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Supporting Information

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Tetraarylphosphonium Salts as Novel Solubility Control Groups: Phosphonium Supported Triphenylphosphine and Azodicarboxylate Reagents

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Contents

General: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH_2Cl_2, benzene, DMF, CH_3CN, toluene, hexane, methanol) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et_3N, $ClCH_2CH_2Cl$, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F_{254}). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.[2] Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^1H, ^{13}C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a Bruker AV 300, AMX 300, AV 400, ARX 400, or DMX 600 spectrometer. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextuplet, m = multiplet and br = broad), coupling constant in Hz, integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, NOESY, HMQC and DEPT experiments. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal. Thermogravimetric experiments were done on a TGA Q500V5.3 Build 151.

(3-Bromophenyl)(diphenyl)phosphine (1).

To a solution of 1,3-dibromobenzene (7.4 mL, 61 mmol, 1.05 equiv) in THF (70 mL) at -90 °C was added *n*-BuLi (2.5 M in hexane, 25.5 mL, 64 mmol, 1.10 equiv) dropwise. The reaction mixture was stirred 45 min then diphenylchlorophosphine (10.7 mL, 58 mmol, 1.0 equiv) was added dropwise, and the resulting dark brown solution was warmed to room temperature for 15 min and filtered through a pad of *celite*. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (Et_2O/hexane, 0:100-5:95) to afford pure **1** (18.1g, 91%) as a viscous colorless oil.[3]

[3-(Diphenylphosphino)phenyl](triphenyl)phosphonium bromide (2).

To a solution of $NiBr_2$ (dry under vacuum for 2 h at 140 °C) (3.6 g, 16 mmol, 0.5 equiv) in benzonitrile (dry overnight over activated molecular sieves 4 Å) (250 mL) was added triphenylphosphine (26.0 g, 49 mmol, 3 equiv). The solution was heated under reflux 15 min and became dark green then was cooled to room temperature. Phosphine **1** (11.1 g, 32.5 mmol, 1.0 equiv) in benzonitrile (20 mL + 5 mL rinse) was added to the solution. The resulting solution was heated under reflux for 4 h then cooled to room temperature, and a 10% (w/w) KBr aqueous solution (250 mL) was added. The layers were separated, and the aqueous layer was washed twice with CH_2Cl_2 (250 mL). The organic solution was washed three times with water (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. To the resulting solution was added hexane (750 mL) to precipitate the crude product. The precipitate was washed with hexane and diluted with CH_2Cl_2 (20 mL). Et_2O (150 mL) was added to the resulting solution and the precipitate was filtered and purified by flash chromatography (0 to 10% MeOH/CH_2Cl_2) to afford **2** (>95% purity) as a white solid (15.3 g, 78%): **mp** 215-220 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60-6.80 (m, 29H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.1 (dd, *J* = 18.5, 11.1 Hz, 1C), 139.4 (dd, *J* = 22.1, 2.3 Hz, 1C), 137.2 (dd, *J* = 13.2, 11.0 Hz, 1C), 135.4 (d, *J* = 2.6 Hz, 3C), 134.5 (d, *J* = 10.6 Hz, 2C), 133.9 (d, *J* = 10.3 Hz, 6C), 133.8 (dd, *J* = 10.4, 1.1 Hz, 1C), 133.4 (d, *J* = 20.2 Hz, 4C), 130.4 (d, *J* = 12.8 Hz, 6C), 129.7 (dd, *J* = 12.6, 6.4 Hz, 1C), 129.5 (s, 2C), 128.7 (d, *J* = 7.4 Hz, 4C), 118.1 (dd, *J* = 86.9, 3.1 Hz, 1C), 116.7 (d, *J* = 88.7 Hz, 3C); **^{31}P NMR** (162 MHZ, $CDCl_3$): δ 23.2, -4.5; **IR** (film) 1974, 1913, 1827, 1585, 1474, 1432, 1433, 1386, 1108 cm^{-1}; **LRMS** (APCI, Pos) calc. for $C_{36}H_{29}P_2$ $[M]^+$: 523.2, found 523.1.

[3-(Diphenylphosphino)phenyl](triphenyl)phosphonium perchlorate (3).
To phosphonium salt **2** (15.0 g, 25 mmol, 1.0 equiv) in CH_3CN (30 mL) and CH_2Cl_2 (10 mL) was added $LiClO_4{\bullet}3H_2O$ (4.2 g, 26 mmol, 1.05 equiv). After 15 min, the mixture was concentrated under reduced pressure and diluted with CH_2Cl_2 (200 mL). The resulting mixture was washed with water (100 mL). The aqueous layer was washed with CH_2Cl_2 (100 mL). The organic solution was washed three times with water (50mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (30 mL) and was crunched with Et_2O (150 mL). This operation was repeated twice to afford pure **3** as a white solid (14.7 g, 95%): **mp** 160-165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): see **2**; **^{13}C NMR** (100 MHz, $CDCl_3$): see **2**; **^{31}P NMR** (162 MHZ, $CDCl_3$): see **2**; **IR** (film) 1585, 1483, 1435, 1388, 1079 cm^{-1}; **LRMS** (APCI, Pos) see **2**; **LRMS** (APCI, Neg) calc. for $^{35}ClO_4$ $[M]^-$: 99.0, found 99.0; calc. for $^{37}ClO_4$ $[M]^-$: 101.0, found 101.1.

[3-(Diphenylphosphino)phenyl](triphenyl)phosphonium hexafluorophosphate (4).
To perchlorate **3** (1.24 g, 2 mmol, 1.0 equiv) in CH_3CN (8 mL) and H_2O (4 mL) was added KPF_6 (442 mg, 2.4 mmol, 1.2 equiv). After 1 h, the mixture was concentrated under reduced pressure and diluted with CH_2Cl_2 (50 mL). The resulting mixture was washed with water (20 mL). The aqueous layer was washed with CH_2Cl_2 (10 mL). The organic solution was washed twice with water (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give pure compound **4** (1.27 g, 95%) as a solid foam: **mp** 80-85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): see **2**; **^{13}C NMR** (100 MHz, $CDCl_3$): see **2**; **^{31}P NMR** (162 MH_Z, $CDCl_3$): δ 23.2, -4.5, -143.9 (sept, *J* = 713 Hz); **^{19}F NMR** (376 MH_Z, $CDCl_3$): δ -76.3 (d, *J* = 713 Hz); **IR** (film) 1586, 1483, 1436, 1388, 1107, 829 cm^{-1}; **LRMS** (APCI, Pos) see **2**; **LRMS** (APCI, Neg) calc. for PF_6 $[M]^-$: 145.0, found 145.0.

[3-(Diphenylphosphoryl)phenyl](triphenyl)phosphonium perchlorate (5).
White solid: **mp** 214-216 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.30 (m, 29H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.3 (dd, *J* = 9.7, 2.9 Hz, 1C), 137.5 (dd, *J* = 10.3, 2.3 Hz, 1C), 137.0 (t, *J* = 11.0 Hz, 1C), 136.6 (dd, *J* = 98.3, 11.2 Hz, 1C), 135.6 (d, *J* = 2.7 Hz, 3C), 134.2 (d, *J* = 10.3 Hz, 6C), 132.5 (d, *J* = 2.5 Hz, 2C), 131.7 (d, *J* = 10.0 Hz, 4C), 130.9 (t, *J* = 11.5 Hz, 1C), 130.6 (d, *J* = 10.6 Hz, 6C), 130.1 (d, *J* = 105.2 Hz, 2C), 128.7 (d, *J* = 12.8 Hz, 4C), 119.0 (dd, *J* = 89.0, 11.6 Hz, 1C), 116.5 (d, *J* = 89.0 Hz, 3C); **^{31}P NMR** (162 MHZ, $CDCl_3$): δ 28.3, 23.3;

IR (film) 1585, 1483, 1435, 1388, 1079 cm^{-1}; **LRMS** (APCI, Pos) calc. for $C_{36}H_{29}P_2O$ $[M]^+$: 539.2, found 539.1.

Recycling of the phosphine oxide (5).

To a 0 °C solution of **5** (200 mg, 0.30 mmol, 1.0 equiv) in benzonitrile (3 mL, 0.1 M) was added *N,N*-dimethylaniline (160 μL, 1.2 mmol, 4.0 equiv) and trichlorosilane (63 μL, 0.62 mmol, 2.0 equiv). The solution was heated to 170 °C over 2 h and it became blue. Precipitation was induced by adding hexane (20 mL). The crude product was redissolved in CH_2Cl_2 (1 mL) and precipitated by adding Et_2O (10 mL). This operation was repeated twice to afford a crude blue solid.

To this crude solid (ca 0.30 mmol, 1.0 equiv) in CH_3CN (1.5 mL) was added $LiClO_4$ (32 mg, 0.30 mmol, 1.0 equiv). After 2 h, the mixture was concentrated under reduced pressure and diluted with CH_2Cl_2 (10 mL). The resulting mixture was washed with water (5 mL). The aqueous layer was washed with CH_2Cl_2 (2 mL). The organic solution was washed three times with water (2 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (1 mL) and was precipitated with Et_2O (10 mL) to afford pure **3** as a white solid (173 mg, 93%).

Typical procedure for the *gem*-dibromoalkene formation.

(4,4-Dibromobut-3-enyl)benzene (6).

To phosphine **3** (1.5 g, 2.5 mmol, 2.5 equiv) under an argon atmosphere was added CH_2Cl_2 (5 mL), CBr_4 (825 mg, 2.5 mmol, 2.5 equiv) and zinc dust < 10 micron (163 mg, 2.5 mmol, 2.5 equiv). The mixture was heated at reflux for 30 min and then cooled to 0 °C. 3-Phenylpropanal (134 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was added. After 3 h of stirring at room temperature, the mixture was filtered on a small pad of silica gel, rinsed with CH_2Cl_2 (2 mL) and with Et_2O (40 mL) that induced the precipitation of the phosphonium salt. The mixture was filtered on a small pad of *celite*. The precipitate was dissolved in CH_2Cl_2 (5 mL) and precipitated by the addition of Et_2O (25 mL). The mixture was filtered on the same pad of *celite* used for the preceding filtration. This operation was repeated once, and the organic liquid phase was concentrated *in vacuo* to afford the nearly pure compound. A quick flash chromatography on silica gel (2% diethyl ether/pentane) gave the *gem*-dibromo olefin **6** (274 mg, 94%).[4]

(2,2-Dibromovinyl)cyclohexane (7).

The title compound (242 mg, 90%)[5] was obtained from cyclohexanecarbaldehyde (112 mg, 1.0 mmol) according to the typical procedure described above.

1,1-Dibromooct-1-ene (8).

The title compound (243 mg, 90%)[6] was obtained from heptanal (114 mg, 1.0 mmol) according to the typical procedure described above.

(2,2-Dibromovinyl)benzene (9).

The title compounds (251 mg, 96%)[7] was obtained from benzaldehyde (106 mg, 1.0 mmol) according to the typical procedure described above.

4-(2,2-Dibromovinyl)benzonitrile (10).

The title compound (276 mg, 96%)[7] was obtained from 4-formylbenzonitrile (131mg, 1.0 mmol) according to the typical procedure described above.

1-Bromo-4-(2,2-dibromovinyl)benzene (11).

The title compound (335 mg, 98%)[8] was obtained from 4-bromobenzaldehyde (185 mg, 1.0 mmol) according to the typical procedure describe above with 3 equiv of each reagents.

1,4-bis(2,2-Dibromovinyl)benzene (12).

The title compound (211 mg, 95%)[9] was obtained from terephthaladehyde (67 mg, 0.5 mmol) according to the typical procedure described above with 6 equiv of each reagent.

4-(2,2-Dibromovinyl)benzaldehyde (13).

The title compound (246 mg, 85%) was obtained from 4-(diethoxymethyl)benzaldehyde (208 mg, 1.0 mmol) according to the typical procedure described above.

White solid: **mp** 60-65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.48 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.5, 140.9, 135.9, 135.8, 129.8, 129.0, 92.8; **IR** (film) 1691, 1587, 1419, 1213, 811 cm^{-1}; **GCMS** (EI) calc. for $C_9H_6{}^{79}Br^{79}BrO$ $[M+H]^+$: 288.9, found 289.0; calc. for $C_9H_6{}^{79}Br^{81}BrO$ $[M+1]^+$: 290.9, found 291.0; calc. for $C_9H_6{}^{81}Br^{81}BrO$ $[M+1]^+$: 292.9, found 293.0.

[(5,5-Dibromopent-4-enyl)oxy](triisopropyl)silane (14).

The title compound (385 mg, 96%)[10] was obtained from 4-(triisopropylsilyloxy)butanal (244 mg, 1.0 mmol) according to the typical procedure described above.

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-nitrobenzoate (15).

(-)-Menthol ((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol) (156 mg, 1.0 mmol, 1.0 equiv) and phosphine **3** (1.0 g, 1.6 mmol, 1.6 equiv) were dissolved in CH_2Cl_2 (5 mL) and then toluene (10 mL) was added. The solution was cooled to -5 °C and DEAD (255 μL, 1.6 mmol, 1.6 equiv) was added dropwise over 5 min. Then 4-nitrobenzoic acid (220 mg, 1.3 mmol, 1.3 equiv) was added and the solution was warmed slowly to room temperature over 3 h during which time a white precipitate appeared (phosphine oxide). After 9 h, Et_2O (25 mL) was added to the solution and the resulting mixture was filtered through a cotton pad and concentrated under reduced pressure. The resulting crude product was dissolved in CH_2Cl_2 (1 mL) and hexane (9 mL) was added. The hydrazine and 4-nitrobenzoic acid residues precipitated and the resulting mixture was filtered through cotton pad, concentrated under reduced pressure and purified by flash chromatography (Et_2O/hexane= 20:80) to afford pure ester as a white crystalline solid **15** (245 mg, 79%): **$[\alpha]_D^{25}$** +17.5 (*c* 1.0, $CHCl_3$); lit **$[\alpha]_D^{25}$** +18.0 (*c* 1.0, $CHCl_3$).[11]

(1*R*)-2-Ethoxy-1-methyl-2-oxoethyl 4-nitrobenzoate (16).

The title compound was obtained as white solid (117 mg, 83%) from ethyl (2*S*)-2-hydroxypropanoate (59 mg, 0.5 mmol) according to the typical procedure described above: **$[\alpha]_D^{25}$** -14.3 (*c* 1.1, EtOH); lit **$[\alpha]_D^{25}$** -13.1 (*c* 1.2, EtOH).[12]

(1*R*)-1-Methylheptyl 4-nitrobenzoate (17).

The title compound was obtained as white solid (163 mg, 91%) from (2*S*)-octan-2-ol (83 mg, 0.64 mmol) scale according to the typical procedure described above with 1.2 equiv of all reactive and warmed to room temperature over 6 h.

White solid: **mp** 28-30 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24-8.14 (m, 4H), 5.14 (sext, *J* = 6.3 Hz, 1H), 1.75-1.71 (m, 1H), 1.71-1.78 (m, 1H), 1.42-1.20 (m, 11H), 0.81 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.3, 150.5, 136.4, 130.7, 123.5, 73.1, 36.0, 31.8, 29.2, 25.4, 22.6, 20.0, 14.1; **IR** (film) 1717, 1607, 1526, 1272, 1101 cm^{-1}; **$[\alpha]_D^{25}$** -43 (*c* 2.2, EtOH).

(3α,5α)-Cholestan-3-yl 4-nitrobenzoate (18).

(+)-Dihydrocholesterol ((3β,5α)-cholestan-3-ol) (389 mg, 1.0 mmol, 1.0 equiv) and phosphine **3** (1.0 g, 1.6 mmol, 1.6 equiv) were dissolved in CH_2Cl_2 (10 mL) and toluene (20 mL) was added. The solution was cooled to -5 °C and DEAD (255 μl, 1.6 mmol, 1.6 equiv) was added dropwise over 5 min. Then 4-nitrobenzoic acid (270 mg, 1.6 mmol, 1.6 equiv) was added and the solution was warmed to room temperature for 6 h during which time a white precipitate of phosphine oxide appeared. Then phosphine **3** (0.5 g, 0.8 mmol, 0.8 equiv) and DEAD (127 μL, 0.8 mmol, 0.8 equiv) were added. After 6 h, 50 mL of Et_2O was added to the solution and the resulting mixture was filtered through a cotton pad and concentrated under reduced pressure. The resulting crude product was dissolved in CH_2Cl_2 (1 mL) and hexane (9 mL) was added. The hydrazine and 4-nitrobenzoic acid residues precipitated and the resulting mixture was filtered through a cotton pad, concentrated under reduced pressure and purified by flash chromatography (0 to 50% CH_2Cl_2/hexane) to afford pure ester **18** as a white crystalline solid (419 mg, 78%).

White solid: **mp** 95-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45-8.15 (m, 4H), 5.28 (br s, 1H), 2.0-0.64 (m, 46H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.1, 150.5, 136.7, 130.8, 123.7, 72.3, 56,7, 56.5, 54.5, 42.7, 40.7, 40.1, 39.7, 36.3, 36.1, 36.0, 35.6, 33.4, 33.1, 32.1, 28.5, 28.4, 28.2, 26.4, 24.3, 24.0, 23.0, 22.7, 21.0, 18.8, 12.2, 11.6; **IR** (film) 2929, 1711, 1606, 1523, 1289, 1105 cm^{-1}; **$[\alpha]_D^{25}$** +17.3 (*c* 1.0, $CHCl_3$).

Ethyl (3β,5β,7α,12α)-7,12-dihydroxy-3-[4-nitrobenzoyl)oxy]cholan-24-oate (19).

The title compound was obtained from ethyl (3α,5β,7α,12a)-3,7,12-trihydroxycholan-24-oate (437 mg, 1.0 mmol) as white solid (524 mg, 89%) according to the typical procedure described above with CH_2Cl_2 (10 mL) and THF (20 mL) as solvents and DIAD (315 μL, 1.6 mmol, 1.6 equiv) and warmed to room temperature over 2 h. **19** could be quantitatively extracted from the phosphonium salt (5 cycles of solubilization in CH_2Cl_2 and precipitation by adding Et_2O). But, in order to eliminate the hydrazine residue, it is more useful in this case to obtain the product directly by flash chromatography (0 to 2% MeOH/CH_2Cl_2/MeOH).

White solid: **mp** 190-195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32-8.19 (m, 4H), 5.33 (br s, 1H), 4.14-4.11 (m, 2H), 4.02 (br s, 1H), 3.91 (br s, 1H), 2.68 (br t, J = 13.9 Hz, 1H), 2.40-1.20 (m, 28H), 1.02 (br s, 6H), 0.73 (br s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.4, 164.0, 150.3, 136.5, 130.6, 123.5, 73.2, 72,8, 68.5, 60.2, 47.3, 46.6, 41.7, 39.3, 37.2, 35.4, 35.2, 34.3, 33.5, 31.4, 30.9, 30.8, 28.5, 27.6, 25.7, 24.9, 23.3, 23.0, 17.3, 14.2, 12.4; **IR** (film) 3453, 2935, 1713, 1606, 1524, 1278, 1105 cm^{-1}; **$[\alpha]_D^{25}$** +21.8 (*c* 1.1, $CHCl_3$).

1-Chloro-4-[(*E*)-2-(4-chlorophenyl)vinyl]benzene (20).

To zinc dust < 10 micron (flame dried under argon) (10.2 g, 156 mmol, 2.19 equiv) was added THF (215 mL) the resulting mixture was cooled to -10 °C. Then $TiCl_4$ (8.3 mL, 76.0 mmol, 1.07 equiv) was carefully added to the solution. After 5 min, 4-chlorobenzaldhyde (9.9 g, 70.0 mmol, 1.0 equiv) was added in one portion. The resulting mixture was heated under reflux for 20 h then cooled to room temperature, and a 10% (w/w) K_2CO_3 aqueous solution (150 mL) was added. The clear organic phase was collected and the aqueous mixture was washed with Et_2O (100 mL). The organic phase was concentrated under reduced pressure to afford a crude crystalline product washed with Et_2O to afford pure **20** as a white solid[13] (7.9 g, 91%).

Triphenyl(4-{(*E*)-2-[4-(triphenylphosphonio)phenyl]vinyl}phenyl)phosphonium dibromide (21).

A solution of $NiBr_2$ (19.0 g, 86 mmol, 2.0 equiv), triphenylphosphine (45.0 g, 172 mmol, 4 equiv) and **20** (10.6 g, 43 mmol, 1.0 equiv) in benzonitrile (300 mL, 0.15 M) was heated under reflux 2 h. The solution was cooled to 60 °C and a 10% (w/w) KBr aqueous solution (100 mL) was added. The layers were separated, the aqueous layer was washed twice with CH_2Cl_2 (100 mL) and once with a solution of CH_2Cl_2 (100 mL) and MeOH (25 mL). The organic solution was washed with a half saturated NaCl aqueous solution (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. To the resulting mixture was added hexane (1 L) to finish precipitating the crude product. The precipitate was filtered on a büchner and washed with Et_2O (2x100 mL) and then dried under reduced pressure overnight to afford a crystalline product **21** as a white solid (38.6 g, ca. 105%) containing some amount of benzonitrile. An aliquot was purified by dissolution in CH_2Cl_2 and precipitation by Et_2O to afford pure **21**: **mp** >250 °C; **^{1}H NMR** (400 MHz, $CDCl_3$+ CD_3OD (trace)): δ 7.97-7.84 (m, 4H), 7.72-7.63 (m, 6H), 7.60-7.46 (m, 14H), 7.38-7.31 (m, 16H); **^{13}C NMR** (100 MHz, $CDCl_3$+ CD_3OD (trace)): δ 143.3 (d, *J* = 2.9 Hz, 2C), 135.2 (d, *J* = 2.5 Hz, 6C), 134.2 (d, *J* = 10.6 Hz, 4C), 133.7 (d, *J* = 10.3 Hz, 12C), 131.1 (s, 2C), 130.2 (d, *J* = 12.8 Hz, 12C), 128.8 (d, *J* = 13.2 Hz, 4C), 117.0 (d, *J* = 89.1 Hz, 2C), 115.1 (d, *J* = 90.8 Hz, 6C); **^{31}P NMR** (162 MHZ, $CDCl_3$+ CD_3OD (trace)): δ 23.3; **IR** (film) 3055, 1821, 1593, 1436, 1106, 917cm^{-1}; **LRMS** (API-ES, Pos) calc. for $C_{50}H_{40}P_2$ $[M]^{2+}$: 351.1, found 351.2.

[4-(Hydroxymethyl)phenyl](triphenyl)phosphonium perchlorate (22).

Dibromide **21** (8.63 g, ca. 9.6 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (60 mL) and dry $LiClO_4$ (3.5 g, 22.0 mmol, 2.3 equiv) was added followed by MeOH (30 mL). After 10 min, saturated aqueous NaCl (40 mL) and water (10 mL) were added. The layers were separated and the aqueous layer was washed with a solution of 60:40 CH_2Cl_2:MeOH (100 mL) and MeOH (30 mL) and with a solution composed of CH_2Cl_2 (30 mL) and MeOH (10 mL). The organic solution was dried over Na_2SO_4, filtered and cooled to -78 °C. O_3 was bubbled through the solution. When the solution became clear blue, O_2 and argon were bubbled into the solution to remove excess ozone. $NaBH_4$ (740 mg, 20 mmol, 2.1 equiv) was added to the solution and after 30 min, the solution was warmed to 0 °C for 1 h. A saturated aqueous solution of NH_4Cl (100 mL) was carefully added. The layers were separated, and the aqueous layer was washed twice with CH_2Cl_2 (50 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (15 mL) and was the desired product was precipitated upon Et_2O (100 mL) addition. Filtration afforded pure **22** as a white solid (6.9 g, 77% 2 steps): **mp** 225-230 °C; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.85-7.70 (m, 3H), 7.63-7.60 (m, 8H), 7.54-7.45 (m, 8H), 4.71 (s, 2H), 4.30 (bs, 1H); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 150.8 (d, *J* = 3.0 Hz, 1C), 135.4 (d, *J* = 1.7 Hz, 3C), 134.4 (d, *J* = 10.2 Hz, 6C), 134.3 (d, *J* = 10.6 Hz, 2C), 130.3 (d, *J* = 12.8 Hz, 6C), 128.1 (d, *J* = 13.2 Hz, 2C), 117.7 (d, *J* = 89.1 Hz, 1C), 115.0 (d, *J* = 90.9 Hz, 3C), 63.4 (s, 1C); **^{31}P NMR** (162 MHZ, CD_2Cl_2): δ 23.3; **IR** (film) 3244, 1436, 1266, 1083 cm^{-1}; **LRMS** (APCI, Pos) calc. for $C_{25}H_{22}O_1P_1$ $[M]^+$: 369.1, found 369.1; **LRMS** (APCI, Neg) calc. for $^{35}ClO_4$ $[M]^-$: 99.0, found 99.0; calc. for $^{37}ClO_4$ $[M]^-$: 101.0, found 101.1; **Elem. Anal.** Calc. (%) for $C_{25}H_{22}ClO_5P$: C 64.04, H 4.73, found: C 64.25, H 4.92.

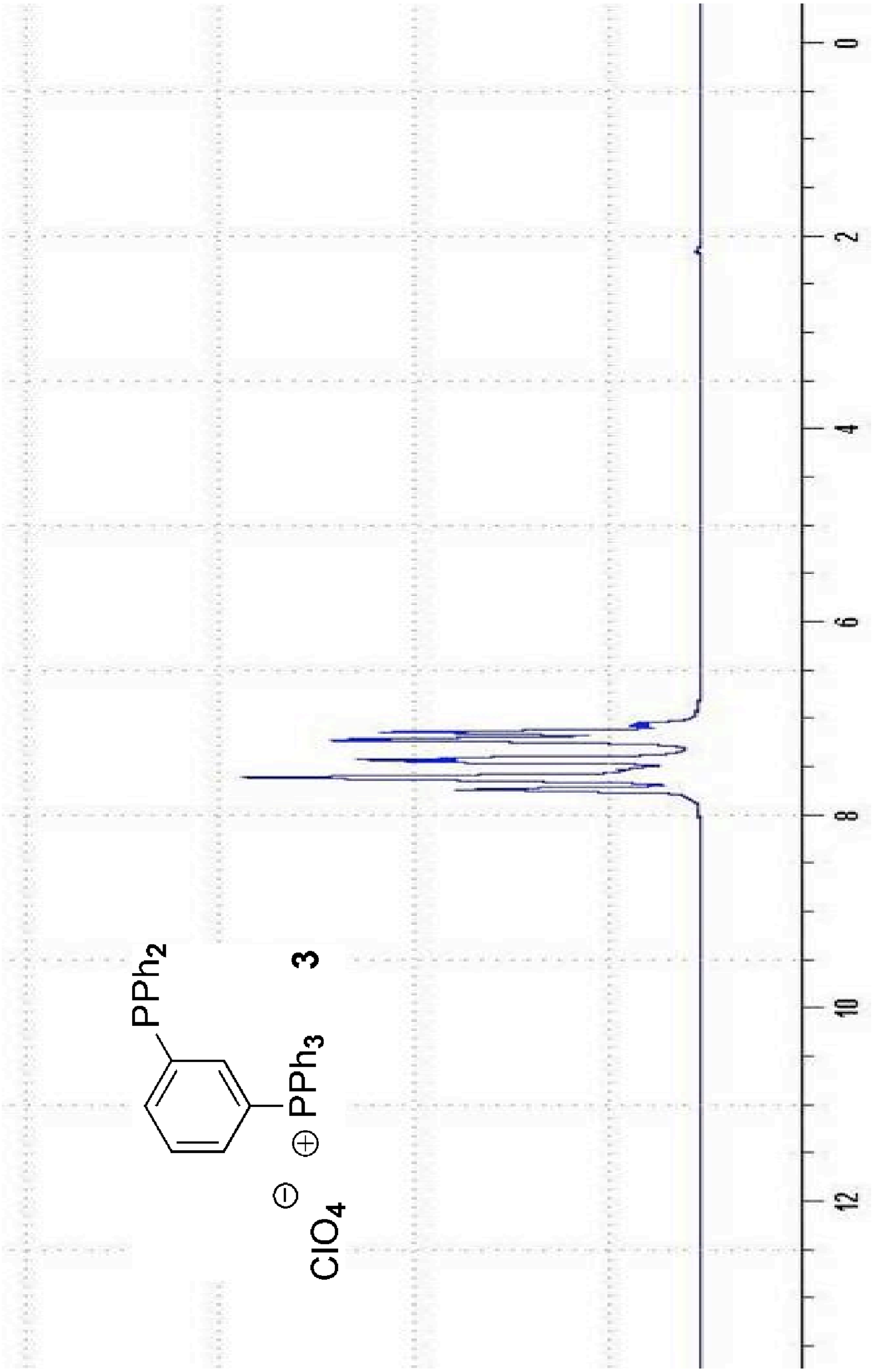
{4-[({[(2-(Etoxycarbonyl)hydrazino]carbonyl}oxy)methyl]phenyl}(triphenyl)phosphonium perchlorate. (23).

To a solution of triphosgene (1.3 g, 4.3 mmol, 0.43 equiv) in CH_2Cl_2 (75 mL) at -30 °C was added dropwise pyridine (2.1 mL, 26 mmol, 2.6 equiv). The resulting mixture was warmed to room temperature for 30 min (it became a clear yellowish homogeneous solution) then was cooled to -78 °C (it became a milky yellowish mixture). A solution of **22** (4.7 g, 10 mmol, 1.0 equiv) in CH_2Cl_2 (75 mL, rinse with 1 mL) at -78 °C was added dropwise for 5 min to the mixture (the mixture had to be kept below -70 °C and became a clear limpid solution at the end of the addition). After 10 min, a solution of ethyl carbazate (2.1 g, 20 mmol, 2.0 equiv) in CH_2Cl_2 (25 mL) at -78 °C was added dropwise to the solution. The solution became yellow and the external bath was warmed to -60 °C and was left to warm to -20 °C over 2 h and to 0 °C over 0.5 h. The resulting solution was washed with water (100 mL). The aqueous layer was washed twice with CH_2Cl_2 (100 mL, 50 mL). The combined organic layers were washed with water (100 mL). The aqueous layer was washed with CH_2Cl_2 (50 mL). The organic solution was washed with a solution of $LiClO_4 \cdot 3H_20$ (1.6 g, 10 mmol, 1.0 equiv) in water (10 mL), with water (20 mL) and was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (25 mL) and the desired product was precipitated with Et_2O (100 mL) and filtration afforded pure **23** as a white solid foam (5.7 g, 95%): **mp** 95-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.85 (m, 3H), 7.85-7.70 (m, 8H), 7.70-7.65 (m, 8H), 7.31 (bs, 1H), 6.82 (bs, 1H), 5.26 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7 (s, 1C), 156.3 (s, 1C), 144.8 (s, 1C), 135.7 (d, *J* = 2.3 Hz, 3C), 134.5 (d, *J* = 10.7 Hz, 2C), 134.3 (d, *J* = 10.3 Hz, 6C), 130.7 (d, *J* = 12.9 Hz, 6C), 129.0 (d, *J* = 12.9 Hz, 2C), 117.5 (d, *J* = 89.0 Hz, 3C), 116.5 (d, *J* = 90.1 Hz, 1C), 65.6 (s, 1C), 61.9 (s, 1C), 14.4 (s, 1C); **IR** (film) 1720, 1437, 1266, 1217, 1067 cm^{-1}; **^{31}P NMR** (162 MHZ, $CDCl_3$): δ 23.2; **LRMS** (APCI, Pos) calc. for $C_{29}H_{28}N_2O_4P_1$ $[M]^+$: 499.2, found 499.1; **LRMS** (APCI, Neg) calc. for $^{35}ClO_4$ $[M]^-$: 99.0, found 98.9; calc. for $^{37}ClO_4$ $[M]^-$: 101.0, found 101.0.

{4-[({[(E)-(Etoxycarbonyl)diazenyl]carbonyl}oxy)methyl]phenyl}(triphenyl)phosphonium perchlorate. (24).

To a solution of **23** (2.4 mg, 4.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) at 0 °C was added pyridine (500 μL, 1.5 mmol, 1.5 equiv) and in one portion NBS (856 mg, 4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C without light for 30 min and was washed with a solution containing water (11 mL) and saturated aqueous $Na_2S_2O_3$ (11 mL). The aqueous layer was washed with CH_2Cl_2 (20 mL). The organic solution was washed once with water (10 mL), twice with a 5% aqueous HCl solution (20 mL) and once with water (10 mL). Each time the aqueous layers were washed with CH_2Cl_2 (5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was diluted with

CH_2Cl_2 (5 mL) and the desired product was precipitated upon the addition of Et_2O (30 mL). Filtration afforded pure **24** as a yellow solid foam (2.2 g, 91%): **mp** 85-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.65 (m, 19H), 5.59 (s, 2H), 4.49 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.2 (s, 1C), 160.0 (s, 1C), 142.1 (d, J = 2.9 Hz, 1C), 135.9 (d, J = 2.6 Hz, 3C), 135.0 (d, J = 10.6 Hz, 2C), 134.6 (d, J = 10.3 Hz, 6C), 130.9 (d, J = 12.9 Hz, 6C), 130.0 (d, J = 13.1 Hz, 2C), 118.3 (d, J = 89.5 Hz, 1C), 117.3 (d, J = 89.1 Hz, 3C), 69.0 (s, 1C), 63.7 (s, 1C), 14.2 (s, 1C); **^{31}P NMR** (162 MHZ, $CDCl_3$): δ 23.2; **IR** (film) 1777, 1439, 1266, 1224, 1090 cm^{-1}; **LRMS** (APCI, Pos) calc. for $C_{29}H_{26}N_2O_4P_1$ $[M]^+$: 497.2, found 497.1; **Elem. Anal.** Calc. (%) for $C_{29}H_{26}ClN_2O_8P$: C 58.35, H 4.39, found: C 58.37, H 4.27.



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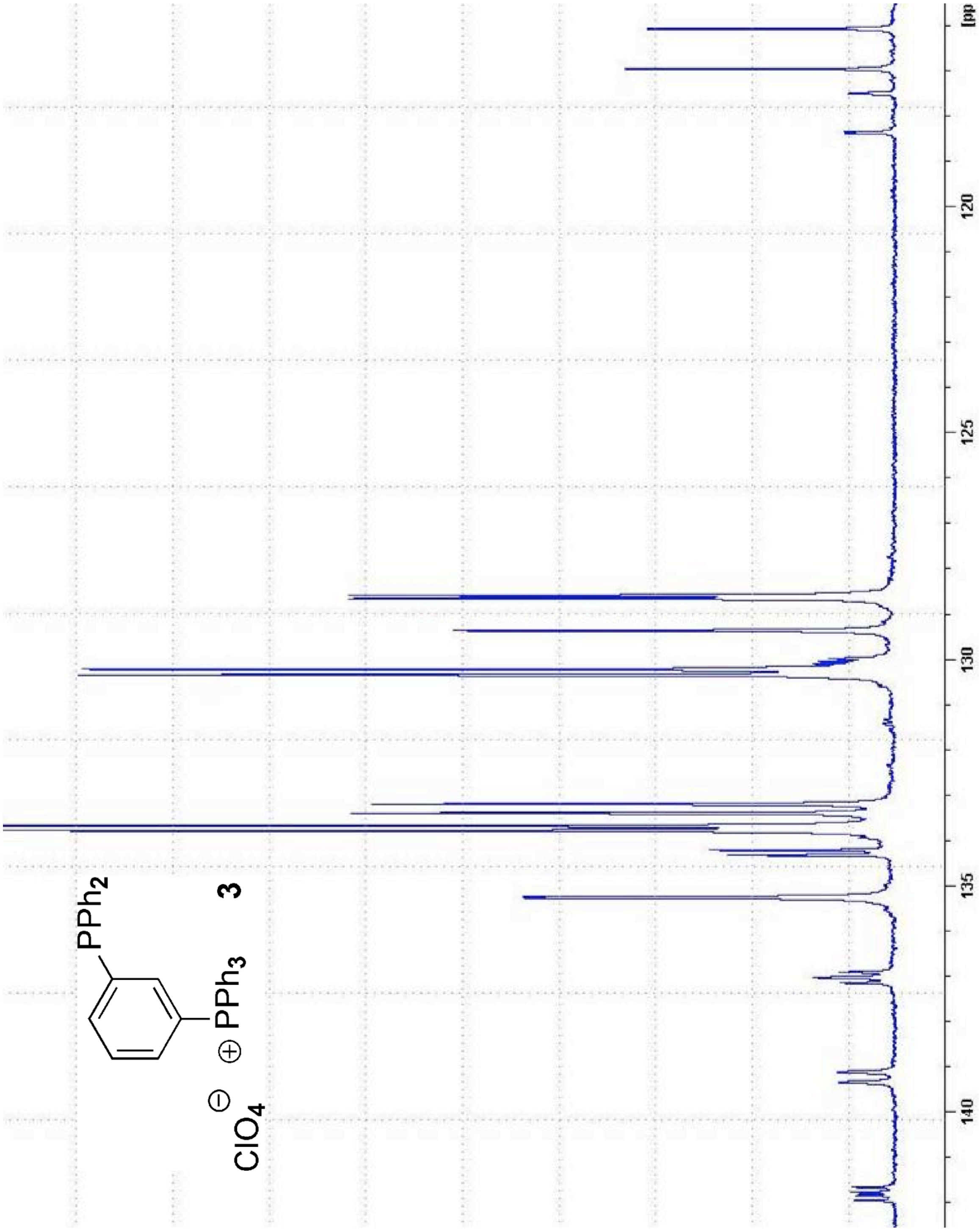
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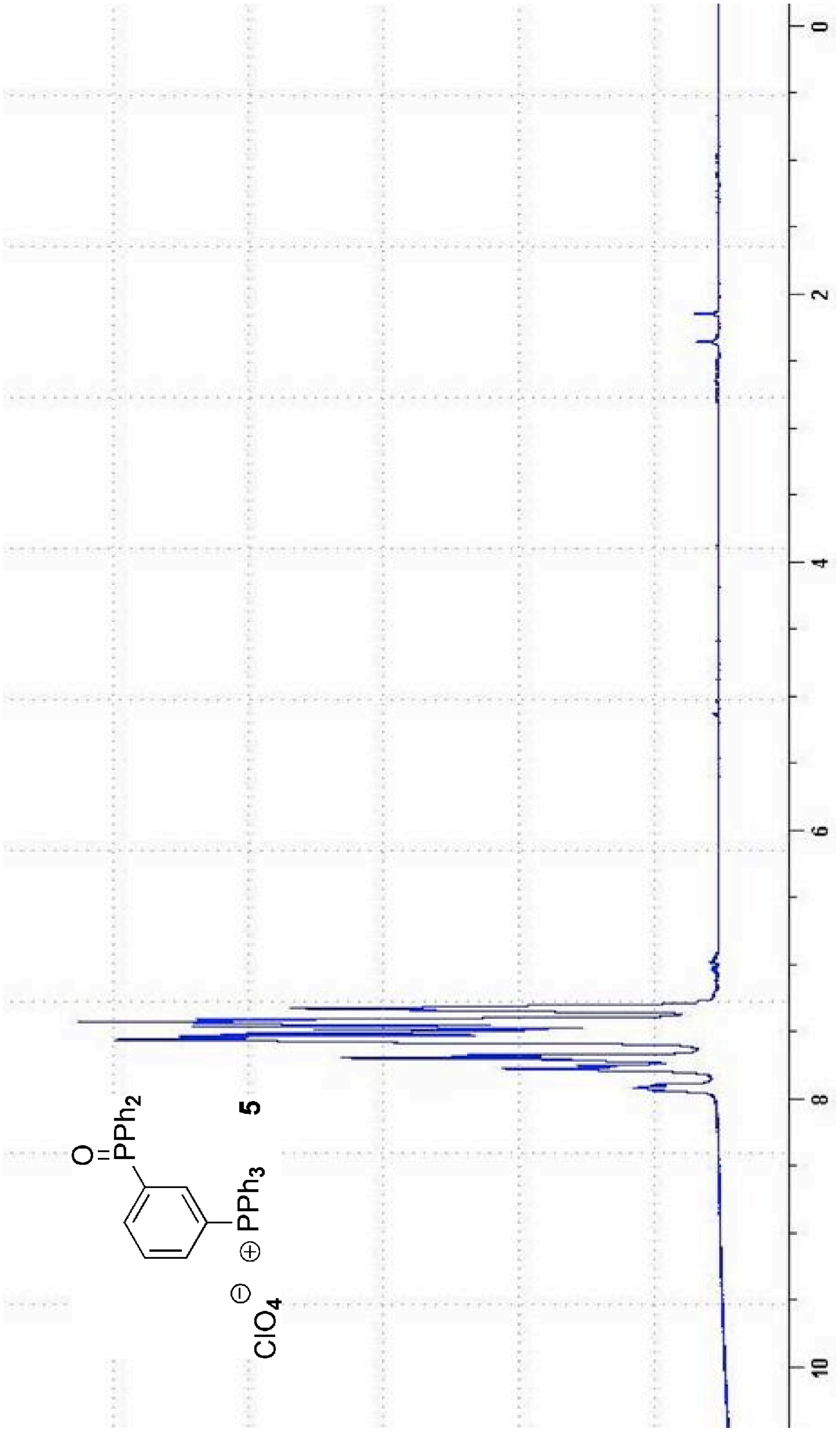
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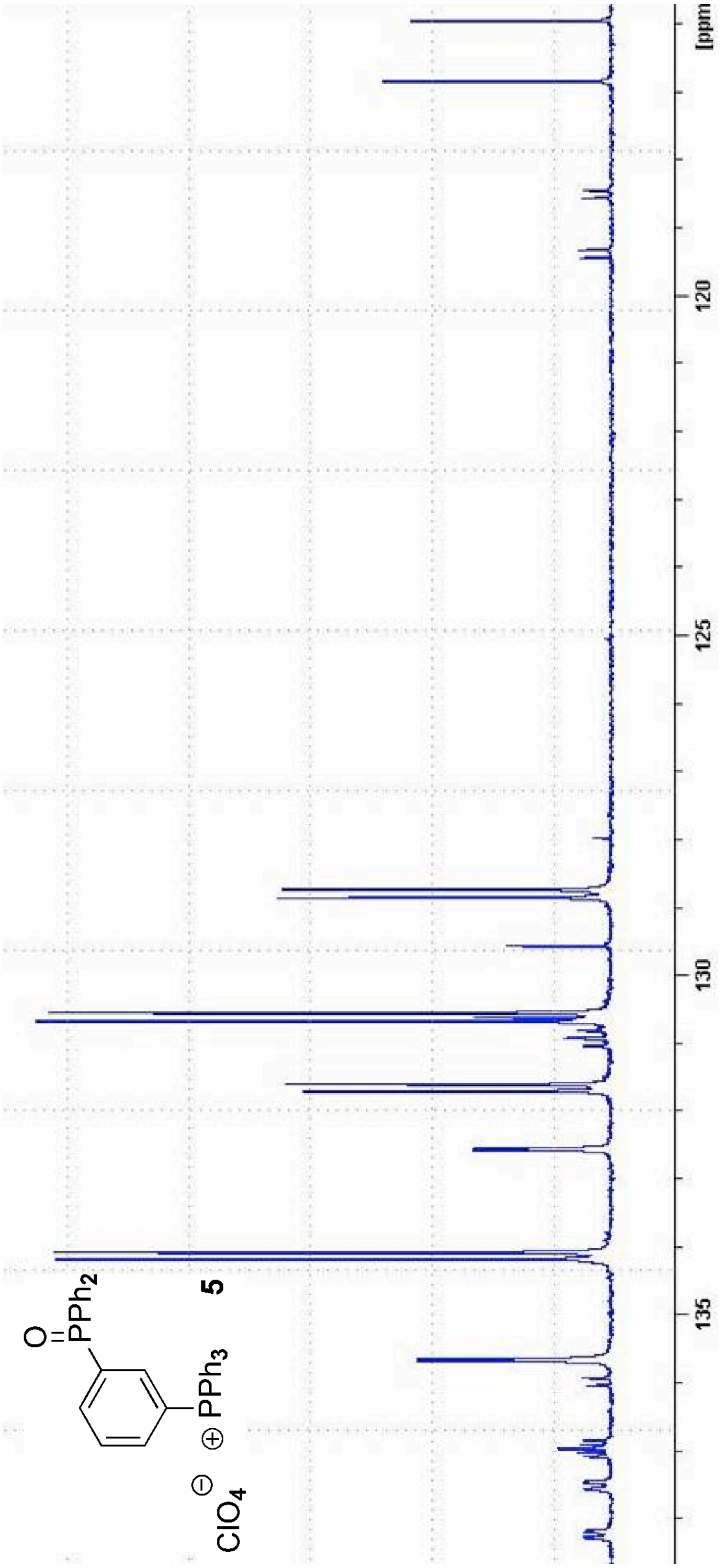
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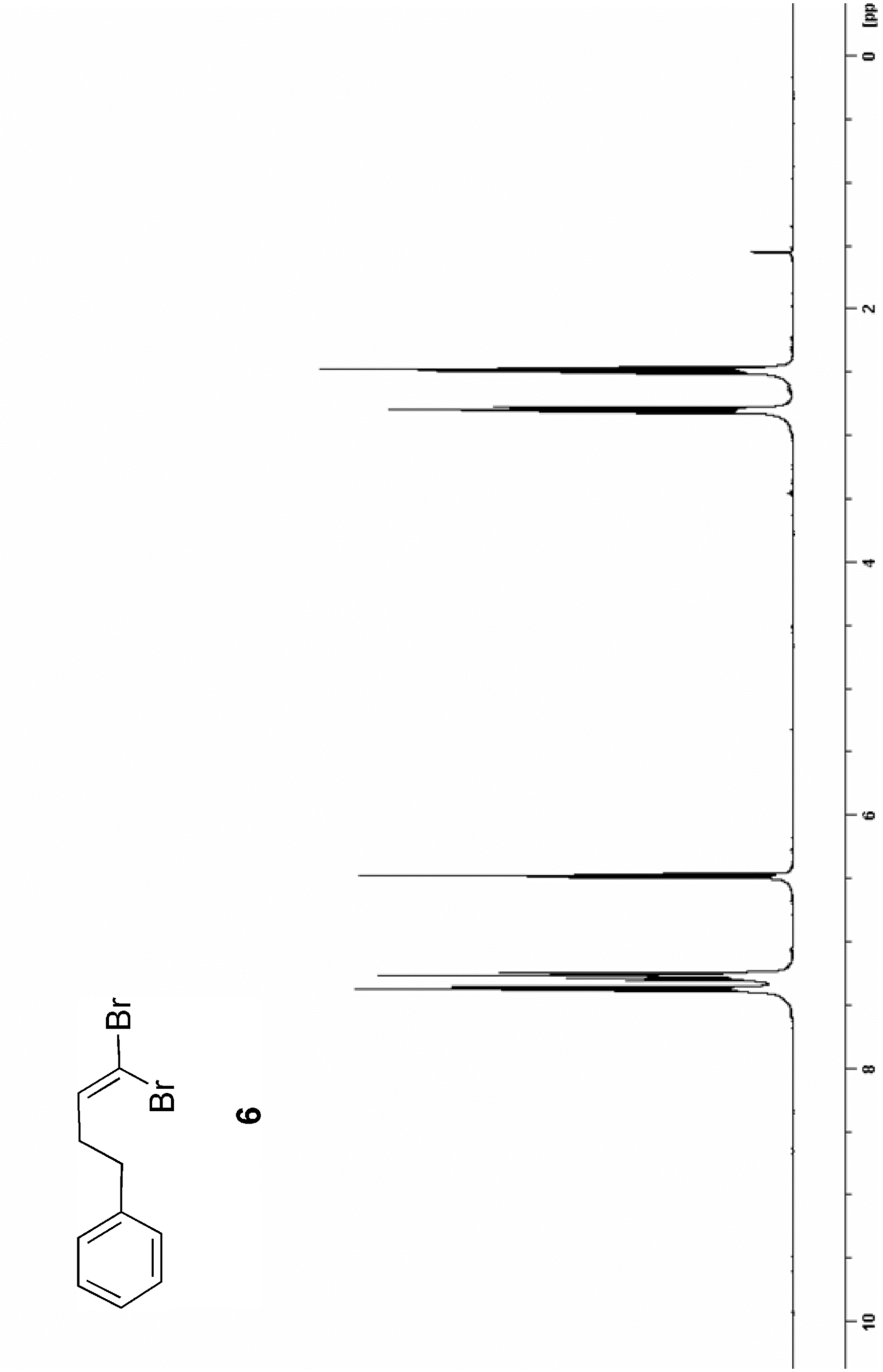

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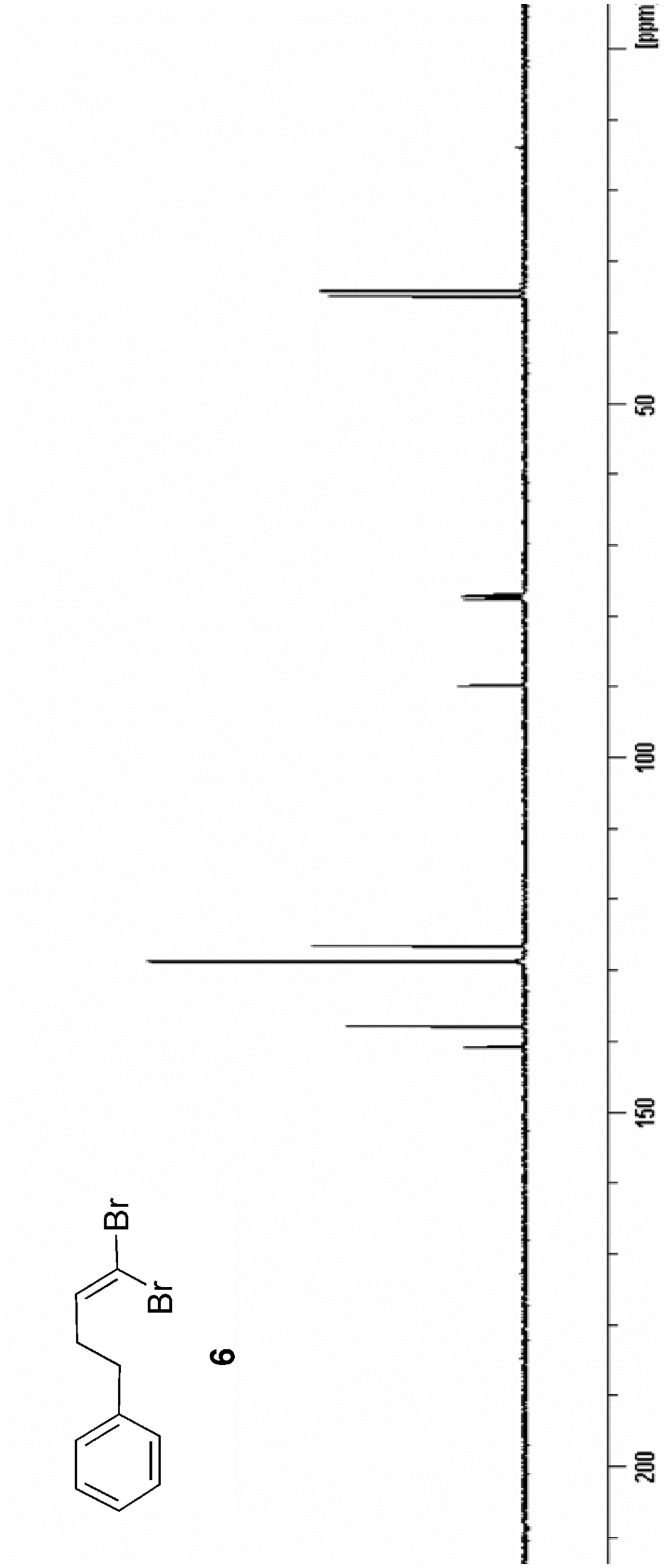

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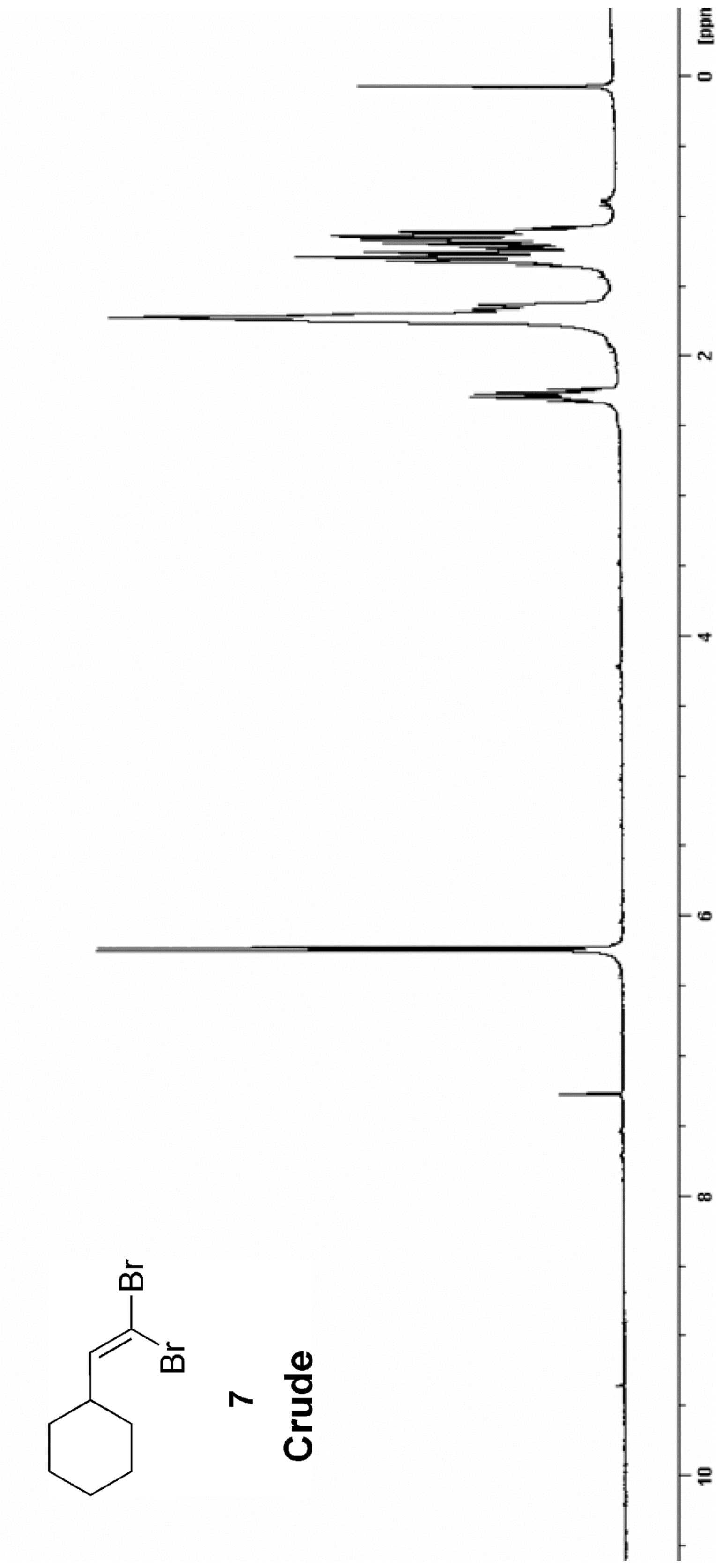

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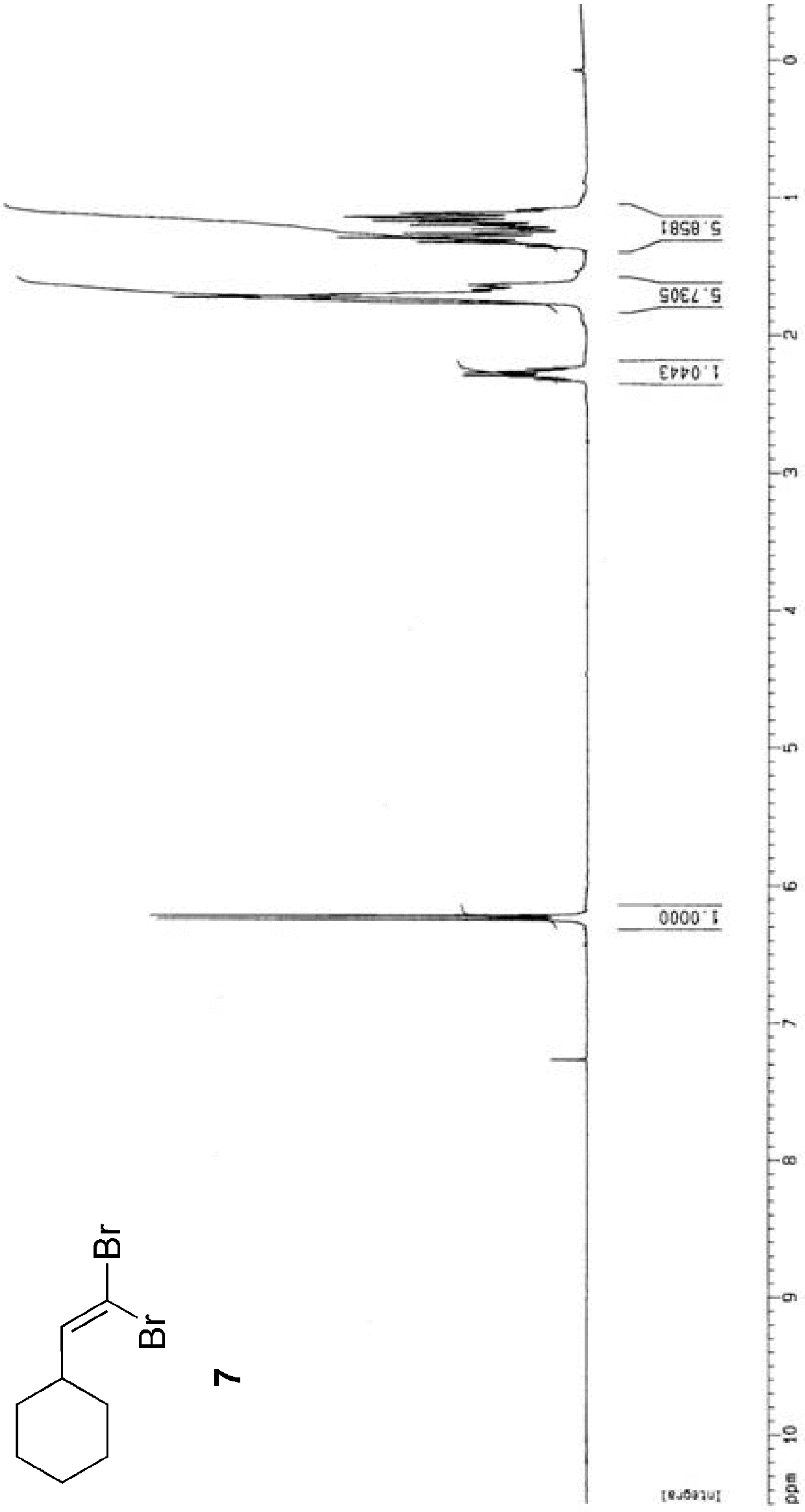
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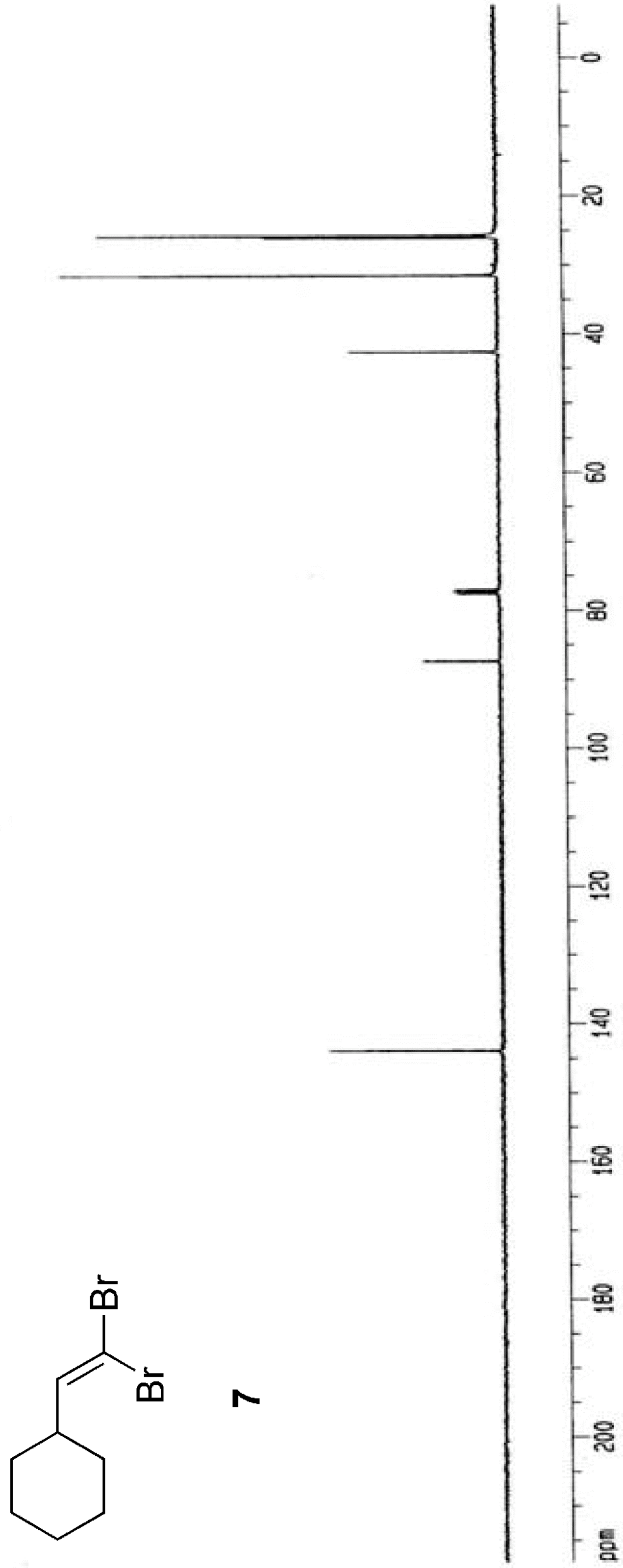

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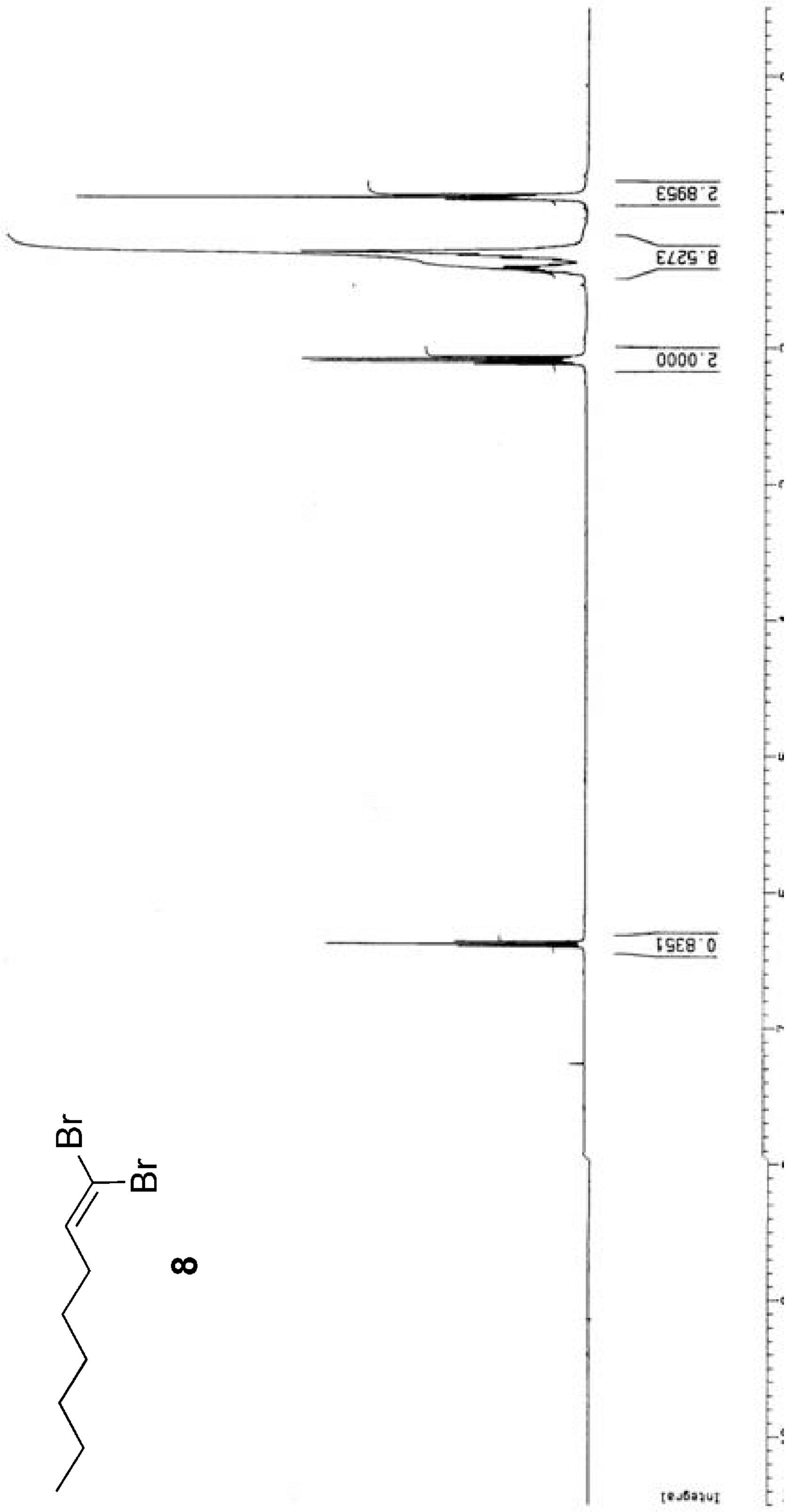

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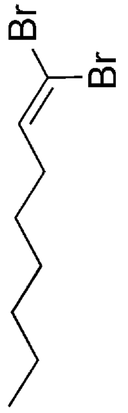

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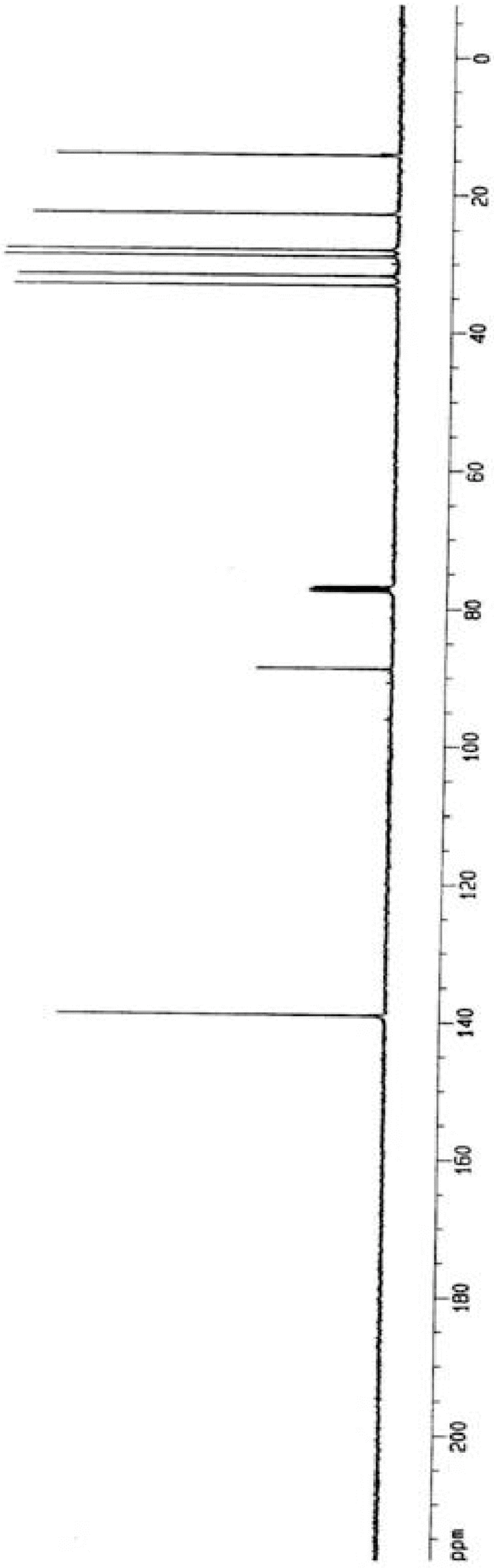

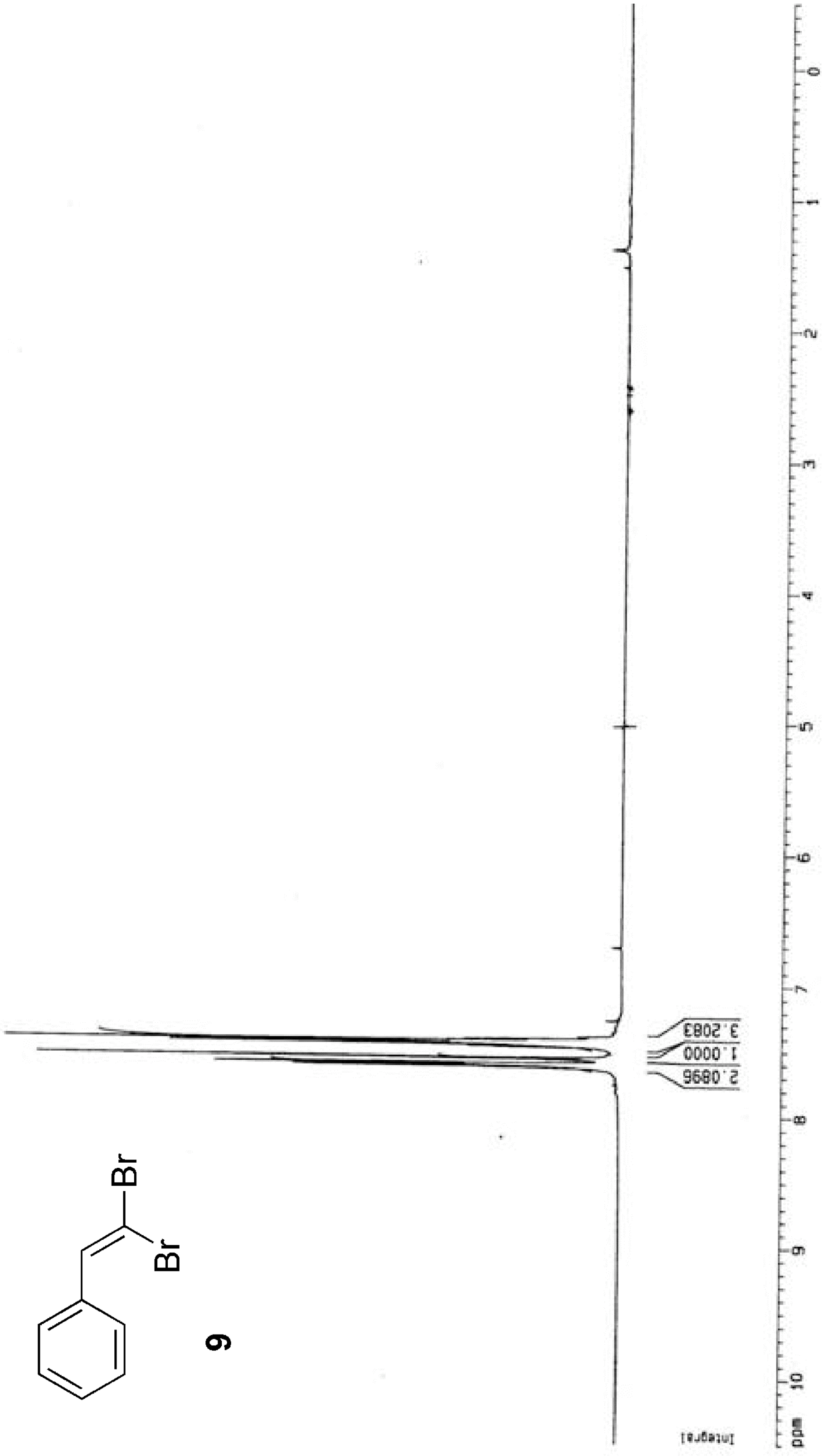

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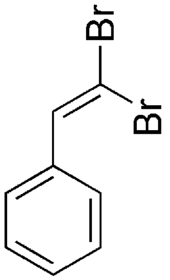

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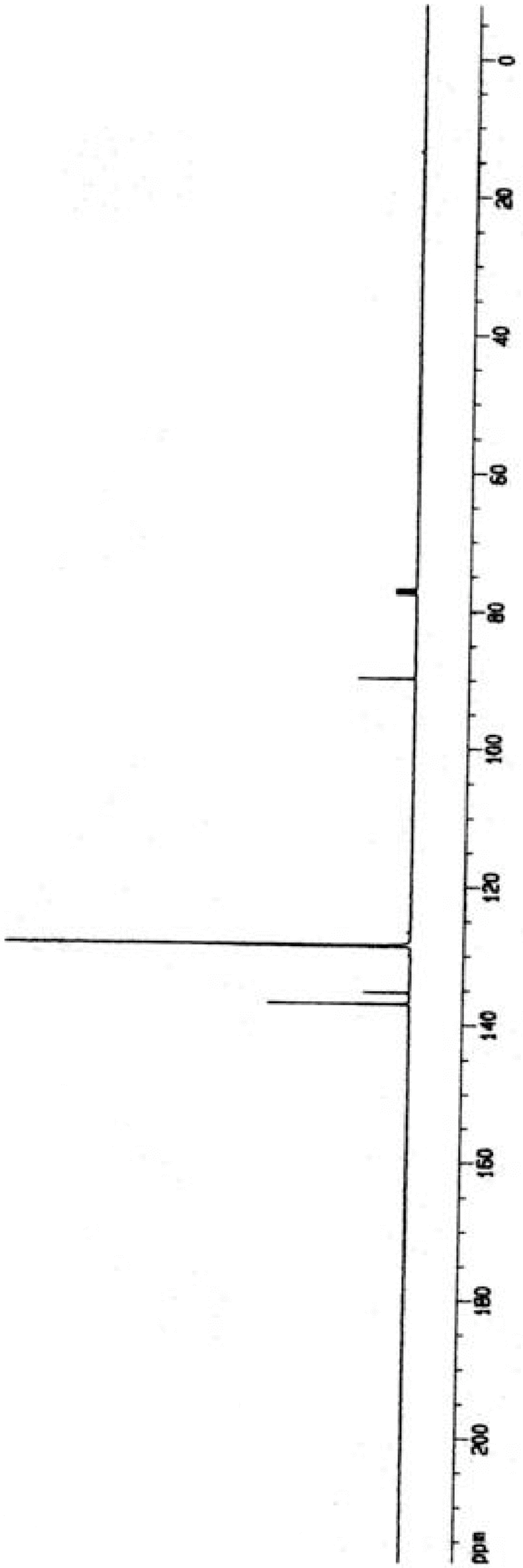

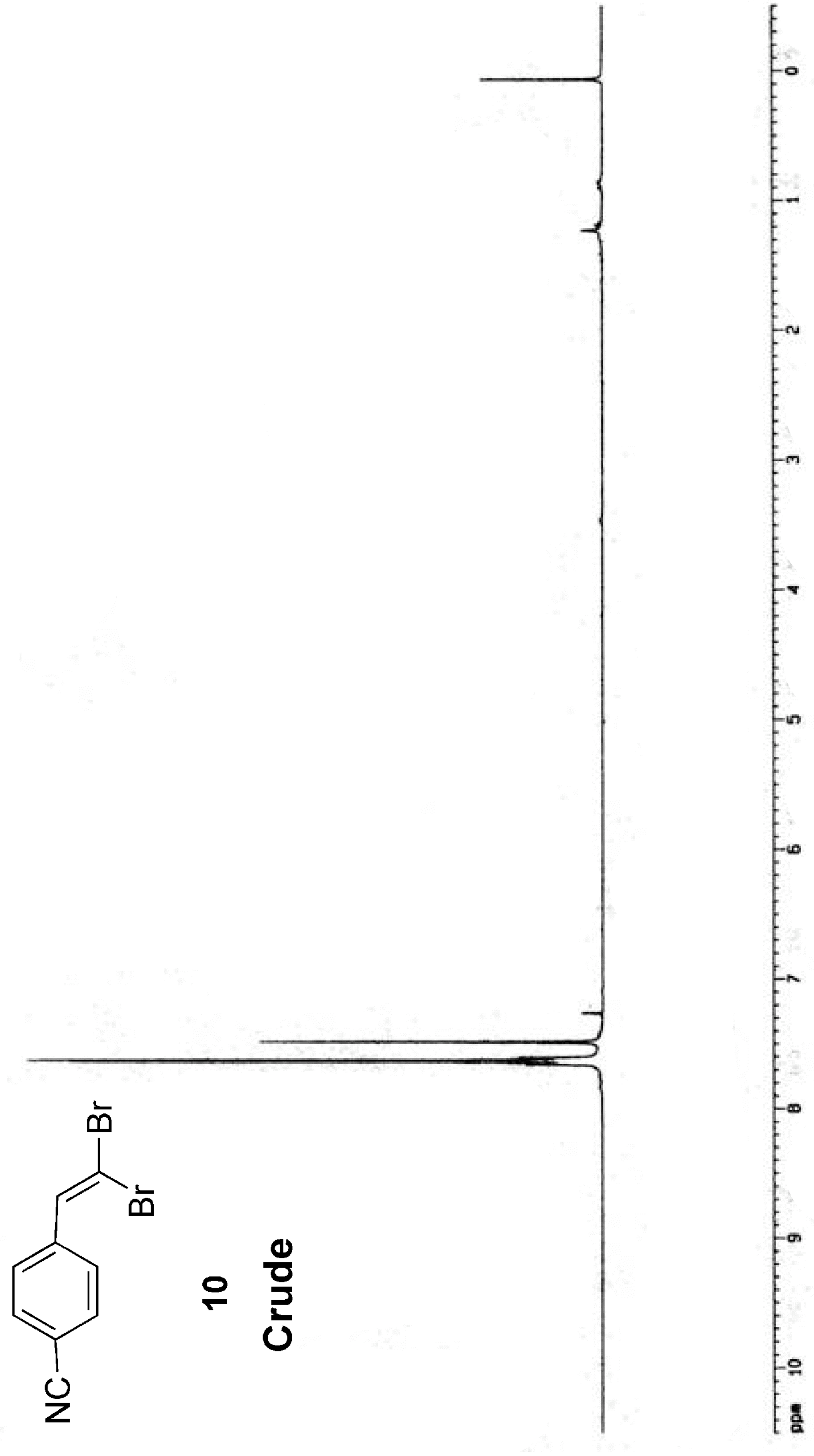

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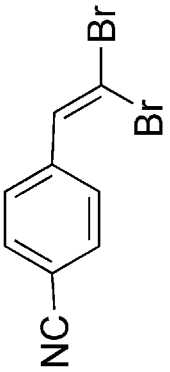

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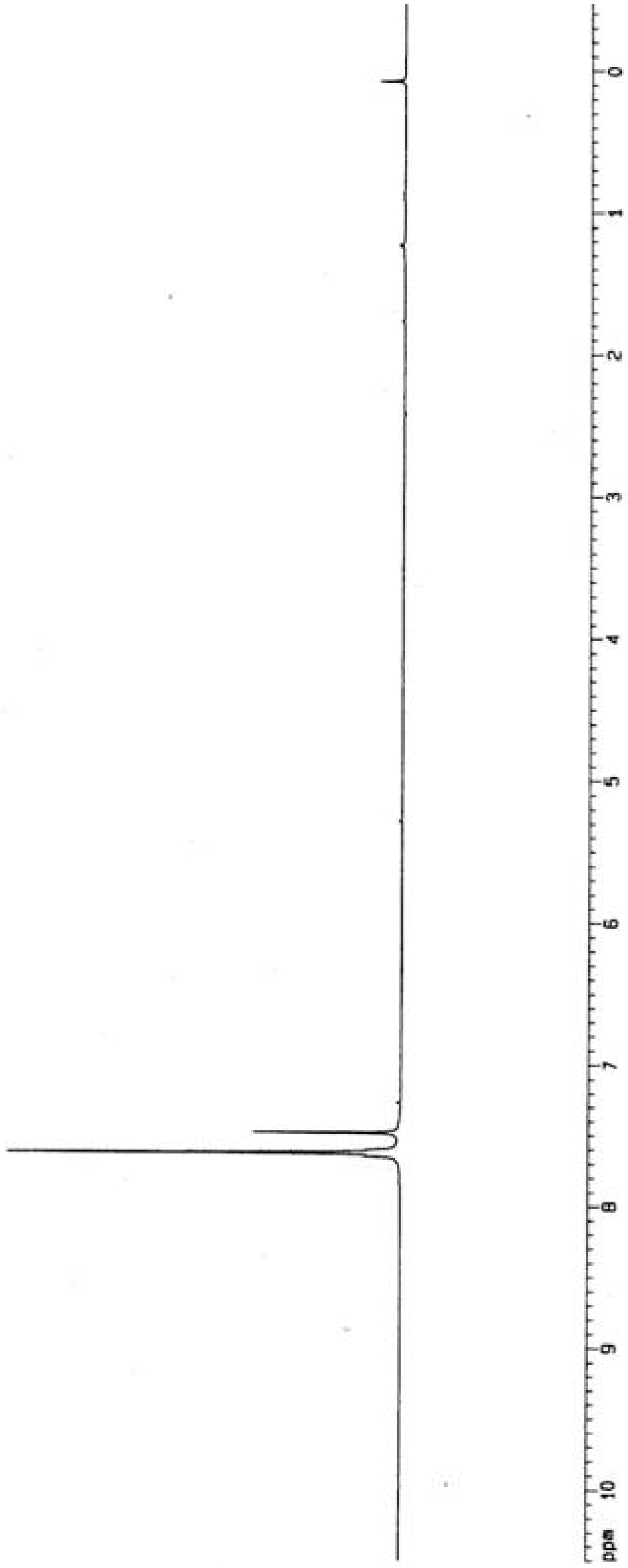

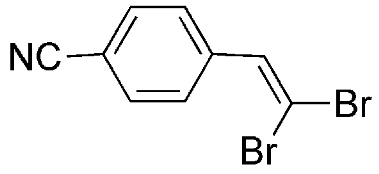

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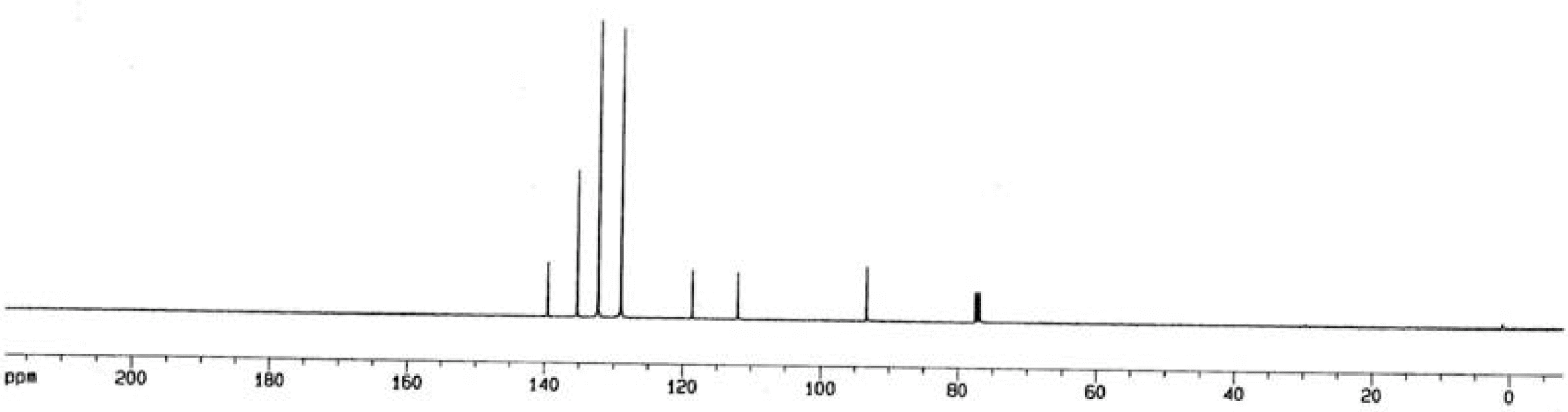

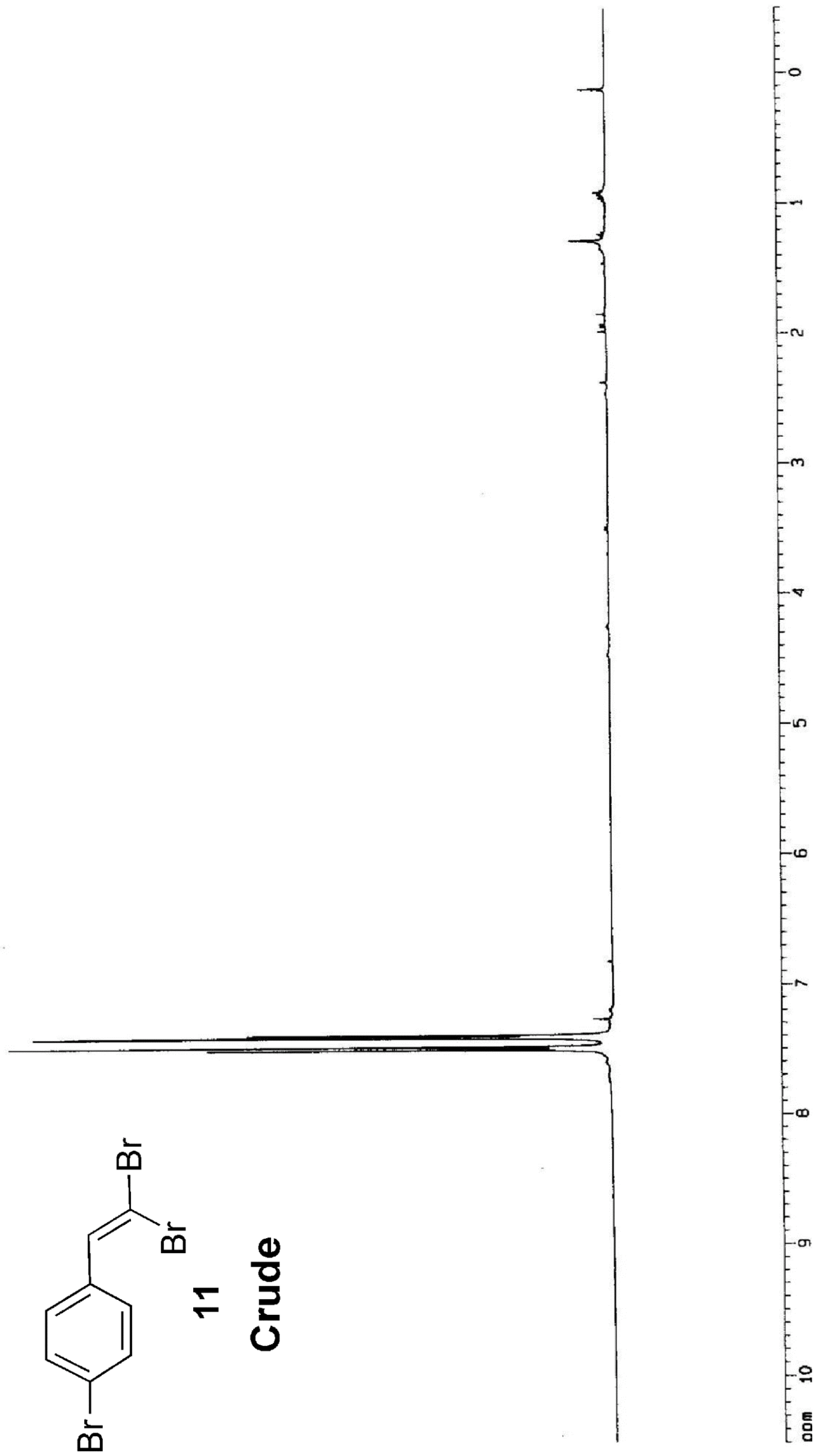

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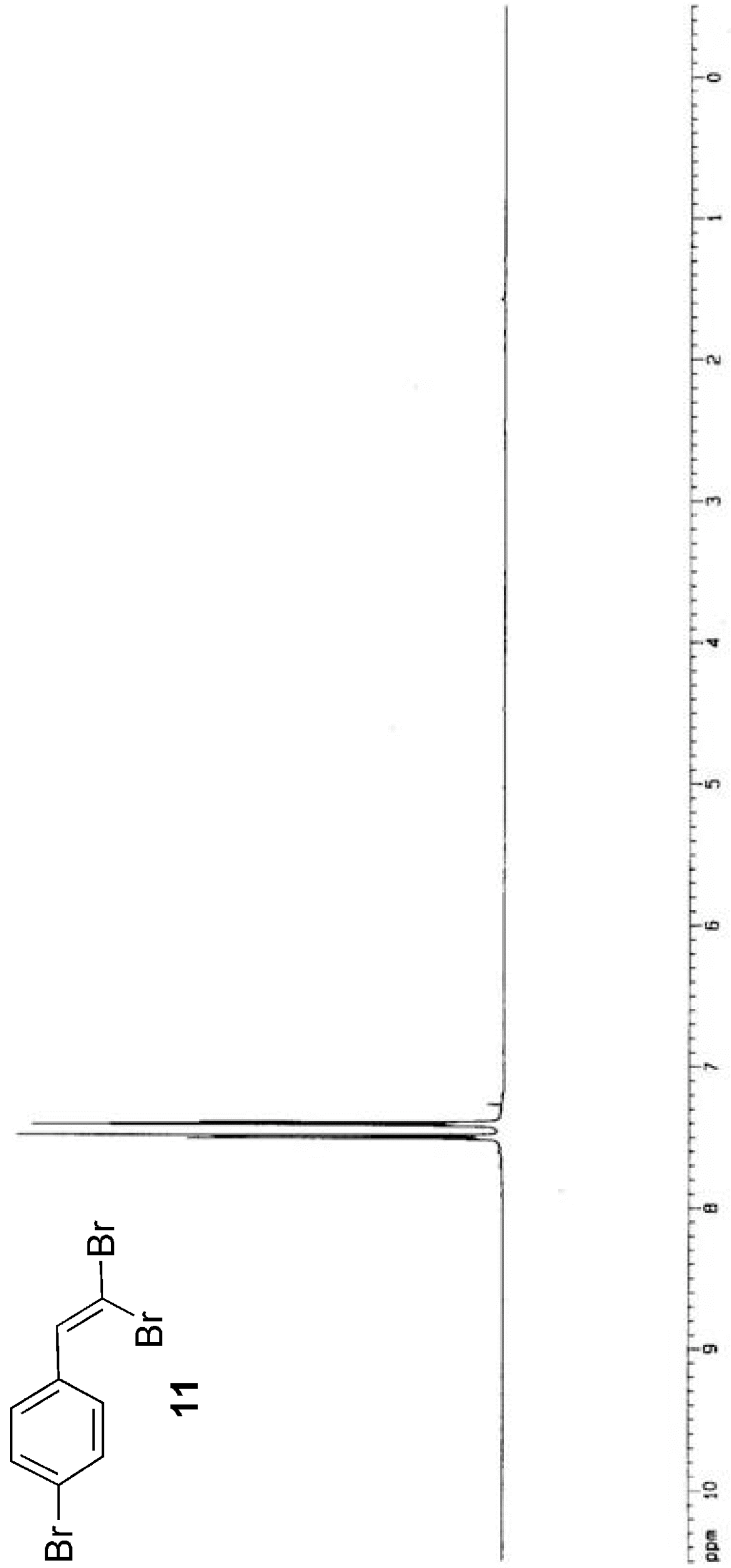

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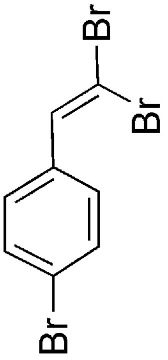

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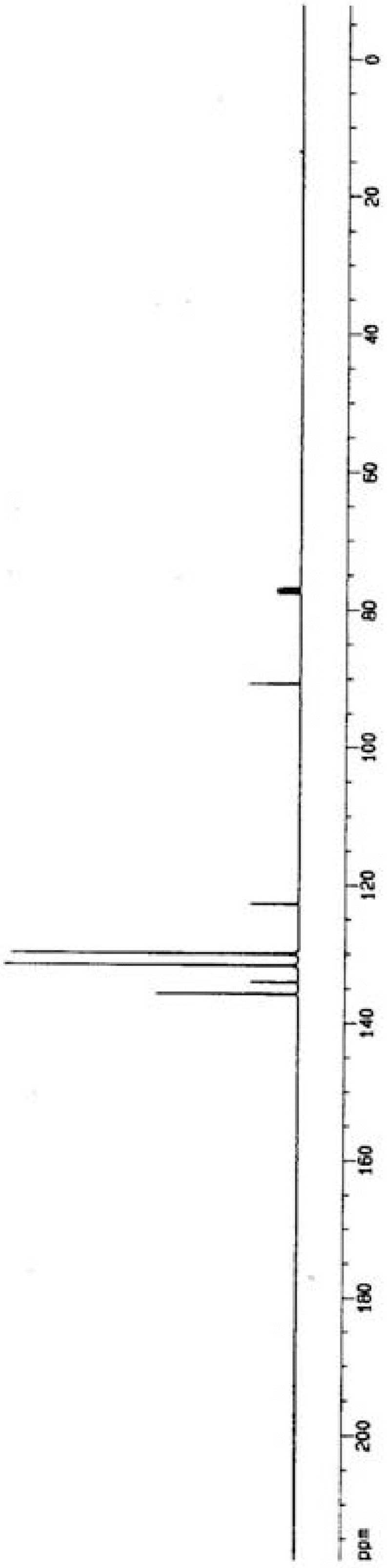

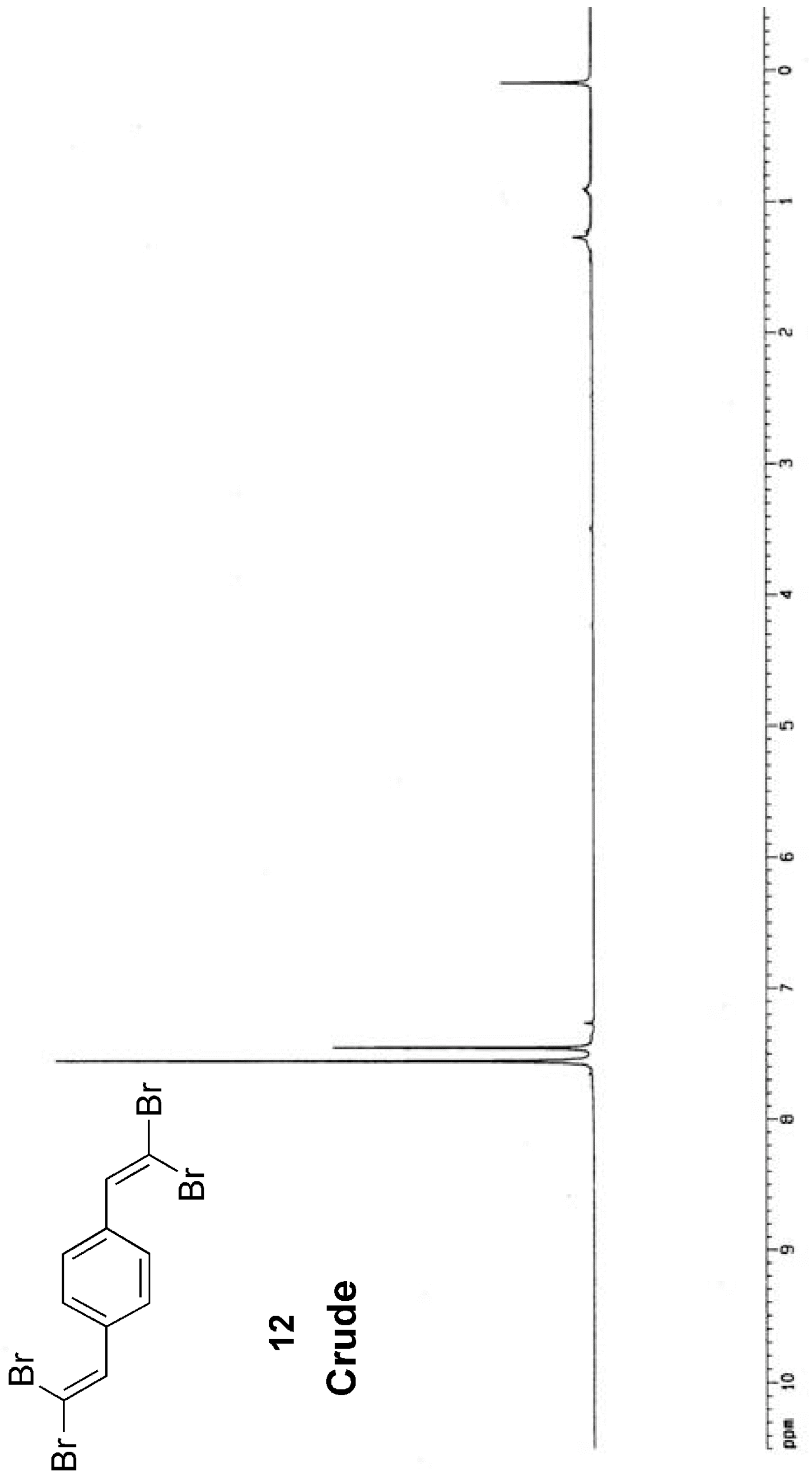

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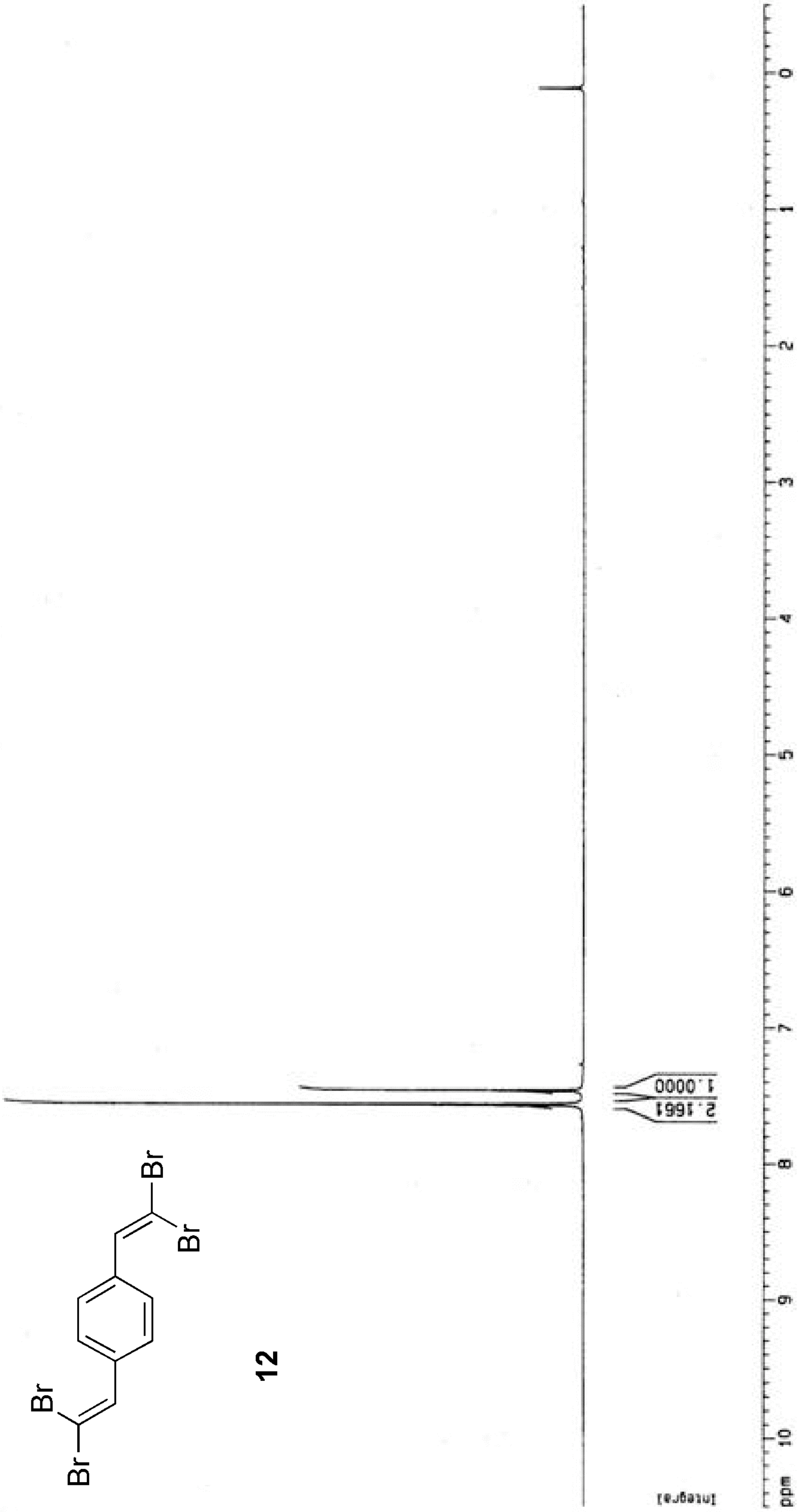

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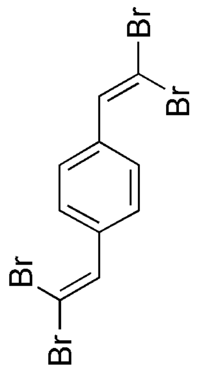

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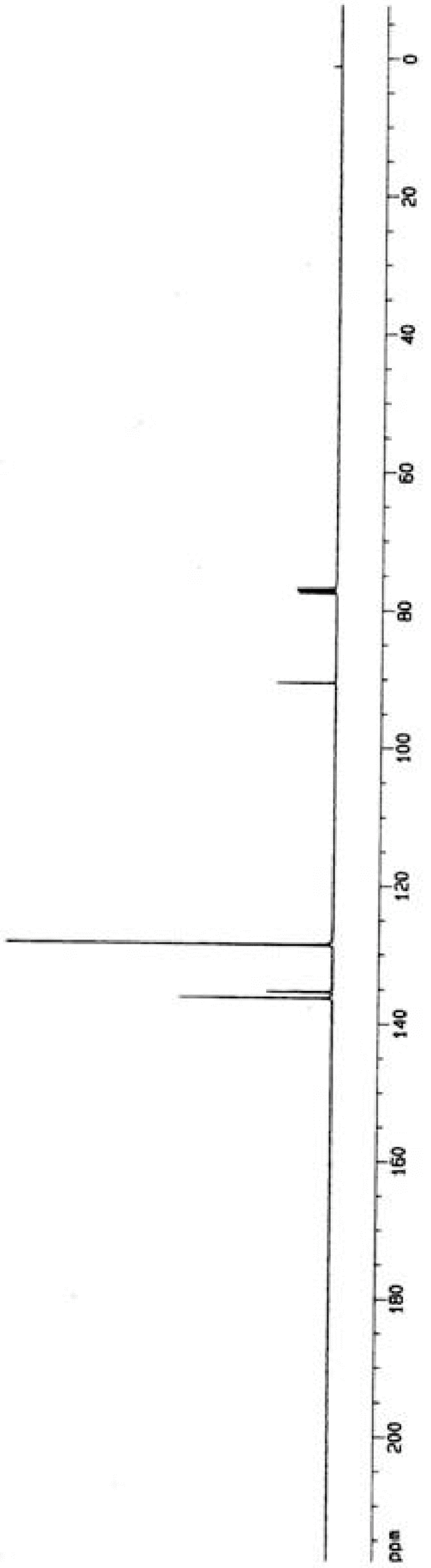

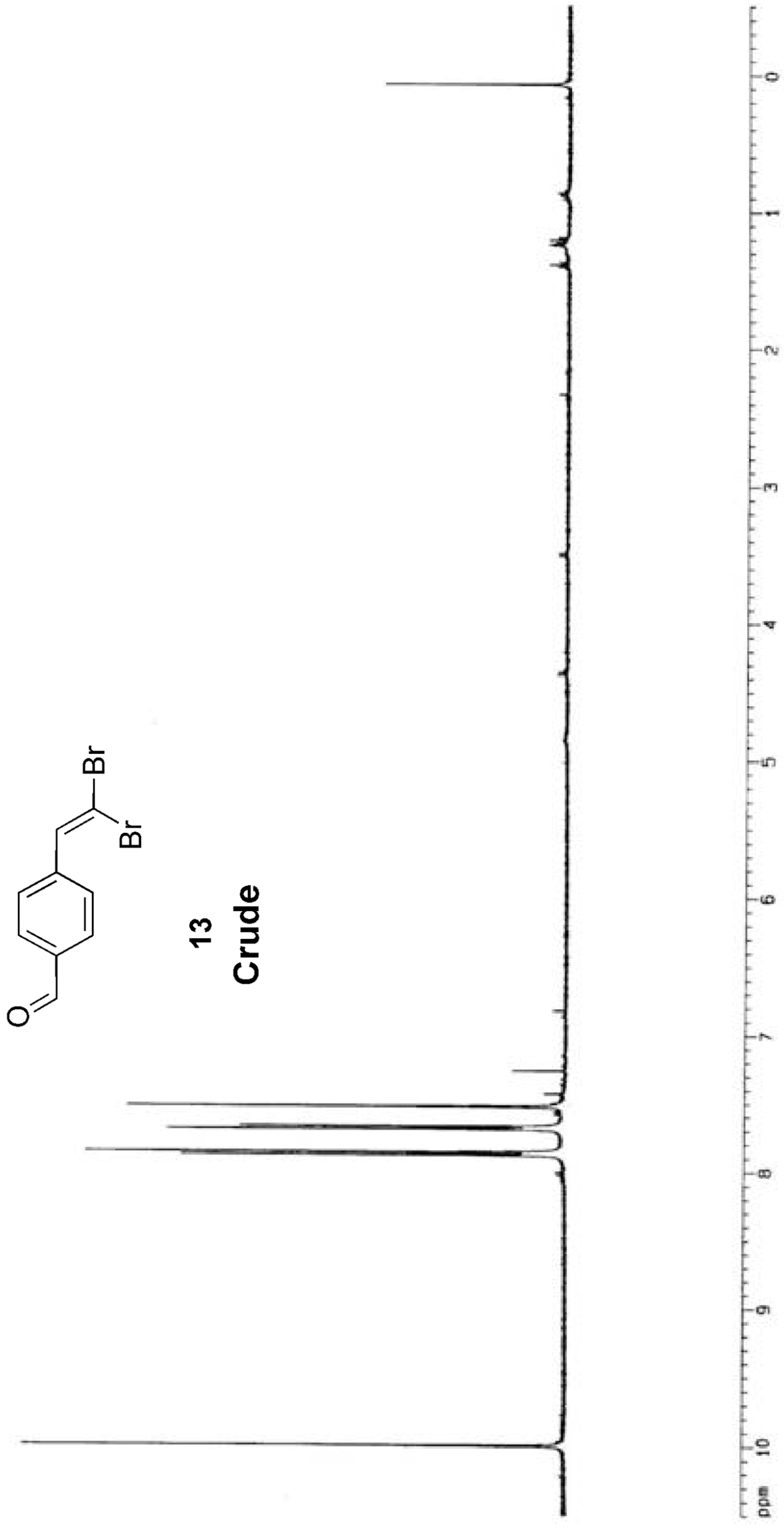

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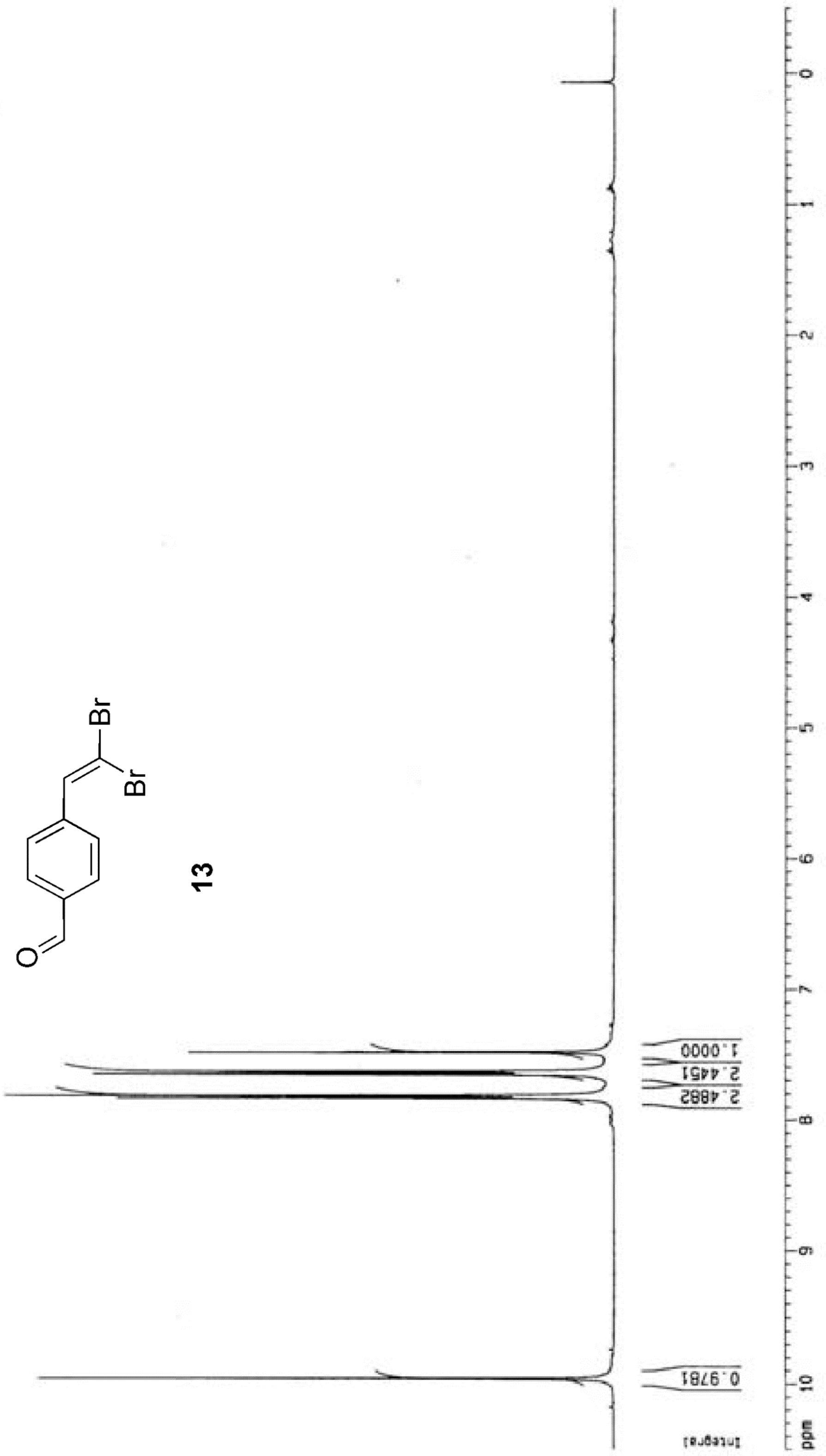

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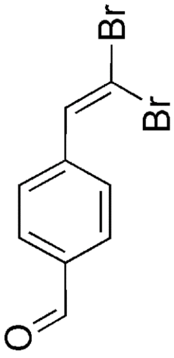

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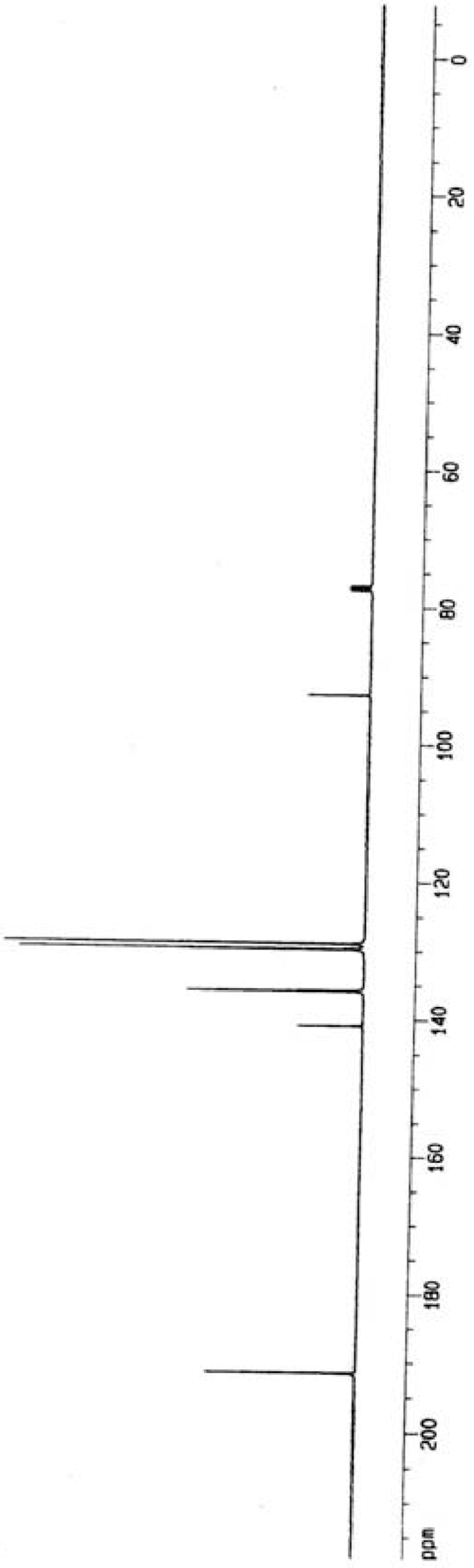

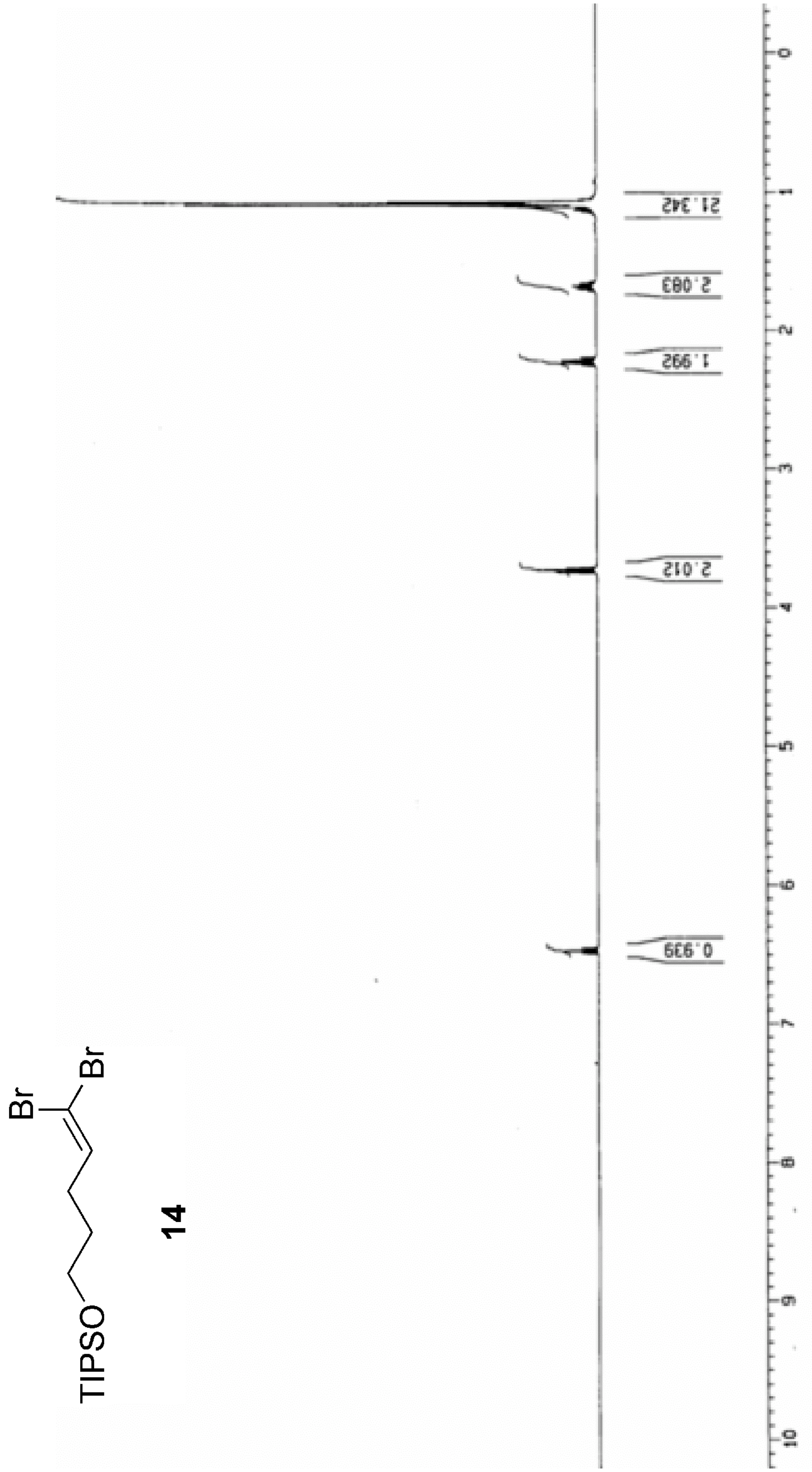

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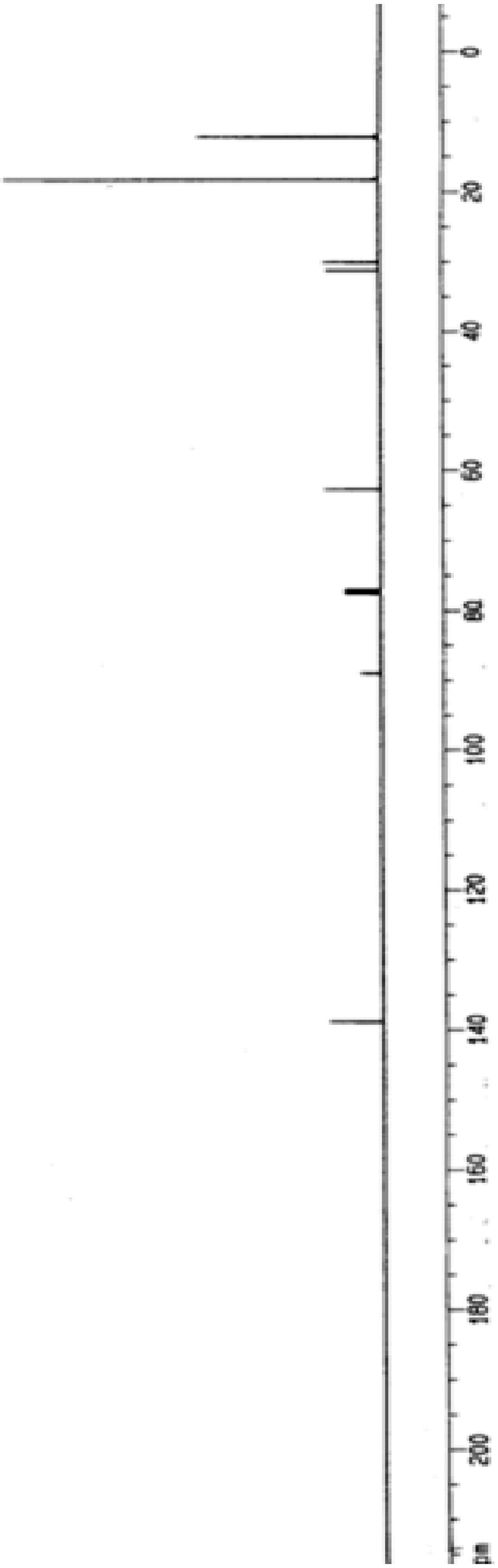

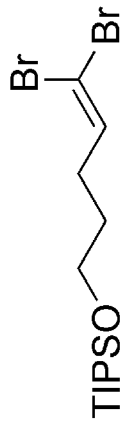

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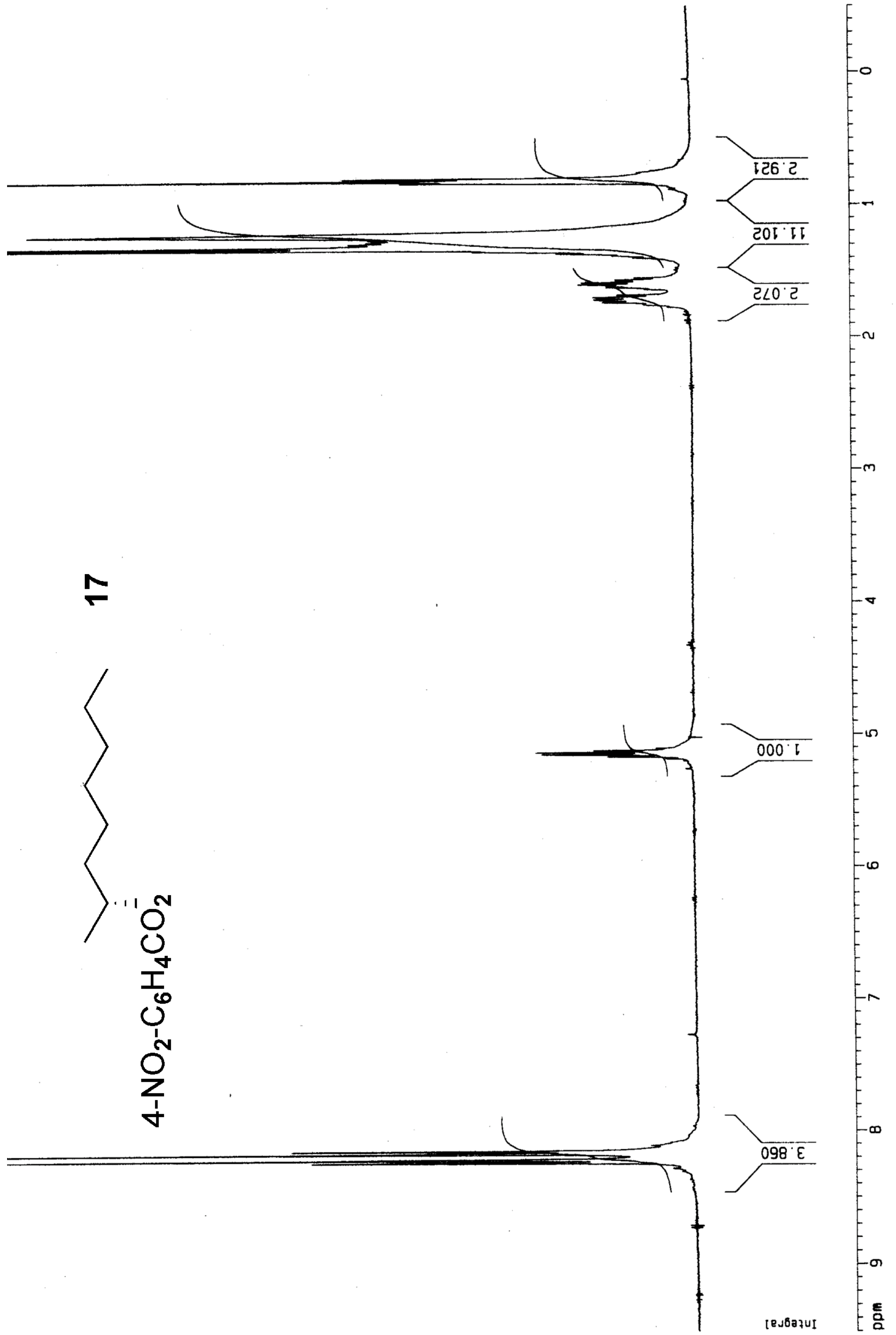
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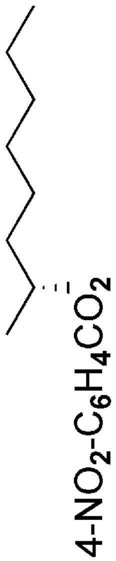

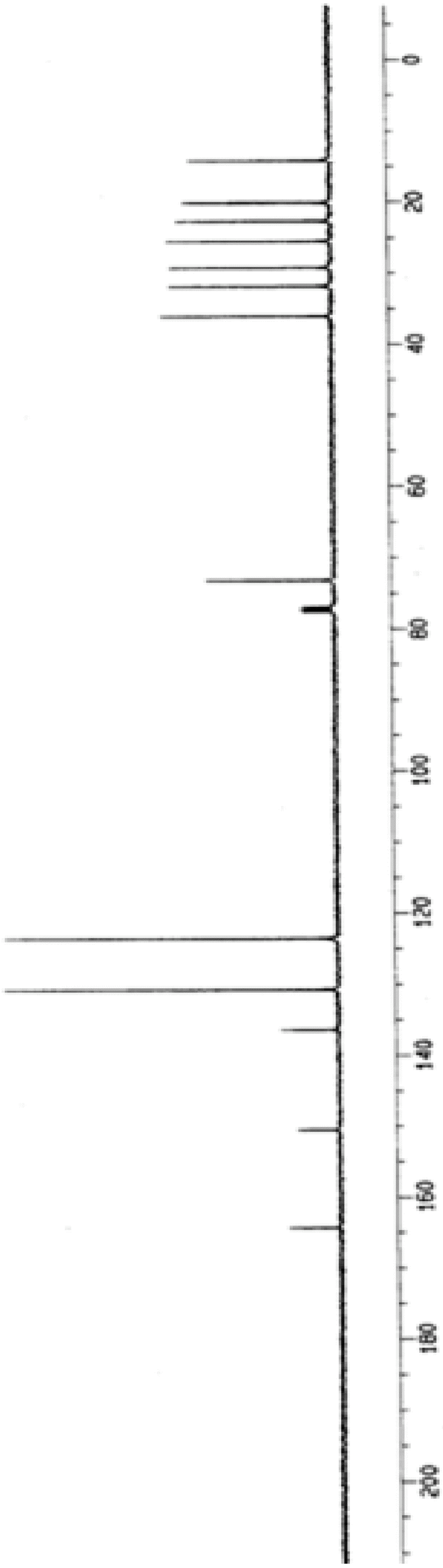

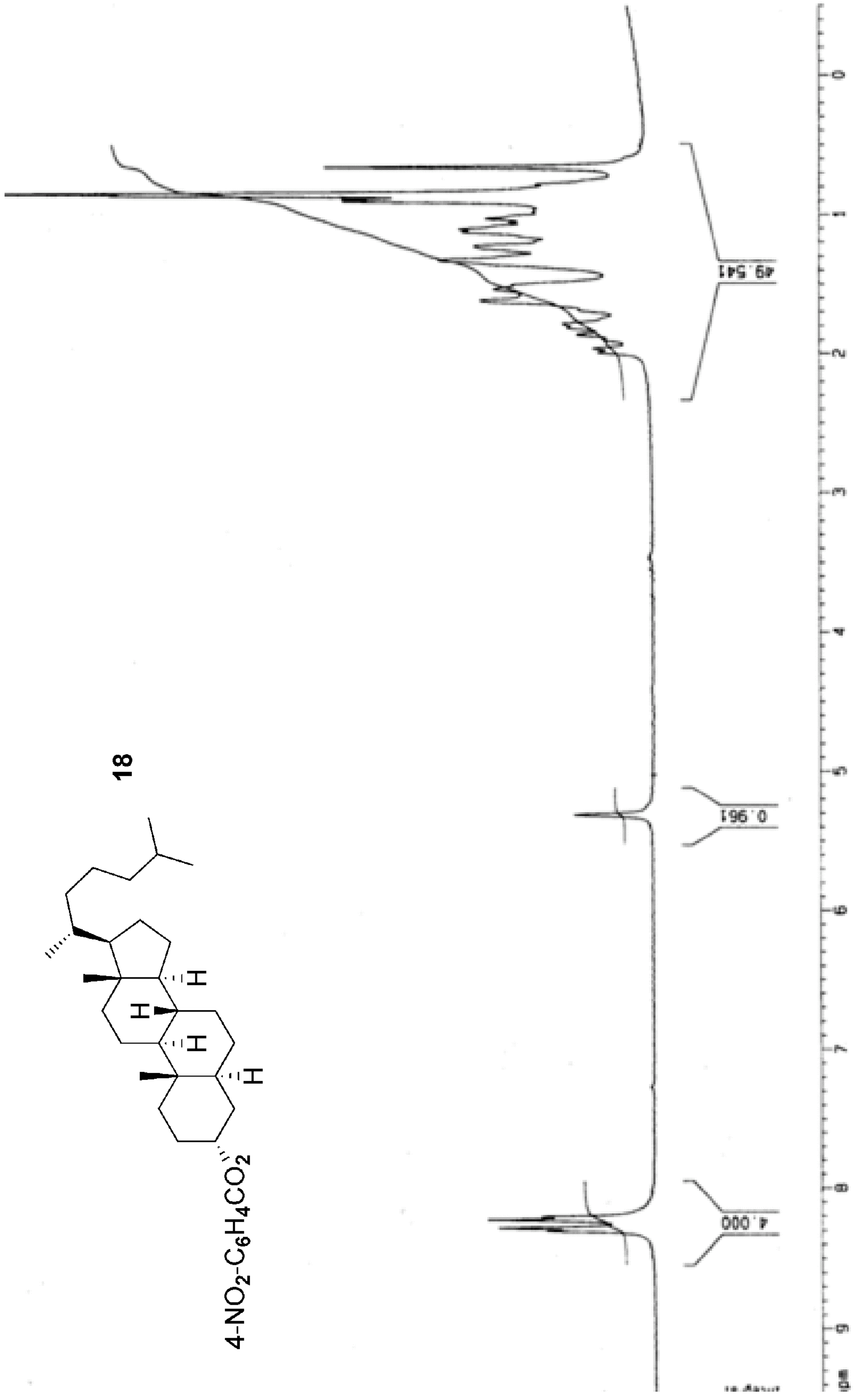

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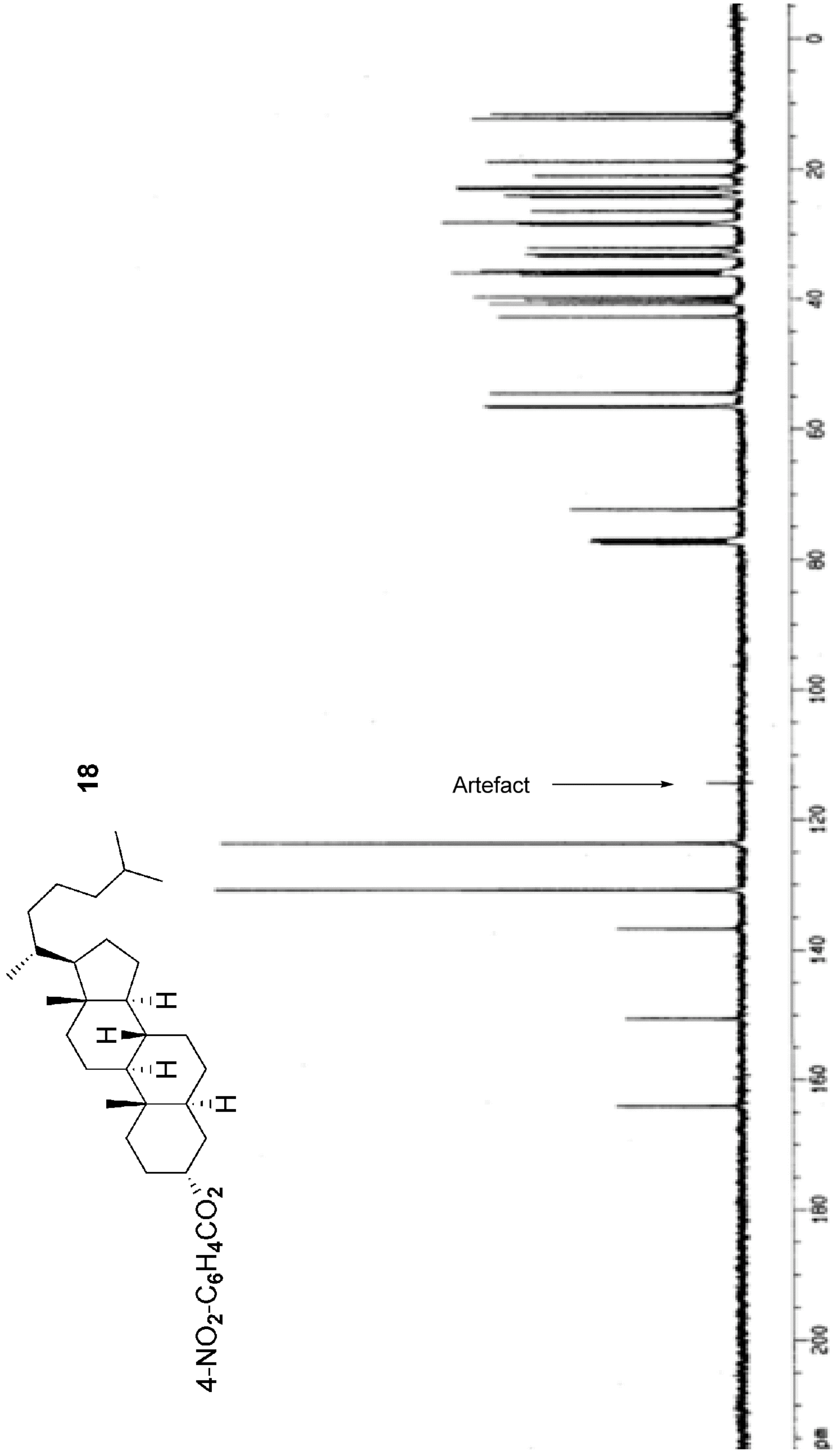

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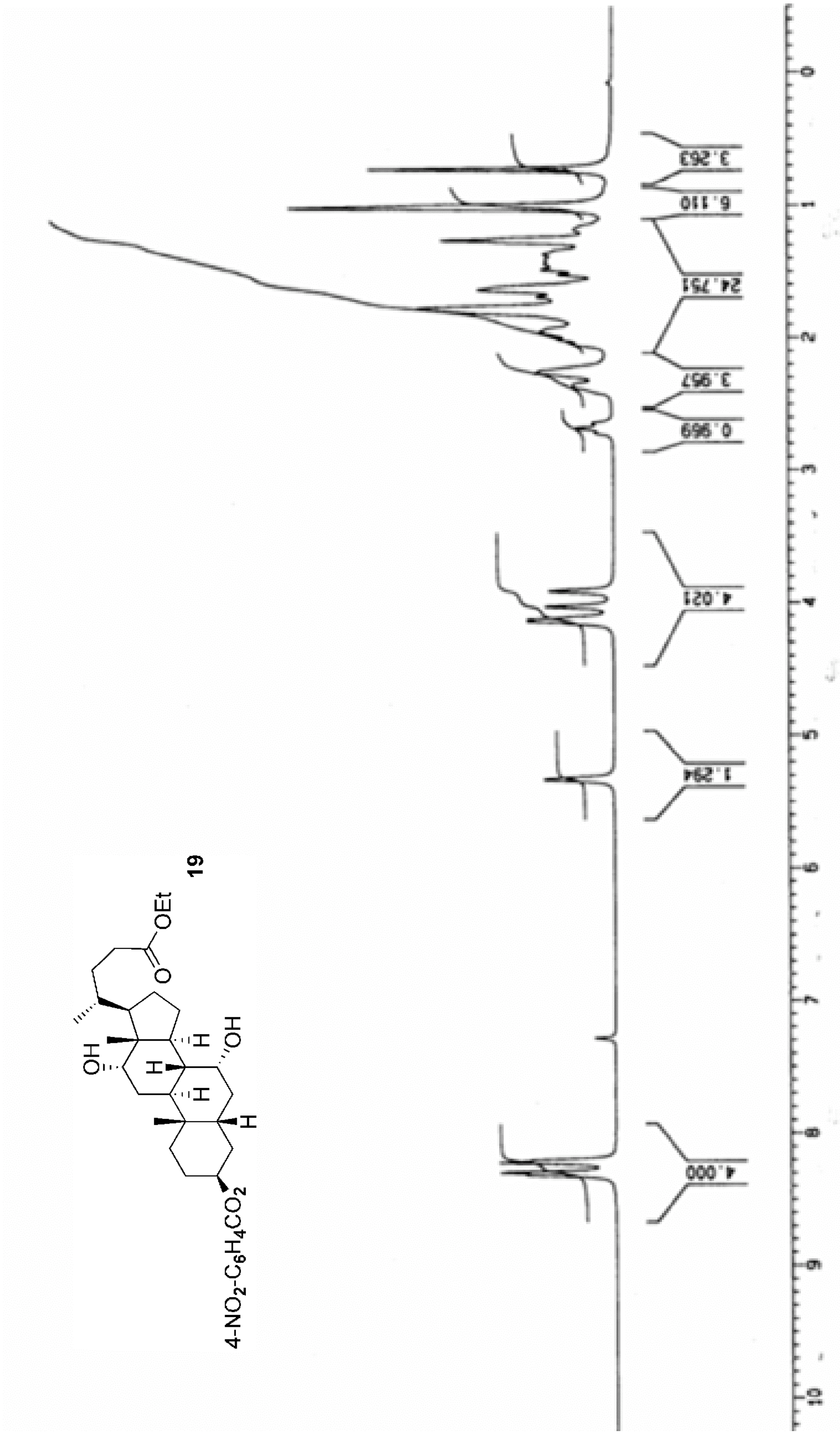
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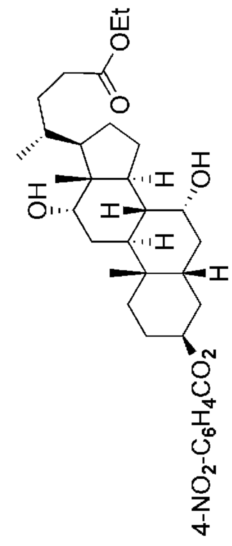
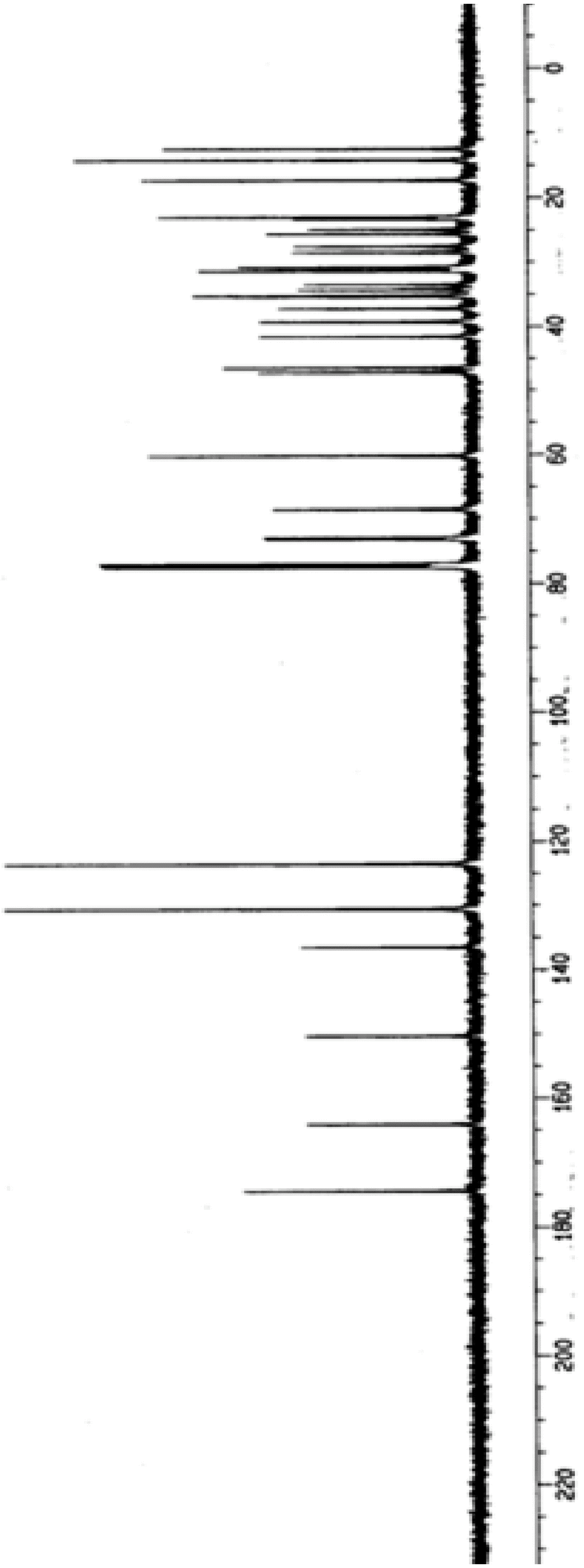
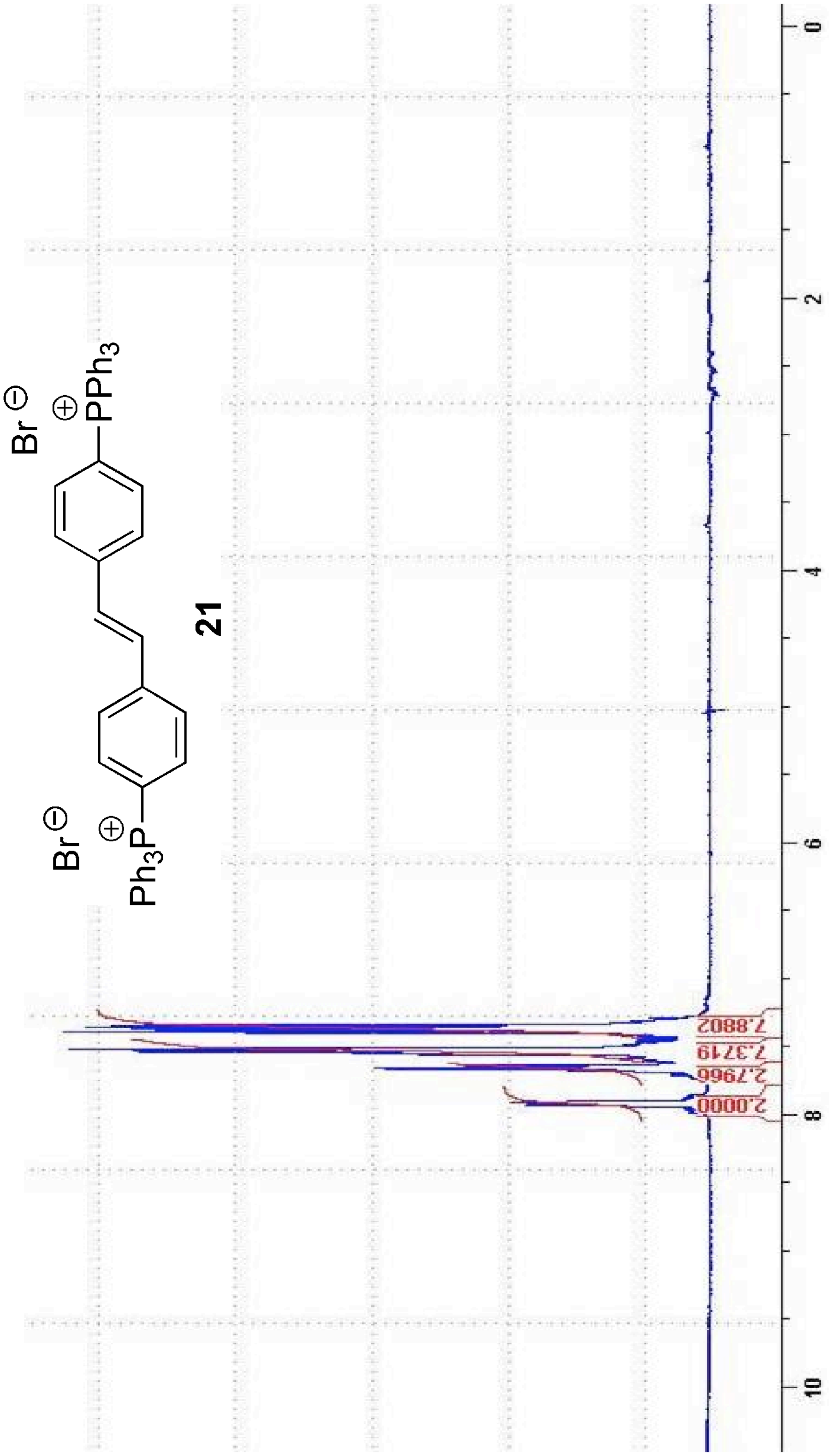
10

19

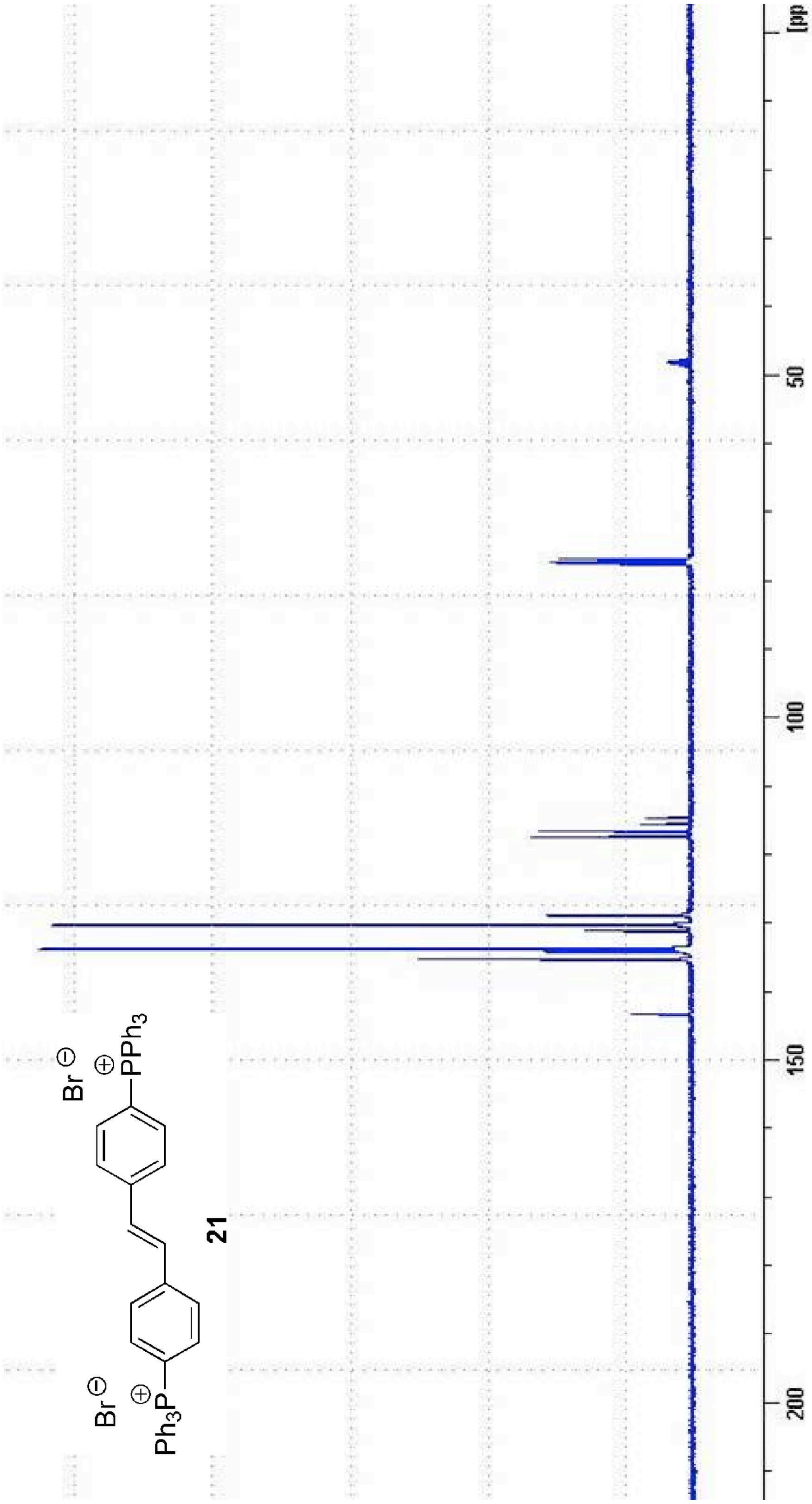

OH
OEt
O
H
OH
$4\text{-}NO_2\text{-}C_6H_4CO_2$

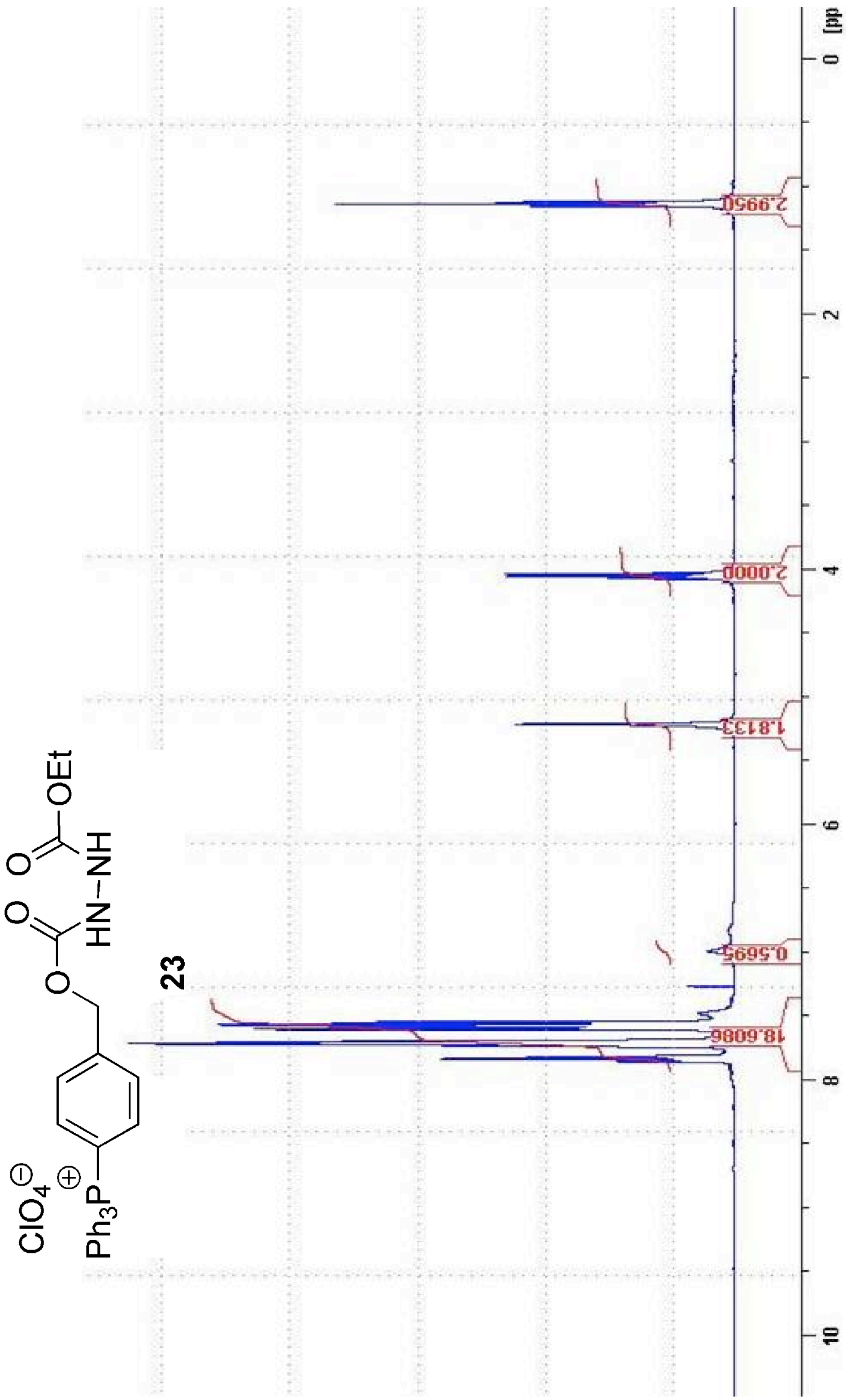
19


0
20
40
60
80
100
120
140
160
180
200
220

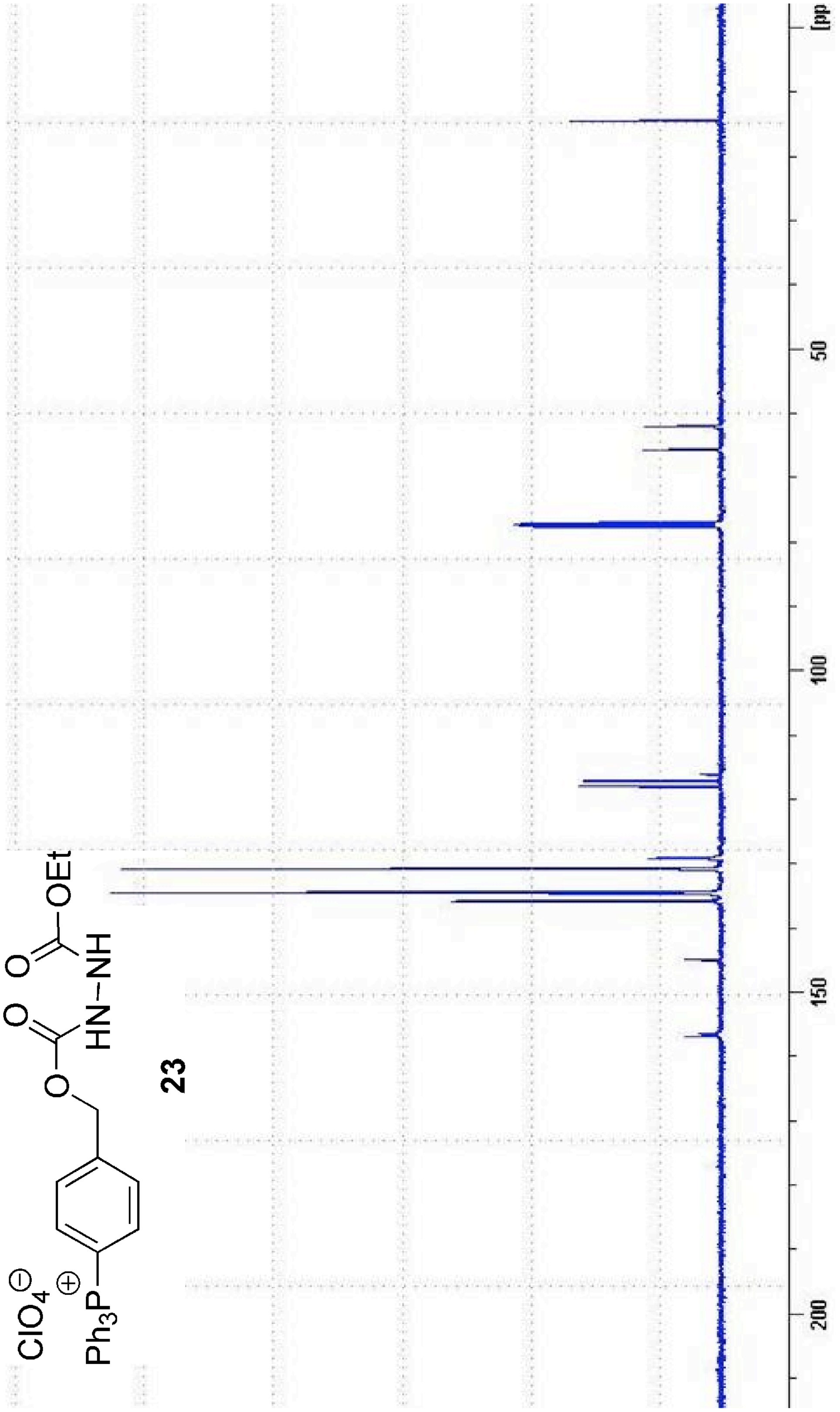


21


21

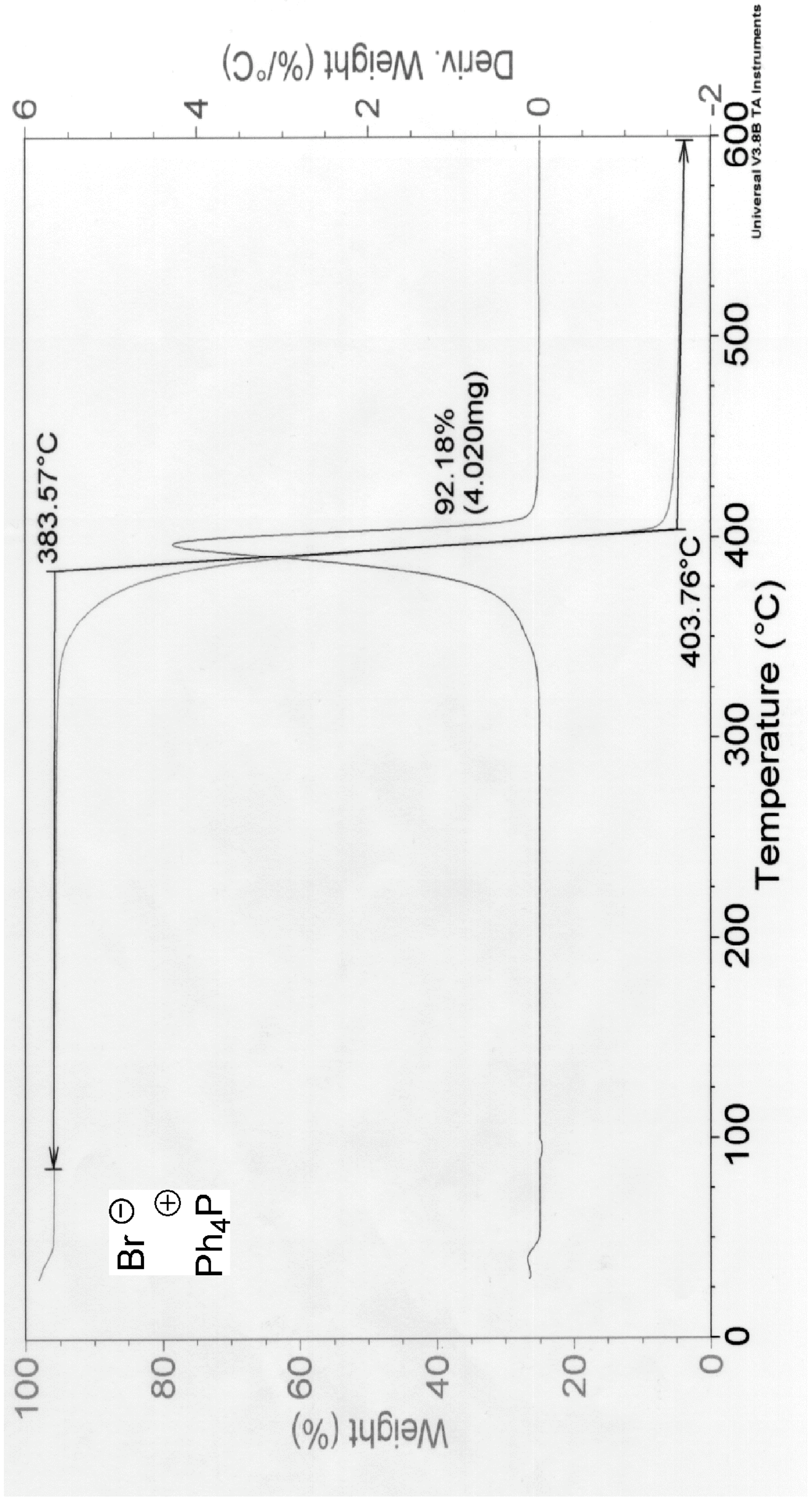

ClO4
Ph3P
O
O
O
HN–NH
OEt
2.9950
2.0000
1.8133
0.5695
18.6086
0
2
4
6
8
10
[ppm]

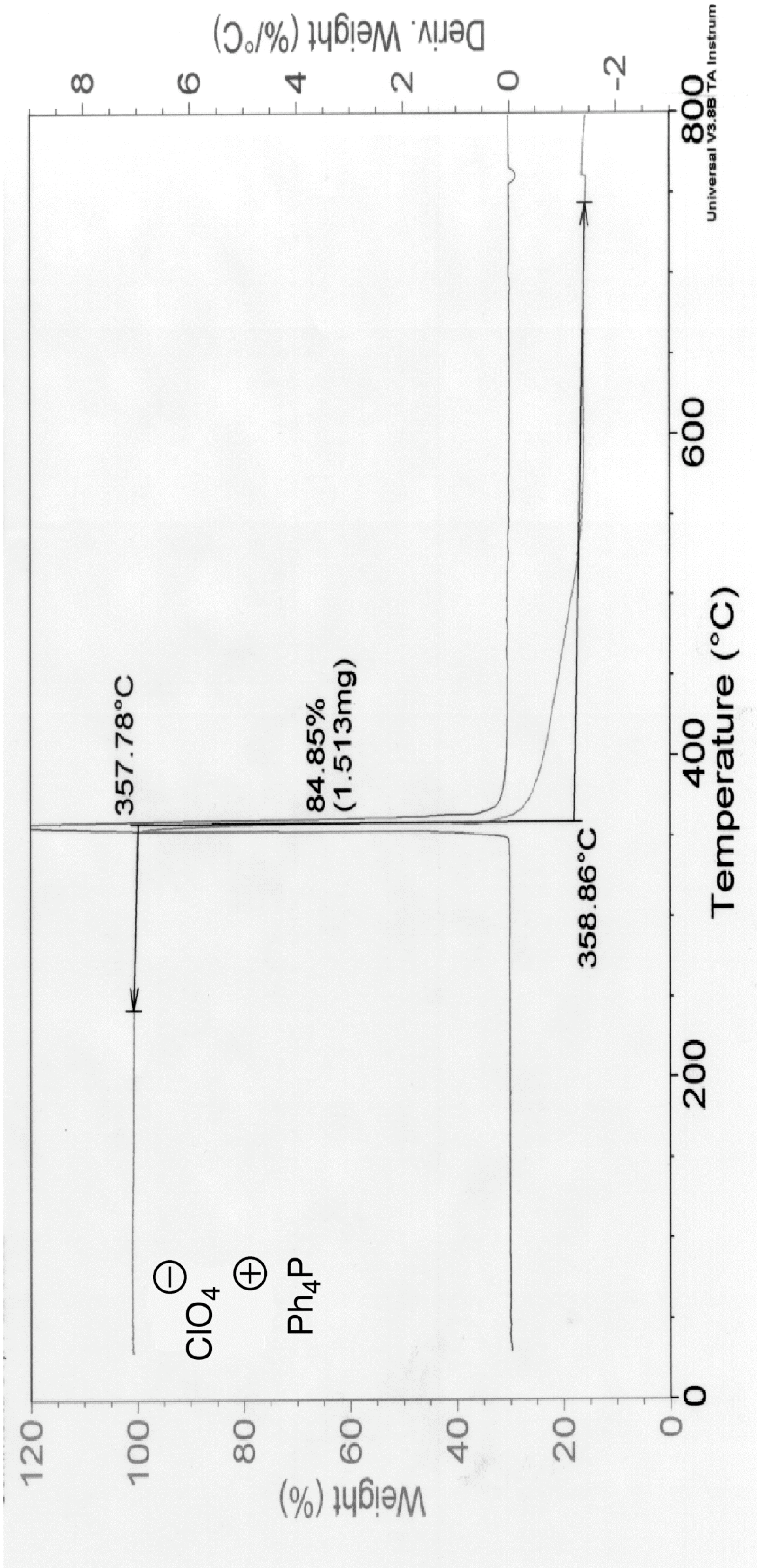
23



23

Themo gravimetric experiment




357.78°C
84.85%
(1.513mg)
358.86°C
$ClO_4^{\ominus}$
$Ph_4P^{\oplus}$
Weight (%)
120
100
80
60
40
20
0
Deriv. Weight (%/°C)
8
6
4
2
0
-2
Temperature (°C)
0
200
400
600
800
Universal V3.8B TA Instrum

References and Notes

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