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**First Stereoselective [4+2] Cycloaddition Reactions of
3-Cyanochromone Derivatives with
Electron Rich Dienes: An Approach to the ABC Tricyclic Frame of
Arisugacin.**

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The General Procedure for the Thermal [4+2] Cycloaddition Reactions.

A 0.1 *M* solution of the appropriate cyanochromone derivative in toluene containing 2.0 eq of the diene was heated at appropriate temperatures in a sand bath supported by a heating mantle (500-mL size). The temperature was measured at the bottom of the sand bath. The reaction was monitored carefully with TLC (50% ether in hexane). When the reaction was completed or when the starting material was mostly consumed as indicated by the TLC analysis, the mixture was concentrated *in vacuo* to provide a crude material that contained the pure product in most cases. Column chromatography was used to further purify the desired product. The diastereomeric ratio of the product was determined from ¹H NMR of the crude mixture prior to the final purification.

The General Procedure for the Lewis Acid Promoted [4+2] Cycloaddition Reactions.

To a 0.2 *M* solution of the appropriate cyanochromone derivative in CH₂Cl₂ containing 2.0 eq of the diene was added 1.0 eq of TiCl₄ (1.0 *M* in CH₂Cl₂). The reaction mixture was stirred at room temperature and monitored carefully with TLC (50% ether in hexane). When the reaction was completed or when the starting material was mostly consumed as indicated by the TLC analysis, the mixture was concentrated *in vacuo* to provide a crude material that contained the desired product. Column chromatography was needed to purify and isolate the final product. The diastereomeric ratio of the product was determined from ¹H NMR of the crude mixture prior to the final purification.

Characterizations for Compounds 7, 9-15, 18, 19, 21, 22, 24, 26-28.

For Compound 7:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 0.24 (s, 3H), 0.25 (s, 3H), 0.97 (s, 9H), 2.44 (dt, 1H, J = 1.3, 4.2 Hz), 2.80 (m, 1H), 3.08 (s, 3H), 4.36 (d, 1H, J = 5.6 Hz), 4.89 (dt, 1H, J = 1.7, 5.5 Hz), 5.25 (d, 1H, J = 5.4 Hz), 7.00 (dd, 1H, J = 1.5, 8.8 Hz), 7.13 (dt, 1H, J = 1.5, 8.1 Hz), 7.52 (dt, 1H, J = 1.7, 8.1 Hz), 7.99 (dd, 1H, J = 1.7, 7.7 Hz);

exo isomer: δ 0.20 (s, 3H), 0.22 (s, 3H), 0.93 (s, 9H), 2.53 (dt, 1H, J = 1.3, 4.5 Hz), 2.75 (d, 1H, J = 1.7 Hz), 3.34 (s, 3H), 4.44 (d, 1H, J = 1.5 Hz), 5.03 (t, 1H, J = 4.5 Hz), 5.14 (quintet, 1H, J = 1.5 Hz), 7.03 (dd, 1H, J = 1.5, 8.8 Hz), 7.13 (dt, 1H, J = 1.5, 8.0 Hz), 7.59 (dt, 1H, J = 1.7, 8.0 Hz), 7.98 (dd, 1H, J = 1.7, 7.5 Hz);

IR (neat) cm^{-1} 2949s, 2933s, 2863m, 1703s, 1663m, 1607s, 1464s, 1364w, 1295w, 1225m, 1095w, 838m, 783w;

mass spectrum (EI): m/e (%relative intensity) 385 (71) M^+ , 354(46), 328 (54), 314 (46), 236 (54), 194 (54), 180(100), 165 (92), 143 (100), 123 (67), 109 (21);

m/e calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_4\text{Si}$ 385.1710, measd 385.1722.

Compound 7 could be hydrolyzed to the correponding methoxy ketone in good yields using 3*N* HCl in THF (1:1) at room temperature.

For the corresponding methoxy ketone:

^1H NMR (200 MHz, CDCl_3) α -isomer (from the *endo* product): δ 2.78 (d, 1H, J = 9.5 Hz), 2.86 (d, 1H, J = 5.8 Hz), 3.05 (m, 2H), 3.08 (s, 3H), 4.41 (dt, 1H, J = 1.1, 2.1 Hz), 5.15 (dd, 1H, J = 3.8, 4.7 Hz), 7.00 (dd, 1H, J = 1.2, 8.8 Hz), 7.11 (dt, 1H, J = 1.2, 7.4 Hz), 7.53 (dt, 1H, J = 1.8, 7.4 Hz), 7.94 (dd, 1H, J = 1.8, 8.8 Hz);

β -isomer (from the *exo* product): δ 2.86 (d, 1H, J = 9.1 Hz), 2.93 (d, 1H, J = 4.4 Hz), 2.97 (m, 2H), 3.32 (s, 3H), 4.16 (dd, 1H, J = 4.7, 9.6 Hz), 5.09 (t, 1H, J = 4.3 Hz), 7.01 (d, 1H, J = 8.4 Hz), 7.18 (t, 1H, J = 7.7 Hz), 7.61 (dt, 1H, J = 1.6, 7.7 Hz), 8.00 (dd, 1H, J = 1.6, 7.8 Hz);

IR (neat) cm^{-1} 2993w, 2933w, 2877w, 1730s, 1701s, 1607s, 1580m, 1463s, 1327m, 1305s, 1267m, 1225m, 1157w, 1104m, 991w;

mass spectrum (EI): m/e (%relative intensity) 271 (63) M^+ , 185 (14), 172 (26), 120 (100), 100 (47), 92 (100);

m/e calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_4$ 271.0845, measd 271.0845.

For Compound 9:

^1H NMR (200 MHz, CDCl_3) δ 4.12 (s, 3H), 7.12 (s, 1H), 7.47 (dt, 1H, J = 1.3, 8.5 Hz), 7.61 (dd, 1H, J = 1.3, 7.5 Hz), 7.74 (dt, 1H, J = 1.7, 7.5 Hz), 8.22 (dd, 1H, J = 1.7, 7.7 Hz);

IR (neat) cm^{-1} 3074w, 3045w, 3019w, 2959w, 1737s, 1659s, 1624m, 1607m, 1462s, 1393w, 1293m, 1262s, 1239m, 1124m, 1082w, 976w;
mass spectrum (EI): m/e (%relative intensity) 204 (100) M^+ , 176 (24), 145 (45), 120 (12), 89 (63);

For Compound 10:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.40 (m, 2H), 1.80 (m, 1H), 2.08 (m, 1H), 2.97 (m, 1H), 3.60 (m, 1H), 5.20 (d, 1H, $J = 2.5$ Hz), 6.29 (m, 2H), 6.85 (dd, 1H, $J = 1.3, 8.3$ Hz), 6.97 (dt, 1H, $J = 1.3, 7.9$ Hz), 7.45 (dt, 1H, $J = 1.8, 7.9$ Hz), 7.75 (dd, 1H, $J = 1.8, 7.5$ Hz);
exo isomer: δ 1.40 (m, 2H), 1.80 (m, 1H), 2.08 (m, 1H), 3.13 (m, 1H), 3.29 (m, 1H), 4.96 (dd, 1H, $J = 3.3, 9.3$ Hz), 6.25 (m, 2H), 6.78 (dd, 1H, $J = 1.4, 8.2$ Hz), 6.94 (dt, 1H, $J = 1.4, 7.9$ Hz), 7.39 (dt, 1H, $J = 1.8, 7.9$ Hz), 7.70 (dd, 1H, $J = 1.8, 7.6$ Hz);
IR (neat) cm^{-1} 3011w, 2933s, 2863s, 1676m, 1646w, 1633w, 1603s, 1581w, 1464s, 1325m, 1308s, 1264w, 1221m, 1147w, 1121w;
mass spectrum (EI): m/e (%relative intensity) 306 (23) M^++2 , 304 (20) M^+ , 196 (47), 168 (16), 147 (100), 121 (20);
m/e calcd for $\text{C}_{15}\text{H}_{13}^{79}\text{BrO}_2$ 304.0099, measd 304.0097; calcd for $\text{C}_{15}\text{H}_{13}^{81}\text{BrO}_2$ 306.0080, measd 306.0064.

For Compound 11:

^1H NMR (200 MHz, CDCl_3) isomer 1: δ 0.20 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 2.28 (s, 2H), 2.70 (d, 1H, $J = 2.7$ Hz), 3.06 (s, 3H), 3.62 (s, 3H), 4.17 (d, 1H, $J = 5.3$ Hz), 5.28 (dd, 1H, $J = 2.7, 5.3$ Hz), 7.04 (m, 2H), 7.46 (m, 1H), 7.83 (m, 1H);
isomer 2: δ 0.17 (s, 3H), 0.18 (s, 3H), 0.90 (s, 9H), 2.08-2.38 (m, 2H), 2.60 (t, 1H, $J = 0.9$ Hz), 3.33 (s, 3H), 3.66 (s, 3H), 4.26 (d, 1H, $J = 4.8$ Hz), 5.09 (d, 1H, $J = 4.8$ Hz), shared the same aromatic region as the isomer 1;
isomer 3: δ 0.26 (s, 3H), 0.27 (s, 3H), 0.99 (s, 9H), 2.23 (s, 2H), 2.51 (d, 1H, $J = 1.2$ Hz), 3.28 (s, 3H), 3.73 (s, 3H), 4.24 (d, 1H, $J = 6.5$ Hz), 5.13 (dd, $J = 1.2, 6.5$ Hz), shared the same aromatic region as the isomer 1;
isomer 4: δ 0.11 (s, 3H), 0.13 (s, 3H), 0.88 (s, 9H), 2.08-2.38 (m, 2H), 2.80 (dd, 1H, $J = 9.5, 10.9$ Hz), 3.26 (s, 3H), 3.71 (s, 3H), 4.45 (d, 1H, $J = 2.3$ Hz), 4.95 (d, 1H, $J = 2.3$ Hz), shared the same aromatic region as the isomer 1;
IR (neat) cm^{-1} 2949s, 2933s, 2889w, 2854m, 2360w, 1746s, 1698s, 1667s, 1607s, 1464s, 1373m, 1303m, 1256s, 1212s, 1086s, 904m, 839s, 783m;
mass spectrum (EI): m/e (%relative intensity) 418 (14) M^+ , 387 (46), 359 (39), 297 (16), 283 (16), 239 (32), 214 (32), 195 (25), 157 (25), 143 (100), 121 (14);
m/e calcd for $\text{C}_{20}\text{H}_{30}\text{O}_6\text{Si}$ 418.1812, measd 418.1813.

For Compound 12:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 2.81 (m, 2H), 3.15 (s, 3H), 4.18 (dd, 1H, J = 1.3, 3.8 Hz), 4.86 (dt, 1H, J = 0.4, 3.3 Hz), 6.09 (m, 2H), 7.00 (dd, 1H, J = 1.3, 9.1 Hz), 7.09 (dt, 1H, J = 1.3, 8.0 Hz), 7.53 (dt, 1H, J = 1.6, 8.0 Hz), 8.00 (dd, 1H, J = 1.6, 7.8 Hz);
exo isomer: δ 2.52 (m, 1H), 2.61 (m, 1H), 3.41 (s, 3H), 4.32 (t, 1H, J = 2.2 Hz), 4.97 (t, 1H, J = 4.1 Hz), 5.91 (m, 1H), 5.99 (m, 1H), 7.05 (dd, 1H, J = 1.4, 8.9 Hz), 7.11 (dt, 1H, J = 1.4, 8.0 Hz), 7.59 (dt, 1H, J = 1.5, 8.0 Hz), 8.02 (dd, 1H, J = 1.5, 7.8 Hz);
IR (neat) cm^{-1} 3037w, 2933m, 2828w, 2238w, 1694s, 1663m, 1607s, 1464s, 1342m, 1308s, 1234m, 1138m, 1091s, 1052w, 930m, 756w;
mass spectrum (EI): m/e (%relative intensity) 255 (30) M^+ , 172 (41), 143 (12), 120 (22), 84 (100);
m/e calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3$ 255.0895, measd 255.0883.

For Compound 13:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.38-1.85 (m, 4H), 2.97 (quintet, 1H, J = 2.7 Hz), 3.18 (s, 3H), 3.52 (dt, 1H, J = 3.7, 7.3 Hz), 4.64 (dd, 1H, J = 2.2, 7.3 Hz), 5.07 (d, 1H, J = 2.7 Hz), 6.88 (dd, 1H, J = 1.4, 8.3 Hz), 6.96 (dt, 1H, J = 1.4, 7.2 Hz), 7.47 (dt, 1H, J = 1.7, 7.2 Hz), 7.70 (dd, 1H, J = 1.7, 7.9 Hz);
exo isomer: δ 1.38-1.85 (m, 4H), 3.01 (m, 1H), 3.52 (m, 1H), 3.63 (s, 3H), 4.93 (dd, 1H, J = 1.1, 3.3 Hz), 5.19 (dd, 1H, J = 1.9, 7.1 Hz), 6.88 (d, 1H, J = 8.3 Hz), 7.05 (t, 1H, J = 7.2 Hz), 7.53 (dt, 1H, J = 1.9, 7.2 Hz), 7.87 (dd, 1H, J = 1.9, 8.0 Hz);
IR (neat) cm^{-1} 2967w, 2932w, 2906w, 1672s, 1650m, 1637s, 1603m, 1464s, 1386w, 1329m, 1299m, 1216m, 1147w, 1130w, 1025w;
mass spectrum (EI): m/e (%relative intensity) 281 (59) M^+ , 220 (21), 172 (30), 149 (34), 133 (60), 110 (100), 92 (19);
m/e calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$ 281.1052, measd 281.1059.

For Compound 14:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.40 (m, 1H), 1.45 (m, 1H), 1.80 (m, 1H), 2.20 (m, 1H), 3.12 (m, 1H), 3.52 (m, 1H), 5.09 (d, 1H, J = 2.5 Hz), 6.16 (dt, 1H, J = 1.5, 6.4 Hz), 6.26 (dt, 1H, J = 1.2, 6.6 Hz), 6.83 (dd, 1H, J = 2.5, 8.6 Hz), 6.98 (dt, 1H, J = 2.5, 7.7 Hz), 7.47 (dt, 1H, J = 1.8, 7.7 Hz), 7.72 (dd, 1H, J = 1.8, 8.1 Hz);
exo isomer: δ selected proton resonances: 4.80 (dd, 1H, J = 1.2, 2.6 Hz), 6.49 (dt, 1H, J = 1.4, 6.2 Hz), 6.58 (dt, 1H, J = 1.3, 6.6 Hz), 6.85 (dd, 1H, J = 2.4, 8.5 Hz), 7.05 (dt, 1H, J = 2.4, 7.7 Hz), 7.55 (dt, 1H, J = 1.8, 7.7 Hz), 7.85 (dd, 1H, J = 1.8, 8.2 Hz);
IR (neat) cm^{-1} 3019w, 2933m, 2880w, 1689s, 1620m, 1603m, 1464s, 1416w, 1331w, 1300m, 1271w, 1238m, 1150w, 1092m, 1047w;
mass spectrum (EI): m/e (%relative intensity) 251 (18) M^+ , 172 (49), 120 (62), 96 (16), 86 (100);
m/e calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_2$ 251.0946, measd 251.0946.

For Compound **15**:

^1H NMR (200 MHz, CDCl_3) δ 1.73 (s, 3H), 1.77 (s, 3H), 2.28-2.85 (m, 4H), 4.84 (dd, 1H, J = 1.7, 4.5 Hz), 7.02 (dd, 1H, J = 1.5, 8.3 Hz), 7.12 (dt, 1H, J = 1.5, 8.1 Hz), 7.58 (dt, 1H, J = 1.6, 8.1 Hz), 7.94 (dd, 1H, J = 1.6, 7.8 Hz);
IR (neat) cm^{-1} 2958w, 2915m, 2863w, 1698s, 1607s, 1577m, 1473s, 1434w, 1355w, 1325m, 1308s, 1264w, 1221m, 1151m, 1117w, 1056m, 930s;
mass spectrum (EI): m/e (%relative intensity) 253 (36) M^+ , 172 (20), 133 (11), 121 (100), 97 (18), 86 (100);
m/e calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ 253.1103, measd 253.1107.

For Compound **18**:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 2.82 (m, 2H), 3.19 (s, 3H), 4.19 (dd, 1H, J = 1.7, 4.0 Hz), 4.85 (t, 1H, J = 3.0 Hz), 6.13 (m, 2H), 6.92 (d, 1H, J = 8.8 Hz), 7.60 (dd, 1H, J = 2.2, 8.8 Hz), 8.09 (d, 1H, J = 2.2 Hz);
exo isomer: δ 2.10 (m, 1H), 2.87 (m, 1H), 3.43 (s, 3H), 4.29 (m, 1H), 4.98 (t, 1H, J = 3.9 Hz), 5.89 (m, 1H), 6.00 (m, 1H), 6.95 (d, 1H, J = 8.8 Hz), 7.67 (dd, 1H, J = 2.5, 8.8 Hz), 8.09 (d, 1H, J = 2.5 Hz);
IR (neat) cm^{-1} 3063w, 3037w, 2993w, 2933m, 2828w, 1698s, 1672m, 1598s, 1468s, 1412s, 1342w, 1308m, 1273s, 1229m, 1203w, 1143m, 1091s, 934m;
mass spectrum (EI): m/e (%relative intensity) 335 (25) $\text{M}^{++}2$, 333 (25) M^+ , 200 (30), 198 (29), 172 (25), 170 (25), 134 (18), 84 (100);
m/e calcd for $\text{C}_{15}\text{H}_{12}{^{79}\text{Br}}\text{NO}_3$ 333.0001, measd 333.0014; calcd for $\text{C}_{15}\text{H}_{12}{^{81}\text{Br}}\text{NO}_3$ 334.9982, measd 334.9998.

For Compound **19**:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.40 (m, 2H), 1.78 (m, 1H), 2.16 (m, 1H), 3.13 (m, 1H), 3.53 (m, 1H), 5.09 (d, 1H, J = 2.7 Hz), 6.16 (dt, 1H, J = 1.2, 5.0 Hz), 6.27 (dt, 1H, J = 2.1, 6.6 Hz), 6.75 (d, 1H, J = 8.7 Hz), 7.53 (dd, 1H, J = 2.5, 8.7 Hz), 7.82 (d, 1H, J = 2.5 Hz);
exo isomer: δ 1.40 (m, 2H), 1.78 (m, 1H), 2.16 (m, 1H), 3.13 (m, 1H), 3.53 (m, 1H), 4.80 (dd, 1H, J = 1.1, 2.7 Hz), 6.51 (dt, 1H, J = 1.4, 5.5 Hz), 6.59 (dt, 1H, J = 2.0, 6.3 Hz), 6.89 (d, 1H, J = 8.7 Hz), 7.62 (dd, 1H, J = 2.3, 8.7 Hz), 7.98 (d, 1H, J = 2.3 Hz);
IR (neat) cm^{-1} 2950m, 2880w, 1689s, 1676s, 1598s, 1577w, 1468s, 1416s, 1377w, 1321w, 1277s, 1229m, 1199m, 1138s, 1034w, 817w;
mass spectrum (EI): m/e (%relative intensity) 331 (14) $\text{M}^{++}2$, 329 (14) M^+ , 252 (9), 250 (9), 198 (15), 196 (15), 80 (100);
m/e calcd for $\text{C}_{16}\text{H}_{12}{^{79}\text{Br}}\text{NO}_2$ 329.0052, measd 329.0056; calcd for $\text{C}_{16}\text{H}_{12}{^{81}\text{Br}}\text{NO}_2$ 331.0033, measd 331.0011.

For Compound **21**:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 2.81 (m, 2H), 3.17 (s, 3H), 4.18 (dd, 1H, J = 1.1, 3.7 Hz), 4.84 (t, 1H, J = 2.9 Hz), 6.11 (m, 2H), 6.97 (d, 1H, J = 8.8 Hz), 7.43 (dd, 1H, J = 2.6, 8.8 Hz), 7.93 (d, 1H, J = 2.6 Hz);

exo isomer: δ 2.55 (m, 1H), 2.87 (m, 1H), 3.41 (s, 3H), 4.27 (t, 1H, J = 2.1 Hz), 4.97 (t, 1H, J = 3.4 Hz), 5.87 (m, 1H), 5.99 (m, 1H), 6.99 (d, 1H, J = 8.8 Hz), 7.50 (dd, 1H, J = 2.4, 8.8 Hz), 7.93 (d, 1H, J = 2.4 Hz);

IR (neat) cm^{-1} 3080w, 3045w, 2993w, 2933m, 2828w, 1694s, 1603s, 1568m, 1468s, 1451m, 1420s, 1347m, 1273s, 1229m, 1203m, 1095s, 1043m, 939m, 826m;

mass spectrum (EI): m/e (%relative intensity) 289 (17) M^+ , 154 (26), 126 (21), 84 (100);
m/e calcd for $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$ 289.0506, measd 289.0509.

For Compound **22**:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.40 (m, 2H), 1.74 (m, 1H), 2.16 (m, 1H), 3.12 (m, 1H), 3.50 (m, 1H), 5.09 (d, 1H, J = 2.3 Hz), 6.15 (dt, 1H, J = 1.4, 6.6 Hz), 6.29 (t, 1H, J = 7.1 Hz), 6.80 (d, 1H, J = 8.9 Hz), 7.41 (dd, 1H, J = 2.7, 8.9 Hz), 7.67 (d, 1H, J = 2.7 Hz);

exo isomer: δ selected proton resonances: 4.79 (dd, 1H, J = 1.3, 2.5 Hz), 6.50 (dt, 1H, J = 1.4, 6.4 Hz), 6.57 (dt, 1H, J = 1.3, 6.7 Hz), 6.95 (d, 1H, J = 8.5 Hz), 7.50 (dd, 1H, J = 2.5, 8.5 Hz), 7.81 (d, 1H, J = 2.5 Hz);

IR (neat) cm^{-1} 3055w, 2944m, 2876w, 1660s, 1606s, 1579w, 1475s, 1423s, 1275s, 1237w, 1202m, 1140m, 1036w, 821m;

mass spectrum (EI): m/e (%relative intensity) 285 (32) M^+ , 206 (21), 154 (27), 126 (24), 80 (100);
m/e calcd for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2$ 285.0557, measd 285.0555.

For Compound **24**:

^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 2.34 (s, 3H), 2.80 (m, 2H), 3.16 (s, 3H), 4.18 (dd, 1H, J = 0.8, 3.8 Hz), 4.81 (t, 1H, J = 4.1 Hz), 6.12 (m, 2H), 6.90 (d, 1H, J = 8.2 Hz), 7.31 (dd, 1H, J = 1.7, 8.2 Hz), 7.76 (d, 1H, J = 1.7 Hz);

exo isomer: δ 2.34 (s, 3H), 2.54 (m, 1H), 2.83 (m, 1H), 3.40 (s, 3H), 4.30 (t, 1H, J = 2.0 Hz), 4.92 (t, 1H, J = 3.3 Hz), 5.86 (m, 1H), 5.97 (m, 1H), 6.92 (d, 1H, J = 8.6 Hz), 7.37 (dd, 1H, J = 1.7, 8.6 Hz), 7.76 (d, 1H, J = 1.7 Hz);

IR (neat) cm^{-1} 3040w, 2930m, 2829w, 1702s, 1618s, 1581m, 1488s, 1460m, 1418s, 1344m, 1289s, 1225s, 1139m, 1092s, 1051s, 945m, 921m, 826m;

mass spectrum (EI): m/e (%relative intensity) 269 (19) M^+ , 234 (6), 186 (9), 135 (36), 109 (11), 84 (100);

m/e calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$ 269.1052, measd 269.1054.

For Compound 26:

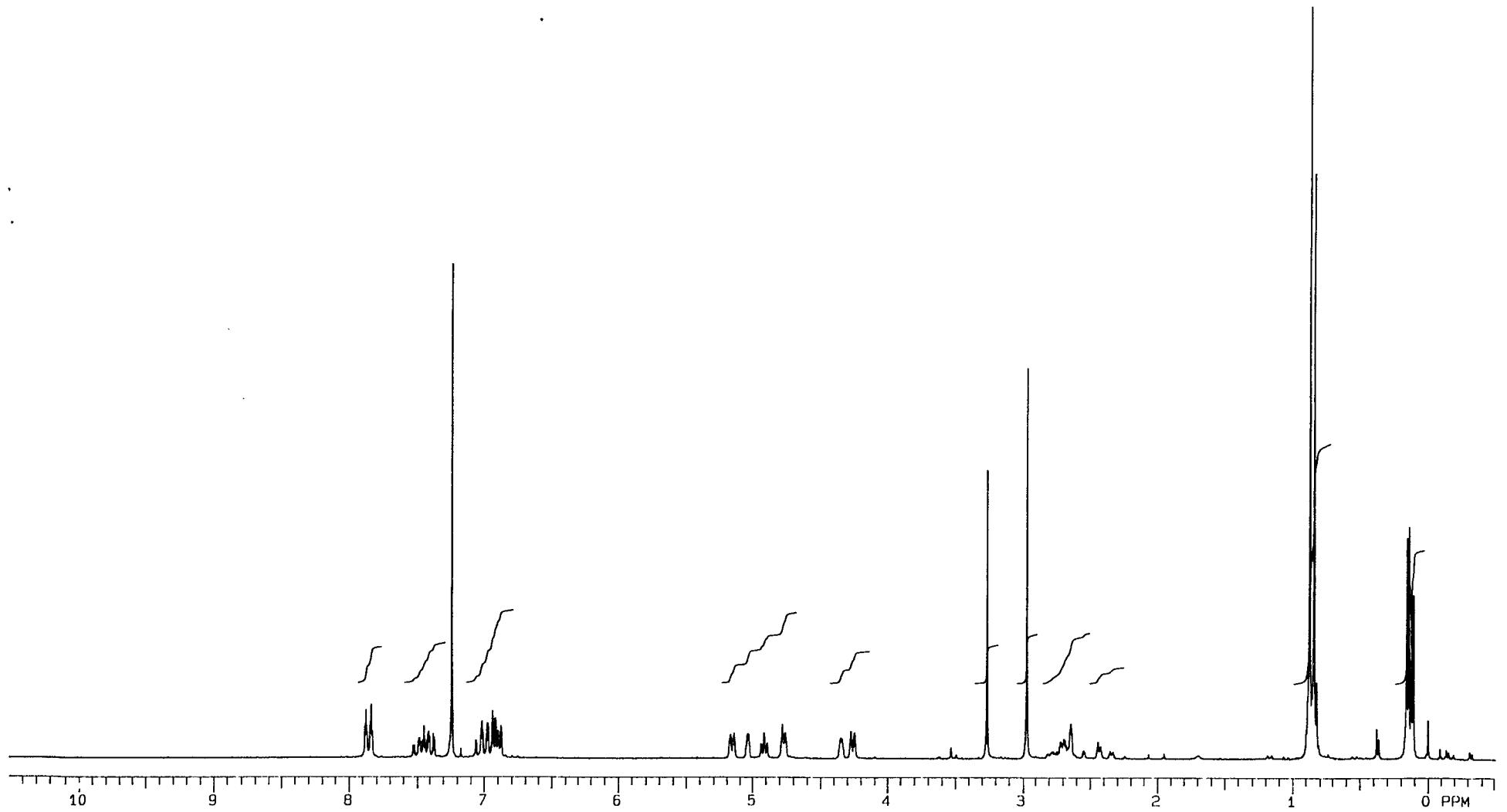
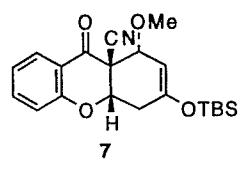
^1H NMR (200 MHz, CDCl_3) *endo* isomer: δ 1.10 (s, 3H), 1.12 (s, 3H), 1.58 (s, 3H), 1.40-1.80 (m, 6H), 2.35 (ddd, 1H, J = 3.9, 9.7, 18.3 Hz), 2.72 (ddd, 1H, J = 3.9, 8.4, 18.3 Hz), 5.25 (t, 1H, J = 3.9 Hz), 5.31 (dd, 1H, J = 8.4, 9.7 Hz), 6.90 (d, 1H, J = 9.0 Hz), 7.59 (dd, 1H, J = 2.4, 9.0 Hz), 7.88 (d, 1H, J = 2.4 Hz);

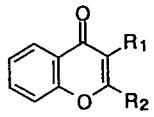
exo isomer: δ 1.15 (s, 3H), 1.18 (s, 3H), 1.27 (s, 3H), 1.40-1.80 (m, 6H), 2.61 (ddd, 1H, J = 1.1, 4.1, 20.2 Hz), 3.10 (ddd, 1H, J = 1.1, 6.5, 20.2 Hz), 4.91 (dd, 1H, J = 1.3, 6.5 Hz), 5.69 (dt, 1H, J = 1.0, 4.0 Hz), 6.92 (d, 1H, J = 8.6 Hz), 7.62 (dd, 1H, J = 2.4, 8.6 Hz), 8.08 (d, 1H, J = 2.4 Hz);

IR (neat) cm^{-1} 2993w, 2926m, 1709s, 1668s, 1634s, 1599s, 1467s, 1411m, 1267s;

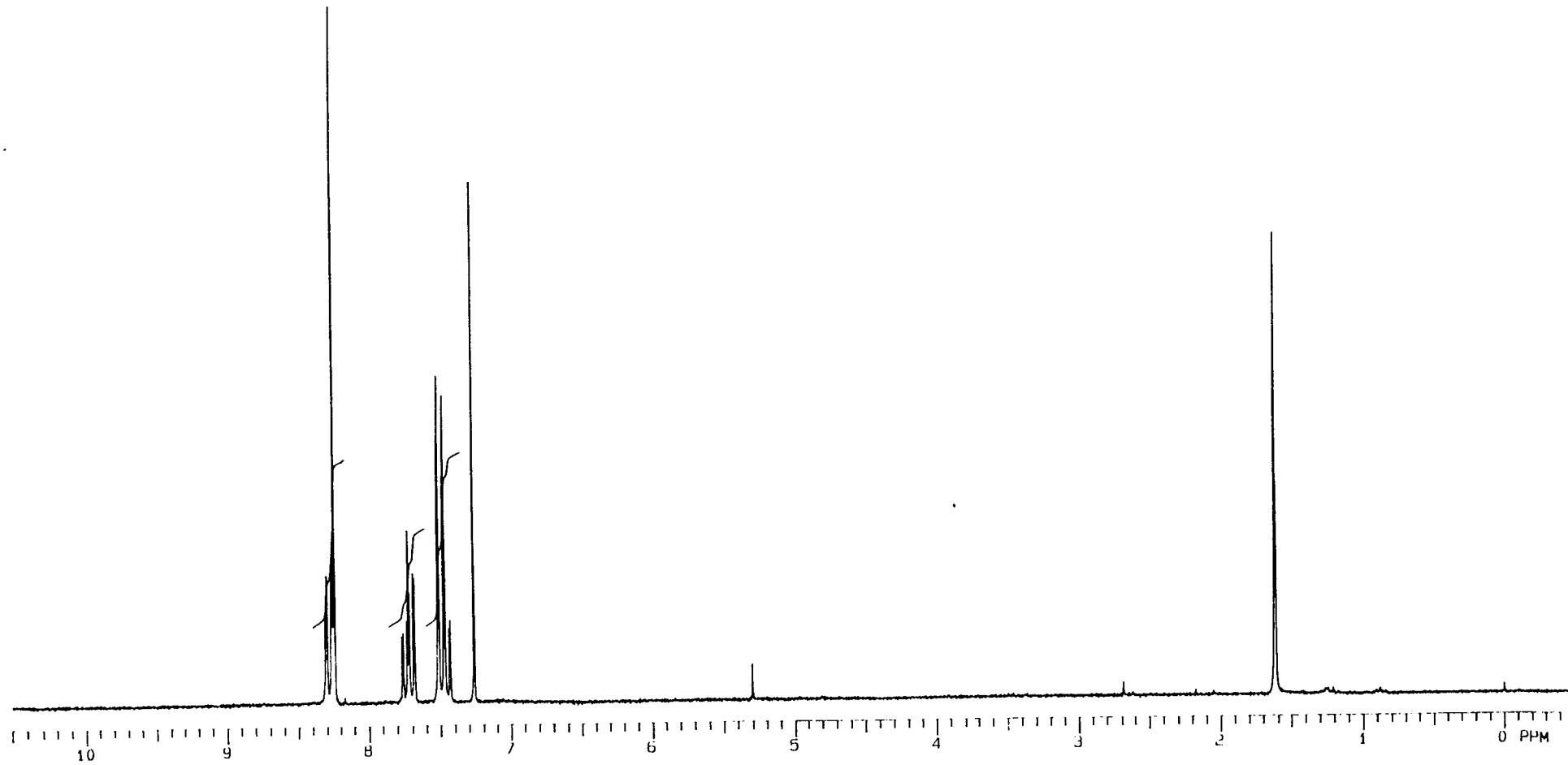
mass spectrum (EI): m/e (%relative intensity) 401 (25) M^++2 , 399 (22) M^+ , 386 (14), 384 (14), 252 (50), 250 (50), 200 (27), 198 (27), 172 (30), 170 (32) 150 (100);

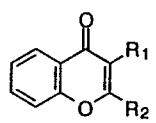
m/e calcd for $\text{C}_{21}\text{H}_{22}^{79}\text{BrNO}_2$ 399.0834, measd 399.0847; calcd for $\text{C}_{21}\text{H}_{22}^{81}\text{BrNO}_2$ 401.0817, measd 401.0821.



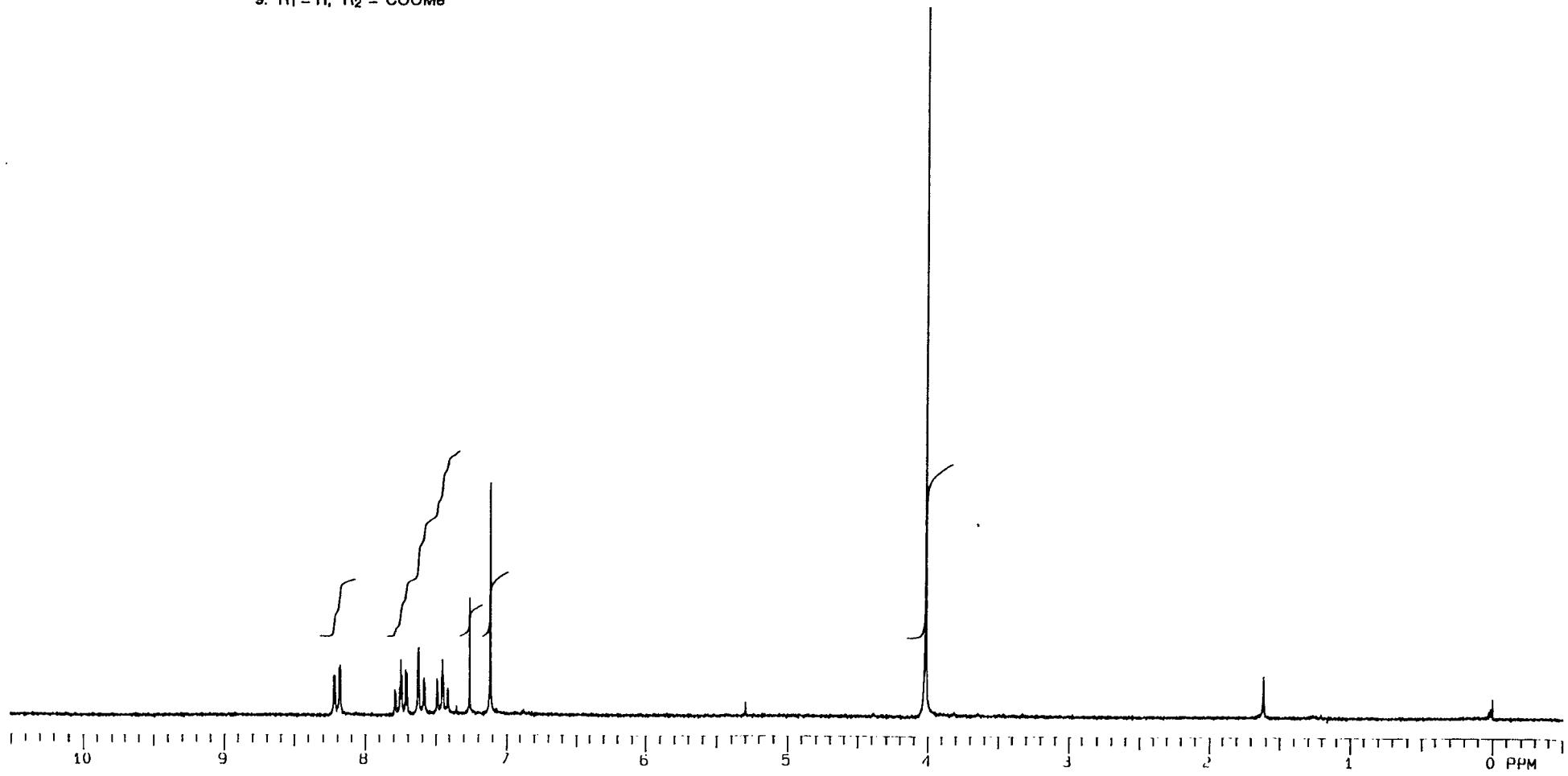


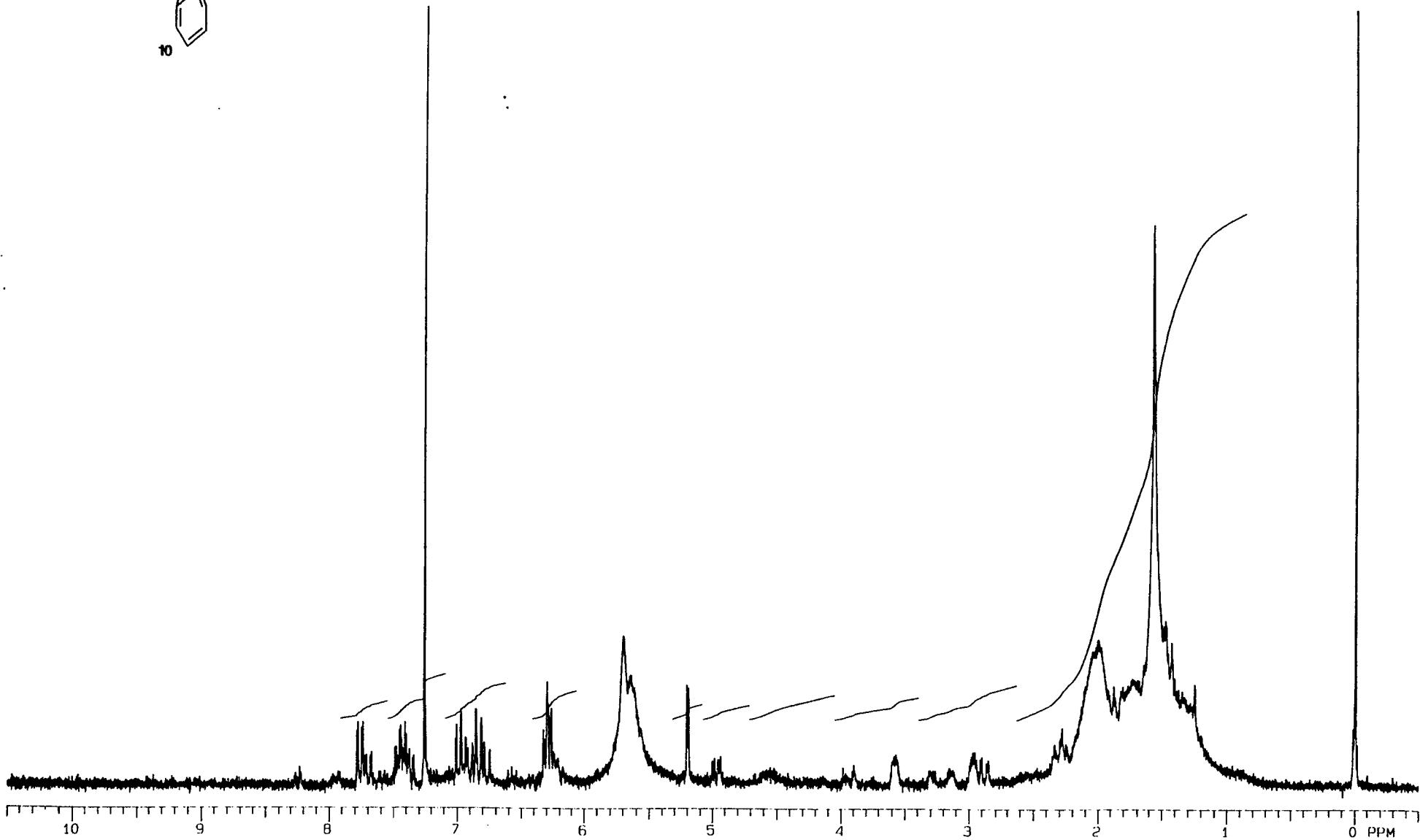
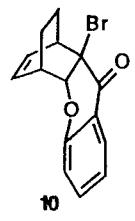
8: R₁ = Br, R₂ = H

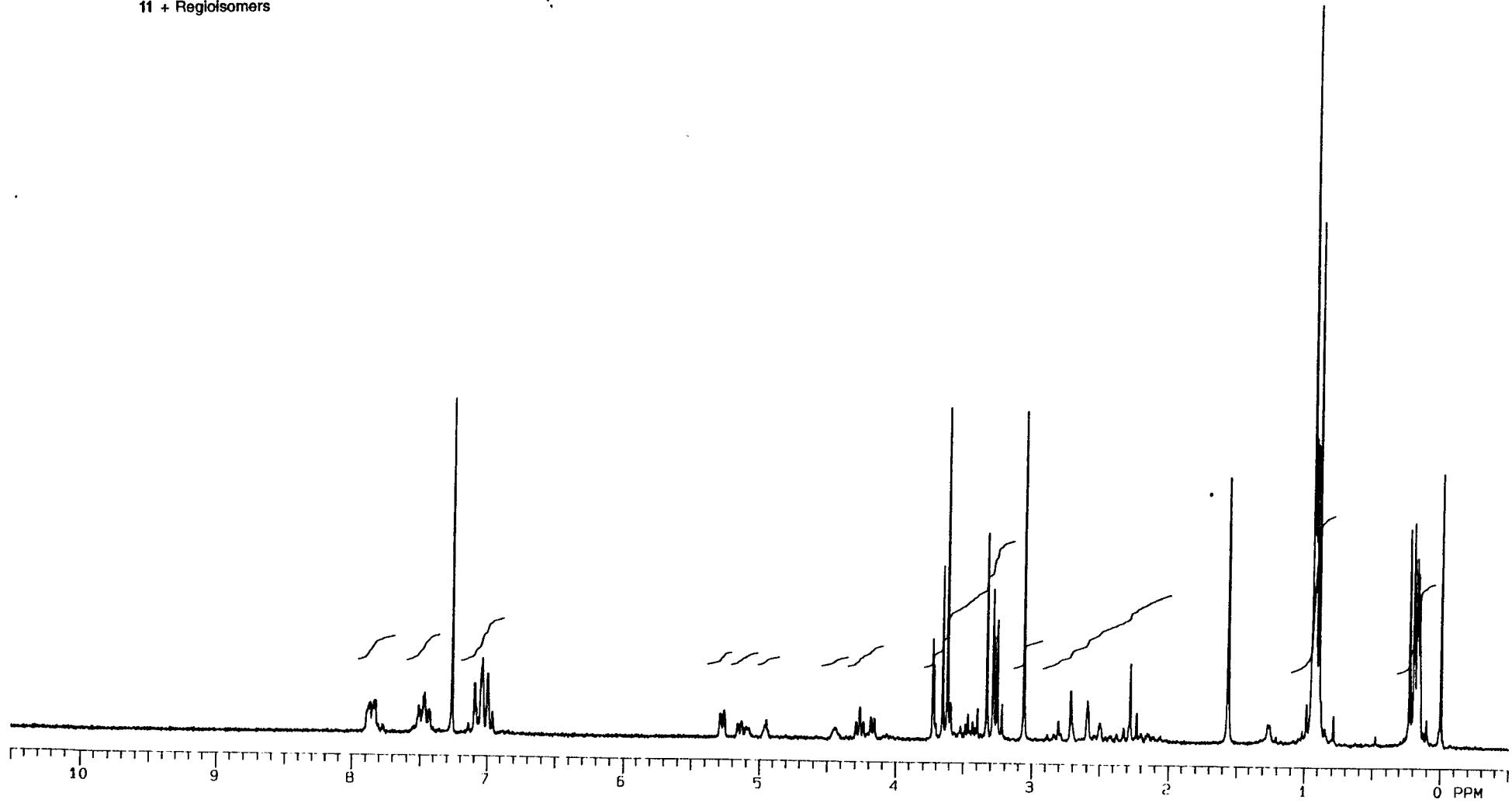
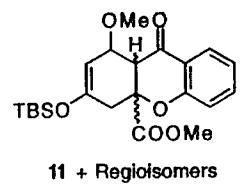


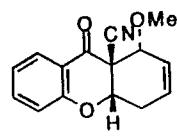


9: R₁ = H, R₂ = COOMe

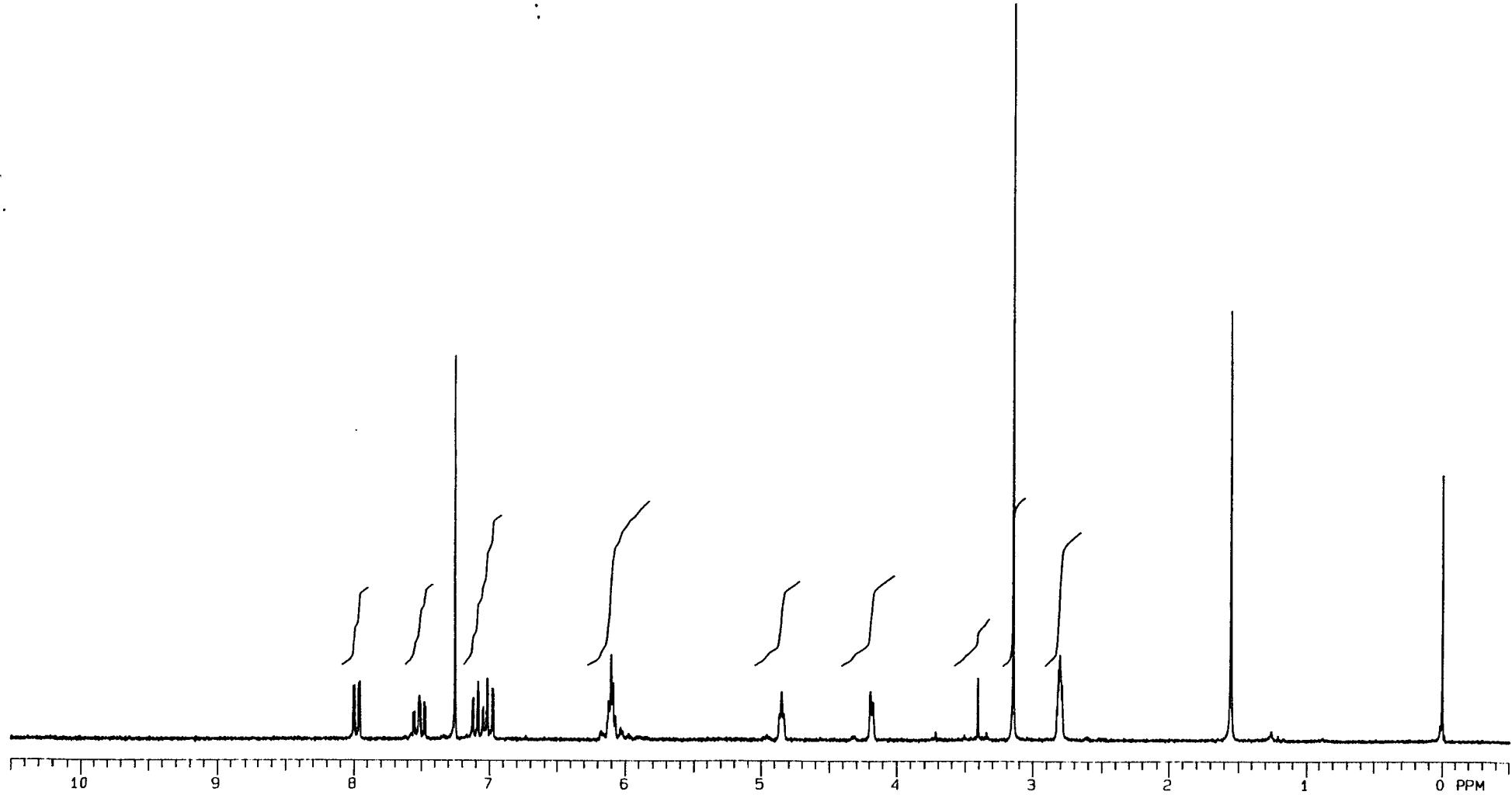


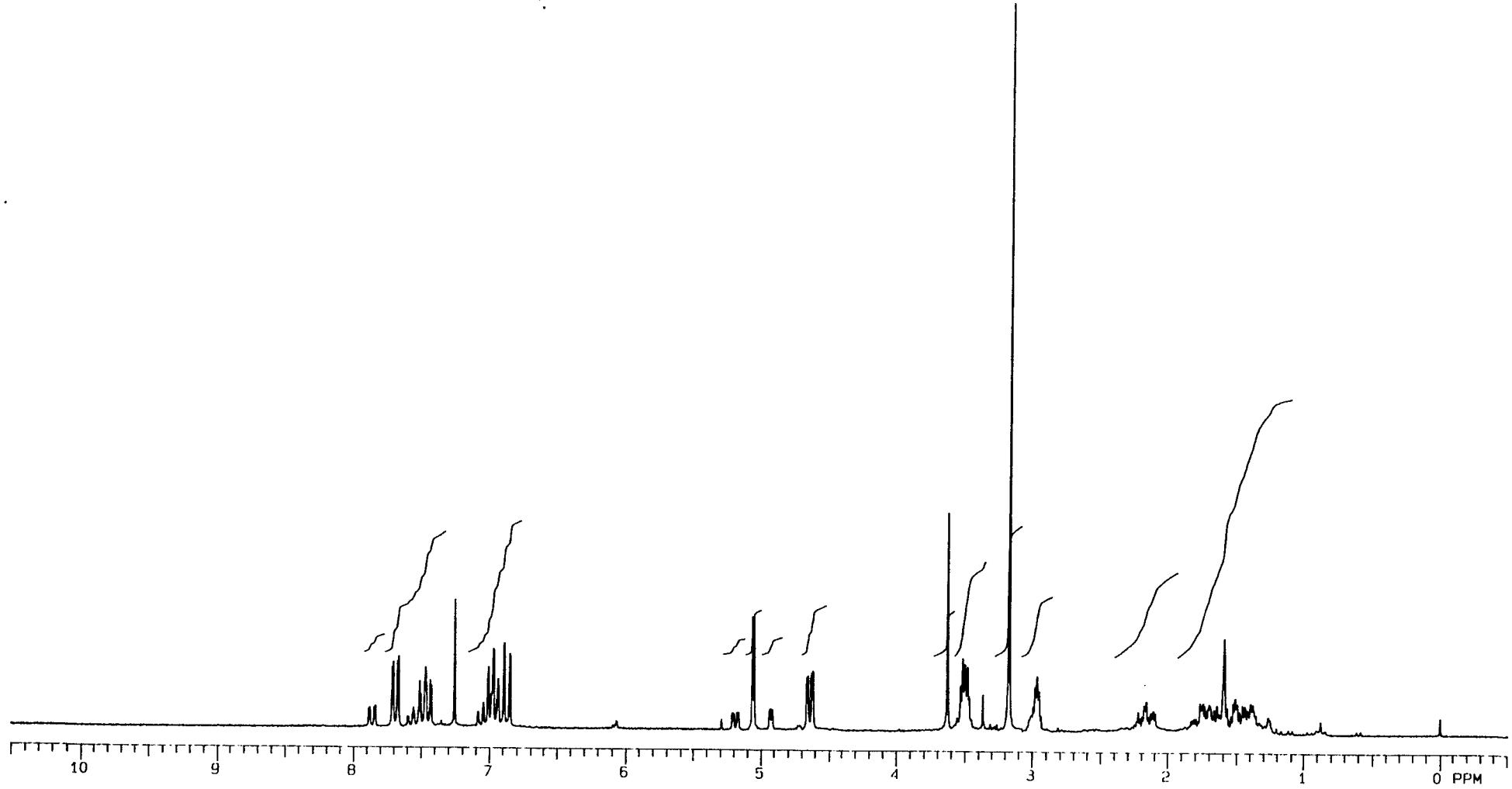
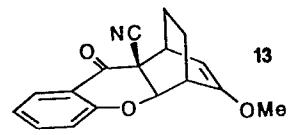


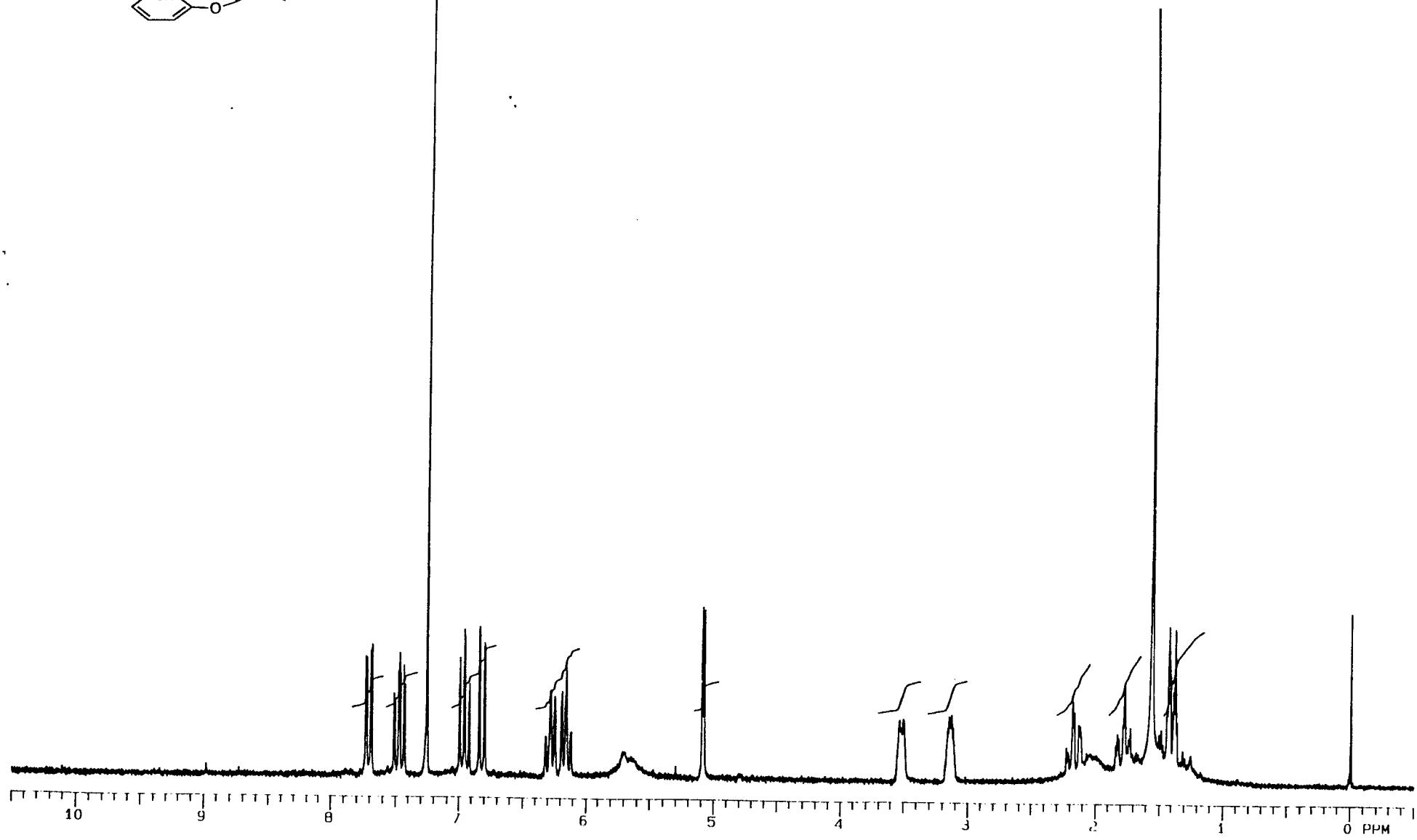
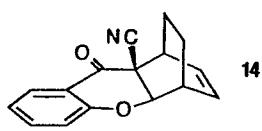


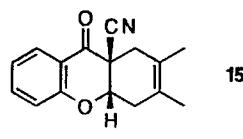


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