Supporting Information

Using Air, Light, Water and Spirulina To Access a Wide Variety of Polyoxygenated Compounds

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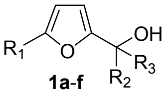
Supporting Information

Part A: Experimental procedures

General procedure for photooxidations. A solution of furanols **1a-f**, **4**, **6**, **13**, or furan-diols **7**, **9** and **11**, (0.5 mmol) in water (10 mL), containing spirulina (20 mg) as photosensitizer, was placed in a test tube and cooled with an ice bath (5 ºC). Oxygen was bubbled through the solution immediately before, and, during, its irradiation by a xenon Variac Eimac Cermax 300 W visible spectrum lamp. More spirulina (20 mg) was added for every 15 min of irradiation. Complete consumption of the starting material was observed by TLC after 20 – 110 mins of irradiation.

In the case of **1a-f**, **6** and **9** the reaction mixture was extracted with EtOAc (3×), the combined organics were dried (Na_2SO_4), concentrated *in vacuo* and purified by flash column chromatography to afford pure **2a-f**, **5** and **10**, respectively.

In the case of furans **4**, **7**, **11** and **13** the EtOAc extracts were treated with catalytic amounts of *p*-TsOH (see below).



1a-f

The photooxidation precursors, furanols **1a-f** shown in Scheme 3, were easily prepared using well-established known synthetic protocols. In particular, primary alcohols **1a** and **1d** were prepared by $NaBH_4$ reduction of the corresponding commercially available furfurals. Secondary alcohols **1c** and **1f** were easily synthesized by *n*-BuLi addition to the same furfurals. Furanol **1e** was prepared by addition of methylfuryllithium, prepared by deprotonation of methylfuran with *n*-BuLi, to acetone. Finally, substrate **1b** was prepared by aldol condensation of the enolate of ethyl acetate (LDA was used as base), to furfural.

1a: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37 (dd, J_1 = 1.8 Hz, J_2 = 0.6 Hz, 1H), 6.32 (dd, J_1 = 3.3 Hz, J_2 = 1.8 Hz, 1H), 6.26 (d, J = 3.3 Hz, 1H), 4.55 (s, 1H), 2.75 (brs, 1 -OH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.0, 142.4, 110.2, 107.6, 57.1 ppm.

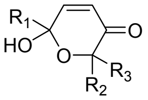
1b: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35 (dd, J_1 = 1.8 Hz, J_2 = 0.9 Hz, 1H), 6.31 (dd, J_1 = 3.3 Hz, J_2 = 1.8 Hz, 1H), 6.26 (d, J = 3.3 Hz, 1H), 5.11 (dd, J_1 = 8.3 Hz, J_2 = 4.5 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H) 3.42 (brs, 1 -OH) 2.88 (dd, J_1 = 16.4 Hz, J_2 = 8.3 Hz, 1H), 2.80 (dd, J_1 = 16.4 Hz, J_2 = 4.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.8, 154.7, 142.1, 110.2, 106.2, 64.1, 60.9, 39.8, 14.0 ppm.

1c: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, J = 1.8 Hz, 1H), 6.32 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 1H), 6.22 (d, J = 3.2 Hz, 1H), 4.65 (t, J = 6.8 Hz, 1H), 2.10 (brs, -OH), 1.84 (m, 2H), 1.35 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.9, 141.8, 110.1, 105.7, 67.8, 35.2, 27.7, 22.5, 14.0 ppm.

1d: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.16 (d, J = 2.9 Hz, 1H), 5.91 (d, J_1 = 2.9 Hz, 1H), 4.53 (d, J = 3.9 Hz, 1H), 2.28 (s, 3H), 1.88 (brs, 1-OH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) = 152.4, 152.2, 108.7, 106.2, 57.5, 13.5 ppm.

1e: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.04 (d, J = 3.0 Hz, 1H), 5.86 (m, 1H), 2.27 (d, J = 0.6 Hz, 3H), 1.56 (s, 6H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.4, 151.1, 105.8, 104.3, 68.7, 28.6, 13.5 ppm.

1f: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.09 (d, J = 2.7 Hz, 1H), 5.89 (d, J = 2.7 Hz, 1H), 4.58 (q, J = 5.1 Hz, 1H), 2.27 (s, 3H), 1.83 (m, 2H plus 1 -OH), 1.33 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H), ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.1, 151.6, 106.6, 105.9, 67.8, 35.1, 27.8, 22.5, 14.0, 13.5 ppm.



2a-f

Solutions of furanols **1a-f** in water were photooxidized according to the general procedure described above. The irradiation times were: 60 min for **1a**, 50 min for **1b**, 50 min for **1c**, 60 min for **1d**, 30 min for **1e** and 30 min for **1f**. For the relative ratios of the products **2** and **3** as well as the isolated yields see Scheme 3.

2a: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.97 (dd, J_1 = 10.4 Hz, J_2 = 3.0 Hz, 1H), 6.17 (d, J = 10.4 Hz, 1H), 5.64 (d, J = 3.0 Hz, 1H), 4.58 (d, J = 16.9 Hz, 1H), 4.14 (d, J = 16.9 Hz, 1H) ppm; ^{13}C (75 MHz, $CDCl_3$): δ = 194.6, 145.8, 127.9, 88.2, 66.6 ppm.

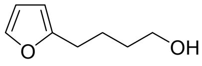
2b: Mixture of two diastereoisomers in 7:3 ratio. ^{1}H-NMR (300 MHz, $CDCl_3$) for the major diastereoisomer: δ = 6.92 (dd, J_1 = 10.3 Hz, J_2 = 3.5 Hz, 1H), 6.15 (d, J = 10.3 Hz, 1H), 5.65 (d, J = 3.3 Hz, 1H), 5.03 (dd, J_1 = 7.5 Hz, J_2 = 3.9 Hz , 1H), 4.17 (q, J = 7.2 Hz, 1H), 3.00 (dd, J_1 = 16.8 Hz, J_2 = 3.8 Hz, 1H), 2.75 (dd, J_1 = 16.8 Hz, J_2 = 7.6 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H) ppm; ^{1}H-NMR (300 MHz, $CDCl_3$) for the minor diastereoisomer: δ = 6.96 (dd, J_1 = 10.4 Hz, J_2 = 1.7 Hz, 1H), 6.20 (dd, J_1 = 10.4 Hz, J_2 = 1.7 Hz, 1H), 5.71 (brs, 1H), 5.03 (dd, J_1 = 8.4 Hz, J_2 = 4.5 Hz , 1H), 4.17 (q, J = 7.2 Hz, 1H), 3.02 (dd, J_1 = 16.8 Hz, J_2 = 3.8 Hz, 1H), 2.81 (dd, J_1 = 16.8 Hz, J_2 = 7.9 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) for the major diastereoisomer: δ = 194.7, 171.0, 144.2, 127.3, 87.8, 70.8, 60.9, 35.3, 14.1 ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) for the minor diastereoisomer: 193.6, 171.0, 147.9, 128.3, 90.8, 75.3, 61.1, 36.2, 14.1 ppm.

2c: Mixture of two diastereoisomers in 7:3 ratio. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.92 (dd, J_1 = 10.2 Hz, J_2 = 1.5 Hz, 1H, minor), 6.89 (dd, J_1 = 10.2 Hz, J_2 = 3.3 Hz, 1H, major), 6.15 (dd, J_1 = 10.2 Hz, J_2 = 1.5 Hz, 1H, *minor*), 6.11 (d, J = 10.2 Hz, 1H, major), 5.66 (m, 2H, both major and minor), 4.56 (dd, J_1 = 8.1 Hz, J_2 = 3.8 Hz, 1H, major), 4.08 (dd, J_1 = 8.2 Hz, J_2 = 3.9 Hz, 1H, minor) 3.12 (d, J = 7.3 Hz, -OH, minor) 2.90 (d, J = 5.1, -OH, major), 1.94 (m, 1H, both major and minor), 1.71 (m, 1H, both major and minor), 1.38 (m, 4H, both major and minor), 0.91 (t, J =7.1, 3H, both major and minor) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) for the major diastereoisomer: δ =196.5, 144.1, 127.7, 87.7, 74.2, 29.3, 27.1, 22.5, 13.9; ^{13}C-NMR (75 MHz, $CDCl_3$) for the minor diastereoisomer: δ = 196.2, 147.4, 128.8, 90.9, 79.0, 30.4, 27.3, 22.4, 13.9.

2d: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.87 (d, *J* = 10.4 Hz, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 4.57 (d, *J* = 16.8 Hz, 1H), 4.12 (d, *J* = 16.8 Hz, 1H), 1.65 (s, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 194.7, 148.6, 126.6, 92.8, 66.6, 28.0 ppm.

2e: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.81 (d, *J* = 10.0 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 2.60 (s, -OH), 1.60 (s, 3H), 1.53 (s, 3H), 1.36 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.3, 147.5, 124.3, 92.6, 78.8, 30.6, 28.0, 25.9 ppm; HRMS (TOFMS ES+): calcd for $C_8H_{12}O_3Na$: 179.0684 $[M + Na]^+$; found: 179.0670.

2f: Mixture of two diastereoisomers in 4:1 ratio. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 10.2 Hz, 1H, minor), 6.80 (d, *J* = 10.1 Hz, 1H, major), 6.03 (d, *J* = 10.2 Hz, 1H, minor), 6.01 (d, *J* = 10.1 Hz, 1H, major), 4.50 (dd, J_1 = 7.7 Hz, J_2 = 3.8 Hz, 1H, major), 4.15 (dd, J_1 = 8.3 Hz, J_2 = 4.6 Hz, 1H, minor), 1.92 (m, 1H, both major and minor), 1.68 (m, 1H, both major and minor), 1.64 (s, 3H, major), 1.61 (s, 3H minor), 1.37 (m, 4H both major and minor), 0.90 (t, *J* = 7.0 Hz, 3H both major and minor) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) for the major diastereoisomer: δ = 196.9, 147.6, 126.6, 92.7, 74.3, 29.3, 29.0, 27.1, 22.5, 13.9 ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) for the minor diastereoisomer: δ = 196.5, 150.1, 126.3, 94.4, 78.0, 31.2, 27.3, 24.7, 22.4, 14.0 ppm; HRMS (TOFMS EI+): calcd for $C_{10}H_{16}O_3$: 184.1099 $[M]^+$; found: 184.1097.



4

To a solution of TBS-protected precursor of alcohol **4**[1] (not shown, 460 mg, 1.74 mmol) in THF (25 mL) at 0 °C, was added dropwise TBAF (2.0 mL 1M in THF, 2.0 mmol). The reaction was then warmed to room temperature and stirred for 1.5 h after which it was partitioned between EtOAc (20 mL) and H_2O (20 mL). The layers were separated and the organic phase dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 5:1) to afford the desired deprotected alcohol **4** (225 mg, 90%).

4: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 1.6 Hz, 1H), 6.27 (dd, J_1 = 3.1 Hz, J_2 = 1.6 Hz, 1H), 5.98 (d, *J* = 3.1 Hz, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.65 (t, *J* = 7.3 Hz,

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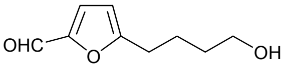
[1] M. Tofi, T. Montagnon, T. Georgiou and G. Vassilikogiannakis, *Org. Biomol. Chem*., 2007, **5**, 772.

2H), 1.89 (s, -OH), 1.66 (m, 4H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.0, 140.8, 110.1, 104.8, 62.5, 32.1, 27.6, 24.3 ppm.



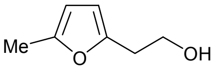
6

To a solution of TBS-protected precursor of alcohol **4**[1] (not shown, 500 mg, 1.97 mmol) in anhydrous THF (10 mL) under an argon atmosphere at 0 °C, was added dropwise a solution of *n*-BuLi (2.46 mL, 1.6 M solution in Hexane, 3.94 mmol). After 20 min stirring at the same temperature, DMF (488 μL, 6.3 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h, after which it was partitioned between Et_2O (10 mL) and NH_4Cl (10 mL). The layers were separated and the organic phase dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, petroleum ether:EtOAc = 30:1) afforded the desired aldehyde (397 mg, 68%).

To a solution of aldehyde (327 mg, 1.16 mmol) in THF (15 mL) at 0 °C, was added dropwise TBAF (1.30 mL 1M in THF, 1.30 mmol). The reaction was then warmed to room temperature and stirred for 1.5 h after which it was partitioned between EtOAc (15 mL) and H_2O (10 mL). The layers were separated and the organic phase dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, petroleum ether:EtOAc = 1:2) to afford the desired alcohol **6** (156 mg, 80%).

6: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 7.16 (d, J = 3.5 Hz, 1H), 6.23 (d, J = 3.5 Hz, 1H), 3.64 (t, J = 6.5 Hz, 2H), 2.74 (t, J = 7.4 Hz, 2H), 2.05 (s, -OH), 1.77 (m, 2H), 1.60 (m, 2H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 177.0, 163.7, 151.8, 123.8, 108.8, 62.2, 32.0, 28.1, 23.9 ppm.

Substrates **7**[1], **9**[2] and **11**[3] have been previously prepared in our laboratory.



13

A free radical coupling of an excess of commercially available sylvan with ethyl iodoacetate according to Bacciochi[4] conditions afforded ethyl 2-(furan-2-yl)acetate.

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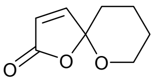
[2] T. Georgiou, M. Tofi, T. Montagnon and G. Vassilikogiannakis, G. *Org. Lett.*, 2006, **8**, 1945.
[3] D. Noutsias, A. Kouridaki and G. Vassilikogiannakis, *Org. Lett.*, 2011, **13**, 1166.

Specifically, to a solution of commercially available sylvan (1.69 mL, 18.7 mmol) in DMSO (8 mL) were added ethyl-iodoacetate (276 µL, 2.34 mmol) and $FeSO_4 \cdot 7H_2O$ (325 mg, 1.17 mmol). Afterwards a solution of H_2O_2 (30% wt in H_2O, 482 µL) was added dropwise. The reaction mixture stirred for 20 h at room temperature after which it was partitioned between Et_2O (10 mL) and brine (3× 8 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to afford the desired ethyl 2-(furan-2-yl)acetate (386 mg, 98%).

To a solution of ethyl 2-(furan-2-yl)acetate (196 mg, 1.17 mmol) in anhydrous Et_2O (10 mL) under an argon atmosphere at 0 °C, was added $LiAlH_4$ (89 mg, 2.33 mmol). The reaction was then warmed to room temperature and stirred for 30 min after which it was partitioned between Et_2O (10 mL) and NH_4Cl (10 mL). The layers were separated and the organic phase dried (Na_2SO_4) and concentrated *in vacuo* to afford the alcohol **13** (133 mg, 90%).

13: ^{1}H-NMR (300 MHz, $CDCl_3$,): δ = 5.97 (d, *J* = 3.0 Hz, 1H), 5.87 (d, *J* = 3.0 Hz, 1H), 3.83 (t, *J* = 6.2 Hz, 2H), 2.83 (t, *J* = 6.2 Hz, 2H), 2.25 (s, 3H), 1.85 (s, -OH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 151.1, 150.8, 107.2, 106.0, 61.1, 31.6, 13.5 ppm.



5

Furan **4** (70 mg, 0.5 mmol) was photooxidised in H_2O (see the general procedure described above) for 20 minutes. The reaction solution was concentrated *in vacuo*. The crude mixture of spiro-hydroperoxides was redissolved in pyridine (3 mL) followed by addition of acetic anhydride (100 µL). The resulting solution was stirred for 10 min at room temperature. EtOAc (10 mL) was then added and the organic phase was washed with saturated aq. solution of $CuSO_4$ (3× 5 mL). The organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, petroleum ether:EtOAc = 2:1) afforded 1,6-dioxaspiro[4,5]dec-3-en-2-one **5** (55 mg, 71%).

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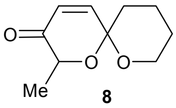
[4] E. Baciocchi, E. Muraglia and G Sleiter *J. Org. Chem.*, 1992, **57**, 6817.

The photooxidation of furfural **6** (84 mg, 0.5 mmol) in H_2O was slower (110 minutes of irradiation), but provides directly and cleanly (no further treatment was needed) the requisite 1,6-dioxaspiro[4,5]dec-3-en-2-one **5** (64 mg, 83 %).

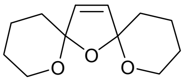
5: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 5.7 Hz, 1H), 6.10 (d, *J* = 5.7 Hz, 1H), 3.98 (m, 2H), 2.00–1.50 (m, 6H), ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.5, 154.2, 123.0, 106.8, 65.0, 32.1, 24.0, 19.0 ppm; HRMS (ESI+): calcd for $C_{16}H_{20}O_6Na$: 331.1152 [2M + Na^+]; found: 331.1148.



8

Furan-diol **7** (92 mg, 0.5 mmol) was photooxidised in H_2O (see the general procedure described above) for 60 minutes. The crude reaction mixture was dissolved in EtOAc (5 mL) followed by addition of catalytic amount of *p*-TsOH. After 1 h stirring at room temperature the reaction mixture was washed with sat. $NaHCO_3$, dried (Na_2SO_4) and purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1 → 1:1) to afford pure 2-methyl-1,7 dioxaspiro[5,5]undec-4-en-3-one **8** (49 mg, 54%, mixture of two diastereoisomers in 2.5:1 ratio) as well as γ-spiroketal δ-lactone **5** (11.5 mg, 15%).

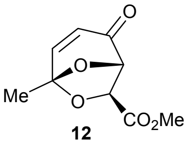
8: Mixture of 2 distereoisomers in 2.5:1 ratio. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ = 6.73 (d, *J* = 10.2 Hz, 1H, minor), 6.67 (d, *J* = 10.1 Hz, 1H, major), 6.02 (d, *J* = 10.2 Hz, 1H, minor), 6.00 (d, *J* = 10.1 Hz, 1H, major), 4.46 (q, *J* = 6.6 Hz, 1H, major), 4.29 (q, *J* = 7.1 Hz, 1H, minor), 4.04 (dt, J_1 = 11.3 Hz, J_2 = 3.8 Hz, 1H, minor), 3.80 (m, 2H major plus 1H minor), 1.89 (m, 2H major plus 2H minor), 1.66 (m, 4H major plus 4H minor), 1.52 (d, *J* = 7.2 Hz, 3H minor), 1.39 (d, *J* = 6.9 Hz, 3H major) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$, for the major): δ = 197.7, 148.4, 126.8, 93.2, 70.0, 62.5, 34.3, 24.7, 17.8, 15.3 ppm; ^{13}C-NMR (75 MHz, $CDCl_3$, for the minor): δ = 197.8, 149.5, 125.8, 93.9, 74.4, 61.6, 32.6, 24.6, 18.5, 18.3 ppm; HRMS (ESI+): calcd for $C_{10}H_{14}O_3Na$ [M + Na^+]: 205.0835; found: 205.0835.



10

Furan-diol **9** (106 mg, 0.5 mmol) was photooxidised in H_2O (see the general procedure described above) for 40 minutes. The residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 2:1) to afford *bis*-spiroketal **10** (71 mg, 68%) as a 55:45 mixture of diastereoisomers.

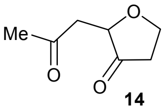
10: Mixture of two diastereoisomers in 55:45 ratio. ^{1}H-NMR (500 MHz, C_6D_6): δ = 5.73 (s, 2H), 5.72 (s, 2H), 4.07 (m, 4H), 3.70 (m, 4H), 1.95 (m, 4H), 1.83 (m, 2H), 1.64 (dd, J_1 = 13.0 Hz, J_2 = 4.3 Hz, 2H), 1.60 (m, 2H), 1.47 (m, 8H), 1.24 (m, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 133.8 (2C), 133.7 (2C), 109.4 (2C), 108.6 (2C), 63.4 (2C), 63.3 (2C), 35.1 (2C), 34.5 (2C), 25.0 (2C), 24.9 (2C), 19.6 (2C), 19.5 (2C) ppm.



12

Furan-diol **11** (100 mg, 0.5 mmol) was photooxidised in H_2O (see the general procedure described above) for 35 minutes. After photooxidation the intermediate pyranulose (not shown) was dissolved in EtOAc (5 mL) at room temperature and treated with catalytic amount of *p*-TsOH for 1 h. The reaction was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 5:1) to afford pure 6,8-dioxabicyclo[3.2.1]oct-3-en-2-one **12** (73 mg, 74%).

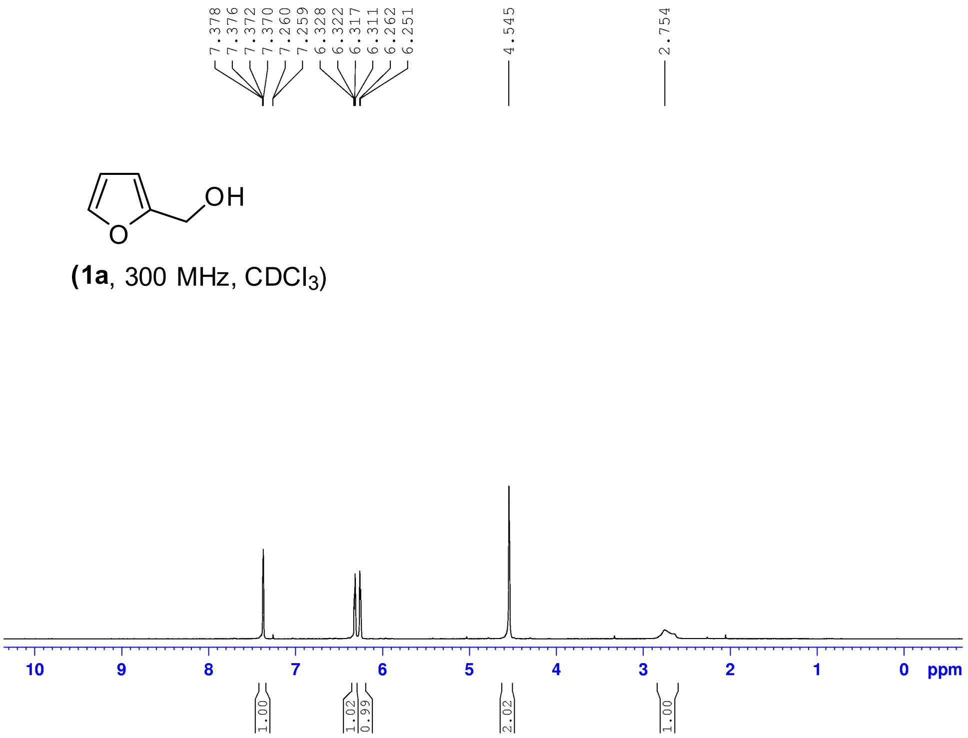
12: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (d, J = 9.6 Hz, 1H), 6.06 (dd, J_1 = 9.6 Hz, J_2 = 1.3 Hz, 1H), 4.89 (d, J = 1.4 Hz, 1H), 4.30 (d, J = 1.4 Hz, 1H), 3.82 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.5, 169.4, 151.3, 126.1, 105.5, 84.0, 73.5, 53.0, 21.6 ppm; HRMS (TOFMS EI+): calcd for $C_9H_{10}O_5$: 198.0528 $[M]^+$; found: 198.0535.



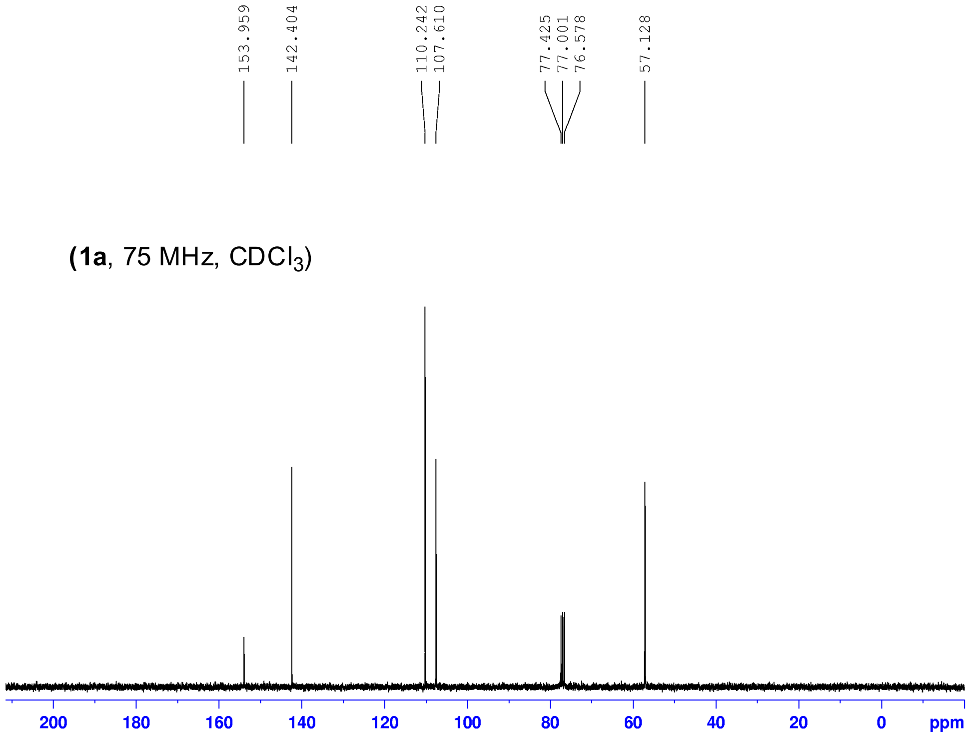
14

Furan **13** (63 mg, 0.5 mmol) was photooxidised in H_2O (see the general procedure described above) for 35 minutes. The aqueous solution containing the intermediate 1,4-enedione (previously isolated in a separate experiment) was treated *in situ* with catalytic amount of *p*-TsOH (at room temperature, overnight). The reaction mixture was extracted with EtOAc. The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 5:1 → 1:1) affording pure 3-keto-tetrahydrofuran **14** (57.5 mg, 81%).

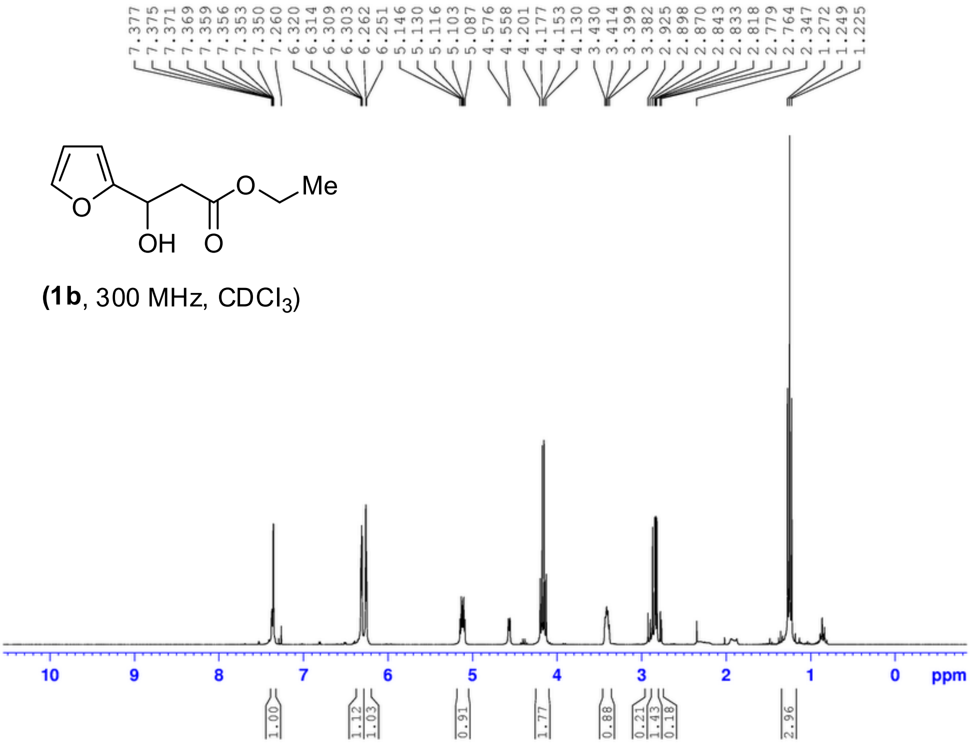
14: ^{1}H-NMR (300 MHz, $CDCl_3$,): δ = 4.34 (dt, J_1 = 9.1 Hz, J_2 = 4.1 Hz, 1H), 4.1 (dt, J_1 = 9.0 Hz, J_2 = 7.5 Hz, 1H), 3.95 (dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 1H), 3.00 (dd, (J_1 = 17.8 Hz, J_2 = 3.6 Hz, 1H), 2.84 (dd, J_1 = 17.8 Hz, J_2 = 5.6 Hz, 1H), 2.75 (q, J = 9.0 Hz, 1H), 2.51 (ddd, J_1 = 17.9 Hz, J_2 = 7.5 Hz, J_3 = 4.1 Hz, 1H), 2.17 (s, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 215.4, 204.6, 75.3, 65.1, 44.9, 36.4, 30.0 ppm;



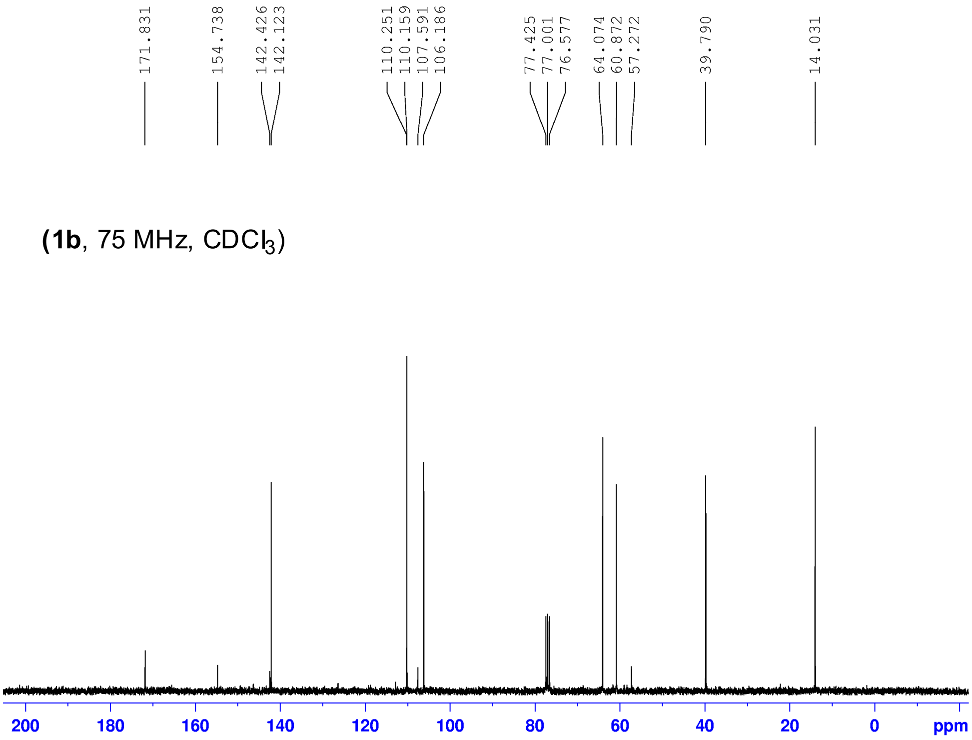
(**1a**, 300 MHz, $CDCl_3$)



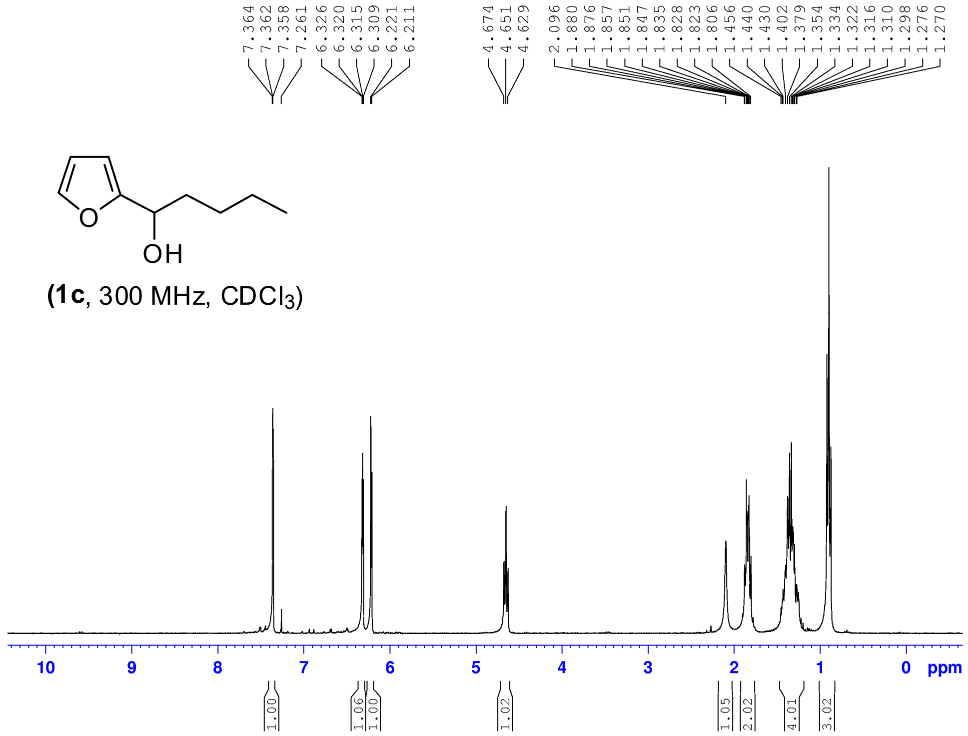
(**1a**, 75 MHz, $CDCl_3$)

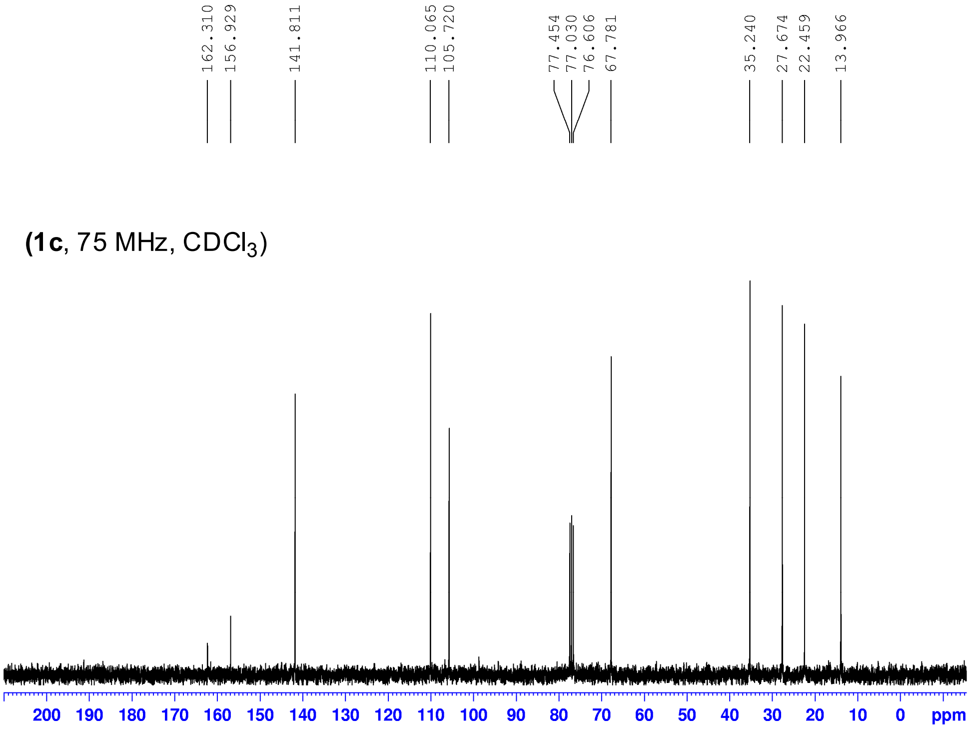


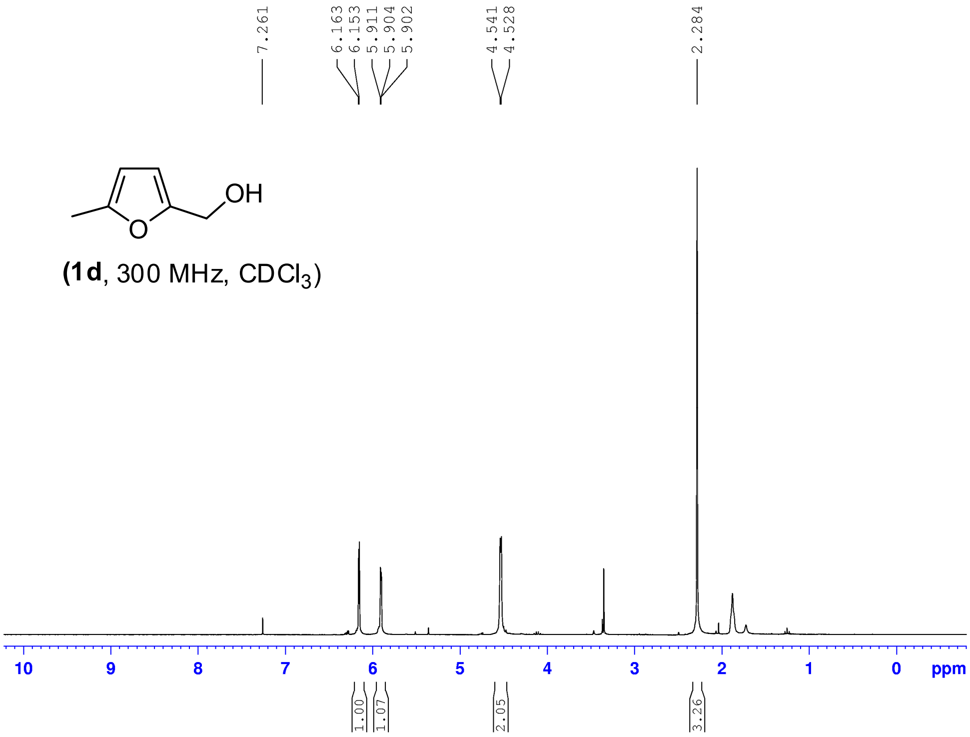
(**1b**, 300 MHz, $CDCl_3$)

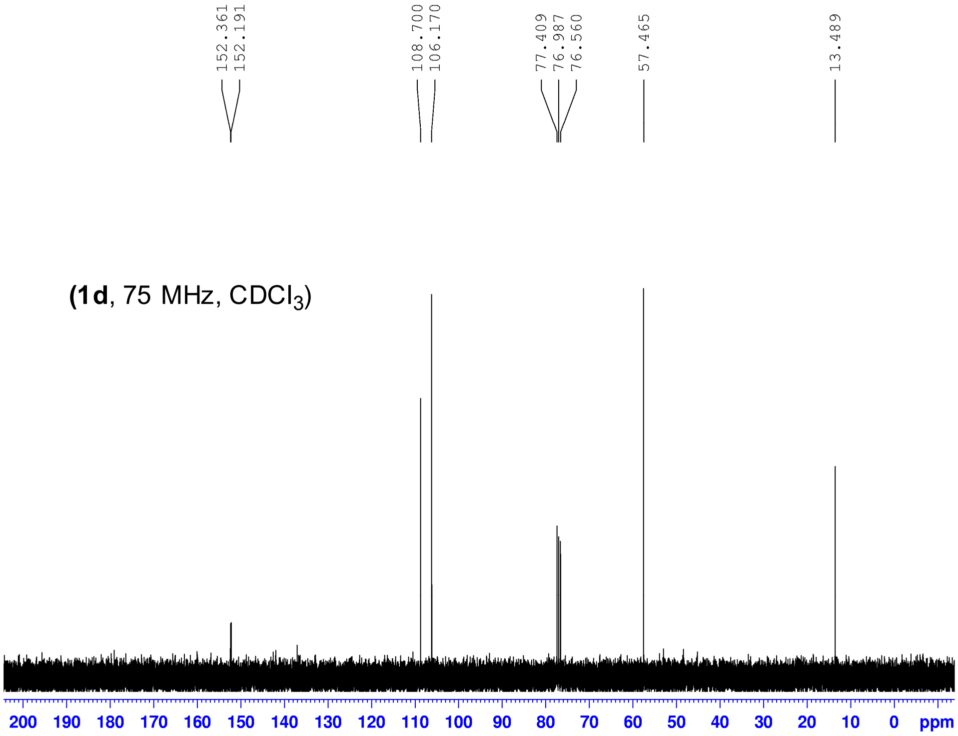


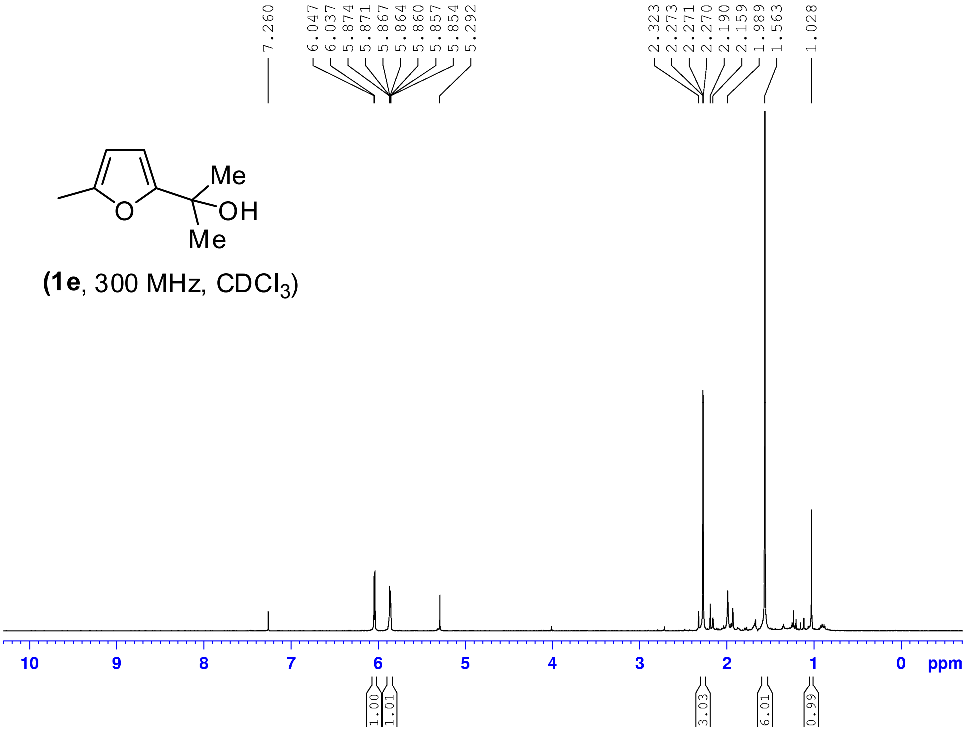
(**1b**, 75 MHz, $CDCl_3$)


7.364
7.362
7.358
7.261
6.326
6.320
6.315
6.309
6.221
6.211
4.674
4.651
4.629
2.096
1.880
1.876
1.857
1.851
1.847
1.835
1.828
1.823
1.806
1.456
1.440
1.430
1.402
1.379
1.354
1.334
1.322
1.316
1.310
1.298
1.276
1.270
O
OH
(1c, 300 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.00
1.02
1.05
2.02
4.01
3.02

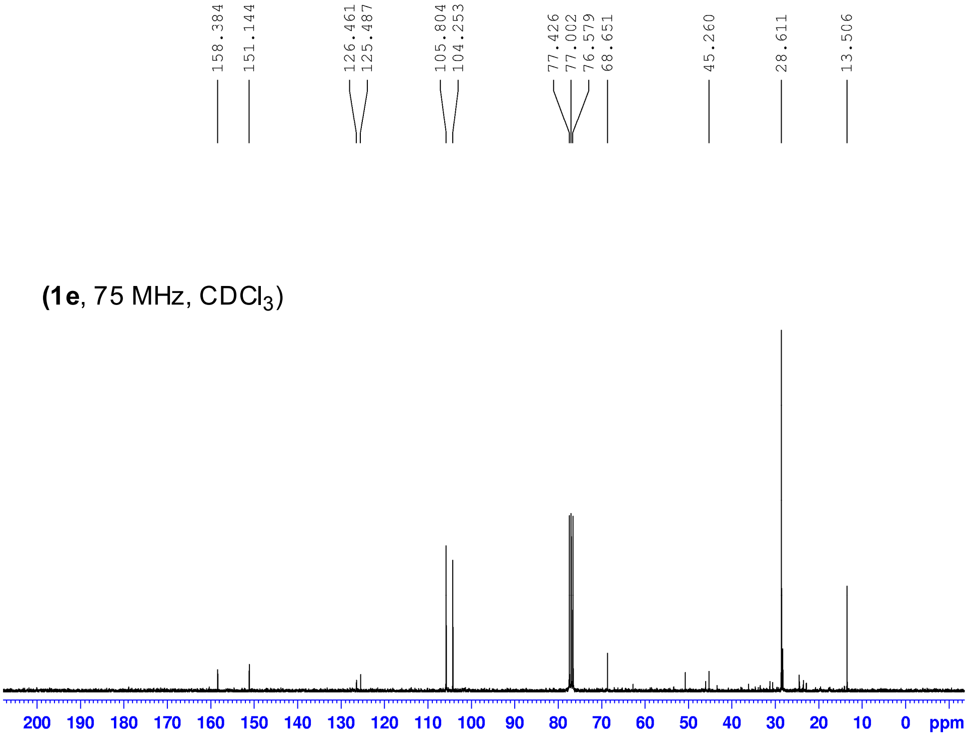

162.310
156.929
141.811
110.065
105.720
77.454
77.030
76.606
67.781
35.240
27.674
22.459
13.966
(1c, 75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


(**1d**, 300 MHz, $CDCl_3$)

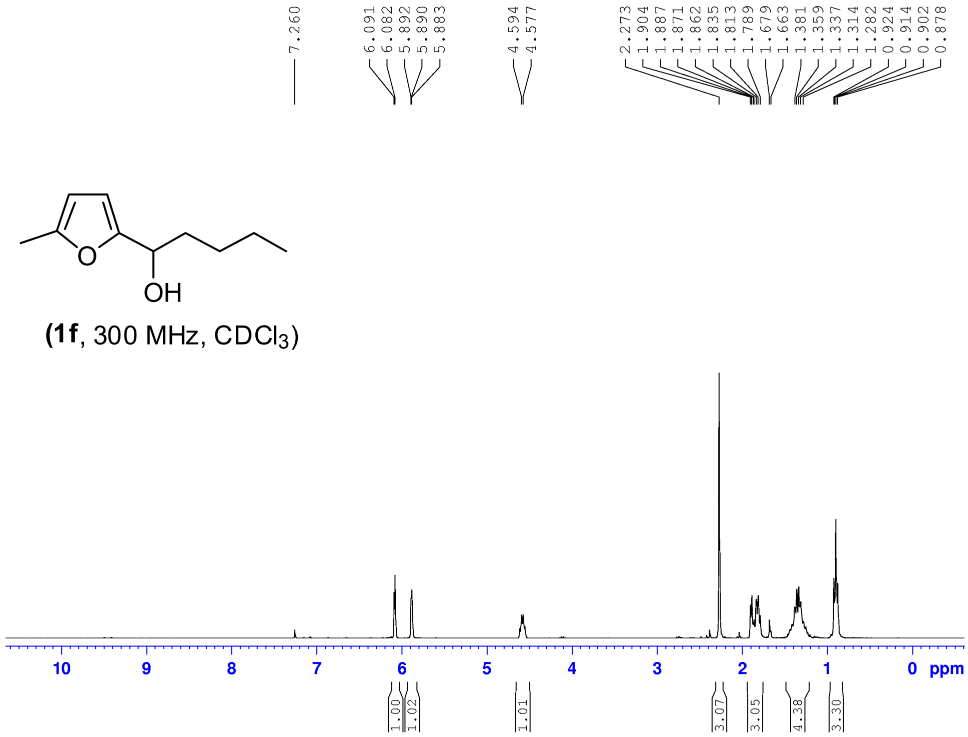

(**1d**, 75 MHz, $CDCl_3$)



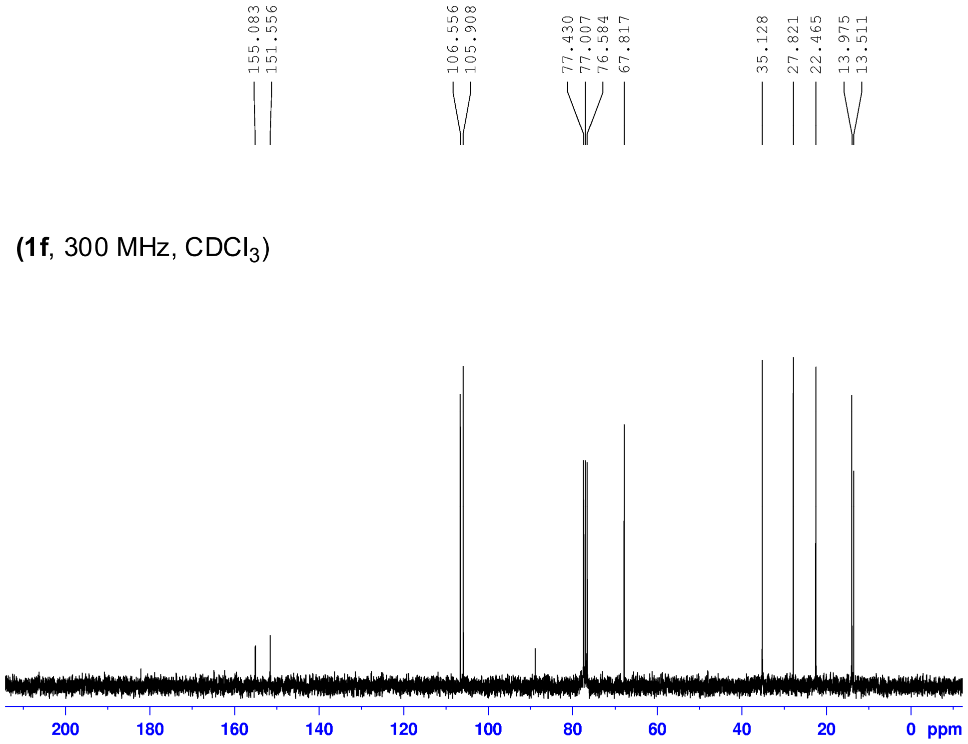
(**1e**, 300 MHz, $CDCl_3$)



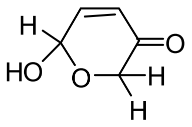
(**1e**, 75 MHz, $CDCl_3$)



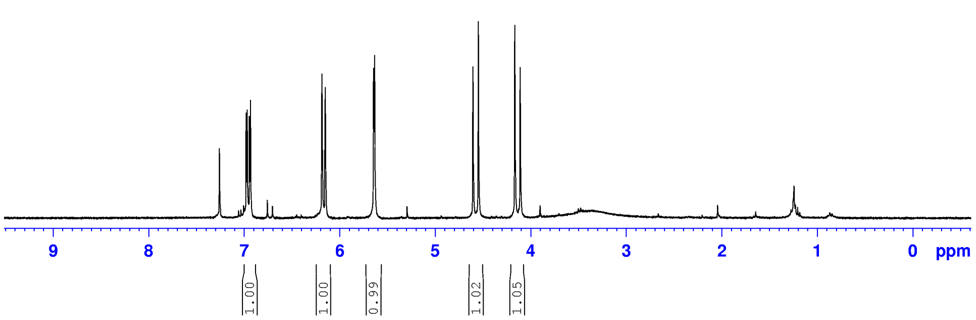
(**1f**, 300 MHz, $CDCl_3$)



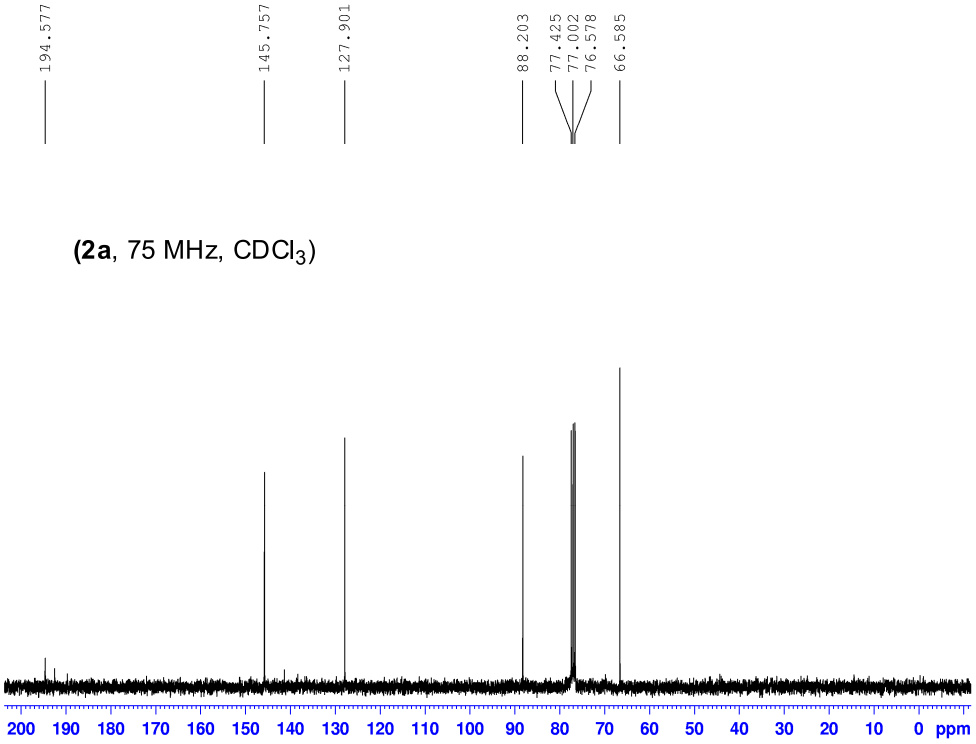
(**1f**, 300 MHz, $CDCl_3$)

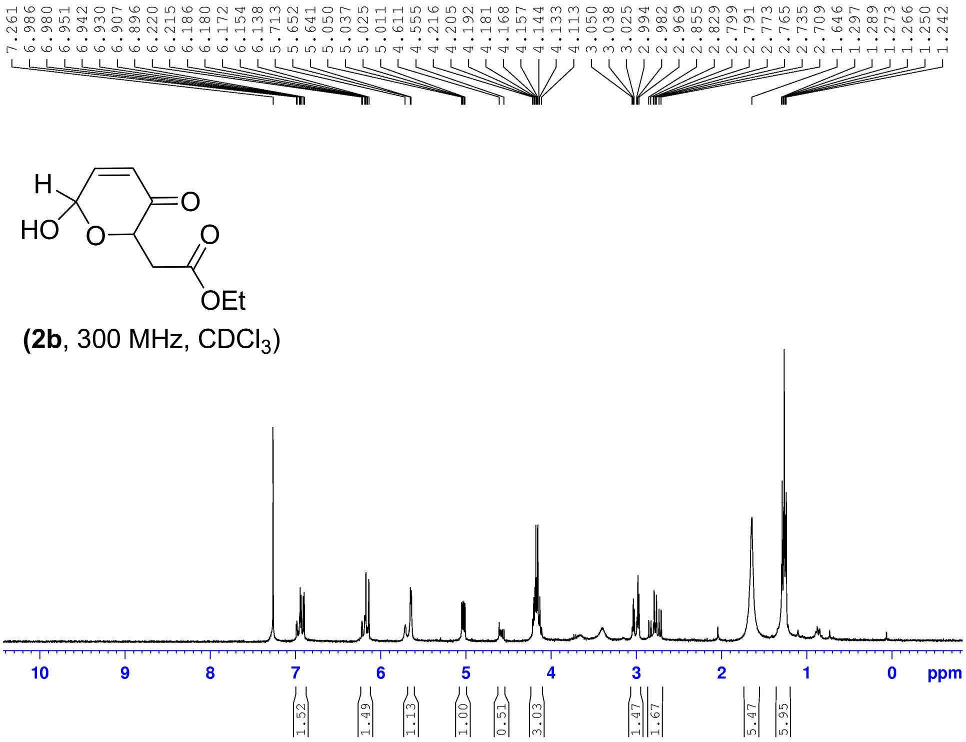


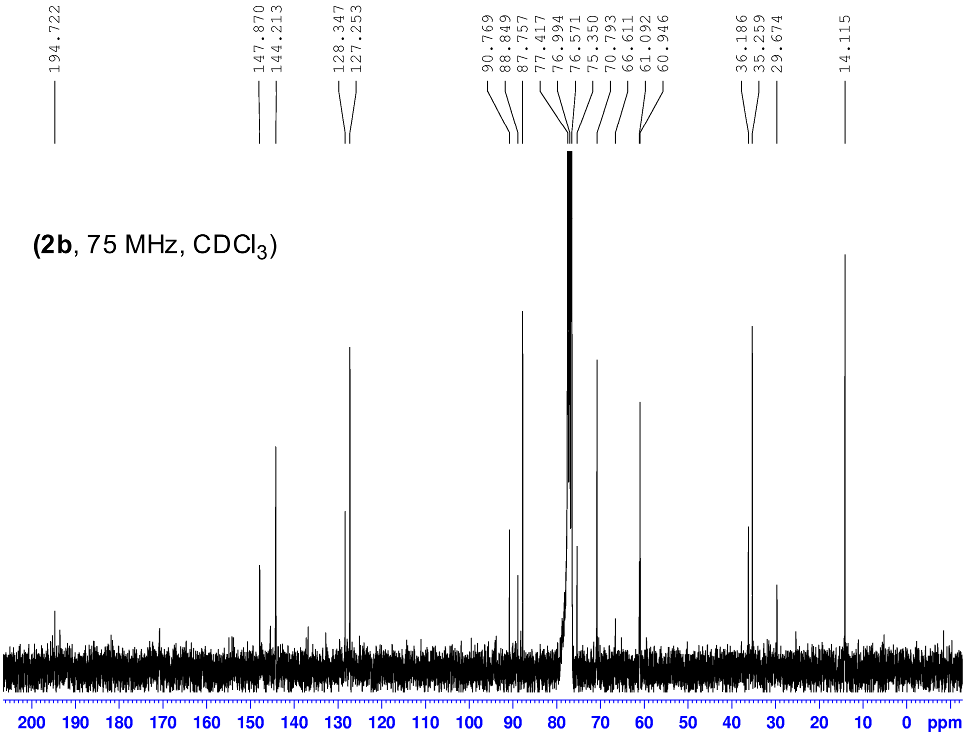
(**2a**, 300 MHz, $CDCl_3$)

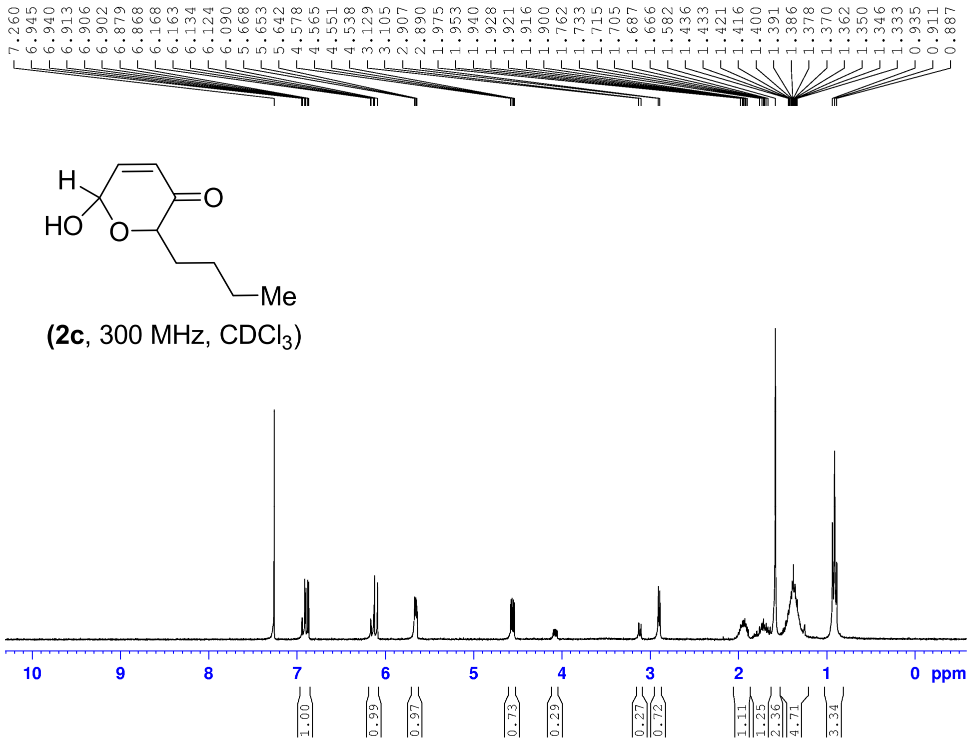


(**2a**, 75 MHz, $CDCl_3$)

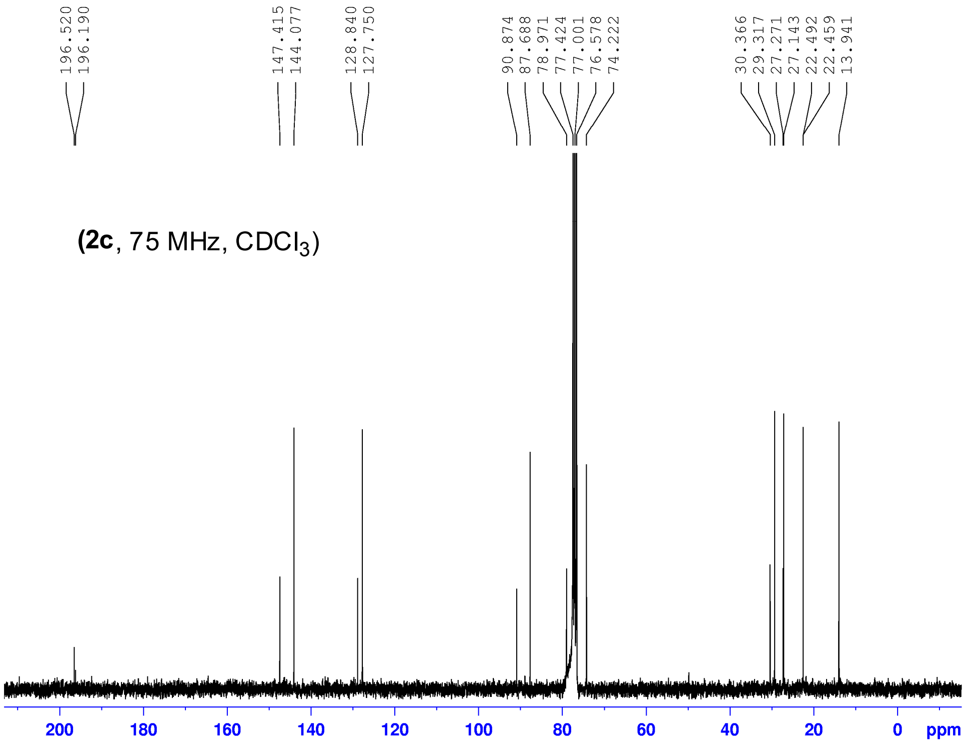



(**2b**, 300 MHz, $CDCl_3$)

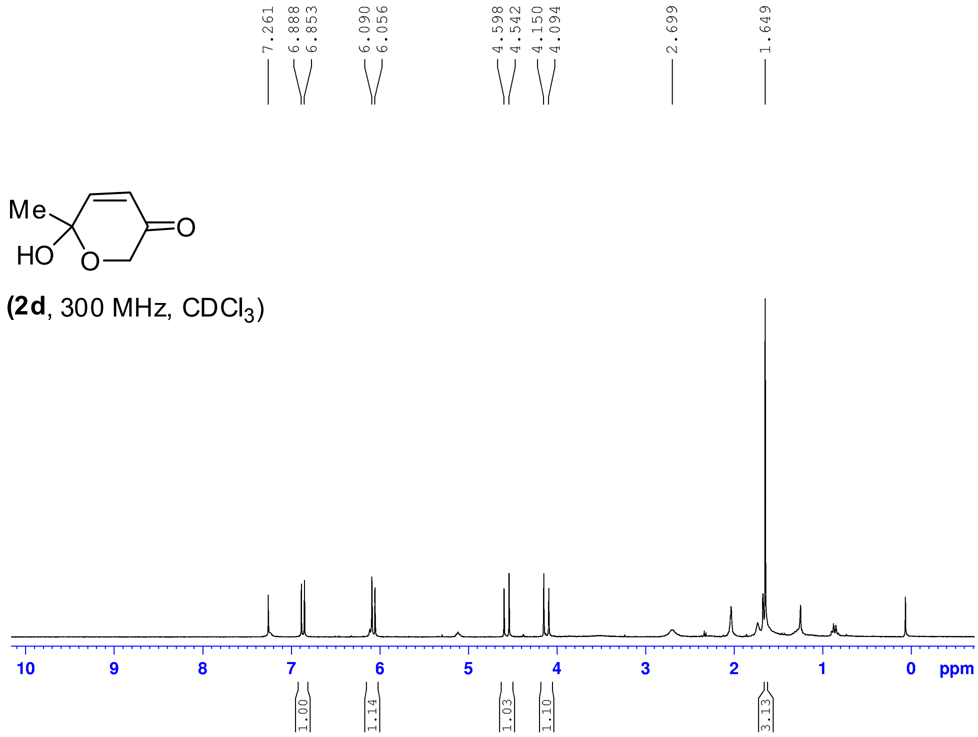

(**2b**, 75 MHz, $CDCl_3$)



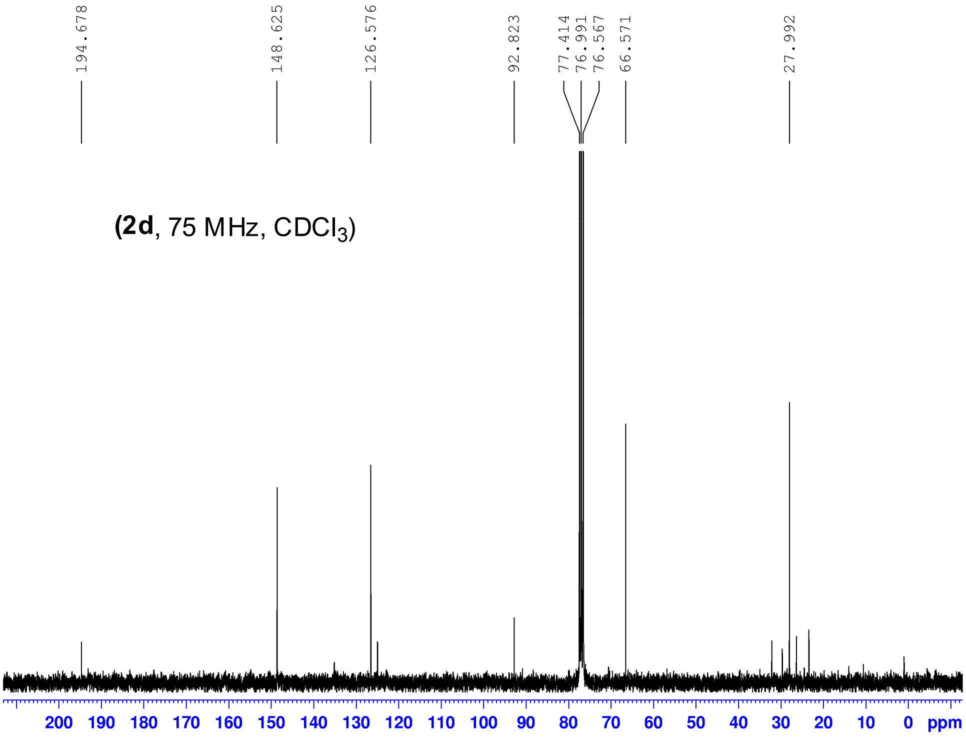
(**2c**, 300 MHz, $CDCl_3$)



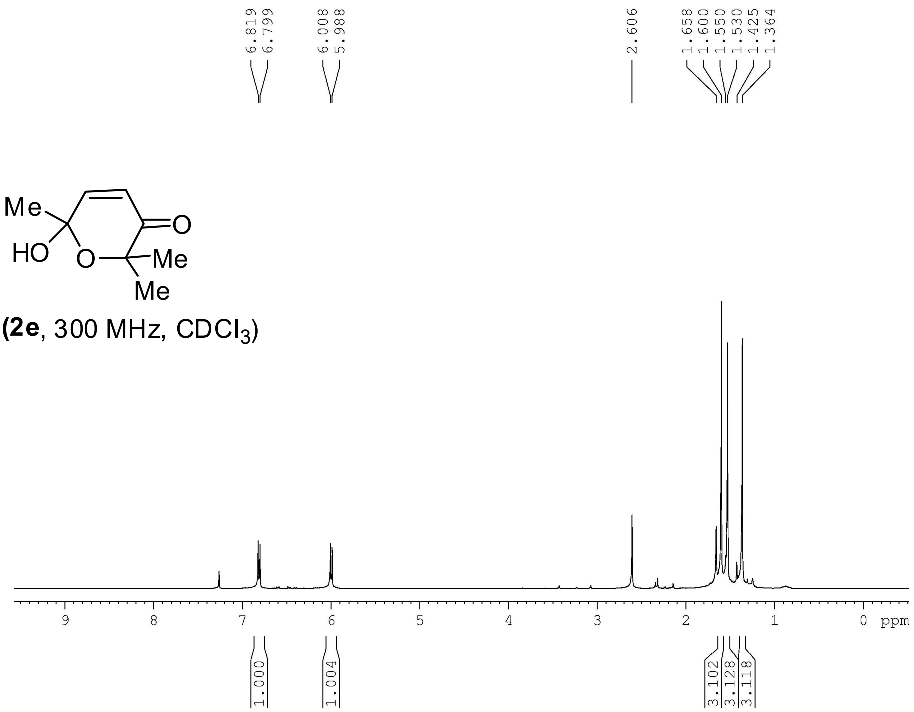
(**2c**, 75 MHz, $CDCl_3$)



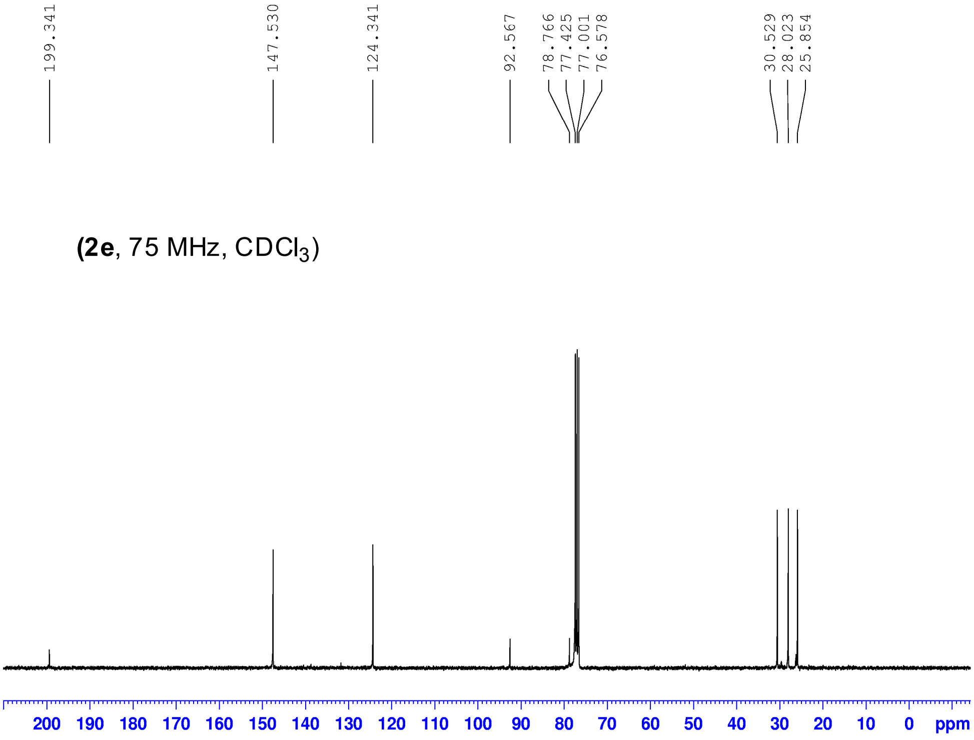
(**2d**, 300 MHz, $CDCl_3$)



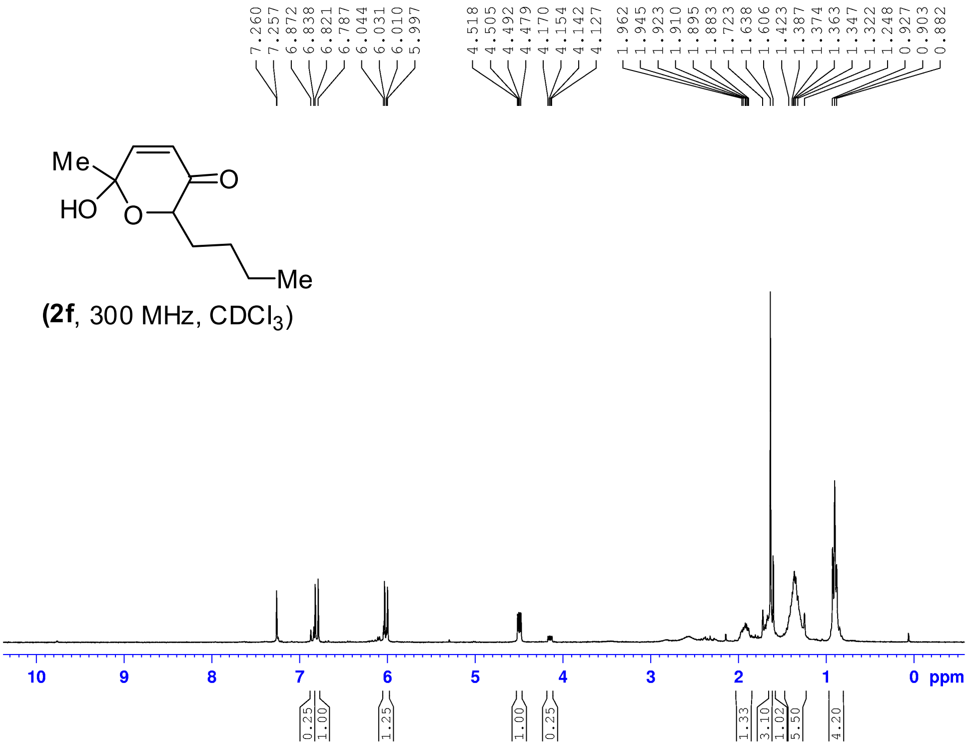
(**2d**, 75 MHz, $CDCl_3$)



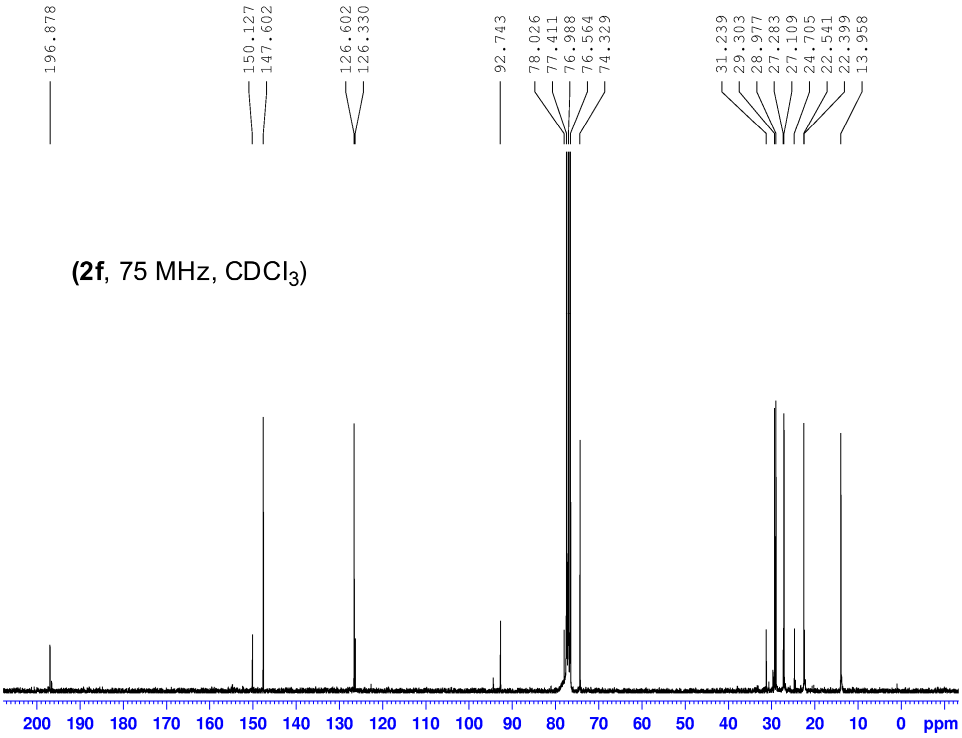
(**2e**, 300 MHz, $CDCl_3$)



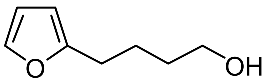
(**2e**, 75 MHz, $CDCl_3$)



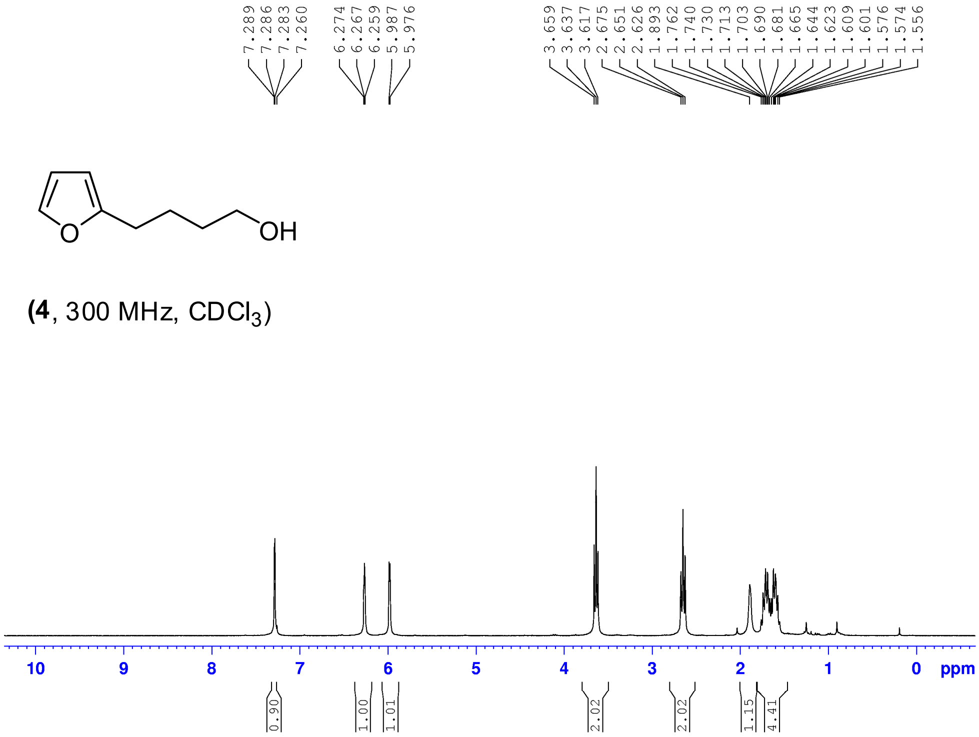
(**2f**, 300 MHz, $CDCl_3$)



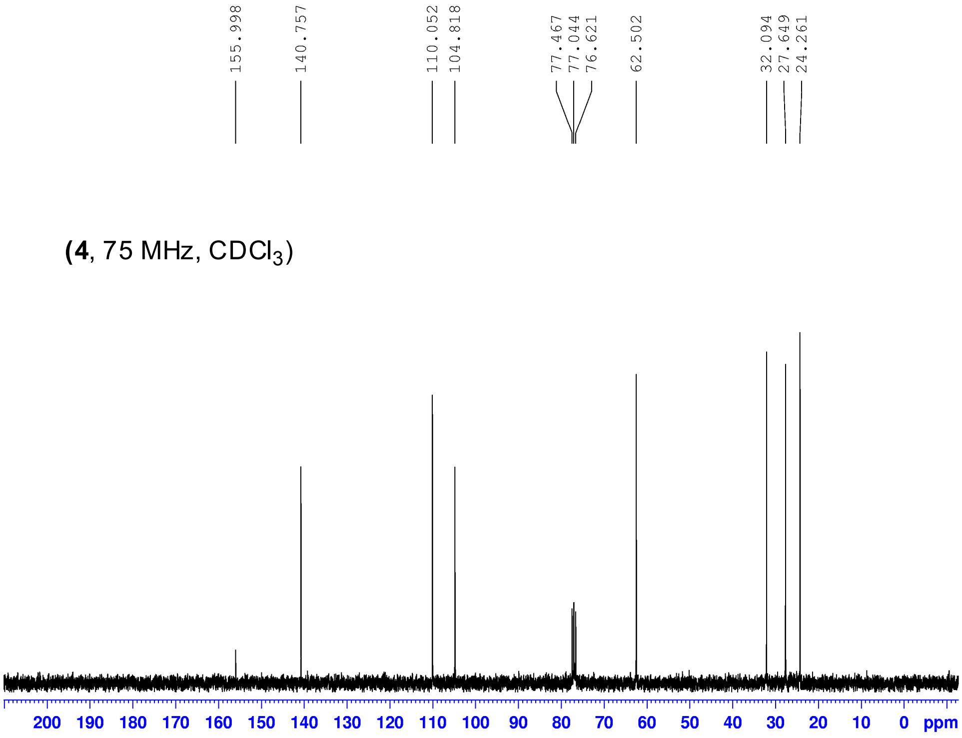
(**2f**, 75 MHz, $CDCl_3$)

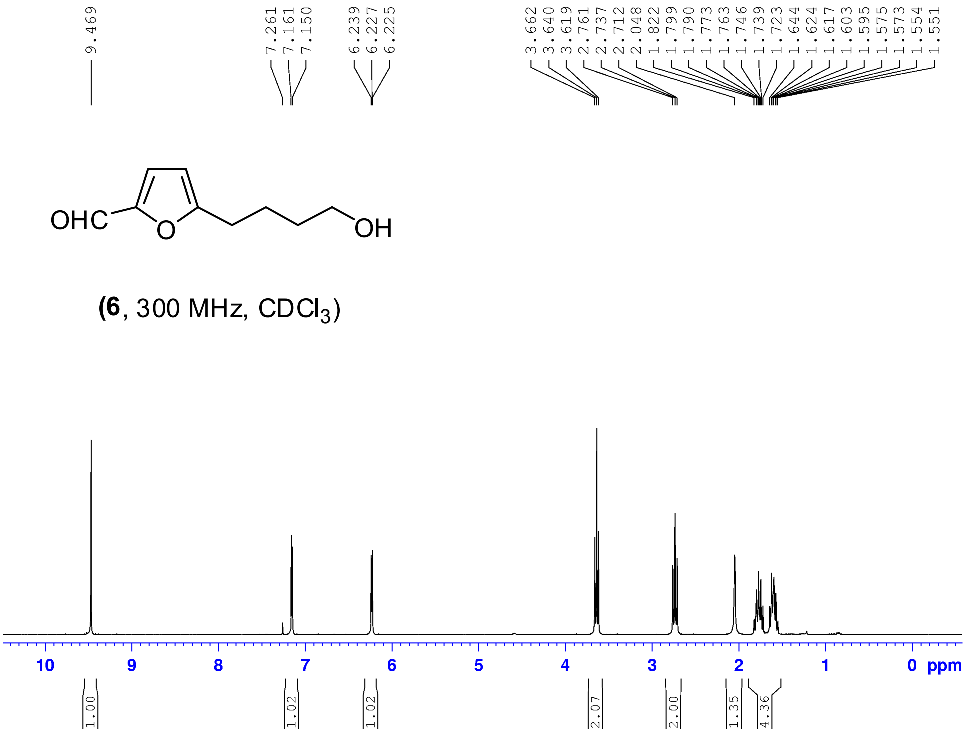


(**4**, 300 MHz, $CDCl_3$)

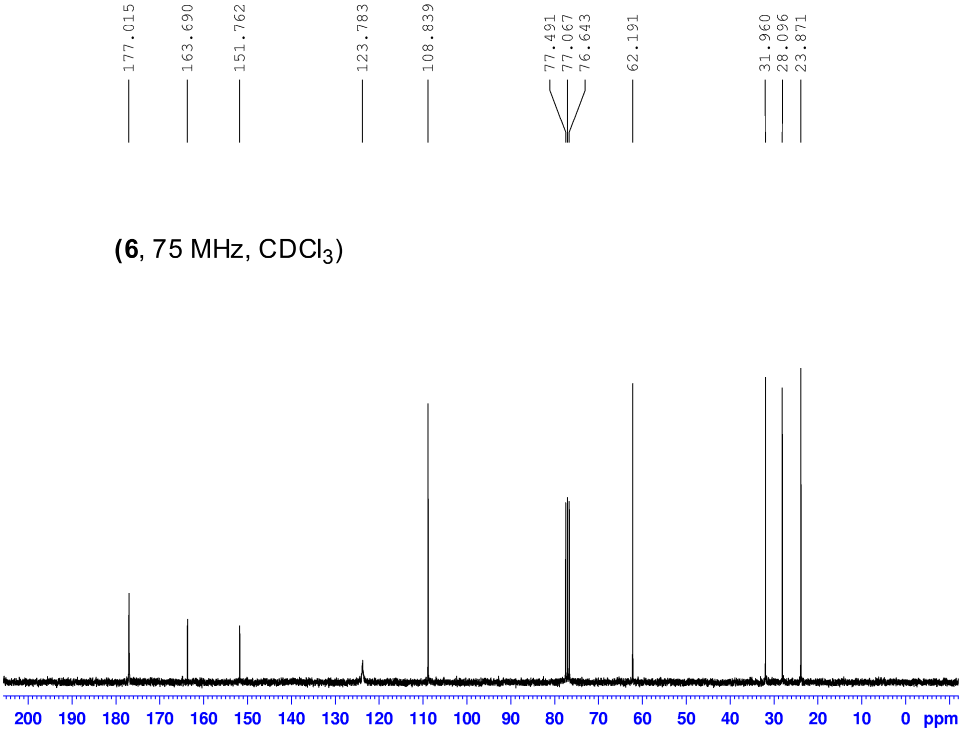


(**4**, 75 MHz, $CDCl_3$)

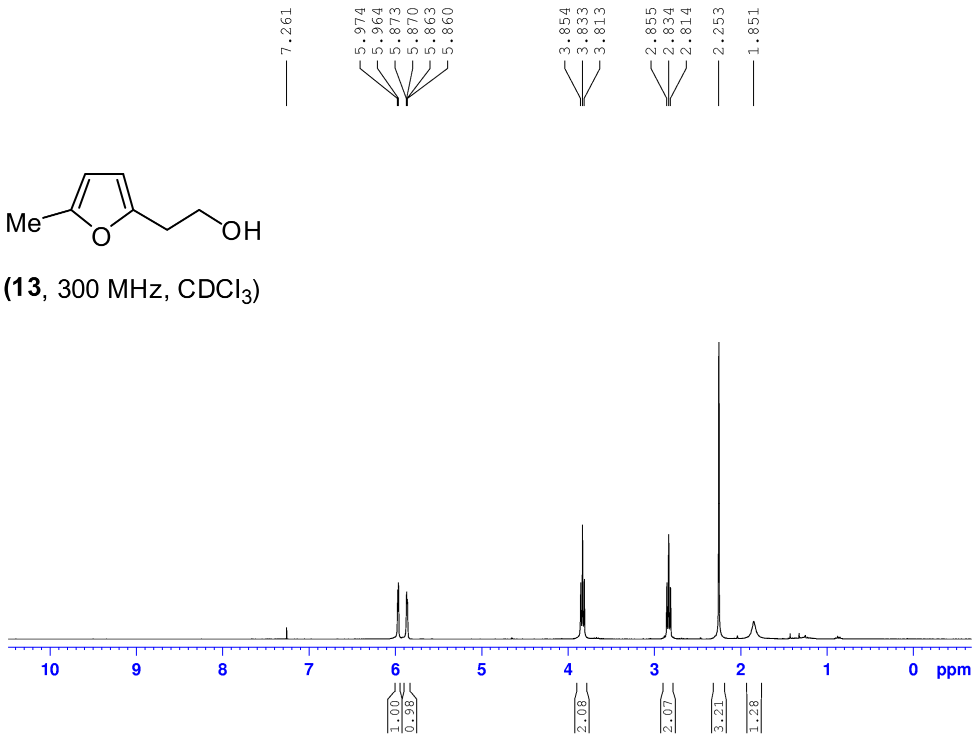




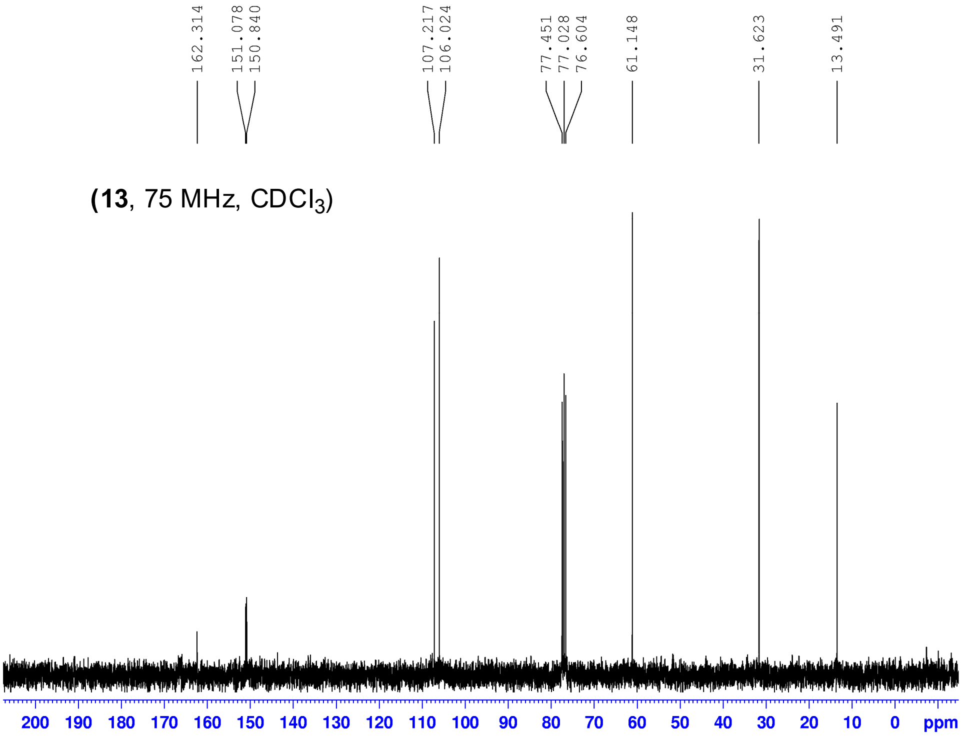
(**6**, 300 MHz, CDCl$_3$)



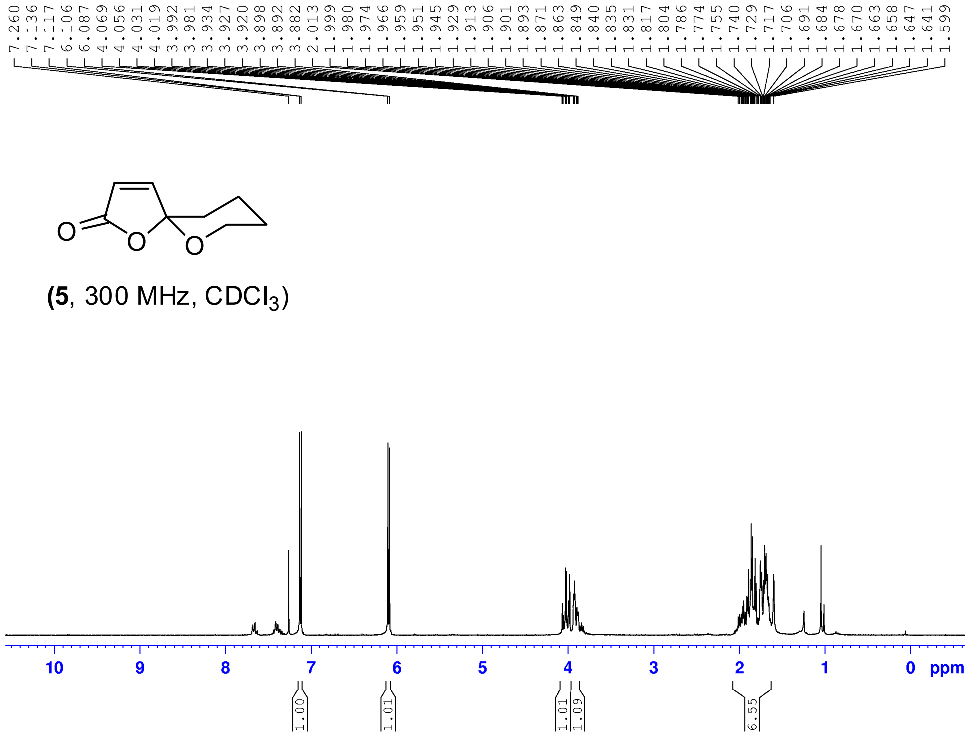
(**6**, 75 MHz, CDCl$_3$)



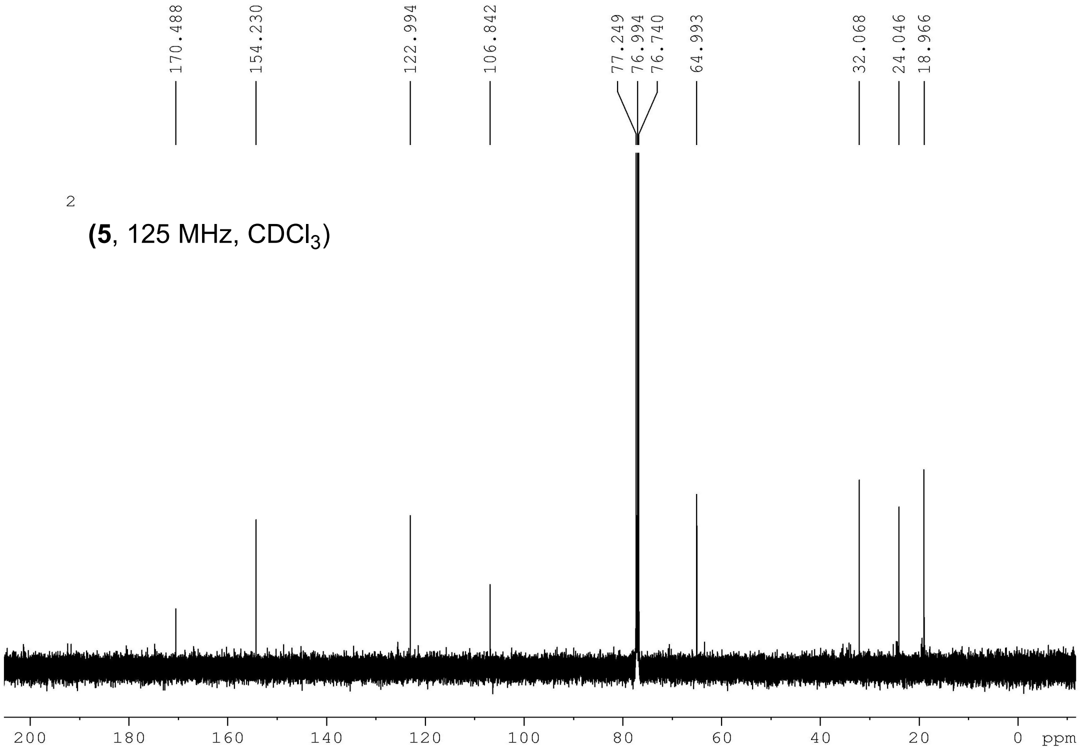
(**13**, 300 MHz, CDCl$_3$)



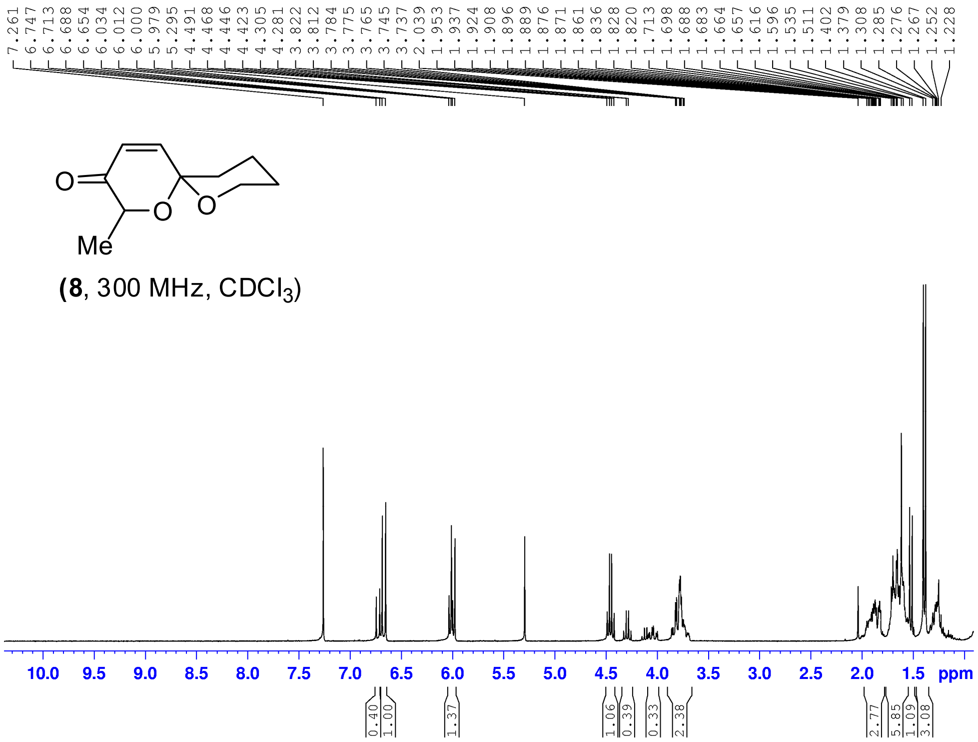
(**13**, 75 MHz, CDCl$_3$)



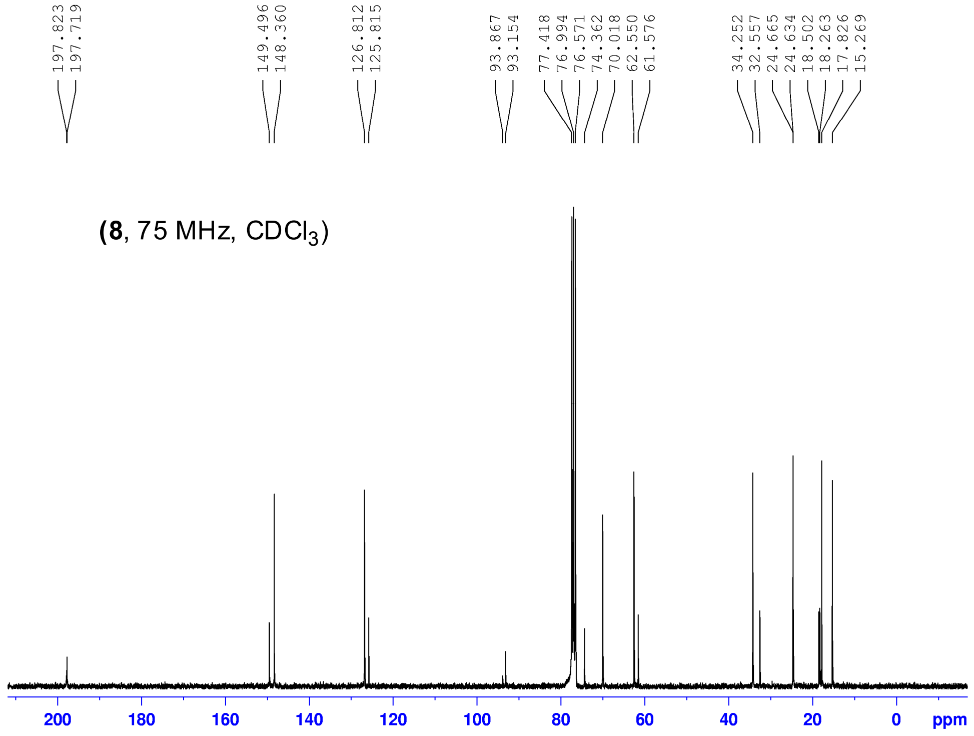
(**5**, 300 MHz, $CDCl_3$)



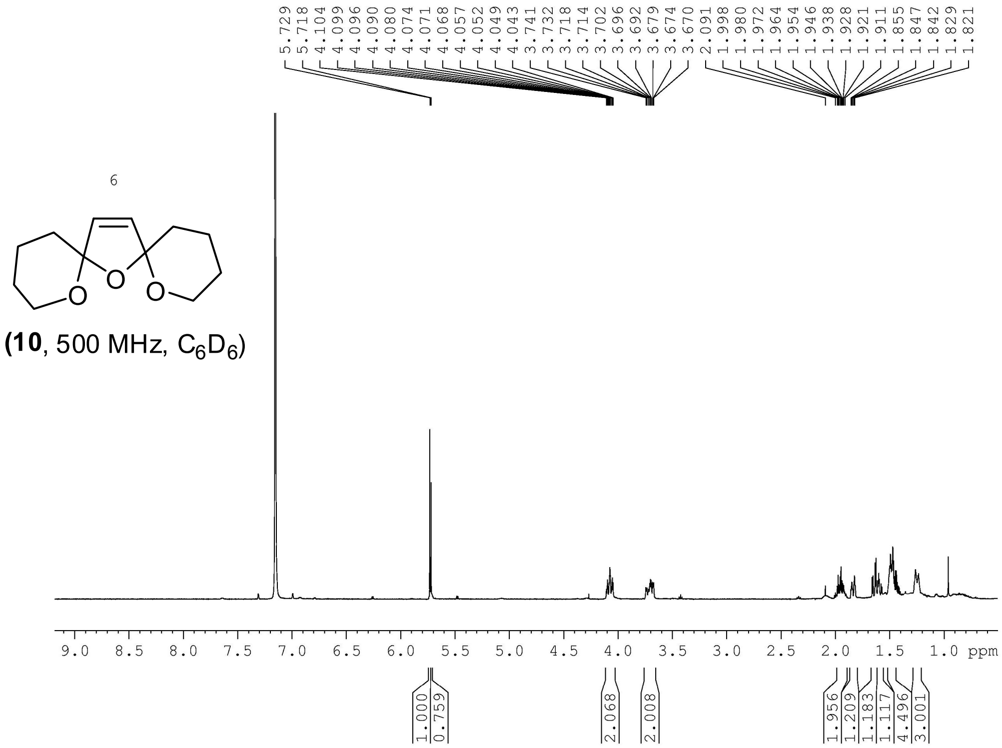
(**5**, 125 MHz, $CDCl_3$)



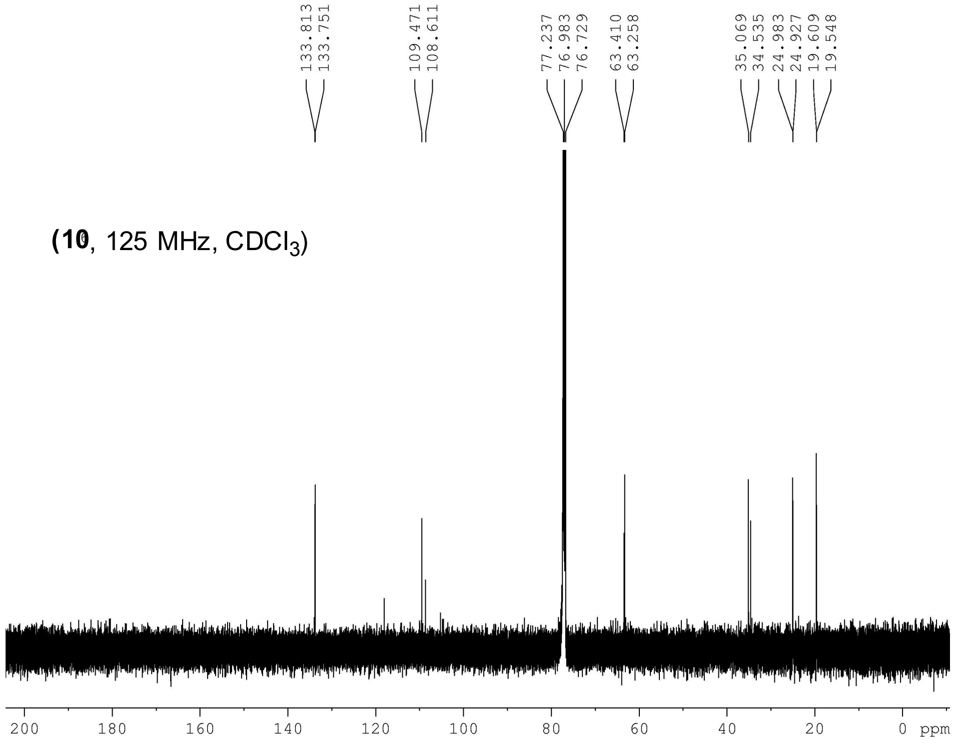
(**8**, 300 MHz, $CDCl_3$)



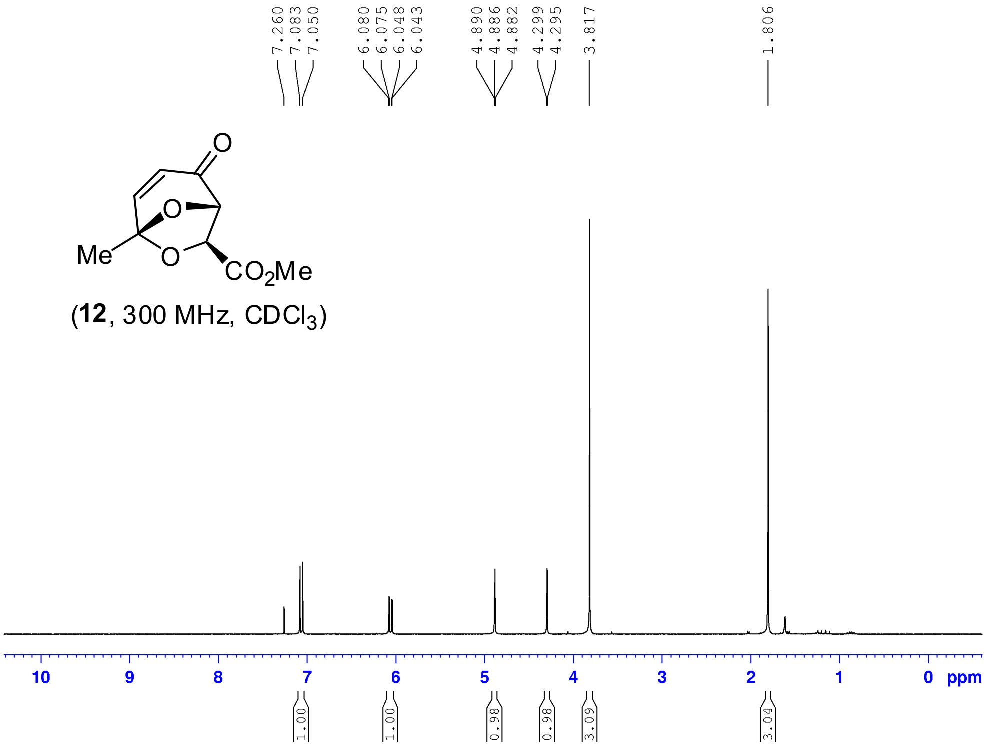
(**8**, 75 MHz, $CDCl_3$)



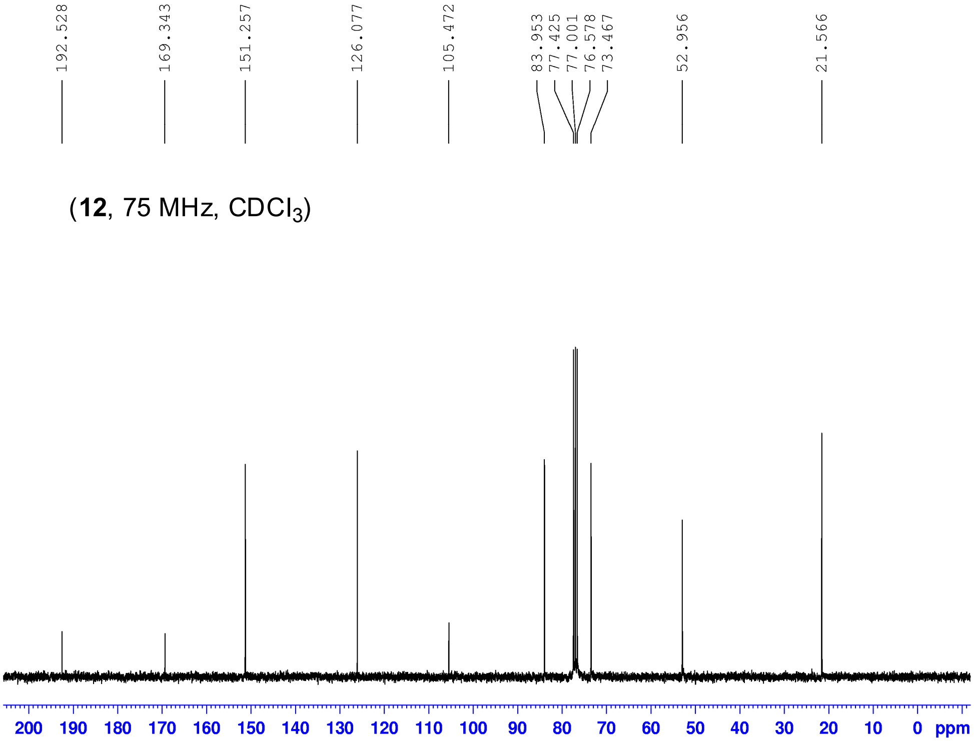
(**10**, 500 MHz, C_6D_6)



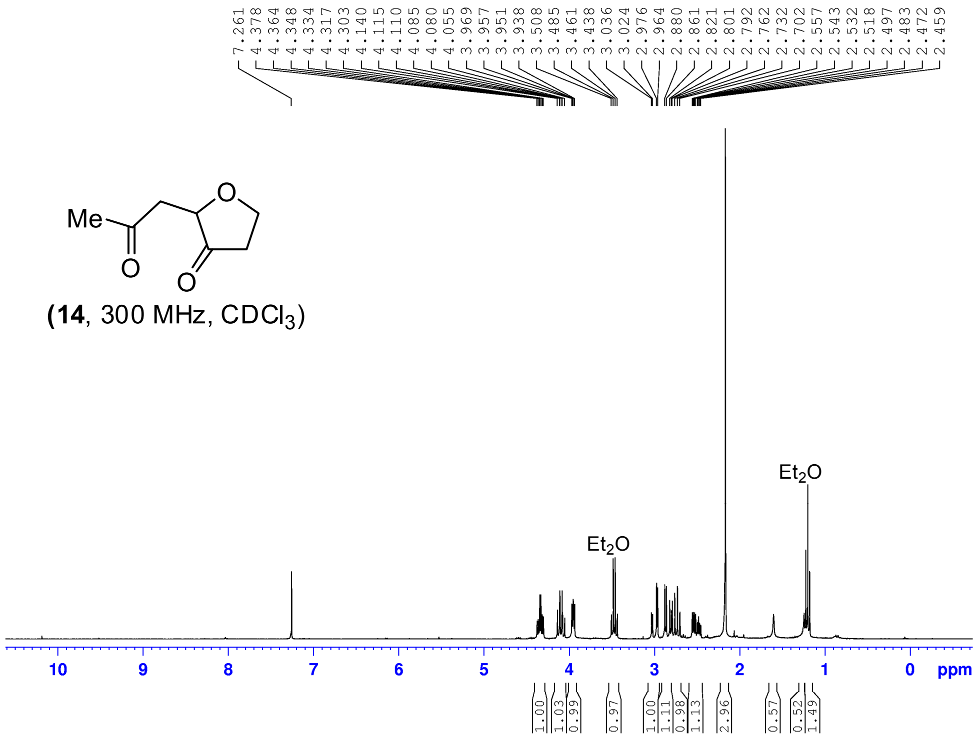
(**10**, 125 MHz, $CDCl_3$)



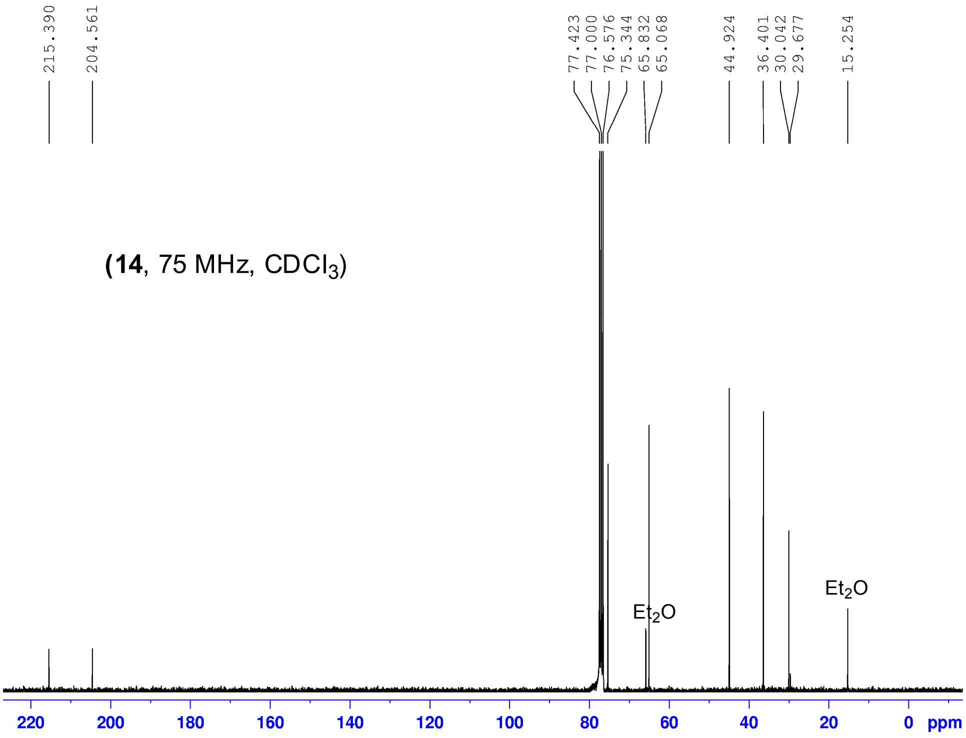
(**12**, 300 MHz, $CDCl_3$)



(**12**, 75 MHz, $CDCl_3$)



(**14**, 300 MHz, $CDCl_3$)



(**14**, 75 MHz, $CDCl_3$)