Supporting Information

Facile butenolide synthesis from functionalized cyclopropenones

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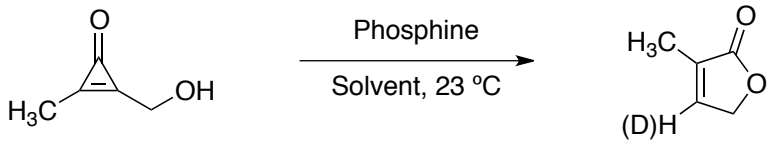
I. General information

Reactions were run at ambient temperature under a nitrogen atmosphere, unless otherwise indicated. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), dimethylformamide (DMF), and acetonitrile (MeCN) were degassed with argon and run through two 4 x 36 inch columns of anhydrous neutral A-2 (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 h). Thin-layer chromatography was performed using Silica Gel 60 F_{254}-coated glass plates (0.25 mm thickness), and visualization was performed with $KMnO_4$ stain and/or UV irradiation. Chromatography was performed with 60 Å (240–400 mesh) silica gel, commercially available from Sorbent Technologies. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. NMR spectra were collected on a Bruker DRX400 instrument (400 MHz ^1H, 376 MHz ^{19}F, 162 MHz ^{31}P), a Bruker DRX500 instrument equipped with a cryo probe (500 MHz ^1H), or an AVANCE600 instrument equipped with a cryo probe (600 MHz ^1H, 151 MHz ^{13}C). Spectra were internally referenced to residual solvent signals ($CDCl_3$ was referenced to 7.26 ppm for ^1H and 77.16 ppm for ^{13}C, CD_3OD was referenced to 3.31 ppm for ^1H and 49.0 ppm for ^{13}C, C_6D_6 was referenced to 7.16 ppm for ^1H and 128.06 ppm for ^{13}C, $(CD_3)_2SO$ was referenced to 2.50 ppm for ^1H, D_2O was referenced to 4.79 ppm for ^1H). ^{19}F and ^{31}P NMR spectra were referenced by indirect absolute chemical shift to residual protio solvent signals. All spectra were collected at 298 K unless stated otherwise. High resolution mass spectrometry (HRMS) was performed by the University of California, Irvine Mass Spectrometry Facility. Crystallographic data were acquired and processed by the University of California, Irvine X-Ray Crystallography Facility.

II. Optimization of butenolide cyclization conditions

Reaction conditions were analyzed using ^{1}H NMR spectroscopy. Cyclopropenone **1a** (25 mM) and phosphine (1–100 mol %) were incubated in the presence of air at ambient temperature. NMR spectra were acquired over 24 h, or until full conversion was observed.

Table S1. Optimization of butenolide cyclization conditions[a]



1a **2a**

entry	phosphine (mol %)	solvent	time	conversion (%)[b]
1	PTA (100)	CD_3OD	10 min	> 95
2	PTA (10)	CD_3OD	2 h	67
3	CyDPP (5)	CD_3OD	2.5 h	90
4	P(*o*-tolyl)$_3$ (5)	CD_3OD	2.5 h	0
5	PPh_3 (100)	CD_3OD	10 min	> 95
6	PPh_3 (100)	DMSO-d_6	22 h	> 95
7	PPh_3 (5)	DMSO-d_6	24 h	16
8	PPh_3 (100)	C_6D_6	1 h	> 95
9	PPh_3 (5)	C_6D_6	24 h	94
10	PPh_3 (10)	CD_3OD	1.5 h	> 95
11	**PPh_3 (5)**	**CD_3OD**	**2.5 h**	**> 95**
12	PTA (1)	CD_3OD	2 h	9
13	PTA (5)	D_2O	2.5 h	52
14	P(*o*-tolyl)$_3$ (5)	CD_3OD	21 h	0
15[c]	P(*o*-tolyl)$_3$ (5)	CH_3OH	18 h	0

[a]Reaction conditions: CpO (15 μmol), TMS-acetylene (3 μmol), solvent (600 μL)

[b]NMR conversion, calculated from integral ratios between starting CpO and butenolide product

[c]Reaction conditions: CpO (0.36 mmol), solvent (14.4 mL), 60 ºC

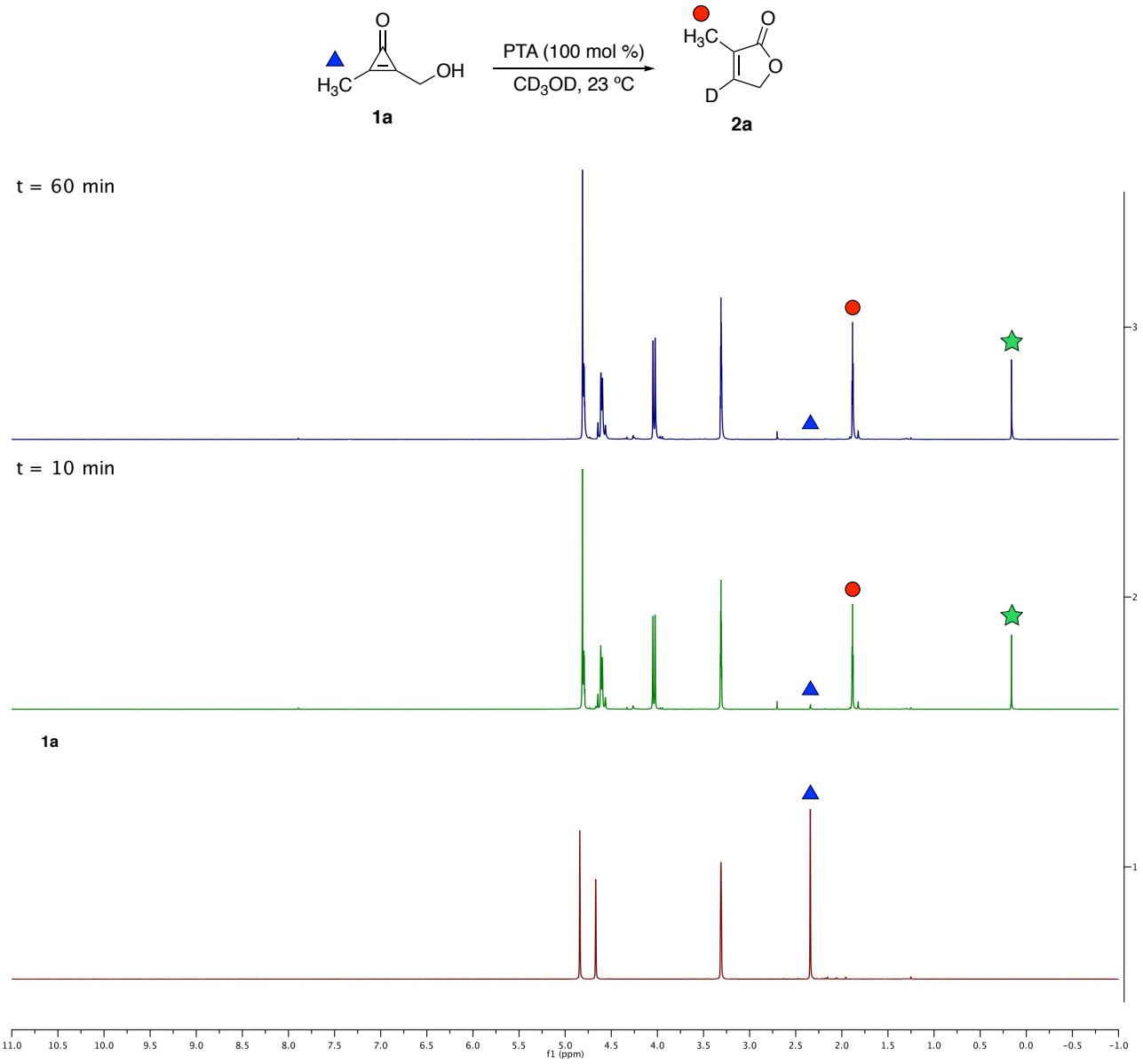


Figure S1. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PTA (100 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

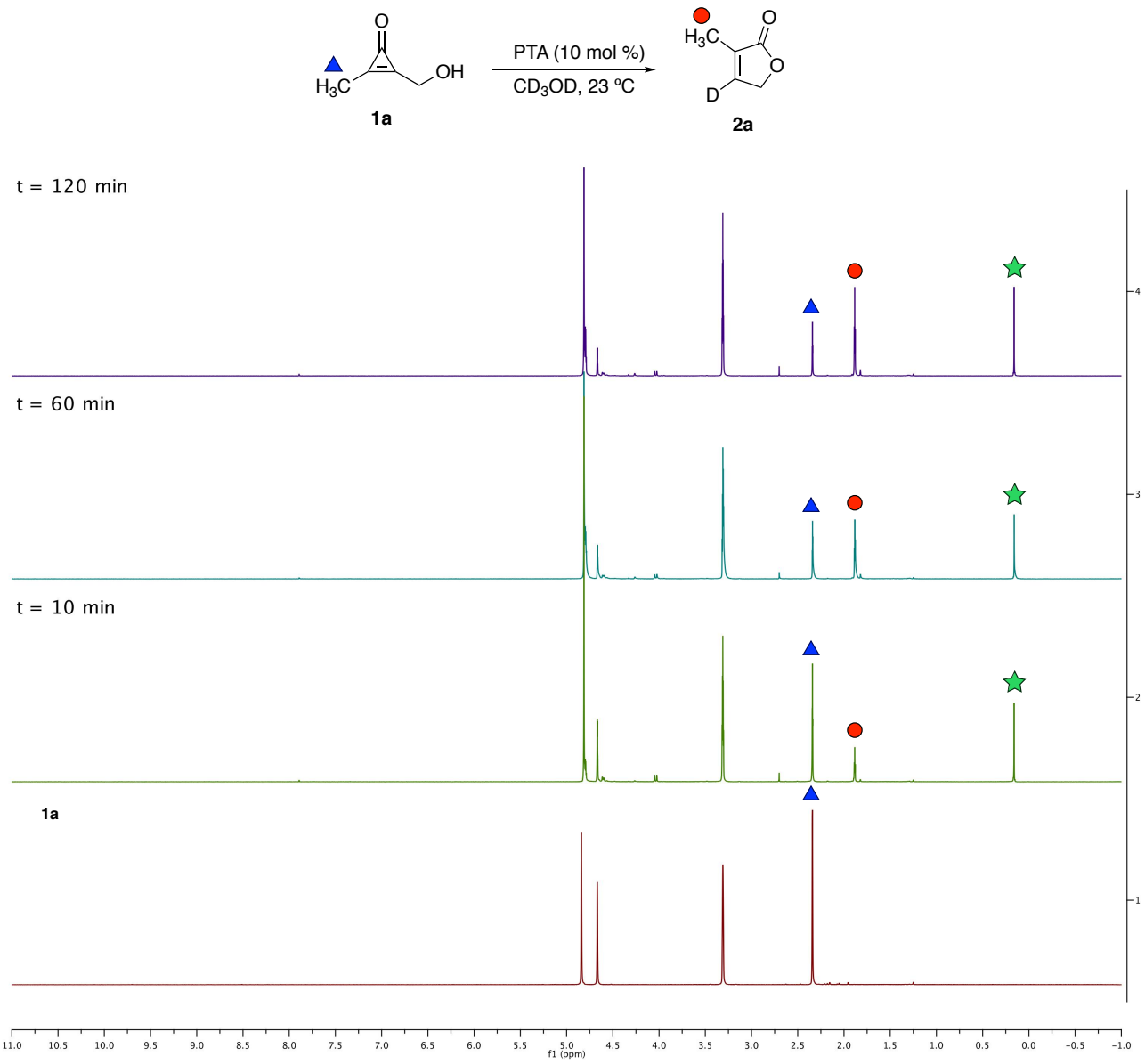


Figure S2. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PTA (10 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

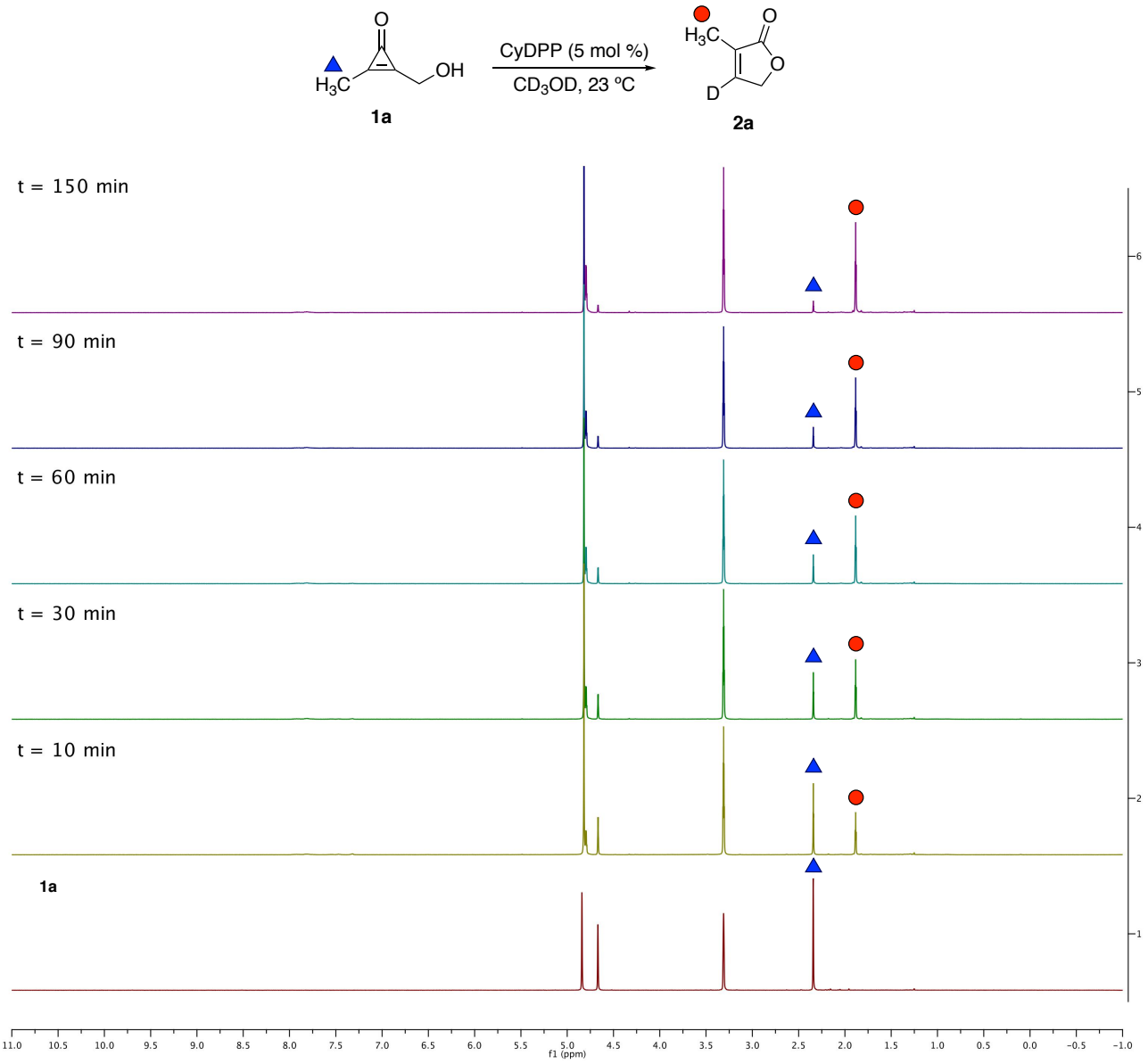


Figure S3. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with cyclohexyldiphenylphosphine (CyDPP, 5 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle).

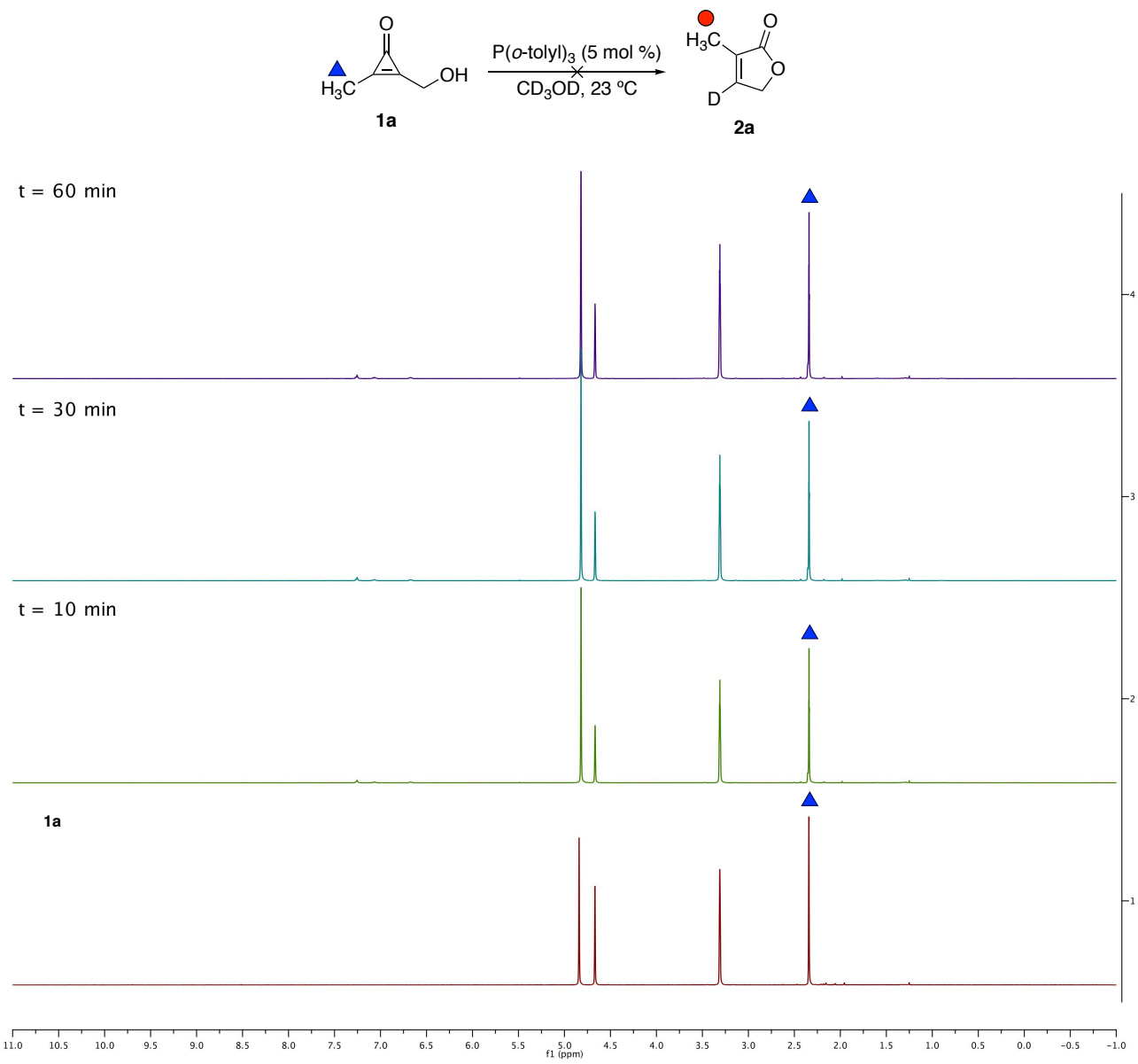


Figure S4. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with P(*o*-tolyl)$_3$ (5 mol %) in CD_3OD (600 μL) at ambient temperature. The reaction was monitored periodically by ^{1}H NMR spectroscopy. No conversion to butenolide **2a** was observed.

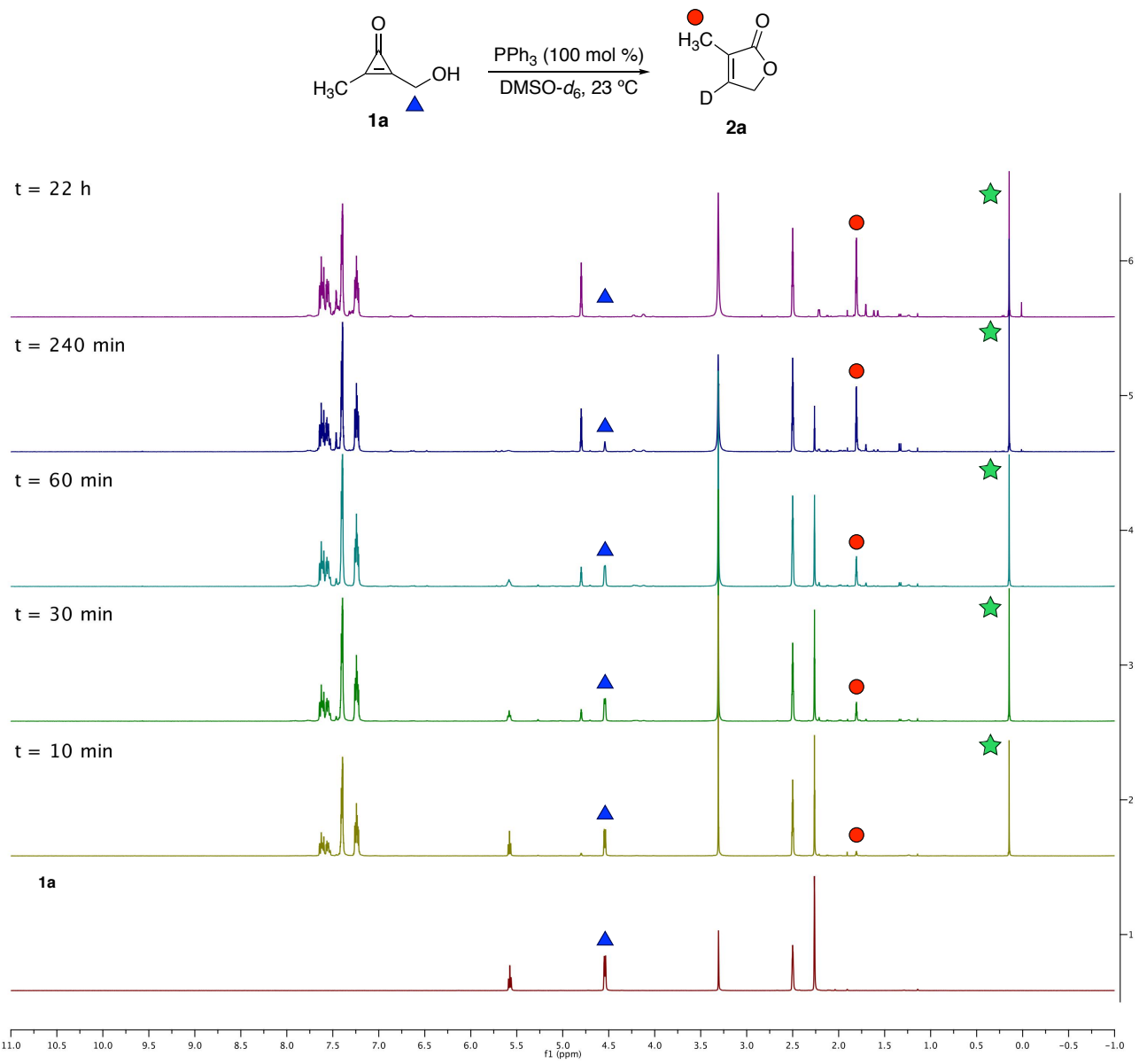


Figure S5. Solvent screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (100 mol %) in DMSO-d_6 (600 µL) at ambient temperature. The reaction was monitored periodically by ^{1}H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

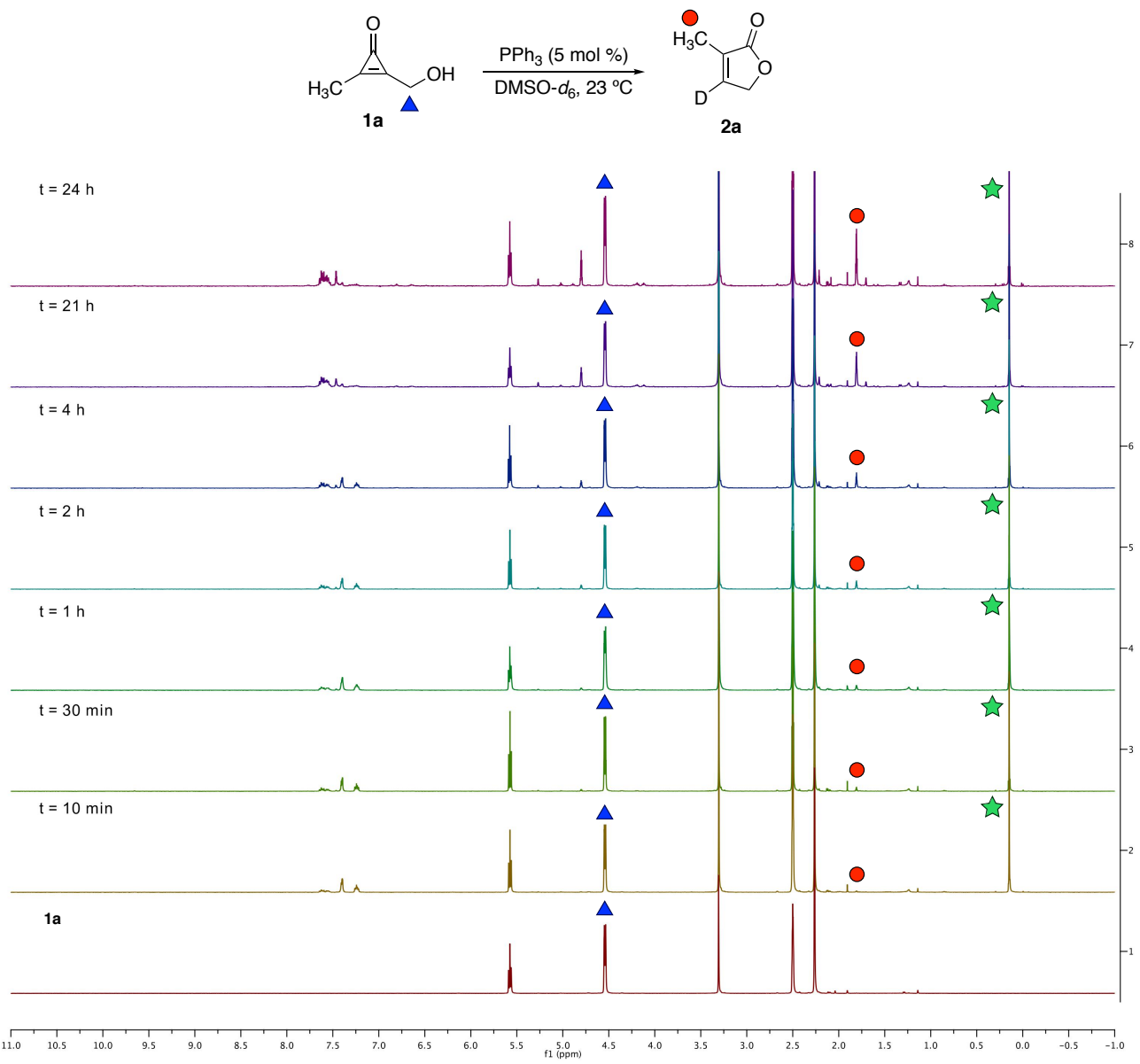


Figure S6. Solvent screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (5 mol %) in DMSO-d_6 (600 µL) at ambient temperature. The reaction was monitored periodically by ^{1}H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

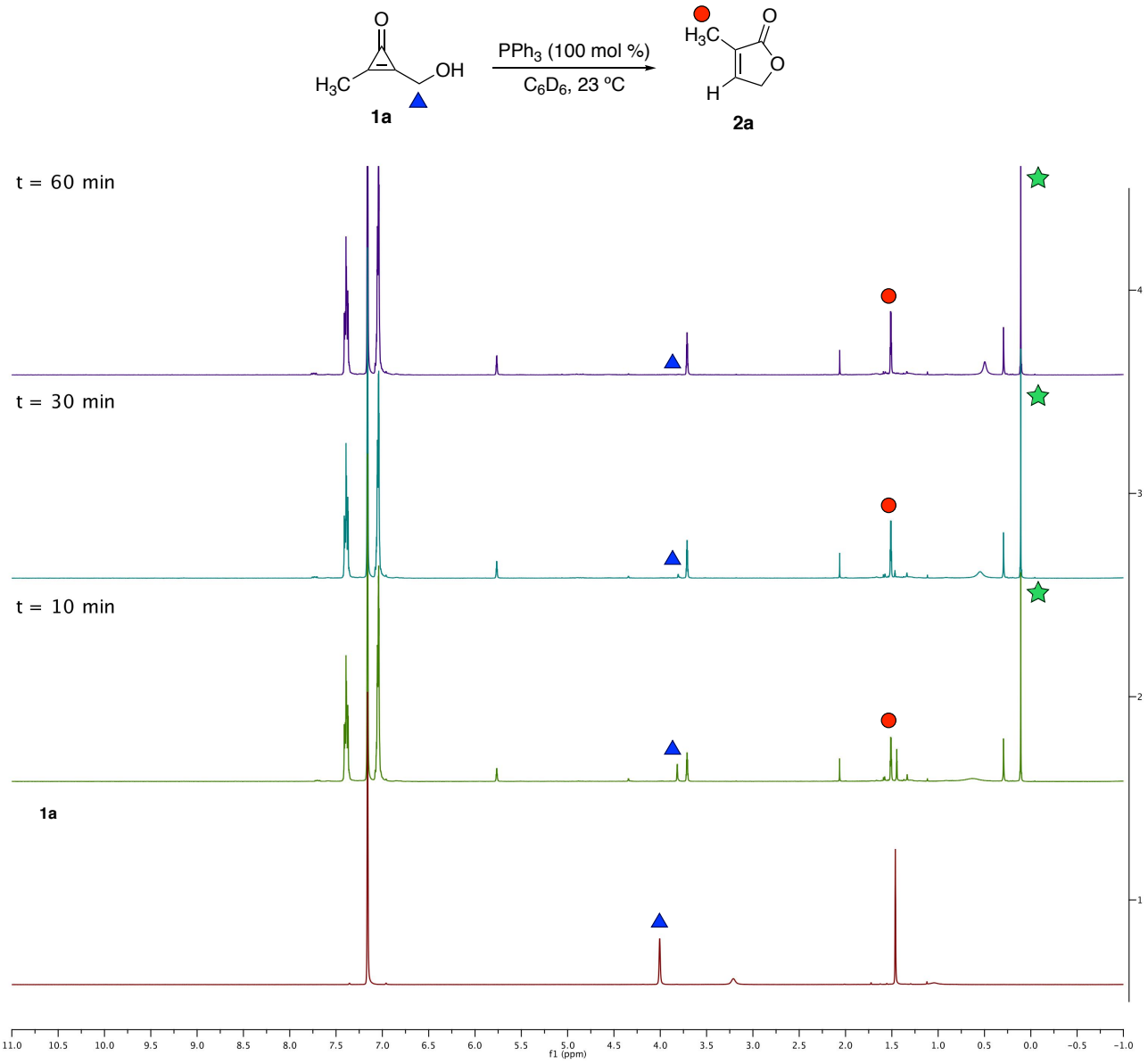


Figure S7. Solvent screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (100 mol %) in C_6D_6 (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

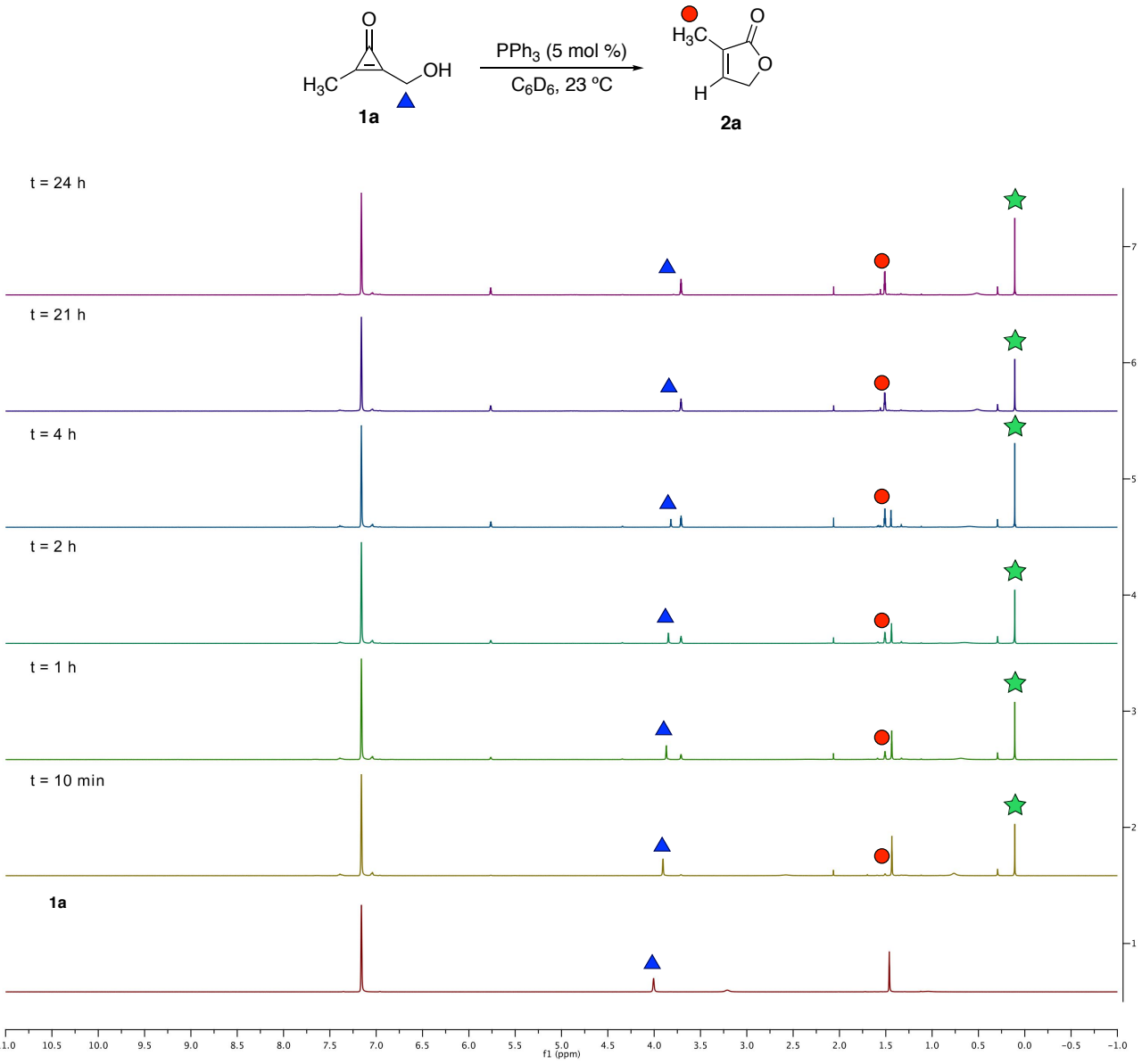


Figure S8. Solvent screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (5 mol %) in C_6D_6 (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

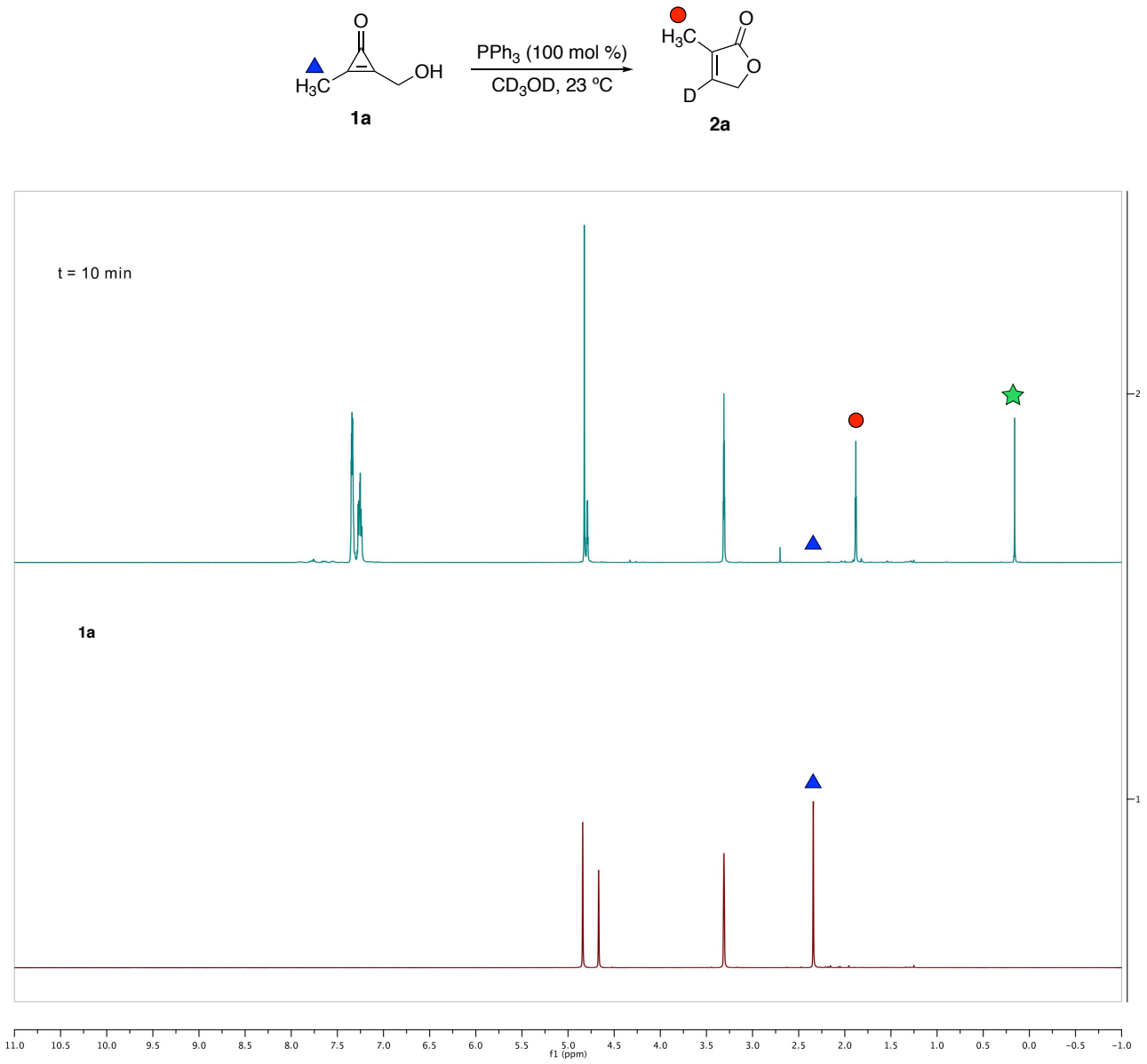
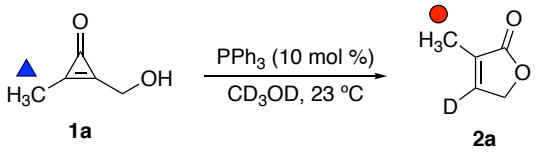


Figure S9. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (100 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.



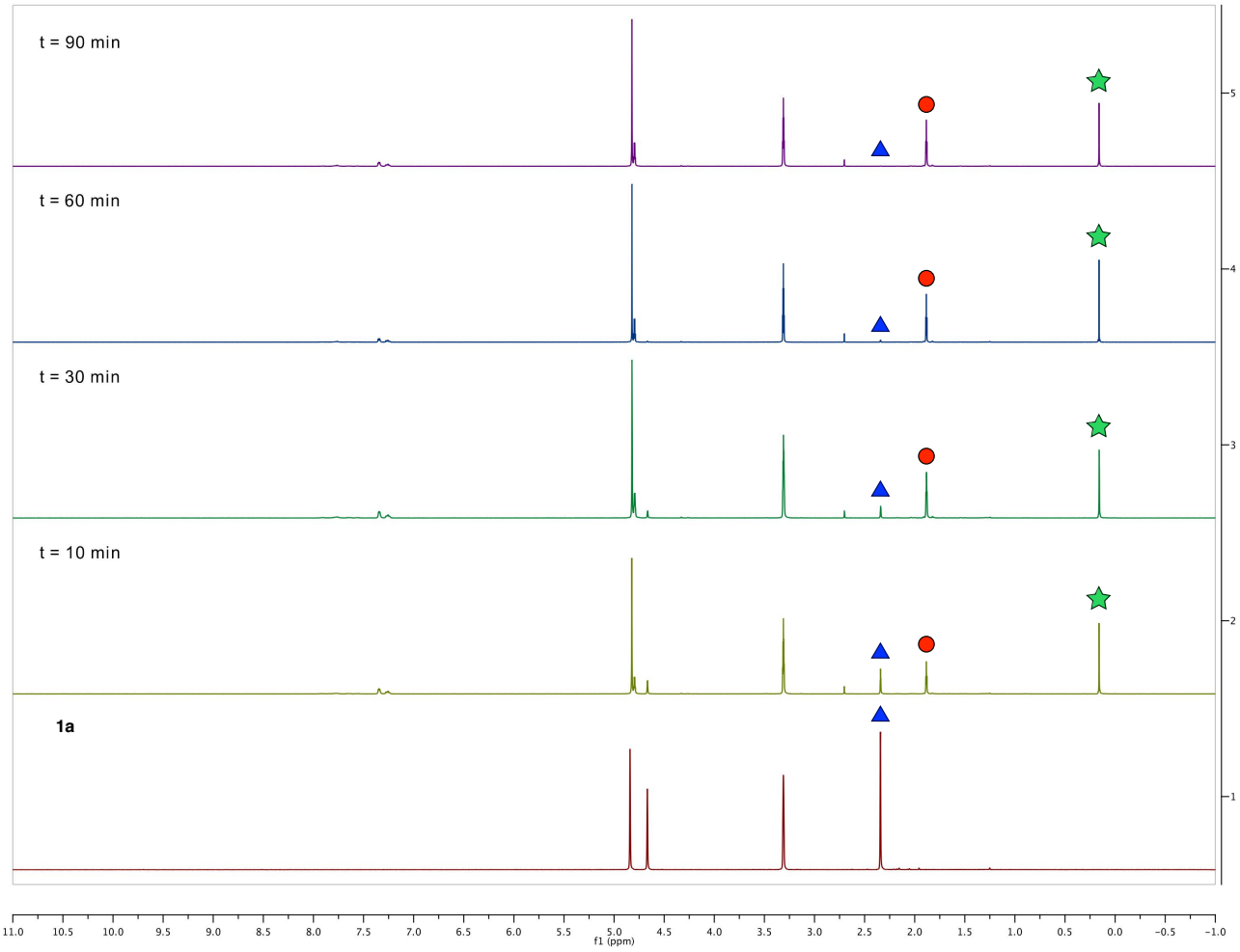


Figure S10. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (10 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

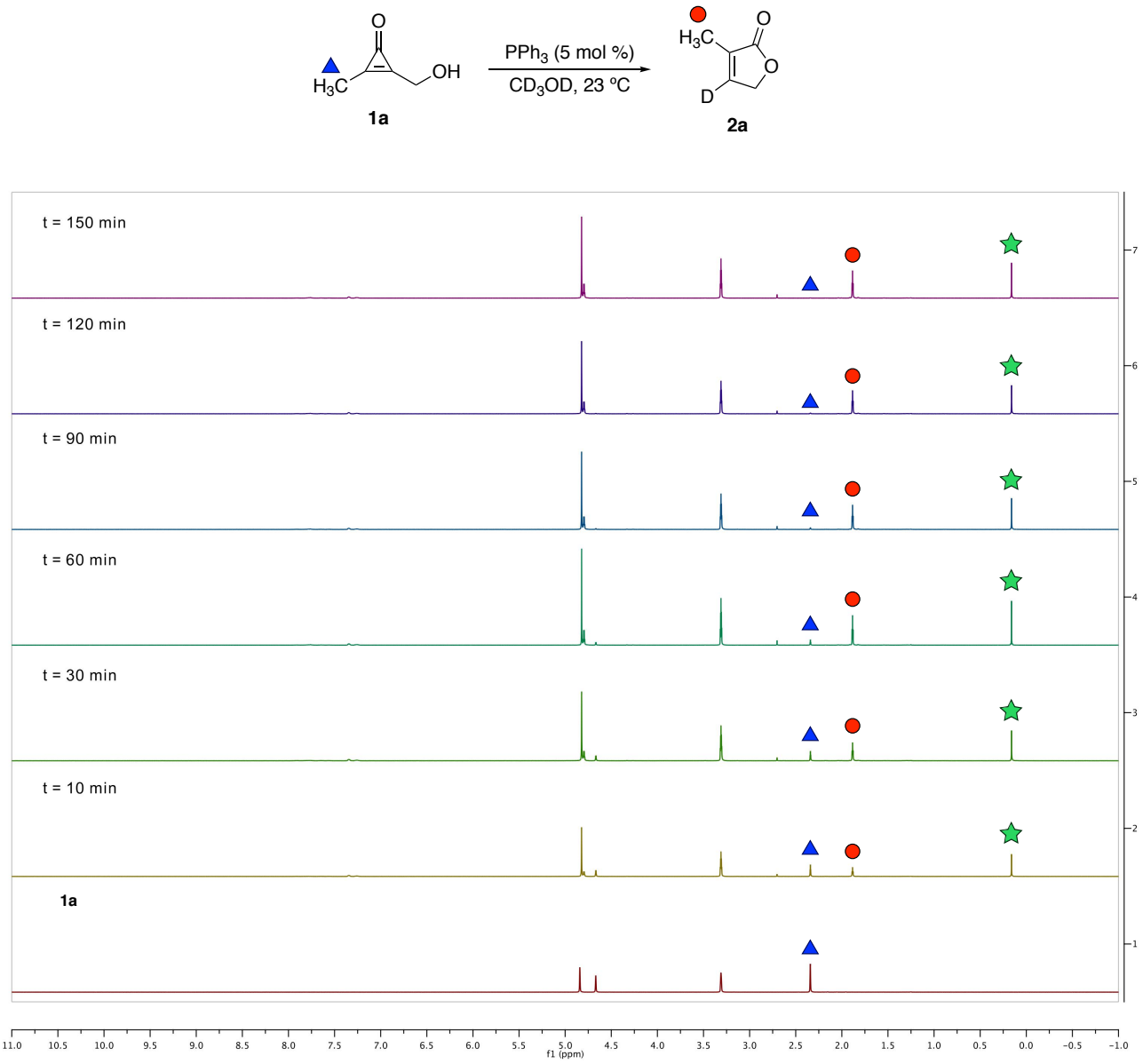


Figure S11. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PPh_3 (5 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

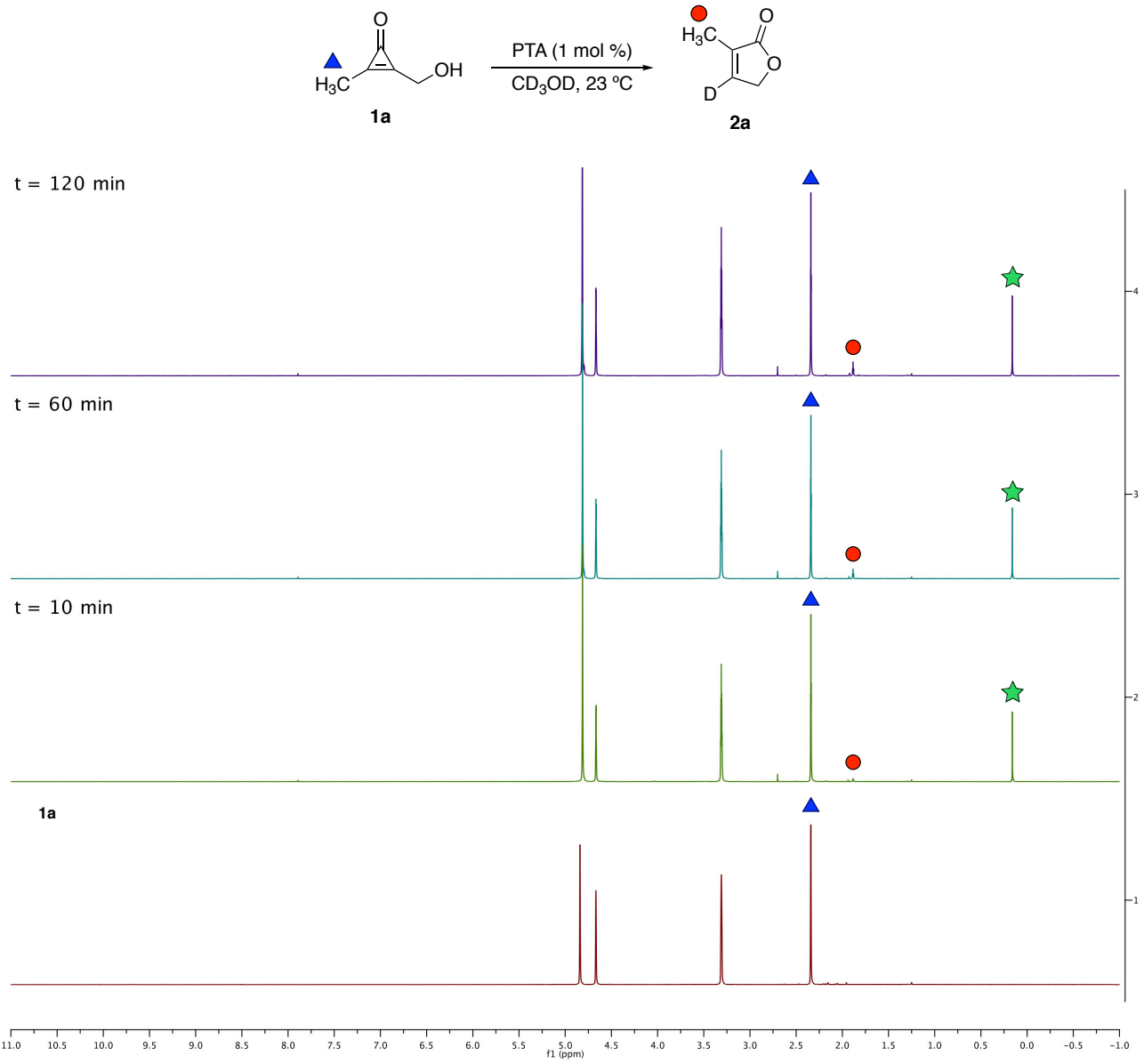


Figure S12. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PTA (1 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle). TMS-acetylene (5 mM, green star) was added as a reference.

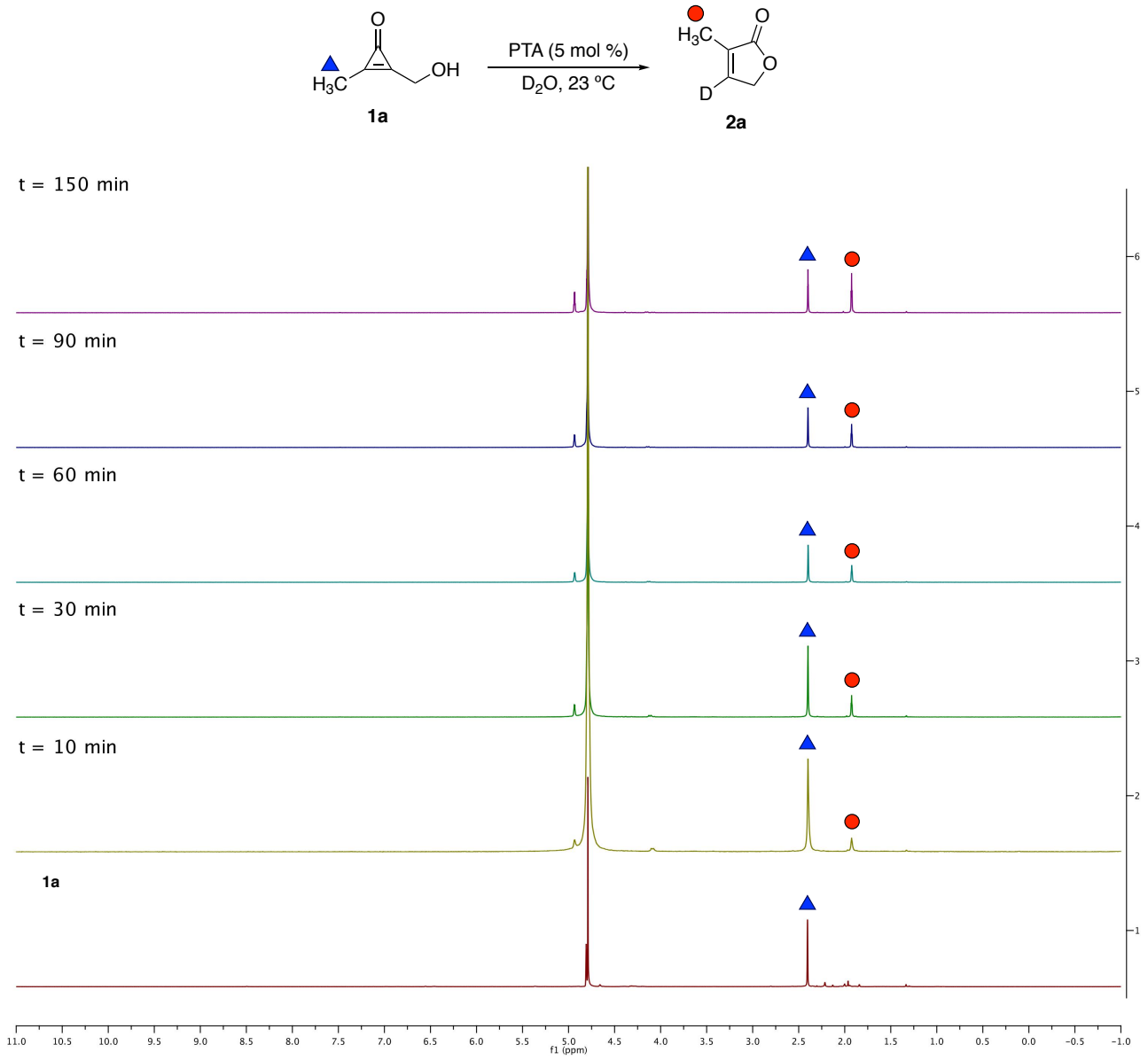


Figure S13. Solvent screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with PTA (5 mol %) in D_2O (600 μL) at ambient temperature. The reaction was monitored periodically by ^1H NMR spectroscopy for the formation of butenolide **2a** (red circle).

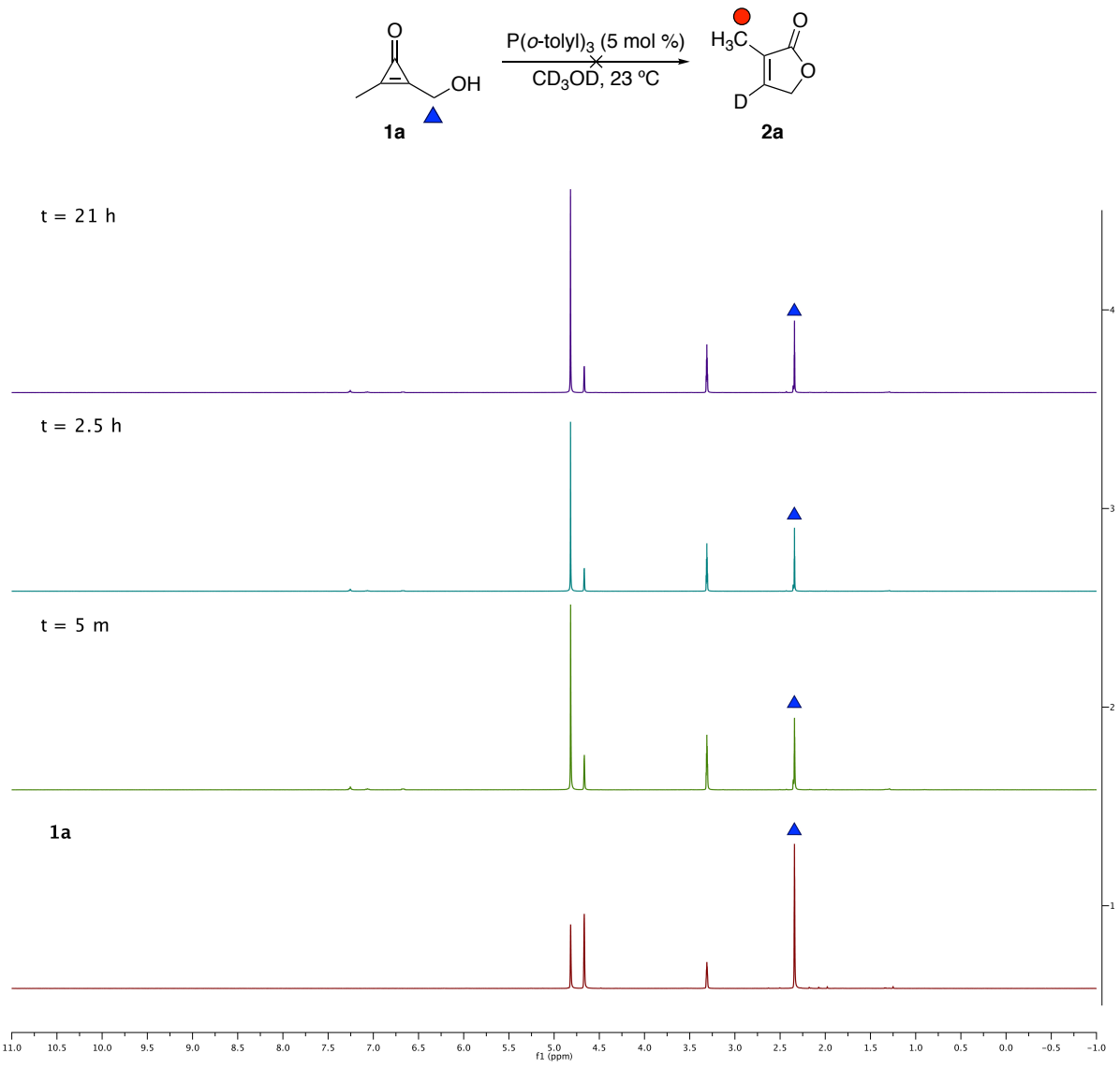


Figure S14. Phosphine screen for butenolide formation. CpO **1a** (25 mM, blue triangle) was incubated with P(*o*-tolyl)$_3$ (5 mol %) in CD_3OD (600 µL) at ambient temperature. The reaction was monitored periodically by ^{1}H NMR spectroscopy. No conversion to butenolide **2a** was observed.

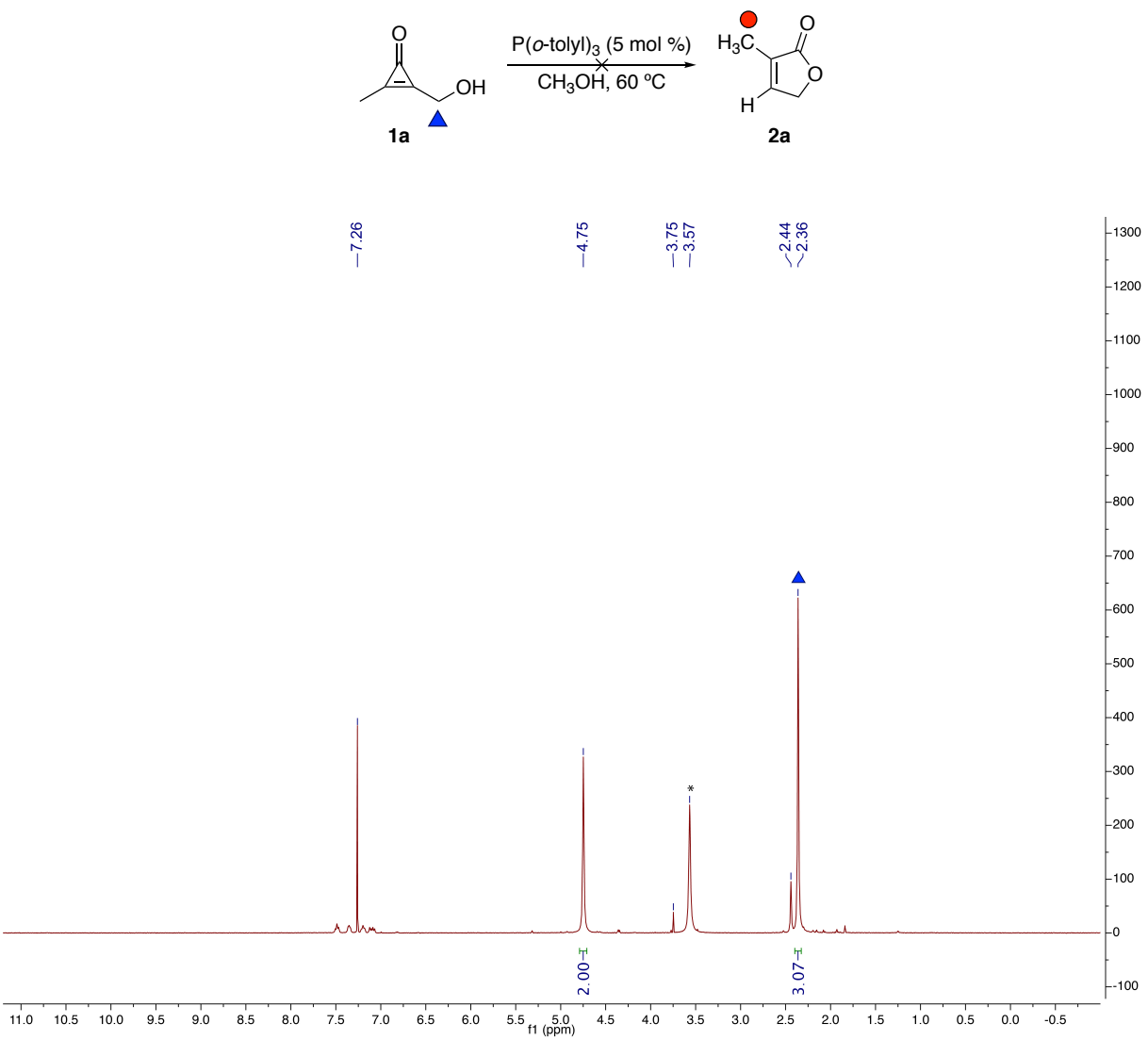


Figure S15. Phosphine screen for butenolide formation. CpO **1a** (35.5 mg, 0.361 mmol, 1.00 equiv., blue triangle) was incubated with P(*o*-tolyl)$_3$ (5.5 mg, 0.021 mmol, 5 mol %) in CH_3OH (14.4 mL) at reflux. After 18 h, the reaction was cooled to ambient temperature and concentrated. The crude mixture was analyzed (in $CDCl_3$) by ^1H NMR spectroscopy. No conversion to butenolide **2a** was observed (* residual methanol).

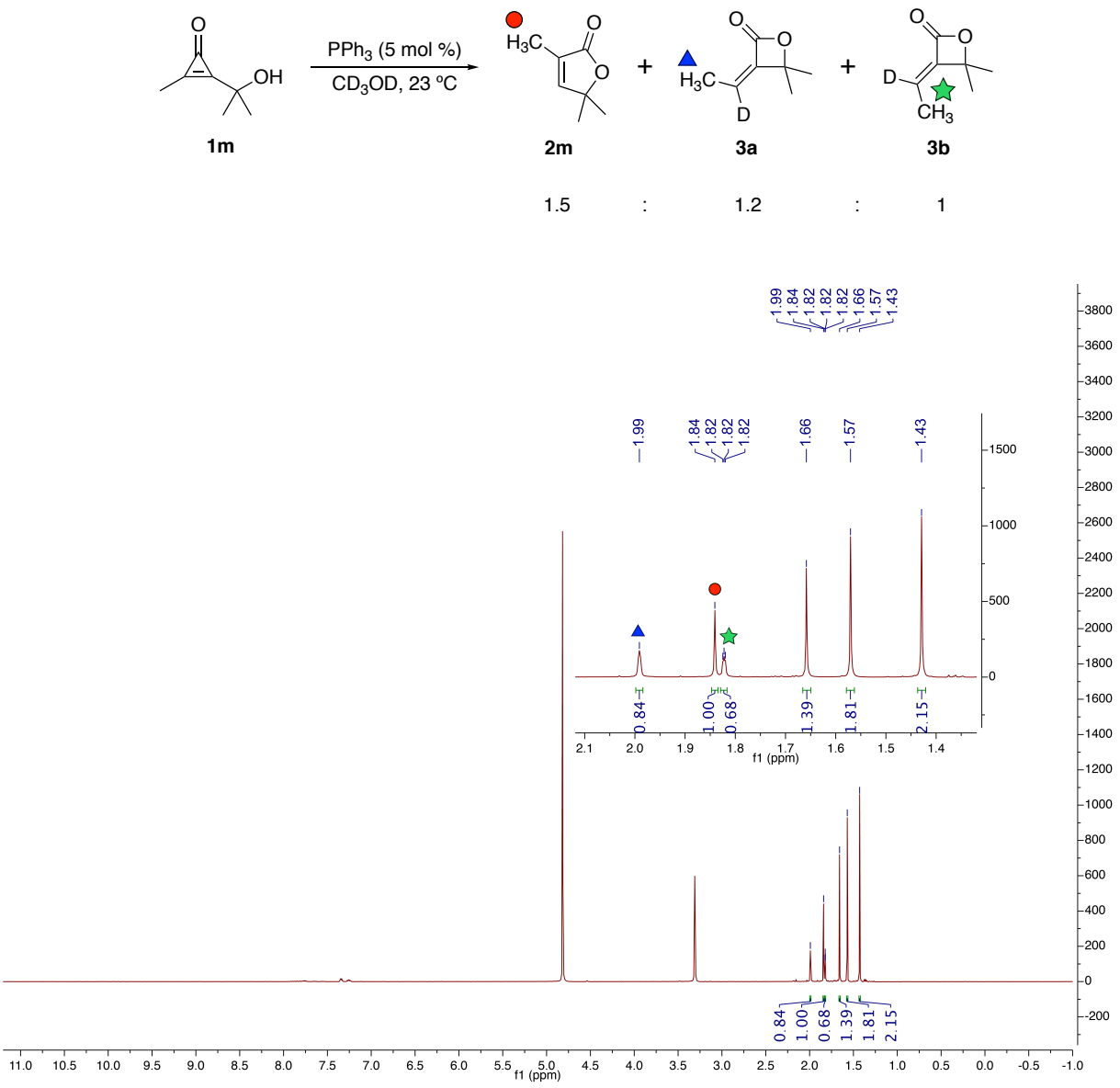


Figure S16. β-Lactone products were only observed with **1m**. CpO **1m** (25 mM) was incubated with PPh_3 (5 mol %) in CD_3OD at ambient temperature. The reaction was monitored by ^1H NMR spectroscopy until full consumption of starting material was observed. CpO **1m** gave a mixture of butenolide **2m** (red circle) and β-lactones **3a**[1] (blue triangle) and **3b**[1] (green star) in an approximate 1.5 : 1.2 : 1.0 molar ratio. Splitting of the β-lactone methyl peaks was attributed to vinylic coupling to deuterium.

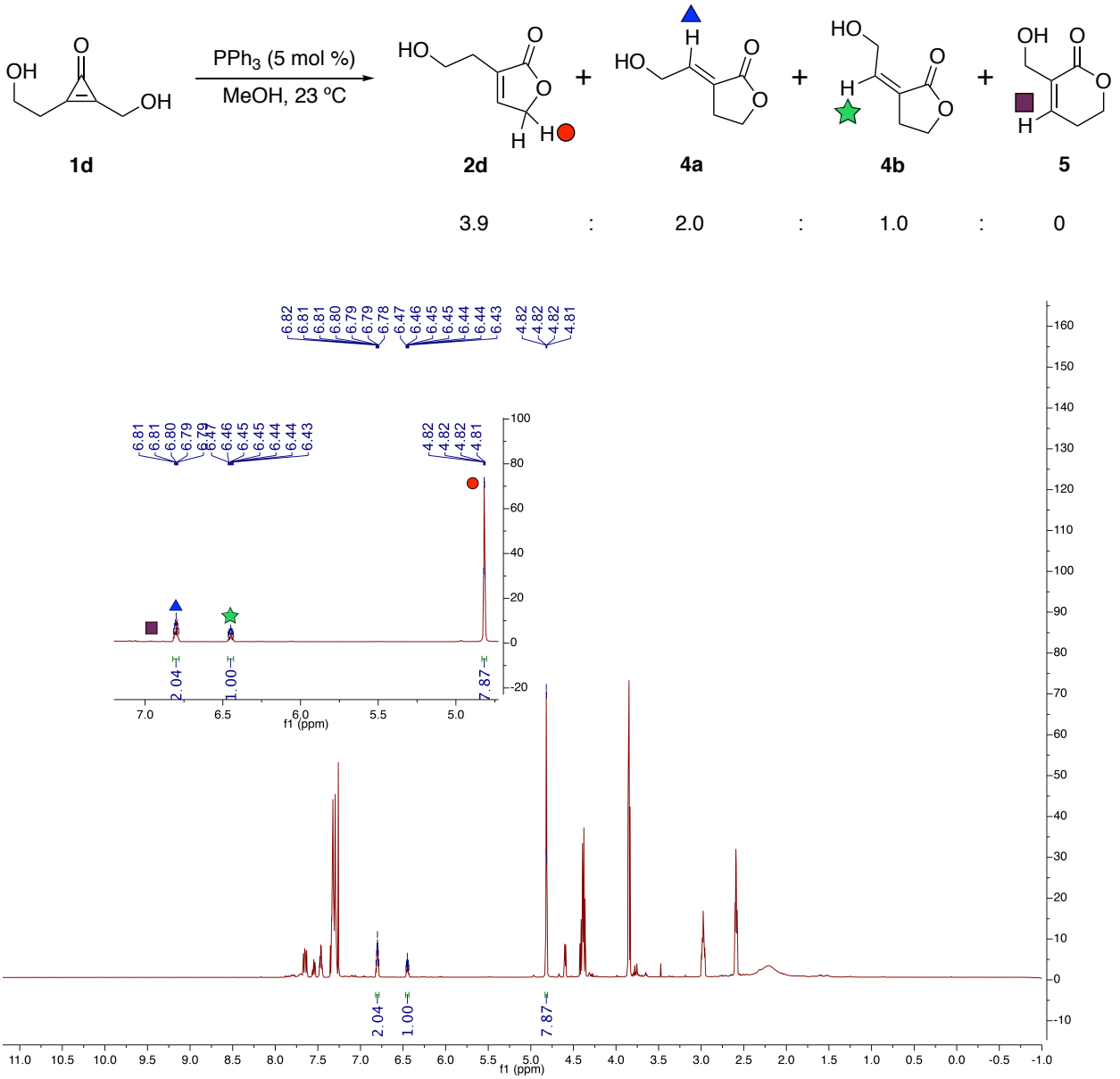


Figure S17. Mechanistic study on butenolide cyclization. Diol-CpO **1d** was incubated with PPh_3 (5 mol %) in CH_3OH. The reaction was concentrated, and the crude mixture was analyzed by ^1H NMR spectroscopy. A mixture of lactones **2d** (red circle), **4a** (blue triangle)[2], and **4b** (green star)[2] was formed in an approximate 3.9 : 2.0 : 1.0 ratio. No δ-lactone **5** (purple square)[3] was observed.

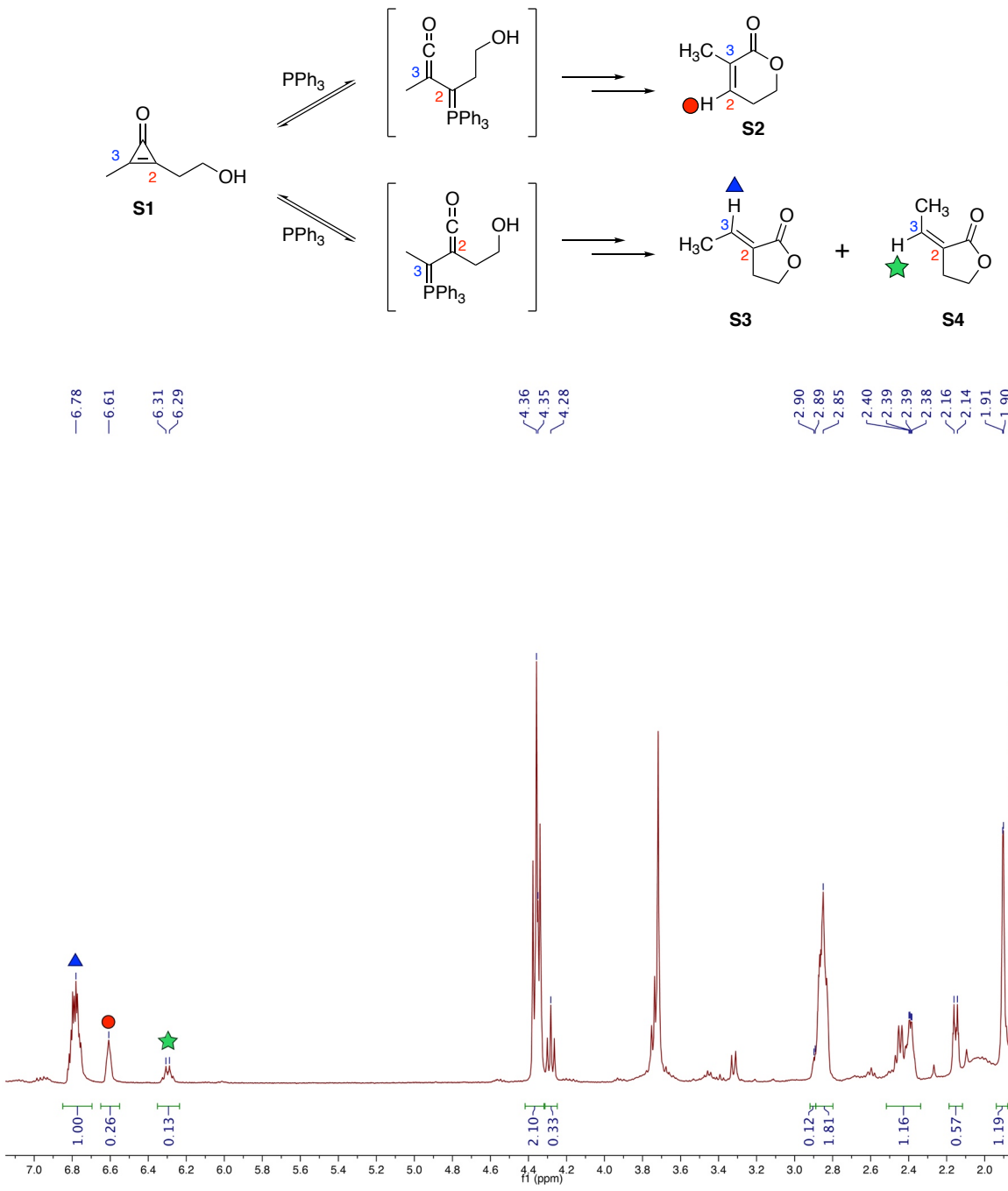
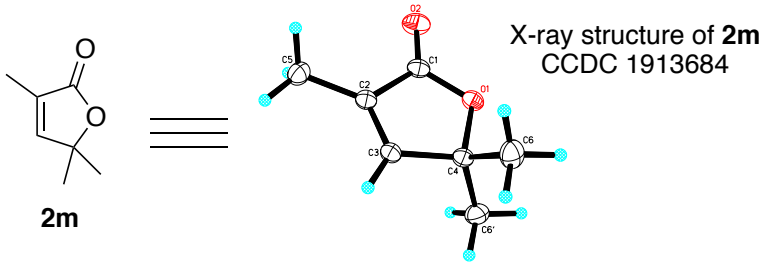


Figure S18. Mechanistic study on ketene-ylide formation. CpO **S1** (25 mM) was incubated with PPh_3 (5 mol %) in CH_3OH. The reaction was concentrated, and the crude mixture was analyzed by ^1H NMR spectroscopy. A mixture of lactones **S2** (red circle)[4], **S3** (blue triangle)[2], and **S4** (green star)[2] was observed. This experiment demonstrates that both ketene-ylides can be formed and trapped.

III. Crystallization of compound 2m

A scintillation vial containing compound **2m** (~60 mg) was dissolved in Et_2O and concentrated *in vacuo* using a Büchi rotary evaporator. The resulting residue was placed under reduced pressure (~0.1 mm Hg). After 2 h, crystals were serendipitously found deposited onto the needle. Crystals were transferred to a new scintillation vial, parafilmed, and stored at –20 ºC until diffraction.

X-ray crystal structure of compound 2m



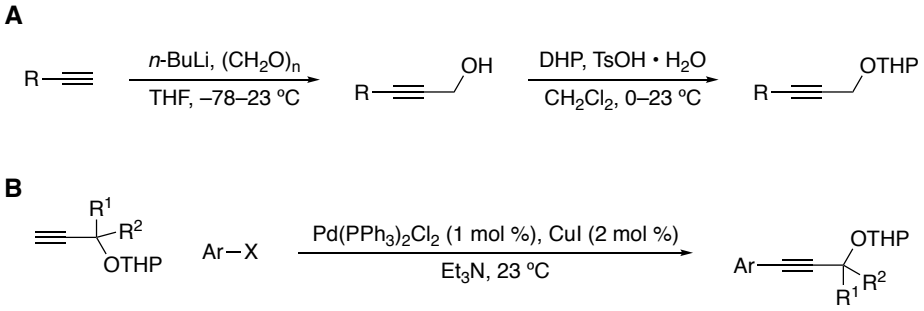
A colorless crystal (0.169 x 0.306 x 0.408 mm) was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[5] program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *C*2, *Cm* and *C*2/*m*. It was later determined that space group *C*2/*m* was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). The molecule was located on a mirror plane.

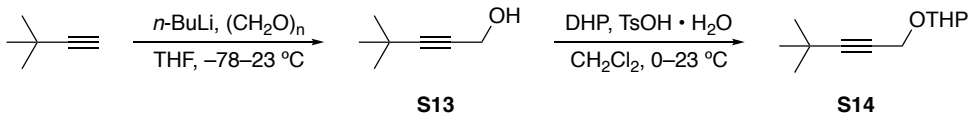
Least-squares analysis yielded wR2 = 0.0922 and Goof = 1.062 for 74 variables refined against 920 data (0.74 Å), R1 = 0.0341 for those 864 data with $I > 2.0\sigma(I)$.

IV. Synthetic procedures

Scheme S1. General synthesis of functionalized alkynes with masked hydroxymethyl tethers. (A) Alkyl-functionalized alkynes were accessed via acetylide addition to formaldehyde, followed by THP protection. (B) Aryl-functionalized alkynes were prepared via Sonogashira cross coupling reactions with THP-protected propargyl alcohols and aryl halides.



Compounds **S1**[10], **S5**[11], **S6**[12], **S7**[13], **S8**[14], **S9**[15], **S10**[16], **S11**[17], and **S12**[18] were synthesized as previously described. All other reagents were obtained from commercial sources and used without further purification.

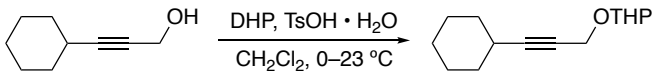


2-((4,4-Dimethylpent-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S14)

To a flame-dried round-bottom flask was added 3,3-dimethylbut-1-yne (0.50 mL, 4.1 mmol, 1.0 equiv.) in anhydrous THF (8.0 mL). The solution was cooled to –78 ºC, and *n*-butyllithium (2.5 M in hexanes, 1.8 mL, 4.5 mmol, 1.1 equiv.) was added dropwise. The solution was stirred at –78 ºC for 1 h. Paraformaldehyde (0.145 g, 4.83 mmol, 1.20 equiv.) was added in one portion, and the reaction was stirred at ambient temperature. When full consumption of the alkyne was observed (as determined by TLC), the solution was quenched with sat. NH_4Cl (90 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were combined, dried with $MgSO_4$ and filtered. The solvent was concentrated *in vacuo*, and the resulting crude oil (**S13**) was used in the next step without further purification.

To a flame-dried round-bottom flask was added 4-toluenesulfonic acid monohydrate (TsOH • H_2O, 5.2 mg, 0.040 mmol, 1 mol %) and a solution of **S9** (0.798 g, 4.07 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (8.0 mL). After cooling to 0 ºC, 3,4-dihydro-2*H*-pyran (DHP, 0.39 mL, 4.5 mmol, 1.1 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting dark solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 5% EtOAc in hexanes) to give compound **S14** (0.65 g, 81% over two steps) as a clear, viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.86 (t, *J* = 3.4 Hz, 1H), 4.31 (d, *J* = 15.4 Hz, 1H), 4.25 (d, *J* = 15.2 Hz, 1H), 3.89 (ddd, *J* = 11.5, 9.3, 2.9 Hz, 1H), 3.52–3.49 (m, 1H), 1.86–1.79 (m, 1H), 1.75–1.70 (m, 1H), 1.64–1.56 (m, 2H), 1.55–1.48 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 96.4, 94.8, 74.2, 62.0, 54.6, 31.0, 30.4, 27.4, 25.4, 19.2. HRMS (ESI^+) calcd. for $C_{12}H_{20}O_2Na$ $[M+Na]^+$ 219.1361 *m/z*, found 219.1360.

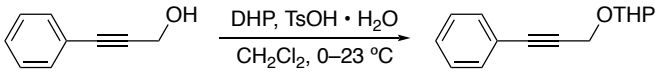


S5 **S15**

2-((3-Cyclohexylprop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S15)

To a flame-dried round-bottom flask was added TsOH • H_2O (5.1 mg, 0.027 mmol, 1 mol %) and a solution of **S5** (0.354 g, 2.56 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (3 mL). After cooling to 0 ºC, DHP (0.24 mL, 2.8 mmol, 1.1 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting dark solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 5% Et_2O in hexanes) to give compound **S15** (0.46 g, 81%) as a colorless oil.

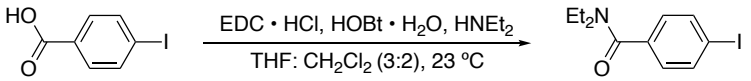
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (t, *J* = 3.4 Hz, 1H), 4.30 (dd, *J* = 15.3, 1.9 Hz, 1H), 4.23 (dd, *J* = 15.3, 1.8 Hz, 1H), 3.85 (ddd, *J* = 11.6, 9.4, 2.8 Hz, 1H), 2.39 (m, 1H), 1.87–1.48 (m, 12H), 1.46–1.40 (m, 2H), 1.34–1.24 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 96.7, 90.9, 75.7, 62.1, 54.8, 32.8, 30.5, 29.3, 26.0, 25.6, 25.0, 19.3. HRMS (ESI^+) calcd. for $C_{14}H_{22}O_2Na$ $[M+Na]^+$ 245.1517 *m/z*, found 245.1512.



S16

2-((3-Phenylprop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S16)

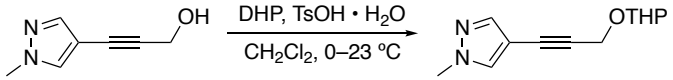
To a flame-dried round-bottom flask was added TsOH • H_2O (28.8 mg, 0.151 mmol, 1 mol %), anhydrous CH_2Cl_2 (30 mL), and 3-phenyl-2-propyn-1-ol (1.86 mL, 15.1 mmol, 1 equiv.). After cooling to 0 ºC, DHP (1.28 mL, 15.1 mmol, 1.00 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting dark solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 0–5% EtOAc in hexanes) to give compound **S16** (2.80 g, 85%) as a pale yellow oil. NMR spectra matched those previously reported.[19]



S17

***N,N*-Diethyl-4-iodobenzamide (S17)**

To a flame-dried round-bottom flask was added 4-iodobenzoic acid (0.496 g, 2.00 mmol, 1.00 equiv.), EDC • HCl (0.461 g, 2.40 mmol, 1.20 equiv.), and HOBt • H_2O (0.367 g, 2.40 mmol, 1.20 equiv.). Anhydrous THF (3.0 mL), anhydrous CH_2Cl_2 (2.0 mL), and diethylamine (0.62 mL, 6.0 mmol, 3.0 equiv.) were added, and the solution was stirred at ambient temperature overnight. The reaction was concentrated *in vacuo* and the crude residue was purified by flash column chromatography (eluting with 0–2% MeOH in CH_2Cl_2) to give compound **S17** (0.58 g, 96%) as a white powder. NMR spectra matched those previously reported.[20]

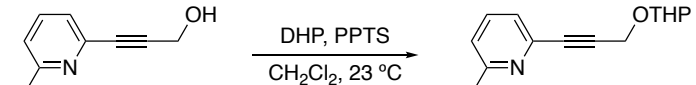


S6 **S18**

1-Methyl-4-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-1*H*-pyrazole (S18)

To a flame-dried round-bottom flask was added TsOH • H_2O (12.2 mg, 0.0641 mmol, 6 mol %) and a solution of **S6** (0.152 g, 1.12 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (3.0 mL). After cooling to 0 ºC, DHP (0.18 mL, 2.0 mmol, 1.8 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 20% EtOAc in hexanes) to give compound **S18** (0.18 g, 74%) as a yellow oil.

^{1}H NMR (400 MHz, C_6D_6) δ 7.64 (s, 1H), 6.81 (s, 1H), 4.97 (t, J = 3.3 Hz, 1H), 4.52 (d, J = 15.7 Hz, 1H), 4.46 (d, J = 15.7 Hz, 1H), 3.75 (ddd, J = 13.5, 11.0, 2.9 Hz, 1H), 3.41–3.36 (m, 1H), 3.02 (s, 3H), 1.80–1.67 (m, 1H), 1.66–1.53 (m, 2H), 1.41–1.31 (m, 1H), 1.30–1.18 (m, 2H). ^{13}C NMR (151 MHz, C_6D_6) δ 142.2, 132.8, 103.2, 96.6, 86.7, 78.0, 61.5, 54.9, 38.2, 30.6, 25.8, 19.2. HRMS (ESI$^+$) calcd. for $C_{12}H_{16}N_2O_2Na$ $[M+Na]^+$ 243.1109 *m/z*, found 243.1106.



S7 **S19**

2-Bromo-6-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)pyridine (S19)

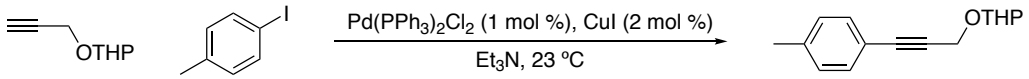
Compound **S14** was synthesized following the general procedure of Duffey, *et al.*[12] To a flame-dried round-bottom flask was added a solution of **S7** (0.201 g, 0.947 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (3.0 mL). DHP (0.17 mL, 1.9 mmol, 2.0 equiv.) was added dropwise, followed by pyridinium *p*-toluenesulfonate (PPTS, 14.2 mg, 0.0577 mmol, 6 mol %). The solution was stirred at ambient temperature overnight. The reaction was poured into a separatory

funnel containing sat. $NaHCO_3$ (40 mL), then extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 10% EtOAc in hexanes) to give compound **S19** (0.21 g, 76%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 4.87 (t, *J* = 3.2 Hz, 1H), 4.52 (d, *J* = 16.1 Hz, 1H), 4.46 (d, *J* = 16.1 Hz, 1H), 3.86 (ddd, *J* = 11.5, 9.3, 2.9 Hz, 1H), 3.57–3.54 (m, 1H), 1.88–1.80 (m, 1H), 1.78–1.73 (m, 1H), 1.67–1.59 (m, 2H), 1.56–1.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 141.8, 138.4, 127.9, 126.2, 97.2, 87.3, 83.9, 62.2, 54.6, 30.3, 25.5, 19.1. HRMS (ESI^+) calcd. for $C_{13}H_{14}BrNO_2Na$ $[M+Na]^+$ 318.0106 *m/z*, found 318.0094.

General procedure A for Sonogashira Coupling

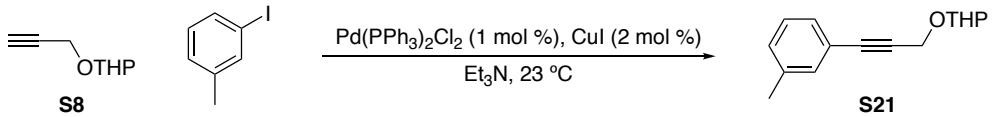
To a flame-dried round-bottom flask was added $Pd(PPh_3)_2Cl_2$ (1 mol %), copper (I) iodide (CuI, 2–3 mol %), anhydrous triethylamine (Et_3N, 0.25–0.31 M aryl halide), aryl halide (1.0 equiv.), and alkyne (1.0–1.1 equiv.). The mixture was stirred at ambient temperature overnight. The resultant slurry was dissolved in CH_2Cl_2 (20 mL) and washed with sat. NH_4Cl (1 x 30 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with hexanes/EtOAc) to afford pure product.



S8 **S20**

2-((3-(*p*-Tolyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S20)

General procedure A was used with the following reagents: 4-iodotoluene (0.654 g, 3.00 mmol, 1.00 equiv.), **S8** (0.42 mL, 3.0 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (21.0 mg, 0.0299 mmol, 1 mol %), CuI (12.0 mg, 0.0630 mmol, 2 mol %), anhydrous Et_3N (12 mL). The crude residue was purified by flash column chromatography (eluting with 1–8% EtOAc in hexanes) to give compound **S16** (0.67 g, 96%) as a yellow oil. NMR spectra matched those previously reported.[19]

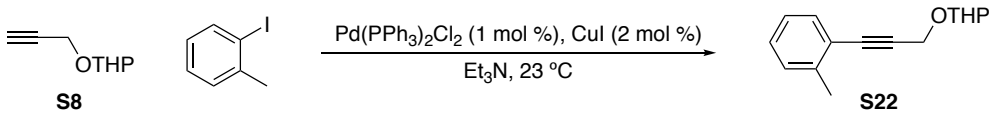


S8 **S21**

2-((3-(*m*-Tolyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S21)

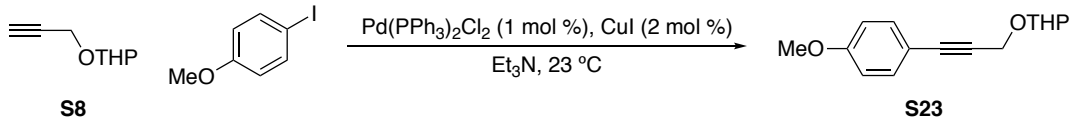
General procedure A was used with the following reagents: 3-iodotoluene (0.13 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.2 mg, 0.010 mmol, 1 mol %), CuI (4.3 mg, 0.023 mmol, 2 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 1–3% EtOAc in hexanes) to give compound **S21** (0.19 g, 80%) as a light brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.91 (t, *J* = 3.4 Hz, 1H), 4.51 (d, *J* = 15.7 Hz, 1H), 4.45 (d, *J* = 15.7 Hz, 1H), 3.89 (ddd, *J* = 11.9, 9.0, 3.1 Hz, 1H), 3.59–3.54 (m, 1H), 2.32 (s, 3H), 1.92–1.73 (m, 2H), 1.70–1.54 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 132.5, 129.4, 129.0, 128.3, 122.7, 96.9, 86.1, 84.9, 62.1, 54.9, 30.4, 25.5, 21.3, 19.2. HRMS (ESI^+) calcd. for $C_{15}H_{18}O_2Na$ $[M+Na]^+$ 253.1205 *m/z*, found 253.1195.



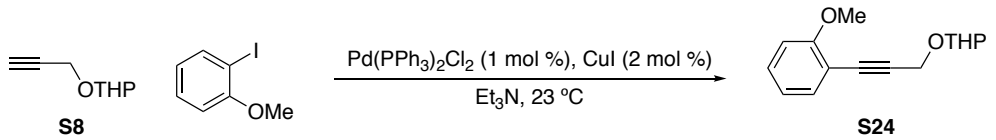
S8 **S22**

2-((3-(*o*-Tolyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S22)
General procedure A was used with the following reagents: 2-iodotoluene (0.13 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (8.1 mg, 0.012 mmol, 1 mol %), CuI (4.2 mg, 0.022 mmol, 2 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 1% EtOAc in hexanes) to give compound **S22** (0.18 g, 78%) as a yellow oil. NMR spectra matched those previously reported.[19]



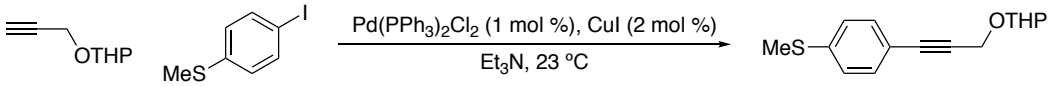
S8 **S23**

2-((3-(4-Methoxyphenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S23)
General procedure A was used with the following reagents: 4-iodoanisole (0.235 g, 1.00 mmol, 1.00 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.2 mg, 0.010 mmol, 1 mol %), CuI (4.1 mg, 0.022 mmol, 2 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 1–3% EtOAc in hexanes) to give compound **S23** (0.22 g, 89%) as a yellow oil. NMR spectra matched those previously reported.[21]



S8 **S24**

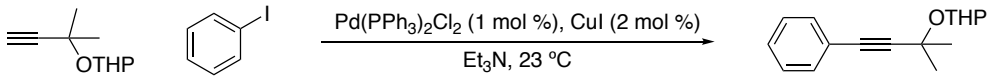
2-((3-(2-methoxyphenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S24)
General procedure A was used with the following reagents: 2-iodoanisole (0.26 mL, 2.0 mmol, 1.0 equiv.), **S8** (0.31 mL, 2.2 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (14.1 mg, 0.0199 mmol, 1 mol %), CuI (7.5 mg, 0.039 mmol, 2 mol %), anhydrous Et_3N (8.0 mL). The crude residue was purified by flash column chromatography (eluting with 2–3% EtOAc in hexanes) to give compound **S24** (0.44 g, 89%) as a brown oil. NMR spectra matched those previously reported.[19]



S8 **S25**

2-((3-(4-(Methylthio)phenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S25)
General procedure A was used with the following reagents: 4-iodothioanisole (0.250 g, 1.00 mmol, 1.00 equiv.), **S8** (0.14 mL, 1.0 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.010 mmol, 1 mol %), CuI (3.8 mg, 0.020 mmol, 2 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 99:0:1–93:6:1 hexanes:EtOAc:C_6H_6) to give compound **S25** (0.24 g, 92%) as an off-white solid.

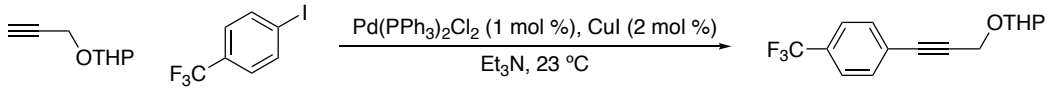
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.16–7.09 (m, 2H), 4.87 (t, J = 3.6 Hz, 1H), 4.50 (d, J = 16.0 Hz, 1H), 4.42 (d, J = 16.0 Hz, 1H), 3.86 (ddd, J = 12.0, 8.8, 3.2 Hz, 1H), 3.57–3.50 (m, 1H), 2.44 (s, 3H), 1.90–1.46 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 132.1, 125.7, 119.0, 96.8, 85.6, 85.2, 62.0, 54.8, 30.3, 25.4, 19.1, 15.3. HRMS (ESI^+) calcd. for $C_{15}H_{18}O_2S$ $[M+Na]^+$ 285.0925 *m/z*, found 285.0925.



S9 **S26**

2-((2-Methyl-4-phenylbut-3-yn-2-yl)oxy)tetrahydro-2*H*-pyran (S26)
General procedure A was used with the following reagents: iodobenzene (0.41 mL, 3.7 mmol, 1.0 equiv.), **S9** (0.683 g, 4.06 mmol, 1.10 equiv.), $Pd(PPh_3)_2Cl_2$ (25.2 mg, 0.0359 mmol, 1 mol %), CuI (16.7 mg, 0.0878 mmol, 2 mol %), anhydrous Et_3N (12 mL). The crude residue was purified by flash column chromatography (eluting with 1% EtOAc in hexanes) to give compound **S26** (0.65 g, 72%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.32–7.28 (m, 3H), 5.16–5.13 (m, 1H), 4.02–3.97 (m, 1H), 3.56–3.50 (m, 1H), 1.92–1.82 (m, 1H), 1.79–1.71 (m, 1H), 1.63 (s, 3H), 1.59 (s. 3H), 1.57–1.52 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.8, 128.4, 128.3, 123.1, 96.5, 91.8, 84.1, 71.7, 63.6, 32.2. 30.9, 30.1, 25.6, 20.8. HRMS (ESI^+) calcd. for $C_{16}H_{20}O_2Na$ $[M+Na]^+$ 267.1361 *m/z*, found 267.1360.

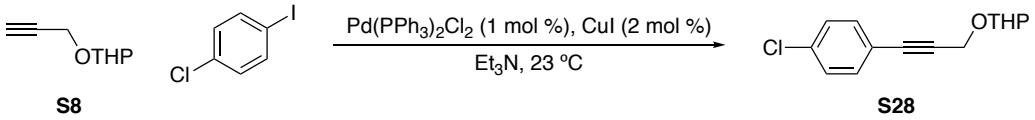


S8 **S27**

2-((3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S27)
General procedure A was used with the following reagents: 4-iodobenzotrifluoride (0.15 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.6 mg, 0.010 mmol, 1 mol %), CuI (5.5 mg, 0.029 mmol, 3 mol %), anhydrous Et_3N (4.0 mL). The crude residue was

purified by flash column chromatography (eluting with 1–2% EtOAc in hexanes) to give compound **S27** (0.18 g, 63%) as a pale yellow oil.

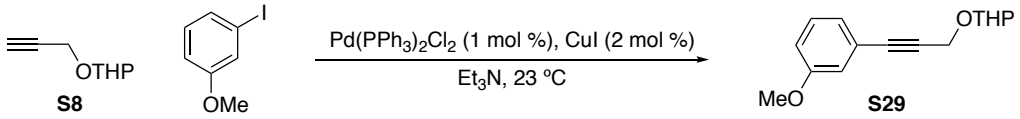
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.52 (m, 4H), 4.88 (t, J = 3.4 Hz, 1H), 4.53 (d, J = 15.9 Hz, 1H), 4.46 (d, J = 16.0 Hz, 1H), 3.88 (ddd, J = 11.8, 9.3, 3.0 Hz, 1H), 3.59–3.54 (m, 1H), 1.89–1.53 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1. ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.1, 130.1 (q, J = 32.7 Hz), 126.7 (d_{app}, J = 1.3 Hz), 125.3 (q, J = 3.7 Hz), 124.0 (q, J = 272.2 Hz), 97.1, 87.9, 84.5, 62.1, 54.7, 30.4, 25.5, 19.1. HRMS (ESI$^+$) calcd. for $C_{15}H_{15}F_3O_2Na$ $[M+Na]^+$ 307.0922, found 307.0920.



S8 **S28**

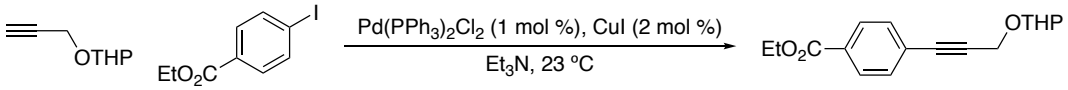
2-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S28)
General procedure A was used with the following reagents: 1-chloro-4-iodobenzene (0.242 g, 1.00 mmol, 1.00 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.2 mg, 0.010 mmol, 1 mol %), CuI (6.2 mg, 0.033 mmol, 3 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 2–5% EtOAc in hexanes) to give compound **S28** (0.19 g, 76%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 4.88 (t, J = 2.8 Hz, 1H), 4.51 (d, J = 15.8 Hz, 1H), 4.44 (d, J = 15.8 Hz, 1H), 3.89 (ddd, J = 12.0, 9.4, 3.0 Hz, 1H), 3.59–3.54 (m, 1H), 1.89–1.56 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.6, 132.2, 128.8, 121.5, 97.2, 86.4, 84.8, 62.2, 54.9, 30.5, 25.6, 19.2. HRMS (ESI$^+$) calcd. for $C_{14}H_{15}ClO_2Na$ $[M+Na]^+$ 273.0658, found 273.0660.



S8 **S29**

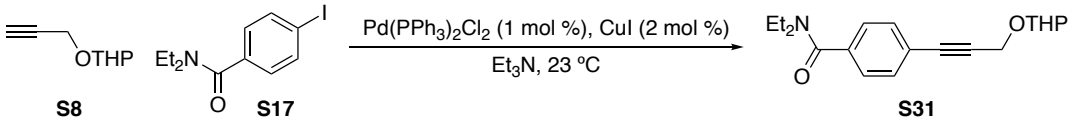
2-((3-(3-Methoxyphenyl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S29)
General procedure A was used with the following reagents: 3-iodoanisole (0.12 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.1 mg, 0.010 mmol, 1 mol %), CuI (3.8 mg, 0.020 mmol, 2 mol %), anhydrous Et_3N (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 1–5% EtOAc in hexanes) to give compound **S29** (0.18 g, 71%) as a yellow oil. NMR spectra matched those previously reported.[19]



S8 **S30**

Ethyl 4-(3-((tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)benzoate (S30)
General procedure A was used with the following reagents: ethyl 4-iodobenzoate (0.26 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.14 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.010 mmol, 1 mol %), CuI (4.0 mg, 0.021 mmol, 2 mol %), anhydrous Et_3N (4 mL). The crude residue was purified by flash column chromatography (eluting with 98:1:1 – 84:15:1 hexanes:EtOAc:C_6H_6) to give compound **S30** (0.24 g, 82%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.93 (m, 2H), 7.52–7.45 (m, 2H), 4.88 (t, *J* = 3.6 Hz, 1H), 4.53 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.88 (ddd, *J* = 12.0, 8.8, 3.2 Hz, 1H), 3.61–3.53 (m, 1H), 1.93–1.46 (m, 7H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 131.7, 130.0, 129.4, 127.3, 97.0, 88.2, 85.1, 62.0, 61.1, 54.7, 30.3, 25.4, 19.0, 14.3. HRMS (ESI^+) calcd. for $C_{17}H_{20}O_4Na$ $[M+Na]^+$ 311.1259 *m/z*, found 311.1264.



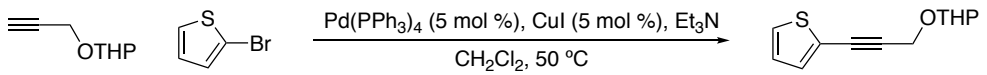
S8 **S17** **S31**

***N*,*N*-Diethyl-4-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)benzamide (S31)**
General procedure A was used with the following reagents: **S17** (0.542 g, 1.8 mmol, 1.00 equiv.), **S8** (0.28 mL, 2.0 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (13.2 mg, 0.019 mmol, 1 mol %), CuI (8.5 mg, 0.045 mmol, 2 mol %), anhydrous Et_3N (8.0 mL). The crude residue was purified by flash column chromatography (eluting with 50% EtOAc in hexanes) to give compound **S31** (0.56 g, >99%, 97% purity).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.89 (t, *J* = 3.3 Hz, 1H), 4.53 (d, *J* = 15.9 Hz, 1H), 4.46 (d, *J* = 15.9 Hz , 1H), 3.89 (ddd, *J* = 11.6, 9.5, 3.0 Hz, 1H), 3.59–3.53 (m, 3H), 3.23 (bs, 2H), 1.89–1.81 (m, 1H), 1.80–1.74 (m, 1H), 1.70–1.62 (m, 2H), 1.59–1.53 (m, 2H), 1.23 (bs, 3H), 1.10 (bs, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 137.2, 132.0, 126.5, 123.8, 97.1, 86.5, 85.3, 62.2, 54.9, 43.4, 39.5, 30.4, 25.5, 19.2, 14.3, 13.0. HRMS (ESI^+) calcd. for $C_{19}H_{25}NO_3Na$ $[M+Na]^+$ 338.1732 *m/z*, found 338.1734.

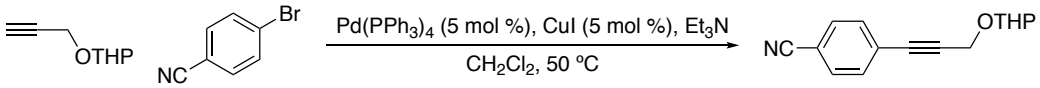
General procedure B for Sonogashira Coupling

To a flame-dried Schlenk tube was added $Pd(PPh_3)_4$ (5 mol %), copper (I) iodide (CuI, 5–8 mol %), a solution of aryl halide (1.0 equiv.) in anhydrous CH_2Cl_2 (0.25 M aryl halide), anhydrous Et_3N (3.0–6.0 equiv.), and alkyne (1.1 equiv.). The tube was sealed, and the solution was stirred at 50 ºC overnight). After cooling to ambient temperature, the reaction was diluted with CH_2Cl_2 (20 mL) and washed with sat. NH_4Cl (1 x 30 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with hexanes/EtOAc) to afford pure product.



S8 **S32**

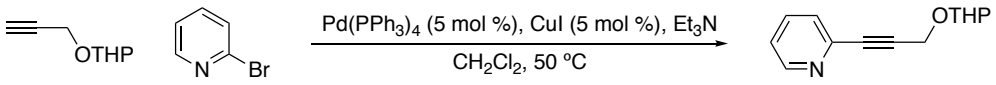
2-((3-(Thiophen-2-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (S32)
General procedure B was used with following reagents: 2-bromothiophene (0.10 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (56.8 mg, 0.0492 mmol, 5 mol %), CuI (15.6 mg, 0.0819 mmol, 8 mol %), anhydrous Et_3N (0.44 mL, 3.1 mmol, 3.0 equiv.), anhydrous CH_2Cl_2 (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 2% EtOAc in hexanes) to give compound **S32** (0.13 g, 57%) as a yellow oil. NMR spectra matched those previously reported.[22]



S8 **S33**

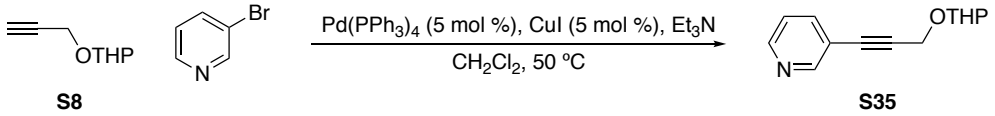
4-(3-((Tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)benzonitrile (S33)
General procedure B was used with the following reagents: 4-bromobenzonitrile (0.203 g, 1.10 mmol, 1.00 equiv.), **S8** (0.17 mL, 1.2 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (64.5 mg, 0.0558 mmol, 5 mol %), CuI (11.1 mg, 0.0583 mmol, 5 mol %), anhydrous Et_3N (0.47 mL, 3.3 mmol, 3.0 equiv.), anhydrous CH_2Cl_2 (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 3–5% Et_2O in hexanes) to give compound **S33** (0.22 g, 82%) as an amber oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 4.87 (t, J = 3.3 Hz, 1H), 4.54 (d, J = 16.0 Hz, 1H), 4.47 (d, J = 16.0 Hz, 1H), 3.88 (ddd, J = 12.0, 9.4, 3.0 Hz, 1H), 3.60–3.54 (m, 1H), 1.91–1.74 (m, 2H), 1.71–1.53 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.5, 132.1, 127.8, 118.6, 112.0, 97.2, 90.0, 84.3, 62.2, 54.8, 30.4, 25.5, 19.1. HRMS (FI^+) calcd. for $C_{11}H_{15}NO_2$ $[M]^+$ 241.1103 *m/z*, found 241.1106.



S8 **S34**

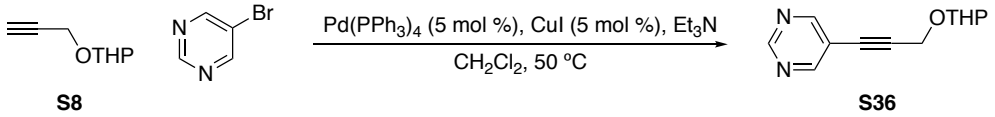
2-(3-((Tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)pyridine (S34)
General procedure B was used with the following reagents: 2-bromopyridine (0.10 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (60.0 mg, 0.0519 mmol, 5 mol %), CuI (11.0 mg, 0.0578 mmol, 5 mol %), anhydrous Et_3N (0.44 mL, 3.2 mmol, 3.0 equiv.), anhydrous CH_2Cl_2 (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 10–50% EtOAc in hexanes) to give compound **S34** (0.13 g, 56%) as a brown oil. NMR spectra matched those previously reported.[23]



S8 **S35**

3-(3-((Tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)pyridine (S35)
General procedure B was used with the following reagents: 3-bromopyridine (0.10 mL, 1.0 mmol, 1.0 equiv.), **S8** (0.16 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (60.4 mg, 0.0523 mmol, 5 mol %), CuI (10.5 mg, 0.0551 mmol, 5 mol %), anhydrous Et_3N (0.88 mL, 6.3 mmol, 6.3 equiv.), anhydrous CH_2Cl_2 (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 2–5% EtOAc in hexanes) to give compound **S35** (0.12 g, 51%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 1.9, 0.6 Hz, 1H), 8.53 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.72 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.23 (ddd, *J* = 7.9, 4.9, 0.8 Hz, 1H), 4.88 (t, *J* = 3.4 Hz, 1H), 4.54 (d, *J* = 15.9 Hz, 1H), 4.46 (d, *J* = 15.9 Hz, 1H), 3.88 (ddd, *J* = 11.8, 9.3, 3.0 Hz, 1H), 3.59–3.55 (m, 1H), 1.90–1.81 (m, 1H), 1.80–1.74 (m, 1H), 1.70–1.52 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.6, 148.9, 138.9, 123.1, 120.0, 97.2, 88.8, 82.6, 62.2, 54.8, 30.4, 25.5, 19.1. HRMS (ESI^+) calcd. for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1181 *m/z*, found 218.1181.



S8 **S36**

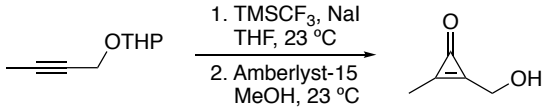
5-(3-((Tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)pyrimidine (S36)
General procedure B was used with the following reagents: 5-bromopyrimidine (0.159 g, 1.00 mmol, 1.00 equiv.), **S8** (0.15 mL, 1.1 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (59.2 mg, 0.0512 mmol, 5 mol %), CuI (15.8 mg, 0.0830 mmol, 8 mol %), anhydrous Et_3N (0.42 mL, 3.0 mmol, 3.0 equiv.), anhydrous CH_2Cl_2 (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 90:9:1 – 85:14:1 hexanes:EtOAc:PhMe) to give compound **S36** (0.15 g, 68%) as a light yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.77 (s, 2H), 4.86 (t, *J* = 3.4 Hz, 1H), 4.54 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 16.1 Hz, 1H), 3.87 (ddd, *J* = 11.5, 9.5, 3.0 Hz, 1H), 3.58–3.55 (m, 1H), 1.88–1.81 (m, 1H), 1.79–1.73 (m, 1H), 1.69–1.54 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 157.1, 119.4, 97.3, 92.8, 79.1, 62.2, 54.6, 30.3, 25.4, 19.0. HRMS (ESI^+) calcd. for $C_{12}H_{15}N_2O_2$ $[M+H]^+$ 219.1134 *m/z*, found 219.1131.

General procedure C for substituted hydroxymethylcyclopropenones

To a flame-dried Schlenk tube was added sodium iodide (NaI, 1.8–2.5 equiv.). The reagent was gently flame-dried under vacuum, then resuspended in a solution of alkyne (1 equiv.) in anhydrous THF (0.25 M alkyne). Trifluoromethyltrimethylsilane ($TMSCF_3$, 2–2.2 equiv.) was added, and the vessel was sealed and stirred vigorously at ambient temperature for 2 d. The slurry was diluted with water (30 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude difluorocyclopropene was used immediately without further purification.

To a flame-dried round-bottom flask was added a solution of crude difluorocyclopropene in anhydrous MeOH (~ 0.5 M w.r.t. alkyne), followed by Amberlyst-15 resin (~70–80 mg $mmol^{-1}$ alkyne). The mixture was stirred until starting material was fully consumed (as observed by TLC, 1:1 CH_2Cl_2:EtOAc). The mixture was filtered to remove the Amberlyst-15 resin, then concentrated *in vacuo*. If necessary, the crude residue was purified by flash column chromatography to afford pure product.

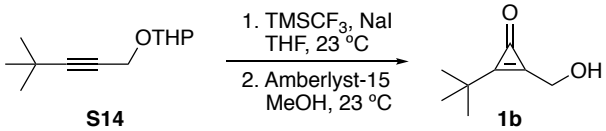


S10 **1a**

2-(Hydroxymethyl)-3-methylcycloprop-2-en-1-one (1a)

General procedure C was used with following reagents: **S10** (1.08 g, 7.00 mmol, 1.00 equiv.), NaI (2.31 g, 15.4 mmol, 2.20 equiv.), $TMSCF_3$ (2.1 mL, 15 mmol, 2.2 equiv.), anhydrous THF (28 mL); Amberlyst-15 (0.150 g), anhydrous MeOH (5 mL). The crude residue was purified by flash column chromatography (eluting with 0–50% acetone in EtOAc) to give compound **1a** (0.44 g, 64% over two steps) as a brown oil.

^1H NMR (400 MHz, CD_3OD) δ 4.67 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 162.4, 160.5, 157.6, 58.5, 10.4. HRMS (ESI^+) calcd. for $C_5H_6O_2Na$ $[M+Na]^+$ 121.0266 *m/z*, found 121.0264.

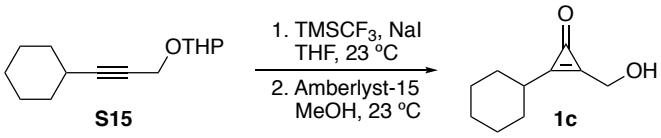


S14 **1b**

2-(*tert*-Butyl)-3-(hydroxymethyl)cycloprop-2-en-1-one (1b)

General procedure C was used with the following reagents: **S14** (0.647 g, 3.30 mmol, 1.00 equiv.), NaI (0.937 g, 6.25 mmol, 1.90 equiv.), $TMSCF_3$ (1.1 mL, 7.3 mmol, 2.2 equiv.), anhydrous THF (8.0 mL); Amberlyst-15 (0.200 g), anhydrous MeOH (6.0 mL). The crude residue was purified by flash column chromatography (eluting with 25% acetone in CH_2Cl_2) to give compound **1b** (0.25 g, 55% over two steps) as a pale yellow solid.

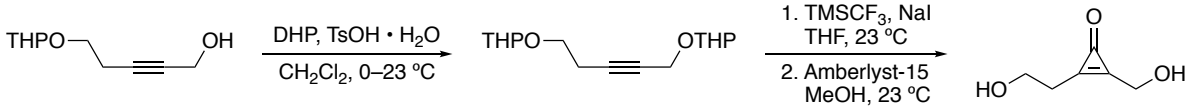
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.69 (s, 2H), 4.49 (bs, 1H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 158.5, 158.3, 57.8, 33.8, 28.0. HRMS (ESI^+) calcd. for $C_8H_{12}O_2Na$ $[M+Na]^+$ 163.0735 *m/z*, found 163.0733.



S15 **1c**

2-Cyclohexyl-3-(hydroxymethyl)cycloprop-2-en-1-one (1c)
General procedure C was used with the following reagents: **S15** (0.218 g, 0.980 mmol, 1.00 equiv.), NaI (0.324 g, 2.16 mmol, 2.20 equiv.), $TMSCF_3$ (0.29 mL, 2.0 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (83.4 mg), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 25–50% EtOAc in CH_2Cl_2) to give compound **1c** (0.11 g, 65% over two steps) as a yellow oil.

^{1}H NMR (500 MHz, CD_3OD) δ 4.66 (s, 2H), 2.90–2.84 (m, 1H), 2.00–1.95 (m, 2H), 1.75–1.68 (m, 2H), 1.66–1.59 (m, 3H), 1.50–1.35 (m, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 163.7, 161.2, 160.8, 58.1, 36.9, 30.9, 26.7, 26.0. HRMS (ESI^+) calcd. for $C_{10}H_{14}O_2Na$ $[M+Na]^+$ 189.0892 *m/z*, found 189.0898.

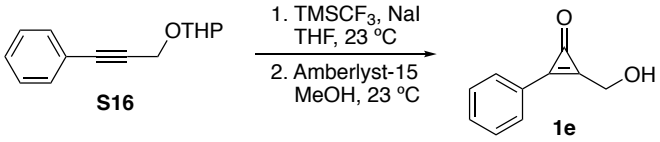


S11 **S37**

2-(2-Hydroxyethyl)-3-(hydroxymethyl)cycloprop-2-en-1-one (1d)
To a flame-dried round-bottom flask was added TsOH • H_2O (1.1 mg, 0.0086 mmol, 1 mol %) and a solution of **S11** (0.160 g, 0.868 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (2.0 mL). After cooling to 0 ºC, DHP (0.083 mL, 0.95 mmol, 1.1 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting dark solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue passed through a plug of silica (eluting with 30% EtOAc in hexanes) to give **S37**, which was used immediately without further purification.

General procedure C was used with the following reagents: **S37** (0.892 g, 3.33 mmol, 1.00 equiv.), NaI (0.945 g, 6.30 mmol, 1.90 equiv.), $TMSCF_3$ (1.1 mL, 7.3 mmol, 2.2 equiv.), anhydrous THF (7.0 mL); Amberlyst-15 (0.300 g), anhydrous MeOH (7.0 mL). The crude residue was purified by flash column chromatography (eluting with 10% MeOH in CH_2Cl_2) to give compound **1d** (0.27 g, 62% over three steps) as an orange oil.

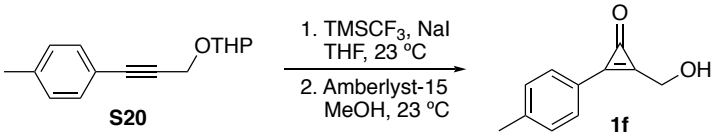
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 2H), 3.97 (t, J = 5.3 Hz, 2H), 2.93 (t, J = 5.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 157.7, 157.5, 58.7, 58.3, 29.7. HRMS (ESI^+) calcd. for $C_6H_8O_3Na$ $[M+Na]^+$ 151.0371 *m/z*, found 151.0371.



S16 1e

2-(Hydroxymethyl)-3-phenylcycloprop-2-en-1-one (1e)
General procedure C was used with the following reagents: **S16** (2.68 g, 12.4 mmol, 1.00 equiv.), NaI (4.10 g, 27.3 mmol, 2.20 equiv.), $TMSCF_3$ (3.7 mL, 25 mmol, 2.0 equiv.), anhydrous THF (52 mL); Amberlyst-15 (0.750 g), anhydrous MeOH (40 mL). The crude residue was purified by flash column chromatography (eluting with 0–100% acetone in EtOAc) to give compound **1e** (1.5 g, 74% over two steps) as a peach solid.

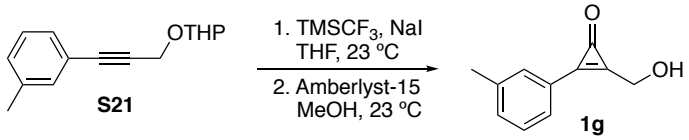
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.53 (m, 3H), 4.93 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 154.4, 154.0, 133.1, 132.4, 129.4, 123.0, 58.9. HRMS (ESI^+) calcd. for $C_{10}H_8O_2$ $[M+Na]^+$ 183.0422 *m/z*, found 183.0422.



S20 1f

2-(Hydroxymethyl)-3-(*p*-tolyl)cycloprop-2-en-1-one (1f)
General procedure C was used with the following reagents: **S20** (0.194 g, 0.842 mmol, 1.00 equiv.), NaI (0.278 g, 1.85 mmol, 2.20 equiv.), $TMSCF_3$ (0.25 mL, 1.7 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (0.145 g), anhydrous MeOH (3.0 mL). After filtration, the resulting solution was concentrated *in vacuo* to give compound **1f** (83 mg, 57% over two steps) as a dark brown solid.

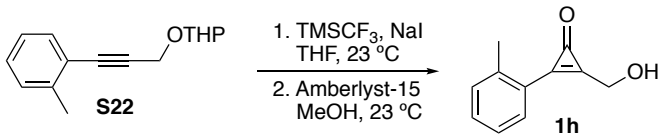
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 153.5, 153.0, 144.1, 132.5, 130.0, 120.2, 58.6, 22.0. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0570.



S21 1g

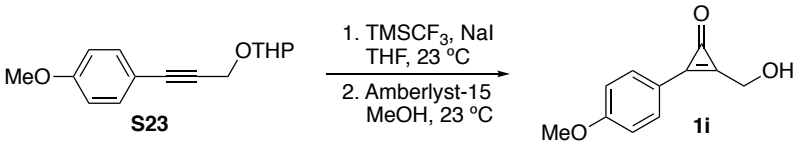
2-(Hydroxymethyl)-3-(*m*-tolyl)cycloprop-2-en-1-one (1g)
General procedure C was used with the following reagents: **S21** (0.183 g, 0.794 mmol, 1.00 equiv.), NaI (0.273 g, 1.82 mmol, 2.29 equiv.), $TMSCF_3$ (0.23 mL, 1.6 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (80.8 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated *in vacuo* to give **1g** (91 mg, 66% over two steps) as a brown solid.

^{1}H NMR (400 MHz, CD_3OD) δ 7.84 (s, 1H), 7.82–7.80 (m, 1H), 7.47–7.46 (m, 2H), 4.85 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 157.9, 156.3, 154.2, 140.6, 135.0, 133.8, 130.6, 130.3, 123.8, 58.4, 21.2. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0577.



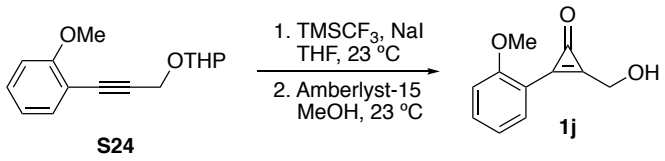
2-(Hydroxymethyl)-3-(*o*-tolyl)cycloprop-2-en-1-one (1h)
General procedure C was used with the following reagents: **S22** (0.183 g, 0.796 mmol, 1.00 equiv.), NaI (0.265 g, 1.77 mmol, 2.22 equiv.), $TMSCF_3$ (0.24 mL, 1.6 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (77.0 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated *in vacuo* to give compound **1h** (92 mg, 67% over two steps) as a peach solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.49 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40–7.33 (m, 2H), 4.88 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 157.7, 155.5, 153.5, 142.9, 134.5, 134.1, 131.7, 127.6, 124.1, 58.4, 20.6. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0587.



2-(Hydroxymethyl)-3-(4-methoxyphenyl)cycloprop-2-en-1-one (1i)
General procedure C was used with the following reagents: **S23** (0.219 g, 0.890 mmol, 1.00 equiv.), NaI (0.299 g, 1.99 mmol, 2.24 equiv.), $TMSCF_3$ (0.26 mL, 1.8 mmol, 2.0 equiv.), anhydrous THF (4.0 mL). After the difluorocarbene insertion, the residue was passed through a plug of silica (eluting with 15–50% EtOAc in CH_2Cl_2) and used in the next step without further purification. Amberlyst-15 (71.2 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated *in vacuo* to give compound **1i** (55 mg, 33% over two steps) as a tan solid.

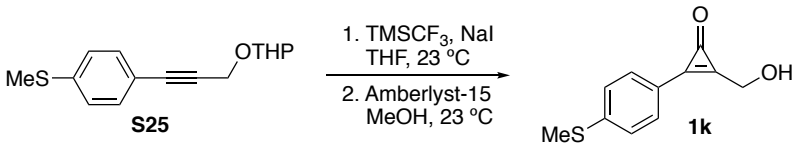
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.85 (s, 2H), 3.85 (s, 3H), 3.66 (br s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 155.5, 153.0, 150.4, 134.5, 115.7, 114.7, 58.5, 55.6. HRMS (ESI^+) calcd. for $C_{11}H_{11}O_3$ $[M+H]^+$ 191.0708 *m/z*, found 191.0704.



S24 1j

2-(Hydroxymethyl)-3-(2-methoxyphenyl)cycloprop-2-en-1-one (1j)
General procedure C was used with the following reagents: **S24** (0.435 g, 1.77 mmol, 1.00 equiv.), NaI (0.538 g, 3.59 mmol, 2.03 equiv.), $TMSCF_3$ (0.52 mL, 3.5 mmol, 2.0 equiv.), anhydrous THF (7.0 mL); Amberlyst-15 (0.136 g), anhydrous MeOH (3.5 mL). The crude residue was purified by flash column chromatography (eluting with 5% MeOH in CH_2Cl_2) to give compound **1j** (0.22 g, 66% over two steps) as an off-white solid.

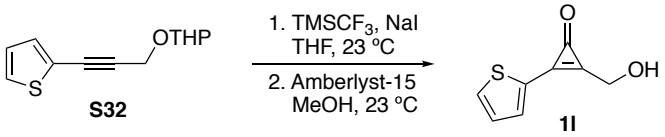
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.9 Hz, 1H), 7.18 (d, J = 8.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 4.84 (s, 2H), 3.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 157.9, 154.4, 150.1, 136.9, 113.1, 112.7, 59.0, 56.5. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528 *m/z*, found 213.0530.



S25 1k

2-(Hydroxymethyl)-3-(4-(methylthio)phenyl)cycloprop-2-en-1-one (1k)
General procedure C was used with the following reagents: **S25** (0.239 g, 0.912 mmol, 1.00 equiv.), NaI (0.308 g, 2.05 mmol, 2.25 equiv.), $TMSCF_3$ (0.27 mL, 1.8 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (72.6 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated *in vacuo* to give compound **1k** (0.15 g, 79% over two steps) as a light beige solid.

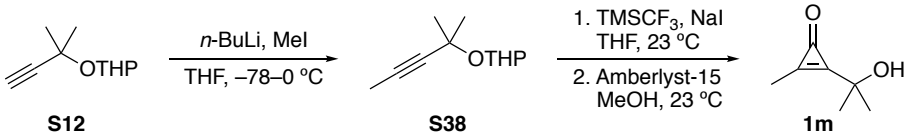
^{1}H NMR (500 MHz, CD_3OD) δ 7.91 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 4.82 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 157.4, 154.3, 153.5, 148.4, 133.7, 126.6, 119.7, 58.3, 14.5. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2SNa$ $[M+Na]^+$ 229.0299 *m/z*, found 229.0291.



S32 1l

2-(Hydroxymethyl)-3-(thiophen-2-yl)cycloprop-2-en-1-one (1l)
General procedure C was used with the following reagents: **S32** (0.132 g, 0.601 mmol, 1.00 equiv.), NaI (0.221 g, 1.47 mmol, 2.45 equiv.), $TMSCF_3$ (0.19 mL, 1.3 mmol, 2.2 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (80.9 mg), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 25–50% EtOAc in CH_2Cl_2) to give **1l** (61 mg, 61% over two steps) as a brown solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.00 (dd, J = 5.1, 1.1 Hz, 1H), 7.88 (dd, J = 3.7, 1.1 Hz, 1H), 7.30 (dd, J = 5.1, 3.8 Hz, 1H), 4.77 (s, 2H). ^{13}C NMR (151 MHz, CD_3OD) δ 154.5, 149.1, 146.9, 138.1, 137.0, 129.9, 124.9, 58.2. HRMS (ESI^+) calcd. for $C_8H_6O_2SNa$ $[M+Na]^+$ 188.9986 *m/z*, found 188.9989.



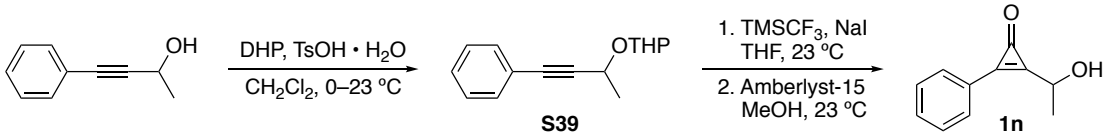
S12 **S38** **1m**

2-(2-Hydroxypropan-2-yl)-3-methylcycloprop-2-en-1-one (1m)

To a flame-dried round-bottom flask was added a solution of **S12** (1.00 g, 5.96 mmol, 1.00 equiv.) in anhydrous THF (12 mL). The solution was cooled to –78 ºC, and *n*-butyllithium was added dropwise (2.5 M in hexanes, 2.6 mL, 6.5 mmol, 1.1 equiv.). The solution was stirred at –78 ºC for 30 min, then methyl iodide was added dropwise (0.45 mL, 7.2 mmol, 1.2 equiv.). The solution was slowly warmed to ambient temperature and stirred overnight. The solution was quenched with sat. NH_4Cl (90 mL), then extracted with Et_2O (2 **x** 50 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude oil **S38** was used in the next step without further purification.

General procedure C was employed using the following amounts of reagents: **S38** (1.05 g, 5.76 mmol, 1.00 equiv.), NaI (1.91 g, 12.7 mmol, 2.21 equiv.), $TMSCF_3$ (1.7 mL, 12 mmol, 2.0 equiv.), anhydrous THF (12 mL); Amberlyst-15 (0.385 g), anhydrous MeOH (10 mL). The crude residue was purified by flash column chromatography (eluting with 50% EtOAc in CH_2Cl_2) to give compound **1m** (0.39 g, 52% over three steps) as a yellow oil.

^{1}H NMR (600 MHz, CD_3OD) δ 2.33 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 166.0, 160.2, 156.3, 71.2, 28.1, 10.1. HRMS (ESI^+) calcd. for $C_7H_{10}O_2Na$ $[M+Na]^+$ 149.0578 *m/z*, found 149.0577.



S39 **1n**

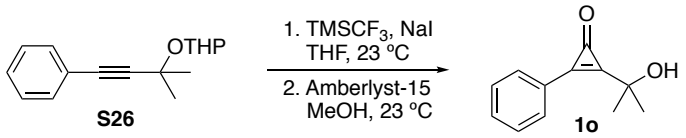
2-(1-Hydroxyethyl)-3-phenylcycloprop-2-en-1-one (1n)

To a flame-dried round-bottom flask was added TsOH • H_2O (3.0 mg, 0.016 mmol, 0.6 mol %) and a solution of 4-phenyl-3-butyn-2-ol (0.369 g, 2.52 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (5.0 mL). After cooling to 0 ºC, DHP (0.24 mL, 2.8 mmol, 1.1 equiv.) was added dropwise, and the solution was slowly warmed to ambient temperature and stirred overnight. The resulting dark solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. $NaHCO_3$ (1 x 50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (eluting with 5–10% EtOAc in hexanes) to give

compound **S39** (0.56 g, 97%) as a colorless oil. The mixture of diastereomers was used in the next step without further purification.

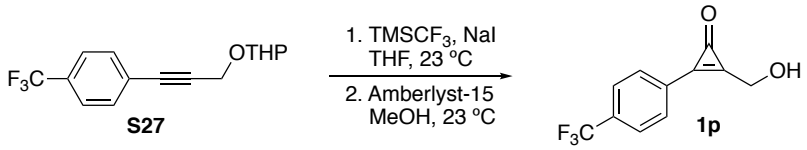
General procedure C was employed using the following amounts of reagents: **S39** (0.460 g, 2.0 mmol, 1.00 equiv.), NaI (0.568 g, 3.78 mmol, 1.89 equiv.), $TMSCF_3$ (0.69 mL, 4.4 mmol, 2.2 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (0.100 g), anhydrous MeOH (5.0 mL). The crude residue was purified by flash column chromatography (eluting with 5–20% acetone in CH_2Cl_2) to give compound **1n** (0.21 g, 59% over two steps) as a tan solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97–7.94 (m, 2H), 7.58–7.49 (m, 3H), 5.14 (qd, J = 6.9, 4.9 Hz, 1H), 2.75 (d, J = 5.0 Hz, 1H), 1.64 (d, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 155.9, 153.1, 133.0, 132.5, 129.3, 123.0, 65.0, 21.4. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0570.



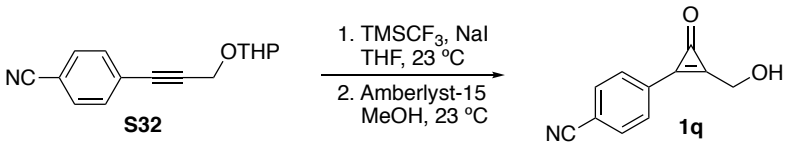
2-(2-Hydroxypropan-2-yl)-3-phenylcycloprop-2-en-1-one (1o)
General procedure C was used with the following reagents: **S26** (0.620 g, 2.54 mmol, 1.00 equiv.), NaI (0.853 g, 5.69 mmol, 2.24 equiv.), $TMSCF_3$ (0.75 mL, 5.1 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (0.173 g), anhydrous MeOH (4.0 mL).The crude residue was purified by flash column chromatography (eluting with 25–50% EtOAc in CH_2Cl_2) to give compound **1o** (0.35 g, 74% over two steps) as a light brown solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.03–8.00 (m, 2H), 7.67–7.62 (m, 1H), 7.60–7.56 (m, 2H), 1.61 (s, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 160.4, 157.9, 152.6, 134.4, 133.7, 130.5, 123.9, 71.3, 28.4. HRMS (ESI^+) calcd. for $C_{12}H_{12}O_2Na$ $[M+Na]^+$ 211.0735 *m/z*, found 211.0728.



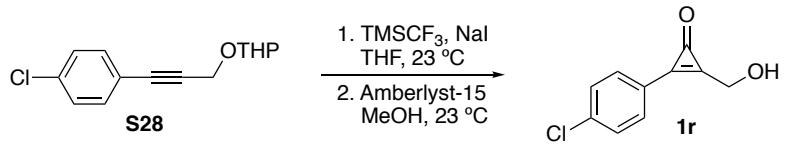
2-(Hydroxymethyl)-3-(4-(trifluoromethyl)phenyl)cycloprop-2-en-1-one (1p)
General procedure C was used with the following reagents: **S27** (0.183 g, 0.644 mmol, 1.00 equiv.), NaI (0.229 g, 1.53 mmol, 2.37 equiv.), $TMSCF_3$ (0.19 mL, 1.9 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (78.6 mg), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 25–50% EtOAc in CH_2Cl_2) to give compound **1p** (45 mg, 31% over two steps) as an off-white solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.20 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 4.90 (s, 2H). ^{19}F NMR (376 MHz, CD_3OD) δ -65.0. ^{13}C NMR (151 MHz, CD_3OD) δ 160.2, 157.2, 152.9, 135.0 (q, J = 32.7 Hz), 133.9, 127.3 (q, J = 3.8 Hz), 127.2 (d_{app}, J = 0.9 Hz), 125.1 (q, J = 271.9 Hz), 58.7. HRMS (ESI^+) calcd. for $C_{11}H_8F_3O_3$ $[M+H]^+$ 229.0476, found 229.0472.



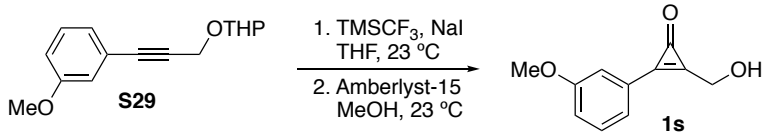
4-(2-(Hydroxymethyl)-3-oxocycloprop-1-en-1-yl)benzonitrile (1q)
General procedure C was used with the following reagents: **S32** (0.217 g, 0.901 mmol, 1.00 equiv.), NaI (0.303 g, 2.02 mmol, 2.24 equiv.), $TMSCF_3$ (0.27 mL, 1.8 mmol, 2.0 equiv.), anhydrous THF (4.0 mL); Amberlyst-15 (75.2 mg), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 50–100% EtOAc in CH_2Cl_2) to give compound **1q** (45 mg, 27% over two steps) as a light tan solid.

^{1}H NMR (400 MHz, $(CD_3)_3SO$) δ 8.07 (s, 4H), 6.02 (t, J = 5.4 Hz, 1H), 4.83 (d, J = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $(CD_3)_3SO$) δ 161.7, 153.5, 151.0, 133.4, 132.0, 126.3, 118.1, 114.4, 57.8. HRMS (ESI^+) calcd. for $C_{11}H_7NO_2Na$ $[M+Na]^+$ 208.0374 *m/z*, found 208.0374.



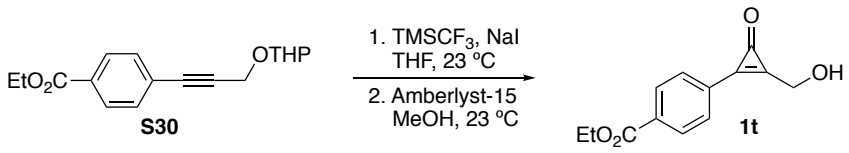
2-(4-Chlorophenyl)-3-(hydroxymethyl)cycloprop-2-en-1-one (1r)
General procedure C was used with the following reagents: **S28** (0.194 g, 0.773 mmol, 1.00 equiv.), NaI (0.258 g, 1.72 mmol, 2.22 equiv.), $TMSCF_3$ (0.23 mL, 1.5 mmol, 2.0 equiv.), anhydrous THF (4.0 mL). The crude residue was passed through a plug of silica (eluting with 10–20% EtOAc in CH_2Cl_2) and used in the next step without further purification. Amberlyst-15 (77.0 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated *in vacuo* to give compound **1r** (35 mg, 23% over two steps) as an off-white solid.

^{1}H NMR (600 MHz, CD_3OD) δ 8.01 (m, 2H), 7.61 (m, 2H), 4.85 (s, 2H). ^{13}C NMR (151 MHz, CD_3OD) δ 157.3, 157.2, 153.0, 140.5, 134.9, 130.8, 122.6, 58.5. HRMS (ESI^+) calcd. for $C_{10}H_7ClO_2Na$ $[M+Na]^+$ 217.0032 *m/z*, found 217.0031.



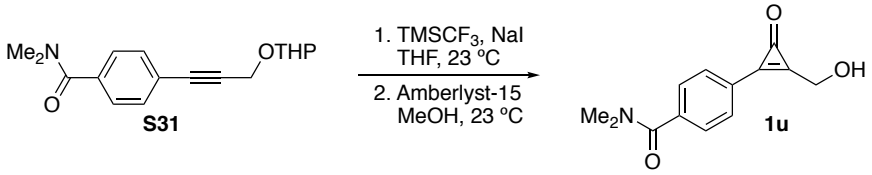
2-(Hydroxymethyl)-3-(3-methoxyphenyl)cycloprop-2-ene-1-one (1s)
General procedure C was used with the following reagents: **S29** (0.176 g, 0.714 mmol, 1.00 equiv.), NaI (0.236 g, 1.57 mmol, 2.21 equiv.), $TMSCF_3$ (0.21 mL, 1.4 mmol, 2.0 equiv.), anhydrous THF (2.9 mL); Amberlyst-15 (60.1 mg), anhydrous MeOH (2.0 mL). After filtration, the solution was concentrated to give compound **1s** (83 mg, 66% over two steps) as a dark yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, J = 7.4 Hz, 1H) 7.47 (s, 1H) 7.39 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H), 4.91 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 155.7, 154.7, 153.7, 124.8, 123.7, 119.7, 116.6, 58.73, 55.6. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528 *m/z*, found 213.0529.



Ethyl 4-(2-(hydroxymethyl)-3-oxocycloprop-1-en-1-yl)benzoate (1t)
General procedure C was used with the following amounts of reagents and modifications: **S30** (0.224 g, 0.777 mmol, 1.00 equiv.), NaI (0.257 g, 1.71 mmol, 2.20 equiv.), $TMSCF_3$ (0.23 mL, 1.6 mmol, 2.0 equiv.), anhydrous THF (3.0 mL). The reaction was sealed and stirred at 85 ºC overnight. Amberlyst-15 (75.0 mg), anhydrous MeOH (4.0 mL). The crude residue was purified by flash column chromatography (eluting with 0–5% acetone in EtOAc) to give compound **1t** (0.11 g, 46% over two steps) as a light brown solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.20 (m, 2H), 8.11 (m, 2H), 4.89 (s, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 166.8, 159.6, 157.4, 153.2, 135.3, 133.3, 131.2, 127.5, 62.7, 58.7, 14.5. HRMS (ESI^+) calcd. for $C_{13}H_{12}O_4Na$ $[M+Na]^+$ 255.0633 *m/z*, found 255.0632.

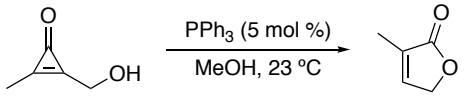


***N*,*N*-Diethyl-4-(2-(hydroxymethyl)-3-oxocycloprop-1-en-1-yl)benzamide (1u)**
General procedure C was used with the following reagents: **S31** (0.564 g, 1.79 mmol, 1.00 equiv.), NaI (0.508 g, 3.39 mmol, 1.89 equiv.), $TMSCF_3$ (0.61 mL, 3.9 mmol, 2.2 equiv.), anhydrous THF (3.6 mL); Amberlyst-15 (0.200 g), anhydrous MeOH (3.6 mL). The crude residue was purified by flash column chromatography (eluting with 10% MeOH in CH_2Cl_2) to give **1u** (0.18 g, 38% over two steps) as a clear orange oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.41 (t, J = 5.8 Hz, 1H), 4.74 (d, J = 5.8 Hz, 2H), 3.52 (q, J = 7.0 Hz, 2H), 3.16 (q, J = 7.0 Hz, 2H), 1.23 (t, J = 7.0 Hz, 3H), 1.06 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 157.3, 155.3, 152.7, 140.5, 132.6, 126.7, 123.5, 58.4, 43.5, 39.7, 14.1, 12.8. HRMS (ESI^+) calculated for $C_{15}H_{17}NO_3Na$ $[M+Na]^+$ 282.1106 *m/z*, found 282.1107.

General procedure D for substituted butenolides

To a scintillation vial containing substituted 2-hydroxymethyl-cyclopropenone (1.0 equiv.) was added anhydrous MeOH (0.25 M) or anhydrous C_6H_6 (0.25 M), followed by triphenylphosphine (PPh_3, 5 mol %, unless otherwise stated). The reaction was stirred at ambient temperature, and monitored until full consumption of starting material was observed (as determined by TLC, 1:1 CH_2Cl_2:EtOAc). The mixture was concentrated *in vacuo*, then purified by flash column chromatography to afford pure product.

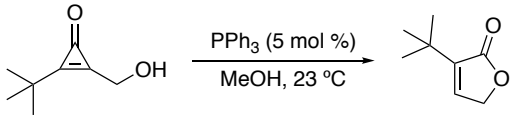


1a **2a**

3-Methylfuran-2(5*H*)-one (2a)

General procedure D was employed using the following reagents: **1a** (48 mg, 0.49 mmol, 1.0 equiv.), triphenylphosphine (PPh_3, 6.2 mg, 0.024 mmol, 5 mol %), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 50% Et_2O in *n*-pentane) to give compound **2a** (20 mg, 62%) as a clear oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 1H), 4.73 (s, 2H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 145.1, 130.0, 70.1, 10.8. HRMS (ESI^+) calcd. for $C_5H_6O_2Na$ $[M+Na]^+$ 121.0266 *m/z*, found 121.0266.

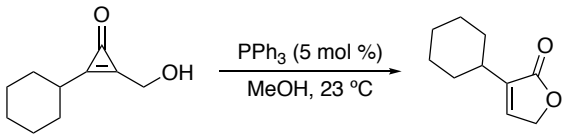


1b **2b**

3-(*tert*-Butyl)furan-2(5*H*)-one (2b)

General procedure D was used with the following reagents: **1b** (0.177 g, 1.26 mmol, 1.00 equiv.), triphenylphosphine (16.5 mg, 0.0629 mmol, 5 mol %), anhydrous MeOH (5.0 mL). The crude residue was purified by flash column chromatography (eluting with 10% EtOAc in hexanes) to give compound **2b** (0.12 g, 69%) as a clear oil.

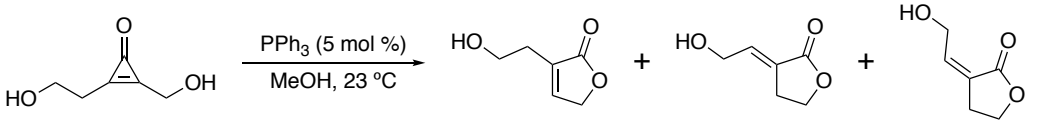
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 1H), 4.71 (s, 2H), 1.26 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 142.6, 142.5, 69.3, 31.7, 28.2. HRMS (ESI^+) calcd. for $C_{12}H_{12}O_2Na$ $[M+Na]^+$ 163.0735 *m/z*, found 163.0731.



1c **2c**

3-Cyclohexylfuran-2(5*H*)-one (2c)
General procedure D was used with the following reagents: **1c** (0.105 g, 0.633 mmol, 1.00 equiv.), PPh_3 (8.7 mg, 0.033 mmol, 5 mol %), anhydrous MeOH (2.5 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2c** (95 mg, 91%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (q_{app}, J = 1.6 Hz, 1H), 4.75 (t, J = 1.7 Hz, 2H), 2.35 ($toct_{app}$, J = 11.6, 1.5 Hz, 1H), 1.97–1.92 (m, 2H), 1.81–1.68 (m, 3H), 1.43–1.30 (m, 2H), 1.26–1.15 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 142.7, 139.5, 70.2, 35.0, 31.6, 26.2, 26.1. HRMS (ESI^+) calcd. for $C_{10}H_{14}O_2Na$ $[M+Na]^+$ 189.0892 *m/z*, found 189.0893.



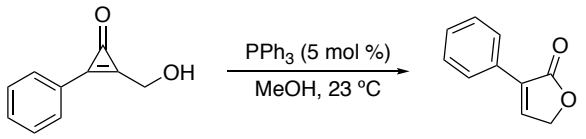
1d **2d** **4a** **4b**

3-(2-Hydroxyethyl)furan-2(5*H*)-one (2d)
General procedure D was used with the following reagents: **1d** (0.102 g, 0.790 mmol, 1.00 equiv.), PPh_3 (42.0 mg, 0.160 mmol, 5 mol %), anhydrous MeOH (3.2 mL). The crude residue was purified by flash column chromatography (eluting with 20% EtOAc in hexanes) to give compound **2d** (50 mg, 52%) as a clear oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (quint, J = 1.6 Hz, 1H) 4.83 (q, J = 1.8 Hz, 2H), 3.85 (q, J = 5.8 Hz, 2H), 2.60 (tq, J = 5.8, 1.6 Hz, 2H), 2.08 (t, J = 5.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 146.8, 131.8, 70.7, 60.6, 29.1. HRMS (ESI^+) calcd. for $C_6H_8O_3Na$ $[M+Na]^+$ 151.0371 *m/z*, found 151.0370.

Compound **4a** (11 mg), was isolated as a colorless oil.[2] Further attempts of purification led to decomposition. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (tt_{app}, J = 5.4, 2.9 Hz, 1H) 4.40–4.36 (m, 4H), 2.98 (dddd, J = 9.8, 5.0, 4.3, 2.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 138.0, 126.1, 65.8, 61.0, 25.5. HRMS (ESI^+) calcd. for $C_6H_8O_3Na$ $[M+Na]^+$ 151.0371 *m/z*, found 151.0367.

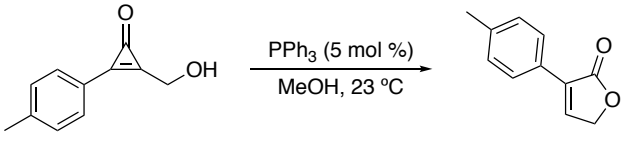
Compound **4b** (8.0 mg), was isolated as a colorless oil.[2] Further attempts of purification led to decomposition. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (tt_{app}, J = 5.7, 2.4 Hz, 1H) 4.60 (ddd, J = 4.8, 3.2, 2.3 Hz, 2H), 4.42 (t, J = 7.4 Hz, 2H), 2.99 (dddd, J = 9.7, 5.1, 4.6, 2.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 142.4, 126.3, 66.5, 59.1, 28.9. HRMS (ESI^+) calcd. for $C_6H_8O_3Na$ $[M+Na]^+$ 151.0371 *m/z*, found 151.0368.



1e **2e**

3-Phenylfuran-2(5*H*)-one (2e)
General procedure D was used with the following reagents: **1e** (15.5 mg, 0.0966 mmol, 1.00 equiv.), PPh_3 (1.3 mg, 0.0050 mmol, 5 mol %), anhydrous MeOH (0.4 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2e** (10 mg, 68%) as a pale yellow solid.

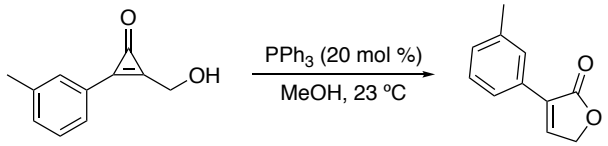
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.83 (m, 2H), 7.64 (t, J = 2.0 Hz, 1H), 7.44–7.36 (m, 3H), 4.92 (d, J = 2.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 144.4, 131.9, 129.7, 129.5, 128.8, 127.1, 69.7. HRMS (ESI^+) calcd. for $C_{10}H_8O_2$ $[M+Na]^+$ 183.0422 *m/z*, found 183.0421.



1f **2f**

3-(*p*-Tolyl)furan-2(5*H*)-one (2f)
General procedure D was used with the following reagents: **1f** (79.6 mg, 0.457 mmol, 1.00 equiv.), PPh_3 (12.0 mg, 0.0458 mmol, 10 mol %), anhydrous MeOH (1.8 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2f** (65 mg, 82%) as a while solid.

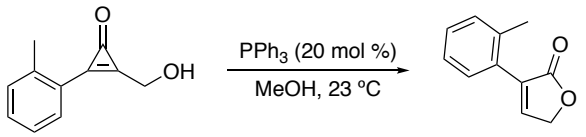
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 2.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 4.90 (d, J = 2.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 143.4, 139.6, 131.6, 129.5, 126.9, 126.8, 69.6, 21.5. HRMS (ESI^+) calcd. for $[M+Na]^+$ 197.0578 *m/z*, found 197.0585.



1g **2g**

3-(*m*-Tolyl)furan-2(5*H*)-one (2g)
General procedure D was used with the following reagents: **1g** (86.8 mg, 0.498 mmol, 1.00 equiv.), PPh_3 (26.3 mg, 0.100 mmol, 20 mol %), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2g** (61 mg, 70%) as an off-white solid.

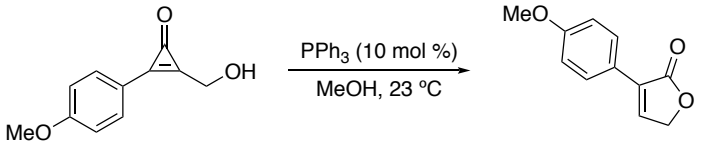
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (br s, 1H), 7.64–7.61 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 4.92 (d, *J* = 2.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 144.2, 138.5, 132.0, 130.3, 129.6, 128.7, 127.7, 124.2, 69.6, 21.6. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0572.



1h **2h**

3-(*o*-Tolyl)furan-2(5*H*)-one (2h)
General procedure D was used with the following reagents: **1h** (86.6 mg, 0.497 mmol, 1.00 equiv.), PPh_3 (26 mg, 0.099 mmol, 20 mol %), anhydrous MeOH (2.0 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2h** (73 mg, 84%) as a clear oil.

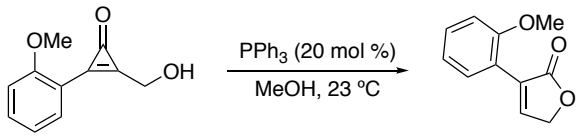
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.32–7.27 (m, 2H), 7.25–7.22 (m, 1H), 4.98 (d, *J* = 1.8 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 147.8, 136.7, 133.6, 130.7, 129.64, 129.60, 129.2, 126.0, 70.1, 20.5. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0570.



1i **2i**

3-(4-Methoxyphenyl)furan-2(5*H*)-one (2i)
Using Procedure D. The following amounts of reagents were used: **1i** (54.6 mg, 0.287 mmol, 1.00 equiv.), PPh_3 (7.4 mg, 0.028 mmol, 10 mol %), anhydrous MeOH (1.2 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2i** (47 mg, 85%) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.52 (t, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.90 (d, *J* = 2.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 160.6, 142.0, 131.2, 128.5, 122.3, 114.2, 69.6, 55.5. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528 *m/z*, found 213.0520.

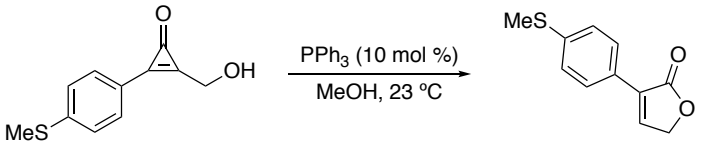


1j **2j**

3-(2-Methoxyphenyl)furan-2(5*H*)-one (2j)

General procedure D was used with the following reagents: **1j** (20.2 mg, 0.106 mmol, 1.00 equiv.), PPh_3 (5.6 mg, 0.021 mmol, 20 mol %), anhydrous MeOH (0.42 mL). The crude residue was purified by flash column chromatography using deactivated silica (deactivated with 1% Et_3N in CH_2Cl_2, then eluting with 15% EtOAc in hexanes) to give compound **2j** (8.6 mg, 43%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.98 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.93 (d, *J* = 1.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 157.8, 148.4, 130.3, 130.8, 129.6, 126.9, 120.8, 118.7, 110.9, 69.8, 55.6. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528 *m/z*, found 213.0527.

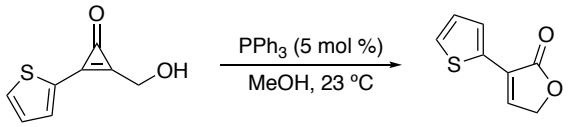


1k **2k**

3-(4-(Methylthio)phenyl)furan-2(5*H*)-one (2k)

General procedure D was used with the following reagents: **1k** (0.142 g, 0.689 mmol, 1.00 equiv.), PPh_3 (18.2 mg, 0.0694 mmol, 10 mol %), anhydrous MeOH (2.8 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2k** (0.12 g, 82%) as a yellow solid.

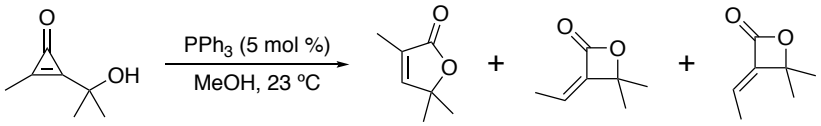
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.92 (d, *J* = 2.0 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 143.3, 140.6, 131.2, 127.4, 126.2, 126.16, 69.6, 15.5. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2SNa$ $[M+Na]^+$ 229.0299 *m/z*, found 229.0305.



1l **2l**

3-(Thiophen-2-yl)furan-2(5*H*)-one (2l)
General procedure D was used with the following reagents: **1l** (58.5 mg, 0.352 mmol, 1.00 equiv.), PPh_3 (5.0 mg, 0.019 mmol, 5 mol %), anhydrous MeOH (2.8 mL). The crude residue was purified by flash column chromatography (eluting with 20% Et_2O in hexanes) to give compound **2l** (50 mg, 85%) as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.4 Hz, 1H), 7.47 (t, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 5.0 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.94 (d, *J* = 2.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 140.5, 131.6, 127.9, 127.5, 127.3, 126.7, 70.1. HRMS (ESI^+) calcd. for $C_8H_6O_2SNa$ $[M+Na]^+$ 188.9986 *m/z*, found 188.9989.



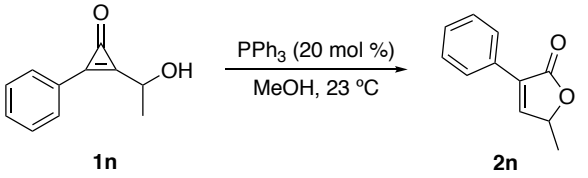
1m **2m** **3a** **3b**

3,5,5-Trimethylfuran-2(5*H*)-one (2m)
General procedure D was used with the following reagents: **1m** (0.101 g, 0.800 mmol, 1.00 equiv.), PPh_3 (10.6 mg, 0.0404 mmol, 5 mol %), anhydrous MeOH (3.2 mL). The crude residue was purified by flash column chromatography (eluting with 3–4 Et_2O in hexanes) to give compound **2m** (47 mg, 46%) as a white solid.

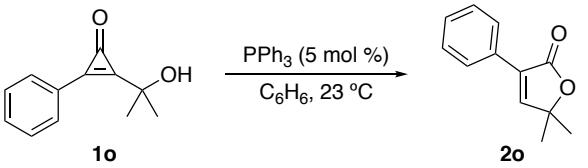
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98–6.97 (m, 1H), 1.88 (d, *J* = 1.4 Hz, 3H), 1.43 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 154.1, 128.3, 84.3, 25.8, 10.6. HRMS (CI^+) calcd. for $C_7H_{10}O_2$ $[M]^+$ 126.0681 *m/z*, found 126.0675.

Compound **3a** (5.4 mg, 5%) was isolated as a volatile, colorless oil.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (q, *J* = 7.2 Hz, 1H), 2.03 (d, *J* = 7.2 Hz, 3H), 1.58 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 142.5, 129.2, 83.8, 25.6, 14.7. HRMS (CI^+) calcd. for $C_7H_{11}O_2$ $[M+H]^+$ 127.0759 *m/z*, found 127.0760.

Compound **3b** (5.0 mg, 5%) was isolated as a volatile, colorless oil.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (q, *J* = 7.3 Hz, 1H), 1.80 (d, *J* = 7.3 Hz, 3H), 1.66 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8, 142.8, 127.2, 84.0, 25.0, 13.3. HRMS (CI^+) calcd. for $C_7H_{11}O_2$ $[M+H]^+$ 127.0759 *m/z*, found 127.0761.

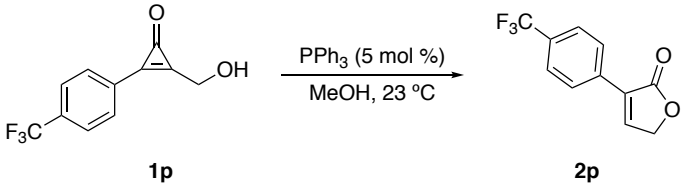


5-Methyl-3-phenylfuran-2(5*H*)-one (2n)
General procedure D was used with the following reagents: **1n** (7.0 mg, 0.039 mmol, 1.0 equiv.), PPh_3 (2.0 mg, 0.0076 mmol, 20 mol %), anhydrous MeOH (0.15 mL). The crude residue was purified by flash column chromatography (eluting with 20% EtOAc in hexanes) to give compound **2n** (4.8 mg, 72%) as a clear oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 1.4 Hz, 1H) 7.43–7.37 (m, 3H), 5.15 (qd, *J* = 6.8, 1.4 Hz, 1H), 1.52 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 149.1, 131.6, 129.7, 129.5, 128.8, 127.2, 76.8, 19.3. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_2Na$ $[M+Na]^+$ 197.0578 *m/z*, found 197.0579.



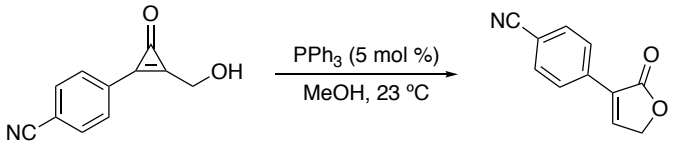
5,5-Dimethyl-3-phenylfuran-2(5*H*)-one (2o)
General procedure D was used with the following reagents and modifications: **1o** (50.2 mg, 0.267 mmol, 1.00 equiv.), PPh_3 (3.6 mg, 0.014 mmol, 5 mol %), anhydrous C_6H_6 (1.1 mL). The crude residue was purified by flash column chromatography (eluting with 5–10% Et_2O in hexanes) to give compound **2o** (28 mg, 55%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.1 Hz, 2H), 7.50 (s, 1H), 7.42–7.36 (m, 3H), 1.56 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 153.1, 130.2, 129.7, 129.4, 128.8, 127.2, 83.5, 25.9. HRMS (ESI^+) calcd. for $C_{12}H_{12}O_2Na$ $[M+Na]^+$ 211.0735 *m/z*, found 211.0736.



3-(4-(Trifluoromethyl)phenyl)furan-2(5*H*)-one (2p)
General procedure D was used with the following reagents: **1p** (44.8 mg, 0.196 mmol, 1.00 equiv.), PPh_3 (2.6 mg, 0.0099 mmol, 5 mol %), anhydrous MeOH (0.78 mL). The crude residue was purified by flash column chromatography (eluting with 50% EtOAc in hexanes) to give compound **2p** (28 mg, 61%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.78 (t, J = 1.9 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 4.99 (d, J = 1.9 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1. ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 146.3, 133.0 (q, J = 1.2 Hz), 131.4 (q, J = 32.7 Hz), 130.9, 125.8 (q, J = 3.8 Hz), 124.0 (q, J = 272.2 Hz), 69.8. HRMS (ESI$^-$) calcd. for $C_{11}H_6F_3O_2$ [M-H]$^-$ 227.0320 *m/z*, found 227.0323.

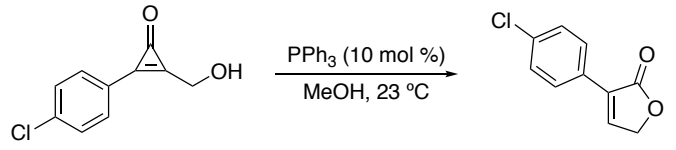


1q **2q**

4-(2-Oxo-2,5-dihydrofuran-3-yl)benzonitrile (2q)

General procedure D was used with the following reagents: **1q** (26.8 mg, 0.145 mmol, 1.00 equiv.), PPh_3 (1.9 mg, 0.0072 mmol, 5 mol %), anhydrous MeOH (0.60 mL). The crude residue was purified by flash column chromatography (eluting with 75% Et_2O in hexanes) to give compound **2q** (17 mg, 62%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.81 (s, 1H), 7.72 (d, J = 8.3 Hz, 2H), 5.00 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 147.1, 133.8, 132.6, 130.5, 127.7, 118.5, 113.1, 69.8. HRMS (ESI$^-$) calcd. for $C_{11}H_6NO_2$ [M-H]$^-$ 184.0399 *m/z*, found 184.0397.

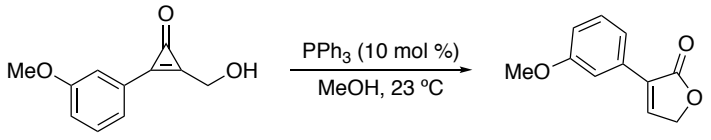


1r **2r**

3-(4-Chlorophenyl)furan-2(5*H*)-one (2r)

General procedure D was used with the following reagents: **1r** (29.9 mg, 0.154 mmol, 1.00 equiv.), PPh_3 (4.0 mg, 0.015 mmol, 10 mol %), anhydrous MeOH (0.60 mL). The crude residue was purified by flash column chromatography (eluting with 50% Et_2O in CH_2Cl_2) to give compound **2r** (12 mg, 41%) as a white solid.

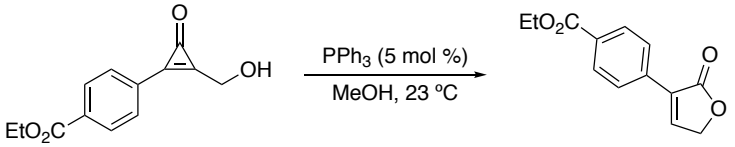
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 2H), 7.66 (t, J = 2.0 Hz, 1H), 7.44–7.37 (m, 2H), 4.94 (d, J = 2.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 144.6, 135.6, 130.8, 129.1, 128.4, 128.1, 69.7. HRMS (ESI$^-$) calcd. for $C_{10}H_9O_2Cl$ [M-H]$^-$ 193.0056 *m/z*, found 193.0064.



1s **2s**

3-(3-Methoxyphenyl)furan-2(5*H*)-one (2s)
General procedure D was used with the following reagents: **1s** (83.0 mg, 0.436 mmol, 1.00 equiv.), PPh_3 (12.0 mg, 0.0458 mmol, 10 mol %), anhydrous MeOH (1.8 mL). The crude residue was purified by flash column chromatography (eluting with 50% EtOAc in hexanes) to give compound **2s** (30 mg, 36%) as a yellow oil.

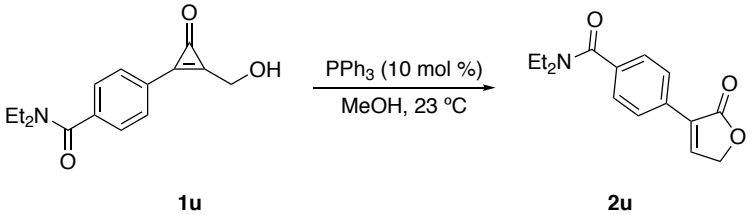
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (t, *J* = 1.8 Hz, 1H) 7.44 (t, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.90 (d, *J* = 1.9 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 159.8, 144.8, 131.4, 130.8, 129.7, 119.4, 115.1, 112.4, 69.5, 55.4. HRMS (ESI^+) calcd. for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528 *m/z*, found 213.0524.



1t **2t**

Ethyl 4-(2-oxo-2,5-dihydrofuran-3-yl)benzoate (2t)
General procedure D was used with the following reagents: **1t** (27.0 mg, 0.116 mmol, 1.00 equiv.), PPh_3 (1.5 mg, 0.0057 mmol, 5 mol %), anhydrous MeOH (0.46 mL). The crude residue was purified by flash column chromatography (eluting with 20–50% Et_2O in hexanes) to give compound **2t** (14 mg, 52%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.06 (m, 2H), 7.99–7.92 (m, 2H), 7.77 (t, *J* = 2.0 Hz, 1H), 4.97 (d, *J* = 2.0 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 166.2, 146.2, 133.7, 131.2, 131.1, 130.0, 127.0, 69.8, 61.3, 14.5. HRMS (ESI^+) calcd. for $C_{13}H_{12}O_4Na$ $[M+Na]^+$ 255.0633 *m/z*, found 255.0635.



1u **2u**

***N*,*N*-Diethyl-4-(2-(hydroxymethyl)-3-oxocycloprop-1-en-1-yl)benzamide (2u)**
General procedure D was used with the following reagents: **1u** (0.110 g, 0.424 mmol, 1.00 equiv.), PPh_3 (11.0 mg, 0.0419 mmol, 10 mol %), anhydrous MeOH (1.7 mL). The crude residue

was purified by flash column chromatography (eluting with 10% acetone in CH_2Cl_2) to give compound **2u** (50 mg, 45%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.69 (t, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 4.96 (d, *J* = 1.9 Hz, 2H), 3.55 (bs, 2H), 3.26 (bs, 2H), 1.25 (bs, 3H), 1.12 (bs, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 170.7, 145.3, 138.2, 132.2, 132.1, 131.1, 130.3, 128.64, 128.56, 127.1, 126.8, 69.7, 43.4, 39.4, 14.4, 13.0. HRMS (ESI^+) calcd. for $C_{15}H_{17}NO_3Na$ $[M+Na]^+$ 282.1106 *m/z*, found 282.1107.

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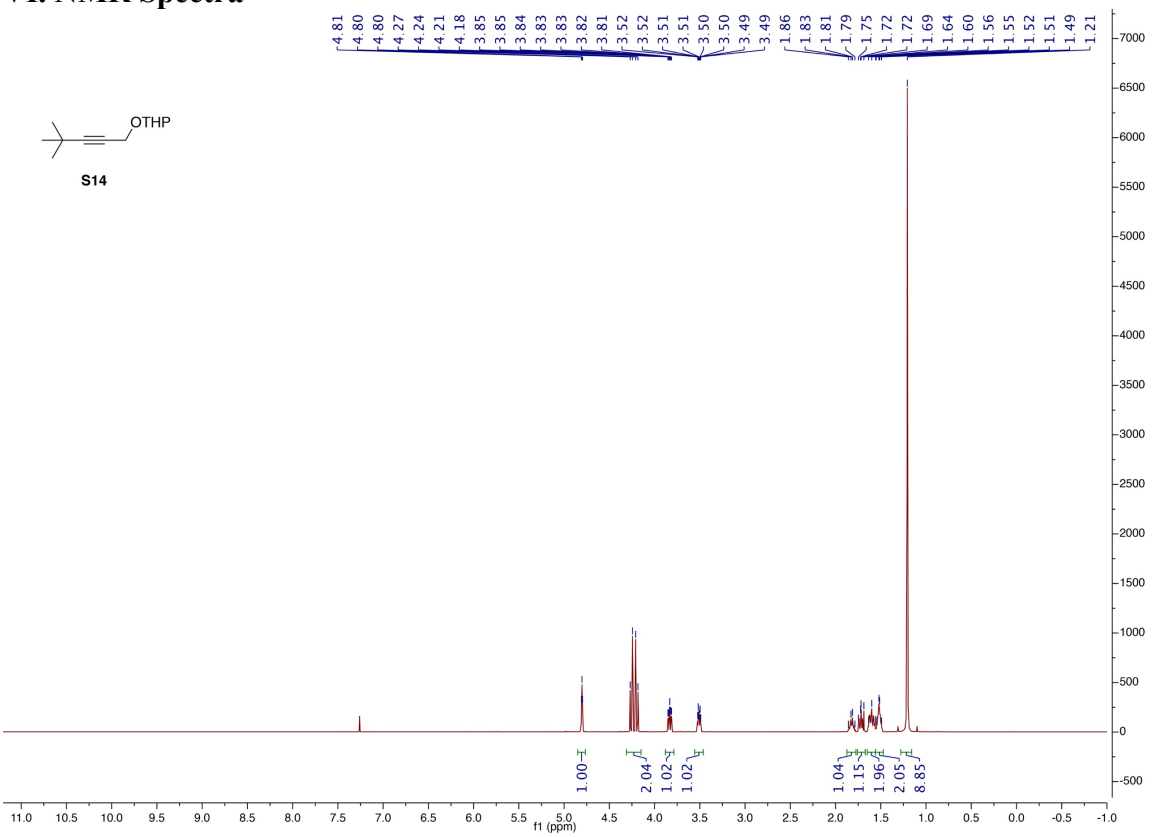
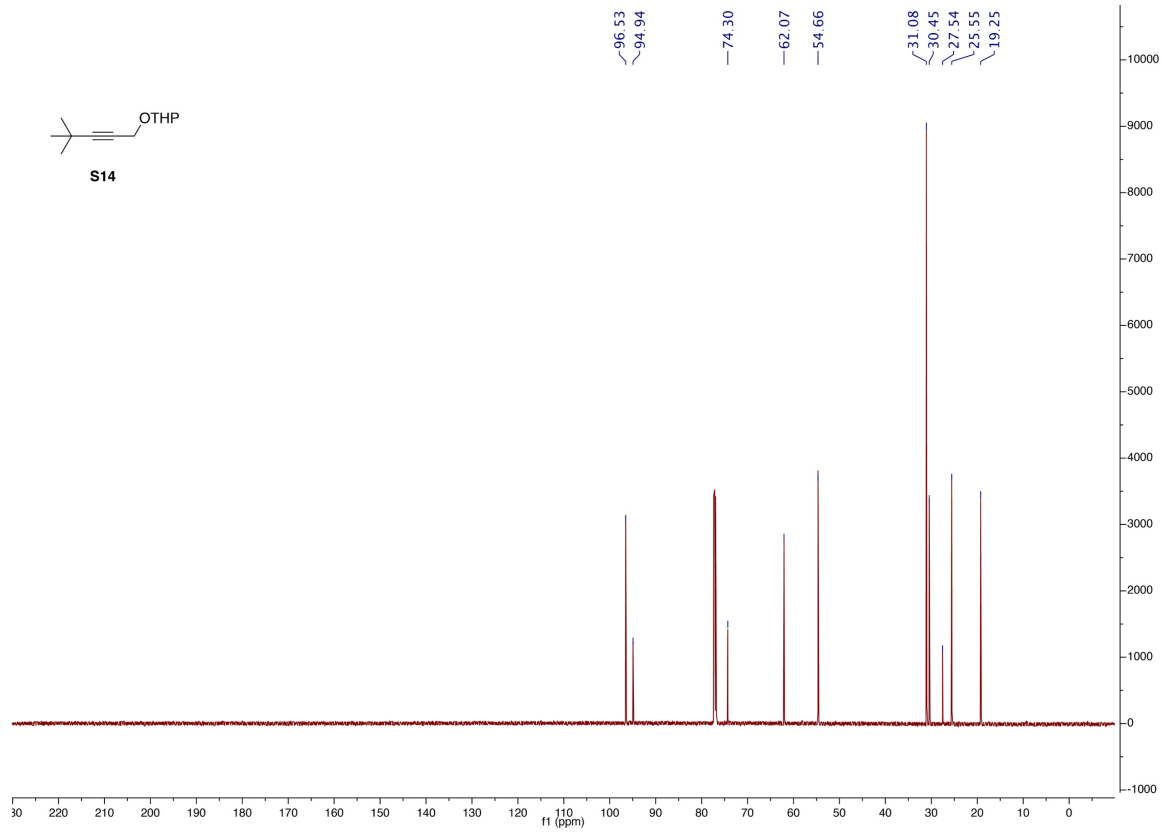
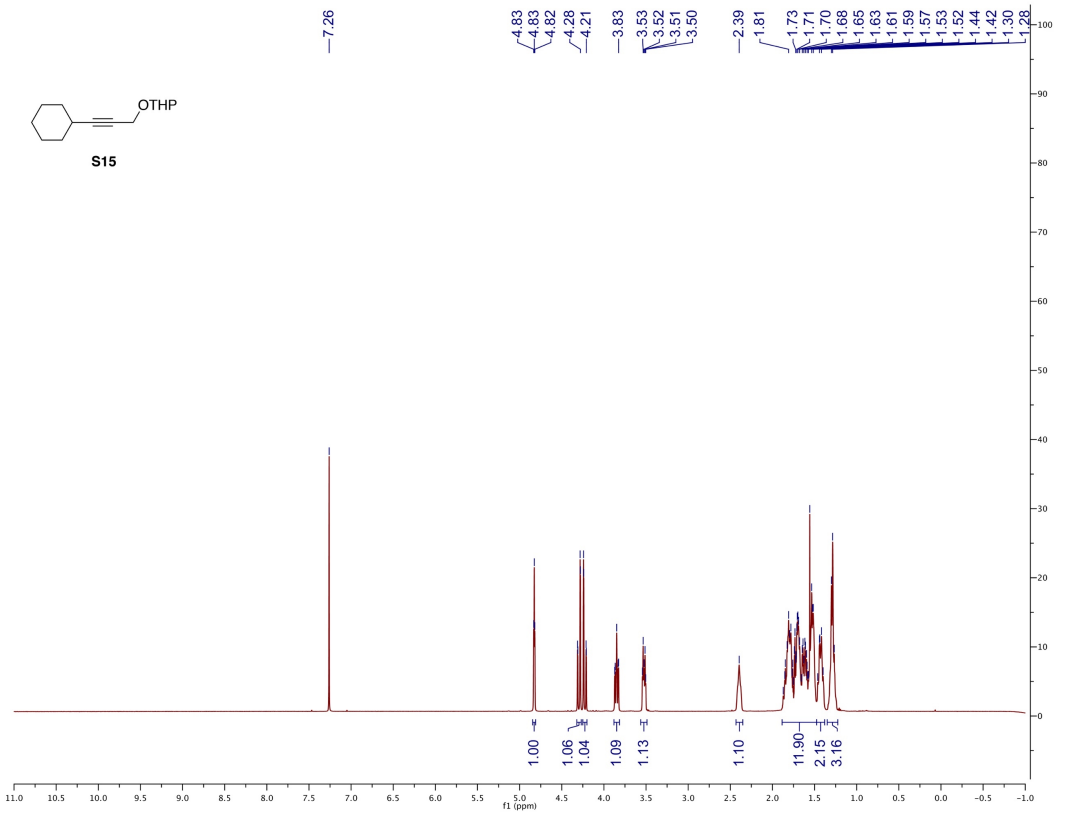
VI. NMR Spectra



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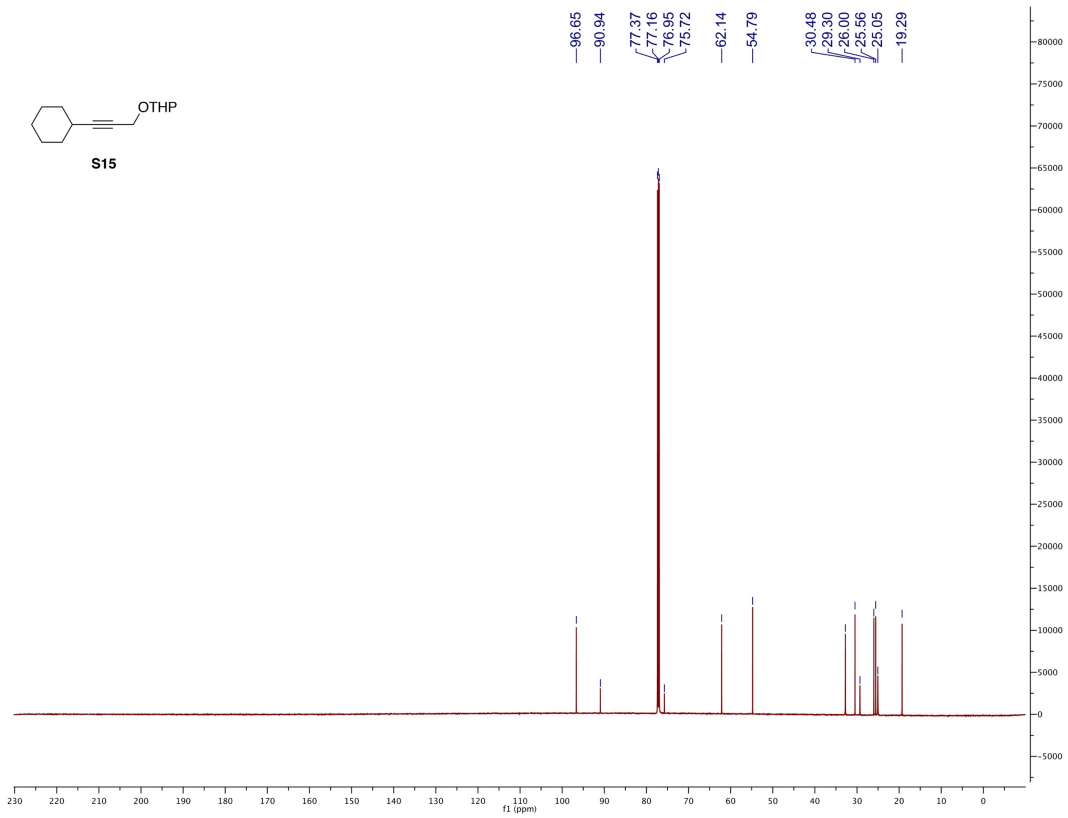
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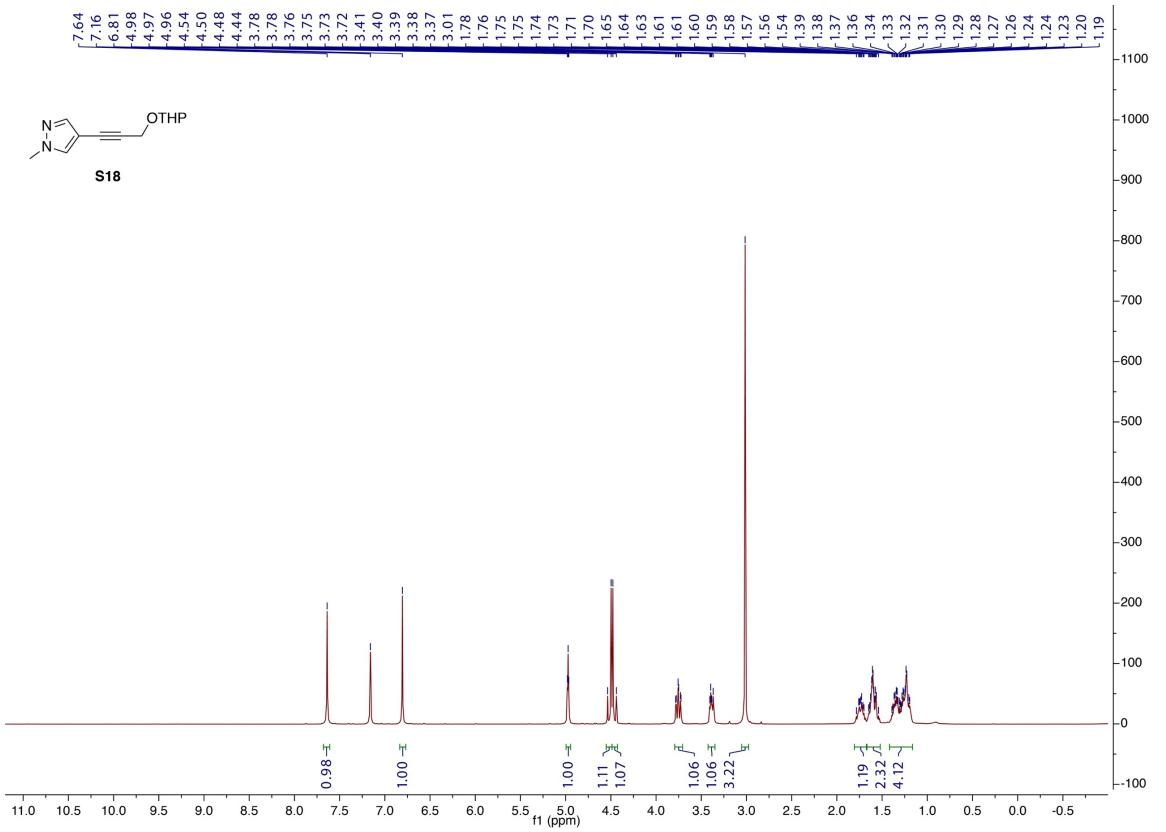
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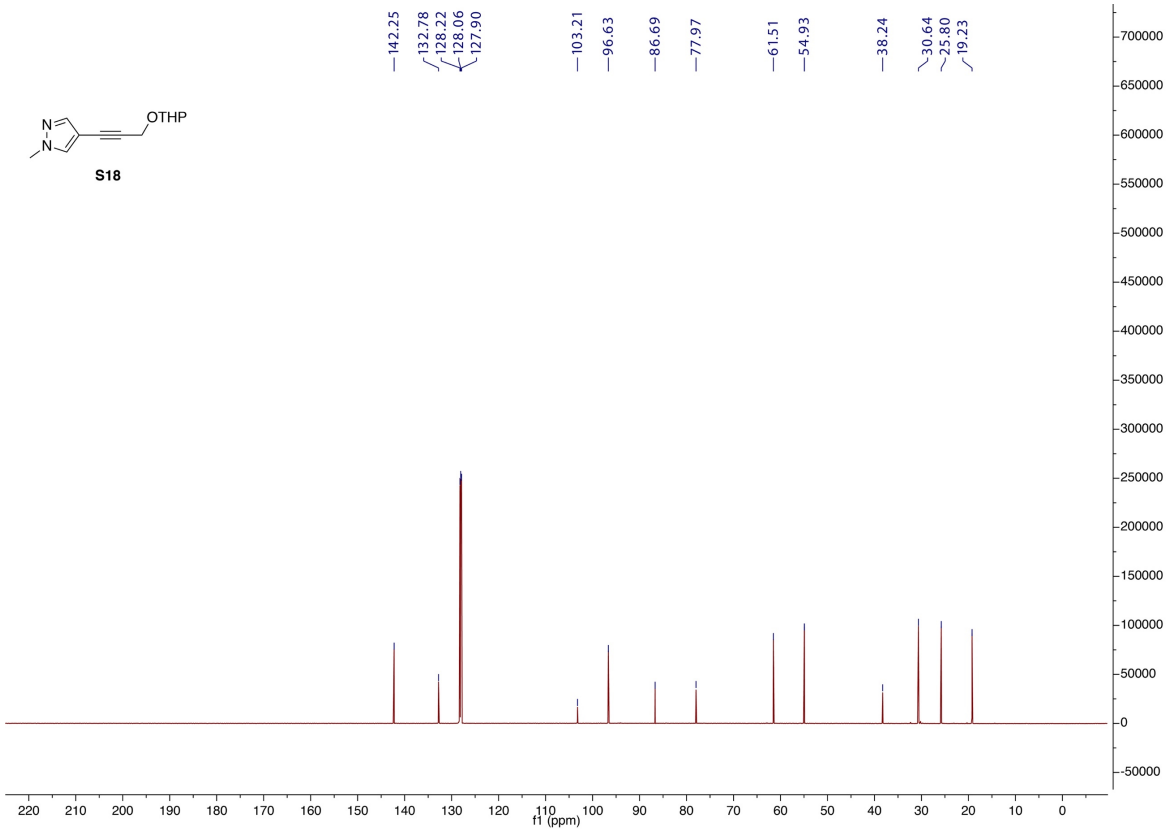
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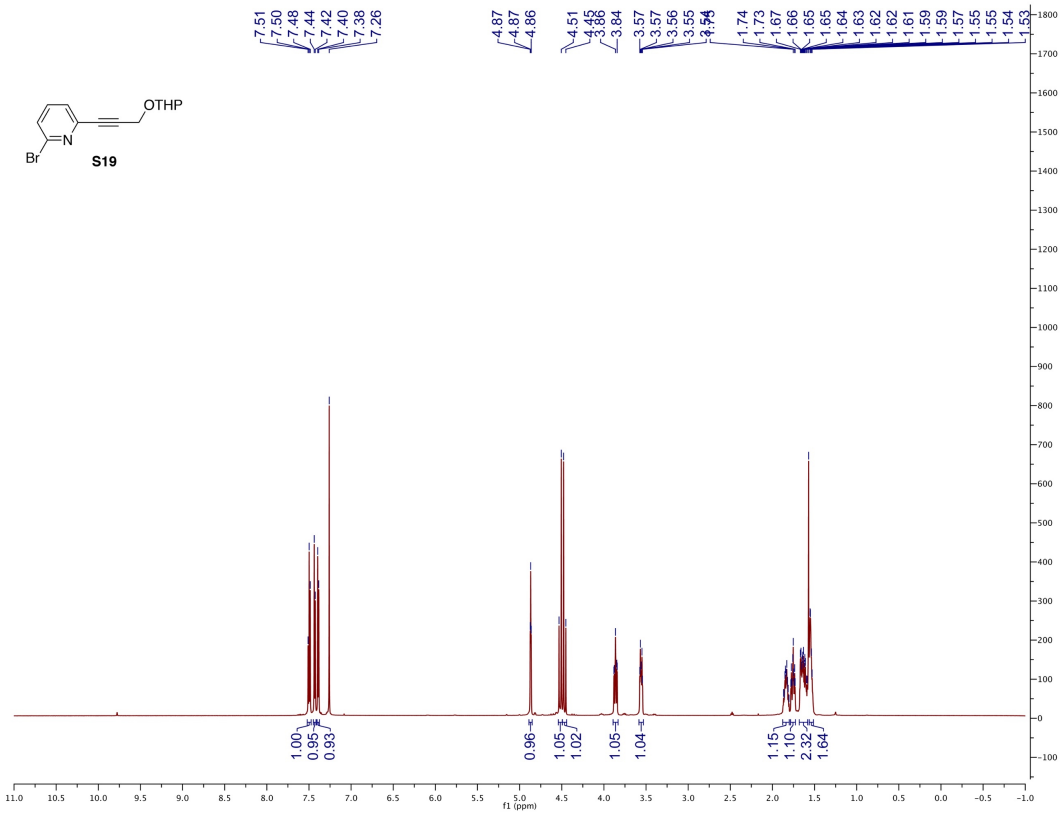
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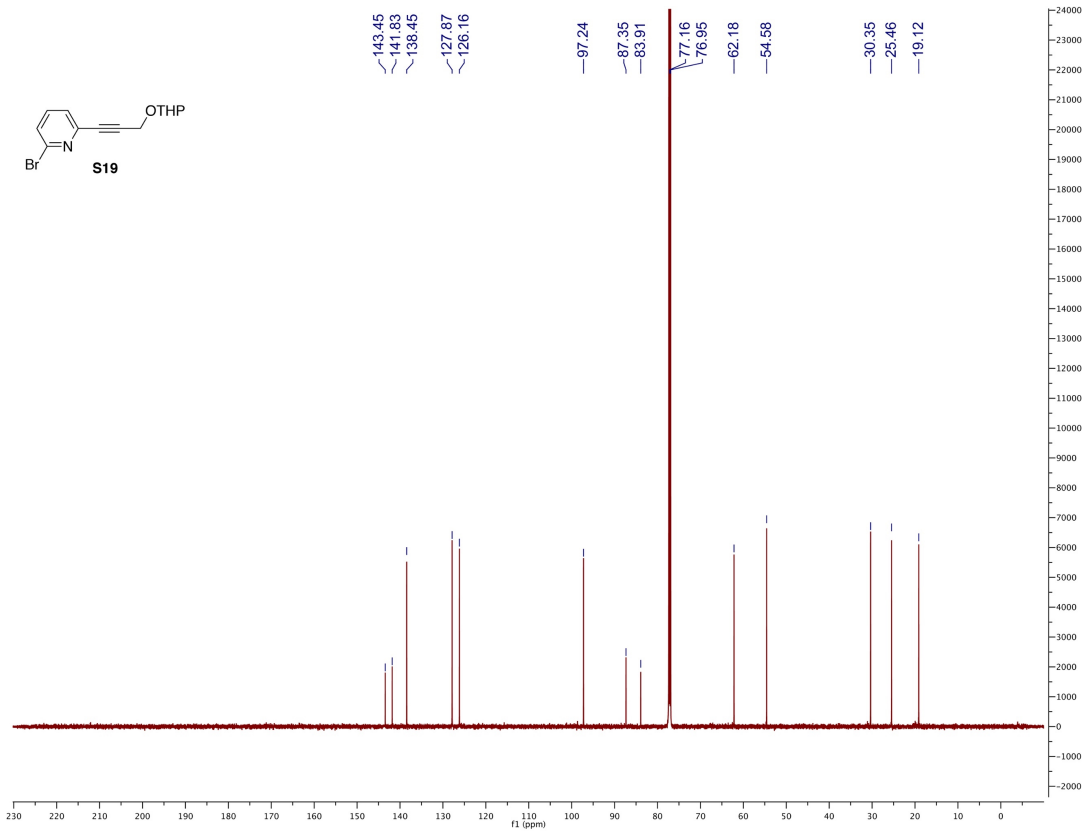
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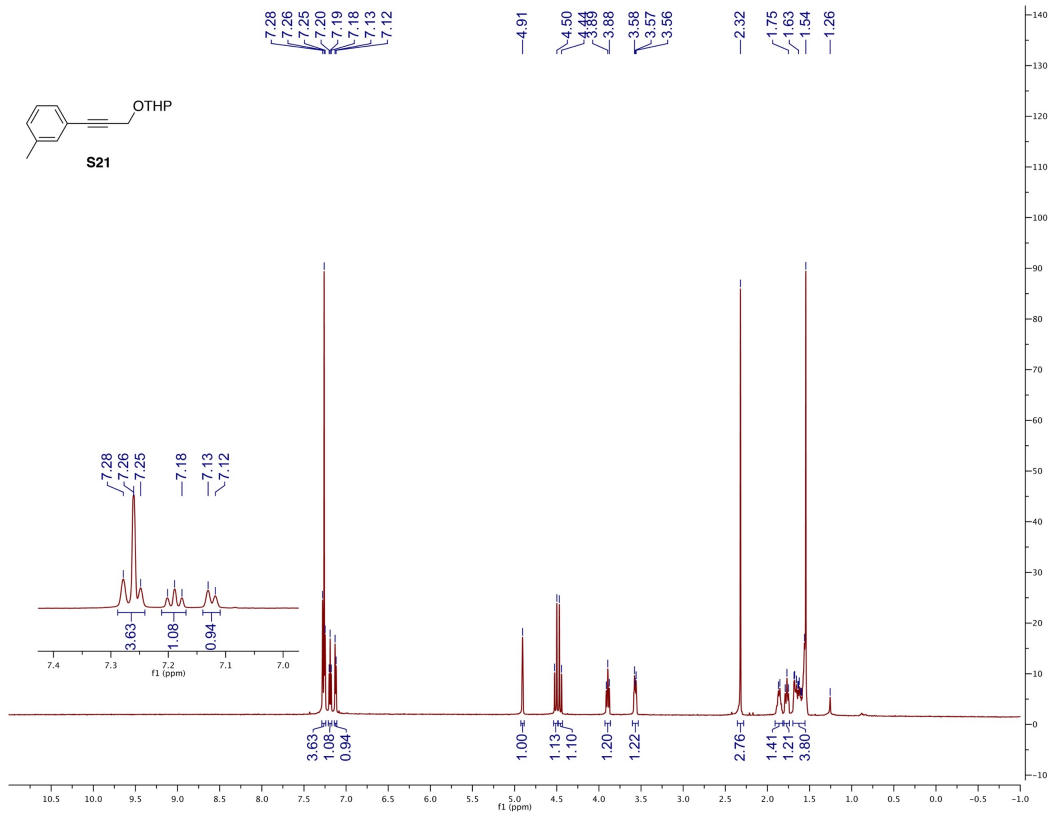
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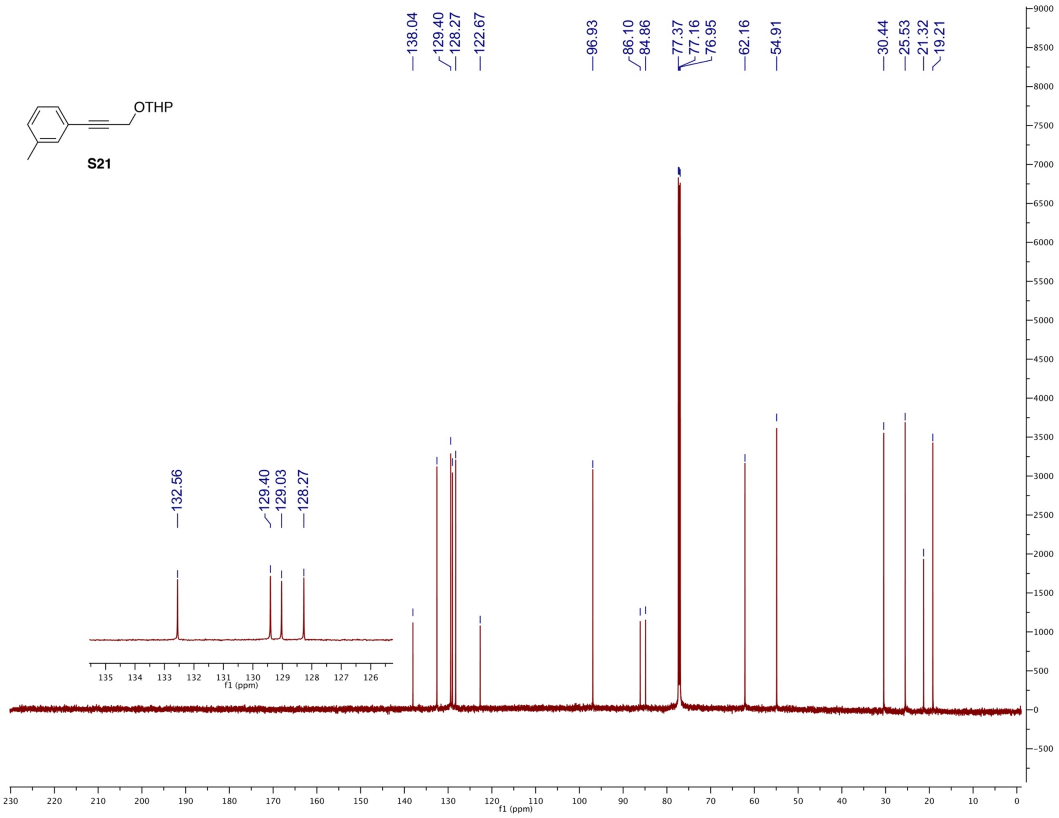
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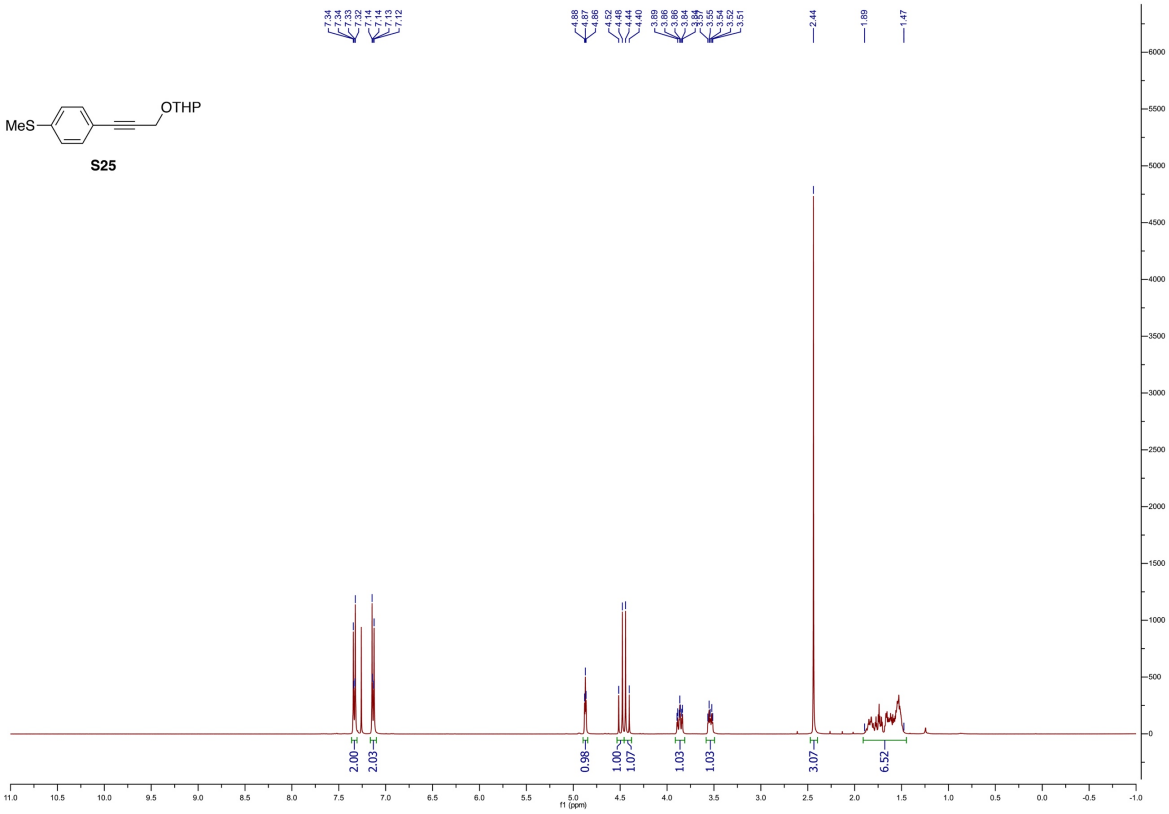
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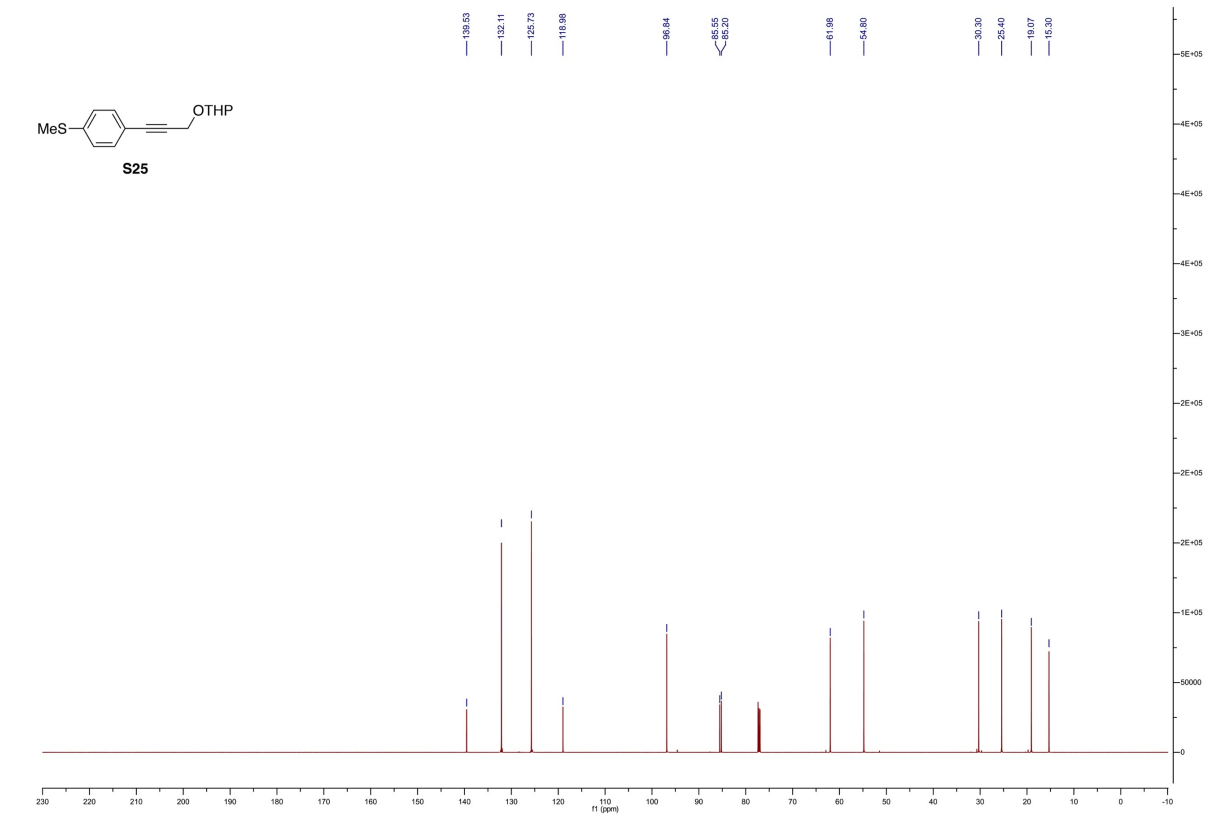
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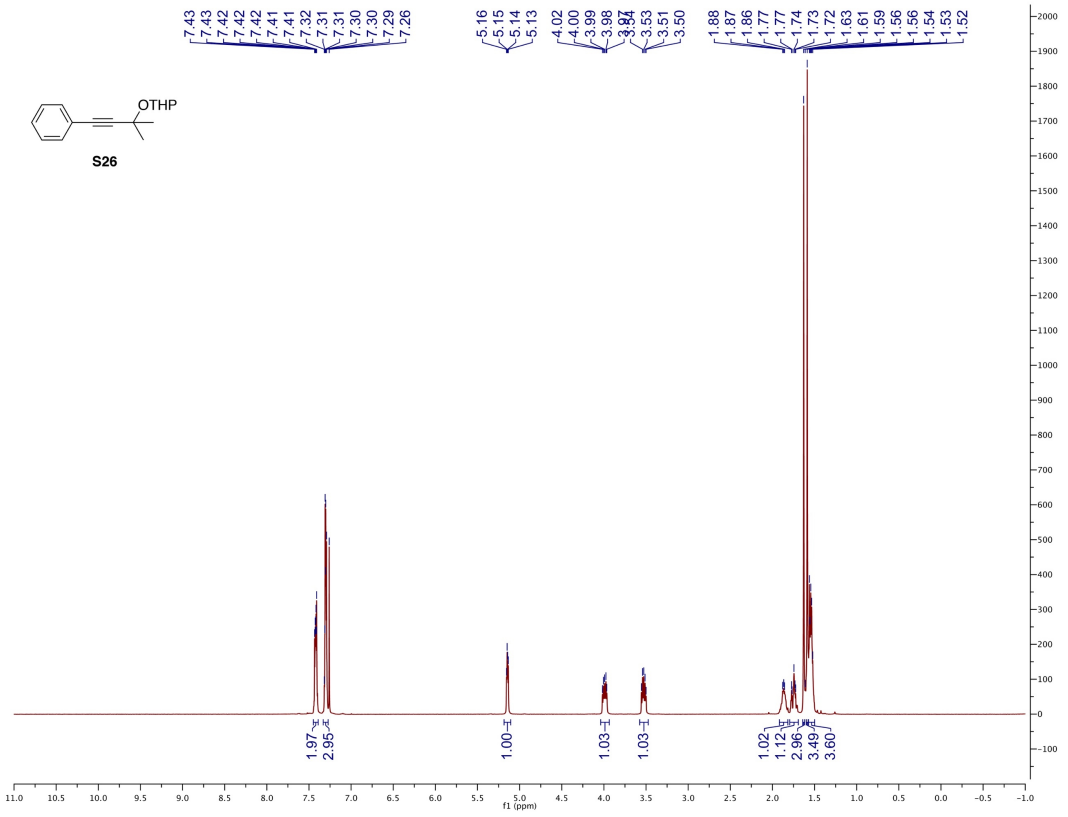
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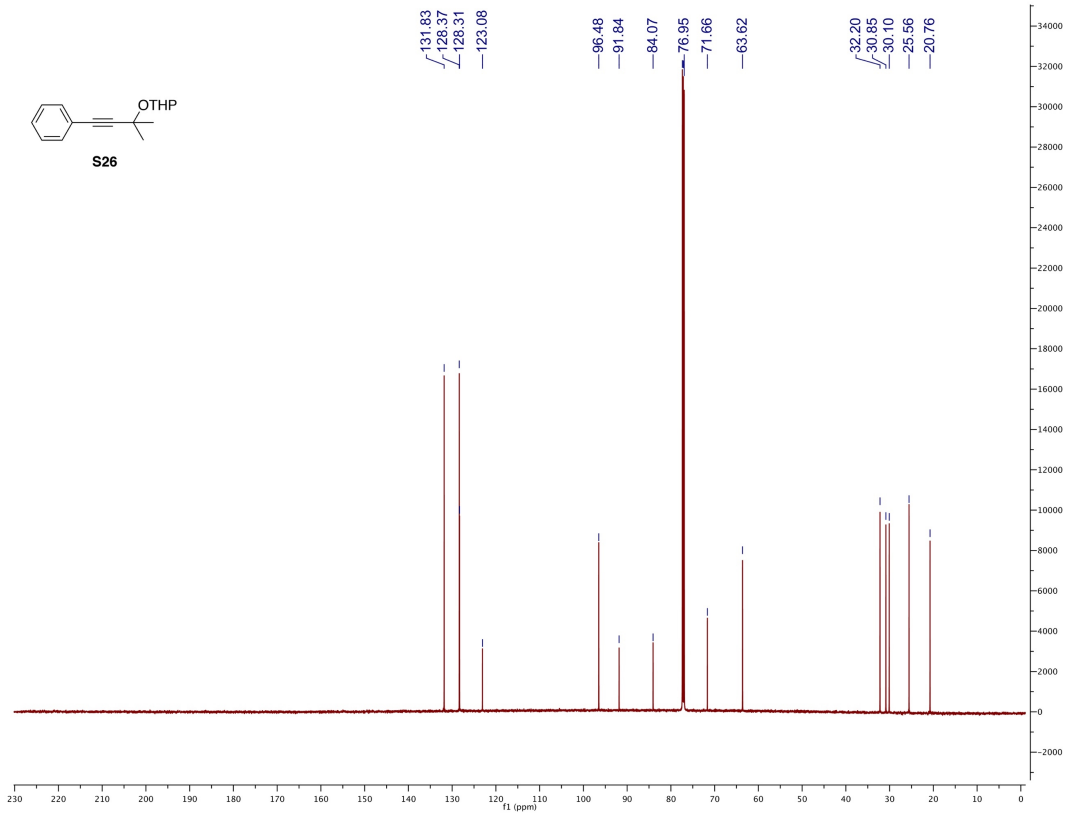
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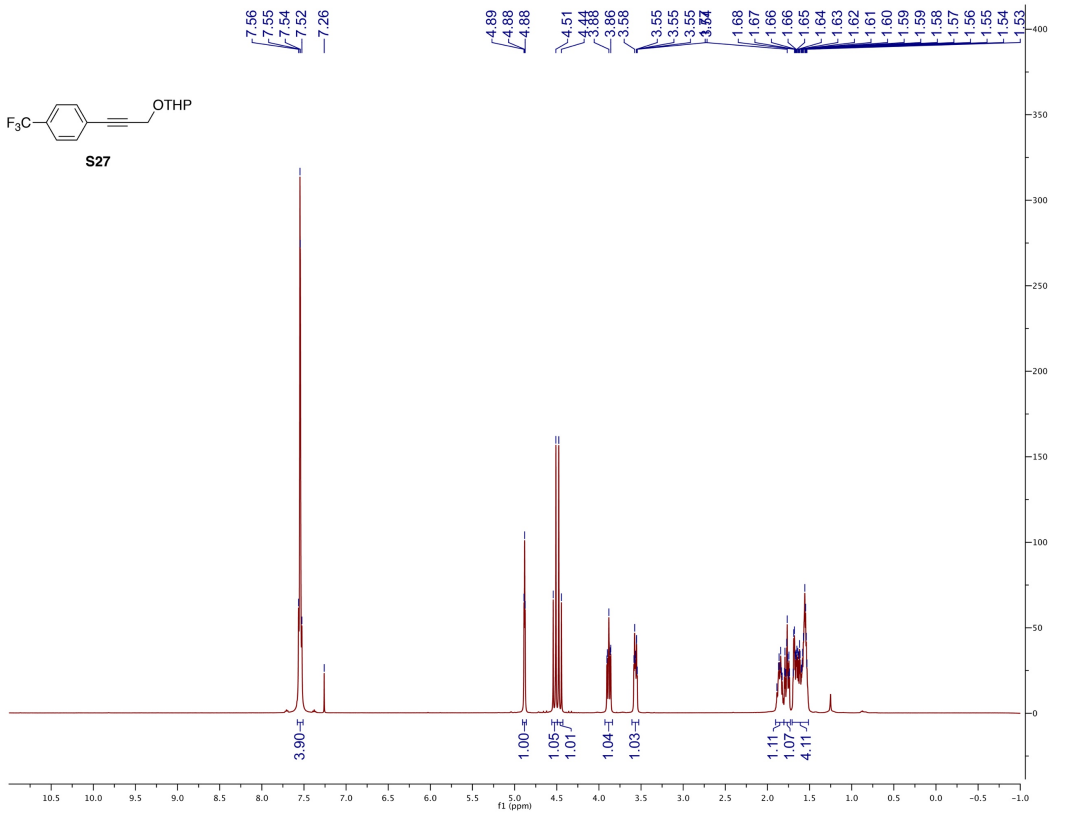
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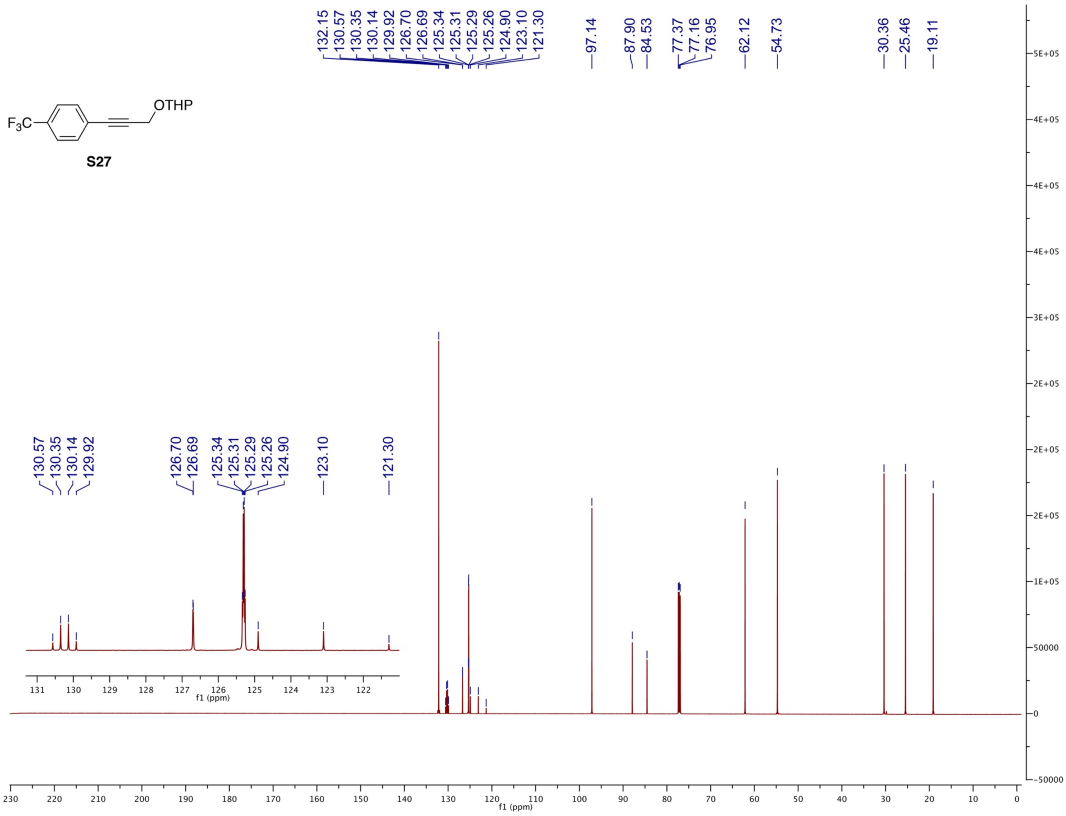
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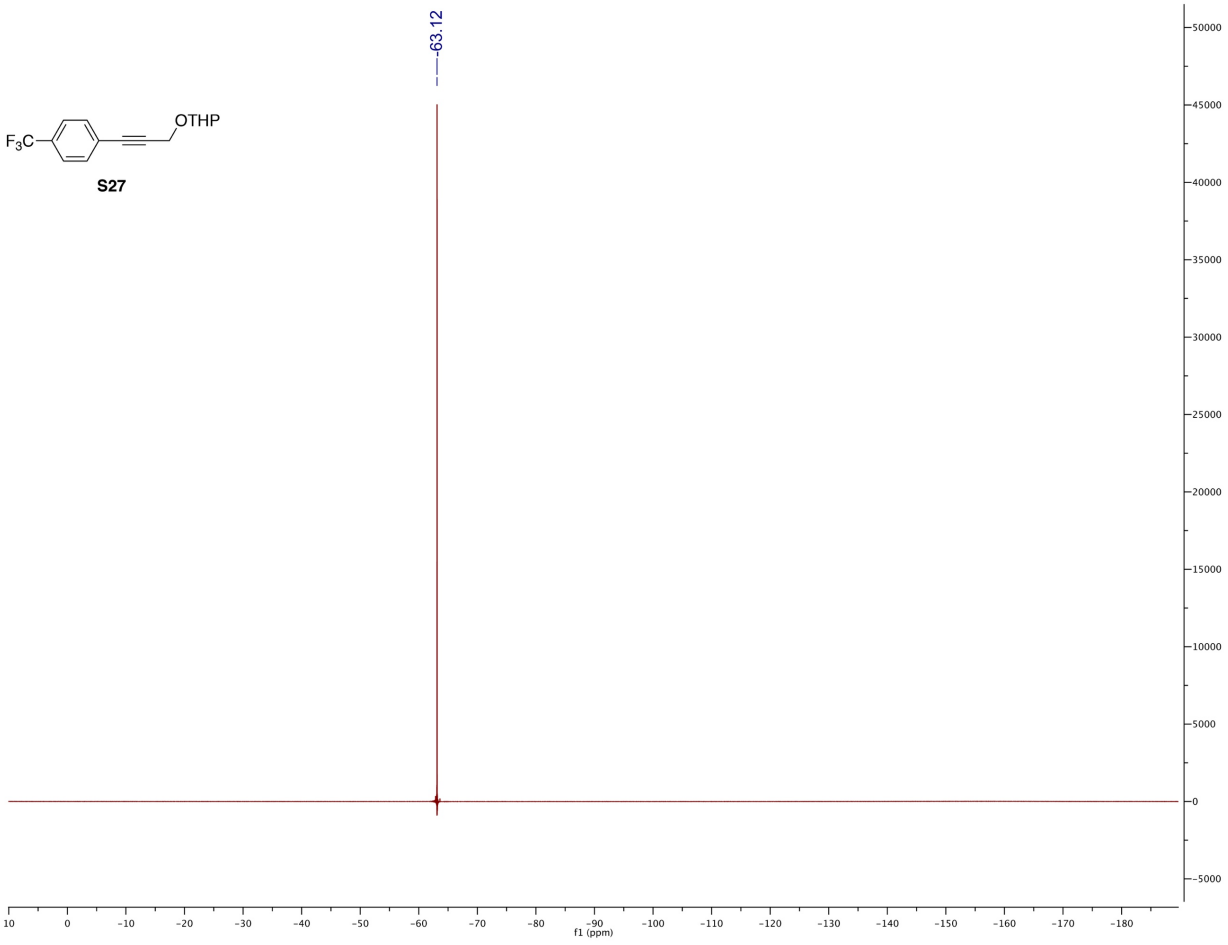
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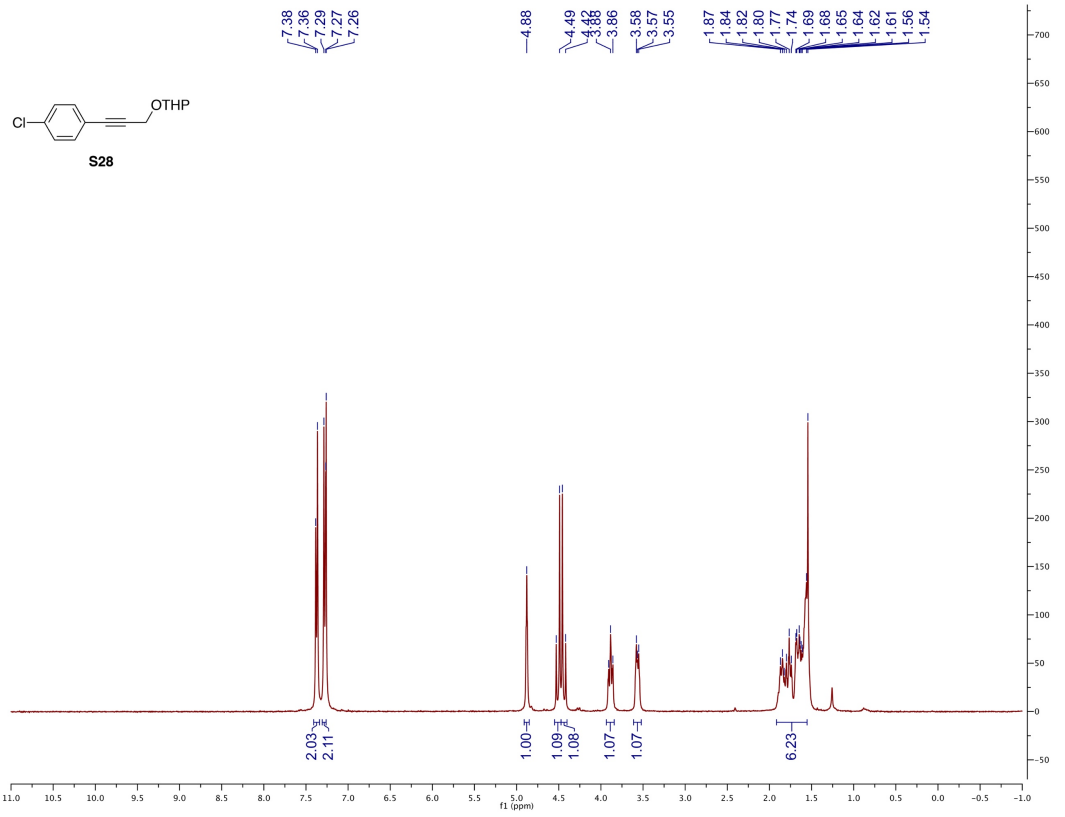
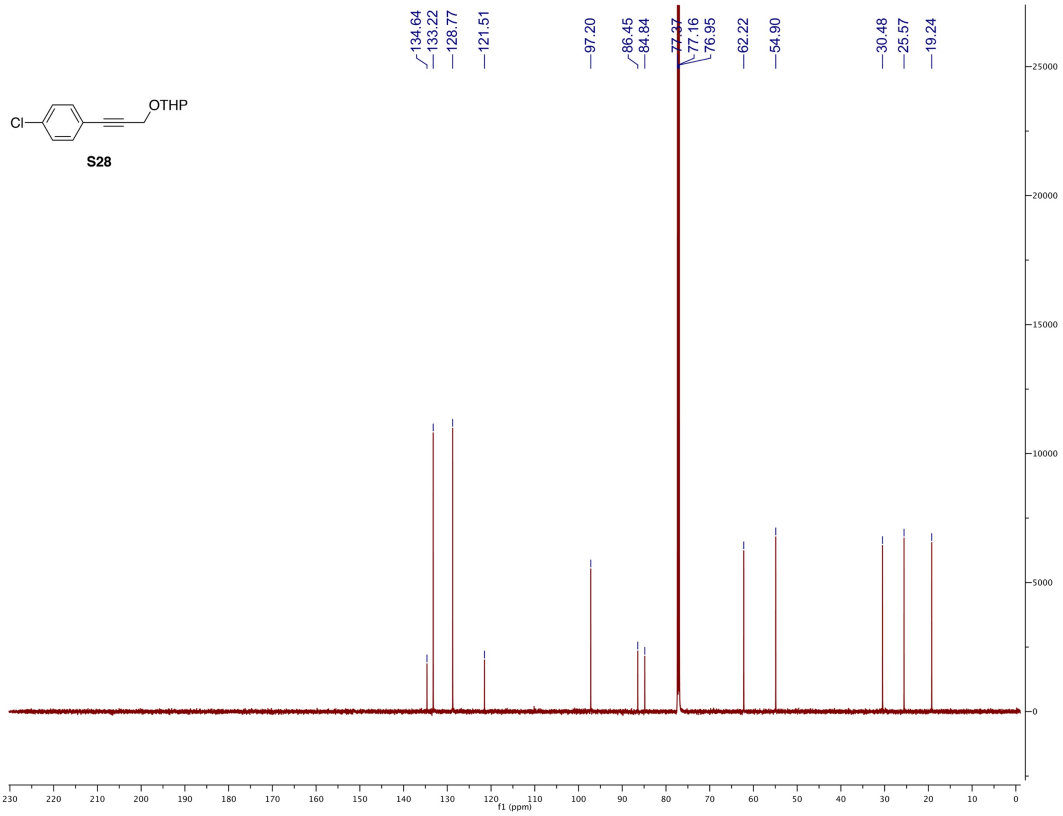
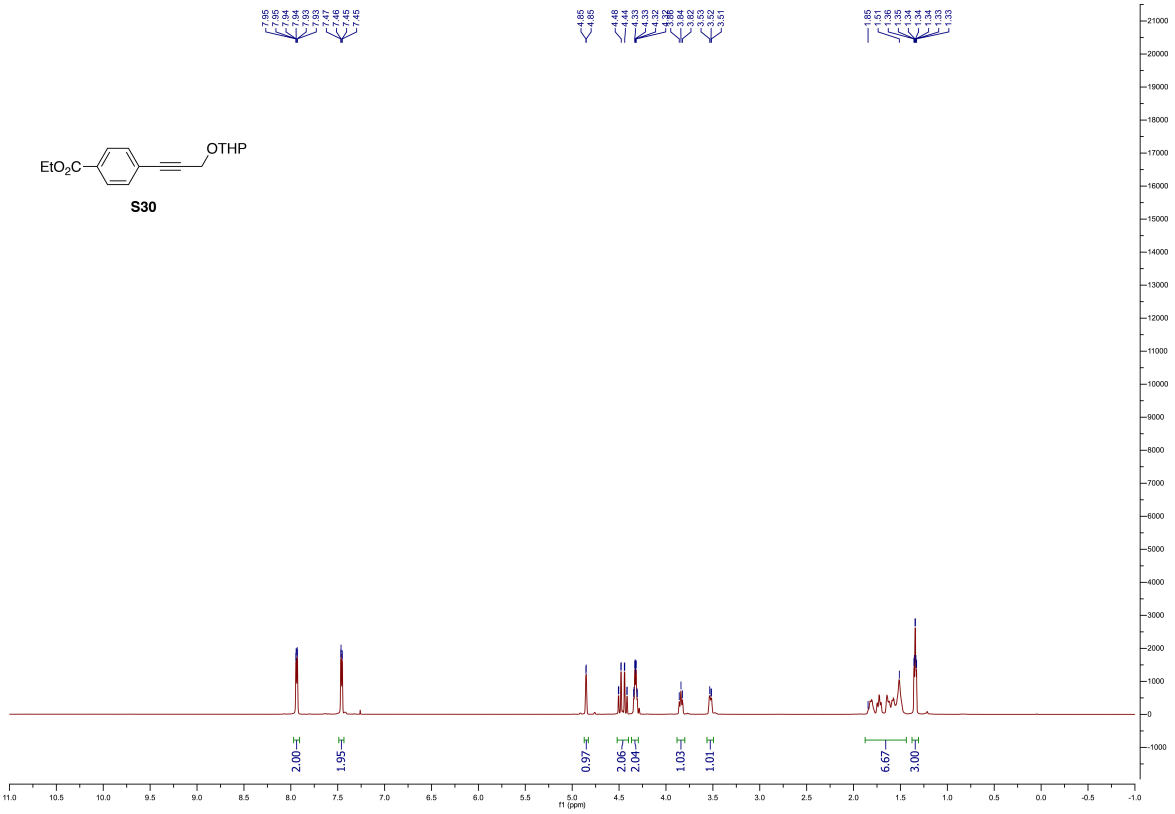
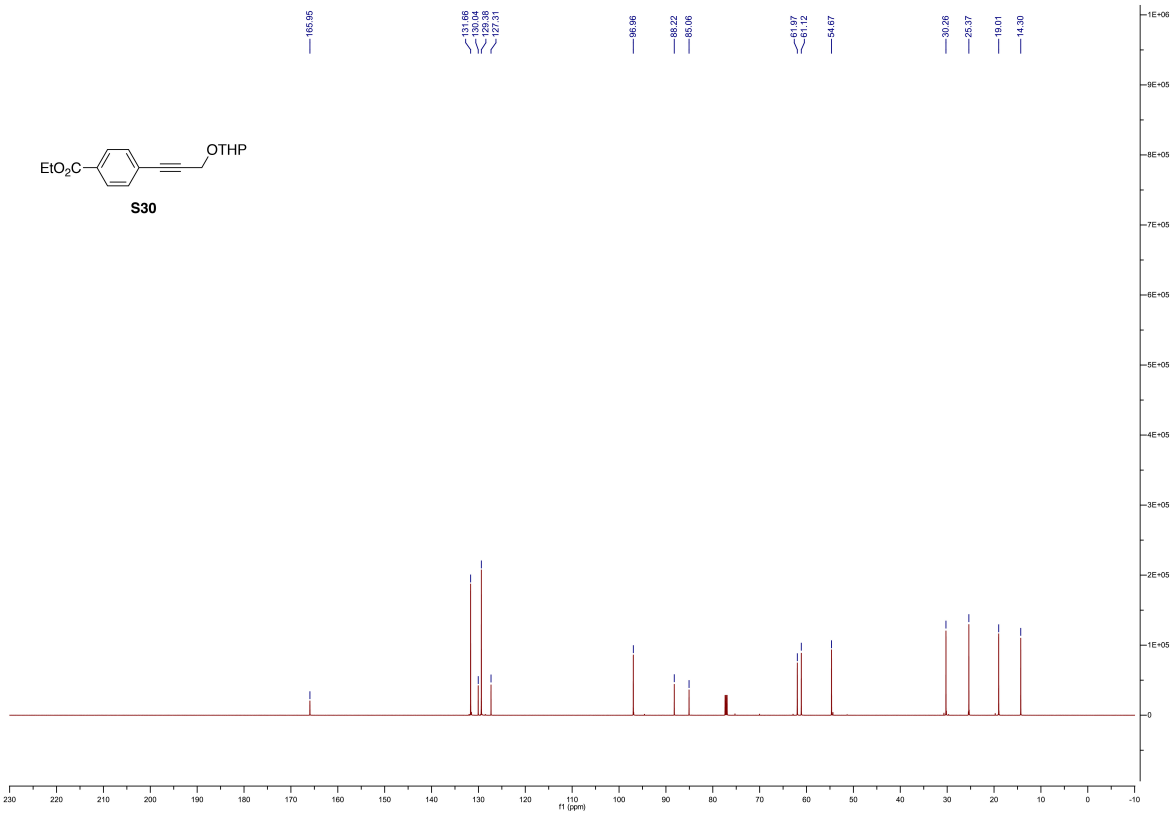
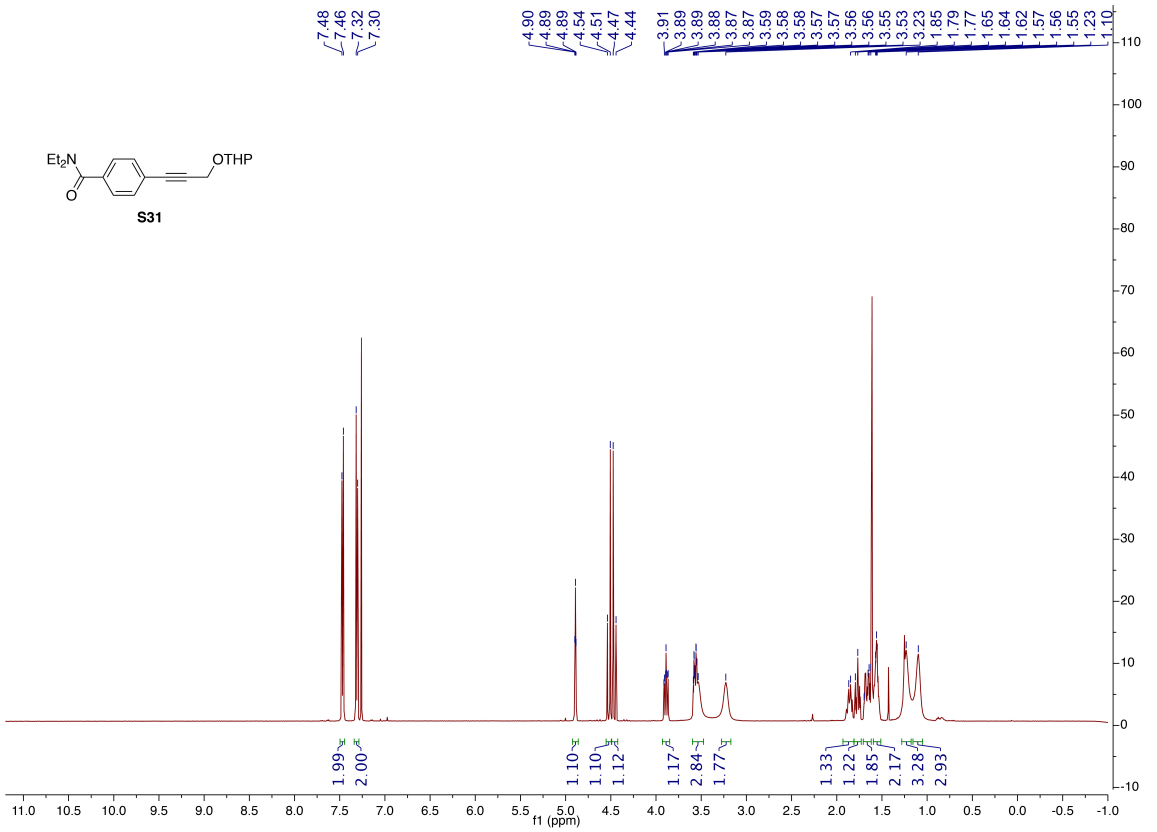
10000
5000
0
-5000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

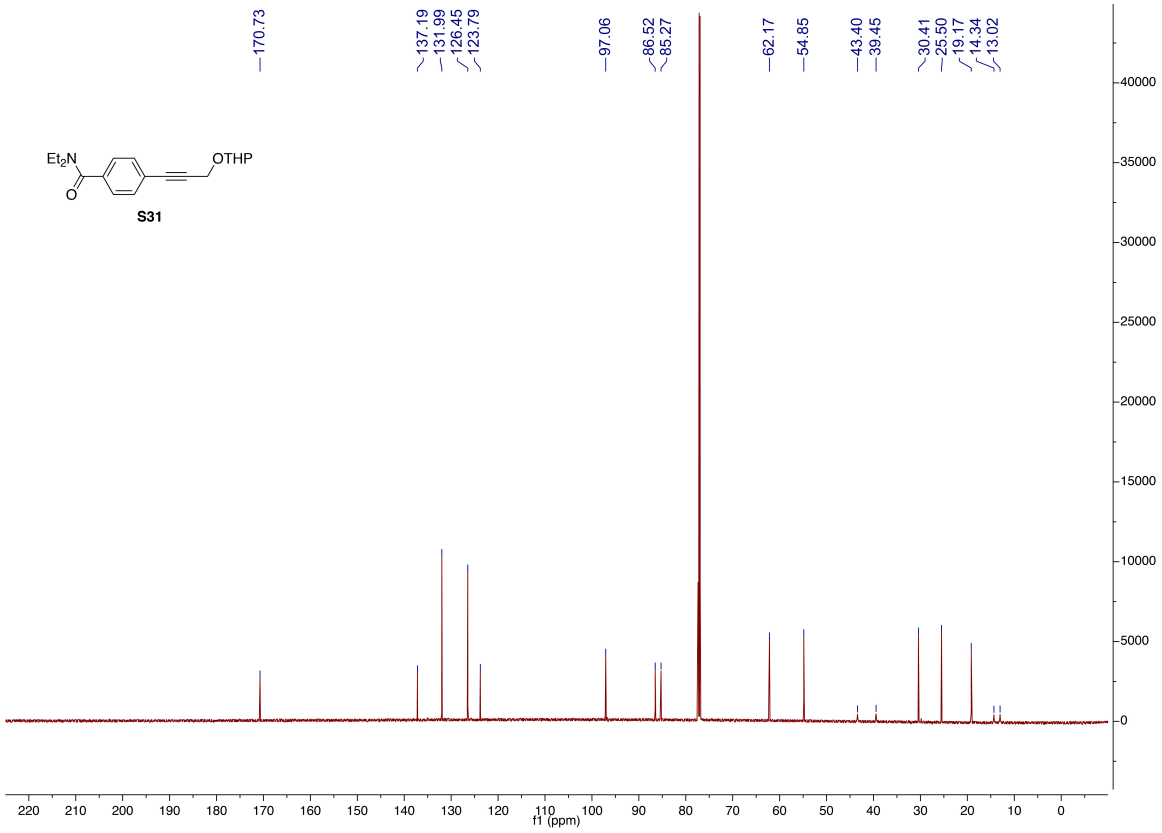

7.38
7.36
7.29
7.27
7.26
4.88
4.49
4.42
3.88
3.86
3.58
3.57
3.55
1.87
1.84
1.82
1.80
1.77
1.74
1.69
1.68
1.65
1.64
1.62
1.61
1.56
1.54
Cl
OTHP
S28
2.03
2.11
1.00
1.09
1.08
1.07
1.07
6.23
f1 (ppm)

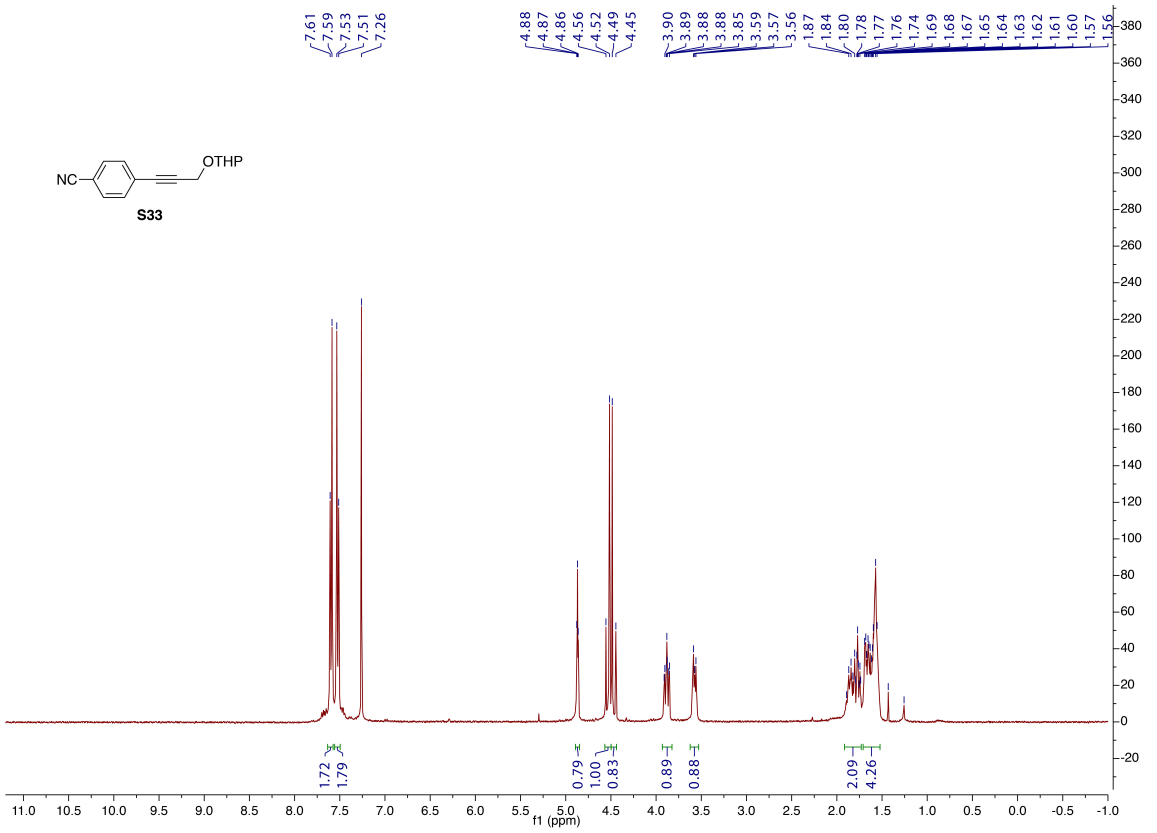

134.64
133.22
128.77
121.51
97.20
86.45
84.84
77.37
77.16
76.95
62.22
54.90
30.48
25.57
19.24
Cl
OTHP
S28
f1 (ppm)

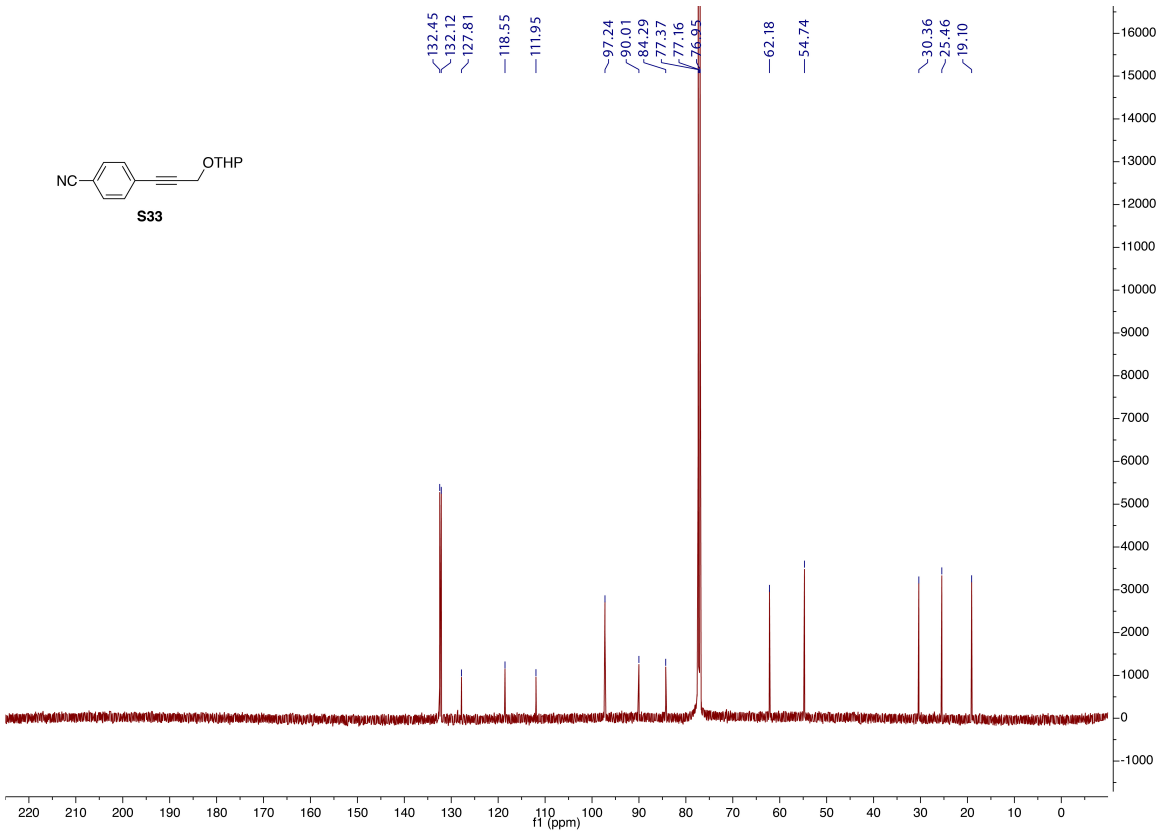

EtO2C
OTHP
S30
7.95
7.95
7.94
7.94
7.93
7.93
7.47
7.46
7.46
7.45
4.85
4.85
4.48
4.44
4.33
4.32
3.92
3.86
3.84
3.82
3.53
3.52
3.51
1.85
1.51
1.36
1.35
1.34
1.34
1.33
1.33
2.00
1.95
0.97
2.06
2.04
1.03
1.01
6.67
3.00
f1 (ppm)

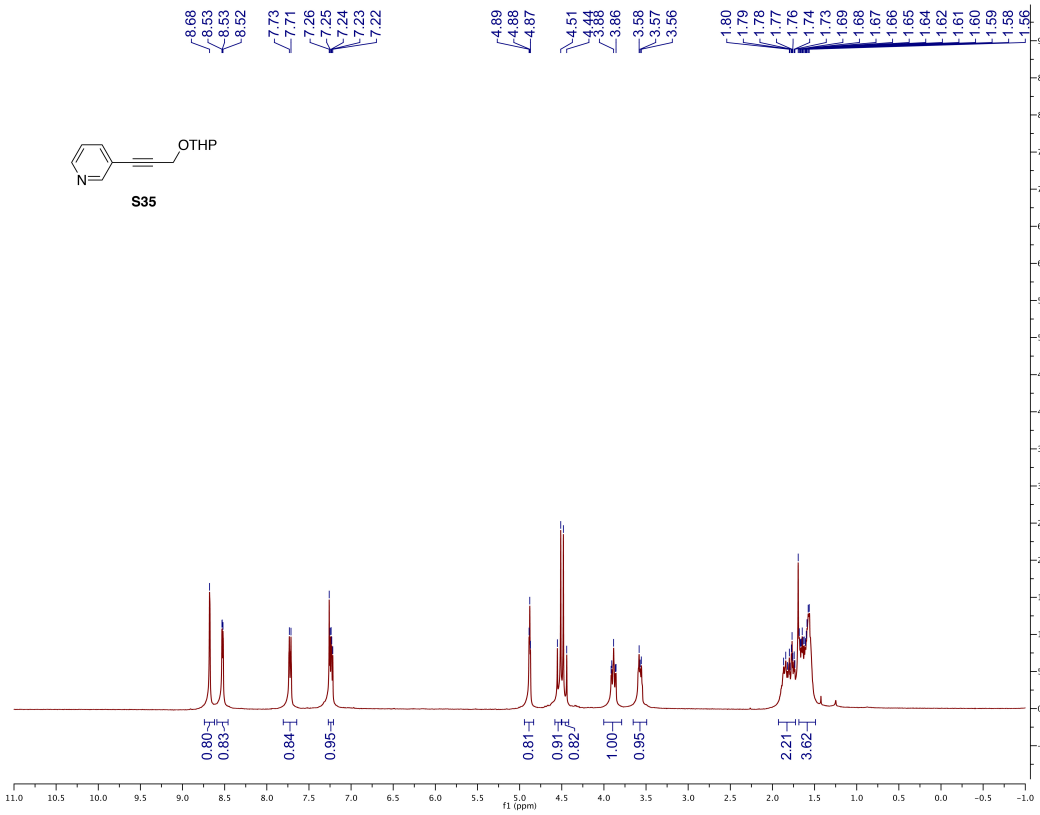

EtO2C
OTHP
S30
165.95
131.66
130.14
129.38
127.31
96.96
88.22
85.06
61.97
61.12
54.67
30.26
25.37
19.01
14.30
f1 (ppm)

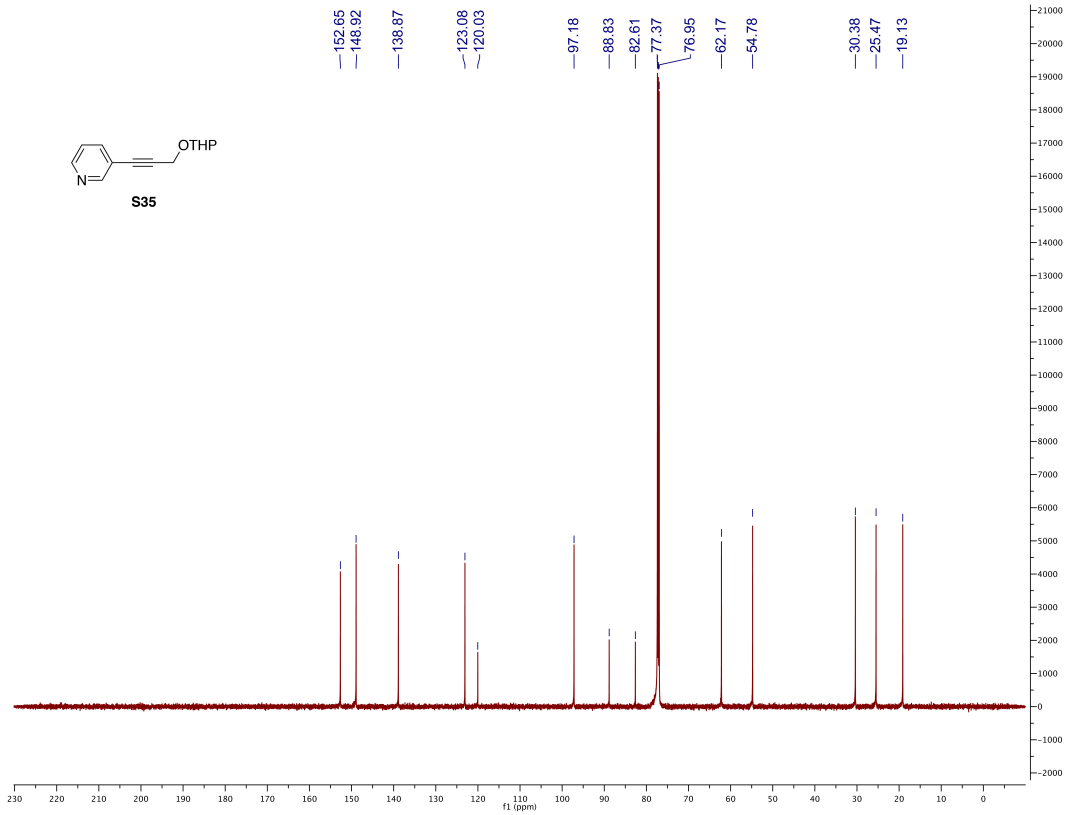

7.48
7.46
7.32
7.30
4.90
4.89
4.89
4.54
4.51
4.47
4.44
3.91
3.89
3.89
3.88
3.87
3.87
3.59
3.58
3.58
3.57
3.57
3.56
3.56
3.55
3.53
3.23
1.85
1.79
1.77
1.65
1.64
1.62
1.57
1.56
1.55
1.23
1.10
Et2N
O
OTHP
S31
1.99
2.00
1.10
1.10
1.12
1.17
2.84
1.77
1.33
1.22
1.85
2.17
3.28
2.93
f1 (ppm)

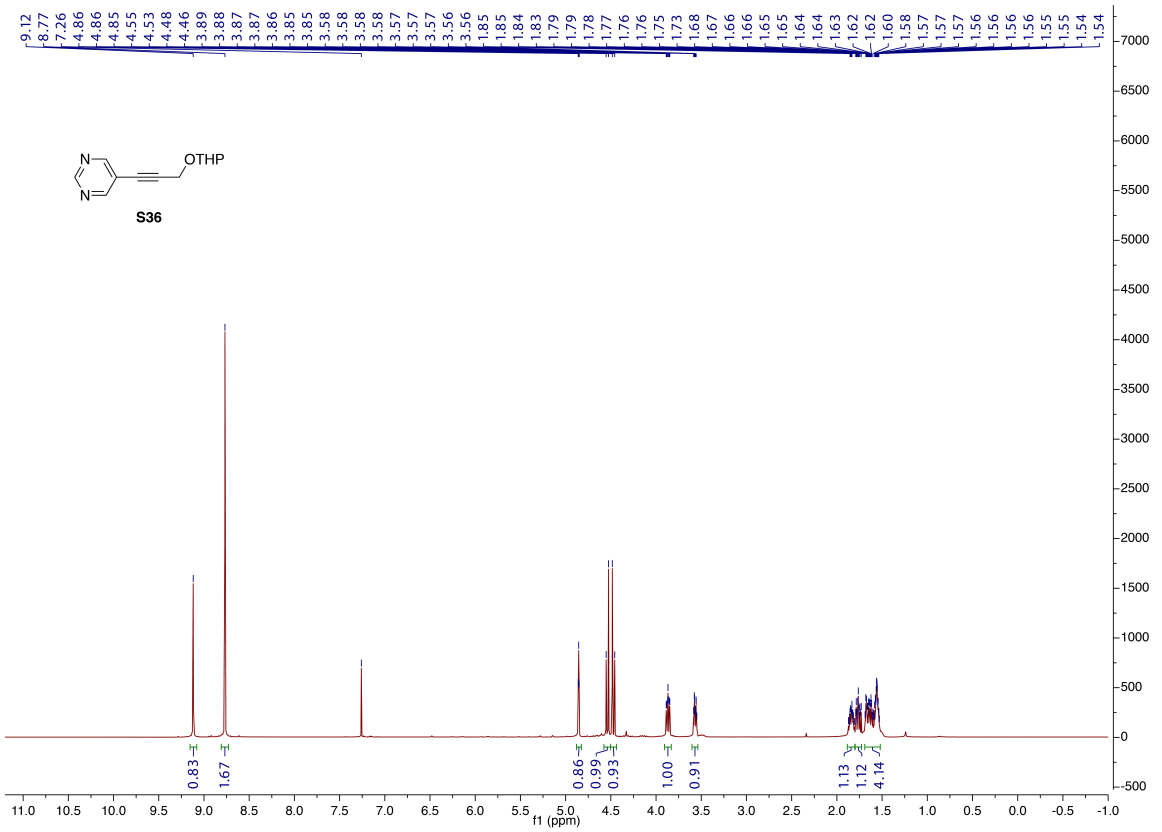

170.73
137.19
131.99
126.45
123.79
97.06
86.52
85.27
62.17
54.85
43.40
39.45
30.41
25.50
19.17
14.34
13.02
Et2N
O
OTHP
S31
f1 (ppm)

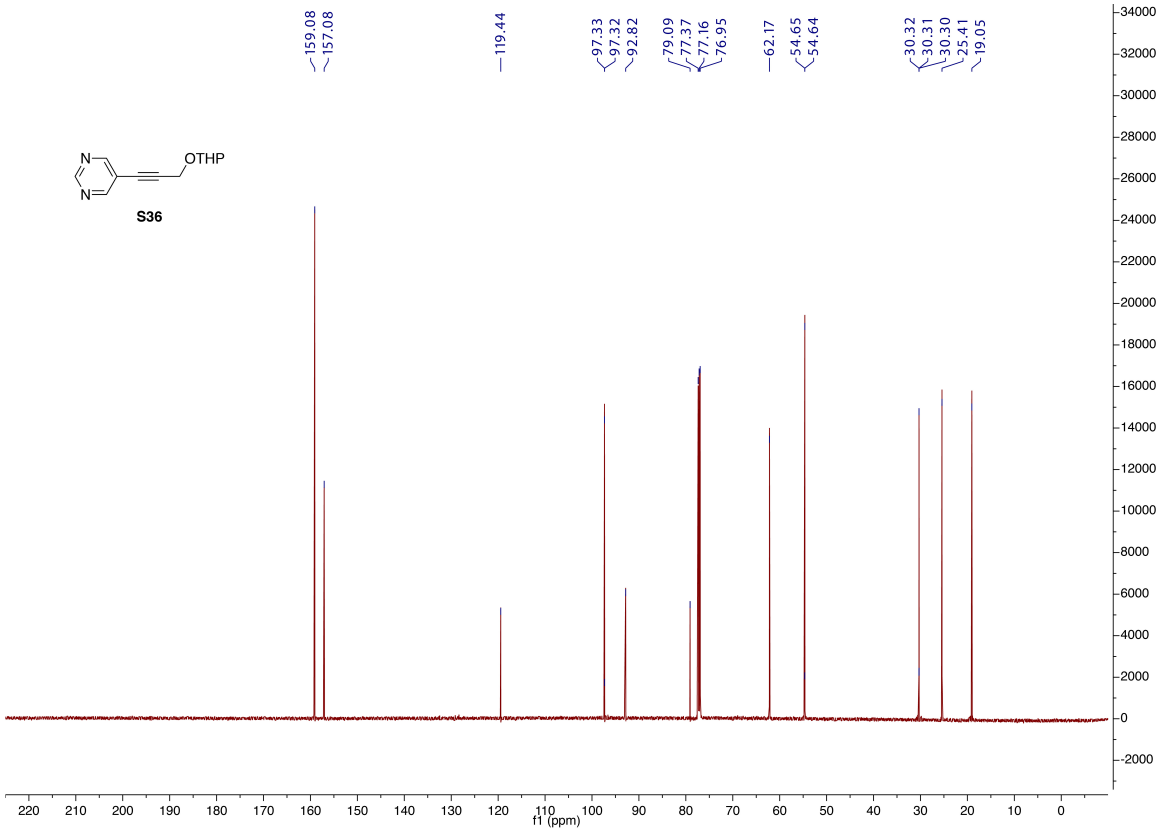

7.61
7.59
7.53
7.51
7.26
4.88
4.87
4.86
4.56
4.52
4.49
4.45
3.90
3.89
3.88
3.88
3.85
3.59
3.57
3.56
1.87
1.84
1.80
1.78
1.77
1.76
1.74
1.69
1.68
1.67
1.65
1.64
1.63
1.62
1.61
1.60
1.57
1.56
NC
OTHP
S33
1.72
1.79
0.79
1.00
0.83
0.89
0.88
2.09
4.26
f1 (ppm)

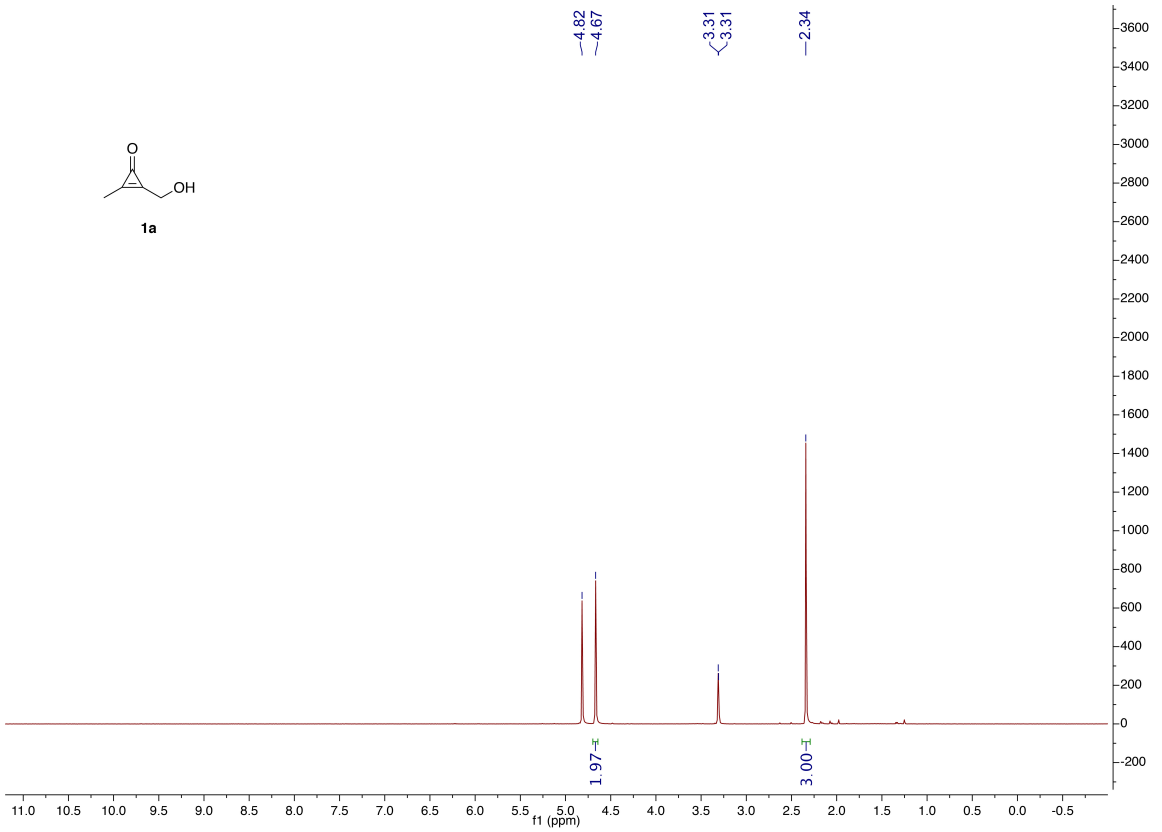

132.45
132.12
127.81
118.55
111.95
97.24
90.01
84.29
77.37
77.16
76.95
62.18
54.74
30.36
25.46
19.10
NC
OTHP
S33
f1 (ppm)

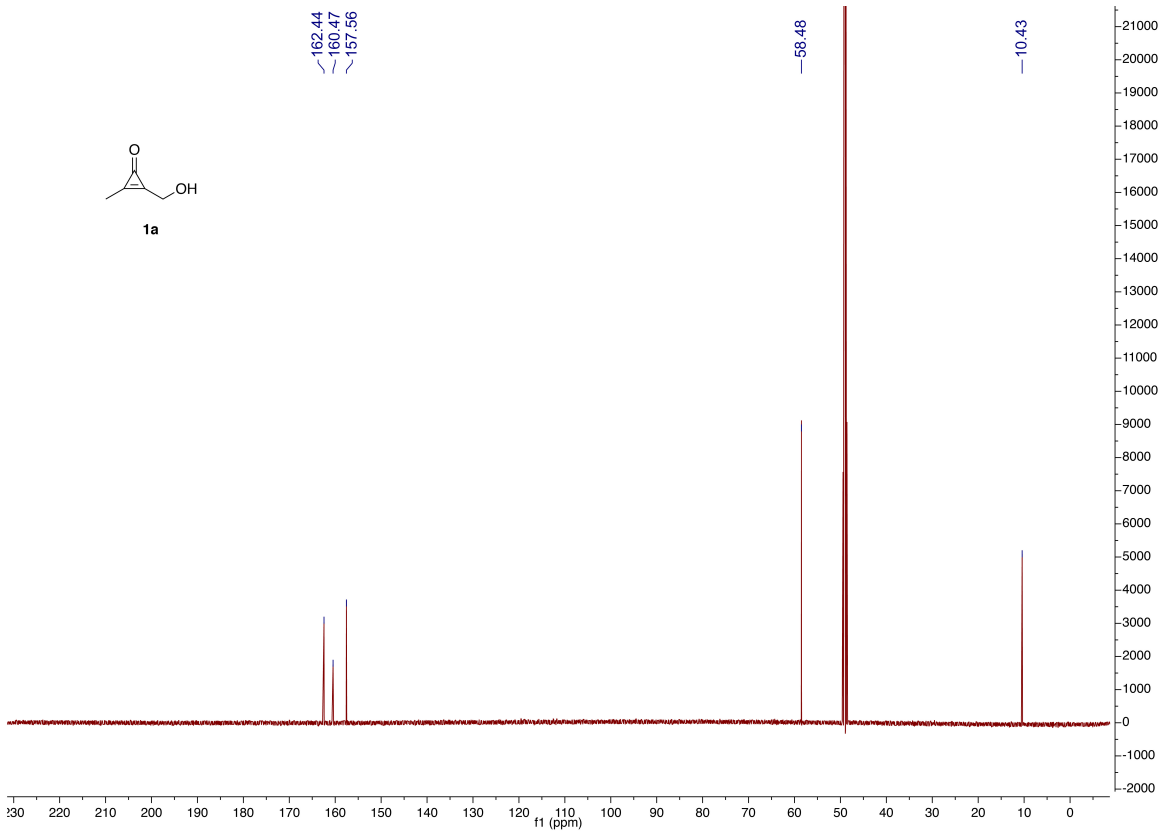

8.68
8.53
8.53
8.52
7.73
7.71
7.26
7.25
7.24
7.23
7.22
4.89
4.88
4.87
4.51
4.44
3.88
3.86
3.58
3.57
3.56
1.80
1.79
1.78
1.77
1.76
1.74
1.73
1.69
1.68
1.67
1.66
1.65
1.64
1.62
1.61
1.60
1.59
1.58
1.56
OTHP
N
S35
0.80
0.83
0.84
0.95
0.81
0.91
0.82
1.00
0.95
2.21
3.62
f1 (ppm)

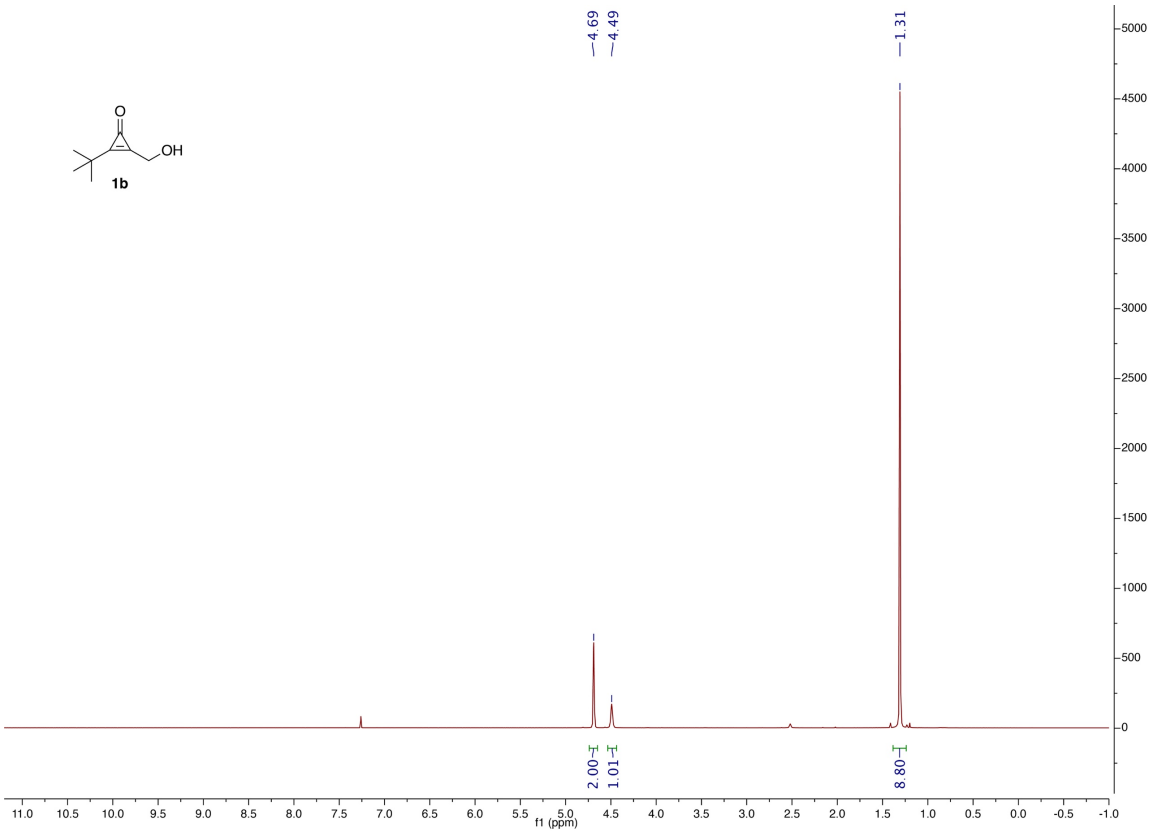

152.65
148.92
138.87
123.08
120.03
97.18
88.83
82.61
77.37
76.95
62.17
54.78
30.38
25.47
19.13
OTHP
N
S35
f1 (ppm)

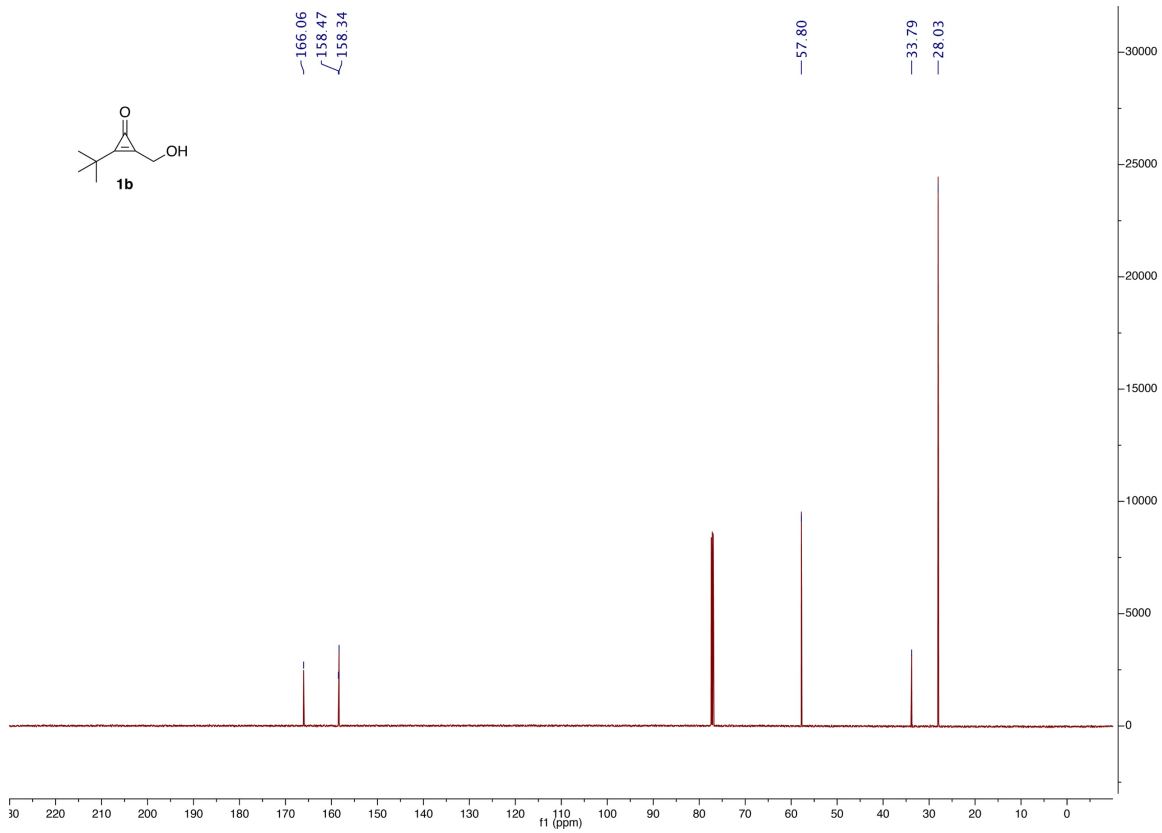

OTHP
S36
f1 (ppm)

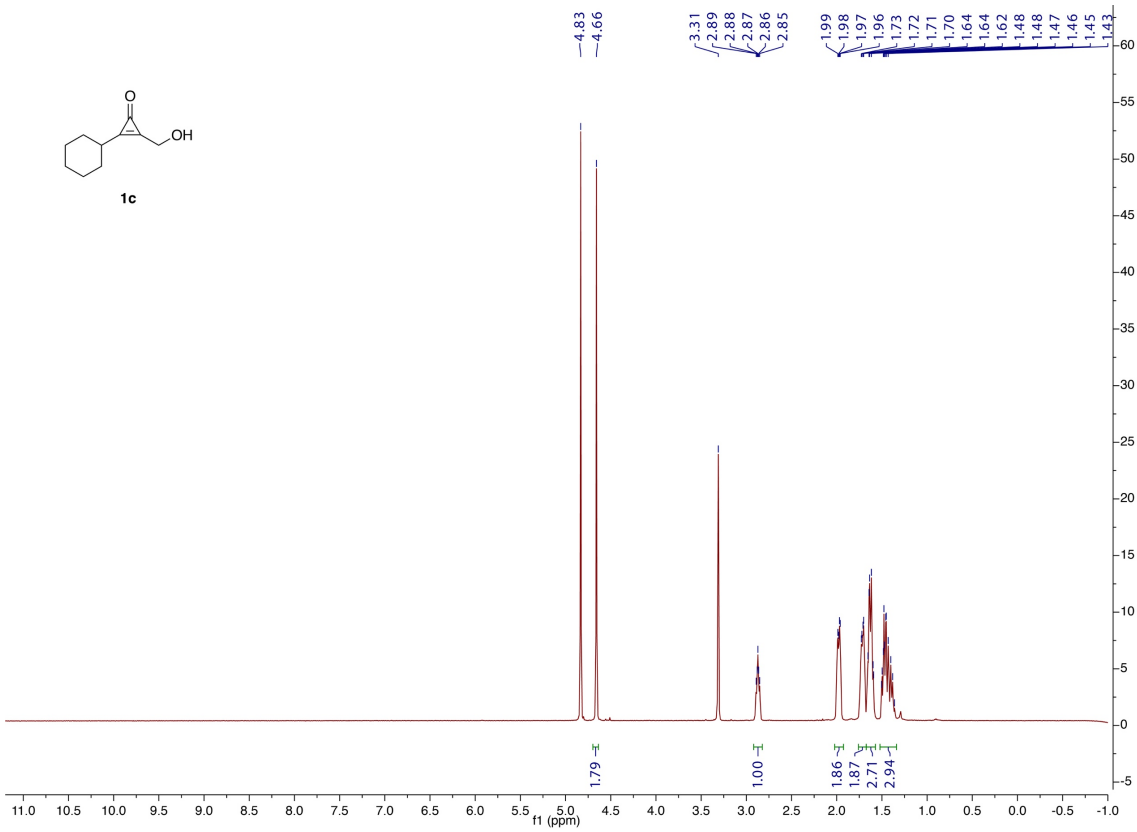

OTHP
S36
f1 (ppm)

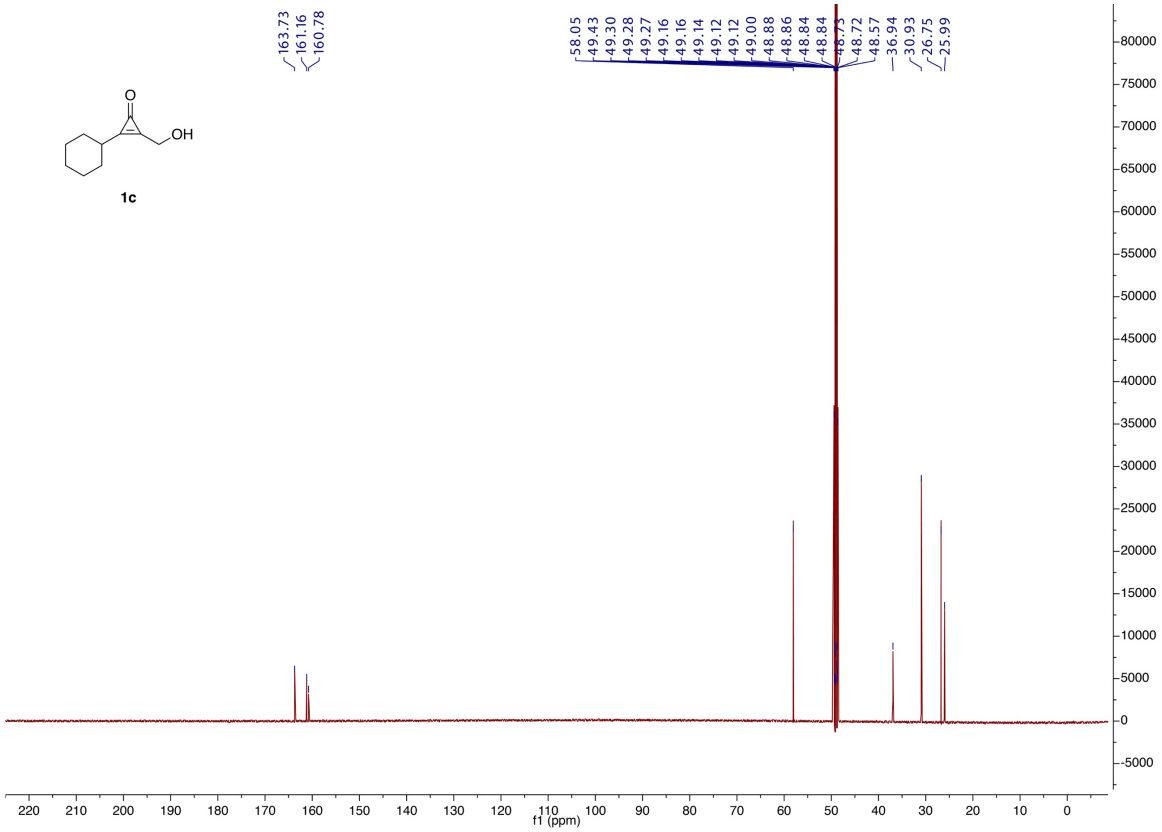

4.82
4.67
3.31
3.31
2.34
O
OH
1a
1.97
3.00
f1 (ppm)

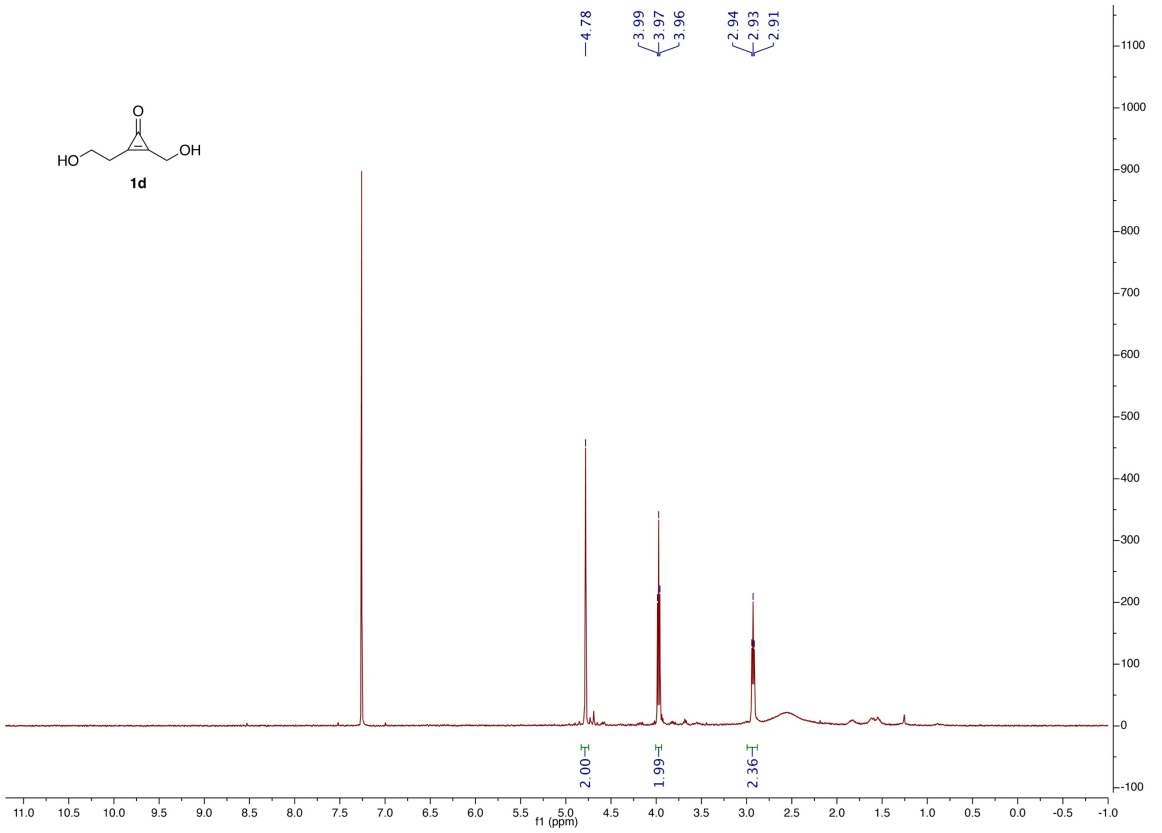

162.44
160.47
157.56
58.48
10.43
O
OH
1a
f1 (ppm)

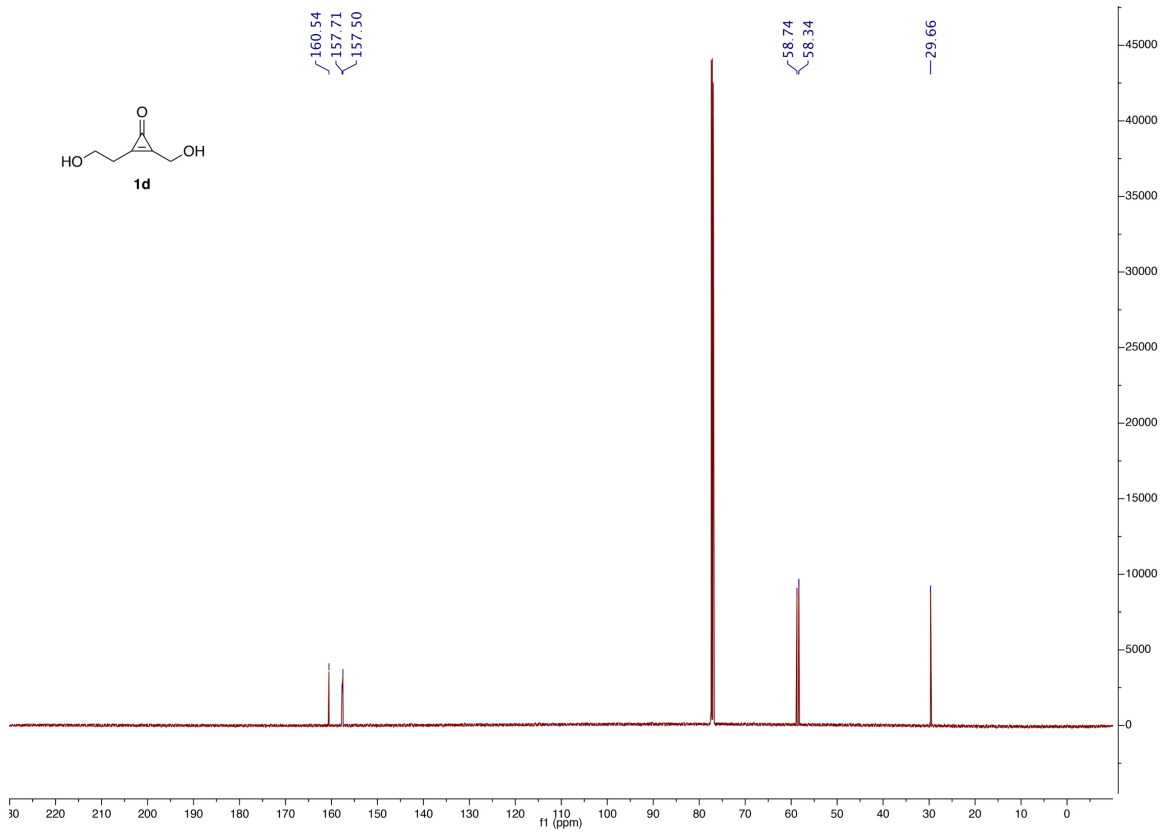

4.69
4.49
1.31
OH
1b
2.00
1.01
8.80
f1 (ppm)

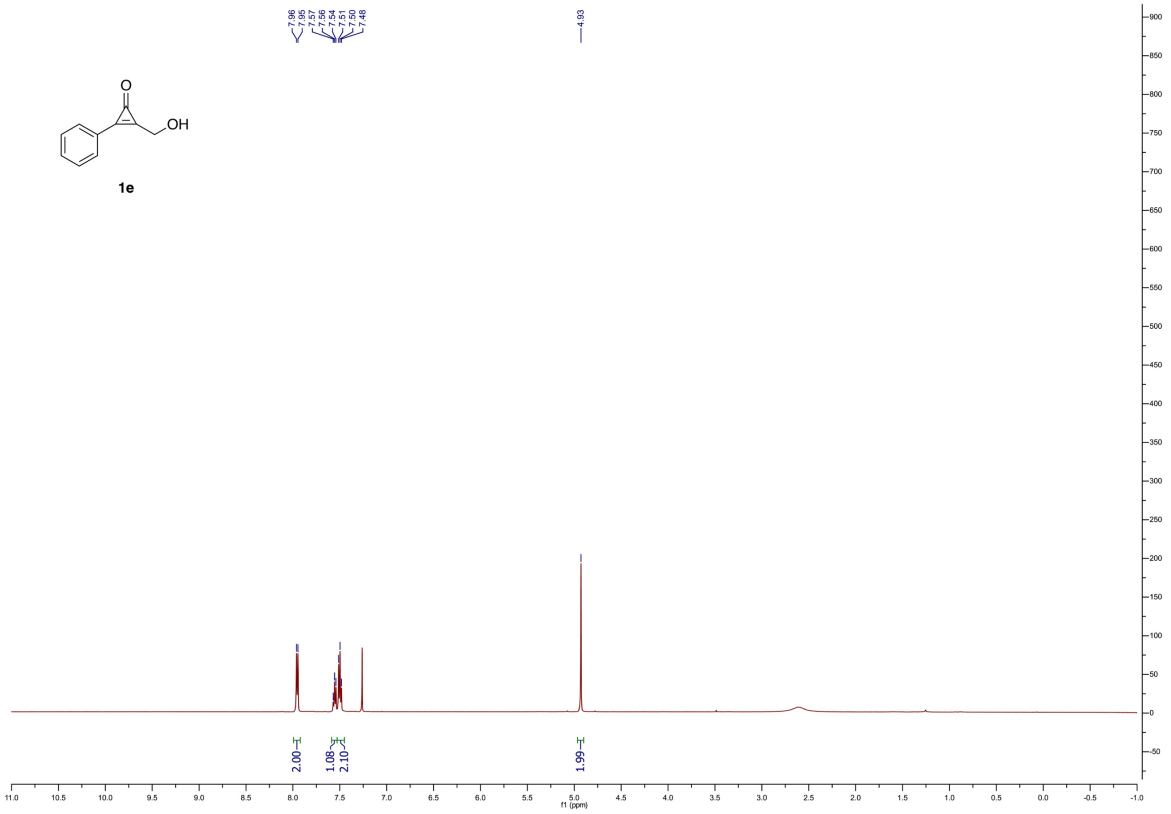

166.06
158.47
158.34
57.80
33.79
28.03
OH
1b
f1 (ppm)

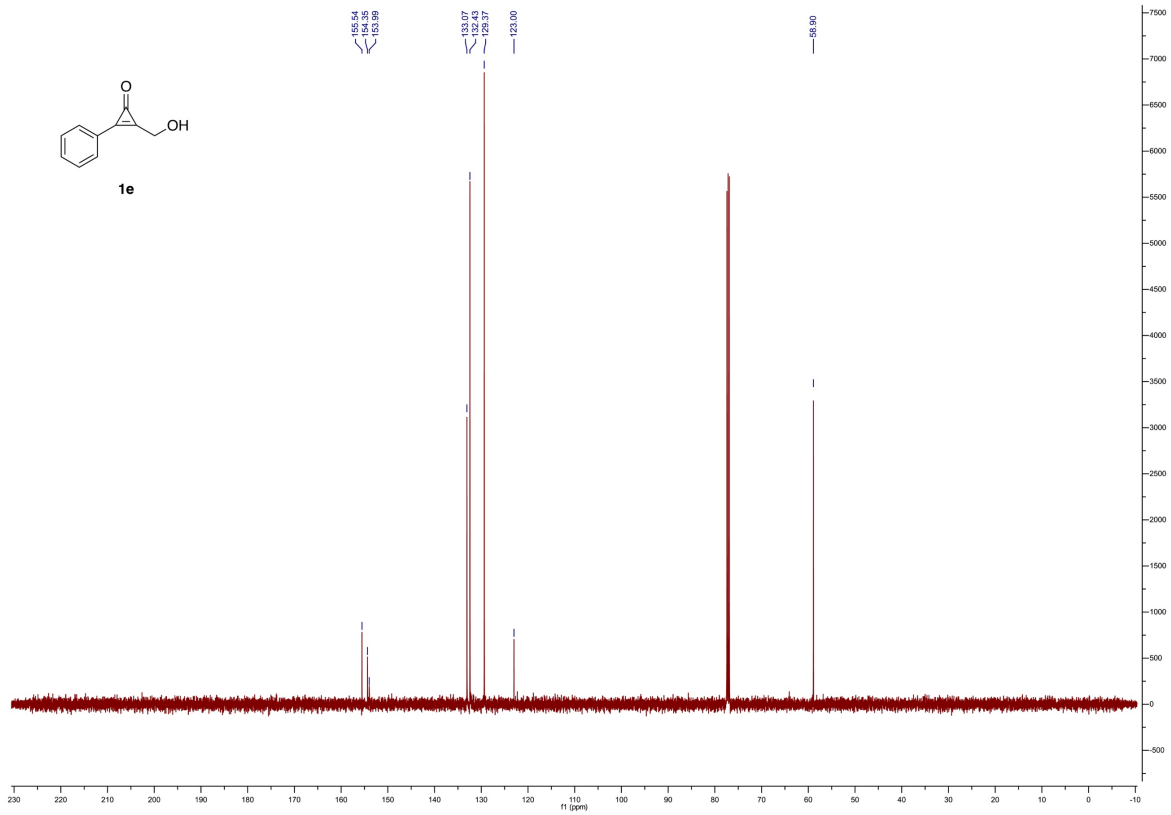

4.83
4.66
3.31
2.89
2.88
2.87
2.86
2.85
1.99
1.98
1.97
1.96
1.73
1.72
1.71
1.70
1.64
1.64
1.62
1.48
1.48
1.47
1.46
1.45
1.43
1.79
1.00
1.86
1.87
2.71
2.94
f1 (ppm)
OH
1c

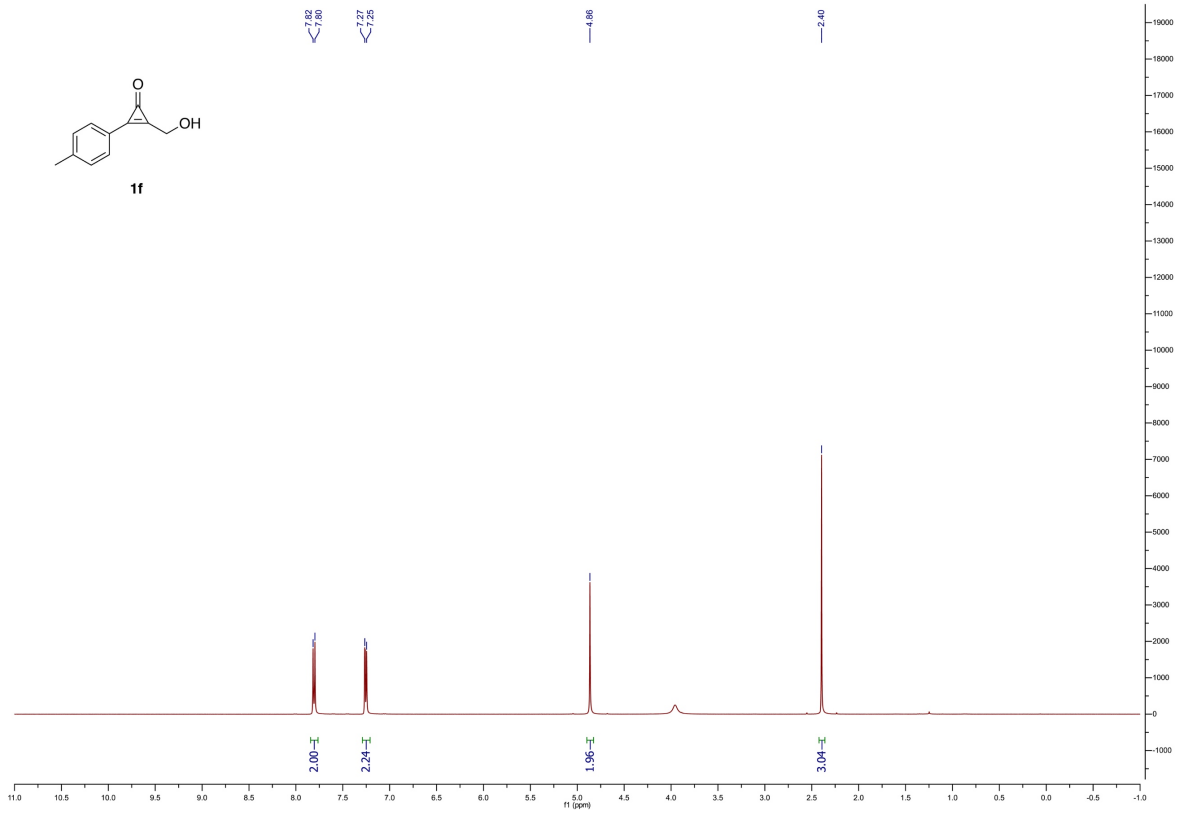

163.73
161.16
160.78
58.05
49.43
49.30
49.28
49.27
49.16
49.16
49.14
49.12
49.12
49.00
48.88
48.86
48.84
48.84
48.73
48.72
48.57
36.94
30.93
26.75
25.99
f1 (ppm)
OH
1c

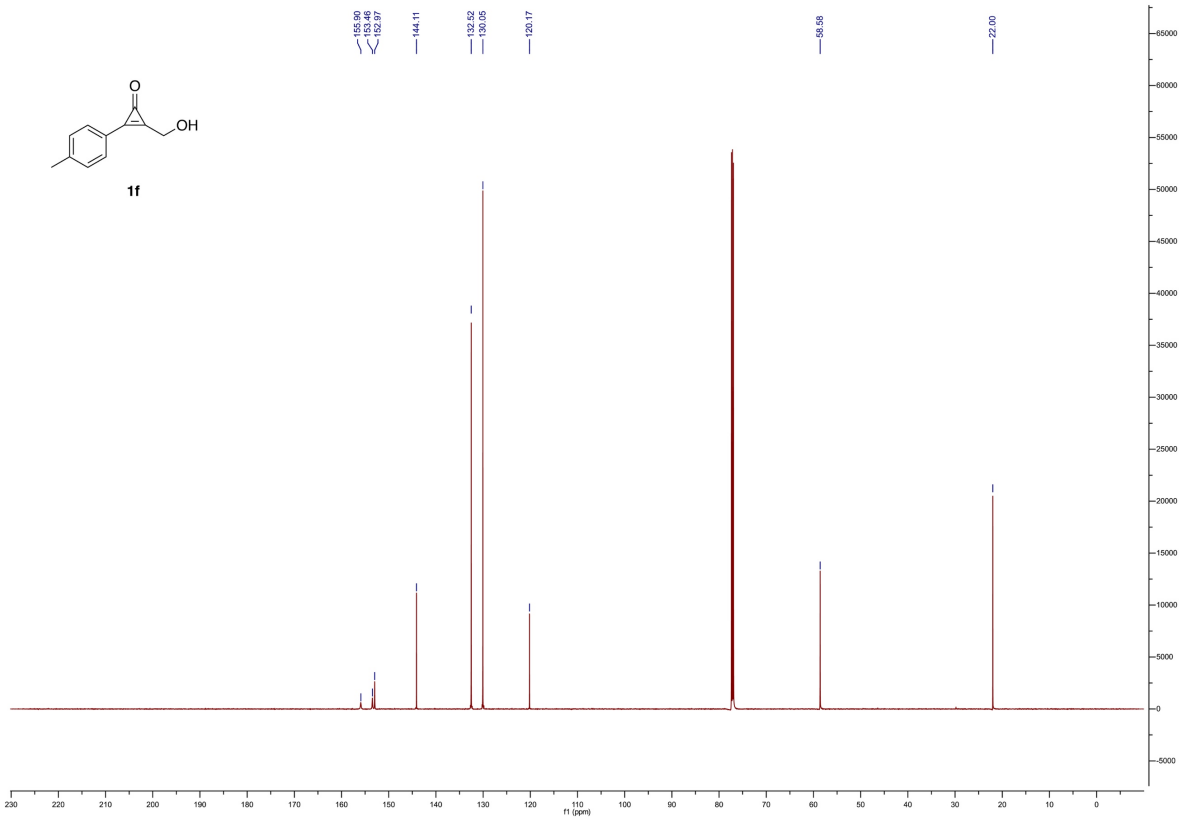

4.78
3.99
3.97
3.96
2.94
2.93
2.91
HO
OH
1d
2.00
1.99
2.36
f1 (ppm)

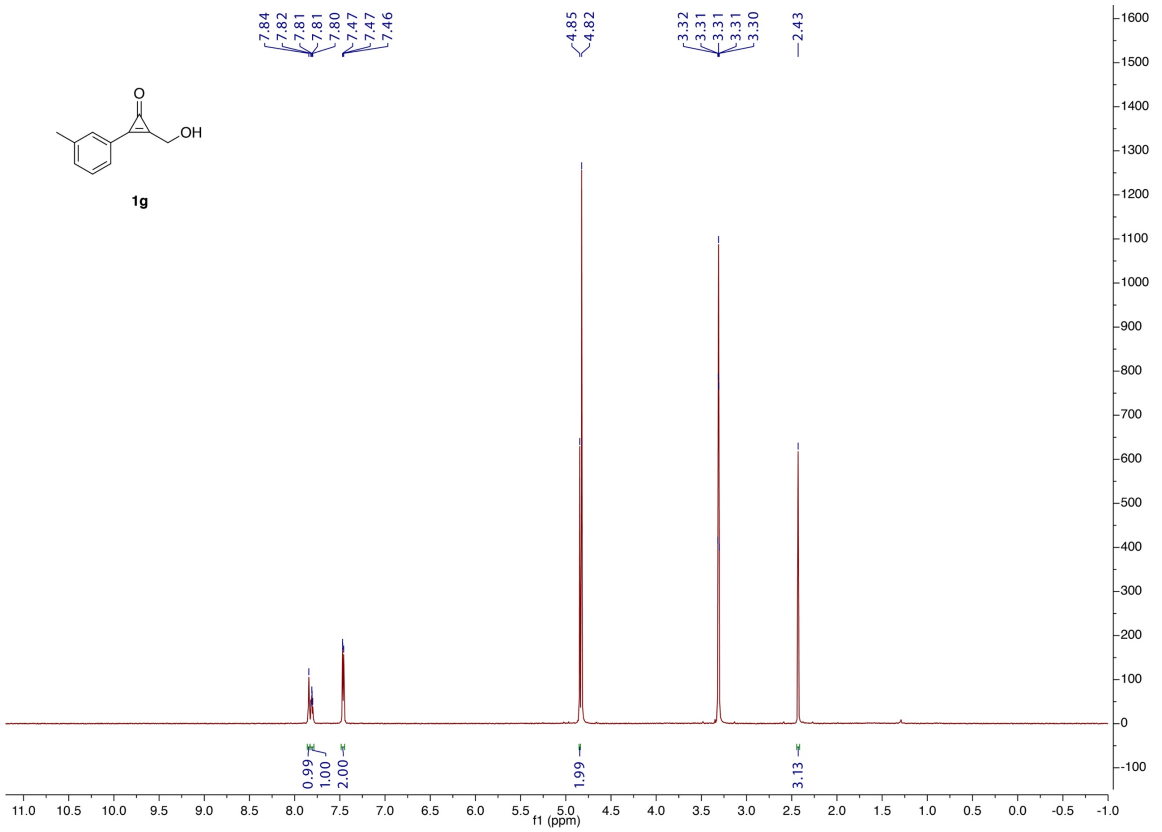

160.54
157.71
157.50
58.74
58.34
29.66
HO
OH
1d
f1 (ppm)


7.96
7.95
7.57
7.56
7.55
7.54
7.51
7.50
7.48
4.93
O
OH
1e
2.00
1.08
2.10
1.99
f1 (ppm)


155.54
154.35
153.99
133.07
132.43
129.37
123.00
58.90
O
OH
1e
f1 (ppm)


7.82
7.80
7.27
7.25
4.86
2.40
O
OH
1f
2.00
2.24
1.96
3.04
f1 (ppm)


155.90
153.46
152.97
144.11
132.52
130.05
120.17
58.58
22.00
O
OH
1f
f1 (ppm)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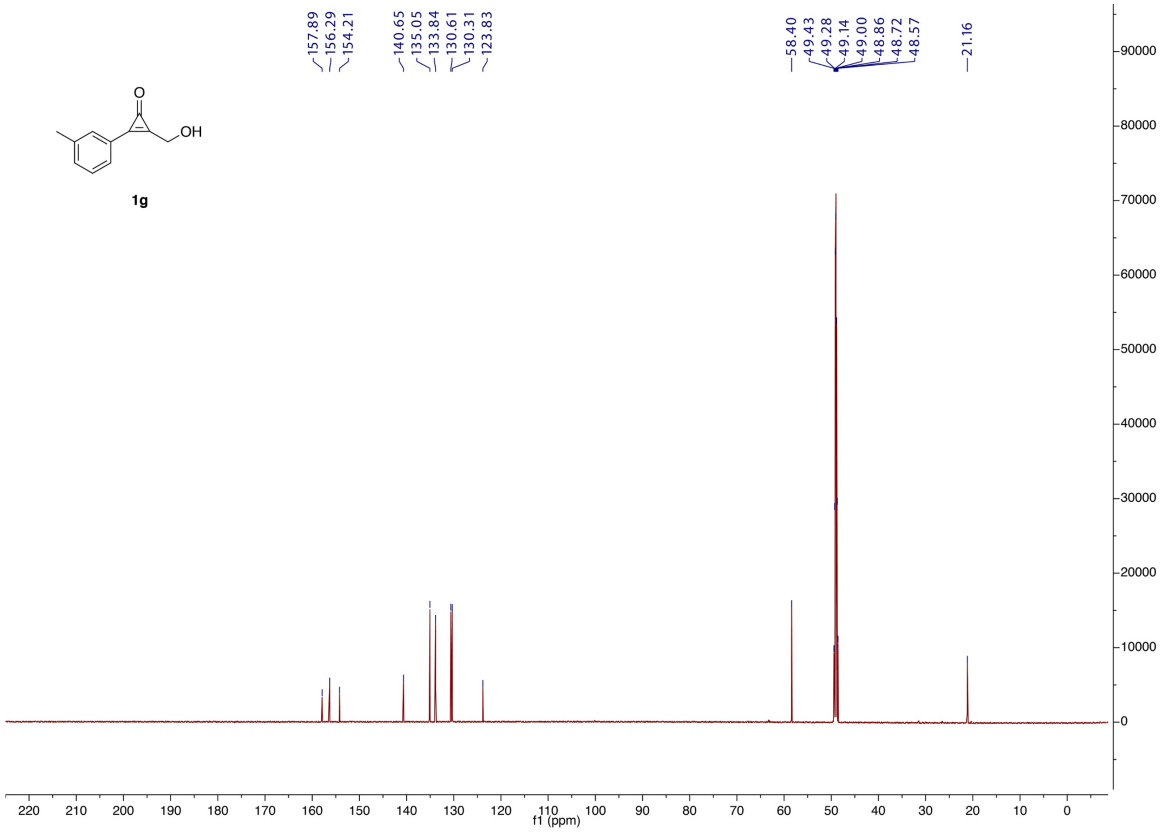
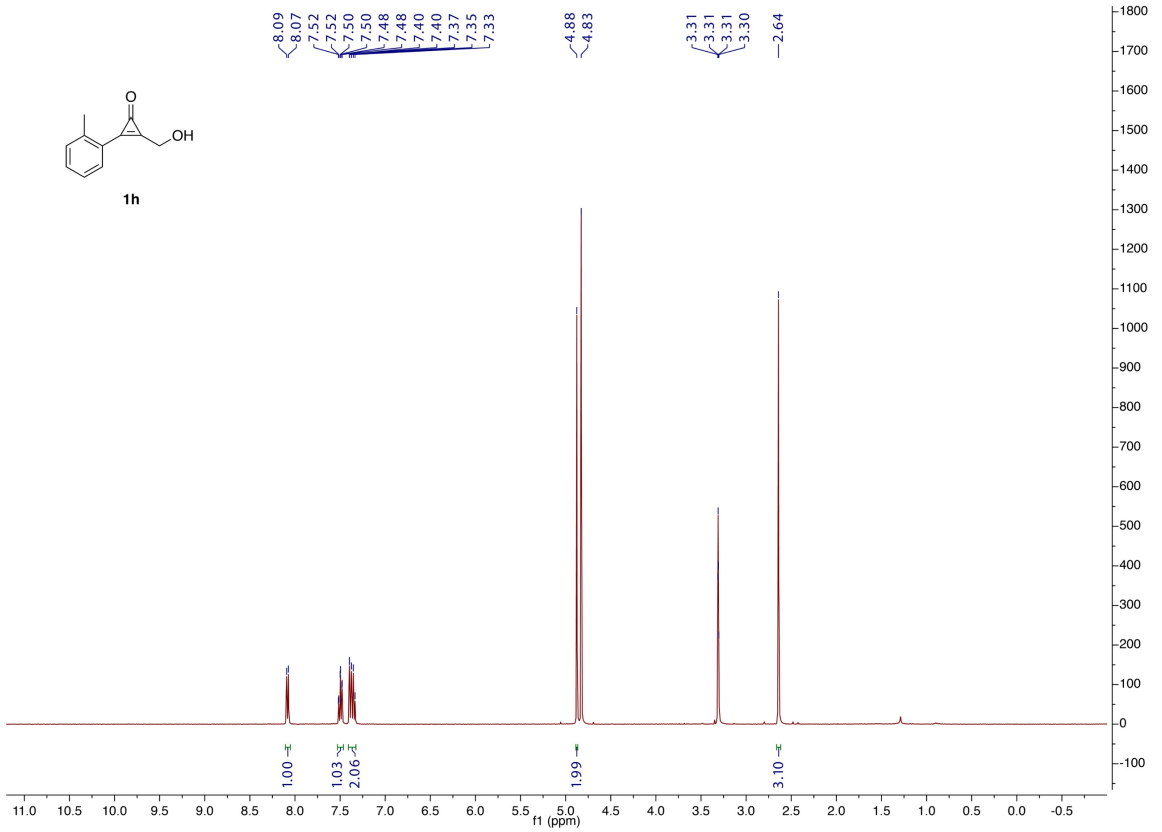
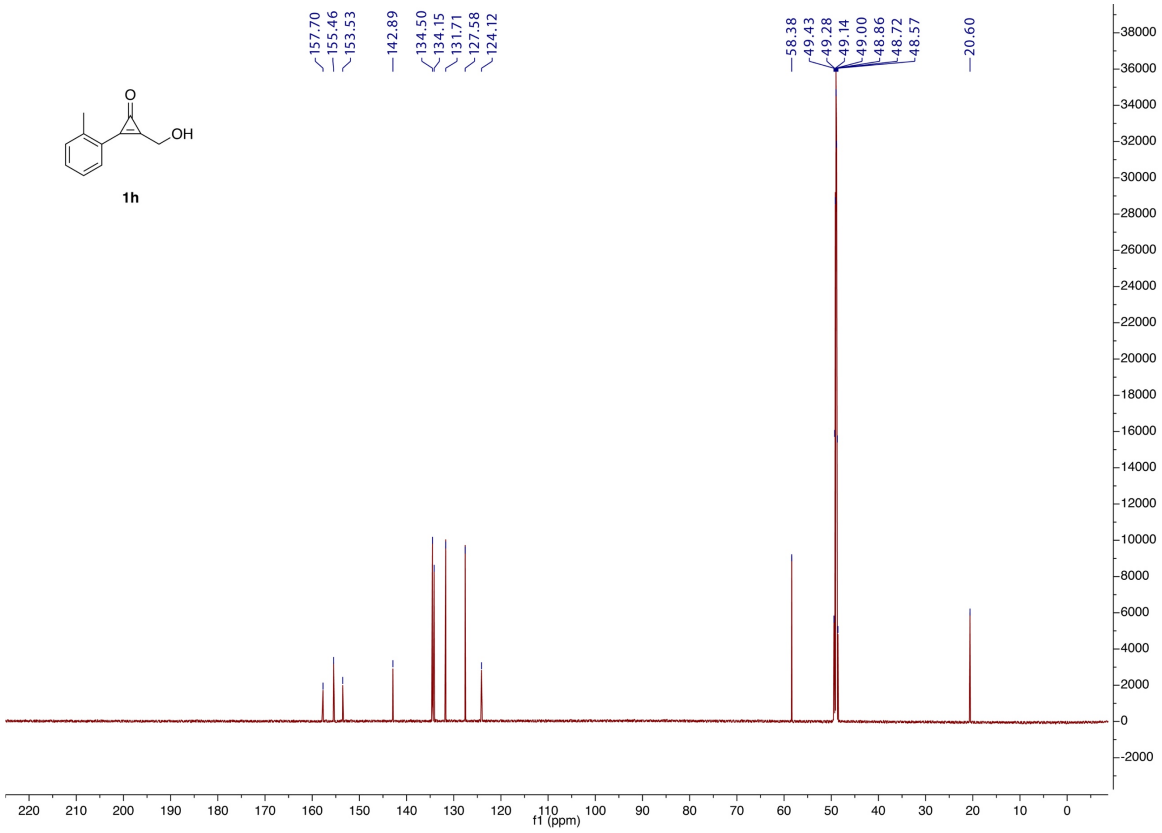
7.82
7.81
7.81
7.80
7.47
7.47
7.46
4.85
4.82
3.32
3.31
3.31
3.31
3.30
2.43
O
OH
1g
0.99
1.00
2.00
1.99
3.13
f1 (ppm)


157.89
156.29
154.21
140.65
135.05
133.84
130.61
130.31
123.83
58.40
49.43
49.28
49.14
49.00
48.86
48.72
48.57
21.16
O
OH
1g
f1 (ppm)


8.09
8.07
7.52
7.52
7.50
7.50
7.48
7.48
7.40
7.40
7.37
7.35
7.33
4.88
4.83
3.31
3.31
3.31
3.30
2.64
O
OH
1h
1.00
1.03
2.06
1.99
3.10
f1 (ppm)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153.53
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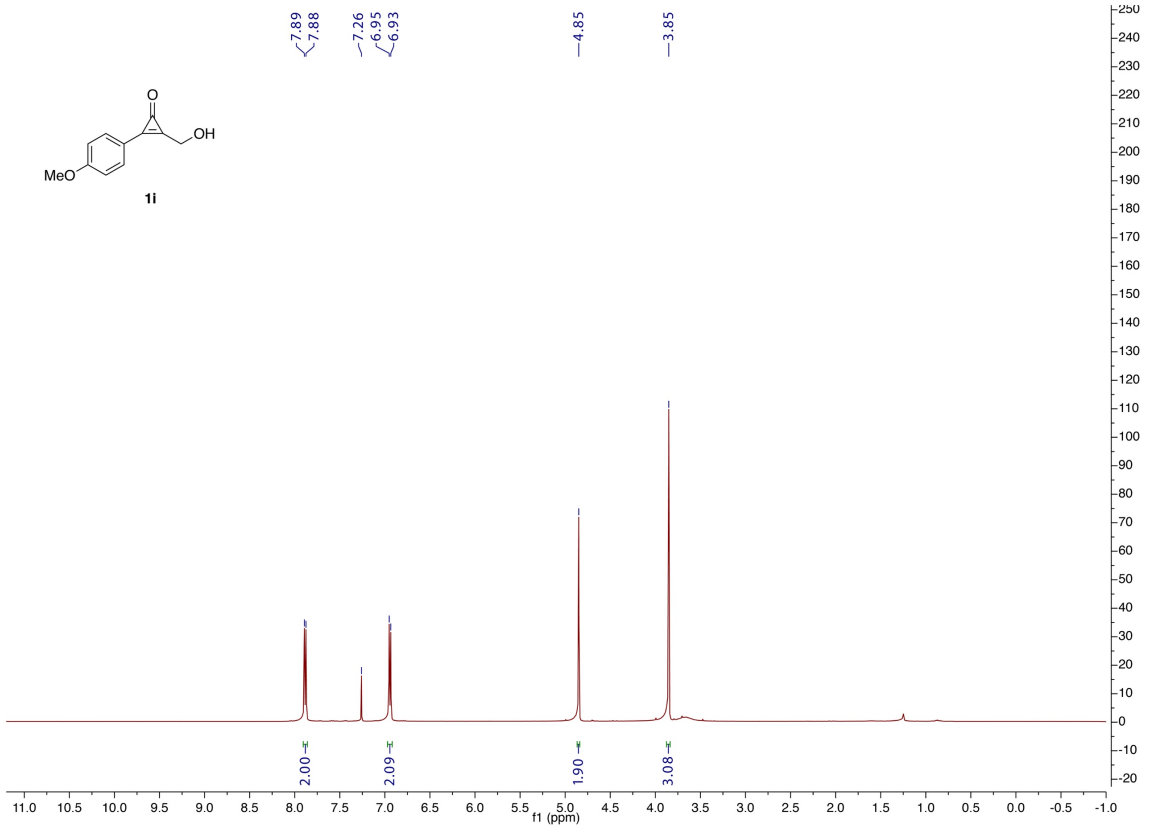
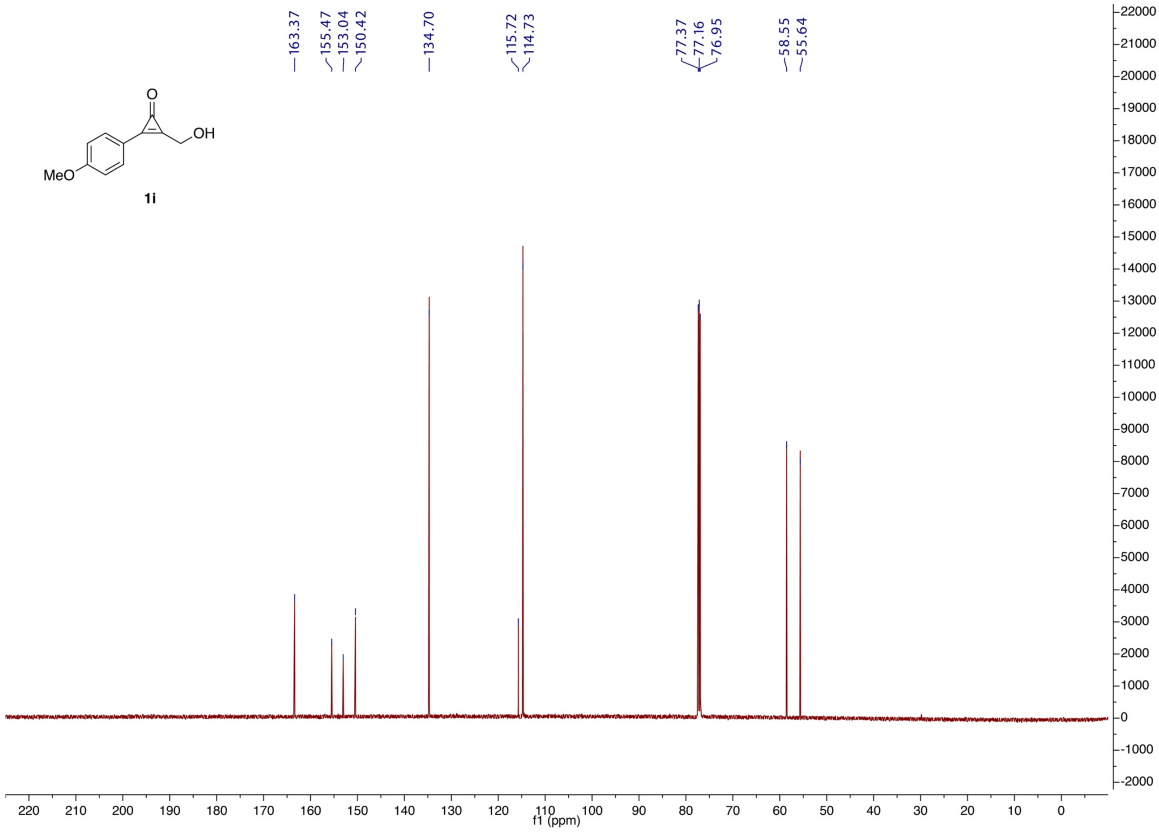
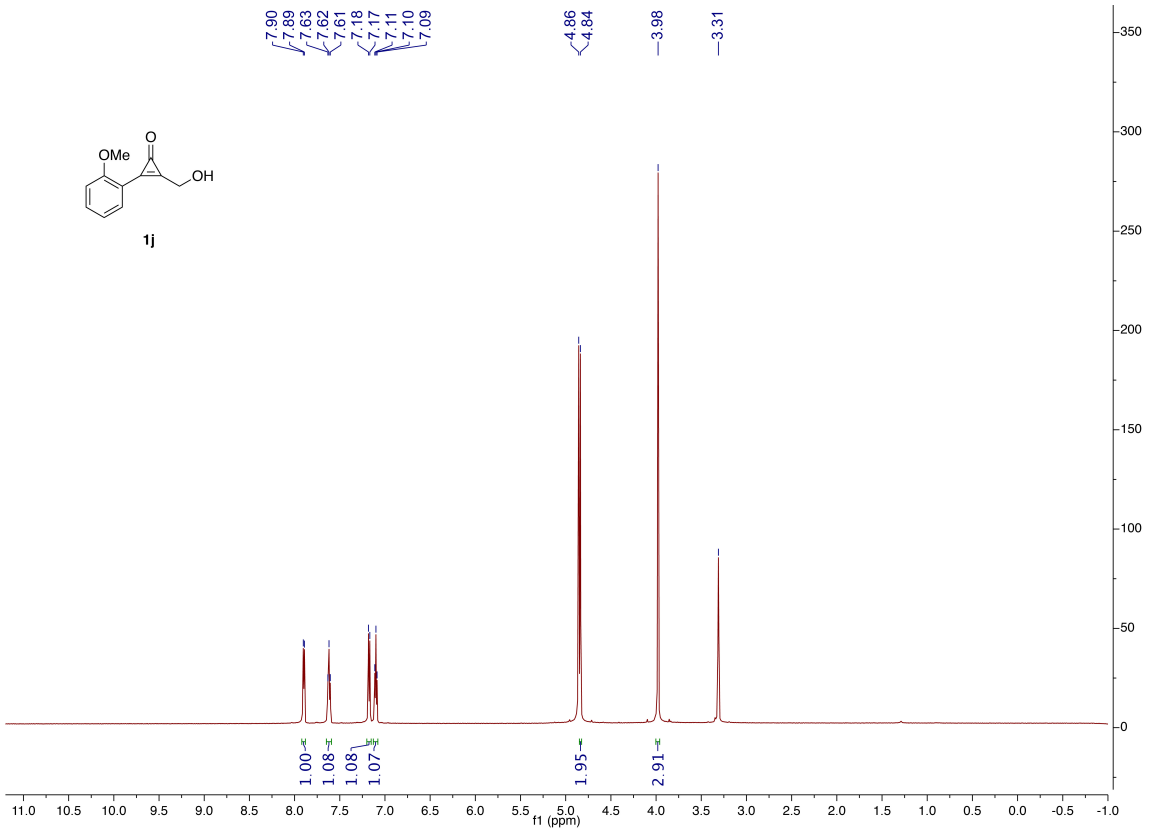
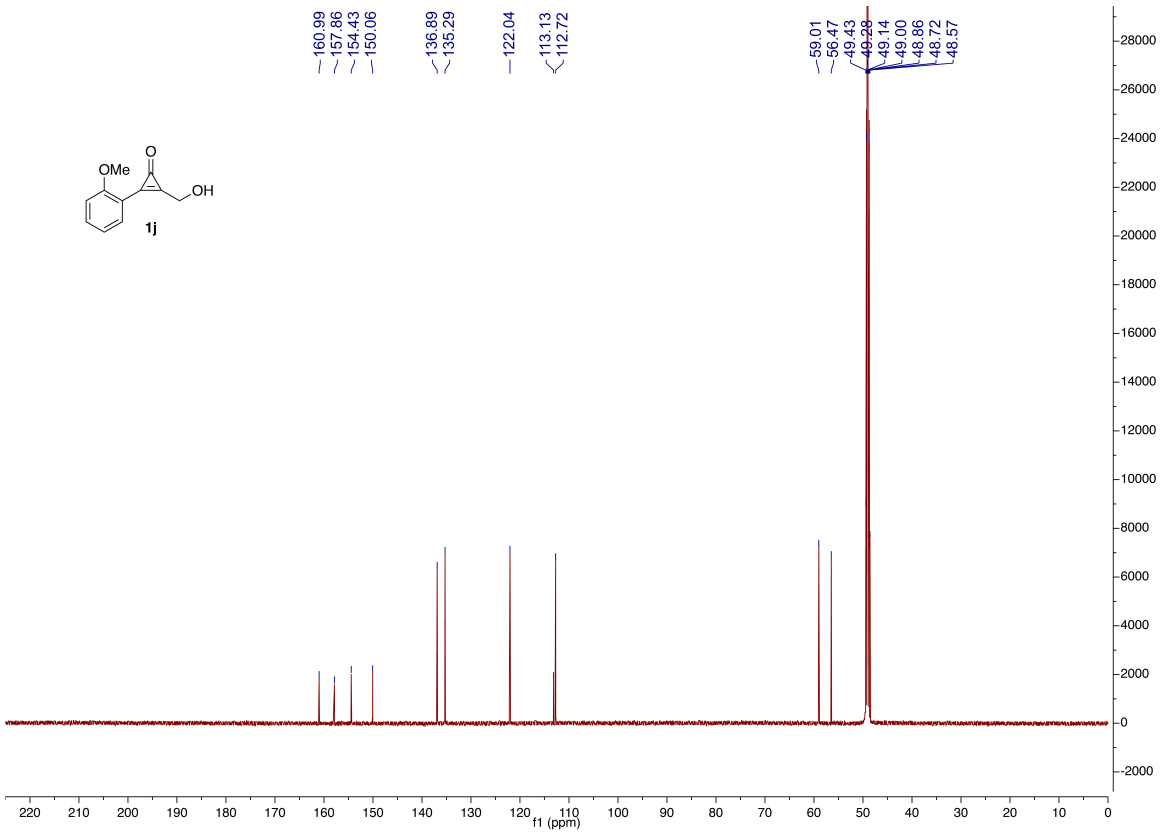
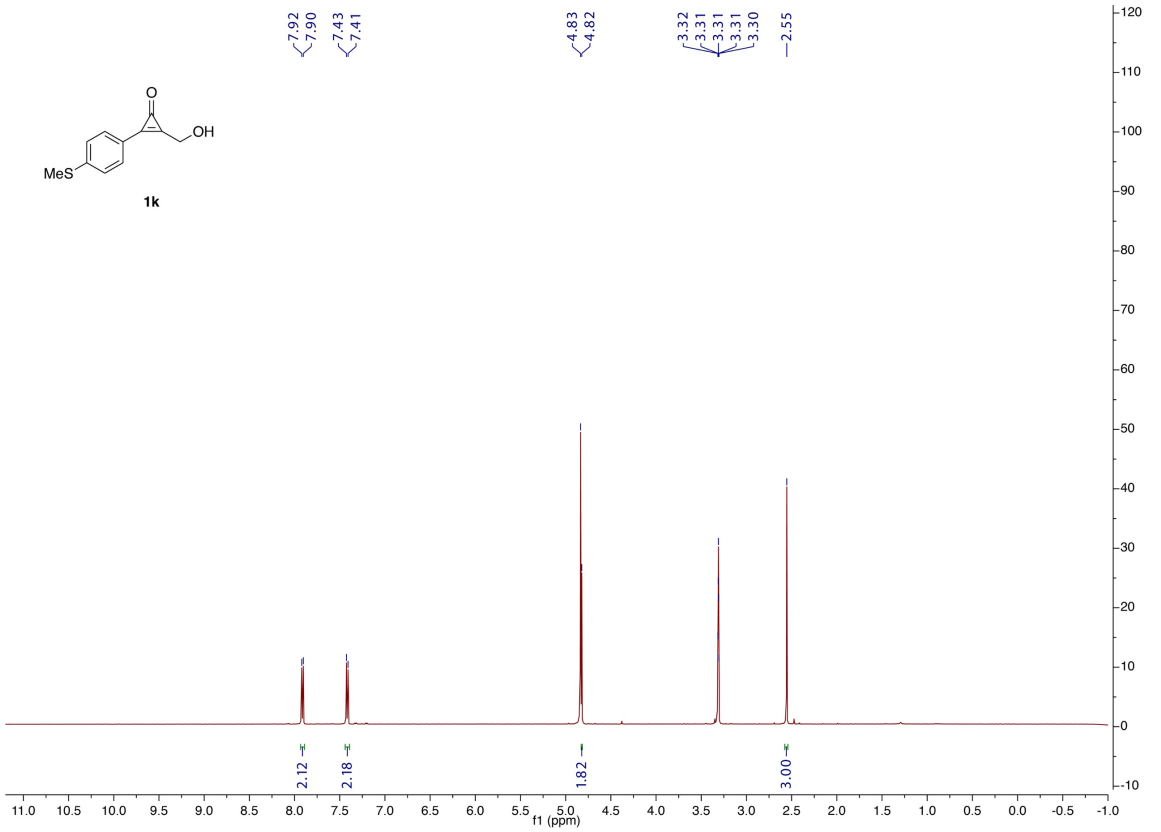
134.50
134.15
131.71
127.58
124.12
58.38
49.43
49.28
49.14
49.00
48.86
48.72
48.57
20.60
O
OH
1h
f1 (ppm)


7.89
7.88
7.26
6.95
6.93
4.85
3.85
O
OH
MeO
1i
2.00
2.09
1.90
3.08
f1 (ppm)


163.37
155.47
153.04
150.42
134.70
115.72
114.73
77.37
77.16
76.95
58.55
55.64
O
OH
MeO
1i
f1 (ppm)


7.90
7.89
7.63
7.62
7.61
7.18
7.17
7.11
7.10
7.09
4.86
4.84
3.98
3.31
OMe
O
OH
1j
1.00
1.08
1.08
1.07
1.95
2.91
f1 (ppm)


160.99
157.86
154.43
150.06
136.89
135.29
122.04
113.13
112.72
59.01
56.47
49.43
49.28
49.14
49.00
48.86
48.72
48.57
OMe
O
OH
1j
f1 (ppm)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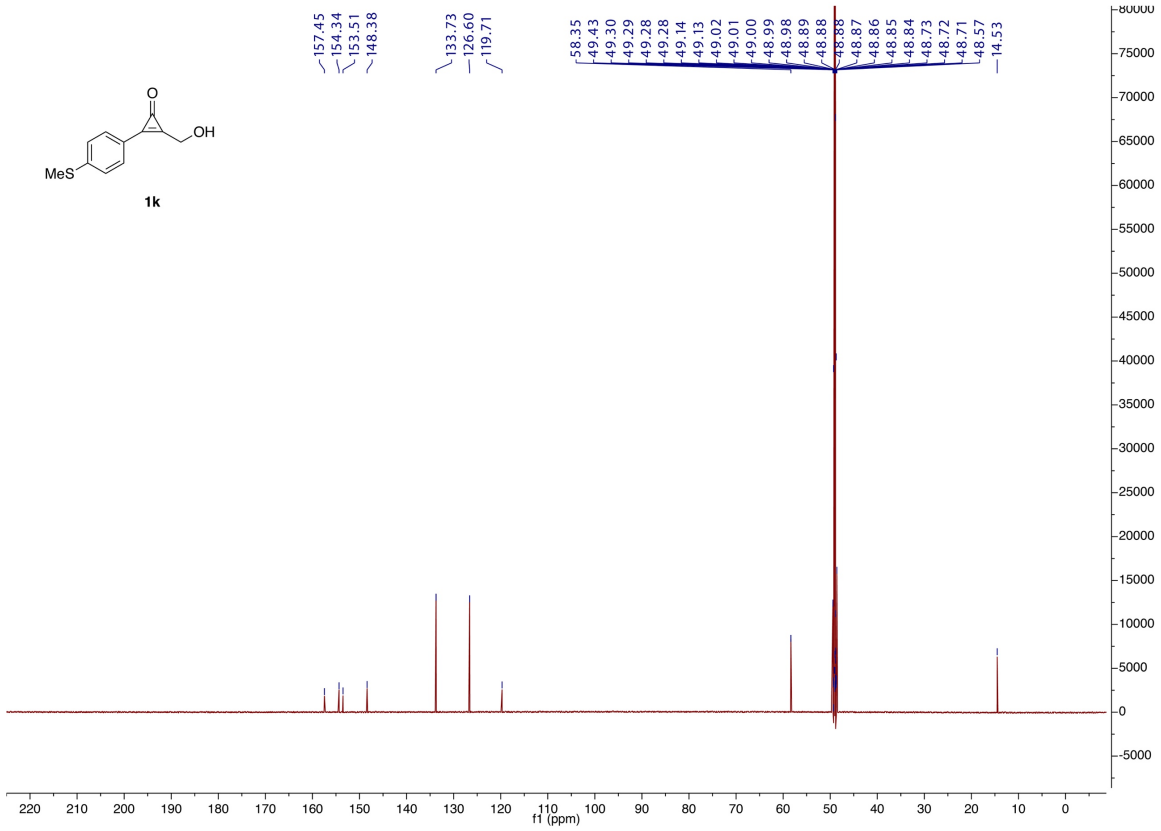
7.90
7.43
7.41
4.83
4.82
3.32
3.31
3.31
3.31
3.30
2.55
O
OH
MeS
1k
2.12
2.18
1.82
3.00
f1 (ppm)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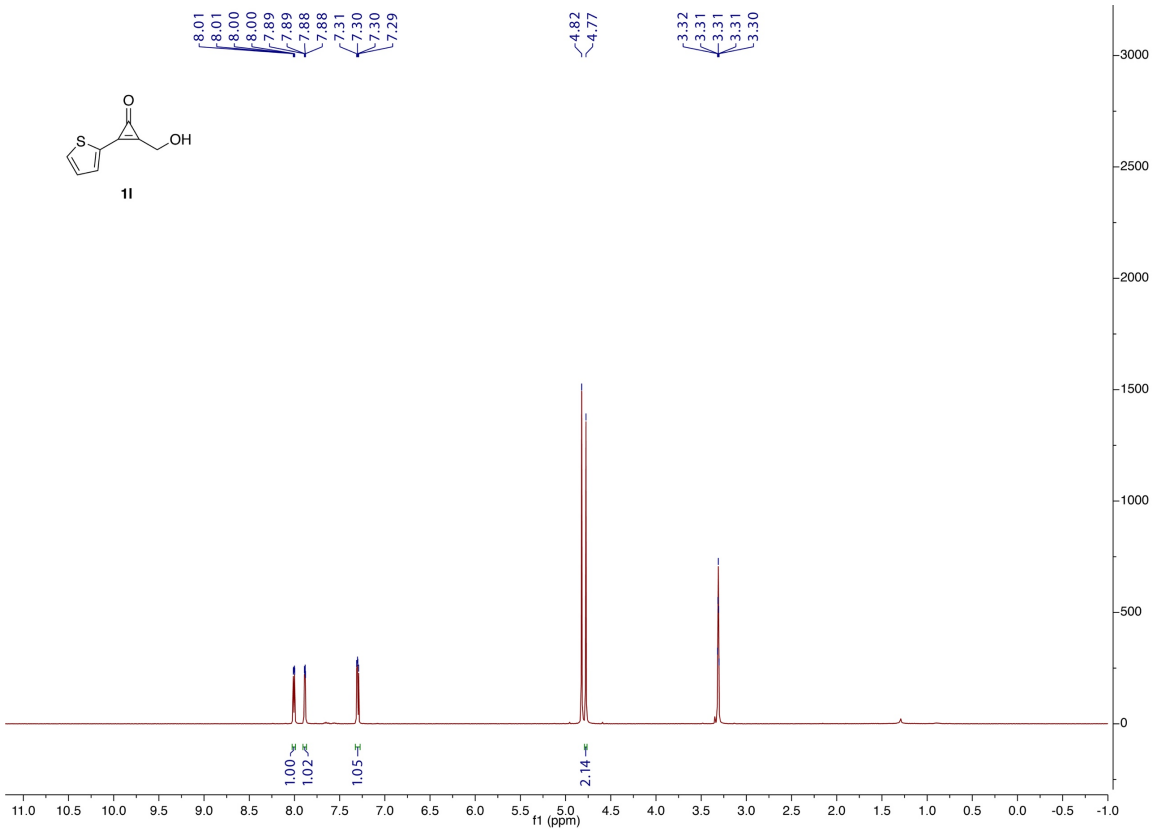
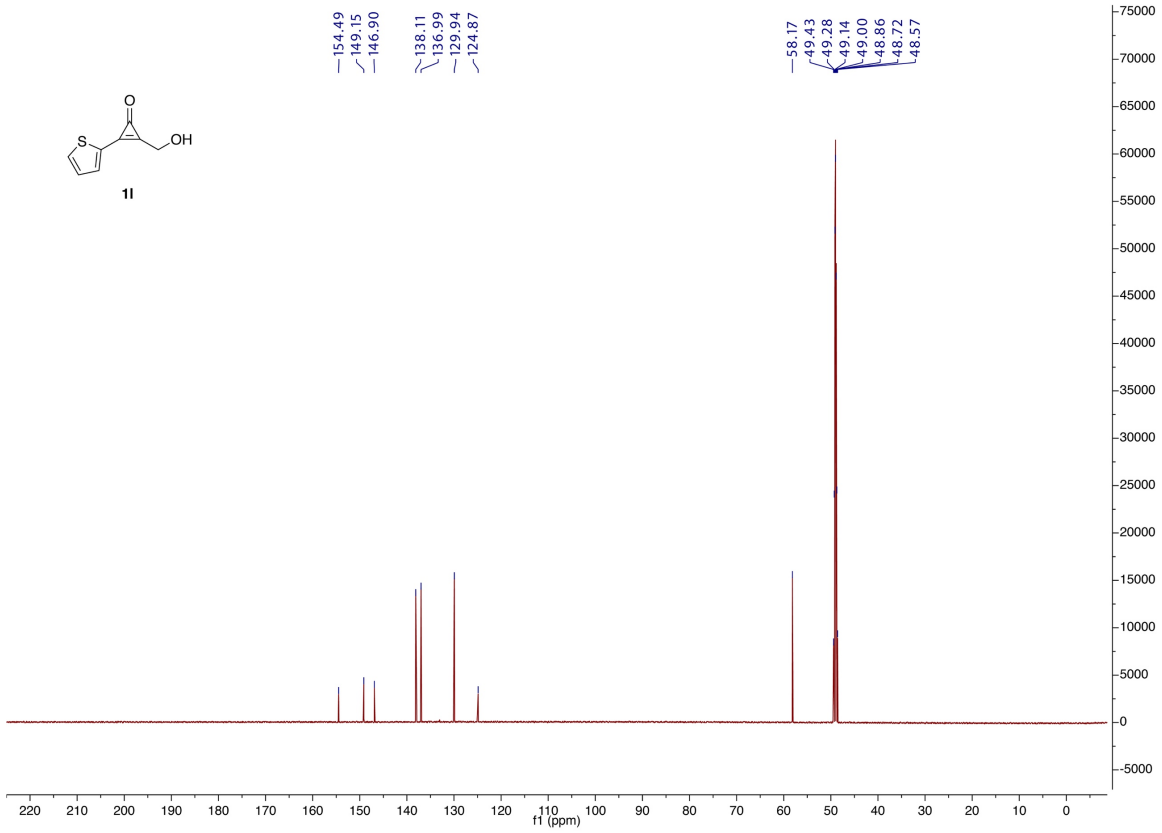
154.34
153.51
148.38
133.73
126.60
119.71
58.35
49.43
49.30
49.29
49.28
49.28
49.14
49.13
49.02
49.01
49.00
48.99
48.98
48.89
48.88
48.88
48.87
48.86
48.85
48.84
48.73
48.72
48.71
48.57
14.53
O
OH
MeS
1k
f1 (ppm)


8.01
8.01
8.00
8.00
7.89
7.89
7.88
7.88
7.31
7.30
7.30
7.29
4.82
4.77
3.32
3.31
3.31
3.31
3.30
O
S
OH
1l
1.00
1.02
1.05
2.14
f1 (ppm)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129.94
124.87
58.17
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49.28
49.14
49.00
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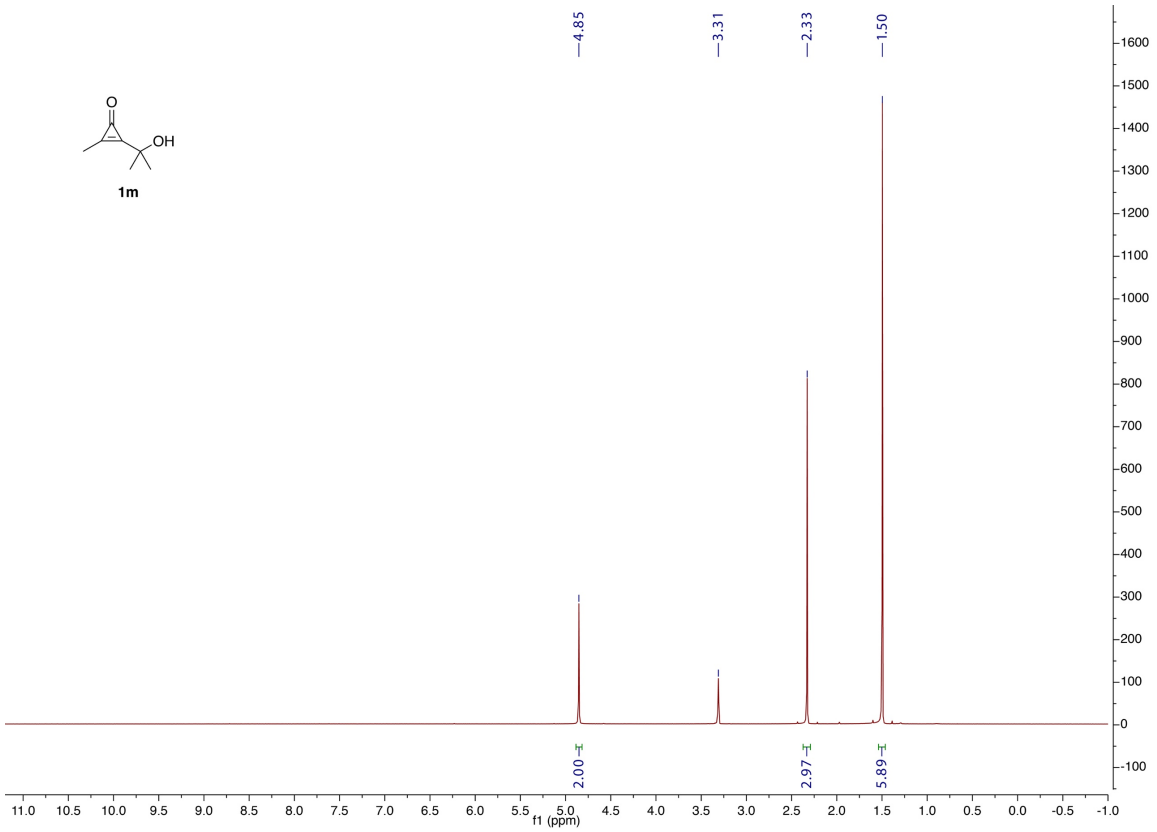
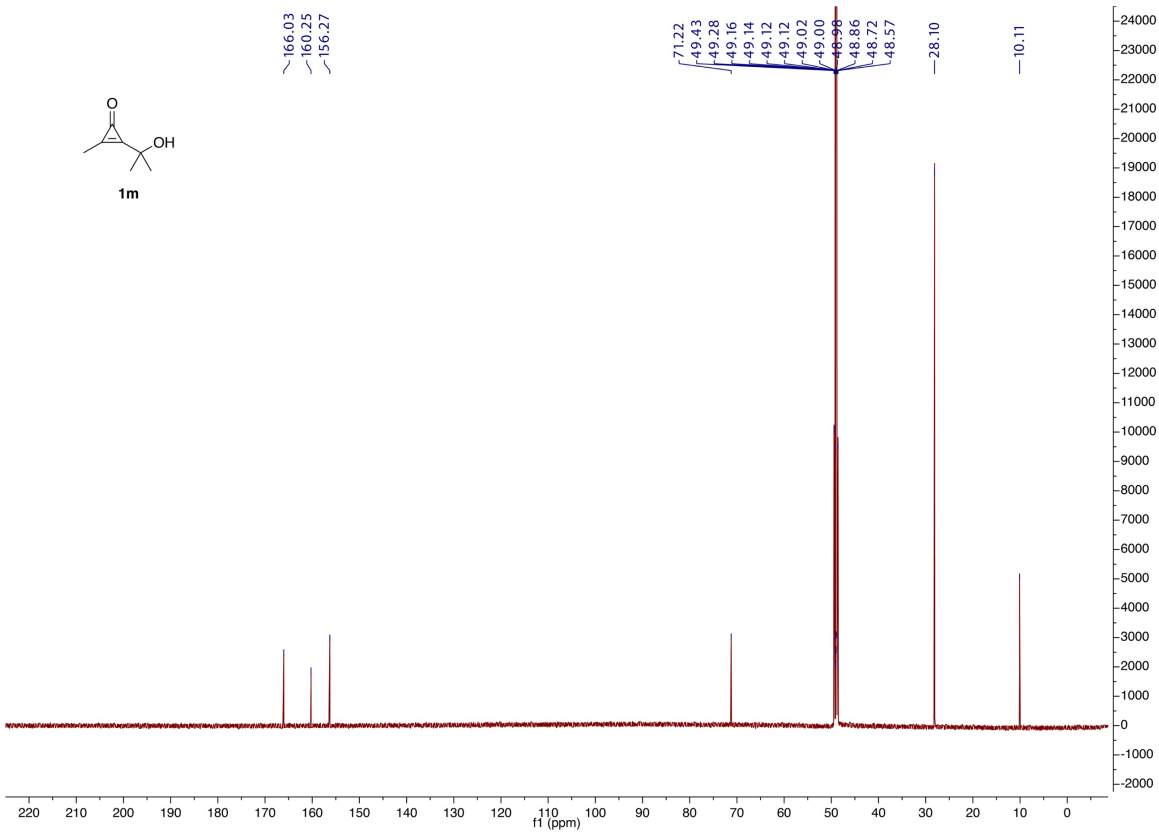
48.72
48.57
O
S
OH
1l
f1 (ppm)


4.85
3.31
2.33
1.50
O
OH
1m
2.00
2.97
5.89
f1 (ppm)


166.03
160.25
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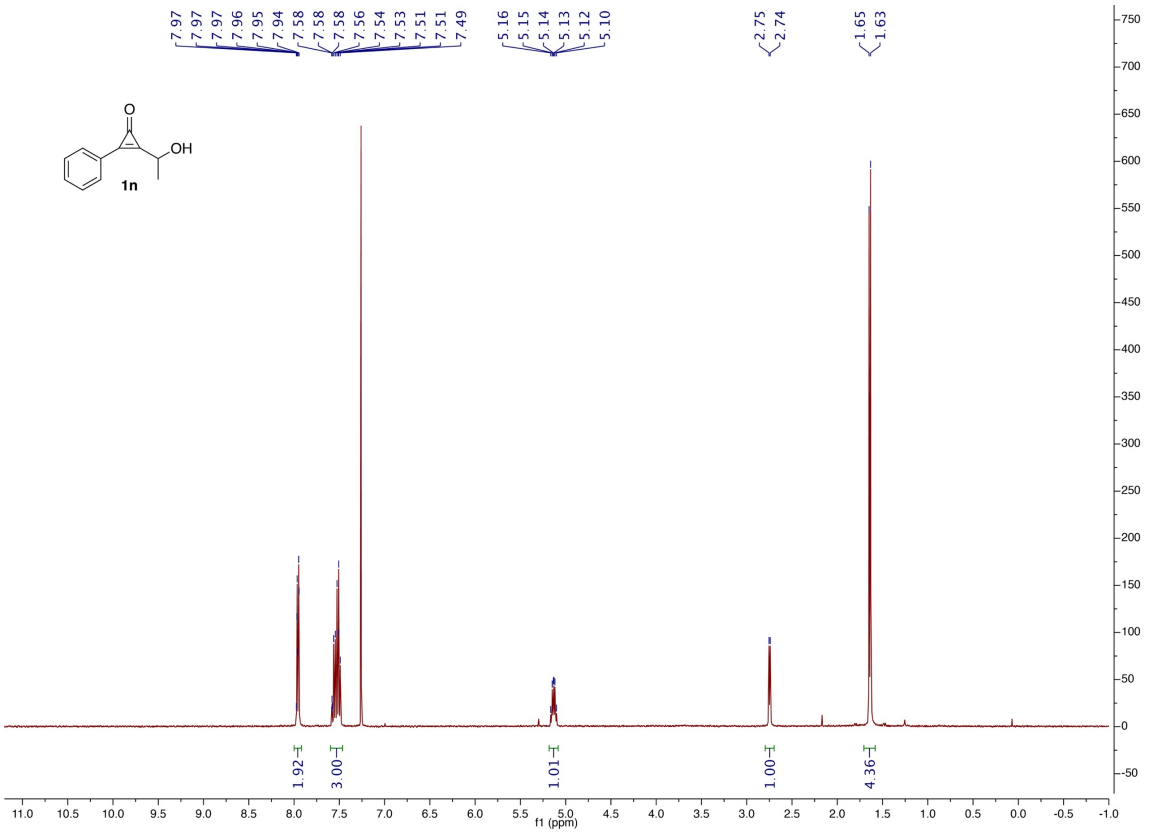
71.22
49.43
49.28
49.16
49.14
49.12
49.12
49.02
49.00
48.98
48.86
48.72
48.57
28.10
10.11
O
OH
1m
f1 (ppm)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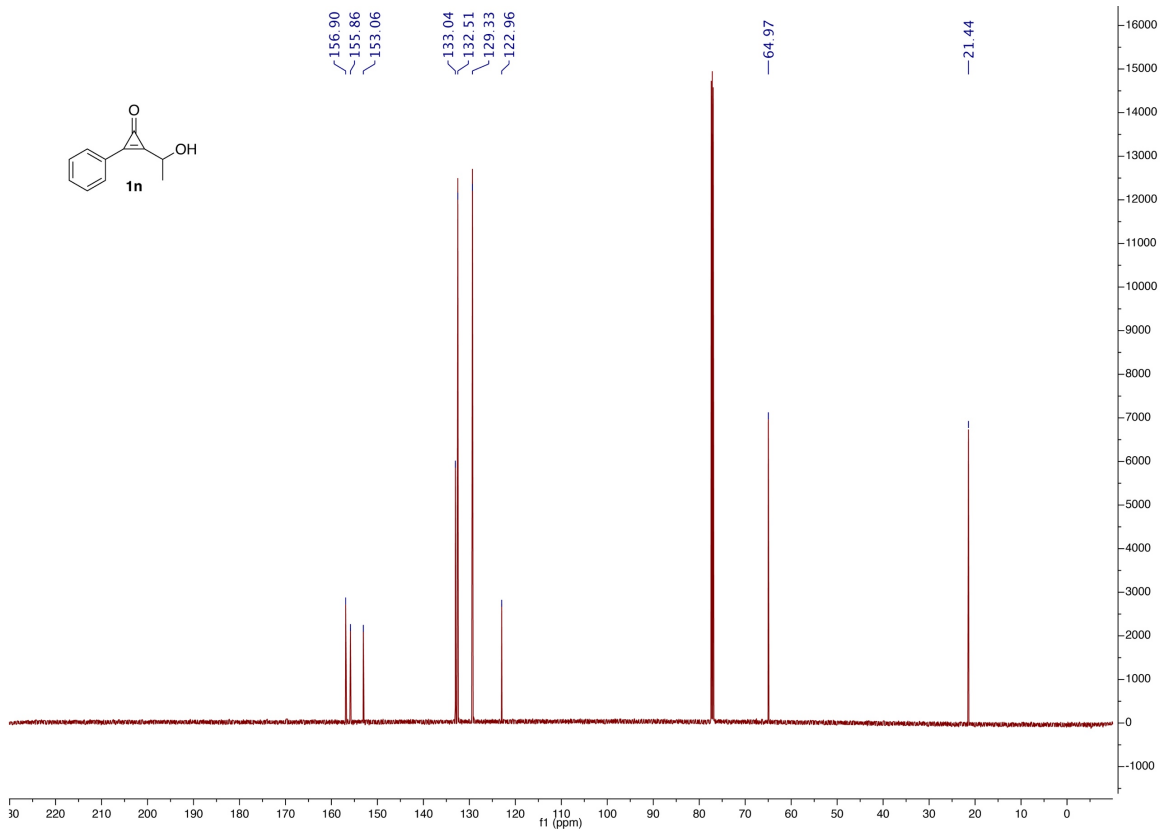
7.97
7.97
7.96
7.95
7.94
7.58
7.58
7.58
7.56
7.54
7.53
7.51
7.51
7.49
5.16
5.15
5.14
5.13
5.12
5.10
2.75
2.74
1.65
1.63
O
OH
1n
1.92
3.00
1.01
1.00
4.36
f1 (ppm)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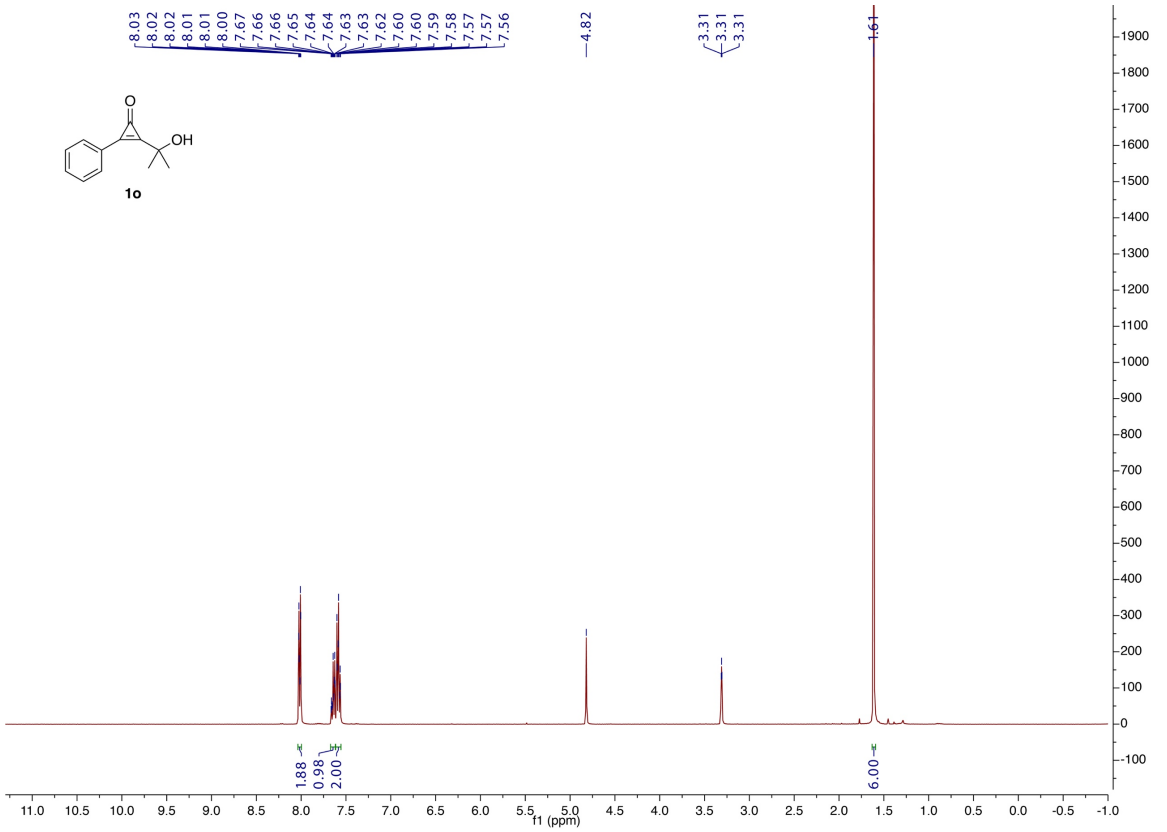
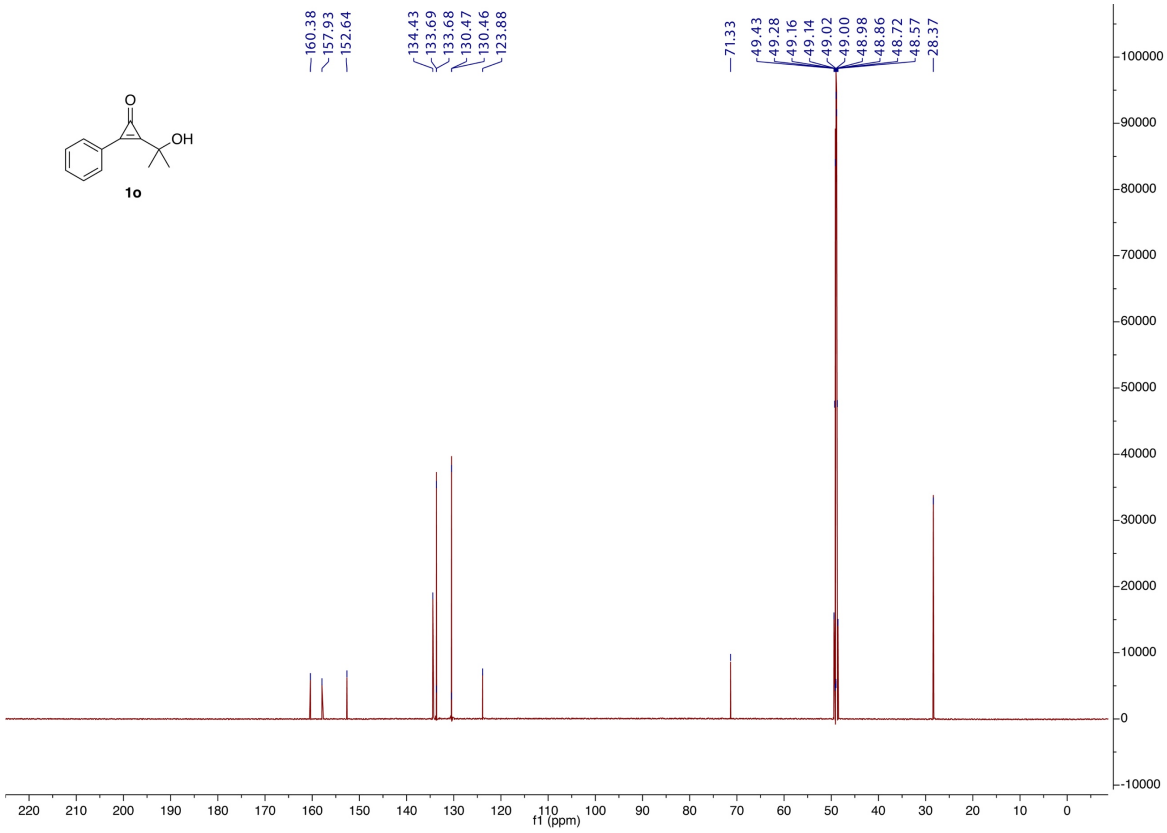
132.51
129.33
122.96
64.97
21.44
O
OH
1n
f1 (ppm)


8.03
8.02
8.02
8.01
8.01
8.00
7.67
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.62
7.60
7.60
7.59
7.58
7.57
7.57
7.56
4.82
3.31
3.31
3.31
1.61
O
OH
1o
1.88
0.98
2.00
6.00
f1 (ppm)


160.38
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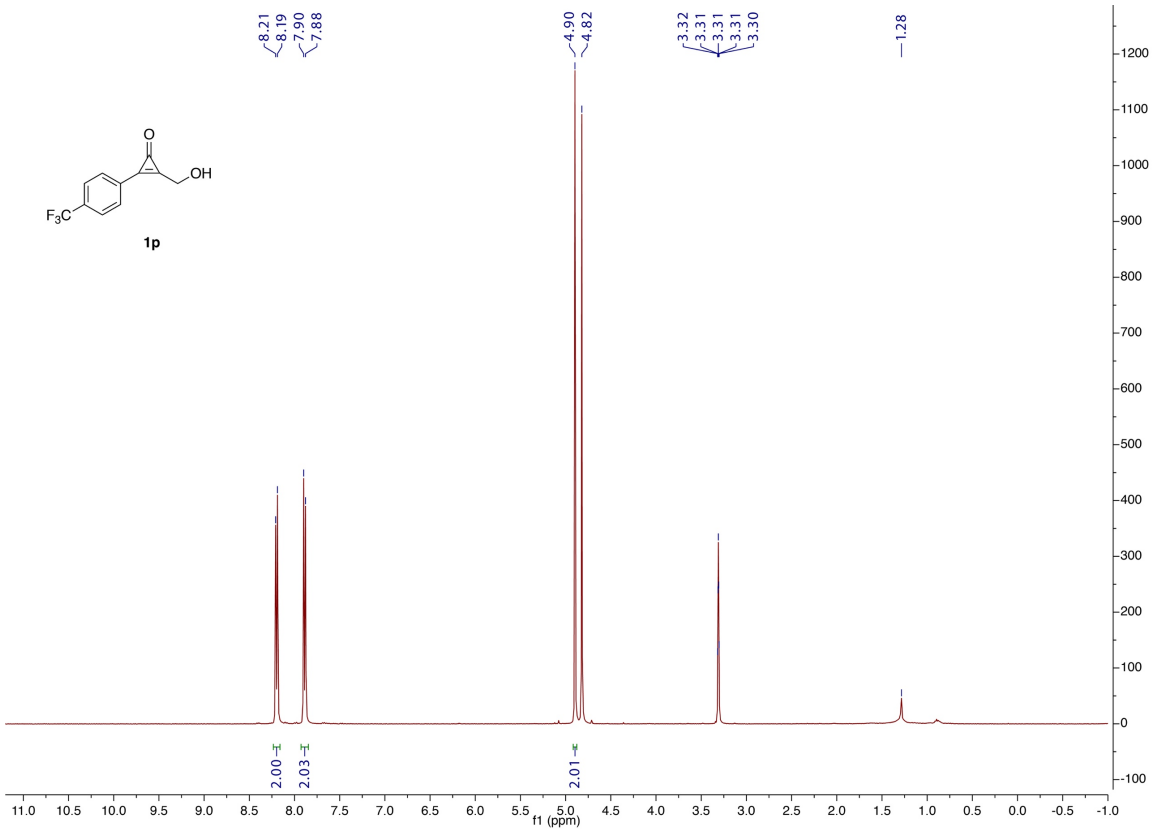
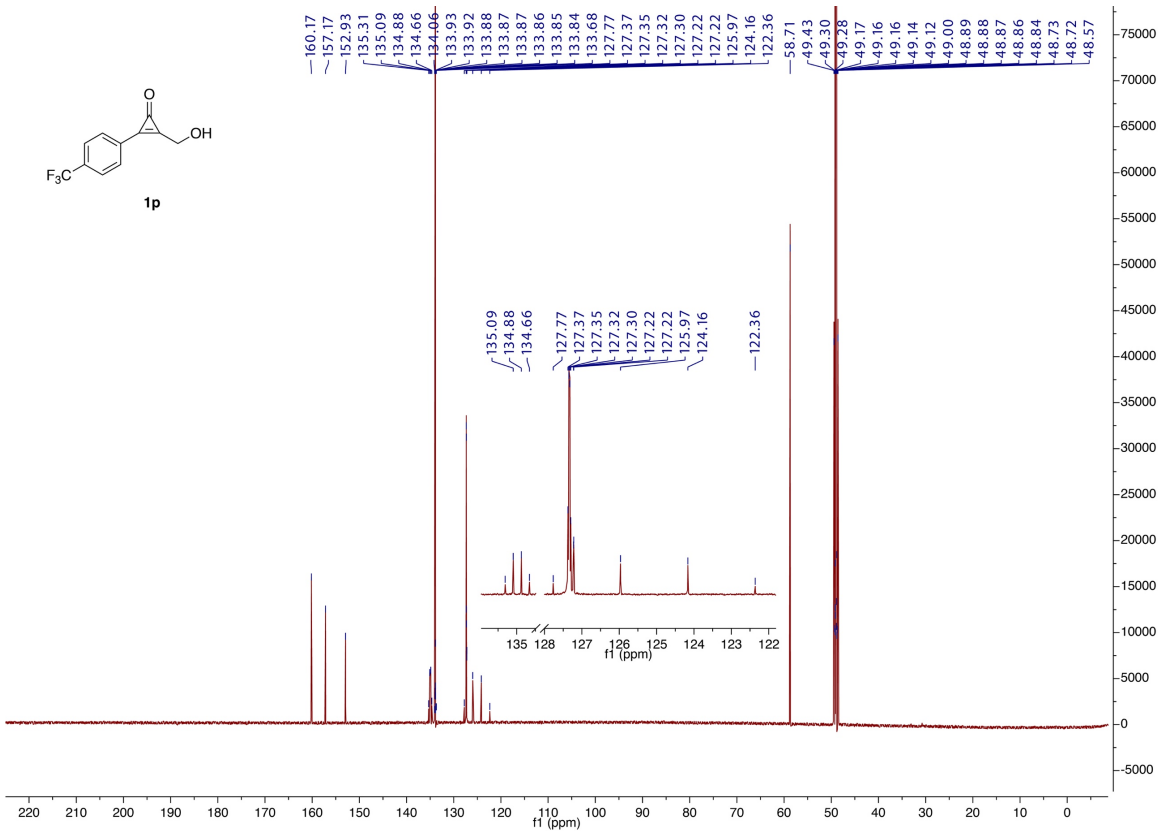
133.68
130.47
130.46
123.88
71.33
49.43
49.28
49.16
49.14
49.02
49.00
48.98
48.86
48.72
48.57
28.37
O
OH
1o
f1 (ppm)


8.21
8.19
7.90
7.88
4.90
4.82
3.32
3.31
3.31
3.31
3.30
1.28
O
OH
F3C
1p
2.00
2.03
2.01
f1 (ppm)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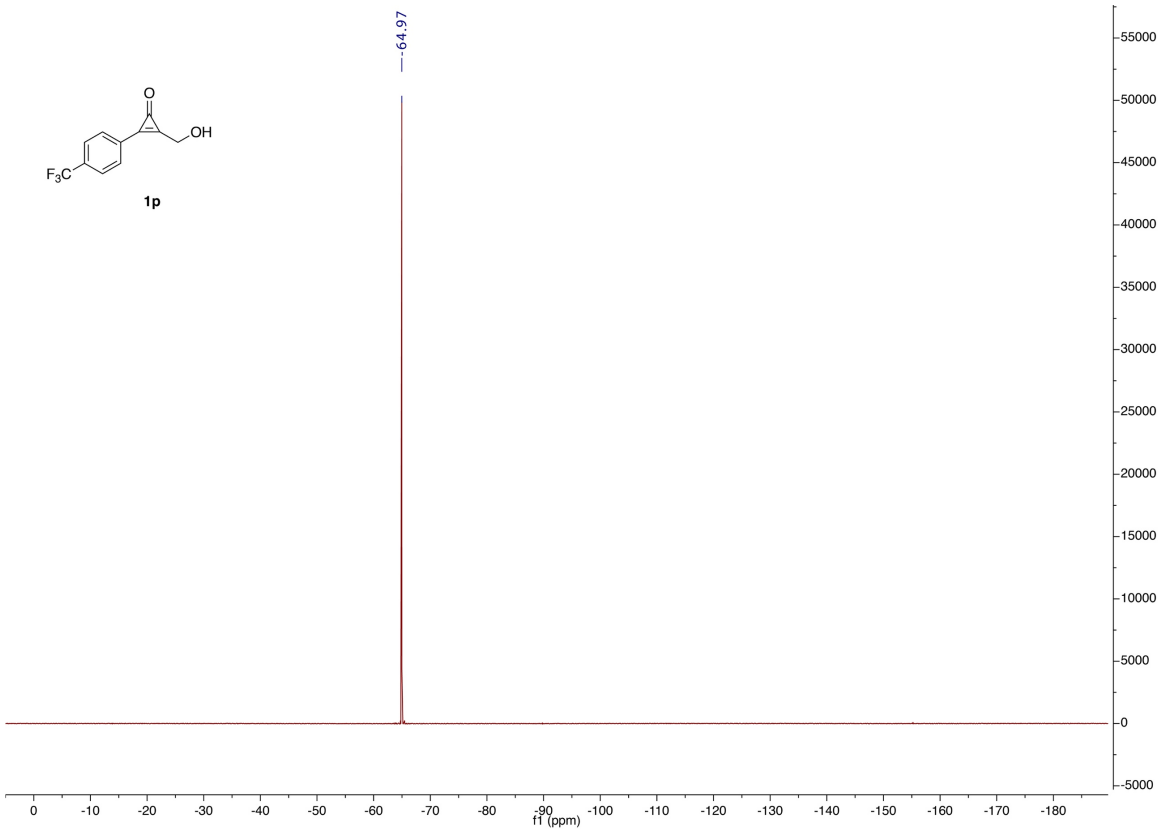
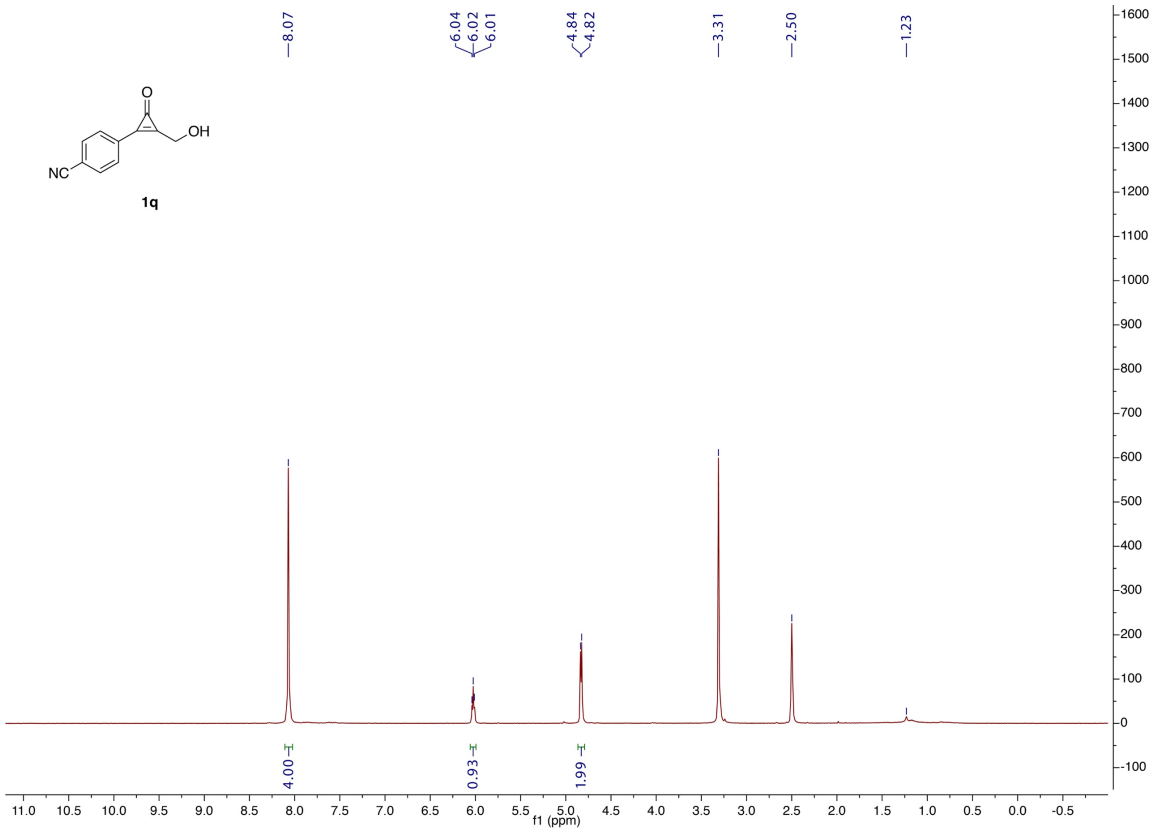
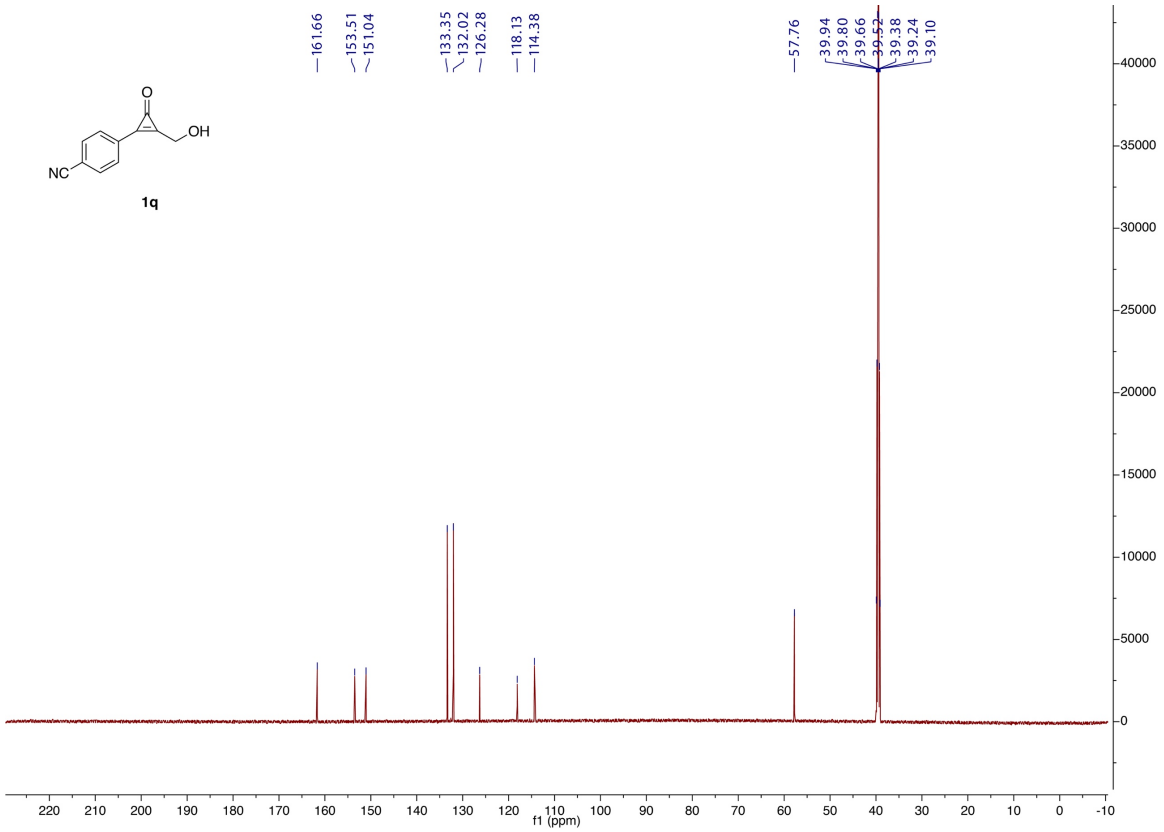
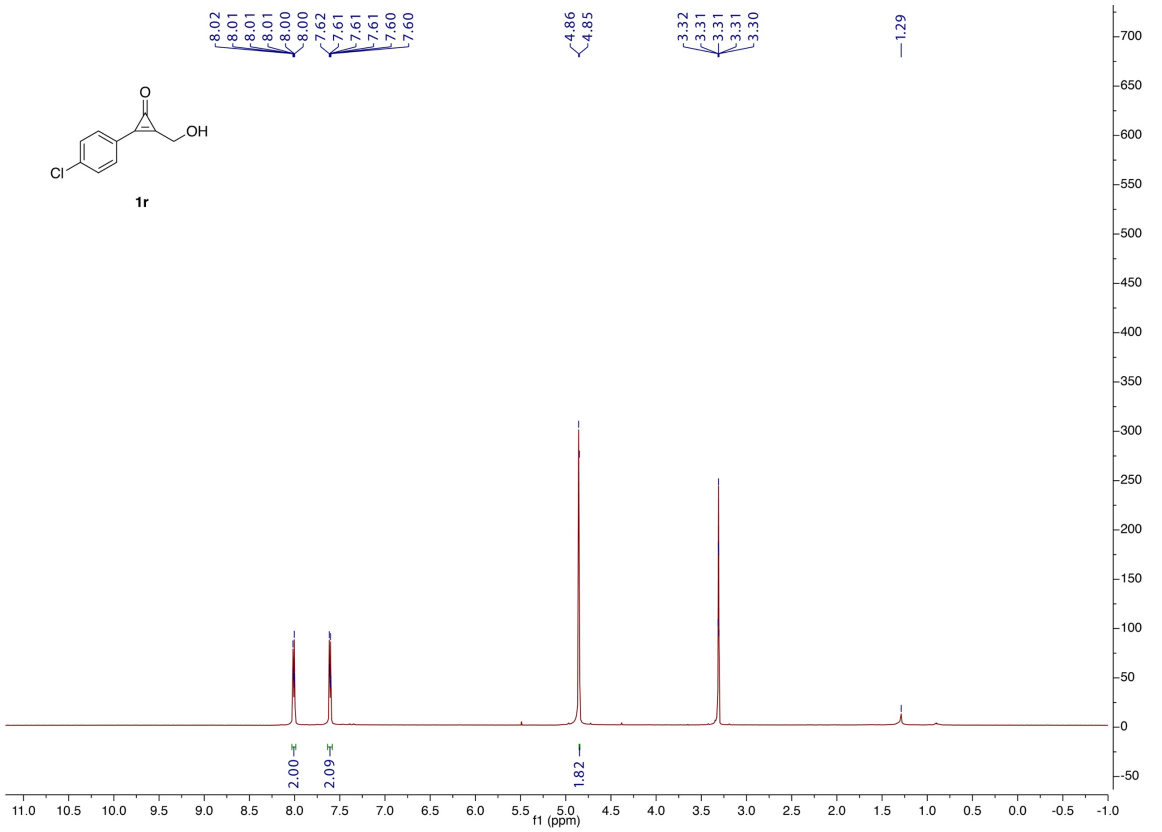
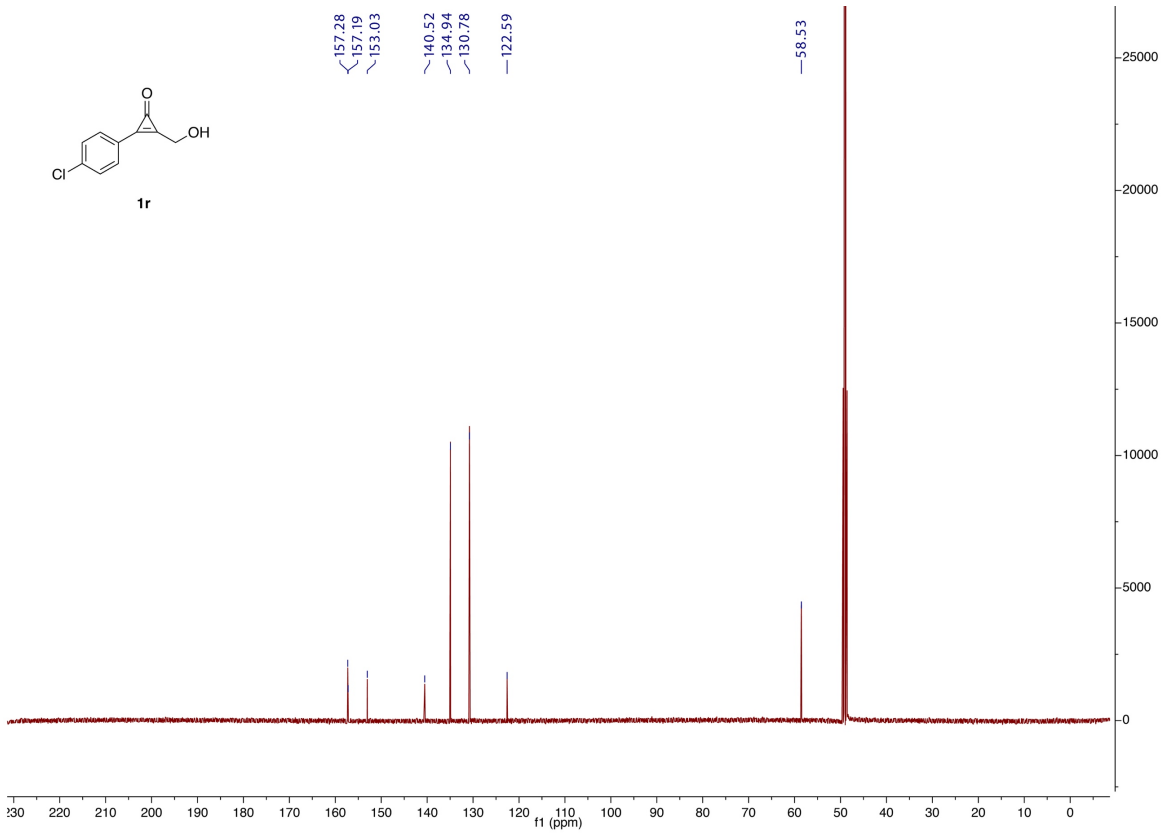
157.17
152.93
135.31
135.09
134.88
134.66
134.06
133.93
133.92
133.88
133.87
133.87
133.86
133.85
133.84
133.68
127.77
127.37
127.35
127.32
127.30
127.22
127.22
125.97
124.16
122.36
58.71
49.43
49.30
49.28
49.17
49.16
49.16
49.14
49.12
49.00
48.89
48.88
48.87
48.86
48.84
48.73
48.72
48.57
O
OH
F3C
1p
f1 (ppm)

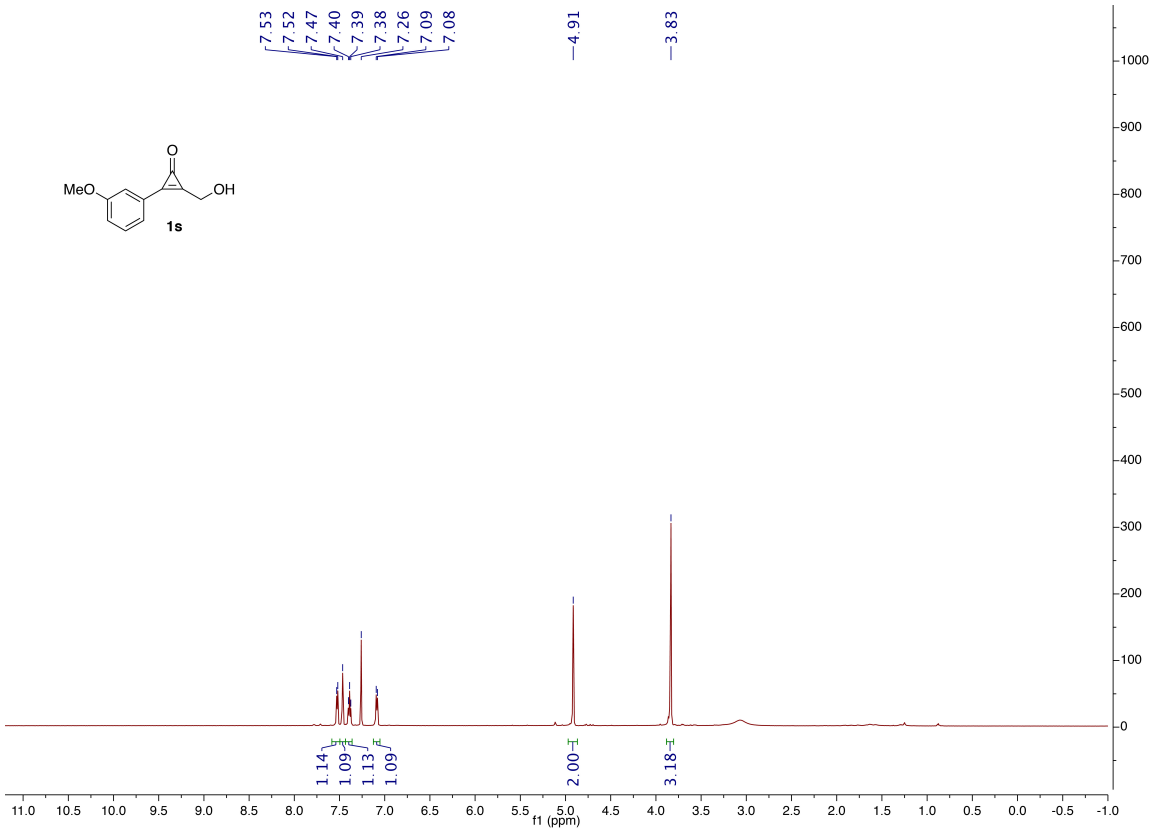

-64.97
O
OH
F3C
1p
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

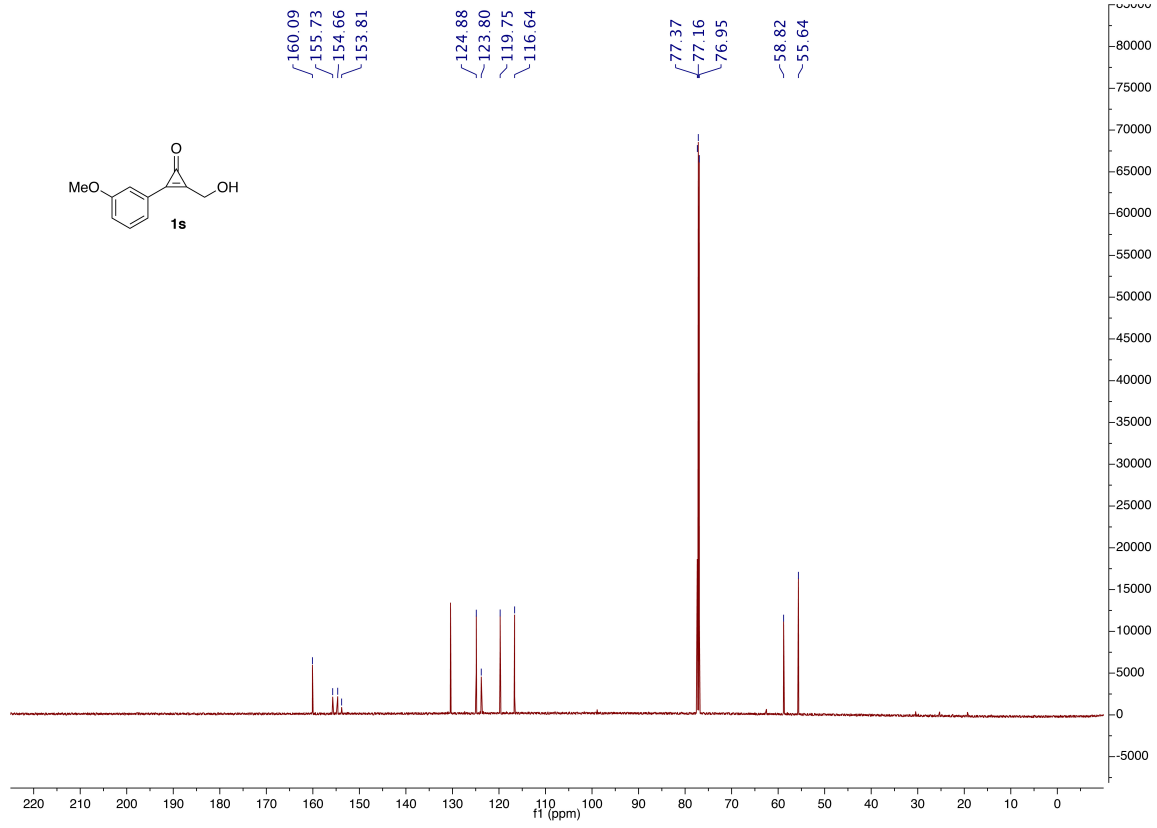

8.07
6.04
6.02
6.01
4.84
4.82
3.31
2.50
1.23
O
OH
NC
1q
4.00
0.93
1.99
f1 (ppm)

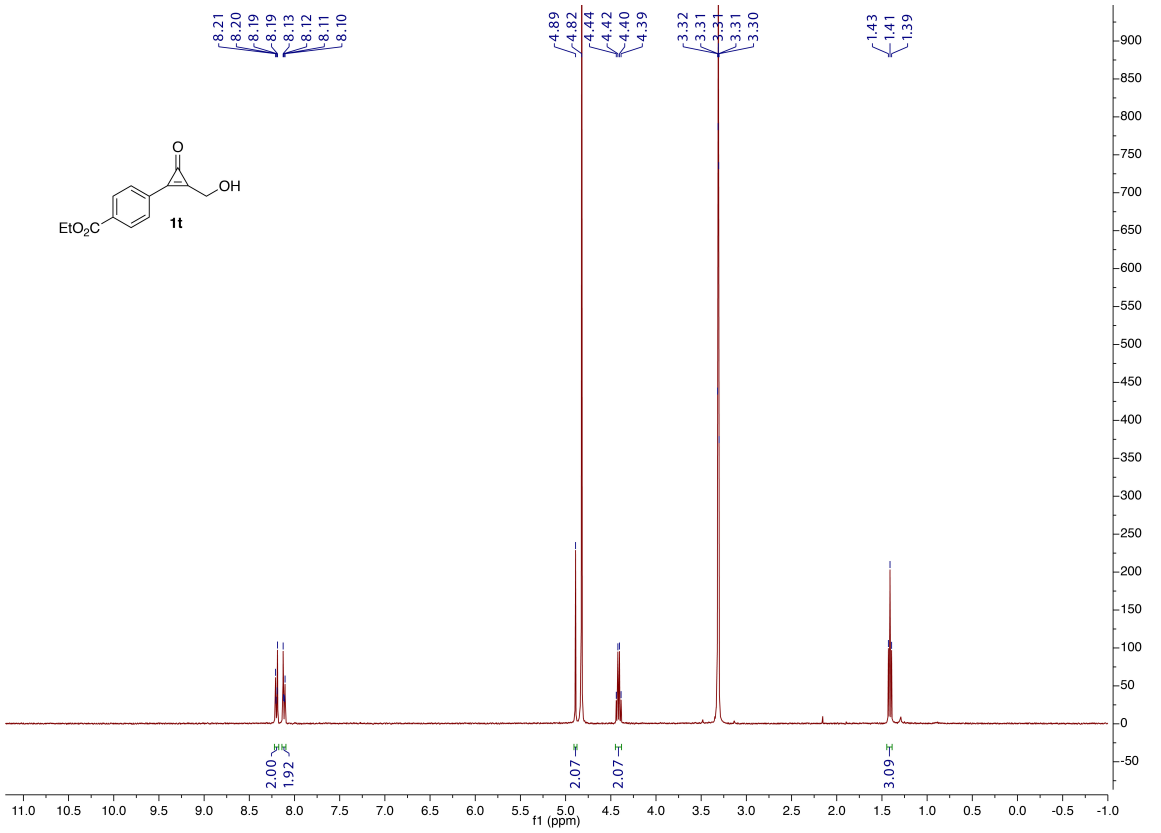

161.66
153.51
151.04
133.35
132.02
126.28
118.13
114.38
57.76
39.94
39.80
39.66
39.52
39.38
39.24
39.10
O
OH
NC
1q
f1 (ppm)


8.02
8.01
8.01
8.01
8.00
8.00
7.62
7.61
7.61
7.61
7.60
7.60
4.86
4.85
3.32
3.31
3.31
3.31
3.30
1.29
O
OH
Cl
1r
2.00
2.09
1.82
f1 (ppm)


157.28
157.19
153.03
140.52
134.94
130.78
122.59
58.53
O
OH
Cl
1r
f1 (ppm)


7.53
7.52
7.47
7.40
7.39
7.38
7.26
7.09
7.08
4.91
3.83
O
MeO
OH
1s
1.14
1.09
1.13
1.09
2.00
3.18
f1 (ppm)


160.09
155.73
154.66
153.81
124.88
123.80
119.75
116.64
77.37
77.16
76.95
58.82
55.64
O
MeO
OH
1s
f1 (ppm)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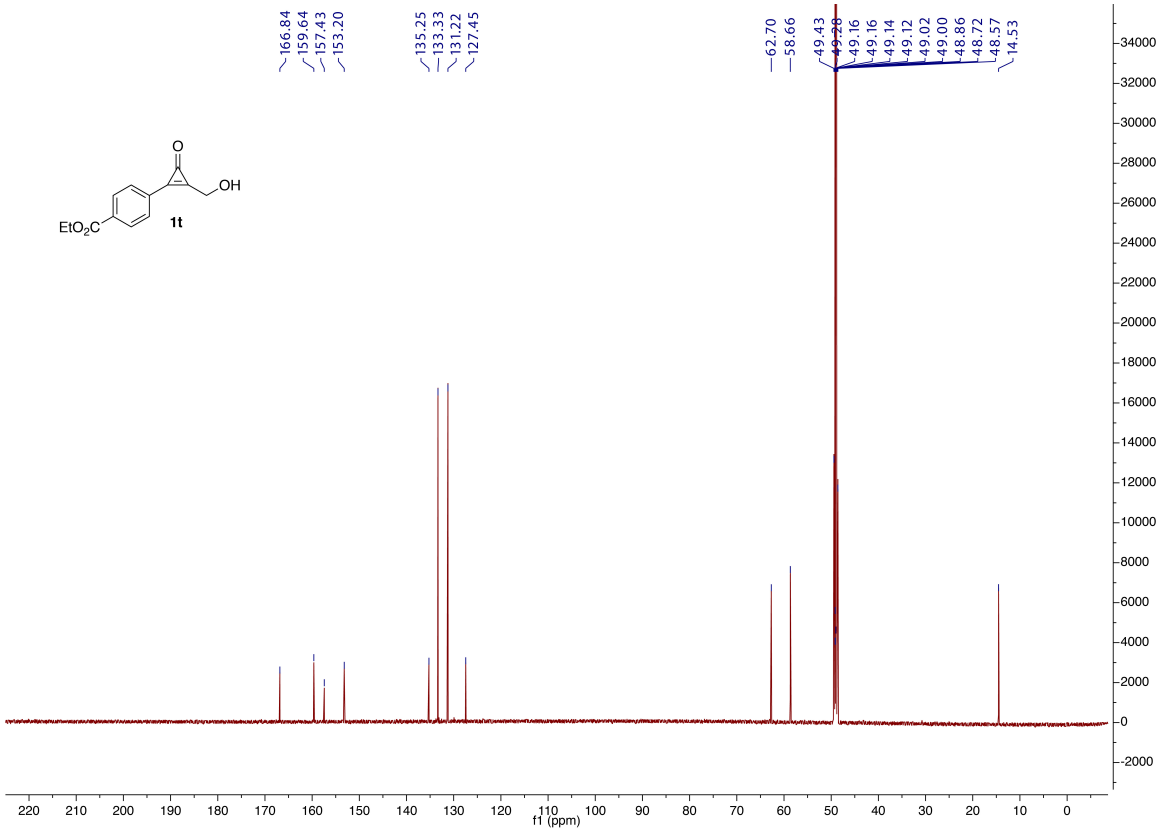
8.20
8.19
8.19
8.13
8.12
8.11
8.10
4.89
4.82
4.44
4.42
4.40
4.39
3.32
3.31
3.31
3.31
3.30
1.43
1.41
1.39
O
OH
EtO2C
1t
2.00
1.92
2.07
2.07
3.09
f1 (ppm)


166.84
159.64
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153.20
135.25
133.33
131.22
127.45
62.70
58.66
49.43
49.28
49.16
49.16
49.14
49.12
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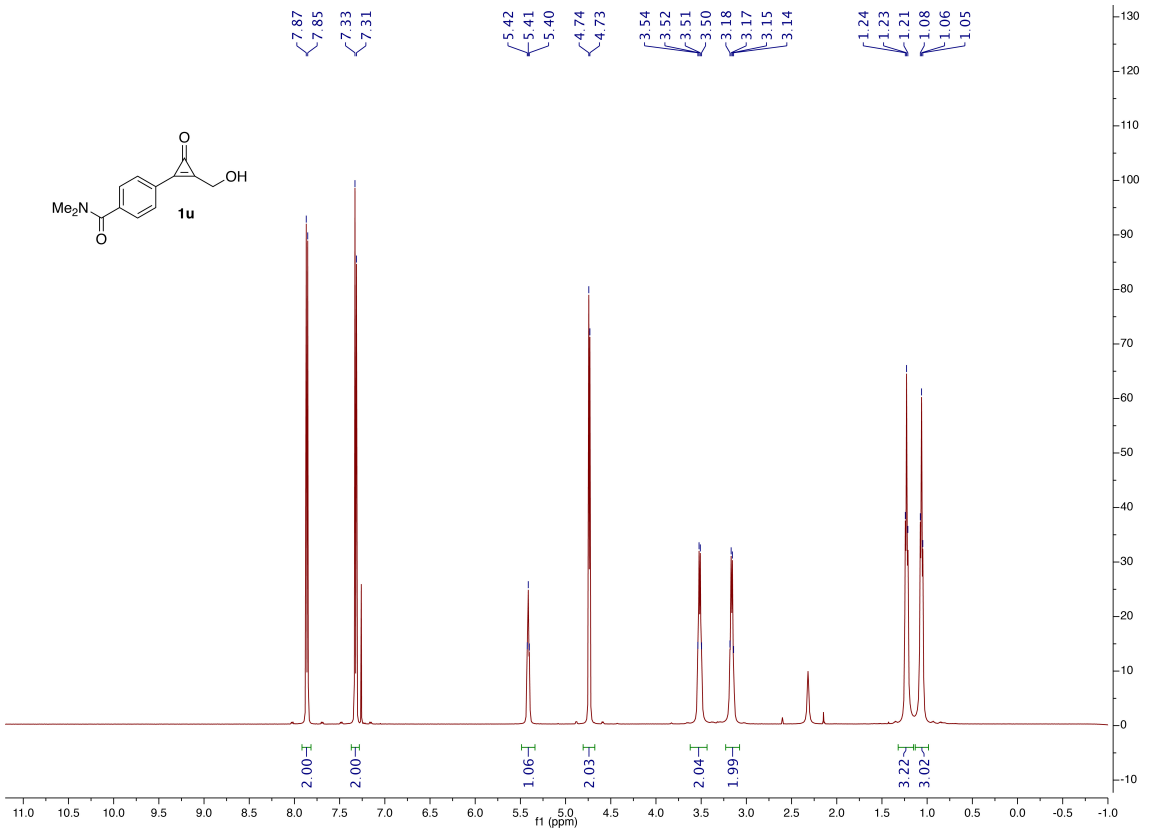
49.00
48.86
48.72
48.57
14.53
O
OH
EtO2C
1t
f1 (ppm)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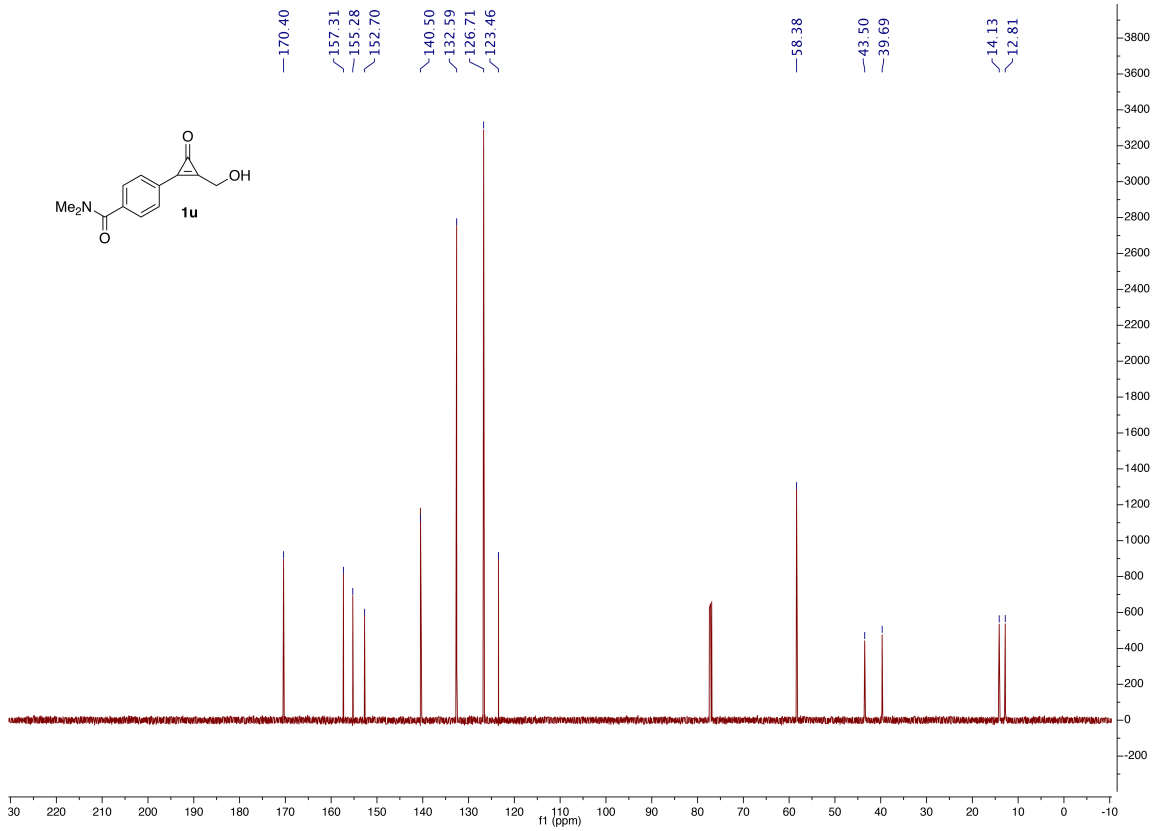
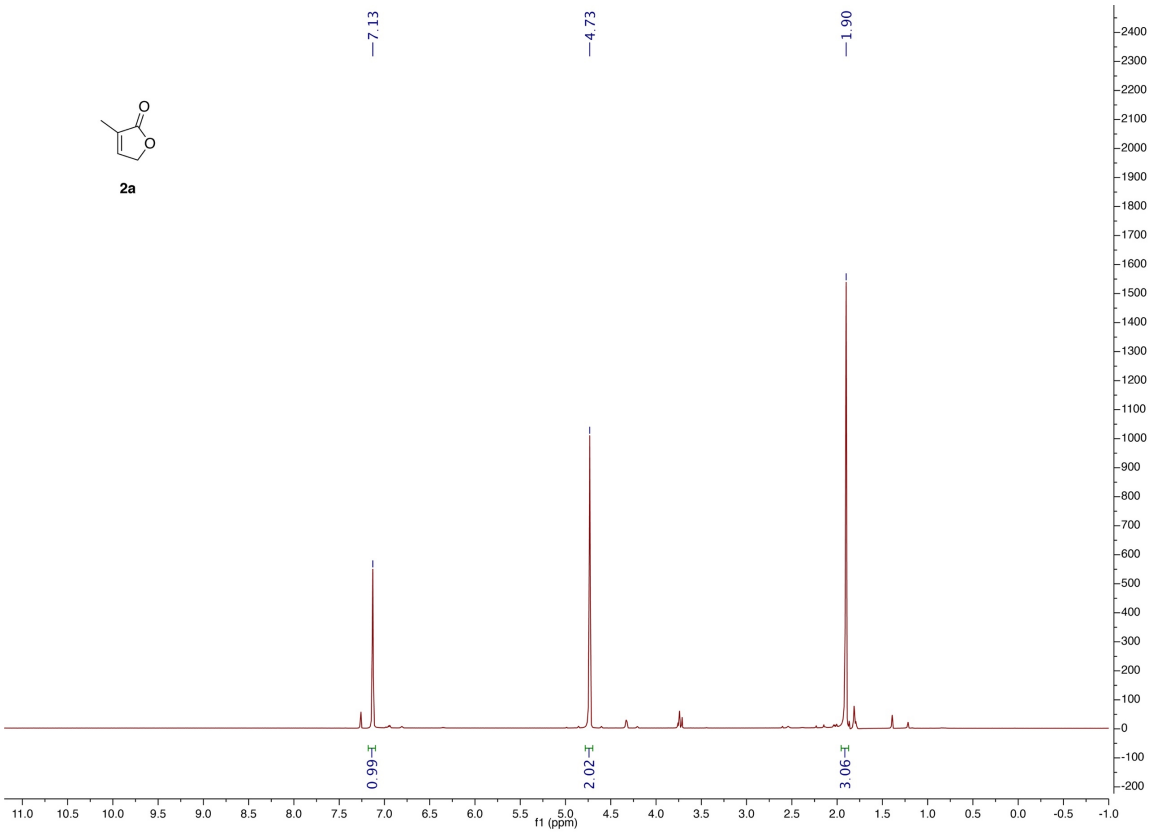
7.85
7.33
7.31
5.42
5.41
5.40
4.74
4.73
3.54
3.52
3.51
3.50
3.18
3.17
3.15
3.14
1.24
1.23
1.21
1.08
1.06
1.05
O
OH
Me2N
O
1u
2.00
2.00
1.06
2.03
2.04
1.99
3.22
3.02
f1 (ppm)


170.40
157.31
155.28
152.70
140.50
132.59
126.71
123.46
58.38
43.50
39.69
14.13
12.81
O
OH
Me2N
O
1u
f1 (ppm)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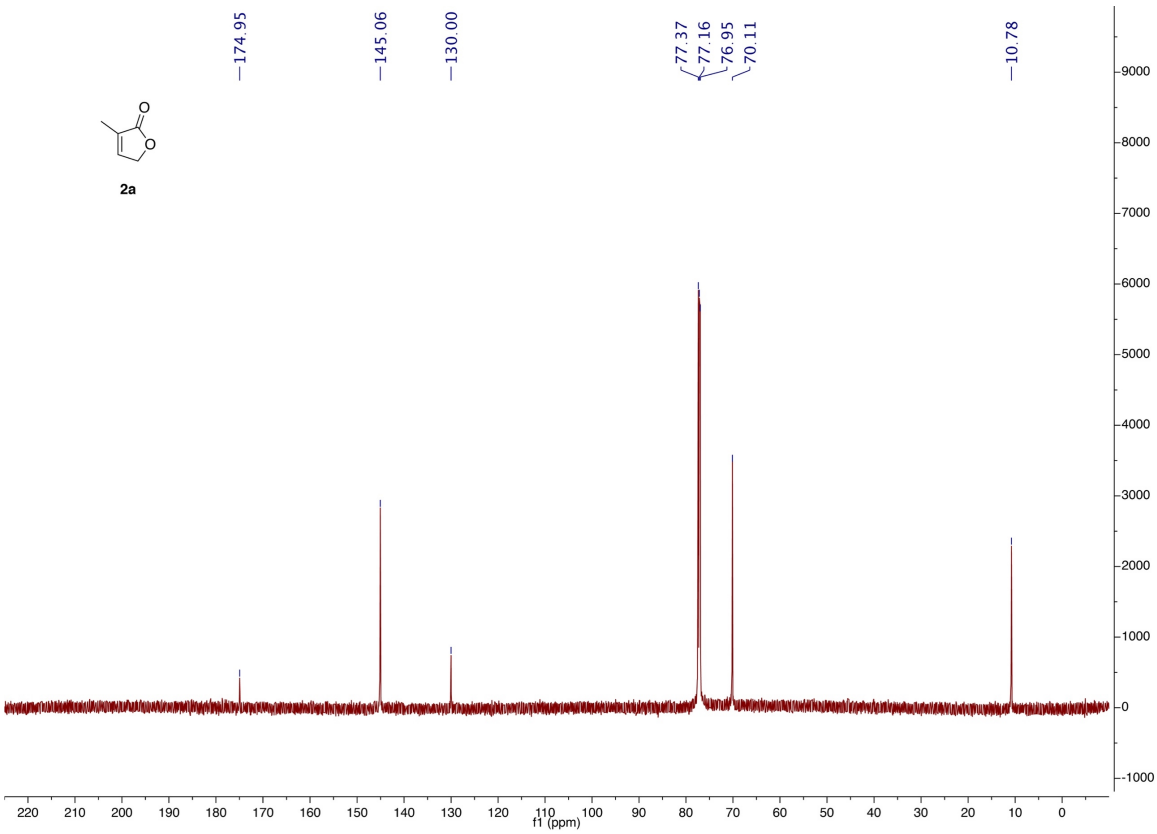
4.73
1.90
2a
0.99
2.02
3.06
f1 (ppm)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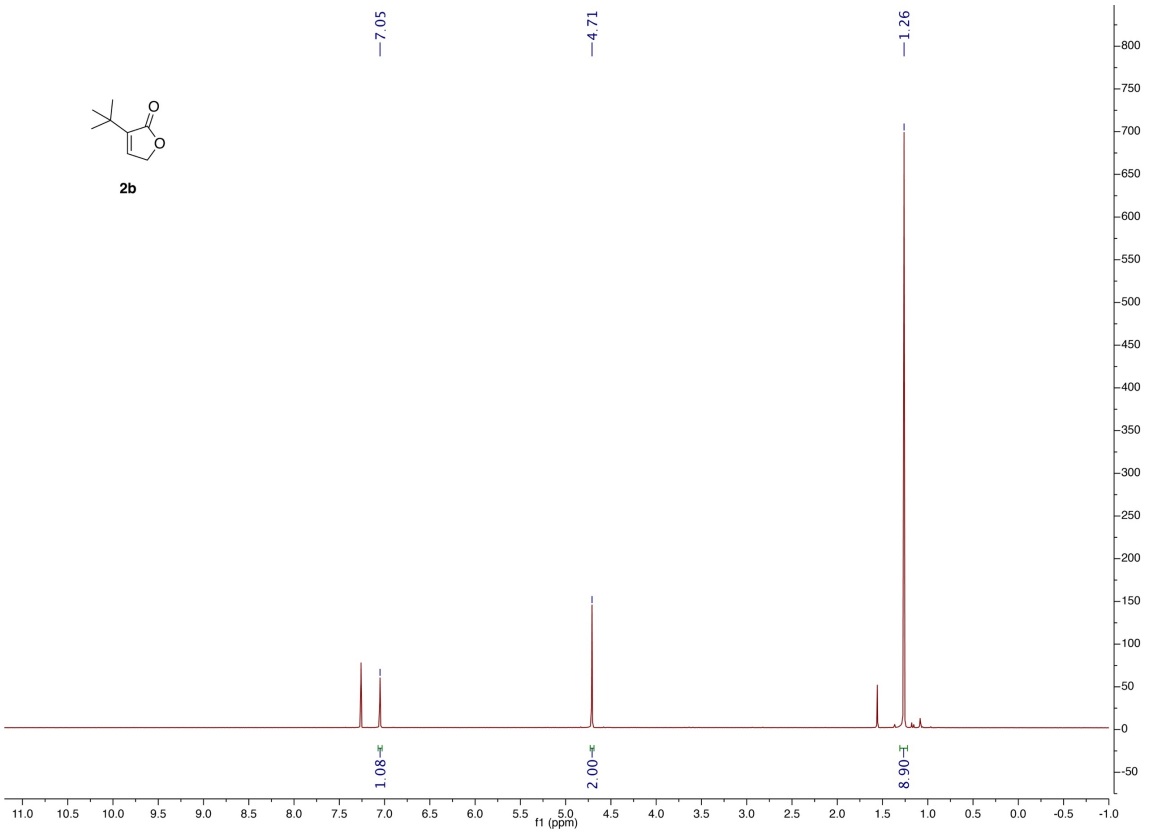
77.37
77.16
76.95
70.11
10.78
2a
f1 (ppm)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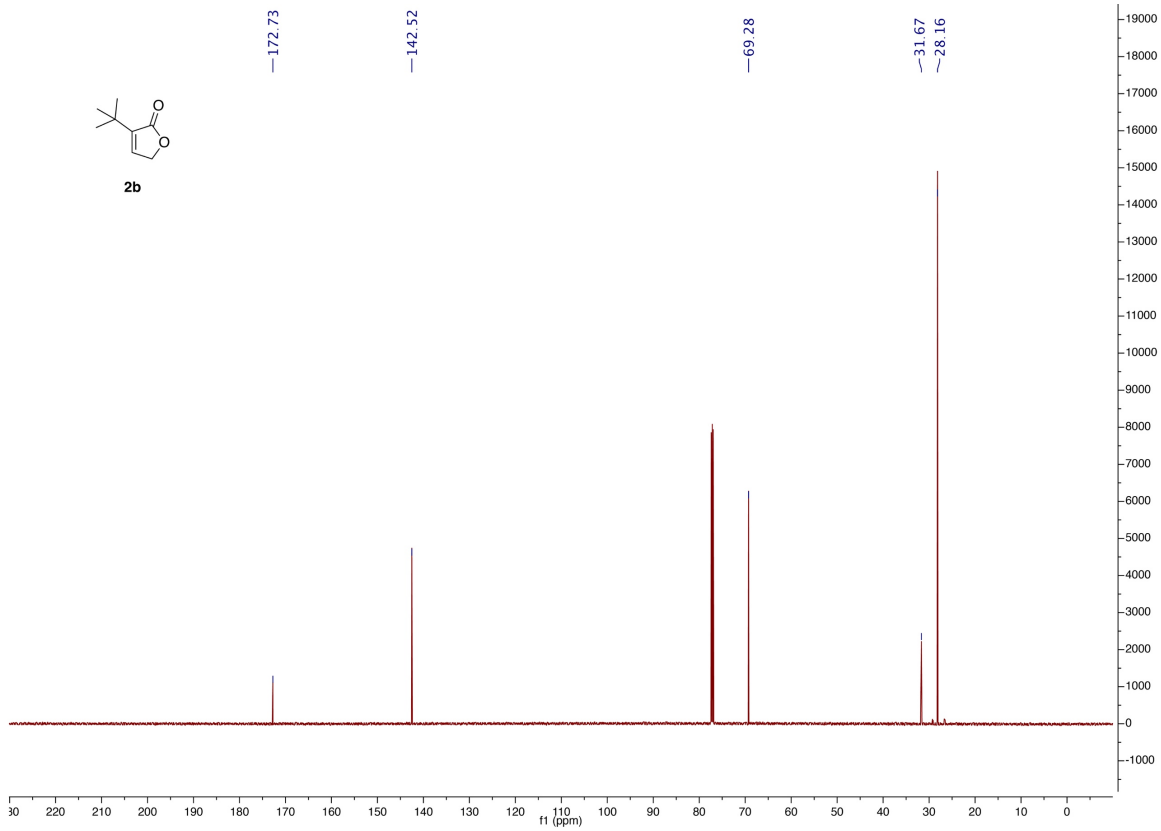
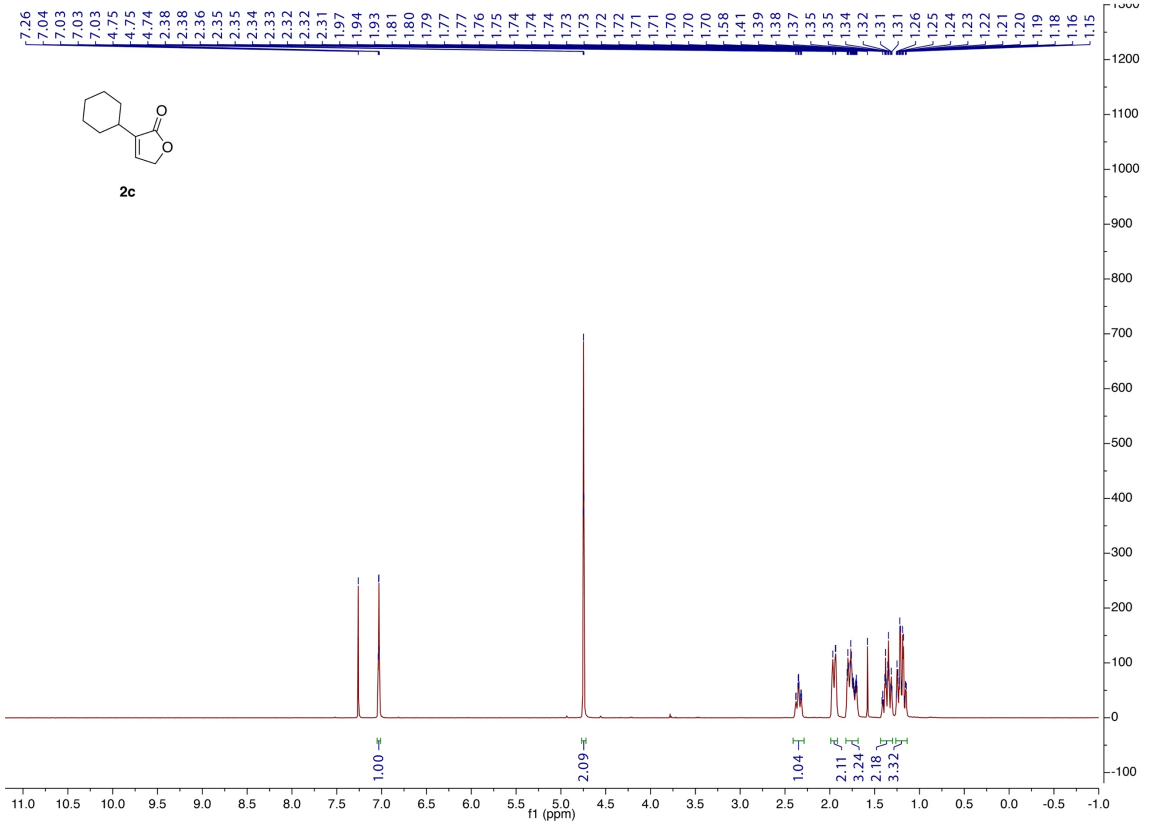
4.71
1.26
2b
1.08
2.00
8.90
f1 (ppm)


172.73
142.52
69.28
31.67
28.16
2b
f1 (ppm)


7.26
7.04
7.03
7.03
7.03
4.75
4.75
4.74
2.38
2.38
2.36
2.35
2.35
2.34
2.33
2.32
2.32
2.31
1.97
1.94
1.93
1.81
1.80
1.79
1.77
1.77
1.76
1.75
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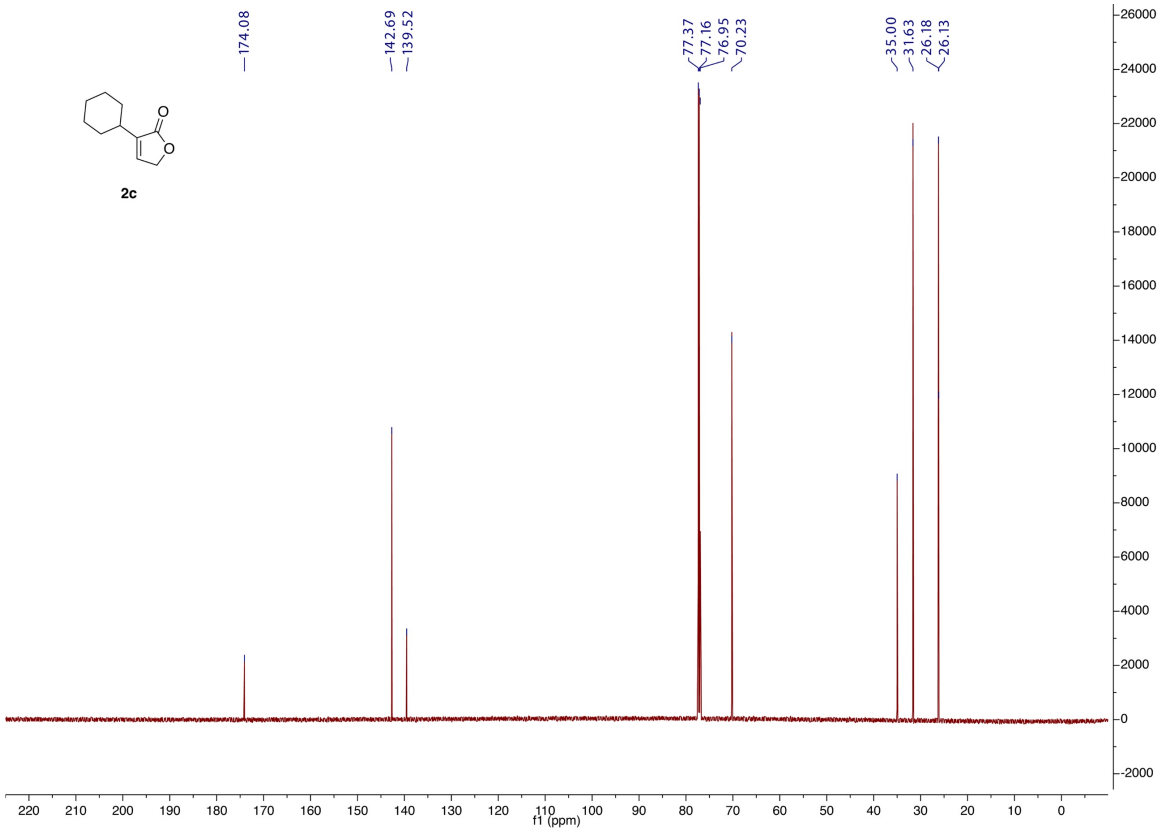
1.35
1.35
1.34
1.32
1.31
1.31
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.18
1.16
1.15
O
O
2c
1.00
2.09
1.04
2.11
3.24
2.18
3.32
f1 (ppm)


174.08
142.69
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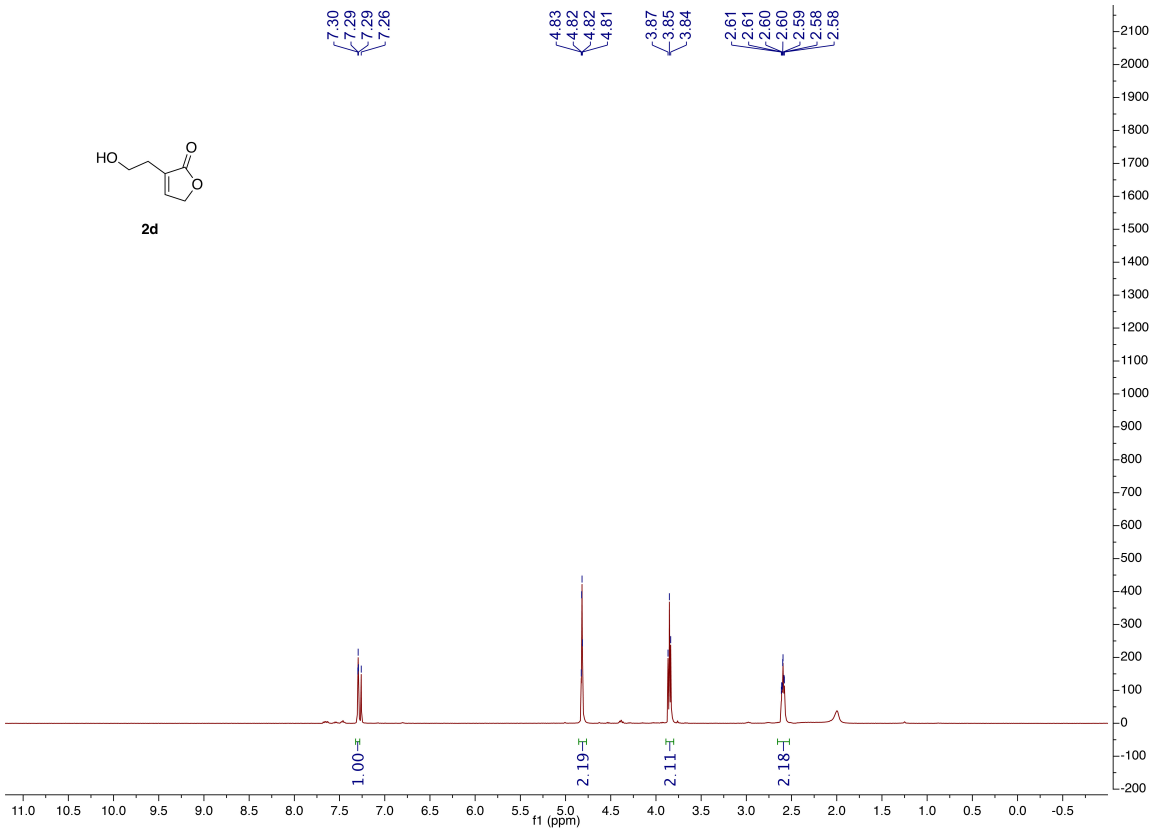
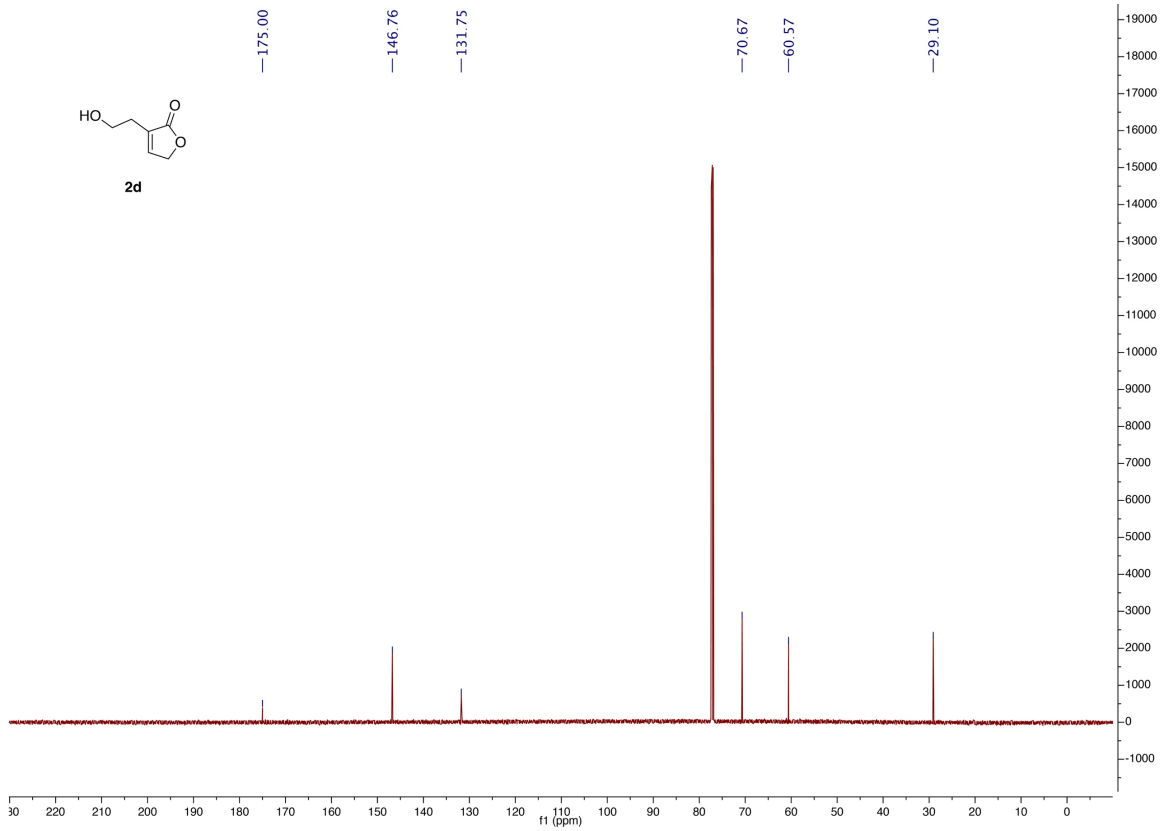
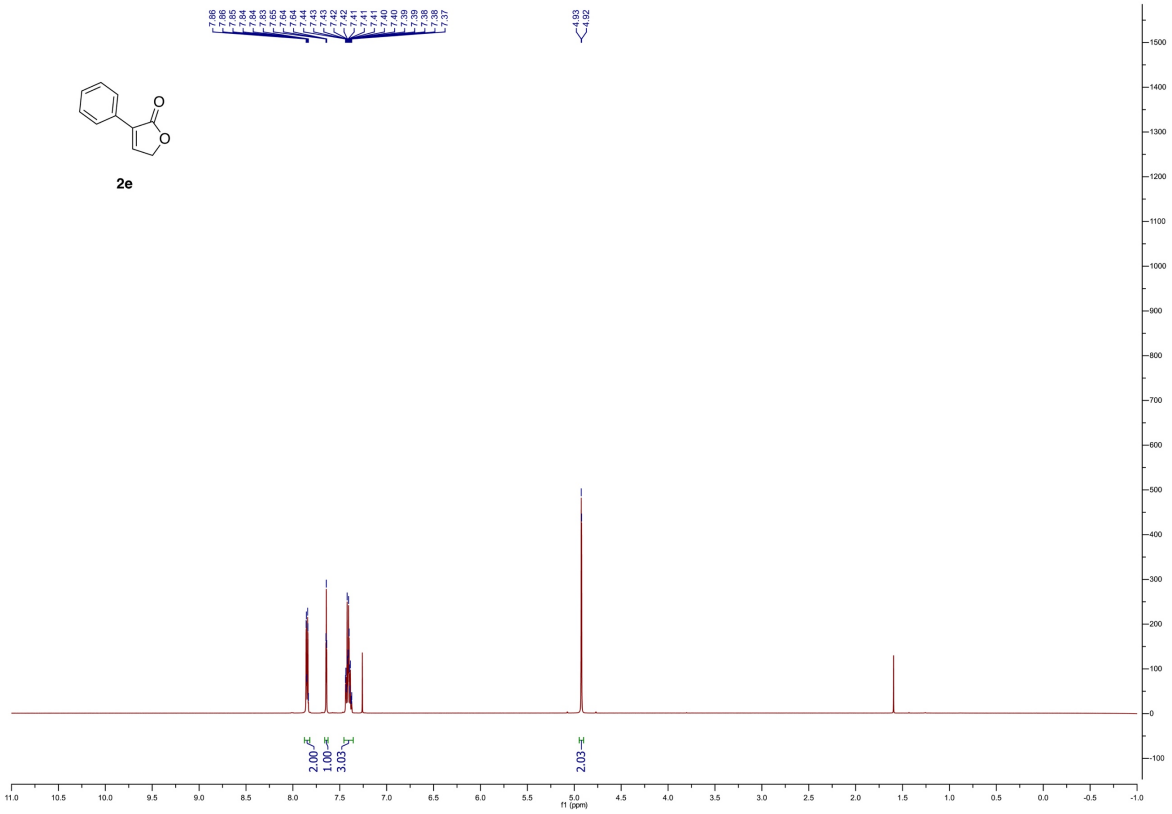
77.37
77.16
76.95
70.23
35.00
31.63
26.18
26.13
O
O
2c
f1 (ppm)


7.30
7.29
7.29
7.26
4.83
4.82
4.82
4.81
3.87
3.85
3.84
2.61
2.61
2.60
2.60
2.59
2.58
2.58
HO
O
O
2d
1.00
2.19
2.11
2.18
f1 (ppm)


175.00
146.76
131.75
70.67
60.57
29.10
HO
O
O
2d
f1 (ppm)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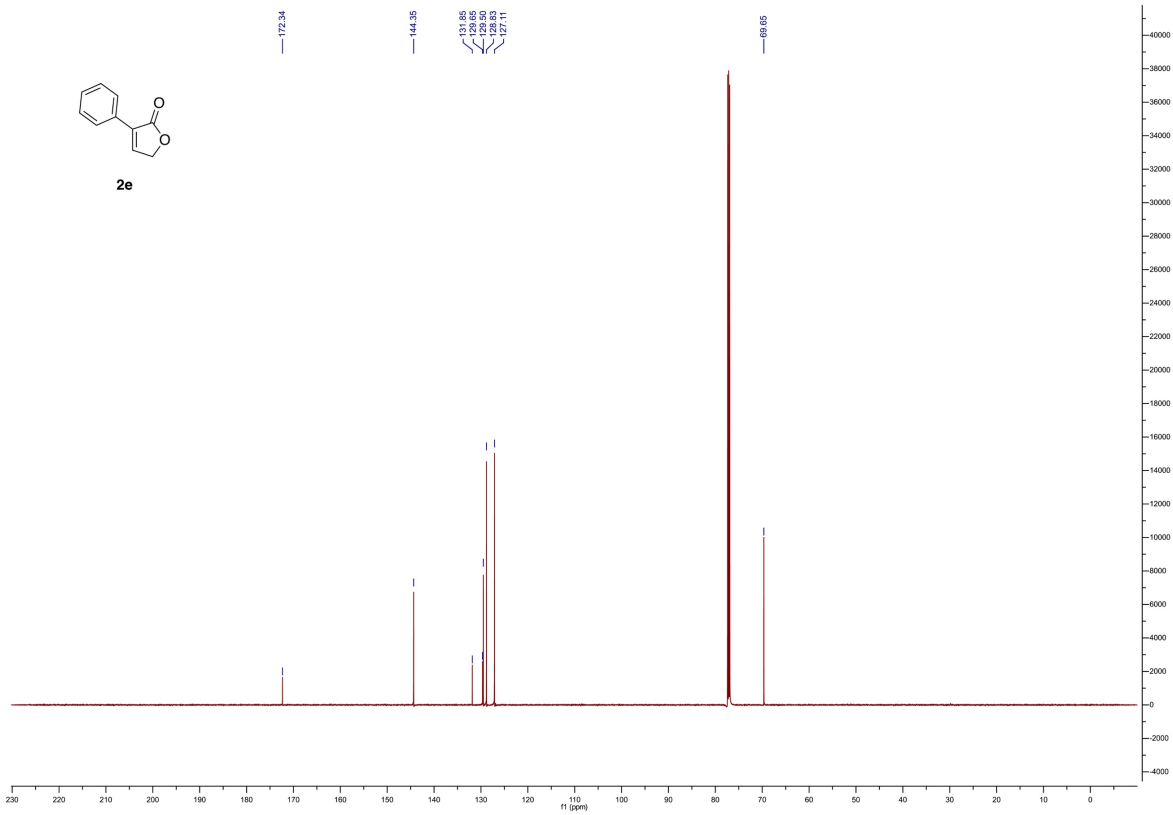
7.86
7.85
7.84
7.84
7.83
7.65
7.64
7.64
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
4.93
4.92
2e
2.00
1.00
3.03
2.03
f1 (ppm)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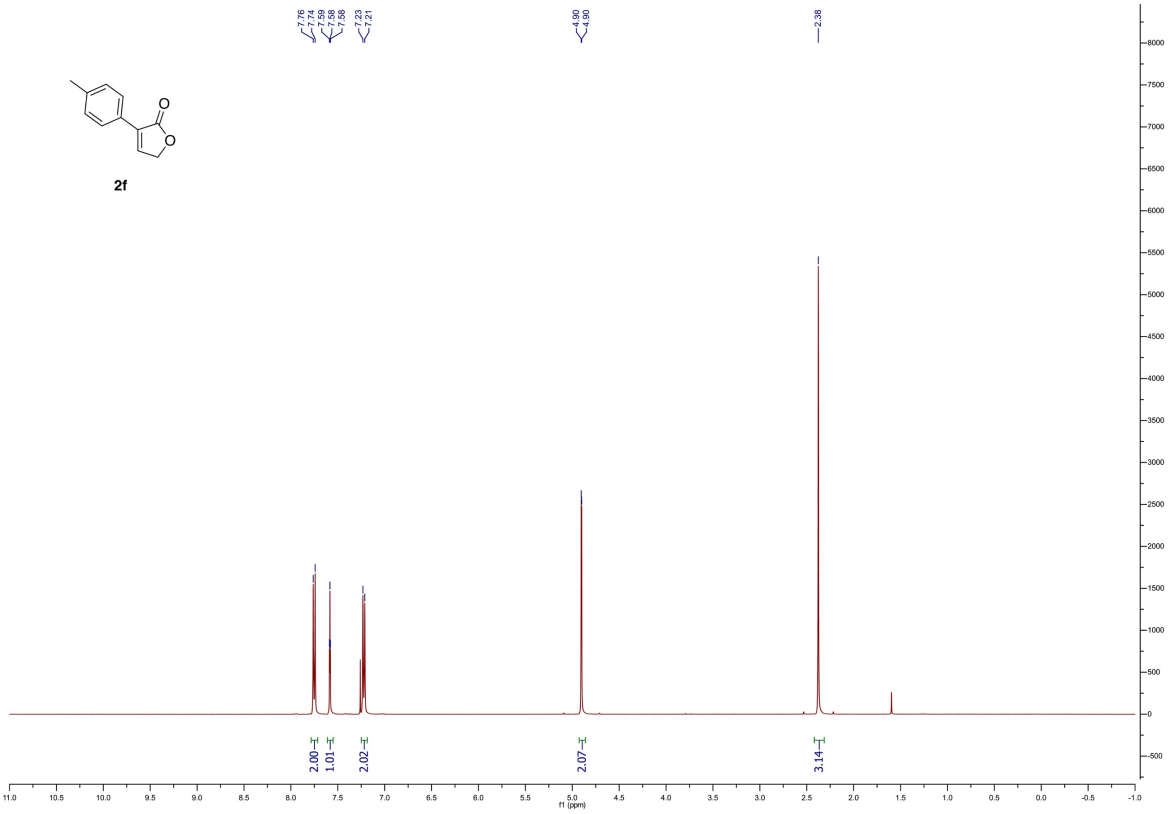
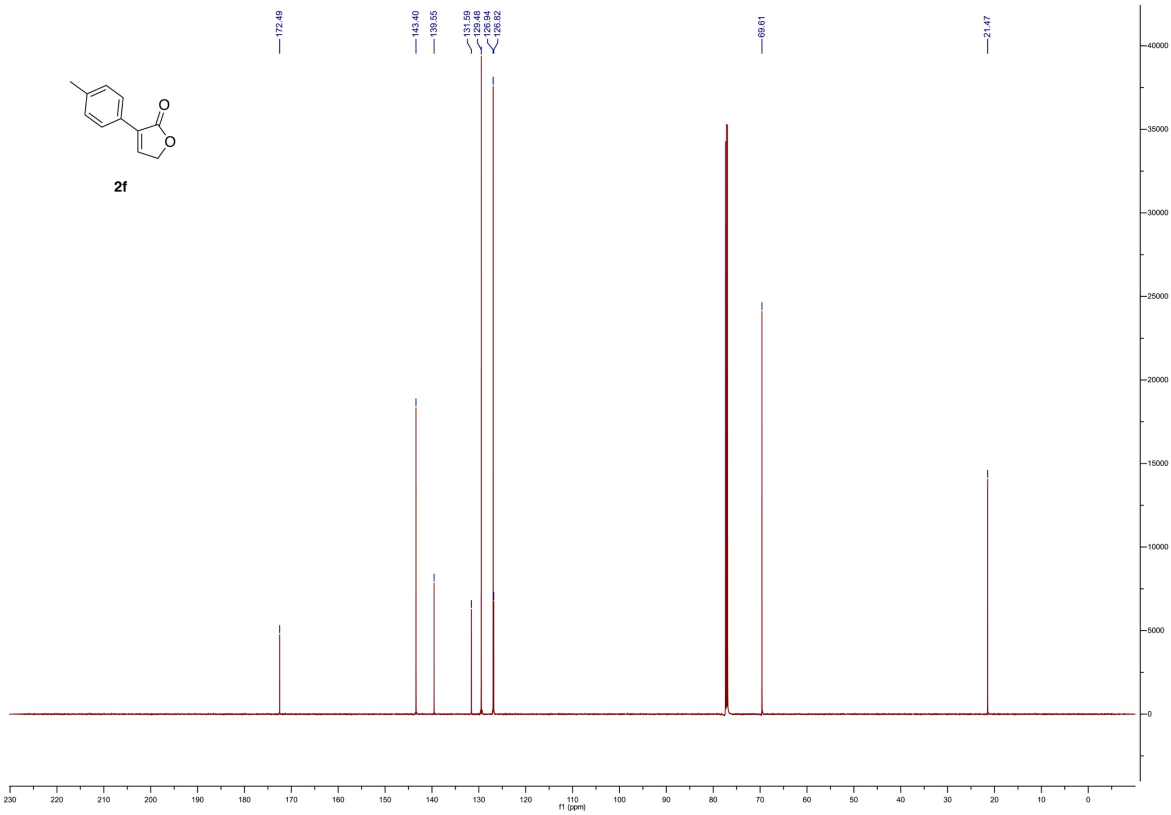
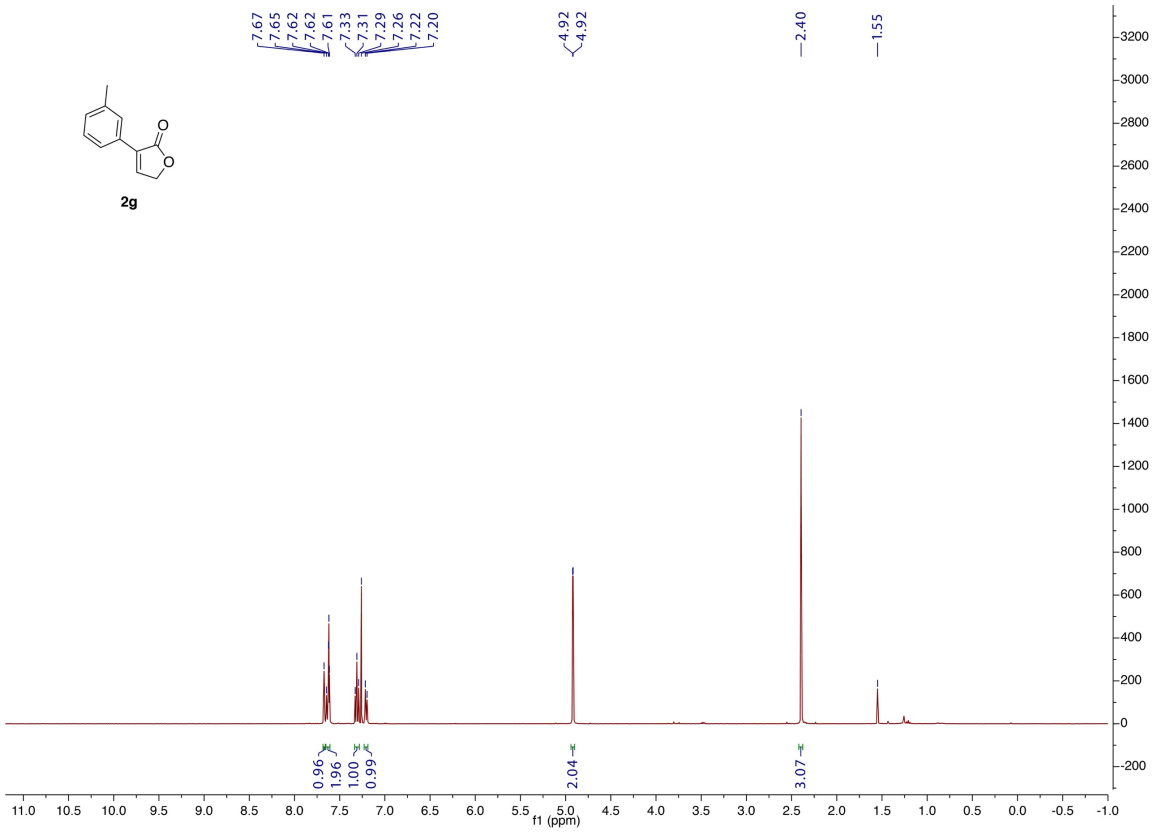
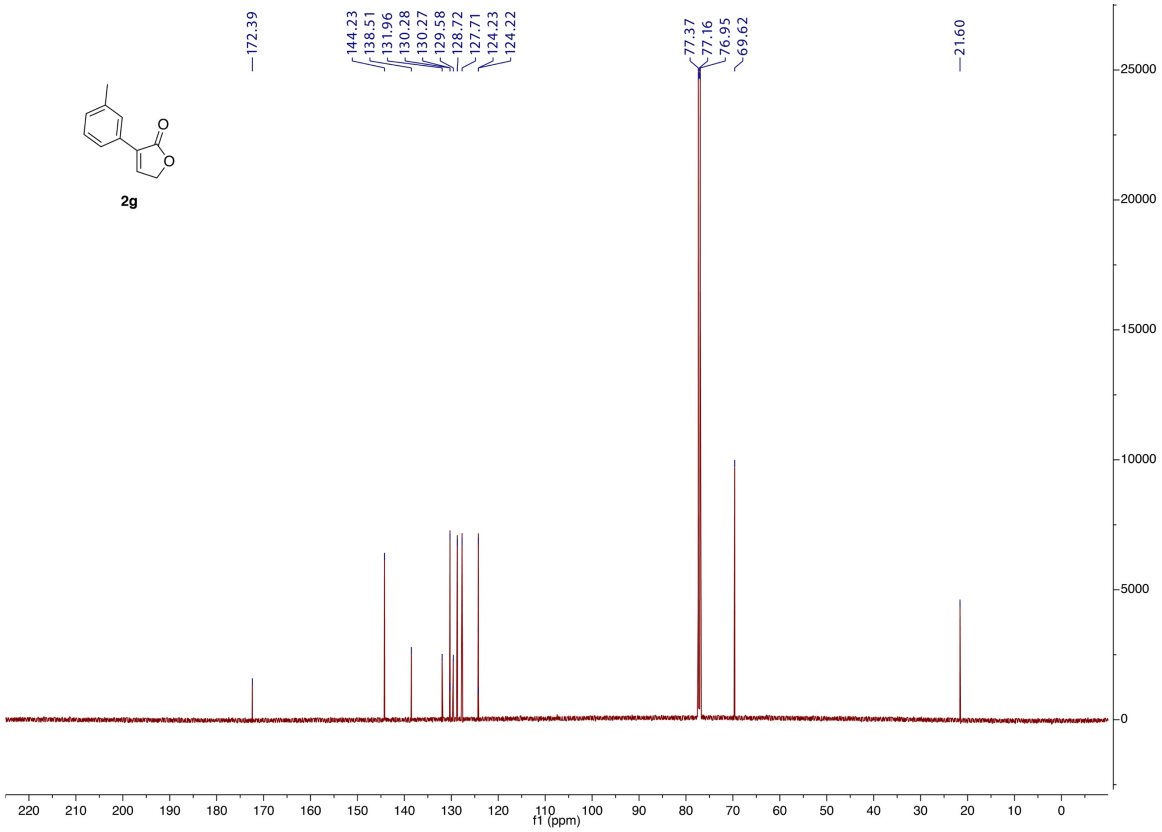
144.35
131.85
129.65
129.50
128.83
127.11
69.65
2e
f1 (ppm)


7.76
7.74
7.59
7.58
7.58
7.23
7.21
4.90
4.90
2.38
2f
2.00
1.01
2.02
2.07
3.14
f1 (ppm)

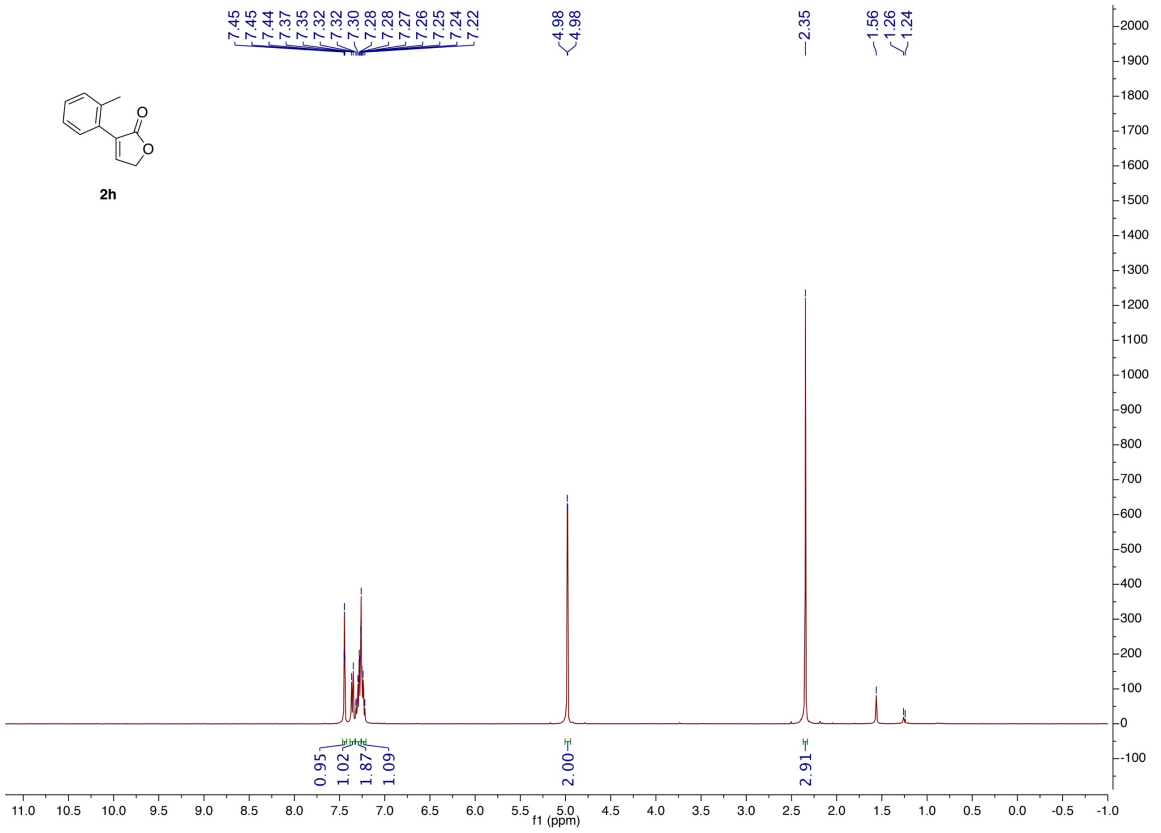

172.49
143.40
139.55
131.59
129.48
128.34
126.82
69.61
21.47
2f
f1 (ppm)

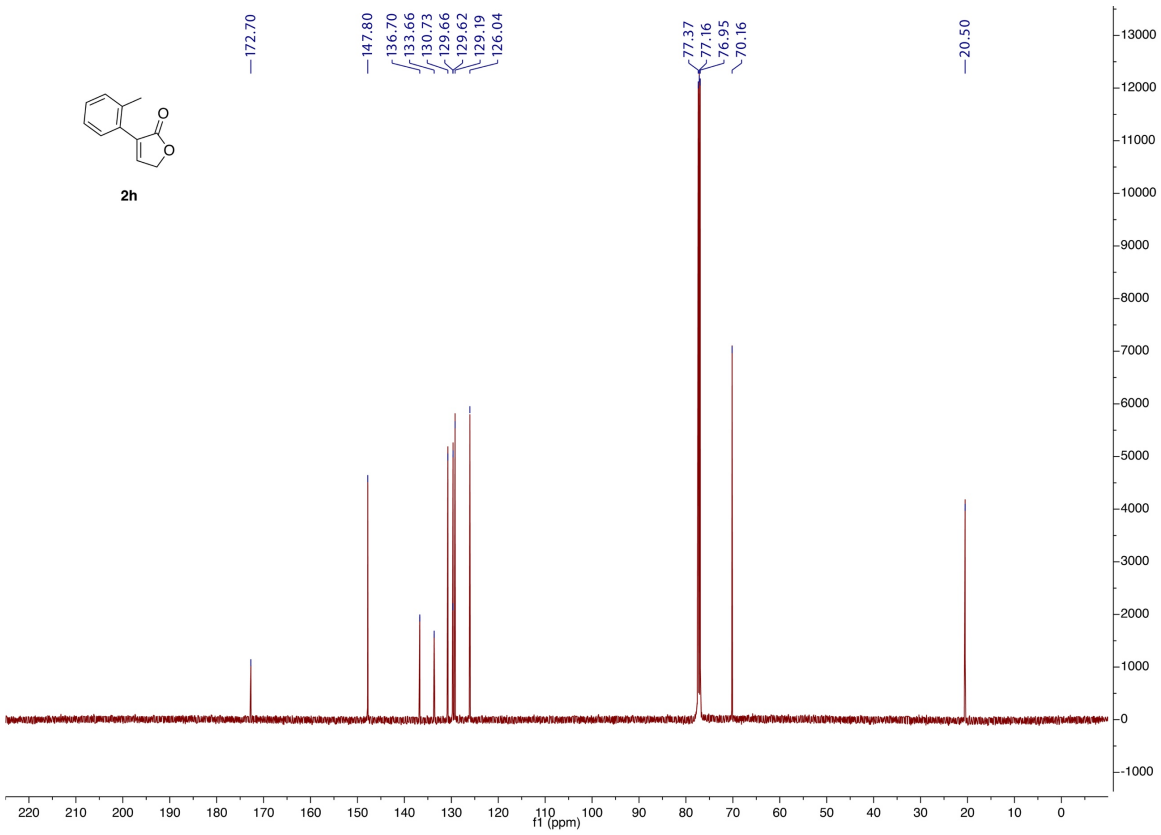

7.67
7.65
7.62
7.62
7.61
7.33
7.31
7.29
7.26
7.22
7.20
4.92
4.92
2.40
1.55
0.96
1.96
1.00
0.99
2.04
3.07
f1 (ppm)

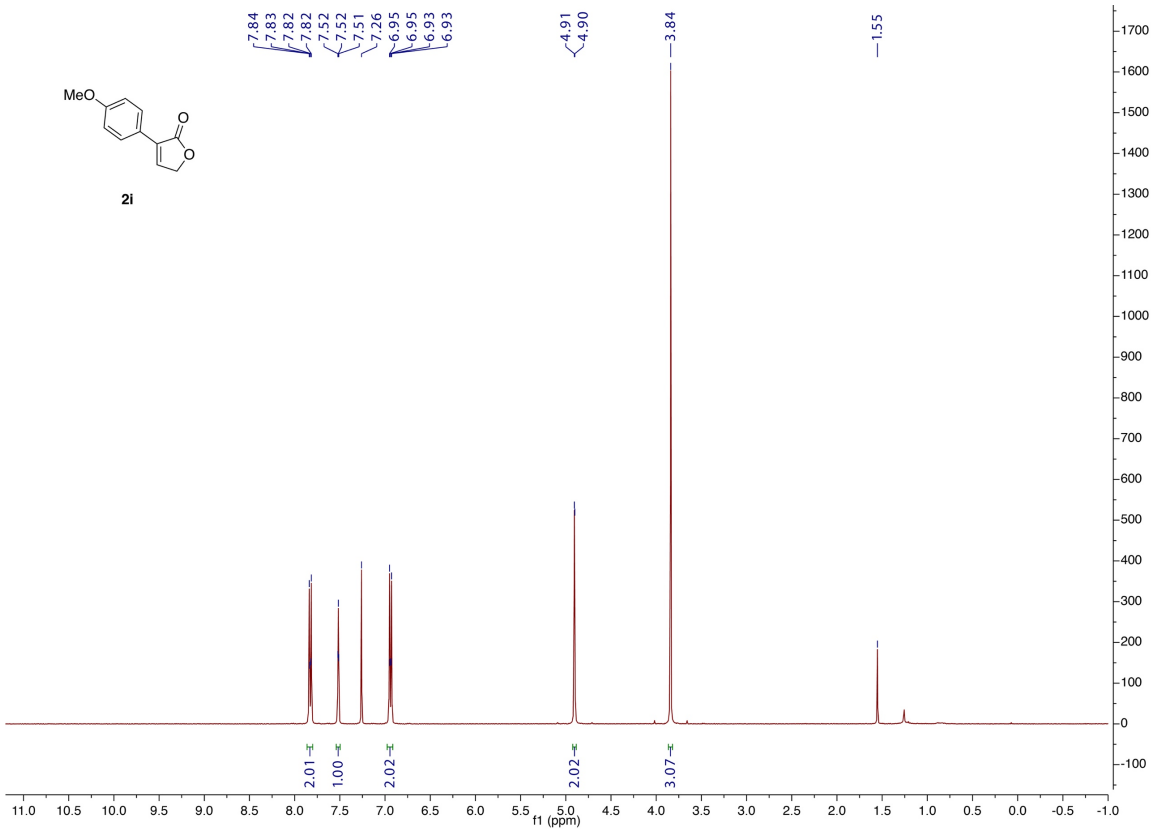
2g

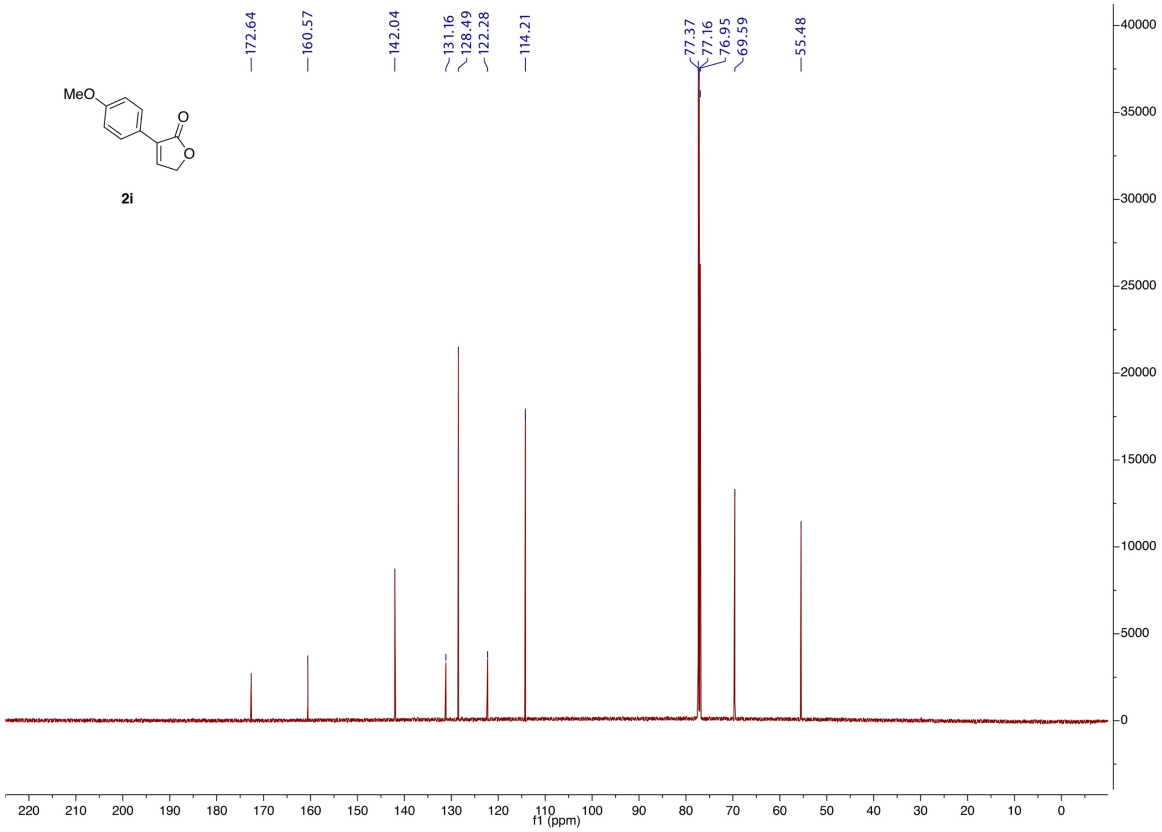

172.39
144.23
138.51
131.96
130.28
130.27
129.58
128.72
127.71
124.23
124.22
77.37
77.16
76.95
69.62
21.60
f1 (ppm)

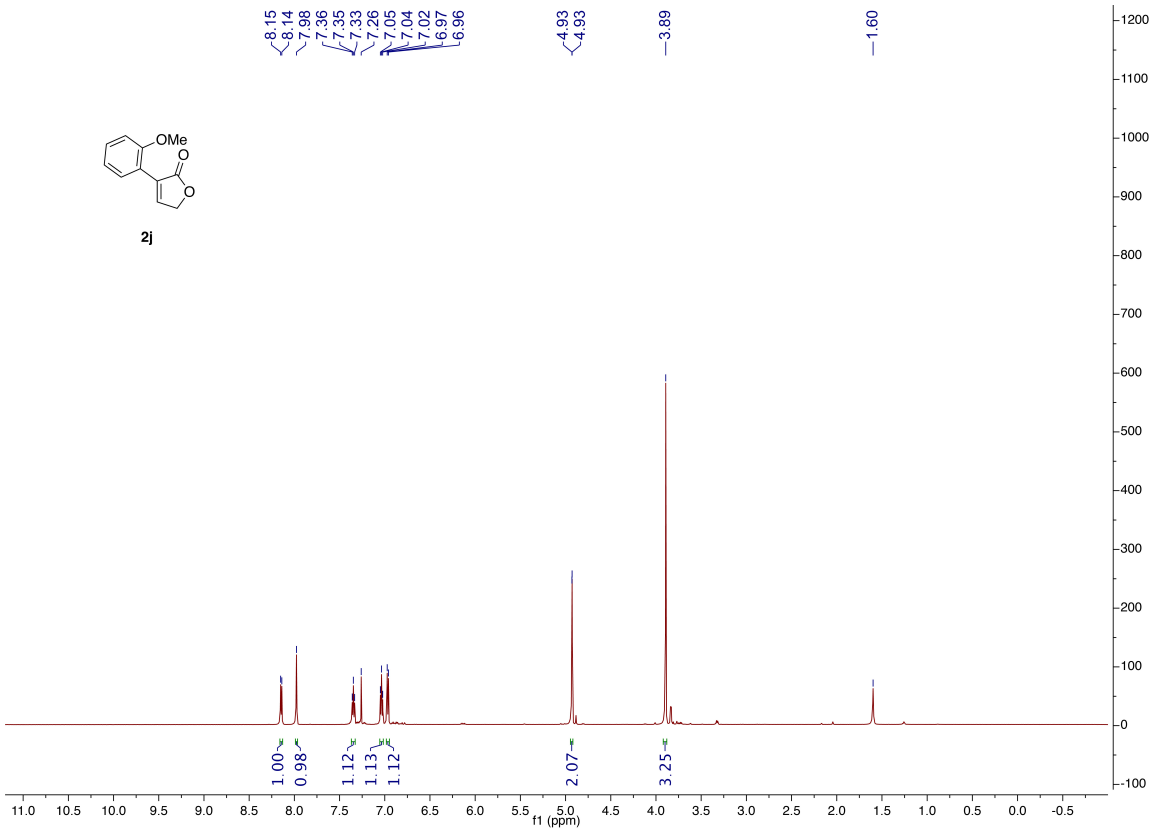
2g

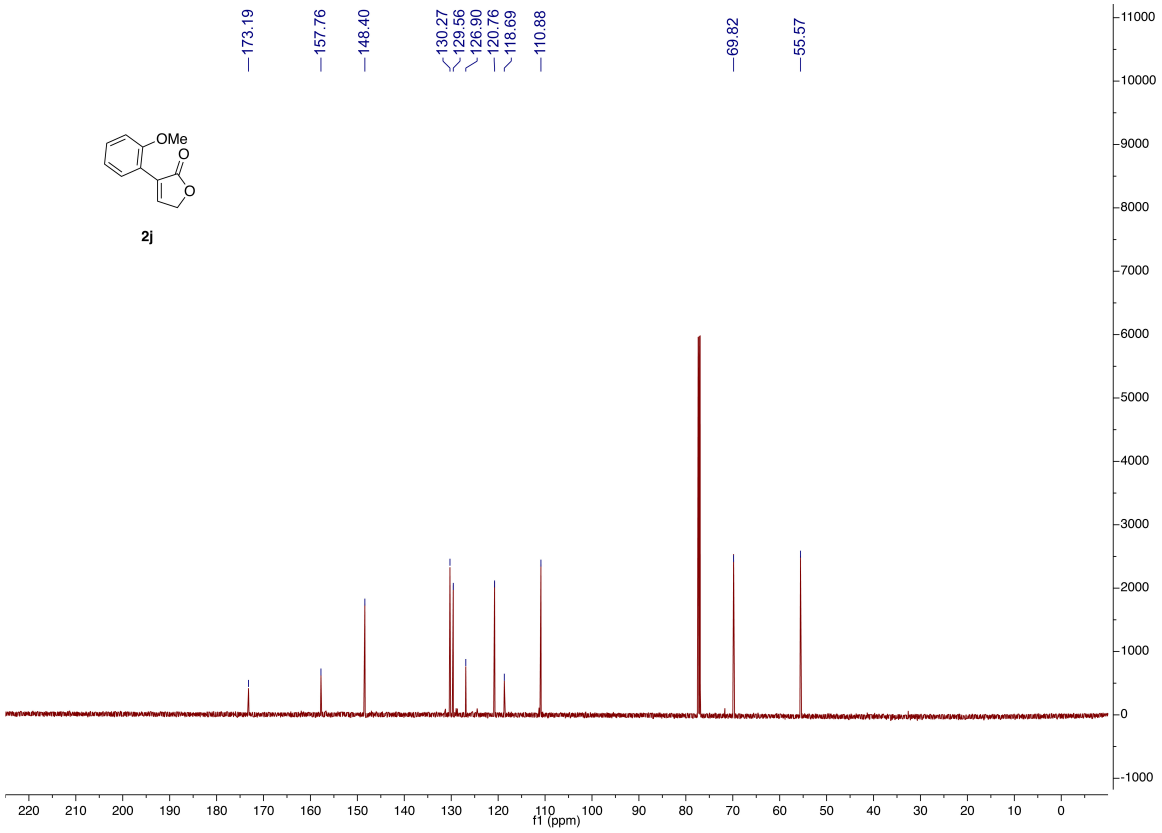

7.45
7.45
7.44
7.37
7.35
7.32
7.32
7.30
7.28
7.28
7.27
7.26
7.25
7.24
7.22
4.98
4.98
2.35
1.56
1.26
1.24
2h
0.95
1.02
1.87
1.09
2.00
2.91
f1 (ppm)

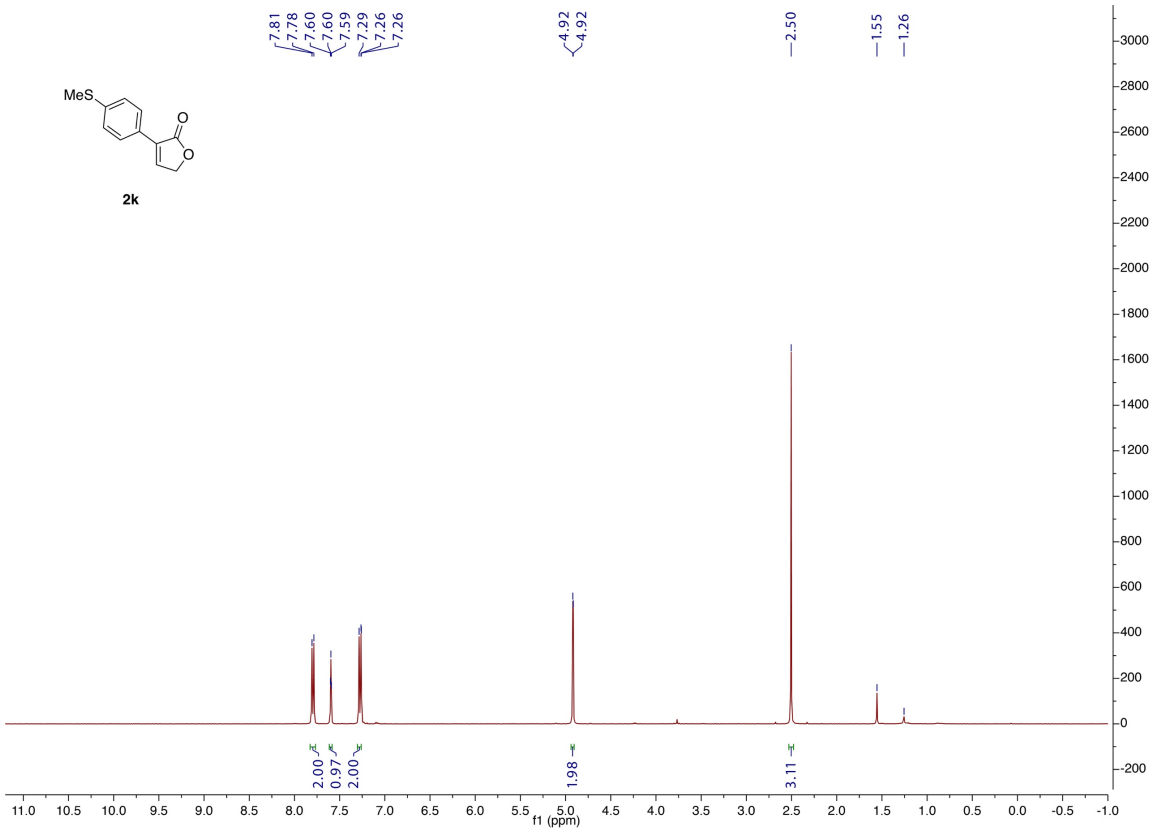

172.70
147.80
136.70
133.66
130.73
129.66
129.62
129.19
126.04
77.37
77.16
76.95
70.16
20.50
2h
f1 (ppm)

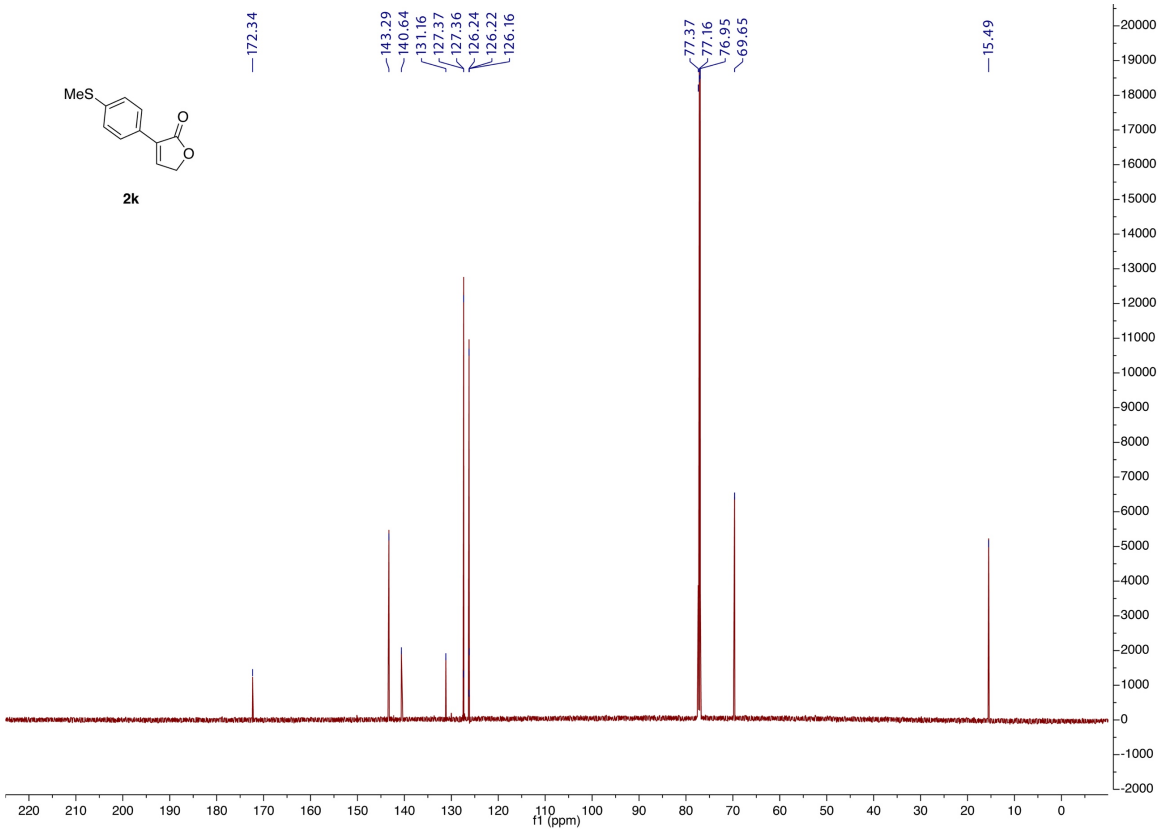

7.84
7.83
7.82
7.82
7.52
7.52
7.51
7.26
6.95
6.95
6.93
6.93
4.91
4.90
3.84
1.55
MeO
O
O
2i
2.01
1.00
2.02
2.02
3.07
f1 (ppm)

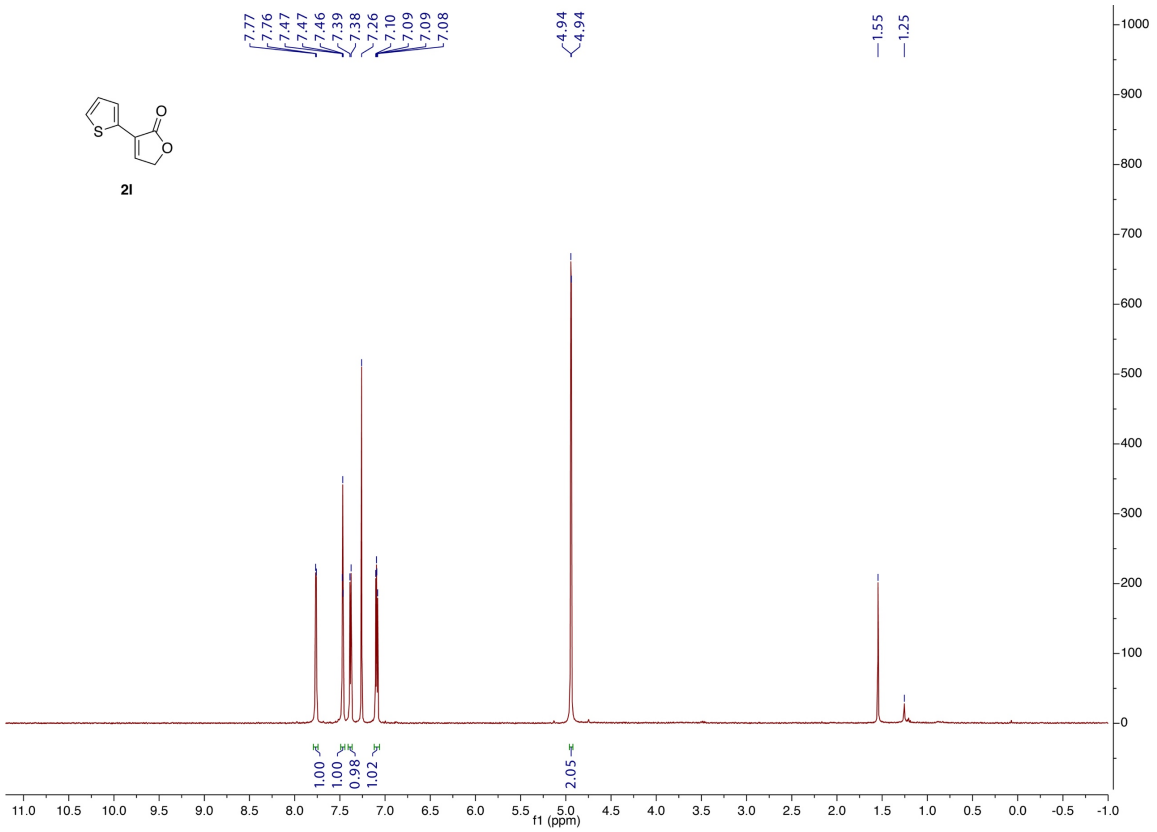

172.64
160.57
142.04
131.16
128.49
122.28
114.21
77.37
77.16
76.95
69.59
55.48
MeO
O
O
2i
f1 (ppm)

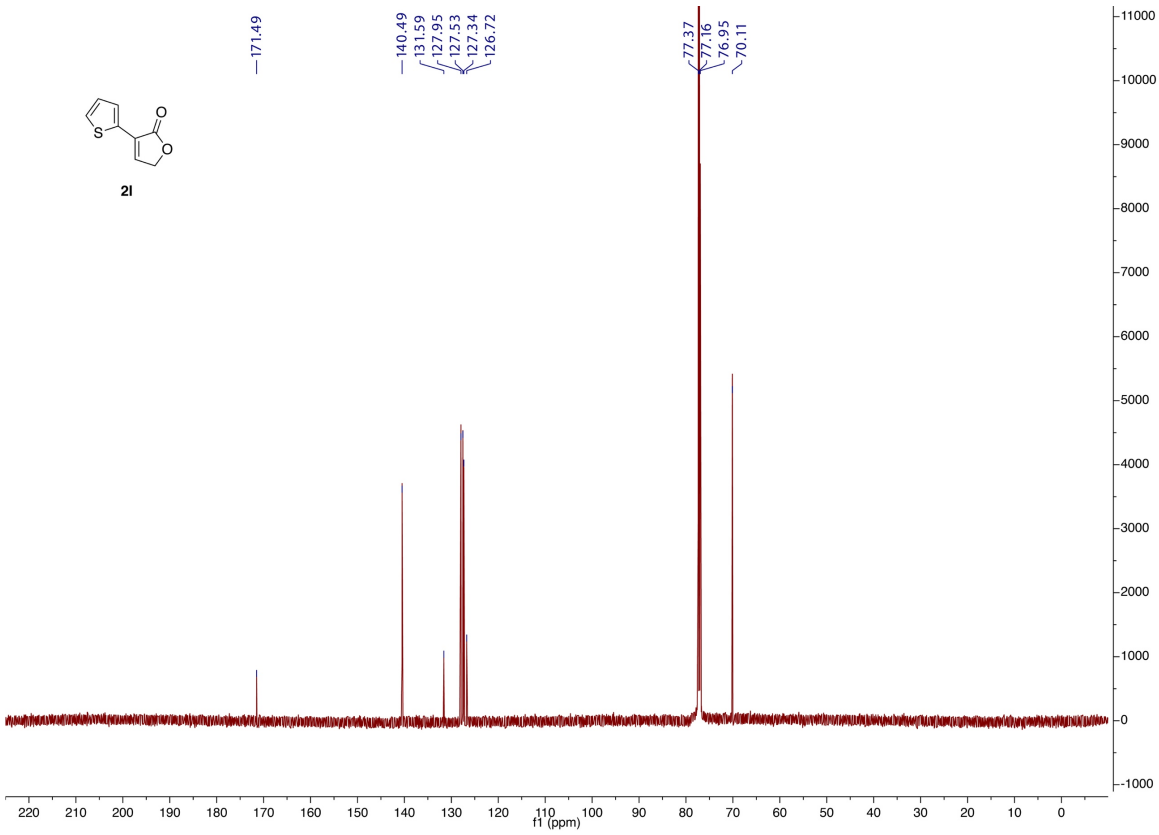

8.15
8.14
7.98
7.36
7.35
7.33
7.26
7.05
7.04
7.02
6.97
6.96
4.93
4.93
3.89
1.60
OMe
O
O
2j
1.00
0.98
1.12
1.13
1.12
2.07
3.25
f1 (ppm)

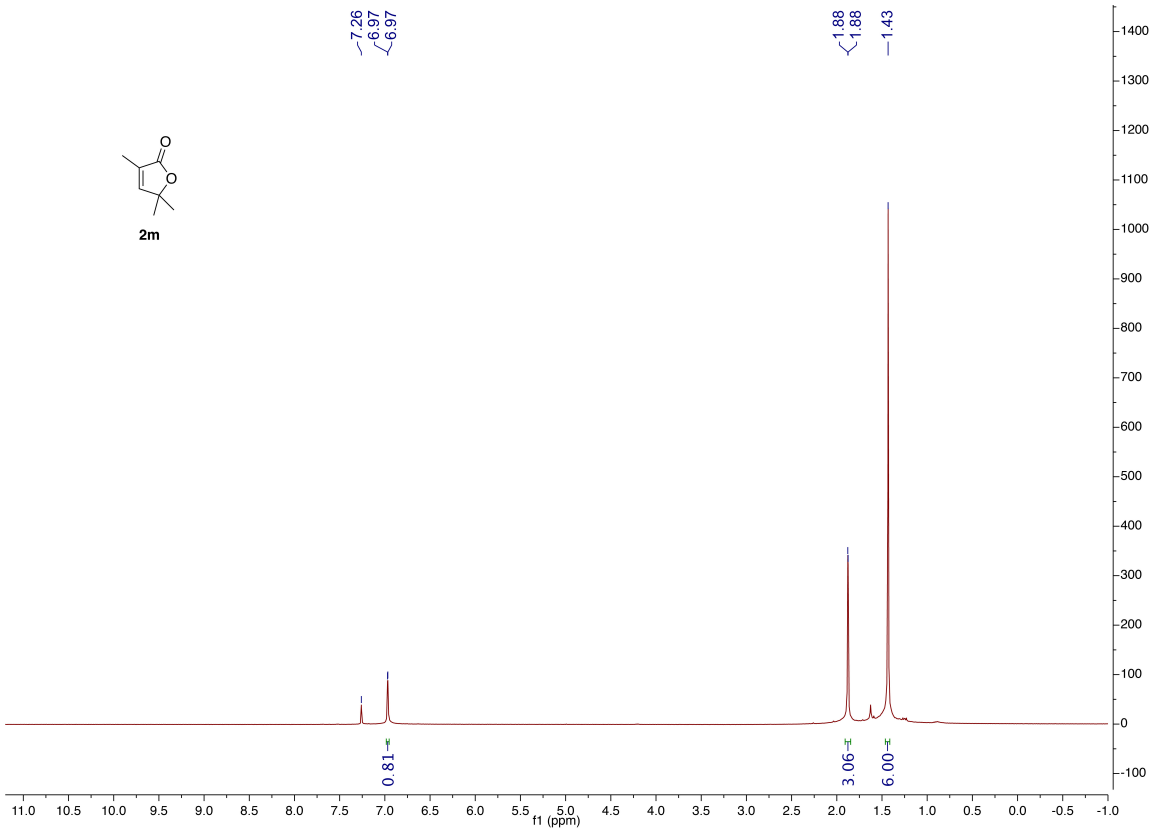

173.19
157.76
148.40
130.27
129.56
126.90
120.76
118.69
110.88
69.82
55.57
OMe
O
O
2j
f1 (ppm)

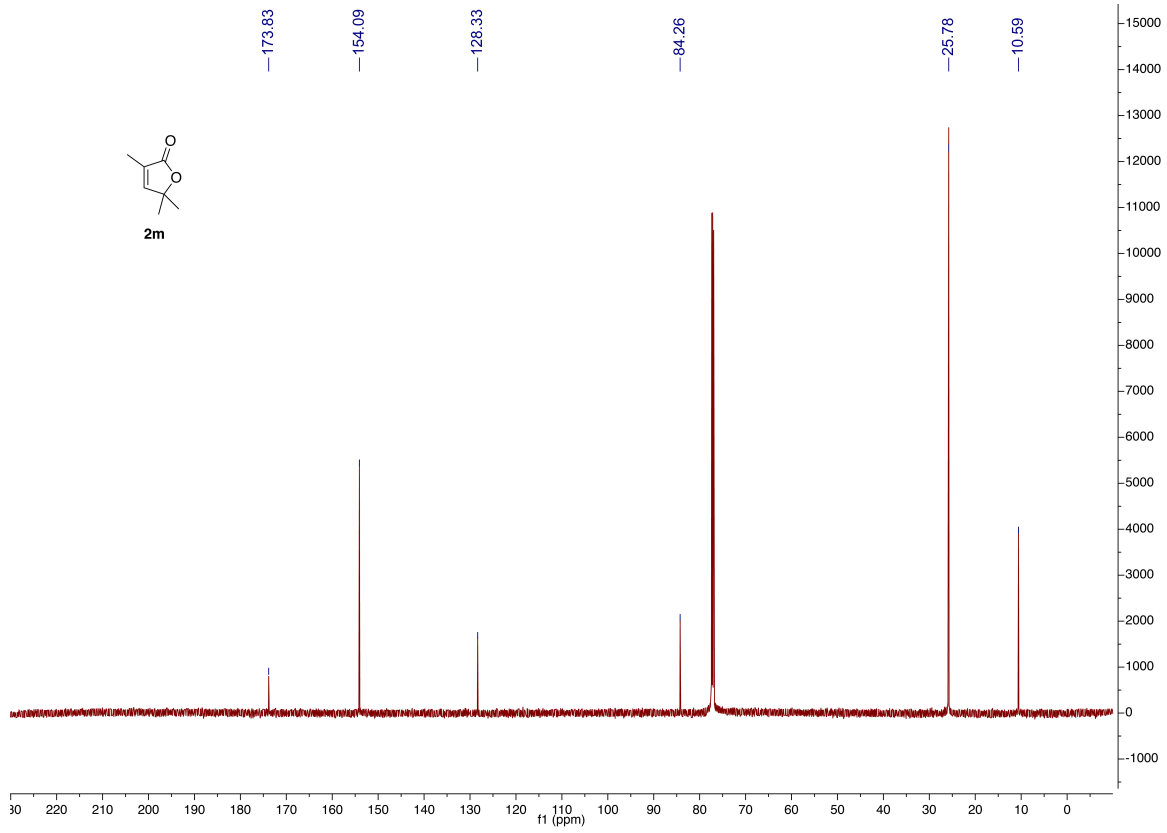

7.81
7.78
7.60
7.60
7.59
7.29
7.26
7.26
4.92
4.92
2.50
1.55
1.26
MeS
O
O
2k
2.00
0.97
2.00
1.98
3.11
f1 (ppm)

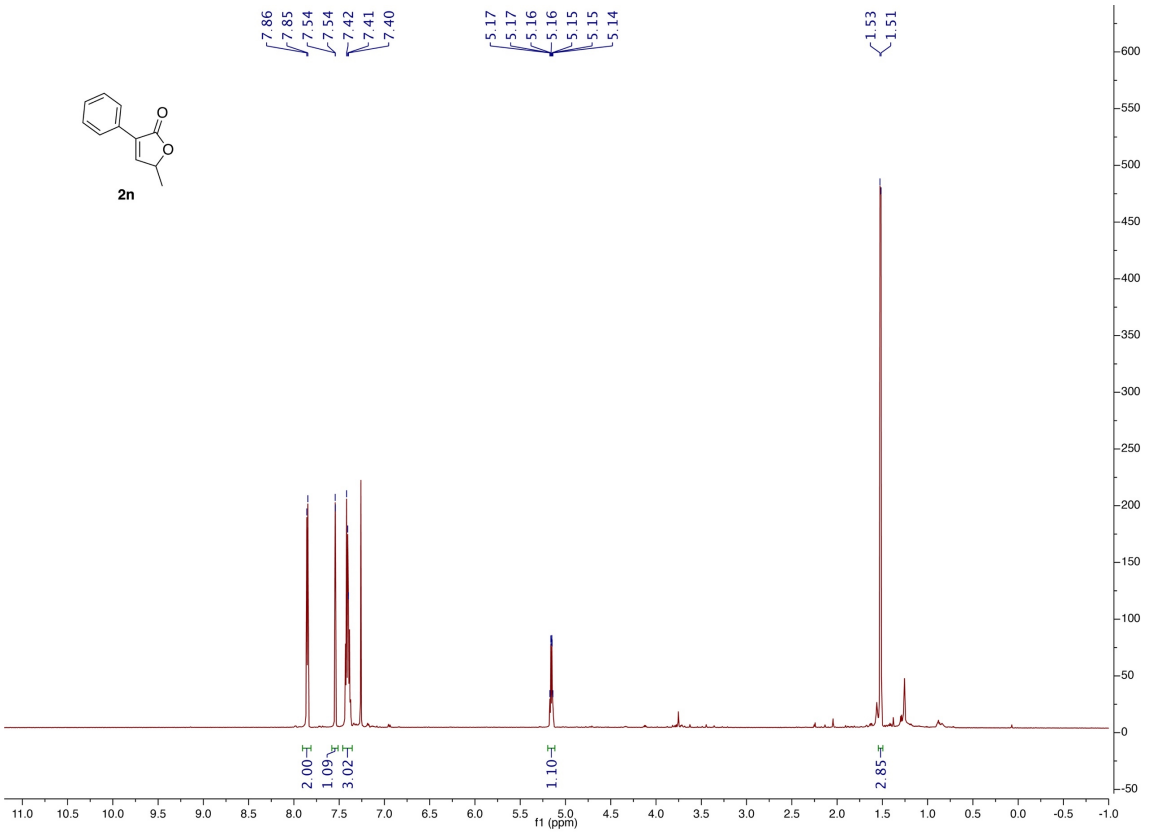

172.34
143.29
140.64
131.16
127.37
127.36
126.24
126.22
126.16
77.37
77.16
76.95
69.65
15.49
MeS
O
O
2k
f1 (ppm)

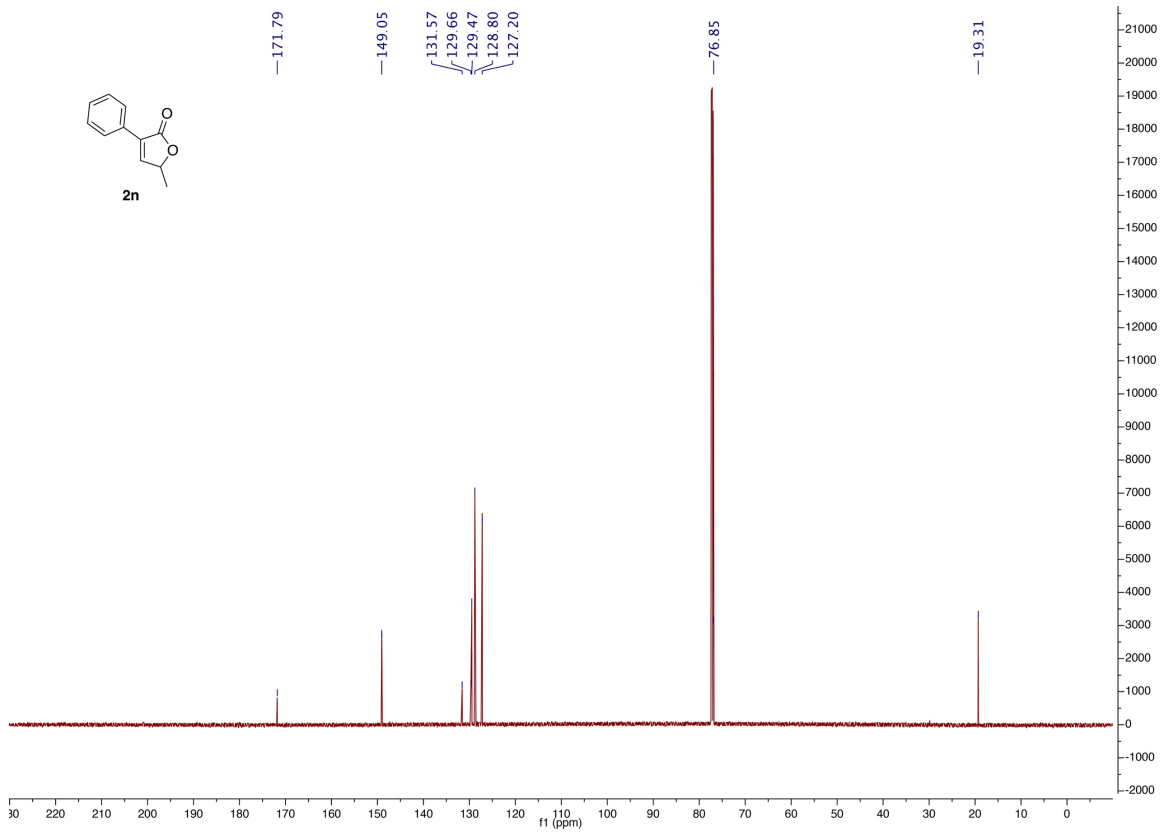

7.77
7.76
7.47
7.47
7.46
7.39
7.38
7.26
7.10
7.09
7.09
7.08
4.94
4.94
1.55
1.25
2l
1.00
1.00
0.98
1.02
2.05
f1 (ppm)

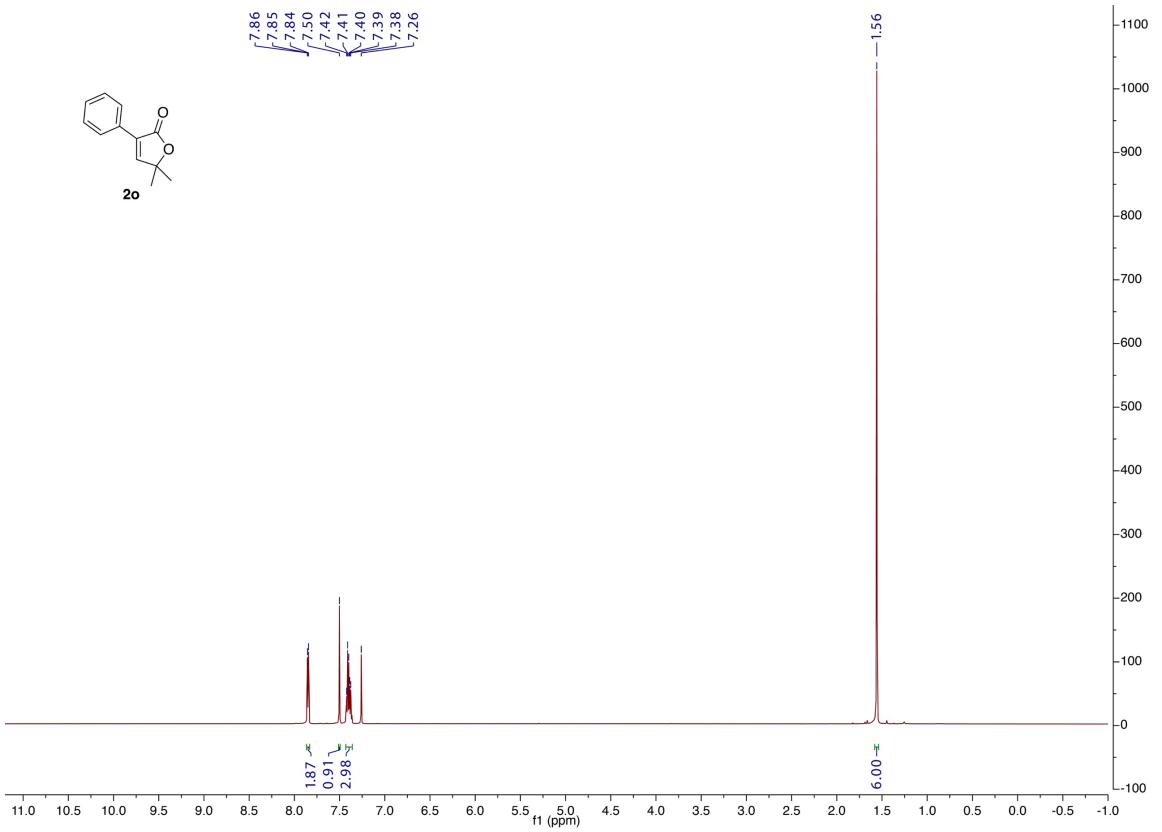

171.49
140.49
131.59
127.95
127.53
127.34
126.72
77.37
77.16
76.95
70.11
2l
f1 (ppm)

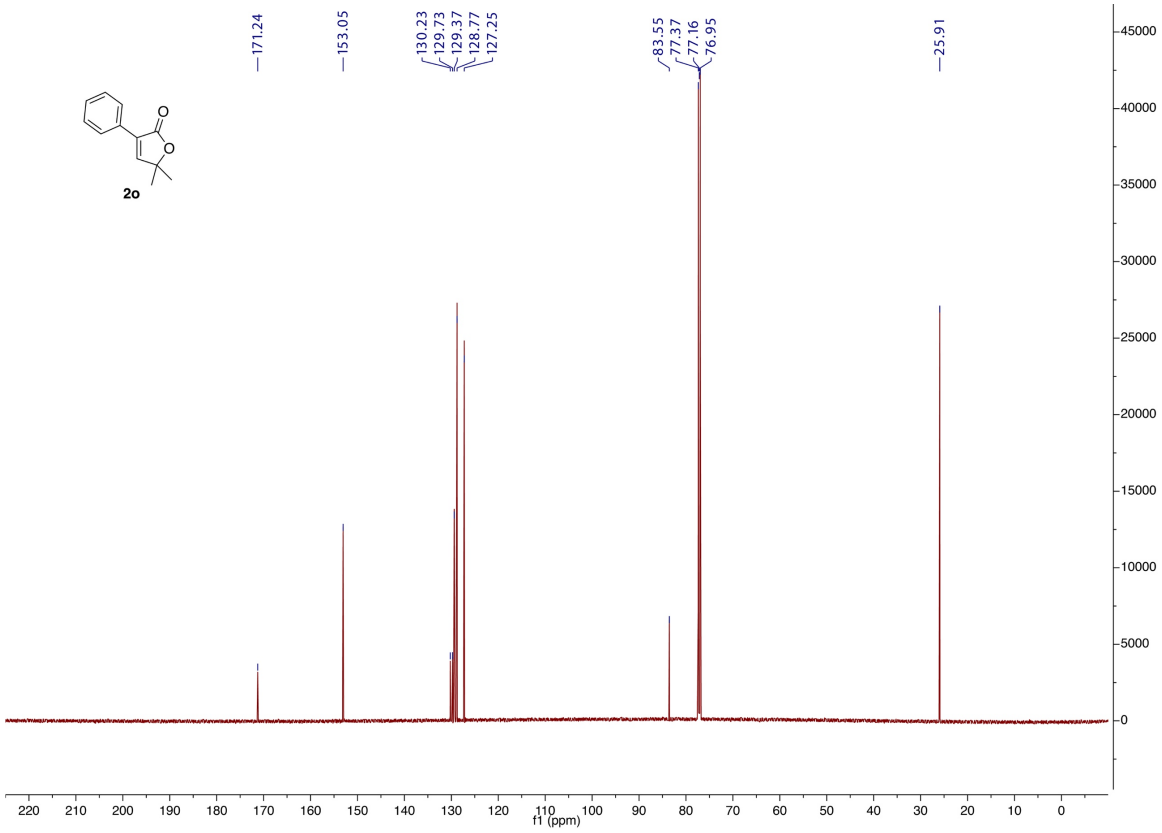

7.26
6.97
6.97
1.88
1.88
1.43
2m
0.81
3.06
6.00
f1 (ppm)

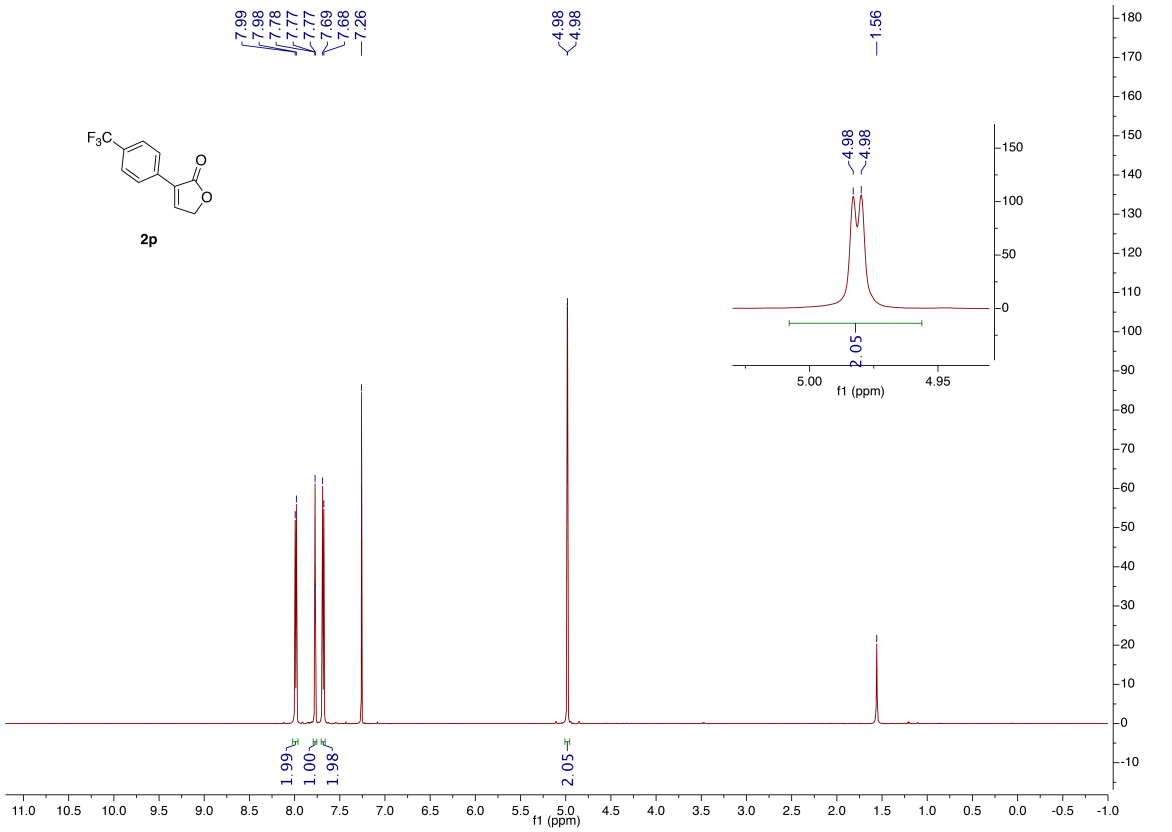

173.83
154.09
128.33
84.26
25.78
10.59
2m
f1 (ppm)

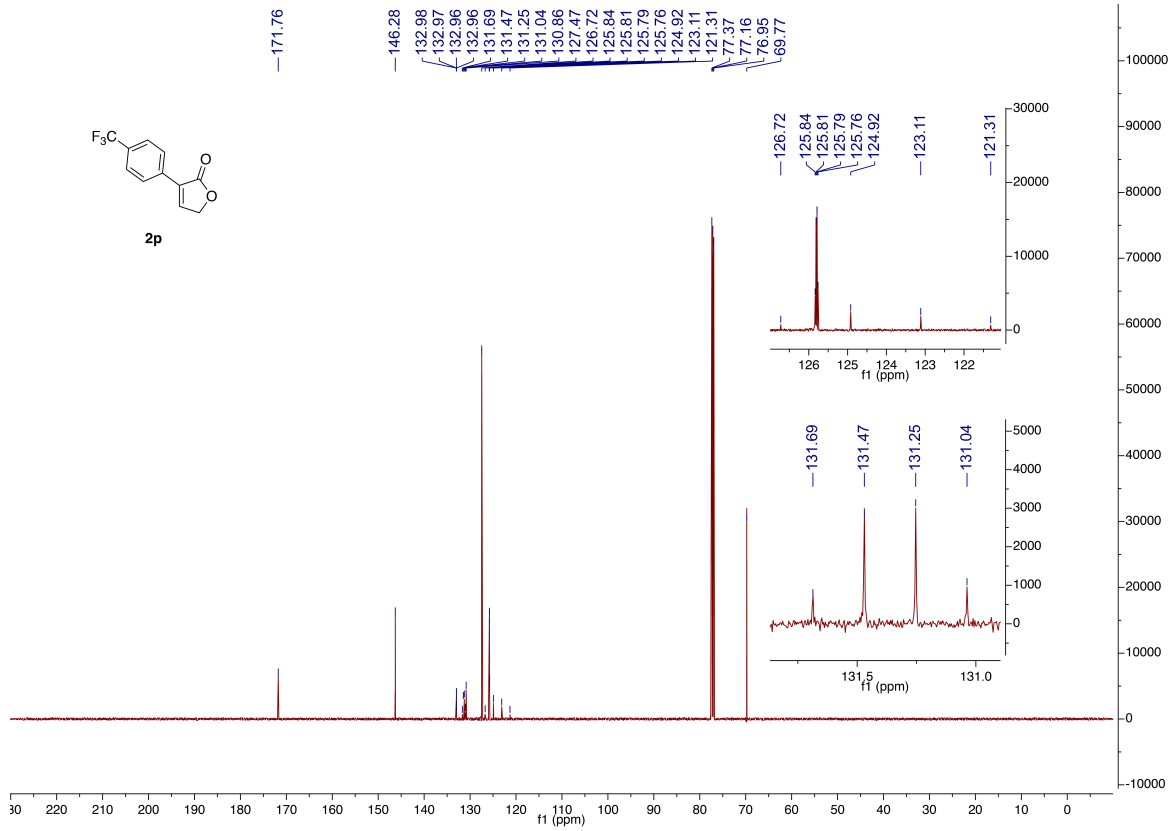

7.86
7.85
7.54
7.54
7.42
7.41
7.40
5.17
5.17
5.16
5.16
5.15
5.15
5.14
1.53
1.51
2n
2.00
1.09
3.02
1.10
2.85
f1 (ppm)

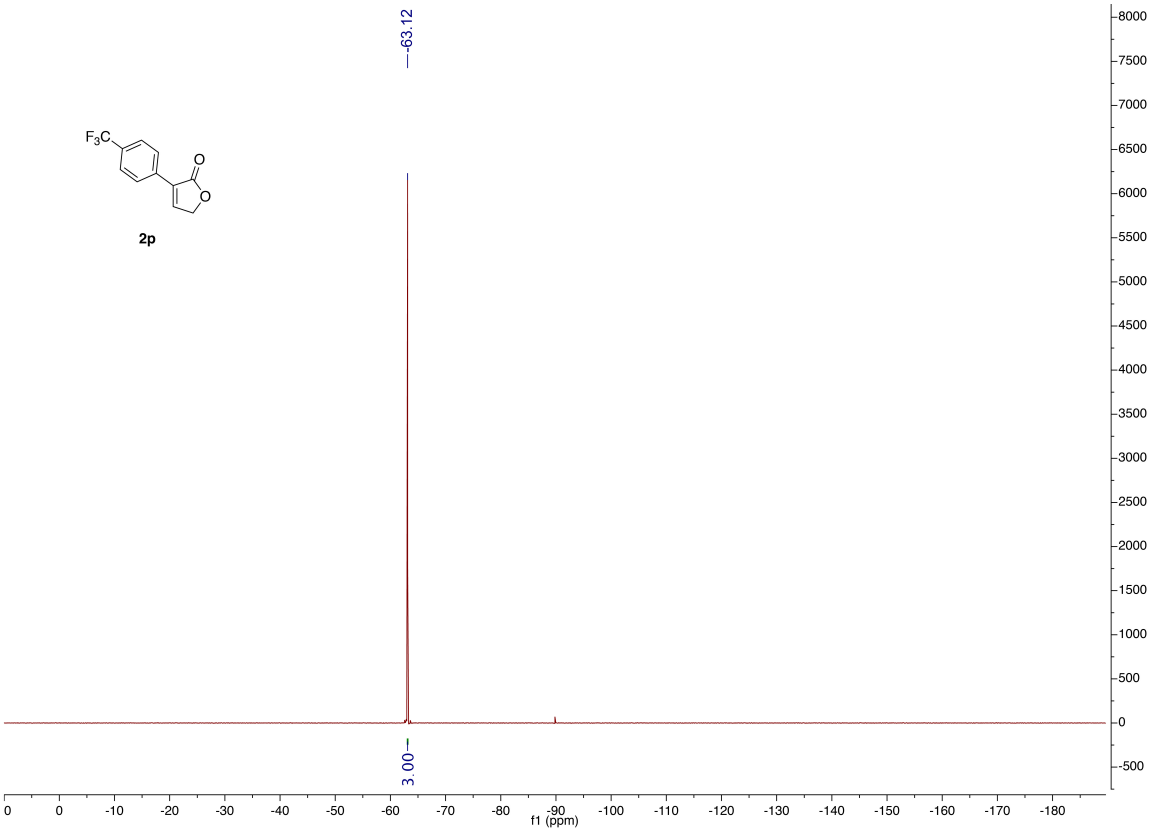

171.79
149.05
131.57
129.66
129.47
128.80
127.20
76.85
19.31
2n
f1 (ppm)

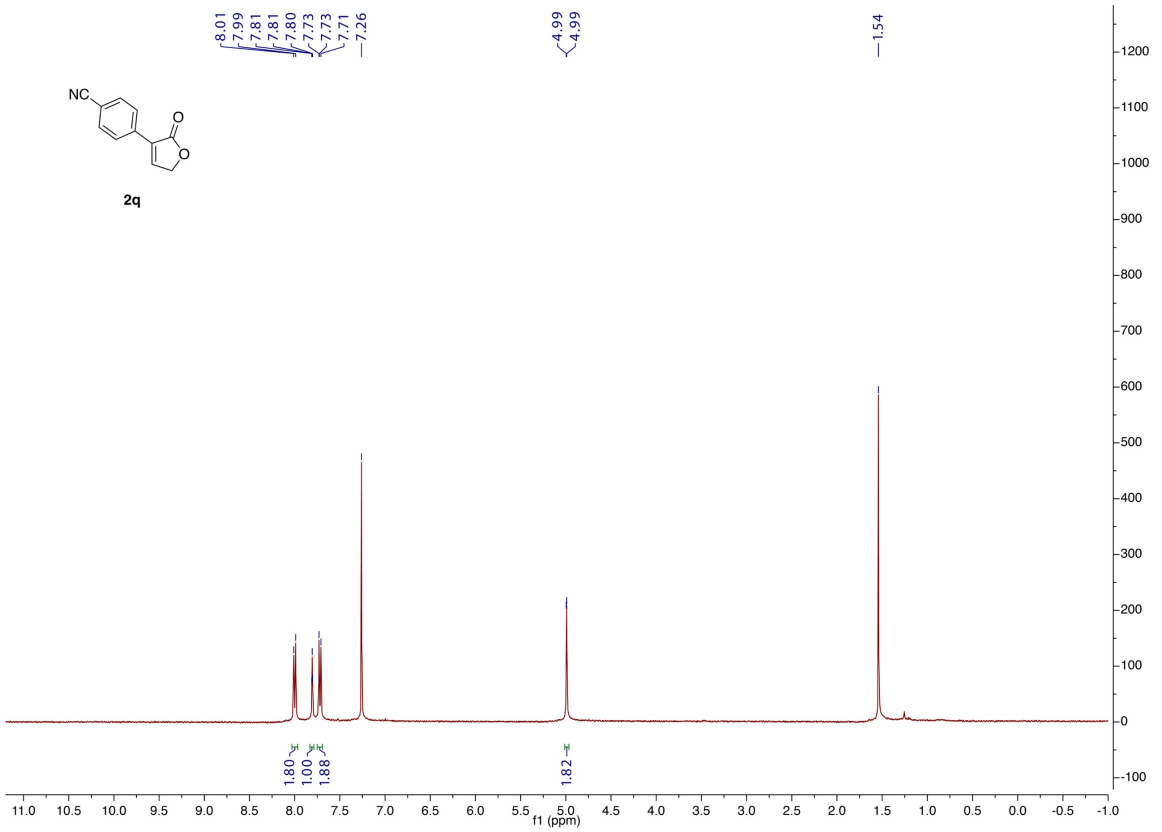

7.86
7.85
7.84
7.50
7.42
7.41
7.40
7.39
7.38
7.26
1.56
2o
1.87
0.91
2.98
6.00
f1 (ppm)

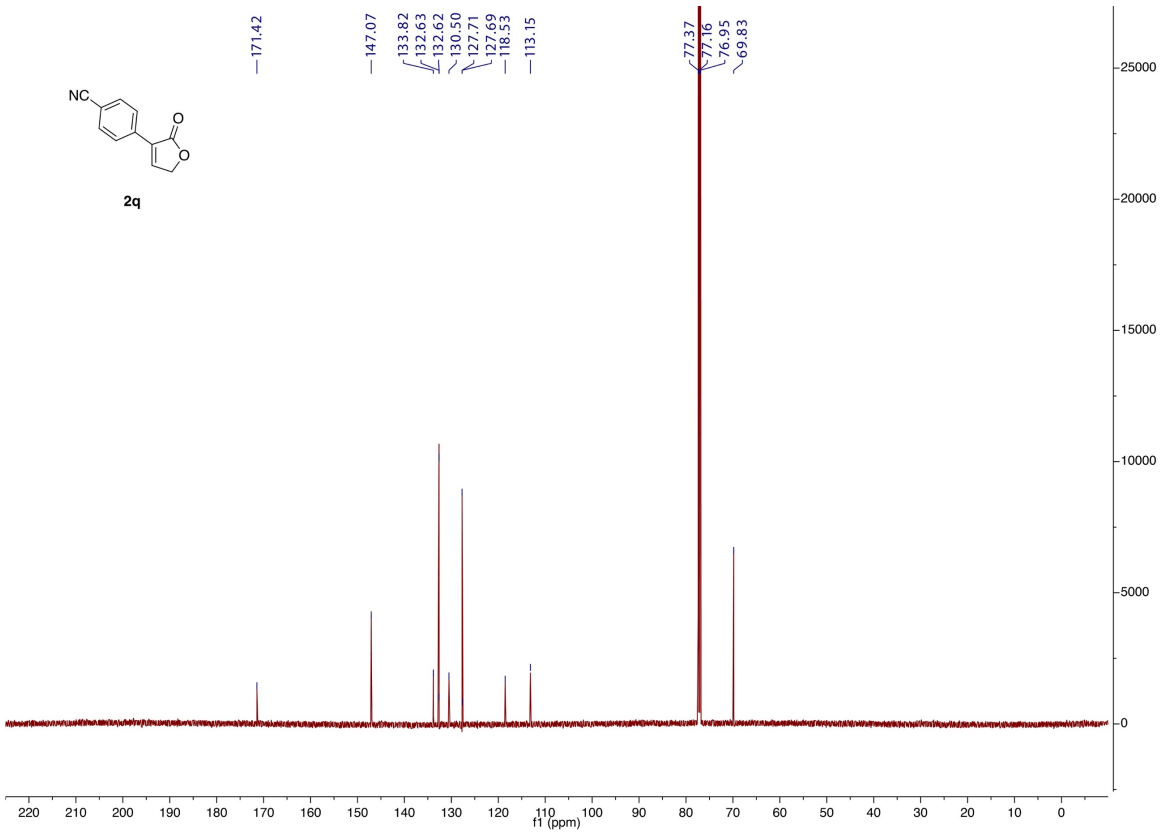

171.24
153.05
130.23
129.73
129.37
128.77
127.25
83.55
77.37
77.16
76.95
25.91
2o
f1 (ppm)

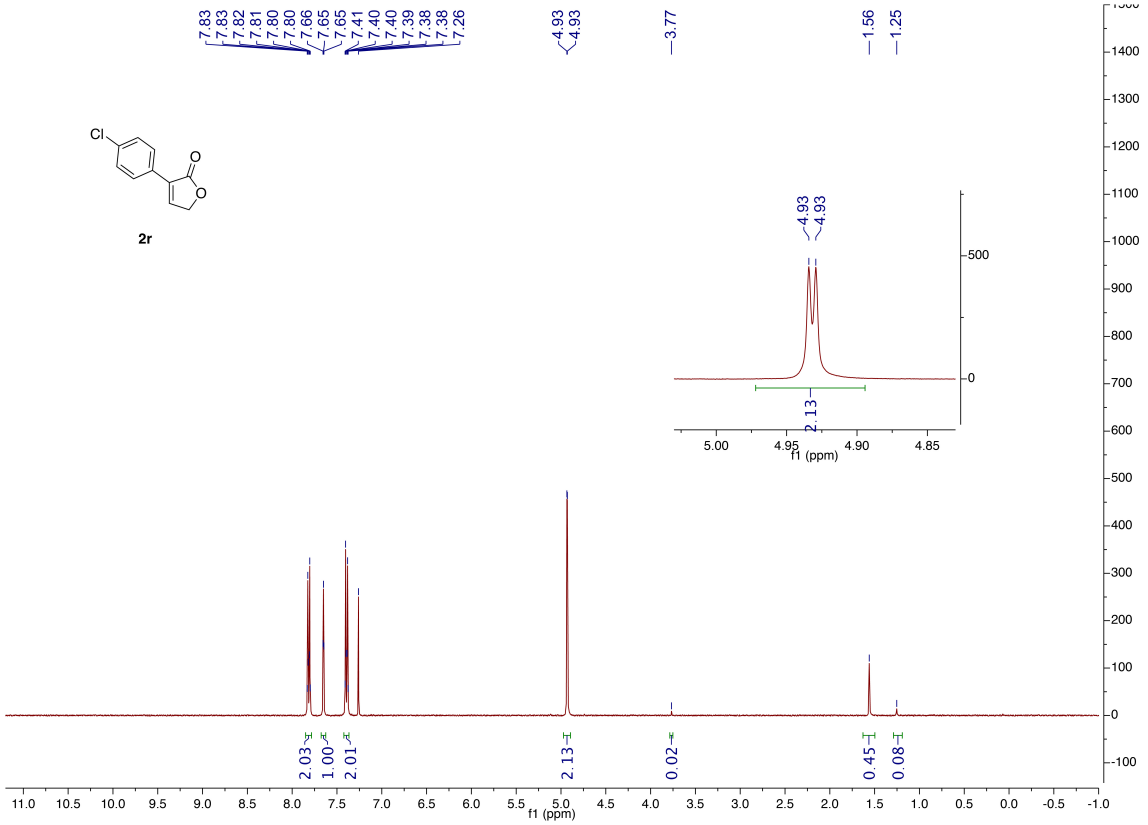

7.99
7.98
7.78
7.77
7.77
7.69
7.68
7.26
4.98
4.98
1.56
F3C
O
O
2p
4.98
4.98
2.05
5.00
4.95
f1 (ppm)
1.99
1.00
1.98
2.05
f1 (ppm)

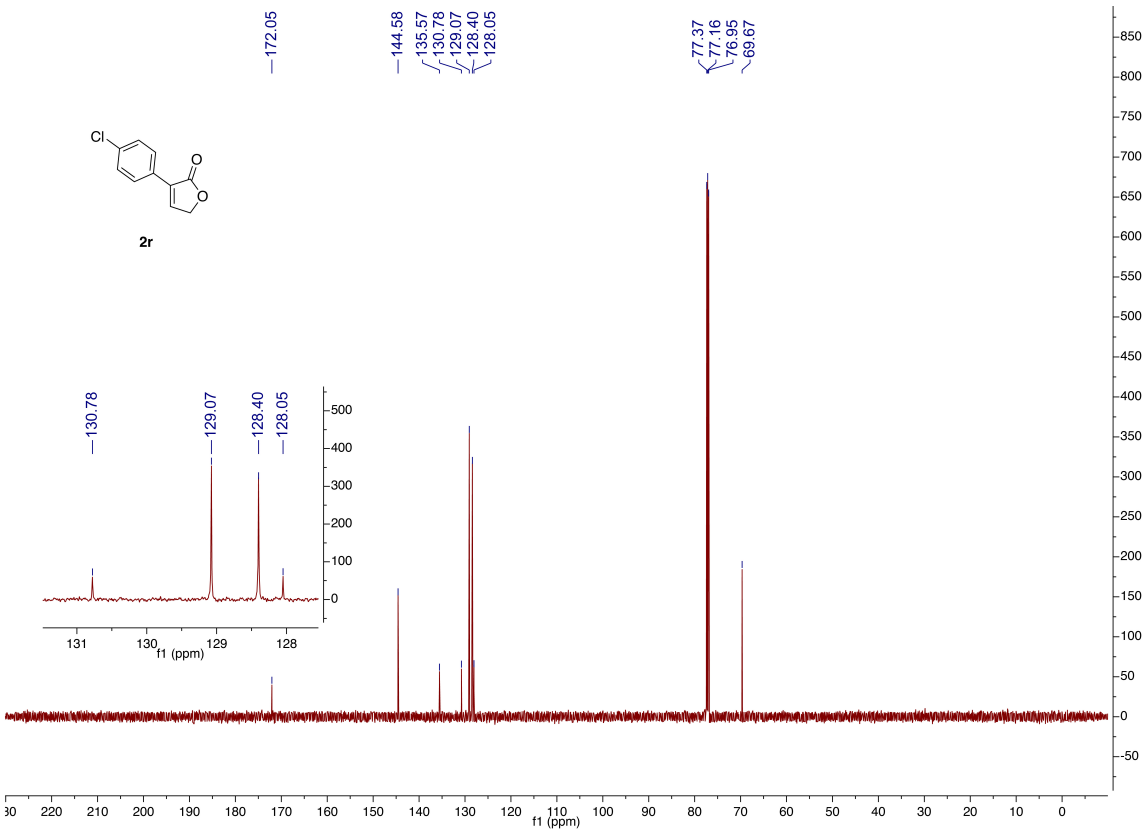

171.76
146.28
132.98
132.97
132.96
132.96
131.69
131.47
131.25
131.04
130.86
127.47
126.72
125.84
125.81
125.79
125.76
124.92
123.11
121.31
77.37
77.16
76.95
69.77
F3C
O
O
2p
126.72
125.84
125.81
125.79
125.76
124.92
123.11
121.31
126
125
124
123
122
f1 (ppm)
131.69
131.47
131.25
131.04
131.5
131.0
f1 (ppm)
f1 (ppm)

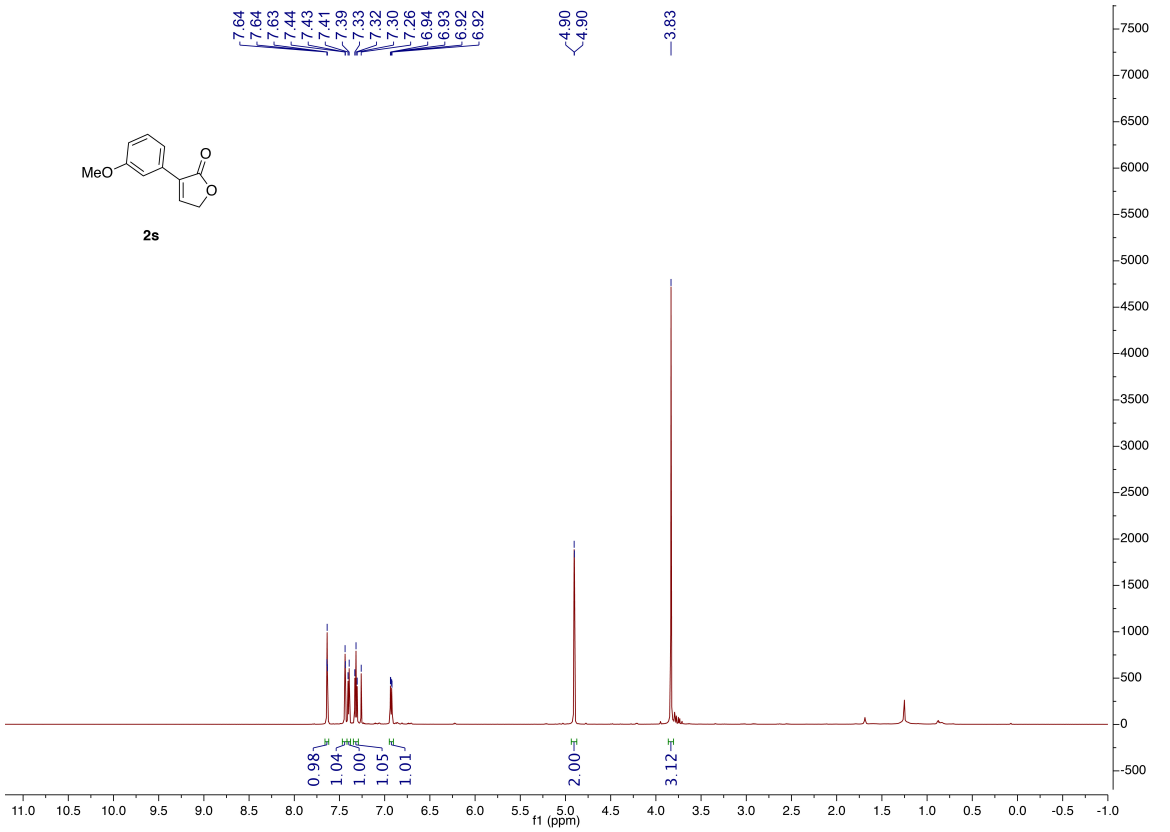

-63.12
F3C
O
O
2p
3.00
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

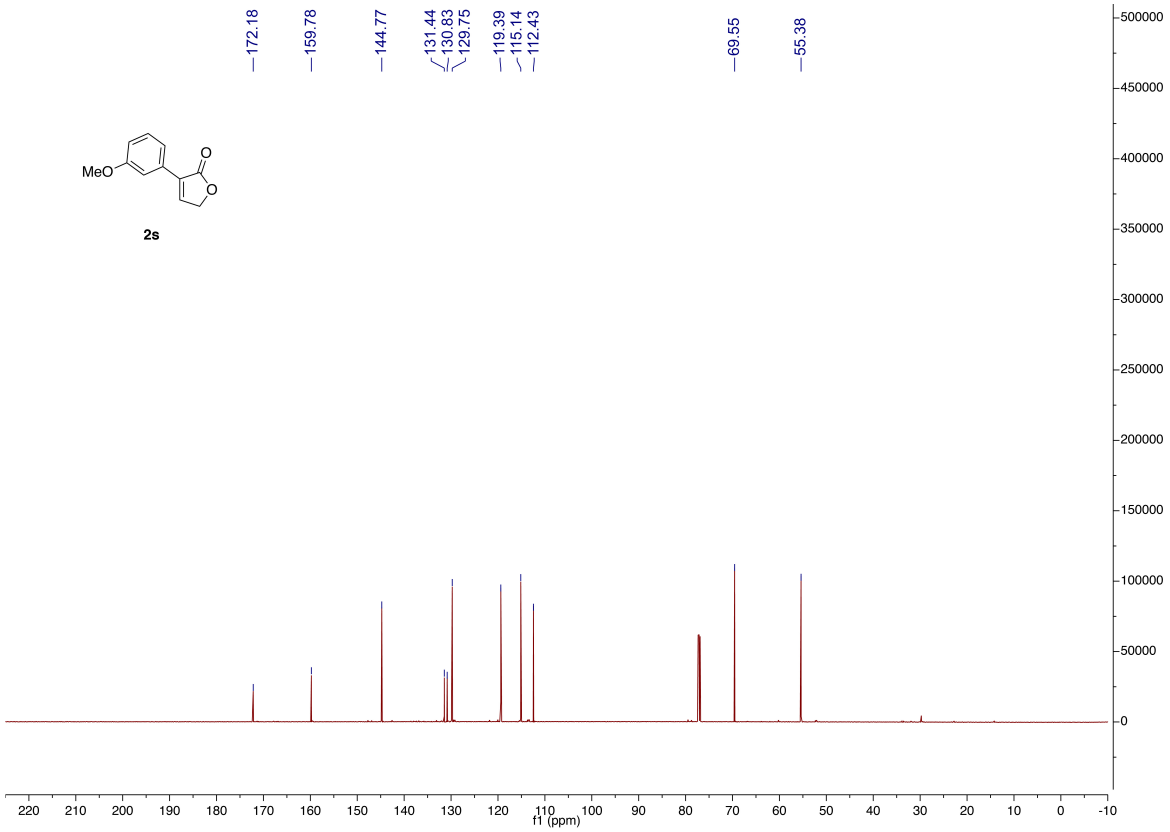

8.01
7.99
7.81
7.81
7.80
7.73
7.73
7.71
7.26
4.99
4.99
1.54
NC
O
O
2q
1.80
1.00
1.88
1.82
f1 (ppm)

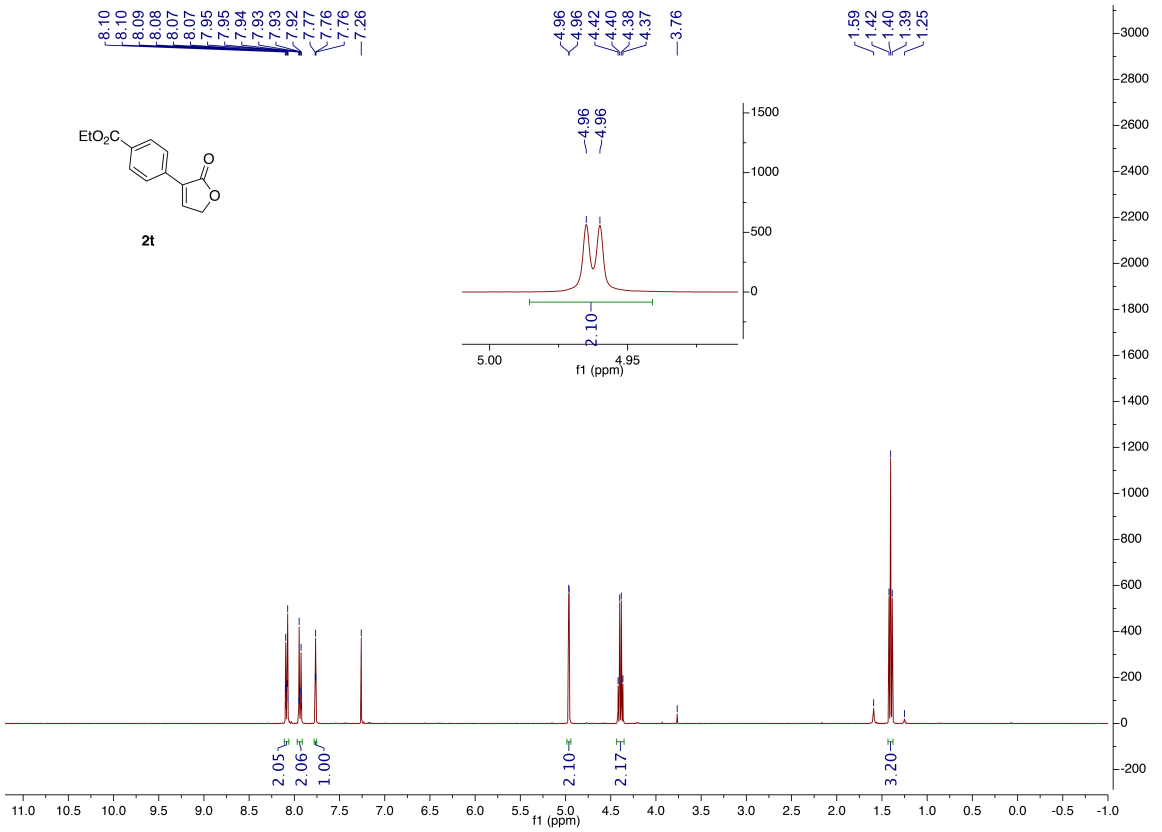

171.42
147.07
133.82
132.63
132.62
130.50
127.71
127.69
118.53
113.15
77.37
77.16
76.95
69.83
NC
O
O
2q
f1 (ppm)

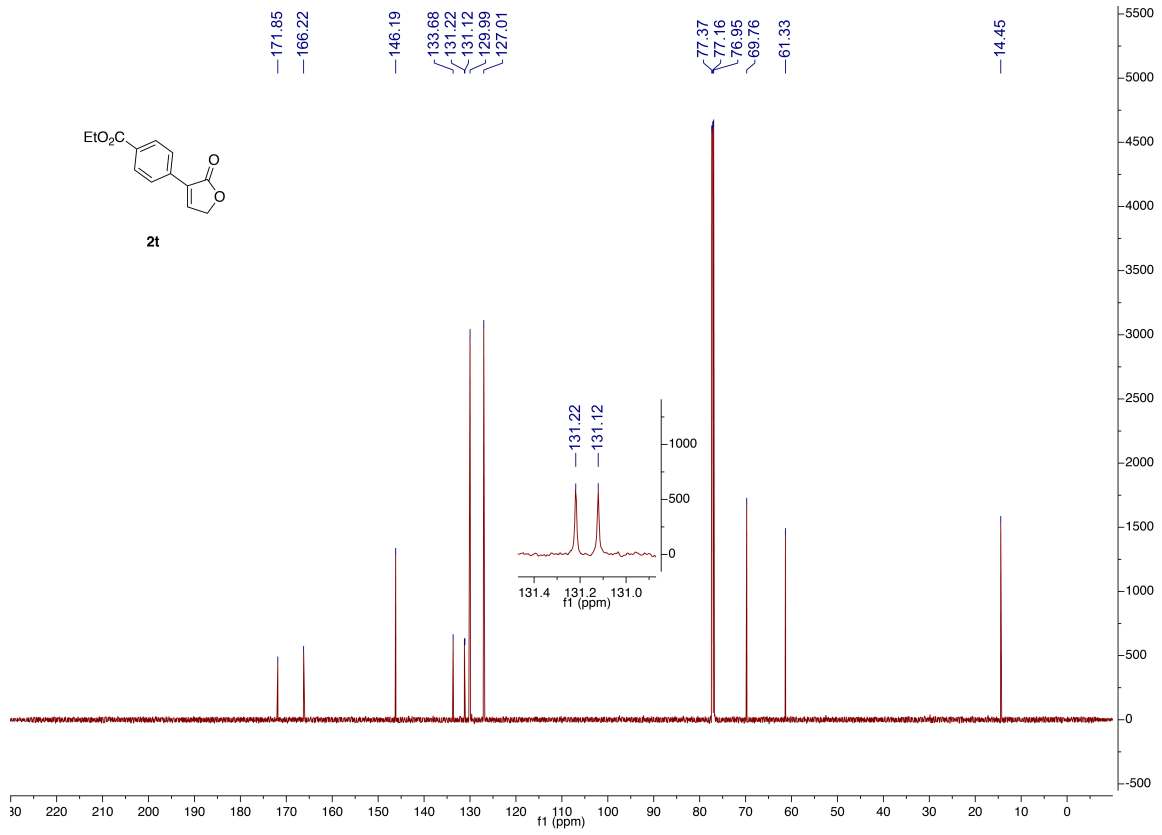

7.83
7.83
7.82
7.81
7.80
7.80
7.66
7.65
7.65
7.41
7.40
7.40
7.39
7.38
7.38
7.26
4.93
4.93
3.77
1.56
1.25
Cl
O
O
2r
4.93
4.93
2.13
f1 (ppm)
2.03
1.00
2.01
2.13
0.02
0.45
0.08
f1 (ppm)

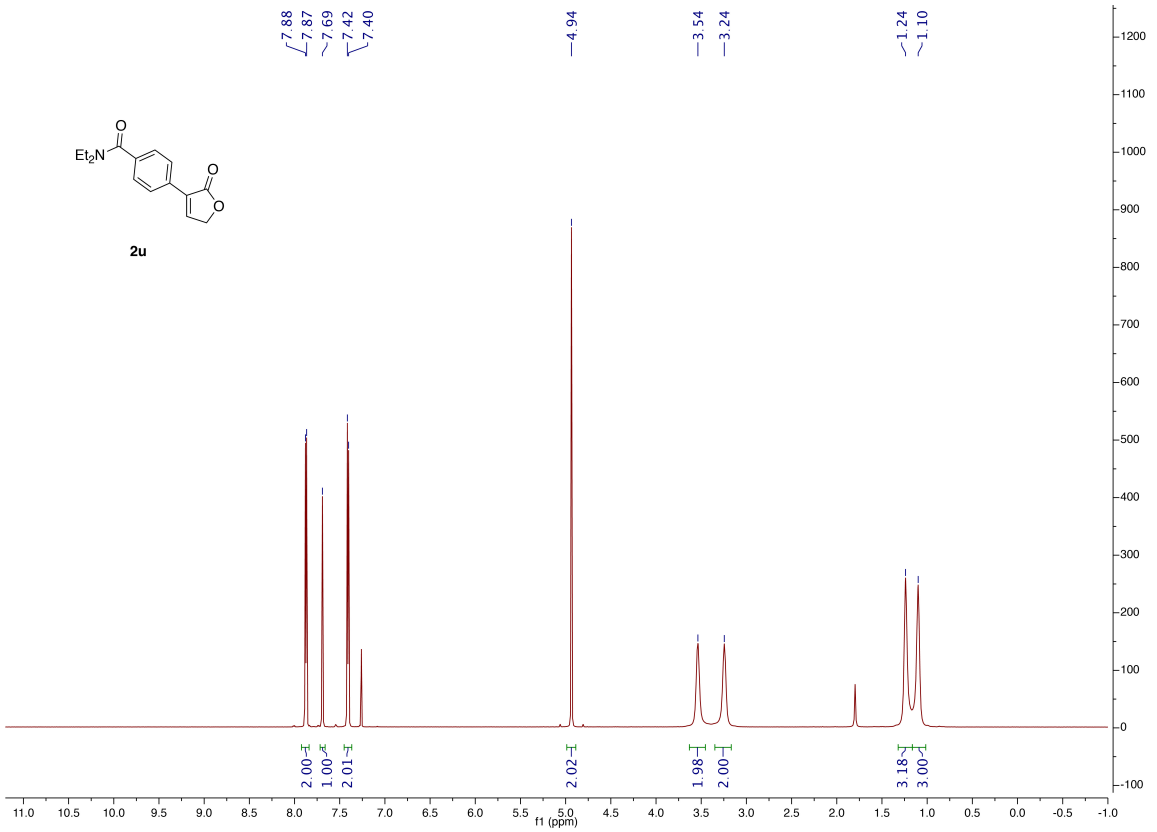

172.05
144.58
135.57
130.78
129.07
128.40
128.05
77.37
77.16
76.95
69.67
Cl
O
O
2r
130.78
129.07
128.40
128.05
f1 (ppm)
f1 (ppm)


7.64
7.64
7.63
7.44
7.43
7.41
7.39
7.33
7.32
7.30
7.26
6.94
6.93
6.92
6.92
4.90
4.90
3.83
MeO
O
O
2s
0.98
1.04
1.00
1.05
1.01
2.00
3.12
f1 (ppm)


172.18
159.78
144.77
131.44
130.83
129.75
119.39
115.14
112.43
69.55
55.38
MeO
O
O
2s
f1 (ppm)

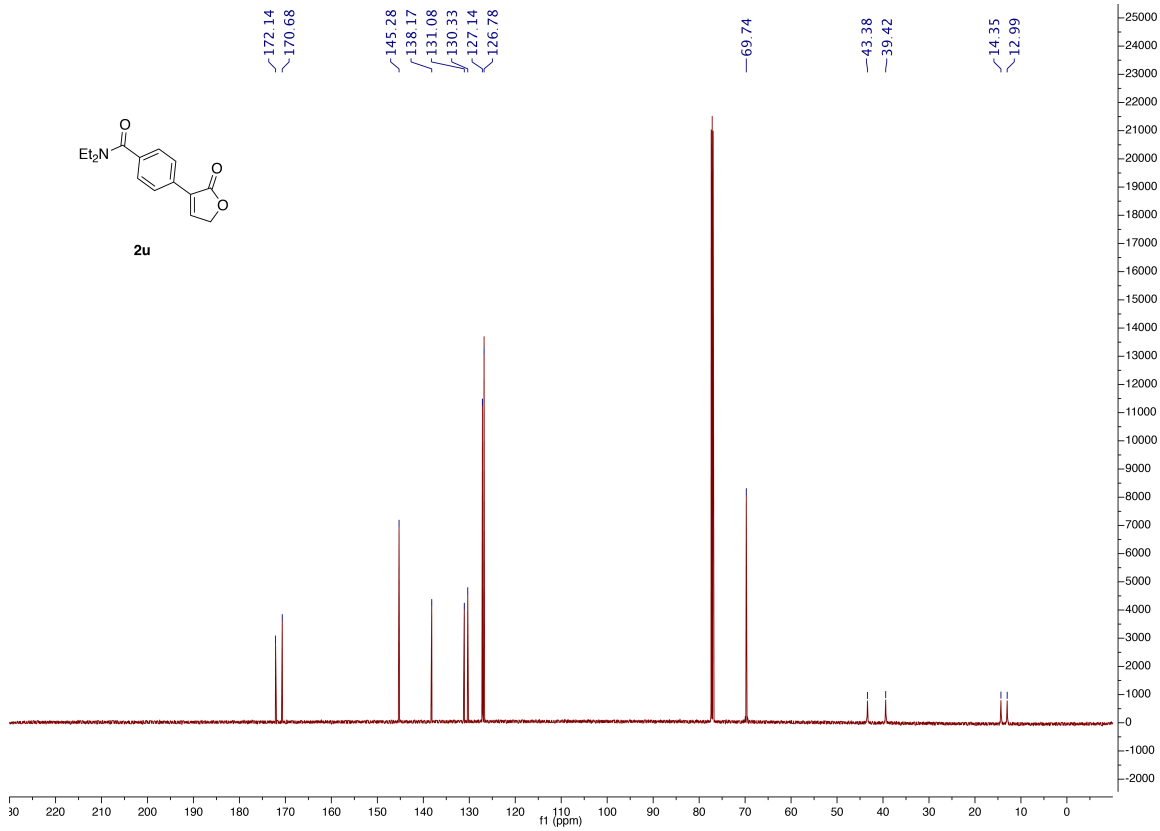

8.10
8.10
8.09
8.08
8.07
8.07
7.95
7.95
7.94
7.93
7.93
7.92
7.77
7.76
7.76
7.26
4.96
4.96
4.42
4.40
4.38
4.37
3.76
1.59
1.42
1.40
1.39
1.25
EtO2C
O
O
2t
4.96
4.96
2.10
f1 (ppm)
2.05
2.06
1.00
2.10
2.17
3.20
f1 (ppm)


171.85
166.22
146.19
133.68
131.22
131.12
129.99
127.01
77.37
77.16
76.95
69.76
61.33
14.45
EtO2C
O
O
2t
131.22
131.12
f1 (ppm)
f1 (ppm)


7.88
7.87
7.69
7.42
7.40
4.94
3.54
3.24
1.24
1.10
2.00
1.00
2.01
2.02
1.98
2.00
3.18
3.00
f1 (ppm)

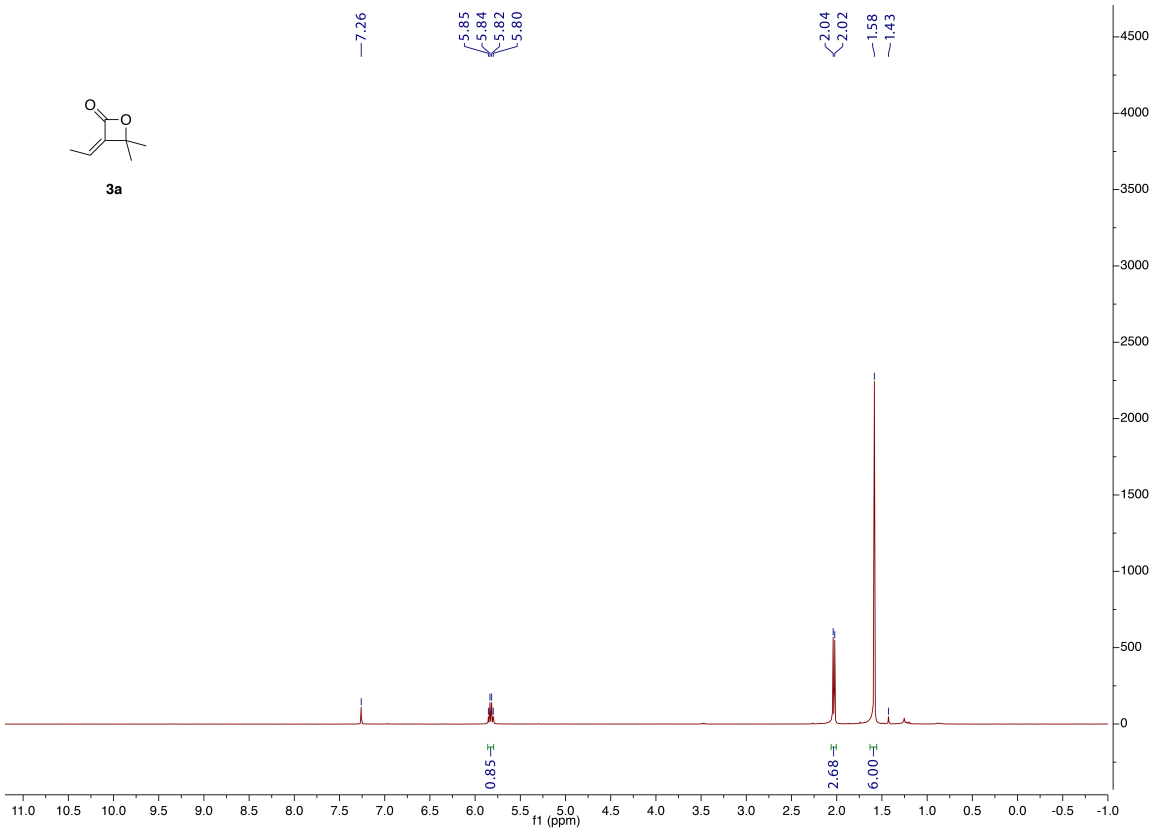
Et2N
O
O
O

2u

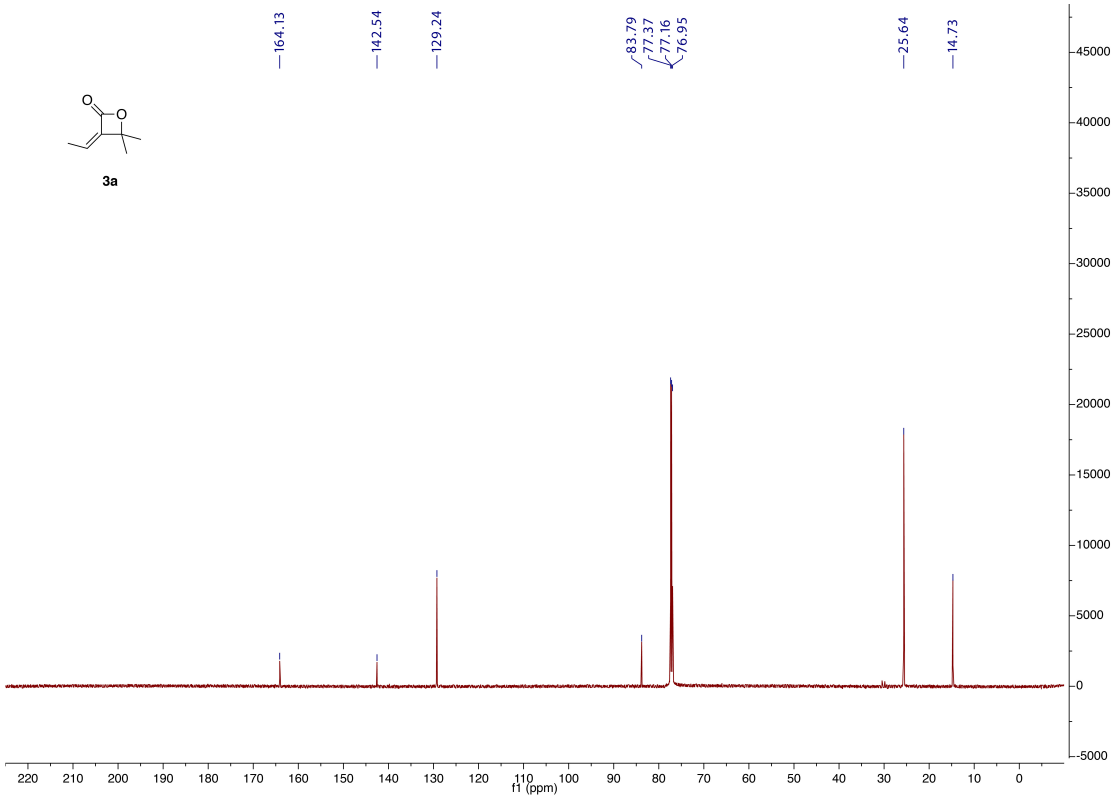

172.14
170.68
145.28
138.17
131.08
130.33
127.14
126.78
69.74
43.38
39.42
14.35
12.99
f1 (ppm)

Et2N
O
O
O

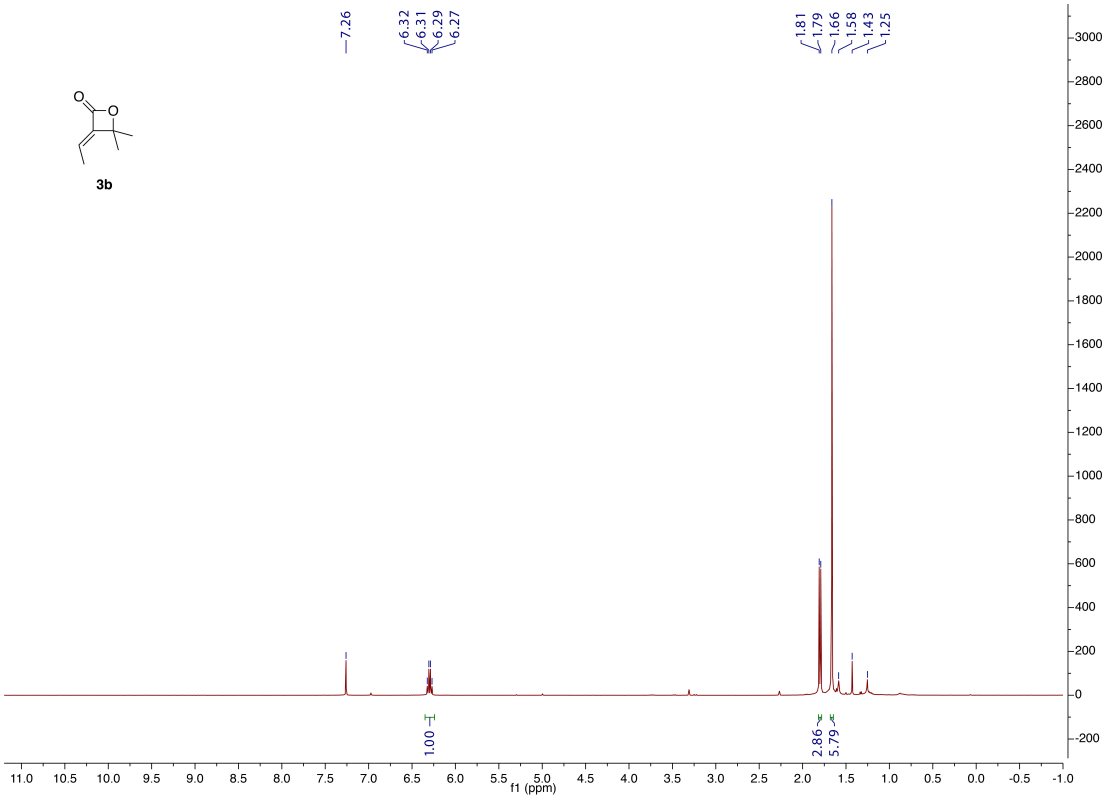
2u

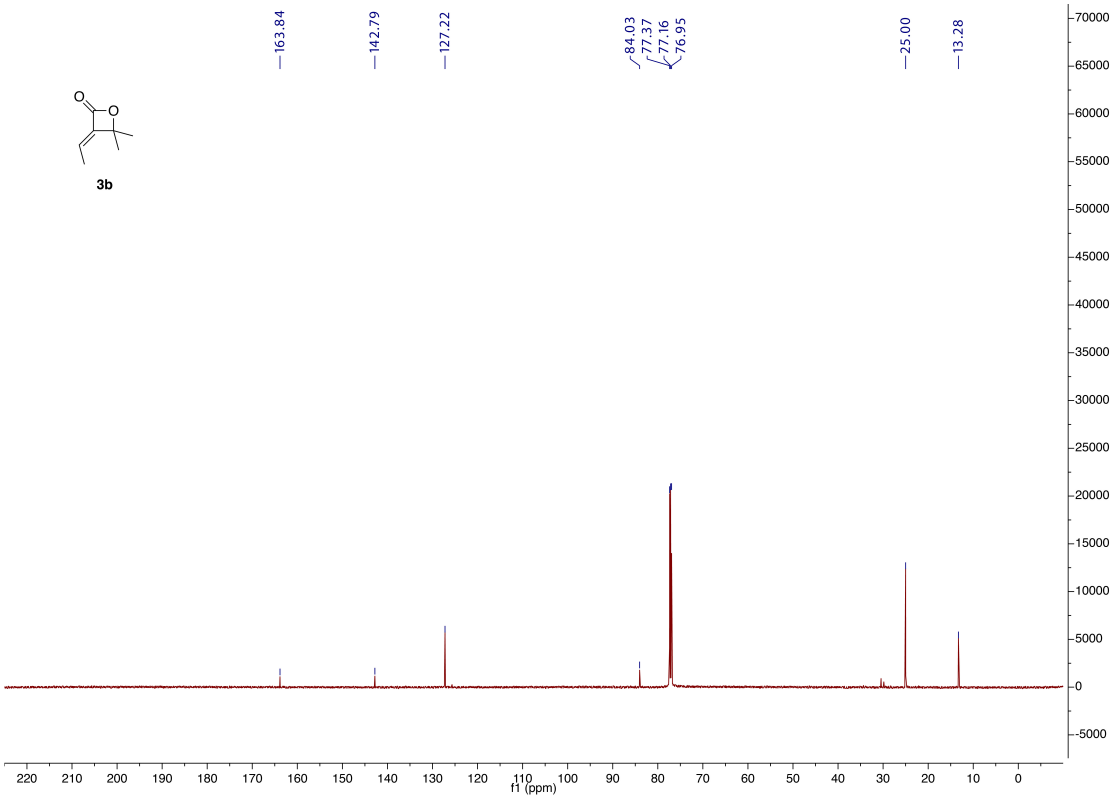

7.26
5.85
5.84
5.82
5.80
2.04
2.02
1.58
1.43
0.85
2.68
6.00
f1 (ppm)

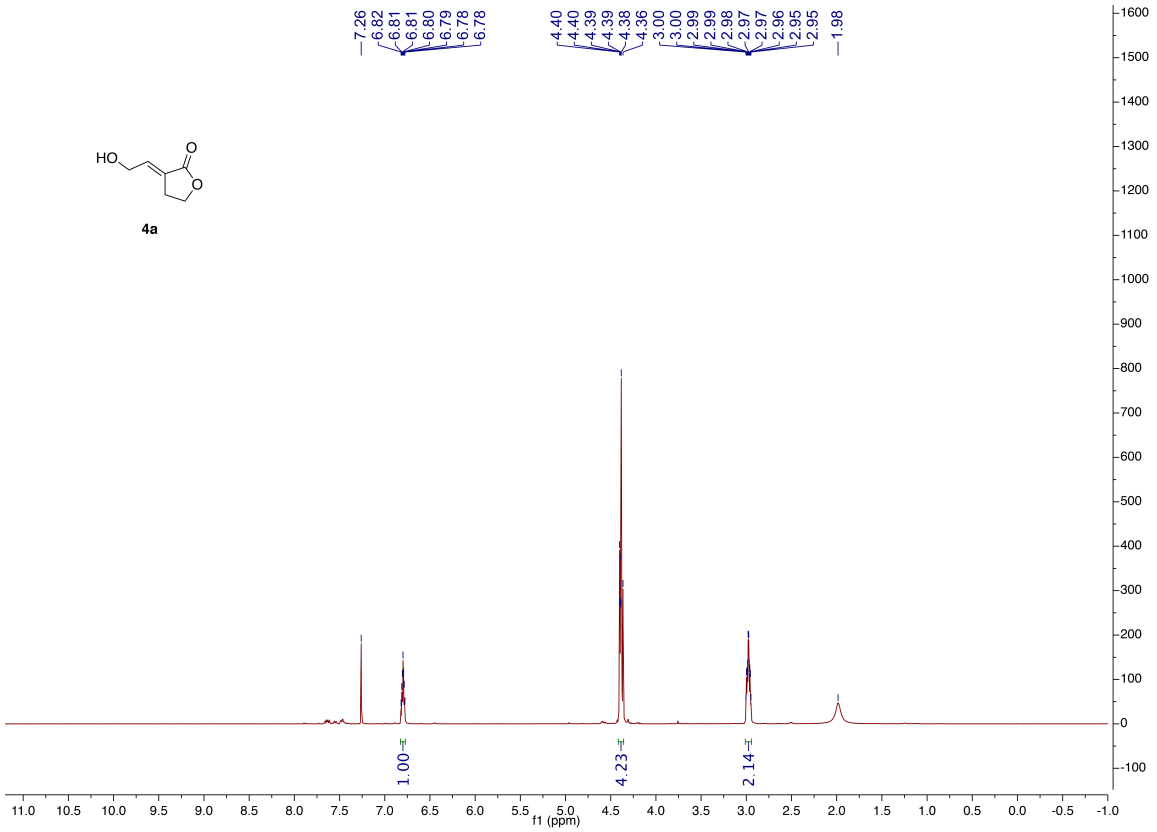
3a

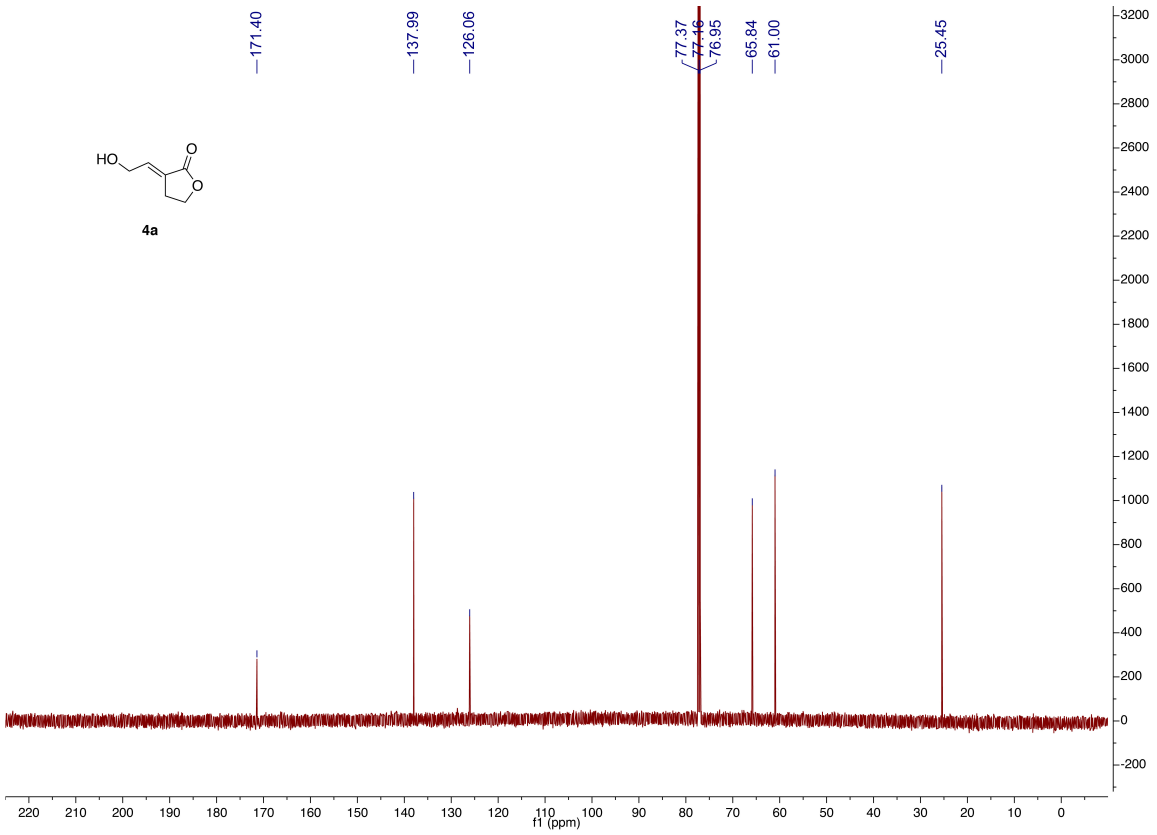

164.13
142.54
129.24
83.79
77.37
77.16
76.95
25.64
14.73
f1 (ppm)

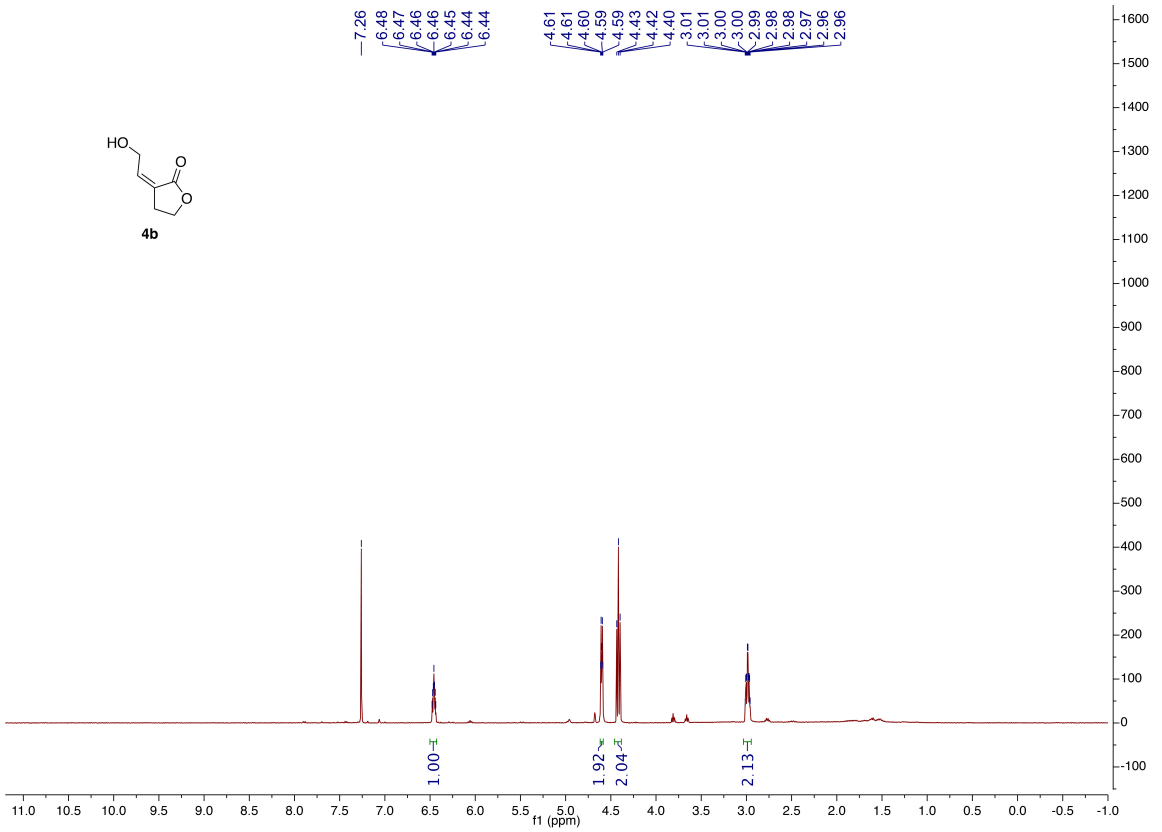
3a

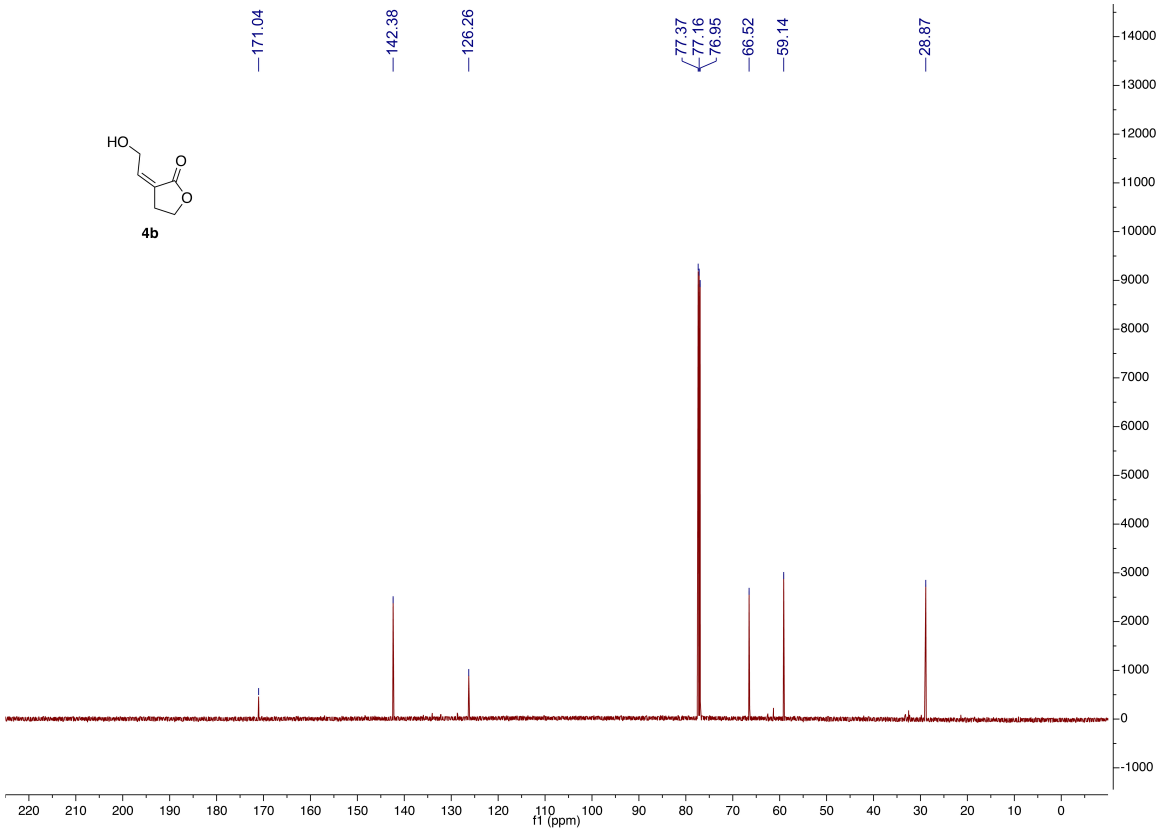

7.26
6.32
6.31
6.29
6.27
1.81
1.79
1.66
1.58
1.43
1.25
3b
1.00
2.86
5.79
f1 (ppm)


163.84
142.79
127.22
84.03
77.37
77.16
76.95
25.00
13.28
3b
f1 (ppm)


7.26
6.82
6.81
6.81
6.80
6.79
6.78
6.78
4.40
4.40
4.39
4.39
4.38
4.36
3.00
3.00
2.99
2.99
2.98
2.97
2.97
2.96
2.95
2.95
1.98
HO
O
O
4a
1.00
4.23
2.14
f1 (ppm)


171.40
137.99
126.06
77.37
77.16
76.95
65.84
61.00
25.45
HO
O
O
4a
f1 (ppm)


7.26
6.48
6.47
6.46
6.46
6.45
6.44
6.44
4.61
4.61
4.60
4.59
4.59
4.43
4.42
4.40
3.01
3.01
3.00
3.00
2.99
2.98
2.98
2.97
2.96
2.96
HO
O
O
4b
1.00
1.92
2.04
2.13
f1 (ppm)


171.04
142.38
126.26
77.37
77.16
76.95
66.52
59.14
28.87
HO
O
O
4b
f1 (ppm)