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<Supporting Information - I>

Experimental Data

General:

^1H NMR and ^{13}C NMR spectra were recorded on GE QE-300 spectrometer at 300 MHz and 75.6 MHz, respectively. ^1H NMR chemical shifts are shown in ppm (δ) using residual CHCl_3 (δ 7.26) or C_6H_6 (δ 7.15) in the perdeuterated solvent as the internal standard. Multiplicities are reported with s (singlet), d (doublet), t (triplet), and m (multiplet). ^{13}C NMR chemical shifts are also shown in ppm (δ) relative to the internal standard CDCl_3 (δ 77.00) or C_6D_6 (δ 128.00). High resolution mass spectrometric data (HRMS) were obtained by using a Hitachi M-80 mass spectrometer.

Synthesis of 1,2-Diethoxy-1,2-di(trimethylsilyloxy)ethylene (**2**) (trans, cis-mixture).

Sodium metal (Na) (220 mmol) and potassium metal (K) (220 mmol) in toluene (ca. 100 mL) were heated up to ca. 100 °C under N_2 atmosphere to prepare Na-K alloy (liquid). After cooling to room temperature (rt), toluene was replaced by Et_2O (200 mL) by decantation. To a suspension of Na-K alloy in Et_2O was added TMSCl (450 mmol) at a rt under N_2 atmosphere. Diethyl oxalate **3** (200 mmol) was added dropwise with vigorous stirring at rate with which Et_2O boiled gently. Following complete addition, the mixture was stirred overnight. The solid material (NaCl and unreacted Na-K) was filtered off and washed twice with Et_2O (50 mL) under N_2 atmosphere. The combined organic layer was fractionally distilled to give **2** as a trans, cis-isomer mixture (47%) (bp 62-64 °C / 1.3 mmHg). Isomer ratio trans/cis (or cis/trans) = 1 / 1. **2**: ^1H NMR (C_6D_6) trans (or cis): 0.22 (s, 18H), 1.10 (t, $J = 7.1$ Hz, 6H), 3.75 (q, $J = 7.1$ Hz, 4H); cis (or trans): 0.23 (s, 18H), 1.12 (t, $J = 7.1$ Hz, 6H), 3.78 (q, $J = 7.1$ Hz, 4H); ^{13}C NMR (C_6D_6) (trans, cis mixture) -0.11, 0.09, 14.72, 14.77, 64.35, 65.42, 134.27, 134.99; IR (liquid film) (trans, cis mixture) 2975 (m), 2960 (m), 2900 (w), 1750 (w), 1250 (s), 1225 (s), 1130 (s), 845 (s) cm^{-1} .

Synthesis of 1,2-Diethoxy-1,2-di(trimethylsilyloxy)cyclopropane (**1**) (trans, cis-mixture).

A magnetically stirred solution of **2** (trans, cis mixture) (23.9 mmol) in Et₂O (120 mL) was cooled to 0 °C to which Et₂Zn (1.0 M in n-hexane) (31.1 mmol) was added. CH₂I₂ (62.1 mmol) was added dropwise by a syringe and the reaction mixture was stirred at 0 °C over 3 days and quenched by bubbling NH₃ for 10 min. The reaction mixture was allowed to warm up to rt and stirred vigorously for additional 10 min. The reaction mixture was filtered through a silica gel column with EtOAc as the eluent and the filtrate was concentrated. The crude mixture was subjected to a flash silica gel column chromatographic separation (0.2-0.3% EtOAc/n-hexane). The fraction containing **1**, which was impure, was subjected to a GPC separation (toluene) to yield pure **1** as a trans, cis mixture (1:1 ratio) in 30%. **1**: trans isomer: ¹H NMR (C₆D₆) 0.19 (s, 18 H), 1.14 (t, *J* = 7.1 Hz, 6H), 1.18 (s, 2 H), 3.75 (dq, *J* = 9.0 and 7.1 Hz, 2H), 3.81 (dq, *J* = 9.0 and 7.1 Hz, 2H); (CDCl₃) 0.17 (s, 18H), 1.16 (s, 2H), 1.17 (t, *J* = 7.1 Hz, 6H), 3.64 (dq, *J* = 9.0 and 7.1 Hz, 2H), 3.75 (dq, *J* = 9.0 and 7.1 Hz, 2H); ¹³C NMR (75.6 MHz, C₆D₆) 0.49, 15.13, 27.74, 62.03, 88.04. cis isomer: ¹H NMR (C₆D₆) 0.23 (s, 18H), 0.99 (d, *J* = 6.5 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 6H), 1.24 (d, *J* = 6.5 Hz, 1H), 3.62 (dq, *J* = 8.7 and 7.1 Hz, 2H), 3.81 (dq, *J* = 8.7 and 7.1 Hz, 2H); (in CDCl₃) 0.18 (s, 18H), 0.93 (d, *J* = 6.5 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.19 (d, *J* = 6.5 Hz, 1H), 3.64 (dq, *J* = 8.7 and 7.1 Hz, 2H), 3.72 (dq, *J* = 8.7 and 7.1 Hz, 2H); ¹³C NMR (C₆D₆) 0.49, 15.06, 26.56, 61.54, 88.52; IR (liquid film) (trans, cis mixture) 2975 (m), 2960 (m), 2900 (w), 1450 (w), 1250 (m), 1190 (m), 1145 (m), 865 (m), 845 (s) cm⁻¹; Anal. Calcd for C₁₃H₃₀O₄Si₂ (trans, cis mixture): C, 50.94; H, 9.86. Found: C, 51.15; H, 10.14.

Nonirradiated Single-Electron-Transfer (SET) Reaction of **1** with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

A reaction flask, in which a stirring bar and DDQ (0.163 mmol) were placed in advance, was dried under vacuum by heating with a dryer and replaced with N₂ atmosphere. To the flask was added a solution of **1** (0.163 mmol) in THF (2.8 mL) at rt and the mixture was stirred for 5 min. At this stage the yield of diethyl malonate (**4**, 81%) was determined based on the GC analysis of the reaction mixture. After removing the solvent under reduced pressure, a part of the mixture was dissolved in n-hexane and subjected to Florisil column chromatographic separation (5% Et₂O/n-pentane) to yield **4** (74%) together with 2,3-dichloro-5,6-dicyanohydroquinone (DDQH₂) (**5**) (95%). Spectroscopic data of **5**: IR (KBr) 2900-3500 (s), 2250 (m),

1570 (w), 1450 (s), 1270 (s), 1185 (s), 885 (m), 620 (w) cm^{-1} ; HRMS calcd for $\text{C}_8\text{H}_2\text{N}_2\text{O}_2\text{Cl}_2$ (M+), 227.9493, found 227.9488.

Nonirradiated SET Reaction of 1 with 2,3,5,6-Tetrachloro-1,4-benzoquinone (Chloranil, CA).

In a reaction flask equipped with a reflux condenser were placed in advance a magnetic stirring bar and CA (0.163 mmol), and the flask was dried under vacuum and replaced with N_2 atmosphere. To the flask was added a solution of **1** (0.163 mmol) in THF (2.8 mL) at rt, the mixture was warmed to 67 °C and stirred for 70 h. GC analysis on the reaction mixture was conducted to calculate the GC yield of diethyl malonate (**4**, 72%). After removing the solvent under reduced pressure, a part of the mixture was dissolved in n-hexane and subjected to Florisil column chromatographic separation (5% Et_2O /n-pentane) to give **4** in 63% yield. Other products were tetrachlorohydroquinone (**5**, X = Cl, Y = H) and CA obtained as a mixture. (**5**): IR (KBr) 3050-3500 (s), 1405 (s), 1305 (s), 1200 (s), 880 (s), 700 (s), 515 (w) cm^{-1} .

Photo-Induced Electron Transfer (PET) Reaction of 1 with CA.

A test-tube-shaped reaction flask in which a stirring magnetic bar and CA (0.163 mmol) were placed in advance was dried under vacuum and replaced with N_2 atmosphere. To the flask was added a solution of **1** (0.163 mmol) in THF (2.8 mL) at rt and the reaction mixture was irradiated with a high-pressure mercury lamp through a Pyrex filter for 1 h. GC analysis on the reaction mixture proved that diethyl malonate (**4**) was formed in 76% yield at this stage. After removing the solvent under reduced pressure, a part of the mixture was dissolved in n-hexane and subjected to Florisil column chromatographic separation (5% Et_2O /n-pentane) to give **4** in 59% yield. Other products were **5** (X = Cl, Y = H) and CA obtained as a mixture.

Nonirradiated SET Reaction of 1 with 7,7,8,8-Tetracyanoquinodimethane (TCNQ).

The reaction procedure was analogous to that described above for the nonirradiated reaction of **1** with CA except the reaction mixture was stirred for 5 h. GC analysis on the reaction mixture was conducted to determine the GC yield of diethyl malonate (**4**) (84%). After removing the solvent under reduced pressure, a part of the mixture was dissolved in n-hexane and subjected to Florisil column chromatographic separation (5%

Et₂O/n-pentane) to give **4** in 72% yield. Other detected product was 1,4-di(dicyanomethyl)benzene (TCNQH₂, **6**) in a mixture. **6**: HRMS calcd for C₁₂H₆N₄ (M⁺) 206.0592, found 206.0587; UV (MeCN) λ_{max} 310 nm). Before the column chromatography, two intermediate products **7** and **8** were detected by ¹H NMR. TCNQ(TMS)₂ (**7**): ¹H NMR (C₆D₆) -0.22 (s, 18H), 7.13 (s, 4H). TCNQH(TMS) (**8**): ¹H NMR (C₆D₆) -0.21 (s, 9H), 6.74 (ddd, *J* = 1.5, 2.1, and 8.4 Hz, 2H), 6.87 (ddd, *J* = 2.1, 2.1, and 8.4 Hz, 2H).

Competitive Reaction of **1 and 1-Methoxy-1-trimethylsilyloxy-2-phenylcyclopropane (CPA) (*E*, *Z*-mixture).**

A reaction flask, in which a stirring bar and DDQ (0.163 mmol) were placed in advance, was dried under vacuum and replaced with N₂ atmosphere. To the flask was added a solution of **1** (0.163 mmol) and CPA (0.163 mmol) dissolved in THF (2.8 mL) at rt and the mixture was stirred for 20 min. GC analysis on the reaction mixture was conducted to determine the GC yield of diethyl malonate (**4**, 6.3%). After removing the solvent under reduced pressure, a part of the mixture was dissolved in n-hexane and subjected to silica column chromatographic separation (1% EtOAc/n-hexane) to yield methyl 3-phenylpropenoate (*E*-isomer) (54%) and recovered **1** (43%) together with **5** (X = CN, Y = H) (100%): ¹H NMR (CDCl₃) 3.80 (s, 3H), 6.44 (d, *J* = 15.9 Hz, 1H), 7.36-7.41 (m, 3H), 7.49-7.55 (m, 2H), 7.70 (d, *J* = 15.9 Hz, 1H).

PET Reaction of **1 with Ketones in the Presence of Mg(ClO₄)₂. A General Procedure.**

A test-tube-shaped reaction flask in which a ketone (0.245 mmol), Mg(ClO₄)₂ (0.163 mmol), and a stirring magnetic bar were placed in advance was dried under vacuum and replaced with N₂ atmosphere. To the flask was added a solution of **1** (0.163 mmol) in deoxygenated MeCN at rt and the reaction mixture was irradiated with a high-pressure mercury lamp through a Pyrex filter. The reaction mixture was washed with a mixture of water and CH₂Cl₂ (or Et₂O) and the organic layer was dried over Na₂SO₄. GC analysis on the reaction mixture was conducted to determine the GC yield of **4**. After removing the solvent under reduced pressure, the product mixture which was dissolved in CHCl₃ (or toluene) was subjected to GPC separation and, if necessary, flash silica gel chromatographic separation. Spectroscopic data of products are as follows.

Ethyl 4-hydroxy-4,4-diphenyl-3-oxobutanoate (9): ^1H NMR (CDCl_3) 1.23 (t, $J = 7.1$ Hz, 3H), 3.47 (s, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 6.93 (s, 2H), 7.19-7.35 (m, 10H); ^{13}C NMR (CDCl_3) 13.94, 41.89, 61.52, 77.94, 127.10, 128.00, 128.44, 139.52, 165.5, 166.2; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ (M^+) 298.1205, found 298.1210.

Ethyl 4-(4-cyanophenyl)-4-hydroxy-3-oxopentanoate (22): ^1H NMR (CDCl_3) 1.25 (t, $J = 7.1$ Hz, 3H), 1.56 (d, $J = 6.7$ Hz, 3H), 3.40 (s, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 5.93 (q, $J = 6.7$ Hz, 1H), 7.45 (ddd, $J = 1.8, 1.8$, and 8.1 Hz, 2H), 7.65 (ddd, $J = 1.8, 1.8$, and 8.1 Hz, 2H); HRMS calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_4$ (M^+) 261.1001, found 261.0995.

3-Ethoxy-4,4-diphenyl-3-trimethylsilyloxy-4-butanolide (10): ^1H NMR (CDCl_3) 0.03 (s, 9H), 1.11 (t, $J = 7.0$ Hz, 3H), 2.71 (d, $J = 16.2$ Hz, 1H), 2.84 (d, $J = 16.2$ Hz, 1H), 3.25 (dq, $J = 8.4$ and 7.1 Hz, 1H), 3.57 (dq, $J = 8.4$ and 7.1 Hz, 1H), 7.22-7.33 and 7.55-7.66 (m, 10H); HRMS calcd for $\text{C}_{21}\text{H}_{26}\text{O}_4\text{Si}$ (M^+) 370.1600, found 370.1596.

4-(4-Cyanophenyl)-3-ethoxy-4-methyl-3-trimethylsilyloxy-4-butanolide (23): (a diastereoisomeric mixture) One isomer: ^1H NMR (CDCl_3) 0.24 (s, 9H), 0.81 (t, $J = 6.9$ Hz, 3H), 1.66 (s, 3H), 2.85 (s, 2H), 3.04 (dq, $J = 8.4$ and 6.9 Hz, 1H), 3.14 (dq, $J = 8.4$ and 6.9 Hz, 1H), 7.54-7.65 (m, 4H); Another isomer: ^1H NMR (CDCl_3) -0.17 (s, 9H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.69 (s, 3H), 2.75 (d, $J = 16.8$ Hz, 1H), 3.04 (d, $J = 16.8$ Hz, 1H), 3.48 (dq, $J = 8.7$ and 7.1 Hz, 1H), 3.70 (dq, $J = 8.7$ and 7.1 Hz, 1H), 7.54-7.65 (m, 4H); HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{Si}$ (M^+) 333.1396, found 333.1394.

1,1,2,2-Tetraphenyl-1,2-ethanediol (Benzopinacol 11): ^1H NMR (CDCl_3) 3.03 (s, 2H), 7.15-7.32 (m, 20H).

2,3-Di-(4-cyanophenyl)-2,3-butanediol (24): (1:1 mixture of diastereomers) ^1H NMR (CDCl_3) 1.55 (s, 6H), 1.57 (s, 6H), 2.23 (s, 2H), 2.49 (s, 2H), 7.24-7.56 (m, 8H x 2).

Diphenylmethanol (Benzhydrol, 12): ^1H NMR (CDCl_3) 2.18 (brs, 1H), 5.85 (s, 1H), 7.23-7.40 (m, 10H).

1-(4-Cyanophenyl)ethanol (25): ^1H NMR (CDCl_3) 1.49 (d, $J = 6.5$ Hz, 3H), 1.91 (brs, 1H), 4.96 (q, $J = 6.5$ Hz, 1H), 7.46-7.52 (m, 2H), 7.61-7.67 (m, 2H).

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<Supporting Information - II>

^1H NMR and ^{13}C NMR Spectra of Products : INDEX

- No.1: ^1H nmr of 1,2-diethoxy-1,2-di(trimethylsilyloxy)cyclopropane (**1**) (mixture of trans, cis isomer) in C_6D_6 .
- No.2: ^{13}C nmr of **1** (mixture of trans, cis isomer).
- No.3: ^1H nmr of cis 1,2-diethoxy-1,2-di(trimethylsilyloxy)cyclopropane (**1**) in CDCl_3 .
- No.4: ^1H nmr of ethyl 4-hydroxy-4,4-diphenyl-3-oxobutanoate (**9**).
- No.5: ^{13}C nmr of ethyl 4-hydroxy-4,4-diphenyl-3-oxobutanoate (**9**).
- No.6: ^1H nmr of 3-ethoxy-4,4-diphenyl-3-trimethylsilyloxy-4-butanolide (**10**).
- No.7: ^1H nmr of ethyl 4-(4-cyanophenyl)-4-hydroxy-3-oxopentanoate (**22**).
- No.8: ^1H nmr of 4-(4-cyanophenyl)-3-ethoxy-4-methyl-3-trimethylsilyloxy-4-butanolide (**23**).

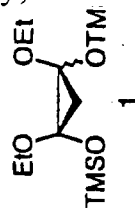


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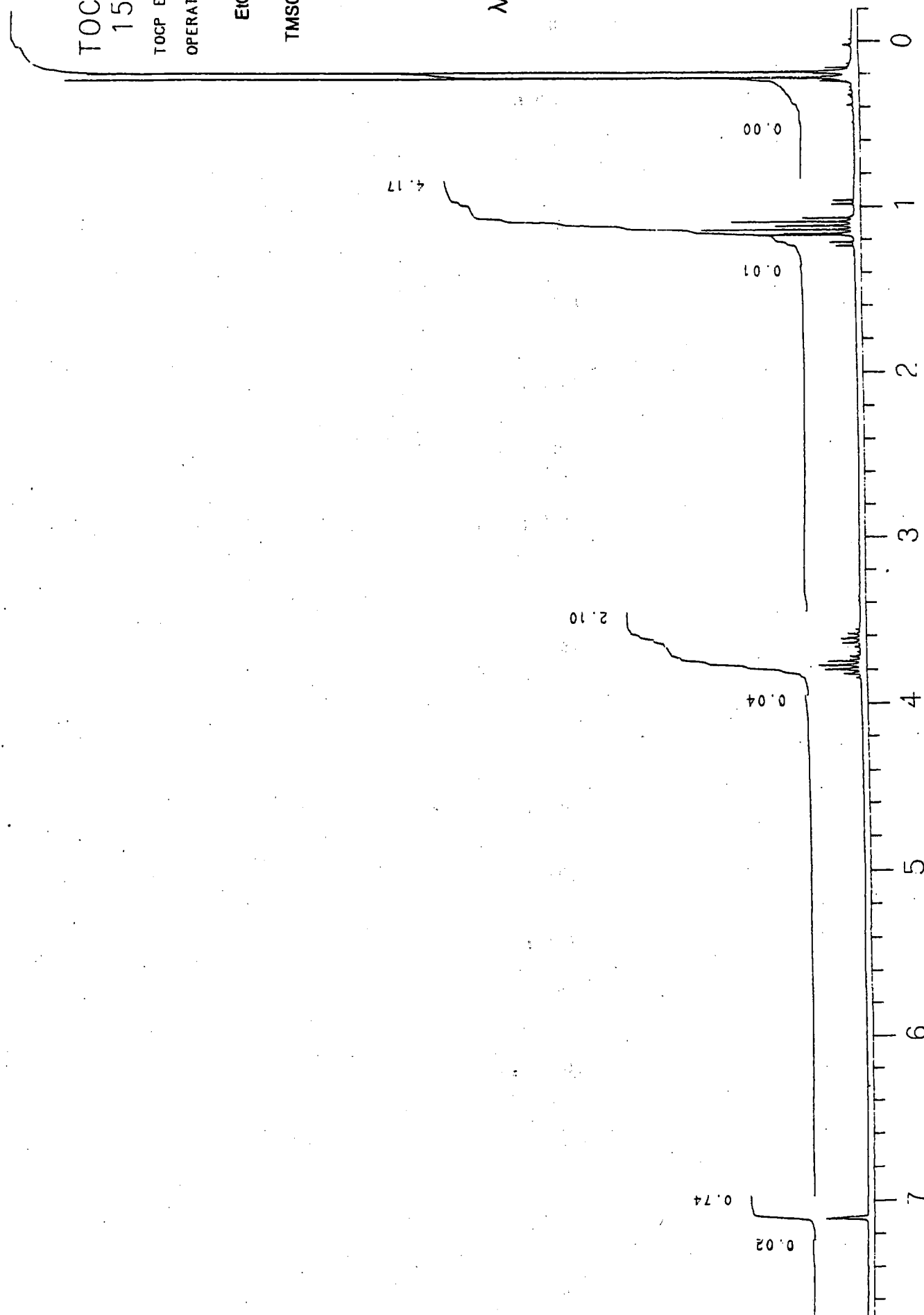
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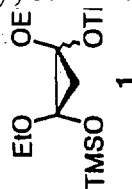




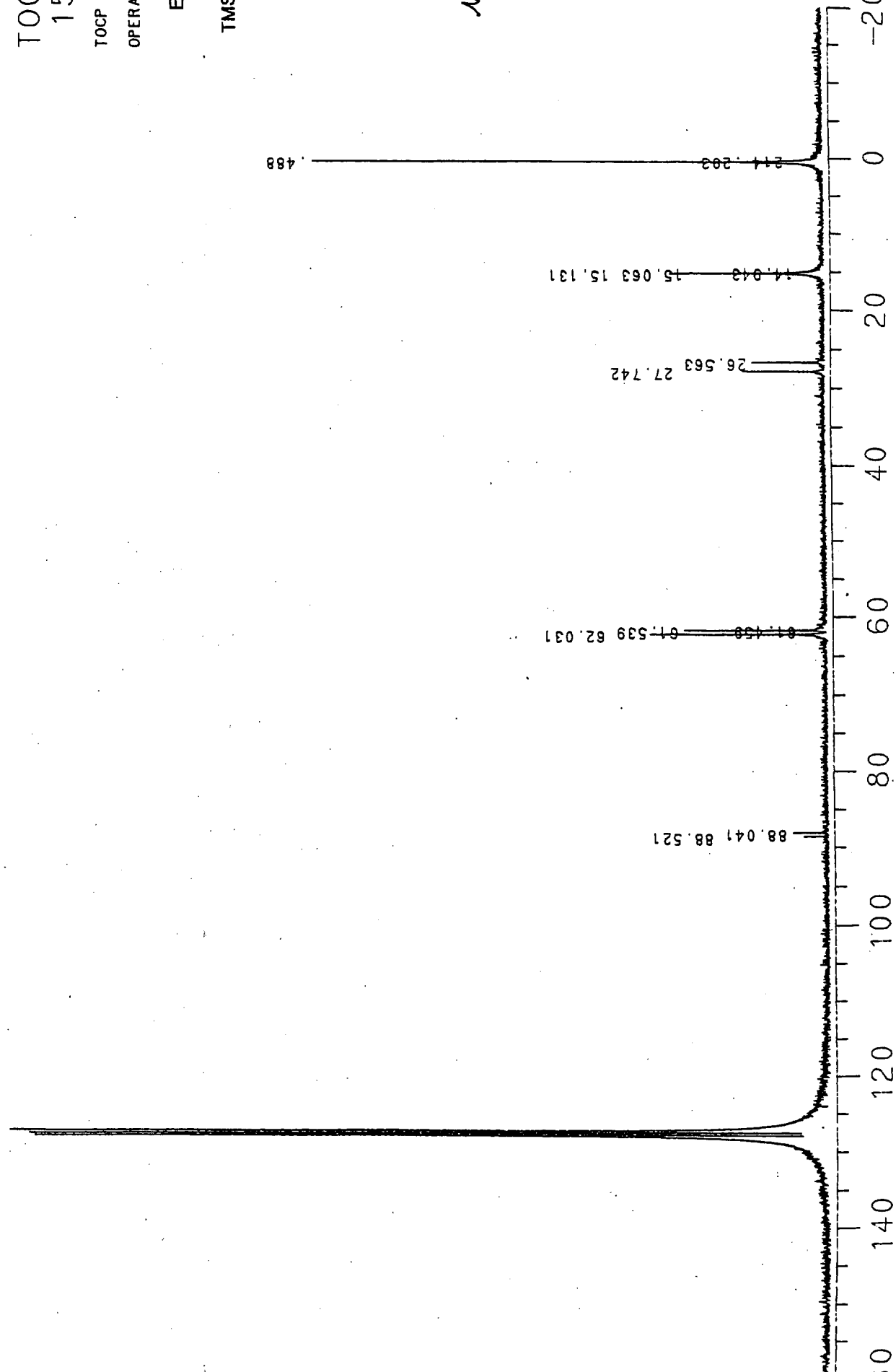
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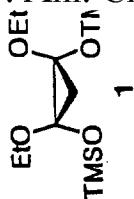




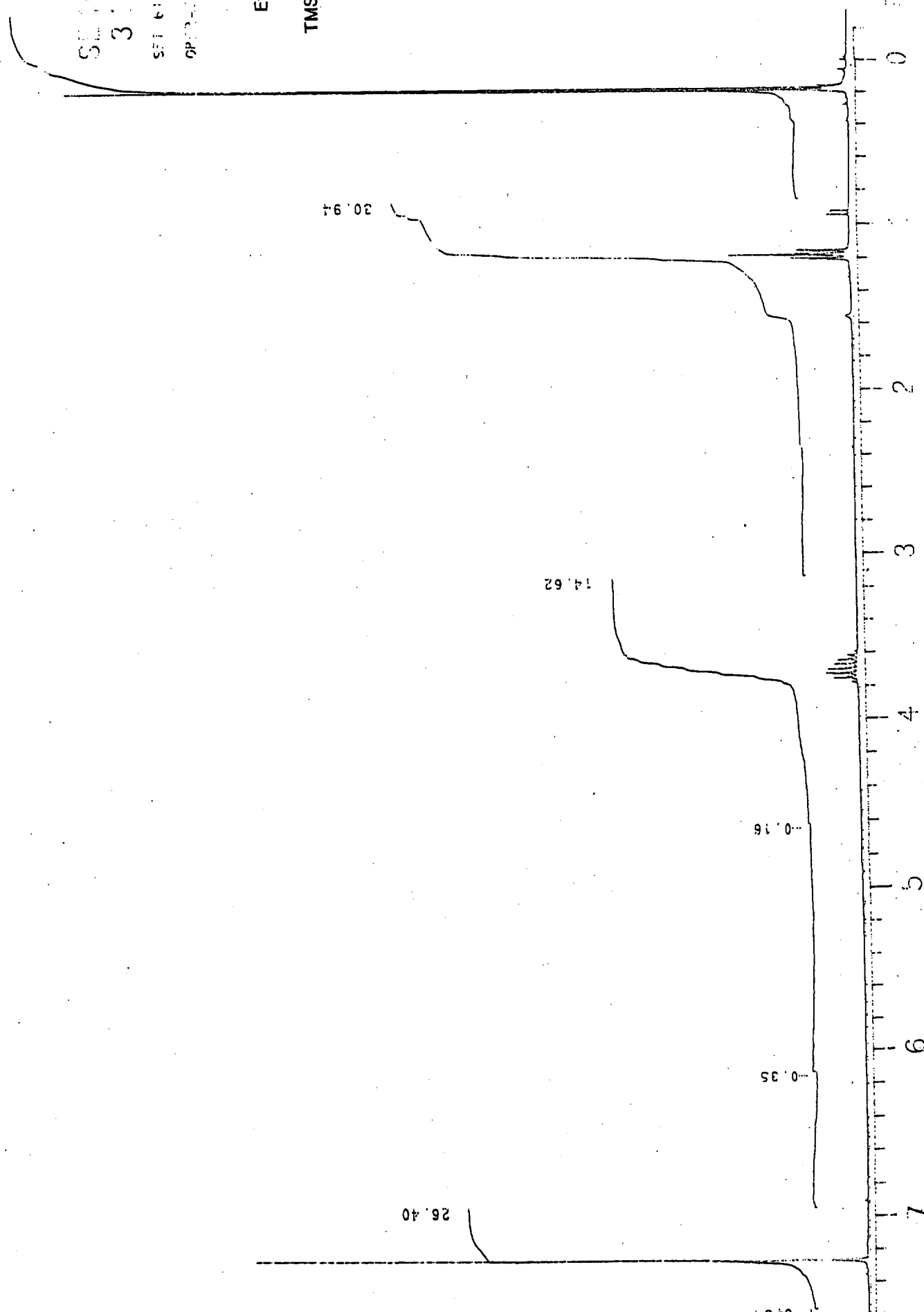
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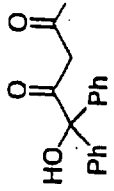
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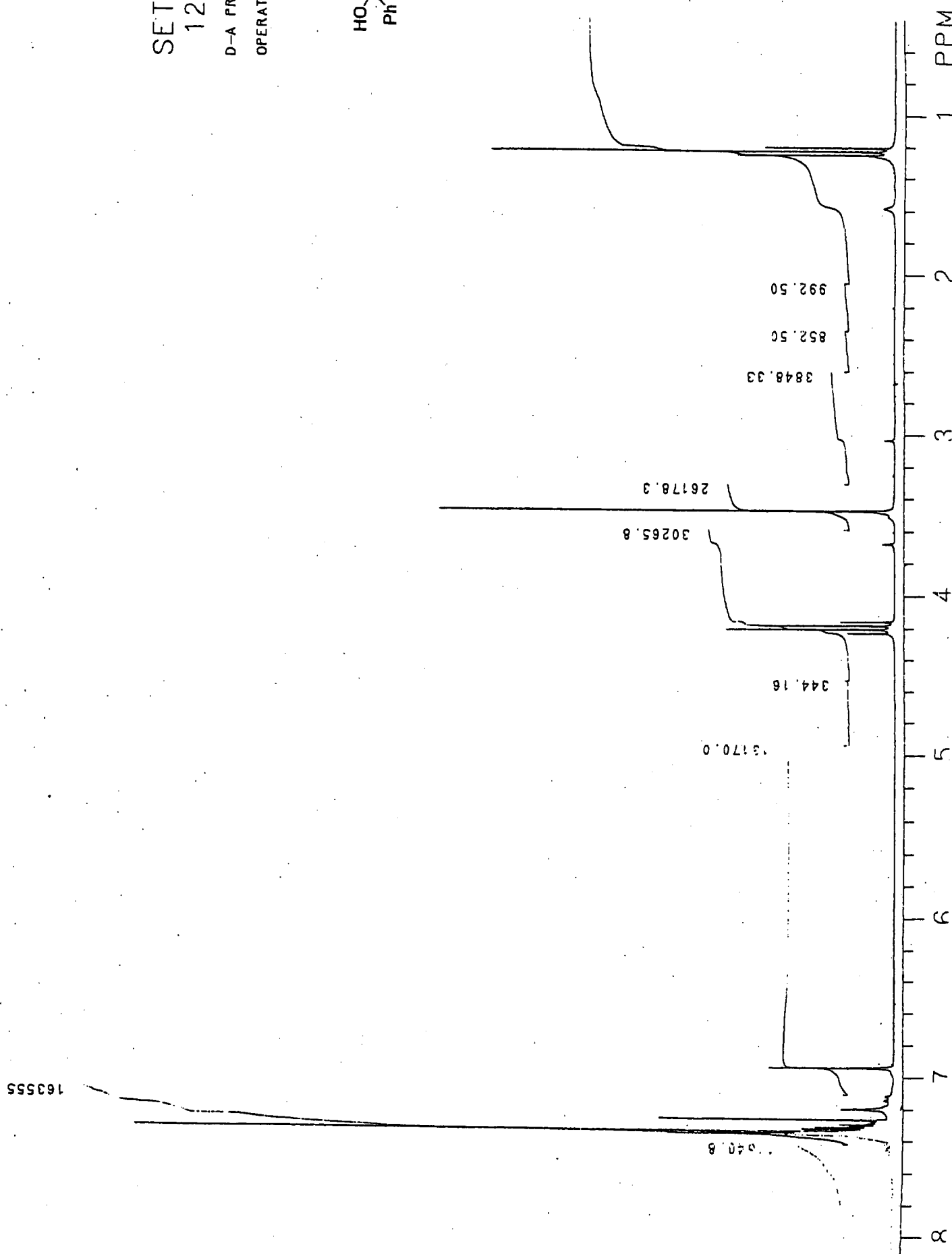
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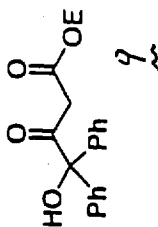




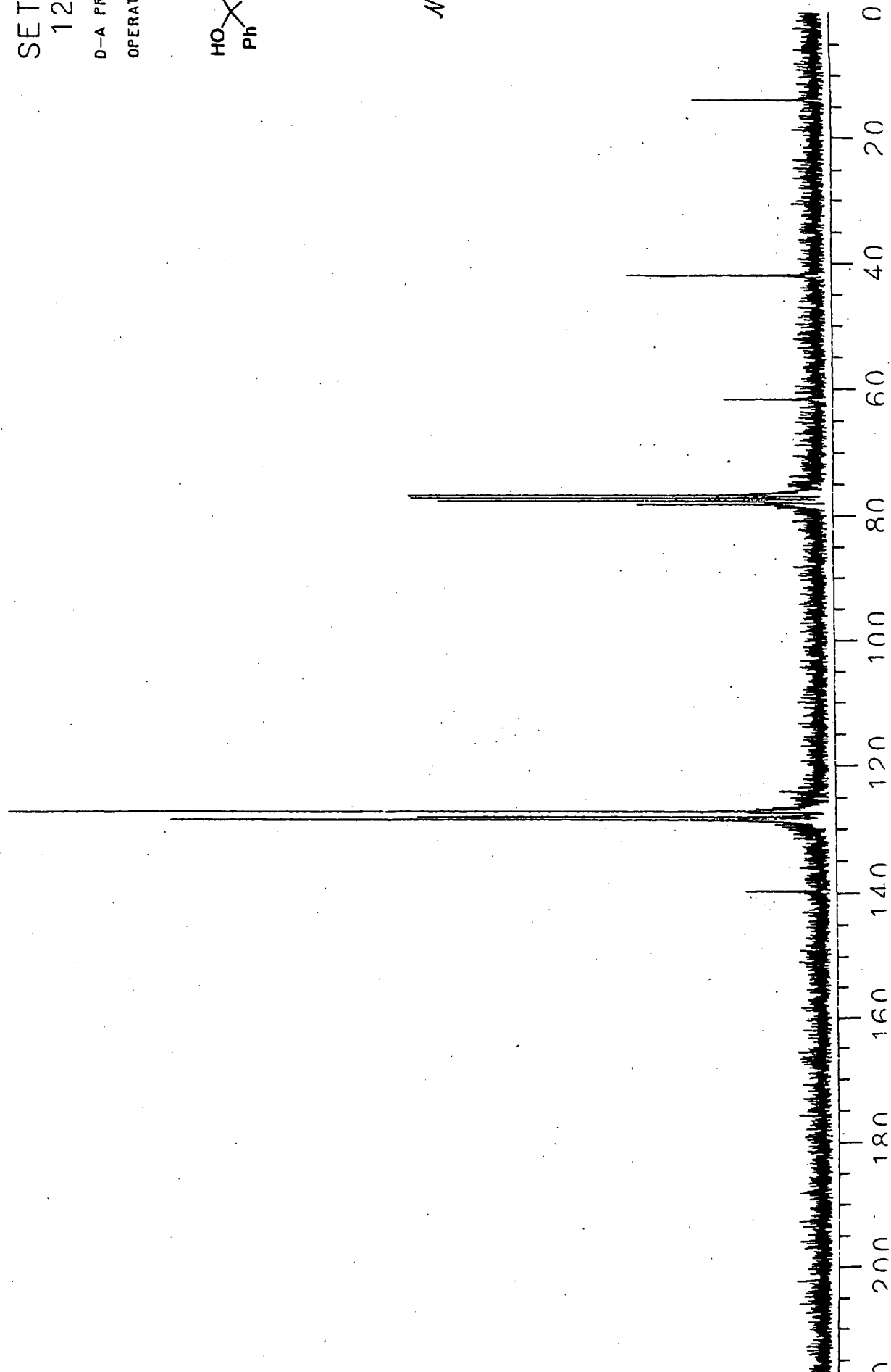
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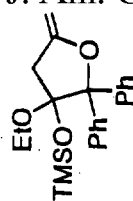




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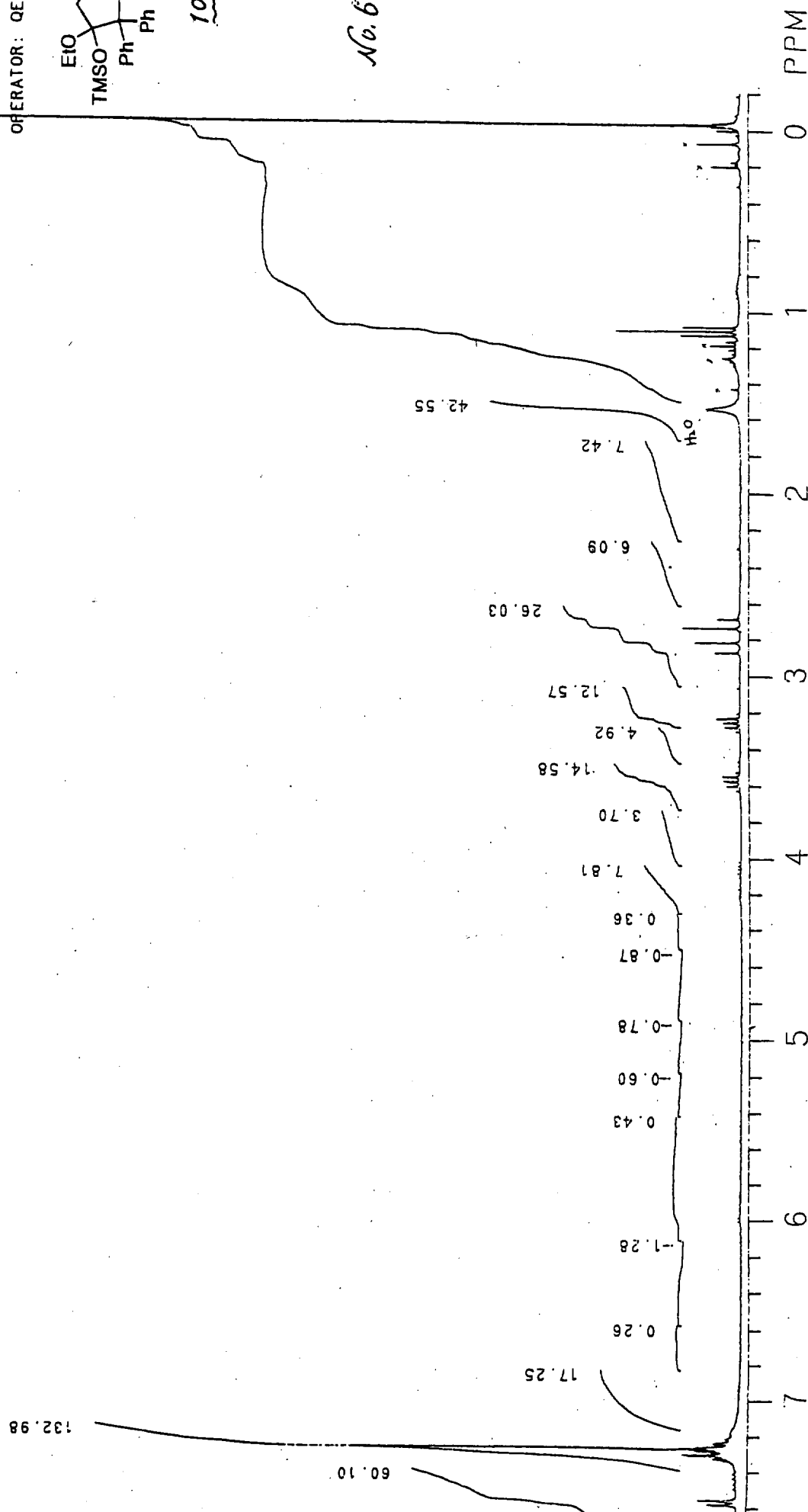
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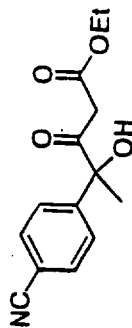
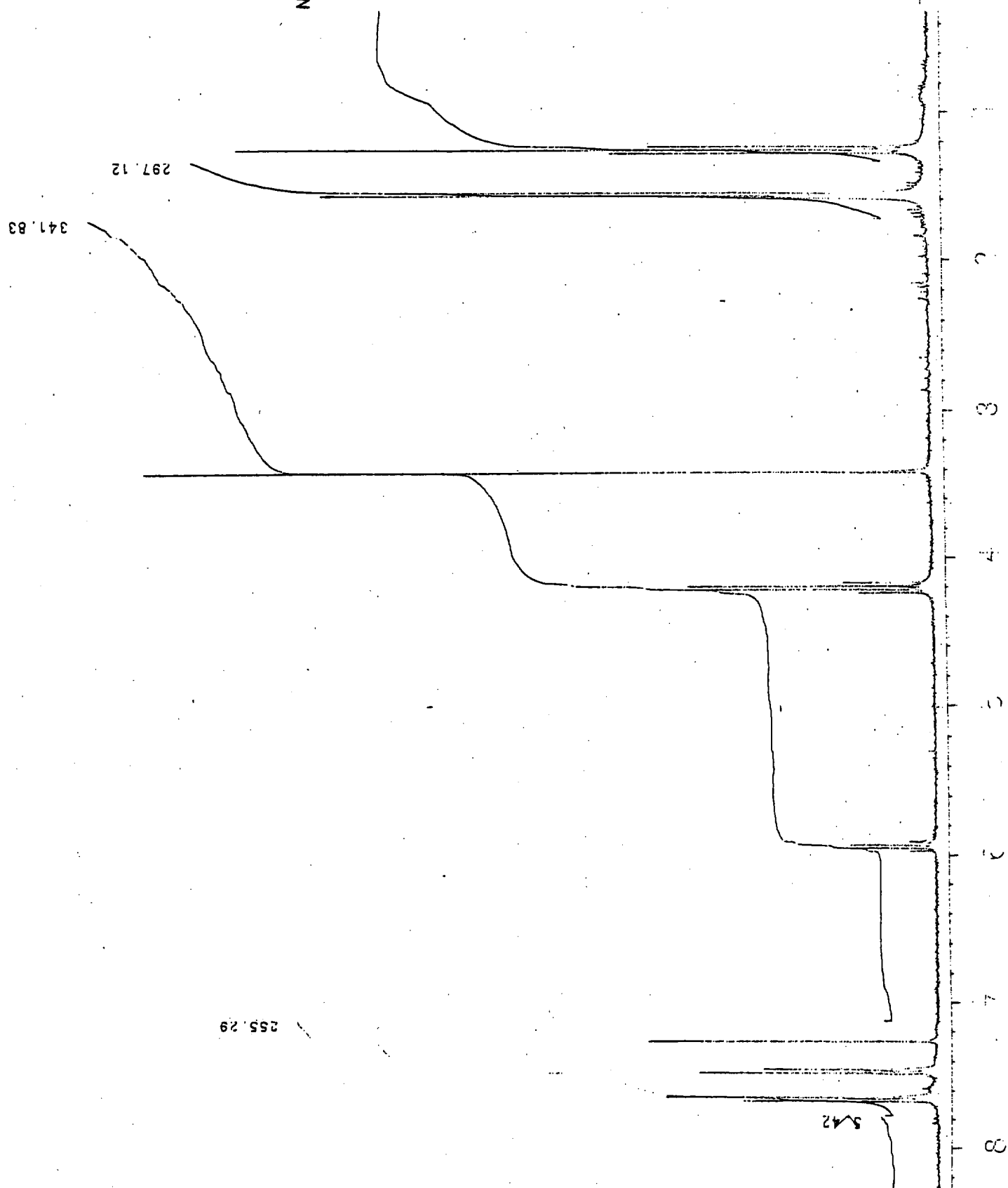
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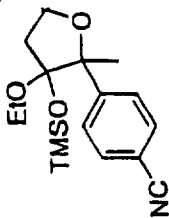
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