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Supporting Information

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Silver-Catalyzed Transmetalation between Chlorosilanes and Aryl and Alkenyl Grignard Reagents for Synthesis of Tetraorganosilanes

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Instrumentation and Chemicals

^{1}H NMR (300 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian Mercury 300 and UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to $SiMe_4$ at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. $AgNO_3$ was purchased from Wako Pure Chemical Industries, Ltd. Arylmagnesium bromide was prepared from magnesium turnings (Nacalai Tesque, Inc.) and the corresponding bromoarene in THF. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Chlorosilanes were purchased from Shin-Etsu Chemical Co., Ltd. and Tokyo Chemical Industry Co., Ltd. The starting material **6**[1] was prepared according to the literature.

[1] Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, 86, 3271–3276.

Experimental Section

Typical procedure for silver-catalyzed reactions: The reaction of **1a** with 4-methylphenylmagnesium bromide (Table 1, entry 2) is representative. $AgNO_3$ (4.2 mg, 0.025 mmol) was placed in a 20-mL reaction flask under argon. Chlorodimethylphenylsilane (85 mg, 0.50 mmol) in THF (5 mL) was added to the flask. Then, 4-methylphenylmagnesium bromide (1.0 M THF solution, 0.75 mL, 0.75 mmol) was added. The mixture was stirred at 20 ˚C for 1.5 h. A saturated aqueous solution of NH_4Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na_2SO_4 and concentrated in vacuo. Chromatographic purification on silica gel by using hexane as an eluent afforded dimethyl(4-methylphenyl)phenylsilane (**2a**, 104 mg, 0.46 mmol) in 92% yield.

Typical procedure for large scale reaction (Table 3, entry 5): $AgNO_3$ (425 mg, 2.5 mmol) was placed in a 300-mL reaction flask under argon, and THF (50 mL) was then added. Chloro(chloromethyl)dimethylsilane (7.15 g, 50 mmol) in THF (50 mL) was added to the flask. The flask was cooled to 0 ˚C. Phenylmagnesium bromide (1.0 M THF solution, 75 mL, 75 mmol) was subsequently added over 0.5 h. After the completion of the addition, the mixture was warmed to 20 ˚C and stirred at the same temperature for 3 h. The reaction mixture was quenched with a ice-cold saturated aqueous solution of NH_4Cl (50 mL). The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na_2SO_4 and concentrated in vacuo. After evaporation, the residue was distilled to give (chloromethyl)dimethylphenylsilane (**3e'**, 7.3 g, 40 mmol, bp 90 ˚C at 9 mmHg) in 79% yield.

Typical procedure for synthesis of diaryldimethylsilanes:

Dichlorodimethylsilane (65 mg, 0.5 mmol) was placed in a 20-mL reaction flask under argon in THF (5 mL). The flask was cooled to –20 ˚C. 4-Methylphenylmagnesium bromide (1.0 M THF solution, 0.6 mL, 0.6 mmol) was slowly introduced to the flask. The reaction mixture was stirred for 5 h at –20 ˚C. After being stirred, 4-methoxyphenylmagnesium bromide (1.0 M THF solution, 0.7 mmol, 0.7 mL) and $AgNO_3$ (4.2 mg, 0.025 mmol) were sequentially added at the same temperature. The mixture was stirred for 13 h at –20 ˚C. A saturated aqueous solution of NH_4Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na_2SO_4 and concentrated in vacuo. Chromatographic purification on silica gel by using hexane / ethyl acetate = 20 : 1 as an eluent afforded (4-methoxyphenyl)dimethyl(4-methylphenyl)silane (**4**, 114 mg, 0.45 mmol) in 89% yield.

Characterization Data of Products

Products **2b**[2]**, 2d**[3]**,** and **3e'**[4] are known compounds and showed the identical spectra according to the literature.

Dimethyl(4-methylphenyl)phenylsilane (2a): oil. IR (neat) 3041, 2959, 1605, 1427, 1106, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57 (s, 6H), 2.38 (s, 3H), 7.20–7.57 (m, 9H) ; ^{13}C NMR ($CDCl_3$) δ –2.13, 21.66, 127.96, 128.84, 129.20, 134.34, 134.42, 134.72, 138.68, 139.17; Found: C, 79.61; H, 8.09%. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01%.

(4-Fluorophenyl)dimethylphenylsilane (2c): oil. IR (neat) 2958, 1895, 1588, 1499, 1104 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 6H), 7.05–7.11 (m, 2H), 7.38–7.56 (m, 7H) ; ^{13}C NMR ($CDCl_3$) δ –2.11, 115.15 (d, J = 19.6 Hz) , 128.06, 129.41, 133.89 (d, J = 3.4 Hz), 134.29, 136.28 (d, J = 7.1 Hz), 138.14, 163.94 (d, J = 247 Hz); Found: C, 72.96; H, 6.83%. Calcd for $C_{14}H_{15}FSi$: C, 73.00; H, 6.56%.

Dimethylphenyl(4-triisopropylsiloxy)silane (2e): oil. IR (neat) 2946, 1591, 1501, 1273, 1112, 814 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.51 (s, 6H), 1.10 (d, J = 6.9 Hz, 18H), 1.09–1.31 (m, 3H), 6.85–6.87 (m, 2H), 7.31–7.37 (m, 5H), 7.48–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.98, 12.88, 18.12, 119.66, 127.90, 129.11, 129.37, 134.34, 135.75, 139.07, 157.25; HRMS Found: 384.2307 (Δ = 0.5 ppm), Calcd for $C_{23}H_{36}OSi_2$: 384.2305.

Dimethyl(2-methylphenyl)phenylsilane (2f): oil. IR (neat) 2959, 2230, 1599, 1385, 1109, 818 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 6H), 2.26 (s, 3H), 7.12–7.50 (m, 9H); ^{13}C NMR ($CDCl_3$) δ –1.21, 23.34, 125.10, 128.00, 129.10, 129.77, 130.04, 134.16, 135.54, 136.32, 139.13, 144.28; Found: C, 79.80; H, 8.29%. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01%.

(3-Trifluoromethylphenyl)dimethylphenylsilane (2g): oil. IR (neat) 1600, 1429, 1327, 1119, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.61 (s, 6H), 7.36–7.86 (m, 9H); ^{13}C NMR ($CDCl_3$) δ –2.38, 124.57 (q, J = 271 Hz), 126.03 (q, J = 3.8 Hz), 128.19, 128.25, 129.65, 130.19 (q, J = 32 Hz), 130.58 (q, J = 3.8 Hz), 131.68 (q, J = 32 Hz), 134.30, 137.74, 139.99; Found: C, 64.27; H, 5.12%. Calcd for $C_{15}H_{15}F_3Si$: C, 64.26; H, 5.39%.

1-Trimethylsilyl-1-dimethylphenylsilylethene (2h): oil. IR (neat) 2956, 1428, 1249, 1111, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.40 (s, 6H), 6.33 (d, J = 4.8 Hz, 1H), 6.42 (d, J = 4.8 Hz, 1H), 7.34–7.37 (m, 3H), 7.48–7.51(m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.56, –0.14, 127.79, 128.97, 134.24, 139.26, 142.07, 152.91; Found: C, 66.30; H, 9.24%. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46%.

Methyl(4-methylphenyl)diphenylsilane (3a): oil. IR (neat) 3068, 1600, 1428, 1110, 788 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3H), 2.35 (s, 3H), 7.16–7.52 (m, 14H); ^{13}C NMR ($CDCl_3$) δ –2.13, 21.71, 128.00, 128.90, 129.49, 132.58, 135.44, 135.52, 136.55, 139.51; Found: C, 83.15; H, 7.01%. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99%.

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[2] Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2006**, 128, 8152–8153.

[3] Yamanoi, Y. *J. Org. Chem.* **2005**, 70, 9607–9609.

[4] Commercially available from Shin-Etsu Chemical Co., Ltd.

Triethyl(4-methylphenyl)silane (3b): oil. IR (neat) 2954, 1605, 1459, 1105, 711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–0.81 (m, 6H), 0.92–0.98 (m, 9H), 2.34 (s, 3H), 7.15–7.18 (m, 2H), 7.37–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 3.57, 7.61, 21.65, 128.71, 133.86, 134.42, 138.66; Found: C, 75.38; H, 10.94%. Calcd for $C_{13}H_{22}Si$: C, 75.65; H, 10.74%.

Allyldimethyl(4-methylphenyl)silane (3c): oil. IR (neat) 2957, 1634, 1248, 1107, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 6H), 1.74 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H), 4.81–4.89 (m, 2H), 5.70–5.85 (m, 1H), 7.16–7.19 (m, 2H), 7.40–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.23, 21.64, 23.96, 113.44, 128.77, 133.85, 134.95, 135.16, 139.04; Found: C, 75.48; H, 9.71%. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53%.

(4-Methylphenyl)diphenylvinylsilane (3d): oil. IR (neat) 3064, 1599, 1428, 1110, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 5.79 (dd, J = 3.6 Hz, 20.1 Hz, 1H), 6.30 (dd, J = 3.6 Hz, 14.4 Hz, 1H), 6.68 (dd, J = 14.4 Hz, 20.1 Hz, 1H), 7.17–7.54 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 21.74, 128.01, 128.93, 129.67, 130.60, 134.22, 134.60, 136.11, 136.18, 136.82, 139.71; Found: C, 84.01; H, 6.68%. Calcd for $C_{21}H_{20}Si$: C, 83.94; H, 6.71%.

(4-Methoxyphenyl)dimethyl(4-methylphenyl)silane (4): oil. IR (neat) 2956, 1595, 1502, 1278, 1113, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (s, 6H), 2.34 (s, 3H), 3.80 (s, 3H), 6.88–6.91 (m, 2H), 7.15–7.18 (m, 2H), 7.39–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –1.92, 21.65, 55.20, 113.74, 128.81 129.45, 134.38, 135.16, 135.81, 139.07, 160.62; HRMS Found: 256.1286 (Δ = 1.0 ppm), Calcd for $C_{16}H_{20}OSi$: 256.1283.

5-[Methyl(4-methylphenyl)phenylsilyl]-1-pentene (5a): oil. IR (neat) 2923, 1639, 1428, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (s, 3H), 1.03–1.08 (m, 2H), 1.42–1.52 (m, 2H), 2.08 (q, J = 6.6 Hz, 2H), 2.34 (s, 3H), 4.91–5.00 (m, 2H), 5.70–5.83 (m, 1H), 7.39–7.74 (m, 9H); ^{13}C NMR ($CDCl_3$) δ –4.19, 14.01, 21.67, 23.51, 37.78, 114.87, 127.94, 128.84, 129.20, 133.76, 134.63, 134.70, 137.77, 138.90, 139.16

2-Methyl-6-methyl(4-methylphenyl)phenylsilyl-2-hexene (5b): oil. IR (neat) 2923, 1603, 1427, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.51 (s, 3H), 1.02–1.08 (m, 2H), 1.35–1.49 (m, 2H), 1.56 (s, 3H), 1.67 (s, 3H), 2.00 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 5.08 (t, J = 7.2 Hz, 1H), 7.15–7.17 (m, 2H), 7.31–7.51 (m, 7H); ^{13}C NMR ($CDCl_3$) δ –4.16, 14.21, 17.94, 21.67, 24.33, 25.93, 32.09, 124.70, 127.92, 128.82, 129.15, 131.79, 133.90, 134.64, 134.71, 137.91, 139.10; HRMS Found: 308.1958 (Δ = –0.7 ppm), Calcd for $C_{21}H_{28}Si$: 308.1960.

(4-methoxyphenyl)methyl(1-naphthyl)phenylsilane (7): oil. IR (neat) 2854, 1591, 1458, 1377, 1107, 783 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (s, 3H), 3.80 (s, 3H), 6.89–6.91 (m, 2H), 7.23–7.54 (m, 11H), 7.84–7.92 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –1.65, 55.18, 113.91, 125.29, 125.58, 125.81, 127.40, 128.09, 129.07, 129.27, 129.45, 130.61, 133.62, 134.49, 135.47, 136.68, 137.00, 137.16, 137.34, 160.83; HRMS Found: 354.1437 (Δ = –0.9 ppm), Calcd for $C_{24}H_{22}OSi$: 354.1140.

Figure S1. ^{1}H NMR spectrum of **2b**.

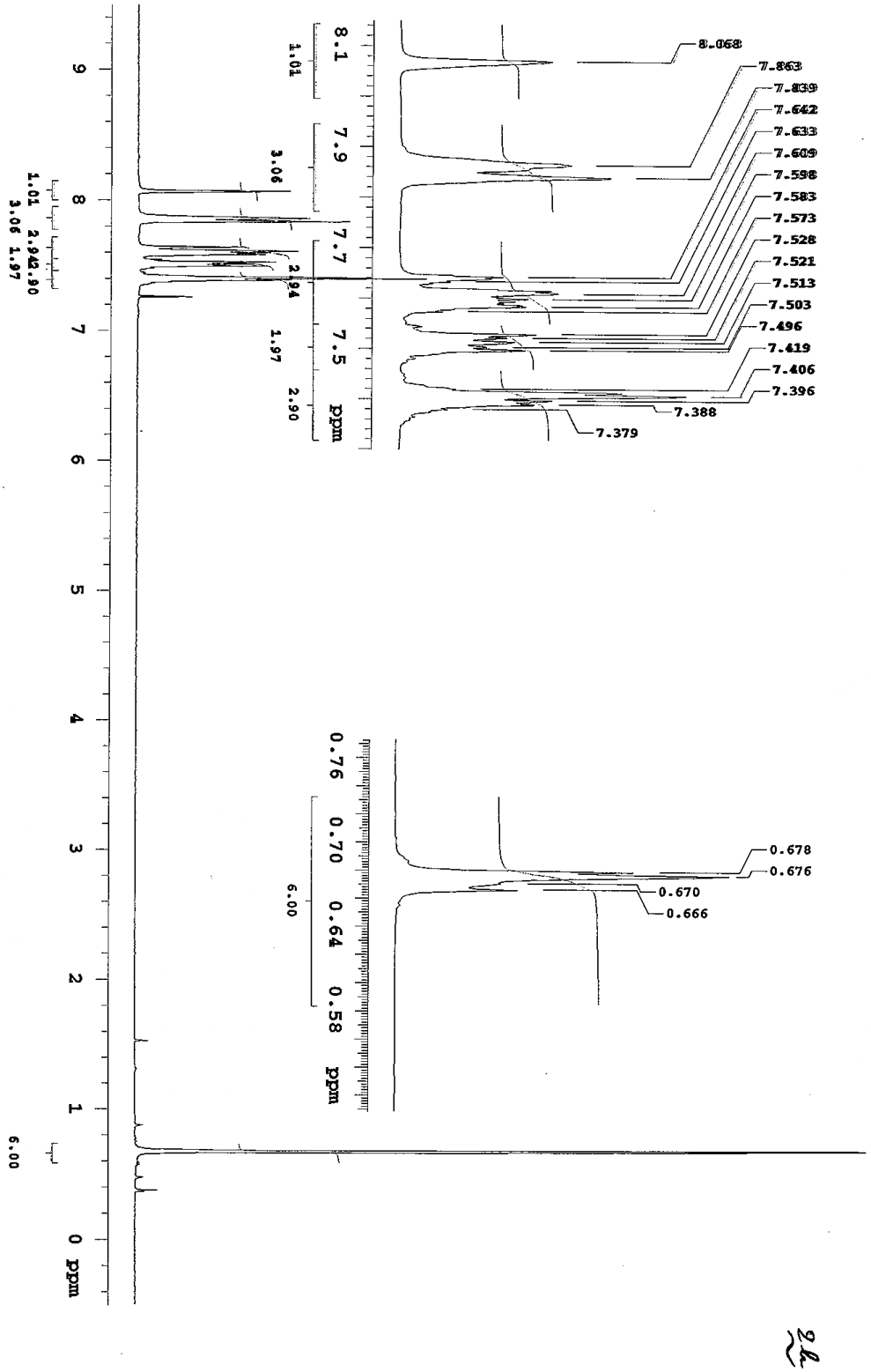


Figure S2. ^{13}C NMR spectrum of **2b**.

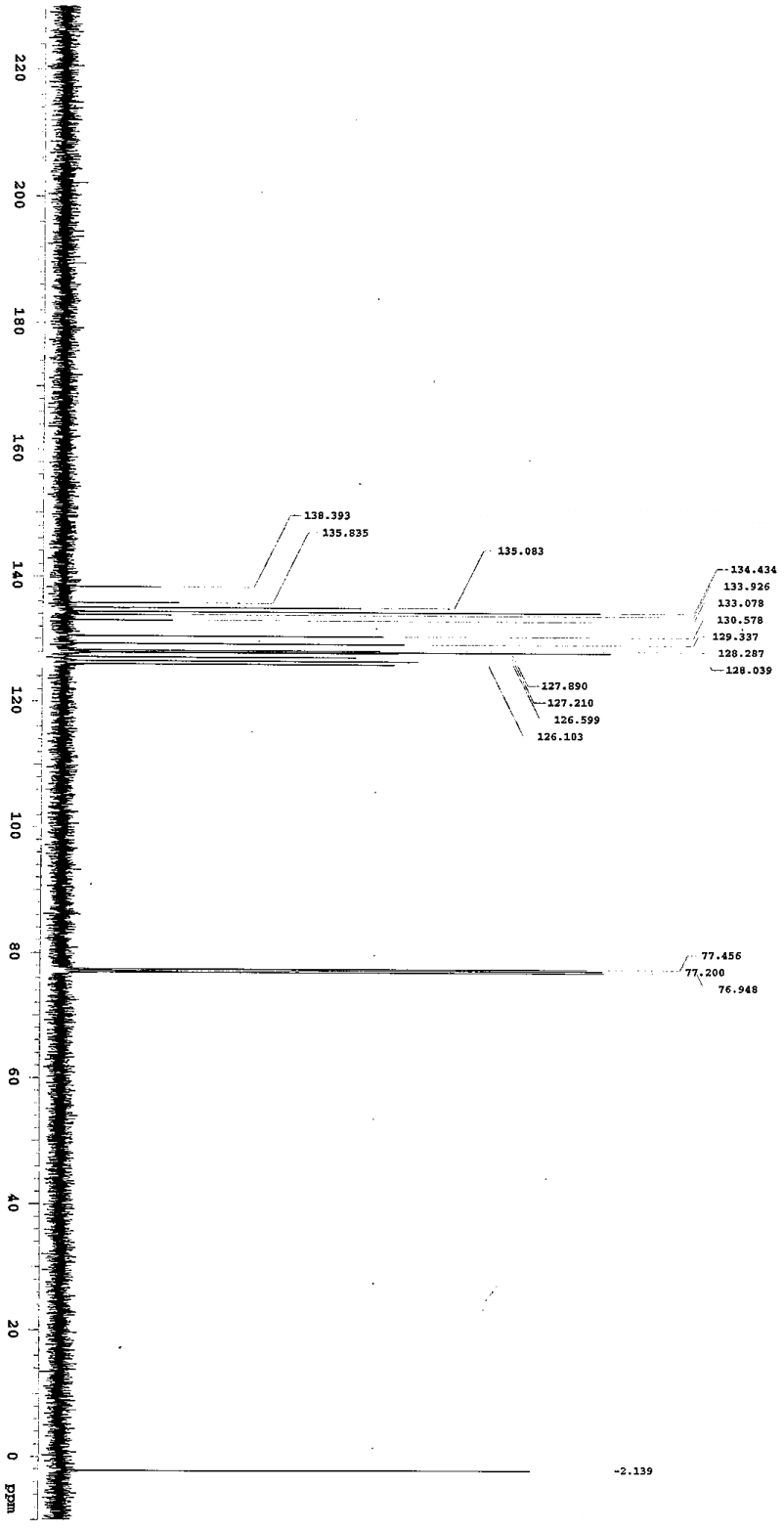


Figure S3. ^{1}H NMR spectrum of **2d**.

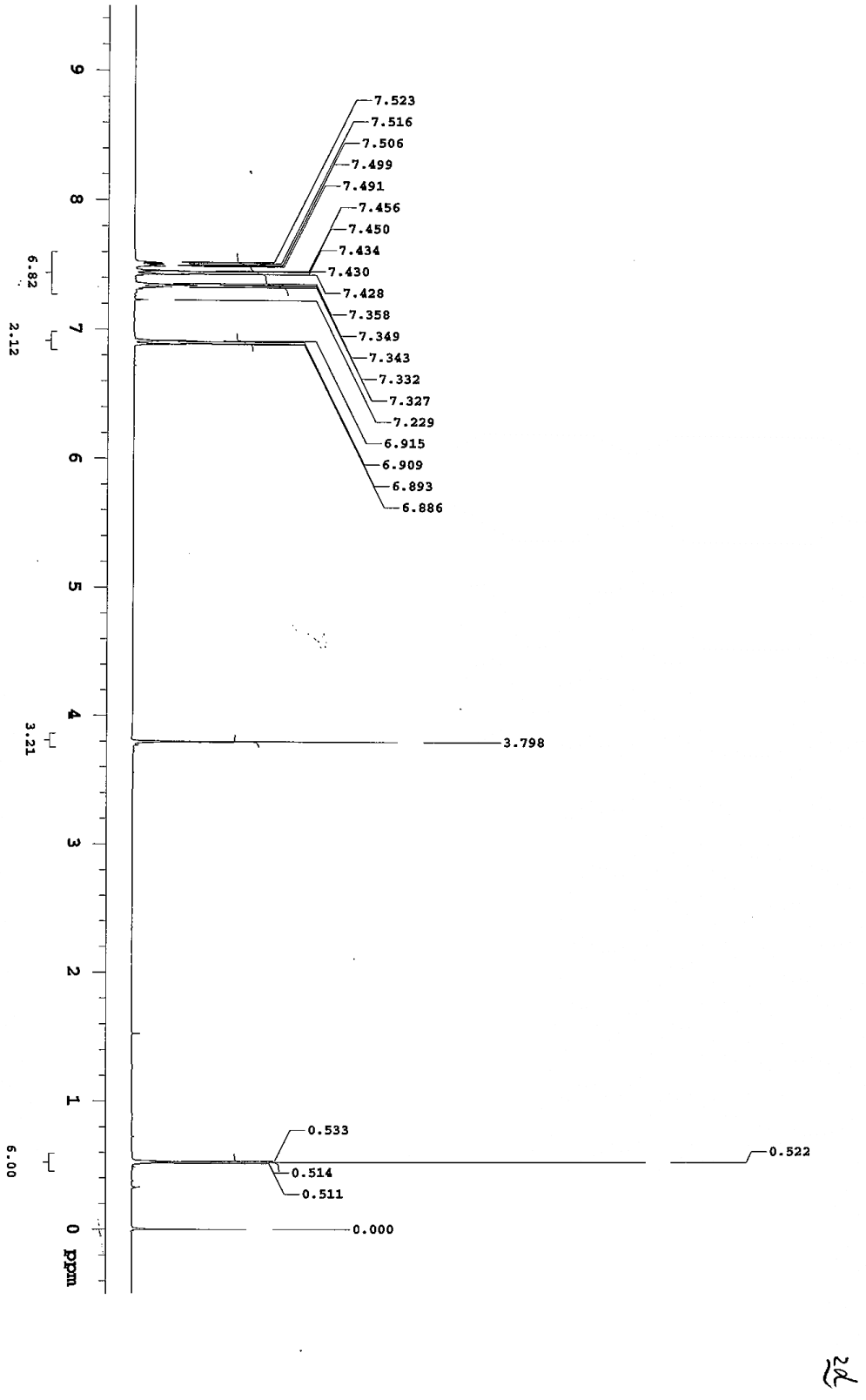
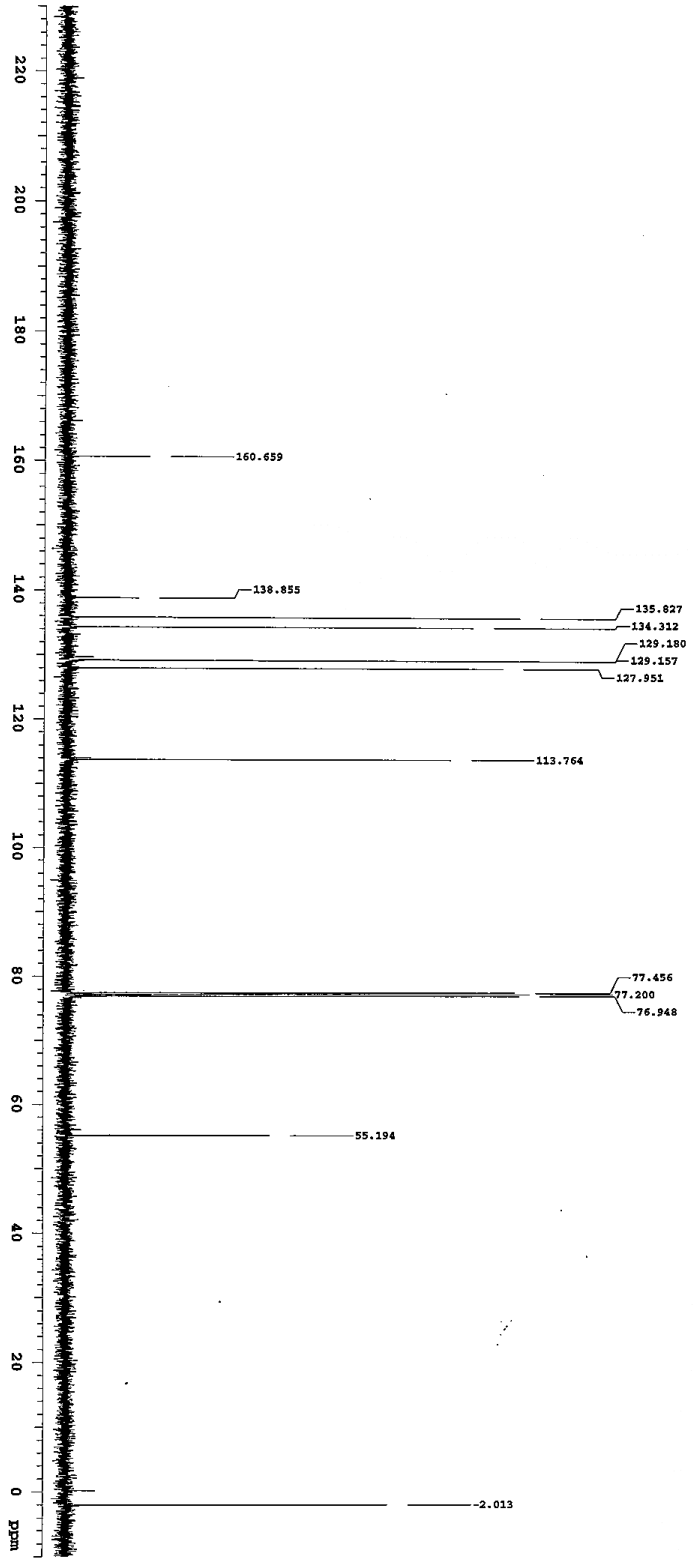


Figure S4. ^{13}C NMR spectrum of **2d**.



2d

Figure S5. ^{1}H NMR spectrum of **2e**.

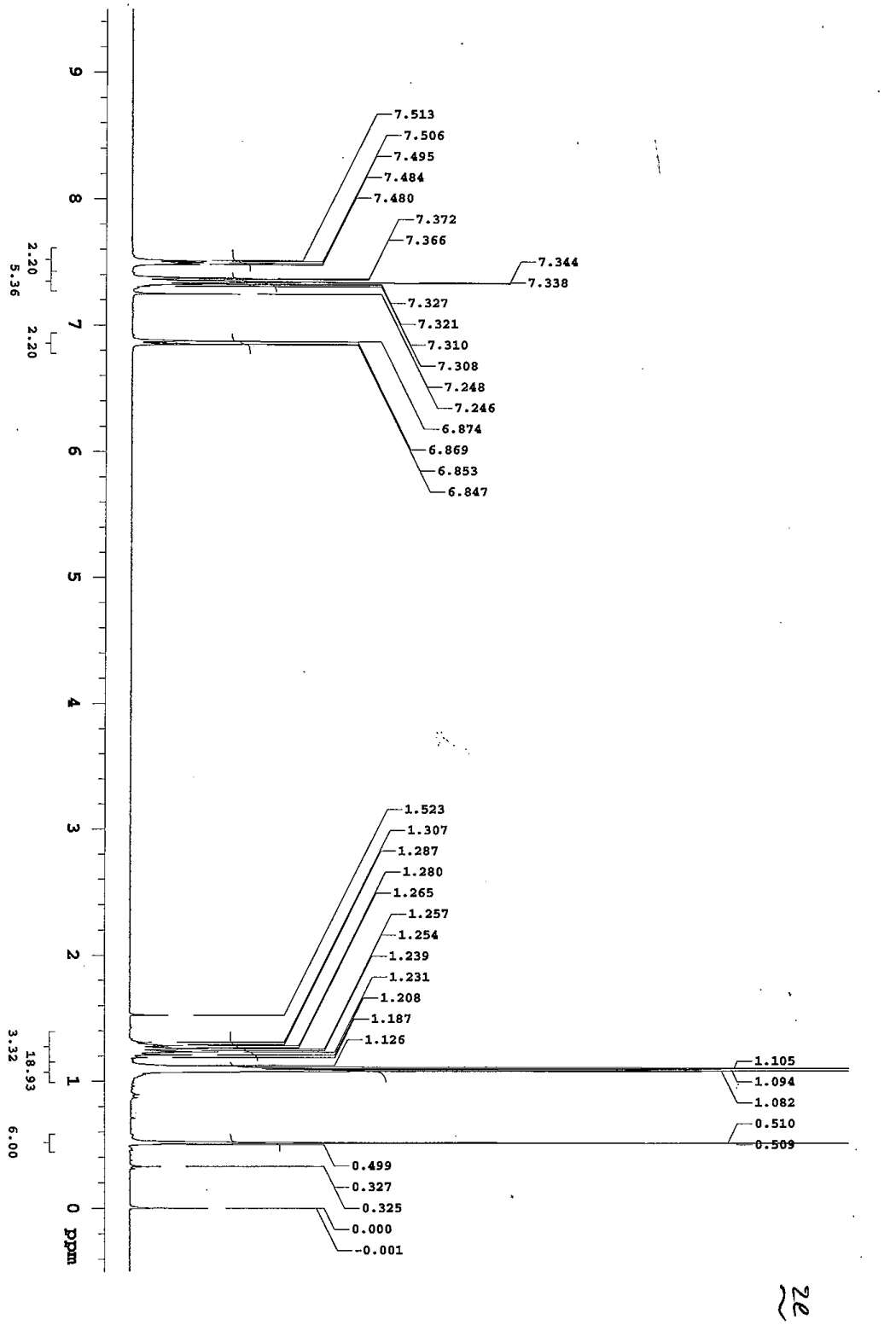


Figure S6. ^{13}C NMR spectrum of **2e**.

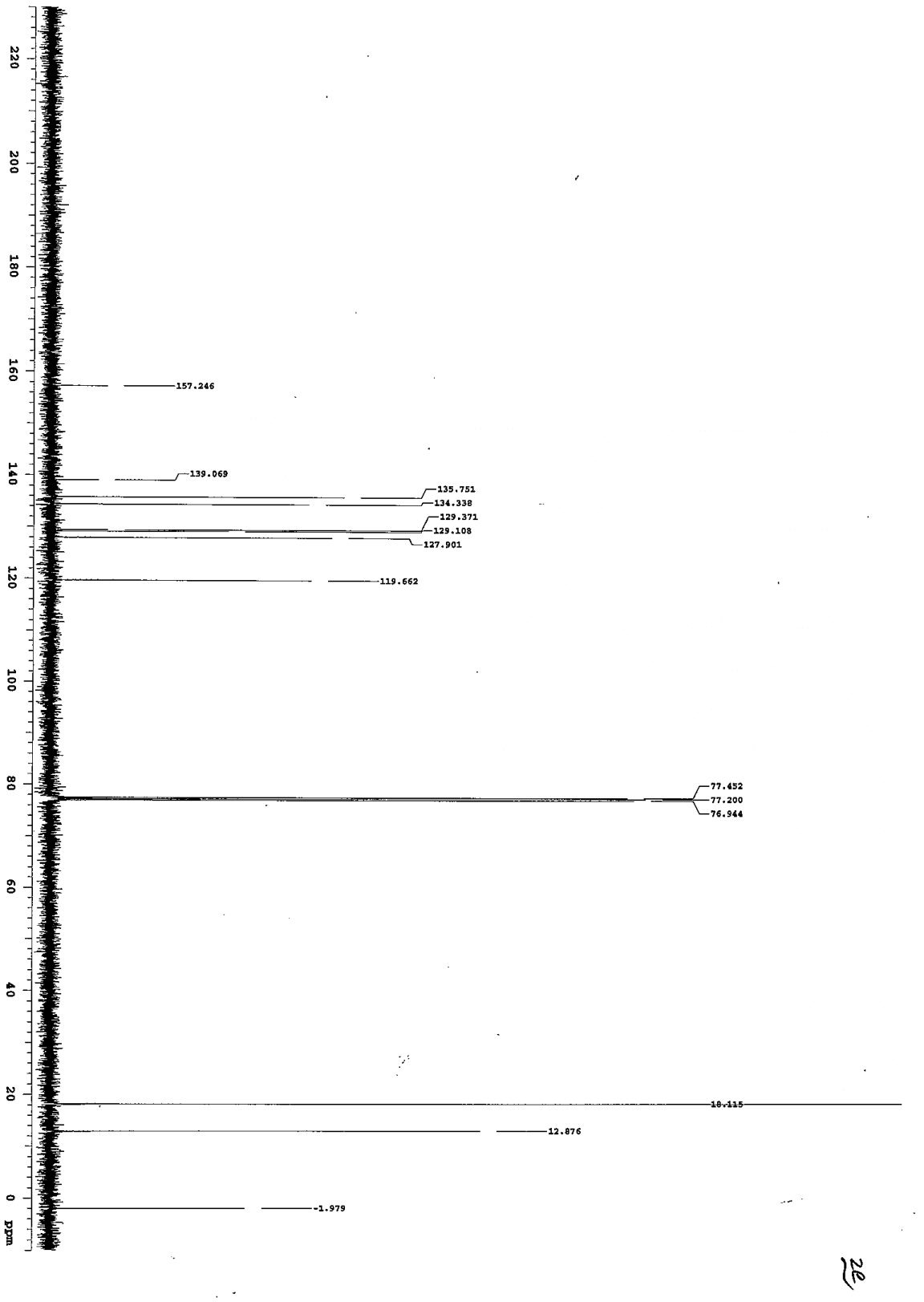


Figure S7. ^{1}H NMR spectrum of **3e'**.

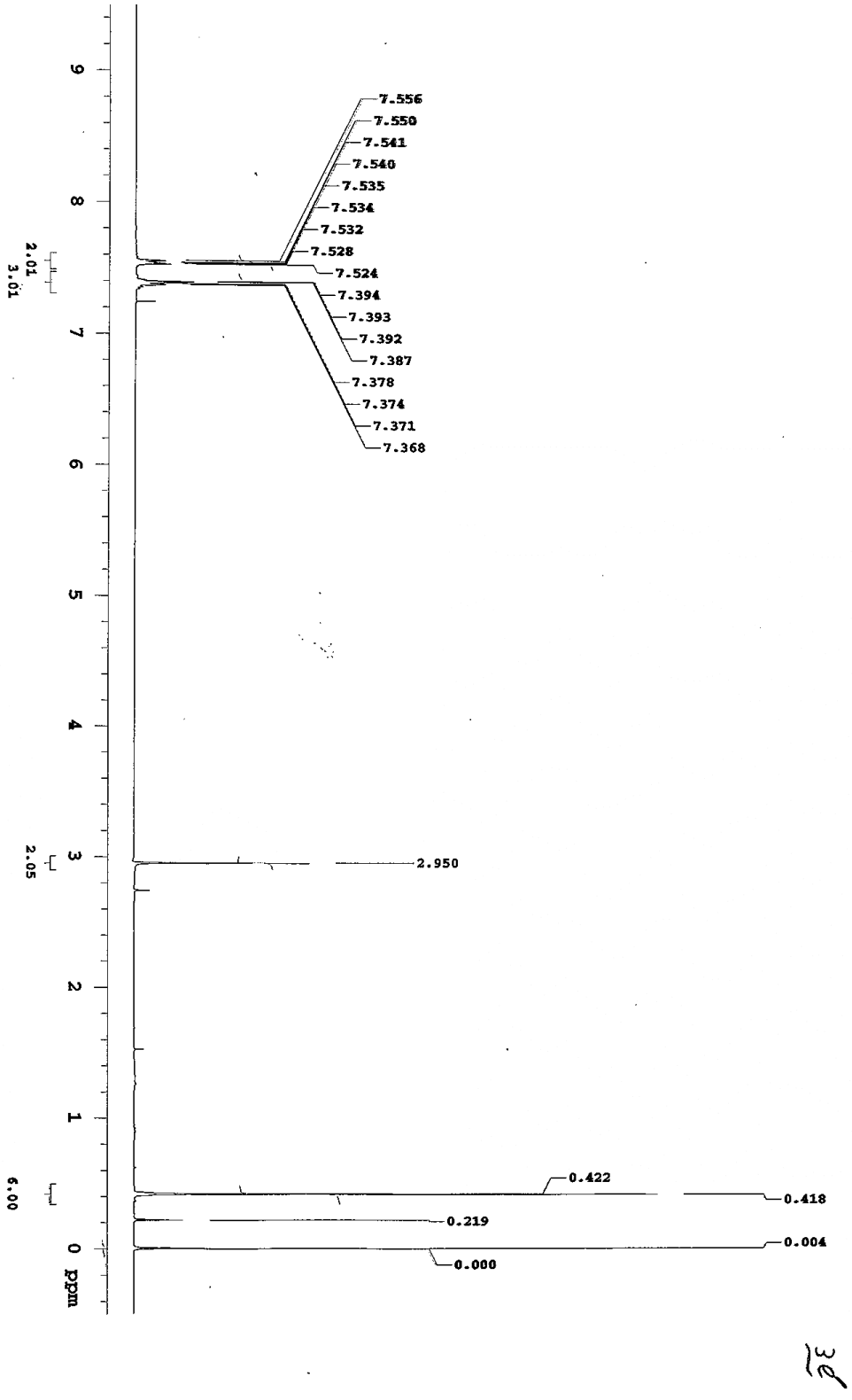


Figure S8. ^{13}C NMR spectrum of **3e'**.

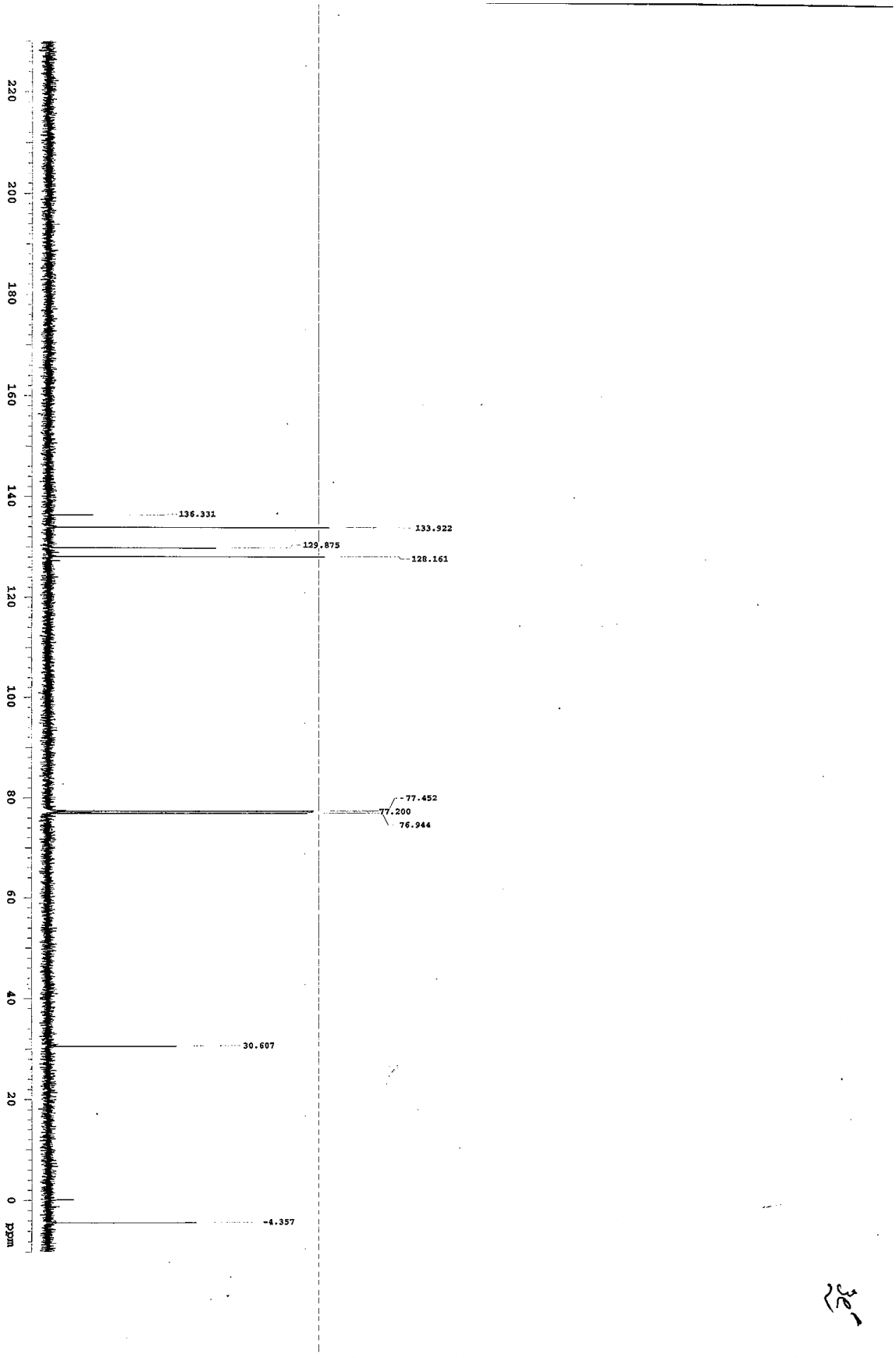


Figure S9. ^{1}H NMR spectrum of **4**.

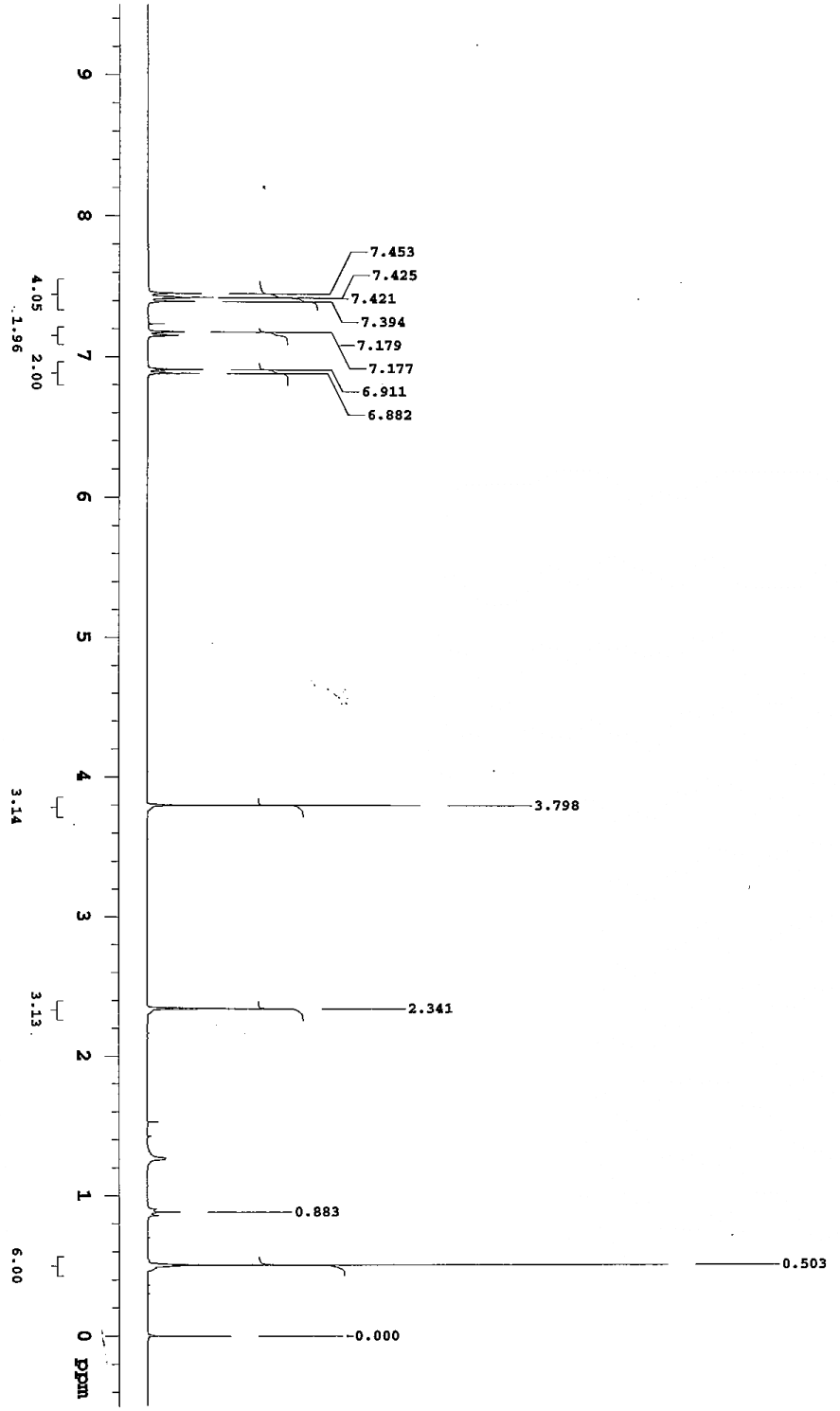


Figure S10. ^{13}C NMR spectrum of **4**.

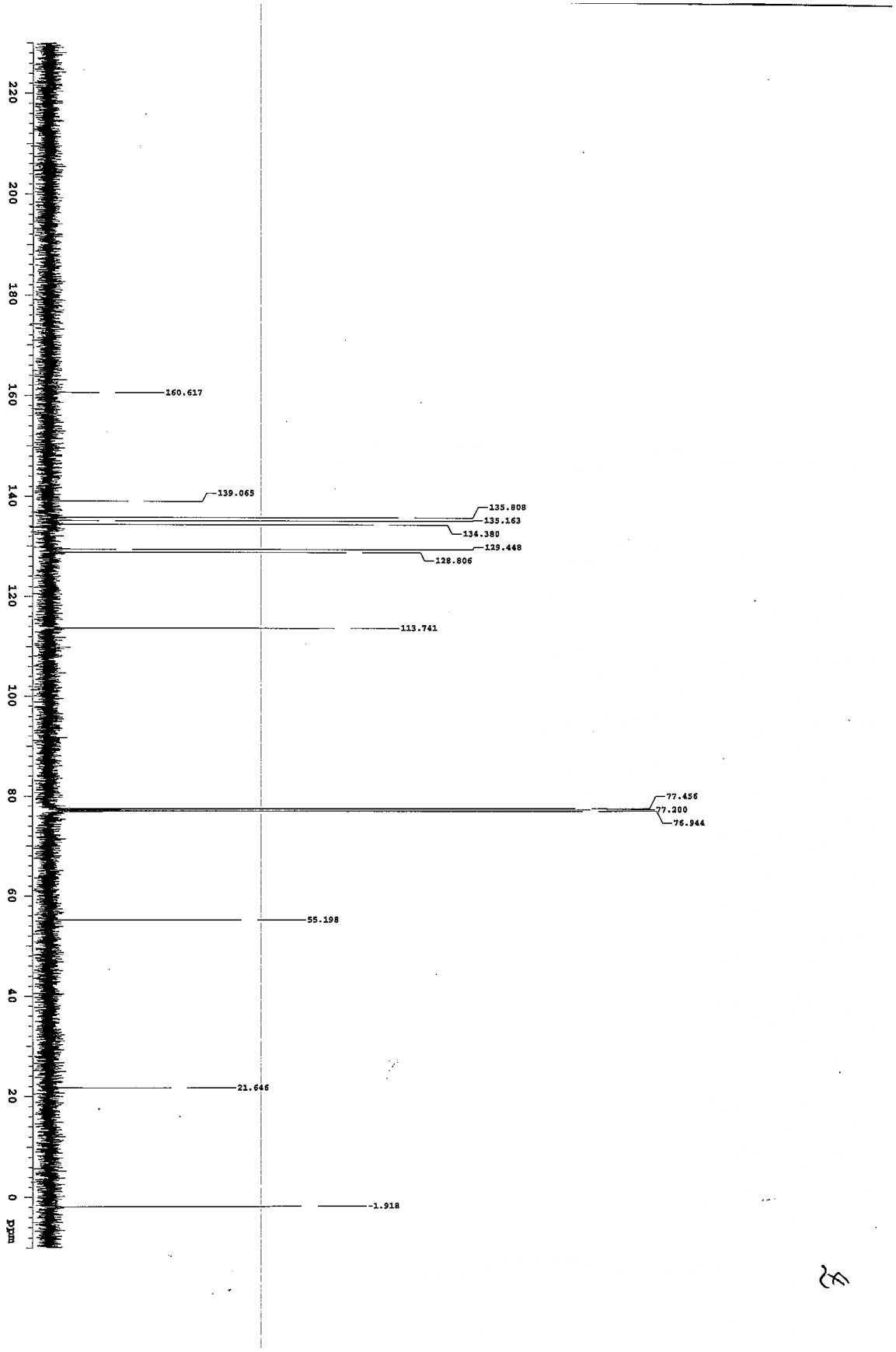


Figure S11. ^{1}H NMR spectrum of **5a**.

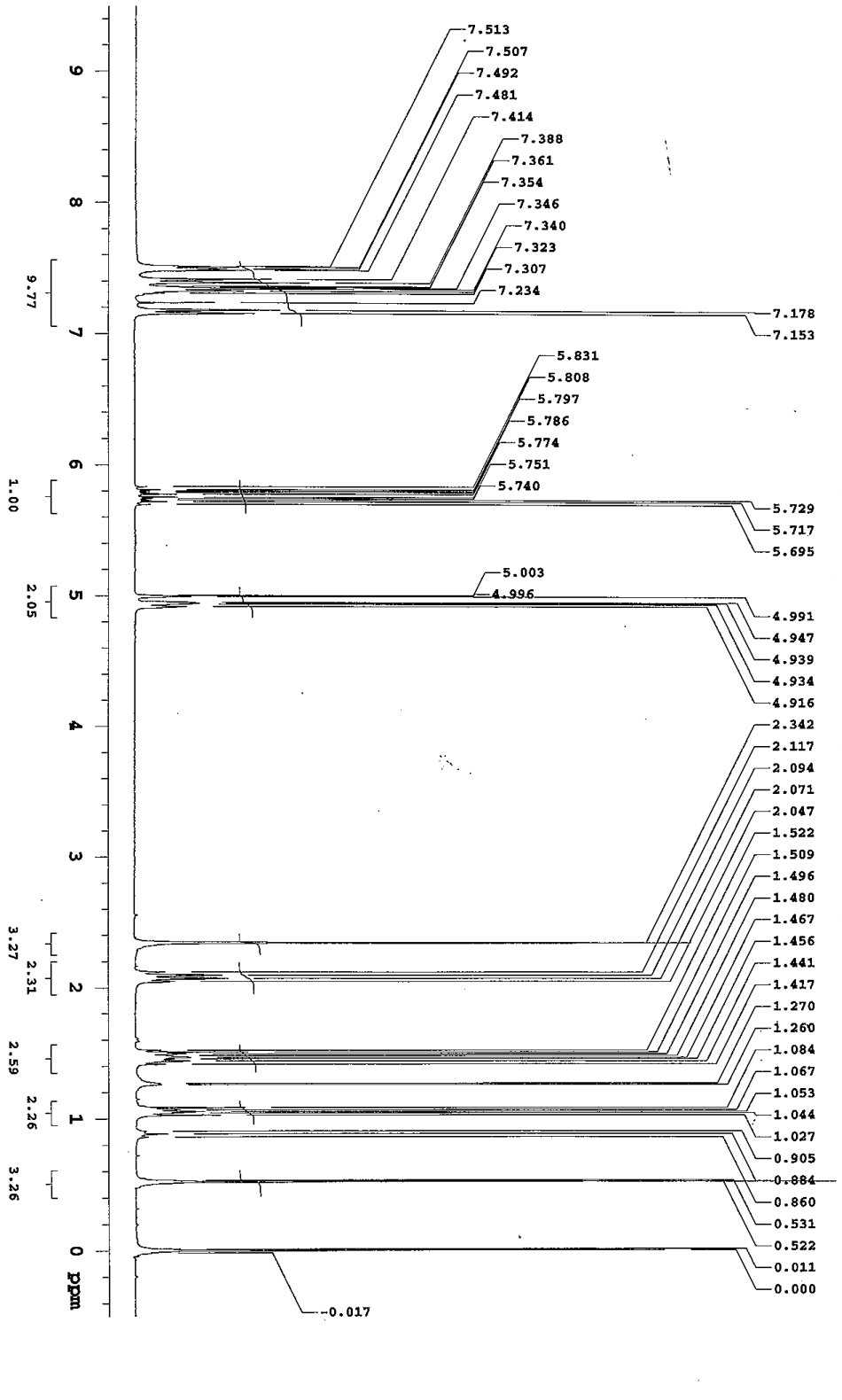


Figure S12. ^{13}C NMR spectrum of **5a**.

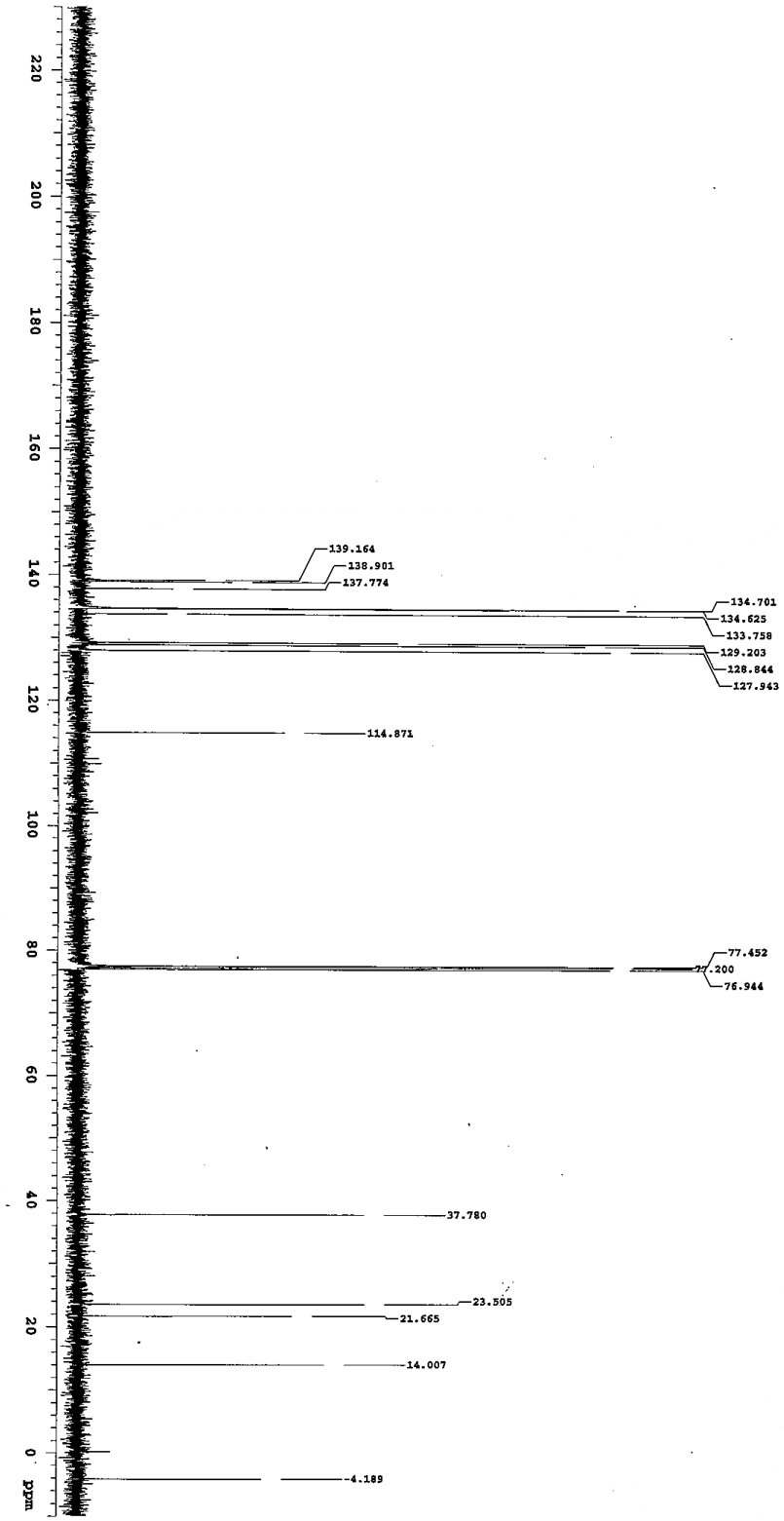


Figure S13. ^{1}H NMR spectrum of **5b**.

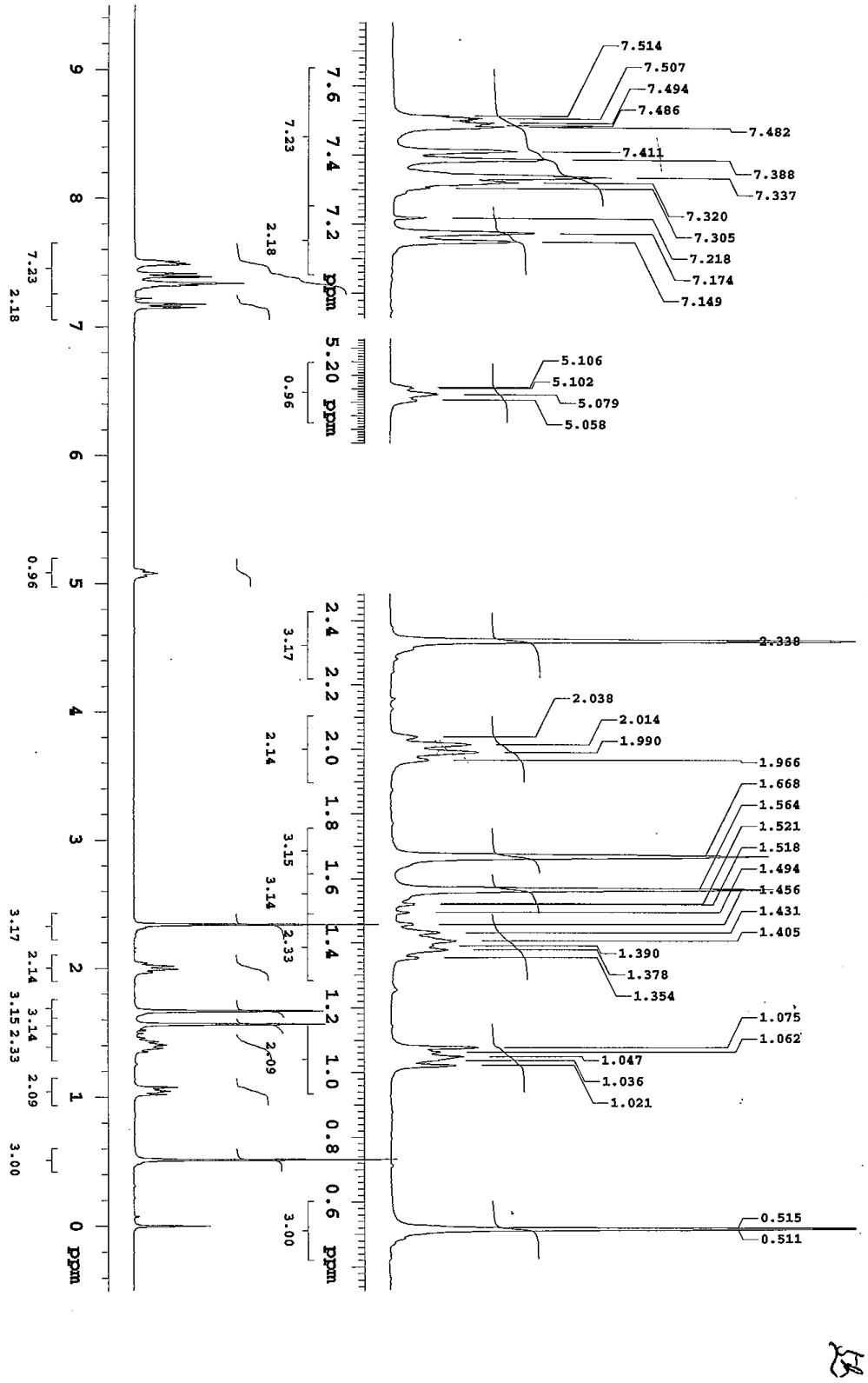


Figure S14. ^{13}C NMR spectrum of **5b**.

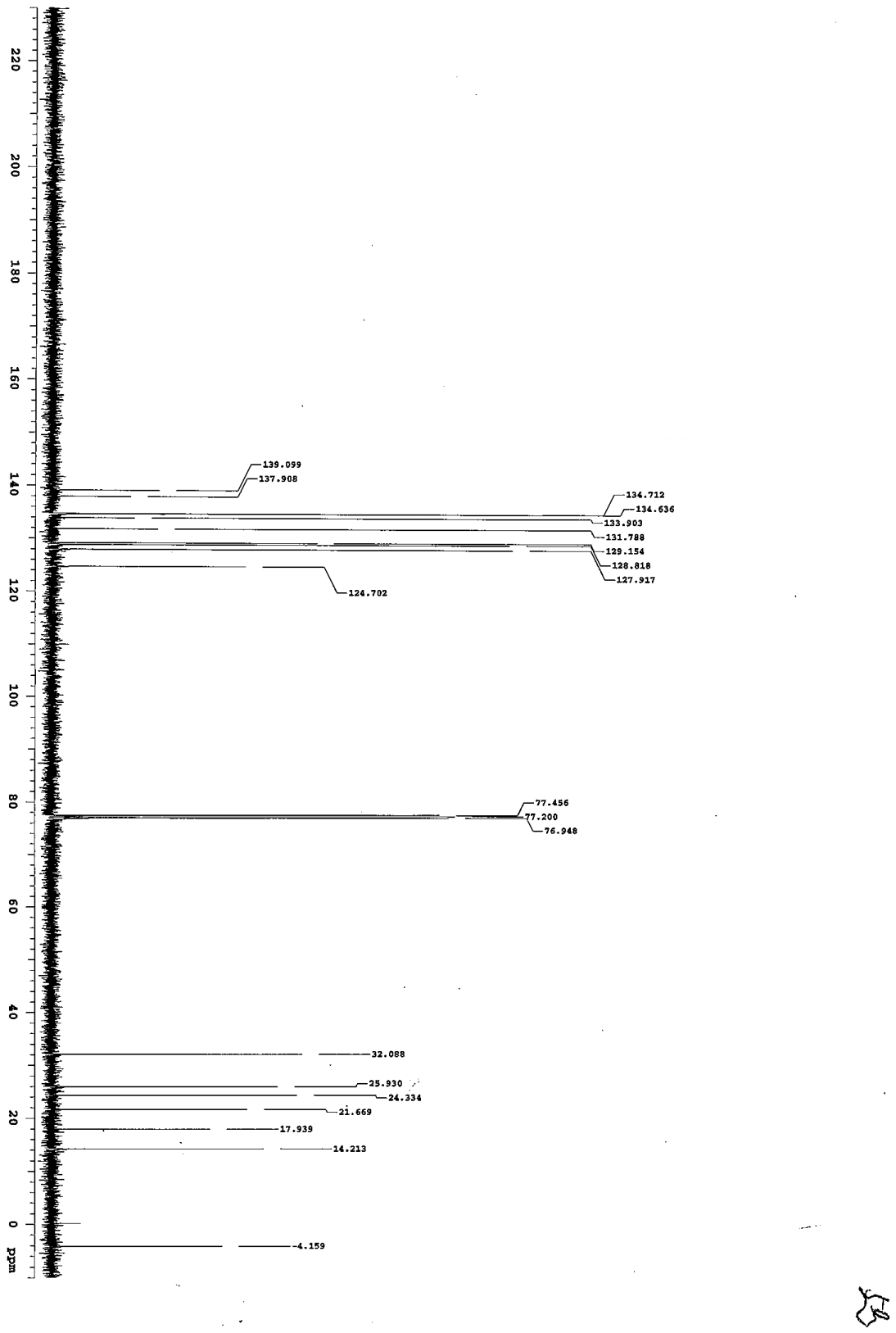


Figure S15. ^{1}H NMR spectrum of **7**.

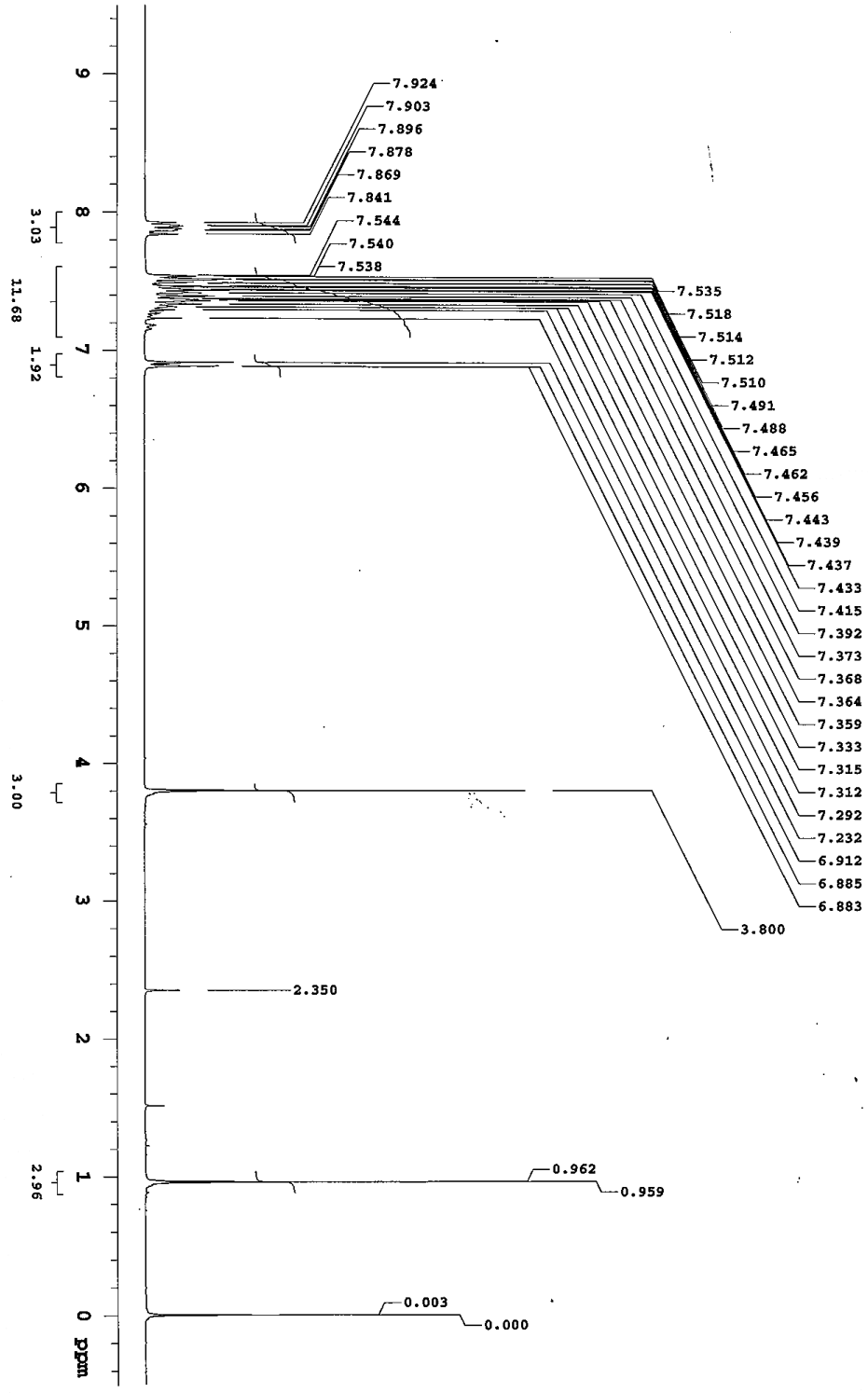


Figure S16. ^{13}C NMR spectrum of **7**.