FACILE ACCESS TO HIGHLY-SUBSTITUTED DIHYDROFURANS USING RESONATED VINYLPENTANEDIONE RADICALS GENERATED BY Mn(III)-BASED OXIDATION

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Measurements.

Melting points were taken using a MP-J3 Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured in $CHCl_3$ using a Shimadzu 8400 or neat using an IRAffinity-1S FT IR spectrometer with MIRacle 10 ATR accessary. All the IR data were expressed in cm^{-1}. The NMR spectra were recorded using a JNM ECX 500 spectrometer at 500 MHz for the ^1H and at 125 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and brs, broad singlet for the ^1H NMR spectra, and also aromatic proton; arom H, aromatic carbon; arom C, aromatic carbon attached to proton; arom CH. The high-resolution mass spectra using a JEOL JMS-700 MStation and the elemental analyses using a J-SCIENCE LAB JM10 were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

Materials.

Manganese(III) acetate dihydrate, $Mn(OAc)_3•2H_2O$, was synthesized according to our modified method.[5] The 1,1-diarylethenes were prepared by the Grignard reaction of the corresponding acetophenones with arylmagnesium bromides followed by dehydration in 20% aqueous sulfuric acid.[4a,5a–d]

Manganese(II) acetate tetrahydrate, $Mn(OAc)_2•4H_2O$, acetic acid, methanol, ethanol were purchased from Wako Pure Chemical Ind., Ltd. Formic acid was purchased from Kishida Chemical Co., Ltd. *n*-Propanol, *n*-butanol, benzyl alcohol, *n*-pentanol, and *n*-hexanol were purchased from Tokyo Kasei Co., Ltd., and all the commercially-available materials were used as received. Flash column chromatography was performed on silica gel 60N (40-50 mm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 and B-5F from Wako Pure Chemical Ind., Ltd. The solvents were commercially-available guaranteed or first-grade and used as received.

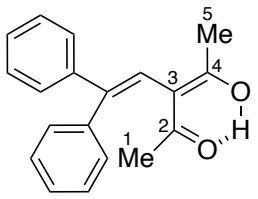
Preparation of Starting Dihydrofurans.[2e]

Pentane-2,4-dione (1.0104 g, 10 mmol) and 1,1-diphenylethene (1.8070, 10 mmol) were dissolved in AcOH (200 mL). The mixture was heated under argon, and $Mn(OAc)_3•2H_2O$ (5.4 g, 20 mmol) was added just before refluxing and continued to stir until the dark-brown color of Mn(III) turned transparent yellow. The solvent was removed in vacuo and the resulting residue was treated with water (100 mL) followed by extraction with chloroform (30 mL × 3).

The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ followed by water, dried over anhydrous $MgSO_4$ then concentrated to dryness. The obtained residue was separated by silica gel column chromatography eluting with chloroform, giving 3-acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (2.3637 g, 85%). A similar procedure of the reaction using 1,1-bis(4-chlorophenyl)ethene, 1,1-bis(4-fluorophenyl)ethene, 1,1-bis(4-methylphenyl)ethene, and 1,1-bis(4,4-methoxyphenyl)ethene was performed giving 3-acetyl-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (1.5919 g, 92%), 3-acetyl-5,5-bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran (1.9265 g, 88%), 3-acetyl-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (1.6843 g, 91%), and 3-acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran (0.2931 g, 86%), respectively.

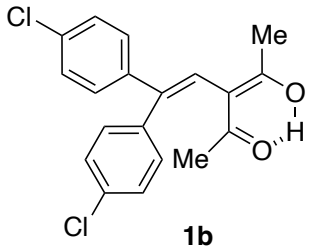
Preparation of Vinylpentanediones 1a-c.[4]

3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (0.8618 g, 3.1 mmol) was dissolved in MeCN (67.5 mL) and conc. HCl (7.5 mL) was added. The mixture was heated at 100 °C under argon with stirring for 12 h, followed by adding water (67.5 mL). The aqueous solution was extracted with chloroform (20 mL × 3), and the combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ followed by water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The obtained residue was separated by silica gel column chromatography eluting with EtOAc-hexane (2:8 v/v), giving 5,5-diphenylpent-4-en-2-one (quant). The obtained pentenone (1.3140 g, 5.6 mmol) in Ac_2O (100 mL) was heated at 80 °C under argon, $BF_3 \cdot Et_2O$ (2.4 mL) was dropwise added, and continued to heat with stirring for 3h. The solvent was removed in vacuo and water (100 mL) was added to the resulting residue. The aqueous solution was extracted with chloroform (20 mL × 3), and the combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ followed by water, dried over anhydrous $MgSO_4$, then concentrated to dryness. The resulting residue was separated by silica gel column chromatography with EtOAc-hexane (1:9 v/v), giving (*Z*)-3-(2,2-diphenylvinyl)-4-hydroxypent-3-en-2-one, as the enol form of 3-(2,2-diphenylvinyl)pentane-2,4-dione (**1a**) **(**0.8867 g, 57%). A similar reaction procedure using 3-acetyl-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran and 3-acetyl-5,5-bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran was carried out to yield 3-(2,2-bis(4-chlorophenyl)vinyl)pentane-2,4-dione (**1b**) (772.1 mg, 71%) and 3-(2,2-bis(4-fluorophenyl)vinyl)pentane-2,4-dione (**1c**) (1.0388 g, 61%). The vinylpentanediones **1b** and **1c** were also isolated as their enol forms.



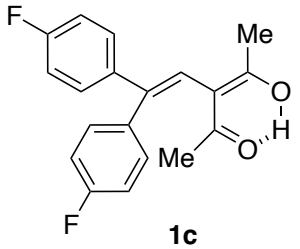
1a

(*Z*)-3-(2,2-Diphenylvinyl)-4-hydroxypent-3-en-2-one (1a):[4a] Yield 57%; yellowish oil; R_f = 0.70 (EtOAc/hexane 1:9 v/v); IR ($CHCl_3$) ν 1596 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.53 (1H, s, OH), 7.34–7.09 (10H, m, arom H), 6.54 (1H, s, =CH-), 1.95 (6H, s, Me × 2); ^{13}C NMR ($CDCl_3$) δ 191.1 (2C) (=C–O), 146.2 (>C=), 143.0, 140.2 (arom C), 130.0 (2C), 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.0, 127.7 (arom CH), 122.4 (=CH-), 110.5 (C-3), 24.2 (2C) (Me); FAB HRMS (acetone/NBA) *m/z*: $[M]^+$ Calcd for $C_{19}H_{18}O_2$ 278.1307; found *m/z* 278.1300. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.93; H, 6.71.



1b

(*Z*)-3-(2,2-Bis(4-chlorophenyl)vinyl)-4-hydroxypent-3-en-2-one (1b):[4a] Yield 71%; pale yellow microcrystals (from CH_2Cl_2-hexane); mp 164.0-166.0 °C; R_f = 0.59 (Et_2O/hexane 3:7 v/v); IR ($CHCl_3$) ν 1593 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.53 (1H, s, OH), 7.32–7.20 (6H, m, arom H), 7.03 (2H, d, J = 8.5 Hz, arom H), 6.54 (1H, s, =CH-), 1.95 (6H, s, Me × 2); ^{13}C NMR ($CDCl_3$) δ 191.0 (2C) (=C-O), 143.8 (>C=), 140.9, 138.2, 134.1, 133.8 (arom C), 131.3 (2C), 129.4 (2C), 128.9 (2C), 128.7 (2C) (arom C), 123.4 (=CH-), 110.3 (C-3), 24.2 (2C) (Me). Anal. Calcd for $C_{19}H_{16}Cl_2O_2$: C, 65.72; H, 4.64. Found: C, 65.43; H, 4.52.



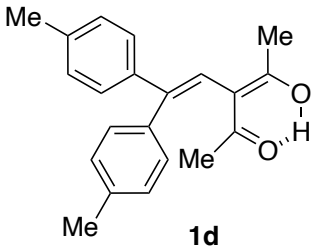
1c

(*Z*)-3-(2,2-Bis(4-fluorophenyl)vinyl)-4-hydroxypent-3-en-2-one (1c): Yield 61%; pale yellow cubes (from CH_2Cl_2-hexane); mp 108.0–109.0 °C; R_f = 0.59 (Et_2O/hexane 3:7 v/v); IR ($CHCl_3$) ν 1602 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.51 (1H, s, OH), 7.27-7.24 (2H, m, arom H), 7.09–6.98 (6H, m, arom H), 6.48 (1H, s, =CH-), 1.95 (6H, s, Me × 2); ^{13}C NMR ($CDCl_3$) δ 191.0 (2C) (=C–O), 162.6 (d, $^1J_{(C,F)}$ = 245 Hz, arom C), 162.0 (d, $^1J_{(C,F)}$ = 248 Hz, arom C),

144.0 (>C=), 138.8 (d, $^4J_{(C,F)}$ = 3 Hz, arom C), 135.9 (d, $^4J_{(C,F)}$ = 3 Hz, arom C), 131.6 (2C) (d, $^3J_{(C,F)}$ = 8 Hz), 129.8 (2C) (d, $^3J_{(C,F)}$ = 8 Hz) (arom CH), 122.4 (=CH-), 115.6 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 115.3 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 110.4 (C-3), 24.2 (2C) (Me); FAB HRMS (acetone/NBA) *m/z*: $[M]^+$ Calcd for $C_{19}H_{16}F_2O_2$ 314.1118; found 314.1185. Anal. Calcd for $C_{19}H_{16}F_2O_2$: C, 72.60; H, 5.13. Found: C, 72.59; H, 5.19.

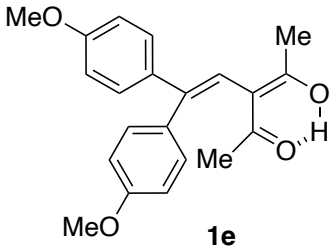
Preparation of Vinylpentanediones 1d and 1e.

3-Acetyl-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (2.2166 g, 7.2 mmol) was dissolved in MeCN (100 mL) and *p*-TsOH·H_2O (1.31 g, 7.6 mmol) was added. The mixture was heated at 80 °C under argon with stirring for 24 h. The reaction was quenched by adding water (100 mL) and the aqueous solution was extracted with chloroform (30 mL × 3). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ followed by water, dried over anhydrous $MgSO_4$, then concentrated to dryness. The resulting residue was separated by silica gel column chromatography eluting with EtOAc-hexane (1:9 v/v), affording (*Z*)-3-(2,2-bis(4-methylphenyl)vinyl)-4-hydroxypent-3-en-2-one as the enol form of 3-(2,2-bis(4-methylphenyl)vinyl)pentane-2,4-dione (**1d**) (0.7489 g, 34%). A similar reaction using 3-acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran was conducted and (*Z*)-3-(2,2-bis(4-methoxyphenyl)vinyl)-4-hydroxypent-3-en-2-one as the enol form of 3-(2,2-bis(4-methoxyphenyl)vinyl)pentane-2,4-dione (**1e**) was obtained in 90% yield (0.9094 g).



1d

(*Z*)-3-(2,2-Bis(4-methylphenyl)vinyl)-4-hydroxypent-3-en-2-one (1d):[4a] Yield 34%; pale yellow needles (from hexane); mp 135.5–137.0 °C; R_f = 0.67 (Et_2O/hexane 3:7 v/v); IR ($CHCl_3$) ν 1595 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.51(1H, s, OH), 7.22 (2H, d, *J* = 7.5 Hz, arom H), 7.14 (2H, d, *J* = 7.5 Hz, arom H), 7.08 (2H, d, *J* = 7.5 Hz, arom H), 6.98 (2H, d, *J* = 8.0 Hz, arom H), 6.46 (1H, s, =CH-), 2.37 (3H, s, Me-C_6H_4), 2.33 (3H, s, Me-C_6H_4), 1.95 (6H, s, Me × 2); ^{13}C NMR ($CDCl_3$) δ 191.1 (2C) (=C–O), 145.9 (>C=), 140.3, 137.8, 137.8, 137.3 (arom CH), 129.9 (2C), 129.1 (2C), 129.0 (2C), 128.2 (2C) (arom C), 121.2 (=CH-), 110.8 (C-3), 24.2 (2C), 21.3, 21.2 (Me). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.37; H, 7.36.

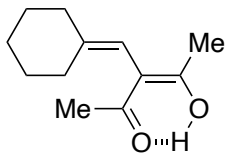


1e

(*Z*)-3-(2,2-Bis(4-methoxyphenyl)vinyl)-4-hydroxypent-3-en-2-one (1e): Yield 64%; dark red liquid; R_f = 0.67 (Et_2O/hexane 3:7 v/v); IR ($CHCl_3$) ν 1606 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.51 (1H, s, OH), 7.24 (2H, d, J = 8.5 Hz, arom H), 7.03 (2H, d, J = 8.5 Hz, arom H), 6.86 (2H, d, J = 9.5 Hz, arom H), 6.82 (2H, d, J = 8.5 Hz, arom H), 6.38 (1H, s, =CH-), 3.83 (3H, s, OMe), 3.80 (3H, s, OMe), 1.96 (6H, s, Me × 2); ^{13}C NMR ($CDCl_3$) δ 191.2 (2C) (=C–O), 159.6, 158.9, 135.8, 132.6 (arom C), 145.1 (>C=), 131.2 (2C), 129.5 (2C), 113.8 (2C), 113.7 (2C) (arom C), 120.0 (=CH-), 110.9 (C-3), 55.5, 55.3 (MeO), 24.2 (2C) (Me); FAB HRMS (acetone/NBA) *m/z*: $[M]^+$ Calcd for $C_{21}H_{22}O_4$ 338.1518; found 338.1504.

Preparation of Vinylpentanedione 1f.[4c]

Cyclohexanecarbaldehyde (1.2722, 11 mmol) and pentane-2,4-dione (1.0079g, 10 mmol) were dissolved in toluene (40 mL), and piperidine (0.1 mL) and AcOH (0.1 mL) were added. The mixture was heated at reflux temperature under argon with stirring for 5 h. The reaction was quenched by adding water (40 mL) and the aqueous solution was extracted with EtOAc (15 mL × 3). The combined extracts were washed with 2M HCl (20 mL) followed by a saturated aqueous solution of $NaHCO_3$, washed with water, dried over anhydrous $MgSO_4$, and then concentrated to dryness. The resulting residue was separated by silica gel column chromatography eluting with EtOAc-hexane (1:9 v/v), giving (*Z*)-3-(cyclohexylidenemethyl)-4-hydroxypent-3-en-2-one as the enol form of 3-(cyclohexylidenemethyl)pentane-2,4-dione (**1f**) (quant).

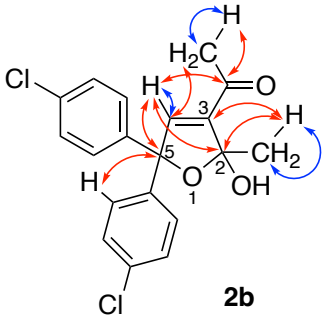


1f

(*Z*)-3-(Cyclohexylidenemethyl)-4-hydroxypent-3-en-2-one (1f):[4c] Yield quantitative; yellow liquid; R_f = 0.5 (EtOAc/hexane 1:9 v/v); IR ($CHCl_3$) ν 1595 (C=O); ^{1}H NMR ($CDCl_3$) δ 16.39 (1H, s, OH), 5.70 (1H, s, =CH-), 2.21 (2H, d, J = 5.6 Hz, CH_2), 2.02 (6H, s, Me × 2), 1.99 (2H, d, J = 6.1 Hz, CH_2), 1.63–1.54 (4H, m, CH_2 × 2), 1.51–1.46 (2H, m, CH_2); ^{13}C

NMR ($CDCl_3$) δ 191.0 (2C) (=C–O), 146.2 (>C=), 115.6 (=CH-), 109.3 (C-3), 36.5, 29.8, 28.5, 27.3, 29.7 (CH_2), 23.9 (2C) (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{18}O_2Na$ 217.1204; found 217.1081.

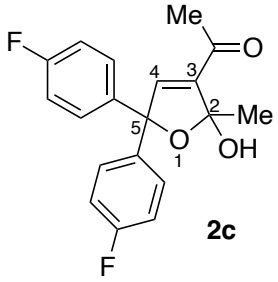
Oxidation Products 2 and 3.



2b

Fig. 1. Selected Correlation Based on HMQC and HMBC of **2b**

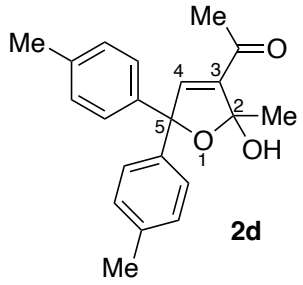
3-Acetyl-5,5-bis(4-chlorophenyl)-2-hydroxy-2-methyl-2,5-dihydrofuran (2b): Yield 22.0 mg, 20%; pale yellow amorphous; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 3425 (OH), 1676 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.33 (2H, d, J = 8.4 Hz, arom H), 7.31 (4H, m, arom H), 7.25 (2H, d, J = 8.4 Hz, arom H), 7.15 (1H, s, H-4), 3.20 (1H, brs, OH), 2.42 (3H, s, COMe), 1.76 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 194.5 (C=O), 144.1 (C-4), 141.8 (C-3), 141.6, 141.0 (arom C), 134.2 (2C) (arom C), 128.92 (2C), 128.88 (2C), 128.2 (2C), 128.0 (2C) (arom CH), 109.1 (C-2), 90.8 (C-5), 28.1 (COMe), 27.1 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{16}Cl_2O_3Na$ 385.0374; found 385.0373.



2c

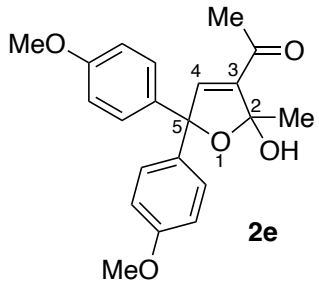
3-Acetyl-5,5-bis(4-fluorophenyl)-2-hydroxy-2-methyl-2,5-dihydrofuran (2c): Pale yellow oil; R_f = 0.36 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 3427 (OH), 1674 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.36–7.34 (2H, m, arom H), 7.30–7.27 (2H, m, arom H), 7.17 (1H, s, H-4), 7.06-7.00 (4H, m, arom H), 3.14 (1H, brs, OH), 2.43 (3H, s, COMe), 1.77 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 194.6 (C=O), 162.4 (2C) (d, $^1J_{(C,F)}$ = 246 Hz, arom C), 144.6 (C-4), 141.5 (C-3), 139.1 (d, $^4J_{(C,F)}$ = 3 Hz, arom CH), 138.5 (d, $^4J_{(C,F)}$ = 3 Hz, arom CH), 128.6 (2C) (d, $^3J_{(C,F)}$ = 9 Hz, arom CH), 128.4 (2C) (d, $^3J_{(C,F)}$ = 9 Hz, arom CH), 115.65 (2C) (d, $^2J_{(C,F)}$ = 21

Hz, arom CH), 115.56 (2C) (d, $^{2}J_{(C,F)}$ = 21 Hz, arom CH), 109.0 (C-2), 90.9 (C-5), 28.1 (CO<u>Me</u>), 27.1 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{16}F_2O_3Na$ 353.0965; found 353.0987.



2d

3-Acetyl-2-hydroxy-5,5-bis(4-methylphenyl)-2-methyl-2,5-dihydrofuran (2d): Yield 13.9 mg, 14%; yellow oil; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 3446 (OH), 1674 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.28 (2H, d, J = 8.2 Hz, arom H), 7.22 (1H, s, H-4), 7.21 (2H, d, J = 8.2 Hz, arom H), 7.15 (2H, d, J = 8.2 Hz, arom H), 7.14 (2H, d, J = 8.2 Hz, arom H), 2.89 (1H, s, OH), 2.41 (3H, s, CO<u>Me</u>), 2.34 (3H, s, Me), 2.33 (3H, s, Me), 1.78 (3H, s, 2-Me); ^{13}C NMR ($CDCl_3$) δ 194.6 (C=O), 145.8 (C-4), 141.2, 140.7, 137.77, 137.45 (arom C), 139.96 (C-3), 129.34 (2C), 129.27 (2C), 126.62 (2C), 126.54 (2C) (arom CH), 108.8 (C-2), 91.5 (C-5), 28.1 (CO<u>Me</u>), 26.9, 21.2 (2C) (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}O_3Na$ 345.1467; found 345.1529.



2e

3-Acetyl-2-hydroxy-5,5-bis(4-methoxyphenyl)-2-methyl-2,5-dihydrofuran (2e): Yield 4.1 mg, 4%; yellow oil; R_f = 0.21 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 3446 (OH), 1676 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.30 (2H, d, J = 8.2 Hz, arom H), 7.23 (2H, d, J = 8.2 Hz, arom H), 7.18 (1H, s, H-4), 6.89–6.85 (4H, m, arom H), 3.80 3H, s, OMe), 3.79 (3H, s, OMe), 2.90 (1H, brs, OH), 2.42 (3H, s, CO<u>Me</u>), 1.78 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 194.7 (C=O), 159.3 (2C) (arom C–O), 145.8 (C-4), 140.9 (C-3), 135.8, 135.0 (arom C), 128.1 (2C), 127.9 (2C), 114.0 (2C), 113.9 (2C) (arom CH), 108.7 (C-2), 91.2 (C-5), 55.4 (2C) (O<u>Me</u>), 28.1 CO<u>Me</u>), 27.0 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}O_5Na$ 377.1365; found 377.1397.

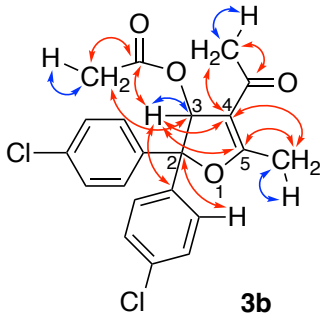
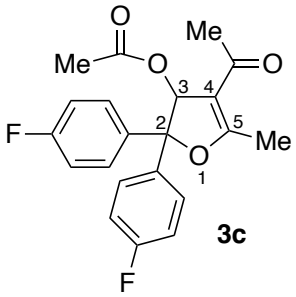


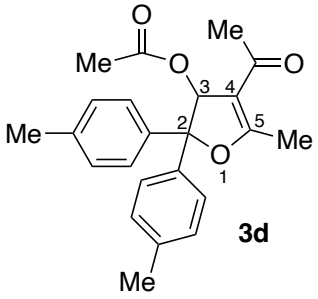
Fig. 2. Selected Correlation Based on HMQC and HMBC of **3b**

4-Acetyl-2,2-bis(4-chlorophenyl)-5-methyl-2,3-dihydrofuran-3-yl acetate (3b): Yield 92.6 mg, 76%; colorless amorphous; R_f = 0.61 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1732, 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.67 (2H, d, J = 8.6 Hz, arom H), 7.40 (2H, d, J = 8.6 Hz, arom H), 7.25 (2H, d, J = 8.6 Hz, arom H), 7.13 (2H, d, J = 8.6 Hz, arom H), 6.68 (1H, s, H-3), 2.46 (3H, s, Me), 2.13 (3H, s, COMe), 1.61 (3H, s, OAc); ^{13}C NMR ($CDCl_3$) δ 193.5 (C=O), 172.2 (C-5), 170.5 (OCOMe), 139.1, 136.0, 135.0, 134.4 (arom C), 129.0 (2C), 128.95 (2C), 128.1 (2C), 127.97 (2C) (arom CH), 111.5 (C-4), 94.4 (C-2), 80.4 (C-3), 29.0 (COMe), 20.5 (OCOMe), 15.6 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{18}O_4Cl_2Na$ 427.0480; found 427.0481.



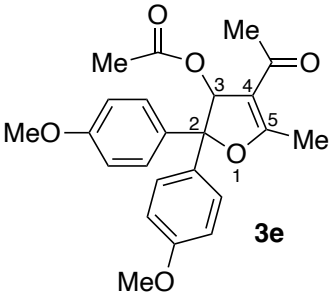
4-Acetyl-2,2-bis(4-fluorophenyl)-5-methyl-2,3-dihydrofuran-3-yl acetate (3c): Yield quantitative; pale yellow oil; R_f = 0.56 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1735, 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.76–7.73 (2H, m, arom H), 7.20–7.17 (2H, m, arom H), 7.14–7.10 (2H, m, arom H), 6.98–6.95 (2H, m, arom H), 6.71 (1H, brs, H-3), 2.48 (3H, s, Me), 2.15 (3H, s, COMe), 1.62 (3H, s, OAc); ^{13}C NMR ($CDCl_3$) δ 193.7 (C=O), 172.3 (C-5), 170.5 (OCOMe), 162.8 (d, $^1J_{(C,F)}$ = 246 Hz, arom C), 162.4 (d, $^1J_{(C,F)}$ = 246 Hz, arom C), 136.5 (d, $^4J_{(C,F)}$ = 6 Hz, arom C), 133.5 (d, $^4J_{(C,F)}$ = 3 Hz, arom C), 129.5 (2C) (d, $^3J_{(C,F)}$ = 8 Hz, arom CH), 128.7 (2C) (d, $^3J_{(C,F)}$ = 8 Hz, arom CH), 115.7 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 114.6 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 111.4 (C-4), 94.6 (C-2), 80.6 (C-3), 29.0 (COMe), 20.4 (OCOMe), 15.6 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M]^+$ Cald for $C_{21}H_{18}F_2O_4$ 372.1173;

found 372.1186.



3d

4-Acetyl-2,2-bis(4-methylphenyl)-5-methyl-2,3-dihydrofuran-3-yl acetate (3d): Yield 83.0 mg, 77%; pale yellow liquid; R_f = 0.64 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1735, 1676 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.62 (2H, d, J = 8.0 Hz, arom CH), 7.22 (2H, d, J = 8.0 Hz, arom H), 7.11 (2H, d, J = 8.2 Hz, arom H), 7.06 (2H, d, J = 8.2 Hz, arom H), 6.75 (1H, brs, H-3), 2.47 (3H, s, 5-Me), 2.36 (3H, s, Me), 2.29 (3H, s, Me), 2.13 (3H, s, COMe), 1.57 (3H, s, OAc); ^{13}C NMR ($CDCl_3$) δ 194.0 (C=O), 172.8 (C-5), 170.6 (O<u>C</u>OMe), 138.5, 138.2, 137.2, 135.1 (arom C), 129.3 (2C), 128.4 (2C), 127.4 (2C), 126.6 (2C) (arom CH), 111.5 (C-4), 95.6 (C-2), 80.6 (C-3), 29.0 (CO<u>Me</u>), 21.2, 21.1 (<u>Me</u>), 20.5 (OCO<u>Me</u>), 15.7 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{24}O_4Na$ 387.1572; found 387.1579.

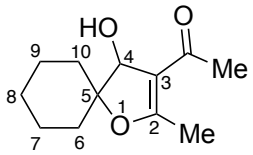


3e

4-Acetyl-2,2-bis(4-methoxyphenyl)-5-methyl-2,3-dihydrofuran-3-yl acetate (3e): Yield 102.2 mg, 95%; pale pink oil; R_f = 0.50 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1737, 1674 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.66 (2H, d, J = 8.8 Hz, arom CH), 7.11 (2H, d, J = 8.8 Hz, arom H), 6.94 (2H, d, J = 8.9 Hz, arom H), 6.79 (2H, d, J = 8.9 Hz, arom H), 6.69 (1H, brs, H-3), 3.87 (3H, s, OMe), 3.76 (3H, s, OMe), 2.46 (3H, s, Me), 2.14 (3H, s, COMe), 1.60 (3H, s, OAc); ^{13}C NMR ($CDCl_3$) δ 194.0 (C=O), 172.8 (C-5), 170.7 (O<u>C</u>OMe), 159.7, 159.3, 133.1, 130.2 (arom C), 129.1 (2C), 128.1 (2C), 113.9 (2C), 112.9 (2C) (arom CH), 111.4 (C-4), 95.4 (C-2), 80.7 (C-3), 55.41, 55.35 (Me), 29.0 (CO<u>Me</u>), 20.5 (OCO<u>Me</u>), 15.7 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{24}O_6Na$ 419.1471; found 419.1503.

Oxidation of Vinylpentanedione Enol 1f. To a boiling AcOH (150 mL) solution including $Mn(OAc)_3$•$2H_2O$ (536.2 mg, 2 mmol) under argon, a mixture of **1f** (97.1 mg, 0.50 mmol) and

AcOH (20 mL) was dropwise added over 40 min. After cooling, the solvent was removed in vacuo and water (150 mL) was added to the resulting residue followed by extraction with $CHCl_3$ (20 mL x 3). The work-up described above was performed and the crude products were purified by column chromatography on silica gel eluting with EtOAc/hexane (4:6 v/v), affording **3f** (37.8 mg, 44%).



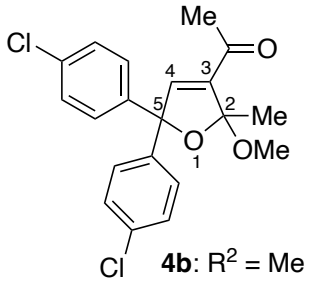
3f

3-Acetyl-4-hydroxy-2-methyl-1-oxaspiro[4.5]dec-2-ene (3f): Brown liquid; R_f = 0.33 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 3352 (OH), 1651 (C=O); ^{1}H NMR ($CDCl_3$) δ 4.70 (1H, d, J = 5.4 Hz, H-4), 2.31 (3H, s, Ac), 2.26 (3H, s, Me), 2.24 (1H, J = 5.4 Hz, OH), 1.89–1.41 (10H, m, CH_2 x 5); ^{13}C NMR ($CDCl_3$) δ 195.9 (C=O), 170.6 (C-2), 116.6 (C-3), 90.7 (C-5), 78.5 (C-4), 35.1, 29.6 (CH_2), 29.0 (CO<u>Me</u>), 25.2, 23.0, 22.7 (CH_2), 16.0 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{18}O_3Na$ 233.1154; found 233.1162.

Treatment of Dihydrofuranyl Acetates 3b–e with H_2O producing Hemiacetals 3b–e.

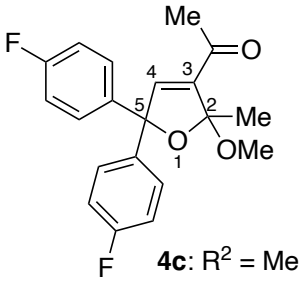
Dihydrofuranyl acetate **3** (0.02–0.15 mmol) was dissolved in AcOH/H_2O (5/5 mL) at room temperature and stirred under argon for 3 h except for **3b** for 24 h. Additional water (10 mL) was added to the mixture and the aqueous solution was extracted with $CHCl_3$ (10 mL × 3). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ followed by water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was separated by column chromatography on silica gel eluting with hexane/EtOAc (3:7 v/v), giving the corresponding hemiacetals **2b** (19.9 mg, 90%), **2c** (35.9 mg, 74%), **2d** (7.0 mg, 94%), and **2e** (19.1 mg, 68%), respectively.

A similar reaction of **3** (0.1 mmol) was carried out in AcOH/R^2OH (5/5 mL) instead of water for the period mentioned in Table 2, producing the corresponding acetal **4**.



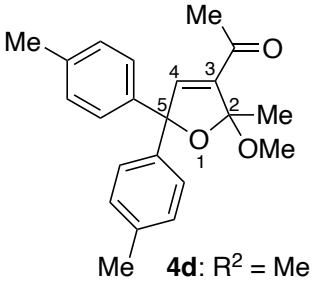
4b: R^2 = Me

3-Acetyl-5,5-bis(4-chlorophenyl)-2-methoxy-2-methyl-2,5-dihydrofuran (4b: R^2 = Me): Yield 41.6 mg, 72%; colorless oil; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.34–7.28 (8H, m, arom H), 7.26 (1H, s, H-4), 3.01 (3H, s, OMe), 2.43 (3H, s, CO<u>Me</u>), 1.72 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 193.4 (C=O), 144.7 (C-4), 141.8, 141.7 (arom C), 140.5 (C-3), 134.0, 133.9 (arom C), 128.94 (2C), 128.90 (2C), 127.9 (2C), 127.4 (2C) (arom CH), 113.1 (C-2), 89.8 (C-5), 50.9 (OMe), 28.2 (CO<u>Me</u>), 25.2 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}Cl_2O_3Na$ 399.0531; found 399.0571.



4c: R^2 = Me

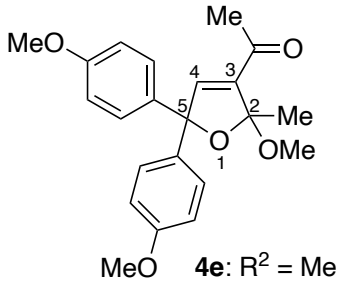
3-Acetyl-5,5-bis(4-fluorophenyl)-2-methoxy-2-methyl-2,5-dihydrofuran (4c: R^2 = Me): Yield 63.1 mg, 97%; yellow oil; R_f = 0.36 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.37 (1H, s, H-4), 7.34–7.31 (4H, m, arom H), 7.05–7.01 (4H, m, arom H), 3.01 (3H, s, OMe), 2.44 (3H, s, CO<u>Me</u>), 1.73 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 193.6 (C=O), 162.1 (2C) (d, $^1J_{(C,F)}$ = 246 Hz, arom C), 145.4 (C-4), 140.1 (C-3), 139.35, 139. 27 (d, $^4J_{(C,F)}$ = 3 Hz, arom C), 128.3 (2C), 127.8 (2C) (d, $^3J_{(C,F)}$ = 8 Hz, arom CH), 115.59 (2C), 115.56 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 113.0 (C-2), 89.9 (C-5), 50.8 (OMe), 28.1 (CO<u>Me</u>), 25.2 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}F_2O_3Na$ 367.1122; found 367.1122.



4d: R^2 = Me

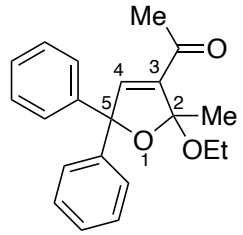
3-Acetyl-2-methoxy-5,5-bis(4-methylphenyl)-2-methyl-2,5-dihydrofuran (4d: R^2 = Me): Yield 32.5 mg, 95%; colorless microcrystals (from $CHCl_3$/hexane); mp 112–114 °C; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1679 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.43 (1H, s, H-4),7.26–7.24 (4H, m, arom H), 7.13 (4H, d, J = 7.9 Hz, arom H), 2.99 (3H, s, OMe), 2.43 (3H, s, CO<u>Me</u>), 2.32 (6H, s, Me × 2), 1.74 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 193.8 (C=O), 146.7 (C-4), 140.9, 140.8 (arom C), 139.4 (C-3), 137.5, 137.4 (arom C), 129.3 (2C), 129.2

(2C), 126.4 (2C), 126.0 (2C) (arom CH), 112.8 (C-2), 90.6 (C-5), 50.9 (OMe), 28.21 (CO<u>Me</u>), 25.6 (2-Me), 21.19, 21.14 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{24}O_3Na$ 359.1623; found 359.1668.



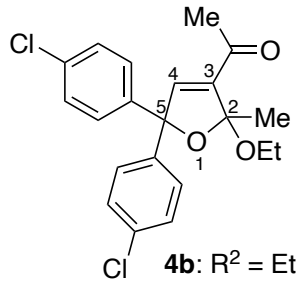
4e: R^2 = Me

3-Acetyl-5,5-bis(4-methoxylphenyl)-2-methoxy-2-methyl-2,5-dihydrofuran (4e: R^2 = Me): Yield 30.1 mg, 41%; colorless microcrystals (from $CHCl_3$/hexane); mp 122–123 °C; R_f = 0.21 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1672 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.38 (1H, s, H-4),7.28–7.25 (4H, m, arom H), 6.87–684 (4H, m, arom H), 3.79 (3H, s, OMe), 3.78 (3H, s, OMe), 3.01 (3H, s, OMe), 2.43 (3H, s, CO<u>Me</u>), 1.74 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 193.8 (C=O), 159.0 (2C) (arom C), 146.7 (C-4), 139.3 (C-3), 135.98, 135.92 (arom C), 127.9 (2C), 127.4 (2C), 113.9 (2C), 113.8 (2C) (arom CH), 112.7 (C-2), 90.3 (C-5), 55.38, 55.35, 50.9 (OMe), 28.1 (CO<u>Me</u>), 25.5 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{24}O_5Na$ 391.1521; found 391.1590.



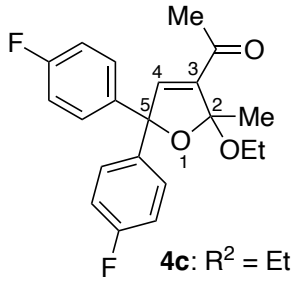
4a: R^2 = Et

3-Acetyl-2-ethoxy-2-methyl-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = Et): Yield 23.1 mg, 58%; yellow oil; R_f = 0.33 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.43 (1H, s, H-4), 7.39–7.31 (8H, m, arom H), 7.28–7.24 (2H, m, arom H), 3.27 (1H, dq, J = 8.3, 7.0 Hz, O–<u>H</u>CH), 3.16 (1H, dq, J = 8.3, 7.0 Hz, O–HC<u>H</u>), 2.43 (3H, s, CO<u>Me</u>), 1.75 (3H, s, Me), 1.02 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.7 (C=O), 146.9 (C-4), 143.8, 143.7 (arom C), 140.4 (C-3), 128.7 (2C), 128.5 (2C), 127.8, 127.7, 126.5 (2C), 126.1 (2C) (arom CH), 112.5 (C-2), 90.5 (C-5), 58.8 (OCH_2), 28.1 (CO<u>Me</u>), 25.8 (2-Me), 15.3 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}O_3Na$ 345.1467; found 345.1464.



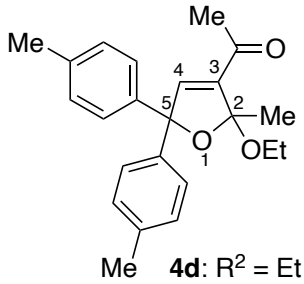
4b: R^2 = Et

3-Acetyl-5,5-bis(4-chlorophenyl)-2-ethoxy-2-methyl-2,5-dihydrofuran (4b: R^2 = Et): Yield 59.2 mg, 62%; pale yellow oil; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.32–7.26 (8H, m, arom H), 7.29 (1H, s, H-4), 3.27 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 3.16 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 2.42 (3H, s, COMe), 1.72 (3H, s, Me), 1.04 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.4 (C=O), 144.4 (C-4), 141.89, 141.85 (arom C), 141.1 (C-3), 133.94, 133.85, 128.91 (2C), 128.82 (2C), 127.86 (2C), 127.46 (2C) (arom CH), 112.7 (C-2), 89.6 (C-5), 58.9 (OCH_2), 28.2 (COMe), 25.6 (2-Me), 15.3 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{20}Cl_2O_3Na$ 413.0687; found 413.0703.



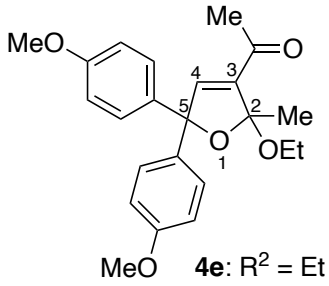
4c: R^2 = Et

3-Acetyl-5,5-bis(4-fluorophenyl)-2-ethoxy-2-methyl-2,5-dihydrofuran (4c: R^2 = Et): Yield 49.1 mg, 47%; yellow oil; R_f = 0.36 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.33–7.29 (4H, m, arom H), 7.33 (1H, s, H-4), 7.05–7.00 (4H, m, arom H), 3.27 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 3.18 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 2.43 (3H, s, COMe), 1.73 (3H, s, Me), 1.03 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.5 (C=O), 162.2 (2C) (d, $^1J_{(C,F)}$ = 246 Hz, arom C), 145.4 (C-4), 140.1 (C-3), 139.35, 139.27 (d, $^4J_{(C,F)}$ = 3 Hz, arom C), 128.3 (2C), 127.8 (2C) (d, $^3J_{(C,F)}$ = 8 Hz, arom CH), 115.60 (2C), 115.44 (2C) (d, $^2J_{(C,F)}$ = 21 Hz, arom CH), 112.5 (C-2), 89.6 (C-5), 58.8 (OCH_2), 28.2 (COMe), 25.5 (2-Me), 15.3 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{20}F_2O_3Na$ 381.1278; found 381.1289.



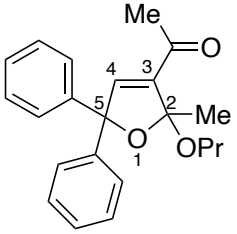
4d: R^2 = Et

3-Acetyl-2-ethoxy-5,5-bis(4-methylphenyl)-2-methyl-2,5-dihydrofuran (4d: R^2 = Et): Yield 33.6 mg, 87%; colorless microcrystals (from $CHCl_3$/hexane); mp 97–98 °C; R_f = 0.41 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.40 (1H, s, H-4),7.26 (4H, m, arom H), 7.12 (4H, d, J = 7.9 Hz, arom H), 3.28 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 3.14 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 2.41 (3H, s, COMe), 2.32 (3H, s, Me), 2.31 (3H, s, Me), 1.73 (3H, s, 2-Me), 1.04 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.8 (C=O), 146.3 (C-4), 141.0, 140.9 (arom C), 140.0 (C-3), 137.42, 137.35 (arom C), 129.3 (2C), 129.2 (2C), 126.4 (2C), 126.0 (2C) (arom CH), 112.4 (C-2), 90.3 (C-5), 58.8 (OCH_2), 28.1 (COMe), 25.9 (2-Me), 21.20, 21.14 (Me), 15.3 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{26}O_3Na$ 373.1780; found 373.1827.



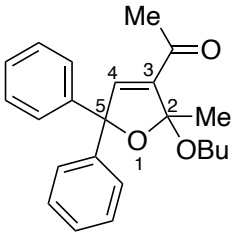
4e: R^2 = Et

3-Acetyl-2-ethoxy-5,5-bis(4-methoxylphenyl)-2-methyl-2,5-dihydrofuran (4e: R^2 = Et): Yield 42.9 mg, 60%; pale yellow oil; R_f = 0.21 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, s, H-4),7.28–7.24 (4H, m, arom H), 6.87–6.84 (4H, m, arom H), 3.79 (3H, s, OMe), 3.78 (3H, s, OMe), 3.29 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 3.16 (1H, dq, J = 8.3, 7.0 Hz, O–HCH), 2.42 (3H, s, COMe), 1.73 (3H, s, 2-Me), 1.04 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.8 (C=O), 146.3 (C-4), 141.0, 140.9 (arom C), 140.0 (C-3), 137.42, 137.35 (arom C), 129.3 (2C), 129.2 (2C), 126.4 (2C), 126.0 (2C) (arom CH), 112.4 (C-2), 90.3 (C-5), 58.8 (OCH_2), 28.1 (COMe), 25.9 (2-Me), 21.20, 21.14 (Me), 15.3 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{26}O_5Na$ 405.1678; found 405.1689.



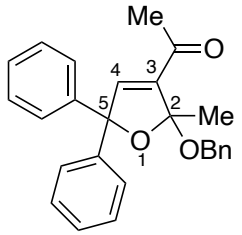
4a: R^2 = Pr

3-Acetyl-2-methyl-2-propoxy-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = Pr): Yield 30.5 mg, 42%; orange oil; R_f = 0.64 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.42 (1H, s, H-4), 7.39–7.31 (8H, m, arom H), 7.28–7.24 (2H, m, arom H), 3.14 (1H, dt, J = 8.8, 6.8 Hz, O–HCH), 3.03 (1H, dt, J = 8.8, 6.8 Hz, O–HCH), 2.42 (3H, s, COMe), 1.75 (3H, s, Me), 1.41 (2H, sext, J = 7.2 Hz, CH_2), 0.71 (3H, t, J = 7.4 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.7 (C=O), 145.8 (C-4), 143.82, 143.78 (arom C), 140.4 (C-3), 128.6 (2C), 128.5 (2C), 127.8, 127.6, 126.6 (2C), 126.1 (2C) (arom CH), 112.5 (C-2), 90.5 (C-5), 65.0 (OCH_2), 28.2 (COMe), 25.8 (2-Me), 23.0 (CH_2), 10.5 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{24}O_3Na$ 359.1623; found 359.1633.



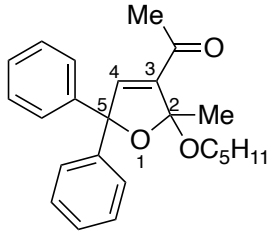
4a: R^2 = Bu

3-Acetyl-2-butoxy-2-methyl-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = Bu): Yield 43.2 mg, 57%; colorless microcrystals (from $CHCl_3$/hexane); mp 66–67 °C; R_f = 0.52 (EtOAc/hexane 2:8 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.44–7.39 (3H, m, arom H), 7.42 (1H, s, H-4), 7.38–7.35 (2H, m, arom H), 7.33－7.30 (3H, m, arom H), 7.25–7.23 (2H, m, arom H), 3.71–3.63 (2H, m, O–CH_2), 2.40 (3H, s, COMe), 1.67–1.58 (2H, m, CH_2), 1.51 (3H, s, Me), 1.42 (2H, sext, J = 7.4 Hz, CH_2), 0.92 (3H, t, J = 7.4 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 196.1 (C=O), 142.7 (C-4), 140.7, 140.1 (arom C), 137.8 (C-3), 128.1, 128.61 (2C), 128.58 (2C), 128.3, 127.98 (2C), 127.69 (2C) (arom CH), 99.8 (C-2), 85.1 (C-5), 62.8 (OCH_2), 32.1 (CH_2), 27.3 (COMe), 19.8 (2-Me), 19.4 (CH_2), 14.0 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{26}O_3Na$ 373.1780; found 373.1795.



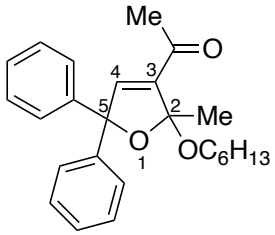
4a: R^2 = Bn

3-Acetyl-2-benzyloxy-2-methyl-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = Bn): Yield 37.4 mg, 54%; colorless microcrystals (from $CHCl_3$/hexane); mp 102–103 °C; R_f = 0.45 ($CHCl_3$); IR ($CHCl_3$) ν 1681 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.46 (1H, s, H-4), 7.42–7.40 (4H, m, arom H), 7.35–7.32 (4H, m, arom H), 7.30–7.19 (5H, m, arom H), 7.08 (2H, d, J = 7.7 Hz, arom H), 4.26 (1H, d, J = 11.3 Hz, O–HCH), 4.16 (1H, d, J = 11.3 Hz, O–HCH), 2.37 (3H, s, COMe), 1.85 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 193.6 (C=O), 145.9 (C-4), 143.72, 143.67 (arom C), 140.3 (C-3), 138.2 (arom C), 128.66 (2C), 128.64 (2C), 128.4 (2C), 127.94 (2C), 127.90, 127.7, 127.3, 126.6 (2C), 126.1 (2C) (arom CH), 112.7 (C-2), 90.9 (C-5), 65.5 (OCH_2), 28.1 (COMe), 25.8 (2-Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{24}O_3Na$ 407.1623; found 407.1594.



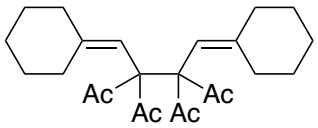
4a: R^2 = C_5H_{11}

3-Acetyl-2-methyl-2-pentyloxyl-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = *n*-C_5H_{11}): Yield 24.3 mg, 54%; orange oil; R_f = 0.58 (EtOAc/hexane 2:8 v/v); IR ($CHCl_3$) ν 1681 (C=O); ^{11}H NMR ($CDCl_3$) δ 7.42 (1H, s, H-4), 7.37 (4H, td, J = 8.6, 1.3 Hz, arom H), 7.32 (4H, t, J = 7.9 Hz, arom H), 7.28–7.24 (2H, m, arom H), 3.17 (1H, dt, J = 8.8, 7.0 Hz, O–HCH), 3.04 (1H, dt, J = 8.8, 7.0 Hz, O–HCH), 2.42 (3H, s, COMe), 1.75 (3H, s, Me), 1.39 (2H, quint, J = 7.2 Hz, CH_2), 1.18–1.03 (4H, m, CH_2 × 2), 0.80 (3H, t, J = 7.0 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.7 (C=O), 145.8 (C-4), 143.83, 143.80 (arom C), 140.4 (C-3), 128.6 (2C), 128.5 (2C), 127.8, 127.6, 126.6 (2C), 126.1 (2C) (arom CH), 112.6 (C-2), 90.5 (C-5), 63.5 (OCH_2), 29.4, 28.19 (CH_2), 28.15 (COMe), 25.8 (2-Me), 22.4 (CH_2), 14.1 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{28}O_3Na$ 387.1936; found 387.1909.

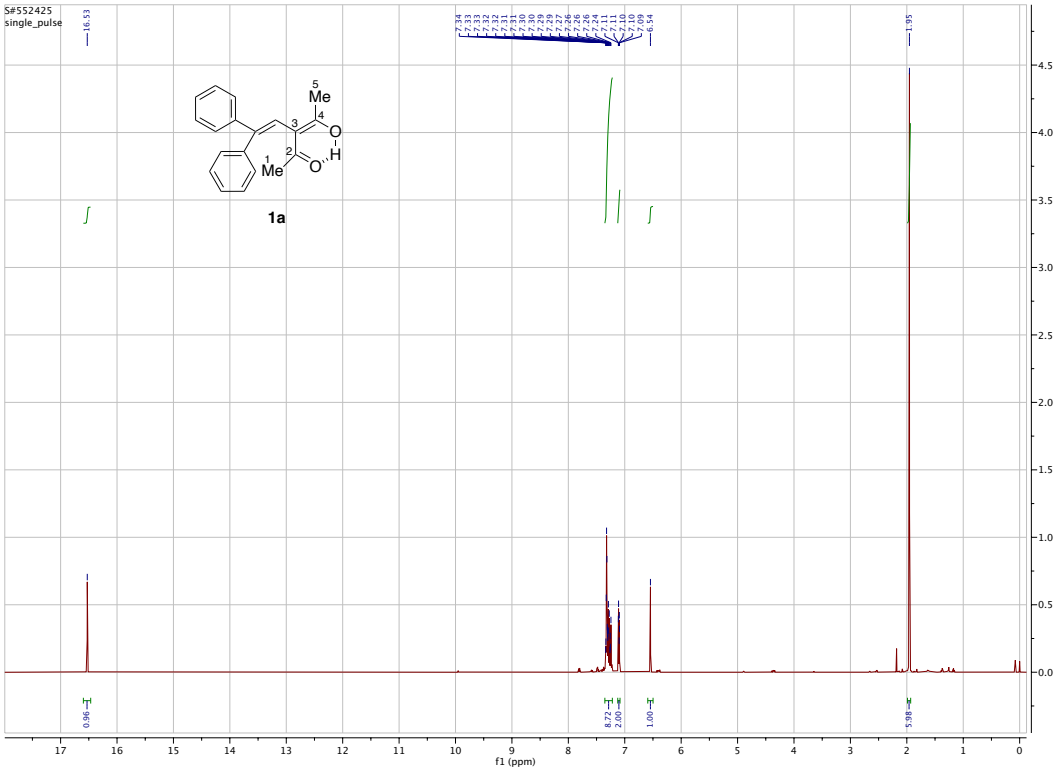


4a: $R^2 = C_6H_{13}$

3-Acetyl-2-methyl-2-hexyloxyl-5,5-diphenyl-2,5-dihydrofuran (4a: R^2 = *n*-C_6H_{13}): Yield 23.7 mg, 30%; pale yellow oil; R_f = 0.50 ($CHCl_3$); IR ($CHCl_3$) ν 1681 (C=O); ^{11}H NMR ($CDCl_3$) δ 7.42 (1H, s, H-4), 7.37 (4H, td, J = 8.2, 1.2 Hz, arom H), 7.32 (4H, t, J = 7.5 Hz, arom H), 7.28–7.24 (2H, m, arom H), 3.16 (1H, dt, J = 8.8, 7.0 Hz, O–HCH), 3.04 (1H, dt, J = 8.8, 7.0 Hz, O–HCH), 2.42 (3H, s, COMe), 1.75 (3H, s, Me), 1.38 (2H, quint, J = 7.2 Hz, CH_2), 1.26–1.05 (6H, m, CH_2 × 3), 0.83 (3H, t, J = 7.2 Hz, Me); ^{13}C NMR ($CDCl_3$) δ 193.7 (C=O), 145.8 (C-4), 143.82, 143.78 (arom C), 140.4 (C-3), 128.6 (2C), 128.5 (2C), 127.8, 127.6, 126.6 (2C), 126.1 (2C) (arom CH), 112.5 (C-2), 90.5 (C-5), 63.5 (OCH_2), 31.6, 29.7 (CH_2), 28.2 (COMe), 25.8 (2-Me), 25.7, 22.6 (CH_2), 14.1 (Me); FAB HRMS (acetone/NBA) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{30}O_3Na$ 401.2093; found 401.2096.



3,4-Diacetyl-3,4-bis(cyclohexylidenemethyl)hexane-2,5-dione: Yield 24.3 mg, 29%; colorless microcrystals (from $CHCl_3$); mp 173.2–176.4 °C; R_f = 0.52 (EtOAc/hexane 3:7 v/v); IR ($CHCl_3$) ν 1688 (C=O); ^{1}H NMR ($CDCl_3$) δ 6.41 (2H, s, =CH– × 2), 2.41 (6H, s, Ac × 2), 2.31 (6H, s, Ac × 2), 1.82 (4H, d, J = 13.2 Hz, CH_2 × 2), 1.64 (6H, d, J = 11.2 Hz, CH_2 × 3), 1.49 (4H, t, J = 13.2 Hz, CH_2 × 2), 1.20 (4H, qt, J = 13.0, 2.6 Hz, CH_2 × 2), 1.09 (2H, tt, J = 12.4, 2.4 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 203.9 (2C), 198.7 (2C) (C=O), 150.7 (2C) (=CH–), 146.2 (2C) (>C=), 50.6 (2C) (>C<), 31.3 (2C), 26.8 (2C) (Ac), 26.2 (4C), 23.8 (6C) (CH_2); FAB HRMS (acetone/NBA) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{35}O_4$ 387.2535; found 387.2524.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7.33
7.33
7.32
7.32
7.31
7.31
7.30
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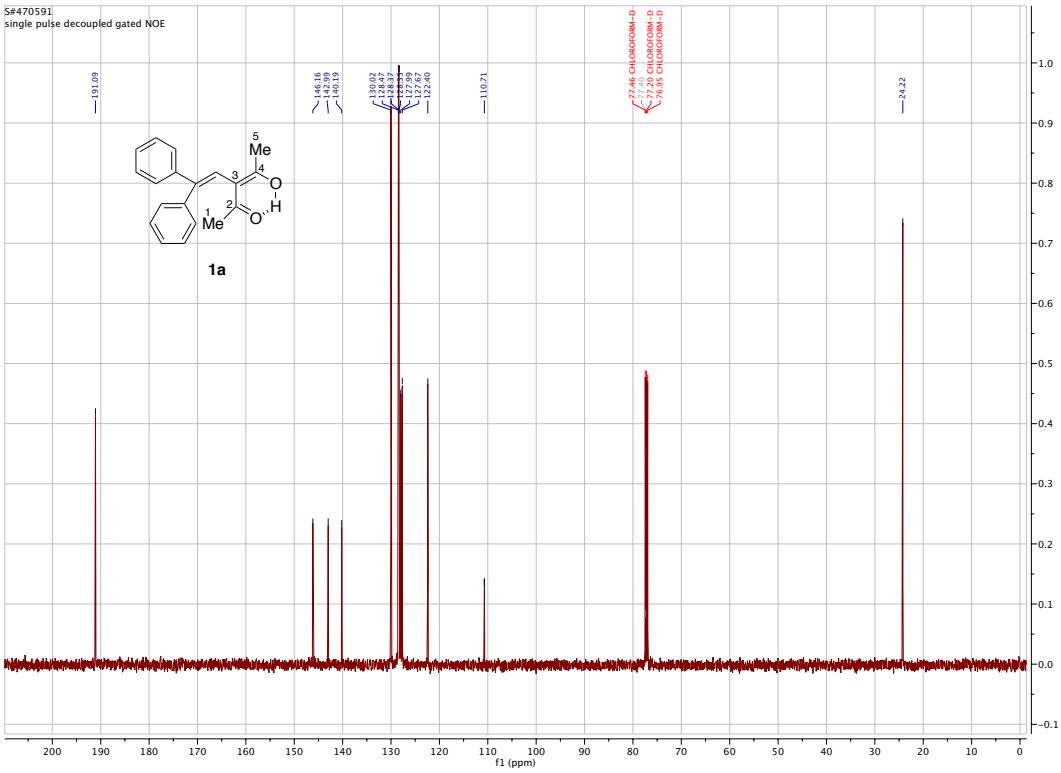
7.28
7.27
7.26
7.26
7.24
7.11
7.11
7.10
7.09
6.54
1.95
Me
Me
O
H
1a
f1 (ppm)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140.19
130.02
128.47
128.37
127.99
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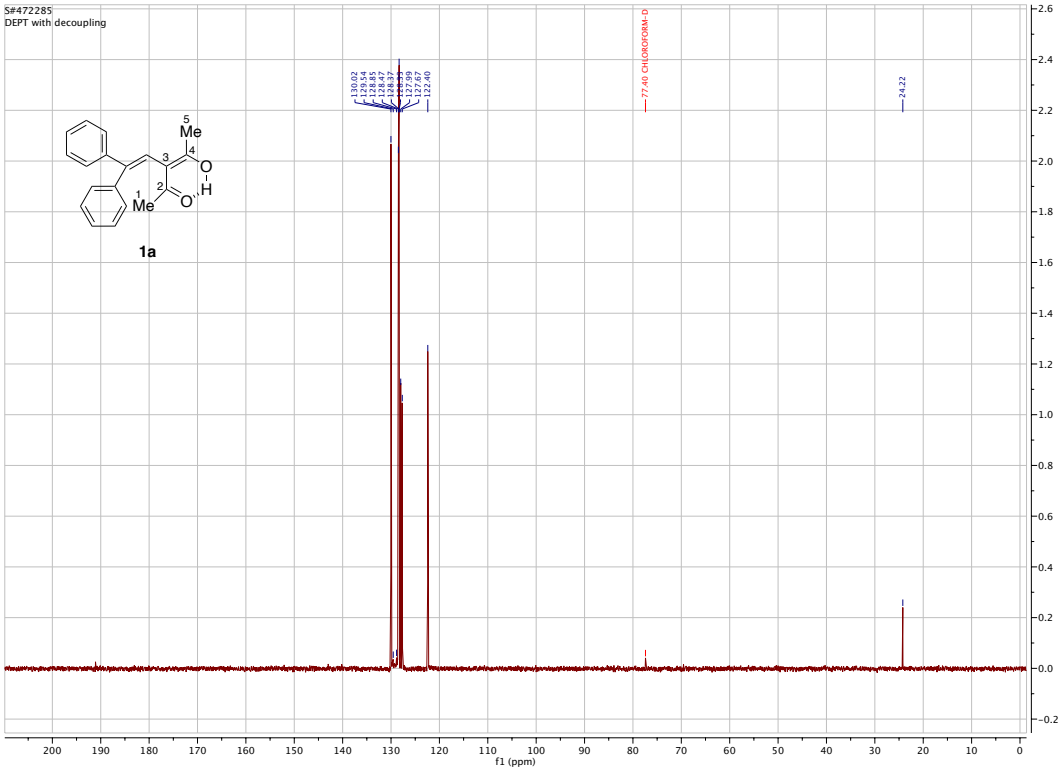
127.67
122.40
110.71
77.46 CHLOROFORM-d
77.20 CHLOROFORM-d
76.95 CHLOROFORM-d
24.22
Me
Me
O
H
1a
f1 (ppm)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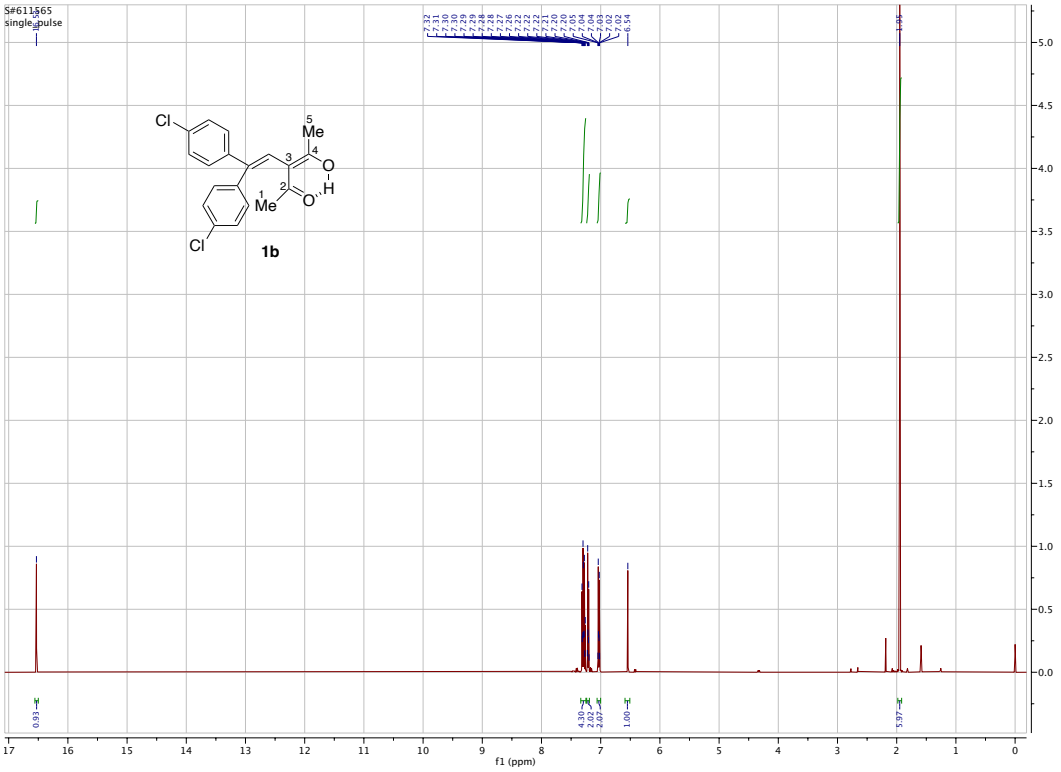
O
H
Me
O
1a
f1 (ppm)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Me
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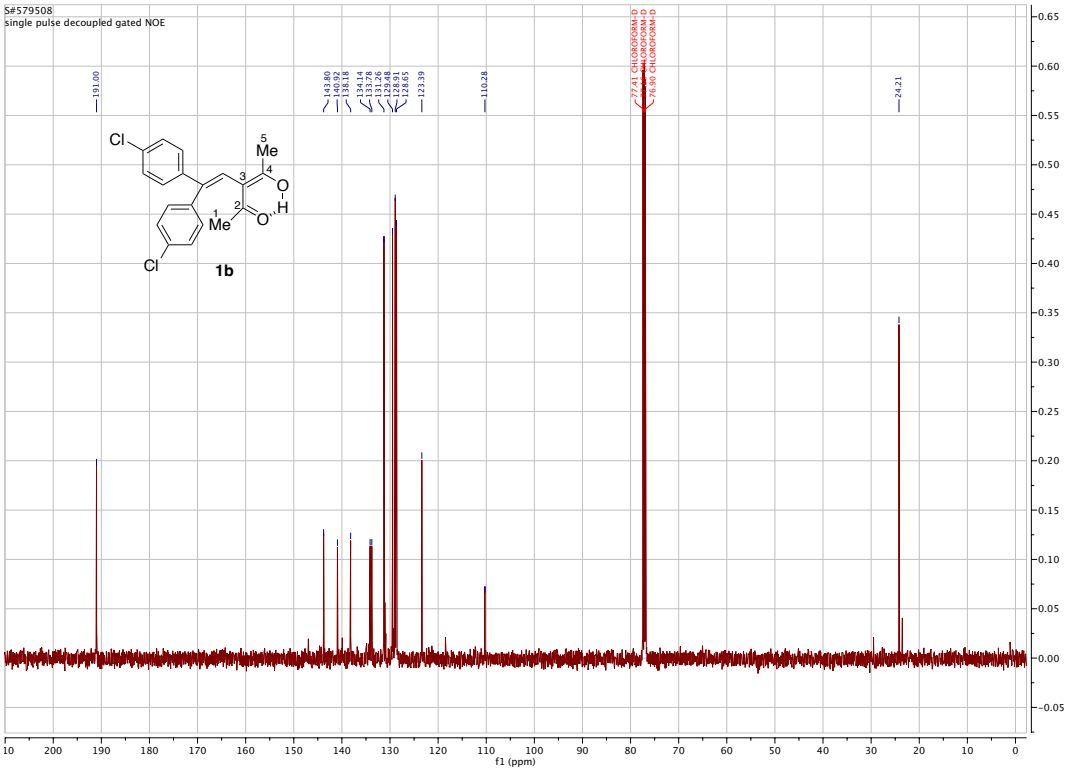
H
Me
O
Cl
1b
f1 (ppm)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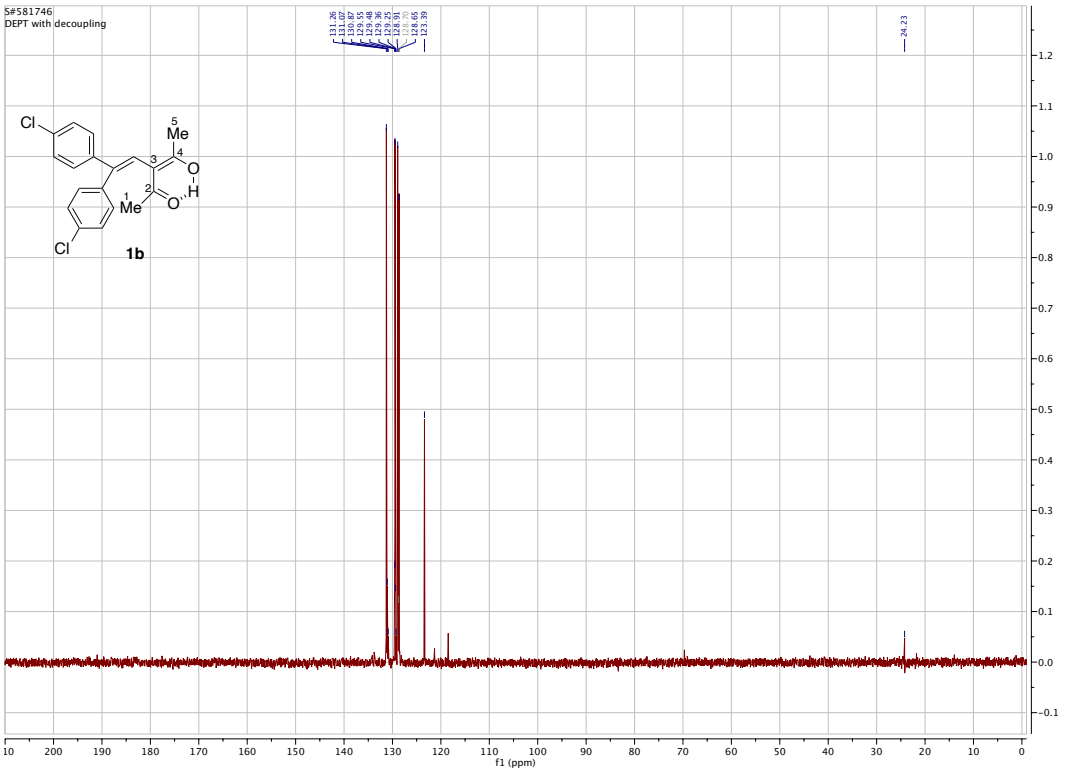
134.14
131.26
129.48
128.91
128.65
123.39
110.28
77.41 CHLOROFORM-D
77.00 CHLOROFORM-D
76.90 CHLOROFORM-D
24.21
Cl
Me
O
H
Me
O
Cl
1b
f1 (ppm)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DEPT with decoupling
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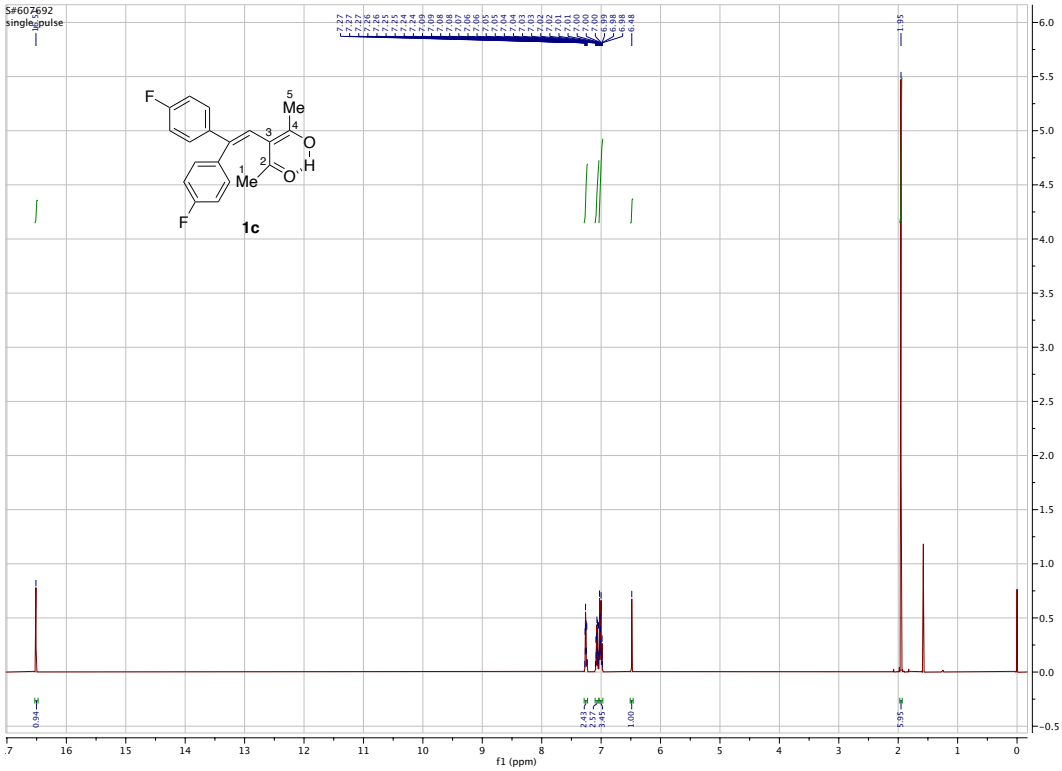
129.55
129.48
129.36
129.25
128.91
128.65
123.39
24.23
Cl
Me
O
H
Me
O
Cl
1b
f1 (ppm)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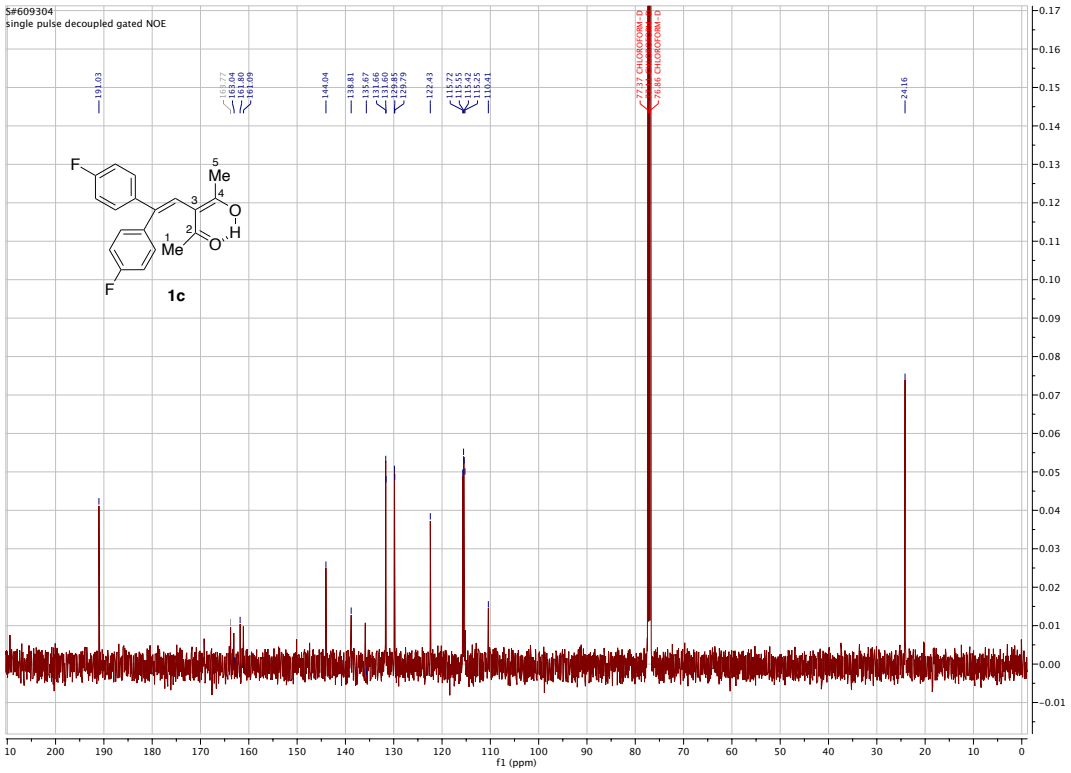
O
H
Me
O
F
1c
f1 (ppm)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single pulse decoupled gated NOE
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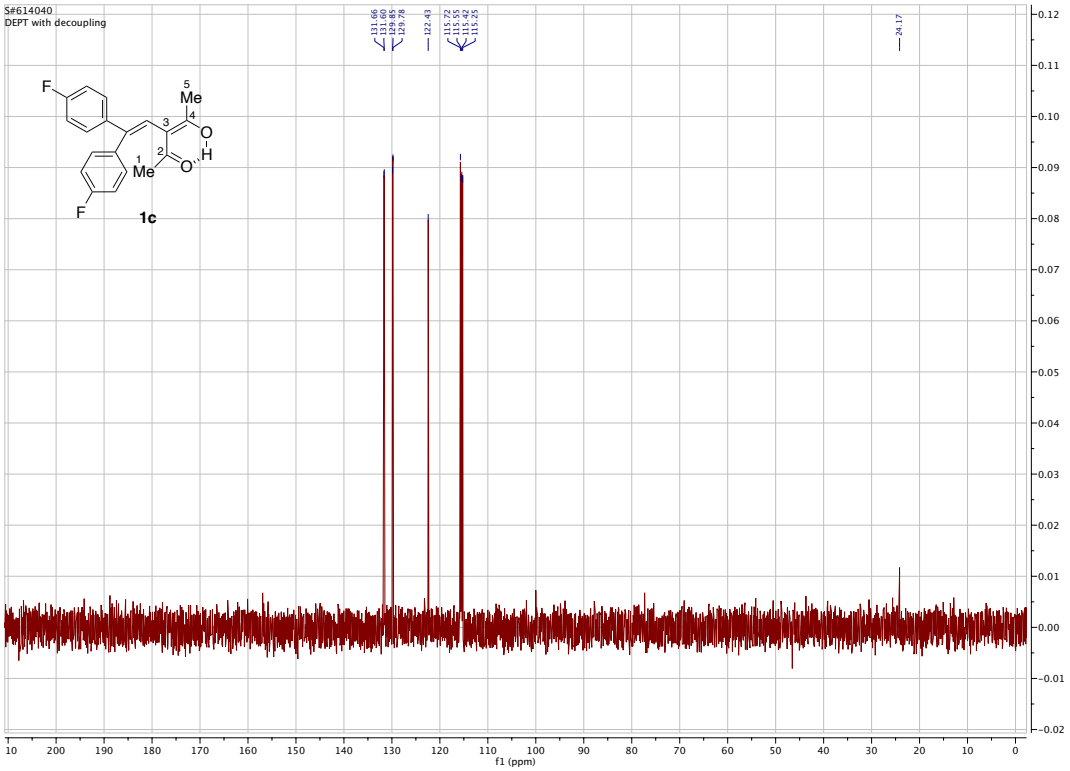
Me
O
H
Me
O
F
1c
f1 (ppm)


S#614040
DEPT with decoupling
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Me
5
4
3
O
H
2
1
Me
O
F
1c
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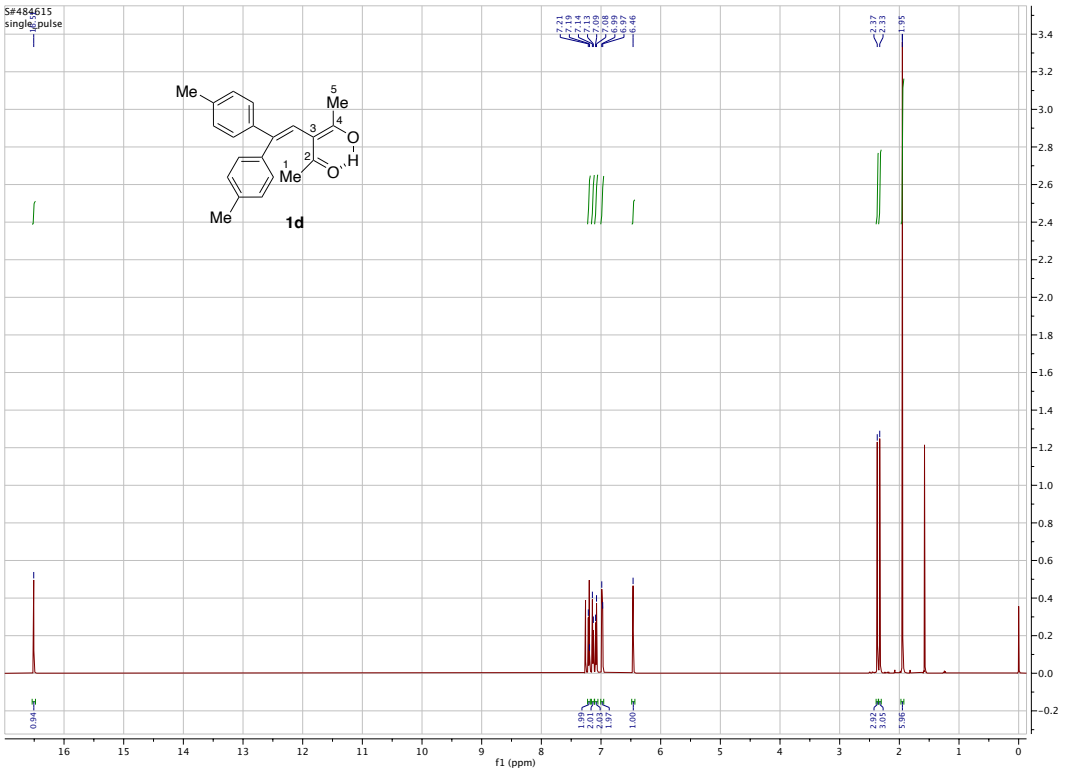
115.55
115.42
115.25
24.17
f1 (ppm)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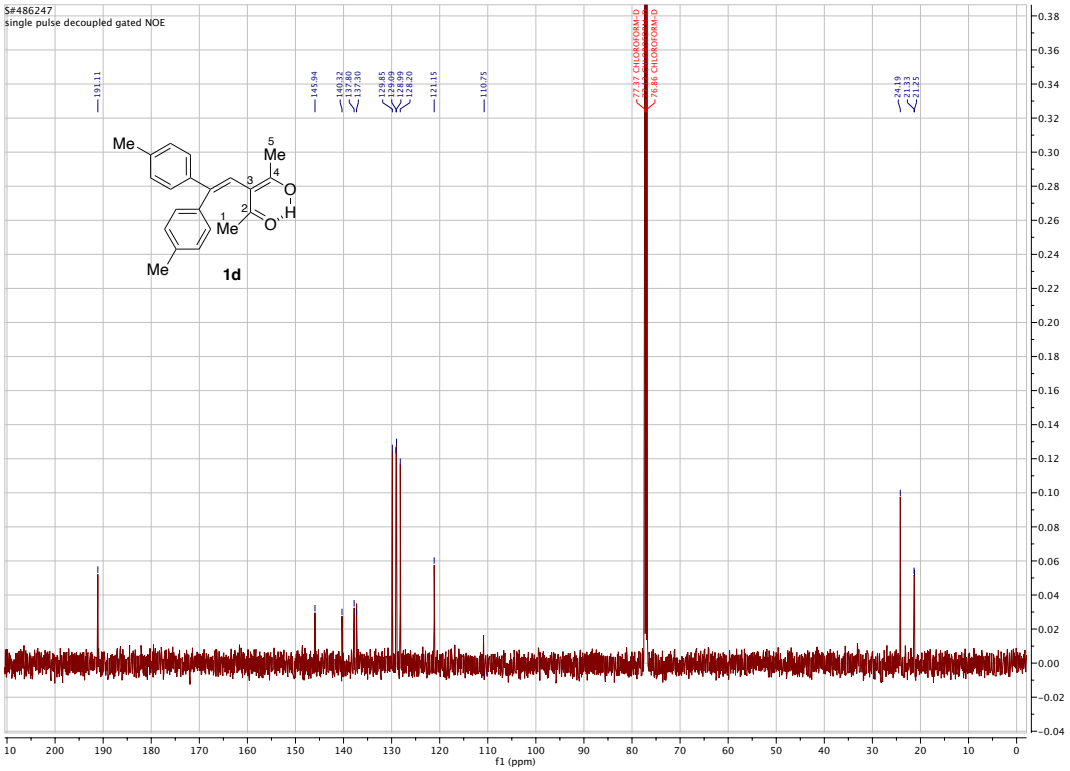
5
Me
4
3
O
H
2
1
Me
O
Me
1d
7.21
7.19
7.14
7.13
7.09
7.08
6.99
6.97
6.46
2.37
2.33
1.95
0.94
1.00
2.82
3.05
5.96
f1 (ppm)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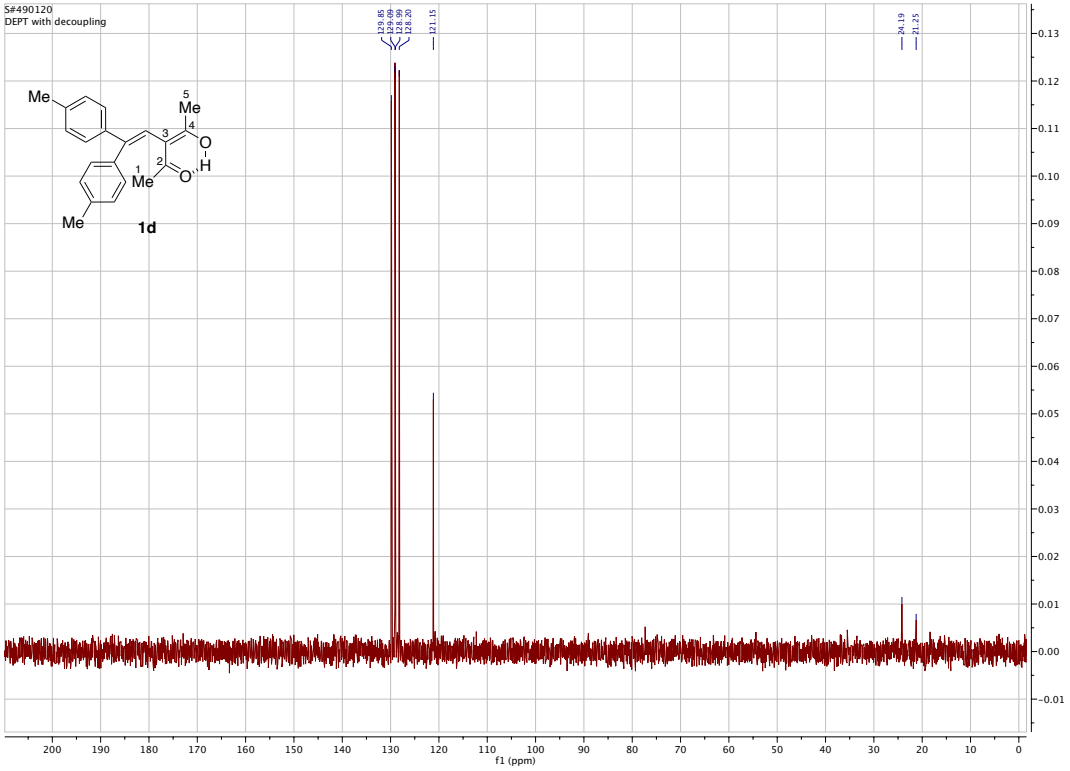
145.94
140.32
137.80
137.30
129.85
129.09
128.99
128.30
121.15
110.75
77.37 CHLOROFORM-D
76.86 CHLOROFORM-D
24.19
21.33
21.25
Me
Me
Me
Me
1d
f1 (ppm)


S#490120
DEPT with decoupling
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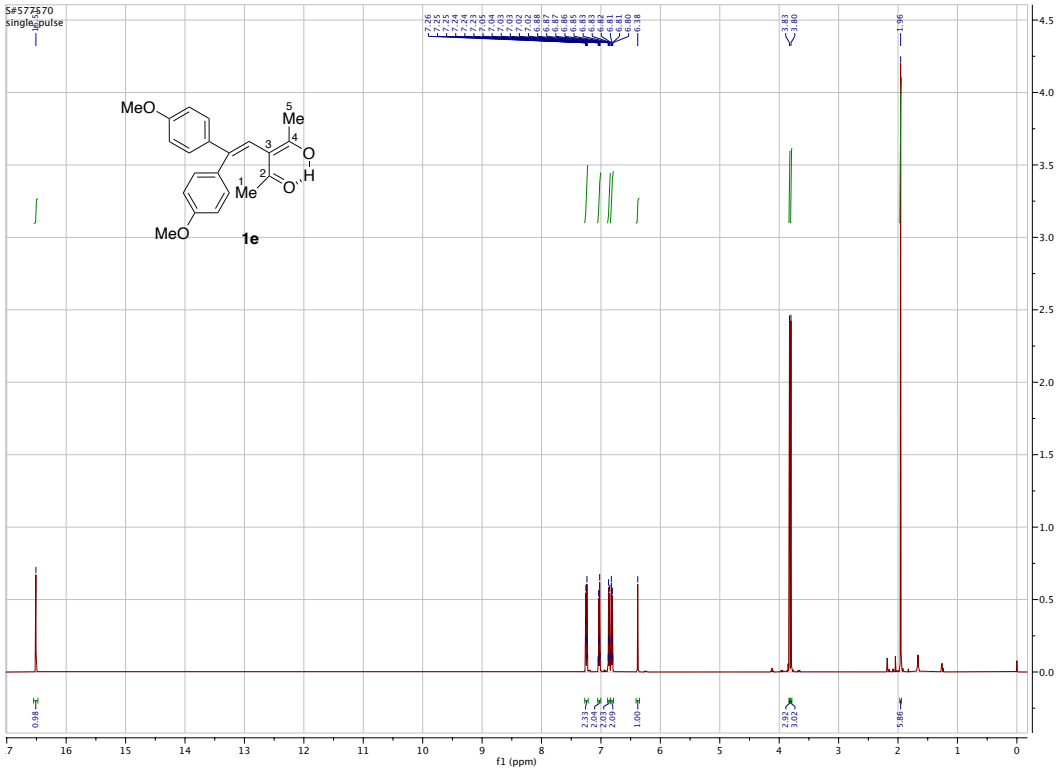
129.09
128.99
128.30
121.15
24.19
21.25
Me
Me
Me
Me
1d
f1 (ppm)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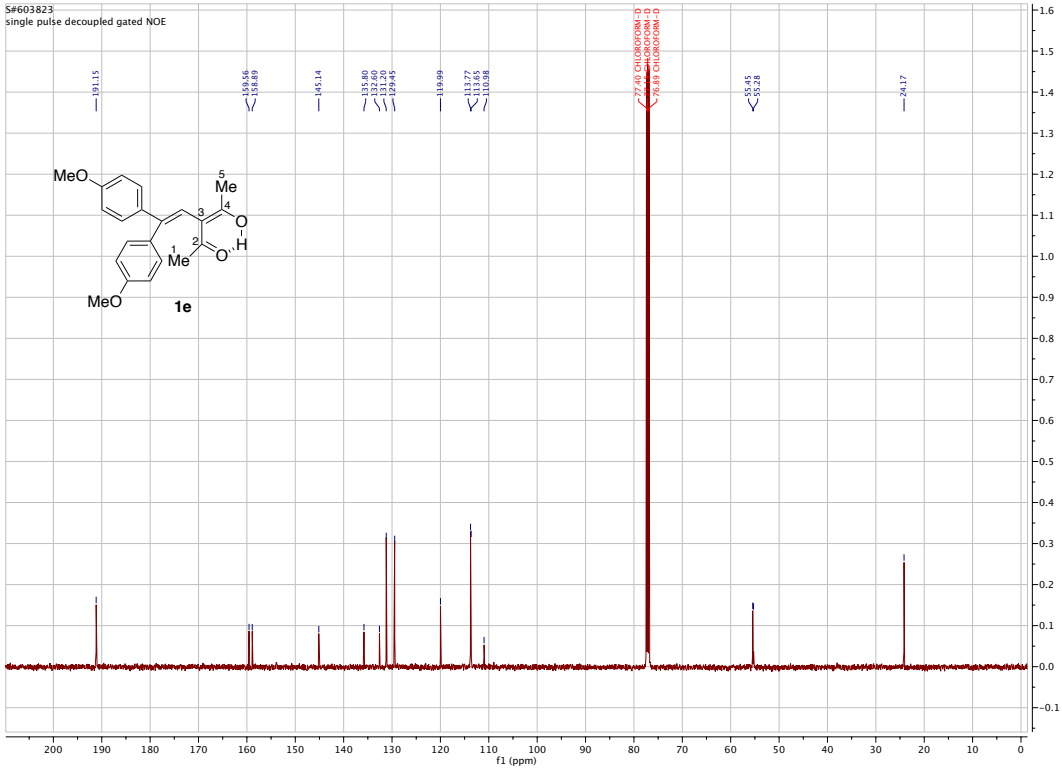
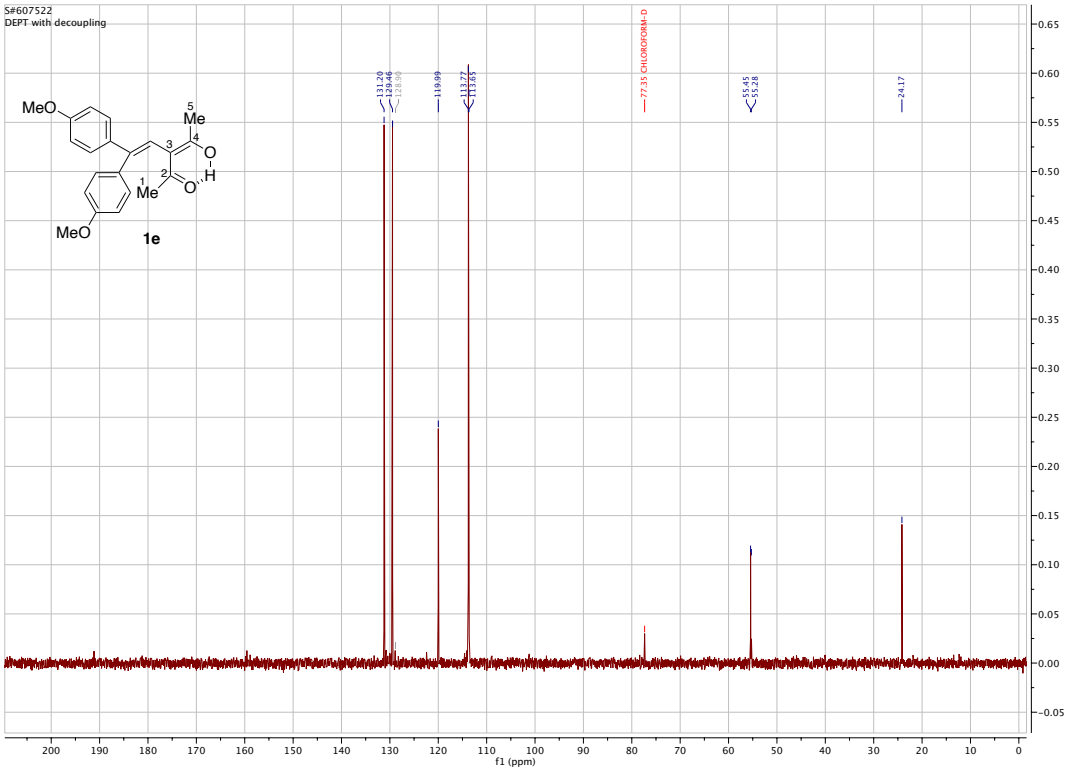
Me
O
H
Me
MeO
1e
f1 (ppm)


S#603823
single pulse decoupled gated NOE
MeO
Me
O
H
Me
MeO
1e
f1 (ppm)


S#607522
DEPT with decoupling
MeO
Me
O
H
Me
O
MeO
1e
131.20
129.46
128.90
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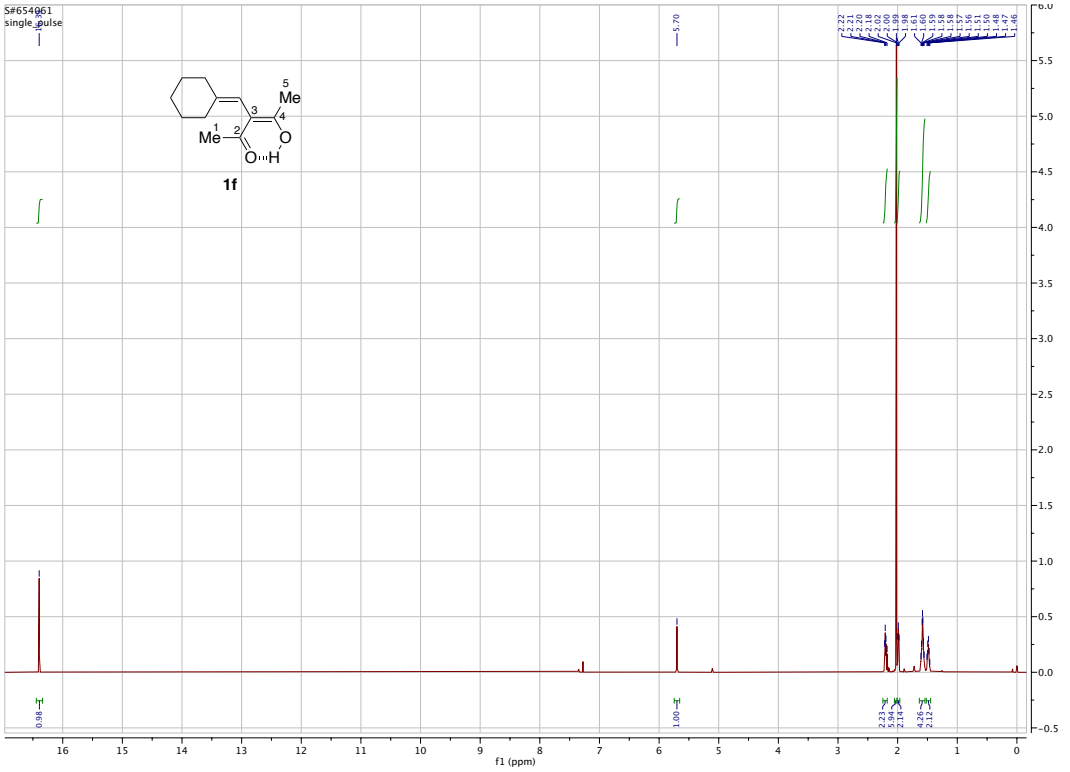
113.65
77.35 CHLOROFORM-D
55.45
55.28
24.17
f1 (ppm)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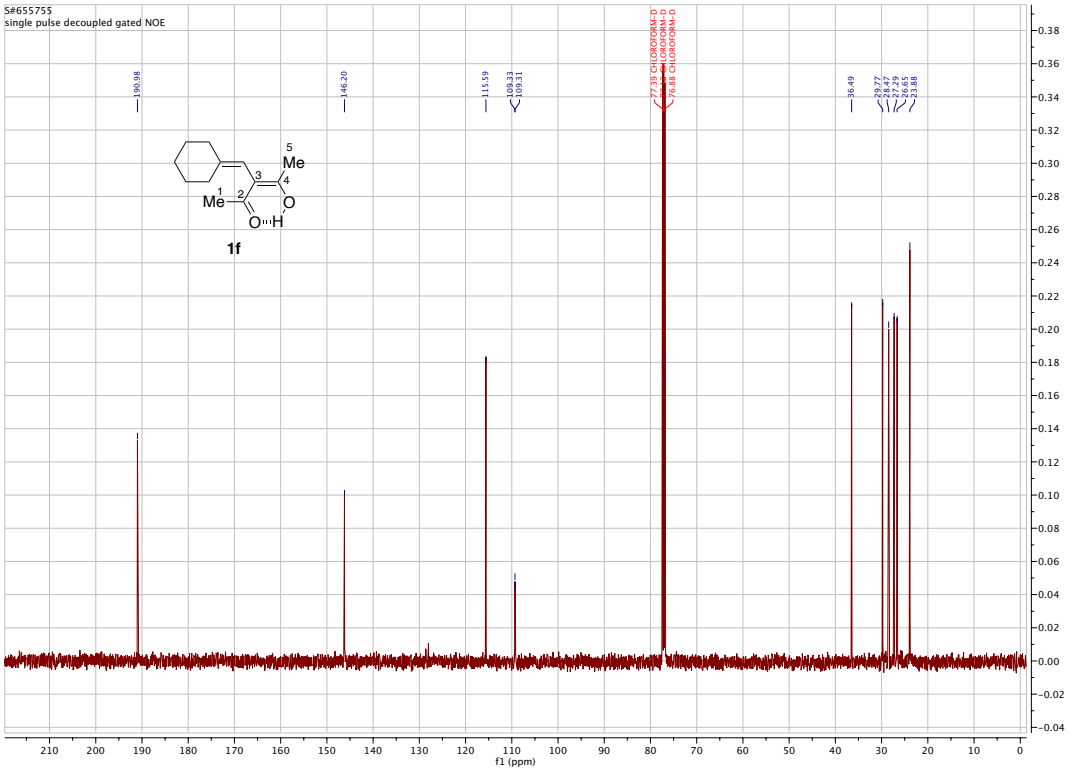
Me
O
H
1f
5.70
f1 (ppm)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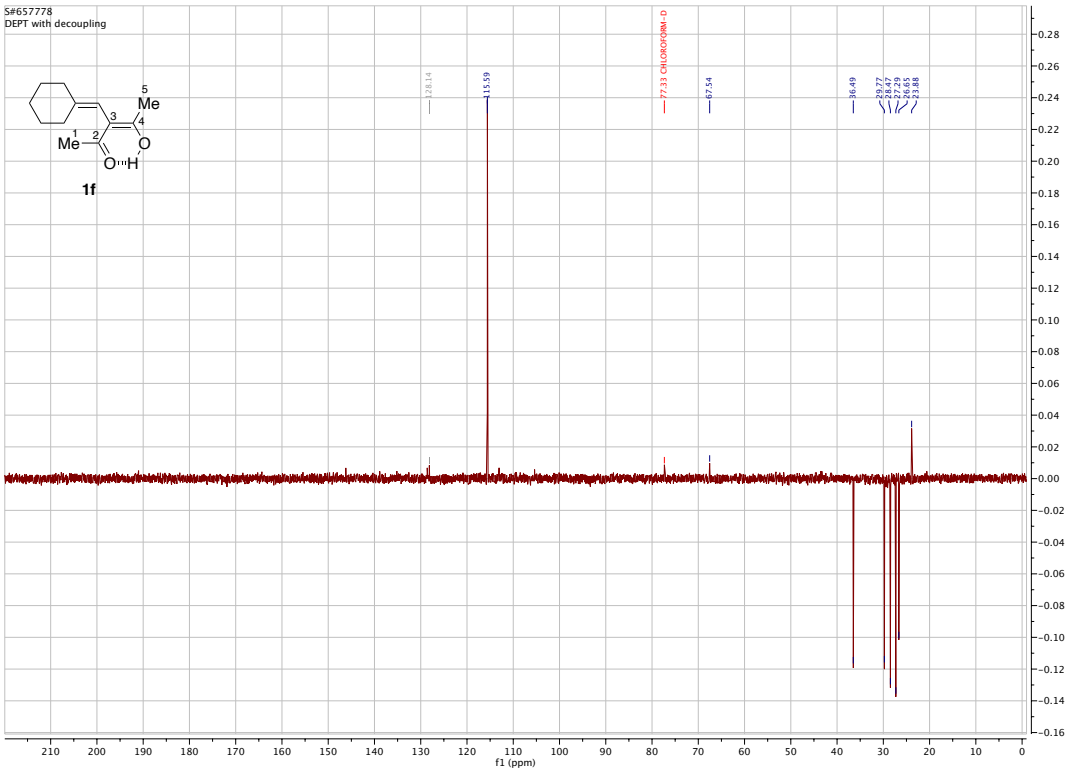
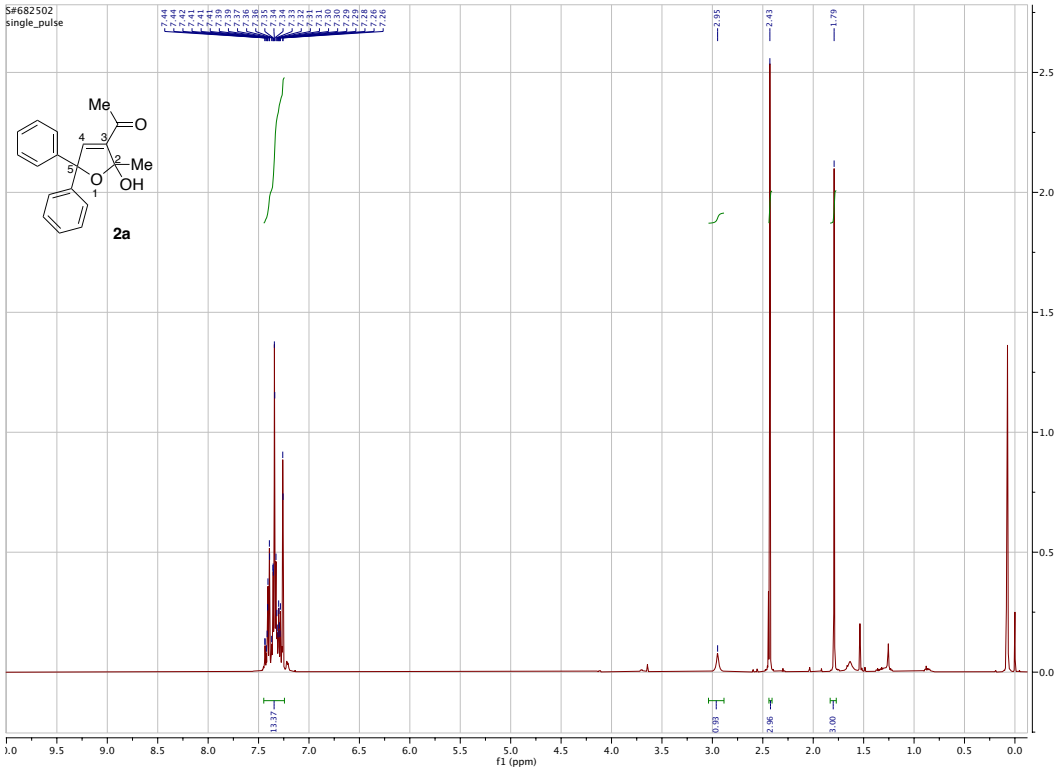
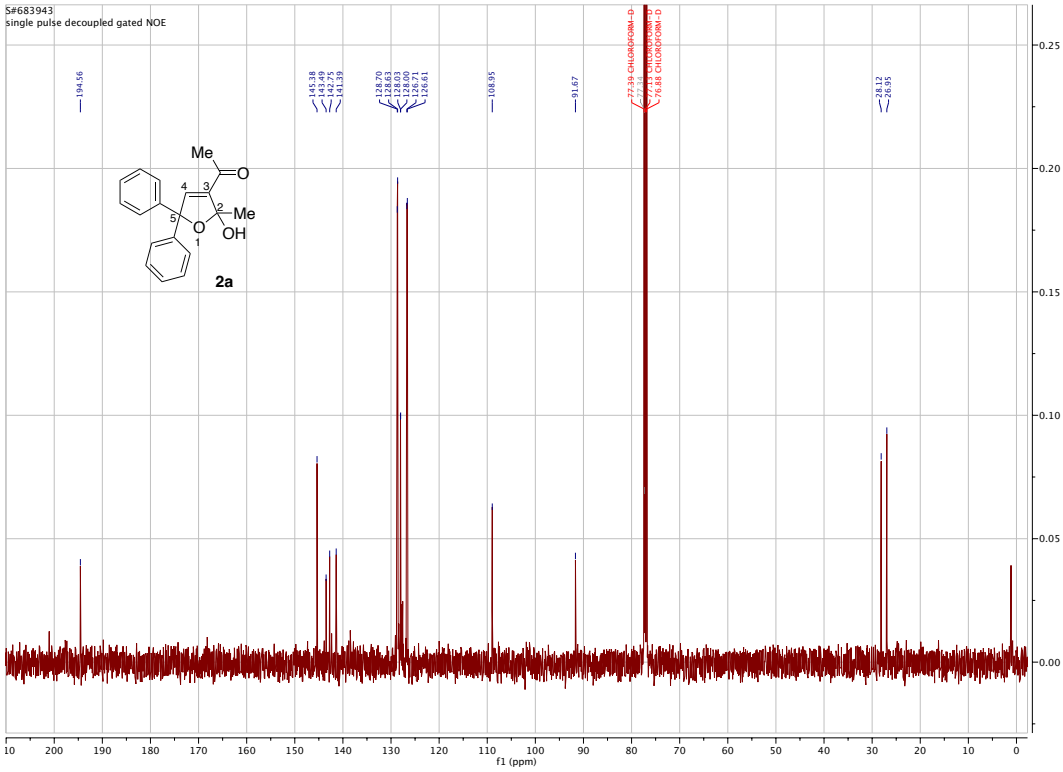
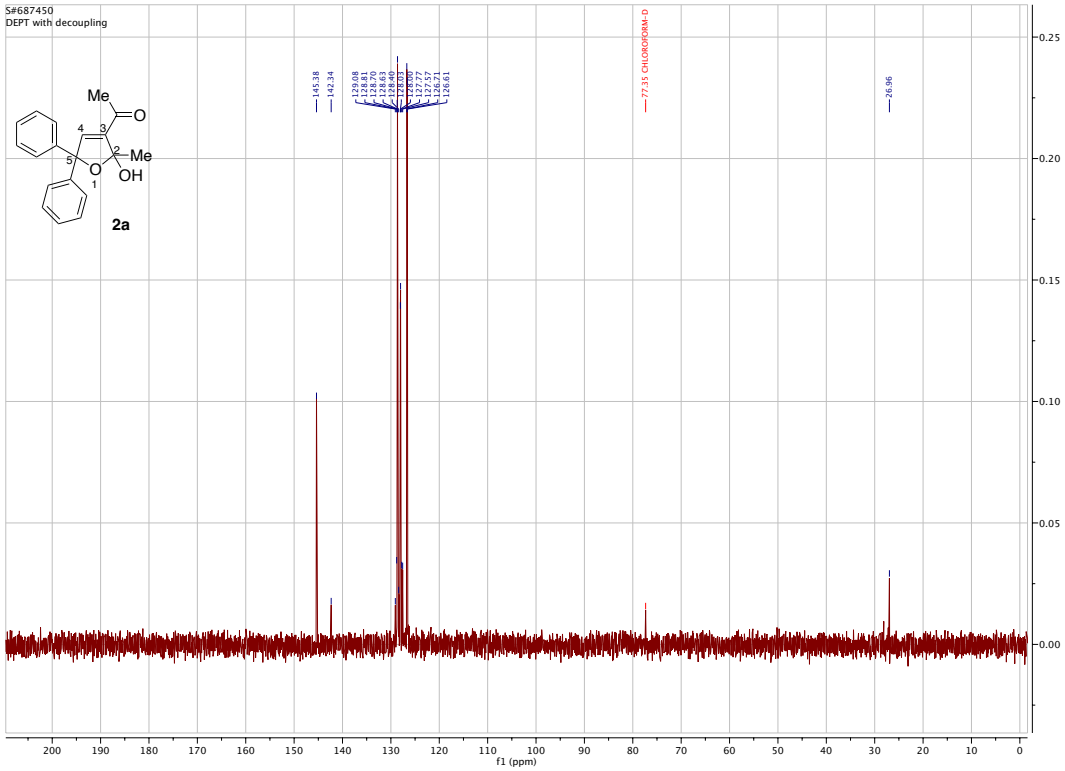
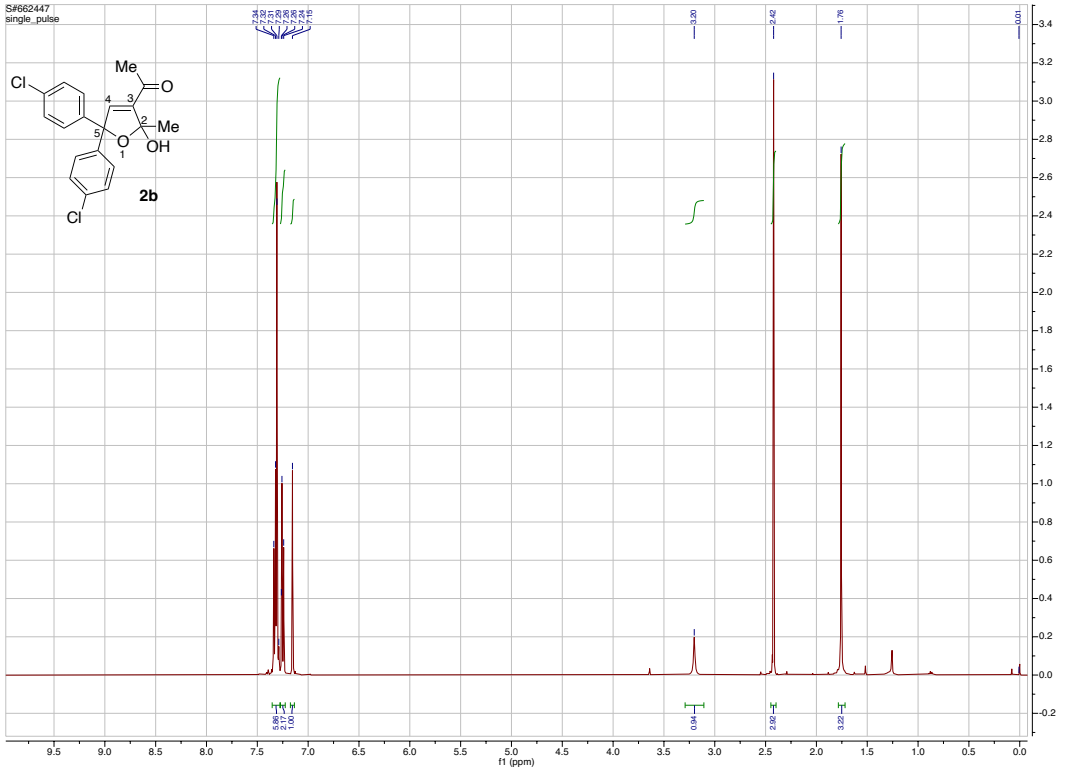
115.59
109.33
109.31
77.33 CHLOROFORM-D
77.00 CHLOROFORM-D
76.68 CHLOROFORM-D
36.49
29.77
28.47
27.29
26.65
23.88
Me
Me
O
O
H
1f
f1 (ppm)

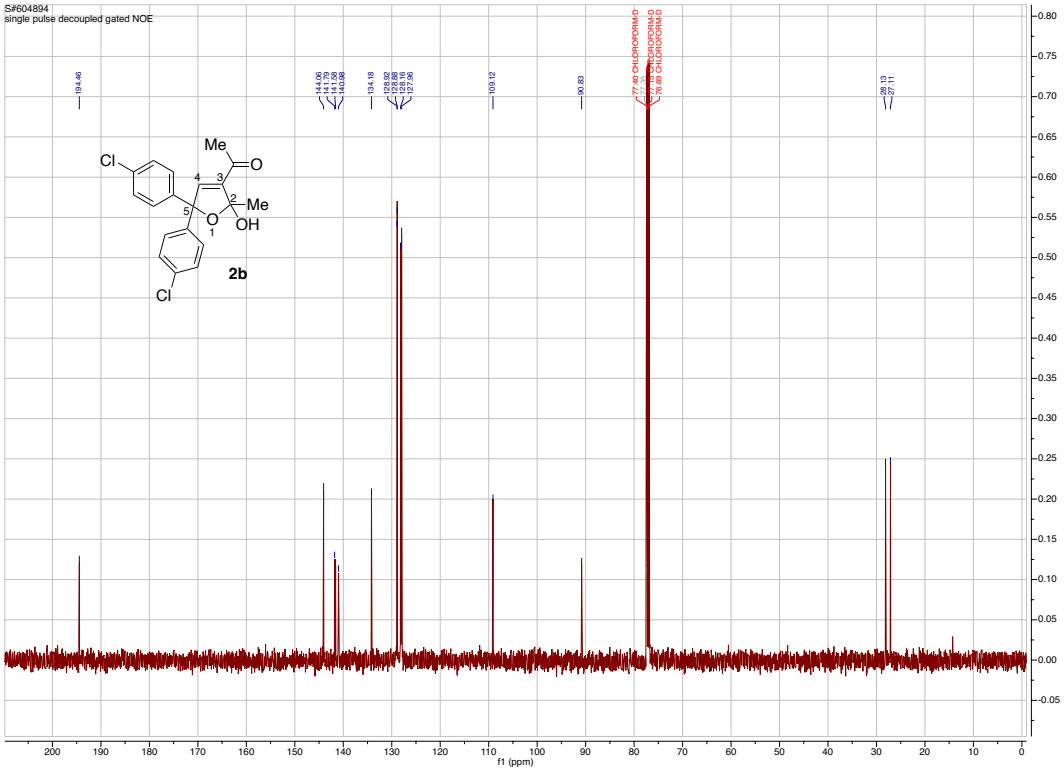

S#657778
DEPT with decoupling
128.14
115.59
77.33 CHLOROFORM-D
67.54
36.49
29.77
28.47
27.29
26.65
23.88
Me
Me
O
O
H
1f
f1 (ppm)

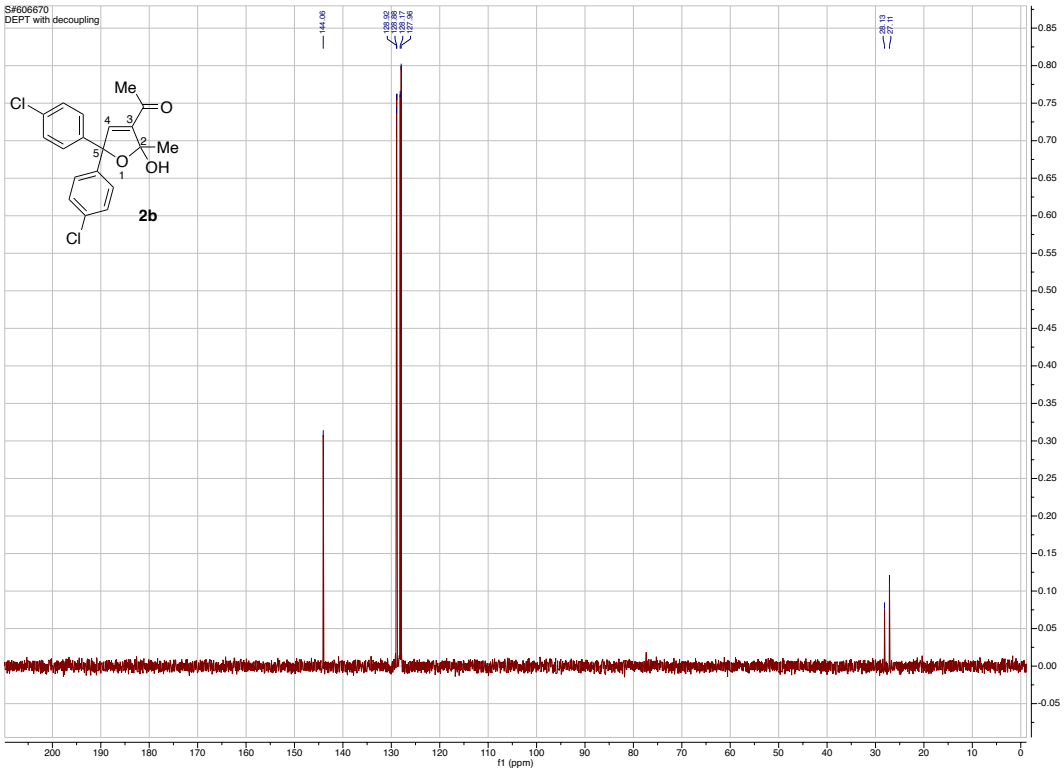

S#682502
single_pulse
Me
O
Me
OH
2a
f1 (ppm)

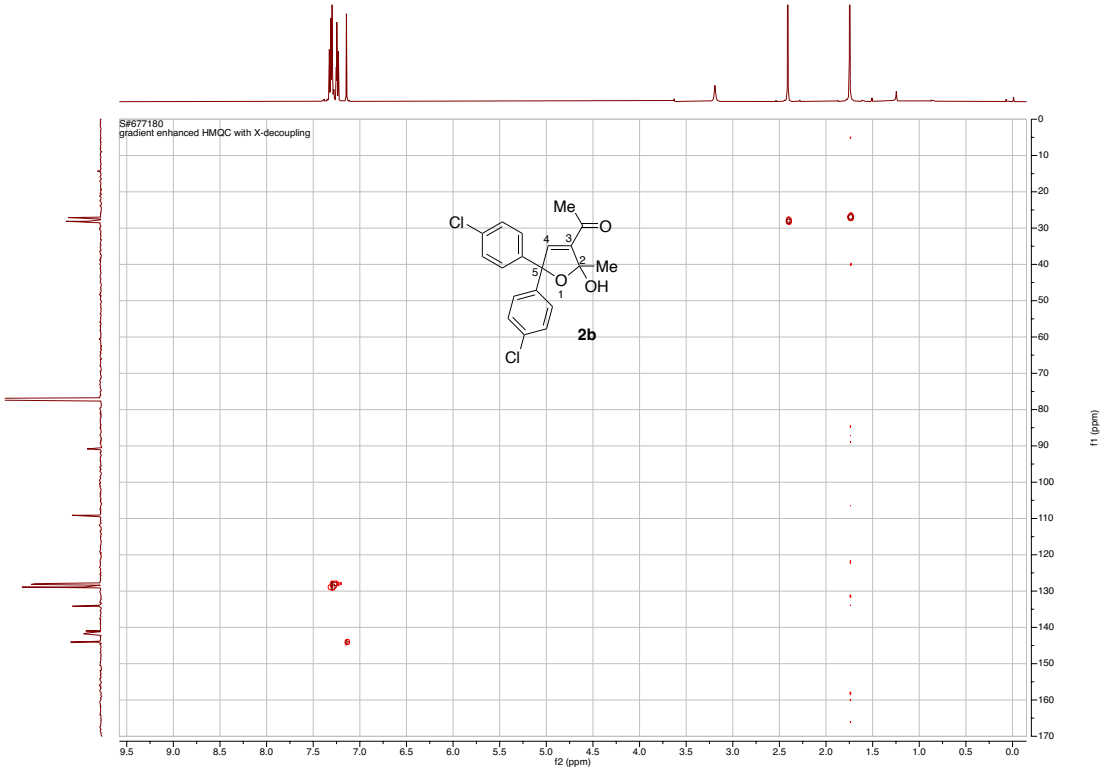

S#683943
single pulse decoupled gated NOE
Me
O
Me
OH
2a
f1 (ppm)

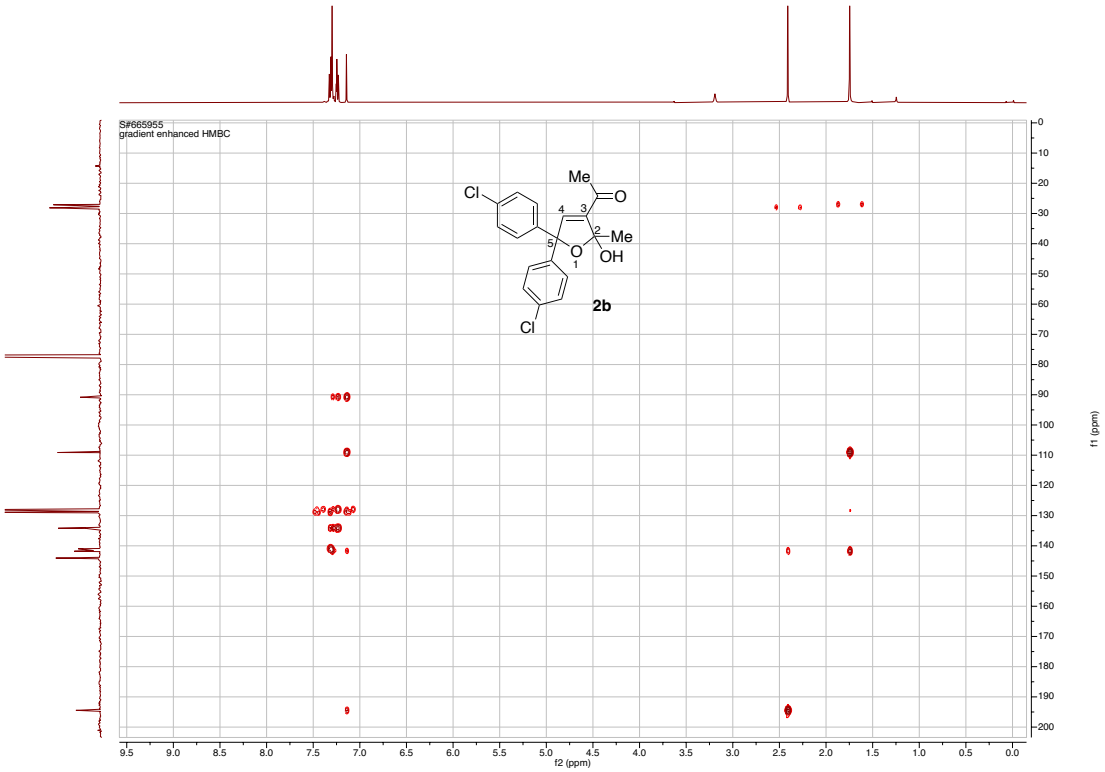

S#687450
DEPT with decoupling
Me
O
4
3
2
Me
5
O
OH
1
2a
145.38
142.34
129.08
128.81
128.70
128.63
128.40
128.07
127.77
127.57
126.71
126.61
77.35 CHLOROFORM-D
26.96
0.25
0.20
0.15
0.10
0.05
0.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

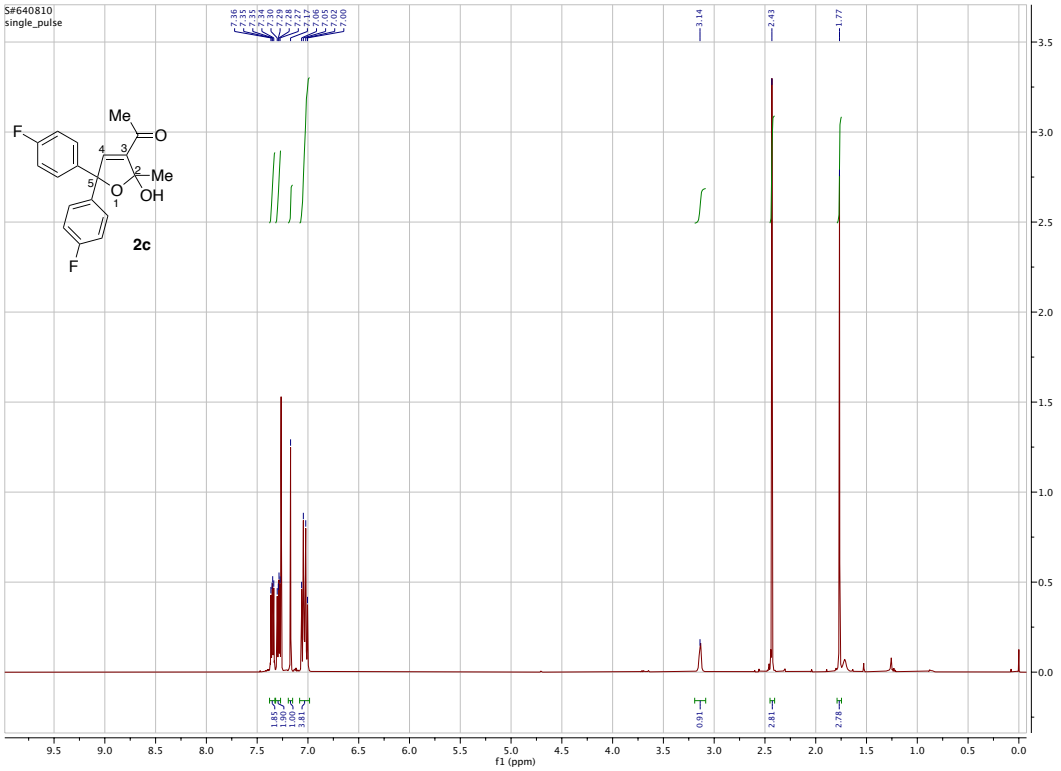

S#662447
single_pulse
Cl
Me
O
4
3
2
Me
5
O
OH
1
2b
Cl
7.34
7.32
7.31
7.29
7.28
7.28
7.26
7.16
3.20
2.42
1.76
0.01
1.00
0.94
2.02
3.22
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

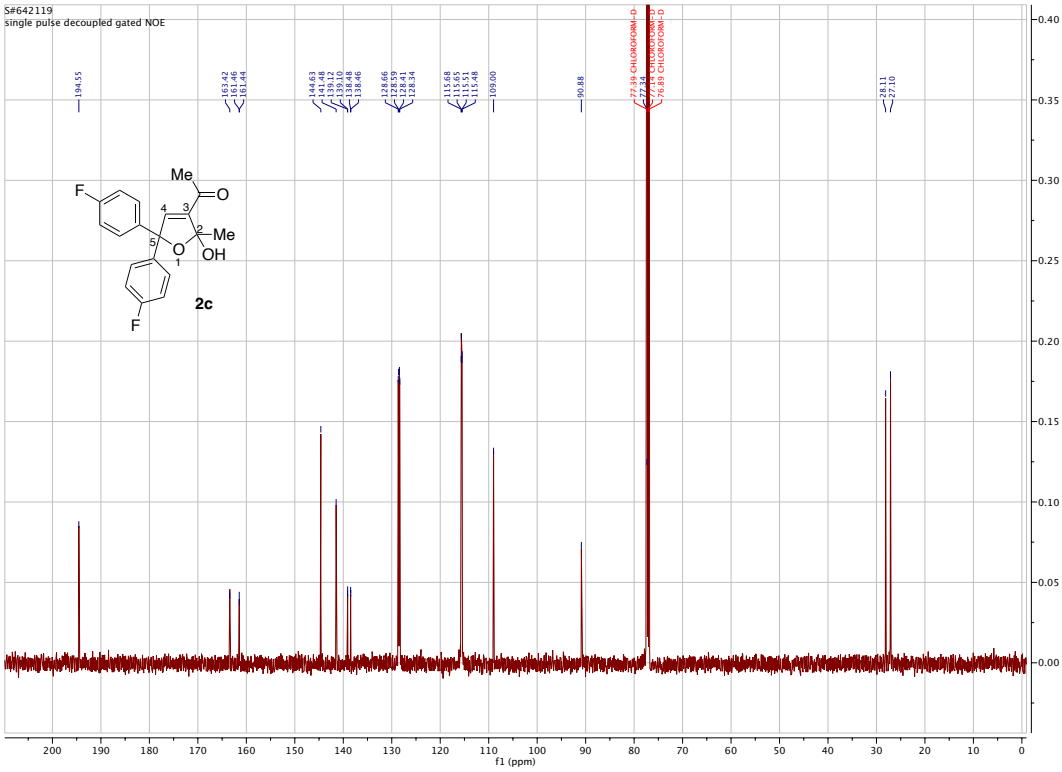

S#604894
single pulse decoupled gated NOE
194.46
144.06
141.59
140.88
134.16
129.92
129.68
129.16
127.96
109.12
90.83
77.40 CHLOROFORM-D
77.16 CHLOROFORM-D
76.89 CHLOROFORM-D
28.13
27.11
Me
O
Cl
4
3
2
Me
5
O
1
OH
Cl
2b
f1 (ppm)

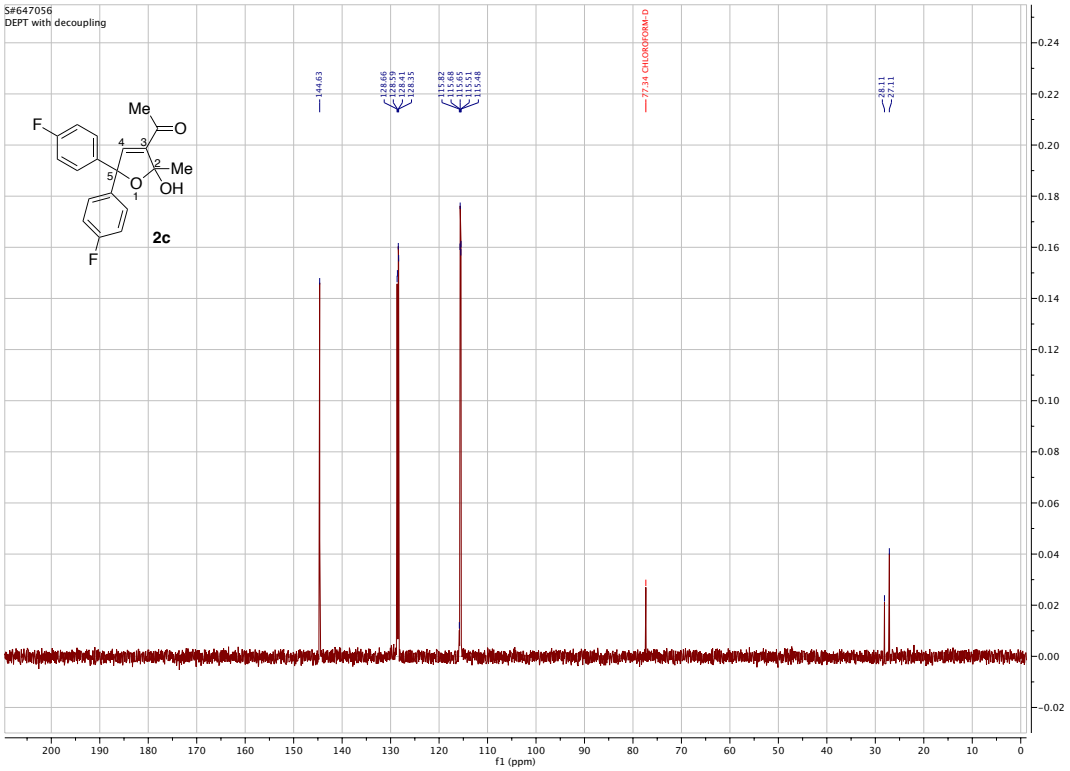

S#606670
DEPT with decoupling
144.06
129.92
129.68
129.17
127.96
28.13
27.11
Me
O
Cl
4
3
2
Me
5
O
1
OH
Cl
2b
f1 (ppm)

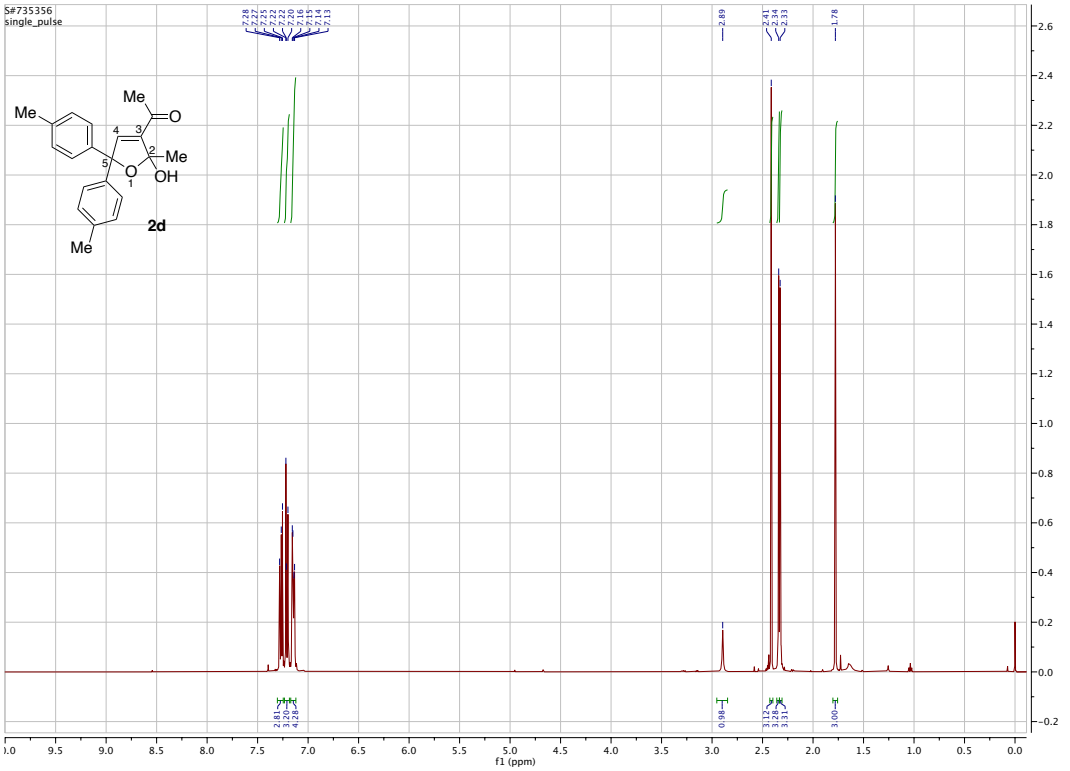

S#677180
gradient enhanced HMQC with X-decoupling
Me
O
Cl
4
3
2
Me
5
O
OH
1
2b
Cl
f2 (ppm)
f1 (ppm)

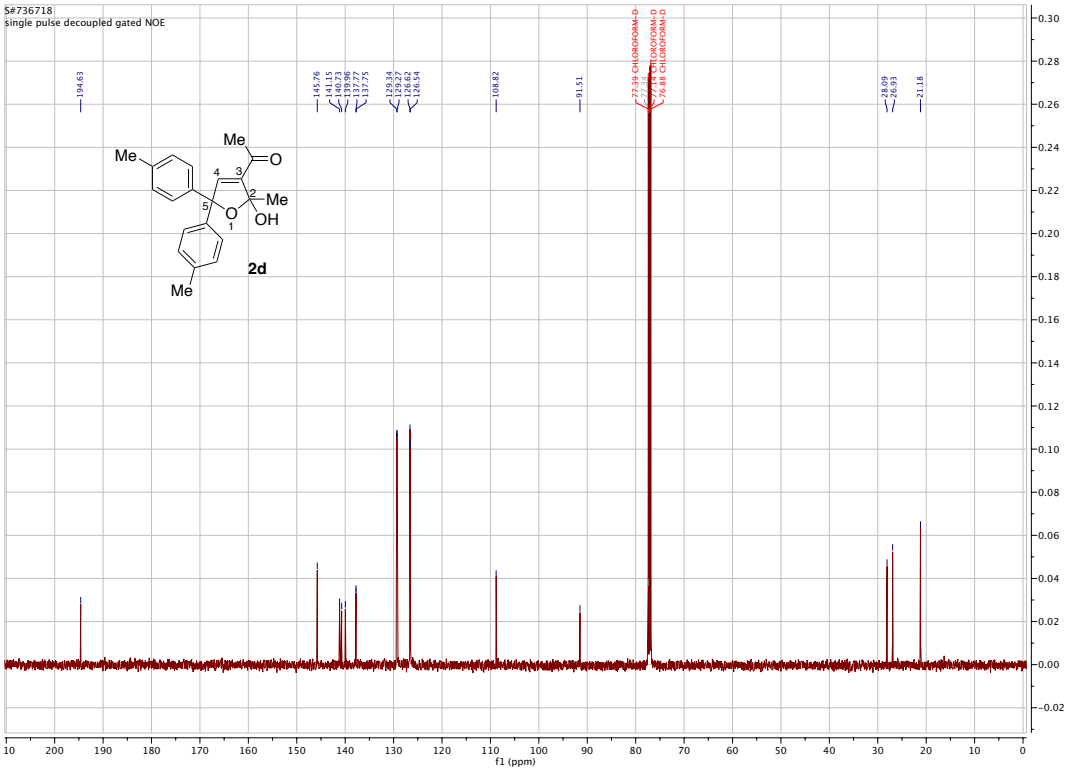

S#665955
gradient enhanced HMBC
Me
O
Cl
4
3
2
Me
5
O
OH
1
2b
Cl
f2 (ppm)
f1 (ppm)

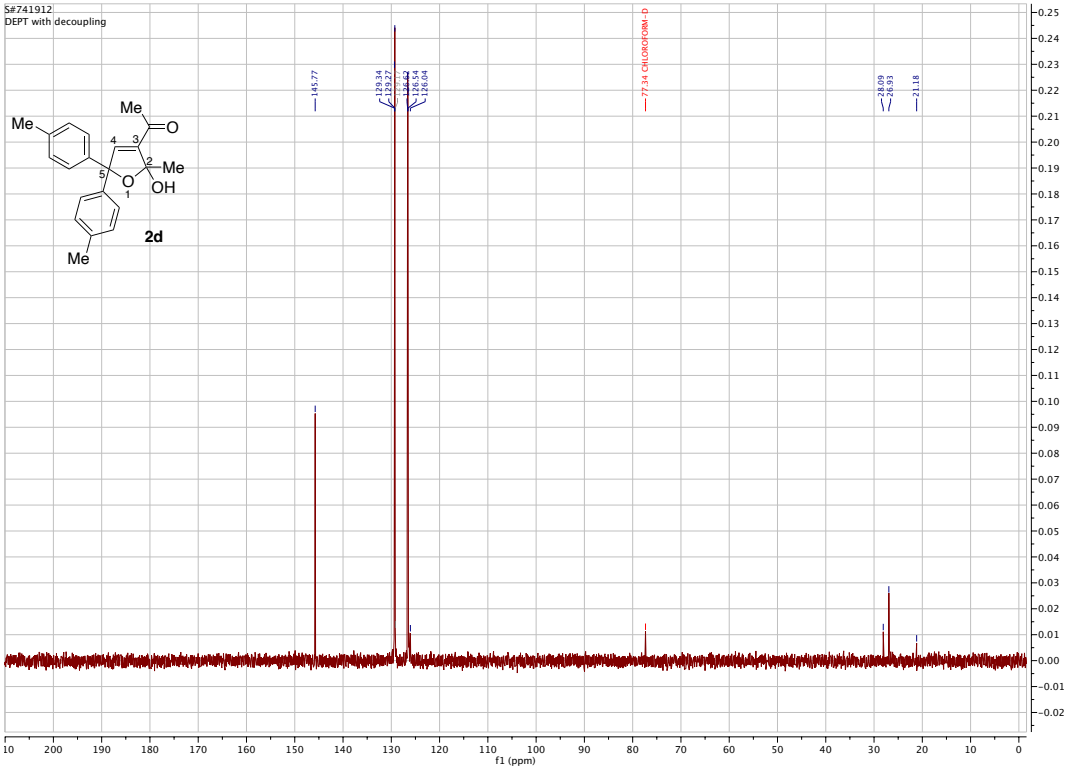

S#640810
single_pulse
Me
O
F
Me
OH
O
2c
F
f1 (ppm)

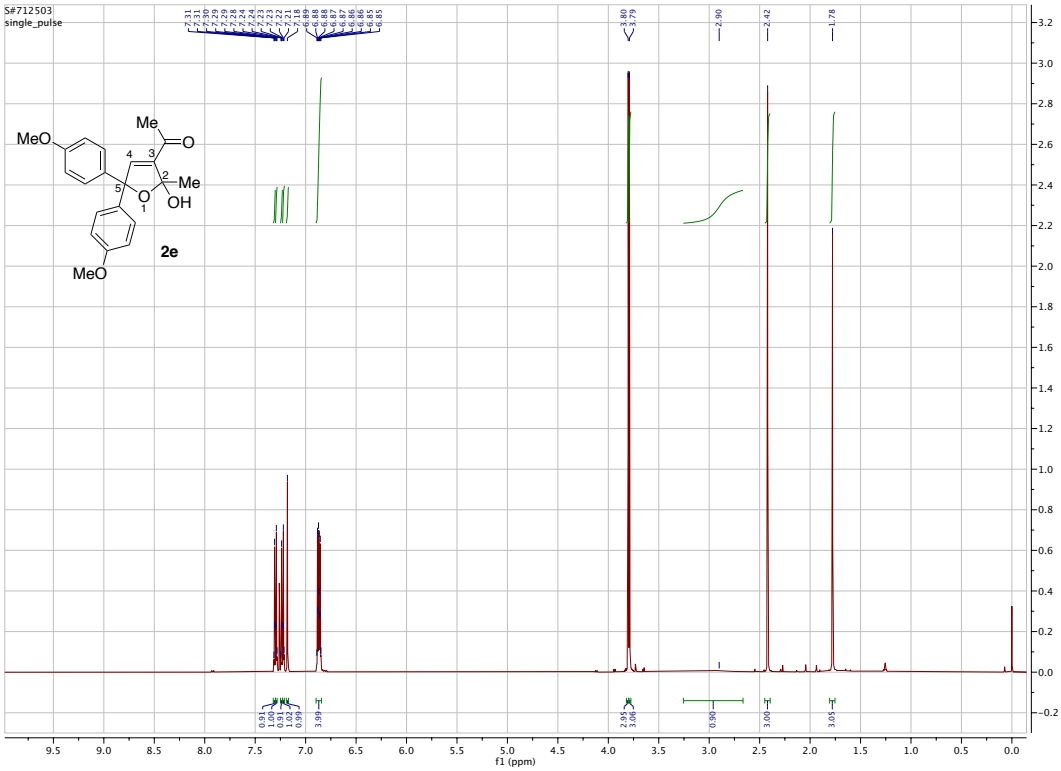

S#642119
single pulse decoupled gated NOE
Me
O
F
Me
OH
O
2c
F
f1 (ppm)

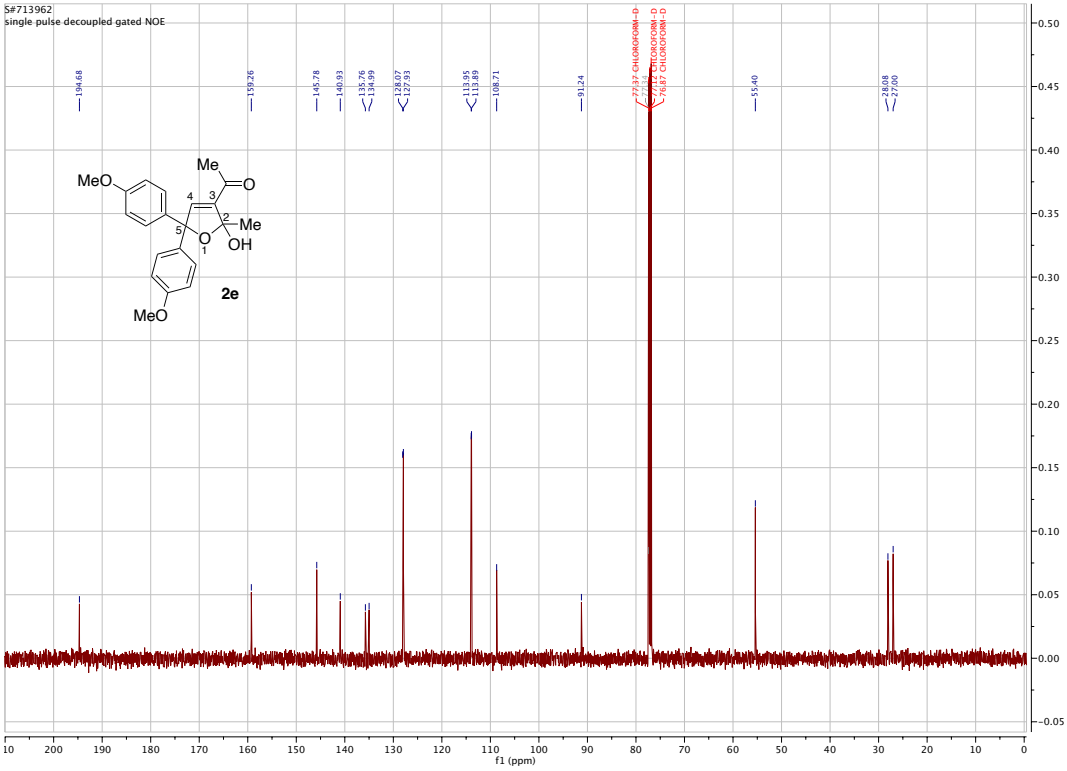

S#647056
DEPT with decoupling
Me
O
F
4
3
2
Me
5
O
OH
1
2c
F
144.63
128.66
128.59
128.41
128.35
115.82
115.68
115.65
115.51
115.48
77.34 CHLOROFORM-D
28.11
27.11
f1 (ppm)

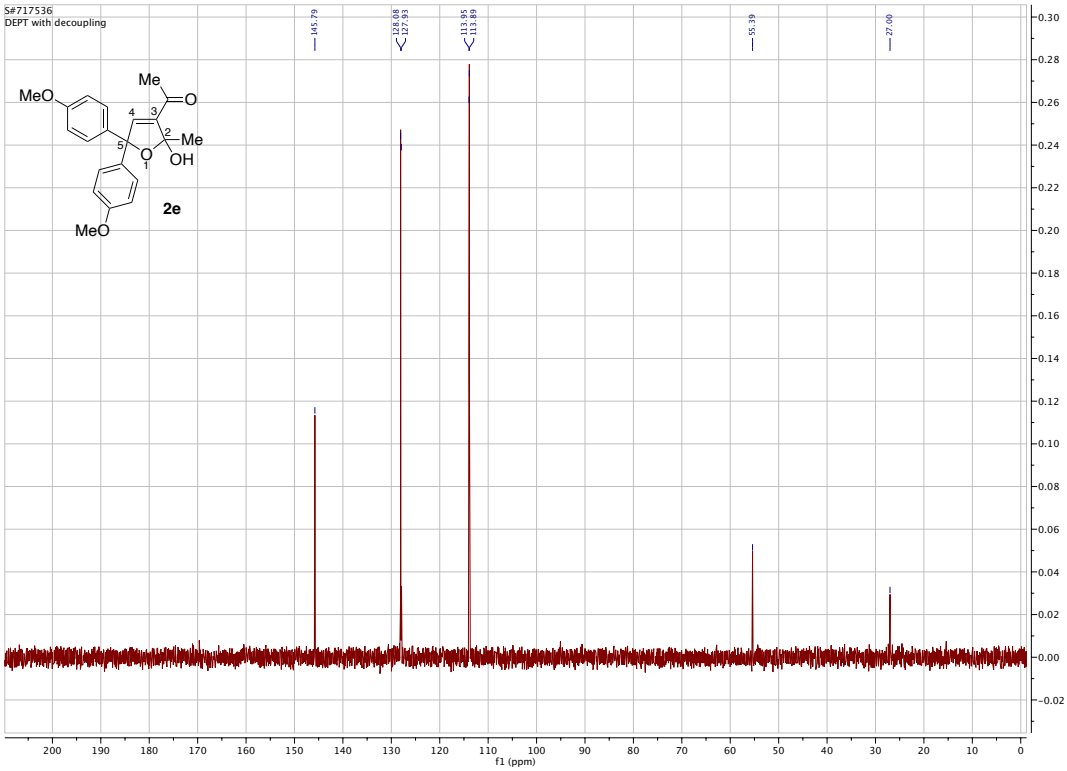

S#735356
single_pulse
Me
Me
O
4
3
2
Me
5
O
OH
1
2d
Me
7.28
7.27
7.25
7.22
7.22
7.20
7.16
7.15
7.14
7.13
2.89
2.41
2.34
2.33
1.78
2.81
2.72
2.72
4.26
0.98
3.12
3.07
3.03
3.01
3.00
f1 (ppm)

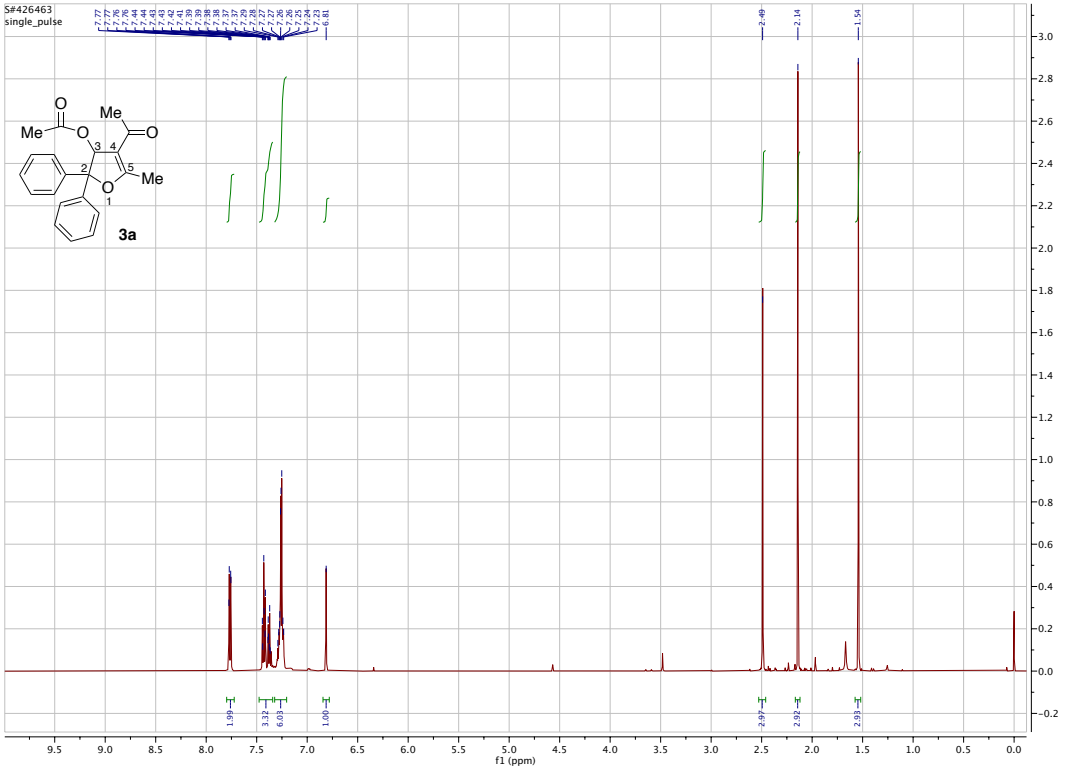

S#736718
single pulse decoupled gated NOE
194.63
145.76
141.15
140.73
139.96
137.77
137.75
129.34
129.27
126.62
126.54
108.82
91.51
77.39 CHLOROFORM-D
77.18 CHLOROFORM-D
76.98 CHLOROFORM-D
28.09
26.93
21.18
Me
Me
O
4
3
5
O
1
2
Me
OH
Me
2d
f1 (ppm)

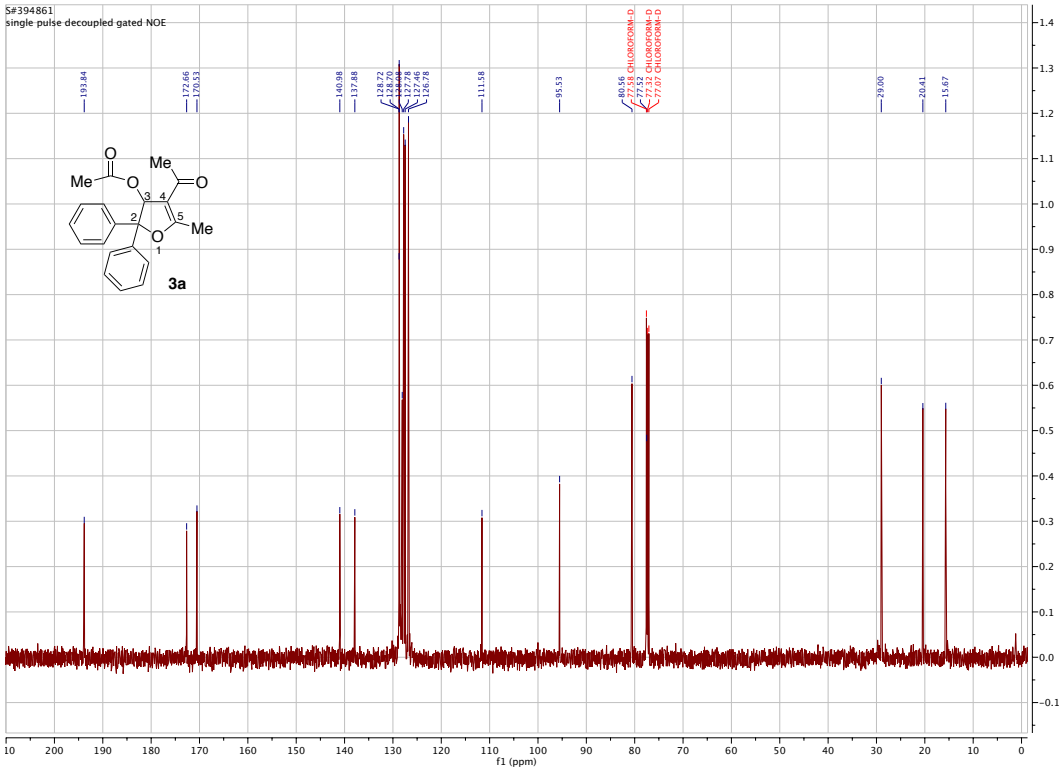

S#741912
DEPT with decoupling
145.77
129.34
129.27
126.62
126.54
126.04
77.34 CHLOROFORM-D
28.09
26.93
21.18
Me
Me
O
4
3
5
O
1
2
Me
OH
Me
2d
f1 (ppm)

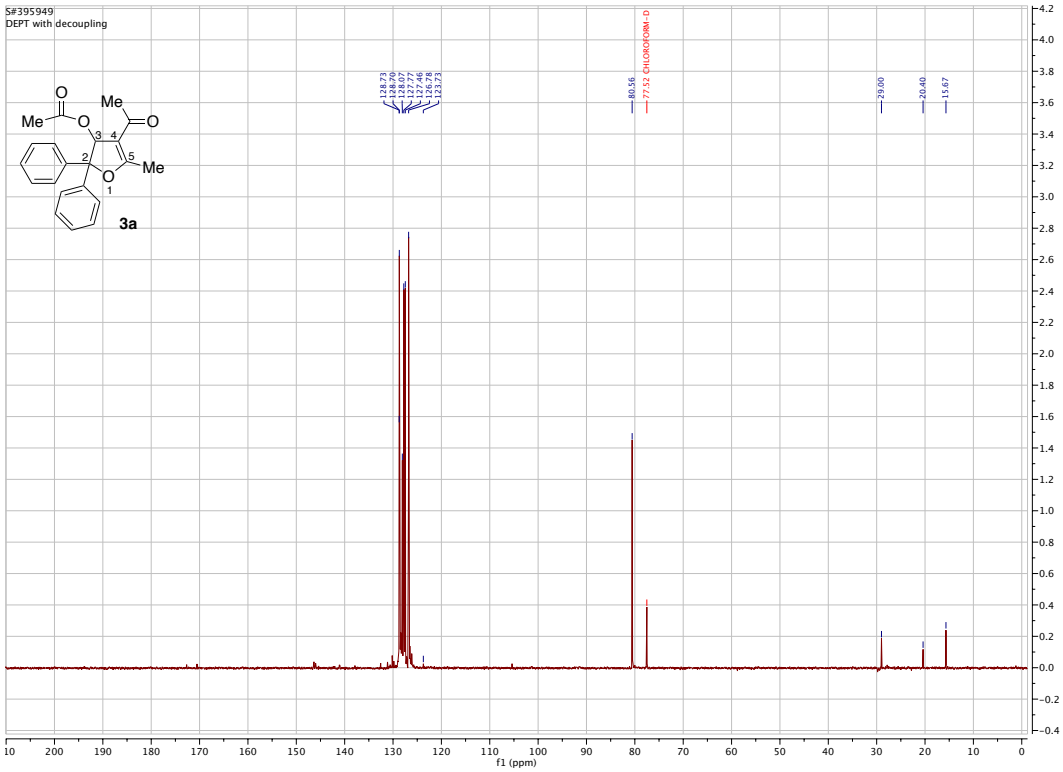

S#712503
single_pulse
MeO
Me
O
Me
OH
MeO
2e
f1 (ppm)

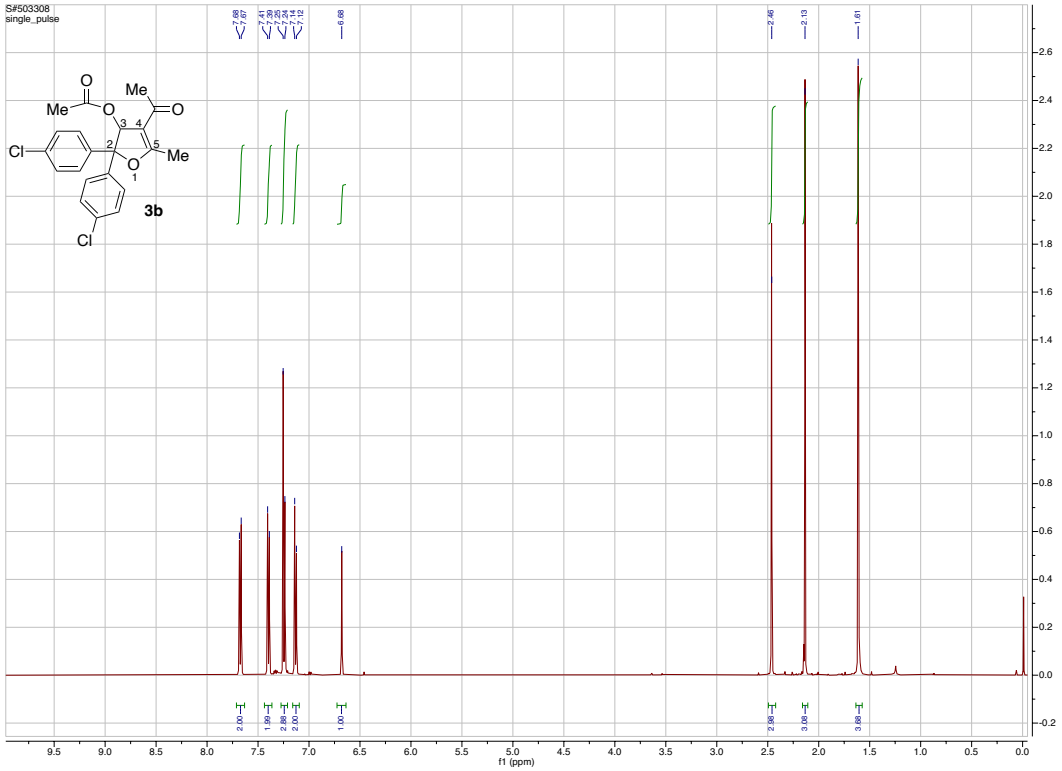

S#713962
single pulse decoupled gated NOE
MeO
Me
O
Me
OH
MeO
2e
f1 (ppm)

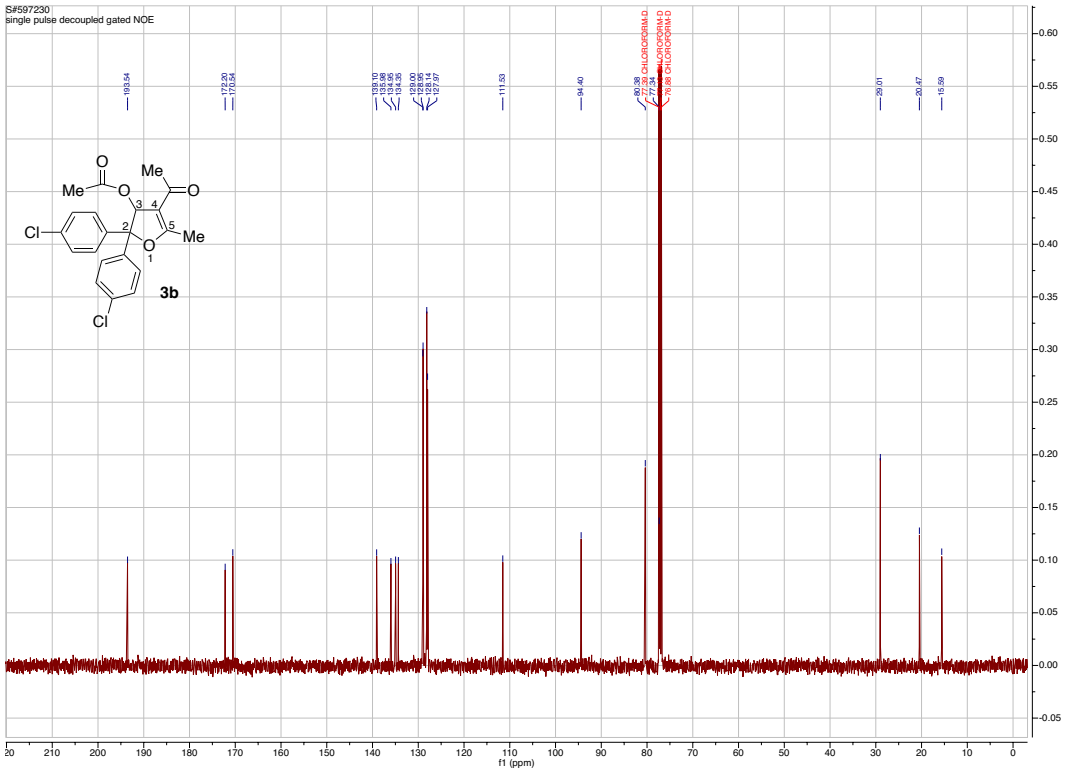

S#717536
DEPT with decoupling
MeO
Me
O
Me
OH
MeO
2e
145.79
128.68
127.93
113.95
113.89
55.39
27.00
f1 (ppm)

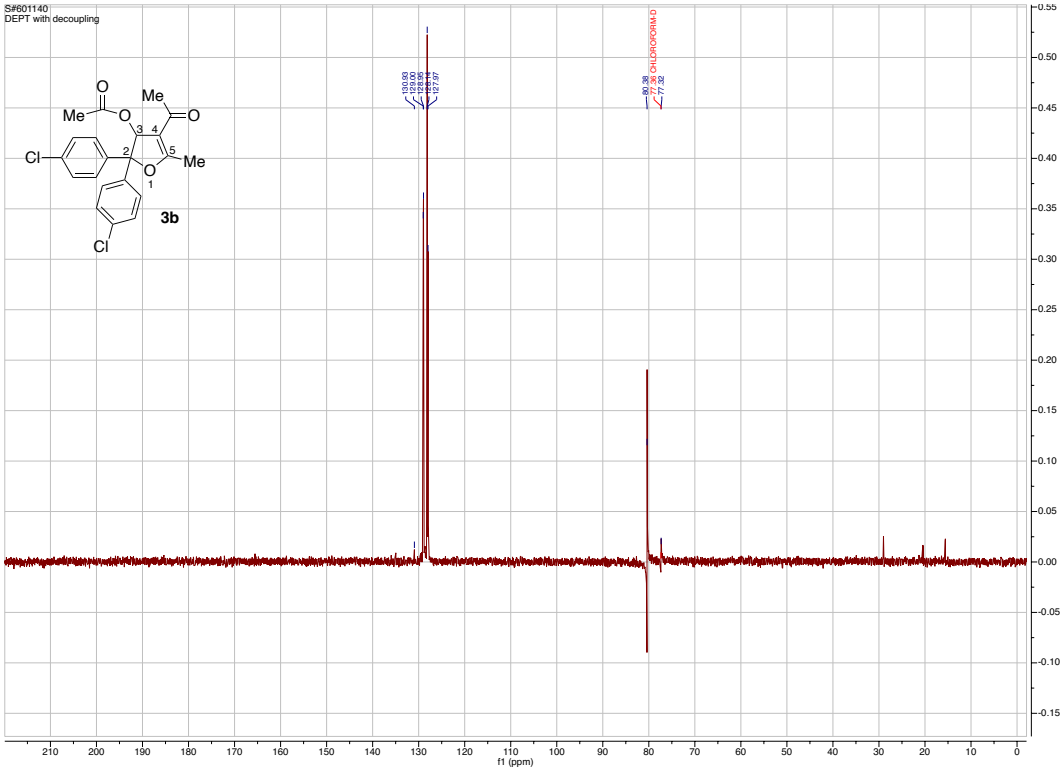

S#426463
single_pulse
Me
O
Me
O
Me
3a
2.49
2.14
1.94
1.99
3.32
6.03
1.00
2.93
2.93
2.93
f1 (ppm)

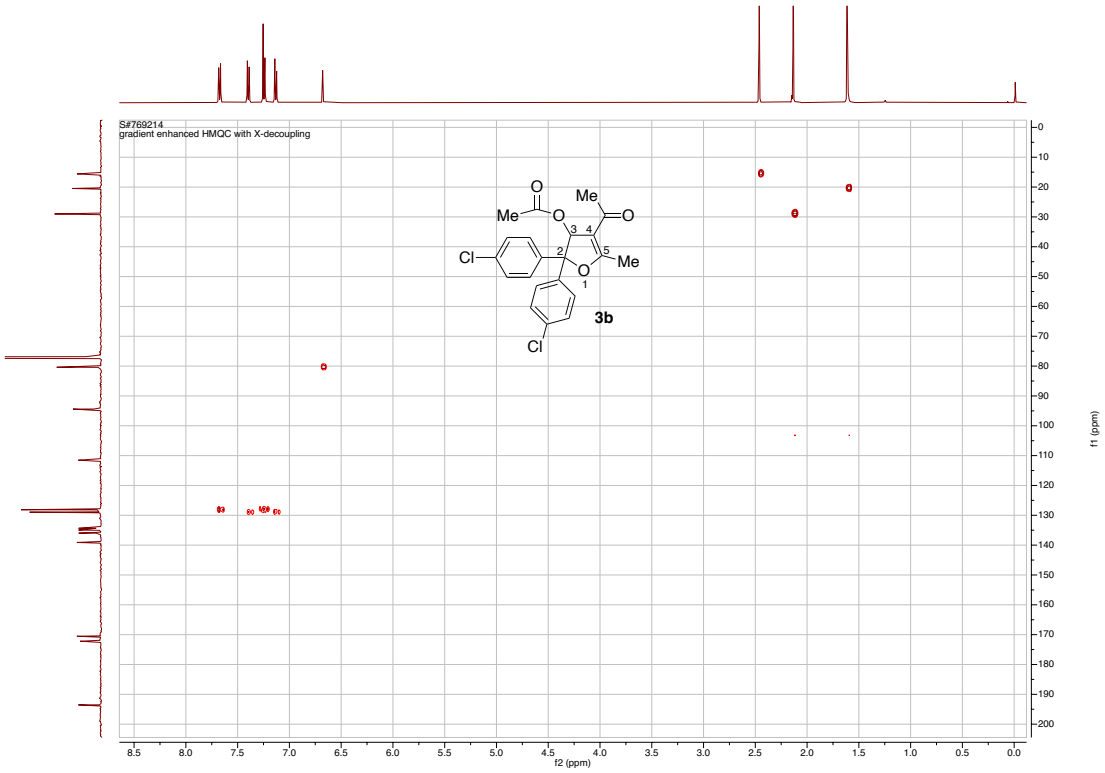

S#394861
single pulse decoupled gated NOE
193.84
172.66
170.53
140.98
137.88
128.72
128.70
128.04
127.78
127.46
126.78
111.58
95.53
80.56
77.58 CHLOROFORM-D
77.32
77.07 CHLOROFORM-D
29.00
20.41
15.67
Me
O
Me
O
3
4
2
5
Me
O
1
3a
f1 (ppm)

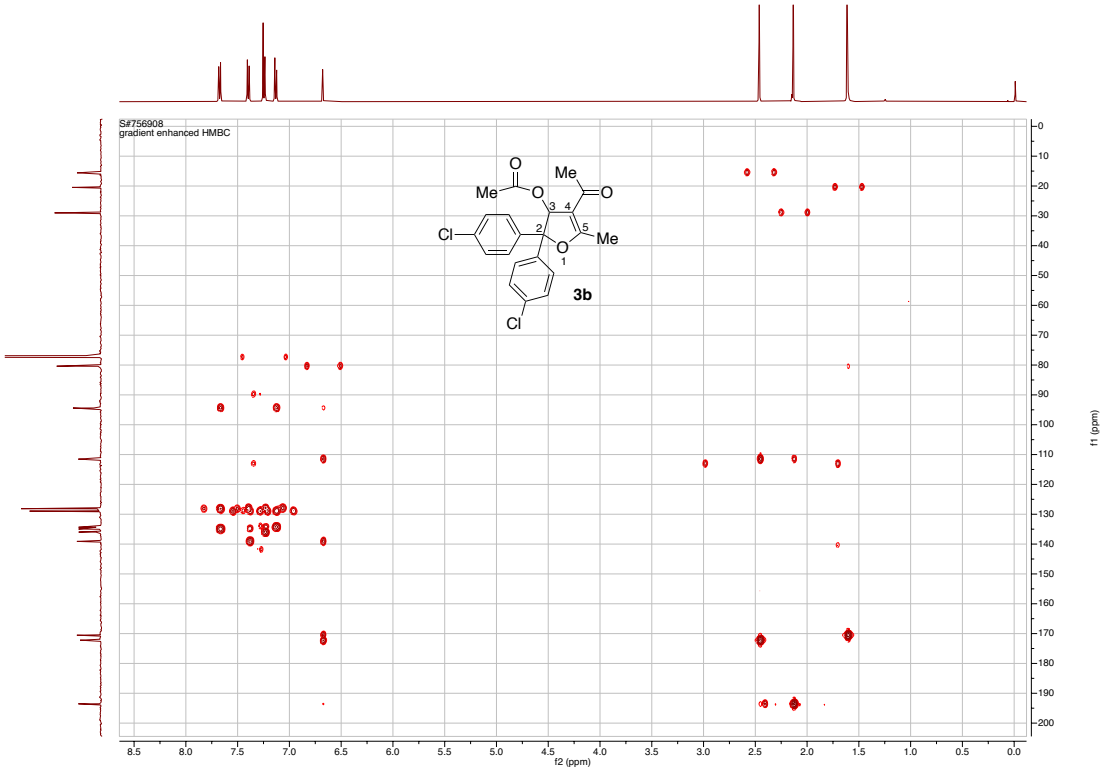

S#395949
DEPT with decoupling
128.73
128.70
128.07
127.77
127.46
126.78
123.73
80.56
77.52 CHLOROFORM-D
29.00
20.40
15.67
Me
O
Me
O
3
4
2
5
Me
O
1
3a
f1 (ppm)

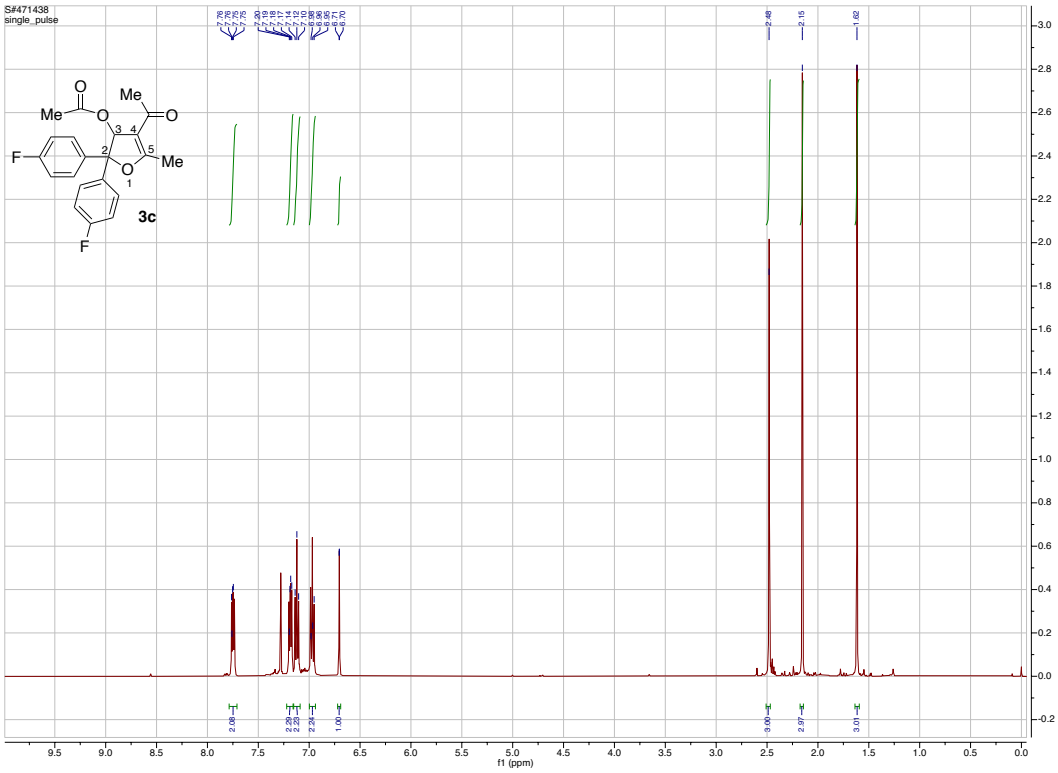

S#503308
single_pulse
3b
f1 (ppm)

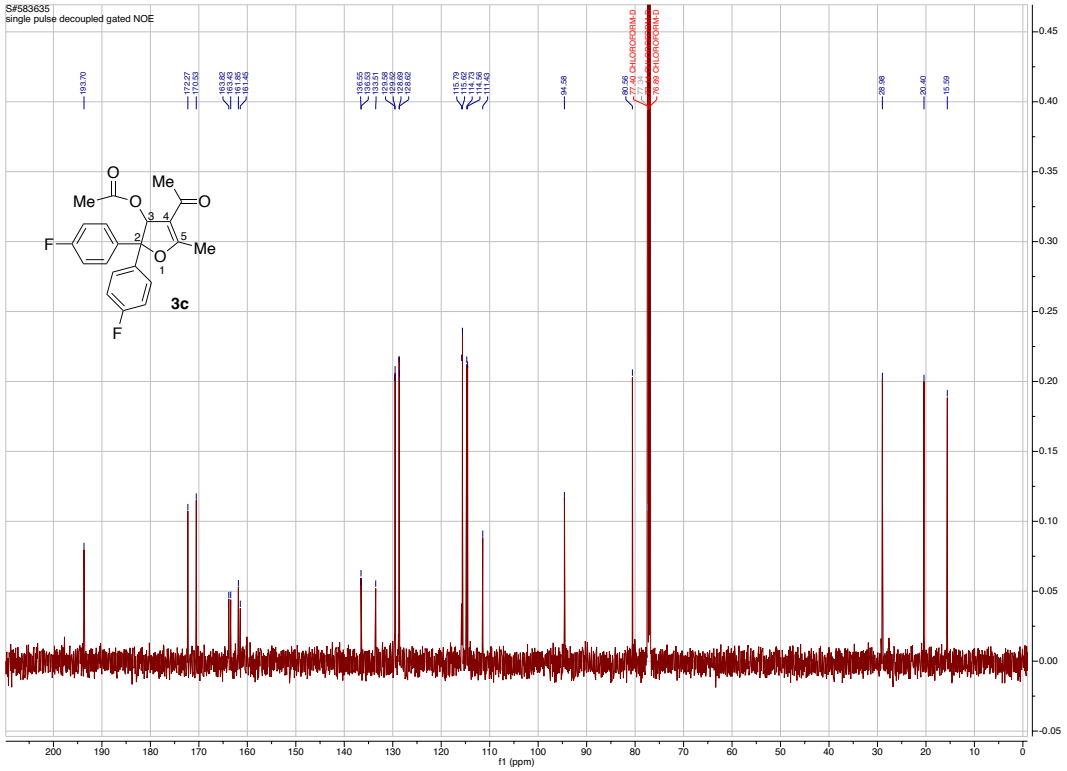

S#597230
single pulse decoupled gated NOE
3b
f1 (ppm)

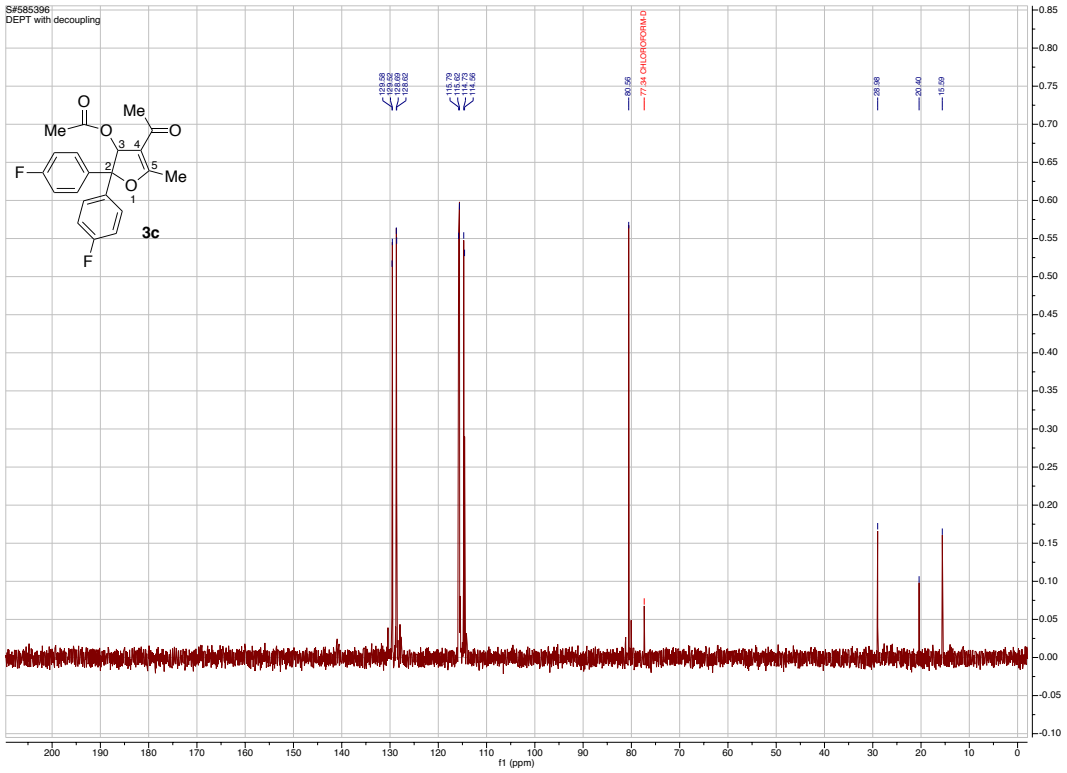

S#601140
DEPT with decoupling
3b
f1 (ppm)

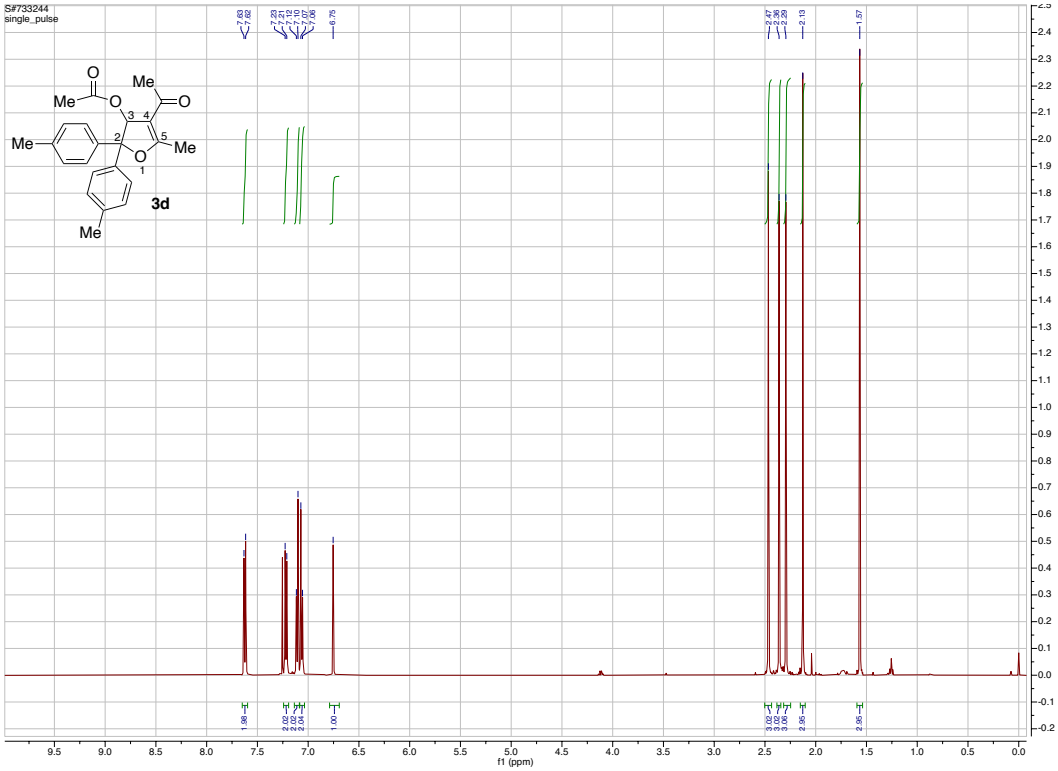

S#769214
gradient enhanced HMQC with X-decoupling
3b
f2 (ppm)
f1 (ppm)

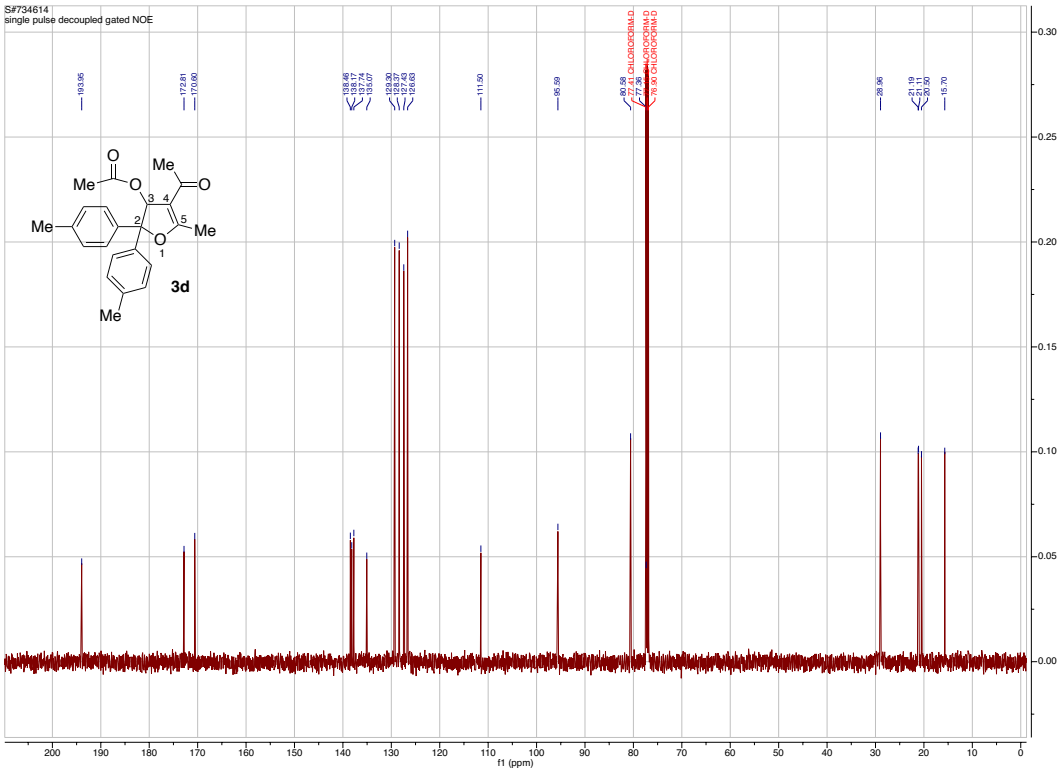

S#756908
gradient enhanced HMBC
3b
f2 (ppm)
f1 (ppm)

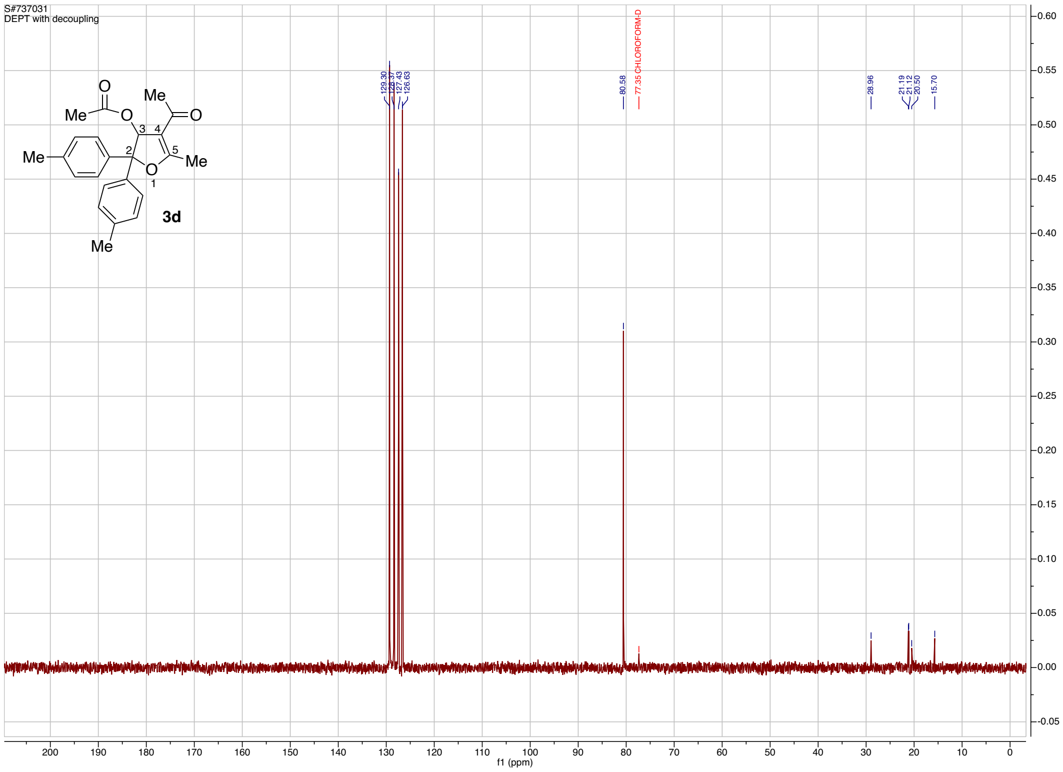

S#471438
single_pulse
3c
f1 (ppm)

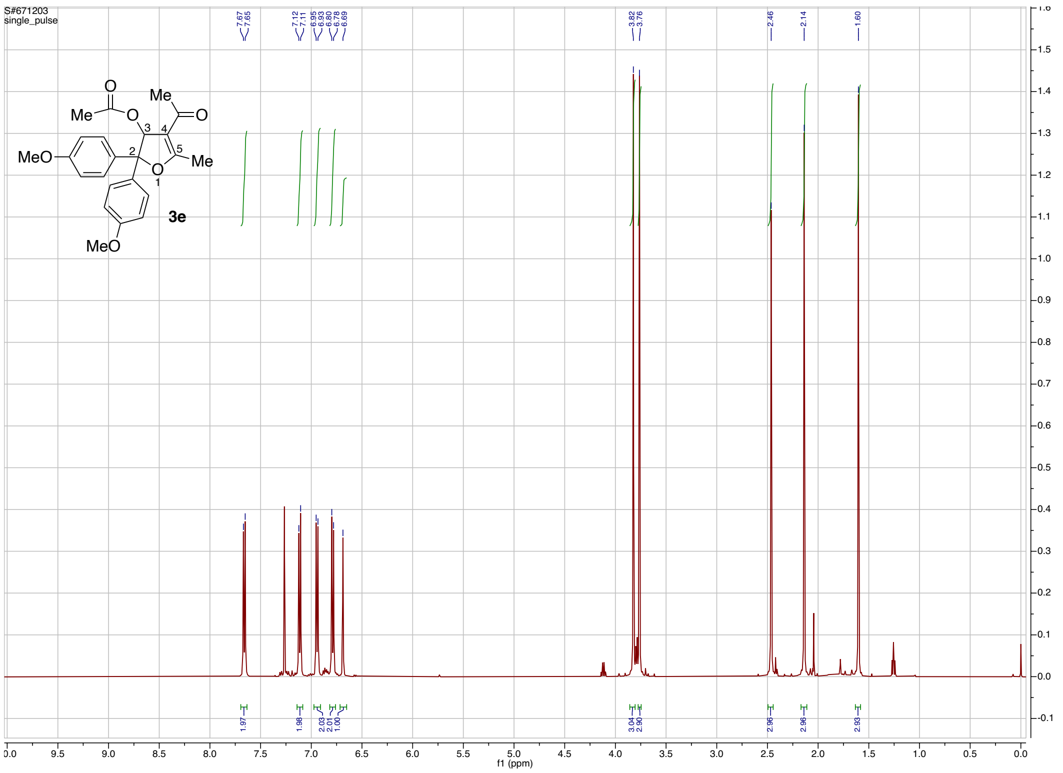

S#583635
single pulse decoupled gated NOE
193.70
172.27
170.53
163.82
161.95
161.45
136.55
133.91
129.69
129.62
128.62
115.79
115.62
114.73
114.56
111.43
94.58
80.96
77.34 CHLOROFORM-D
78.89 CHLOROFORM-D
28.98
20.40
15.69
3c
f1 (ppm)

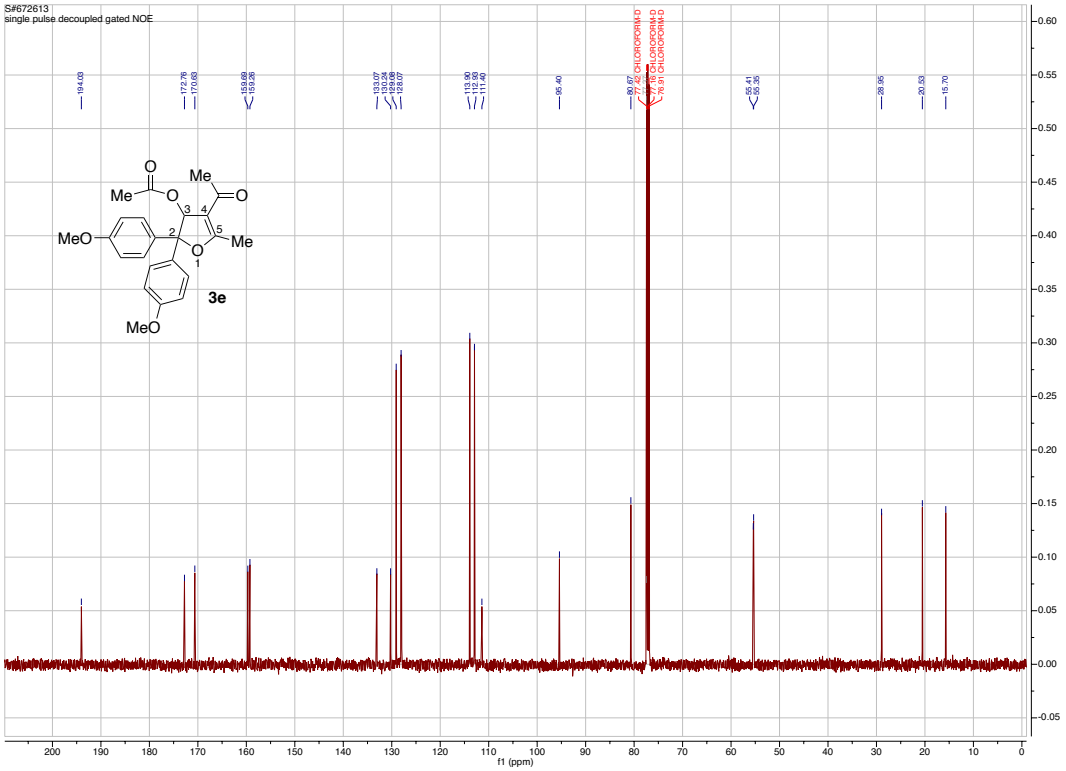

S#585396
DEPT with decoupling
129.58
129.62
129.69
128.62
115.79
115.62
114.73
114.56
80.96
77.34 CHLOROFORM-D
28.98
20.40
15.69
3c
f1 (ppm)

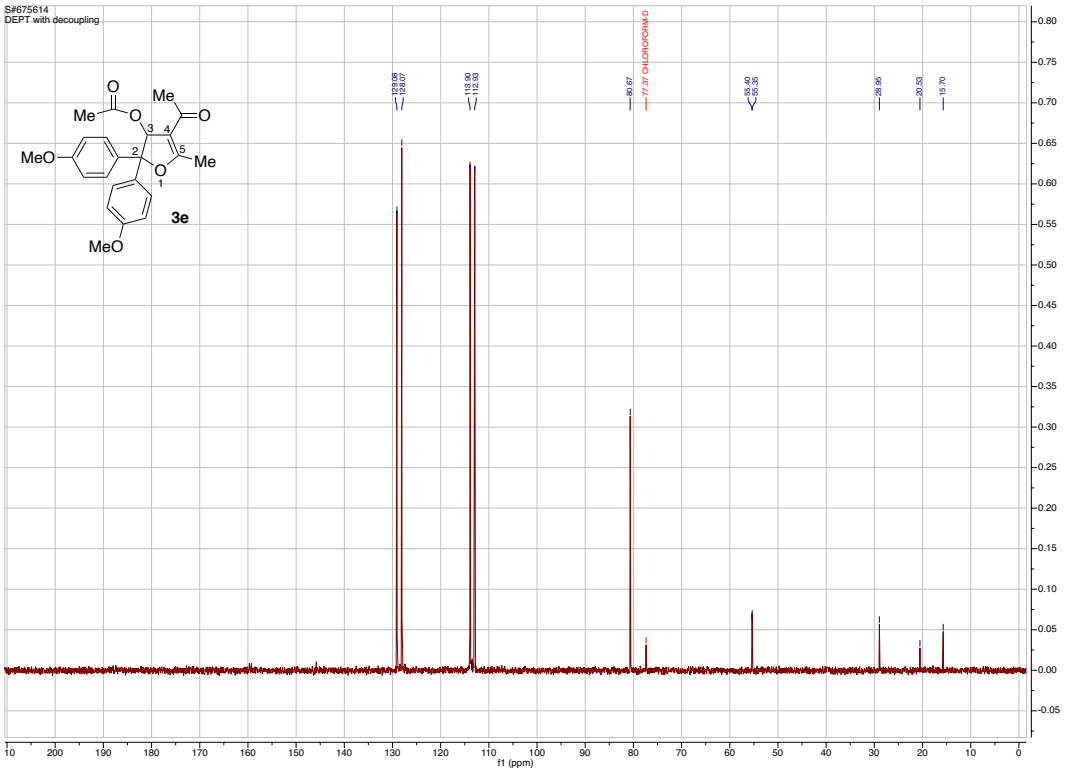

S#733244
single_pulse
3d
f1 (ppm)


S#734614
single pulse decoupled gated NOE
3d
f1 (ppm)

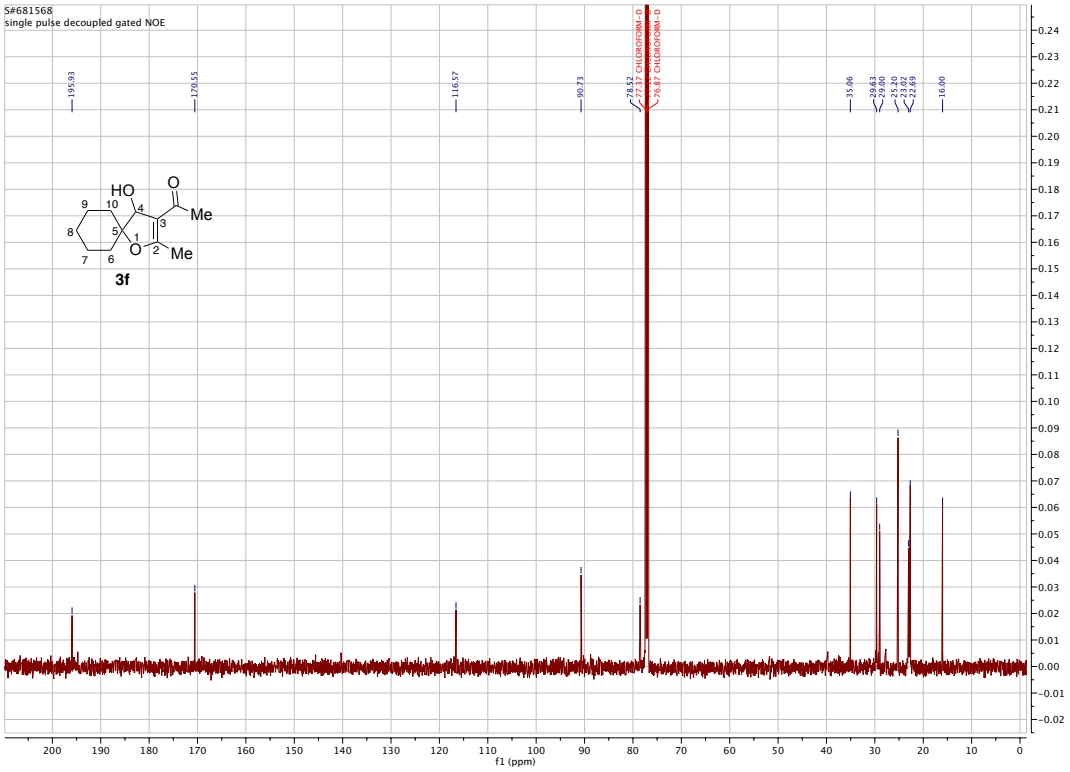

S#737031
DEPT with decoupling
129.30
128.37
127.43
126.63
80.58
77.35 CHLOROFORM-D
28.96
21.19
21.12
20.50
15.70
3d
f1 (ppm)

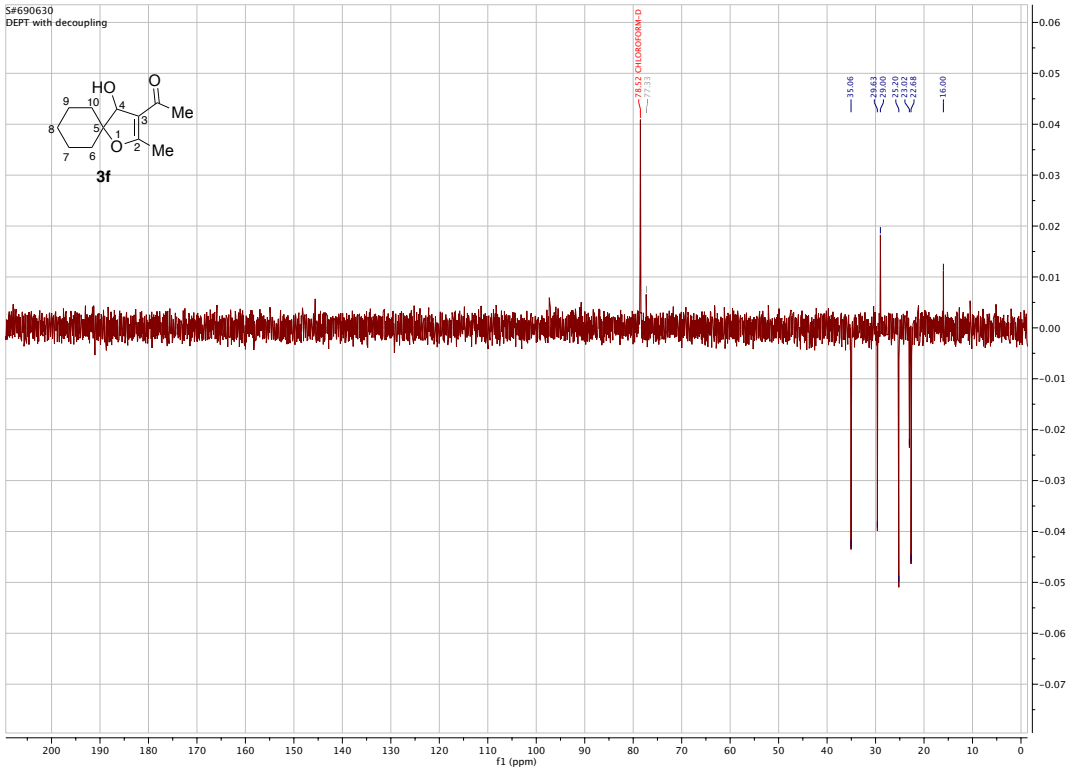

S#671203
single_pulse
7.67
7.65
7.12
7.11
6.95
6.93
6.80
6.78
6.69
3.82
3.76
2.46
2.14
1.60
3e
1.97
1.98
2.03
2.01
1.00
3.04
2.90
2.96
2.96
2.93
f1 (ppm)

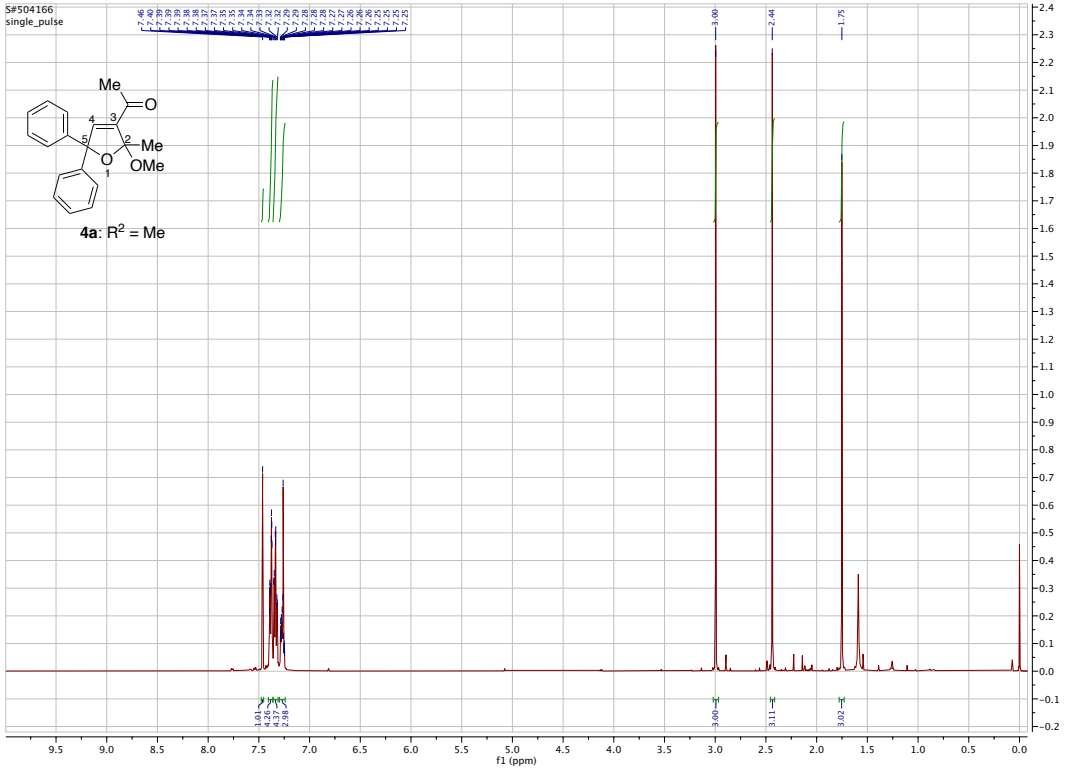

S#672613
single pulse decoupled gated NOE
194.03
172.76
170.68
159.69
159.36
133.07
130.34
129.08
128.07
113.90
112.93
111.40
86.40
80.67
77.42 CHLOROFORM-D
77.16 CHLOROFORM-D
76.91 CHLOROFORM-D
55.41
55.35
28.95
20.53
15.70
3e
f1 (ppm)

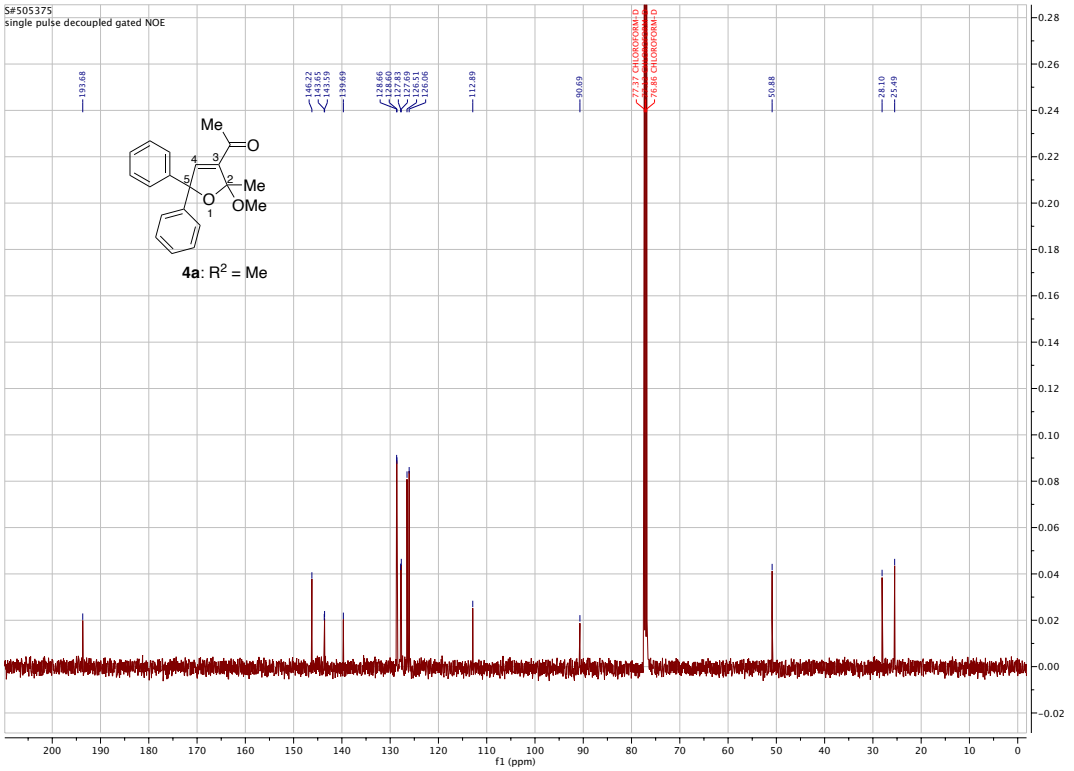

S#675614
DEPT with decoupling
129.08
128.07
113.90
112.93
80.67
77.37 CHLOROFORM-D
55.40
55.35
28.95
20.53
15.70
3e
f1 (ppm)

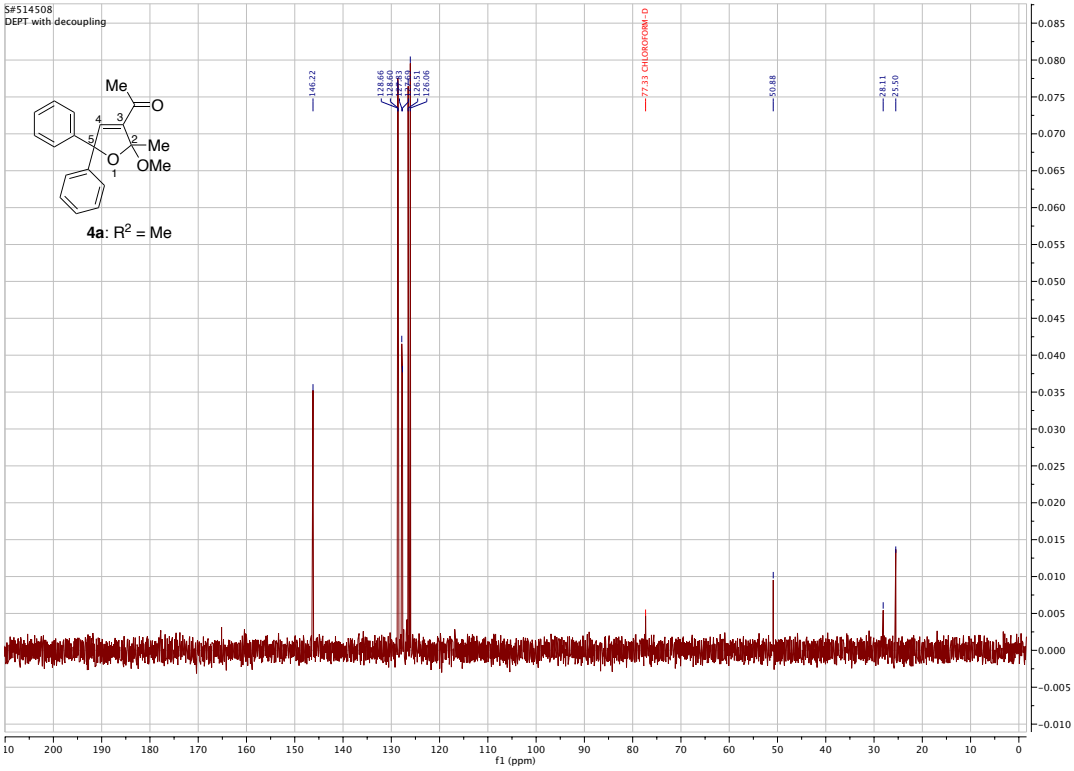

S#680246
single_pulse
HO
O
Me
Me
3f
f1 (ppm)

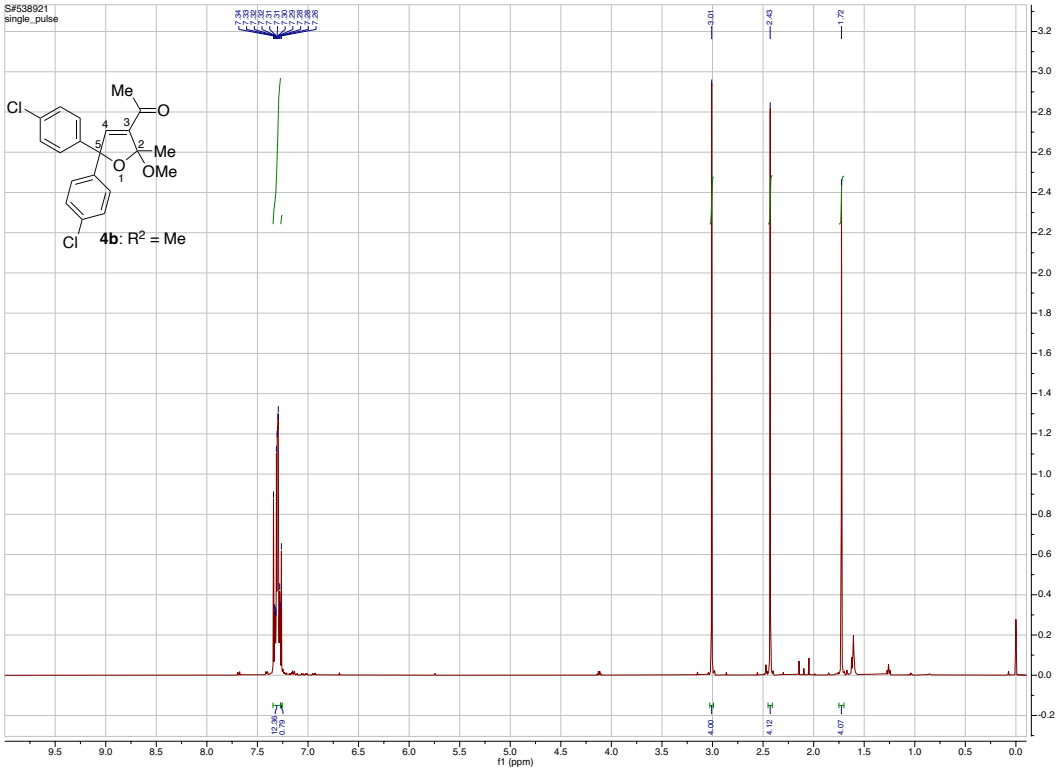

S#681568
single pulse decoupled gated NOE
195.93
170.55
116.57
90.73
78.32
77.37 CHLOROFORM-D
76.87 CHLOROFORM-D
35.06
29.63
29.00
25.20
23.30
22.49
16.60
HO
O
Me
Me
3f
f1 (ppm)

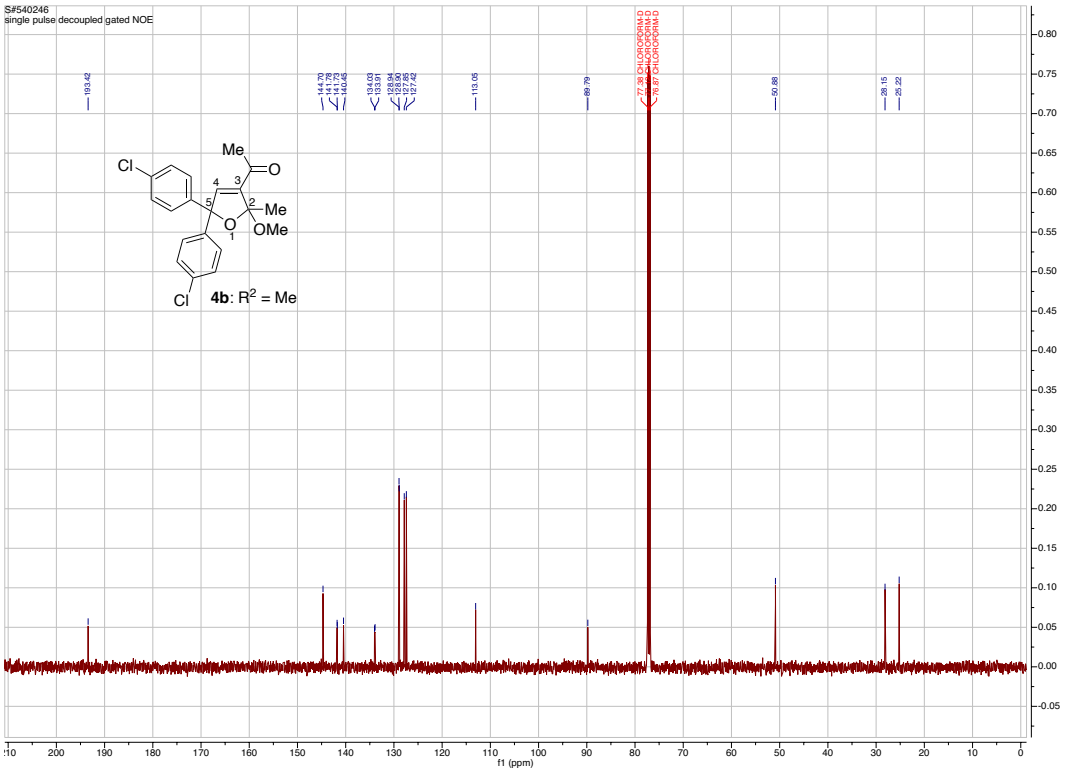

S#690630
DEPT with decoupling
HO
O
Me
Me
3f
f1 (ppm)

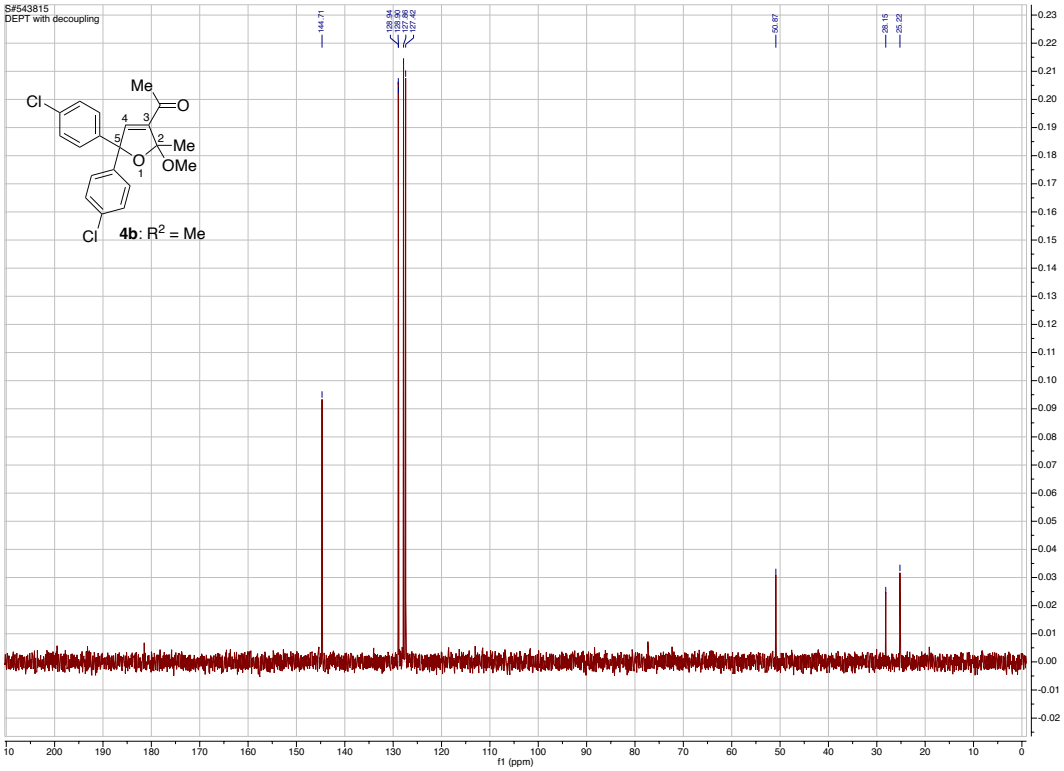

S#504166
single_pulse
Me
O
Me
OMe
4a: R2 = Me
f1 (ppm)

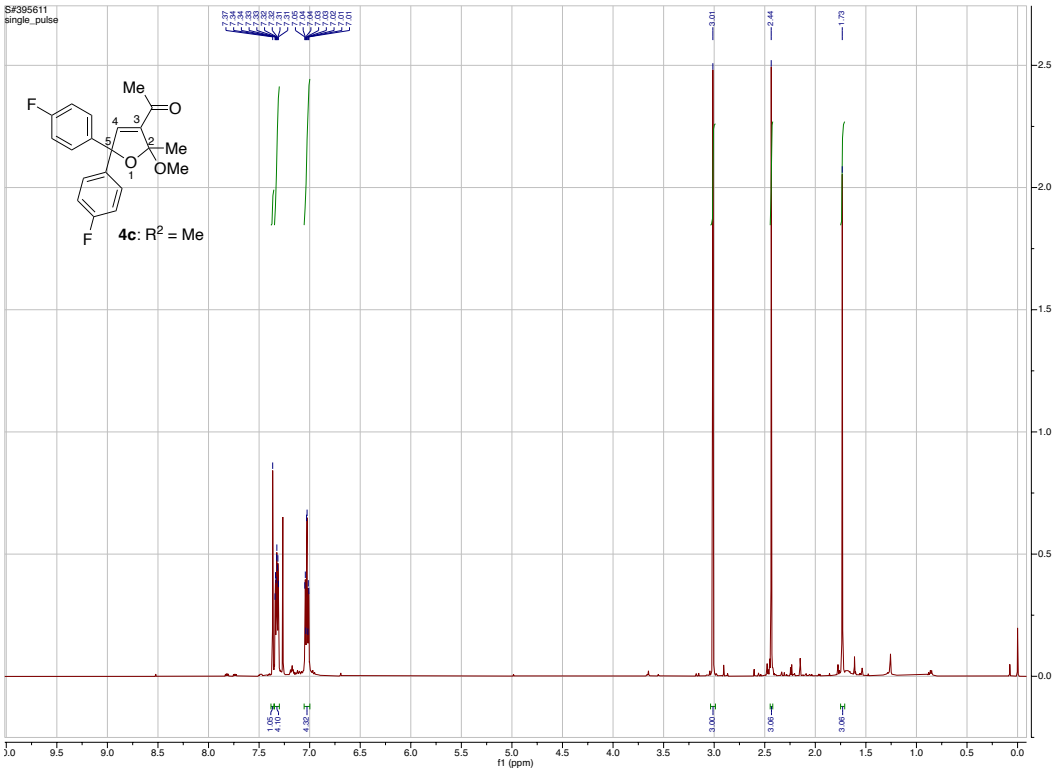

S#505375
single pulse decoupled gated NOE
193.68
146.22
143.65
143.59
139.69
128.66
128.60
128.23
127.69
126.51
126.06
112.89
90.69
77.37 CHLOROFORM-D
76.86 CHLOROFORM-D
50.88
28.10
25.49
Me
O
Me
OMe
4a: R2 = Me
f1 (ppm)

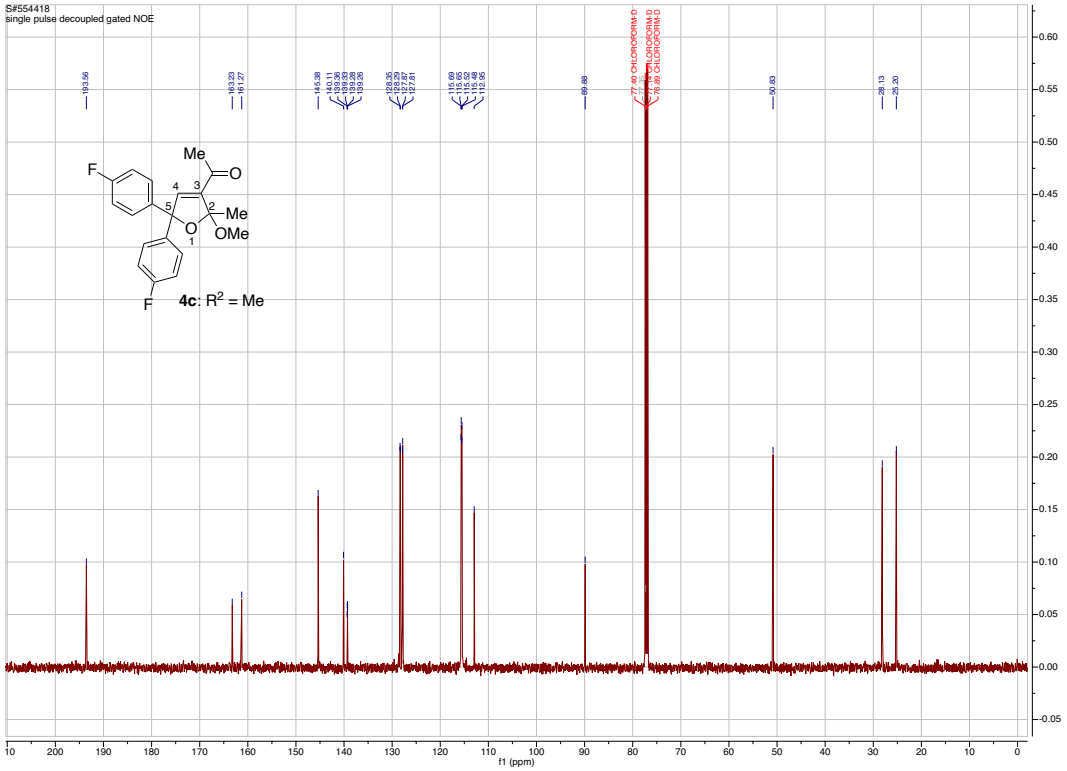

S#514508
DEPT with decoupling
146.22
128.66
128.60
128.23
127.69
126.51
126.06
77.33 CHLOROFORM-D
50.88
28.11
25.50
Me
O
Me
OMe
4a: R2 = Me
f1 (ppm)

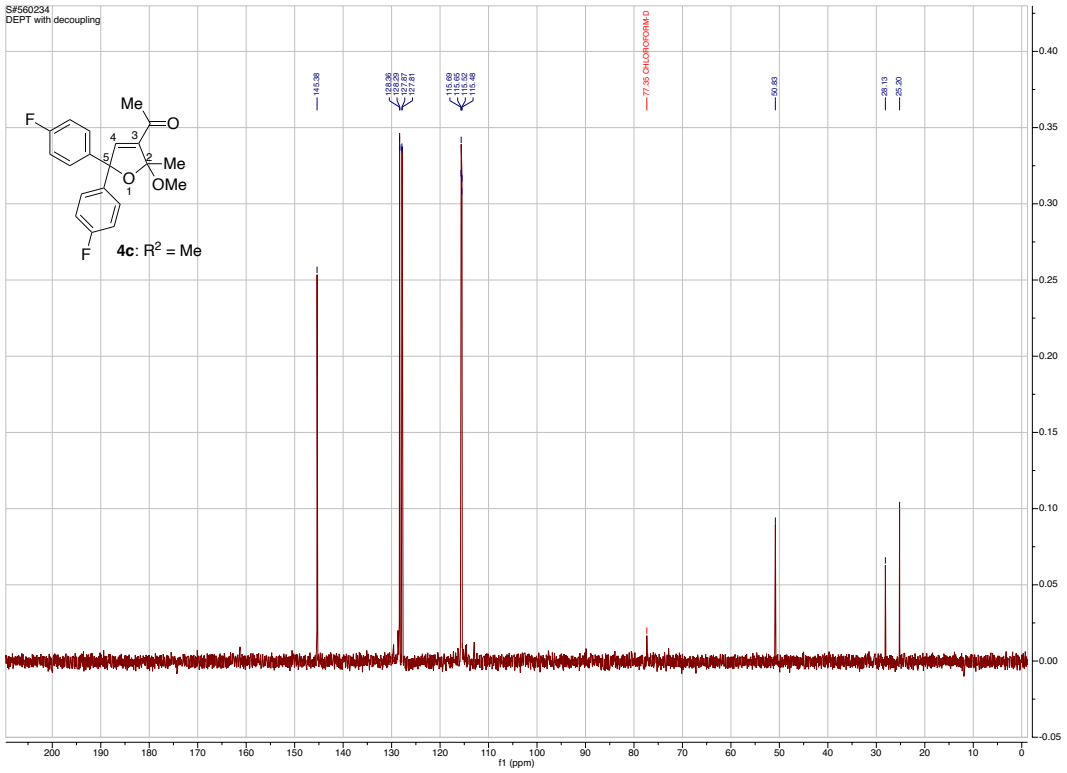

S#538921
single_pulse
Me
O
Cl
4
3
5
2
Me
O
1
OMe
Cl
4b: R2 = Me
f1 (ppm)

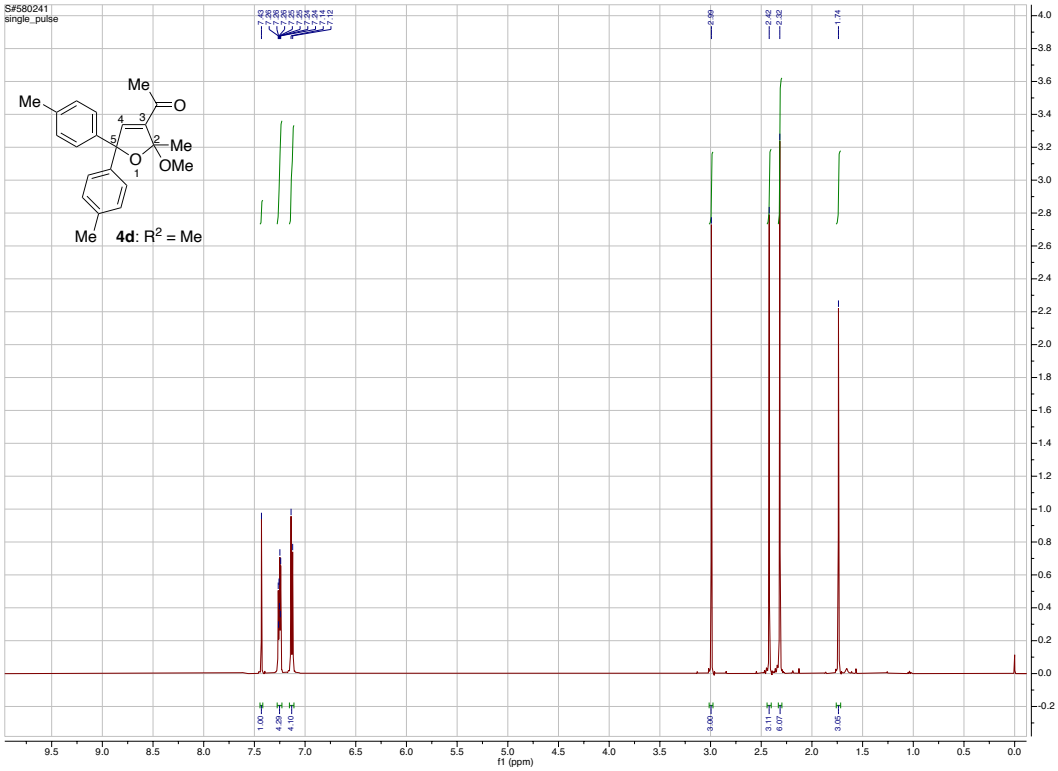

S#540246
single pulse decoupled gated NOE
193.42
144.70
141.78
141.73
140.45
134.03
133.91
128.84
128.60
127.93
127.42
113.05
89.79
77.24 CHLOROFORM-D
77.45 CHLOROFORM-D
76.87 CHLOROFORM-D
50.88
28.15
25.22
Me
O
Cl
4
3
5
2
Me
O
1
OMe
Cl
4b: R2 = Me
f1 (ppm)

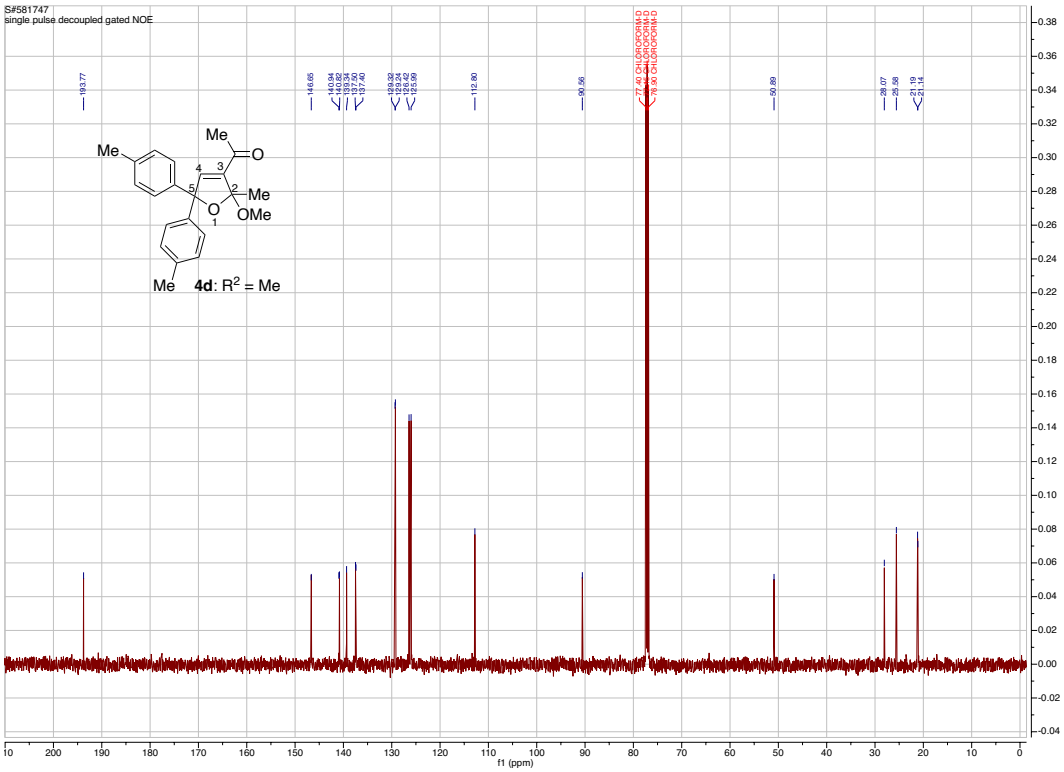

S#543815
DEPT with decoupling
Me
O
Cl
Me
OMe
Cl
4b: R2 = Me
144.71
128.84
128.50
127.86
127.42
50.67
28.15
25.22
f1 (ppm)

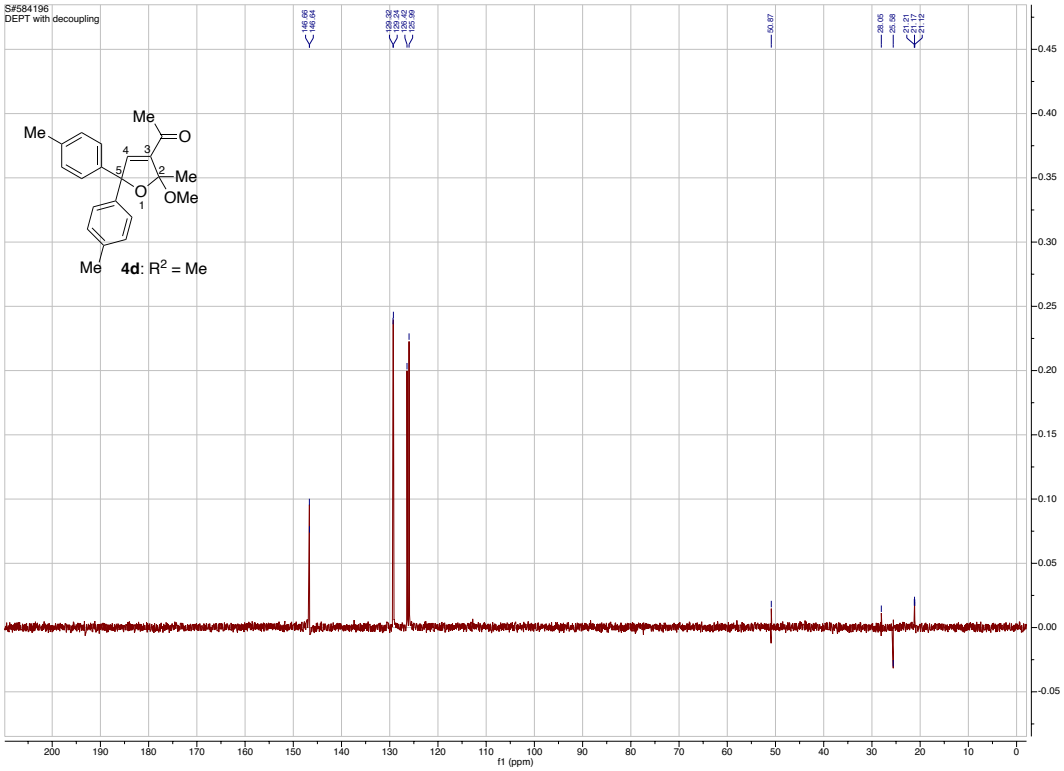

S#395611
single_pulse
Me
O
F
Me
OMe
F
4c: R2 = Me
3.01
2.44
1.73
1.05
4.10
4.32
3.00
3.06
3.06
f1 (ppm)

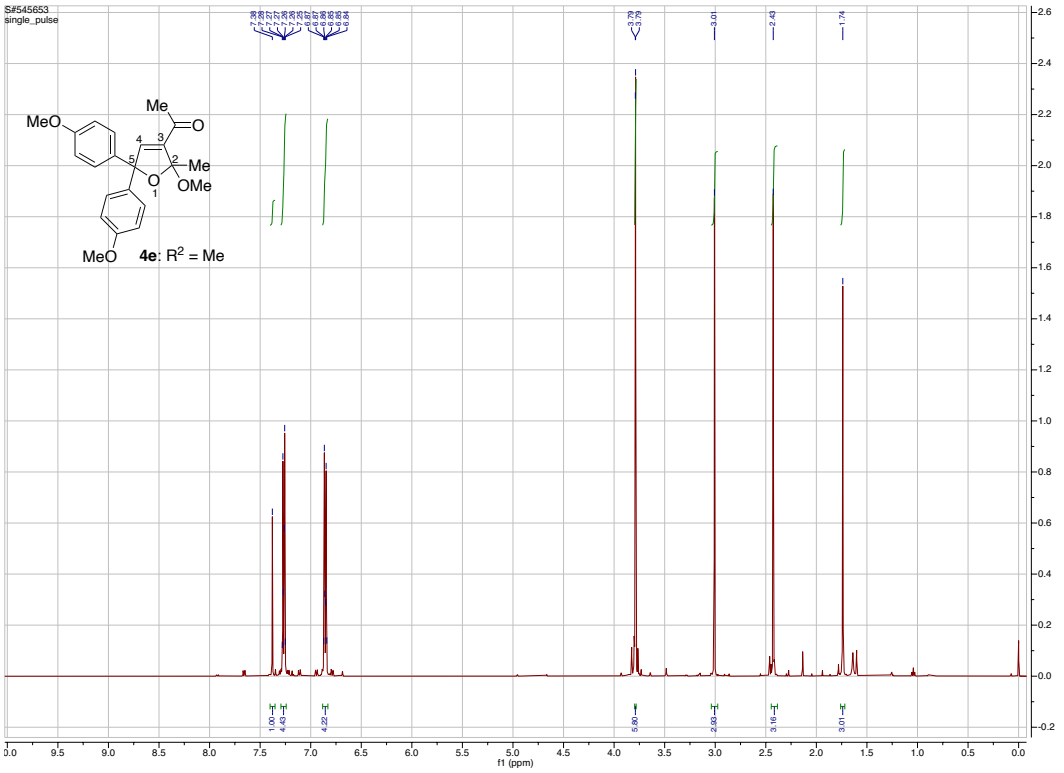

S#554418
single pulse decoupled gated NOE
193.56
163.03
161.27
145.38
141.11
139.46
139.33
139.23
139.06
128.35
128.30
127.87
127.81
115.69
115.62
115.55
115.48
112.95
89.88
77.40 CHLOROFORM-D
77.15 CHLOROFORM-D
76.89 CHLOROFORM-D
50.83
28.13
25.20
Me
O
F
4
3
5
2
Me
O
1
OMe
F
4c: R2 = Me
f1 (ppm)

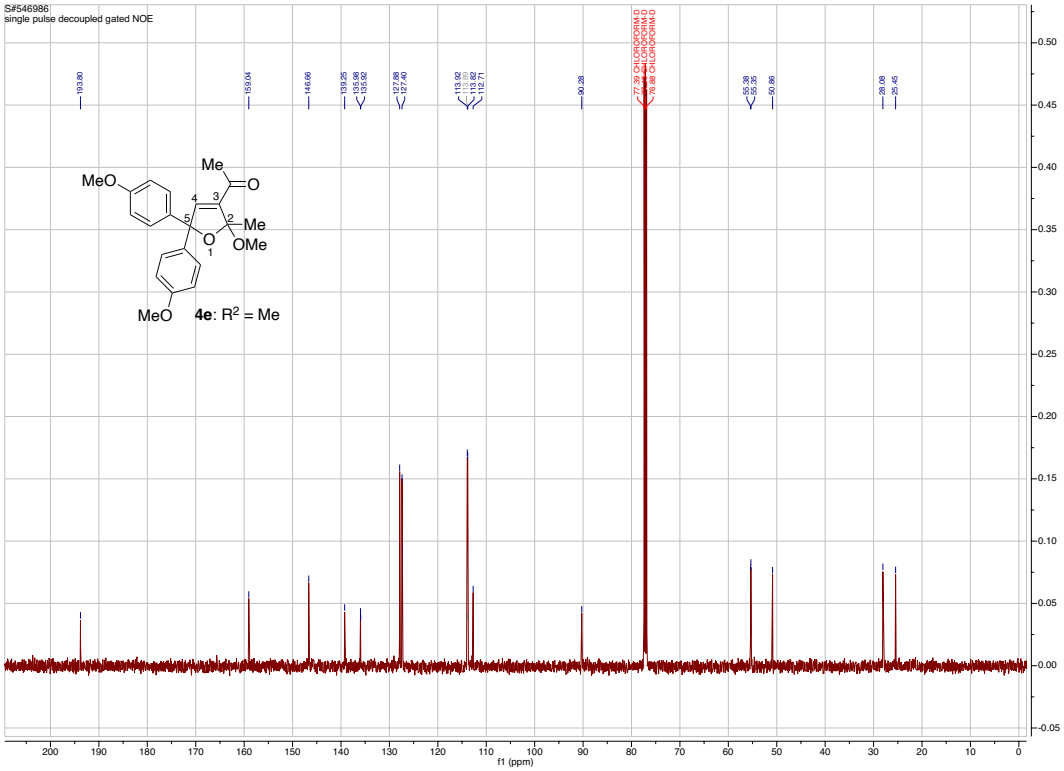

S#560234
DEPT with decoupling
145.38
128.35
128.30
127.87
127.81
115.69
115.62
115.55
115.48
77.35 CHLOROFORM-D
50.83
28.13
25.20
Me
O
F
4
3
5
2
Me
O
1
OMe
F
4c: R2 = Me
f1 (ppm)

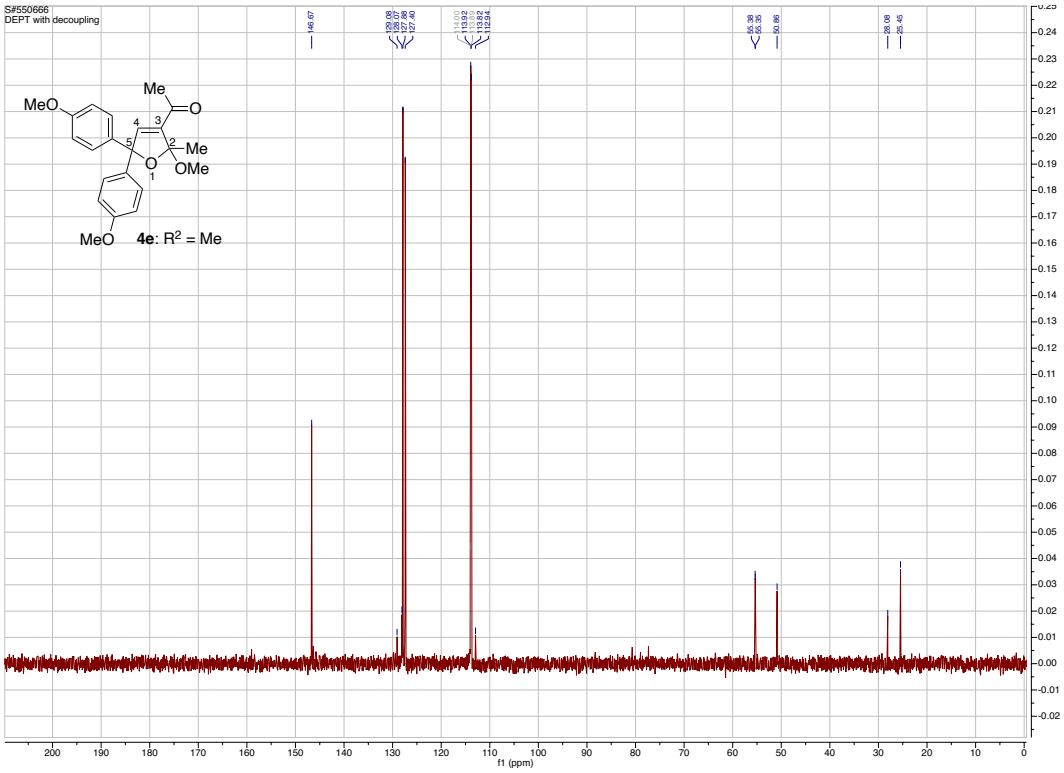

S#580241
single_pulse
Me
O
Me
OMe
Me
Me
4d: R2 = Me
f1 (ppm)

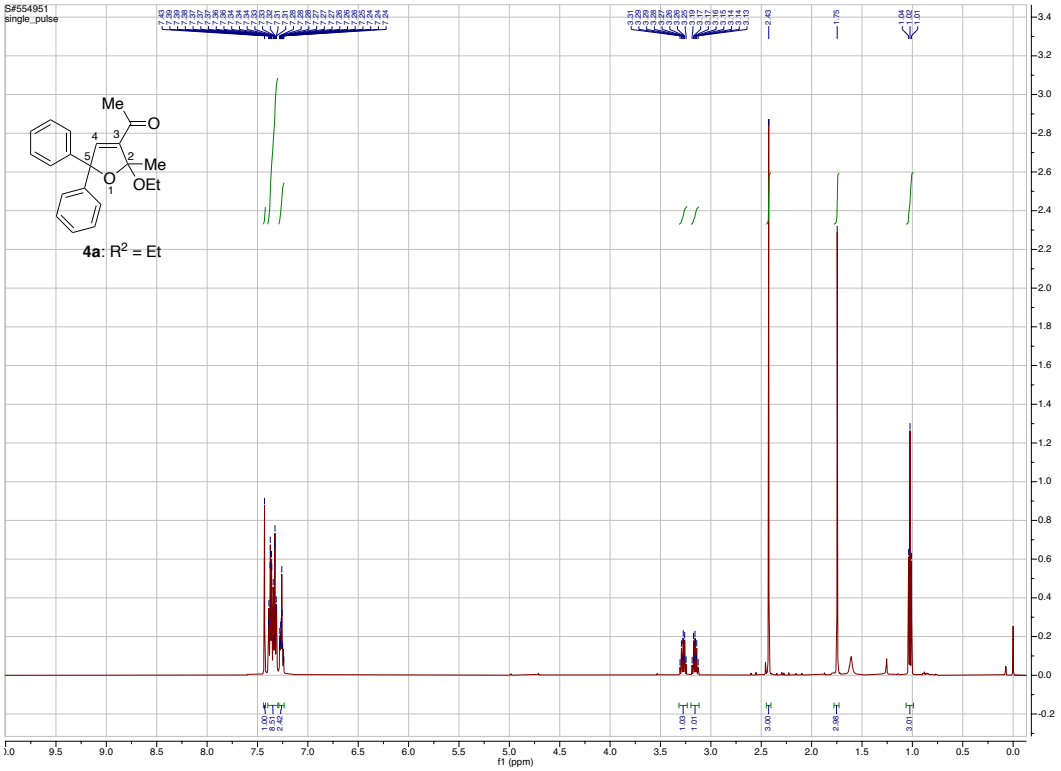

S#581747
single pulse decoupled gated NOE
Me
O
Me
OMe
Me
Me
4d: R2 = Me
f1 (ppm)

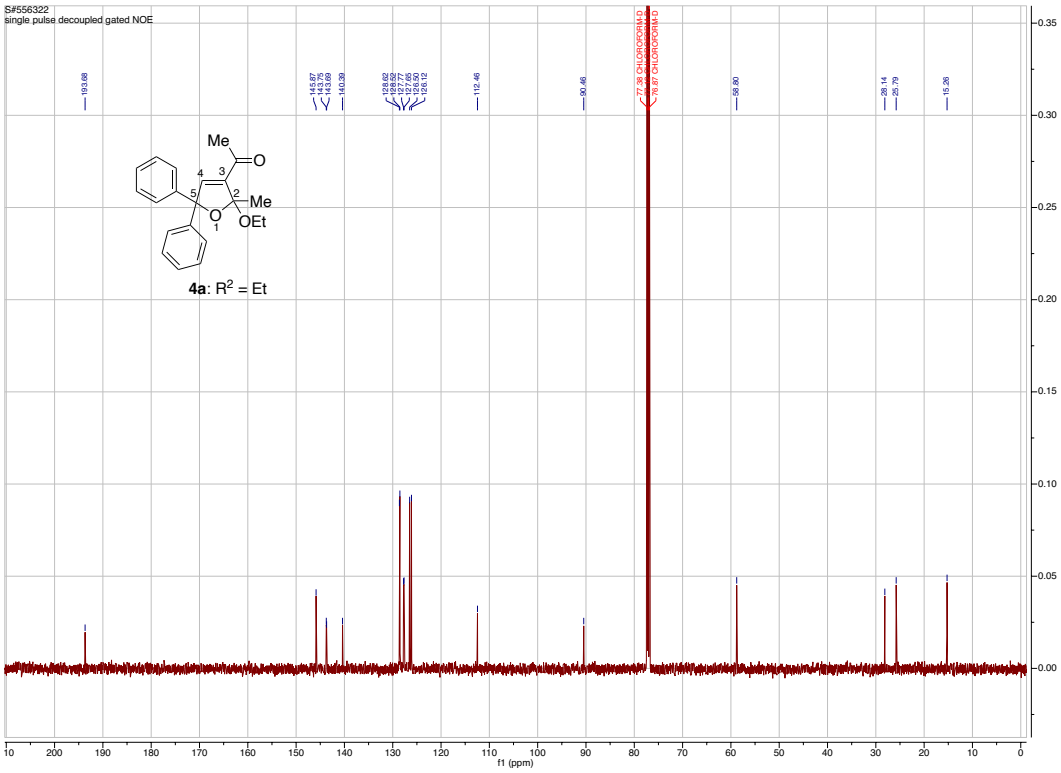

S#584196
DEPT with decoupling
Me
Me
O
Me
OMe
Me
4d: R2 = Me
f1 (ppm)

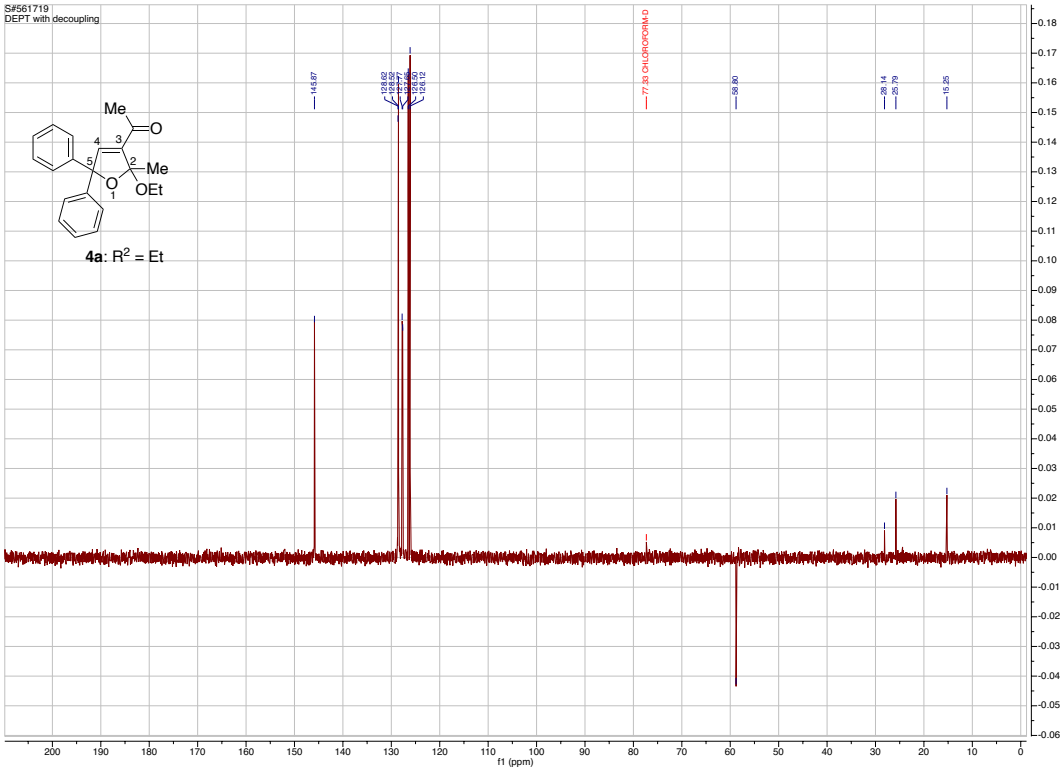

S#545653
single_pulse
MeO
Me
O
Me
OMe
MeO
4e: R2 = Me
f1 (ppm)

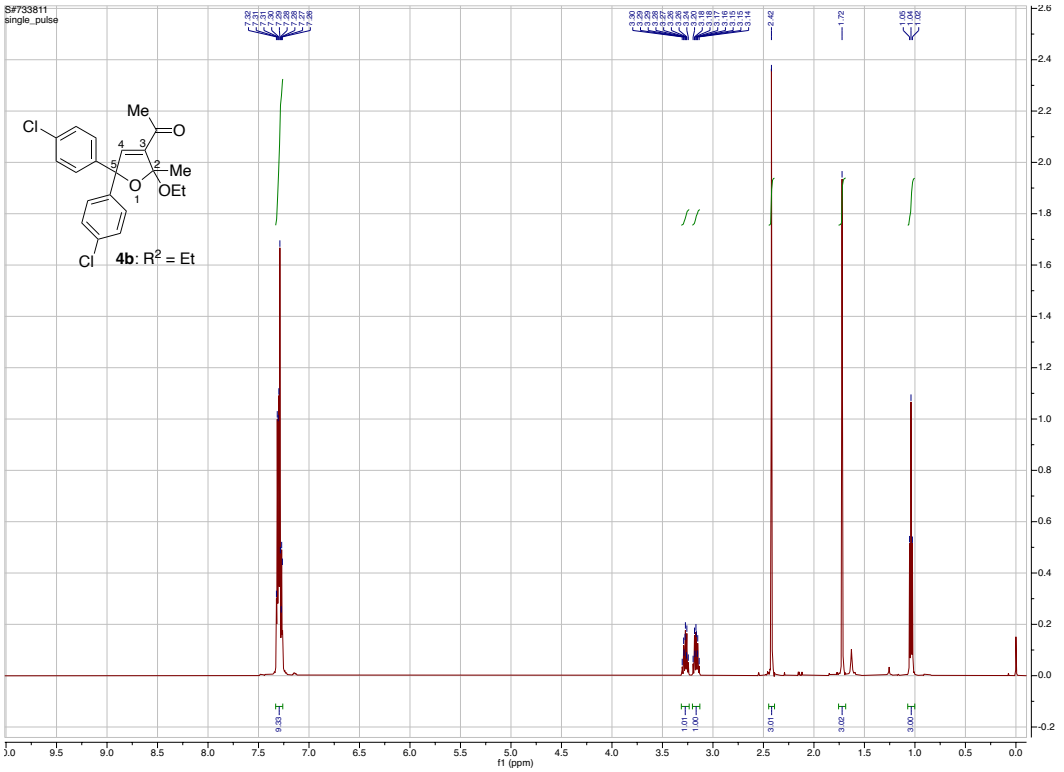

S#546986
single pulse decoupled gated NOE
MeO
Me
O
4
3
5
2
Me
O
1
OMe
MeO
4e: R2 = Me
f1 (ppm)

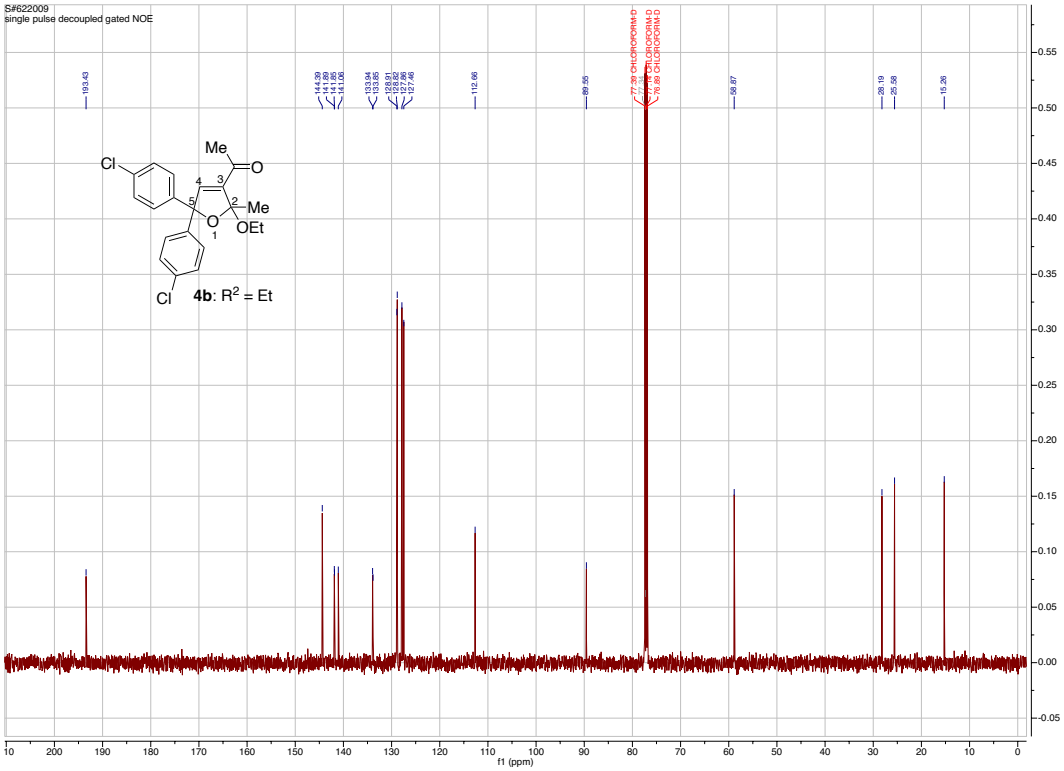

S#550666
DEPT with decoupling
MeO
Me
O
4
3
5
2
Me
O
1
OMe
MeO
4e: R2 = Me
f1 (ppm)

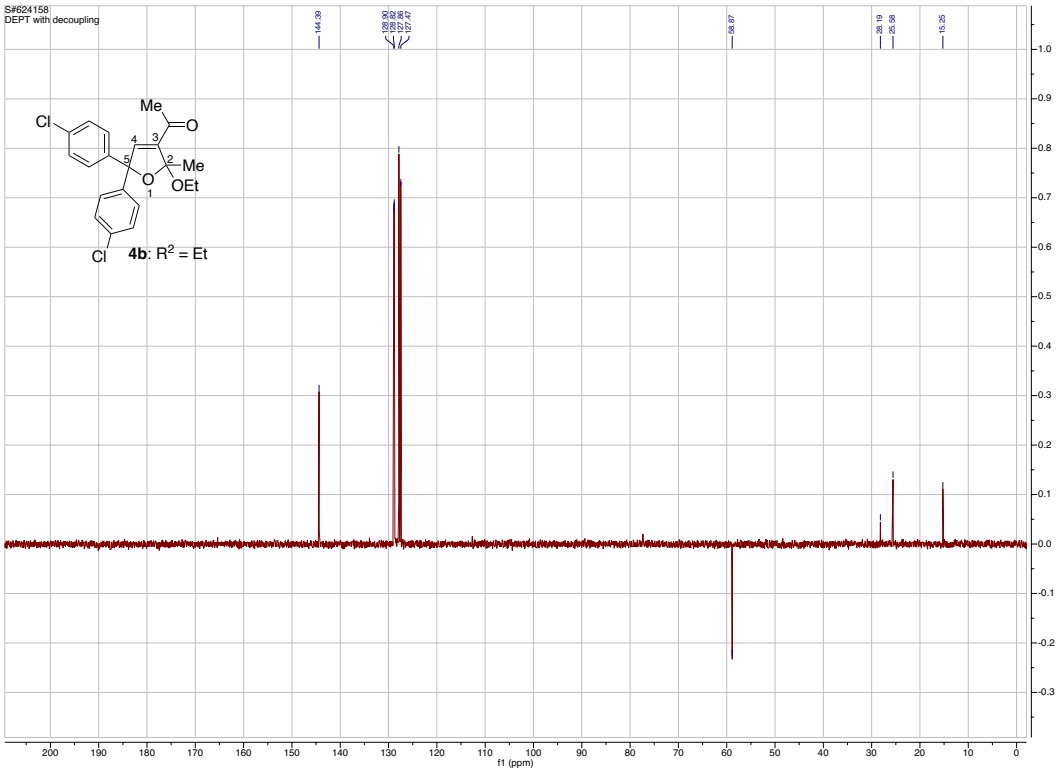

S#554951
single_pulse
Me
O
4
3
5
2
Me
O
1
OEt
4a: R2 = Et
f1 (ppm)

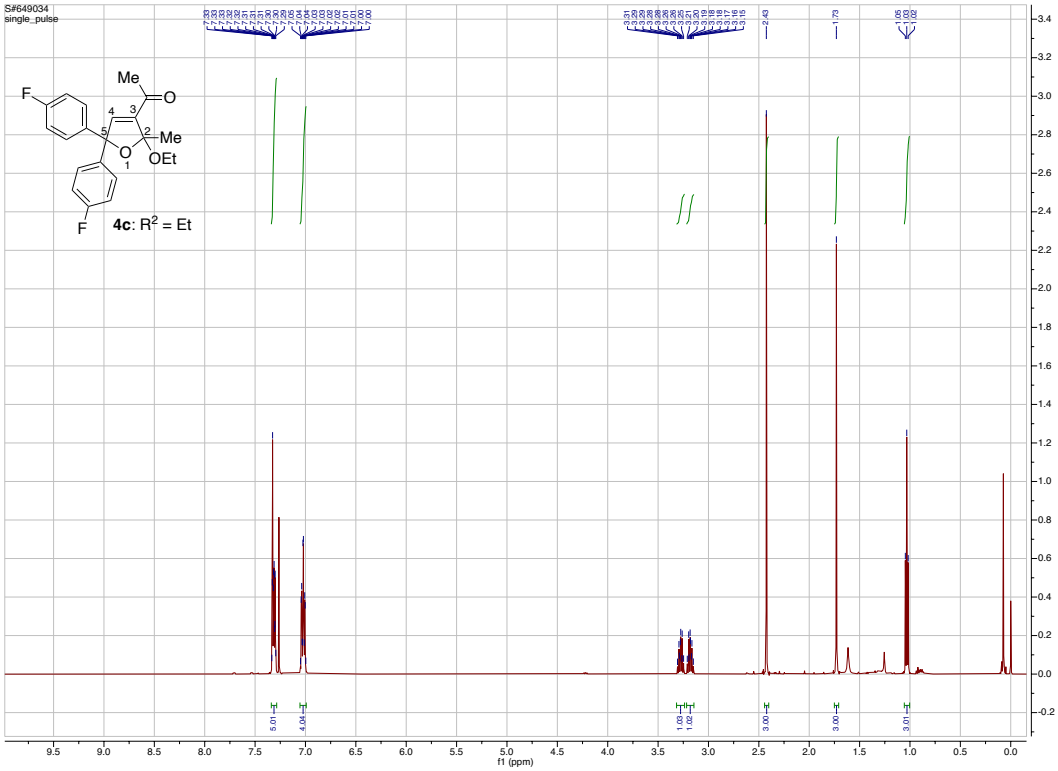

S#556322
single pulse decoupled gated NOE
193.69
145.67
143.75
143.69
140.39
128.62
128.52
127.77
127.65
126.50
126.12
112.46
90.46
77.28 CHLOROFORM-D
77.03
76.87 CHLOROFORM-D
58.80
28.14
25.79
15.26
Me
O
4
3
5
2
Me
O
1
OEt
4a: R2 = Et
f1 (ppm)

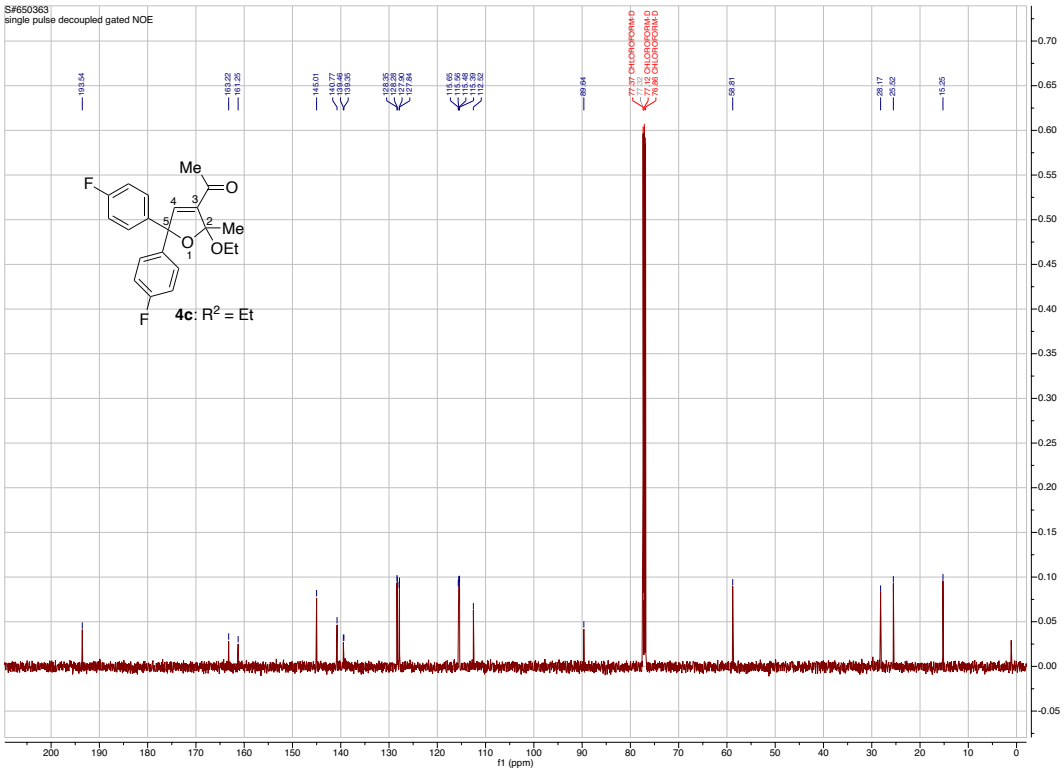

S#561719
DEPT with decoupling
Me
O
Me
OEt
4a: R2 = Et
145.67
128.62
128.32
127.77
126.92
126.10
77.33 CHLOROFORM-D
58.80
28.14
25.79
15.25
f1 (ppm)

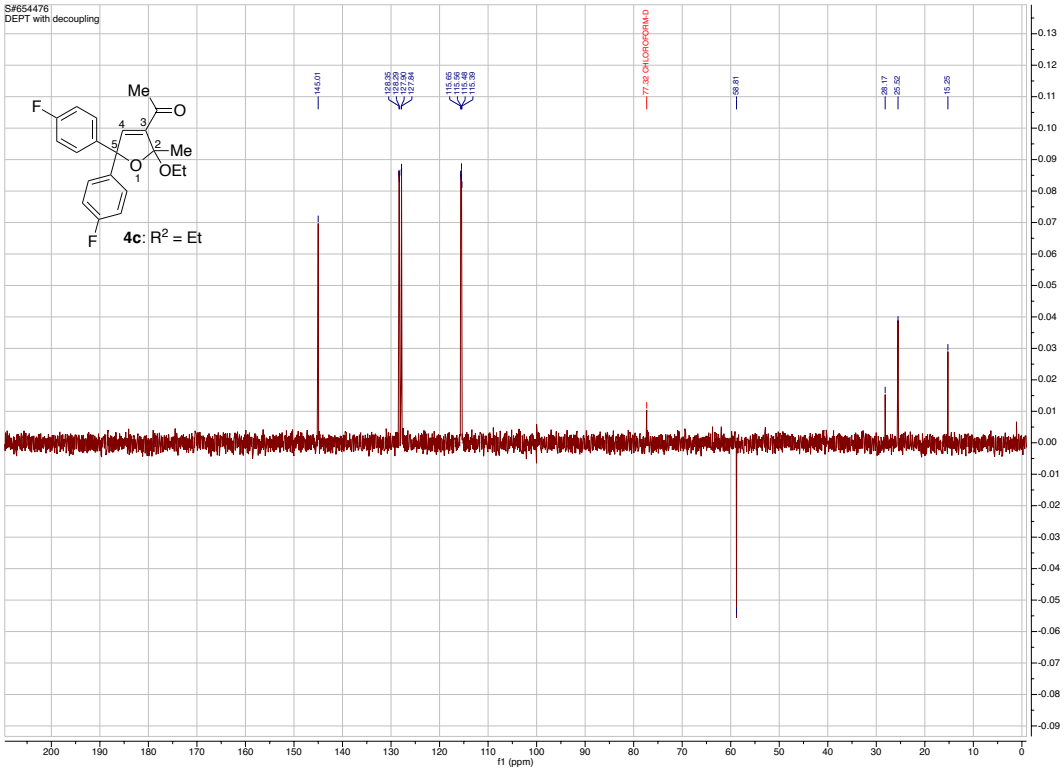

S#733811
single_pulse
Cl
Me
O
Me
OEt
Cl
4b: R2 = Et
7.32
7.31
7.30
7.29
7.28
7.27
7.26
3.30
3.29
3.28
3.27
3.26
3.25
3.24
3.23
3.22
3.21
3.20
3.19
3.17
3.16
3.15
3.14
2.42
1.72
1.05
1.04
1.02
9.33
1.01
1.00
3.01
3.02
3.00
f1 (ppm)

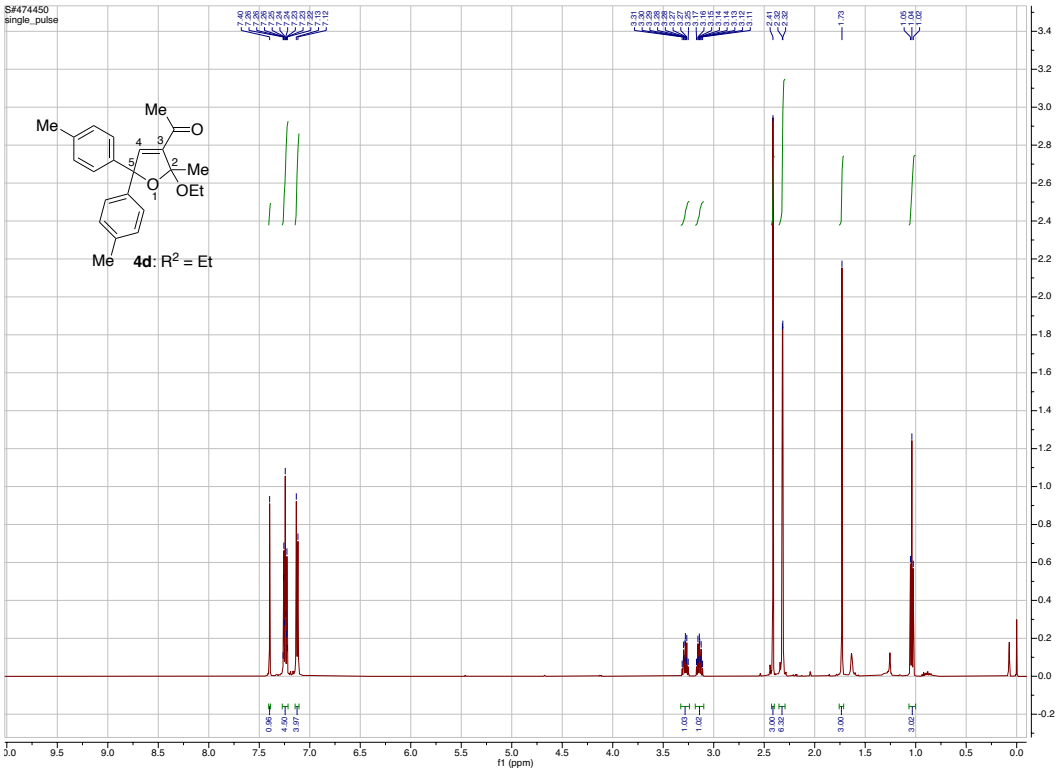

S#622009
single pulse decoupled gated NOE
193.43
144.39
141.85
141.06
133.94
133.85
128.91
128.82
127.96
127.46
112.66
89.55
77.39 CHLOROFORM-D
77.15
76.89 CHLOROFORM-D
58.87
28.19
25.58
15.26
Me
O
Cl
4
3
5
2
Me
O
1
OEt
Cl
4b: R2 = Et
f1 (ppm)

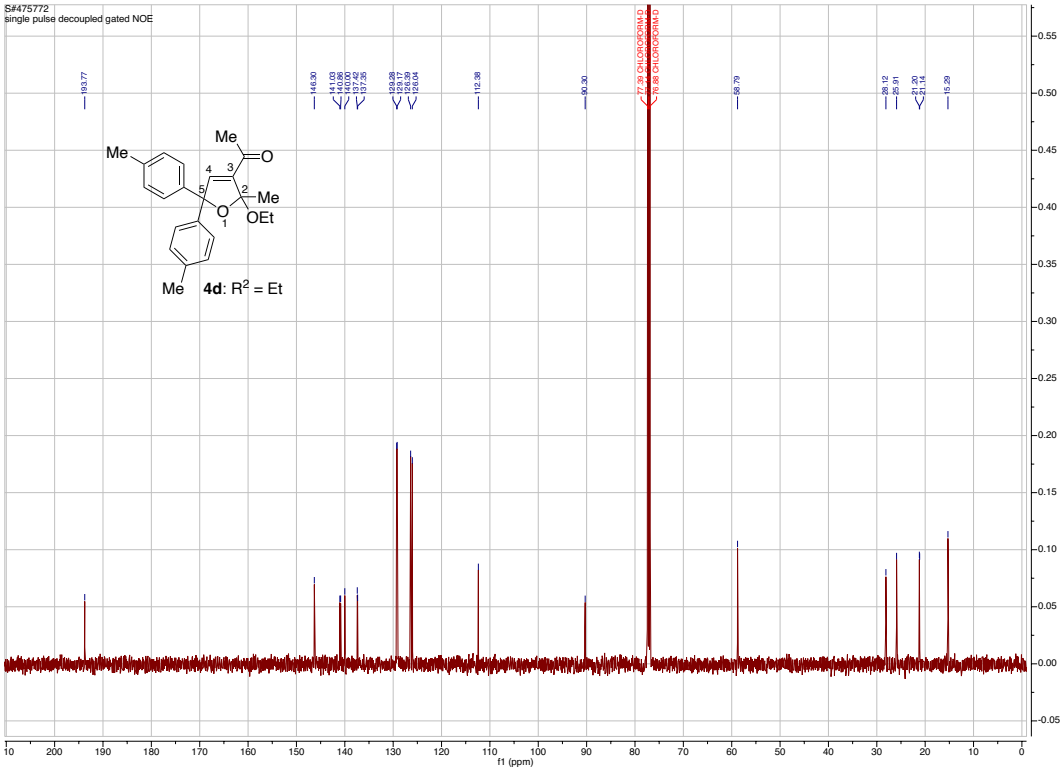

S#624158
DEPT with decoupling
144.39
128.90
128.82
127.96
127.46
58.87
28.19
25.58
15.25
Me
O
Cl
4
3
5
2
Me
O
1
OEt
Cl
4b: R2 = Et
f1 (ppm)

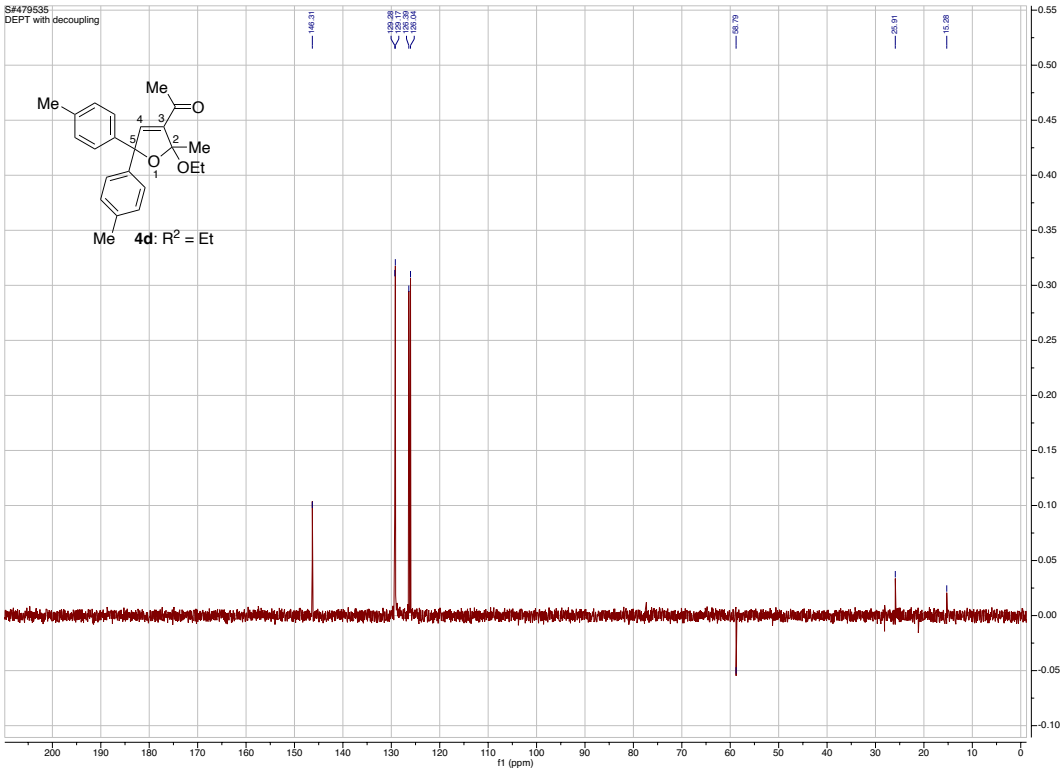

S#649034
single_pulse
Me
O
F
4
3
5
2
Me
O
1
OEt
F
4c: R2 = Et
f1 (ppm)

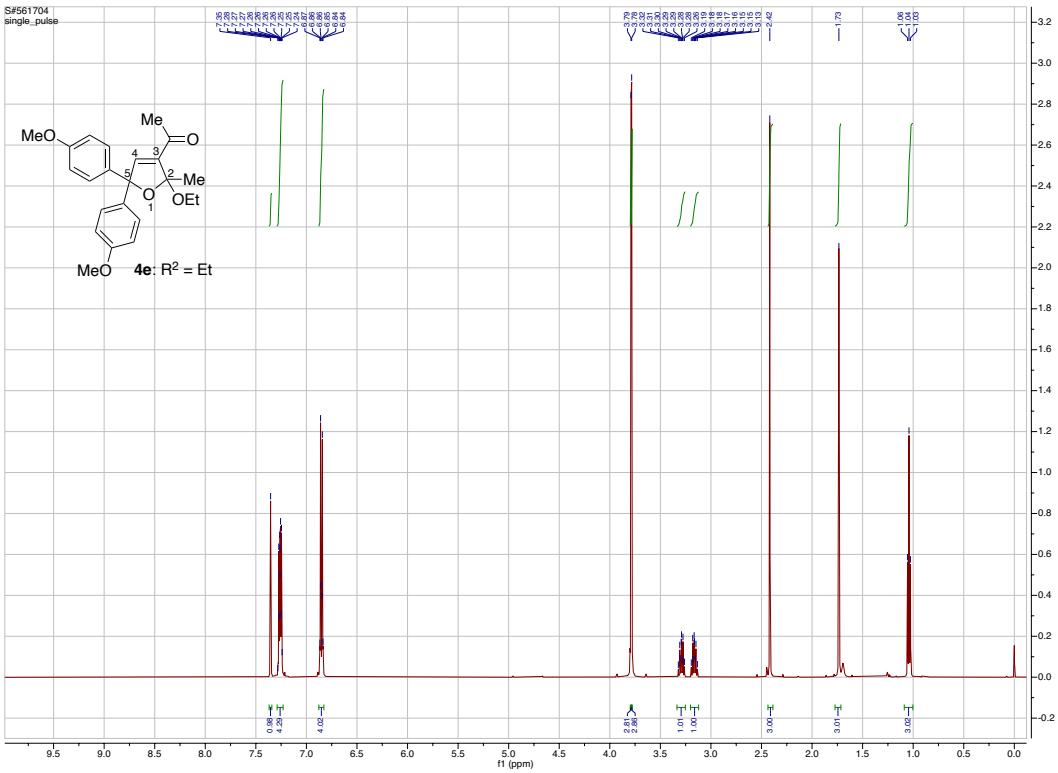

S#650363
single pulse decoupled gated NOE
Me
O
F
4
3
5
2
Me
O
1
OEt
F
4c: R2 = Et
f1 (ppm)

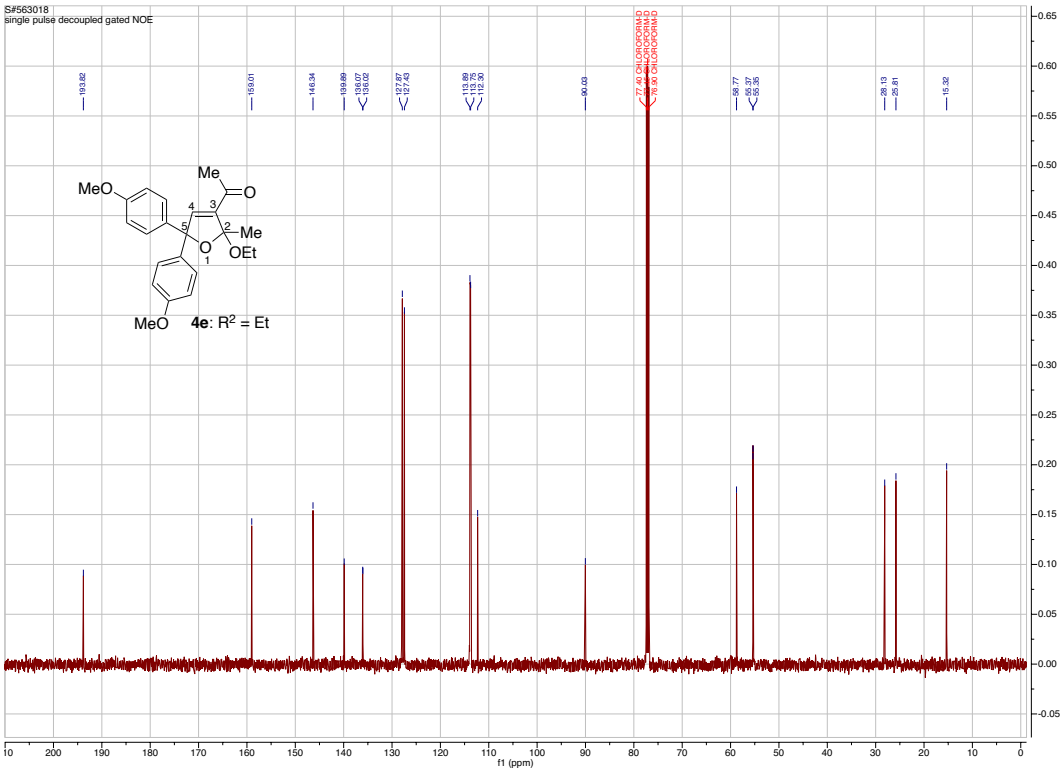

S#654476
DEPT with decoupling
Me
O
F
4
3
5
2
Me
O
1
OEt
F
4c: R2 = Et
145.01
128.35
128.30
127.90
127.84
115.65
115.56
115.49
115.39
77.32 CHLOROFORM-D
58.81
28.17
25.92
15.25
f1 (ppm)

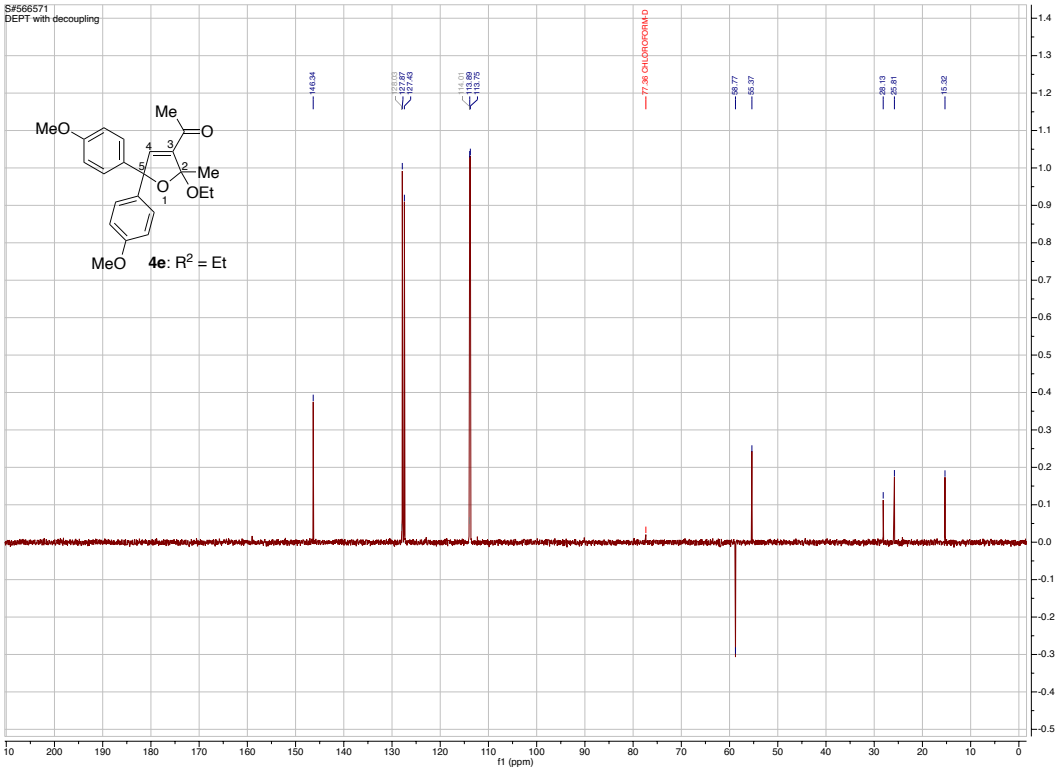

S#474450
single_pulse
Me
Me
O
4
3
5
2
Me
O
1
OEt
Me
4d: R2 = Et
f1 (ppm)

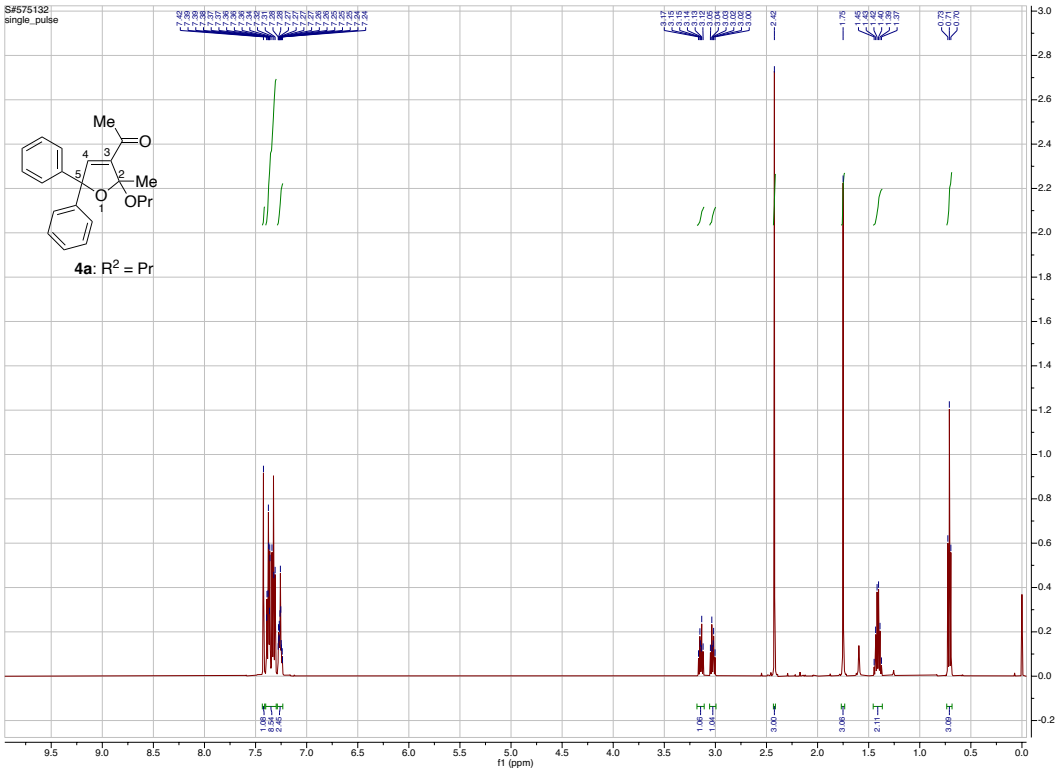

S#475772
single pulse decoupled gated NOE
193.77
146.30
141.03
140.66
140.00
137.67
137.26
129.28
128.77
128.39
126.04
112.38
90.30
77.39 CHLOROFORM-D
76.88 CHLOROFORM-D
58.79
28.12
25.91
21.20
21.14
15.29
Me
Me
O
4
3
5
2
Me
O
1
OEt
Me
4d: R2 = Et
f1 (ppm)

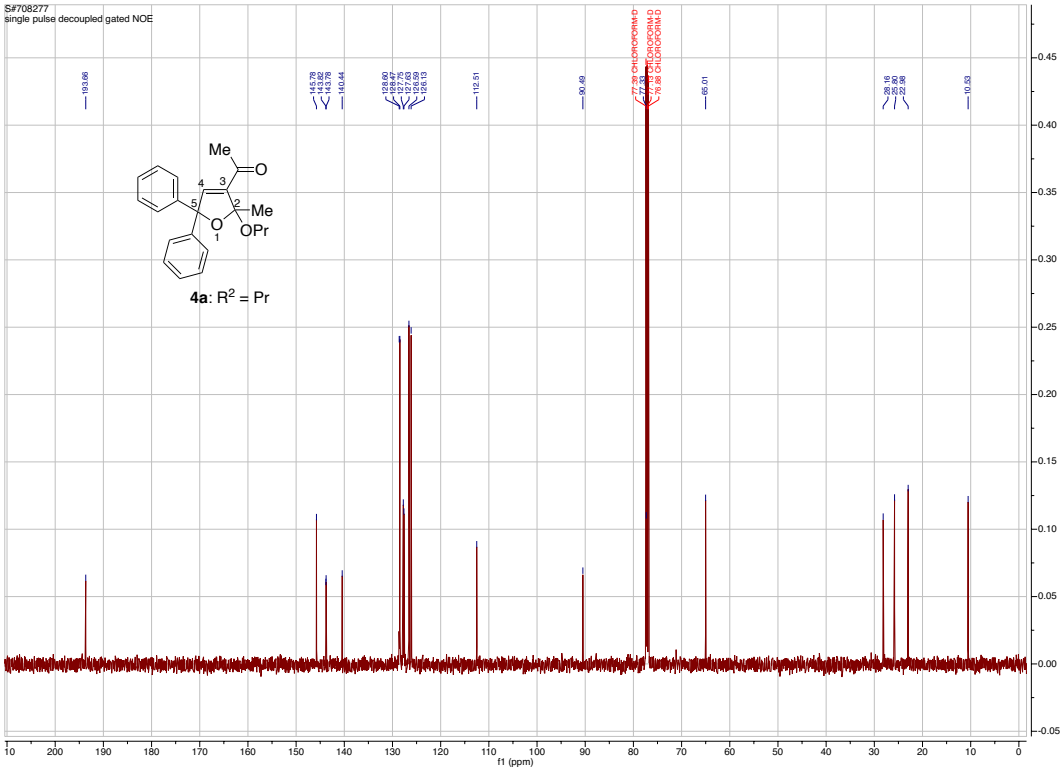

S#479535
DEPT with decoupling
146.31
129.28
128.77
128.39
126.04
58.79
25.91
15.28
Me
Me
O
4
3
5
2
Me
O
1
OEt
Me
4d: R2 = Et
f1 (ppm)

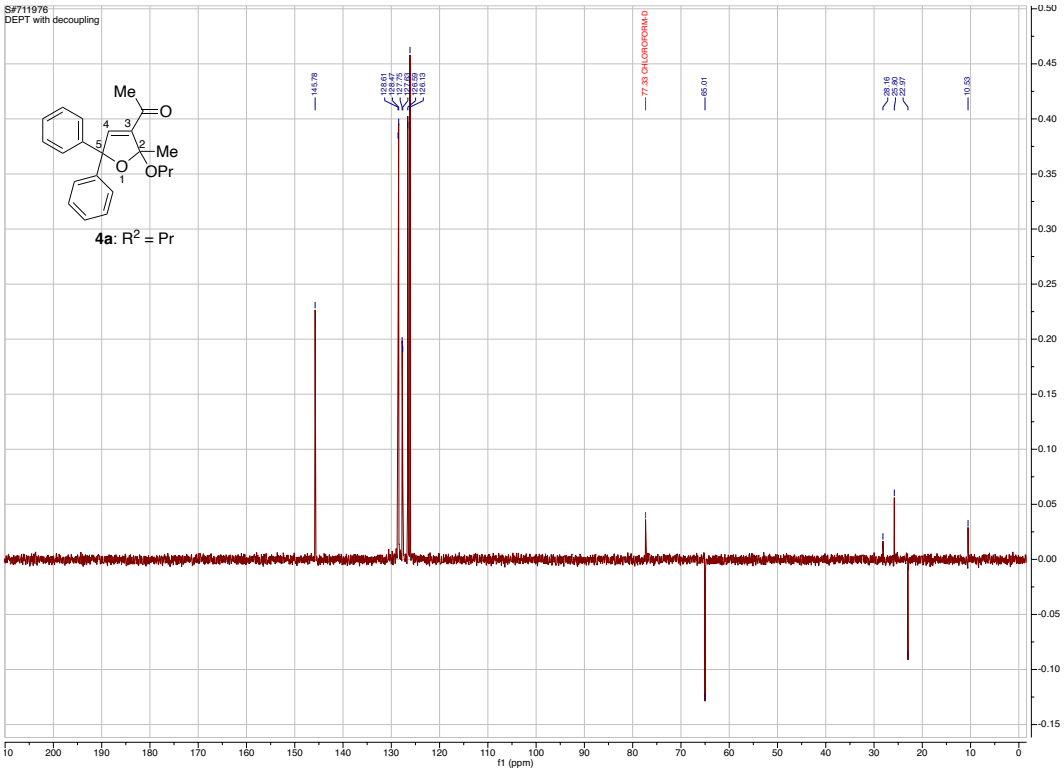

S#561704
single_pulse
MeO
Me
O
4
3
5
2
Me
O
1
OEt
MeO
4e: R2 = Et
f1 (ppm)


S#563018
single pulse decoupled gated NOE
193.82
159.01
146.34
139.89
136.07
130.02
127.87
127.43
113.89
113.75
112.36
90.03
77.40 CHLOROFORM-D
77.08 CHLOROFORM-D
76.90 CHLOROFORM-D
58.77
55.37
55.35
28.13
25.81
15.32
MeO
Me
O
4
3
5
2
Me
O
1
OEt
MeO
4e: R2 = Et
f1 (ppm)

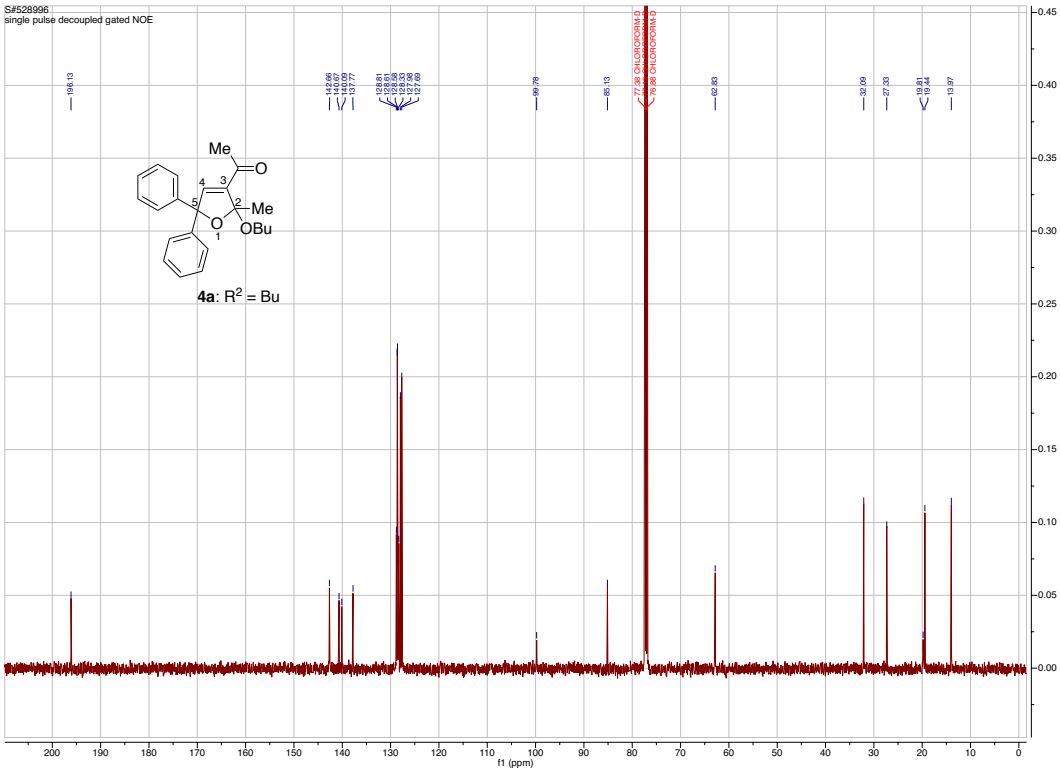

S#566571
DEPT with decoupling
Me
MeO
O
Me
OEt
MeO
4e: R2 = Et
146.34
128.03
127.67
127.45
114.01
113.89
113.75
77.36 CHLOROFORM-D
56.77
55.37
29.13
25.81
15.32
f1 (ppm)

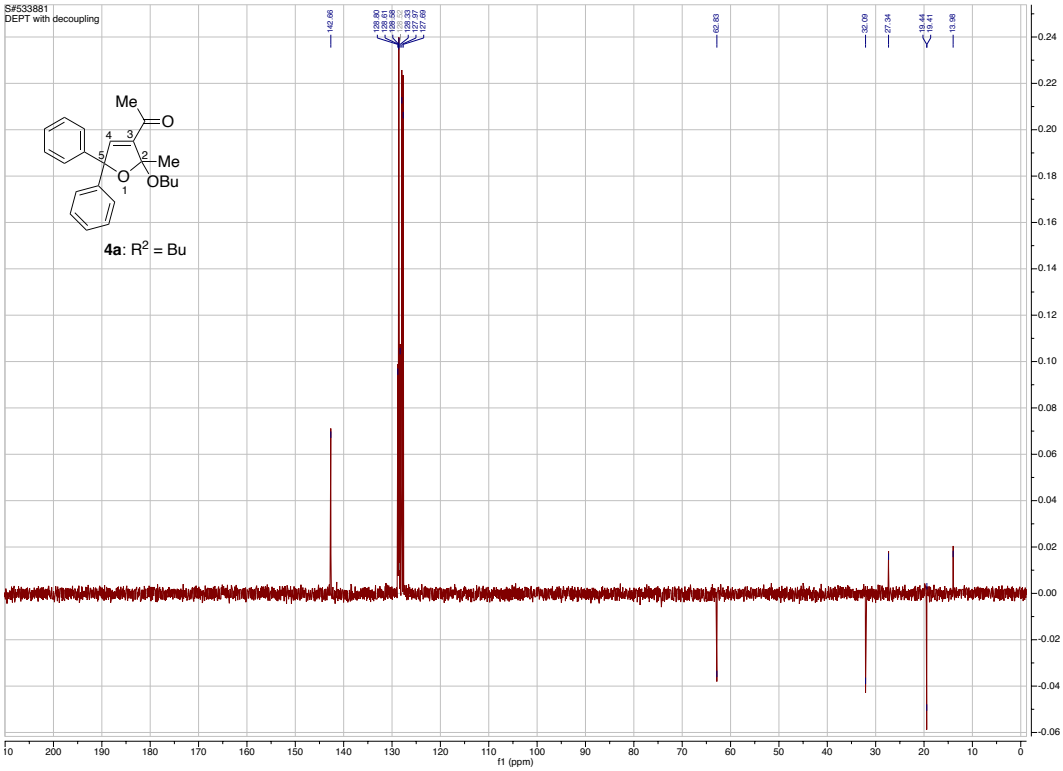

S#575132
single_pulse
Me
O
Me
OPr
4a: R2 = Pr
7.62
7.39
7.37
7.36
7.34
7.31
7.28
7.27
7.26
7.25
7.24
3.17
3.15
3.14
3.13
3.05
3.04
3.03
3.02
3.00
2.42
1.75
1.45
1.43
1.40
1.39
1.37
0.73
0.71
0.70
f1 (ppm)

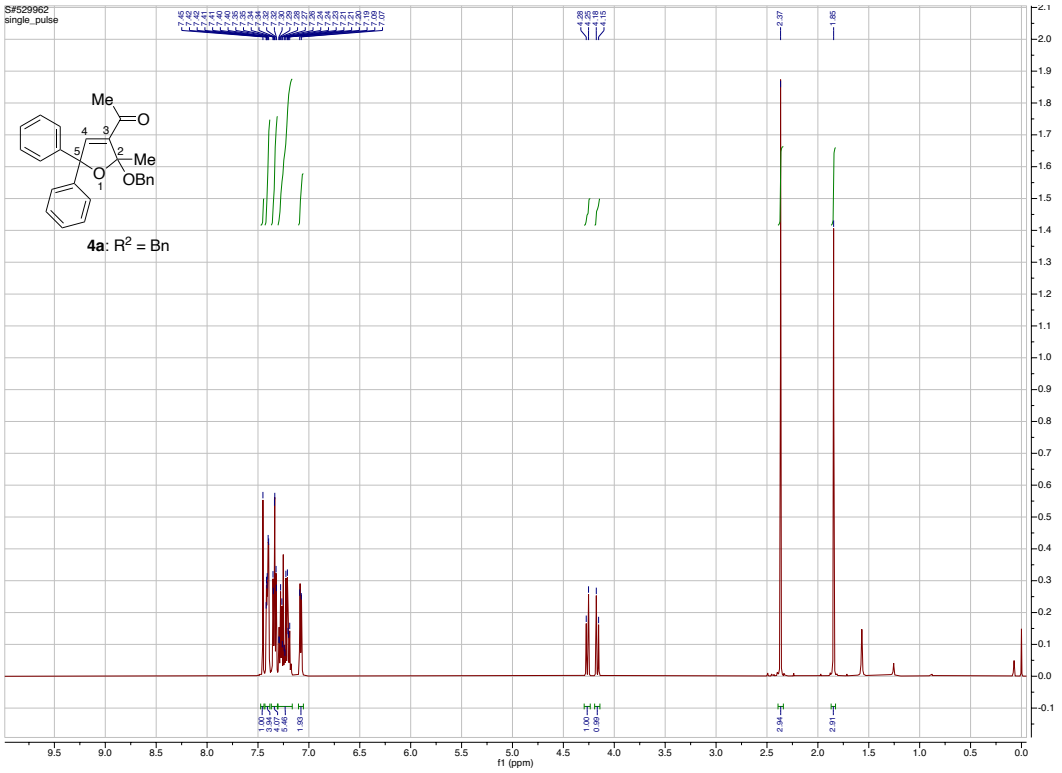

S#708277
single pulse decoupled gated NOE
193.66
145.78
143.82
143.78
140.44
128.60
128.47
127.75
127.63
126.59
126.10
112.51
90.49
77.33 CHLOROFORM-D
77.33
77.00 CHLOROFORM-D
76.68 CHLOROFORM-D
65.01
28.16
25.90
22.98
10.53
Me
O
4
3
5
2
Me
O
1
OPr
4a: R2 = Pr
f1 (ppm)

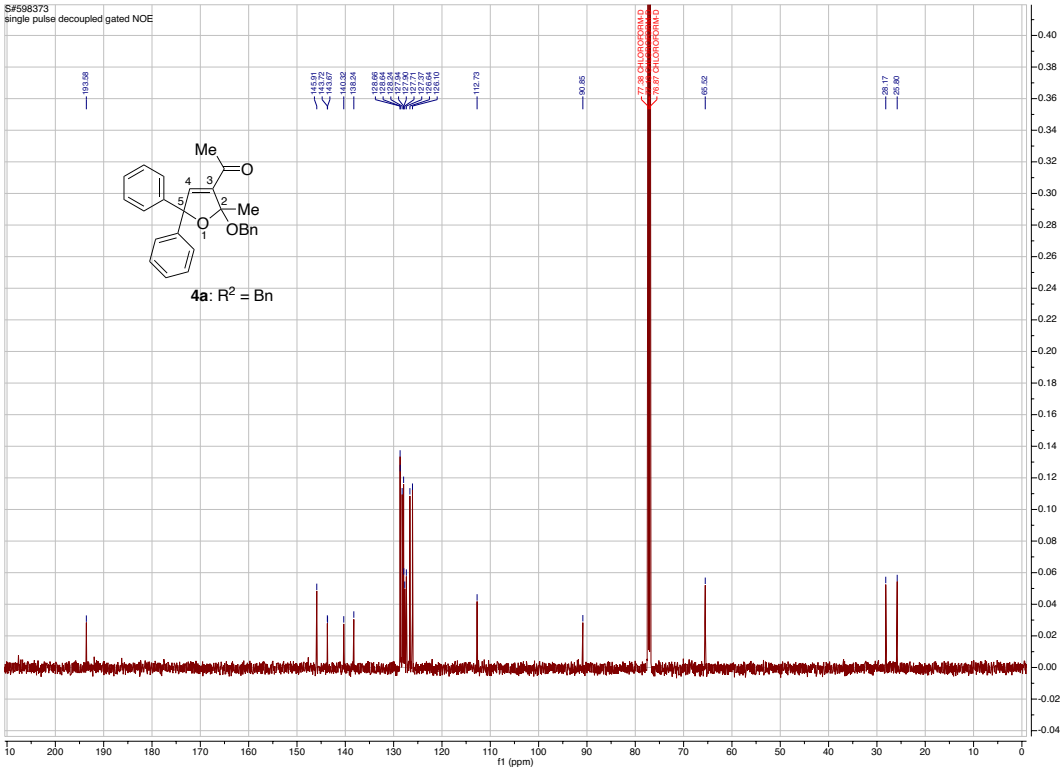

S#711976
DEPT with decoupling
145.78
128.61
128.47
127.75
127.63
126.59
126.10
77.33 CHLOROFORM-D
65.01
28.16
25.90
22.97
10.53
Me
O
4
3
5
2
Me
O
1
OPr
4a: R2 = Pr
f1 (ppm)

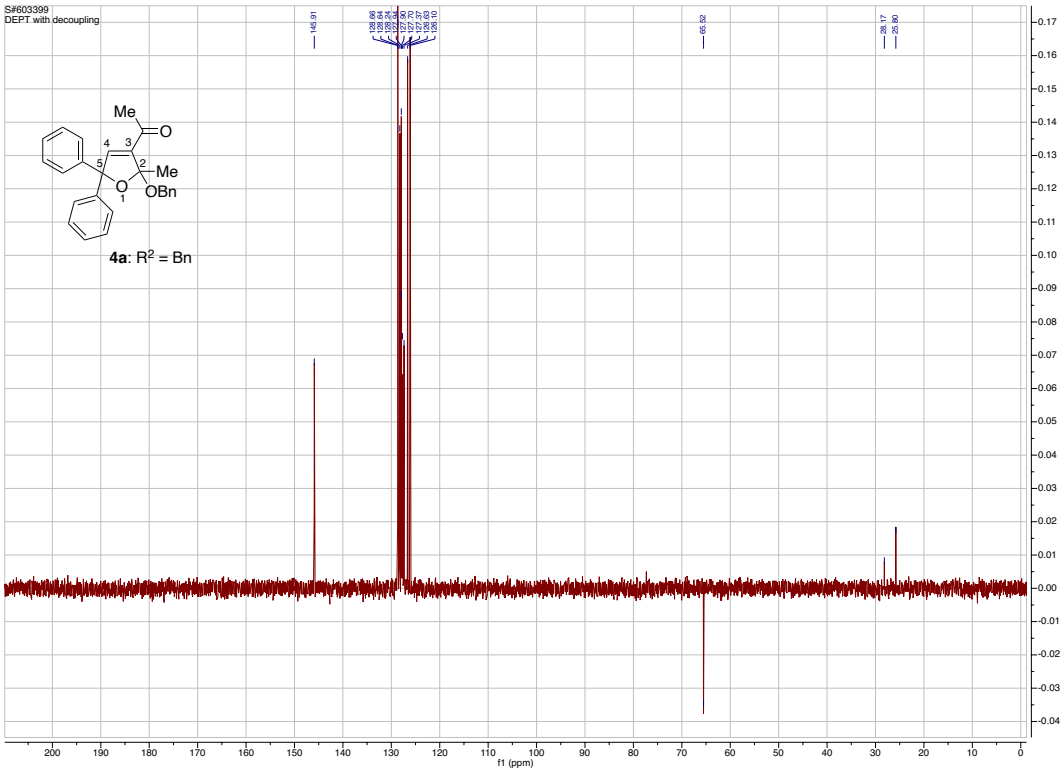

S#527649
single_pulse
Me
O
Me
OBu
4a: R2 = Bu
f1 (ppm)

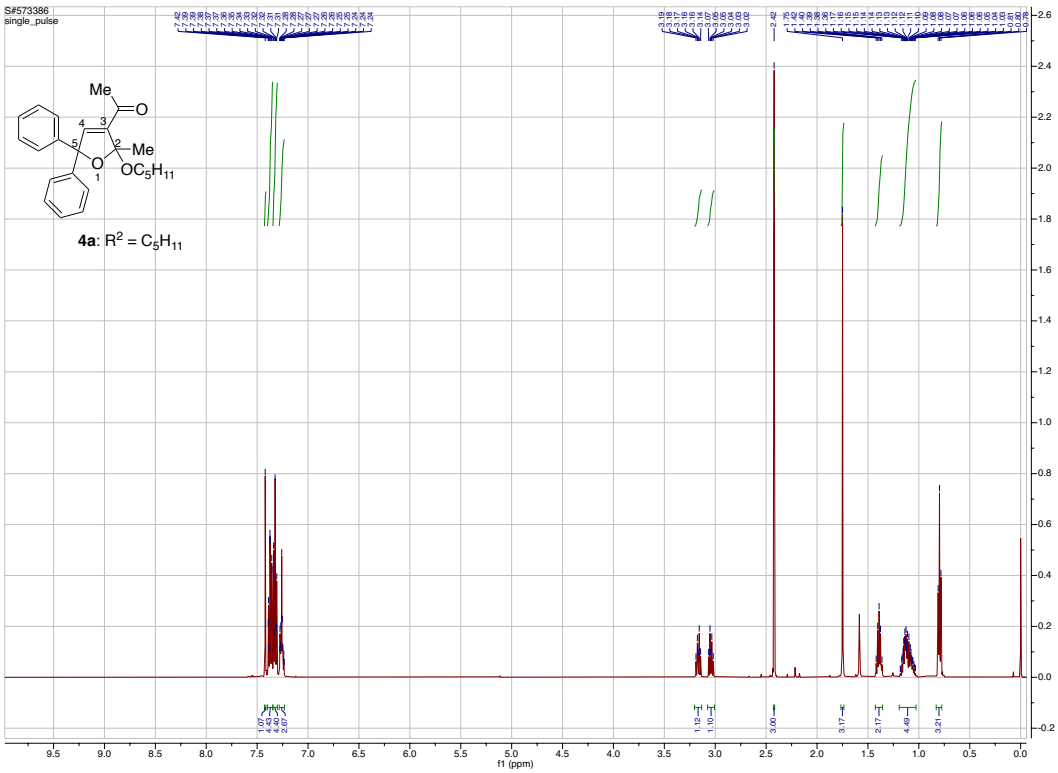

S#528996
single pulse decoupled gated NOE
Me
O
Me
OBu
4a: R2 = Bu
f1 (ppm)

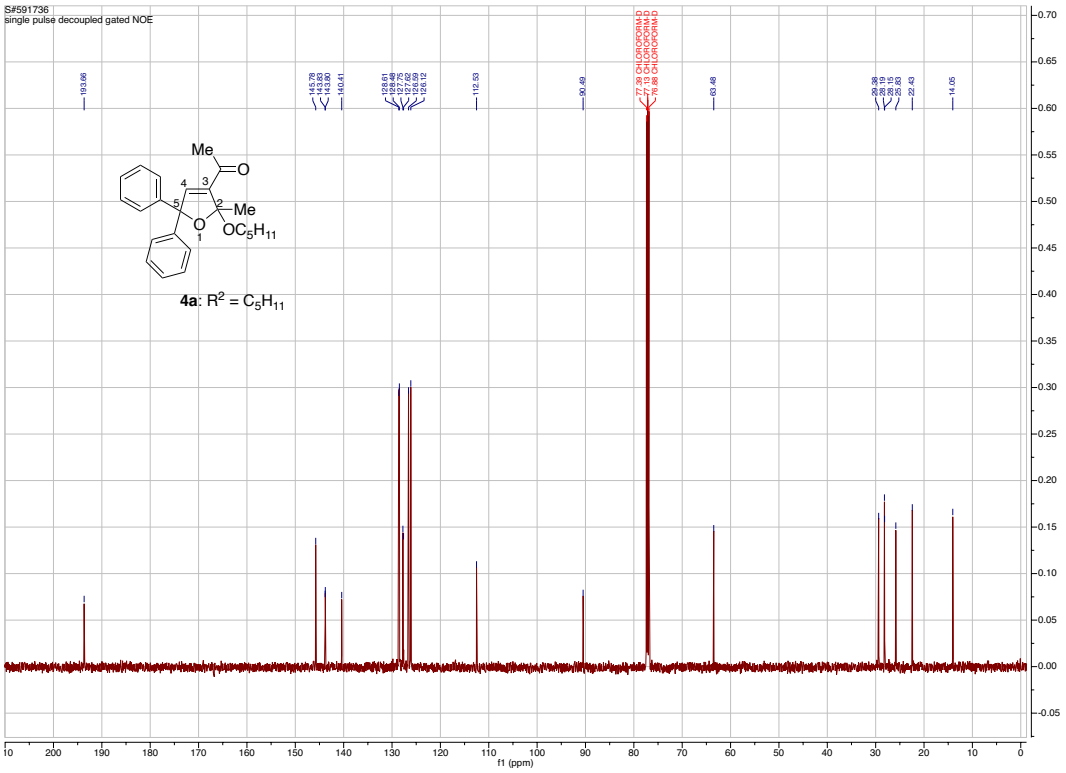

S#533881
DEPT with decoupling
Me
O
Me
OBu
4a: R2 = Bu
f1 (ppm)

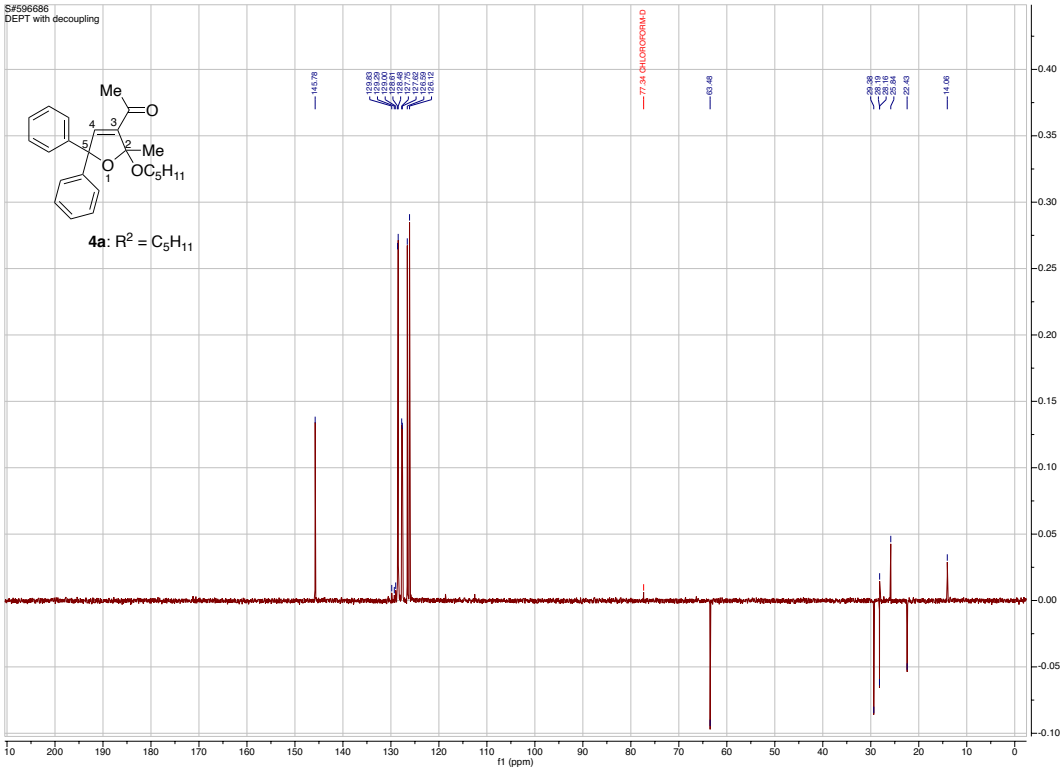

S#529962
single_pulse
Me
O
Me
OBn
4a: R2 = Bn
f1 (ppm)

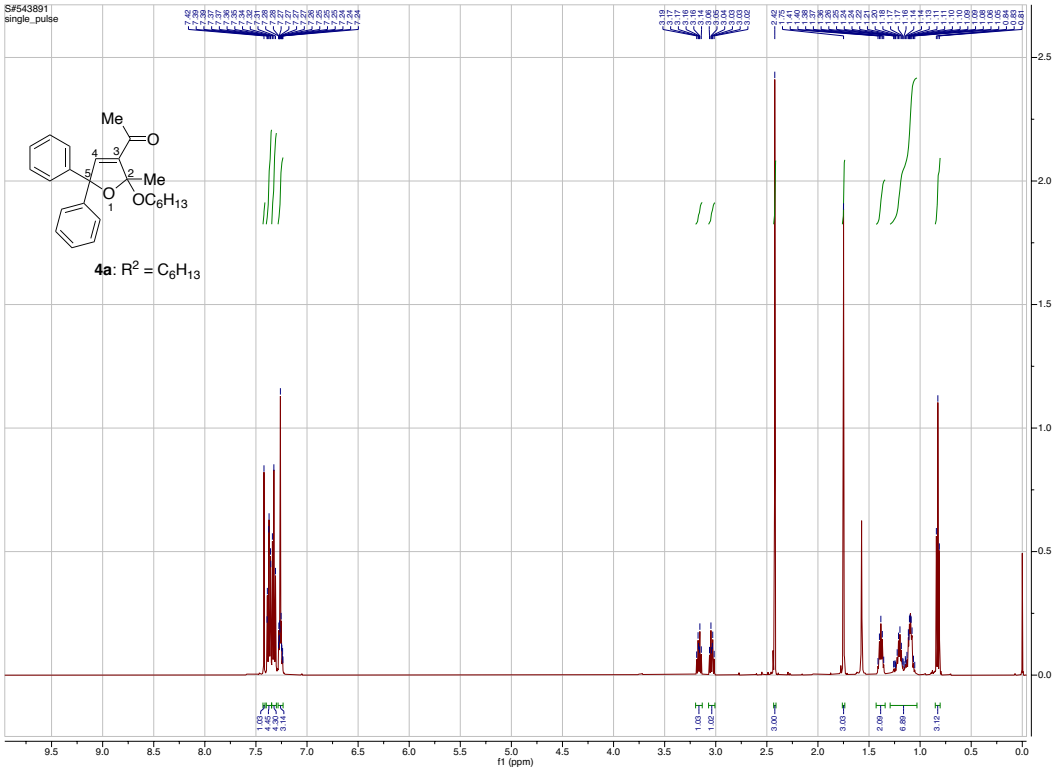

S#598373
single pulse decoupled gated NOE
193.98
145.91
143.72
143.67
141.69
139.84
128.66
128.54
128.24
127.90
127.77
127.27
126.64
126.10
112.73
90.85
77.38 CHLOROFORM-D
78.87 CHLOROFORM-D
65.52
28.17
25.80
Me
O
4
3
5
2
Me
O
1
OBn
4a: R2 = Bn
f1 (ppm)

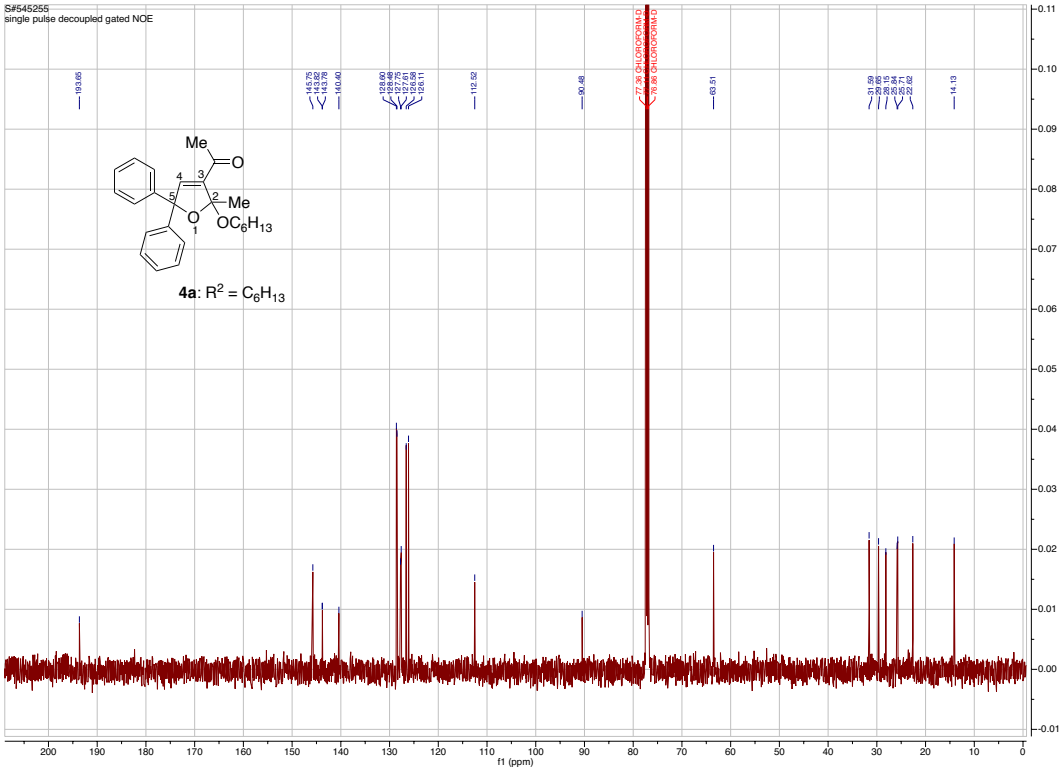

S#603399
DEPT with decoupling
145.91
128.66
128.54
128.24
127.90
127.77
127.27
126.64
126.10
65.52
28.17
25.80
Me
O
4
3
5
2
Me
O
1
OBn
4a: R2 = Bn
f1 (ppm)

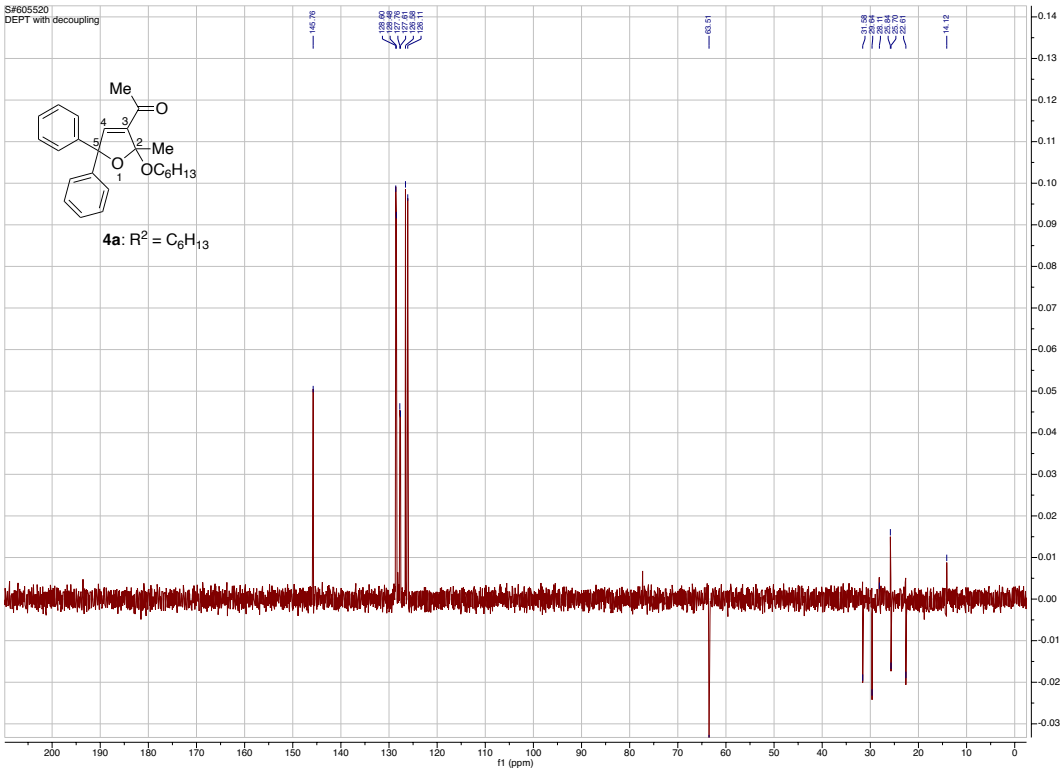

S#573386
single_pulse
Me
O
Me
OC5H11
4a: R2 = C5H11
f1 (ppm)

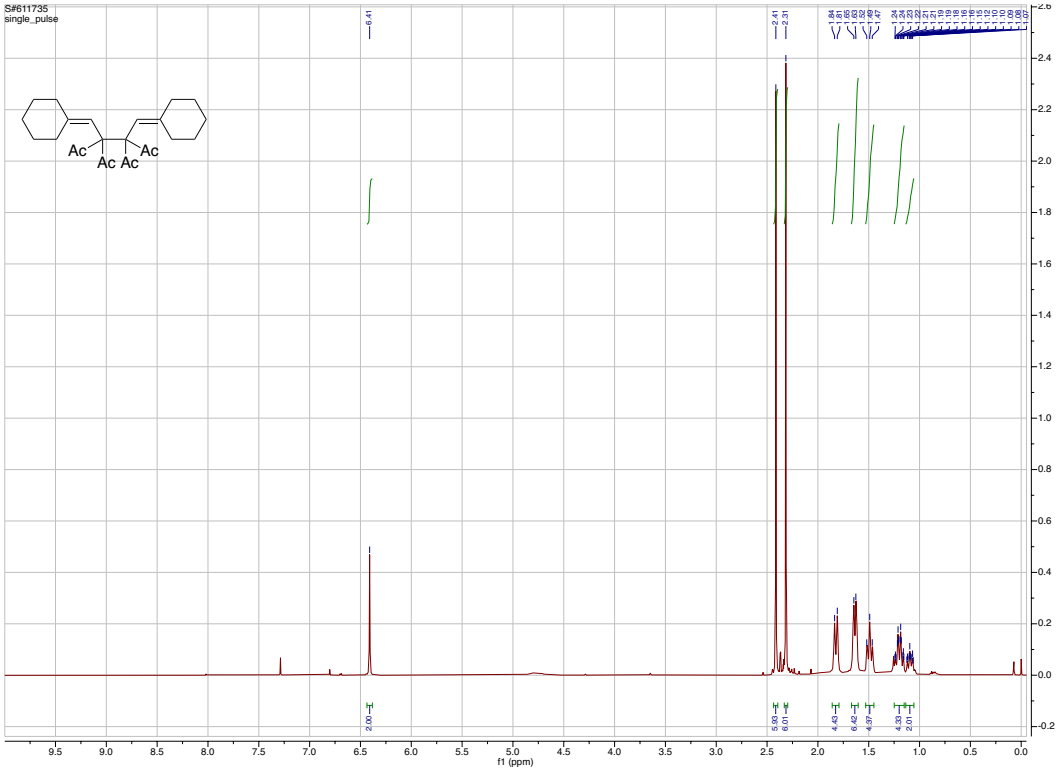

S#591736
single pulse decoupled gated NOE
Me
O
Me
OC5H11
4a: R2 = C5H11
f1 (ppm)

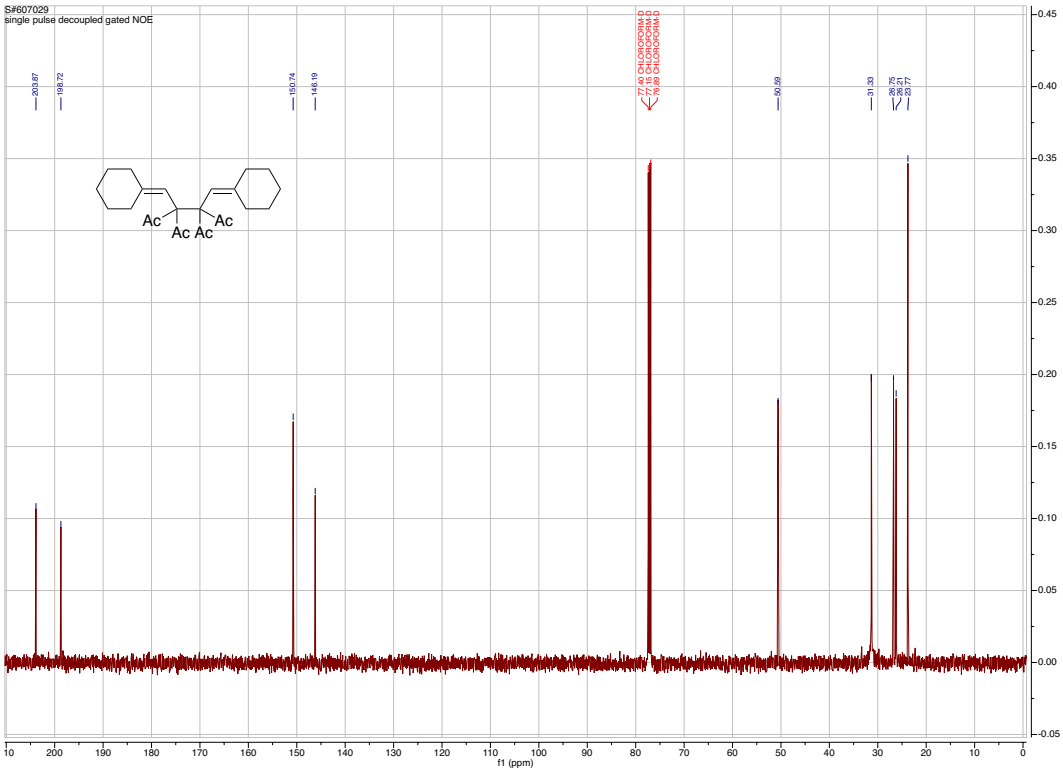

S#596686
DEPT with decoupling
Me
O
Me
OC5H11
4a: R2 = C5H11
145.78
129.83
129.39
129.00
128.81
127.45
127.02
126.69
126.12
77.34 CHLOROFORM-D
63.48
29.38
28.19
25.55
25.84
22.43
14.06
f1 (ppm)

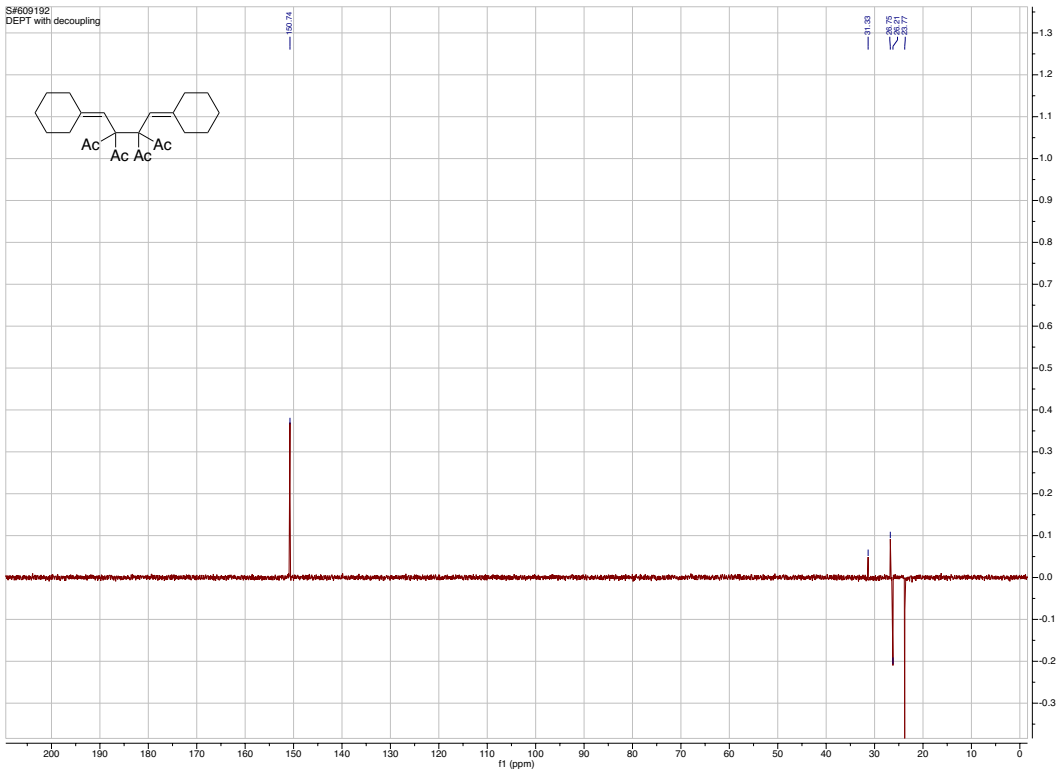

S#543891
single_pulse
Me
O
Me
OC6H13
4a: R2 = C6H13
f1 (ppm)


S#545255
single pulse decoupled gated NOE
193.65
145.75
143.92
143.28
140.40
128.60
128.49
127.77
127.61
126.83
126.11
112.52
90.48
77.30 CHLOROFORM-D1
77.04
76.86 CHLOROFORM-D
63.51
31.59
29.65
29.15
25.84
22.71
22.62
14.13
Me
O
4
3
5
2
Me
O
1
OC6H13
4a: R2 = C6H13
f1 (ppm)


S#605520
DEPT with decoupling
145.78
128.60
128.49
127.77
127.61
126.83
126.11
63.51
31.58
29.64
29.15
25.84
25.70
22.61
14.12
Me
O
4
3
5
2
Me
O
1
OC6H13
4a: R2 = C6H13
f1 (ppm)


S#611735
single_pulse
Ac
Ac Ac
Ac
f1 (ppm)


S#607029
single pulse decoupled gated NOE
203.87
198.72
150.74
146.19
77.16 CHLOROFORM-D
77.00 CHLOROFORM-D
76.89 CHLOROFORM-D
50.89
31.33
26.75
26.57
23.77
Ac
Ac Ac
Ac
f1 (ppm)


S#609192
DEPT with decoupling
150.74
31.93
26.75
26.21
23.77
Ac
Ac Ac
Ac
f1 (ppm)