Supporting Information

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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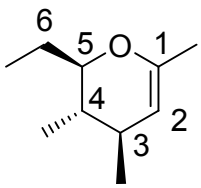
1. General Methods.

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 $MgSO_4$ or Na_2SO_4 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_2SO_4 (200 mL) in AcOH (800 mL). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ 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 ($CHCl_3$: 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 ^{13}C spectra are proton-decoupled. The numbering pattern used for the ^1H NMR is illustrated below.



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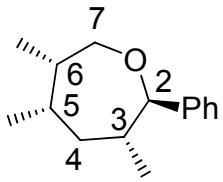

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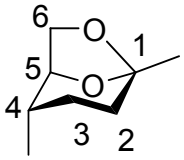

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Mass spectra were recorded by direct injection with a mass spectrometer *Agilent 6250 Accurate Mass Q-TOF LC/MS* equipped with an electrospray ion source in positive mode. Optical rotations $[\alpha]_D$ were measured for solutions in chloroform with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

Starting glycals **6a**[11], **6b**[12] and lactone **7a**[13] 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 80ºC and stirred for 6 h. The mixture was then allowed to cool, diluted with Et_2O and filtered though 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**: $[\alpha]^{25}_D$ +30.7 (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.32-7.16 (m, 10 H), 4.63 (d, *J* = 11.3 Hz, CH_2Ph), 4.56 (d, *J* = 11.7 Hz, CH_2Ph), 4.55 (d, *J* = 11.4 Hz, CH_2Ph), 4.47 (d, *J* = 11.8 Hz, CH_2Ph),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); ^{13}C NMR ($CDCl_3$, 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+): found 499.2876 $(M + H)^+$; calcd. for $[C_{29}H_{42}O_5Si + H]^+$ 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 ºC, and then treated with n-butyllithium (3.05 equiv). After 30 minutes at -78 ºC 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; $[\alpha]^{25}_{D}$ -3.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ph), 4.60 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.59 (d, *J* = 11.1 Hz, 1 H, CH_2Ph), 4.57 (d, *J* = 12.1 Hz, 1 H, CH_2Ph), 4.52 (s, 2 H, CH_2Ph), 4.46 (d, *J* = 14.8 Hz, 1 H, CH_2Ph) 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); ^{13}C NMR ($CDCl_3$, 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+): found: 539.2193 $(M+Na)^+$, calcd. for $[C_{35}H_{32}O_4 + Na]^+$ 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**: $[\alpha]^{28}_{D}$ -17.4 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ph), 4.85 (d, *J* = 11.2 Hz, 1 H, CH_2Ph), 4.74 (d, *J* = 11.7 Hz, 1 H, CH_2Ph), 4.67 (d, *J* = 11.7 Hz, 1 H, CH_2Ph), 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); ^{13}C NMR ($CDCl_3$, 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+): found: 605.3054 $(M+Na)^+$, calcd. for $[C_{37}H_{46}O_4Si + Na]^+$ 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. $NaHCO_3$ 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. 98-100ºC; $[\alpha]^{29}_D$ -16.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ph), 4.66 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.61 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 4.50 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 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); ^{13}C NMR ($CDCl_3$, 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+): found: 427.1894 $(M+H)^+$; 465.1468 $(M+K)^+$, calcd. for $[C_{28}H_{26}O_4 + H]^+$ 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_2SO_4, 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. $[\alpha]^{25}_D$ +6.71º (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ar), 4.68 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.66 (d, *J* = 11.2 Hz, 1 H, CH_2Ar), 4.60 (d, *J* = 11.7 Hz, 1 H, CH_2Ar), 4.59 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.51

(d, *J* = 11.7 Hz, 1 H, CH_2Ar), 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_3O); ^{13}C NMR ($CDCl_3$, 75MHz) δ 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 $(M+H)^+$; 569.2394 $(M+Na)^+$, calcd. for $[C_{36}H_{34}O_5 + H]^+$ 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. $[\alpha]^{25}_D$ +7.8 (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 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_2Ar), 4.77 – 4.62 (m, 4 H, CH_2Ar), 4.59 (d, *J* = 12.5 Hz, 1 H, CH_2Ar), 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); ^{13}C NMR ($CDCl_3$, 75MHz) δ 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 $(M+H)^+$; 553.2368 $(M+Na)^+$, calcd. for $[C_{36}H_{34}O_5 + H]^+$ 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. 97-100ºC; $[\alpha]^{25}_D$ -6.9 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 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_2Ar), 4.82 (d, *J* = 12.3 Hz, 1 H, CH_2Ar), 4.74 (d, *J* = 12.3 Hz, 1 H, CH_2Ar), 4.68 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.66 (d, *J* = 11.2 Hz, 1 H, CH_2Ar), 4.58 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 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); ^{13}C NMR ($CDCl_3$, 75MHz) δ 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 $(M+H)^+$; 1150.5274 $(2M+NH_4)^+$, calcd. for $[C_{39}H_{34}O_4 + H]^+$ 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 ºC, $[\alpha]^{25}_D$ +1.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2 H, *o* I-C_6H_4), 7.45 – 7.11 (m, 15 H), 7.00 (d, *J* = 8.1 Hz, 2 H, *m* I-C_6H_4), 5.36 (d, *J* = 3.1 Hz, 1 H, H-2), 4.76 (d, *J* = 11.3 Hz, 1 H, CH_2Ar), 4.59 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.57 (d, *J* = 11.4 Hz, 1 H, CH_2Ar), 4.49 (d, *J* = 11.7 Hz, 1 H, CH_2Ar), 4.48 (d, *J* = 12.0 Hz, 1 H, CH_2Ar), 4.41 (d, *J* = 12.0 Hz, 1 H, CH_2Ar), 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); ^{13}C NMR ($CDCl_3$, 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 $(M+H)^+$; 1302.2869 $(2M+NH_4)^+$, calcd. for $[C_{35}H_{31}IO_4 + H]^+$ 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 ºC; $[\alpha]^{25}_D$ -0.3 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ar), 4.69 (d, *J* = 11.5 Hz, 1 H, CH_2Ar), 4.67 (d, *J* = 11.3 Hz, 1 H, CH_2Ar), 4.64 – 4.47 (m, 3 H, CH_2Ar), 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); ^{13}C NMR ($CDCl_3$, 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 $(M+H)^+$, calcd. for $[C_{35}H_{31}BrO_4 + H]^+$ 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. 82-86ºC; $[\alpha]^{25}_{D}$ -3.60 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 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_2Ar), 4.57 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.56 (d, *J* = 11.6 Hz, 1 H, CH_2Ar), 4.49 (d, *J* = 5.6 Hz, 1 H, CH_2Ar), 4.45 (d, *J* = 5.3 Hz, 1 H, CH_2Ar), 4.41 (d, *J* = 12.2 Hz, 1 H, CH_2Ar), 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; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4 ($^1J_{C,F}$ = 245.5 Hz), 138.3 (x 2), 138.2 (x 2), 133.9 ($^4J_{C,F}$ = 3.1 Hz), 131.9 (x 2), 129.6 ($^3J_{C,F}$ = 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 ($^2J_{C,F}$ = 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+): found: 535.2285 $(M+H)^+$, calcd. for $[C_{35}H_{31}FO_4 + H]^+$ 535.2285.

General Procedure C. Preparation of cobalt-complexed enynes 9 and 19. A solution of $Co_2(CO)_8$ (1.2 eq) in anhydrous CH_2Cl_2 (1 ml/mmol) was added to a solution of the corresponding enyne in CH_2Cl_2 (10 ml/mmol). The dark solution was stirred at room temperature until TLC showed complete formation of the comple (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 $Co_2(CO)_8$ (2 g, 6 mmol) in dry CH_2Cl_2. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 95:5) to give a brownish oil (3.45 g, 86 %); ^{1}H NMR ($CDCl_3$) 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_2Ph), 4.78 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 4.66 (s, 2 H, CH_2Ph), 4.63 (d, *J* = 12.0 Hz, 1 H, CH_2Ph), 4.56 (d, *J* = 12.0 Hz, 1 H, CH_2Ph),

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}C NMR (75 MHz, $CDCl_3$) δ 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 $Co_2(CO)_8$ (600 mg, 1.76 mmol) in dry CH_2Cl_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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.73 (d, *J* = 11.4 Hz, 1 H, CH_2Ph), 4.55 (s, 2 H, CH_2Ph), 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}C-NMR (75 MHz, $CDCl_3$) δ 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 CH_2Cl_2 (100 mL/mmol) under an argon atmosphere and in the presence of 4Å molecular sieves was cooled to -20ºC, and treated with $BF_3{\cdot}OEt_2$ (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 $NaHCO_3$. The cooling bath was removed and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.42 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 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_{ax}), 2.49 (d, J = 2.2 Hz, 1 H, OH), 2.14 (d, *J* = 14.6 Hz, 1 H, H-4_{eq}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 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_{ax}, H-4_{ax} and OH.
For **12**: ^{1}H NMR ($CDCl_3$) δ 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}C NMR (75 MHz, $CDCl_3$) δ 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 0º C was treated with an excess of 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 $NaHCO_3$ solution, and extracted with AcOEt. The combined organic layers were washed with 10% aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_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%). $[\alpha]^{25}_{D}$ +10.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.56 (d, *J* = 11.7 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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+): found: 427.1907 $(M+H)^+$, calcd. for $[C_{28}H_{26}O_4 + H]^+$ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.34 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 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, CH_3), 2.05 (d, *J* = 14.3 Hz, 1 H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.46 (d, *J* = 11.4 Hz, 1 H, CH_2Ph), 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}C NMR (101 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2 H, *o* I-C_6H_4), 7.51 – 7.20 (m, 10 H), 7.09 (d, *J* = 8.2 Hz, 2 H, *m* I-C_6H_4), 4.99 (d, *J* = 10.7 Hz, 1 H, H-2), 4.57 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 4.45 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.41 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.45 (d, *J* = 11.4 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 204.1, 198.0 (x 6), 162.5 ($^1J_{C,F}$ = 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 ($^2J_{C,F}$ = 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 CH_2Cl_2 and cooled to -20 ºC, $BF_3{\cdot}OEt_2$ (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 $NaHCO_3$. The cooling bath was removed and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*.

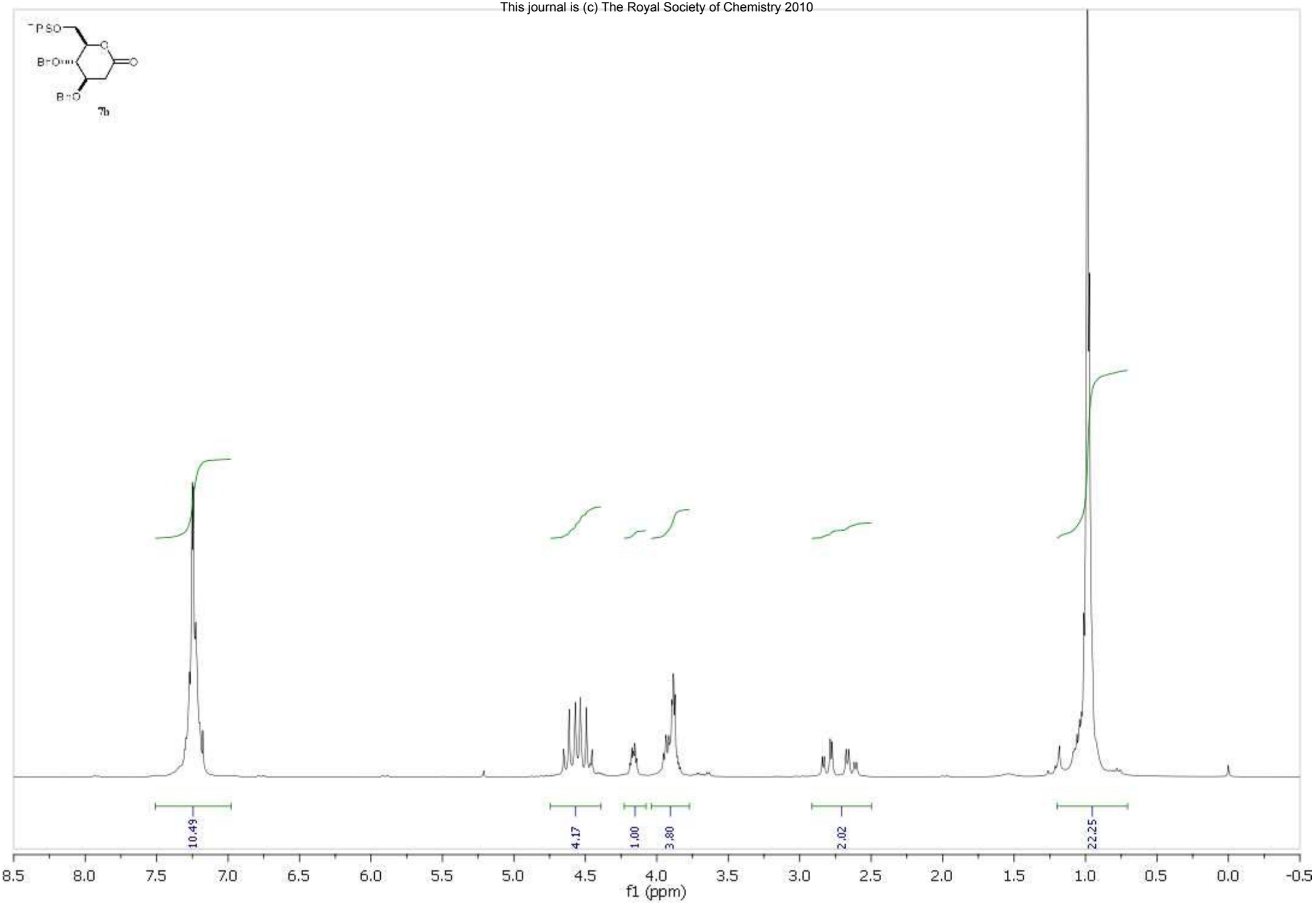
Glycal **21a**. This compound was prepared from dicobalt hexacarbonyl complex **9b** (70 mg, 0.08 mmol) and allyltrimethylsilane (27 mg, 0.24 mmol) according to the general procedure E. The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 99:1) to give compound **21a** (45.3 mg, 70%) as a brownish oil: ^{1}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.63 (d, *J* = 11.8 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.45 (d, *J* = 11.3 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) δ 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, CH_2Ph), 4.47 (d, *J* = 12.9 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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}H NMR ($CDCl_3$) 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, CH_2Ph), 4.55 (d, *J* = 11.1 Hz, 1 H, CH_2Ph), 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}C NMR (75 MHz, $CDCl_3$) δ 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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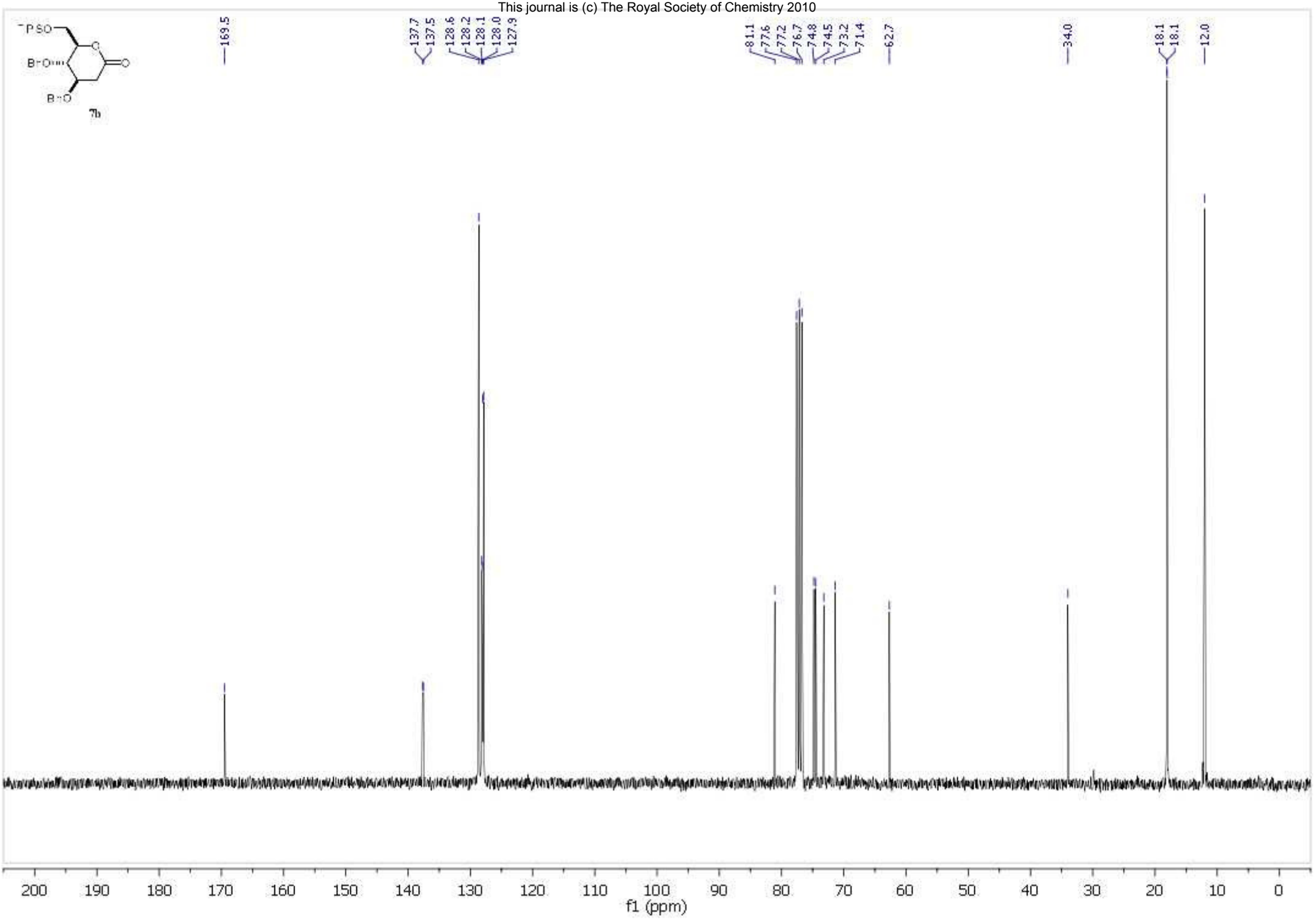
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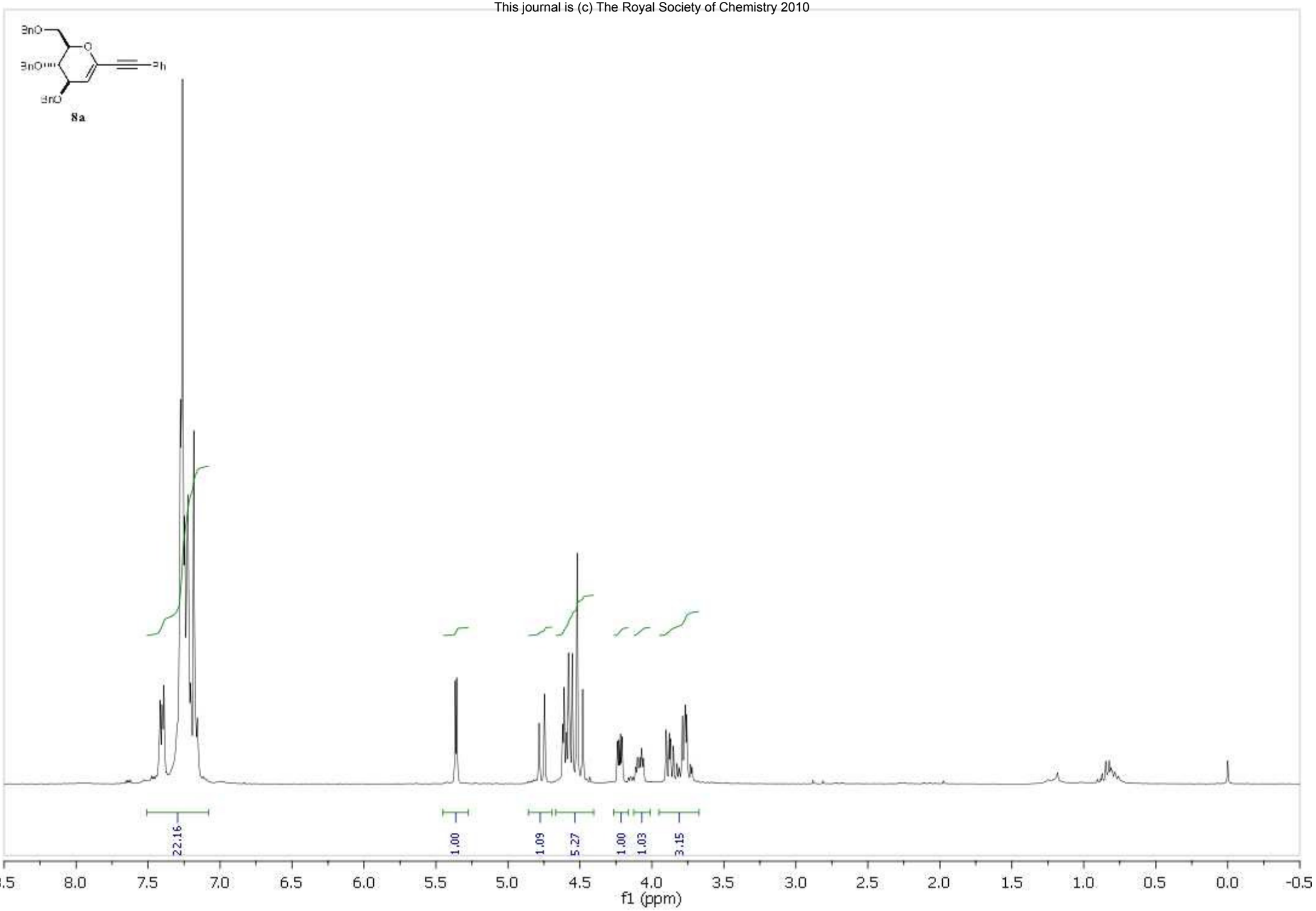
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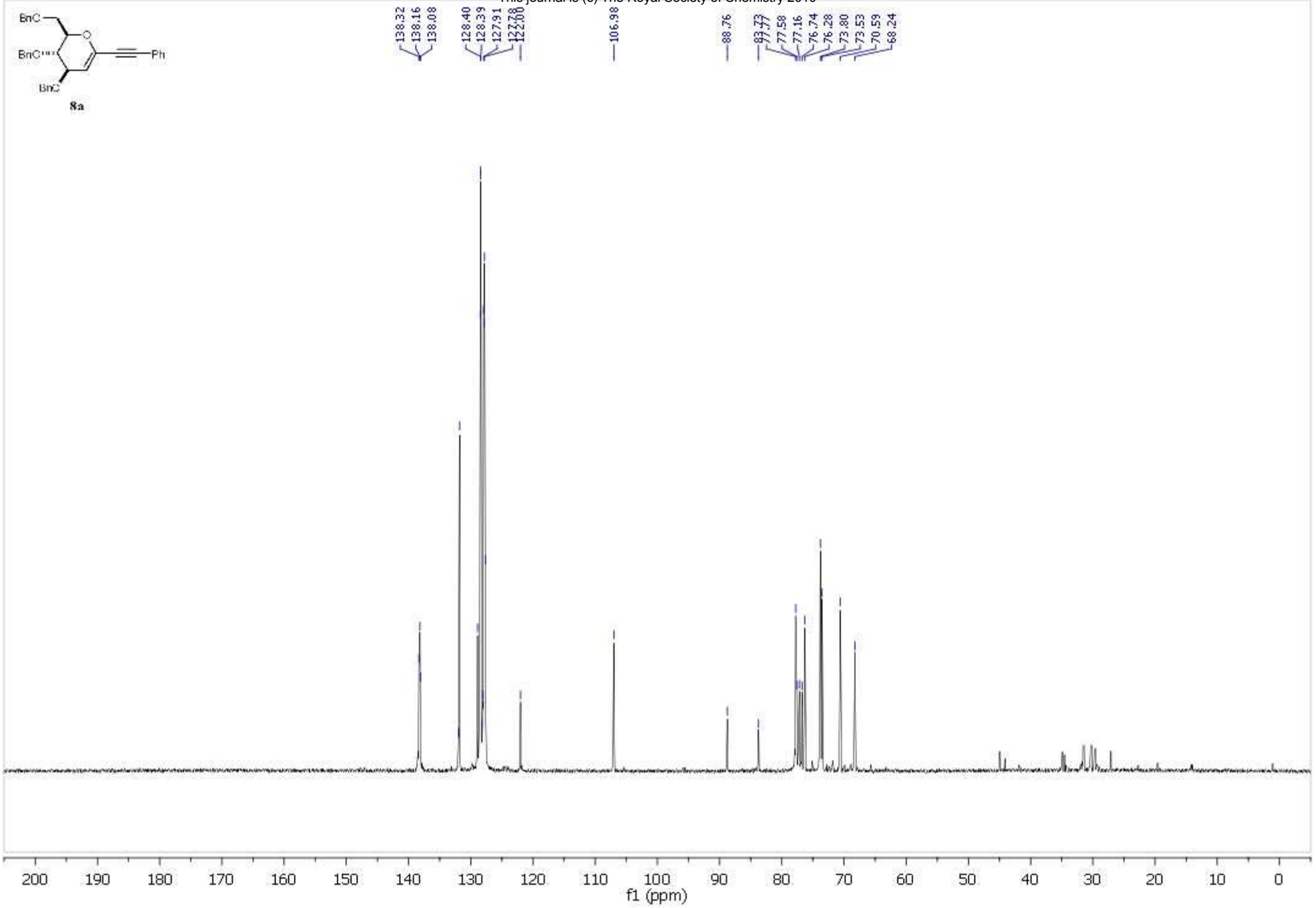
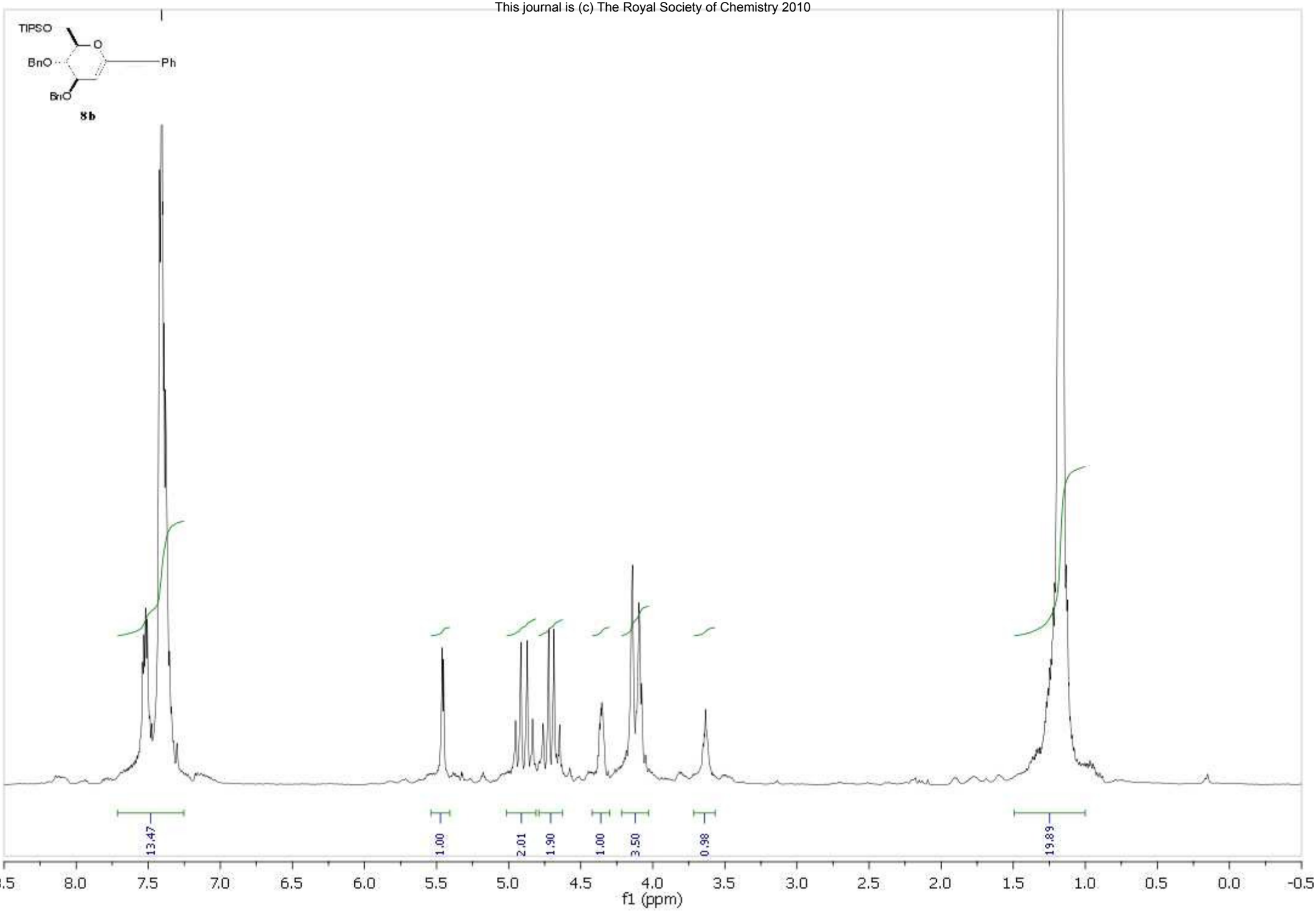
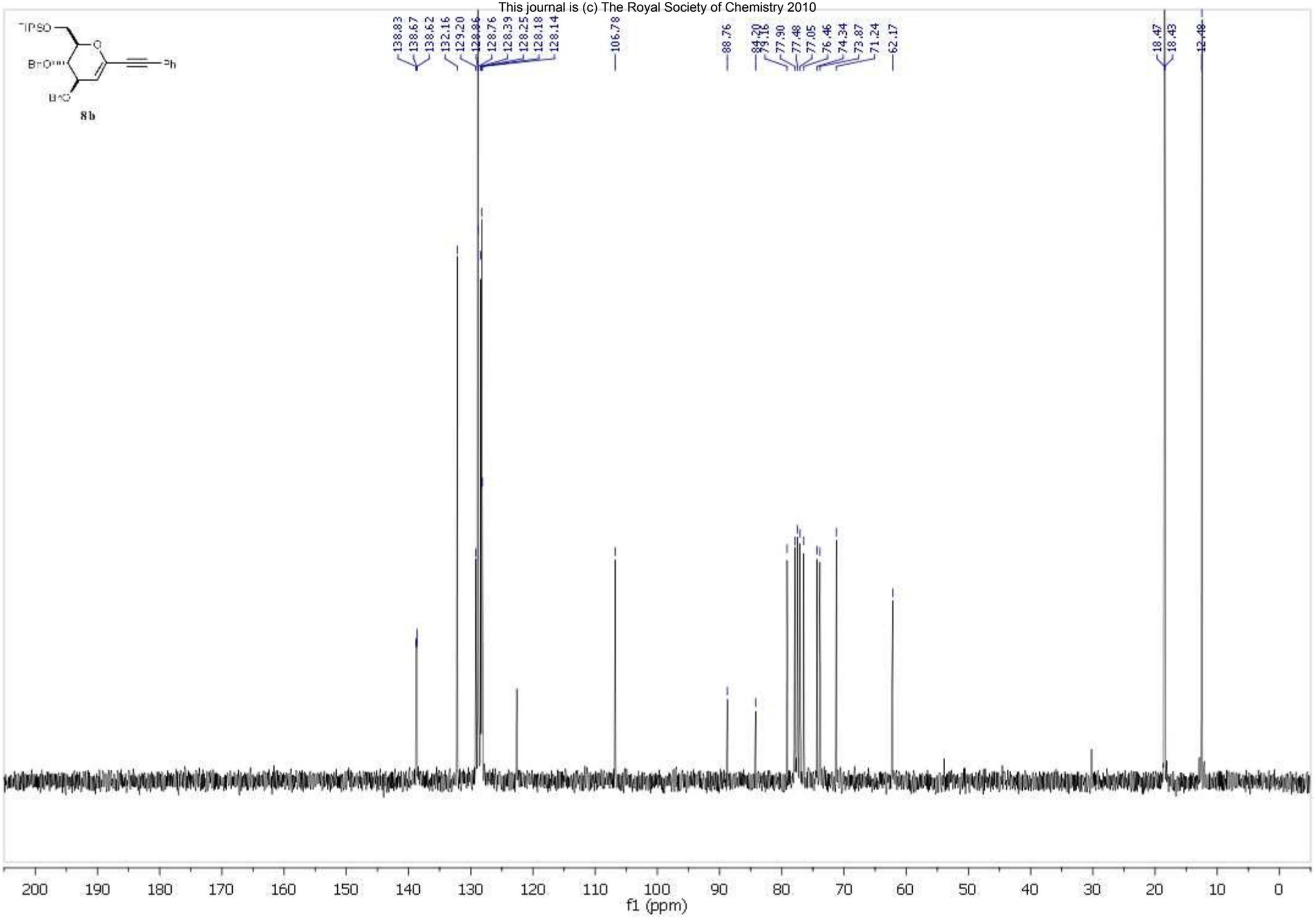
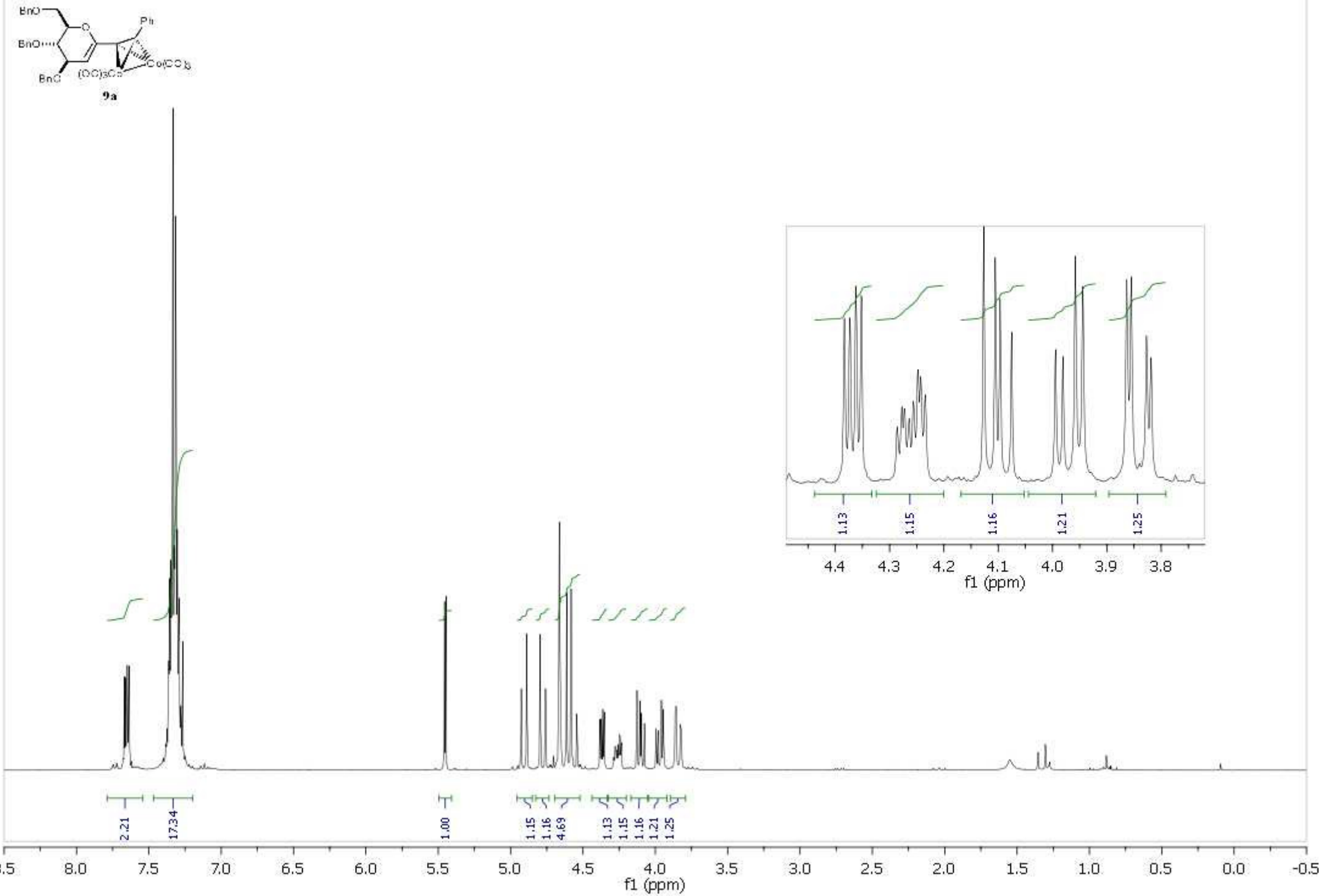
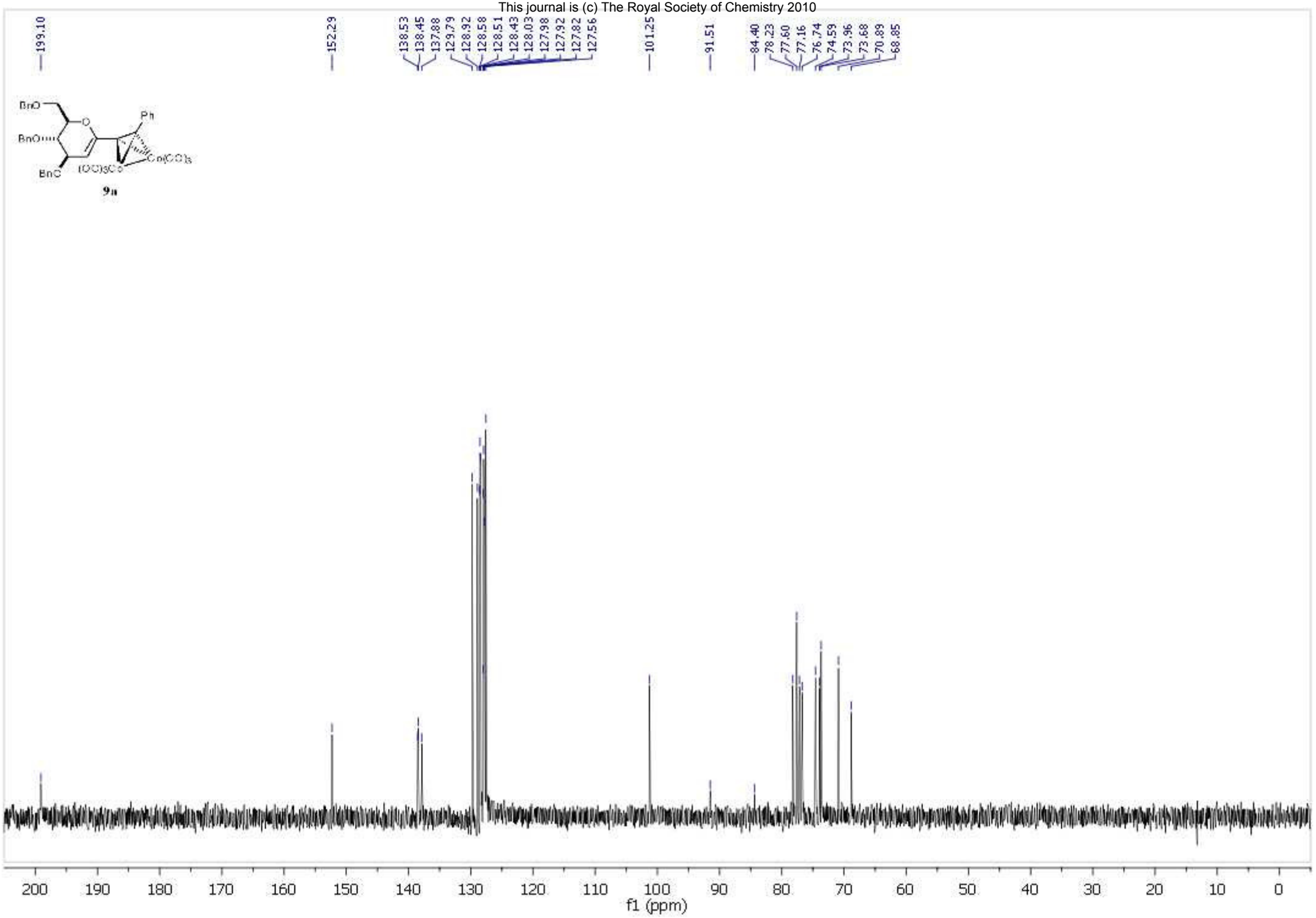
f1 (ppm)

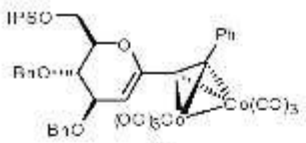

BnO
BnO
BnO
Ph
8a
138.32
138.16
138.08
128.40
128.39
127.91
106.98
88.76
77.58
77.16
76.74
76.28
73.80
73.53
70.59
68.24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TIPSO
O
BnO
Ph
BnO
8b
13.47
1.00
2.01
1.90
1.00
3.50
0.98
19.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


TIPSO
BnO
BnO
Ph
8b
138.83
138.67
138.62
132.16
129.20
128.86
128.76
128.39
128.25
128.18
128.14
106.78
88.76
84.20
77.90
77.48
77.05
76.46
74.34
73.87
71.24
62.17
18.47
18.43
12.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

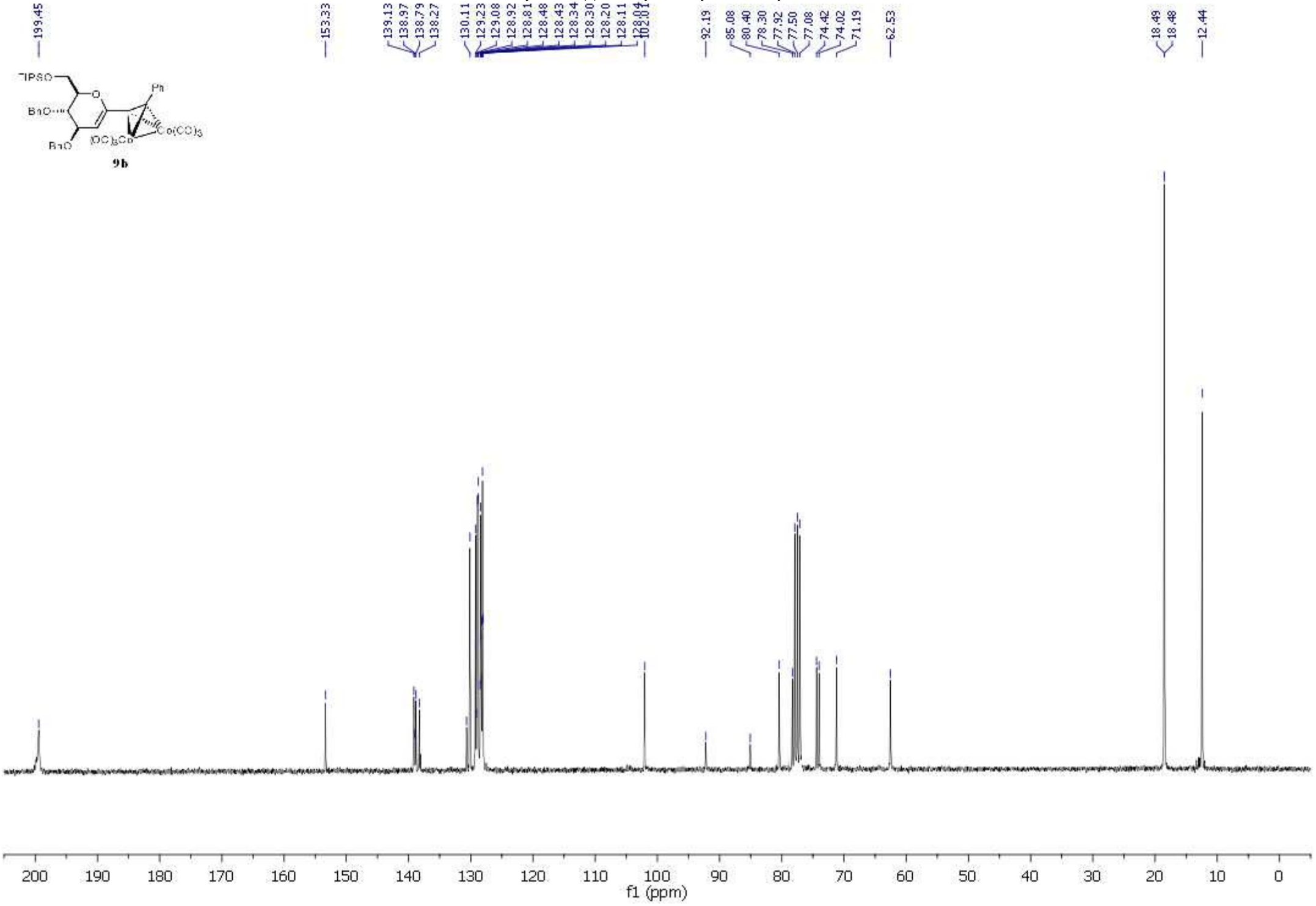

BnO
BnO
BnO
O
Ph
(OC)3Co
Co(CO)3
9a
2.21
17.34
1.00
1.15
1.16
4.69
1.13
1.15
1.16
1.21
1.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.13
1.15
1.16
1.21
1.25
4.4
4.3
4.2
4.1
4.0
3.9
3.8
f1 (ppm)

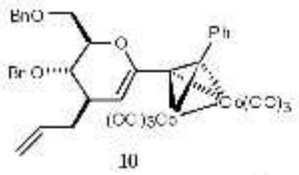

199.10
152.29
138.53
138.45
137.88
129.79
128.92
128.58
128.51
128.43
128.03
127.98
127.92
127.82
127.56
101.25
91.51
84.40
78.23
77.60
77.16
76.74
74.59
73.96
73.68
70.89
68.85
BnO
BnO
BnO
Ph
(OC)3Co
Co(CO)3
9a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


IPSO
BnO
BnO
Ph
Co(CO)3
(OC)3Co

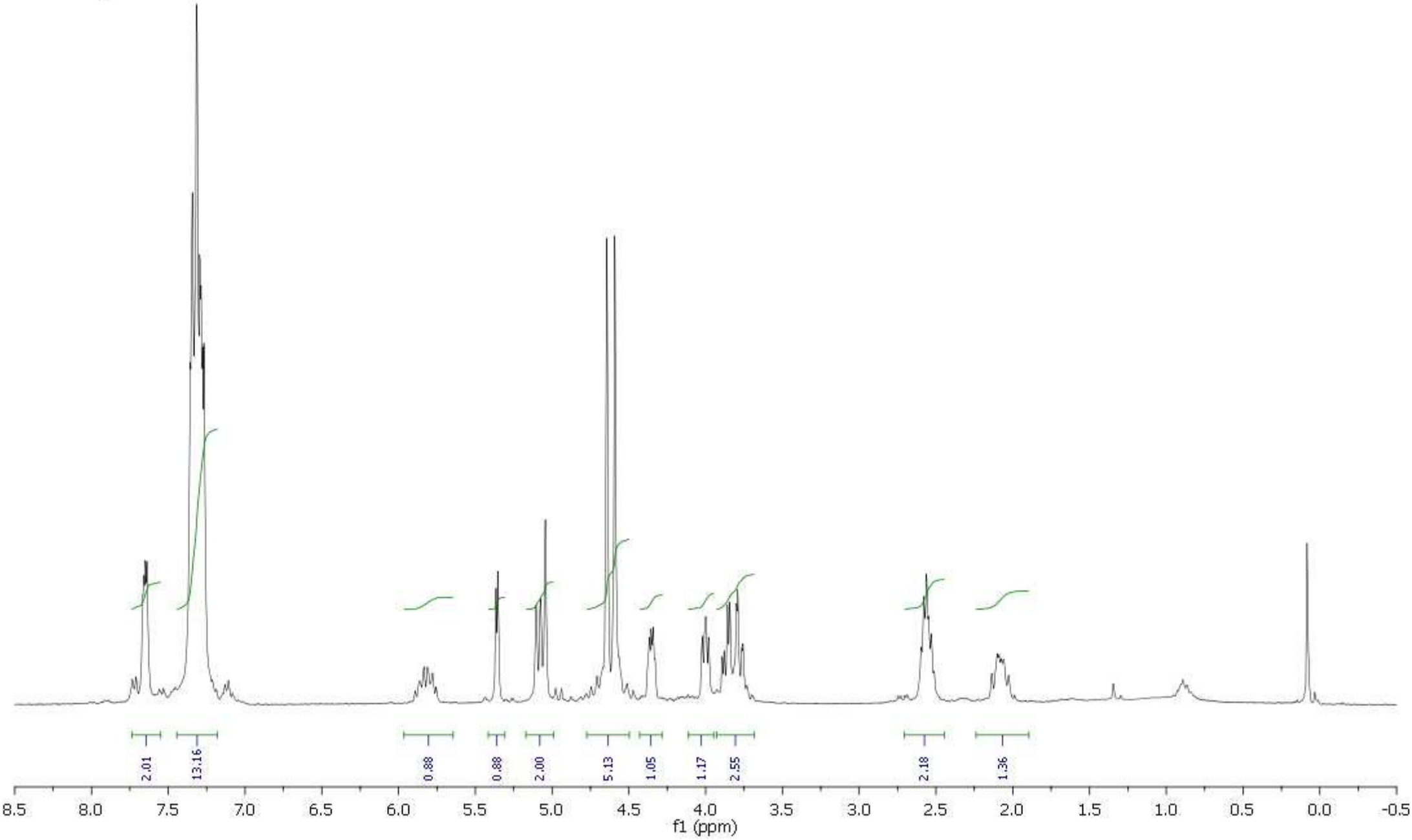
9b

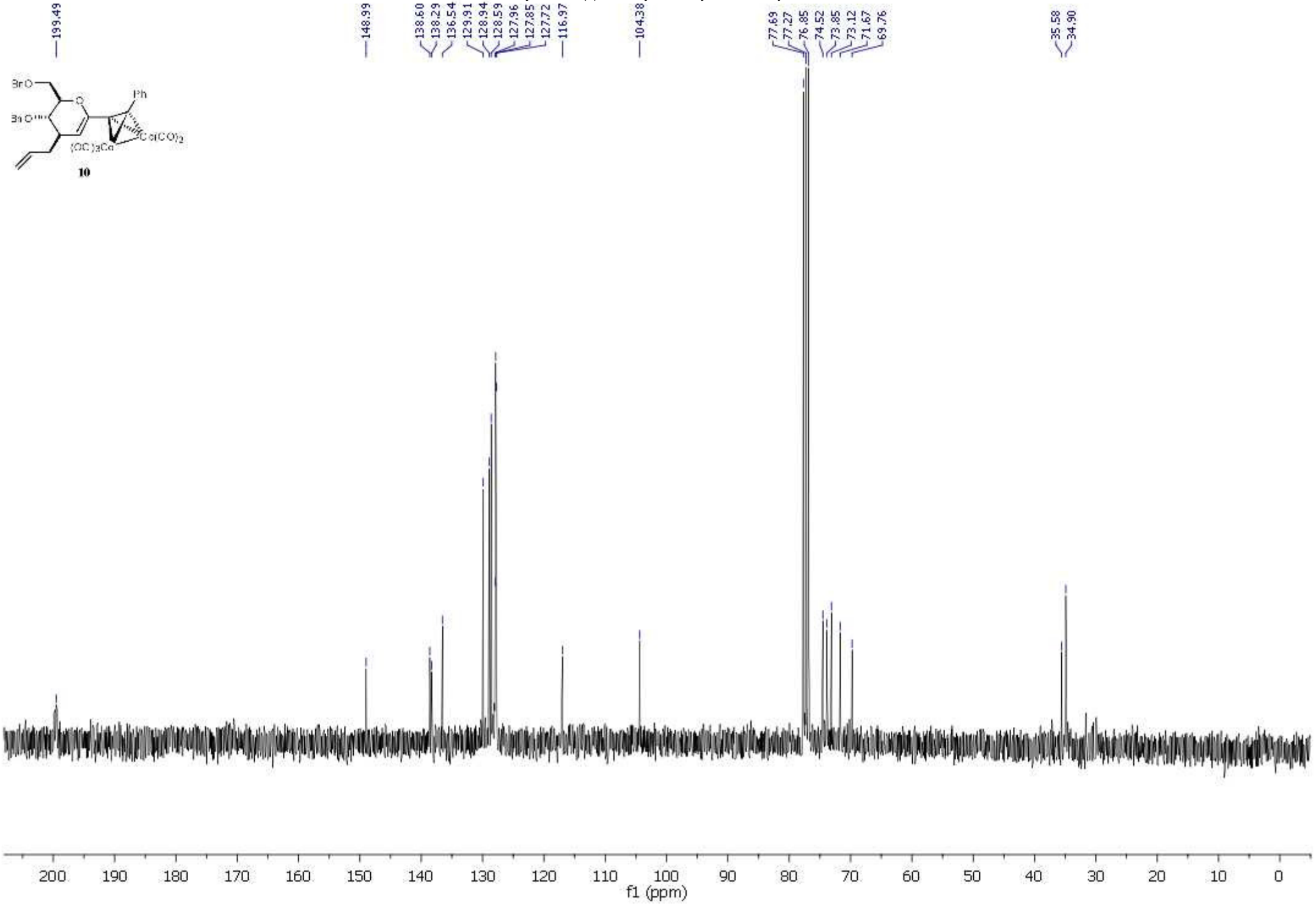
2.55
14.60
1.00
1.10
1.20
1.81
1.04
4.26
19.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

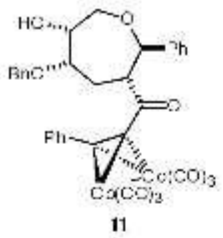

199.45
153.33
139.13
138.97
138.79
138.27
130.11
129.23
129.08
128.92
128.81
128.48
128.43
128.34
128.30
128.20
128.11
128.04
127.81
92.19
85.08
80.40
78.30
77.92
77.50
77.08
74.42
74.02
71.19
62.53
18.49
18.48
12.44
TIPSO
BnO
BnO
Ph
Co(CO)3
(OC)3Co
9b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
Br
O
Ph
$Co_2(CO)_6$
$(OC)_3Co$

10

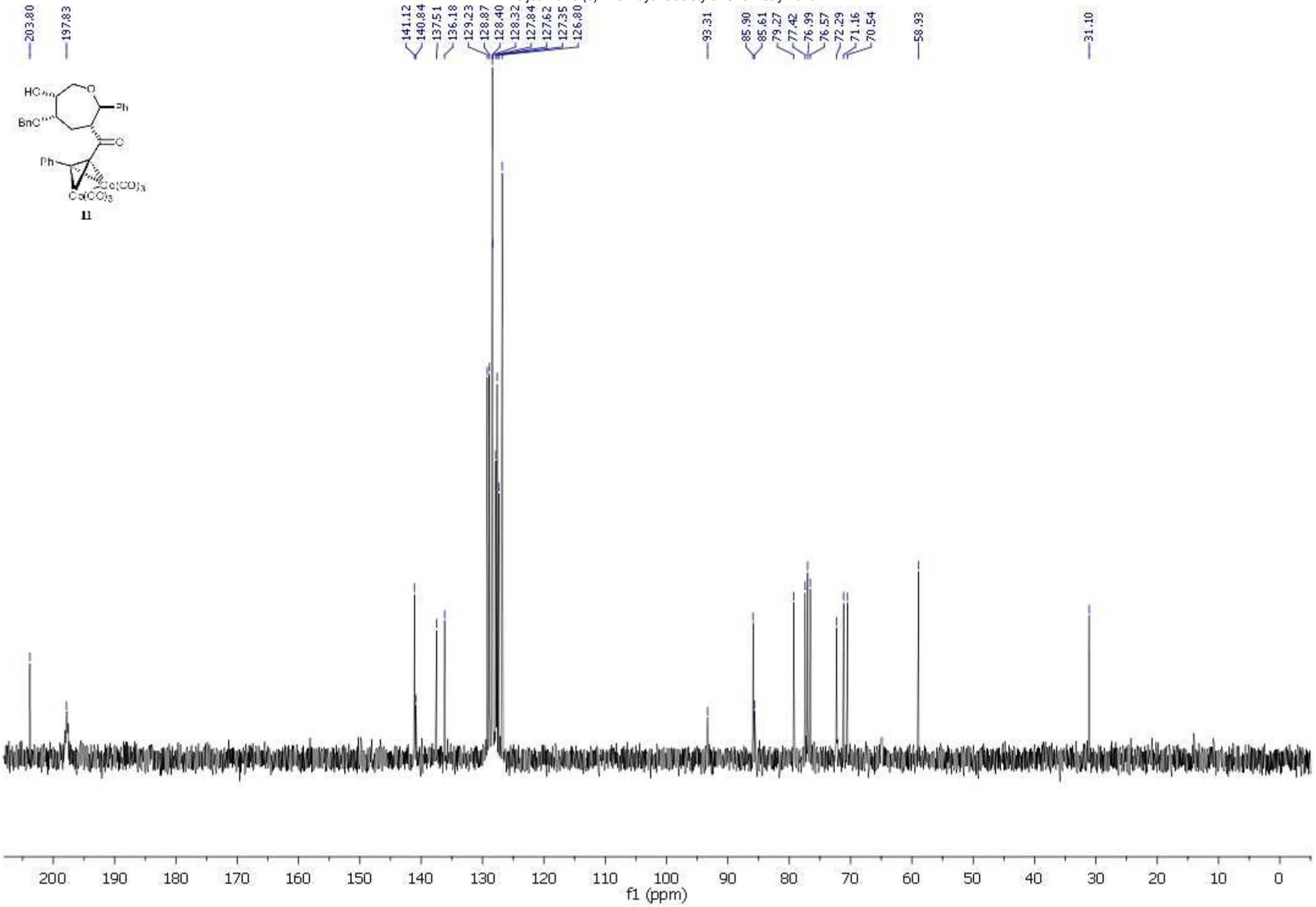

2.01
13.16
0.88
0.88
2.00
5.13
1.05
1.17
2.55
2.18
1.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

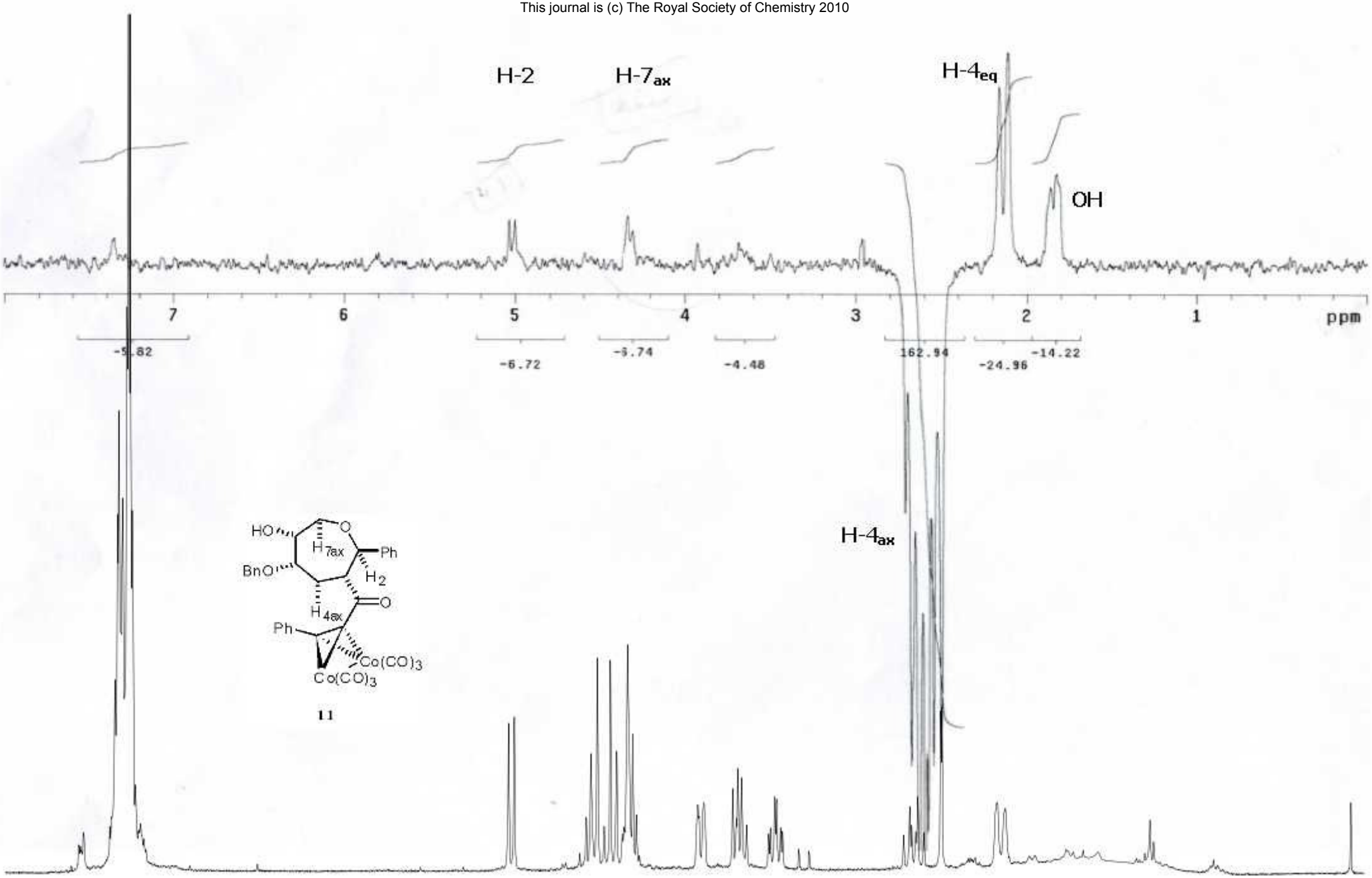

199.49
148.99
138.60
138.29
136.54
129.91
128.94
128.59
127.96
127.85
127.72
116.97
104.38
77.69
77.27
76.85
74.52
73.85
73.12
71.67
69.76
35.58
34.90
BnO
BnO
O
Ph
Co(CO)3
(OC)3Co
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
BnO
Ph
Ph
Co(CO)3
Co(CO)3
Co(CO)3

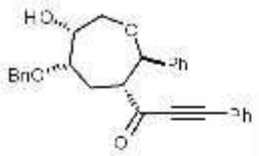
11

14.54
0.89
4.86
0.93
1.21
0.92
1.00
0.90
1.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

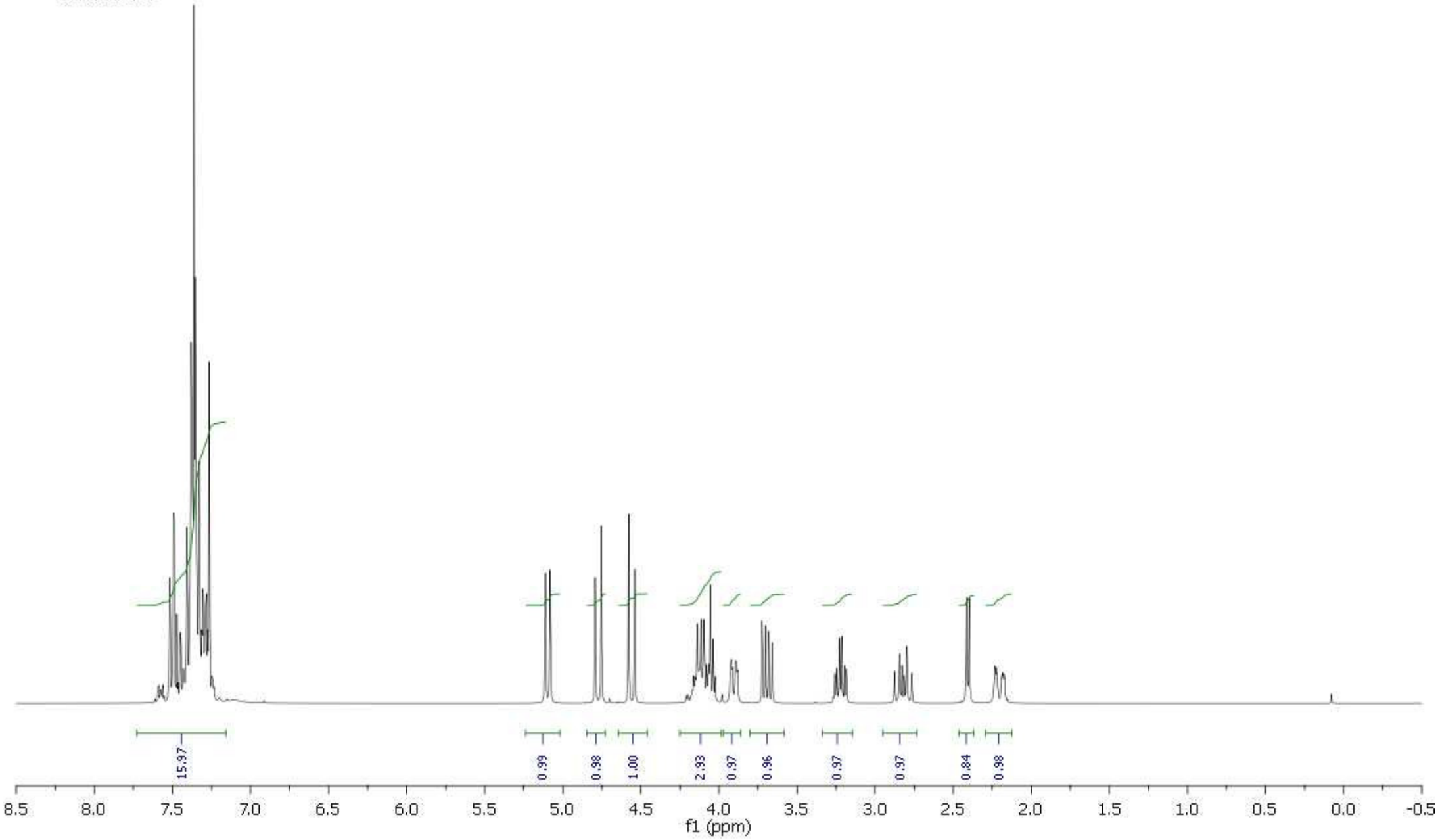

203.80
197.83
141.12
140.84
137.51
136.18
129.23
128.87
128.40
128.32
127.84
127.62
127.35
126.80
93.31
85.90
85.61
79.27
77.42
76.99
76.57
72.29
71.16
70.54
58.93
31.10
HO
BnO
O
Ph
Ph
Co(CO)3
Co(CO)3
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

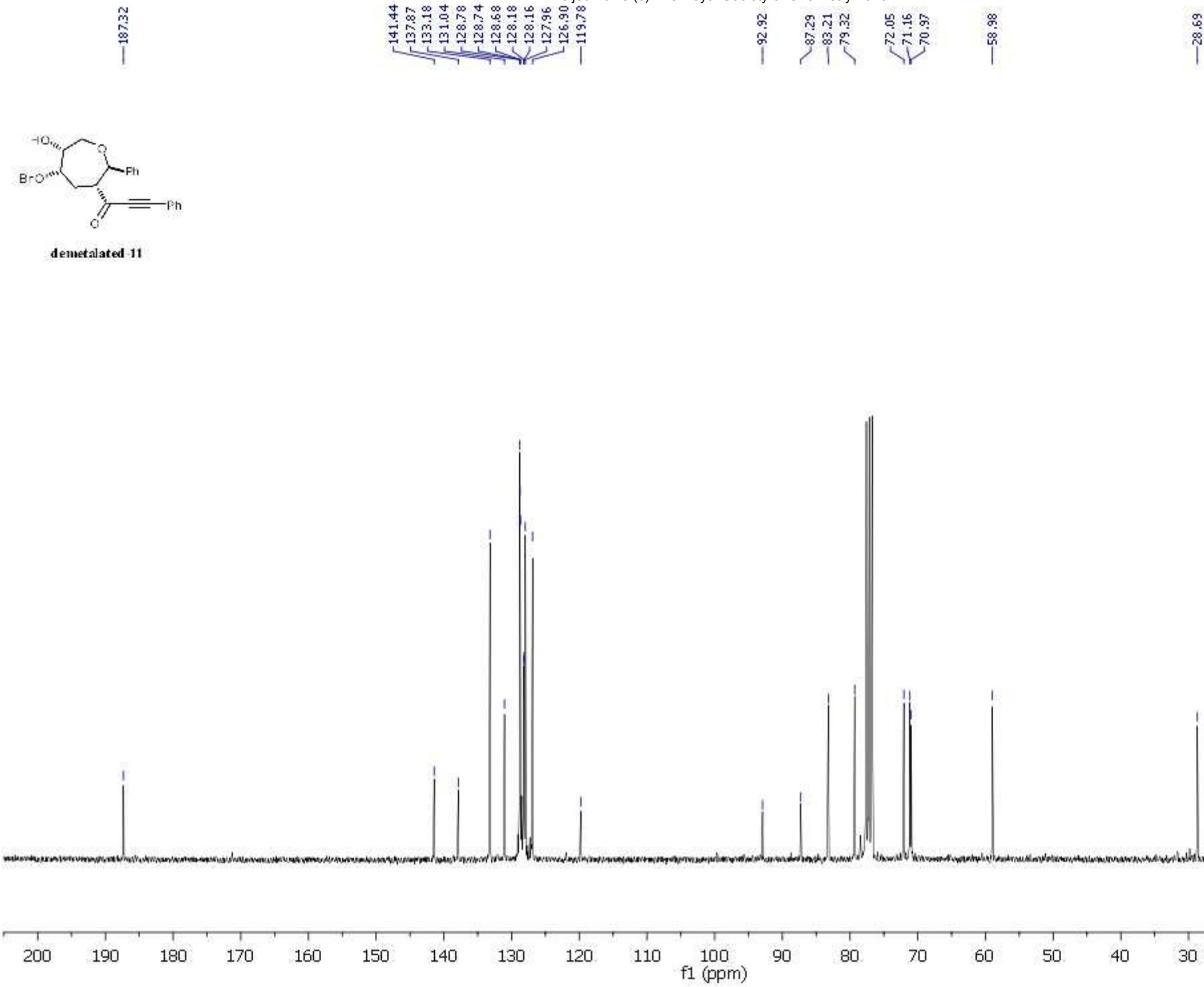

H-2
H-7ax
H-4eq
OH
H-4ax
7
6
5
4
3
2
1
ppm
-5.82
-6.72
-5.74
-4.48
162.94
-24.96
-14.22
HO
BnO
H7ax
Ph
H2
O
H4ax
Ph
Co(CO)3
Co(CO)3

11

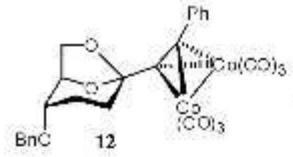


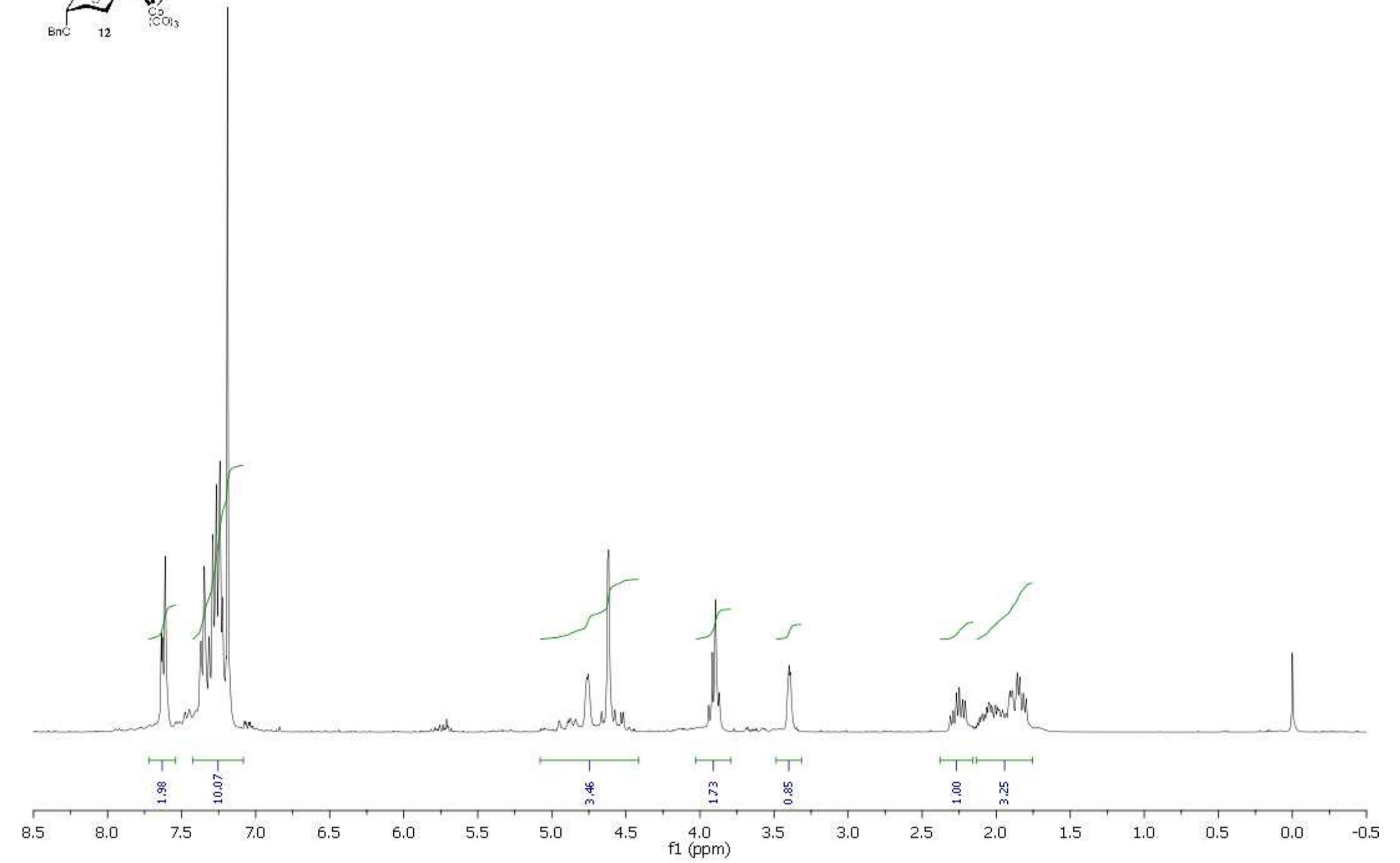
demetalated-f1

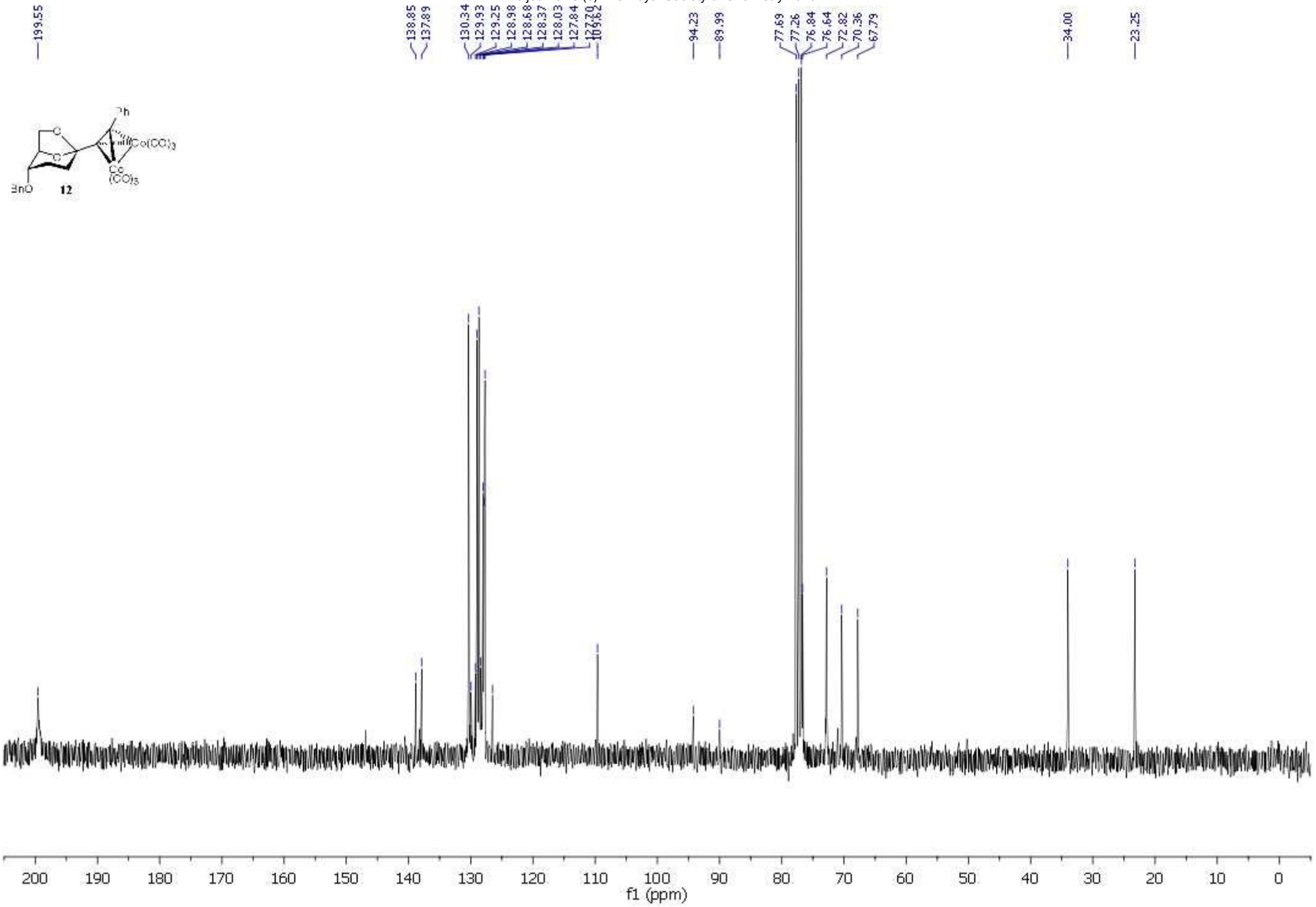


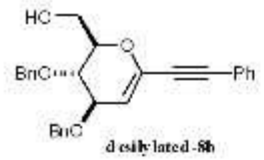


demetalated 11

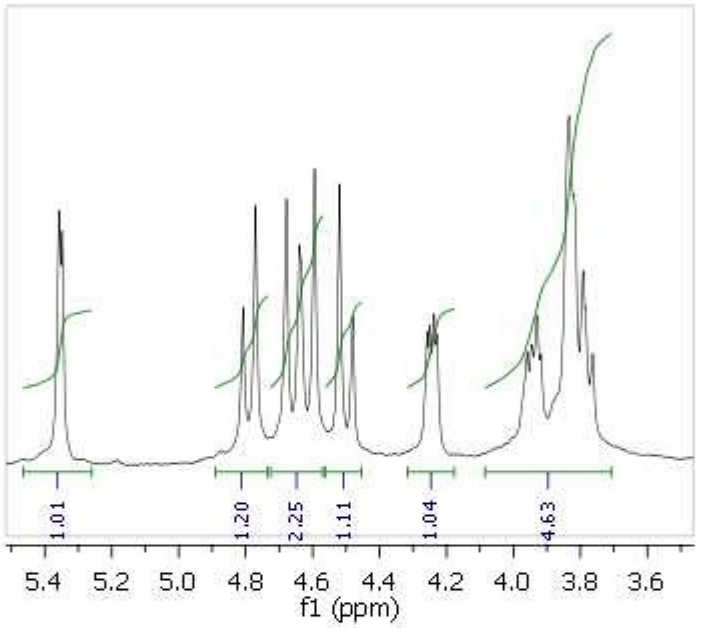

Ph
Co(CO)3
Co
(CO)3
BnC
12

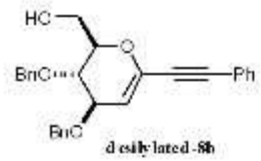

1.98
10.07
3.46
1.73
0.85
1.00
3.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


199.55
138.85
137.89
130.34
129.93
129.25
128.98
128.68
128.37
128.03
127.84
127.70
109.62
94.23
89.99
77.69
77.26
76.84
76.64
72.82
70.36
67.79
34.00
23.25
Ph
Co(CO)3
Co
(CO)3
BnO
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

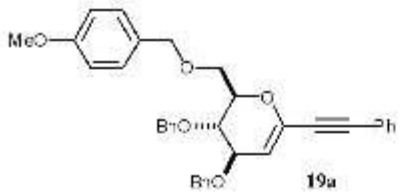


desilylated-8h



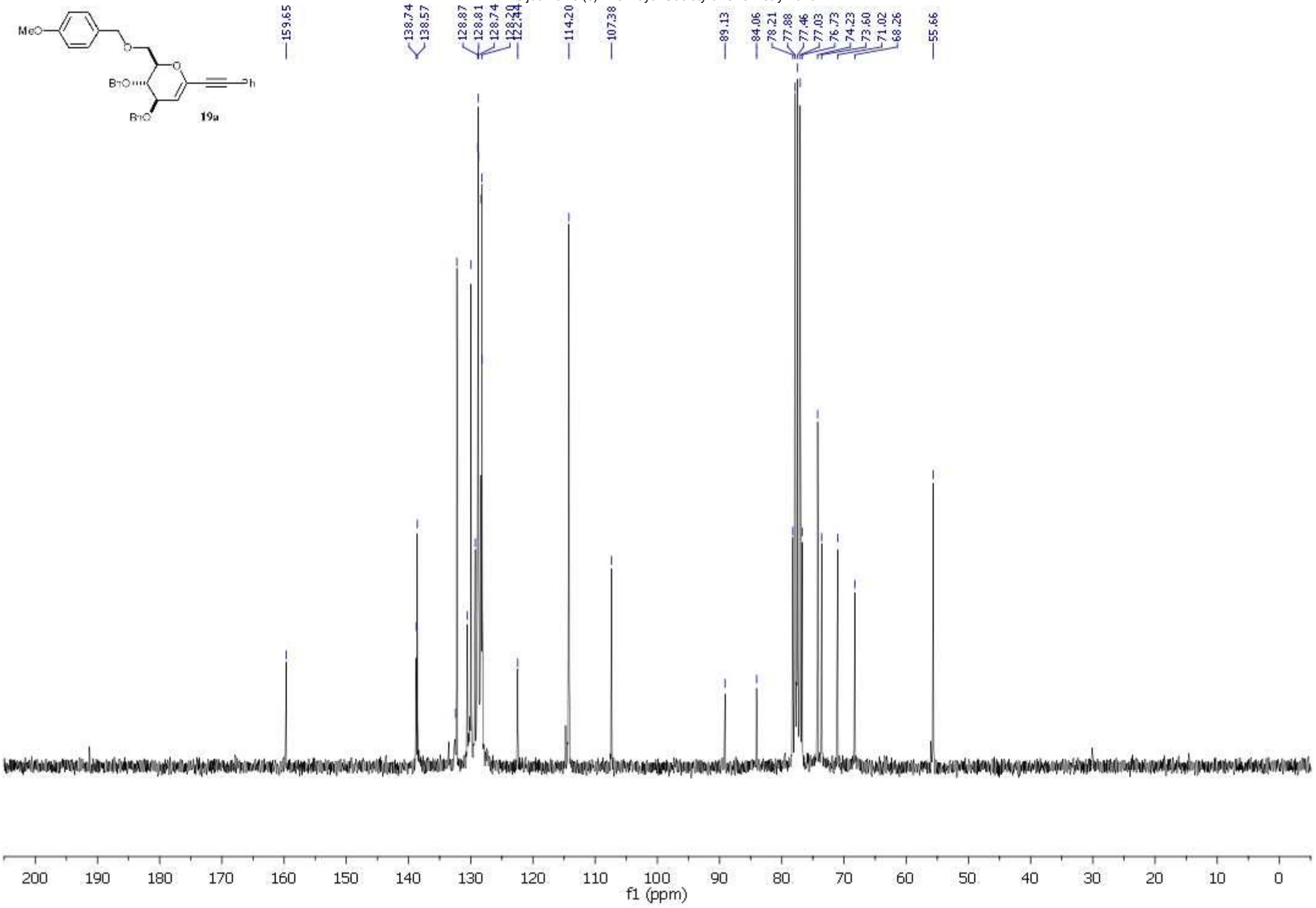


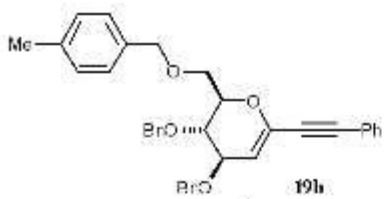
desilylated-8h


MeO
BnO
BnO
Ph

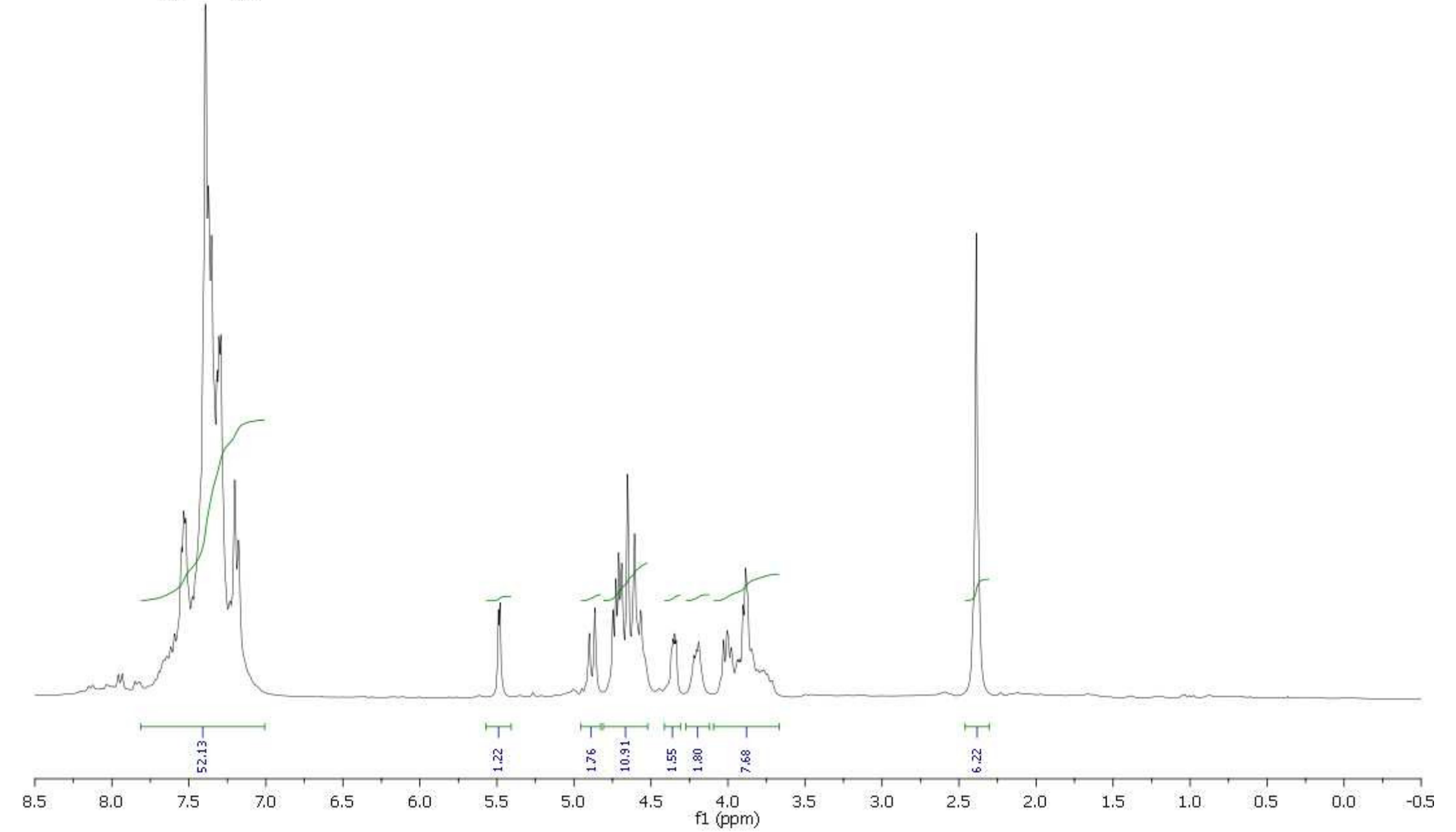
19a

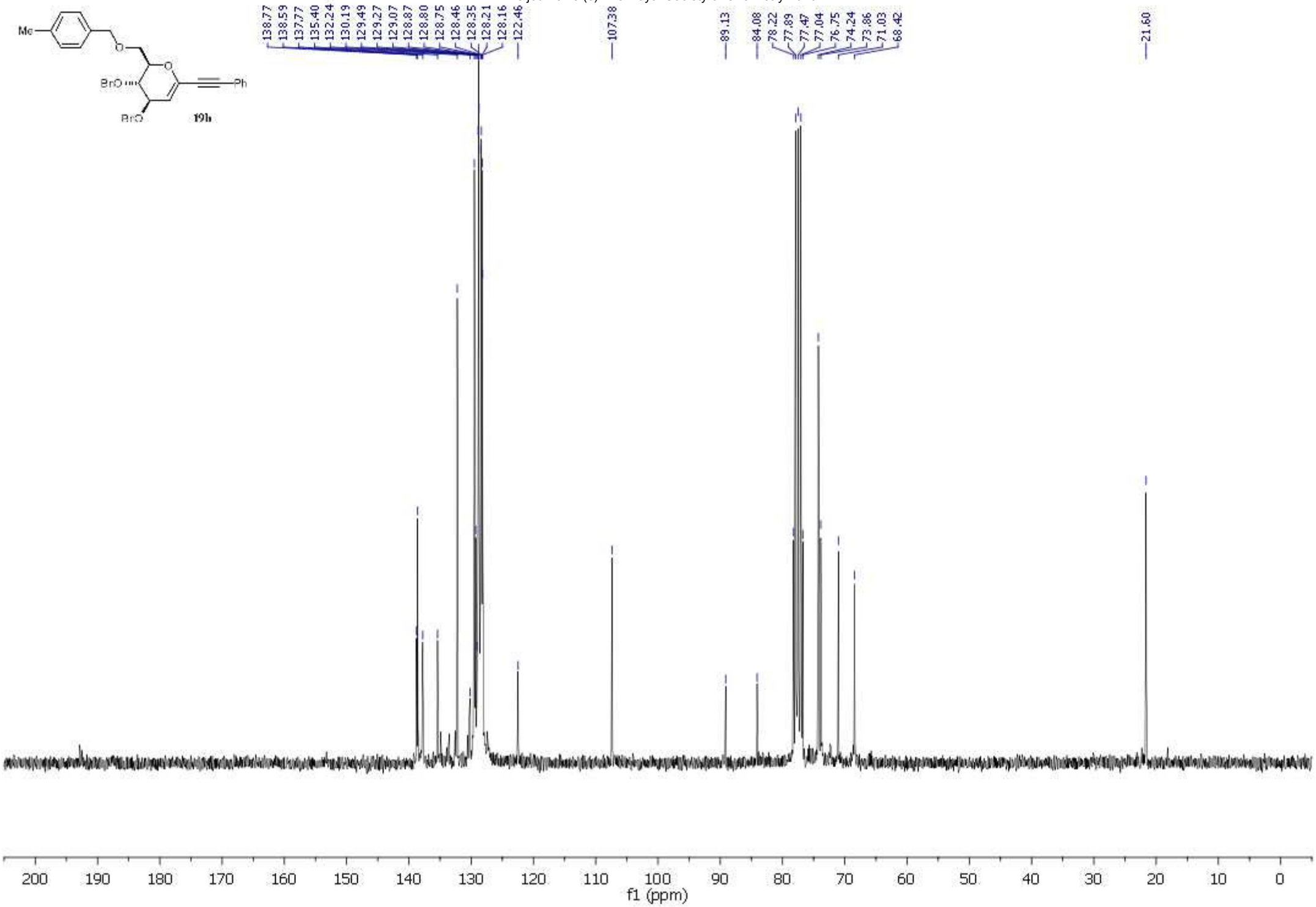
25.50
1.00
1.56
7.07
1.35
1.31
9.74
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

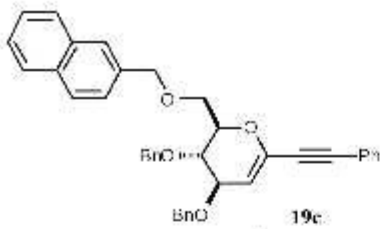

MeO
BnO
BnO
Ph
19a
159.65
138.74
138.57
128.87
128.81
128.74
128.20
127.44
114.20
107.38
89.13
84.06
78.21
77.88
77.46
77.03
76.73
74.23
73.60
71.02
68.26
55.66
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
O
BnO
Ph
BnO

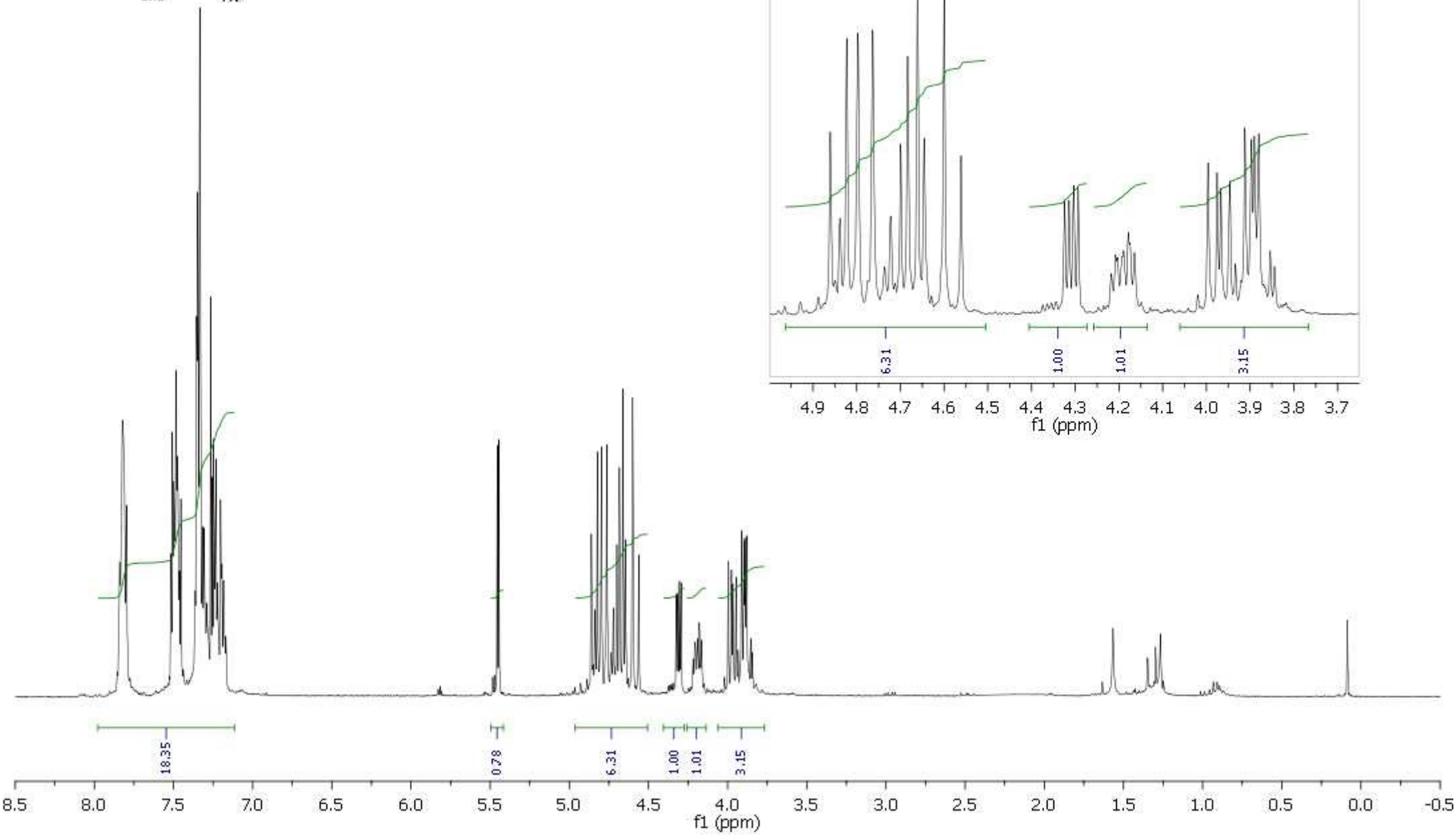
19h

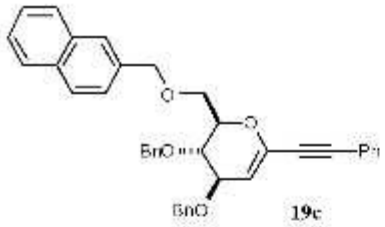

52.13
1.22
1.76
10.91
1.55
1.80
7.68
6.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
O
O
BnO
Ph
BnO
19h
138.77
138.59
137.77
135.40
132.24
130.19
129.49
129.27
129.07
128.87
128.80
128.75
128.46
128.35
128.21
128.16
122.46
107.38
89.13
84.08
78.22
77.89
77.47
77.04
76.75
74.24
73.86
71.03
68.42
21.60
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
BnO
Ph

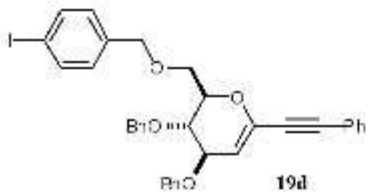
19c


18.35
0.78
6.31
1.00
1.01
3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
6.31
1.00
1.01
3.15
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7
f1 (ppm)

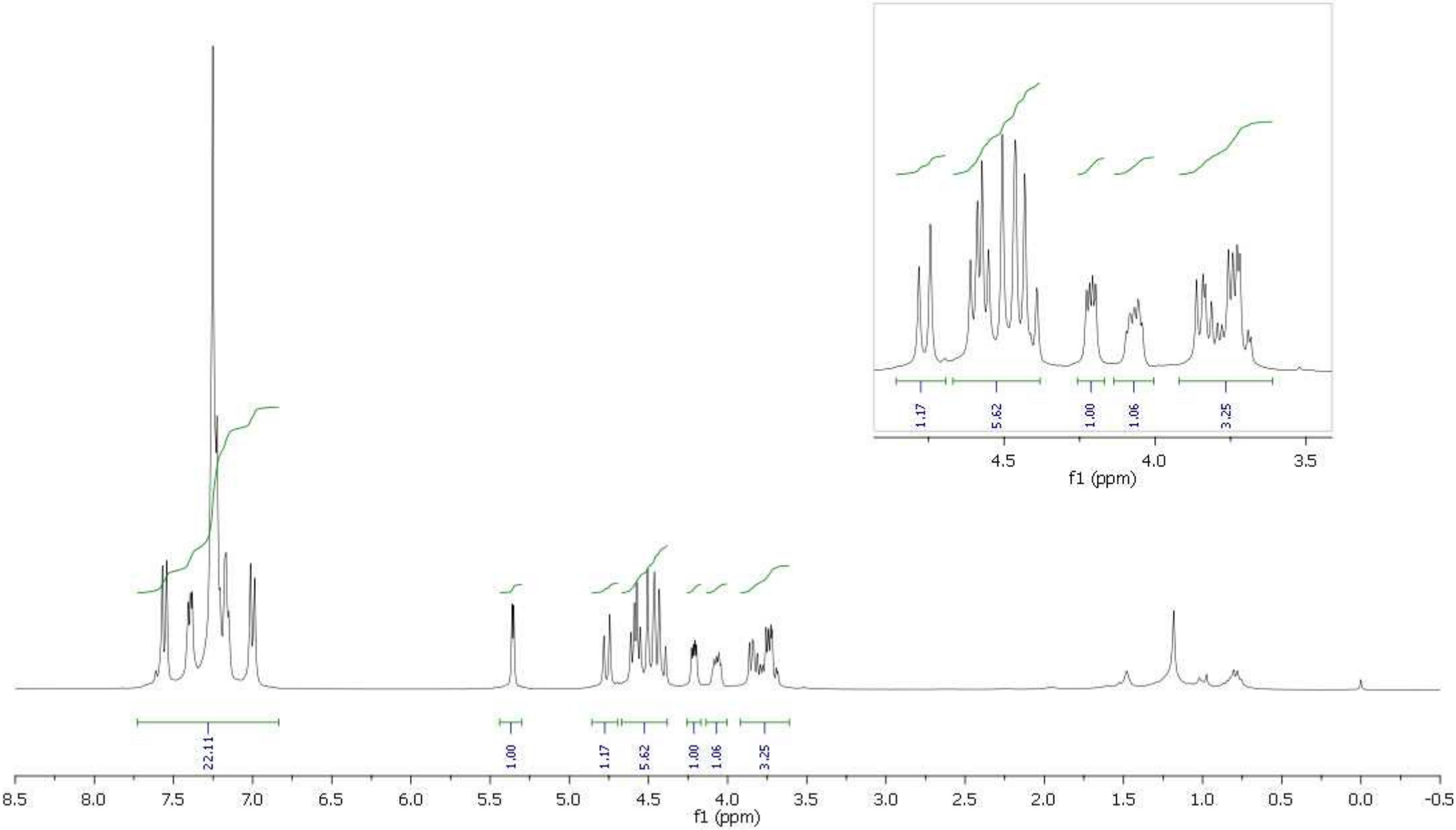

BnO
BnO
Ph

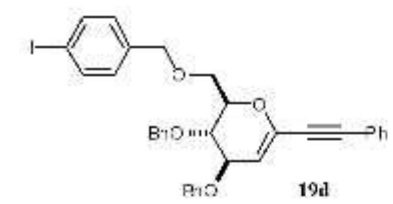
19c

138.83
138.65
138.60
136.07
133.80
133.53
132.33
129.40
128.96
128.87
128.69
128.47
128.36
128.28
128.24
127.08
126.58
126.37
122.52
107.50
89.31
84.27
78.30
78.06
77.63
77.21
76.81
74.33
74.30
74.09
71.10
68.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


I
O
O
BnO
Ph
BnO

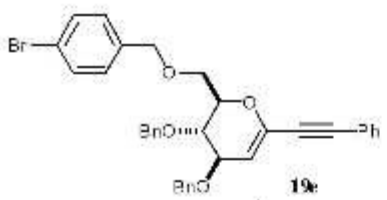
19d


22.11
1.00
1.17
5.62
1.00
1.06
3.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.17
5.62
1.00
1.06
3.25
4.5
4.0
3.5
f1 (ppm)

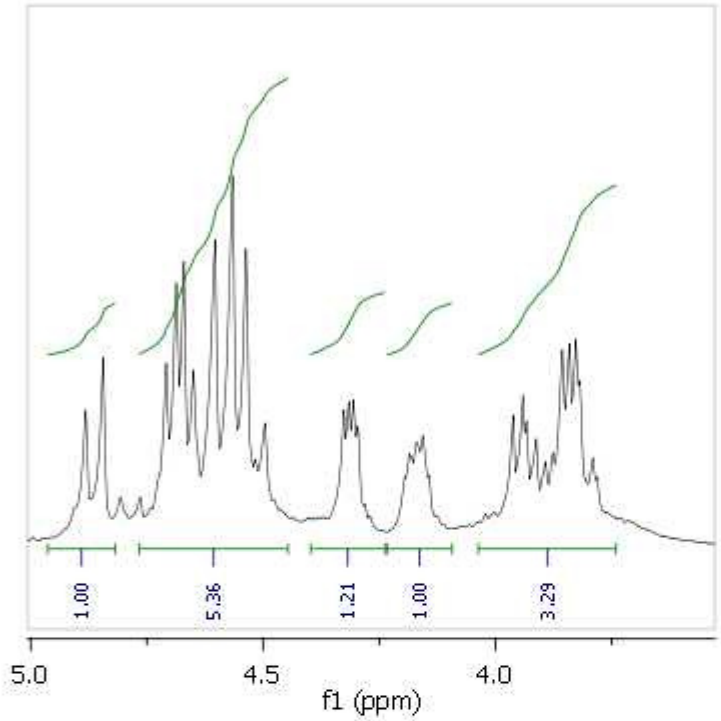

I
O
BnO
Ph
BnO

19d

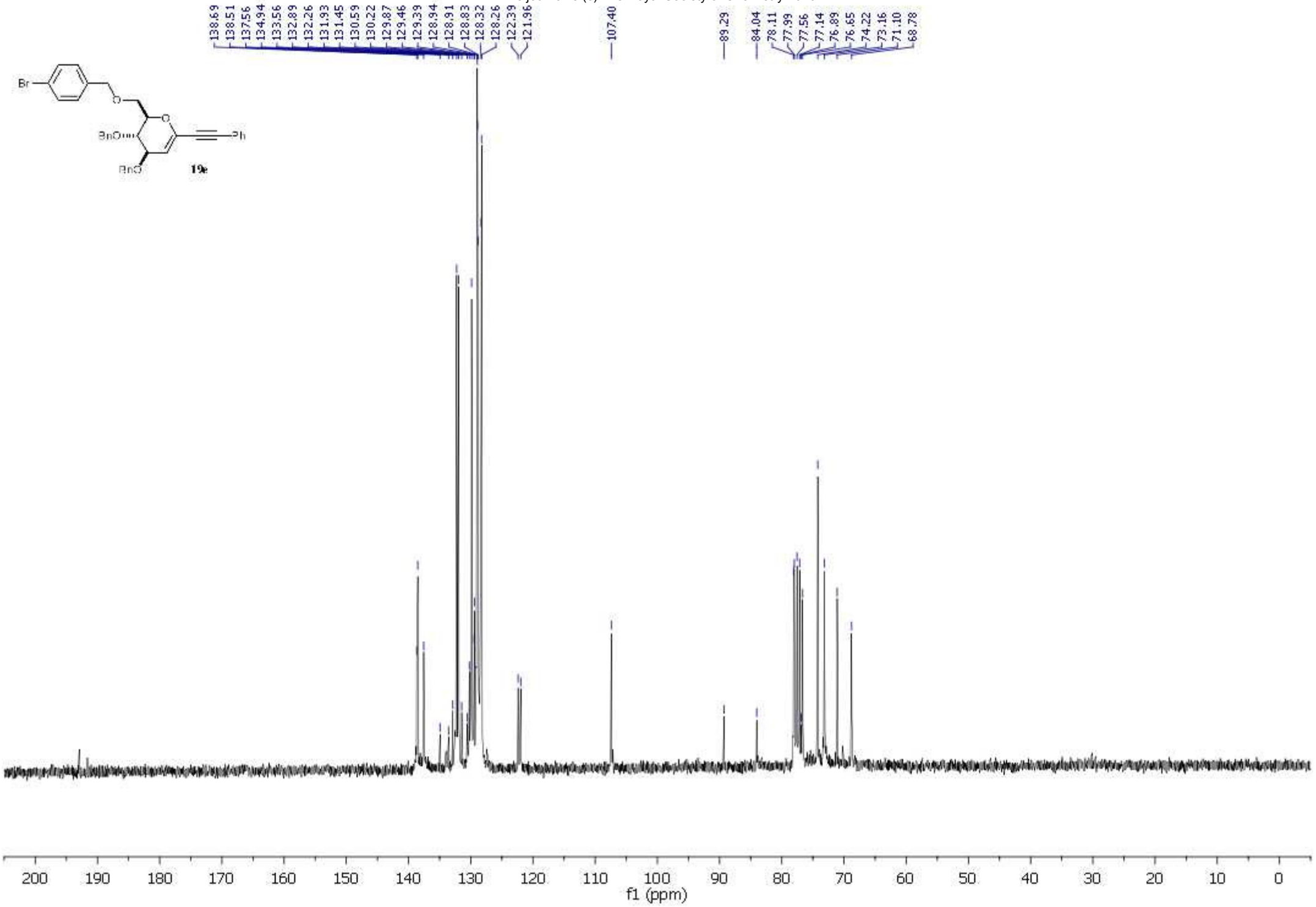
138.67
138.50
138.22
137.88
128.90
128.88
128.28
128.22
122.38
107.35
93.51
89.22
83.97
78.10
77.88
77.46
77.04
76.65
74.19
73.22
71.08
68.77
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

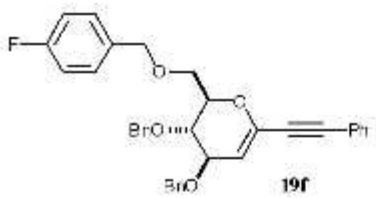

Br
O
O
BnO
Ph
BnO

19e

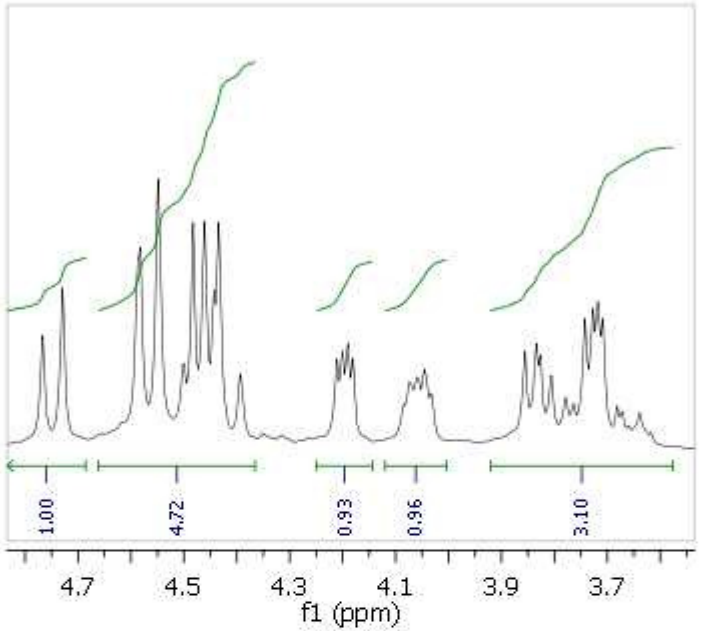

1.00
5.36
1.21
1.00
3.29
5.0
4.5
4.0
f1 (ppm)

19.55
0.79
1.00
5.36
1.10
1.00
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

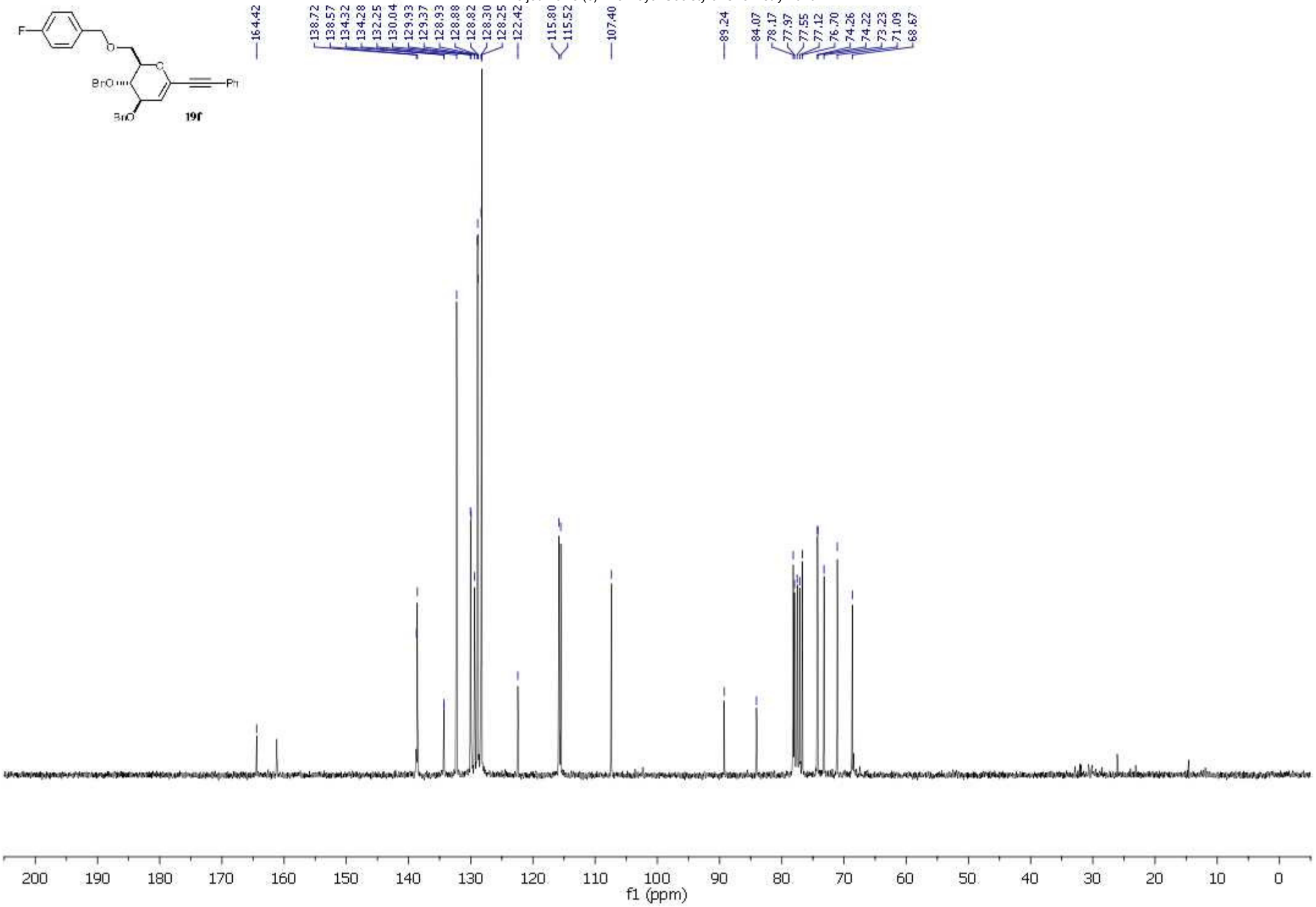

138.69
138.51
137.56
134.94
133.56
132.89
132.26
131.93
131.45
130.59
130.22
129.87
129.46
129.39
128.94
128.91
128.83
128.32
128.26
122.39
121.96
107.40
89.29
84.04
78.11
77.99
77.56
77.14
76.89
76.65
74.22
73.16
71.10
68.78
Br
O
O
BnO
BnO
Ph
19e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

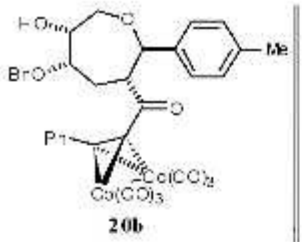

F
O
O
BnO
BnO
Ph

19f

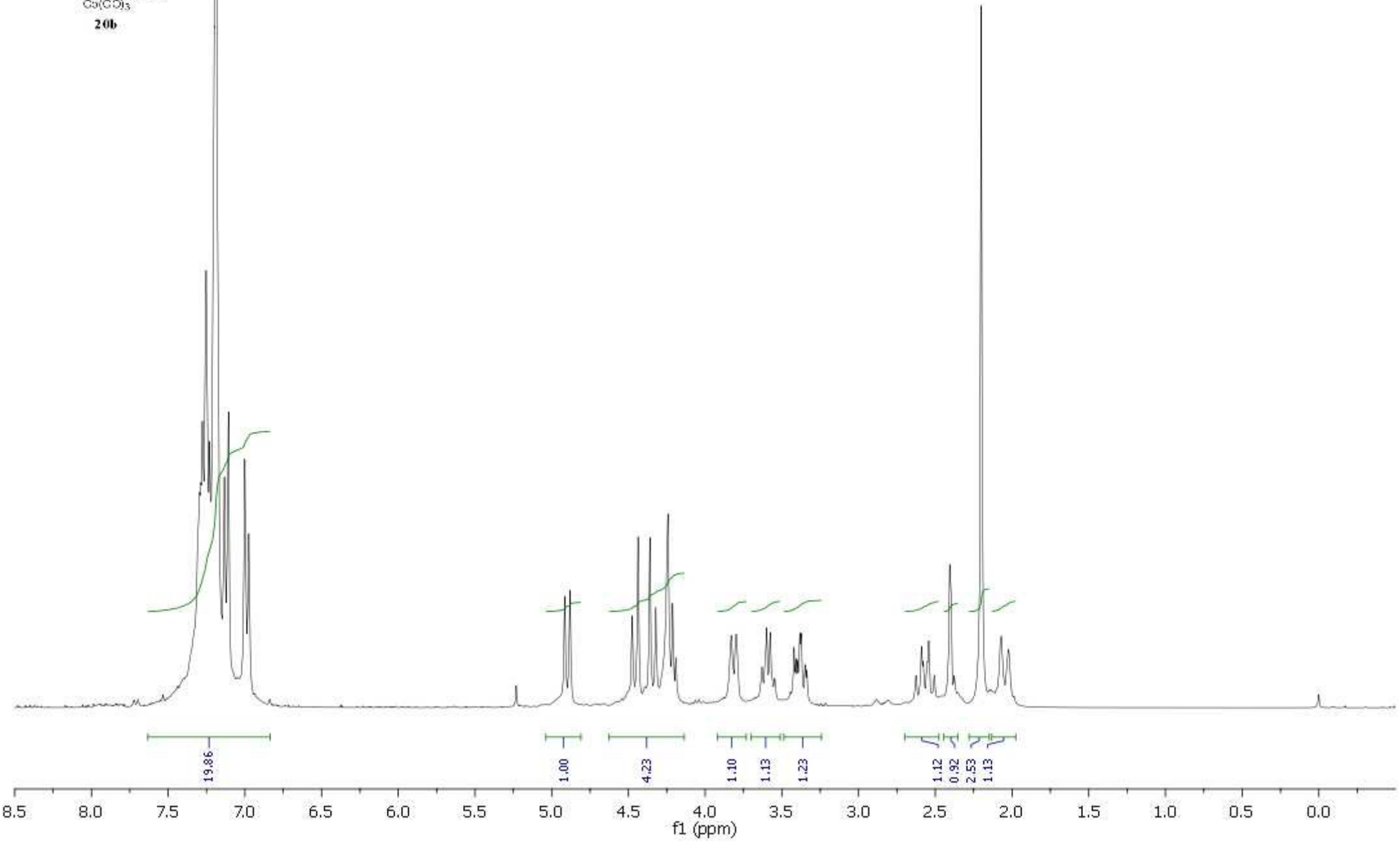

1.00
4.72
0.93
0.96
3.10
4.7
4.5
4.3
4.1
3.9
3.7
f1 (ppm)

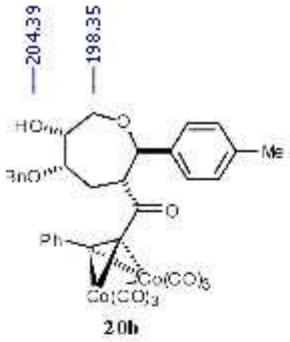
18.90
0.83
1.00
4.72
0.93
0.96
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


F
O
O
BnO
BnO
Ph
19f
164.42
138.72
138.57
134.32
134.28
132.25
130.04
129.93
129.37
128.93
128.88
128.82
128.30
128.25
122.42
115.80
115.52
107.40
89.24
84.07
78.17
77.97
77.55
77.12
76.70
74.26
74.22
73.23
71.09
68.67
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
BnO
O
Me
O
Pr
Co(CO)3
Co(CO)3

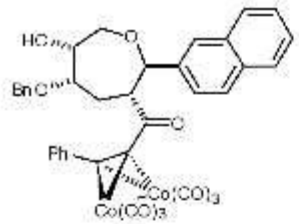
20b


19.86
1.00
4.23
1.10
1.13
1.23
1.12
0.92
2.53
1.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
BnO
O
Me
O
Ph
Co(CO)3
Co(CO)3

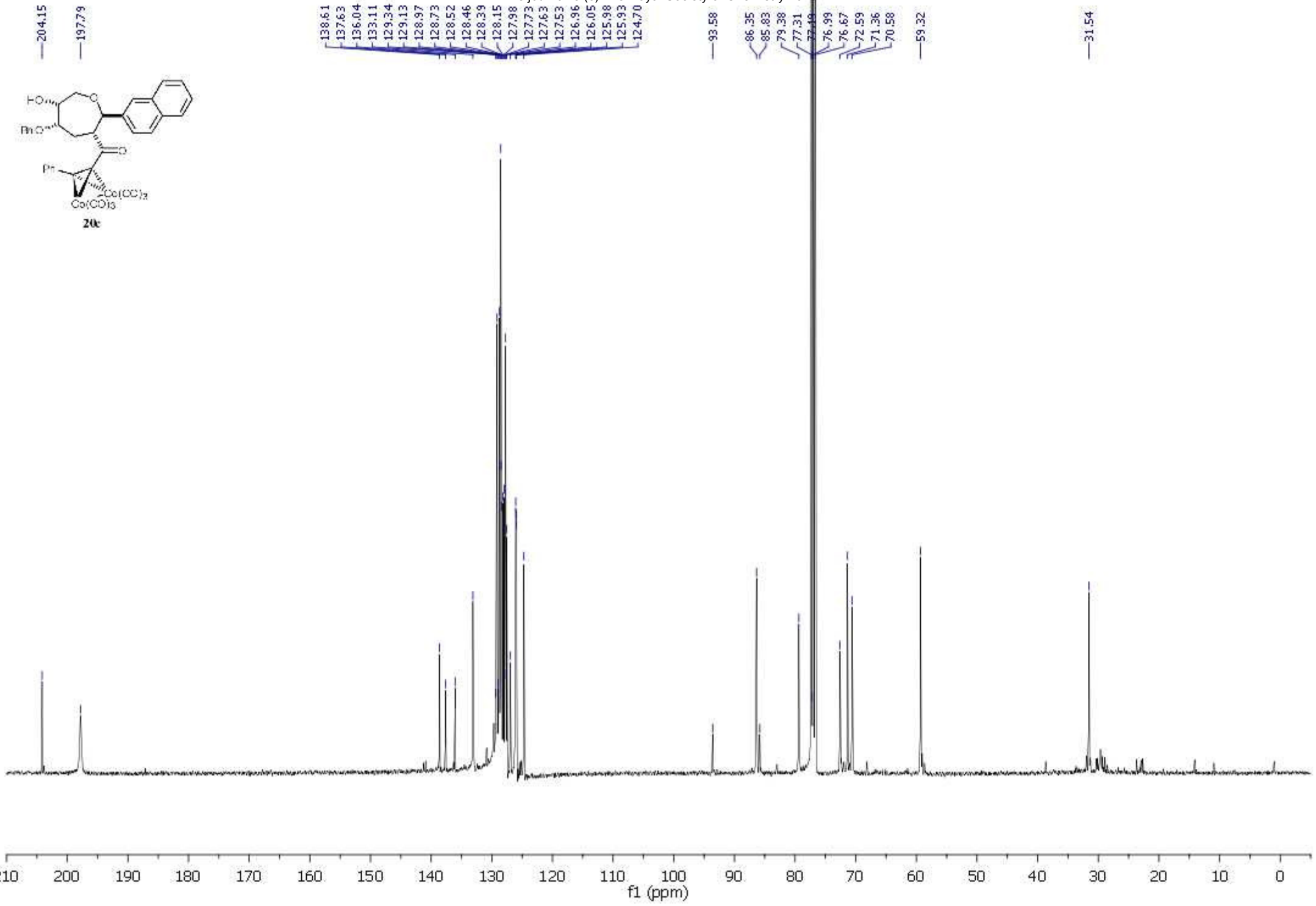
20b

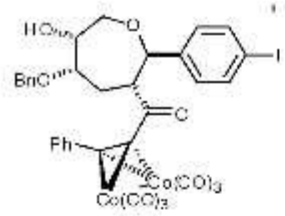
204.39
198.35
138.71
138.14
138.10
136.81
129.81
129.60
129.35
128.94
128.38
128.15
127.22
93.97
86.57
79.87
77.87
77.45
77.02
72.72
71.74
70.98
59.51
31.74
21.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
BnO
O
Ph
Co(CO)3
Co(CO)3

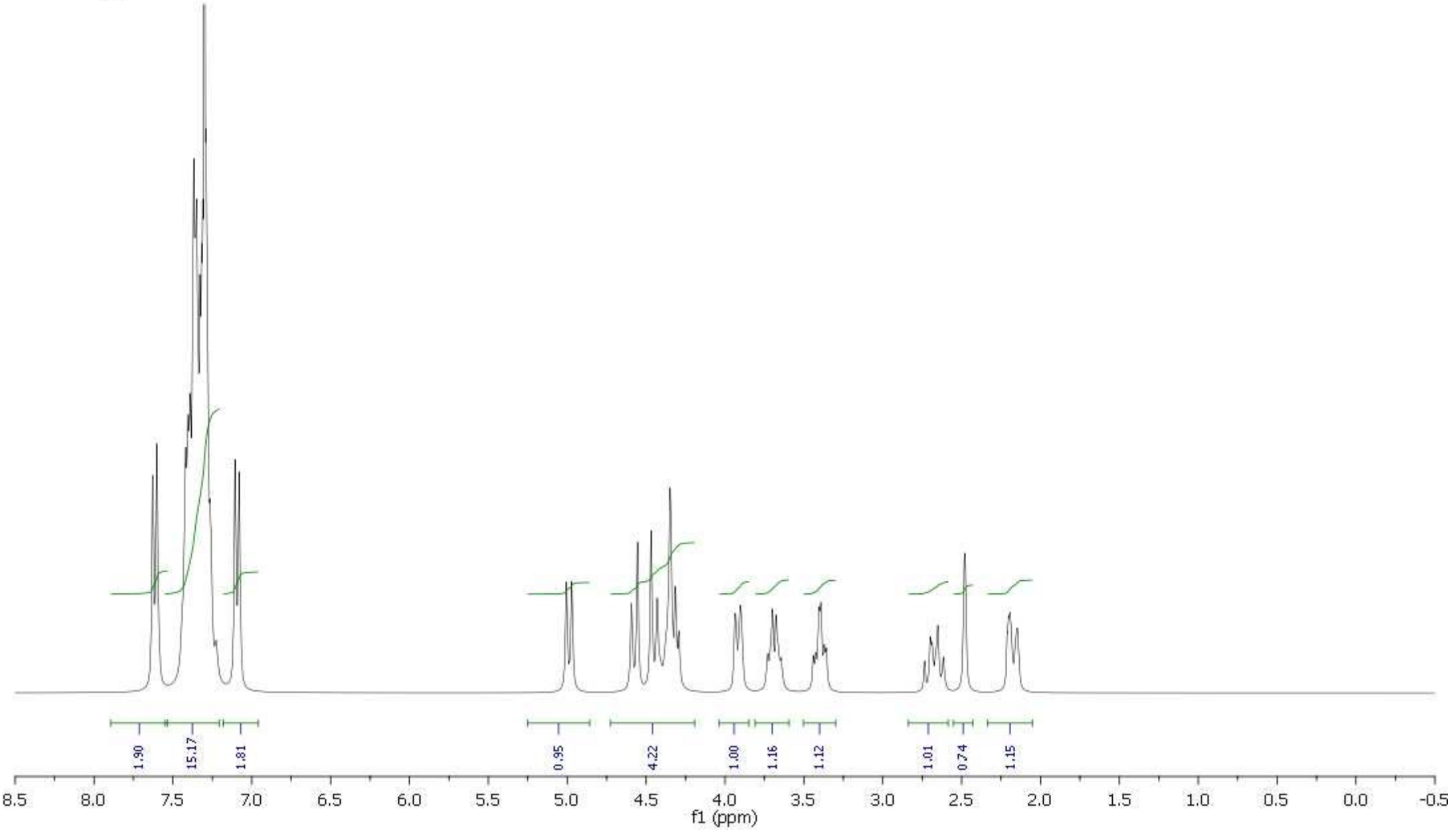
20k

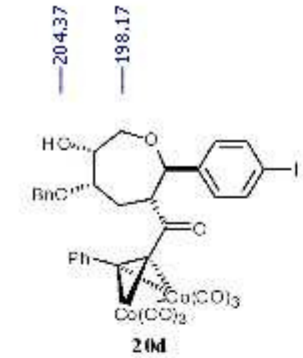
22.53
1.00
1.05
1.07
3.20
1.11
1.10
1.11
1.05
1.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


204.15
197.79
138.61
137.63
136.04
133.11
129.34
129.13
128.97
128.73
128.52
128.46
128.39
128.15
127.98
127.73
127.63
127.53
126.96
126.05
125.98
125.93
124.70
93.58
86.35
85.83
79.38
77.31
77.19
76.99
76.67
72.59
71.36
70.58
59.32
31.54
HO
BnO
Pr
Co(CO)3
Co(CO)3
20c
f1 (ppm)


BnO
Ph
Co(CO)3
Co(CO)3

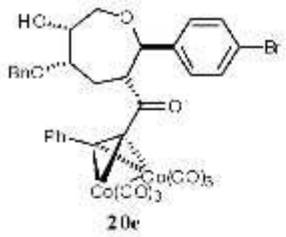
20d


1.90
15.17
1.81
0.95
4.22
1.00
1.16
1.12
1.01
0.74
1.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

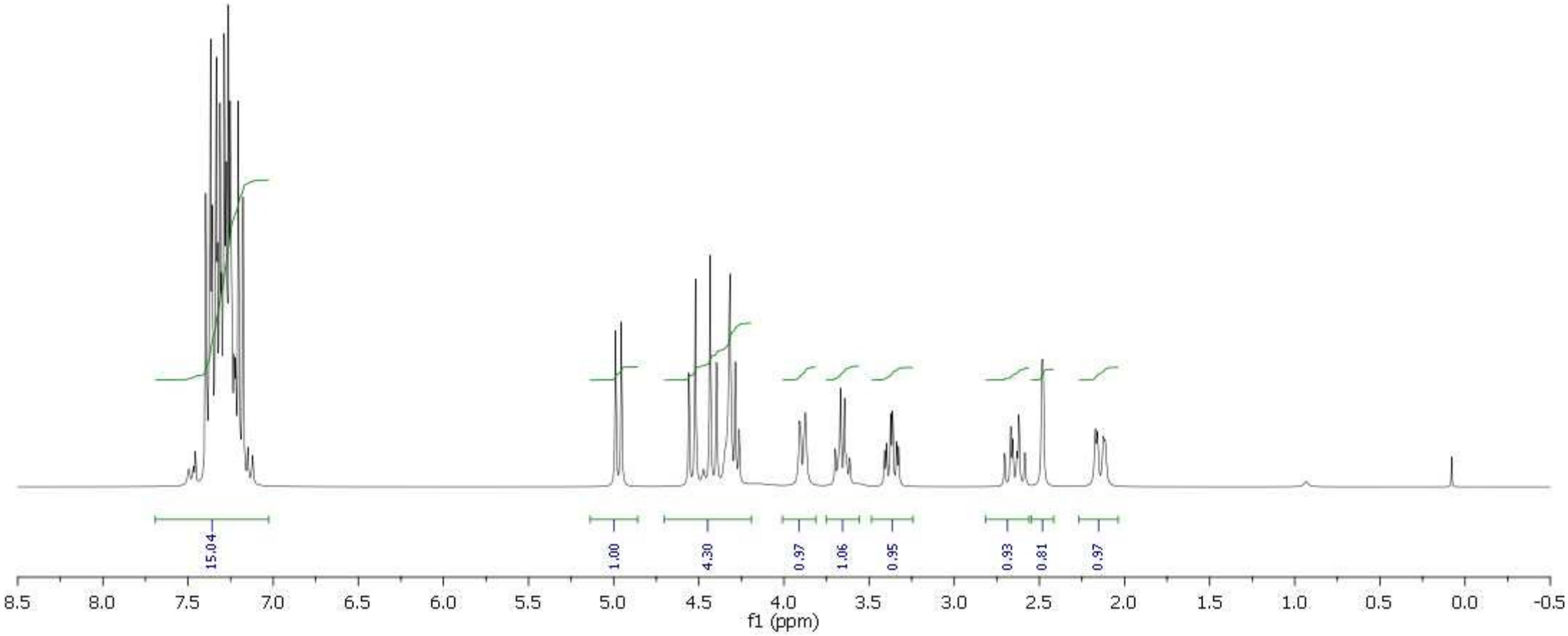

HC
BnO
O
I
O
Ph
Co(CO)3
Co(CO)3

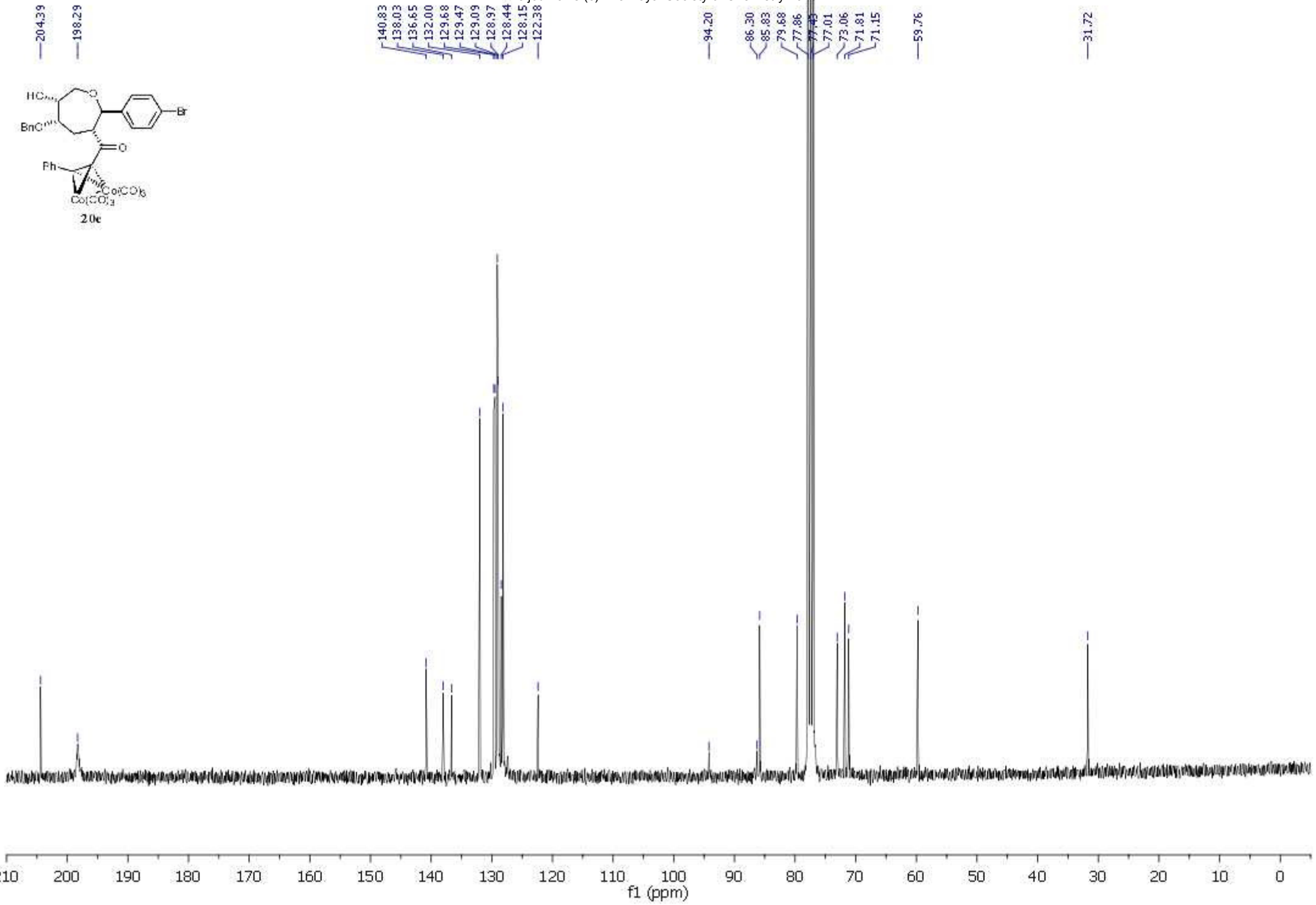
20d

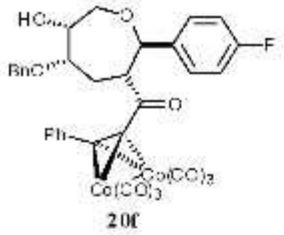
204.37
198.17
141.46
137.96
136.65
132.41
129.68
129.50
129.30
129.10
128.97
128.65
128.44
128.15
94.07
86.30
85.89
79.67
77.86
77.44
77.02
73.04
71.81
71.14
66.27
31.74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HC
BnO
Br
O
Ph
Co(CO)3
Co(CO)3

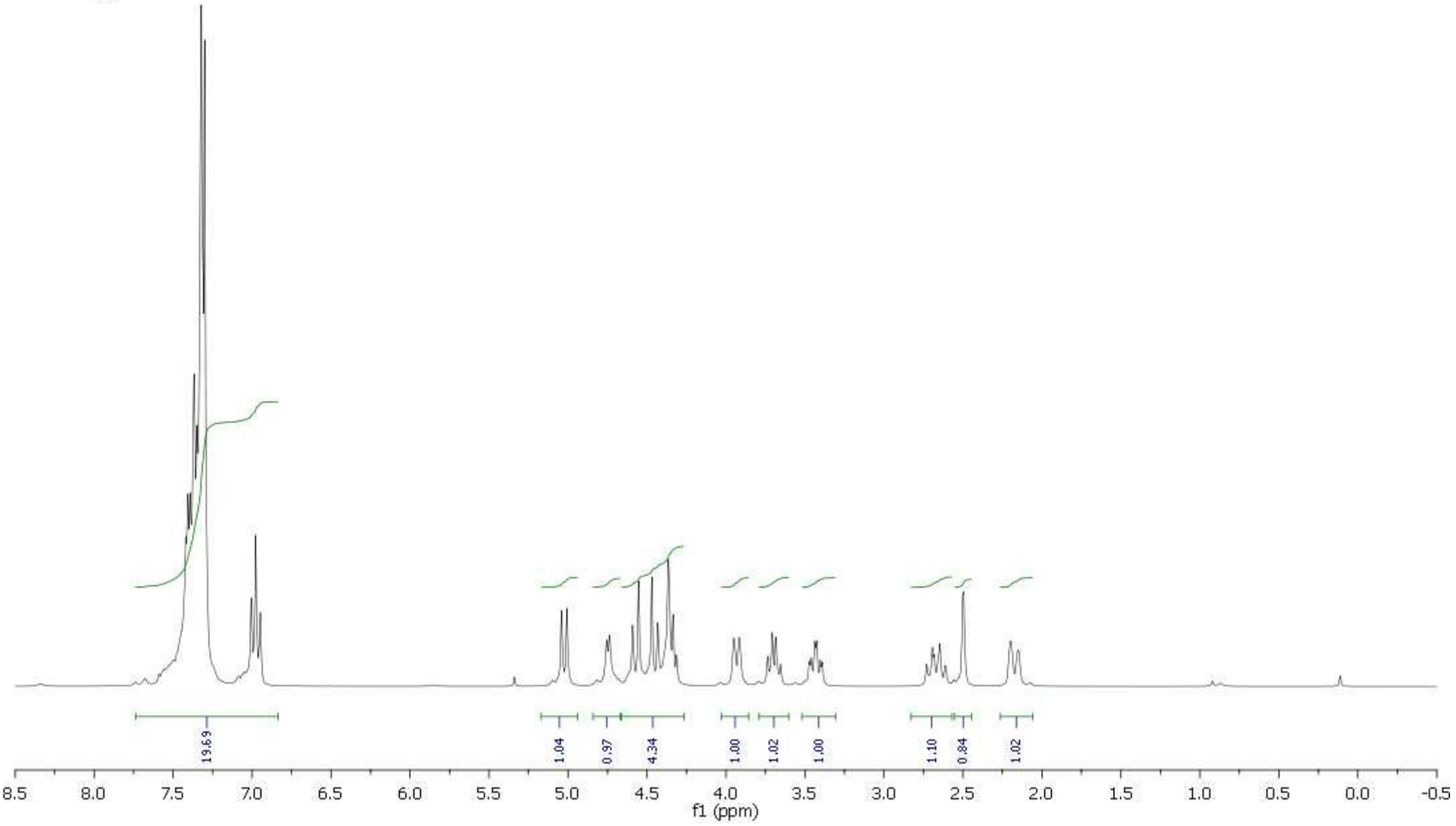
20e

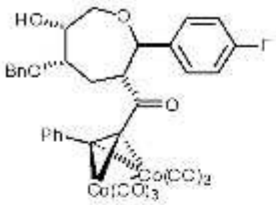

15.04
1.00
4.30
0.97
1.06
0.95
0.93
0.81
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


204.39
198.29
140.83
138.03
136.65
132.00
129.68
129.47
129.09
128.97
128.44
128.15
122.38
94.20
86.30
85.83
79.68
77.86
77.45
77.01
73.06
71.81
71.15
59.76
31.72
HC
BnO
O
Br
O
Ph
Co(CO)3
Co(CO)3
20e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HC
BnO
O
F
Ph
Co(CO)3
Co(CO)3

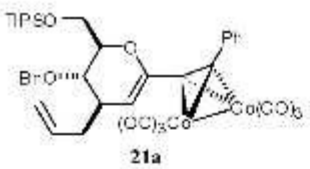
20f


19.69
1.04
0.97
4.34
1.00
1.02
1.00
1.10
0.84
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


HO
BnO
O
Ph
Co(CO)3
Co(CO)3

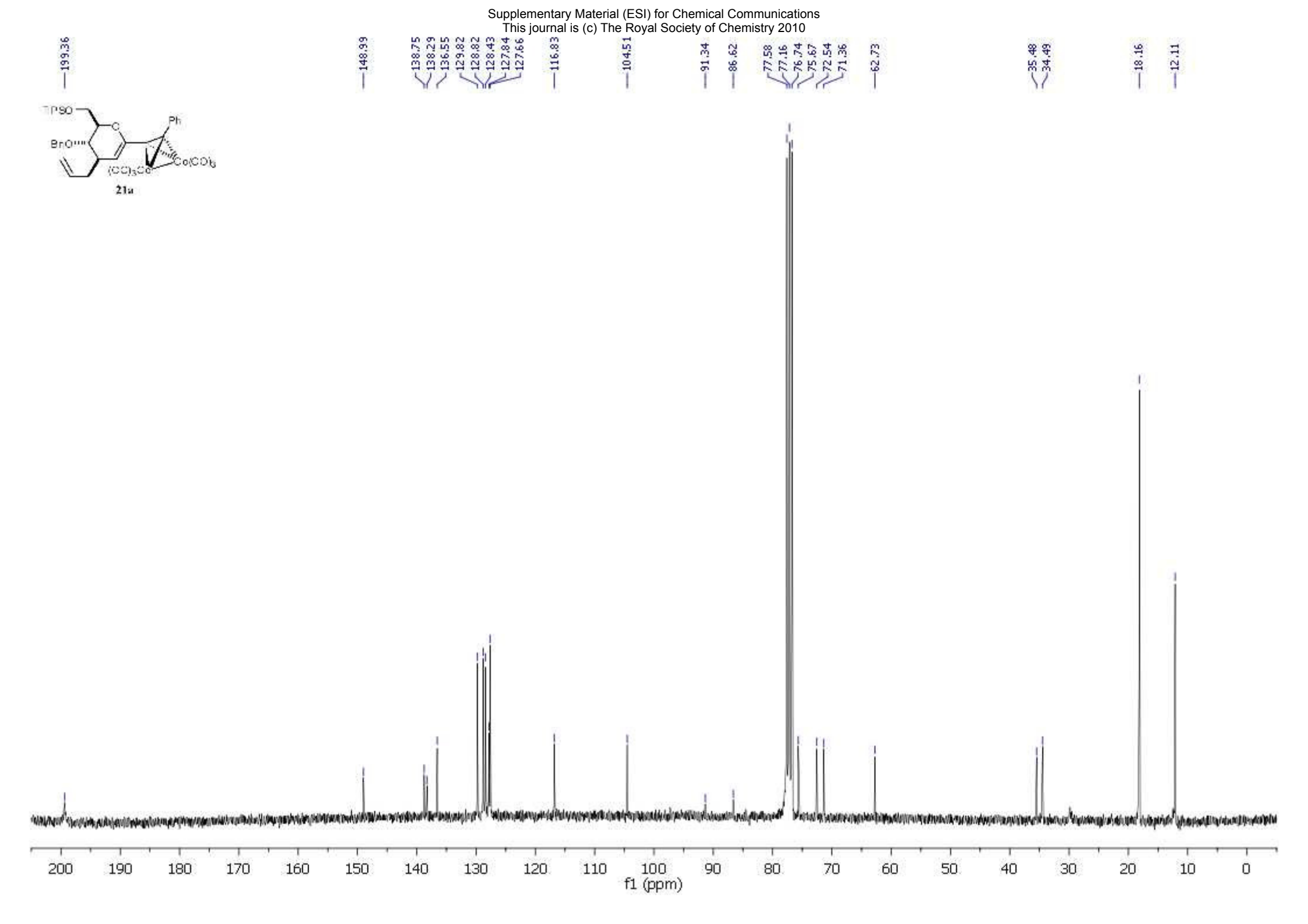
20f

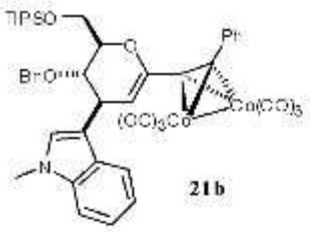
204.33
198.24
164.39
161.12
138.03
137.72
136.68
129.70
129.40
128.95
128.40
94.08
86.33
85.88
79.70
77.85
77.43
77.00
73.05
71.77
31.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TIPSO
Ph
BnO
$(OC)_3Co$
$Co(CO)_3$

21a

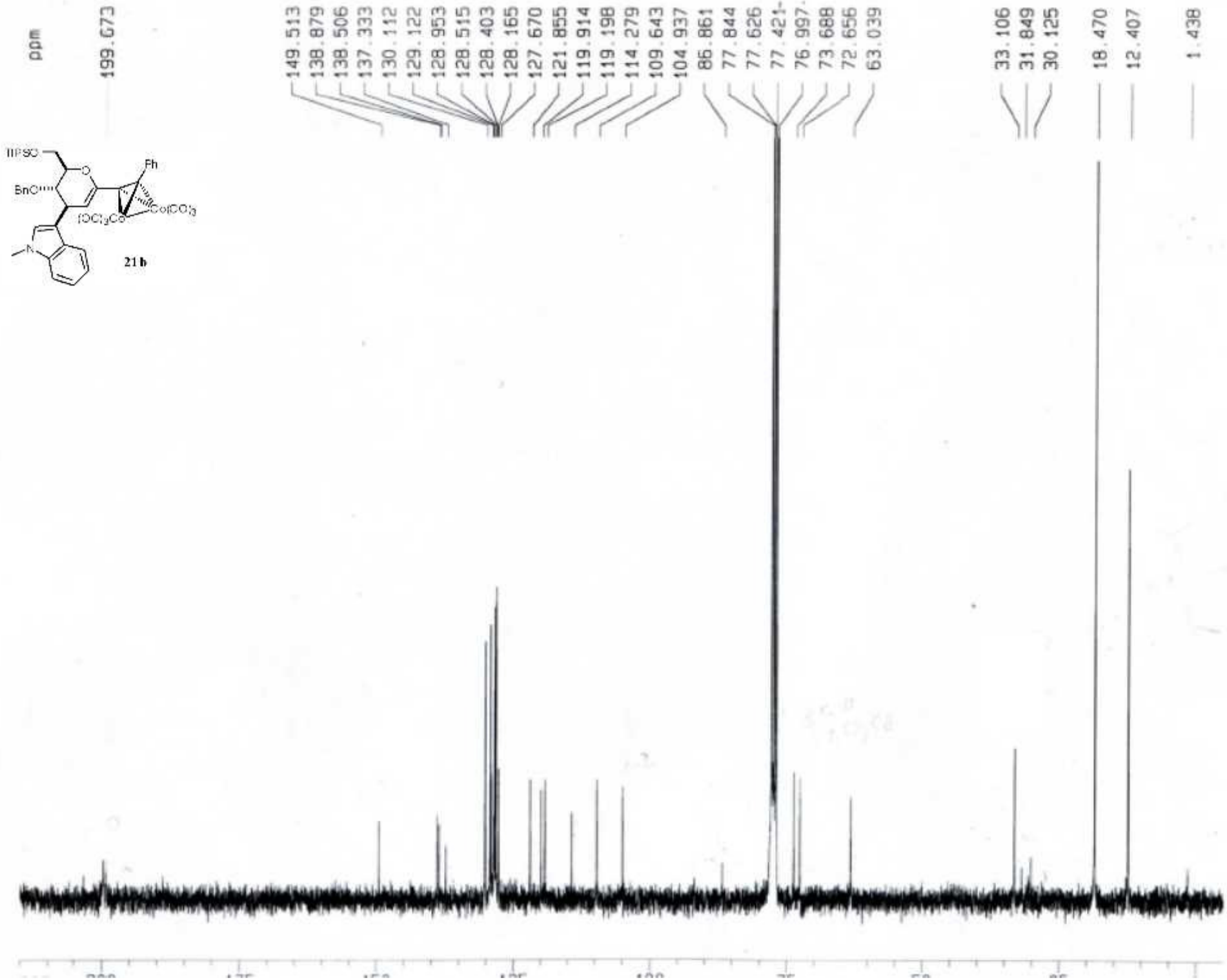
9.06
0.87
0.97
1.93
2.22
0.99
3.12
2.06
1.09
21.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

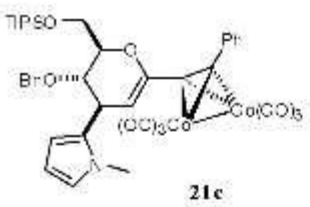

199.36
148.99
138.75
138.29
136.55
129.82
128.82
128.43
127.84
127.66
116.83
104.51
91.34
86.62
77.58
77.16
76.74
75.67
72.54
71.36
62.73
35.48
34.49
18.16
12.11
TPSO
BnO
Ph
Co(CO)3
(CO)3Co
21a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TIPSO
BrO
Ph
$(OC)_3Co$
$Co(CO)_3$
N

21b

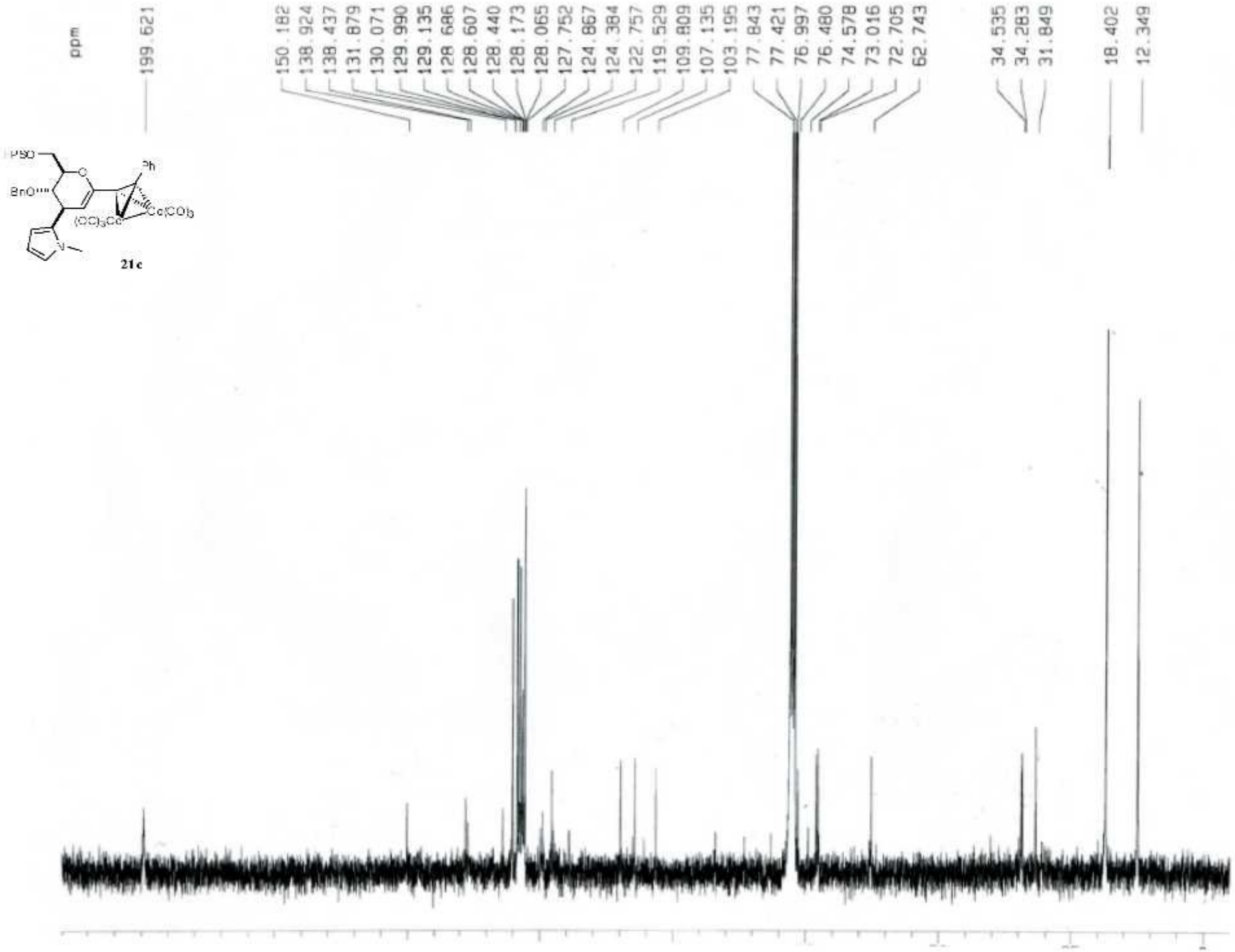
17.56
0.91
2.12
3.88
2.04
2.79
21.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ppm
199.673
149.513
138.879
138.506
137.333
130.112
129.122
128.953
128.515
128.403
128.165
127.670
121.855
119.914
119.198
114.279
109.643
104.937
86.861
77.844
77.626
77.421-
76.997-
73.688
72.656
63.039
33.106
31.849
30.125
18.470
12.407
1.438
TIPSO
BnO
Ph
(OC)3Co
Co(CO)3
N
21b

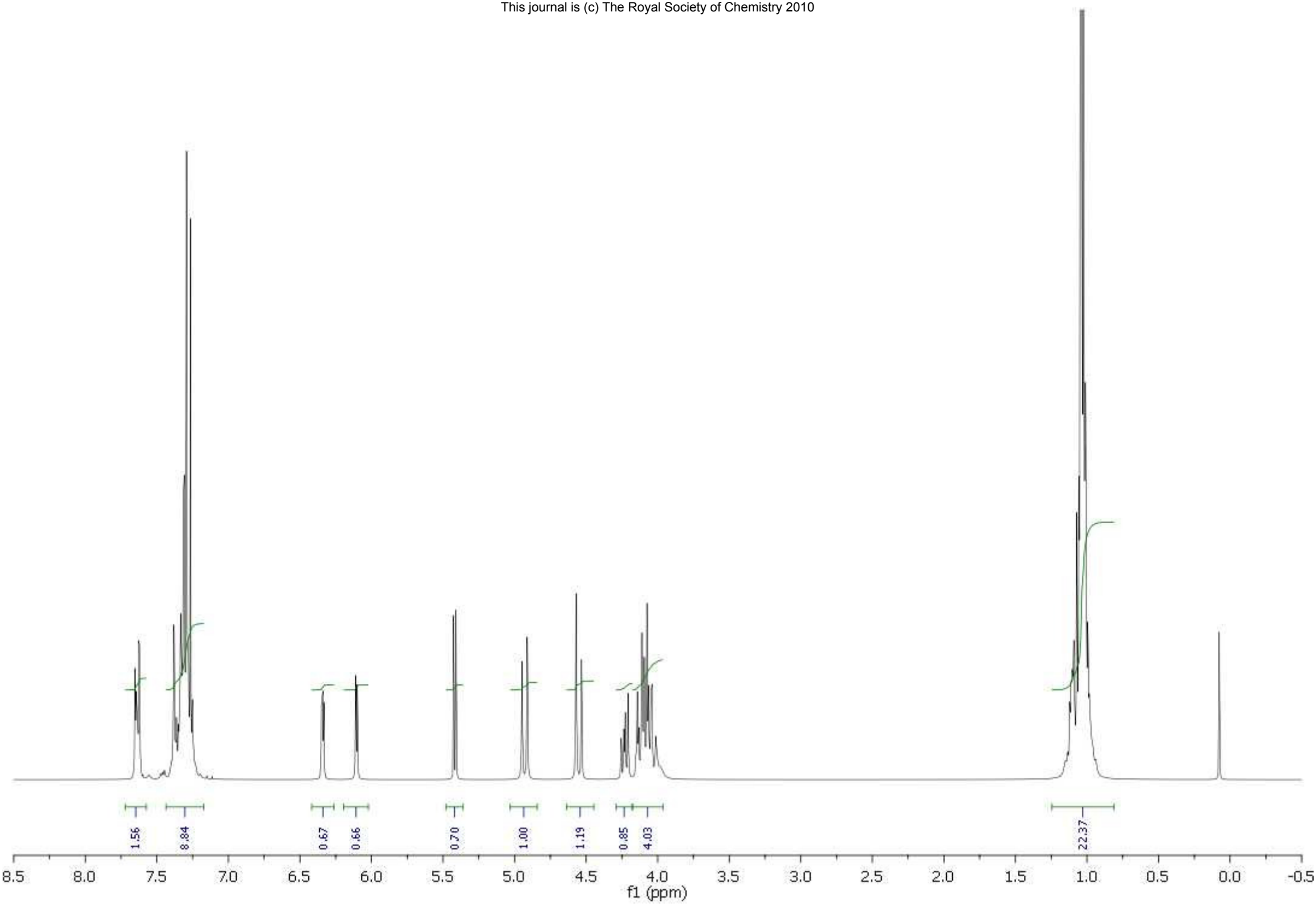

TIPSO
BnO
Ph
$(OC)_3Co$
$Co(CO)_3$

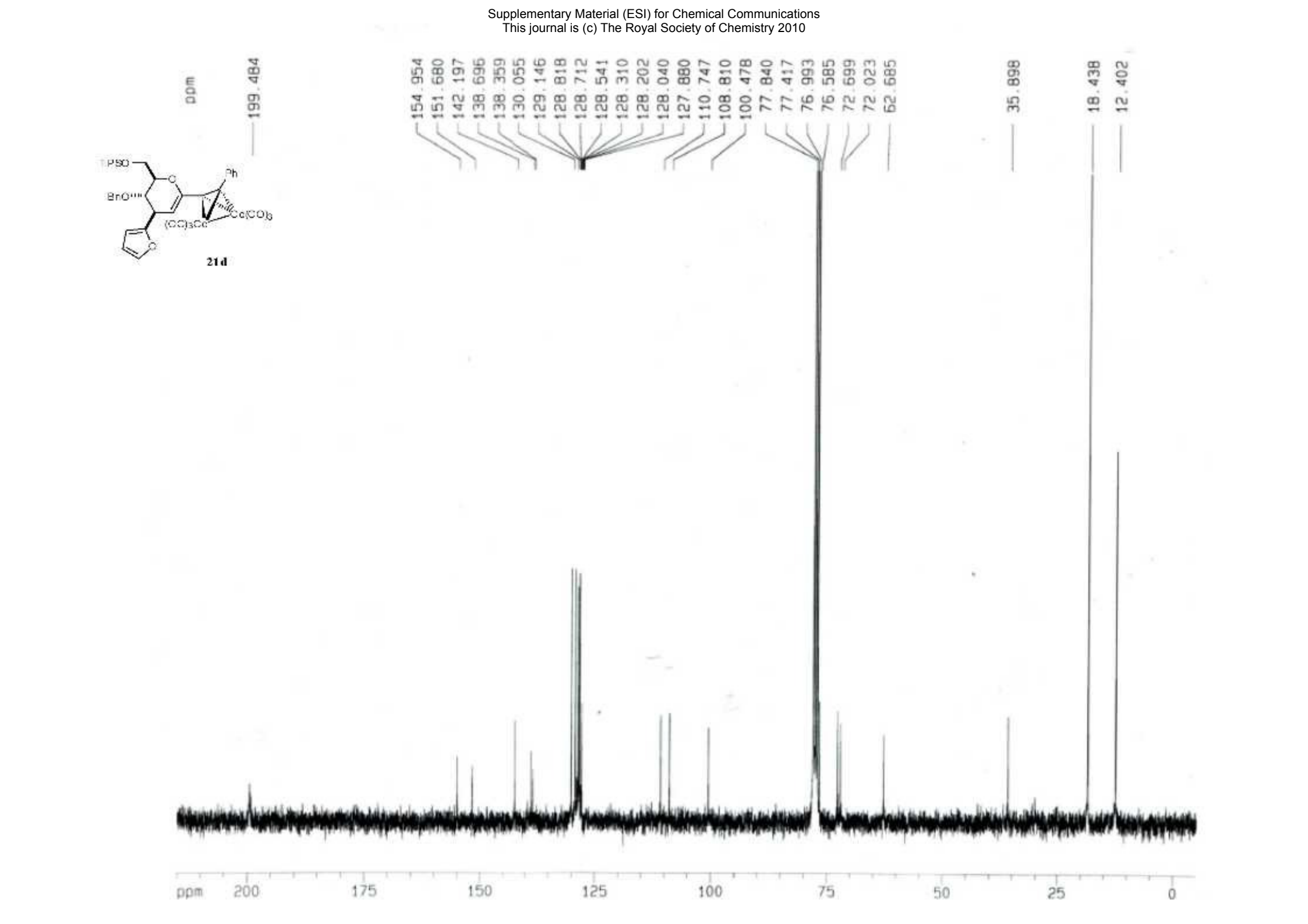
21c

19.72
1.00
0.84
0.67
0.70
2.56
1.05
5.72
3.36
29.52
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ppm
199.621
150.182
138.924
138.437
131.879
130.071
129.990
129.135
128.686
128.607
128.440
128.173
128.065
127.752
124.867
124.384
122.757
119.529
109.809
107.135
103.195
77.843
77.421
76.997
76.480
74.578
73.016
72.705
62.743
34.535
34.283
31.849
18.402
12.349
PSO
BnO
Ph
Co(CO)3
(OC)3Co
N

21c




ppm
199.484
154.954
151.680
142.197
138.696
138.359
130.055
129.146
128.818
128.712
128.541
128.310
128.202
128.040
127.880
110.747
108.810
100.478
77.840
77.417
76.993
76.585
72.699
72.023
62.685
35.898
18.438
12.402
TIPSO
BnO
Ph
Co(CO)3
(OC)3Co
O
21d
ppm
200
175
150
125
100
75
50
25
0