Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z53535

69451 Weinheim, Germany

A Novel 1,2-Migration of Acyl, Phosphatyl, and Sulfonyl Groups in Allenes: Efficient Synthesis of Tri- and Tetrasubstituted Furans

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Instrumentation. NMR spectra were recorded on Bruker Avance DPX-400 (400 MHz) and Bruker Avance DRX-500 (500 MHz) instruments. GC/MS analyses were performed on a Hewlett-Packard Model 6890 GC interfaced to a Hewlett-Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Elemental analyses were performed at Midwest Microlabs, Indianapolis, Indiana.

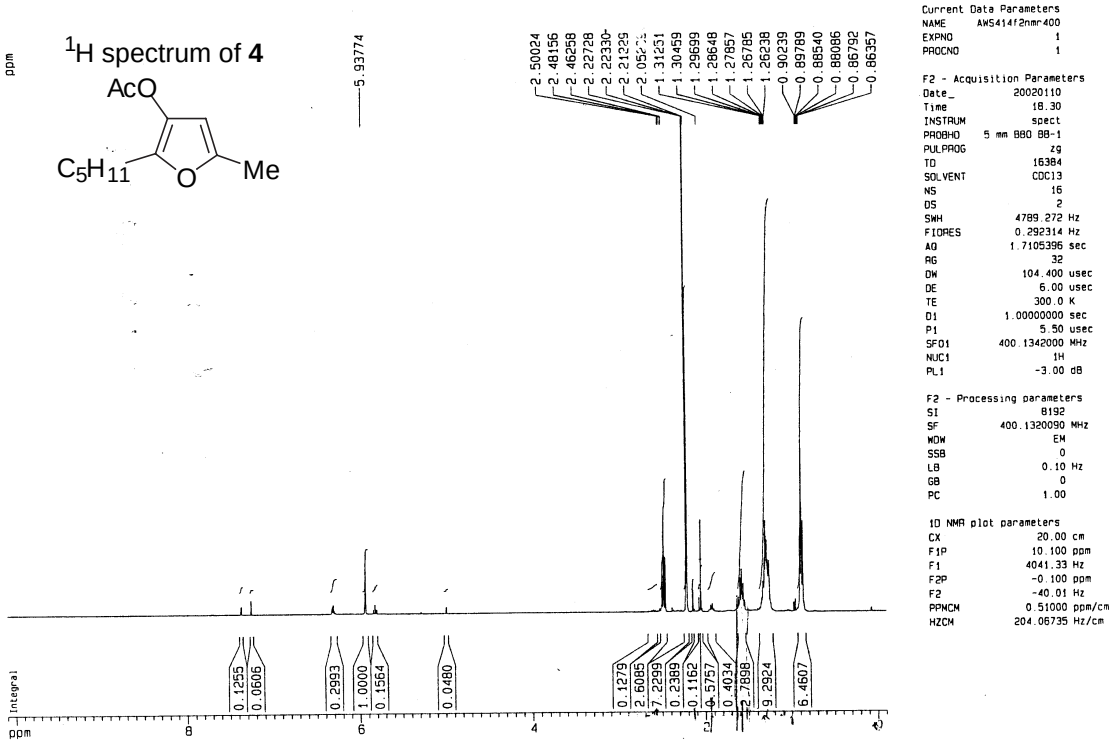
Purification and analysis. Purification was carried out through column chromatography using Merck and ICN silica gels (40-63 μm and 63-100 μm) and Fluka aluminum oxide (neutral, Brockmann I). Analytical thin layer chromatography was performed using precoated using Merck 0.2 mm precoated silca gel plates (60 F_{254}).

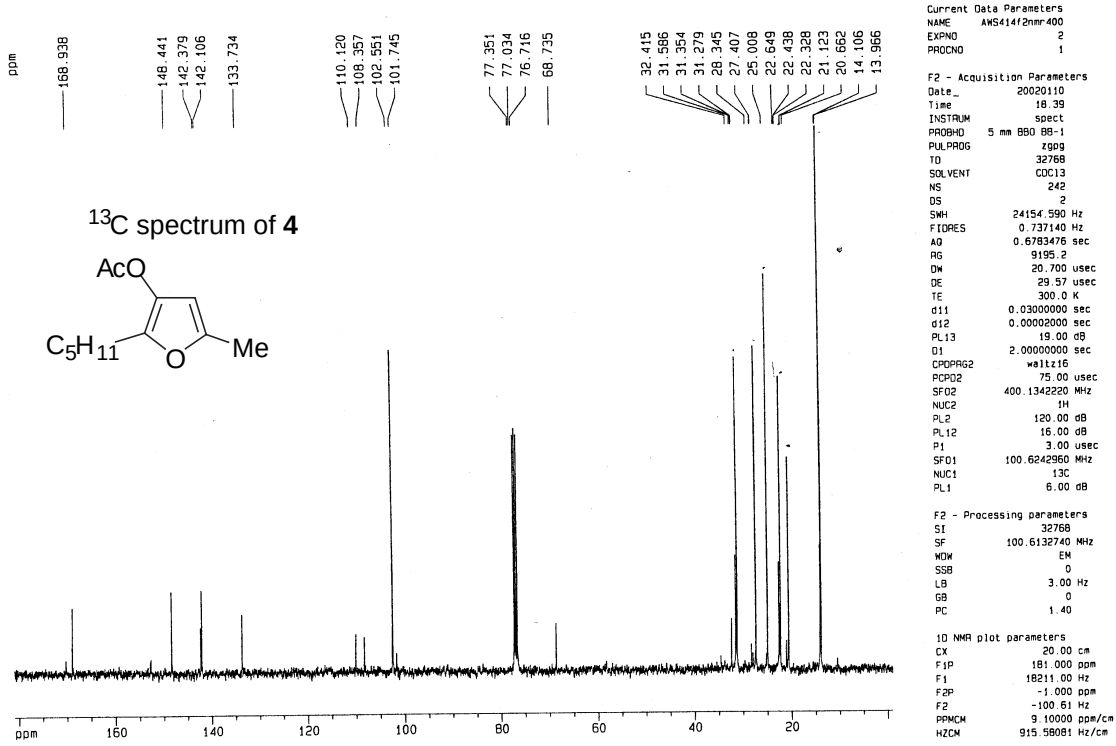
Chemicals. Alkynes, propargylic alcohols, acid chlorides, acid anhydrides, *n*-butyllithium, DMAP, and diones were purchased from Aldrich, Acros Organics, and TCI and used without further purification. Triethylamine was stored over calcium hydride prior to use. Triethyl orthoformate was distilled prior to use. Anhydrous DMA, THF, and ether were purchased from Aldrich and additionally stored over calcium hydride prior to use. Bis(triphenylphosphine)dichloropalladium (II) was prepared in our lab. Copper chloride, copper iodide, and silver tetrafluoroborate were purchased from Aldrich and stored in a glovebox. Acetals[1] and (4-*t*-butyldimethylsiloxy)-1-pentyn-3-ol[2] were prepared using published procedures.

3 (acetic acid 2-methyl-5-pentyl-furan-2-yl ester): Copper chloride (0.5 mmol, 51 mg) was loaded in a glovebox into an oven-dried 3 mL Wheaton microreactor equipped with a spin vane and Teflon septum. Anhydrous DMA (2.5 mL) and **1** (1.0 mmol, 230 μL) were sequentially added. The microreactor was capped with a Mininert valve, shielded from light, and placed in a preheated aluminum block (130°C) and stirred until the reaction was judged complete by GC/MS and TLC (12 hours). The microreactor was allowed to cool, and the mixture was poured into 15 mL of water and thoroughly extracted with hexanes (3x3 mL). The organic layer was dried by filtering through anhydrous Na_2CO_3, then concentrated and purified by column chromatography using 1:20 ethyl acetate:hexanes as eluent to afford 29% of a 6.7:1 mixture of **3**:**4**. ^{1}H NMR (400.13 MHz): δ5.95 (s, 1H); 2.51 (t, 2H, J = 7.7 Hz); 2.23 (s, 3H); 2.15 (s, 3H); 1.62-1.58 (m, 2H); 1.34-1.29 (m, 4H); 0.89 (t, 3H; J = 7.3 Hz). ^{13}C NMR (100.61 MHz): δ168.8; 152.9; 137.8; 134.0; 101.7; 31.3; 28.4; 27.4; 22.4; 20.7; 14.0; 10.6. GC/MS *m/z*: 210 (M^+, 8); 168 (49); 111 (100).

4 (acetic acid 2-methyl-5-pently-furan-3-yl ester): Copper chloride (18 mg, 0.2 mmol) was loaded in a glovebox into an oven-dried 3 mL Wheaton microreactor equipped with a spin vane and Teflon septum. Anhydrous DMA (2.5 mL), anhydrous triethylamine (0.2 mmol, 28 μL), and **1** (1.0 mmol, 230 μL) were sequentially added. The microreactor was capped with a Mininert valve, shielded from light, and placed in a preheated aluminum block (130°C), and stirred until the reaction was judged complete by TLC and GC/MS (12 hours). The microreactor was allowed to cool, and the mixture was poured into 15 mL of water and extracted thoroughly with hexanes (3x3 mL). The organic layer was dried by filtering through anhydrous Na_2CO_3, and then concentrated and purified by column chromatography using 1:20 ethyl acetate:hexanes as eluent to afford 33% of a

6.7:1 mixture of **4**:**3**. ^{1}H NMR (400.13 MHz): δ5.94 (s, 1H); 2.48 (t, 2H, J = 7.5 Hz); 2.23 (s 3H); 2.21 (s, 3H); 1.64-1.52 (m, 2H); 1.31-1.26 (m, 4H); 0.88 (t, 3H, J = 7.1 Hz). ^{13}C NMR (100.61 MHz): δ168.9; 148.4; 142.1; 133.7; 102.6; 31.3; 27.4; 25.0; 22.3; 20.7; 14.0 (x 2). GC/MS *m/z*: 210 (M^+, 6); 168 (16); 111 (100).

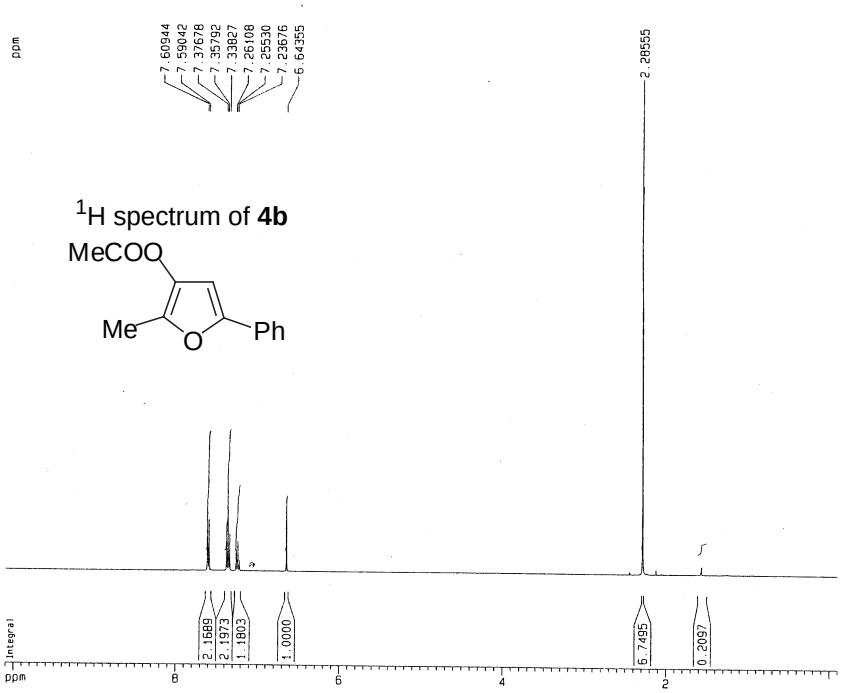




Synthesis of 2,3,5-trisubstituted furans (General Procedure): Copper chloride (0.05 mmol, 5 mg) was loaded into an oven-dried 3 mL Wheaton microreactor in a glovebox. Anhydrous DMA (1 mL), anhydrous triethylamine (0.2 mmol, 28 μL), and acyloxy alkynyl ketone (1 mmol) were successively added. The reactor was capped with a Mininert valve and then placed in a preheated aluminum block (130^{o}C), shielded from light, and stirred from 2 to 24 hours. Progress of the reaction was monitored by TLC and GC/MS. After the reaction was judged to be complete, the microreactor was allowed to cool and the mixture was poured into 10 mL of water and thoroughly extracted with hexanes (3x3 mL). The organic layer was dried with anhydrous Na_2CO_3, concentrated, and chromatographed over silica gel using hexanes-ethyl acetate as the eluent.

4a (benzoic acid 2-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 8.21 (d, 2H, *J* = 8.4 Mz); 7.65 (d, 3H, *J* = 8.5 Hz); 7.53 (t, 2H, *J* = 9.8 Hz); 7.38 (t, 2H, *J* = 7.8 Hz); 7.26 (pst, 1H, *J* = 3.8 Hz); 6.78 (s, 1H); 2.36 (s, 3H). ^{13}C NMR (125.76 MHz): δ 164.6; 150.5; 140.5; 136.1; 134.1(x2); 131.2; 130.6(x2); 129.3(x3); 129.0(x2); 123.8(x2); 102.4; 11.4. Anal. calcd.: C, 77.68; H, 5.07. Found: C, 77.29; H, 5.07. GC/MS *m/z*: 278 (M^{+}, 18); 105 (PhCO, 100).

4b (acetic acid 2-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (400.13 MHz): δ 7.60 (d, 2H, *J* = 7.6 Hz); 7.36 (t, 2H, *J* = 7.7 Hz); 7.25 (t, 1H, *J* = 7.4 Hz); 2.29 (s, 6H). ^{13}C NMR (100.61 MHz): δ 168.6; 150.0; 139.8; 130.7; 128.6 (x 2); 127.2; 123.3 (x 2); 101.9; 20.7; 10.8. GC/MS *m/z*: 174 (100); 105 (PhCO, 82).



^{1}H spectrum of **4b**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PL1                -3.00 dB

F2 - Processing parameters
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1D NMR plot parameters
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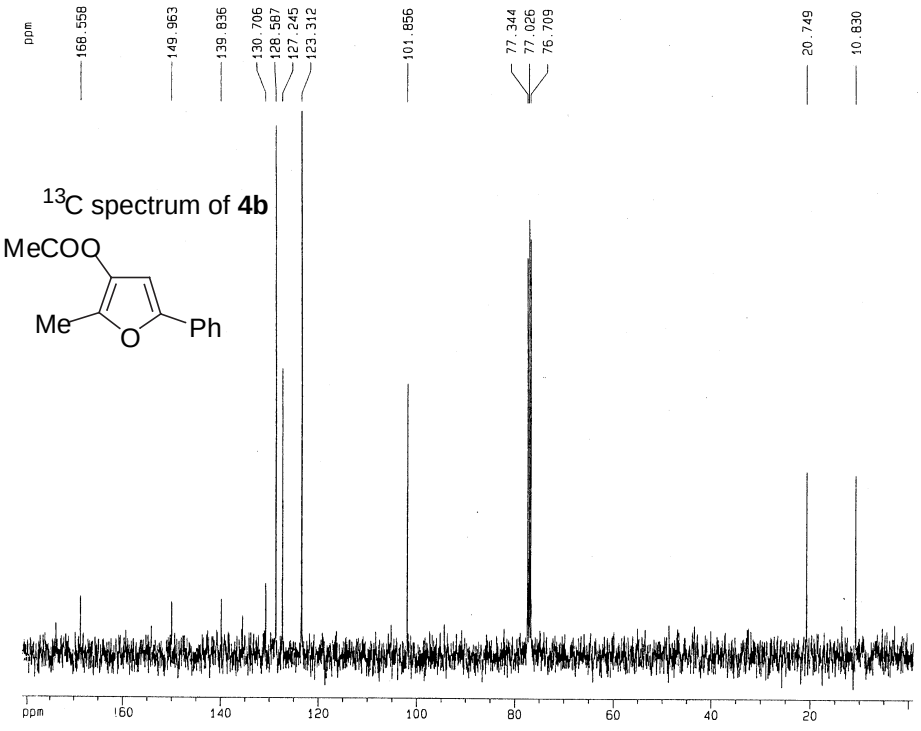

^{13}C spectrum of **4b**


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PL13                19.00 dB
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NUC2                   1H
PL2               120.00 dB
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P1                 3.00 usec
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NUC1                  13C
PL1                6.00 dB

F2 - Processing parameters
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1D NMR plot parameters
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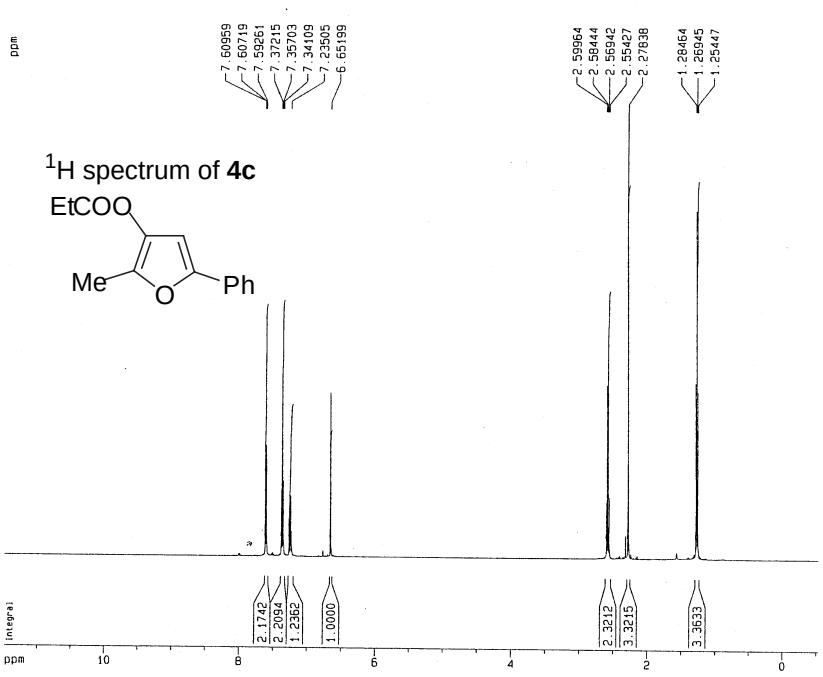
F1              18211.00 Hz
F2P              -1.000 ppm
F2               -100.61 Hz
PPMCM          9.[illegible]0000 ppm/cm
HZCM          9      )81 Hz/cm
```

4c (propionic acid-2-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.61 (d, 2H, *J* = 7.3 Hz); 7.36 (d, 2H, *J* = 7.3 Hz); 7.23 (t, 1H, *J* = 7.4 Hz); 6.65 (s, 1H,); 2.58 (q, 2H, *J* = 7.6 Hz); 2.28 (s, 3H); 1.27 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR (125.76 MHz): δ 172.5; 150.3; 140.2; 135.9; 131.2; 129.0; 127.6; 123.7; 102.4; 27.8; 11.2; 9.5. GC/MS *m/z*: 230 (M^{+}, 14); 174 (100).



^{1}H spectrum of **4c**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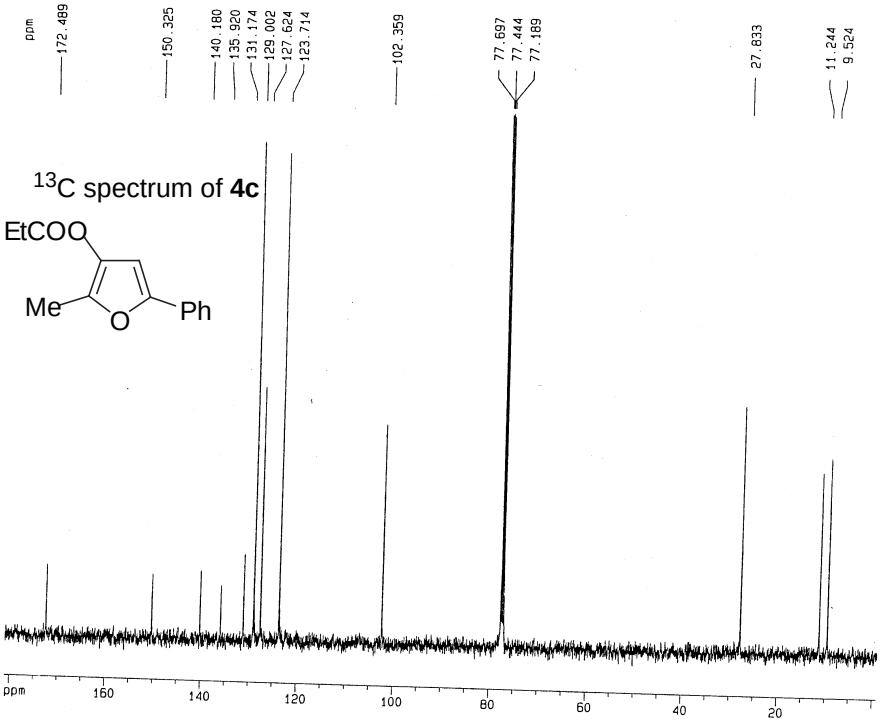

^{13}C spectrum of **4c**


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NUC2               1H
PL2            3.00 dB
PL12           22.00 dB
P1             3.80 usec
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NUC1               13C
PL1            3.00 dB

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1D NMR plot parameters
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F1          22762.15 Hz
F2P           -1.000 ppm
F2          -125.76 Hz
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HZCM      1144.39539 Hz/cm
```

4d (isobutyric acid 2-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (400.13 MHz): δ 7.60 (dd, 2H, J_1 = 8.4, J_2 = 1.2 Hz); 7.36 (t, 2H, J = 7.7 Hz); 7.23 (t, 1H, J = 7.5 Hz); 6.65 (s, 1H); 2.80 (sept, 1H, J = 7.0 Hz); 2.27 (s, 3H); 1.32 (d, 6H, J = 7.0 Hz). ^{13}C NMR (100.61 MHz): δ 174.7; 149.9; 139.7; 135.6; 130.8; 128.6(x 2); 127.2; 123.3(x 2); 102.0; 34.0; 19.0; 10.8. Anal. calcd.: C, 73.75; H, 6.60. Found: C, 74.09; H, 6.81. GC/MS *m/z*: 244 (M^+, 12); 174 (100).

4e (2,2-dimethylpropionic acid-2-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.63 (d, 2H, J = 7.2 Hz); 7.38 (t, 2H, J = 7.8 Hz); 7.29 (t, 1H, J = 7.4 Hz); 6.67 (s, 1H,); 2.29 (s, 3H); 1.40 (s, 9H). ^{13}C NMR (125.76 MHz): δ 176.6; 150.3; 140.1; 136.1; 131.2; 129.0 (x 2); 127.6 (x 2); 124.0; 102.4; 39.5; 27.6 (x 3); 11.2. Anal. calcd.: C, 74.39; H, 7.02. Found: C, 74.47; H, 7.07. GC/MS *m/z*: 258 (M^+, 21); 174 (100); 57 (*t*Bu, 81).

4f (benzoic acid 2-pentyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (400.13 MHz): δ 8.19 d, 2H, J = 8.4 Hz); 7.65 (d, 3H, J = 7.8 Hz); 7.53 (t, 2H, J = 7.7 Hz); 7.37 (t, 2H, J = 7.8 Hz); 7.26 (t, 1H, J = 3.7 Hz); 6.80 (s, 1H); 2.71 (t, 2H, J = 7.5 Hz); 1.73 (quint, 2H, J = 7.4 Hz); 1.40-1.34 (m, 4H); 0.89 (t, 3H, J = 7.1 Hz). ^{13}C NMR (100.61 MHz): 164.3; 150.0; 144.0; 135.4; 133.7; 130.9; 130.1(x2); 129.2; 128.6(x4); 127.2; 123.3(x2); 102.0; 31.3; 27.4; 25.4; 22.3; 14.0. Anal. calcd.: C, 79.02; H, 6.63. Found: C, 78.76; H, 6.80. GC/MS *m/z*: 334 (M^+, 9); 105 (PhCO, 100).

4g (2,2-dimethylpropionic acid-5 *tert*-butyl-2-pentyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 5.98 (s, 1H); 2.52 (t, 2H, J = 7.4 Hz); 1.62 (quint, 2H, J = 7.4 Hz); 1.37-1.29 (m, 4H); 1.33 (s, 9H); 1.26 (s, 9H); 0.91 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125.76 MHz): δ 176.8; 160.5; 141.8; 134.3; 99.4; 39.4; 33.1; 31.7; 29.2 (x 3); 27.7; 27.6 (x 3); 25.5; 22.7; 14.4. Anal. calcd.: C, 73.43; H, 10.27. Found: C, 73.42; H, 10.37. GC/MS *m/z*: 294 (M^+, 13); 153 (98); 57 (*t*Bu, 100).

4h (benzoic acid-2[1-(*tert*-butyldimethylsilanyloxy)-ethyl]-5-phenyl-furan-3-yl ester: ^{1}H NMR (500.13 MHz): δ 8.20 (dd, 2H, J_1 = 8.5; J_2 = 1.4 Hz); 7.68 (dd, 2H, J_1 = 8.2; J_2 = 0.9 Hz); 7.66 (d, 1H, J = 7.5 Hz); 7.53 (t, 2H, J = 7.8 Hz); 7.40 (t, 2H, J = 7.8 Hz); 7.29 (t, 1H, J = 7.4 Hz); 6.81 (s, 1H); 5.03 (q, 1H, J = 6.6 Hz); 1.60 (d, 3H, J = 6.6 Hz); 0.88 (s, 9H); 0.088 (s, 3H); 0.006 (s, 3H). ^{13}C NMR (125.76 MHz): δ 164.5; 151.1; 144.8; 135.5; 134.2; 131.0; 130.6 (x 2); 129.4; 129.09 (x 4); 129.06; 128.1; 124.1 (x 2); 102.4; 62.6; 26.2 (x 3); 22.6; 18.6; -4.4; -4.6. Anal. calcd.: C, 71.05; H, 7.16. Found: C, 71.03; H, 7.13. GC/MS *m/z*: 422 (M^+, 1); 105 (PhCO, 100).

Synthesis of tetrasubstituted furans. General procedure. Silver tetrafluoroborate (0.05 mmol, 5 mg) was loaded into an oven-dried, cooled 3 mL Wheaton microreactor in a glovebox under argon atmosphere. The microreactor was capped with a Mininert valve, shielded from light. Anhydrous dichloromethane (1 mL) and propargyl ketone acetate (1 mmol) were added successively while stirring. The solution was allowed to stir at room temperature from 2 to 15 minutes and monitored by TLC and GCMS. Reactions were

generally complete within 5 minutes. The solution was then filtered over a pad of aluminum oxide to yield rather pure crude product. Products were additionally purified by silica gel column chromatography using ethyl acetate:hexanes as eluent.

10a (acetic acid 2-*tert*-butyl-4,5-diphenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.42 (d, 2H, J = 7.2 Hz); 7.37-7.33 (m, 6H); 7.23 (t, 2H, J = 7.6 Hz); 7.19 (tt, 1H, J_1 = 7.2, J_2 = 1.3 Hz); 2.07 (s, 3H); 1.39 (s, 9H). ^{13}C NMR (125.76 MHz): δ 169.8; 149.9; 145.2; 132.0; 131.4; 130.0 (x 2); 129.1 (x 2); 128.7 (x 2); 127.9; 127.6; 125.7 (x 2); 118.9; 33.5; 29.0 (x 3); 20.9. Anal. calcd.: C, 79.02; H, 6.63. Found: C, 78.95; H, 6.57. GC/MS *m/z*: 334 (M^+, 8); 277 (M^+ - *t*Bu, 100).

10b (acetic acid 2-*tert*-butyl-5-methyl-4-phenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.36 (t, 2H, J = 7.6 Hz); 7.27 (t, 3H, J = 7.1 Hz); 2.30 (s, 3H); 2.11 (s, 3H); 1.31 (s, 9H). ^{13}C NMR (125.76 MHz): δ 170.0; 148.5; 145.1; 132.2; 131.1; 128.9 (x 2); 128.8 (x 2); 127.1; 117.6; 33.2; 29.0 (x 3); 21.0; 13.3. Anal. calcd.: C, 74.97; H, 7.40. Found: C, 75.02; H, 7.37. GC/MS *m/z*: 272 (M^+, 5); 215 (M^+ - *t*Bu, 100).

10c (acetic acid 2-*tert*-butyl-4-methyl-5-phenyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.59 (dd, 2H, J_1 = 8.5, J_2 = 0.9 Hz); 7.39 (t, 2H, J = 7.8 Hz); 7.24 (t, 1H, J = 7.4 Hz); 2.31 (s, 3H); 2.05 (s, 3H); 1.34 (s, 9H). ^{13}C NMR (125.76 MHz): δ 169.8; 148.0; 145.1; 134.2; 132.3; 128.9 (x 2); 127.0; 125.3 (x 2); 112.9; 33.3; 21.0 (x 3); 9.0. Anal. calcd.: C, 74.97; H, 7.40. Found: C, 74.60; H, 7.55. GC/MS *m/z*: 272 (M^+, 11); 215 (M^+ - *t*Bu, 100).

10d (acetic acid 2-*tert*-butyl-4,5-dimethyl-furan-3-yl ester): ^{1}H NMR (500.13 MHz): δ 7.25 (s, 3H); 2.14 (s, 3H); 1.73 (s, 3H); 1.24 (s, 9H). ^{13}C NMR (125.76 MHz): δ 170.0; 147.5; 144.0; 132.8; 110.7; 32.6; 29.1 (x 3); 20.9. Anal. calcd.: C, 68.54; H, 8.63. Found: C, 68.45; H, 8.73. GC/MS m/z: 210 (**M**+, 7); 153 (M+ - tBu, 100).

10e (acetic acid 2-tert-butyl-4,5,6,7-tetrahydrobenzofuran-3-yl ester): 1H NMR (500.13 MHz): δ 2.50 (tt, 2H, J_1 = 6.4, J_2 = 1.7 Hz); 2.23 (s, 3H); 2.21 (tt, 2H, J_1 = 6.0, J_2 = 1.8 Hz); 1.79 (dquint, 2H, J_1 = 6.1, J_2 = 2.5 Hz); 1.68 (dquint, 2H, J_1 = 5.9, J_2 = 2.4 Hz); 1.26 (s, 9H). ^{13}C NMR (125.76 MHz): δ 169.7; 147.8; 147.4; 132.0; 113.8; 33.1; 29.2 (x 3); 23.6; 23.2; 22.9; 21.0; 20.4. Anal. calcd.: C, 71.16; H, 8.53. Found: C, 70.86; H, 8.79. GC/MS m/z: 236 (M^+, 7); 179 (M^+ - *t*Bu, 100).

12 (phosphoric acid 2-tert-butyl-4,5-diphenyl-furan-3-yl ester diethyl ester):
*Preparation of **12** from **11***: Silver tetrafluoroborate (0.04 mmol, 8 mg) was added to an oven-dried 3 mL Wheaton microreactor in the glovebox under argon atmosphere. Dichloroethane (1 mL) and **11** (0.94 mmol, 403 mg) were successively added. The microreactor was capped with a Mininerty valve and shielded from light, and the reaction was stirred at 60°C for 16 hours. After the reaction was judged to be complete by TLC analysis, the reactor was cooled, and the solution was filtered through a short pad of aluminum oxide and concentrated. The residue was purified by column chromatography over 50 mL silica gel using 1:3 ethyl acetate:hexanes as eluent to afford 263 mg (65%) pure **12**.

*Preparation of **12** from **13***: Silver tetrafluoroborate (0.005 mmol, 1 mg) was added to an oven-dried 3 mL Wheaton microreactor in the glovebox under argon atmosphere. Dichloroethane (0.20 mL) and **13** (0.1 mmol, 43 mg) were successively added. The microreactor was capped with a Mininert valve, shielded from light and the solution was stirred for 1.25 h at room temperature, and then at 60°C for 20 h. Once the reaction was complete by TLC analysis, the solution was cooled, filtered through a short pad of aluminum oxide, and concentrated. Analysis of the crude residue indicated a 76% NMR yield of **12** with dibromomethane as the standard. ^{1}H NMR (500.13 MHz): δ 7.44-7.32 (m, 7H); 7.22-7.14 (m, 3H); 3.86-3.81 (m, 2H); 3.74-3.65 (m, 2H); 1.47 (s, 9H); 1.13 (t, 3H, J = 7.0 Hz); 1.12 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125.76 MHz): δ 49.5; 144.6; 132.1; 131.5; 131.0 (x 2); 128.8 (x 2); 128.6 (x 2); 127.9; 127.5; 125.6 (x 2); 118.7; 64.4 (J_{CP} = 6.0 Hz); 33.6; 29.2 (x 3); 16.3 (J_{CP} = 6.9 Hz). Anal. calcd.: C, 67.28; H, 6.82. Found: C, 67.09; H, 6.92. GC/MS *m/z*: 428 (M^+, 12); 105 (PhCO, 100).

16 (toluene-4-sulfonic acid 2-*tert*-butyl-4,5-diphenyl-furan-3-yl ester): Silver tetrafluoroborate (0.01 mmol, 1.8 mg) and **15** (1.03 mmol, 461 mg) were successively added to an oven-dried, 3 mL Wheaton microreactor in the glovebox under argon atmosphere. Dichloroethane (1 mL) was added, the microreactor was capped with a Mininert valve, shielded from light, and the reaction was stirred at 60°C for 45 h. After the reaction was judged complete by TLC analysis, the microreator was cooled, and the solution was filtered through a short pad of aluminum oxide, concentrated, and purified by column chromatography over 50 mL silica gel with 1:10 ethyl acetate:hexanes as eluent to afford 376 mg (82%) pure **16**. ^{1}H NMR (500.13 MHz): δ 7.33 (dd, 2H, J_1 = 8.3, J_2 = 1.4 Hz); 7.29 (d, 2H, J = 8.3 Hz); 7.23-7.15 (m, 4H), 7.10-7.07 (m, 4H); 6.94 (d, 2H, J = 8.1 Hz); 2.33 (s, 3H); 1.52 (s, 9H). ^{13}C NMR (125.76 MHz): δ 153.3; 145.1; 144.9; 133.4; 131.8; 131.4; 131.2; 130.4(x 2); 129.7(x 2); 128.7 (x 4); 128.4 (x 2); 127.8; 127.4; 125.9 (x 2); 118.4; 34.0; 29.3 (x 3); 22.0. Anal. calcd.: C, 72.62; H, 5.87. Found: C, 72.83; H, 5.93.

Synthesis of acyloxy alkynyl ketones. General procedures.

Procedure A. To a 250 mL round-bottomed, two-necked, flash-dried, argon flushed flask equipped with a Teflon coated magnetic stir bar, addition funnel, and T-shaped stopcock with an argon balloon, were successively added: 1-octyn-3-ol (50 mml, 7.3 mL) and anhydrous THF (100 mL). The solution was cooled while stirring to -78°C and *n*-butyllithium (0.11 mol, 44mL of 2.5M solution in hexanes) was added dropwise *via* addition funnel (*ca*. 30 minutes). The resulting solution was allowed to warm to room temperature. To a 500 mL round bottomed, two-necked flask, also flash-dried and flushed with argon, equipped with a Teflon coated magnetic stir bar, addition funnel, and T-shaped stopcock with argon balloon were successively added: acid anhydride (0.25 mol) and anhydrous ether (150 mL). The resulting solution was cooled to -78°C while stirring, and the dianion solution from the first flask was slowly added via addition funnel. The solution was allowed to warm to room temperature overnight, and was quenched with a mixture of 1% NH_4OH and 200 mL saturated NH_4Cl, adjusted to reach pH 8. After thorough extraction with hexanes and 1:1 hexanes:diethyl ether (50 mL each); the organic extracts were combined and dried with anhydrous Na_2SO_4 and then

concentrated. The resulting residue was purified either by high vacuum distillation or by column chromatography using ethyl acetate:hexanes as eluent.

Procedure B. Sonogashira coupling.[3] (Representative procedure). To an oven-dried, 3 mL Wheaton microreactor equipped with a triangular Teflon coated spin vane and Teflon septum with open phenolic cap were successively added copper iodide (0.0013 mmol, 2.5 mg) and dichlorobis(triphenylphosphine)palladium (0.0035 mmol, 2.5 mg) in a glovebox under argon atmosphere. Anhydrous triethylamine (2.5 mL) was added and the mixture was stirred. The propargylacyloxyalkyne (2.33 mmol) was added *via* syringe and the mixture was briefly stirred. Benzoyl chloride (2.5 mmol, 290 μL) was then added dropwise. The reaction was stirred overnight at room temperature and monitored by TLC and GC/MS. The reaction was quenched by filtration through a pad of silica gel with ethyl acetate. The washings were concentrated and purified by column chromatography using silica gel and hexanes: ethyl acetate as eluent.

1 (acetic acid-2-oxo-3-decyn-5-yl ester): Procedure A (62% y.): ^{1}H NMR (400.13 MHz): δ 5.45 (t, 1H, J = 6.7 Hz); 2.34 (s, 3H); 2.09 (s, 3H); 1.82-1.77 (m, 2H); 1.44-1.41 (m, 2H); 1.33-1.29 (m, 4H); 0.89 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125.76 MHz): δ 184.0; 170.0; 88.4; 84.1; 63.3; 33.9; 32.6; 31.1; 24.6; 22.4; 20.8; 13.9. GC/MS *m/z*: 195 (M^+-15, 1); 168 (44); 111 (100).

5a (benzoic acid 1-methyl-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (74% y.): ^{1}H NMR (500.13 MHz): δ 8.13-8.09 (m, 4H); 7.62-7.59 (m, 2H); 5.93 (q, 1H, J = 6.8 Hz); 1.78 (d, 3H, J = 6.8 Hz). ^{13}C NMR (125.76 MHz): δ 177.9; 165.8; 136.7; 134.8; 133.9; 130.3(x 2); 130.1(x 2); 129.8; 129.1(x 2); 128.9(x 2); 91.9; 82.6; 60.8; 21.1. GC/MS *m/z*: 278 (M^+, 18); 105 (PhCO, 100).

5b (acetic acid 1-methyl-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (42% y.): ^{1}H NMR (500.13 MHz): δ 8.10 (d, 2H, J = 7.7 Hz); 7.62 (t, 1H, J = 7.4 Hz); 7.48 (t, 2H, J = 7.7 Hz); 5.66 (q, 1H, J = 6.8 Hz); 2.13 (s, 3H); 1.63 (d, 3H, J = 6.8 Hz). ^{13}C NMR (125.76 MHz): δ177.9; 170.2; 136.7; 134.8; 130.1(x 2); 129.1(x 2); 91.8; 82.3; 60.2; 21.3; 20.9. GC/MS *m/z*: 215 (M^+-1; 1); 174 (100); 128 (77); 105 (PhCO, 96); 77 (Ph, 75); 51 (47).

5c (propionic acid 1-methyl-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (43% y.): ^{1}H NMR (500.13 MHz): δ 8.10 (dd, 2H, J_1 = 8.3; J_2 = 1.3 Hz); 7.62 (t, 1H, J = 7.4 Hz); 7.49 (t, 2H, J = 7.8 Hz); 5.68 (q, 1H, J = 6.8 Hz); 2.41 (q, 1H, J = 7.6 Hz); 2.40 (q, 1H, J = 7.6 Hz); 1.63 (d, 3H, J = 6.8 Hz); 1.18 (t, 3H, J = 7.6 Hz). ^{13}C NMR (125.76 MHz): δ 177.9; 173.6; 136.7; 134.8; 130.1 (x 2); 129.1 (x 2); 92.1; 82.3; 60.0; 27.9; 21.0; 9.4. GC/MS *m/z*: 229 (M^+-1, 0.1); 175 (87); 128 (100); 105 (PhCO, 94); 77 (Ph, 64); 57 (66).

5d (isobutyric acid 1-methyl-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (76% y.): ^{1}H NMR (500.13 MHz): δ 8.12 (dd, 2H, J_1 = 8.4; J_2 = 1.3 Hz); 7.64 (t, 1H, J = 7.5 Hz); 7.51 (t, 2H, J = 7.8 Hz); 5.70 (q, 1H, J = 6.8 Hz); 2.65 (sept, 1H, J = 7.0 Hz); 1.66 (d, 3H, J = 6.9 Hz); 1.23 (d, 6H, J = 7.0 Hz). ^{13}C NMR (125.76 MHz): δ 177.9; 176.3; 136.8; 134.7;

130.0 (x 2); 129.0 (x 2); 92.2; 82.3; 60.0; 34.3; 20.9; 19.2 (x 2). GC/MS *m/z*: 243 (M^+-1, 0.4); 175 (98); 128 (100); 105 (PhCO, 68); 77(Ph, 79).

5e (2,2-dimethylpropionic acid 1-methyl-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (78% y.): ^{1}H NMR (500.13 MHz): δ 8.09 (dd, 2H, J_1 = 8.1; J_2 = 1.9 Hz); 7.61 (t, 1H, J = 7.4 Hz); 7.48 (t, 2H, J = 7.8 Hz); 5.65 (q, 1H; J = 6.8 Hz); 1.62 (d, 3H, J = 6.8 Hz); 1.25 (s, 9H). ^{13}C NMR (125.76 MHz): δ 177.9; 177.7; 136.8; 134.8; 130.0 (x 2); 129.0 (x 2); 92.3; 82.2; 60.1; 39.2; 27.4 (x 3); 20.8. GC/MS *m/z*: 258 (M^+; 0.1); 57 (*t*Bu, 100).

5f (benzoic acid 4-oxo-1-pentyl-4-phenyl-but-2-ynyl ester): Procedure B (69% y.): ^{1}H NMR (500.13 MHz): δ 8.11 (t, 4H, J = 6.8 Hz); 7.61 (t, 2H, J = 7.4 Hz); 7.48 (q, 4H, J = 7.0 Hz); 5.85 (t, 1H, J = 6.7 Hz); 2.10-2.03 (m, 2H); 1.62 (quint, 2H, J = 7.4 Hz); 1.43-1.34 (m, 4H); 0.92 (t, 3H, J = 6.9 Hz). ^{13}C NMR (125.76 MHz): δ 177.9; 165.9; 136.8; 134.8; 133.9; 130.3 (x 2); 130.1 (x 2); 129.8; 129.1 (x 2); 128.9 (x 2); 91.4; 83.2; 64.6; 34.6; 31.7; 25.2; 22.9; 14.4. GC/MS *m/z*: 334 (M^+, 2); 105 (PhCO, 100).

5g (2,2-dimethyl propionic acid 5,5-dimethyl-4-oxo-1-pentyl-hex-2-ynyl ester): Procedure A (41% y.): ^{1}H NMR (500.13 MHz): δ 5.45 (t, 1H, J = 6.7 Hz); 1.85-1.92 (m, 2H); 1.48-1.42 (m, 2H); 1.34-1.28 (m, 4H); 1.21 (s, 9H); 1.17 (s, 9H); 0.88 (t, 3H, J = 6.9 Hz). ^{13}C NMR (125.76 MHz): δ 194.0; 177.6; 91.1; 82.1; 63.7; 45.3; 39.2; 34.3; 31.5; 27.4 (x 3); 26.3 (x 3); 25.0; 22.8; 14.3. GC/MS *m/z*: 294 (M^+, 0.1); 57 (*t*Bu, 100).

5h (benzoic acid 1-[1-(*tert*-butyldimethylsilanyloxy)-ethyl]-4-oxo-4-phenyl-but-2-ynyl ester): Procedure B (85% y.): ^{1}H NMR (500.13 MHz): δ 8.16 (d, 2H, J = 8.4 Hz); 8.10 (dd, 2H, J_1 = 8.4, J_2 = 1.4 Hz); 7.61 (t, 2H, J = 7.4 Hz); 7.50-7.45 (m, 4H); 5.83 (d, 0.2 H, J = 6.2 Hz); 5.78 (d, 0.8 H, J = 4.1 Hz); 4.29 (dquint, 0.8 H, J_1 = 6.3; J_2 = 2.1 Hz); 4.24 (quint, 0.2 H, J = 6.2 Hz); 1.44 (d, 0.6 H, J = 6.2 Hz); 0.097 (s, 2.4 H); 0.093 (s, 0.6 H). ^{13}C NMR (125.76 MHz): δ 177.8; 165.8; 136.9; 134.7; 133.9; 130.3 (x 2); 130.1 (x 2); 129.7; 129.1 (x 2); 128.9 (x 2); 89.5 (x 0.2); 89.4 (x 0.8); 84.0 (x 0.2); 83.8 (x 0.8); 69.9 (x 0.8); 69.3 (x 0.8); 69.1 (x 0.2); 68.7 (x 0.2); 26.1; 20.4 (x 0.8); 20.1 (x 0.2); 18.4; -4.2; -4.4. GC/MS *m/z*: 407 (M^+ -15, 0.1); 179 (44); 105 (PhCO, 100).

Synthesis of acetoxy propargyl ketones. General procedure.

To a flash dried, argon flushed, round bottomed two-necked flask equipped with a Teflon coated stir bar and a T-shaped stopcock with an argon filled balloon, were successively added 10 mL anhydrous THF and 3,3-dimethyl-1-butyne (0.62 mL, 5.0 mmol). The solution was cooled to -78^{o}C in a dry ice/acetone bath while stirring. *n*-Butyllithium (5.2 mmol, 2.1 mL of 2.5 M solution in hexanes) was added dropwise to the cooled solution. The resulting solution was allowed to warm to room temperature. To an additional flash dried 50 mL round bottomed two-necked flask, flushed with argon and equipped with a stir bar and T-shaped stopcock with argon balloon, were successively added the appropriate dione (4.8 mmol) and anhydrous THF (10 mL). The dione solution was cooled to -78^{o}C while stirring. The acetylide solution from the first flask was added slowly via cannula to the dione solution under argon pressure at -78^{o}C. The resulting solution was allowed to warm to room temperature and then cooled down again to -78^{o}C.

Acetic anhydride (8.0 mmol, 0.76 mL) was added to the flask while stirring, and the flask was removed from the cooling bath and allowed to warm to room temperature. The solution was then poured into a separatory funnel containing 200 mL of saturated NH_4Cl solution and 50 mL of ether. After extraction, the organic layer was separated, dried with anhydrous $MgSO_4$, concentrated, and purified by silica gel column chromatography with hexanes:ethyl acetate as eluent to afford pure acetoxy propargyl ketone.

8a (acetic acid 1-benzoyl-4,4-dimethyl-1-phenyl-pent-2-ynyl ester) (83% y.): ^{1}H NMR (500.13 MHz): δ 7.88 (dd, 2H, J_1 = 8.3; J_2 = 1.0 Hz); 7.77 (dd, 2H, J_1 = 8.0; J_2 = 1.1 Hz); 7.45-7.35 (m, 4H); 7.31 (t, 2H, J = 7.7 Hz); 2.15 (s, 3H); 1.20 (s, 9H). ^{13}C NMR (125.76 MHz): δ 192.3; 169.0; 136.5; 134.9; 132.8; 130.3 (x 2); 129.6; 129.2 (x 2); 128.0 (x 2); 127.8 (x 2); 101.5; 81.3; 75.9; 30.7 (x 3); 28.2; 21.8. GC/MS *m/z*: 334 (M^+, 10); 277 (M^+ - *t*Bu, 100); 105 (PhCO, 63).

8c (acetic acid 1-benzoyl-1,4,4-trimethyl-pent-2-ynyl ester) (43%): ^{1}H NMR (500.13 MHz): δ 8.15 (dd, 2H, J_1 = 8.2, J_2 = 0.9 Hz); 7.51 (t, 3H, J = 7.4 Hz); 7.41 (t, 2H, J = 8.0 Hz); 1.93 (s, 3H); 1.90 (s, 3H); 1.18 (s, 9H). ^{13}C NMR (125.76 MHz): δ 193.7; 169.7; 134.4; 133.0; 129.8 (x 2); 128.4 (x 2); 99.1; 78.4; 76.8; 30.8 (x 3); 28.0; 25.1; 21.6. GC/MS *m/z*: 272 (M^+, 12); 215 (M^+-*t*Bu, 100); 105 (PhCO, 73).

8d (acetic acid 1-acetyl-1,4,4-trimethyl-pent-2-ynyl ester) (51%): ^{1}H NMR (500.13 MHz): δ 2.35 (s, 3H); 2.08 (s, 3H); 1.61 (s, 3H); 1.22 (s, 9H). ^{13}C NMR (125.76 MHz): δ 202.7; 169.7; 96.8; 77.4; 76.5; 30.9 (x 3); 27.9; 25.6; 25.0; 21.3. GC/MS *m/z*: 210 (M^+, 7); 153 (M^+-*t*Bu, 100).

8b (acetic acid 1-acetyl-4,4-dimethyl-1-phenyl-pent-2-ynyl ester) To a flash-dried, 10 mL, argon-flushed, round-bottomed, two-necked flask equipped with a Teflon-coated stir bar and T-shaped stopcock with an argon balloon were sequentially added anhydrous THF (6 mL) and 3,3-dimethyl-1-butyne (3.3 mmol, 406 μL). The solution was cooled to -78^{o}C while stirring, and *n*-butyllithium (1.4 mL, 2.5 M in hexanes) was added dropwise. The resulting solution was allowed to warm to room temperature. Another flash-dried, two-necked, round-bottomed, 25 mL flask with argon atmosphere equipped with a Teflon coated stir bar and T-shaped stopcock with argon balloon was loaded with anhydrous THF (6 mL) and 1-phenyl-1-propanone-2,2-diethylacetal[1] (3.0 mmol, 650 mg). The flask was cooled while stirring and the acetylide solution from the first flask was transferred dropwise *via* cannula. The resulting alkoxide solution was allowed to warm to room temperature and cooled again to -78^{o}C and quenched with acetic anhydride (5.0 mmol, 410 μL). The solution was allowed to warm to room temperature, and was poured into a separatory funnel containing 120 mL saturated NH_4Cl and 30 mL ether. The mixture was extracted, and the organic layer was separated and dried with anhydrous $MgSO_4$. The organic extract was then concentrated and purified over 100 mL flash silica gel with 1:30 ethyl acetate:hexanes as eluent to afford 502 mg (48%) of the acetal. The acetal was hydrolyzed using a known procedure to afford **8b** in 86% yield.[4] ^{1}H NMR (500.13 MHz): δ 7.71 (dd, 2H, J_1 = 8.1, J_2 = 1.6 Hz); 7.41-7.35 (m, 3H); 2.27 (s, 3H); 2.16 (s, 3H); 1.33 (s, 9H). ^{13}C NMR (125.76 MHz): δ 199.7; 169.2; 135.6; 129.6; 129.0

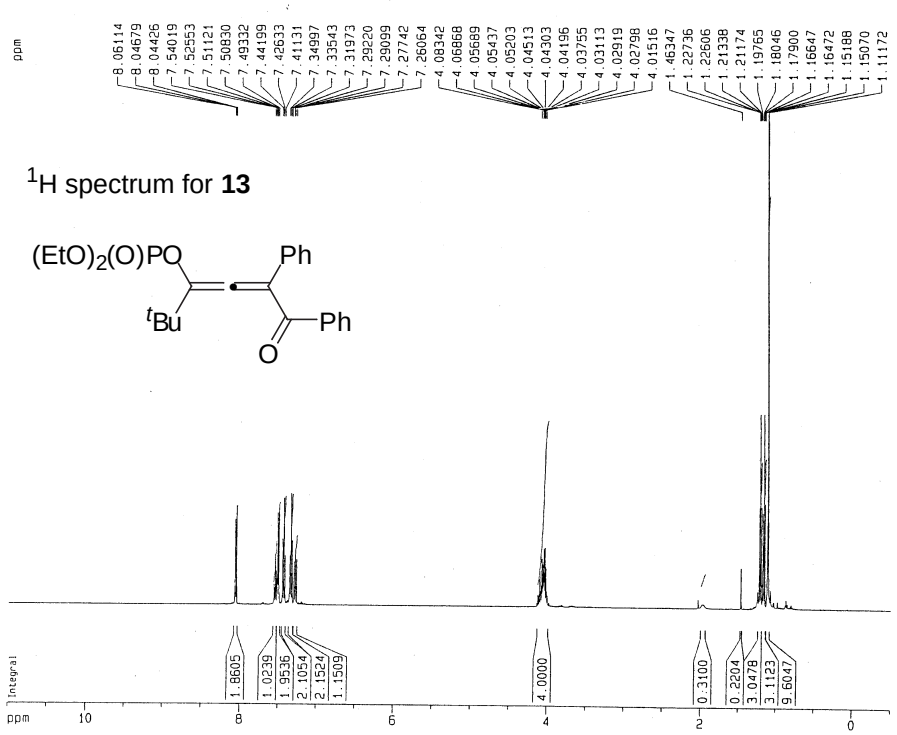
(x 2); 127.3 (x 2); 99.7; 77.7; 75.2; 30.9 (x 3); 28.2; 25.7; 21.5. GC/MS *m/z*: 272 (M^+, 7); 215 (M^+-*t*Bu, 100).

8e (acetic acid 1-(3,3-dimethyl-but-2-ynyl)-2-oxocyclohexyl ester): To a flash-dried, argon flushed, round bottomed two-necked flask equipped with a T-shaped stopcock, argon balloon, and bubbler was added ethyl magnesium bromide (11 mL, 1.0 M in THF) and the flask was cooled to 0°C. 3,3-Dimethyl-1-butyne (1.4 mL, 11. mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and observed until evolution of ethane ceased (*ca.* 30 min.) and stirred for an additional 30 minutes. The flask was cooled to 0°C and a solution of 1,2-cyclohexanedione (560 mg, 5.0 mmol) in 3 mL anhydrous THF was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for another 30 minutes. After TLC and GC/MS analysis showed the reaction was complete, the contents of the flask were poured into 130 mL saturated NH_4Cl solution and extracted with 30 mL ether. The organic layer was separated and the aqueous layer was acidified with 2N HCl and extracted a second time with 30 mL 2N HCl. The organic extracts were combined, dried with anhydrous $MgSO_4$, concentrated, and purified over 75 mL of silica gel with 1:10 ethyl acetate:hexanes as the eluent to afford 492 mg (51%) pure alcohol.[5] This compound was acylated using a known procedure.[6] ^{1}H NMR (500.13 MHz): δ 2.86 (dt, 1H, J_1 = 13.2, J_2 = 5.9 Hz); 2.41 (td, 1H, J_1 = 13.2, J_2 = 3.3 Hz); 2.28 (qd, 1H, J_1 = 12.7, J_2 = 2.6 Hz); 2.12 (dt, 1H, J_1 = 12.0, J_2 = 3.8 Hz); 2.12 (s, 3H); 2.05-1.97 (m, 1H); 1.86-1.82 (m, 1H); 1.76-1.70 (m, 1H); 1.60-1.49 (m, 1H); 1.23 (s, 9H). ^{13}C NMR (125.76 MHz): δ202.3; 168.9; 99.4; 79.9; 75.3; 40.7; 38.8; 31.4; 31.2; 31.0 (x 3); 28.0; 27.9; 22.8; 21.8. GC/MS *m/z*: 236 (M^+, 6); 179 (M^+-*t*Bu, 100).

11 (phosphoric acid 1-benzoyl-4,4-dimethyl-1-phenyl-pent-2-ynyl ester): To a flash-dried, argon flushed, round bottomed, two-necked flask equipped with a Teflon coated magnetic stir bar and T-shaped stopcock with an argon balloon were successively added anhydrous THF (10 mL) and 3,3-dimethyl-1-butyne (5.0 mmol, 0.62 mL). The solution was cooled to -78°C while stirring. *n*-Butyllithium (5.5 mmol, 2.2 mL of 2.5 M solution in hexanes) was added slowly dropwise. The flask was removed from the cooling bath and allowed to warm to room temperature. A flash-dried, argon flushed, 50 mL round bottomed, two-necked flask equipped with a Teflon-coated stir bar and T-shaped stopcock with an argon balloon was sequentially loaded with benzil (5.0 mmol, 1.05 g) and anhydrous THF (10 mL). The solution was cooled to -78°C while stirring, and the acetylide solution from the first flask was transferred dropwise via cannula under positive argon pressure. The resulting purple-black solution was allowed to warm to room temperature while stirring and then placed back into the dry ice/acetone bath to cool to -78°C again. Next, diethylchlorophosphate (5.5 mmol, 0.8 mL) and anhydrous triethylamine[7] (5.5 mmol, 0.8 mL) were successively added. The solution was removed from the bath and allowed to return to room temperature. The resulting amber solution was then poured into a separatory funnel containing 300 mL saturated NH_4Cl solution and 50 mL diethyl ether. After thorough extraction, the organic layer was separated, dried with anhydrous $MgSO_4$, and concentrated. The resulting residue was purified over 150 mL flash silica gel with 1:3 ethyl acetate:hexanes as the eluent to afford 653 mg (30%) pure **11** (and 878 mg (41%) slightly contaminated **11)**. ^{1}H NMR (500.13 MHz): δ 7.89 (d,

2H, J = 8.4 Hz); 7.70 (dd, 2H, J_1 = 7.8, J_2 = 0.9 Hz); 7.43-7.34 (m, 4H); 7.26 (t, 2H, J = 7.7 Hz); 4.24-4.10 (m, 2H); 4.07-3.97 (m, 2H); 1.31 (t, 3H, J = 7.1 Hz); 1.24 (t, 3H, J = 8.1 Hz); 1.23 (s, 9H). ^{13}C NMR (125.76 MHz): δ 191.6; 137.8; 134.1; 133.0; 131.0 (x 2); 129.7; 129.1 (x 2); 128.0 (x 2); 127.8 (x 2); 103.8; 82.6; 75.3; 64.1 (d, J_{CP} = 38.9 Hz); 64.1 (d, J_{CP} = 39.0 Hz); 30.6 (x 3); 28.3; 16.5 (d, J_{CP} = 12.7 Hz); 16.4 (d, J_{CP} = 12.8 Hz). ^{31}P NMR (202.46 MHz): δ -7.30 ppm. GC/MS *m/z*: 428 (M^+, 15); 155 (66); 105 (PhCO, 100).

13 (phosphoric acid 1-*tert*-butyl-4-oxo-3,4-diphenyl-buta-1,2-dienyl ester): Silver tetrafluoroborate (0.01 mmol, 1.9 mg) was added to an oven-dried 1 mL Wheaton microreactor equipped with a Teflon-coated spin vane and Teflon septum in the glovebox under argon atmosphere. Anhydrous dichloromethane (0.20 mL) and **15** (0.2 mmol, 88 mg) were successively added. The microreactor was shielded from light and the solution was allowed to stir at room temperature for one hour and monitored by TLC. The solution was then filtered through a short pad of aluminum oxide, concentrated, and purified by column chromatography over 20 mL silica gel and 1:3 ethyl acetate:hexanes as eluent to afford 48 mg (56%) of pure **13**. ^{1}H NMR (500.13 MHz): δ 8.05 (d, 2H, J = 7.2 Hz); 7.54 (t, 1H, J = 7.3 Hz); 7.50 (d, 2H, J = 7.5 Hz); 7.43 (d, 2H, J = 7.6 Hz); 7.34 (t, 2H, J = 7.6 Hz); 7.28 (t, 1H, J = 7.9 Hz); 4.07-3.99 (m, 4H); 1.21 (t, 3H, J = 7.1 Hz); 1.16 (t, 3H, J = 7.0 Hz); 1.11 (s, 9H). ^{13}C NMR (125.76 MHz): δ 196.3; 193.2; 137.5; 137.0 (d, J_{CP} = 11.4 Hz); 133.9; 133.7; 130.4 (x 2); 129.0; 128.9 (x 2); 128.7 (x 2); 128.2 (x 2); 120.3; 64.8 (d, J_{CP} = 6.5 Hz); 64.7 (d, J_{CP} = 6.3 Hz); 36.4 (d, J_{CP} = 6.3 Hz); 27.9 (x 2); 16.4 (d, J_{CP} = 12.6 Hz); 16.3 (d, J_{CP} = 12.5 Hz). ^{31}P NMR (202.46 MHz): δ -7.01 ppm.



^{1}H spectrum for **13**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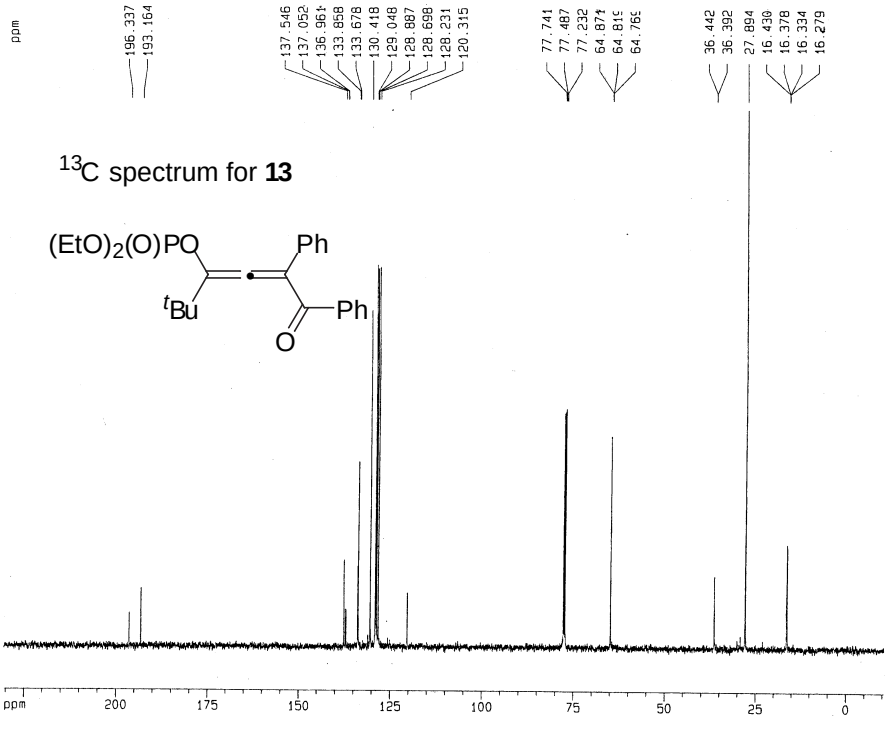
NUC1                    1H
PL1                  3.00 dB

F2 - Processing parameters
SI                     16384
SF              500.1300130 MHz
WDW                       EM
SSB                        0
LB                   0.20 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 11.000 ppm
F1                 5501.43 Hz
F2P                 -0.500 ppm
F2                 -250.07 Hz
PPMCM              0.57500 ppm/cm
HZCM              287.57477 Hz/cm
```



^{13}C spectrum for **13**

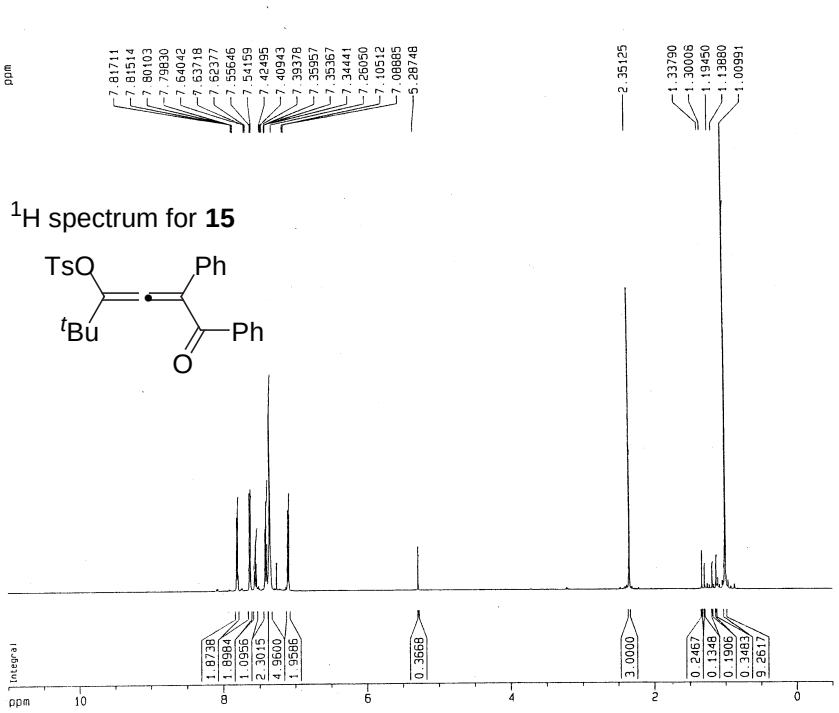

```
Current Data Parameters
NAME        AWS0890f2nmr50
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20030619
Time                  13.04
INSTRUM               spect
PROBHD    5 mm BBO BB-1
PULPROG              zgpg
TD                   32768
SOLVENT              CDCl3
NS                     128
DS                       2
SWH              30303.031 Hz
FIDRES            0.924775 Hz
AQ                0.5407220 sec
RG                  10321.3
DW                 16.500 usec
DE                  6.00 usec
TE                  300.0 K
d11               0.03000000 sec
d12               0.00002000 sec
PL13                22.00 dB
D1                2.00000000 sec
CPDPRG2              waltz16
PCPD2               80.00 usec
SFO2            500.1320000 MHz
NUC2                    1H
PL2                  3.00 dB
PL12                22.00 dB
P1                   3.80 usec
SFO1            125.7715724 MHz
NUC1                   13C
PL1                  3.00 dB

F2 - Processing parameters
SI                     32768
SF              125.7577390 MHz
WDW                       EM
SSB                        0
LB                   3.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                230.482 ppm
F1                28984.87 Hz
F2P                -10.482 ppm
F2                -1318.16 Hz
PPMCM             12.04818 ppm/cm
HZCM              1515.15161 Hz/cm
```

15 (toluene-4-sulfonic acid 1-*tert*-butyl-4-oxo-3,4-diphenyl-buta-1,2-dienyl ester): To a flash-dried, argon flushed, 25 mL round-bottomed, two-necked flask equipped with a Teflon coated magnetic stir bar and T-shaped stopcock with an argon balloon were successively added anhydrous THF (10 mL) and 3,3-dimethyl-1-butyne (5.0 mmol, 0.62 mL). The solution was allowed to cool to -78^{o}C while stirring. *n*-Butyllithium (5.5 mmol, 2.2 mL of 2.5 M solution in hexanes) was added slowly dropwise and the solution gradually turned purple-black with the addition of butyllithium. The flask was removed from the cooling bath and allowed to warm to room temperature. A flash-dried, argon filled, round bottomed, two-necked 50 mL flask equipped with a Teflon coated magnetic stir bar and T-shaped stopcock with argon balloon was successively loaded with benzil (5.0 mmol, 1.05 g) and anhydrous THF (10 mL). The solution was stirred and cooled to -78^{o}C, and the acetylide solution was then transferred slowly dropwise to the benzil solution via cannula under positive argon pressure. The resulting solution was allowed to reach room temperature before being placed back into the dry ice/acetone bath. When the solution was cooled to -78^{o}C, *p*-toluenesulfonyl chloride (5.5 mmol, 1.05 g) in anhydrous THF (1 mL) and anhydrous triethylamine (5.5 mmol, 0.77 mL) were successively added. The flask was then removed from the cooling bath and allowed to warm to room temperature. The solution was then poured into a separatory funnel containing 300 mL saturated NH_4Cl solution and 50 mL diethyl ether. After thorough extraction, the organic layer was separated, dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography over 150 mL silica gel with 1:10 ethyl acetate:hexanes as eluent to afford 1.32 g (60%) of pure **15** (yellow oil which solidifies upon refrigeration). ^{1}H NMR (500.13 MHz): δ 7.81 (dd, 2H, J_1 = 8.4, J_2 = 1.4 Hz); 7.63 (d, 2H, J = 8.3 Hz); 7.55 (t, 1H, J = 7.4 Hz); 7.41 (t, 2H, J = 7.8 Hz); 7.38-7.32 (m, 5H); 7.09 (d, 2H, J = 8.2 Hz); 2.35 (s, 3H); 1.01 (s, 9H). ^{13}C NMR (125.76 MHz): δ 197.1; 192.7; 145.6; 137.5; 136.7; 133.8; 133.3; 133.2; 130.1 (x 2); 130.0 (x 2); 129.3; 129.0 (x 2); 128.8 (x 4); 128.5 (x 2); 121.0; 36.5; 27.8 (x 3); 22.1.



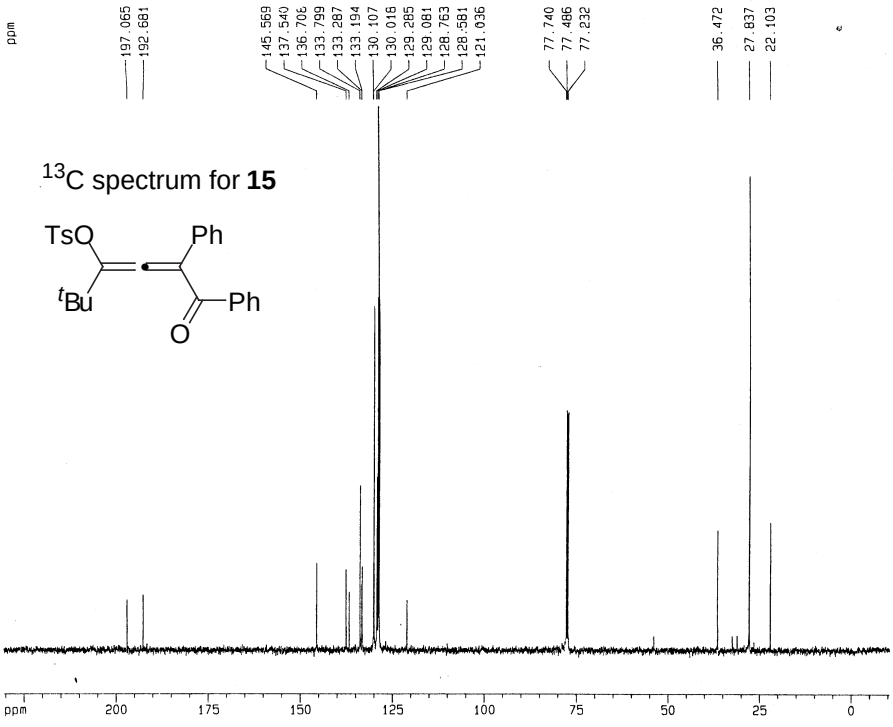
^{1}H spectrum for **15**


```
Current Data Parameters
NAME      AWS0896pnmr500
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030621
Time               15.45
INSTRUM            spect
PROBHD     5 mm BBO BB-1
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                  35.9
DW             83.200 usec
DE              6.00 usec
TE              300.0 K
D1           1.00000000 sec
P1             5.00 usec
SFO1       500.1327507 MHz
NUC1               1H
PL1             3.00 dB

F2 - Processing parameters
SI                 16384
SF         500.1300130 MHz
WDW                   EM
SSB                    0
LB              0.20 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                20.00 cm
F1P              11.000 ppm
F1             5501.43 Hz
F2P              -0.500 ppm
F2             -250.07 Hz
PPMCM         0.57500 ppm/cm
HZCM          287.57477 Hz/cm
```



^{13}C spectrum for **15**

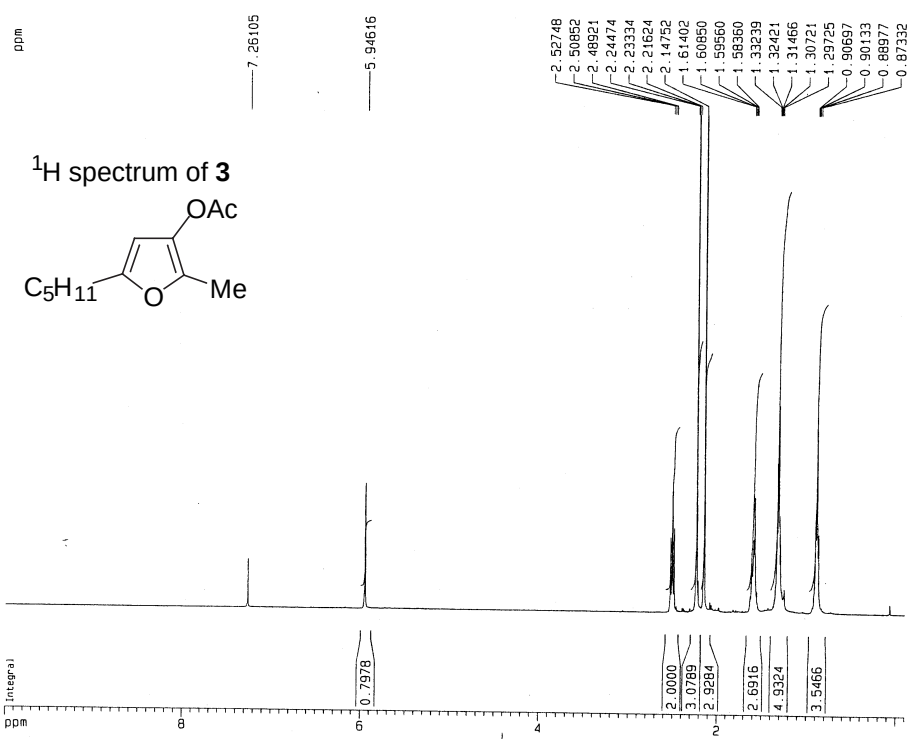

```
Current Data Parameters
NAME      AWS0896pnmr500
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030621
Time               15.49
INSTRUM            spect
PROBHD     5 mm BBO BB-1
PULPROG            zgpg
TD                 32768
SOLVENT            CDCl3
NS                   132
DS                     2
SWH          30303.031 Hz
FIDRES        0.924775 Hz
AQ            0.5407220 sec
RG                  8192
DW             16.500 usec
DE              6.00 usec
TE              300.0 K
d11          0.03000000 sec
d12          0.00002000 sec
PL13            22.00 dB
D1           2.00000000 sec
CPDPRG2         waltz16
PCPD2           80.00 usec
SFO2       500.1320000 MHz
NUC2               1H
PL2             3.00 dB
PL12            22.00 dB
P1              3.80 usec
SFO1       125.7715724 MHz
NUC1               13C
PL1             3.00 dB

F2 - Processing parameters
SI                 32768
SF         125.7577390 MHz
WDW                   EM
SSB                    0
LB              3.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
F1P             230.482 ppm
F1           28984.87 Hz
F2P             -10.482 ppm
F2           -1318.16 Hz
PPMCM         12.04818 ppm/cm
HZCM          1515.15161 Hz/cm
```

^{1}H, ^{13}C, HMQC, and HMBC of 3:

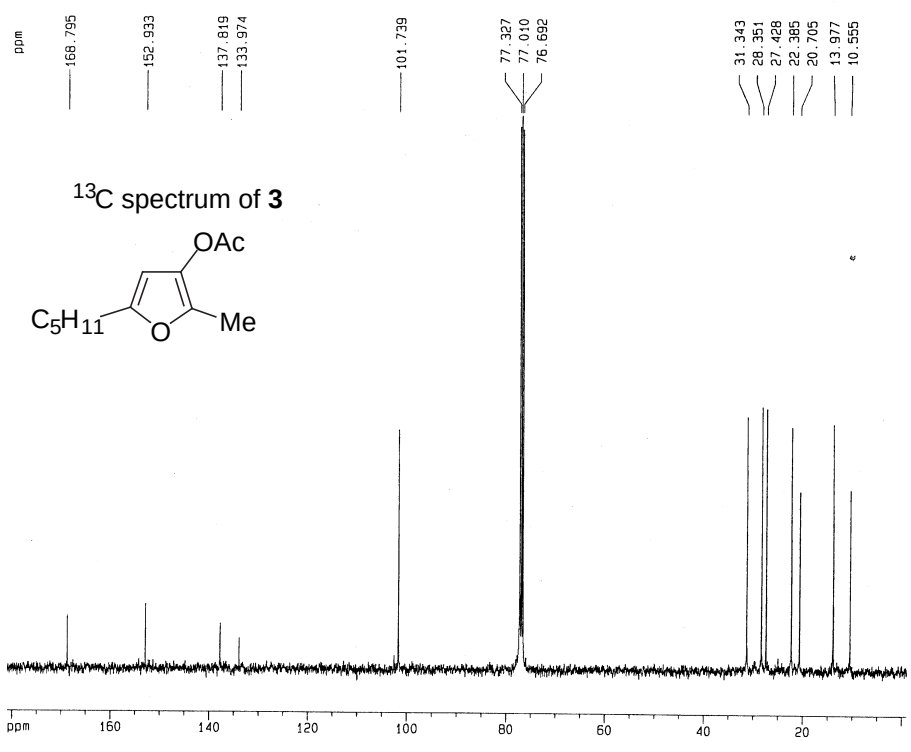


Current Data Parameters
NAME ak677fr2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010807
Time 19.13
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 90.5
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 5.50 usec
SFO1 400.1342000 MHz
NUC1 1H
PL1 -3.00 dB

F2 - Processing parameters
SI 8192
SF 400.1320090 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.32 Hz
F2P -0.100 ppm
F2 -40.01 Hz
PPMCM 0.50500 ppm/cm
HZCM 202.06668 Hz/cm

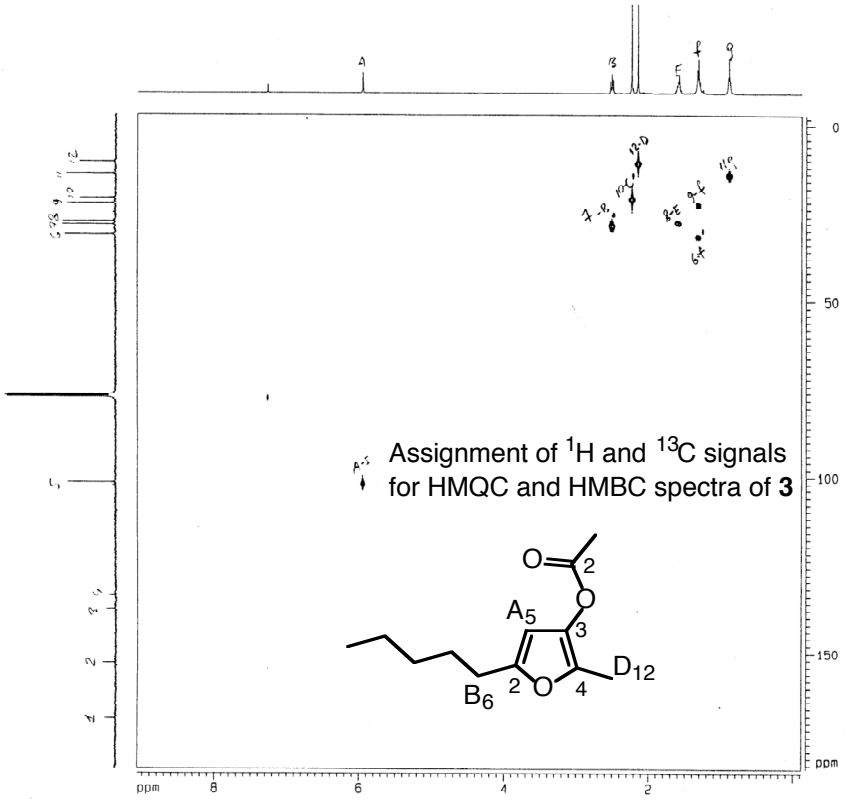


Current Data Parameters
NAME ak677fr2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010807
Time 20.00
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 1024
DS 2
SWH 24154.590 Hz
FIDRES 0.737140 Hz
AQ 0.6783476 sec
RG 14596.5
DW 20.700 usec
DE 29.57 usec
TE 300.0 K
d11 0.03000000 sec
d12 0.00002000 sec
PL13 19.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 75.00 usec
SFO2 400.1342220 MHz
NUC2 1H
PL2 120.00 dB
PL12 16.00 dB
P1 3.00 usec
SFO1 100.6242960 MHz
NUC1 13C
PL1 6.00 dB

F2 - Processing parameters
SI 32768
SF 100.6132740 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 181.000 ppm
F1 18211.00 Hz
F2P -1.000 ppm
F2 -100.61 Hz
PPMCM 9.10000 ppm/cm
HZCM 915.58081 Hz/cm



Assignment of ^{1}H and ^{13}C signals for HMQC and HMBC spectra of **3**

Current Data Parameters
NAME ak677r2
EXPNO 3
PROCNO 1

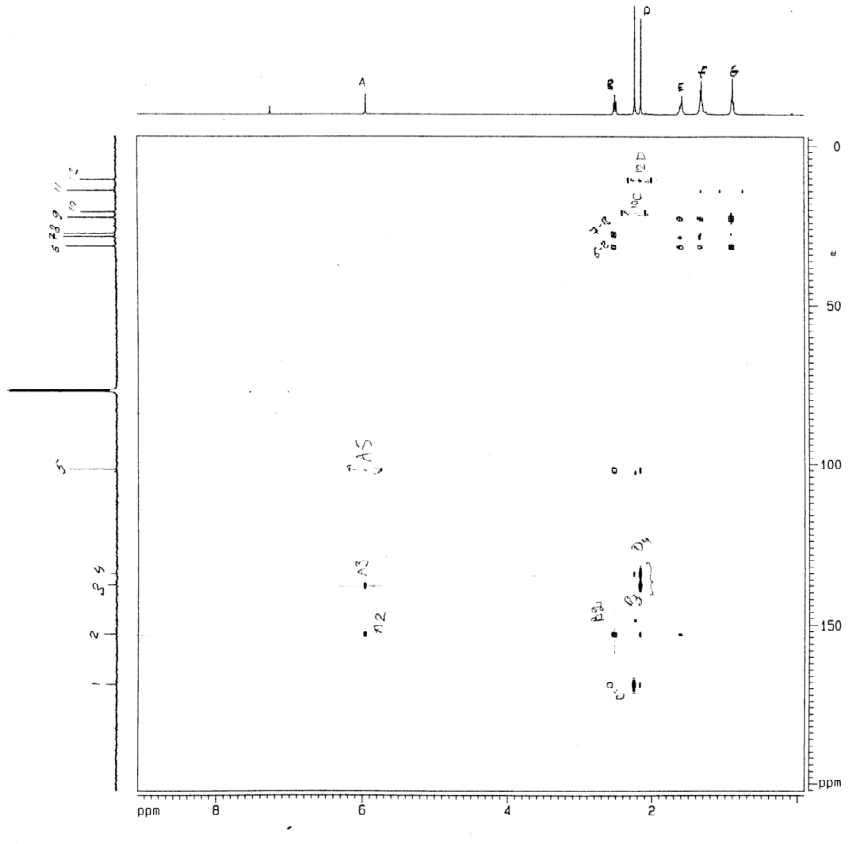
F2 - Acquisition Parameters
Date_ 20010809
Time 17.30
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG inv4gslsirnd
TD 2048
SOLVENT CDCl3
NS 16
DS 8
SWH 3676.471 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 8192
DW 136.000 usec
DE 6.00 usec
TE 300.0 K
P1 11.00 usec
p2 22.00 usec
d0 0.00000300 sec
CNST2 150.0000000
d2 0.00333333 sec
d12 0.00020000 sec
d13 0.00000300 sec
P16 2000.00 usec
d20 0.00131033 sec
D1 2.00000000 sec
SFO1 400.1338000 MHz
NUC1 1H
PL1 -3.00 dB
PL2 0.00 dB
P3 6.00 usec
SFO2 100.6228862 MHz
NUC2 13C
D16 0.00010000 sec
PL12 27.00 dB
CPDPRG2 garp
PCPD2 70.00 usec
INO 0.00002571 sec

F1 - Acquisition parameters
ND0 2
TD 256
SFO1 100.6223 MHz
FIDRES 73.110316 Hz
SW 186.021 ppm

F2 - Processing parameters
SI 2048
SF 400.1300090 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 100.6132320 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 9.070 ppm
F2LO 3629.24 Hz
F2PHI -0.118 ppm
F2HI -47.24 Hz
F1PLO 183.008 ppm
F1LO 18413.08 Hz
F1PHI -3.028 ppm
F1HI -304.75 Hz
F2PPMCM 0.51251 ppm/cm
F2HZCM 245.09805 Hz/cm
F1PPMCM 13.49250 ppm/cm
F1HZCM 1247.83562 Hz/cm



Current Data Parameters
NAME ak677r2
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010810
Time 16.30
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG inv4gslsirnd
TD 2048
SOLVENT CDCl3
NS 16
DS 8
SWH 3676.471 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 8192
DW 136.000 usec
DE 6.00 usec
TE 300.0 K
P1 11.00 usec
p2 22.00 usec
d0 0.00000300 sec
CNST2 150.0000000
d2 0.00333333 sec
d13 0.00000300 sec
D1 2.00000000 sec
SFO1 400.1338000 MHz
NUC1 1H
PL1 -3.00 dB
P3 6.00 usec
SFO2 100.6228362 MHz
NUC2 13C
PL2 6.00 dB
D6 0.00330000 sec
P16 2000.00 usec
D16 0.00010000 sec
INO 0.00002424 sec

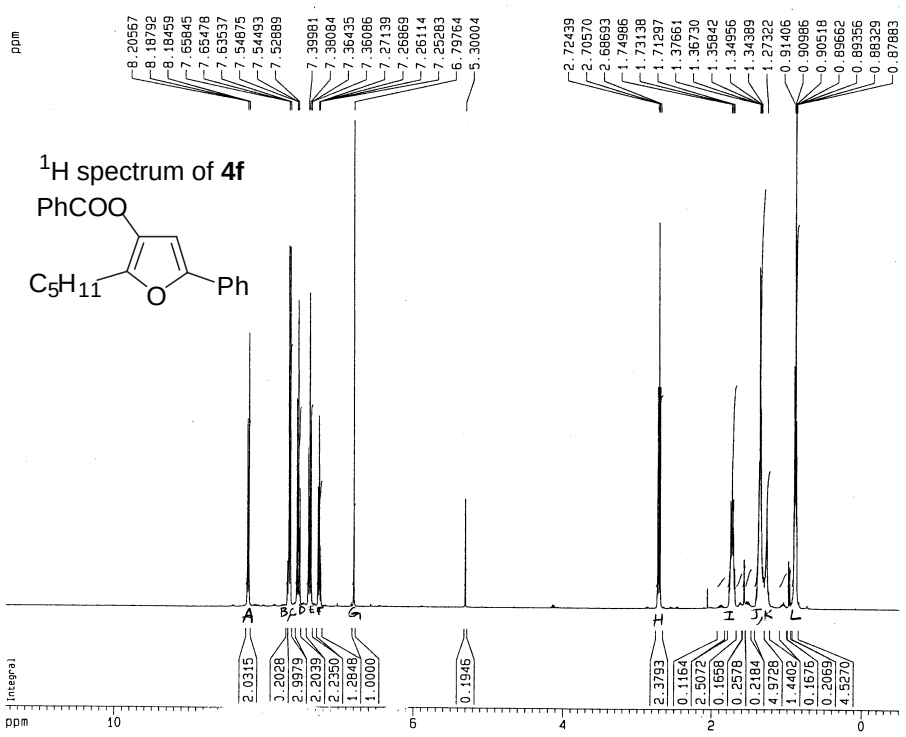
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 100.6233 MHz
FIDRES 90.582771 Hz
SW 205.014 ppm

F2 - Processing parameters
SI 2048
SF 400.1300000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 100.6132547 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 9.093 ppm
F2LO 3636.24 Hz
F2PHI -0.098 ppm
F2HI -38.74 Hz
F1PLO 202.282 ppm
F1LO 20352.22 Hz
F1PHI -2.753 ppm
F1HI -276.97 Hz
F2PPMCM 0.51254 ppm/cm
F2HZCM 245.09804 Hz/cm
F1PPMCM 13.66897 ppm/cm
F1HZCM 1375.27942 Hz/cm

^{1}H, ^{13}C, HMQC, and HMBC spectra of 4f:

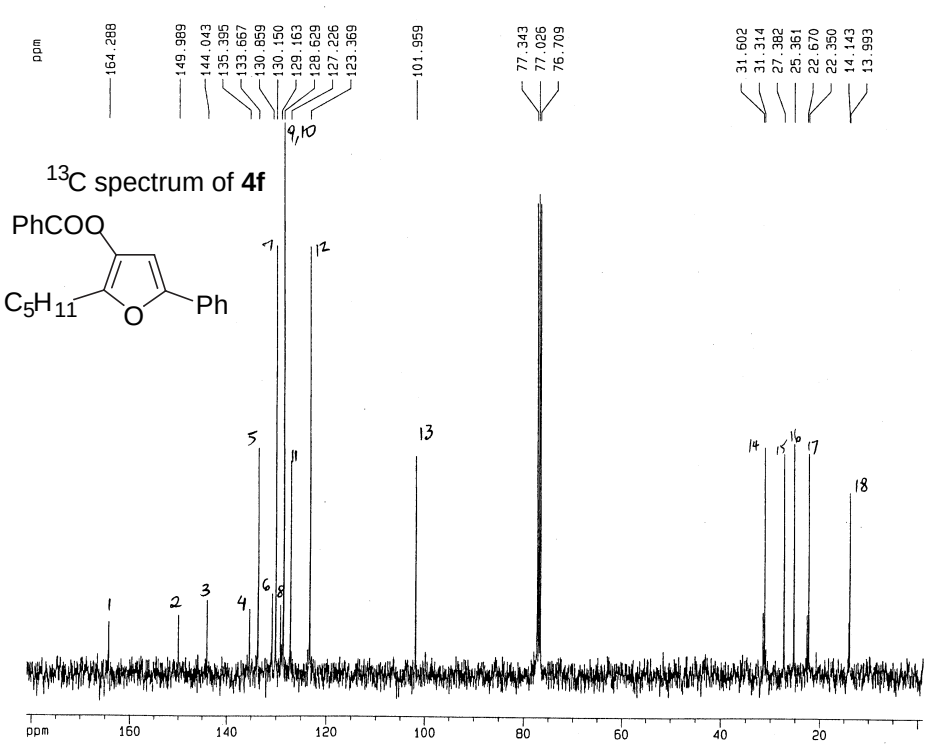



```
Current Data Parameters
NAME      AWS0433cnmr400
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020214
Time               12.38
INSTRUM            spect
PROBHD     5 mm BBO BB-1
PULPROG               zg
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            4789.272 Hz
FIDRES         0.292314 Hz
AQ             1.7105396 sec
RG                  71.8
DW                104.400 usec
DE                  6.00 usec
TE                300.0 K
D1             1.00000000 sec
P1                  5.50 usec
SFO1          400.1342000 MHz
NUC1                  1H
PL1                -3.00 dB

F2 - Processing parameters
SI                  8192
SF            400.1320090 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                11.460 ppm
F1               4585.64 Hz
F2P                -0.509 ppm
F2               -203.64 Hz
PPMCM           0.59846 ppm/cm
HZCM          239.46362 Hz/cm
```

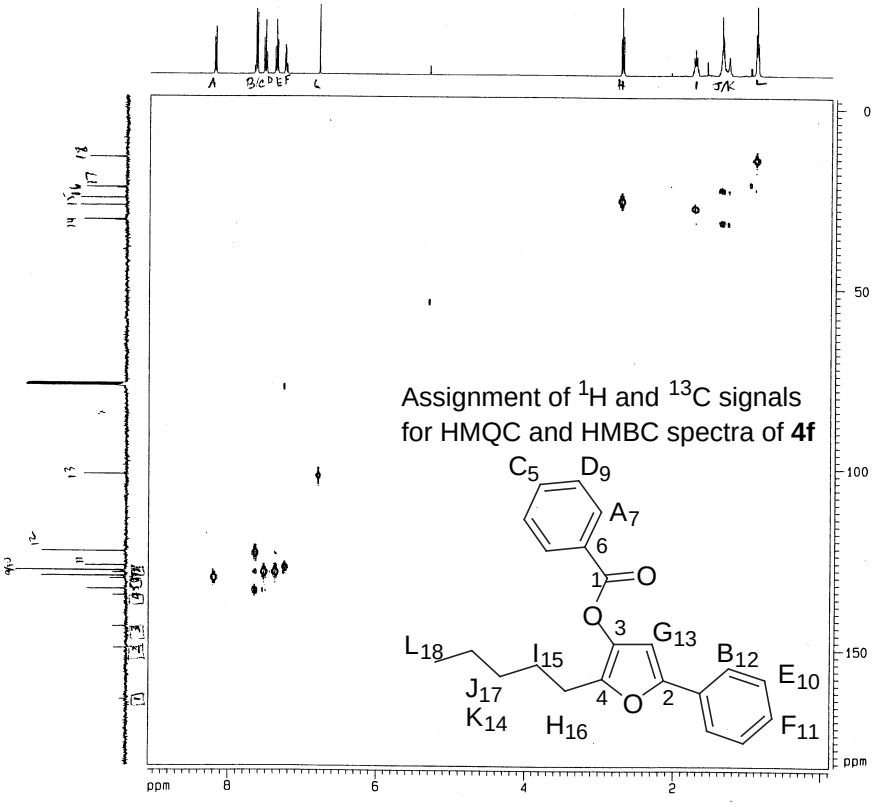



```
Current Data Parameters
NAME      AWS0433cnmr400
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020214
Time               13.15
INSTRUM            spect
PROBHD     5 mm BBO BB-1
PULPROG            zgpg
TD                 32768
SOLVENT            CDCl3
NS                  1024
DS                     2
SWH            24154.590 Hz
FIDRES         0.737140 Hz
AQ             0.6783476 sec
RG                  6502
DW                20.700 usec
DE                29.57 usec
TE                300.0 K
d11            0.03000000 sec
d12            0.00002000 sec
PL13               19.00 dB
D1             2.00000000 sec
CPDPRG2          waltz16
PCPD2              75.00 usec
SFO2          400.1342220 MHz
NUC2                  1H
PL2               120.00 dB
PL12               16.00 dB
P1                  3.00 usec
SFO1          100.6242960 MHz
NUC1                  13C
PL1                6.00 dB

F2 - Processing parameters
SI                 32768
SF            100.6132740 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               181.000 ppm
F1              18211.00 Hz
F2P                -1.000 ppm
F2              -100.61 Hz
PPMCM           9.10000 ppm/cm
HZCM          915.58081 Hz/cm
```




```
Current Data Parameters
NAME                  AWS0433nmr400
EXPNO                            7
PROCNO                           1

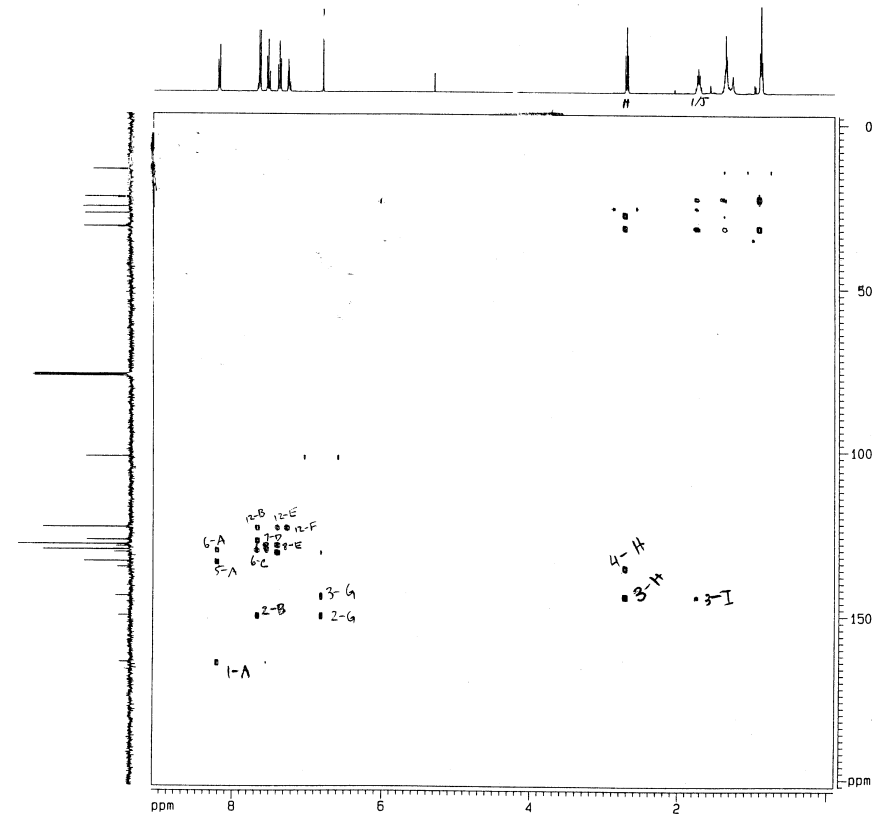
F2 - Acquisition Parameters
Date_                     20020213
Time                         15.46
INSTRUM                      spect
PROBHD     5 mm BBO BB-1
PULPROG                    inv4gs
TD                           2048
SOLVENT                     CDCl3
NS                               4
DS                               8
SWH                       3676.471 Hz
FIDRES                    1.795152 Hz
AQ                        0.2785780 sec
RG                            8192
DW                         136.000 usec
DE                           6.00 usec
TE                          300.0 K
P1                           11.00 usec
p2                           22.00 usec
d0                       0.00000300 sec
CNST2                    150.0000000
d2                       0.00333333 sec
d12                      0.00002000 sec
d13                      0.00001300 sec
P16                         2000.00 usec
d00                      0.00131033 sec
D1                       2.00000000 sec
SFO1                    400.1338000 MHz
NUC1                            1H
PL1                          -3.00 dB
PL2                           6.00 dB
P3                           6.00 usec
SFO2                    100.6222862 MHz
NUC2                            13C
D16                      0.00010000 sec
PL12                         27.00 dB
CPDPRG2                      garp
PCPD2                       70.00 usec
IN0                      0.00002671 sec

F1 - Acquisition parameters
ND0                              2
TD                             256
SFO1                    100.6223 MHz
FIDRES                  73.116516 Hz
SW                        186.021 ppm

F2 - Processing parameters
SI                            2048
SF                      400.1320090 MHz
WDW                           SINE
SSB                              0
LB                            0.00 Hz
GB                               0
PC                            1.00

F1 - Processing parameters
SI                            1024
MC2                             QF
SF                      100.6132320 MHz
WDW                           SINE
SSB                              0
LB                            0.00 Hz
GB                               0

2D NMR plot parameters
CX2                          15.00 cm
CX1                          15.00 cm
F2PLO                        9.070 ppm
F2LO                      3629.24 Hz
F2PH1                       -0.118 ppm
F2H1                        -47.24 Hz
F1PLO                      183.006 ppm
F1LO                     18413.08 Hz
F1PH1                       -3.029 ppm
F1H1                       -304.75 Hz
F2PPMCM                   0.61254 ppm/cm
F2HZCM                  245.09805 Hz/cm
F1PPMCM                  12.40250 ppm/cm
F1HZCM                  1247.85522 Hz/cm
```




```
Current Data Parameters
NAME                  AWS0433nmr400
EXPNO                            3
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20020214
Time                         13.28
INSTRUM                      spect
PROBHD     5 mm BBO BB-1
PULPROG                 inv4gslprnd
TD                           2048
SOLVENT                     CDCl3
NS                               4
DS                               8
SWH                       3676.471 Hz
FIDRES                    1.795152 Hz
AQ                        0.2785780 sec
RG                            8192
DW                         136.000 usec
DE                           6.00 usec
TE                          300.0 K
P1                           11.00 usec
p2                           22.00 usec
d0                       0.00000300 sec
CNST2                    150.0000000
d2                       0.00333333 sec
d13                      0.00001300 sec
D1                       2.00000000 sec
SFO1                    400.1338000 MHz
NUC1                            1H
PL1                          -3.00 dB
P3                           6.00 usec
SFO2                    100.6232923 MHz
NUC2                            13C
PL2                           6.00 dB
D6                       0.08330000 sec
P16                         2000.00 usec
D16                      0.00010000 sec
IN0                      0.00002424 sec

F1 - Acquisition parameters
ND0                              2
TD                             256
SFO1                    100.6233 MHz
FIDRES                  80.587771 Hz
SW                        205.014 ppm

F2 - Processing parameters
SI                            2048
SF                      400.1320000 MHz
WDW                           SINE
SSB                              0
LB                            0.00 Hz
GB                               0
PC                            1.40

F1 - Processing parameters
SI                            1024
MC2                             QF
SF                      100.6132547 MHz
WDW                           SINE
SSB                              0
LB                            0.00 Hz
GB                               0

2D NMR plot parameters
CX2                          15.00 cm
CX1                          15.00 cm
F2PLO                        9.093 ppm
F2LO                      3638.24 Hz
F2PH1                       -0.096 ppm
F2H1                        -38.24 Hz
F1PLO                      202.262 ppm
F1LO                     20352.22 Hz
F1PH1                       -2.753 ppm
F1H1                       -276.97 Hz
F2PPMCM                   0.81254 ppm/cm
F2HZCM                  245.09804 Hz/cm
F1PPMCM                  13.86897 ppm/cm
F1HZCM                  1375.27942 Hz/cm
```

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