

Supporting Information

Rhodium-Catalyzed *anti*-Markovnikov Intermolecular Hydroalkoxylation of Terminal Acetylenes

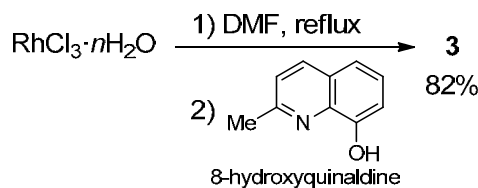
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General Information

Reactions were carried out under nitrogen unless otherwise noted. Substrates **1a**, **1b**, **1g**, **1h**, **1i**, **1k** and **1o** were purchased and distilled prior to use. **1c**,¹ **1d**,^{2,3} **1e**,^{2,4} **1f**,⁵ **1j**,⁶ **1l**,^{1,7} **1m**,⁸ **1n**,⁹ and **1p**¹⁰ were prepared according to literature procedures. Catalysts RhCl(PPh₃)₃, RhCl(CO)(PPh₃)₂, [Rh(CO)₂Cl]₂, [IrCl(cod)]₂, [Ru(CO)₃Cl₂]₂, and CpRuCl(PPh₃)₂ were purchased and used directly. [RhCl(cod)]₂¹¹ and Rh(acac)(CO)₂¹² were prepared according to literature procedures. MeOH and ⁱPrOH were dried over Drierite[®] and distilled prior to use. EtOH was treated with Mg/I₂ and distilled, then distilled again over sulfanilic acid prior to use. Anhydrous solvents were purchased and used directly. All other reagents were purchased and used directly. Column chromatography was carried out on Chromatorex NH[®] gel (Fuji Silysia Chemical Ltd.) by eluting with hexane unless otherwise noted. ¹H (392 MHz), ¹³C{¹H} (98.5 MHz), and ¹⁹F (369 MHz) NMR measurements were performed on a JEOL ECX-400 spectrometer. For ¹H and ¹³C NMR, chemical shifts were reported in ppm relative to TMS, with TMS as an internal reference, or to residual solvent peak. For ¹⁹F NMR, chemical shifts were reported in ppm relative to CFCl₃, with CFCl₃ as an external reference. *Z/E* ratios were calculated from ¹H NMR integrations of vinylic protons of enol ether products. Gas chromatography (GC) analyses were performed using a CBP-10 capillary column (25 m × 0.22 mm, film thickness 0.25 μm). ESI- and APCI-MS were performed on a JEOL JMS-T100LCS. EI-MS was performed on a SHIMADZU GCMS-QP2010. IR measurements were performed on a JASCO FT/IR-410 or FT/IR 4200. Melting points were measured on a Yamato MP-21 apparatus and were uncorrected. They were obtained in sealed glass tubes.

Preparation of **3**¹³



$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (801 mg, 3.0 mmol) and DMF (25 mL) were reacted at 170 °C for 30 min and cooled in an ice-water bath to obtain yellow solution. To this, DMF (5 mL) solution of 8-hydroxyquinaldine (573 mg, 3.6 mmol) was added at rt and a green suspension was obtained immediately. After 1 h, the suspension was poured into water (400 mL) under air. The resulting precipitate was collected by filtration with suction and washed with water (3 times, total 200 mL). After drying under air, the solid was dissolved in CH_2Cl_2 (500 mL), dried over Na_2SO_4 , and filtered through a Celite pad. Hexane (500 mL) was added to the filtrate and reduced the volume to ca. 500 mL by rotary evaporation. The resulting precipitate was collected by filtration with suction, washed with hexane (3 times, total 300 mL) then Et_2O (3 times, total 200 mL) and dried under vacuum to obtain **3** as a green solid with bronze shine (779 mg, 82% yield). ^1H NMR (CDCl_3) δ 3.04 (s, 3 H), 7.03 (dd, $J = 1.1, 7.9$ Hz, 1 H), 7.08 (dd, $J = 1.1, 7.9$ Hz, 1 H), 7.36 (d, $J = 8.4$ Hz, 1 H), 7.41 (t, $J = 7.9$ Hz, 1 H), 8.19 (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 29.9, 113.2, 116.0 (d, $J_{\text{Rh-C}} = 1.9$ Hz), 122.6, 128.5, 129.6, 140.3, 143.3, 158.7, 167.0, 183.7 (d, $J_{\text{Rh-C}} = 70$ Hz, CO), 185.9 (d, $J_{\text{Rh-C}} = 70$ Hz, CO); IR (KBr) ν_{CO} 2067, 2006 cm^{-1} ; mp 227 °C (dec); HRMS (APCI) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{12}\text{H}_9\text{NO}_3\text{Rh}$) m/z 317.9638. Found 317.9647. Anal. calcd for $\text{C}_{12}\text{H}_8\text{NO}_3\text{Rh}$: C, 45.45; H, 2.54; N, 4.42. Found: C, 45.39; H, 2.70; N, 4.36.

$\text{Rh}(\text{CO})_2$ complexes having other *N*-O anionic ligands in Scheme 1 were prepared similarly.¹⁴ Rh complexes having PPh_3 ¹⁵ and COD¹⁶ in Scheme 1 were prepared according to the literature.

8-Quinolinolato rhodium complexes have been used as catalysts for hydroformylation of olefins,¹⁷ hydrosilylation of olefins,¹⁸ hydrogenation of olefins,¹⁹ hydrogenation of O_2 ,²⁰ cyclotrimerization of phenylacetylene,²¹ and polymerization of diazocarbene.²² Surprisingly, the reaction conditions of the cyclotrimerization of phenylacetylene²¹ are quite similar to those of hydroalkoxylation reaction, but the authors did not comment on any formation of enol ethers.

Table S1. Screening of catalysts

$ \begin{array}{c} \text{Ph} \text{---} \text{C} \equiv \text{C} \\ \textbf{1a} \\ 1 \text{ mmol} \end{array} + \begin{array}{c} \text{MeOH} \\ \textbf{2a} \\ 1 \text{ mL} \end{array} \xrightarrow[65 \text{ }^\circ\text{C, 24 h sealed tube}]{5 \text{ mol \% catalyst}} \begin{array}{c} \text{Ph} \text{---} \text{C} \equiv \text{C} \text{---} \text{OMe} \\ \textbf{4aa} \end{array} $			
entry	catalyst	GC conv. of 1a	GC yield of 4aa
1	3	91%	22%
2	RhCl(PPh ₃) ₃	92%	nd
3	RhCl(CO)(PPh ₃) ₂	0%	nd
4	[RhCl(cod)] ₂ (2.5 mol %)	79%	nd
5	Rh(acac)(CO) ₂	81%	nd
6	[Rh(CO) ₂ Cl] ₂ (2.5 mol %)	90%	<5%
7	[IrCl(cod)] ₂ (2.5 mol %)	91%	nd
8	[Ru(CO) ₃ Cl ₂] ₂ (2.5 mol %)	59%	nd
9	CpRuCl(PPh ₃) ₂	35%	nd
10	CpRuCl(dppm)	23%	nd

Table S2. Screening of solvents

$ \begin{array}{c} \text{Ph} \text{---} \text{C} \equiv \text{C} \\ \textbf{1a} \\ 1 \text{ mmol} \end{array} + \begin{array}{c} \text{MeOH} \\ \textbf{2a} \\ 1 \text{ mL} \end{array} \xrightarrow[1 \text{ mL solvent, 65 }^\circ\text{C, 24 h sealed tube}]{5 \text{ mol \% } \textbf{3}} \begin{array}{c} \text{Ph} \text{---} \text{C} \equiv \text{C} \text{---} \text{OMe} \\ \textbf{4aa} \end{array} $			
entry	solvent	GC conv. of 1a	GC yield of 4aa
1	–	91%	22%
2	DMF	–	44%
3	DMA	>99%	59% (62% at 70 °C)
4	MeCN	90%	17%
5	DMSO	96%	18%
6	acetone	93%	23%
7	THF	96%	29%
8	DCE	>99%	31%
9	toluene	>99%	32%
10	Et ₃ N	>99%	7%
11	pyridine	27%	nd

Table S3. Optimization of catalyst loading and reaction time

$ \begin{array}{c} \text{Ph}-\text{C}\equiv\text{C}-\text{H} \\ \mathbf{1a} \\ 1 \text{ mmol} \end{array} + \begin{array}{c} \text{MeOH} \\ \mathbf{2a} \\ 1 \text{ mL} \end{array} \xrightarrow[\substack{1 \text{ mL DMA} \\ 70^\circ\text{C, time} \\ \text{sealed tube}}]{\text{cat. } \mathbf{3}} \begin{array}{c} \text{Ph}-\text{CH}=\text{CH}-\text{OMe} \\ \mathbf{4aa} \end{array} $				
entry	catalyst	time	GC conv. of 1a	GC yield of 4aa
1	5 mol %	24 h	>99%	62%
2	3 mol %	24 h	>99%	66%
3	2 mol %	24 h	80%	55%
4	2 mol %	48 h	>99%	80%
5	1 mol %	24 h	37%	22%
6	1 mol %	120 h	65%	41%

General Procedure for Hydroalkoxylation

Catalyst **3** (0.02 mmol), DMA (1 mL), alcohol (1 mL), and acetylene (1 mmol) were charged in a 10 mL Schlenk flask with a magnetic stirring bar and heated at 70 °C for 48 h. The resulting mixture was diluted with EtOAc and/or Et₂O and analyzed by GC. Water was then added and the organic layer was collected. The aqueous layer was extracted three times with Et₂O or EtOAc. Combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and carefully concentrated to remove volatile materials. The crude material obtained was analyzed by NMR. Finally, enol ether product was isolated by column chromatography using Chromatorex NH[®] gel with hexane as an eluent unless otherwise noted.

(2-Methoxyethenyl)-benzene (4aa, Table 1, entry 12)

Colorless oil (80% GC yield, *Z/E* = 90/10; 82.8 mg, 60% isolated yield, *Z/E* = 90/10). Spectroscopic data was compatible with literature.²³ ¹H NMR (CDCl₃) δ 3.68 (s, 0.35 H, CH₃ (*E*-isomer)), 3.78 (s, 3.0 H, CH₃ (*Z*-isomer)), 5.22 (d, *J* = 7.0 Hz, 1.0 H, ArCH (*Z*-isomer)), 5.81 (d, *J* = 13.1 Hz, 0.11 H, ArCH (*E*-isomer)), 6.13 (d, *J* = 7.0 Hz, 1.0 H, OCH (*Z*-isomer)), 7.05 (d, *J* = 13.1 Hz, 0.11 H, OCH (*E*-isomer)), 7.12-7.56 (m, 5.6 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 60.6, 105.7, 125.7, 128.1, 128.2, 135.9, 147.9; IR (neat) 3085 w, 3055 w, 3030 m, 2935 m, 2867 w, 2829 w, 1651 s, 1600 m, 1493 m, 1456 m, 1444 m, 1402 m, 1318 w, 1301 m, 1272 s, 1238 w, 1203 m, 1152 w, 1098 s, 1075 s, 1030 w, 983 w, 937 w, 912 w, 779 s, 751 w, 729 w, 695 s cm⁻¹; LRMS (EI) *m/z* (% relative intensity) 134 (M⁺, 71), 119 (16), 105 (3), 91 (100), 77 (7), 65 (21), 51 (10).

1-(2-Methoxyethenyl)-4-(trifluoromethyl)-benzene (4ba, Table 2, entry 1)

Colorless oil (92% GC yield, *Z/E* = 94/6; 92.1 mg, 48% isolated yield, *Z/E* = 94/6). ¹H NMR (CDCl₃) δ 3.72 (s, 0.18 H, CH₃ (*E*-isomer)), 3.82 (s, 3.0 H, CH₃ (*Z*-isomer)), 5.25 (d, *J* = 7.1 Hz, 1.0 H, ArCH (*Z*-isomer)), 5.81 (d, *J* = 12.9 Hz, 0.06 H, ArCH (*E*-isomer)), 6.24 (d, *J* = 7.1 Hz, 1.0 H, OCH (*Z*-isomer)), 7.13 (d, *J* = 12.9 Hz, 0.06 H, OCH (*E*-isomer)), 7.30 (d, *J* = 8.2 Hz, 0.12 H, ArH), 7.51 (d, *J* = 8.2 Hz, 2.1 H, ArH), 7.65 (d, *J* = 8.2 Hz, 2.0 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 61.0, 104.4, 124.4 (q, *J*_{C-F} = 272 Hz), 124.9 (q, *J*_{C-F} = 3.8 Hz), 127.3 (q, *J*_{C-F} = 32.3 Hz), 128.1, 139.5, 150.6; ¹⁹F NMR (CDCl₃) δ -62.2; IR (neat) 3042 w, 3013 w, 2941 m, 2879 w, 2837 w, 1651 s, 1617 s, 1457 m, 1415 s, 1326 s, 1275 s, 1207 m, 1187 s, 1164 s, 1117 s, 1097 s, 1068 s, 1016 m, 985 w, 849 s, 764 m, 734 w, 602 m cm⁻¹; HRMS (ESI) calcd for [M-H]⁻ (C₁₀H₈F₃O) 201.0527. Found 201.0500.

4-(2-Methoxyethenyl)-benzonitrile (4ca, Table 2, entry 2)

Colorless solid (85% GC yield, *Z/E* = 95/5; 87.1 mg, 54% isolated yield, *Z/E* = 99/1). ¹H NMR (CDCl₃) δ 3.73 (s, 0.02 H, CH₃ (*E*-isomer)), 3.84 (s, 3.0 H, CH₃ (*Z*-isomer)), 5.23 (d, *J* = 7.0 Hz, 1.0 H, ArCH (*Z*-isomer)), 5.79 (d, *J* = 12.7 Hz, 0.01 H, ArCH (*E*-isomer)), 6.28 (d, *J* = 7.0 Hz, 1.0 H, OCH (*Z*-isomer)), 7.54 (d, *J* = 8.4 Hz, 2.0 H, ArH), 7.63 (d, *J* = 8.4 Hz, 2.0 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 61.2, 104.3, 108.5, 119.5, 128.4, 131.9, 140.6, 150.9; IR (KBr) 2972 w, 2947 w, 2842 w, 2218 s, 1649 s, 1604 s, 1503 w, 1457 w, 1419 m, 1323 w, 1299 m, 1276 s, 1207 w, 1176 w, 1128 w, 1094 s, 986 w, 847 s, 774 w cm⁻¹; mp 50-51 °C; HRMS (ESI) calcd for [M+Na]⁺ (C₁₀H₉NNaO) 182.0582. Found 182.0586.

4-(2-Methoxyethenyl)-benzoic acid, methyl ester (4da, Table 2, entry 3)

Colorless oil (82% GC yield, *Z/E* = 94/6; 123.1 mg, 64% isolated yield, *Z/E* = 95/5). Spectroscopic data was compatible with literature.²⁴ ¹H NMR (CDCl₃) δ 3.72 (s, 0.15 H, CH₃OCH (*E*-isomer)), 3.83 (s, 2.9 H, CH₃OCH (*Z*-isomer)), 3.90 (s, 3.0 H, CH₃OCO), 5.26 (d, *J* = 7.0 Hz, 0.95 H, OCH (*Z*-isomer)), 5.82 (d, *J* = 12.9 Hz, 0.05 H, OCH (*E*-isomer)), 6.24 (d, *J* = 7.0 Hz, 0.95 H, ArCH (*Z*-isomer)), 7.17 (d, *J* = 12.9 Hz, 0.05 H, ArCH (*E*-isomer)), 7.61 (d, *J* = 8.5 Hz, 2.0 H, ArH), 7.95 (d, *J* = 8.5 Hz, 2.0 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 51.9, 61.0, 104.9, 127.9, 129.5, 130.0, 140.6, 150.0, 167.1; IR (neat) 3036 m, 2994 m, 2950 m, 2877 m, 2837 m, 1720 s, 1649 s, 1606 s, 1561 m, 1456 m, 1435 s, 1415 m, 1313 s, 1283 s, 1180 s, 1155 m, 1109 s, 1092 s, 1018 m, 967 w, 863 s, 784 s, 701 m cm⁻¹; HRMS (ESI) calcd for [M+Na]⁺ (C₁₁H₁₂NaO₃) 215.0684. Found 215.0685.

1-[4-(2-Methoxyethenyl)-phenyl]-ethanone (4ea, Table 2, entry 4)

Colorless oil (78% GC yield, *Z/E* = 94/6; 96.4 mg, 55% isolated yield, *Z/E* = 94/6). ¹H NMR (CDCl₃) δ 2.58 (s with a shoulder peak at δ 2.57, 3.0 H, CH₃CO), 3.73 (s, 0.19 H, CH₃O (*E*-isomer)),

3.84 (s, 2.8 H, CH₃O (*Z*-isomer)), 5.27 (d, *J* = 7.2 Hz, 0.94 H, ArCH (*Z*-isomer)), 5.83 (d, *J* = 13.0 Hz, 0.06 H, ArCH (*E*-isomer)), 6.26 (d, *J* = 7.2 Hz, 0.94 H, OCH (*Z*-isomer)), 7.19 (d, *J* = 13.0 Hz, 0.06 H, OCH (*E*-isomer)), 7.29 (d, *J* = 8.5 Hz, 0.12 H, ArH) 7.63 (d, *J* = 8.5 Hz, 1.9 H, ArH), 7.85-7.89 (m, 2.0 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 26.5, 61.1, 104.8, 128.0, 128.4, 134.2, 140.9, 150.3, 197.7; IR (neat) 3036 w, 3003 w, 2938 m, 2875 w, 2835 w, 1677 s, 1648 s, 1600 s, 1556 m, 1456 m, 1412 s, 1358 s, 1306 m, 1272 s, 1206 w, 1182 s, 1156 m, 1095 s, 1016 w, 984 w, 956 m, 849 s, 765 w, 751 w, 728 w cm⁻¹; HRMS (ESI) calcd for [M+Na]⁺ (C₁₁H₁₂NaO₂) 199.0735. Found 199.0734.

1-(2-Methoxyethenyl)-4-nitrobenzene (4fa, Table 2, entry 5)

Yellow solid (73% NMR yield, *Z/E* = 94/6; 102.0 mg, 57% isolated yield, *Z/E* = 93/7). ¹H NMR (CDCl₃) δ 3.75 (s, 0.22 H, CH₃O (*E*-isomer)), 3.87 (s, 3.0 H, CH₃O (*Z*-isomer)), 5.30 (d, *J* = 7.0 Hz, 1.0 H, ArCH (*Z*-isomer)), 5.84 (d, *J* = 12.9 Hz, 0.07 H, ArCH (*E*-isomer)), 6.34 (d, *J* = 7.0 Hz, 1.0 H, OCH (*Z*-isomer)), 7.23 (d, *J* = 12.9 Hz, 0.07 H, OCH (*E*-isomer)), 7.32 (d, *J* = 8.9 Hz, 0.14 H, ArH), 7.67 (d, *J* = 8.9 Hz, 2.0 H, ArH), 8.13 (d, *J* = 8.9 Hz, 2.1 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 61.3, 104.0, 123.6, 128.4, 142.8, 145.1, 151.6; IR (KBr) 3103 w, 3075 w, 2979 w, 2940 w, 2877 w, 2838 w, 1639 s, 1590 s, 1506 s, 1454 w, 1411 w, 1394 w, 1344 s, 1322 m, 1311 m, 1277 s, 1249 w, 1206 w, 1186 w, 1161 w, 1110 m, 1091 s, 987 w, 939 w, 861 m, 844 w, 795 w, 778 w, 750 w, 697 w cm⁻¹; mp 63 °C (dec); HRMS (ESI) calcd for [M+Na]⁺ (C₉H₉NNaO₃) 202.0480. Found 202.0474.

1-(2-Methoxyethenyl)-4-methylbenzene (4ga, Table 2, entry 6)

Colorless oil (64% GC yield, *Z/E* = 88/12; 79.0 mg, 53% isolated yield, *Z/E* = 88/12). ¹H NMR (CDCl₃) δ 2.31 (s with a shoulder peak at δ 2.306, 3.0 H, CH₃Ar), 3.67 (s, 0.37 H, CH₃O (*E*-isomer)), 3.76 (s, 2.6 H, CH₃O (*Z*-isomer)), 5.20 (d, *J* = 7.0 Hz, 0.88 H, ArCH (*Z*-isomer)), 5.79 (d, *J* = 13.0 Hz, 0.12 H, ArCH (*E*-isomer)), 6.09 (d, *J* = 7.0 Hz, 0.88 H, OCH (*Z*-isomer)), 7.00 (d, *J* = 13.0 Hz, 0.12 H, OCH (*E*-isomer)), 7.06-7.14 (m, 2.3 H, ArH), 7.46 (d, *J* = 8.3 Hz, 1.7 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 21.2, 60.6, 105.6, 128.1, 128.9, 133.0, 135.3, 147.2; IR (neat) 3032 m, 2934 s, 2869 m, 2829 m, 1649 s, 1512 s, 1453 m, 1400 m, 1320 m, 1299 m, 1266 s, 1240 m, 1201 m, 1184 m, 1151 m, 1097 s, 978 w, 941 w, 827 s, 752 w, 712 w cm⁻¹; HRMS (APCI) calcd for [M+H]⁺ (C₁₀H₁₃O) 149.0966. Found 149.0970.

1-(2-Methoxyethenyl)-2-methylbenzene (4ha, Table 2, entry 7)

Orange oil (65% GC yield, *Z/E* = 70/30; 85.8 mg, 58% isolated yield, *Z/E* = 72/28). ¹H NMR (CDCl₃) δ 2.30 (s, 3.0 H, CH₃Ar), 3.70 and 3.75 (s and s, 3.0 H, CH₃O), 5.32 (d, *J* = 7.2 Hz, 0.72 H, ArCH (*Z*-isomer)), 5.92 (d, *J* = 12.8 Hz, 0.28 H, ArCH (*E*-isomer)), 6.18 (d, *J* = 7.2 Hz, 0.72 H, OCH (*Z*-isomer)), 6.87 (d, *J* = 12.8 Hz, 0.28 H, OCH (*E*-isomer)), 7.04-7.28 (m, 3.3 H, ArH), 7.87

(d, $J = 7.9$ Hz, 0.72 H, ArH); ^{13}C NMR (CDCl_3 , Z-isomer) δ 20.1, 60.5, 102.7, 124.8, 125.9, 128.9, 129.8, 134.1, 134.8, 147.7; IR (neat) 3058 m, 3018 m, 2933 m, 2864 w, 2830 w, 1648 s, 1600 m, 1486 s, 1461 s, 1402 m, 1379 w, 1338 w, 1308 m, 1274 s, 1421 s, 1222 s, 1207 s, 1189 w, 1158 s, 1111 s, 1090 s, 1052 w, 982 w, 938 m, 814 w, 768 s, 752 s, 717 m cm^{-1} ; HRMS (APCI) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{10}\text{H}_{13}\text{O}$) 149.0966. Found 149.0988.

1-Methoxy-4-(2-methoxyethenyl)-benzene (4ia, Table 2, entry 8)

Colorless oil (64% GC yield, Z/E = 87/13; 91.9 mg, 55% isolated yield, Z/E = 86/14). Spectroscopic data was compatible with literature.²⁵ ^1H NMR (CDCl_3) δ 3.66-3.80 (m, 6.0 H, 2 x CH_3), 5.18 (d, $J = 7.1$ Hz, 0.86 H, ArCH (Z-isomer)), 5.78 (d, $J = 13.0$ Hz, 0.14 H, ArCH (E-isomer)), 6.05 (d, $J = 7.1$ Hz, 0.86 H, OCH (Z-isomer)), 6.81-6.84 (m, 2.0 H, ArH), 6.93 (d, $J = 13.0$ Hz, 0.14 H, OCH (E-isomer)), 7.16 (d, $J = 9.0$ Hz, 0.28 H, ArH), 7.51 (d, $J = 9.0$ Hz, 1.7 H, ArH); ^{13}C NMR (CDCl_3 , Z-isomer) δ 55.2, 60.5, 105.2, 113.6, 128.7, 129.4, 146.3, 157.6; IR (neat) 3033 w, 3001 w, 2935 m, 2833 m, 1653 s, 1606 s, 1572 w, 1510 s, 1455 m, 1399 m, 1319 m, 1301 m, 1269 s, 1246 s, 1201 w, 1178 s, 1151 m, 1095 s, 1034 s, 837 s, 691 w cm^{-1} ; LRMS (EI) m/z (% relative intensity) 164 (M^+ , 92), 149 (63), 121 (100), 106 (4), 91 (20), 77 (23), 63 (10), 51 (16).

2-(2-Methoxyethenyl)-naphthalene (4ja, Table 2, entry 9)

Colorless oil (55% GC yield, Z/E = 91/9; 82.3 mg, 45% isolated yield, Z/E = 90/10). ^1H NMR (CDCl_3) δ 3.74 (s, 0.32 H, CH_3 (E-isomer)), 3.84 (s, 3.0 H, CH_3 (Z-isomer)), 5.37 (d, $J = 7.0$ Hz, 1.0 H, ArCH (Z-isomer)), 5.98 (d, $J = 13.0$ Hz, 0.11 H, ArCH (E-isomer)), 6.22 (d, $J = 7.0$ Hz, 1.0 H, OCH (Z-isomer)), 7.19 (d, $J = 13.0$ Hz, 0.11 H, OCH (E-isomer)), 7.36-7.44 (m, 2.3 H, ArH), 7.59 (s, 0.11 H, ArH), 7.71-7.79 (m, 4.3 H, ArH), 8.00 (s, 1.0 H, ArH); ^{13}C NMR (CDCl_3 , Z-isomer) δ 60.8, 105.7, 125.1, 125.8, 126.4, 127.0, 127.5, 127.5, 127.9, 131.8, 133.5, 133.6, 148.4; IR (neat) 3053 m, 2934 m, 2866 w, 2828 w, 1650 s, 1625 m, 1596 m, 1504 m, 1453 m, 1403 m, 1282 s, 1190 m, 1155 m, 1126 s, 1092 s, 949 m, 894 m, 858 s, 822 s, 740 s cm^{-1} ; HRMS (APCI) calcd for $[\text{M}]^+$ ($\text{C}_{13}\text{H}_{12}\text{O}$) 185.0966. Found 185.0968.

3-(2-Methoxyethenyl)-thiophene (4ka, Table 2, entry 10)

Yellow oil (64% GC yield, Z/E = 88/12; 75.0 mg, 52% isolated yield, Z/E = 90/10). ^1H NMR (CDCl_3) δ 3.66 (s, 0.33 H, CH_3 (E-isomer)), 3.78 (s, 3.0 H, CH_3 (Z-isomer)), 5.36 (d, $J = 6.7$ Hz, 1.0 H, ArCH (Z-isomer)), 5.85 (d, $J = 13.0$ Hz, 0.11 H, ArCH (E-isomer)), 6.09 (d, $J = 6.7$ Hz, 1.0 H, OCH (Z-isomer)), 6.92-6.93 (m, 0.11 H, ArH), 6.99 (d, $J = 13.0$ Hz, 0.11 H, OCH (E-isomer)), 7.04-7.06 (m, 0.22 H, ArH), 7.21-7.25 (m, 2.0 H, ArH), 7.38-7.39 (m, 1.0 H, ArH); ^{13}C NMR (CDCl_3 , Z-isomer) δ 60.4, 100.5, 121.4, 124.4, 128.4, 136.3, 146.8; IR (neat) 3097 w, 3037 w, 3004 m, 2934 s, 2873 m, 2834 m, 1650 s, 1517 w, 1452 s, 1415 s, 1402 m, 1384 m, 1351 m, 1332 w, 1271

s, 1240 s, 1216 s, 1183 m, 1152 s, 1098 s, 996 m, 980 w, 923 m, 867 s, 833 s, 791 s, 739 m, 687 w, 641 s cm⁻¹; HRMS (APCI) calcd for [M+H]⁺ (C₇H₉OS) 141.0374. Found 141.0344.

2-(2-Methoxyethenyl)-thiophene (4la, Table 2, entry 11)

Orange oil (32% NMR yield, Z/E = 96/4; 36.3 mg, 25% isolated yield, Z/E = 96/4). ¹H NMR (CDCl₃) δ 3.67 (s, 0.12 H, CH₃ (E-isomer)), 3.82 (s, 3.0 H, CH₃ (Z-isomer)), 5.64 (d, J = 6.5 Hz, 1.0 H, ArCH (Z-isomer)), 5.97 (d, J = 12.8 Hz, 0.04 H, ArCH (E-isomer)), 6.13 (d, J = 6.5 Hz, 1.0 H, OCH (Z-isomer)), 6.94-6.99 (m, 2.1 H, ArH, OCH (E-isomer)), 7.15-7.17 (m, 1.0 H, ArH); ¹³C NMR (CDCl₃, Z-isomer) δ 60.5, 100.5, 124.0, 124.6, 126.3, 138.2, 145.7; IR (neat) 3103 w, 3066 w, 3004 w, 2933 m, 2856 m, 2828 m, 1646 s, 1453 m, 1430 w, 1389 s, 1273 s, 1230 s, 1203 m, 1165 w, 1126 w, 1096 s, 1046 w, 850 m, 825 m, 744 m, 696 s cm⁻¹; HRMS (APCI) calcd for [M+H]⁺ (C₇H₉OS) 141.0374. Found 141.0374.

2-(2-Methoxyethenyl)-1-methyl-1H-indole (4ma, Table 2, entry 12)

Yellow solid (66% GC yield, Z/E = 80/20; 72.5 mg, 39% isolated yield, Z/E = 81/19). Spectroscopic data was compatible with literature.²⁶ ¹H NMR (CDCl₃) δ 3.69 (s with a shoulder peak at δ 3.68, 3.7 H, NCH₃), 3.75 (s, 0.70 H, OCH₃ (E-isomer)), 3.87 (s, 3.0 H, OCH₃ (Z-isomer)), 5.40 (d, J = 7.0 Hz, 1.0 H, ArCH (Z-isomer)), 5.81 (d, J = 12.8 Hz, 0.23 H, ArCH (E-isomer)), 6.30 (d, J = 7.0 Hz, 1.0 H, OCH (Z-isomer)), 6.38 (s, 0.23 H, ArH), 6.91 (s, 1.0 H, ArH), 7.03-7.24 (m, 3.9 H, ArH, OCH (E-isomer)), 7.51-7.56 (m, 1.2 H, ArH); ¹³C NMR (CDCl₃, Z-isomer) δ 29.5, 60.9, 94.6, 101.9, 108.7, 119.3, 120.2, 121.0, 128.5, 134.6, 136.7, 148.8; IR (KBr) 3051 w, 2937 w, 2840 w, 1648 s, 1527 w, 1466 m, 1412 w, 1328 m, 1317 m, 1277 s, 1232 m, 1148 w, 1138 m, 1097 s, 781 s, 751 m, 734 m, 730 m, 659 w cm⁻¹; mp 56 °C; HRMS (ESI) calcd for [M+H]⁺ (C₁₂H₁₄NO) 188.1075. Found 188.1076.

2-(2-Methoxyvinyl)-benzofuran (4na, Table 2, entry 13)

Yellow oil (29% NMR yield, Z/E = 90/10; 49.5 mg, 28% isolated yield, Z/E = 90/10). Spectroscopic data was compatible with literature.²⁷ ¹H NMR (CDCl₃) δ 3.73 (s, 0.33 H, CH₃ (E-isomer)), 3.88 (s, 3.0 H, CH₃ (Z-isomer)), 5.46 (d, J = 6.7 Hz, 1.0 H, ArCH (Z-isomer)), 5.76 (d, J = 12.8 Hz, 0.11 H, ArCH (E-isomer)), 6.29 (d, J = 6.7 Hz, 1.0 H, OCH (Z-isomer)), 6.35 (s, 0.11 H, ArH), 6.87 (s, 1.0 H, ArH), 7.14-7.22 (m, 2.2 H, ArH), 7.32-7.51 (m, 2.3 H, ArH, OCH (Z-isomer)); ¹³C NMR (CDCl₃, Z-isomer) δ 61.1, 95.9, 104.1, 110.7, 120.4, 122.5, 123.3, 129.7, 149.5, 152.9, 153.5; IR (neat) 3065 w, 3010 w, 2937 m, 2866 w, 2830 w, 1650 s, 1568 m, 1473 m, 1451 s, 1399 m, 1308 m, 1274 s, 1257 s, 1189 s, 1166 s, 1140 m, 1099 s, 1008 m, 996 m, 934 m, 889 w, 850 w, 802 s, 751 s, 666 m, 611 w cm⁻¹; HRMS (APCI) calcd for [M+H]⁺ (C₁₁H₁₁O₂) 175.0759. Found 175.0757.

1-(2-Methoxyethenyl)-cyclohexene (40a, Table 2, entry 14)

Isolated by column chromatography using SiO₂ gel with hexane as an eluent. Orange oil (27% NMR yield, Z/E = 50/50; 23.0 mg, 17% isolated yield, Z/E = 49/51). ¹H NMR (CDCl₃) δ 1.56-2.30 (m, 15.7 H, CH₂), 3.57 and 3.61 (s and s, 5.9 H, CH₃), 4.69 (d, *J* = 7.6 Hz, 0.96 H, C₆H₉CH (*Z*-isomer)), 5.52-5.55 (m, 2.0 H, C₆H₉CH (*E*-isomer), CH₂CH (*Z*-isomer)), 5.77-5.81 (m, 2.0 H, OCH (*Z*-isomer), CH₂CH (*E*-isomer)), 6.51 (d, *J* = 12.8 Hz, 1.0 H, OCH (*E*-isomer)); ¹³C NMR (CDCl₃) δ 22.1, 22.5, 22.6, 23.0, 24.8, 25.7, 25.7, 28.8, 56.3, 60.2, 108.7, 109.1, 123.9, 125.4, 132.8, 133.6, 145.3, 145.8; IR (neat) 3068 w, 3025 m, 2929 s, 2831 s, 1651 s, 1620 s, 1449 s, 1438 s, 1400 m, 1378 m, 1333 s, 1313 m, 1276 s, 1220 s, 1197 s, 1186 s, 1155 s, 1126 s, 1096 s, 1078 s, 1046 m, 988 m, 921 s, 845 m, 802 m, 788 m, 762 w, 744 m, 703 m cm⁻¹; HRMS (APCI) calcd for [M+H]⁺ (C₉H₁₅O) 139.1123. Found 139.1097.

1-Methoxy-3,3,3-triphenyl-1-propene (4pa, Table 2, entry 15)

Colorless solid (69% GC yield, Z/E = 100/0; 200.4 mg, 66% isolated yield, Z/E = 100/0). ¹H NMR (CDCl₃) δ 3.26 (s, 3.0 H, CH₃), 5.38 (d, *J* = 7.0 Hz, 1.0 H, ArCH), 6.01 (d, *J* = 7.0 Hz, 1.0 H, OCH), 7.15-7.26 (m, 15 H, ArH); ¹³C NMR (CDCl₃) δ 58.8, 59.2, 115.4, 125.7, 127.5, 129.7, 146.5, 147.9; IR (KBr) 3080 w, 3056 w, 3016 w, 2966 w, 2930 w, 2855 w, 2821 w, 1660 s, 1598 w, 1489 m, 1444 m, 1391 w, 1310 m, 1216 m, 1112 s, 1083 m, 1044 w, 965 w, 933 w, 894 w, 759 s, 731 m, 701 s, 639 w, 610 w cm⁻¹; mp 113 °C; HRMS (ESI) calcd for [M+H]⁺ (C₂₂H₂₁O) 301.1592. Found 301.1579.

(2-Ethoxyethenyl)-benzene (4ab, eq 1)

Colorless oil (72% GC yield, Z/E = 91/9; 76.8 mg, 51% isolated yield, Z/E = 91/9). Spectroscopic data was compatible with literature.²⁸ ¹H NMR (CDCl₃) δ 1.32-1.39 (m, 3.0 H, CH₃CH₂), 3.90 (q, *J* = 7.1 Hz, 0.18 H, CH₃CH₂ (*E*-isomer)), 3.98 (q, *J* = 7.1 Hz, 1.8 H, CH₃CH₂ (*Z*-isomer)), 5.22 (d, *J* = 7.1 Hz, 0.91 H, ArCH (*Z*-isomer)), 5.84 (d, *J* = 13.0 Hz, 0.09 H, ArCH (*E*-isomer)), 6.21 (d, *J* = 7.1 Hz, 0.91 H, OCH (*Z*-isomer)), 6.99 (d, *J* = 13.0 Hz, 0.09 H, OCH (*E*-isomer)), 7.11-7.61 (m, 5.0 H, ArH); ¹³C NMR (CDCl₃, *Z*-isomer) δ 15.4, 69.1, 105.4, 125.6, 128.1, 128.1, 136.1, 146.5; IR (neat) 3089 w, 3055 m, 3025 m, 2979 s, 2931 m, 2885 m, 1649 s, 1600 m, 1493 m, 1476 w, 1448 s, 1417 w, 1385 s, 1360 m, 1307 s, 1258 s, 1200 m, 1165 m, 1099 s, 1074 s, 1031 m, 912 m, 779 s, 750 m, 714 m, 695 s cm⁻¹; LRMS (EI) *m/z* (% relative intensity) 148 (M⁺, 44), 120 (45), 91 (100), 77 (6), 65 (14), 51 (8).

[2-(1-Methylethoxy)-ethenyl]-benzene (4ac, eq 1)

Colorless oil (62% GC yield, Z/E = 93/7; 77.9 mg, 48% isolated yield, Z/E = 93/7). Spectroscopic data was compatible with literature.²⁹ ¹H NMR (CDCl₃) δ 1.30 (d, *J* = 6.3 Hz, 0.45 H, (CH₃)₂CH (*E*-isomer)), 1.34 (d, *J* = 6.3 Hz, 6.0 H, (CH₃)₂CH (*Z*-isomer)), 4.02-4.17 (m, 1.1 H, (CH₃)₂CH), 5.21

(d, $J = 7.1$ Hz, 1.0 H, ArCH (*Z*-isomer)), 5.91 (d, $J = 12.8$ Hz, 0.07 H, ArCH (*E*-isomer)), 6.25 (d, $J = 7.0$ Hz, 1.0 H, $^i\text{PrOCH}$ (*Z*-isomer)), 6.87 (d, $J = 12.8$ Hz, 0.07 H, $^i\text{PrOCH}$ (*E*-isomer)), 7.10-7.61 (m, 5.4 H, ArH); ^{13}C NMR (CDCl_3 , *Z*-isomer) δ 22.6, 75.8, 105.3, 125.4, 128.1, 128.1, 136.3, 145.5; IR (neat) 3086 w, 3055 w, 3025 m, 2976 s, 2933 m, 2893 w, 1649 s, 1600 m, 1493 m, 1449 m, 1419 w, 1385 w, 1373 m, 1339 m, 1301 w, 1265 s, 1220 w, 1200 m, 1180 m, 1119 s, 1083 s, 1030 w, 943 w, 911 w, 779 s, 695 s cm^{-1} ; LRMS (EI) m/z (% relative intensity) 162 (M^+ , 25), 120 (99), 91 (100), 77 (5), 65 (11), 51 (6).

Procedure for Hydroaryloxylation (**4ad**, eq 2)

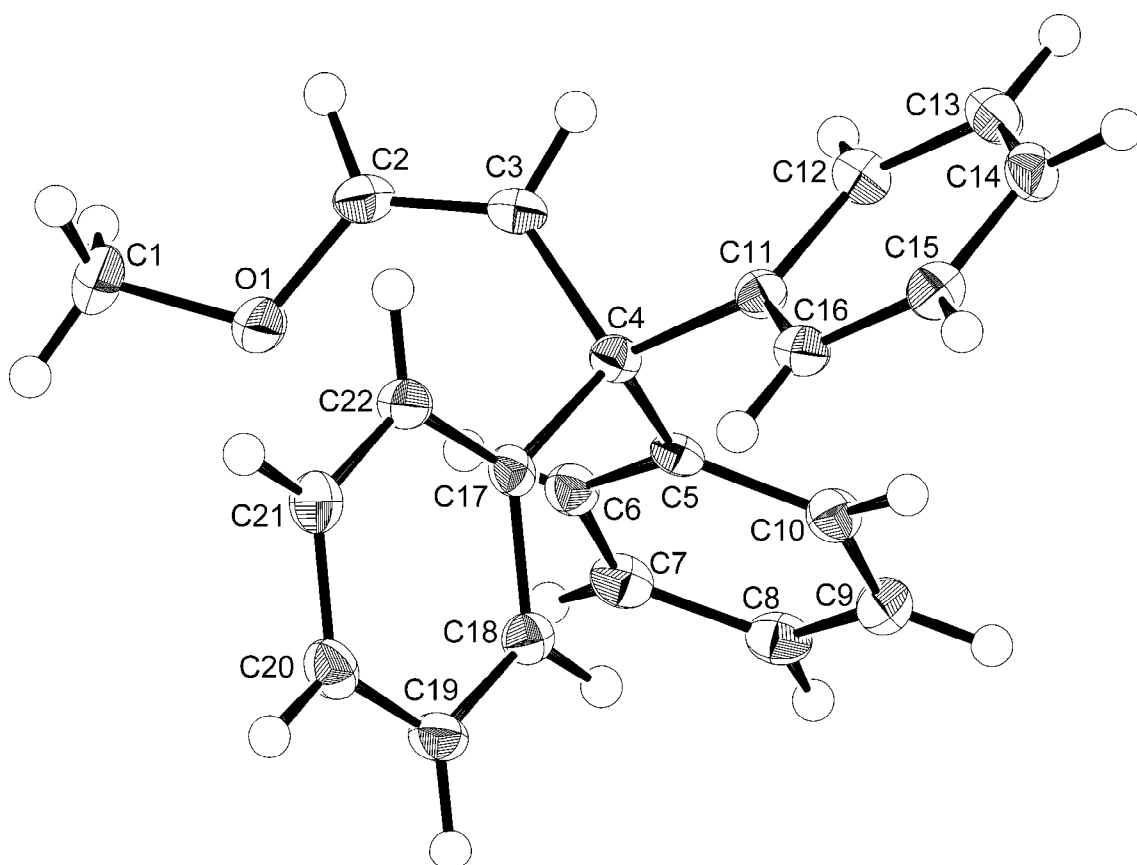
Catalyst (**3**, 0.025 mmol), *p*-methoxyphenol (**2d**, 2.5 mmol), chlorobenzene (0.5 mL), phenylacetylene (**1a**, 0.5 mmol), and 2,6-lutidine (0.025 mmol) were charged in a sealed tube with a magnetic stirring bar and heated at 70 °C for 24 h. The reaction was analyzed by GC.

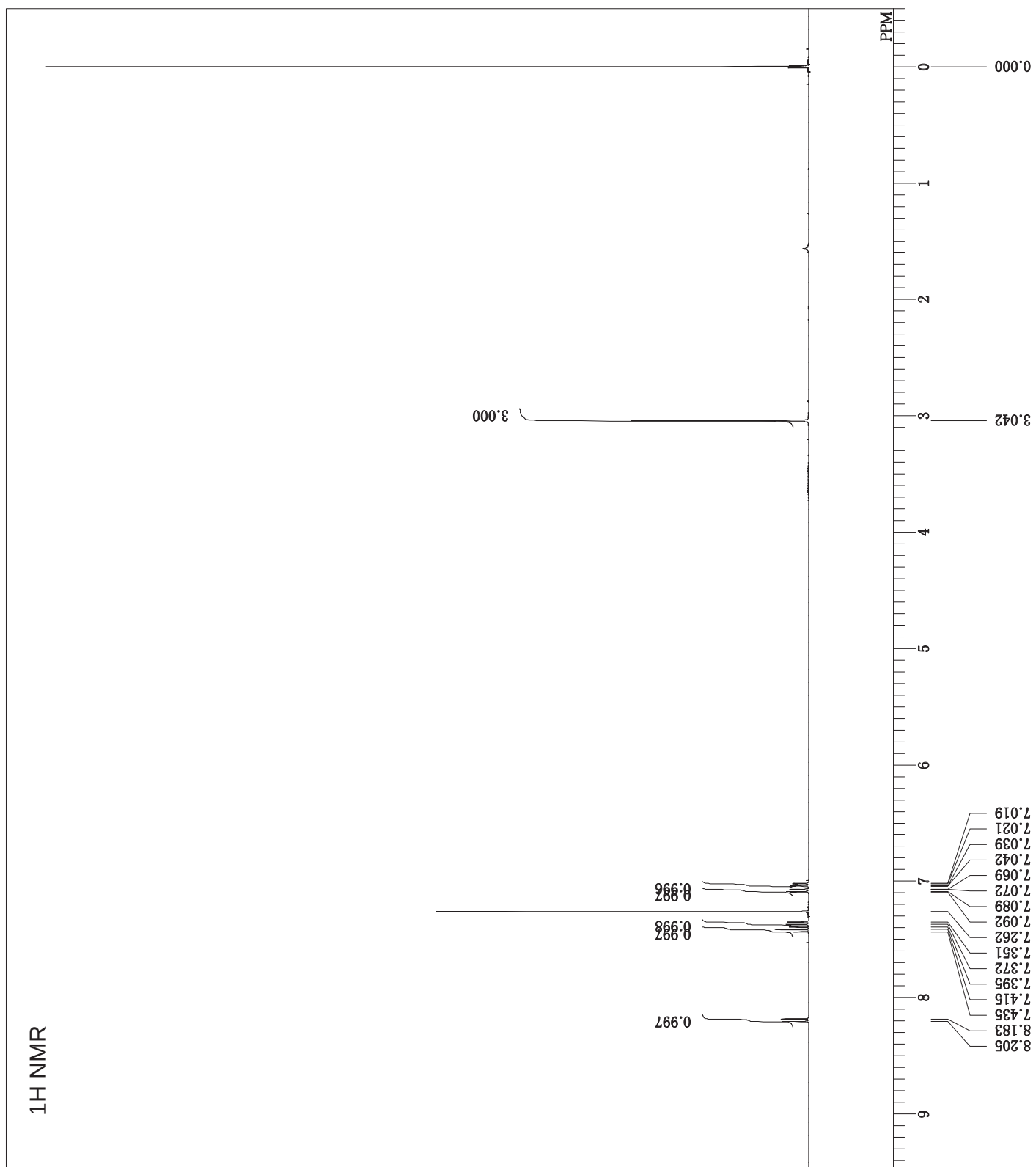
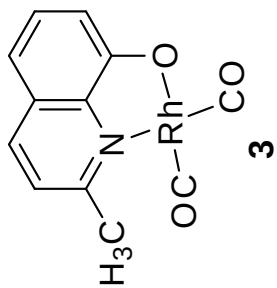
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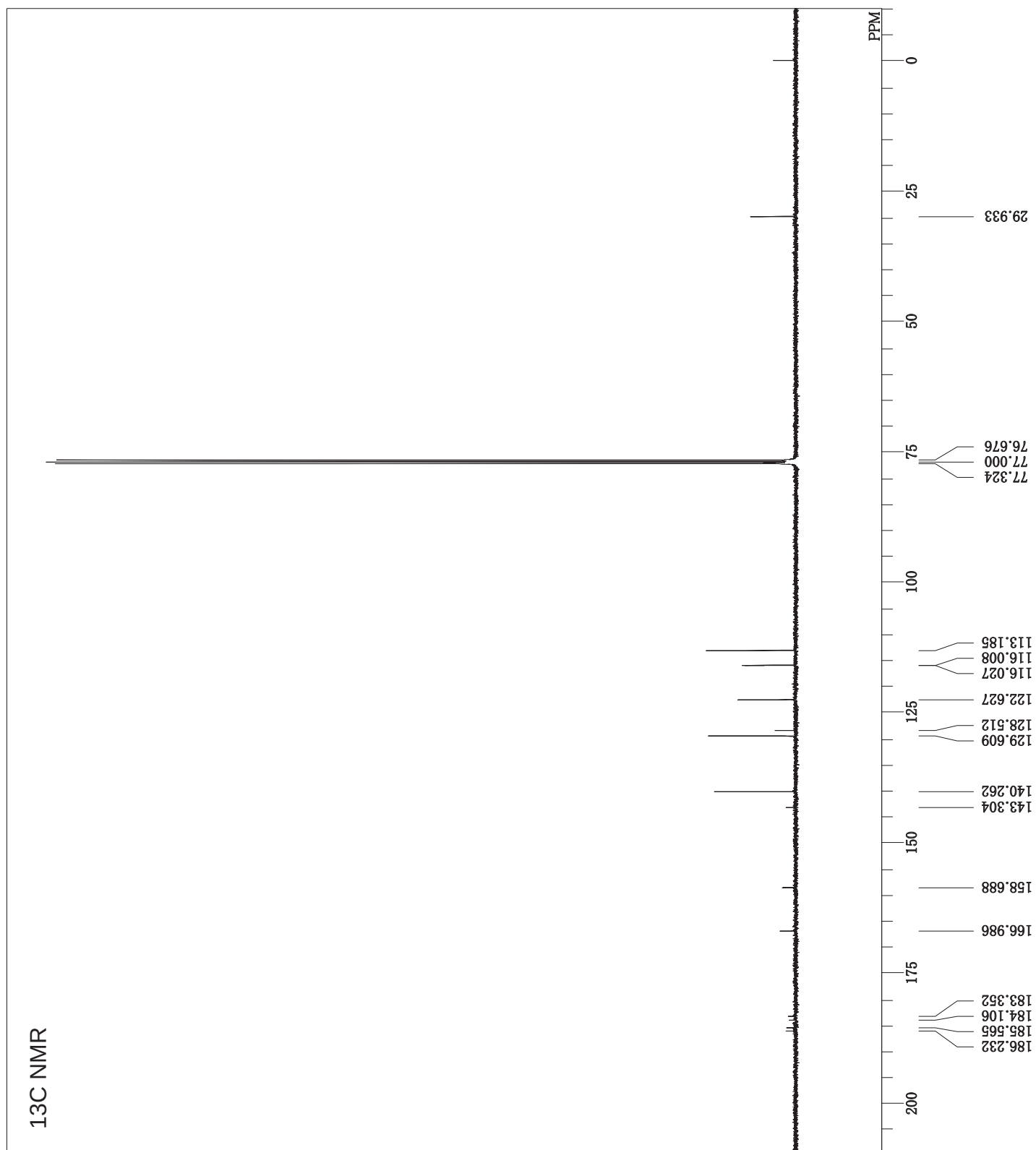
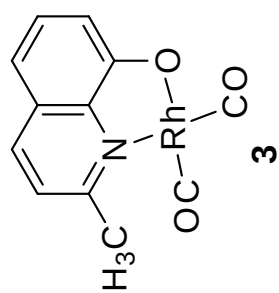
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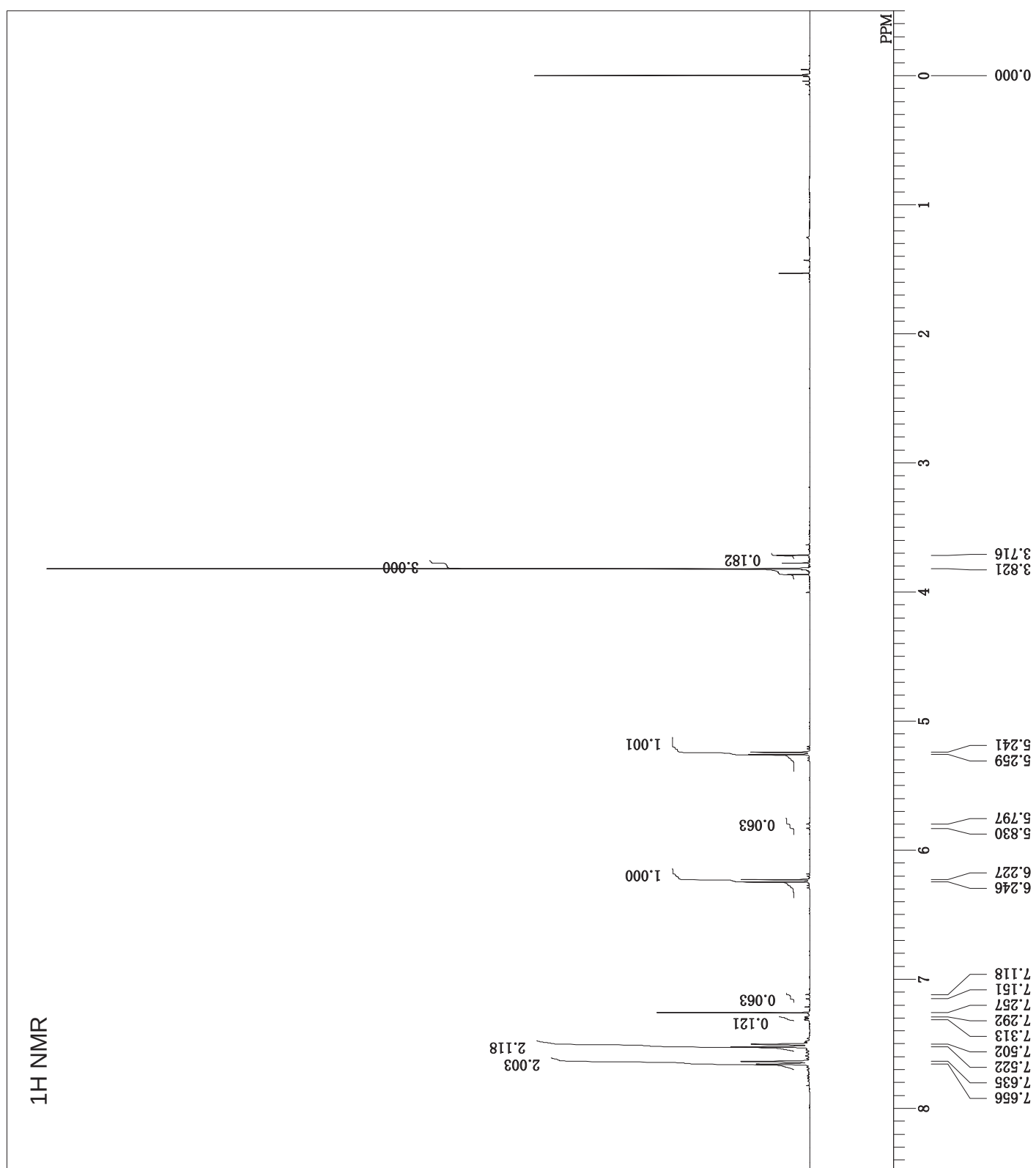
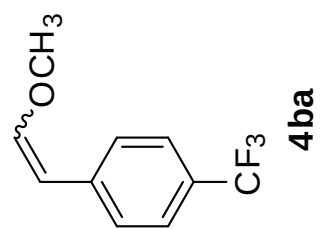
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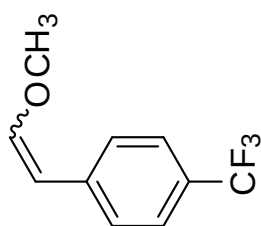
Figure S1. X-ray Structure of **4pa**





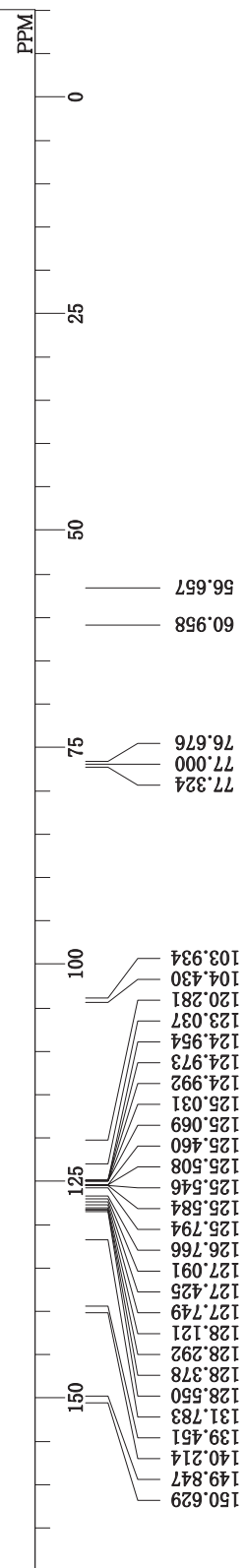


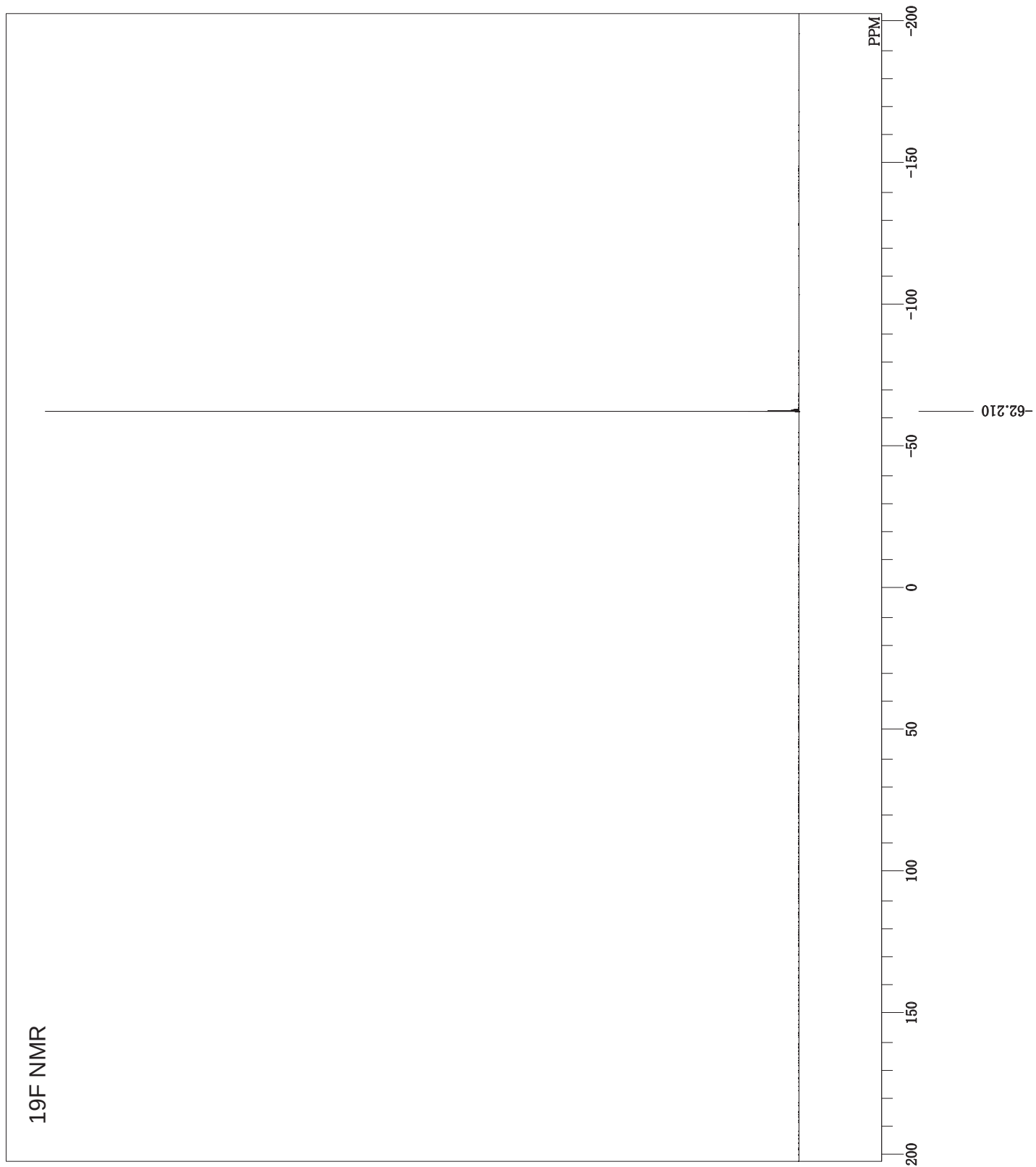
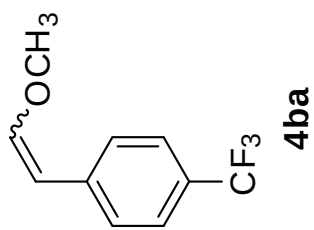


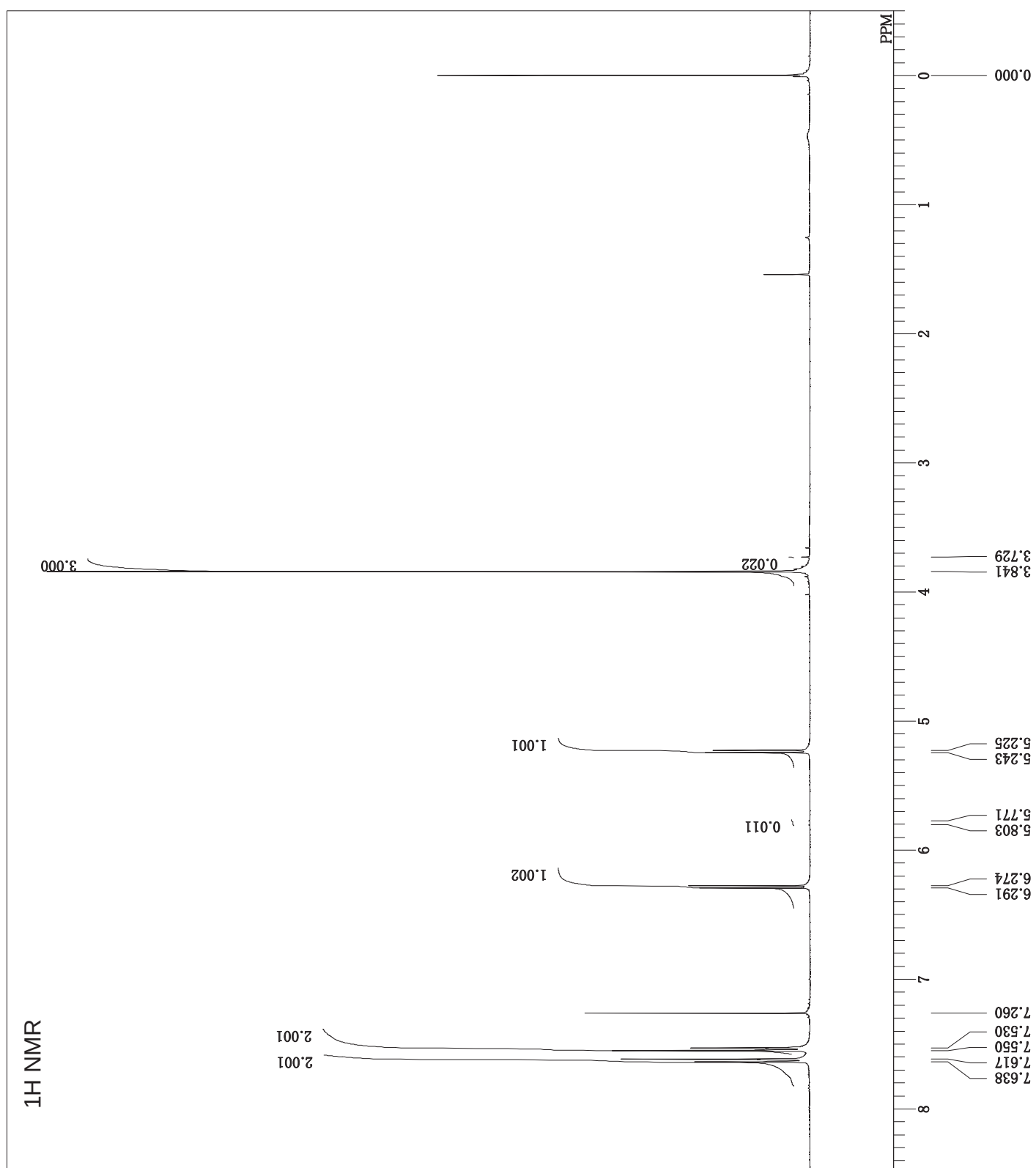
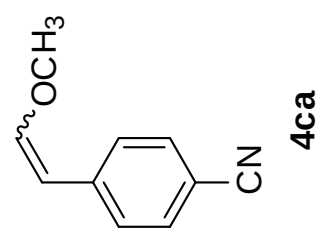


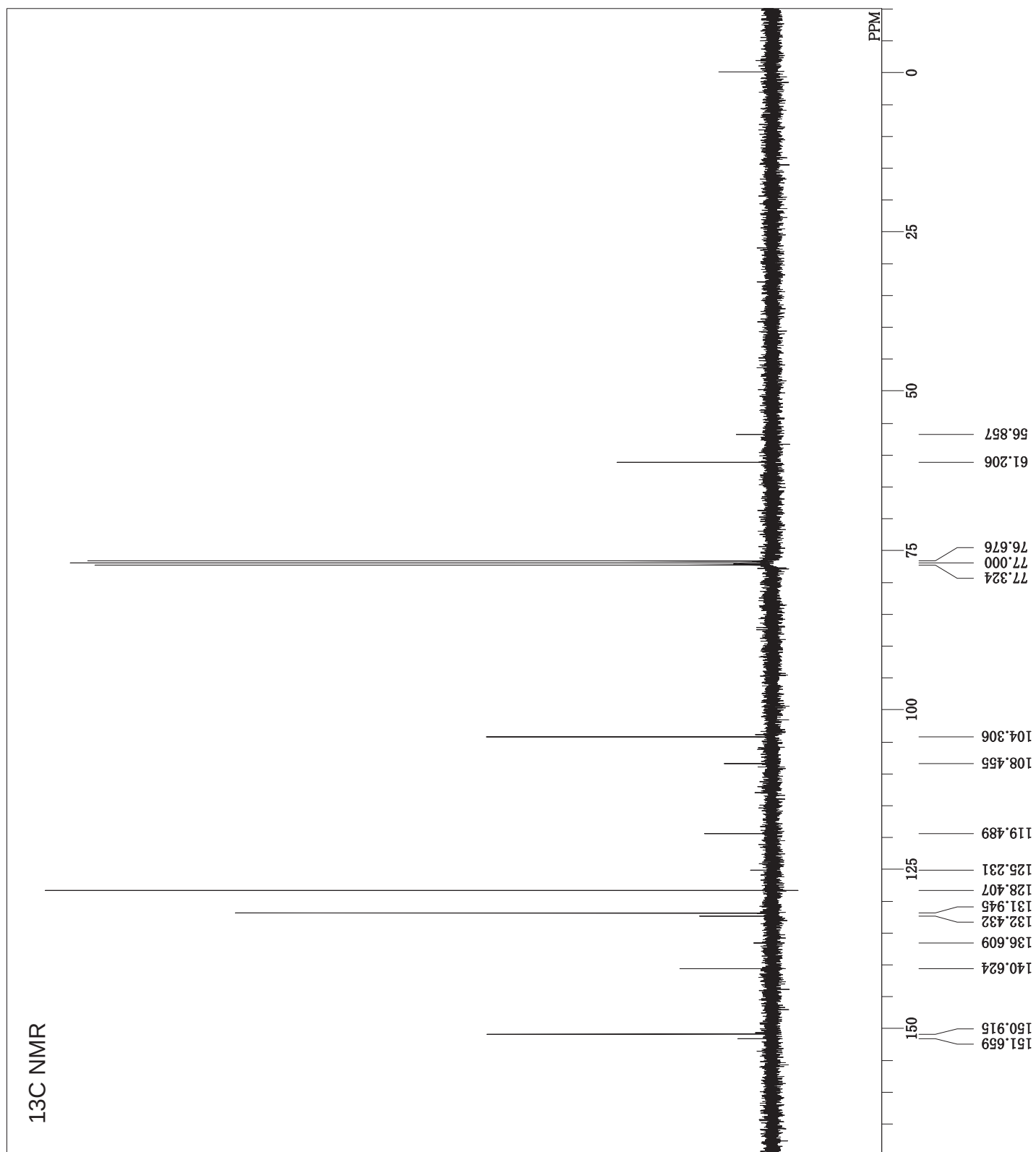
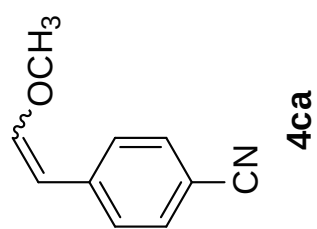
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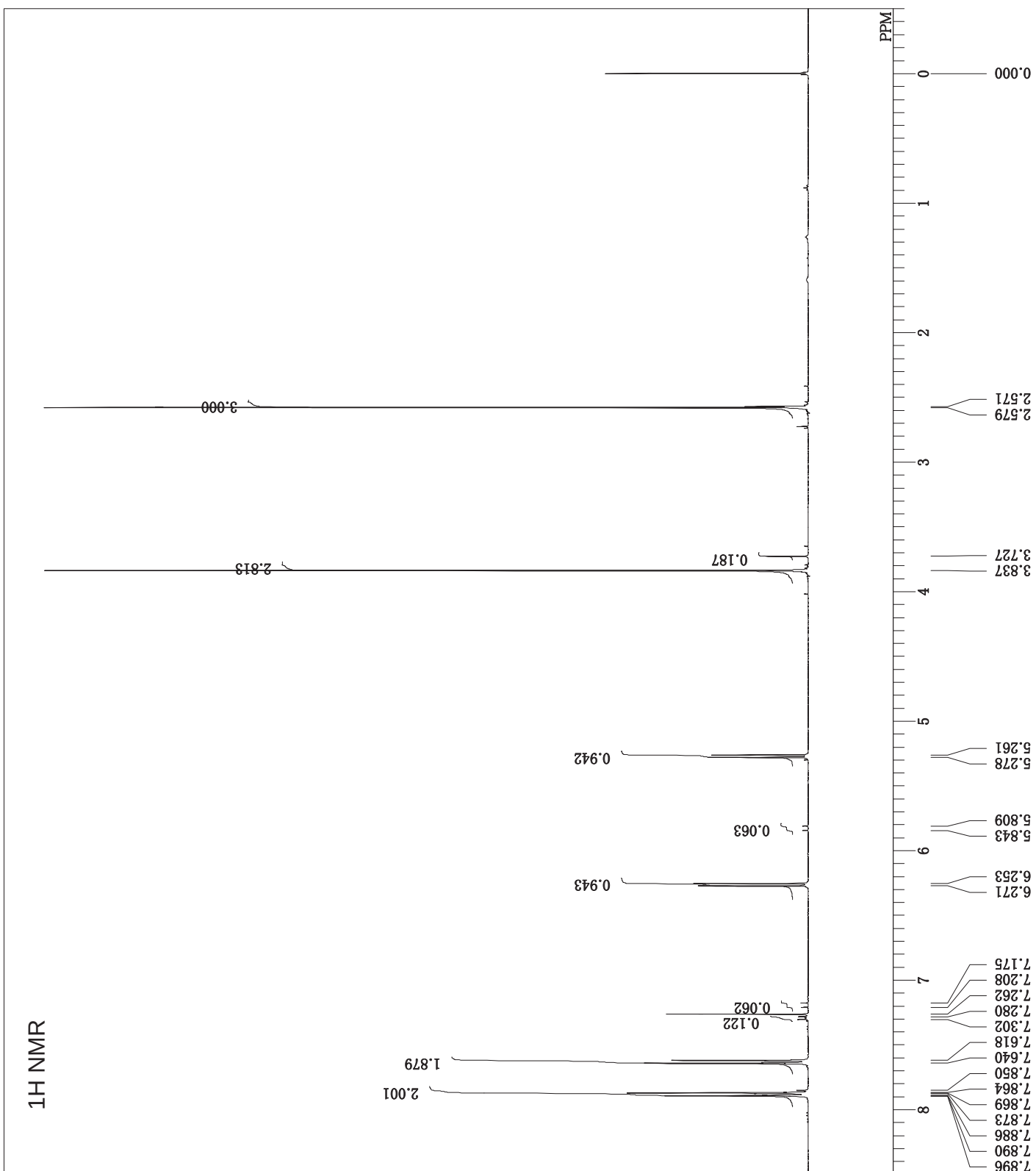
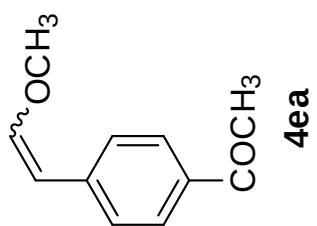
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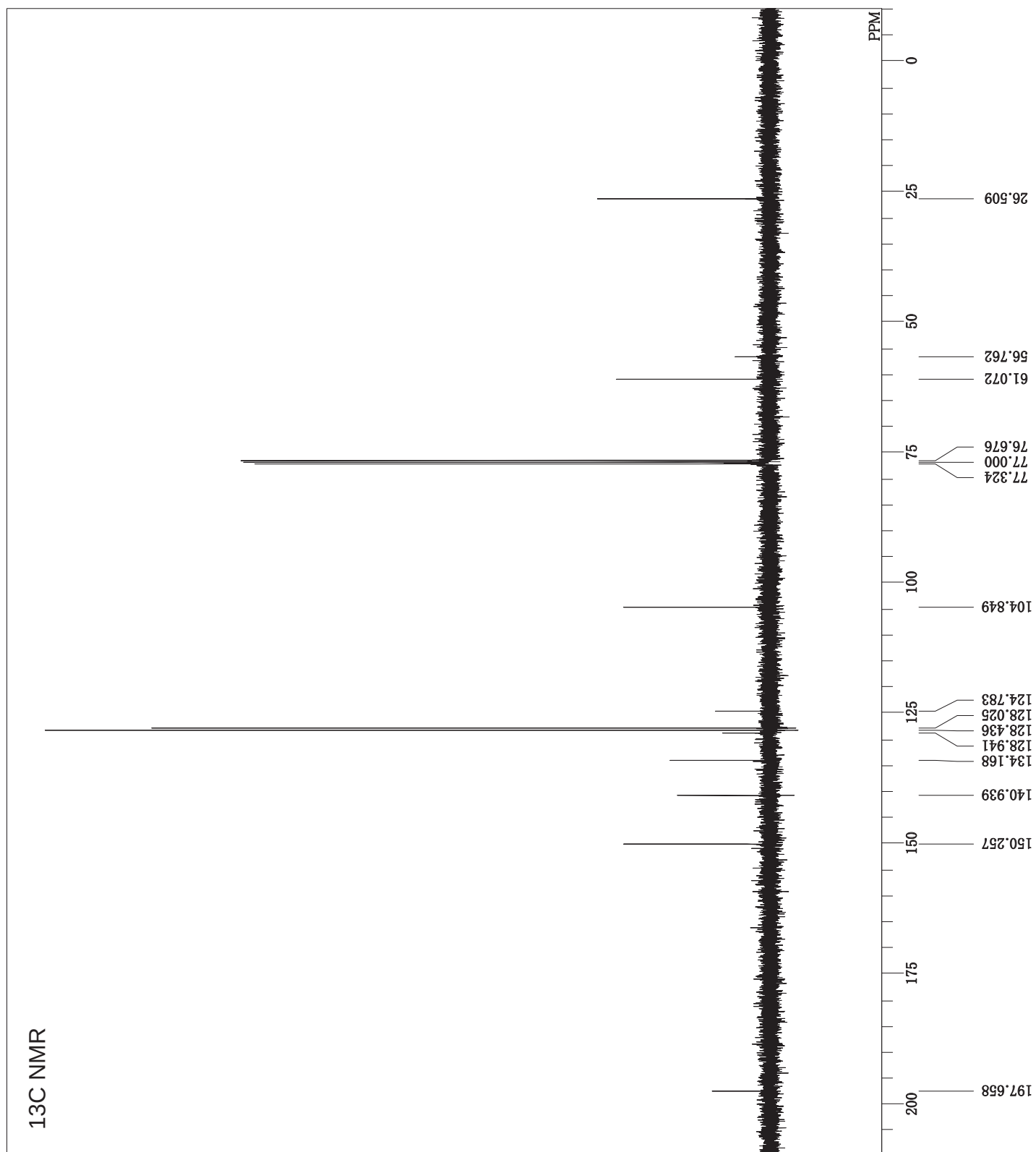
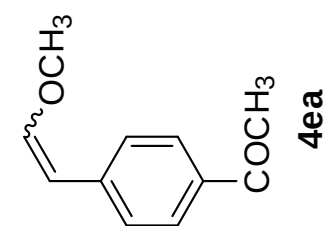


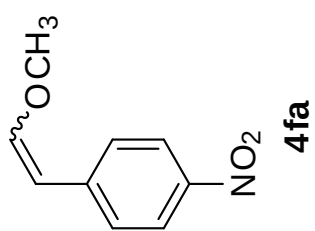
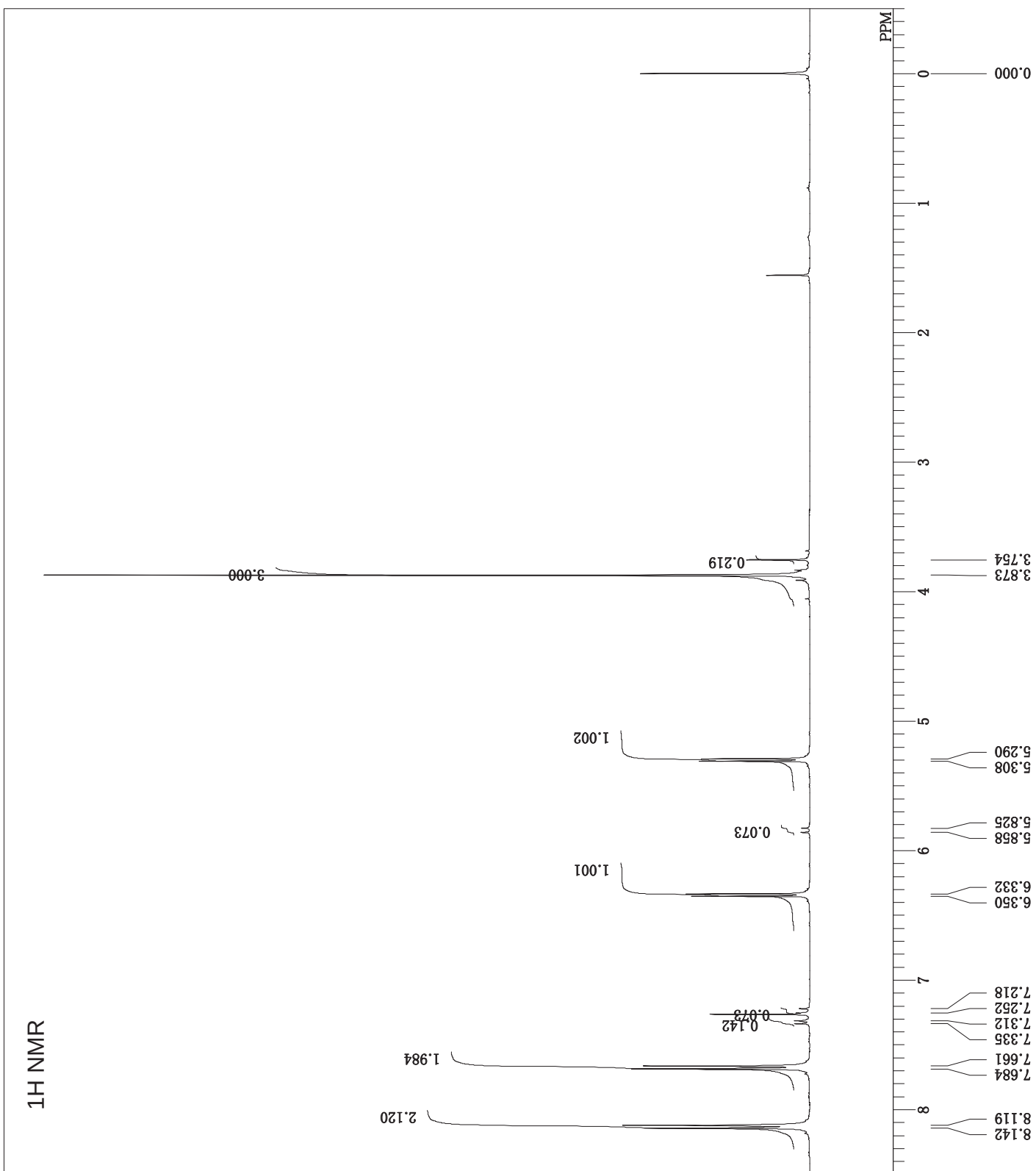


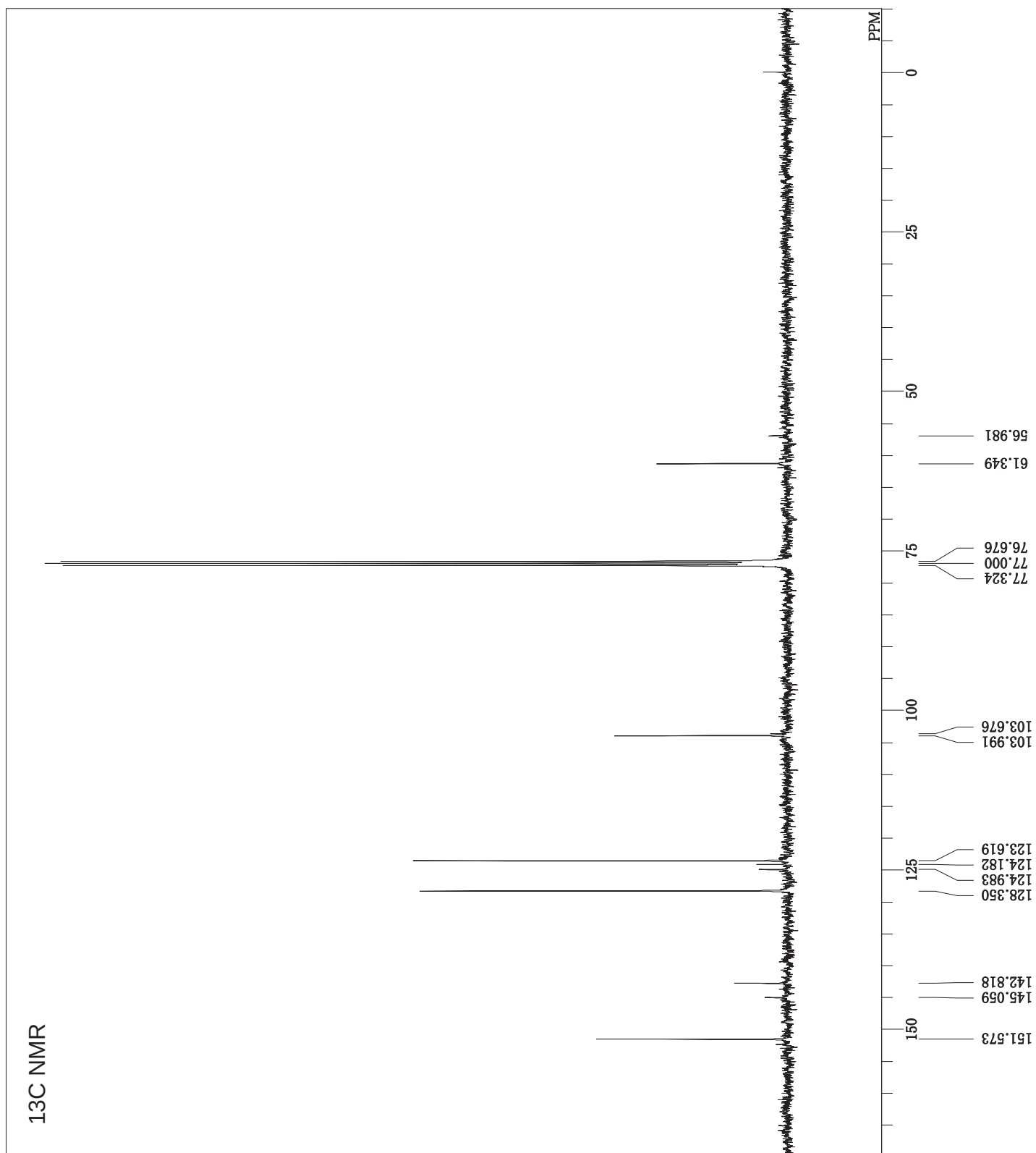
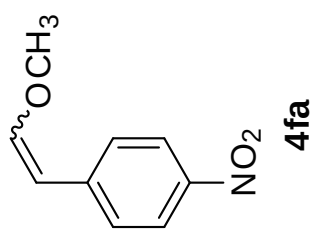


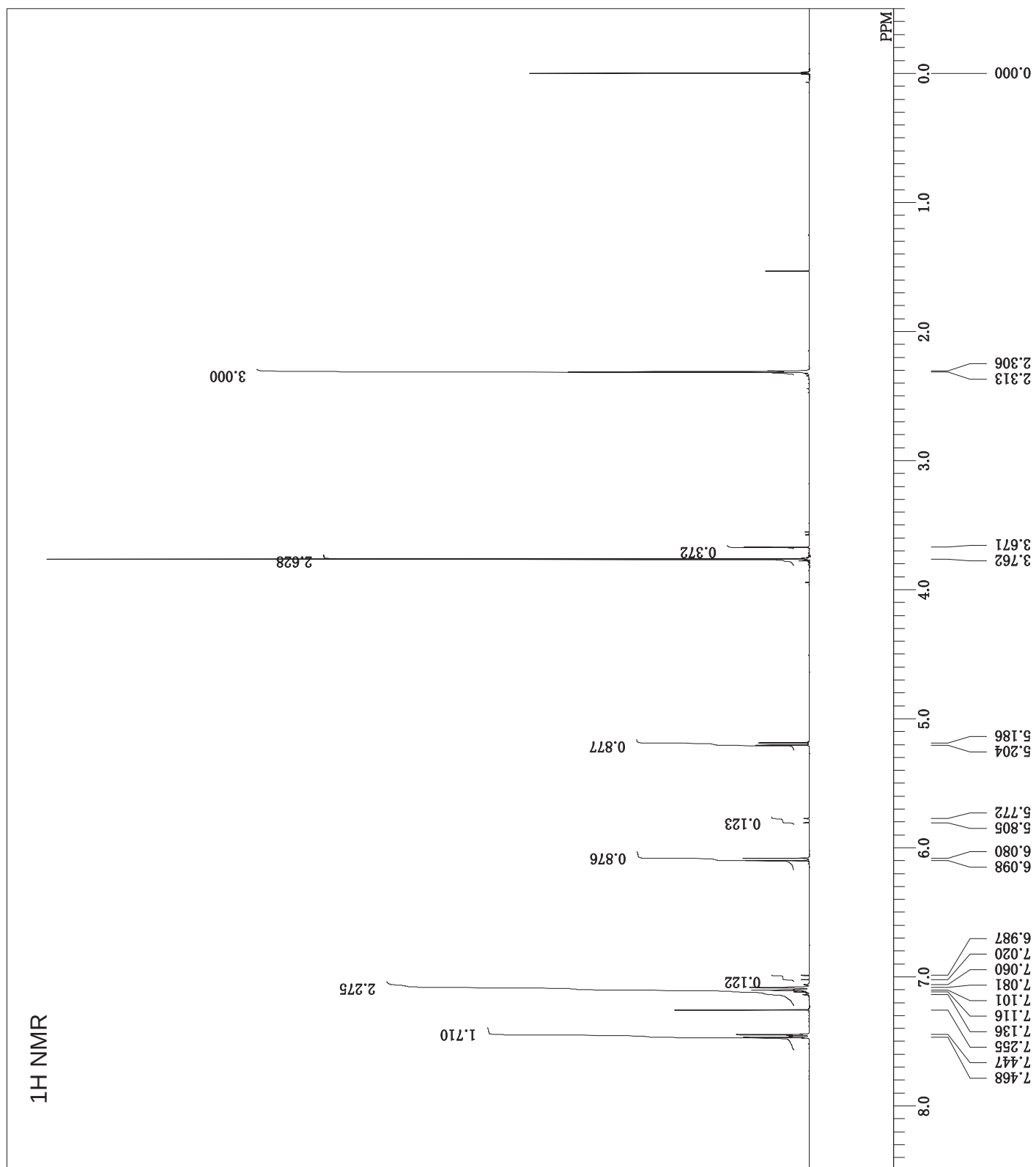
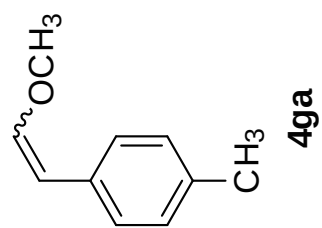


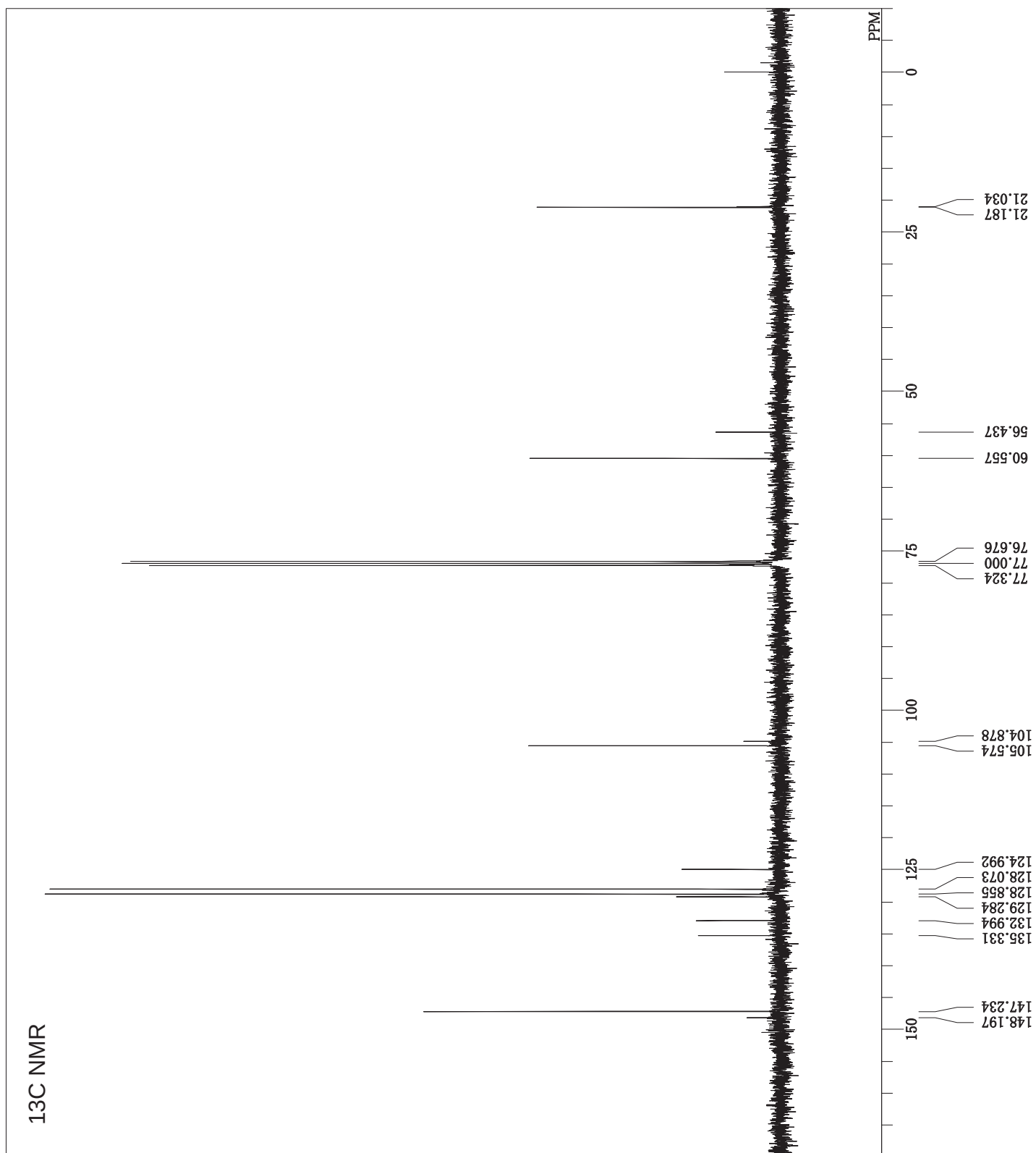
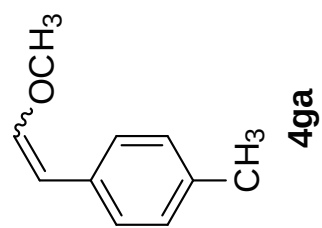


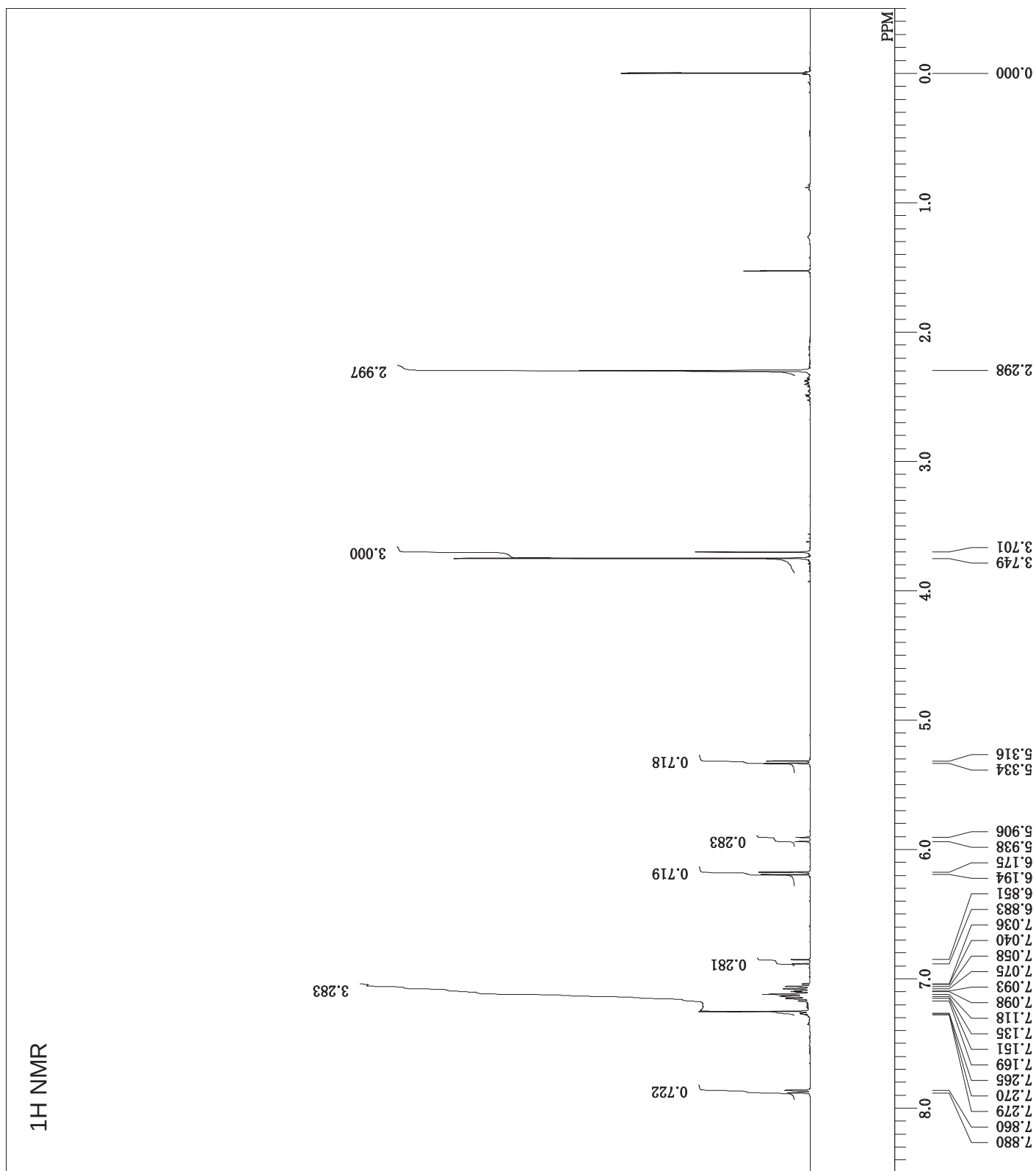
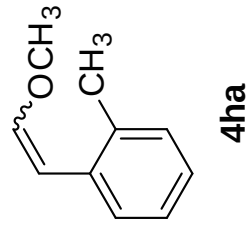


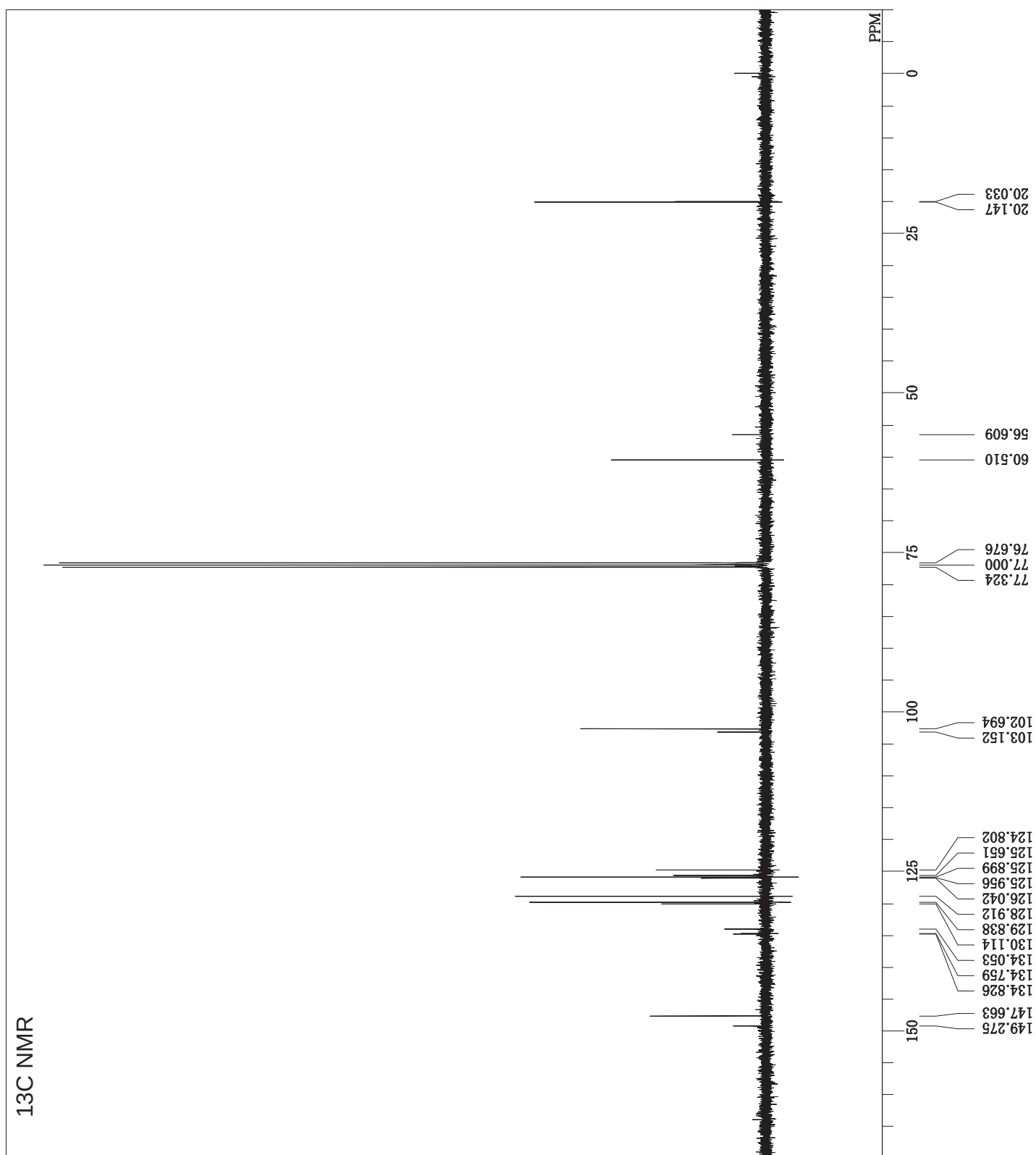
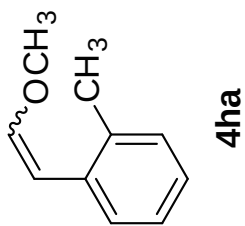


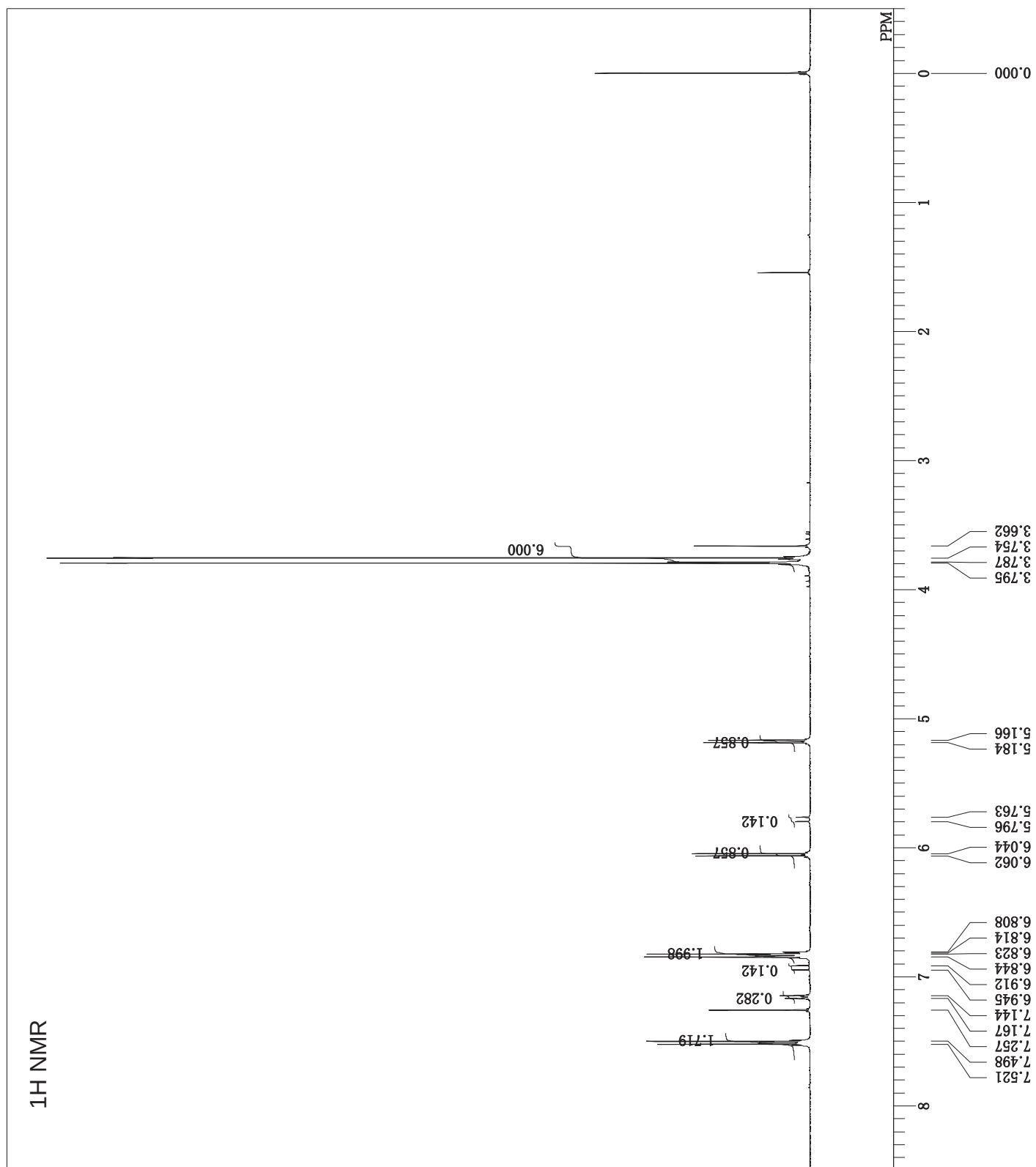
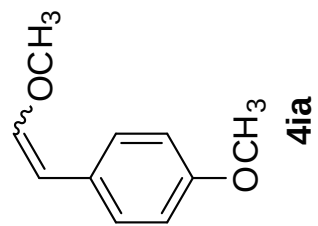


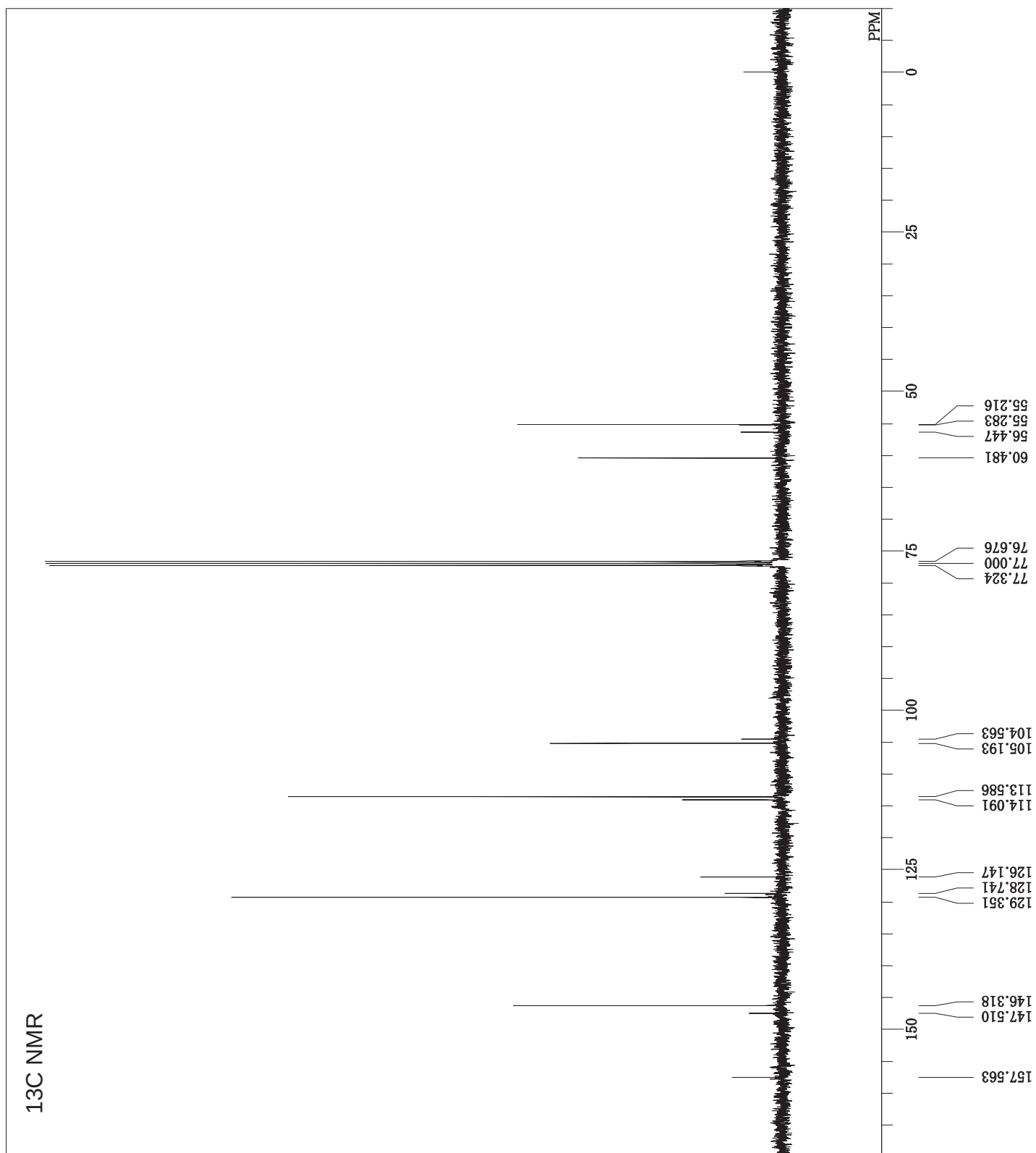
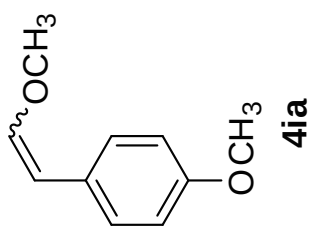


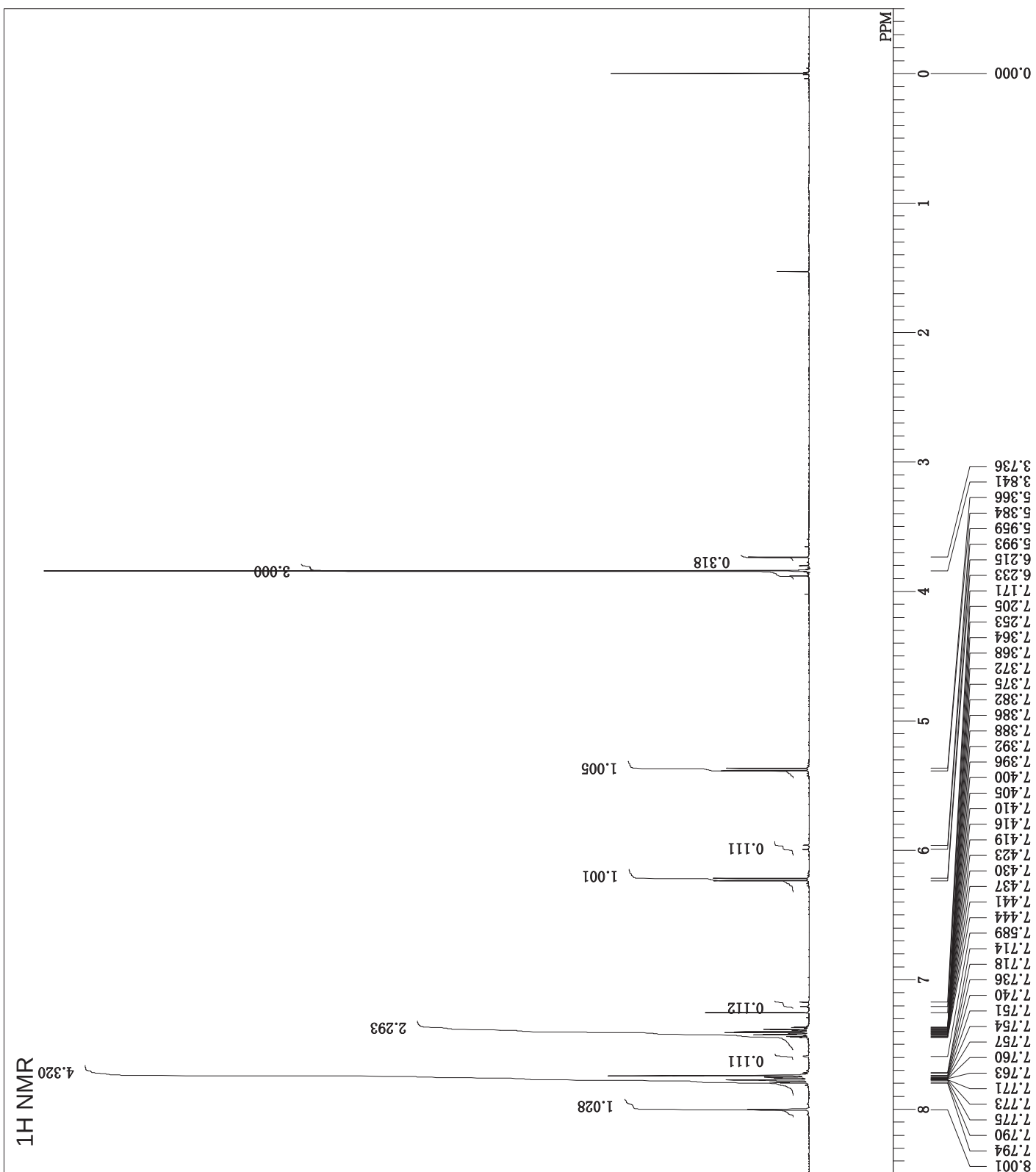






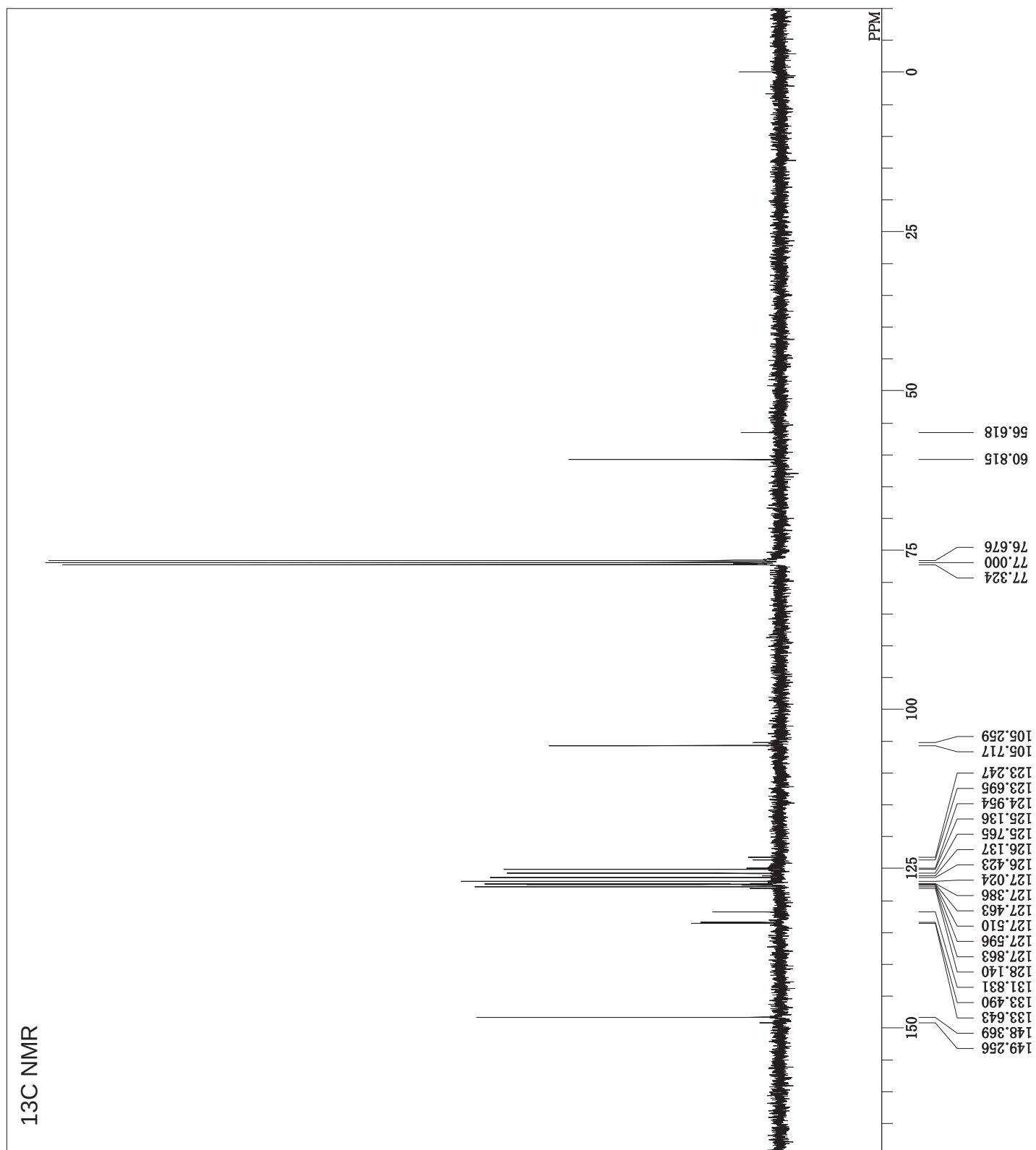
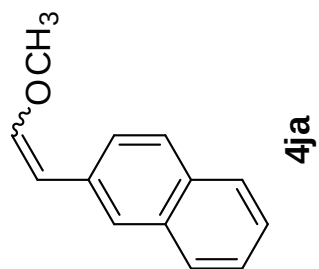


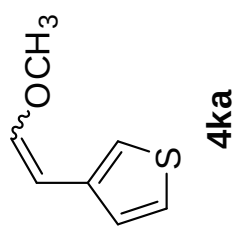
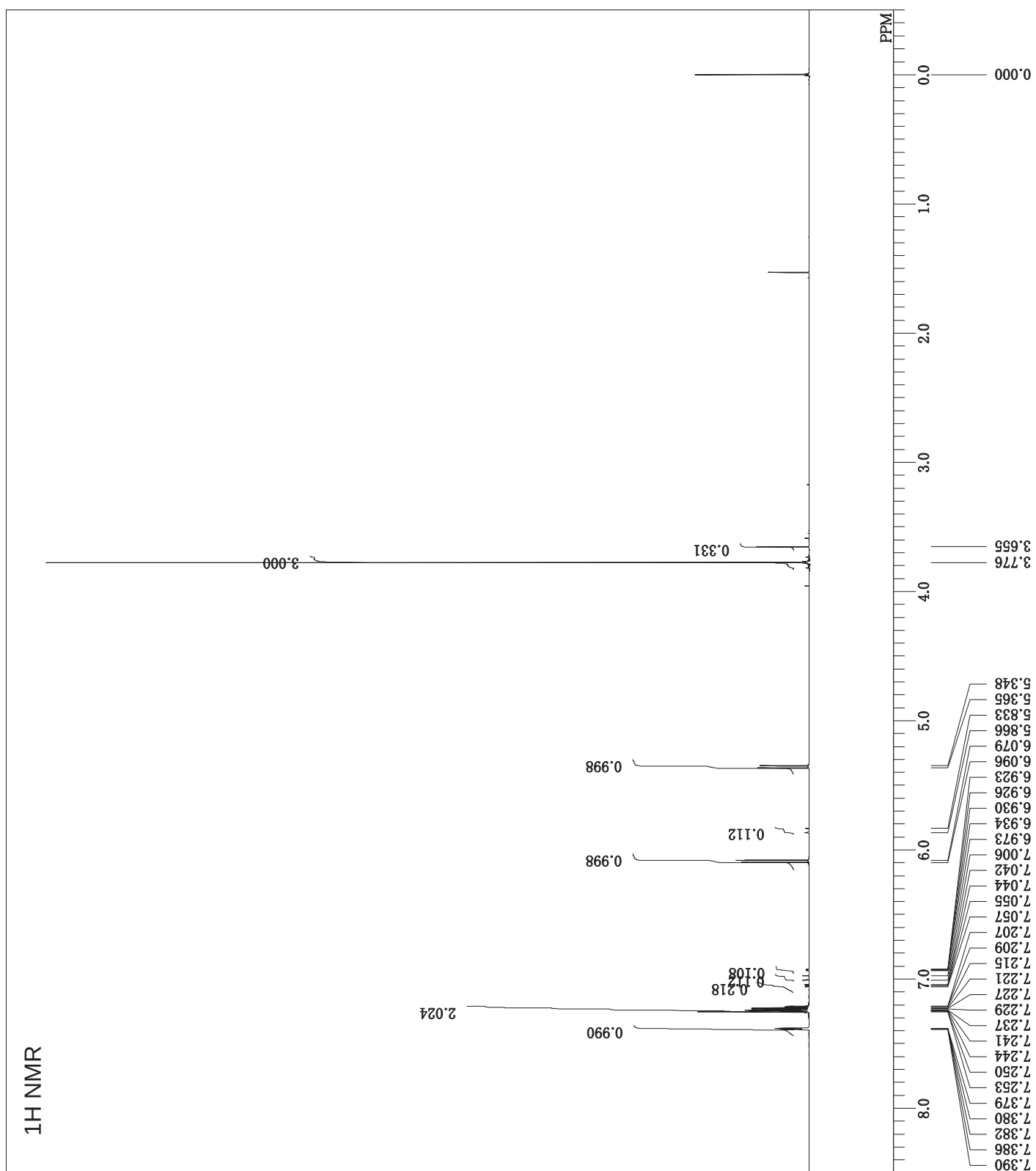


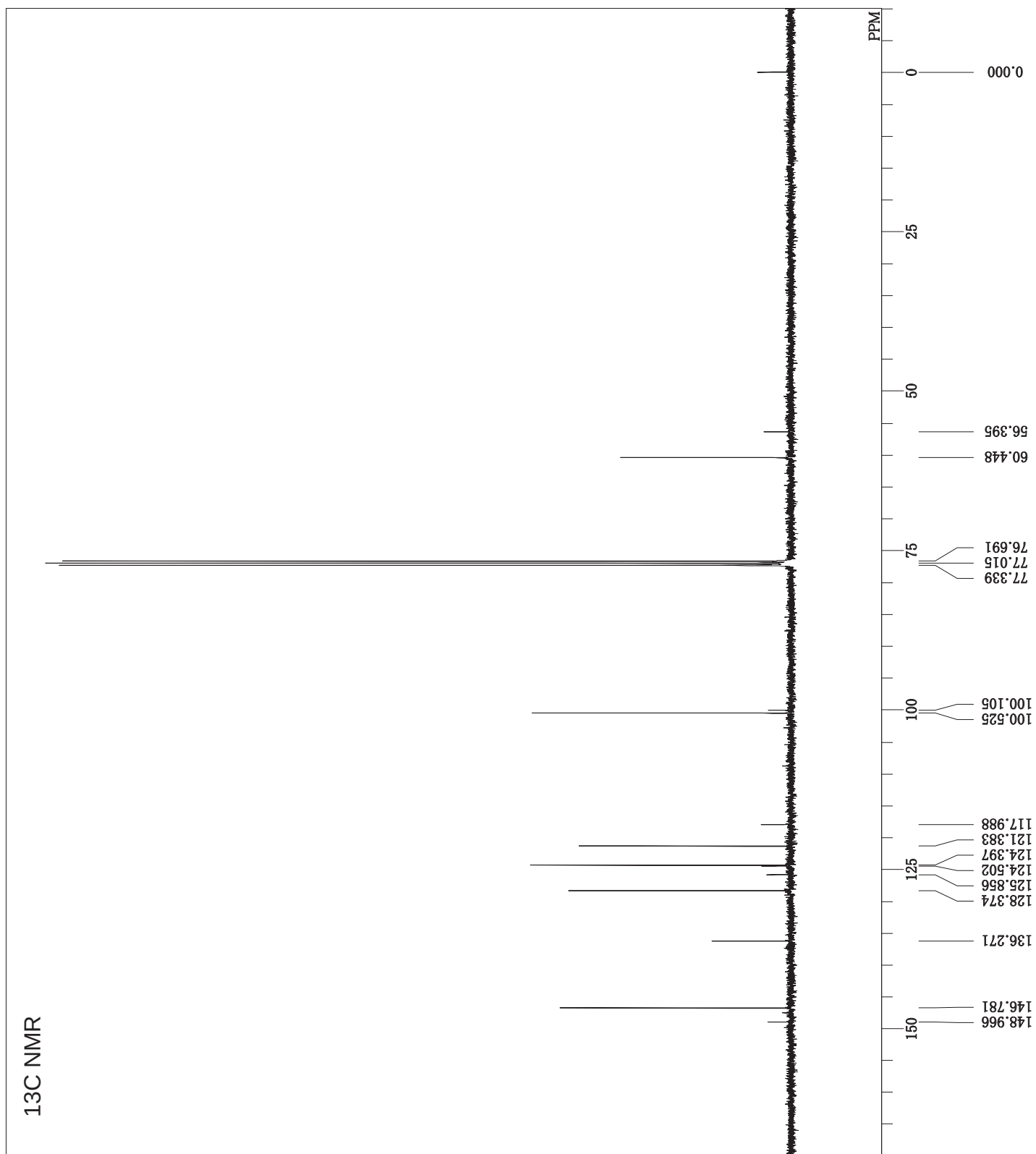
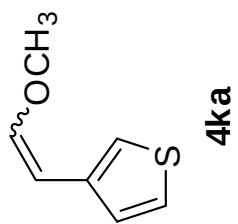


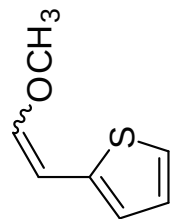
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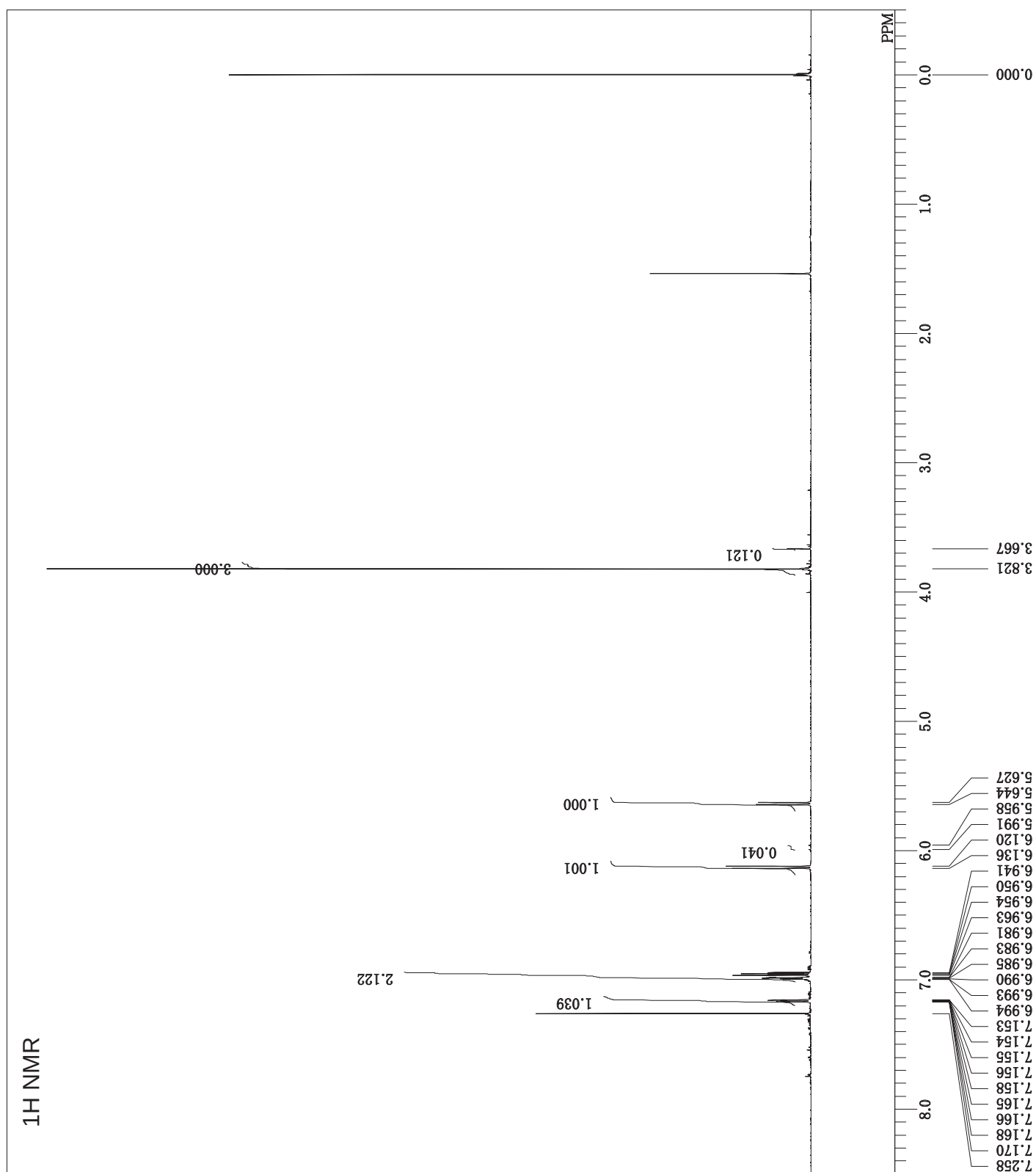


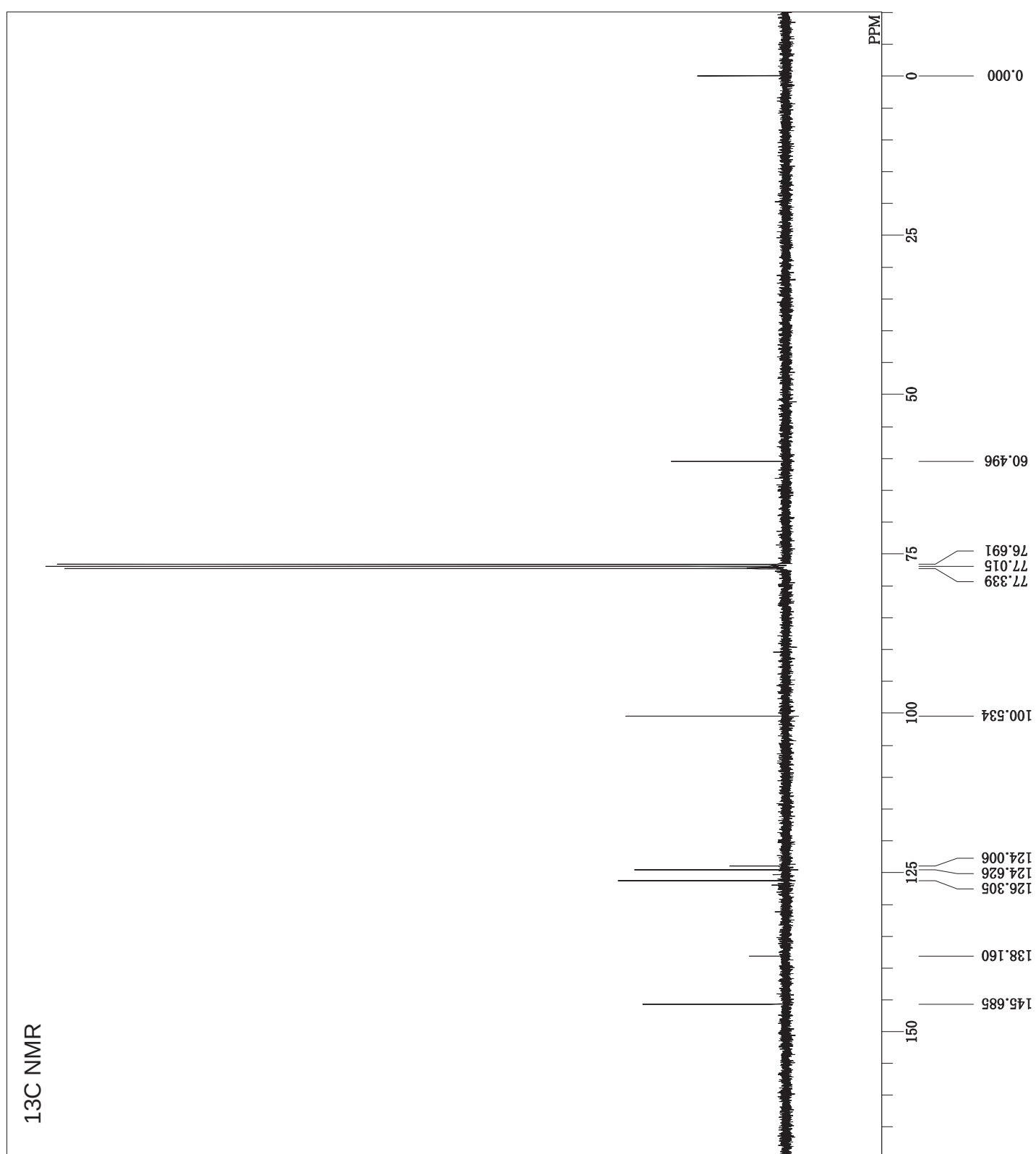
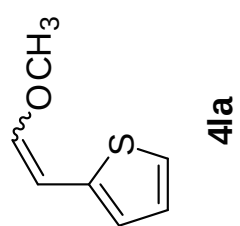


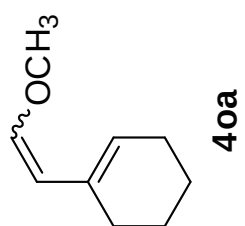
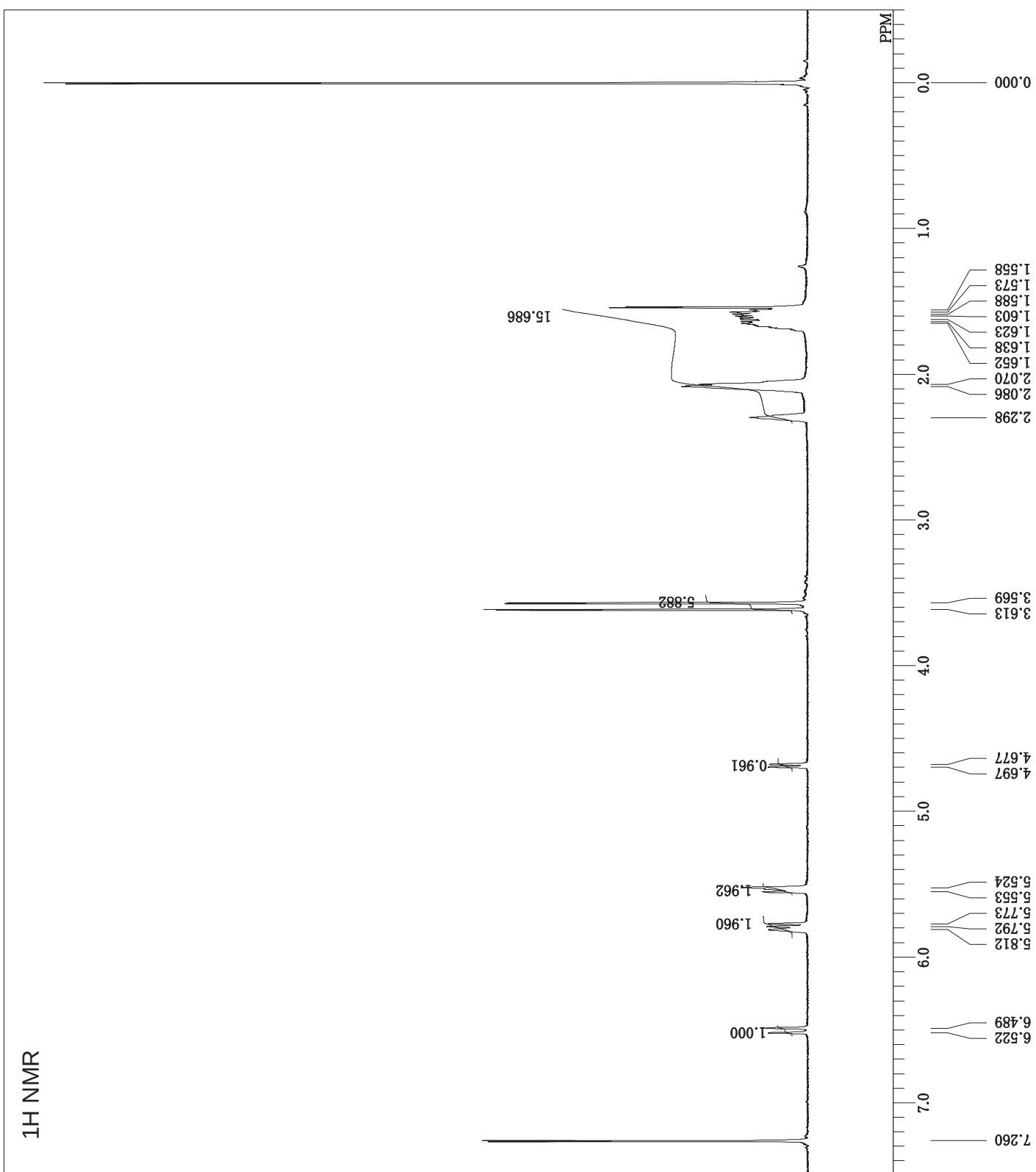


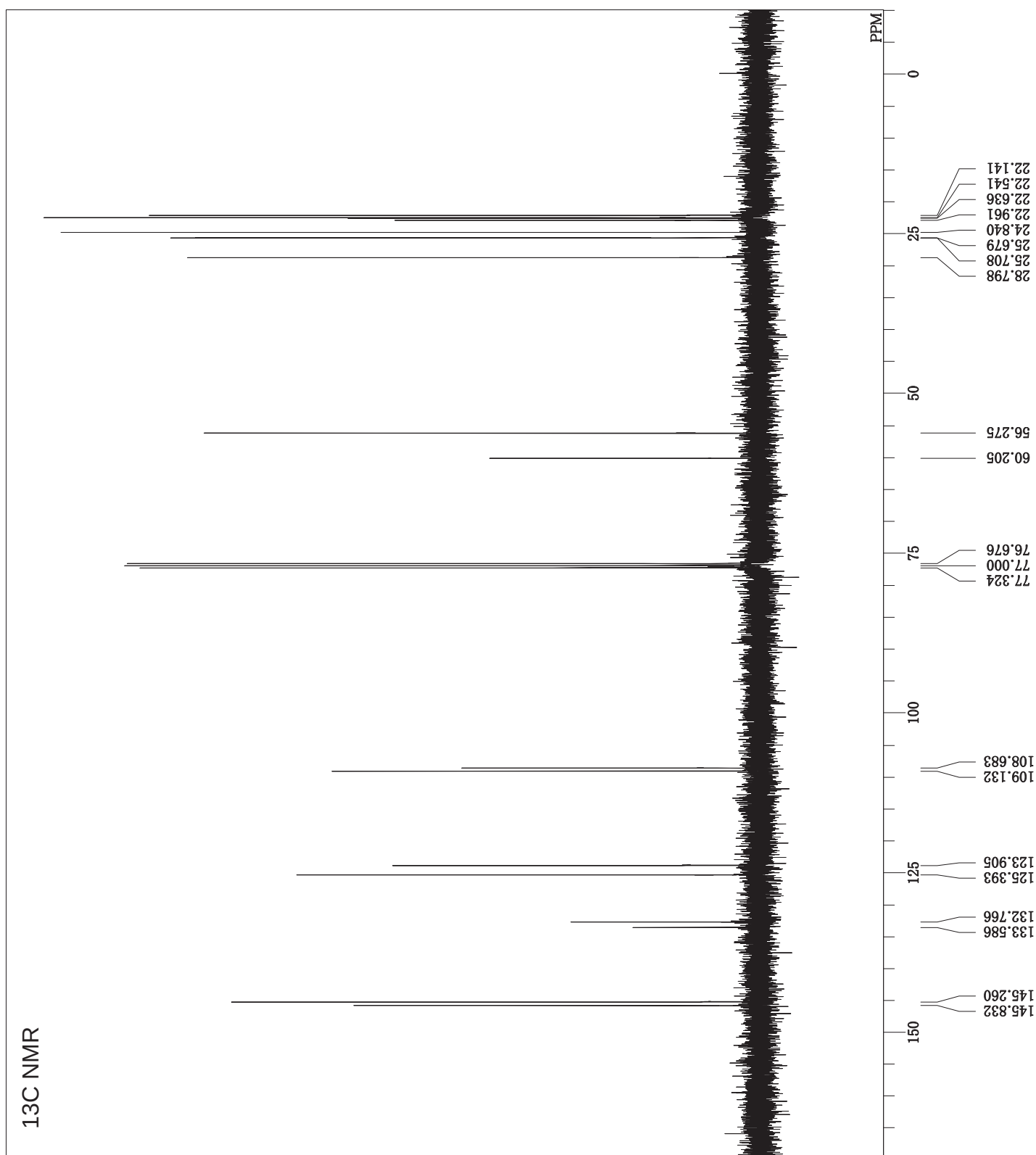
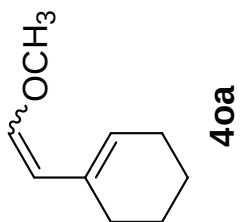


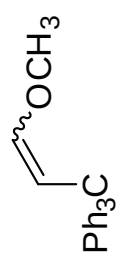
41a











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