7.47-7.22 (m, 8 H), 4.84 (d,  $J$  = 3.0 Hz, 1 H, H-5), 4.72 (d,  $J$  = 12.4 Hz, 1 H, Bn), 4.67 (d,  $J$  = 12.3 Hz, 1 H, Bn), 4.03-3.94 (m, 2 H, H-6), 3.47 (td,  $J$  = 3.9, 1.9 Hz, 1 H, H-4), 2.34 (dt,  $J$  = 12.4, 5.6 Hz, 1 H, H-2), 2.20-2.05 (m, 1 H, H-3), 2.00-1.86 (m, 2 H, H-2, H-3);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 138.8, 137.8, 130.3 (x 2), 128.9 (x 2), 128.6 (x 2), 128.0, 127.8, 127.6 (x 2), 109.6, 94.2, 89.9, 76.6, 72.8, 70.3, 67.7, 34.0, 23.2.

Confirmation of the proposed structure of **11**. A solution of **11** (100 mg, 0.14 mmol) in THF (5 mL) at 0° C was treated with an excess of  $\text{I}_2$  (70 mg, 0.28 mmol). The mixture was stirred at this temperature until no starting material was left (TLC analysis), quenched with saturated aqueous  $\text{NaHCO}_3$  solution, and extracted with AcOEt. The combined organic layers were washed with 10% aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 8:2) to give **demetalated-11** (44 mg, 74%).  $[\alpha]_D^{25} +10.2$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.67 – 7.00 (m, 15 H), 5.10 (d,  $J$  = 9.3 Hz, 1 H, H-2), 4.77 (d,  $J$  = 11.7 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.56 (d,  $J$  = 11.7 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.26 – 4.00 (m, 2 H, H-6, H-7), 3.90 (ddd,  $J$  = 9.3, 3.2, 1.6 Hz, 1 H, H-5), 3.69 (dd,  $J$  = 12.7, 6.6 Hz, 1 H, H-7), 3.22 (td,  $J$  = 9.3,

4.0 Hz, 1 H, H-3), 2.82 (dt,  $J = 14.3, 9.3$  Hz, 1 H, H-4), 2.41 (d,  $J = 4.9$  Hz, 1 H, OH), 2.20 (ddd,  $J = 14.3, 4.0, 1.6$  Hz, 1 H, H-4);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  187.3, 141.4, 137.9, 133.2 (x 2), 131.0, 128.8 (x 2), 128.7 (x 2), 128.7 (x 2), 128.2, 128.2, 128.0 (x 2), 126.9 (x 2), 119.8, 92.9, 87.3, 83.2, 79.3, 72.0, 71.2, 71.0, 59.0, 28.7. HRMS (ESI<sup>+</sup>): found: 427.1907 ( $\text{M}+\text{H}$ )<sup>+</sup>, calcd. for  $[\text{C}_{28}\text{H}_{26}\text{O}_4 + \text{H}]^+$  427.1904.

Oxepane **20b**. Dicobalt hexacarbonyl complex **19b** (130 mg, 0.16 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (25 mg, 27%) followed by oxepane **20b** (43 mg, 38%). For **20b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.59 – 6.85 (m, 14 H), 4.90 (d,  $J = 10.6$  Hz, 1 H, H-2), 4.46 (d,  $J = 11.5$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.34 (d,  $J = 11.5$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.29 – 4.17 (m, 2 H, H-5, H-7), 3.81 (ddd,  $J = 9.2, 2.9, 1.8$  Hz, 1 H, H-6), 3.59 (dd,  $J = 15.9, 9.2$  Hz, 1 H, H-7), 3.38 (td,  $J = 10.6, 3.5$  Hz, 1 H, H-3), 2.57 (dt,  $J = 14.3, 10.6$  Hz, 1 H, H-4), 2.40 (d,  $J = 2.9$  Hz, 1 H, OH), 2.20 (s, 3 H,  $\text{CH}_3$ ), 2.05 (d,  $J = 14.3$  Hz, 1 H, H-4);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.1, 198.1 (x 6), 138.4, 137.8, 137.8, 136.5, 129.5 (x 2), 129.3 (x 2), 129.1 (x 2), 128.6 (x 2), 128.6, 128.1, 127.9 (x 2), 126.9 (x 2), 93.7, 86.3 (x 2), 79.6, 72.4, 71.4, 70.7, 59.2, 31.5, 21.2.

Oxepane **20c**. Dicobalt hexacarbonyl complex **19c** (75 mg, 0.09 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (17 mg, 30%) followed by oxepane **20c** (44 mg, 62%). For **20c**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.91 – 6.87 (m, 17 H), 5.19 (d,  $J = 10.4$  Hz, 1 H, H-2), 4.59 (d,  $J = 11.4$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.46 (d,  $J = 11.4$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.42 – 4.32 (m, 2 H, H-5, H-7), 3.98 (dt,  $J = 8.7, 1.9$  Hz, 1 H, H-6), 3.73 (dd,  $J = 15.3, 8.7$  Hz, 1 H, H-7), 3.57 (td,  $J = 10.4, 3.5$  Hz, 1 H, H-3), 2.73 (dt,  $J = 14.1, 10.4$  Hz, 1 H, H-4), 2.20 (d,  $J = 14.1$  Hz, 1 H, H-4);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.3, 198.0 (x 6), 138.8, 137.8, 136.2, 133.3 (x 2), 129.3 (x 2), 128.9 (x 2), 128.7 (x 2), 128.6, 128.6, 128.3, 128.2, 127.9 (x 2), 127.1, 126.2, 126.2, 126.1, 124.9, 93.8, 86.5, 86.0, 79.6, 72.8, 71.5, 70.8, 59.5, 31.7.

Oxepane **20d**. Dicobalt hexacarbonyl complex **19d** (100 mg, 0.11 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (35 g, 43%) followed by oxepane **20d** (25 mg, 49%). For **20c**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J$  = 8.2 Hz, 2 H, *o* I- $\text{C}_6\text{H}_4$ ), 7.51 – 7.20 (m, 10 H), 7.09 (d,  $J$  = 8.2 Hz, 2 H, *m* I- $\text{C}_6\text{H}_4$ ), 4.99 (d,  $J$  = 10.7 Hz, 1 H, H-2), 4.57 (d,  $J$  = 11.3 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.45 (d,  $J$  = 11.3 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.39 – 4.27 (m, 2 H, H-5, H-7), 3.92 (d,  $J$  = 9.7 Hz, 1 H, H-6), 3.69 (dd,  $J$  = 16.3, 9.7 Hz, 1 H, H-7), 3.40 (td,  $J$  = 10.7, 4.2 Hz, 1 H, H-3), 2.67 (dt,  $J$  = 14.6, 10.7 Hz, 1 H, H-4), 2.48 (d,  $J$  = 2.4 Hz, 1 H, OH), 2.17 (d,  $J$  = 14.6 Hz, 1 H, H-4).;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.1, 197.9 (x 6), 141.2, 137.7 (x 2), 136.4, 132.1, 129.4 (x 2), 129.2 (x 2), 129.0 (x 2), 128.8, 128.7 (x 2), 128.4, 128.2, 127.9 (x 2), 93.8, 86.0, 85.6, 79.4, 72.8, 71.5, 70.9, 66.0, 31.5.

Oxepane **20e**. Dicobalt hexacarbonyl complex **19e** (100 mg, 0.11 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (14 mg, 21%) followed by oxepane **20e** (48 mg, 54%). For **20e**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.55 – 7.09 (m, 14 H), 4.97 (d,  $J$  = 10.6 Hz, 1 H, H-2), 4.54 (d,  $J$  = 11.4 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.41 (d,  $J$  = 11.5 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.36 – 4.24 (m, 2 H, H-5, H-7), 3.89 (d,  $J$  = 10.6 Hz, 1 H, H-6), 3.66 (dd,  $J$  = 16.1, 9.3 Hz, 1 H, H-7), 3.37 (td,  $J$  = 10.6, 3.5 Hz, 1 H, H-3), 2.64 (dt,  $J$  = 13.2, 10.6 Hz, 1 H, H-4), 2.48 (d,  $J$  = 2.7 Hz, 1 H, OH), 2.14 (d,  $J$  = 13.2 Hz, 1 H, H-4);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.1, 198.0 (x 6), 140.6, 137.8, 136.4, 131.7 (x 2), 129.4 (x 2), 129.2 (x 2), 128.8 (x 3), 128.7 (x 2), 128.2, 127.9 (x 2), 122.1, 93.9, 86.0, 85.6, 79.4, 72.8, 71.5, 70.9, 59.5, 31.4.

Oxepane **20f**. Dicobalt hexacarbonyl complex **19f** (125 mg, 0.15 mmol) was subjected to general procedure D to produce after silica gel column purification (hexane/Ethyl acetate in gradient from 95:5 to 8:2) compound **12** (14 mg, 15%) followed by oxepane **20f** (76 mg, 69%). For **20f**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.85 – 6.85 (m, 14 H), 5.02 (d,  $J$  = 10.6 Hz, 1 H, H-2), 4.57 (d,  $J$  = 11.4 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.45 (d,  $J$  = 11.4 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.40 – 4.30 (m, 2 H, H-5, H-7), 3.93 (dt,  $J$  = 9.6, 2.4 Hz, 1

H, H-6), 3.70 (dd,  $J = 15.6, 9.6$  Hz, 1 H, H-7), 3.43 (td,  $J = 10.6, 3.7$  Hz, 1 H, H-3), 2.67 (dt,  $J = 14.3, 10.6$  Hz, 1 H, H-4), 2.50 (d,  $J = 2.4$  Hz, 1 H, OH), 2.17 (d,  $J = 14.3$  Hz, 1 H, H-4).;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.1, 198.0 (x 6), 162.5 ( $^1J_{\text{C,F}} = 246.7$  Hz), 137.8, 137.4, 136.4, 129.4 (x 2), 129.1 (x 2), 128.8 (x 2), 128.7 (x 3), 128.1, 127.9 (x 2), 115.4 ( $^2J_{\text{C,F}} = 21.5$  Hz) (x 2), 93.8, 86.1, 85.6, 79.4, 72.8, 71.5, 70.8, 59.6, 31.3.

**General Procedure E. General procedure for the coupling reaction of cobalt-complexed enyne **9b** with nucleophiles.** To a solution of the cobalt complex in dry  $\text{CH}_2\text{Cl}_2$  and cooled to  $-20^\circ\text{C}$ ,  $\text{BF}_3\cdot\text{OEt}_2$  (1 equiv) and the corresponding nucleophile (3 equiv) were added. The mixture was kept at that temperature until no further progress was revealed by TLC analysis, and then quenched with saturated aqueous  $\text{NaHCO}_3$ . The cooling bath was removed and the layers were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*.

**Glycal **21a**.** This compound was prepared from dicobalt hexacarbonyl complex **9b** (70 mg, 0.08 mmol) and allyltrimethylsilane (27 mg, 0.24 mmol) according to the general procedure E. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 99:1) to give compound **21a** (45.3 mg, 70%) as a brownish oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.66-7.23 (m, 10 H), 5.80 (tdd,  $J = 14.3, 10.1, 7.2$  Hz, 1 H, H-2'), 5.30 (d,  $J = 4.0$  Hz, 1 H, H-2), 5.09-5.01 (m, 2 H, H-3'), 4.67 (d,  $J = 11.8$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.63 (d,  $J = 11.8$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.26 (dd,  $J = 11.0, 4.6$  Hz, 1 H, H-5), 4.07-3.83 (m, 3 H, H-4, 2 x H-6), 2.63-2.47 (m, 2 H, H-1'), 2.09 (td,  $J = 14.0, 8.2$  Hz, 1 H, H-3), 1.11-1.00 (m, 21 H, TIPS);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4 (x 6), 149.0, 138.8, 138.3, 136.6, 129.8 (x 2), 128.8 (x 2), 128.4 (x 2), 127.8, 127.7 (x 2), 127.6, 116.8, 104.5, 91.3, 86.6, 75.7, 72.5, 71.4, 62.7, 35.5, 34.5, 18.2 (x 6), 12.1 (x 3).

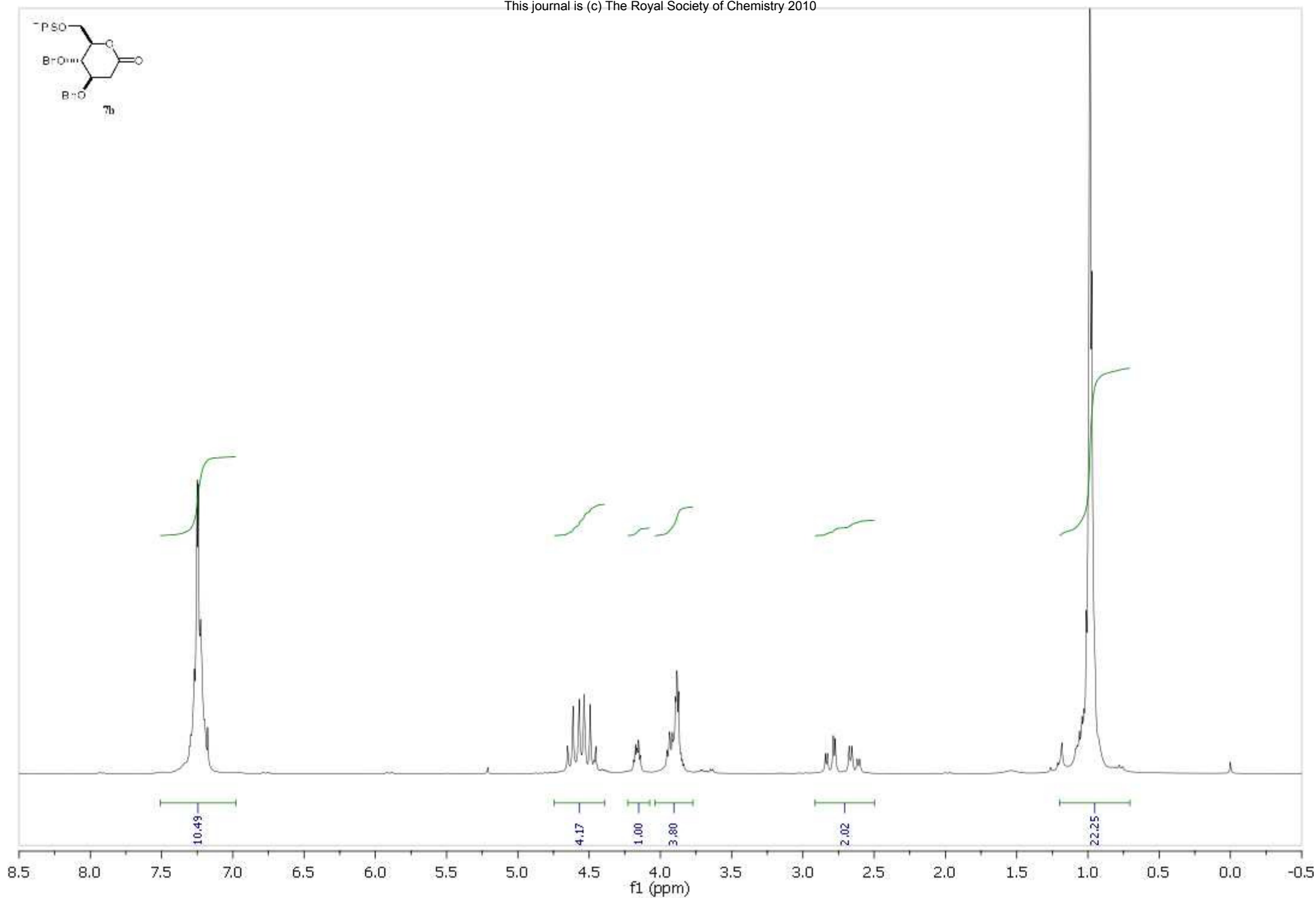
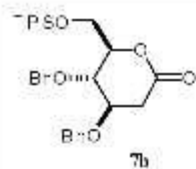
Glycal **21b**. This compound was prepared from dicobalt hexacarbonyl complex **9b** (92 mg, 0.10 mmol) and N-methylindol (39 mg, 0.30 mmol) according to the general procedure E. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 99:1) to give compound **21b** (52 mg, 59%) as a brownish oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.63-6.73 (m, 15 H), 5.48 (d,  $J$  = 3.6 Hz, 1 H, H-2), 4.54 (d,  $J$  = 11.4 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.45 (d,  $J$  = 11.3 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.28 (dd,  $J$  = 9.6, 4.4 Hz, 1 H, H-5), 4.22-4.11 (m, 3 H, H-4, H-6), 3.98 (d,  $J$  = 4.3 Hz, 1 H, H-3), 3.63 (s, 3 H, Me), 1.01-0.95 (m, 21 H, TIPS);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7 (x 6), 149.5, 138.9, 138.5, 137.3, 130.1 (x 2), 129.1, 128.9 (x 2), 128.5, 128.4 (x 2), 128.2 (x 3), 127.7, 121.8, 119.9, 119.2, 114.3, 109.6, 104.9, 92.3, 86.9, 77.6, 73.7, 72.6, 63.0, 33.1 (x 2), 18.5 (x 6), 12.4 (x 3).

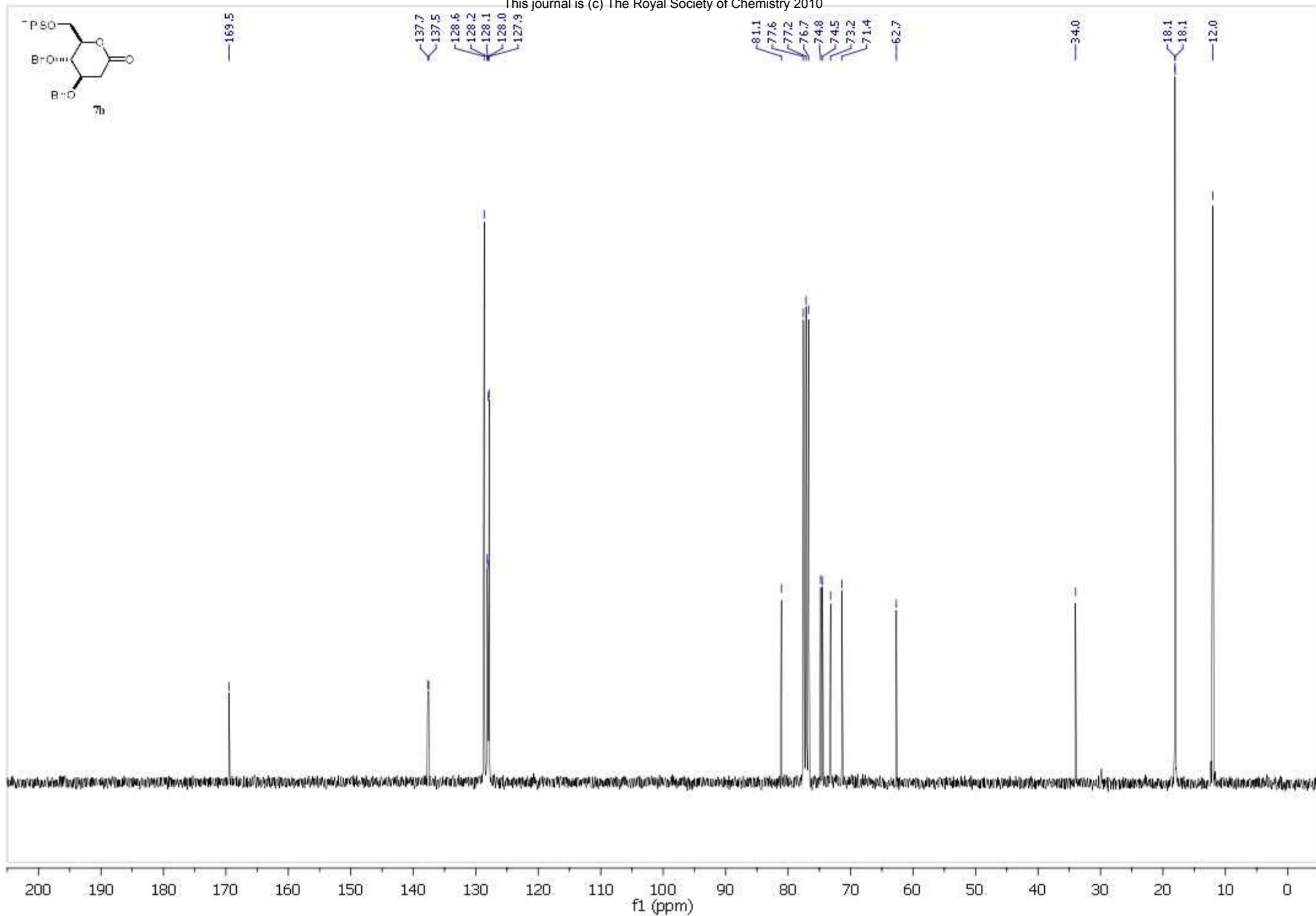
Glycal **21c**. This compound was prepared from dicobalt hexacarbonyl complex **9b** (84 mg, 0.10 mmol) and N-methylpyrrole (24 mg, 0.29 mmol) according to the general procedure E. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 99:1) to give compound **21c** (47 mg, 57%) as a brownish oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.61-6.96 (m, 10 H), 6.48 (s, 1 H, H-5'), 6.04-6.01 (m, 1 H, H-3'), 5.90 (dd,  $J$  = 3.2, 1.6 Hz, 1 H, H-4'), 5.39 (d,  $J$  = 4.0 Hz, 1 H, H-2), 4.57 (d,  $J$  = 12.0 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.47 (d,  $J$  = 12.9 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.33-3.70 (m, 4 H, H-4, H-5, H-6), 3.48-3.42 (m, 1 H, H-3), 3.35 (s, 3 H, Me);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.6 (x 6), 150.2, 138.9, 131.9, 130.0 (x 2), 129.1 (x 2), 128.7, 128.6 (x 2), 128.2, 128.1, 122.8 (x 2), 109.8, 107.1, 103.2, 91.6, 86.5, 76.5, 74.6, 73.0, 72.7, 62.7, 34.3, 31.8, 18.4 (x 6), 12.3 (x 3).

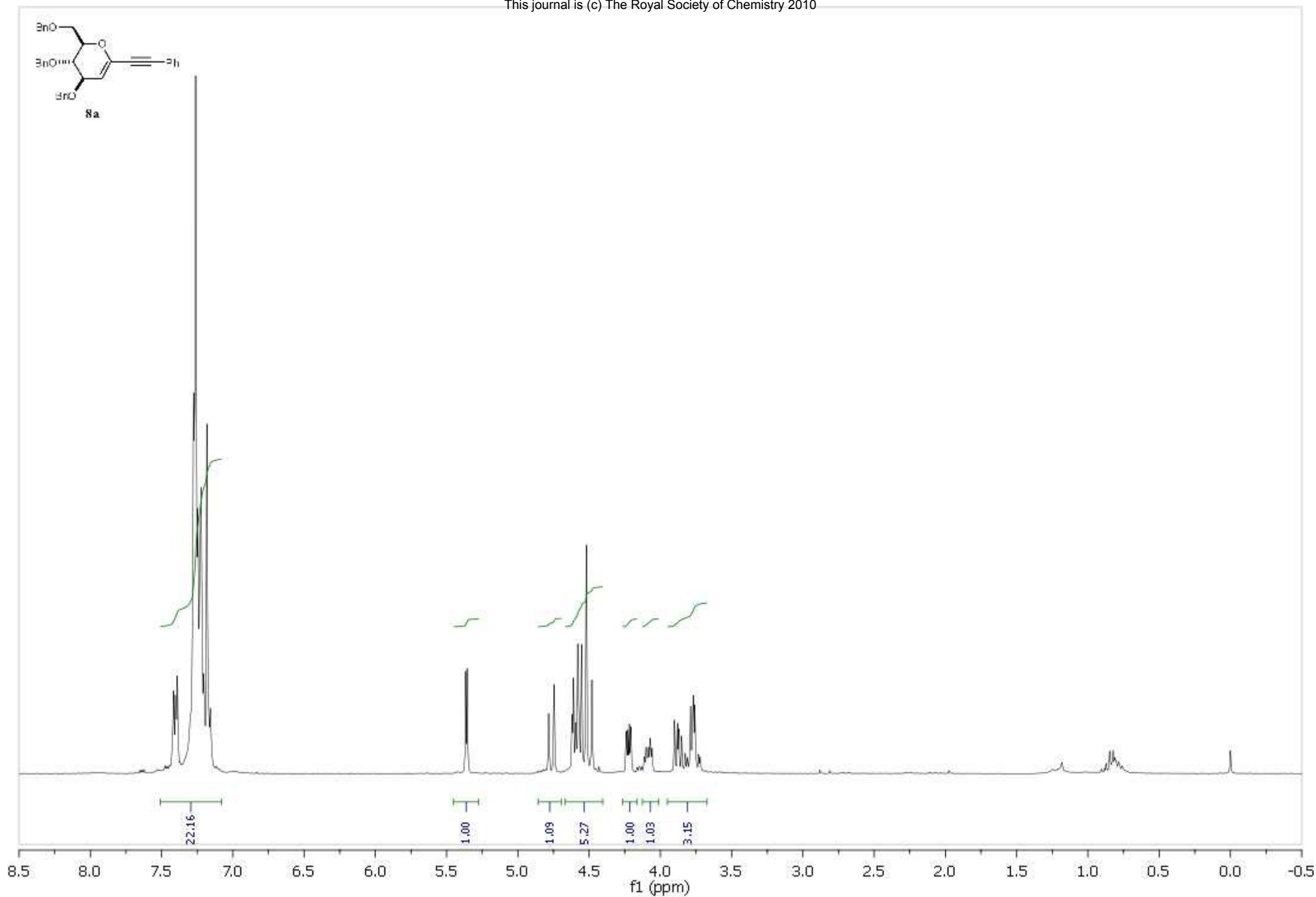
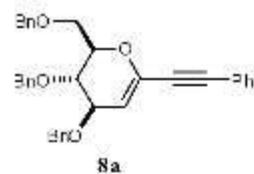
Glycal **21d**. This compound was prepared from dicobalt hexacarbonyl complex **9b** (73 mg, 0.08 mmol) and furan (17 mg, 0.24 mmol) according to the general procedure E. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 99:1) to give compound **21d** (62 mg, 57%) as a brownish oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.67-7.61 (m, 1 H, H-5'), 7.41-7.24 (m, 10 H, arom.), 6.34 (dd,  $J$  = 3.1, 1.9 Hz, 1H, H-4'), 6.11 (d,  $J$  = 3.2 Hz, 1 H, H-3'), 5.42 (d,  $J$  = 5.0 Hz, 1 H, H-2), 4.93 (, d,  $J$  = 11.0 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.55 (d,  $J$  = 11.1 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 4.23 (dd,  $J$

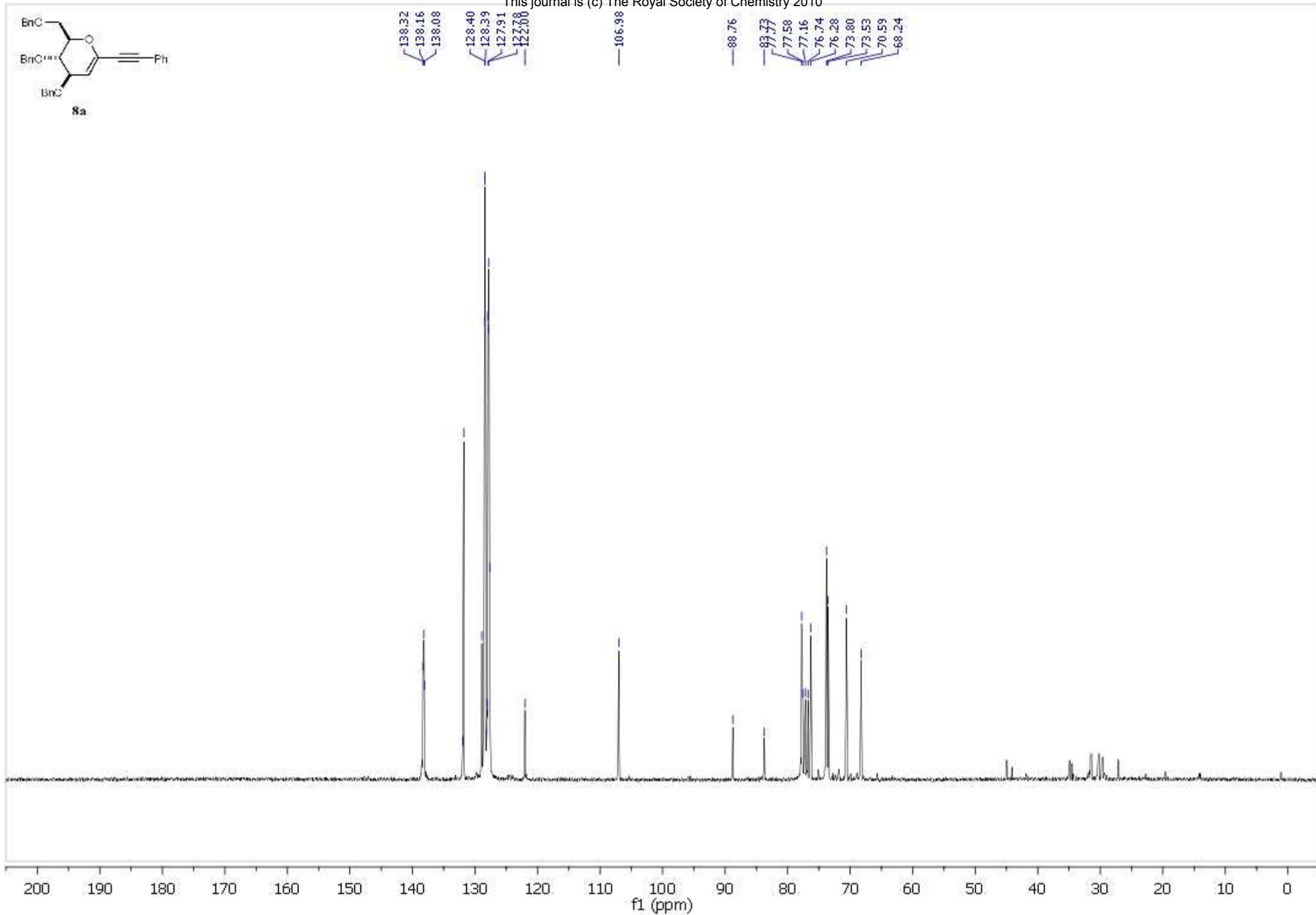
= 8.4, 5.8 Hz, 1 H, H-5), 4.16-4.00 (m, 4 H, H-3, H-4, H-6), 1.07-1.00 (m, 21 H, TIPS);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5 (x 6), 155.0, 151.7, 142.2, 138.7, 130.0 (x 2), 129.10 (x 2), 128.5 (x 2), 128.3 (x 2), 128.2, 128.0, 127.9, 110.7, 108.8, 100.5, 92.0, 85.8, 76.6, 72.7, 72.0, 62.7, 35.9, 18.4 (x 6), 12.4 (x 3).

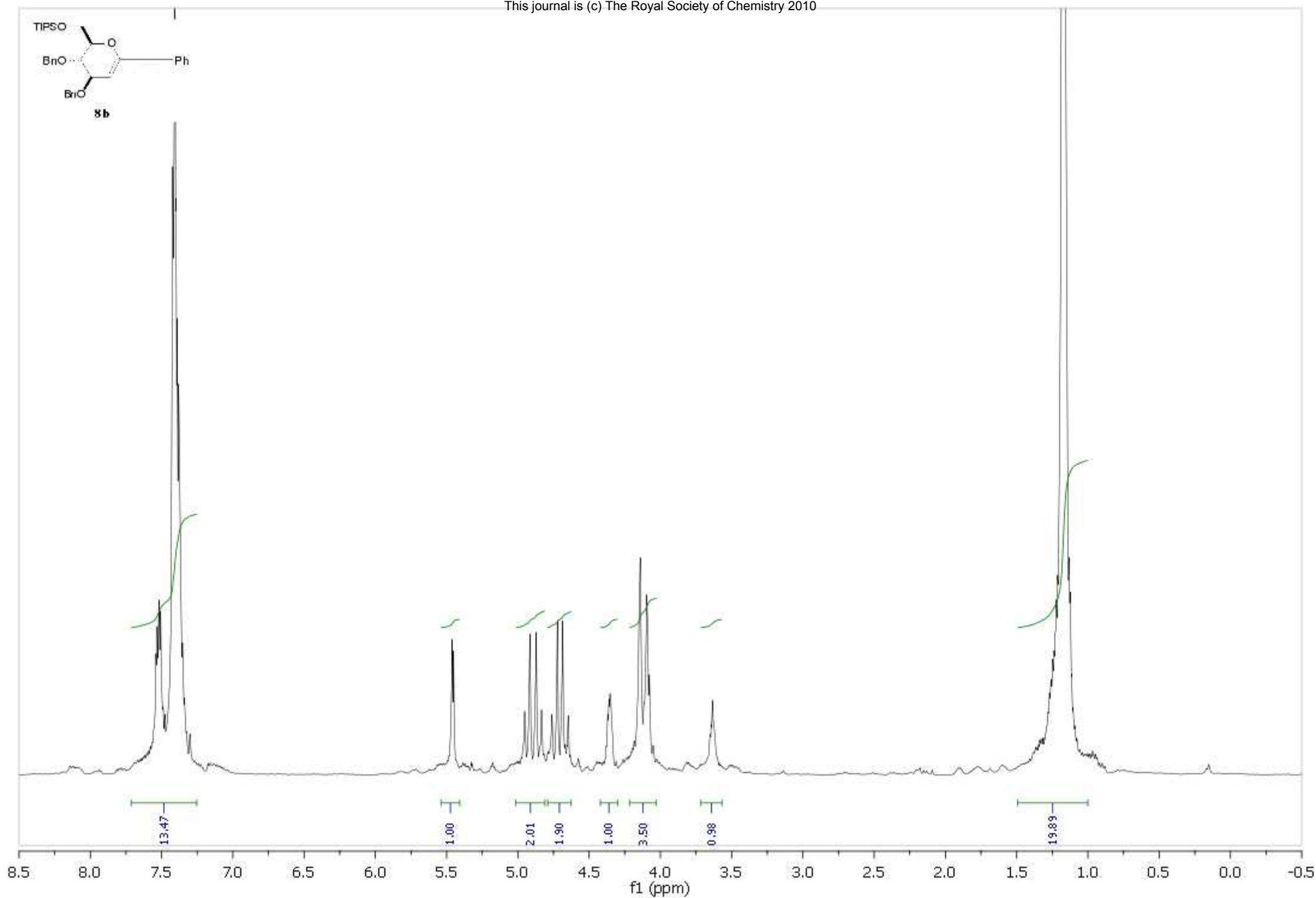
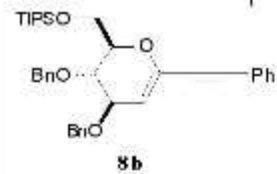


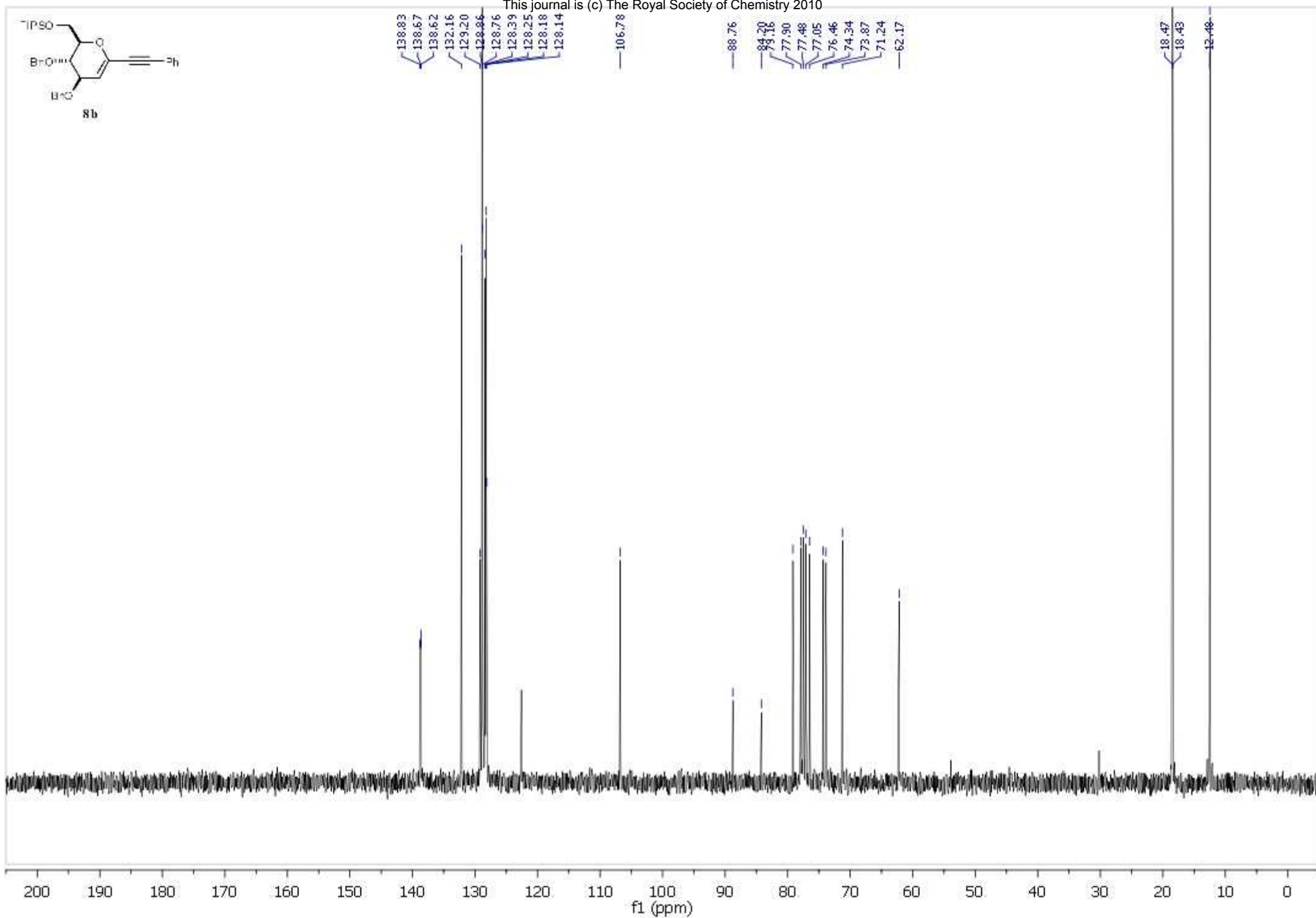


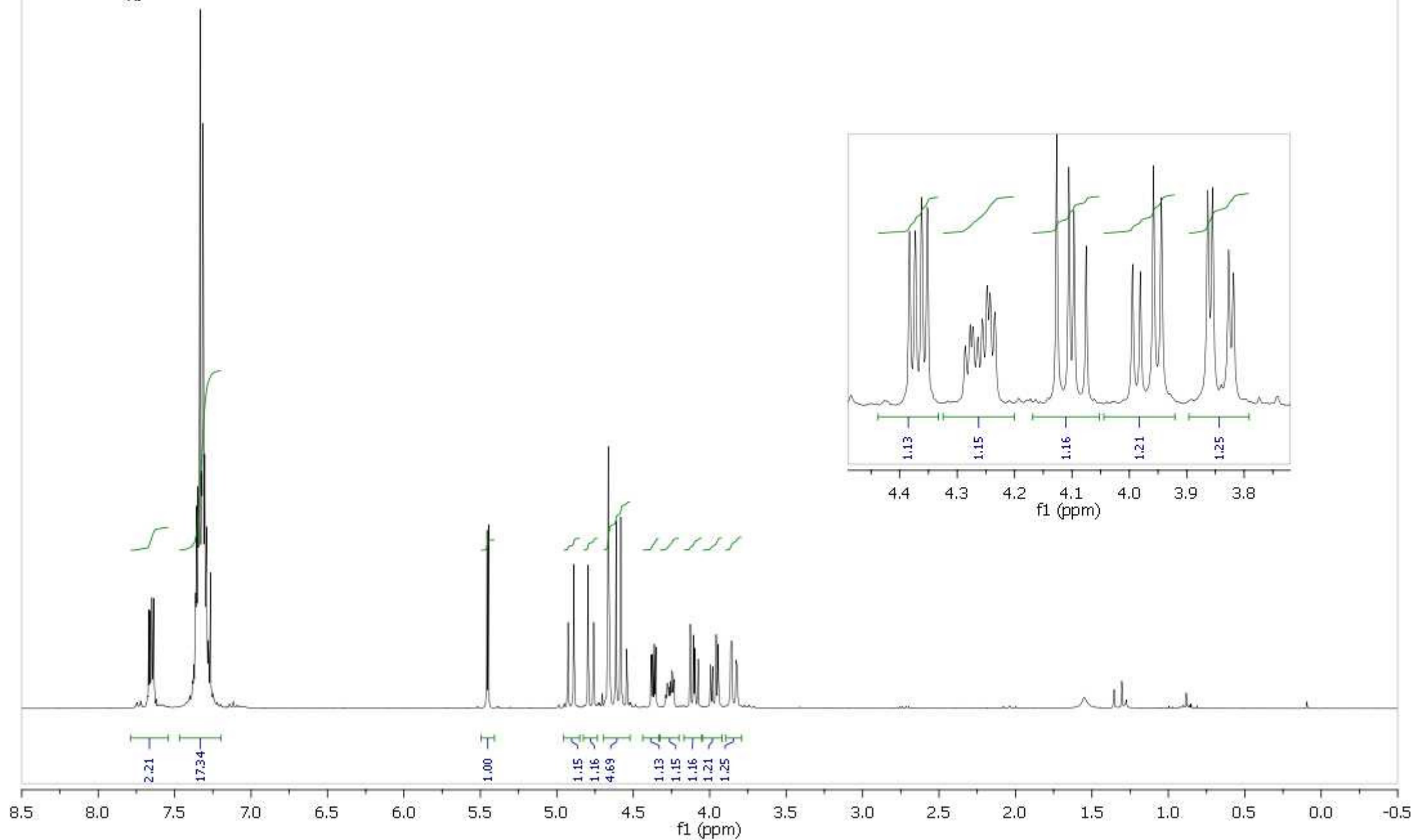
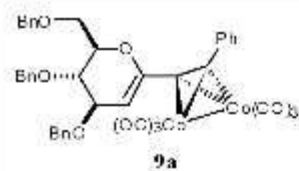


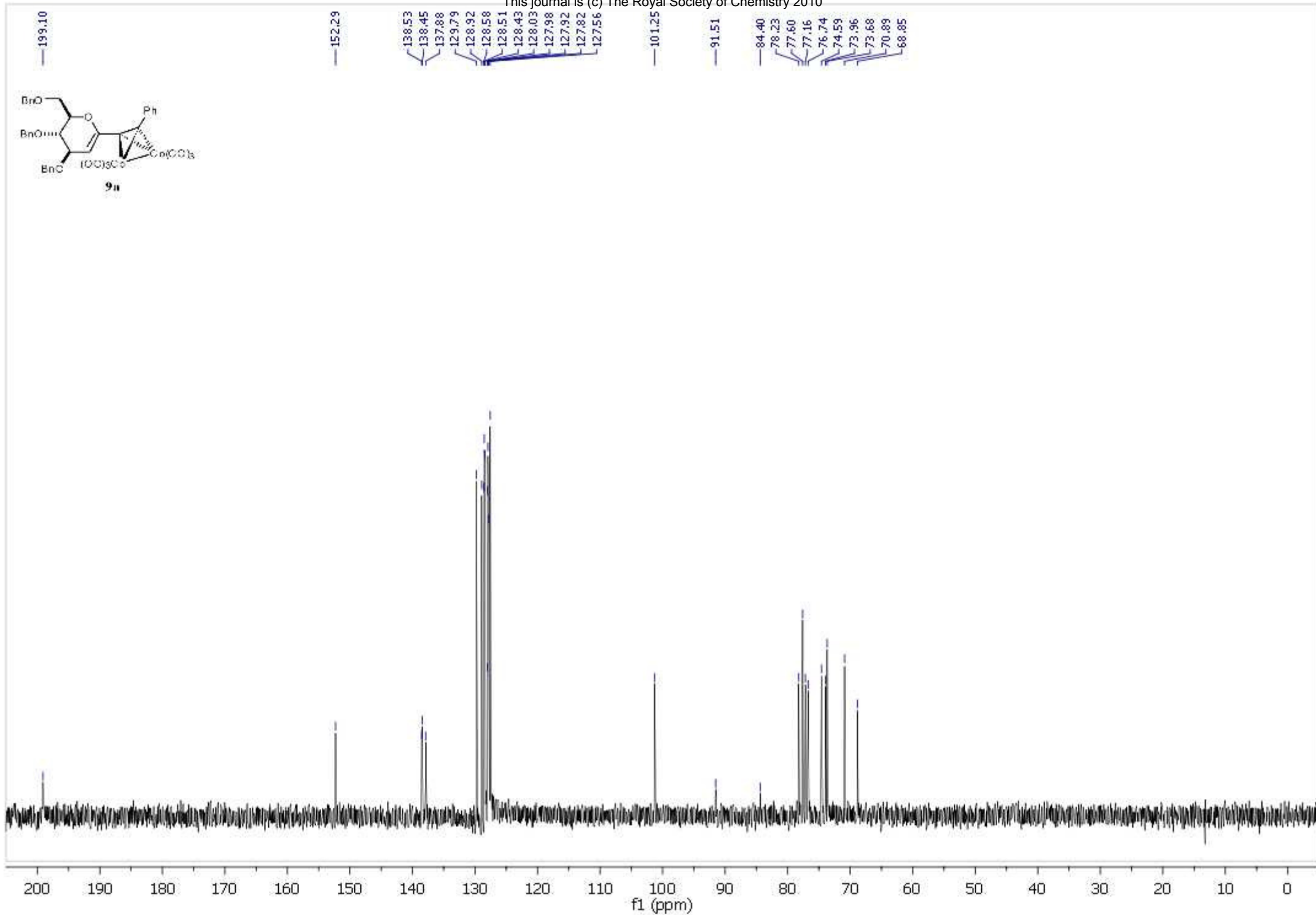




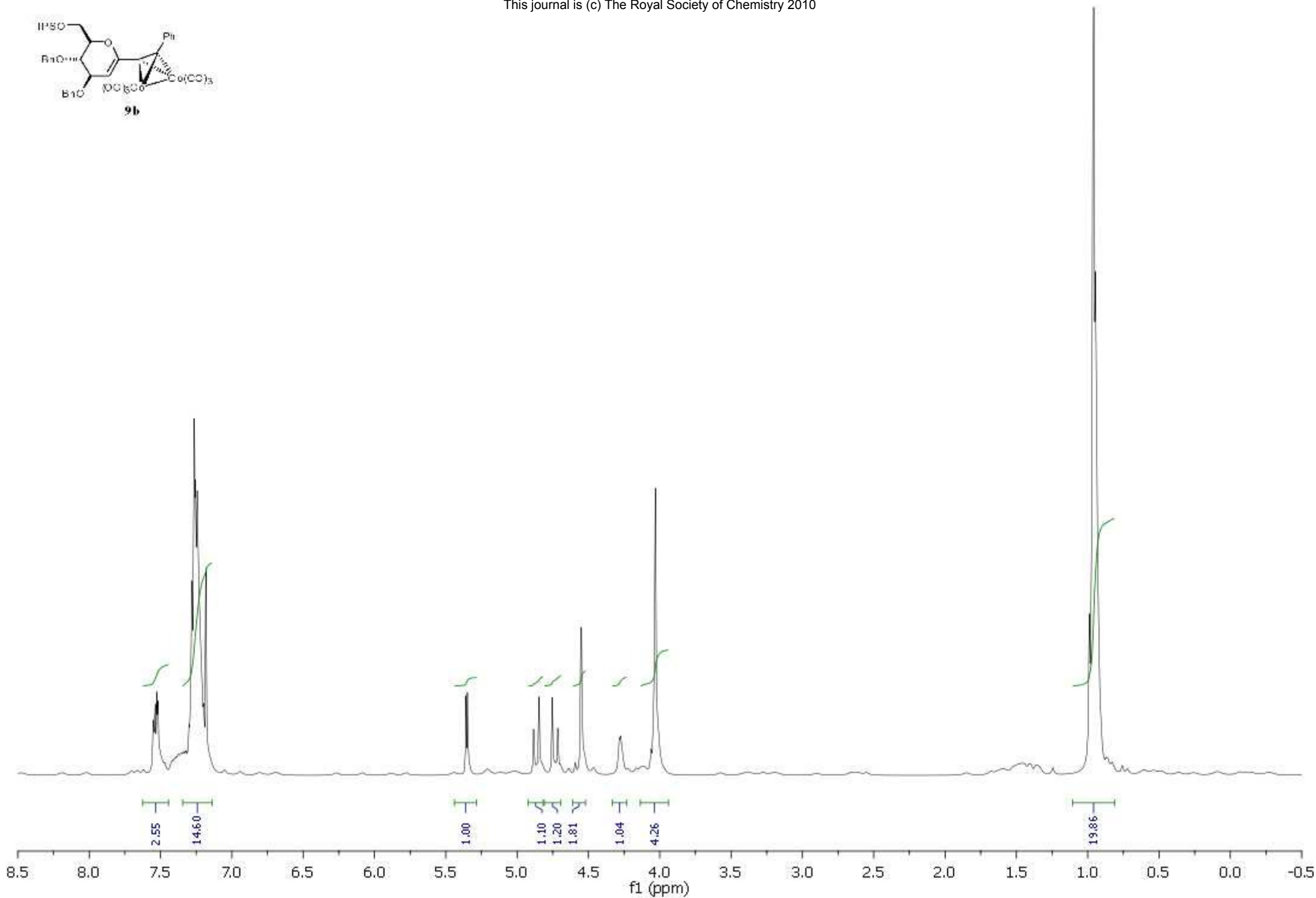
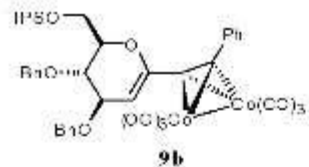


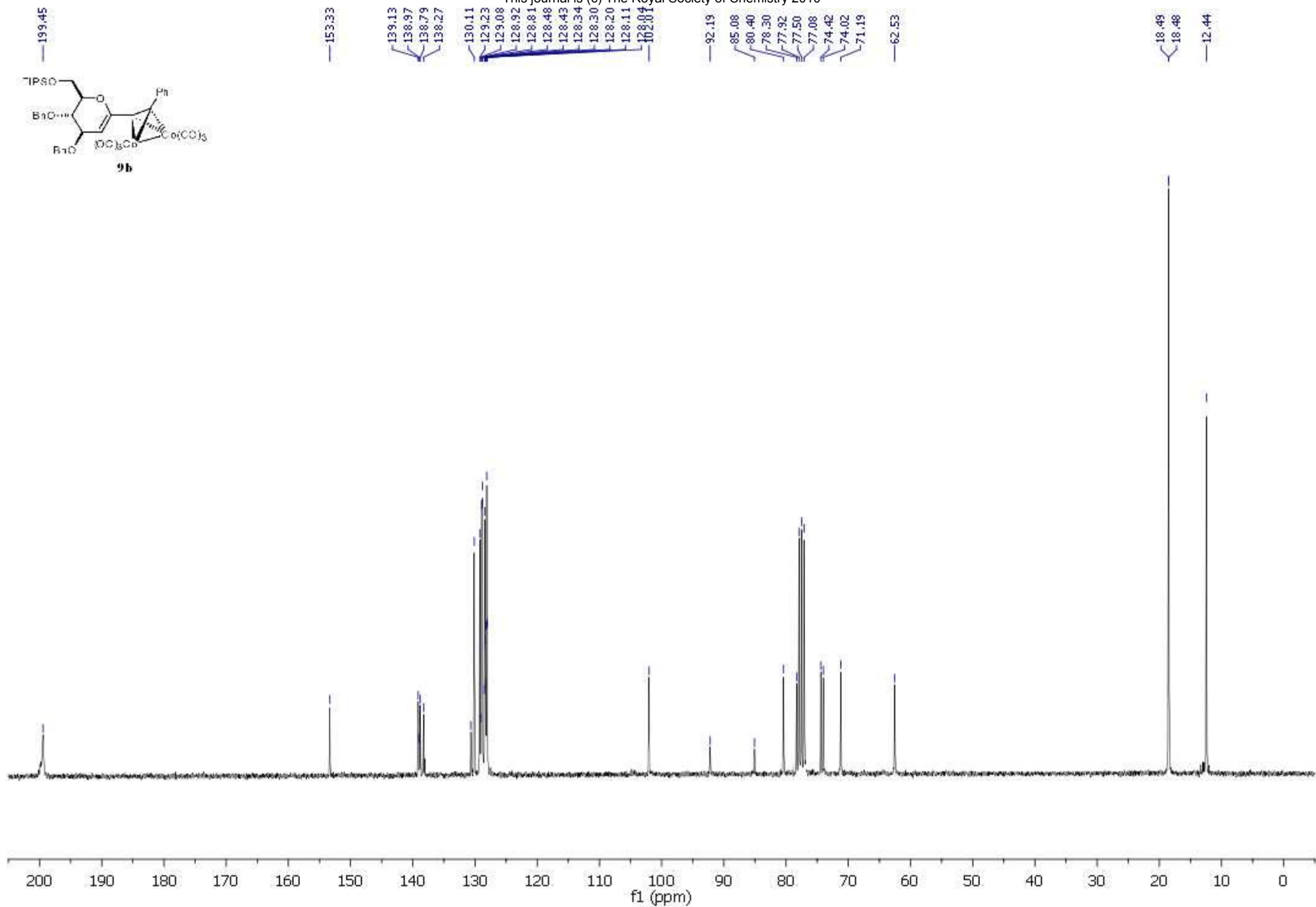
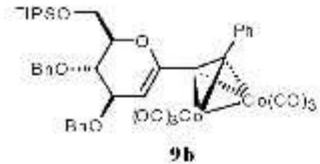


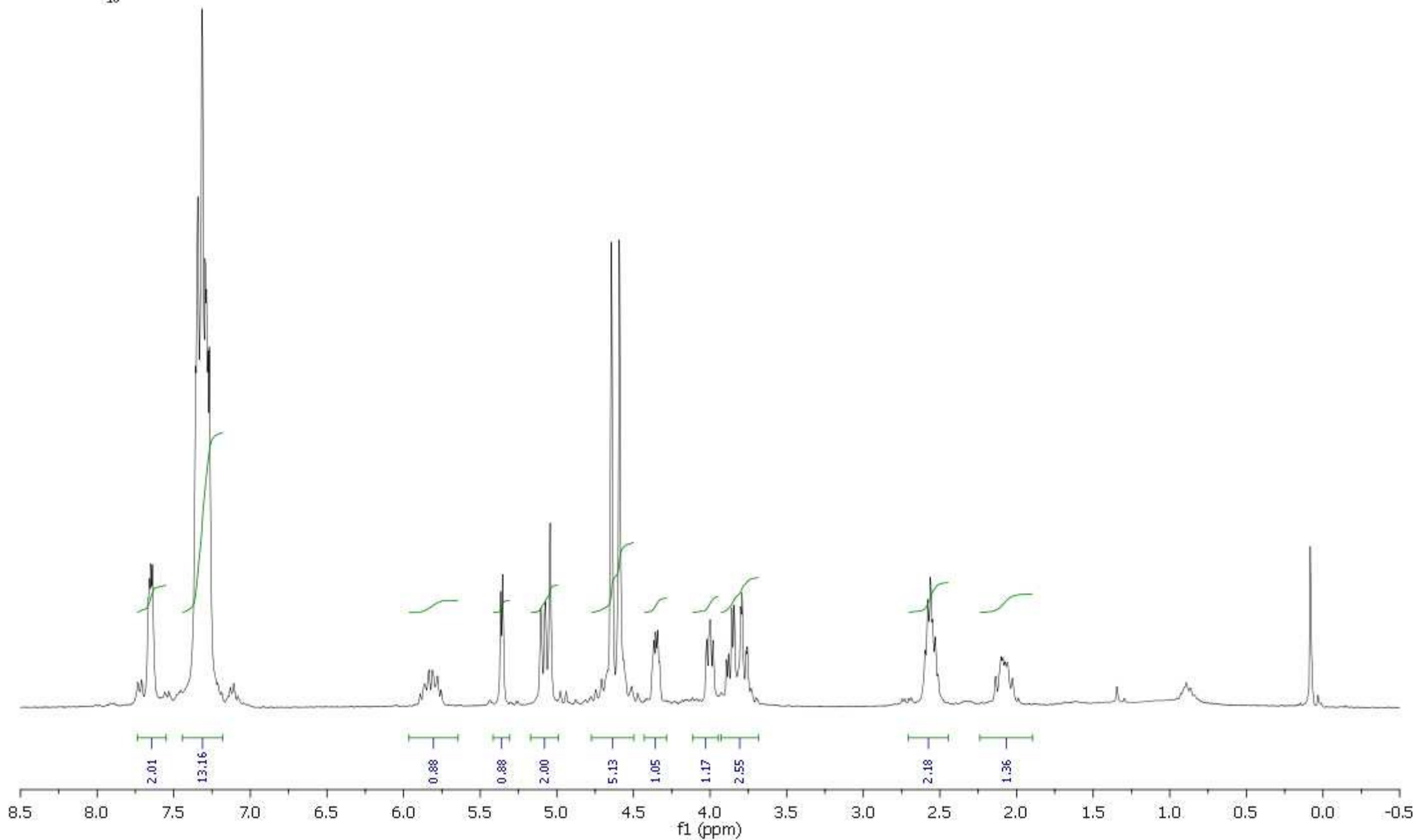
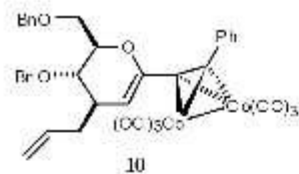


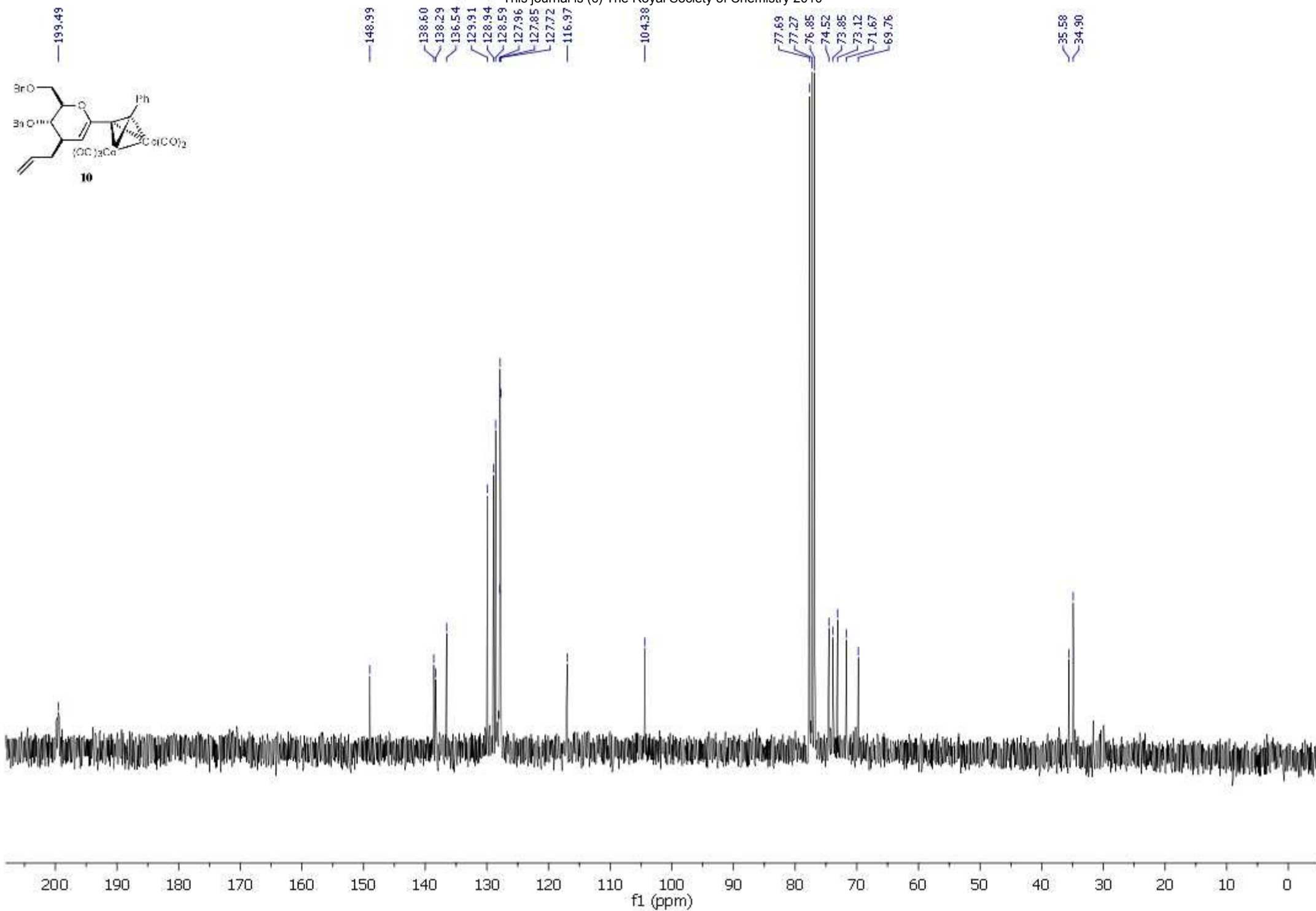


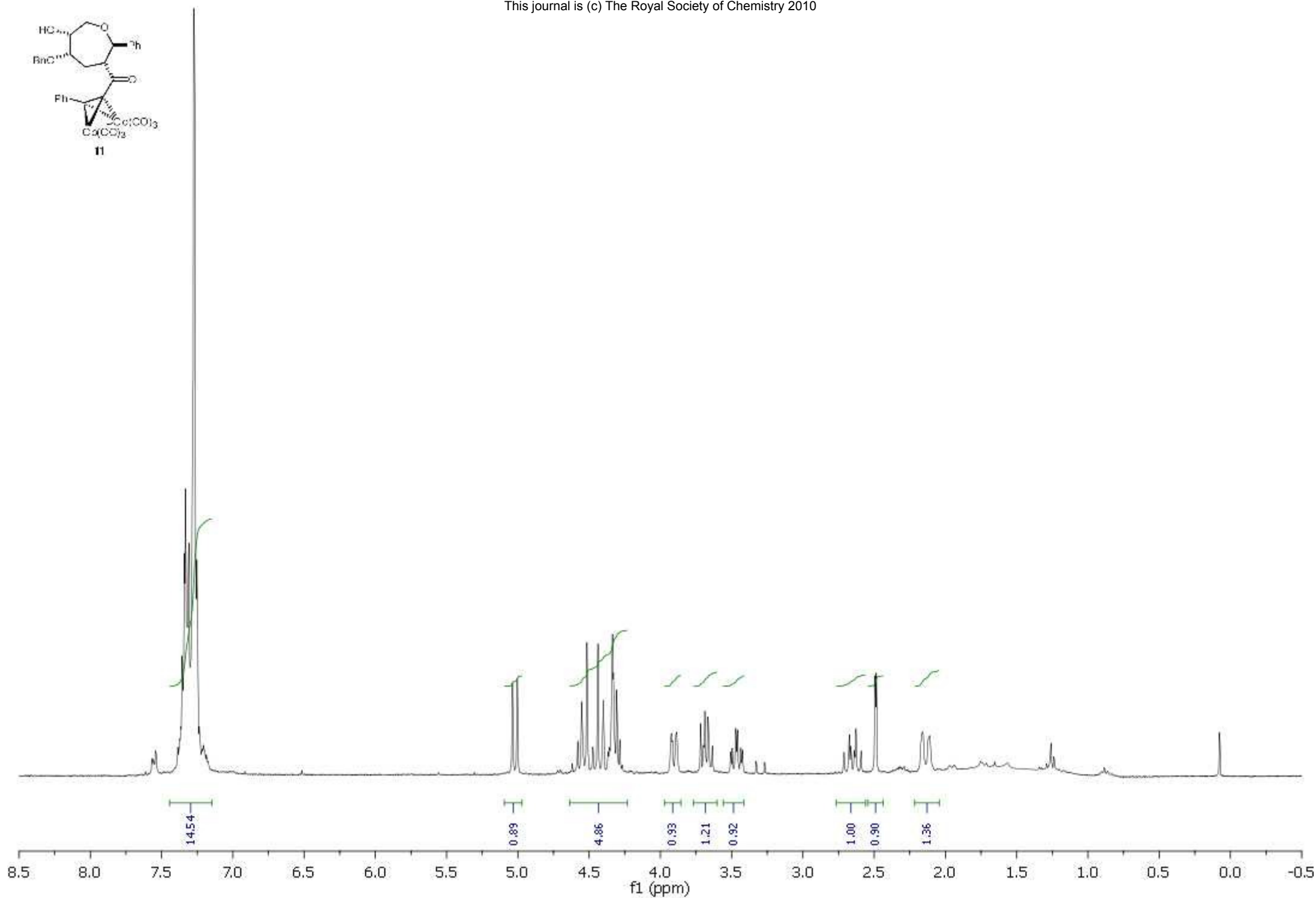
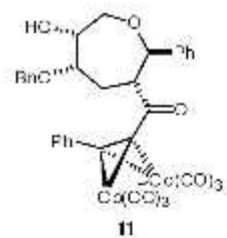


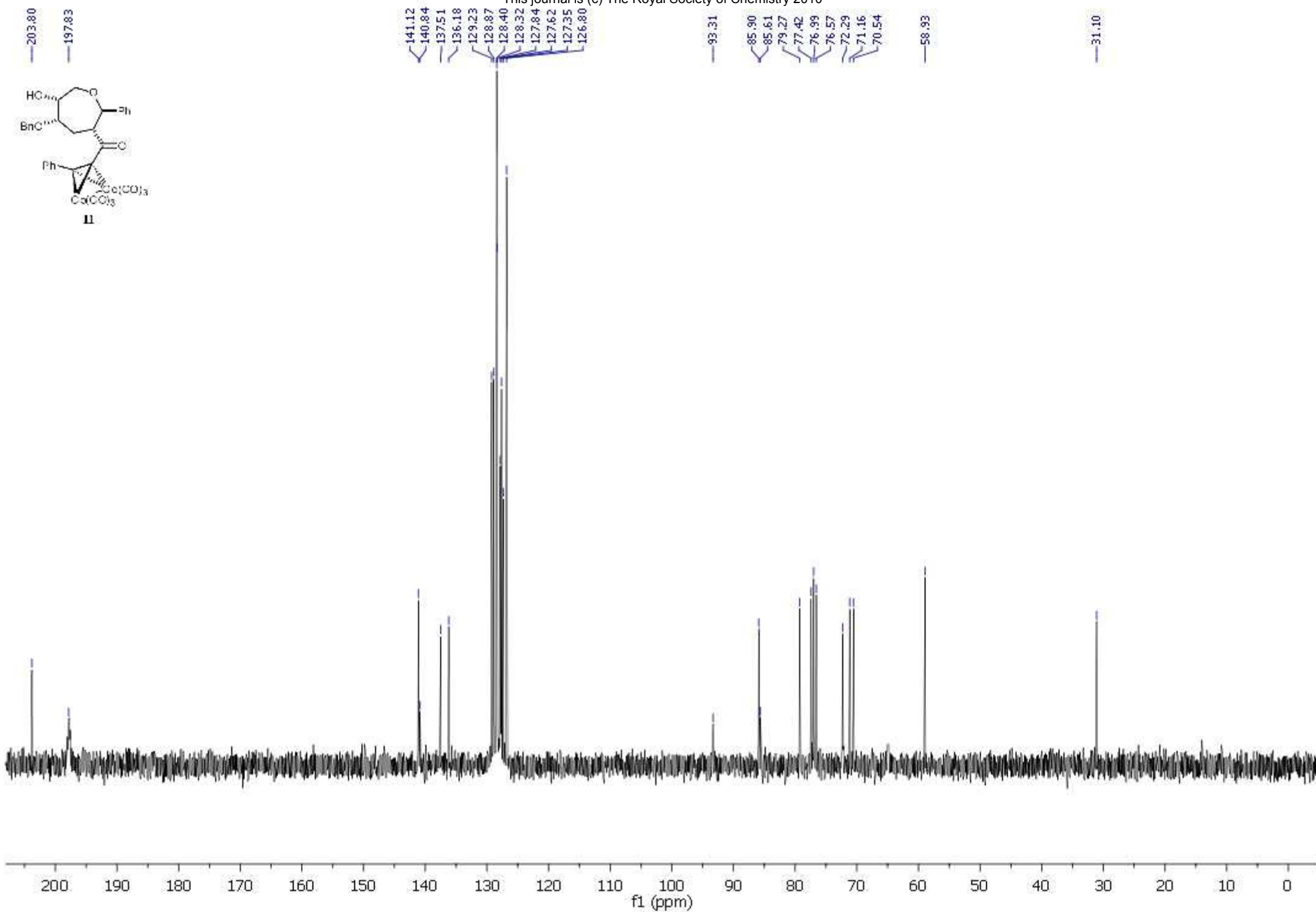


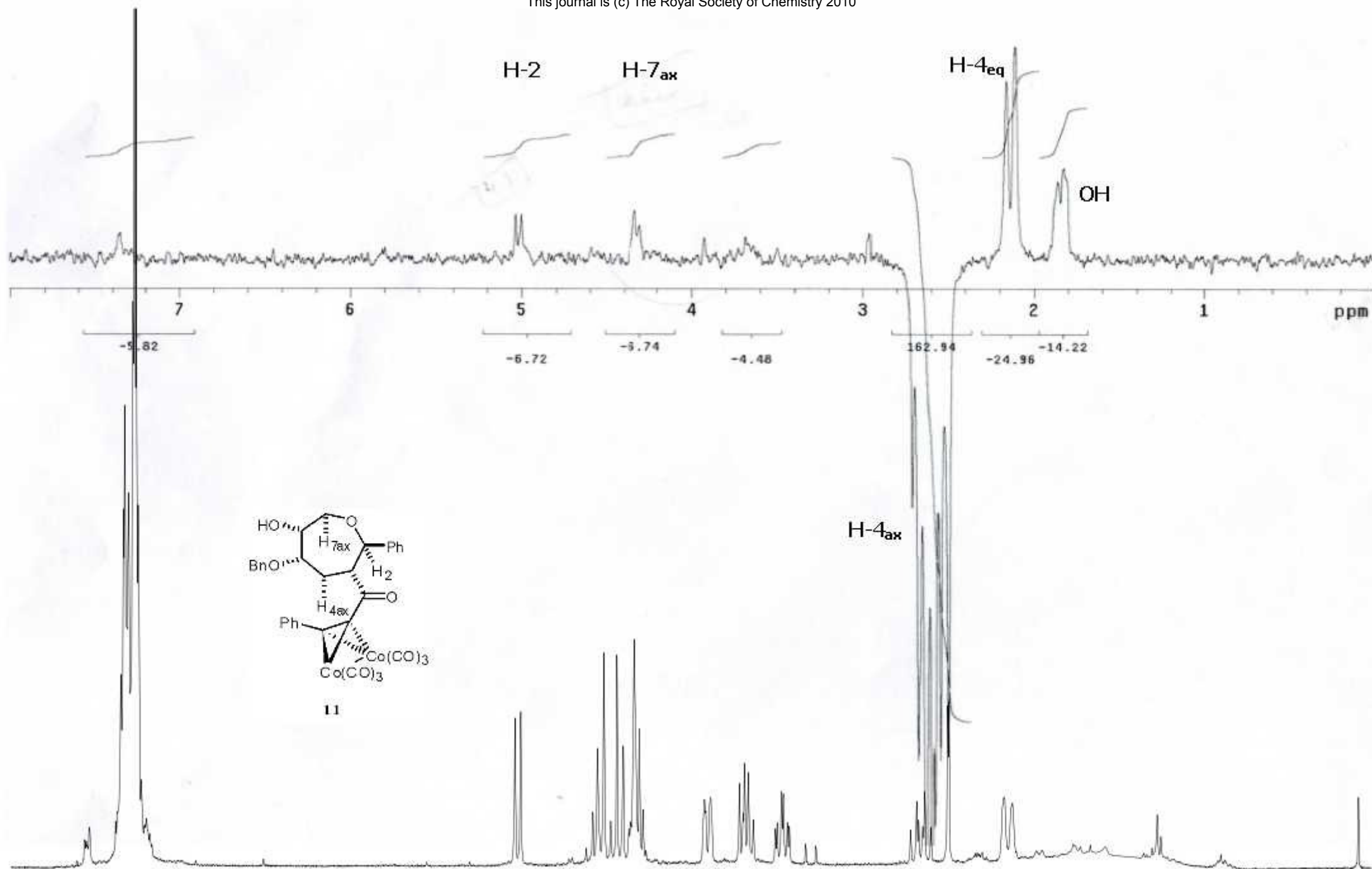


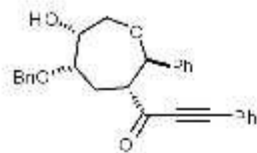




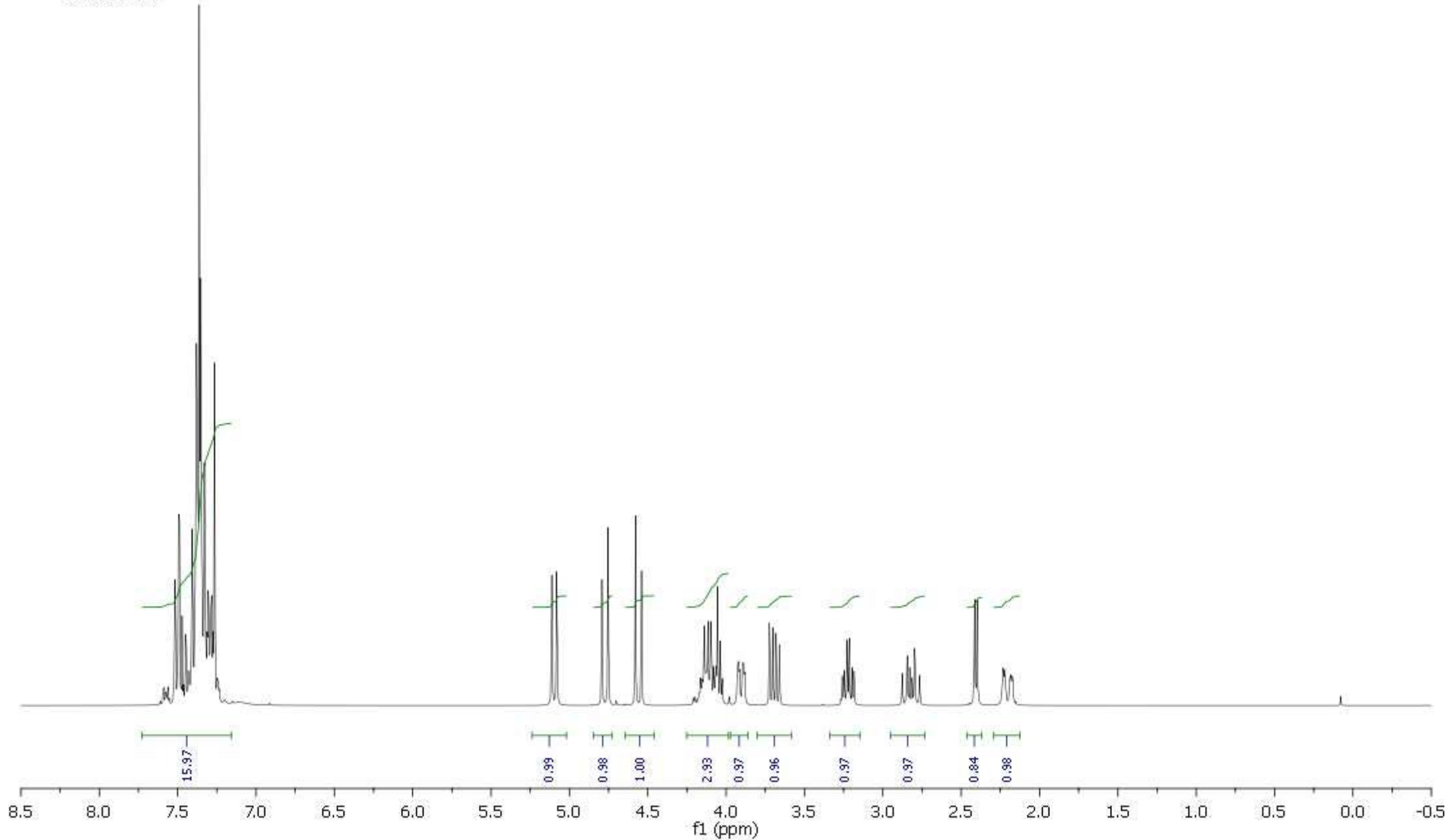




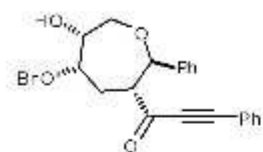




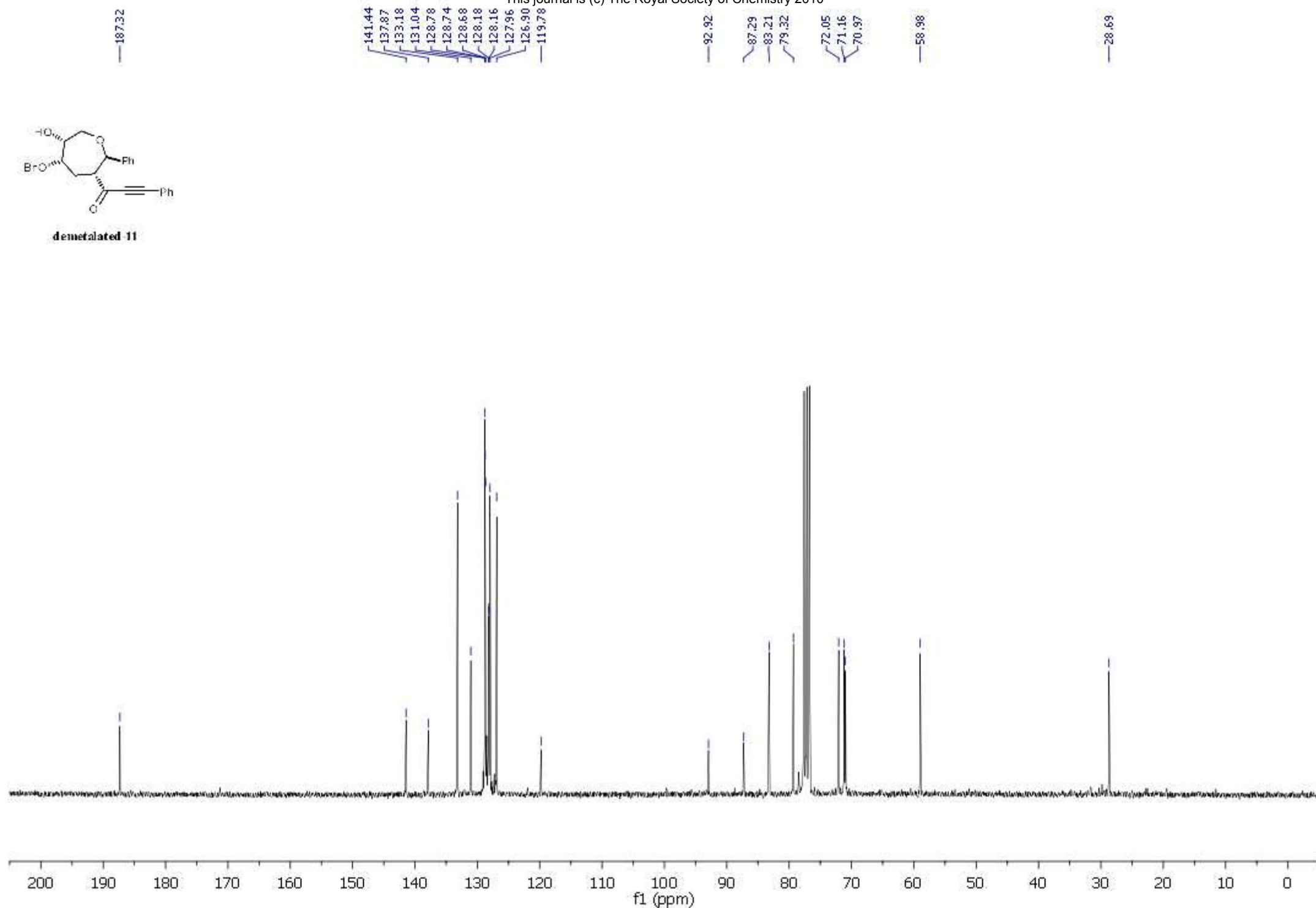
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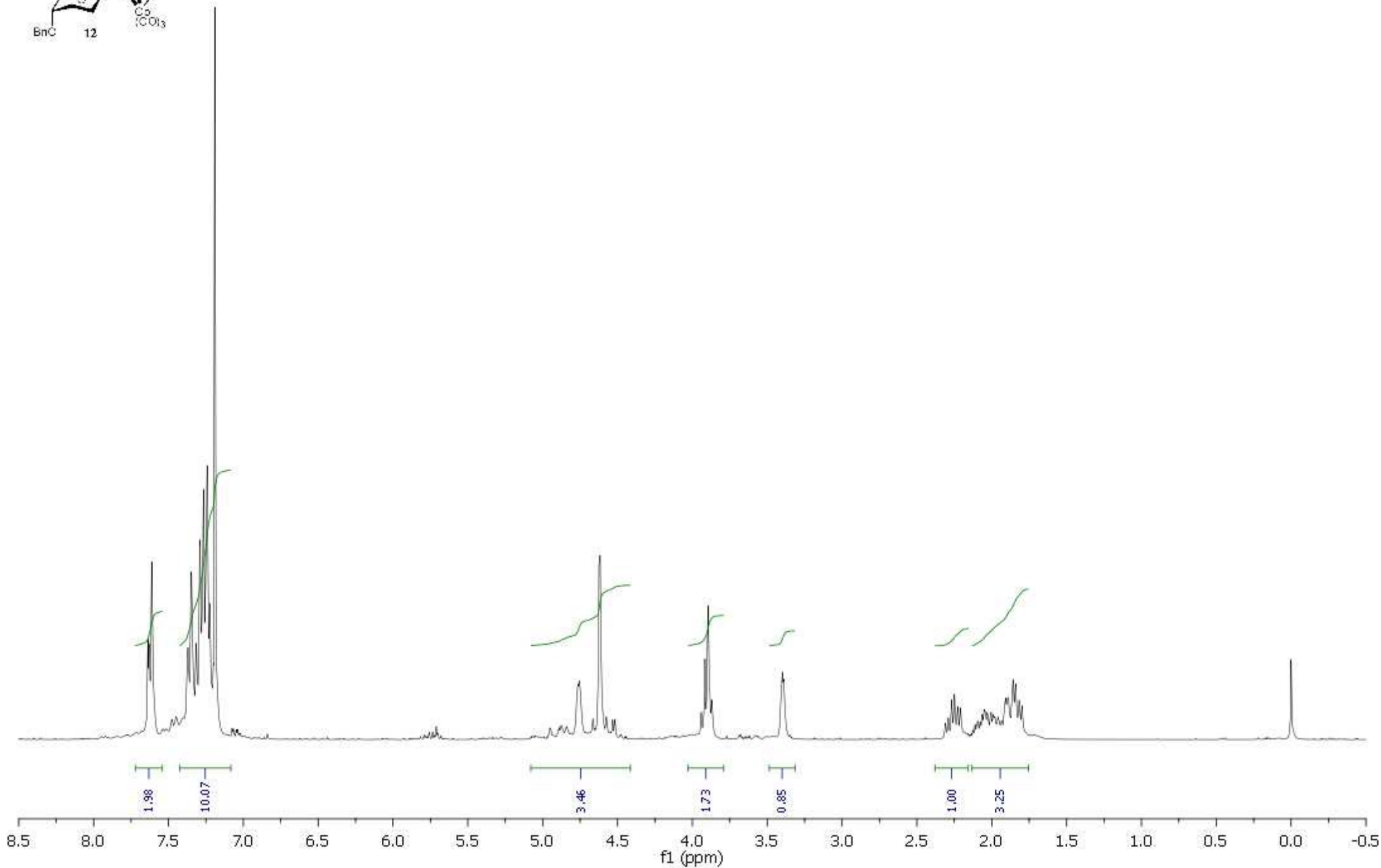
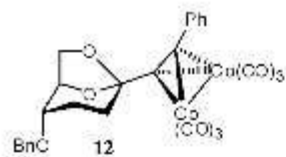


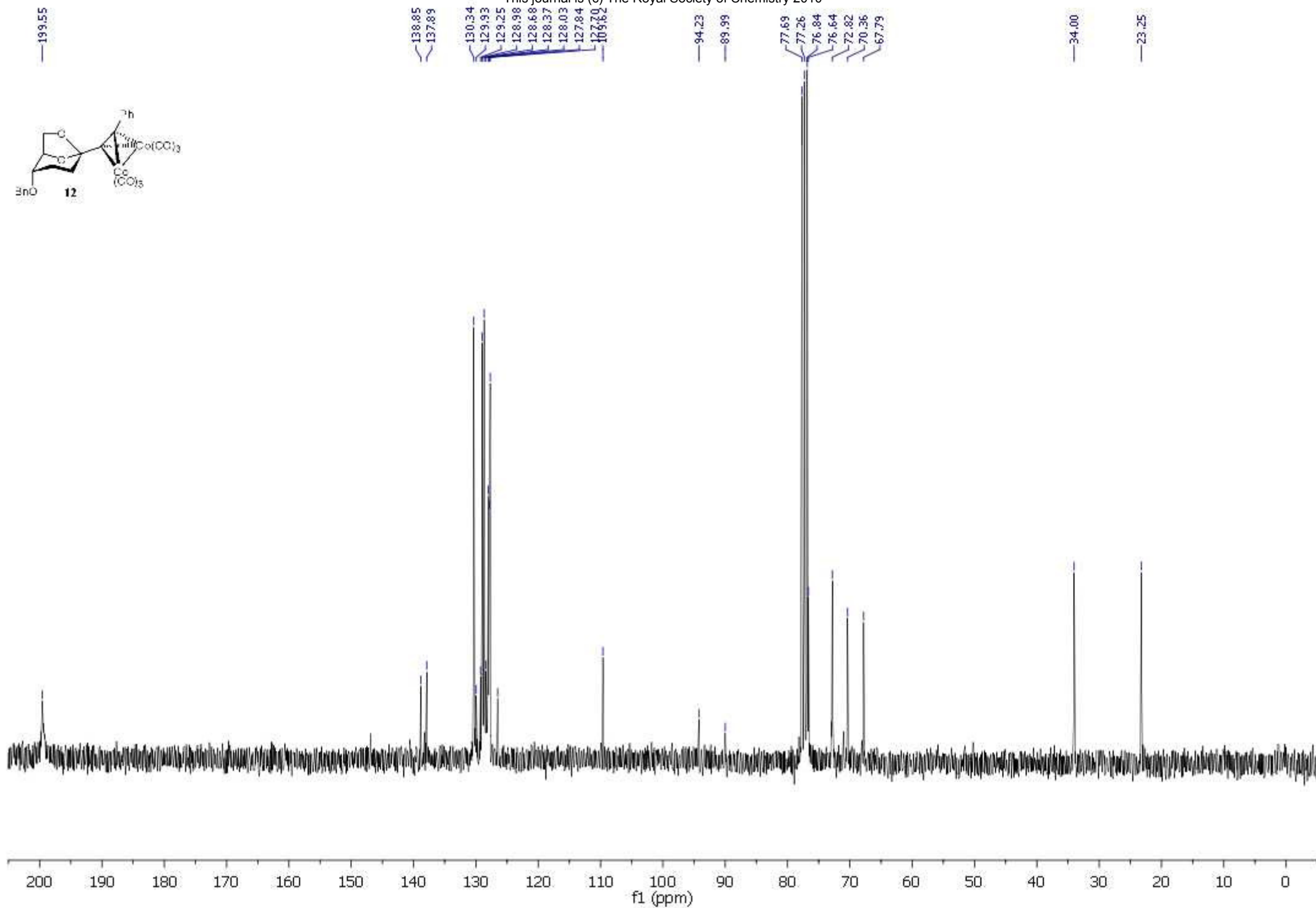
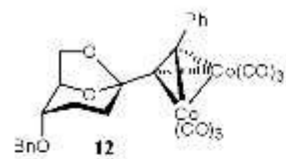


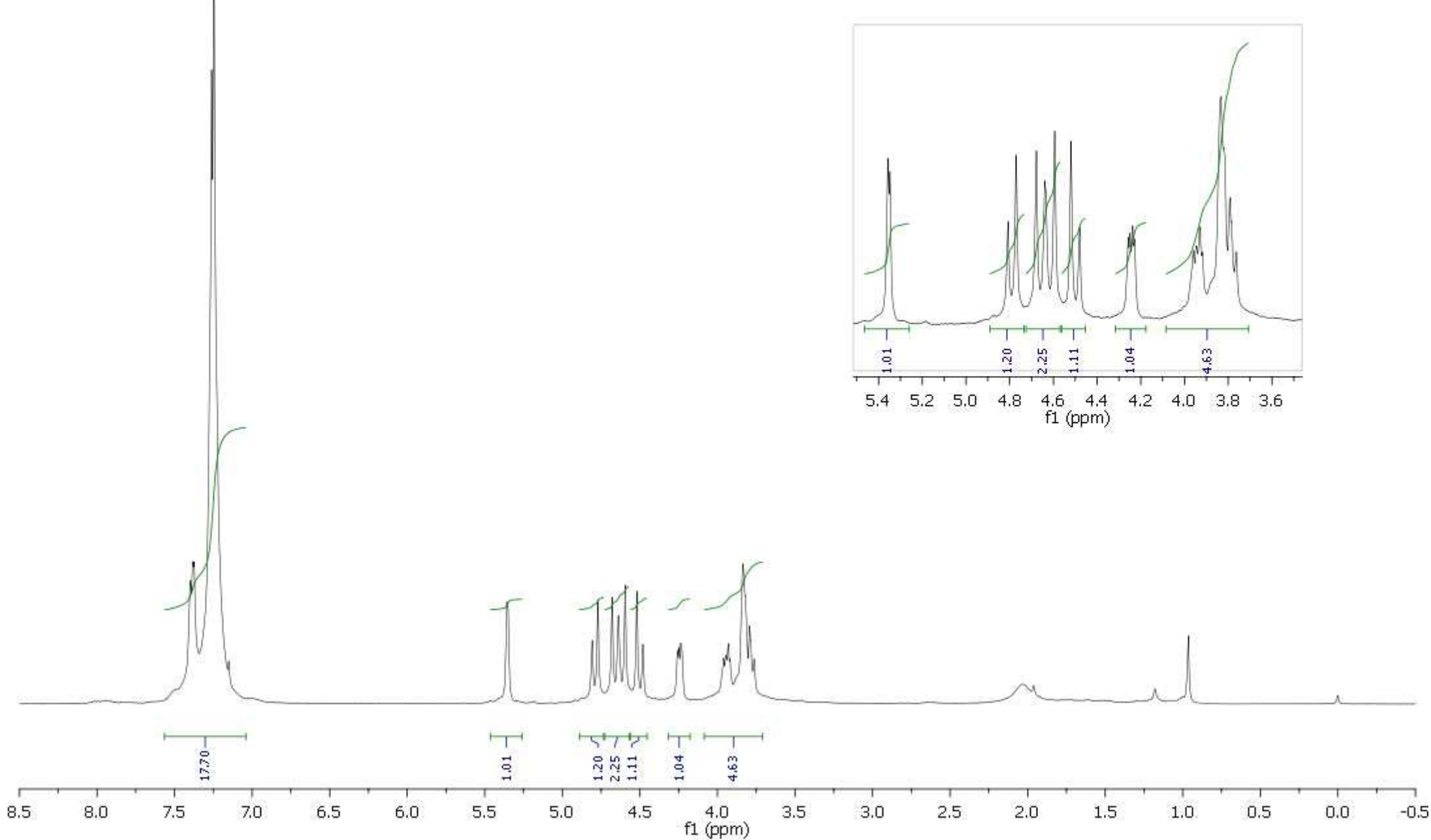
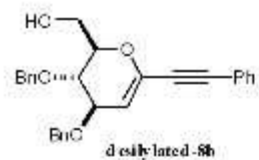


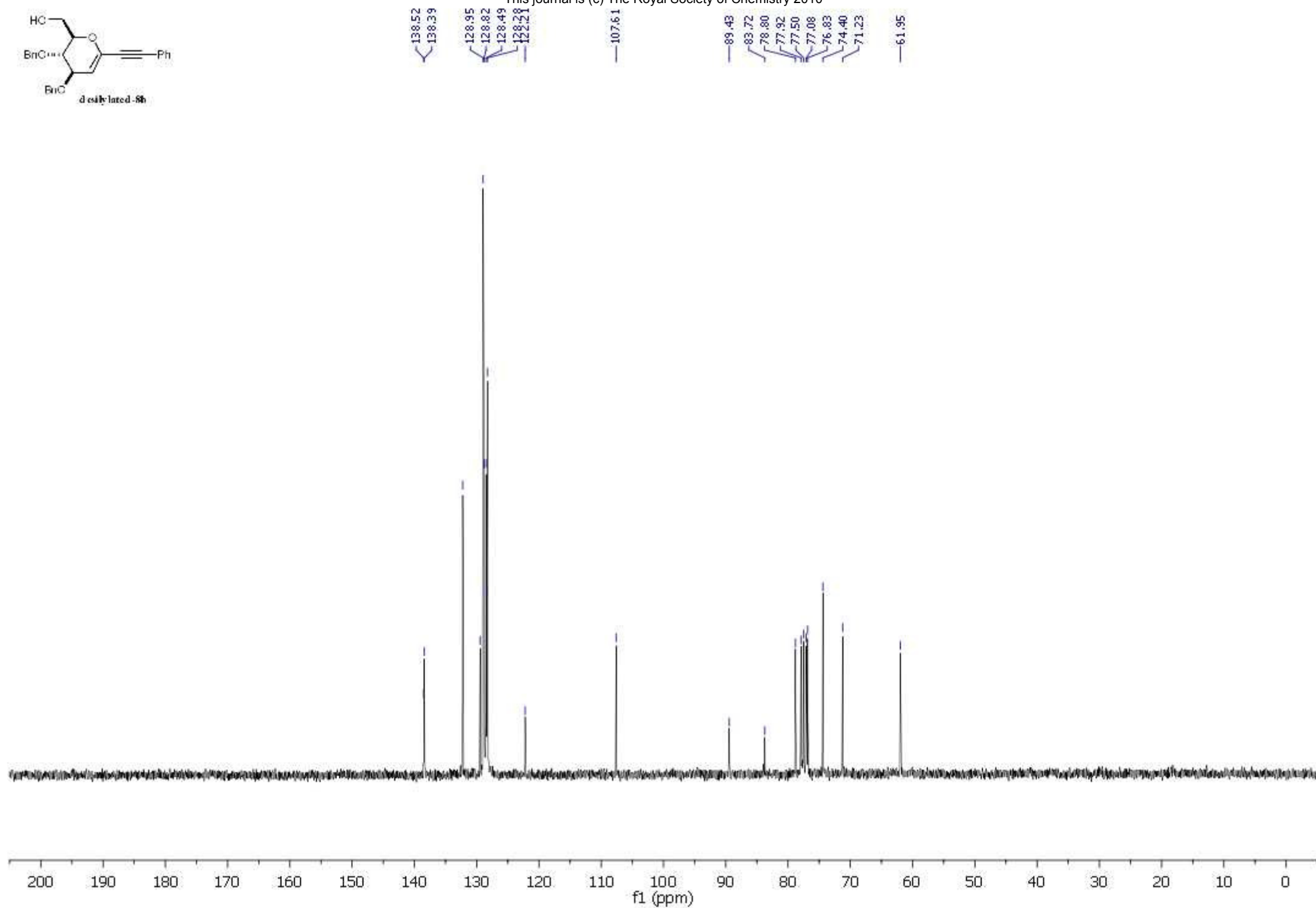
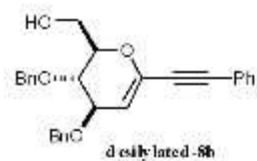
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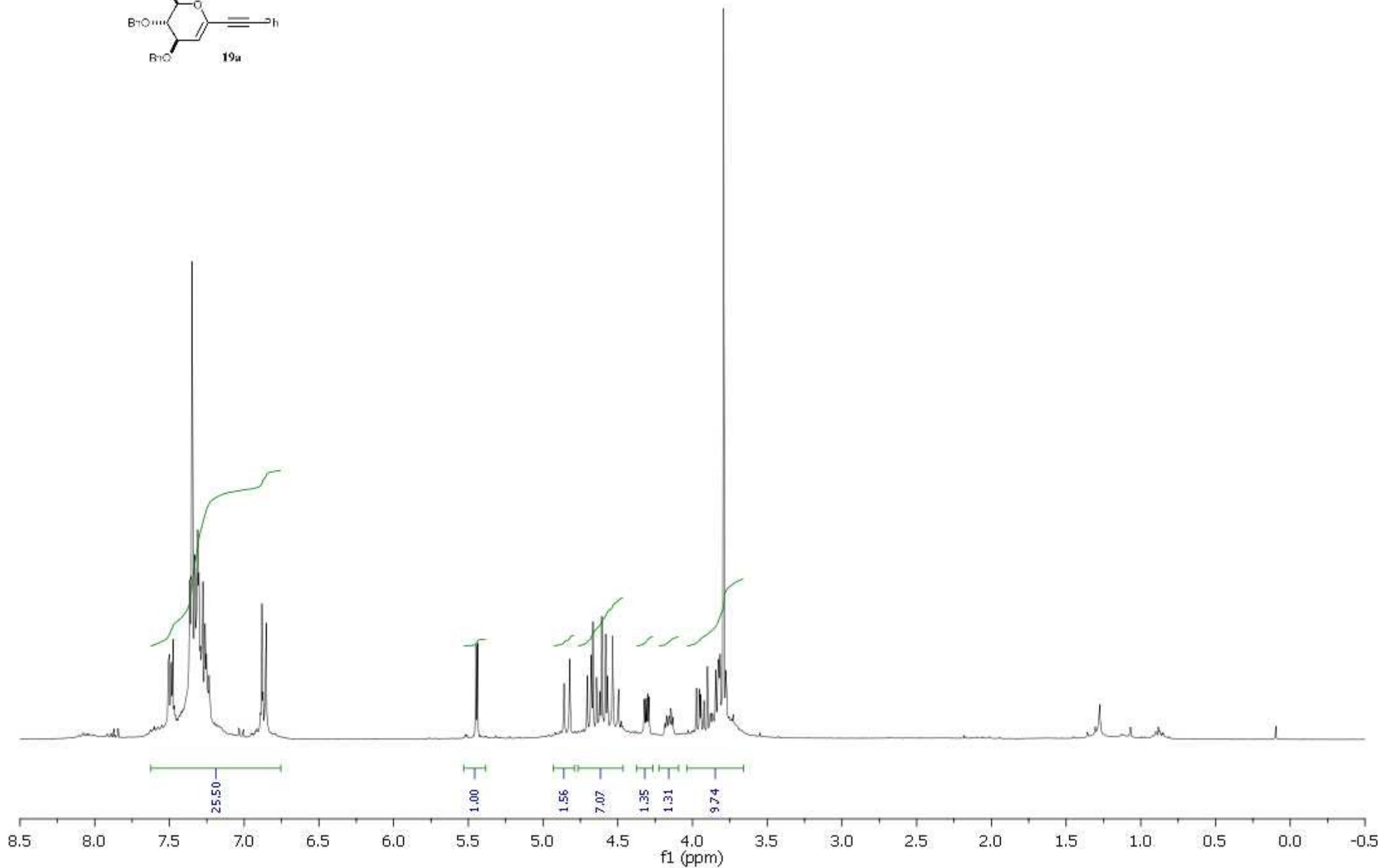
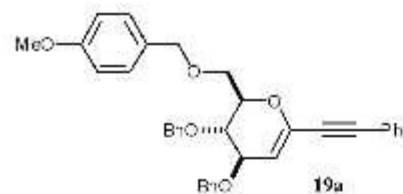


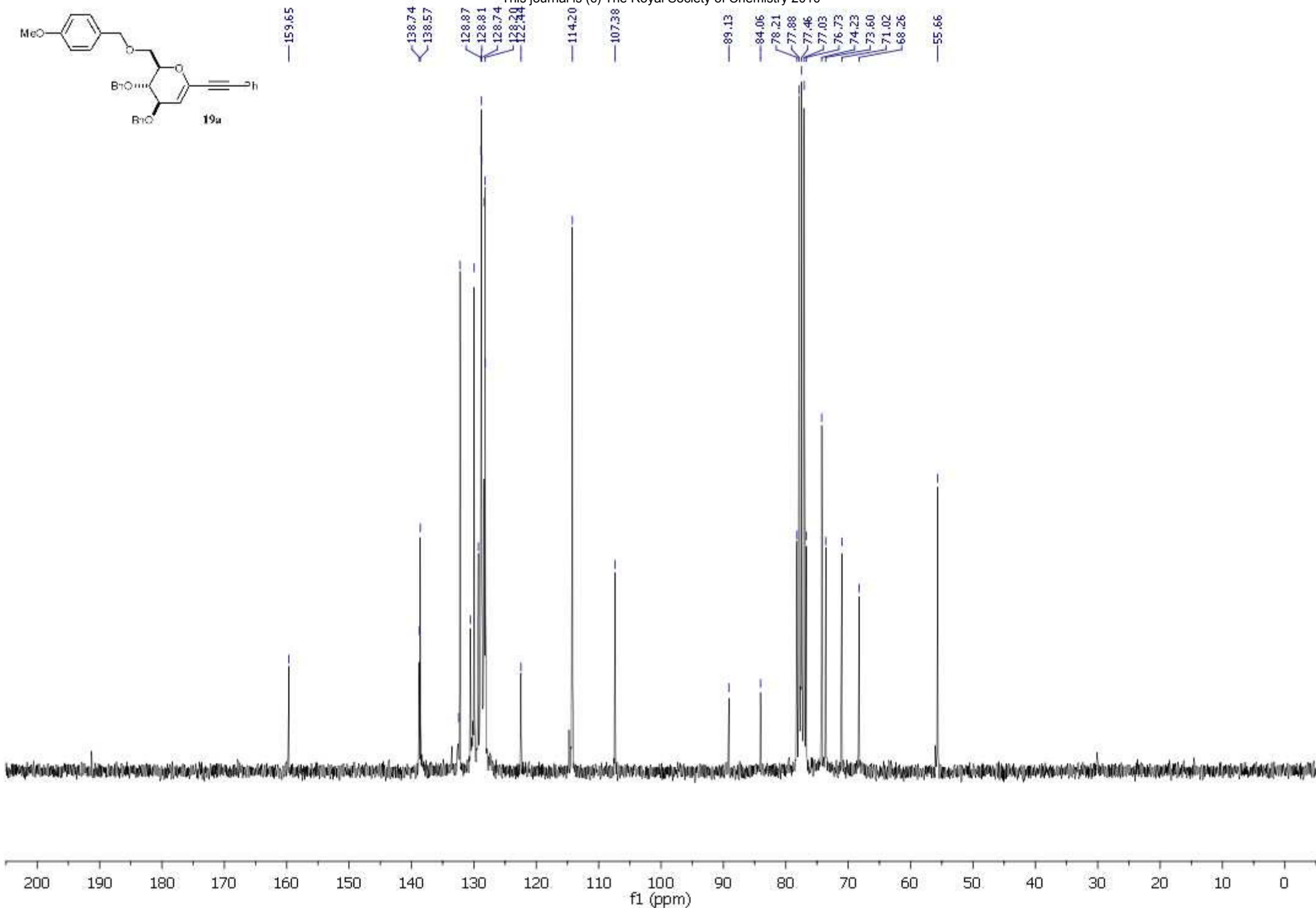


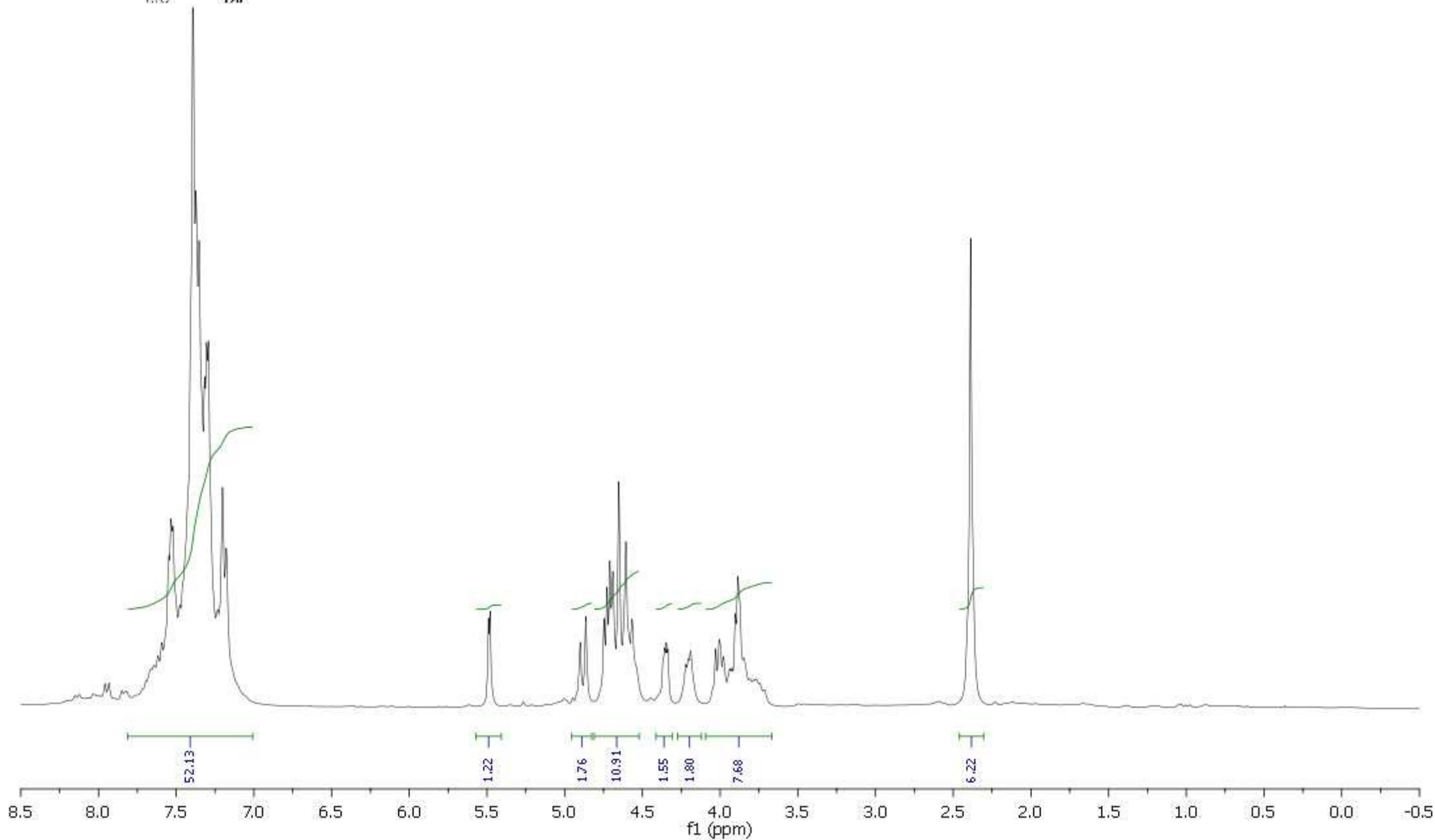
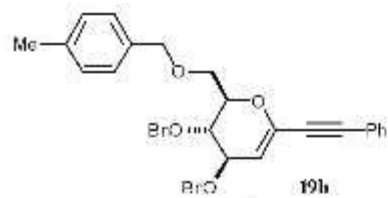




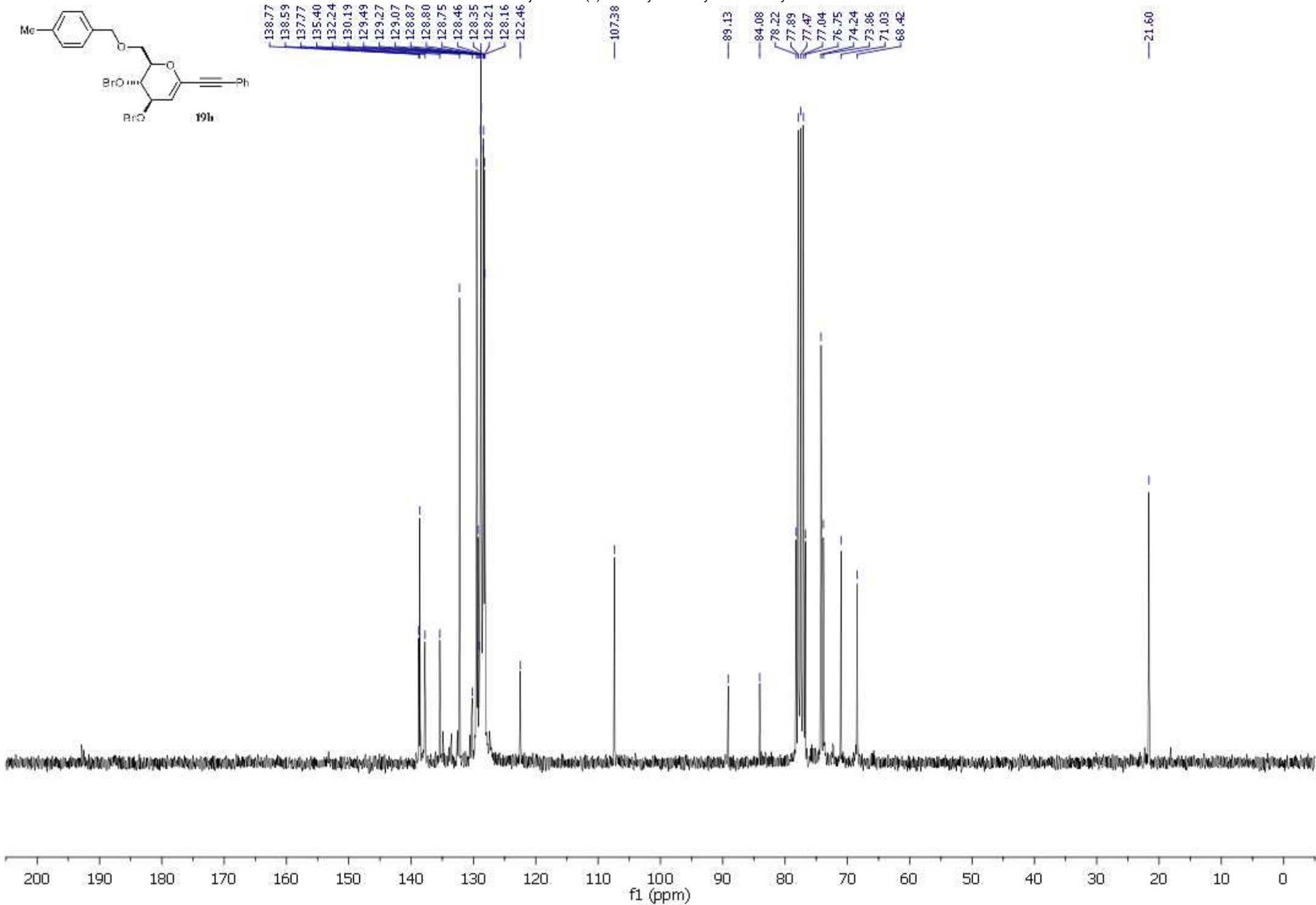


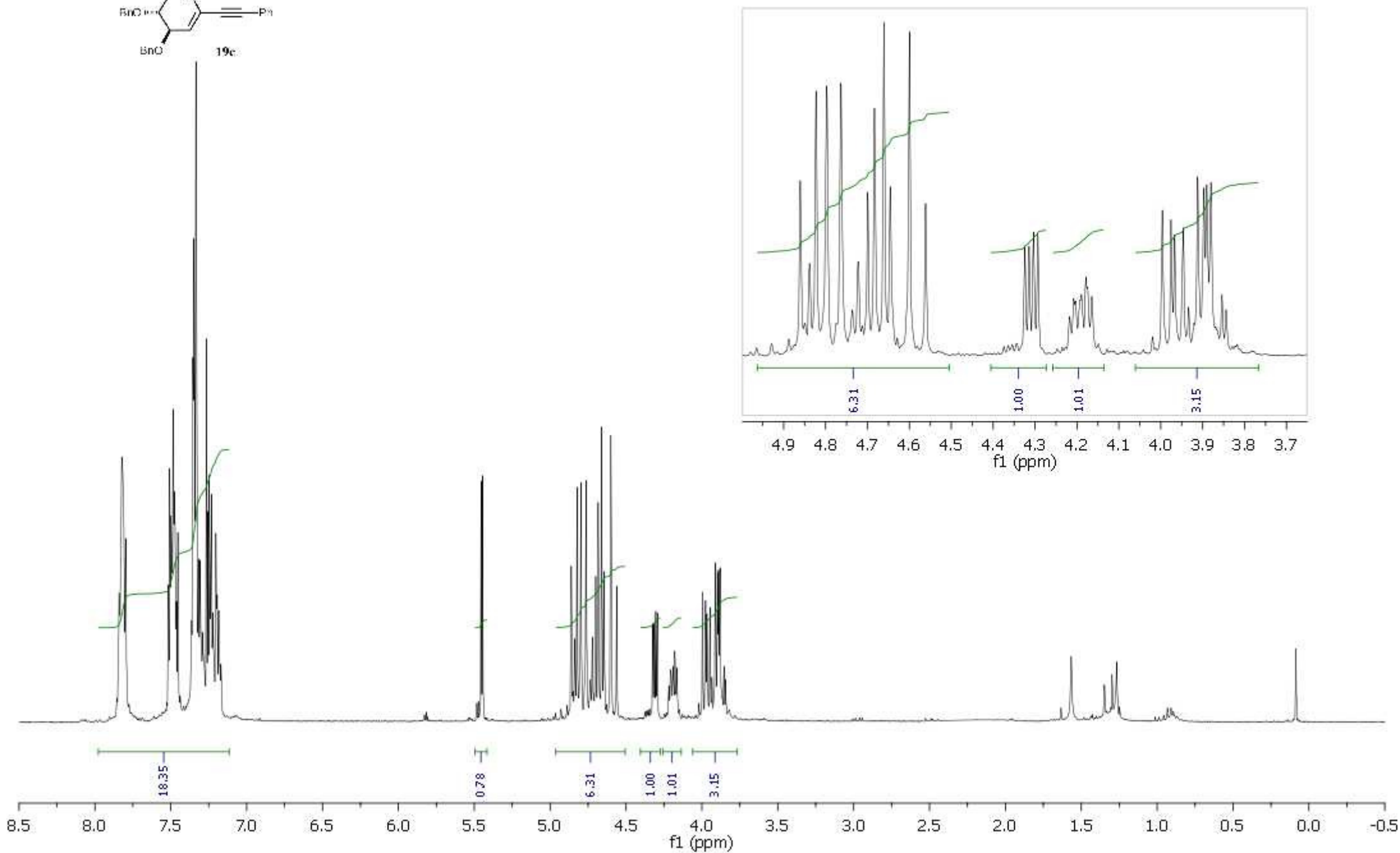
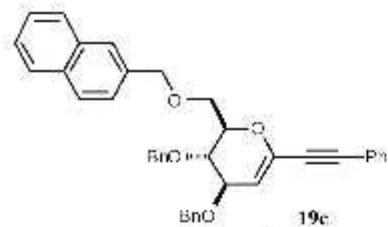


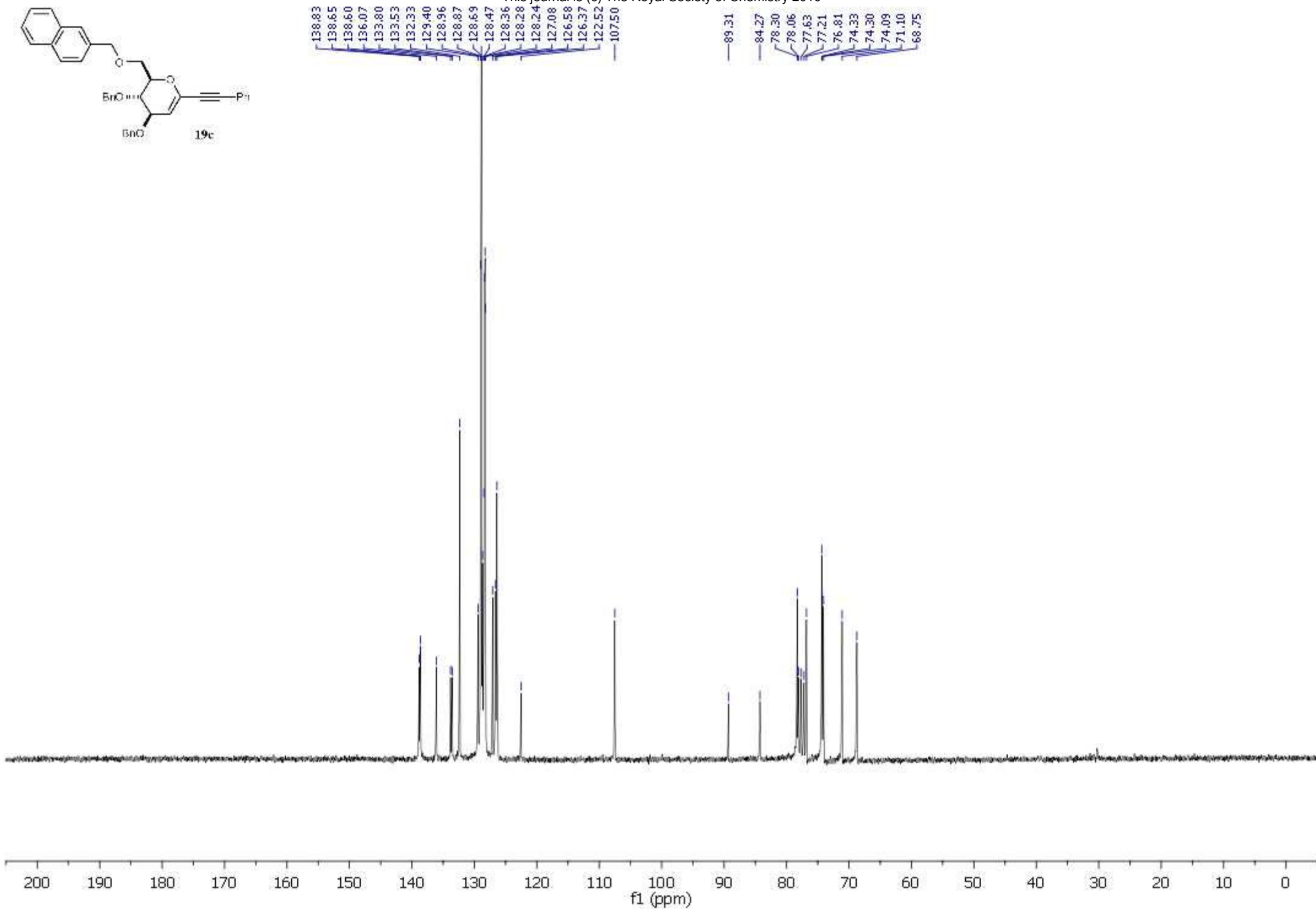


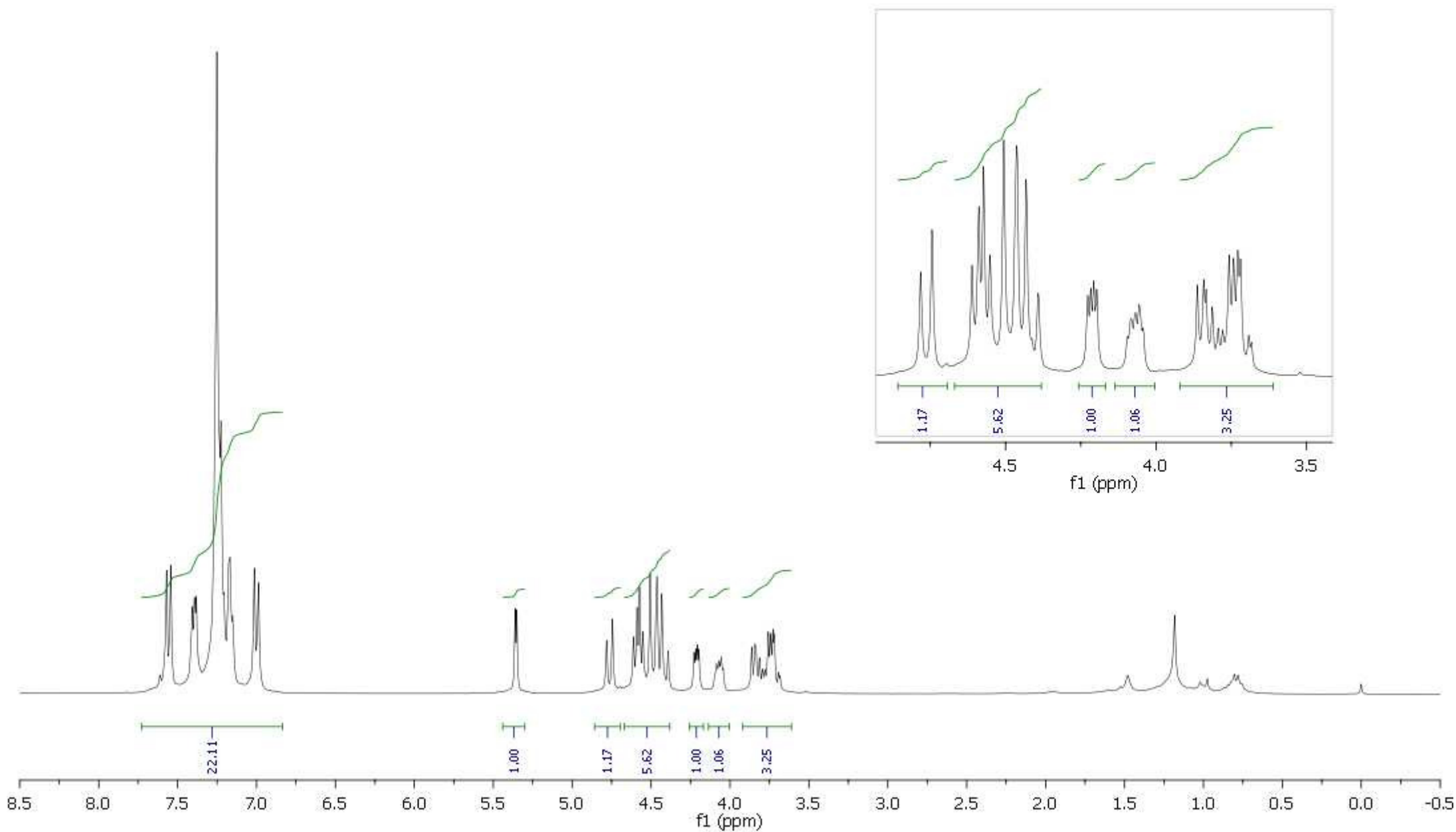
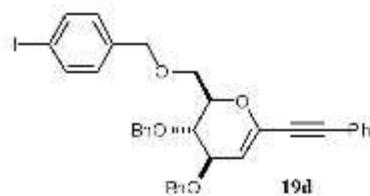


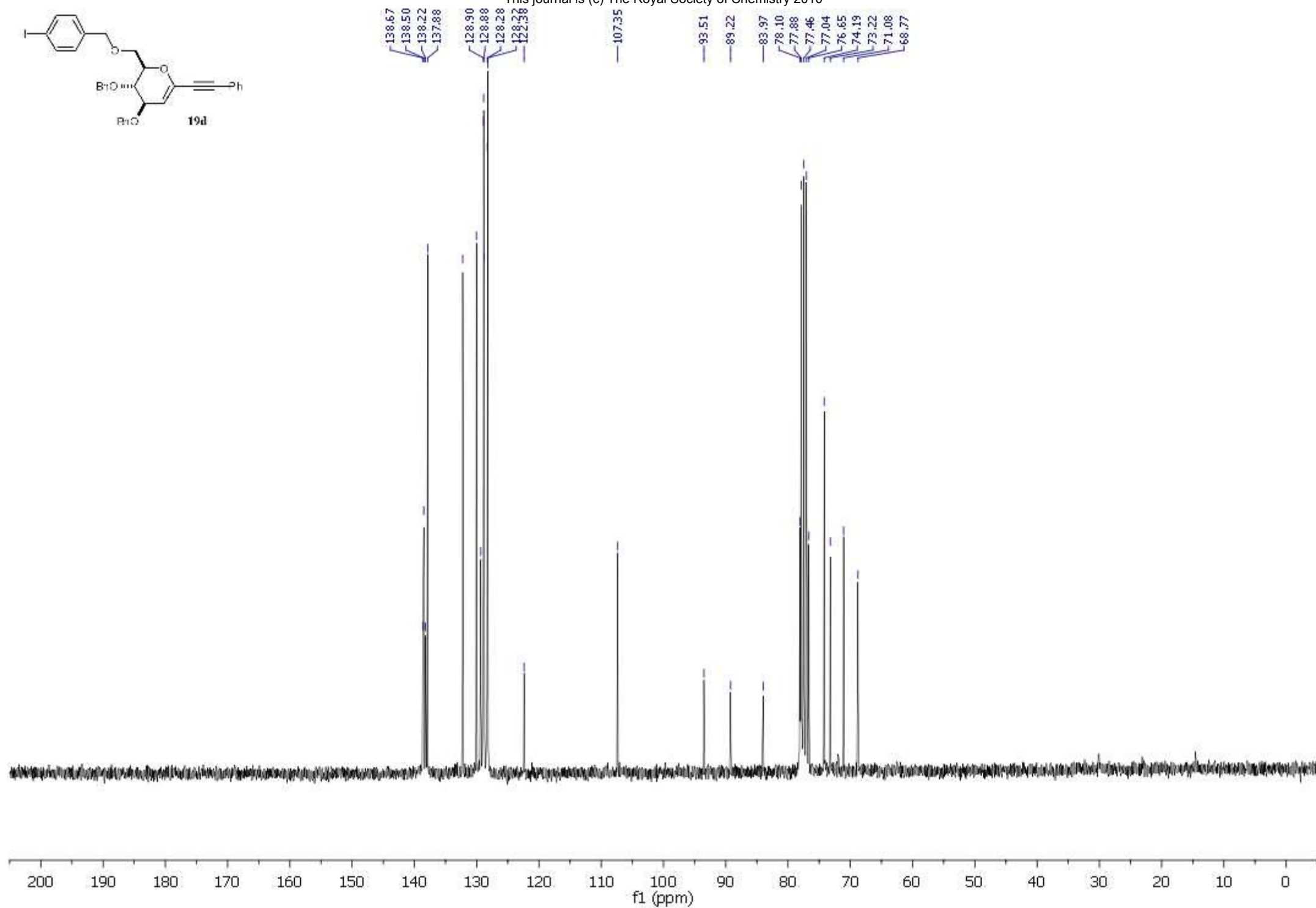
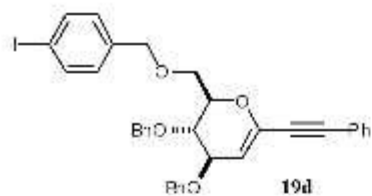


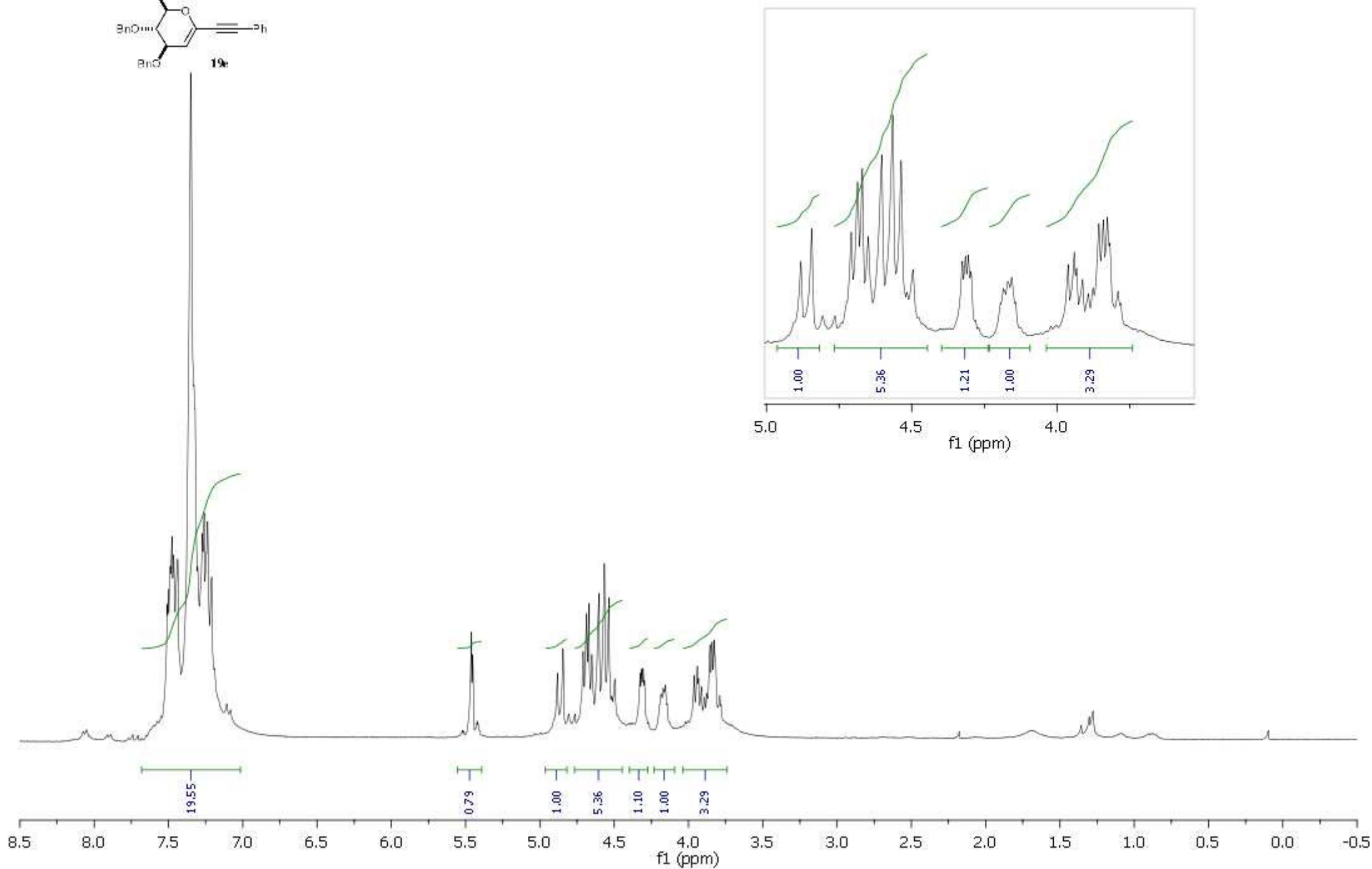
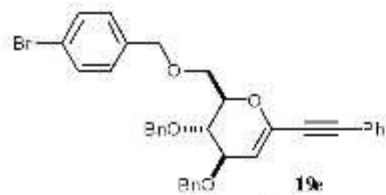


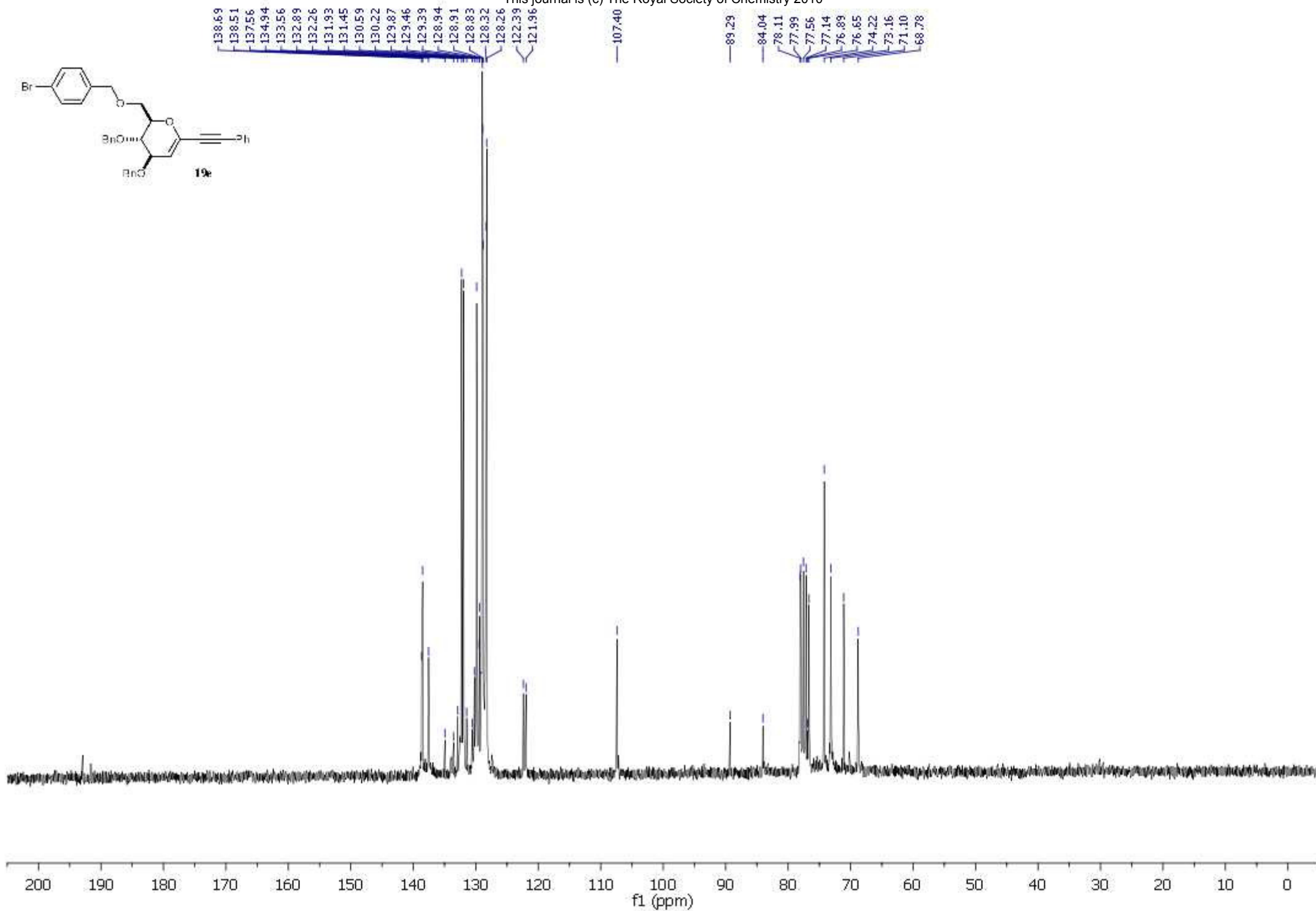


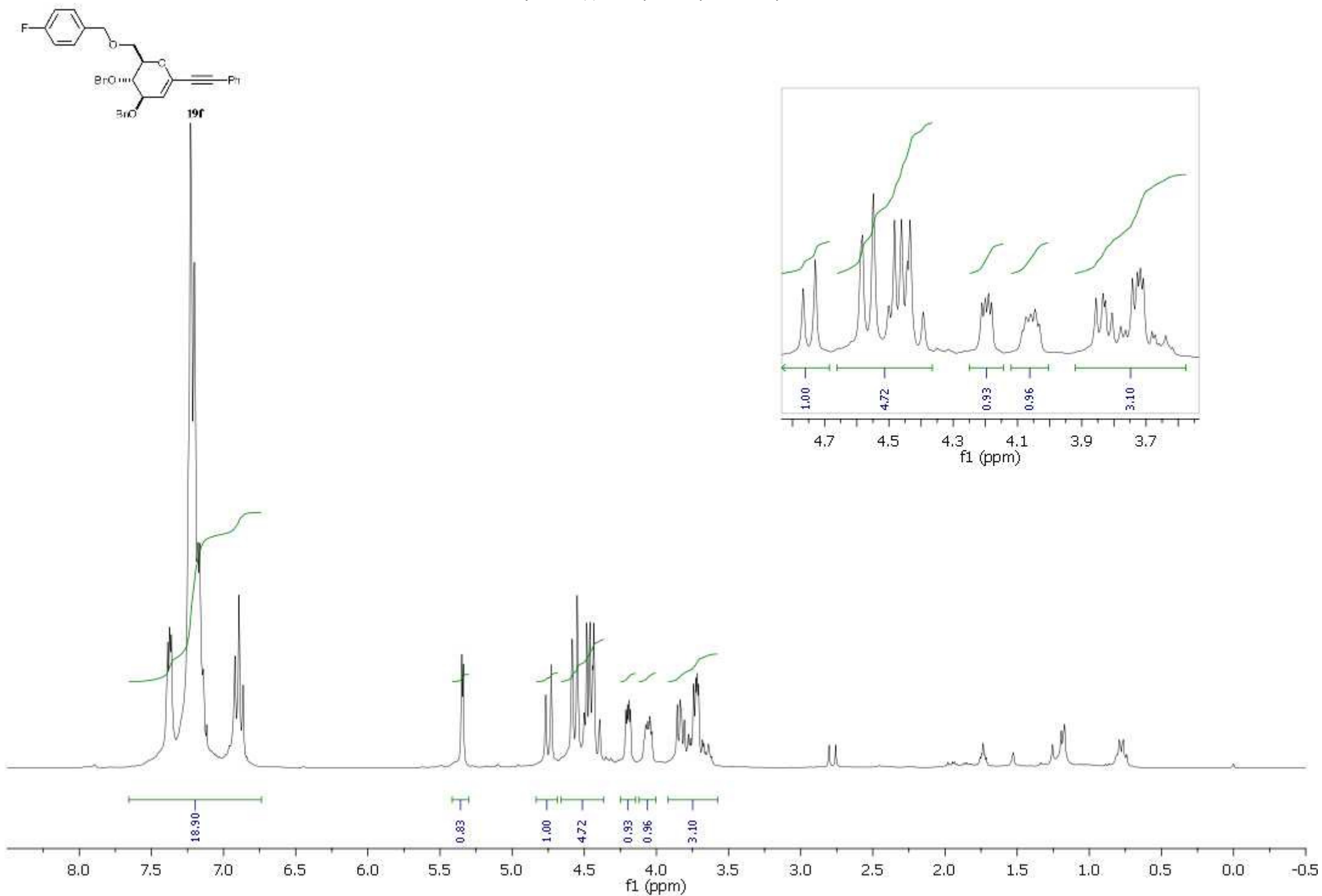




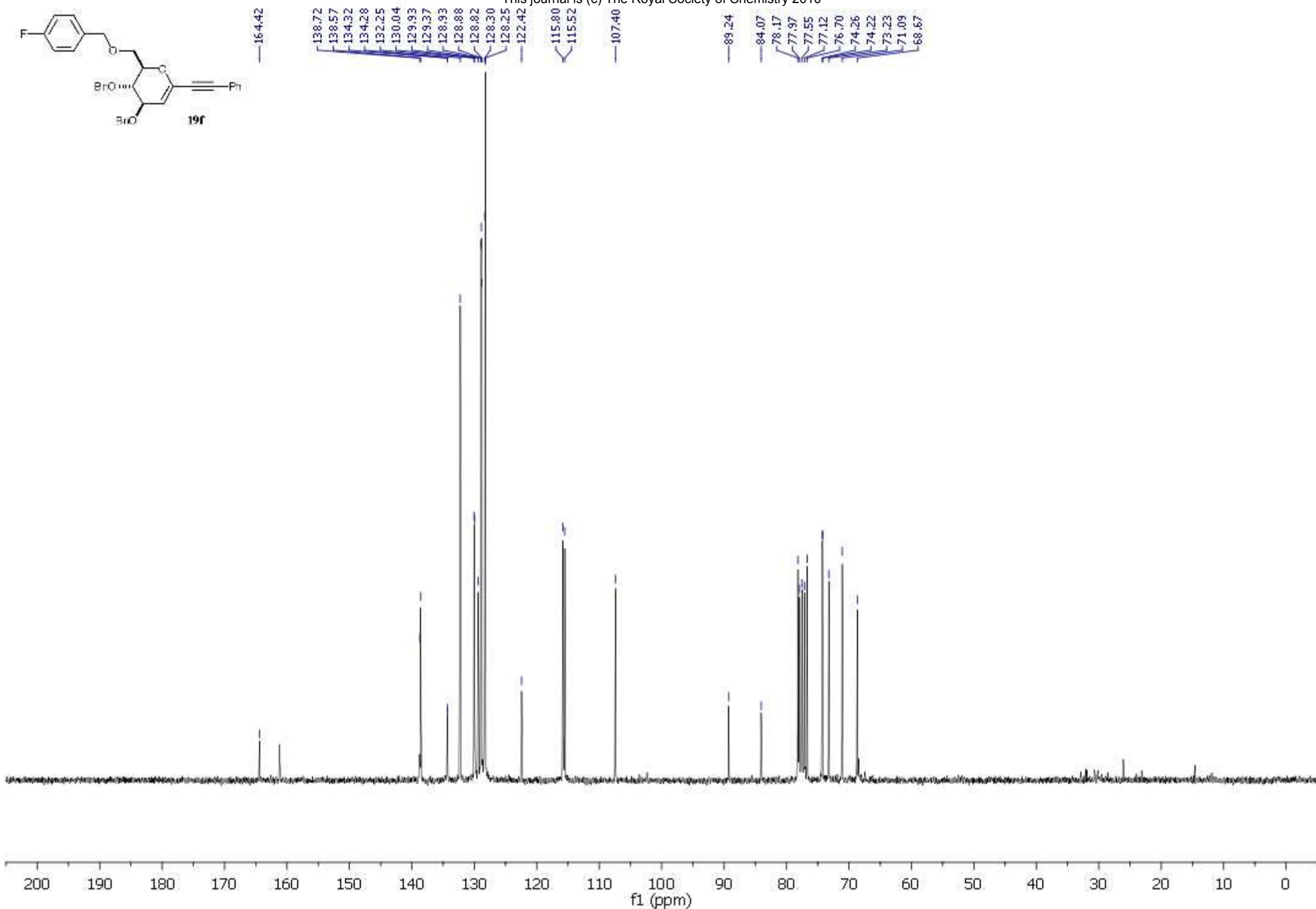


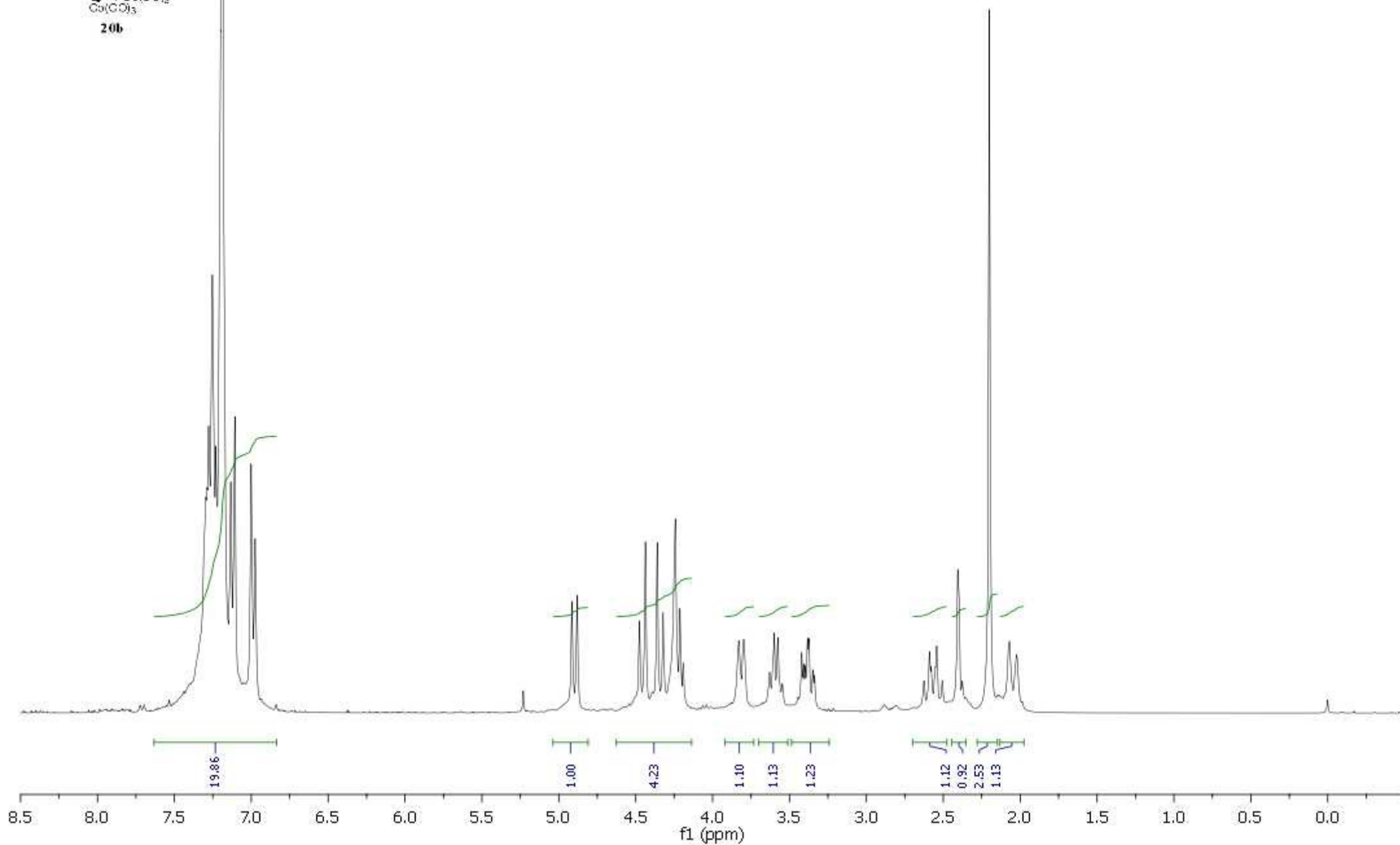
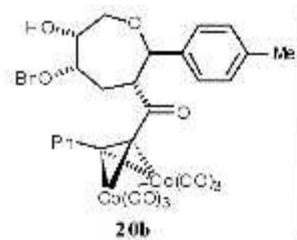


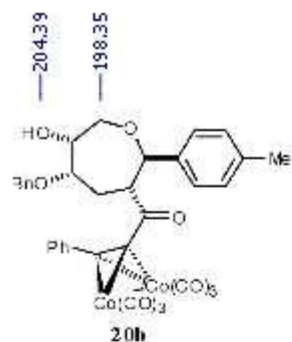












138.71  
138.14  
138.10  
136.81  
129.81  
129.60  
129.35  
128.94  
128.38  
128.15  
127.22

93.97  
86.57  
79.87  
77.87  
77.45  
77.02  
72.72  
71.74  
70.98

59.51

31.74

21.49

