## Supporting Information.

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## **Experimental section**

**Compound 2d.** Compound **1** (0.16 g, 0.6 mmol) was treated as above but with 2,2diphenylacetic acid. Flash chromatography (pentane:Et<sub>2</sub>O, 75:25) gave 0.13 g (46%) of **2d**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz) 7.5-7.2 (m, 10 H), 6.08 (dd, J = 9.9, 4.7 Hz, 1 H), 5.96 (ddd, J = 9.9, 5.4, 2.2 Hz), 5.43 (br s, 1 H), 5.20 (td, J = 5.5, 3.3 Hz, 1H), 5.38 (s, 1 H), 3.74 (s, 6H), 3.57 (m, 1 H), 3.37 (td, J = 11.0, 6.3 Hz, 1H), 2.29 (br pent, J = 6.8 Hz, 1H), 1.55 (m, 2H), 1.10 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 75 MHz) 172.0, 170.3 (2C), 155.4, 138.7, 138.6, 131.7, 130.4, 128.8, 128.5, 128.4, 127.0, 125.3, 124.8, 118.6, 67.6, 65.9, 56.8, 52.5, 52.1, 45.0, 38.3, 27.8, 26.4, 21.2, 20.5 MS (EI): m/z = 167 (100), 157 (88).

**Compound 2e. 1** (0.16 g, 0.6 mmol) was treated as above but with 2-chloroacetic acid. Flash chromatography (pentane:Et<sub>2</sub>O, 75:25) gave 0.10 g (49%) of **2e**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz) 6.17 (dd, J = 9.9, 4.5 Hz, 1 H), 5.97 (ddd, J = 9.9, 5.3, 2.2 Hz, 1 H), 5.27 (br s, 1H), 5.20 (td, J = 5.5, 3.3 Hz, 1 H), 4.08 (s, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 3.59 (m, 1 H), 3.42 (td, J = 11.3, 6.4 Hz, 1H), 2.30 (br pent, J = 6.9 Hz, 1H), 1.55 (m, 2H), 1.10 (d, J = 6.7 Hz 3H), 1.03 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 100 MHz) 170.6 (2C), 167.2, 155.5, 132.7, 124.6, 119.0, 68.0, 67.6, 53.0, 52.6, 45.3, 41.4, 38.5, 28.1, 26.7, 21.6, 20.9 MS (EI): m/z = 212 (100), 157 (89).

**Compound 2f. 1** (0.16 g, 0.6 mmol) was treated as above but with 3-butenoic acid. Flash chromatography (pentane:Et<sub>2</sub>O, 75:25) gave 0.09 g (43%) of **2f**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz) 6.10 (dd, J = 10.3, 4.8 Hz, 1 H), 6.0-5.8 (m, 2 H), 5.44 (br s, 1H) 5.2-5.1 (m, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 3.58 (m, 1 H), 3.43 (td, J = 10.9, 7.1 Hz, 1H), 3.10 (d, J = 7.1 Hz, 2H), 2.29 (br pent, J = 6.8 Hz, 1H), 1.55 (m, 2H), 1.10 (d, J = 6.7 Hz 3H), 1.02 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 75 MHz) 171.2, 170.4, 155.4, 131.4, 128.8, 125.0, 118.6, 118.4, 65.4, 52.6, 52.2, 45.0, 44.4, 39.1, 38.3, 27.8, 26.5, 21.2, 20.5 MS (EI): *m/z* = 212 (100), 157 (84).

**Compound 2g. 1** (0.13 g, 0.5 mmol) was treated as above but with sorbic acid. Flash chromatography (pentane:Et<sub>2</sub>O, 75:25) gave 0.13 g (71%) of **2g**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz) 7.25 (m, 1H), 6.17 (m, 2H), 6.10 (dd, J = 10.1, 4.6 Hz), 1 H), 6.00 (ddd, J = 10.1, 5.5, 2.2 Hz, 1 H), 5.78 (d, J = 15.4 Hz, 1H), 5.44 (br s, 1H) 5.20 (dt, J = 5.3, 3.3 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.59 (m, 1 H), 3.47 (td, J = 11.9, 5.8 Hz, 1H), 2.32 (br pent, J = 7.1, 1H), 1.85 (d, J = 5.2 Hz, 3H), 1.57 (br s, 2H), 1.11 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 100 MHz) 170.4 (2C), 166.2, 155.5, 145.0, 139.3, 131.2, 129.6, 125.4, 119.0, 118.5, 67.8, 64.7, 52.5, 52.2, 45.0, 38.4, 27.8, 26.6, 21.2, 20.5, 18.5. MS (EI): m/z = 212 (100), 157 (84).

**Compound 2h. 1** (0.060 g, 0.22 mmol) was treated as above but with pentafluorophenol. Flash chromatography (pentane:Et<sub>2</sub>O, 90:10) gave 0.044 g (44%) of **2h**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz) 6.19 (dd, J = 9.8, 3.7 Hz, 1H), 5.94 (dd, J = 9.8, 5.1 Hz, 1 H), 5.47 (br s, 1H), 4.54 (td, J = 5.1, 3.0 Hz, 1H), 3.8-3.6 (m including singlets at 3.72 and 3.70, 8H), 2.28 (br pent, J = 6.8 Hz, 1H), 1.8-1.4 (m, 2H), 1.11 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 100 MHz) 170.7, 170.5, (Aromatic carbons are not clearly detectable due to C-F coupling), 155.5, 133.4, 124.7, 119.2, 76.0 (broaden due to C-F coupling), 68.0, 52.9, 52.4, 45.6, 38.2, 28.2, 27.3, 21.6, 20.9.; MS (EI): m/z = 341 (10), 217 (48), 157 (100).

**Compound 2i.** To a solution of **1** (0.075 g, 0.27 mmol) in 3 mL of BnOH was added lithium carbonate (0.07 g, 1.0 mmol) and Pd(dba)<sub>2</sub> (0.008 g, 0.014 mmol). The reaction was stirred at room temperature for 24 h. H<sub>2</sub>O was added and the aqueous layer extracted with Et<sub>2</sub>O (3 x 30 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), evaporation followed by flash chromatography (pentane:Et<sub>2</sub>O, 1:1) bulb to

bulb distillation and again flash chromatography (pentane:Et<sub>2</sub>O, 1:1) gave 0.055 g (53%) of **2i**. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz) 8.03 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.0 Hz, 2H), 6.12 (m, 2H), 5.48 (br s, 1 H), 5.38 (td, J = 5.0, 3.3 Hz, 1 H), 3.74 (s, 3H), 3.71 (s, 3H), 3.65 (m, 1 H), 3.55 (m, 1H), 2.35 (br pent, J = 6.8 Hz, 1H), 1.7-1.6 (m, 2H), 1.13 (d, J = 6.7 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H); MS (EI): m/z = 197 (17), 107 (40), 91 (100).

**Compound 2j and 2j'. 1** (0.075 g, 0.27 mmol) was treated using the general procedure as for **2a**. Flash chromatography (pentane:Et<sub>2</sub>O, 75:25) gave 0.082 g (78%) of a mixture of **2j** (55%) and **2j'** (45%) (unseparable on HPLC). <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz) 7.45 (m, 2H), 7.35 (m, 3H), 6.10 (dd, J = 9.8, 3.3 Hz, 0.5H), 5.98 (d, J = 3.0 Hz, 1H), 5.87 (dd, J = 9.8, 5.7, 2.1 Hz, 0.5H), 5.42 (br s, 1H), 3.9-3.4 (m, 8H, including singlets at 3.74, 3.70 and 3.57), 3.00 (br d, J = 16.6 Hz, 1 H), 2.80 (br d, J = 16.3 Hz, 1 H), 2.32 (br pent, J = 6.8 Hz, 1H), 1.70 (br s, 3H), 1.62 (br s, 3H), 1.6-1.4 (m, 2H), 1.11 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub> 100 MHz) 170.4, 156.6, 135.1, 132.9, 132.8, 131.4, 131.0, 128.8, 128.7, 128.3, 127.6, 127.2, 125.5, 124.8, 118.2, 67.8, 62.5, 52.6, 52.5, 52.1, 45.2, 43.4, 43.0, 41.0, 38.4, 37.9, 36.5, 29.5, 27.7, 26.6, 26.0, 22.0, 21.2, 21.0, 20.5. MS (EI): m/z = first peak: 386 (15), 277 (35), 217 (70), 157 (100), second peak: 386 (10), 277 (22), 258 (70), 217 (55), 157 (100).

**Compound 3c.** The reaction was carried out as above, using benzoic acid as nucleophile, to give **3c** in 50% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz) 8.05(dd, J = 8.4, 1.4 Hz, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 6.24 (ddd, J = 10.4, 4.0, 1.0 Hz, 1H), 5.97 (ddd, J = 10.2, 4.6, 2.5 Hz, 1H) 5.77 (d, J = 2.4 Hz, 1H) 5.36 (q, J = 4.5 Hz, 1H), 5.12 (bs, 1H), 5.10 (s, 1H), 3.84 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.65 (m, 1H) 1.98 (ddd, J = 13.9, 10.4, 4.4 Hz, 1H) 1.96 (s, 3H), 1.82 (dt, J = 13.8, 10.0, 5.0 Hz, 1H);

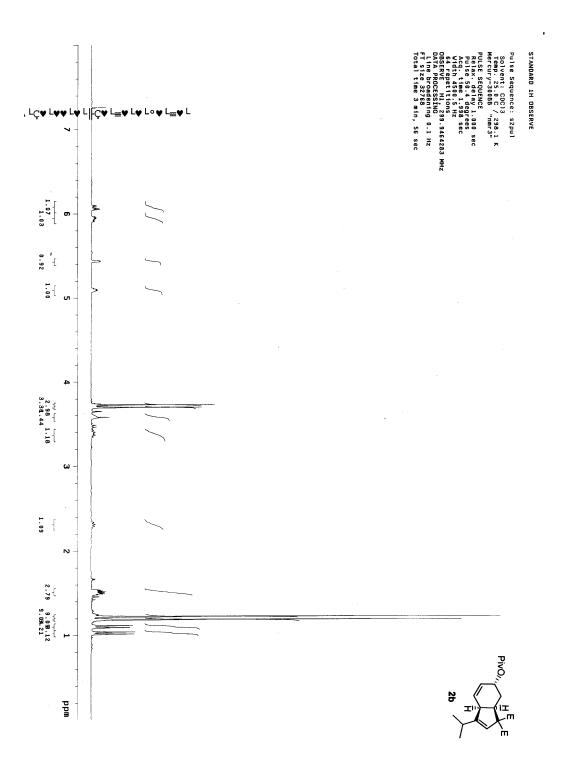
<sup>13</sup>C NMR (CDCl<sub>3</sub> 75 MHz) 170.7, 170.3, 166.2, 149.0, 138.5, 133.1, 131.7, 130.6, 129.8, 128.5, 125.5, 124.2, 115.4, 68.2, 65.8, 53.0, 52.8, 44.2, 39.1, 27.4, 21.7. Anal. Calcd. for C<sub>23</sub>H<sub>24</sub>O<sub>6</sub>: C, 69.68; H, 6.10. Found: C, 69.64; H, 6.20.

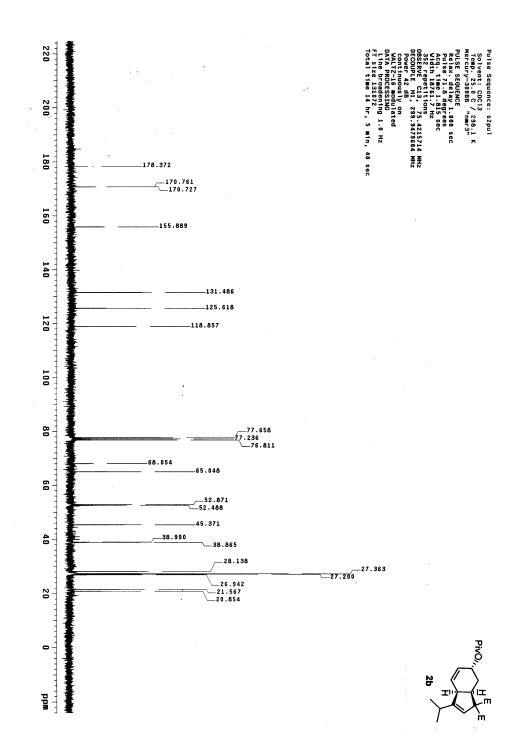
**Compound 3d.** The reaction was carried out as above, using propionic acid as nucleophile, to give **3d** in 42% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300MHz) 6.18 (ddd, J = 10.3, 3.9, 0.9 Hz, 1H), 5.83 (ddd, J = 10.2, 4.5, 2.5 Hz, 1H), 5.73 (d, J = 2.3 Hz, 1H) 5.10 (consealed q,  $J \sim 4.8$  Hz, 1H), 5.09 (bs, 1H), 5.07 (bs, 1H) 3.77 (s, 3H) 3.75 (m, 1H) 3.72 (s, 3H), 3.55 (ddd, J = 15.3, 6.7, 5.1 Hz, 1H), 2.32 (q, J = 7.6 Hz, 2H), 1.93 (s, 3H), 1.87 (ddd, J = 14.6, 10.3, 4.61 Hz, 1H), 1.66 (m, 1H) 1.13 (t, J = 7.54 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 75 MHz): 174.2, 170.7, 170.3, 149.0, 138.5, 131.4, 125.6, 124.2, 115.4, 68.2, 65.0, 53.0, 52.8, 44.1, 39.0, 29.8, 27.9, 27.2, 21.6.

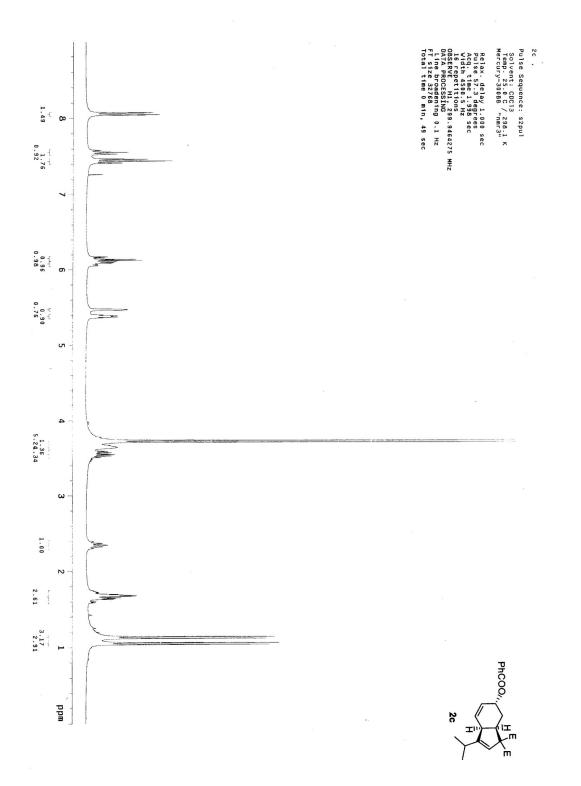
**Compound 3e.** The reaction was carried out as above, using 3-butenoic acid as nucleophile, to give **3e** in 19% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub> 300 MHz): 6.19 (ddd, J = 10.2, 3.9, 1.0 Hz, 1H), 5.84 (ddd, J = 10.4, 4.6, 2.4 Hz, 1H), 5.74 (d, J = 2.4 Hz, 1H), 5.17 (m, 3H), 5.11 (br s, 1H), 5.07 (s, 1H), 3.75 (m, 7H), 3.55 (ddd, J = 10.0, 6.8, 5.2 Hz, 1H), 3.09 (dt J = 6.9, 1.5 Hz, 2H), 1.99 (s, 3H), 1.89 (m, 1H), 1.67 (dt, J = 14.0, 5.1 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 75 MHz): 171.4, 170.8, 170.4, 149.0, 138.5, 131.6, 130.5, 125.5, 124.3, 118.8, 115.5, 68.2, 65.6, 53.1, 52.9, 44.1, 39.5, 39.1, 27.3, 21.7.

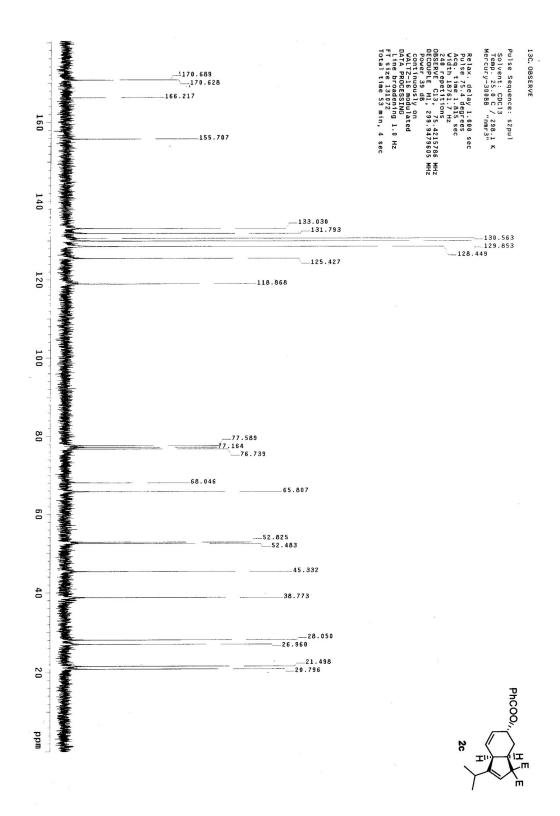
**Compound 3f.** The reaction was carried out as above, using 2-methyl-propionic acid as nucleophile, to give **3f** in 15% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz): 6.17 (dd, J = 10.3, 3.9 Hz, 1H), 5.82 (ddd, J = 10.3, 4.4, 2.5 Hz, 1H) 5.74 (d, J = 2.3 Hz, 1H), 5.09 (m,3H), 3.78 (s, 3H), 3.76 (m, 1H), 3.73 (s, 3H), 3.54 (ddd, J = 11.9, 9.9, 6.9 Hz, 1H), 2.54 (hept, J = 7.0 Hz, 1H), 1.93 (s, 3H), 1.89 (ddd, J = 14.5, 9.9, 4.6 Hz, 1H) 1.65 (ddd, J = 13.9, 10.2, 4.9 Hz, 1H) 1.16 (d, J = 2.6 Hz, 3H) 1.15 (d, J = 2.6 Hz,

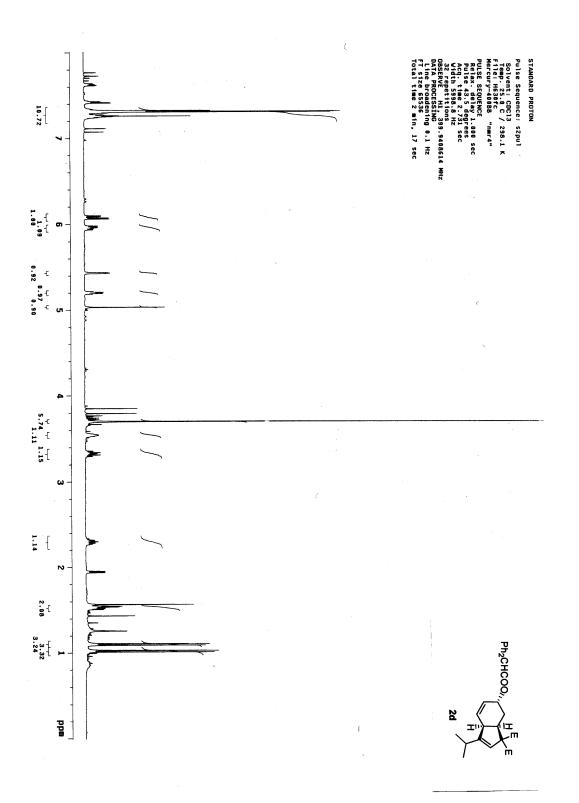
3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 400 MHz): 176.9, 170.8, 170.3, 149.0, 138.4, 131.3, 125.6, 124.2, 115.4, 68.1, 64.9, 53.0, 52.9, 44.0, 39.1, 34.1, 27.2, 21.6, 19.2, 19.1.

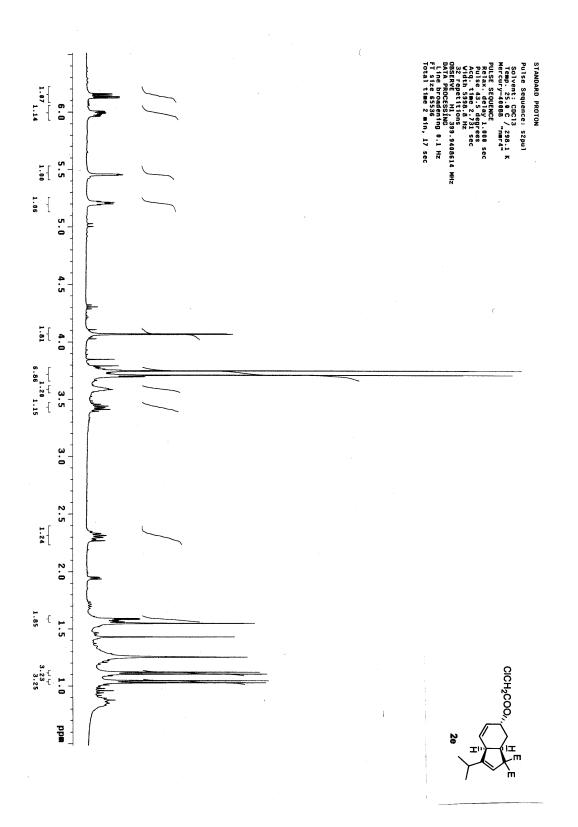


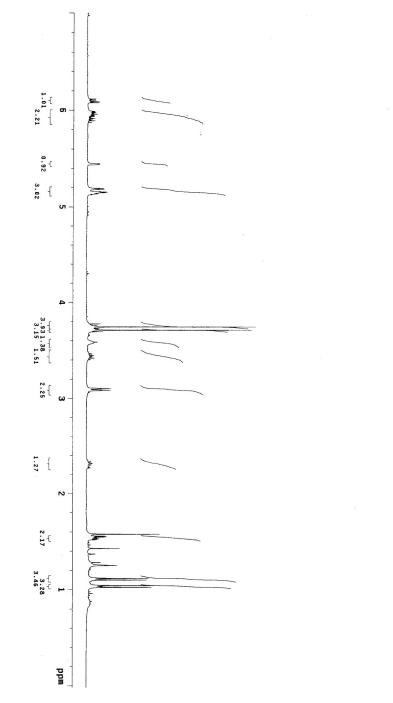




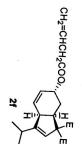


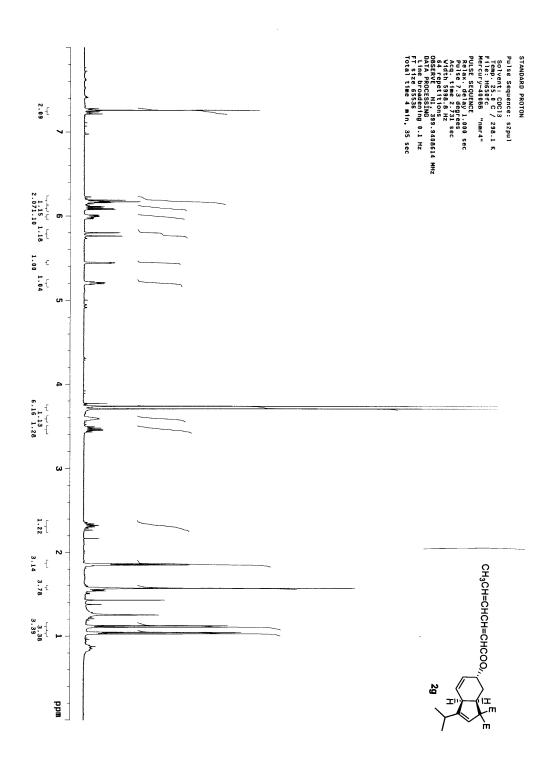


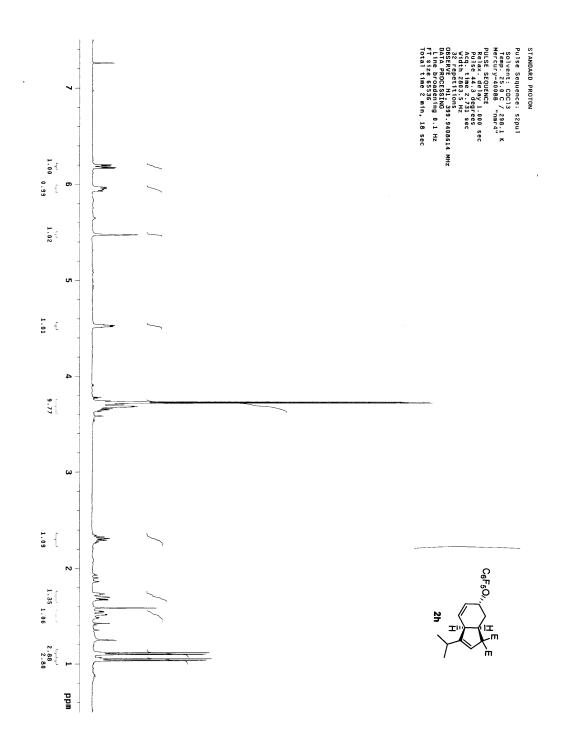


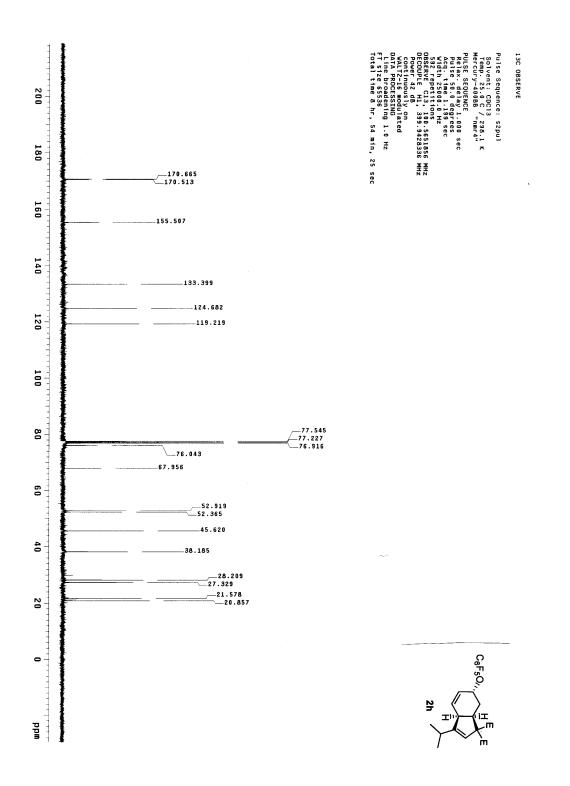


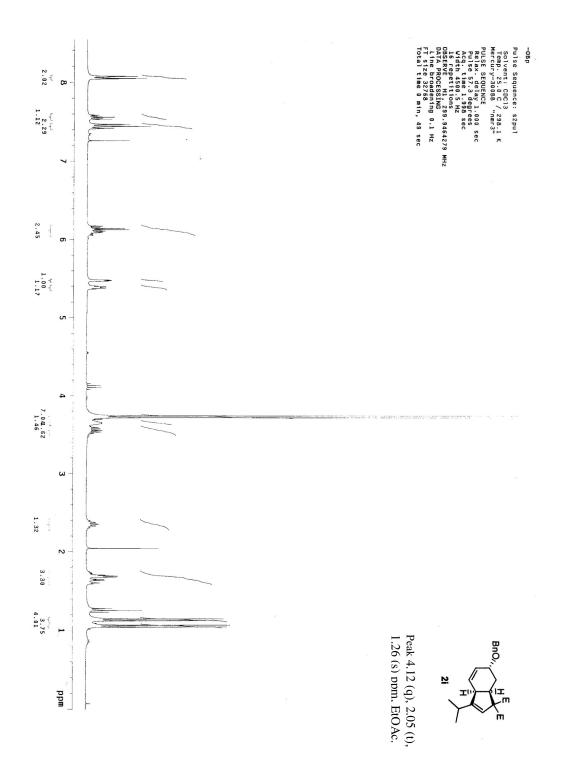
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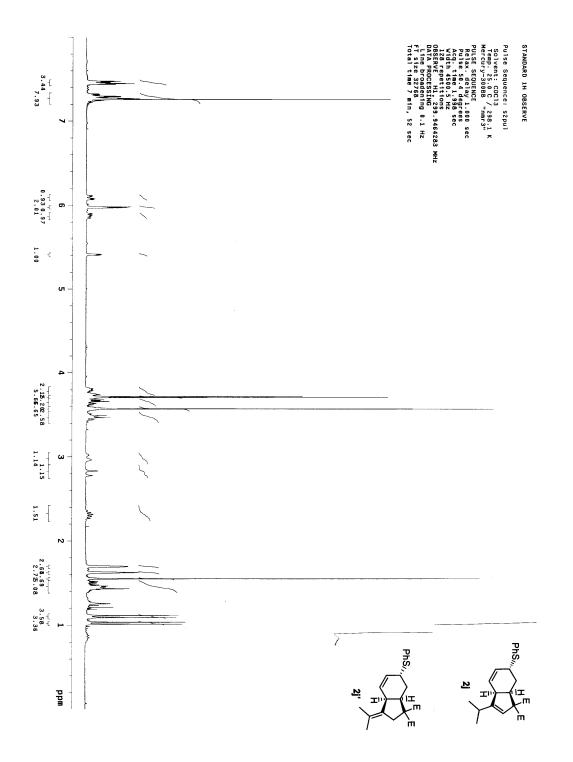


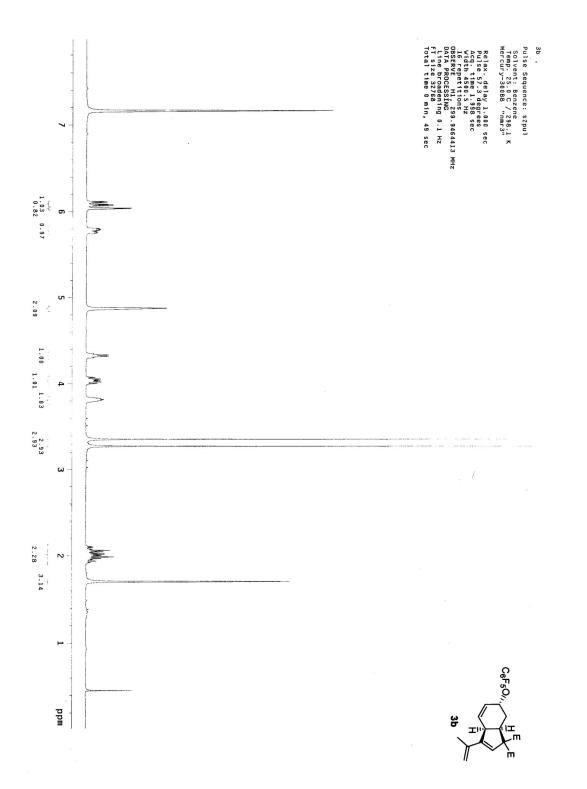


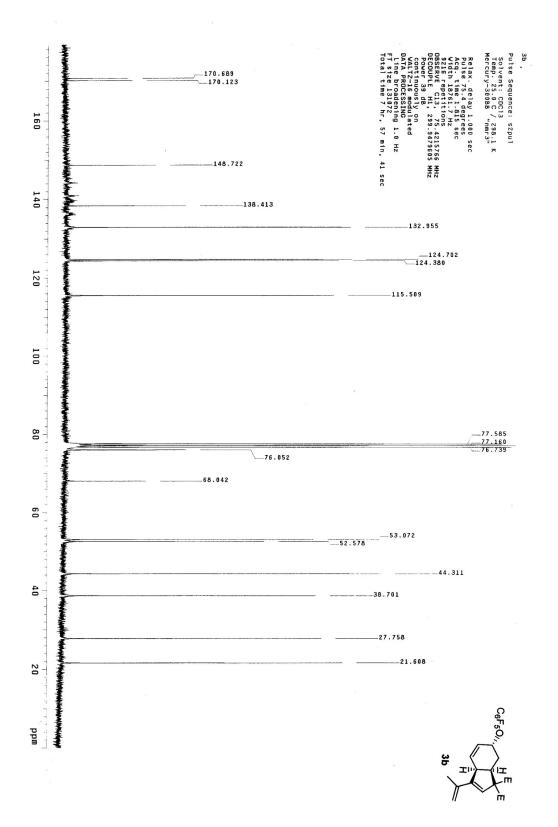


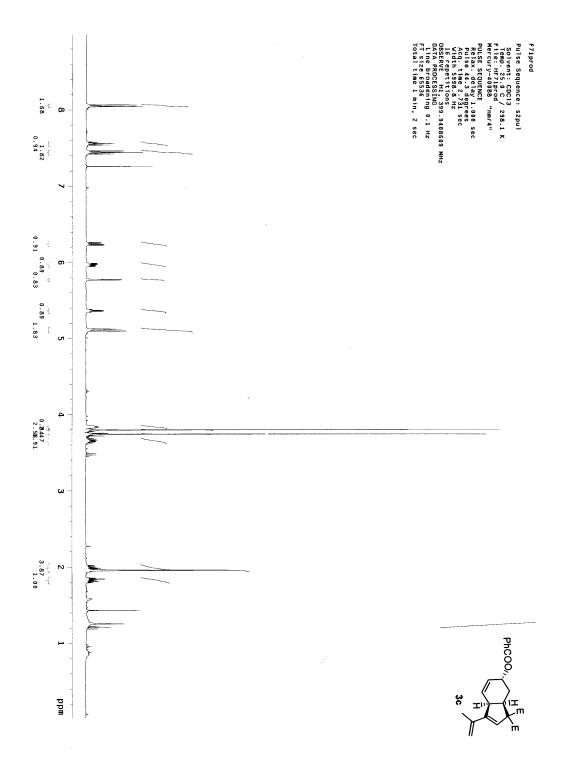


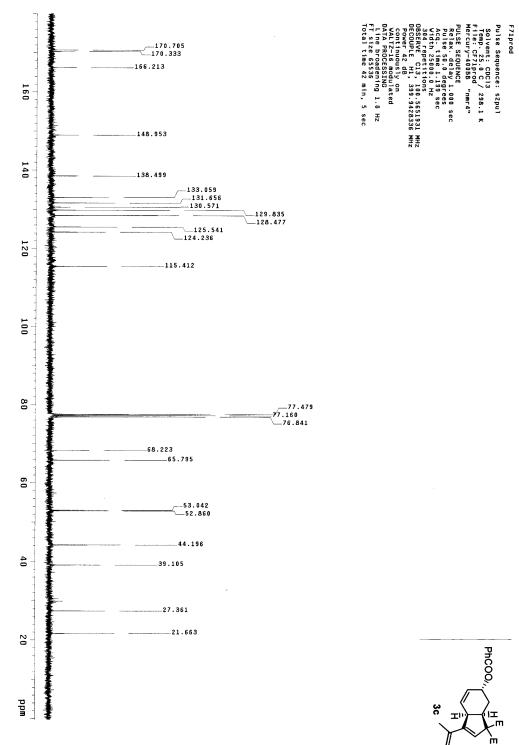












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