Supporting Information

Allylation of Carbon Pronucleophiles with Alkynes in the Presence of Palladium/Acetic Acid Catalyst

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Contents of Supporting Information

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General

Spectroscopic measurements were carried out with the following instruments: JEOL LA-300 (^{1}H and ^{13}C NMR), SHIMAZU FTIR-8200A (IR), HITACHI M-2500S (HRMS). Dehydrated 1,4-dioxane and all other solvents were purchased from Wako Pure Chemical Inc. For experimental details, characterization data of compounds **14**-**17**, **19**, **20**, **31**, **32**, **34**, **35**, **37**, **39** and **40**, see ref 5a in text. Structure of **41**,[1] **42**,[2] **43**,[3] **44**,[4] **45**,[5] **46**[5] were confirmed by comparison with published spectral data.

Typical Procedure for the allylation of diethyl malonate (8) with 1-phenyl-1-propyne (13). To a mixture of 1-phenyl-1-propyne **13** (0.20 g, 1.72 mmol), diethyl malonate **8** (0.33 g, 2.07 mmol), $Pd(PPh_3)_4$ (0.099 g, 0.086 mmol) in dry 1,4-dioxane (5 mL) was added acetic acid (0.010 g, 0.17 mmol), and the mixture was stirred for 12h at 100 °C. The reaction mixture was then filtered through a short silica gel column using ether as an eluent, and the filtrate was concentrated. The residue was purified by a silica gel column chromatography (hexane/AcOEt, 4:1) to give **43** (0.44 g, 92%).

(E)-(3-phenyl-prop-2-enyl)malononitrile (41): solid, mp = 55-56 °C, IR (KBr) 3690, 2995, 2943, 2228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.40-7.20 (m, 5H), 6.72 (d, J = 15.3 Hz, 1H), 6.19 (dt, J = 15.3, 7.1 Hz, 1H), 3.84 (t, J = 7.7 Hz, 1H), 2.92 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) *d* 137.3, 135.5, 135.1, 128.8, 128.6, 126.7, 119.7, 34.3, 23.4; Anal calcd for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.25; H, 5.63; N, 15.07

(E)-bis-(3-phenyl-prop-2-enyl)malononitrile (42): solid, mp = 115-116 °C, IR (KBr) 3686, 3019, 2930, 2230 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.48-7.25 (m, 10H), 6.71 (d, J = 15.7 Hz, 2H), 6.26 (dt, J = 15.7, 7.7 Hz), 2.90 (dd, J = 7.7, 1.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 138.0, 135.7, 128.7, 128.6, 126.7, 119.0, 115.0, 40.4, 37.9; Anal calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found C, 84.59; H, 6.02; N, 9.41.

2-(3-Phenyl-allyl)-malonic acid diethyl ester (43): oil; IR (KBr) 3029, 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.18-7.32 (m, 5H), 6.46 (d, J = 15.9 Hz, 1H), 6.14 (ddd, 15.9, 7.8, 7.8 Hz, 1H), 4.18 (2q, J = 7.3 Hz, 4H), 3.47 (t, J = 7.5 Hz, 1H), 2.78 (t, J = 7.5 Hz, 2H), 1.24 (2t, J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 168.6, 136.9, 132.6, 128.4, 128.3, 127.9, 127.2, 126.0, 125.4, 61.4, 51.9, 32.2, 14.09; HRMS (EI) Calcd for $C_{16}H_{20}O_4$: (M^+) 276.1356, found 276.1356.

2-Benzoyl-5-phenyl-pent-4-enoic acid ethyl ester (44): oil; IR (KBr) 3061, 1735, 1686 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.96 (d, J = 12 Hz, 2H), 7.12-7.56 (m, 8H), 6.42 (d, J = 15.5 Hz, 1H), 6.18 (ddd, J = 15.5, 8.0, 8.0 Hz, 1H), 4.41 (t, J = 8.0 Hz, 1H), 4.11 (q, J = 7.5 Hz, 2H), 2.86 (m, 2H), 1.12 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 194.1, 169. 1, 136.8, 136.0, 133.3, 132.4, 128.5, 128.4, 128.4, 128.3, 128.0, 127.1, 125.9, 125.9, 61.33, 54.2, 32.3, 14.0; HRMS (EI) Calcd for $C_{20}H_{20}O_3$: (M^+) 308.1407, found 308.1407.

1,3-Diphenyl-2-(3-phenyl-allyl)-propane-1,3-dione (45): Solid, mp 72-74 °C; IR (KBr) 3085, 1690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.99 (d, J = 8 Hz, 4H), 7.11-7.72 (m, 11H), 6.48 (d, J = 16.0 Hz, 1H), 6.26 (ddd, J = 16.0, 8.0, 8.0 Hz, 1H), 5.37 (t, J = 8.0 Hz, 1H), 3.04 (t, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 195.3, 136.8, 135.8, 133.4, 132.3, 128.8, 128.4, 128.3, 127.2, 126.6, 126.0, 57.0, 33.0; HRMS (EI) Calcd for $C_{24}H_{20}O_2$: (M^+) 340.1458, found 340.1455.

2-Benzenesulfonyl-1,5-diphenyl-pent-4-en-1-one (46): Solid, mp 116-117 °C; IR (KBr) 3061, 1686, 1596 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.91 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.12-7.67 (m, 11H), 6.39 (d, J = 16.0 Hz, 1H), 5.91 (ddd, J = 16.0, 7.5, 7.5 Hz,

1H), 5.18 (dd, J = 12.0, 4.0 Hz, 1H), 2.89-3.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 191.6, 136.7, 136.3, 136.2, 134.1, 133.9, 133.8, 129.5, 128.7, 128.5, 128.2, 127.4, 125.9, 122.8, 69.3, 31.5; HRMS (EI) Calcd for $C_{23}H_{20}O_3S$: (M^+) 376.1128, found (M-SO_2Ph) 235.1117.

(1-Acetyl-4-phenyl-but-3-enyl)-phosphonic acid dimethyl ester (47): oil; 3045, 1742 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.13-7.26 (m, 5H), 6.38 (d, J = 16.0 Hz, 1H), 6.01 (ddd, J = 16.0, 8.0, 8.0 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.21-3.33 (m, 1H), 2.81-2.85 (m, 1H), 2.61-2.66 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 202.4, 136.5, 132.2, 131.7, 131.6, 128.2, 128.1, 127.7, 127.1, 125.8, 125.8, 125.7, 125.6, 53.2, 52.0, 31.3, 29.6; HRMS (EI) Calcd for $C_{14}H_{19}O_4P$: (M^+) 282.1015, found 282.1015.

[1-Acetyl-4-phenyl-1-(3-phenyl-allyl)-but-2-enyl]-phosphonic acid dimethyl ester (48): oil; IR 3050, 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.18-7.35 (m, 10H), 6.46 (d, J = 16.0 Hz, 2H), 6.18 (ddd, J = 16.0, 7.8, 7.8 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 2.86 (dd, J = 16.0, 7.8 Hz, 4H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 204.6, 136.9, 133.8, 128.4, 127.3, 126.0, 124.4, 124.3, 77.3, 76.7, 53.4, 34.8, 28.5; HRMS (EI) Calcd for $C_{23}H_{27}O_4P$: (M^+) 398.1601, found (M+H) 399.1602.

5-Ethoxycarbonyl-hex-2-enedioic acid diethyl ester (50): oil; IR (neat) 3065, 1735, 1710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 6.85 (ddd, J = 12.9, 7.5, 7.5 Hz, 1H), 5.85 (d, J = 12.9 Hz, 1H), 4.18 (3q, J = ~7.3 Hz, 6H), 3.45 (t, J = 7.5 Hz, 1H), 2.77 (t, J = 7.5 Hz, 2H), 1.25 (3t, J = ~7.3 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 167.9, 165.6, 143.5, 123.6, 61.5, 60.1, 50.5, 30.9, 14.1, 13.9; HRMS (EI) Calcd for $C_{13}H_{20}O_6$: (M^+) 272.1254, found (M+H) 273.1333.

5-Benzoyl-hex-2-enedioic acid diethyl ester (51): oil; IR (neat) 3089, 1735, 1711, 1690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.98 (d, J = 8.0 Hz, 2H), 7.50-7.59 (m, 1H), 7.44-7.49 (m, 2H), 6.89 (ddd, J = 12.7, 7.5, 7.5 Hz, 1H), 5.88 (d, J = 12.7 Hz, 1H), 4.42 (t, J = 8.0 Hz, 1H), 4.14 (2q, J = 7.3 Hz, 4H), 2.88 (m, 2H), 1.25 (t, J = 7.3 Hz, 3H), 1.15 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 190.3, 168.5, 165.8, 144.1, 135.6, 133.9, 128.5, 123.6, 61.7, 60.2, 52.8, 31.08, 14.2, 13.9; HRMS (EI) Calcd for $C_{17}H_{20}O_5$: (M^+) 304.1305, found (M+H) 305.1384.

5-Benzenesulfonyl-6-oxo-6-phenyl-hex-2-enoic acid ethyl ester (52): oil; IR (neat) 2931, 1710, 1690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.89 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.41-7.73 (m, 6H), 6.65 (ddd, J = 12.8, 7.9, 7.9 Hz, 1H), 5.78 (d, J = 12.8 Hz, 1H), 5.15 (t, J = 8.0 Hz, 1H), 4.07 (q, 7.3 Hz, 2H), 2.95 (dd, J = 8.0, 7.9 Hz, 2H), 1.19 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 190.6, 165.2, 141.2, 136.3, 135.9, 134.3, 134.0, 129.4, 128.9, 128.8, 128.6, 124.8, 124.8, 68.1, 60.3, 30.2, 14.0; HRMS (EI) Calcd for $C_{20}H_{20}O_5S$: (M^+) 372.1026, found (M+H) 373.1104.

^{t}Butyl-3-phenyl-2-propynylcarbamate (53):[6] To a mixture of ^{t}Butyl 2-propynylcarbamate (0.2 g, 1.29 mmol), prepared by the usual Cbz protection of propargyl amine in quantitative yield, CuI (0.019 g, 0.10 mmol), $Pd(PPh_3)_4$ (0.029 g, 0.02 mmol), and diethylamine (0.5 mL) in ether (3 mL) was added iodobenzene (0.14 mL, 1.29 mmol), and the mixture was stirred for 2 h at 35 °C. The reaction mixture was diluted with ether, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/AcOEt, 3:1) to give **20** (0.28 g, 94 %): White solid, mp 98 °C; IR (neat) 3320, 1690, 1540 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.16-7.24 (m, 3H), 7.32-7.36 (m, 2H), 4.70 (bs, 1H), 4.09 (bs, 2H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 155.2, 131.5, 128.1, 128.0, 122.6, 85.4, 82.9, 79.8, 31.2, 28.3; HRMS (EI) Calcd for $C_{14}H_{17}O_2N$: (M^+) 231.1254, found (M-C_4H_8) 175.0628.

2-(1-tert-Butoxycarbonylamino-3-phenyl-allyl)-malonic acid diethyl ester (54): Solid, mp 65-67 °C; IR (neat) 3315, 1735, 1689 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.20-7.35 (m, 5H),

6.57 (d, J = 16.0 Hz, 1H), 6.20 (dd, J = 16.0, 7.9 Hz, 1H), 5.62-5.75 (bs, 1H), 4.91-5.02 (bs, 1H), 4.14-4.25 (m, 4H), 3.35 (bs, 1H), 1.45 (s, 9H), 1.24 (t, J = 7.6 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 167.7, 167.1, 136.1, 131.8, 128.3, 127.6, 126.5, 126.4, 79.5, 61.7, 61.3, 55.7, 28.3, 13.9; HRMS (EI) Calcd for $C_{21}H_{29}O_6N$: (M^+) 391.1989, found (M-C_4H_8) 335.1363.

References for supporting information

(1) Yamamoto, Y.; Al-Masum, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 6019-6020.
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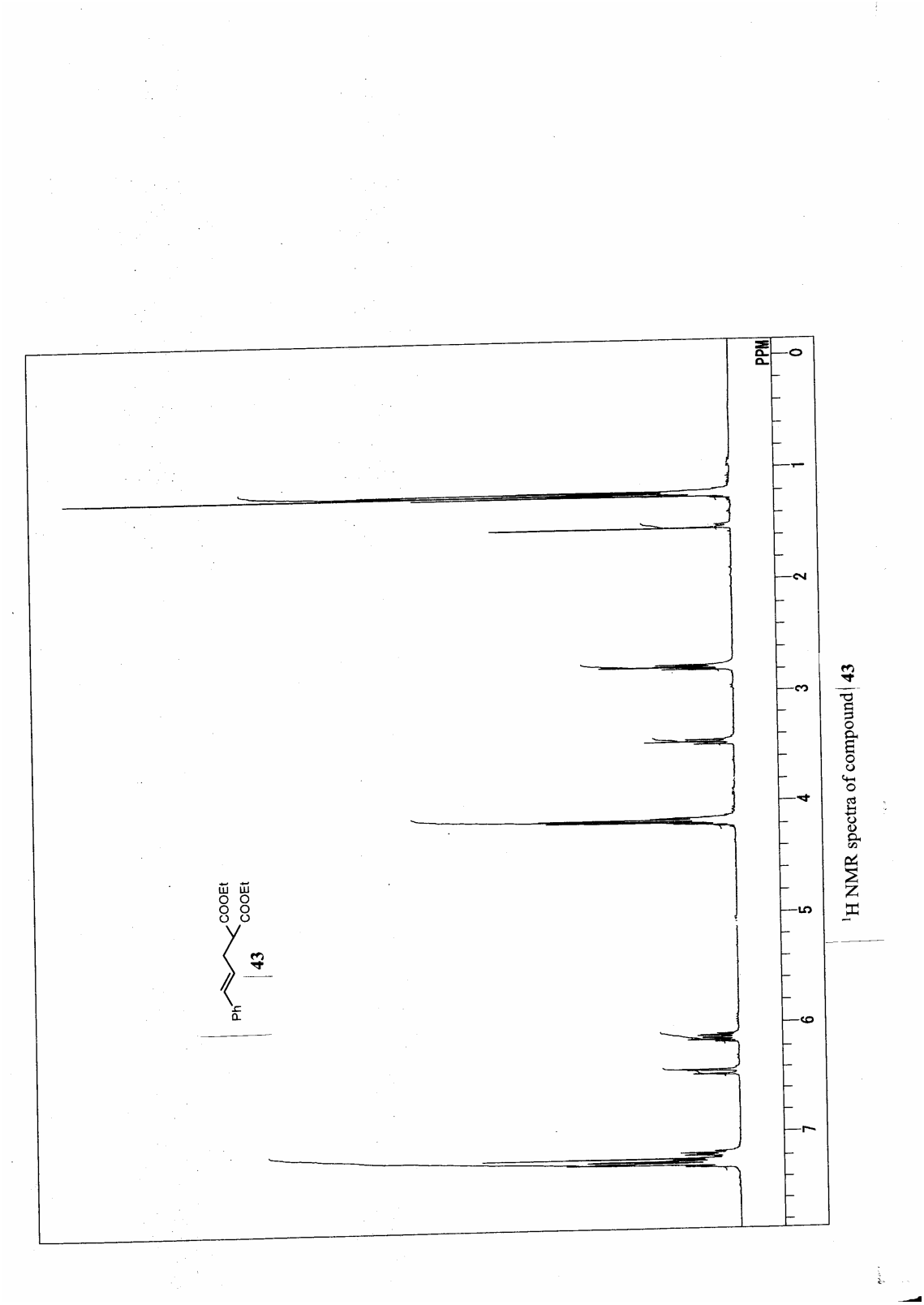
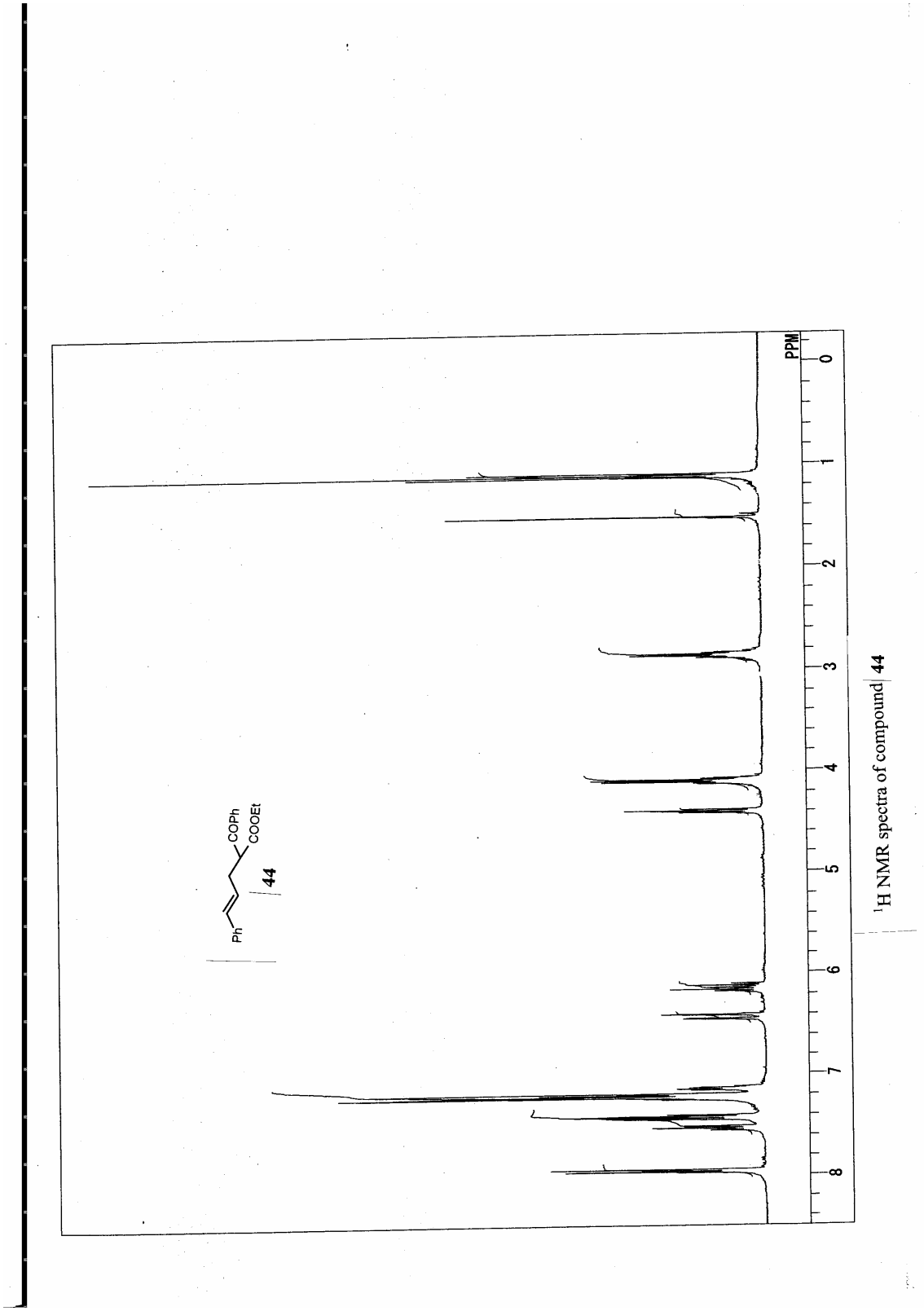
(6) Miller, K. M.; Huang, W-S.; Jamison, T. F. *J. Am. Chem. Soc.* **2003**, *125*, 3442-3443



^{1}H NMR spectra of compound **43**



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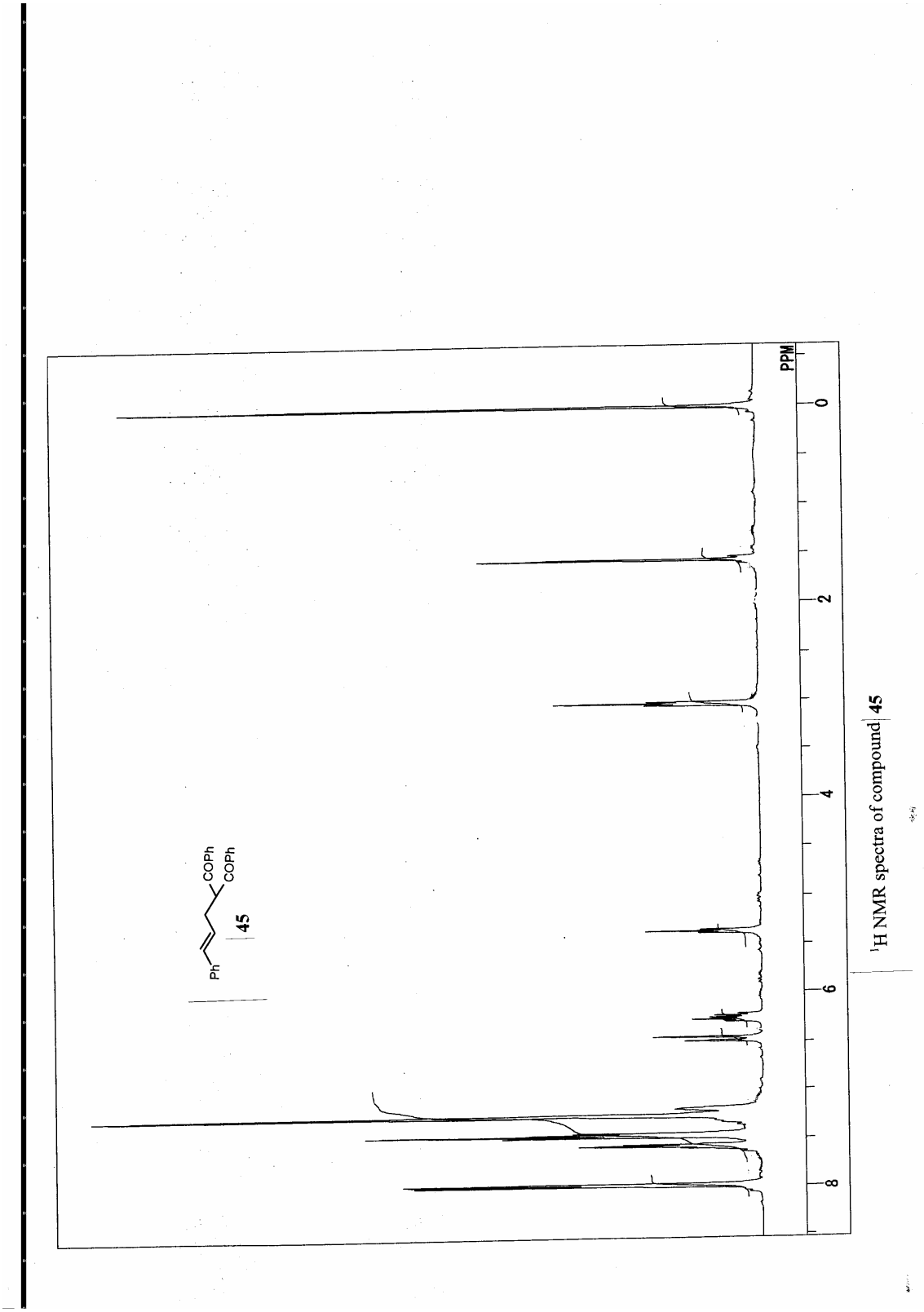

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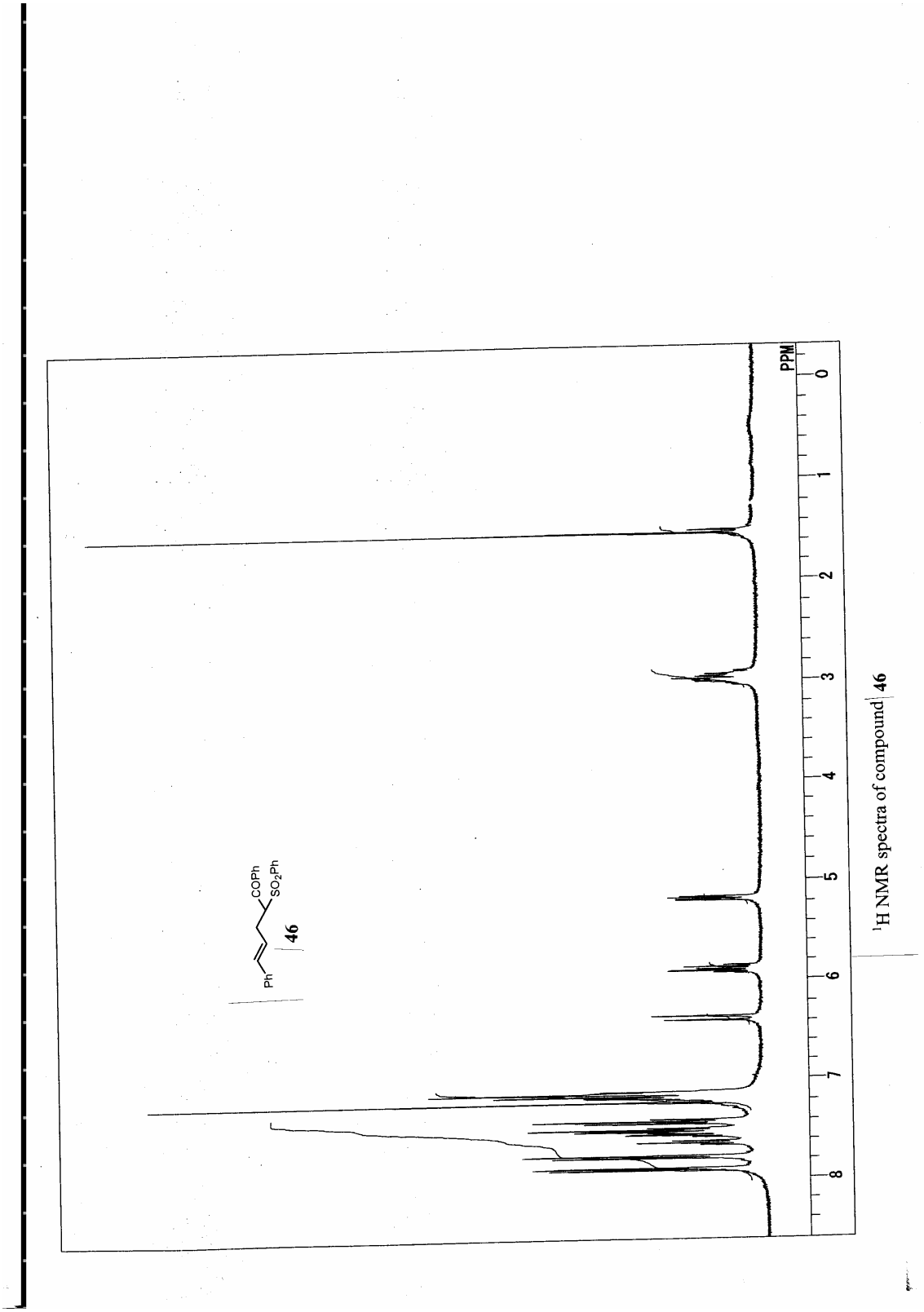

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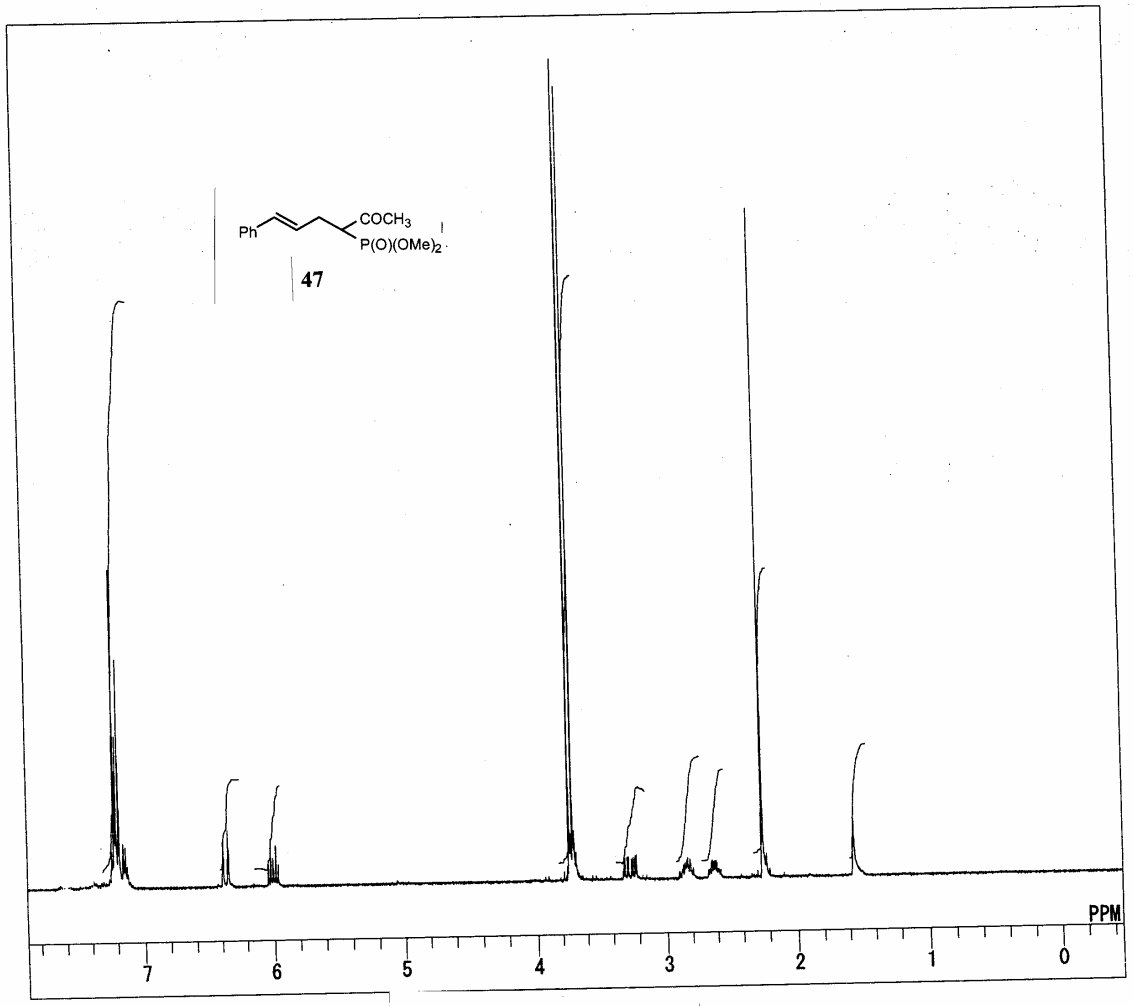

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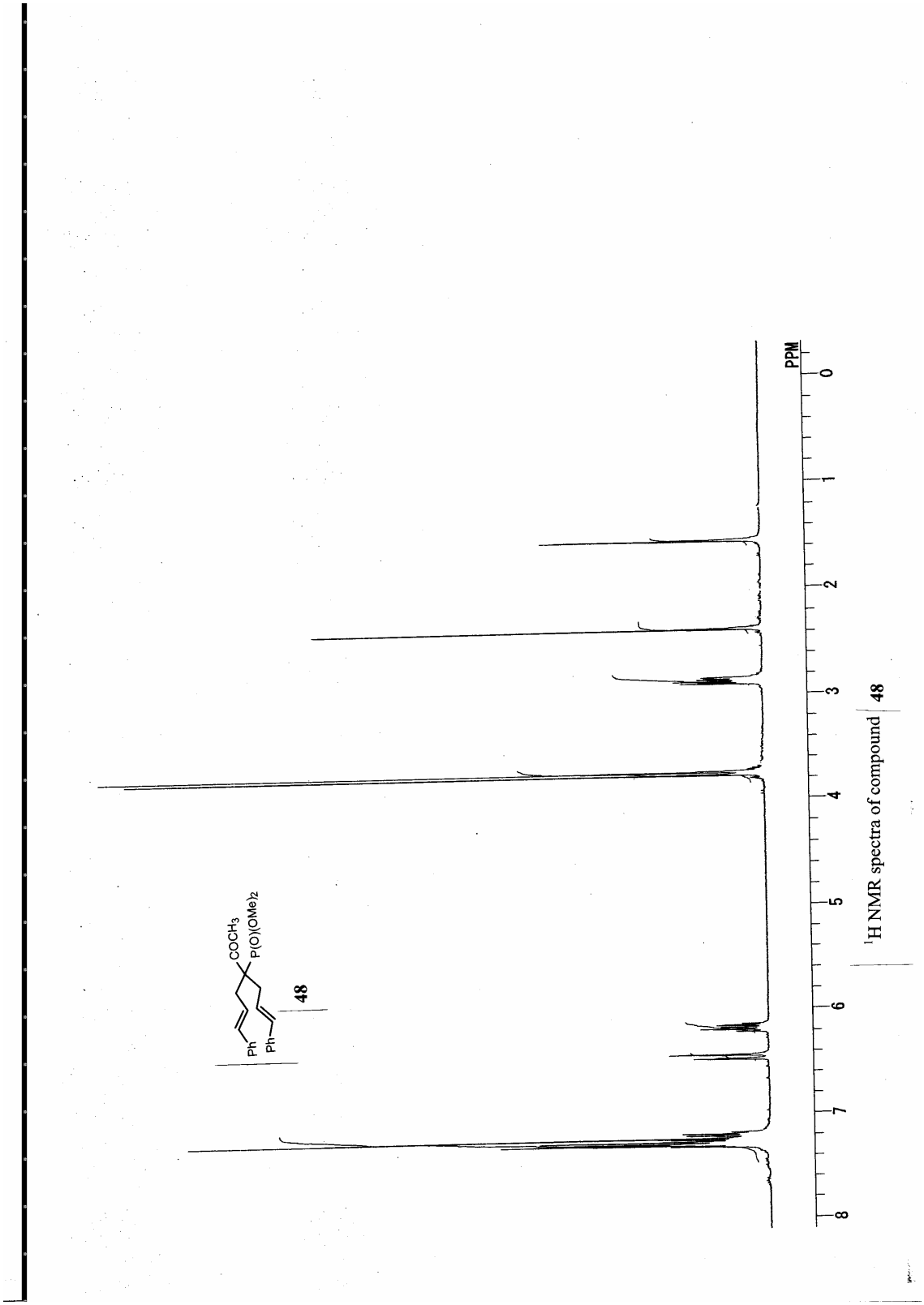

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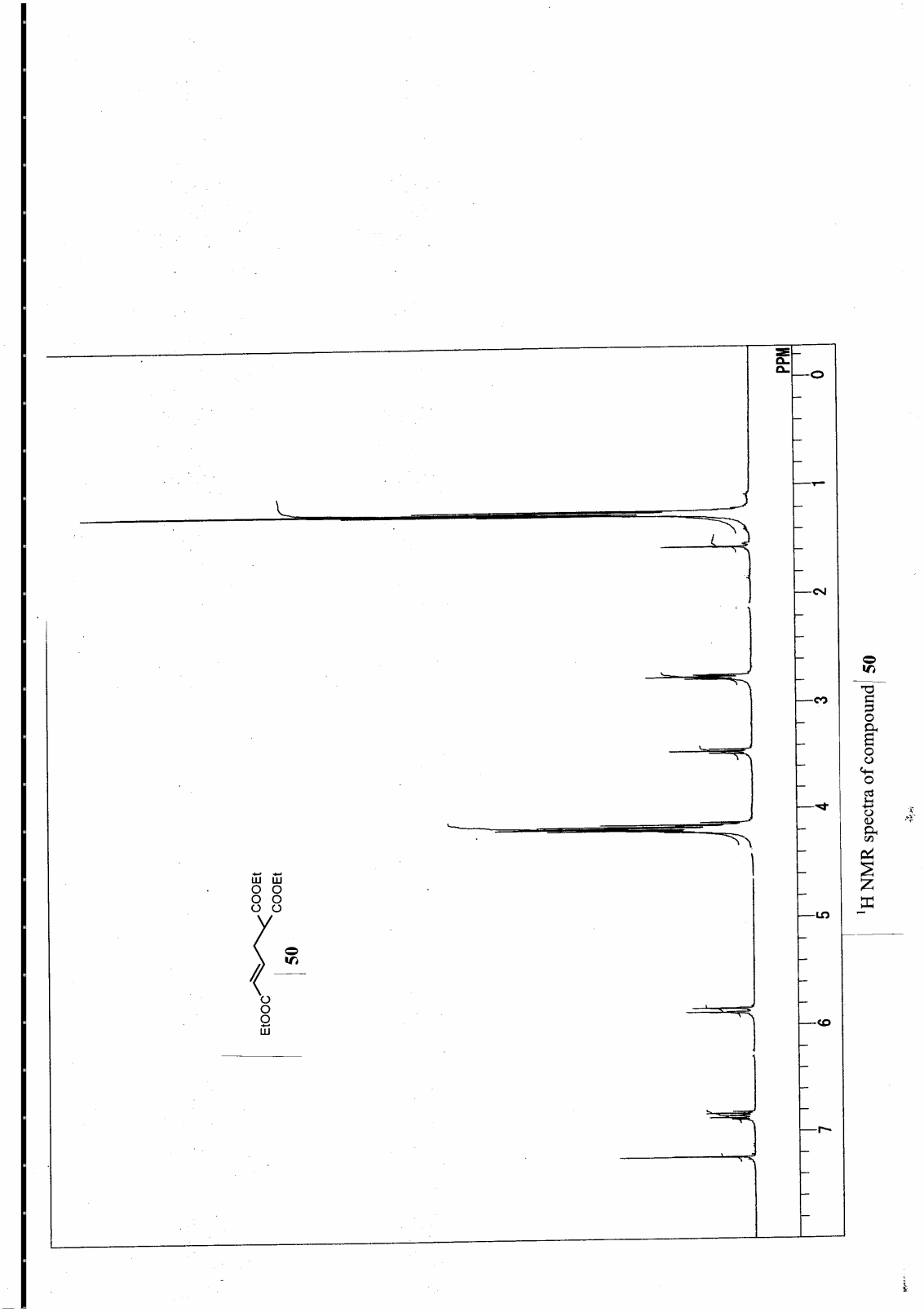

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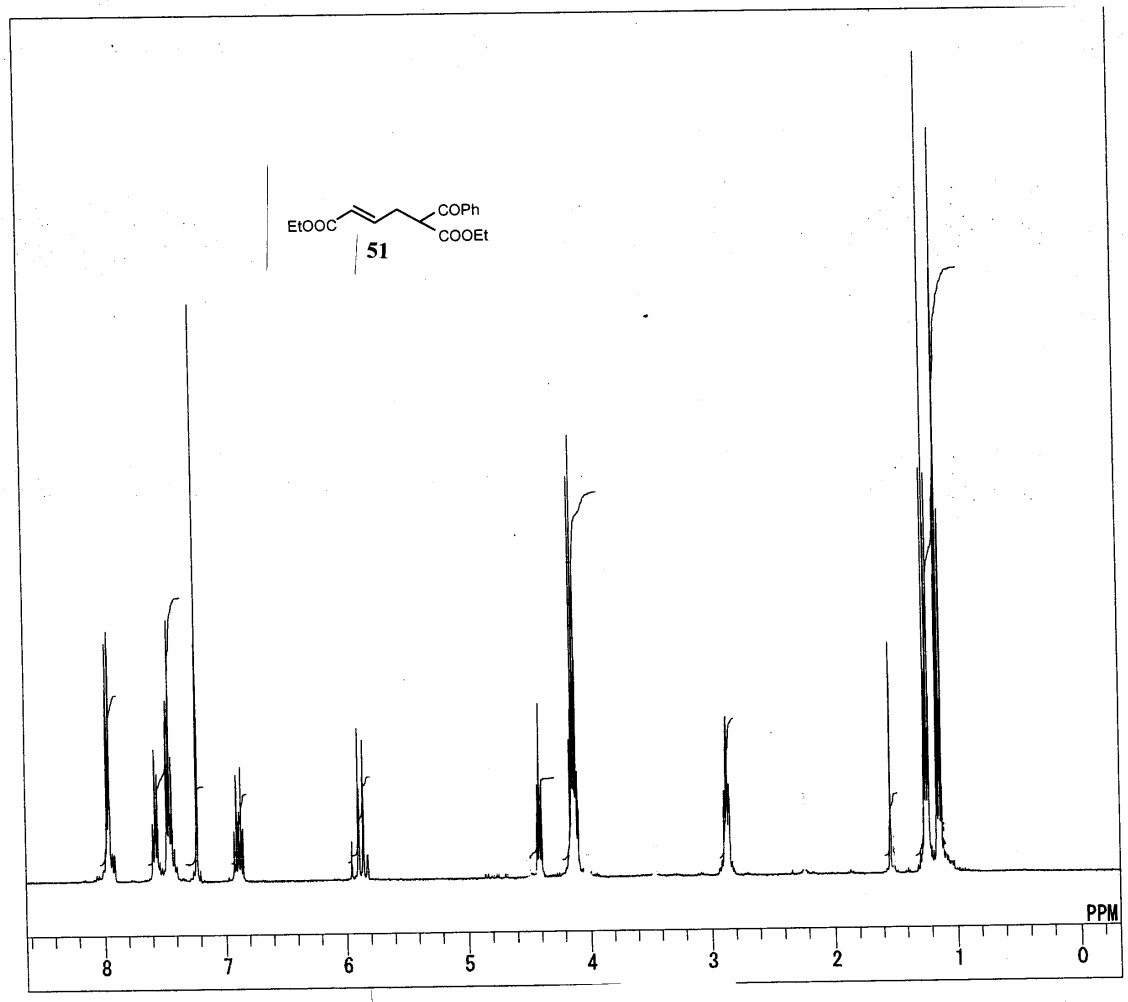

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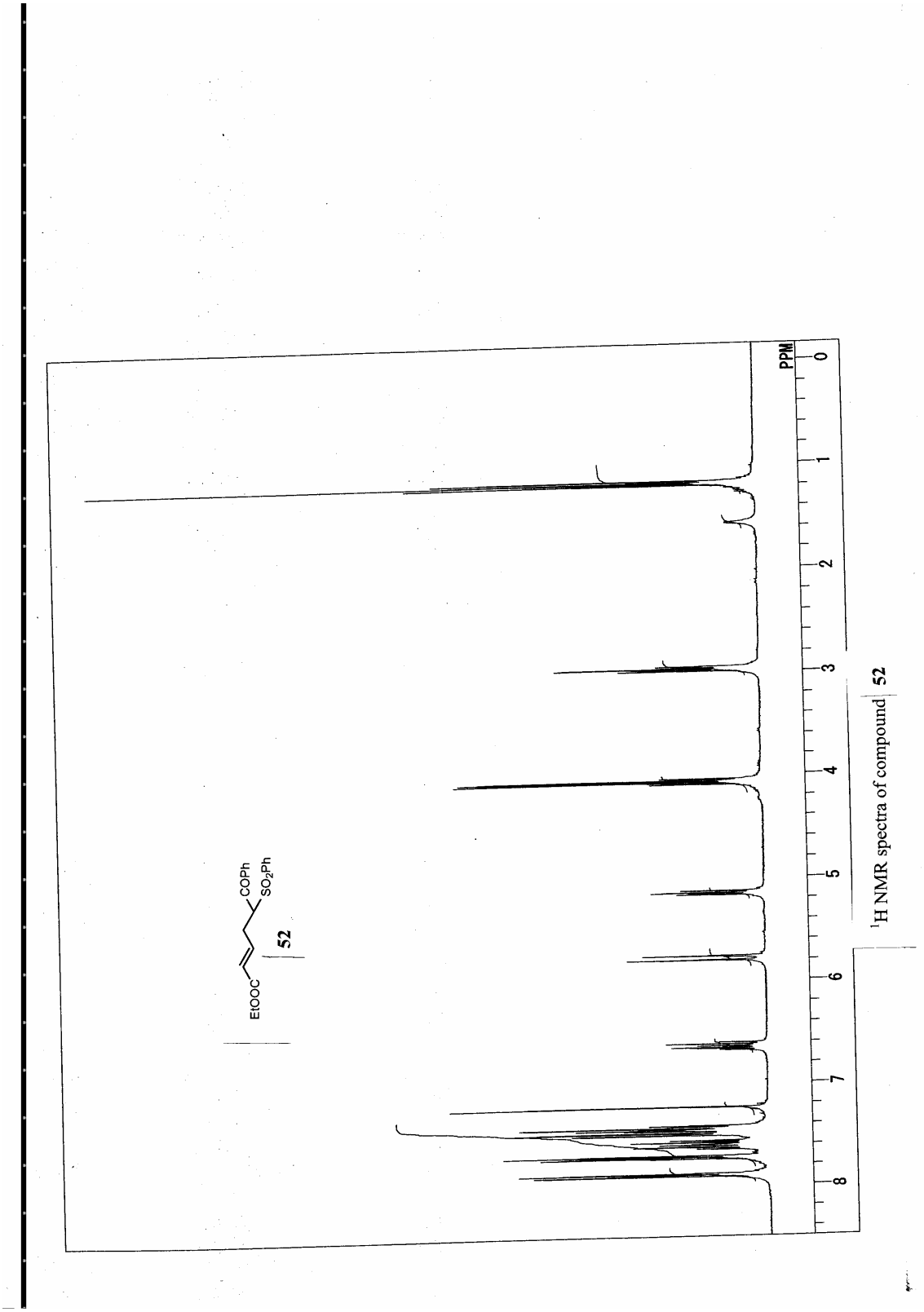

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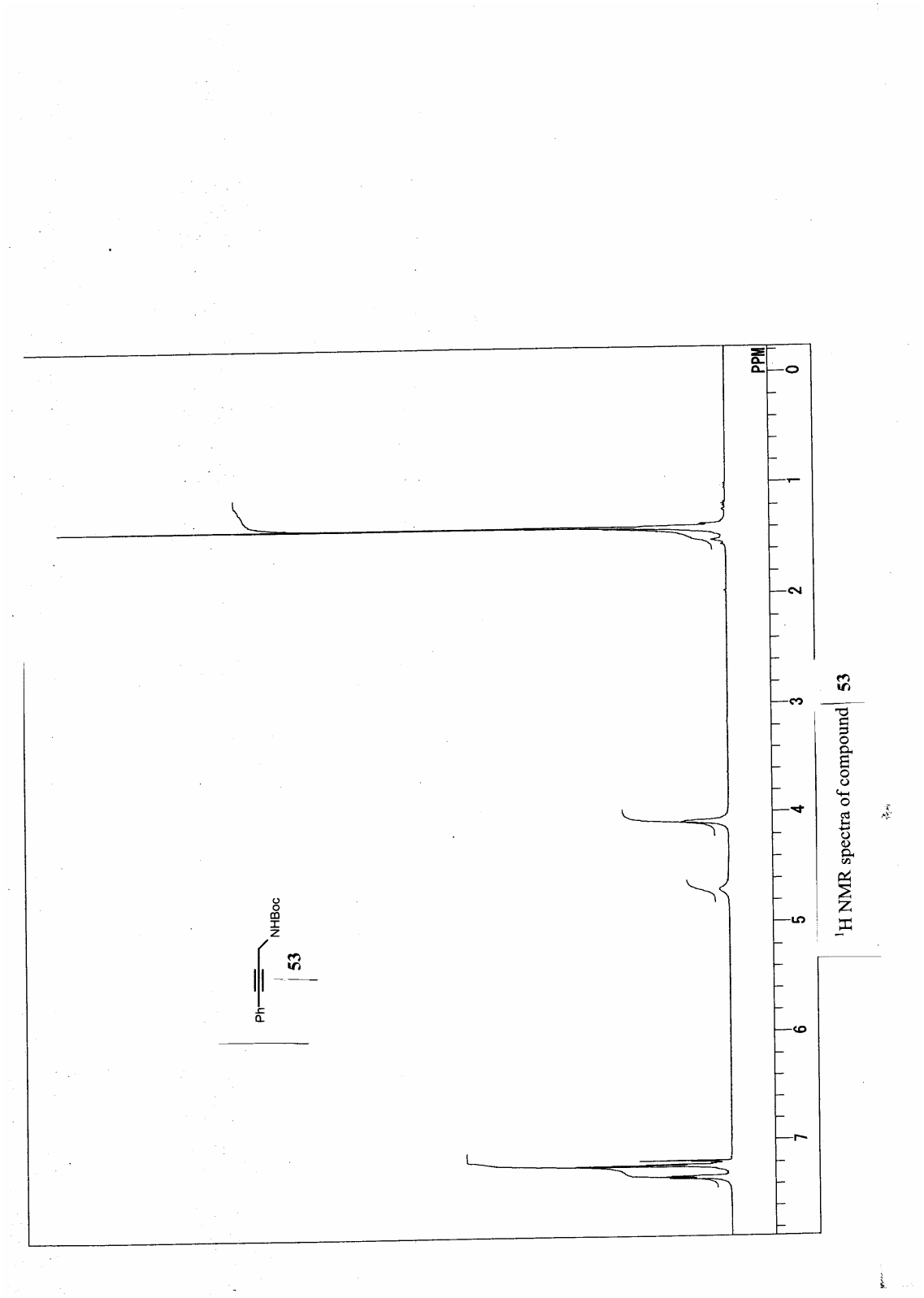

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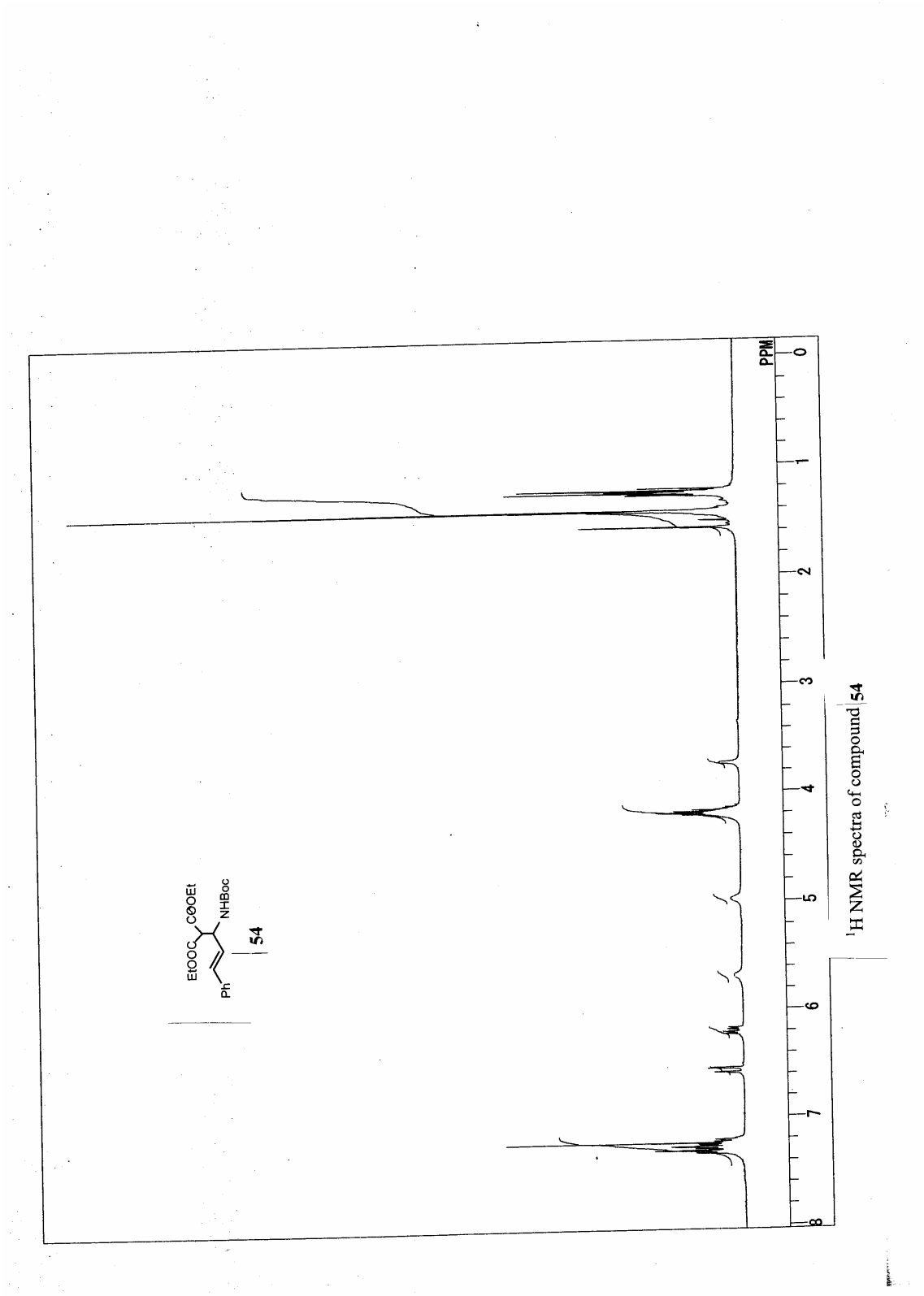

^{1}H NMR spectra of compound **54**