Regio- and Enantiospecific Rhodium-Catalyzed Arylation of Unsymmetrical Fluorinated Acyclic Allylic Carbonates: Inversion of Absolute Configuration

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Representative Experimental Procedures and Supplemental Data

General Information: Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Optical rotation was recorded on a Perkin Elmer Mode 1343 polarimeter. ^{1}H NMR spectra were recorded on a Varian VXR400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance ($CDCl_3$, 7.24 ppm) as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, br = broad, m = multiplet) and coupling constants (Hz), integration. ^{13}C NMR spectra were recorded on a Varian VXR400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance ($CDCl_3$, 77.0 ppm) as the internal standard. All ^{13}C NMR spectral data using the descriptors *o* and *e* refer to whether the peak is odd or even respectively, and correlate to an attached proton test (APT) experiment. ^{19}F NMR spectra were recorded on a Varian Gemini-2000 (282 MHz) spectrometer and chemical shifts are reported in ppm from trifluoroacetic acid resonance (-78.5 ppm) as the external standard. Mass spectra analyses were obtained using a Kratos MS-80 spectrometer using the ionization technique indicated. Analytical thin layer chromatography (TLC) was performed on Merck 25 TLC plastic sheets silica gel 60 F_{254}. Flash column chromatography was performed on silica gel (Sorbent technologies, Silica gel, 60 Å, 32-63 μ, standard grade).

All reactions were carried out under an argon (Ar) atmosphere in oven-dried glassware. All substrate were purified by column chromatography or distillation. $ZnBr_2$ and LiBr were dried at 100-200 °C under high-vaccum for 2 hours and stored in the glove box. Diethyl ether and dichloromethane were used from Grubbs' still solvent system.

Bis(ethylene)hydrotris(pyrazolyl)borate rhodium(I).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.0 Hz, 3H), 7.58 (d, *J* = 2.0 Hz, 3H), 6.18 (t, *J* = 2.0 Hz, 3H), 2.51 (bs, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (o), 134.8 (o), 104.8 (o), 48.7 (e; $J_{C\text{-}Rh}$ = 12.9 Hz).

General Method for Preparation of the Fluorinated Carbonates.[2] To a solution of carbonyldiimidazole (1.2 eq) in dichloromethane (*ca*. 1M) was added corresponding allylalcohol (1.0 eq) at room temperature and the resulting solution was allowed to stir for ≥3 hours. The yellow solution (or suspension) was partitioned between dichloromethane and water, and the organic phase washed with water (2x) to remove any residual imidazole. The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford a crude oil. The residue was re-dissolved into dichloromethane (*ca*. 1M) and treated with hexafluoro-2-propanol (>2 eq.) and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine at room temperature for *ca*. 12 hours (t.l.c. control). Purification by flash chromatography (eluting with a 100/0-10/1 pentane/dichloromethane gradient) furnished the allyl carbonates **1a-i** (~60% yield) as a colorless oil.

1-(2-Phenylethyl)prop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 5.82 (ddd, *J* = 17.4, 10.4, 6.8 Hz, 1H), 5.54 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 5.10 (brq, *J* = 6.8 Hz, 1H), 2.74-2.62 (m, 2H), 2.10 (dddd, *J* = 14.0, 8.8, 7.6, 6.4 Hz, 1H), 1.97 (dddd, *J* = 10.0, 8.8, 6.8, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (e), 140.4 (e), 134.3 (o), 128.6 (o), 128.3 (o), 126.3 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 280.1 Hz), 119.2 (e), 81.5 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 35.5 (e), 31.0 (e); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.3 (m, 6F); IR (liquid film) 3030 (w), 2972 (w), 1776 (vs), 1650 (w), 1605 (w), 1498 (m), 1456 (m), 1386 (s), 1364 (s), 1302 (vs), 1262 (vs), 1202 (vs), 1140 (s), 1112 (s), 1008 (s), 937 (s), 909 (s), 781 (m), 754 (m), 700 (s), 690 (s) cm^{-1}.

1-Methylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.53 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.25 (brquin, *J* = 6.4 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 1.43 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (e), 135.6 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 280.8 Hz), 117.9

(e), 78.5 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 19.7 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.4 (s, 6F); IR (liquid film) 2991 (m), 1775 (vs), 1651 (w), 1455 (w), 1386 (s), 1364 (s), 1303 (vs), 1263 (vs), 1203 (vs), 1141(s), 1114 (vs), 1041 (s), 1007 (m), 909 (s), 782 (m), 756 (m), 690 (m) cm^{-1}.

1-Nonylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd, *J* = 17.2, 10.8, 6.8 Hz, 1H), 5.31 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.31 (dt, *J* = 17.2, 1.0 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.10 (brq, *J* = 6.8 Hz, 1H), 1.79-1.60 (m, 1H), 1.64 (tt, *J* = 8.4, 6.4 Hz, 1H), 1.38-1.20 (brm, 14H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (e), 134.7 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 281.6 Hz), 118.7 (e), 82.5 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 34.0 (e), 31.9 (e), 29.5 (e), 29.4 (e), 29.3 (e), 29.2 (e), 24.8 (e), 22.7 (e), 14.0 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.3 (d, *J* = 6.0 Hz, 6F); IR (liquid film) 2929 (s), 2859 (s), 1776 (vs), 1650 (w), 1469 (m), 1386 (s), 1363 (s), 1303 (vs), 1262 (vs), 1202 (vs), 1140 (s), 1113 (vs), 1011 (m), 935 (s), 908 (s), 781 (m), 756 (w), 689 (m) cm^{-1}.

1-Isopropylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.54 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.90 (t, *J* = 6.8 Hz, 1H), 1.96 (octet, *J* = 6.8 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (e), 132.9 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 280.8 Hz), 119.6 (e), 87.0 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 31.8 (o), 17.8 (o), 17.7 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.4 (s, 6F); IR (liquid film) 2975 (s), 1776 (vs), 1650 (w), 1473 (m), 1387 (s), 1364 (s), 1304 (vs), 1260 (vs), 1203 (vs), 1139 (s), 1114 (vs), 1012 (s), 939 (vs), 908 (s), 781 (m), 753 (m), 689 (s) cm^{-1}.

1-Cyclohexylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.6, 10.4, 7.6 Hz, 1H), 5.53 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.89 (t, *J* = 7.2 Hz, 1H), 1.82-1.58 (m, 6H), 1.28-1.07 (m, 3H), 1.06-0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (e), 133.2 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 280.8 Hz), 119.6 (e), 86.6 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 41.3 (o), 28.3 (e), 28.2 (e), 26.1 (e), 25.7_3 (e), 25.6_7 (e); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.4 (d, *J* = 6.0 Hz, 6F); IR (liquid film) 2935 (s), 2859 (s), 1775 (vs), 1648 (w), 1454 (m), 1386 (s), 1363 (s), 1303 (vs),

1260 (vs), 1202 (vs), 1139 (s), 1113 (vs), 1010 (s), 950 (s), 909 (s), 780 (m), 755 (m), 689 (s) cm^{-1}.

1-Isobutylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.2, 10.4, 7.0 Hz, 1H), 5.53 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.18 (brq, J = 6.8 Hz, 1H), 1.73-1.62 (m, 2H), 1.46 (sept, J = 6.0 Hz, 1H), 0.92 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (e), 134.9 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 280.9 Hz), 118.7 (e), 81.1 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 42.8 (e), 24.3 (o), 22.5 (o), 22.2 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.4 (m, 6F); IR (liquid film) 2966 (s), 2877 (m), 1772 (vs), 1651 (w), 1472 (m), 1387 (s), 1364 (s), 1303 (vs), 1260 (vs), 1202 (vs), 1140 (s), 1114 (vs), 1009 (s), 940 (s), 909 (s), 781 (m), 756 (m), 690 (s) cm^{-1}.

1-Benzylprop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate (1g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.2 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 2H), 5.84 (ddd, J = 17.2, 10.6, 6.6 Hz, 1H), 5.45 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.33 (brq, J = 6.8 Hz, 1H), 5.30 (d, J = 13.2 Hz, 1H), 5.26 (d, J = 10.8 Hz, 1H), 3.05 (dd, A of ABX, J_{AB} = 14.0 Hz, J_{AX} = 7.6 Hz, 1H), 2.96 (dd, B of ABX, J_{AB} = 14.0 Hz, J_{BX} = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (e), 135.6 (e), 133.9 (o), 129.5 (o), 128.5 (o), 127.0 (o), 120.2 (e; q, $J_{C\text{-}F}$ = 280.8 Hz), 119.0 (e), 82.3 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 40.7 (e); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.3 (d, J = 6.0 Hz, 6F); IR (liquid film) 3034 (w), 2974 (w), 1775 (vs), 1650 (w), 1606 (w), 1498 (m), 1456 (m), 1386 (s), 1364 (s), 1303 (vs), 1260 (vs), 1202 (vs), 1139 (s), 1113 (vs), 971 (s), 940 (s), 909 (s), 781 (m), 749 (m), 700 (s), 689 (s) cm^{-1}.

1-[6-(*tert*-Butyldimethylsiloxy)hexyl]prop-2-en-1-yl 2,2,2-trifluoro-1-(trifluoro-methyl)ethyl carbonate (1h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.2, 10.4, 7.0 Hz, 1H), 5.53 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.10 (q, J = 6.8 Hz, 1H), 3.58 (t, J = 6.4 Hz, 2H), 1.80-1.70 (m, 1H), 1.70-1.61 (m, 1H), 1.52-1.44 (m, 2H), 1.40-1.28 (m, 4H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (e), 134.6 (o), 120.3 (e; q, $J_{C\text{-}F}$ = 282.6 Hz), 118.8 (e), 82.4 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 62.9 (e), 33.9 (e), 32.6 (e), 25.9 (o), 25.5 (e), 24.6 (e), 18.3 (e), -5.4 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.3 (d, J = 6.0 Hz, 6F); IR (liquid film) 2934 (s), 2861 (s), 1777 (vs), 1650 (w), 1473 (m), 1464 (m),

1386 (s), 1363 (s), 1303 (vs), 1260 (vs), 1202 (vs), 1140 (s), 1113 (vs), 1008 (m), 937 (s), 908 (s), 836 (s), 777 (s), 756 (m), 689 (m) cm^{-1}.

6-({[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]carbonyl}oxy)oct-7-en-1-yl acetate (1i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.53 (sept, $J_{H\text{-}F}$ = 6.0 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.26 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.10 (q, *J* = 6.8 Hz, 1H), 4.02 (t, *J* = 6.8 Hz, 2H), 2.01 (s, 3H), 1.78-1.55 (m, 4H), 1.40-1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 (e), 152.2 (e), 134.4 (o), 120.2 (e; q, $J_{C\text{-}F}$ = 280.5 Hz), 118.9 (e), 82.2 (o), 70.1 (o; sept, $J_{C\text{-}F}$ = 34.9 Hz), 64.2 (e), 33.8 (e), 28.4 (e), 25.6 (e), 24.4 (e), 20.9 (o); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.3 (d, *J* = 6.0 Hz, 6F); IR (liquid film) 2947 (m), 2865 (w), 1776 (s), 1741 (s), 1652 (w), 1465 (m), 1387 (s), 1367 (s), 1301 (s), 1257 (vs), 1200 (vs), 1138 (s), 1112 (s), 1011 (m), 935 (s), 908 (s), 781 (m), 689 (m) cm^{-1}.

3,5-Diphenylpent-1-ene (2a, Ar = Ph).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 4H), 7.22-7.12 (m, 6H), 5.97 (ddd, *J* = 13.6, 9.6, 7.6 Hz, 1H), 5.05 (d, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 13.6 Hz, 1H), 3.27 (brq, *J* = 7.6 Hz, 1H), 2.63-2.49 (m, 2H), 2.05 (quin, *J* = 7.6 Hz, 1H), 2.02 (dq, *J* = 6.4, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 (e), 142.2 (e), 142.1 (o), 128.5 (o), 128.4 (o), 128.3 (o), 127.6 (o), 126.2 (o), 125.7 (o), 114.3 (e), 49.2 (o), 36.9 (e), 33.6 (e); IR (liquid film) 3027 (s), 2925 (m), 1637 (m), 1602 (m), 1495 (s), 1453 (s), 1077 (m), 1030 (m), 994 (m), 915 (s), 747 (s), 699 (vs) cm^{-1}.

3-(4-Methoxyphenyl)-5-phenylpent-1-ene (2a, Ar = *p*-MeO-C_6H_4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 2H), 7.19-7.12 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.94 (ddd, *J* = 16.8, 10.8, 7.6 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 5.01 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H), 3.22 (brq, *J* = 7.2 Hz, 1H), 2.58 (ddd, *J* = 13.6, 9.2, 7.2 Hz, 1H), 2.52 (ddd, *J* = 13.6, 8.8, 7.2 Hz, 1H), 2.02 (ddt, *J* = 13.6, 9.2, 7.2 Hz, 1H), 1.98 (ddt, *J* = 13.6, 8.8, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (e), 142.4 (o), 142.3 (e), 136.1 (e), 128.5 (o), 128.4 (o), 128.3 (o), 125.7 (o), 113.9 (e), 113.9 (o), 55.2 (o), 48.3 (o), 37.0 (e), 33.6 (e); IR (liquid film) 3027 (m), 2934 (s), 2857 (m), 2835 (m), 1636 (m), 1610 (s), 1511 (vs), 1454 (s), 1247 (vs), 1178 (s), 1037 (s), 914 (s), 829 (s), 750 (s), 699 (s) cm^{-1}; HRMS (EI, M^+) calcd for $C_{18}H_{20}O$ 252.1514, found 252.1508.

3-(4-Methylphenyl)-5-phenylpent-1-ene (2a, Ar = *p*-Me-C_6H_4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.18-7.07 (m, 7H), 5.95 (ddd, *J* = 17.2, 9.6, 7.6 Hz, 1H), 5.05-5.00 (m, 2H), 3.24 (brq, *J* = 7.2 Hz, 1H), 2.63-2.48 (m, 2H), 2.32 (s, 3H), 2.08-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3 (e), 142.3 (o), 141.0 (e), 135.7 (e), 129.2 (o), 128.4 (o), 128.3 (o), 127.5 (o), 125.7 (o), 114.1 (e), 48.9 (o), 36.9 (e), 33.7 (e), 21.0 (o); IR (liquid film) 3026 (s), 2923 (s), 2859 (s), 1636 (m), 1604 (m), 1513 (s), 1496 (s), 1454 (s), 1111 (m), 994 (m), 913 (s), 816 (s), 749 (s), 699 (vs) cm^{-1}; HRMS (EI, M+) calcd for $C_{18}H_{20}$ 236.1565, found 236.1566.

3-(4-Fluorophenyl)-5-phenylpent-1-ene (2a, Ar = *p*-F-C_6H_4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 8.4 Hz, 2H), 5.92 (ddd, *J* = 17.4, 10.4, 7.6 Hz, 1H), 5.04 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.01 (dt, *J* = 17.4, 1.2 Hz, 1H), 3.25 (brq, *J* = 7.2 Hz, 1H), 2.56 (ddd, *J* = 14.0, 9.2, 6.4 Hz, 1H), 2.52 (ddd, *J* = 14.0, 9.2, 6.4 Hz, 1H), 2.03 (ddt, *J* = 13.6, 9.2, 6.8 Hz, 1H), 1.97 (dddd, *J* = 13.6, 9.2, 7.2, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (e; d, $J_{C\text{-}F}$ = 242.8 Hz), 142.0 (o), 141.9 (e), 139.6 (e; d, $J_{C\text{-}F}$ = 3.1 Hz), 129.0 (o; d, $J_{C\text{-}F}$ = 7.6 Hz), 128.4 (o), 128.3 (o), 125.8 (o), 115.2 (o; d, $J_{C\text{-}F}$ = 21.3 Hz), 114.5 (e), 48.4 (o), 37.0 (e), 33.6 (e); ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.6 (brs, 1F); IR (liquid film) 3028 (m), 2926 (m), 2859 (m), 1637 (m), 1603 (s), 1509 (vs), 1455 (s), 1223 (s), 1158 (s), 1095 (m), 995 (m), 917 (s), 833 (s), 750 (s), 699 (s) cm^{-1}; HRMS (EI, M^+) calcd for $C_{17}H_{17}F$ 240.1314, found 240.1323.

3-Phenylbut-1-ene (2b).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.23-7.15 (m, 3H), 6.00 (ddd, *J* = 16.8, 10.4, 6.8 Hz, 1H), 5.04 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.02 (dd, *J* = 10.4, 1.2 Hz, 1H), 3.46 (brquin, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 (e), 143.2 (o), 128.4 (o), 127.2 (o), 126.1 (o), 113.1 (e), 43.2 (o), 20.7 (o); IR (liquid film) 3028 (m), 2967 (s), 2929 (s), 1638 (m), 1602 (m), 1493 (s), 1452 (s), 1371 (m), 1016 (m), 997 (m), 913 (s), 756 (m), 699 (vs) cm^{-1}.

3-Phenyldodec-1-ene (2c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20-7.14 (m, 3H), 5.93 (ddd, *J* = 16.8, 10.8, 7.6 Hz, 1H), 4.99 (d, 16.8 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 3.21 (q, *J* = 7.6 Hz, 1H), 1.70-1.64 (m, 2H), 1.32-1.12 (brm, 14H), 0.85 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (e), 142.5 (o), 128.4 (o), 127.6 (o), 126.0 (o), 113.8 (e), 49.9

(o), 35.4 (e), 31.9 (e), 29.6 (e), 29.5 (e), 29.3 (e), 27.5 (e), 22.7 (e), 14.1 (o); IR (liquid film) 3028 (m), 2926 (vs), 2855 (vs), 1637 (m), 1602 (m), 1493 (m), 1466 (s), 1453 (s), 1074 (w), 1030 (w), 992 (m), 911 (s), 757 (m), 736 (m), 699 (s) cm^{-1}; HRMS (CI, M^+) calcd for $C_{18}H_{28}$ 244.2191, found 244.2186.

4-Methyl-3-phenylpent-1-ene (2d).[7] ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.2 Hz, 2H), 7.16 -7.13 (m, 3H), 5.97 (dt, *J* = 18.0, 9.2 Hz, 1H), 5.00 (d, *J* = 18.0 Hz, 1H), 4.99 (d, *J* = 9.2 Hz, 1H), 2.86 (t, *J* = 8.8 Hz, 1H), 1.92 (dsept, *J* = 9.2, 6.8 Hz, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3 (e), 141.2 (o), 128.3 (o), 127.9 (o), 125.9 (o), 114.9 (e), 58.5 (o), 32.6 (o), 21.0 (o), 20.7 (o); IR (liquid film) 3028 (m), 2957 (s), 2926 (s), 1637 (m), 1601 (m), 1491 (m), 1453 (m), 1385 (m), 1367 (m), 992 (m), 912 (s), 757 (s), 700 (vs), 673 (m) cm^{-1}.

3-Cyclohexyl-3-phenylprop-1-ene (2e).[8] ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.97 (dt, *J* = 17.2, 9.6 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 9.6 Hz, 1H), 2.92 (t, *J* = 9.2 Hz, 1H), 1.93-1.84 (m, 1H), 1.78-1.67 (m, 1H), 1.67-1.52 (m, 3H), 1.45-1.35 (m, 1H), 1.28-1.04 (m, 3H), 0.92 (dq, *J* = 12.0, 3.6 Hz, 1H), 0.80 (dq, *J* = 11.2, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 (e), 141.2 (o), 128.3 (o), 127.9 (o), 125.9 (o), 114.8 (e), 57.6 (o), 42.1 (o), 31.3_1 (e), 31.3_0 (e), 26.5 (e), 26.4 (e); IR (liquid film) 3027 (m), 2923 (vs), 2852 (s), 1637 (m), 1601 (m), 1491 (m), 1449 (s), 1066 (w), 991 (m), 911 (s), 756 (s), 700 (s), 677 (m) cm^{-1}; HRMS (EI, M^+) calcd for $C_{15}H_{20}$ 200.1565, found 200.1555.

5-Methyl-3-phenylhex-1-ene (2f).[6] ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.21 Hz, 2H), 7.21-7.15 (m, 3H), 5.93 (ddd, *J* = 17.6, 10.0, 7.6 Hz, 1H), 5.00 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 3.35 (brq, *J* = 7.6 Hz, 1H), 1.58 (t, *J* = 6.8 Hz, 1H), 1.48 (sept, *J* = 6.8 Hz, 1H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (e), 142.7 (o), 128.4 (o), 127.6 (o), 126.1(o), 113.7 (e), 47.6 (o), 44.7 (e), 25.3 (o), 22.6 (o), 22.5 (o); IR (liquid film) 2956 (vs), 2925 (s), 2869 (m), 1637 (m), 1602 (m), 1493 (m), 1467 (m), 1453 (m), 1384 (m), 1367 (m), 1069 (w), 1030 (w), 993 (m), 912 (m), 752 (m), 699 (vs) cm^{-1}; HRMS (EI , M^+) calcd for $C_{13}H_{18}$ 174.1409, found 174.1407.

3,4-Diphenylprop-1-ene (2g).[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 6.8 Hz, 2H), 7.22-7.17 (m, 4H), 7.14 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 6.8 Hz, 2H), 6.01 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.00 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.94 (dt, *J* = 17.2, 1.2 Hz, 1H), 3.56 (brq, *J* = 7.2 Hz, 1H), 3.03 (dd, A of ABX, J_{AB} = 13.6 Hz, J_{AX} = 7.6 Hz, 1H), 2.99 (dd, B of ABX, J_{AB} = 13.6 Hz, J_{BX} = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6 (e), 141.3 (o), 140.0 (e), 129.2 (o), 128.4 (o), 128.0 (o), 127.8 (o), 126.3 (o), 125.9 (o), 114.7 (e), 51.6 (o), 42.2 (e); IR (liquid film) 3028 (s), 2923 (m), 1637 (m), 1602 (m), 1495 (s), 1453 (s), 1070 (m), 1030 (m), 992 (m), 915 (s), 755 (s), 744 (s), 698 (vs) cm^{-1}.

8-*tert*-Butyldimethysilyloxy-3-phenyloct-1-ene (2h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.22-7.14 (m, 3H), 5.93 (ddd, *J* = 16.8, 10.4, 7.6 Hz, 1H), 5.00 (d, *J* = 16.8 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.21 (brq, *J* = 7.6 Hz, 1H), 1.76-1.62 (m, 2H), 1.47 (sept, *J* = 6.8 Hz, 2H), 1.40-1.14 (m, 4H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (e), 142.5 (o), 128.4 (o), 127.5 (o), 126.1 (o), 113.8 (e), 63.2 (e), 49.9 (o), 35.4 (e), 32.7 (e), 27.3 (e), 26.0 (o), 25.7 (e), 18.4 (e), -5.3 (o); IR (liquid film) 3028 (m), 2930 (vs), 2857 (vs), 1637 (m), 1602 (m), 1472 (m), 1463 (m), 1255 (s), 1102 (vs), 1005 (m), 913 (s), 836 (vs), 775 (s), 700 (s) cm^{-1}; HRMS (FAB, M-$C_4H_9^+$) calcd for $C_{16}H_{25}OSi$ 261.1675, found 261.1672.

6-Phenyloct-7-en-1-yl acetate (2i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.21-7.12 (m, 3H), 5.92 (ddd, *J* = 17.6, 9.6, 7.6 Hz, 1H), 5.00 (d, *J* = 17.6 Hz, 1H), 4.99 (d, *J* = 9.6 Hz, 1H), 4.00 (t, *J* = 6.4 Hz, 1H), 3.21 (brq, *J* = 7.6 Hz, 1H), 2.01 (s, 3H), 1.74-1.64 (m, 2H), 1.64-1.53 (m, 2H), 1.38-1.16 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 (e), 144.4 (e), 142.3 (o), 128.4 (o), 127.5 (o), 126.1 (o), 114.0 (e), 64.5 (e), 49.8 (o), 35.2 (e), 28.4 (e), 27.1 (e), 25.9 (e), 21.0 (o); IR (liquid film) 3028 (m), 2934 (s), 2859 (s), 1739 (vs), 1637 (m), 1601 (m), 1493 (m), 1453 (m), 1388 (m), 1366 (s), 1239 (vs), 1046 (s), 995 (m), 913 (s), 734 (s), 701 (s) cm^{-1}; HRMS (CI, M^+) calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1631.

(*S*)-1-Methylprop-en-1-yl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl carbonate ((*S*)-1b). $[\alpha]_D^{20}$ -15.2 ($CHCl_3$, c = 0.56). The enantiomeric excess (95% ee) was determined by chiral GLC on the corresponding methyl carbonate using an Astec CHIRALDEX™ G-TA column.

(*R*)-3-(4-Isobutylphenyl)-1-butene ((*R*)-4).[5,9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.99 (ddd, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.02 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.99 (dt, *J* = 10.0, 1.2 Hz, 1H), 3.42 (brquin, *J* = 6.8 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (nonet, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 (o), 142.7 (e), 139.4 (e), 129.1 (o), 126.9 (o), 112.8 (e), 45.0 (e), 42.8 (o), 30.2 (o), 22.4 (o), 20.7 (o); IR (liquid film) 2957 (vs), 2926 (s), 2869 (s), 1637 (m), 1512 (m), 1465 (m), 1418 (m), 1367 (m), 1168 (w), 1116 (w), 1018 (m), 912 (s), 844 (m), 797 (m) cm^{-1}.

(*S*)-2-(4-Isobutylphenyl)-propanoic acid (6).[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (nonet, *J* = 6.8 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 6H). The enantiomeric excess (96% ee) was determined on the corresponding methyl ester using chiral HPLC.[10]

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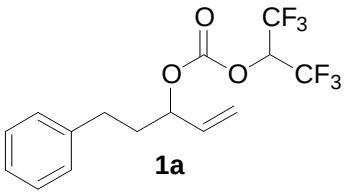

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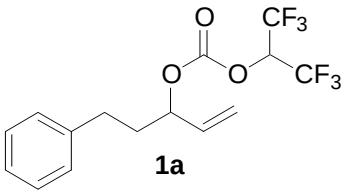

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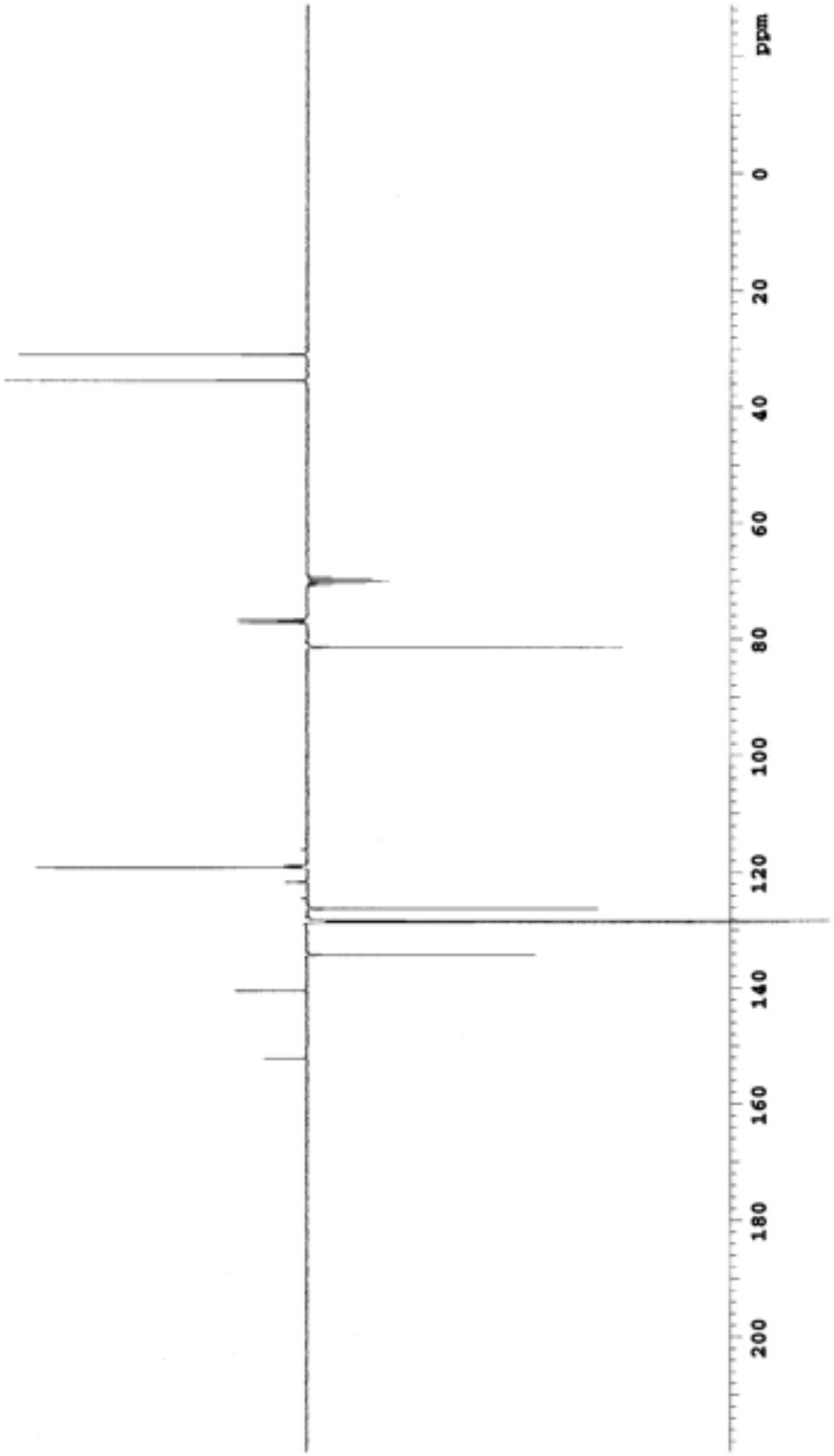

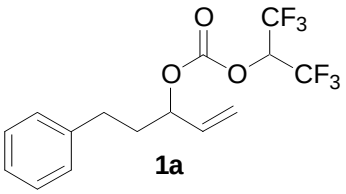

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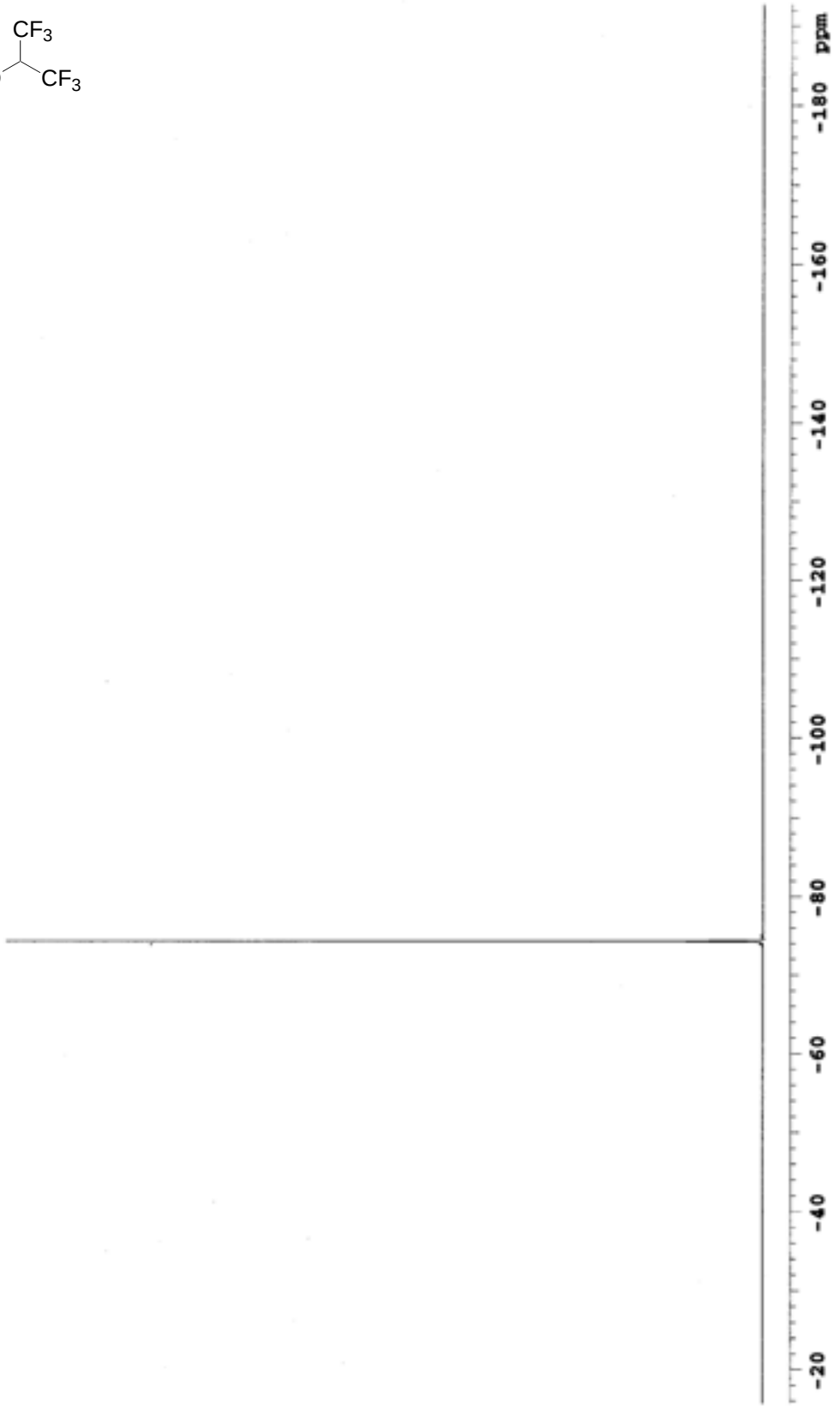

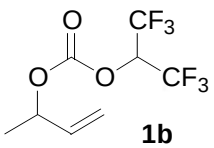

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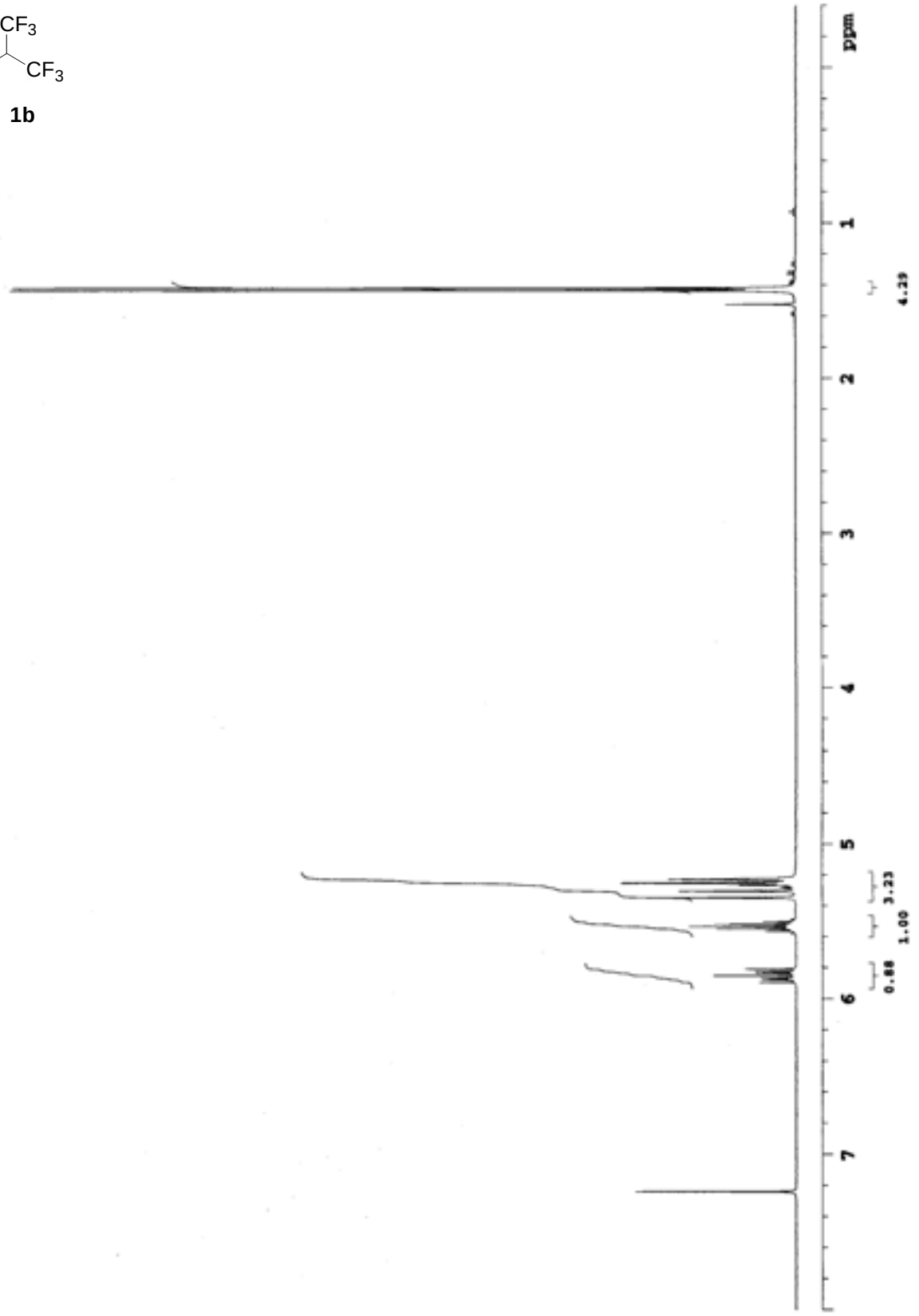

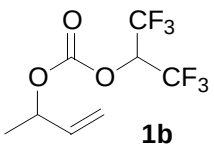

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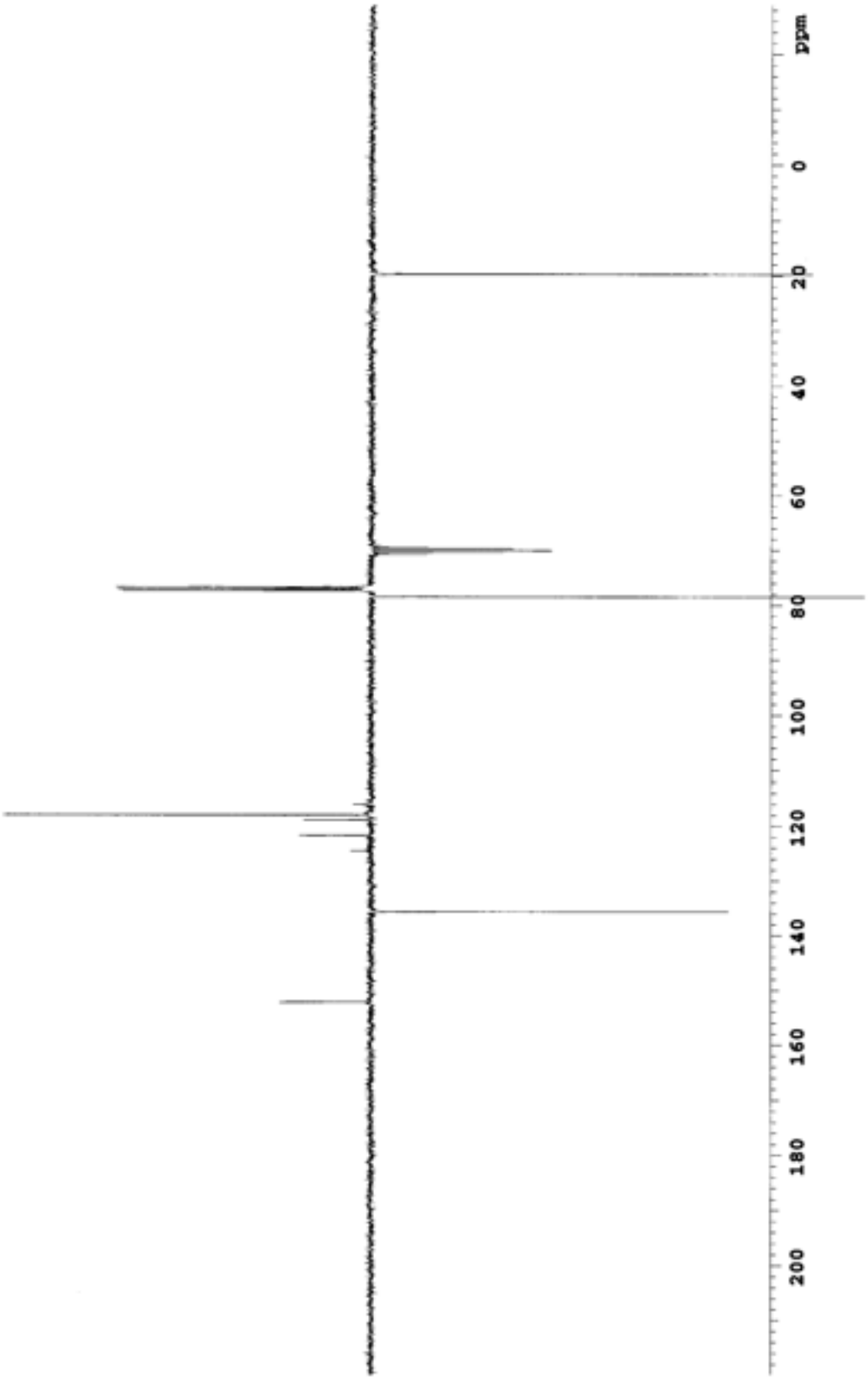

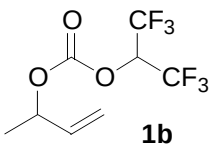

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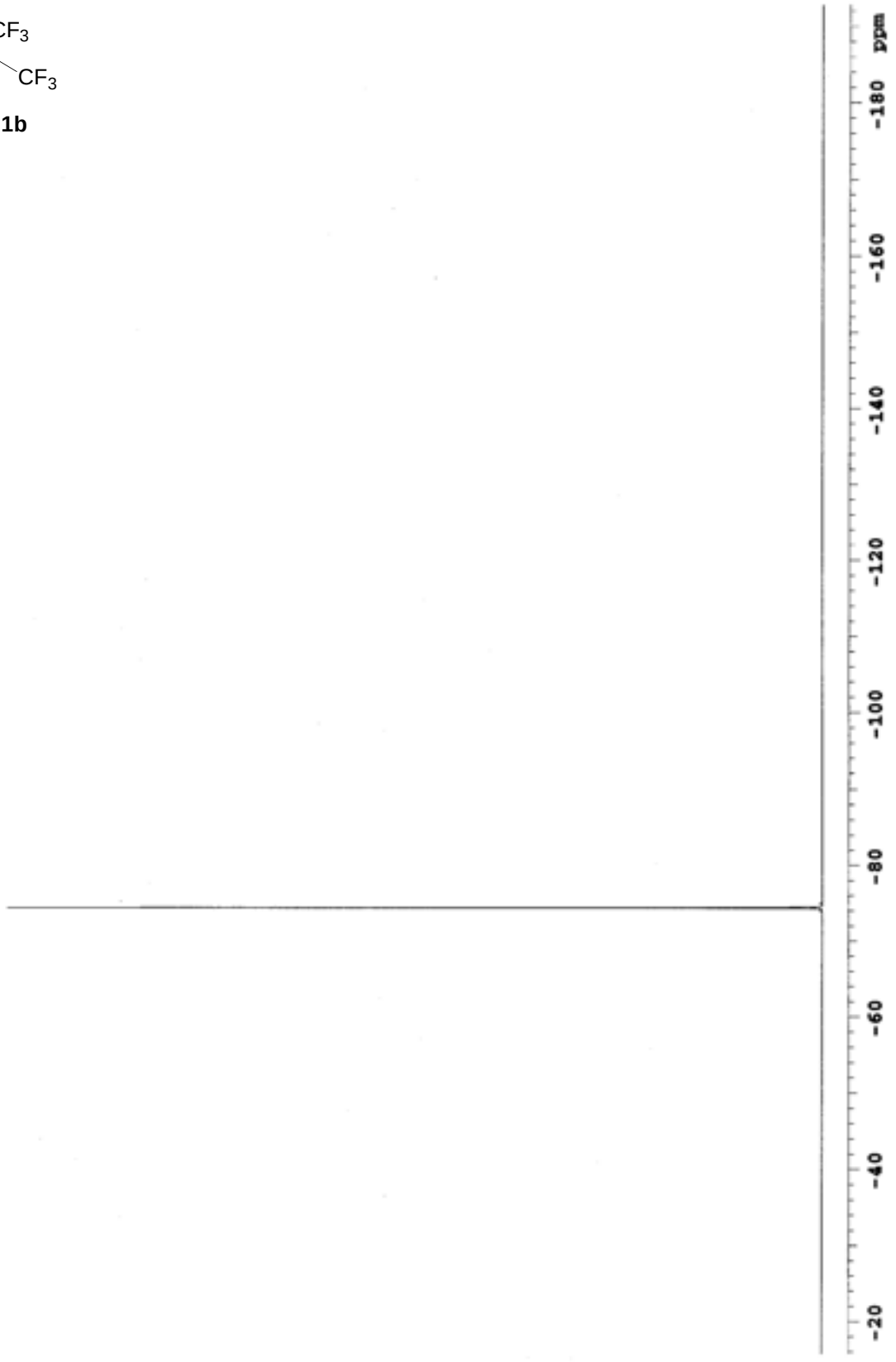

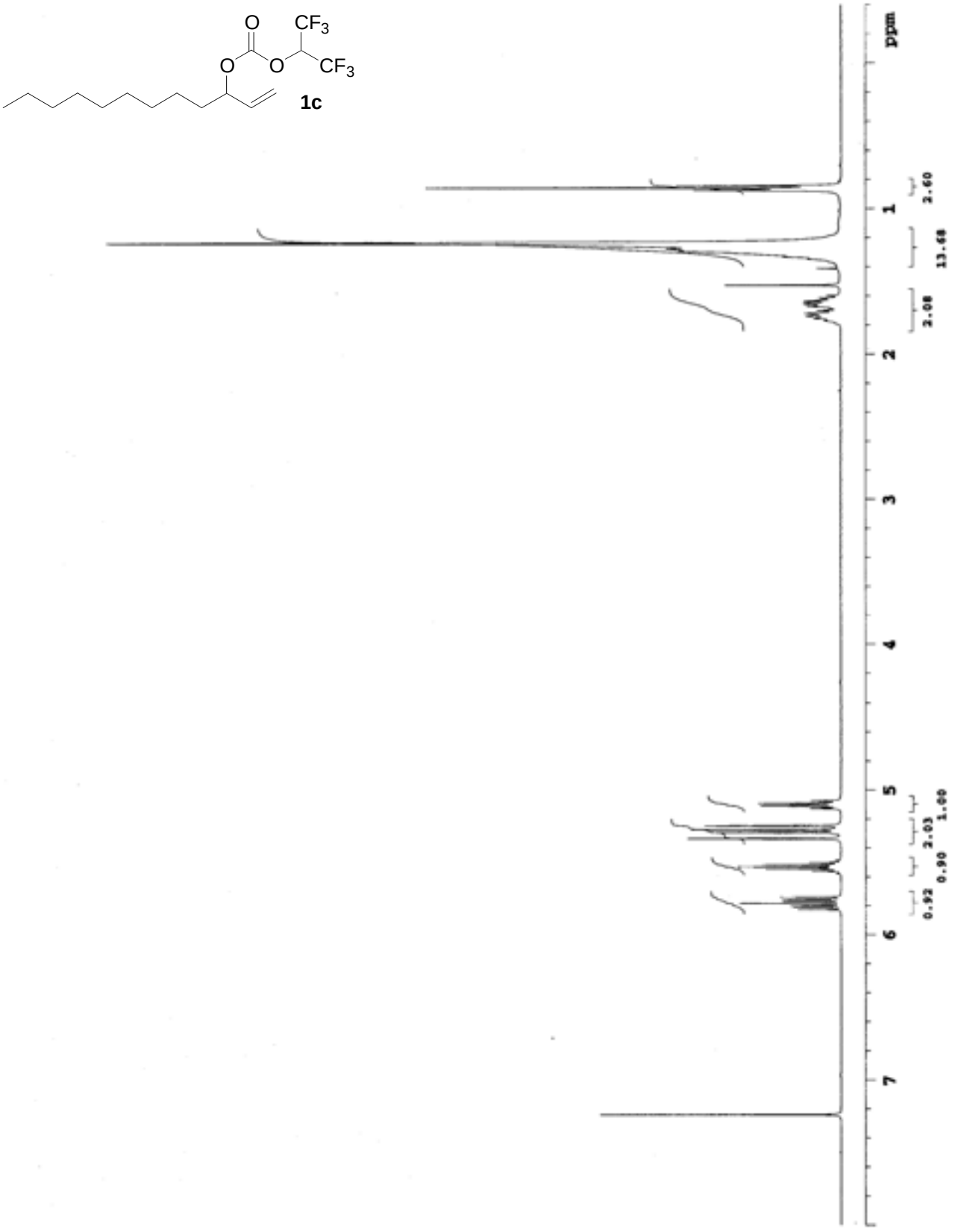
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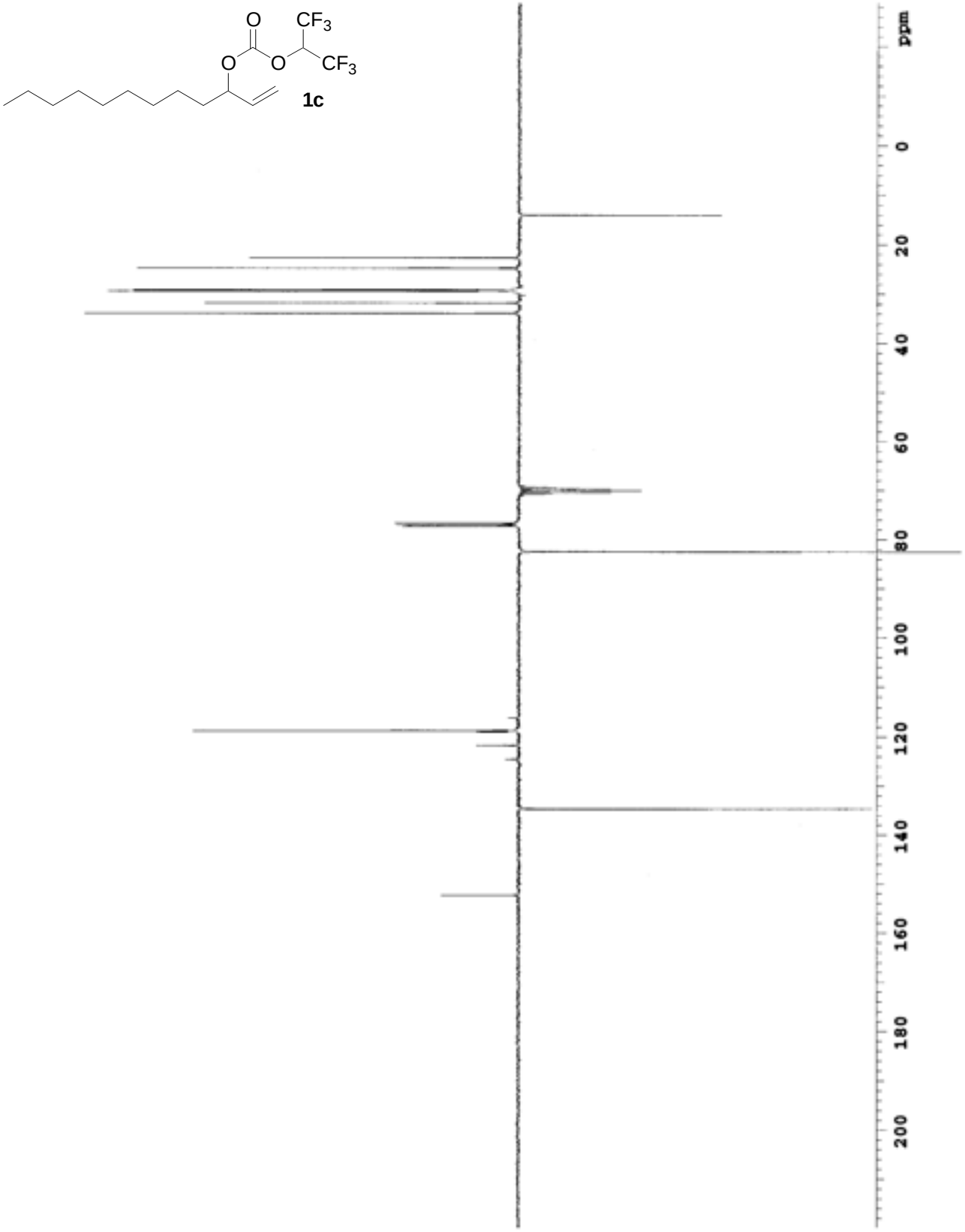
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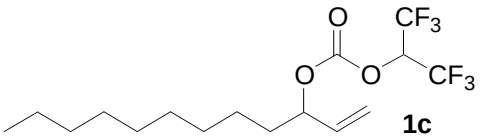

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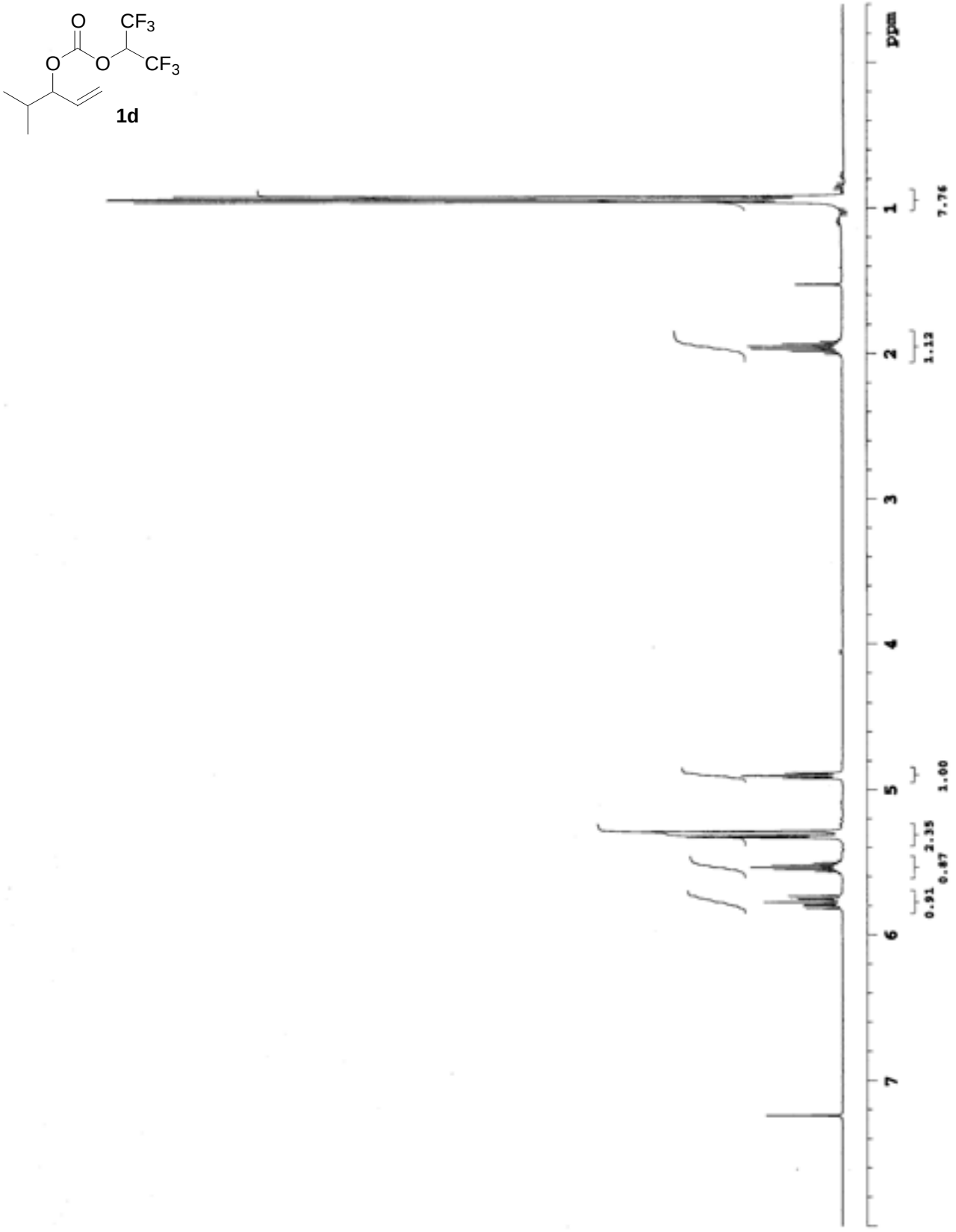
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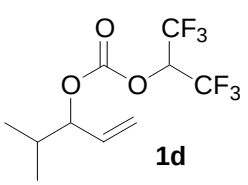

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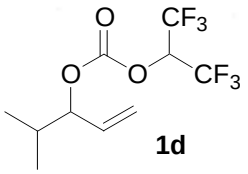

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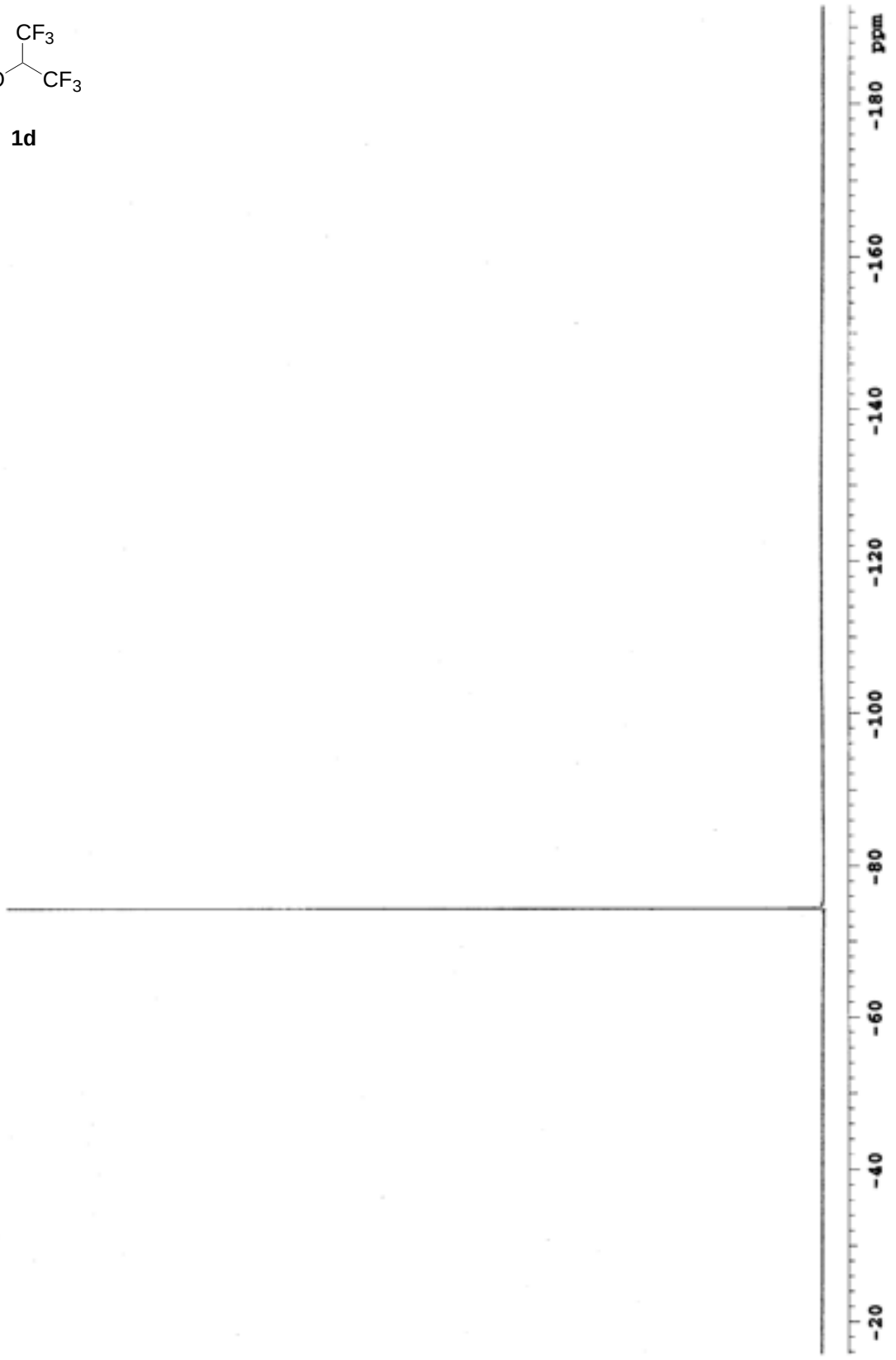

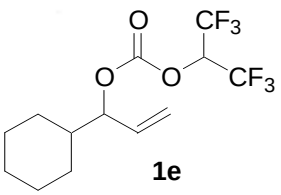

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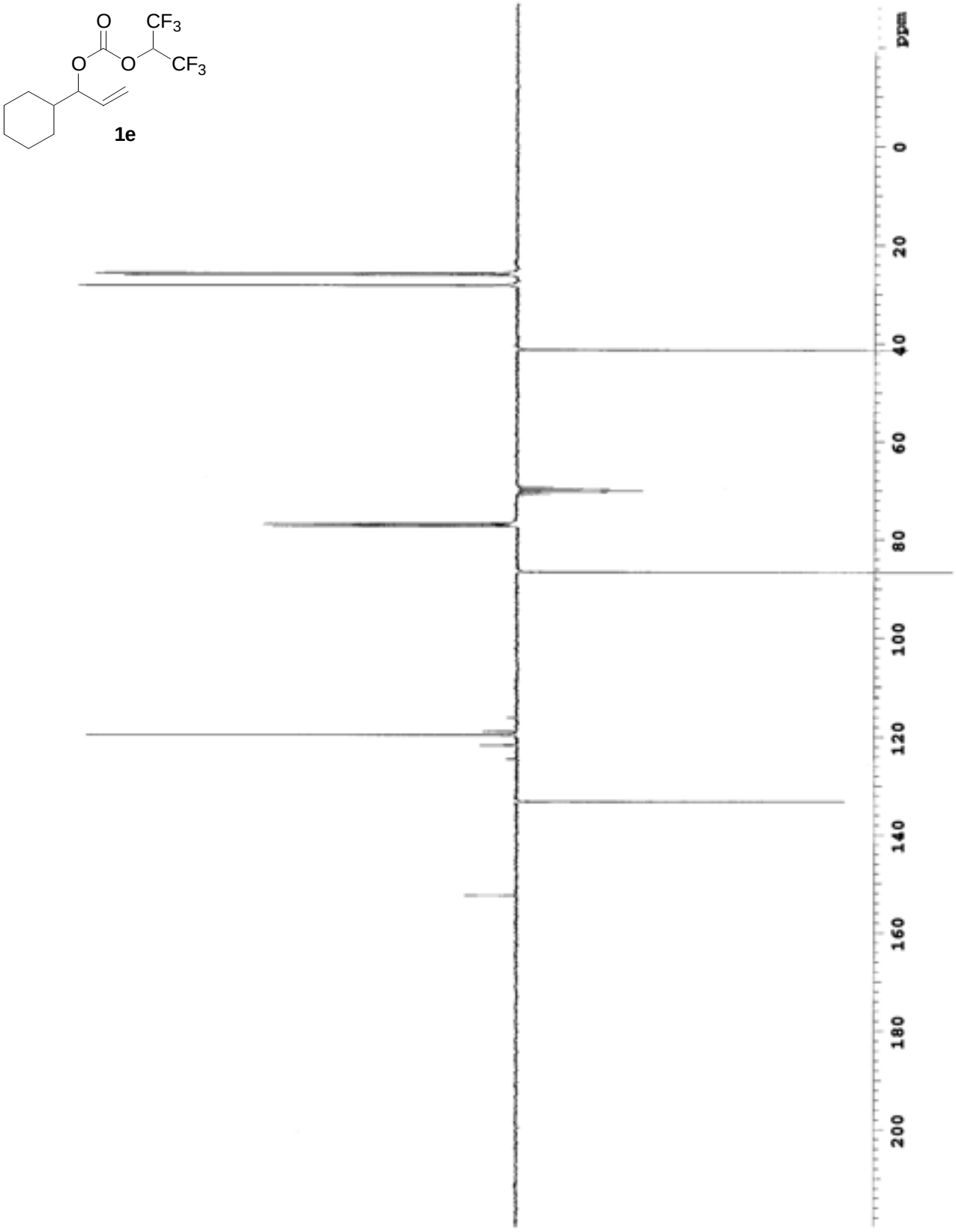
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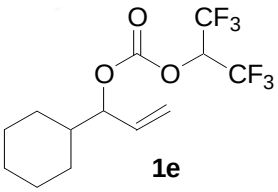

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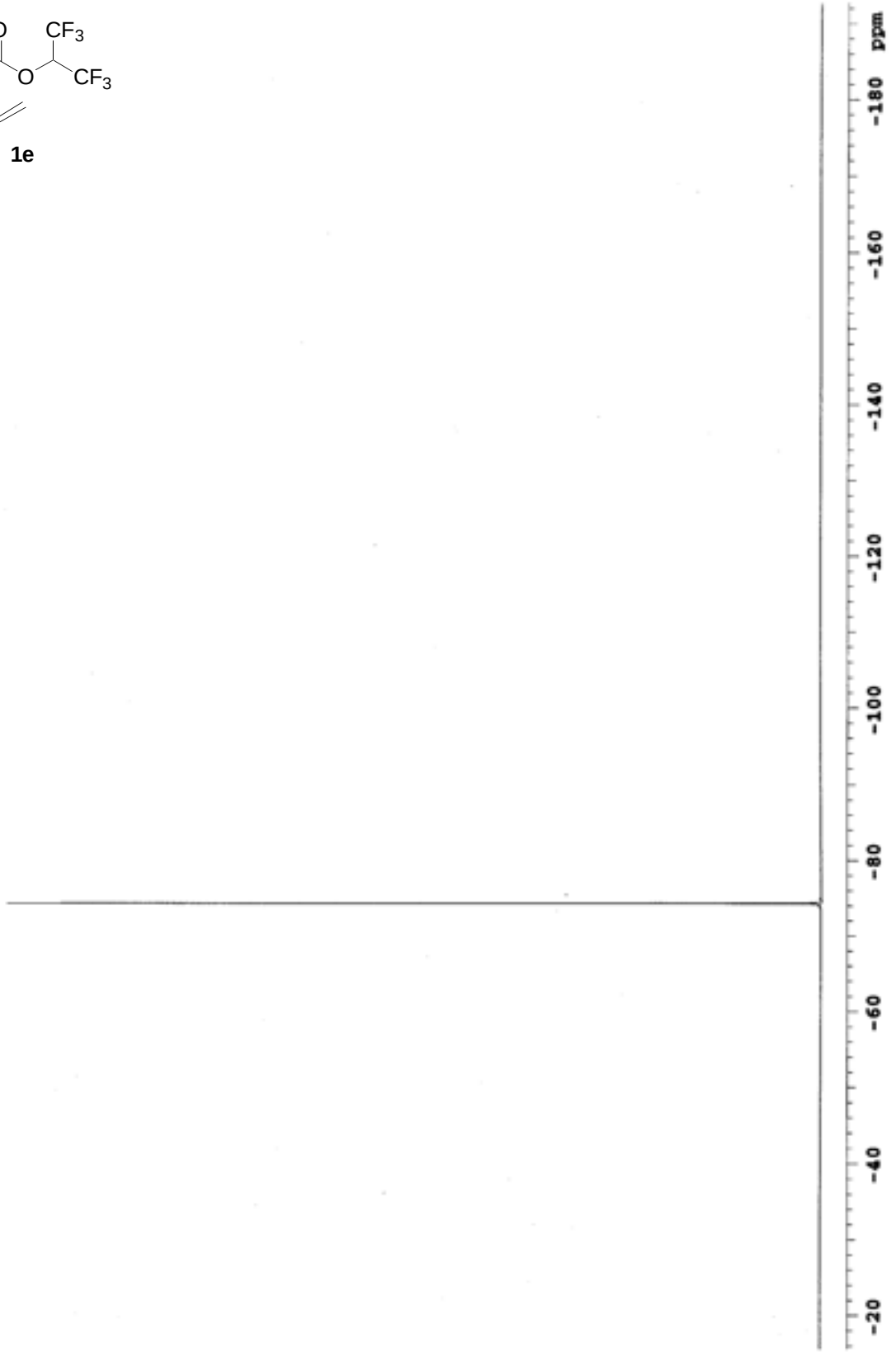

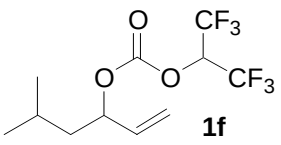

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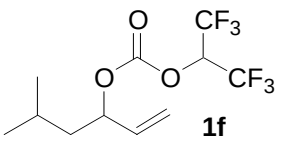

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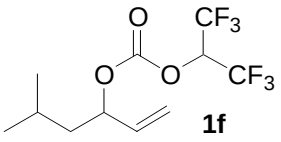

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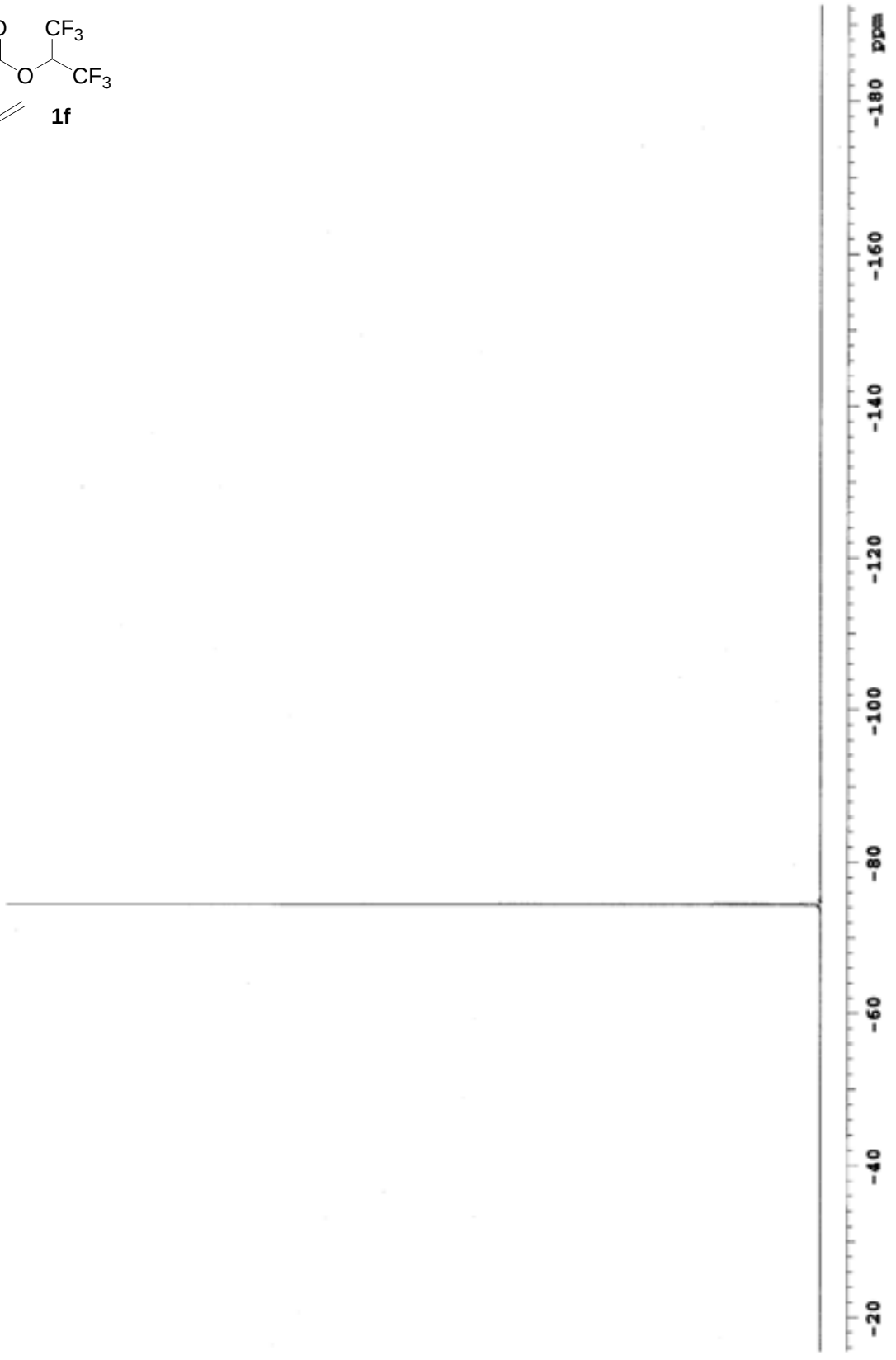

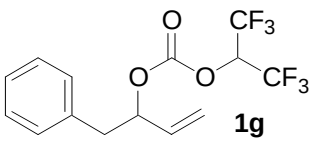

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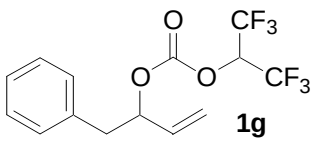

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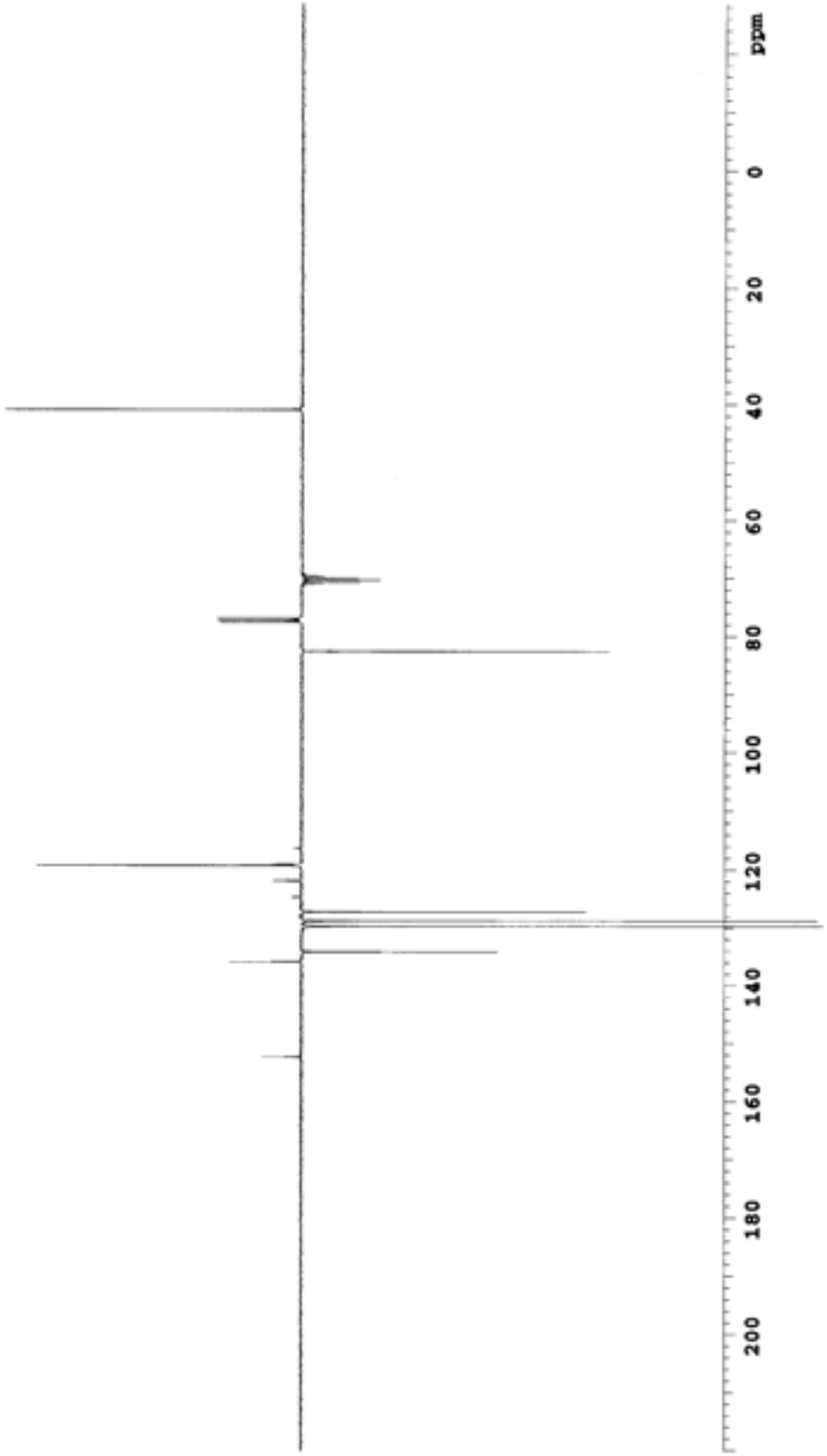

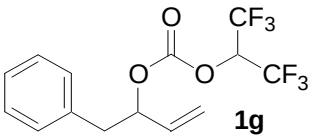

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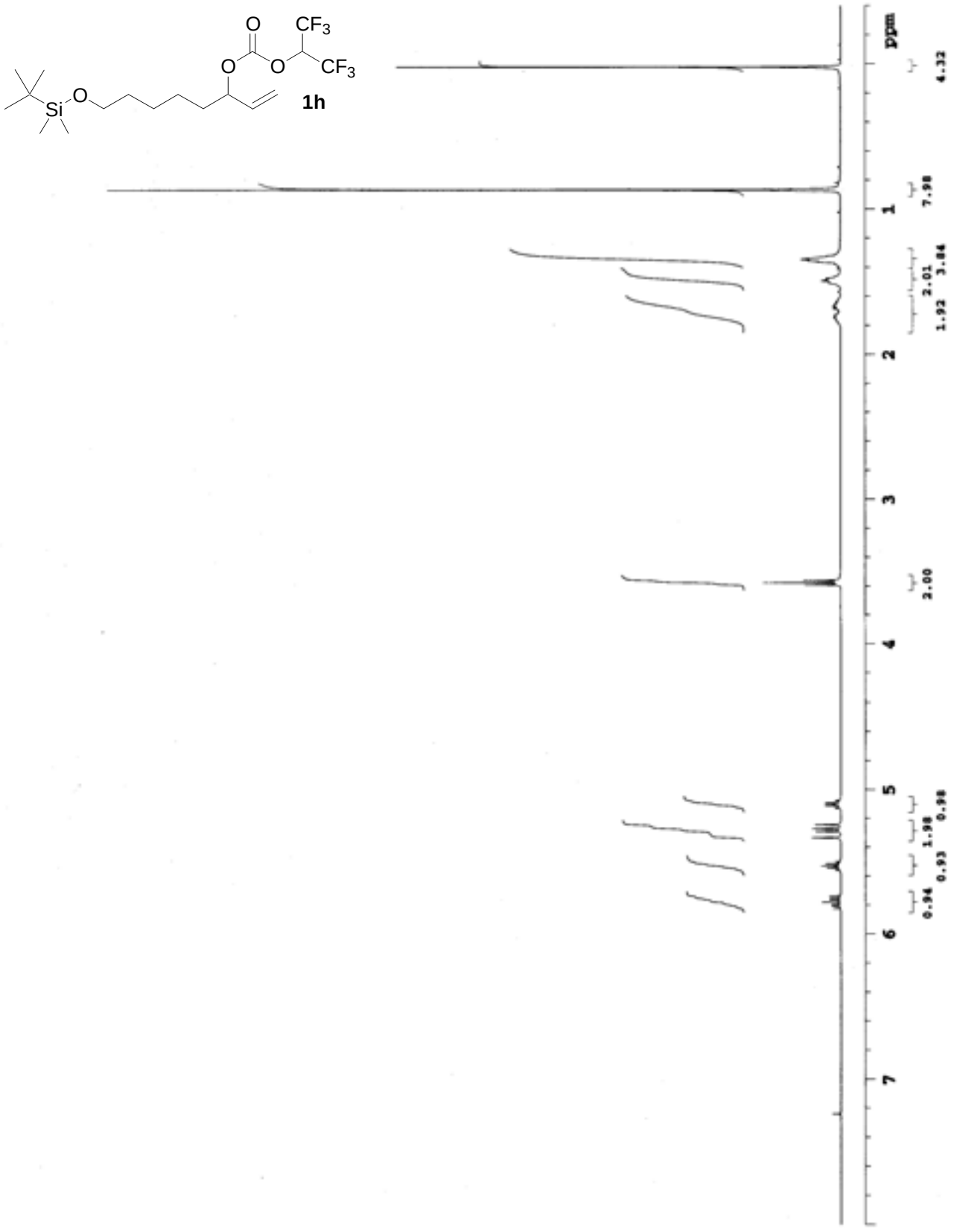
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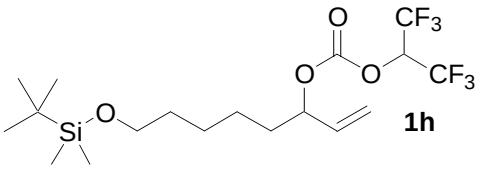

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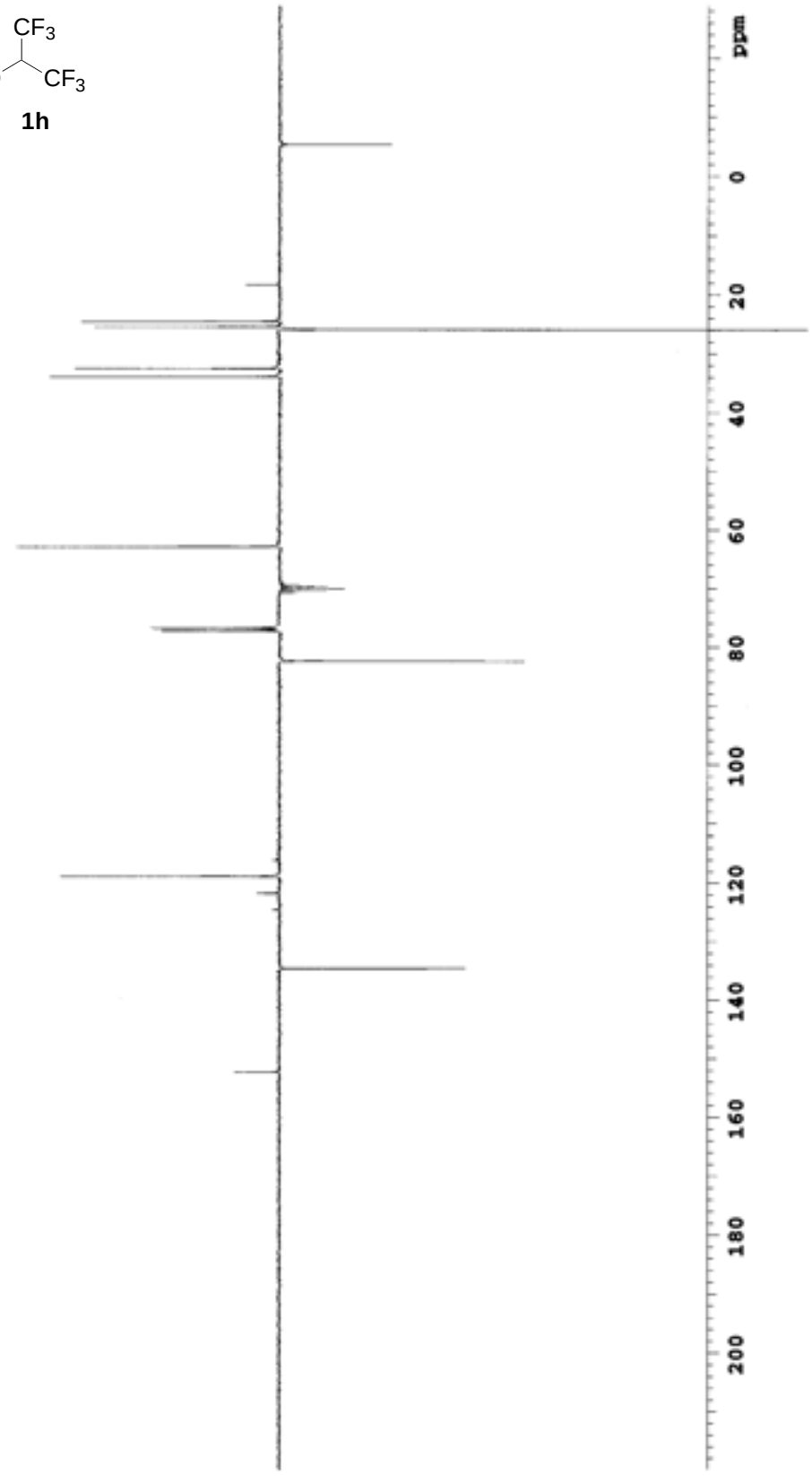

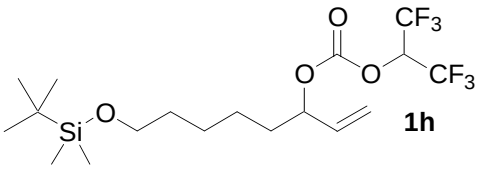

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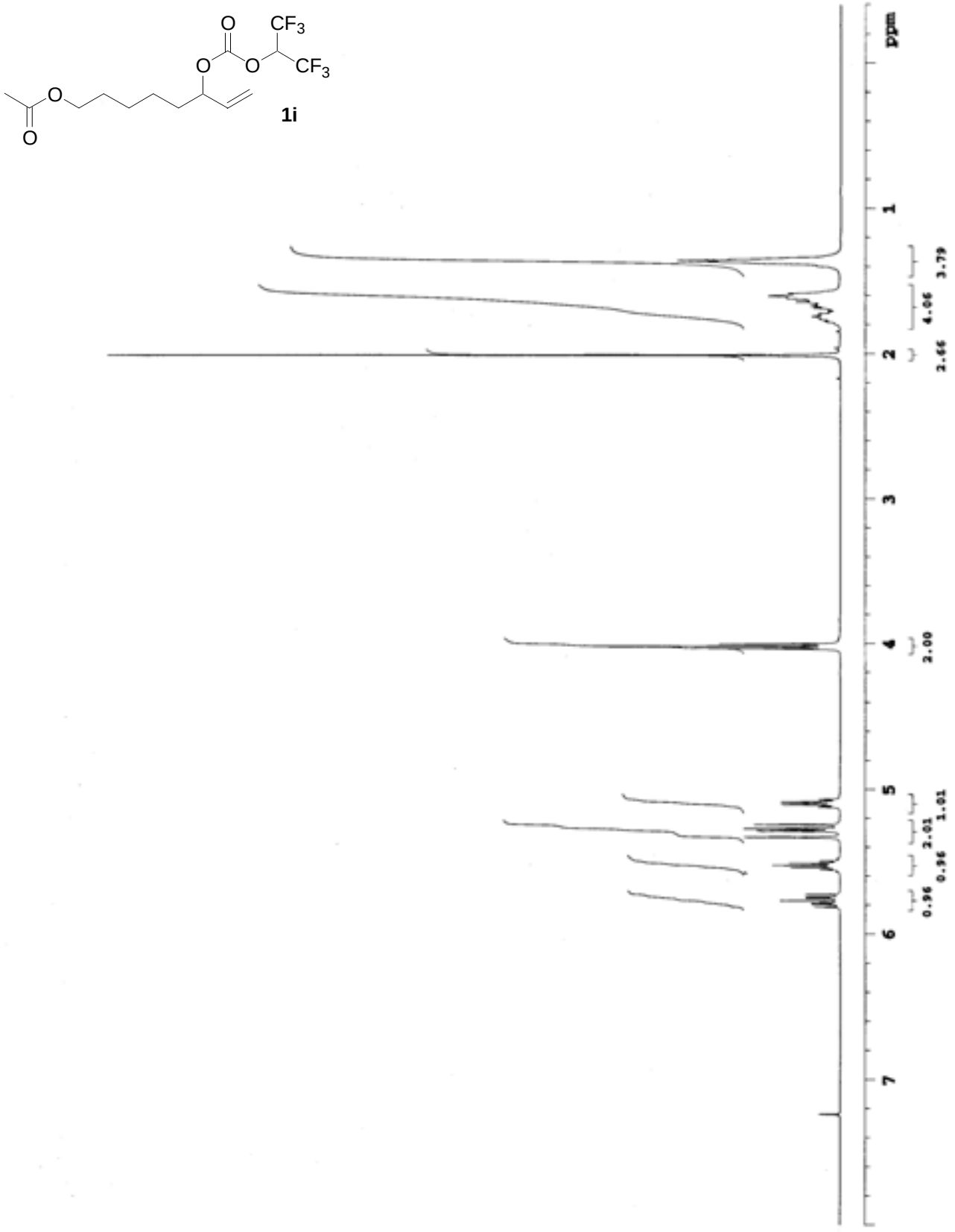
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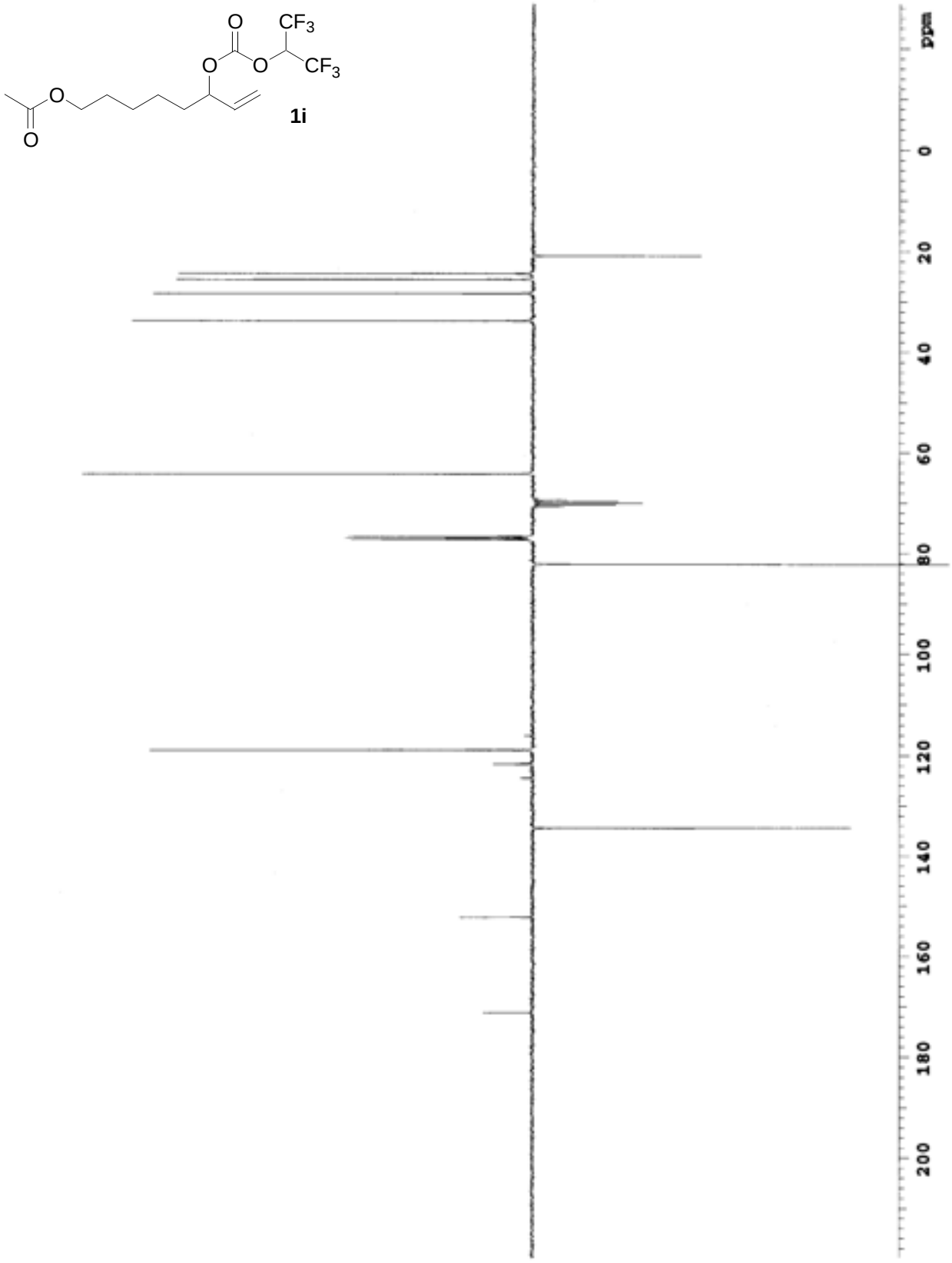
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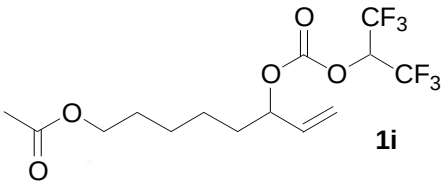

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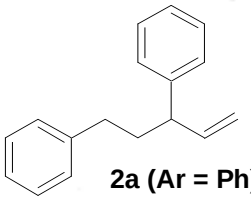

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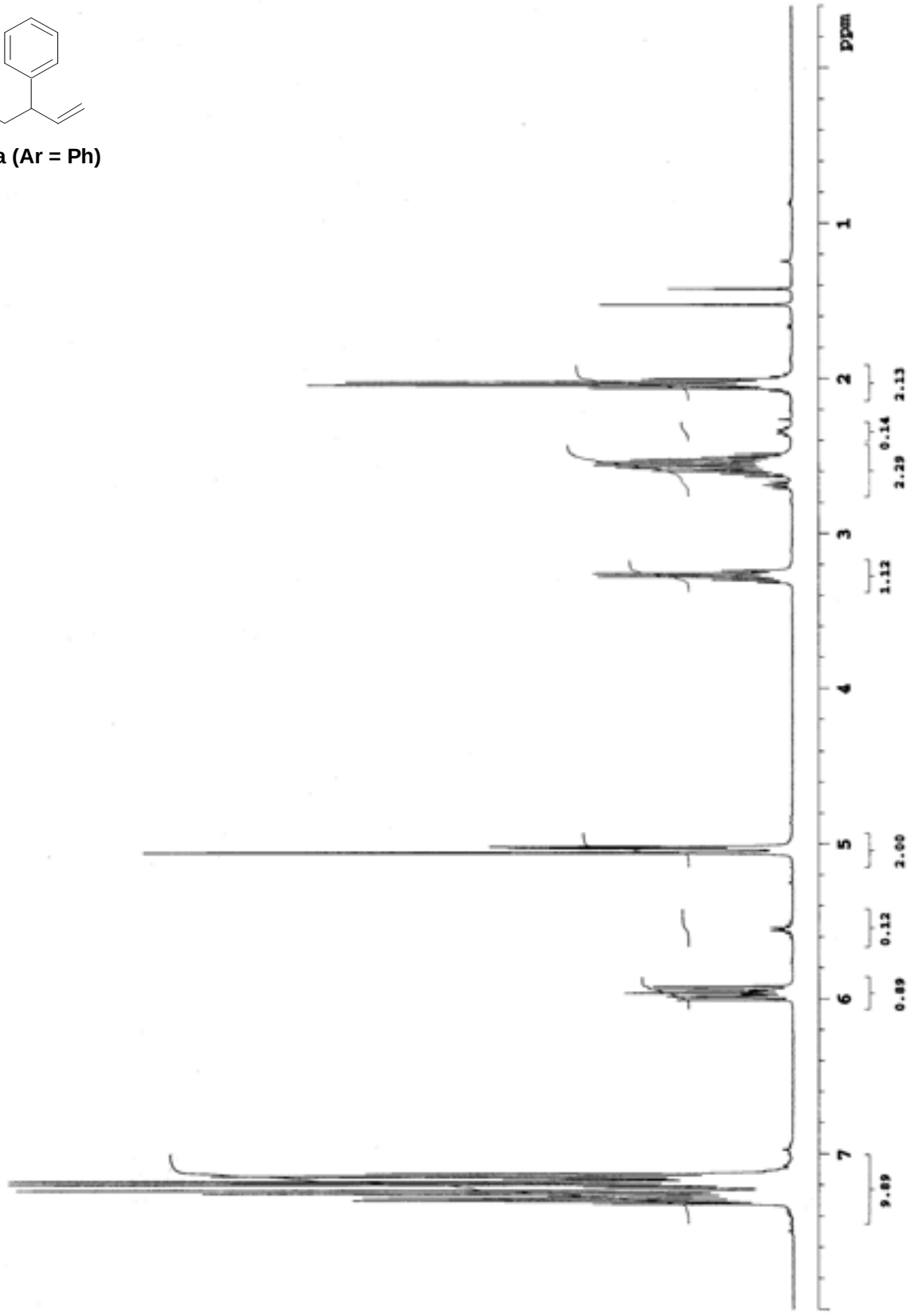

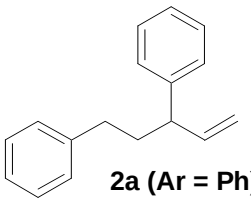

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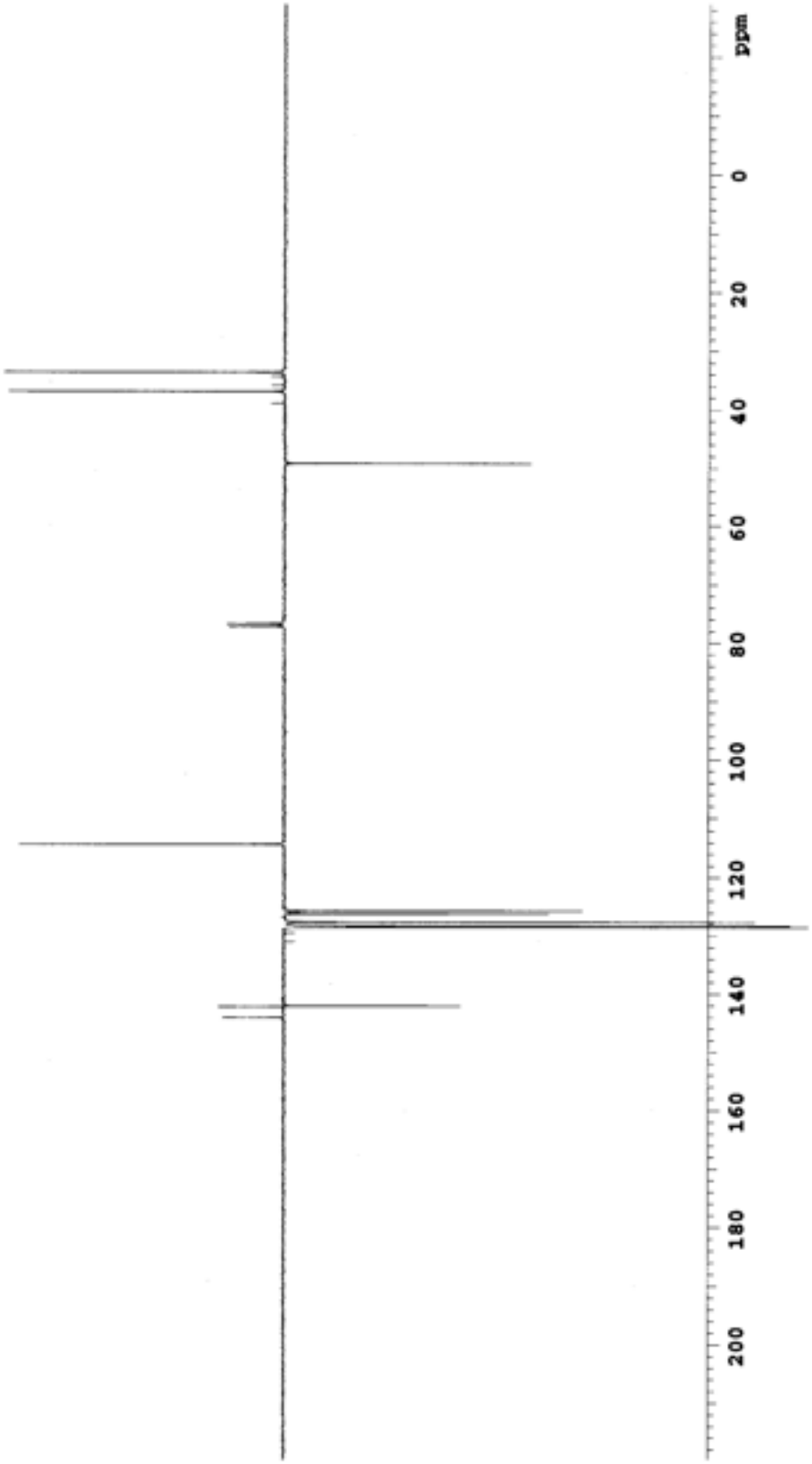

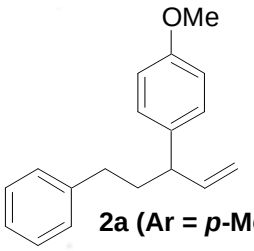

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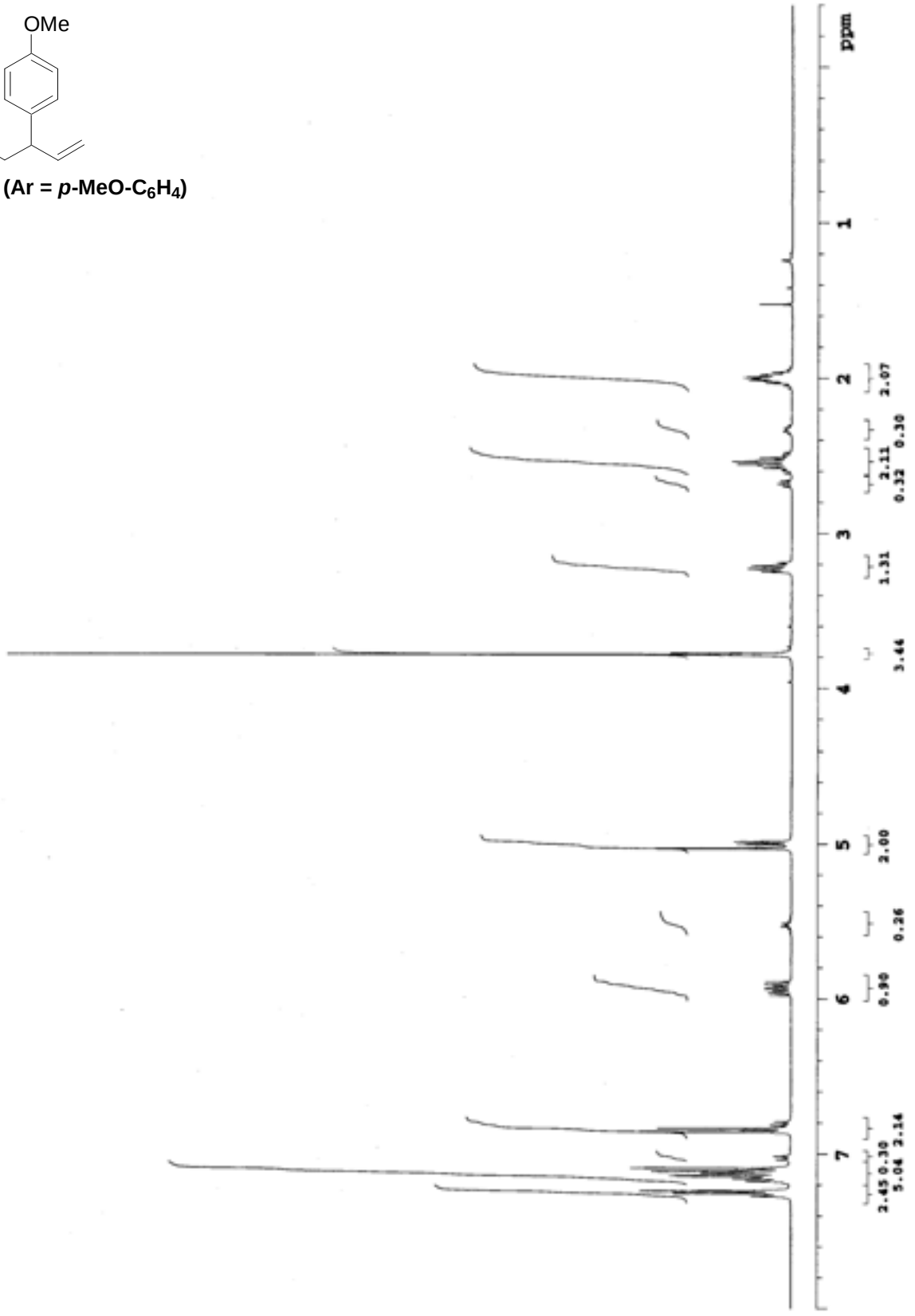

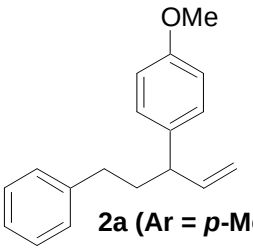

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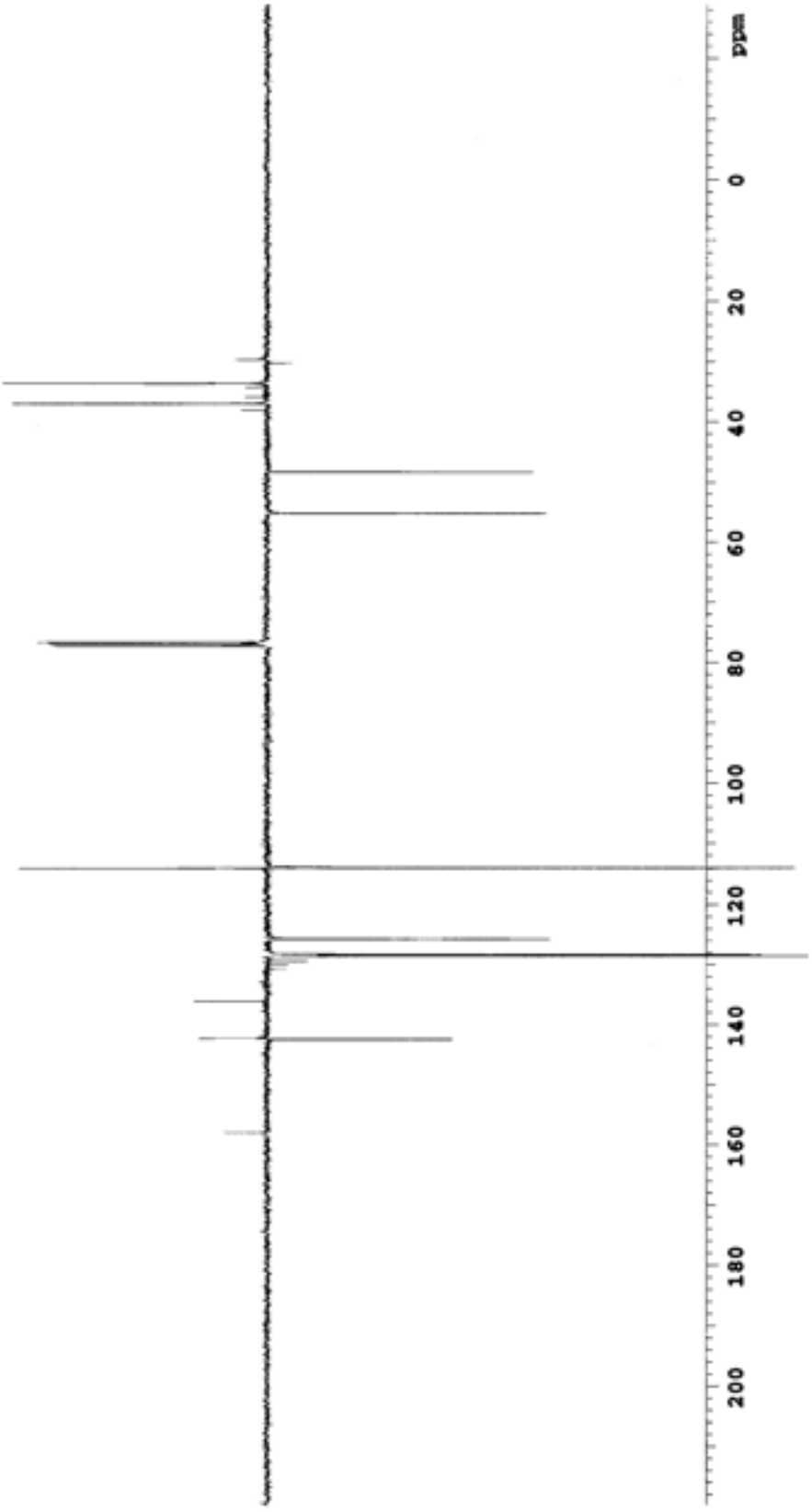

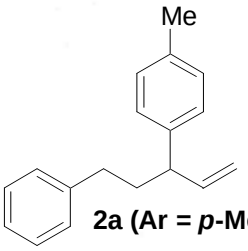

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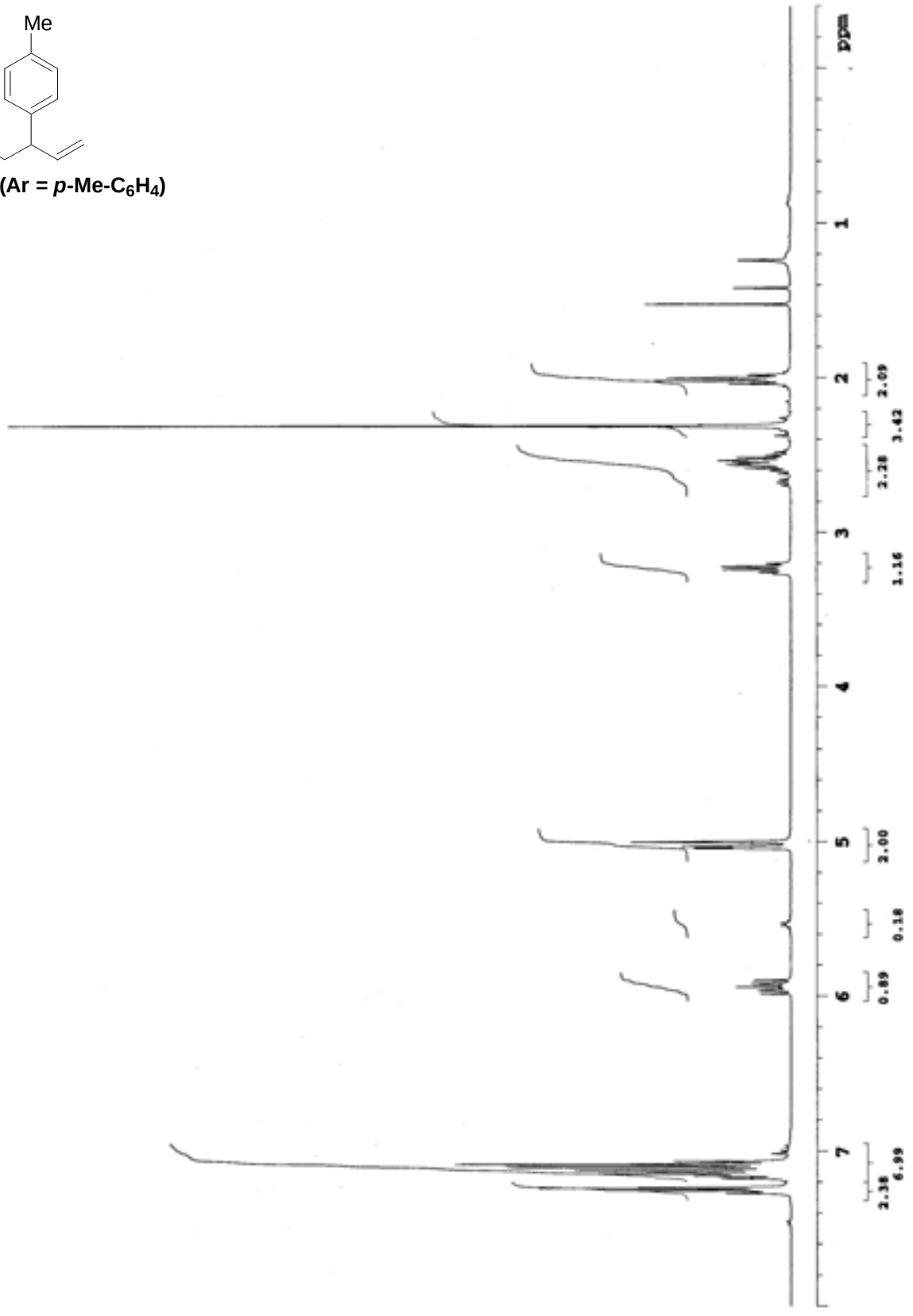

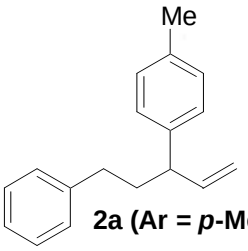

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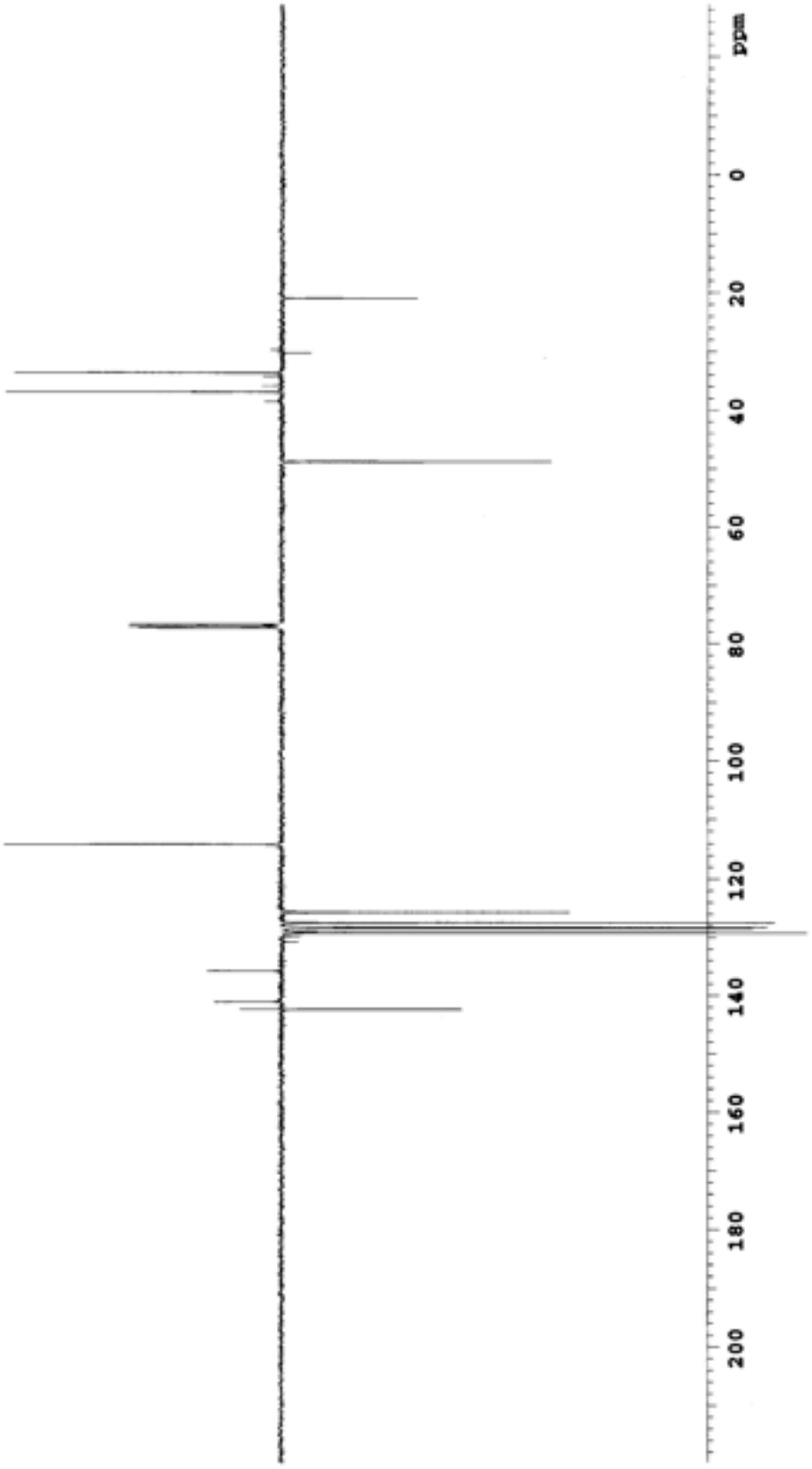

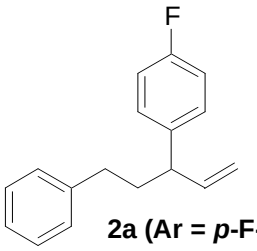

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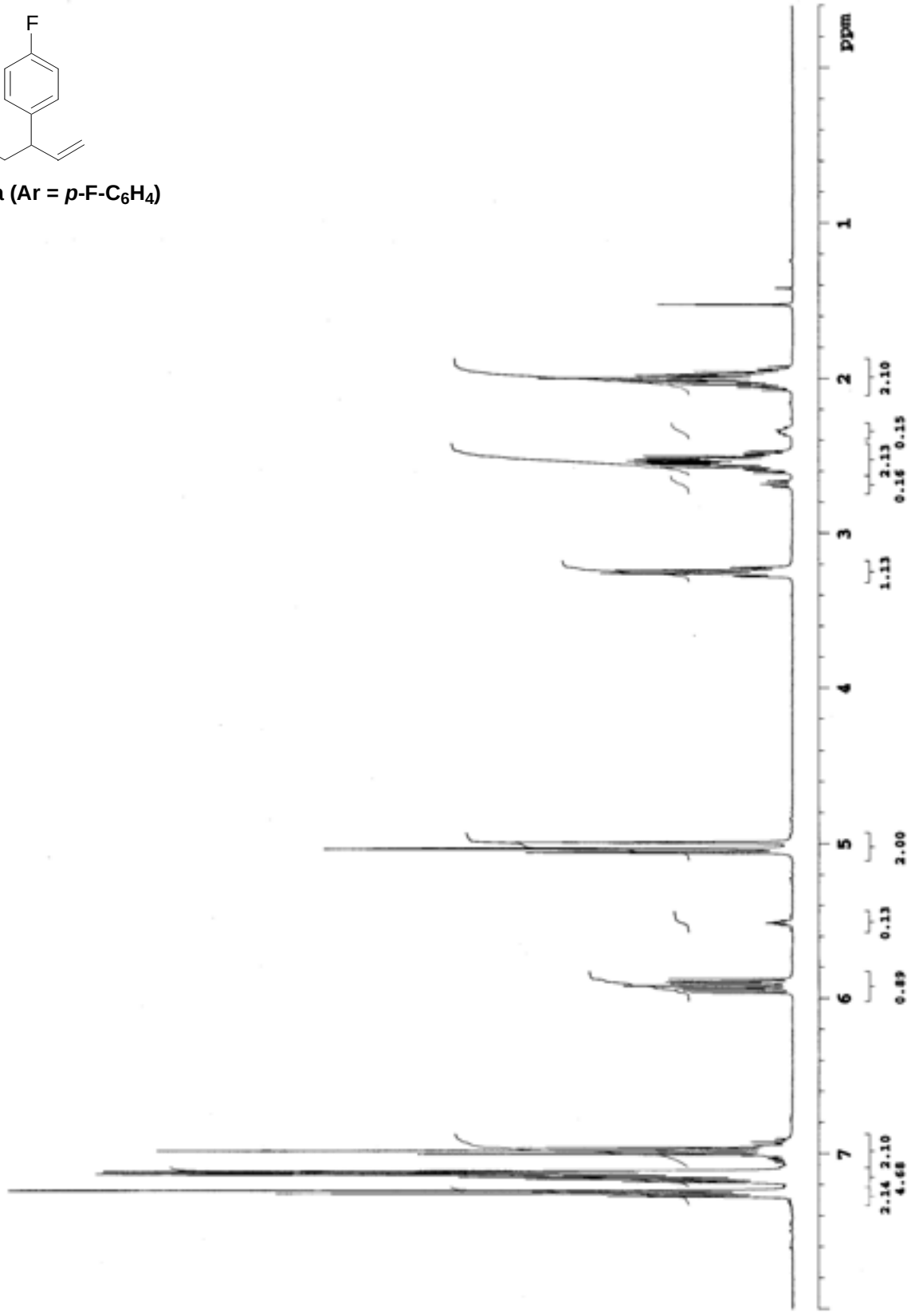

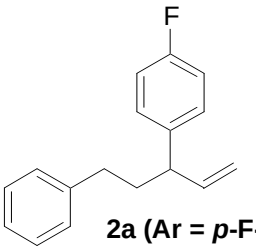

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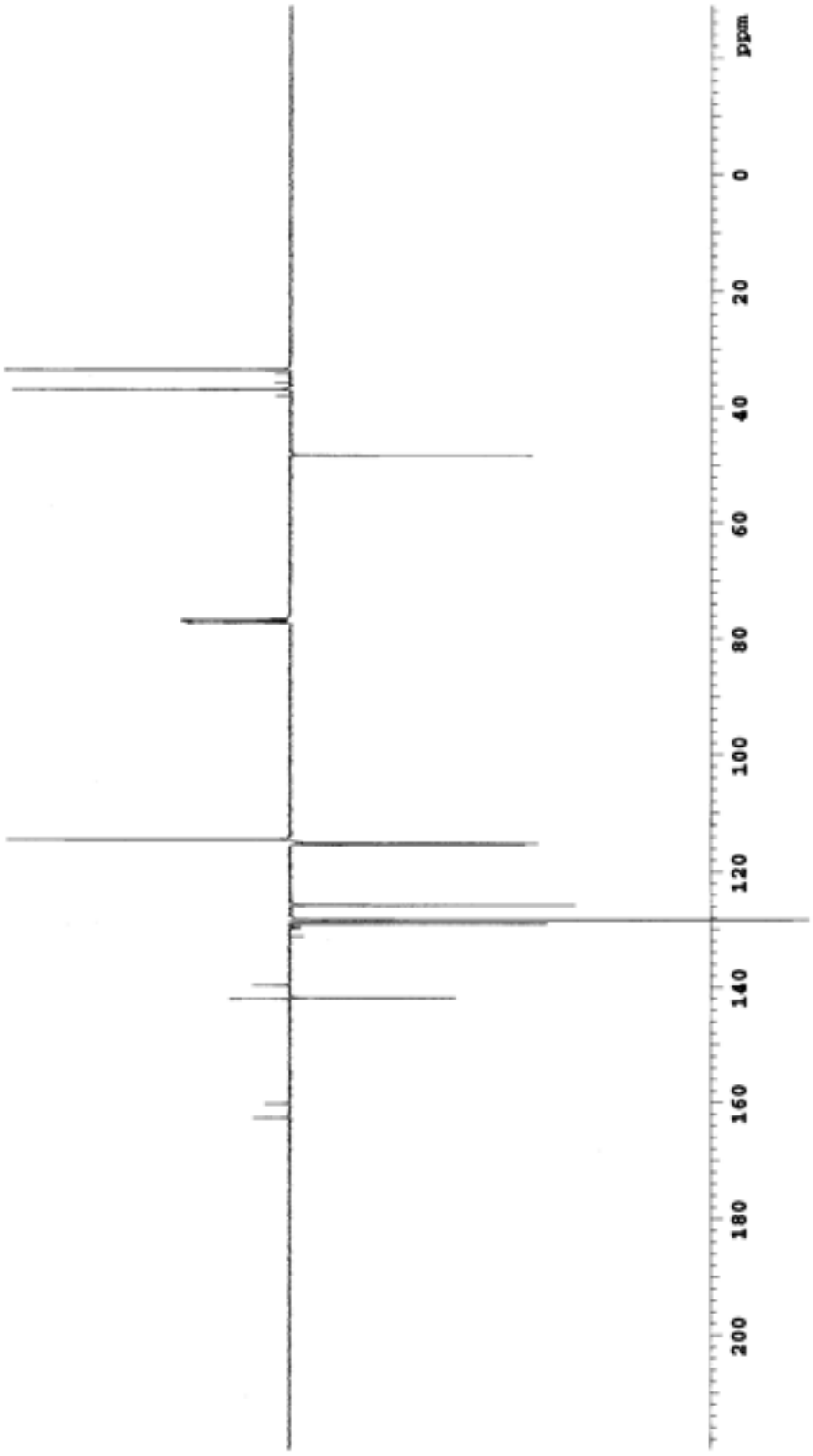

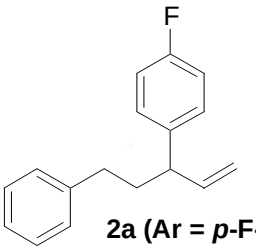

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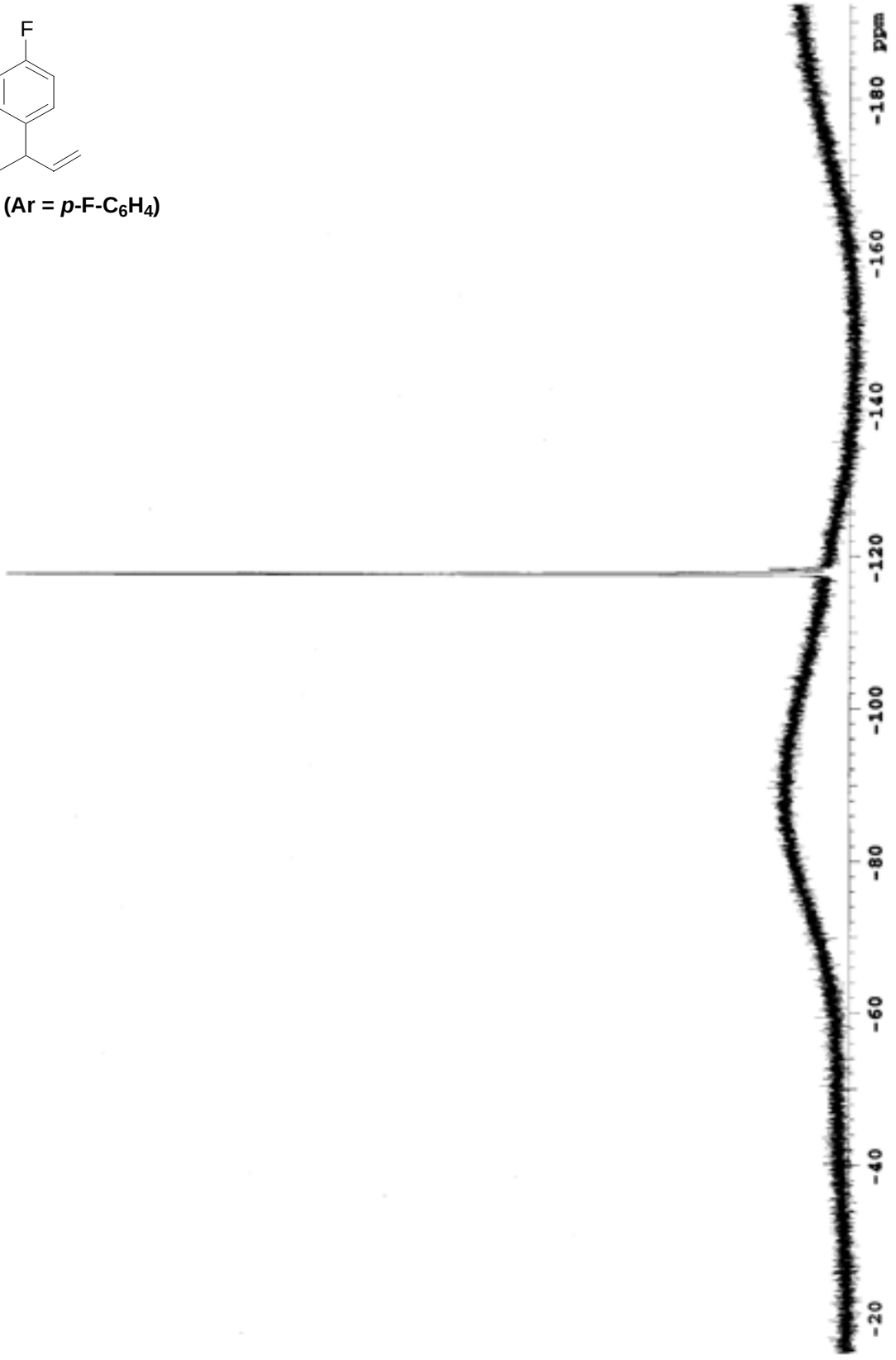

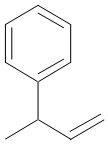

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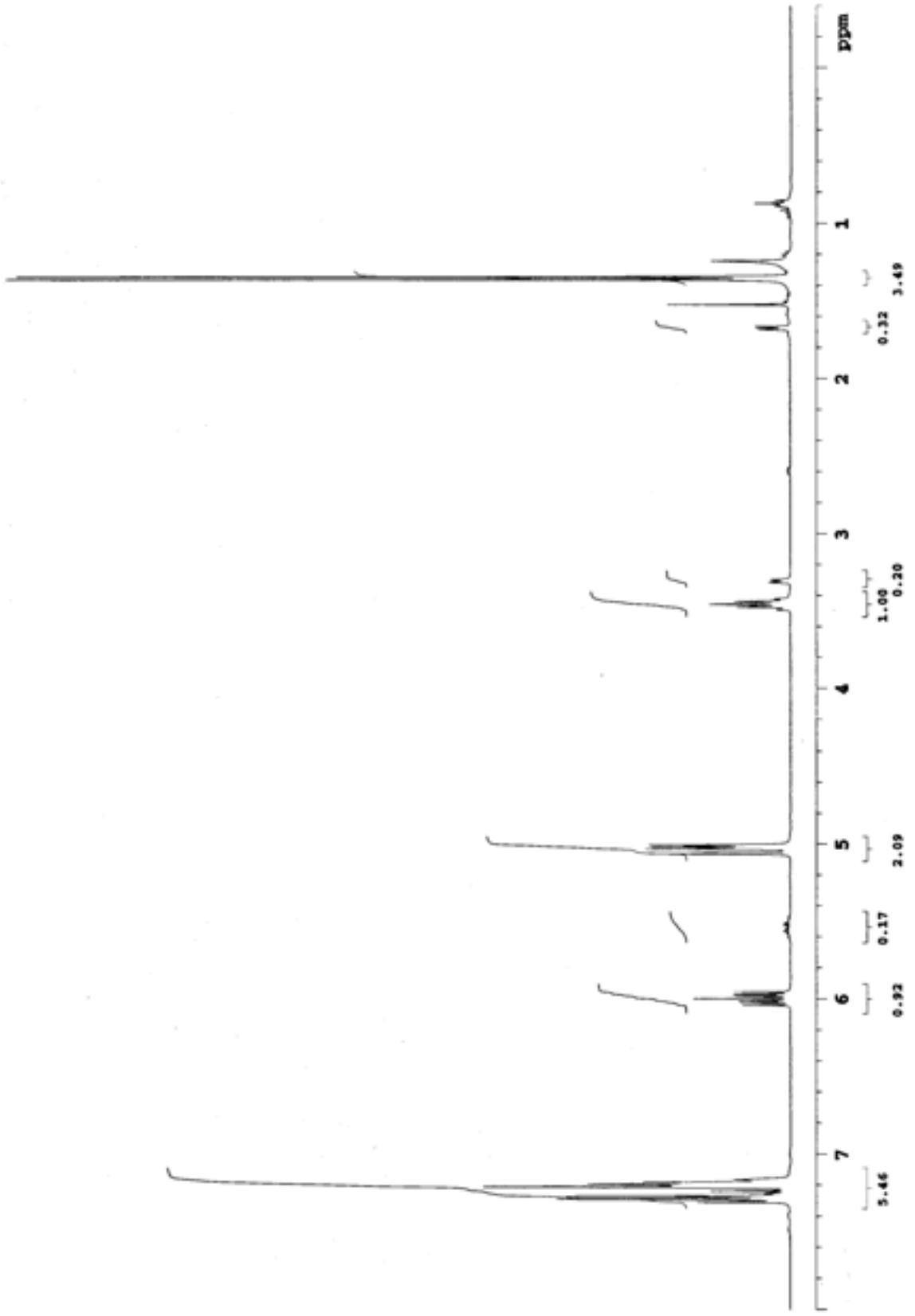

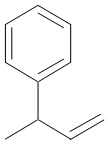

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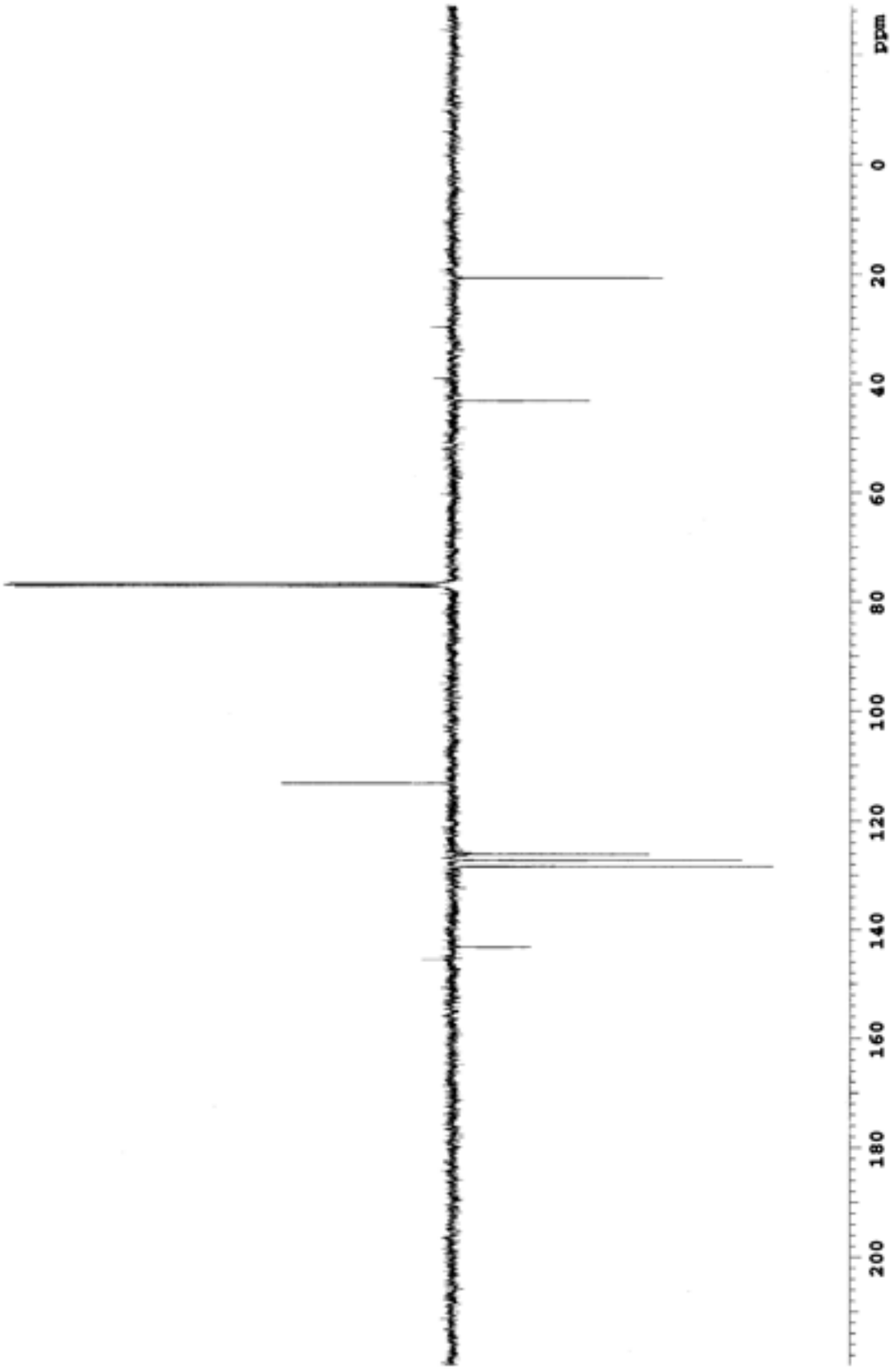

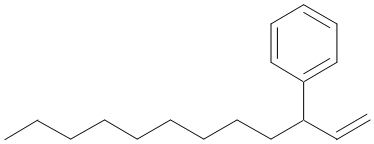

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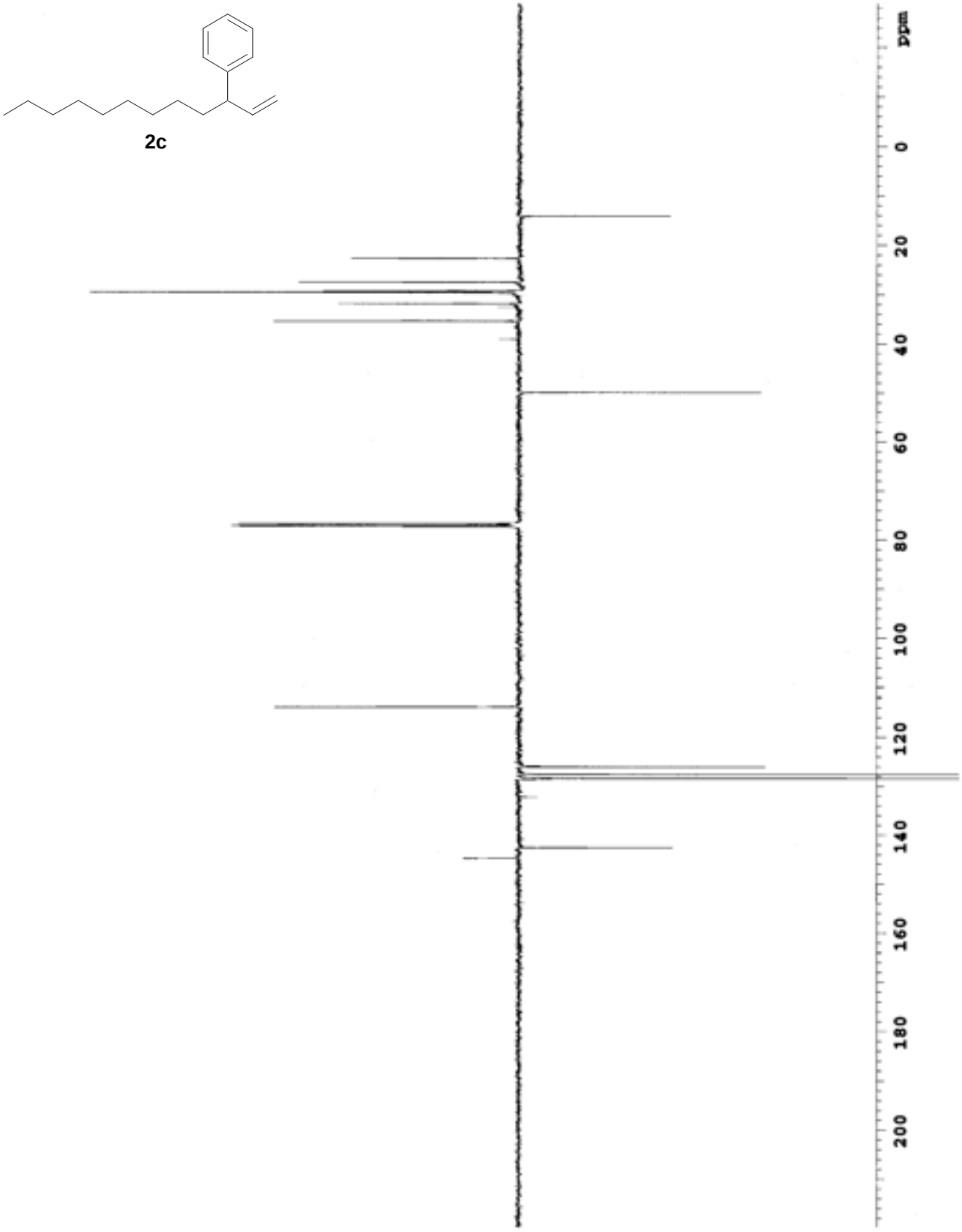
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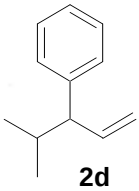

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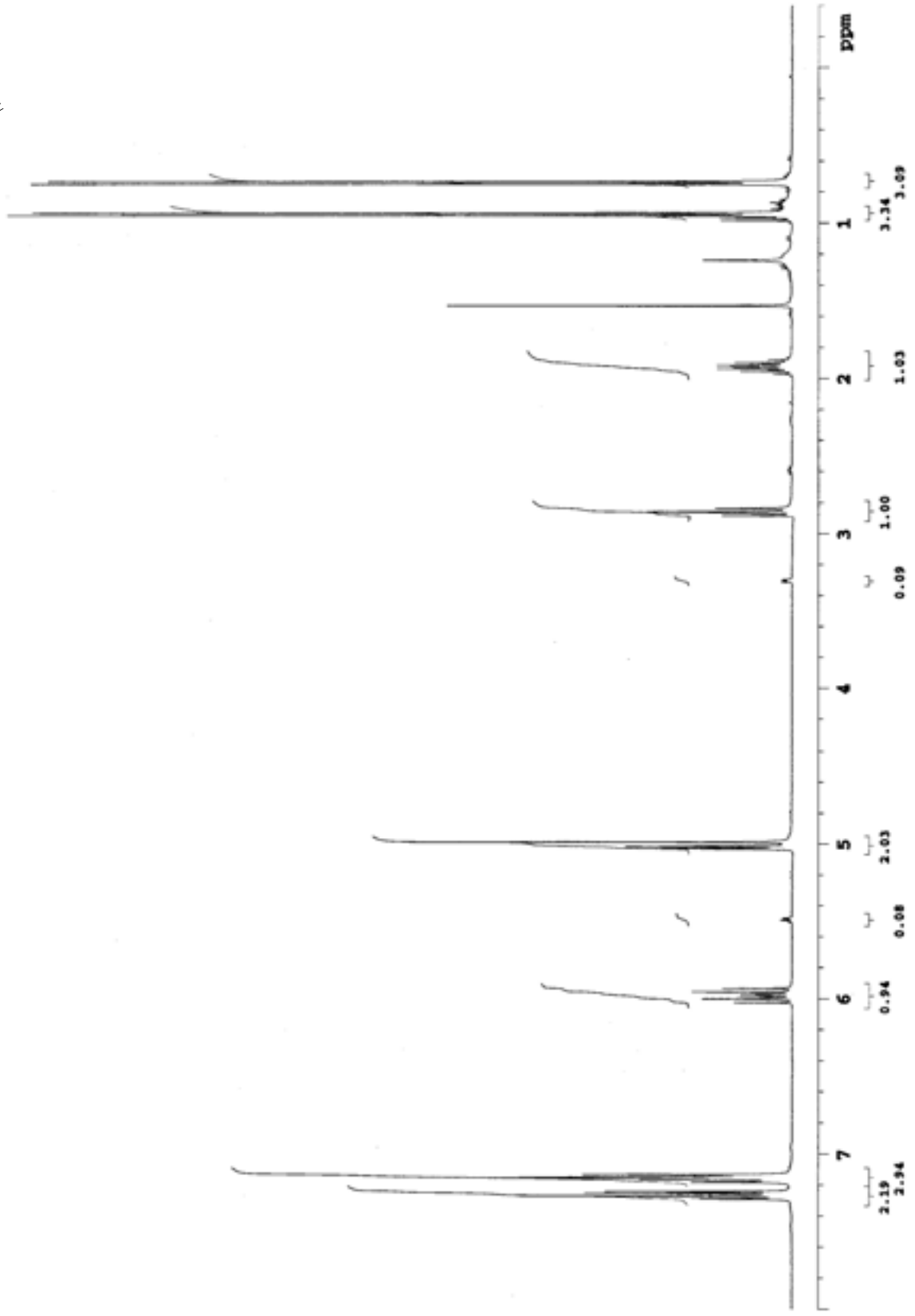

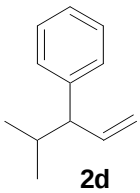

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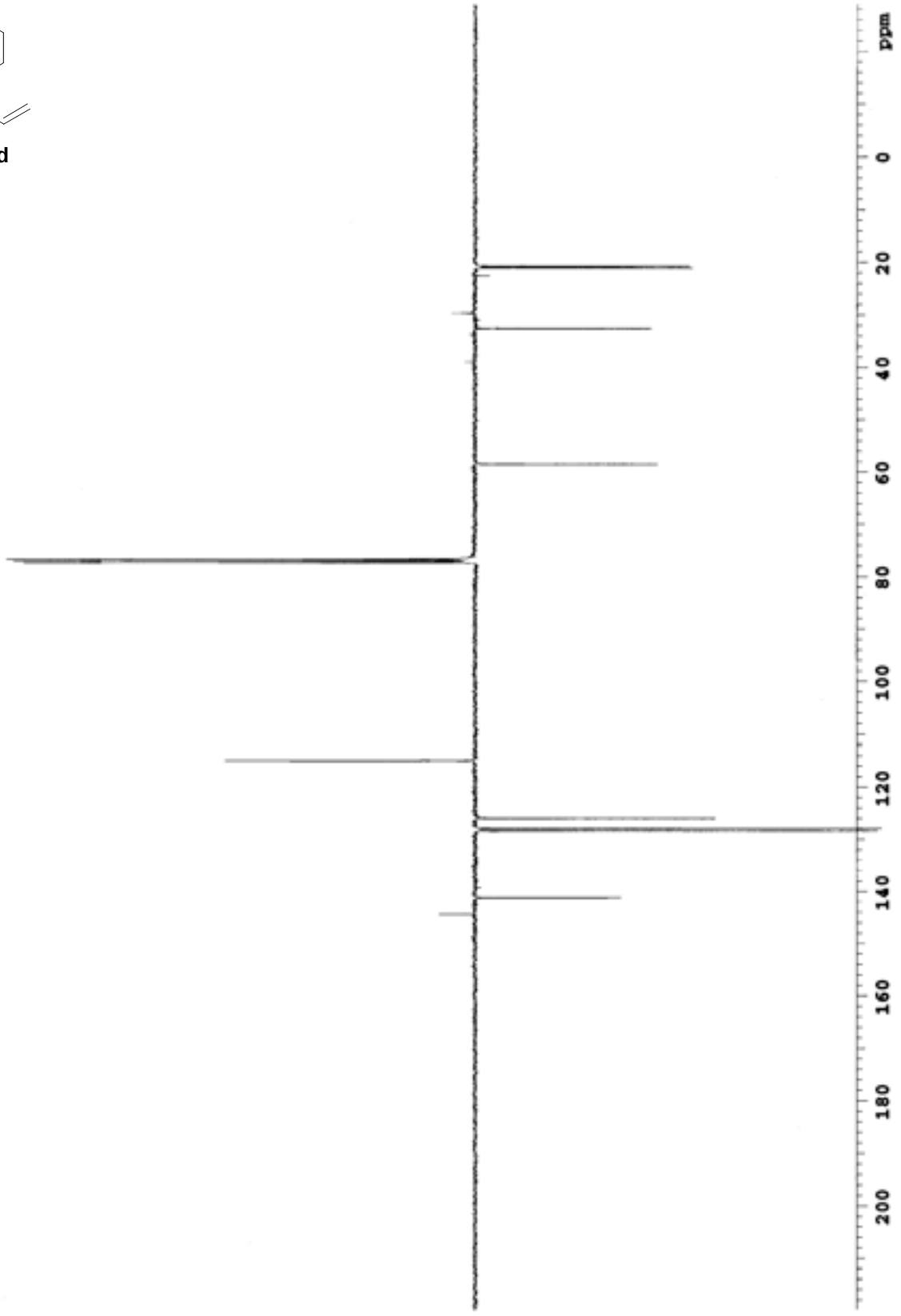

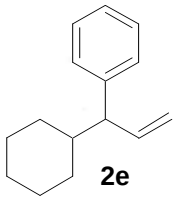

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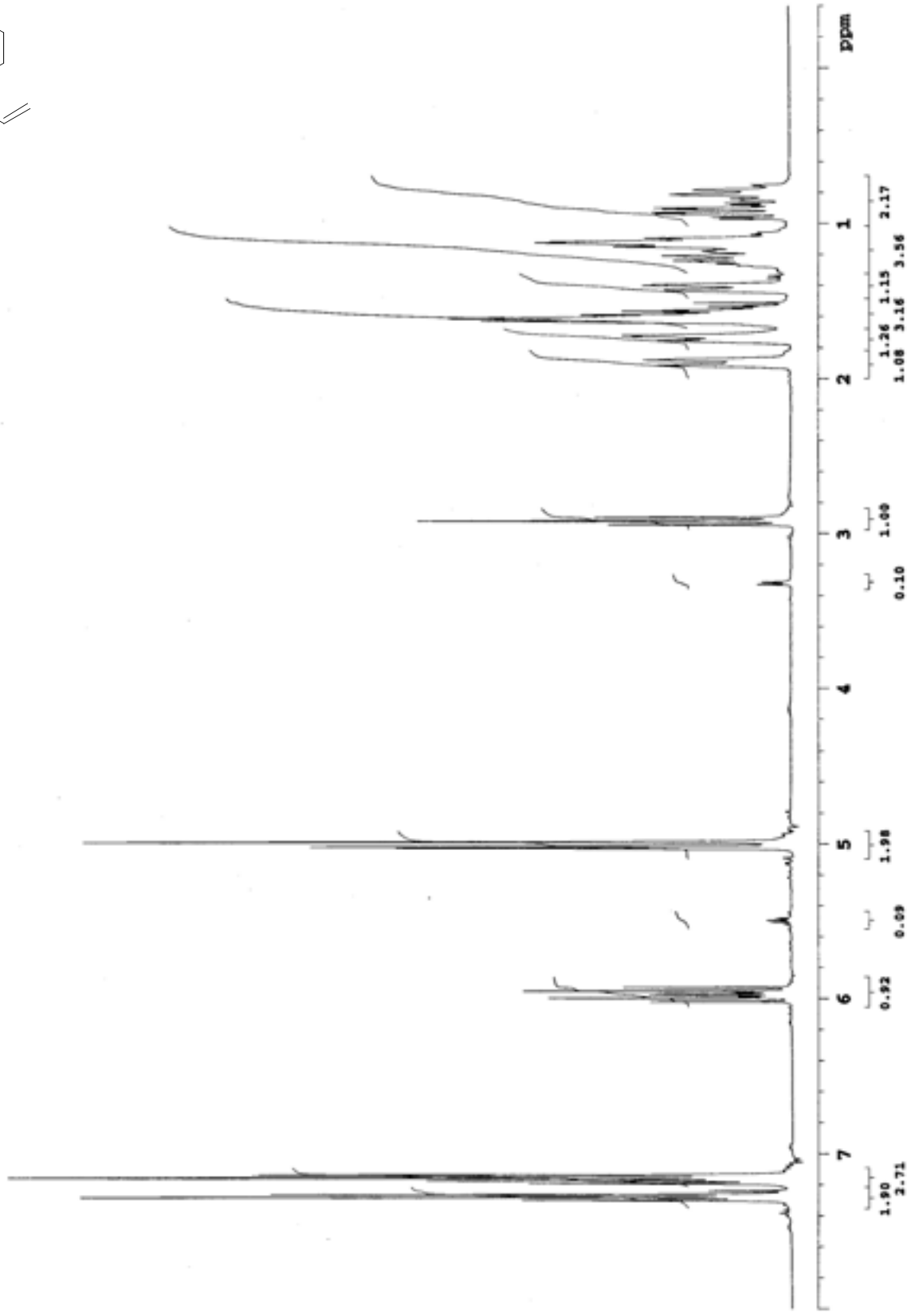

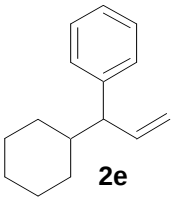

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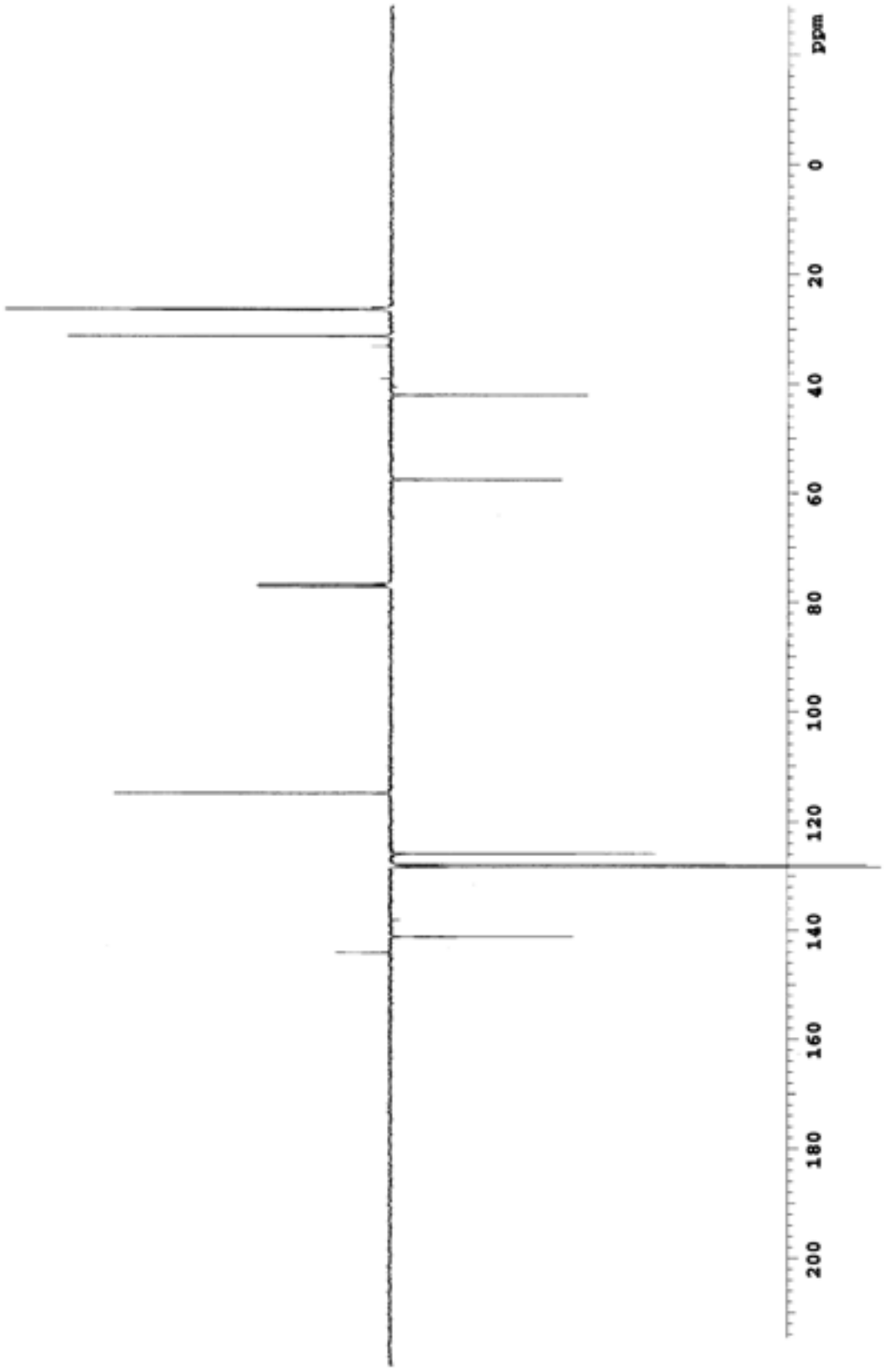

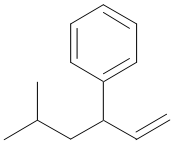

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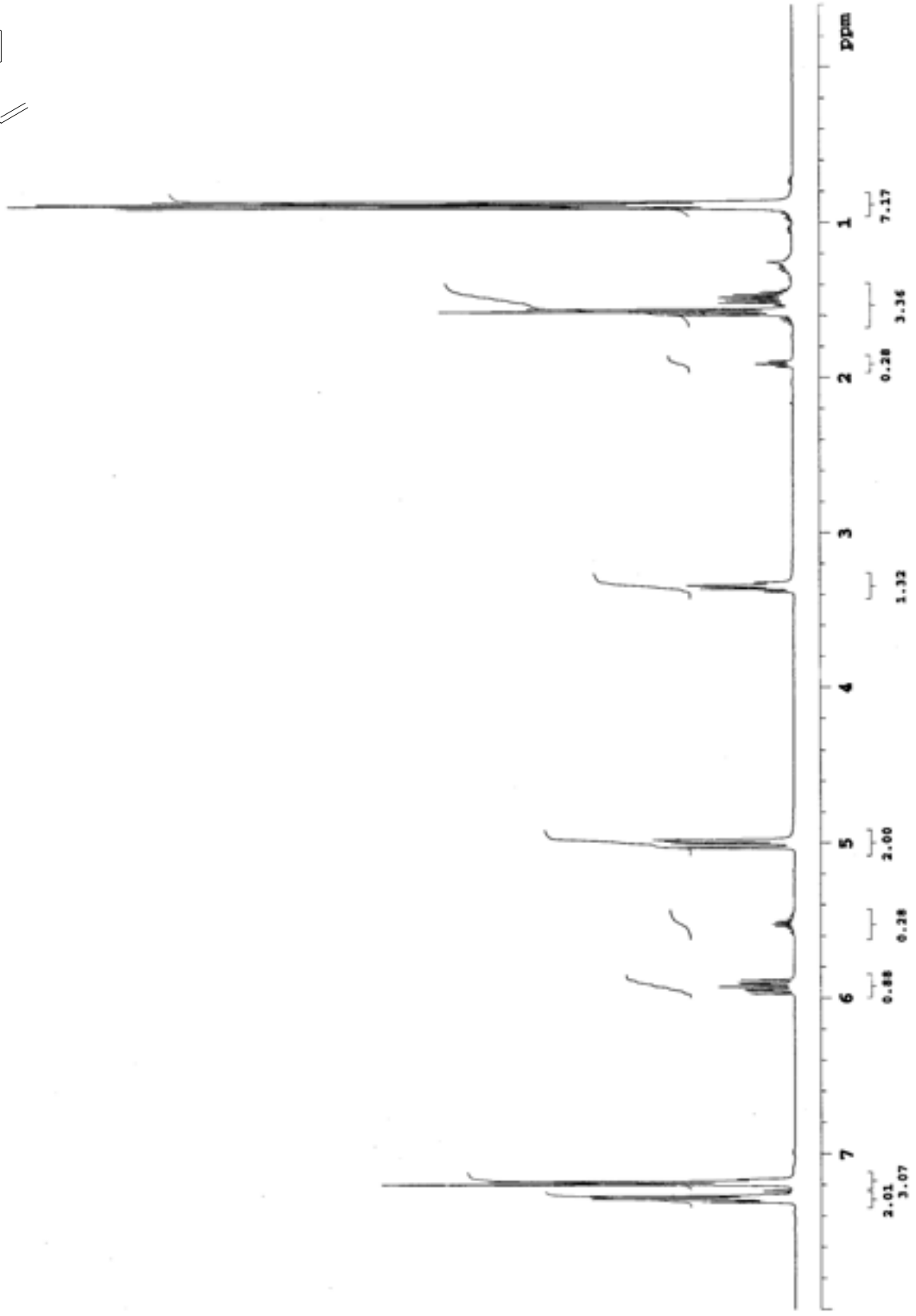

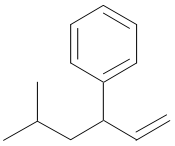

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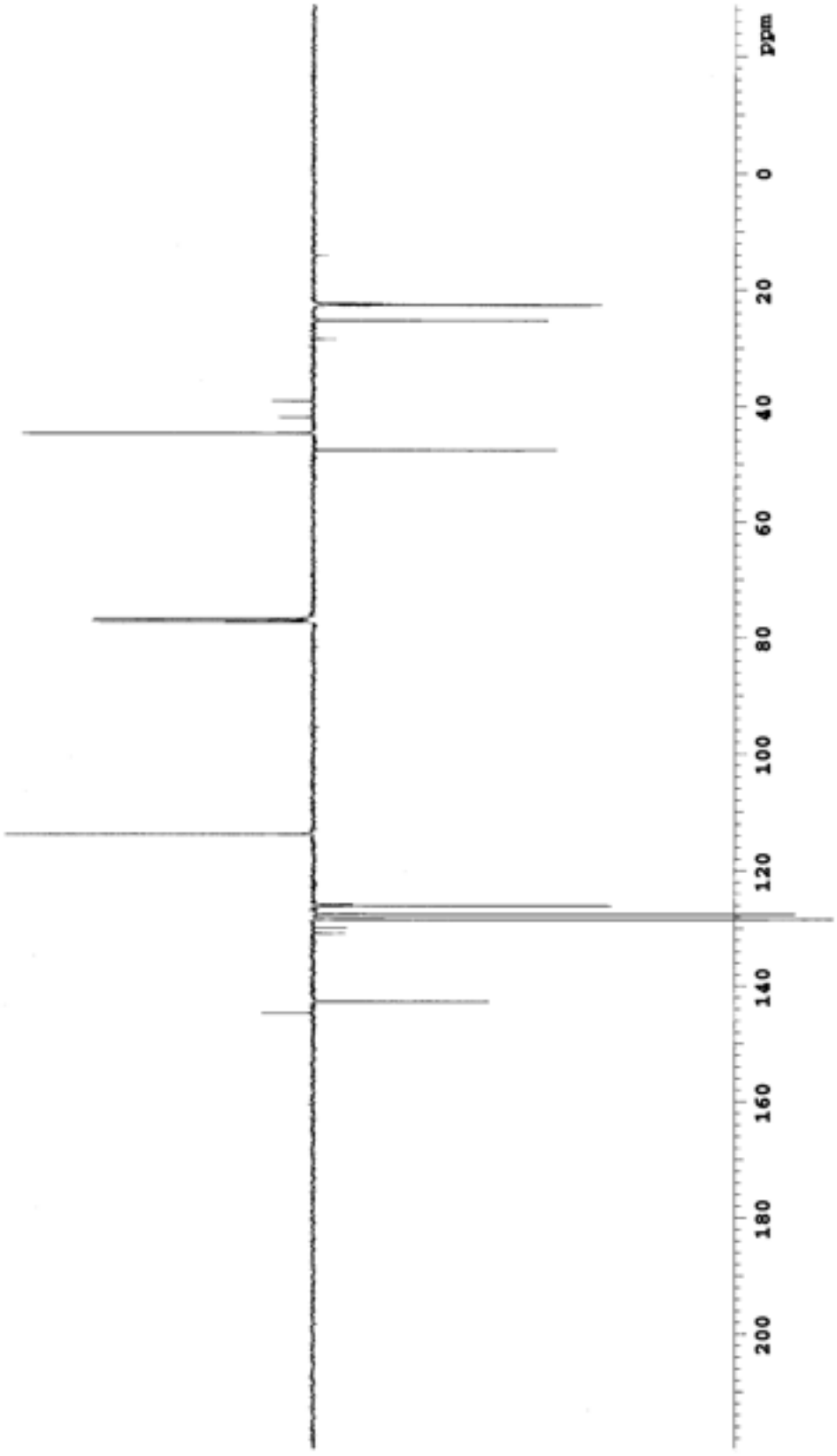

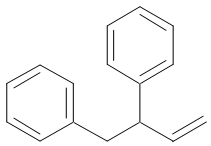

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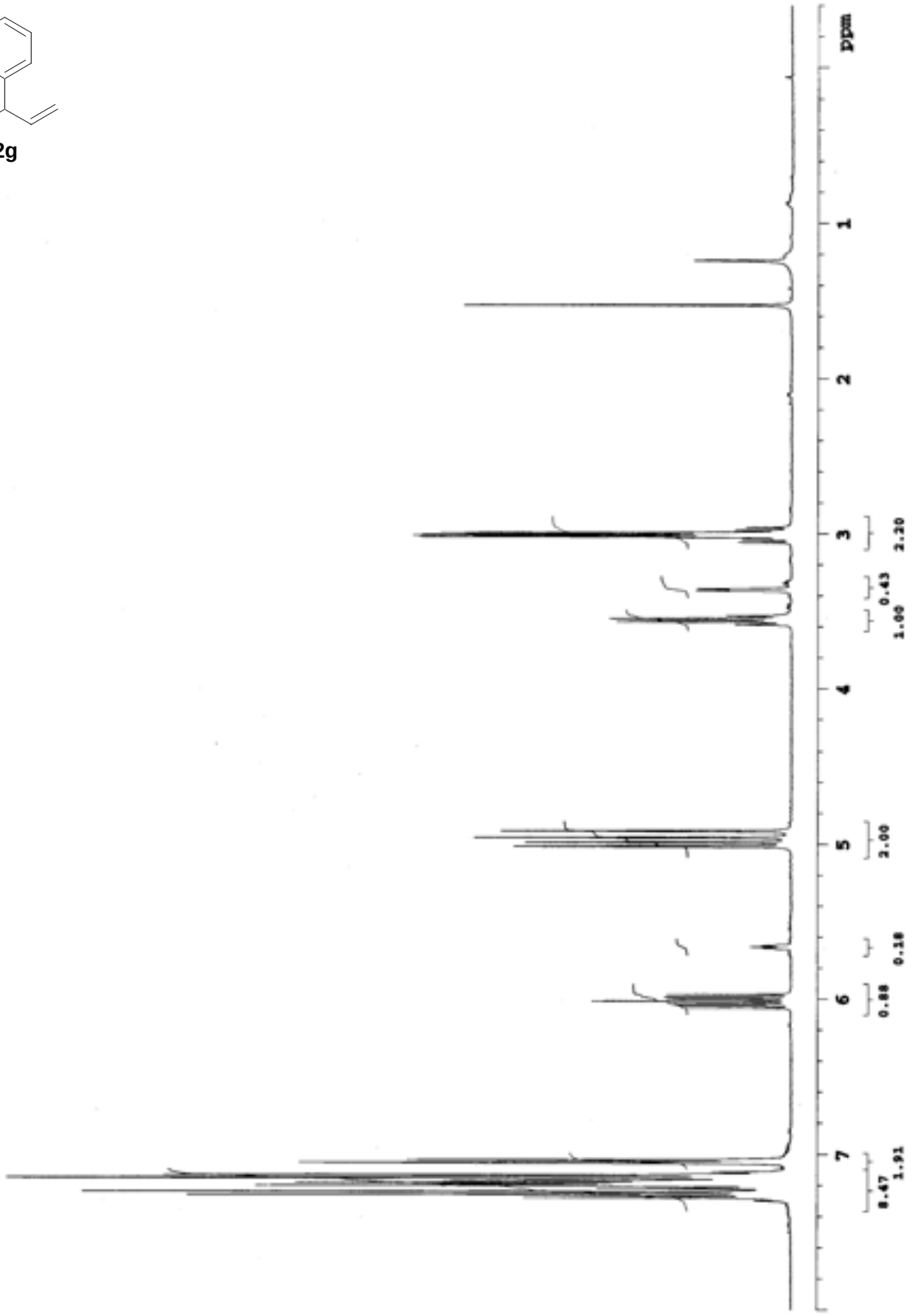

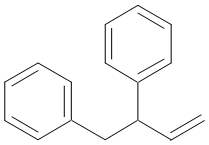

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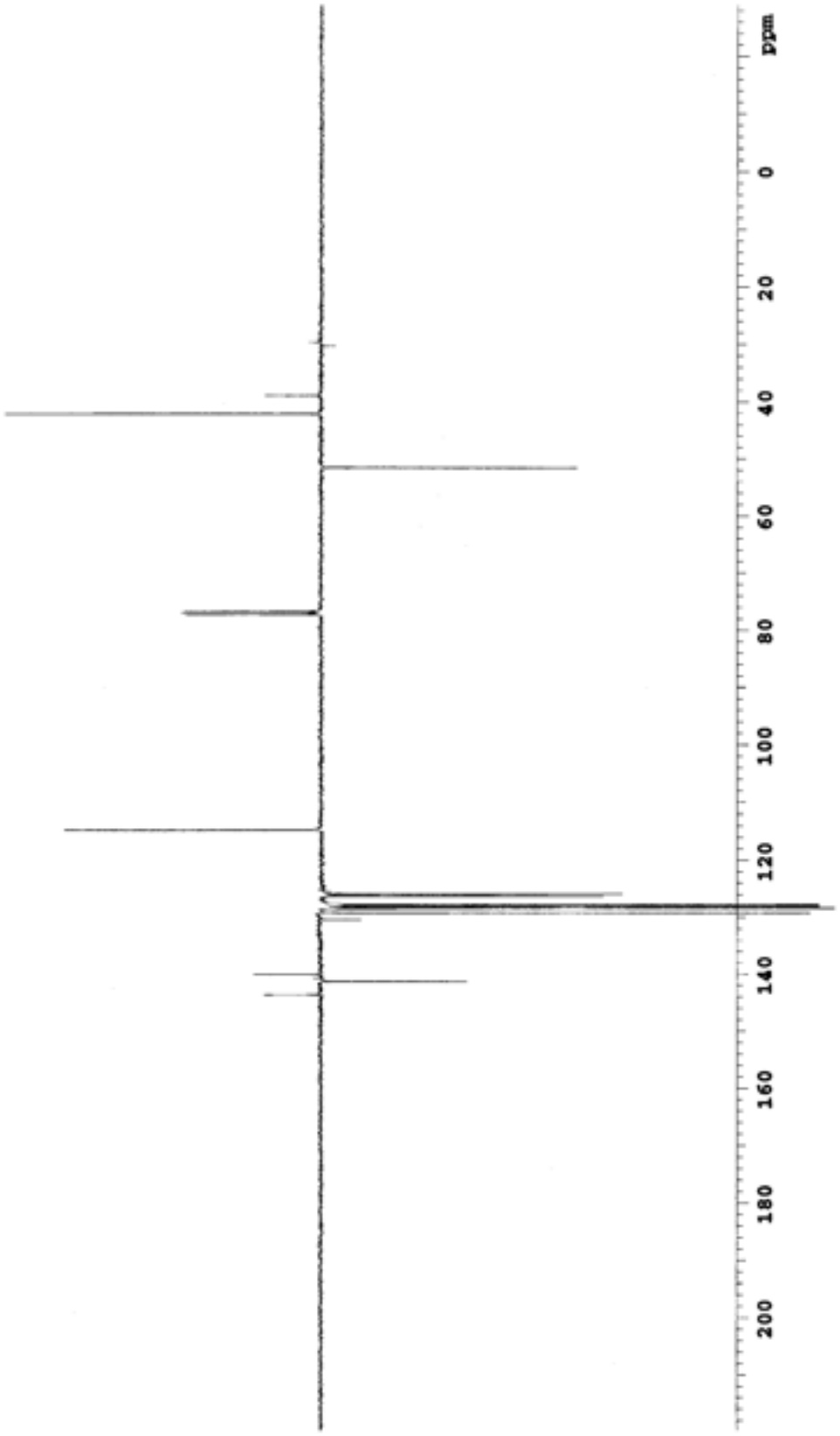

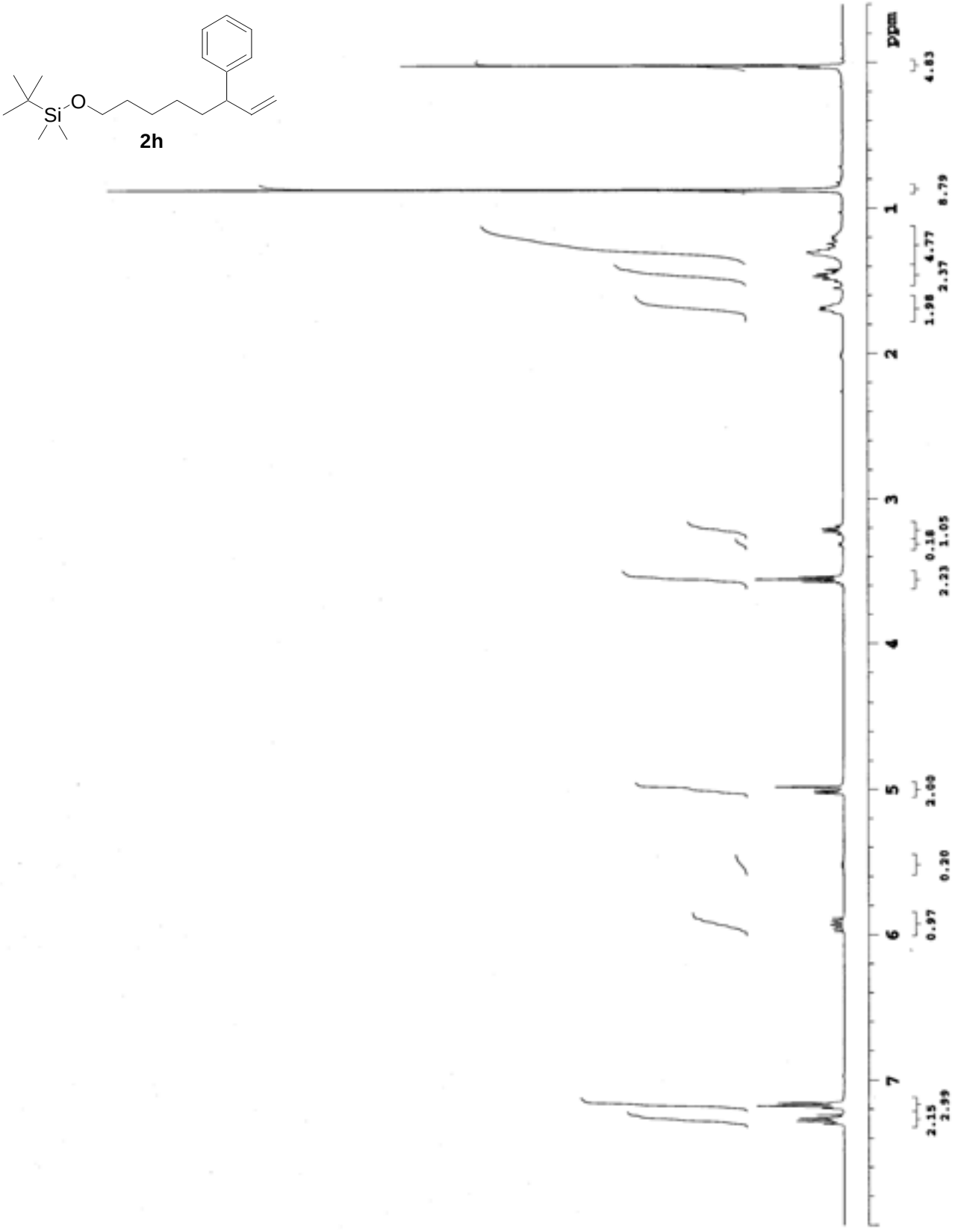
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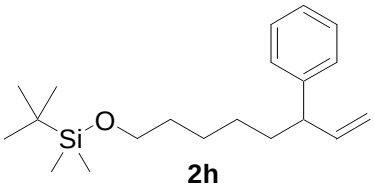

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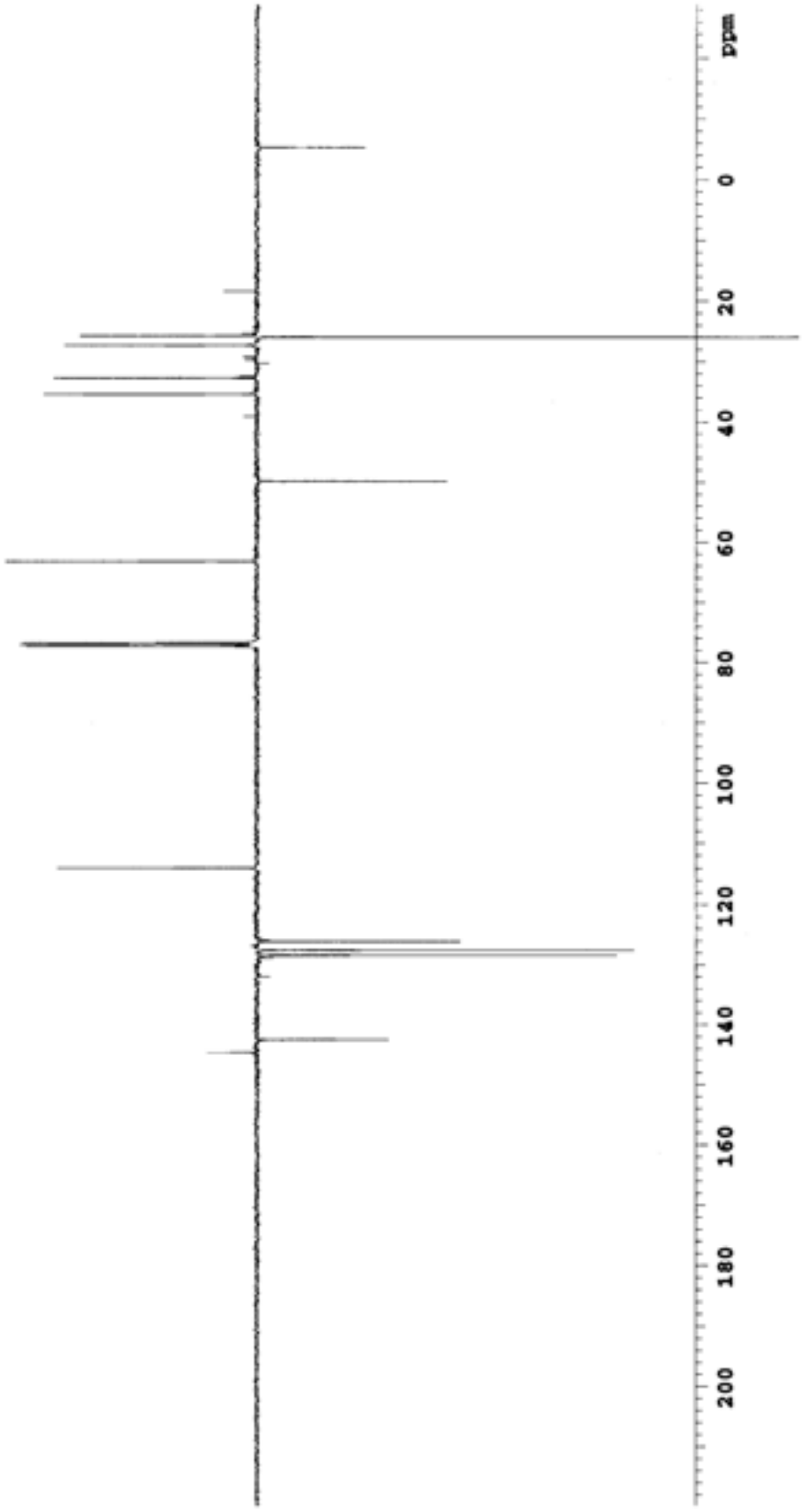

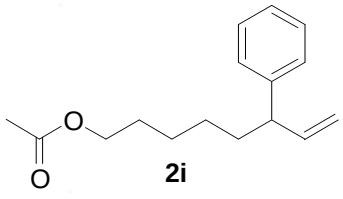

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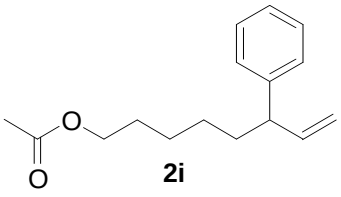

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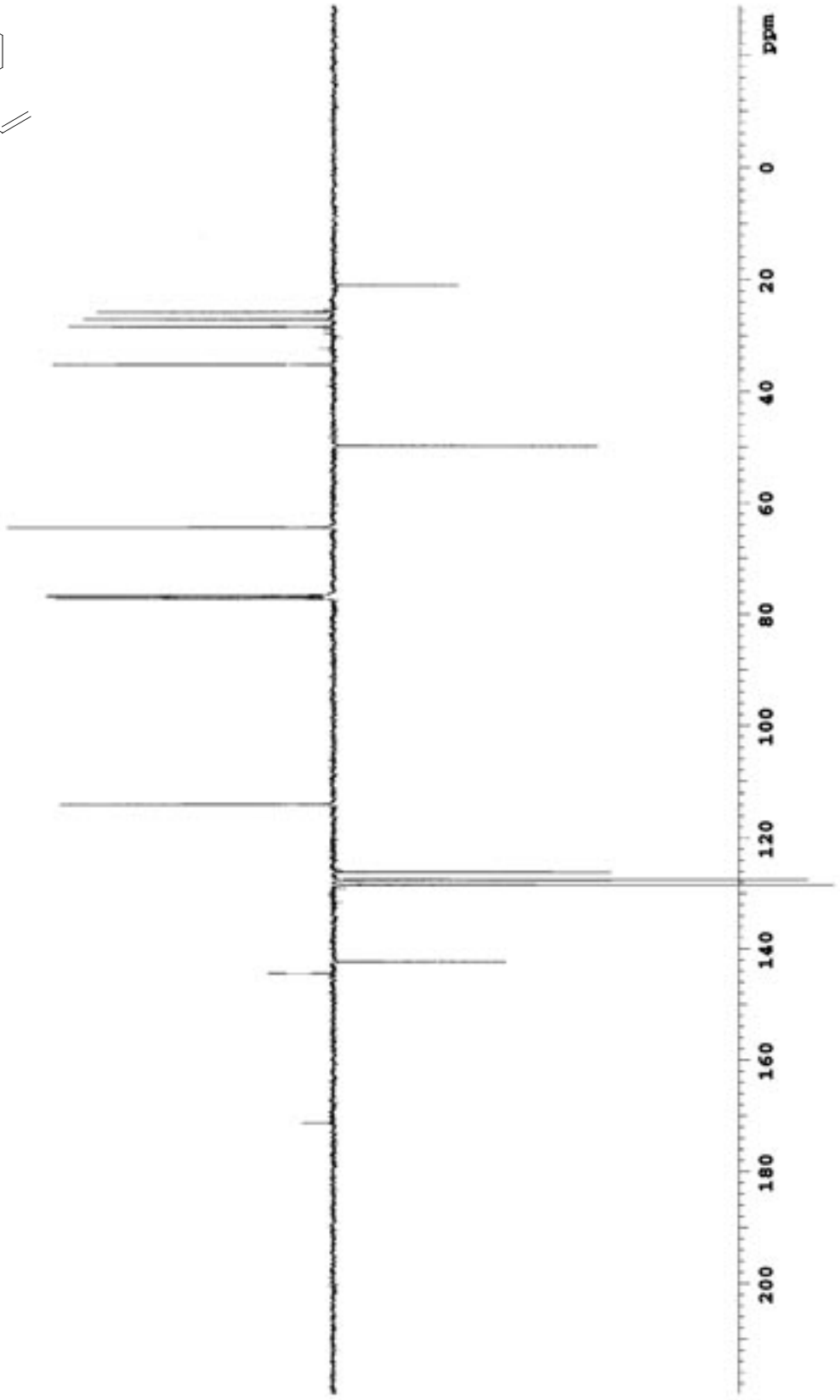

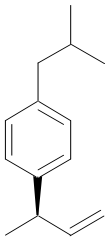

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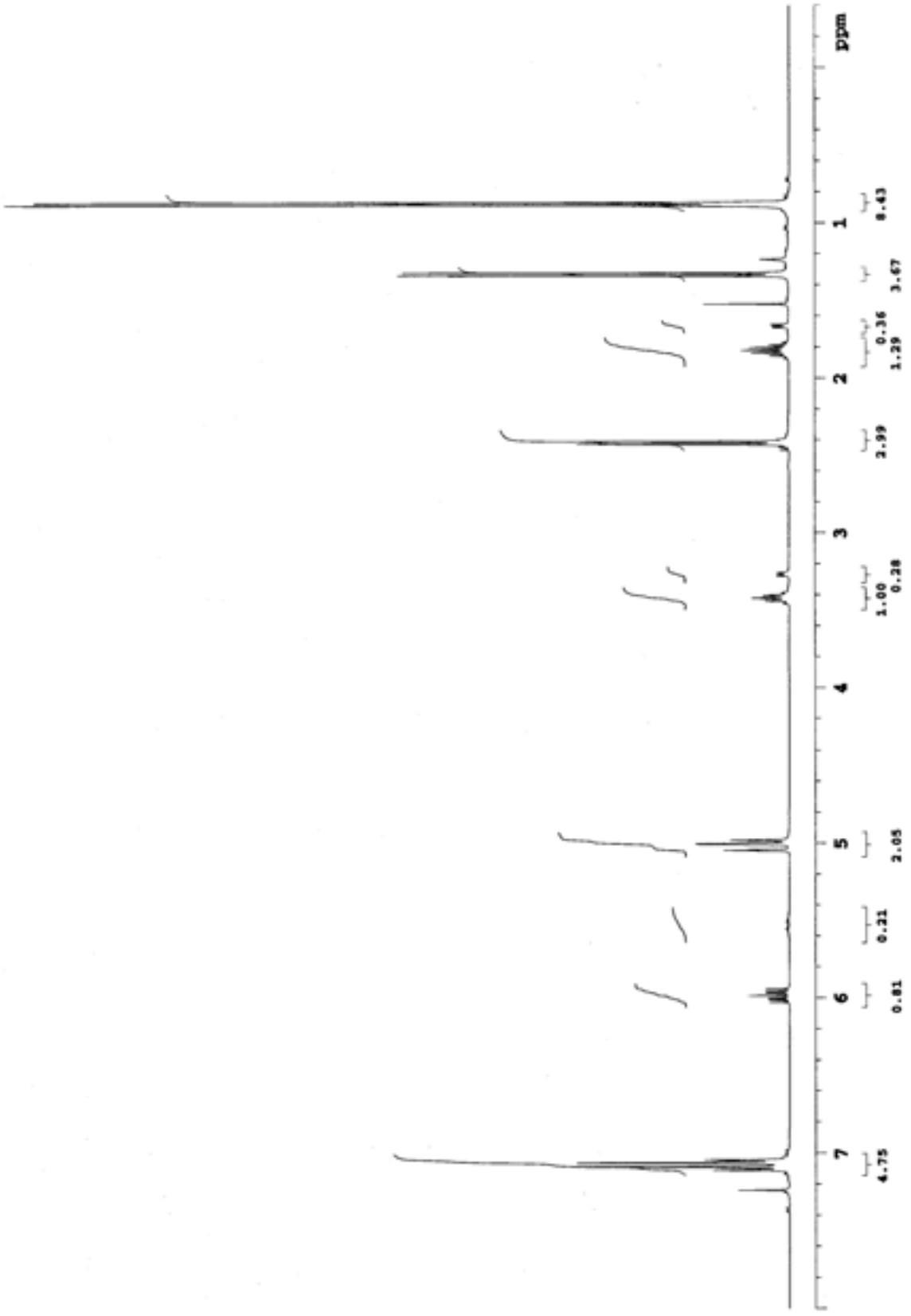

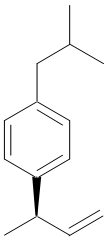

(*R*)-4