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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:Et₂O, 75:25) gave 0.13 g (46%) of **2d**. ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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:Et₂O, 75:25) gave 0.10 g (49%) of **2e**. ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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:Et₂O, 75:25) gave 0.09 g (43%) of **2f**. ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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:Et₂O, 75:25) gave 0.13 g (71%) of **2g**. ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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:Et₂O, 90:10) gave 0.044 g (44%) of **2h**. ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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)₂ (0.008 g, 0.014 mmol). The reaction was stirred at room temperature for 24 h. H₂O was added and the aqueous layer extracted with Et₂O (3 x 30 mL). The combined organic layers were dried (Na₂SO₄), evaporation followed by flash chromatography (pentane:Et₂O, 1:1) bulb to

bulb distillation and again flash chromatography (pentane:Et₂O, 1:1) gave 0.055 g (53%) of **2i**. ¹H NMR (CDCl₃ 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:Et₂O, 75:25) gave 0.082 g (78%) of a mixture of **2j** (55%) and **2j'** (45%) (unseparable on HPLC). ¹H NMR (CDCl₃ 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); ¹³C NMR (CDCl₃ 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. ¹H NMR (CDCl₃ 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);

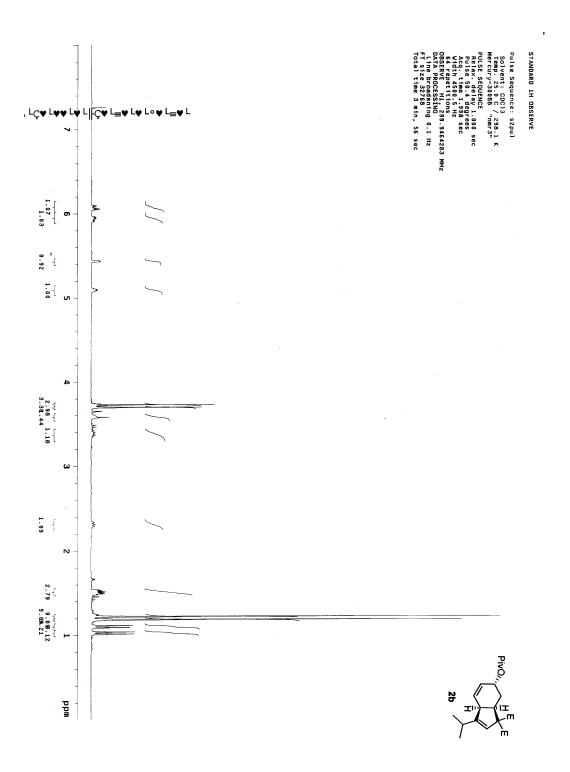
¹³C NMR (CDCl₃ 75 MHz) 170.7, 170.3, 166.2, 149.0, 138.5, 133.1, 131.7, 130.6, 129.8, 128.5, 125.5, 124.2, 115.4, 68.2, 65.8, 53.0, 52.8, 44.2, 39.1, 27.4, 21.7. Anal. Calcd. for C₂₃H₂₄O₆: C, 69.68; H, 6.10. Found: C, 69.64; H, 6.20.

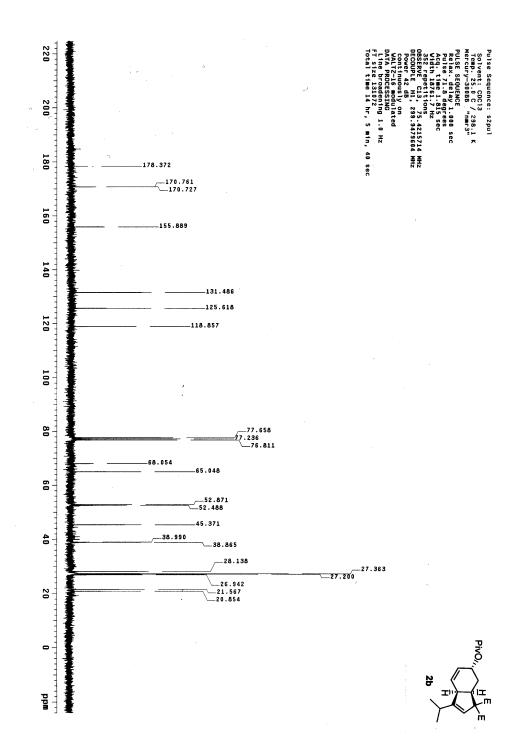
Compound 3d. The reaction was carried out as above, using propionic acid as nucleophile, to give **3d** in 42% yield. ¹H NMR (CDCl₃ 300MHz) 6.18 (ddd, J = 10.3, 3.9, 0.9 Hz, 1H), 5.83 (ddd, J = 10.2, 4.5, 2.5 Hz, 1H), 5.73 (d, J = 2.3 Hz, 1H) 5.10 (consealed q, $J \sim 4.8$ Hz, 1H), 5.09 (bs, 1H), 5.07 (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). ¹³C NMR (CDCl₃ 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.

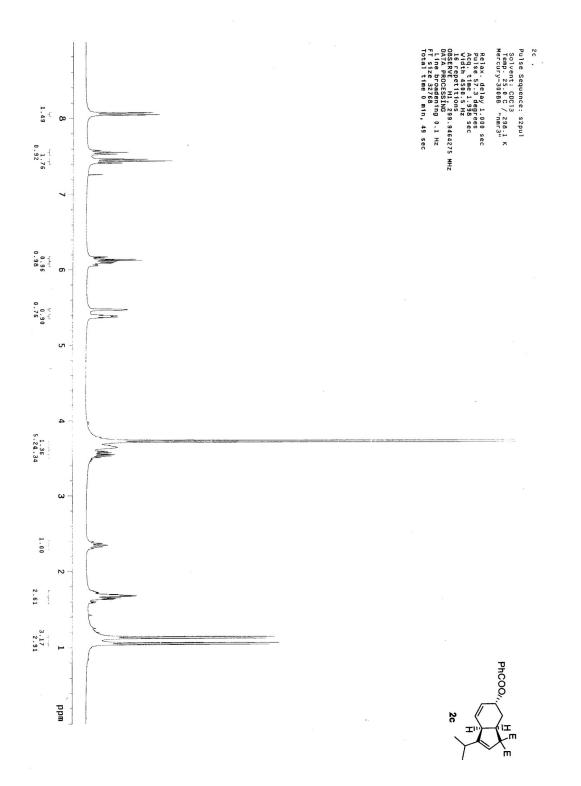
Compound 3e. The reaction was carried out as above, using 3-butenoic acid as nucleophile, to give **3e** in 19% yield. ¹H NMR (CDCl₃ 300 MHz): 6.19 (ddd, J = 10.2, 3.9, 1.0 Hz, 1H), 5.84 (ddd, J = 10.4, 4.6, 2.4 Hz, 1H), 5.74 (d, J = 2.4 Hz, 1H), 5.17 (m, 3H), 5.11 (br s, 1H), 5.07 (s, 1H), 3.75 (m, 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). ¹³C NMR (CDCl₃ 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.

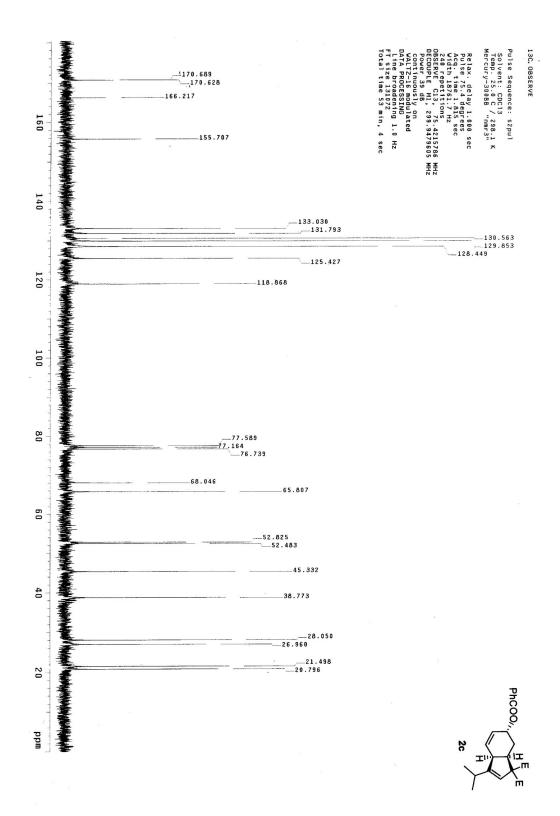
Compound 3f. The reaction was carried out as above, using 2-methyl-propionic acid as nucleophile, to give **3f** in 15% yield. ¹H NMR (CDCl₃ 400 MHz): 6.17 (dd, J = 10.3, 3.9 Hz, 1H), 5.82 (ddd, J = 10.3, 4.4, 2.5 Hz, 1H) 5.74 (d, J = 2.3 Hz, 1H), 5.09 (m,3H), 3.78 (s, 3H), 3.76 (m, 1H), 3.73 (s, 3H), 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,

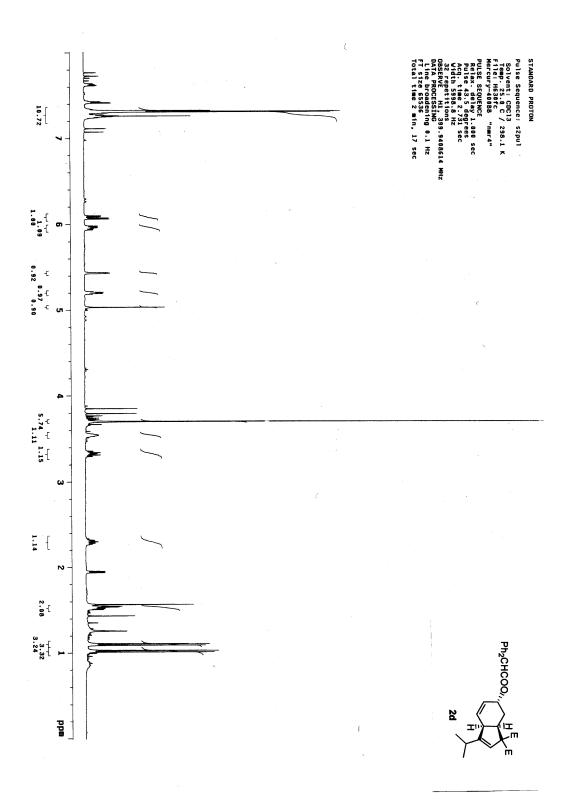
3H). ¹³C NMR (CDCl₃ 400 MHz): 176.9, 170.8, 170.3, 149.0, 138.4, 131.3, 125.6, 124.2, 115.4, 68.1, 64.9, 53.0, 52.9, 44.0, 39.1, 34.1, 27.2, 21.6, 19.2, 19.1.

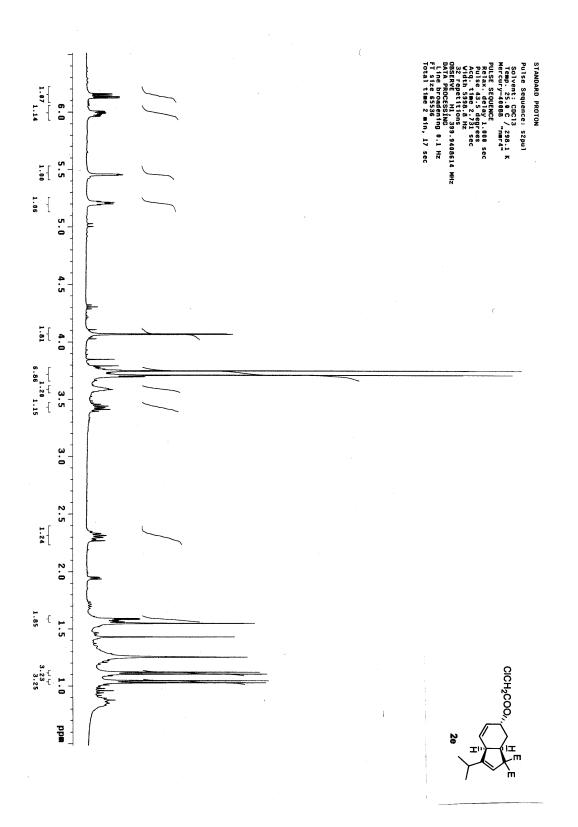


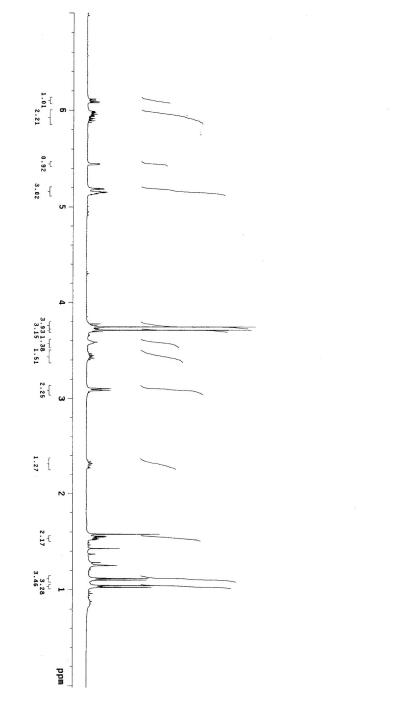




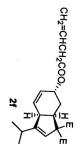


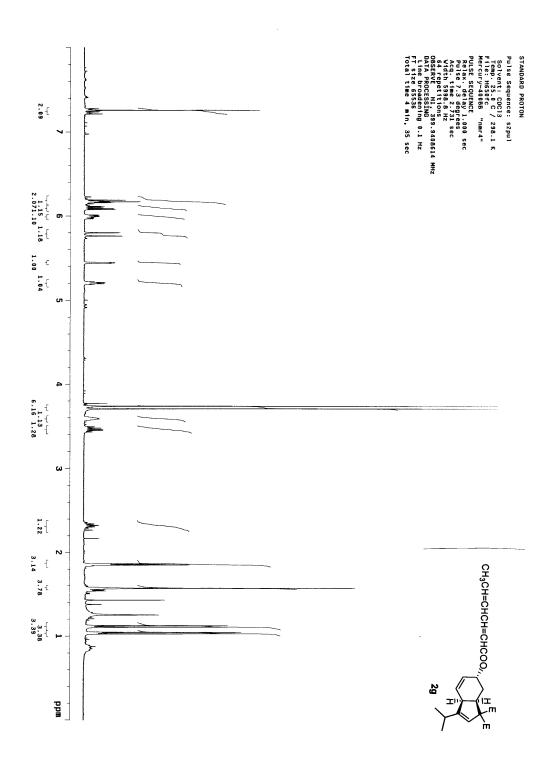


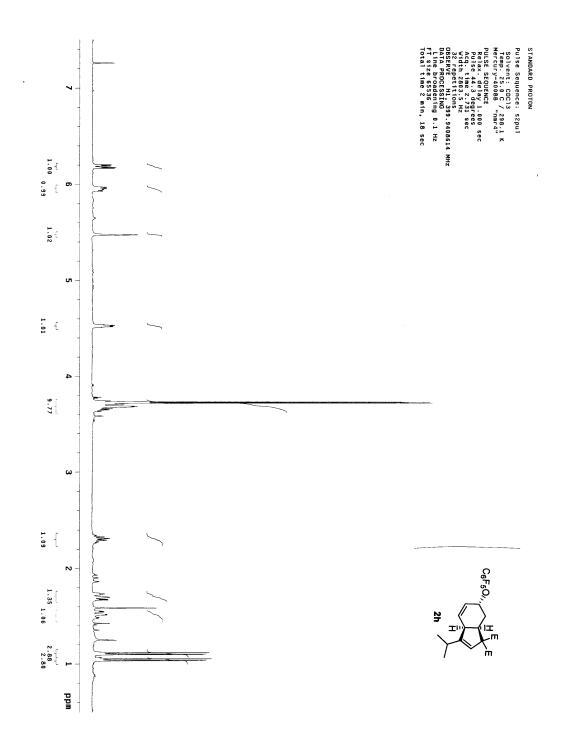


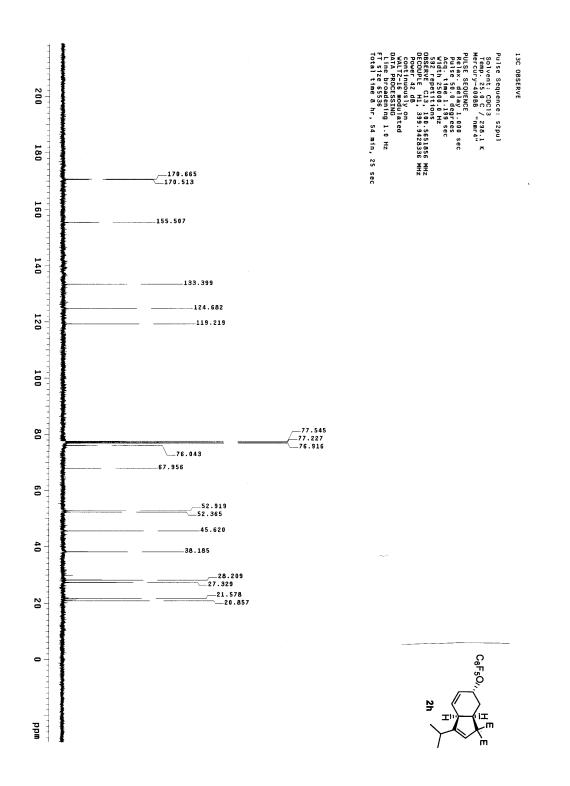


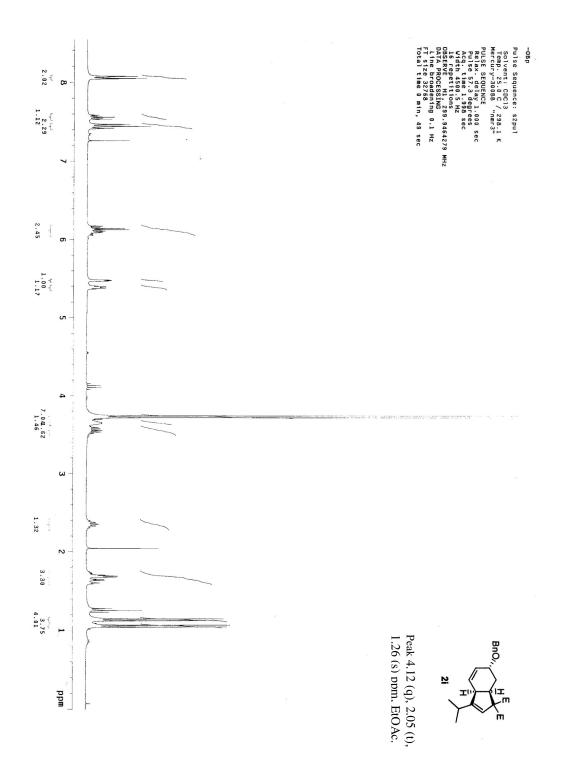
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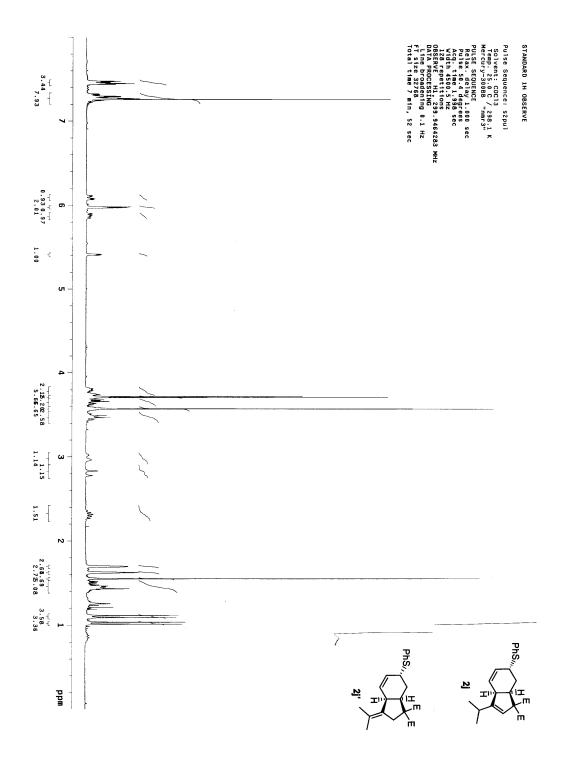


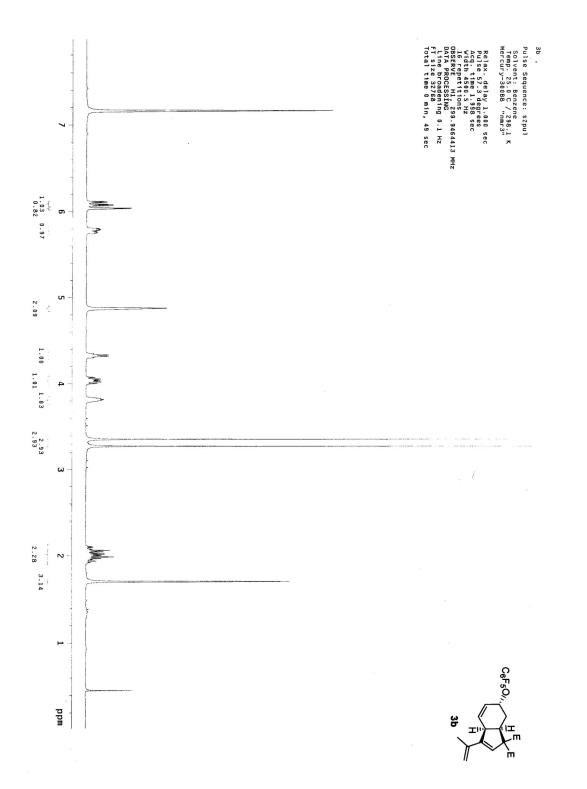


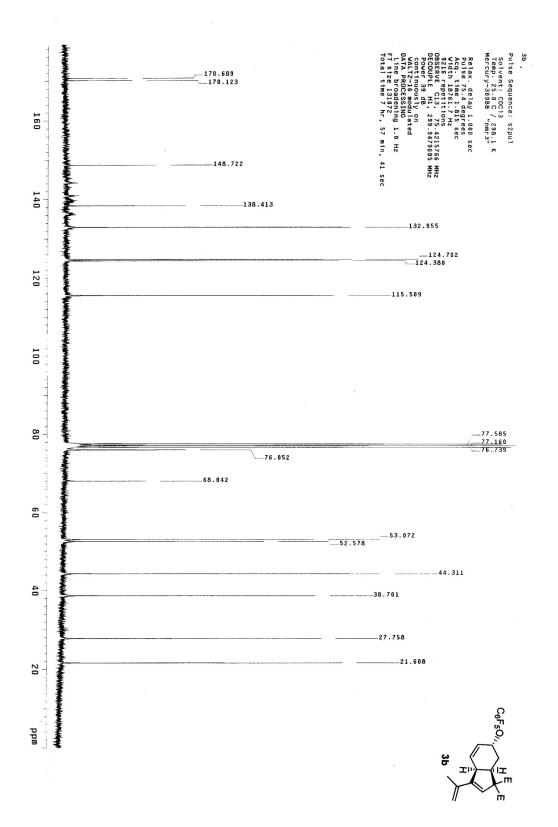


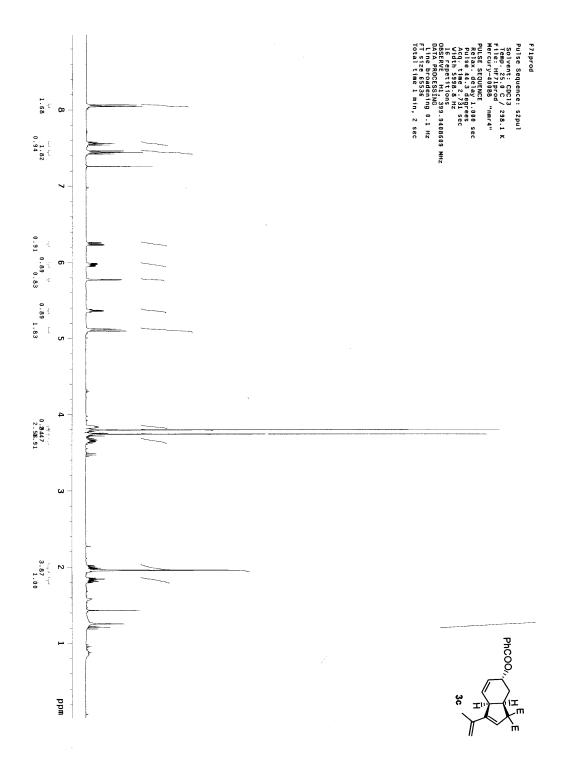


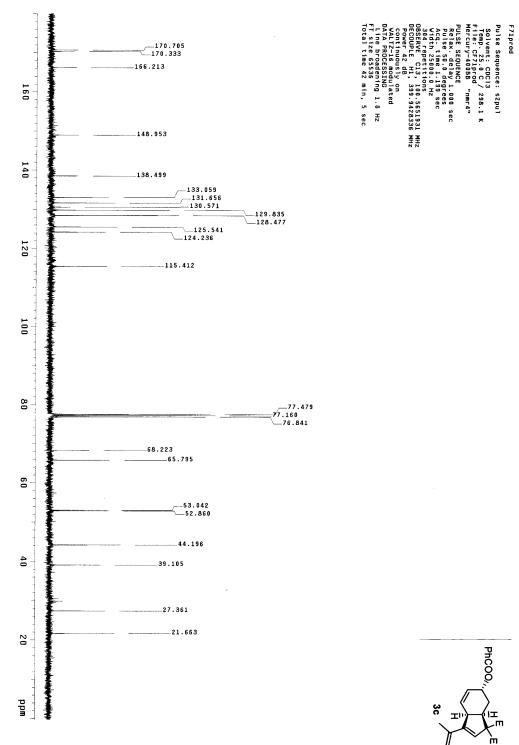












S22

