Au(III)-Catalyzed Ring opening Reaction of 1-Cyclopropyl-2-yn-1-ols with Nucleophiles : Highly Efficient Approach to (*Z*)-conjugated Enynes

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General Remarks:

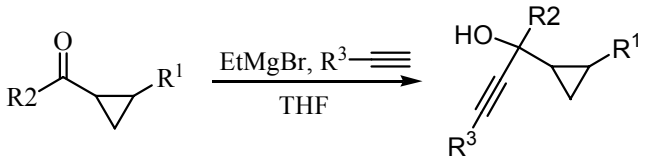
Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 300 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 75 and 100 MHz in $CDCl_3$. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All compounds were further characterized by element analysis; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Room temperature is 23-25 °C. Commercially available reagents and solvents were used without further purification. THF was distilled immediately before use from Na/benzophenone.

Cyclopropyl ketones are prepared according to the literature.[1]

Reference:

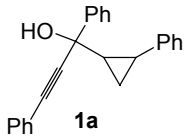
1. E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc*. **1965**, *87*, 1353.

Typical procedure A for the preparation of 1-cyclopropyl-2-propyn-1-ols 1a-1g, 1k:



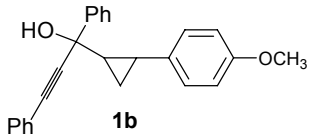
To a stirring solution of appropriate terminal alkyne (1.2 equiv) in THF (1.0 M) was added ethylmagnesium bromide (1.0 M in THF, 1.1 equiv) at room temperature. The resulting solution was stirred for 1 h at 50 °C. Then corresponding ketones (1.0 equiv) in THF (0.35 M) was added slowly by syringe to the resulting solution at room temperature and stirred for 3 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2×40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by

chromatography on silica gel to obtain the pure 1-cyclopropyl-2-propyn-1-ol as a mixture of diastereoisomers (petroleum ether–ethyl acetate, 20:1)



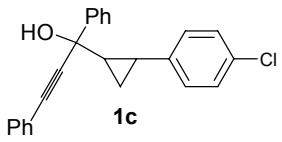
1a

Compound **1a** (cis and trans) was prepared according to the procedure A in 89% yield as an oil. **1a** (cis): oil, ^{1}H NMR (300 MHz; DCl_3): δ 0.98-1.04 (m, 1 H), 1.35-1.42 (m, 1 H), 1.71-1.77 (m, 1 H), 2.40-2.45 (m, 1 H), 2.67 (s, 1 H), 7.06-7.47 (m, 11 H), 7.72-7.74 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3): δ13.4, 20.7, 34.8, 74.0, 74.3, 86.4, 89.1, 122.2, 125.4, 125.7, 126.2, 127.8, 128.2, 128.3, 128.3, 128.6, 131.7, 141.9, 144.4. Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21; Found: C, 88.78; H, 6.30.
1a (trans): oil, ^{1}H NMR (400 MHz; DCl_3): δ 1.02-1.07 (m, 1 H), 1.48-1.53 (m, 1 H), 1.71-1.75 (m, 1 H), 2.28-2.33 (m, 1 H), 2.62 (s, 1 H), 7.02-7.47 (m, 11 H), 7.73-7.75 (m, 2 H); ^{13}C NMR (100 MHz, DCl_3): δ12.1, 21.4, 34.1, 74.1, 86.4, 89.3, 122.3, 125.4, 125.7, 126.4, 127.8, 128.3, 128.6, 131.8, 141.7, 144.4. Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21; Found: C, 88.78; H, 6.30.



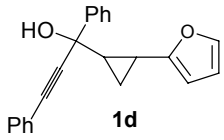
1b

Compound **1b** (1:1 mixture of diastereoisomers) was prepared according to the procedure A in 92% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (1:1 mixture of diastereoisomers): δ 0.95-0.96 (m, 1 H), [1.32-1.33 (m), 1.43-1.45 (m), 1 H], 1.62-1.68 (m, 1 H), [2.24-2.26 (m), 2.38-2.40 (m), 1 H], 2.86 (s,1 H), 3.68 (s, 3 H), 6.71-6.77 (m, 3 H), 6.91-7.01 (m, 2 H), 7.28-7.46 (m, 8 H), 7.72-7.74 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (1:1 mixture of diastereoisomers): δ 11.6, 12.9, 19.9, 20.5, 33.8, 34.4, 55.1, 74.0, 74.3, 86.3, 89.3, 113.6, 113.7, 122.2, 125.3, 127.3, 127.5, 127.7, 128.2, 128.2, 128.5, 131.7, 133.6, 133.9, 144.5, 144.5, 157.6; IR (neat): 3540, 3443, 2226, 1610, 1514, 1490, 1447cm^{-1}. Anal.Calcd for $C_{25}H_{22}O_2$: C,84.72; H, 6.26. Found: C, 84.75; H, 6.29.



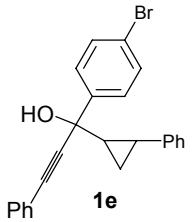
1c

Compound **1c** (2:1 mixture of diastereoisomers) was prepared according to the procedure A in 93% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (2:1 mixture of diastereoisomers): δ 0.96-1.02 (m, 1 H), [1.37-1.41(m), 1.50-1.55(m), 1 H], 1.65-1.74 (m, 1 H), [2.23-2.28 (m), 2.41-2.44 (m), 1 H], [2.64(s), 2.65(s), 1 H], 6.92-7.17 (m, 4 H), 7.20-7.49 (m, 8 H), 7.71-7.74 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (2:1 mixture of diastereoisomers): δ 12.2, 13.5, 20.2, 20.7, 34.4, 34.9, 73.8, 74.2, 86.5, 86.6, 88.9, 89.0, 122.1, 125.3, 127.5, 127.8, 127.9, 128.1, 128.4, 128.5, 128.7, 133.6, 131.3, 131.8, 140.2, 140.5, 144.3; Anal.Calcd for $C_{24}H_{19}O$: C, 80.33; H, 5.34. Found: C, 80.43; H, 5.25.



1d

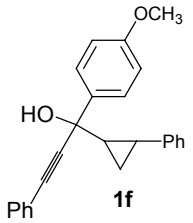
Compound **1d** (2:1 mixture of diastereoisomers) was prepared according to the procedure A in 86% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (2:1 mixture of diastereoisomers): δ 1.05-1.11 (m, 1 H), [1.27-1.32(m), 1.38-1.45(m), 1 H], 1.83-1.90 (m, 1 H), [2.27-2.34 (m), 2.45-2.51 (m), 1 H], [2.69(s), 2.80(s), 1 H], 5.91-5.98 (m, 1 H), 6.19-6.24 (m, 1 H), 7.18-7.47 (m, 8 H), 7.72-7.75 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (2:1 mixture of diastereoisomers): δ 10.6, 11.5, 14.2, 14.8, 31.8, 32.3, 73.5, 74.0, 86.4, 86.3, 88.6, 89.0, 104.0, 110.2, 110.3, 122.0, 125.4, 127.8, 128.2, 128.6,131.7, 140.6, 144.1, 155.3, 155.4; IR (neat): 3543, 3431, 2227, 1598, 1490, 1447cm^{-1}. Anal.Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.00; H, 5.69.



1e

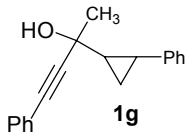
Compound **1e** (1:1 mixture of diastereoisomers) was prepared according to the procedure A in 91% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (1:1 mixture of

diastereoisomers): δ 0.95-1.06 (m, 1 H), [1.35-1.40(m), 1.46-1.50(m), 1 H], 1.59-1.69 (m, 1 H), [2.27-2.29 (m), 2.41-2.43 (m), 1 H], [2.77(s), 2.79(s), 1 H], 6.93-7.60 (m, 14 H); ^{13}C NMR (75 MHz, DCl_3) (1:1 mixture of diastereoisomers): δ 12.0, 13.4, 20.7, 21.4, 34.0.8, 34.7, 73.7.3, 73.9, 86.7, 88.6, 121.8, 121.9, 125.8, 126.1, 126.3, 127.2, 127.5, 128.2, 128.3, 138.8, 131.0, 131.3, 131.8, 141.3, 141.6, 143.5; IR (neat): 3549, 3418, 2227, 1601, 1487, 1487cm^{-1}. Anal.Calcd for $C_{24}H_{19}BrO$: C, 71.47; H, 4.75. Found: C, 71.53; H, 4.68.



1f

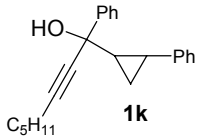
Compound **1f** (1:1 mixture of diastereoisomers) was prepared according to the procedure A in 89% yield as solid: mp, 38-39℃, ^{1}H NMR (300 MHz; DCl_3) (1:1 mixture of diastereoisomers): δ 0.99-1.05 (m, 1 H), [1.32-1.39(m), 1.45-1.52(m), 1 H], 1.69-1.79 (m, 1 H), [2.23-2.29 (m), 2.39-2.45 (m), 1 H], 2.82(s,1 H), 3.73 (s, 3 H), 6.83-6.90 (m, 2 H), 7.01-7.28 (m, 8 H), 7.42-7.47 (m, 2 H), 7.65-7.67 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (1:1 mixture of diastereoisomers): δ 12.2, 13.3, 20.7, 20.2, 34.0, 34.7, 55.1, 73.7, 73.9, 86.1, 89.4, 89.5, 113.5, 122.2, 125.6, 126.1, 126.3, 126.7, 128.2, 128.2, 128.5, 128.5, 131.7, 136.7, 141.8, 142.0, 159.0; IR (neat): 3555, 3438, 2226, 1606, 1508, 1460cm^{-1}. Anal.Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.68; H, 6.35.



1g

Compound **1g** (4:1 mixture of diastereoisomers) was prepared according to the procedure A in 94% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (4:1 mixture of diastereoisomers): δ. [0.79-0.88 (m), 0.94-1.03 (m), 1 H], 1.30-1.39 (m, 1 H), 1.50-1.57 (m, 1 H), [1.67 (s), 1.71 (s), 3 H], [2.00-2.06 (m), 2.10-2.16 (m), 1H], [2.28 (s), 2.30 (s), 1H], 7.05-7.32 (m, 8 H), 7.41-7.45 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (4:1 mixture of diastereoisomers): δ 12.2, 21.0, 29.8, 30.0, 33.0, 33.2, 70.0, 84.4, 90.0,

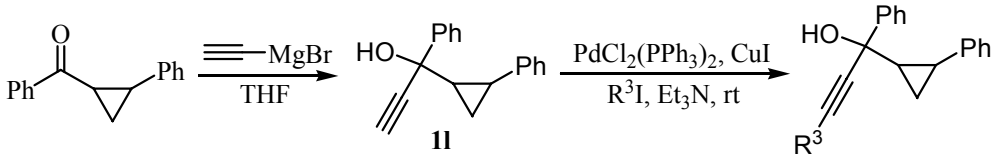
122.3, 125.7, 125.9, 126.1, 126.2, 128.3, 128.3, 128.5, 131.7, 142.1; IR (neat): 3415, 3059, 2981, 2929, 1673, 1603, 1494, 1120, 754 cm^{-1}; Anal.Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.87; H, 6.94.



1k

Compound **1k** (cis) was prepared according to the procedure A in 76% yield as an oil: ^{1}H NMR (300 MHz; DCl_3) (cis): δ 0.88-1.01 (m, 4 H), 1.29-1.46 (m, 5 H), 1.50-1.67 (m, 3 H), 2.17-2.29 (m, 3 H), 2.45 (s, 1 H), 6.99-7.01 (d, *J* = 7.5 Hz, 2 H), 7.11-7.36 (m, 6 H), 7.65-7.68 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, DCl_3) (cis): δ 12.1, 14.0, 18.6, 21.4, 22.1, 28.3, 31.0, 34.1, 73.8, 80.3, 87.4, 125.3, 125.6, 126.4, 127.5, 128.1, 128.2, 141.9, 145.0. IR (neat): 3432, 2930, 2362, 1604, 1452, 752, 697 cm^{-1}; Anal.Calcd for $C_{23}H_{26}O$: C, 86.75; H, 8.23. Found: C, 86.81; H, 8.14.

Typical procedure B for the preparation of 1-cyclopropyl-2-propyn-1-ols 1h-j, 1l-m:

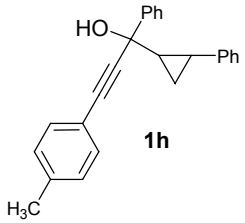


1l

To a stirring solution of ethynylmagnesium bromide solution (3 equiv, 0.35 M in THF) was added ketones (20 mmol, 0.35 M in THF) at room temperature and stirred for 3 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride (60 mL) and extracted with ethyl ether (2×80 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to obtain **1l** as a mixture of diastereoisomers in 76% yield.

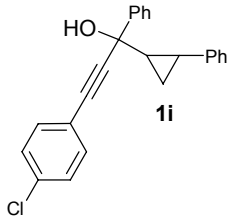
To a solution of compound **1l** (1.2 equiv) and R^3I (1 equiv) in Et_3N was added $PdCl_2(PPh_3)_2$ (3 mol %). The mixture was stirred for 5 min and CuI (6 mol %) was added. The resulting mixture was then stirring under an argon atmosphere at room temperature for 12 h. The ammonium salt was removed by filtration. The solvent was

removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding propargylic alcohols.



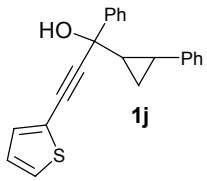
1h

Compound **1h** (1:1 mixture of diastereoisomers) was prepared according to the procedure B as solid: mp, 68-70℃, ^{1}H NMR (300 MHz; DCl_3) (1:1 mixture of diastereoisomers): δ 0.94-1.03 (m, 1 H), [1.34-1.39(m), 1.40-1.48(m), 1 H], 1.62-1.68 (m, 1 H), 2.32(s, 3 H), [2.24-2.29 (m), 2.40-2.47 (m), 1 H], 2.61(s,1 H), 6.75-7.51 (m, 12 H), 7.97-8.00(m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (1:1 mixture of diastereoisomers): δ 12.0, 13.5, 20.7, 21.4, 34.1, 34.8, 74.1, 74.4, 86.6, 88.5, 119.1, 125.4, 125.7, 126.5, 127.8, 128.2, 128.3, 129.1, 131.7, 138.8, 141.7, 144.6; IR (neat): 3555, 3438, 2226, 1606, 1508, 1460cm^{-1}. Anal.Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.78; H, 6.45.



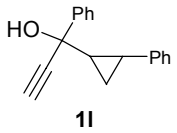
1i

Compound **1i** (1:1 mixture of diastereoisomers) was prepared according to the procedure B as solid: mp, 80-81℃, ^{1}H NMR (300 MHz; DCl_3) (1:1 mixture of diastereoisomers): δ 0.99-1.06 (m, 1 H), [1.33-1.39(m), 1.45-1.49(m), 1 H], 1.70-1.77 (m, 1 H), [2.26-2.31 (m), 2.37-2.44 (m), 1 H], [2.65(s) , 2.66(s), 1 H], 7.06-7.40 (m, 12 H), 7.70-7.73 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (1:1 mixture of diastereoisomers): δ 12.0, 13.4, 20.7, 21.3, 34.1, 34.7, 73.9, 74.3, 85.2, 90.4, 120.7, 125.3, 125.7, 126.1, 127.9, 128.3, 128.6, 133.0, 134.7, 141.7, 144.2; IR (neat): 3545, 3435, 2227, 1602, 1490, 1449cm^{-1}. Anal.Calcd for $C_{24}H_{19}ClO$: C, 80.33; H, 5.84. Found: C, 80.38; H, 5.74.



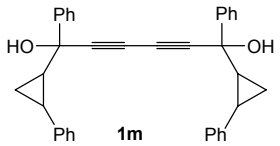
1j

Compound **1j** (10:1 mixture of diastereoisomers) was prepared according to the procedure B as solid: mp, 70-71℃, ^{1}H NMR (300 MHz; DCl_3) (10:1 mixture of diastereoisomers): δ 0.96-1.06(m, 1 H), [1.26-1.39(m), 1.42-1.49(m), 1 H], 1.68-1.78 (m, 1 H), [2.26-2.29 (m), 2.37-2.42 (m), 1 H], [2.58(s), 2.59(s), 1 H], 6.93-7.40 (m, 3 H), 6.91-7.01 (m, 11 H), 7.60-7.72 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (10:1 mixture of diastereoisomers): δ 13.3, 14.1, 20.7, 22.7, 34.7, 74.4, 79.7, 93.0, 122.1, 125.4, 125.7, 126.2, 126.4, 127.0, 127.5, 127.9, 128.3, 132.5, 141.8, 144.1; Anal.Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 79.95; H, 5.55.



1l

Compound **1l** (2:1 mixture of diastereoisomers) was prepared according to the first step of procedure B as solid: mp, 59-60℃, ^{1}H NMR (300 MHz; DCl_3) (2:1 mixture of diastereoisomers): δ 0.96-1.02(m, 1 H), [1.28-1.33(m), 1.38-1.45(m), 1 H], 1.62-1.69 (m, 1 H), [2.21-2.26 (m), 2.34-2.40 (m), 1 H], [2.54(s, 1 H), 2.63(s), 1 H], [2.64(s), 2.65(s), 1 H], 6.99-7.38 (m, 8 H), 6.91-7.01 (m, 2 H), 7.65-7.68 (m, 2 H); ^{13}C NMR (75 MHz, DCl_3) (2:1 mixture of diastereoisomers): δ 11.9, 13.3, 20.5, 21.2, 33.7, 34.3, 73.3, 73.8, 74.5, 84.0, 125.3, 125.7, 126.1, 126.3, 127.9, 128.3, 141.5, 141.8, 143.8; IR (neat): 3541, 3429, 2112, 1602, 1494, 1447cm^{-1}. Anal.Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.18; H, 6.43.



1m

Compound **1m** was isolated as a byproduct in preparation of compound **1h:** mp,48-49℃, ^{1}H NMR (300 MHz; DCl_3): δ 1.00-1.02(m, 1 H), 1.33-1.34(m, 1 H), 1.66-1.69 (m, 1 H), 2.32-2.38 (m, 1 H), 2.66(s, 1 H), 7.03-7.35 (m, 8 H), 7.62-7.65(m,

2 H); ^{13}C NMR (75 MHz, DCl_3): δ 13.2, 20.5, 34.4, 69.9, 74.1, 80.5, 125.3, 125.8, 126.1, 126.3, 128.1, 128.3, 128.4, 141.5, 143.2; IR (neat): 3530, 3418, 2248, 1603, 1494, 1449cm^{-1}. Anal.Calcd for $C_{36}H_{30}O_2$: C, 87.42; H, 6.11. Found: C, 87.37; H, 6.22.

General experimental procedure for the preparation of (*Z*)-conjugated enynes 2aa-2ah, 2ba-2ma:

To a solution of a cis-trans mixture of 1-cyclopropyl-2-propyn-1-ols **1a** (0.3 mmol) in alcohols (1 mL) was added 3 mol % of $HAuCl_4 \cdot 4H_2O$ under air at room temperature. When the reaction was considered complete as determined by TLC analysis，30 mL of ethyl ether was added and the mixture was washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding conjugated enynes. (petroleum ether–ethyl acetate, 40:1).

2aa: oil, IR (neat): 3028, 2930, 2821, 2204, 1951, 1598, 1490, 1447 cm^{-1}.
^{1}H NMR (300 MHz; DCl_3): δ 2.96-3.06 (m, 2 H), 3.26 (s, 3 H, OCH_3), 4.33-4.37 (m, 1 H), 6.44-6.69 (t, *J* = 7.8 Hz 1 H), 7.26-7.37 (m, 11 H), 7.47-7.5 1(m, 2 H), 7.60-7.64 (d, *J* = 8.7 Hz ,2H). ^{13}C NMR (75 MHz, DCl_3): δ 39.7, 56.9, 83.3, 86.6, 95.5, 123.3, 125.0, 126.0, 126.6, 127.6, 128.2, 128.3, 128.4, 131.5, 134.0, 138.0, 141.6**.** Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55; Found: C, 88.65; H, 6.59.

2ab: oil, IR (neat): 3028, 2972, 2868, 2203, 1951, 1598, 1490, 1447, 1059 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 1.08-1.13 (t, *J* = 6.9 Hz, 3 H), 2.88-2.95 (m, 2 H), 3.28-3.36 (m, 2 H), 4.34-4.38 (t, *J* = 7.8 Hz,1 H), 6.37-6.42 (t, *J* = 7.8 Hz, 1 H), 7.14-7.26 (m,11 H), 7.30-7.42 (m, 2 H)，7.51-7.54 (m, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 15.3, 40.0, 64.2, 81.4, 86.7, 95.4, 123.3, 124.9, 126.0, 126.5, 127.5, 127.6, 128.2, 128.2, 128.3, 128.3, 131.4, 131.5, 131.9, 134.4, 138.0, 142.3. Anal. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86; Found: C, 88.52; H, 6.94.

2ac: oil, IR (neat): 3028, 2969, 2926, 2204, 1948, 1598, 1491, 1448, 1064 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 1.03-1.05 (d, *J* = 5.7 Hz, 3 H), 1.08-1.10 (d, *J* =6.0 Hz, 3H),

2.85-2.89 (t, *J* = 6.6 Hz, 2H), 3.44-3.48 (m, 1 H), 4.47-4.51 (t, , *J* = 6.6 Hz, 1 H), 6.39-6.44 (t, *J* = 7.5 Hz, 1 H), 7.14-7.32 (m, 11 H), 7.39-7.43 (m, 2 H), 7.52-7.54 (d, *J* =7.2 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3) δ 21.3, 23.3, 40.3, 69.1, 78.7, 86.6, 95.3, 123.3, 124.7, 126.0, 126.5, 127.3, 127.5, 128.2, 128.2, 128.3, 131.4, 134.7, 138.1, 143.0. Anal. Calcd for $C_{27}H_{27}O$: C, 88.48; H, 7.15; Found: C, 88.44; H, 7.20.

2ad: oil. IR (neat): 3059, 3028, 2972, 2929, 2203, 1953, 1598, 1491, 1448, 1092 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 0.98 (s, 9 H), 2.77-2.82 (m, 2 H), 4.58-4.63 (t, J = 7.2 Hz, 1 H), 6.39-6.44 (t, *J* = 7.5 Hz, 1 H), 7.11-7.20 (m, 11 H), 7.39-7.44 (m, 2 H), 7.52-7.56 (m, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 28.7, 41.9, 74.1, 74.5, 86.9, 95.2, 123.4, 124.6, 126.0, 126.8, 127.5, 128.1, 128.2, 128.3, 128.4, 131.5, 135.3, 138.1, 146.0. Anal. Calcd for $C_{28}H_{28}O$: C, 88.38; H, 7.42; Found: C, 88.28; H, 7.50.

2ae: oil. IR (neat): 3029, 2959, 2862, 2202, 1951, 1598, 1491, 1448, 1112 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.98-3.05 (m, 2 H), 3.55-3.77 (m, 4 H), 4.48-4.53 (m, 1 H), 6.50-6.55 (t, *J* = 7.5 Hz),7.21-7.39 (m,11 H), 7.46-7.50 (m, 2 H), 7.61-7.64 (m, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.9, 43.1, 82.2, 86.6, 95.6, 123.3, 125.1, 126.0, 126.5, 127.6, 127.9, 128.3, 128.3, 128.5, 131.5, 133.9, 138.0, 141.4. Anal. Calcd for $C_{26}H_{23}ClO$: C, 88.71; H, 5.99; Found: C, 88.62; H, 6.05,

2af: oil. IR (neat), 3079, 3060, 3029, 2857, 2204, 1951, 1598, 1491, 1448, 1084 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.94-3.12 (m, 2 H), 3.80-4.00 (m, 2 H), 4.51-4.54 (t, *J* = 6.6 Hz, 1 H), 5.13-5.28 (dd, *J* =17.4 Hz, *J* = 10.5 Hz, 2 H), 5.85-5.97 (m, 1 H), 6.46-6.50 (t, *J* = 7.8 Hz), 7.19-7.39 (m, 11 H), 7.47-7.50 (m, 2 H), 7.60-7.62 (d, *J* = 6.9 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.9, 69.5, 80.8, 86.6, 95.5, 116.8, 123.3, 125.0, 126.0, 126.6, 127.6, 127.7, 128.8, 128.3, 128.4, 131.5, 134.1, 134.8, 138.0, 141.8**.** Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64; Found: C, 88.89; H, 6.70.

2ag: oil, IR (neat): 3294, 3059, 3030, 2899, 2856, 2204, 2118, 1491, 1447 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.35-2.38 (m, 1 H), 2.98-3.12 (m, 2 H), 3.87-3.94 (m, 1 H), 4.12-4.19 (m, 1 H), 4.71-4.75 (t, *J* = 6.6 Hz, 1 H), 6.63-6.50 (m, 1 H), 7.21-7.37 (m, 11 H), 7.47-7.49 (m, 2 H), 7.60-7.63 (d, *J* = 6.9 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.5, 55.7, 74.2, 79.9, 80.2, 86.6, 95.6, 123.3, 125.2, 126.1, 126.9, 127.6, 128.0,

128.3, 128.5, 131.5, 133.7, 138.0, 140.5. Anal. Calcd for C27H22O: C, 89.47; H, 6.12; Found: C, 89.35.; H, 6.17.

2ah: oil. IR (neat): 3060, 3029, 2863, 2202, 1954, 1599, 1491, 1450, 1090 cm^{-1}.

1H NMR (300 MHz; DCl_3): δ 2.97-3.13 (m, 2 H), 4.30-4.34 (d, *J* = 12.3 Hz, 2 H), 4.51-4.60 (m, 2 H), 6.45-6.47 (t, *J* = 7.8 Hz, 1 H), 7.26-7.40 (m, 16 H), 7.43-7.49 (m, 2 H), 7.58-7.60 (m, 2 H); 13C NMR (75 MHz, DCl_3): δ 40.0, 70.4, 80.8, 86.6, 95.5, 123.3, 125.0, 126.0, 126.8, 127.5, 127.6, 127.7, 127.7, 128.0, 128.2, 128.3, 128.5, 131.5, 134.2, 138.1, 138.4, 141.8. Anal. Calcd for $C_{31}H_{26}O$: C, 89.82; H, 6.32; Found: C, 89.73; H, 6.36.

2ba: oil. IR(neat): 3058, 3030, 2931, 2207, 1956, 1511, 1491, 1445, 1096 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.89-3.11 (m, 2 H), 3.22 (s, 3 H), 3.76 (s, 3 H), 6.42-6.47 (m, 1 H), 6.86-6.87 (m, 2 H), 7.22-7.35 (m, 8 H), 7.46-7.50 (m, 2 H), 7.60-7.63 (m, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.7, 56.1, 56.4, 82.8, 86.6, 95.5, 113.7, 123.3, 124.9, 126.0, 127.5, 127.8, 128.2, 128.3, 131.5, 133.5, 134.2, 138.0, 159.1. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57; Found: C, 84.66; H, 6.59.

2ca: oil. IR(neat): 3058, 3029, 2930, 2204, 1950, 1597, 1489, 1445, 1093 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.90-3.04 (m, 2 H), 3.25 (s, 3 H), 4.30-4.34 (t, *J*=7.2 Hz, 1 H), 6.40-6.45 (t, *J* = 7.8 Hz, 1 H), 7.20-7.34 (m, 11 H), 7.45-7.49 (m, 2 H), 7.59-7.62 (m, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.6, 56.8, 82.6, 86.4, 95.6, 123.2, 125.4, 126.0, 127.7, 128.0, 128.6, 131.5, 133.3, 137.8, 140.1. Anal. Calcd for $C_{25}H_{21}ClO$: C, 80.53; H, 5.68; Found: C, 88.49; H, 5.70.

2da: oil. IR (neat): 3058, 3029, 2927, 2204, 1597, 1491, 1092 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 3.12-3.18 (m, 2 H), 3.33 (s, 3 H), 4.40-4.44 (s, 3 H), 6.34-6.46 (m, 3 H), 7.23-7.41 (m, 8 H), 7.51-7.54 (m, 2 H), 7.61-7.62 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 35.8, 56.5, 75.7, 86.4, 95.8, 108.2, 110.0, 123.3, 125.3, 126.0, 127.7, 128.3, 131.5, 133.1, 137.9, 142.4, 153.7.Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14; Found: C, 84.10.; H, 6.21.

2ea: oil. IR (neat): 3059, 3029, 2927, 2205, 1951, 1599, 1487, 1448, 1099 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.95-3.06 (m, 2 H), 3.27 (s, 3 H), 4.33-4.37 (t, *J* = 5.7 Hz,

1 H), 6.44-6.49 (t, *J* = 6.9 Hz, 1 H), 7.22-7.50 (m, 14 H).^{13}C NMR (75 MHz, DCl_3): δ 39.8, 56.7, 83.1, 86.0, 95.8, 121.5, 123.0, 124.0, 126.6, 127.6, 127.7, 128.3, 128.4, 128.5, 131.3, 131.5, 134.5, 136.9, 141.4. Anal. Calcd for $C_{25}H_{21}BrO$: C, 71.95; H, 5.07; Found: C, 71.84; H, 5.14.

2fa: oil. IR(neat): 3059, 3031, 2931, 2204, 1606, 1510, 1490, 1250, 1099 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.91-3.03 (m, 2 H), 3.27 (s, 3 H), 3.80 (s, 3 H), 4.31-4.36 (m, 1 H), 6.33-6.38 (t, *J* = 7.2 Hz, 1 H), 6.85-6.89 (d, *J* 9 Hz, 2 H), 7.27-7.36 (m, 8 H), 7.47-7.50 (m, 2 H), 7.53-7.56 (d, *J* = 9 Hz, 2 H). ^{13}C NMR (75 MHz, DCl3): δ 39.7, 55.2, 56.7, 83.4, 86.8, 95.3, 113.7, 123.4, 124.4, 126.6, 127.2, 127.6, 128.2, 128.3, 130.7, 131.5, 132.1, 141.7, 159.2. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57; Found: C, 84.69; H, 6.66.

2ga: oil. IR(neat): 3451, 2924, 2822, 1491, 1449, 1103, 756, 697 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 1.91 (s, 3 H), 2.72-2.82 (m, 2 H), 3.23 (m, 3 H), 4.20-4.25 (m, 1 H), 5.71-5.75 (m, 1 H), 7.27-7.42 (m, 10 H); ^{13}C NMR (75 MHz, DCl3): δ 23.1, 39.1, 56.6, 83.4, 88.6, 93.2, 119.8, 123.5, 116.6, 127.5, 127.9, 128.2, 128.3, 131.4, 133.7, 141.7. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.97; H, 7.22.

2ha: oil. IR (neat, cm^{-1}), 3060, 3029, 2928, 2201, 1489, 1094 cm^{-1}. ^{1}H NMR (300 MHz; DCl_3): δ 2.34 (s, 3 H), 2.93-3.07 (m, 2 H), 3.27 (s, 3 H), 4.32-4.37 (m, 1 H), 6.41-6.46 (t, *J* = 7.5 Hz, 1 H), 7.11-7.14 (d, *J* = 7.8 Hz, 2 H), 7.20-7.39 (m, 10 H), 7.60-7.63 (m, 2 H)**.** ^{13}C NMR (75 MHz, DCl_3): δ 21.5, 39.7, 56.7, 83.4, 85.9, 95.8, 120.2, 125.2, 126.1, 126.6, 127.5, 127.7, 128.3, 128.4, 129.1, 131.4, 133.7, 138.1, 138.4, 141.7. Anal. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86; Found: C, 88.50; H, 6.90.

2ia: oil. IR (neat): 3060, 3029, 2932, 2821, 2204, 1489, 1094 cm^{-1}. ^{1}H NMR (300 MHz; DCl3): δ 2.94-3.03 (m, 2 H), 3.26 (s, 3 H), 4.31-4.46 (t, *J* = 6.9 Hz, 1 H), 6.45-6.50 (t, *J* = 7.2 Hz, 1 H), 7.26-7.40 (m, 12 H), 7.57-7.60 (t, *J* = 7.8 Hz, 2 H). ^{13}C NMR (75 MHz, DCl3): δ 39.8, 56.7, 83.3, 87.6, 94.3, 121.8, 124.9, 126.0, 126.6, 127.7, 128.3, 128.4, 128.6, 132.7, 134.2, 134.5, 137.8, 141.5. Anal. Calcd. for $C_{25}H_{21}ClO$: C, 80.53; H, 5.68; Found: C, 80.50; H, 5.75.

2ja: oil. IR (neat): 3060, 3028, 2926, 2195, 1492, 1101 cm^{-1}. ^1H NMR (300 MHz; DCl_3): δ 2.84-2.95 (m, 2 H), 3.18 (s, 3 H), 4.23-4.28 (t, *J* = 6.9 Hz, 1 H), 6.35-6.39 (t, *J* = 7.5 Hz, 1 H), 6.88-6.91 (m, 1 H), 7.12-7.28 (m, 10 H), 7.47-7.50 (d, *J* = 7.5 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.8, 56.7, 83.3, 88.5, 90.4, 123.3, 124.9, 126.0, 126.6, 127.1, 127.3, 128.3, 128.4, 131.7, 134.3, 137.7, 141.5. Anal. Calcd. for $C_{23}H_{20}OS$: C, 80.19; H, 5.85; Found: C, 80.13; H, 5.93.

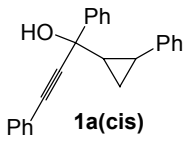
2ka: oil. IR (neat): 3325, 3221, 1685, 1651, 1539, 1358, 1176, 668 cm^{-1}. ^1H NMR (300 MHz; DCl_3): δ 0.85-0.92 (m, 3 H), 1.25-1.48 (m, 4 H), 1.55-1.64 (m, 2 H), 2.40-2.44 (t, *J* = 7.2 Hz, 2 H), 2.85-2.98 (m, 2 H), 3.25 (s, 3 H), 4.27-4.31 (m, 1 H), 6.30-6.35 (t, *J* = 7.2 Hz, 1 H), 7.20-7.39 (m, 8 H), 7.54-7.56 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (75 MHz, DCl3): δ 14.0, 19.5, 22.2, 28.5, 31.1, 39.6, 56.7, 76.6, 83.4, 96.9, 125.3, 126.0, 126.6, 127.3, 127.6, 128.1, 128.4, 132.5, 138.6, 141.8. Anal. Calcd. for $C_{24}H_{28}O$: C, 86.70; H, 8.49; Found: C, 86.59; H, 8.52.

2la: oil. IR (neat): 3064, 3028, 2980, 2206, 1958, 1731, 1508, 1248 cm^{-1}. ^1H NMR (300 MHz; DCl_3): δ 2.88-2.98 (m, 2 H), 3.24 (s, 3 H), 3.29 (s, 1 H), 4.27-4.31 (t, *J* = 7.5Hz, 1 H), 6.48-6.53 (t, *J* = 6.9 Hz, 1 H), 7.23-7.35 (m, 8 H), 7.54-7.56 (d, *J* = 6.9 Hz, 2 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.7, 56.7, 80.7, 83.1, 83.4, 124.0, 125.9, 126.6, 127.6, 127.7, 128.3, 128.4, 128.6, 135.8, 137.5, 141.5. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; Found: C, 84.10; H, 7.01.

2ma: solid; mp 90–91 °C. IR (KBr): 3060, 3029, 2931, 2822, 2204, 1492, 1449, 1101 cm^{-1}. ^1H NMR (300 MHz; DCl_3): δ 2.13-3.05 (m, 4 H), 3.25 (s, 6 H), 4.30-4.34 (m, 2 H), 6.55-6.60 (t, *J* = 7.5 Hz, 2 H), 7.19-7.36 (m, 16 H), 7.52-7.61 (m, 4 H). ^{13}C NMR (75 MHz, DCl_3): δ 39.8, 56.7, 79.6, 79.9, 83.1, 124.3, 126.0, 126.6, 127.7, 127.8, 128.4, 128.5, 137.2, 137.9, 141.3. Anal. Calcd for $C_{38}H_{34}O_2$: C, 87.32; H, 5.65; Found: C, 87.33; H, 5.71.

2lb: oil. IR(neat): 3058, 3028, 2928, 1671, 1622 cm^{-1}. ^1H NMR (300 MHz; DCl_3): δ 2.25 (s, 3 H), 2.39-2.56 (m, 2 H), 3.21 (s, 3 H), 4.21-4.25 (m, 1 H), 6.91-6.96 (m, 3 H), 7.18-7.35 (m, 8 H).^{13}C NMR (75 MHz, DCl_3): δ 27.2, 38.2, 56.7, 82.6, 126.4, 127.4,

128.1, 128.4, 129.3, 135.7, 139.8, 140.9, 144.3, 198.5. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19; Found: C, 81.30.; H, 7.22.



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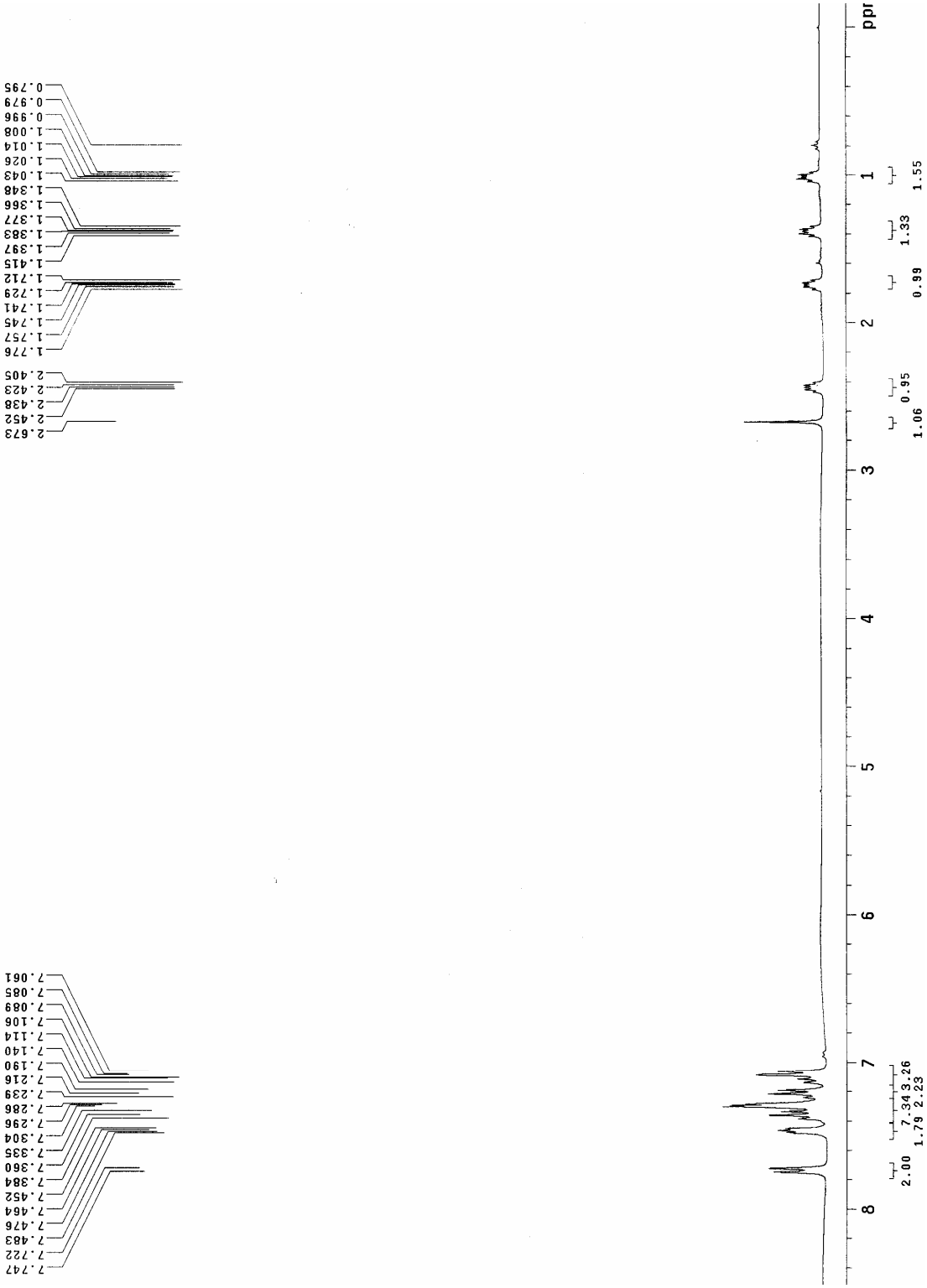

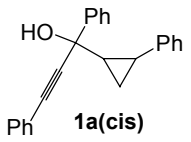

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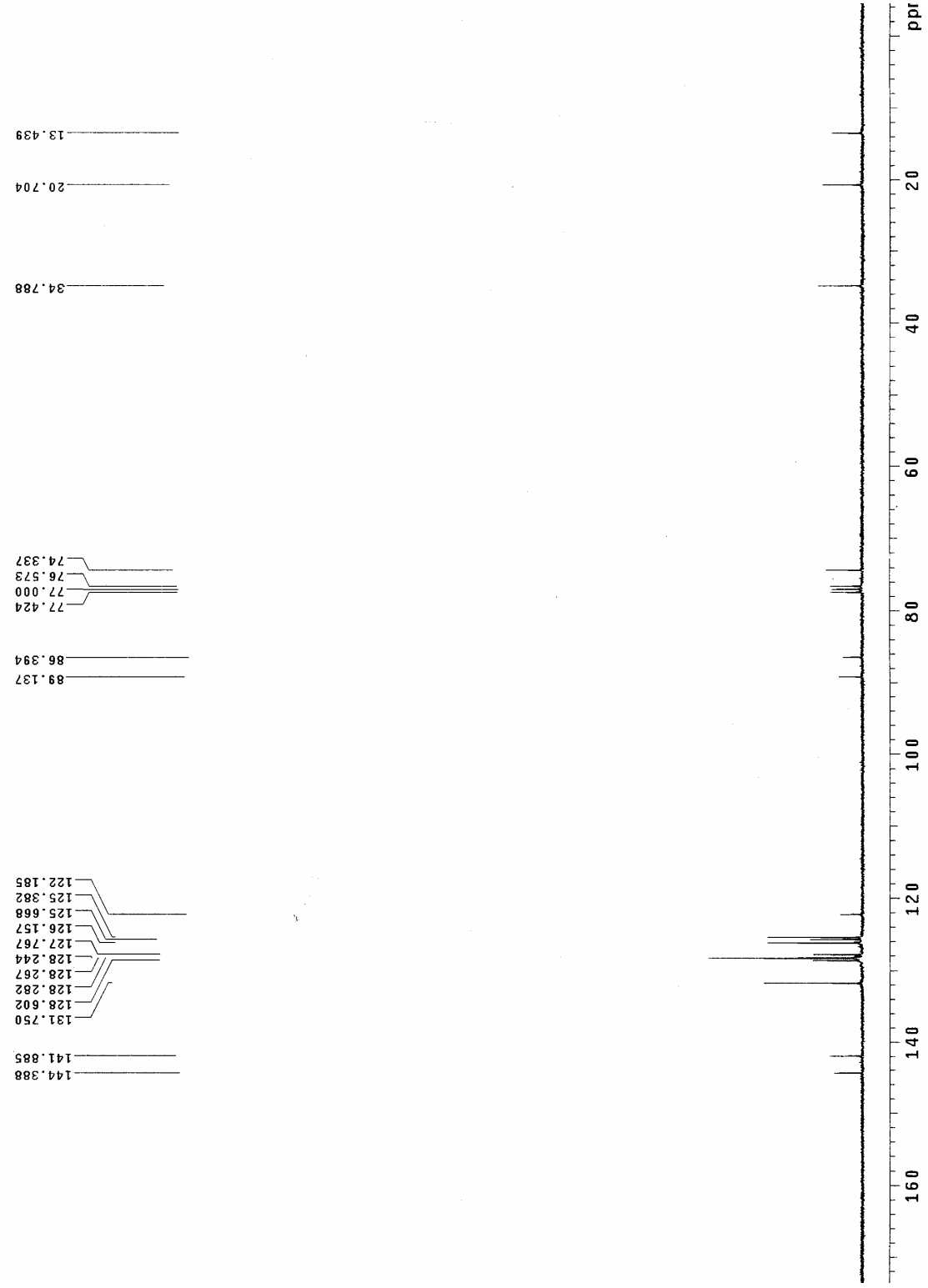

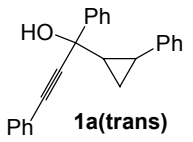

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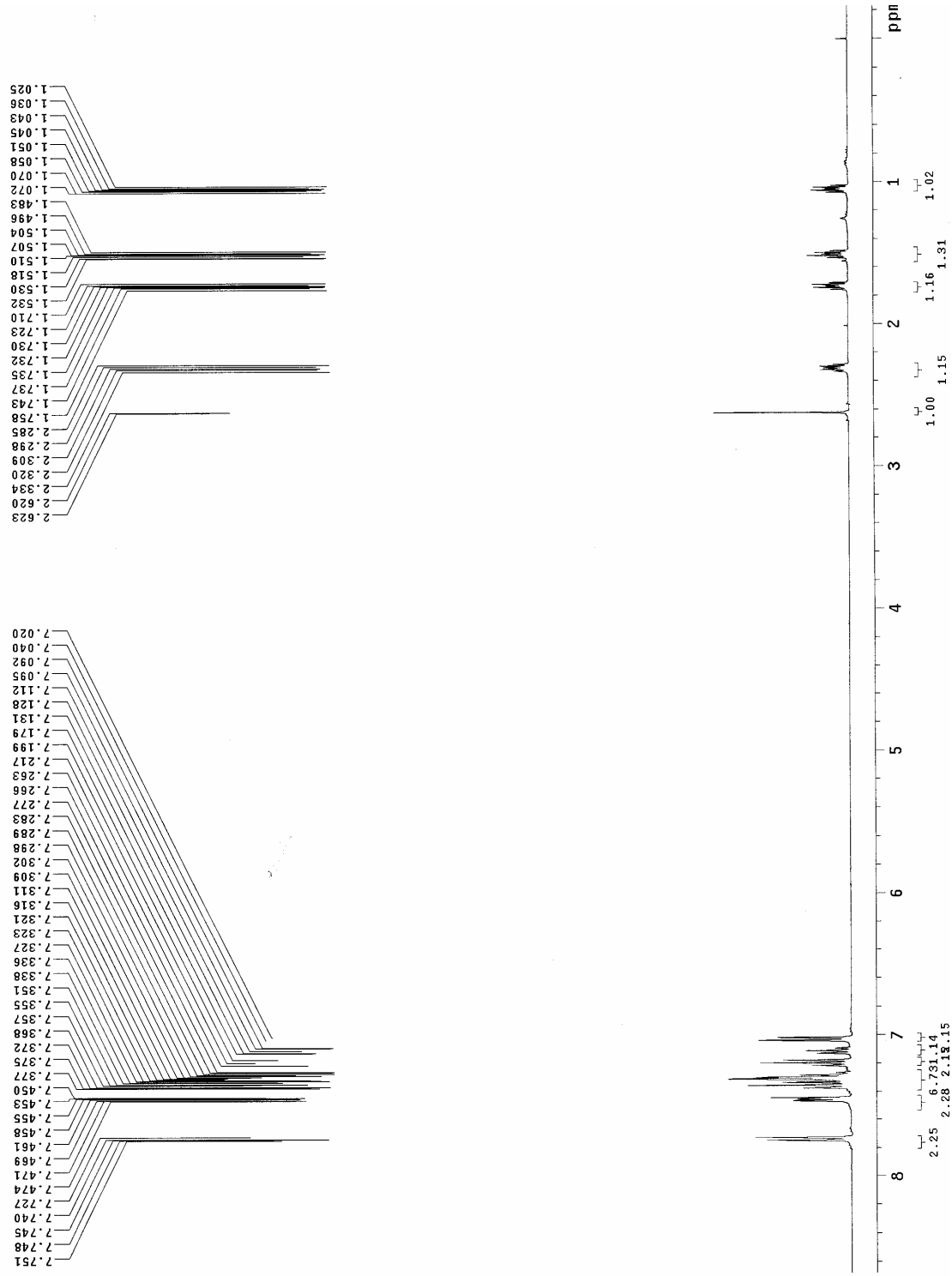

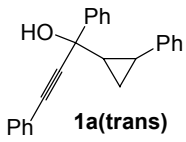

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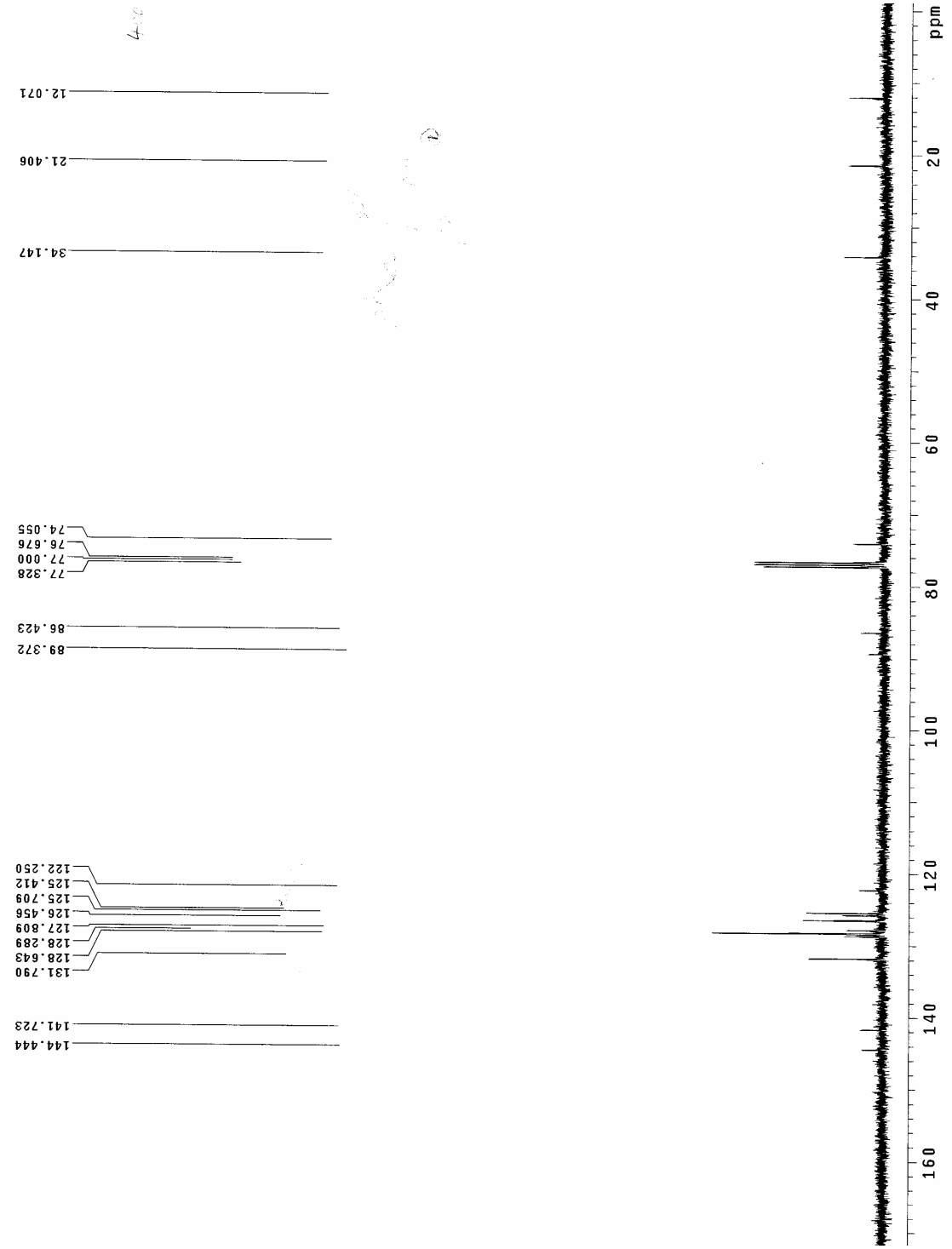

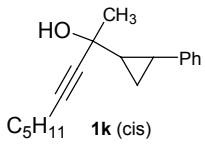

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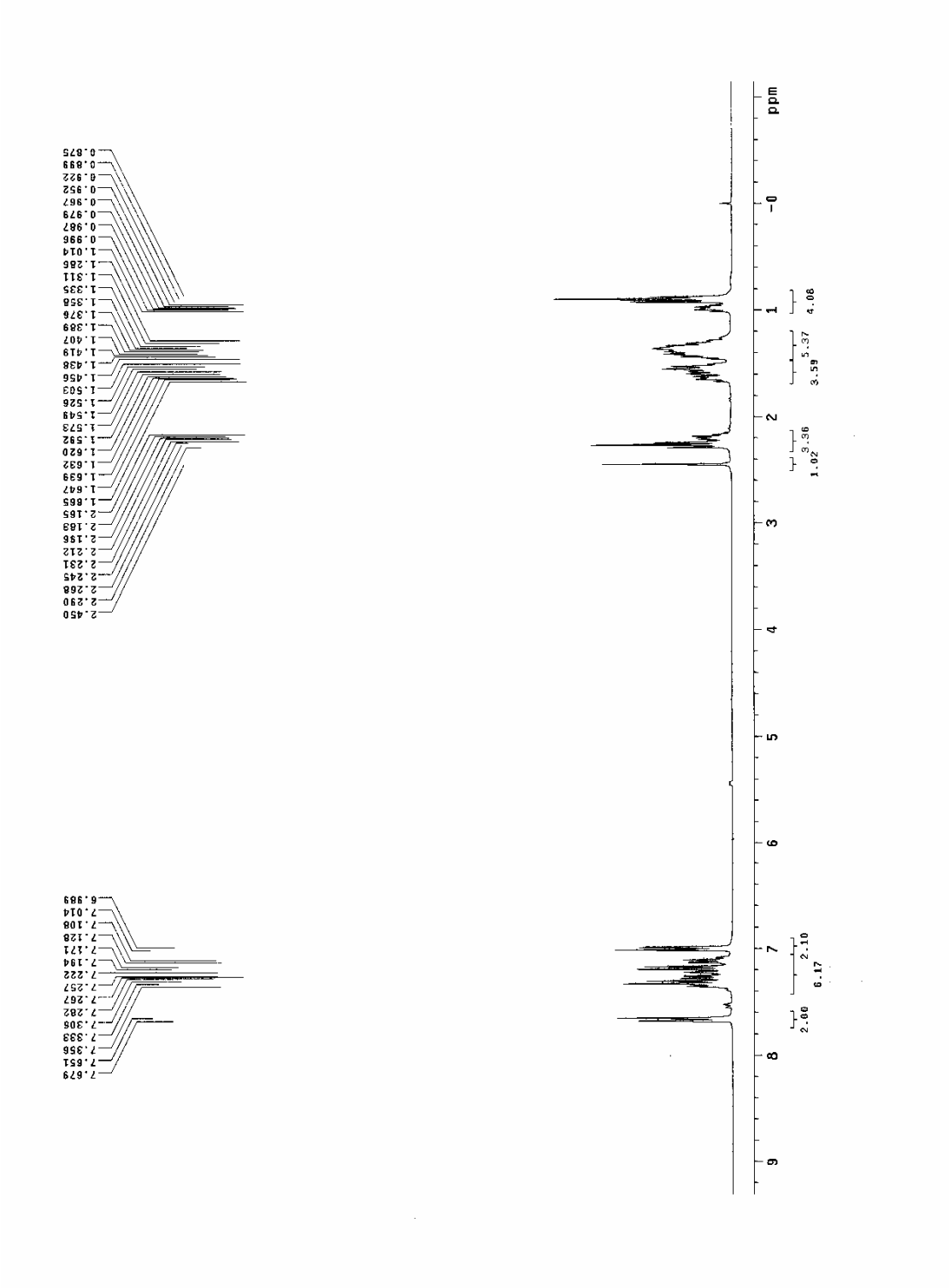

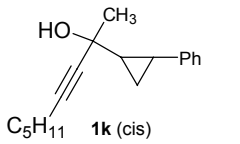

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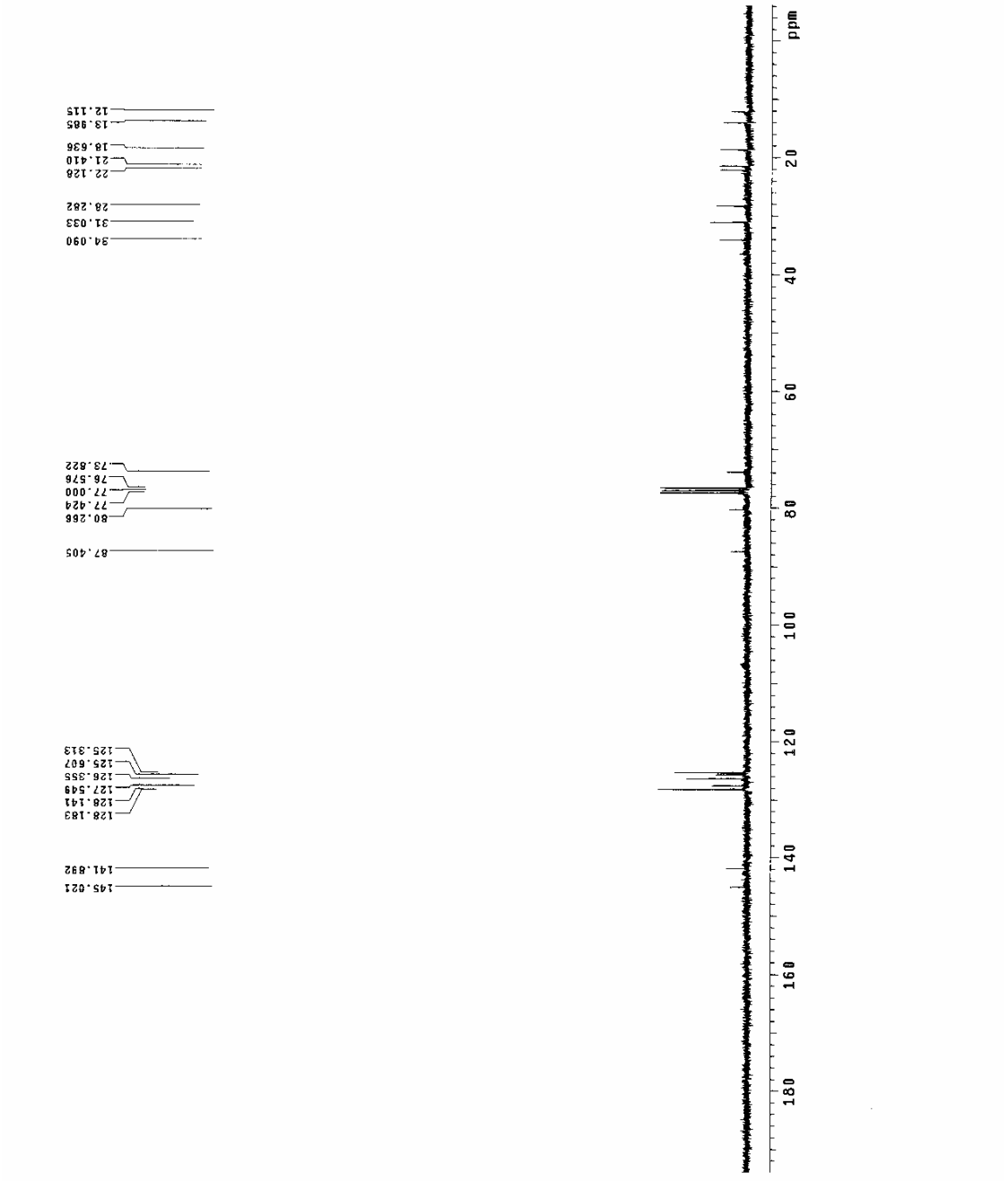

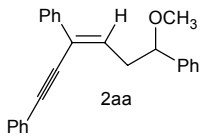

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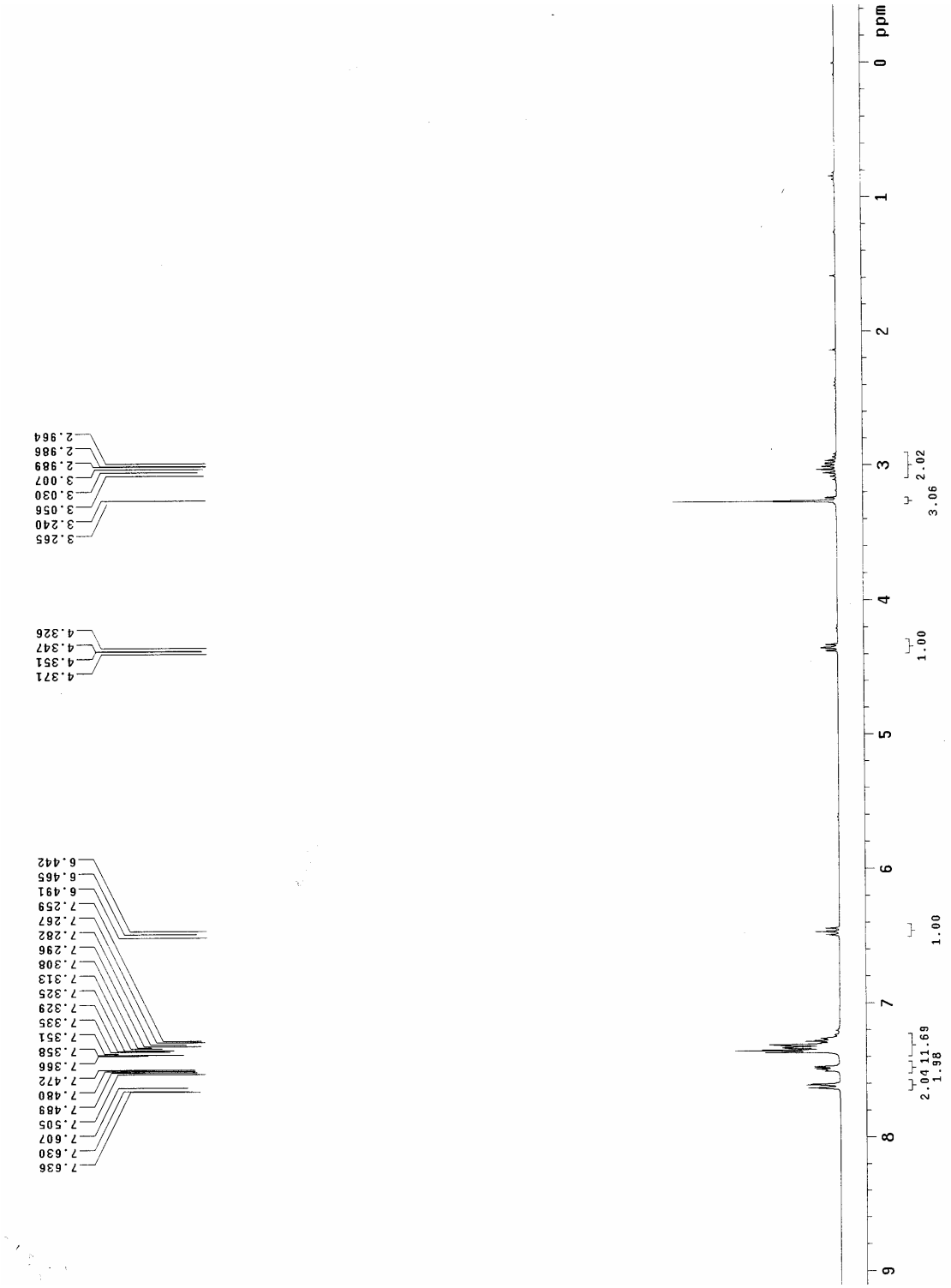

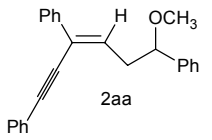

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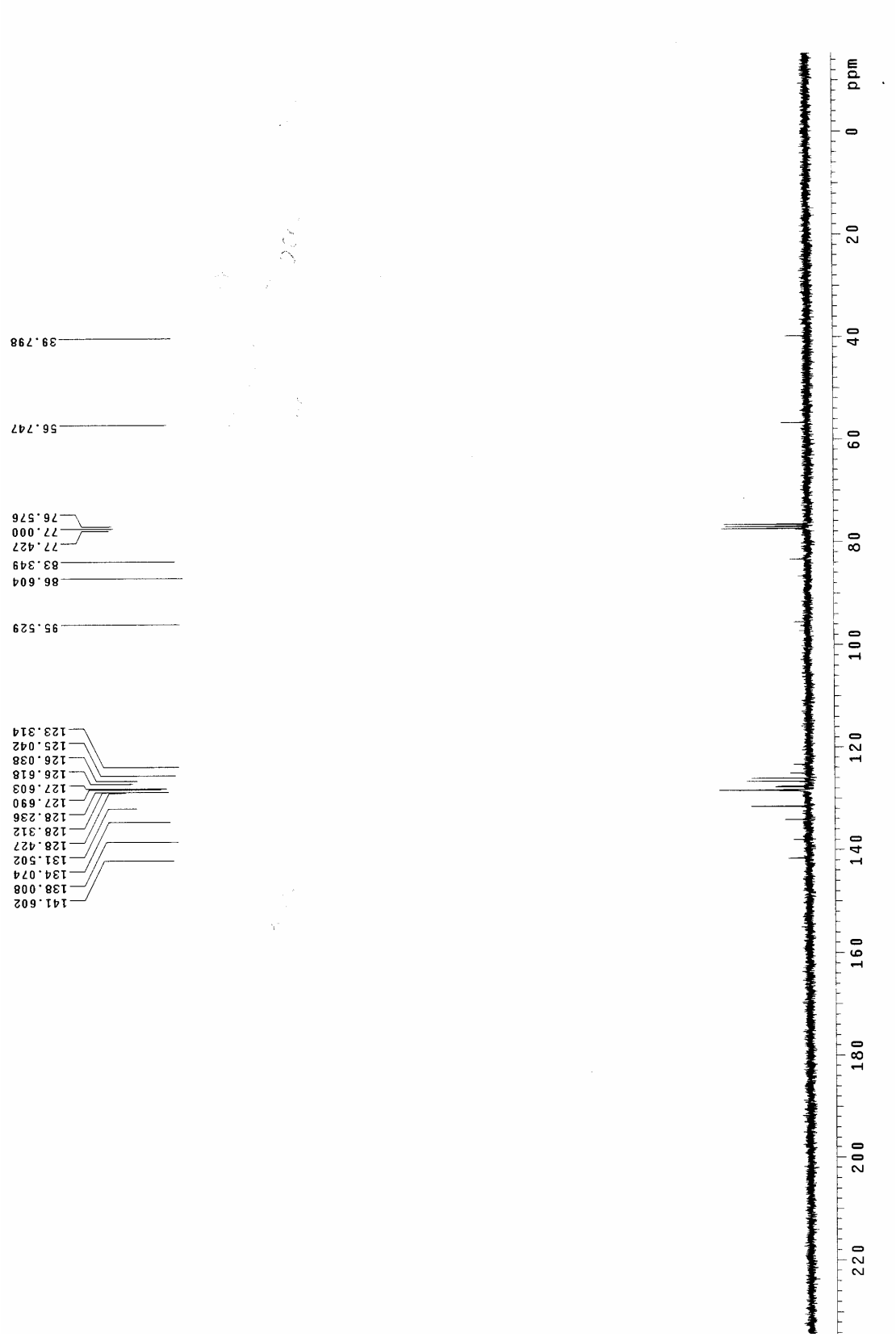

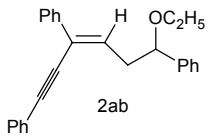

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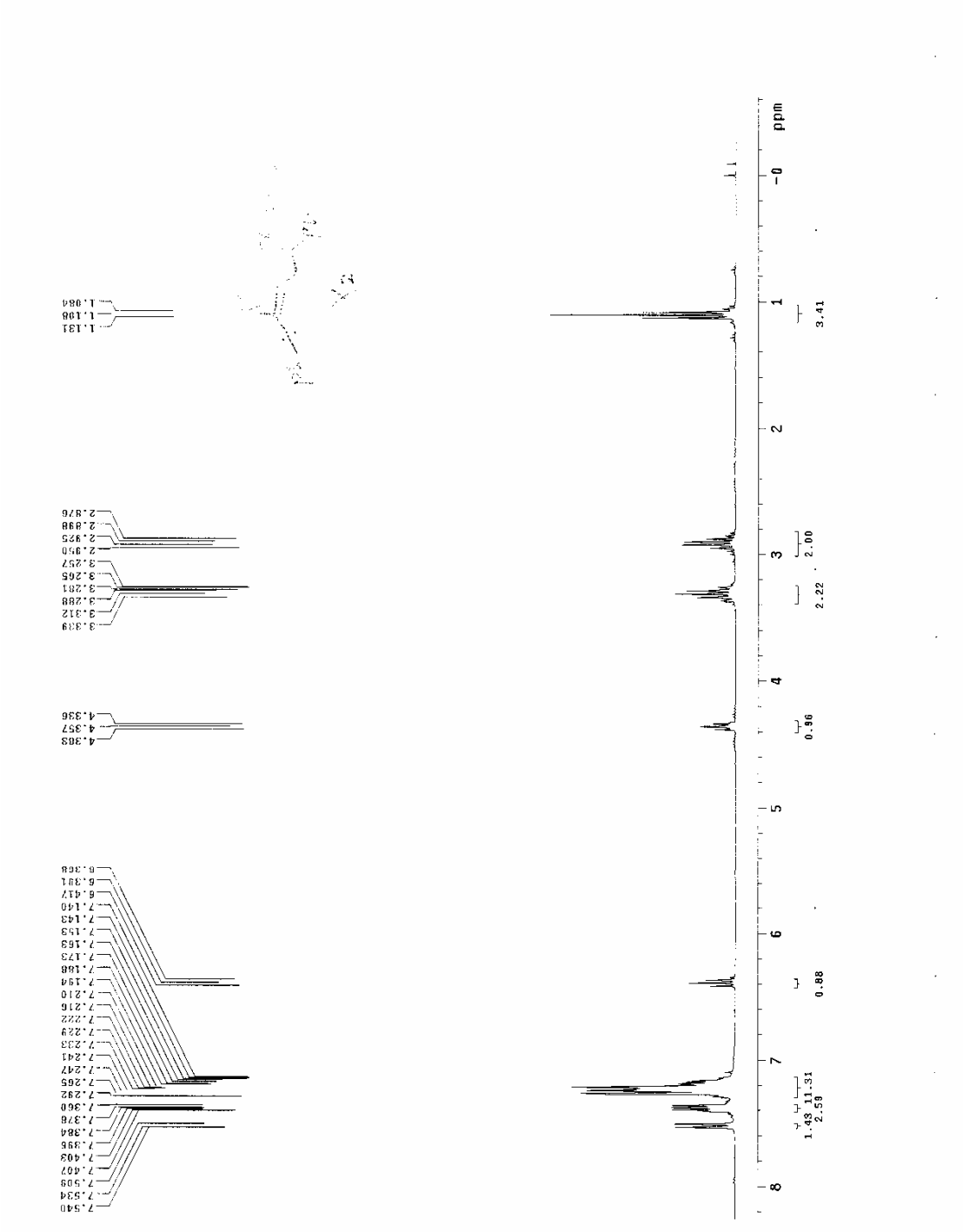

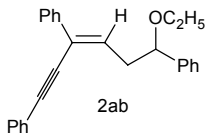

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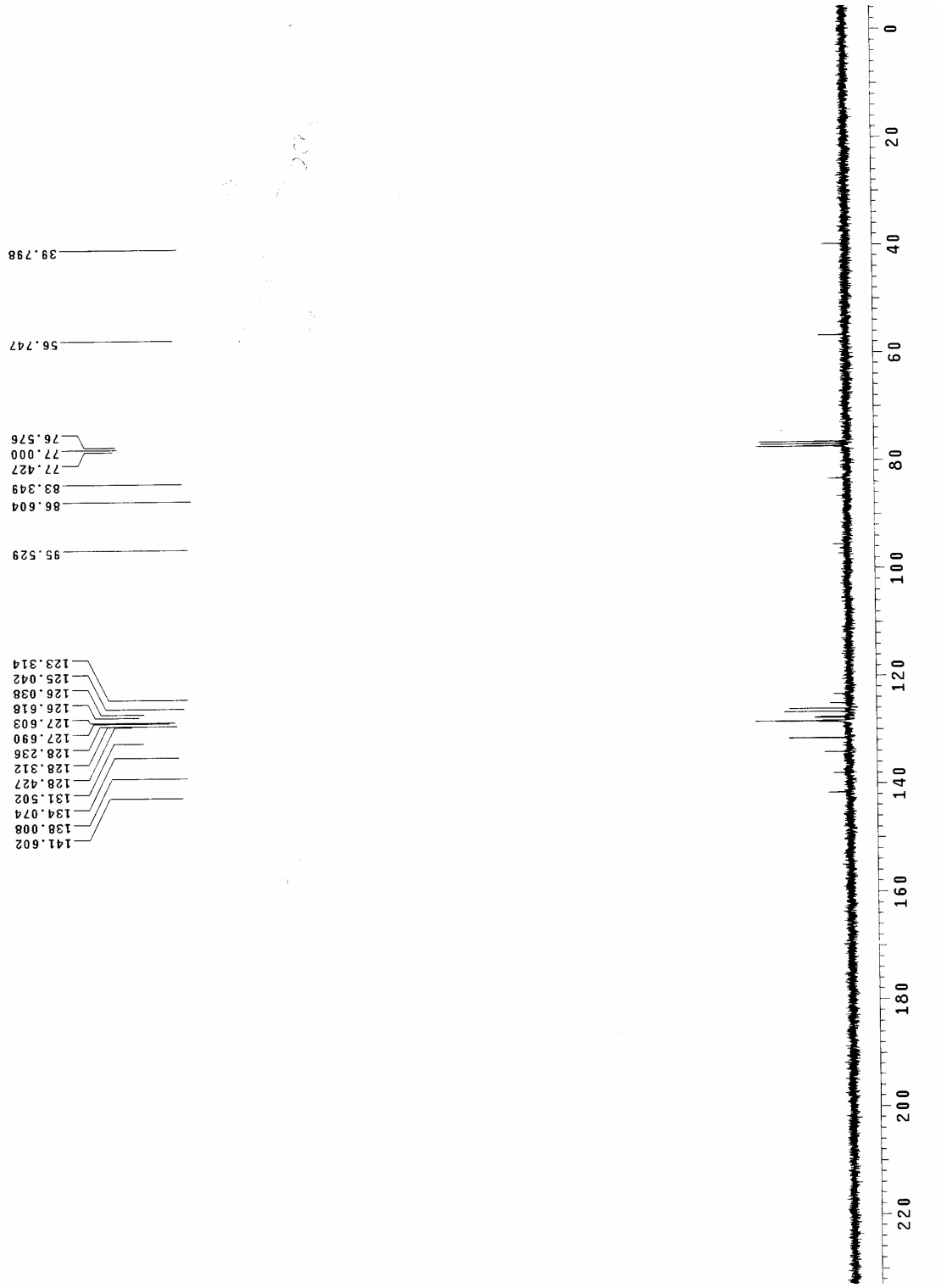

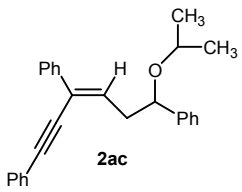

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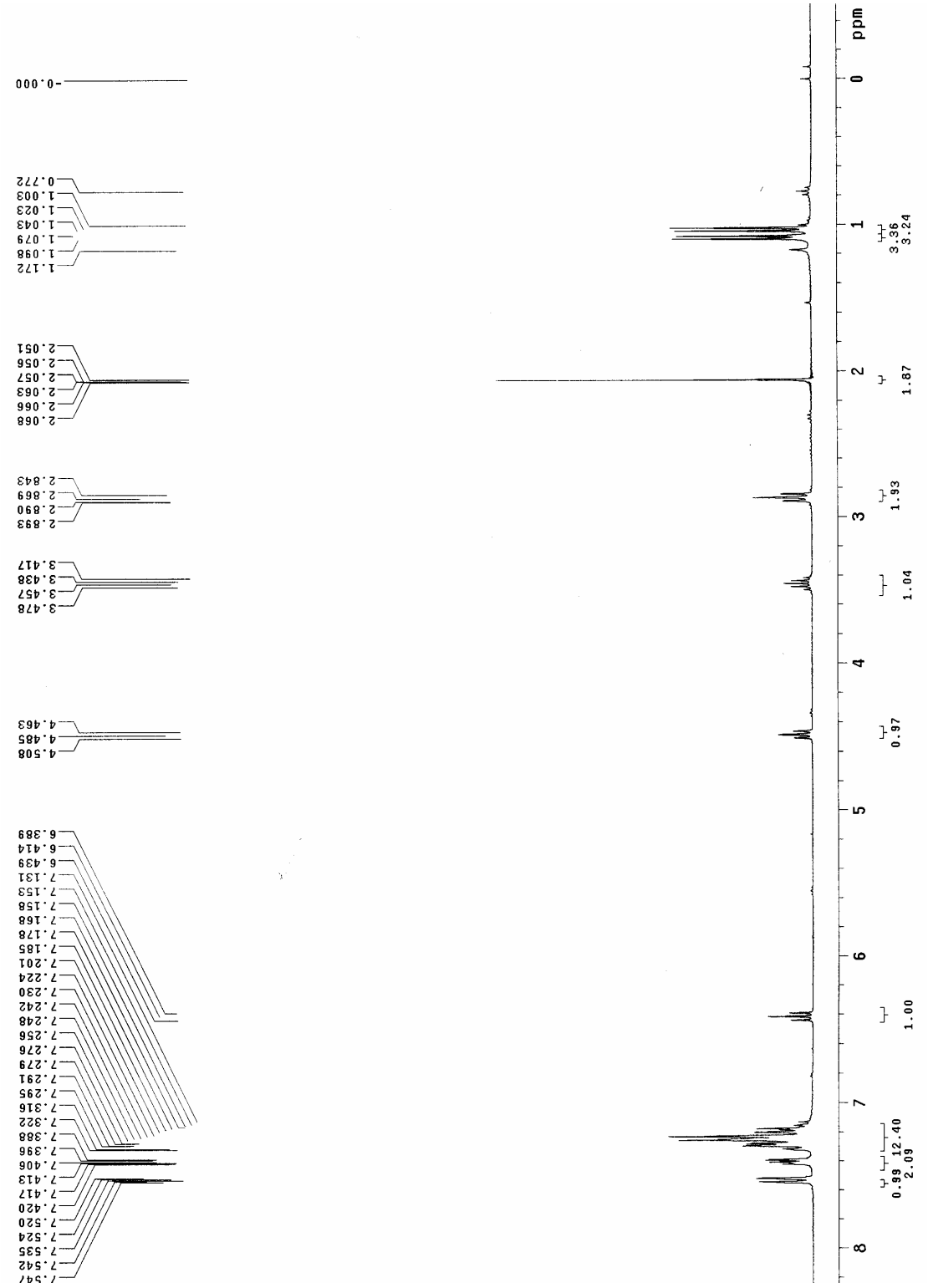

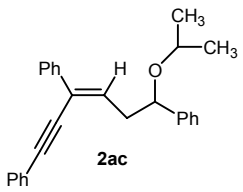

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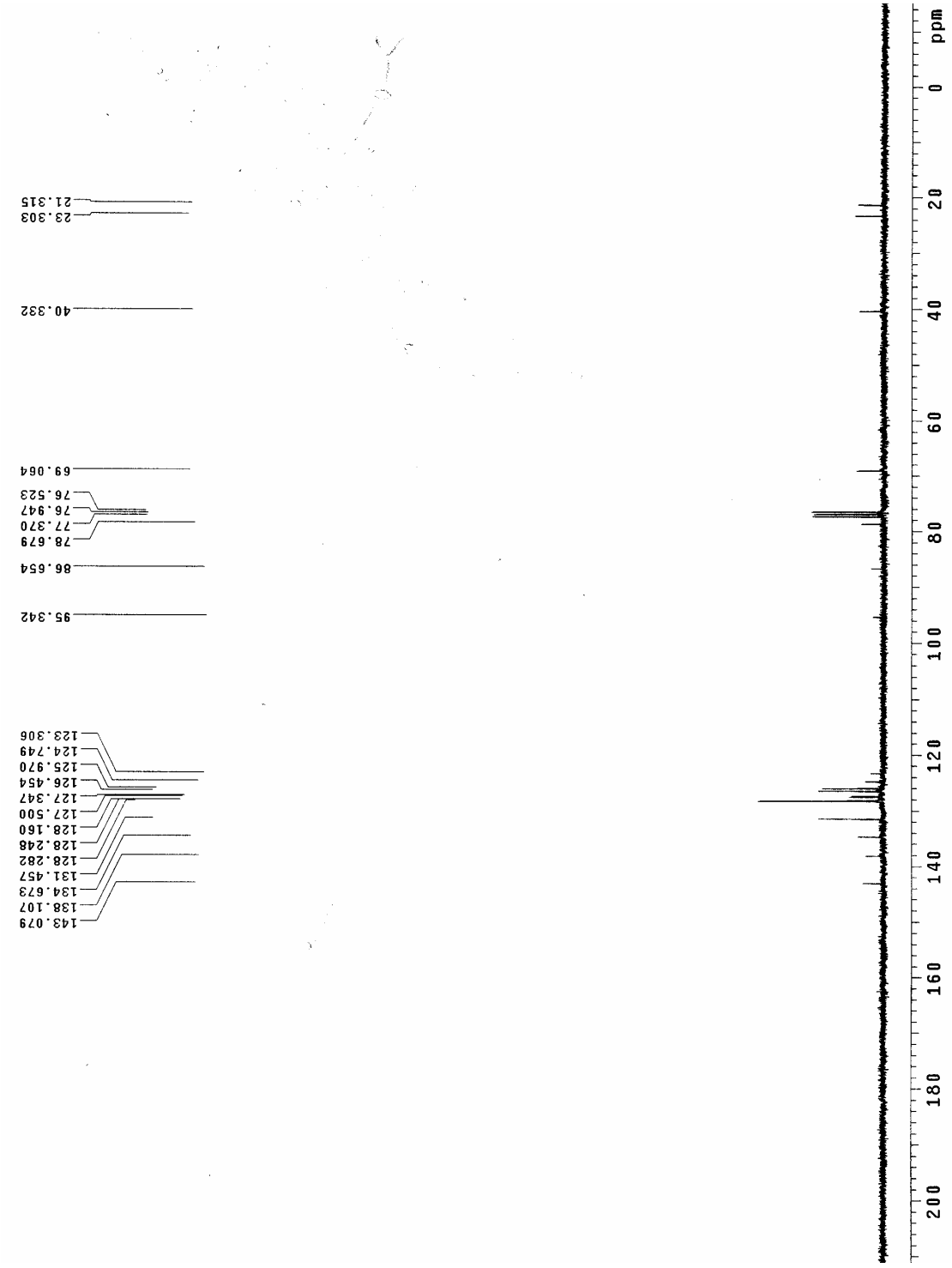

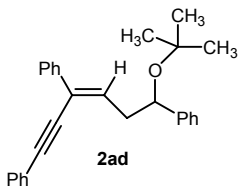

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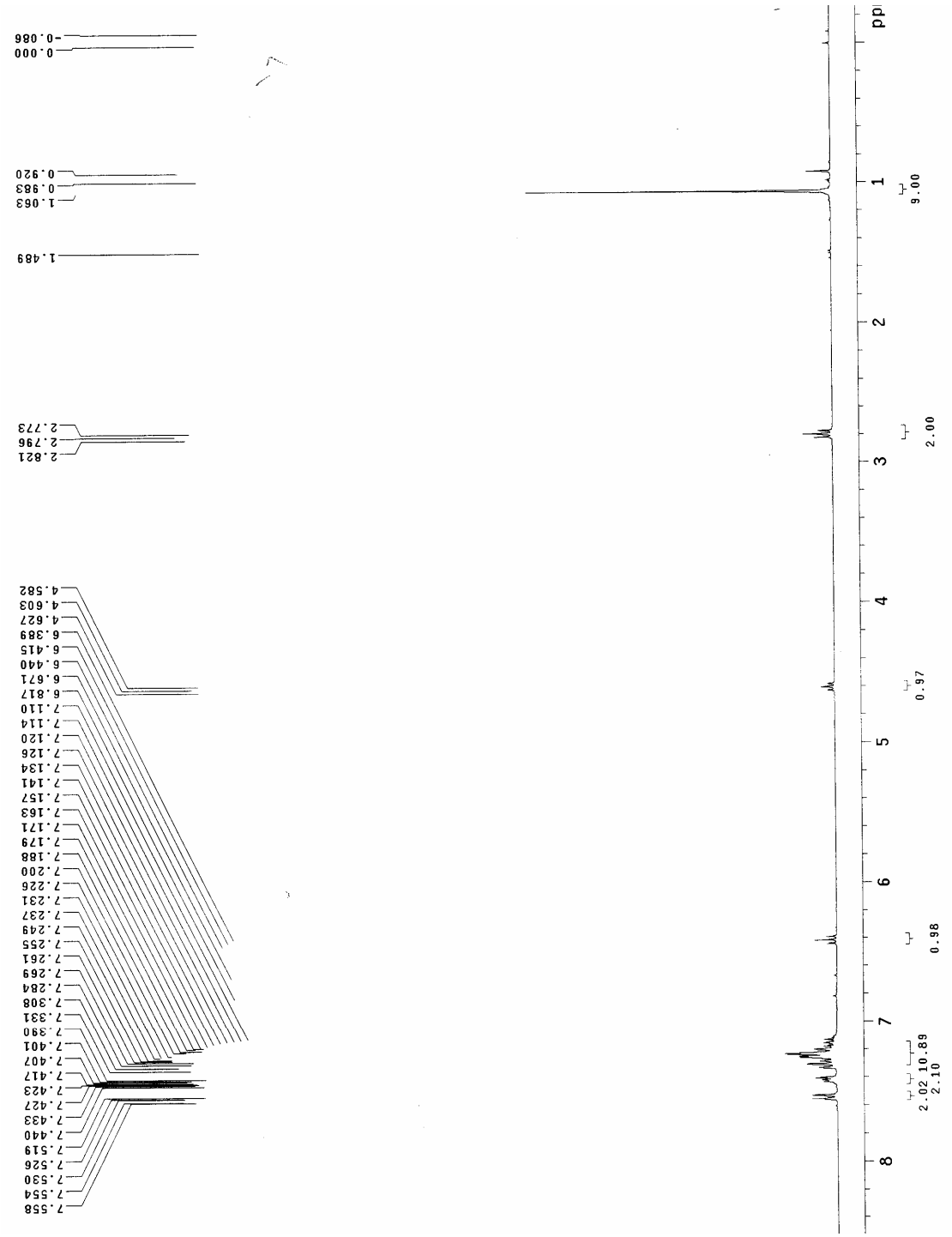

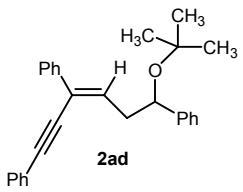

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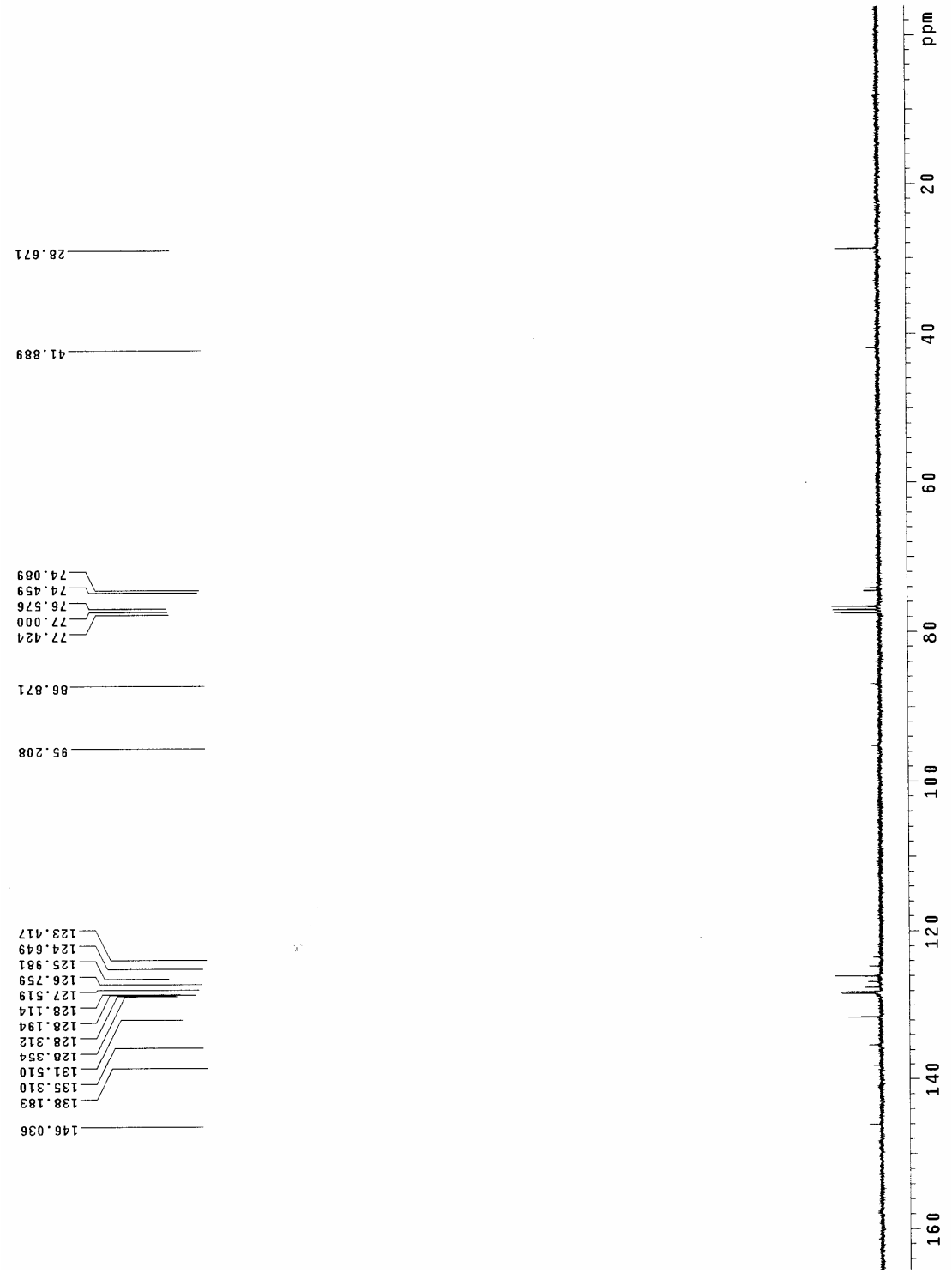

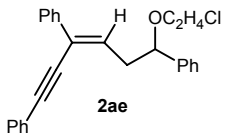

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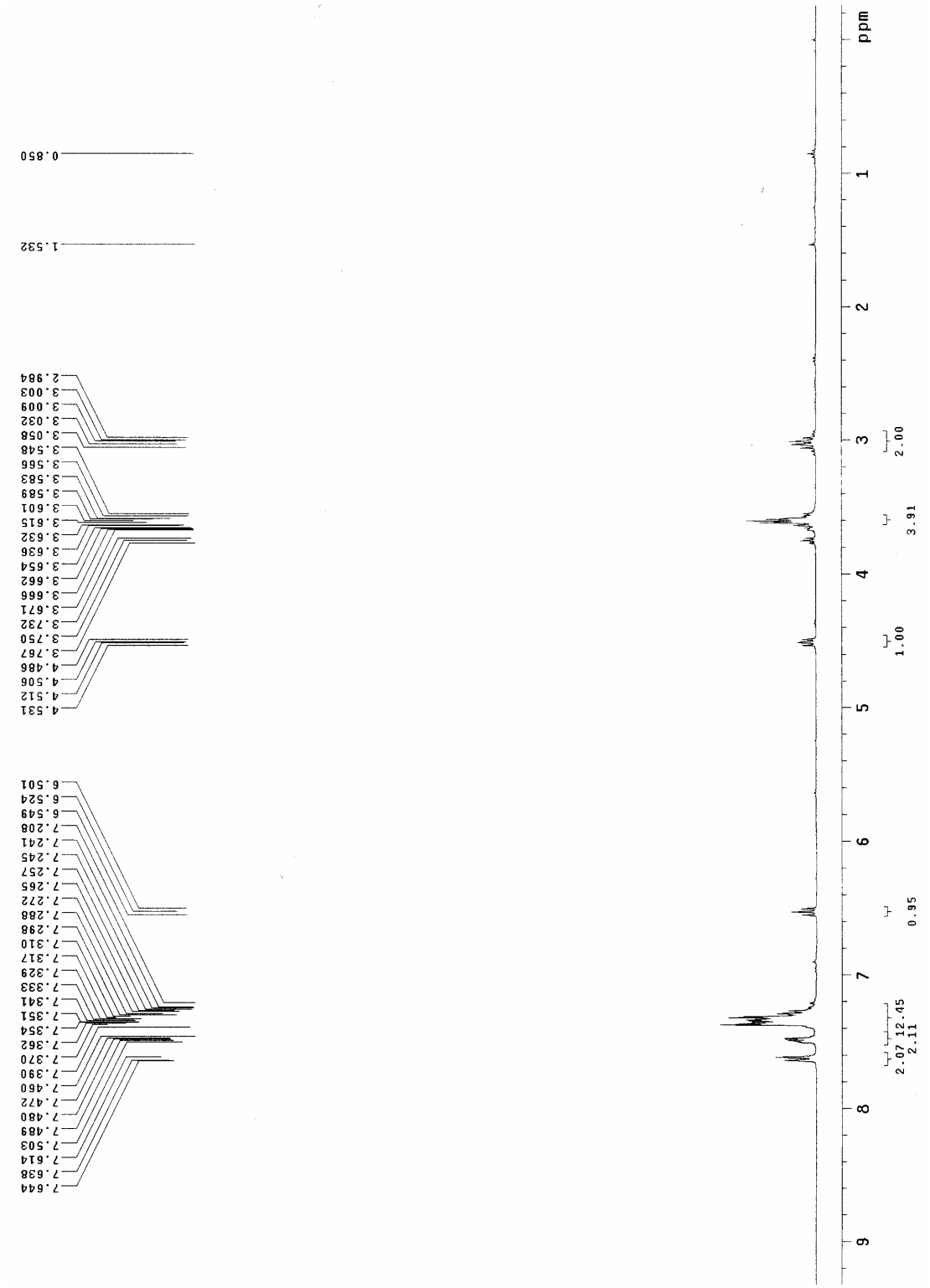

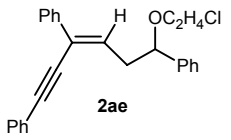

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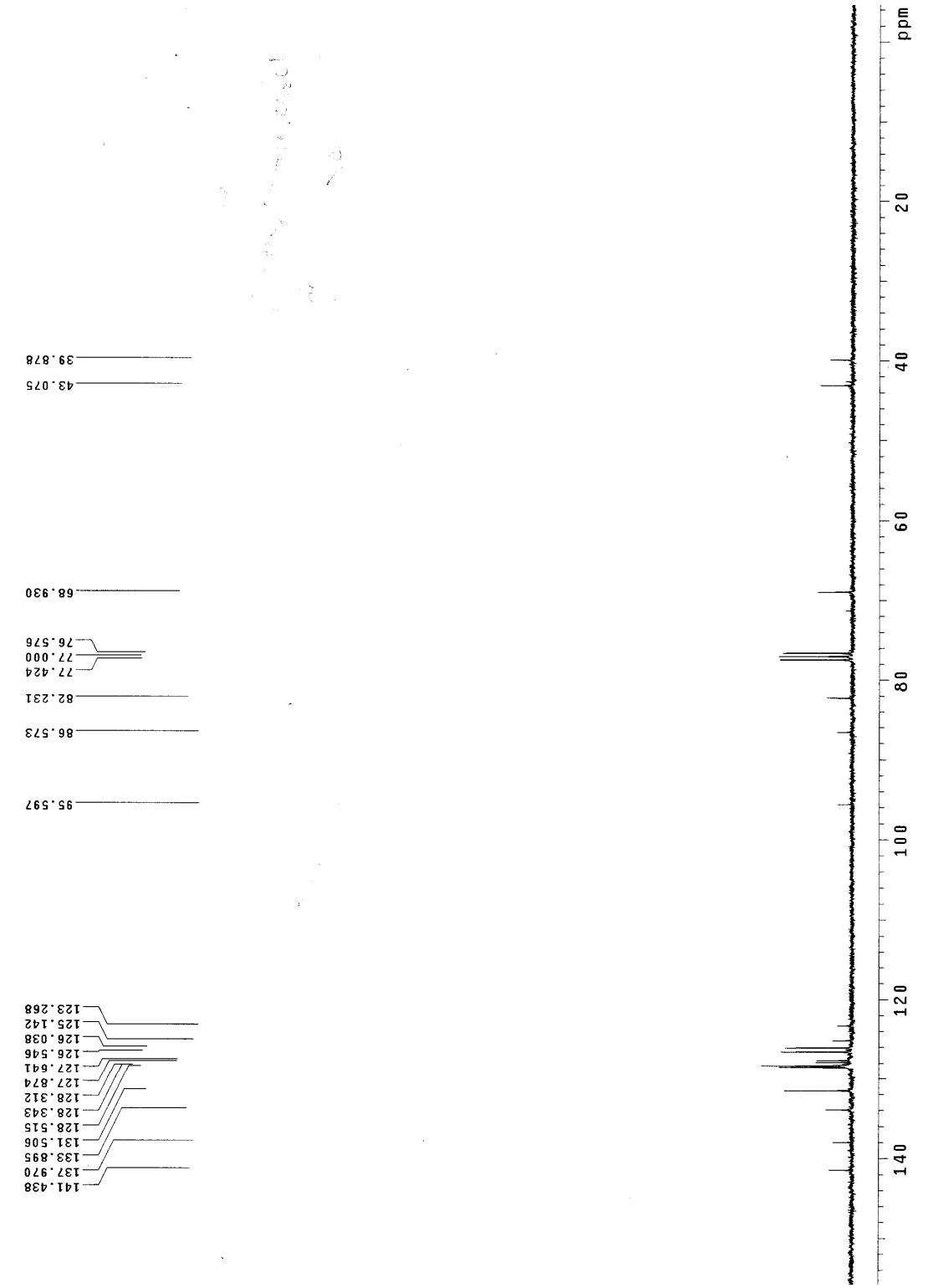

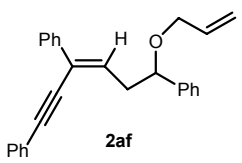

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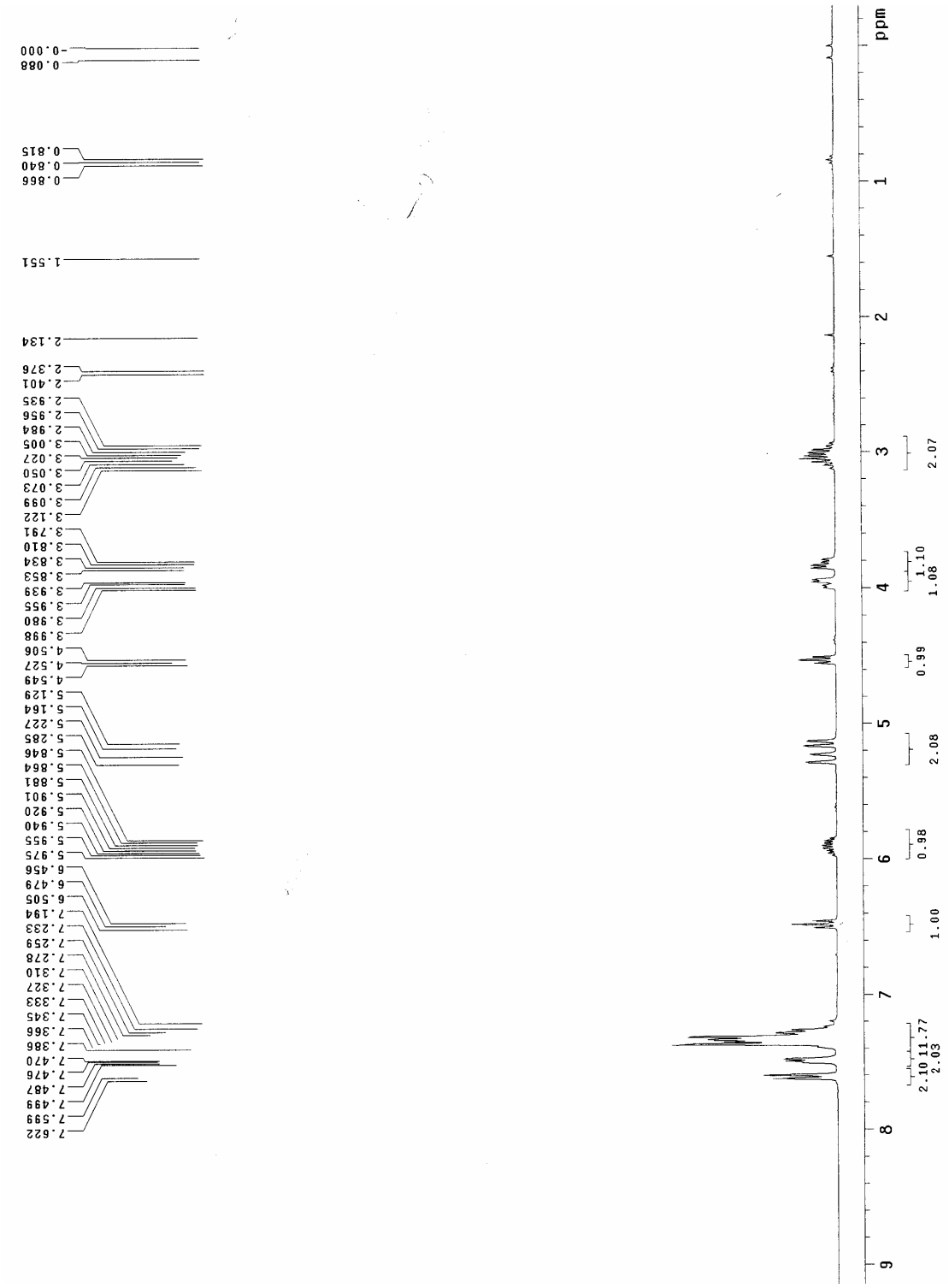

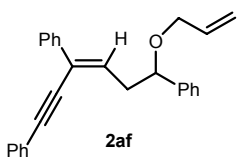

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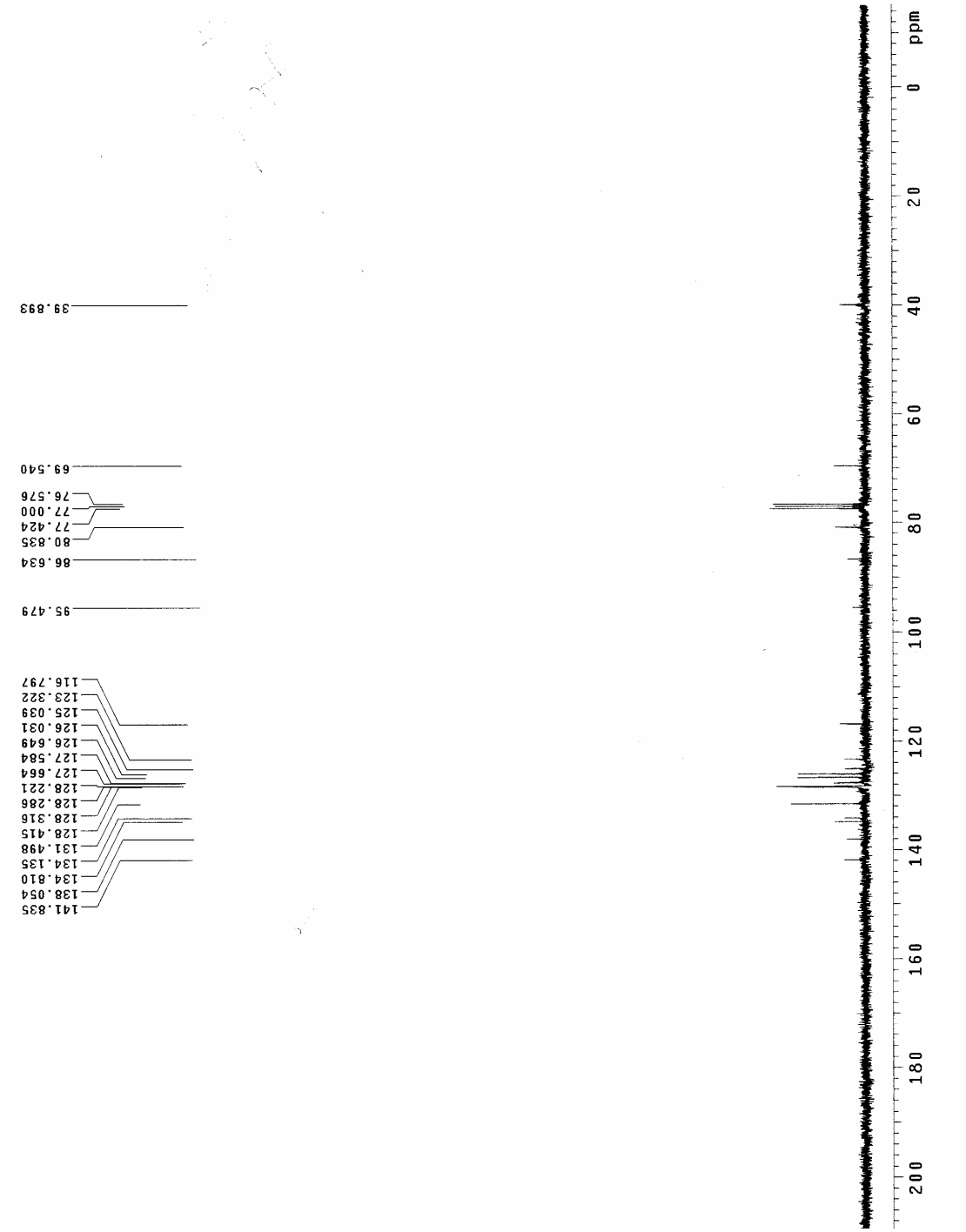

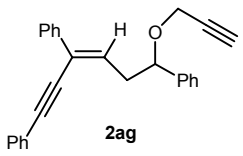

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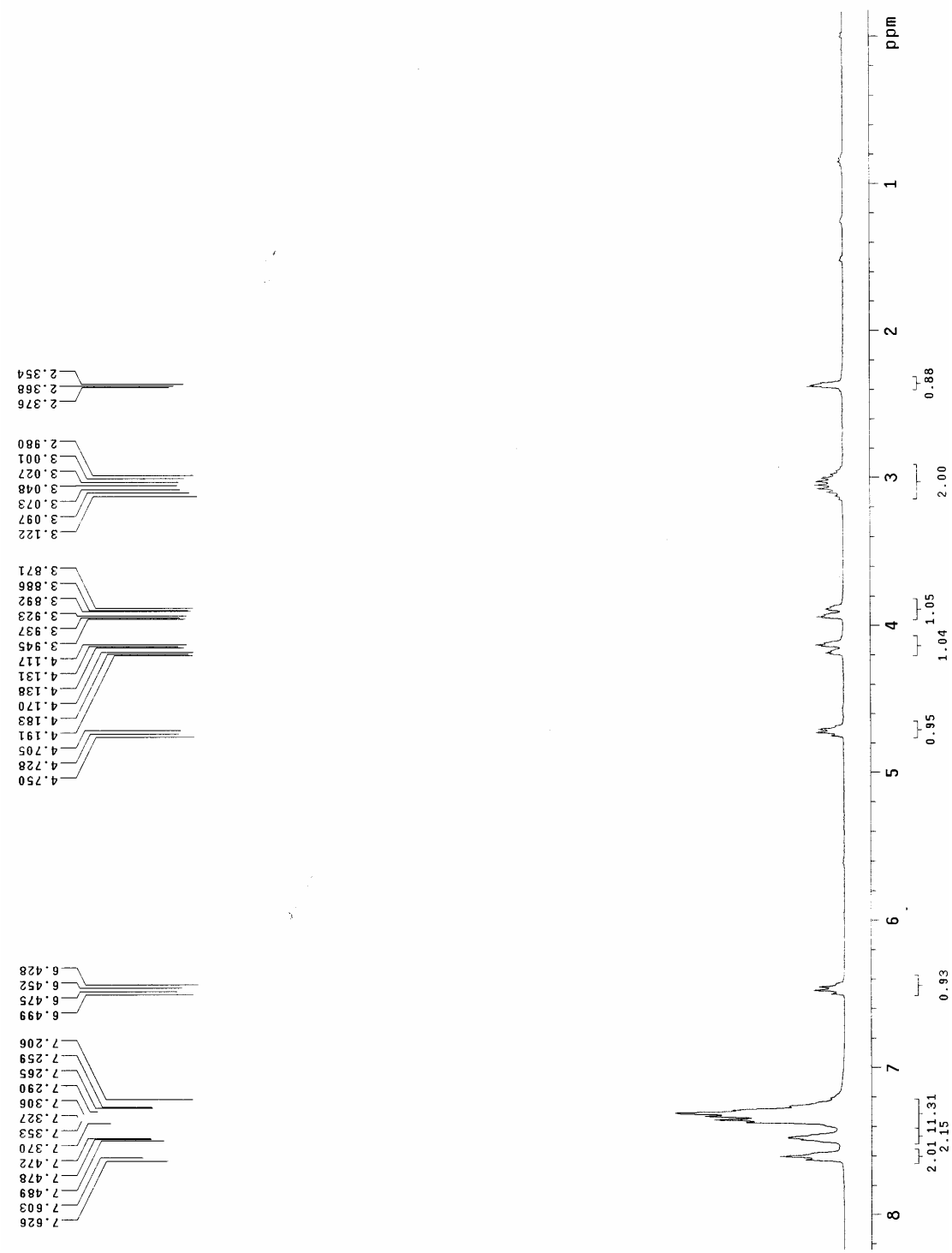

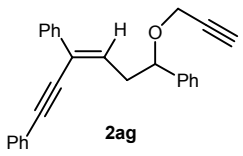

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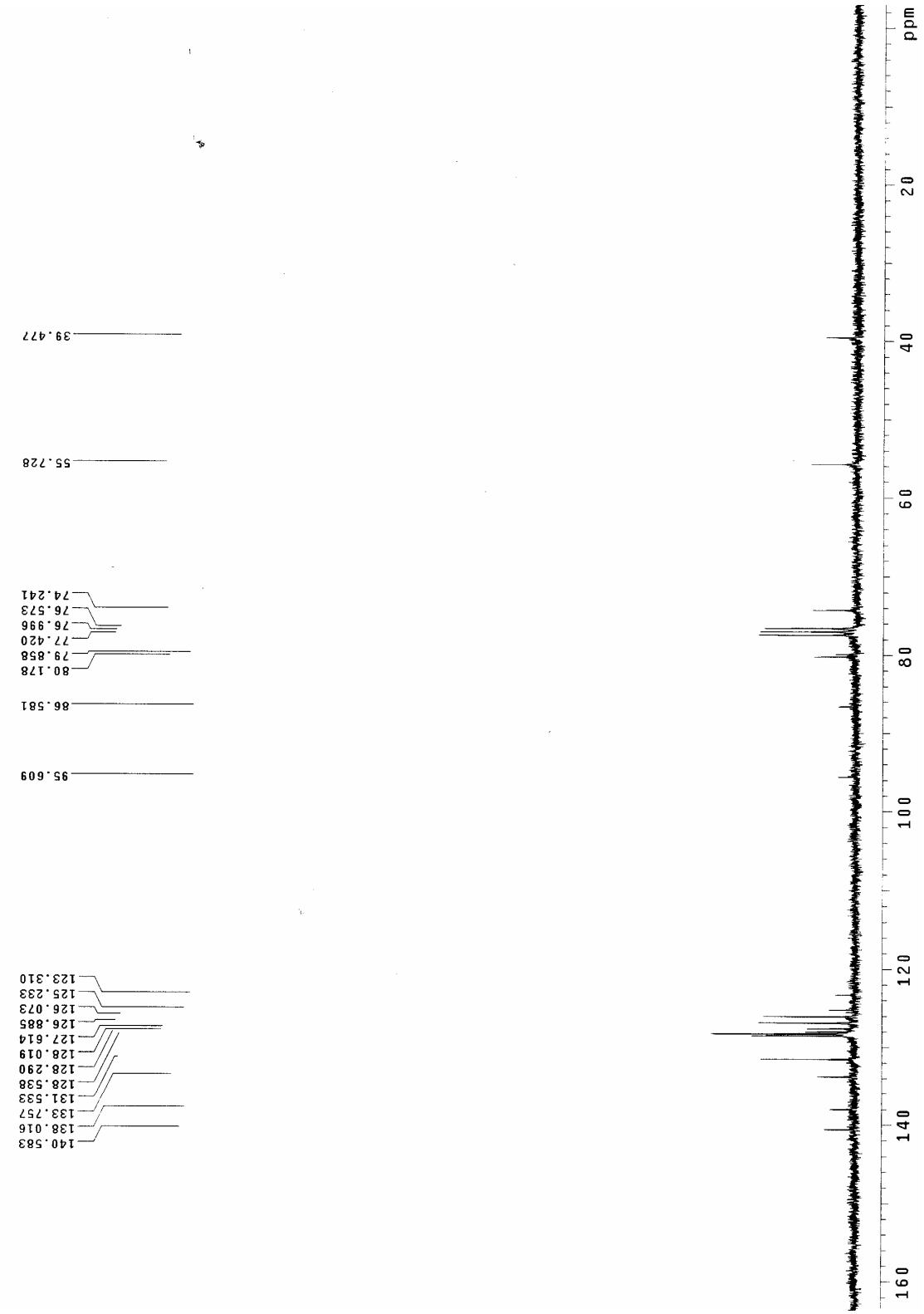

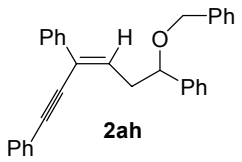

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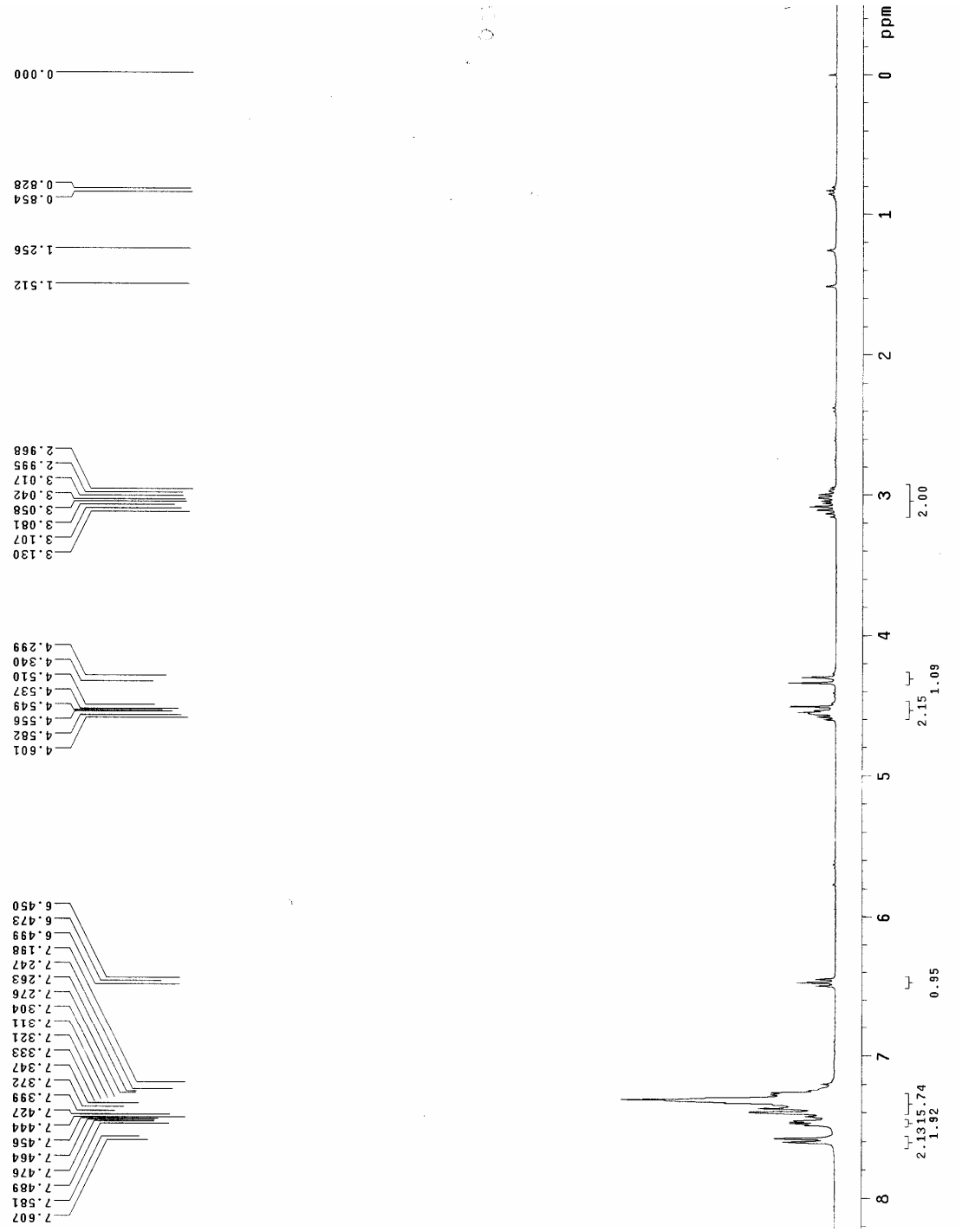

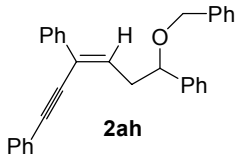

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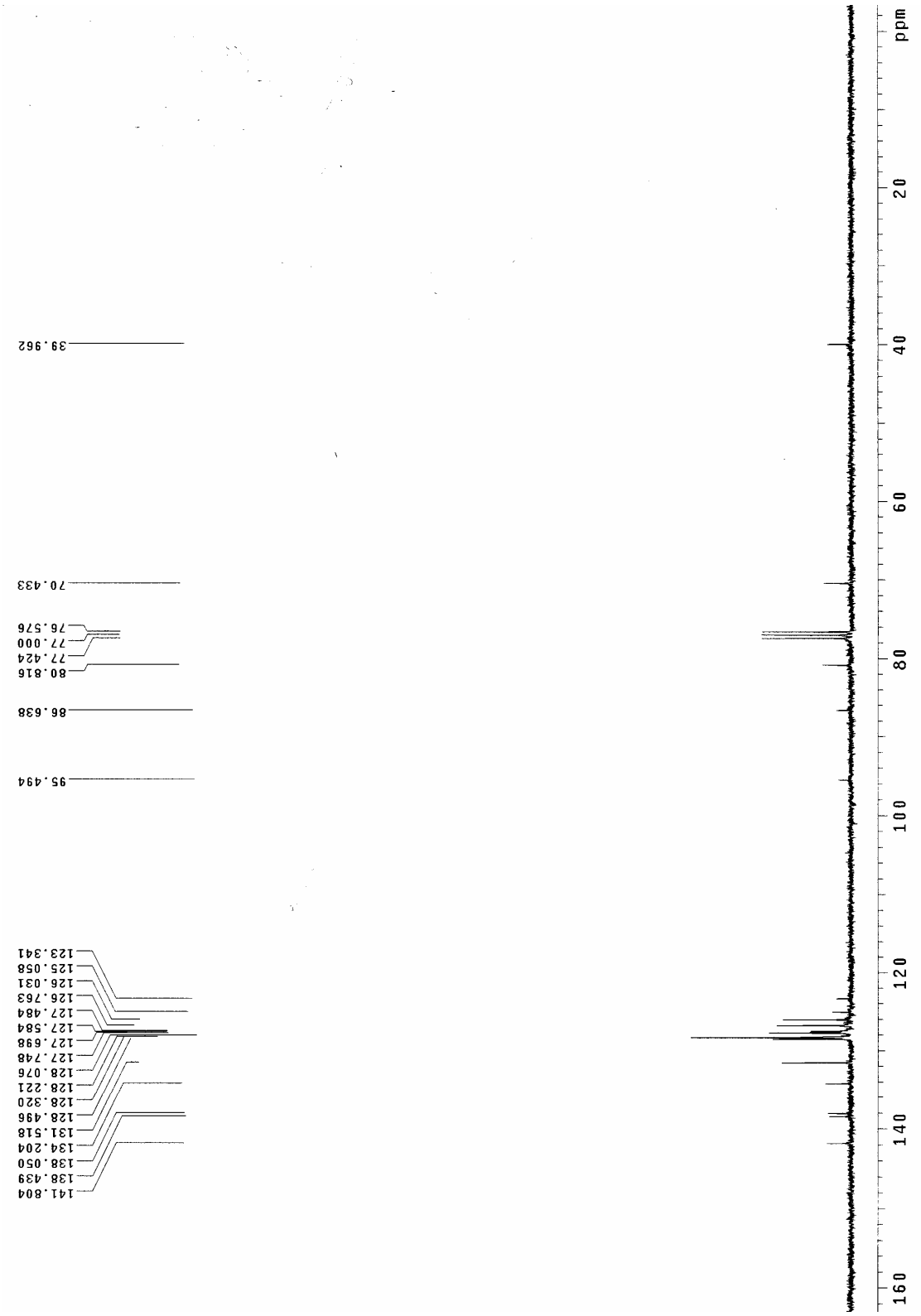

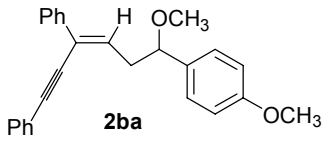

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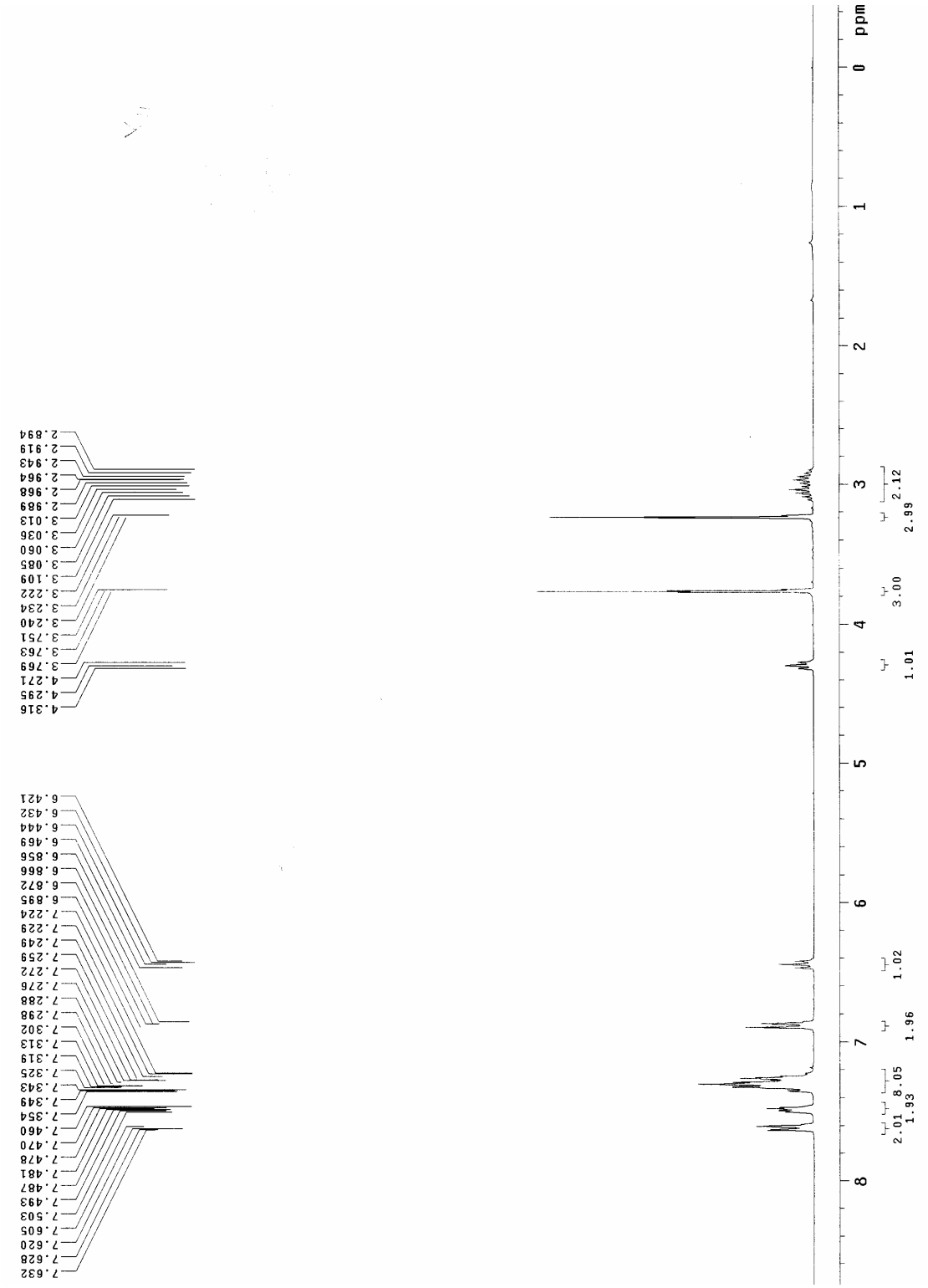

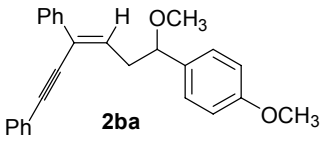

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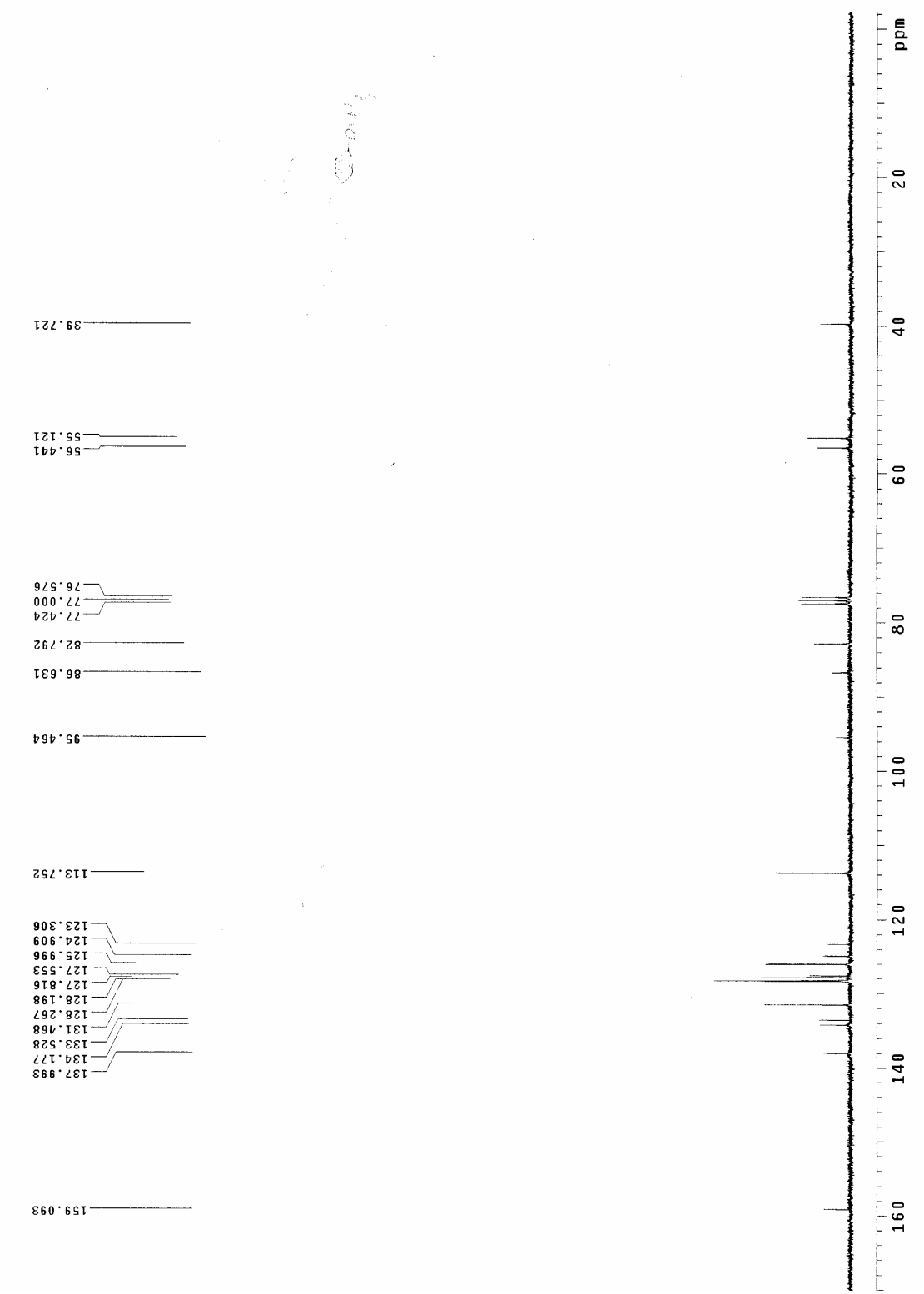

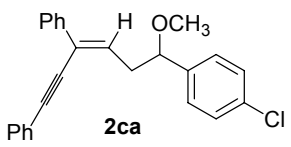

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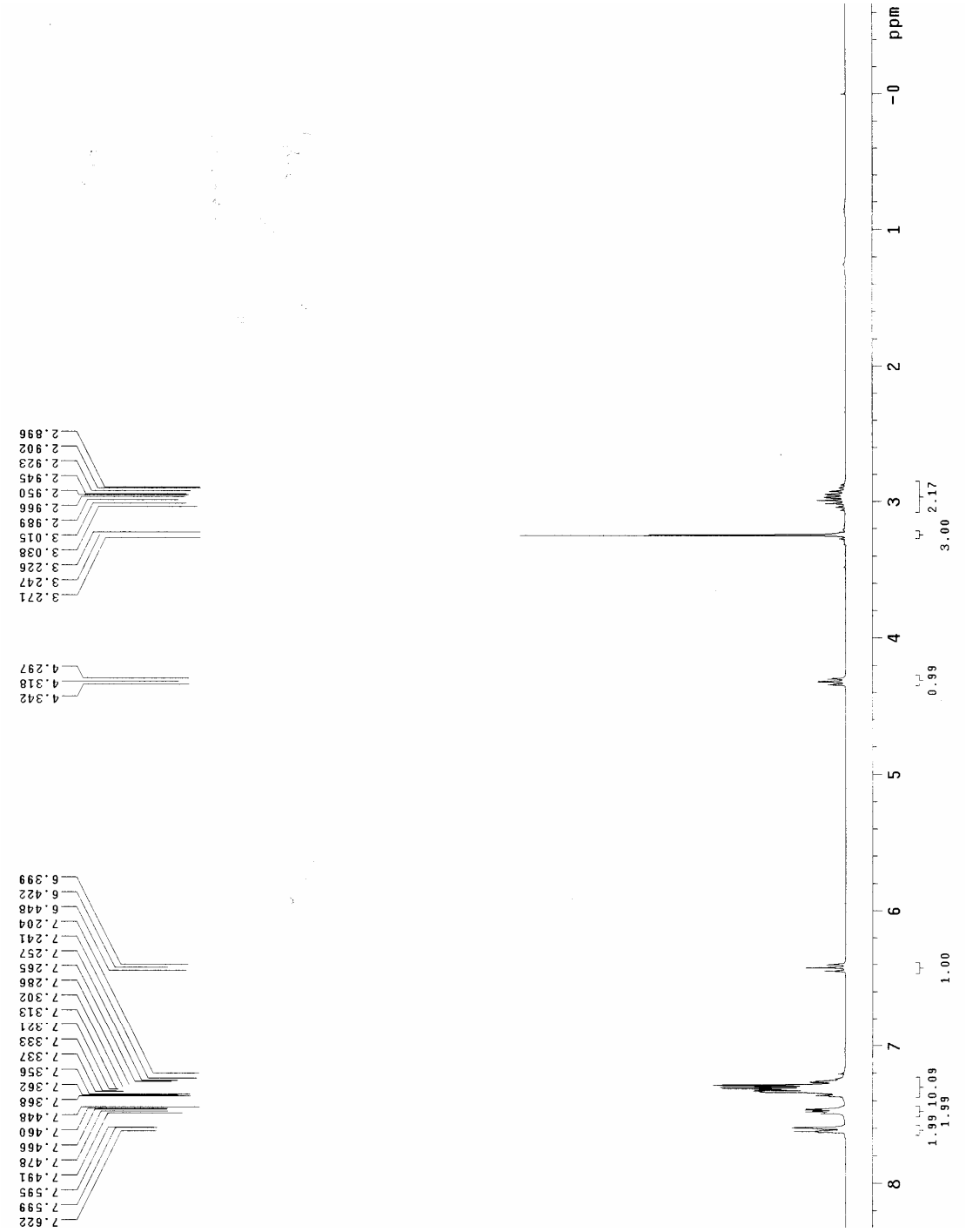

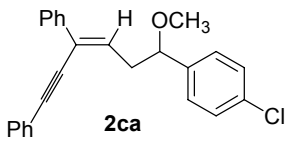

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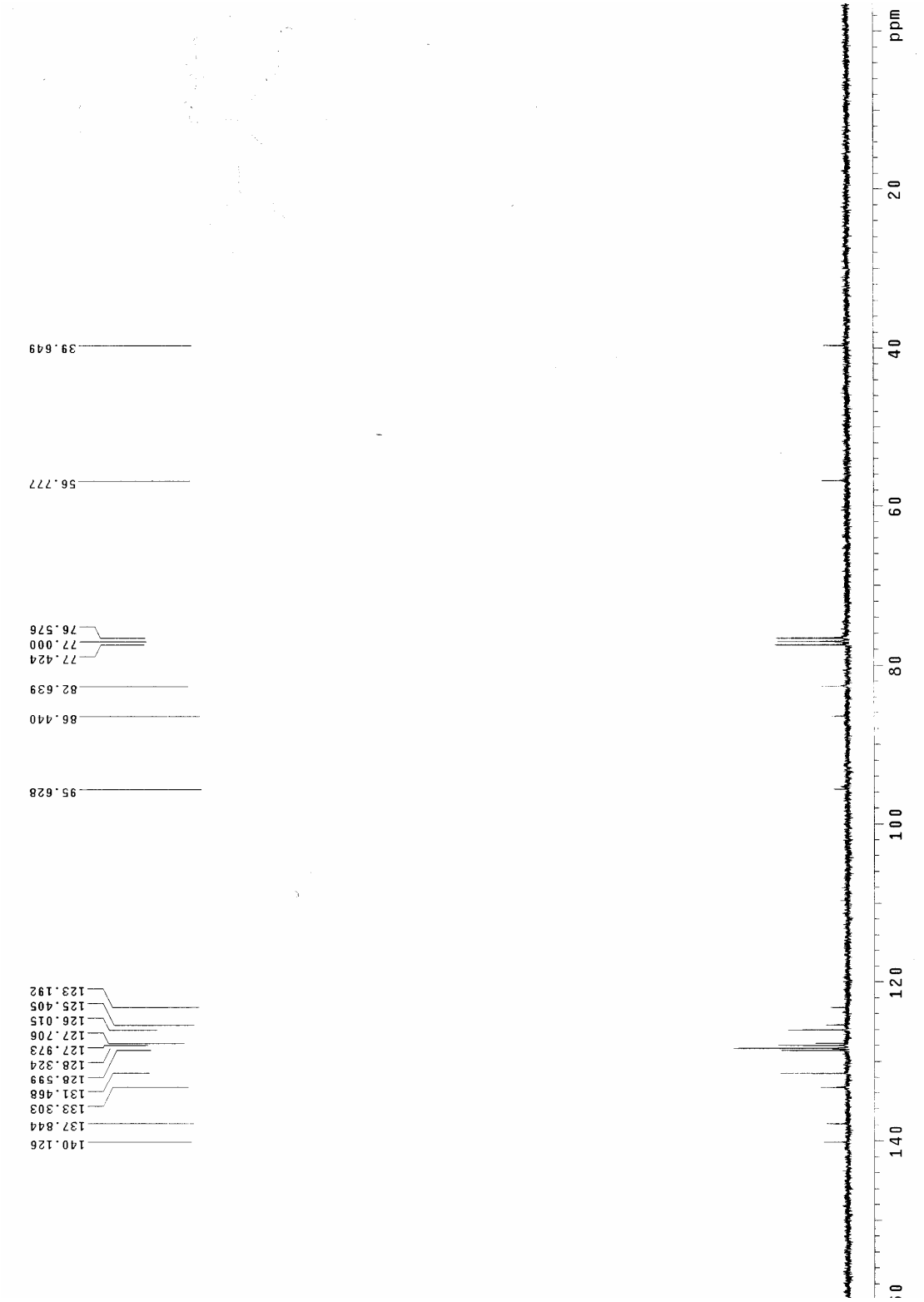

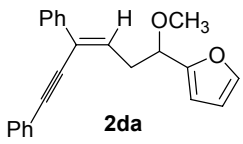

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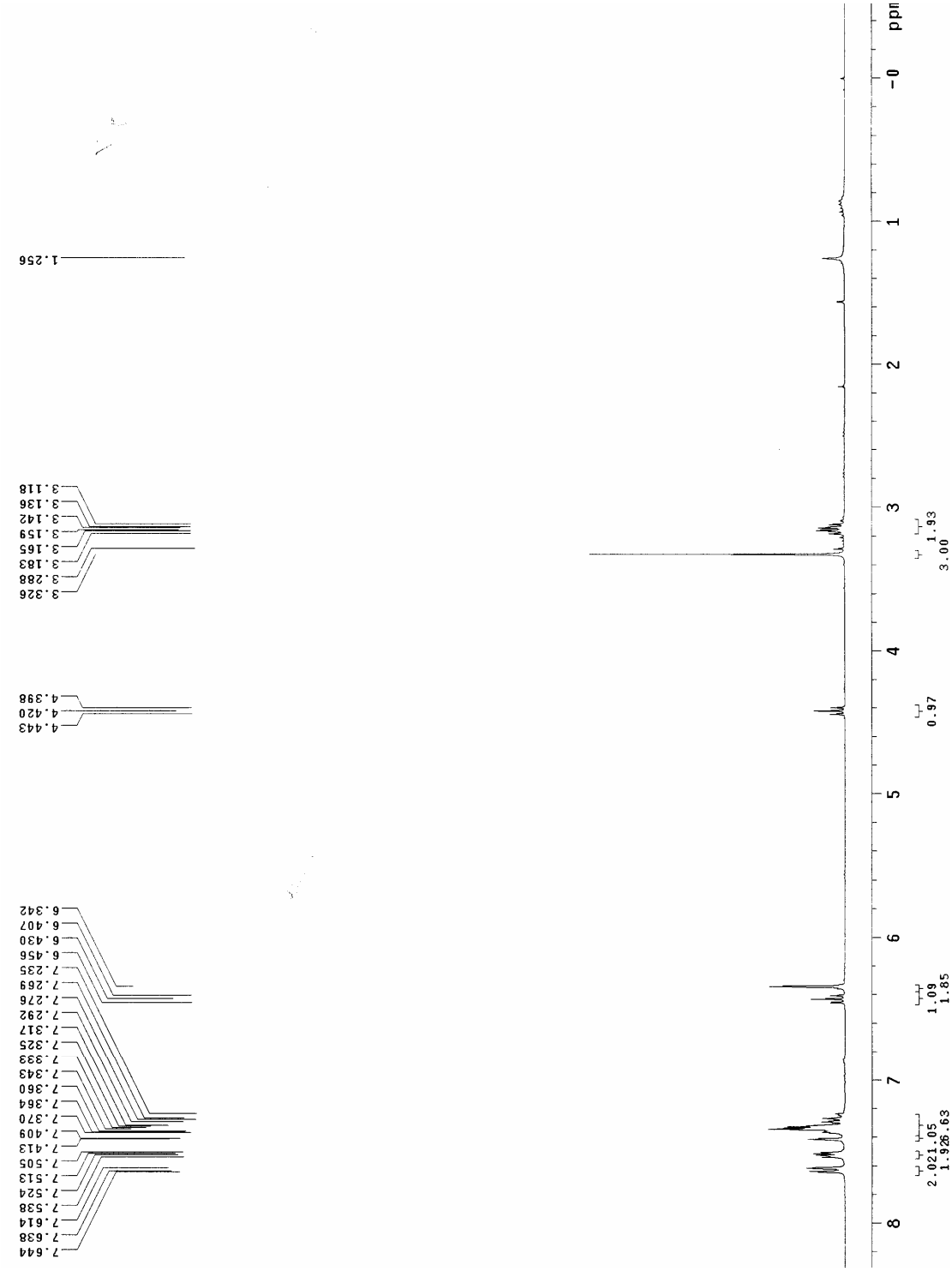

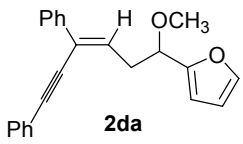

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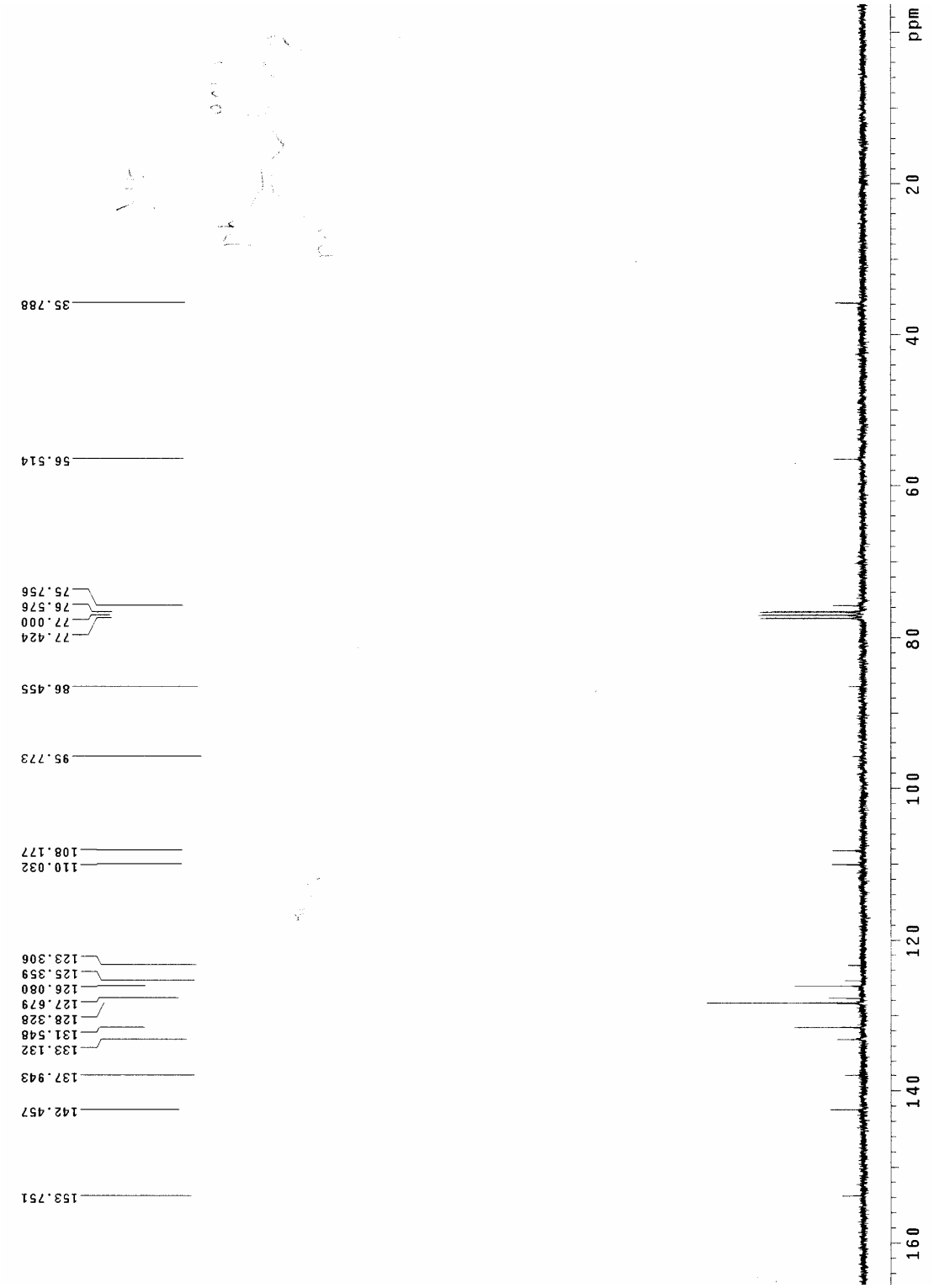

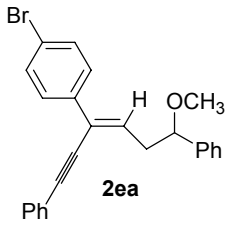

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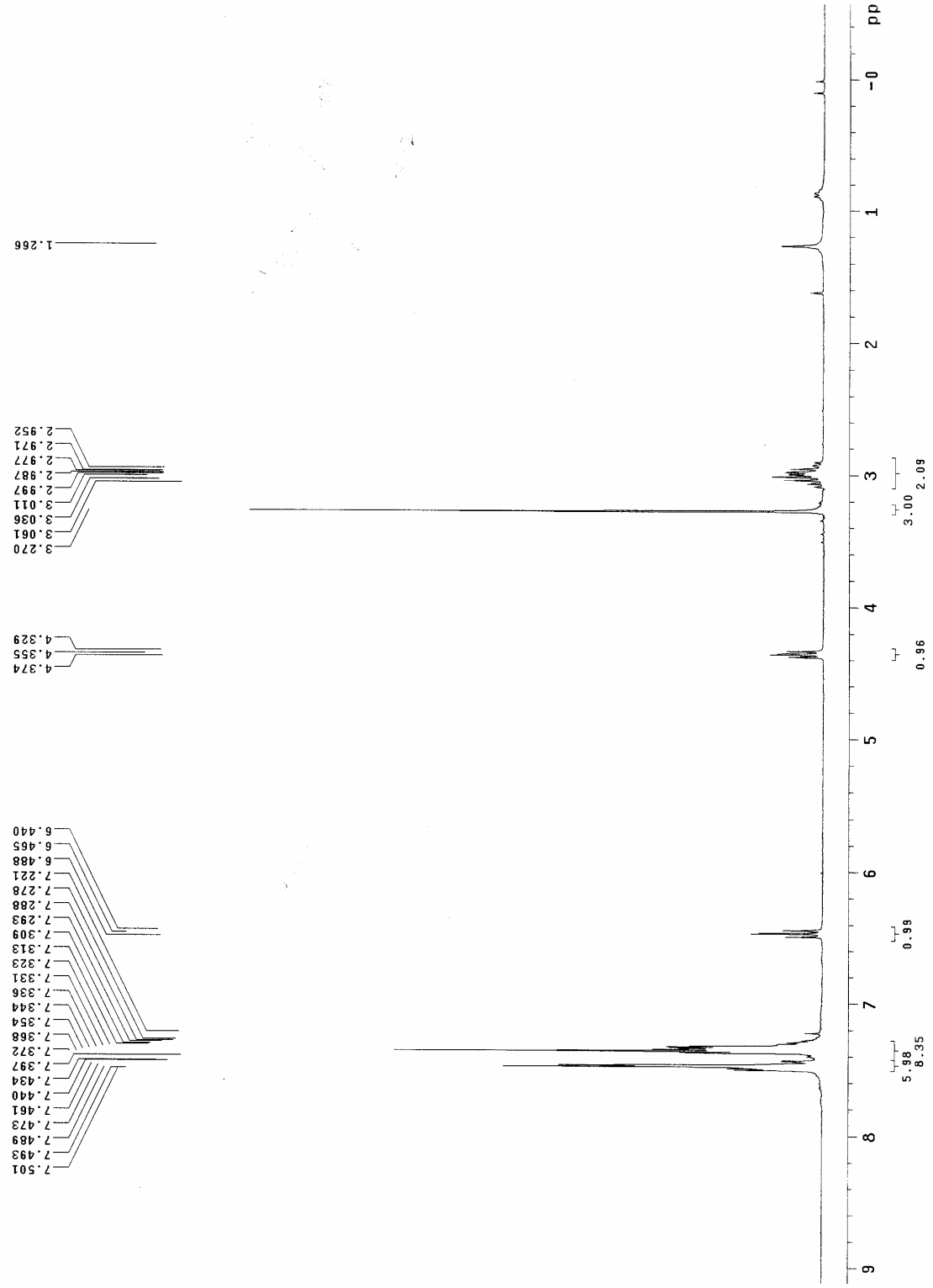

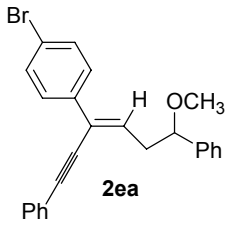

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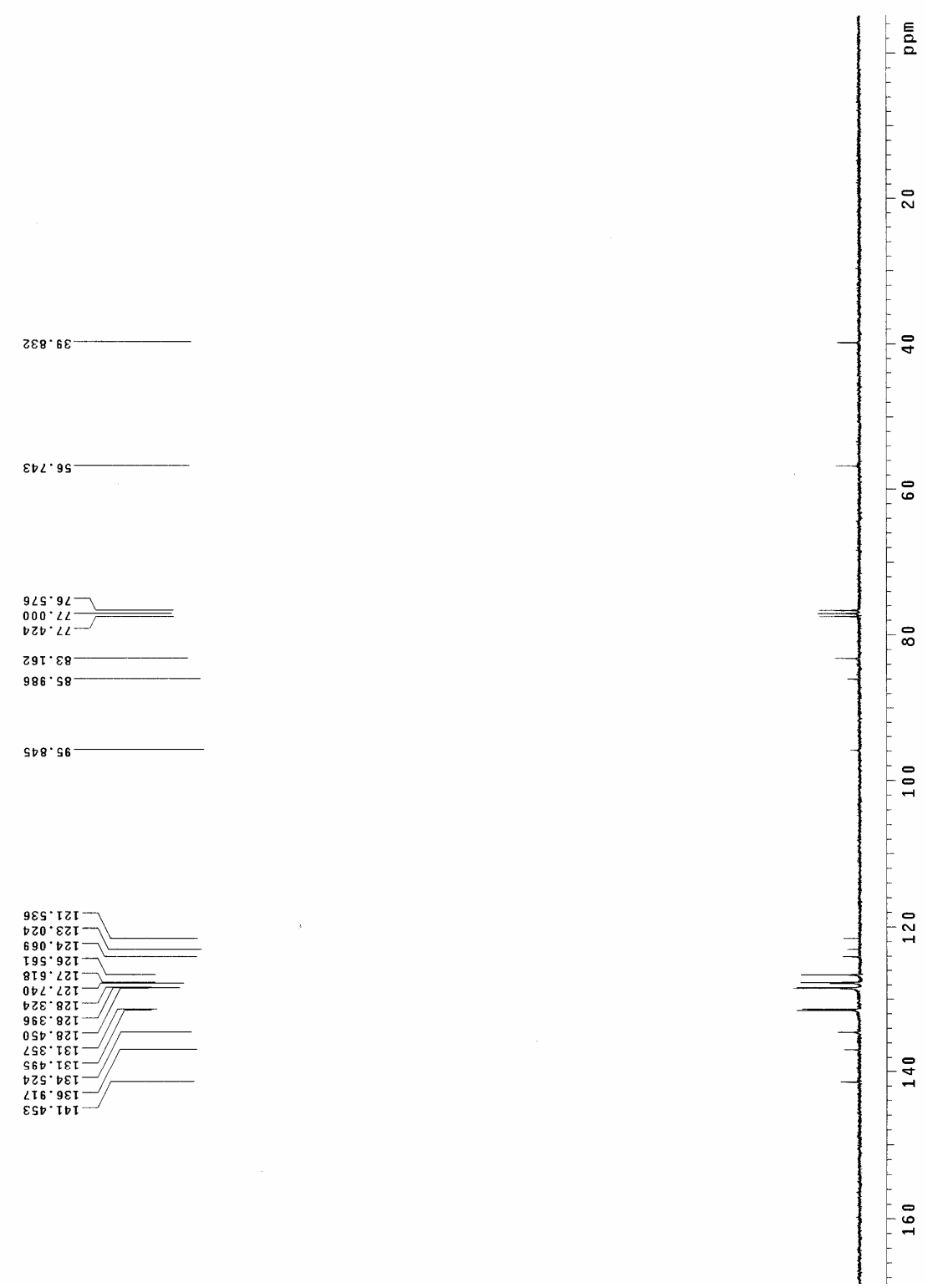

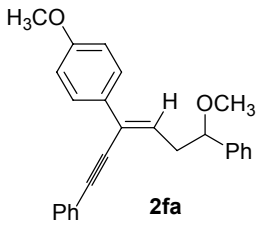

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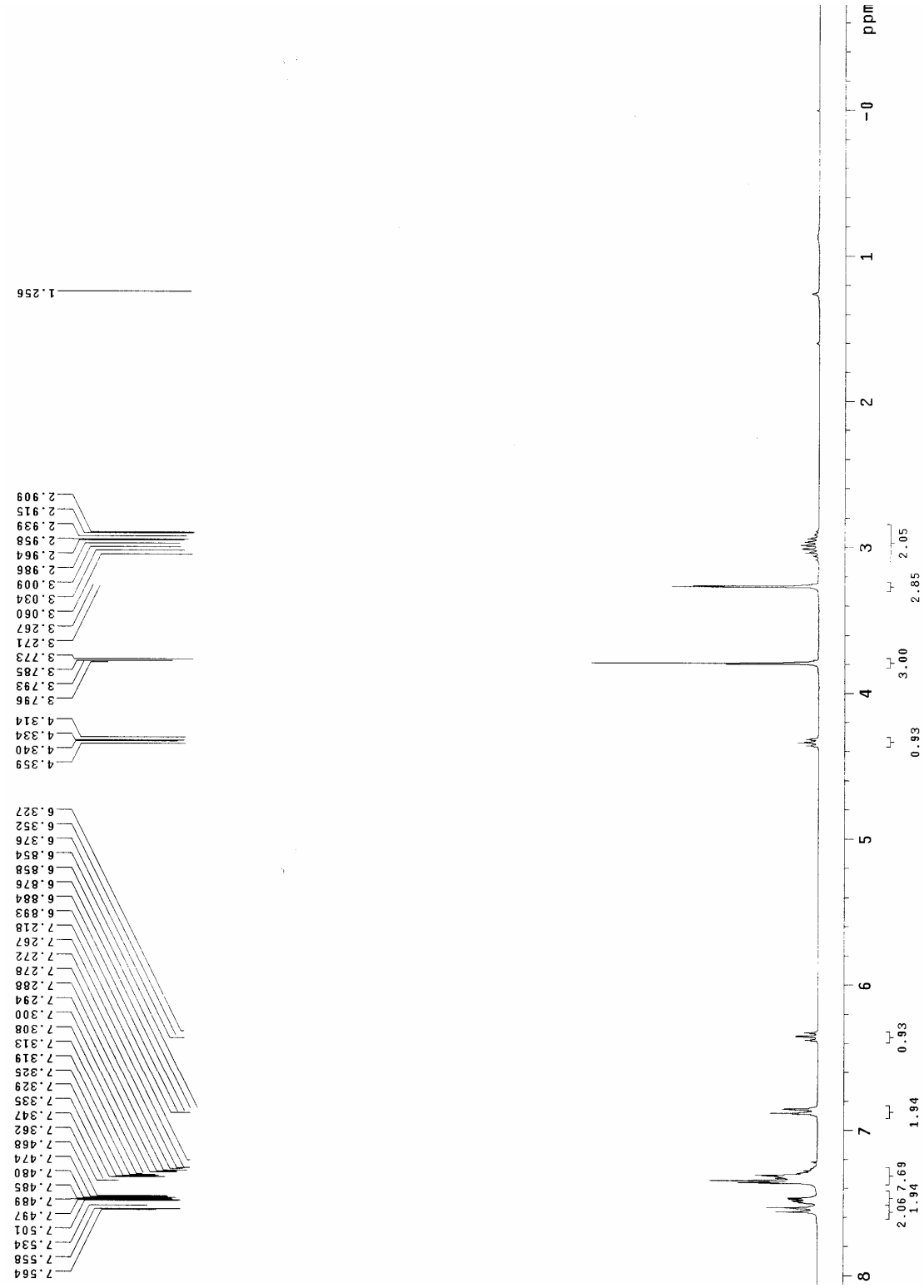

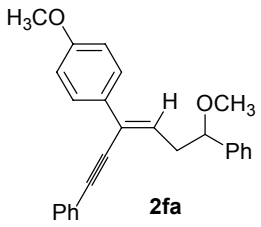

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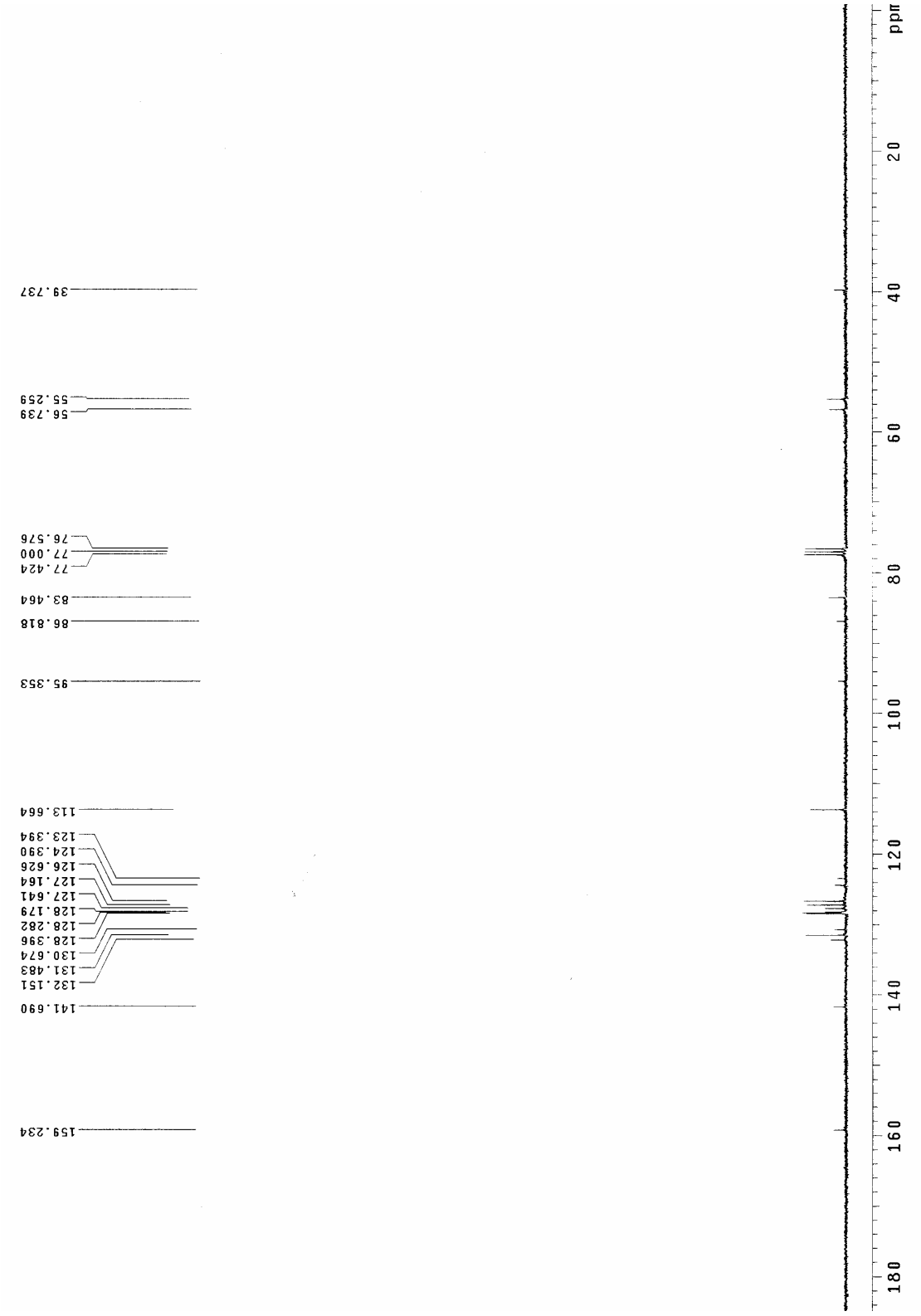

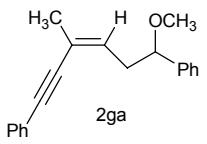

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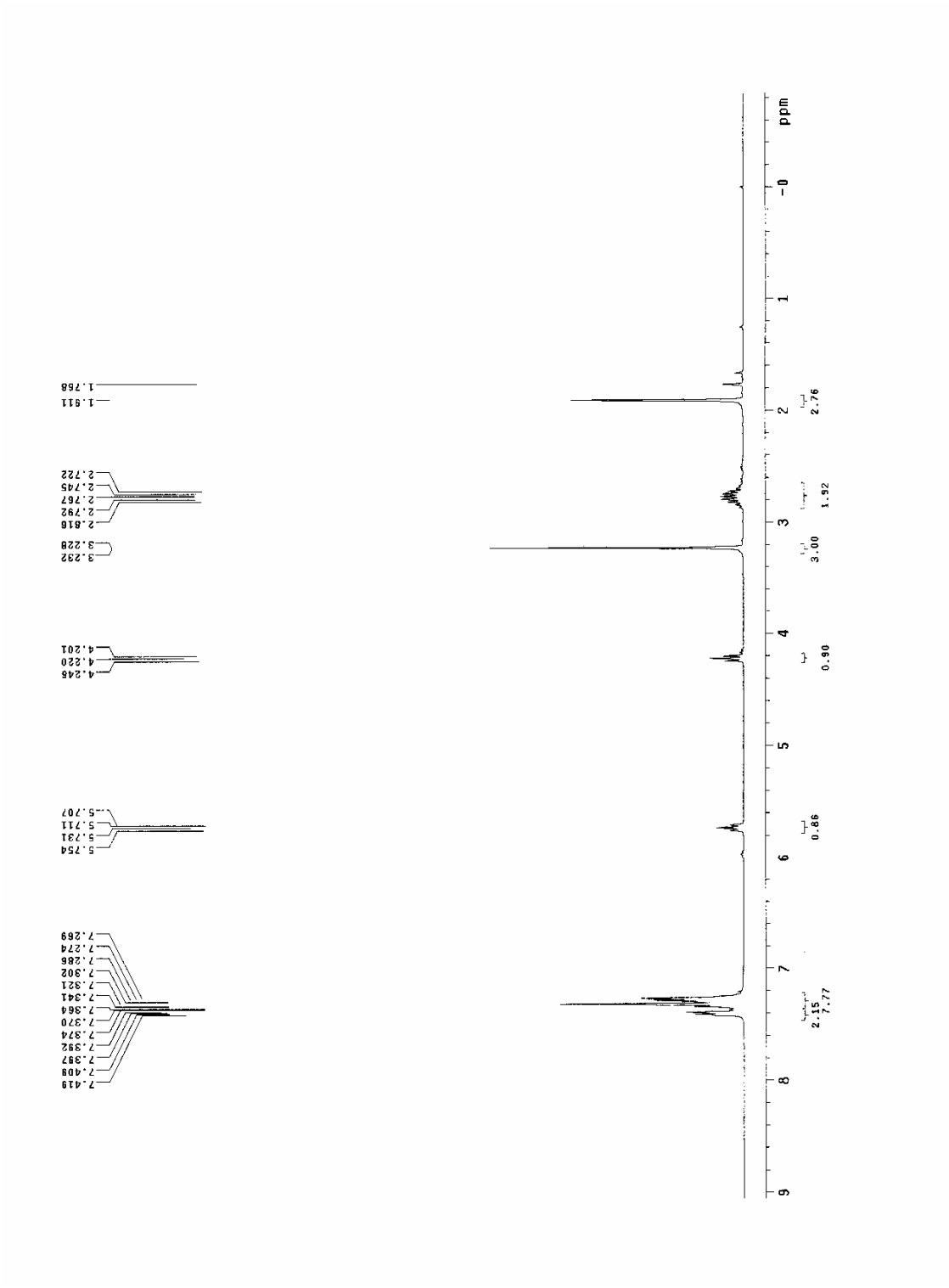

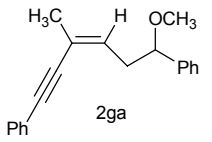

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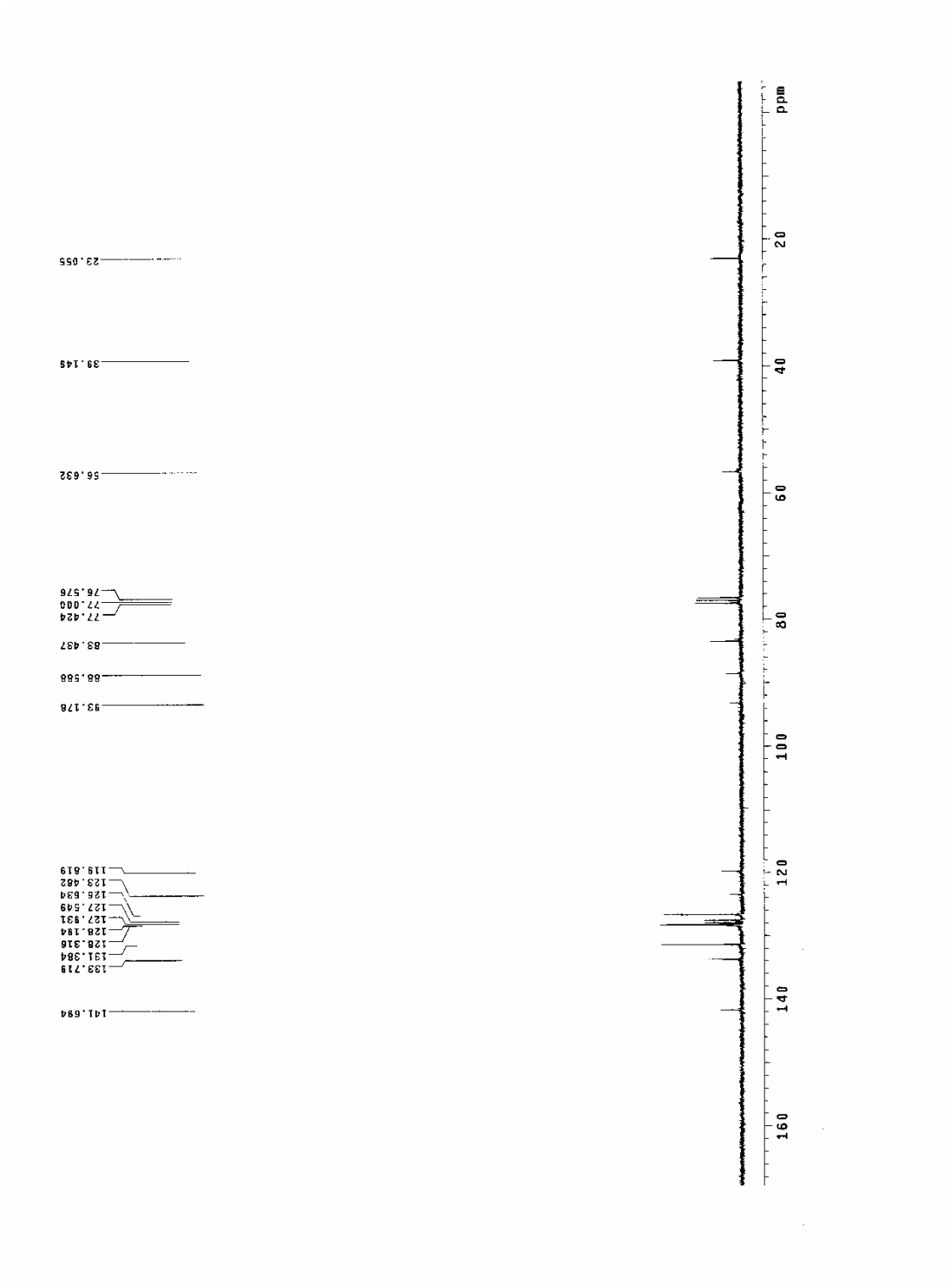

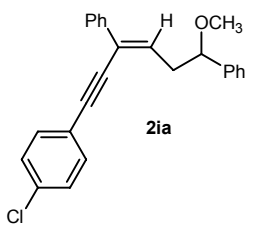

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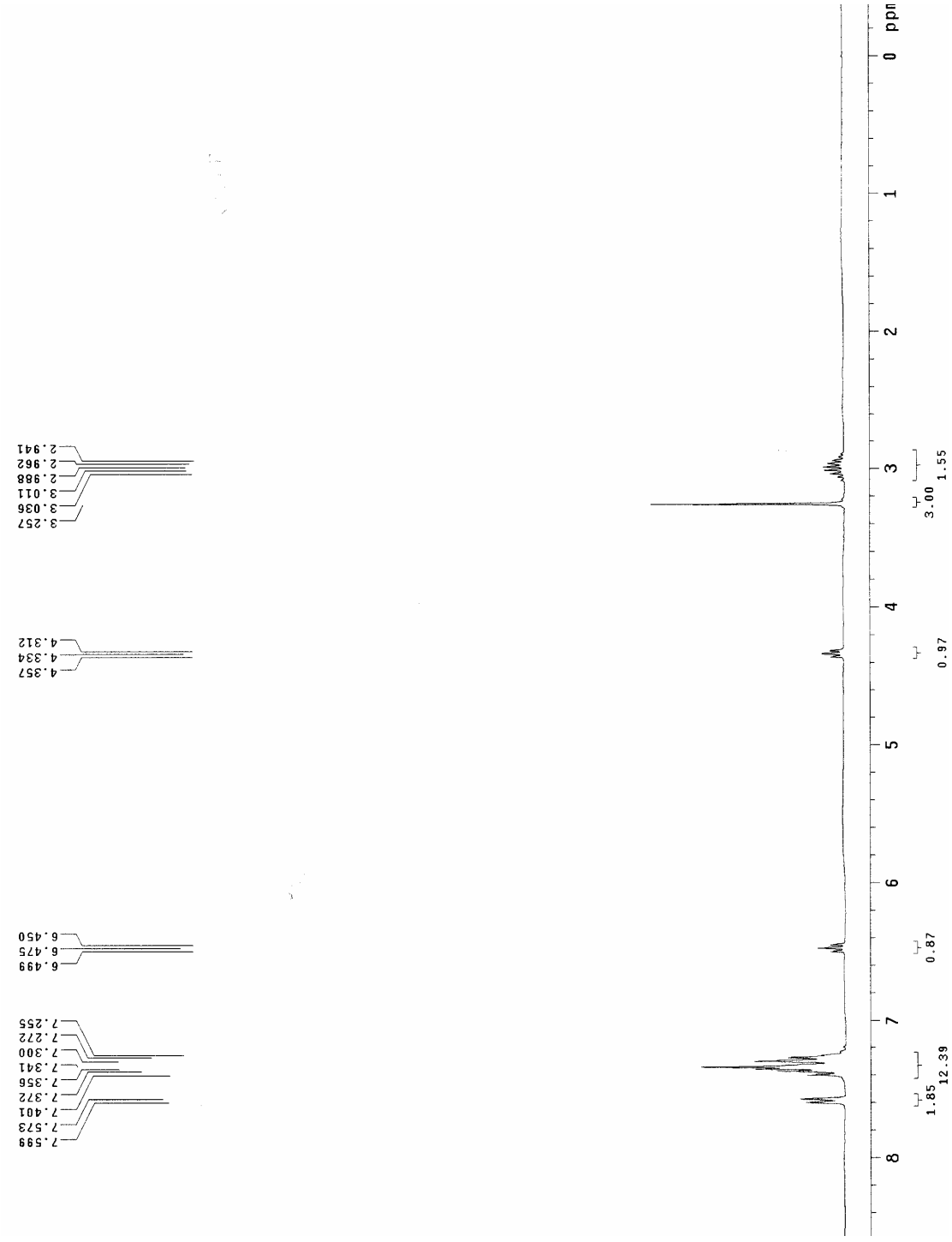

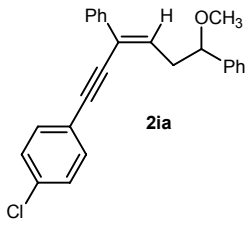

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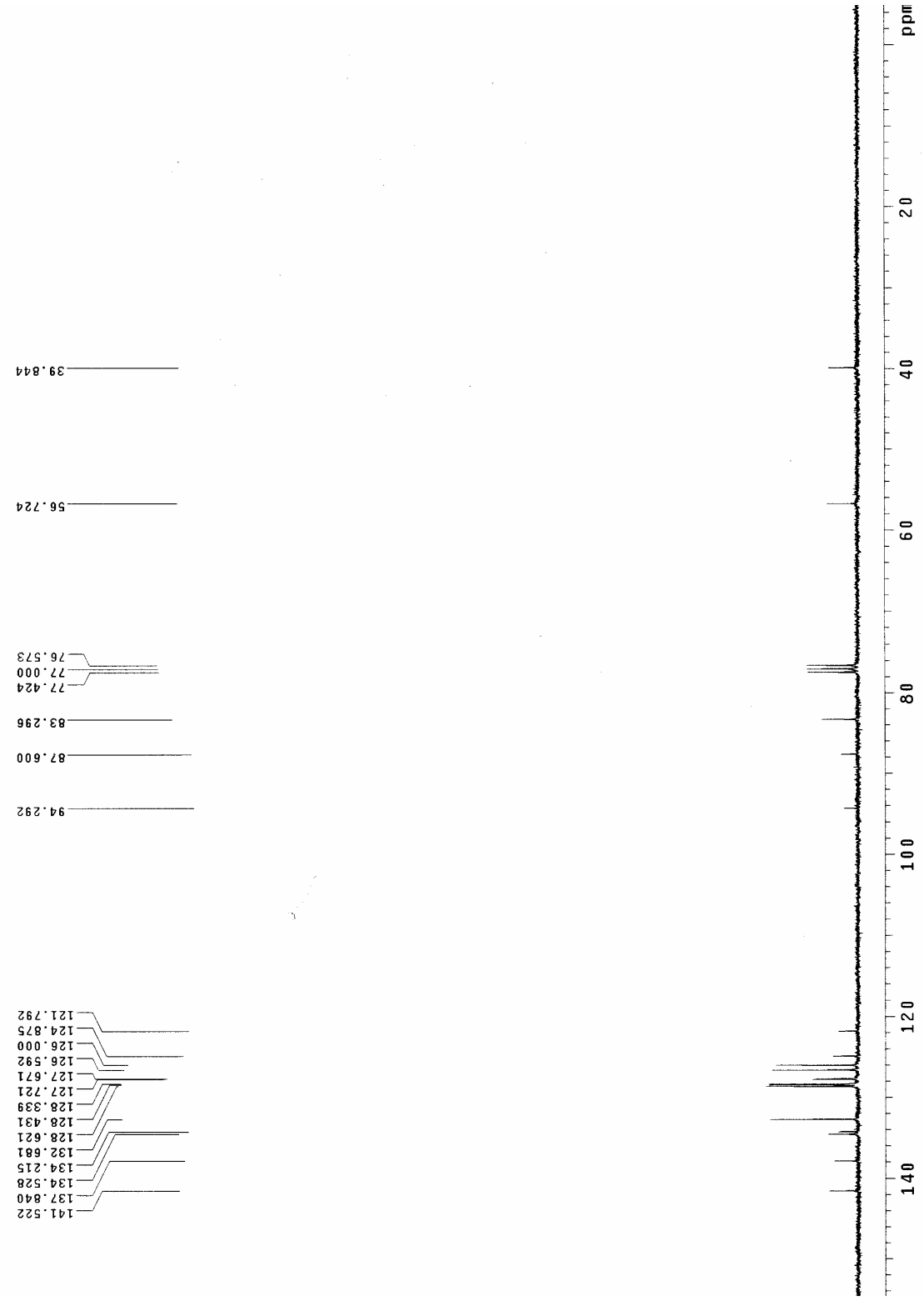

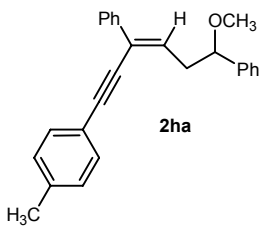

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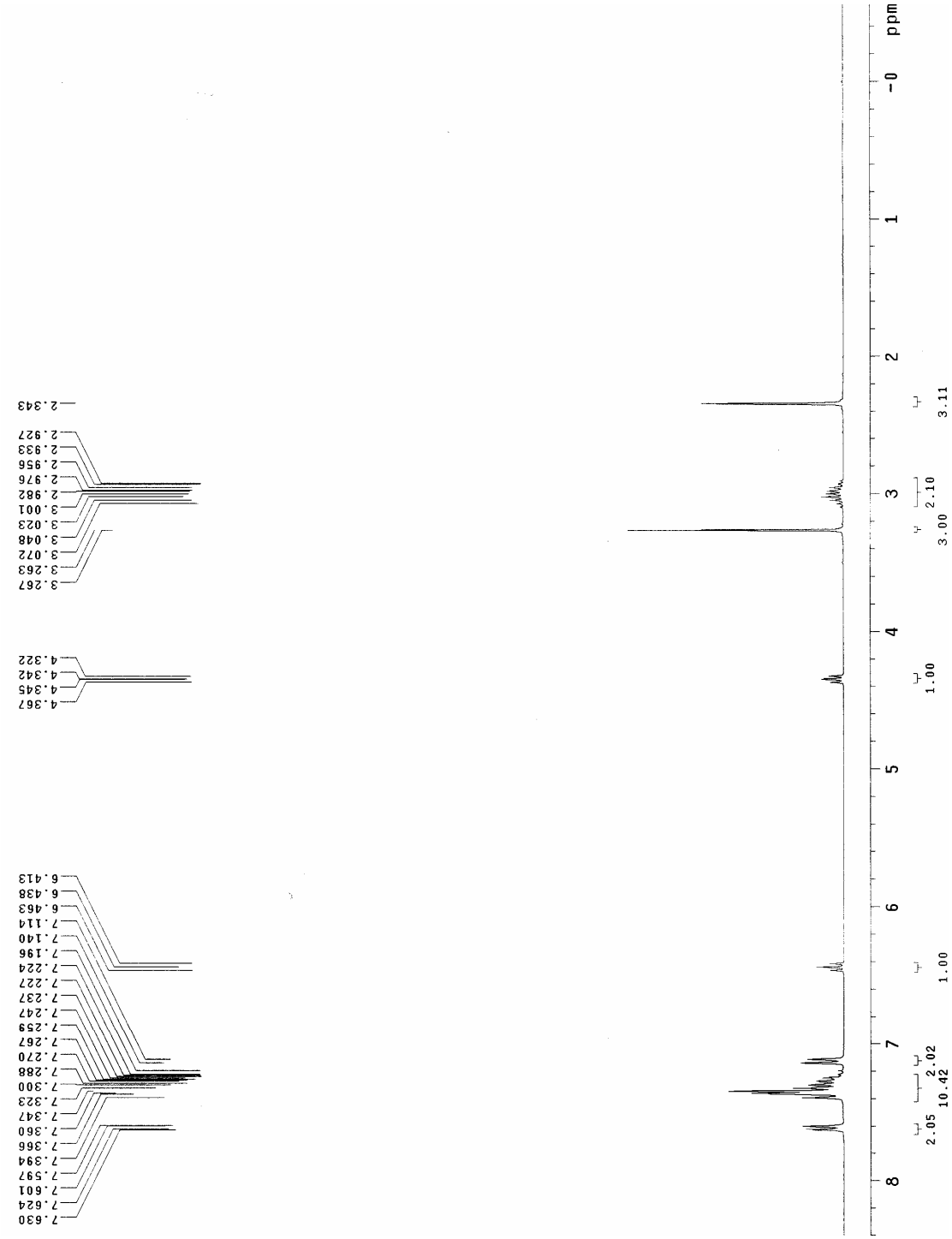

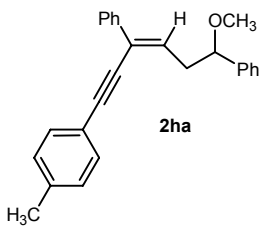

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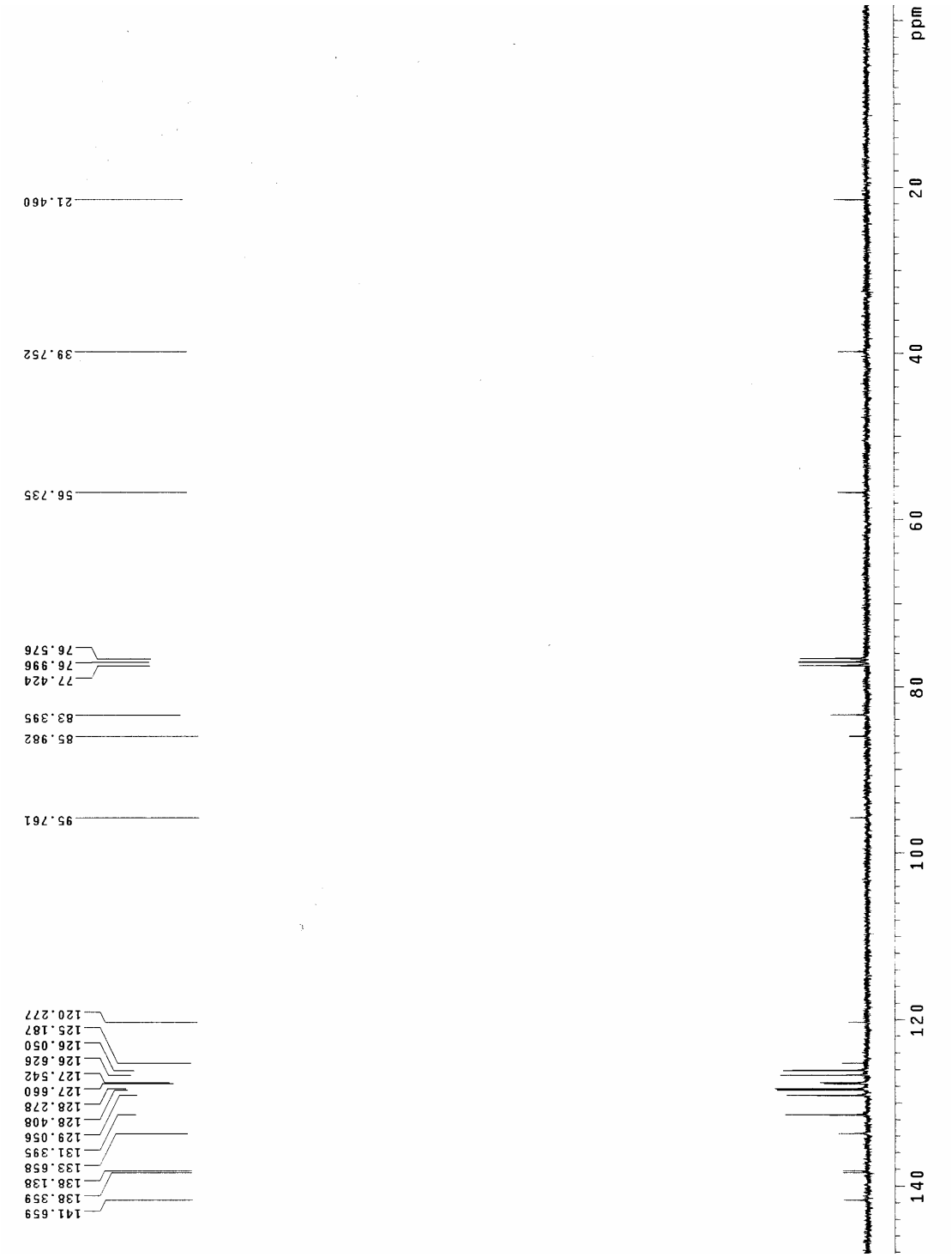

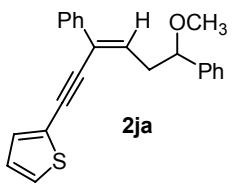

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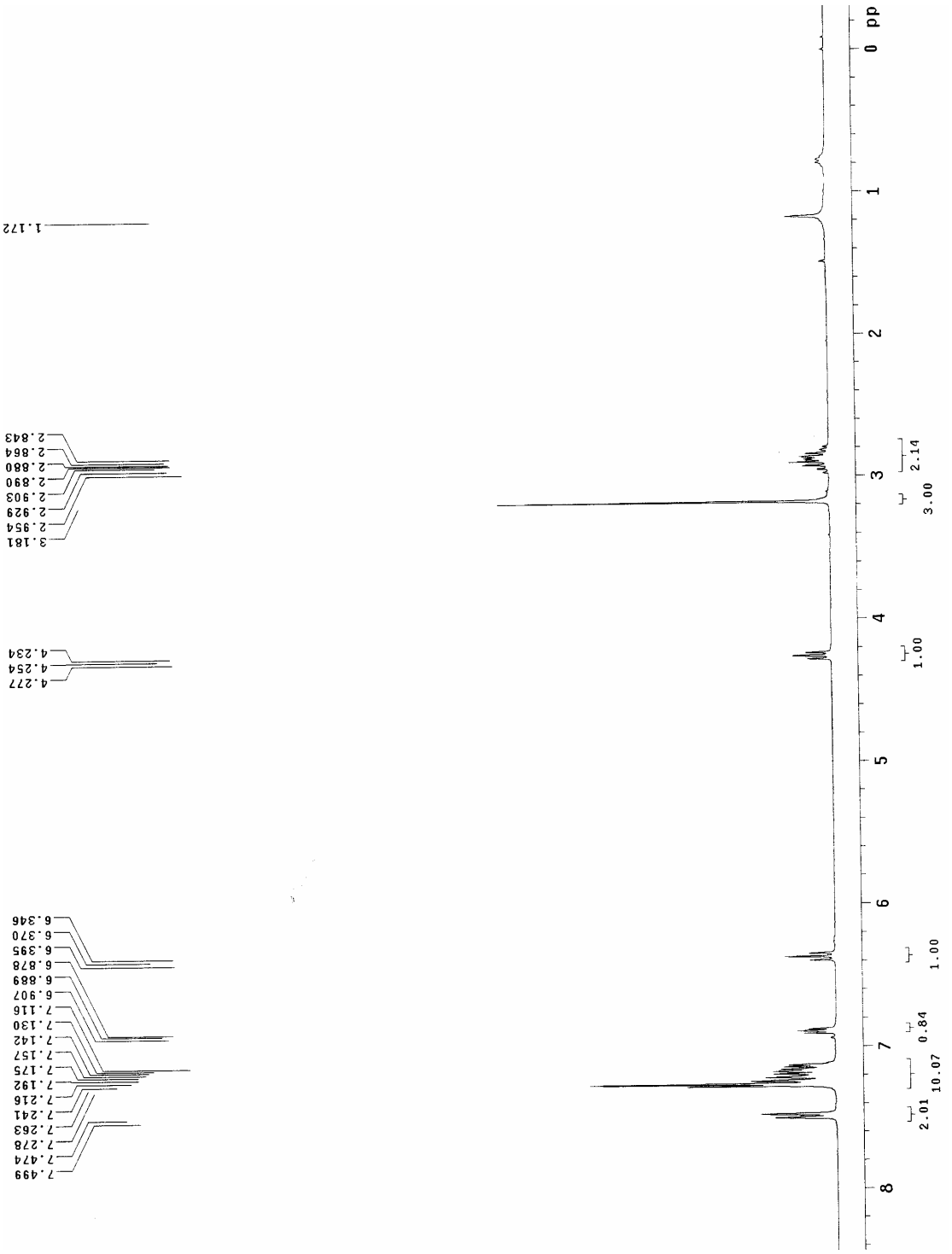

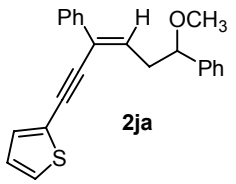

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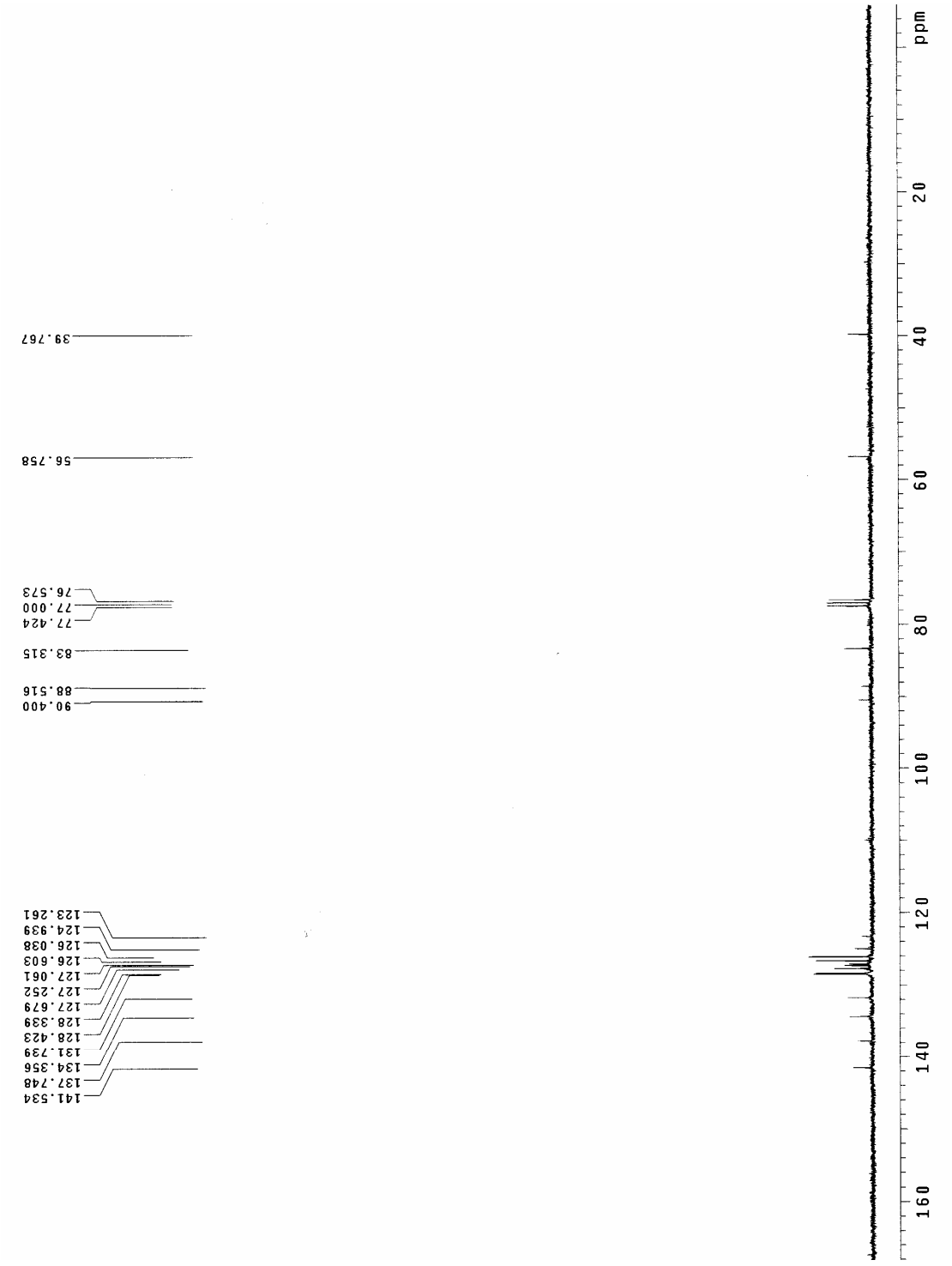

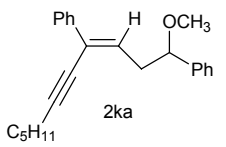

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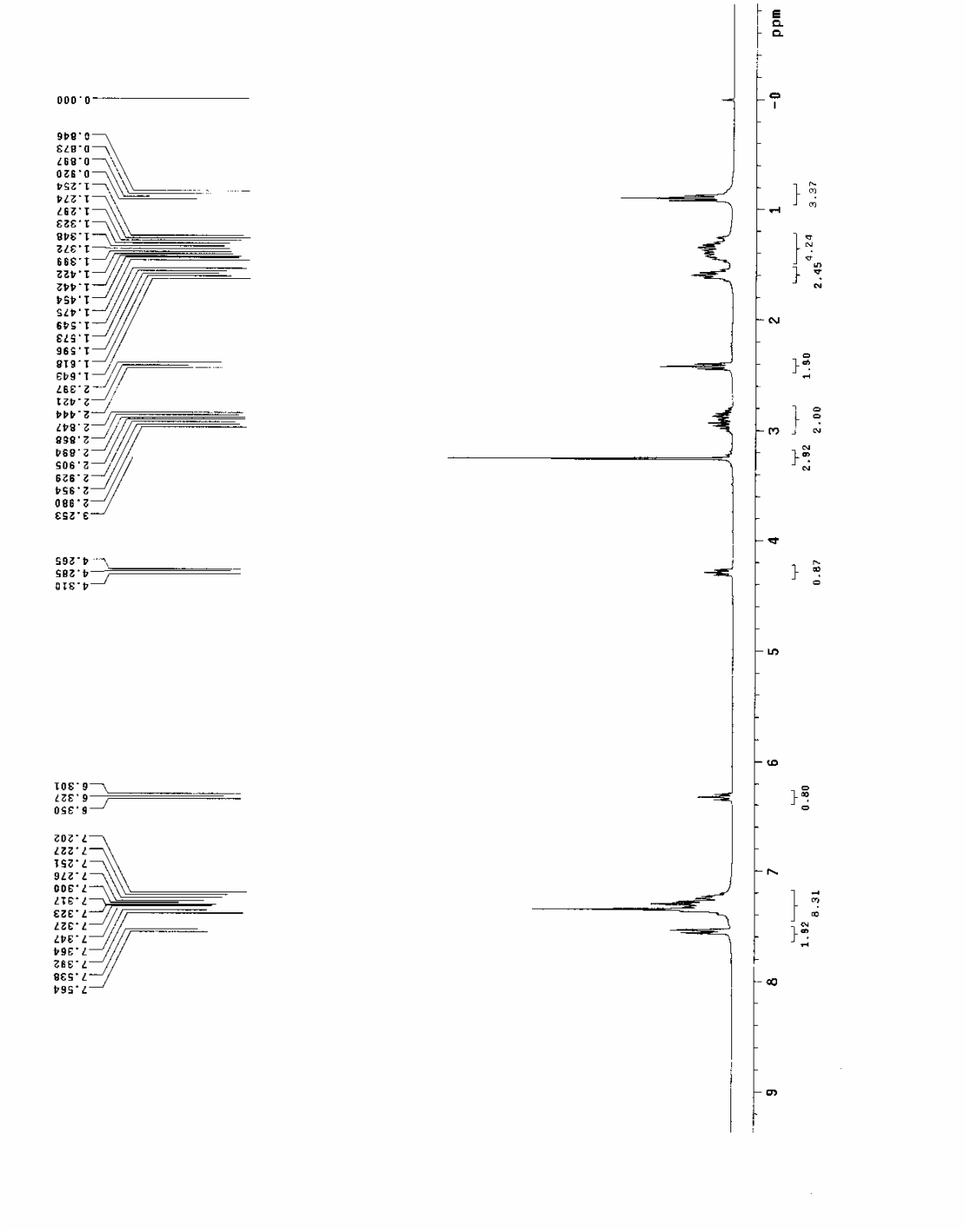

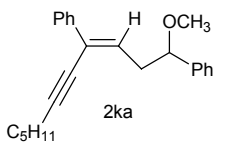

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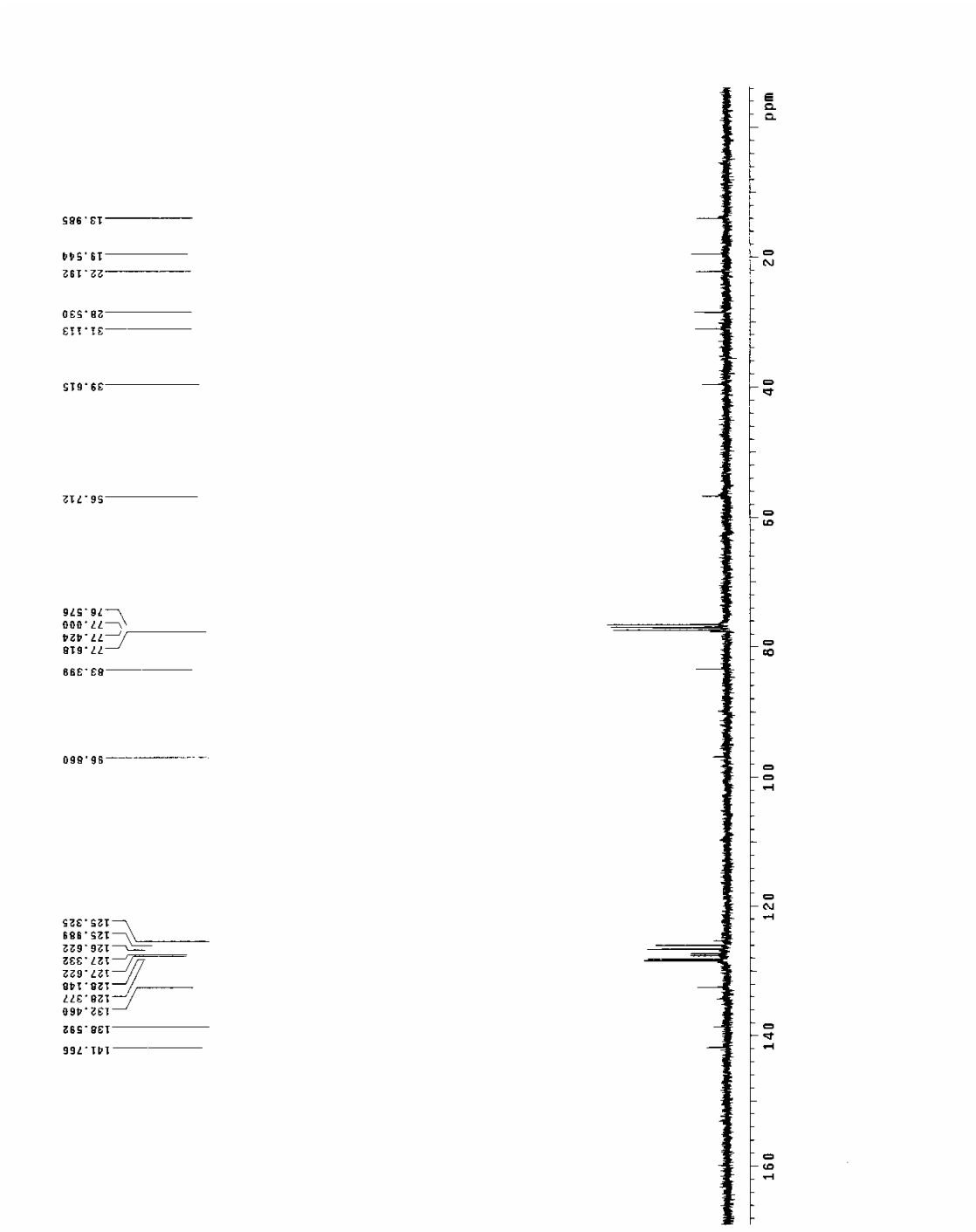

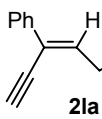

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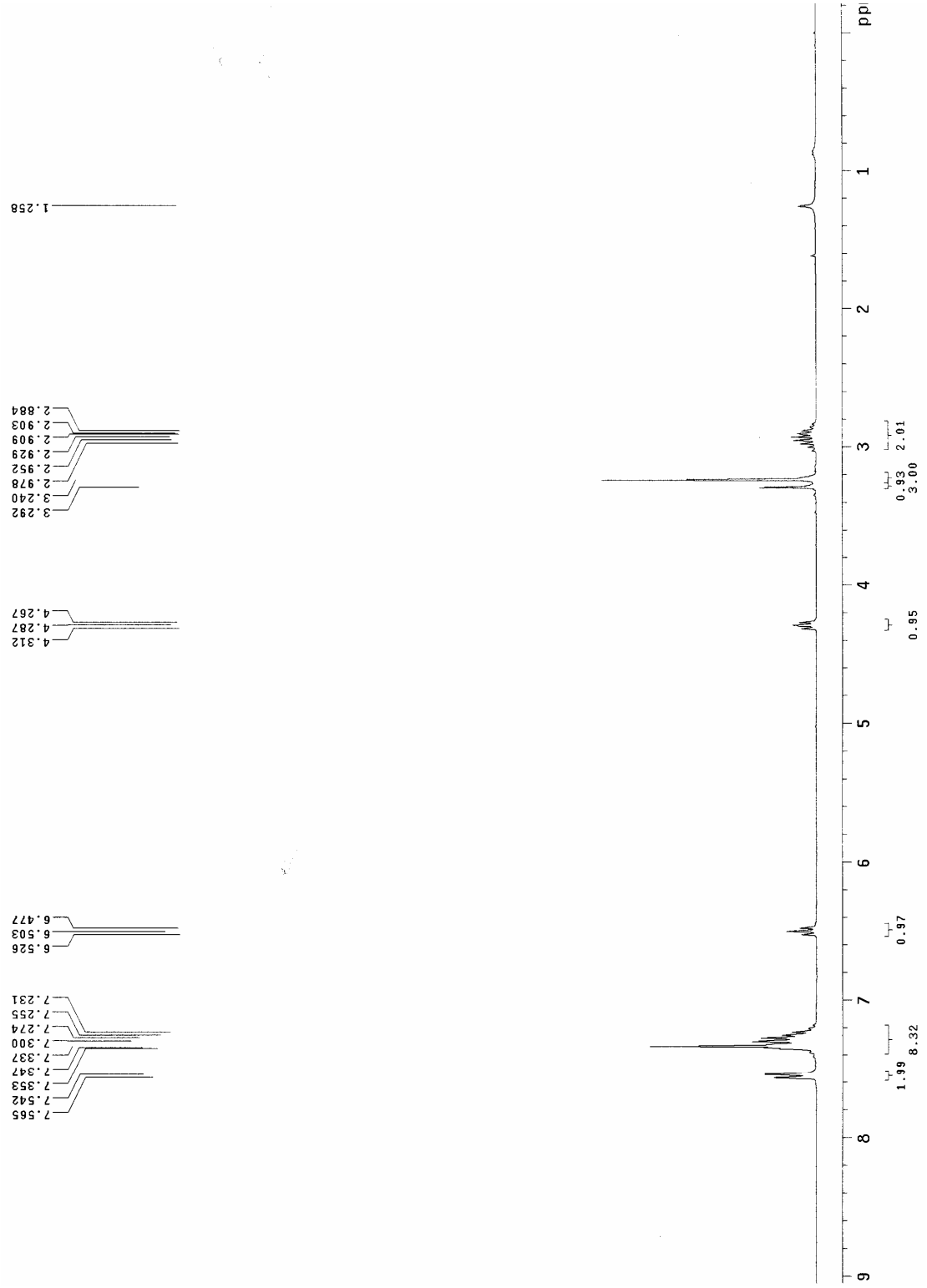

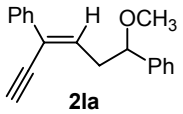

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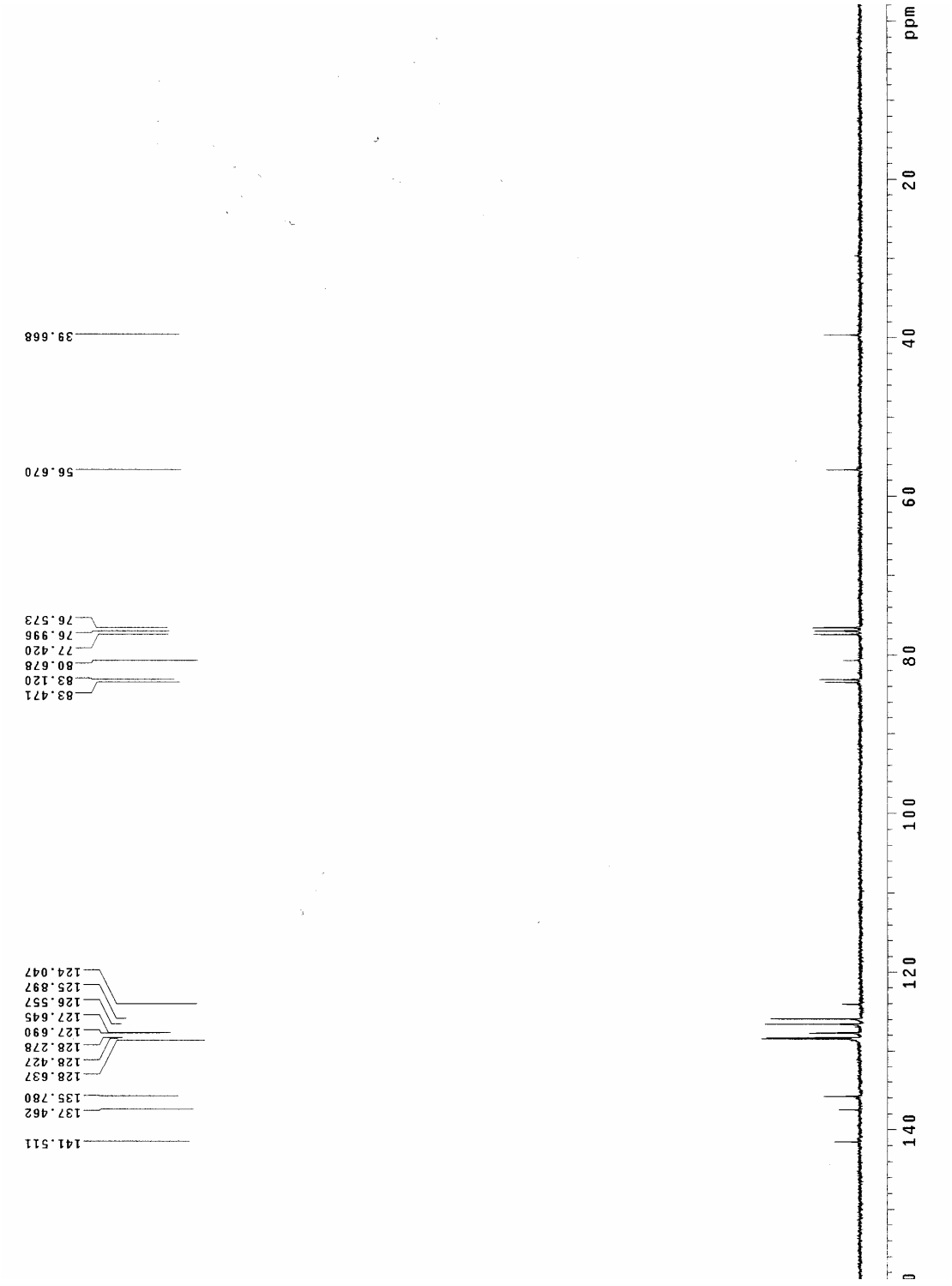

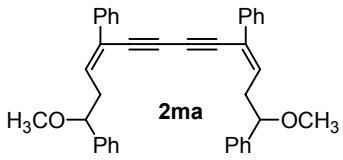

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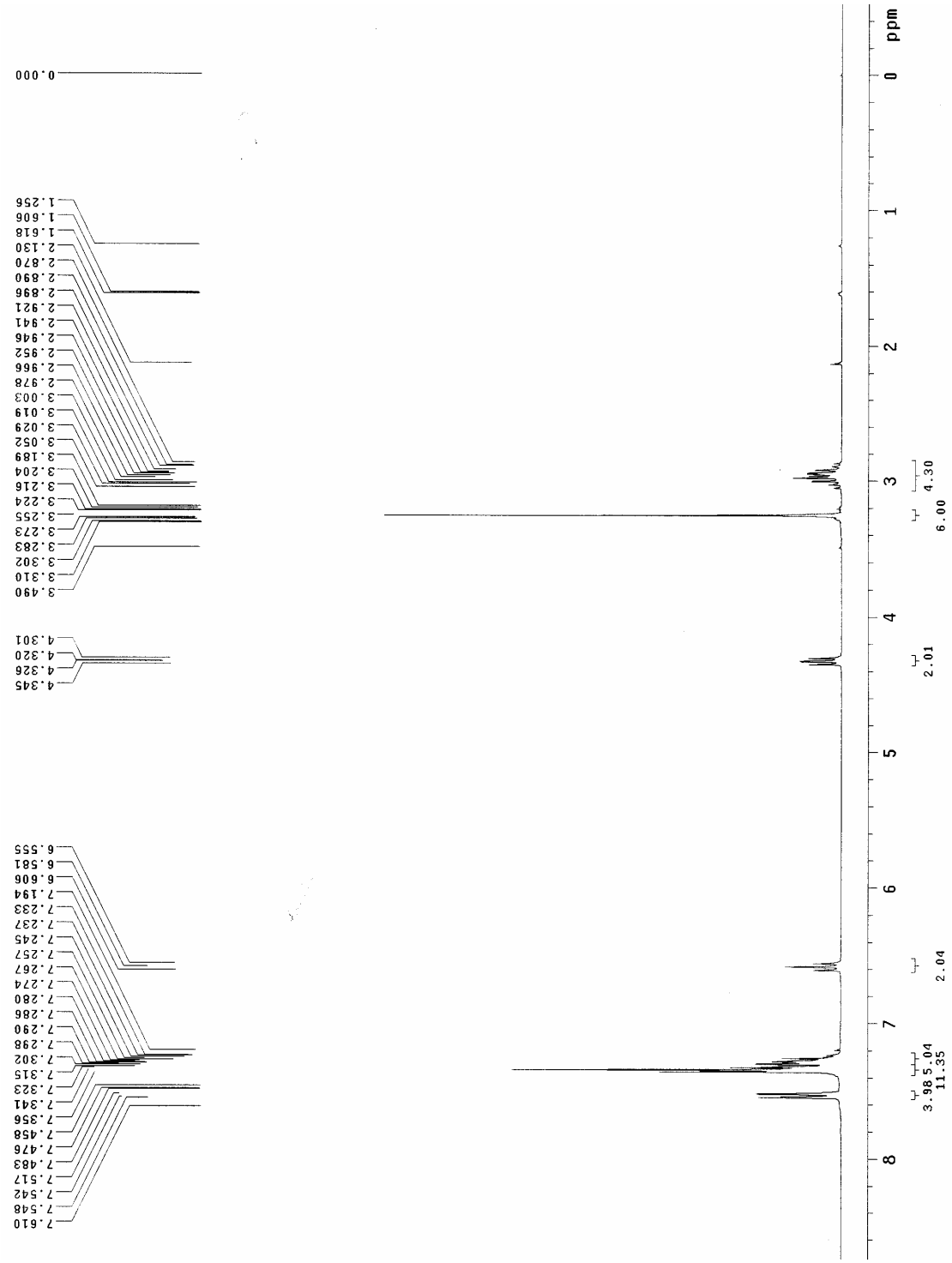

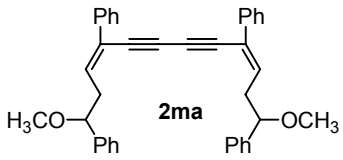

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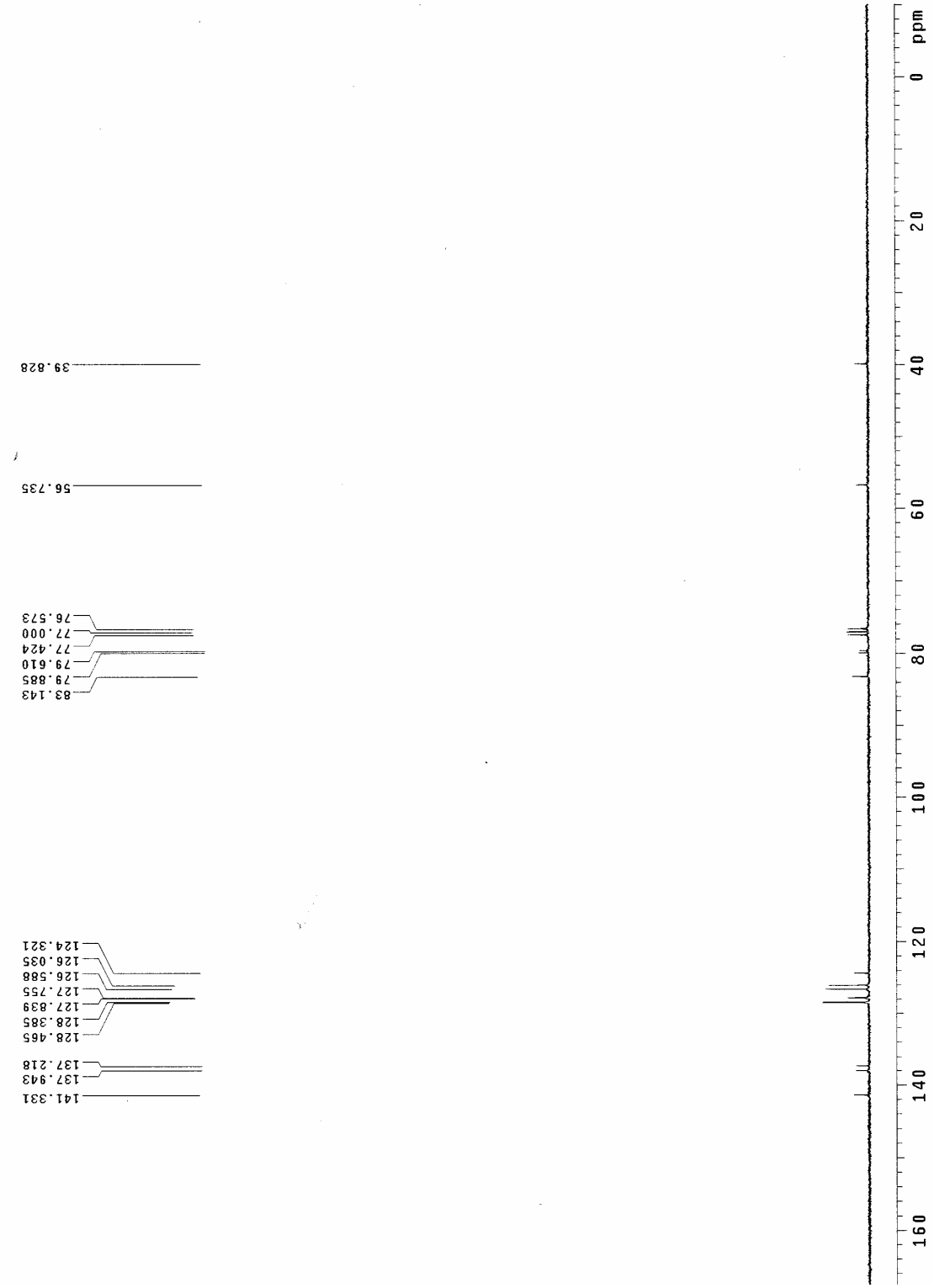

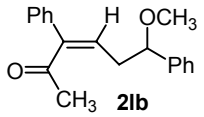

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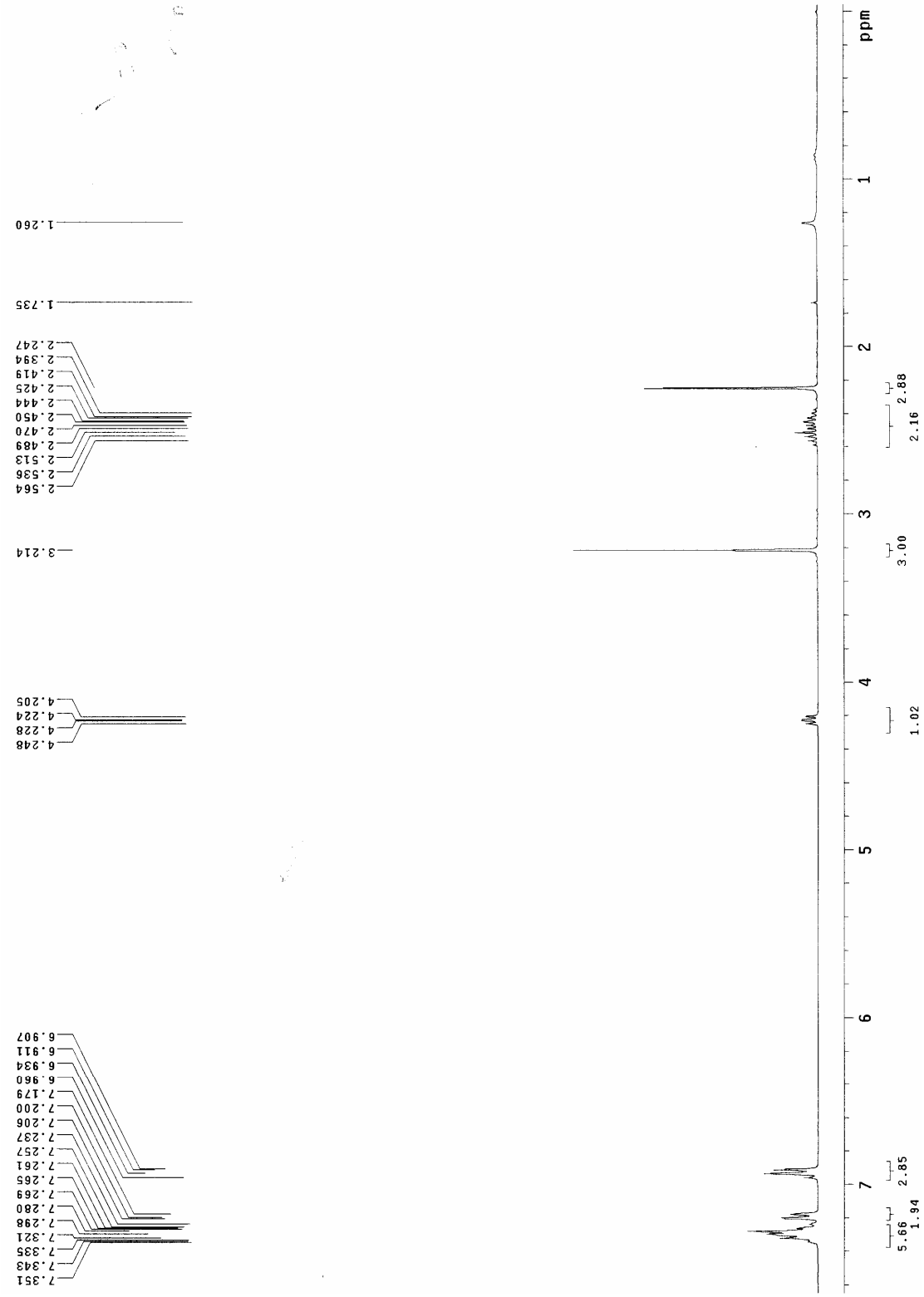

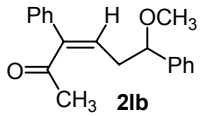

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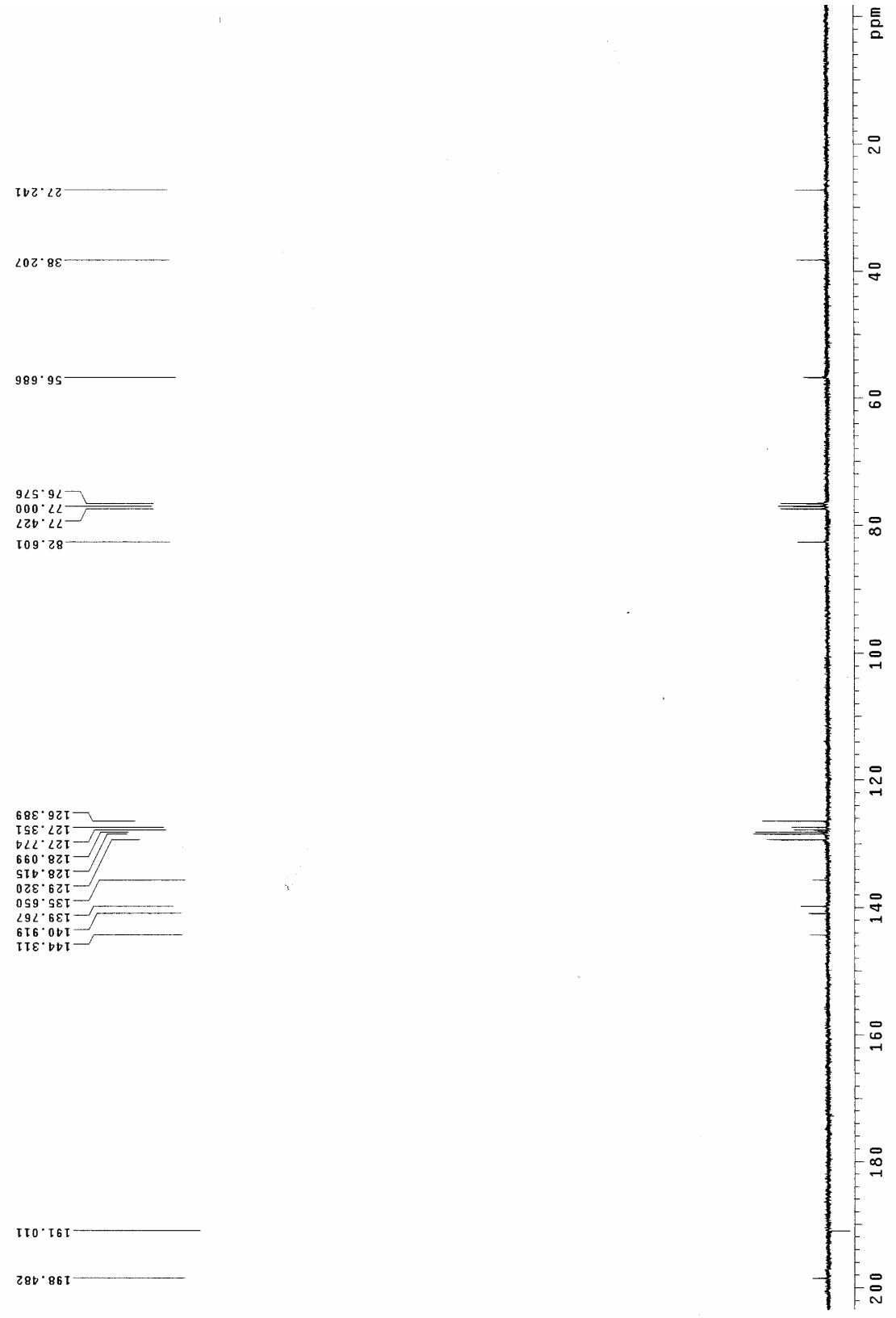
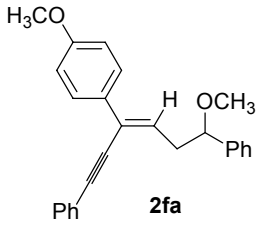


The NOE spectra of compound 2fa:



2fa