General Procedure for Deprotonation and Alkylation.

To a cooled (-78°C) solution of a given allenamide (1.0 mmol) and HMPA (1.0 mmol) in anhydrous THF (15 ml) was added, dropwise, *n*-BuLi (1.2 mmol, 2.2M in Hexanes). After stirring for one hour for complete deprotonation, a solution of electrophile (1.1 mmol) in anhydrous THF was added. The resulting solution was stirred at –78°C for 2-4 hours. The cooled reaction mixture was quenched with water, and the aqueous layer was extracted with ether (3x). The combined organic layers were washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by flash column chromatography on silica gel (85:15 Hexane/EtOAc).

For Compound **5**

R_f = 0.22 (33% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, 3H, J = 6.6 Hz), 2.74 (s, 3H), 3.79 (dq, 1H, J = 6.6, 9.0 Hz), 4.63 (d, 1H, J = 9.0 Hz), 4.76 (d, 1H, J = 9.5 Hz), 5.01 (d, J = 9.5 Hz), 7.02-7.28 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 36.7, 55.2, 60.8, 86.7, 127.8, 128.0, 128.1, 136.0, 157.9, 202.3 (missing one carbon); IR (neat) cm^{-1} 3031m, 2977m, 1959w, 1690s, 1426s, 1195m, 882m; mass spectrum (EI): m/e (%relative intensity) 229 (93) M^+, 228 (89), 171(46), 144 (26), 130 (16), 117 (100), 110 (70);

For Compound **10**.

R_f = 0.18 (33% EtOAc in hexane);

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, 3H, J = 6.6 Hz), 2.12 (t, 3H, J = 3.3 Hz), 2.77 (s, 3H), 3.77 (dq, 1H, J = 6.6, 8.7 Hz), 4.69 (dq, 1H, J = 3.3, 9.0 Hz), 4.75 (d, 1H, J = 8.7 Hz), 4.85 (dq, 1H, J = 3.3, 9.0 Hz), 7.13-7.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 28.7, 36.7, 55.5, 60.8, 86.7, 96.3, 127.8, 127.9, 128.2, 136.0, 157.8, 202.3; IR (neat) cm^{-1} 3391s, 2360.8w, 1959.7m, 1682s, 1419s, 1261m; mass spectrum (EI): m/e (%relative intensity) 242 (100) M^+, 156 (20), 125 (45), 118 (30), 112 (48), 104 (49), 94 (42);

For Compound **11**.

R_f = 0.22 (33% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (t, 3H, J = 3.3 Hz), 3.64 (t, 2H, J = 8.0 Hz), 4.31 (t, 2H, J = 8.0 Hz), 5.17 (q, 2H, J = 3.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.5, 46.0, 61.5, 83.8, 107.0, 155.4, 202.8; IR (neat) cm^{-1} 3927s, 2922s, 1960w, 1754s 1403s, 1121m; mass spectrum (EI): m/e (%relative intensity) 139 (100) M^+, 112 (20), 80 (24), 53 (98);

For Compound **12**.

R_f = 0.44 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 3.65 (t, 2H, J = 8.4 Hz), 4.39 (t, 2H, J = 8.4 Hz), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.3, 45.4, 62.3, 80.7, 105.9, 155.6, 205.5; IR (neat) cm^{-1} 3051m, 2957s, 1927m, 1752s, 1479s, 1250s; mass spectrum (EI): m/e (%relative intensity) 197 (22) M^+, 182 (91), 97 (50), 73 (100);

For Compound **13**.

R_f = 0.42 (33% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 9H, J = 7 Hz), 1.26-1.36 (m, 12H) 1.64 (t, 6H, J = 8.6 Hz), 3.66 (t, 2H, J = 8.4 Hz) 4.36 (t, 2H, J = 8.4 Hz) 4.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 13.7, 27.2, 28.9, 44.9, 62.0, 78.1, 101.2, 156.5, 201.2; IR (neat) cm^{-1} 2955.7s, 2360w, 1928m, 1746.9s, 1439.7m, 1182m; mass spectrum (EI): m/e (%relative intensity) 414 (5) M^+, 358 (100), 244 (36), 159 (12);

For Compound **14**.

R_f = 0.57 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 4.13 (dd, 1H, J = 6.0, 9.0 Hz), 4.53 (d, 1H, J = 10.8 Hz), 4.67 (t, 1H, J = 9.0 Hz), 4.80 (d, 1H, J = 10.8 Hz), 4.97 (dd, 1H, J = 6.0, 9.0 Hz), 7.22-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2, 60.5, 70.5, 80.9, 104.0, 126.4, 128.4, 129.0, 139.6, 156.1, 206.5; IR (neat) cm^{-1} 3033m, 2955s, 1929s, 1760s, 1434s, 1069s, 843s; mass spectrum (EI): m/e (%relative intensity) 273 (2) M^+, 258 (22), 104 (100), 97 (25), 73 (48);

For Compound **15**.

R_f = 0.66 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (dt, 1H, J = 1.8, 15.3 Hz), 3.98 (t, 1H, J = 8.7 Hz), 4.01 (dt, 1H, J = 3.3, 15.3 Hz), 4.52 (t, 1H, J = 8.7 Hz), 4.80 (t, 1H, J = 8.7 Hz), 4.90 (ddd, 1H, J = 1.8, 3.3, 10.5 Hz), 4.98 (ddd, 1H, J = 1.8, 3.3, 10.5 Hz), 6.90-6.94 (m, 2H), 7.09-7.13 (m, 2H), 7.18-7.31 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.6, 61.4, 69.9, 84.0, 102.8, 126.6, 127.1, 128.3, 128.6, 128.7, 129.4, 137.6, 137.64, 156.0, 204.8; IR (neat) cm^{-1} 3064m, 2961m, 1954w, 1750s, 1391s, 1210s, 700s; mass spectrum (EI): m/e (%relative intensity) 291 (20) M^+, 246 (21), 156 (33), 128 (37), 104 (100), 91 (32);

For Compound **16a**.

R_f = 0.70 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.86 (s, 9H), 1.14-1.38 (m, 6H), 1.43 (pentet, 2H, J = 7.0 Hz), 2.34-2.47 (m, 2H), 3.55 (t, 2H, J = 7.0 Hz), 4.14 (dd, 1H, J = 8.0, 9.0 Hz), 4.63 (t, 1H, J = 9.0 Hz), 4.91 (dd, 1H, J = 8.0, 9.0 Hz), 4.93 (dt, 1H, J = 3.5, 10.0 Hz), 5.01 (dt, 1H, J = 3.5, 10.0 Hz), 7.29-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.4, 25.5, 25.9, 26.6, 28.6, 29.5, 32.7, 53.5, 61.0, 63.0, 69.7, 84.2, 109.1, 127.0, 128.6, 128.8, 138.6, 155.8, 204.4; IR (neat) cm^{-1} 3046w, 2938s, 1955m, 1759s, 1454s,

1095s, 848s; mass spectrum (EI): m/e (%relative intensity) 358 (70) $(M\text{-}t\text{-}Bu)^+$, 281 (17), 238 (18), 207 (100), 104 (34), 75 (58);

For Compound **16b**.

R_f = 0.48 (33% EtOAc in hexane);

^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.89 (s, 9H), 1.24-1.66 (m, 6H), 2.51-2.56 (m, 2H), 2.65 (dd, 1H, J = 10.0, 13.5 Hz), 3.23 (dd, 1H, J = 4.0, 13.5 Hz), 3.61 (t, 2H, J = 7.0 Hz), 4.06 (dd, 1H, J = 5.5, 8.0 Hz), 4.09-4.15 (m, 1H), 4.20 (t, 1H, J = 8.0 Hz), 5.24 (dt, 1H, J = 3.5, 10.5 Hz), 5.36 (dt, 1H, J = 3.5, 10.5 Hz), 7.14-7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.2, 18.4, 25.4, 26.0, 26.9, 29.6, 32.7, 38.5, 57.8, 63.2, 66.7, 84.4, 109.4, 127.2, 128.9, 129.1, 135.7, 155.6, 204.0; IR (neat) cm^{-1} 2930m, 1761s, 1663w, 1454m, 1398m, 1097m; mass spectrum (EI): m/e (%relative intensity) 400 (5) $(M\text{-}Me)^+$, 358 (100), 170 (10), 91 (44);

For Compound **17.**

R_f = 0.63 (50% EtOAc in hexane);

^1H NMR (500 MHz, $CDCl_3$) δ 2.22 (t, 3H, J = 3.0 Hz), 2.71 (dd, 1H, J = 9.0, 13.5 Hz), 3.22 (dd, 1H, J = 3.5, 13.5 Hz), 4.08 (dd, 1H, J = 5.5, 8.0 Hz), 4.12 (dddd, 1H, J = 3.5, 5.5, 8.0, 9.0 Hz), 4.20 (t, 1H, J = 8.0 Hz), 5.21 (dq, 1H, J = 3.0, 10.5 Hz), 5.32 (dq, 1H, J = 3.0, 10.5 Hz), 7.15-7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 38.1, 57.7, 66.4, 83.4, 105.2, 127.2, 128.9, 129.0, 135.6, 155.6, 204.0; IR (neat) cm^{-1} 3024m, 2957s, 1959w, 1756s, 1402s, 1031m, 700m; mass spectrum (EI): m/e (%relative intensity) 229 (12) M^+, 138 (100), 117 (31), 86 (70);

For Compound **18**.

R_f = 0.58 (50% EtOAc in hexane);

^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (t, 3H, J = 3.3 Hz), 4.11 (dd, 1H, J = 7.5, 9.0 Hz), 4.63 (t, 1H, J = 9.0 Hz), 4.84 (dq, 1H, J = 3.3, 9.6 Hz), 4.92 (dd, 1H, J = 7.5, 9.0 Hz), 4.97 (dq, 1H, J = 3.3, 9.6 Hz), 7.26-7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 61.2, 70.0, 83.5, 104.9, 126.7, 128.8, 129.1, 138.8, 156.1, 204.7; IR (neat) cm^{-1} 3053m, 2956s, 1956w, 1755s, 1457m, 1386s, 1262s, 1051s; mass spectrum (EI): m/e (%relative intensity) 215 (27) M^+, 170 (80), 156 (40), 129 (33), 104 (100);

For Compound **19**.

R_f = 0.58 (50% EtOAc in hexane);

^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (d, 3H, J = 3.3 Hz), 4.10 (dd, 1H, J = 7.2, 8.7 Hz), 4.63 (t, 1H, J = 8.7 Hz), 4.90-4.95 (m, 2H), 7.29-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 61.1, 69.8, 83.2 (t, J = 25.5 Hz), 104.9, 126.6, 128.7, 129.0, 138.7, 156.0, 204.6; IR (neat) cm^{-1} 3032m, 2956s, 2924s, 1957w,

1760s, 1458s, 1396s, 1288m, 1049m; mass spectrum (EI): m/e (%relative intensity) 216 (20) M^+, 171 (57), 157 (28), 130 (22), 104 (100);

For Compound **20**.

R_f = 0.64 (50% EtOAc in hexane);

^1H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.70 (pentet, 2H, J = 7.2 Hz), 2.27 (t, 2H, J = 7.2 Hz), 2.67 (tt, 2H, J = 3.0, 7.2 Hz), 3.65 (t, 2H, J = 7.2 Hz), 4.35 (t, 2H, J =7.2 Hz), 5.26 (t, 2H, J = 3.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.05, 19.1, 26.2, 28.0, 46.1, 61.7, 84.7, 85.0, 106.7, 110.3, 155.3, 202.5; IR (neat) cm^{-1} 2959s, 1957w, 1739s, 1260m; mass spectrum (EI): m/e (%relative intensity) 253 (1) M^+-CH_3, 238 (100), 160 (48), 151 (40), 144 (30), 100 (83);

For Compound **21**.

R_f = 0.66 (50% EtOAc in hexane);

^1H NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.58 (m, 2H), 2.07 (t, 2H, J = 7.0 Hz), 2.52 (m, 2H), 4.15 (dd, 1 H, J = 7.0, 8.5 Hz), 4.65 (t, 1H, J = 8.5 Hz), 4.94 (dd, 1H, J = 7.0, 8.5 Hz), 4.96 (dt, 1H, J = 3.5, 10.0 Hz), 5.04 (dt, 1H, J = 3.5, 10.0 Hz), 7.26-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 19.5, 27.6, 29.0, 61.2, 69.8, 84.4, 84.6, 107.2, 108.7, 127.0, 128.8, 128.9, 138.4, 156.0, 204.4; IR (neat) cm^{-1} 3033m, 2957s, 2173s, 1955m, 1761s, 1395s, 1249s; mass spectrum (EI): m/e (%relative intensity) 339 (45) M^+, 324 (24), 280 (23), 228 (18), 104 (100);

For Compound **22**.

R_f = 0.47 (50% EtOAc in hexane);

^1H NMR (300 MHz, $CDCl_3$) δ 1.72 (pentet, 2H, J = 7.2 Hz), 1.96 (t, 1H, J = 2.4 Hz), 2.26 (dt, 2H, J = 2.4, 7.2 Hz), 2.66-2.73 (tt, 2H, J = 3.0, 7.2 Hz), 3.65 (t, 2H, J = 8.4 Hz), 4.35 (t, 2H, J =8.4 Hz), 5.27 (t, 2H, J = 3.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ; IR (neat) cm^{-1} 3299m, 2931m, 2173m, 1933w, 1748s, 1402s; mass spectrum (EI): m/e (%relative intensity) 191 (20) M^+, 190 (48), 152 (52), 146 (100), 132 (88), 118 (64), 104 (83), 91 (77);

General Procedure for Pauson-Khand [2+2+1] Cycloaddition Reactions.

To a solution of a given alkynyl allenamide (1.0 mmol) in toluene (13 mL) and DMSO (781 mg, 10.0 mmol) was added $Mo(CO)_6$ (320 mg, 1.2 mmol). The suspension was heated to 100 °C (oil bath) after which it became a homogeneous solution. The resulting reaction mixture was stirred at 100 °C for 3-6 hours and then cooled to room temperature and filtered through a pad of silica gel, eluting with EtOAc. Then solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel (70:30 Hexane/EtOAc).

For Compound **23**.

R_f = 0.19 (67% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9H), 1.93 (pentet, 2H, J = 6.3 Hz), 2.52 (t, 2H, J = 6.3 Hz), 2.70 (t, 2H, J = 6.3 Hz), 2.97 (s, 2H), 3.87 (t, 2H, J = 8.7 Hz) 4.44 (t, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.5, 22.2, 26.4, 26.7, 38.6, 45.4, 62.5, 129.8, 131.8, 142.1, 154.8, 177.0, 208.0; IR (neat) cm^{-1} 2949s, 1752s, 1675s, 1547s, 1406s, 1479m; mass spectrum (EI): m/e (%relative intensity) 291 (72) M^+, 276 (100), 230 (22), 202 (40), 188 (42);

For Compound **24**.

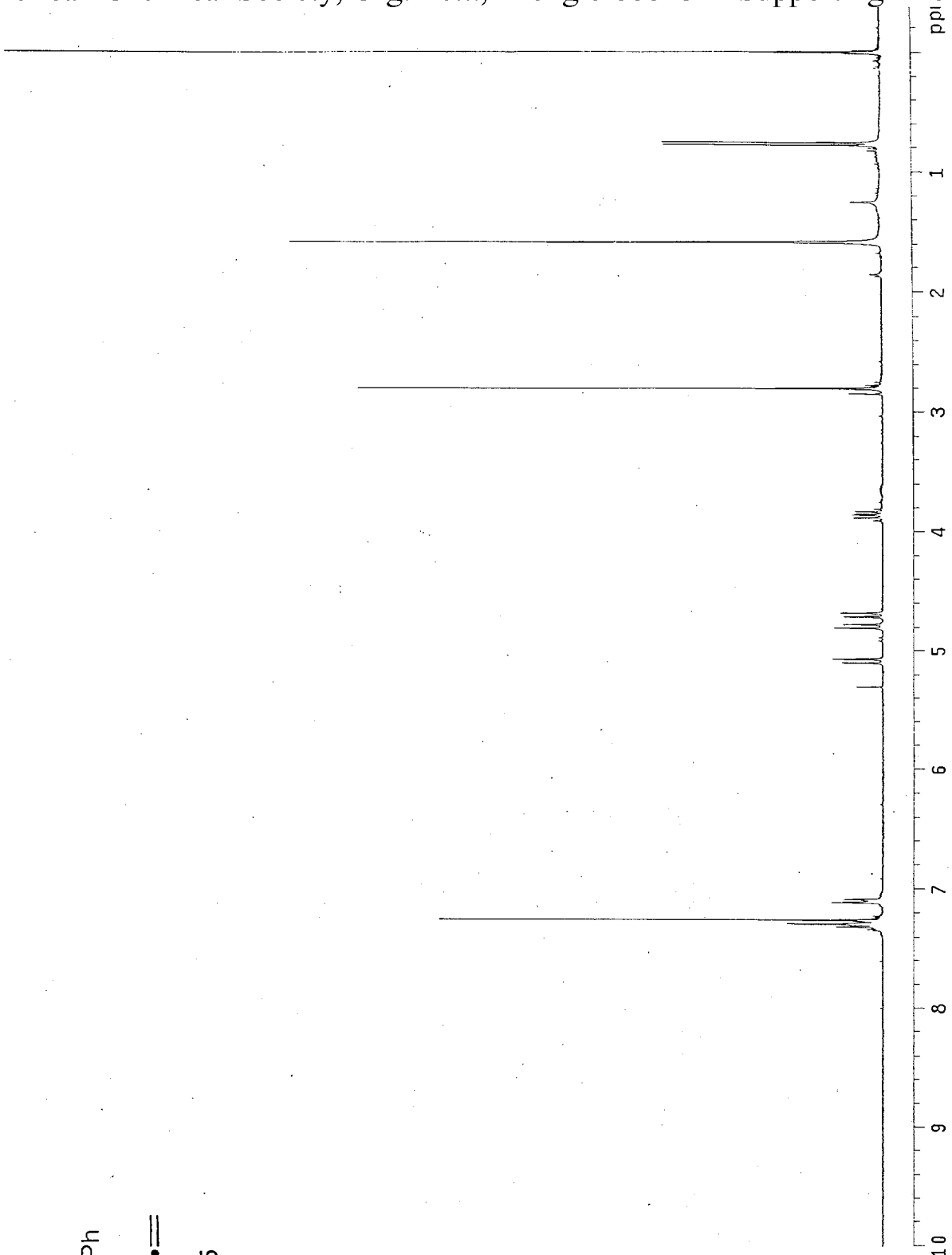
R_f = 0.35 (50% EtOAc in hexane);

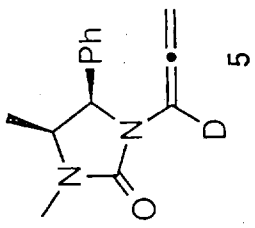
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.52-1.64 (m, 1H), 1.75-1.87 (m, 1H), 2.16 (ddd, 1H, J = 5.1, 8.1, 17.4 Hz), 2.36 (dt, 1H, J = 5.1, 17.4 Hz), 2.50 (ddd, 1H, J = 5.0, 9.3, 17.4 Hz), 2.64 (dt, 1H, J = 5.0, 17.4 Hz), 2.78 (d, 1H, J = 20.7 Hz), 3.19 (d, 1H, J = 20.7 Hz), 4.17 (t, 1H, J = 8.7 Hz), 4.71 (t, 1H, J =8.7 Hz), 5.20 (t, 1H, J = 8.7 Hz), 7.26-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.6, 22.1, 26.5, 26.6, 38.7, 60.3, 70.4, 126.6, 129.3, 129.5, 129.9, 133.1, 137.2, 138.8, 154.5, 176.2, 208.1; IR (neat) cm^{-1} 2949m, 1752s, 1675s, 1551m; mass spectrum (EI): m/e (%relative intensity);

For Compound **25**.

R_f = 0.16 (67% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (pentet, 2H, J = 6.0 Hz), 2.57 (t, 2H, J = 6.0 Hz), 2.68 (t, 2H, J = 6.0 Hz), 3.04 (s, 2H), 3.91 (t, 2H, J = 8.0 Hz), 4.47 (t, 2H, J = 8.0 Hz), 5.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 25.8, 26.6, 38.3, 45.6, 62.5, 126.8, 127.7, 132.8, 155.0, 171.6, 204.1; IR (neat) cm^{-1} 2957w, 1739s, 1675s, 1573m; mass spectrum (EI): m/e (%relative intensity) 219 (100) M^+, 174 (18), 160 (47), 146 (19), 132 (39);





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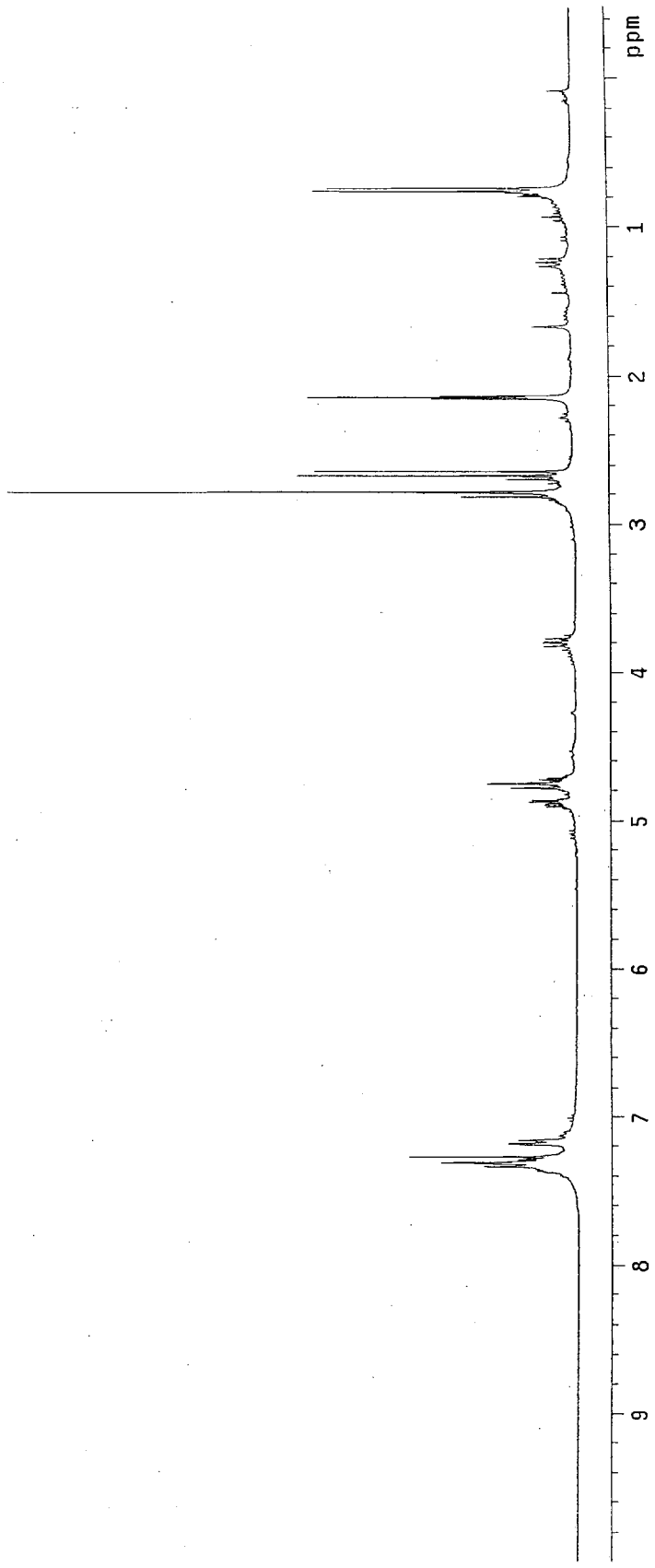

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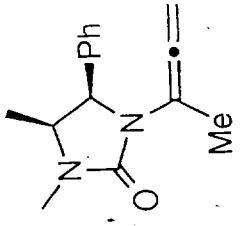

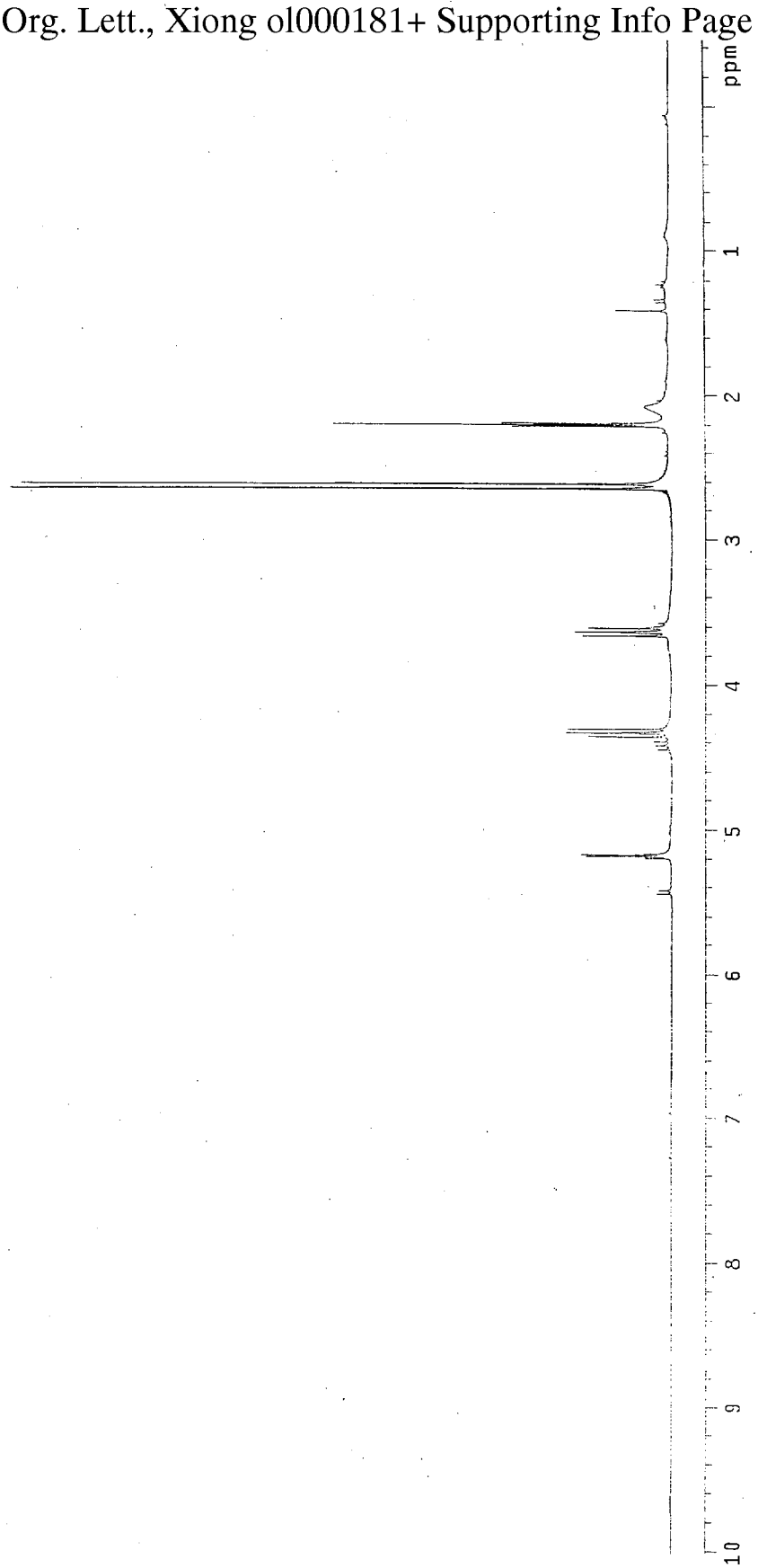

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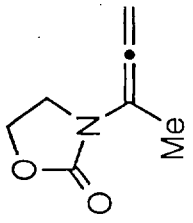

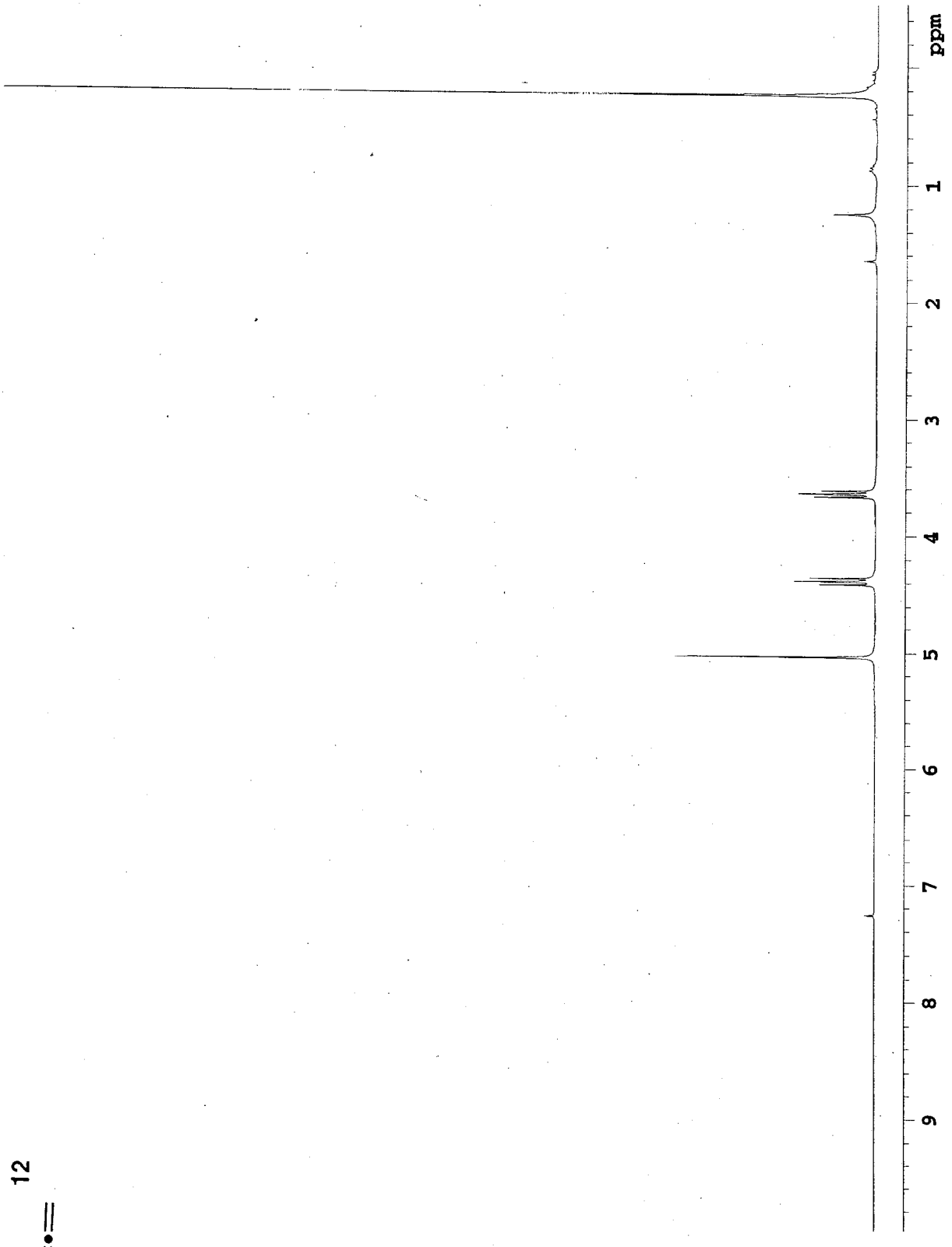

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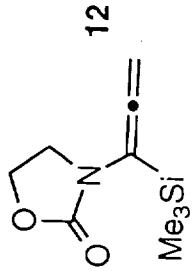

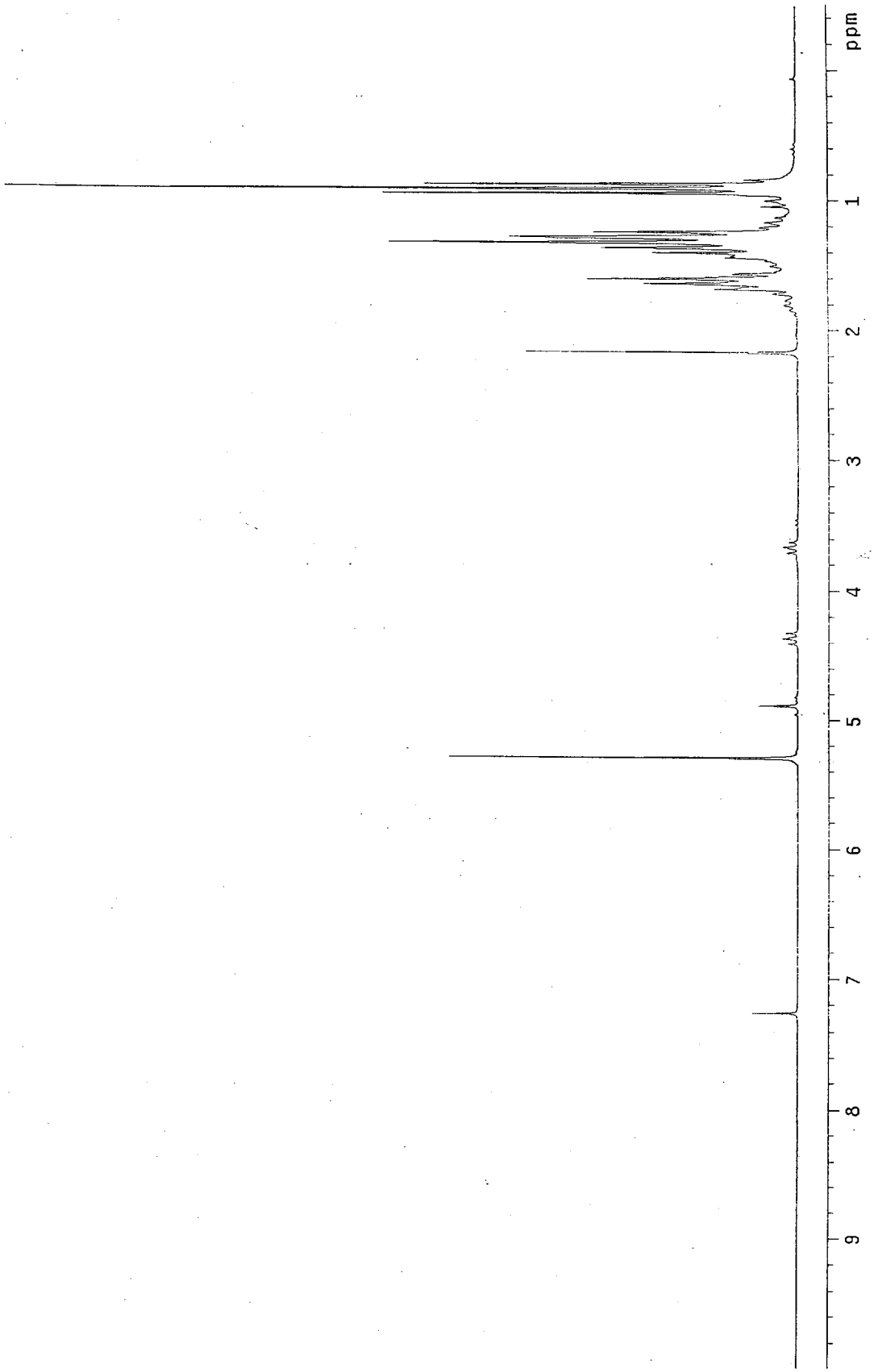

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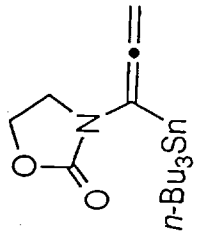

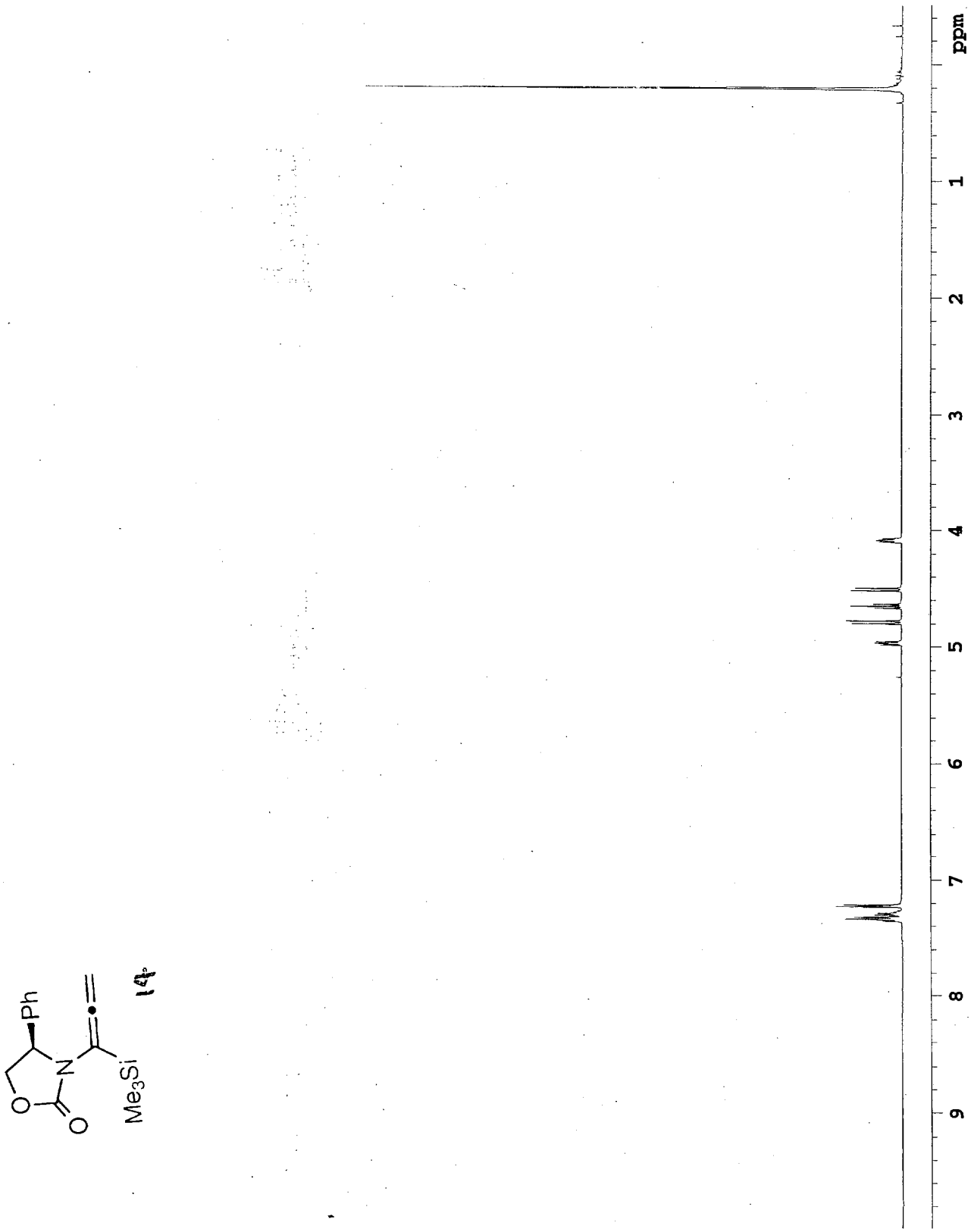

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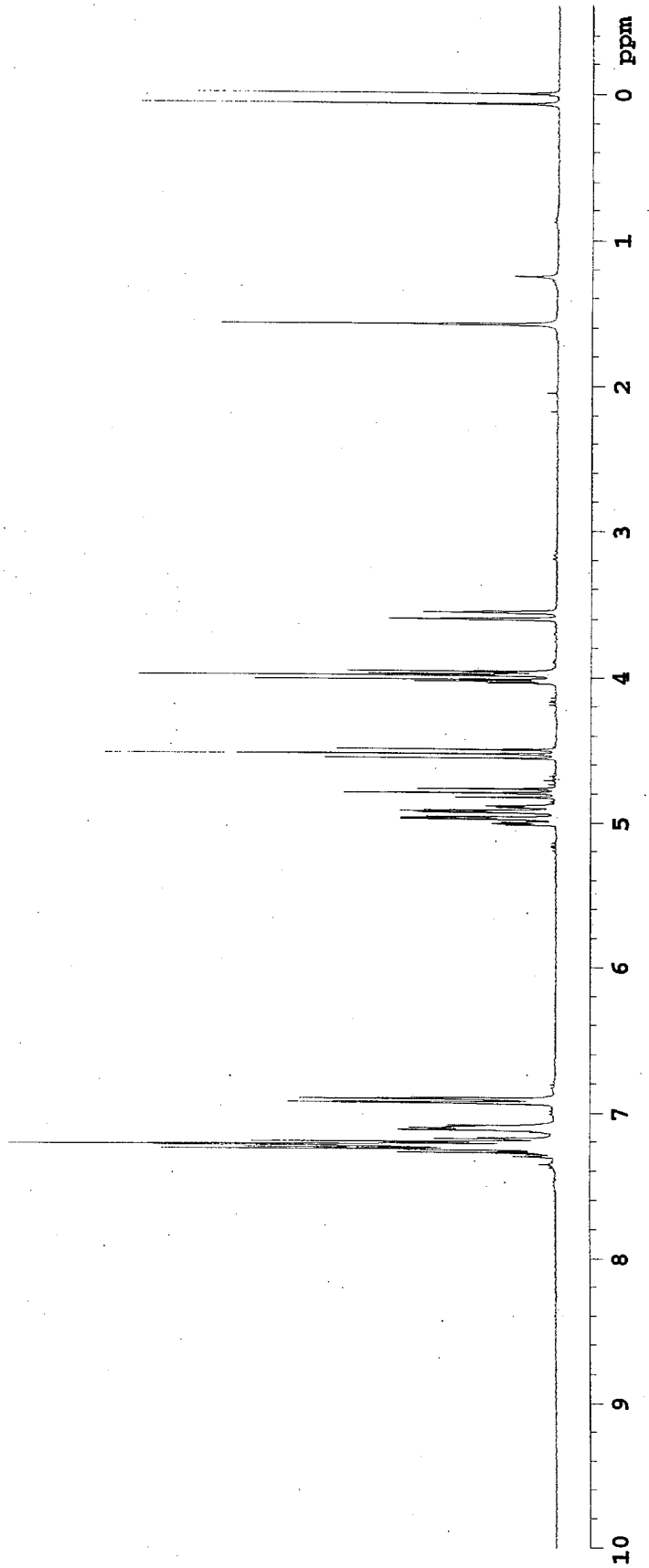

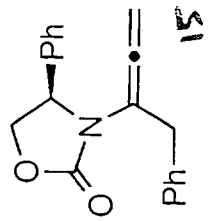

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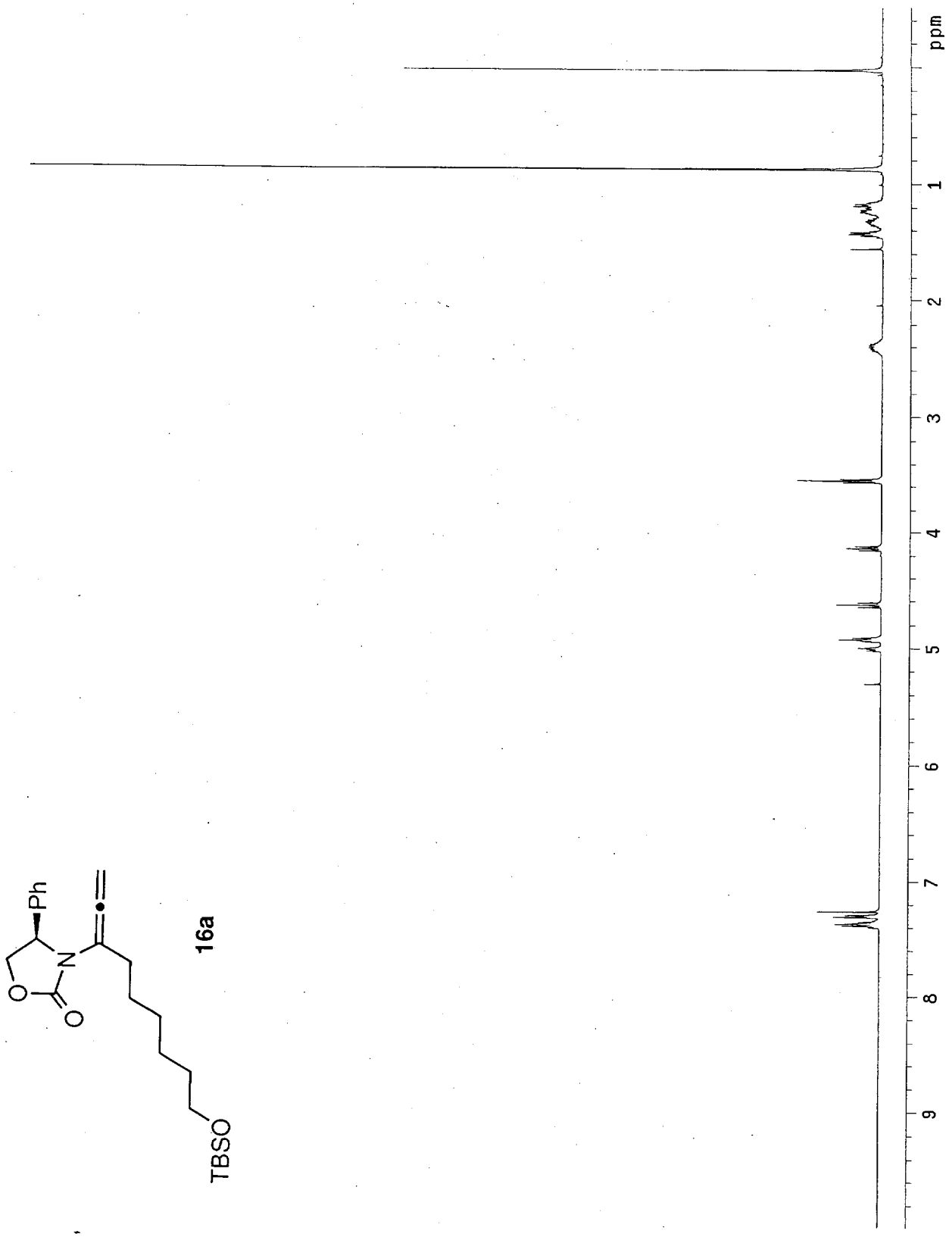
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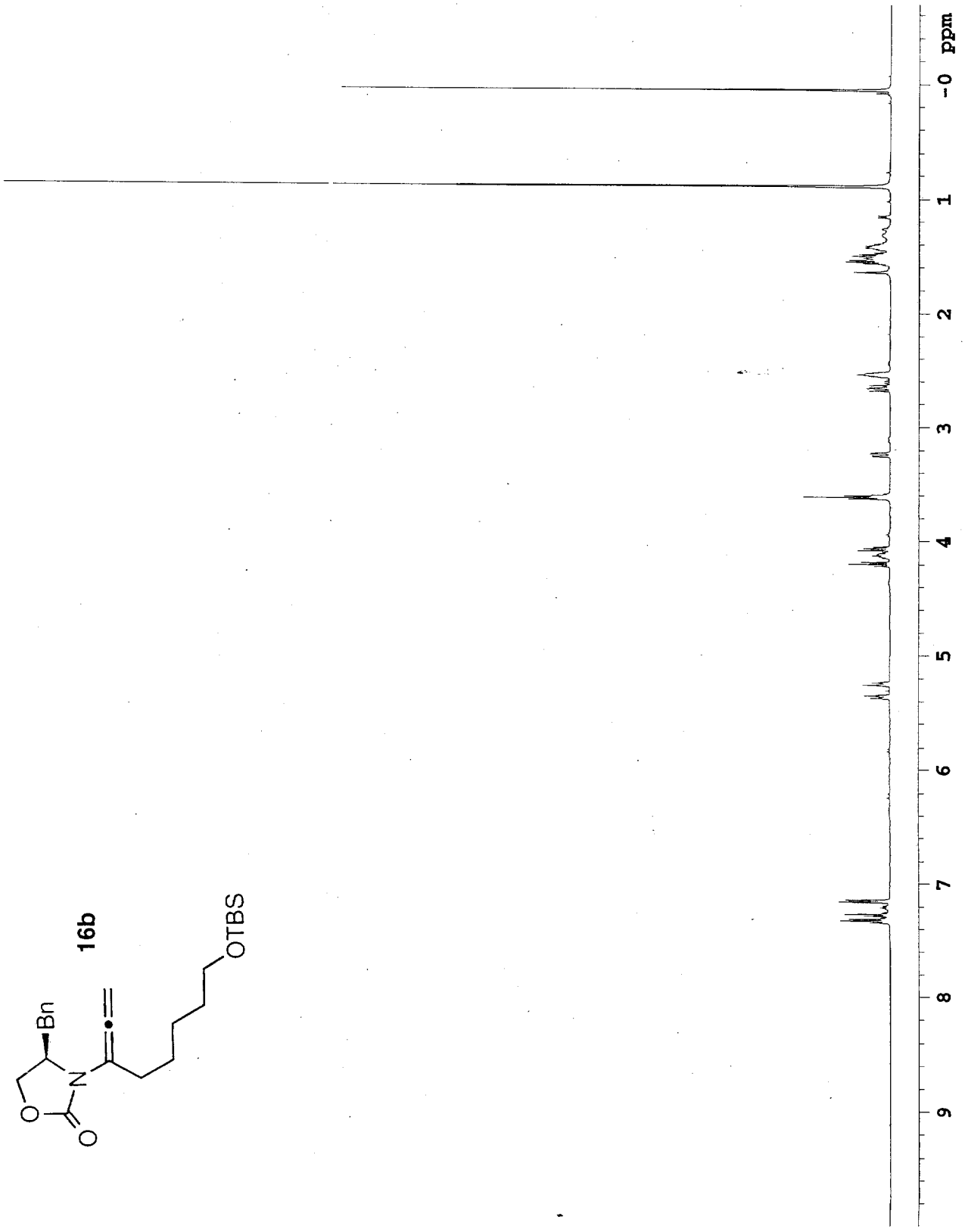
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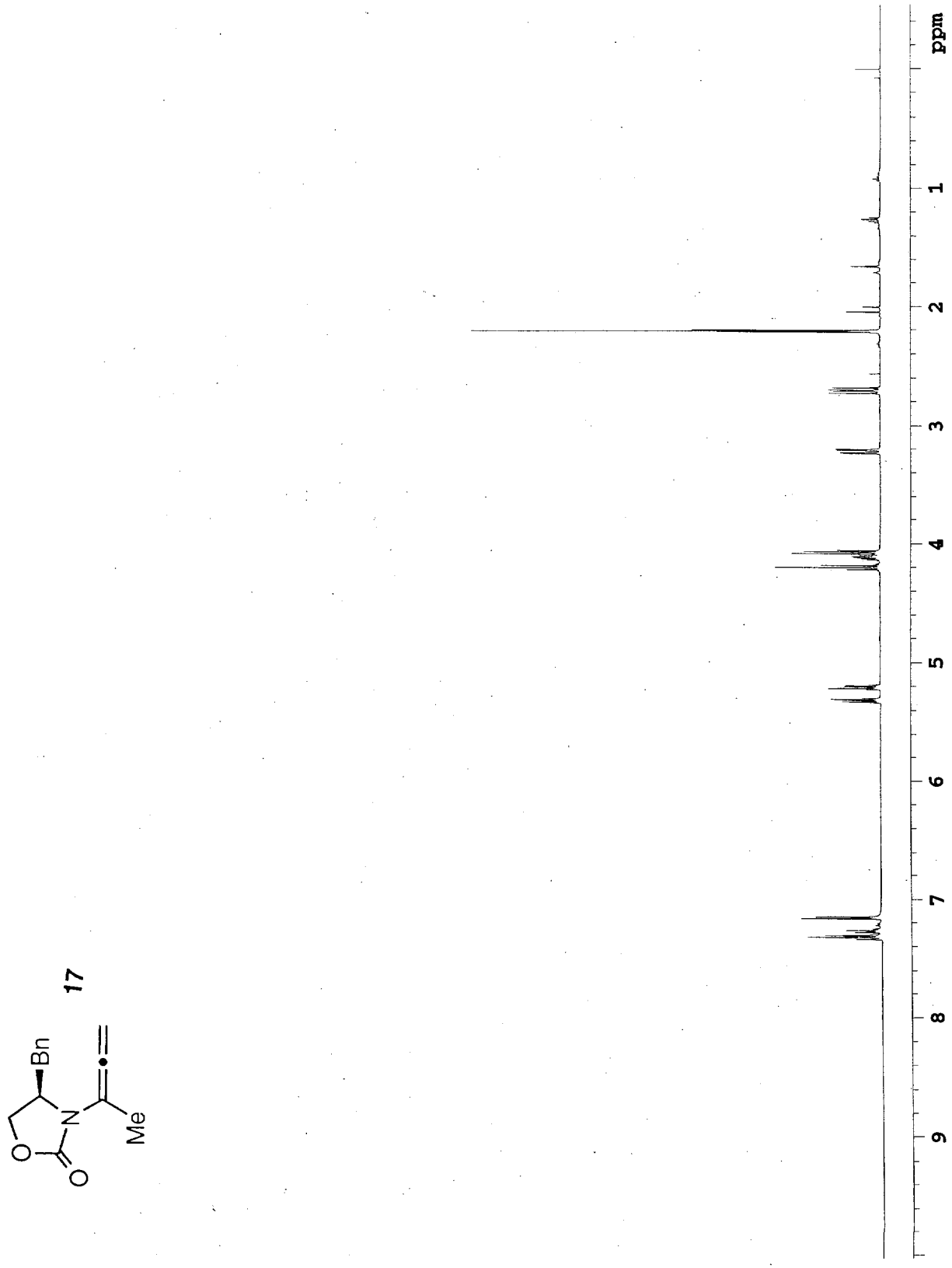

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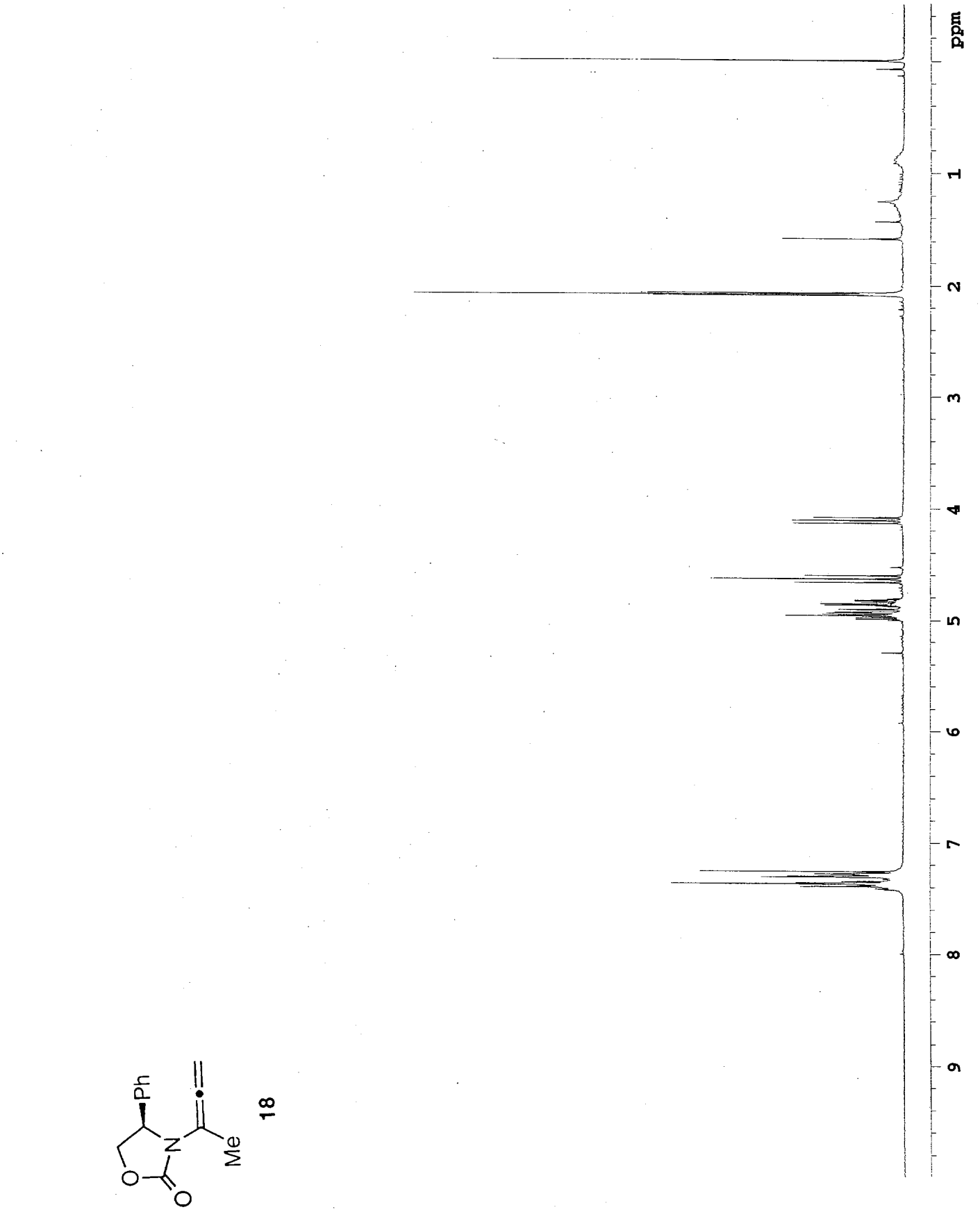

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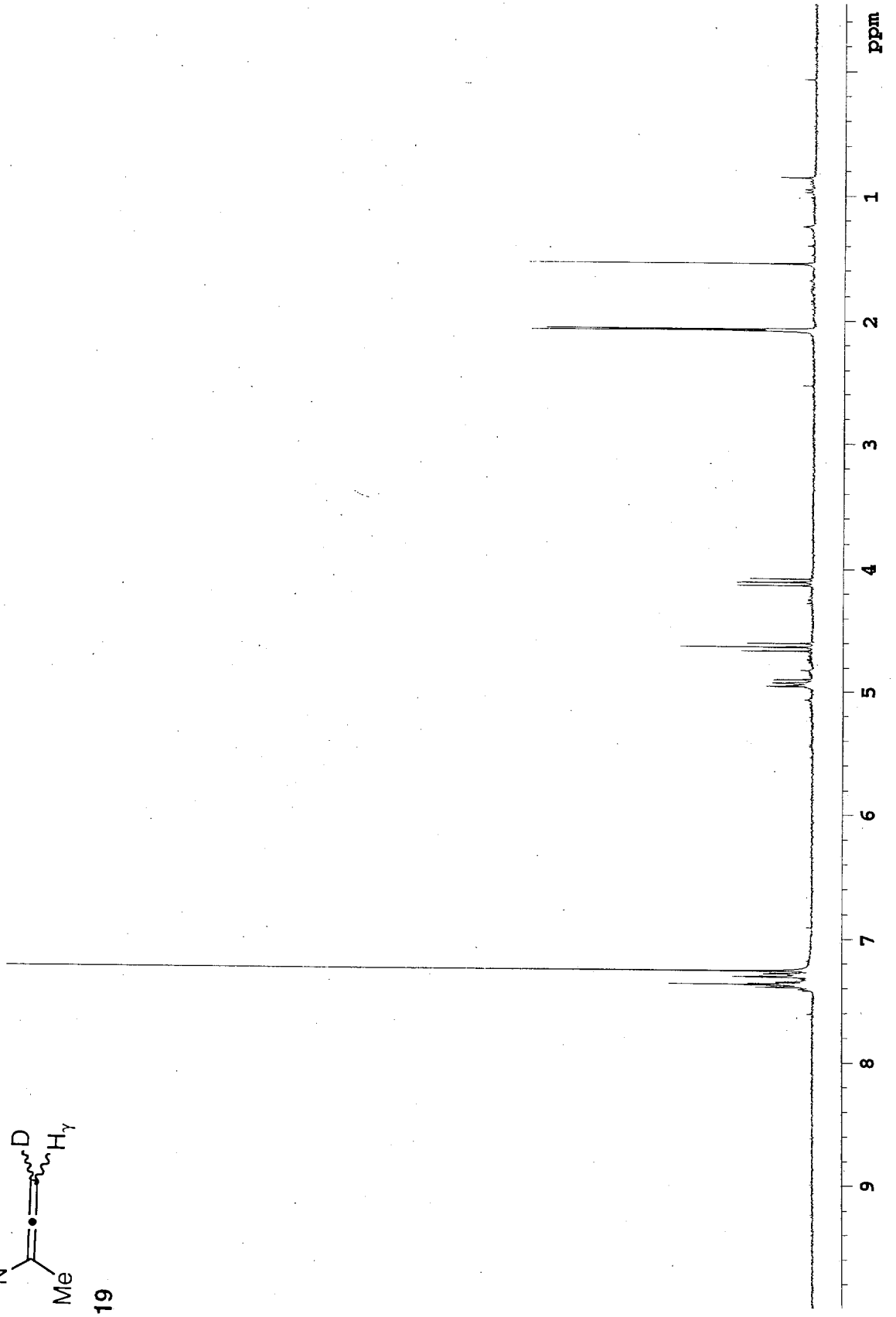

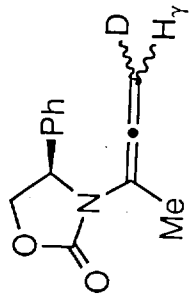

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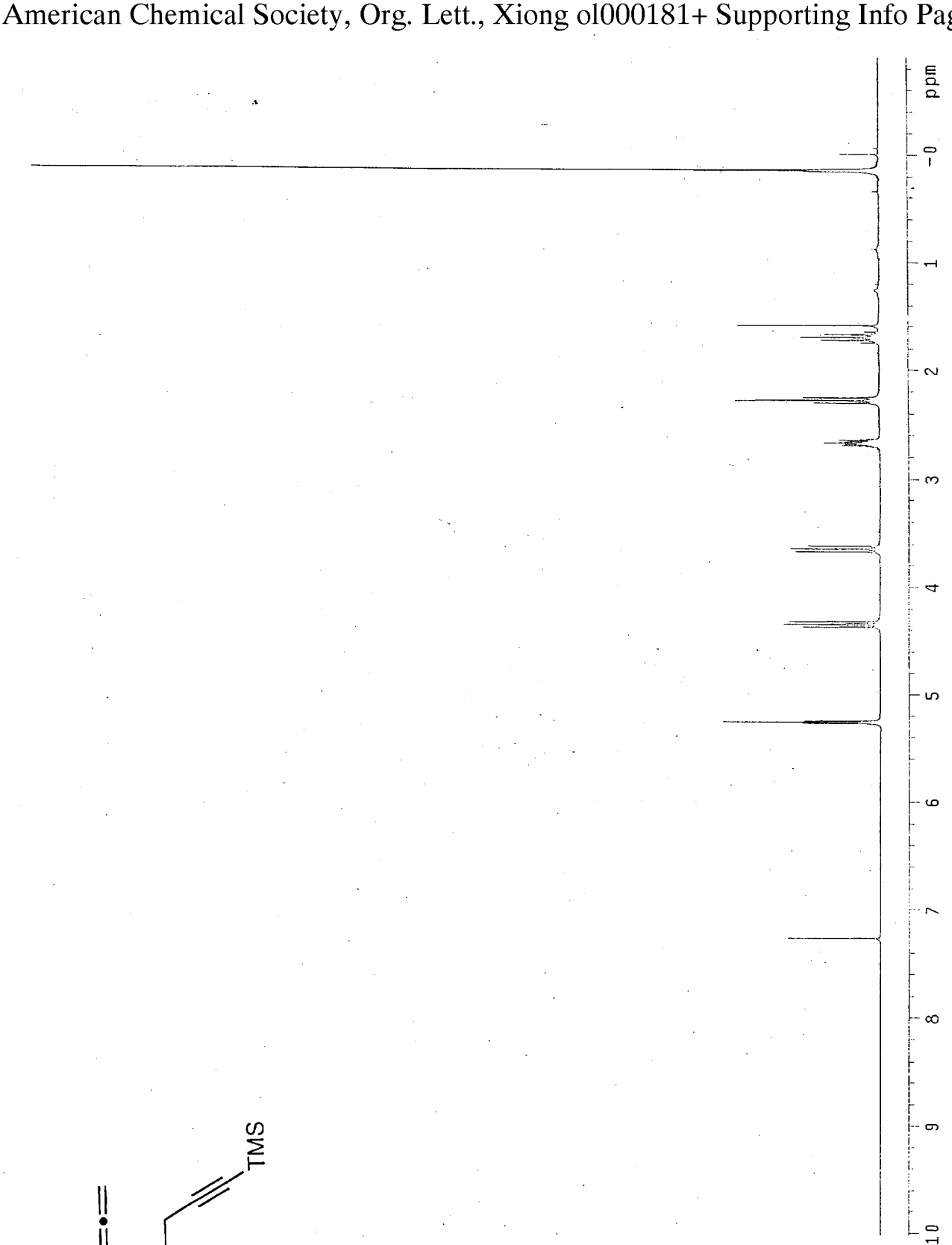

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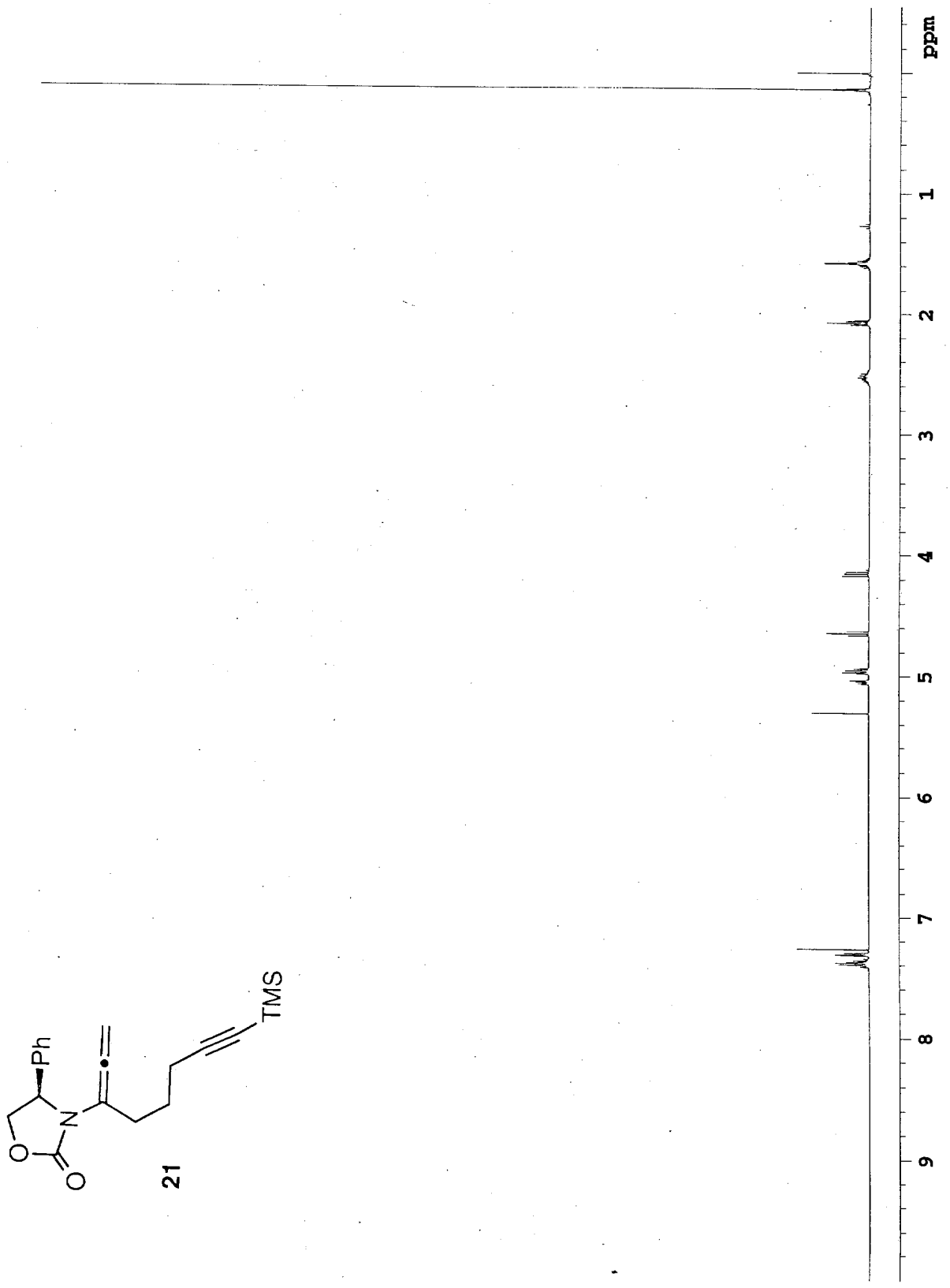
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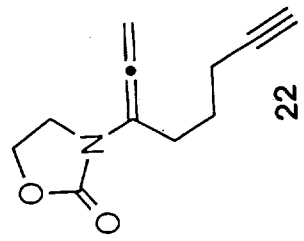

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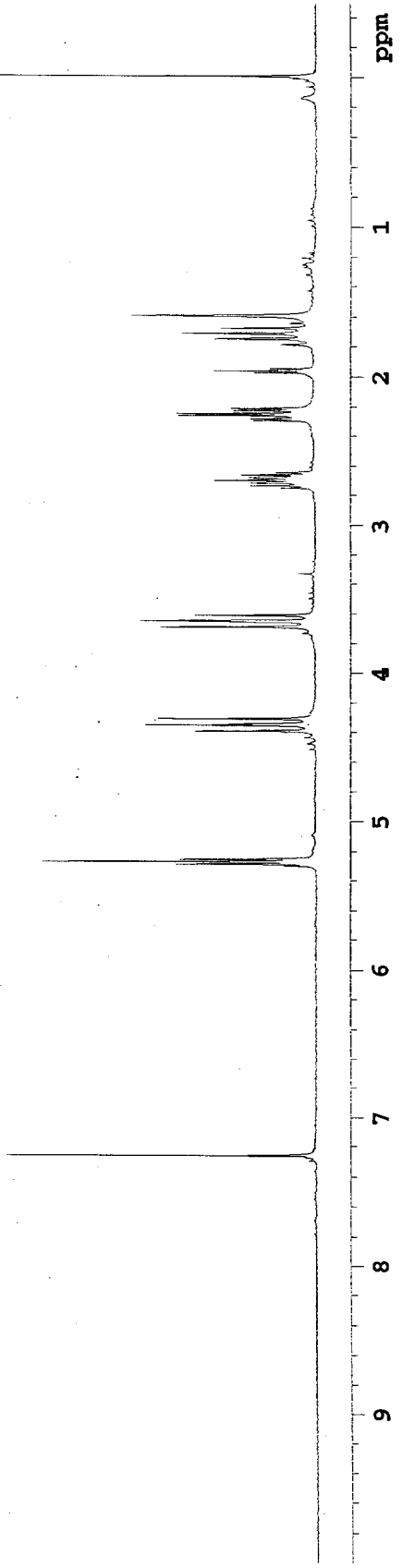

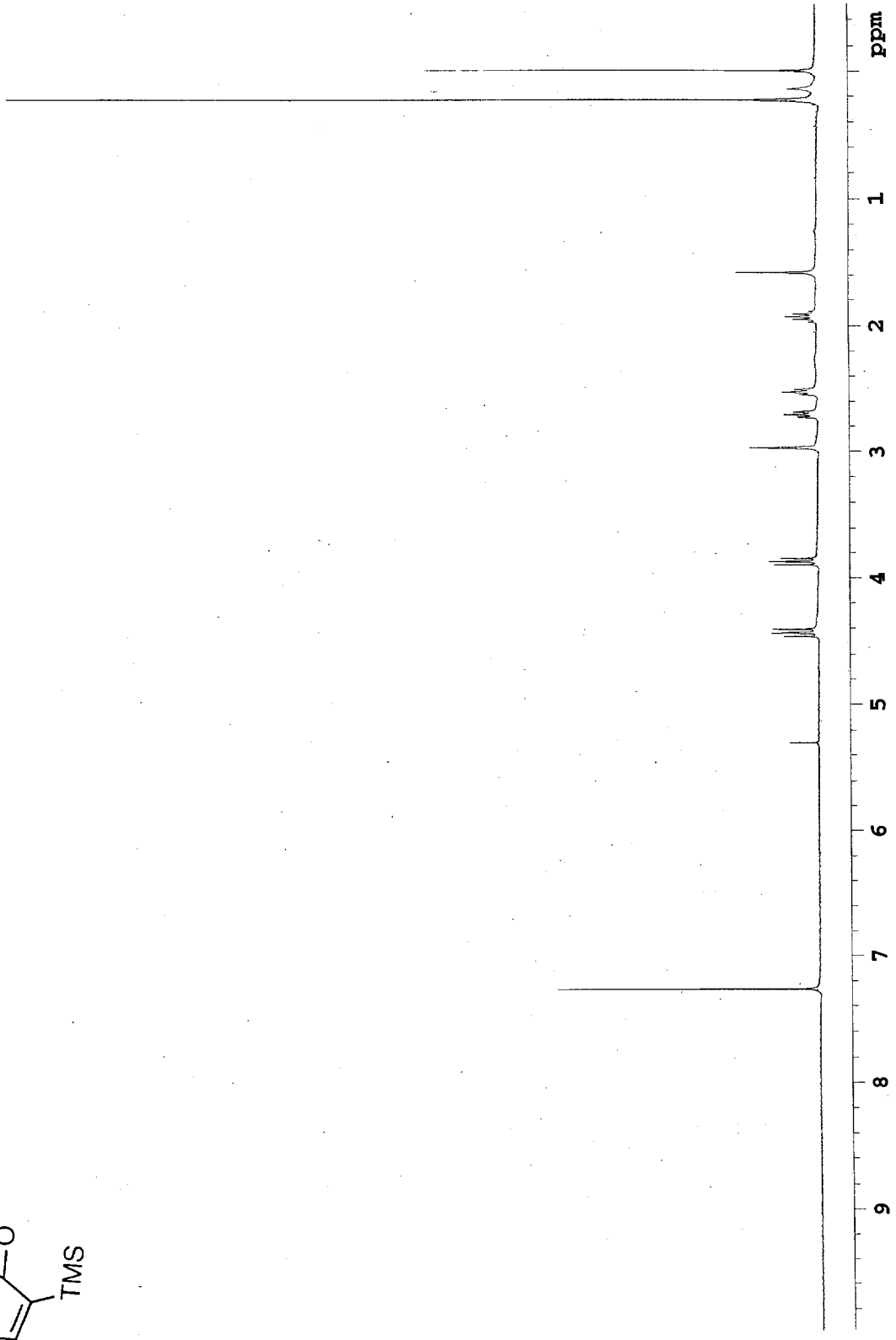

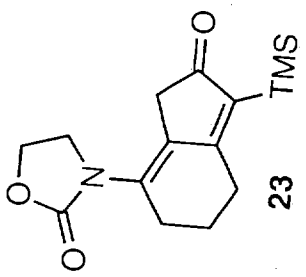

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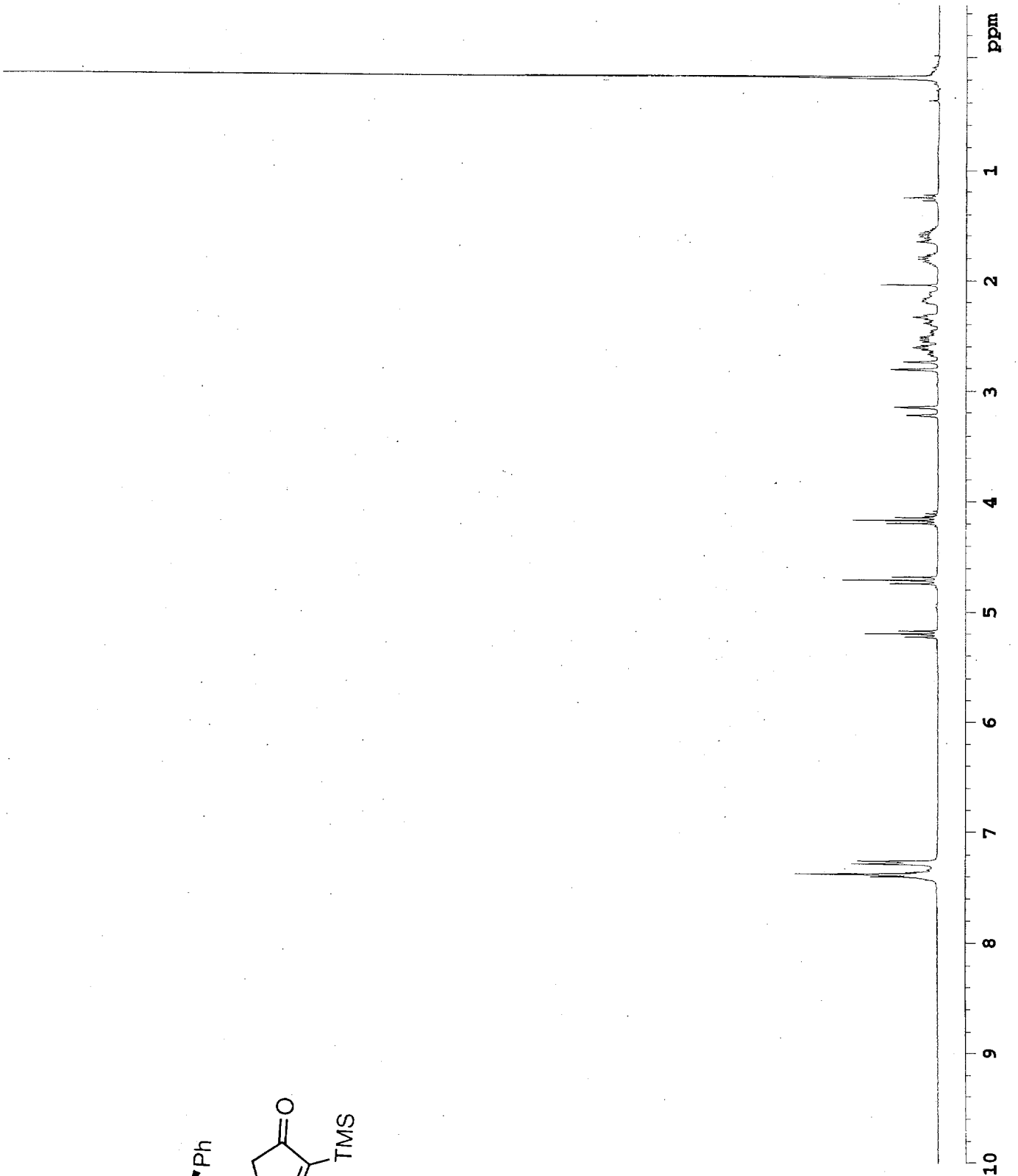

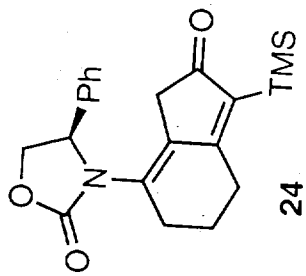

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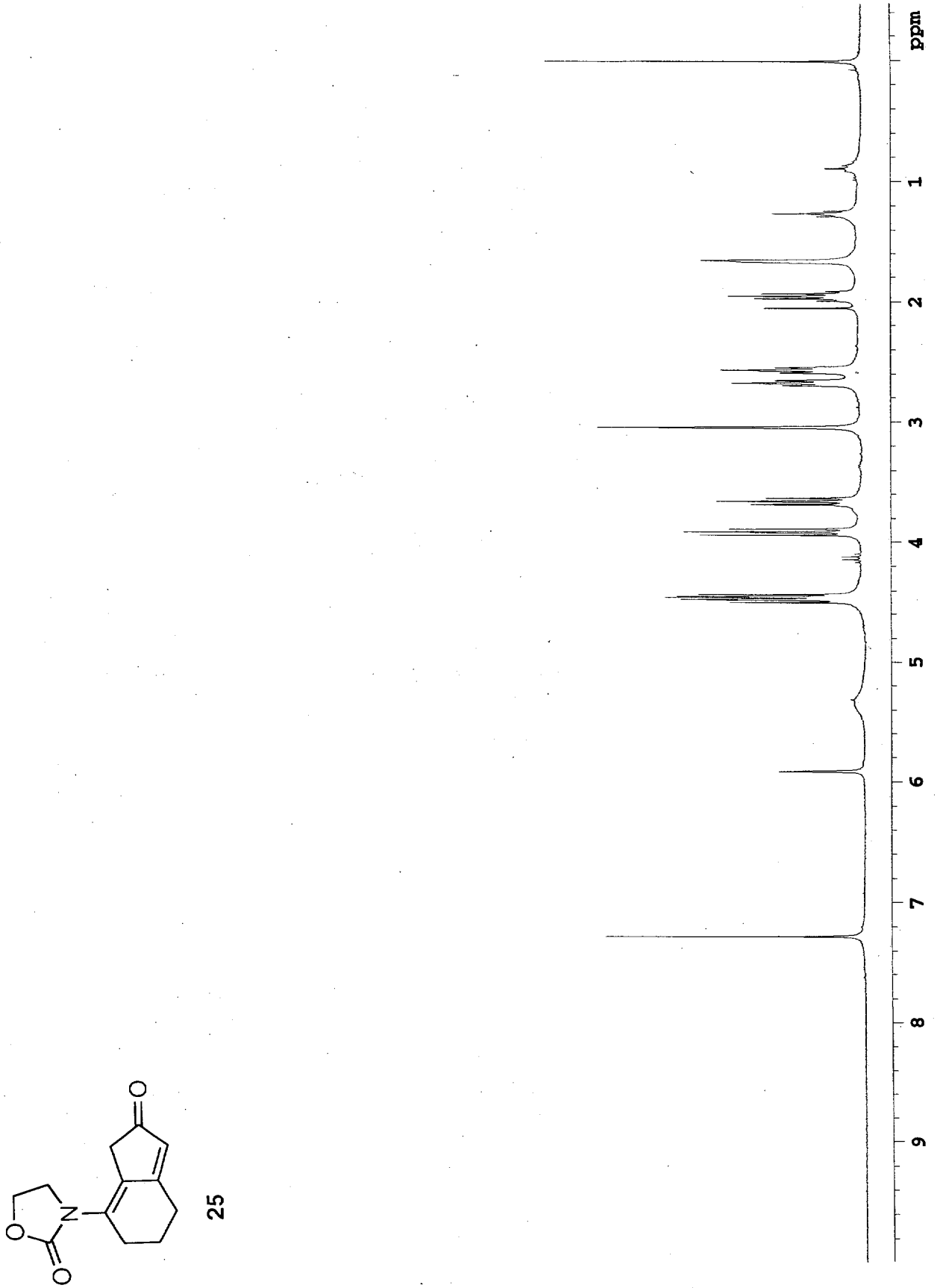

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