Electronic Supplementary Information (ESI)

Cellulose sulfonic acid as a green, efficient, and reusable catalyst for Nazarov cyclization of unactivated dienones and pyrazoline synthesis

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Contents

I) General methods

Reactions were carried out under air-conditioned environment. Solvents were distilled before use. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F254 (Merck). Flash chromatography column was packed with 230-400 mesh silica gel (Merck). Melting points were measured on an Electrothermal 9200 apparatus. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. Infrared (IR) spectra were recorded on a Shimadzu IR-470 spectrometer. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker DRX-300 Avance spectrometer 300.13 MHz; chemical shifts (δ scale) are reported in parts per million (ppm) downfield from tetramethylsilane and referenced to residual protium in the NMR solvent (DMSO: δ 2.50, $CDCl_3$: δ 7.24). ^{1}H NMR Spectra are reported in order: number of

protons, multiplicity and approximate coupling constant (*J* value) in hertz (Hz); signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and br s (broad signal). The ^{13}C NMR spectra were recorded at 75.47 MHz and 100 MHz; chemical shifts (δ scale) are reported in parts per million (ppm). The elemental analyses were performed with an Elementar Analysen systeme GmbH VarioEL. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation (λ =1. 5406 Å). TG/DTA experiments were carried out by a BÄHR Thermo analysis with a temperature program from 10 °C to 800 °C at a constant rate of 20 °C per min. Scanning electron microscopy was carried out by Philips XL-30 ESEM.

II) Preparation of catalysts:

Synthesis of cellulose sulfonic acid (CSA):

To a magnetically stirred mixture of cellulose (5.00 g, DEAE for column chromatography, Merck) in *n*-Hexanes (20 mL), chlorosulfonic acid (1.00 g, 9 mmol) was added dropwise at 0 °C during 2 h. After addition was completed, the mixture was stirred for 2 h until HCl was removed from the reaction vessel. Then, the mixture was filtered and washed with methanol (30 mL) and dried at room temperature to obtain cellulose sulfonic acid as white powder (5.20 g). Sulfur content of the sample measured by conventional elemental analysis and it was found to be 0.35 mmol/g for cellulose sulfonic acid. The number of H^+ site of cellulose sulfonic acid determined by acid–base titration was 0.30 meq/g. (0.2 g cellulose sulfonic acid was dissolved in deionized water (10 ml) and titration was carried out by NaOH (0.1 N) and phenolphthalein was used as an indicator). The XRD-diffraction patterns of the cellulose sulfonic acid (scheme 3. Fig (xiii), b) shows five characteristic peaks (2θ = 11.08, 16.70, 22.63, 27.63, 34.58). The weight loss was found from TGA measurements and agreed well with those expected for the decomposition of cellulose sulfonic acid to cellulose and the sulfonic acid group. As shown in scheme 2. Fig (vii), (b), the TG curve seems to indicate three-stage decomposition with a weight loss of 11.52 % between 73.17 °C and 123.28 °C which could be attributed to the evaporation of surface-physisorbed water. Another weight loss of 30.30 % between 291.37 °C–399.43 °C could be due to the decomposition of the loaded sulfonic acid along with the cellulose polymer the third weight loss of 26.70 % between 467.78 °C-534.71 °C could be due to the decomposition of cellulose. Further evidence for the loss of physisorbed water and

loaded sulfonic acid on cellulose was provided by DTA measurements (scheme 2. Fig (viii), b). The FT-IR spectrum of the catalyst (scheme 1. Fig (i), b) exhibited a broad peak for an OH absorption band at 3440 cm^{-1}. The peaks at 1158, 1055 and 904 cm^{-1} represented C–O stretching, C–C skeletal vibrations, and C–H ring stretching of the glucose unit. The three new bands appeared in FT-IR spectrum at 1163, 1048 and 674 cm^{-1} corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic acid groups.

Synthesis of silica sulfonic acid (SSA):

The synthesis of silica sulfonic acid was carried out similar to the procedure of cellulose sulfonic acid synthesis to afford silica sulfonic acid as a white powder (5.10 g). Sulfur content of the samples probed by conventional elemental analysis and it was found to be 0.18 mmol/g for silica sulfonic acid. The number of H^+ site of silica sulfonic acid determined by acid–base titration was 0.15 meq/g. (0.2 g silica sulfonic acid was dissolved in deionized water (10 ml) and titration was carried out by NaOH (0.1 N) and phenolphthalein was used as an indicator). The XRD-diffraction patterns of the silica sulfonic acid (scheme 3. Fig (xv), d) shows three characteristic peaks (2θ = 23.00, 25.01, 26.94). As shown in scheme 2. Fig (ix), (d), the TG curve seems to indicate three-stage decomposition with a weight loss of 8.60 % between 129.67 $^{\circ}C$ and 173.79 $^{\circ}C$, which could be attributed to the evaporation of surface-physisorbed water. Another weight loss of 5.57 % between 261.56 $^{\circ}C$-332.61 $^{\circ}C$ could be due to the decomposition of the loaded sulfonic acid along with the silica and the third weight loss of 5.59 % between 554.74 $^{\circ}C$-769.44 $^{\circ}C$ could be due to the decomposition of silica. Further evidence for the loss of physisorbed water and loaded sulfonic acid on silica was presented by DTA measurements (scheme 2. Fig (x), d). The FT-IR spectrum of the catalyst (scheme 1. Fig (ii), d) exhibited a broad peak for an OH absorption band at 3421 cm^{-1}. The three new bands appeared in FT-IR spectrum at 1083, 943 and 804 cm^{-1} corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic acid groups.

Synthesis of galactose sulfonic acid:

The synthesis of galactose sulfonic acid was carried out similar to the procedure of cellulose sulfonic acid synthesis to afford galactose sulfonic acid as a white powder (5.10 g). Sulfur content of the samples probed by conventional elemental analysis, and it was found to be 0.21 mmol/g for galactose sulfonic acid. The number of H^+ site of galactose sulfonic acid determined by acid–base titration was 0.20 meq/g. (0.2 g galactose sulfonic acid was dissolved in deionized water (10 ml) and titration was carried out by NaOH (0.1 N) and phenolphthalein was used as an indicator). The XRD-diffraction patterns of the galactose sulfonic acid (scheme 3. Fig (xvii), h) shows twelve characteristic peaks (2θ = 11.08, 15.76, 18.56, 19.40, 21.72, 22.43, 25.12, 27.62, 36.37, 39.51, 41.15, 43.28). As shown in scheme 2. Fig (xi), (h), the TG curve seems to indicate three-stage decomposition with a weight loss of 0.57 % between 42.72 $^{\circ}$C and 117.28 $^{\circ}$C, which could be attributed to the evaporation of surface-physisorbed water. Another weight loss of 25.23 % between 145.55 °C–172.45 °C could be due to the decomposition of the loaded sulfonic acid along with the galactose and the third weight loss of 56.84 % between 451.67 $^{\circ}$C-659.47 $^{\circ}$C. Further evidence for the loss of physisorbed water and loaded sulfonic acid on galactose was presented by DTA measurements (scheme 2. Fig (xii), h). The FT-IR spectrum of the catalyst (scheme 1. Fig (iv), h) exhibited a broad peak for an OH absorption band at 3393 cm^{-1}. The three new bands appeared in FT-IR spectrum at 1144, 1057 and 766 cm^{-1} corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic acid groups.

Synthesis of MCM-41 sulfonic acid

The synthesis of MCM-41 sulfonic acid was carried out similar to the procedure of cellulose sulfonic acid synthesis to afford MCM-41 sulfonic acid as a white powder (5.10 g). Sulfur content of the samples by conventional elemental analysis, was 0.31 mmol/g for MCM-41 sulfonic acid. The number of H^+ site of MCM-41 sulfonic acid determined by acid–base titration was 0.30 meq/g (0.2 g MCM-41 sulfonic acid was dissolved in deionized water (10 ml) and titration was carried out by NaOH (0.1 N) and phenolphthalein was used as an indicator).The XRD-diffraction patterns of the MCM-41sulfonic acid (scheme 3. Fig (xiv), f) shows four characteristic peaks (2θ = 2.46, 4.24, 4.72, 6.44). As shown in scheme 2. Fig (ix),

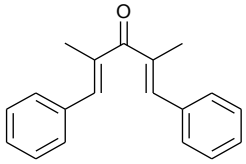
(f), the TG curve seems to indicate three-stage decomposition with a weight loss of 1.99 % between 68.45 °C and 101.30 °C, which could be attributed to the evaporation of surface-physisorbed water. Another weight loss of 1.36 % between 189.90 °C–276.91 °C could be due to the decomposition of the loaded sulfonic acid along with the MCM-41 and the third weight loss of 6.65 % between 279.94 °C-747.15 °C. Further evidence for the loss of physisorbed water and loaded sulfonic acid on MCM-41 was presented by DTA measurements (scheme 2. Fig (x), f). The FT-IR spectrum of the catalyst (scheme 1. Fig (iii), f) exhibited a broad peak for an OH absorption band at 3440 cm^{-1}. The three new bands appeared in FT-IR at 1222, 1097 and 801 cm^{-1} corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic acid groups.

Synthesis of SBA-15 sulfonic acid

The synthesis of SBA-15 sulfonic acid was carried out similar to the procedure of cellulose sulfonic acid synthesis to afford SBA-15 sulfonic acid as a white powder (5.10 g). Sulfur content of the samples by conventional elemental analysis, was 0.18 mmol/g for SBA-15 sulfonic acid. The number of H^+ site of SBA-15 sulfonic acid determined by acid–base titration was 0.20 meq/g. (0.2 g SBA-15 sulfonic acid was dissolved in deionized water (10 ml) and titration was carried out by NaOH (0.1 N) and phenolphthalein was used as an indicator). The XRD-diffraction patterns of the SBA-15 sulfonic acid (scheme 3. Fig (xvi), j) shows three characteristic peaks (2θ = 1.54, 2.8, 3.04). As shown in scheme 2. Fig (ix), (j), the TG curve seems to indicate three-stage decomposition with a weight loss of 16.51 % between 86.68 °C and 155.05 °C, which could be attributed to the evaporation of surface-physisorbed water. Another weight loss of 1.36 % between 403.92 °C–450.10 °C could be due to the decomposition of the loaded sulfonic acid along with the cellulose polymer and the third weight loss of 39.3 % between 491.41 °C-773.34 °C. Further evidence for the loss of physisorbed water and loaded sulfonic acid on SBA-15 was presented by DTA measurements (scheme 2. Fig (x), j). The FT-IR spectrum of the catalyst (scheme 1. Fig (v), j) exhibited a broad peak for an OH absorption band at 3434 cm^{-1}. The three new bands appeared in FT-IR at 1223, 1098 and 765 cm^{-1} corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic acid groups.

III) Preparation of dienones:

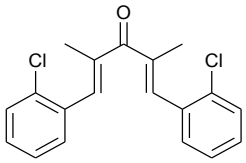
(1*E*,4*E*)-1,5-Di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one (1a):



1a

A 250 mL round-bottom flask fitted with a reflux condenser and magnetic stir bar was charged with KOH (6.9 g, 122 mmol), H_2O (20 mL) and MeOH (40 mL) at room temperature. At this temperature a mixture of 3-pentanone (5.0 g, 58 mmol) and benzaldehyde (12.2 mL, 122 mmol) was added. The resulting solution was refluxed overnight. The reaction mixture was cooled to room temperature, and neutralized with 2 M HCl solution. Organic compounds were extracted with DCM (20 ml× 2), rinsed with brine, and dried with $MgSO_4$. Subsequent recrystalization with MeOH afforded **1d**, as a white solid in 45 % yield. White solid; 45 % yield; **mp:** 120 °C; **TLC R_f** = 0.4 (9:1 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.35-7.5 (m, 12H), 2.27 (s, 6H); **^{13}C NMR (75 MHz, $CDCl_3$):** 201.08, 139.06, 136.91, 135.97, 129.65, 128.48, 128.32, 14.97; **IR (KBr, cm^{-1})** 3051, 3025, 1604, 1478, 1432, 1239, 1200, 1043, 921, 689, 510; **Ms m/z (%):** 262(M^+), 247, 219, 185, 145, 115, 91, 65, 39. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; found C, 86.98; H, 6.91.

(1E,4E)-1,5-bis(2-chlorophenyl)-2,4-dimethylpenta-1,4-dien-3-one(1b):

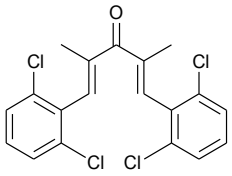


1b

Compound **1b** was prepared by following the procedure for the preparation of **1a**. White solid; 51 % yield; **mp: 68-69 °C**; **TLC R_f** = 0.66 (9:1 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.26-7.46 (m, 10H), 2.08 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** 201.50, 138.32, 136.34, 134.54, 134.06, 130.34, 129.60, 129.36, 126.50, 14.58; **IR (KBr, cm^{-1}):** 3065, 2919, 1626, 1467, 1420, 1361, 1295, 1235, 1202, 1129, 1043, 976, 903, 758, 698, 579, 472; **Ms m/z (%):** 3065, 2919, 1626, 1467, 1420, 1361, 1295, 1235, 1202, 1129, 1043, 976, 903,

758, 698, 579, 472; **Ms m/z(%):** 331(M^+), 315, 295, 267, 232, 216, 179, 151, 115, 89, 63, 39. Anal. Calcd for $C_{19}H_{16}Cl_2O$: C, 68.89; H, 4.87; found C, 68.57; H, 5.34.

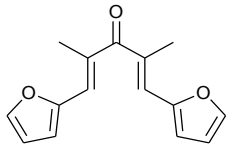
(1E,4E)-1,5-bis(2,6-dichlorophenyl)-2,4-dimethylpenta-1,4-dien-3-one (1c):



1c

Compound **1c** was prepared by following the procedure for the preparation of **1a**. White solid; 65 % yield; **mp: 105-106 °C**; **TLC R_f** = 0.55 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.20-7.38 (m, 8H), 1.86 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** 199.32, 140.93, 134.35, 134.33, 134.11, 129.44, 127.96, 14.70; **IR (KBr, cm^{-1}):** 2908, 1634, 1553, 1428, 1346, 1234, 1190, 1147, 1090, 1040, 978, 778, 690, 597, 516; **Ms m/z(%):** 400(M^+), 363, 335, 213, 236, 185, 149, 115, 87, 63, 39. Anal. Calcd for $C_{19}H_{14}Cl_4O$: C, 57.03; H, 3.53; found C, 57.08; H, 3.43.

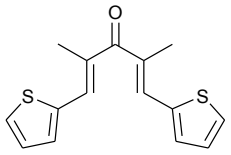
(1*E*,4*E*)-1,5-Di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one (1d):



1d

Compound **1d** was prepared by following the procedure for the preparation of **1a**. Yellow solid; 28% yield; **mp:** 83-84 °C; **TLC R_f** = 0.46 (9:1 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) δ 7.54-6.50 (m, 4H), 2.26 (s, 6H); **IR (KBr, cm^{-1}):** 3104, 1613, 1474, 1361, 1275, 1149, 1089, 1036, 950, 870, 764, 744, 724, 645, 598, 459; **Ms m/z(%):** 242(M^+), 199, 171, 135, 107, 77, 39.

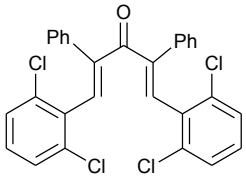
(1E,4E)-2,4-dimethyl-1,5-di(thiophen-2-yl)penta-1,4-dien-3-one (3e):



1e

Compound **1e** was prepared by following the procedure for the preparation of **1a**. Yellow solid; 65 % yield; **mp:** 81-82 °C; **TLC R_f** = 0.80 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.54-7.13 (m, 8H), 2.30 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** 200.84, 139.44, 133.63, 131.92, 131.32, 129.11, 127.42, 15.52; **IR (KBr, cm^{-1}):** 3071, 2906, 1600, 1420, 1354, 1268, 1195, 1029, 857, 830, 711, 585, 512; **Ms m/z (%):** 274(M^+), 259, 231, 190, 151, 123, 97, 79, 45. Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14, S, 23.37; found C, 67.62; H, 5.30, S, 23.67.

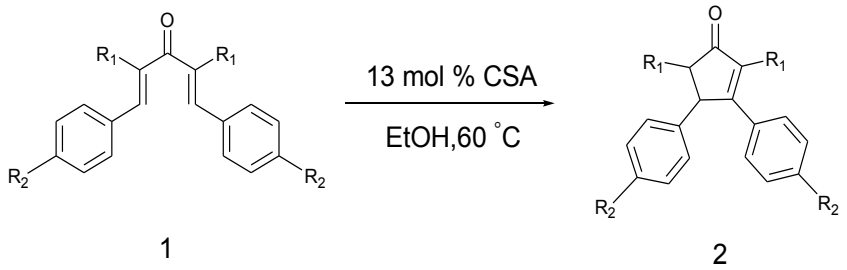
(1E,4E)-1,5-bis(2,6-dichlorophenyl)-2,4-diphenylpenta-1,4-dien-3-one (1f):



1f

Compound **1f** was prepared by following the procedure for the preparation of **1a**. White solid; 65 % yield; **mp:** 178-179 °C; **TLC R_f** = 0.50 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.20-7.38 (m, 8H),1.86 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** 200.84, 139.44, 133.63, 131.92, 131.32, 129.11, 127.423, 15.52; **IR (KBr, cm^{-1}):** 3736, 3065, 2361, 1716, 1558, 1499, 1433, 1334, 1235, 775, 702, 564; **Ms m/z (%):** 524(M^+), 247, 212, 176, 150, 105, 91, 77, 51. Anal. Calcd for $C_{29}H_{18}Cl_4O$: C, 66.44; H, 3.46; found C, 66.43; H, 3.45.

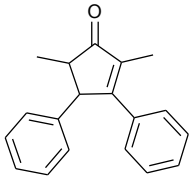
IV) General procedure for the cellulose sulfonic acid catalyzed Nazarov cyclization:



1 2

To a solution of divinyl ketone **1a-f** (1 mmol) in EtOH (10 mL) was added cellulose sulfonic acid (0.4 g, 13 mol %) and the reaction was let to stir at 60 ºC for 12 h. After completion of the reaction, the reaction mixture was filtered to separate the catalyst. The solid catalyst was washed with EtOH (2 mL × 2), dried in an oven at 60 °C and reused for further catalytic cycles. The filtrate was concentrated under reduced pressure, and the crude compound was purified by thin layer chromatography performed on glass plates pre-coated with silica (2:18, EtOAc/hexanes) to afford the desired Nazarov product **2a-f**.

2,5-dimethyl-3,4-diphenylcyclopent-2-enone (2a):[2]

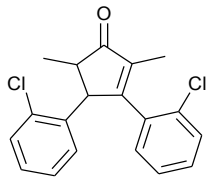


2a

Trans-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (2a′): white solid; 97 % yield; **mp:128 °C**; **TLC R_f =** 0.55 (9:1 n-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.07-7.38 (m, 10H), 3.99 (d, 1H, *J* = 2.7 Hz), 2.43 (qd, 1H, *J* = 7.5, 2.7 Hz), 2.10 (s, 3H), 1.38 (d, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 210.9, 167.0, 142.0, 136.7, 135.1, 128.9, 128.4 (2C), 128.3, 127.7, 126.6, 56.3, 51.2, 15.2, 10.1; **IR (KBr, cm^{-1}):** 3045, 3032, 2965, 2919, 2866, 1745, 1692, 1633, 1487, 1454, 1334, 1228, 1009, 903, 797, 751, 691, 539, 512, 459; **Ms m/z(%):** 262(M^+), 219, 185, 162, 143, 115, 91, 51. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; found C, 86.95; H, 6.89.

Cis-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (2a′′): white solid; 97 % yield; **mp:128 °C.**; **TLC R_f =** 0.50 (9:1 *n*-Hexanes: EtOAc); **^{1}HNMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.04-7.43 (m, 10H), 4.60 (d, 1H, *J* = 6.9 Hz), 2.95 (qd, 1H, *J* = 7.5, 6.9 Hz), 2.11 (s, 3H), 0.79 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 211.4, 166.3, 139.2, 136.7, 128.9, 128.4, 128.3, 128.2, 127.5, 127.6, 126.8, 52.5, 45.5, 12.2, 10.2; **IR (KBr, cm^{-1}):** 3045, 3032, 2965, 2919, 2866, 1745, 1692, 1633, 1487, 1454, 1334, 1228, 1009, 903, 797, 751, 691, 539, 512, 459; **Ms m/z(%):** 262(M^+), 219, 185, 162, 143, 115, 91, 51. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; found C, 86.95; H, 6.89.

3,4-bis(2-chlorophenyl)-2,5-dimethylcyclopent-2-enone (2b):



2b

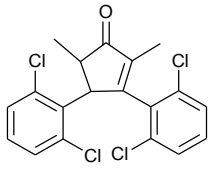
Compound **2b** was prepared by following the procedure for the preparation of **2a** and the mixture of diastereiomers were inseparable.

Trans-3,4-bis(2-chlorophenyl)-2,5-dimethylcyclopent-2-enone (2b′): white solid; 96 % yield; **mp: 109-110 °C**; **TLC R_f =** 0.46 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.97-7.33 (m, 8H), 4.76 (br s, 1H), 2.49 (q, 1H, *J* = 7.2 Hz), 1.76 (s, 3H), 1.39 (d, 3H, *J* = 7.2 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 210.5, 165.7, 139.7, 135.8, 134.6, 134.2, 134.1, 132.1, 130.2, 129.9, 129.7, 129.5, 129.0, 128.1, 126.7, 52.6, 49.0, 15.5, 9.9; **IR (KBr, cm^{-1}):** 2959, 2919, 2859, 1699, 1646, 1480, 1420, 1381, 1341, 1222, 1102, 1043, 837, 791, 751, 698, 645, 565, 453; **Ms m/z(%):** 331(M^+), 295, 267, 232, 202, 179, 152, 115, 75, 39. Anal. Calcd for $C_{19}H_{16}Cl_2O$: C, 68.89; H, 4.87; found C, 68.52; H, 5.38.

Cis-3,4-bis(2-chlorophenyl)-2,5-dimethylcyclopent-2-enone (2b′′): white solid; 96 % yield; **mp: 109-110 °C**; **TLC R_f =** 0.46 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.97-7.33 (m, 8H), 5.36 (d, 1H, *J* = 5.7 Hz), 3.05 (qd, 1H, *J* = 7.5, 5.7 Hz), 0.76 (d, 3H,

J = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 211.0, 164.8, 140.7, 134.9, 134.0, 134.6, 132.3, 129.9, 129.7, 129.1, 128.1, 127.1, 126.7, 126.5, 126.3; **IR (KBr, cm^{-1}):** 2959, 2919, 2859, 1699, 1646, 1480, 1420, 1381, 1341, 1341, 1222, 1102, 1043, 837, 791, 751, 698, 645, 565, 453; **Ms m/z(%):** 331(M^+), 295, 267, 232, 202, 179, 152, 115, 75, 39; Anal. Calcd for $C_{19}H_{16}Cl_2O$: C, 68.89; H, 4.87; found C, 68.52; H, 5.38.

3,4-bis(2,6-dichlorophenyl)-2,5-dimethylcyclopent-2-enone (2c):



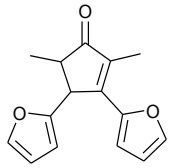
2c

Compound **2c** was prepared by following the procedure for the preparation of **2a** and the mixture of diastereiomers were inseparable.

Trans-3,4-bis(2,6-dichlorophenyl)-2,5-dimethylcyclopent-2-enone (2c′): white solid; 95 % yield; **mp: 130-131 °C**; **TLC R_f** = 0.66 (9:1 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.07-7.34 (m, 6H), 5.13 (d, 1H, *J* = 3.4 Hz), 3.01 (qd, 1H, *J* = 6.9, 3.4 Hz), 1.69 (s, 3H), 1.40 (d, 1H, *J* = 6.9 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 211.5, 160.4, 136.9, 134.2, 134.0, 130.0, 129.9, 128.6, 128.2, 128.1, 128.0, 52.4, 45.2, 17.9, 9.0; **IR (KBr, cm^{-1}):** 2965, 2925, 2846, 1712, 1646, 1560, 1427, 1374, 1328, 1182, 1082, 956, 771; **Ms m/z(%):** 400(M^+), 372, 335, 300, 236, 215, 186, 149, 115, 63, 43. Anal. Calcd for $C_{19}H_{14}Cl_4O$: C, 57.03; H, 3.53; found C, 57.09; H, 3.48.

Cis-3,4-bis(2,6-dichlorophenyl)-2,5-dimethylcyclopent-2-enone (2c′′): white solid; 95 % yield; **mp:130-131 °C**; **TLC R_f** = 0.66 (9:1 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.07-7.34 (m, 6H), 5.71 (d, 1H, *J* = 3.4 Hz), 3.01 (qd, 1H, *J* = 6.3, 3.4 Hz), 1.72 (s, 3H), 1.21 (d, 3H, *J* = 6.3 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 209.6, 157.4, 142.4, 137.9, 137.2, 134.0, 131.1, 130.3, 128.7, 128.5, 128.0, 48.6, 45.1, 10.1, 9.3; **IR (KBr, cm^{-1}):** 2965, 2925, 2846, 1712, 1646, 1560, 1427, 1374, 1328, 1182, 1082, 956, 771; **Ms m/z (%):** 400(M^+), 372, 335, 300, 236, 215, 186, 149, 115, 63, 43 Anal. Calcd for $C_{19}H_{14}Cl_4O$: C, 57.03; H, 3.53; found C, 57.09; H, 3.48.

3,4-di(furan-2-yl)-2,5-dimethylcyclopent-2-enone (2d):



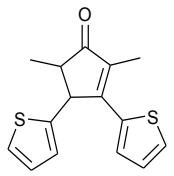
2d

Compound **2d** was prepared by following the procedure for the preparation of **2a** and the mixture of diastereiomers were separated by silica gel plate (2:18, EtOAc/hexanes).

Trans-3,4-di(furan-2-yl)-2,5-dimethylcyclopent-2-enone (2d′): Orange solid; 96 % yield; **mp: 70-71 °C**; **TLC R_f =** 0.45 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.10-7.55 (m, 8H), 3.95 (d, 1H, J = 3.0 Hz), 2.55 (qd, 1H, *J* = 7.5, 3.0 Hz), 2.16 (s, 3H), 1.30 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 209.5, 154.7, 150.8, 150.5, 144.8, 141.6, 133.3, 114.7, 112.0, 110.3, 106.1, 47.4, 46.9, 29.6, 16.0, 9.9; **IR (KBr, cm^{-1}):** 3124, 2972, 2925, 2866, 1798, 1692, 1626, 1460, 1374, 1341, 1222, 1142, 1069, 1003, 983, 910, 817, 744, 698, 585; **Ms m/z(%):** 242(M^+), 199, 171, 128, 108, 77, 39. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82; found C, 74.28; H, 5.78.

Cis-3,4-di(furan-2-yl)-2,5-dimethylcyclopent-2-enone (2d′′): Orange solid; 96 % yield; **mp: 70-71 °C**; **TLC R_f =** 0.46 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.04-7.56 (m, 8H), 4.60 (d, 1H, *J* = 7.2 Hz), 2.80 (qd, 1H, *J* = 7.5, 7.2 Hz), 2.18 (s, 3H), 0.9 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 209.7, 153.3, 151.1, 150.4, 144.7, 141.6, 133.6, 114.3, 112.0, 110.2, 107.7, 44.7, 43.3, 29.7, 11.3, 9.9; **IR (KBr, cm^{-1}):** 3124, 2972, 2925, 2866, 1798, 1692, 1626, 1460, 1374, 1341, 1222, 1142, 1069, 1003, 983, 910, 817, 744, 698, 585; **Ms m/z (%):** 242(M^+), 199, 171, 128, 108, 77, 39. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82; found C, 74.28; H, 5.78.

2,5-dimethyl-3,4-di(thiophen-2-yl)cyclopent-2-enone (2e):



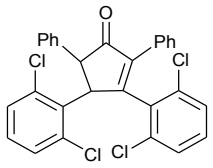
2e

Compound **2e** was prepared by following the procedure for the preparation of **2a** and the mixture of diastereiomers were separated by silica gel plate (2:18, EtOAc/hexanes).

Trans-2,5-dimethyl-3,4-di(thiophen-2-yl)cyclopent-2-enone (2e′): White solid; 92 % yield; **mp: 93-94 °C**; **TLC R_f =** 0.50 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.80-7.51 (m, 8H), 4.26 (d, 1H, *J* = 2.4 Hz), 2.50 (qd, 1H, *J*=7.5, 2.4 Hz), 2.17 (s, 3H), 1.35 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 209.2, 157.4, 146.5, 138.0, 133.7, 130.2, 126.9, 124.7, 124.2, 51.7, 51.1, 16.3, 10.5; **IR (KBr, cm^{-1}):** 3098, 2965, 2919, 2866, 1745, 1692, 1606, 1414, 1381, 1334, 1208, 1049, 996, 857, 698.; **Ms m/z (%):** 274(M^+), 207, 185, 150, 115, 75, 57, 39; Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14; S, 23.37; found C, 65.52; H, 5.38; S, 23.32.

Cis-2,5-dimethyl-3,4-di(thiophen-2-yl)cyclopent-2-enone (2e′′): White solid; 92 % yield; **mp: 93-94 °C**; **TLC R_f =** 0.50 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.79-7.25 (m, 8H), 4.86 (d, 1H, *J* = 7.2 Hz), 2.90 (qd, 1H, *J* = 7.5, 7.2 Hz), 2.20 (s, 3H), 0.90 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** 209.2, 157.5, 143.5, 138.5, 133.5, 129.7, 127.6, 127.0, 47.4, 45.9, 11.2, 10.4; **IR (KBr, cm^{-1}):** 3098, 2965, 2919, 2866, 1745, 1692, 1606, 1414, 1381, 1334, 1208, 1049, 996, 857, 698; **Ms m/z (%):** 274(M^+), 207, 185, 150, 115, 75, 57, 39; Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14; S, 23.37; found C, 65.52; H, 5.38; S, 23.32.

Cis-3,4-bis(2,6-dichlorophenyl)-2,5-diphenylcyclopent-2-enone (2f):

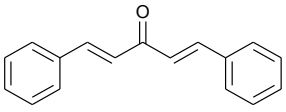


2f

To a solution of divinyl ketone **3a** (0.262 g, 1 mmol) in EtOH (10 mL) was added cellulose sulfonic acid (0.4 g, 13 mol %). The reaction was stirred at 60 ºC. After completion of the reaction, the reaction mixture was filtered. The solution was cooled at room temperature and the precipitate was slowly formed, filtered off and washed with *n*-Hexanes. White solid; 95 % yield; **mp: 103-104 °C**; **TLC** R_f = 0.48 (8:2 *n*-Hexanes: EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.88-7.67 (m, 16H), 6.28 (d, 1H, *J* = 7.5 Hz), 4.61 (d, 1H, *J* = 7.5 Hz); **^{13}C NMR (75 MHz, $CDCl_3$):** 203.4, 156.8, 144. 2, 131.1, 130.6, 130.1, 130.0, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 126.4, 53.2, 48.8; **IR (KBr, cm^{-1}):** 2434, 1713, 1557, 1430, 1337, 1225, 1167, 1055, 884, 782, 684, 606, 563; **Ms m/z(%):** 524(M^+), 489, 335, 276, 246, 212, 176, 150, 105, 77, 39; Anal. Calcd for $C_{29}H_{18}Cl_4O$: C, 66.44; H, 3.46; found C, 66.42; H, 3.44.

V) Preparation of α,β-unsaturated ketone 3a−3f

(1E,4E)-1,5-diphenylpenta-1,4-dien-3-one (3a):[3a]

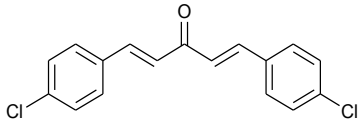


3a

To a solution of NaOH (2.0 g, 50.0 mmol) in aqueous ethanol (1:1) at ambient temperature, benzaldehyde (4.24 g, 40.0 mmol) was added dropwise. After additional stirring for 10 min, acetone (1.17 g, 20.0 mmol) was added dropwise and stirred for 30 min. Water (20 ml) was added to the reaction mixture, which was then filtered. The product was washed with water

(20 ml x 3) and purified by re-crystallizing from ethanol and allowed to dry. Yellow solid; 90 % yield; **mp: 113-114 °C**; **^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.09-7.79 (m, 14H).

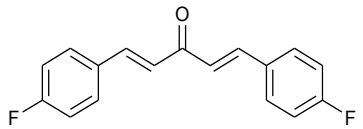
(1E,4E)-1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one (3b):[3a]



3b

Compound **3b** was prepared by following the procedure for the preparation of **3a.** Yellow solid; 93 % yield; **mp: 185-186 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.02-7.73 (m, 12H).

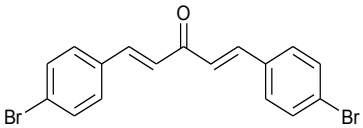
(1E,4E)-1,5-bis(4-fluorophenyl)penta-1,4-dien-3-one (3c):[3a]



3c

Compound **3c** was prepared by following the procedure for the preparation of **3a.** Yellow solid; 91 % yield; **mp: 91-92 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.97-7.74 (m, 12H).

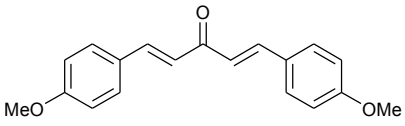
(1E,4E)-1,5-bis(4-bromophenyl)penta-1,4-dien-3-one (3d):[3b]



3d

Compound **3d** was prepared by following the procedure for the preparation of **3a.** Yellow solid; 91 % yield; **mp: 212-213 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.70-7.72 (m, 12H).

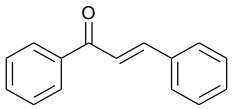
(1E,4E)-1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one (3e):[3b]



3e

Compound **3e** was prepared by following the procedure for the preparation of **3a.** Yellow solid; 90 % yield; **mp: 130-131 °C**; **^{1}H NMR (300 MHz, CDCl3):** δ_H (ppm) 6.70-7.72 (m, 12H), 3.84 (s, 6H).

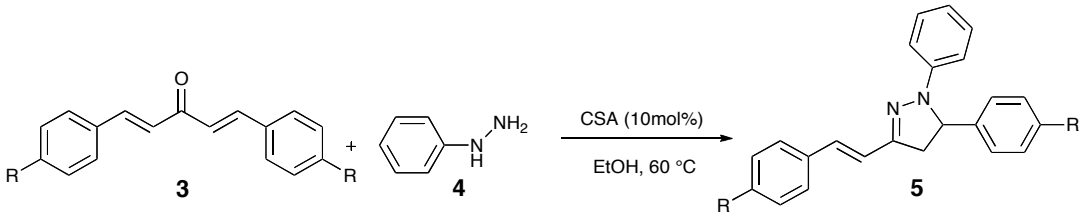
Chalcone (3f):[4]



3f

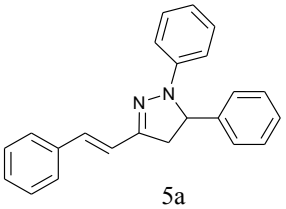
To a solution of NaOH (50.0 mmol, 2.0 g) in aqueous ethanol (1:1) at ambient temperature, benzaldehyde (2.12 g, 20.0 mmol) was added dropwise. After additional stirring for 10 min, acetophenone (2.4 g, 20.0 mmol) was added dropwise and stirred for 24 h. Water (20 ml) was added to the reaction mixture, which was then filtered. The product was washed with water (20 ml × 3) and purified by re-crystallizing from ethanol and allowed to dry. Yellow solid; 90 % yield; **mp: 56-57 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 7.43-8.06 (m, 12H).

VI) General procedure for the cellulose-SO_3H catalyzed pyrazoline synthesis



To a suspension of (**3a-f**) (1 mmol) and cellulose sulfonic acid (0.3 g, 10 mol %) in EtOH (10 ml), phenylhydrazine (0.21 g, 2 mmol) was added and stirred at 60 °C. After completion of the reaction that was monitored by TLC, the reaction mixture was poured into cold water and the precipitate was filtered, afterwards ethyl acetate was added to the precipitate in order to dissolve the product and it was filtered to separate the catalyst. The solid catalyst was washed with EtOH (2 x 2 mL), dried in oven at 60 °C and reused for further catalytic cycles. The filtrate was concentrated under reduced pressure and purified by re-crystallizing from ethanol and dried under high vacuum to afford the desired products (**5a-f**).

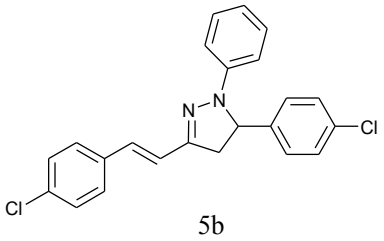
4,5-dihydro-1,5-diphenyl-3-styryl-1H-pyrazole (5a):[5a]



5a

Compound **5a** was prepared by following the general procedure. Yellow solid; 96 % yield; **mp: 152-153 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.76-7.56 (m, 16H), 6.55 (d, 1H, *J* = 15.9 Hz), 5.27 (dd, 1H, *J* = 12.6, 6.9 Hz), 3.69 (dd, 1H, *J* = 16.9, 12.6 Hz), 3.07 (dd, 1H, *J* = 16.9, 6.9 Hz).

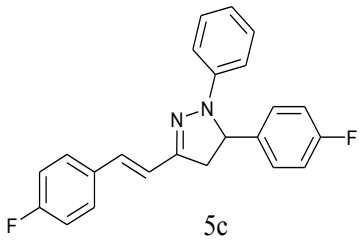
3-(4-chlorostyryl)-1-(4-chlorophenyl)-4,5-dihydro-5-phenyl-1H-pyrazole (5b):[5a]



5b

Compound **5b** was prepared by following the general procedure. Yellow solid; 98 % yield; **mp: 211-212 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.73-7.47 (m, 14H), 6.48 (d, 1H, *J* = 16.2 Hz), 5.25 (dd, 1H, *J* = 12.3, 6.6 Hz), 3.70 (dd, 1H, *J* = 16.7, 12.3 Hz), 2.97 (dd, 1H, *J* = 16.7, 6.6 Hz).

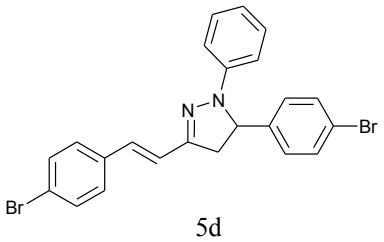
3-(4-fluorostyryl)-5-(4-fluorophenyl)-4,5-dihydro-1-phenyl-1H-pyrazole (5c):[5b]



5c

Compound **5c** was prepared by following the general procedure. Yellow solid; 96 % yield; **mp: 200-201 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.80-7.50 (m, 14H), 6.52 (d, 1H, *J* = 16.5Hz), 5.26 (dd, 1H, *J* = 12.3, 6.6 Hz), 3.71 (dd, 1H, *J* = 16.8, 12.3 Hz), 2.99 (dd, 1H, *J* = 16.8, 6.6 Hz).

3-(4-bromostyryl)-5-(4-bromophenyl)-4,5-dihydro-1-phenyl-1H-pyrazole (5d):[5c]

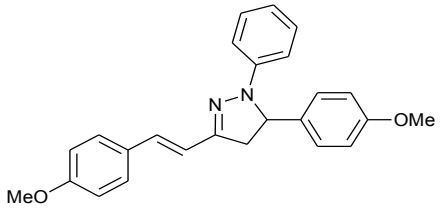


5d

Compound **5d** was prepared by following the general procedure. Yellow solid; 93 % yield; **mp: 227-228 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.80-7.60 (m, 14H), 6.47 (d, 1H, *J*

= 16.2 Hz), 5.25 (dd, 1H, *J* = 12.3, 6.6 Hz), 3.71 (dd, 1H, *J* = 16.9, 12.3 Hz), 2.98 (dd, 1H, *J* = 16.9, 6.6 Hz).

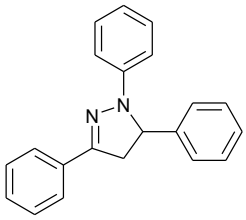
3-(4-methoxystyryl)-4,5-dihydro-5-(4-methoxyphenyl)-1-phenyl-1H-pyrazole (5e):[5a]



5e

Compound **5e** was prepared by following the general procedure. Yellow solid; 92 % yield; **mp: 159-160 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.82-7.45 (m, 14H), 6.55 (d, 1H, *J* = 16.2Hz), 5.20 (dd, 1H, *J* = 12.3, 6.6 Hz), 3.84 (s, 3H), 3.81 (s, 3H), 3.69 (dd, 1H, *J* = 16.8, 12.3 Hz), 3.00 (dd, 1H, *J* = 16.8, 6.6 Hz); **^{13}C NMR (75 MHz, $CDCl_3$):** 159.71, 158.99, 148.86, 144.38, 134.59, 132.38, 129.53, 129.01, 127.97, 127.05, 119.68, 119.13, 114.53, 114.32, 113.40, 63.60, 55.36, 55.31, 42.42.

4,5-dihydro-1,3,5-triphenyl-1H-pyrazole (5f):[6]



5f

Compound **5f** was prepared by following the general procedure. Yellow solid; 91 % yield; **mp: 134-135 °C; ^{1}H NMR (300 MHz, $CDCl_3$):** δ_H (ppm) 6.81-7.78 (m, 15H), 5.30 (dd, 1H, *J* = 12.3, 7.2 Hz), 3.86 (dd, 1H, *J* = 17.1, 12.3 Hz), 3.17 (dd, 1H, *J* = 17.1, 7.2 Hz).

VII) References:

1) Y. Kwon, F. G. West and R. McDonald, *Angew. Chem*., 2013, **125**, 8778 – 8781.

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FT−IR, XRD, TG/DTA spectra for different catalysts

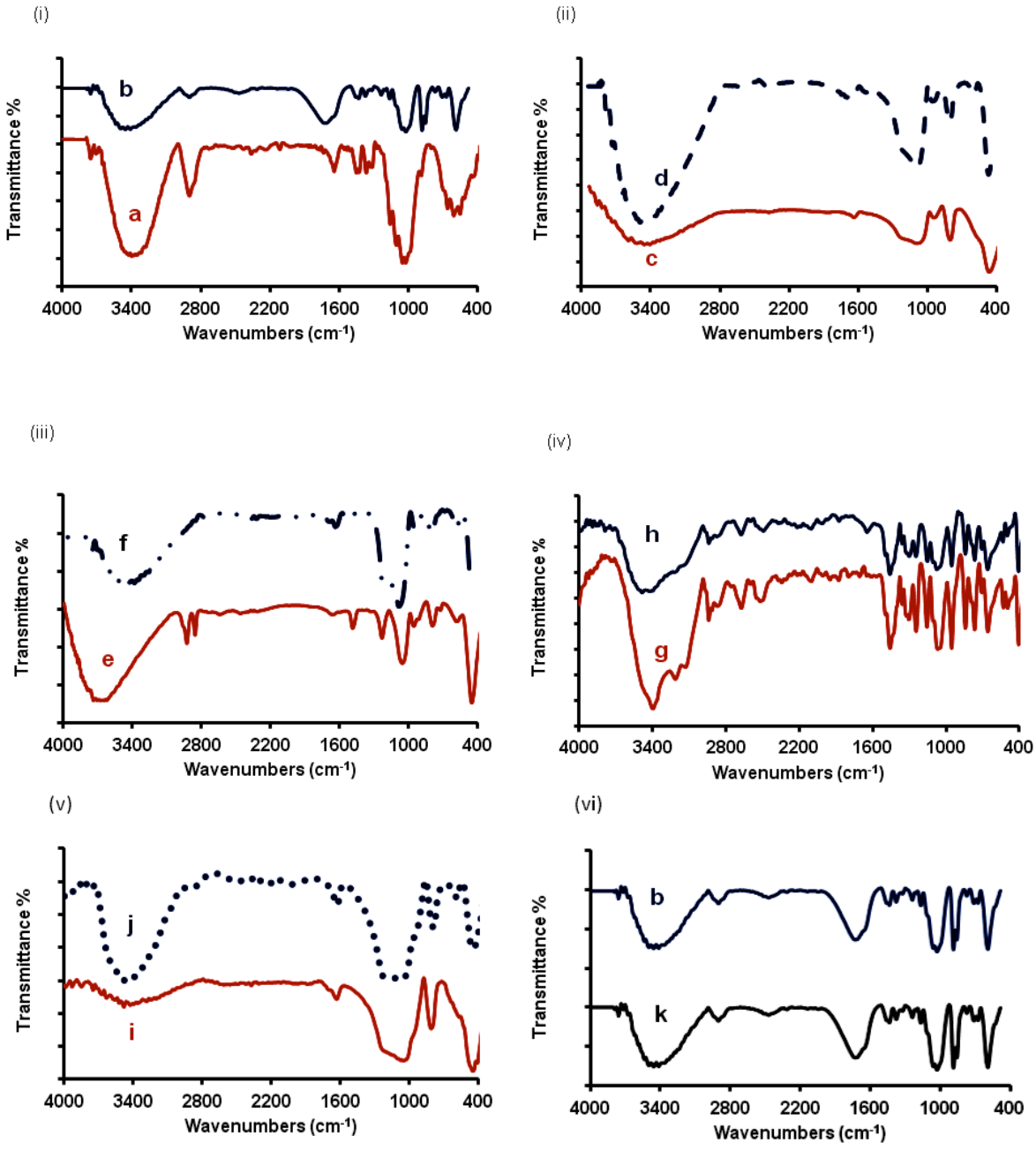


Fig. S1. (i) FT-IR spectrums of (a) cellulose, (b) cellulose sulfonic acid; (ii) FT-IR spectrums of (c) silica, (d) silica sulfonic acid; (iii) FT-IR spectrums of (e) MCM-41, (f) MCM-41 sulfonic acid; (iv) FT-IR spectrums of (g) galactose, (h) galactose sulfonic acid; (v) FT-IR spectrums of (i) SBA-15, (j) SBA-15 sulfonic acid; (vi) FT-IR spectrums of (b) fresh cellulose sulfonic acid, (k) reused cellulose sulfonic acid.

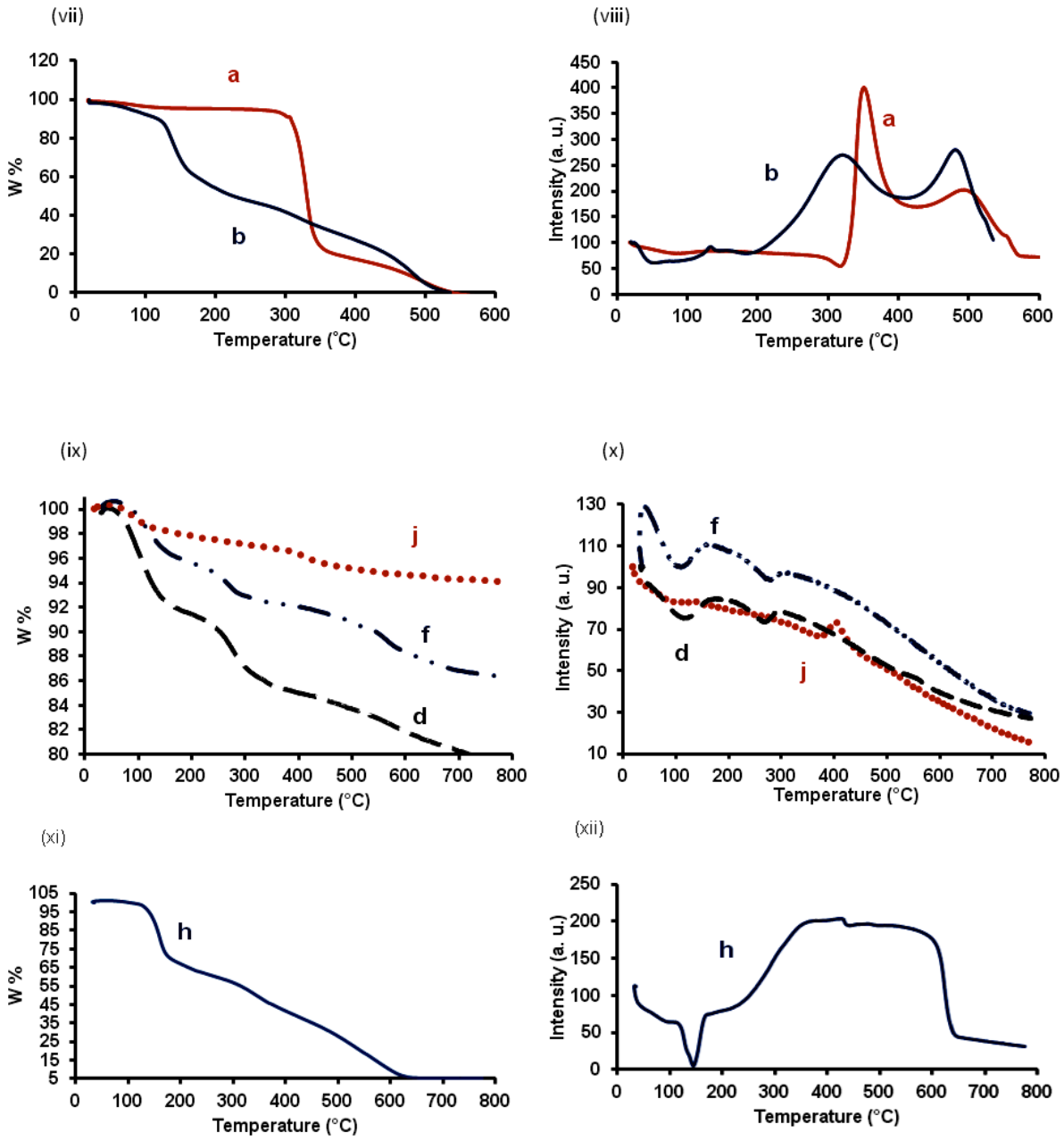


Fig. S2. (vii) TGA curves for (a) cellulose (b) cellulose sulfonic acid; (viii) DTA curves for (a) cellulose (b) cellulose sulfonic acid; (ix) TGA curves for (j) SBA-15 sulfonic acid (f) MCM-41 sulfonic acid (d) silica sulfonic acid; (x) DTA curves for (j) SBA-15 sulfonic acid (f) MCM-41 sulfonic acid; (d) silica sulfonic acid; (xi) TGA curves for (h) galactose sulfuric acid; (xii) DTA curves for (h) galactose sulfuric acid.

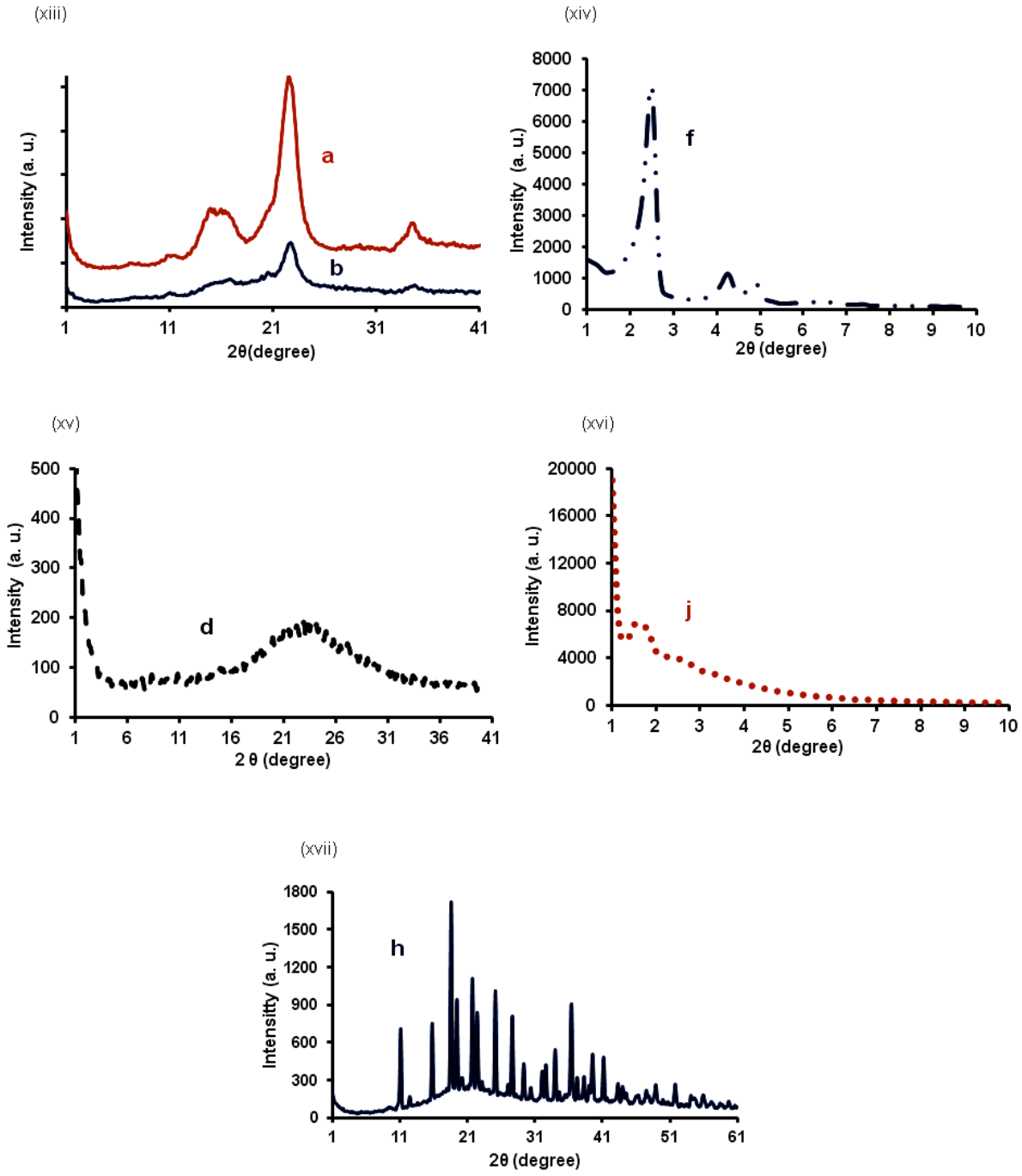
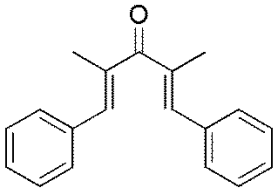
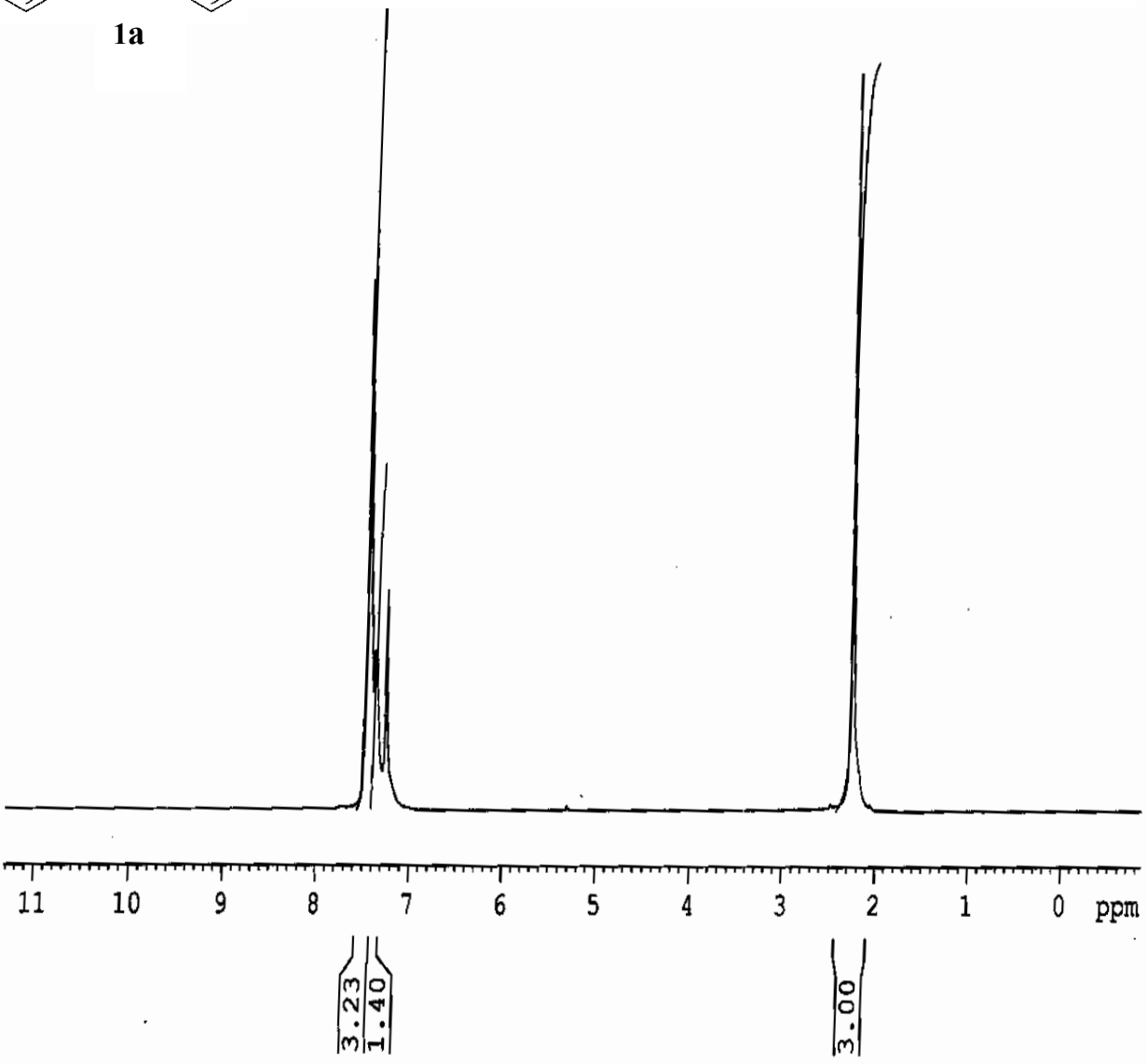


Fig. S3. (xiii) XRD of (a) cellulose (b) cellulose sulfonic acid; (xiv) XRD of (f) MCM-41 sulfonic acid; (xv) XRD of (d) silica sulfonic acid; (xvi) XRD of (j) SBA-15 sulfonic acid; (xvii) XRD of (h) galactose sulfonic acid.

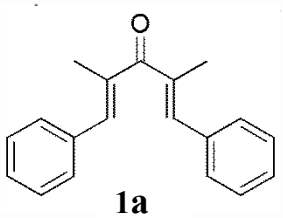
VIII) Selected ^{1}H NMR and ^{13}C NMR spectra



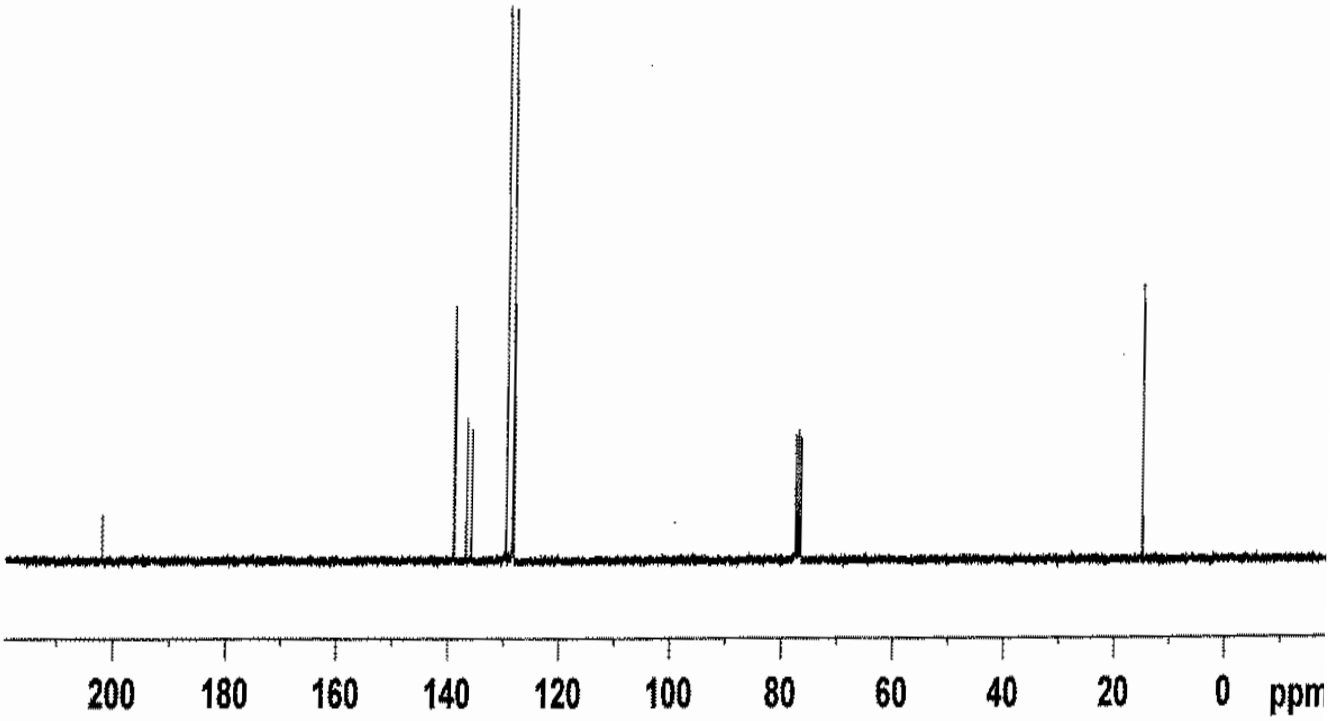
1a



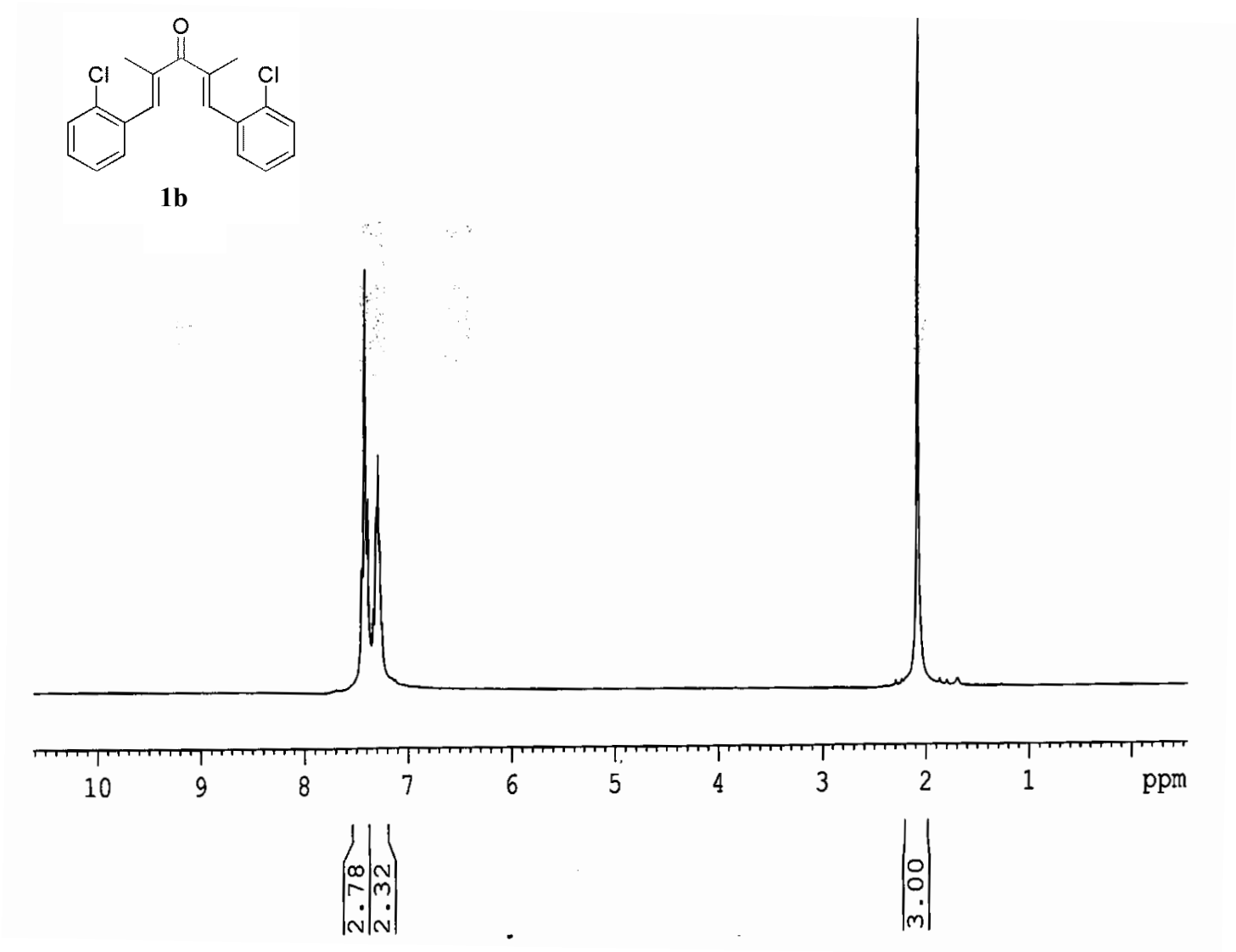
^{1}H NMR of **1a** ($CDCl_3$, 300 MHz)



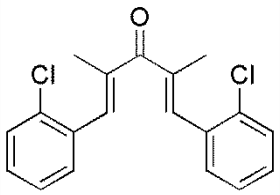
1a



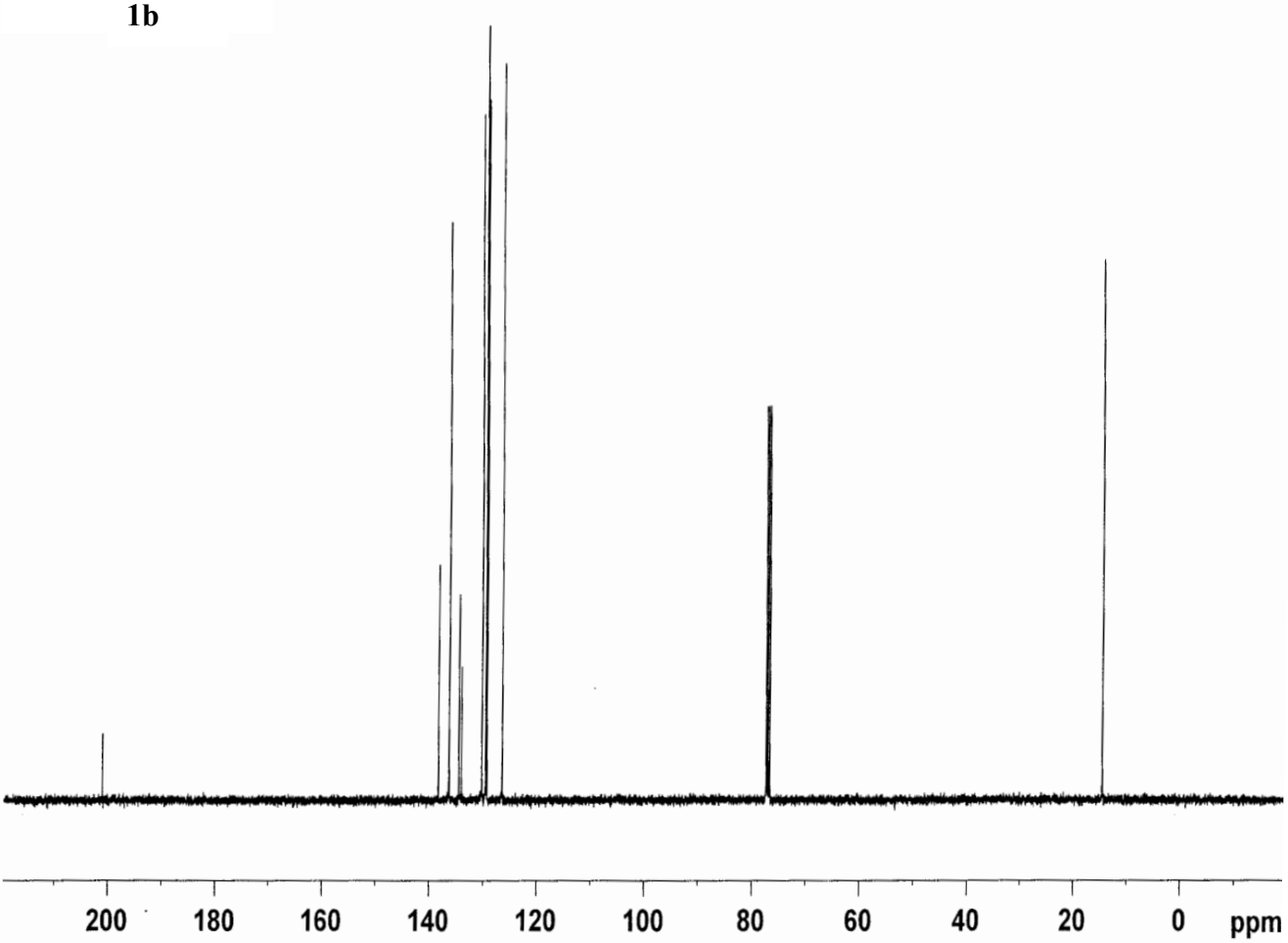
^{13}C NMR of **1a** ($CDCl_3$, 75 MHz)



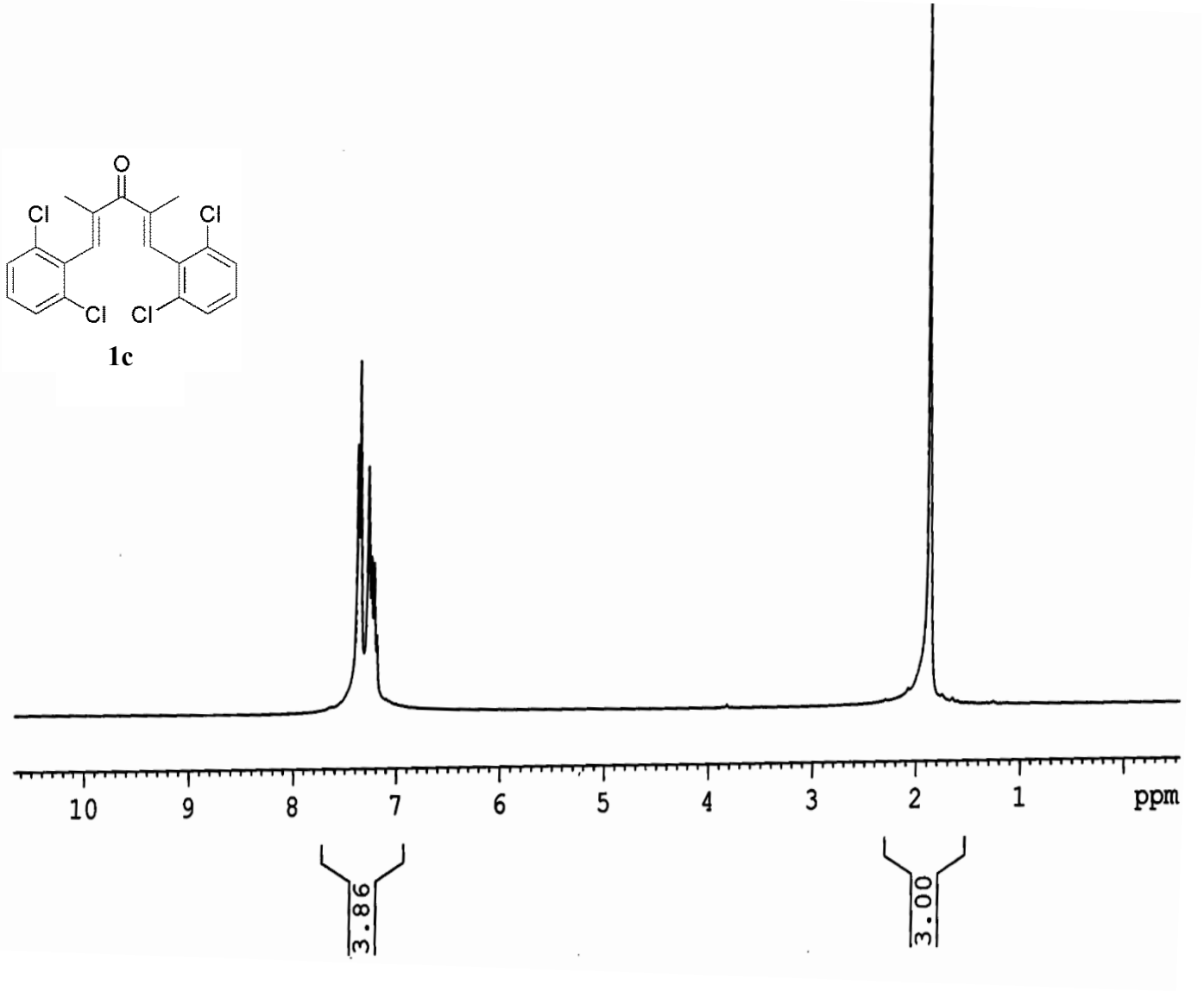
^{1}H NMR of **1b** ($CDCl_3$, 300 MHz)



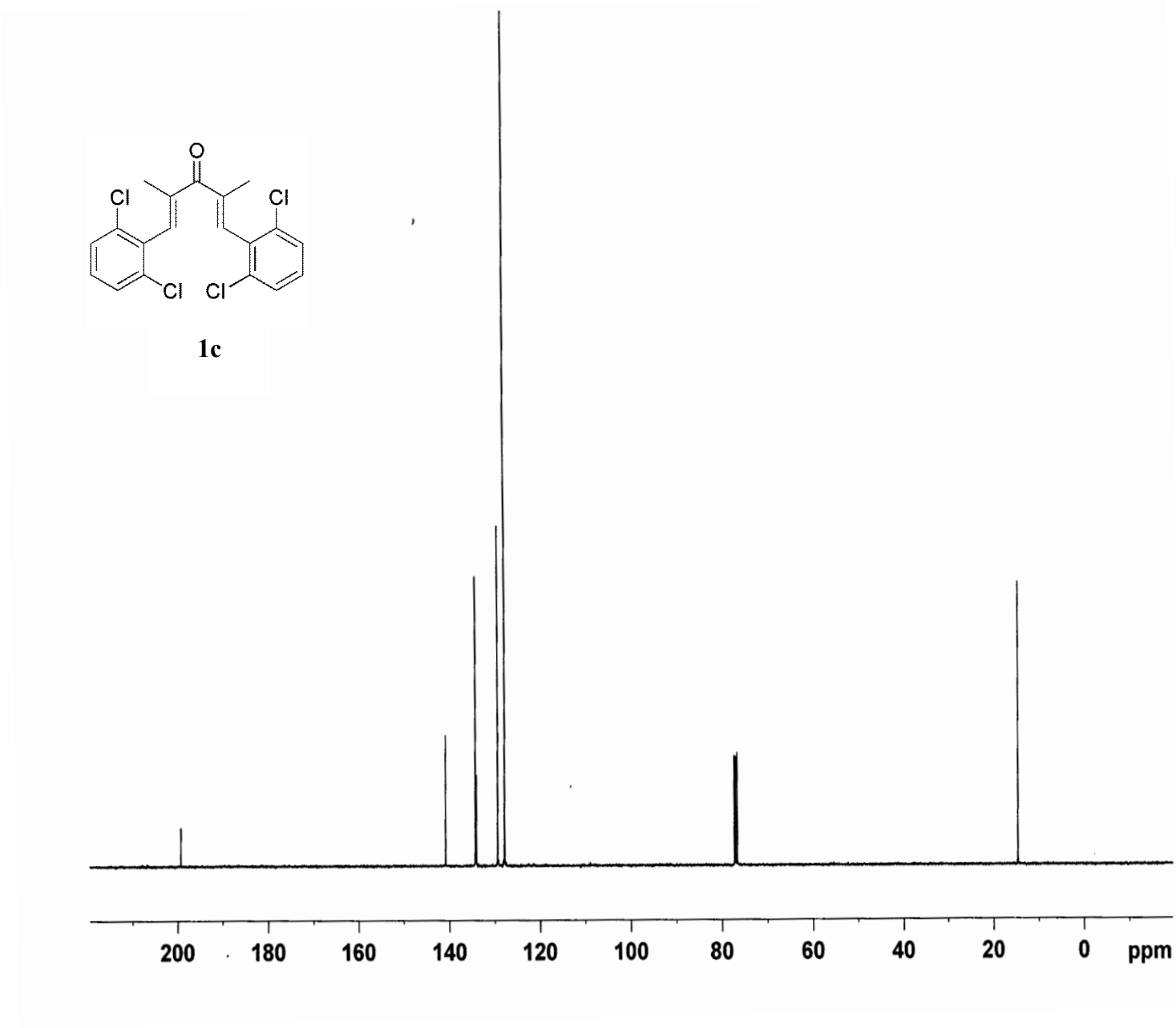
1b



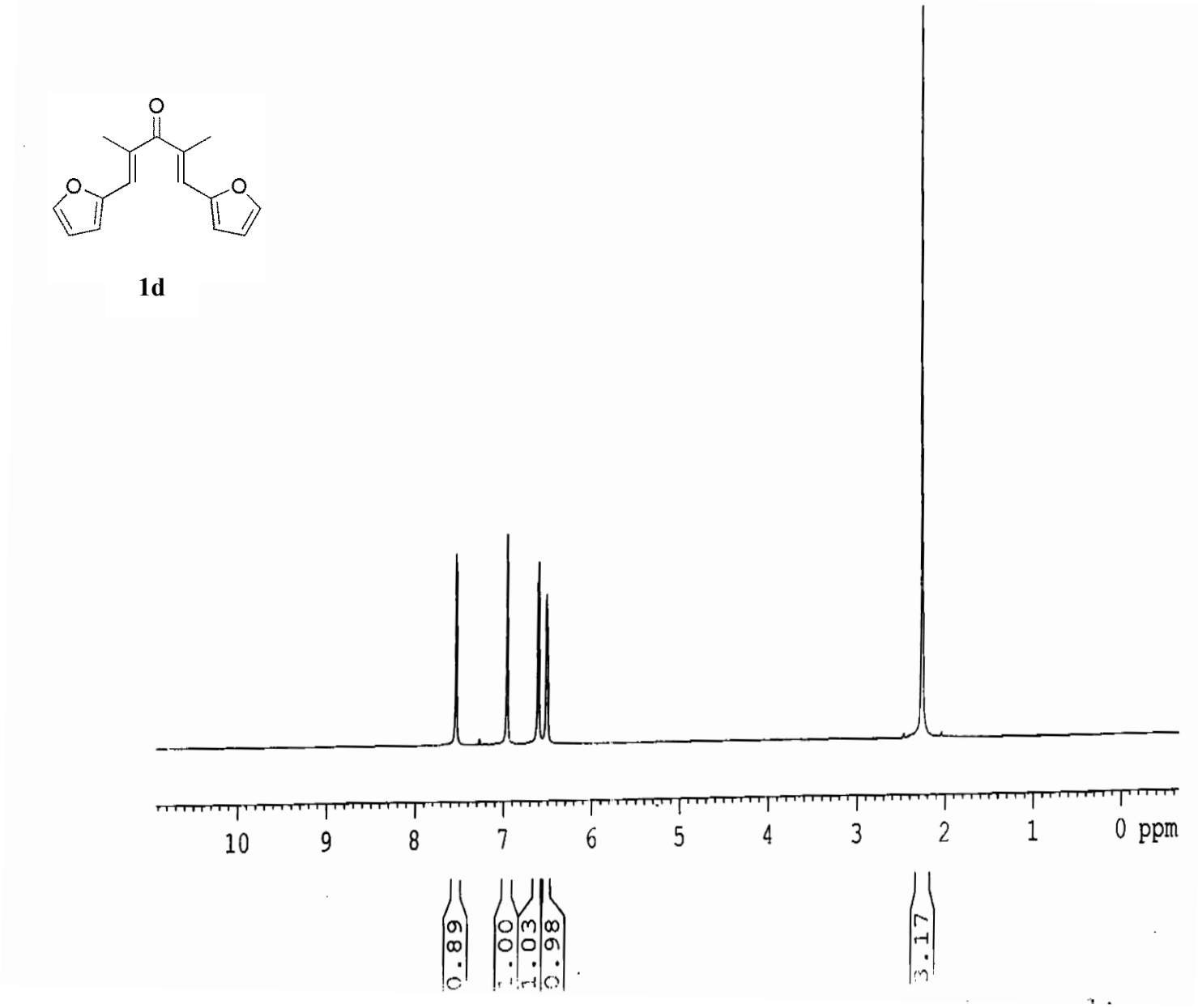
^{13}C NMR of **1b** ($CDCl_3$, 100 MHz)



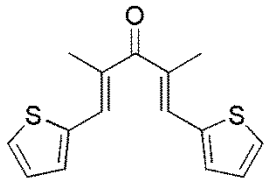
^{1}H NMR spectrum of **1c** ($CDCl_3$, 300 MHz)



^{13}C NMR spectrum of **1c** ($CDCl_3$, 100 MHz)

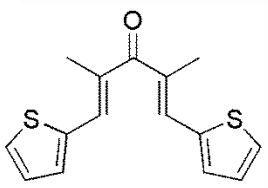


^{1}H NMR spectrum of **1d** ($CDCl_3$, 300 MHz)



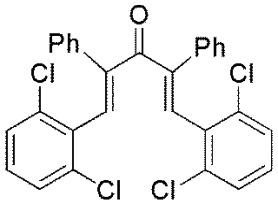
1e

^{1}H NMR spectrum of **1c** ($CDCl_3$, 300 MHz)

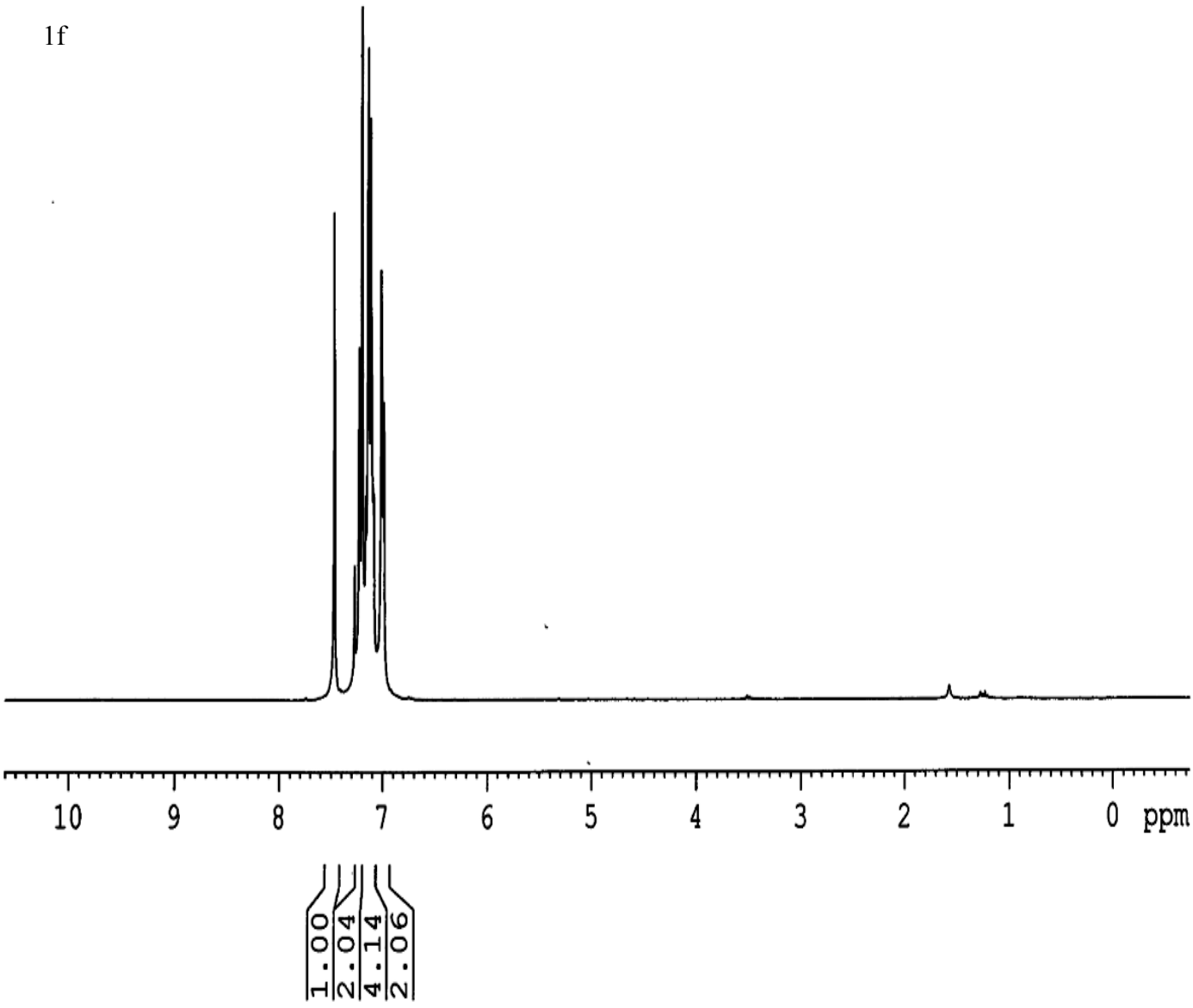


1e

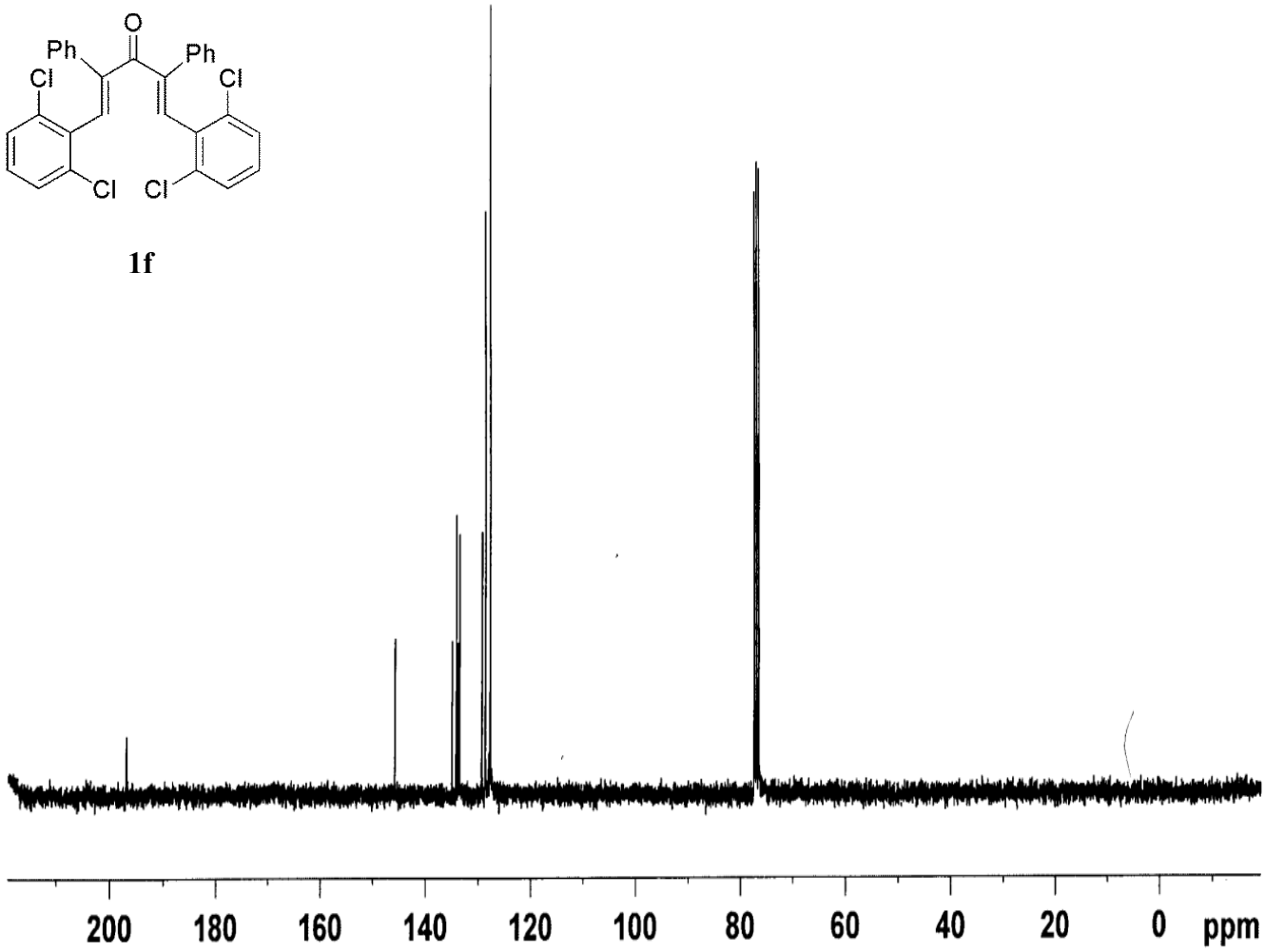
^{13}C NMR spectrum of **1a** ($CDCl_3$, 100 MHz)



1f

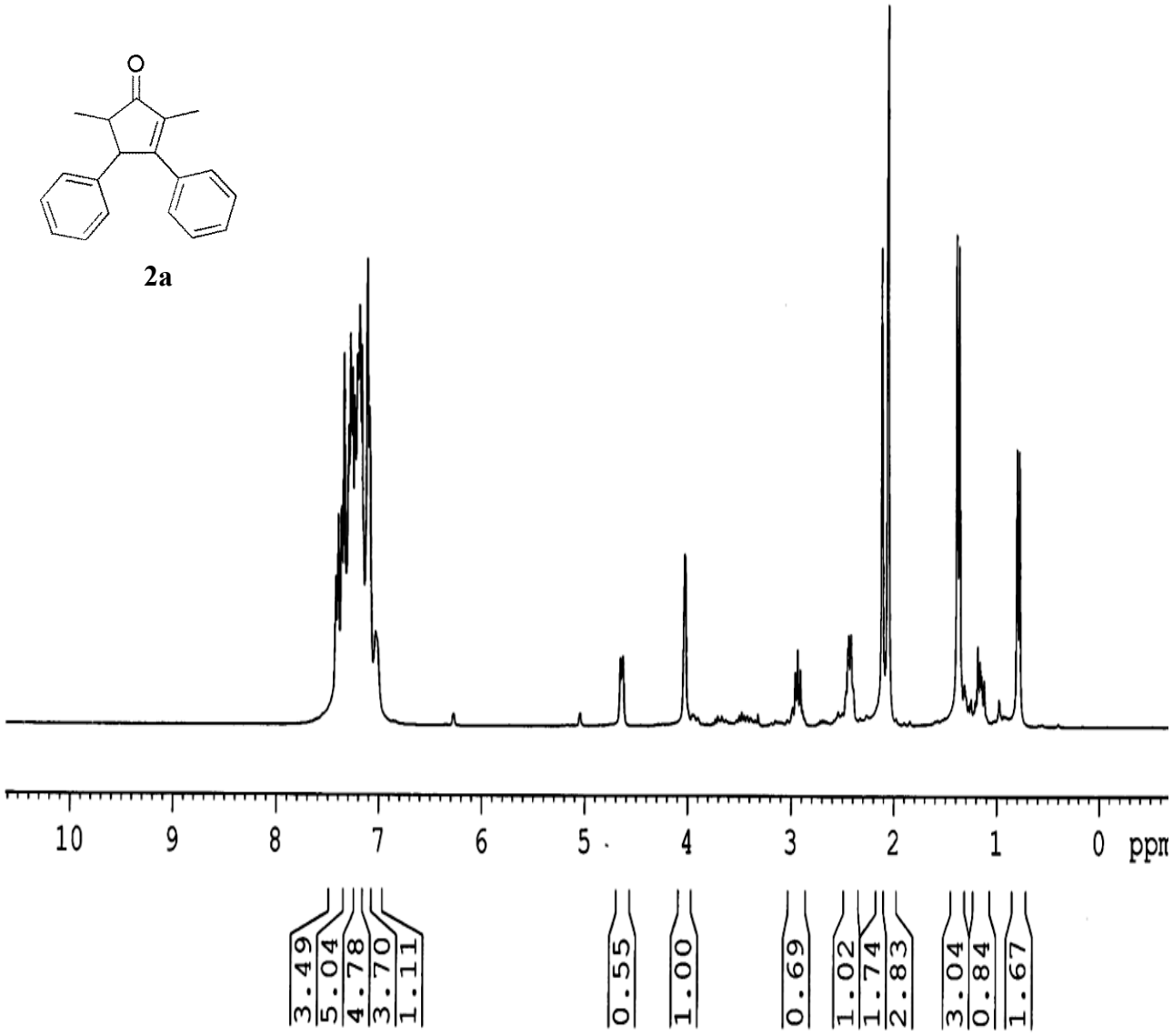


^{1}H NMR spectrum of **1f** ($CDCl_3$, 300 MHz)

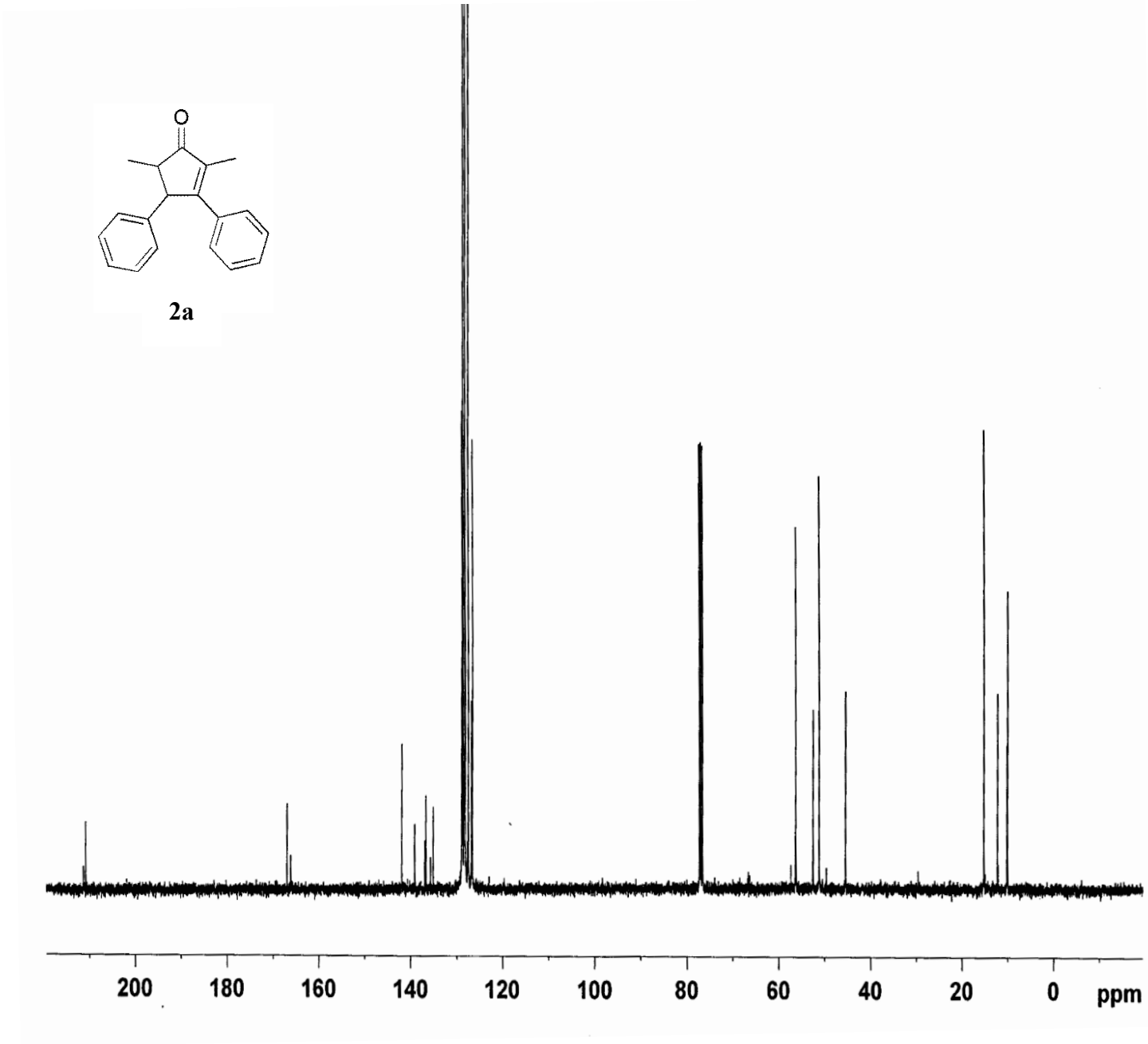


1f

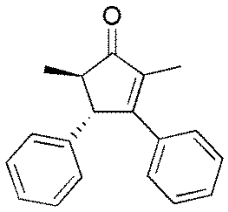
^{13}C NMR spectrum of **1f** ($CDCl_3$, 75 MHz)



^{1}H NMR spectrum of **2a** ($CDCl_3$, 300 MHz)

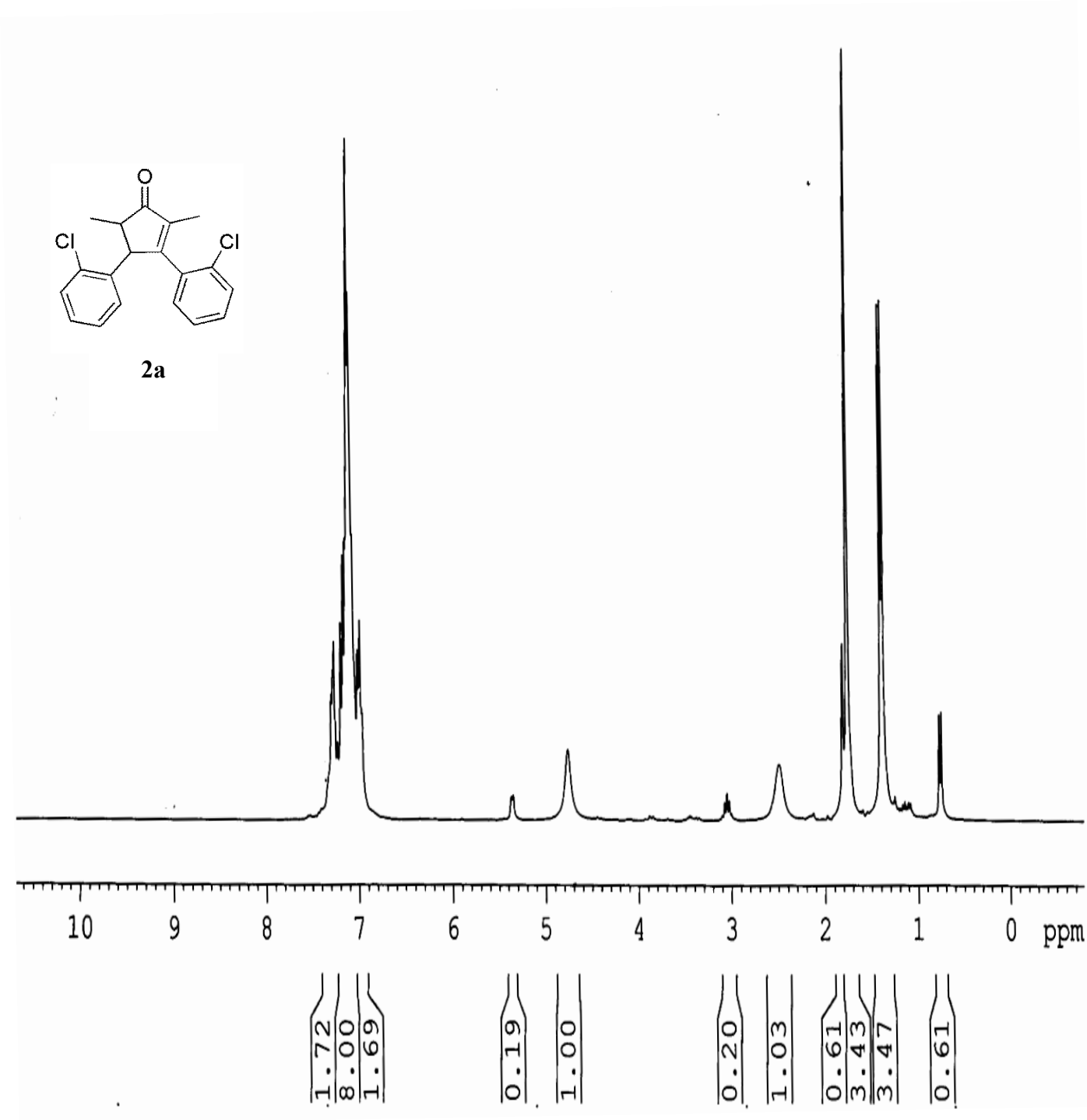


^{13}C NMR spectrum of **2a** ($CDCl_3$, 100 MHz)

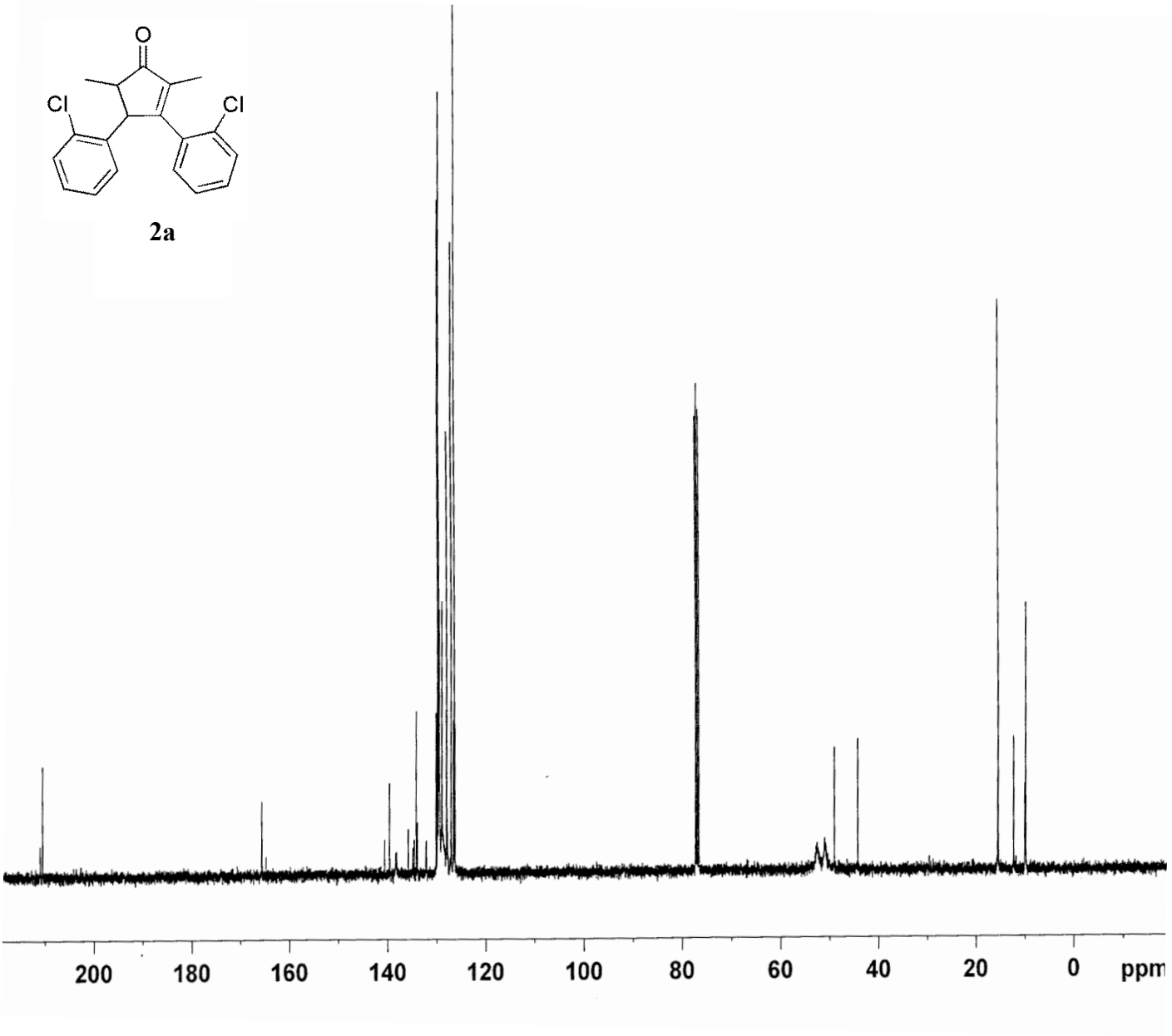


2a´

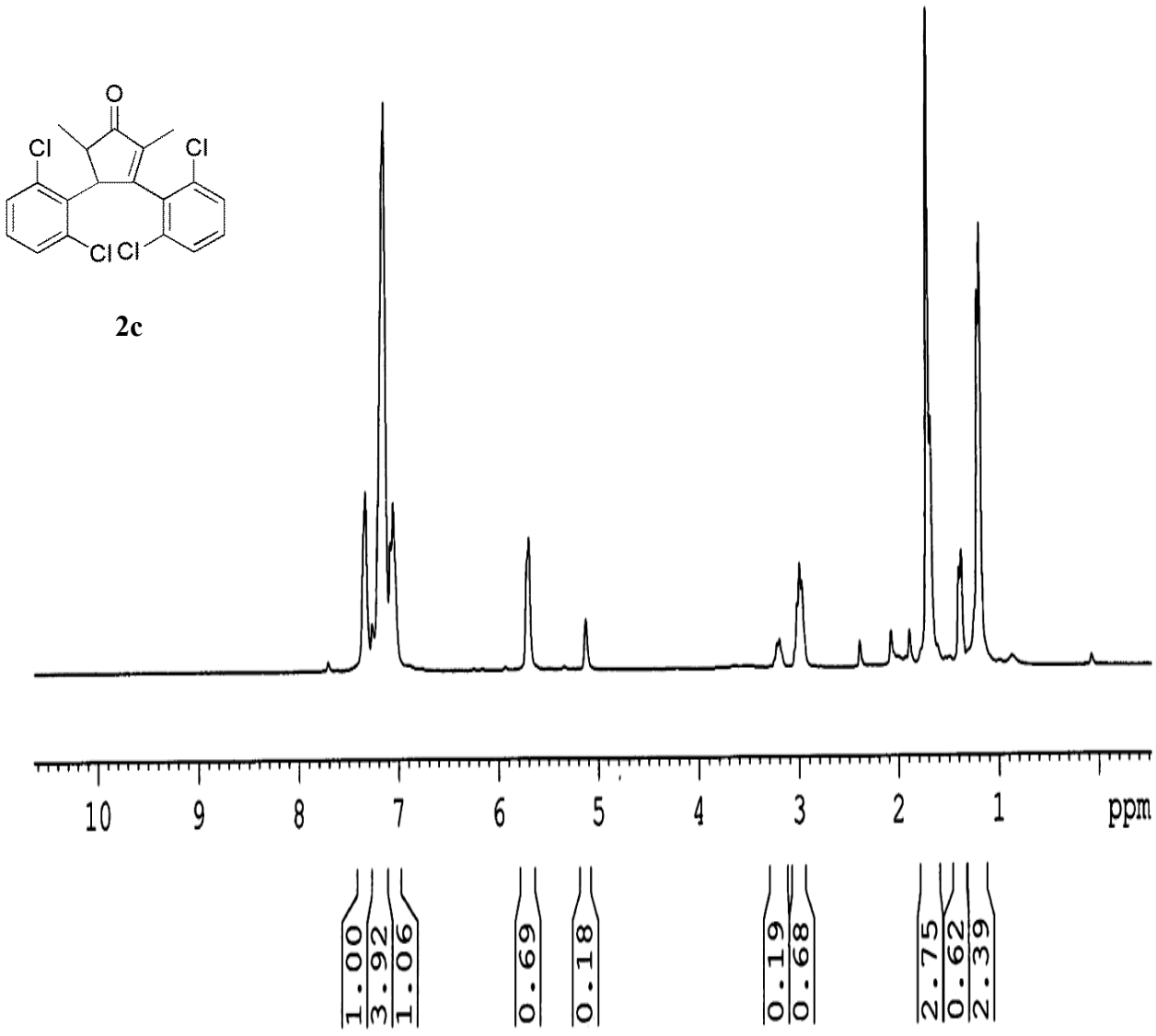
^{1}H NMR spectrum of **2a´** ($CDCl_3$, 300 MHz)



^{1}H NMR spectrum of **2b** ($CDCl_3$, 300 MHz)

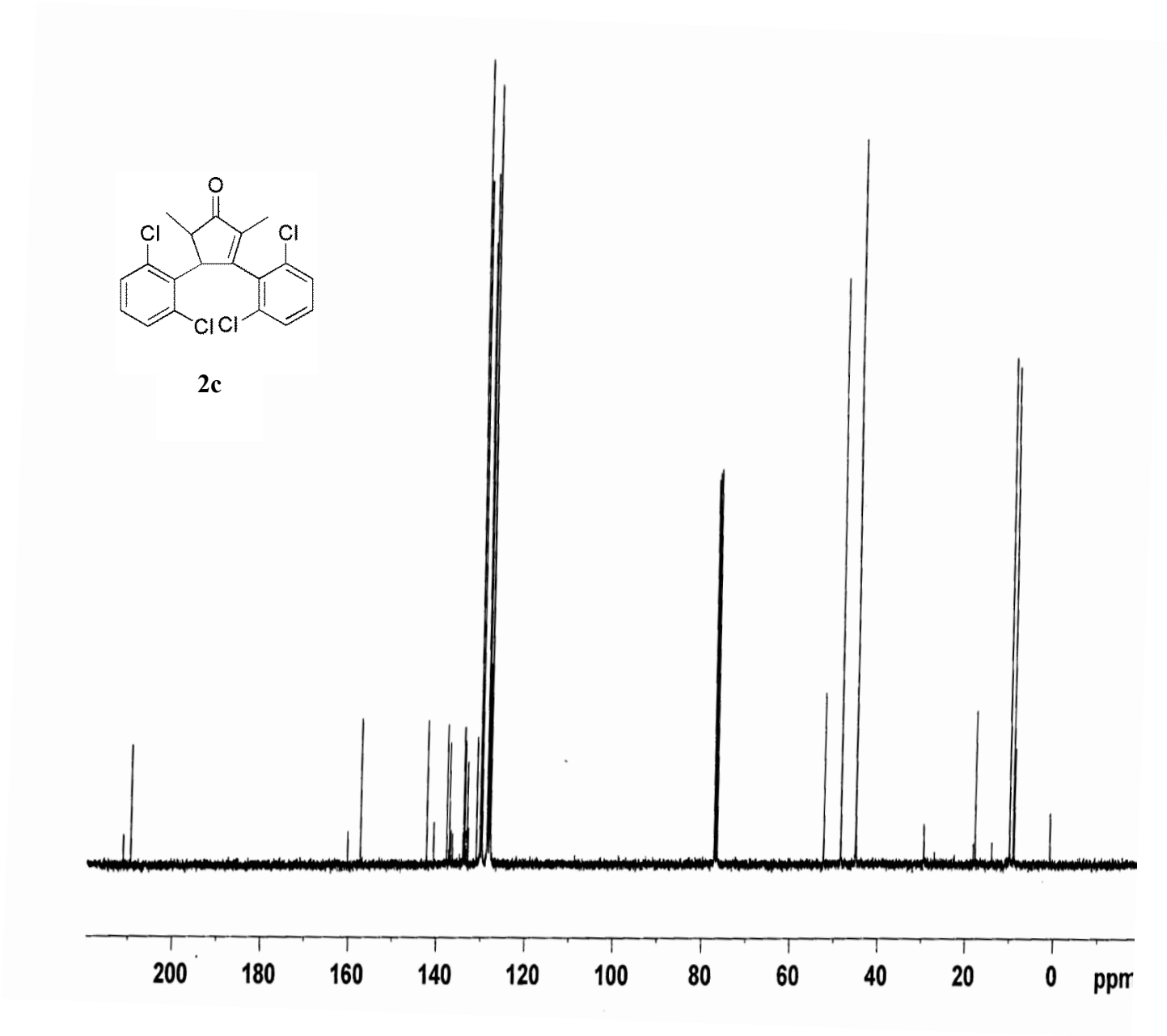


^{13}C NMR spectrum of **2a** ($CDCl_3$, 100 MHz)

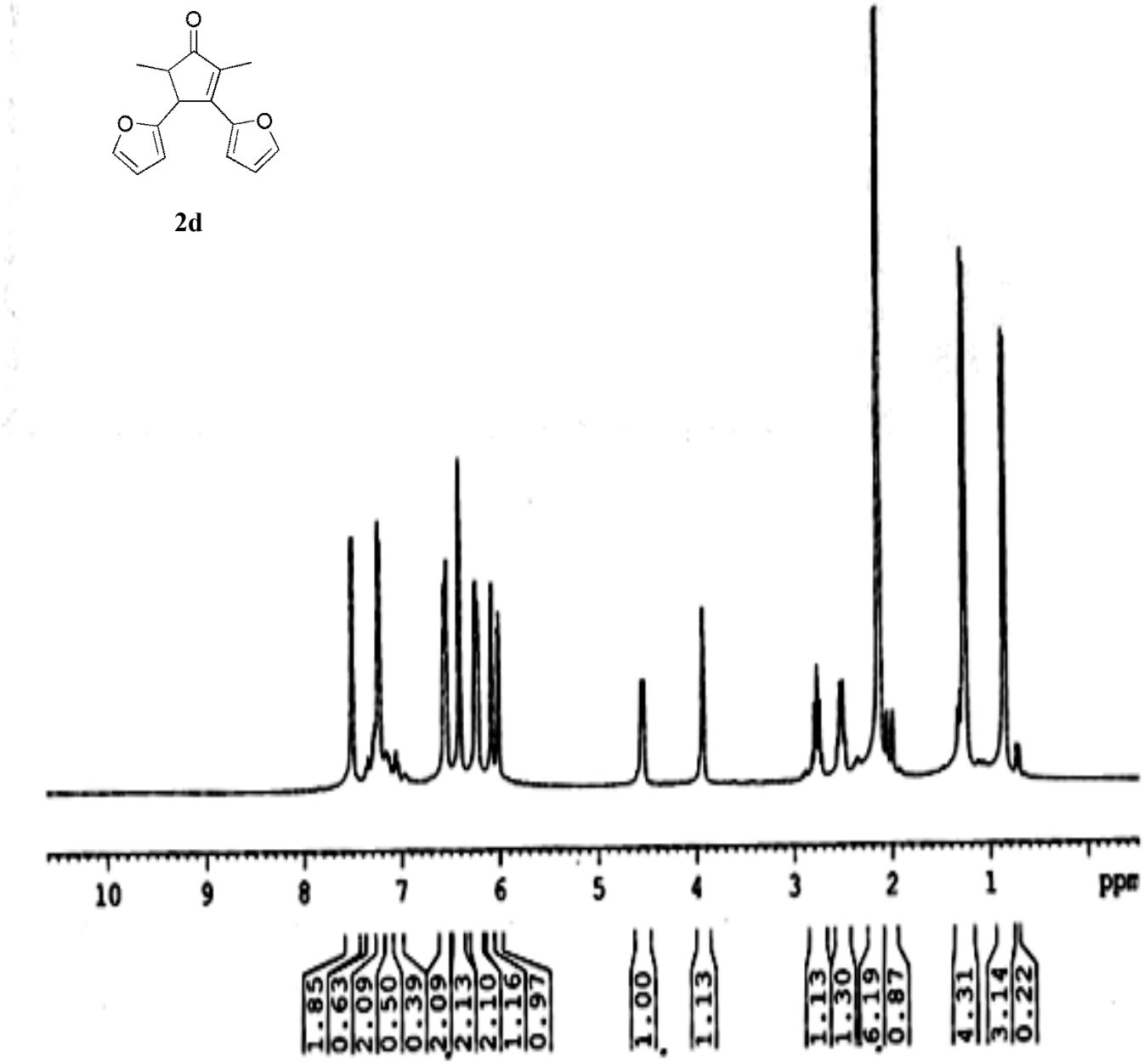


2c

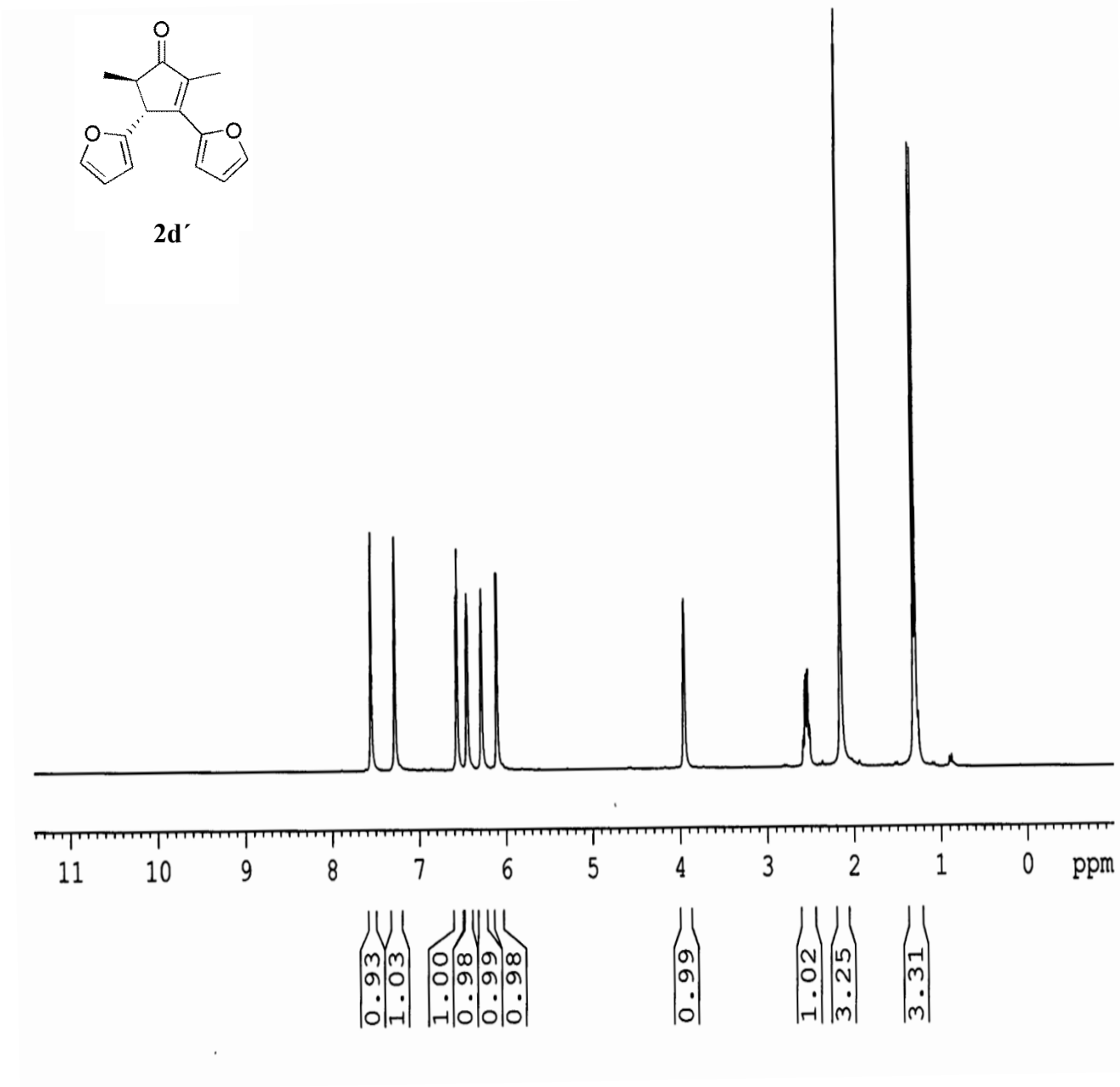
^{1}H NMR spectrum of **2c** ($CDCl_3$, 300 MHz)



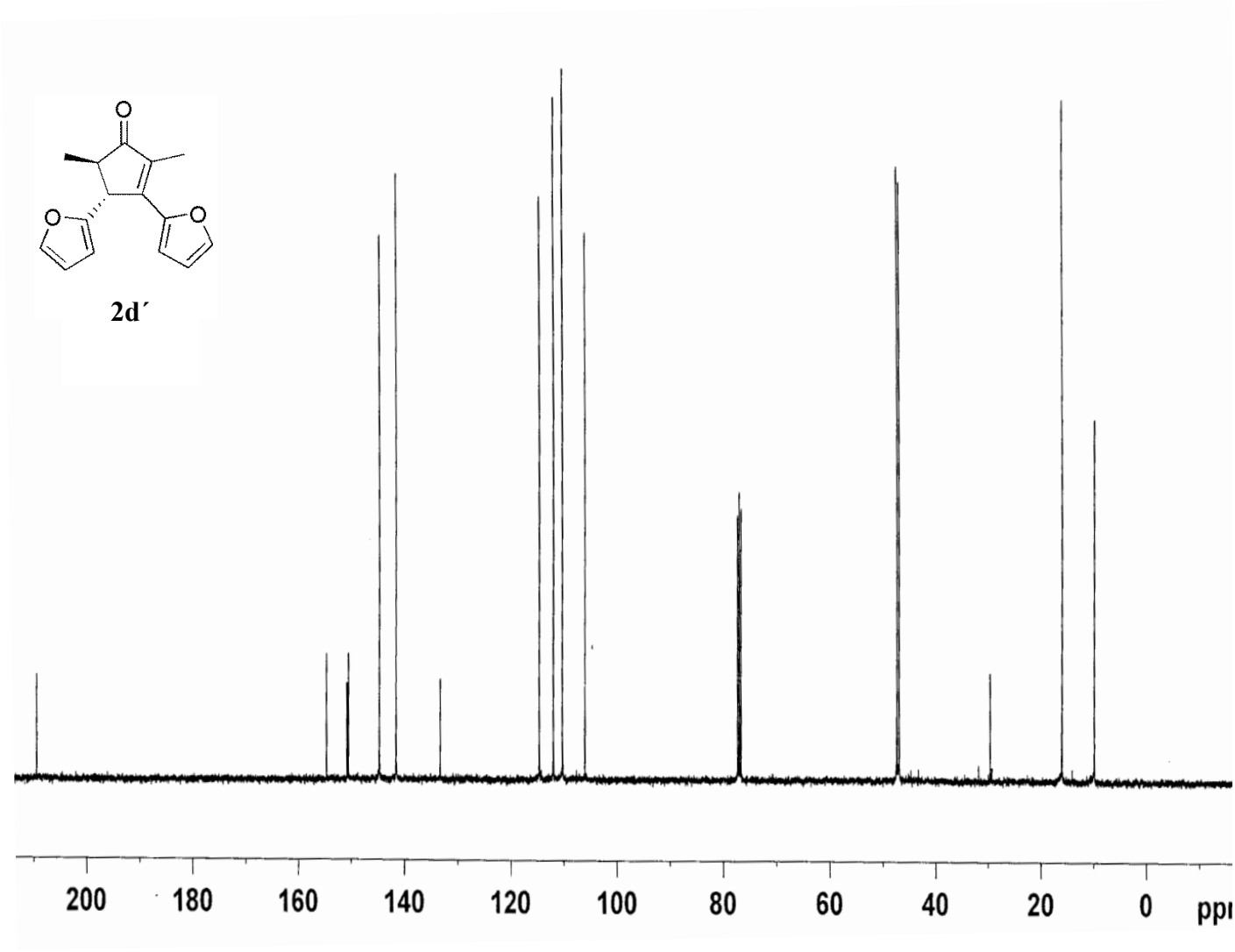
^{13}C NMR spectrum of **2b** ($CDCl_3$, 100 MHz)



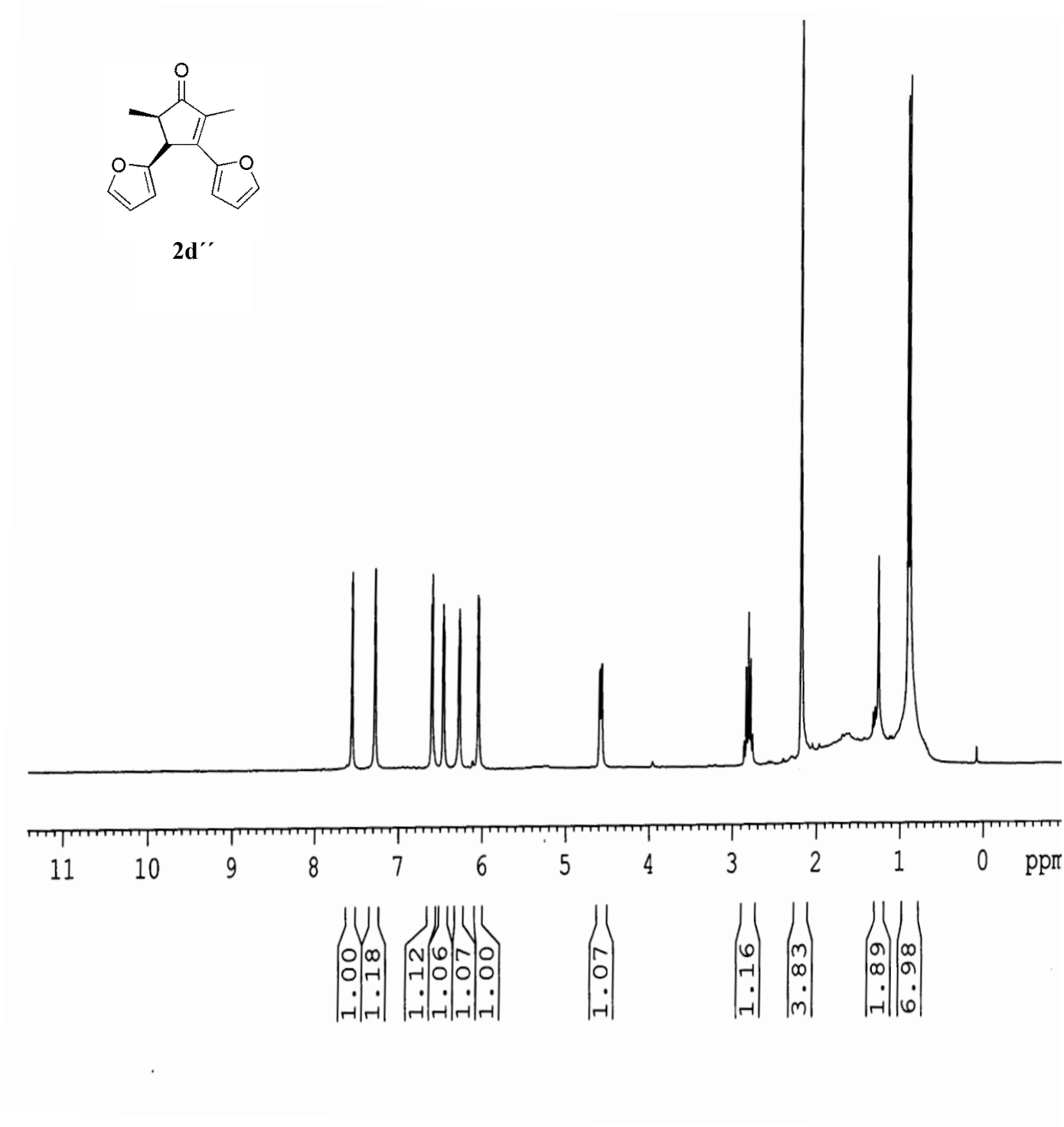
^{1}H NMR spectrum of **2d** ($CDCl_3$, 300 MHz)



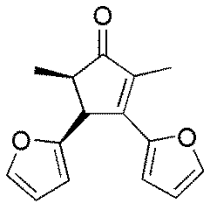
^{1}H NMR spectrum of **2d´** ($CDCl_3$, 300 MHz)



^{13}C NMR spectrum of **2d´** ($CDCl_3$, 100 MHz)

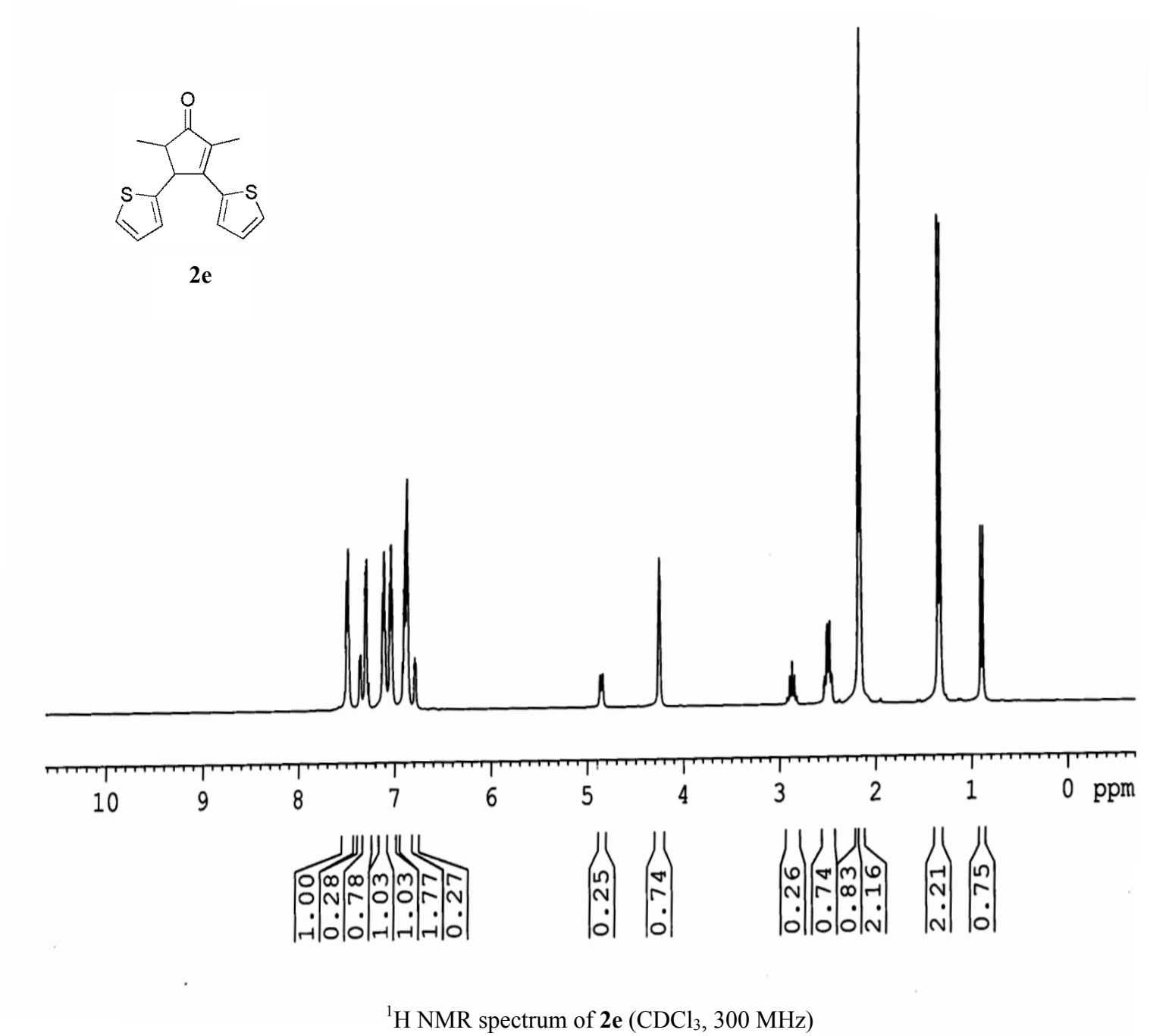


^{1}H NMR spectrum of **2d´´** ($CDCl_3$, 300 MHz)

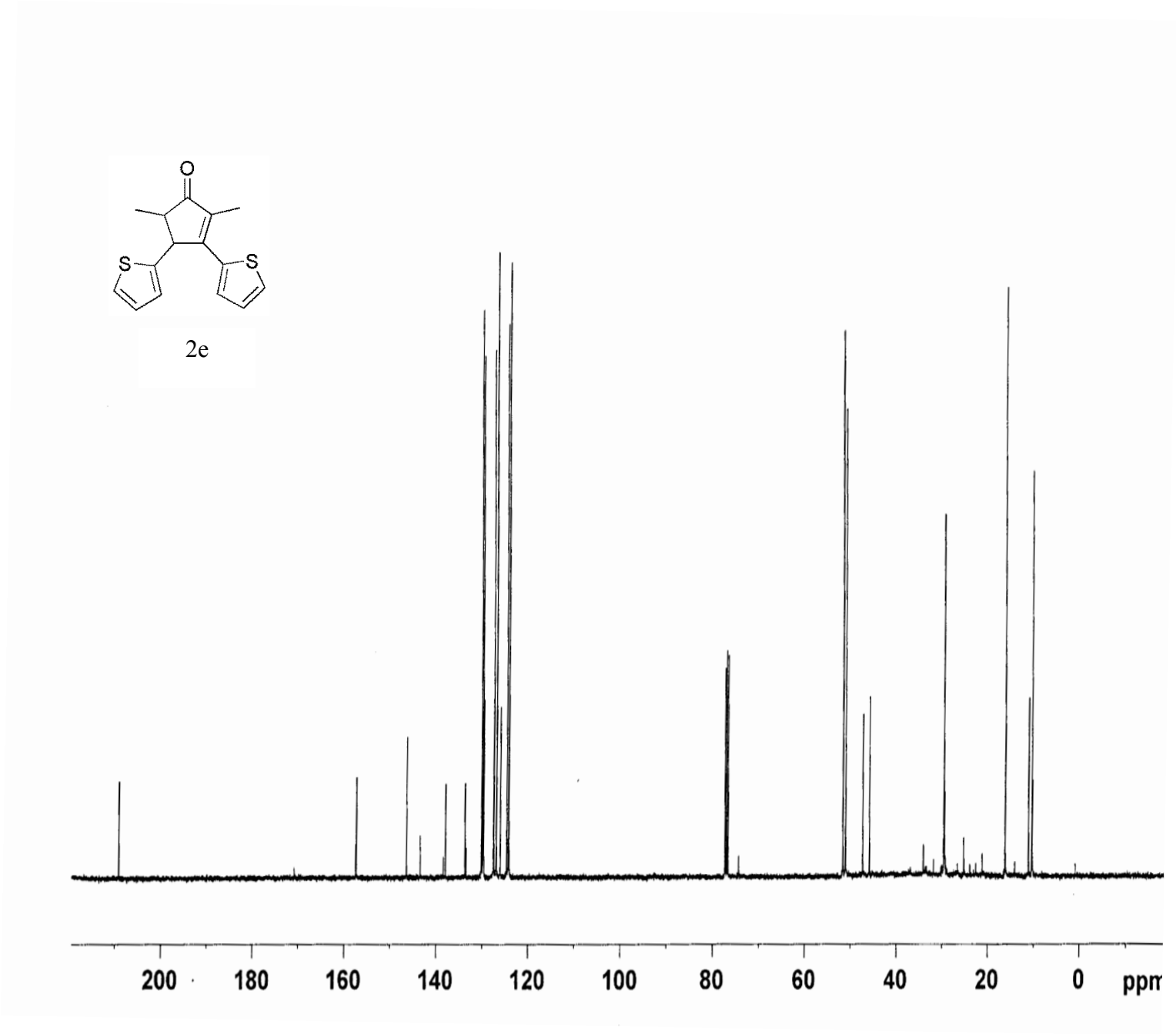


2d´´

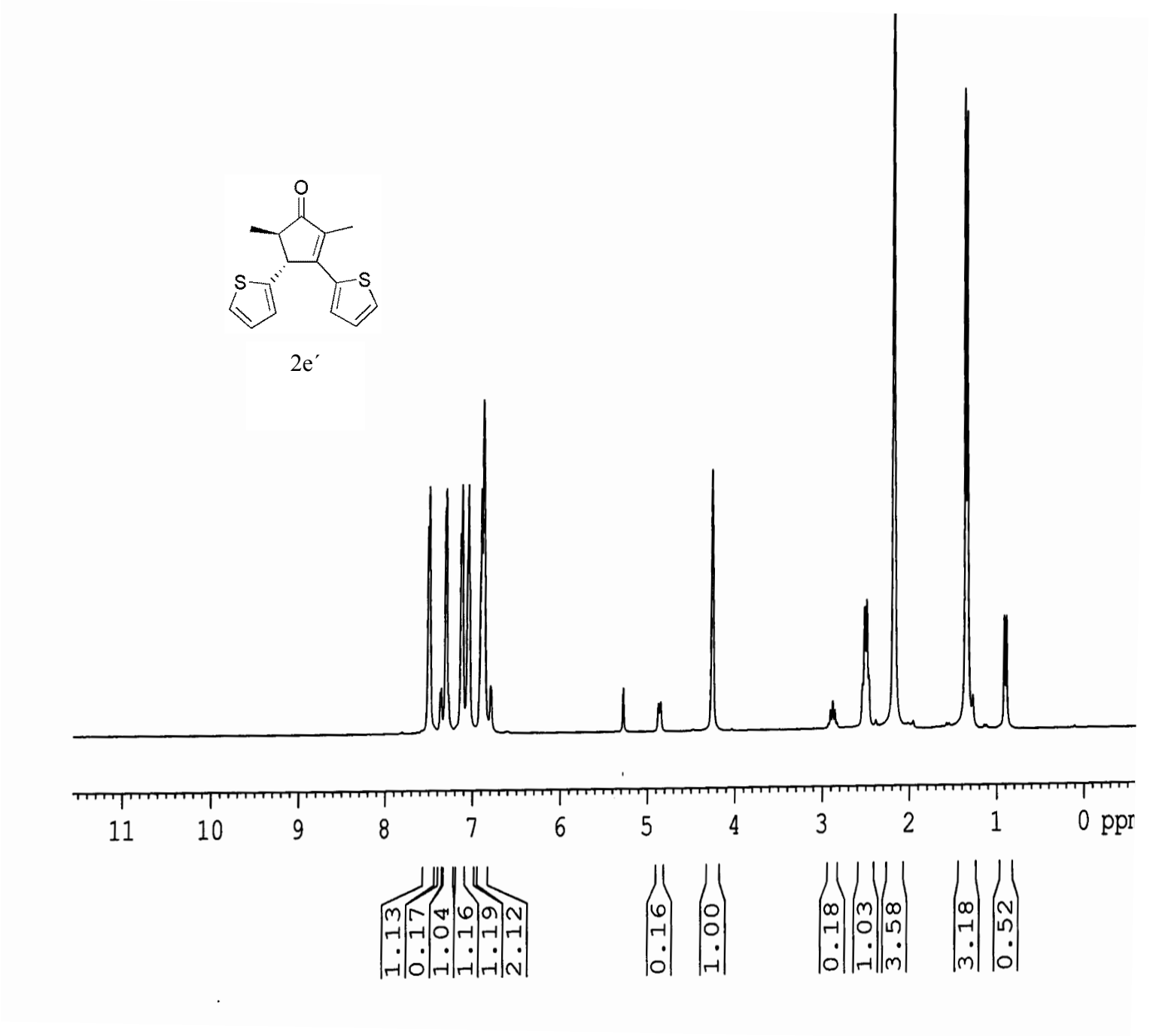
^{13}C NMR spectrum of **2d´** ($CDCl_3$, 100 MHz)



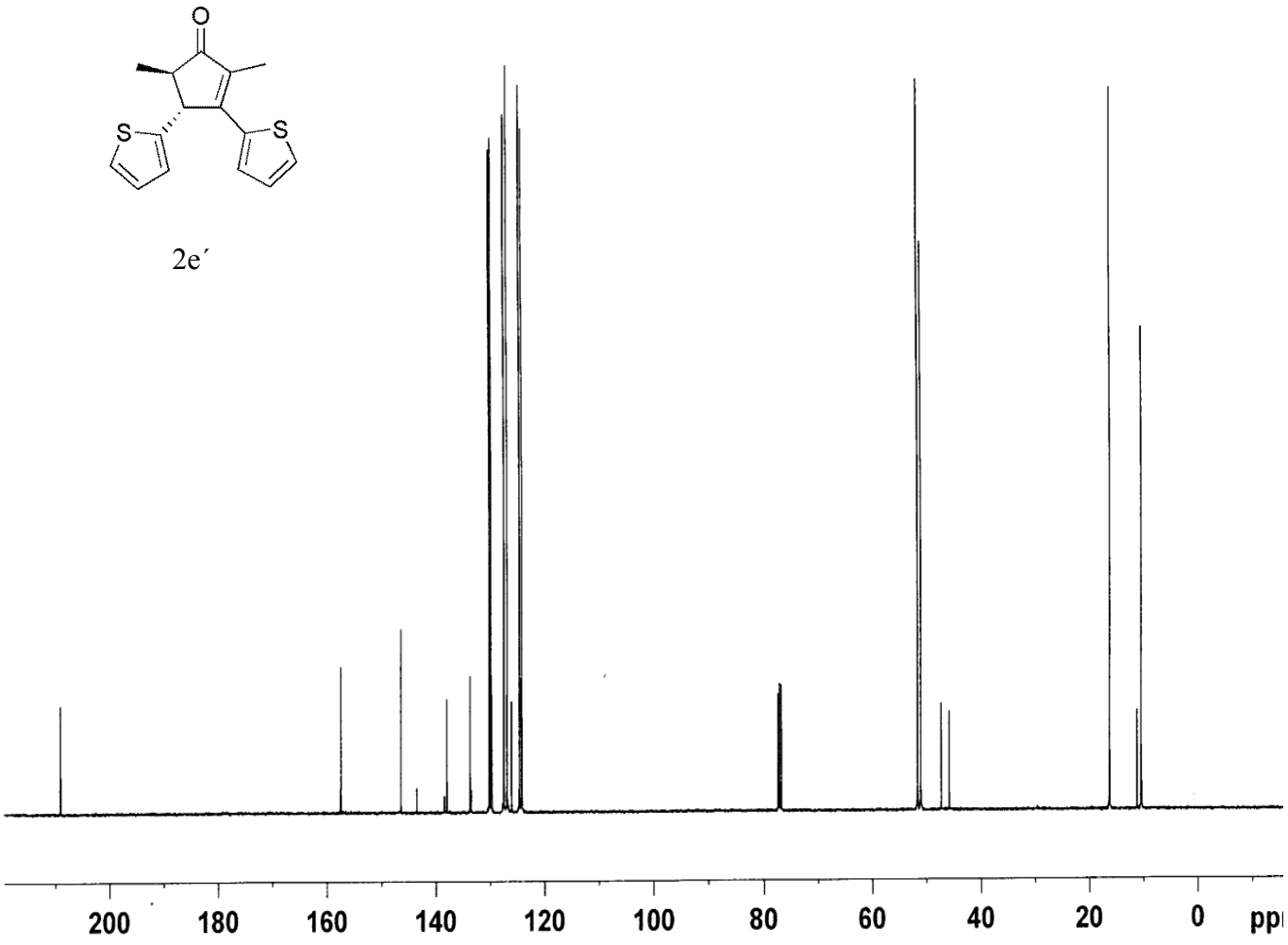
^{1}H NMR spectrum of **2e** ($CDCl_3$, 300 MHz)



^{13}C NMR spectrum of **2e** ($CDCl_3$, 100 MHz)

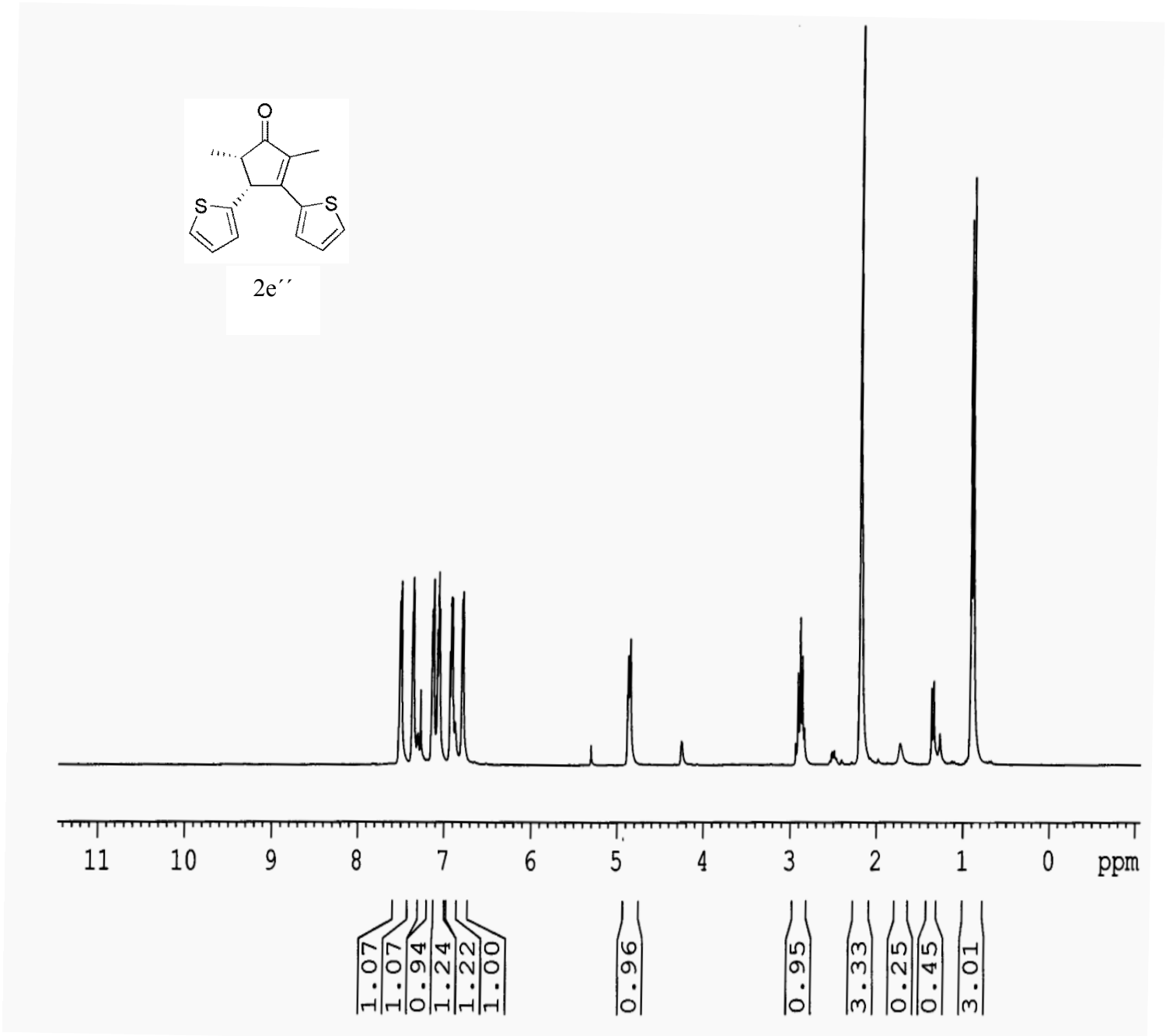


^{1}H NMR spectrum of **2e´** ($CDCl_3$, 300 MHz)

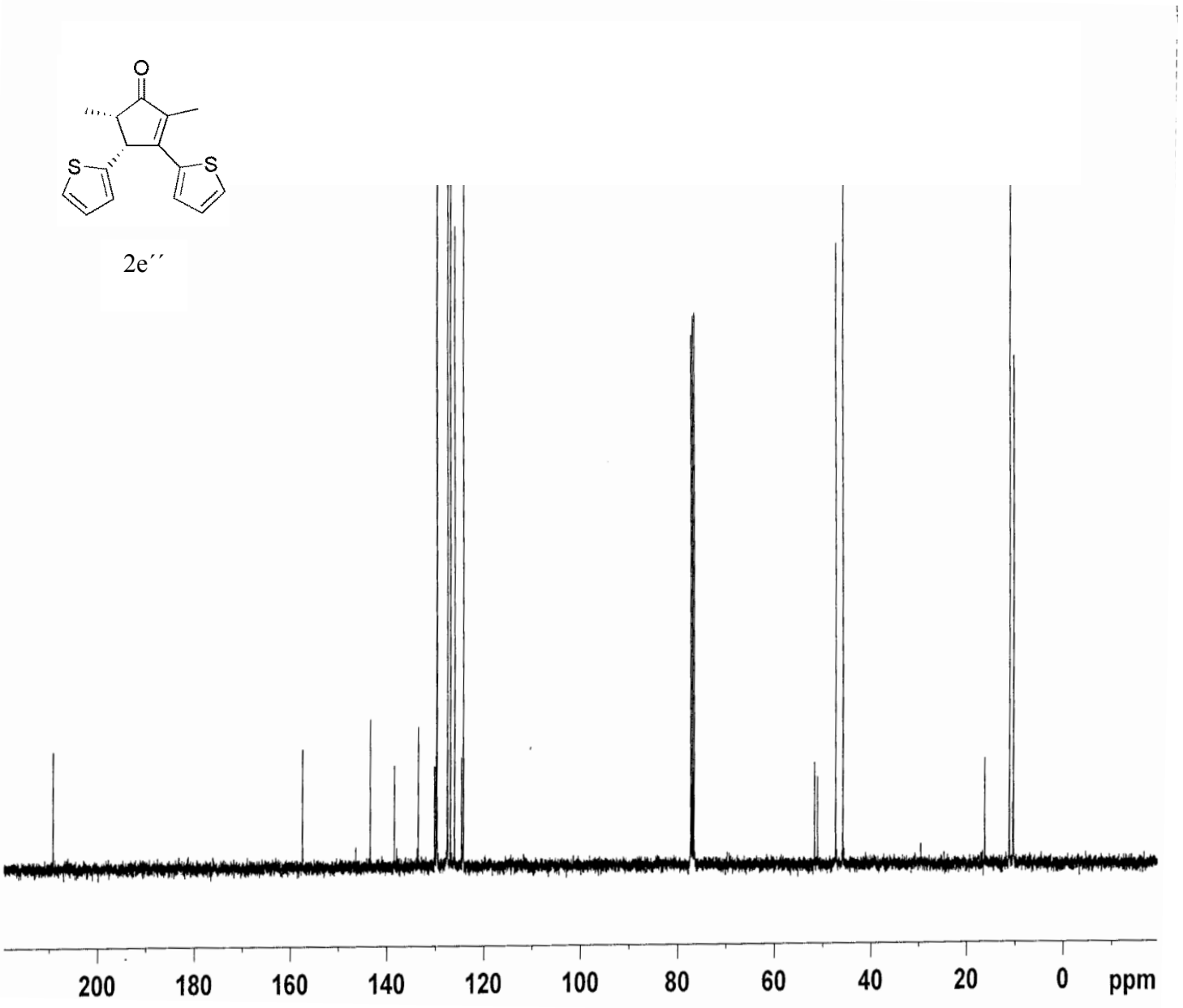


2e´

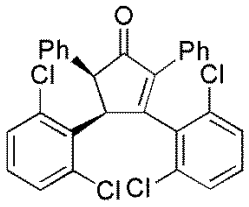
^{13}C NMR spectrum of **2e´** ($CDCl_3$, 100 MHz)



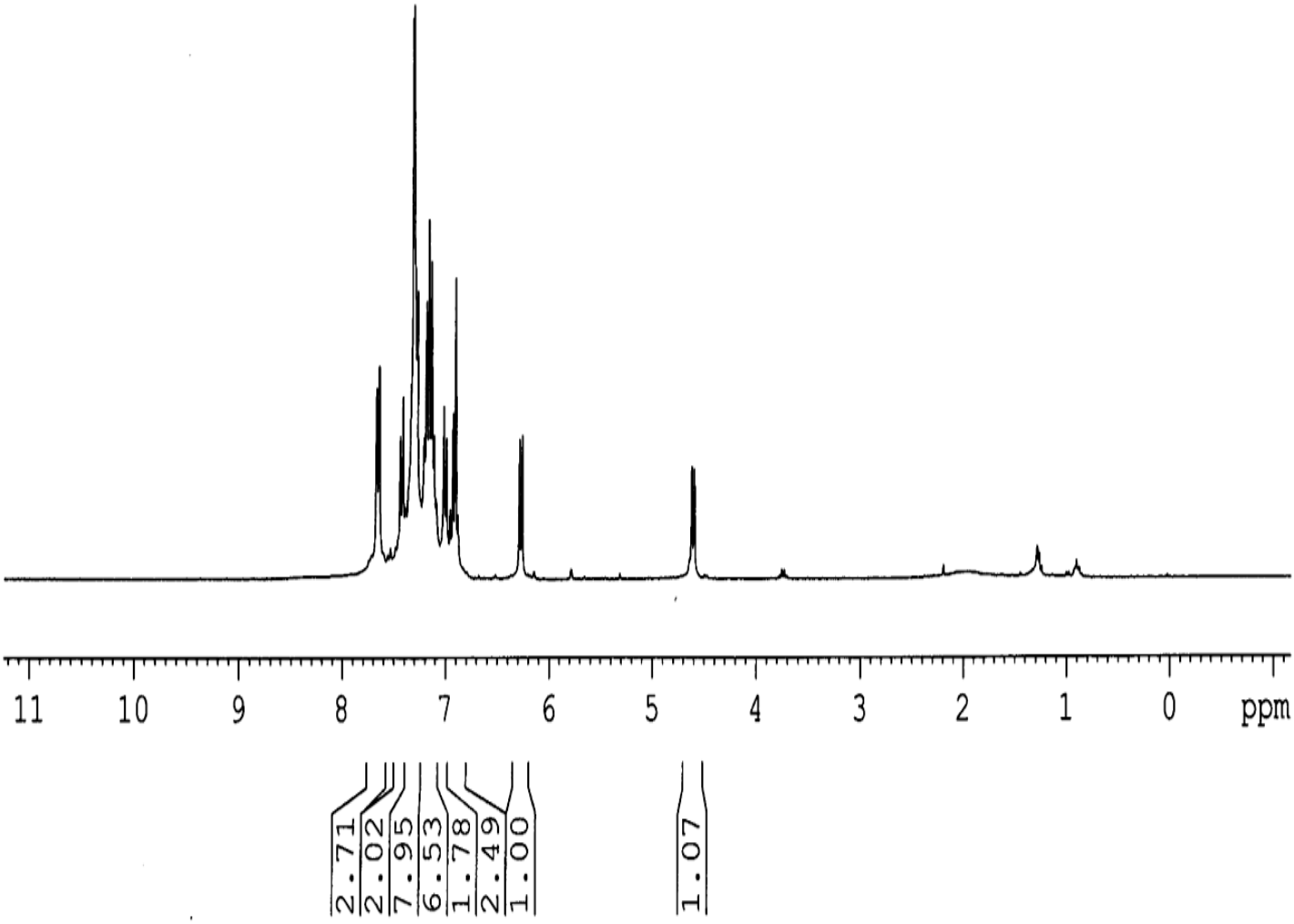
^{1}H NMR spectrum of **2e´´** ($CDCl_3$, 300 MHz)



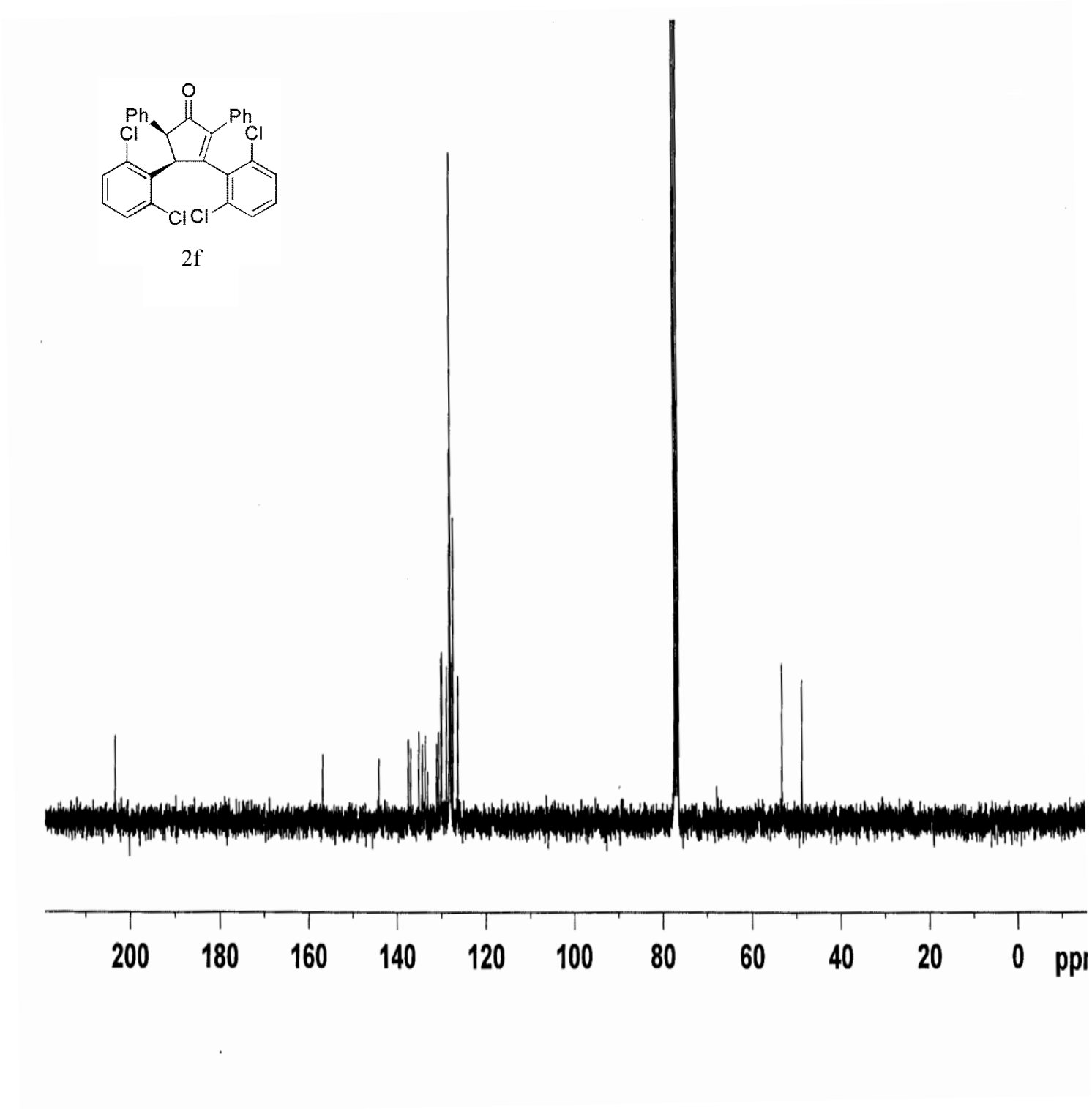
^{13}C NMR spectrum of **2e´´** ($CDCl_3$, 100 MHz)



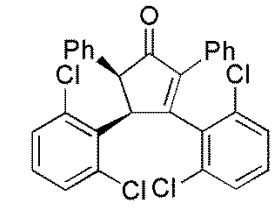
2f



^{1}H NMR spectrum of **2f** ($CDCl_3$, 300 MHz)

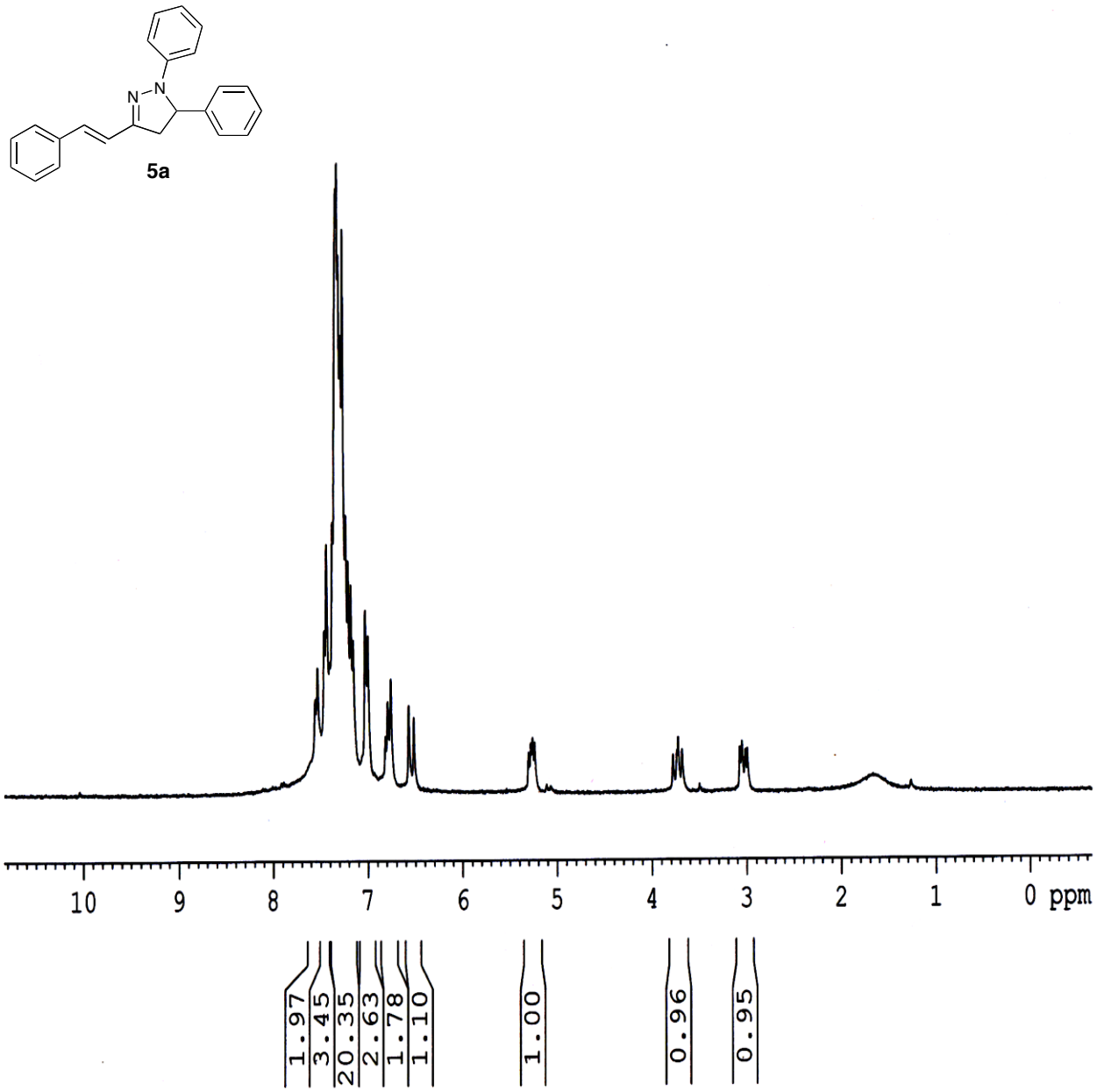


^{13}C NMR spectrum of **2f** ($CDCl_3$, 75 MHz)

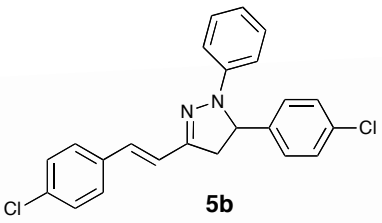


2f

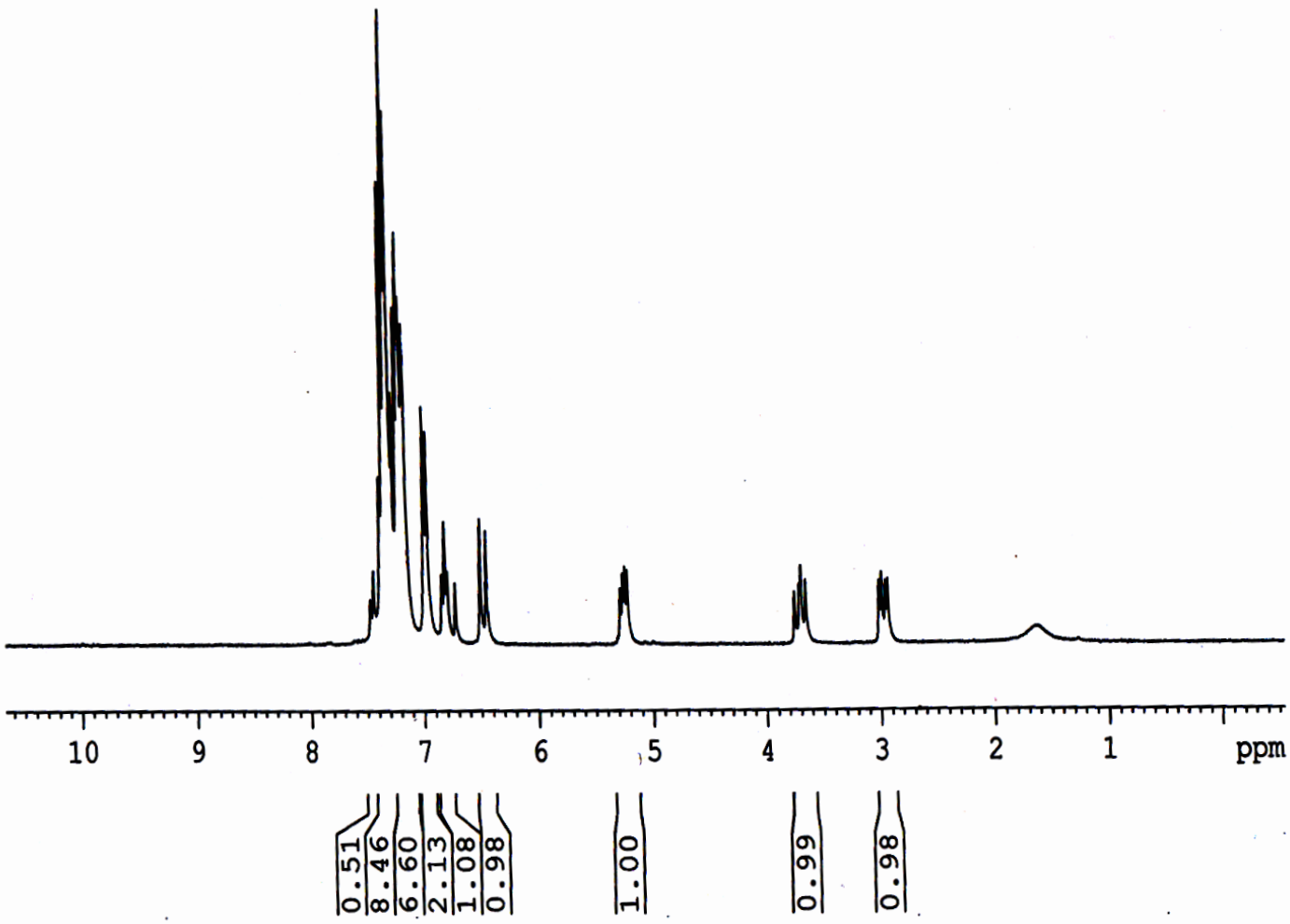
NOE spectrum of **2f** ($CDCl_3$, 300 MHz)



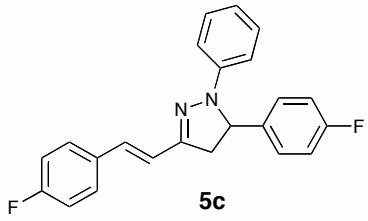
^{1}H NMR spectrum of **5a** ($CDCl_3$, 300 MHz)



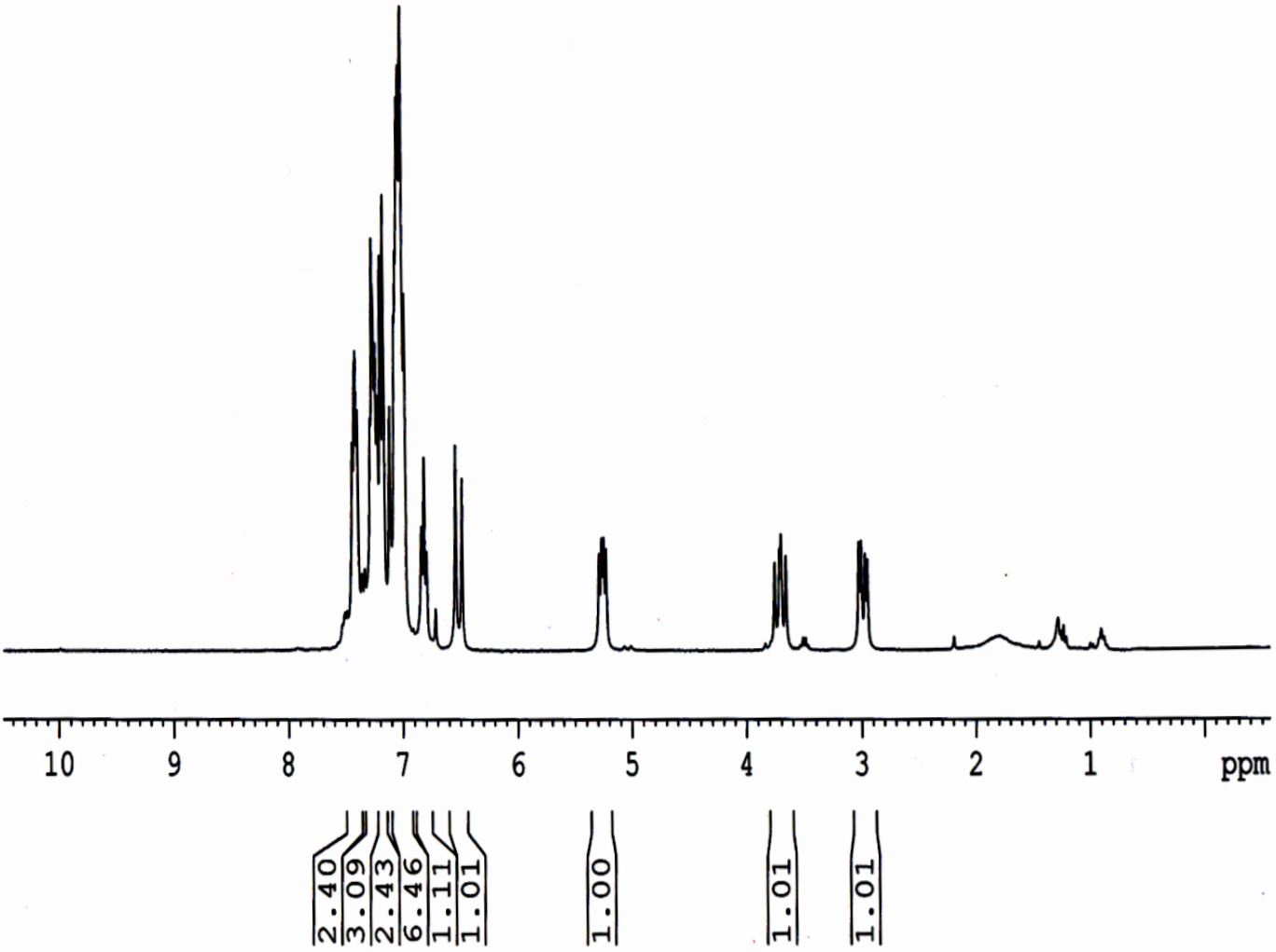
5b



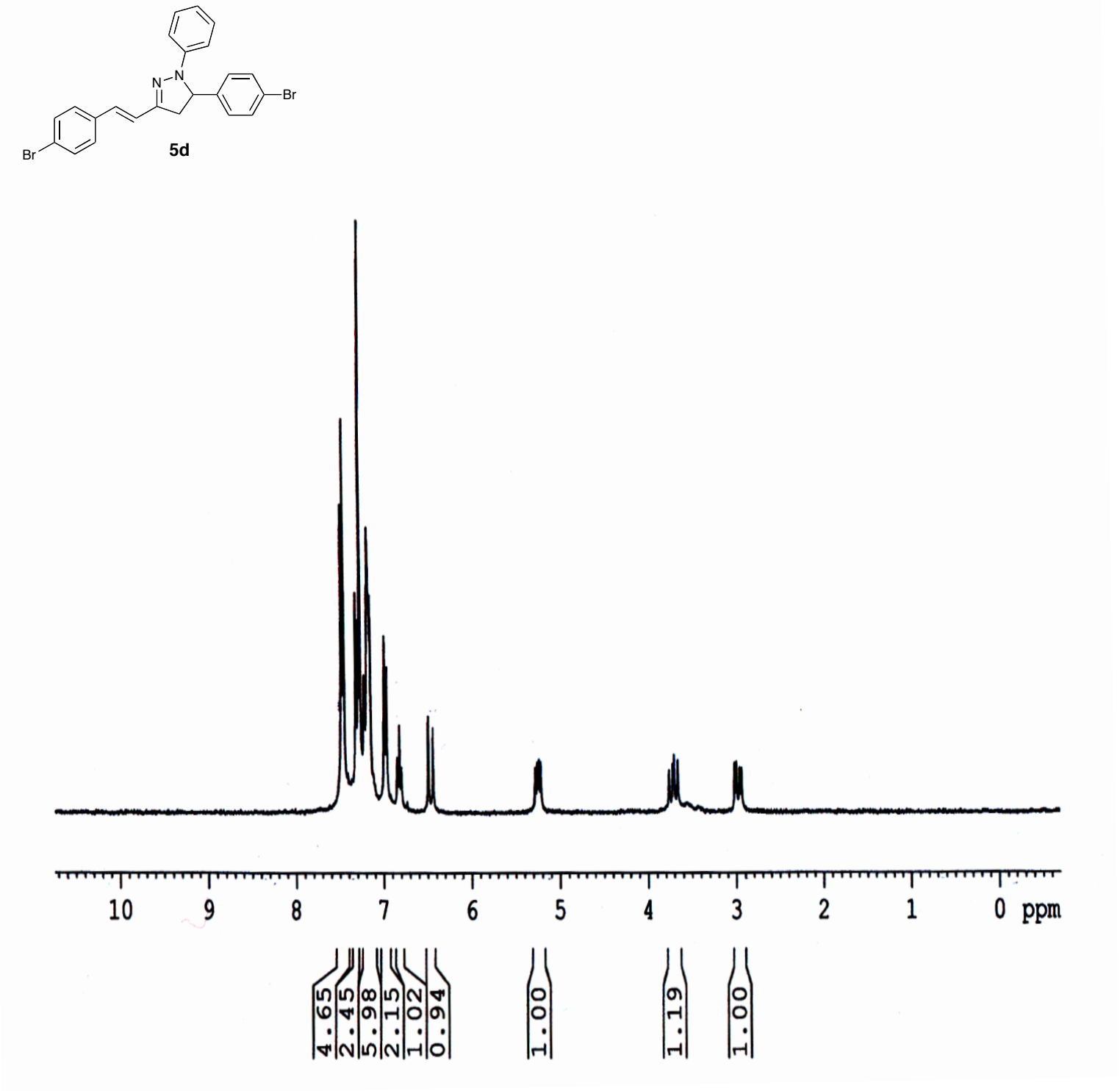
^{1}H NMR spectrum of **5b** ($CDCl_3$, 300 MHz)



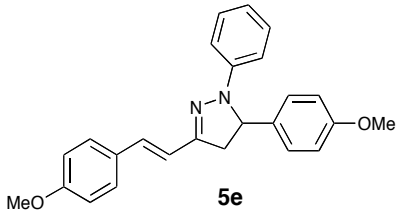
5c



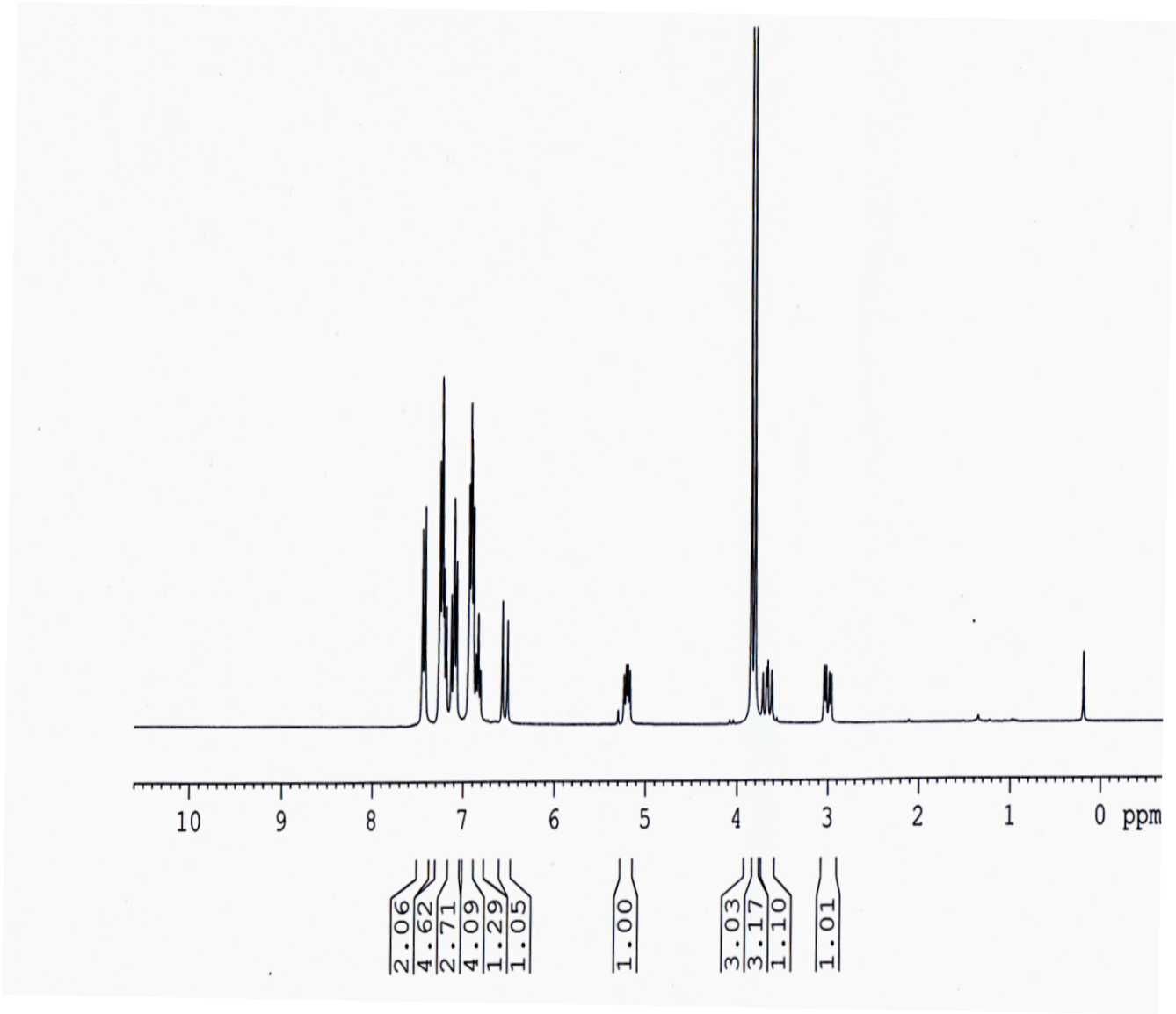
^{1}H NMR spectrum of **5c** ($CDCl_3$, 300 MHz)



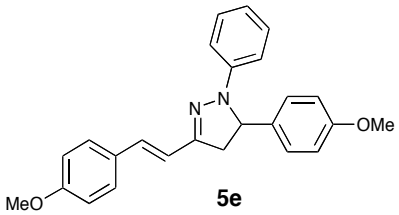
^{1}H NMR spectrum of **5d** ($CDCl_3$, 300 MHz)



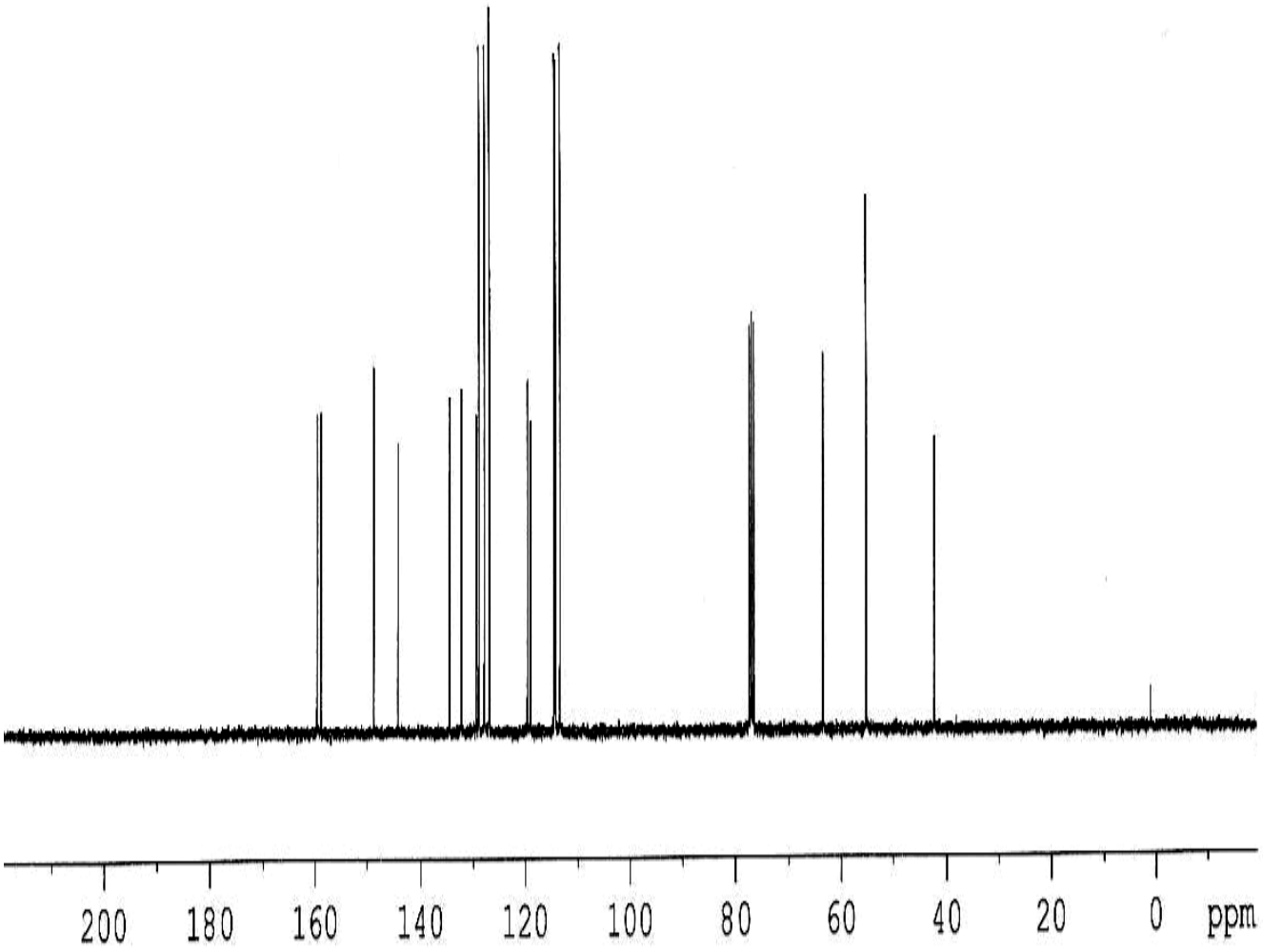
5e



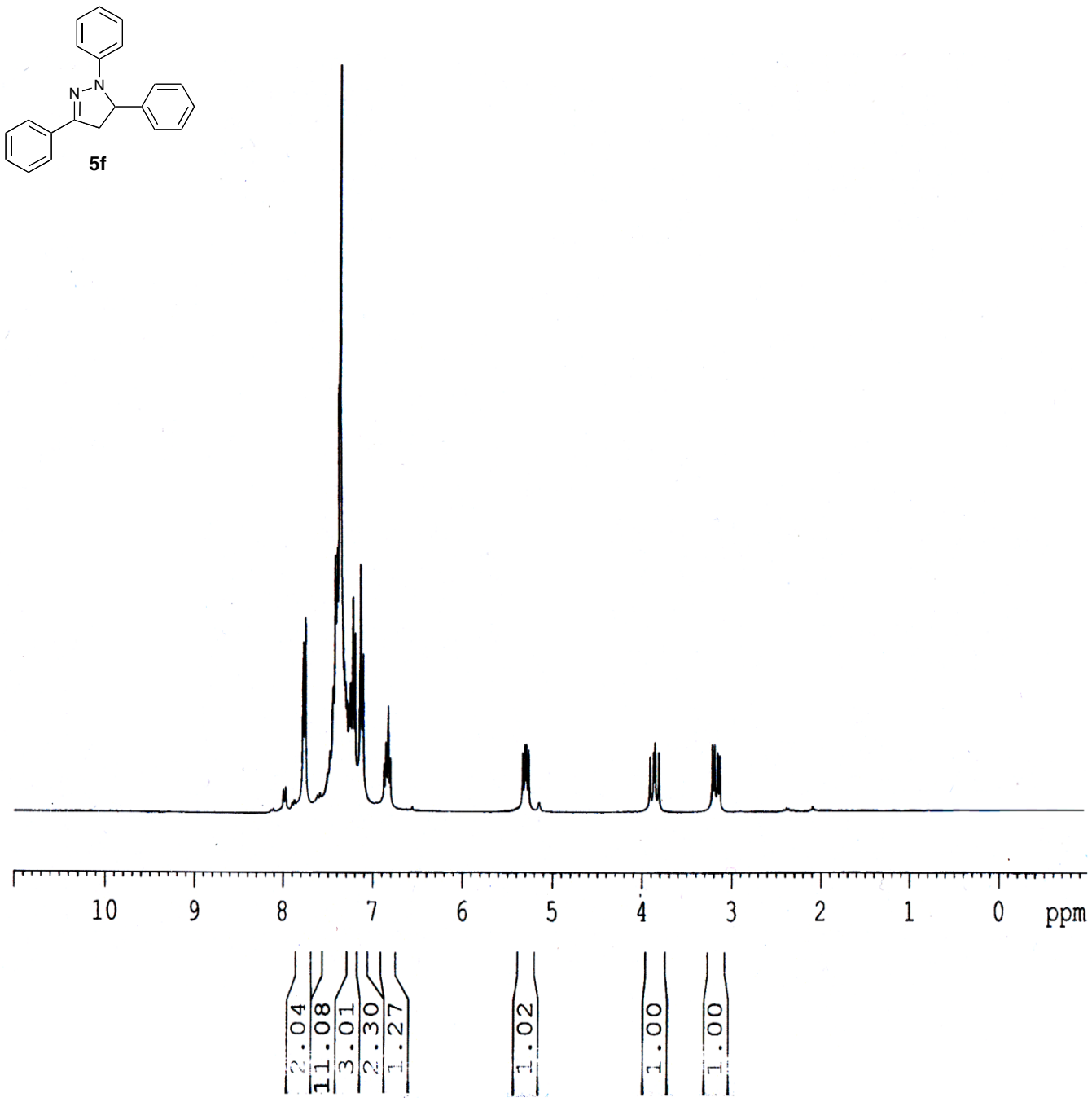
^{1}H NMR spectrum of **5e** ($CDCl_3$, 300 MHz)



5e



^{13}C NMR spectrum of **5e** ($CDCl_3$, 75 MHz)



^{1}H NMR spectrum of **5f** ($CDCl_3$, 300 MHz)