Experimental Section

General Procedure for Preparation of *N*-Allenyl Imidazolidinones/Oxazolidinones.

Preparation of N-propargyl Imidazolidinones/oxazolidinones:

To a homogeneous solution of an imidazolidinone / oxazolidinone (5.0 mmol) in anhydrous THF (30 mL) was added NaH (60%w in miner oil, 1.2 equiv) in small portions (Cautions!). The resulting slur was stirred for 30 min at room temperature before the addition of propargyl bromide (2 equiv). The precipitate of sodium salt didnot affect the reaction. The mixture was stirred at rt for 16-24 h. After when, the concentrated mixture was re-dissolved into ether (~ 20-50 mL) and filtered through a small bed of celite. The solvent was concentrated under the reduced pressure, and the residue was purified by flash silica gel column chromatography (gradient solvent system: 0% to 20% EtOAc in hexane) to provide the desired propargyl products in high yields (> 90%).

Preparation of Allenamides.

To a homogeneous solution of the propargyl product prepared above (5.0 mmol) in anhydrous THF (5.0 mL) was added freshly made ^{t}BuOK-^{t}BuOH (200 mg, 20 mol%) under nitrogen. The reaction mixture was stirred at rt for 16-24 h. The reaction progress was monitored by TLC (25% or 50% EtOAc in hexane) or ^{1}H NMR. After removing the solvent under reduced pressure, the crude mixture was redissolved in ether (~ 20-50 mL) and filtered through a small bed of celite or basic Al_2O_3 (25 % EtOAc in hecaxe as eluent). The solvent was removed under reduced pressure to provide pure allenamides in high yields (> 90%). For allenamides **2-5**, further purification can be achieved by flash silica gel column chromatography (gradient solvent system: 0% to 50% EtOAc in hexane). However, allenamide **1** couldnot survive on silica gel column.

General Procedure of [4 + 2] Cycloadditions:

In a flame-dried sealed tube (25 ml, previously soaked with 5%w 1,1,1,3,3,3-Hexamethyldisilazane in anhydrous hexane for 4-16 h) equipped with a magnetic stirring bar, an appropriate allenamide (0.5 mmol), 2.5 ml of anhydrous acetonitrile, and an appropriate enone/enal (0.5-0.6 mmol for **8-14** and **16**; 1.0 mmol for **15**; and 1.0-1.5 mmol for acrolein and MVK which were filtrated through a short-pad of silica gel before use) were mixed under nitrogen at rt or 0 °C (for bromoacrolein only). Then the sealed tube was simply submerged into an oil bath and heated to suitable temperature. The reaction was monitored by TLC and/or ^{1}H NMR. After the reaction was complete, the mixture was concentrated under reduced pressure and purified by silica gel column chromatography (gradient solvent system: 0 to 50 % EtOAc in hexane). to provide the desired cycloaddition products.

Characterizations

*For the allenamide **1**:*

R_f = 0.45 (50% EtOAc in hexane, mostly decomposed); mp 113-115 °C; $[\alpha]_D^{20}$ -96.9 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74 (d, 3 H, J = 6.6 Hz), 2.77 (s, 3 H), 3.84 (dq, 1 H, J = 6.6, 8.7 Hz), 4.68 (d, 1 H, J = 8.7 Hz), 4.75 (dd, 1 H, J= 6.3, 9.0 Hz), 5.04 (dd, 1 H, J = 6.3, 9.0 Hz), 6.96 (t, 1 H, J = 6.3 Hz), 7.06-7.31 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 15.0, 28.8, 55.6, 60.9, 86.7, 96.4, 127.9, 128.2, 128.6, 136.1, 157.9, 202.4;

IR (neat) cm^{-1} 3052 (s), 2924 (s), 1961 (m), 1709 (s), 1456 (s), 1401 (s), 880 (m);

mass spectrum (EI) for $C_{14}H_{16}N_2O$: m/e (%relative intensity) 228 (77) M^+, 111 (70), 227 (72), 170 (29), 118 (77), 117 (100);

*For the allenamide **2**:*

R_f = 0.57 (50% EtOAc in hexane, mostly decomposed); $[\alpha]_D^{20}$ -156.4 °;

^{1}H NMR (300 MHz, CDCl3) δ 4.10 (dd, 1 H, J = 6.0, 8.7 Hz), 4.64 (t, 1 H, J = 6.0 Hz), 4.78-4.84 (m, 2 H), 5.10 (dd, 1 H, J = 6.3, 9.6 Hz), 6.73 (t, 1 H, J= 6.3 Hz), 7.16-7.33 (m, 5 H);

^{13}C NMR (75 MHz, CDCl3) δ (total peakes) 59.0, 70.6, 87.7, 95.6, 126.5, 128.7, 129.0, 138.4, 155.5, 201.9;

IR (neat) cm^1 3063 (m), 3035 (s), 2979 (s), 1963 (w), 1767 (s), 1494 (s), 1462 (s), 1216 (s), 966 (m), 911 (s), 881 (s);

mass spectrum (EI) for $C_{12}H_{11}N_1O_2$: m/e (%relative intensity) 201 (15) M^+, 200 (14), 156 (100), 129 (17), 115 (19), 104 (45);

*For the allenamide **3**:*

R_f = 0.66 (50% EtOAc in hexane); mp 108-112 °C; $[\alpha]_D^{20}$ -60.7 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.85 (dd, 1 H, J = 6.3, 10.0 Hz), 5.13 (d, 1 H, J = 8.1 Hz), 5.17 (dd, 1 H, J= 6.3, 10.0 Hz), 5.92 (d, 1 H, J = 8.1 Hz), 6.80-6.84 (m, 2 H), 6.93 (t, 1 H, J = 6.3 Hz), 6.96-7.09 (m, 8 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 64.0, 80.3, 87.6, 95.8, 126.2, 127.3, 127.9, 128.05, 128.09, 128.14, 133.9, 134.0, 155.2, 202.22;

IR (neat) cm^{-1} 3036 (m), 2982 (w), 1961 (w), 1754 (s), 1456 (s), 1396 (s), 1266 (s), 1032 (s), 885 (m);

mass spectrum (EI) for $C_{18}H_{15}N_1O_2$: m/e (%relative intensity) 277 (2) M^+, 233 (100), 179 (51), 165 (36), 115 (46);

*For the allenamide **4**:*

R_f = 0.59 (50% EtOAc in hexane); $[\alpha]_D^{20}$ -22.7 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.74 (dd, 1 H, J = 8.7, 14.0 Hz), 3.23 (dd, 1 H, J = 3.0, 14.0 Hz), 4.05-4.25 (m, 3 H), 5.51 (dd, 1 H, J = 6.3, 9.9 Hz), 5.57 (dd, 1 H, J = 6.3, 9.9 Hz), 6.90 (t, 1 H, J = 6.3 Hz), 7.15-7.35 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 37.1, 55.6, 66.7, 88.0, 96.0, 127.3, 128.9, 129.3, 135.4, 154.97, 201.6;

IR (neat) cm^{-1} 3062 (m), 3030 (s), 1961 (m), 1760 (s), 1496 (s), 1456 (s), 1233 (s), 1067 (s), 863 (s), 800 (m);

mass spectrum (EI) for $C_{13}H_{13}N_1O_2$: m/e (%relative intensity) 215 (60) M^+, 170 (32), 124 (100), 117 (38), 91 (58);

*For the allenamide **5***

R_f = 0.64 (50% EtOAc in hexane); $[\alpha]_D^{20}$ -318.3 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.39 (dd, 1 H, J = 3.6, 8.7 Hz), 4.49 (dd, 1 H, J = 8.7, 8.7 Hz), 4.64 (ddd, 1 H, J = 3.6, 3.9, 8.7 Hz), 4.72 (d, 1 H, J = 3.9 Hz), 5.36 (dd, 1 H, J = 6.6, 10.2 Hz), 5.43 (dd, 1H, J = 6.6, 10.2 Hz), 6.86 (t, I H, J = 6.6 Hz), 7.07-7.38 (m, 10H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 49.3, 57.2, 64.9, 88.2, 96.1, 127.2, 127.7, 128.5, 128.7, 128.9, 129. 2, 138.0, 139.7, 155.0, 201.4;

IR (neat) cm^{-1} 3055 (m), 3031 (m), 2924 (m), 1960 (w), 1757 (s), 1458 (s), 1266 (s), 889 (m);

mass spectrum (EI) for $C_{19}H_{17}N_1O_2$: m/e (%relative intensity) 291 (53) M^+, 167 (61), 165 (39), 152 (25), 124 (100), 115 (14);

*For the pyranyl product **6**:*

R_f = 0.45 (50% EtOAc in hexane); mp 96-98 °C; $[\alpha]_D^{20}$ +189.0 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, 3 H, J = 6.5 Hz), 2.12-2.18 (m, 1 H), 2.45-2.50 (m, 1H), 2.78 (s, 3H), 3.84 (dq, 1 H, J = 6.5, 9.0 Hz) 4.62 (dt, 1 H, J = 3.5, 6.5 Hz), 4.78 (d, 1 H, J = 1.0 Hz), 4.88 (d, 1 H, J = 9.0 Hz), 5.00 (d, 1 H, J = 1.0 Hz), 6.20 (s, 1 H), 6.41 (dt, 1 H, J = 2.0, 6.5 Hz), 7.14-7.28 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 15.0, 26.3, 28.7, 56.8, 59.8, 81.1, 99.3, 115.6, 127.8, 127.9, 128.0, 137.5, 137.8, 142.6, 161.5;

IR (neat) cm^{-1} 3066 (w), 3033 (w), 2958 (m), 2924 (m), 1694 (s), 1662 (m), 1426 (s), 1399 (s), 1225 (m), 1049 (s);

mass spectrum (EI) for $C_{17}H_{20}N_2O_2$: m/e (%relative intensity) 284 (59) M^+, 267 (40), 255 (32), 240 (60), 189 (51), 170 (32), 132 (34), 118 (90), 117 (100), 115 (65), 94 (100);

*For the pyranyl product **7**:*

R_f = 0. 47 (50% EtOAc in hexane); mp 90-93 °C; $[\alpha]_D^{20}$ +158.0 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, 3 H, J = 4.2 Hz), 1.73 (d, 3 H, J = 0.9 Hz), 2.07-2.16 (m, 1 H), 2.43 (brd, 1 H, J = 20.4 Hz), 2.76 (s, 3 H), 3.82 (dq, 1 H, J = 4.2, 8.7 Hz), 4.36 (brs, 1 H), 4.76 (brs, 1 H), 4.79 (d, 1 H, J = 8.7 Hz), 4.99 (brs, 1 H), 6.18 (s, 1 H), 7.12-7.26 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 15.0, 20.0, 26.9, 28.7, 56.9, 59.8, 81.5, 94.5, 114.8, 127.8, 127.9, 128.0, 137.6, 137.8, 149.7, 161.5;

IR (neat) cm^{-1} 3062 (w), 3031 (w), 2980 (m), 1919 (m), 1702 (s), 1606 (m), 1399 (s), 1383 (s), 1349 (s), 1253 (s), 1172 (s), 1060 (s), 914 (m);

mass spectrum (EI) for $C_{18}H_{22}N_2O_2$: m/e (%relative intensity) 298 (36) M^+, 283 (58), 255 (66), 240 (25), 227 (21), 117 (58), 109 (64), 108 (100), 91 (37);

*For the pyranyl product **17***

R_f = 0.32 (33% EtOAc in hexanes); mp 117-119 °C; $[\alpha]_D^{20}$ +104.8 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, 3 H, J = 6.6 Hz), 2.33 (ddd, 1 H, J = 2.4, 4.9, 20.0 Hz), 2.71 - 2.82 (m, 1 H), 2.76 (s, 3 H), 3.83 (dq, 1 H, J = 6.6, 9.0 Hz), 4.82 (m, 1 H), 4.83 (d, 1 H, J = 9.0 Hz), 5.07 (brs, 1 H), 6.22 (s, 1 H), 6.62 (t, 1 H, J = 2.4 Hz), 7.12 - 7.17 (m, 2 H), 7.25 - 7.30 (m, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ major: 15.0, 28.7, 35.6, 56.5, 59.8, 80.6, 97.1, 117.0, 127.9, 128.1, 128.3, 136.5, 137.4, 141.7, 161.1; minor: 14.6, 28.6, 36.4, 56.1, 60.9, 80.8, 96.8, 115.2, 127.9, 128.1, 128.2, 136.4, 136.5, 141.0, 160.0;

IR (neat) cm^{-1} 3079 (w), 3031 (w), 2978 (w), 1694 (s), 1430 (s), 1135 (s), 1008 (s), 887 (s);

mass spectrum (EI) for $C_{17}H_{19}BrN_2O_2$: m/e (%relative intensity) 363 (2) M^+, 283 (100), 227 (9), 189 (10), 170 (9), 117 (32), 91 (17), 65 (9);

*For the pyranyl product **18***

R_f = 0.47 (50% EtOAc in hexane); mp 118-120 °C; $[\alpha]_D^{20}$ +161.8 °;

^{1}H NMR (300 MHz, CDCl3) δ 0.68 (d, 3 H, J = 6.6 Hz), 2.33 (ddd, 1 H, J = 2.6, 4.8, 21.2 Hz), 2.70 (dd, 1 H, J = 4.8, 21.2 Hz), 2.78 (s, 3 H), 3.77 (dq, 1 H, J = 6.6, 8.5 Hz), 4.82 (d, 1 H, J = 8.5 Hz), 4.83 (brs, 1 H), 5.05 (brs, 1 H), 5.24 (t, 1 H, J = 4.8 Hz), 6.42 (s, 1 H), 7.12-7.59 (m, 10 H)

^{13}C NMR (125 MHz, CDCl3) δ (total peakes) 15.0, 27.3, 28.8, 56.9, 59.9, 81.9, 96.4, 115.1, 124.7, 127.9, 128.0, 128.1, 128.2, 135.4, 137.6, 137.8, 150.5, 161.6; * one aromatic carbon missing due to overlap.

IR (neat) cm^{-1} 3064 (w), 2972 (w), 1706 (s), 1662 (m), 1427 (m), 1397 (m), 1058 (m);

mass spectrum (EI) for $C_{23}H_{24}N_2O_2$: m/e (%relative intensity) 360 (18) M^+ , 345 (23), 255 (50), 170 (100), 117 (32), 77 (24);

*For the pyranyl product **19**:*

R_f = 0.20 (25% EtOAc in hexanes); mp 166-169 °C; $[\alpha]_D^{20}$ +91.7 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, 3 H, J = 6.6 Hz), 2.49 (dd, 1 H, J = 4.0, 21.0 Hz), 2.78 (dd, 1 H, J = 4.0, 21.0 Hz), 2.78 (s, 3 H), 3.79 (dq, 1 H, J = 6.6, 8.7 Hz), 4.74 (d, 1 H, J = 8.7 Hz), 4.87 (brs, 1 H), 5.05 (brs, 1 H), 5.49 (t, 1 H, J = 4.0 Hz), 6.34 (s, 1 H), 7.10 - 7.17 (m, 2 H), 7.24 - 7.29 (m, 3 H), 7.66 (d, 2 H, J = 9.0 Hz), 8.15 (d, 2 H, J = 9.0 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9, 27.7, 28.7, 56.8, 60.4, 82.4, 100.8, 115.7, 123.6, 125.1, 127.9, 128.1, 132.5, 136.6, 137.5, 141.1, 147.2, 148.7, 161.2;

IR (neat) cm^{-1} 3082 (w), 2971 (w), 1707 (s), 1596 (m), 1515 (m), 1427 (m), 1397 (m), 1342 (s), 1059 (m);

mass spectrum (EI) for $C_{23}H_{23}N_3O_4$: m/e (% relative intensity);

*For the pyranyl product **20**:*

R_f = 0.50 (50% EtOAc in hexane); mp 133-136 °C; $[\alpha]_D^{20}$ +151.4 °;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, 3 H, J = 6.3 Hz), 2.35 (ddd, 1 H, J =2.4, 4.0, 21.0 Hz), 2.68 (dd, 1 H, J = 4.0, 21.0 Hz), 2.77 (s, 3 H), 3.76 (dq, 1 H, J = 6.3, 8.3 Hz), 4.76 (d, 1 H, J = 8.3 Hz), 4.83 (brs, 1 H), 5.03 (brs, 1 H), 5.24 (t, 1 H, J = 4.0 Hz), 6.36 (s, 1 H), 7.11-7.44 (m, 9 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (total peakes) 14.9, 27.4, 28.7, 56.8, 60.1, 82.0, 97.0, 115.3, 121.9, 126.2, 127.9, 127.9, 128.0, 131.3, 134.3, 137.2, 137.6, 149.5, 161.4;

IR (neat) cm^{-1} 3075 (m), 3034 (m), 2981 (m), 1693 (s), 1427 (s), 1070 (m), 1005 (s), 912 (m);

mass spectrum (EI) for $C_{23}H_{23}N_2O_2Br$: m/e (%relative intensity) 440 (2) and 438 (2) M^+, 281 (45), 253 (72), 207 (100);

*For the pyranyl product **21**:*

R_f = 0.47 (50% EtOAc in hexane); mp 80-83 °C; $[\alpha]_D^{20}$ +90.0 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.67 (d, 3 H, J = 6.6 Hz), 2.36 (dd, 1 H, J = 2.5, 4.0 , 21.0 Hz), 2.69 (dd, 1 H, J = 4.0, 21.0 Hz), 2.76 (s, 3 H), 3.76 (dq, 1 H, J = 6.6, 8.4 Hz), 4.78 (d, 1 H, J = 8.4 Hz), 4.80 (brs, 1 H), 5.01 (brs, 1 H), 5.16 (t, 1 H, J = 4.0 Hz), 6.36 (s, 1 H), 6.95-7.53 (m, 9 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes, ^{19}F-coupling) 14.9, 27.3, 28.7, 56.8, 60.1, 82.0, 96.1 (d, J = 2.3 Hz), 114.9, 115.2 (d, J = 4.0 Hz), 126.4 (d, J = 7.9 Hz), 127.8, 127.9, 128.0, 131.6 (d, J = 3.2 Hz), 137.3, 137.7, 149.6, 161.0, 161.4, 164.3;

IR (neat) cm^{-1} 3053 (w), 2974 (w), 1708 (s), 1665 (m), 1508 (s), 1475 (m), 14280 (s), 1010 (s), 842 (m);

mass spectrum (EI) for $C_{23}H_{23}N_2O_2F$: m/e (%relative intensity) 379 (4) M^+, 378 (17), 363 (24), 255 (52), 188 (100), 17 (33), 77 (10);

*For the pyranyl product **22**:*

R_f = 0.42 (50% EtOAc in hexane); mp 120-122 °C; $[\alpha]_D^{20}$ +150.0 °;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, 3 H, J = 6.8 Hz), 2.29 (ddd, 1 H, J = 2.5, 4.4, 21.5 Hz), 2.69 (dd, 1 H, J = 4.4, 21.5 Hz), 2.77 (s, 3 H), 3.77 (dq, 1 H, J = 6.8, 8.8 Hz), 3.82 (s, 3 H), 4.81 (d, 1 H, J = 8.8 Hz), 4.82 (brs, 1 H), 5.05 (brs, 1 H), 5.23 (t, 1 H, J = 4.4 Hz), 6.42 (s, 1 H), 6.84 (dd, 1 H, J= 2.6, 8.0 Hz), 7.12-7.27 (m, 8 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (total peakes) 15.0, 27.3, 28.7, 55.3, 56.9, 60.0, 81.9, 96.8, 110.2, 113.7, 115.1, 117.2, 127.9, 128.0, 129.2, 137.0, 137.6, 137.8, 150.3, 159.6, 161.5; * one aromatic carbon missing due to overlap.

IR (neat) cm^{-1} 2957 (m), 2931 (m), 1704 (s), 1665 (m), 1600 (m), 1489 (m), 1428 (s), 1052 (s);

mass spectrum (EI) for $C_{24}H_{26}N_2O_3$: m/e (%relative intensity) 375 (6) $(M - CH_3)^+$, 281 (10), 255 (52), 200 (100), 117 (30), 77 (10).

*For the pyranyl product **23**:*

R_f = 0.48 (50% EtOAc in hexane); mp 118-120 °C; $[\alpha]_D^{20}$ +42.6 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, 3 H, J = 6.6 Hz), 2.48 (ddd, 1 H, J =2.6, 5.0, 20.5 Hz), 2.84 (dd, 1H, J = 5.0, 20.5 Hz), 2.78 (s, 3 H), 3.85 (dq, 1 H, J = 6.6, 8.4 Hz), 4.89 (s, 1 H), 5.01-5.04 (m, 1 H), 5.02 (d, 1 H, J = 8.4 Hz), 5.09 (s, 1 H), 6.51 (s, 1 H), 7.16-7.35 (m, 9 H), 7.81-7.86 (m, 2 H), 8.24-8.28 (m, 1 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 15.1, 28.0, 28.8, 57.0, 60.1, 82.3, 100.6, 100.7, 115.2, 125.2, 125.8, 125.9, 126.0, 126.6, 127.9, 128.0, 128.3, 129.0, 131.2, 133.8, 134.4, 137.5, 138.0, 152.0, 161.8;

IR (neat) cm^{-1} 3058 (w), 2927 (w), 1709 (s), 1474 (m), 1427 (m), 1397 (m), 993 (m);

mass spectrum (EI) for $C_{27}H_{26}N_2O_2$: m/e (%relative intensity) 410 (20) M^+, 395 (20), 281 (45), 255 (28), 220 (40), 207 (100), 117 (20);

*For the pyranyl product **24**:*

R_f = 0.56 (50% EtOAc in hexane); mp 152-156 °C; $[\alpha]_D^{20}$ +188.4 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.69 (d, 3 H, J = 6.6 Hz), 1.89-1.11 (m, 11 H), 2.14 (dd, 1H, J = 2.2, 20.5 Hz), 2.59 (dd, 1 H, J = 4.0, 20.5 Hz), 2.75 (s, 3 H), 3.76 (qt, 1 H, J = 6.6, 8.8 Hz), 4.36 (dd, 1 H, J = 2.2, 4.0 Hz), 4.72 (brs, 1 H), 4.82 (d, 1 H, J = 8.8 Hz), 4.96 (brs, 1 H), 6.17 (s, 1 H), 7.09-7.26 (m, 5 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (total peakes) 15.0, 26.1, 26.2, 26.3, 26.6, 28.8, 30.5, 31.0, 42.2, 56.9, 60.0, 81.0, 92.1, 114.7, 127.8, 127.9, 138.0, 157.8, 161.5;

IR (neat) cm^{-1} 2924 (m,), 2854 (m), 1693 (s), 1422 (m), 1400 (m), 1004 (m), 989 (w) 888 (w);

mass spectrum (EI) for $C_{23}H_{30}N_2O_2$: m/e (%relative intensity) 366 (25) M^+, 351 (20), 283 (32), 255 (43), 176 (100), 117 (40).

*For the pyranyl product **25**:*

R_f = 0.64 (50% EtOAc in hexane); mp 77-81 °C; $[\alpha]_D^{20}$ +138.3 °;

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (d, 3 H, J = 6.5 Hz), 0.83-1.46 (m, 11 H), 1.98 (t, 2 H, J = 7.3 Hz), 2.15 (brd, 1 H, J = 20.2 Hz), 2.44 (dd, 1 H, J = 3.4, 20.2 Hz), 2.73 (s, 3 H), 3.77 (dq, 1 H, J = 6.5, 8.6 Hz), 4.36 (dd, 1 H, J = 3.4, 3.6 Hz), 4.71 (brs, 1 H), 4.80 (d, 1 H, J = 8.6 Hz), 4.95 (brs, 1 H), 6.16 (s, 1 H), 7.09-7.26 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 14.1, 15.0, 22.7, 26.8, 27.0, 28.7, 28.9, 31.7, 34.0, 56.9, 59.9, 81.2, 93.9, 114.8, 127.8, 127.9, 137.7, 137.9, 153.4, 161.5; * one aromatic carbon missing due to overlap.

IR (neat) cm^{-1} 2954 (m), 2857 (m), 1706 (s), 1456 (m), 1425 (s), 1198 (m), 1039 (m), 765 (m), 750 (m);

mass spectrum (EI) for $C_{23}H_{32}N_2O_2$: m/e (%relative intensity) 368 (30) M^+, 353 (28), 283 (50), 255 (62), 178 (100), 117 (52).

*For the pyranyl product **26**:*

R_f = 0.48 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 1.91-2.00 (m, 1 H), 2.44-2.51 (m, 1 H), 4.10 (dd, 1 H, J= 5.6, 9.0 Hz), 4.59-4.66 (m, 2 H), 4.85-4.87 (m, 1 H), 5.07-5.08 (m, 1 H), 5.36 (dd, 1 H, J = 5.6, 9.0 Hz), 6.03 (s, 1 H), 6.35 (td, 1 H, J = 2.2, 6.2 Hz), 7.25-7.40 (m, 5 H); minor: 2.70-2.94 (m, 2 H), 4.15 (dd, 1H, J = 8.6, 5.1 Hz), 4.59-4.66 (m, 2 H), 4.94 (dd, 1 H, J = 8.6, 5.1 Hz), 5.21-5.17 (m, 2 H), 5.62 (s, 1 H), 5.96 (td, 1 H, J = 2.2, 6.1 Hz), 7.25-7.40 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) mixture 25.7, 26.7, 57.8, 58.8, 70.4, 70.9, 81.72[two carbons overlap], 100.0, 100.5, 114.3, 115.9, 126.8, 126.9, 128.7, 128.8, 129.0, 129.3, 136.6, 137.0, 139.1, 139.5, 141.0, 141.8, 156.7, 158.6;

IR (neat) cm^{-1} 3066 (s), 2988 (s), 1761 (s), 1458 (s), 1401 (s), 1209 (s), 1057 (s), 918 (s);

mass spectrum (EI) for $C_{15}H_{15}NO_3$: m/e (%relative intensity) 257 (2) M^+, 184 (3), 153 (37), 104 (64), 94 (100).

*For the pyranyl product **27**:*

R_f = 0.55 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 2.08-2.14 (m, 1 H), 2.51-2.46 (m, 1 H), 4.51-4.71 (m, 1 H), 4.89 (brs, 1 H), 5.15 (brs, 1 H), 5.22 (d, 1 H, J = 7.8 Hz), 5.87 (d, 1 H, J = 7.8 Hz), 6.16 (s, 1 H), 6.44 (td, 1 H, J = 2.2, 6.2 Hz), 6.83-7.12 (m, 10 H); minor: 2.77-3.04 (m, 2 H), 4.51-4.71 (m, 1 H), 5.12 (d, 1 H, J = 7.8 Hz),

5.26 (d, 1 H, J = 0.6 Hz,), 5.29 (d, 1 H, J = 0.6 Hz), 5.76 (s, 1 H), 5.84 (d, 1 H, J = 7.8 Hz), 5.98 (td, 1 H, J = 2.1, 6.1 Hz), 6.83-7.12 (m, 10 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) mixture: 25.7, 26.5, 63.2, 64.0, 80.5, 81.3, 81.6, 82.1, 99.9, 100.9, 114.8, 116.8, 126.1, 126.2, 127.4, 127.5, 127.8, 127.9, 128.0, 128.1, 128.2, 133.8, 133.9, 134.9, 135.5, 136.2, 137.3, 140.9, 142.0, 156.5, 158.0;

IR (neat) cm^{-1} 3065 (m), 2919 (m), 1756 (s), 1661 (m), 1217 (m), 1052 (m), 863 (w), 717 (m);

mass spectrum (EI) for $C_{21}H_{19}NO_3$: m/e (%relative intensity) 333 (1) M^+, 288 (2), 260 (4), 180 (100), 165 (18), 94 (47).

*For the pyranyl product **29**:*

R_f = 0.58 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 1.80 (s, 3 H), 2.09-2.50 (m, 2 H), 4.36-4.44 (m, 1 H), 4.85-5.30 (m, 3 H), 5.85 (d, 1 H, J = 7.7 Hz), 6.14 (s, 1 H), 6.82-7.10 (m, 10 H); minor: 1.80 (s, 3 H), 2.70-3.00 (m, 2 H), 4.36-4.44 (m, 1 H), 4.85-5.30 (m, 3 H), 5.82 (d, 1 H, J = 6:5 Hz), 5.96 (s, 1 H), 6.82-7.10 (m, 10 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) 18.9, 19.9, 26.3, 26.9, 63.4, 63.9 80.2, 80.7, 81.2, 82.1, 94.8, 95.0, 114.2, 115.9, 116.2, 126.0, 126.2, 126.3, 127.3, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 133.9, 135.5, 136.2, 137.3, 148.6, 149.2, 158.0; * four aromatic carbons missing due to overlap

IR (neat) cm^{-1} 3035 (w), 2987 (w), 1760 (s), 1456 (m), 1382 (m), 1218 (m), 1024 (m);

mass spectrum (EI) for $C_{22}H_{21}NO_3$: m/e (%relative intensity) 347 (1) M^+, 180 (100), 179 (28), 167 (17), 108 (81).

*For the pyranyl product **30**:*

R_f = 0.53 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 1.82 (brs, 3 H), 2.54-3.36 (m, 4 H), 4.04-4.42 (m, 3 H), 4.62-4.68 (m, 1 H), 5.21 (brs, 1 H), 5.31 (brs, 1 H), 6.02 (brs, 1 H), 7.10-7.36 (m, 5 H); minor: 1.80 (brs, 3 H), 2.54-3.36 (m, 4 H), 4.04-4.42 (m, 3 H), 4.62-4.68 (m, 1 H), 5.11 (brs, 1 H), 5.21 (brs, 1 H), 6.10 (brs, 1 H), 7.10-7.36 (m, 5 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (total peakes) mixture: 19.6, 19.7, 27.7, 27.8, 39.5, 40.5, 55.0, 55.4, 66.7, 68.2, 82.0, 95.2, 95.4, 112.3, 112.6, 127.1, 127.1, 128.7, 128.8, 128.9, 129.4, 136.1, 136.2, 137.2, 137.9, 149.3, 149.4, 158.2;

IR (neat) cm^{-1} 2988 (m), 1920 (s), 1748 (s), 1693 (s), 1496 (s), 1219 (s), 1083 (s);

mass spectrum (EI) for $C_{17}H_{19}NO_3$: m/e (%relative intensity) 285 (3) M^+, 194 (2.5), 167 (6), 109 (30), 108 (100), 91 (21).

*For the pyranyl product **31**:*

R_f = 0.50 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 2.60 (dd, 1 H, J = 10.9, 13.3 Hz), 2.87-3.35 (m, 3 H), 4.05-4.39 (m, 3 H), 4.86-4.92 (m, 1 H), 5.14-5.25 (m, 2 H), 6.01 (s, 1 H), 6.40-6.47 (m, 1 H), 7.12-7.35 (m, 5 H); minor: 2.79 (dd, 1 H, J = 10.1, 13.7 Hz), 2.87-3.35 (m, 3 H), 4.05-4.39 (m, 3 H), 4.86-4.92 (m, 1 H), 5.14-5.25 (m, 2 H), 6.08 (s, 1 H), 6.40-6.47 (m, 1 H), 7.12-7.35 (m, 5 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) mixture: 27.1, 27.2, 39.6, 40.4, 55.1, 55.4, 66.8, 68.11, 81.7, 81.8, 100.5, 112.9, 113.3, 127.1, 127.2, 128.8, 128.9, 129.3, 136.0, 136.1, 137.2, 137.7, 141.8, 142.1, 158.1;

IR (neat) cm^{-1} 3064 (w), 3028 (w), 1754 (s), 1416 (m), 1225 (m);

mass spectrum (EI) for $C_{16}H_{17}NO_3$: m/e (%relative intensity) 271 (1) M^+, 180 (10), 154 (13), 117 (13), 94 (100), 91 (30).

*For the pyranyl product **32**:*

R_f = 0.63 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ major: 1.73 (brs, 3 H), 2.64-2.84 (m, 2 H), 4.22-4.89 (m, 5 H), 5.15 (brs, 1 H), 5.3 (brs, 1 H), 5.75 (s, 1 H), 7.11-7.37 (m, 10 H); minor: 1.81 (brs, 3 H), 2.64-2.84 (m, 2 H), 4.22-4.89 (m, 5 H), 5.06 (brs, 1 H), 5.14 (brs, 1 H), 5.79 (s, 1 H), 7.11-7.37 (m, 10 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (total peakes) mixture: 19.7, 19.9, 29.4, 27.0, 29.7, 27.5, 52.7, 3.7, 56.7, 57.4, 65.2, 65.8, 82.0, 82.8, 94.8, 95.7, 112.9, 114.4, 127.0, 127.1, 127.4, 128.3, 128.4, 128.6, 128.7, 128.8, 128.9, 129.1, 136.8,136.9, 139.0, 139.3, 140.6, 140.7, 148.8, 149.4, 156.8, 157.9;

IR (neat) cm^{-1} 3061 (w), 2921 (w), 1759 (s), 1495 (m), 1219 (m), 1031 (m);

mass spectrum (EI) for $C_{23}H_{23}NO_3$: m/e (%relative intensity) 361 (2) M^+, 194 (20), 167 (45), 152 (21), 108 (100).

*For the pyranyl product **33***

R_f = 0. 34 (33% EtOAc in hexane); mp 148-150 °C; $[\alpha]_D^{20}$ -36.0 °;

^{1}H NMR (500 MHz, CDCl3) δ 0.70 (d, 3 H, J = 6.4 Hz), 0.94 (d, 3 H, J = 6.8 Hz), 1.62 (ddd, 1 H, 4.0, 4.4, 17.1 Hz), 2.04 (m, 1 H), 2.49 (ddd, 1 H, J = 4.0, 5.9, 17.1 Hz), 2.74 (s, 3 H), 3.80 (dq, 1 H, J = 6.4, 9.0 Hz), 4.93 (d, 1 H, J = 9.0 Hz), 4.99 (t, 1 H, J = 4.0 Hz), 6.16 (d, 1 H, J = 2.0 Hz), 7.56-7.30 (m, 9 H), 7.84 (t, 2 H, J =9.0 Hz), 8.35 (d, 1 H, J = 8.5 Hz);

^{13}C NMR (125.7 MHz, CDCl3) δ (total peakes) 14.0, 15.2, 28.8, 29.3, 30.9, 57.3, 58.7, 83.3, 100.8, 125.2, 125.8, 126.2, 126.3, 126.6, 127.9, 128.1, 128.8, 131.4, 133.8, 134.7, 138.8, 152.2, 162.5; * two aromatic carbons missing due to overlap.

IR (neat) cm^{-1} 2969 (w), 2931 (w), 1709 (s), 1454 (w), 1427 (m), 1252 (m), 1050 (m), 976 (w);

mass spectrum (EI) for $C_{27}H_{28}N_2O_2$: m/e (%relative intensity) 412 (5) M^+, 281 (18), 230 (100), 207 (30), 118 (35);

*For the pyranyl product **34**:*

R_f = 0.32 (33% EtOAc in hexane); mp 166-168 °C; $[\alpha]_D^{20}$ -98.0 °;

^{1}H NMR (300 MHz, CDCl3) 0.68 (d, 3 H, J = 6.6 Hz), 0.86 (d, 3 H, J = 6.7 Hz), 1.61-2.20 (m, 5 H), 2.70 (s, 3 H), 3.75 (dq, 1 H, J = 6.6, 8.6 Hz), 4.89 (d, 1 H, J = 8.6 Hz), 5.33 (dd, 1 H, J = 3.5, 10.5 Hz), 5.62 (d, 1 H, J = 1.8 Hz), 7.29-7.85 (m, 11 H), 8.09 (d, 1 H, J = 8.2 Hz)

^{13}C NMR (75 MHz, CDCl3) δ (total peakes) 12.8, 15.3, 26.8, 28.8, 31.0, 32.4, 57.3, 59.0, 77.8, 86.7, 122.9, 123.9, 125.4, 125.9, 127.5, 127.8, 128.2, 128.6, 130.5, 133.7, 138.3, 139.4, 162.9; * two aromatic carbons missing due to overlap.

IR (neat) cm^{-1} 2926 (s), 2855 (m), 1698 (s), 1364 (m), 1350 (m), 1252 (m), 1170 (w), 1000 (m);

mass spectrum (EI) for $C_{27}H_{30}N_2O_2$: m/e (%relative intensity) 414 (10) M^+, 281 (52), 253 (25), 207 (100), 189 (20), 91 (35);

SUPPLEMENTARY ^{1}H NMR SPECTRA

for the

communication

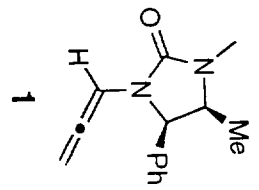
entitled

The First Stereoselective Inverse Demand [4 + 2] Cycloaddition Reactions of Novel Chiral Allenamides with Heterodienes. Preparation of Highly Functionalized 2-Arylpyranyl Heterocycles.

authored by

Lin-Li Wei, Richard P. Hsung*, Hui Xiong, Jason A. Mulder, and Nancy T. Nkansah

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455



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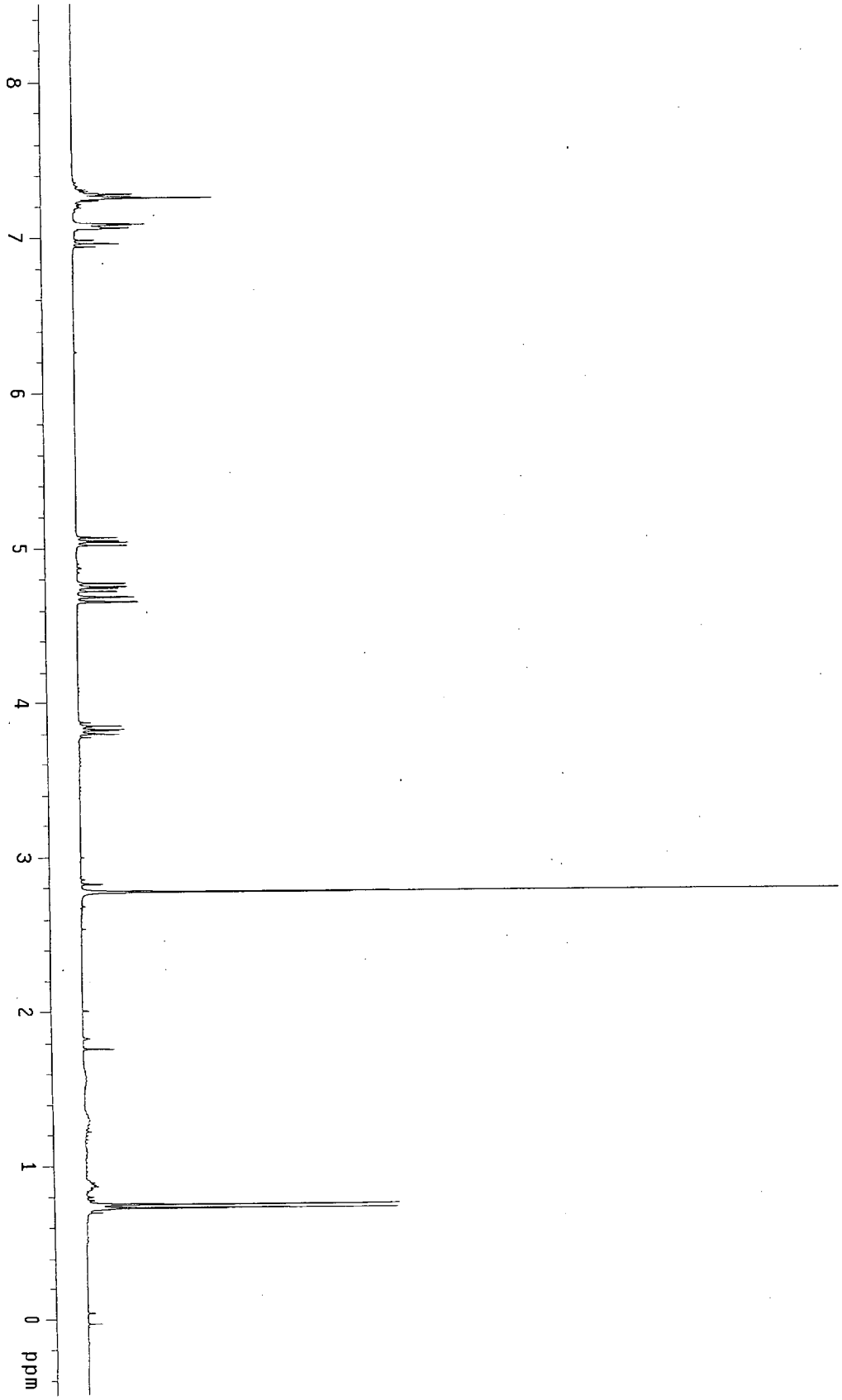

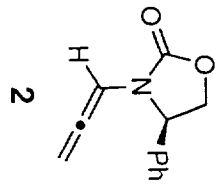

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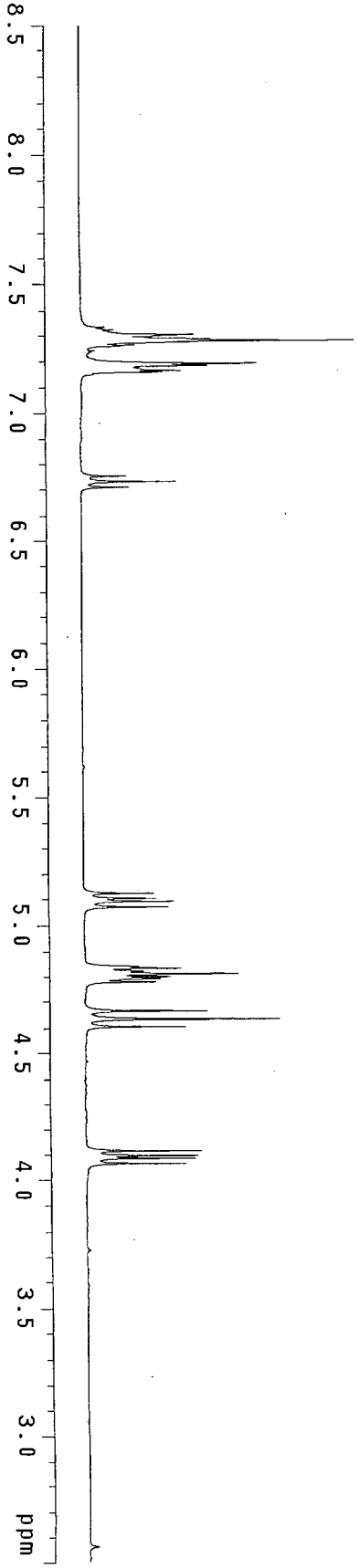

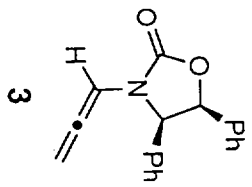

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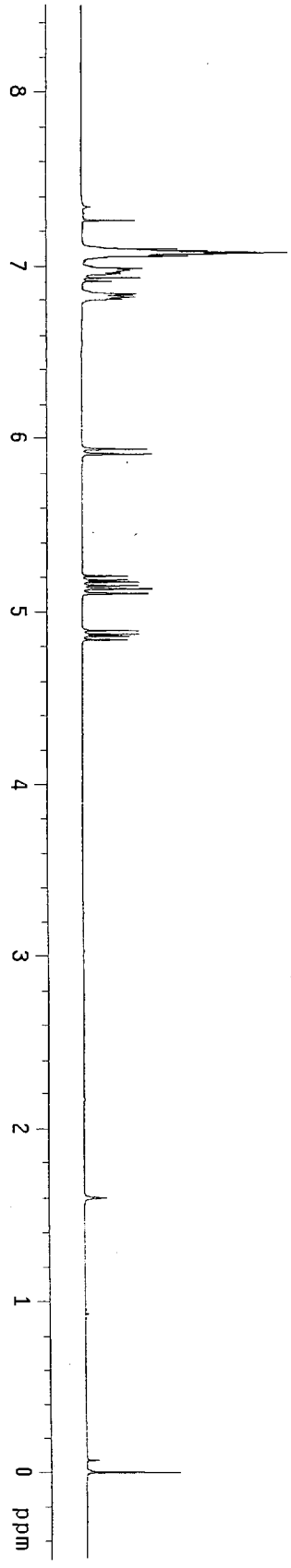

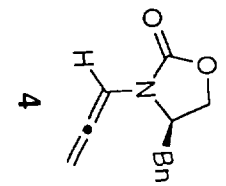

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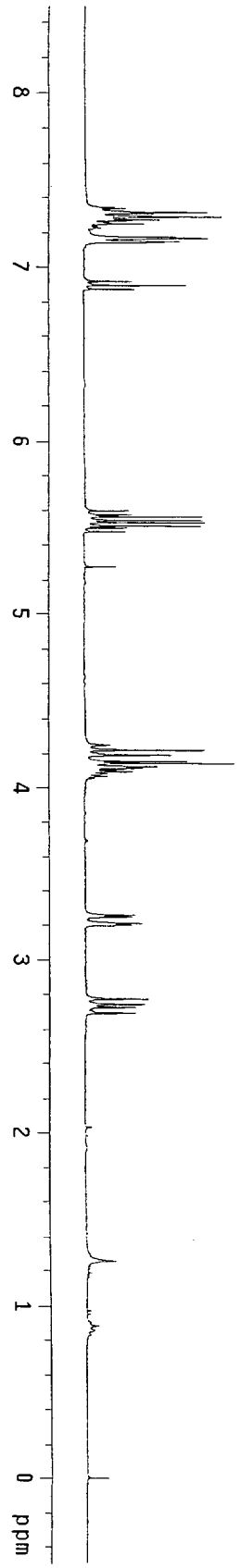

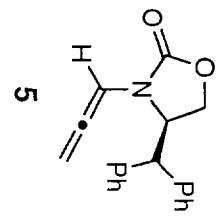

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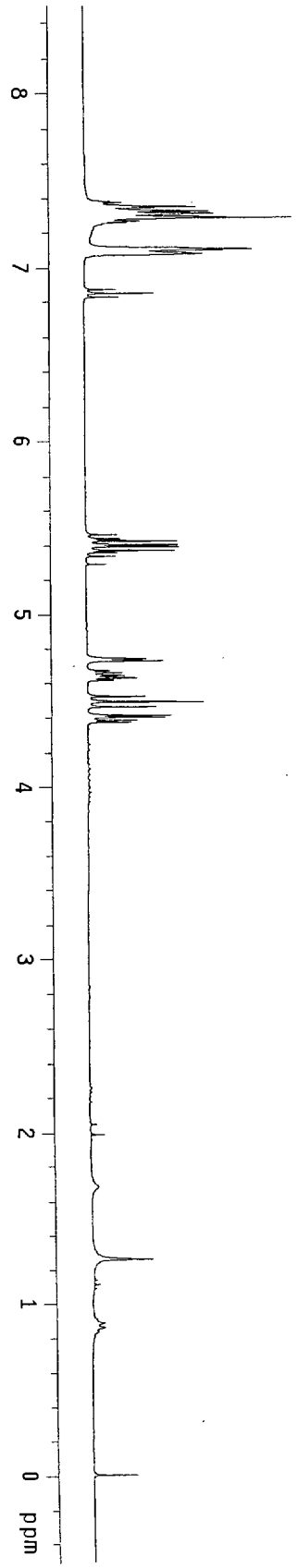

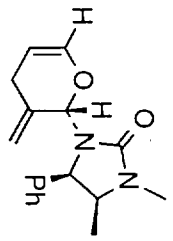

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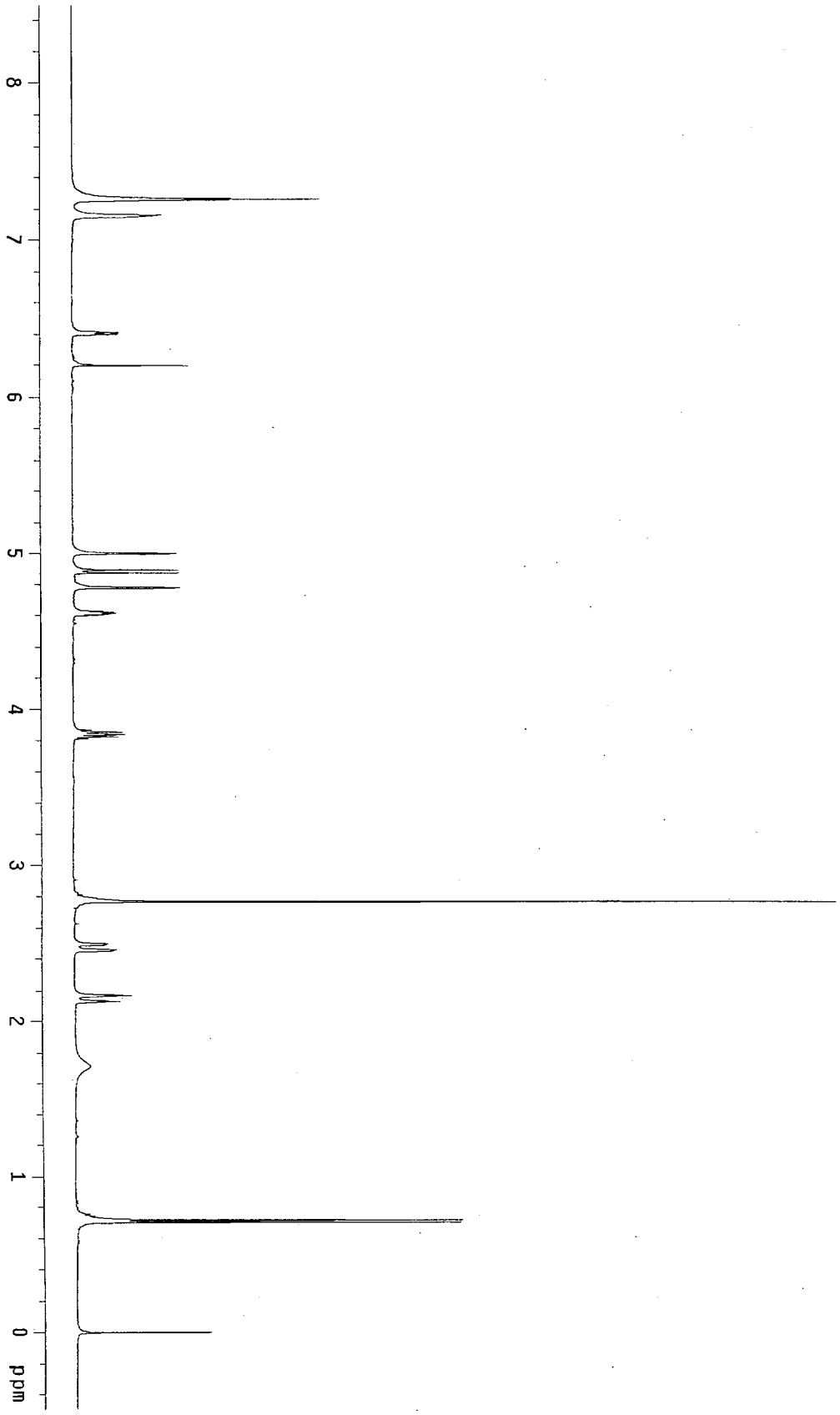

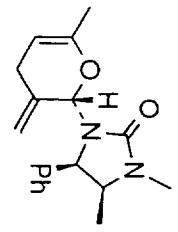

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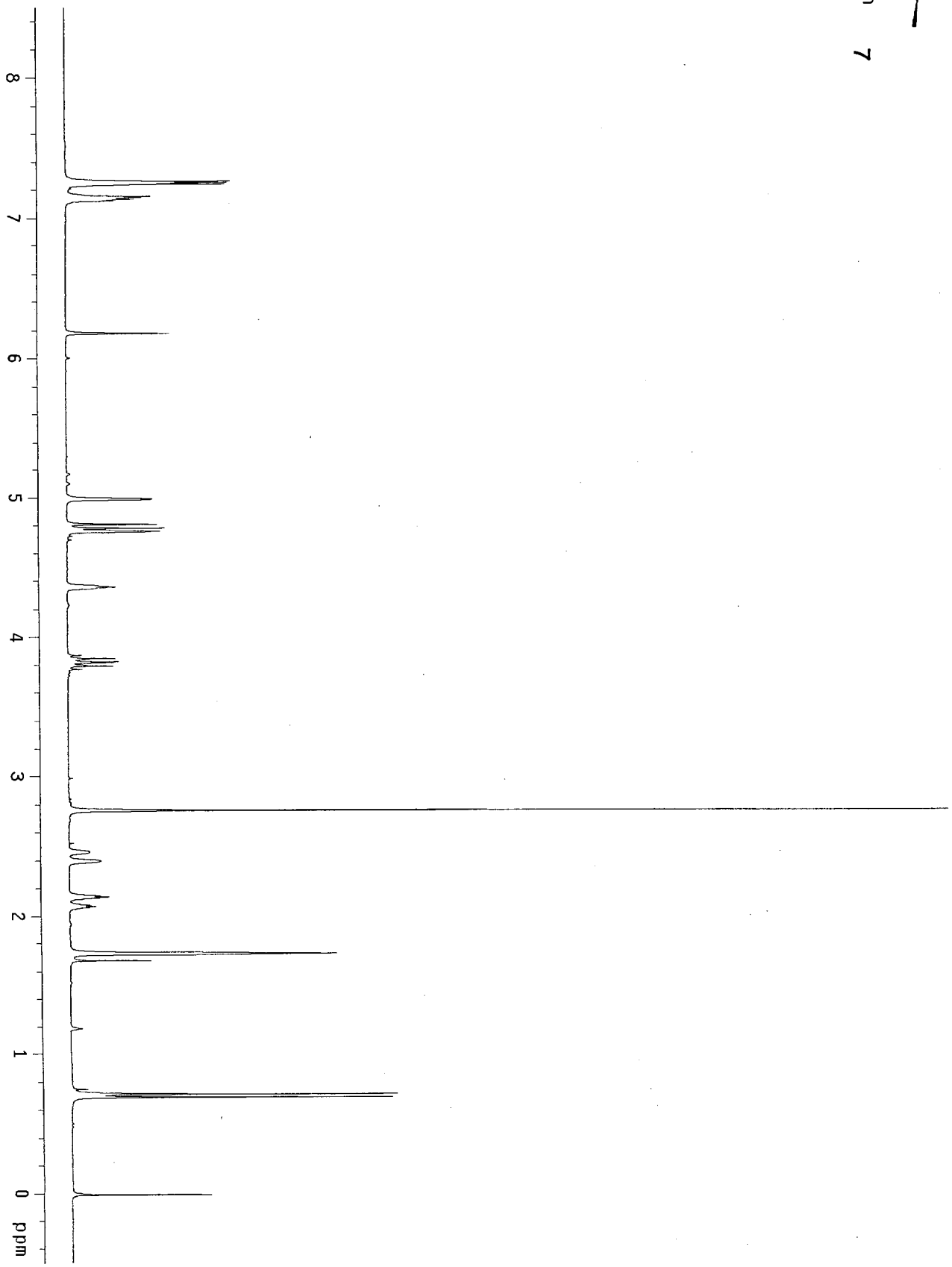

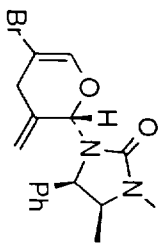

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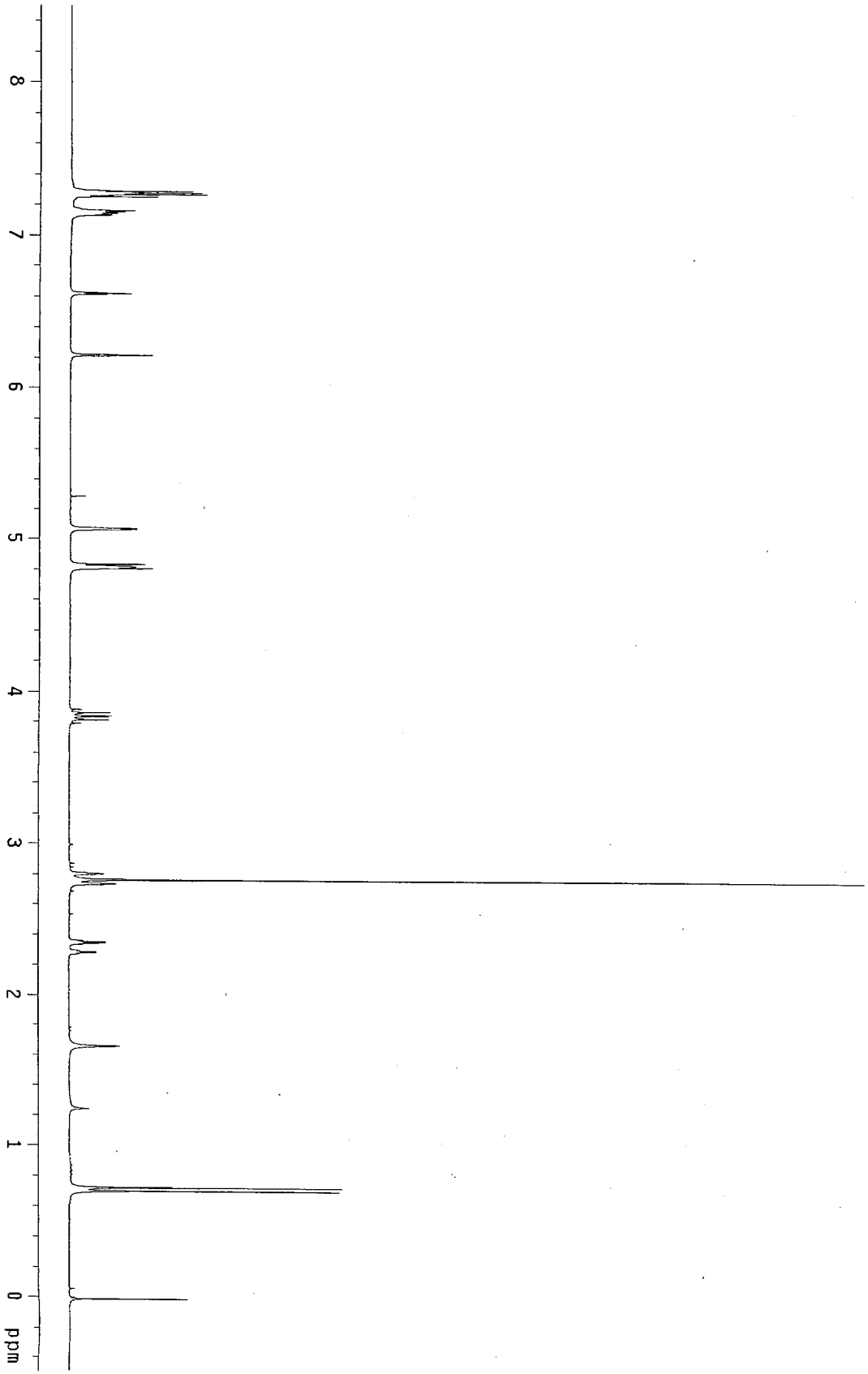

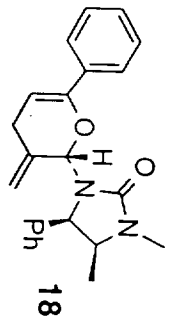

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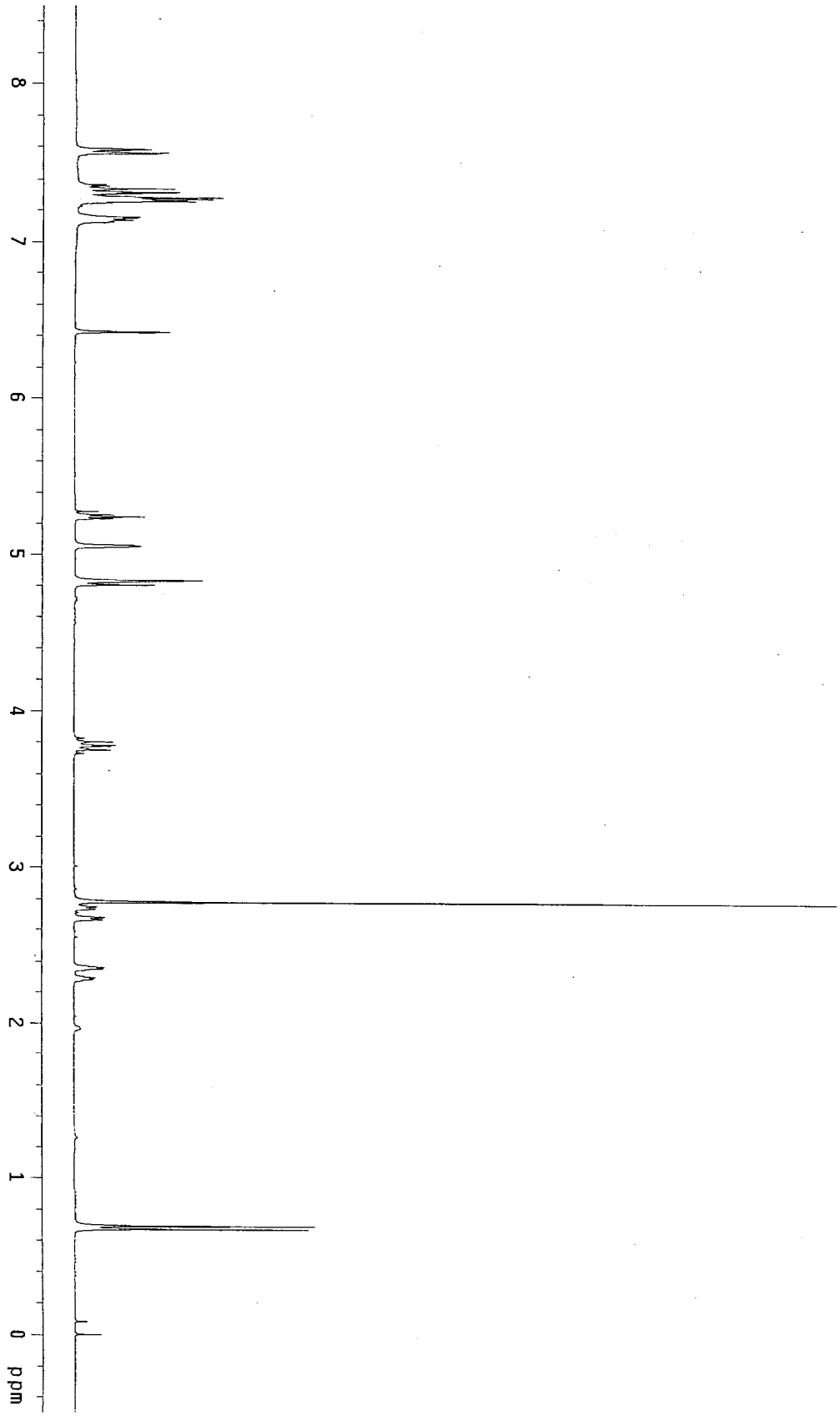

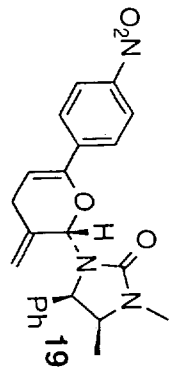

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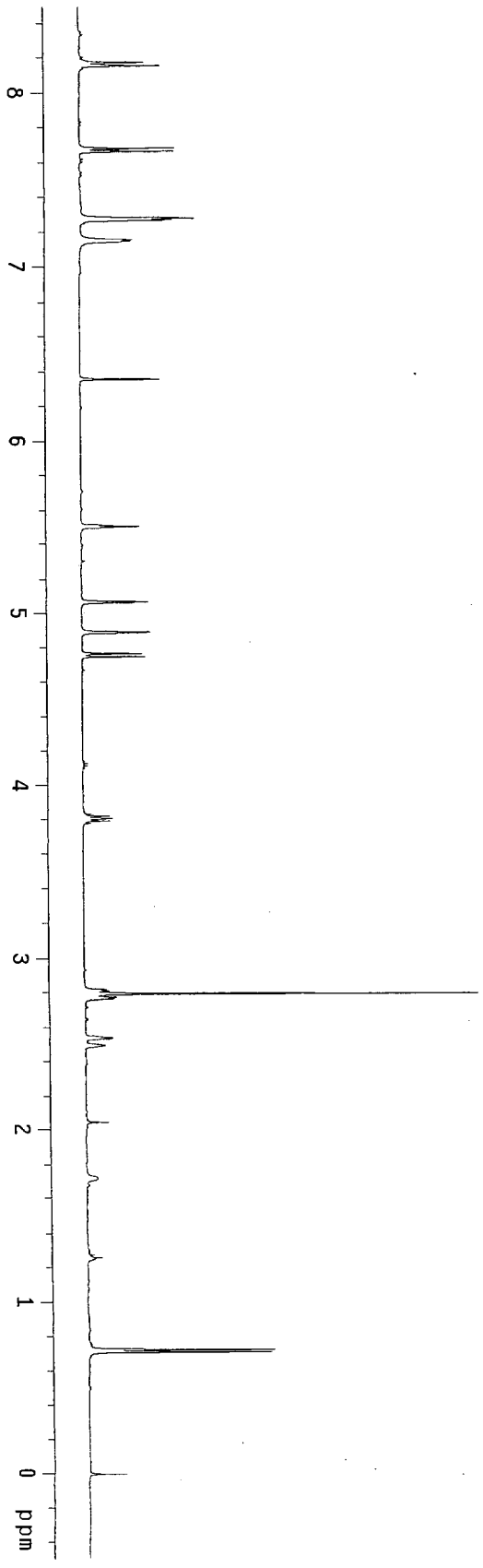

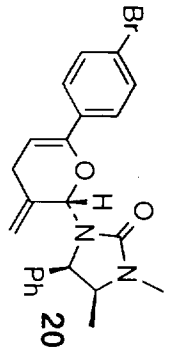

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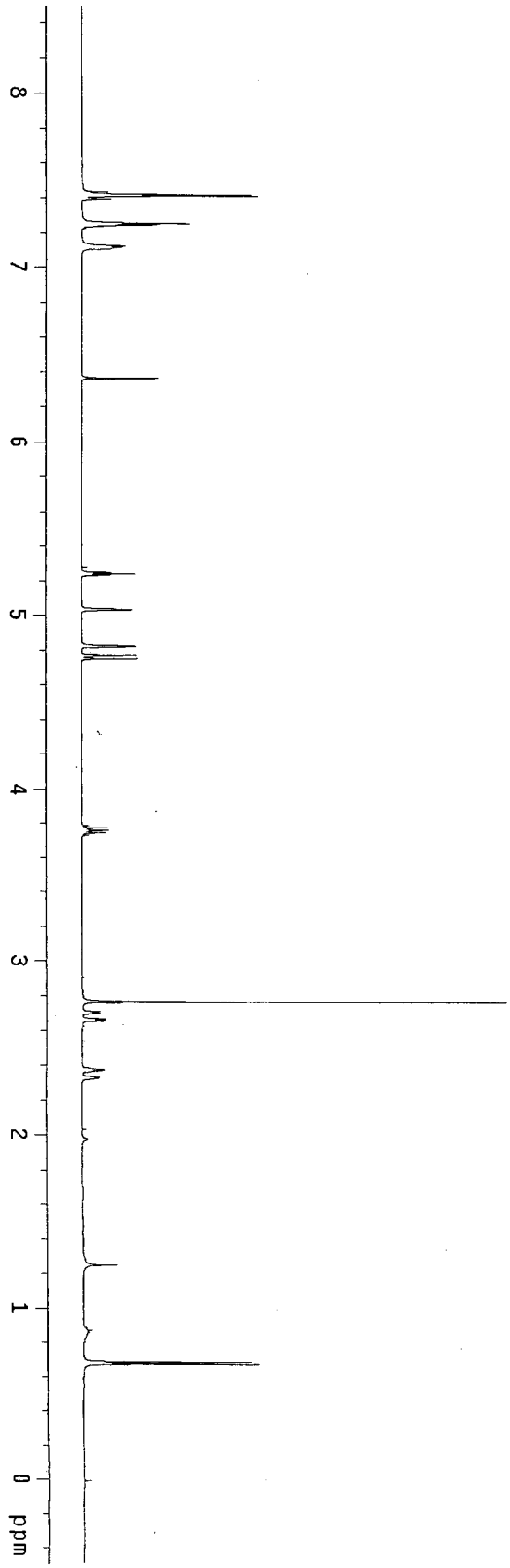

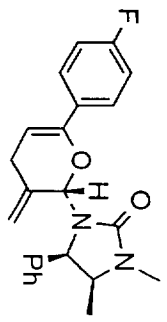

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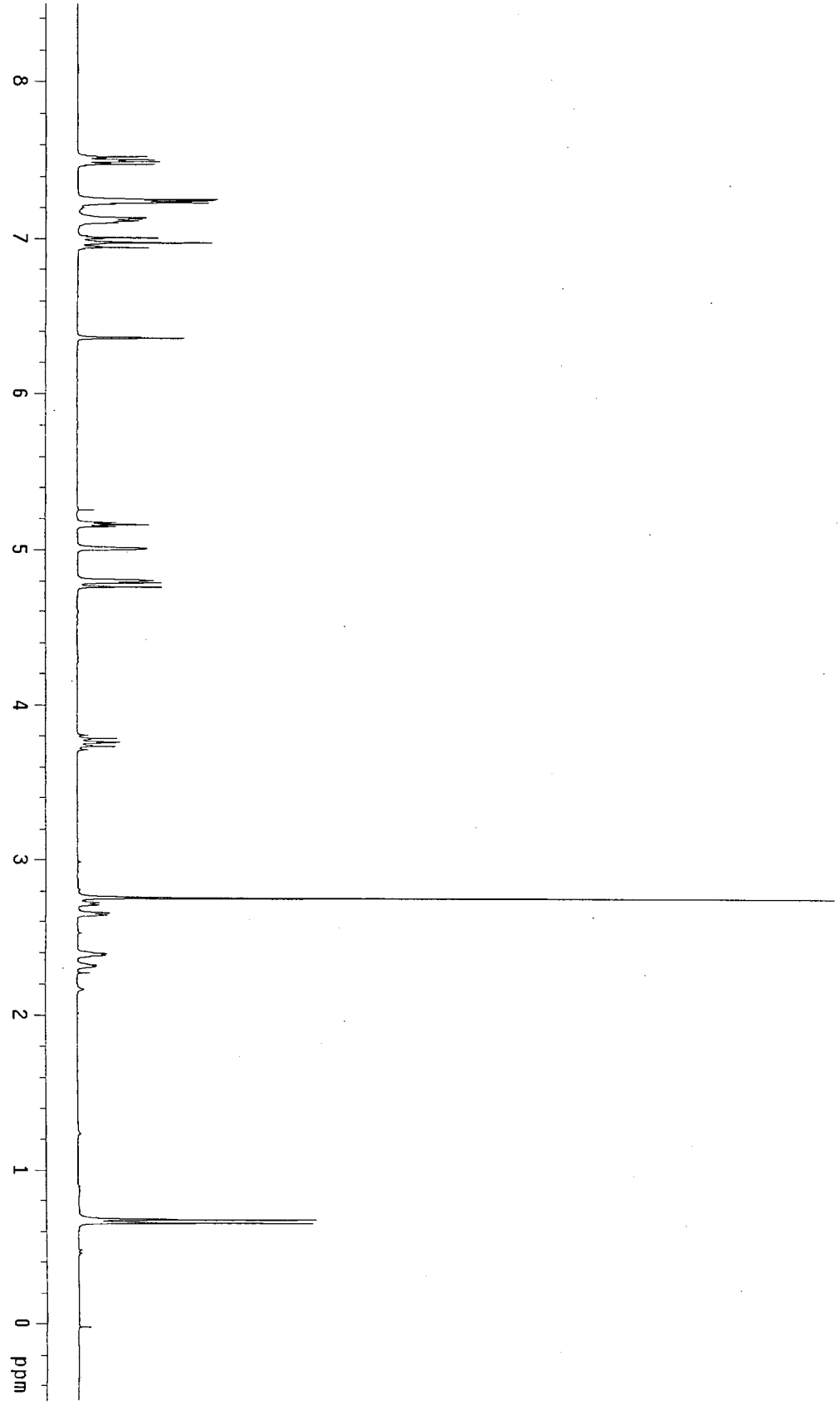

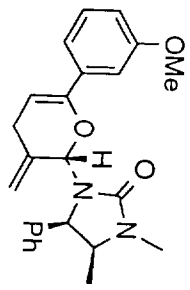

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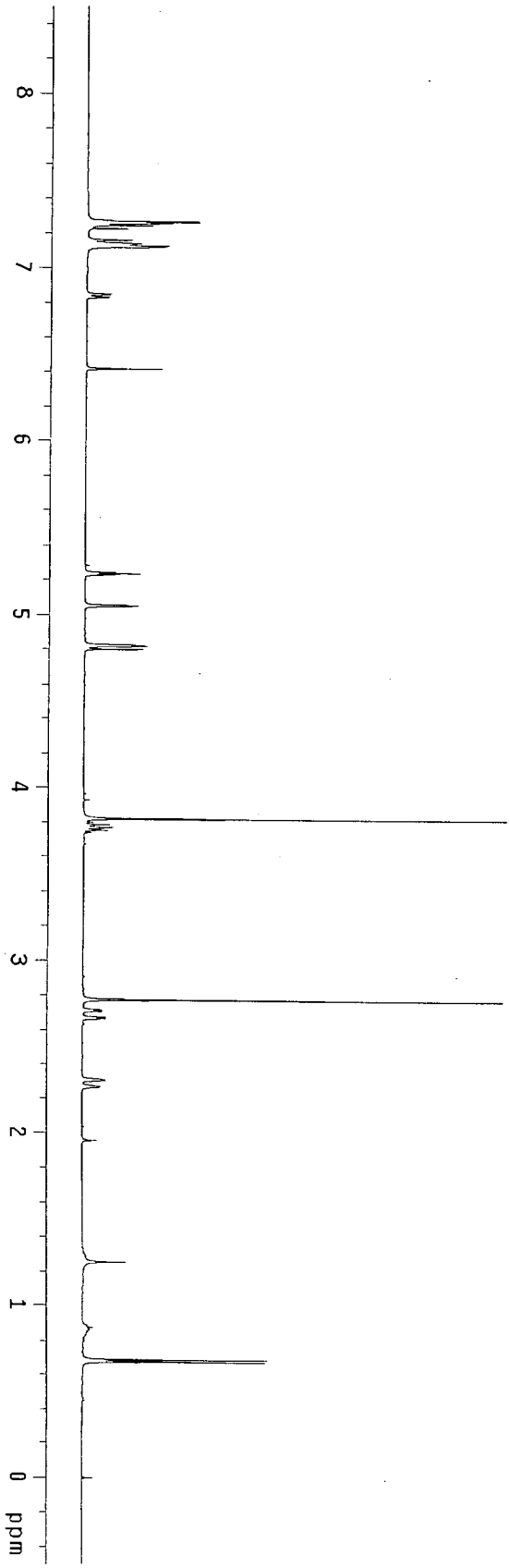

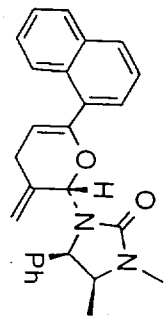

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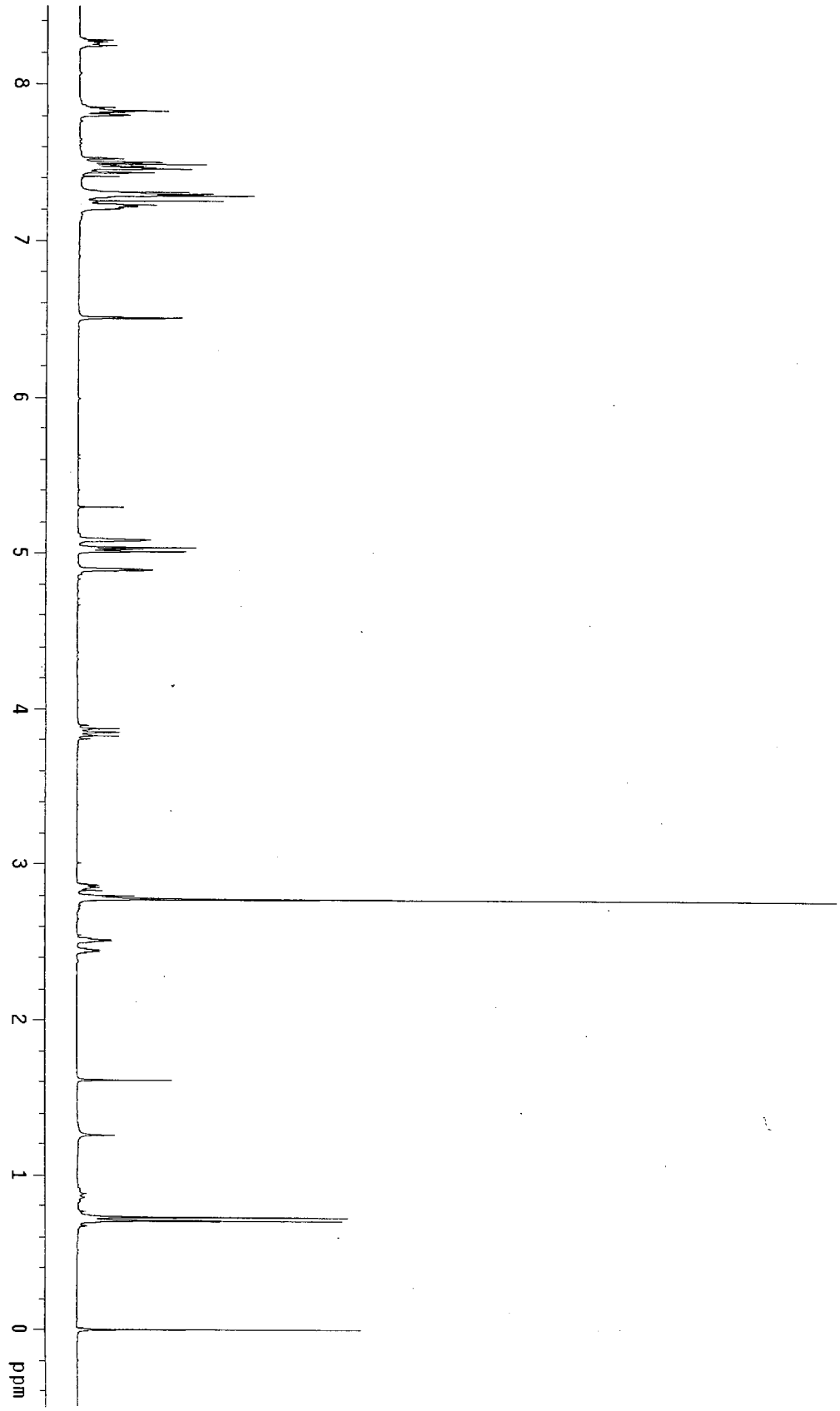

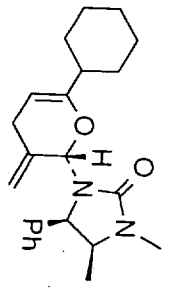

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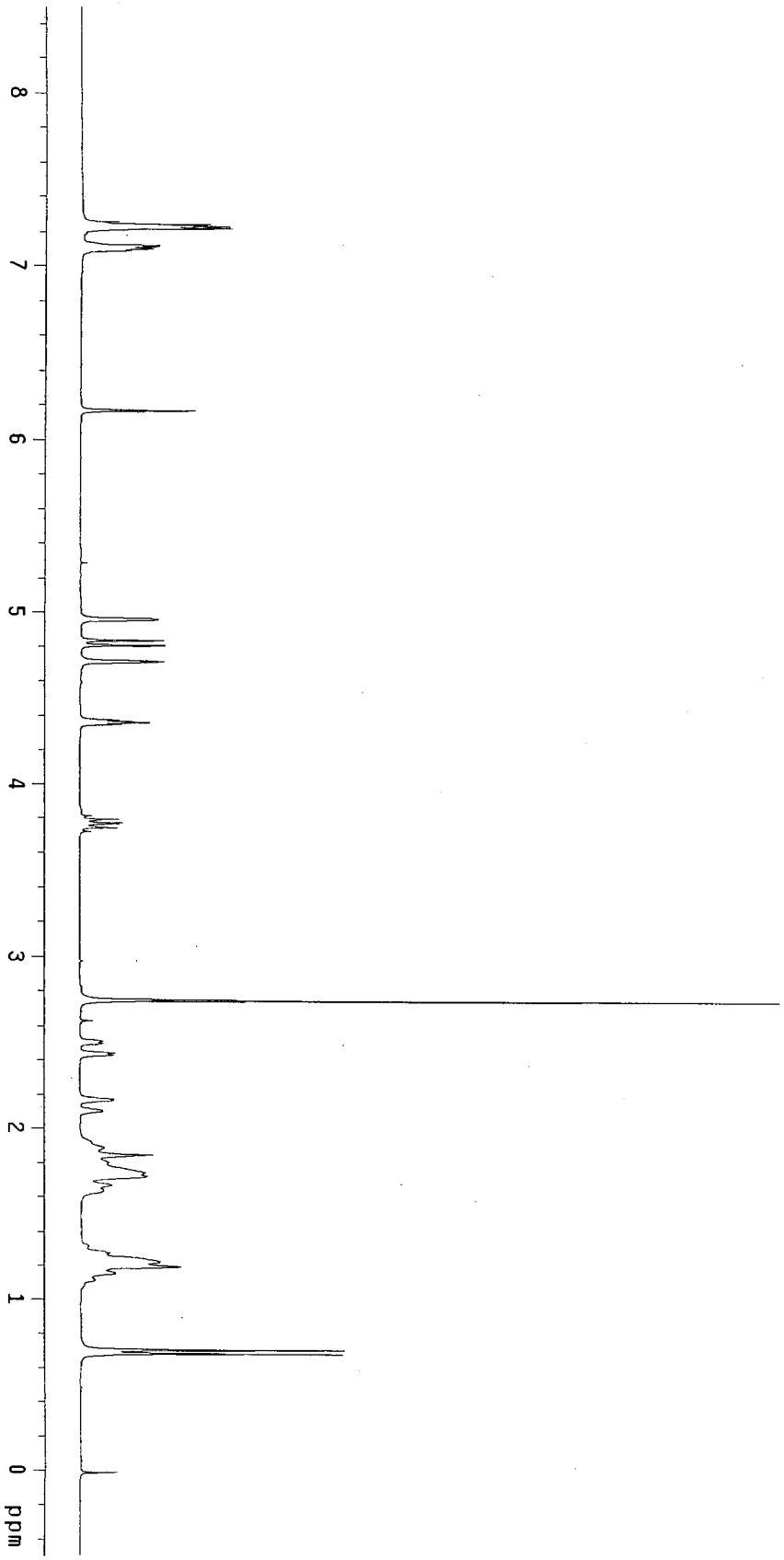

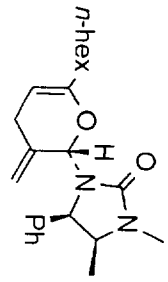

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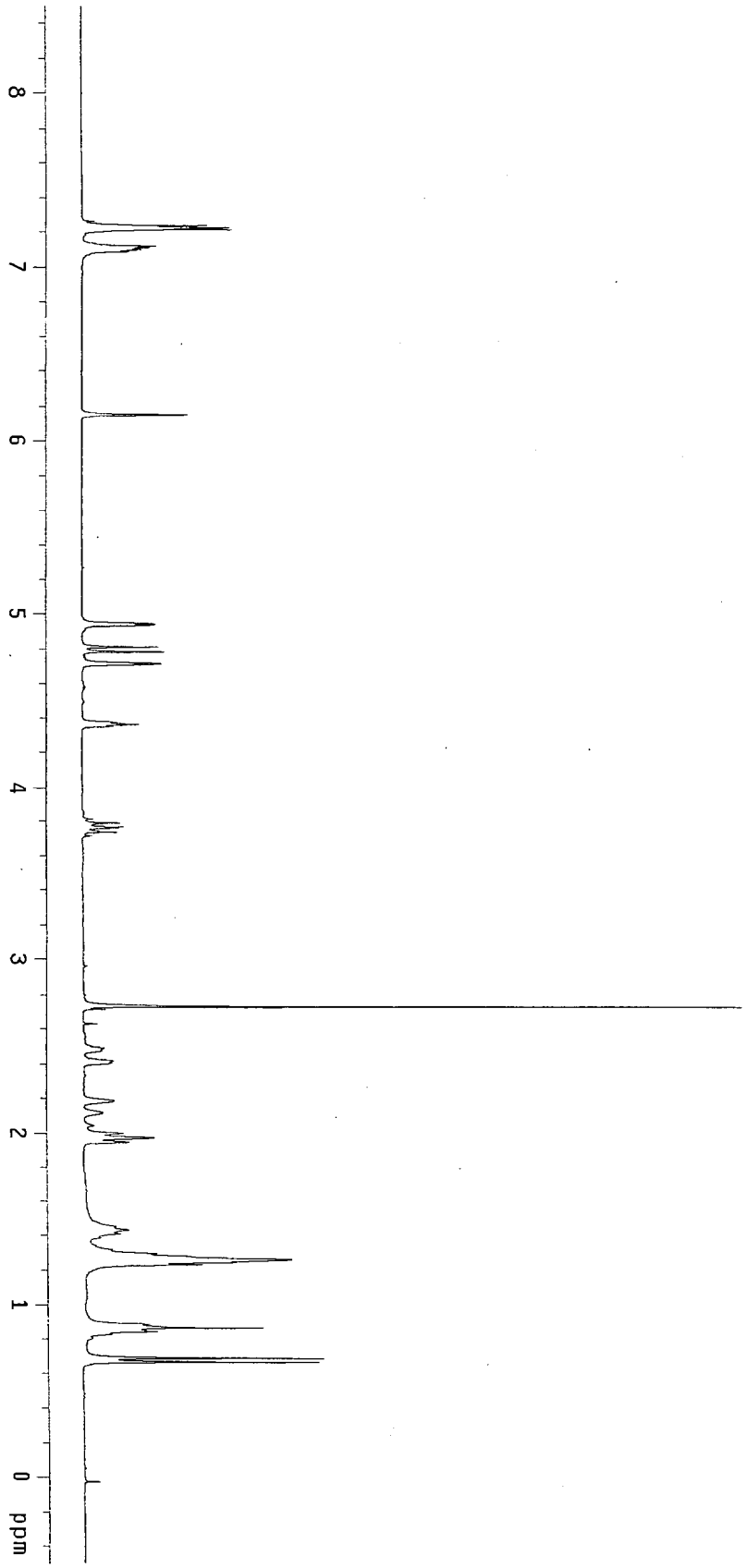

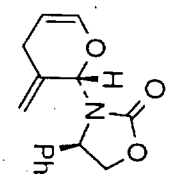

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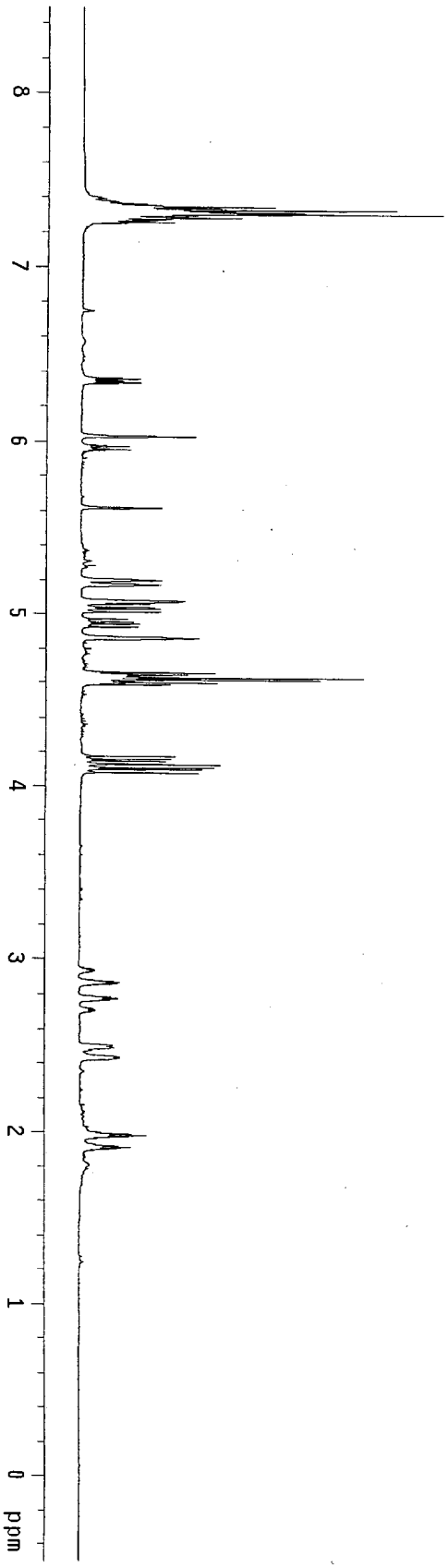

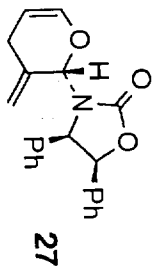

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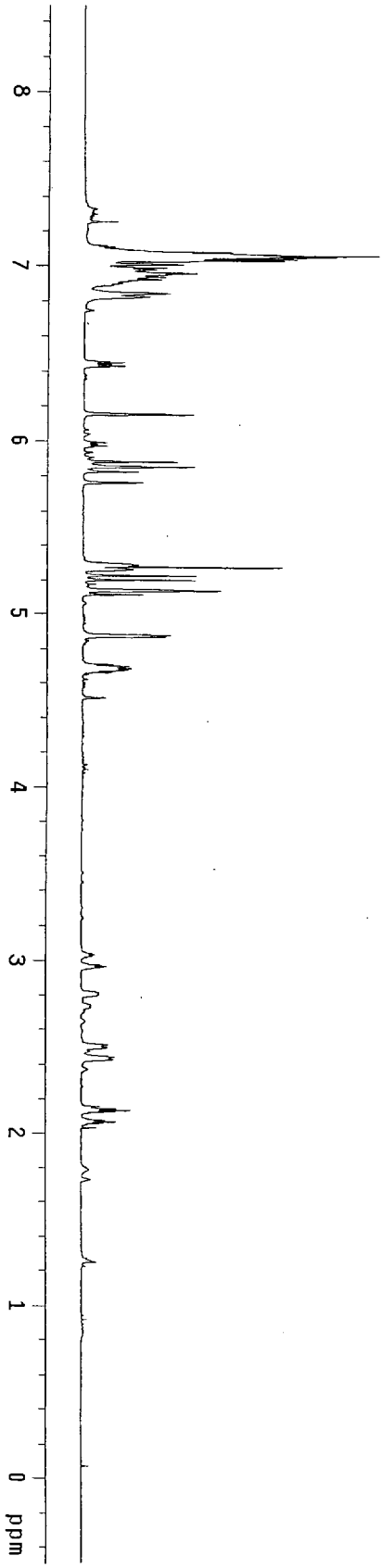

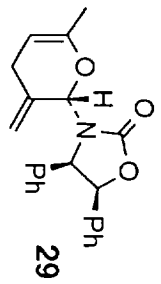

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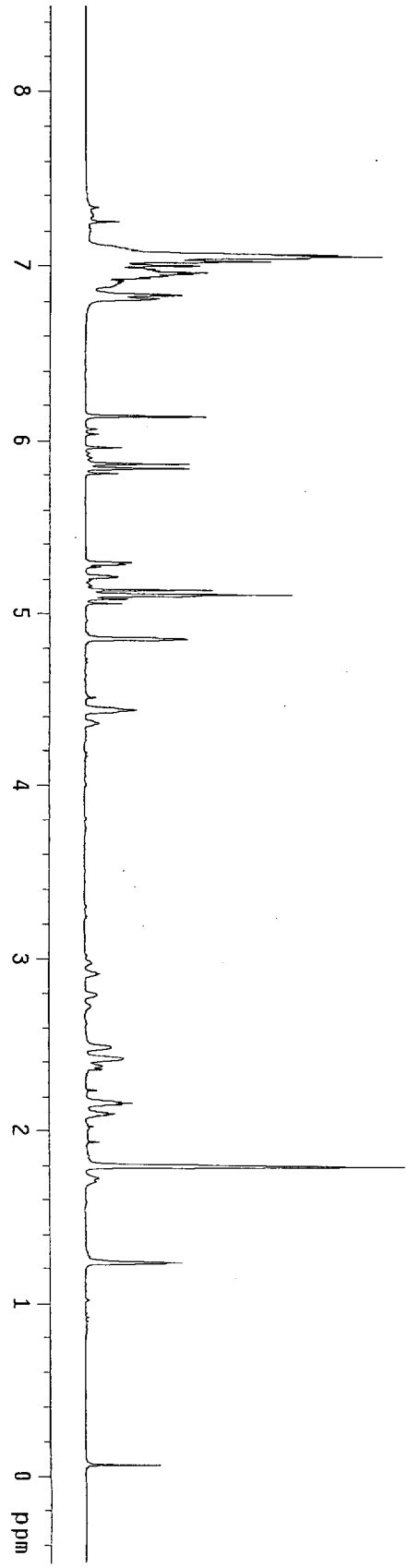

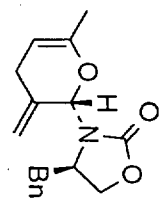

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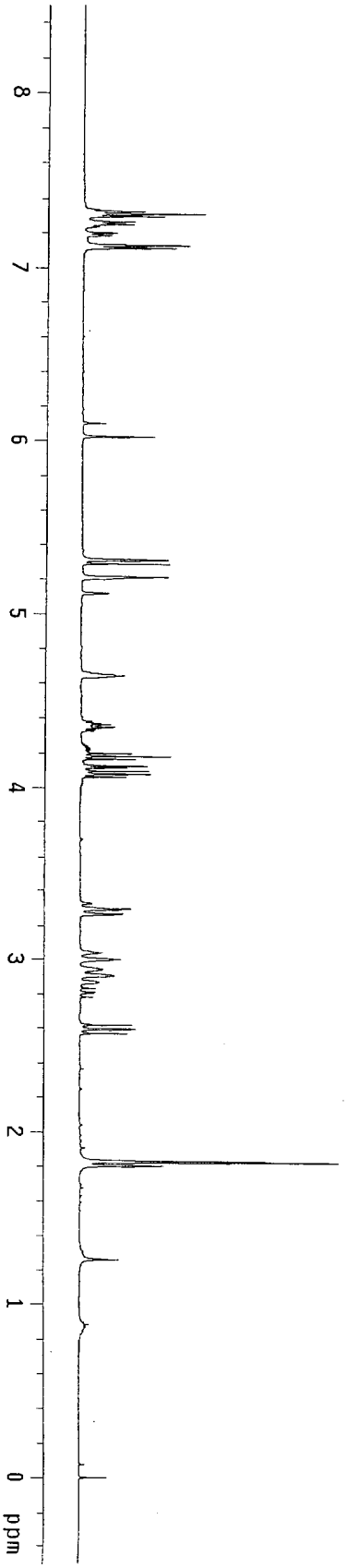

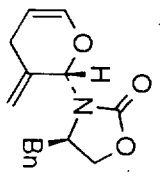

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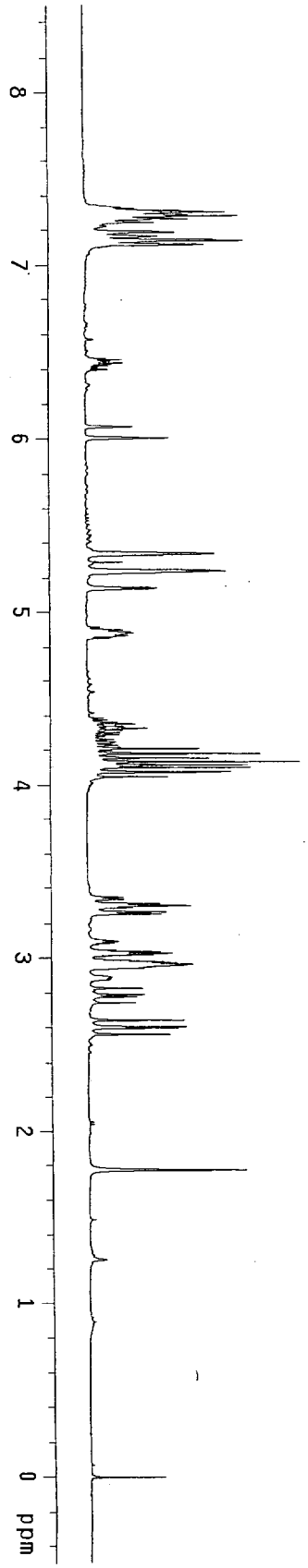

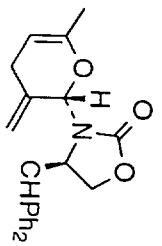

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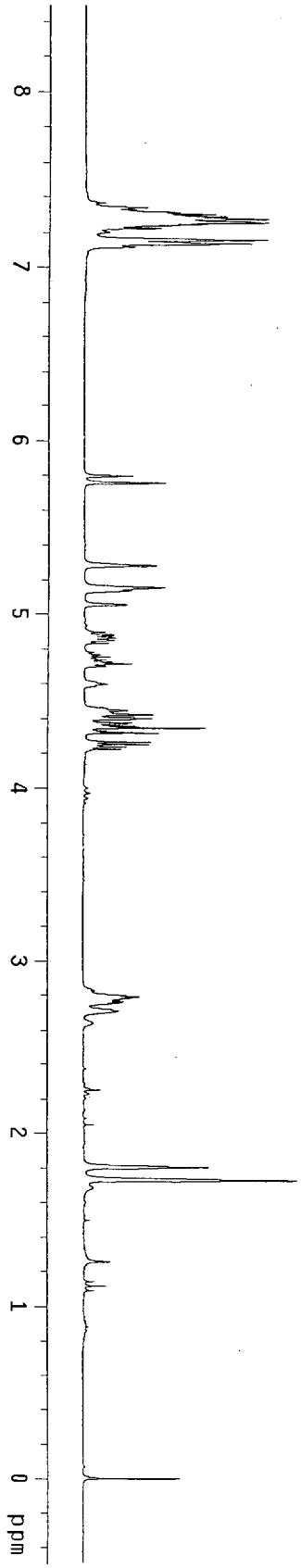

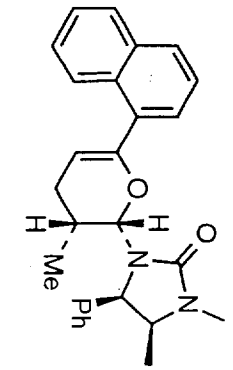

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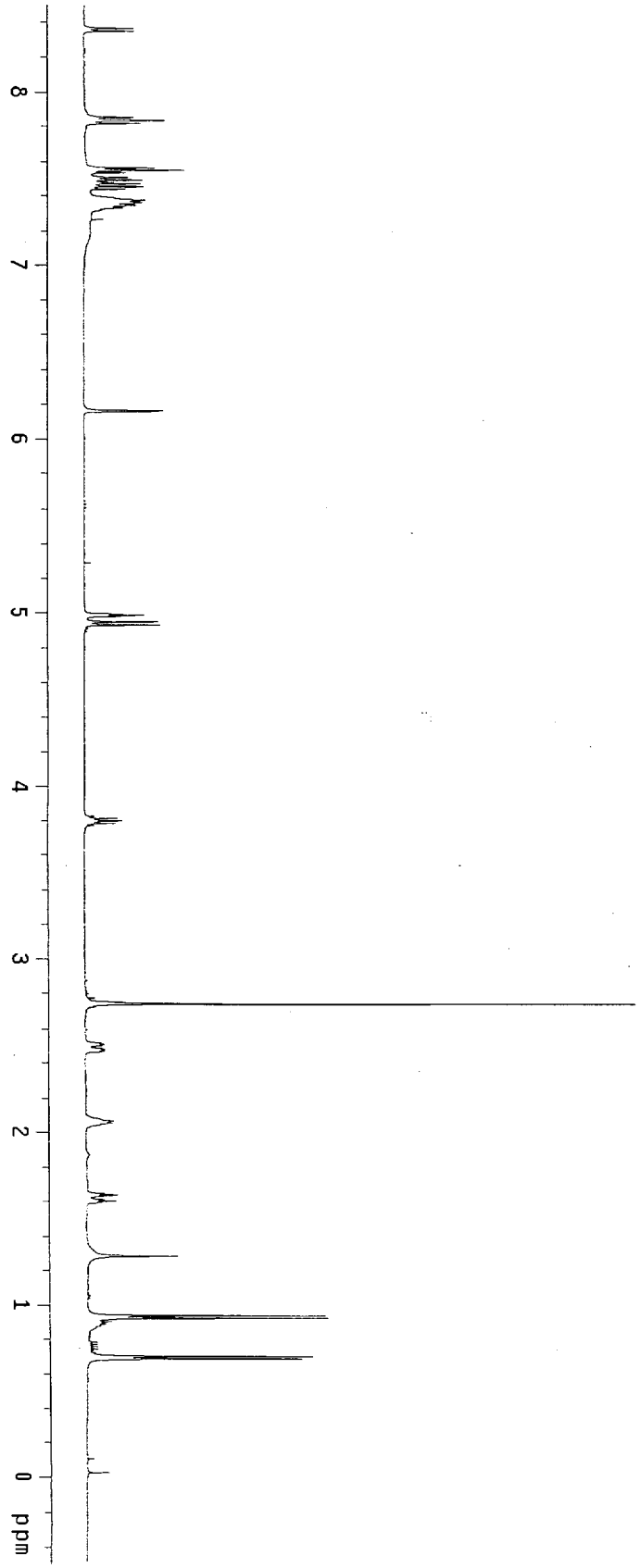

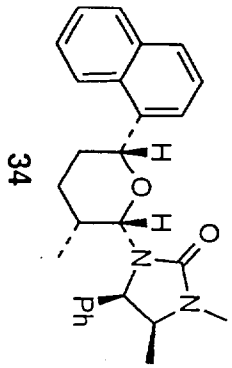
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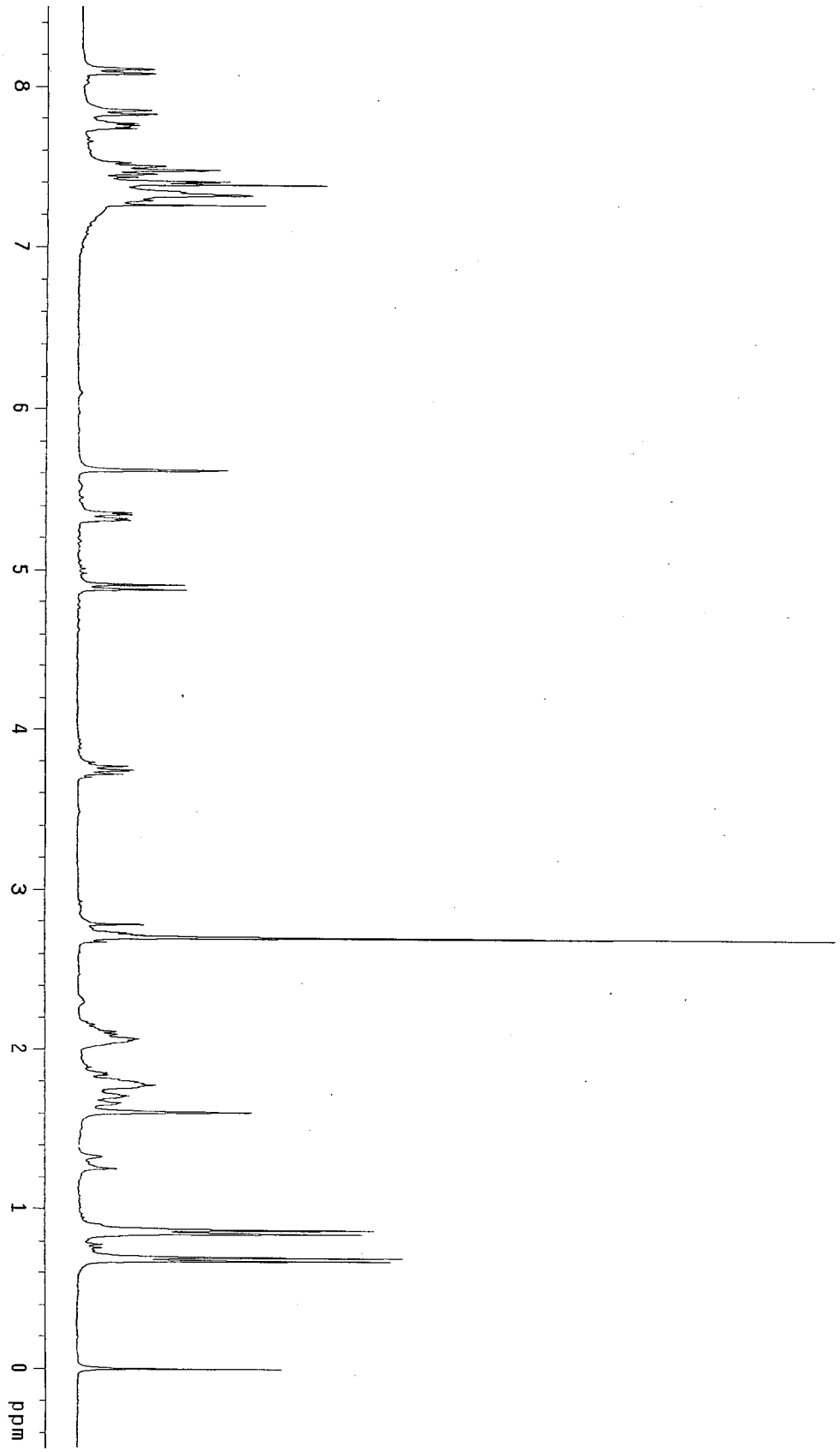
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