SUPPLEMENTARY MATERIAL FOR

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Lewis Acid Promoted Hetero [2+2] Cycloaddition Reactions of Aldehydes with 10-Propynyl-9(10*H*)-acridone. A Highly Stereoselective Synthesis of Trisubstituted Alkenes and 1,3-Dienes From An Electron Deficient Variant of Ynamine.

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General Procedure for the Reaction of 10-Propynyl-9(10*H*)-acridone with Aldehydes.

In a flame dried round bottom flask, the appropriate aldehyde (1-1.5 mmol) (filtered through silica gel if from a commercial source) was dissolved in 5 mL anhydrous dichloromethane (or toluene) and $BF_3 \bullet Et_2O$ (0.125 mmol as a 0.2 M solution in dry dichloromethane) was added. The solution was then cooled to -10 °C (ice in acetone, or -78 °C, dry ice in acetone) and after 10 minutes the 10-propynyl-9(10*H*)-acridone (0.5 mmol) was added all at once as a solid. The solution was stirred for 1 h before being brought to room temperature, and the reaction progress was monitored by TLC analysis (15:1 hexanes:ethyl acetate, multiple elutions). When the reaction was completed, the mixture was diluted with dichloromethane and poured into a solution of saturated sodium bicarbonate. Separation and extraction of the aqueous phase twice with equal volumes of dichloromethane was followed by washing the combined organic extracts with brine. Drying of the dichloromethane solution ($MgSO_4$ or Na_2SO_4) and evaporation of the solvent afforded a crude oil. Silica gel column chromatography (triethylamine doped silica gel, 20:1 or 15:1 hexanes:ethyl acetate eluent) provided the alkene as a yellow-green solid or oil.

Procedure for the Reaction of 10-Propynyl-9(10*H*)-acridone Methyl Vinyl Ketone.

In a flame dried round bottom flask, $BF_3 \bullet Et_2O$ (0.5 mmol as a 0.1 M solution in toluene) was added to a solution of 10-propynyl-9(10*H*)-acridone (0.5 mmol) in 2.5 mL anhydrous toluene. After the flask was cooled to -10 °C (ice in acetone), MVK (1.5 mmol) was added dropwise. The solution was stirred for 1 h before being brought to room temperature, and the reaction was monitored by TLC analysis (1:1 hexanes:ether). Upon reaction completion and normal work-up procedures (see above), the [4+2] product was obtained in 64% yield (97 mg).

Characterizations for Isolated Products:

For the alkene **5**.

R_f = 0.33 (25% EtOAc in hexanes);
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80 (dq, 3 H, J = 1.2, 7.0 Hz), 2.13 (quintet, 3 H, J = 1.2 Hz), 6.56 (qq, 1 H, J = 1.2, 7.0 Hz), 7.08 (d, 2 H, J = 8.7 Hz), 7.31 (ddd, 2 H, J = 0.9, 7.2, 8.1 Hz), 7.61 (ddd, 2 H, J = 1.5, 7.2, 8.7 Hz), 8.53 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.0, 15.8, 116.0, 121.2, 122.5, 127.8, 133.4, 133.9, 140.2, 147.7, 174.5, 178.1;
IR (neat) cm^{-1} 3068w, 1699m, 1636s, 1605s, 1482s, 1464m;
mass spectrum (EI): $C_{18}H_{15}NO_2$ m/e (%relative intensity) 277 (5) M^+, 195 (11), 166 (11), 83 (100), 55 (69).

For the alkene **6**.

R_f = 0.28 (25% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, 3 H, J = 7.5 Hz), 2.12 (q, 3 H, J = 0.75 Hz), 2.21 (quintet, 2 H, J = 7.5 Hz), 6.34 (qq, 1 H, J = 0.75, 7.5 Hz), 7.10 (d, 2 H, J = 8.7 Hz), 7.35 (ddd, 2 H, J = 0.9, 7.2, 8.1 Hz), 7.63 (ddd, 2 H, J = 1.5, 7.2, 8.7 Hz), 8.55 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 11.9, 12.1, 22.9, 115.9, 121.2, 122.3, 127.4, 131.7, 133.6, 140.1, 153.9, 174.5, 177.8;
IR (neat) cm^{-1} 3069w, 2967m, 1703s, 1641s, 1605s, 1482s, 1465s, 1360s, 1293m;
mass spectrum (EI): $C_{19}H_{17}NO_2$ m/e (%relative intensity) 291 (0.1) M^+, 195 (5), 166 (7), 140 (6), 97 (100), 69 (42).

For the alkene **7**.

R_f = 0.40 (25% EtOAc in hexanes);
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (d, 3 H, J = 1.1 Hz), 7.21 (d, 2 H, J = 8.7 Hz), 7.29 (m, 6 H), 7.31 (ddd, 2 H, J = 1.0, 6.9, 8.1 Hz), 7.62 (ddd, 2 H, J = 1.5, 6.9, 8.7 Hz), 8.56 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 116.1, 121.5, 122.6, 127.7, 128.7, 130.2, 130.4, 131.7, 133.9, 134.2, 140.2, 146.6, 175.4, 178.0;
IR (neat) cm^{-1} 3070w, 1695s, 1637s, 1602s, 1480s, 1464s;
mass spectrum (EI): $C_{23}H_{17}NO_2$ m/e (%relative intensity) 339 (2) M^+, 146 (11), 145 (100), 117 (51), 115 (39).

For the alkene **8**.

R_f = 0.62 (25% EtOAc in hexanes);
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, 3 H, J = 6.6 Hz), 1.00-1.30 (m, 8 H), 2.11 (d, 3 H, J = 1.2 Hz), 2.16 (q, 2 H, J = 7.5 Hz), 6.42 (tq, 1 H, J = 1.2, 7.5 Hz), 7.10 (d, 2 H, J = 8.6 Hz), 7.31 (ddd, 2 H, J = 0.9, 7.0, 8.1 Hz), 7.61 (ddd, 2 H, J = 1.6, 7.0, 8.6 Hz), 8.54 (ddd, 2 H, J = 0.5, 1.6, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 14.0, 22.4, 27.8, 28.8, 29.6, 31.4, 116.1, 121.4, 122.4, 127.6, 132.2, 133.7, 140.2, 153.0, 174.5, 178.0;
IR (neat) cm^{-1} 3069w, 2954m, 2928m, 2856m, 1703s, 1644s, 1606s, 1481s, 1465s;
mass spectrum (EI): $C_{23}H_{25}NO_2$ m/e (%relative intensity) 347 (4) M^+, 246 (8), 153 (100), 83 (13), 69 (38), 55 (39).

For the alkene **9**.

R_f = 0.49 (25% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ -0.03 (s, 6 H), 0.83 (s, 9 H), 1.29 (m, 4 H), 2.11 (brs, 3 H), 2.21 (q, 2 H, J = 7.2 Hz), 3.46 (t, 2 H, J = 6.0 Hz), 6.42 (tq, 1 H, J = 1.2, 7.2 Hz), 7.09 (d, 2 H, J = 8.6 Hz), 7.32 (ddd, 2 H, J = 0.9, 7.0, 8.1 Hz), 7.61 (ddd, 2 H, J = 1.6, 7.0, 8.6 Hz), 8.53 (ddd, 2 H, J = 0.5, 1.6, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ -5.2, 0.2, 12.2, 24.6, 26.1, 29.5, 32.38, 62.7, 116.2, 121.6, 122.6, 127.8, 132.5, 133.9, 140.4, 152.6, 174.4, 178.2;
IR (neat) cm^{-1} 3068w, 2949w, 1703m, 16 42s, 1605s, 1481s, 1360m;
mass spectrum (EI): $C_{27}H_{35}NO_3Si$ m/e (%relative intensity) 434 (2) M^+-CH_3, 392 (23), 390 (49), 255 (13), 246 (23), 195 (14), 115 (12), 95 (34), 75 (40), 73 (100), 59 (14).

For the alkene **10**.

R_f = 0.51 (25% EtOAc in hexanes); .
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, 6 H, J = 6.6 Hz), 2.11 (d, 3 H, J = 1.2 Hz), 2.69 (d-septet, 1 H, J = 6.6, 9.6 Hz), 6.21 (dq, 1 H, J = 1.2, 9.6 Hz), 7.11 (d, 2 H, J = 8.7 Hz), 7.32 (ddd, 2 H, J = 0.8, 7.2, 8.1 Hz), 7.62 (ddd, 2 H, J = 1.5, 7.2, 8.7 Hz), 8.54 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 21.2, 28.8, 116.1, 121.5, 122.5, 127.6, 130.1, 133.7, 140.3, 158.4, 175.0, 178.1;
IR (neat) cm^{-1} 3072w, 2962m, 2871w, 1704s, 1636s, 1606s, 1482s, 1464s;
mass spectrum (EI): $C_{20}H_{19}NO_2$ m/e (%relative intensity) 305 (1) M^+, 112 (8), 111 (100), 83 (19), 69 (13), 55 (49).

For the alkene **11**.

R_f = 0.55 (25% EtOAc in hexanes); .
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 9 H), 2.22 (d, 3 H, J = 1.2 Hz), 6.43 (q, 1 H, J = 1.2 Hz), 7.13 (d, 2 H, J = 8.7 Hz), 7.32 (ddd, 2 H, J = 0.9, 6.9, 8.1 Hz), 7.63 (ddd, 2 H, J = 1.5, 6.9, 8.7 Hz), 8.54 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 29.5, 34.0, 116.2, 121.5, 122.6, 127.6, 130.9, 133.7, 140.3, 160.4, 176.0, 178.1;
IR (neat) cm^{-1} 3070w, 2961m, 2869w, 1700s, 1645s, 1606s, 1482s, 1464s;
mass spectrum (EI): $C_{21}H_{21}NO_2$ m/e (%relative intensity) 319 (1) M^+, 166 (8), 125 (100), 97 (19), 69 (20), 55 (53).

For the alkene **12**.

R_f = 0.58 (25% EtOAc in hexanes);
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80-1.70 (m, 10 H), 2.12 (d, 3 H, J = 0.9 Hz), 2.38 (tdt, 1 H, J = 3.6, 9.6, 11.1 Hz), 6.23 (dq, 1 H, J = 1.2, 9.6 Hz), 7.11 (d, 2 H, J = 8.7 Hz), 7.31 (ddd, 2 H, J = 0.8, 7.2, 8.1 Hz), 7.61 (ddd, 2 H, J = 1.5, 7.2, 8.7 Hz), 8.54 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.2, 25.1, 25.5, 31.0, 38.6, 116.1, 121.4, 122.4, 127.6, 130.3, 133.7, 140.39, 157.0, 175.0, 178.1;
IR (neat) cm^{-1} 3070w, 2926m, 2851m, 1701s, 1637s, 1605s, 1481m, 1465m;
mass spectrum (EI): $C_{23}H_{23}NO_2$ m/e (%relative intensity) 345 (4) M^+, 166 (7), 152 (11), 151 (100), 81 (21), 69 (25), 67 (16), 55 (25).

For the diene **14**.

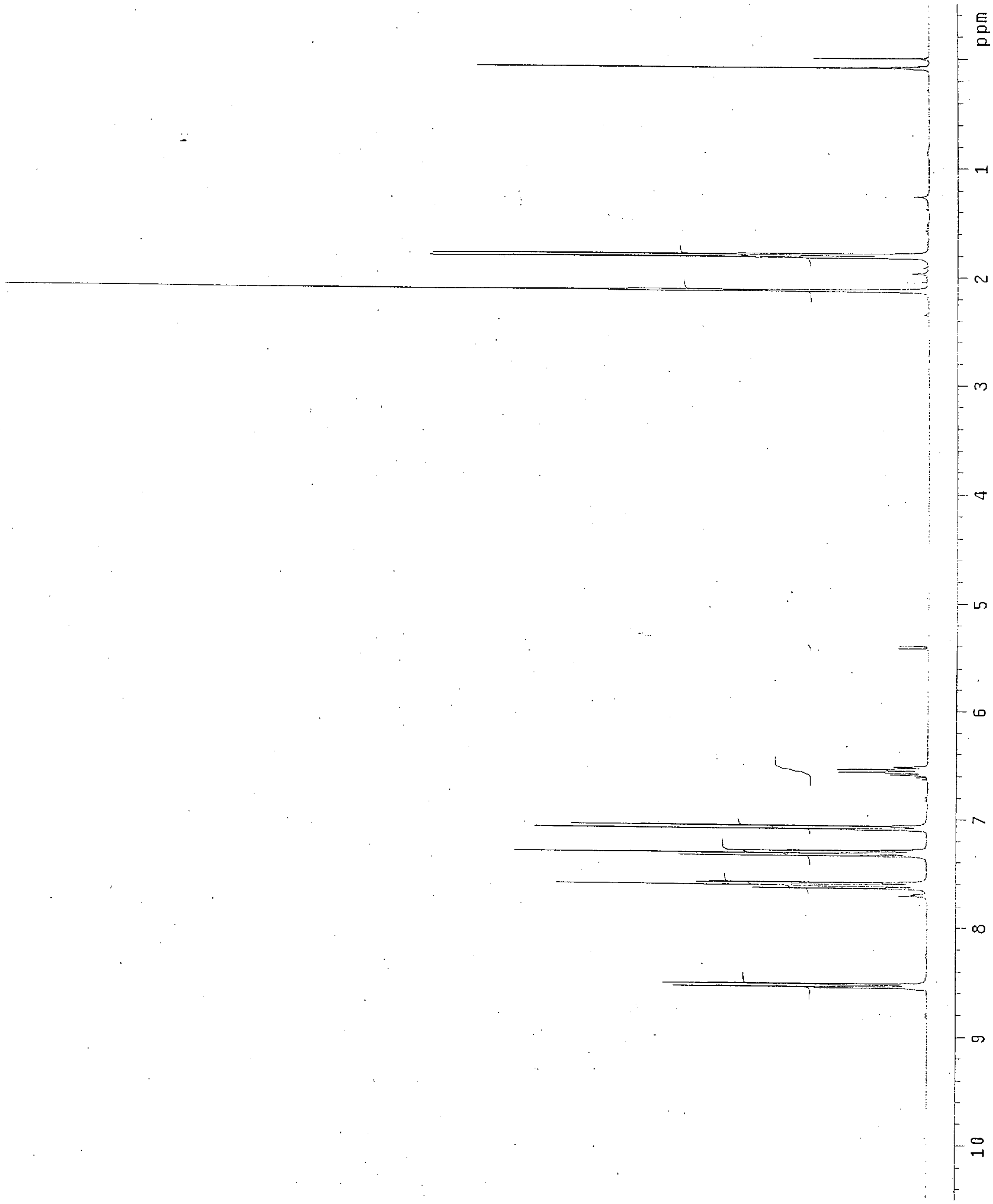
Rf = 0.42 (33% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3 H), 5.45 (m, 1 H), 5.56 (d, 1 H, J = 9.0 Hz), 6.71 (m, 2 H), 7.09 (d, 2 H, J = 8.4 Hz), 7.32 (ddd, 2 H, J = 0.5, 7.5, 8.4 Hz), 7.62 (ddd, 2 H, J = 1.5, 6.9, 8.4 Hz), 8.55 (dd, 2 H, J = 1.2, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 115.9, 122.5, 127.7, 129.6, 131.8, 133.8, 140.0, 145.8, 174.8, 178.0;
IR (neat) cm^{-1} 3051m, 2985w, 2305w, 1688s, 1641s, 1467s, 1267s, 1170s, 720s;
mass spectrum (EI): $C_{19}H_{15}NO_2$ m/e (%relative intensity) 289 (5) M^+, 195 (5), 166 (6), 140 (5), 95 (100), 67 (41).

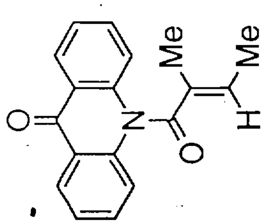
For the diene **15**.

Rf = 0.44 (33% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (d, 3 H, J = 6.9 Hz), 2.18 (s, 3 H), 6.00 (m, 1 H), 6.43 (ddd, 1 H, J = 1.5, 11.1, 14.4 Hz), 6.72 (d, 1 H, J = 11.1 Hz), 7.09 (d, 2 H, J = 8.4 Hz), 7.32 (ddd, 2 H, J = 0.9, 7.5, 8.4 Hz), 7.61 (ddd, 2 H, J = 1.5, 7.2, 8.4 Hz), 8.52 (dd, 2 H, J = 1.2, 7.8 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 12.2, 19.3, 116.0, 122.3, 127.4, 127.6, 133.7, 140.1, 144.8, 146.9, 174.7, 178.0;
IR (neat) cm^{-1} 3054s, 2986w, 2361w, 1695s, 1634s, 1485s, 1264s, 738s;
mass spectrum (EI): $C_{20}H_{17}NO_2$ m/e (%relative intensity) 303 (3) M^+, 195 (3), 166 (5), 140 (3), 109 (100), 81 (31), 53 (10).

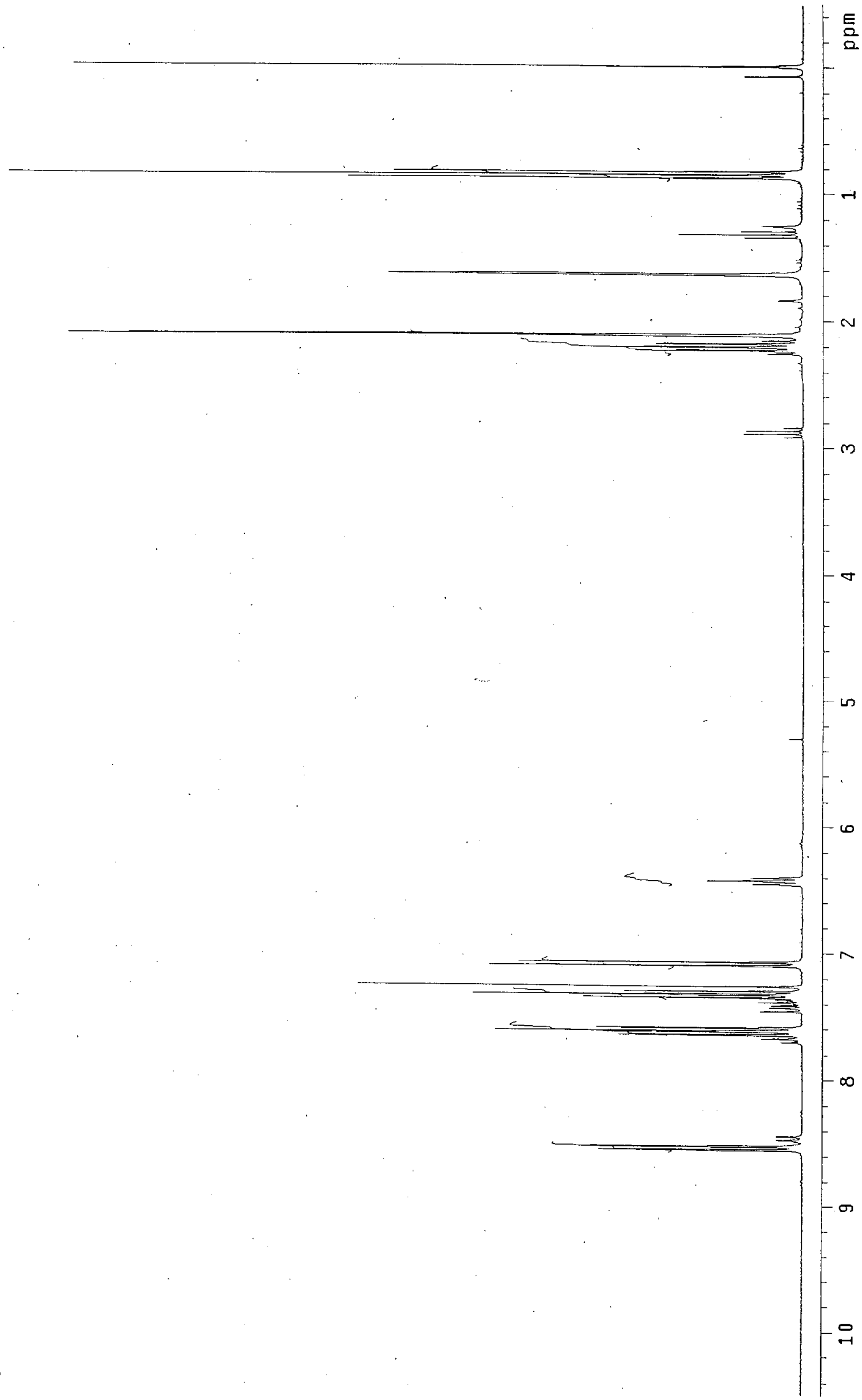
For the cycloadduct **16**.

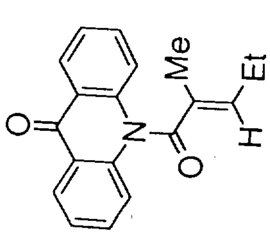
Rf = 0.28 (33% EtOAc in hexane);
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3 H), 1.81 (t, 3 H, J = 1.0 Hz), 2.64-3.00 (m, 2 H), 4.31 (t, 1 H, J = 2.1Hz), 7.34 (ddd, 2 H, J = 0.9, 7.2, 8.1 Hz), 7.45 (d, 2 H, J = 8.7 Hz), 7.70 (ddd, 2 H, J = 1.5, 7.2, 8.7 Hz), 8.55 (dd, 2 H, J = 1.5, 8.1 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 29.7, 54.5, 116.1, 121.9, 122.2, 127.6, 129.3, 133.9, 134.0, 140.9, 149.2, 177.9;
IR (neat) cm^{-1} 3067m, 1973s, 1699s, 1627s, 1475s, 1161s, 921s, 720s;
mass spectrum (EI): $C_{20}H_{17}NO_2$ m/e (%relative intensity) 303 (76) M^+, 288 (16), 260 (100), 244 (34), 220 (26), 195 (48), 167 (24), 140 (18), 108 (19).





E - **5**





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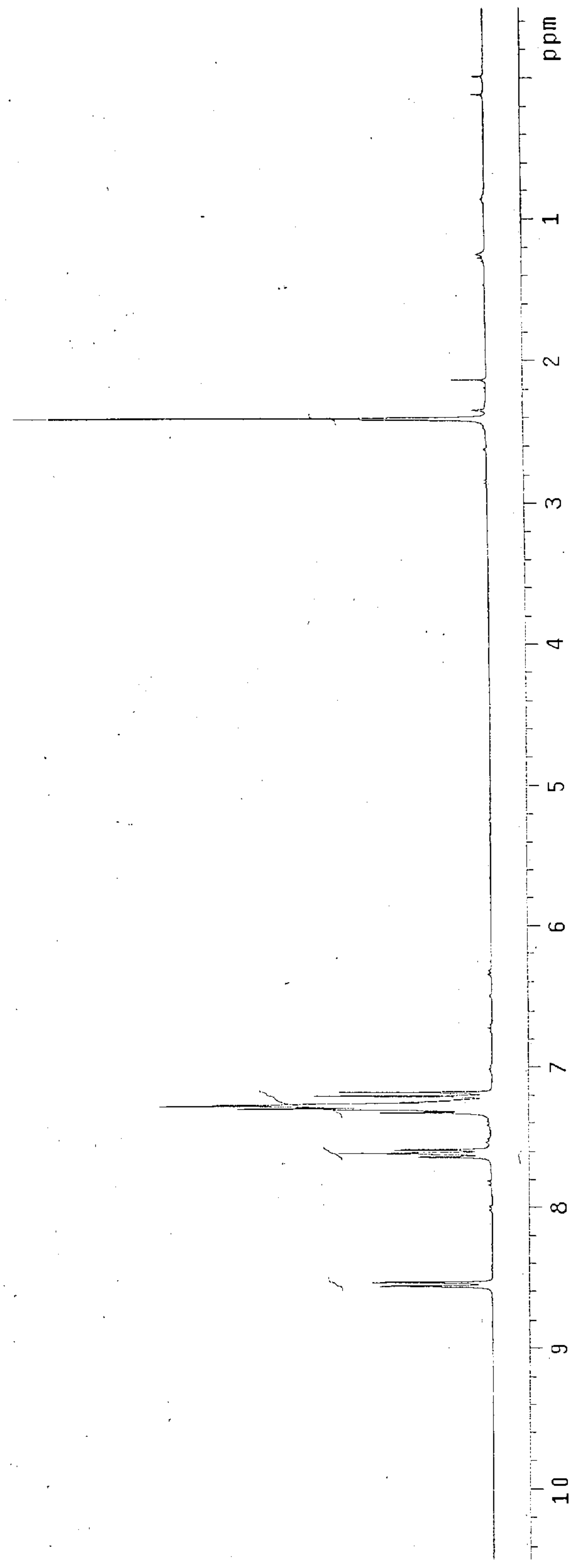

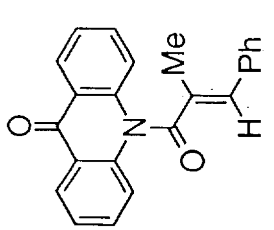

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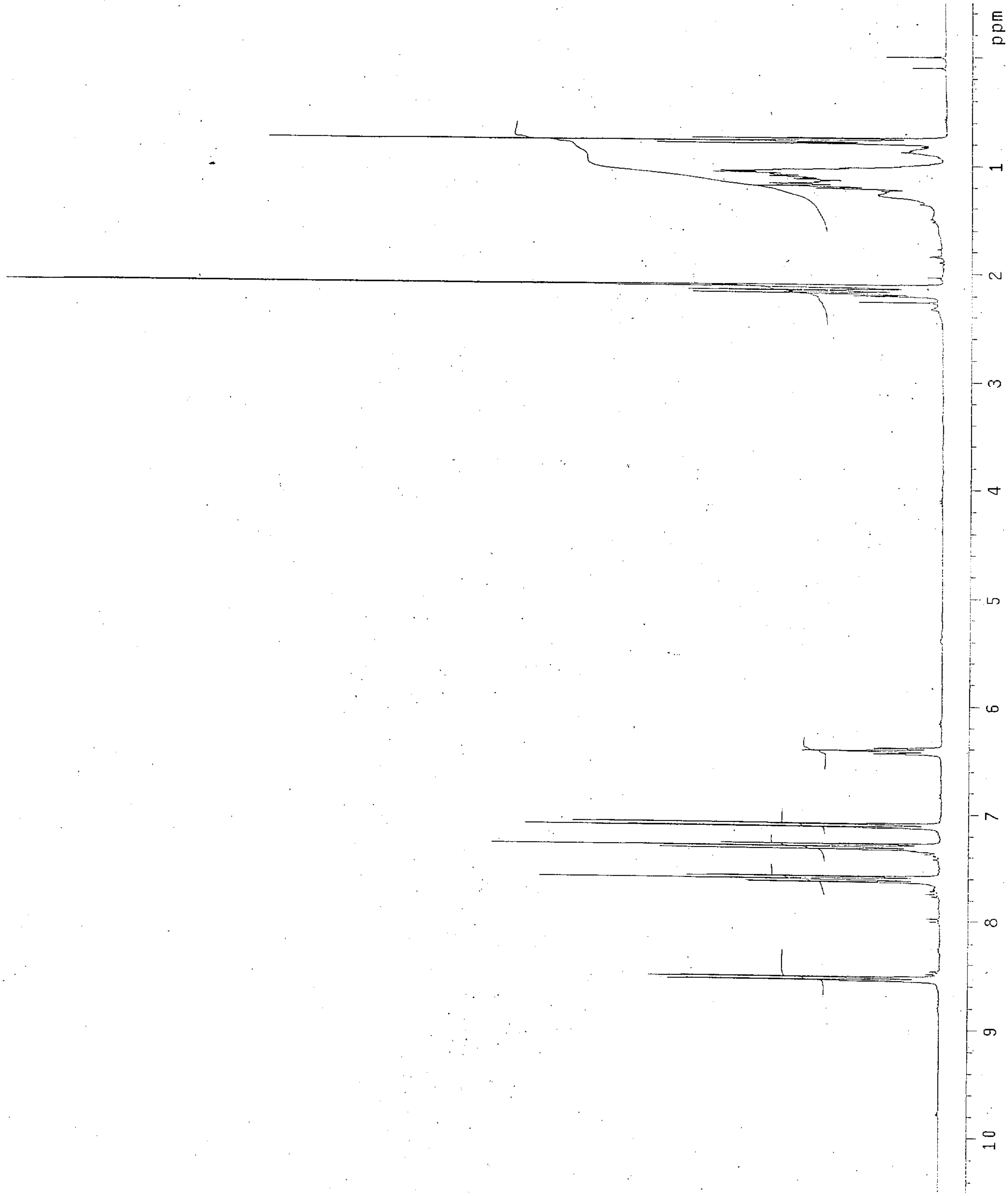

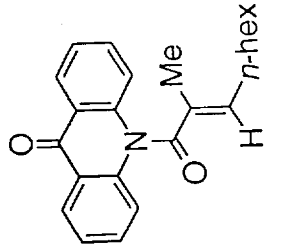

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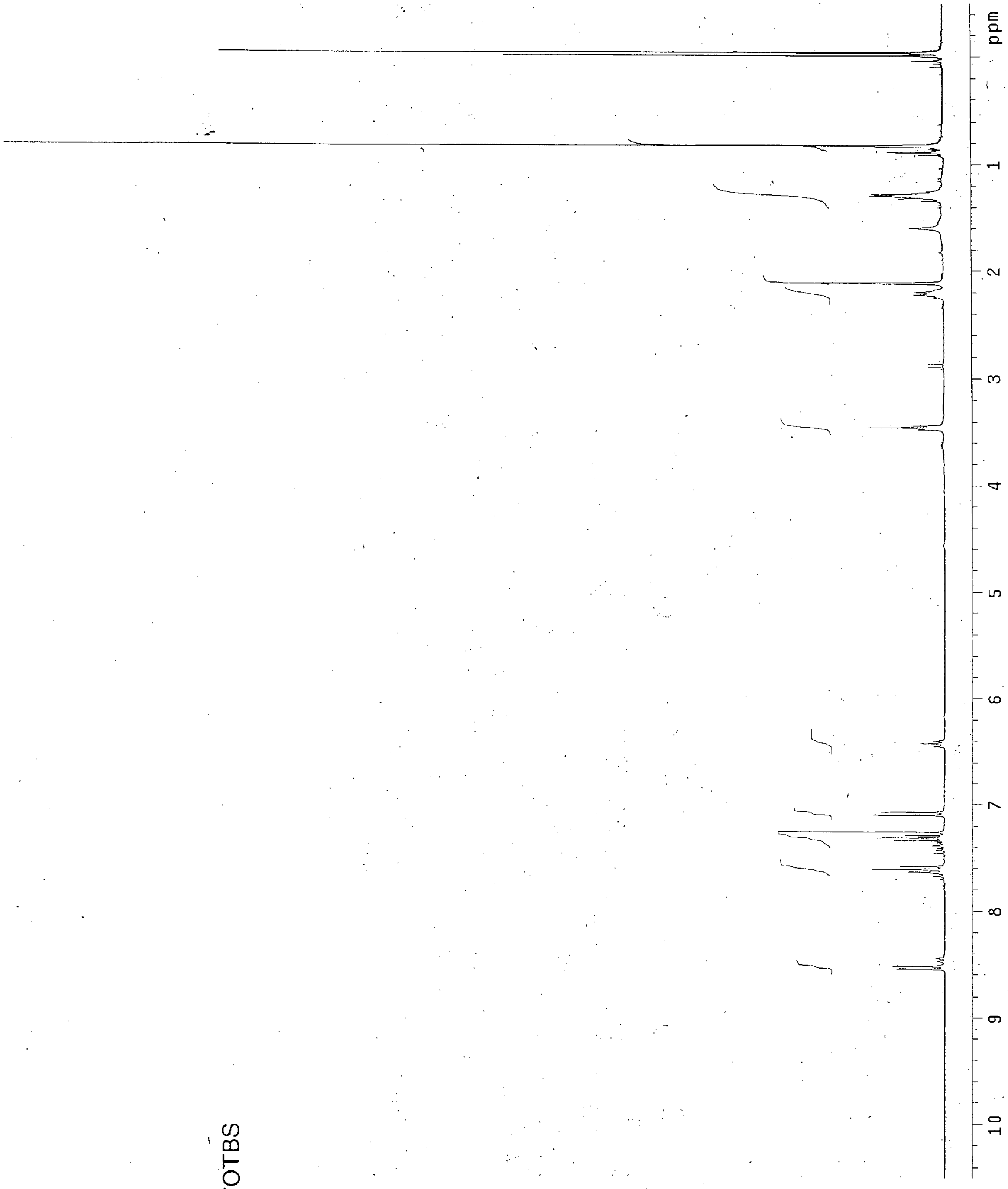

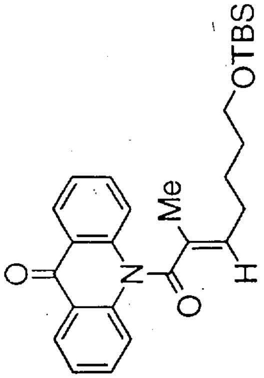

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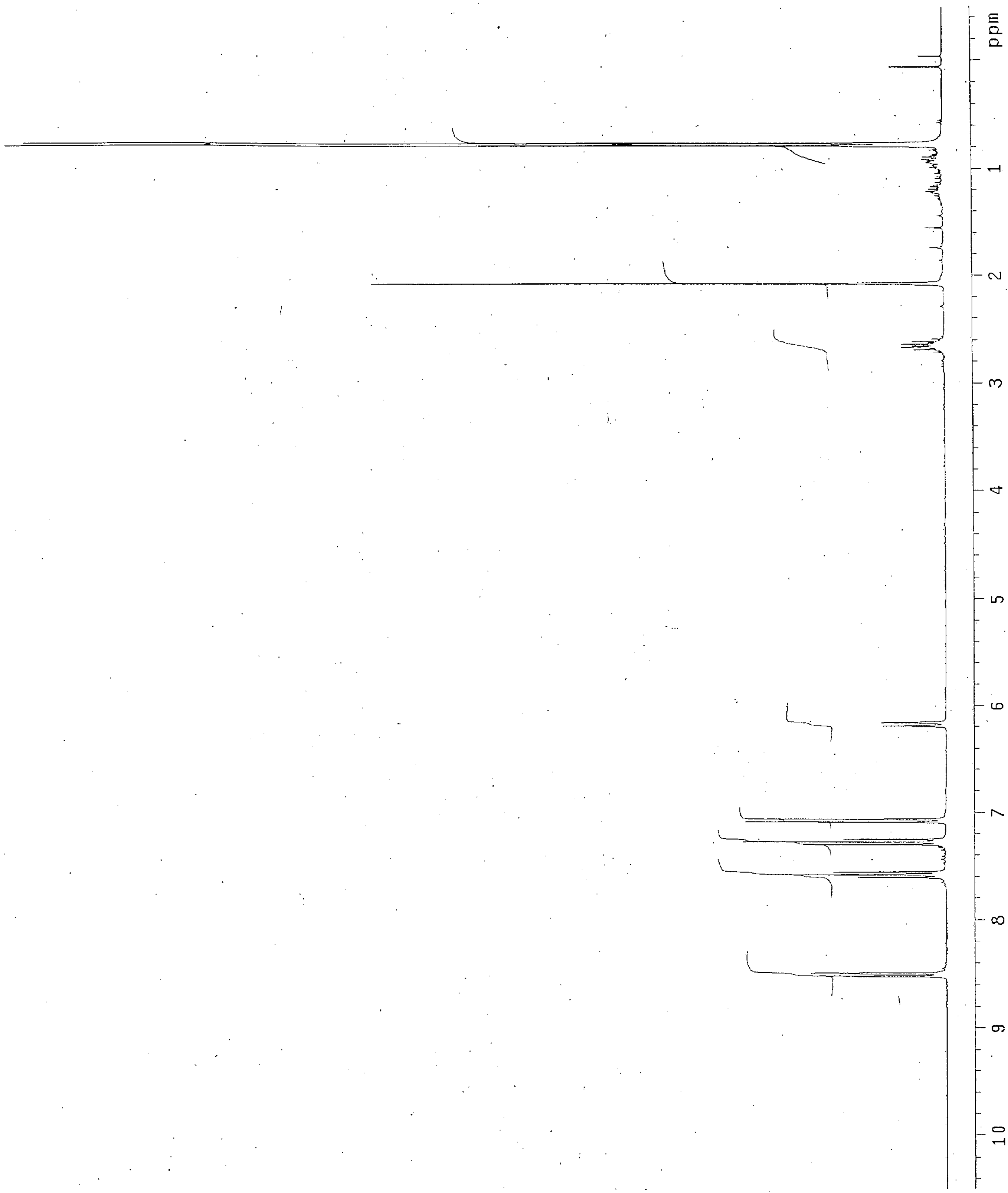

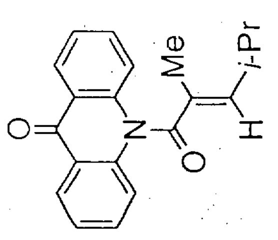

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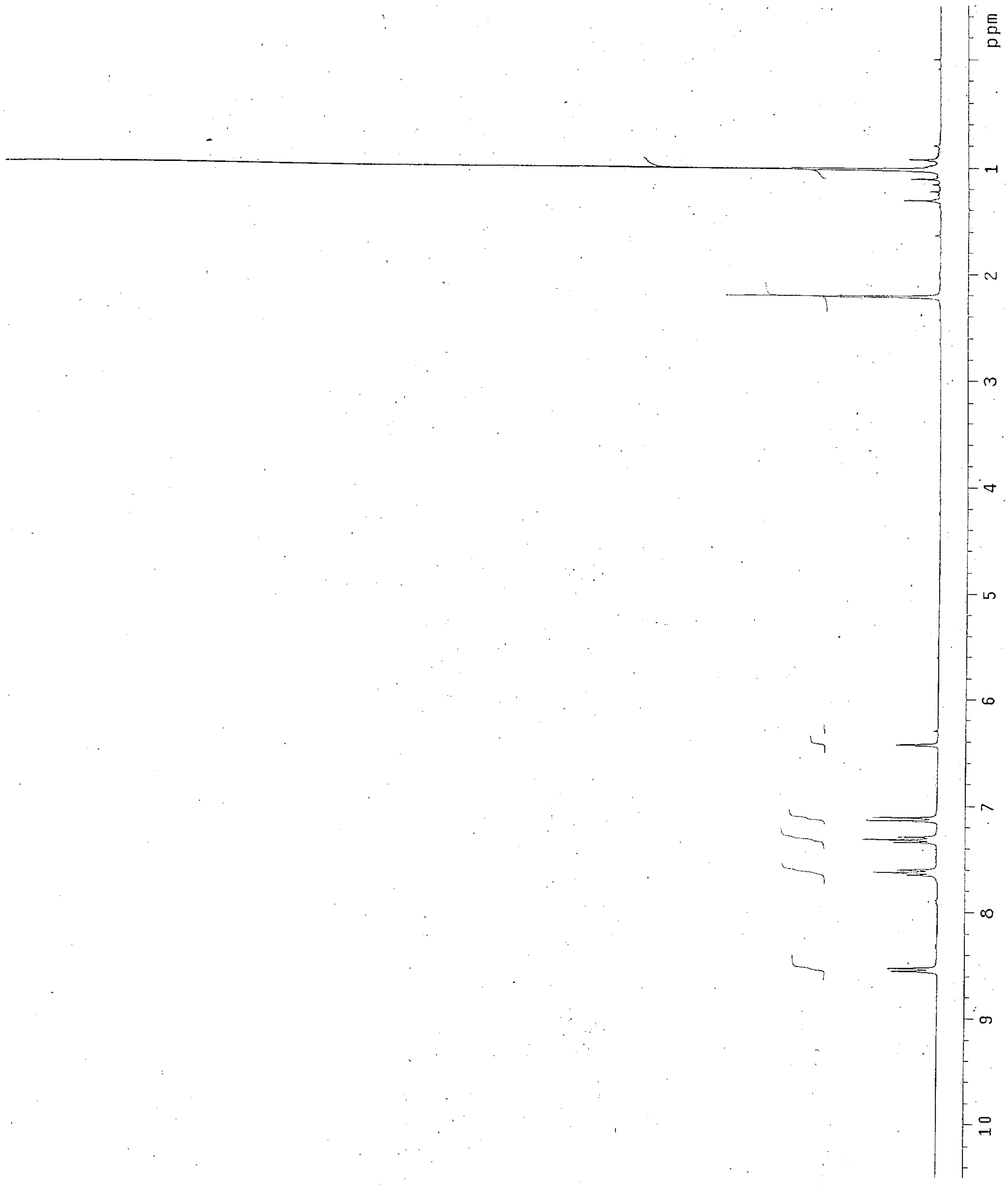

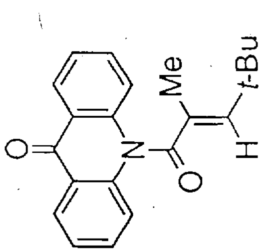

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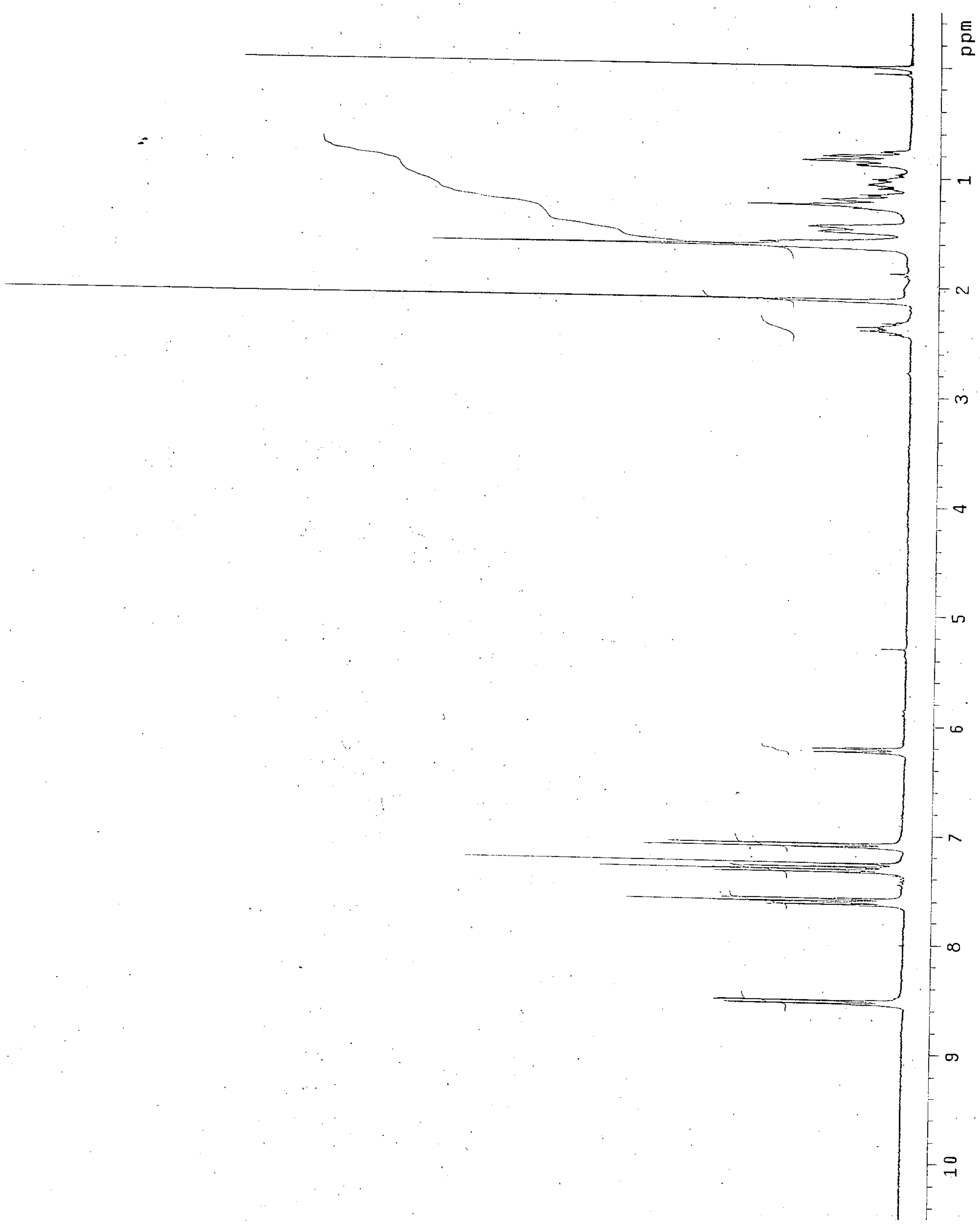

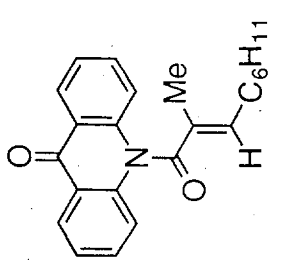

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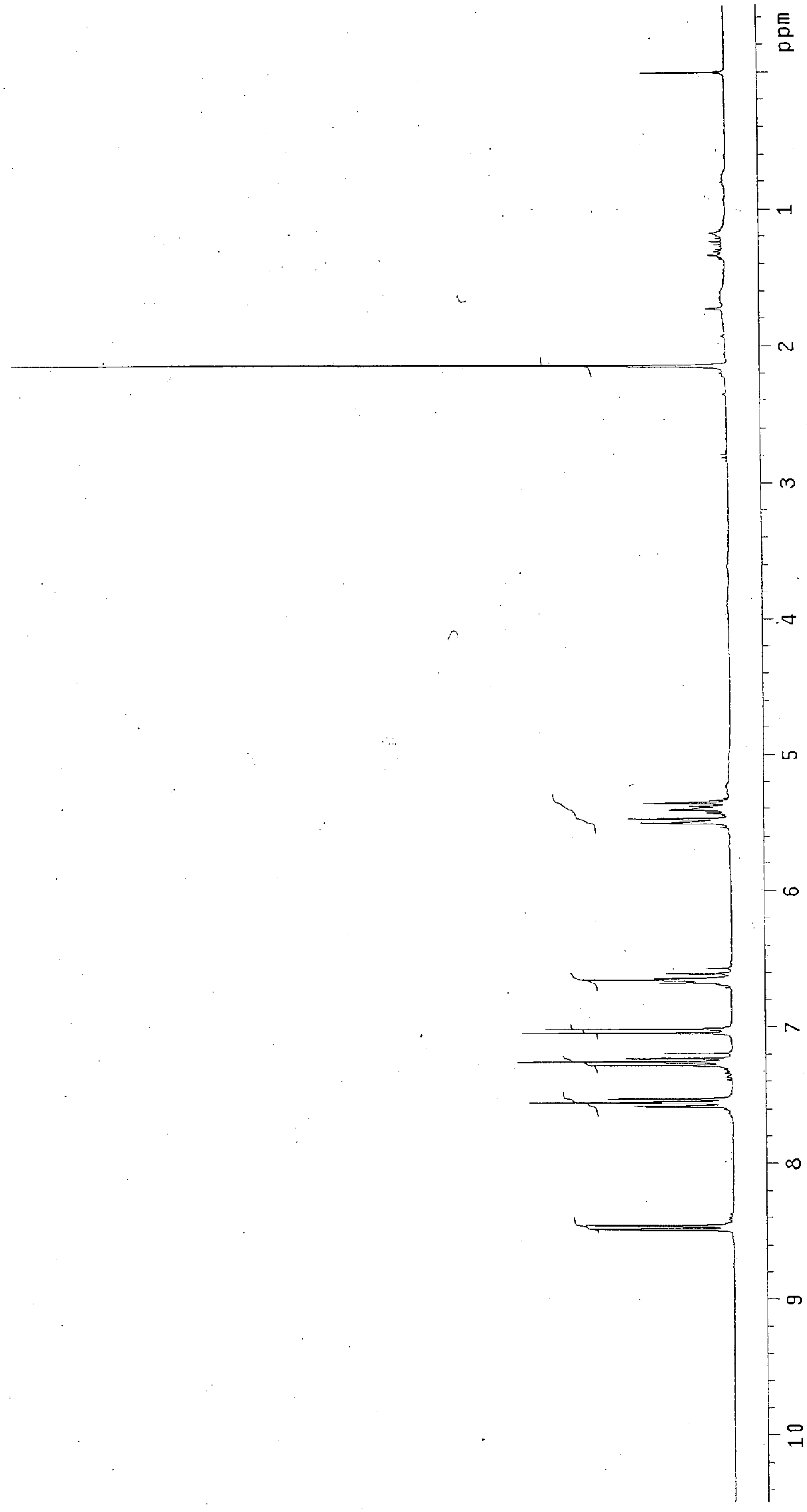

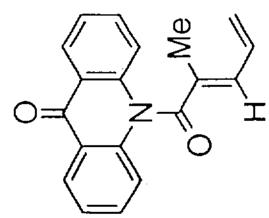

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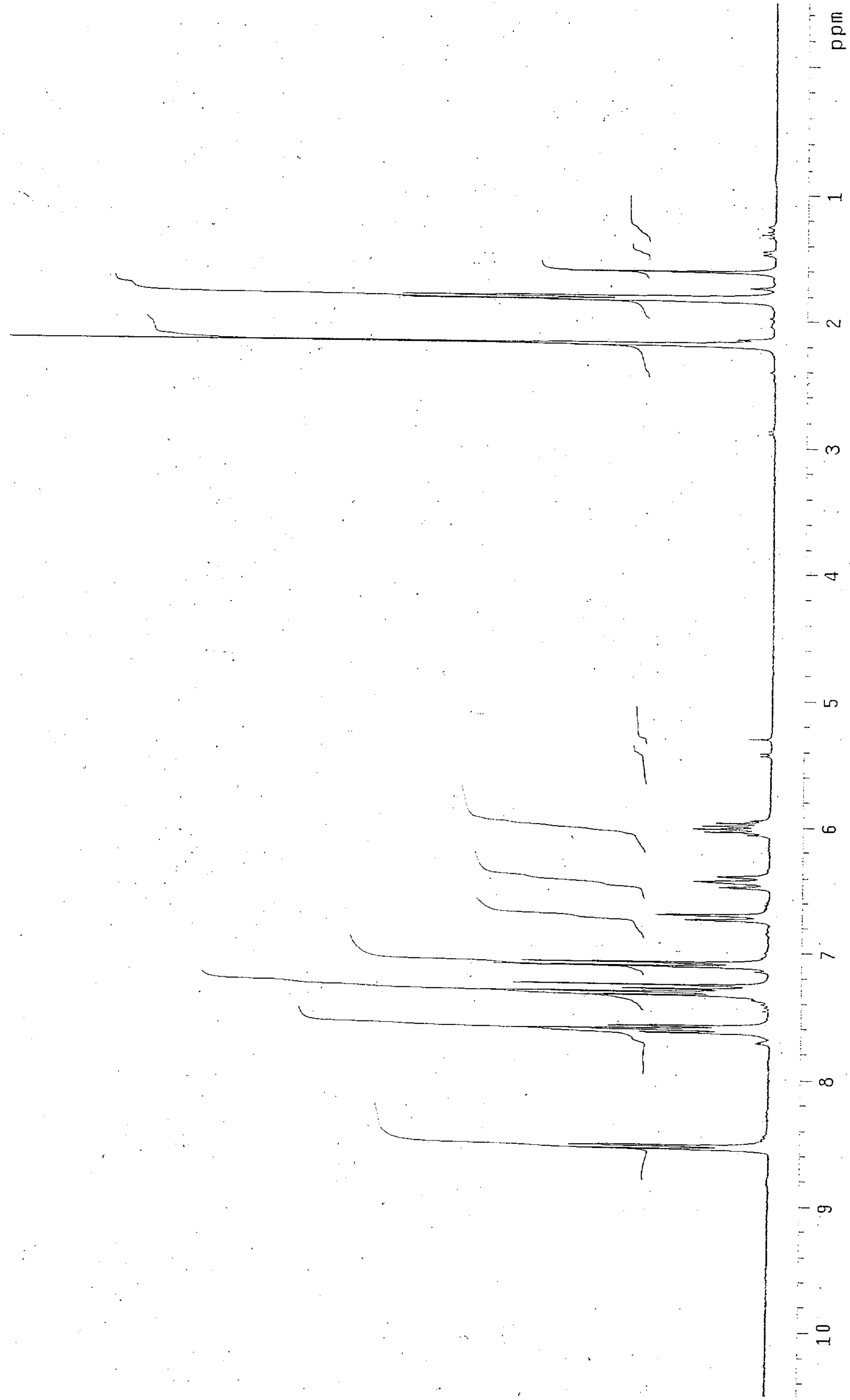

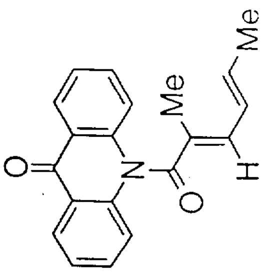

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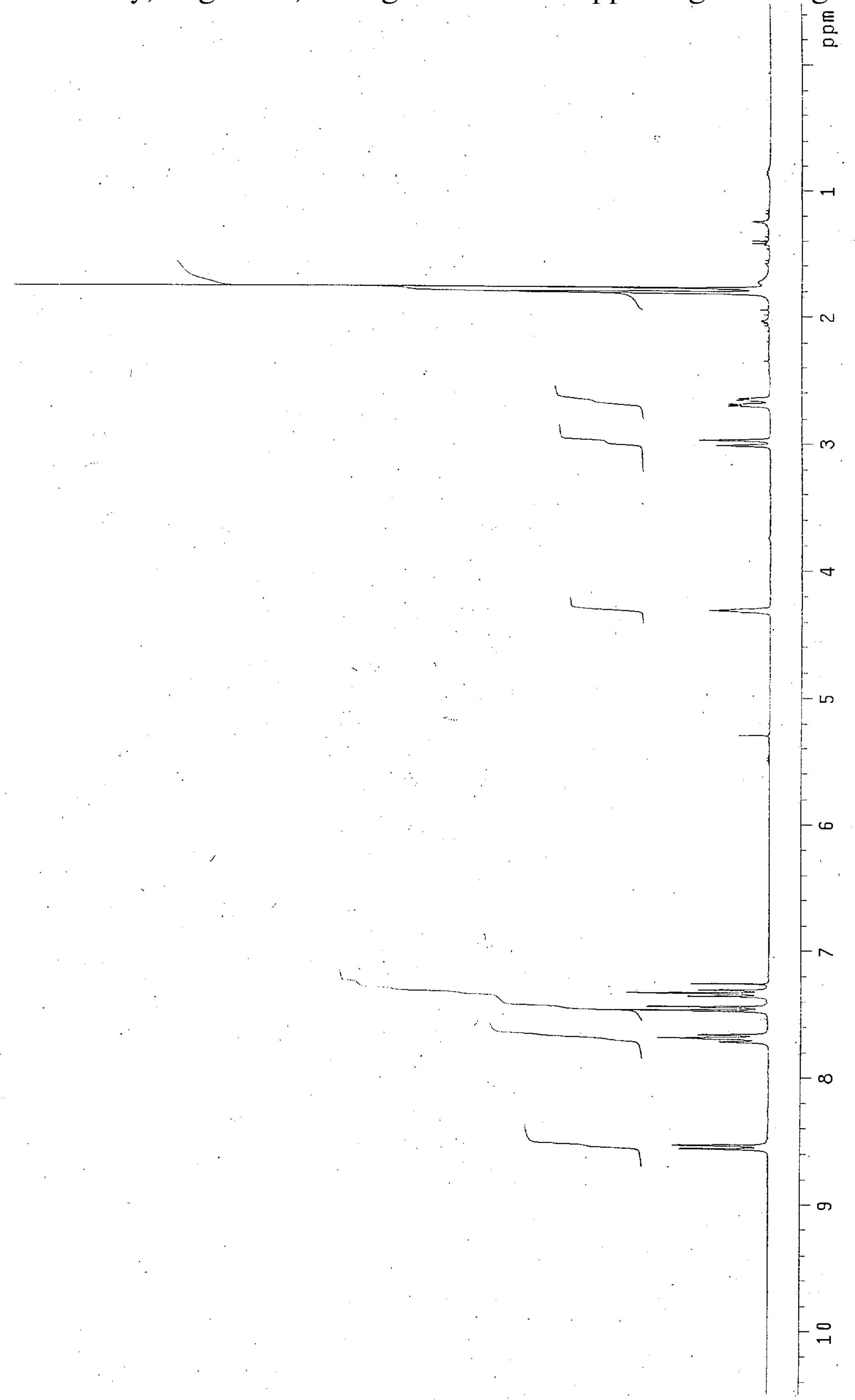

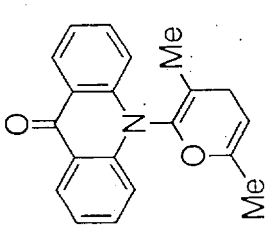

16