Supporting Information

Consecutive Palladium-Catalyzed Hiyama–Heck Reactions in Aqueous Media Under Ligand-Free Conditions

Álvaro Gordillo, Ernesto de Jesús and Carmen López-Mardomingo

Departamento de Química Orgánica and Departamento de Química Inorgánica, Campus Universitario, Universidad de Alcalá. 28871 Alcalá de Henares (Madrid), Spain
ernesto.dejesus@uah.es

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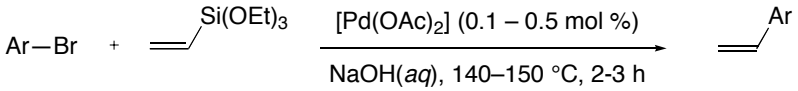
General experimental procedures

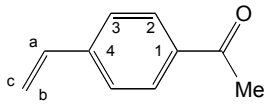
All the reactions were carried out in Ace pressure tubes in air, unless otherwise stated. Deionized water (type II quality) was obtained with a Millipore Elix 10 UV Water Purification System. All other reagents, catalysts, and solvents (synthesis grade) were obtained from commercial sources and used as received. Column chromatography was carried out on silica gel 60 (particle size 0.04–0.063 mm) from Fluka and thin layer chromatography (TLC) on ALUGRAM SIL G/UV$_{254}$ from Macherey–Nagel. ^{1}H and ^{13}C NMR spectra were recorded with Varian Mercury 300, Unity 300, or Unity 500 Plus spectrometers. Chemical shifts (δ, ppm) are quoted relative to SiMe$_4$ and were measured by internal referencing to the deuterated solvent (^{13}C or residual ^{1}H resonances). Coupling constants (J) are given in hertz. When required, two-dimensional ^{1}H-^{13}C HMQC, ^{1}H-^{13}C gHMBC, or ^{1}H-^{1}H TOCSY experiments were carried out for the unequivocal assignment of ^{1}H and ^{13}C resonances. IR spectra were recorded in KBr pellets (solids) or between NaCl crystal windows (liquids) with a Perkin Elmer FT-IR Spectrum 2000 spectrometer. Data are given in cm^{-1}. Melting points were measured with a GallenKamp apparatus. The Analytical Services of the Universidad de Alcalá recorded the EI and ESI mass spectra with a Hewlett-Packard 5988A and an Agilent 6210 LC/MS TOF spectrometer, respectively. Elemental analyses were performed in duplicate by the above Services with a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of vinylarenes (Table 1)



In a 35-mL Ace pressure tube, triethoxy(vinyl)silane (see quantities below) was added to a 0.5 M sodium hydroxide solution in water containing, where appropriate, 20% (w/w) of PEG 2000 and the mixture was stirred vigorously for 5 min at room temperature. The aryl bromide reagent and the palladium acetate catalyst were subsequently added and the tube was placed in a silicone bath previously warmed to the reaction temperature. Vigorous stirring was maintained during the reaction time indicated below. The reaction mixture was then allowed to cool to room temperature and extracted with dichloromethane, ethyl acetate or diethyl ether (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and, after filtration, the solvent eliminated on a rotary evaporator connected to a water aspirator pump. The products were isolated and purified from this residue as described below.

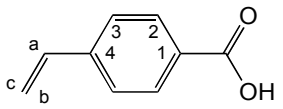
(4-Vinylphenyl)ethanone (1).[1] Following the above procedure, triethoxy(vinyl)silane (1.17 mL, 5.38 mmol), a 0.50 M solution of sodium hydroxide in water (13.50 mL, 6.75 mmol), PEG 2000 (2.7 g), 1-(4-bromophenyl)ethanone (0.2742 g, 1.35 mmol), and palladium(II) acetate (0.3 mg, 1.4 μmol) were warmed for 3 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 6:1 (R_f = 0.30) on silica gel to give **1** as a colorless oil (0.1878 g, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.58 (s, 3 H; CH_3), 5.38 (d, $^3J_{c,a}$ = 11.0, 1 H; H^c), 5.86 (d, $^3J_{b,a}$ = 17.6, 1 H; H^b), 6.74 (dd, $^3J_{a,b}$ = 17.6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 7.46 (d, $^3J_{3,2}$ = 8.2, 2 H; H^3), 7.90 (d, $^3J_{2,3}$ = 8.2, 2 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 26.6 (CH_3), 116.7 (CH_2), 126.2 (C^3), 128.6 (C^2), 135.9 (CH), 136.2 (C^1), 142.0 (C^4), 197.5 (CO). IR (NaCl): ν 3088 w, 3007 m, 2927 w, 1682 s, 1629 m, 1605 s, 1561 m, 1426 m, 1403 s, 1358 s, 1307 m, 1267 s, 1181 m, 1119 m, 1076 w, 1013 w, 991 m, 957 m, 918 m, 846 s, 733 m and 668 m. EI-MS (70 eV): *m/z* (%) 146 (42) [M$^+$], 131 (100) [M$^+$ – CH_3], 103 (45) [M$^+$ – COMe], 77 (35) [Ph$^+$].



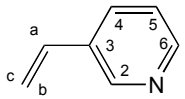
4-Vinylbenzoic acid (2).[2] Following the above procedure, triethoxy(vinyl)silane (1.30 mL, 5.98 mmol), a 0.50 M solution of sodium hydroxide in water (18.0 mL, 9.00 mmol), 4-bromobenzoic acid (0.3077 g, 1.50 mmol), and palladium(II) acetate (1.0 mg, 4.5 μmol) were warmed for 3 h at 140 ºC. Before extraction with diethyl ether, 3 M hydrochloric acid was dropwise added to the solution to reach an acid pH. After extraction, the crude product was purified by flash chromatography with hexane/ethyl acetate 1:10 (R_f = 0.47) on silica gel to give **2** as a white solid (0.2169 g, 97%). M. p.: 143–144 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.40 (d, $^3J_{c,a}$ = 11.0, 1 H; H^c), 5.88 (d, $^3J_{b,a}$ = 17.6, 1 H; H^b), 6.76 (dd, $^3J_{a,b}$ = 17.6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 7.48 (d, $^3J_{3,2}$ = 8.4, 2 H; H^3), 8.06 (d, $^3J_{2,3}$ = 8.4, 2 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 117.0 (CH_2), 126.2 (C^3), 128.2 (C^1), 130.5 (C^2), 135.9 (CH), 142.8 (C^4), 170.6 (COOH). IR (KBr): ν 2500-3300 br, 1679 s,

[1] S. E. Denmark, C. R. Butler, *Org. Lett.* **2006**, *8*, 63-66.
[2] Identical to authentic material (Aldrich).

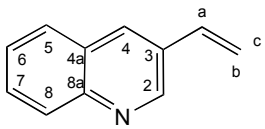
1608 m, 1566 m, 1426 s, 1323 s, 1290 s, 1182 m, 1128 w, 988 w, 908 m, 859 m, 783 m, 755 m, 710 m. EI-MS (70 eV): *m/z* (%) 148 (96) [M^+], 131 (100) [M^+ – OH], 103 (59) [M^+ – COOH], 77 (49) [Ph^+].



3-Vinylpyridine (3).[3] Following the above procedure, triethoxy(vinyl)silane (1.55 mL, 7.13 mmol), a 0.50 M solution of sodium hydroxide in water (17.80 mL, 8.90 mmol), 3-bromopyridine (0.178 mL, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.78 μmol) were warmed for 3 h at 140 ºC. The final product was extracted with dichloromethane and purified by distillation in ball tube oven (82 ºC, 32 mmHg) with to give **3** as a colorless oil (0.1801 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.35 (d, $^3J_{c,a}$ = 11.0, 1 H; H^c), 5.80 (d, $^3J_{b,a}$ = 17.6, 1 H; H^b), 6.68 (dd, $^3J_{a,b}$ = 17.6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 7.22 (dd, $^3J_{5,4}$= 7.9, $^3J_{5,6}$ = 4.9, 1 H; H^5), 7.70 (ddd, $^3J_{4,5}$ = 7.9, $^4J_{4,2}$ = 2.3, $^4J_{4,6}$ = 1.6, 1 H; H^4), 8.46 (dd, $^3J_{6,5}$ = 4.9, $^4J_{6,4}$ = 1.6, 1 H; H^6), 8.73 (d, $^4J_{2,4}$ = 2.3, 1 H; H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 116.2 (CH_2), 123.4 (C^5), 132.6 (C^4), 133.0 (C^3), 133.5 (CH), 148.3, 148.9 (C^2, C^6). IR (NaCl): ν 3029 w, 1632 m, 1587 w, 1567 m, 1481 m, 1475 s, 1411 m, 1400 s, 1125 w, 1104 w, 1025 m, 990 m, 916 s, 815 s, 714 s, 628 m. EI-MS (70 eV): *m/z* (%) 105 (100) [M^+], 78 (36) [M^+ – C_2H_3].

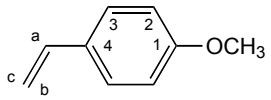


3-Vinylquinoline (4).[1,4] Following the above procedure, triethoxy(vinyl)silane (1.55 mL, 7.13 mmol), a 0.50 M solution of sodium hydroxide in water (17.80 mL, 8.90 mmol), PEG 2000 (3.56 g), 3-bromoquinoline (0.246 mL, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.78 μmol) were warmed for 3 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 1:1 (R_f = 0.46) on silica gel to give **4** as a colorless oil (0.2584 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.44 (d, $^3J_{c,a}$ = 11.0, 1 H; H^c), 5.95 (d, $^3J_{b,a}$ = 17.6, 1 H; H^b), 6.84 (dd, $^3J_{a,b}$ = 17.6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 7.50 (ddd, $^3J_{6,5}$ = 8.1, $^3J_{6,7}$ = 6.9, $^4J_{6,8}$ = 1.1, 1 H; H^6), 7.65 (ddd, $^3J_{7,8}$ = 8.4, $^3J_{7,6}$ = 6.9, $^4J_{7,5}$ = 1.5, 1 H; H^7), 7.76 (dd, $^3J_{8,7}$ = 8.2, $^4J_{8,6}$ = 1.1, 1 H; H^8), 8.03 (d, $^4J_{4,2}$ = 2.2, 1 H; H^4), 8.05 (dd, $^3J_{5,6}$ = 8.2, $^4J_{5,7}$ = 1.5, 1 H; H^5), 9.00 (d, $^4J_{2,4}$ = 2.2, 1 H; H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 116.3 (CH_2), 126.9 (C^6), 127.8 (C^5), 127.9 (C^3), 129.22 (C^7), 129.23 (C^{4a}), 130.3 (C^8), 132.4 (C^4), 133.8 (CH), 147.7 (C^{8a}), 149.1 (C^2). IR (KBr): 3090 w, 3065 w, 3033 w, 3006 w, 1633 w, 1618 w, 1569 w, 1493 s, 1462 w, 1429 w, 1370 w, 1327 w, 1125 w, 1024 w, 988 m, 909 s, 861 w, 787 s, 753 s, 700 w, 609 w. EI-MS (70 eV): *m/z* (%) 155 (100), [M^+], 127 (15).

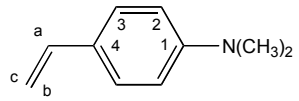


[3] E. Negishi, *Heterocycles*, **1982**, *18*, 117-122.
[4] M. C. Hsu, A. J. Junia, A. R. Haight, W. Zhang, *J. Org. Chem.* **2004,** *69*, 3907-3911.

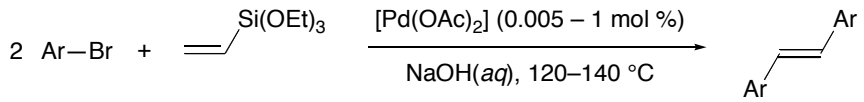
4-Vinylanisole (5).[1,5] Following the above procedure, triethoxy(vinyl)silane (1.94 mL, 8.93 mmol), a 0.50 M solution of sodium hydroxide in water (22.30 mL, 11.15 mmol), PEG 2000 (4.46 g), 4-bromoanisole (0.282 mL, 2.23 mmol), and palladium(II) acetate (0.5 mg, 2.2 μmol) were warmed for 3 h at 150 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 10:1 (R_f = 0.49) on silica gel to give **5** as a colorless oil (0.2243 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.80 (s, 3 H; CH_3), 5.11 (dd, $^3J_{c,a}$ = 11.0, $^2J_{c,b}$ = 0.9, 1 H; H^c), 5.59 (dd, $^3J_{b,a}$ = 17.6, $^2J_{b,c}$ = 0.9, 1 H; H^b), 6.65 (dd, $^3J_{a,b}$ = 17,6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 6.85 (d, $^3J_{2,3}$ = 8.8, 2 H; H^2), 7.33 (d, $^3J_{3,2}$ = 8.8, 2 H; H^3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 55.3 (CH_3), 111.5 (CH_2), 113.9 (C^2), 127.3 (C^3), 130.4 (C^4), 136.1 (CH), 159.3 (C^1). IR (NaCl): ν 3087 w, 3004 m, 2957 w, 2937 w, 2910 w, 2837 m, 1604 s, 1511 s, 1462 m, 1249 s, 1175 s, 1038 s, 902 m, 835 s. EI-MS (70 eV): *m/z* (%) 134 (100) [M$^+$], 119 (36) [M$^+$ – CH_3], 91 (59), 77 (22) [Ph$^+$].



4-Vinyl-*N*,*N*-dimethylaniline (6).[4,5] Following the above procedure, triethoxy(vinyl)silane (0.87 mL, 4.00 mmol), a 0.50 M solution of sodium hydroxide in water (10.00 mL, 5.00 mmol), PEG 2000 (2.00 g), 4-bromo-*N*,*N*-dimethylaniline (0.2063 g, 1.00 mmol), and palladium(II) acetate (1.1 mg, 5.0 μmol) were warmed for 2 h at 150 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 10:1 (R_f = 0.41) on silica gel to give **6** as a colorless oil (0.1270 g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.95 (s, 6 H; CH_3), 5.01 (dd, $^3J_{c,a}$ = 11.0, $^2J_{c,b}$ = 1.1, 1 H; H^c), 5.53 (dd, $^3J_{b,a}$ = 17.6, $^2J_{b,c}$ = 1.1, 1 H; H^b), 6.63 (dd, $^3J_{a,b}$ = 17.6, $^3J_{a,c}$ = 11.0, 1 H; H^a), 6.68 (d, $^3J_{2,3}$ = 8.8, 2 H; H^2), 7.30 (d, $^3J_{3,2}$ = 8.8, 2 H; H^3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 40.52 (CH_3), 109.29 (CH_2), 112.27 (C^2), 126.14 (C^4), 127.08 (C^3), 136.53 (CH), 150.18 (C_1). IR (NaCl): ν 3083 m, 3000 w, 2978 w, 2887 m, 2802 m, 1613 s, 1556 w, 1523 s, 1480 m, 1445 m, 1416 w, 1407 m, 1353 s, 1327 m, 1222 s, 1187 s, 1167 s, 1129 m, 1062 m, 990 s, 947 s, 887 s, 821 s. EI-MS (70 eV): *m/z* (%) 147 (100) [M$^+$], 131 (15), 104 (5), 77 (15) [Ph$^+$].



Synthesis of symmetric (*E*)-1,2-Diarylethenes

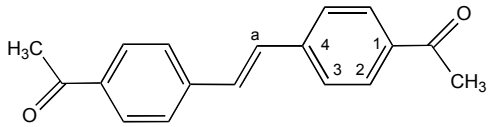


The same general procedure described above for the synthesis of vinylarenes was used for the preparation of symmetric *trans*-stilbenes. Details for each product are given below.

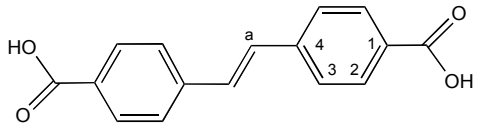
(*E*)-1,2-Bis-[4-acetylphenyl]ethene (7). Following the above procedure, triethoxy(vinyl)silane (0.11 mL, 0.50 mmol), a 0.50 M solution of sodium hydroxide in water (5.00 mL, 2.50 mmol), 1-(4-bromophenyl)ethanone (0.2031 g, 1.00 mmol), and palladium(II) acetate (0.7

[5] S. Weiping, S. Urgaonkar, P. A. McLauglin, J. G. Verkade, *J. Am. Chem. Soc.* **2004**, *126*, 16433-16439.

mg, 3.1 μmol) were warmed for 3 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 6:1 (R_f = 0.35) on silica gel to give **7** as a white solid (0.1301 g, 98%). M. p.: 196–198 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.60 (s, 3 H; CH_3), 7.23 (s, 1 H; H^a), 7.60 (d, $^3J_{3,2}$ = 8.5, 2 H; H^3), 7.96 (d, $^3J_{2,3}$ = 8.5, 2 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 26.6 (CH_3), 126.8 (C^3), 128.9 (C^2), 130.1 (C^a), 136.4 (C^1), 141.2 (C^4), 197.4 (CO). IR (KBr): ν 3050 w, 3034 w, 3018 w, 1676 s, 1603 s, 1566 w, 1413 m, 1358 s, 1332 w, 1309 w, 1267 s, 1220 w, 1184 m, 966 s, 852 w, 837 m, 692 m. EI-MS (70 eV): *m/z* (%) 264 (48) [M$^+$], 249 (100) [M$^+$ – CH_3], 178 (13) [M$^+$ – COMe].



(*E*)-1,2-Bis-[4-carboxyphenyl]ethene (8). Following the above procedure, triethoxy(vinyl)silane (0.26 mL, 1.20 mmol), a 0.50 M solution of sodium hydroxide in water (10.00 mL, 5.00 mmol), PEG 2000 (4.00 g), 4-bromobenzoic acid (0.4102 g, 1.00 mmol), and palladium(II) acetate (1.1 mg, 4.9 μmol) were warmed for 5 h at 140 ºC. The crude of reaction was filtered through silica gel and 3 M hydrochloric acid was dropwise added to the solution to obtain an acid pH. The precipitated solid was filtered and washed with ethanol (3 × 20 mL) to eliminate the 1,1-bis-[4-carboxyphenyl]ethene isomer formed, and dried *in vacuo* to give **8** as a white solid (0.2149 g, 80%). M. p. > 300 ºC. ^{1}H NMR (DMSO, 300 MHz): δ = 7.48 (s, 1 H; H^a), 7.75 (d, $^3J_{3,2}$ = 8.4, 2 H; H^3), 7.95 (d, $^3J_{2,3}$ = 8.4, 2 H; H^2), 12.94 (s, 1 H; COOH). ^{13}C{^{1}H} NMR (DMSO, 75 MHz): δ = 126.3 (C^3), 129.25 (C^2), 129.36 (C^a), 129.42 (C^1), 140.4 (C^4), 166.5 (CO). IR (KBr): ν 3200-2200 br, 1678 s, 1606 s, 1562 m, 1517 w, 1424 s, 1322 s, 1292 s, 1222 w, 1179 s, 1128 w, 1114 w, 1015 w, 950 m, 856 m, 777 s, 699 m, 639 w, 626 w. EI-MS (70 eV): *m/z* (%) 268 (61) [M$^+$], 179 (89), 178 (95) [M$^+$ – 2 COOH], 77 (62) [Ph], 51 (100).

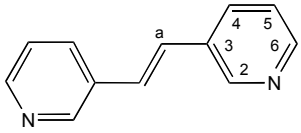


(*E*)-1,2-Bis-(3-piridyl)ethene (9).[6,7] Following the above procedure, triethoxy(vinyl)silane (0.13 mL, 0.60 mmol), a 0.50 M solution of sodium hydroxide in water (5.00 mL, 2.50 mmol), 3-bromopyridine (0.10 mL, 1.00 mmol), and palladium(II) acetate (0.7 mg, 3.1 μmol) were warmed for 3 h at 140 ºC. The final product was extracted with ethyl acetate and purified by dissolution in hexane/ethyl acetate 20:1 to give **9** as a white solid (0.0879 g, 96%). M. p.: 88–89 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.12 (s, 1 H; H^a), 7.30 (ddd, $^3J_{5,4}$= 7.7, $^3J_{5,6}$ = 4.9, $^5J_{5,2}$ = 0.7, 1 H; H^5), 7.84 (ddd, $^3J_{4,5}$ = 7.7, $^4J_{4,2}$ = 2.3, $^4J_{4,6}$ = 1.6, 1 H; H^4), 8.51 (dd, $^3J_{6,5}$ = 4.9, $^4J_{6,4}$ = 1.6, 1 H; H^6), 8.73 (dd, $^4J_{2,4}$ = 2.3, $^5J_{2,5}$ = 0.7, 1 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 123.6 (C^5), 127.1 (C^a), 132.3 (C^3), 132.8 (C^4), 148.7, 149.2 (C^2, C^6). IR (KBr): ν 3022 w, 1571 s, 1484 s, 1422 s, 1292 s, 1246 w,

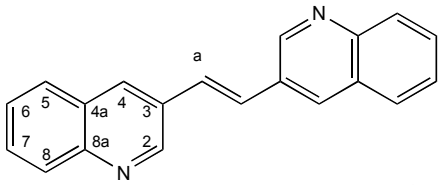
[6] S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Botsmanova, L. G. Kuz`mina, A. V. Churakov, Y. A. Strelenko, M. V. Alfimov, J. A. K. Howard, D. Johnels, U. G. Edlund, *New. J. Chem.* **2005**, *29*, 881-894.

[7] P. Y. White, L. A. Summers, *Aust. J. Chem.* **1977**, *30*, 1153-1156.

1220 w, 1188 w, 1123 m, 1097 w, 1045 w, 1022 s, 967 s, 948 m, 828 m, 814 s, 709 s, 627 m. EI-MS (70 eV): *m/z* (%) 182 (100) [M$^+$], 154 (54), 127 (11).



(*E*)-1,2-Bis-(3-quinolyl)ethene (10).[4,8] Following the above procedure, triethoxy(vinyl)silane (0.20 mL, 0.92 mmol), a 0.50 M solution of sodium hydroxide in water (7.5 mL, 3.75 mmol), 3-bromoquinoline (0.208 mL, 1.50 mmol), and palladium(II) acetate (1.0 mg, 4.5 μmol) were warmed for 3 h at 140 ºC. After cooling to room temperature, compound **10** almost pure after its ^{1}H NMR spectrum (Figure S1) was recuperated from the water suspension by simple filtration, washed with water (3 × 5 mL) and dried in vacuo. Alternatively, the final product was extracted with ethyl acetate and washed with ethyl acetate/chloroform 10:1 to give **10** as a yellow solid (0.2074 g, 98%). M. p.: 236–237 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.46 (s, 1 H; H^a), 7.56 (ddd, $^3J_{6,5}$ = 8.1, $^3J_{6,7}$ = 6.8, $^4J_{6,8}$ = 0.9, 1 H; H^6), 7.70 (ddd, $^3J_{7,6}$ = 8.4, $^3J_{7,8}$ = 7.0, $^4J_{7,5}$ = 1.5, 1 H; H^7), 7.84 (d, $^3J_{8,7}$ = 7.9, 1 H; H^8), 8.10 (d, $^3J_{5,6}$ = 8.4, 1 H; H^5), 8.24 (d, $^4J_{4,2}$ = 2.1, 1 H; H^4), 9.17 (d, $^4J_{2,4}$ = 2.1, 1 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 127.2, 127.4, 127.90, 127.97 (C^3), 129.3, 129.55, 129.65 (C^{4a}), 132.8, 147.7 (C^{8a}), 149.2 (C^2). IR (KBr): ν 3053 m, 3033 m, 3010 m, 1600 m, 1572 s, 1495 s, 1466 w, 1435 m, 1382 m, 1343 m, 1294 m, 1213 w, 1138 w, 1129 m, 980 s, 947 m, 903 s, 867 w, 787 s, 781 s, 772 s, 749 s, 728 s, 611 m. EI-MS (70 eV): *m/z* (%) 282 (100) [M$^+$], 254 (12).



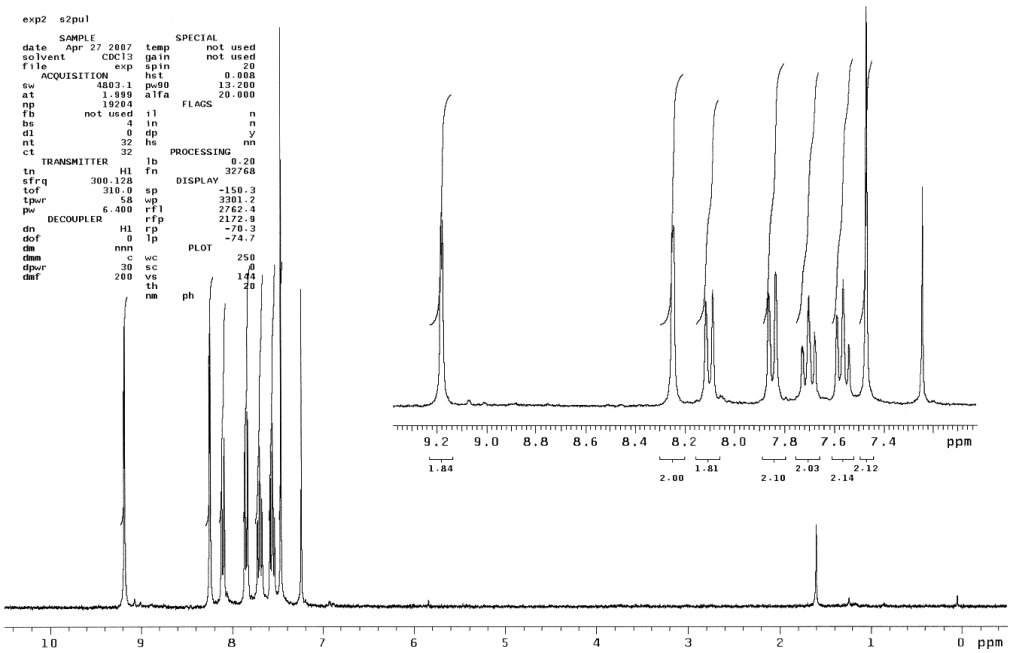
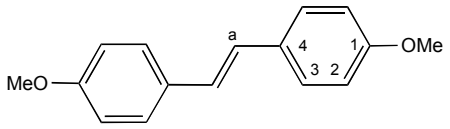


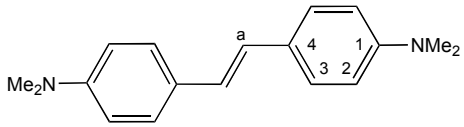
Figure S1. ^{1}H NMR spectrum of crude product **10** separated from the reaction mixture by simple filtration.

[8] C. Bazzini, S. Brovelli, T. Caronna, C. Gambarotti, M. Giannone, P. Macchi, F. Meinardi, A. Mele, W. Panzeri, F. Recupero, A. Sironi, R. Tubito, *Eur. J. Org. Chem.* **2005**, 1247-1257.

(*E*)-1,2-Bis-(4-methoxyphenyl)ethene (11).[9,10] Following the above procedure, triethoxy(vinyl)silane (0.22 mL, 1.01 mmol), a 0.50 M solution of sodium hydroxide in water (3.00 mL, 1.50 mmol), 4-bromoanisole (0.126 mL, 1.00 mmol), and palladium(II) acetate (2.2 mg, 9.8 μmol) were warmed for 22 h at 130 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 10:1 (R_f = 0.27) on silica gel to give **11** as a white solid (0.1692 g, 70%). M. p.: 213–214 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.81 (s, 3 H; CH_3), 6.87 (d, $^3J_{2,3}$ = 8.8, 2 H; H^2), 6.91 (s, 1 H; H^a), 7.41 (d, $^3J_{3,2}$ = 8.8, 2 H; H^3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 55.3 (CH_3), 114.1 (C^2), 126.2 (C^a), 127.4 (C^3), 130.5 (C^4), 159.0 (C^1). IR (KBr): ν 3015 w, 2956 m, 2937 m, 2911 m, 2838 m, 1608 s, 1577 m, 1515 s, 1469 m, 1441 m, 1421 m, 1307 m, 1271 s, 1250 s, 1215 m, 1178 s, 1112 m, 1030 s, 968 s, 956 s, 834 s, 825 s, 745 m, 728 w. EI-MS (70 eV): *m*/*z* (%) 240 (100) [M^+], 225 (62) [$M^+ - CH_3$], 165 (50), 153 (45).

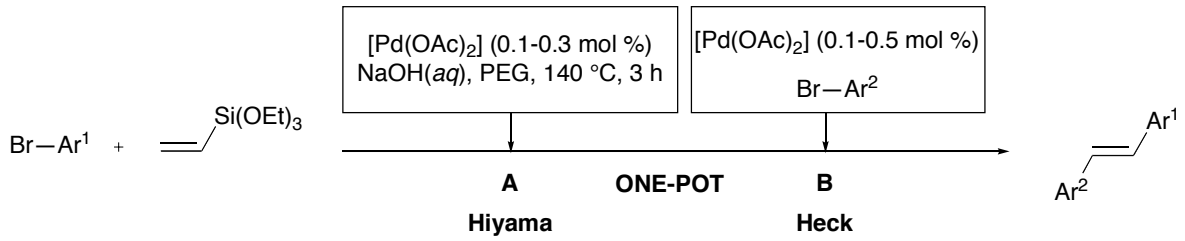


(*E*)-1,2-Bis-[4-(dimethylamino)phenyl]ethene (12).[11,12] Following the above procedure, triethoxy(vinyl)silane (0.435 mL, 2.00 mmol), a 0.50 M solution of sodium hydroxide in water (6.00 mL, 3.00 mmol), 4-bromo-*N*,*N*-dimethylaniline (0.4126 g, 2.00 mmol), and palladium(II) acetate (4.5 mg, 20.0 μmol) were warmed for 5 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 10:1 (R_f = 0.22) on silica gel to give **12** as a pale green solid (0.1341 g, 50%). M. p.: 256-260 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.95 (s, 6 H; CH_3), 6.70 (d, $^3J_{2,3}$ = 8.8, 2 H; H^2), 6.84 (s, 1 H; H^a), 7.36 (d, $^3J_{3,2}$ = 8.8, 2 H; H^3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 40.6 (CH_3), 112.7 (C^2), 124.8 (C^a), 126.9 (C^4), 127.0 (C^3), 149.6 (C^1). IR (KBr): ν 3014 m, 2977 w, 2891 m, 2804 m, 1611 s, 1557 w, 1523 s, 1478 m, 1446 m, 1360 s, 1235 w, 1223 m, 1186 s, 1168 m, 1122 m, 1068 m, 960 m, 947 m, 817 s. EI-MS (70 eV): *m*/*z* (%) 266 (100) [M^+], 251 (25) [$M^+ - CH_3$], 236 (22) [$M^+ - 2\ CH_3$], 178 (16).



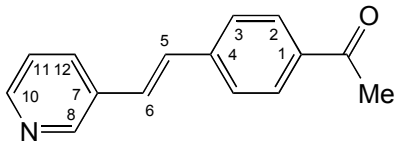
[9] K. Ferré-Filmon, L Delaude, A Demonceau, A. F. Noels, *Eur. J. Org. Chem.* **2005**, 3319-3325.
[10] M. Tsukamoto, M. Schlosser, *Synlett*, **1990**, 605-608.
[11] J.-S. Yang, C.-Y. Hwang, C.-C. Hsieh, S.-Y. Chiou, *J. Org. Chem.* **2004**, *69*, 719-726.
[12] W. Tadros, L. Ekladius, A. B. Sakle, *J. Chem. Soc.* **1954**, 2351-2353.

Synthesis of asymmetric (*E*)-1,2-Diarylethenes (Table 3)

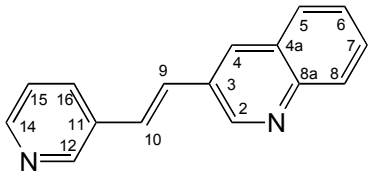


In a 35-mL Ace pressure tube, triethoxy(vinyl)silane (see quantities below) was added to a 0.5 M sodium hydroxide solution in water containing 20% (w/w) of PEG 2000 and the mixture was vigorously stirred for 5 min at room temperature. Aryl bromide **A** and palladium acetate were subsequently added to the mixture, which was placed in a silicone bath previously warmed to the reaction temperature **A** and stirred vigorously for the reaction time **A**. The reaction mixture was then allowed to cool to room temperature and the procedure was repeated after addition of the aryl bromide **B** and a second load of palladium acetate catalyst dissolved in 1 mL of a 20% (w/w) aqueous solution of PEG 2000 at the reaction temperature **B** and for time **B**. The reaction mixture was again allowed to cool to room temperature and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and, after filtration, the solvent eliminated on a rotary evaporator connected to a water aspirator pump. The products were isolated and purified from this residue as described below.

(*E*)-1-(4-Acetylphenyl)-2-(3-pyridyl)ethene (13). Following the above procedure, triethoxy(vinyl)silane (0.77 mL, 3.54 mmol), a 0.50 M solution of sodium hydroxide in water (10.70 mL, 5.35 mmol), PEG 2000 (2.14 g), (**A**) 3-bromopyridine (0.178 mL, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.8 μmol) were warmed for 3 h at 140 ºC. Subsequently (**B**), 1-(4-bromophenyl)ethanone (0.3615 g, 1.78 mmol) and palladium(II) acetate (0.4 mg, 1.8 μmol) were added and the mixture warmed for a further 6 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 1:5 (R_f = 0.24) on silica gel to give **13** as a white solid (0.3467 g, 87%). M. p.: 99–101 ºC. Anal. Calcd for $C_{15}H_{13}NO$: C; 80.69, H, 5.87; N, 6.27. Found: C, 80.57; H, 6.00; N, 6.29. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.60 (s, 3 H; CH_3), 7.18 (s, 2 H; H^5, H^6), 7.31 (dd, $^3J_{11,12}$ = 7.7, $^3J_{11,10}$ = 4.8, 1 H; H^{11}), 7.59 (d, $^3J_{2,3}$ = 8.3, 2 H; H^2), 7.85 (dt, $^3J_{12,11}$ = 7.7, $^4J_{12,10} \approx {}^4J_{12,8}$ = 2.0, 1 H; H^{12}), 7.96 (d, $^3J_{3,2}$ = 8.3, 2 H; H^3), 8.51 (dd, $^3J_{10,11}$ = 4.8, $^4J_{10,12}$ = 1.5, 1 H; H^{10}), 8.74 (d, $^4J_{8,12}$ = 2.0, 1 H; H^8). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 26.6 (CH_3), 123.60 (C^{11}), 126.62 (C^3), 127.5 (C^6), 128.8 (C^2), 129.5 (C^5), 132.4 (C^7), 133.0 (C^{12}), 136.3 (C^1), 141.1 (C^4), 148.6, 148.9 (C^8, C^{10}), 197.2 (CO). IR (KBr): ν 3045 w, 3019 w, 3000 w, 2919 w, 1669 s, 1598 s, 1582 m, 1571 w, 1561 w, 1476 m, 1429 m, 1410 m, 1359 s, 1336 m, 1311 m, 1287 m, 1266 s, 1182 m, 1124 w, 1113 w, 1009 w, 1103 w, 1042 w, 1022 m, 976 s, 958 m, 879 w, 847 m, 823 s, 705 s, 634 m, 613 w. ESI-TOF HRMS: *m/z* 224.1102 [M^+ + H]. Calcd for $C_{15}H_{13}NO{\cdot}H^+$: 224.1075.

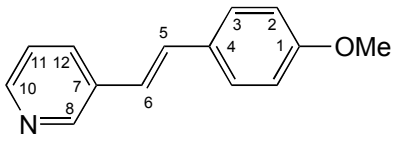


(*E*)-1-(3-Pyridyl)-2-(3-quinolyl)ethene (14). Following the above procedure, triethoxy(vinyl)silane (0.77 mL, 3.54 mmol), a 0.50 M solution of sodium hydroxide in water (10.70 mL, 5.35 mmol), PEG 2000 (2.14 g), (**A**) 3-bromopyridine (0.178 mL, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.8 μmol) were warmed for 3 h at 140 ºC. Subsequently (**B**), 3-bromoquinoline (0.247 mL, 1.78 mmol) and palladium(II) acetate (0.4 mg, 1.8 μmol) were added and the mixture warmed for other 6 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with ethyl acetate/ethanol 10:1 (R_f = 0.19) on silica gel and recrystallized from to give **14** as white needles (0.3349 g, 81%). M. p.: 134–135 ºC. Anal. Calcd for $C_{16}H_{12}N_2$: C; 82.73, H, 5.21; N, 12.06. Found: C, 82.82; H, 5.43; N, 12.00. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (s, 2 H; H^9, H^{10}), 7.32 (ddd, $^3J_{15,16}$ = 8.1, $^3J_{15,14}$ = 4.9, $^5J_{15,12}$ = 0.7, 1 H; H^{15}), 7.55 (ddd, $^3J_{6,5}$ = 8.1, $^3J_{6,7}$ = 7.0, $^4J_{6,8}$ = 1.3, 1 H; H^6), 7.69 (ddd, $^3J_{7,8}$ = 8.4, $^3J_{7,6}$ = 7.0, $^4J_{7,5}$ = 1.6, 1 H; H^7), 7.83 (d, $^3J_{8,7}$ = 8.1, 1 H; H^8), 7.89 (dt, $^3J_{16,15}$ = 7.9, $^4J_{16,12} \approx {}^4J_{16,14}$ = 2.0, 1 H; H^{16}), 8.09 (d, $^3J_{5,6}$ = 8.2, 1 H; H^5), 8.20 (d, $^4J_{4,2}$ = 2.0, 1 H; H^4), 8.51 (dd, $^3J_{14,15}$ = 4.8, $^4J_{14,16}$ = 1.5, 1 H; H^{14}), 8.79 (d, $^4J_{12,16}$ = 1.6, 1 H; H^{12}), 9.12 (d, $^4J_{2,4}$ = 2.2, 1 H; H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 123.5 (C^{15}), 126.9, 127.0, 127.2 (C^6, C^9, C^{10}), 127.80 (C^8), 127.84 (C^{4a}), 129.2 (C^5), 129.43 (C^7), 129.46 (C^3), 132.3 (C^{11}), 132.61 (C^4), 132.68 (C^{16}), 147.6 (C^{8a}), 148.6 (C^{14}), 149.0 (C^2), 149.1 (C^{12}). IR (KBr): ν 3022 w, 1594 w, 1566 m, 1493 m, 1482 m, 1409 s, 1343 w, 1297 m, 1209 w, 1170 w, 1125 m, 1098 w, 1021 m, 989 s, 980 s, 912 m, 896 w, 856 m, 801 m, 785 s, 772 s, 756 s, 708 s, 649 m, 620 m, 603 m. ESI-TOF HRMS: *m/z* 233.1099 [M^+ + H]. Calcd for $C_{16}H_{12}N_2 \cdot H^+$: 233.1079.

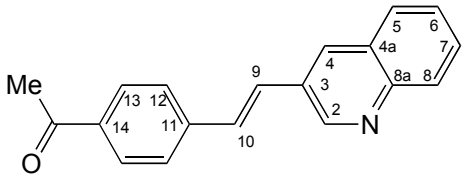


(*E*)-1-(4-Methoxyphenyl)-2-(3-pyridyl)ethene (15).[13] Following the above procedure, triethoxy(vinyl)silane (0.77 mL, 3.54 mmol), a 0.50 M solution of sodium hydroxide in water (10.70 mL, 5.35 mmol), PEG 2000 (2.14 g), (**A**) 3-bromopyridine (0.178 mL, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.8 μmol) were warmed for 3 h at 140 ºC. Subsequently (**B**), 4-bromoanisole (0.3615 g, 1.78 mmol) and palladium(II) acetate (2.0 mg, 8.9 μmol) were added and the mixture warmed for other 6 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 1:1 (R_f = 0.22) on silica gel to give **15** as a white solid (0.2667 g, 71%). M. p.: 98–99 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.82 (s, 3 H; CH_3), 6.90 (d, $^3J_{2,3}$ = 8.6, 2 H; H^2), 6.91 (d, $^3J_{6,5}$ = 16.3, 1 H; H^6), 7.10 (d, $^3J_{5,6}$ = 16.3, 1 H; H^5), 7.25 (dd, $^3J_{11,12}$ = 7.7, $^3J_{11,10}$ = 4.9, 1 H; H^{11}), 7.45 (d, $^3J_{3,2}$ = 8.6, 2 H; H^3), 7.78 (dt, $^3J_{12,11}$ = 8.1, $^4J_{12,10} \approx {}^4J_{12,8}$ = 1.8, 1 H; H^{12}), 8.44 (dd, $^3J_{10,11}$ = 4.8, $^4J_{10,12}$ = 1.5, 1 H; H^{10}), 8.68 (d, $^4J_{8,12}$ = 2.0, 1 H; H^8). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 55.3 (CH_3), 114.2 (C^2), 122.7 (C^6), 123.5 (C^{11}), 127.9 (C^3), 129.5 (C^4), 130.3 (C^5), 132.3 (C^{12}), 133.3 (C^7), 148.2, 148.4 (C^8, C^{10}), 159.7 (C^1). EI-MS (70 eV): *m/z* (%) 211 (100) [M^+], 180 (7) [M^+ – OMe], 167 (59), 115 (17). IR (KBr): ν 3014 w, 2968 w, 2940 w, 2907 w, 2840 w, 1603 s, 1574 m, 1512 s, 1471 m, 1445 m, 1423 m, 1330 w, 1304 m, 1281 s, 1258 s, 1175 s, 1110 m, 1022 s, 965 s, 861 w, 826 s, 763 w, 719 m, 704 s, 612 w.

[13] S. A. Haroutounian, J. A. Katzenellenbogen, *Photochem. Photobiol.* **1988**, *47*, 503-516.

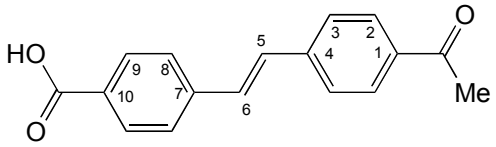


(*E*)-1-(4-Acetylphenyl)-2-(3-quinolyl)ethene (16). Following the above procedure, triethoxy(vinyl)silane (0.77 mL, 3.54 mmol), a 0.50 M solution of sodium hydroxide in water (10.70 mL, 5.35 mmol), PEG 2000 (2.14 g), (**A**) 1-(4-bromophenyl)ethanone (0.3615 g, 1.78 mmol), and palladium(II) acetate (0.4 mg, 1.8 μmol) were warmed for 3 h at 140 ºC. Subsequently (**B**), 4-bromoquinoline (0.247 mL, 1.78 mmol) and palladium(II) acetate (2.0 mg, 8.9 μmol) were added and the mixture warmed for other 6 h at 140 ºC. The final product was extracted with ethyl acetate and purified by flash chromatography with hexane/ethyl acetate 1:1 (R_f = 0.29) on silica gel to give **16** as a yellow solid (0.4381 g, 90%). M. p.: 177–178 ºC. Anal. Calcd for $C_{19}H_{15}NO$: C; 83.49, H, 5.53; N, 5.12. Found: C, 83.41; H, 5.54; N, 5.04. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.61 (s, 3 H; CH_3), 7.35 (s, 2 H; H^9, H^{10}), 7.55 (ddd, $^3J_{6,5}$ = 8.1, $^3J_{6,7}$ = 6.8, $^4J_{6,8}$ = 1.1, 1 H; H^6), 7.64 (d, $^3J_{13,12}$ = 8.4, 2 H; H^{13}), 7.69 (ddd, $^3J_{7,8}$ = 8.1, $^3J_{7,6}$ = 6.8, $^4J_{7,5}$ = 1.5, 1 H; H^7), 7.82 (dd, $^3J_{8,7}$ = 8.1, $^4J_{8,6}$ = 1.1, 1 H; H^8), 7.98 (d, $^3J_{12,13}$ = 8.4, 2 H; H^{12}), 8.08 (dd, $^3J_{5,6}$ = 8.1, $^4J_{5,7}$ = 1.5, 1 H; H^5), 8.20 (d, $^4J_{4,2}$ = 2.2, 1 H; H^4), 9.13 (d, $^4J_{2,4}$ = 2.2, 1 H; H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 26.6 (CH_3), 126.7 (C^{13}), 127.2 (C^6), 127.94, 127.98 ($C^{9/10}$, C^8), 128.00 (C^3), 128.96 (C^{12}), 129.36 (C^5), 129.56, 129.60 ($C^{9/10}$, C^7), 129.68 (C^{4a}), 132.9 (C^4), 136.4 (C^{14}), 141.3 (C^{11}), 147.8 (C^{8a}), 149.3 (C^2), 197.3 (CO). IR (KBr): ν 3063 w, 3023 w, 3000 w, 2920 w, 1675 s, 1600 s, 1568 m, 1492 m, 1429 m, 1410 m, 1373 m, 1353 s, 1268 s, 1184 m, 1112 w, 1018 m, 960 s, 915 m, 859 s, 839 w, 814 m, 789 s, 753 s, 703 m, 640 w, 616 w. ESI-TOF HRMS: *m/z* 274.1221 [M^+ + H]. Calcd for $C_{19}H_{15}NO{\cdot}H^+$: 274.1232.



(*E*)-1-(4-Acetylphenyl)-2-(4-carboxyphenyl)ethene (17). Following the above procedure, triethoxy(vinyl)silane (0.77 mL, 3.54 mmol), a 0.50 M solution of sodium hydroxide in water (14.50 mL, 7.25 mmol), PEG 2000 (2.90 g), (**A**) 4-bromobenzoic acid (0.3651 g, 1.78 mmol), and palladium(II) acetate (1.2 mg, 5.3 μmol) were warmed for 4 h at 140 ºC. Subsequently (**B**), 1-(4-bromophenyl)ethanone (0.3615 g, 1.78 mmol) and palladium(II) acetate (2.0 mg, 8.9 μmol) were added and the mixture warmed for other 3 h at 140 ºC. The final product was extracted with large amounts of ethyl acetate (6 × 30 mL) due to its scarce solubility. It was washed with chloroform and recrystallized from ethyl acetate to give **17** as a yellow solid (0.4219 g, 89%). M. p.: 259–262 ºC. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.01; H, 5.28. ^{1}H NMR (DMSO, 500 MHz): δ = 2.58 (s, 3 H; CH_3), 7.493, 7.495 (*AB* system, $^3J_{5,6}$ = 16.6, 2 H; H^5, H^6), 7.76 (d, ^3J = 8.5, 2 H; $H^{3/8}$), 7.78 (d, ^3J = 8.5, 2 H; $H^{3/8}$), 7.95 (d, ^3J = 8.7, 2 H; $H^{2/9}$), 7.97 (d, ^3J = 8.7, 2 H; $H^{2/9}$), 12.93 (s, 1 H; COOH). ^{13}C{^{1}H} NMR (DMSO, 125 MHz): δ 26.2 (CH_3), 126.31, 126.36 (C^3, C^8), 128.23 (C^2), 129.25 (C^9), 129.29 ($C^{5/6}$), 129.54 (C^{10}), 129.61 ($C^{5/6}$), 135.5 (C^1), 140.4, 140.7 (C^4, C^7), 166.5 (COOH), 196.7 (CO). IR (KBr): ν 3200-2500 br, 3008 m, 2974 m, 2928 m, 2877 w, 2824 w, 1676 s, 1604 s, 1560 m, 1422 s, 1359 m, 1319 s, 1292 s, 1274 s, 1225 m, 1179 s, 1113 m,

958 m, 849 m, 816 m, 767 m, 714 w, 690.9 w. ESI-TOF HRMS: *m*/*z* 267.1027 [M^+ + H]. Calcd for $C_{17}H_{14}O_3 \cdot H^+$: 267.1021.



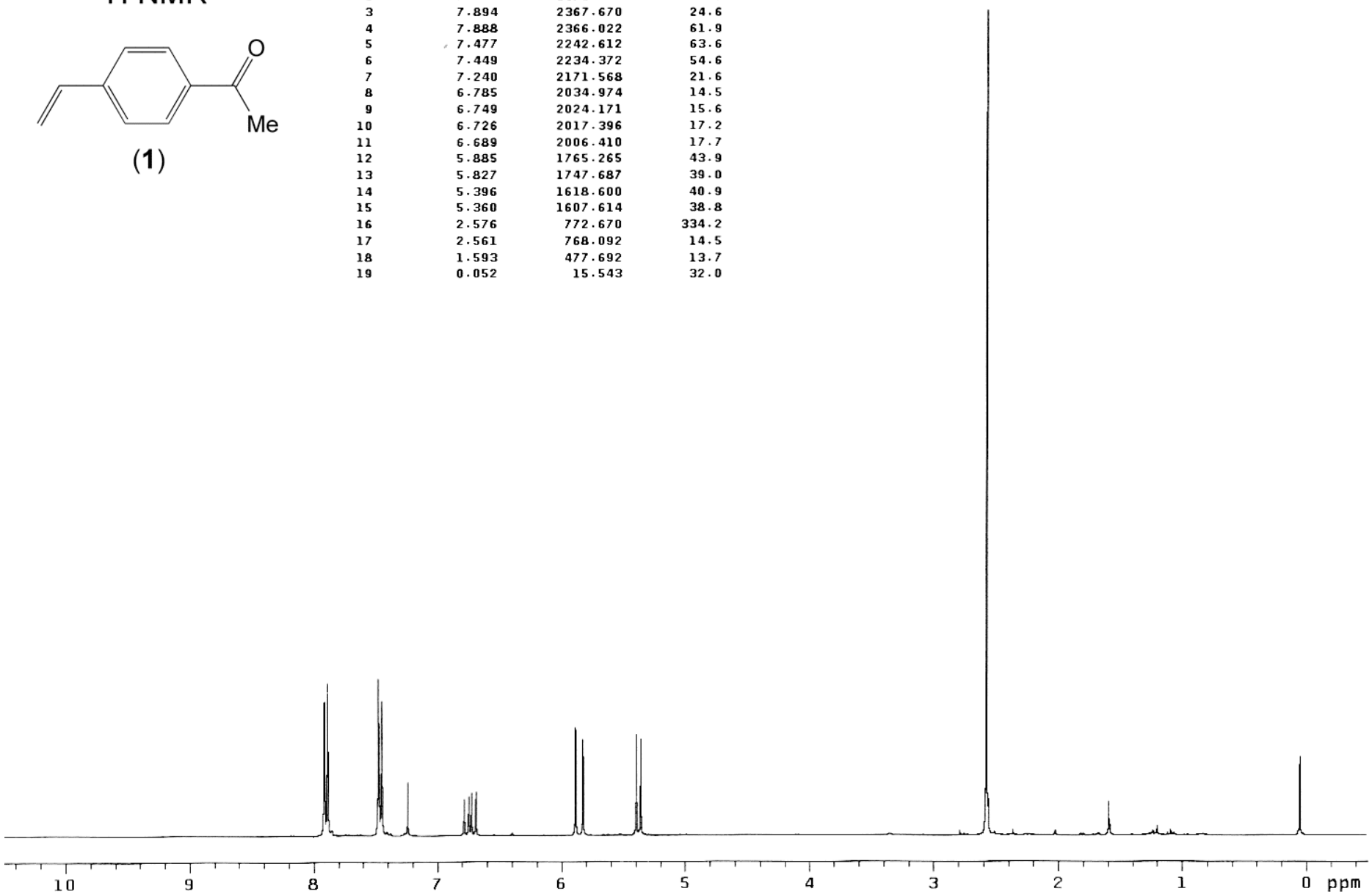
FIGURES REPRODUCING

^{1}H AND ^{13}C{^{1}H} NMR SPECTRA

^{1}H NMR

(**1**)

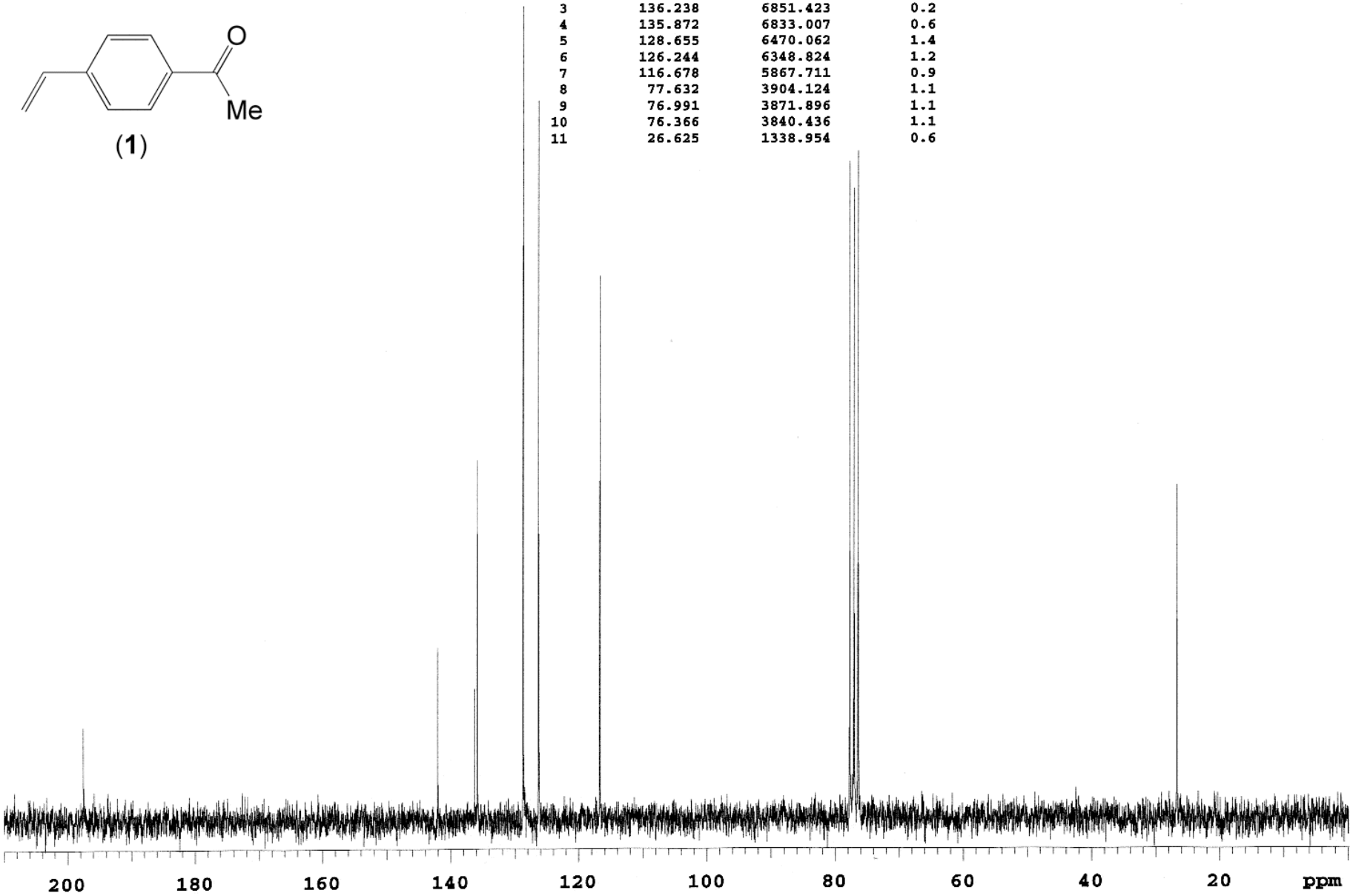
INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	7.916	2374.262	54.1
2	7.910	2372.614	20.0
3	7.894	2367.670	24.6
4	7.888	2366.022	61.9
5	7.477	2242.612	63.6
6	7.449	2234.372	54.6
7	7.240	2171.568	21.6
8	6.785	2034.974	14.5
9	6.749	2024.171	15.6
10	6.726	2017.396	17.2
11	6.689	2006.410	17.7
12	5.885	1765.265	43.9
13	5.827	1747.687	39.0
14	5.396	1618.600	40.9
15	5.360	1607.614	38.8
16	2.576	772.670	334.2
17	2.561	768.092	14.5
18	1.593	477.692	13.7
19	0.052	15.543	32.0



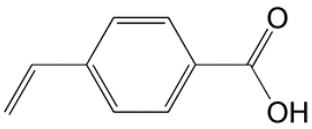
$^{13}C\{^{1}H\}$ NMR

(**1**)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	197.484	9931.468	0.2
2	142.021	7142.239	0.3
3	136.238	6851.423	0.2
4	135.872	6833.007	0.6
5	128.655	6470.062	1.4
6	126.244	6348.824	1.2
7	116.678	5867.711	0.9
8	77.632	3904.124	1.1
9	76.991	3871.896	1.1
10	76.366	3840.436	1.1
11	26.625	1338.954	0.6

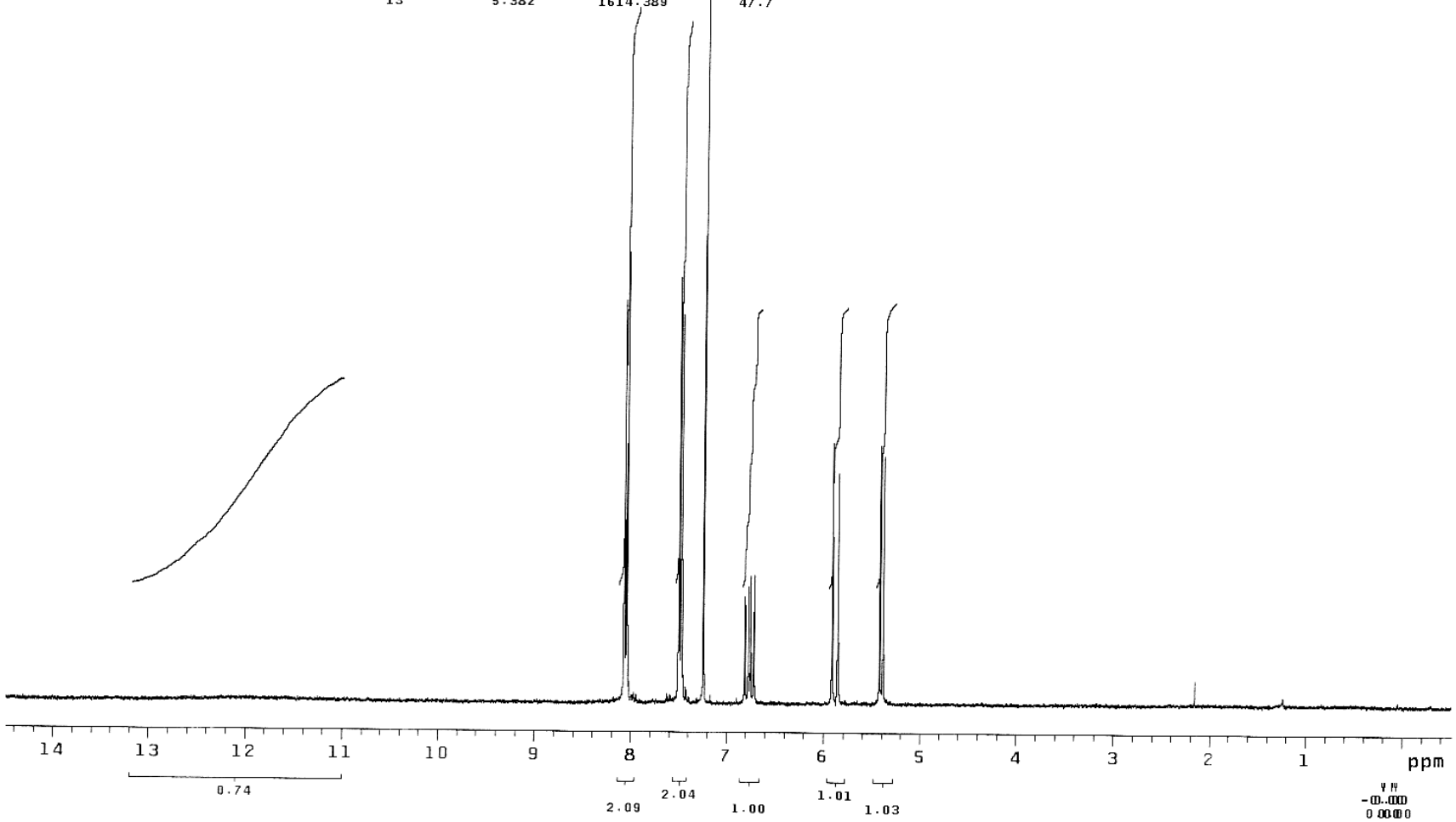


^{1}H NMR



(**2**)

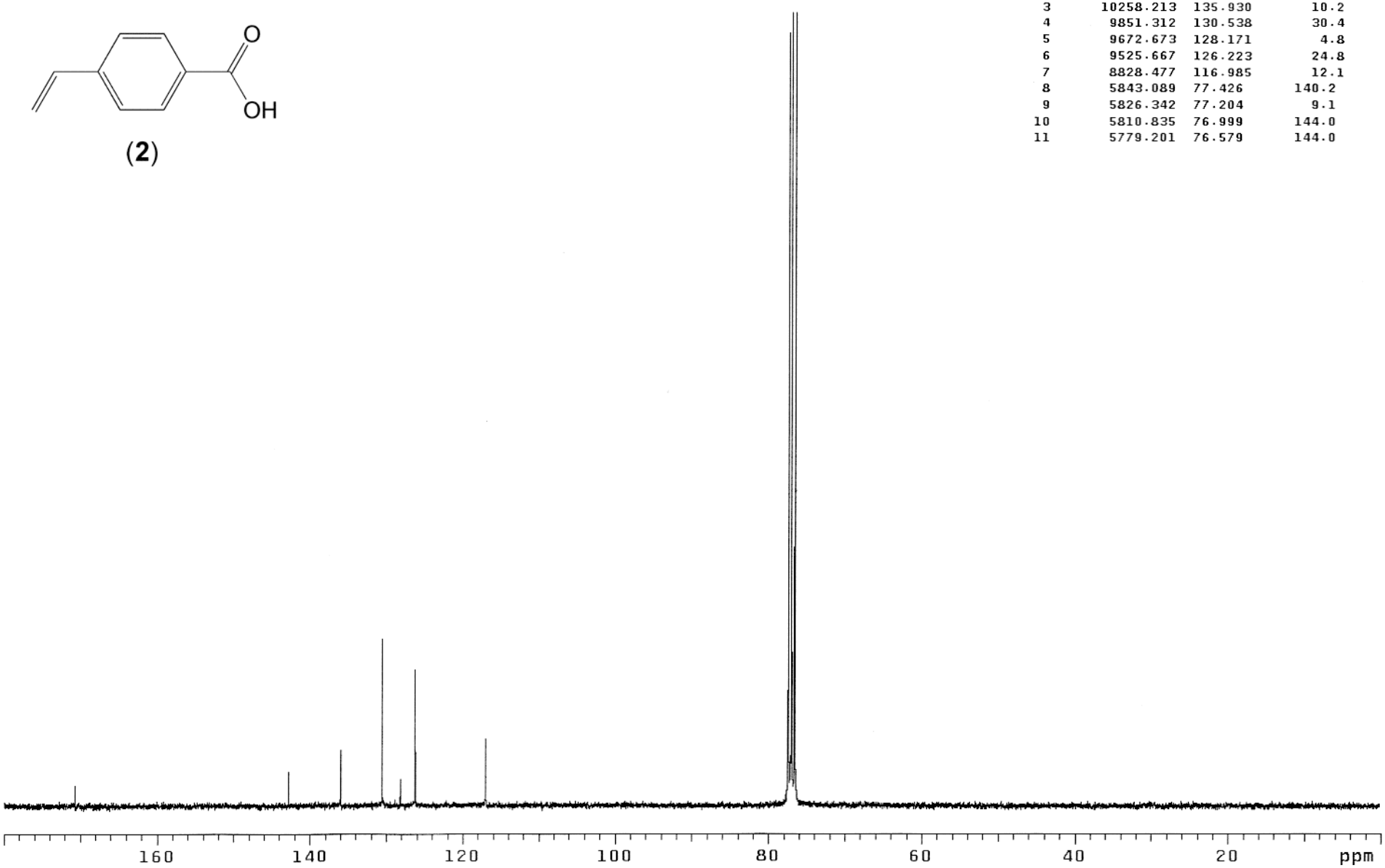
INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	8.071	2420.770	77.6
2	8.043	2412.347	86.9
3	7.497	2248.654	82.2
4	7.469	2240.231	74.9
5	7.240	2171.568	168.9
6	6.804	2040.833	20.6
7	6.767	2029.847	22.6
8	6.745	2023.256	24.5
9	6.709	2012.269	24.7
10	5.909	1772.406	50.4
11	5.851	1754.828	44.4
12	5.419	1625.375	49.7
13	5.382	1614.389	47.7



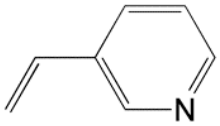
$^{13}C\{^{1}H\}$ NMR

(**2**)

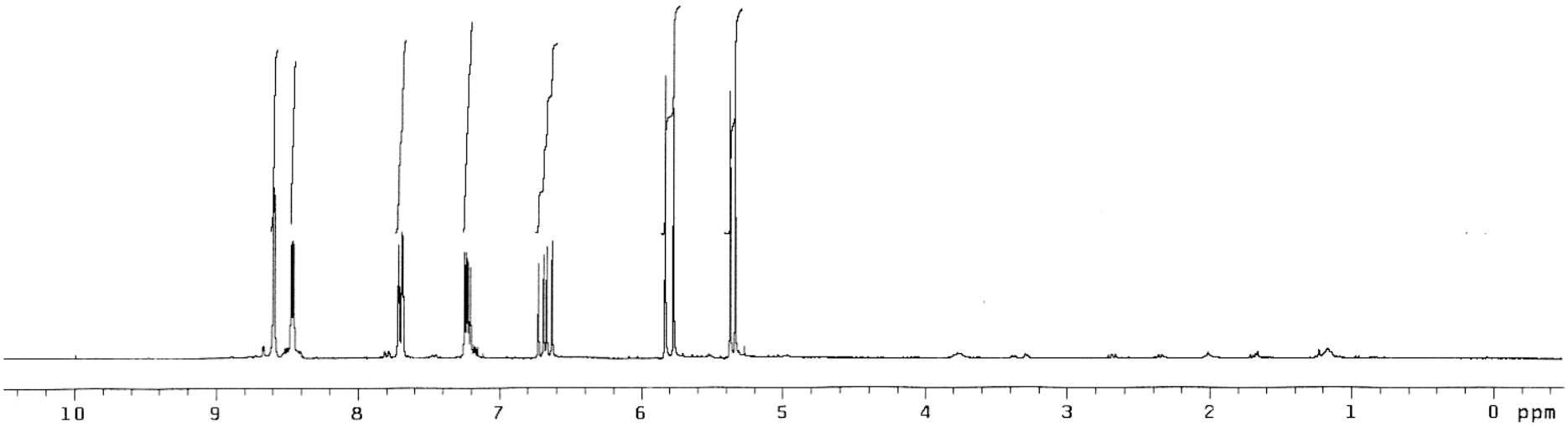
INDEX	FREQUENCY	PPM	HEIGHT
1	12878.259	170.648	3.6
2	10774.283	142.769	6.3
3	10258.213	135.930	10.2
4	9851.312	130.538	30.4
5	9672.673	128.171	4.8
6	9525.667	126.223	24.8
7	8828.477	116.985	12.1
8	5843.089	77.426	140.2
9	5826.342	77.204	9.1
10	5810.835	76.999	144.0
11	5779.201	76.579	144.0



^{1}H NMR



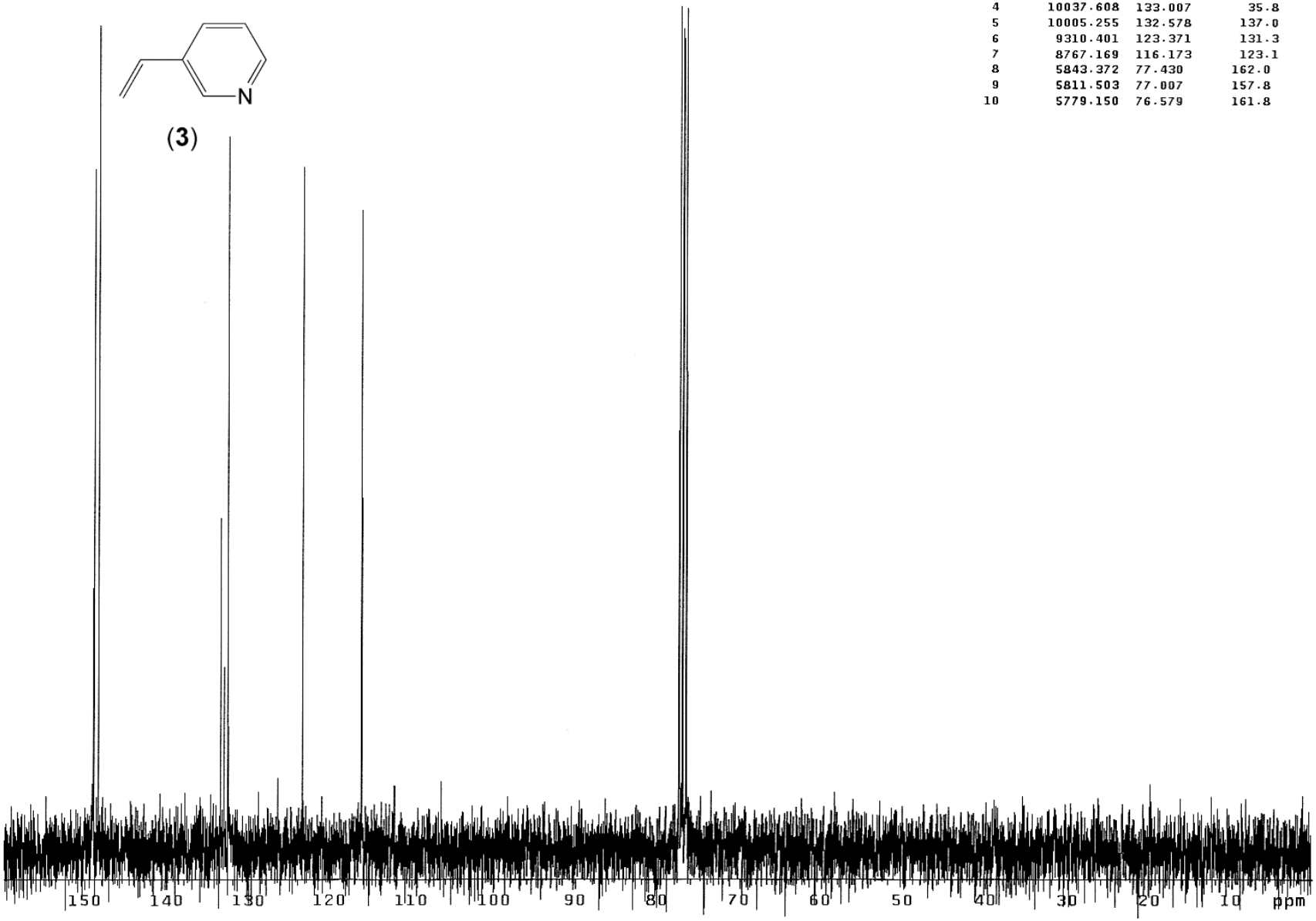
(**3**)



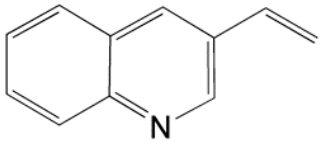
$^{13}C\{^{1}H\}$ NMR

(**3**)

INDEX	FREQUENCY	PPM	HEIGHT
1	11238.030	148.914	130.9
2	11192.157	148.306	158.3
3	10072.858	133.474	64.4
4	10037.608	133.007	35.8
5	10005.255	132.578	137.0
6	9310.401	123.371	131.3
7	8767.169	116.173	123.1
8	5843.372	77.430	162.0
9	5811.503	77.007	157.8
10	5779.150	76.579	161.8



^{1}H NMR



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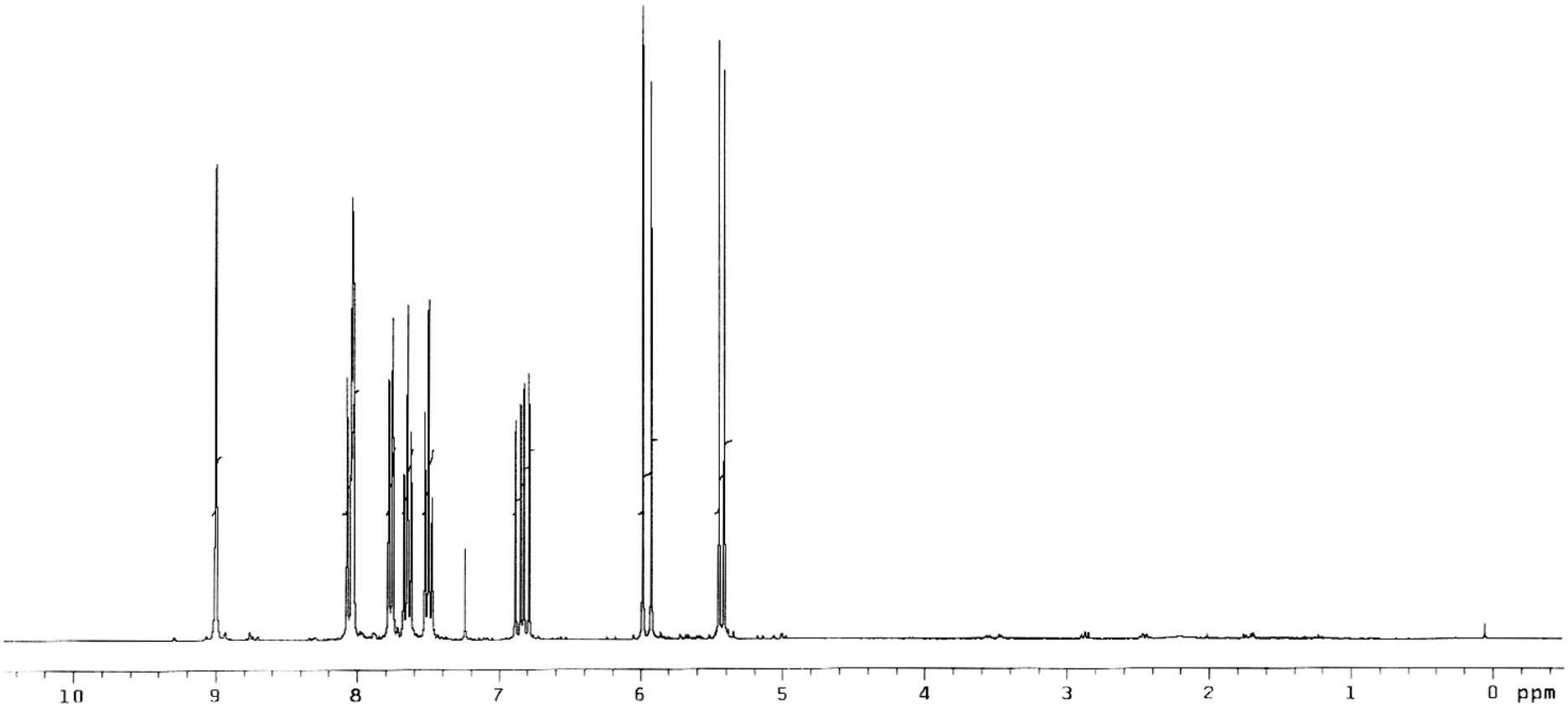
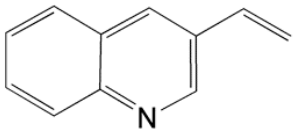
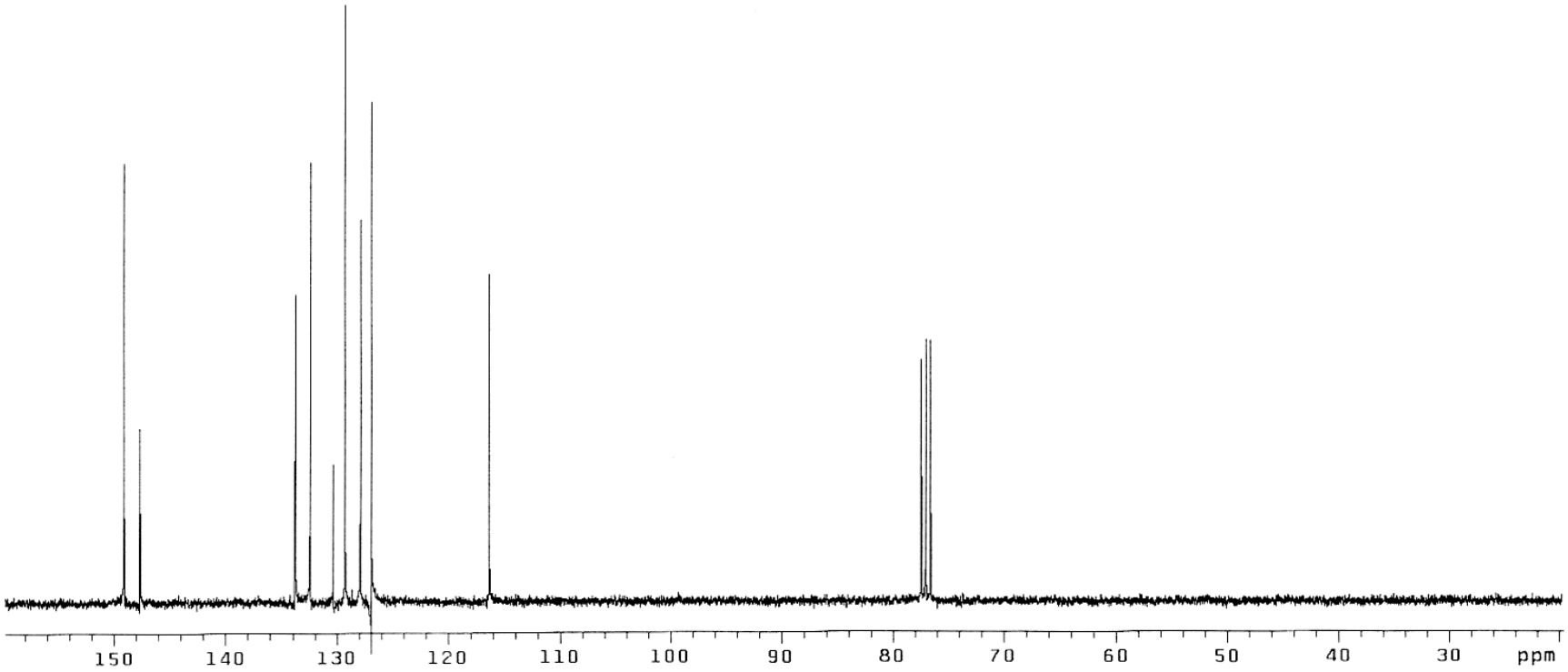


$^{13}C\{^{1}H\}$ NMR



(**4**)

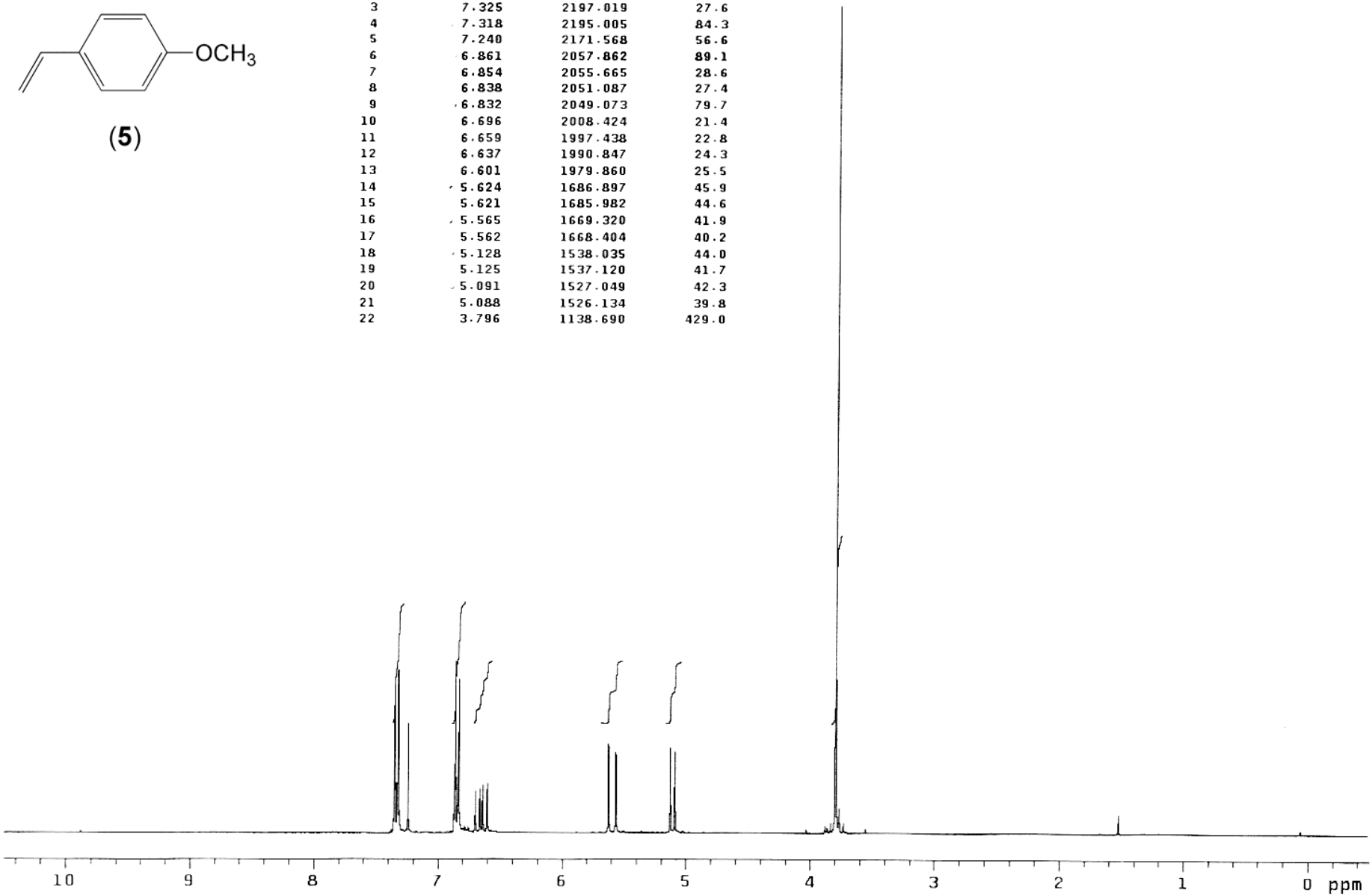
INDEX	FREQUENCY	PPM	HEIGHT
1	11250.997	149.085	70.4
2	11143.288	147.658	28.1
3	10093.872	133.753	49.4
4	9992.147	132.405	70.7
5	9832.827	130.294	22.3
6	9752.045	129.223	95.8
7	9654.060	127.925	12.8
8	9647.328	127.835	61.5
9	9574.026	126.864	80.2
10	8776.679	116.299	52.6
11	5843.102	77.426	39.0
12	5810.939	77.000	42.1
13	5778.776	76.574	42.0



^{1}H NMR

(**5**)

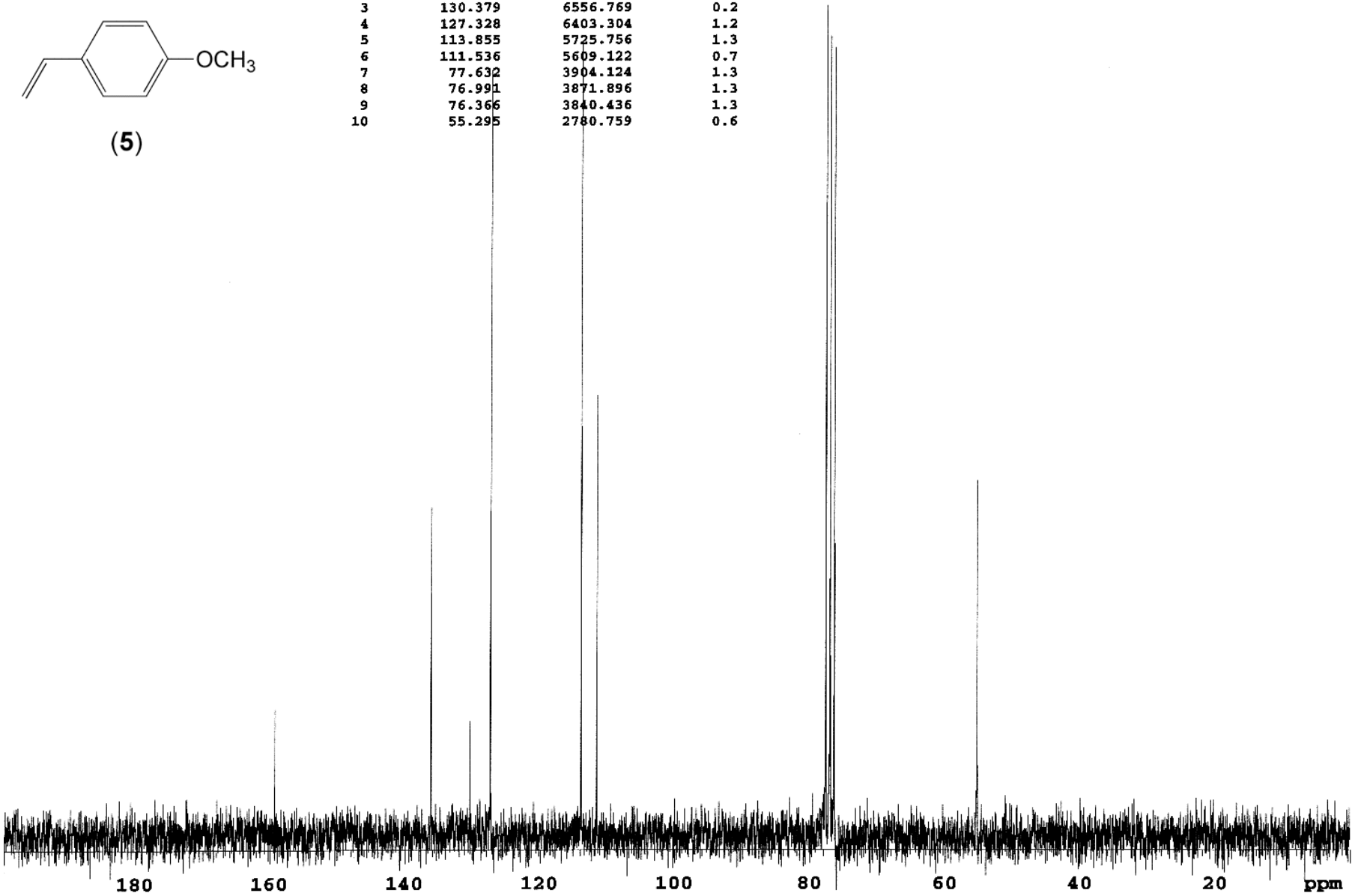
INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	7.347	2203.794	75.9
2	7.341	2201.780	26.0
3	7.325	2197.019	27.6
4	7.318	2195.005	84.3
5	7.240	2171.568	56.6
6	6.861	2057.862	89.1
7	6.854	2055.665	28.6
8	6.838	2051.087	27.4
9	6.832	2049.073	79.7
10	6.696	2008.424	21.4
11	6.659	1997.438	22.8
12	6.637	1990.847	24.3
13	6.601	1979.860	25.5
14	5.624	1686.897	45.9
15	5.621	1685.982	44.6
16	5.565	1669.320	41.9
17	5.562	1668.404	40.2
18	5.128	1538.035	44.0
19	5.125	1537.120	41.7
20	5.091	1527.049	42.3
21	5.088	1526.134	39.8
22	3.796	1138.690	429.0



$^{13}C\{^{1}H\}$ NMR

(**5**)

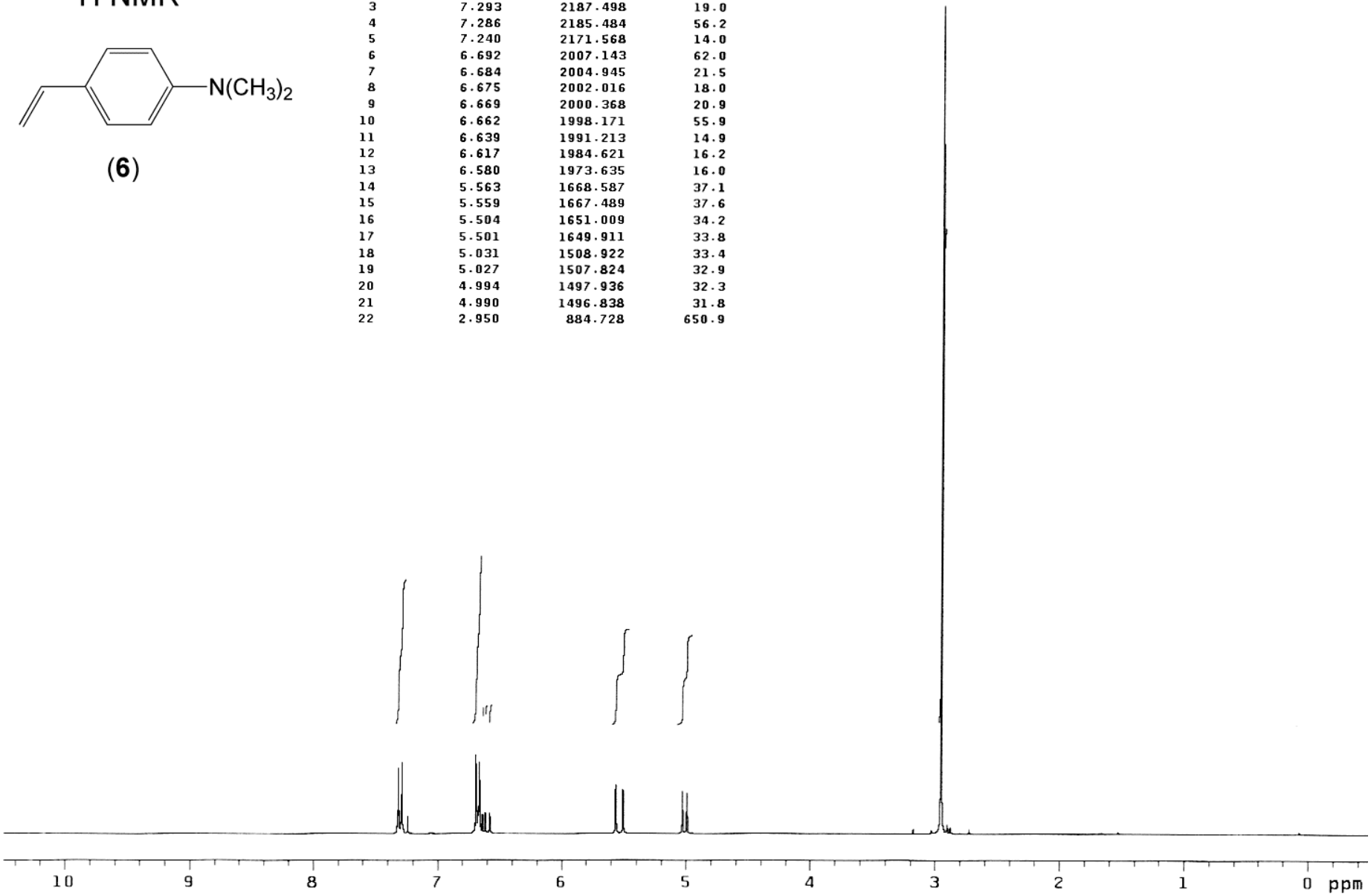
INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	159.278	8010.085	0.2
2	136.147	6846.819	0.5
3	130.379	6556.769	0.2
4	127.328	6403.304	1.2
5	113.855	5725.756	1.3
6	111.536	5609.122	0.7
7	77.632	3904.124	1.3
8	76.991	3871.896	1.3
9	76.366	3840.436	1.3
10	55.295	2780.759	0.6



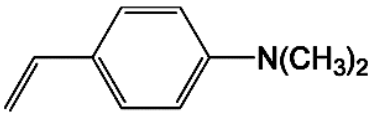
^{1}H NMR

(**6**)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	7.316	2194.273	51.6
2	7.309	2192.259	18.0
3	7.293	2187.498	19.0
4	7.286	2185.484	56.2
5	7.240	2171.568	14.0
6	6.692	2007.143	62.0
7	6.684	2004.945	21.5
8	6.675	2002.016	18.0
9	6.669	2000.368	20.9
10	6.662	1998.171	55.9
11	6.639	1991.213	14.9
12	6.617	1984.621	16.2
13	6.580	1973.635	16.0
14	5.563	1668.587	37.1
15	5.559	1667.489	37.6
16	5.504	1651.009	34.2
17	5.501	1649.911	33.8
18	5.031	1508.922	33.4
19	5.027	1507.824	32.9
20	4.994	1497.936	32.3
21	4.990	1496.838	31.8
22	2.950	884.728	650.9

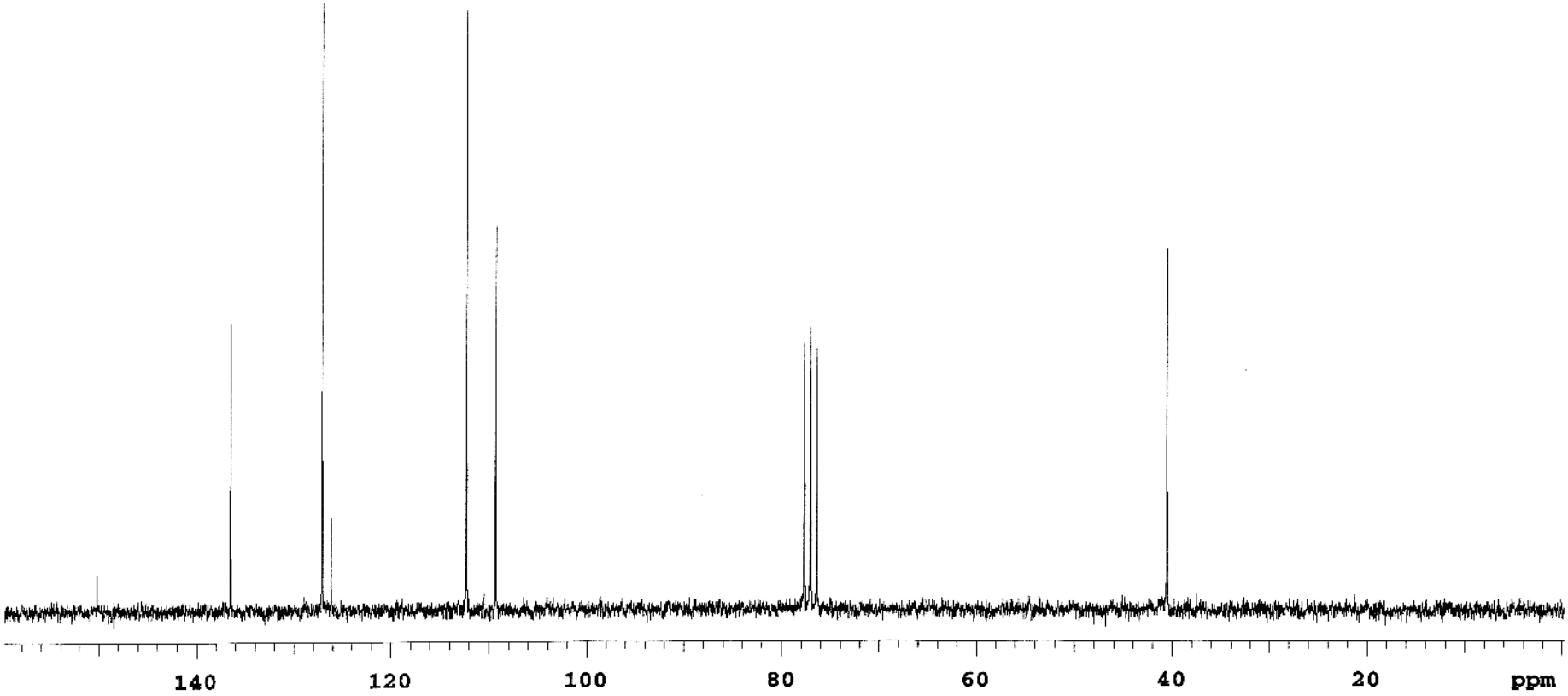


$^{13}C\{^{1}H\}$ NMR

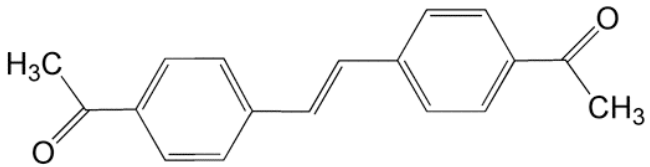


(6)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	150.184	7552.758	0.1
2	136.528	6866.002	0.7
3	127.084	6391.027	1.4
4	126.138	6343.453	0.2
5	112.268	5645.954	1.4
6	109.293	5496.325	0.9
7	77.632	3904.124	0.6
8	76.991	3871.897	0.7
9	76.351	3839.669	0.6
10	40.525	2037.988	0.8

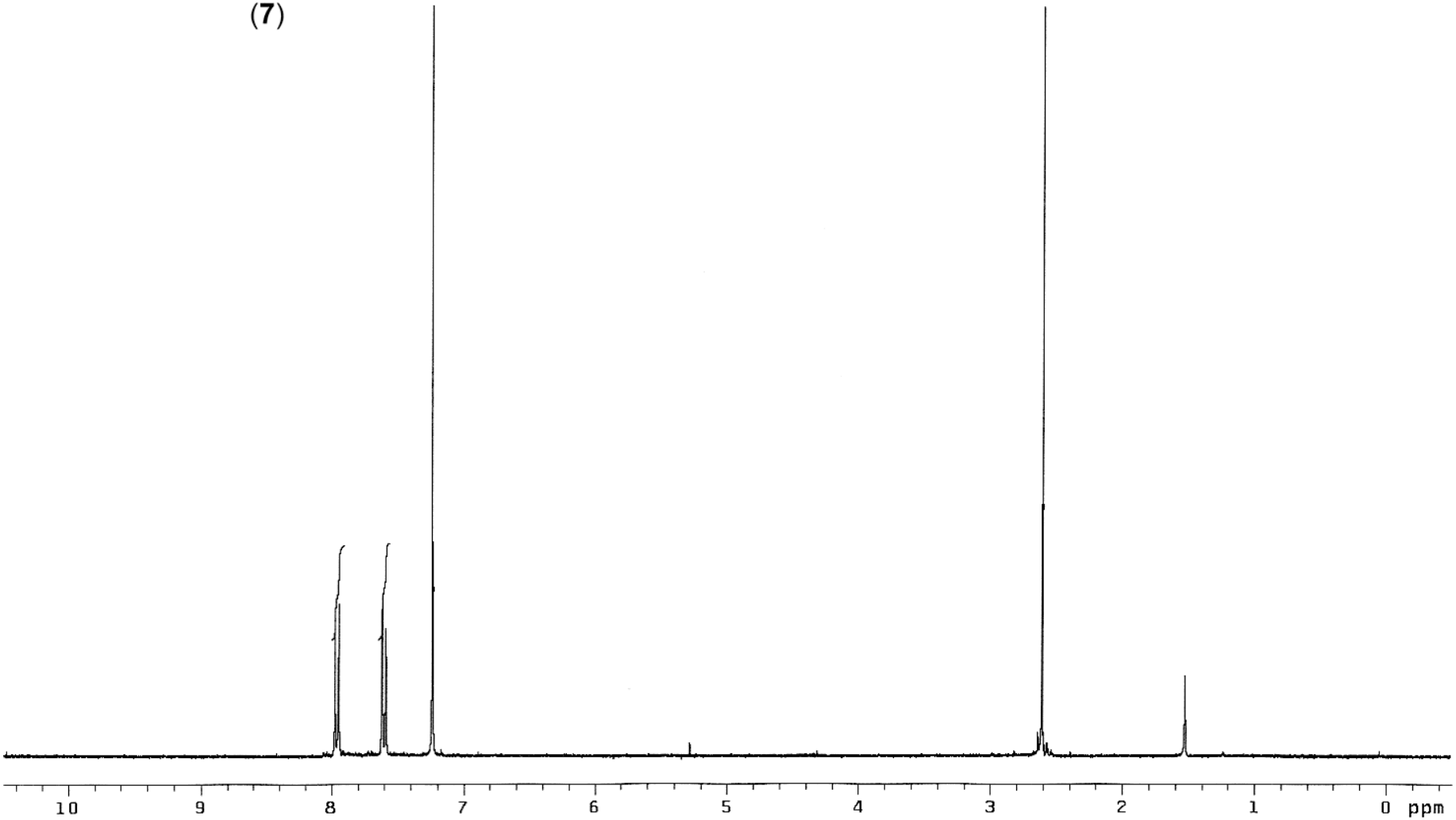


^{1}H NMR

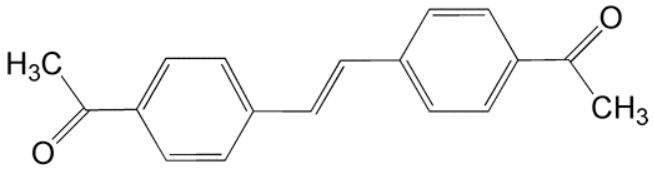


(**7**)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	7.972	2391.213	29.0
2	7.944	2382.778	34.8
3	7.617	2284.617	34.4
4	7.589	2276.132	29.1
5	7.240	2171.568	200.3
6	7.235	2169.942	49.0
7	2.604	781.197	170.6

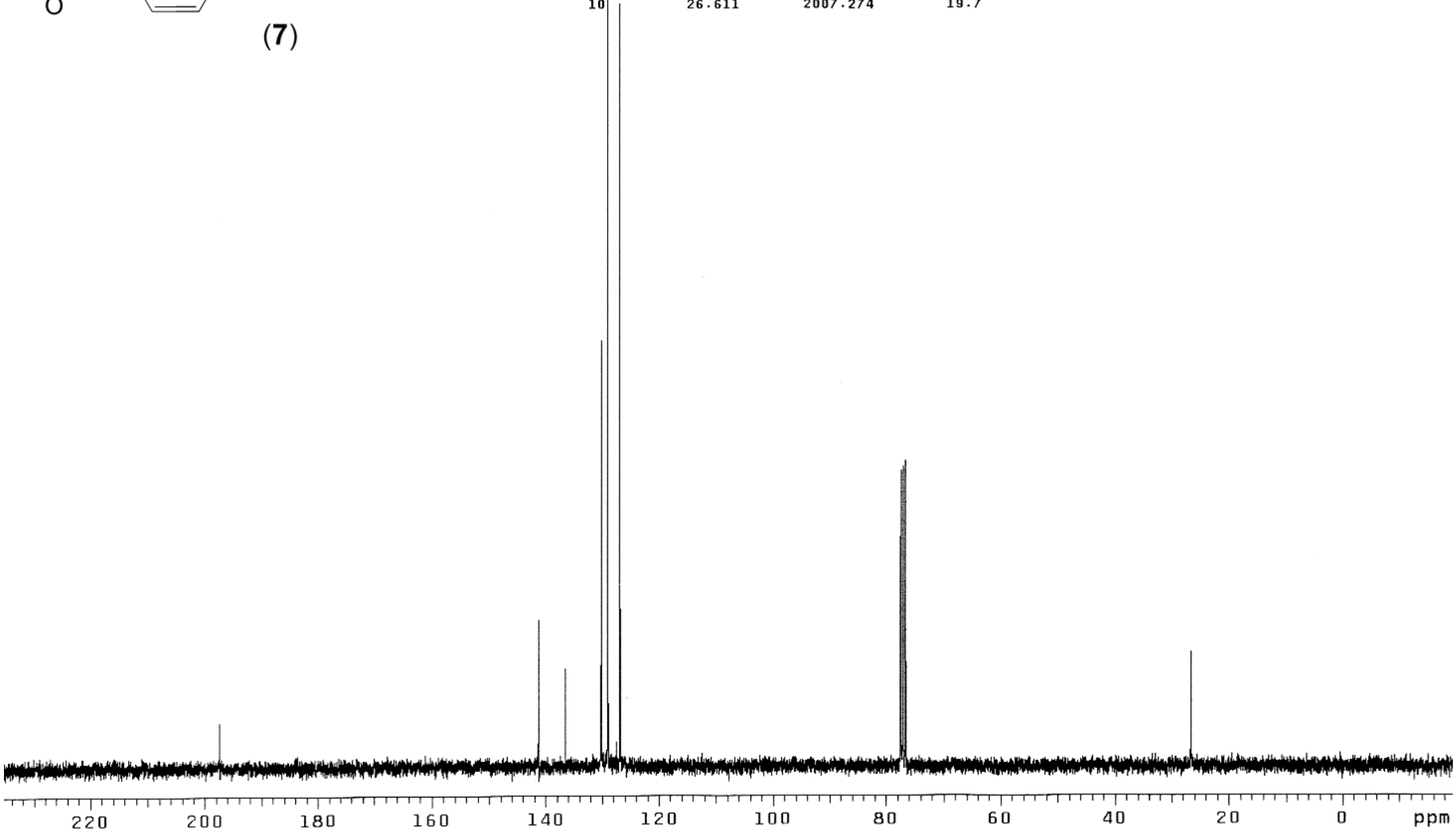


$^{13}C\{^{1}H\}$ NMR

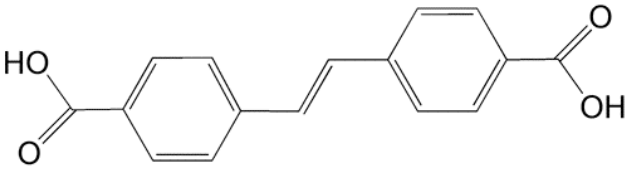


(**7**)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	197.379	14888.444	7.8
2	141.245	10654.185	25.3
3	136.427	10290.764	16.9
4	130.084	9812.346	72.9
5	128.902	9723.149	147.7
6	126.801	9564.659	129.8
7	77.409	5839.042	50.6
8	76.989	5807.344	51.3
9	76.559	5774.909	52.3
10	26.611	2007.274	19.7



^{1}H NMR



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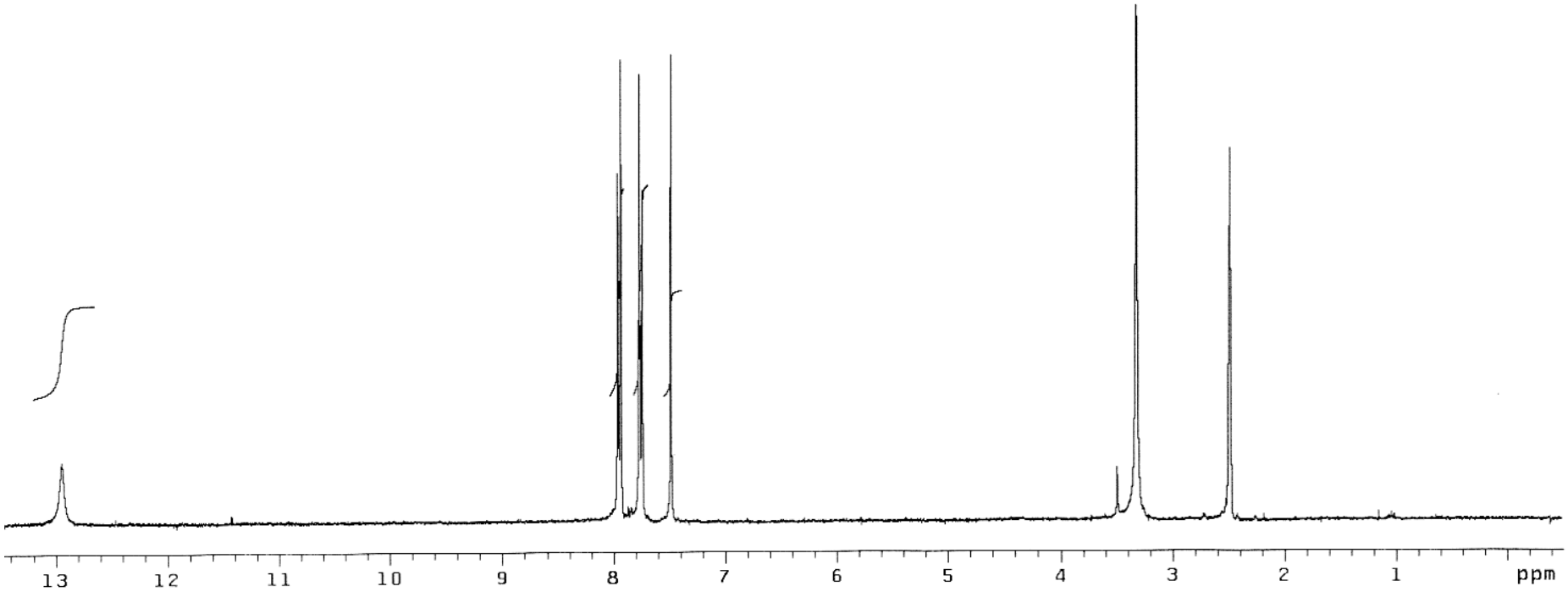
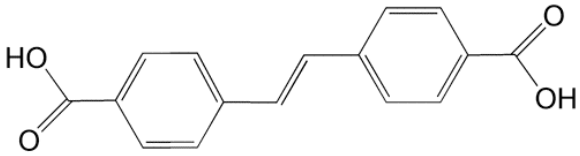
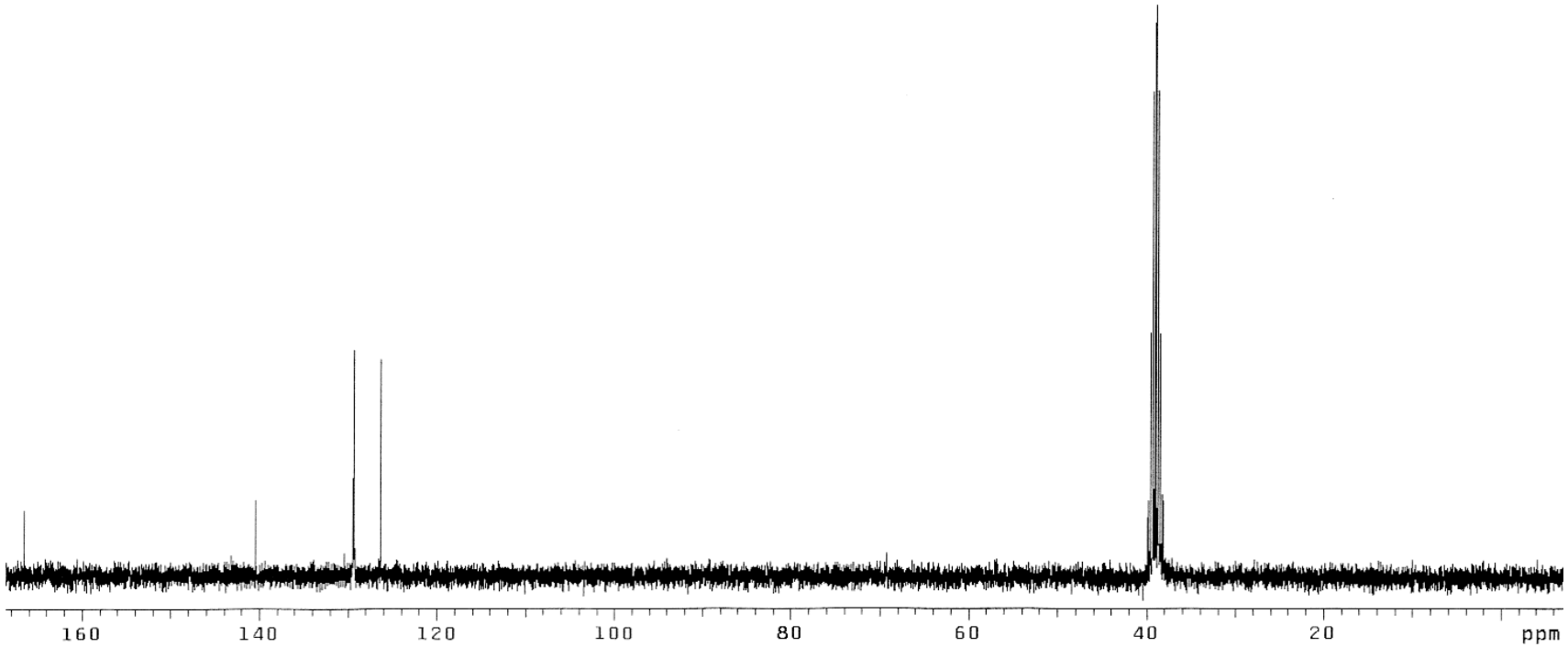


$^{13}C\{^{1}H\}$ NMR

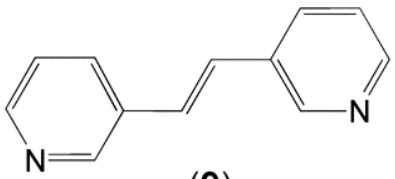


(**8**)

INDEX	FREQUENCY	PPM	HEIGHT
1	12563.500	166.476	11.0
2	10597.724	140.428	12.7
3	9767.182	129.423	10.3
4	9762.836	129.365	16.3
5	9754.144	129.250	36.7
6	9530.091	126.281	35.2
7	3005.993	39.832	12.6
8	2985.230	39.557	39.4
9	2964.466	39.282	78.1
10	2943.220	39.000	92.0
11	2922.456	38.725	78.2
12	2901.210	38.443	39.2
13	2880.446	38.168	13.6

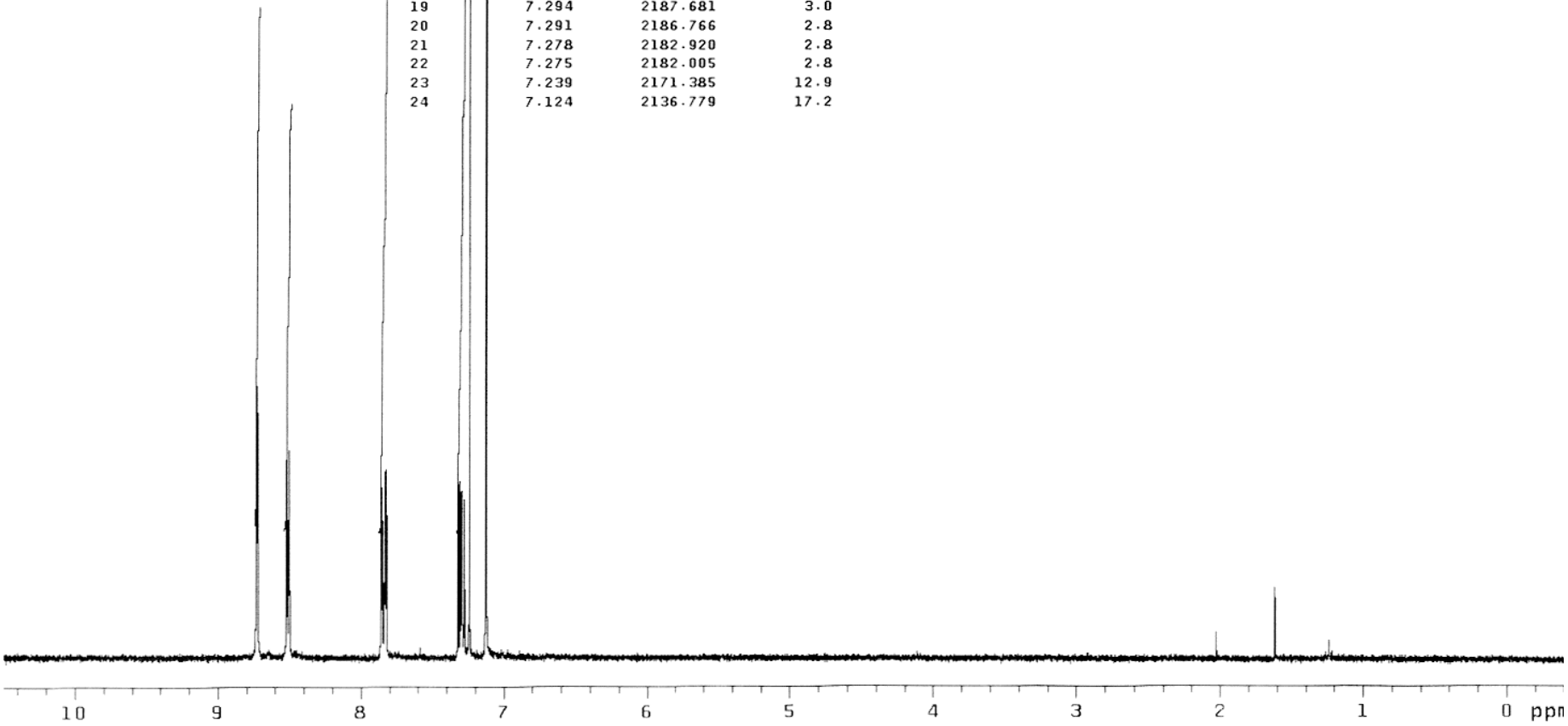


^{1}H NMR



(**9**)

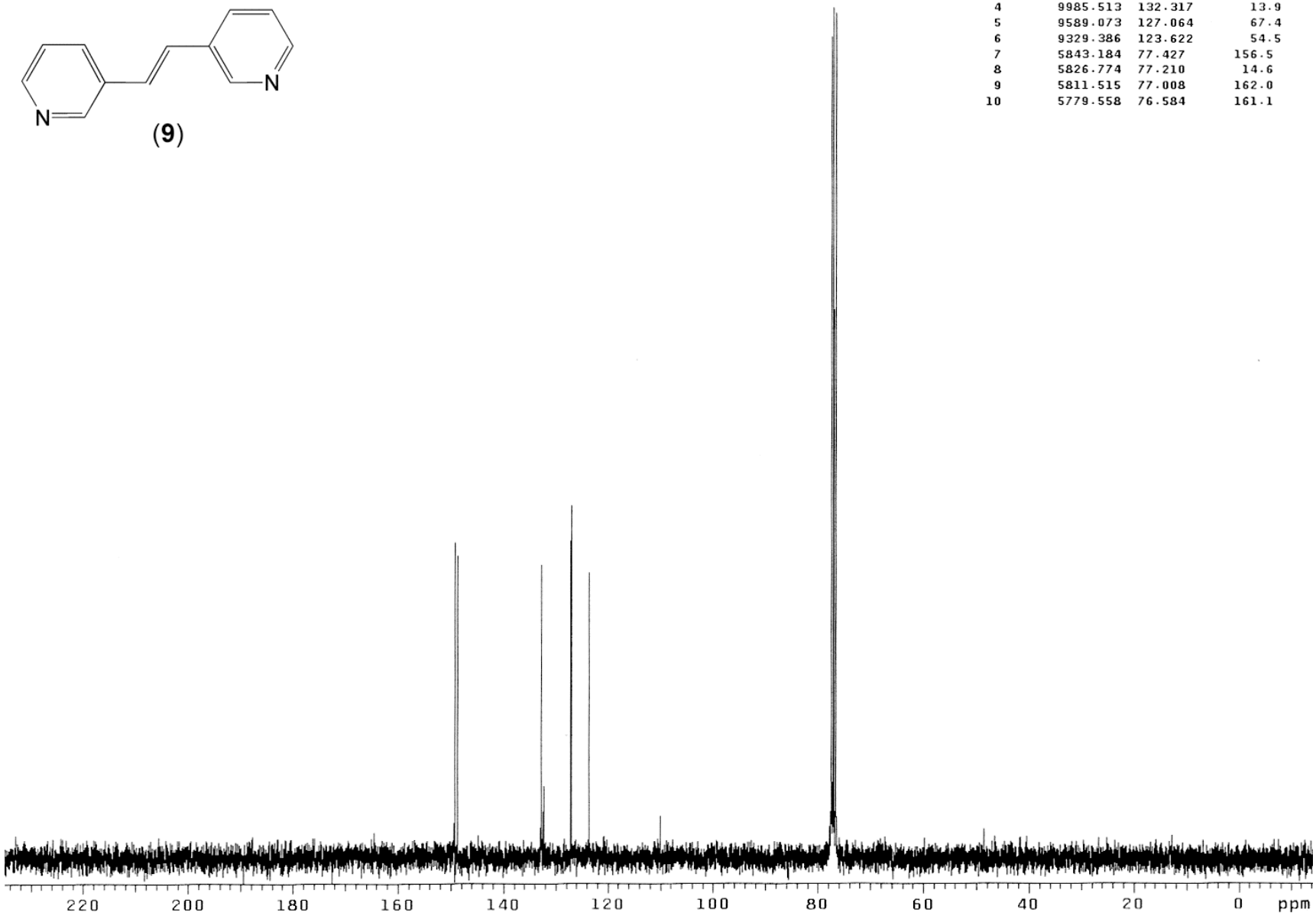
INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	8.732	2619.069	4.6
2	8.729	2618.154	4.7
3	8.724	2616.689	4.9
4	8.722	2615.956	4.4
5	8.521	2555.899	3.5
6	8.516	2554.251	3.7
7	8.505	2550.955	3.7
8	8.500	2549.490	3.5
9	7.859	2357.233	2.5
10	7.852	2355.036	3.0
11	7.846	2353.205	2.4
12	7.832	2349.177	2.8
13	7.826	2347.346	3.4
14	7.819	2345.332	2.6
15	7.320	2195.554	3.1
16	7.317	2194.822	3.1
17	7.304	2190.794	3.2
18	7.302	2190.061	3.0
19	7.294	2187.681	3.0
20	7.291	2186.766	2.8
21	7.278	2182.920	2.8
22	7.275	2182.005	2.8
23	7.239	2171.385	12.9
24	7.124	2136.779	17.2

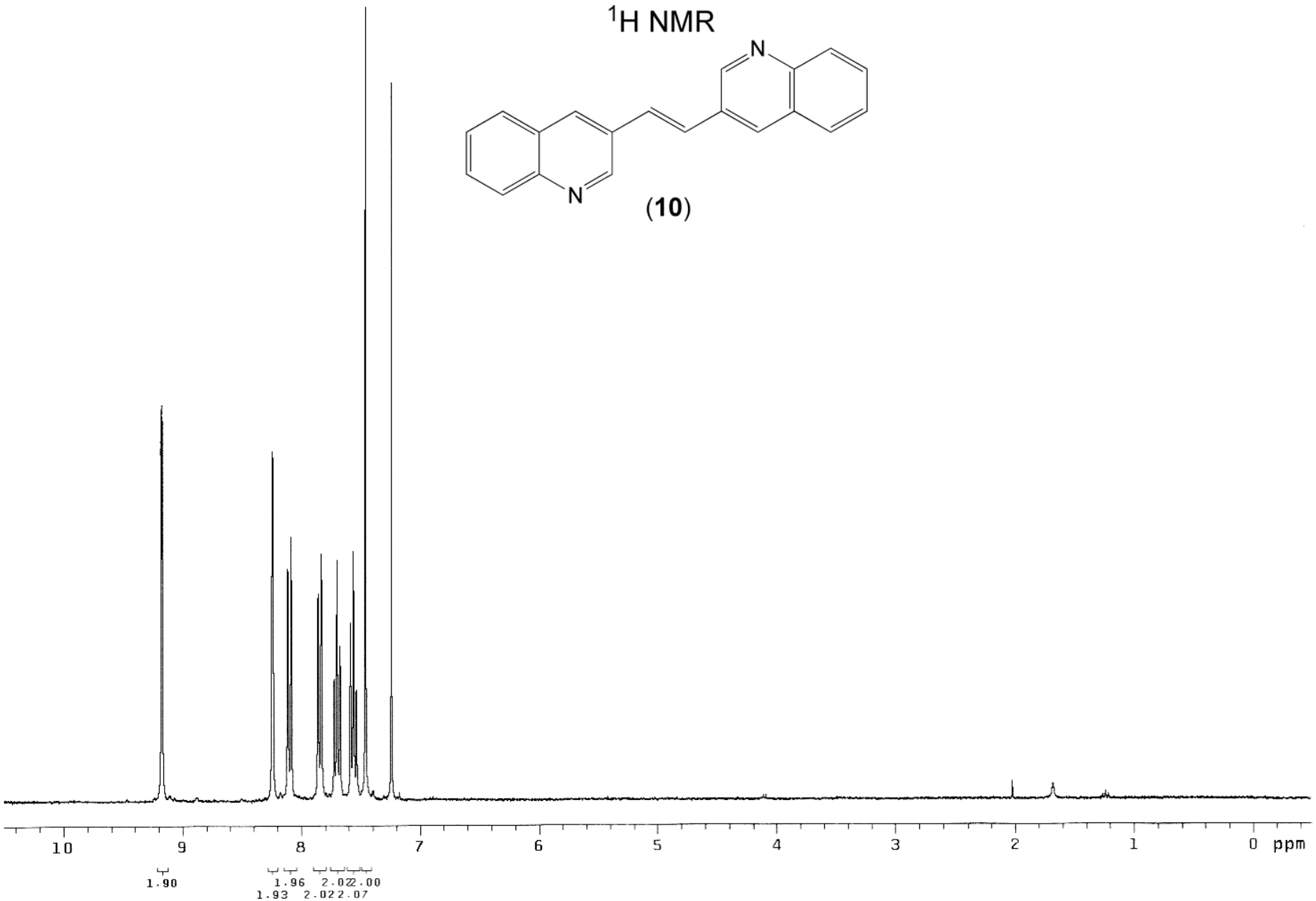


$^{13}C\{^{1}H\}$ NMR

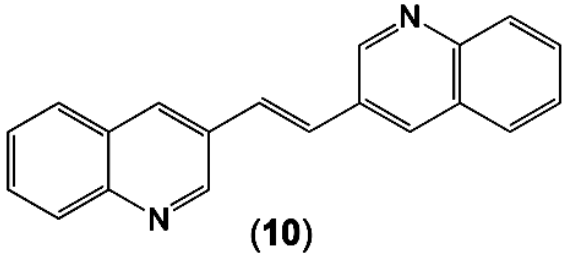
(**9**)

INDEX	FREQUENCY	PPM	HEIGHT
1	11257.463	149.171	60.2
2	11221.475	148.694	57.7
3	10022.077	132.801	56.0
4	9985.513	132.317	13.9
5	9589.073	127.064	67.4
6	9329.386	123.622	54.5
7	5843.184	77.427	156.5
8	5826.774	77.210	14.6
9	5811.515	77.008	162.0
10	5779.558	76.584	161.1



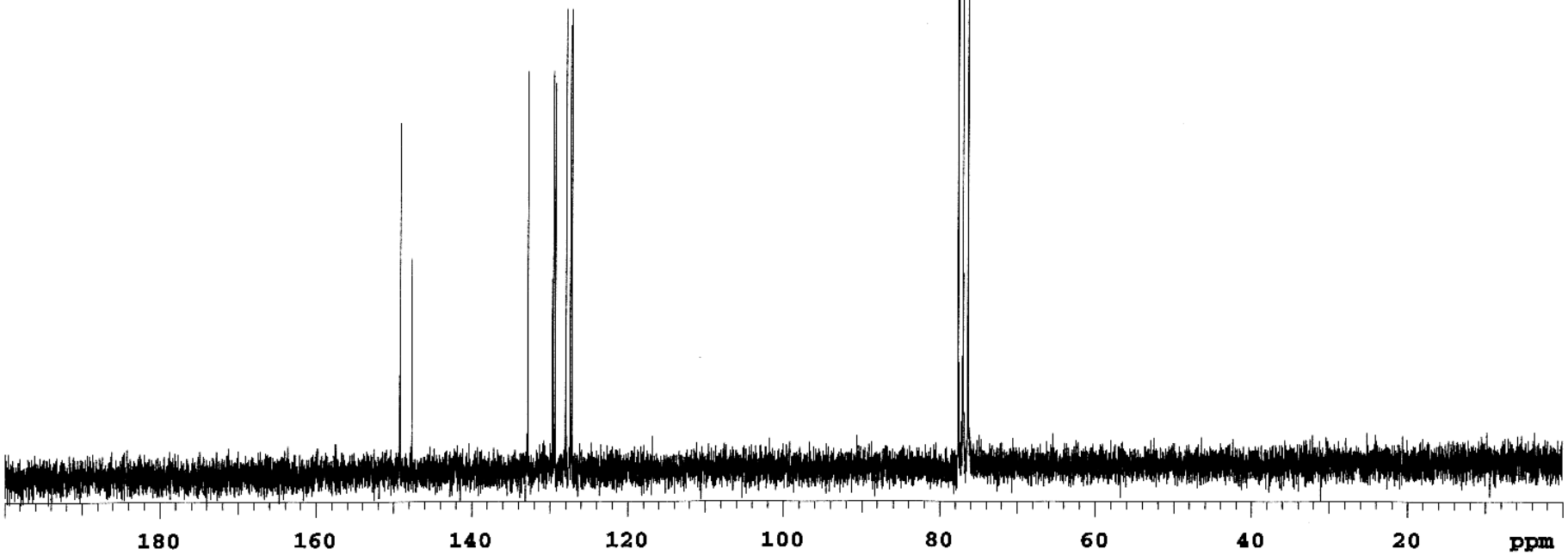

1H NMR
N
N
(10)
10
9
8
7
6
5
4
3
2
1
0 ppm
1.90
1.96
2.02
2.00
1.93
2.02
2.07

$^{13}C\{^{1}H\}$ NMR



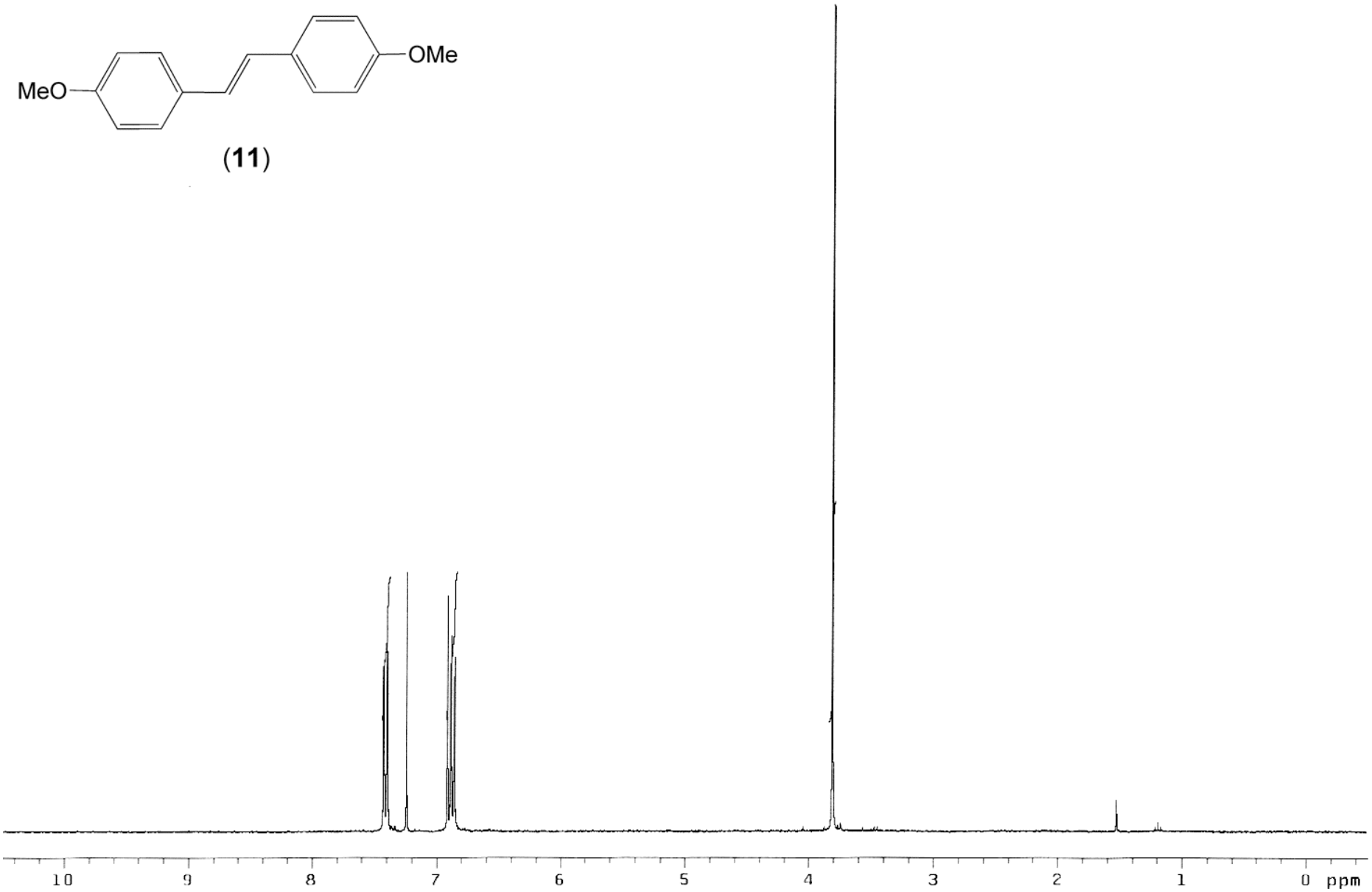
(10)

INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	149.160	7501.237	0.8
2	147.665	7426.041	0.5
3	132.788	6677.921	0.9
4	129.653	6520.241	0.4
5	129.546	6514.870	0.9
6	129.302	6502.593	0.9
7	127.967	6435.454	0.3
8	127.898	6432.001	1.0
9	127.357	6404.762	1.0
10	127.158	6394.787	1.0
11	77.625	3903.740	2.2
12	76.991	3871.897	2.3
13	76.358	3840.053	2.2



^{1}H NMR

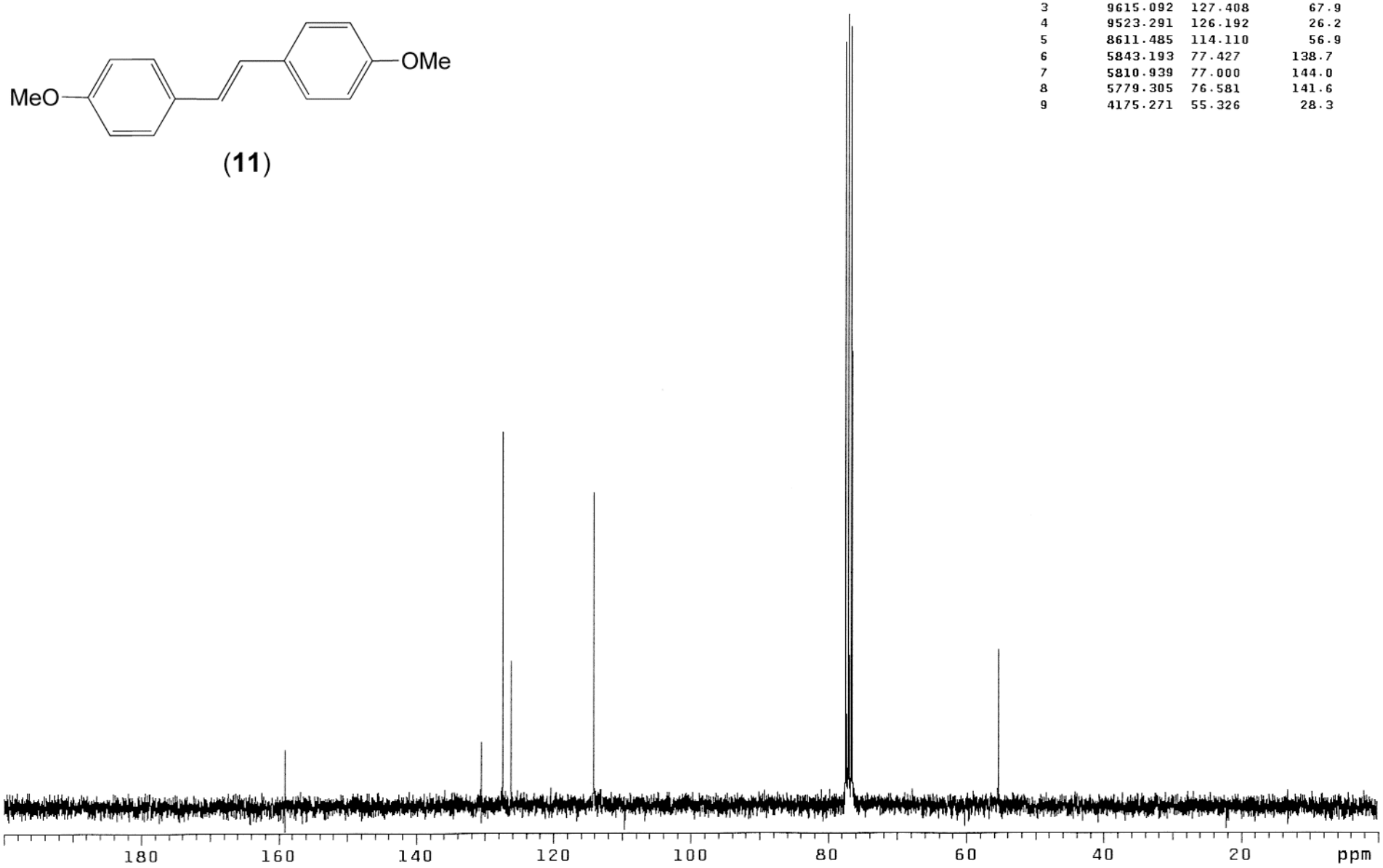
(**11**)



$^{13}C\{^{1}H\}$ NMR

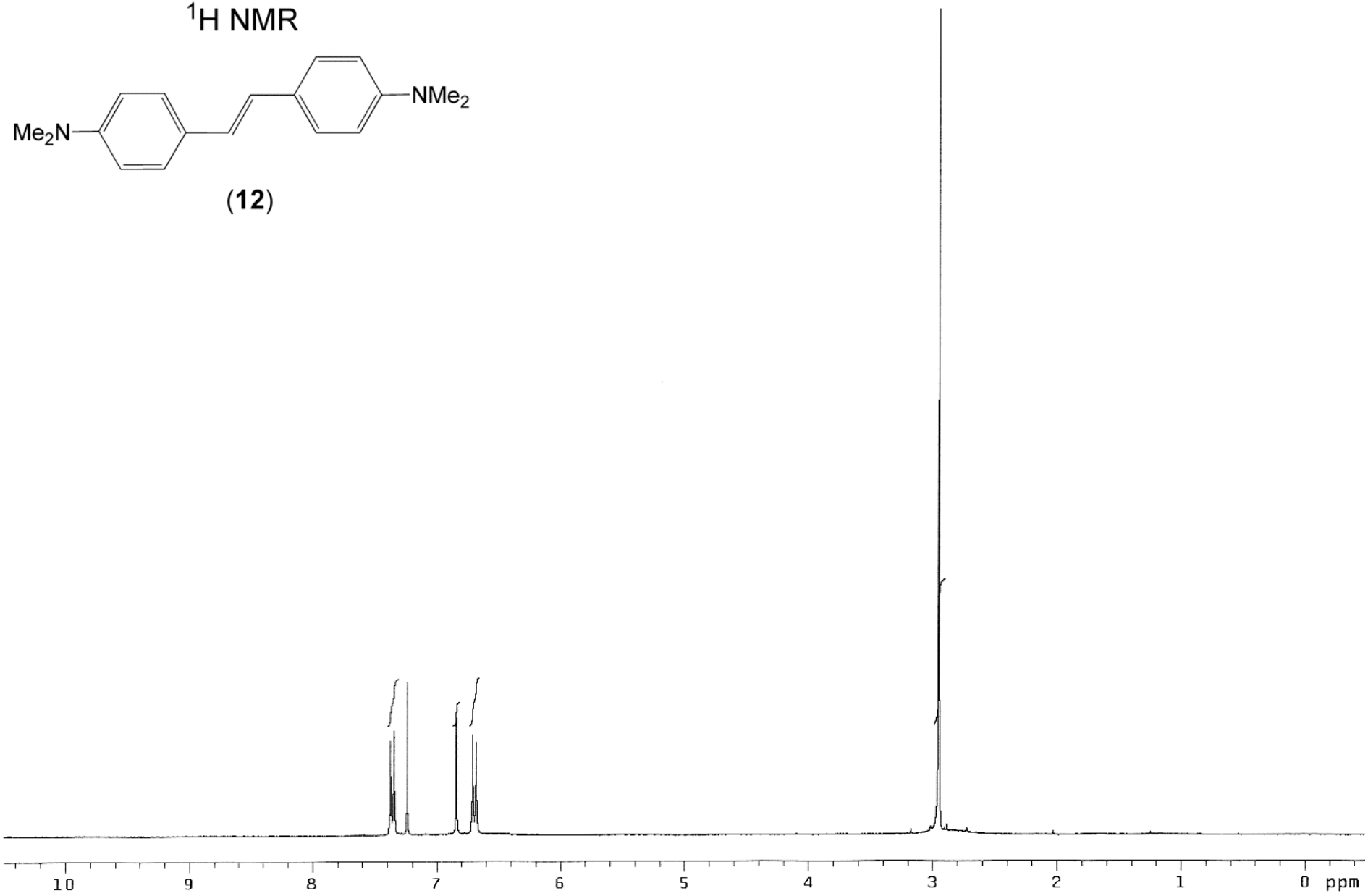
(**11**)

INDEX	FREQUENCY	PPM	HEIGHT
1	12000.673	159.019	10.2
2	9848.936	130.507	11.5
3	9615.092	127.408	67.9
4	9523.291	126.192	26.2
5	8611.485	114.110	56.9
6	5843.193	77.427	138.7
7	5810.939	77.000	144.0
8	5779.305	76.581	141.6
9	4175.271	55.326	28.3

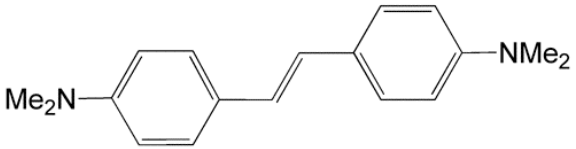


^{1}H NMR

(**12**)

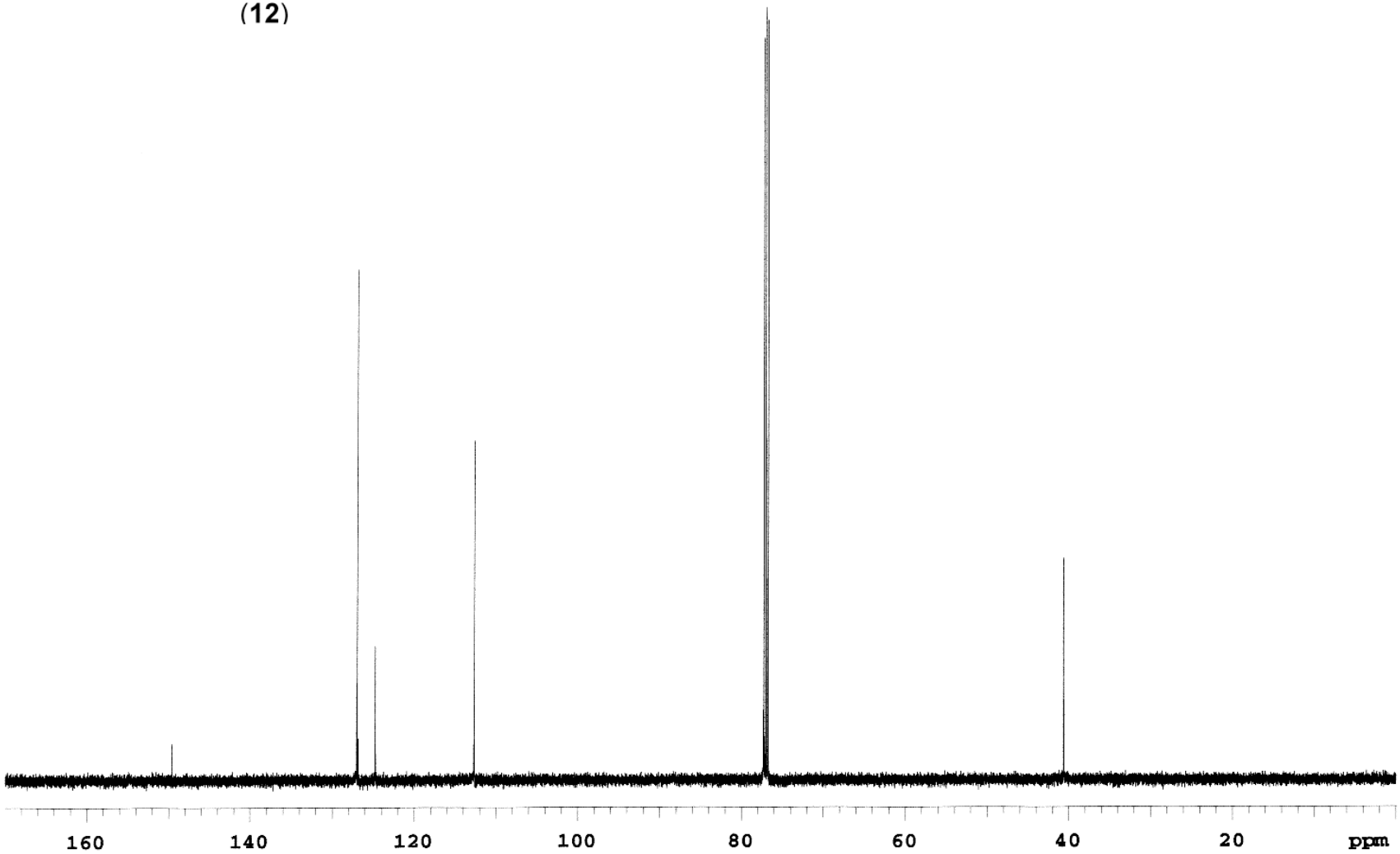


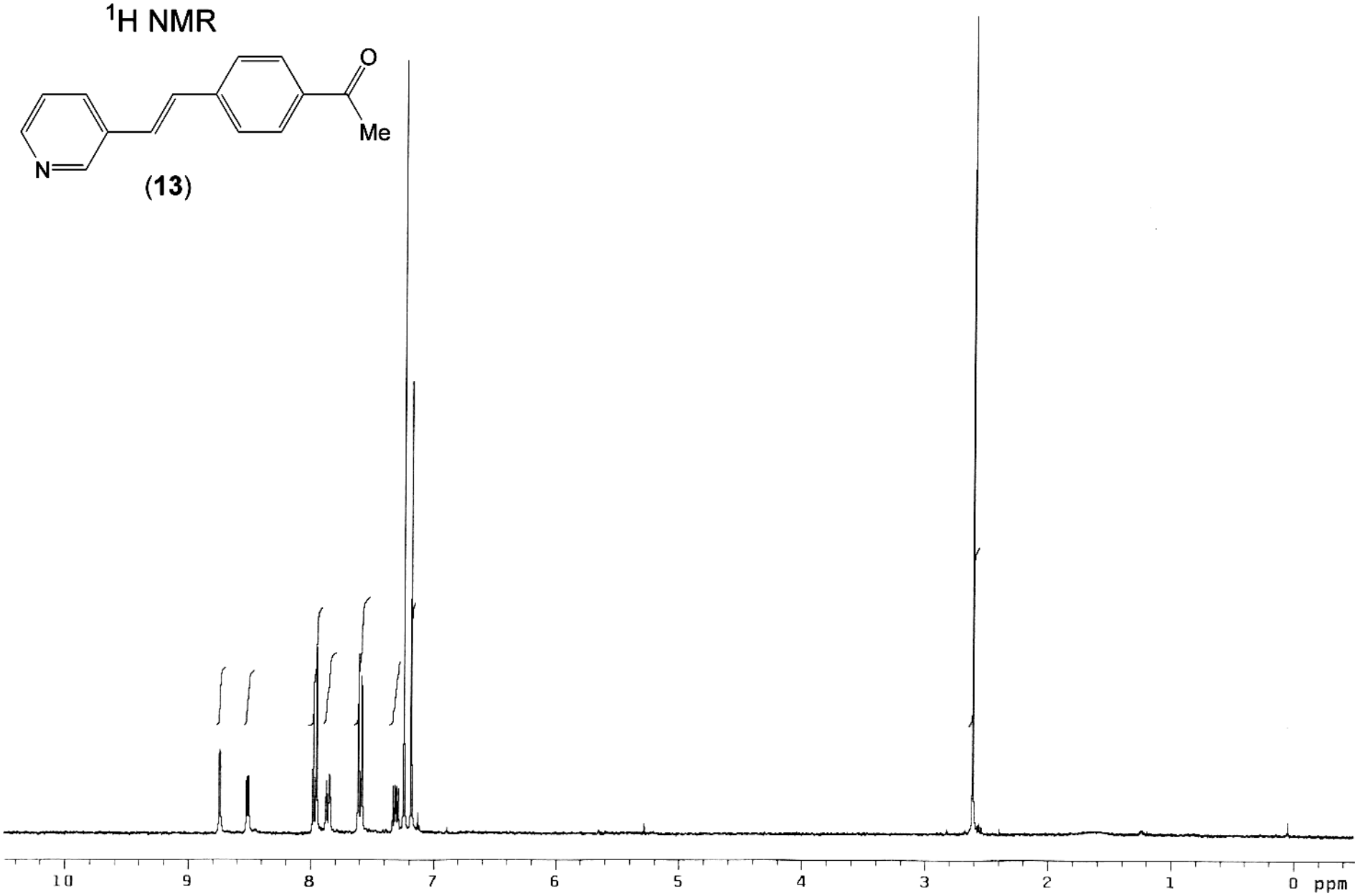
$^{13}C\{^{1}H\}$ NMR



(**12**)

INDEX	FREQUENCY	PPM	HEIGHT
1	18801.073	149.631	6.6
2	15955.471	126.984	91.8
3	15938.427	126.848	7.6
4	15675.456	124.755	24.3
5	14156.882	112.670	61.2
6	9706.672	77.252	133.2
7	9674.613	76.997	138.7
8	9642.553	76.742	136.4
9	5101.846	40.604	40.0

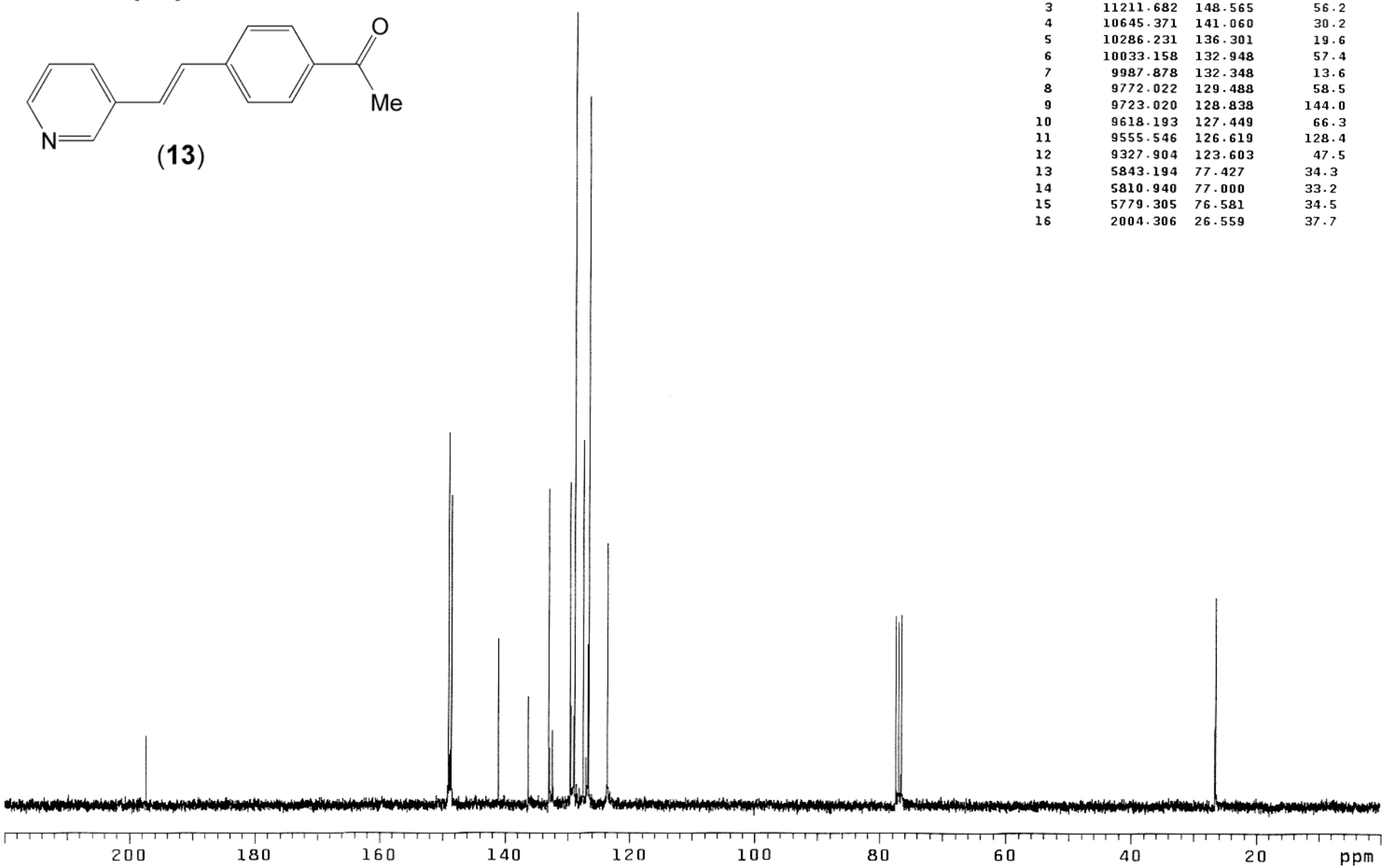


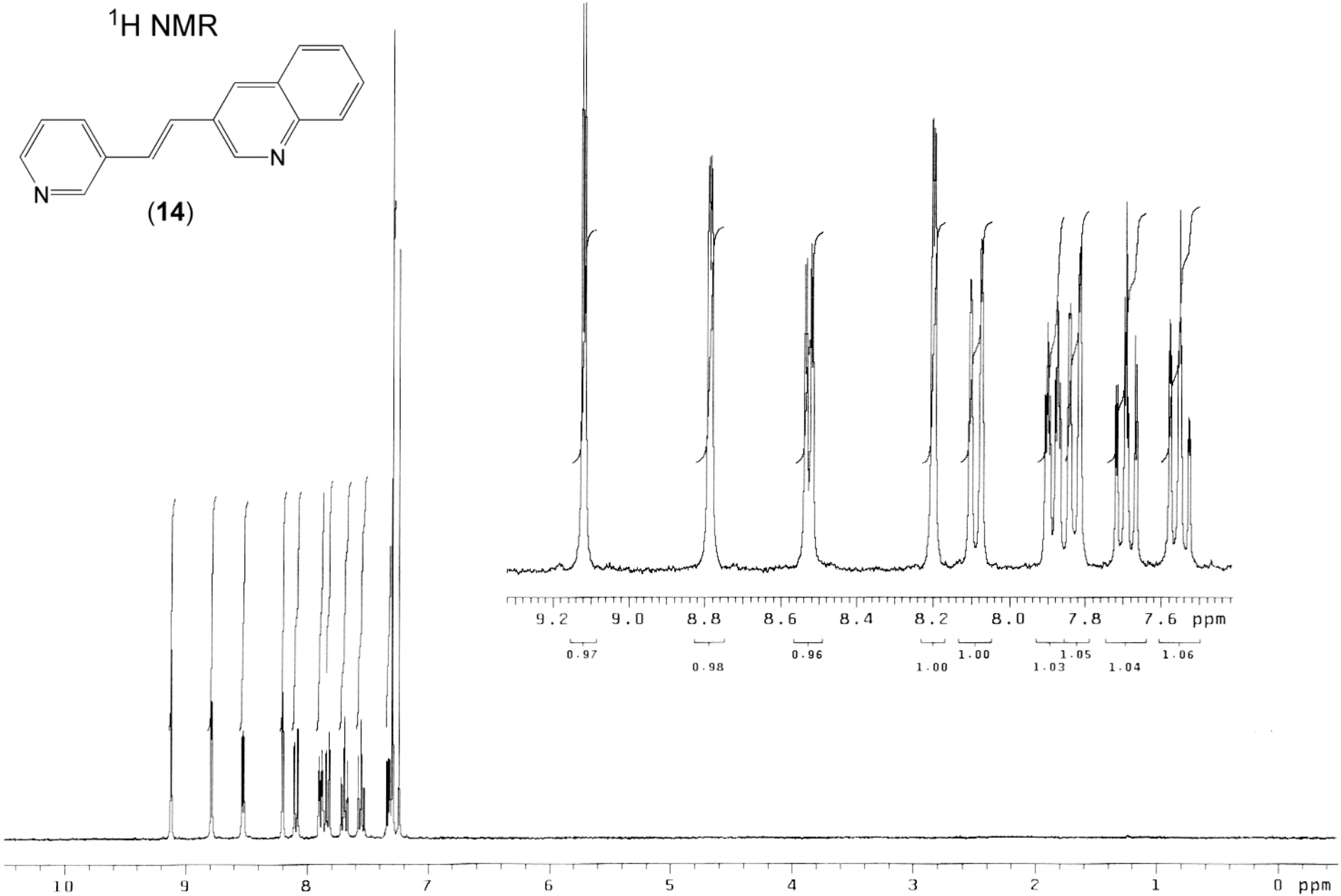

1H NMR
O
Me
N
(13)
10
9
8
7
6
5
4
3
2
1
0 ppm

$^{13}C\{^{1}H\}$ NMR

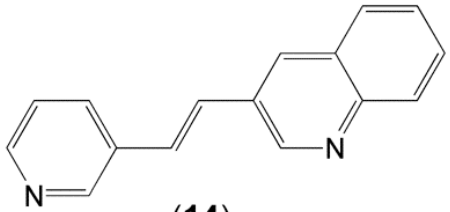
(**13**)

INDEX	FREQUENCY	PPM	HEIGHT
1	14893.020	197.345	12.5
2	11239.595	148.934	67.5
3	11211.682	148.565	56.2
4	10645.371	141.060	30.2
5	10286.231	136.301	19.6
6	10033.158	132.948	57.4
7	9987.878	132.348	13.6
8	9772.022	129.488	58.5
9	9723.020	128.838	144.0
10	9618.193	127.449	66.3
11	9555.546	126.619	128.4
12	9327.904	123.603	47.5
13	5843.194	77.427	34.3
14	5810.940	77.000	33.2
15	5779.305	76.581	34.5
16	2004.306	26.559	37.7



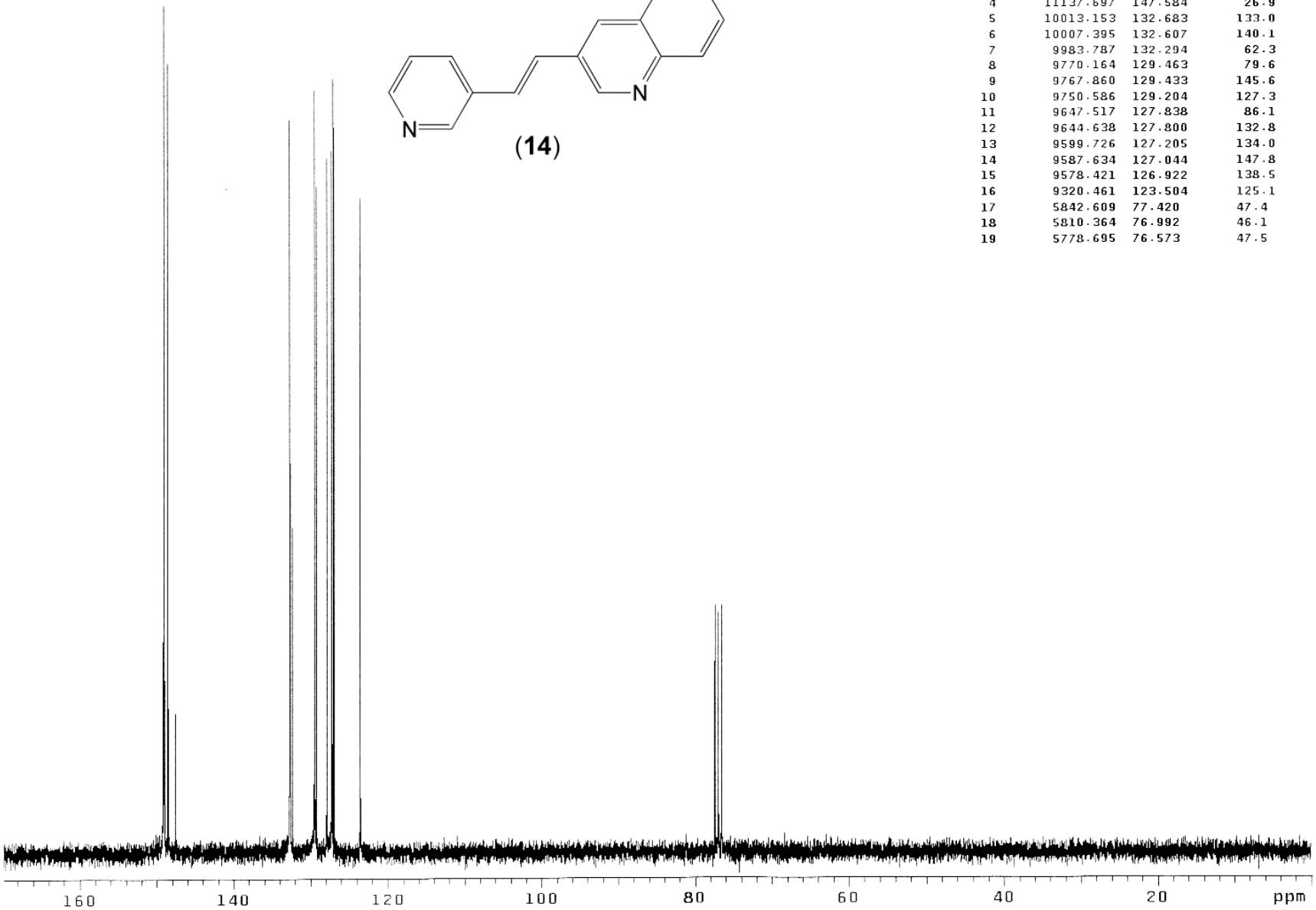

1H NMR
N
N
(14)
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm
0.97
0.98
0.96
1.00
1.00
1.03
1.05
1.04
1.06
10
9
8
7
6
5
4
3
2
1
0
ppm

$^{13}C\{^{1}H\}$ NMR



(**14**)

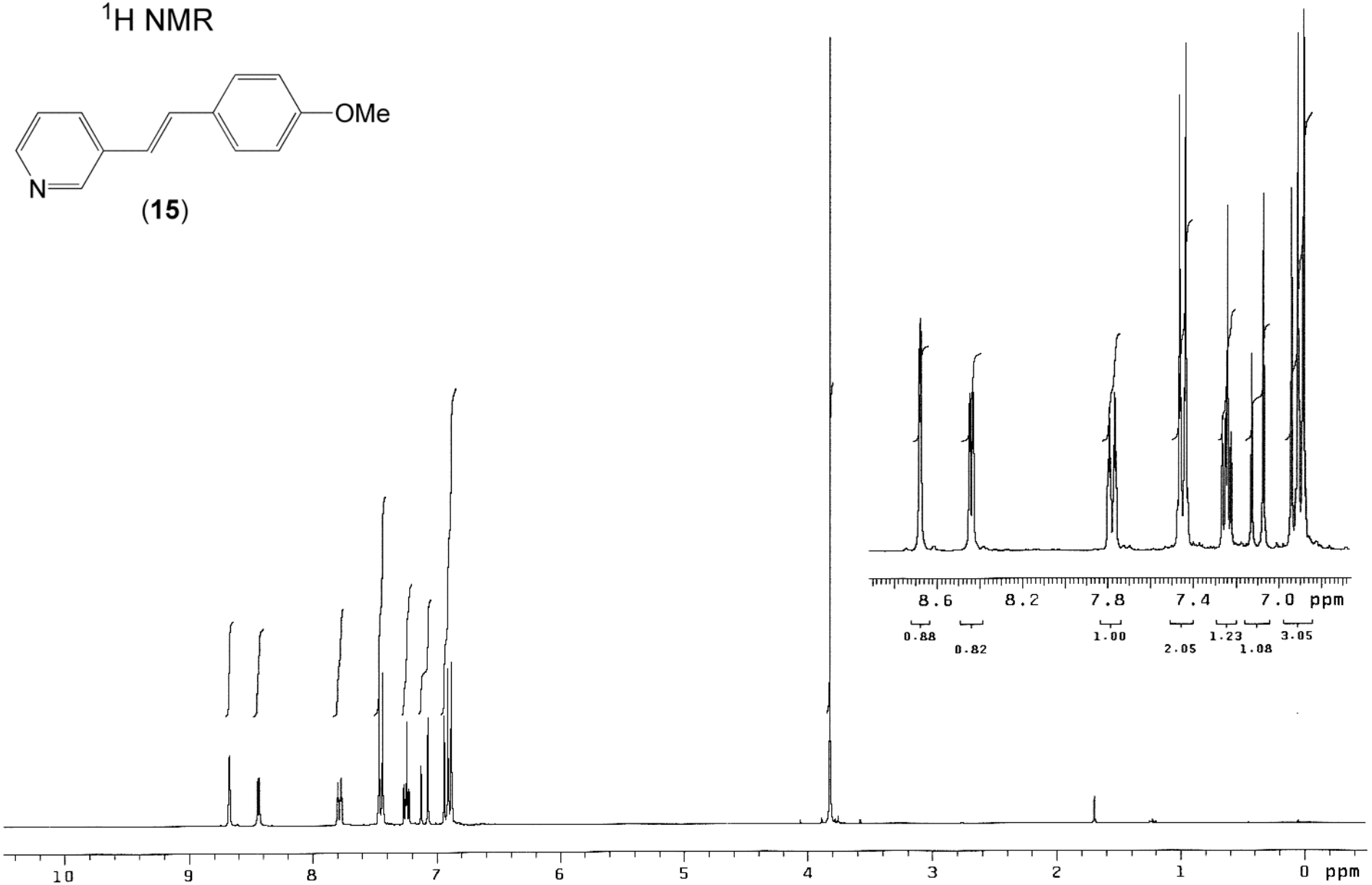
INDEX	FREQUENCY	PPM	HEIGHT
1	11251.706	149.095	162.0
2	11244.796	149.003	148.7
3	11210.248	148.546	150.9
4	11137.697	147.584	26.9
5	10013.153	132.683	133.0
6	10007.395	132.607	140.1
7	9983.787	132.294	62.3
8	9770.164	129.463	79.6
9	9767.860	129.433	145.6
10	9750.586	129.204	127.3
11	9647.517	127.838	86.1
12	9644.638	127.800	132.8
13	9599.726	127.205	134.0
14	9587.634	127.044	147.8
15	9578.421	126.922	138.5
16	9320.461	123.504	125.1
17	5842.609	77.420	47.4
18	5810.364	76.992	46.1
19	5778.695	76.573	47.5



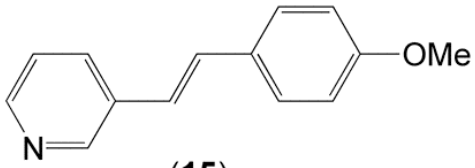
^{1}H NMR

OMe
N

(**15**)

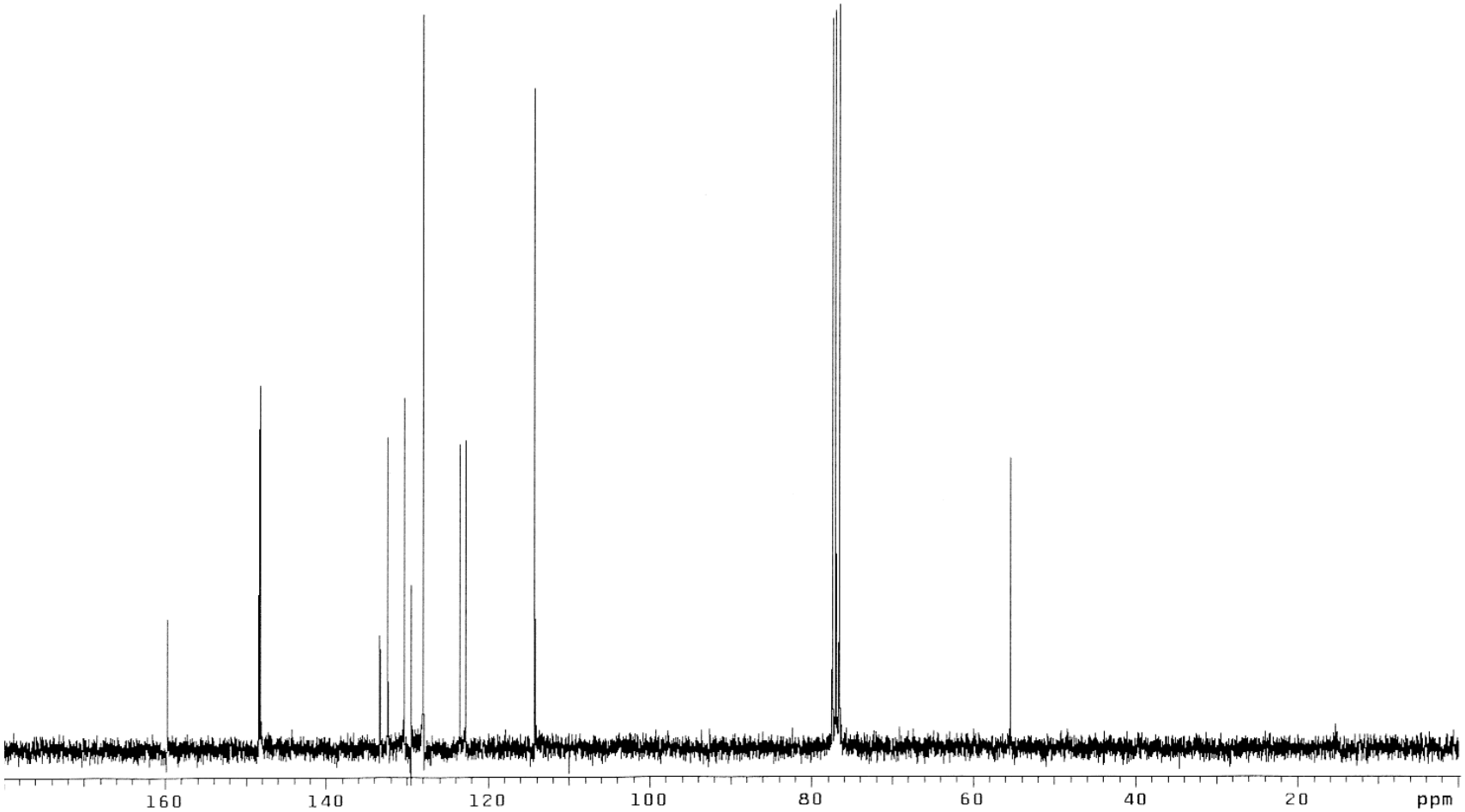

8.6
8.2
7.8
7.4
7.0 ppm
0.88
0.82
1.00
2.05
1.23
1.08
3.05
10
9
8
7
6
5
4
3
2
1
0 ppm

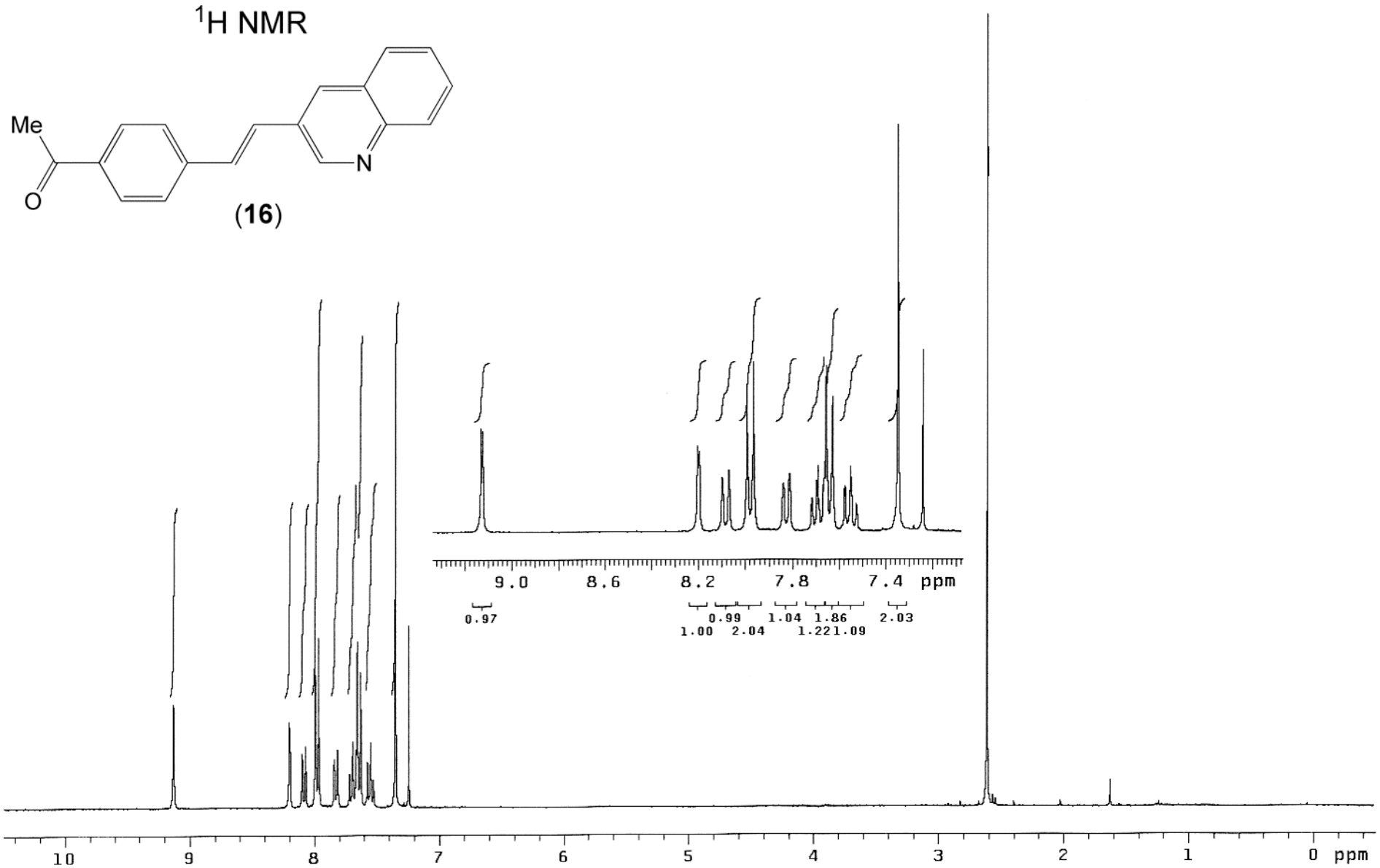
$^{13}C\{^{1}H\}$ NMR



(**15**)

INDEX	FREQUENCY	PPM	HEIGHT
1	12054.999	159.739	22.5
2	11195.900	148.355	55.0
3	11182.081	148.172	62.5
4	10059.840	133.302	19.6
5	9986.713	132.333	53.5
6	9834.701	130.318	60.2
7	9770.211	129.464	28.3
8	9654.475	127.930	125.8
9	9317.630	123.467	52.3
10	9261.777	122.727	53.0
11	8620.332	114.227	113.2
12	5842.657	77.420	125.1
13	5810.987	77.001	126.5
14	5778.742	76.573	127.5
15	4175.706	55.332	50.0

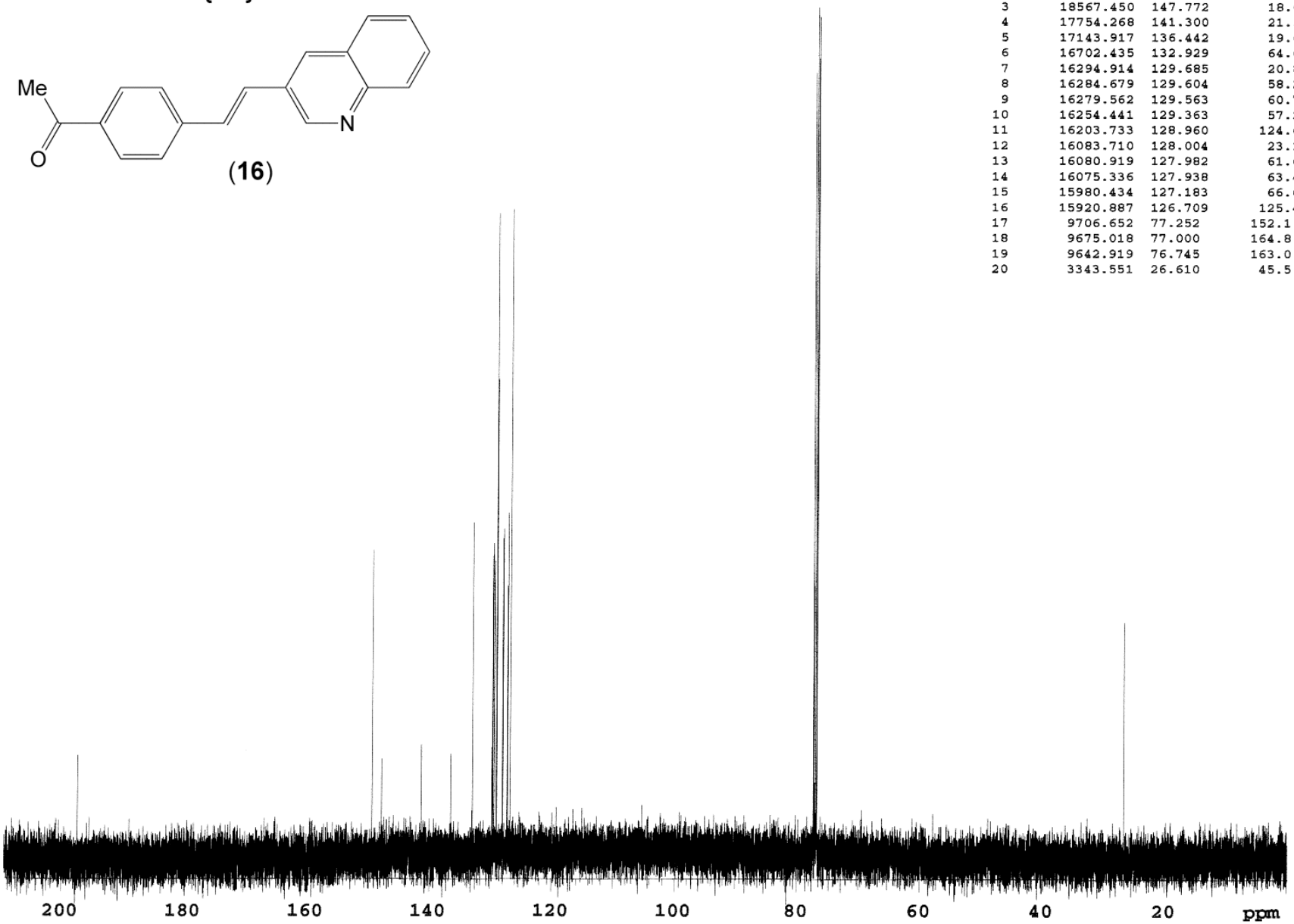



1H NMR
Me
O
N
(16)
9.0
8.6
8.2
7.8
7.4
ppm
0.97
1.00
0.99
2.04
1.04
1.86
1.22
1.09
2.03
10
9
8
7
6
5
4
3
2
1
0
ppm

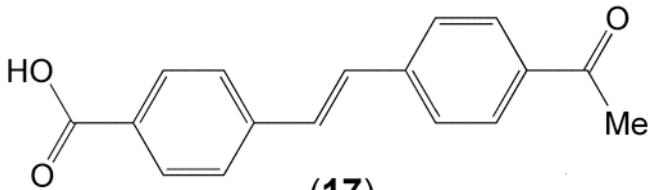
$^{13}C\{^{1}H\}$ NMR

(**16**)

INDEX	FREQUENCY	PPM	HEIGHT
1	24800.293	197.377	19.2
2	18762.837	149.327	59.2
3	18567.450	147.772	18.6
4	17754.268	141.300	21.5
5	17143.917	136.442	19.6
6	16702.435	132.929	64.6
7	16294.914	129.685	20.8
8	16284.679	129.604	58.2
9	16279.562	129.563	60.7
10	16254.441	129.363	57.2
11	16203.733	128.960	124.6
12	16083.710	128.004	23.1
13	16080.919	127.982	61.6
14	16075.336	127.938	63.4
15	15980.434	127.183	66.6
16	15920.887	126.709	125.4
17	9706.652	77.252	152.1
18	9675.018	77.000	164.8
19	9642.919	76.745	163.0
20	3343.551	26.610	45.5

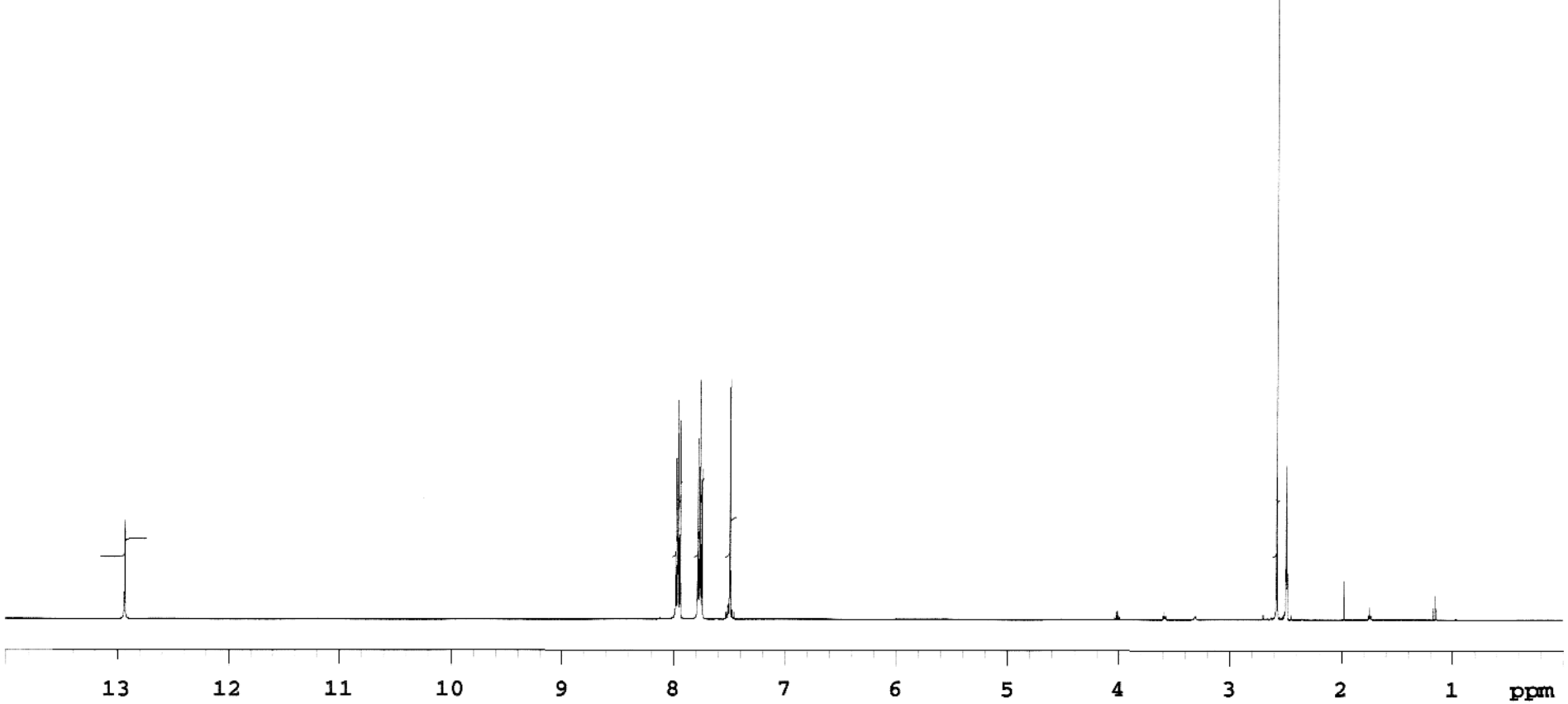


^{1}H NMR

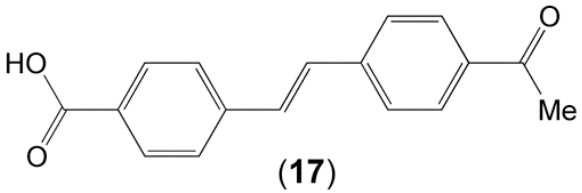


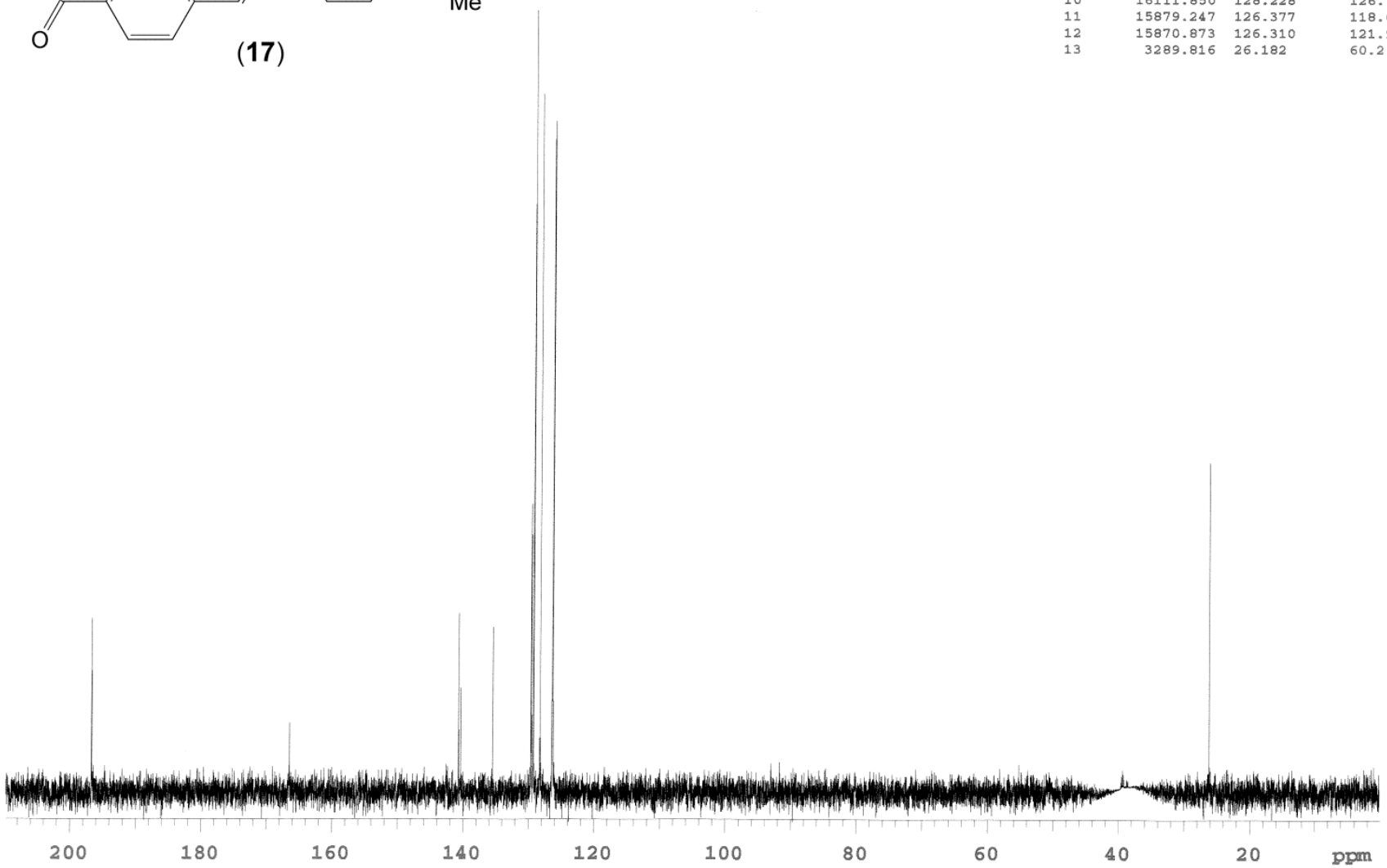
(**17**)

INDEX	FREQUENCY	PPM	HEIGHT
1	6463.302	12.934	15.9
2	3986.439	7.978	25.8
3	3979.592	7.964	11.8
4	3977.880	7.961	35.1
5	3975.924	7.957	29.7
6	3974.212	7.953	9.9
7	3969.321	7.943	10.1
8	3967.610	7.940	32.0
9	3888.626	7.782	29.1
10	3879.578	7.764	38.4
11	3877.622	7.760	11.4
12	3870.775	7.746	24.1
13	3745.086	7.495	38.5
14	3744.108	7.493	37.3
15	1287.296	2.576	144.0
16	1246.214	2.494	17.9
17	1244.258	2.490	24.7
18	1242.546	2.487	16.6



$^{13}C\{^{1}H\}$ NMR



(**17**)

INDEX	FREQUENCY	PPM	HEIGHT
1	24720.040	196.737	31.7
2	20919.299	166.488	12.7
3	17680.528	140.712	32.7
4	17637.729	140.372	19.2
5	17019.934	135.455	30.3
6	16285.838	129.612	52.6
7	16276.534	129.538	16.8
8	16244.900	129.287	57.9
9	16240.248	129.250	141.9
10	16111.850	128.228	126.7
11	15879.247	126.377	118.6
12	15870.873	126.310	121.9
13	3289.816	26.182	60.2