

## Supporting Material

### Application of the Excited State *meta*-Effect in Photolabile Protecting Group Design

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### Experimental Procedures

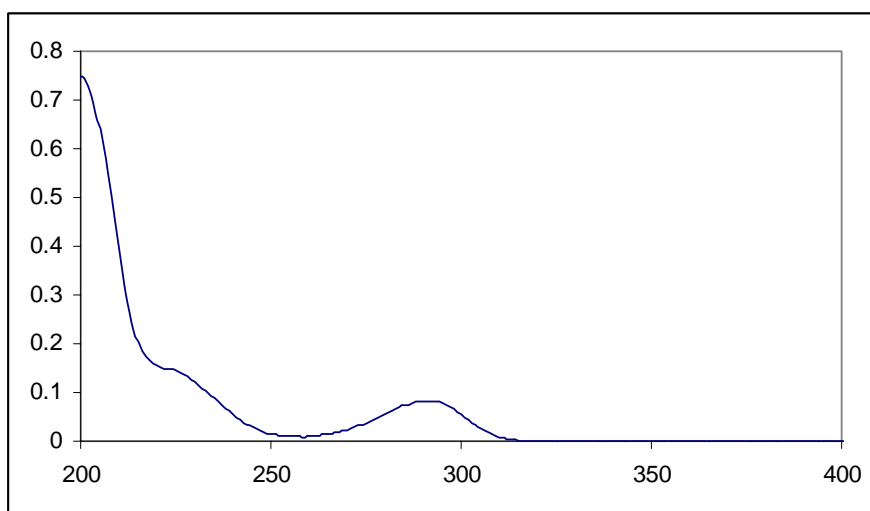
**General Procedures.** All organic solutions were concentrated by rotary evaporation under reduced pressure. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography was performed using plates pre-coated to a depth of 0.25mm with 230-400 mesh silica gel impregnated with a fluorescent indicator. All chemicals and solvents were obtained from commercial vendors and used without further purification. Infrared spectra were obtained using a Bruker Vector 22. Data were presented as frequency of absorption ( $\text{cm}^{-1}$ ). UV-visible spectra were obtained using a Varian Cary 100 Bio UV-visible spectrophotometer, with the sample concentration of  $2.0 \times 10^{-5}$  M and light path length of 1 cm.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 and Bruker 400 NMR spectrometer, chemical shifts are expressed in parts per million ( $\delta$  scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CHCl}_3$ :  $\delta$  7.26). Data were presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and /or multiple resonances), coupling constant in Hertz (Hz), integration. Photolysis was with 450W medium pressure mercury lamp without exclusion of air.

**Preparation of 3,5-dimethoxysalicylic alcohol (2).** 3,5-dimethoxybenzoic acid (3.643g, 20 mmol) with 0.1ml of concentrated  $\text{H}_2\text{SO}_4$  in 60 ml of MeOH was refluxed for 24 h. The solution was concentrated and neutralized with  $\text{NaHCO}_3$  (aq.). The aqueous layer was extracted with Ethyl acetate (50 ml x2) and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated to afford methyl 3,5-dimethoxybenzoate (3.761g, 92%) which was used directly for the next step without further purification.

Methyl 3,5-dimethoxybenzoate (3.924 g, 20 mmol) in 200 ml of MeCN was treated with NBS (3.916g, 22 mmol) at  $0^\circ\text{C}$ , and then stirred at R.T. for 3h. The reaction was quenched with  $\text{Na}_2\text{S}_2\text{O}_3$  (aq.) and concentrated to remove MeCN. The residue was extracted with Ethyl acetate (50 ml x2) and the organic layers were combined and washed by saturated  $\text{NH}_4\text{Cl}$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified with flash chromatography (petroleum ether/Ethyl acetate = 7/1,  $R_f$  = 0.3) to provide methyl 2-bromo-3,5-dimethoxybenzoate (**11**) (4.402g, 80%).

**11** (4.13 g, 15 mmol),  $\text{K}_2\text{CO}_3$  (10.37 g, 75 mmol) and  $\text{Bu}_4\text{NBr}$  (97 mg, 0.3 mmol) in 20 ml of water were refluxed for 9h. Pyridine (2.43 ml, 30 mmol) and Cu powder (190 mg, 3mmol) were added and the reflux continued for 13 h. The reaction mixture was cooled down, poured into ice-cooled water and acidified with HCl to pH = 1~2. The aqueous was extracted with Ethyl acetate (50x3), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The crude 3,5-dimethoxysalicylic acid was dissolved in 30 ml of THF and treated with  $\text{LiAlH}_4$  (1.14g, 30 mmol) in 20 ml of THF under  $\text{N}_2$ . The reaction mixture was stirred at R.T. for 2 h and then poured into ice-water and acidified with HCl to pH = 3~4. The mixture was extracted with Ethyl acetate (30 ml x2), washed with saturated  $\text{NaHCO}_3$  aq. and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was

purified with flash chromatography (petroleum ether/Ethyl acetate = 3/2,  $R_f$  = 0.26) to provide 1.36 g of pure **2** (49%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  6.39 (d,  $J$  = 2.8 Hz, 1 H), 6.36 (d,  $J$  = 2.8 Hz, 1 H), 6.28 (s, 1 H), 4.67 (s, 2 H), 3.77 (s, 3 H), 3.71 (s, 3 H), 3.37 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  153.3, 147.7, 138.1, 126.8, 104.1, 99.2, 62.0, 56.4, 56.1; IR (neat) 3476, 3253, 3004, 2959, 2840, 1615, 1500, 1465, 1433, 1368, 1286, 1244; HRMS (FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 185.0814, found 185.0812. UV of **2** (in general, the sample concentration is  $2.0 \times 10^{-5}$  M and light path length is 1 cm):



**Preparation of 8.** A solution of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  (2.86 ml, 22.6 mmol) in 10 ml of THF was added drop wise to a solution of 2-hydroxy-5-methoxybenzoic acid (2.536 g, 15.1 mmol) and  $\text{NaBH}_4$  (1.155 g, 30.5 mmol) in 40 ml of THF and refluxed for 11 h. The reaction mixture was cooled, poured into 80 ml of water and extracted with Ethyl acetate (70 ml $\times$ 2), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified with flash chromatography (Hexanes/Ethyl acetate = 2/1,  $R_f$  0.2) to provide 5-methoxysalicylic alcohol (1.573g, 68%).

5-methoxysalicylic alcohol (0.462 g, 3 mmol), 3-Phenylpropionaldehyde (**1a**) (0.278 ml, 2 mmol) and p-TsOH (38 mg, 0.2 mmol) in 8 ml of DCM was stirred at R.T. for 24 h. The reaction mixture was concentrated and directly purified with flash chromatography (petroleum ether/Ethyl acetate = 7/1,  $R_f$  = 0.45) to afford **8** (0.475g, 88%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.34-7.21 (m, 5 H), 6.83 (d,  $J$  = 9.0 Hz, 1 H), 6.74 (dd,  $J$  = 9.0, 3.0 Hz, 1 H), 6.51 (d,  $J$  = 3.0 Hz, 1 H), 5.00-4.94 (m, 2 H), 4.84 (d,  $J$  = 14.7 Hz, 1 H), 3.76 (s, 3 H), 2.88 (t,  $J$  = 7.8 Hz, 2 H), 2.20-2.14 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  154.3, 147.4, 141.8, 129.0, 128.9, 126.4, 121.9, 117.9, 114.4, 109.9, 99.4, 66.9, 56.1, 36.3, 30.3; IR (neat) 3031, 2953, 2929, 2863, 1600, 1497, 1454, 1372, 1323, 1259, 1223; HRMS (FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 271.1334, found 271.1330.

**Preparation of 9.** Salicylic alcohol (77 mg, 0.60 mmol), **1a** (0.0278 ml, 0.20 mmol) and  $\text{ZnCl}_2$  (85 mg, 0.60 mmol) in 1 ml of benzene was stirred at 23°C for 18 h. The reaction mixture was concentrated and purified with flash chromatography (petroleum ether/Ethyl acetate = 20/1,  $R_f$  0.39) to provide **9** (22 mg, 46%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.35-7.16 (m, 6 H), 7.00-6.88 (m, 3 H), 5.05-4.98 (m, 2 H), 4.88 (dd,  $J$  = 14.4,

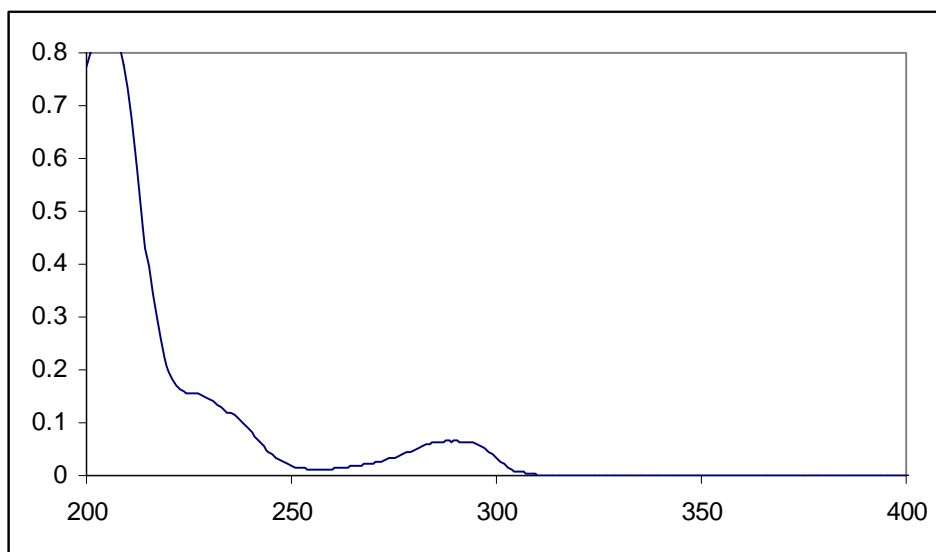
3.0 Hz, 1 H), 2.90 (t,  $J$  = 8.0 Hz, 2 H), 2.25-2.16 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  153.0, 141.3, 128.51, 128.48, 128.0, 126.0, 124.9, 121.03, 120.97, 116.7, 99.0, 66.5, 35.9, 29.8; IR(neat) 3027, 2931, 2857, 1615, 1588, 1490, 1462, 1406, 1272, 1240; HRMS(FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 241.1229, found 241.1228.

**Preparation of 12.** 3,5-dimethoxysalicylic acid was reflux for 24 h in MeOH in the presence of  $\text{H}_2\text{SO}_4$  (conc.). The reaction mixture was cooled and concentrated. Flash chromatography (petroleum ether/ethyl acetate = 7:1,  $R_f$  0.37) afforded the methyl ester. The ester (213 mg, 1 mmol) in 3 ml of THF was treated with LiMe (3.6 ml, 1.4 M in  $\text{Et}_2\text{O}$ ) and stirred at  $-78^\circ\text{C}$  for 1.5 h. The reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (aq.), extracted with ethyl acetate (15 ml x 2), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified with flash chromatography (petroleum ether/ethyl acetate = 2:1,  $R_f$  0.3) to provide the 3,5-dimethoxy- $\alpha,\alpha$ -dimethylsalicylic alcohol (200mg, 94%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  6.89 (s, 1 H), 6.44 (d,  $J$  = 2.8 Hz, 1 H), 6.39 (d,  $J$  = 2.8 Hz, 1 H), 3.87 (s, 3 H), 3.77 (s, 3 H), 3.49 (s, 1 H), 1.63 (s, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  153.1, 148.2, 138.0, 133.3, 102.3, 98.4, 74.4, 56.5, 56.2, 30.0; IR (neat): 3421, 2975, 2838, 1602, 1491, 1460, 1430, 1375, 1324, 1204; HRMS(FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 213.1127, found 213.1128.

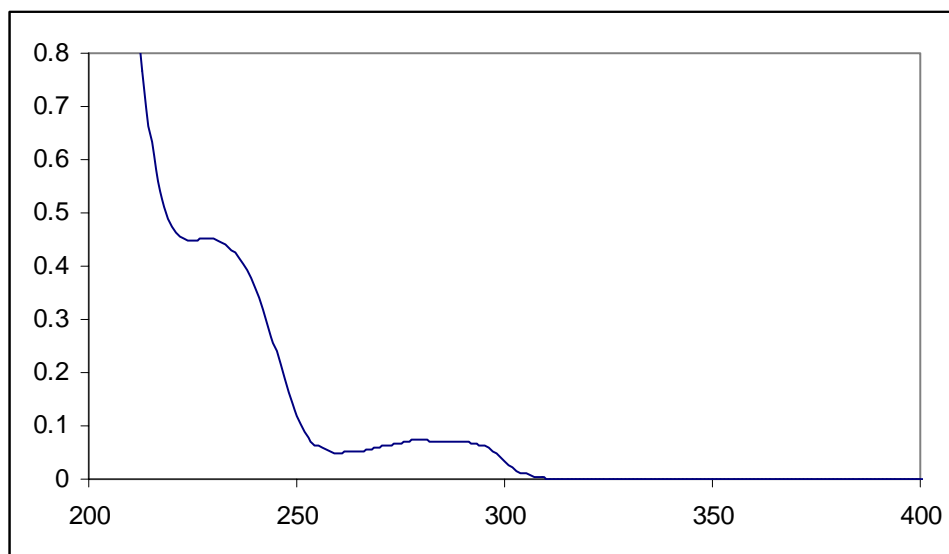
3,5-dimethoxy- $\alpha,\alpha$ -dimethylsalicylic alcohol (33 mg, 0.15mmol), **1a** (0.014 ml 0.10 mmol),  $\text{ZnCl}_2$  (28 mg) in 0.8 ml of MeCN were stirred at  $23^\circ\text{C}$  for 24 h. Flash chromatography (Hexanes/ benzene = 2/3,  $R_f$  0.17) afforded **12** (15mg, 46%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.27-7.18 (m, 5 H), 6.37 (d,  $J$  = 2.4 Hz, 1 H), 6.15 (d,  $J$  = 2.7 Hz, 1 H), 5.01 (dd,  $J$  = 6.3, 4.2 Hz, 1 H), 3.85 (s, 3 H), 3.77 (s, 3 H), 2.92-2.83 (m, 2 H), 2.30-2.20 (m, 2 H), 1.55(s, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz)  $\delta$  154.1, 149.1, 141.7, 136.5, 131.2, 129.0, 128.7, 126.3, 100.9, 98.5, 94.6, 75.5, 56.4, 56.1, 36.0, 31.1, 30.4, 29.3; IR(neat): 2974, 2933, 1603, 1493, 1456, 1401, 1358, 1284, 1257, 1202; HRMS(FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 329.1753, found 329.1751.

**General Procedure of Preparation of 3a, 3b, 3c, 3d, 3e, and 3f.** **2** (28mg, 0.15 mmol) was added to a flame dry flask under Ar, followed by 1.0 ml of freshly distilled toluene and cooled to  $0^\circ\text{C}$ . The carbonyl compound (0.10 mmol),  $p\text{-TsOH}$  (0.4 mg, 0.002 mmol) and  $\text{P}_2\text{O}_5$  (30 mg) was added and stirred at  $0^\circ\text{C}$ . When the carbonyl compound was consumed, the reaction was poured into saturated  $\text{NaHCO}_3$  (aq.) and extracted with Ethyl acetate (15 mlx2), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified with flash chromatography.

**3a**, 92%,  $R_f$  0.27 (petroleum ether/ethyl acetate = 7/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.30-7.19 (m, 5 H), 6.38 (d,  $J$  = 2.7 Hz, 1 H), 6.07 (d,  $J$  = 2.7 Hz, 1 H), 4.97-4.95 (m, 2 H), 4.82 (d,  $J$  = 14.7 Hz, 1 H), 3.85 (s, 3 H), 3.74 (s, 3 H), 2.91-2.84 (m, 2 H), 2.24-2.20 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  154.0, 148.8, 141.2, 136.8, 128.5, 128.4, 125.9, 121.6, 99.2, 99.1, 98.8, 66.4, 56.0, 55.6, 35.6, 29.9; IR (neat): 3059, 3026, 3002, 2933, 2841, 1606, 1499, 1455, 1404, 1369, 1282, 1225; HRMS(FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 301.1440, found 301.1438. UV of **3a**:

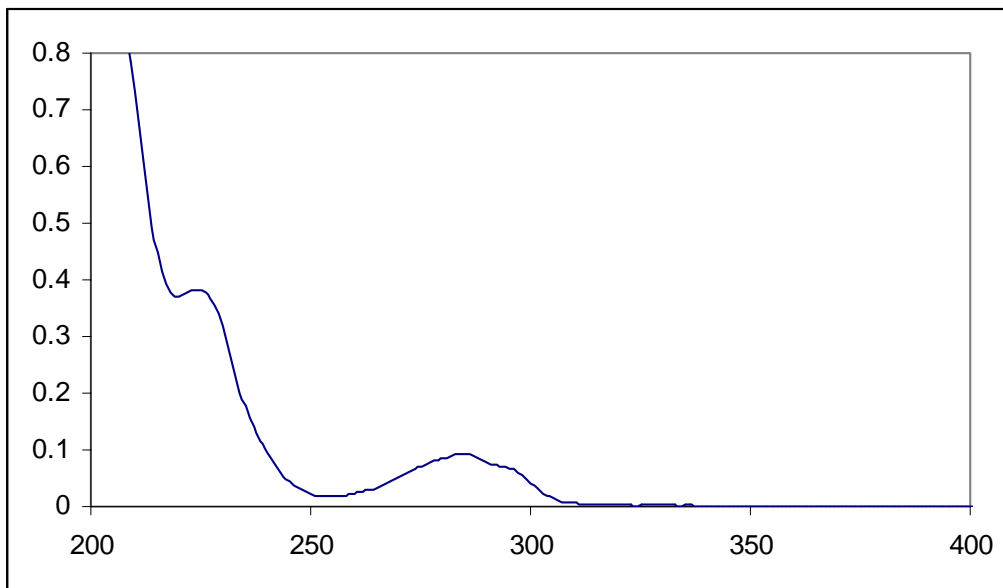


**3b**, 99%, Rf 0.5 (petroleum ether/ethyl acetate = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.58 (d,  $J = 8.6$  Hz, 2 H), 7.34 (t,  $J = 7.6$  Hz, 2 H), 7.11 (t,  $J = 7.3$  Hz, 1 H), 7.05-7.00 (m, 4 H), 6.41 (d,  $J = 2.4$  Hz, 1 H), 6.12 (d,  $J = 2.3$  Hz, 1 H), 5.93 (s, 1 H), 5.16 (d,  $J = 14.8$  Hz, 1 H), 4.94 (d,  $J = 15.0$  Hz, 1 H), 3.84 (s, 3 H), 3.76 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  158.6, 157.4, 154.7, 149.5, 137.3, 132.4, 130.2, 128.8, 123.9, 121.9, 119.5, 119.1, 99.5, 99.4, 99.3, 67.1, 56.4, 56.1; IR (neat): 2997, 2958, 2840, 1610, 1592, 1494, 1457, 1387, 1367, 1336, 1283, 1241; HRMS(FT-ICR)  $m/e$  calcd. for ( $\text{M} + \text{H}^+$ ) 365.1389, found 365.1383. UV of **3b**:

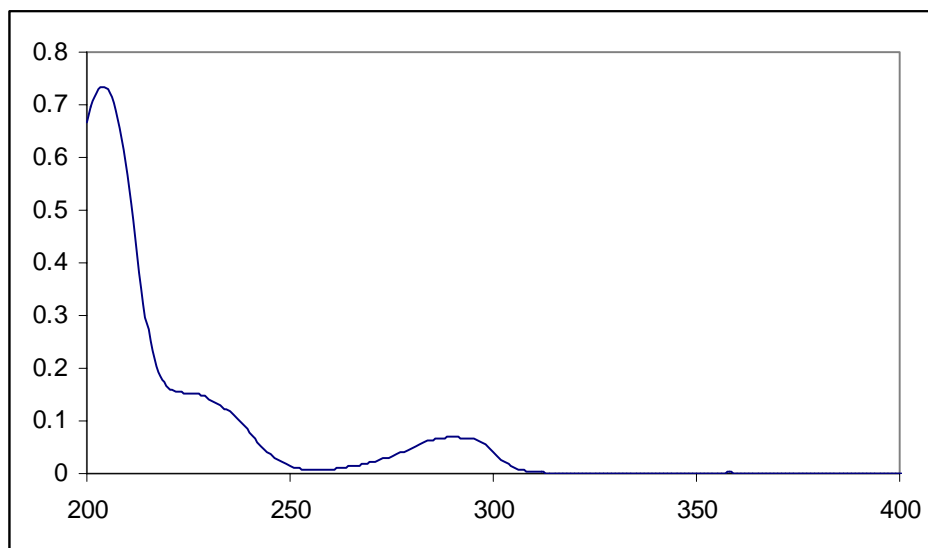


**3c**, 93%, Rf 0.43 (petroleum ether/ethyl acetate = 5/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.04 (d,  $J = 8.6$  Hz, 2 H), 6.74 (d,  $J = 8.6$  Hz, 2 H), 6.32 (d,  $J = 2.7$  Hz, 1 H), 6.01 (d,  $J = 2.5$  Hz, 1 H), 4.78 (d,  $J = 15.2$  Hz, 1 H), 4.72 (d,  $J = 15.1$  Hz, 1 H), 3.77 (s, 3 H), 3.71 (s, 3 H), 3.68 (s, 3 H), 2.68 (t,  $J = 8.6$  Hz, 2 H), 2.14-2.00 (m, 2 H), 1.51 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  156.7, 152.4, 148.3, 133.7, 132.8, 128.2, 119.0, 112.7, 99.6, 98.0, 97.9, 59.8, 55.0, 54.6, 54.2, 38.6, 27.7, 21.3; IR (neat): 2939, 2837, 2730, 1700,

1609, 1584, 1495, 1453, 1372, 1245, 1201; HRMS(FT-ICR)  $m/e$  calcd. for (M + H<sup>+</sup>) 345.1702, found 345.1700. UV of **3c**:

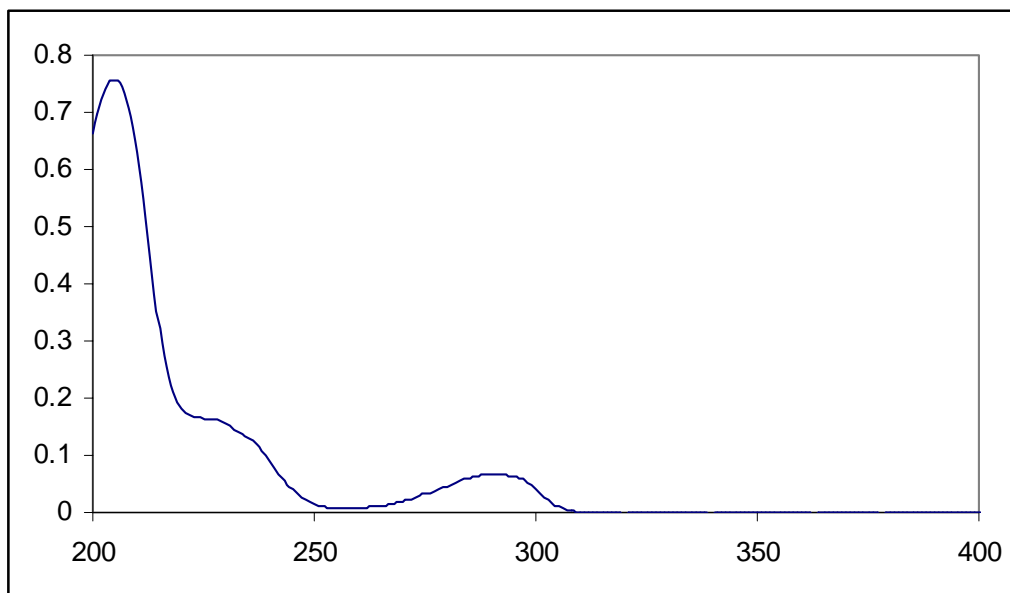


**3d**, 91%, R<sub>f</sub> 0.27 (petroleum ether/ethyl acetate = 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 6.39 (d,  $J$  = 2.7 Hz, 1 H), 6.08 (d,  $J$  = 2.7 Hz, 1 H), 4.81 (d,  $J$  = 15.1 Hz, 1 H), 4.75 (d,  $J$  = 15.1 Hz, 1 H), 3.84 (s, 3 H), 3.75 (s, 3 H), 1.93-1.75 (m, 2 H), 1.52 (s, 3 H), 1.52-1.40 (m, 2 H), 1.31-1.20 (m, 28 H), 0.88 (t,  $J$  = 6.7 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 153.2, 149.2, 134.7, 120.0, 101.2, 98.74, 98.69, 60.7, 55.9, 55.6, 37.7, 31.9, 29.8, 29.71, 29.67, 29.6, 29.5, 29.4, 23.4, 22.7, 22.1, 14.2; IR (neat): 2916, 2848, 1603, 1496, 1462, 1363, 1280, 1245; HRMS(FT-ICR)  $m/e$  calcd. for (M + H<sup>+</sup>) 449.3631, found 449.3642. UV of **3d**:



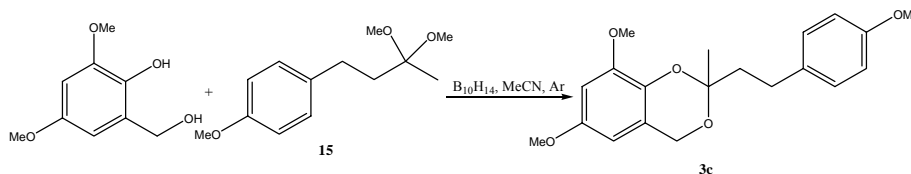
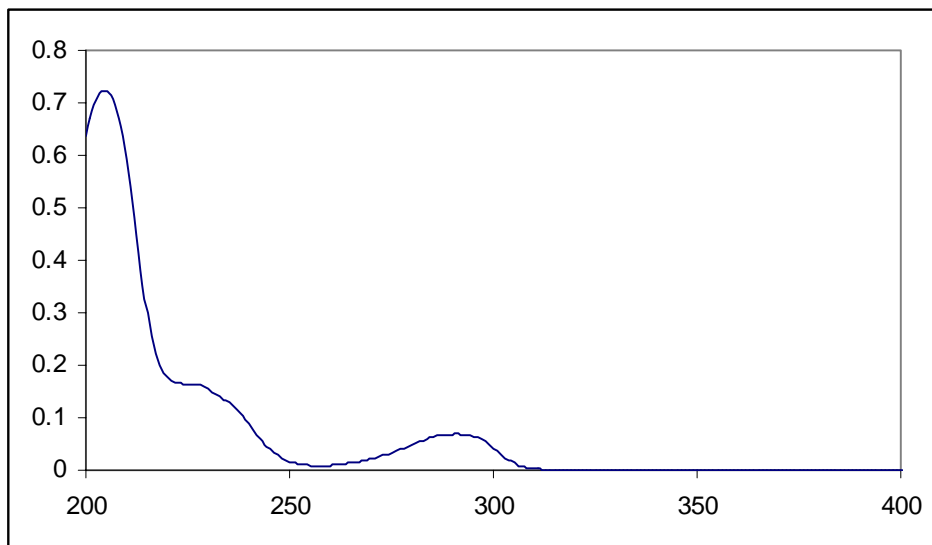
**3e**, 96%, R<sub>f</sub> 0.4 (petroleum ether/ethyl acetate = 7/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 6.38 (d,  $J$  = 2.8 Hz, 1 H), 6.07 (d,  $J$  = 2.8 Hz, 1 H), 4.78 (s, 2 H), 3.83 (s, 3 H), 3.74 (s, 3 H), 2.20 (s, 2 H), 2.12 (d,  $J$  = 12.5 Hz, 2 H), 2.02 (d,  $J$  = 11.9 Hz, 2 H), 1.89-1.85 (m, 2

H), 1.71-1.63 (m, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  152.4, 148.6, 133.5, 120.1, 100.7, 98.0, 97.9, 58.8, 55.1, 54.6, 36.2, 32.8, 32.54, 32.46, 26.05, 26.03; IR (neat): 2910, 2854, 1610, 1498, 1452, 1363, 1283, 1239; HRMS(FT-ICR)  $m/e$  calcd. for  $(\text{M} + \text{H}^+)$  317.1753, found 317.1749. UV of **3e**:



**3f** (isomer a+b = 93%), isomer a (28%), Rf 0.16 (petroleum ether/ ethyl acetate = 20/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.39 (d,  $J = 2.6$  Hz, 1 H), 6.06 (d,  $J = 2.7$  Hz, 1 H), 4.82 (s, 2 H), 3.85 (s, 3 H), 3.75 (s, 3 H), 2.02-0.74 (m, 43 H), 0.65 (s, 3 H);  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75 MHz)  $\delta$  153.3, 149.5, 134.5, 120.7, 99.8, 98.9, 98.7, 60.6, 56.4, 56.2, 56.1, 55.6, 53.7, 42.5, 41.7, 39.9, 39.5, 36.6, 36.1, 35.8, 35.7, 35.4, 34.7, 31.7, 28.7, 28.3, 28.2, 28.0, 24.2, 23.8, 22.9, 22.6, 21.2, 18.6, 12.1, 11.5; IR (neat): 2931, 2864, 1603, 1496, 1451, 1364, 1277, 1230; HRMS(FT-ICR)  $m/e$  calcd. for  $(\text{M} + \text{H}^+)$  553.4257, found 553.4270.

Isomer b (65%), Rf 0.11 (petroleum ether/ ethyl acetate = 20/1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.38 (d,  $J = 2.7$  Hz, 1 H), 6.07 (d,  $J = 2.7$  Hz, 1 H), 4.74 (s, 2 H), 3.84 (s, 3 H), 3.74 (s, 3 H), 2.06-0.68 (m, 43 H), 0.64 (s, 3 H);  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75 MHz)  $\delta$  153.2, 149.1, 134.8, 120.1, 100.5, 98.7, 98.6, 60.2, 56.4, 56.2, 55.9, 55.6, 53.9, 42.5, 42.2, 39.9, 39.5, 36.1, 35.82, 35.78, 35.4, 34.7, 31.9, 29.7, 29.2, 28.3, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.6, 12.0, 11.8; IR (neat): 2933, 2867, 1610, 1498, 1465, 1373, 1228; HRMS(FT-ICR)  $m/e$  calcd. for  $(\text{M} + \text{H}^+)$  553.4257, found 553.4262. UV of **3f**:



**Preparation of 3c from dimethyl ketal. 2** (170 mg, 0.88 mmol), dimethyl ketal **15** (173 mg, 0.72 mmol) and  $B_{10}H_{14}$  (3.6 mg) in 1.5 ml of freshly distilled MeCN was stirred at R. T. under Ar for 3.5 h. The reaction mixture was poured into saturated  $NaHCO_3$  (aq.) and extracted with  $CH_2Cl_2$  (50ml\*2), dried over  $Na_2SO_4$ , filtered and concentrated. The residue was purified with flash chromatography (petroleum ether/ethyl acetate = 5/1, Rf 0.43) to afford **3c** (248 mg, 99%).

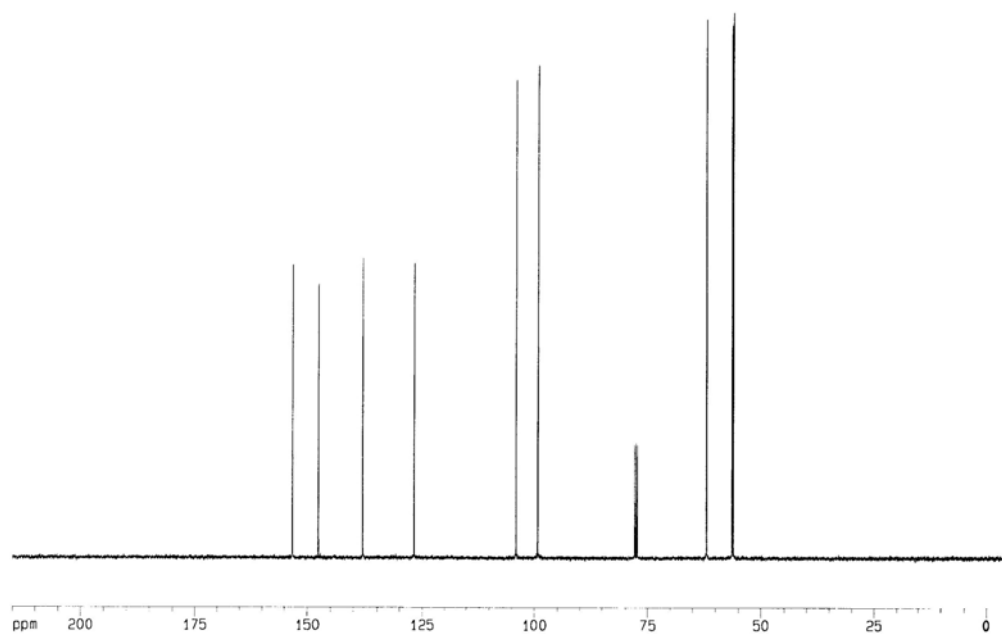
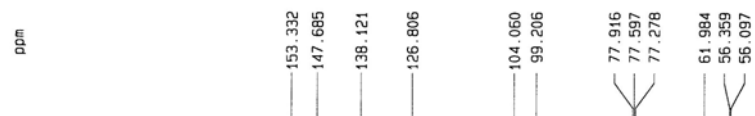
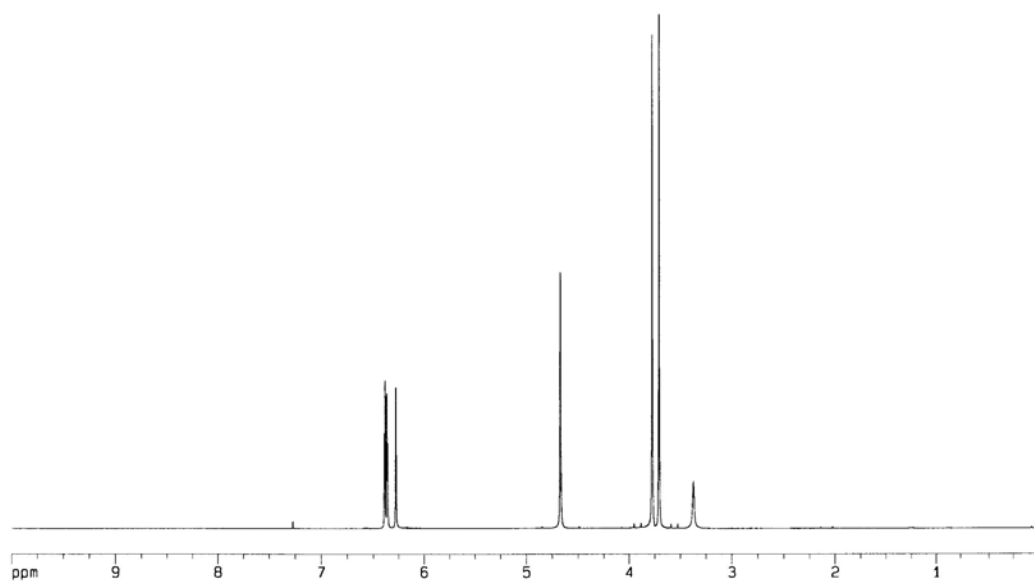
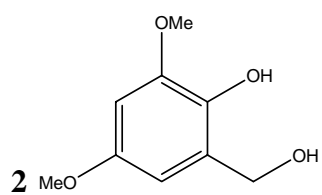
**General procedures of photolysis.** Ketal/acetal (0.20 mmol) in 200 ml of acetonitrile and 50 ml of water was irradiated a 450W medium pressure mercury lamp equipped with a Pyrex filter sleeve, without exclusion of air (for **1d** and **1f**, 240 ml of acetonitrile and 10 ml of water were used because of the solubility). The reaction mixture was then concentrated and the residue was purified with flash column chromatography. Carbonyl compounds **1a** and **1c** were further derivatized. The reaction solution was transferred to a 500 ml round bottom flask containing  $HONH_3Cl$  (1.112 g, 16.0 mmol) and  $NaOAc$  (1.690 g, 19.2 mmol) and stirred at room temperature for 24 h. The reaction mixture was concentrated and extracted with  $CH_2Cl_2$  (30 mlx2). The organic layers were combined, dried over  $Na_2SO_4$ , filtered and concentrated. The residue was purified with flash chromatography to provide the corresponding oximes. The yields of the obtained **1b** and **1e** were calculated the same way as in other cases and without any adjustment for their conversions.

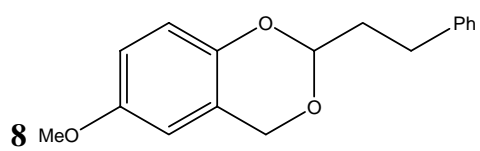
### Stability of 3a under various conditions

entry	reagent <sup>a</sup>	solvent	conditions	3a (%) <sup>d</sup>
1	PhLi <sup>b</sup>	THF	-78°C, 2h	100
2	LiAlH <sub>4</sub> <sup>c</sup>	THF	23°C, 24h	100
3	NaBH <sub>4</sub> <sup>c</sup>	THF	23°C, 24h	100
4	t-BuOK	MeCN	23°C, 24h	100
		MeCN	Reflux, 2h	100
5	DDQ	MeCN	23°C, 24h	25
		MeCN	Reflux, 2h	0
6	TFA	MeCN	23°C, 24h	25
		MeCN	Reflux, 2h	0
7	p-TsOH·H <sub>2</sub> O	MeCN	23°C, 24h	0
		MeCN	Reflux, 2h	0
8	HCl (37%)	MeCN	23°C, 24h	50
		MeCN	Reflux, 2h	0
9	CAN	MeCN	23°C, 24h	0
		MeCN	Reflux, 2h	0
10	AcOH	MeCN	23°C, 24h	100
		MeCN	Reflux, 2h	100

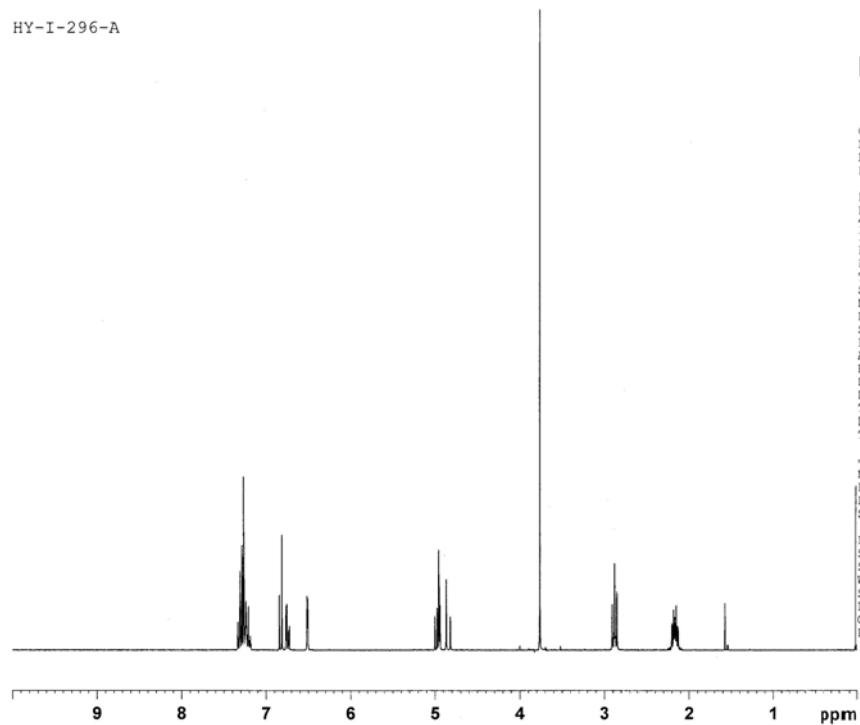
<sup>a</sup> **3a** (2mg) in 1.0ml MeCN treated with reagent (>20 eq.). <sup>b</sup> **3a**(0.05mmol) in 1.0ml dry THF treated with 0.4ml of PhLi (2.0M Bu<sub>2</sub>O solution) under Ar. <sup>c</sup> **3a**(5mg) in 1ml THF as treated with reagent (>20eq.). <sup>d</sup> Yields determined by <sup>1</sup>H NMR of the crude reaction mixture.





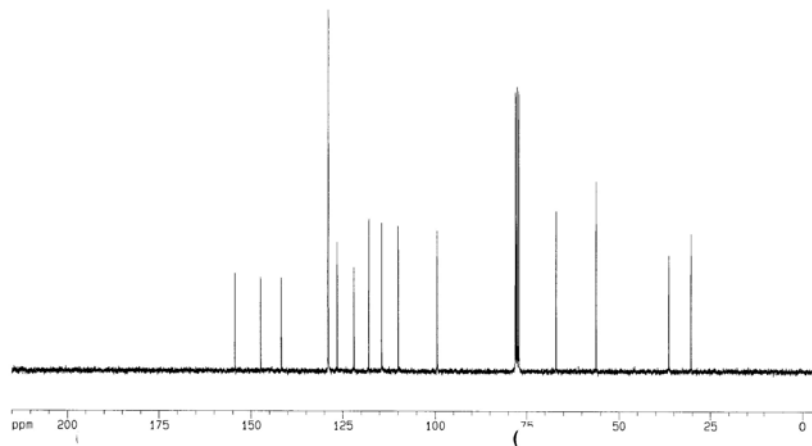


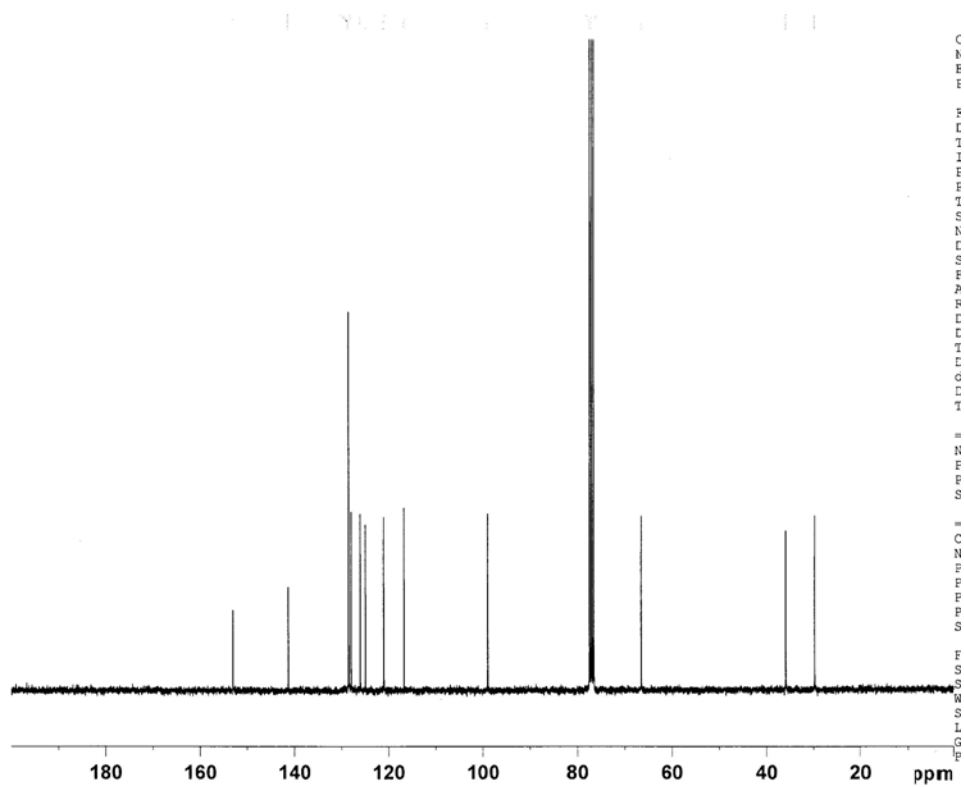
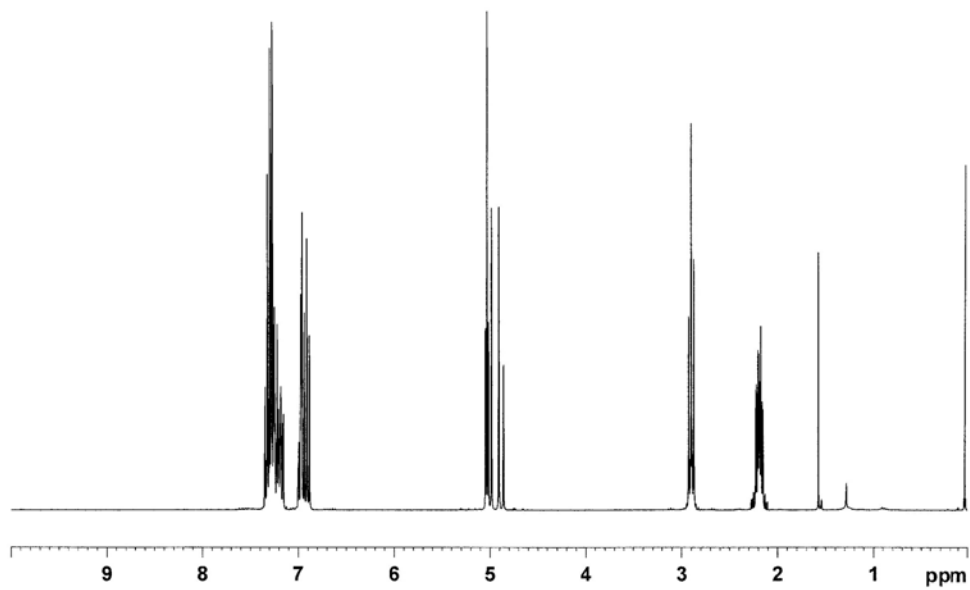
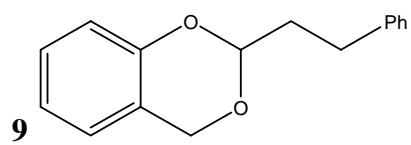
HY-I-296-A

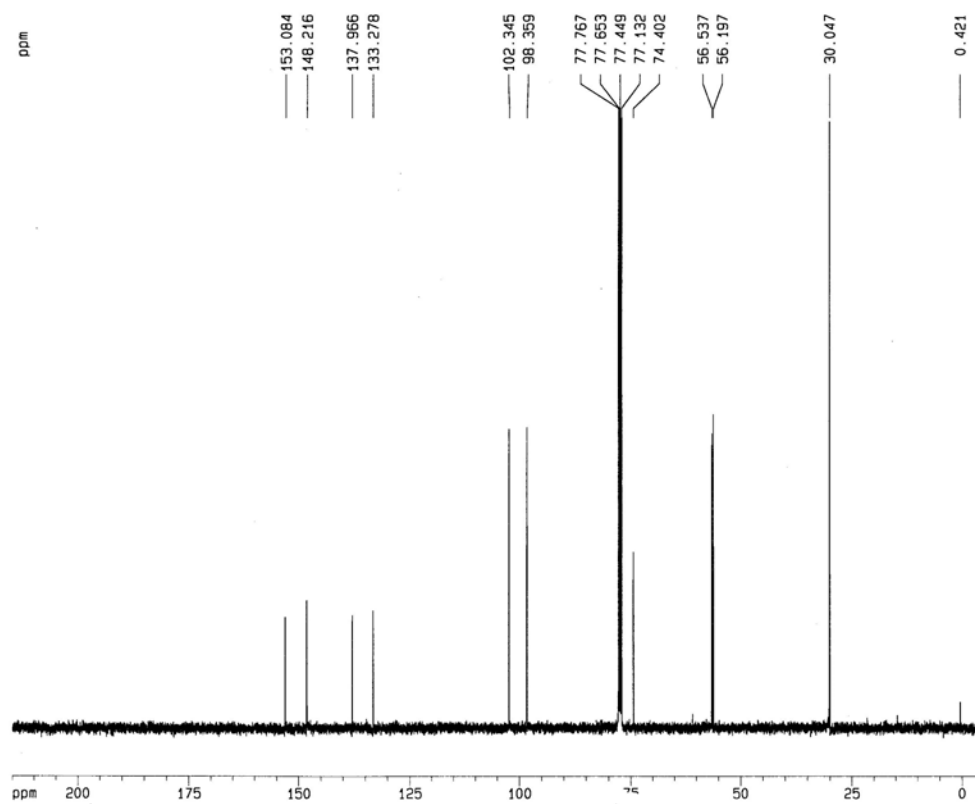
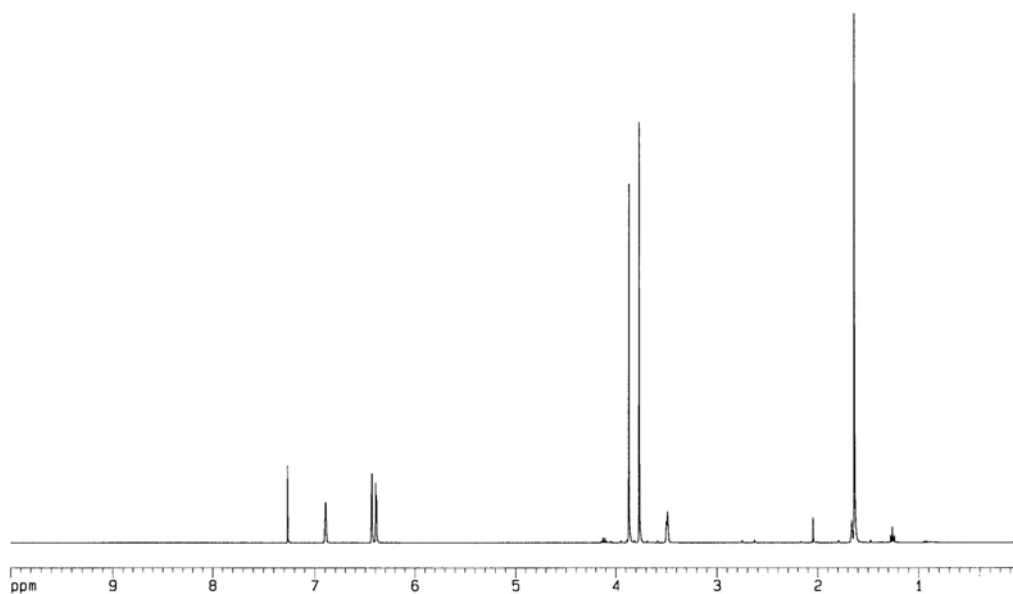
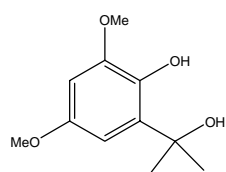


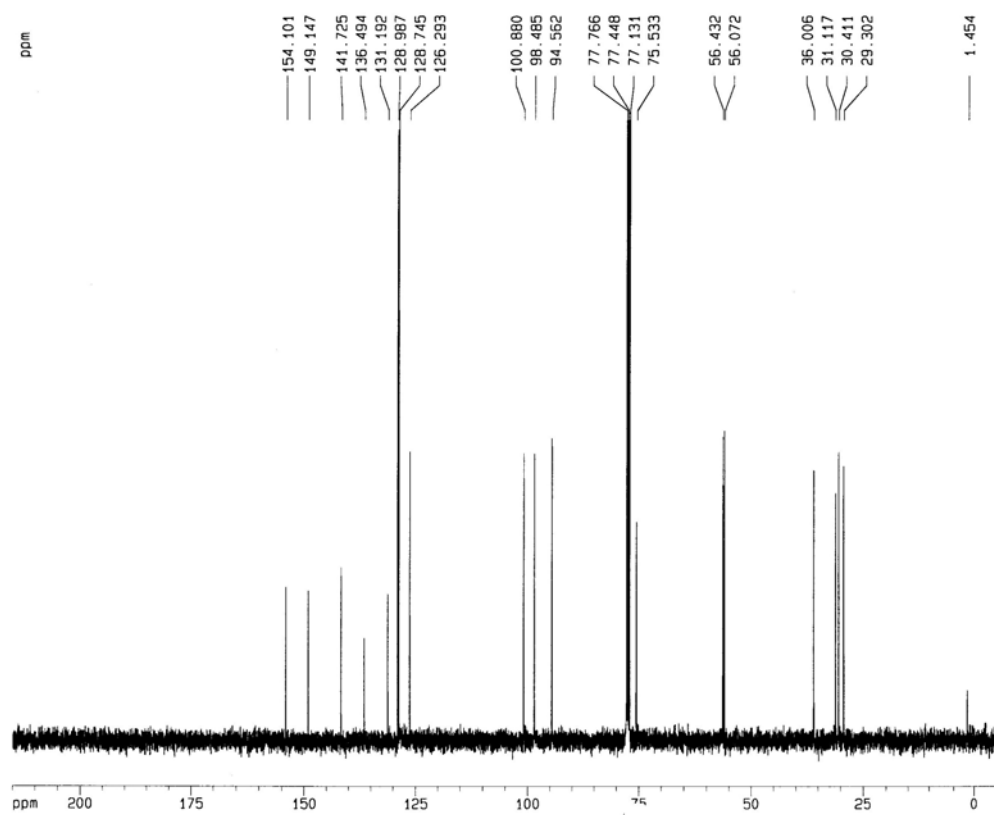
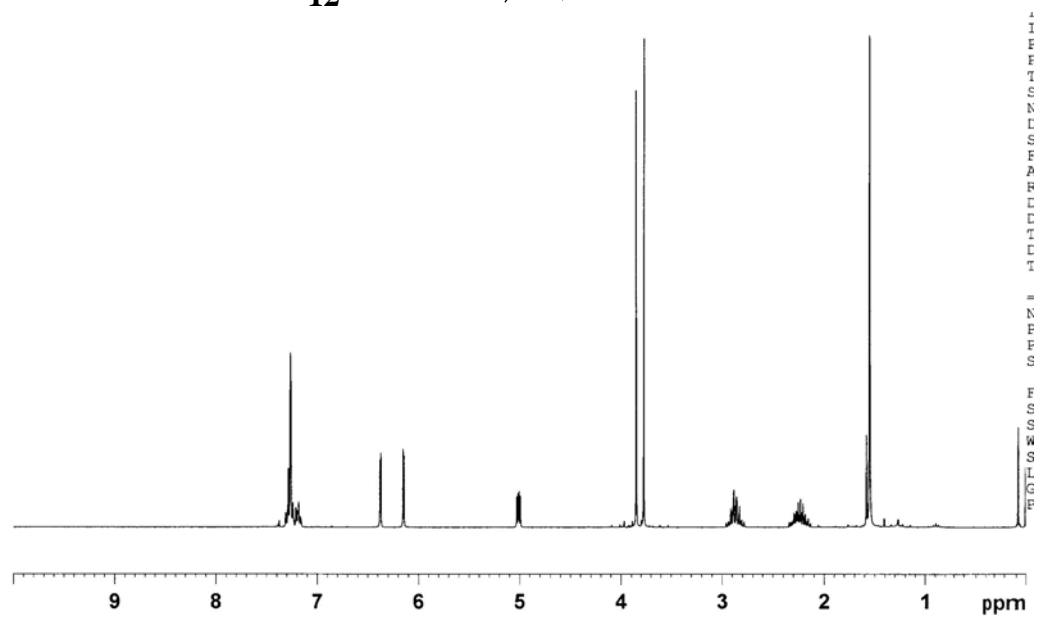
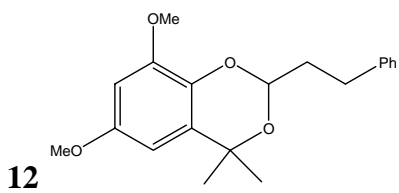
ppm

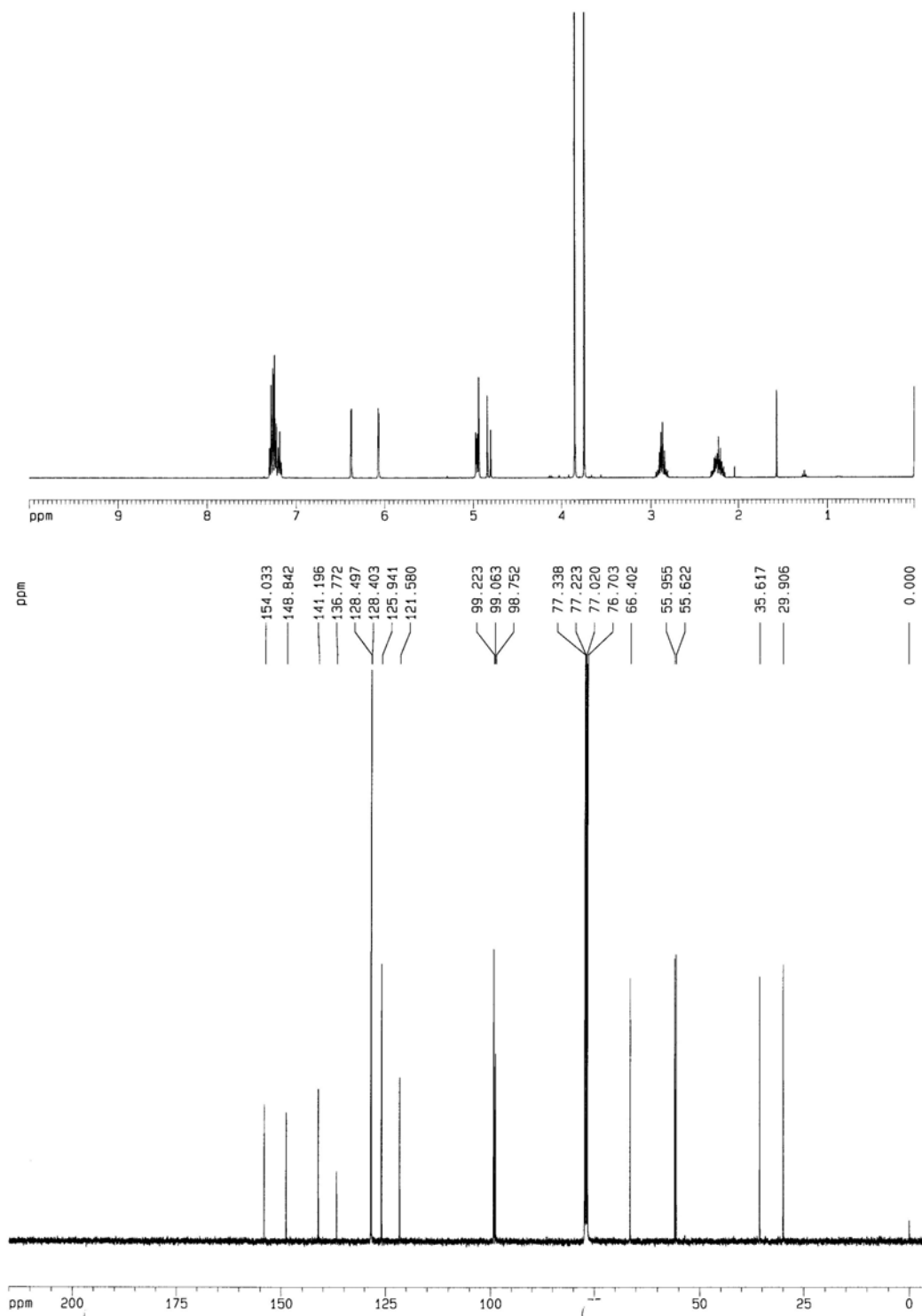
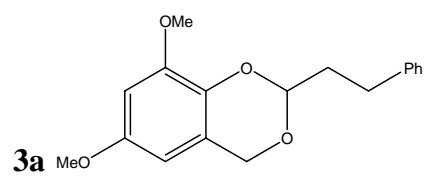
154.347  
147.378  
141.756  
128.950  
128.924  
126.448  
121.956  
117.857  
114.388  
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99.384  
77.950  
77.535  
77.112  
66.899  
56.112  
36.316  
30.289

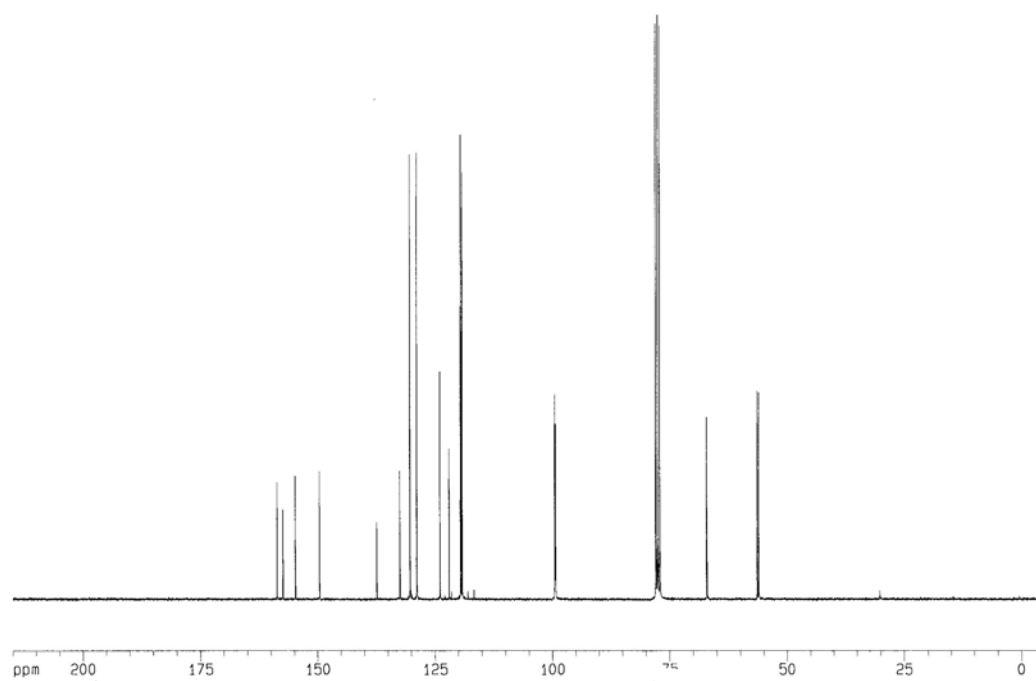
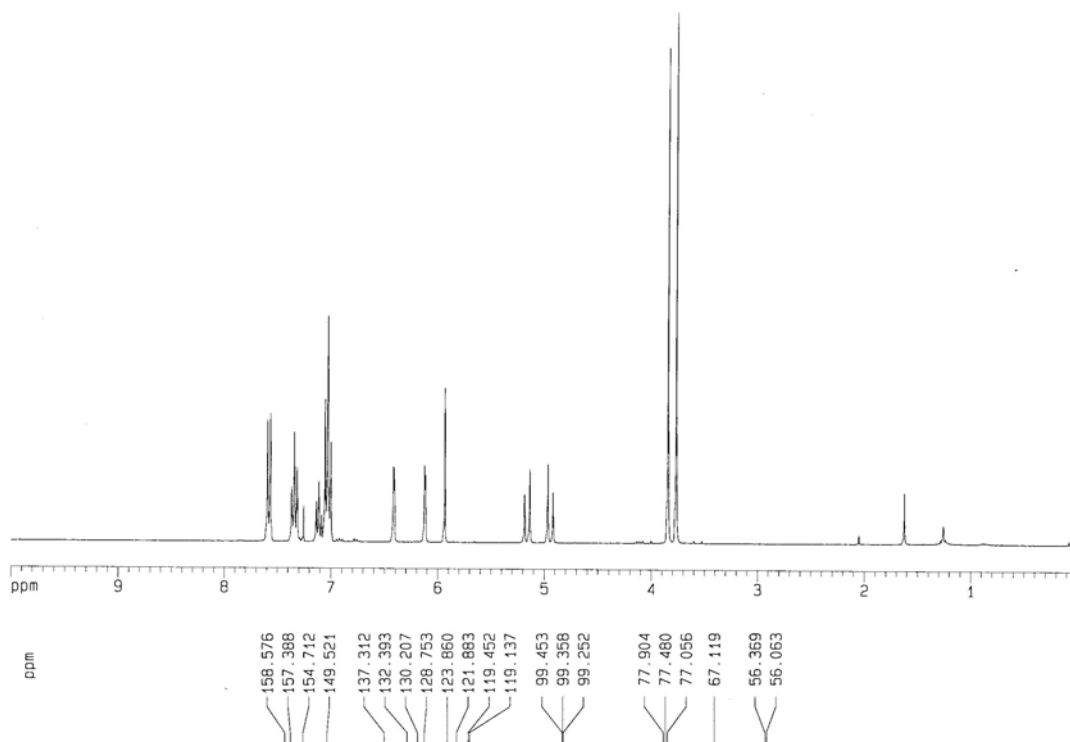
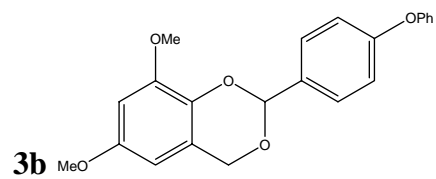


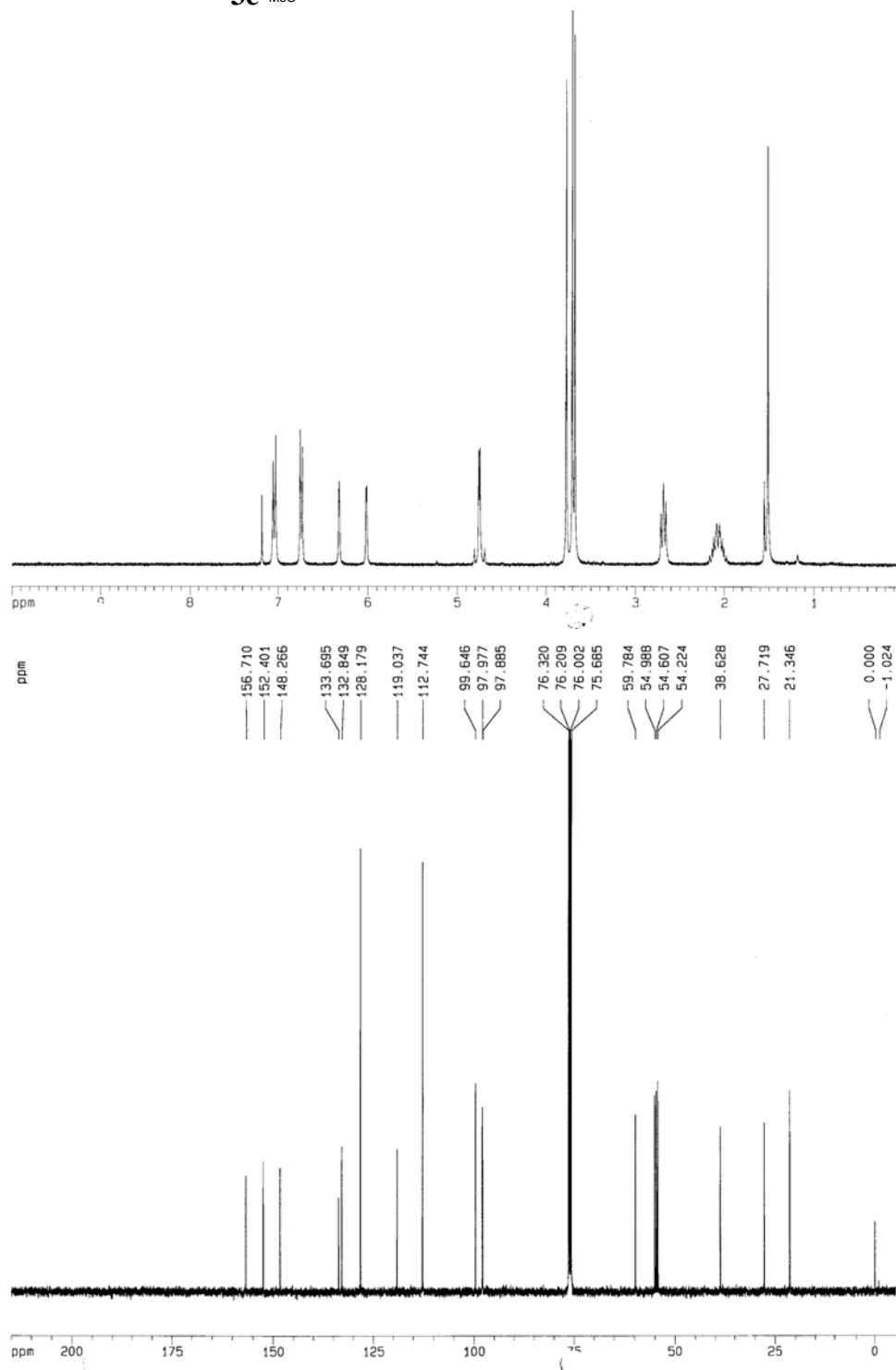
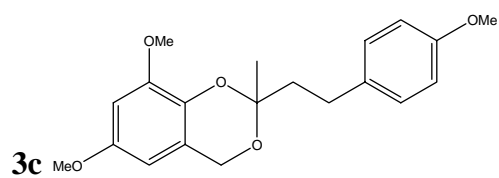




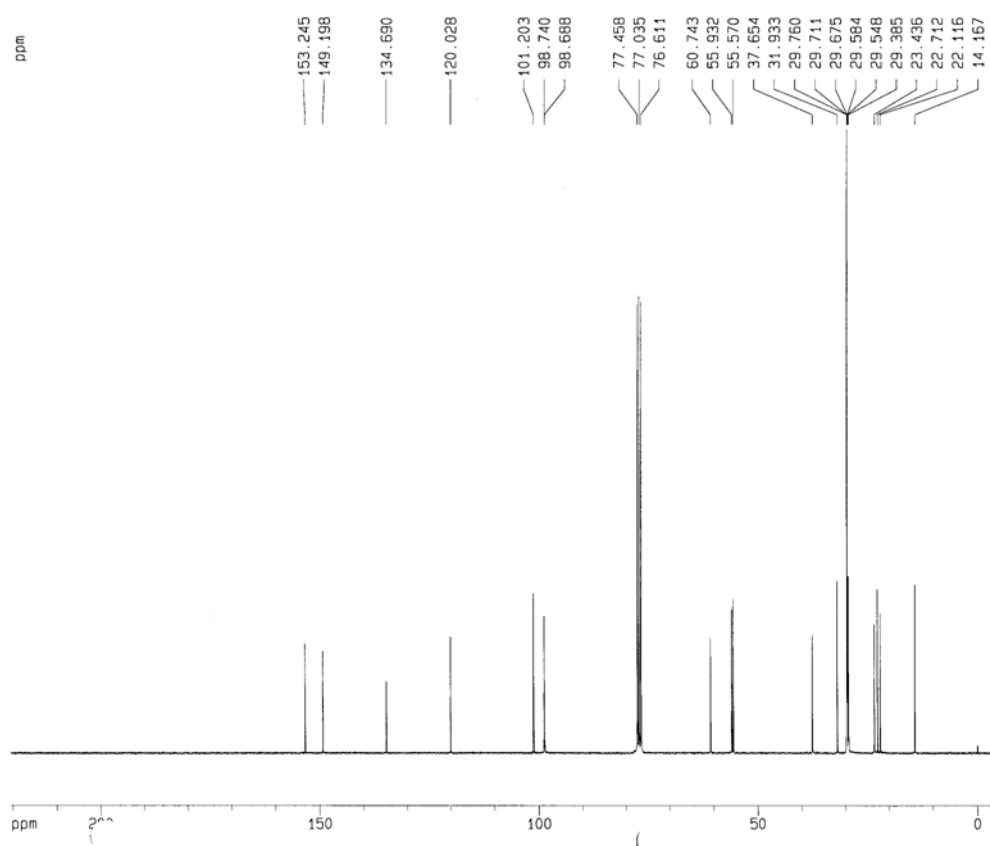
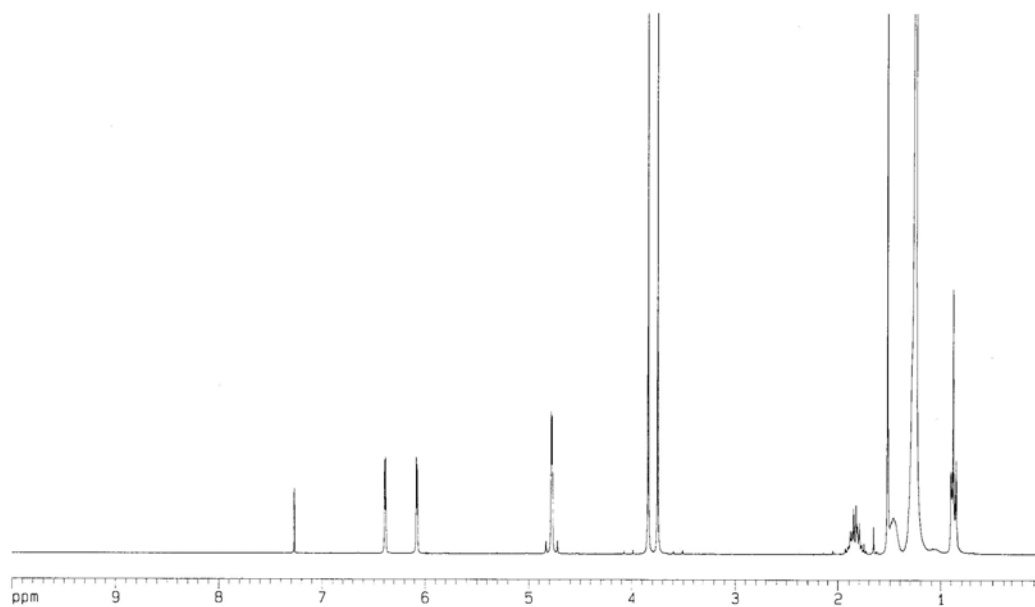
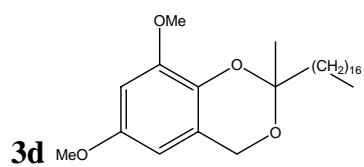


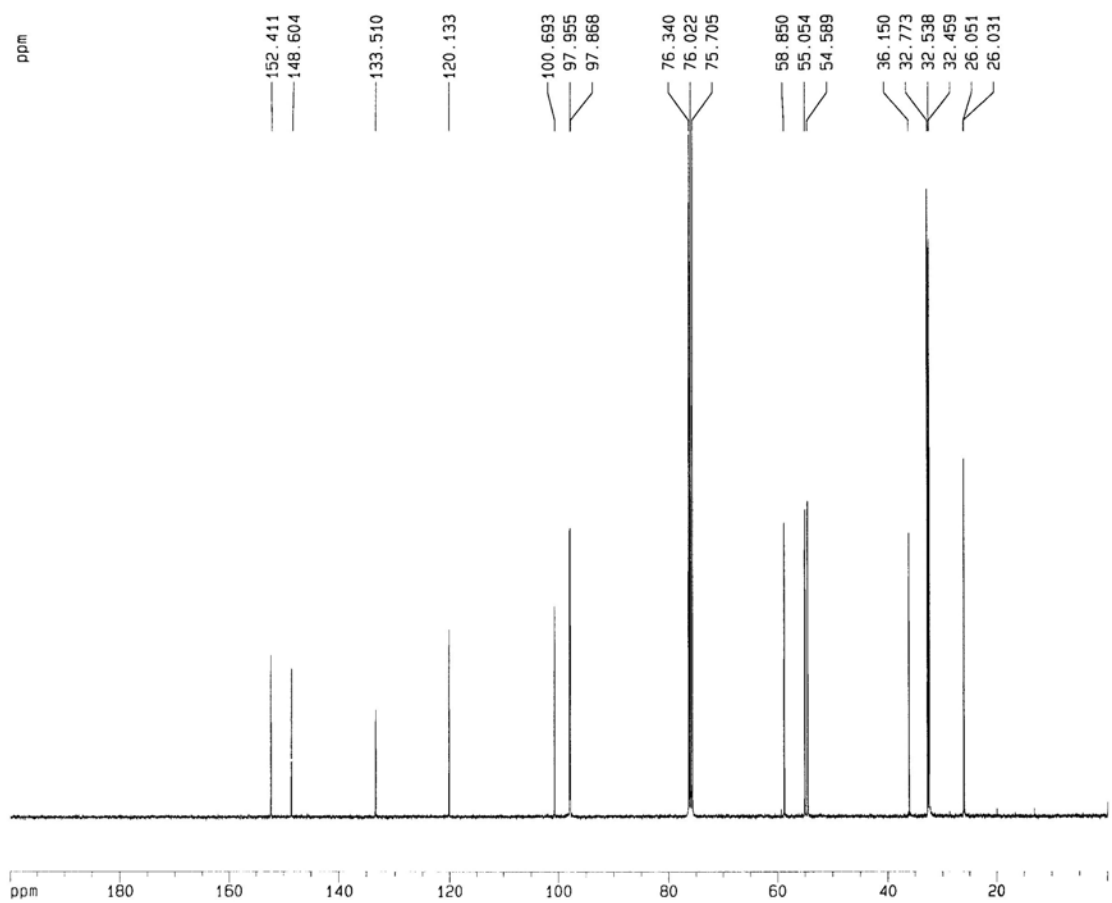
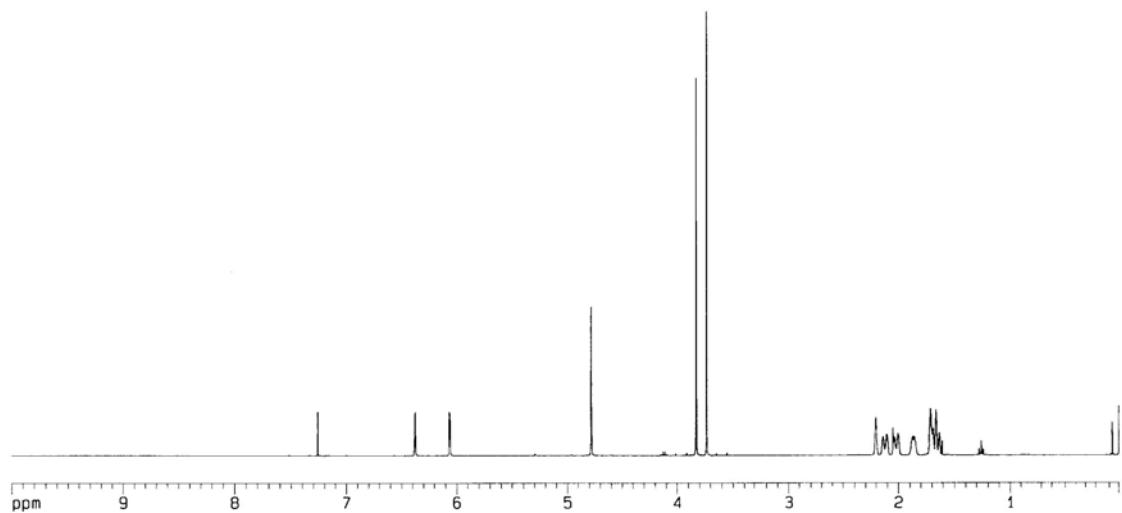
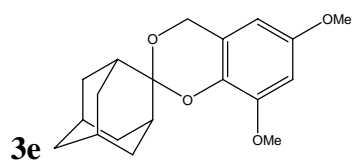


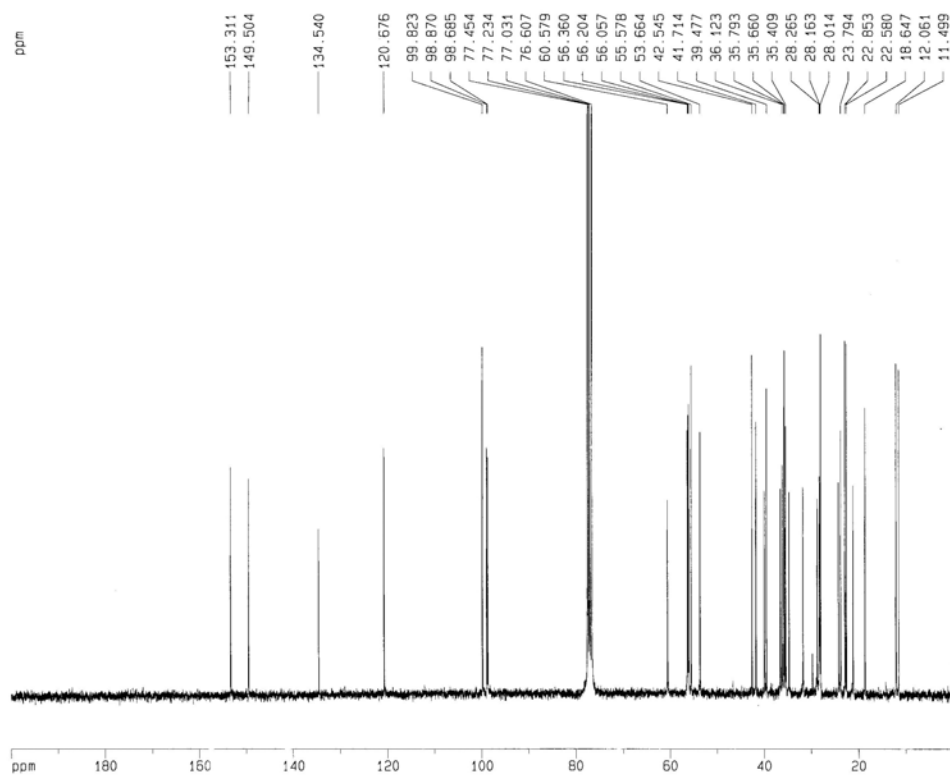
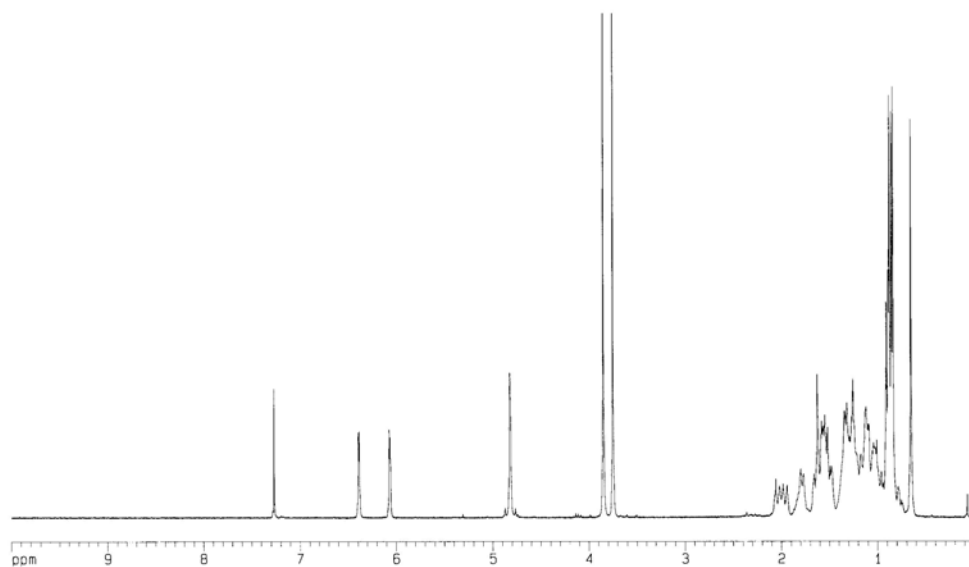
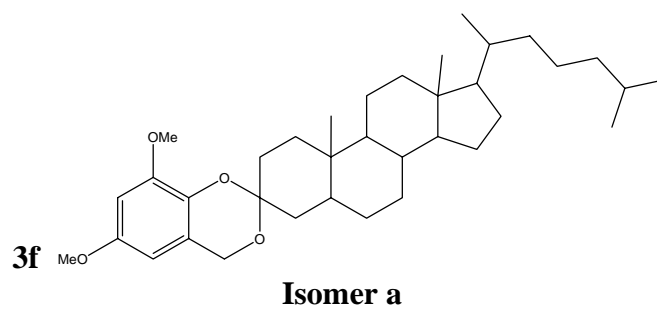












# Isomer b

