6-Endo Heck Cyclization of 3-(2-iodophenoxy)methylbenzofurans: A Useful Approach to Pterocarpenes

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Supplementary Information

General Procedures: All NMR spectra were recorded at 300 MHz (^{1}H) and 125 MHz (^{13}C) on a Bruker Avance spectrometer and were measured in deuteriochloroform with tetramethylsilane (TMS) as internal standard unless otherwise specified. Signals are reported in δ values (ppm) downfield from TMS. Melting points were determined in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were provided by Galbraith Laboratories, Knoxville, TN. HRMS data were provided by the Chemical Instrumentation Center, The Ohio State University. Standard workup refers to extraction of the material into the indicated solvent, washing the organic layer with brine solution, drying over Drierite ($CaSO_4$), concentration *in vacuo*, and drying to constant weight under vacuum (1-2 Torr). The following abbreviations are using throughout the experimental section: thin layer chromatography (TLC), ethyl acetate (EtOAc), dimethyl formamide (DMF), tetrahydrofuran (THF) hexane (Hxa), diisobutylaluminum hydride (DIBAL-H), diisopropylazodicarboxylate (DIAD). All commercially available compounds and reagents were obtained from the Aldrich Chemical Co.

*Preparation of 6-hydroxybenzo[*d*][1,3]dioxole-5-carbaldehyde* (**5c**)

Sesamol (5.7 g, 41.0 mmol), paraformaldehyde (8.6 g, 287 mmol), and anhydrous magnesium chloride (5.9 g, 61.5 mmol) were dissolved in dry CH_3CN (200 mL). Triethylamine (15.5 g, 154 mmol, 22 mL) was added and the mixture was heated at reflux under N_2 with stirring for 6 h. The reaction mixture was then concentrated to ~ ¼ volume, diluted with 100 mL H_2O, 50 mL of 20% HCl (aq), and 100 mL Et_2O. The layers were shaken and separated and the aqueous phase extracted with additional Et_2O (2 x 100 mL). The combined organic layers were washed with brine (100 mL), filtered through a $CaSO_4$ cone, then concentrated in vacuo to give a dark brown solid that was recrystallized from CH_2Cl_2 to yield 1.76 g (26%) of **5c** as a light brown solid, m.p. 125-126 ^{o}C (lit.[1] mp 125–126 ^{o}C). ^{1}H NMR ($CDCl_3$): 6.01 (s, 2H), 6.46 (s, 1H), 6.85 (s, 1H), 9.62 (s, 1H), 11.53 (s, 1H).

[1.] K. Fukui and M. Nakayama, *Bull. Soc. Chem. Jpn.*, 1962, **35**, 1321.

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Preparation of 2-iodo-5-methoxyphenol **(2b)**

To a solution of silver trifluoroacetate (5.52 g, 25 mmol) and 3-methoxyphenol (3.1 g, 25 mmol, 2.74 mL) in $CHCl_3$ (25 mL) was added dropwise a solution of I_2 (6.35 g, 25 mmol) in $CHCl_3$ (200 mL) under N_2 over 1.5 h. After an additional hour, AgI precipitate was removed by vacuum filtration and the resulting filtrate was shaken with 1.0M $NaHSO_3$ solution (50 mL) to discharge excess I_2. The organic phase was then washed with saturated $NaHCO_3$ solution (100 mL) then brine (50 mL) and was dried through a $CaSO_4$ cone. After concentration in vacuo, the resulting dark brown solid was chromatographed on silica gel with $CHCl_3$ as the eluent to afford **2b** (1.9 g, 48%) as a crystalline solid, m.p. 71-72.5 ^oC (lit.[2] mp 71.5-72.5 ^oC). ^1H NMR ($CDCl_3$): 3.77 (s, 3H), 5.27 (s, 1H), 6.33 (dd, J = 8.8, 2.8 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H).

[2.] Winkle, M. R. and Ronald, R. C., *J. Org. Chem*. 1982, **47**, 2101-08

Preparation of ethyl benzofuran-3-carboxylate (**6a**)

To a solution of **5a** (16.4 mmol) in CH_2Cl_2 (5 mL) was added HBF_4-Et_2O complex (0.223 mL). To the resulting dark red mixture was added a solution of ethyl diazoacetate (85%, 3.18 mL) in CH_2Cl_2 (25 mL) dropwise at 25-30°C via addition funnel with evolution of N_2. After 1h, the mixture was concentrated to approx. 2/3 original volume and 1.0 mL of conc. H_2SO_4 was added. After stirring for 15 min, solid $NaHCO_3$ was added until CO_2 evolution ceased. The mixture was then filtered through a Celite pad, concentrated in vacuo and the residue chromatographed on silica gel (3% EtOAc/Hxa as eluent) to afford **6a** as a clear, colorless oil (2.09 g, 67%); ^1H NMR: 1.42 (t, J = 7.1 Hz, 3H), 4.40 (q, J = 7.1 Hz, 2H), 7.35 (m, 2H) 7.51 (m, 1H), 8.07 (m, 1H). 8.25 (s, 1H); ^{13}C NMR: 14.39, 60.56, 111.67, 114.73, 122.05, 124.13, 124.63, 125.25, 150.95, 155.59, 163.46. All data consistent with literature values.[3]

[3.] Dudley, M. E., Morshed, M. M., Hossain, M. M., *Synthesis,* **2006**, 1711–1714.

Preparation of ethyl 6-methoxybenzofuran-3-carboxylate (**6b**)

To a solution of **5b** (16.4 mmol) in CH_2Cl_2 (5 mL) was added HBF_4-Et_2O complex (0.223 mL). To the resulting mixture was added a solution of ethyl diazoacetate (85%, 3.18 mL) in CH_2Cl_2 (25 mL) dropwise at 25-30°C with evolution of N_2. After 1h, the mixture was concentrated to approx. 2/3 original volume and 1.0 mL of conc. H_2SO_4 was added. After stirring for 15 min, solid $NaHCO_3$ was added until CO_2 evolution ceased. The mixture was then filtered through a Celite pad, concentrated in vacuo and the residue chromatographed on silica gel (20% EtOAc/Hxa as eluent) to afford **6b** as white needles (1.16 g, 40%); m.p. 55-57°C (lit[4] mp 55-56°C); ^1H NMR: 1.42 (t, J = 7.1 Hz, 3H), 3.86 (s, 3H), 4.39 (q, J = 7.1 Hz, 2H), 7.00 (m, 1H) 7.90 (d, J = 8.6 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR: 14.37, 55.67, 60.49, 95.93, 113.24, 114.66, 117.86, 122.11, 149.93, 156.60, 158.56, 163.53. All data consistent with literature values.[4]

[4]. Noyce, D. S, Nichols, R. W., *J. Org. Chem.,* **1972**, *37,* 4311-4315

Ethyl 5,6-methylenedioxybenzofuran-3-carboxylate (**6c**)

To a solution of **5c** (16.4 mmol) in CH_2Cl_2 (5 mL) was added HBF_4-Et_2O complex (0.223 mL). To the resulting mixture was added a solution of ethyl diazoacetate (85%, 3.18 mL) in CH_2Cl_2 (25 mL) dropwise at 25-30°C with evolution of N_2. After 1h, the mixture was concentrated to approx. 2/3 original volume and 1.0 mL of conc. H_2SO_4 was added. After stirring for 15 min, solid $NaHCO_3$ was added until CO_2 evolution ceased. The mixture was then filtered through a Celite pad, concentrated in vacuo and the residue chromatographed on silica gel *(*10% EtOAc/Hxa as eluent) to afford **6c** as white needles, m.p. 83-84°C (2.07 g, 73%); ^{1}H NMR: 1.41 (t, *J* = 7.13 Hz, 3H); 4.38 (q, *J* = 7.13 Hz, 2H); 6.02 (s, 2H); 6.99 (s, 1H); 7.42 (s, 1H), 8.15 (s, 1H). ^{13}C NMR: 14.37, 60.51, 93.58, 100.36, 101.62, 115.02, 118.23, 145.65, 146.84, 150.07, 150.83, 163.48.
Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.18; H, 4.21.

Preparation of 3-hydroxymethylbenzofuran (**1a**)

To a -78°C solution of **6a** (1.72 g, 9.05 mmol) in CH_2Cl_2 (20 mL) was added DIBAL-H (1.0 M in hexanes, 22.62 mL in 50 mL CH_2Cl_2) dropwise. After 1 h, the mixture was warmed to room temperature and slowly poured into 5% HCl(aq) solution (75 mL). EtOAc (100 mL) was added, the layers shaken and separated and the organic phase washed with 5% HCl (aq) (2 x 50 mL), then brine (2 x 50 mL), dried through a $CaSO_4$ cone, then concentrated in vacuo to give 1.26 g (94%) of a white solid, m.p. 44-45°C. (lit.[5] m.p. 45-46°C); ^{1}H NMR: 2.70 (br s, 1H), 4.67 (s, 2H), 7.1-7.56 (m, 5H); ^{13}C NMR: 55.93, 111.61, 119.94, 120.41, 122.79, 124.66, 126.68, 142.35, 155.62. All data consistent with literature values.[5]

[5.] Katritzky, A., Kirichenko, K., Ji, Y., Steel, P., Karelson, M., *ARKIVOC*, **2003** *6*, 49-56.

Preparation of 6-methoxy-3-hydroxymethylbenzofuran (**1b**)

To a -78°C solution of **6b** (2.0 g, 9.08 mmol) in CH_2Cl_2 (20 mL) was added DIBAL-H (1.0 M in hexanes, 22.62 mL in 50 mL CH_2Cl_2) dropwise. After 1 h, the mixture was warmed to room temperature and slowly poured into 5% HCl(aq) solution (75 mL). EtOAc (100 mL) was added, the layers shaken and separated and the organic phase washed with 5% HCl (aq) (2 x 50 mL), then brine (2 x 50 mL), dried through a $CaSO_4$ cone, then concentrated in vacuo to give 1.57 g (97%) as an off-white solid, m.p. 67-68.5°C. (lit.[5] m.p. 69-70°C); ^{1}H NMR: 1.65 (br s, 1H), 3.85 (s, 3H), 4.80 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 7.01 (s, 1H), 7.51 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H). Data consistent with literature values.[5]

Preparation of 5,6-methylenedioxy-3-hydroxymethylbenzofuran (**1c**)

To a -78°C solution of **6c** (2.0 g, 8.54 mmol) in CH_2Cl_2 (20 mL) was added DIBAL-H (1.0 M in hexanes, 21.35 mL in 50 mL CH_2Cl_2) dropwise. After 1 h, the mixture was warmed to room temperature and slowly poured into 5% HCl(aq) solution (75 mL). EtOAc (100 mL) was added, the layers shaken and separated and the organic phase washed with 5% HCl (aq) (2 x 50 mL), then brine (2 x 50 mL), dried through a $CaSO_4$ cone, then concentrated in vacuo to give 1.51 g of 1**c** (97%) as a white solid, m.p. 106-107°C; ^{1}H NMR: 1.96 (s, 1H); 4.72 (s, 2H); 5.97 (s, 2H); 6.95 (s, 1H); 6.70 (s, 1H); 7.90 (s, 1H). ^{13}C NMR: 55.84, 93.69, 98.40, 101.36, 119.95, 120.72, 141.78, 144.58, 146.40, 150.78; HRMS, m/z 194.0427, calc'd for $C_{10}H_8O_4$ 194.0422.

Preparation of 3-((2-iodophenoxy)methyl)benzofuran (**3a**)

To a solution of *o*-iodophenol (**2a**, 1.034 g, 4.70 mmol), **1a** (0.663 g, 4.48 mmol), and triphenylphosphine (1.23 g, 4.70 mmol) in THF (12 mL) was added DIAD (0.95 g, 4.70 mmol, 0.925 mL) dropwise at room temperature. The resulting mixture was stirred for 20 min, then heated at reflux for 2h. Concentration in vacuo gave an amber oil which was chromatographed on silica gel (5% EtOAc/Hxa) to give **3a** (0.943 g, 60%) as a clear, thick oil. ^{1}H NMR: 5.24 (s, 2H); 6.71 (m, 1H); 6.97 (d, J = 8.13 Hz, 1H); 7.30-7.27 (m, 3H), 7.51-7.48 (m, 1H); 7.80-7.73 (m, 3H). ^{13}C NMR: 62.69, 86.96, 111.65, 112.63, 116.49, 120.47, 122.93, 123.13, 124.80, 126.58, 129.51, 139.72, 143.20, 155.60, 157.08; HRMS m/z 349.9790, calc'd for $C_{15}H_{11}IO_2$ 349.9804.

Preparation of 3-((2-iodo-5-methoxyphenoxy)methyl)-6-methoxybenzofuran (**3b**)

To a solution of *o*-iodophenol (**2b**, 1.0 g, 4.0 mmol), **1b** (0.678 g, 2.8 mmol), and triphenylphosphine (1.04 g, 4.0 mmol) in THF (12 mL) was added DIAD (0.81 g, 4.0 mmol, 0.787 mL) dropwise at room temperature. The resulting mixture was stirred for 20 min, then heated at reflux for 2h. Concentration in vacuo gave an oil which was chromatographed on silica gel (5% EtOAc/Hxa) to give **3b** (0.831 g (53%) as a white solid: m.p. 103-105°C. ^{1}H NMR: 3.78 (s, 3H); 3.86 (s, 3H); 5.19 (s, 2H); 6.34 (dd, J = 8.63, 2.65 Hz, 1H); 6.55 (d, J = 2.65 Hz, 1H), 6.92 (dd, J = 8.57, 2.39 Hz, 1H); 7.02 (d, J = 2.16 Hz, 1H); 7.65-7.60 (m, 3H). ^{13}C NMR: 55.55, 55.73, 62.70, 75.59, 96.08, 100.69, 107.61, 111.97, 116.25, 119.87, 120.57, 139.32, 142.15, 156.62, 157.79, 158.36, 161.22. HRMS, m/z 410.0001, calc'd for $C_{17}H_{15}IO_4$, 410.0015.

Preparation of 3-((2-iodo-5-methoxyphenoxy)methyl)-5,6-methylene-dioxybenzofuran (**3c**)

To a solution of *o*-iodophenol (**2b**, 1.0 g, 4.0 mmol), **1c** (0.538 g, 2.8 mmol), and triphenylphosphine (1.04 g, 4.0 mmol) in THF (12 mL) was added DIAD (0.81 g, 4.0 mmol, 0.787 mL) dropwise at room temperature. The resulting mixture was stirred for 20 min, then heated at reflux for 2h. Concentration in vacuo gave an oil which was chromatographed on silica

gel (5% EtOAc/Hxa) to give **3c** (0.544 g (46%) as a white solid: m.p. 129.5-132°C. ^{1}H NMR: 3.80 (s, 3H); 5.15 (s, 2H); 5.99 (s, 2H); 6.34 (dd, *J* = 8.6 Hz, 2.6 Hz, 1H); 6.54 (d, *J* = 2.6 Hz, 1H); 6.97 (s, 1H); 7.13 (s, 1H); 7.61-7.64 (m, 2H); ^{13}C NMR: 55.56, 62.60, 75.60, 93.68, 98.97, 100.71, 101.41, 107.62, 116.66, 119.86, 139.34, 142.56, 144.69, 146.59, 150.83, 157.72, 161.20; HRMS, m/z 423.9821, calc'd for $C_{17}H_{13}IO_5$ 423.9808.

*Preparation of 6*H*-benzofuro[3,2-*c*]chromene* (**4a**)

To a solution of **3a** (0.150 g, 0.428 mmol) in DMF (2.0 mL) was added Bu_4NBr (0.276 g, 0.856 mmol, 2.0 equiv), and KOAc (0.210 g, 2.14 mmol, 5.0 equiv) followed by $Pd(OAc)_2$ (0.276 g, 0.856 mmol, 0.1 equiv) and the resulting mixture was heated to 100°C with stirring. After 3 h, TLC (4:1 Hxa/EtOAc), indicated no **3** remaining. After standard workup (EtOAC), the residue was chromatographed on silica gel (5% EtOAc/Hxa) to give **4** (85 mg, 89%) as a white solid, m.p. 89.5-91°C (lit.[5,6] m.p. 76-76.9°C, 87-89°C); all NMR data (^{1}H, ^{13}C) were in good agreement with literature values.[5]

[5.] Takeda, N., Miyata, O., Naito, T., *Eur. J. Org. Chem.* **2007,** 1491–1509.
[6.] Suginome, H., Iwadare, T., *Bull. Chem. Soc. Japan*, **1966**, *39*, 1535-1541.

Preparation of 3,9-dimethoxypterocarpene (**4b**) *(anhydrovariabilin)*

To a solution of **7** (0.150 g, 0.366 mmol), Bu_4NBr (0.236 g, 2.0 equiv.) and KOAc (0.180 g, 5.0 equiv., 1.83 mmol) in DMF (2.0 mL) was added $Pd(OAc)_2$ (8.2 mg, 0.1 equiv., 0.0366 mmol) and the resulting mixture was heated to 100°C for 3 h. After cooling and standard workup (EtOAC), the residue was chromatographed on silica gel (5% EtOAc/Hxa) to give **8** (71.4 mg, 69%) as a white solid: m.p. 110-112°C (lit.[7] m.p. 109-111°C); ^{1}H NMR: 3.81 (s, 3H); 3.87 (s, 3H); 5.57 (s, 2H); 6.50 (d, *J* = 2.2 Hz, 1H); 6.54 (dd, *J* = 2.2 Hz, 8.4 Hz, 1H); 6.87 (dd, *J* = 2.2 Hz, 8.4 Hz, 1H); 7.22 (d, *J* = 8.4, 1H); 7.39 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (d_6 acetone): 55.78, 55.42, 65.63, 96.67, 102.43, 105.74, 107.12, 109.85, 111.67, 118.49, 119.30, 121.01, 147.23, 155.04, 156.30, 157.68, 160.85.

[7.] Miki, Y., Kobyashi, S., Ogawa, N., Hachikin, H., *SynLett,* **1994**, 1001-1002.

Preparation of flemichapparin B (**4c**) *(anhydropisatin)*

To a solution of **13** (0.150 g, 0.354 mmol), Bu_4NBr (0.228 g, 0.708 mmol, 2.0 equiv), and KOAc (0.174 g, 1.77 mmol, 5.0 equiv) in 2.5 mL DMF was added $Pd(OAc)_2$ (0.0079 g, 0.0354 mmol, 0.1 equiv) and the mixture was heated to 100°C for 3.5 hours. After cooling and standard workup (EtOAC), the residue was chromatographed on silica gel (5% EtOAc/Hxa) to give the title compound (0.067 g, 64%) as a white solid, m.p. 178-179°C (lit.[8] m.p. 179-180°C). ^{1}H NMR (d_6 acetone): 3.80 (s, 3H); 5.51 (s, 2H); 5.99 (s, 2H); 6.49 (d, *J* = 2.4 Hz, 1H); 6.53 (dd, *J* = 8.3 Hz,

2.4 Hz, 1H); 6.72 (s, 1H); 7.01 (s, 1H); 7.36 (d, J = 8.3 Hz, 1H). ^{13}C NMR (d_6 acetone): 55.77, 65.95, 99.58, 98.54, 102.48, 103.28, 107.77, 108.03, 110.49, 120.02, 121.54, 145.67, 146.85, 148.23, 151.28, 155.99, 162.01.

[8.] Fukui, K., Nakayama, M., *Bull. Chem. Soc. Japan,* **1969**, *42*, 1408-1411.

Preparation of coumestan (**7**)

To a solution of **4a** (50 mg, 0.225 mmol) in CH_2Cl_2 (4.5 mL) was added pyridinium chlorochromate (97.0 mg, 2.0 equiv) all at once. After 20 h, TLC showed reaction was complete. Concentration in vacuo and purification of the residue by chromatography on silica gel (10% EtOAc/Hxa) gave **7** as a white powder (39.3 mg, 74%) mp 180-181°C (lit.[9] mp 179-180°C); all analytical data (IR, ^{1}H NMR, ^{13}C NMR) were in good agreement with literature values.[9]

[9.] Kraus, G. A., Zhang, N., *J. Org. Chem*., **2000**, 65, 5644-5646.

Preparation of 6,6'-dimethoxy-3,3'(2H,2'H)-spirobibenzofuran (**8**)

To a solution of **3b** (0.150 g, 0.366 mmol) in DMF (1 mL) was added NaOAc (0.079 g, 0.96 mmol), HCO_2Na (0.031 g, 0.46 mmol), Et_4NCl-H_2O (0.085 g, 0.46 mmol) and $Pd(OAc)_2$ (1.0 mg) and the resulting mixture was heated with stirring at 85-95°C for 1 h. Standard workup and chromatography on silica gel (15% EtOAc/Hxa) gave **8** (0.062 g, 60%) as a white waxy solid; mp 88.5-90°C; ^{1}H NMR: 6.92 (d, J = 7.1 Hz, 2H), 6.51 (dd, J = 7.1 Hz, J = 2.4 Hz, 2H), 6.46 (d, J = 2.4 Hz, 2H), 4.73 (d, J = 9.2 Hz, 2H), 4.49 (d, J = 9.2 Hz, 2H), 3.78 (s, 6H); ^{13}C NMR: 162.3 (2C), 162.2 (2C), 124.8 (2C), 124.5 (2C), 108.2 (2C), 96.7 (2C), 84.7 (2C), 55.9 (1C), 55.8 (2C); HRMS, m/z 284.1041, calc'd for $C_{17}H_{16}O_4$ 284.1048.

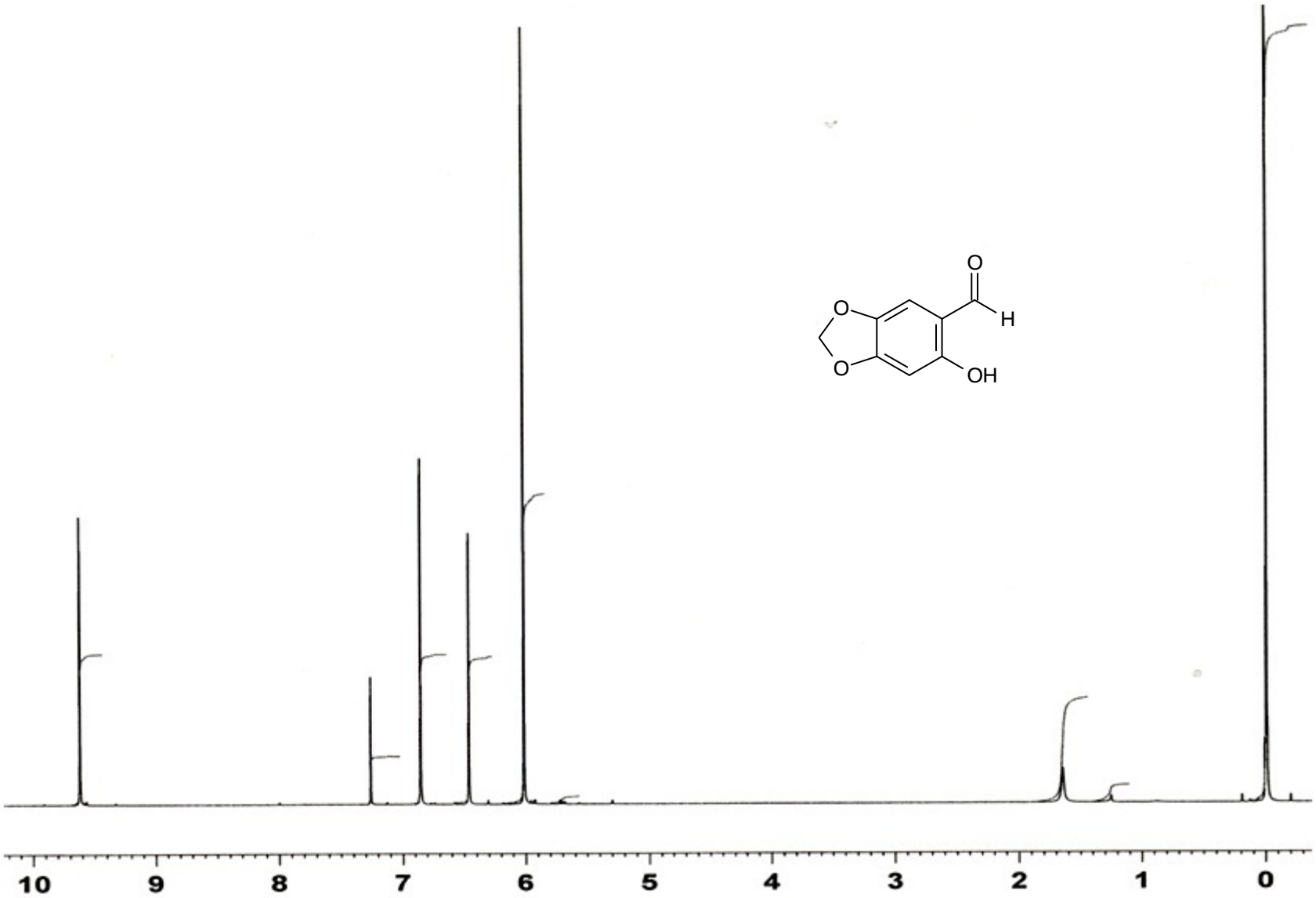

Figure S1: ^{1}H NMR spectrum of 6-hydroxybenzo[d][1,3]dioxole-5-carbaldehyde (**5c**), $CDCl_3$.

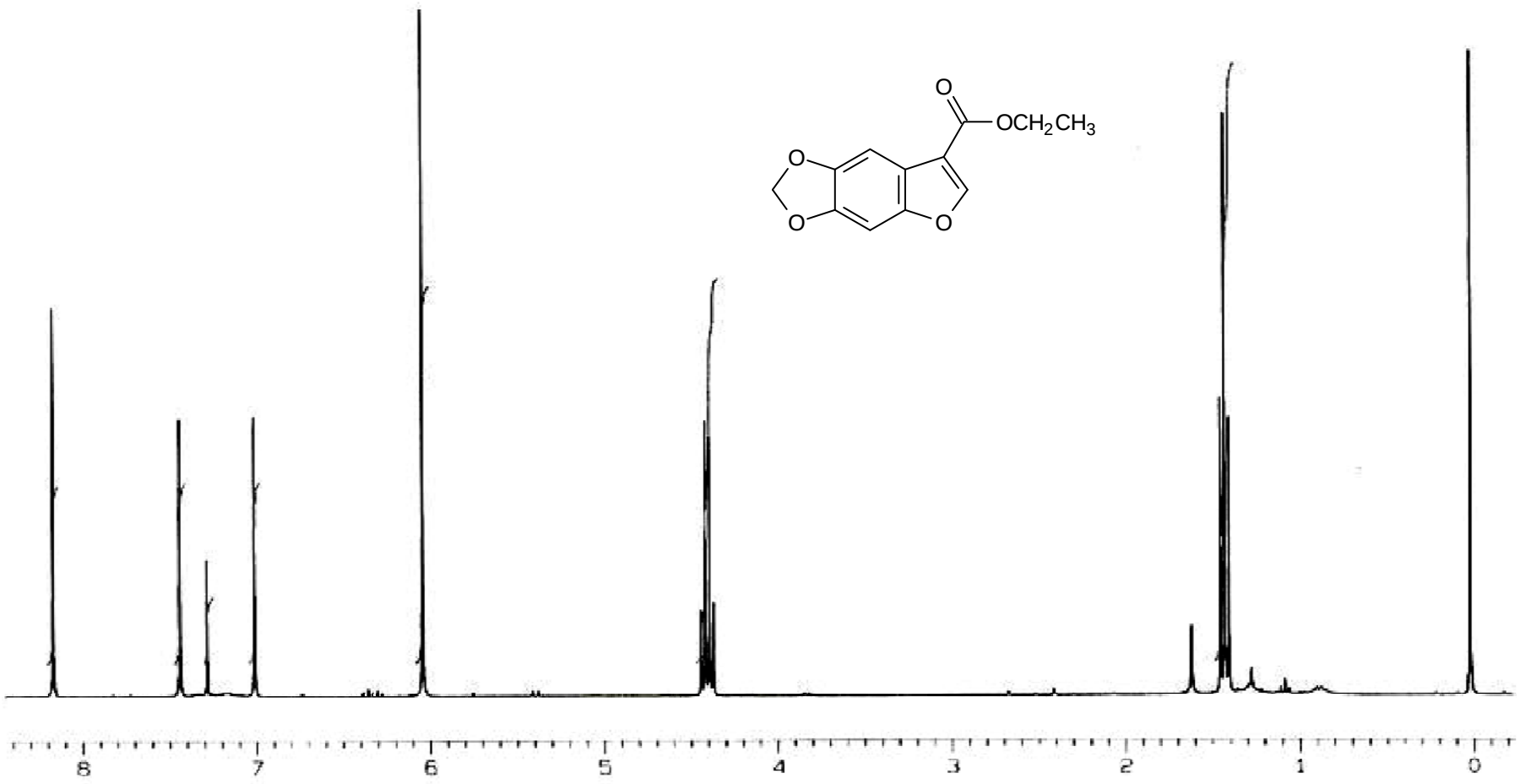

Figure S2: ^{1}H NMR spectrum of Ethyl 5,6-methylenedioxybenzofuran-3-carboxylate (**6c**), $CDCl_3$.

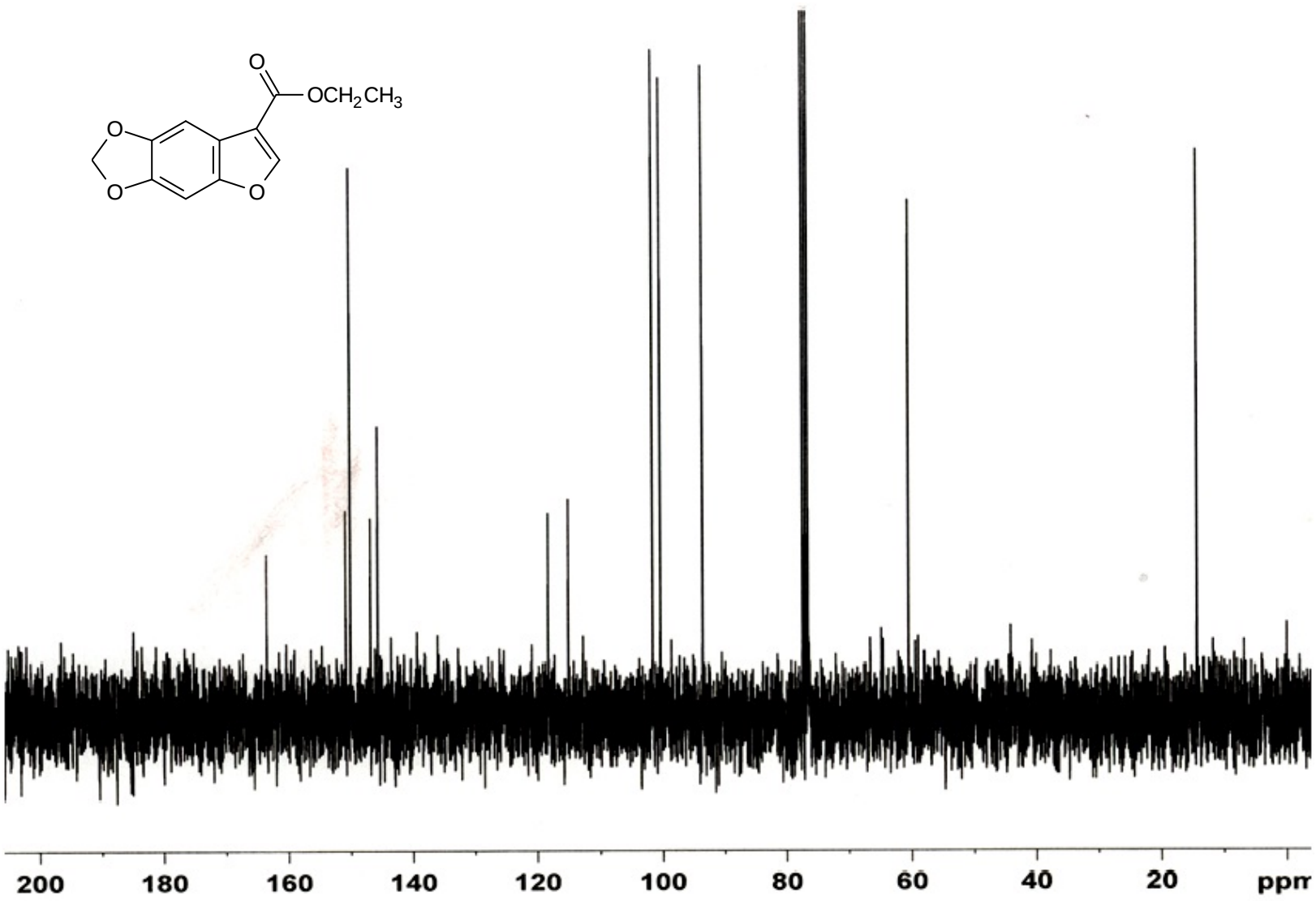

Figure S3: ^{13}C NMR spectrum of ethyl 5,6-methylenedioxybenzofuran-3-carboxylate (**6c**), $CDCl_3$.

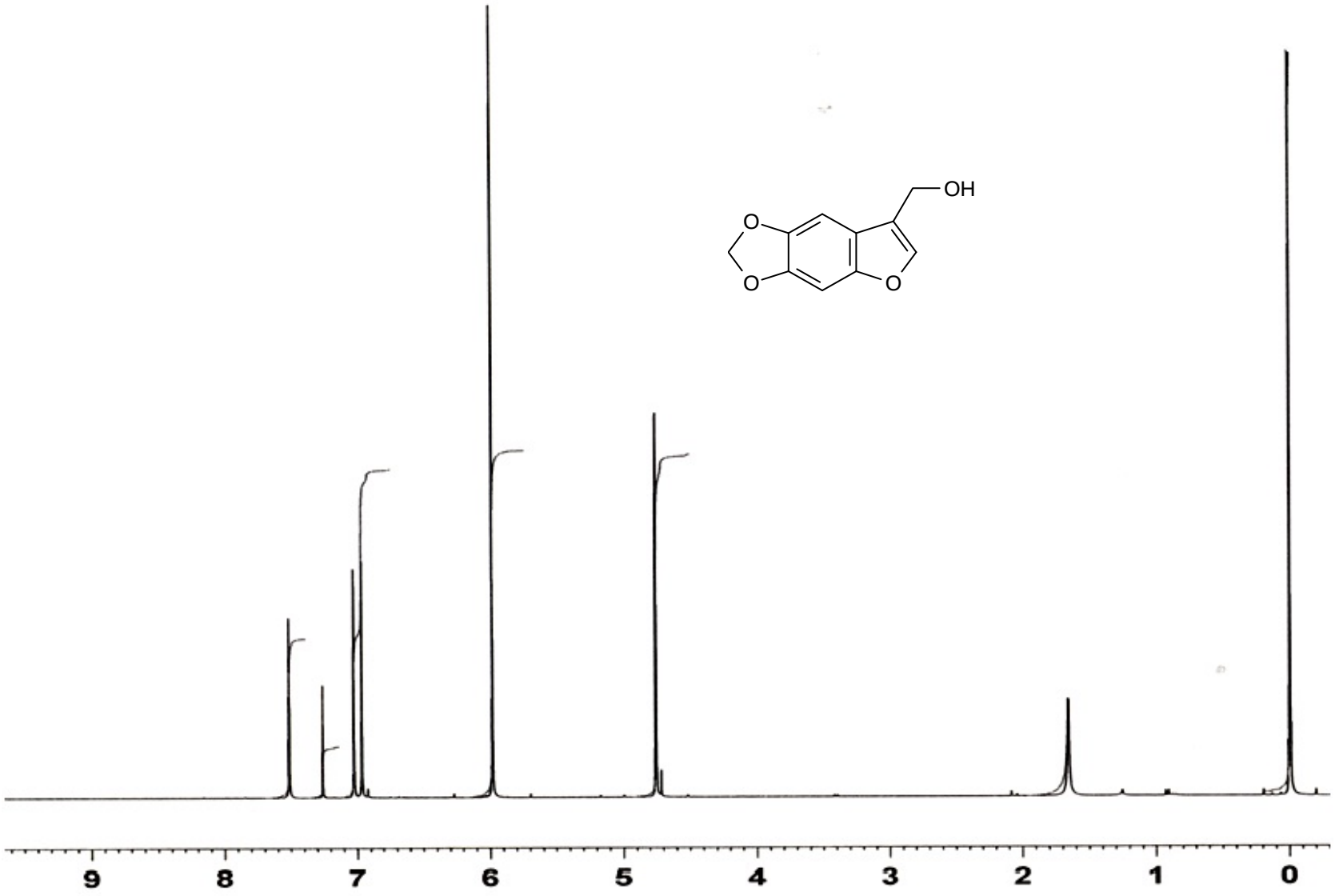

Figure S4: ^{1}H NMR spectrum of 5,6-methylenedioxy-3-hydroxymethylbenzofuran (**1c**), $CDCl_3$.

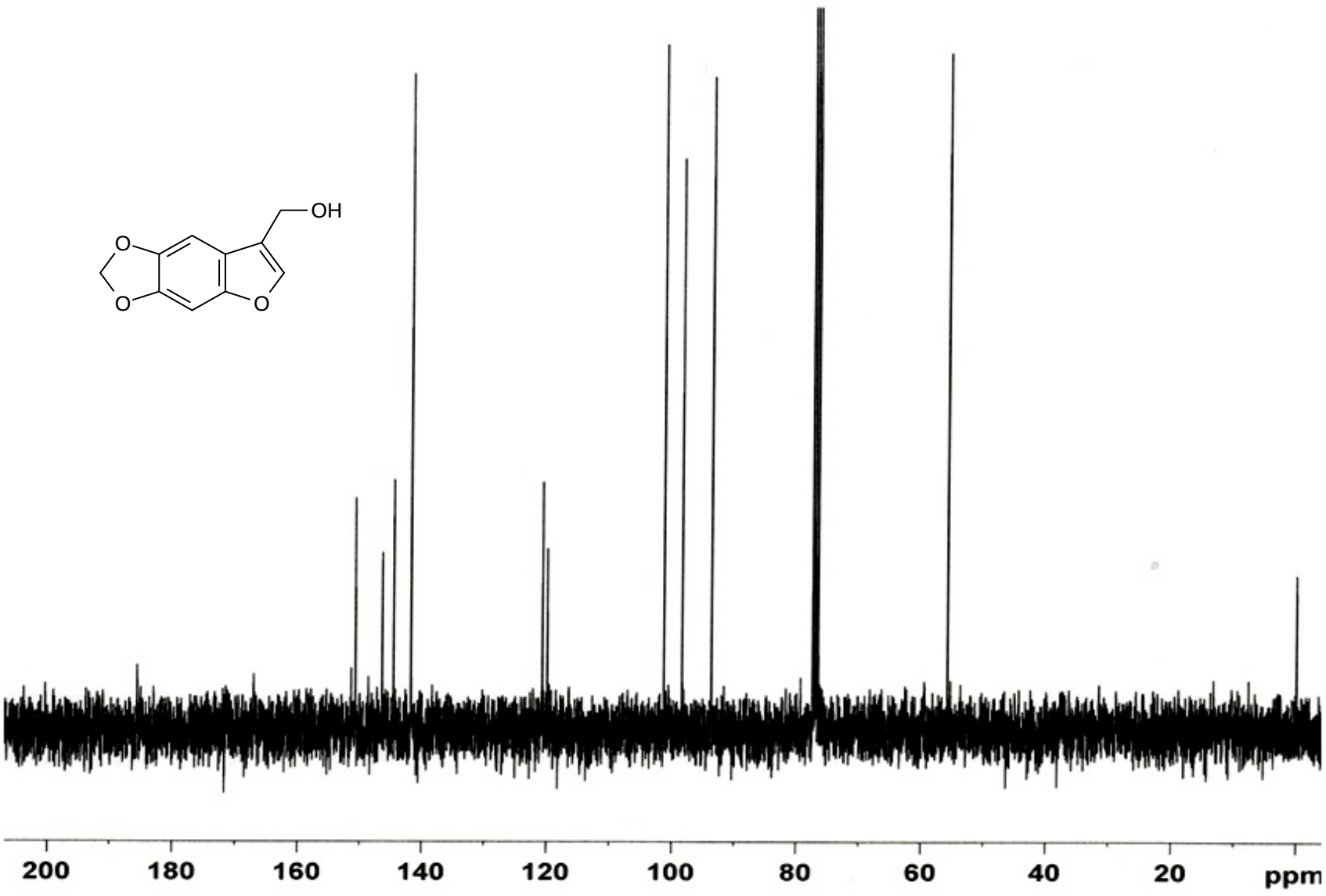

Figure S5: ^{13}C NMR spectrum of 5,6-methylenedioxy-3-hydroxymethylbenzofuran (**1c**), $CDCl_3$

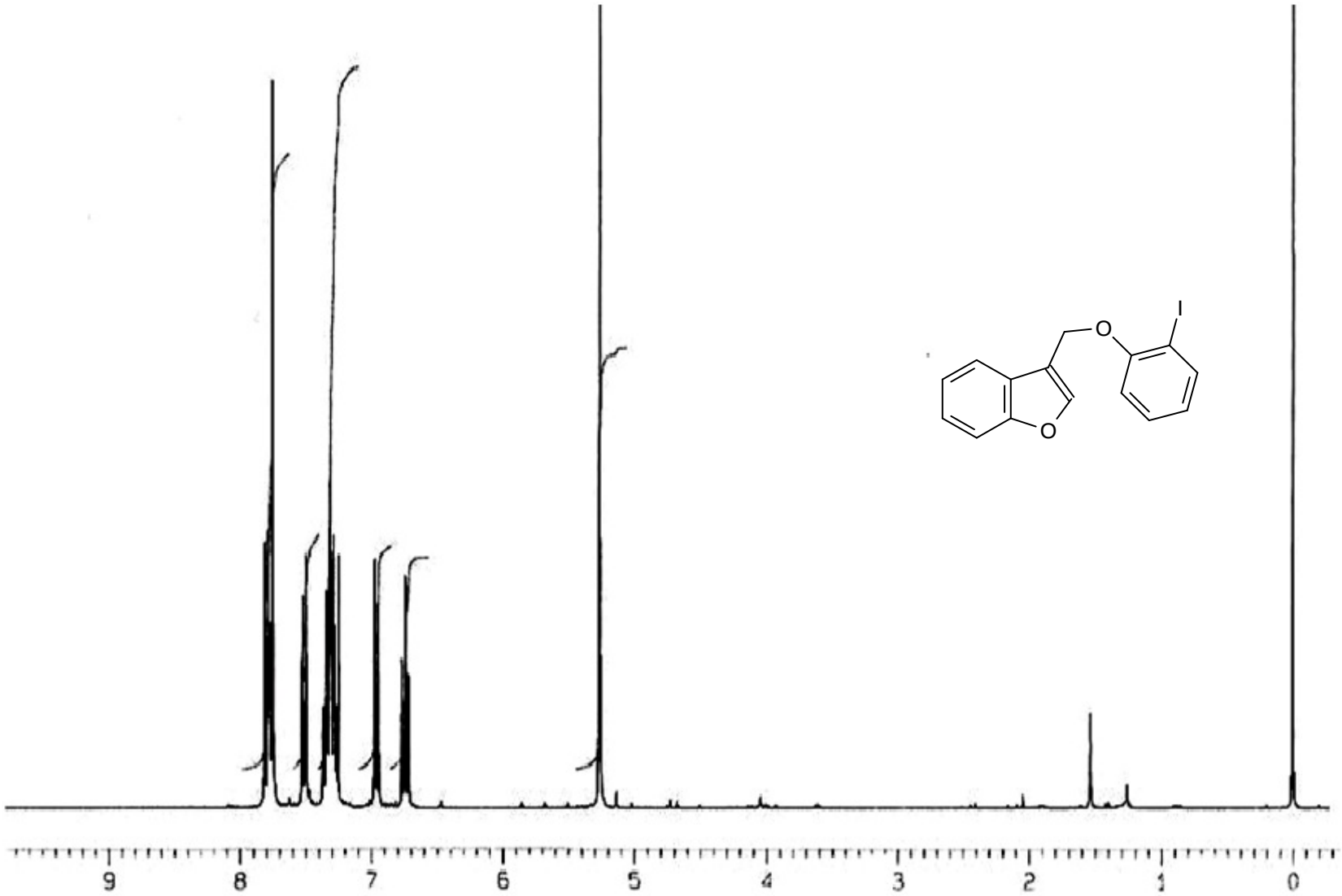

Figure S6: ^{1}H NMR spectrum of 3-((2-iodophenoxy)methyl)benzofuran (**3a**), $CDCl_3$

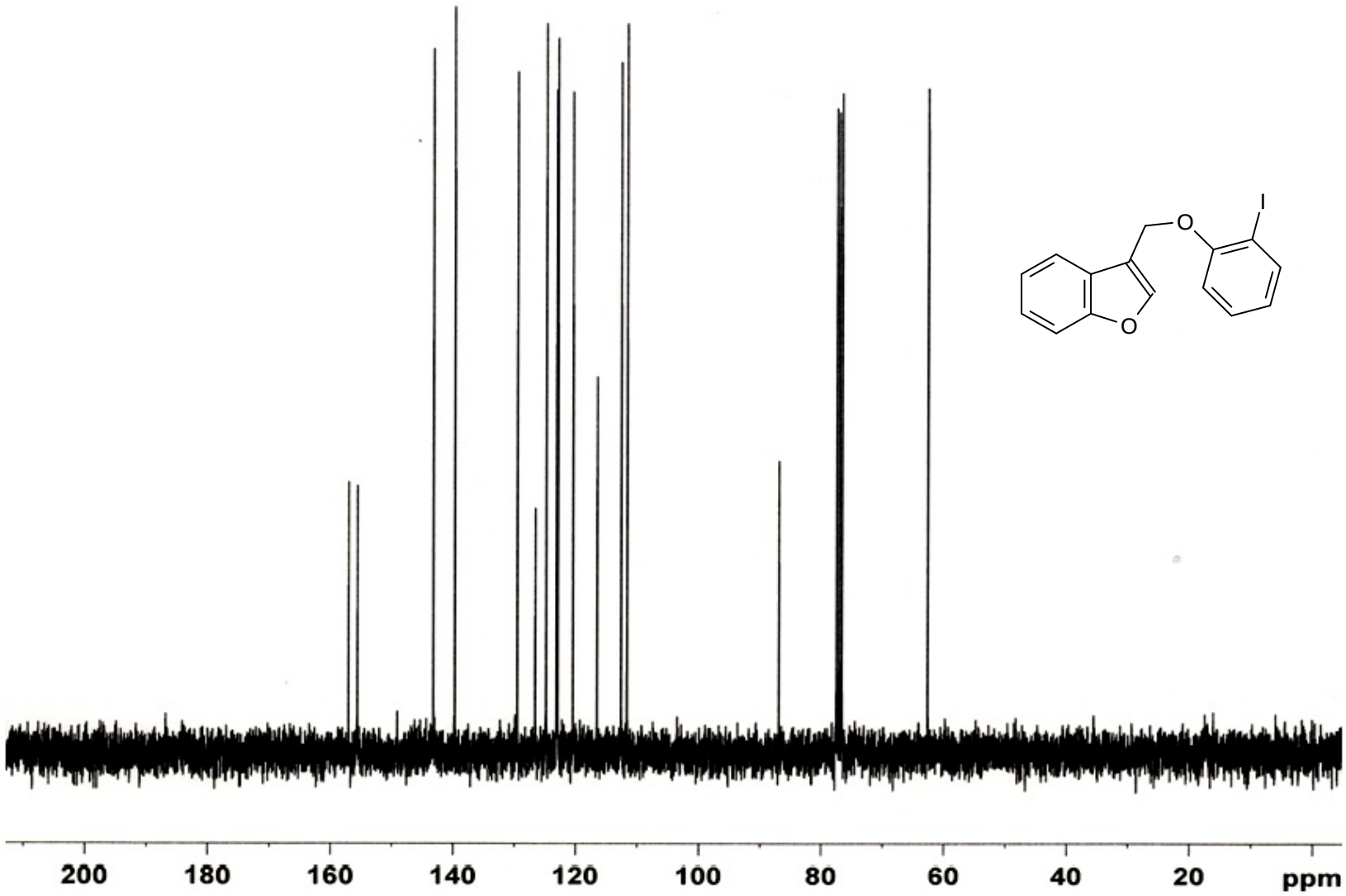

Figure S7: ^{13}C NMR spectrum of 3-((2-iodophenoxy)methyl)benzofuran (**3a**), $CDCl_3$

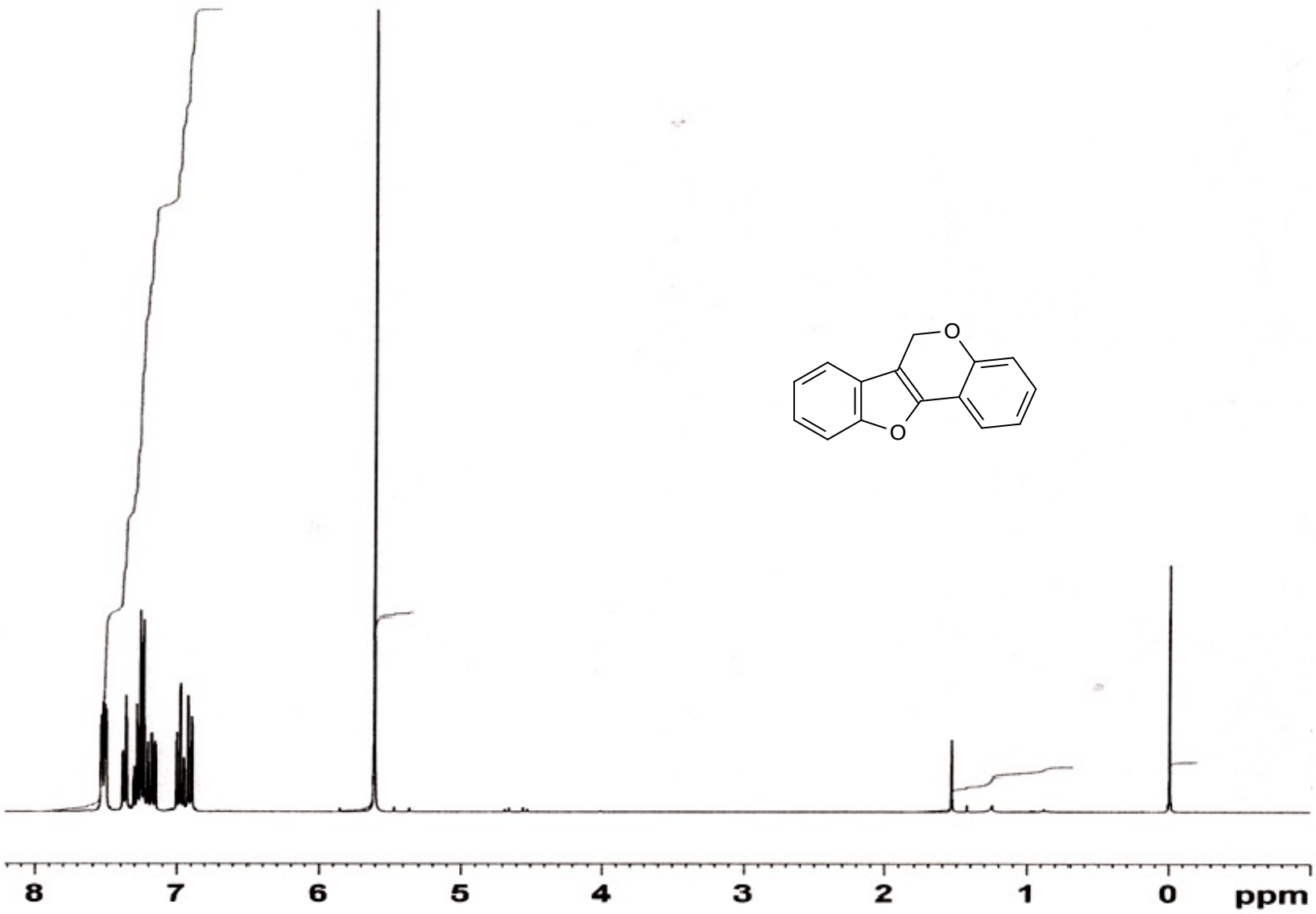

Figure S8: ^{1}H NMR spectrum of 6*H*-benzofuro[3,2-c]chromene (**4a**), $CDCl_3$

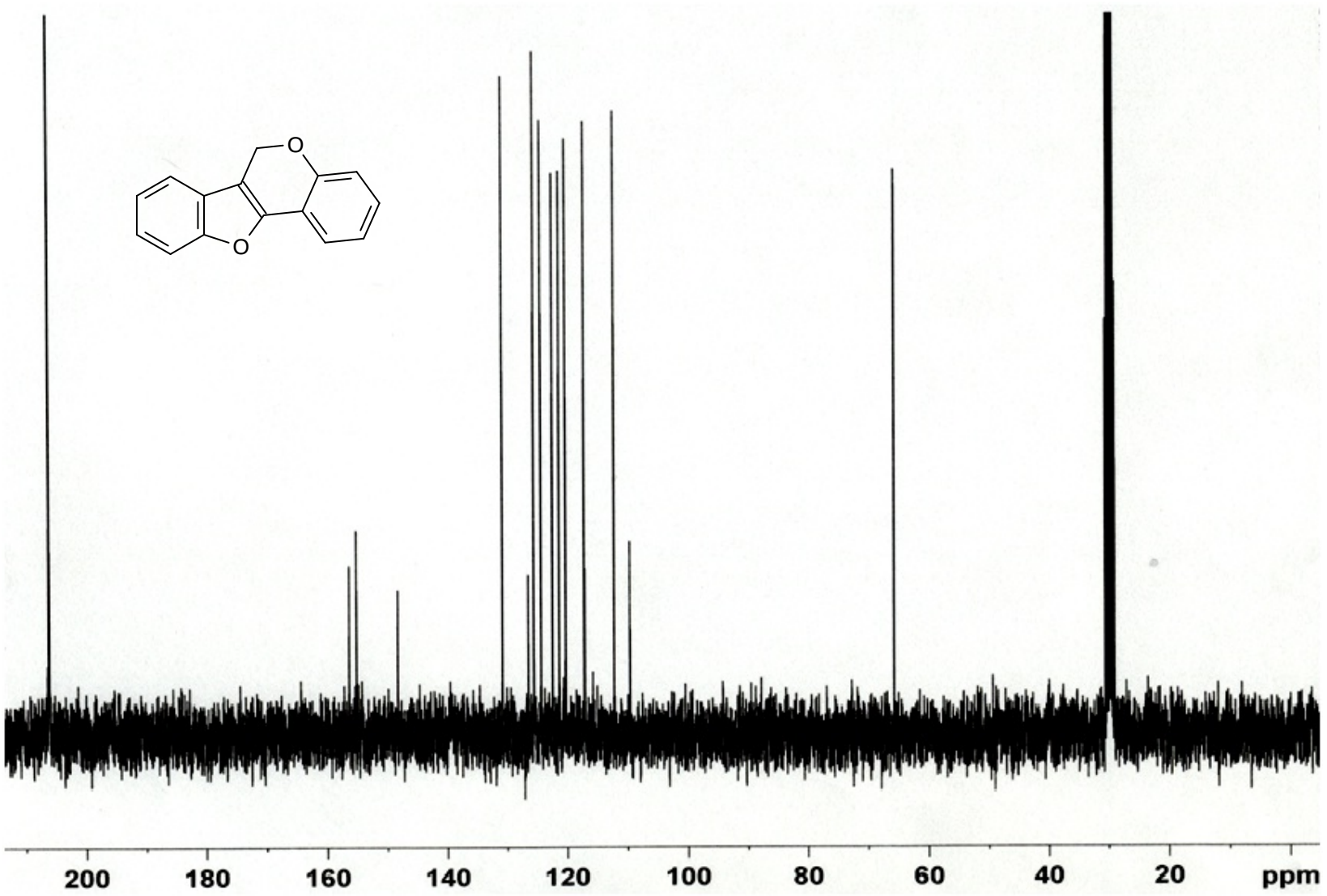

Figure S9: ^{13}C NMR spectrum of 6*H*-benzofuro[3,2-c]chromene (**4a**), d_6 acetone

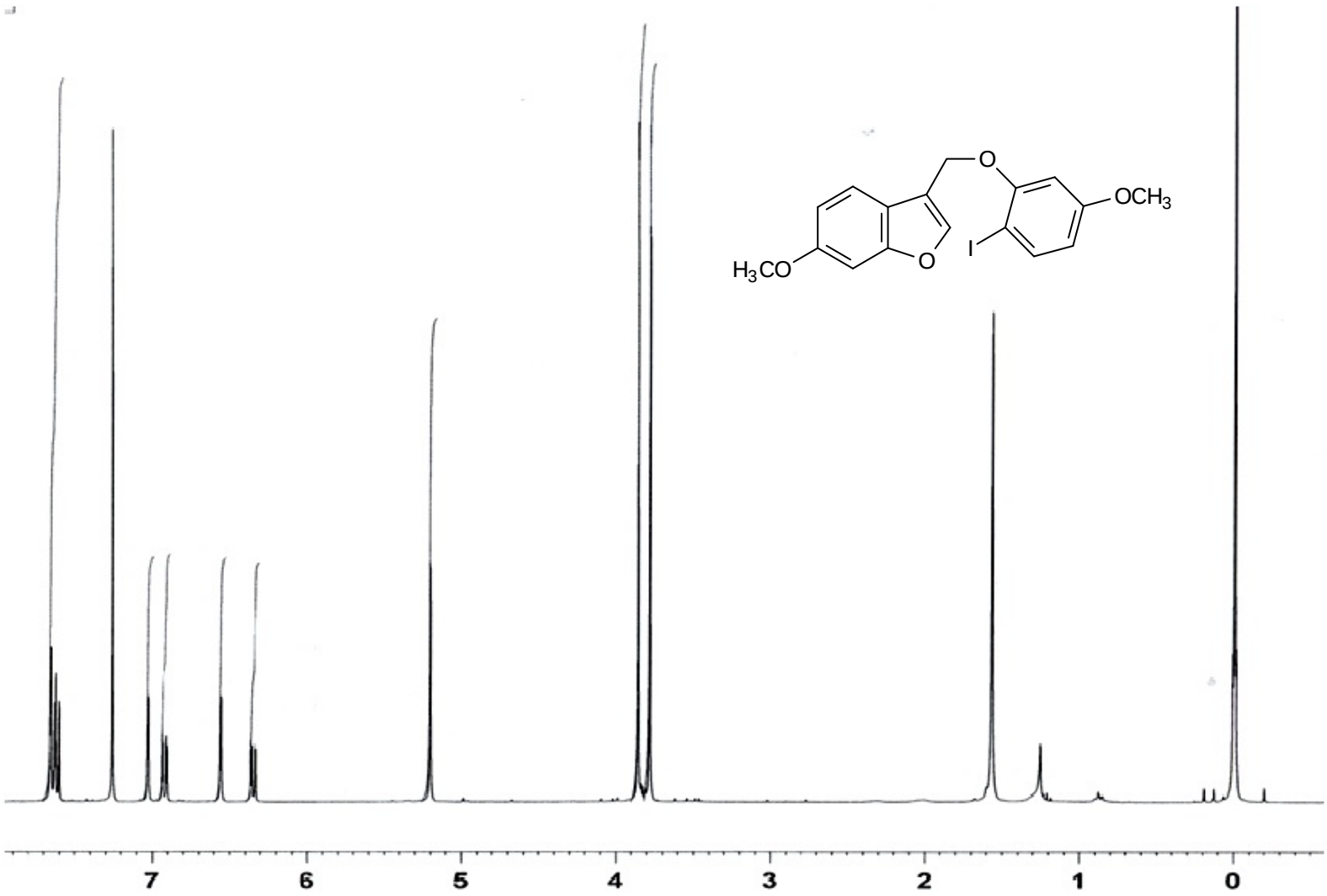

Figure S10: ^{1}H NMR spectrum of 3-((2-iodo-5-methoxyphenoxy)methyl)-6-methoxybenzofuran (**3b**), $CDCl_3$

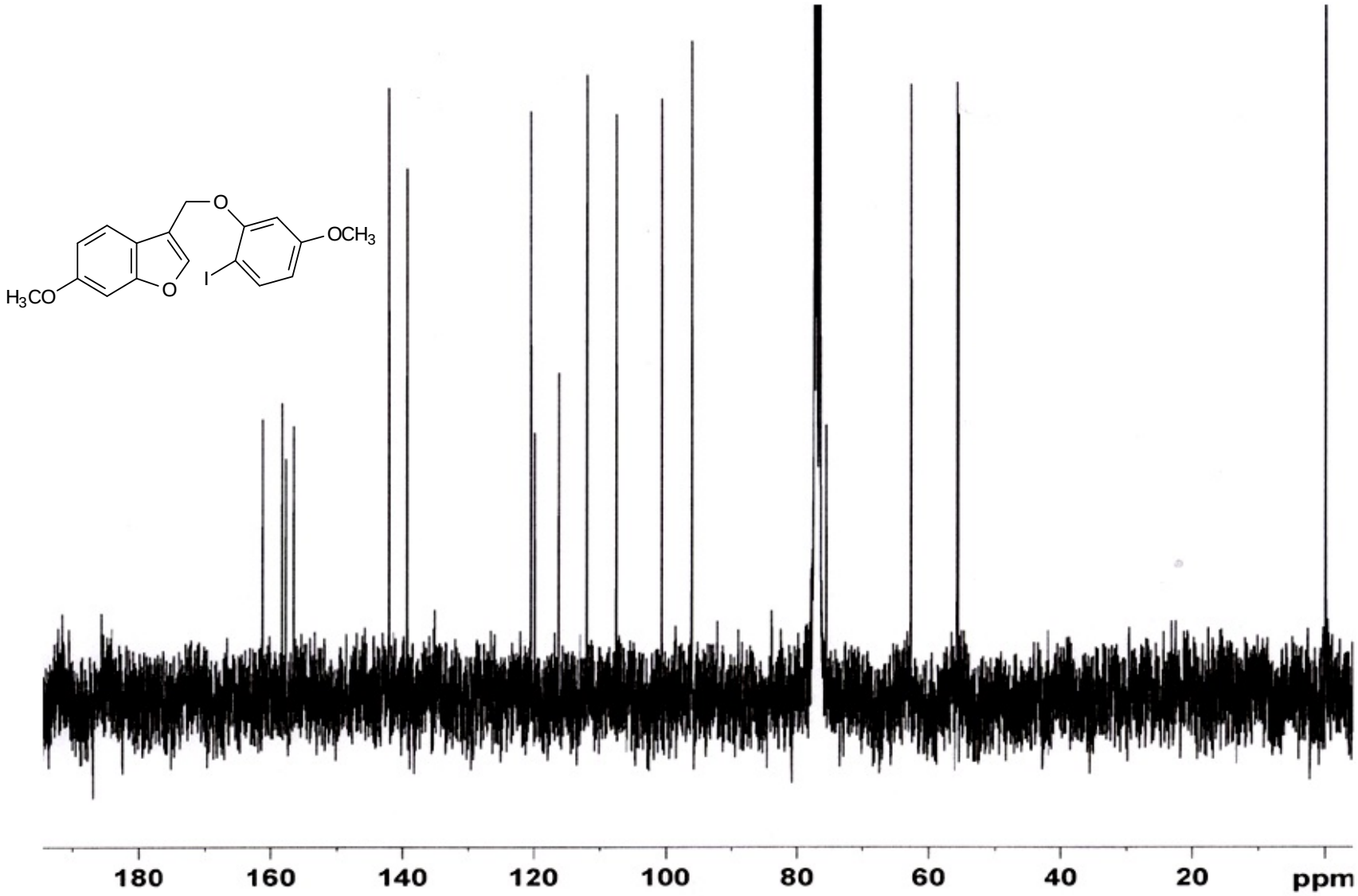

Figure S11: ^{13}C NMR spectrum of 3-((2-iodo-5-methoxyphenoxy)methyl)-6-methoxybenzofuran (**3b**), $CDCl_3$

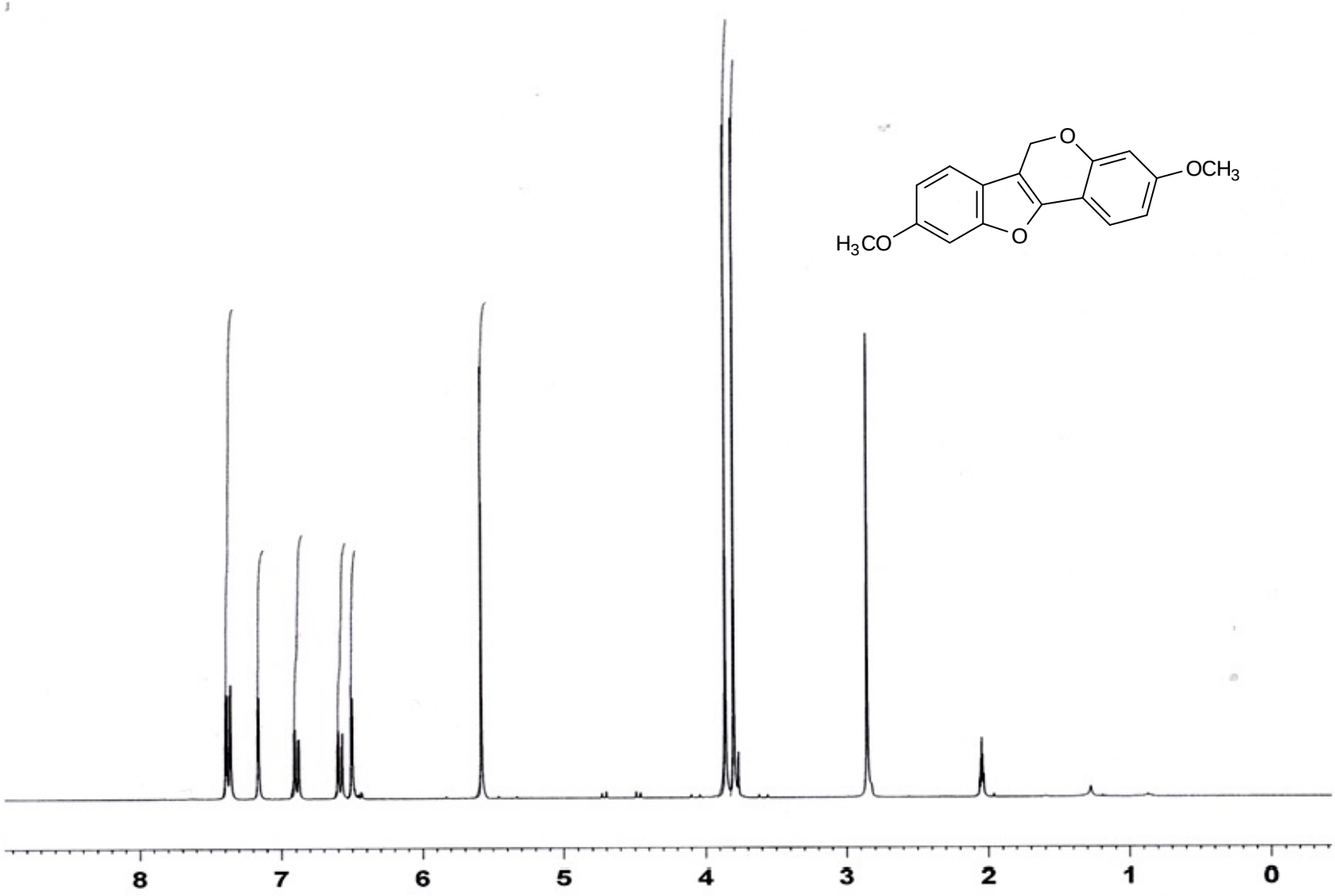

Figure S12: ^{1}H NMR spectrum of 3,9-dimethoxypterocarpene (**4b**) (anhydrovariabilin), d_6 acetone

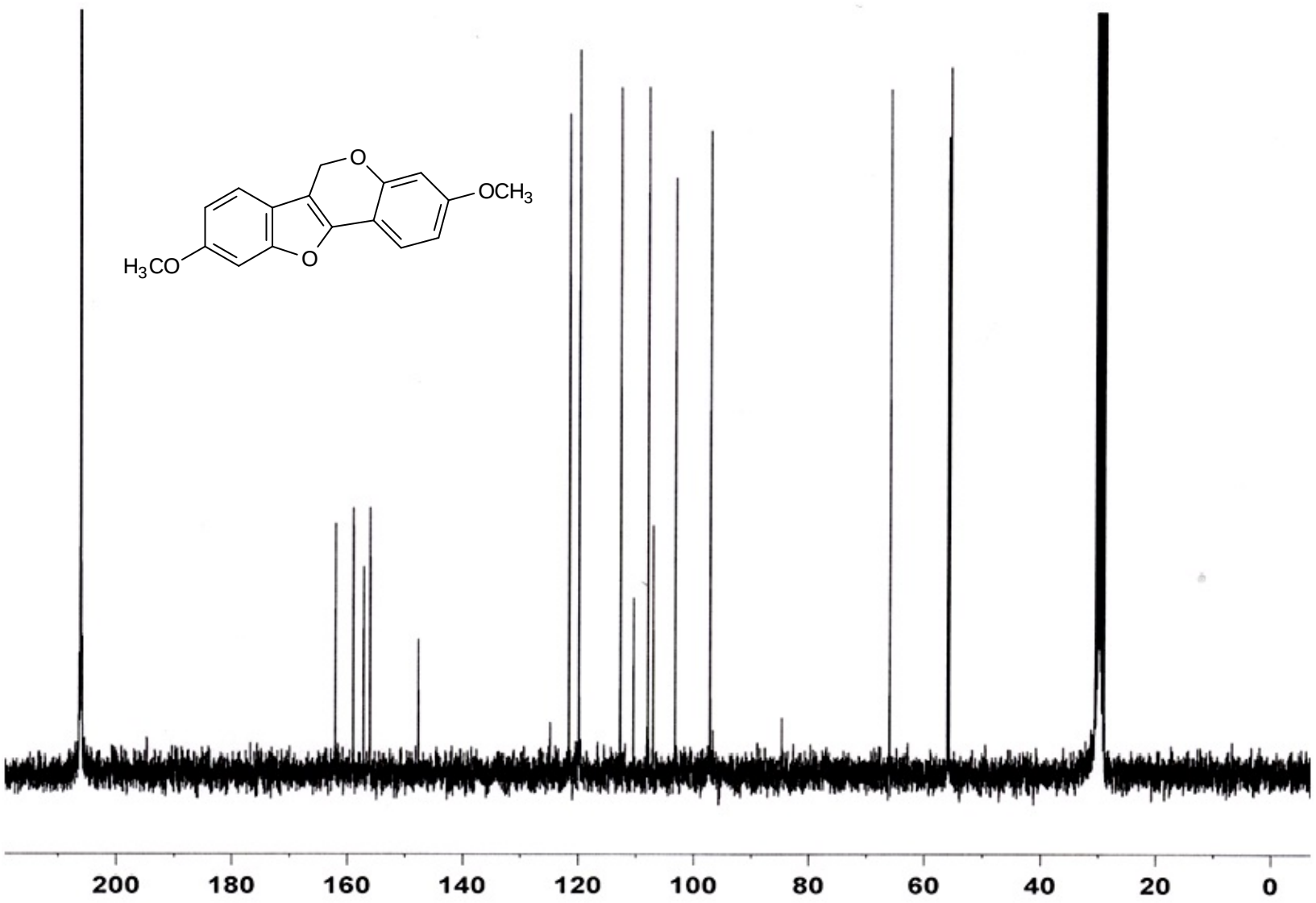

Figure S13: ^{13}C NMR spectrum of 3,9-dimethoxypterocarpene (**4b**) (anhydrovariabilin), d_6 acetone

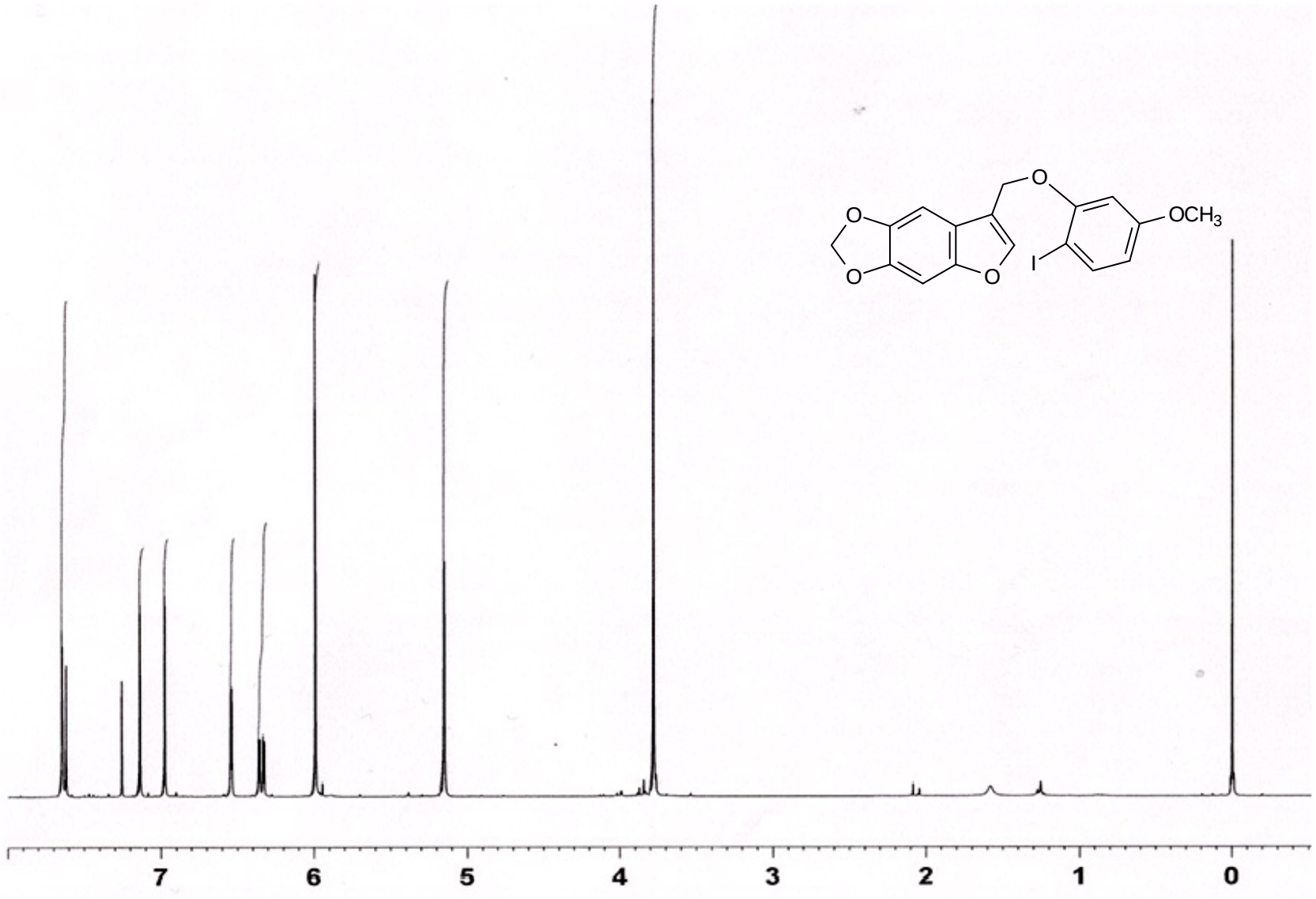

Figure S14: ^{1}H NMR spectrum of 3-((2-iodo-5-methoxyphenoxy)methyl)-5,6-methylene-dioxybenzofuran (**3c**), $CDCl_3$

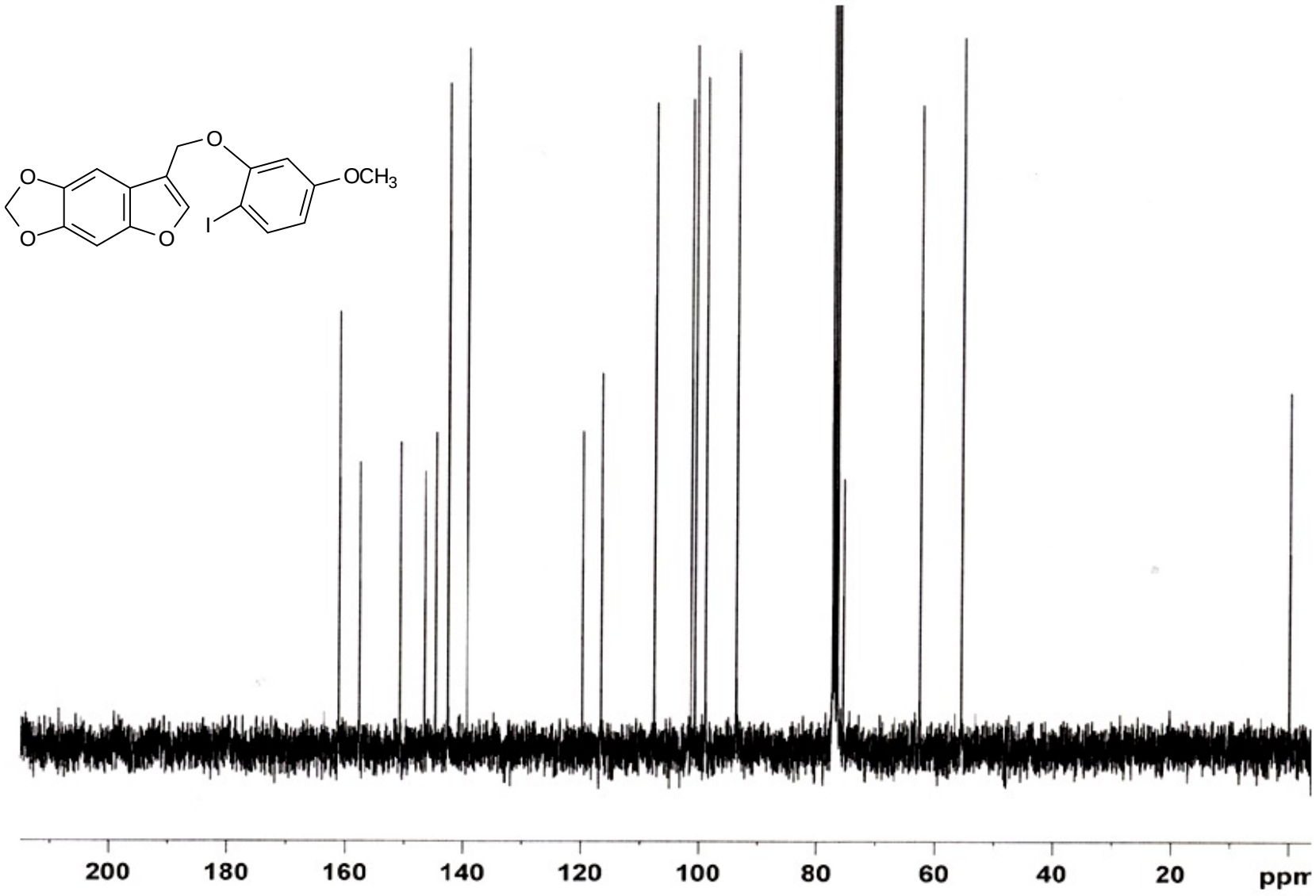

Figure S15: ^{13}C NMR spectrum of 3-((2-iodo-5-methoxyphenoxy)methyl)-5,6-methylene-dioxybenzofuran (**3c**), $CDCl_3$

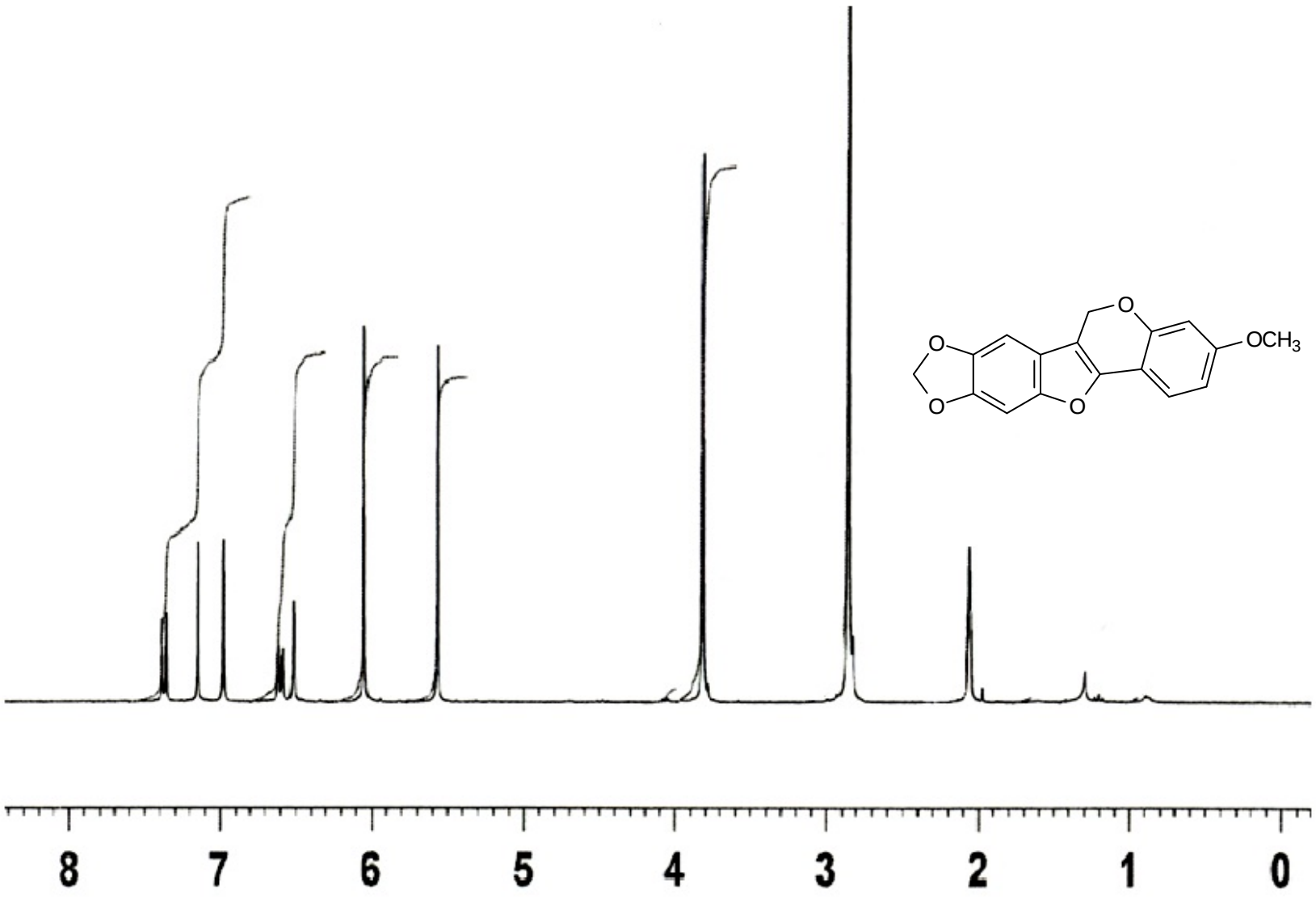

Figure S16: ^{1}H NMR spectrum of flemichapparin B (**4c**) *(anhydropisatin)*, d_6 acetone

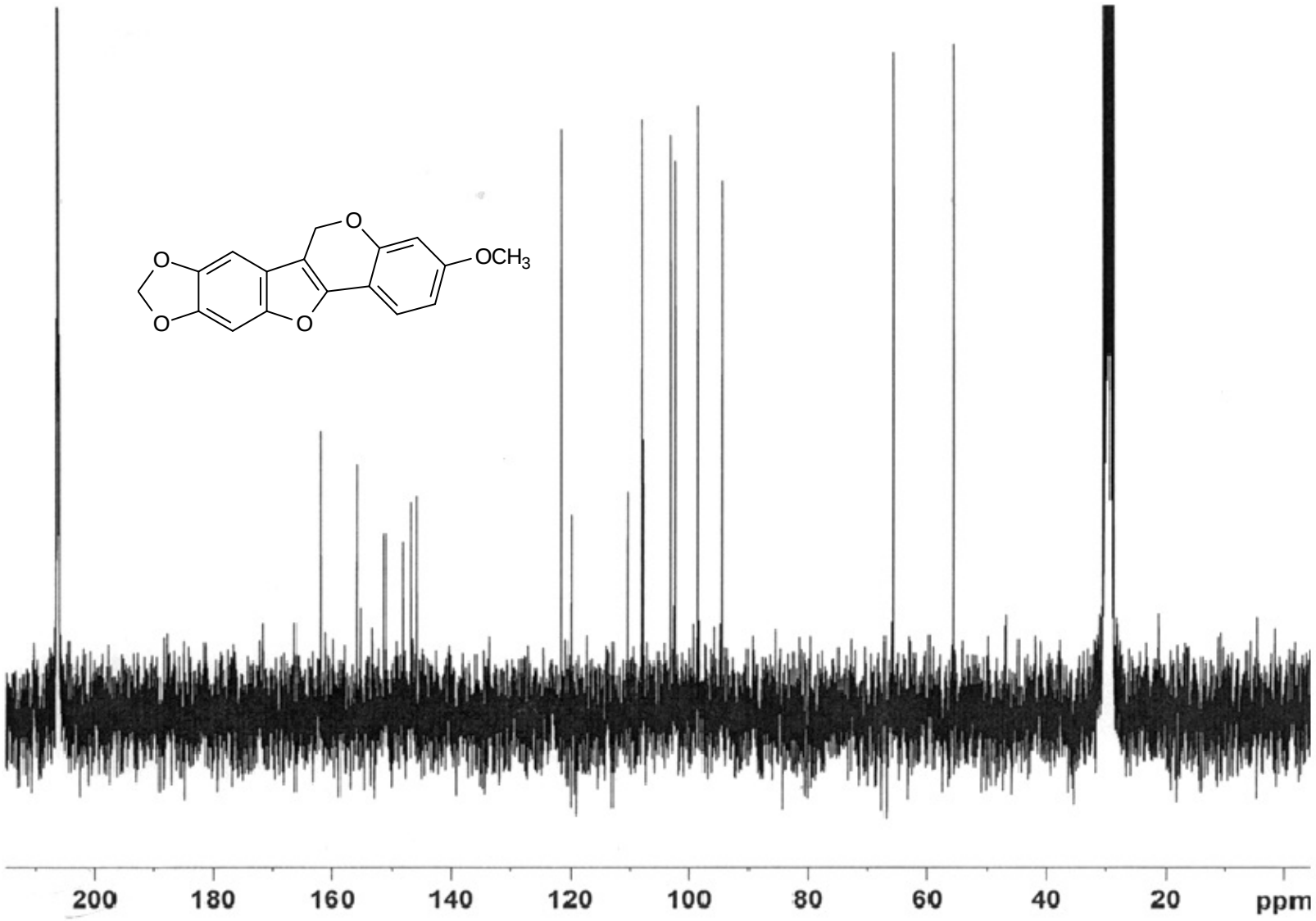

Figure S17: ^{13}C NMR spectrum of flemichapparin B (**4c**) *(anhydropisatin)*, d_6 acetone

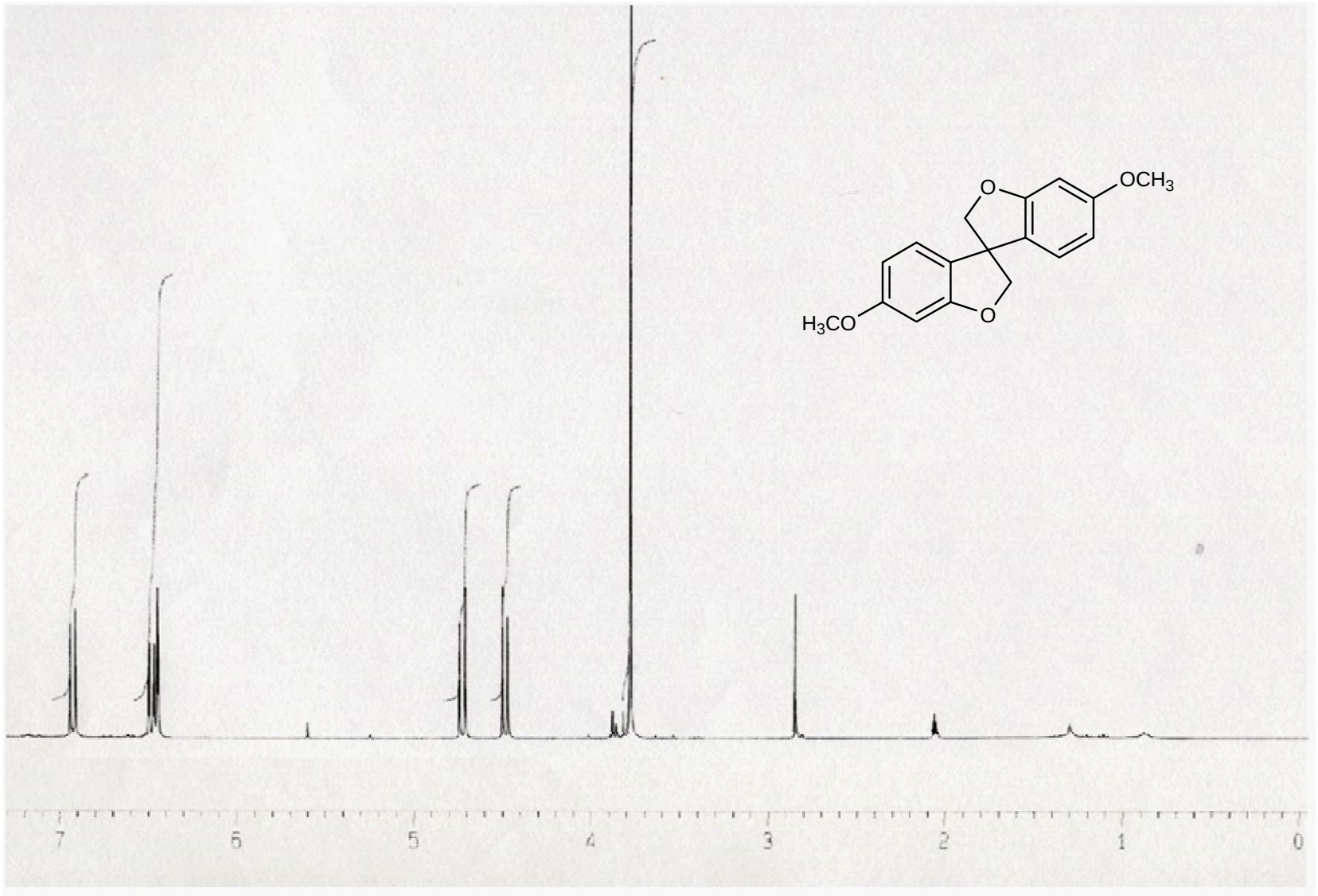

Figure S18: ^{1}H NMR spectrum of 6,6’-dimethoxy-3,3'(2H,2'H)-spirobibenzofuran (**8**)*)*, d_6 acetone

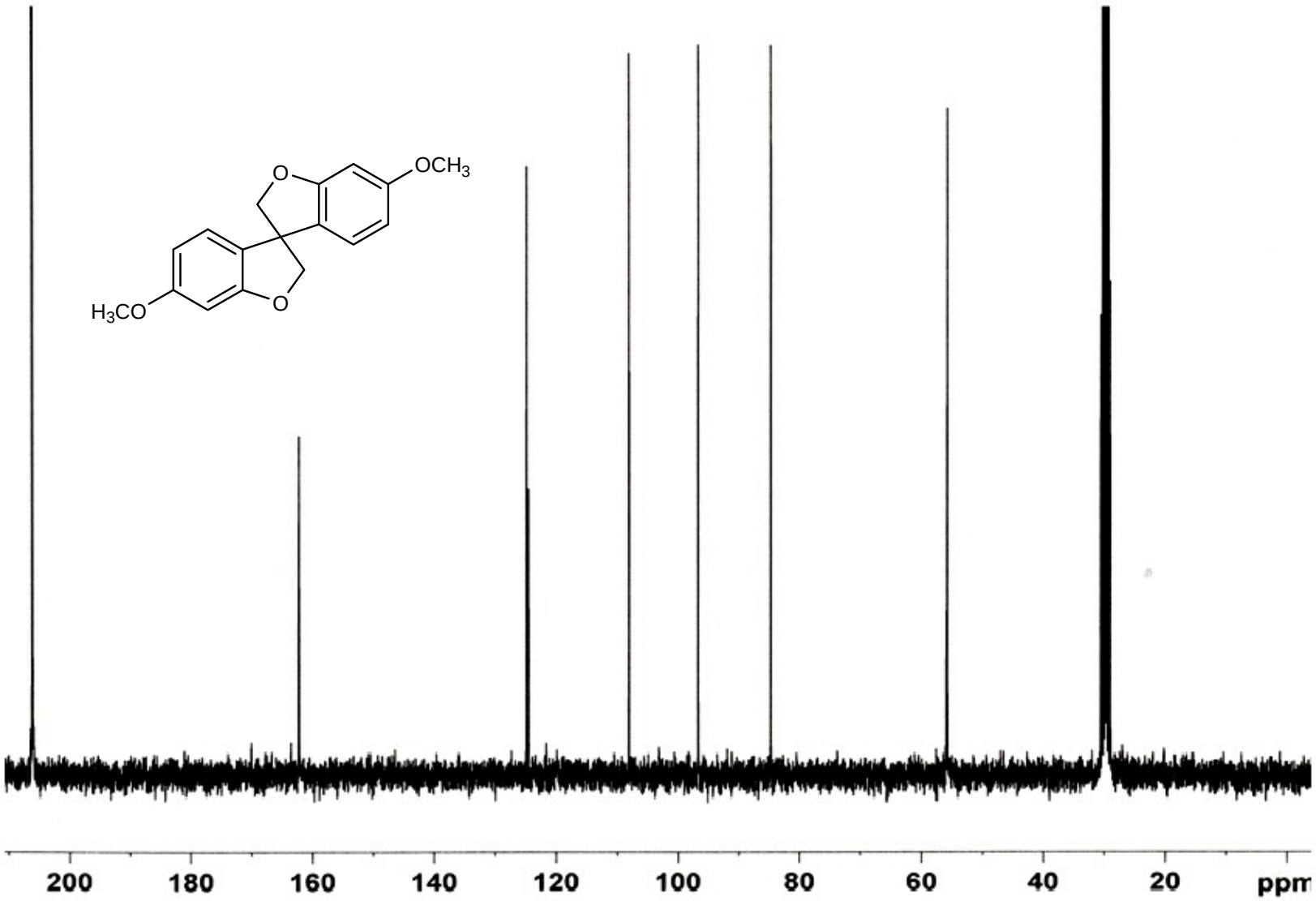

Figure S19: ^{13}C NMR spectrum of 6,6'-dimethoxy-3,3'(2H,2'H)-spirobibenzofuran (**8**), d_6 acetone

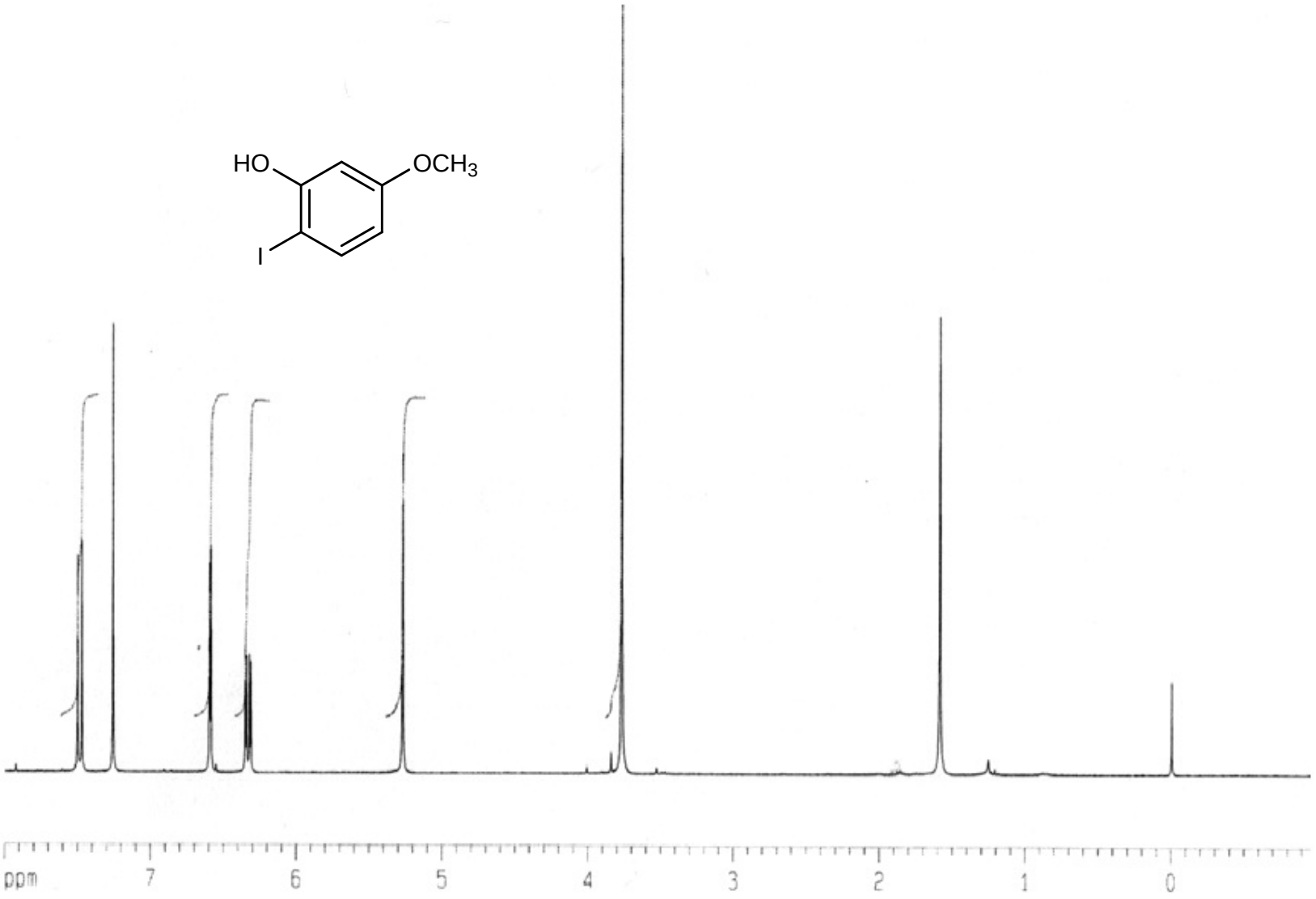

Figure S20: ^{1}H NMR spectrum of 2-iodo-5-methoxyphenol (**2a**), $CDCl_3$