Supporting Information for:

Cascade Transformation of Carbon Dioxide and Alkyne-1,*n*-diols into Densely Substituted Cyclic Carbonates

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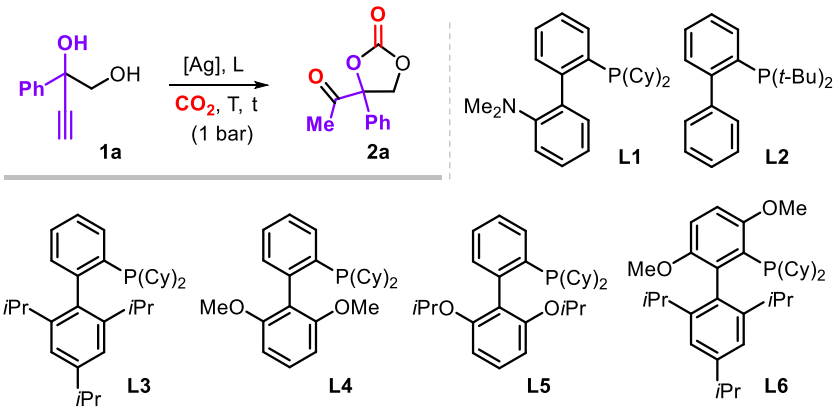
1. General information

Unless otherwise noted, all commercially available reagents and solvents were purchased from Sigma-Aldrich, TCI, Strem Chemicals, ABCR GmbH, Acros Organics or Alfa Aesar and were used without further purification. Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. Carbon dioxide was purchased from PRAXAIR and used without further purification. Reactions were performed in a Schlenk tube or a stainless-steel HEL-multireactor under CO_2 atmosphere. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. NMR spectra were recorded on Bruker Bruker 400 MHz and Bruker 500 MHz at room temperature (25 ºC). The residual solvent signals were used as references for ^{1}H and ^{13}C spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm, DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). ^{19}F NMR spectra were obtained with ^{1}H decoupling unless stated otherwise. FT-IR measurements were carried out on a Bruker Optics FTIR-ATR TR0 spectrometer. Exact mass analyses and X-ray diffraction studies were performed by the Research Support Area (RSA) at ICIQ.

2. Optimization of the reaction conditions

Table S1:

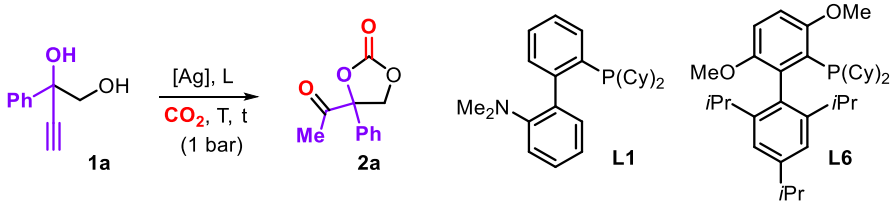


Entry[a]	Catalyst	Ligand	Time/[h]	T/[ºC]	Conv. [%][b]	Yield [%][b]
1	AgOAc (10 mol%)	–	24	35	0	0
2	**L1** (10 mol%)	–	24	35	0	0
3	AgOAc (10 mol%)	**L1** (5 mol%)	24	35	50	12
4	AgOAc (5 mol%)	**L1** (10 mol%)	24	35	80	50
5	AgOAc (10 mol%)	**L1** (10 mol%)	24	35	96	56
6	AgOAc (10 mol%)	**L1** (10 mol%)	48	25	83	62
7	AgOAc (10 mol%)	PPh_3 (10 mol%)	24	25	<10%	<10%
8	AgOAc (10 mol%)	$P(OPh)_3$ (10 mol%)	24	25	0	0
9	AgOAc (10 mol%)	**L2** (10 mol%)	24	25	77	66(63)[c]
10	AgOAc (10 mol%)	**L3** (10 mol%)	24	25	82	74(66)[c]
11	AgOAc (10 mol%)	**L4** (10 mol%)	24	25	84	73(68)[c]
12	AgOAc (10 mol%)	**L5** (10 mol%)	24	25	85	63
13	AgOAc (10 mol%)	**L6** (10 mol%)	24	25	100	91(85)[c]
14	AgOAc (10 mol%)	**L7** (5 mol%)	24	25	0	0
15	AgOAc (10 mol%)	**L8** (5 mol%)	24	25	0	0
16	AgOAc (5 mol%)	**L6** (5 mol%)	24	25	73	69
17	AgOAc (25 mol%)	**L6** (25 mol%)	24	25	88	87
18	AgOAc (5 mol%)	**L6** (5 mol%)	24	40	93	85
19	AgOAc (2.5 mol%)	**L6** (2.5 mol%)	24	40	58	49
20	AgOAc (2.5 mol%)	**L6** (2.5 mol%)	24	50	83	68
21	AgF (5 mol%)	**L6** (5 mol%)	24	40	100	90
22	AgOTf (5 mol%)	**L6** (5 mol%)	24	40	-	Not detected
23	$AgNO_3$ (5 mol%)	**L6** (5 mol%)	24	40	0	0
24	Ag_2CO_3 (5 mol%)	**L6** (5 mol%)	24	40	67	37
25	$AgBF_4$ (5 mol%)	**L6** (5 mol%)	24	40	-	Not detected

- Table continued						
26	AgF_6Sb (5 mol%)	**L6** (5 mol%)	24	40	0	0
27	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	91(88)[c]
28	AgF (5 mol%)	**L6** (5 mol%)	12	40	100	89
29	AgF (5 mol%)	**L6** (5 mol%)	18	40	100	87
30	AgF (2.5 mol%)	**L6** (2.5 mol%)	6	40	12	<5%
31	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	17[d]
32	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	Not detected[e]
33	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	Not detected[f]
34	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	18[g]
35	AgF (5 mol%)	**L6** (5 mol%)	6	40	100	Not detected[h]

[a] Reaction condition: **1a** (0.3 mmol), ACN (0.6 mL). [b] Determined by ^{1}H NMR. [c] Isolated yield of **2a**. [d] MeOH as solvent. [e] DMF as solvent. [f] Toluene as solvent. [g] THF as solvent. [h] DCM as solvent. **L7** stands for DPEPhos, **L8** for dppe.

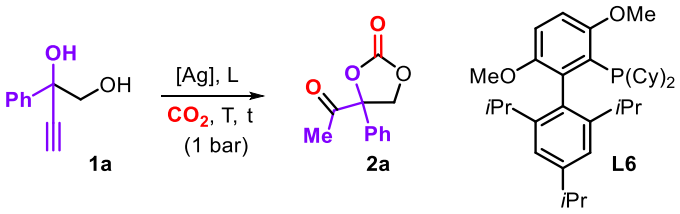
Table S2:[a]



Entry	Catalyst	Ligand	Time, pressure [h, bar]	T [ºC]	Conv. [%][b]	Yield [%][b]
1	AgF (5 mol%)	**L6** (5 mol%)	6, 1	40	52	29
2	AgF (5 mol%)	**L6** (5 mol%)	6, 1	60	22	No detected
3	AgF (5 mol%)	**L6** (5 mol%)	24, 1	40	83	10
4	AgF (5 mol%)	**L6** (5 mol%)	24, 10	rt	100	85(90)[c]
5	AgOAc (10 mol%)	**L1** (10 mol%)	24, 1	rt	37	18
6	AgOAc (10 mol%)	**L1** (10 mol%)	24, 1	50	30	<10%
7	AgOAc (10 mol%)	**L1** (10 mol%)	48, 1	50	77	<10%
8	AgOAc (10 mol%)	**L1** (10 mol%)	24, 10	rt	100	25(19)[c]

[a] Reaction conditions: **1a** (0.3 mmol), ACN (0.6 mL). [b] Determined by ^{1}H NMR. [c] Isolated yield of **2a** in brackets.

Table S3:[a]

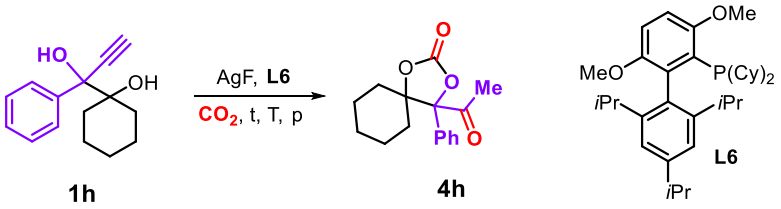


Entry	Catalyst	Ligand	Time, pressure [h, bar]	T [ºC]	Conversion [%][b]	Yield [%][b]
1	AgF (5 mol%)	**L6** (5 mol%)	6, 1	40	45	Not detected
2	AgF (5 mol%)	**L6** (5 mol%)	6, 1	60	42	Not detected
3	AgF (5 mol%)	**L6** (5 mol%)	24, 10	rt	51	trace
4	AgF (10 mol%)	**L6** (10 mol%)	24, 10	rt	100	<10%
5	AgF (5 mol%)	**L6** (5 mol%)	24, 30	rt	100	<10%

[a] Reaction conditions: **1a** (0.3 mmol), ACN (0.6 mL). [b] Determined by ^{1}H NMR.

Table S4:[a]

Screening data with substrate **1h.**



1h 4h

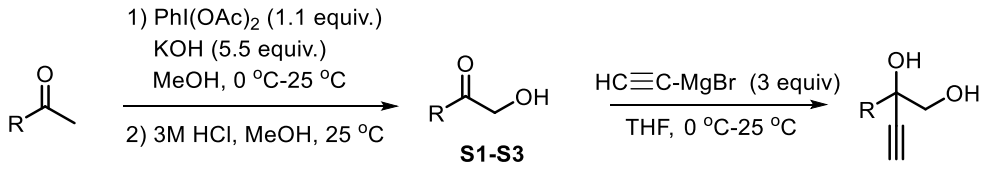
Entry	Catalyst	Ligand	Time, pressure [h , bar]	T [ºC]	Conv. [%][b]	Yield [%][b]
1	AgF (10 mol%)	**L6** (10 mol%)	24, 30	rt	100	95
2	AgF (10 mol%)	**L6** (10 mol%)	24, 10	rt	100	93
3	AgF (5 mol%)	**L6** (5 mol%)	6, 1	40	78	74
4	AgF (5 mol%)	**L6** (5 mol%)	24, 1	40	100	90(87)[c]
5	AgF (5 mol%)	**L6** (5 mol%)	24, 1	rt	93	83

[a] Reaction conditions: **1h** (0.3 mmol), ACN (0.6 mL). [b] Determined by ^{1}H NMR. [c] Isolated yield of **4h**.

3. Experimental procedures and characterization data for substrates

The known alkyne-1,2-diols were synthesized as reported in the literature.[1] Below the preparation of new alkyne-1,2-diols.

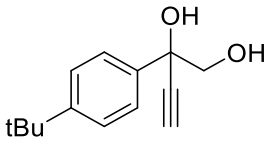
General Procedure A for alkyne-1,2-diol synthesis:



S1-S3 were synthesized according to a literature procedure.[2] To a solution of the ketone derivative (30.0 mmol, 1.0 equiv) in MeOH (60 mL), (diacetoxyiodo)benzene (33.0 mmol, 1.1 equiv) and KOH (165.0 mmol, 5.5 equiv) were slowly added at 0 °C in an open round-bottomed flask. After the mixture had been stirred for 0.5 h at the same temperature it was allowed to reach room temperature over night after which TLC analysis showed complete consumption of the starting material. The reaction mixture was concentrated, water (100 mL) was added and the mixture was extracted with EtOAc (3 × 100 mL). The combined organic extracts were evaporated in vacuo and the residue was dissolved in a mixture of MeOH (20 mL) and aqueous 3 M HCl (20 mL). After stirring overnight at rt, the crude product was concentrated and further purified by column chromatography on silica gel to afford the corresponding α-hydroxy ketones.

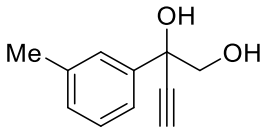
The alkyne-1,2-diols **1d**, **1k** and **1r** in this section were prepared according to a literature procedure.[1] In an oven-dried Schleck flask conditioned under a nitrogen atmosphere was introduced the appropriate α-hydroxy carbonyl compound (5 mmol, 1.0 equiv) in anhydrous THF (40 mL). The solution was cooled down to 0 °C (ice/water) and ethynyl magnesium bromide (0.5 M in THF, 3.0 equiv, 30 mL) was added dropwise via a syringe. The reaction mixture was allowed to warm to room temperature and further stirred for 16 h. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl. The organic phase was extracted with EtOAc (3 × 50 mL). All the organic fractions were combined, dried with anhydrous $NaSO_4$, filtered and concentrated. The crude products were purified by flash chromatography on silica gel to afford the corresponding alkyne-1,2 diols.

2-(4-(*tert*-Butyl)phenyl)but-3-yne-1,2-diol (1d)



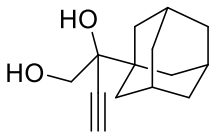
Yellow solid (794.0 mg, 73% yield). Eluent hexanes/ EtOAc = 5/1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 2H), 7.42 – 7.40 (m, 2H), 3.77 (d, *J* = 11.3 Hz, 1H), 3.68 (d, *J* = 11.3 Hz, 1H), 2.70 (s, 1H), 2.25 (brs, 2H), 1.32 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 137.1, 125.6, 125.5, 84.6, 74.8, 73.6, 72.1, 34.7, 31.4. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{14}H_{18}NaO_2$ $[M + Na]^+$ 241.1199; Found 241.1203.

2-(*m*-Tolyl)but-3-yne-1,2-diol (1k)



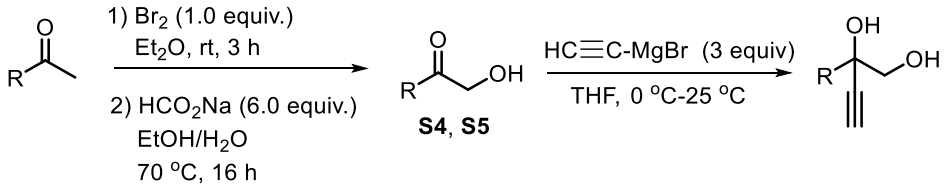
Yellow solid (537.0 mg, 61% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.30 – 7.26 (m, 1H), 7.16 – 7.14 (m, 1H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 1H), 2.38 (s, 3H), 2.17 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.3, 129.3, 128.5, 126.5, 123.0, 84.6, 74.9, 73.7, 72.1, 21.7. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{12}NaO_2$ $[M + Na]^+$ 199.0730; Found 199.0735.

2-(Adamantan-1-yl)-but-3-yne-1,2-diol (1r)



White solid (511.0 mg, 50% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.75 (d, *J* = 10.9 Hz, 1H), 3.67 (d, *J* = 10.9, 1H), 2.49 (s, 1H), 2.04 – 2.01 (m, 4H), 1.77 – 1.65 (m, 13H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 84.4, 77.8, 74.7, 65.6, 38.5, 37.1, 36.8, 28.5. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{14}H_{20}NaO_2$ $[M + Na]^+$ 243.1356; Found 243.1352.

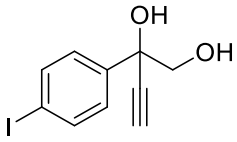
General Procedure B for alkyne-1,2-diol synthesis:



S4 and **S5** were synthesized according to the literature procedure.[3] Bromine (1.0 mL, 1.0 equiv) was added dropwise to a solution of the respective ketone derivative (20.0 mmol, 1.0 equiv) in Et_2O (30 mL) at 0 °C in a round-bottomed flask. Then the mixture was allowed to warm to room temperature and stirred for 3 h. When the starting material had disappeared (followed by TLC), the reaction mixture was quenched with ice water (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (40 mL), and dried over Na_2SO_4. After being filtered and concentrated, the residue was dissolved in a mixture of EtOH (80 mL) and H_2O (40 mL), and sodium formate (120.0 mmol, 6.0 equiv) was added. This mixture was stirred for 16 h at 70 °C, then concentrated under vacuum, diluted with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). The combined layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel to obtain the respective *α*-hydroxy ketone.

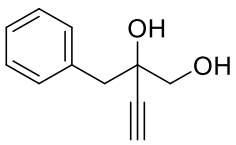
NB: The alkyne-1,3-diols **1h** and **1s** were obtained according to the final one step from **General Procedure A**.

2-(4-Iodophenyl)but-3-yne-1,2-diol (1h)



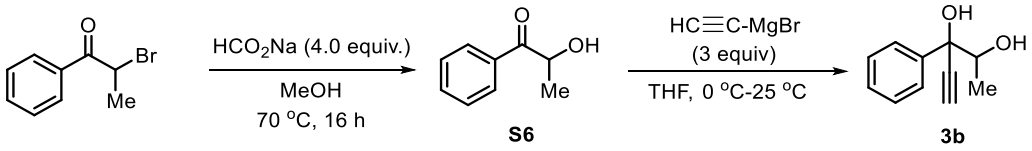
Brown solid (743.8 mg, 51% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.38 – 7.35 (m, 2H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.60 (d, *J* = 11.3 Hz, 1H), 2.71 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.0, 137.6, 127.9, 94.4, 83.9, 75.3, 73.4, 71.9. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{10}H_9INaO_2$ $[M + Na]^+$ 310.9539; Found 310.9533.

2-Benzyl-but-3-yne-1,2-diol (1s)



Yellow solid (474.1 mg, 52% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.60 (d, *J* = 11.2 Hz, 1H), 3.01 (dd, *J* = 16.3, 13.4 Hz, 2H), 2.52 (s, 1H), 2.22 (brs, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.3, 130.9, 128.4, 127.3, 84.3, 75.0, 71.6, 69.2, 43.8. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{12}NaO_2$ $[M + Na]^+$ 199.0730; Found 199.0723.

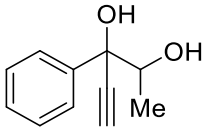
Procedure C for the synthesis of alkyne-1,2-diol 3b:



S6 was synthesized according to the literature procedure.[4] To a solution of 2-bromopropiophenone (16.4 mmol, 1.0 equiv) in MeOH (17 mL) was added sodium formate (64.8 mmol, 4.0 equiv), and the reaction mixture was stirred for 16 h at 70 °C. Then, it was concentrated under vacuum, diluted with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). The combined layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo.* The crude product was purified by flash chromatography on silica gel to obtain the corresponding *α*-hydroxy ketone **S6**.

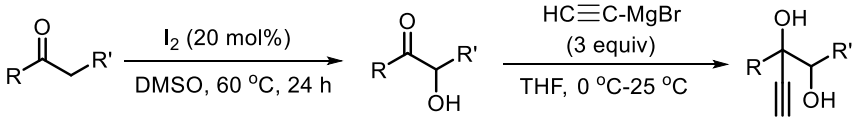
NB: Alkyne-1,2-diol **3b** was obtained according to the final step **General Procedure A**.

<u>3-Phenyl-pent-4-yne-2,3-diol (3b)</u>



Yellow oil (485.6 mg, 55% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.40-7.30 (m, 3H), 4.04 (q, *J* = 6.3 Hz, 1H), 2.68 (s, 1H), 1.06 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 128.29, 128.27, 126.3, 85.5, 75.9, 74.9, 74.7, 16.2. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{12}NaO_2$ $[M + Na]^+$ 199.0730; Found 199.0733.

General Procedure D for alkyne-1,2-diol synthesis:

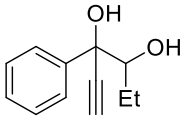


S7-S10

S7-S10 were synthesized according to the literature procedure.[5] To a solution of the respective ketone (10.0 mmol, 1.0 equiv) in DMSO (10 mL) was added I_2 (2.0 mmol, 20 mol %) under air, and the reaction mixture was stirred for 24 h at 60 °C while followed by TLC. When complete consumption of the starting material was observed, the mixture was allowed to cool down to room temperature, and the solution was diluted with ethyl acetate (200 mL), washed with 0.1 M $Na_2S_2O_3$ (100 mL) aqueous solution and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo.* The crude product was purified by flash chromatography on silica gel to obtain the respective *α*-hydroxy ketone.

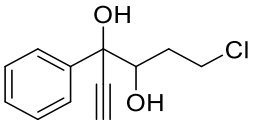
NB: Alkyne-1,2-diols **3c**, **3d**, **3e** and **3g** were obtained according to the final of **General Procedure A**.

3-Phenylhex-1-yne-3,4-diol (3c)



Yellow oil (855.7 mg, 90% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.31 (m, 1H), 3.75 (dd, *J* = 10.3, 2.3 Hz, 1H), 2.93 (brs, 1H), 2.68 (s, 1H), 1.53 – 1.45 (m, 1H), 1.31 – 1.22 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.2, 128.30, 128.26, 126.3, 85.7, 80.3, 75.9, 74.6, 23.4, 10.9. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{14}NaO_2$ $[M + Na]^+$ 213.0886; Found 213.0887.

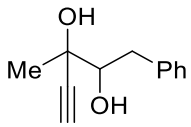
6-Chloro-3-phenyl-hex-1-yne-3,4-diol (3d)



Brown oil (940.1 mg, 84% yield). Eluent hexanes/ EtOAc = 3/1.

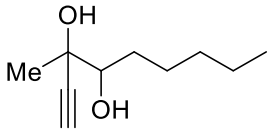
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.43 – 7.32 (m, 3H), 4.09 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.68 – 3.58 (m, 2H), 2.94 (brs, 1H), 2.71 (s, 1H), 2.40 (brs, 1H), 1.90 – 1.76 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 128.6, 128.5, 126.2, 85.1, 75.54, 75.50, 75.1, 42.0, 33.1. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{13}ClNaO_2$ $[M + Na]^+$ 247.0496; Found 247.0498.

3-Methyl-1-phenyl-pent-4-yne-2,3-diol (3e)



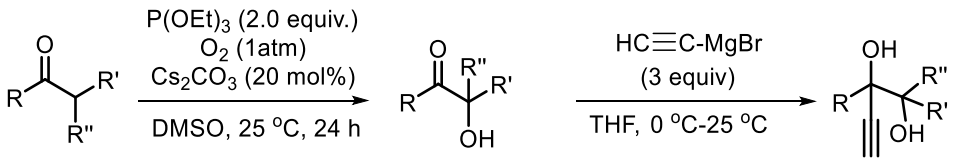
Yellow solid (287.1 mg, 30% yield, 77:23 *dr*). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 3.84 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.09 (dd, *J* = 14.0, 2.3 Hz, 1H), 2.65 (dd, *J* = 14.0, 10.5 Hz, 1H), 2.54 (s, 1H), 2.34 (brs, 2H), 1.55 (s, 3H); **^{1}H NMR** (400 MHz, $CDCl_3$) (minor) δ 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 3.70 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.07 (dd, *J* = 14.0, 2.7 Hz, 1H), 2.80 (dd, *J* = 14.0, 10.3 Hz, 1H), 2.56 (s, 1H), 2.34 (brs, 2H), 1.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 138.7, 129.4, 128.7, 126.7, 86.0, 78.5, 73.2, 70.8, 37.7, 24.1; **^{13}C NMR** (101 MHz, $CDCl_3$) (minor) δ 138.2, 129.5, 128.8, 126.8, 85.0, 78.8, 73.6, 71.0, 38.9, 26.0. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{14}NaO_2$ $[M + Na]^+$ 213.0886; Found 213.0889.

3-Methyl-non-1-yne-3,4-diol (3g)



Yellow oil (299.5 mg, 35% yield, 4:1 *dr*). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 3.60 – 3.58 (m, 1H), 2.48 (s, 1H), 2.41 (brs, 1H), 2.23 (brs, 1H), 1.69 – 1.49 (m, 3H), 1.44 (s, 3H), 1.38 – 1.30 (m, 5H), 0.90 (t, *J* = 6.8 Hz, 3H); **^{1}H NMR** (400 MHz, $CDCl_3$) (minor) δ 3.41 – 3.38 (m, 1H), 2.96 (brs, 1H), 2.47 (s, 1H), 1.87 (brs, 1H), 1.69 – 1.49 (m, 3H), 1.45 (s, 3H), 1.38 – 1.30 (m, 5H), 0.90 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 86.4, 77.6, 72.9, 71.1, 31.90, 30.8, 26.3, 23.6, 22.7, 14.2; **^{13}C NMR** (101 MHz, $CDCl_3$) (minor) δ 85.1, 78.5, 73.4, 71.6, 32.3, 31.87, 26.0, 25.6, 22.7, 14.2. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{10}H_{18}NaO_2$ $[M + Na]^+$ 193.1199; Found 193.1198.

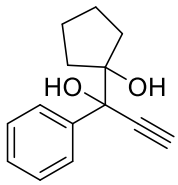
General Procedure E for alkyne-1,2-diol synthesis:



The α-hydroxy ketones of this section were synthesized according to the literature procedure.[6] Cs_2CO_3 (2.0 mmol, 20 mol %), $P(OEt)_3$ (20.0 mmol, 2.0 equiv), the respective ketone (10.0 mmol, 1.0 equiv.) were added to a 100 mL Schlenk tube under air. DMSO (40 mL) was added, the reaction mixture was stirred for 24-72 h at room temperature under air (1 atm). When complete consumption of the starting material had been observed (TLC), the solution was diluted with ethyl acetate (200 mL), washed with brine (50 mL), and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo.* The crude product was purified by flash chromatography on silica gel to obtain the respective *α*-hydroxy ketone.

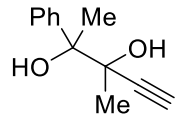
NB: Alkyne-1,2-diols (**3i-3l**) were obtained according to the final one step of **General Procedure A**.

1-(1-Hydroxy-1-phenyl-prop-2-yn-1-yl)cyclopentan-1-ol (3i)



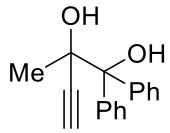
Brown solid (872.0 mg, 80% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.38 – 7.29 (m, 3H), 2.67 (s, 1H), 2.17 – 2.10 (m, 1H), 1.92 – 1.85 (m, 1H), 1.84 – 1.72 (m, 2H), 1.65 – 1.47 (m, 3H), 1.45 – 1.37 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 128.2, 127.8, 127.3, 87.8, 85.9, 77.8, 74.3, 36.2, 34.9, 24.13, 24.07. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{14}H_{16}NaO_2$ $[M + Na]^+$ 239.1043; Found 239.1051.

3-Methyl-2-phenyl-pent-4-yne-2,3-diol (3k)



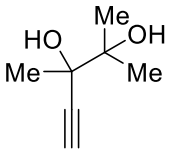
Yellow solid (446.7 mg, 47% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.36 – 7.28 (m, 3H), 4.98 (brs, 1H), 2.71 (brs, 1H), 2.56 (s, 1H), 1.80 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 127.8, 127.4, 126.8, 86.3, 77.9, 74.0, 73.9, 25.5, 25.0; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{14}NaO_2$ $[M + Na]^+$ 213.0886; Found 213.0885.

2-Methyl-1,1-diphenylbut-3-yne-1,2-diol (3l)



Yellow oil (516.9 mg, 41% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 4H), 7.33 – 7.26 (m, 6H), 3.15 (brs, 1H), 2.67 (s, 1H), 2.53 (brs, 1H), 1.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 128.5, 128.1, 127.8, 127.64, 127.56, 127.4, 86.5, 26.8. **HRMS** (ESI/TOF) *m/z* Calcd for $C_{17}H_{16}NaO_2$ $[M + Na]^+$ 275.1043; Found 275.1046.

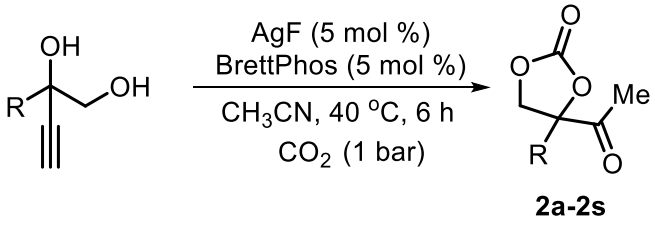
2,3-Dimethylpent-4-yne-2,3-diol (3m)



Yellow oil (448.9 mg, 70% yield). Eluent hexanes/ EtOAc = 3/1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.48 (s, 1H), 2.21 (brs, 2H), 1.47 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 86.3, 75.3, 74.0, 73.0, 25.7, 24.3, 22.8. **HRMS** (ESI/TOF) *m/z* Calcd for $C_7H_{12}NaO_2$ $[M + Na]^+$ 151.0730; Found 151.0729.

4. Procedures and characterization data for the carbonate products

General Procedure F for the synthesis of the cyclic carbonates 2a-2s:

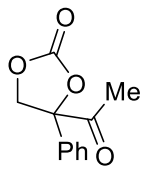


2a-2s

The respective 1,2-diol (0.3 mmol, 1.0 equiv), AgF (0.015 mmol, 5 mol %), BrettPhos (0.015 mmol, 5 mol%) were added to a 25 mL reaction tube. The tube was purged three times with CO_2 and then charged with a CO_2 balloon (1 bar). Hereafter, MeCN (0.6 mL) was added using a syringe. The reaction mixture was stirred at 40 °C for 6 h. When complete consumption of the starting material had been observed by TLC, the mixture was transferred to a round-bottom flask, concentrated and purified by flash column chromatography on silica to afford the corresponding cyclic carbonate product. **Note**: only the characteristic *carbonyl*/*carbonate* IR frequencies are provided in the analytical data descriptions.

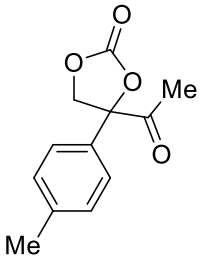
Gram-scale reaction: The 1,2-diol **1a** (6.5 mmol, 1.0 equiv), AgF (0.325 mmol, 5 mol %), BrettPhos (0.325 mmol, 5 mol%) were added to an oven-dried Schleck flask. The tube was purged three times with CO_2 and then charged with a CO_2 balloon (1 bar). Hereafter, MeCN (13.0 mL) was added using a syringe. The reaction mixture was stirred at 40 °C for 6 h. When complete consumption of the starting material had been observed by TLC, the mixture was transferred to a round-bottom flask, concentrated and purified by flash column chromatography on silica to afford the corresponding cyclic carbonate product **2a** with a 85% isolated yield.

4-Acetyl-4-phenyl-1,3-dioxolan-2-one (2a)



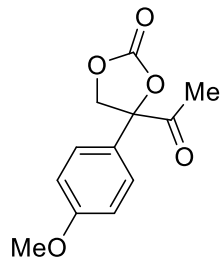
Colorless solid (54.5 mg, 88% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 5.26 (d, *J* = 8.6 Hz, 1H), 4.38 (d, *J* = 8.6 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.9, 153.1, 135.0, 129.8, 129.6, 124.1, 88.6, 72.5, 24.9; **IR (neat)**: ν = 1803, 1729 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{10}NaO_4$ $[M + Na]^+$ 229.0471; Found 229.0474. This compound was further characterized by X-ray crystallography.

4-Acetyl-4-(*p*-tolyl)-1,3-dioxolan-2-one (2b)



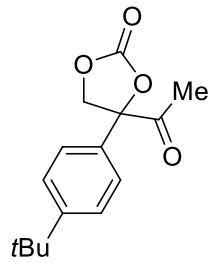
Colorless oil (58.6 mg, 88% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 4H), 5.23 (d, *J* = 8.6 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 153.2, 140.0, 132.0, 130.3, 124.0, 88.7, 72.5, 24.8, 21.3; **IR (neat)**: *v* = 1806, 1724 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{12}NaO_4$ $[M + Na]^+$ 243.0628; Found 243.0626.

4-Acetyl-4-(4-methoxyphenyl)-1,3-dioxolan-2-one (2c)



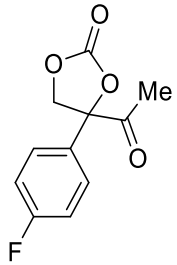
White solid (64.0 mg, 91% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.97 – 6.93 (m, 2H), 5.22 (d, *J* = 8.6 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 1H), 3.82 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.1, 160.7, 153.2, 126.7, 125.6, 115.0, 88.6, 72.6, 55.6, 24.8; **IR (neat)**: *v* = 1796, 1721 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{12}NaO_5$ $[M + Na]^+$ 259.0577; Found 259.0575.

4-Acetyl-4-(4-(tert-butyl)phenyl)-1,3-dioxolan-2-one (2d)



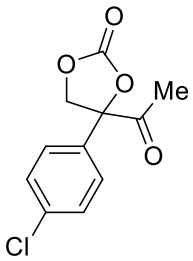
Yellow solid (56.3 mg, 71% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.31 – 7.29 (m, 2H), 5.23 (d, *J* = 8.6 Hz, 1H), 4.38 (d, *J* = 8.6 Hz, 1H), 2.27 (s, 3H), 1.32 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.1, 153.2, 153.1, 131.9, 126.6, 123.9, 88.8, 72.5, 34.9, 31.3, 24.9; **IR (neat)**: *v* = 1809, 1725 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{15}H_{18}NaO_4$ $[M + Na]^+$ 285.1097; Found 285.1085.

4-Acetyl-4-(4-fluorophenyl)-1,3-dioxolan-2-one (2e)



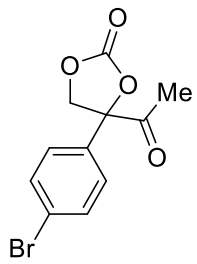
White solid (59.1 mg, 87% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.17 – 7.13 (m, 2H), 5.23 (d, *J* = 8.6 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 163.5 (d, *J* = 250.2 Hz), 152.9, 130.8 (d, *J* = 3.1 Hz), 126.2 (d, *J* = 8.3 Hz), 116.8 (d, *J* = 22.1 Hz), 88.2, 72.6, 24.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.96; **IR (neat)**: *v* = 1809, 1736 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_9FNaO_4$ $[M + Na]^+$ 247.0377; Found 247.0383.

4-Acetyl-4-(4-chlorophenyl)-1,3-dioxolan-2-one (2f)



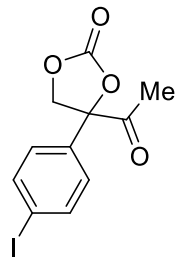
White solid (62.2 mg, 86% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.35 – 7.32 (m, 2H), 5.22 (d, *J* = 8.6 Hz, 1H), 4.35 (d, *J* = 8.6 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.8, 152.8, 136.2, 133.4, 129.9, 125.6, 88.2, 72.5, 24.9; **IR (neat)**: *v* = 1810, 1727 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_9ClNaO_4$ $[M + Na]^+$ 263.0082; Found 263.0084.

4-Acetyl-4-(4-bromophenyl)-1,3-dioxolan-2-one (2g)



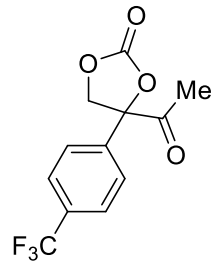
White solid (71.2 mg, 83% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.22 – 7.19 (m, 2H), 5.15 (d, *J* = 8.6 Hz, 1H), 4.28 (d, *J* = 8.6 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.7, 152.7, 134.0, 132.9, 125.8, 124.3, 88.2, 72.4, 24.9; **IR (neat)**: *v* = 1809, 1725 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_9BrNaO_4$ $[M + Na]^+$ 306.9576; Found 306.9581.

4-Acetyl-4-(4-iodophenyl)-1,3-dioxolan-2-one (2h)



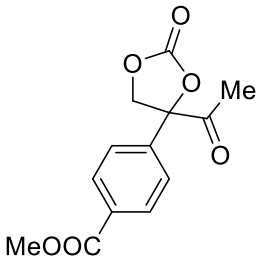
White solid (89.2 mg, 80% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.15 – 7.11 (m, 2H), 5.21 (d, *J* = 8.7 Hz, 1H), 4.34 (d, *J* = 8.7 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.6, 152.8, 138.8, 134.7, 125.9, 96.0, 88.2, 72.3, 24.9; **IR (neat)**: *v* = 1805, 1725 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_9INaO_4$ $[M + Na]^+$ 354.9438; Found 354.9433.

4-Acetyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (2i)



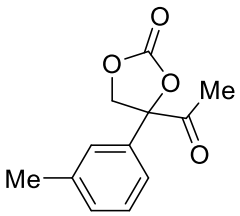
White solid (48.6 mg, 59% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.57 – 7.54 (m, 2H), 5.26 (d, *J* = 8.7 Hz, 1H), 4.38 (d, *J* = 8.7 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 152.6, 138.8, 132.3 (d, *J* = 32.9 Hz), 126.7 (d, *J* = 3.7 Hz), 124.8, 123.6 (d, *J* = 272.5 Hz), 88.2, 72.4, 25.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.10; **IR (neat)**: *v* = 1813, 1727 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_9F_3NaO_4$ $[M + Na]^+$ 297.0345; Found 297.0351.

Methyl 4-(4-acetyl-2-oxo-1,3-dioxolan-4-yl)benzoate (2j)



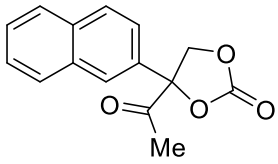
White solid (61.6 mg, 84% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 7.48 – 7.45 (m, 2H), 5.25 (d, *J* = 8.7 Hz, 1H), 4.37 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 166.1, 152.7, 139.4, 131.7, 130.9, 124.3, 88.4, 72.3, 52.6, 25.0; **IR (neat)**: *v* = 1811, 1714 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{12}NaO_6$ $[M + Na]^+$ 287.0526; Found 287.0531.

4-Acetyl-4-(*m*-tolyl)-1,3-dioxolan-2-one (2k)



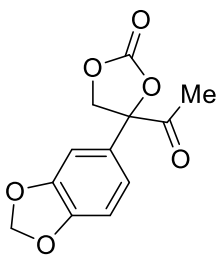
Yellow solid (62.1 mg, 95% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.15 (m, 2H), 5.24 (d, *J* = 8.5 Hz, 1H), 4.36 (d, *J* = 8.5 Hz, 1H), 2.38 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.9, 153.2, 139.7, 134.9, 130.5, 129.5, 124.5, 121.1, 88.7, 72.5, 24.9, 21.6; **IR (neat)**: *v* = 1805, 1726 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{12}NaO_4$ $[M + Na]^+$ 243.0628; Found 243.0623.

4-Acetyl-4-(naphthalen-2-yl)-1,3-dioxolan-2-one (2l)



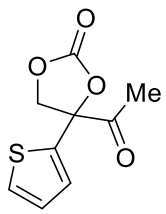
White solid (42.9 mg, 57% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 4H), 7.59 – 7.56 (m, 2H), 7.38 – 7.35 (m, 1H), 5.34 (d, *J* = 8.6 Hz, 1H), 4.47 (d, *J* = 8.6 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.9, 153.1, 133.6, 133.1, 132.1, 130.0, 128.4, 128.0, 127.6, 127.5, 123.8, 120.8, 88.8, 72.4, 24.9; **IR (neat)**: *v* = 1820, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{15}H_{12}NaO_4$ $[M + Na]^+$ 279.0628; Found 279.0633.

4-Acetyl-4-(benzo[d][1,3]dioxol-5-yl)-1,3-dioxolan-2-one (2m)



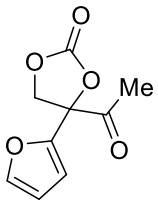
Yellow solid (67.9 mg, 90% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.83 – 6.82 (m, 3H), 6.00 – 5.99 (m, 2H), 5.18 (d, *J* = 8.6 Hz, 1H), 4.33 (d, *J* = 8.6 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.8, 153.0, 148.95, 148.93, 128.5, 118.0, 109.2, 104.7, 101.9, 88.4, 72.5, 24.7; **IR (neat)**: *v* = 1796, 1721 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{10}NaO_6$ $[M + Na]^+$ 273.0370; Found 273.0374.

4-Acetyl-4-(thiophen-2-yl)-1,3-dioxolan-2-one (2n)



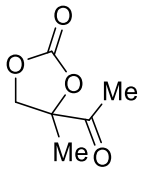
Brown solid (52.1 mg, 81% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.41 (m, 1H), 7.08 – 7.04 (m, 2H), 5.11 (d, *J* = 8.8 Hz, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 152.7, 137.4, 128.0, 127.7, 125.8, 87.0, 73.0, 25.1; **IR (neat)**: *v* = 1791, 1719 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_9H_8SNaO_4$ $[M + Na]^+$ 235.0036; Found 235.0039.

4-Acetyl-4-(furan-2-yl)-1,3-dioxolan-2-one (2o)



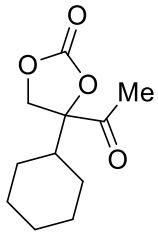
Yellow solid (45.5 mg, 77% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.51 (m, 1H), 6.54 – 6.53 (m, 1H), 6.46 – 6.45 (m, 1H), 4.91 (d, *J* = 9.1 Hz, 1H), 4.71 (d, *J* = 9.1 Hz, 1H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.4, 152.9, 146.6, 145.2, 111.2, 110.9, 84.0, 69.9, 26.3; **IR (neat)**: *v* = 1784, 1726 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_9H_8NaO_5$ $[M + Na]^+$ 219.0264; Found 219.0260.

4-Acetyl-4-methyl-1,3-dioxolan-2-one (2p)



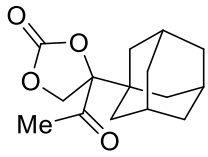
Colorless oil (34.8 mg, 78% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.65 (d, *J* = 8.9 Hz, 1H), 4.17 (d, *J* = 8.9 Hz, 1H), 2.36 (s, 3H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 153.5, 85.9, 72.0, 25.2, 22.3; **IR (neat)**: *v* = 1776, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_6H_9O_4$ $[M + H]^+$ 145.0495; Found 145.0494.

4-acetyl-4-cyclohexyl-1,3-dioxolan-2-one (2q)



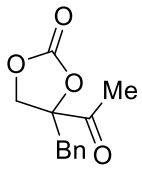
Colorless oil (55.3 mg, 86% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.48 (d, *J* = 9.1 Hz, 1H), 4.32 (d, *J* = 9.1 Hz, 1H), 2.34 (s, 3H), 1.91 – 1.81 (m, 3H), 1.73 – 1.64 (m, 3H), 1.28 – 1.15 (m, 4H), 1.04 – 0.98 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.6, 153.8, 90.7, 69.0, 43.4, 27.4, 26.2, 25.83, 25.77, 25.6; **IR (neat)**: *v* = 1802, 1718 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{16}NaO_4$ $[M + Na]^+$ 235.0941; Found 235.0941.

4-Acetyl-4-(adamantan-1-yl)-1,3-dioxolan-2-one (2r)



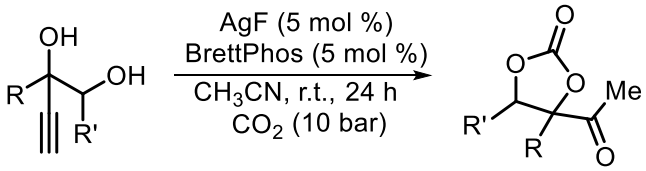
White solid (45.3 mg, 57% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 (d, *J* = 9.3 Hz, 1H), 4.35 (d, *J* = 9.3 Hz, 1H), 2.34 (s, 3H), 2.07 – 2.05 (m, 3H), 1.75 – 1.71 (m, 6H), 1.65 – 1.61 (m, 3H), 1.54 – 1.49 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.9, 153.9, 92.7, 68.1, 38.7, 36.4, 35.5, 29.5, 27.8; **IR (neat)**: *v* = 1789, 1717 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{15}H_{20}NaO_4$ $[M + Na]^+$ 287.1254; Found 287.1259.

4-Acetyl-4-benzyl-1,3-dioxolan-2-one (2s)



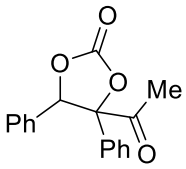
White solid (63.0 mg, 95% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 3H), 7.23 – 7.21 (m, 2H), 4.54 (d, *J* = 9.0 Hz, 1H), 4.29 (d, *J* = 9.0 Hz, 1H), 3.24 (d, *J* = 14.3 Hz, 1H), 3.04 (d, *J* = 14.3 Hz, 1H), 2.15 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.5, 153.4, 132.0, 130.4, 129.1, 128.3, 88.2, 70.4, 41.8, 26.9; **IR (neat)**: *v* = 1807, 1719 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{12}NaO_4$ $[M + Na]^+$ 243.0628; Found 243.0631.

General Procedure G for synthesis of cyclic carbonates 4a-4g:



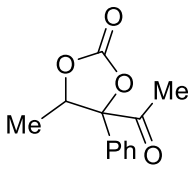
In a stainless-steel HEL-multireactor, the respective 1,2- diol (0.3 mmol, 1.0 equiv), AgF (0.015 mmol, 5 mol%), BrettPhos (0.015 mol%) were dissolved in MeCN (0.2 mL). The reactor was purged three times with CO_2 (10 bar) and then charged with CO_2 (10 bar). The reaction mixture was stirred at room temperature for 24 h. The mixture was then transferred to a round-bottom flask, concentrated and purified by flash column chromatography on silica to afford the corresponding carbonate product.

4-Acetyl-4,5-diphenyl-1,3-dioxolan-2-one (4a)



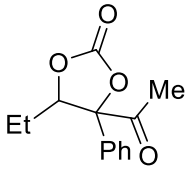
White solid (77.5 mg, 90% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 6H), 7.04 – 6.98 (m, 4H), 6.33 (s, 1H), 2.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.2, 153.0, 133.0, 131.3, 129.2, 129.1, 128.6, 128.3, 127.3, 125.2, 92.4, 83.3, 25.6; **IR (neat)**: ν = 1798, 1719 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{17}H_{14}NaO_4$ $[M + Na]^+$ 305.0784; Found 305.0790. This compound was further characterized by X-ray crystallography.

4-Acetyl-5-methyl-4-phenyl-1,3-dioxolan-2-one (4b)



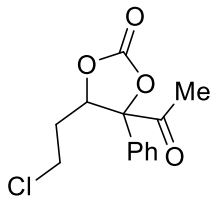
Colorless oil (56.0 mg, 85% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.34 – 7.31 (m, 2H), 5.47 (q, J = 6.6 Hz, 1H), 2.23 (s, 3H), 1.02 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.7, 152.8, 131.2, 129.7, 129.3, 125.1, 91.5, 78.3, 25.4, 17.4; **IR (neat)**: ν = 1807, 1722 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{12}H_{12}NaO_4$ $[M + Na]^+$ 243.0628; Found 243.0626.

4-Acetyl-5-ethyl-4-phenyl-1,3-dioxolan-2-one (4c)



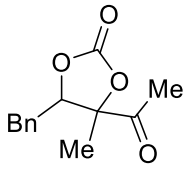
Yellow oil (53.8 mg, 76% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 3H), 7.34 – 7.29 (m, 2H), 5.22 (dd, J = 10.5, 3.1 Hz, 1H), 2.23 (s, 3H), 1.32 – 1.22 (m, 1H), 1.16 – 1.04 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.8, 152.9, 131.3, 129.7, 129.3, 125.1, 91.4, 83.1, 25.4, 25.3, 9.8; **IR (neat)**: ν = 1807, 1722 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784; Found 257.0790.

4-Acetyl-5-(2-chloroethyl)-4-phenyl-1,3-dioxolan-2-one (4d)



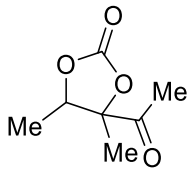
White solid (64.4 mg, 77% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 3H), 7.34 – 7.30 (m, 2H), 5.58 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.60 – 3.52 (m, 2H), 2.24 (s, 3H), 1.63 – 1.48 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 152.3, 130.8, 130.1, 129.6, 125.0, 91.0, 78.4, 39.8, 34.8, 25.4; **IR (neat)**: *v* = 1811, 1726 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{13}ClNaO_4$ $[M + Na]^+$ 291.0395; Found 291.0394.

4-Acetyl-5-benzyl-4-methyl-1,3-dioxolan-2-one (4e)



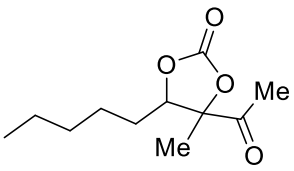
Yellow oil (54.4 mg, 77% yield, 76:24 *dr*). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.35 – 7.24 (m, 5H), 4.85 – 4.77 (m, 1H), 3.03 – 2.99 (m, 2H), 2.37 (s, 3H), 1.57 (s, 3H); **^{1}H NMR** (400 MHz, $CDCl_3$) (minor) δ 7.35 – 7.24 (m, 3H), 7.21 – 7.19 (m, 2H), 4.62 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.03 – 2.99 (m, 1H), 2.73 (dd, *J* = 14.8, 9.5 Hz, 1H), 2.29 (s, 3H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 206.68, 152.7, 135.4, 129.2, 128.9, 127.5, 88.1, 81.8, 36.2, 25.4, 17.8; **^{13}C NMR** (101 MHz, $CDCl_3$) (minor) δ 206.72, 153.1, 134.9, 129.6, 128.9, 127.6, 88.5, 85.9, 36.3, 28.1, 23.1; **IR (neat)**: *v* = 1802, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784; Found 257.0784.

4-Acetyl-4,5-dimethyl-1,3-dioxolan-2-one (4f)



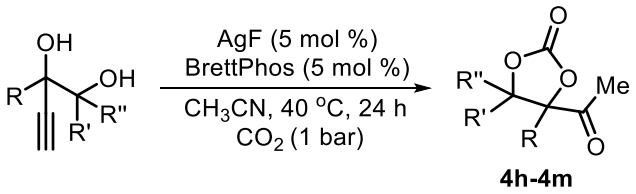
Colorless oil (35.7 mg, 73% yield, 68:32 *dr*). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 4.79 (q, *J* = 6.6 Hz, 1H), 2.35 (s, 3H), 1.45 (s, 3H), 1.43 (d, *J* = 6.6 Hz, 3H); **^{1}H NMR** (400 MHz, $CDCl_3$) (minor) δ 4.54 (q, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 1.57 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 206.9, 152.9, 88.2, 77.5, 25.4, 17.4, 15.3; **^{13}C NMR** (101 MHz, $CDCl_3$) (minor) δ 206.5, 153.3, 88.9, 81.6, 28.0, 22.5, 16.0; **IR (neat)**: *v* = 1800, 1721 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_7H_{10}NaO_4$ $[M + Na]^+$ 181.0471; Found 181.0471.

4-Acetyl-4-methyl-5-pentyl-1,3-dioxolan-2-one (4g)



Colorless oil (40.8 mg, 62% yield, 76:24 *dr*). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 4.57 (dd, *J* = 10.1, 3.1 Hz, 1H), 2.35 (s, 3H), 1.74 – 1.53 (m, 3H), 1.45 (s, 3H), 1.34 – 1.25 (m, 5H), 0.89 (t, *J* = 6.9 Hz, 3H); **^{1}H NMR** (400 MHz, $CDCl_3$) (minor) δ 4.35 (dd, *J* = 10.1, 3.1 Hz, 1H), 2.33 (s, 3H), 1.74 – 1.53 (m, 3H), 1.57 (s, 3H), 1.34 – 1.25 (m, 5H), 0.89 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 207.0, 153.0, 88.2, 81.4, 31.4, 29.9, 25.53, 25.4, 22.5, 17.6, 14.0; **^{13}C NMR** (101 MHz, $CDCl_3$) (minor) δ 206.4, 153.5, 88.7, 85.7, 31.3, 30.3, 28.0, 25.51, 22.7, 22.4, 13.97; **IR (neat)**: *v* = 1805, 1722 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{18}NaO_4$ $[M + Na]^+$ 237.1097; Found 237.1092.

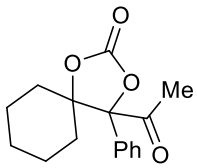
General Procedure H for synthesis of cyclic carbonates 4h-4m:



4h-4m

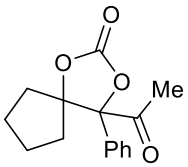
The respective 1,2-diol (0.3 mmol, 1.0 equiv), AgF (0.015 mmol, 5 mol%), BrettPhos (0.015 mmol, 5 mol%) were added to a 25 mL reaction tube. The tube was purged three times with CO_2 and then charged with a CO_2 balloon (1 bar). Hereafter, MeCN (0.6 mL) was added using a syringe. The reaction mixture was stirred at 40 °C for 24 h. When complete consumption of the starting material had been observed by TLC, the mixture was transferred to a round-bottom flask, concentrated and purified by flash column chromatography on silica to afford the corresponding carbonate product.

4-Acetyl-4-phenyl-1,3-dioxaspiro[4.5]decan-2-one (4h)



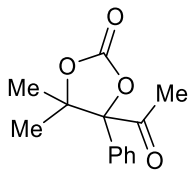
White solid (72.0 mg, 87% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 3H), 2.29 (s, 3H), 1.92 – 1.77 (m, 2H), 1.74 – 1.53 (m, 4H), 1.50 – 1.34 (m, 2H), 1.24 – 1.14 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.6, 152.8, 132.0, 129.4, 128.8, 126.1, 93.6, 90.1, 33.1, 32.9, 28.7, 24.7, 22.2, 22.0; **IR (neat)**: ν = 1798, 1712 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{16}H_{18}NaO_4$ $[M + Na]^+$ 297.1097; Found 297.1094.

4-Acetyl-4-phenyl-1,3-dioxaspiro[4.4]nonan-2-one (4i)



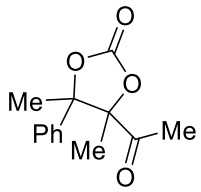
Yellow oil (69.5 mg, 89% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.44 – 7.38 (m, 3H), 2.32 (s, 3H), 2.29 – 2.21 (m, 1H), 1.98 – 1.74 (m, 3H), 1.72 – 1.52 (m, 3H), 1.46 – 1.40 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.7, 152.9, 132.8, 129.4, 129.0, 125.3, 99.3, 91.3, 35.6, 34.0, 28.0, 23.2, 22.1; **IR (neat)**: ν = 1805, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{15}H_{16}NaO_4$ $[M + Na]^+$ 283.0941; Found 283.0932.

4-Acetyl-5,5-dimethyl-4-phenyl-1,3-dioxolan-2-one (4j)



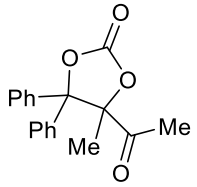
Colorless oil (59.5 mg, 85% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.43 – 7.40 (m, 3H), 2.32 (s, 3H), 1.58 (s, 3H), 1.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.3, 152.8, 132.3, 129.6, 129.0, 125.8, 93.2, 88.4, 28.2, 24.9, 24.7; **IR (neat)**: ν = 1803, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784; Found 257.0779.

4-Acetyl-4,5-dimethyl-5-phenyl-1,3-dioxolan-2-one (4k)



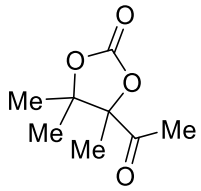
White solid (58.4 mg, 83% yield, *dr* >95:5). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.43 – 7.34 (m, 3H), 2.48 (s, 3H), 1.69 (s, 3H), 1.10 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.2, 152.2, 137.5, 128.8, 128.7, 125.4, 91.7, 88.8, 28.3, 25.3, 22.3; **IR (neat)**: ν = 1803, 1723 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784; Found 257.0778.

4-Acetyl-4-methyl-5,5-diphenyl-1,3-dioxolan-2-one (4l)



White solid (84.3 mg, 95% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.46 – 7.36 (m, 3H), 7.34 – 7.30 (m, 5H), 1.87 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 152.7, 137.6, 136.2, 129.1, 129.0, 128.8, 128.6, 127.0, 126.4, 93.8, 91.3, 27.5, 22.8; **IR (neat)**: ν = 1809, 1720 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{18}H_{16}NaO_4$ $[M + Na]^+$ 319.0941; Found 319.0934.

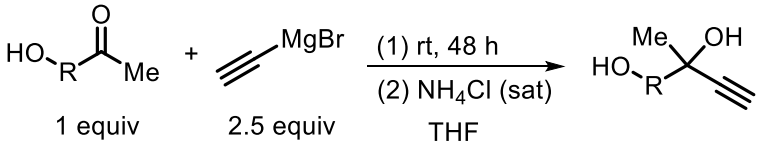
4-Acetyl-4,5,5-trimethyl-1,3-dioxolan-2-one (4m)



White solid (46.0 mg, 91% yield). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 1.52 (s, 3H), 1.49 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.1, 152.7, 91.0, 85.8, 27.8, 23.8, 22.4, 19.7; **IR (neat)**: ν = 1783, 1715 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_8H_{12}NaO_4$ $[M + Na]^+$ 195.0628; Found 195.0629.

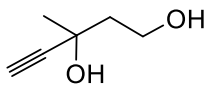
5. Catalytic screening towards larger ring cyclic carbonates

General procedure for the synthesis of 1,3- and 1,4-diols 5a and 5b



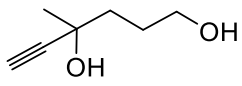
For 5a: In a clean dry double-neck 2L round bottom flask conditioned under an inert atmosphere was introduced ethynyl magnesium bromide (800 mL, 0.5 M in THF, 0.4 mole). Then, 4-hydroxy-2-butanone (13.8 mL, 0.16 mole) was added dropwise using a syringe. The reaction mixture was stirred at room temperature for 48 h, during which the conversion of the ketone was monitored by ATR-IR. Then, a saturated solution of NH_4Cl was added and the mixture was transferred into a separating funnel to recover the organic phase. The aqueous phase was extracted with diethyl ether (200 + 150 mL). The combined organic fractions were dried with anhydrous $MgSO_4$ and filtered. Then the organic phase was evaporated in vacuo and the residue purified by fractional distillation. A transparent to light yellow oil was recovered in a yield of around 60% at 55°C with a vacuum of 1 mbar. A similar procedure was applied for the synthesis of **5b** using the appropriate hydroxy ketone precursor giving a similar isolated yield.

3-Methylpent-4-yne-1,3-diol (5a)



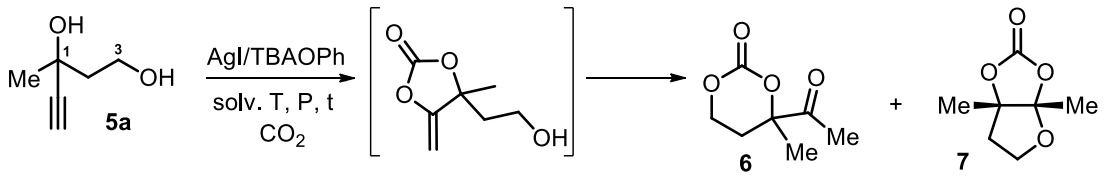
Light yellow oil. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 5.29 (s, 1H), 4.44 (s, 1H), 3.59 (s, 2H), 3.23 (s, 1H), 1.74 (s, 2H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 73.10, 65.62, 58.21, 46.12, 39.56, 30.71.

4-Methylhex-5-yne-1,4-diol (5b)



Light orange oil. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 5.23 (s, 1H), 4.42 (t, *J* = 5.2 Hz, 1H), 3.40 (t, *J* = 5.7 Hz, 2H), 3.16 (s, 1H), 1.70 – 1.46 (m, 4H), 1.33 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 89.69, 72.83, 66.44, 61.47, 40.60, 30.33, 28.43.

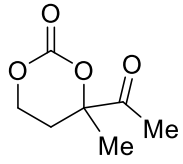
Screening of reaction parameters for the carboxylative coupling of CO_2 to 3-methylpent-4-yne-1,3-diol (5a)



In a clean dry reactor, equipped with a magnetic rod, a manometer and a gas inlet/outlet were introduced 3-methylpent-4-yne-1,3-diol (1 g, 8.76 mmol), tetrabutylammonium phenolate TBAOPh (0.147 g, 0.438 mmol), silver iodide (AgI) (0.102 g, 0.438 mmol) and dried DMSO (2-4 mL). The reactor was closed and placed in a silicon oil bath set heated at the desired temperature. After 30 minutes, CO_2 gas was added at a constant pressure. The reaction ran for 24-72 h after which the reactor was depressurized and placed in a water bath to cool it down to room temperature. The crude reaction mixture was characterized by ^{1}H NMR spectroscopy in DMSO-d_6.

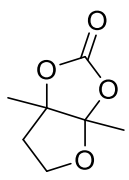
Isolation of products was achieved by extraction of the crude mixture with 80 mL of salted water and 80 mL of CH_2Cl_2, followed by a silica gel chromatography (5-50% ethyl acetate/petroleum ether (40/60)).

4-Methyl-4-(prop-1-en-2-yl)-1,3-dioxan-2-one (6)



White solid, 51%. Eluent petroleum ether /EtOAc = 1/1 **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.37 (dt, *J* = 11.3, 4.7 Hz, 1H), 4.10 (ddd, *J* = 11.3, 10.2, 4.1 Hz, 1H), 2.41 (dt, *J* = 14.7, 4.1 Hz, 1H), 2.28 (s, 3H), 2.12 (ddd, *J* = 14.7, 10.2, 5.0 Hz, 1H), 1.53 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 206.91, 147.83, 87.28, 65.52, 39.57, 28.20, 25.15, 23.35; **IR (neat)** ν = 1750, 1720 cm^{-1}; **HRMS** (QTOF) *m/z* Calcd for $C_7H_{10}NaO_4$ $[M + Na]^+$ 181.0477; Found 181.0472.

3a,6a-Dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-2-one (7)



White solid, 70% Eluent hexanes/EtOAc = 5/1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.05 (dd, *J* = 9.3, 7.9 Hz, 1H), 3.77 (ddd, *J* = 11.9, 9.4, 4.7 Hz, 1H), 2.29 (dd, *J* = 13.9, 4.6 Hz, 1H), 2.05 (ddd, *J* = 13.9, 11.9, 7.9 Hz, 1H), 1.57 (d, *J* = 4.7 Hz, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 152.7, 114.8, 91.8, 65.6, 38.2, 20.3, 20.0; **IR (neat)**: ν = 1802 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_7H_{10}NaO_4$ $[M + Na]^+$ 181.0471; Found 181.0472. This compound was further characterized by X-ray crystallography.

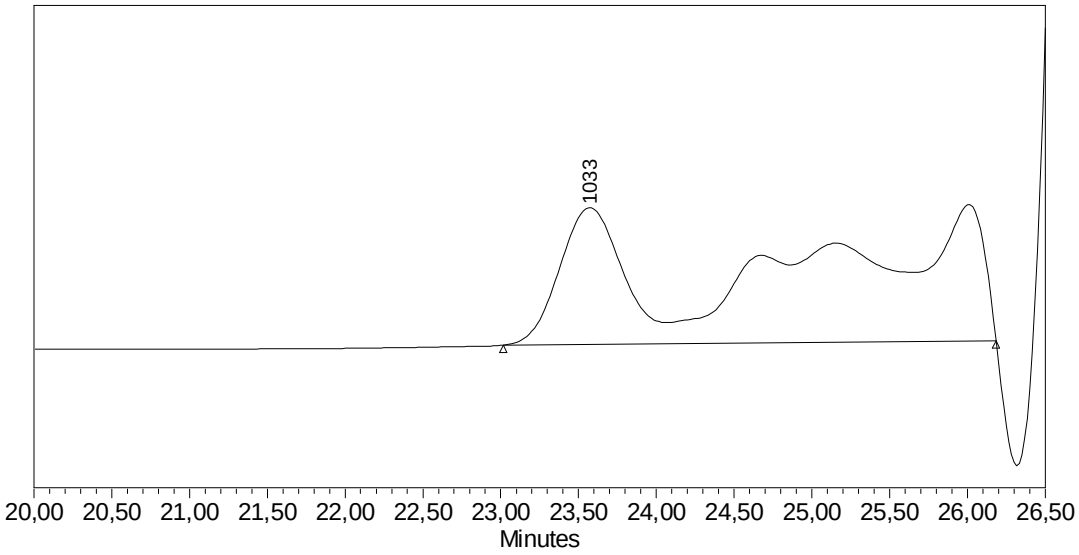
Table S5: Screening of the carboxylative coupling of 1,3-diol **5a** with CO_2 to give **6** and **7**.[a]

Entry	Solvent	Conc. [mol/L]	T [°C]	Conv. of 5a [%] [b]	Sel. for 6 [%] [b]	Sel. for 7 [%] [b]
1[c]	**DMSO**	**2.2**	**25**	**100**	**98 (51)**[d]	**–**
2	DMSO	2.2	25	100	85	–
3	DMSO	4.4	25	34	84	–
4	ACN	2.2	25	0	–	–
5	–	–	25	0	–	–
6[e]	DMSO	2.2	60	100	98	–
7	DMSO	4.4	60	100	85	6
8[f]	DMSO	4.4	60	100	44	49
9	ACN	4.4	60	100	57	21
10	–	–	60	100	13	42
11	DMSO	2.2	80	100	32	35
12	**DMSO**	**4.4**	**80**	**100**	**13**	**69**
13	DMF	4.4	80	100	5	86
14	**ACN**	**4.4**	**80**	**100**	**0**	**90 (70)**[d]
15	–	–	80	70	0	67
16[f]	–	–	80	100	0	90

[a] Conditions: 1,3-diol **5a** (1 g, 8.76 mmol), TBAOPh (0.147 g, 0.438 mmol), AgI (0.102 g, 0.438 mmol), $p(CO_2)$ = 15 bar and t = 24 h. [b] Determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. [c] Reaction time was 16 h. [d] Yields in brackets refer to *isolated* yield after purification by silica gel column chromatography. [e] Reaction time was 3.5 h. [f] Reaction time was 72 h.

Description of the procedure for the SEC analysis: Number-average molecular weight (M_n) and dispersity ($Đ$) of the different polymers were determined by size exclusion chromatography (SEC) in dimethyl formamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) with a Waters chromatograph equipped with two columns dedicated to the analysis of low molar mass polymers (PSS gram analytical 100 Å, separation range 300-60000 Da) and a pre-column (100 Å), a dual λ absorbance detector (Waters 2487) and a refractive index detector (Waters 2414). The system was calibrated by polystyrene (PS) standards.

The crude sample of Table S5, entry 12 was injected in SEC equipment and the corresponding SEC chromatogram is shown in Figure S1. It reveals that the crude product contains a small amount of oligomers of very low molar mass (apparent M_n = 440 g/mol). It is important to note that the tailing at very low molar mass is out of calibration and contains products **6** and **7**, as well as dimers/trimers.



	SampleName	RT	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Polydispersity
1	chng f40a	*15,212*				
2	chng f40a	*19,750*				
3	chng f40a	23,571	443	591	1033	1,332618

Figure S1. SEC trace and data for the crude mixture of **Table S5**, **entry 12**.

Monitoring of the carboxylative coupling of CO_2 to 3-methylpent-4-yne-1,3-diol 5a by FT-IR spectroscopy

In a clean and dry reactor of 40 mL equipped with a manometer, a heating mantle, gas inlet/outlets, a mechanical stirrer and a high-pressure FT-IR probe were introduced 3-methylpent-4-yne-1,3-diol **5a** (3 g, 26.28 mmol), tetrabutylammonium phenolate TBAOPh (0.4410 g, 1.3141 mmol), AgI (0.3085 g, 1.3141 mmol) and dry DMSO (12 mL). The reactor was closed and heated to the desired temperature after which the FT-IR acquisition was initiated. Then, CO_2 gas was added and the pressure maintained at 15 bar. Spectra were recorded every 1-5 min. Once the reaction was complete, the reactor was cooled down to room temperature and depressurized. The crude reaction mixture was recovered and analyzed by ^{1}H NMR spectroscopy.

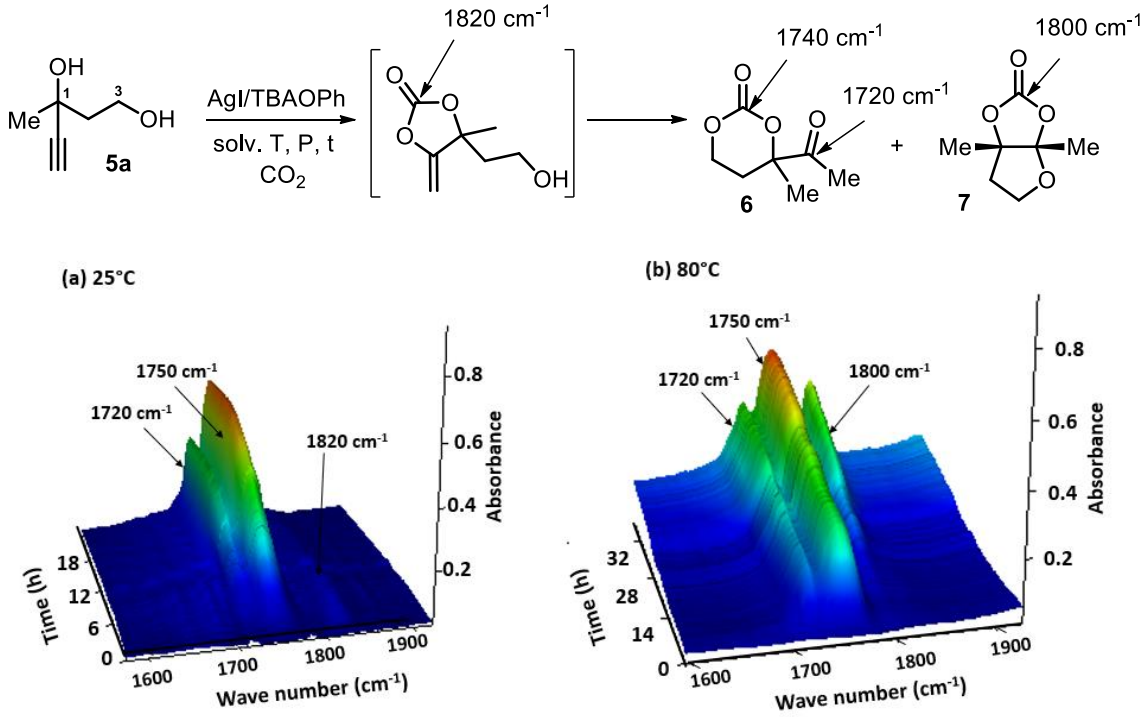


Figure S2. Online monitoring via operando FT-ATR spectroscopy at 25 °C (a) or 80 °C (b) of the carboxylative coupling of 3-methylpent-4-yne-1,3-diol **5a** with CO_2 to afford carbonates **6** and **7**.

At 25°C, we briefly observed the formation of the alkylidene cyclic carbonate as attested by the presence of the band at 1820 cm^{-1}, which disappeared after few hours in favour of the six-membered keto-carbonate **6** with the characteristic bands at 1750 cm^{-1} (carbonate) and 1720 cm^{-1} (ketone). At 80 °C, a new bicyclic tetrasubstituted five-membered cyclic carbonate **7**, with a characteristic band at 1802 cm^{-1}, was formed together with the 6-membered keto-carbonate **6**

(Figure S2) The formation of both products, **6** and **7,** was also confirmed by ^{1}H NMR spectroscopy (Figure S3).

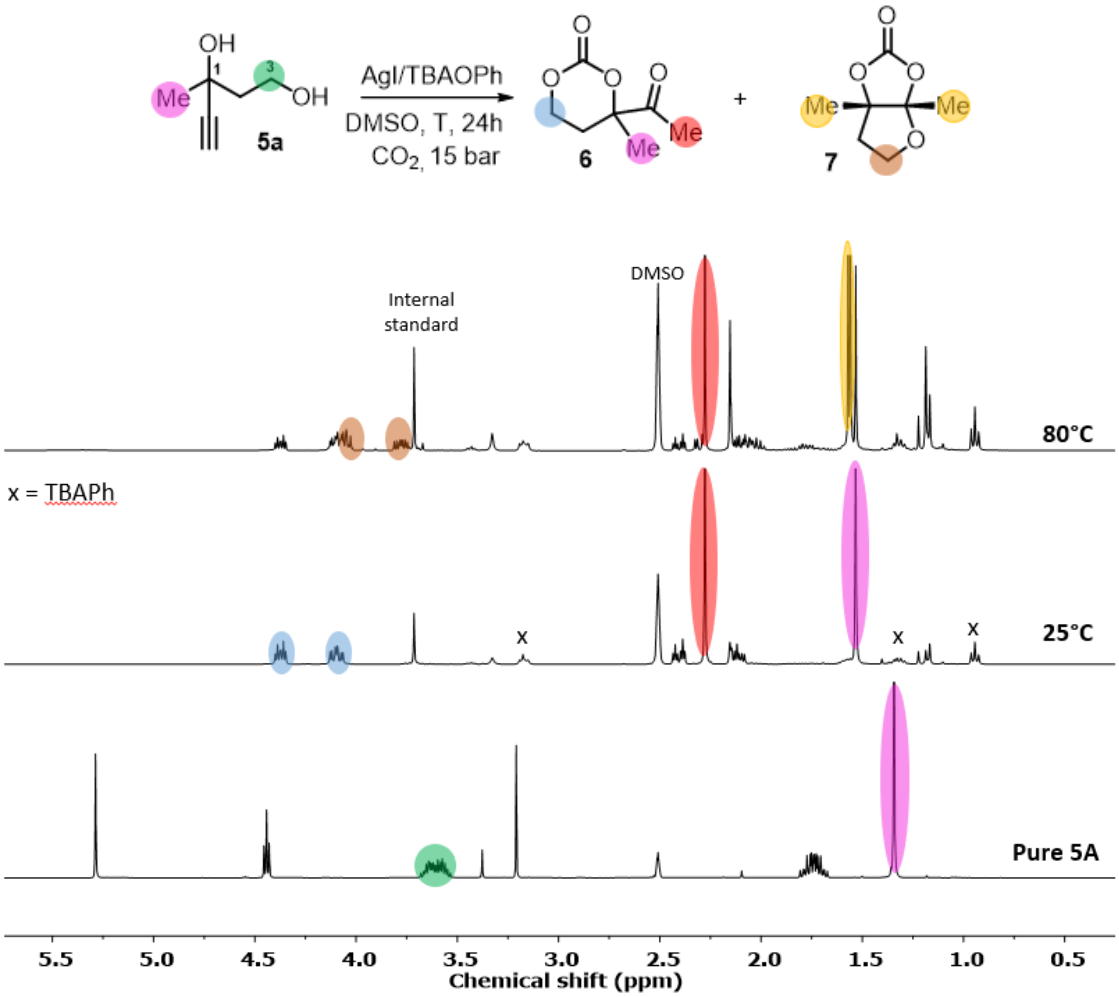
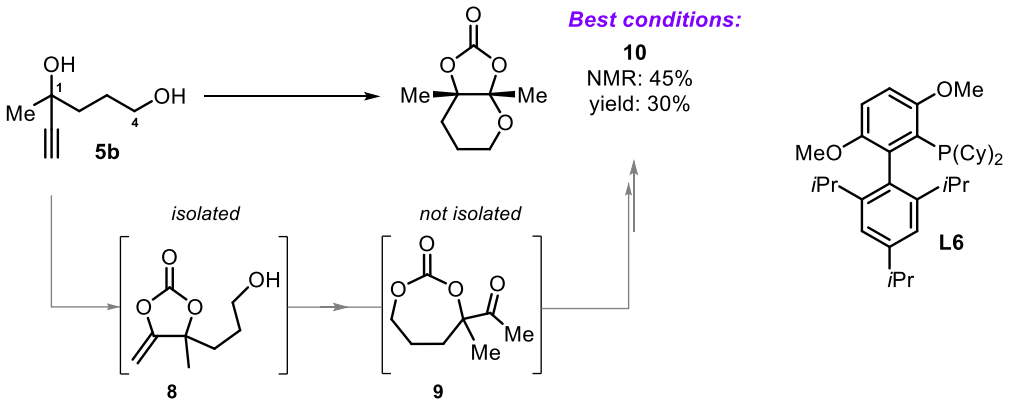


Figure S3. ^{1}H NMR overlay of pure alcohol **5a** (bottom), the crude reaction mixtures obtained at 25 ºC (middle) and 80 ºC (top) for the carboxylative coupling of CO_2 to 3-methylpent-4-yne-2,3-diol **5a**.

Screening of reaction parameters for the carboxylative coupling of CO_2 to 4-methylhex-5-yne-1,4-diol (5b)

Table S6:[a] Screening of parameters for the carboxylative coupling of 1,4-diol **5b** with CO_2 to give **8**, **9** and **10**.



Entry	[Ag] [mol%]	Ligand [mol%]	T/pressure [ºC]/[bar]	Conv. 5b [%][b]	8 [%][b]	9 [%][b]	10 [%][b]
1	AgF, 10	**L6**, 5	rt, 30	>99	66	30	–
2	AgF, 10	**L6**, 5	50, 30	>99	–	–	–
3	AgF, 5	**L1**, 5	rt, 30	>99	31	16	27
4	AgF, 5	**L2**, 5	rt, 30	>99	–	trace	41
5	AgF, 5	**L3**, 5	rt, 30	>99	25	32	14
6	AgF, 5	**L4**, 5	rt, 30	>99	–	10	28
7[c]	AgI, 5	TBAOPh, 5	rt, 15	>99	75, 50[d]	21	–
8[c]	AgI, 5	TBAOPh, 5	80, 15	>99	7	1	24
9	AgI, 5	TBAOPh, 5	80, 15	>99	7	3	16
10	AgI, 5	DBU, 5	80, 15	>99	3	5	25
11	–	DBU, 10	80, 15	>99	–	–	24[d]
12	AgI, 5	DBU, 10	80, 15	>99	–	12	45, 33[d]
13	–	DBU, 10	80, 15	>99	–	–	9

[a] Reaction conditions: **5b** (0.3 mmol), ACN (0.2 mL), CO_2 (pressure indicated), 24 h. [b] Determined by ^{1}H NMR using mesitylene as internal standard. [c] DMSO as solvent [d] Isolated yield.

Description of the procedure for the SEC analysis: Number-average molecular weight (M_n) and dispersity ($Đ$) of the polymers were determined by size exclusion chromatography (SEC) in dimethyl formamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) with a SECcurity GPC1260 chromatograph from PSS equipped with three columns (PSS gram 1000 Å (x2), 30 Å) and a pre-column, a SECcurity refractive index detector, a SECcurity variable wavelength UV-Vis detector and a MALLS detector SLD7000. The system was calibrated by polystyrene (PS) standards.

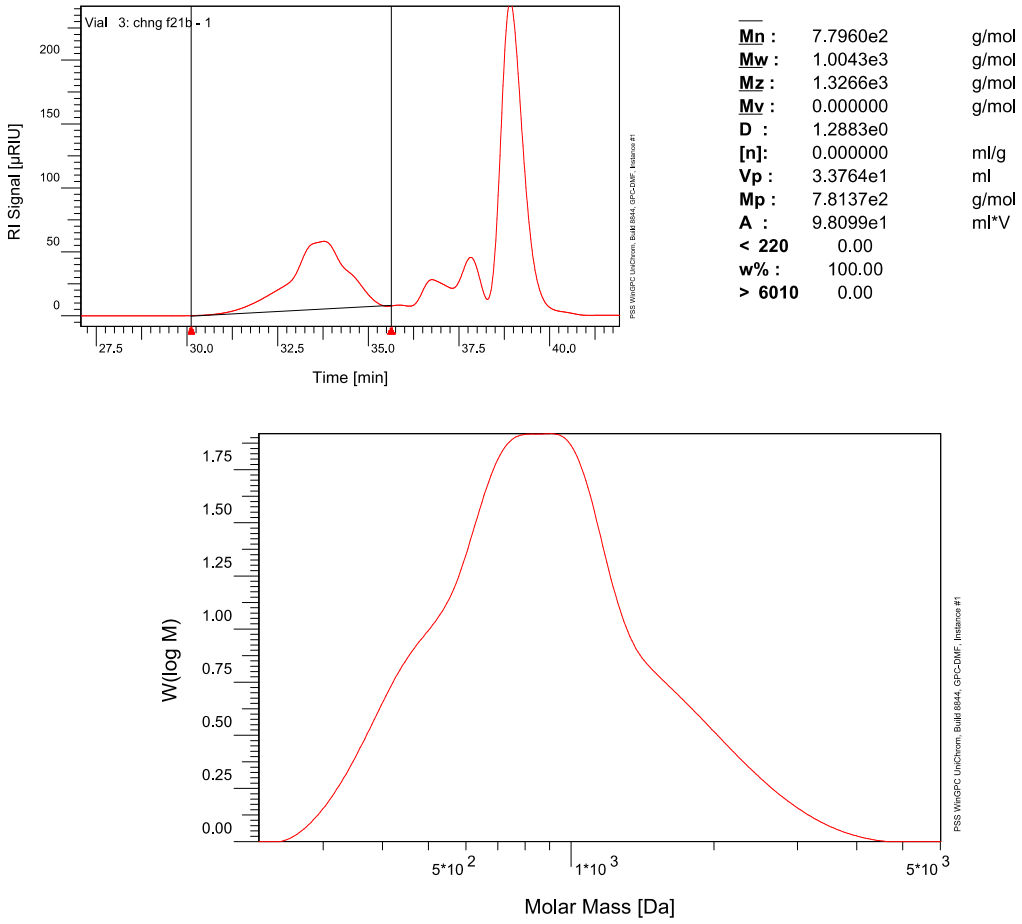
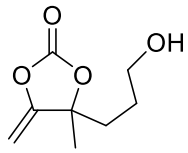


Figure S4. SEC chromatogram and data of the crude mixture (Table S6, entry 9).

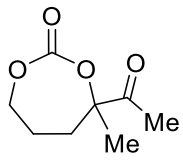
The reaction of alkyne-1,4 diol (**5b**) provides the tetrasubstituted carbonate **10** at lower yield and favors the formation of some oligomeric compounds (Figure S4). The oligomers have an apparent M_n of 780 g/mol and a dispersity of 1.29. All attempts to push the polymerization further to reach higher molar masses were unsuccessful as the formation of product **10** could not be avoided. Products appearing at elution volumes higher than 36 min are out of calibration and correspond to a mixture of products **8**, **9** and **10**. The intense sharp peak at around 39 min corresponds to DMSO, which was used as the solvent for the reaction.

4-(3-Hydroxypropyl)-4-methyl-5-methylene-1,3-dioxolan-2-one (8)



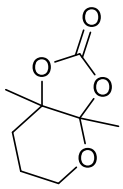
Yellow oil, NMR yield 75%, isolated: 50%. Eluent petroleum ether/ EtOAc 1:1 **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.85 (d, *J* = 3.9 Hz, 1H), 4.63 (d, *J* = 3.9Hz, 1H), 4.53 (t, *J* = 5.2 Hz, 1H), 3.41 (td, *J* = 6.3, 5.1 Hz, 2H), 1.89 (qdd, *J* = 14.4, 9.8, 6.0, 2H), 1.60 (s, 3H), 1.43 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 157.43, 151.46, 87.99, 86.46, 60.56, 36.68, 26.72, 25.94; **IR (neat)** ν = 1686, 1818 cm^{-1}; **HRMS** (QTOF) *m/z* Calcd for $C_8H_{12}NaO_4$ $[M + Na]^+$ 195.1698; Found 195.0633.

4-Acetyl-4-methyl-1,3-dioxepan-2-one (9)



Note: This compound was isolated as a mixture with **8**. The data are here provided for completion. Selected features: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.07 (m, 2H), 2.39 (m, 2H), 2.25 (s, 3H, C(O)Me), 1.80 (m, 2H), 1.49 (s, 3H, Me); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 206.51, 153.07, 90.31, 70.04, 36.88; **IR (neat)** ν = 1720, 1752 cm^{-1}.

3*a*,7*a*-Dimethyltetrahydro-5*H*-[1,3]dioxolo[4,5-b]pyran-2-one (10)

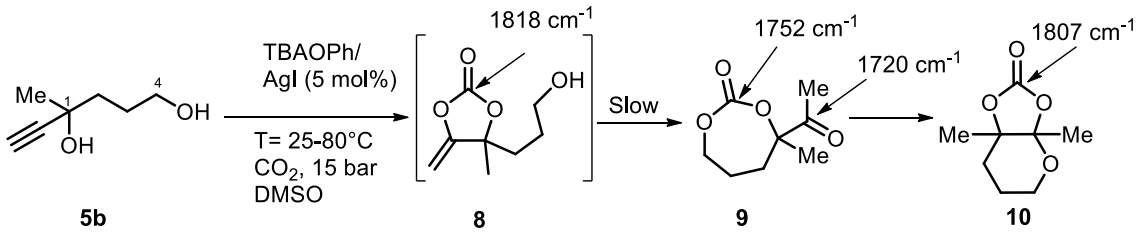


White solid, NMR yield 45%, isolated 30%. Eluent hexanes/ EtOAc = 5/1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 3.72 (td, *J* = 6.4, 1.9 Hz, 2H), 1.97 (ddd, *J* = 14.8, 5.5, 4.1 Hz, 1H), 1.85 (ddd, *J* = 14.7, 10.6, 6.4 Hz, 1H), 1.76 – 1.60 (m, 2H), 1.54 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.1, 107.3, 83.6, 60.7, 28.6, 22.9, 19.8, 18.6; **IR (neat)**: ν = 1803 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_8H_{12}NaO_4$ $[M + Na]^+$ 195.0628; Found 195.0628.

Monitoring of the carboxylative coupling of CO_2 to 4-methylhex-5-yne-1,4-diol (5b) by FT-IR spectroscopy

A similar procedure to that used for **5a** was followed.

At 25 °C, we observed the formation of the alkylidene cyclic carbonate **8** (1818 cm^{-1} and 1685 cm^{-1}) which could be isolated at 50% yield. The seven-membered carbonate **9**, with its characteristic carbonyl vibration at 1752 cm^{-1}, was also formed at the two investigated temperatures, 25 and 80 °C. Note that the progressive broadening of the band at 1818 cm^{-1} with time (for the reaction carried out at 80 °C) results from the appearance of a band at 1807 cm^{-1}, the signature of the tetrasubstituted carbonate **10.**



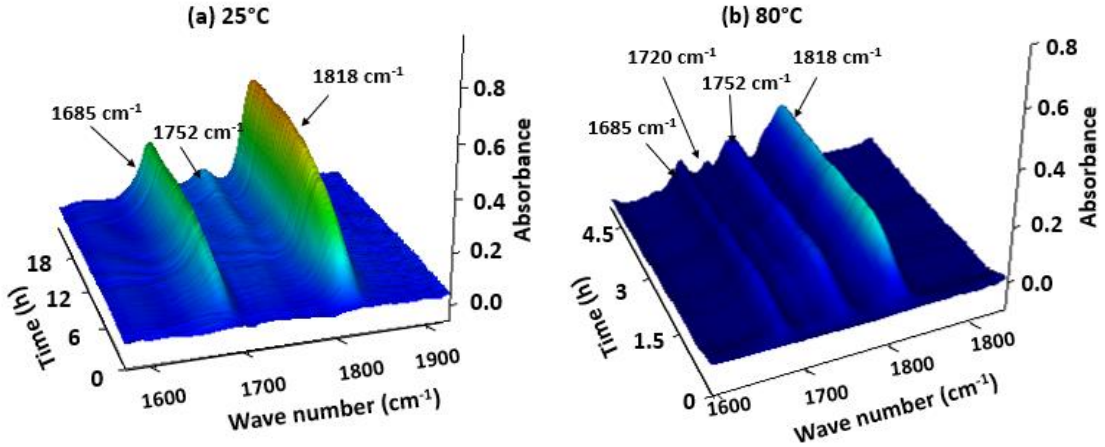


Figure S5. Online monitoring of the carboxylative coupling of 4-methylhex-5-yne-1,4-diol **5b** with CO_2 via operando FT-ATR spectroscopy at (a) 25 °C and (b) 80 °C showing the seven-membered carbonate **9** with absorptions at **1752** and **1720** cm^{-1}.

6. References

[1] Gómez, J. E.; Cristòfol, A.; Kleij, A. W. Copper-Catalyzed Enantioselective Construction of Tertiary Propargylic Sulfones. *Angew. Chem. Int. Ed.* **2019**, *58*, 3903–390.

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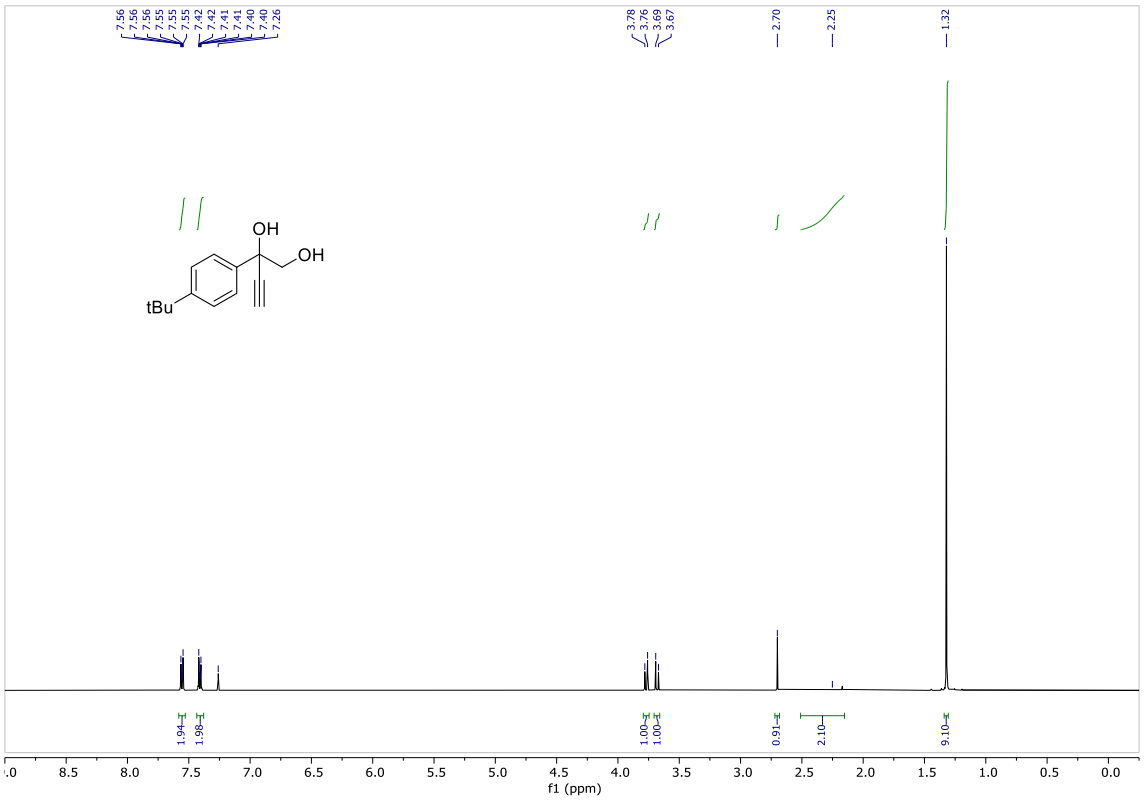
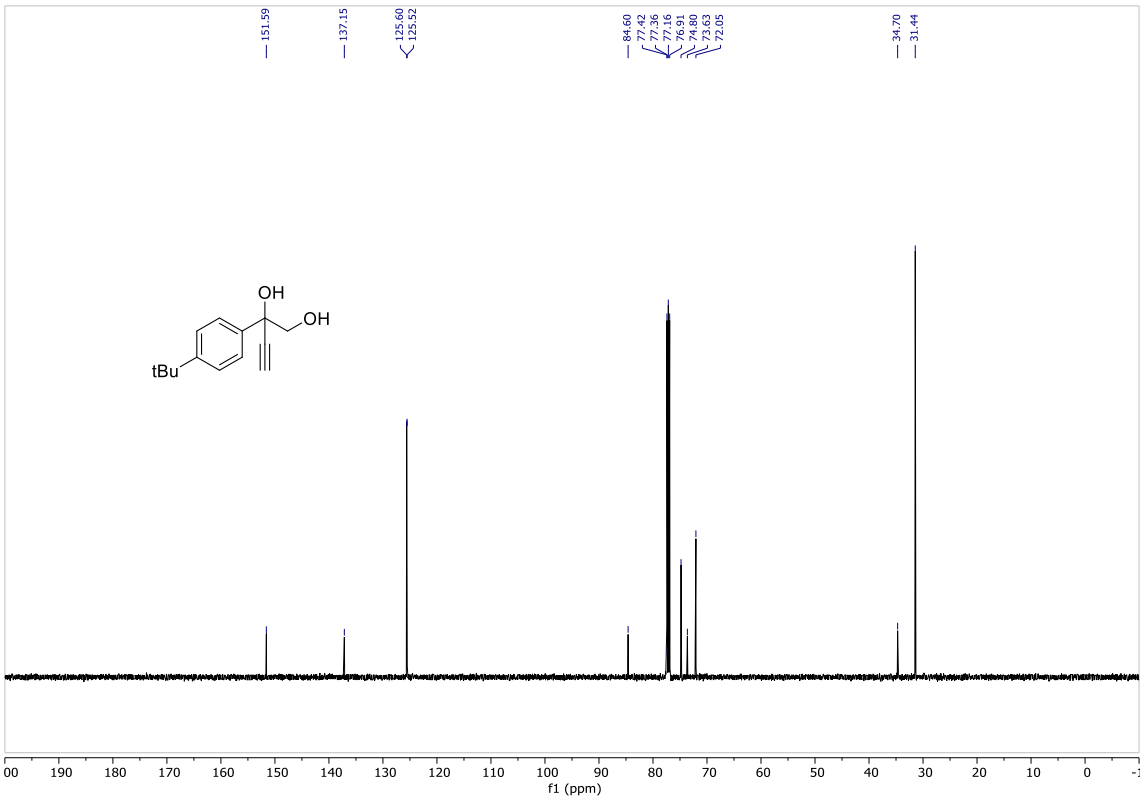
[6] Liang, Y. F.; Jiao, N. Highly Efficient C–H Hydroxylation of Carbonyl Compounds with Oxygen under Mild Conditions. *Angew. Chem. Int. Ed.* **2014**, *53*, 548-552.

7. NMR and IR spectra of all compounds

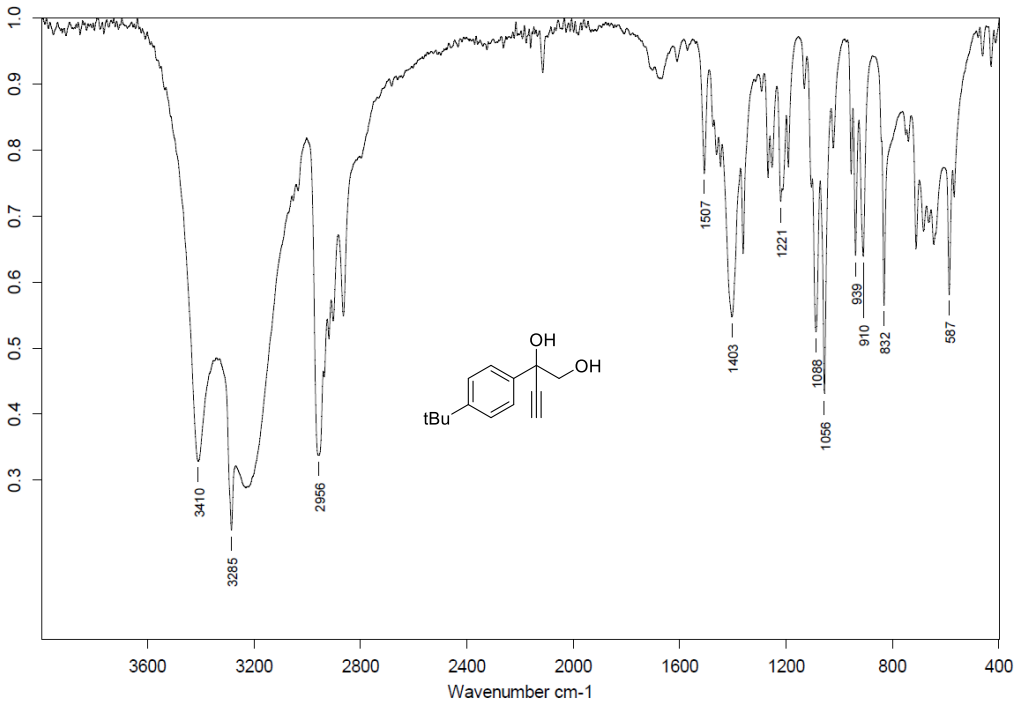
Alkyne-1,2-diols:



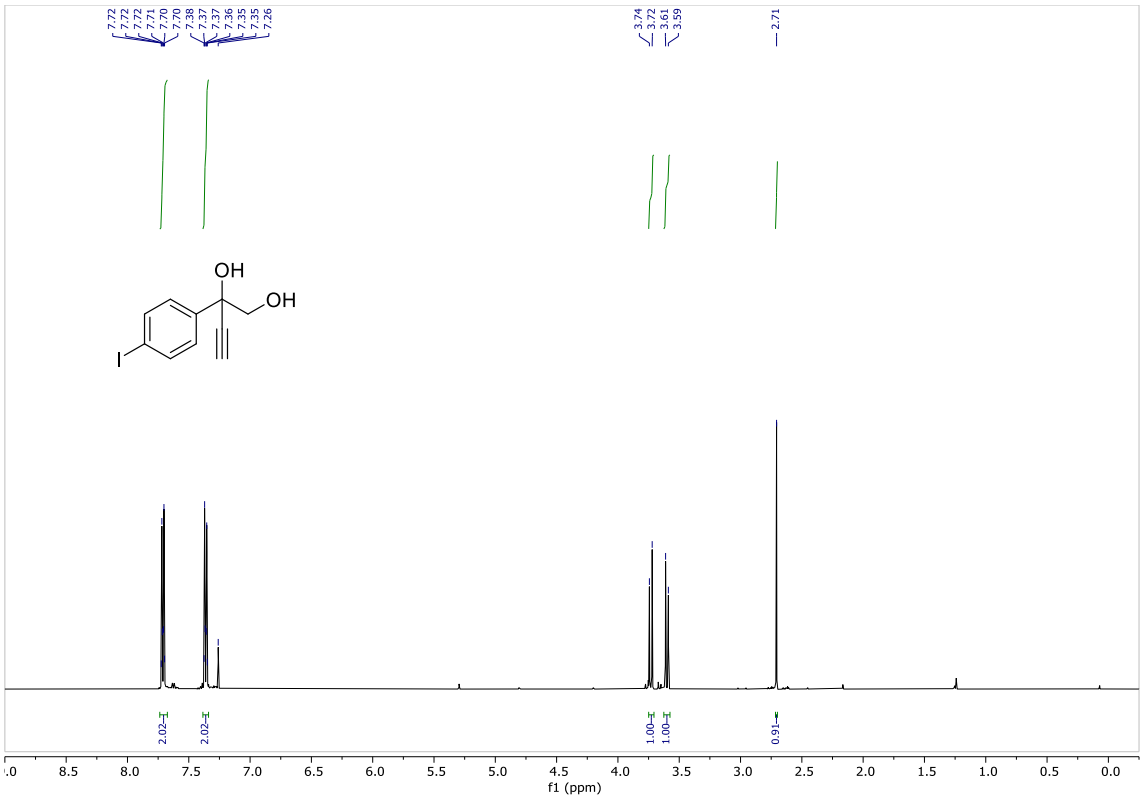
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **1d**



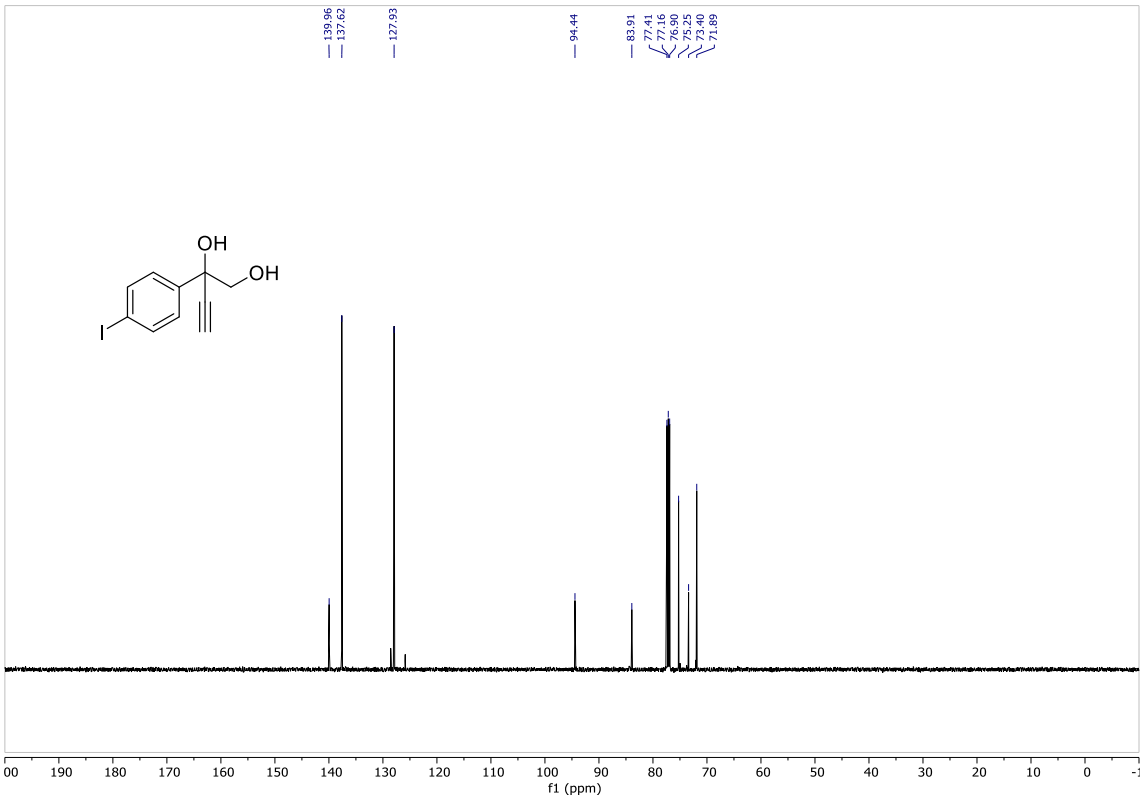
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **1d**



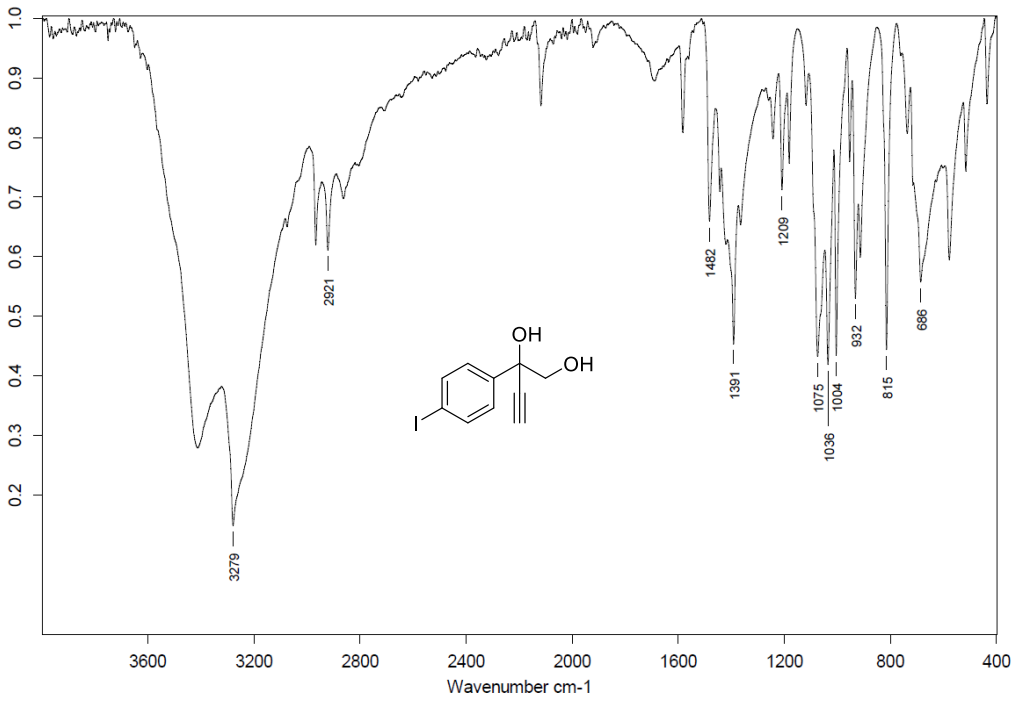
IR (neat) spectrum for **1d**



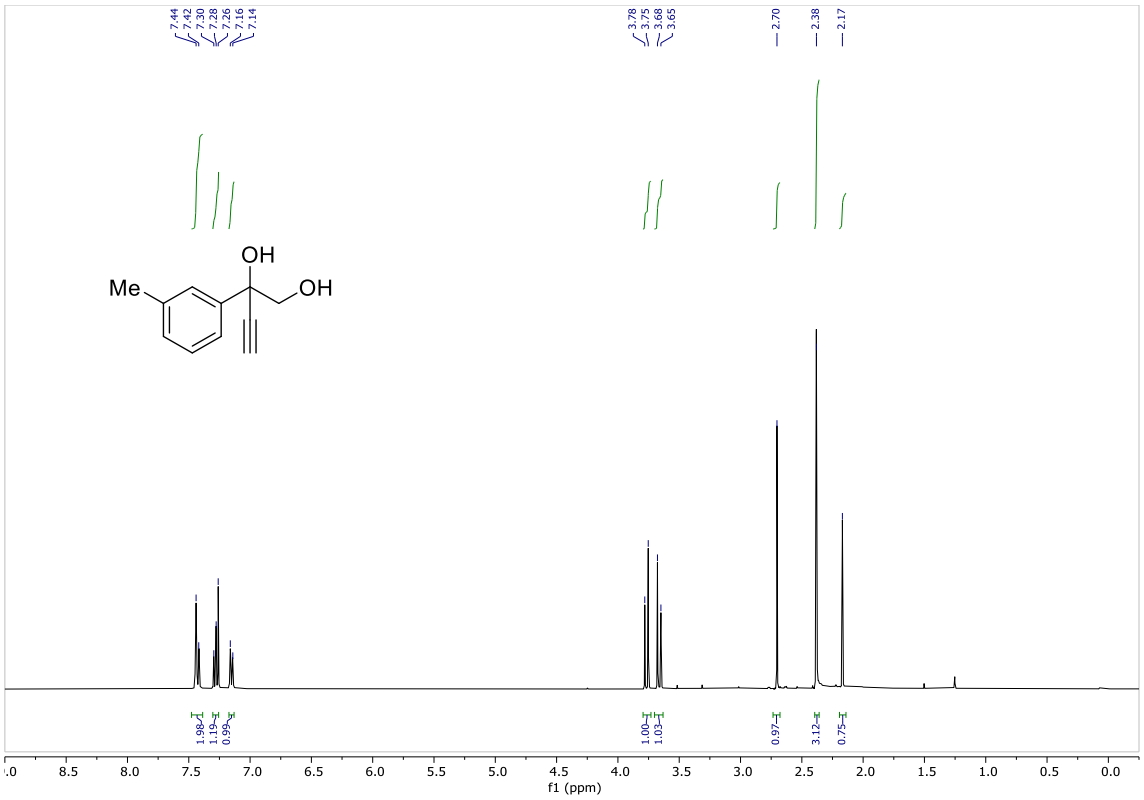
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **1h**



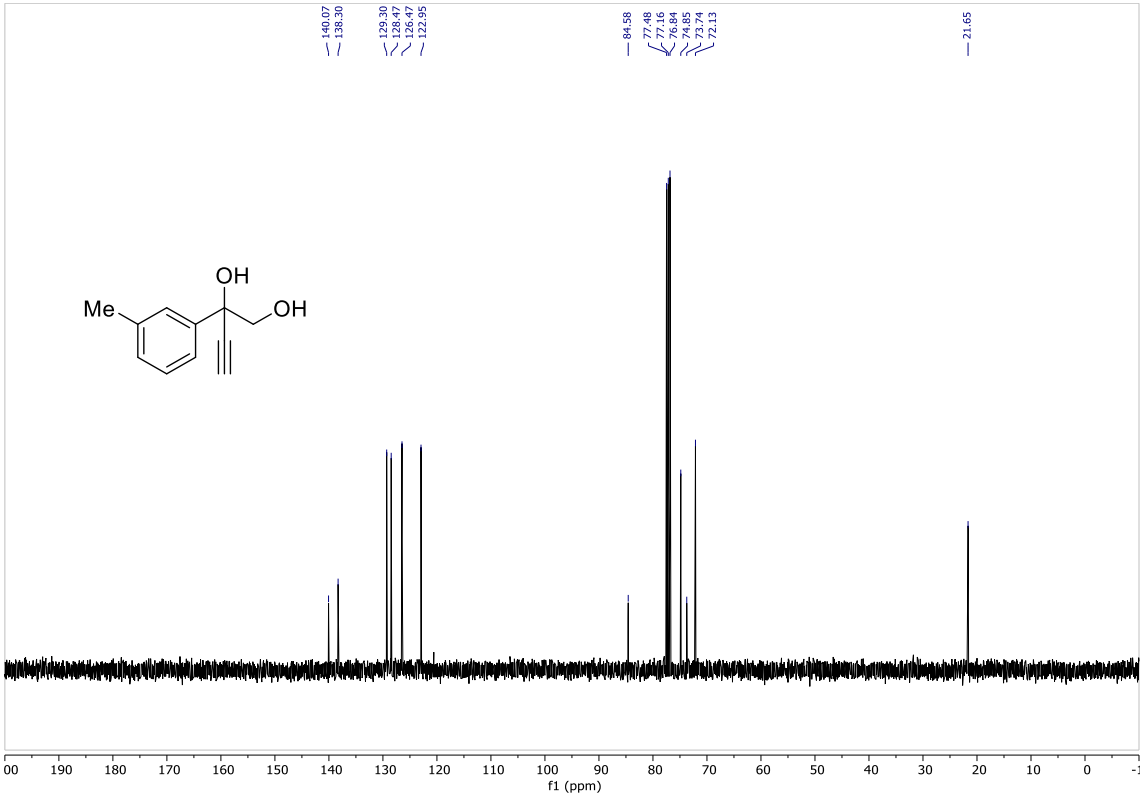
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **1h**



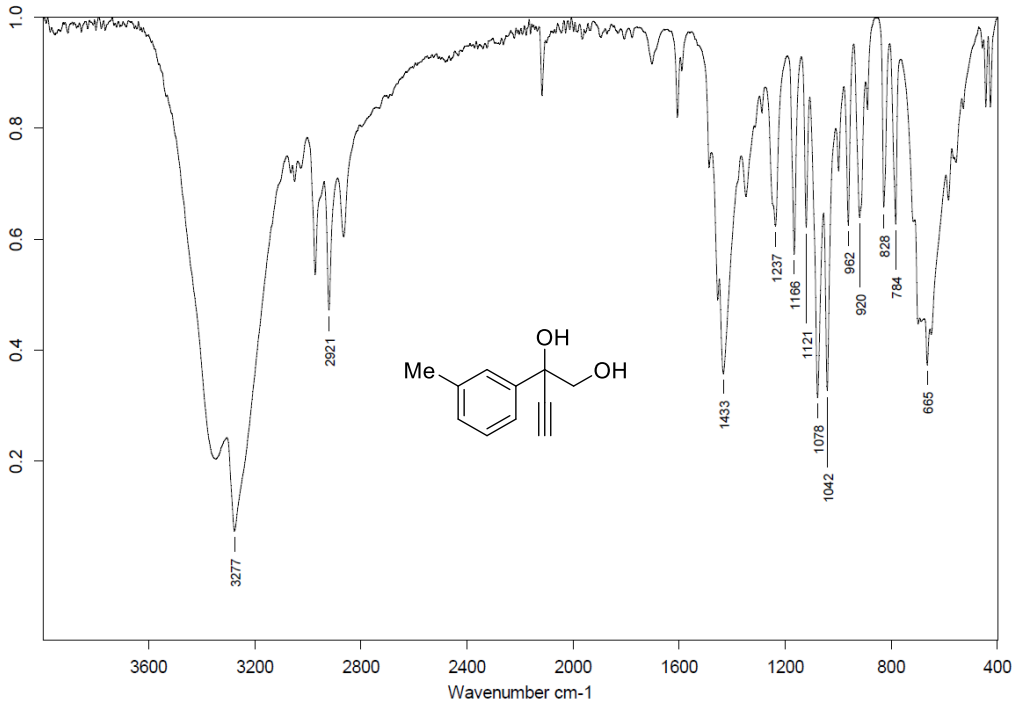
IR (neat) spectrum for **1h**



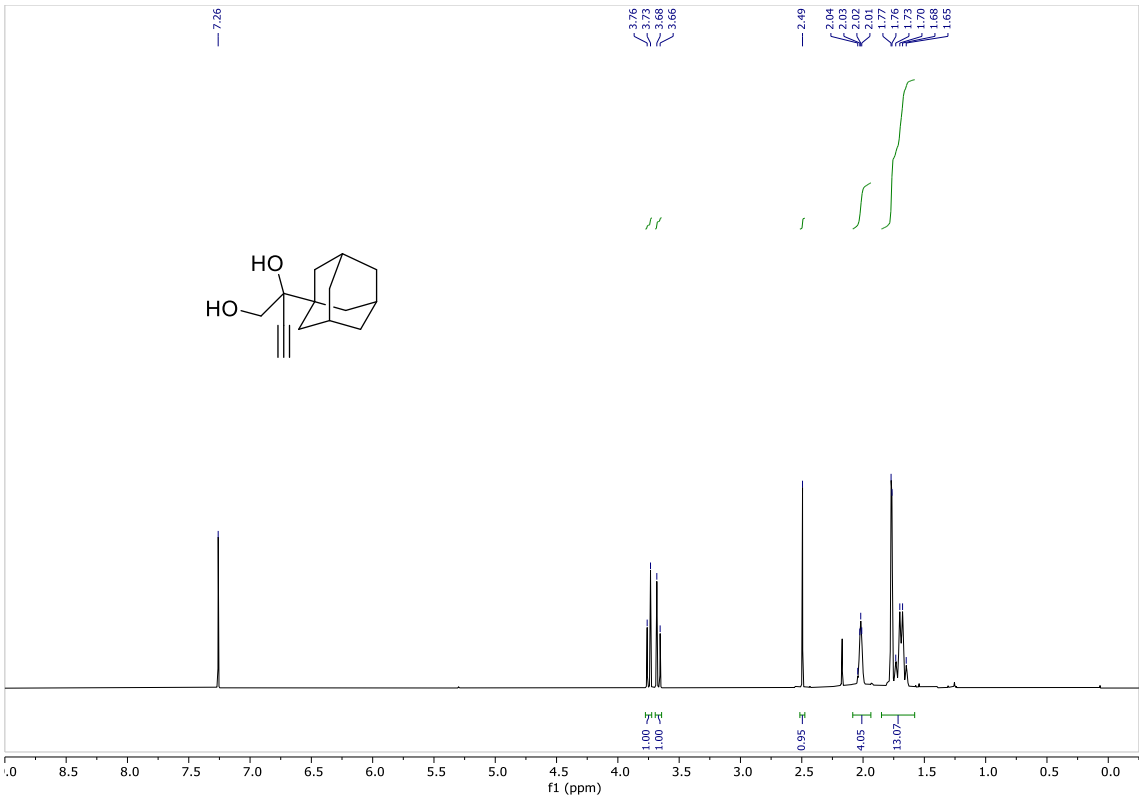
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1k**



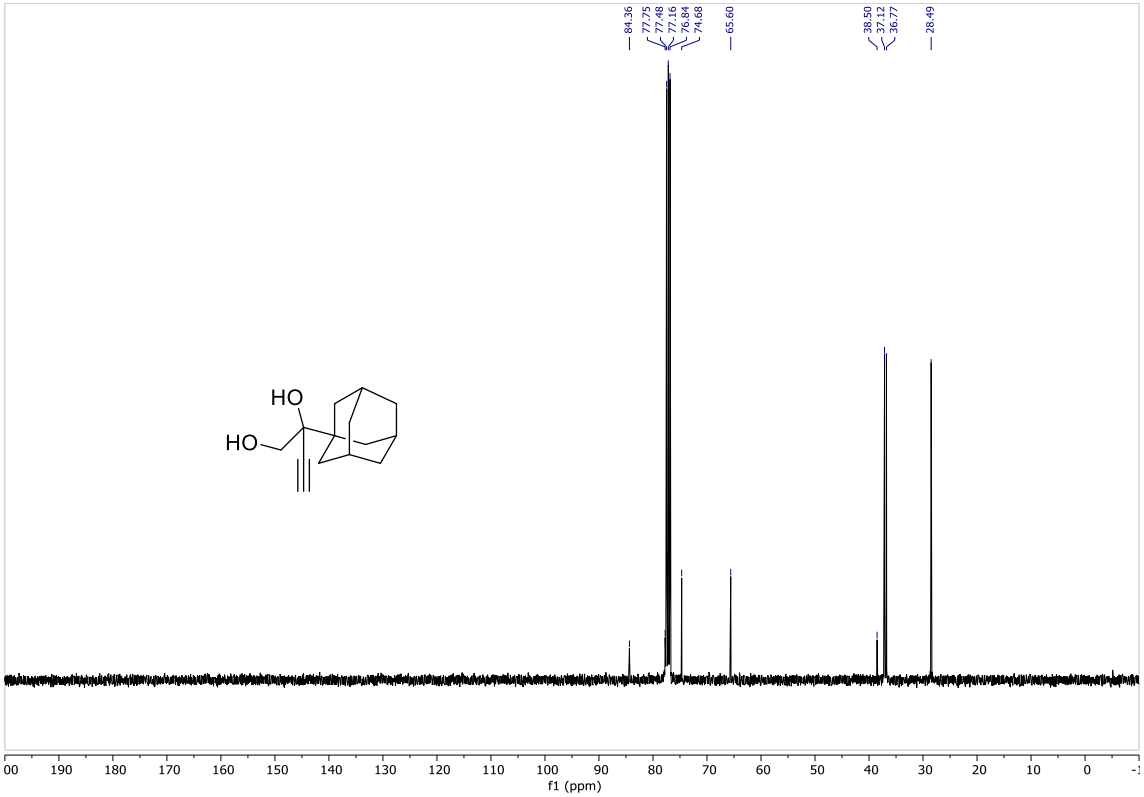
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1k**



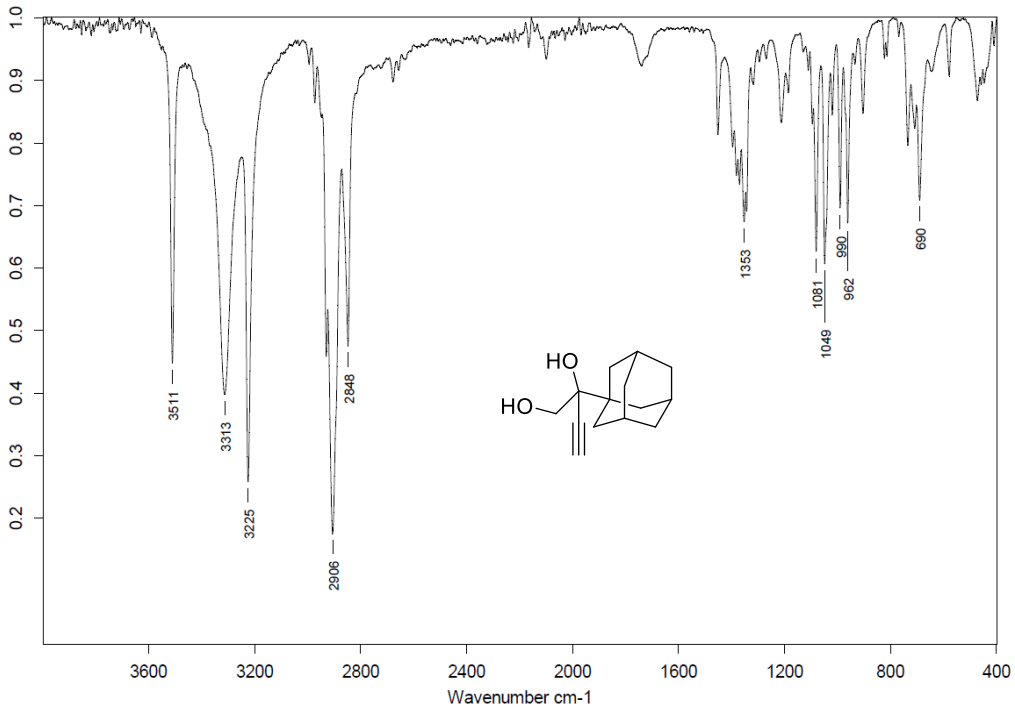
IR (neat) spectrum for **1k**



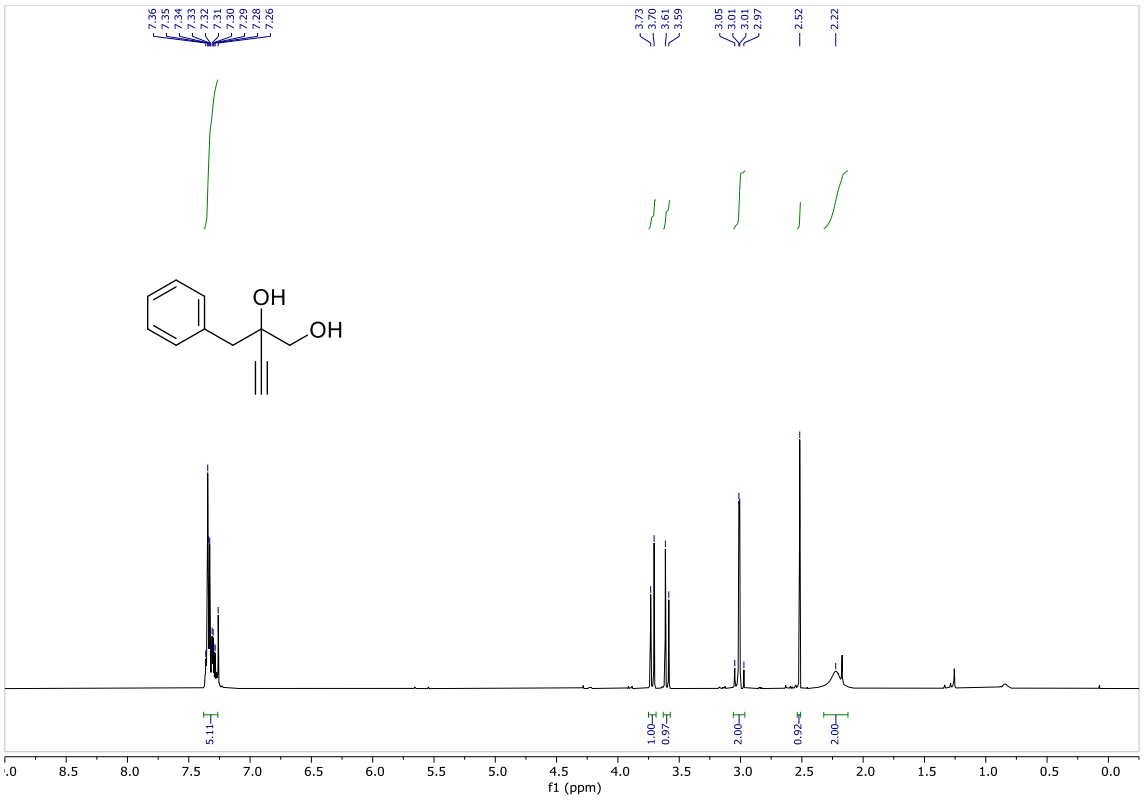
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1r**



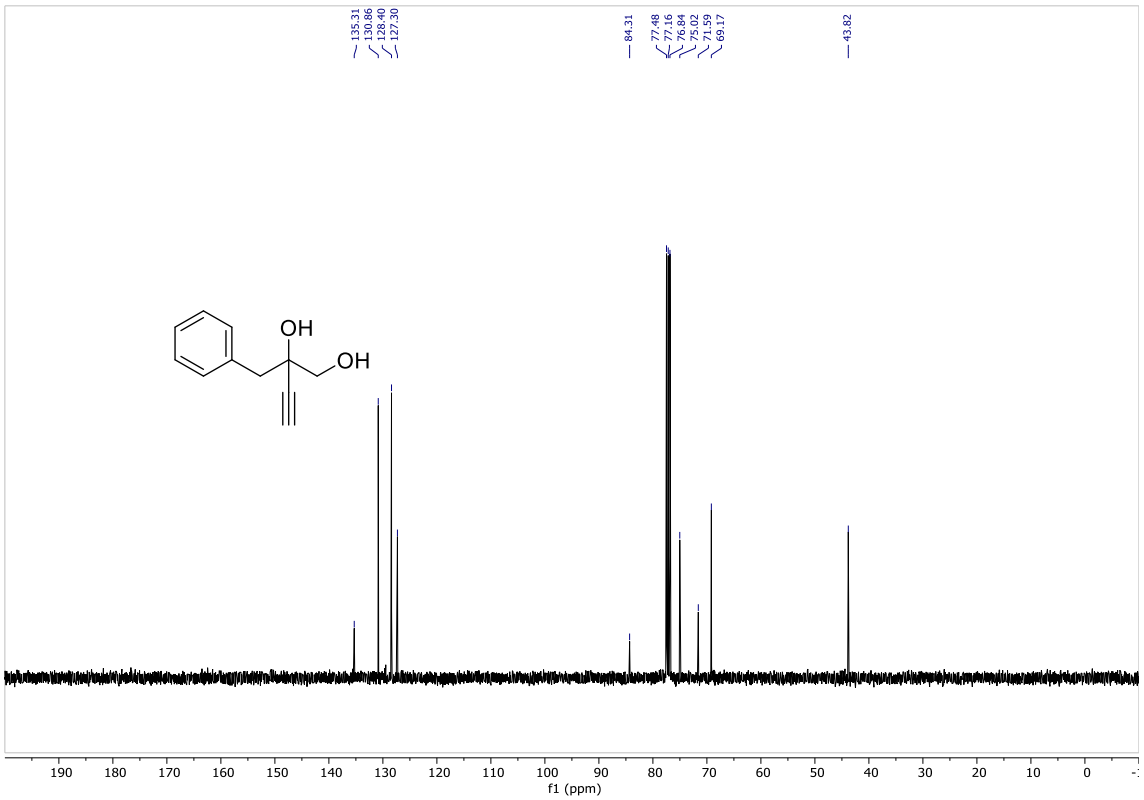
^{13}H NMR (101 MHz, $CDCl_3$) spectrum for **1r**



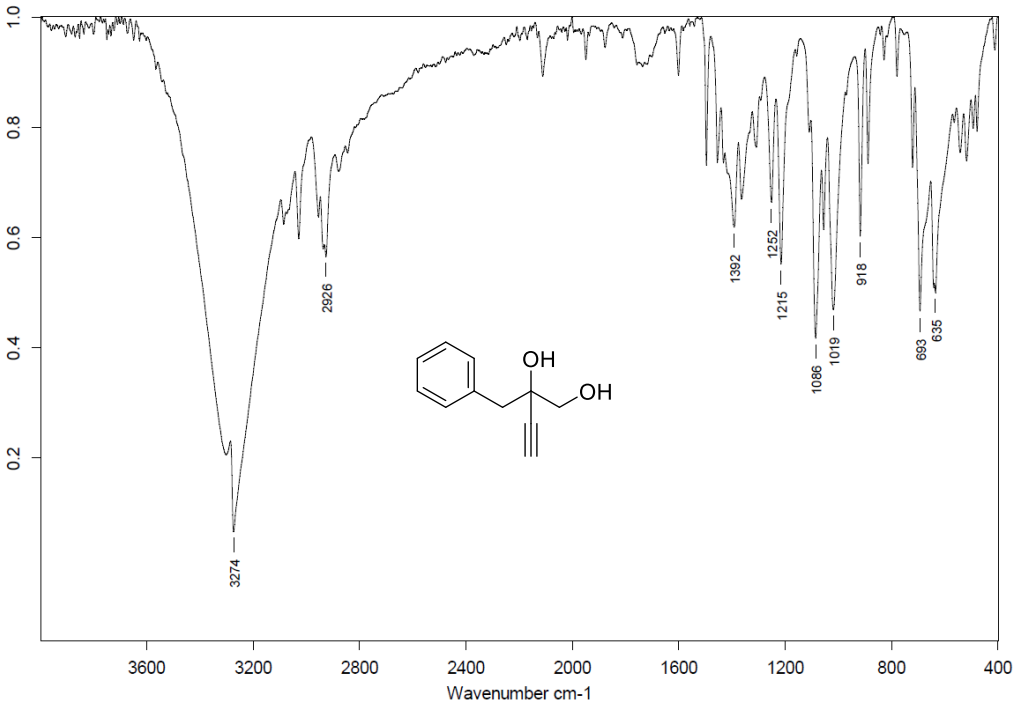
IR (neat) spectrum for **1r**



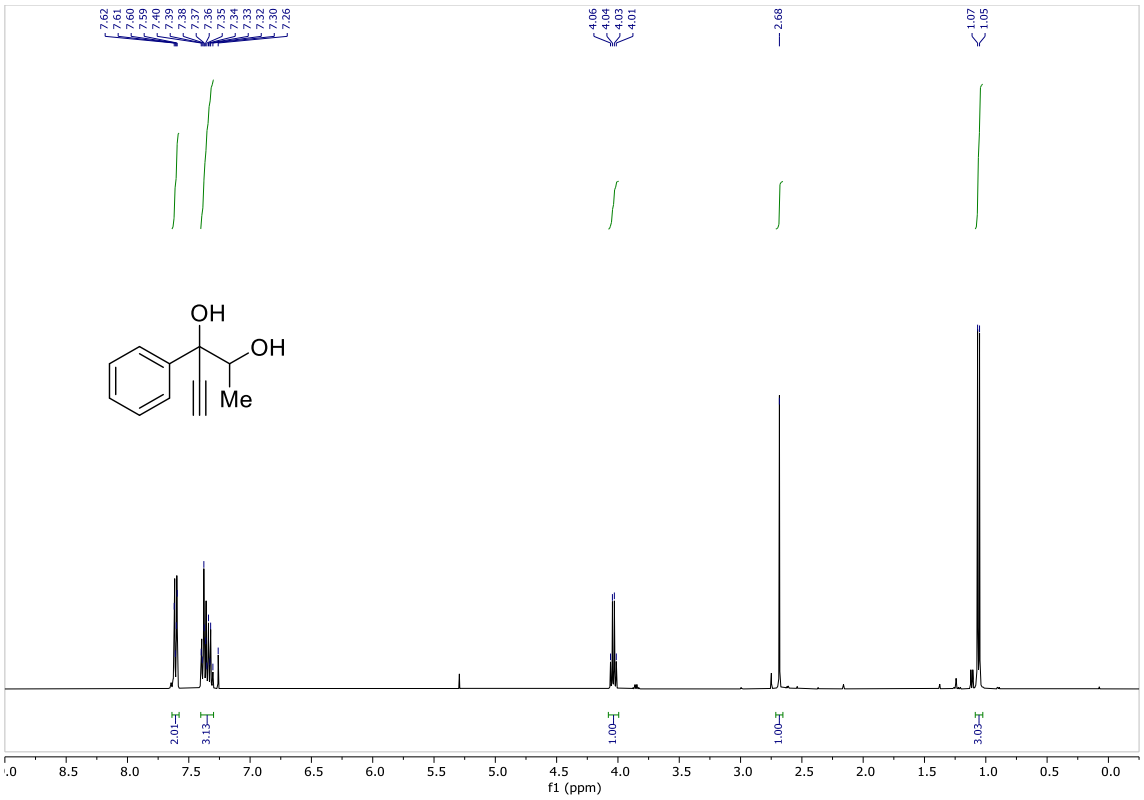
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1s**



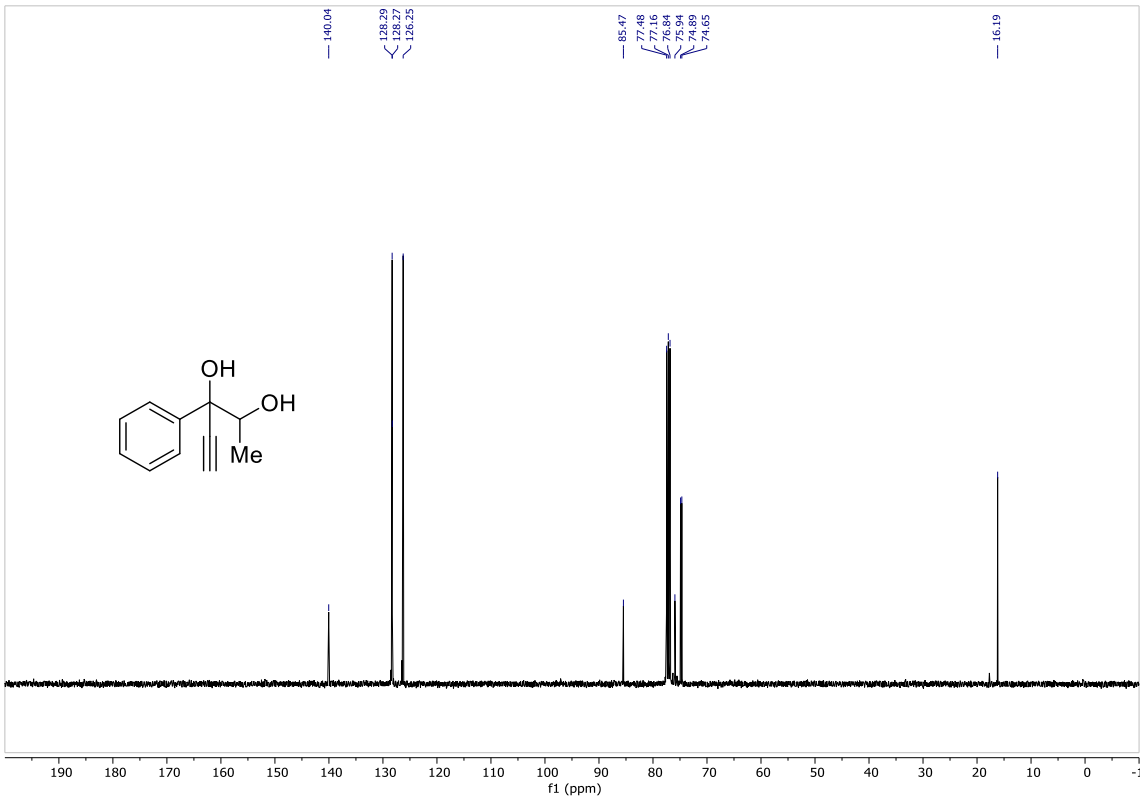
^{13}C NMR (400 MHz, $CDCl_3$) spectrum for **1s**



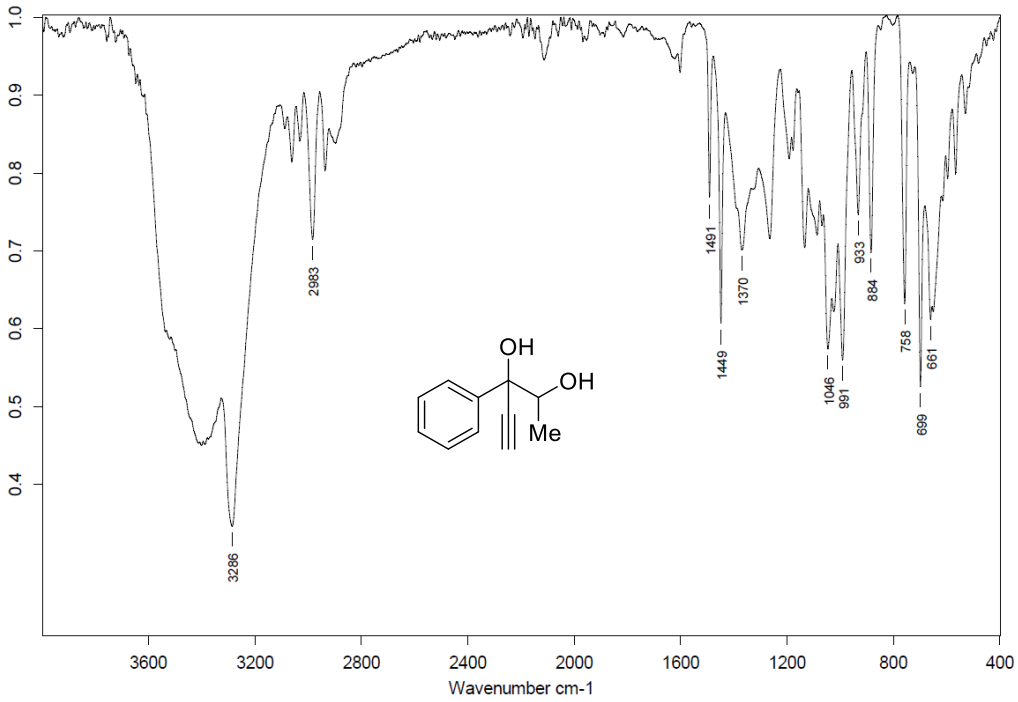
IR (neat) spectrum for **1s**



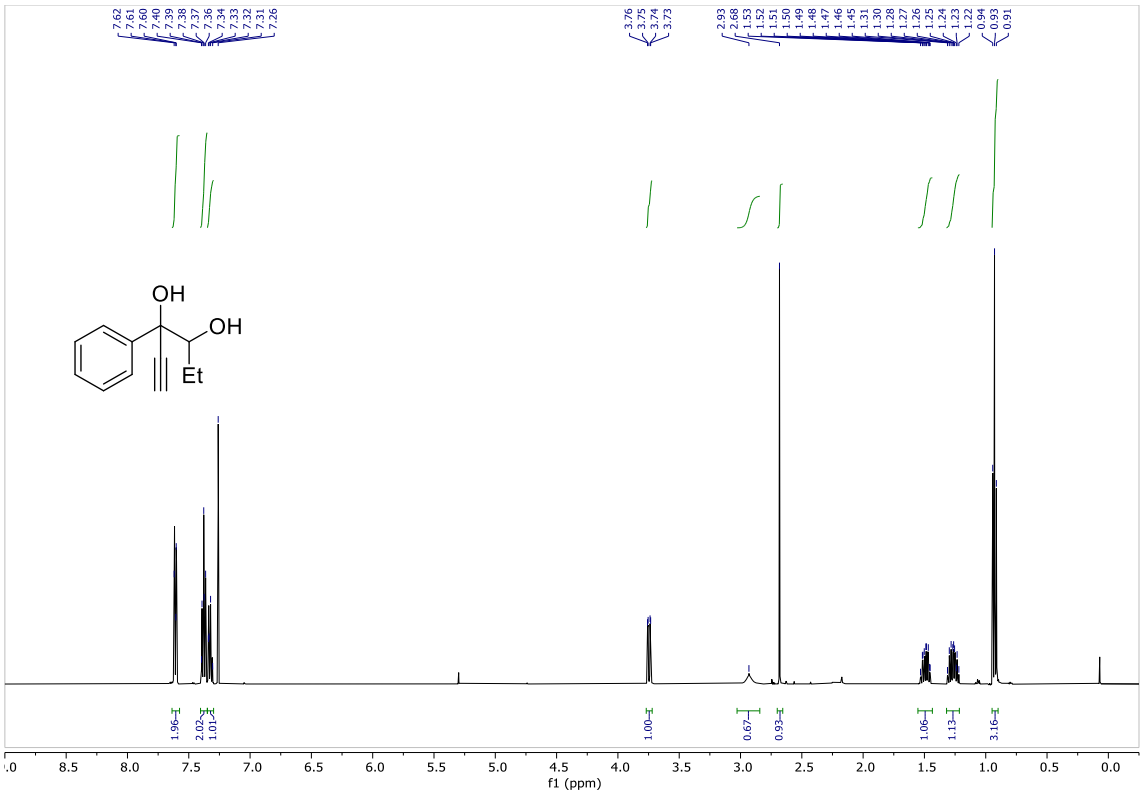
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3b**



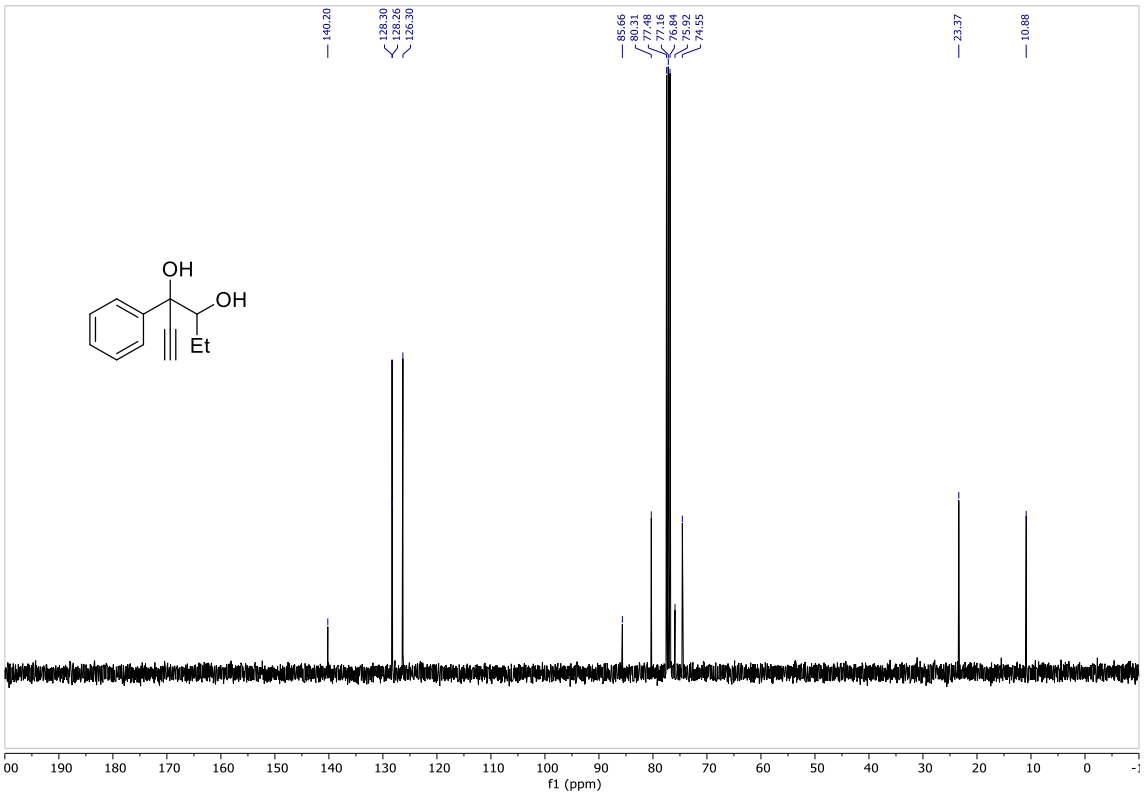
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3b**



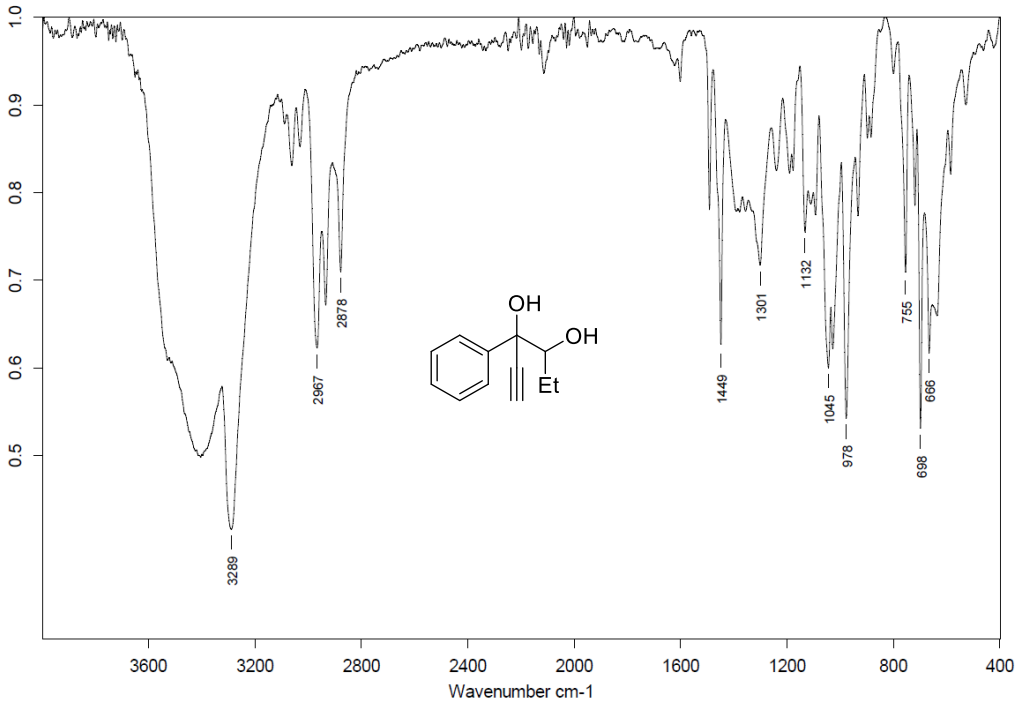
IR (neat) spectrum for **3b**



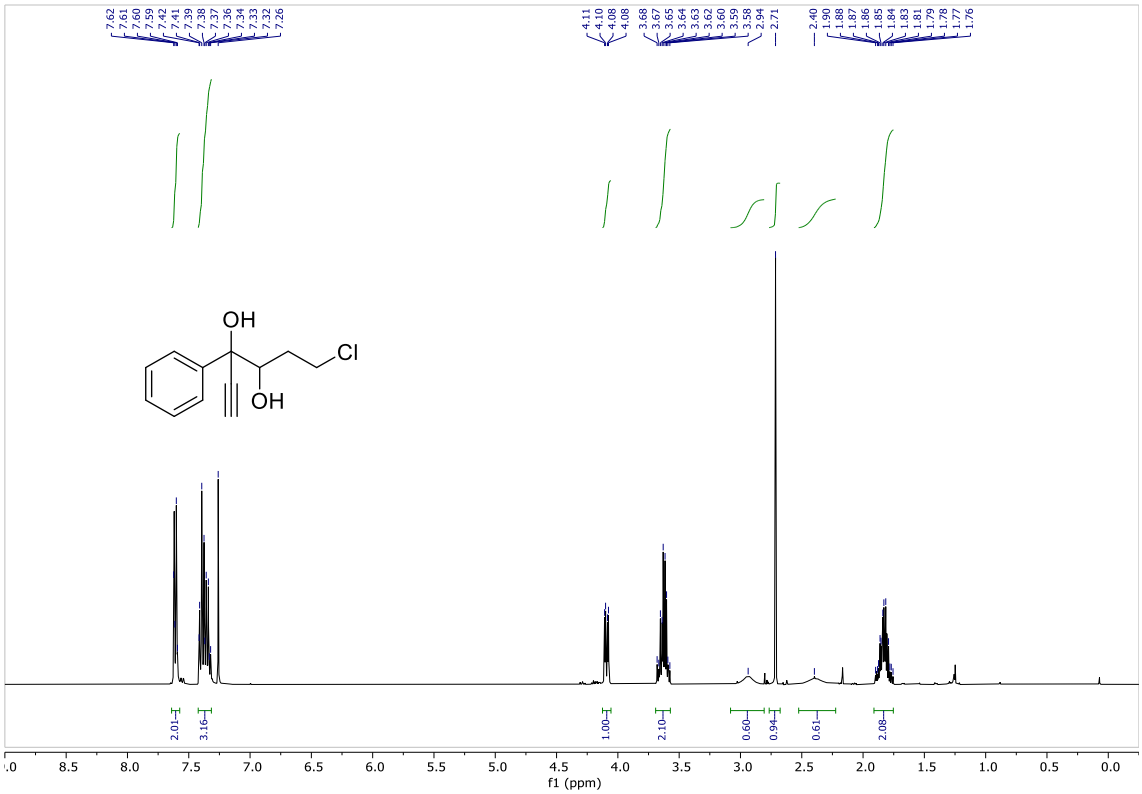
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **3c**



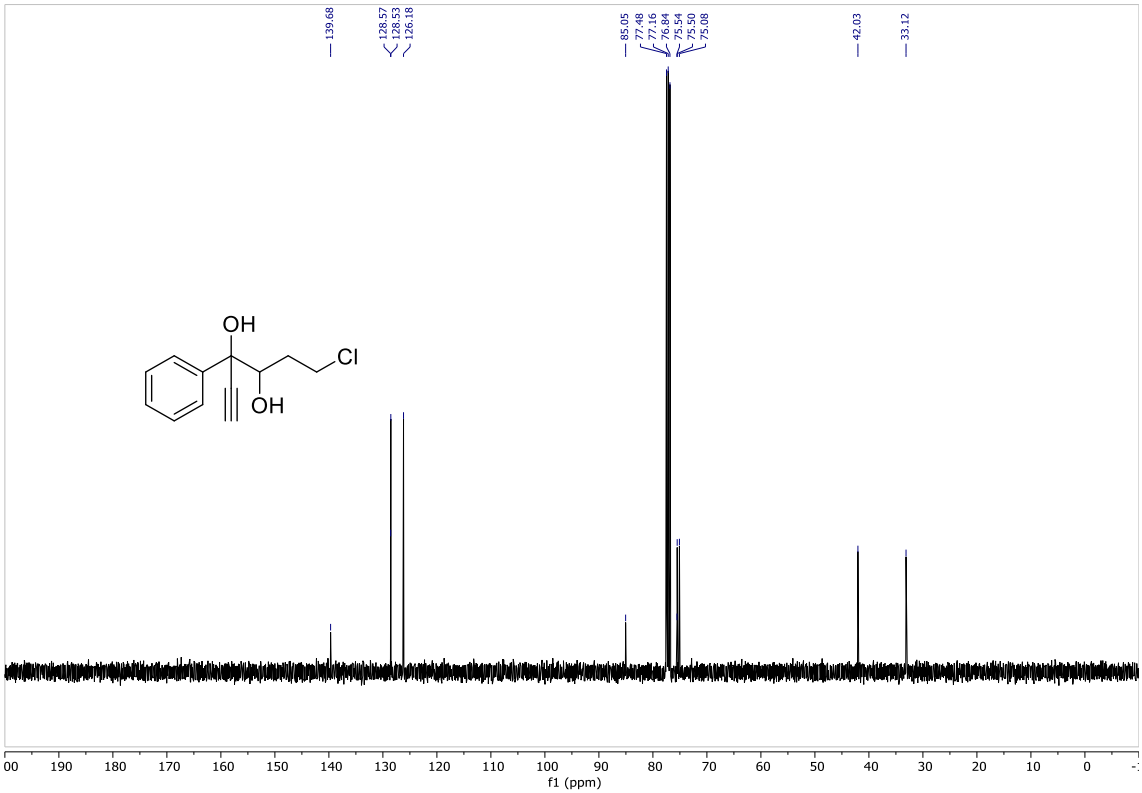
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **3c**



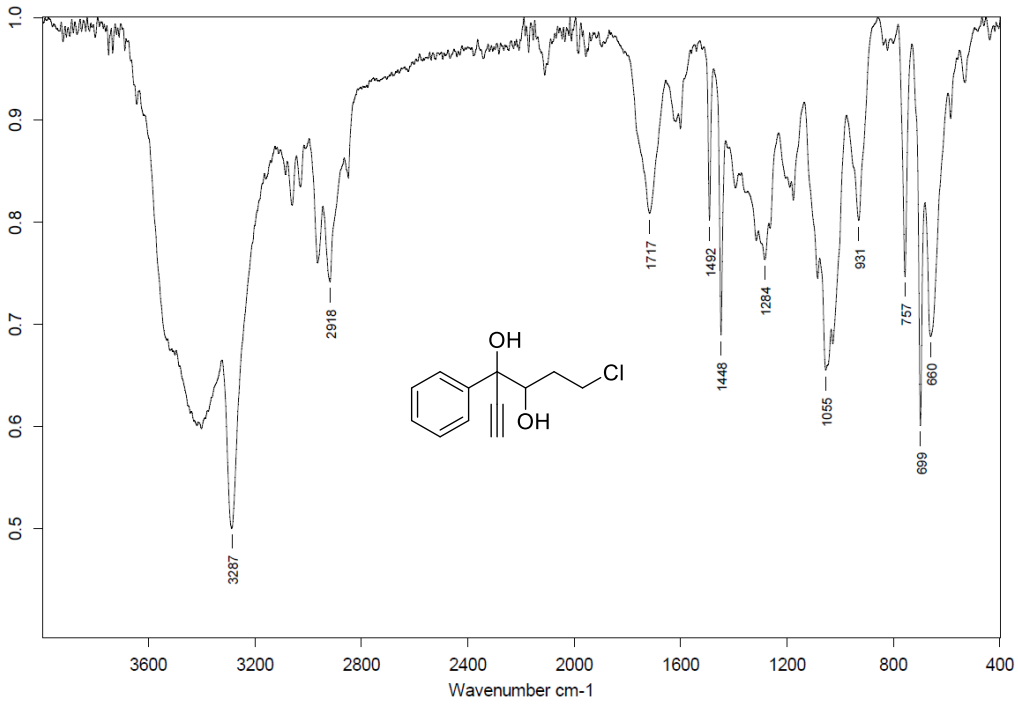
IR (neat) spectrum for **3c**



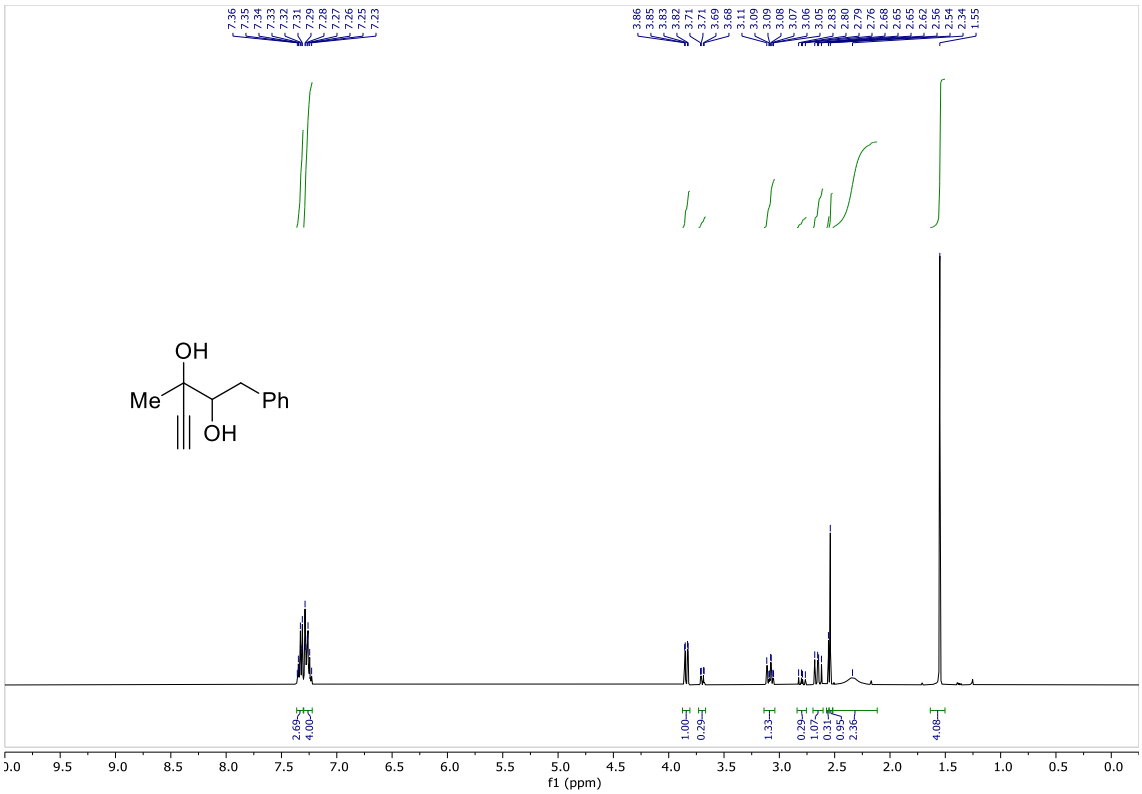
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3d**



^{13}H NMR (101 MHz, $CDCl_3$) spectrum for **3d**



IR (neat) spectrum for **3d**



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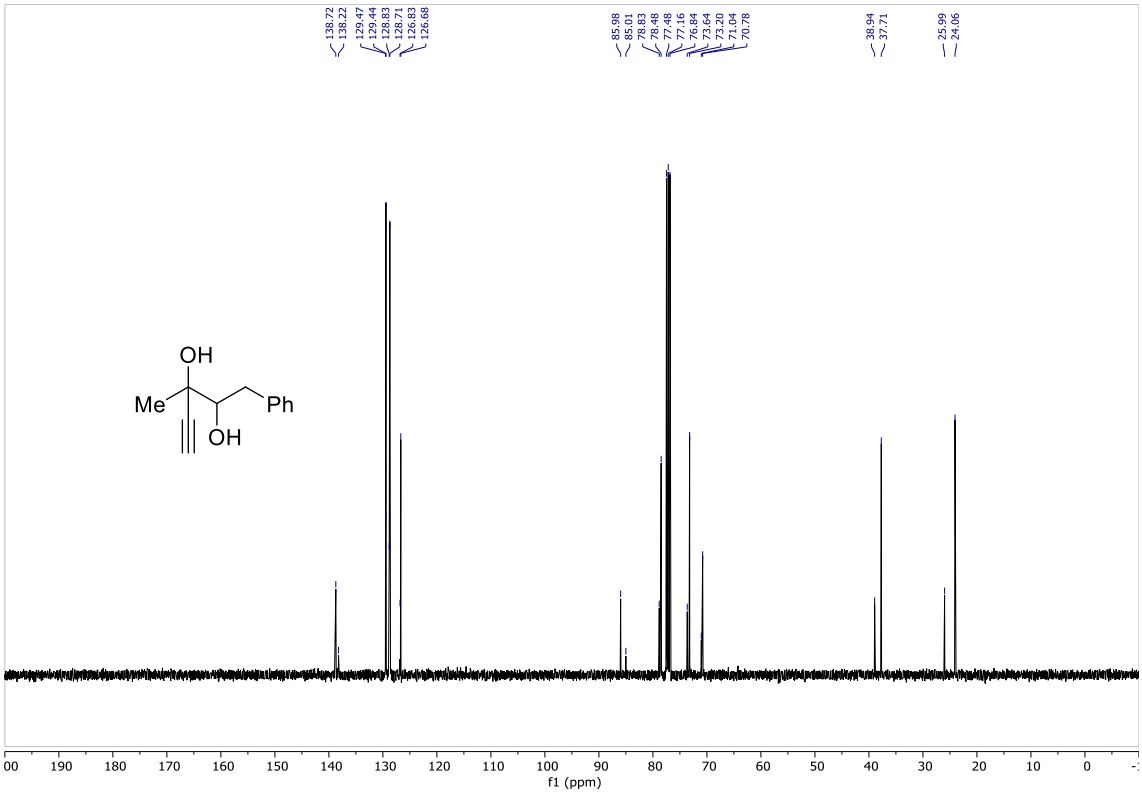
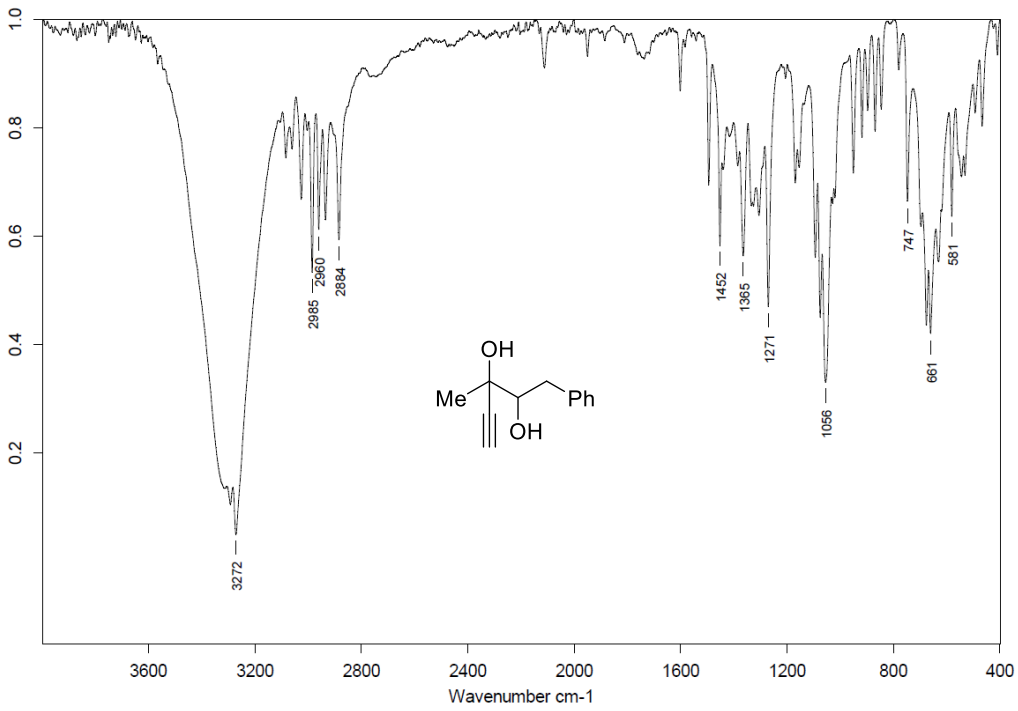
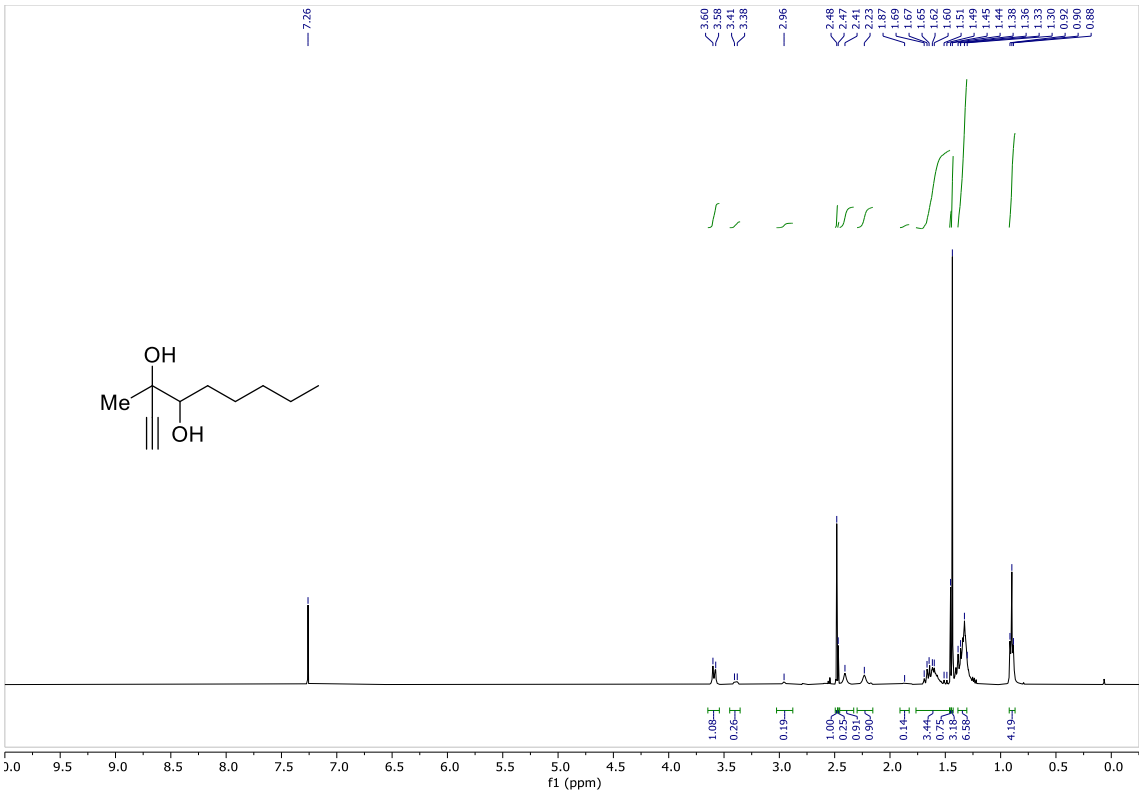


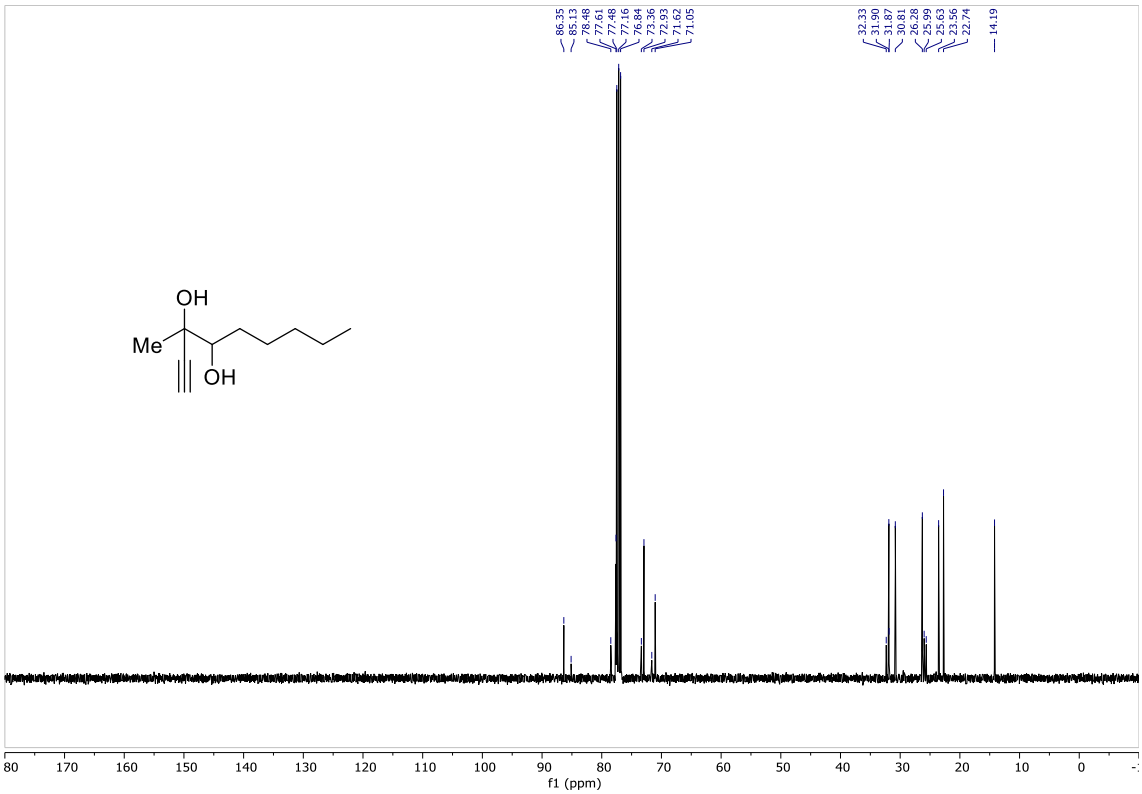
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3e**



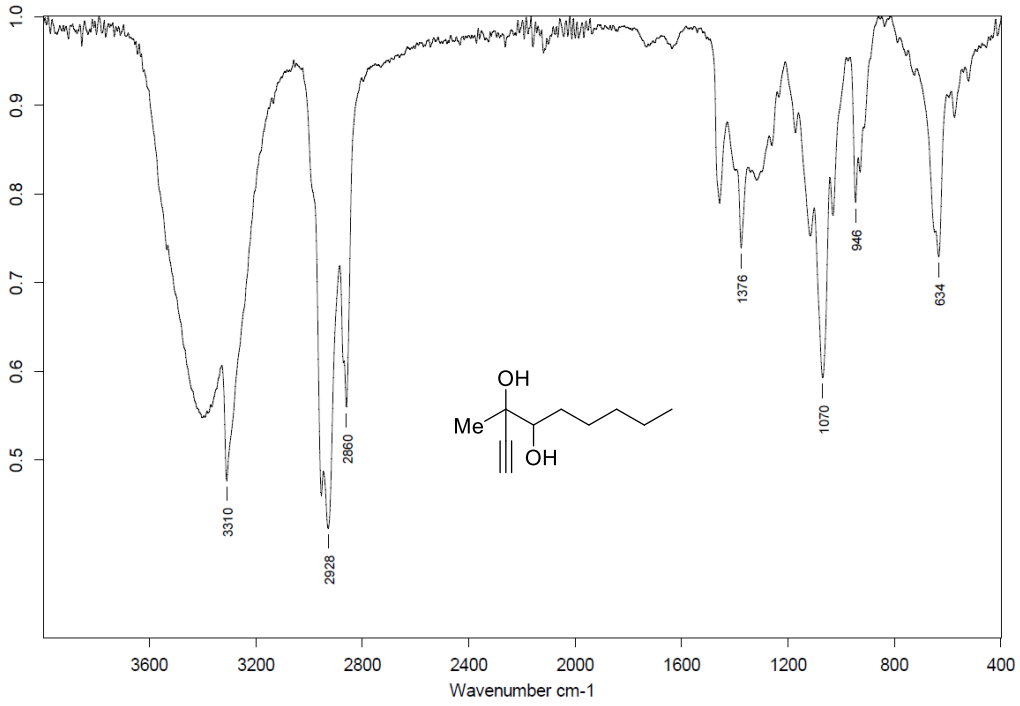
IR (neat) spectrum for **3e**



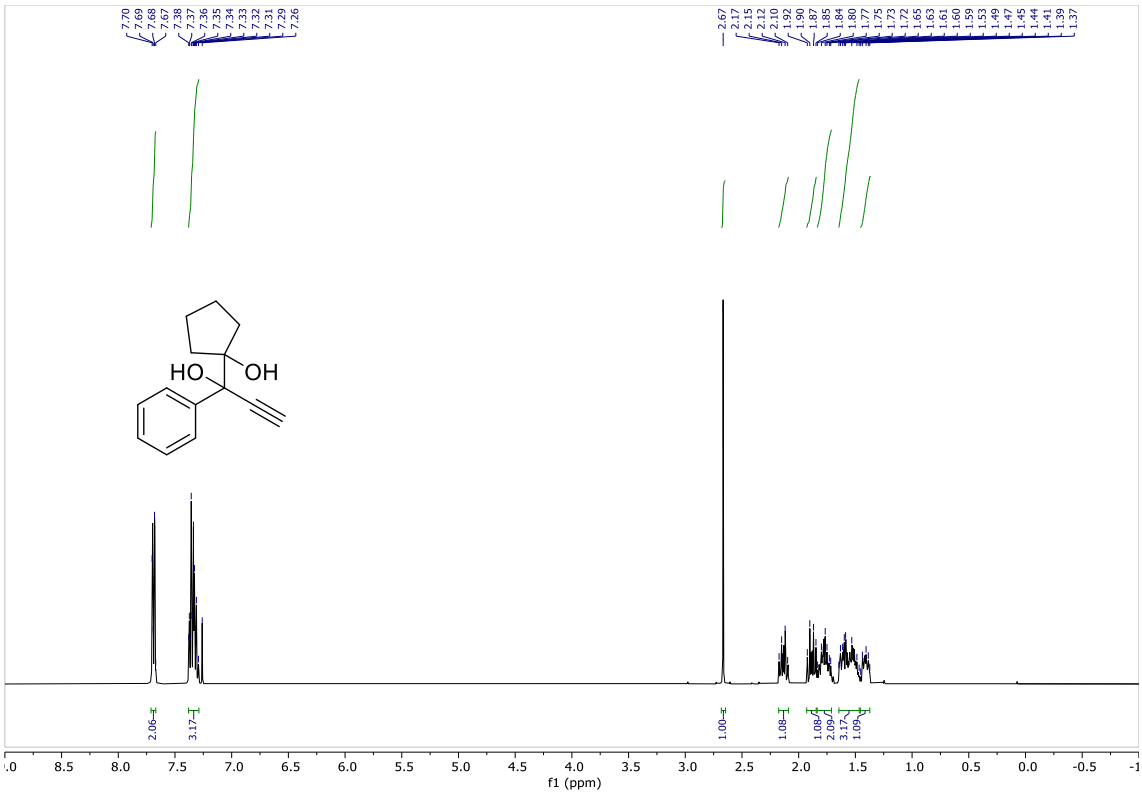
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3g**



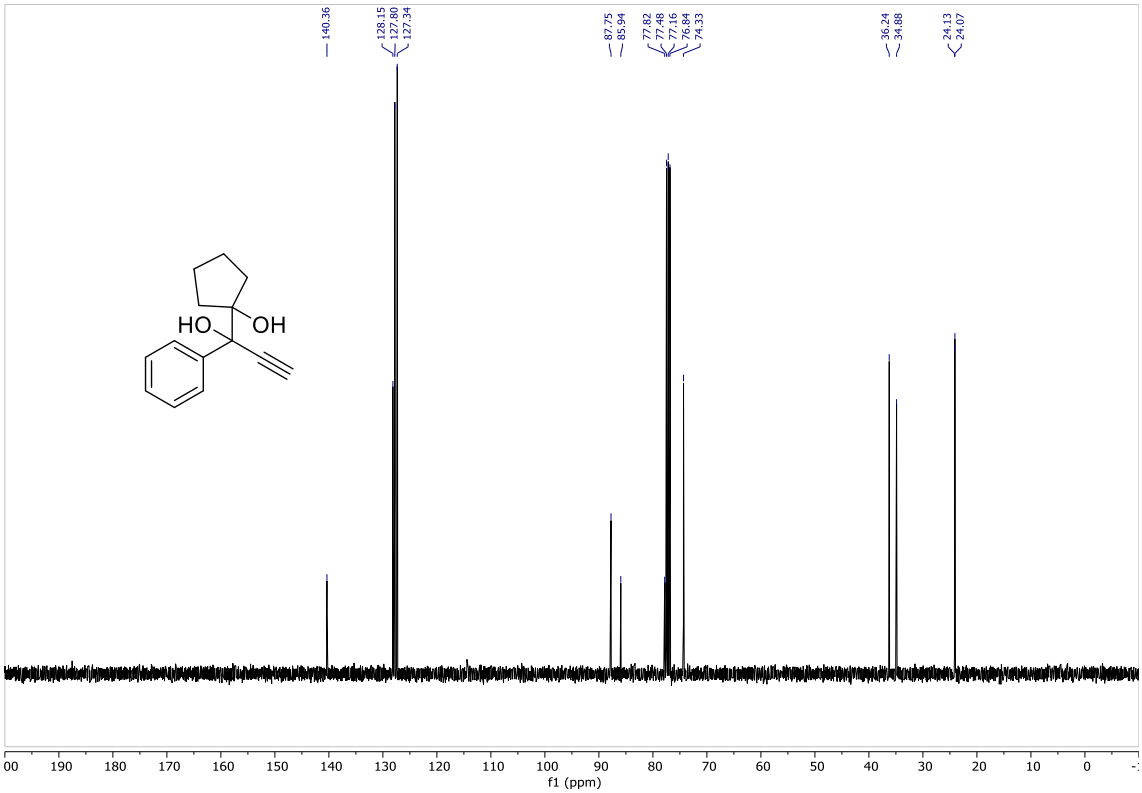
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3g**



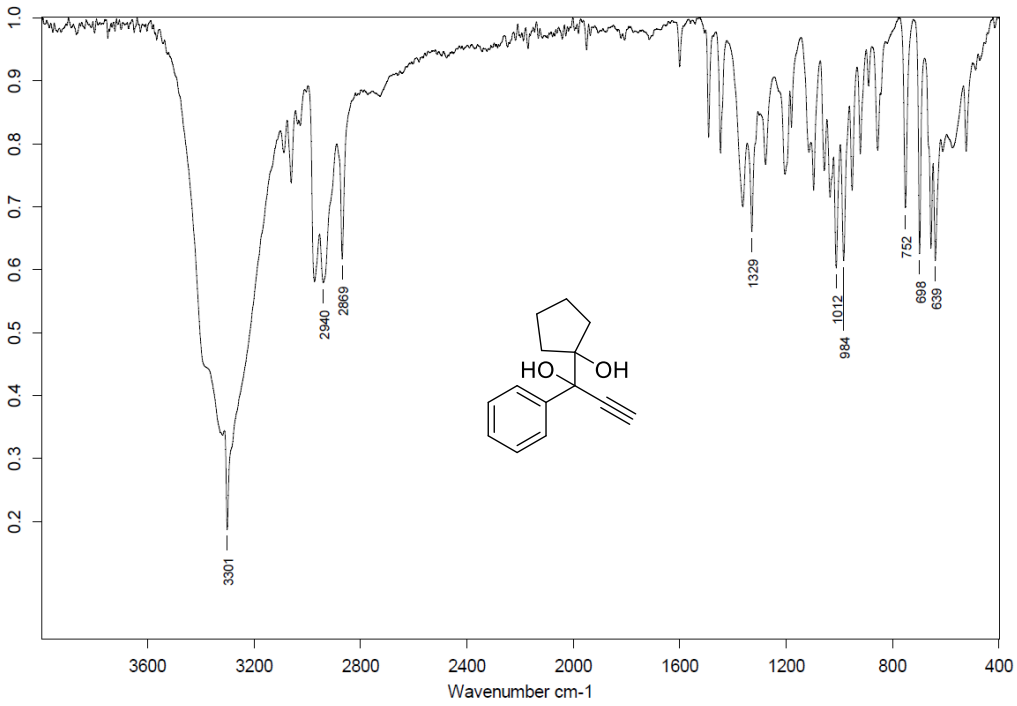
IR (neat) spectrum for **3g**



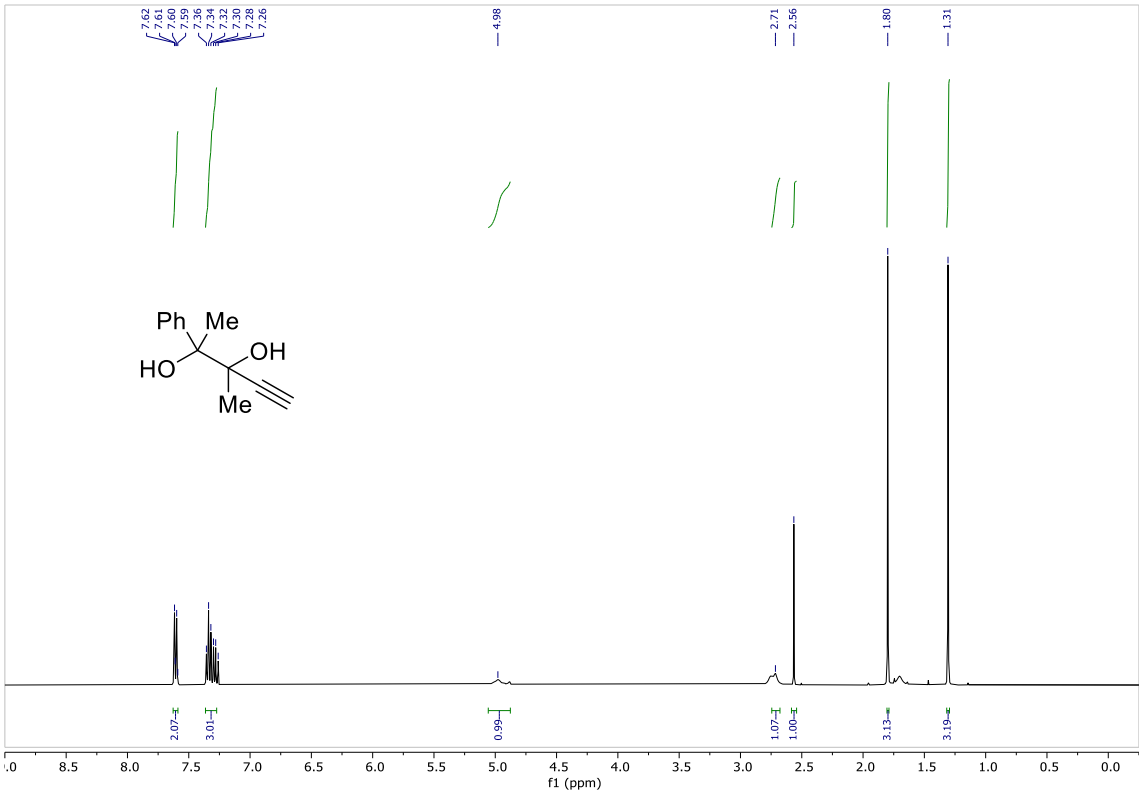
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3i**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3i**



IR (neat) spectrum for **3i**



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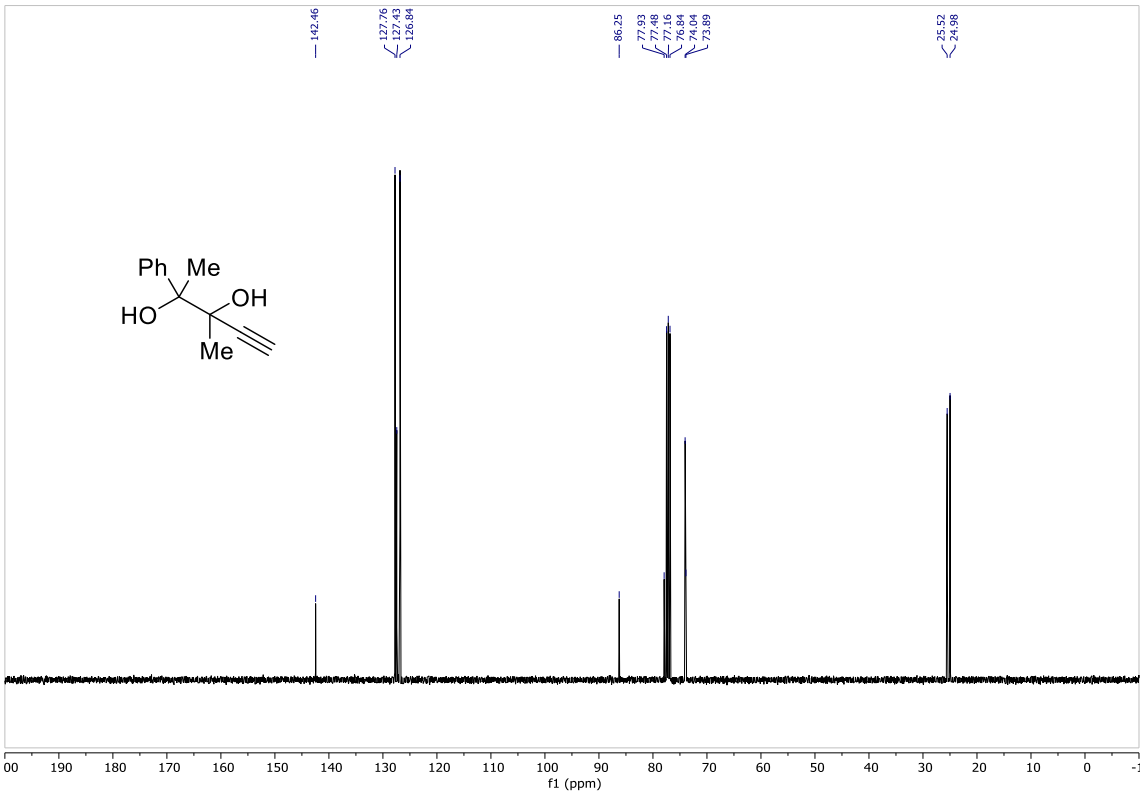
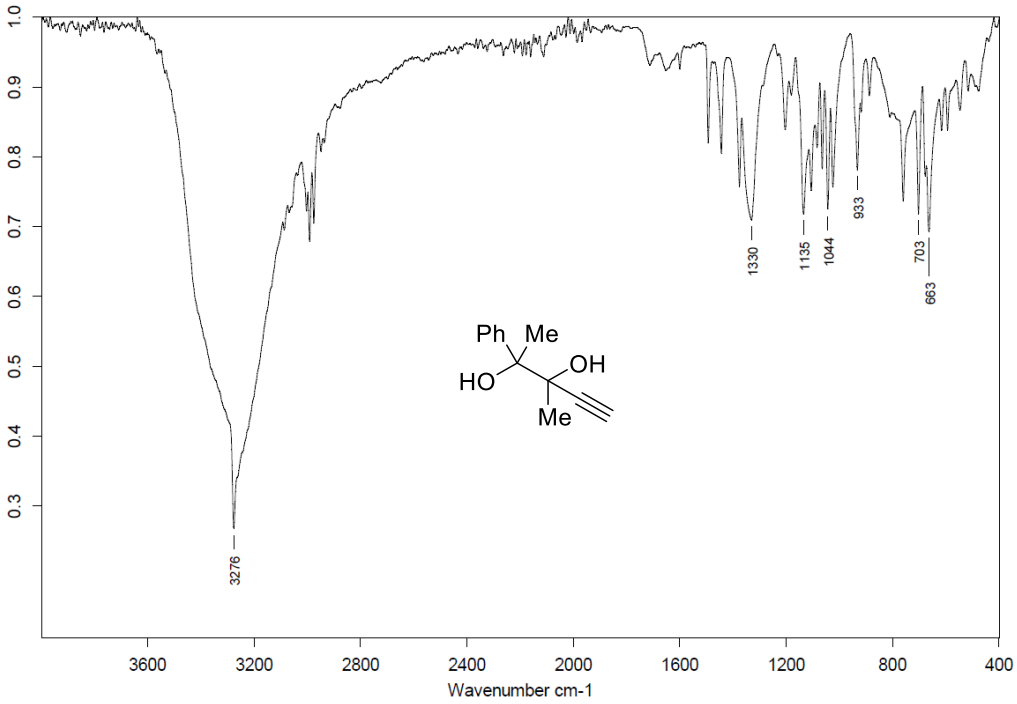
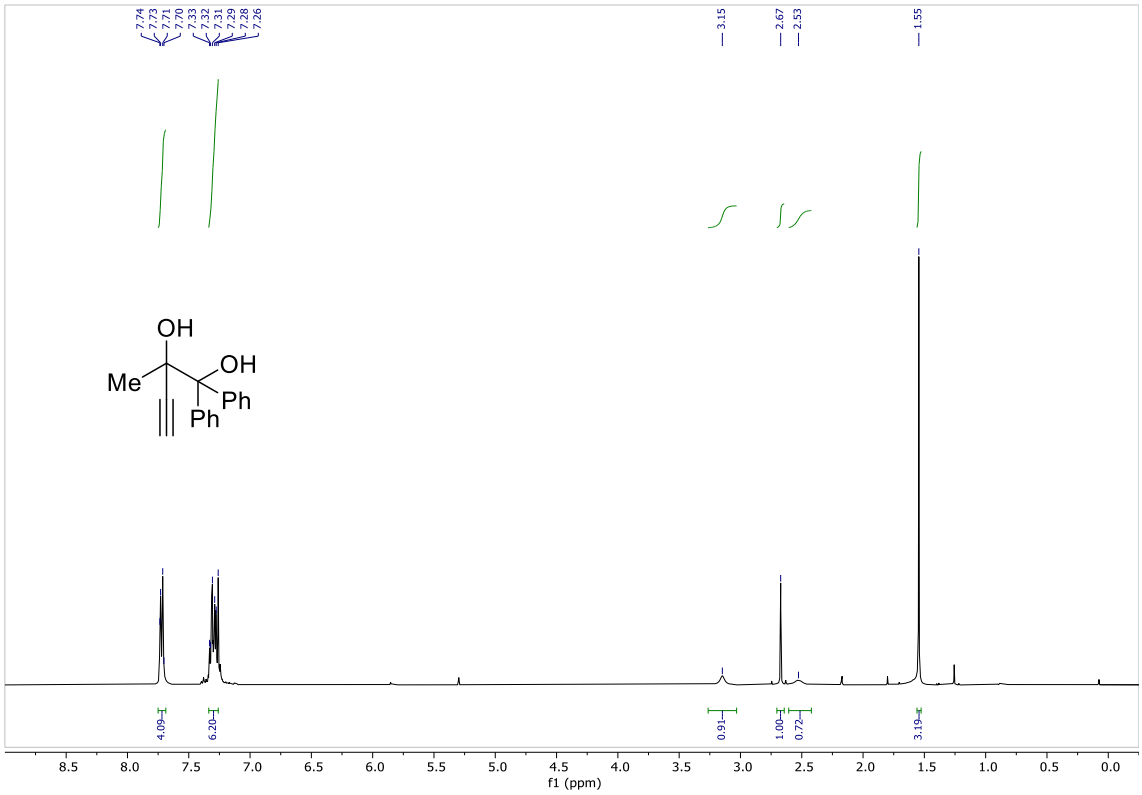


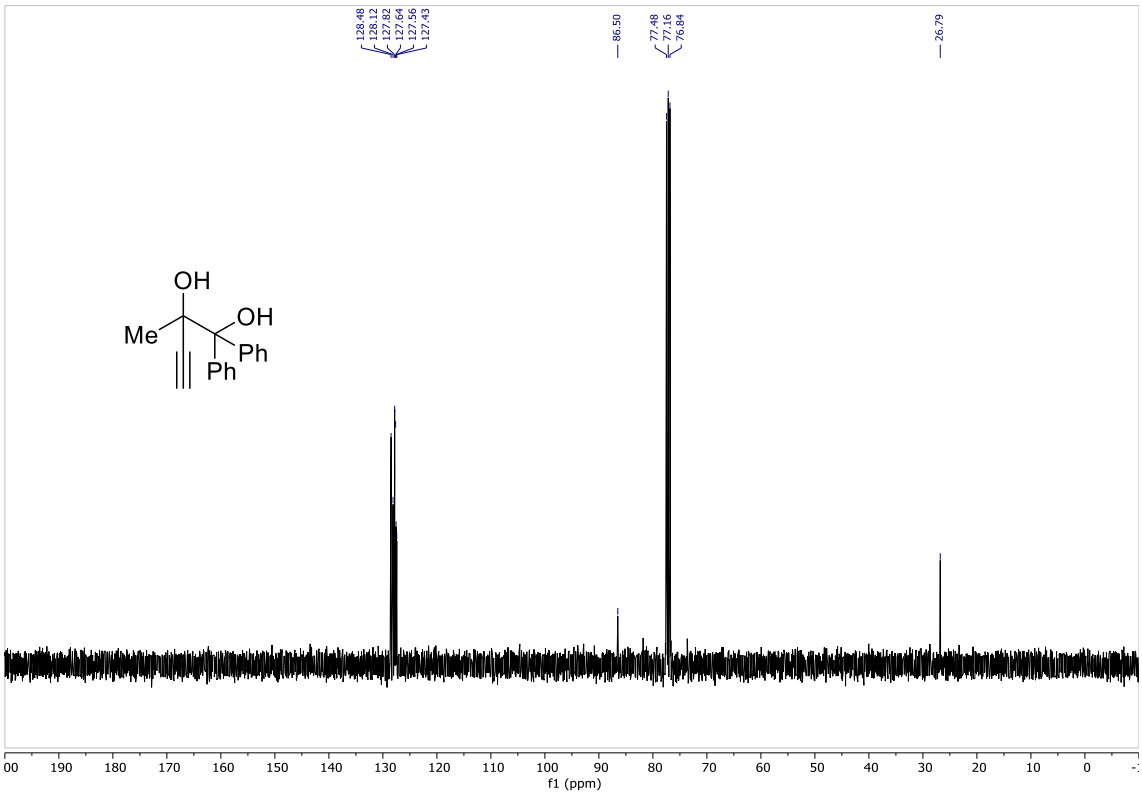
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3k**



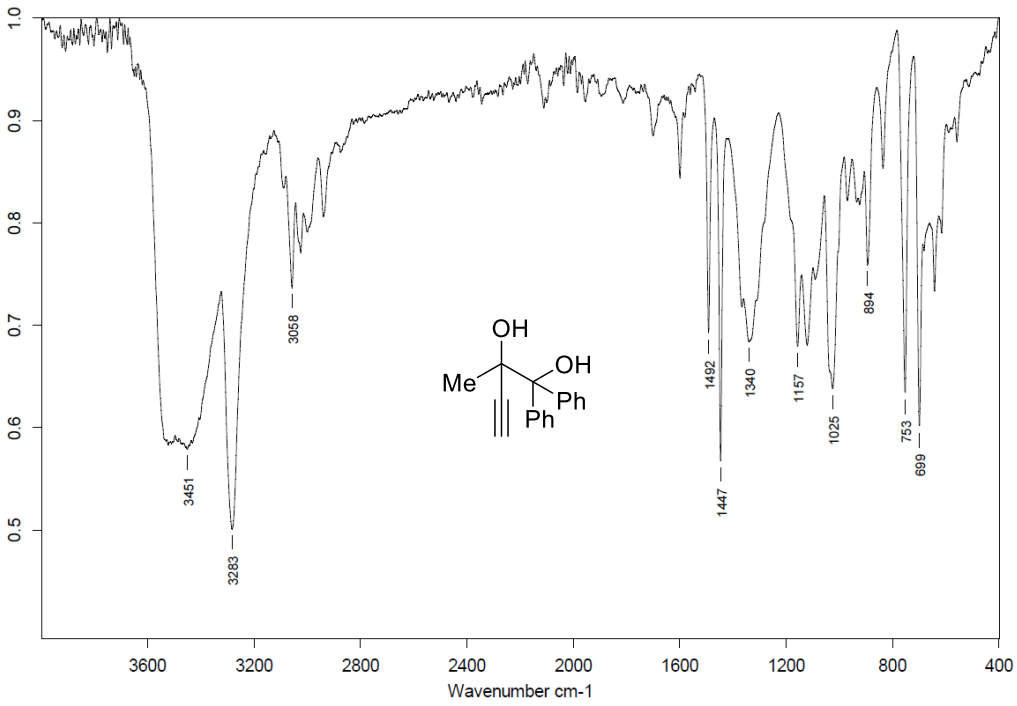
IR (neat) spectrum for **3k**



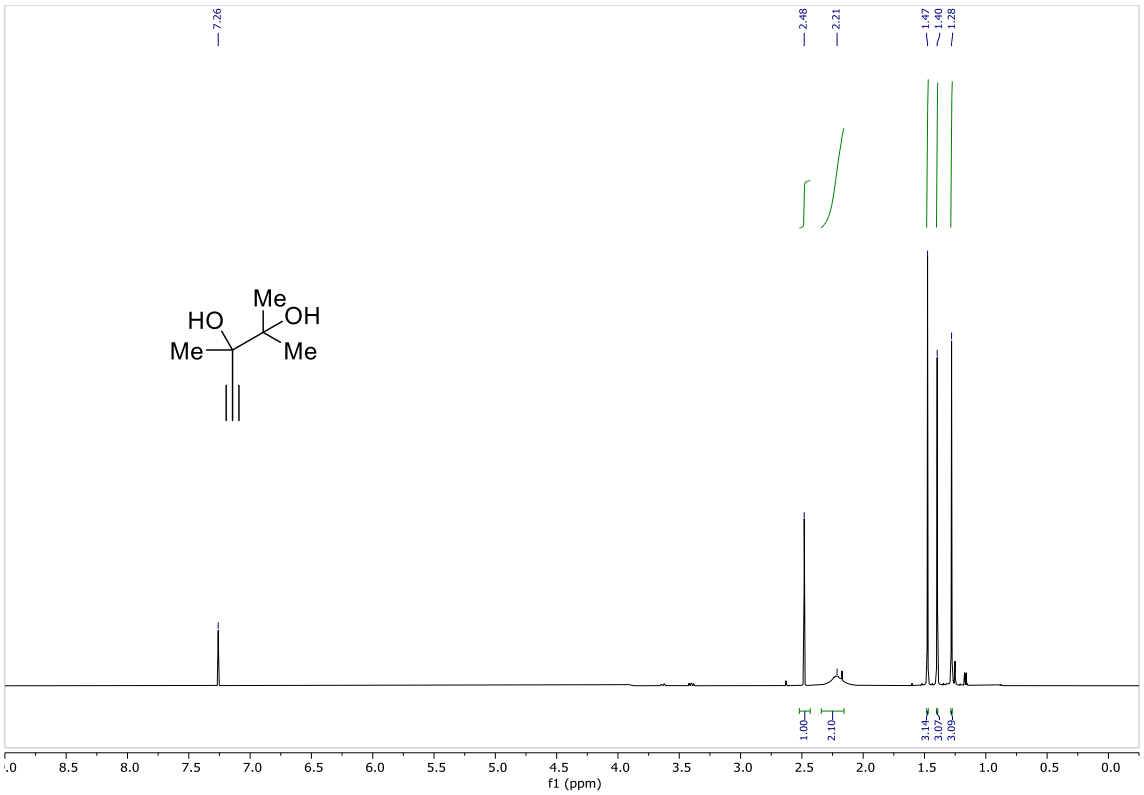
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3l**



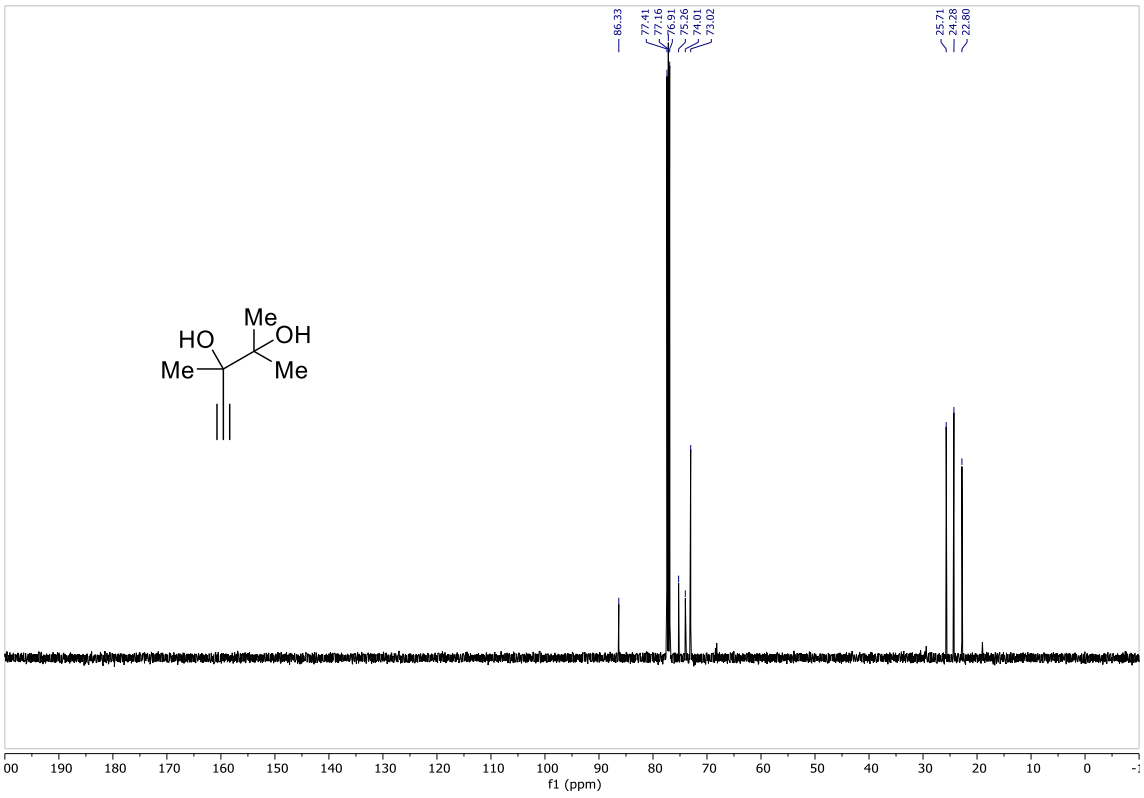
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3l**



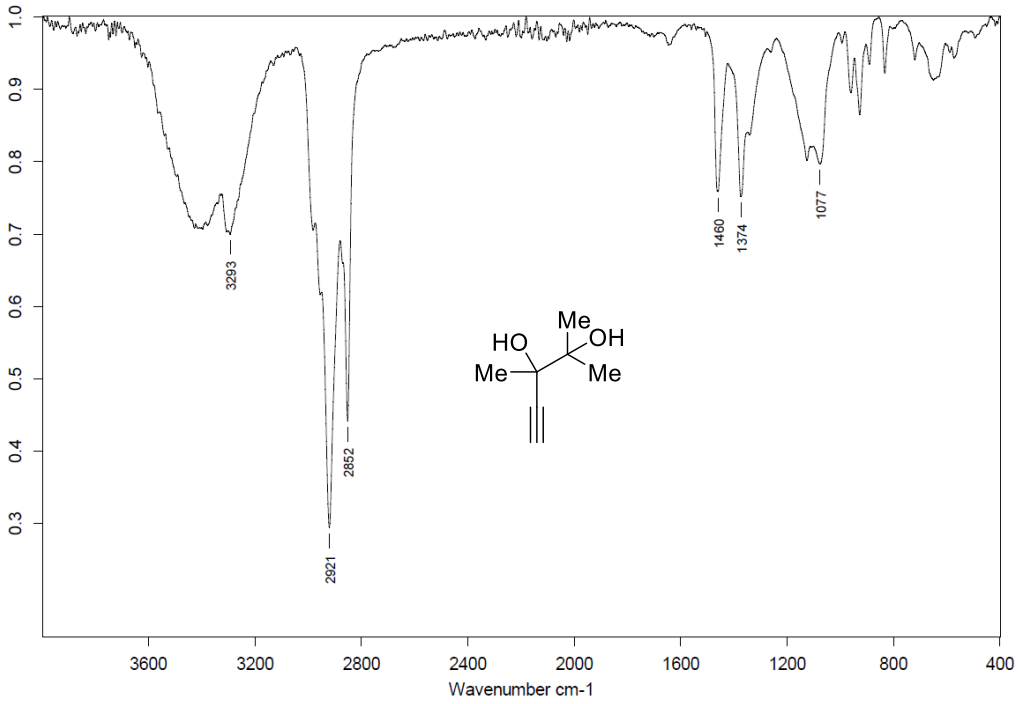
IR (neat) spectrum for **3l**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **3m**

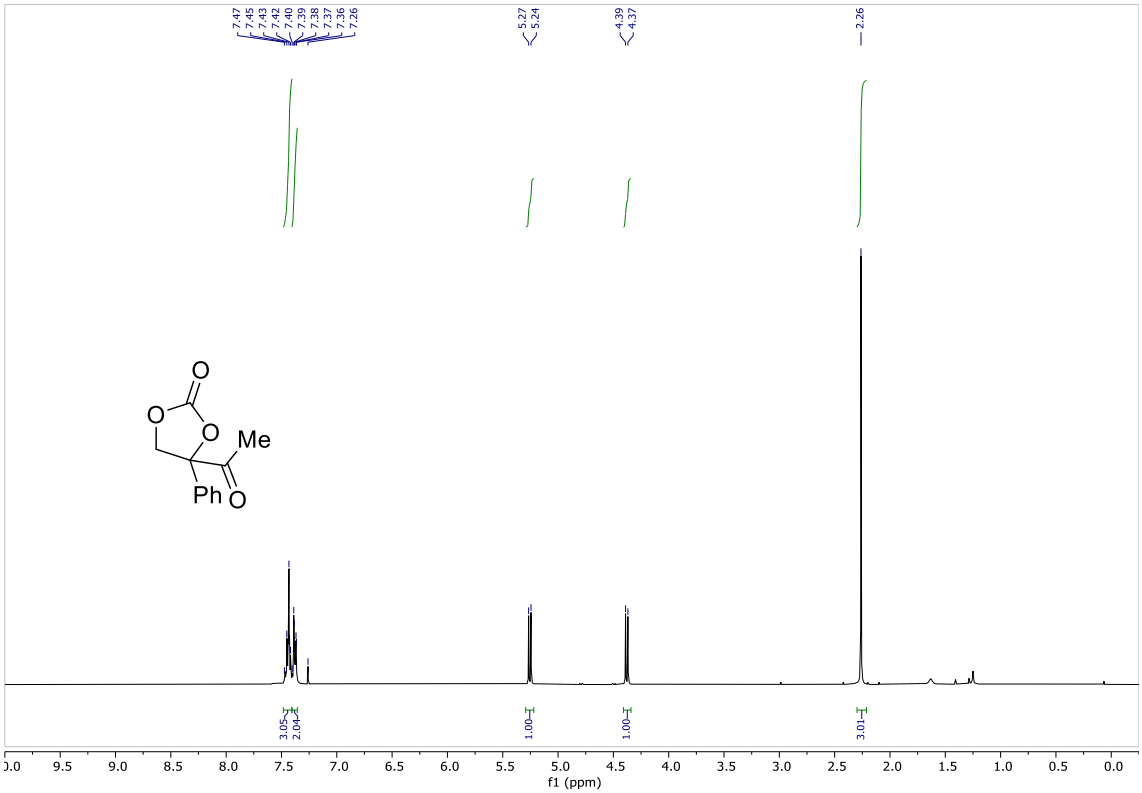


^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **3m**

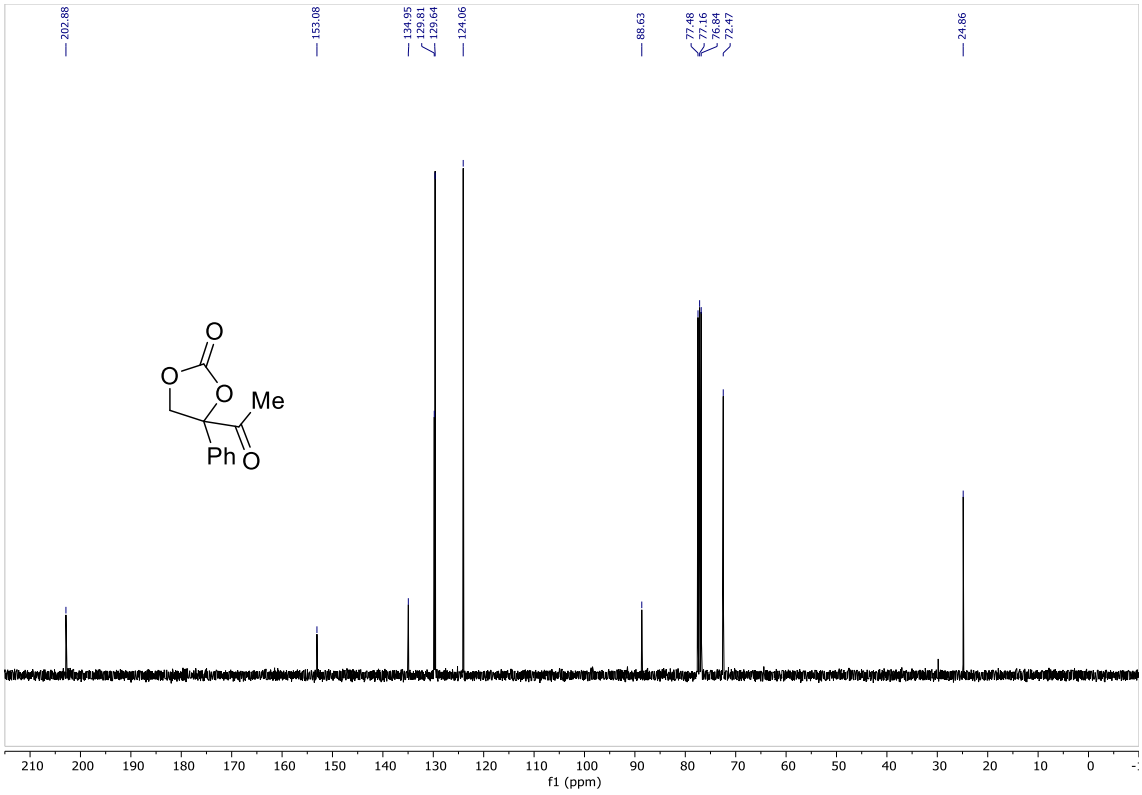


IR (neat) spectrum for **3m**

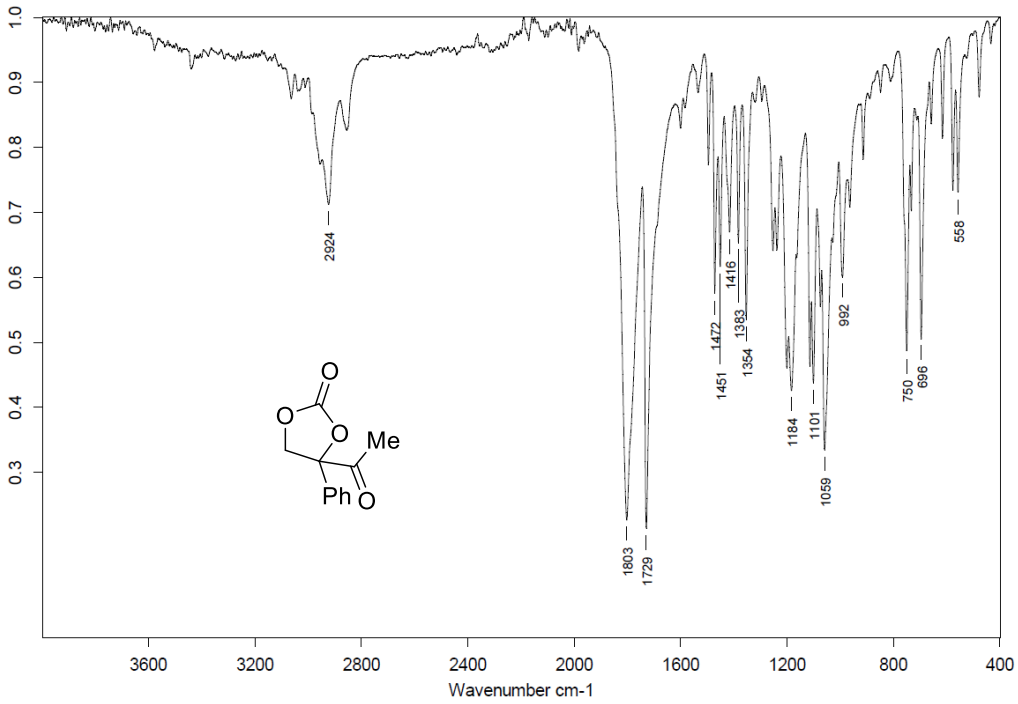
Spectra for the cyclic carbonates:



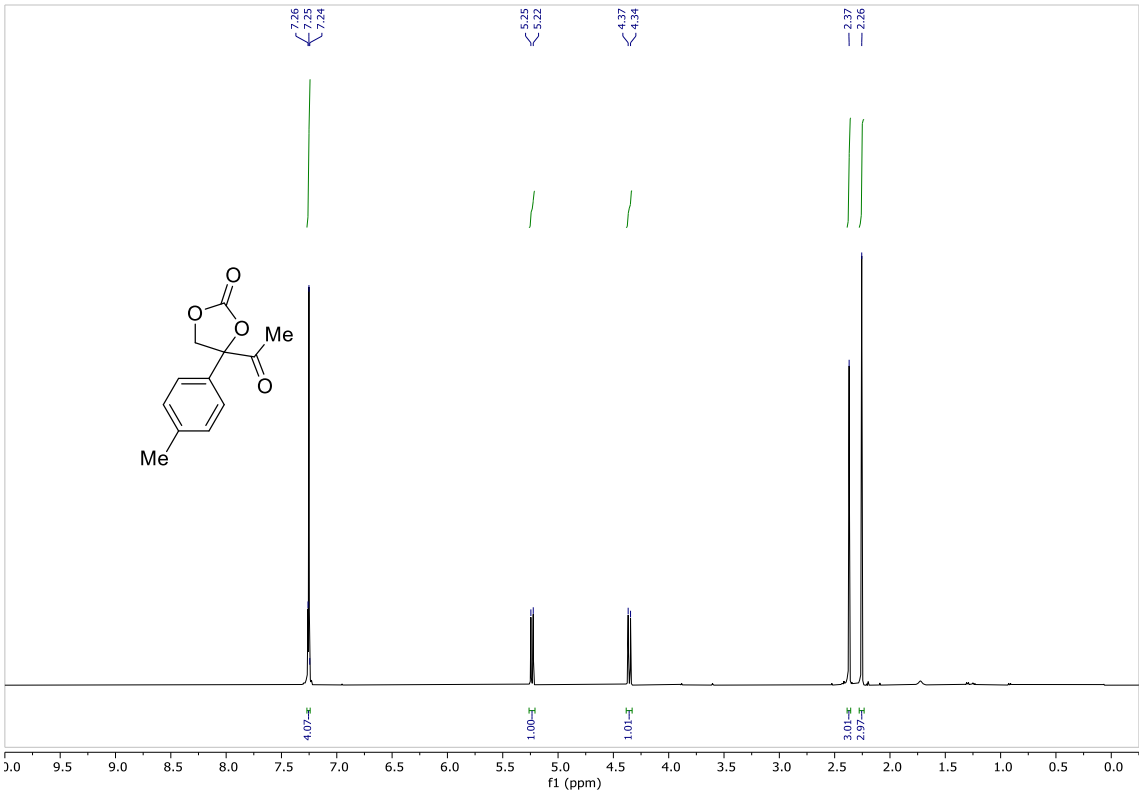
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2a**



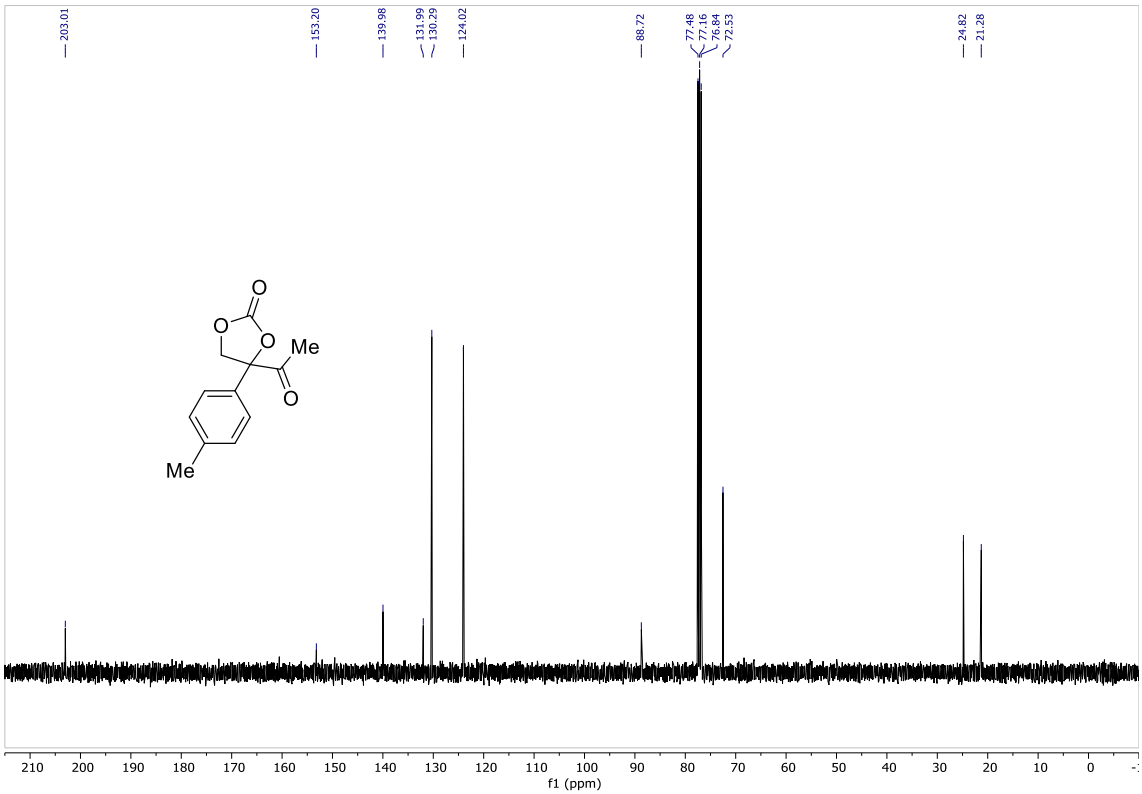
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2a**



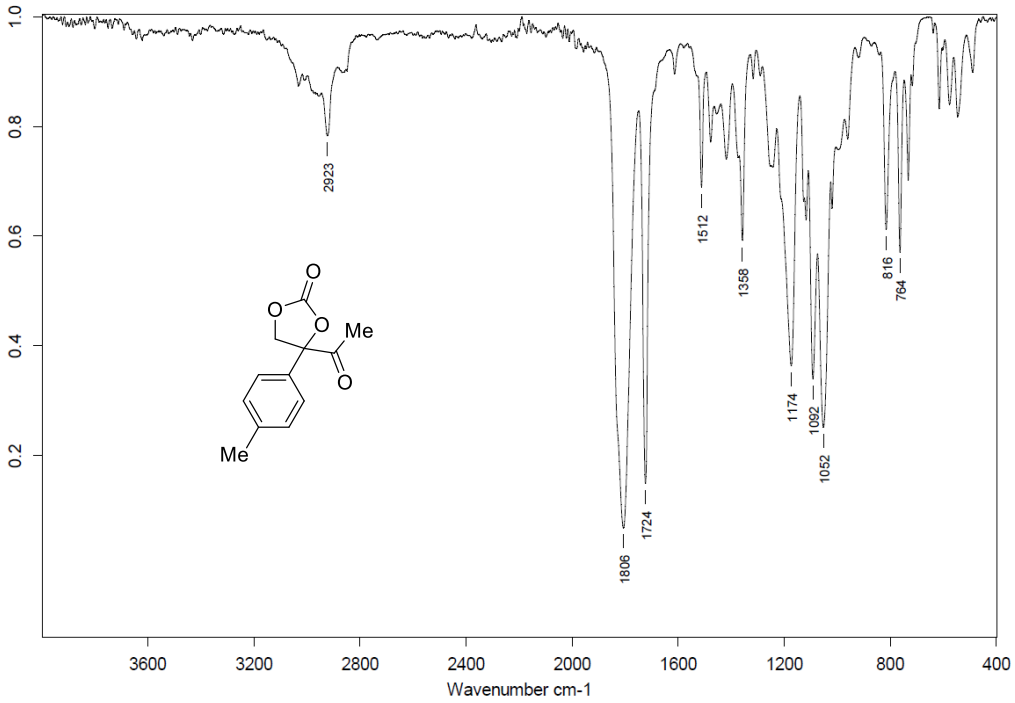
IR (neat) spectrum for **2a**



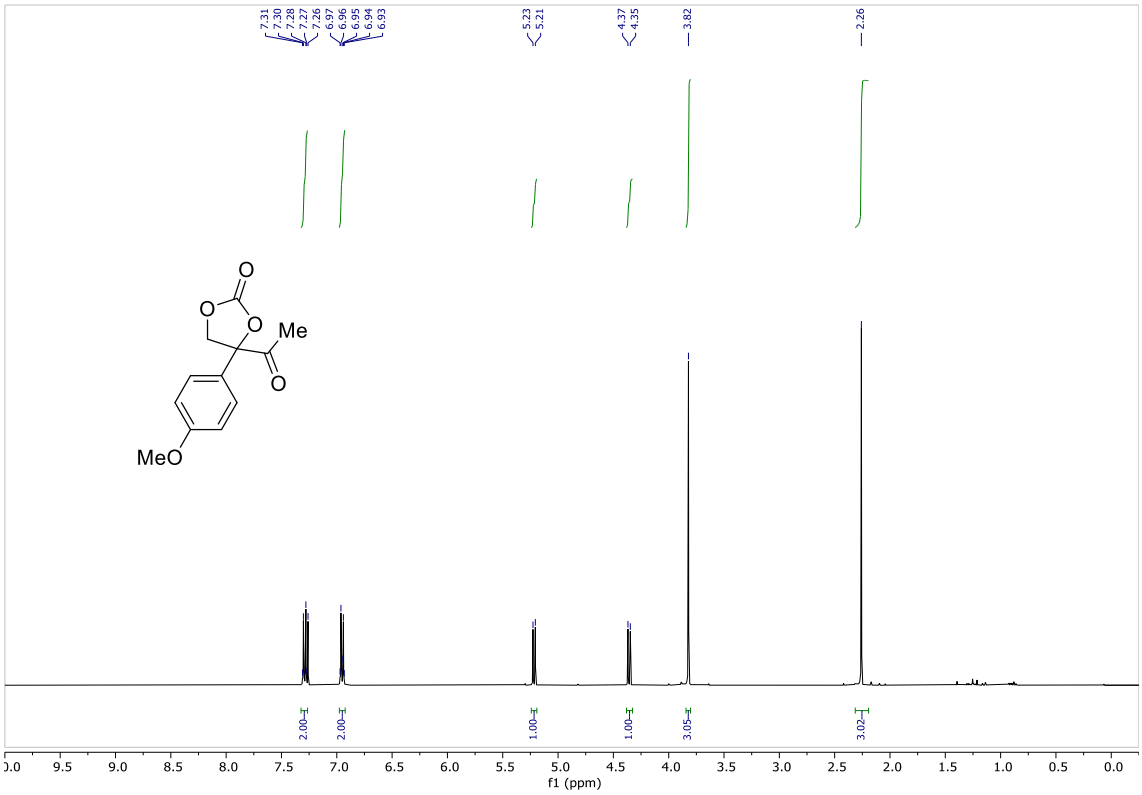
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2b**



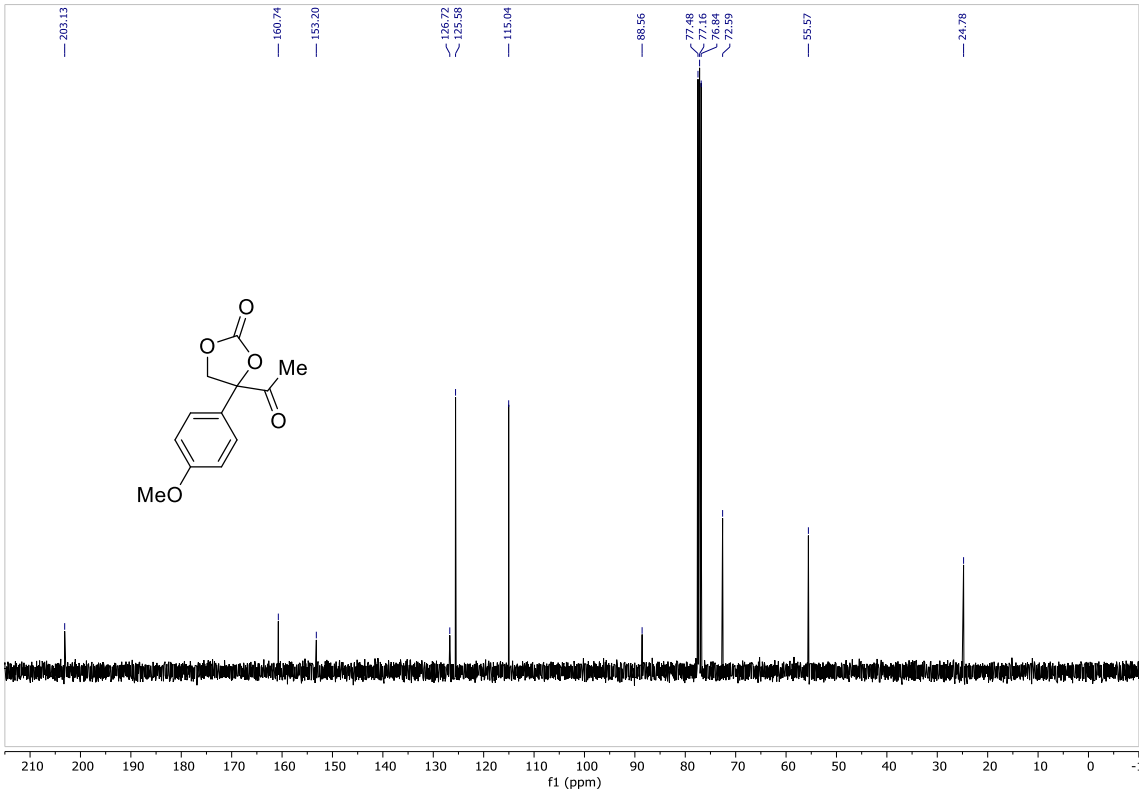
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2b**



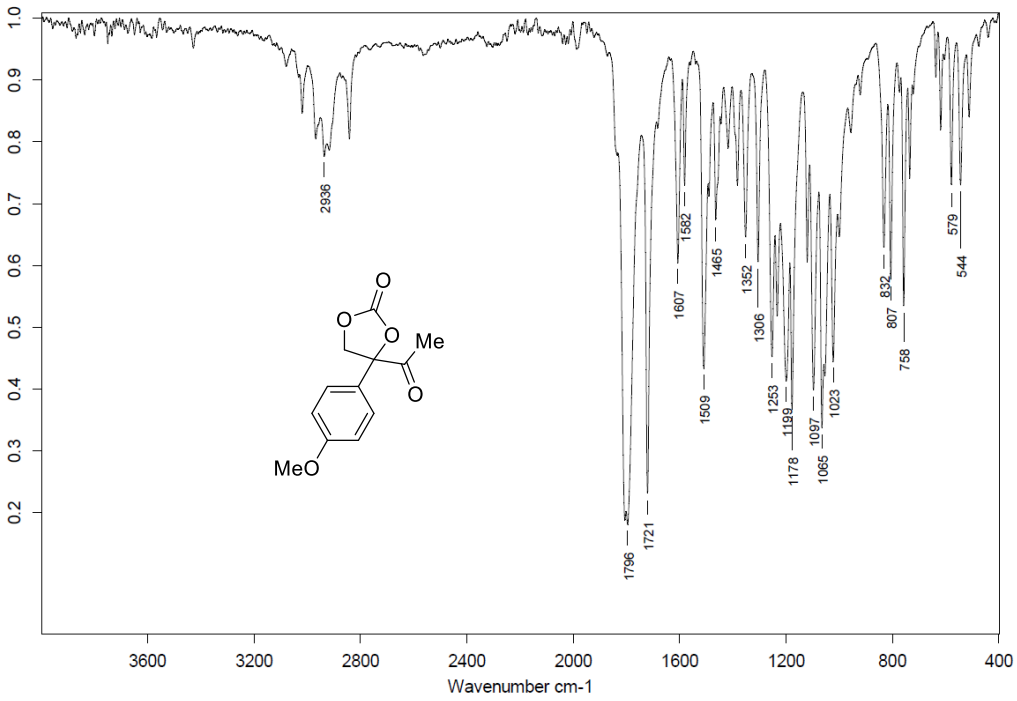
IR (neat) spectrum for **2b**



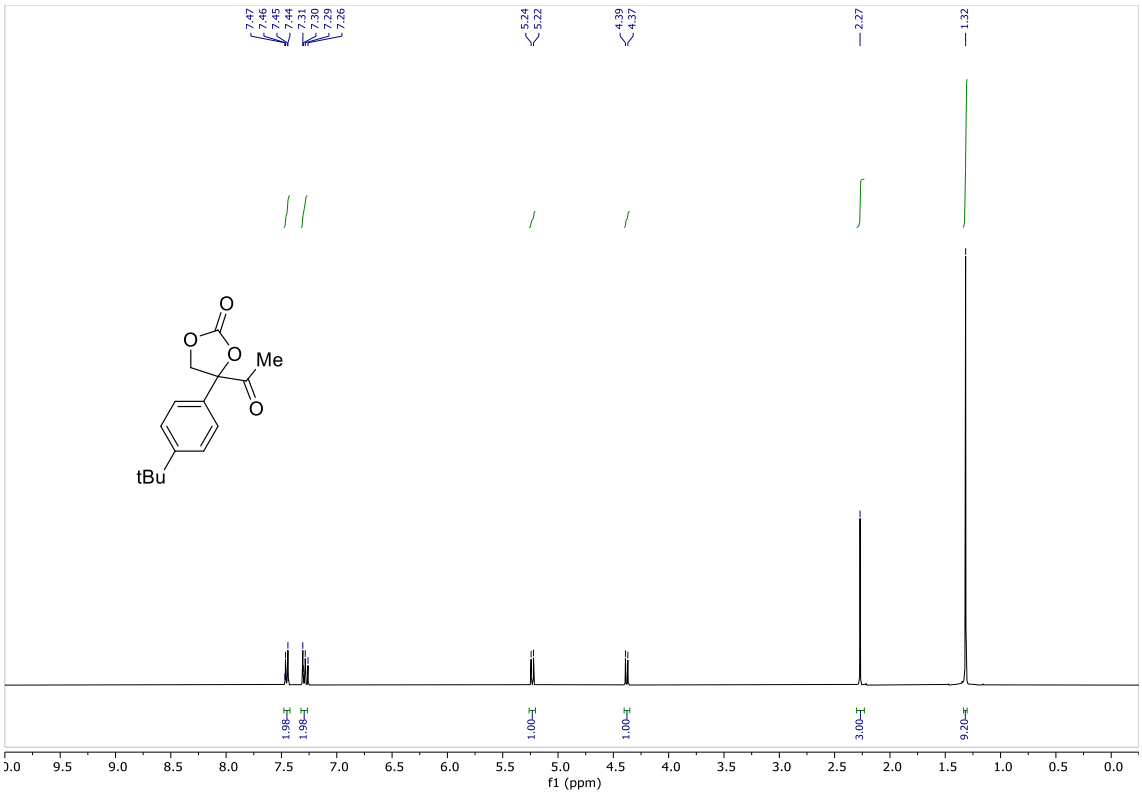
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2c**



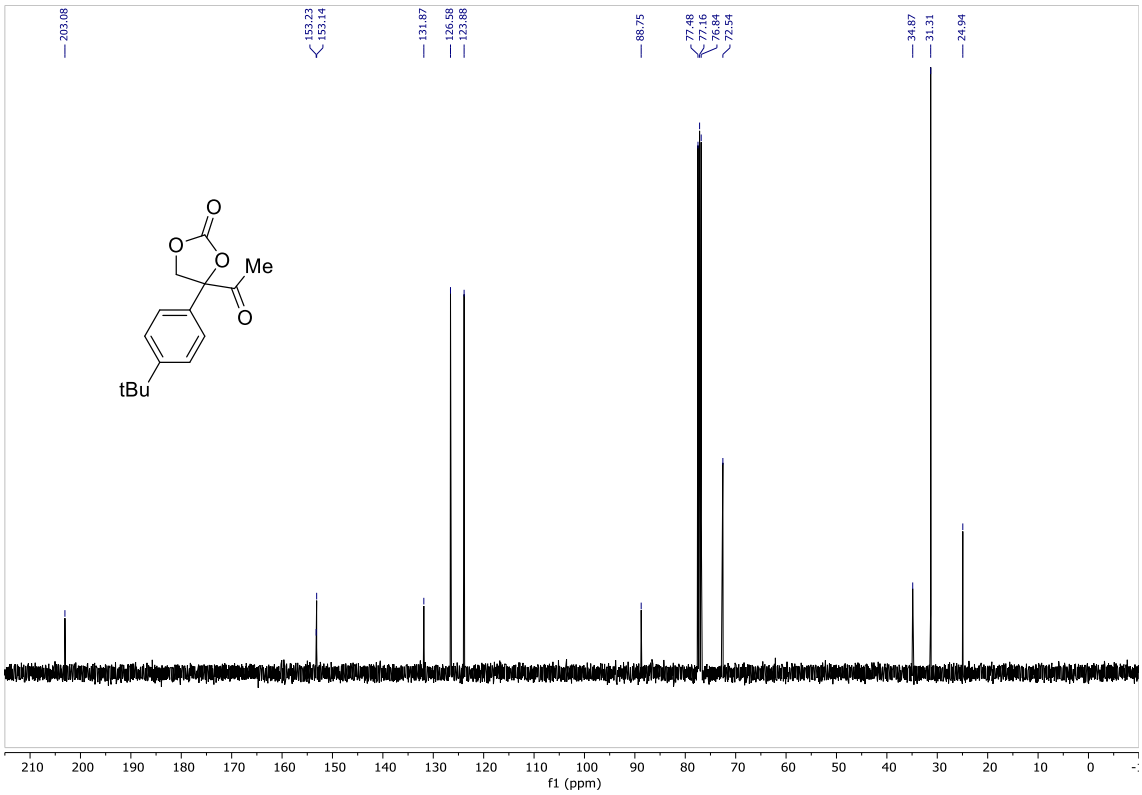
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2c**



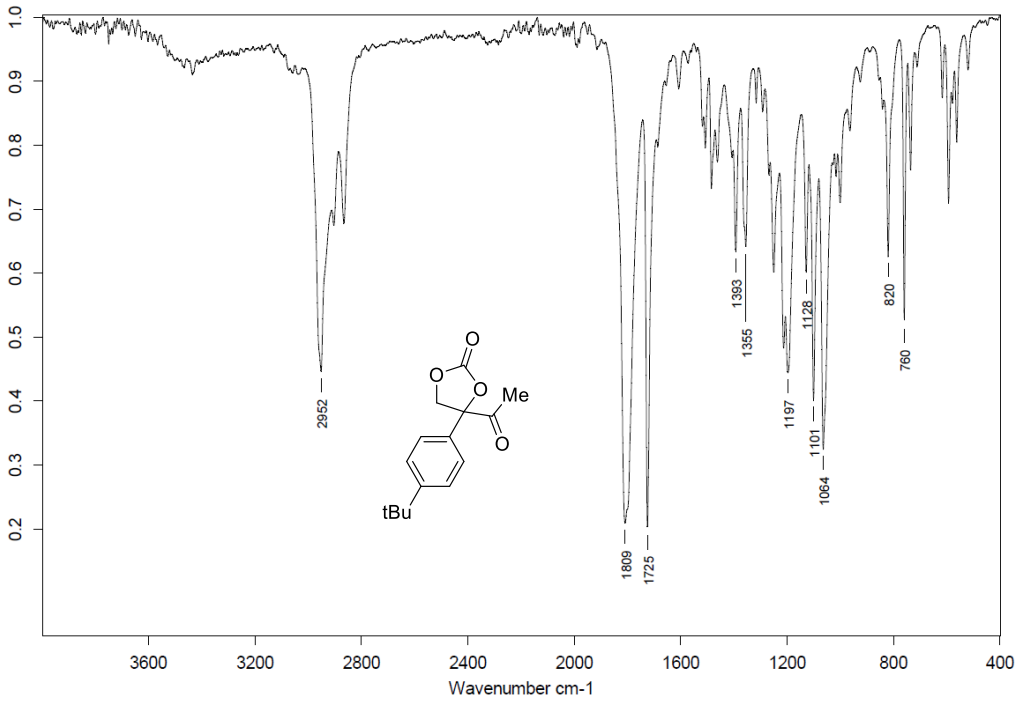
IR (neat) spectrum for **2c**



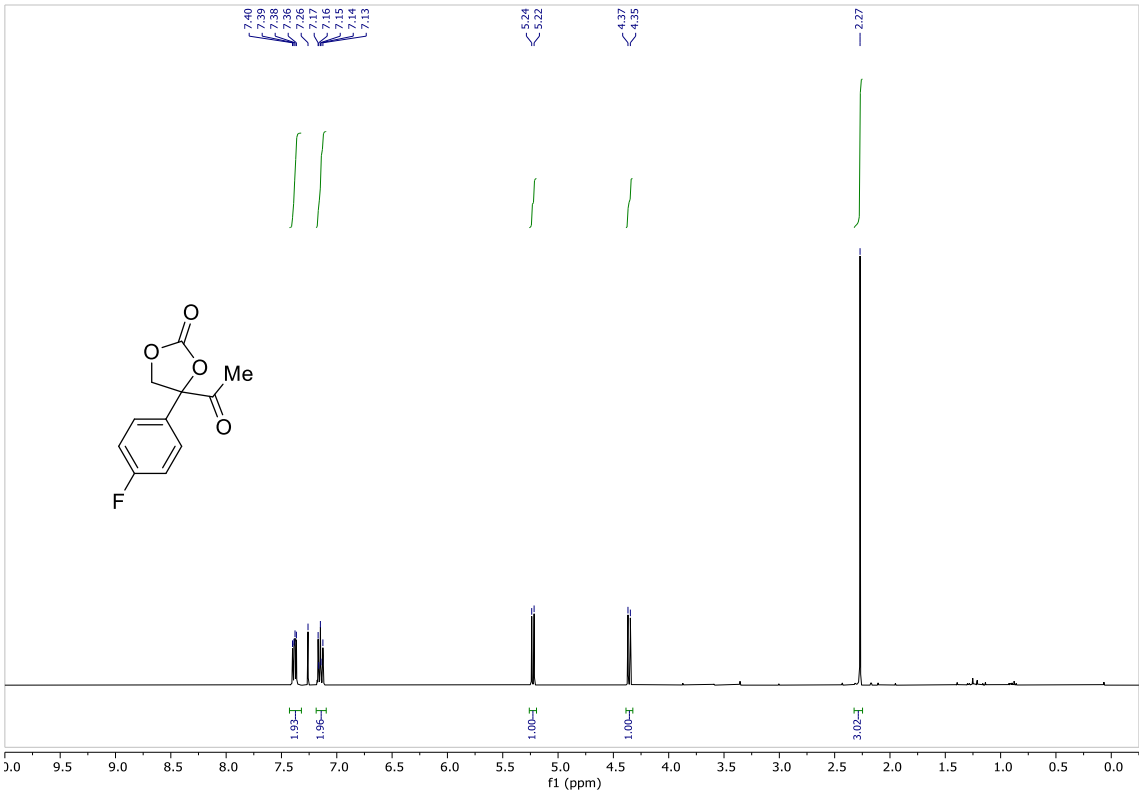
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2d**



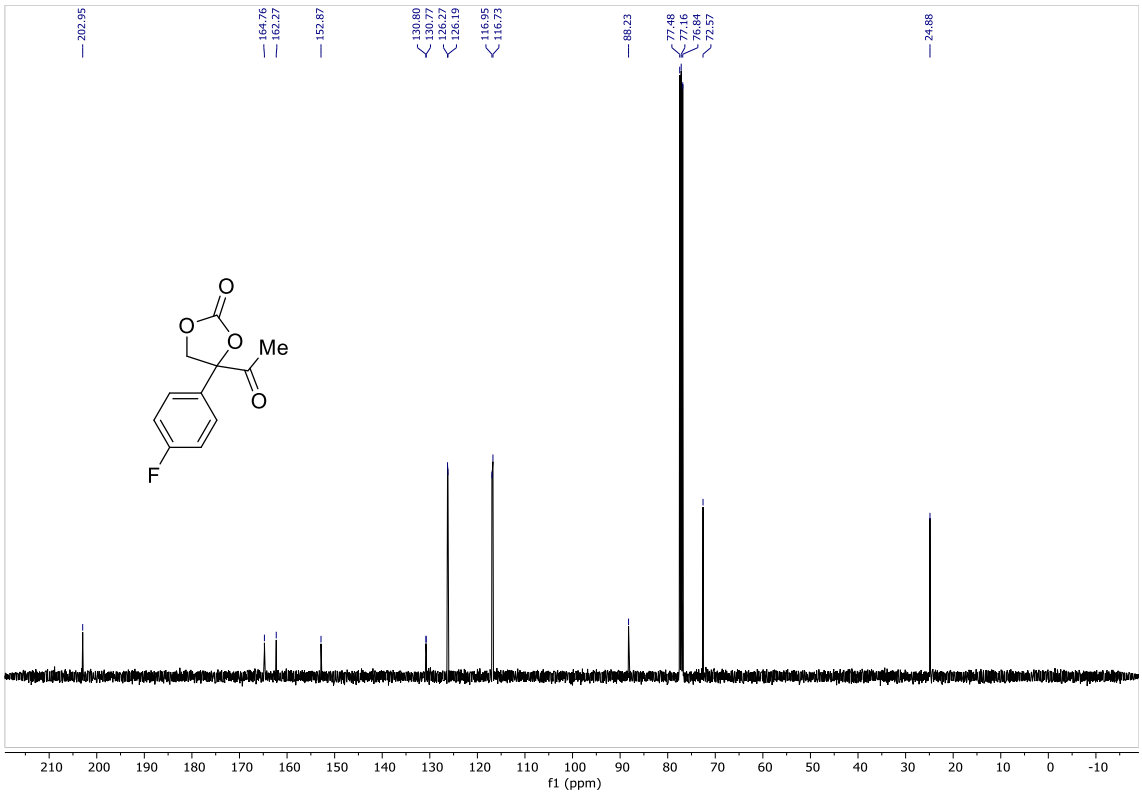
^{13}C NMR (101MHz, $CDCl_3$) spectrum for **2d**



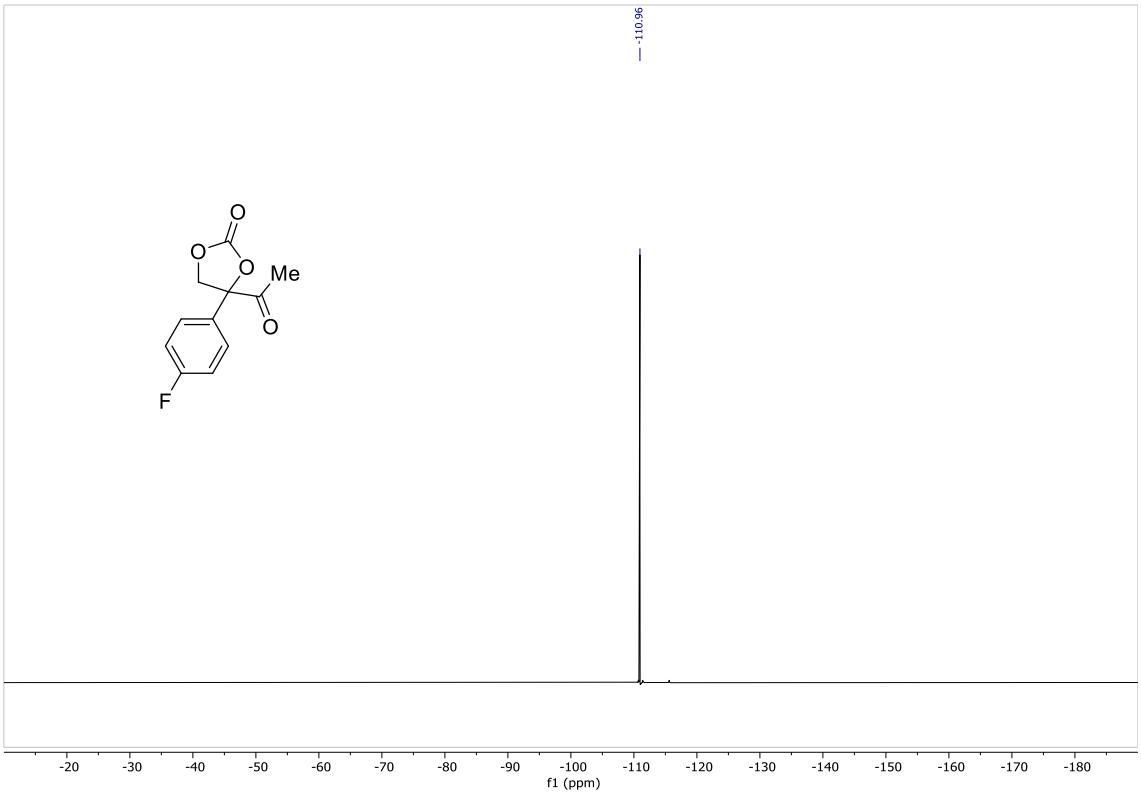
IR (neat) spectrum for **2d**



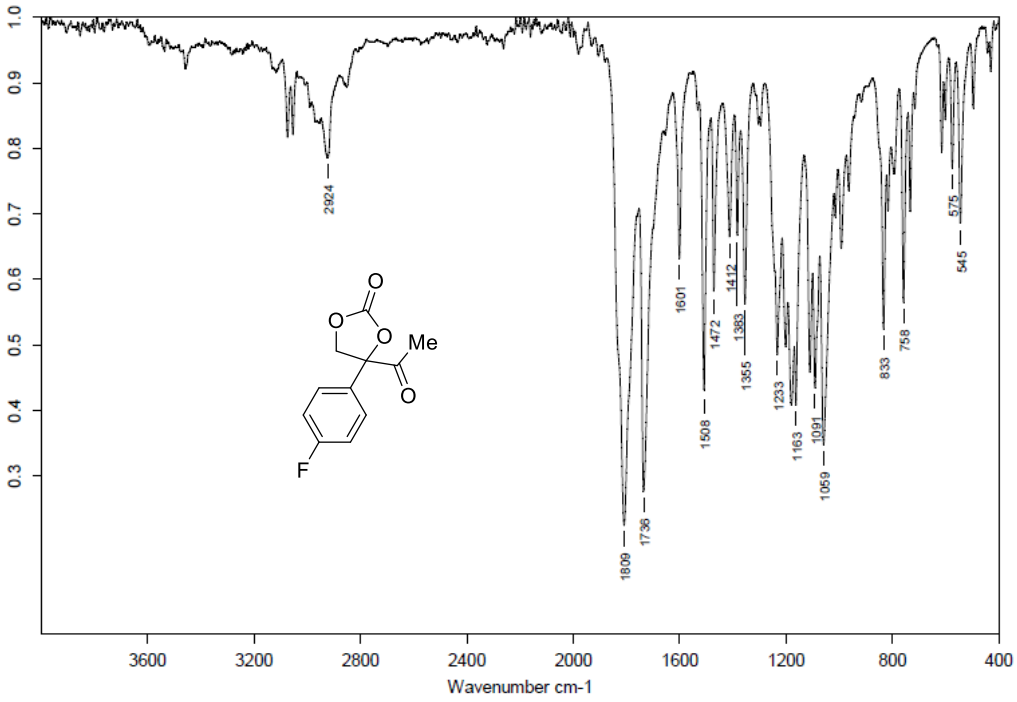
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2e**



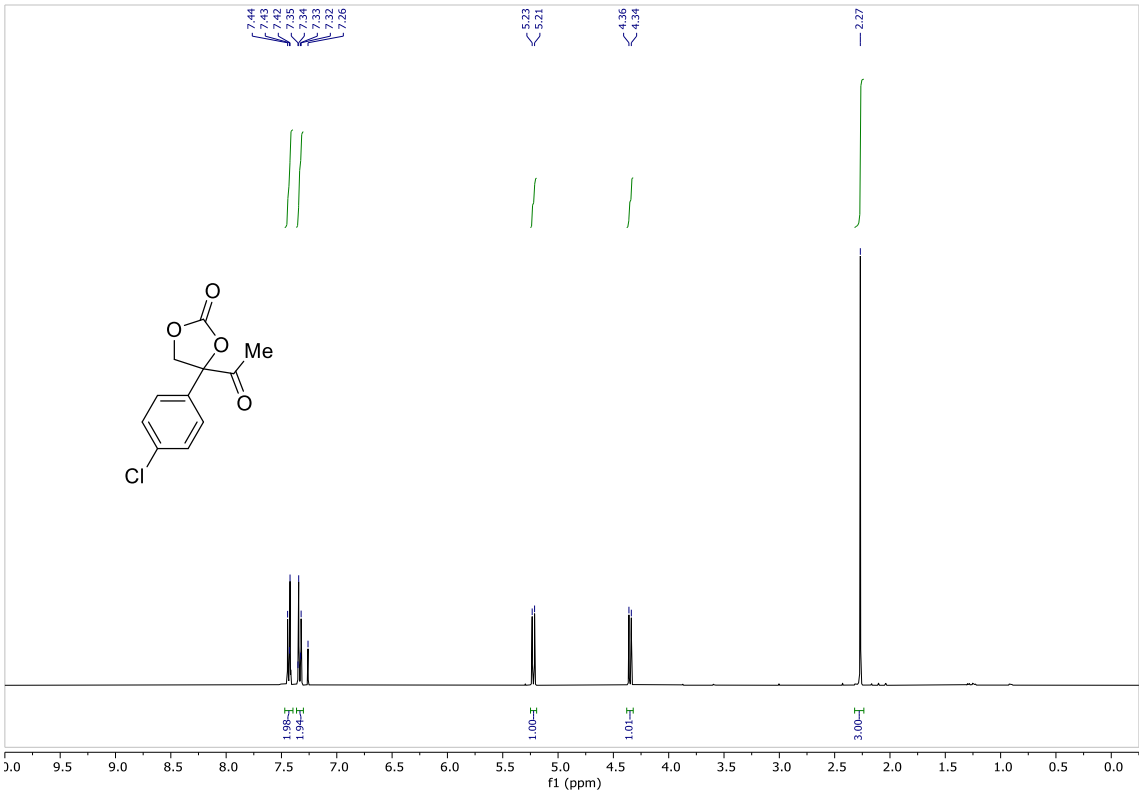
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2e**



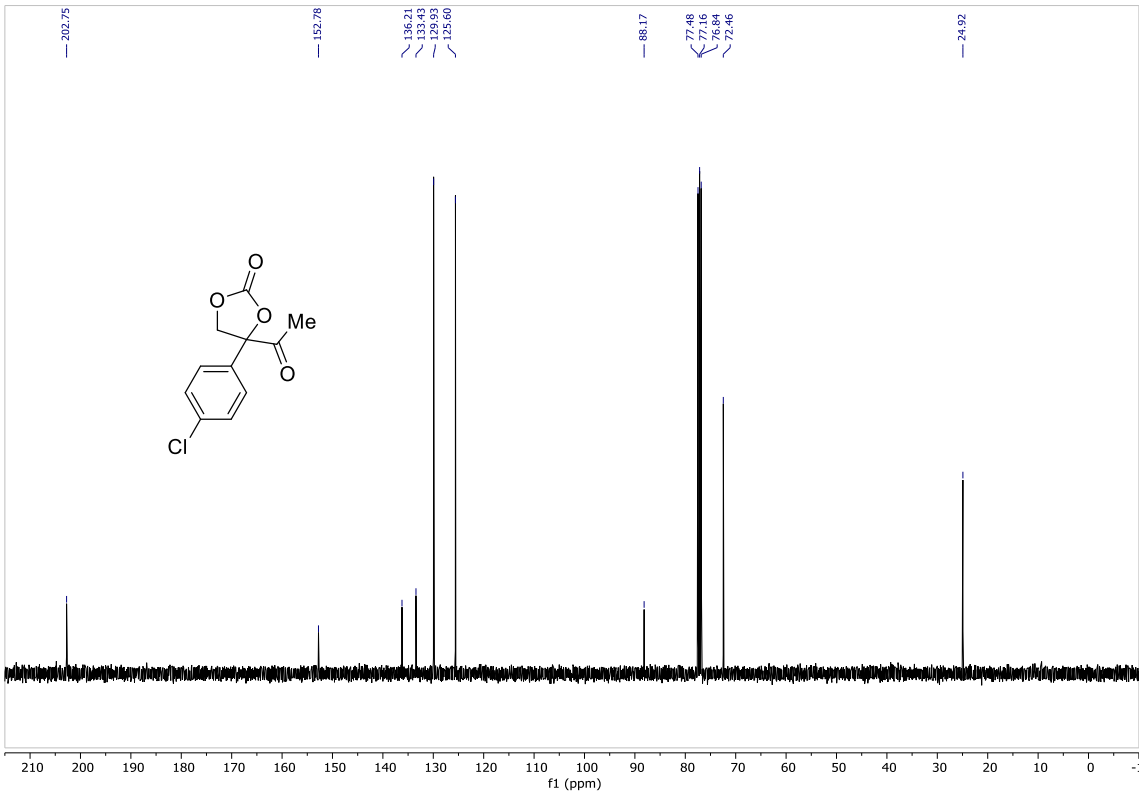
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **2e**



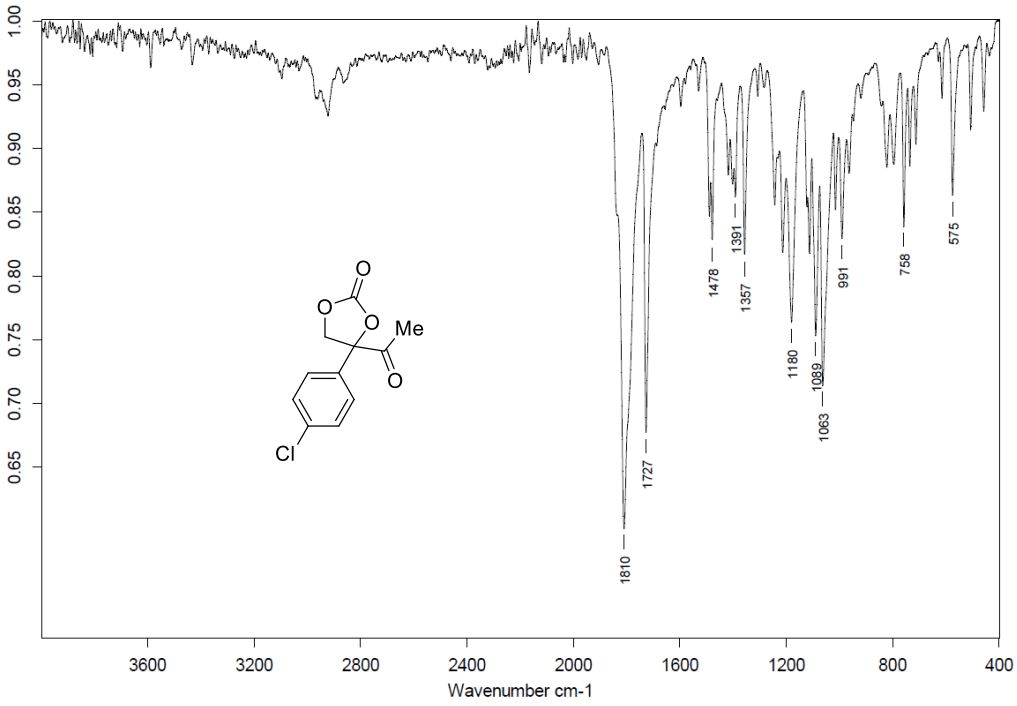
IR (neat) spectrum for **2e**



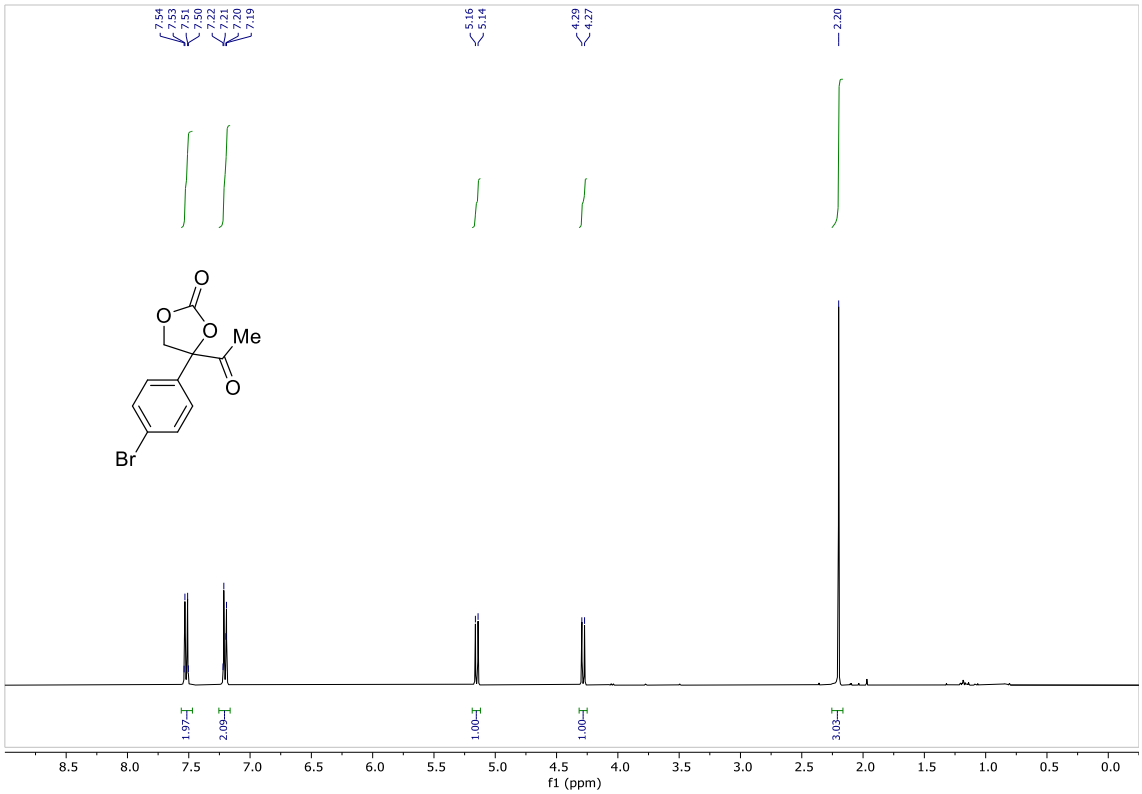
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2f**



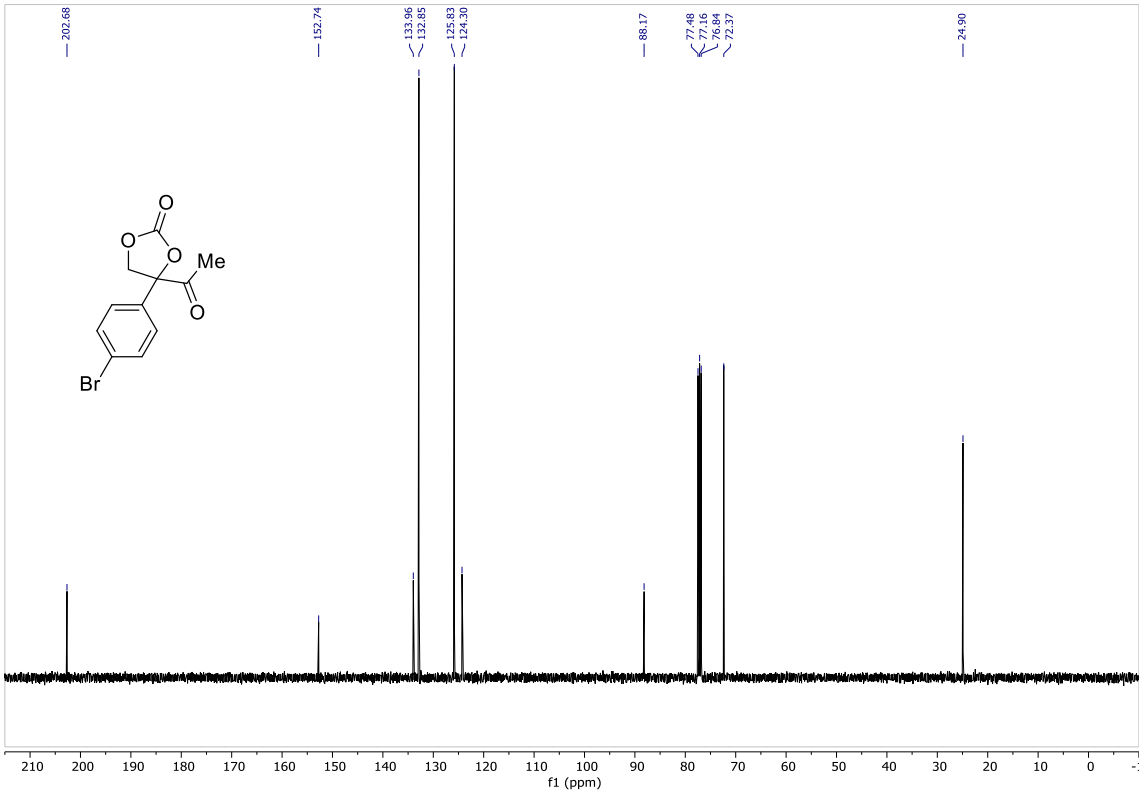
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2f**



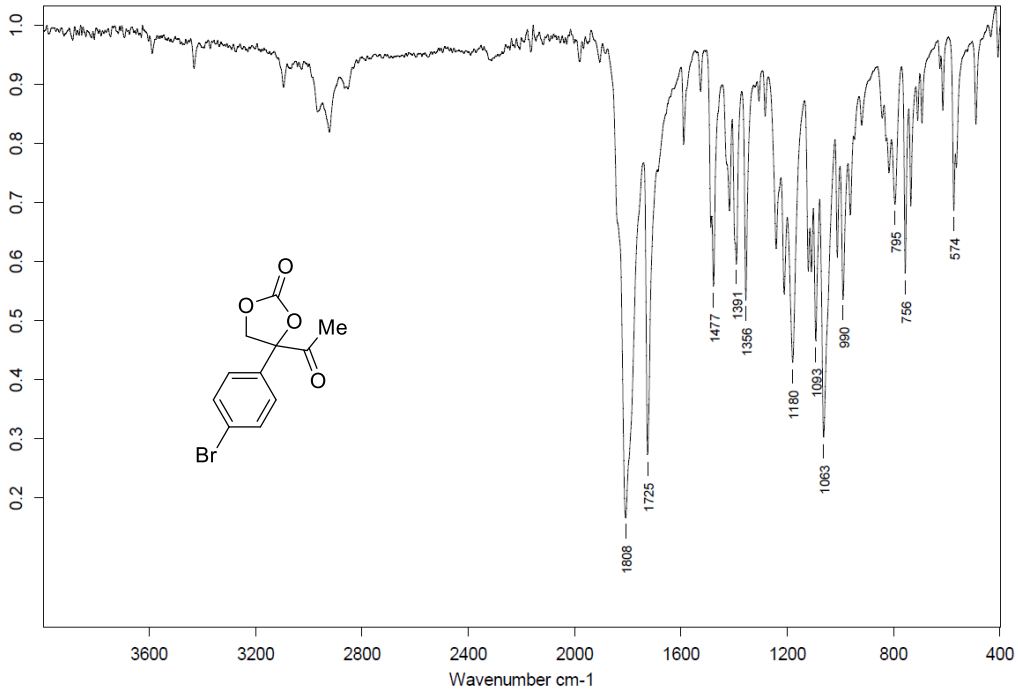
IR (neat) spectrum for **2f**



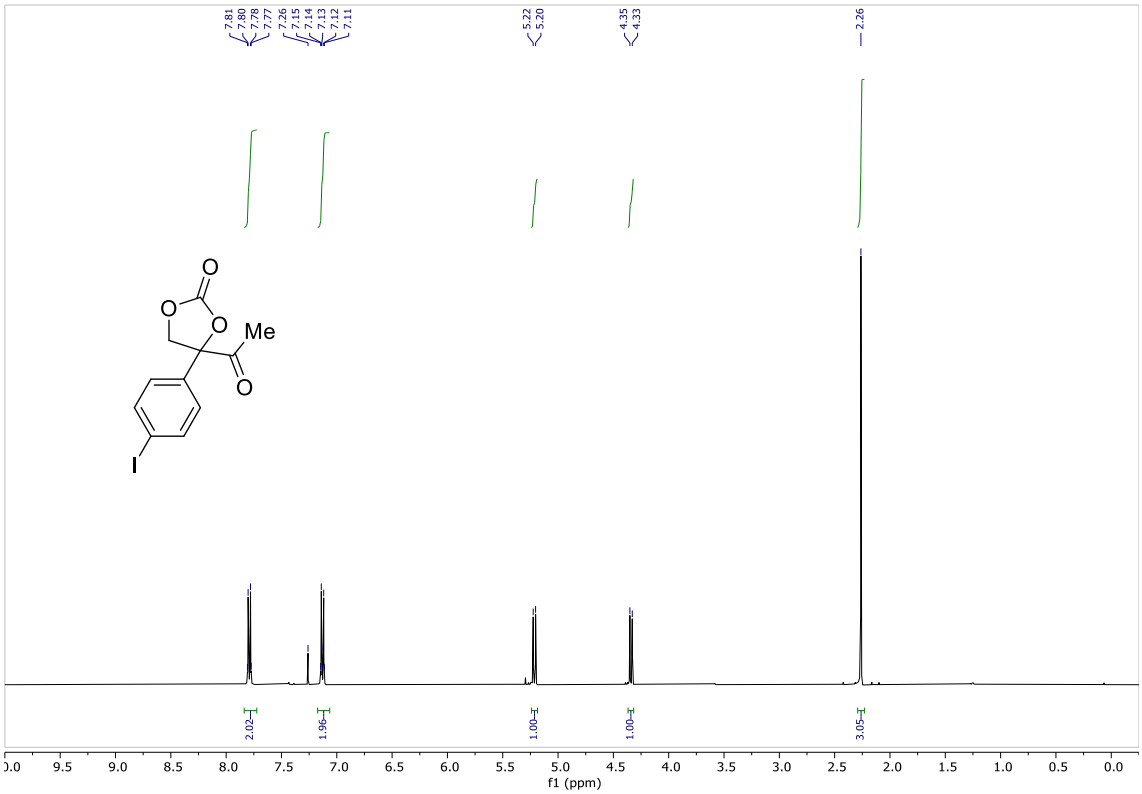
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2g**



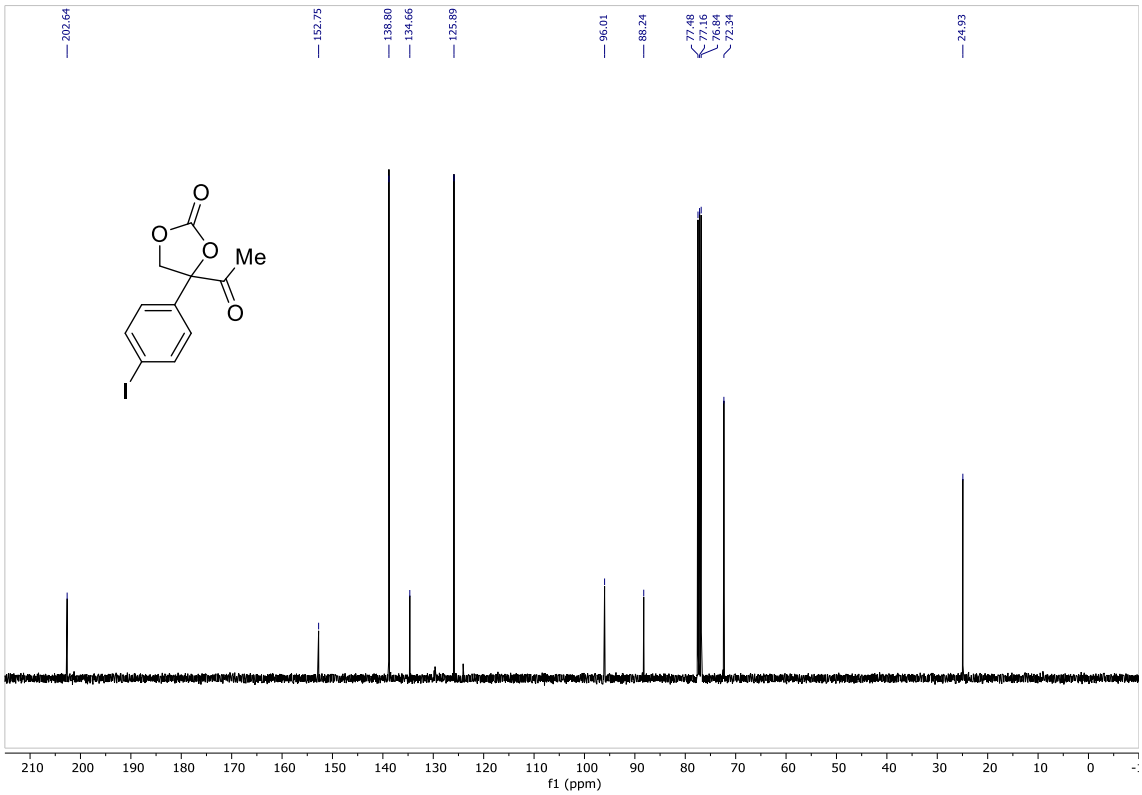
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2g**



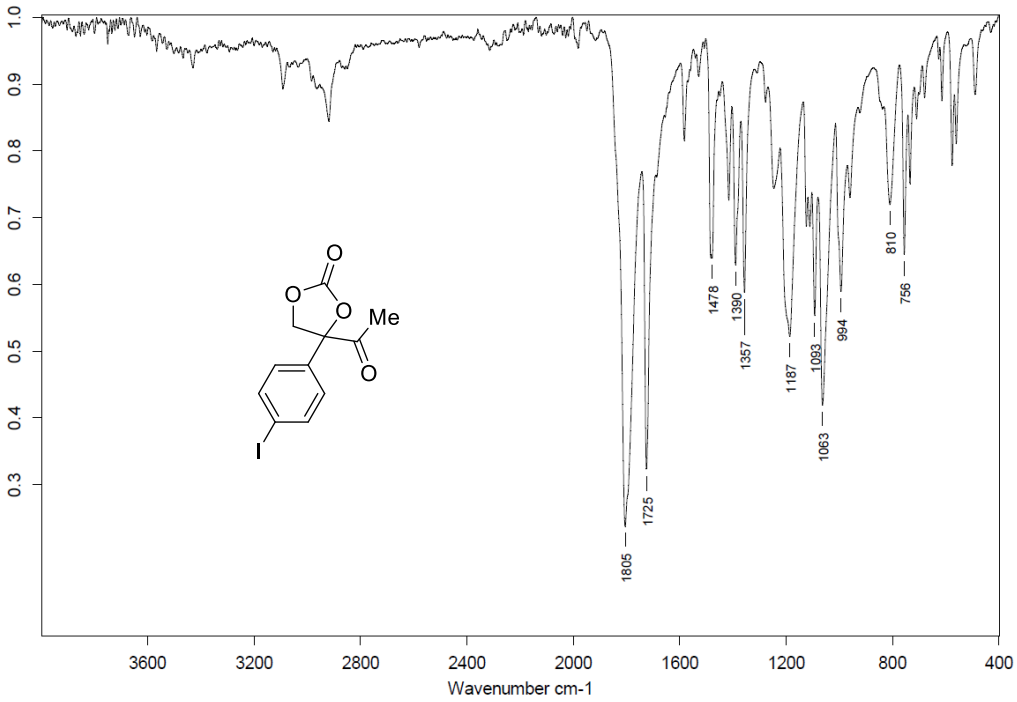
IR (neat) spectrum for **2g**



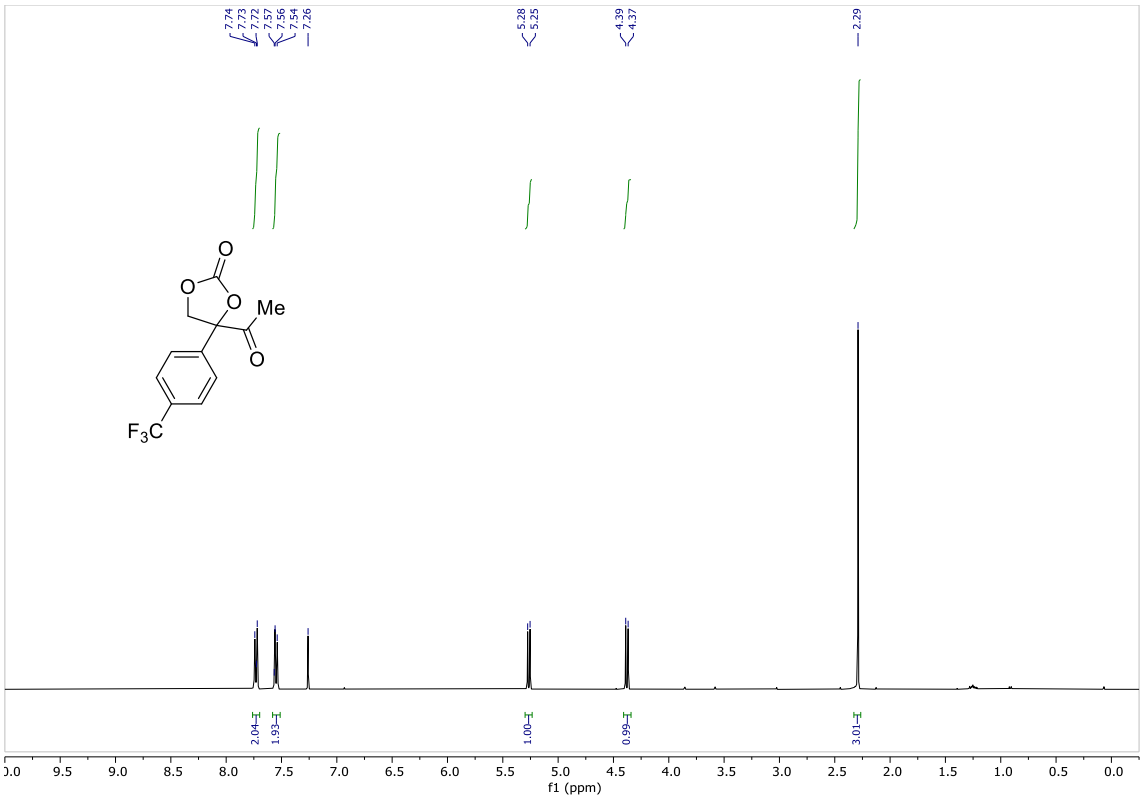
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2h**



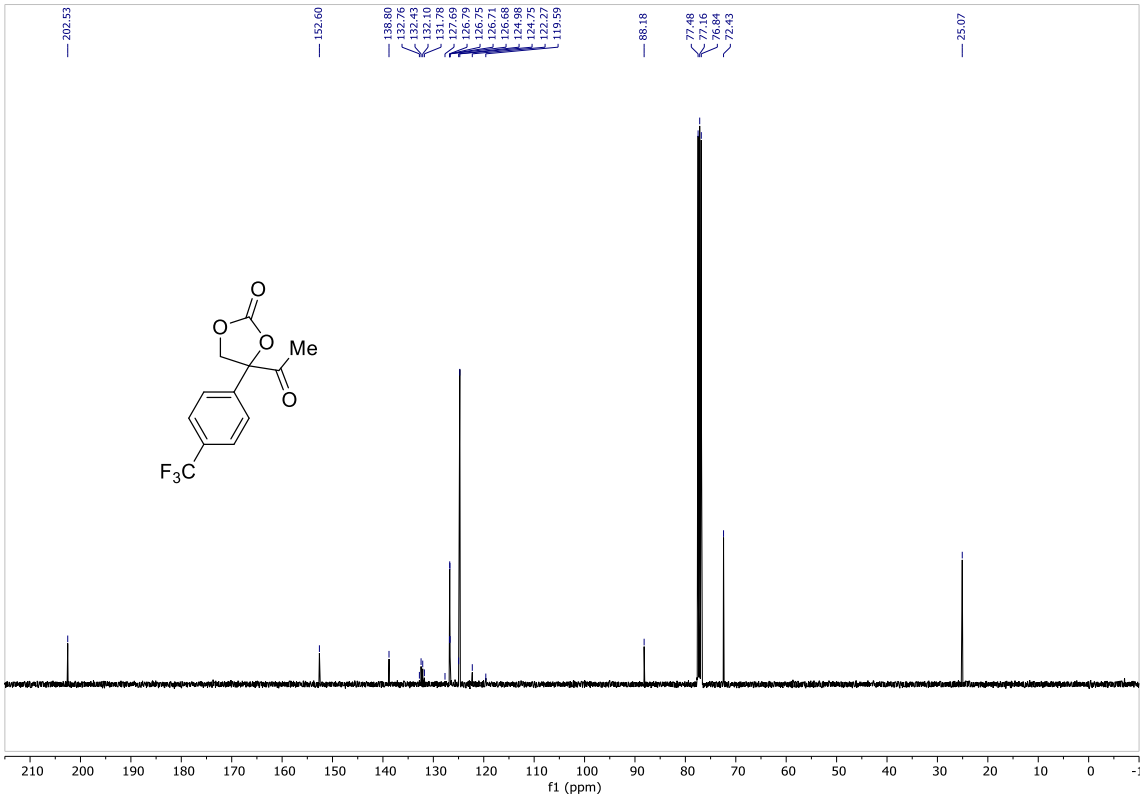
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2h**



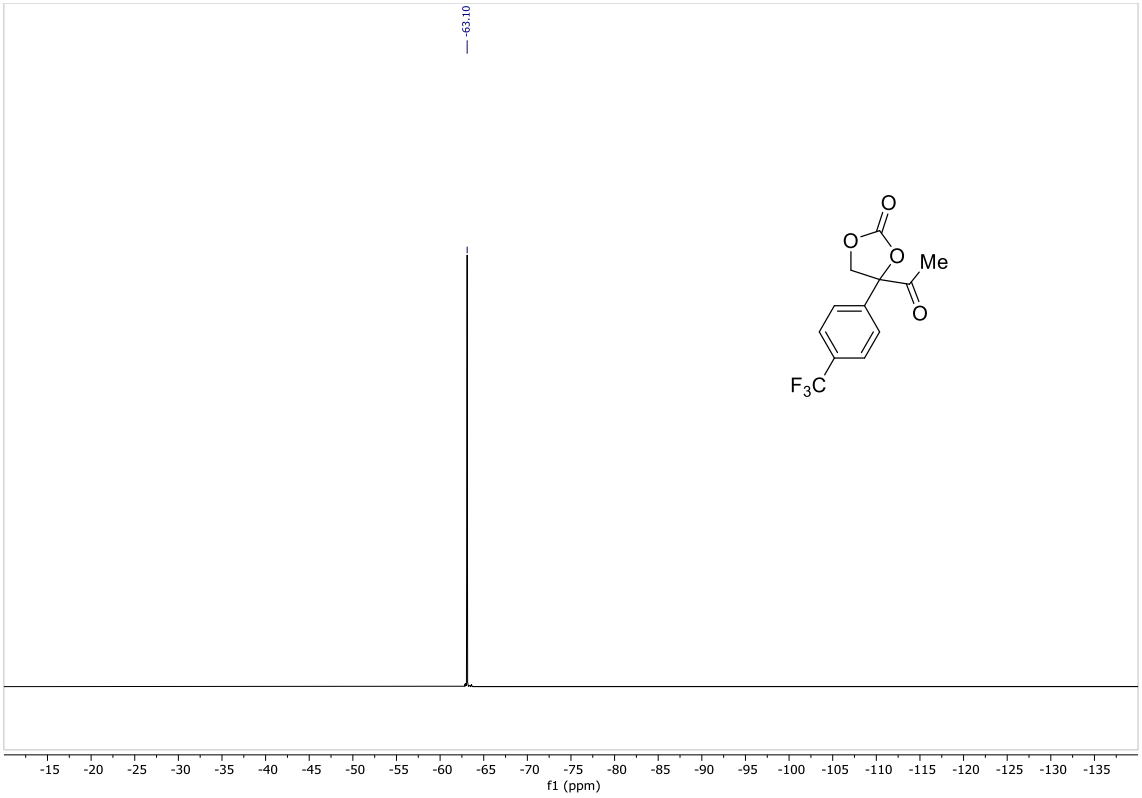
IR (neat) spectrum for **2h**



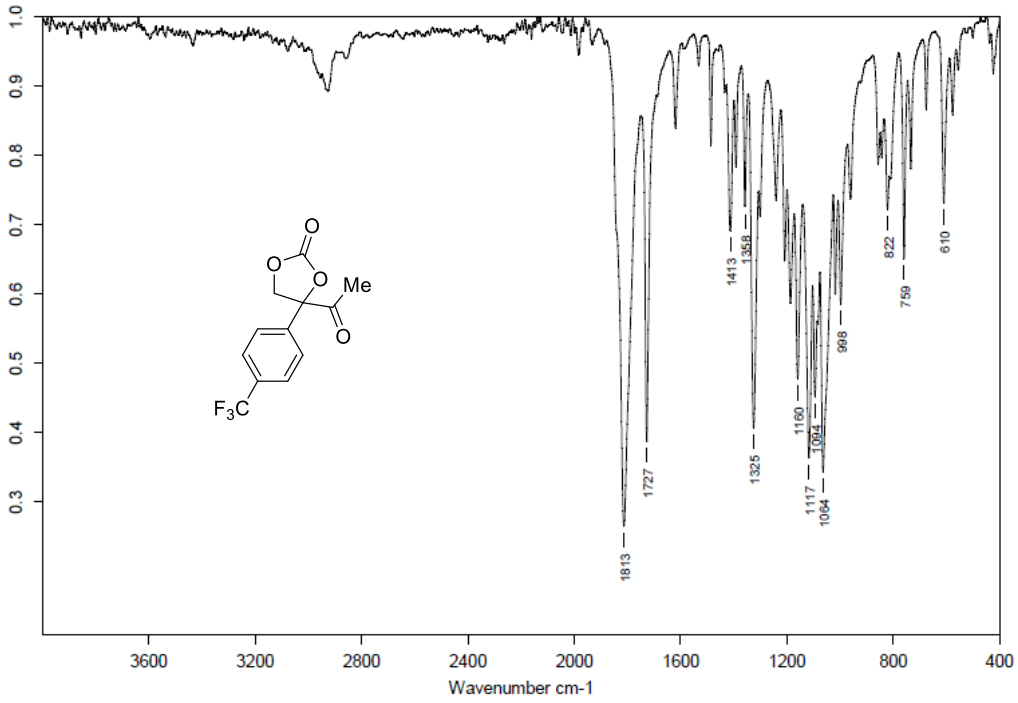
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2i**



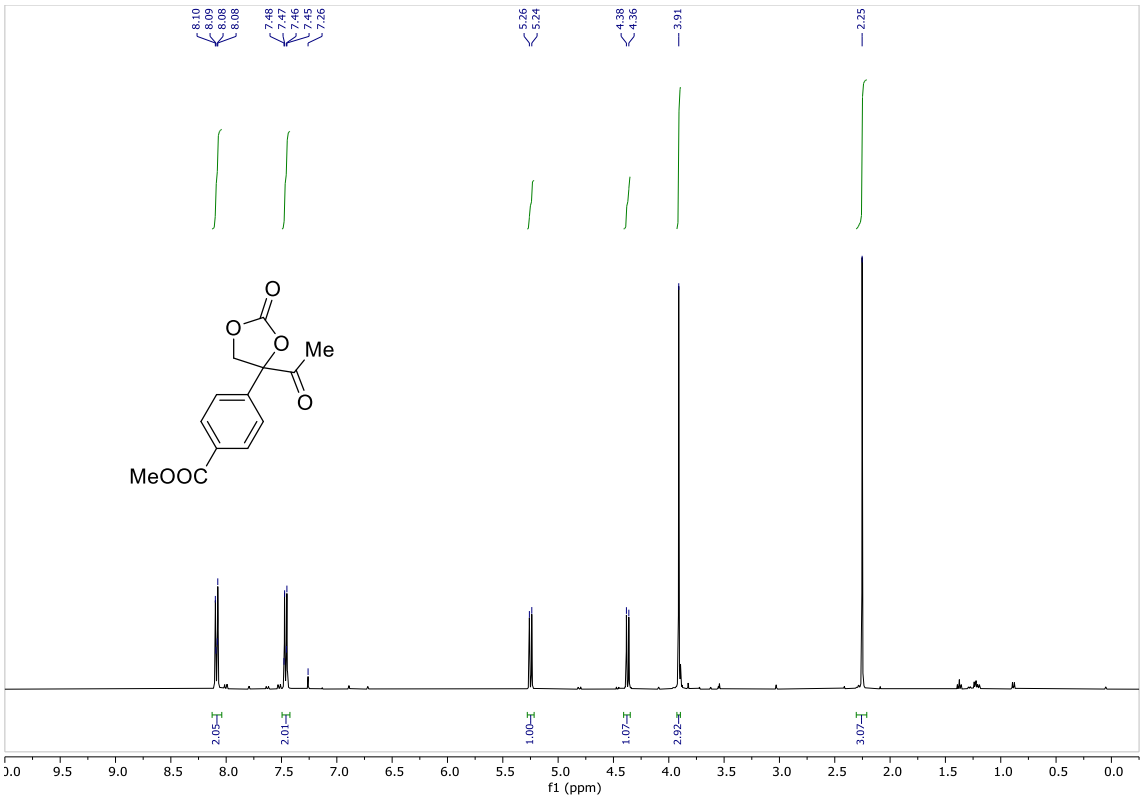
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2i**



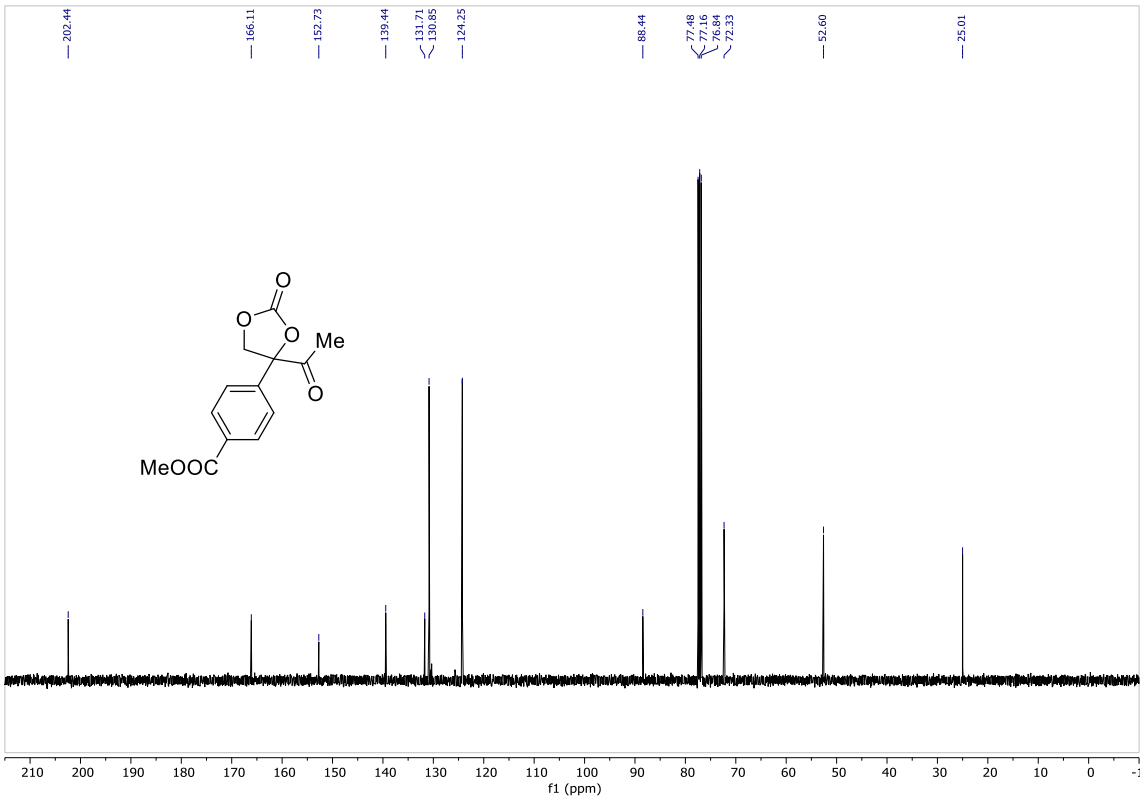
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **2i**



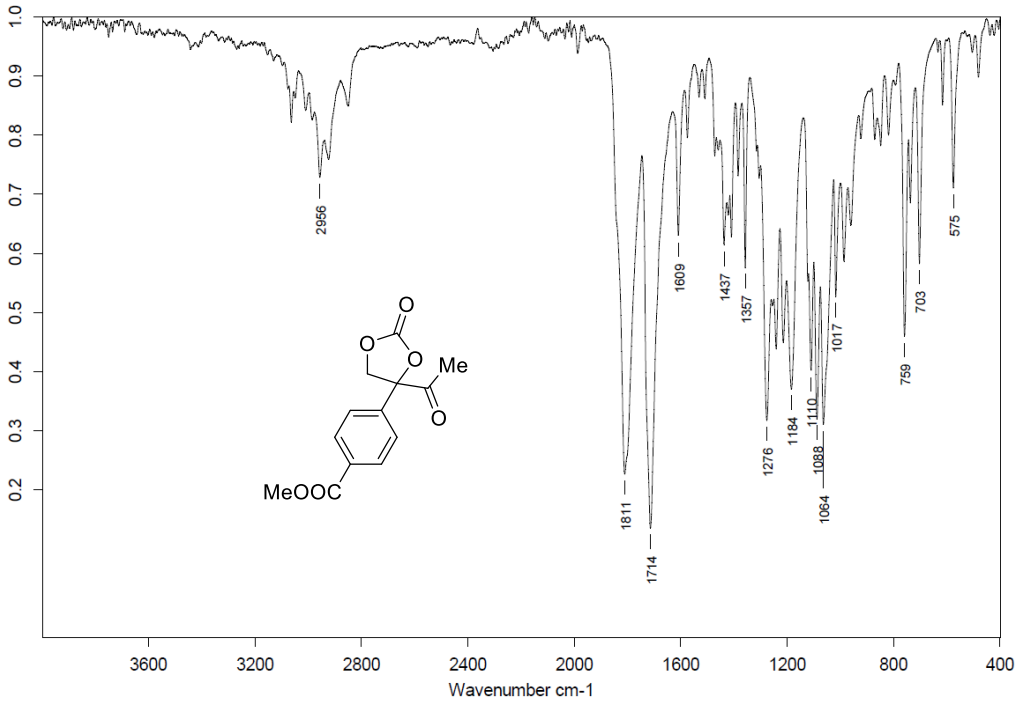
IR (neat) spectrum for **2i**



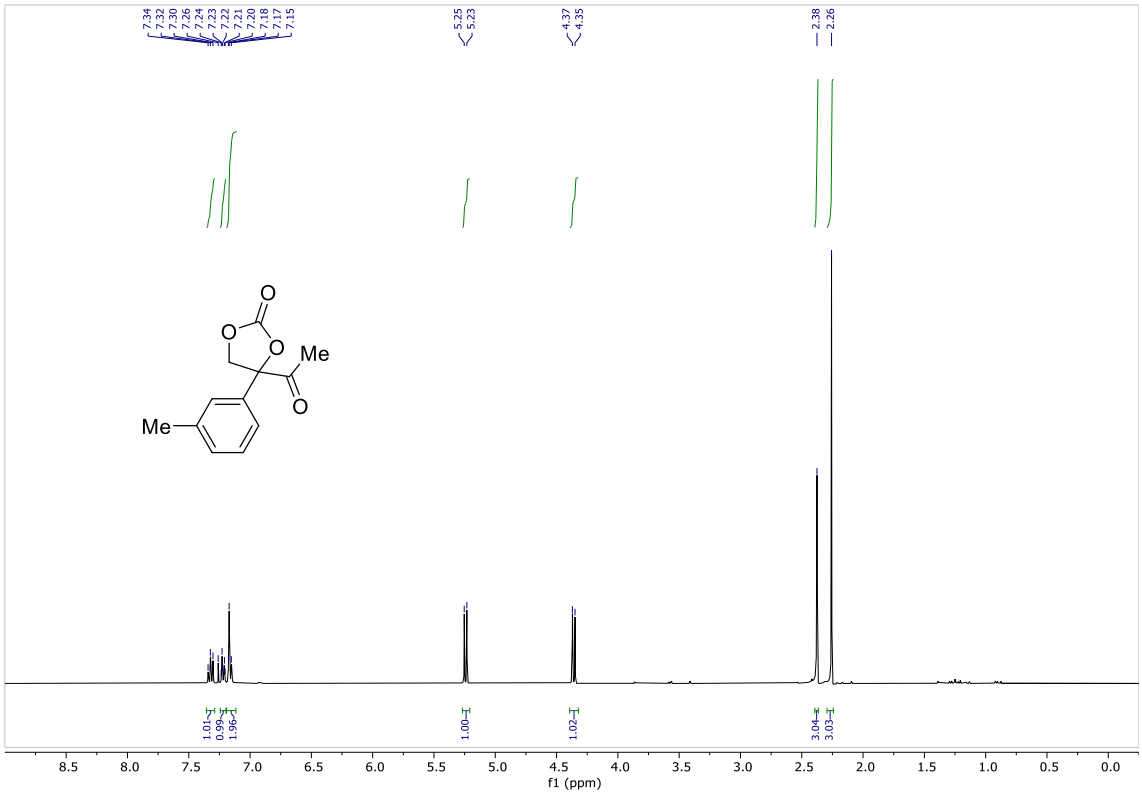
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2j**



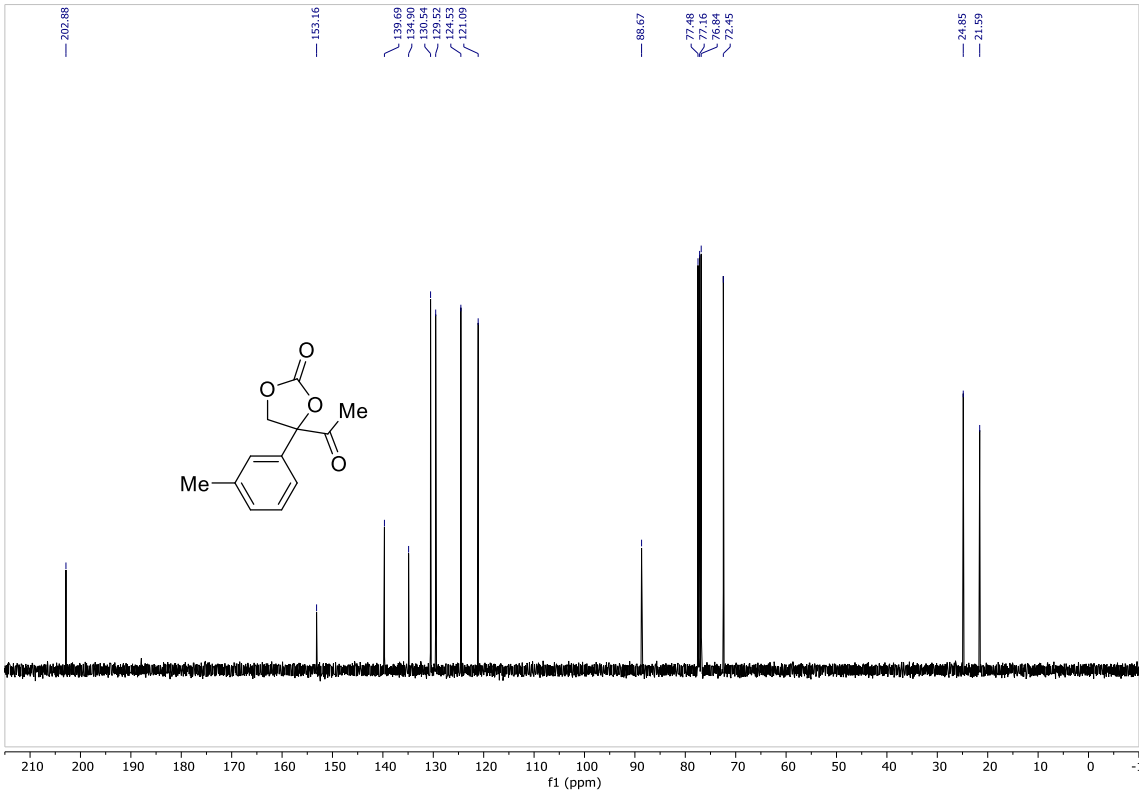
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2j**



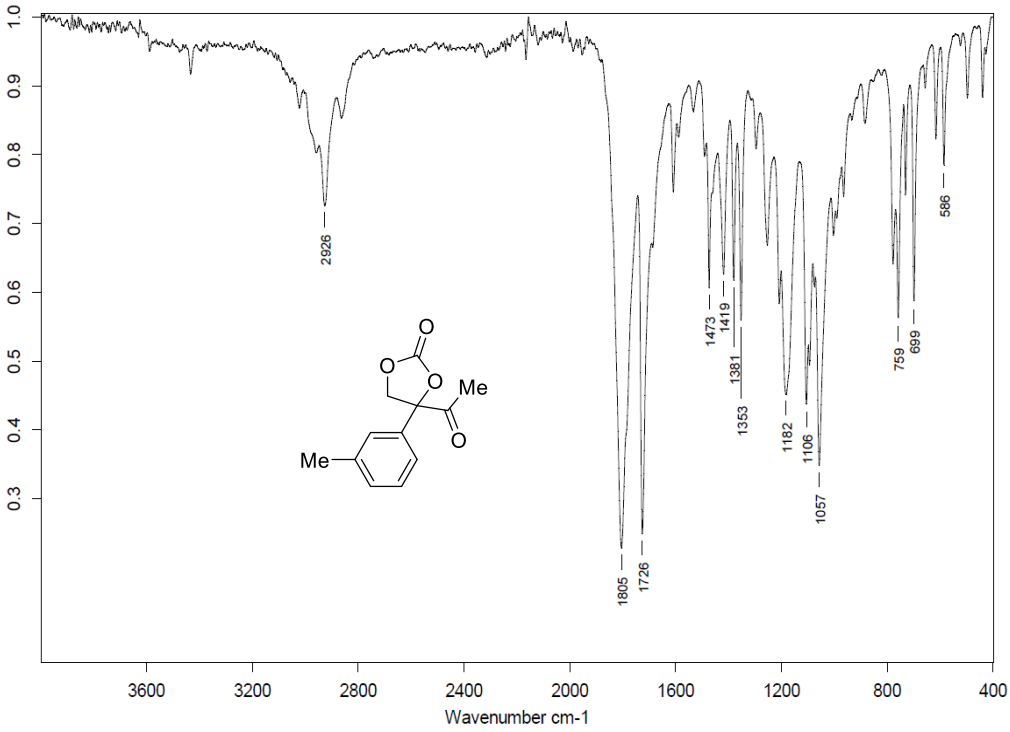
IR (neat) spectrum for **2j**



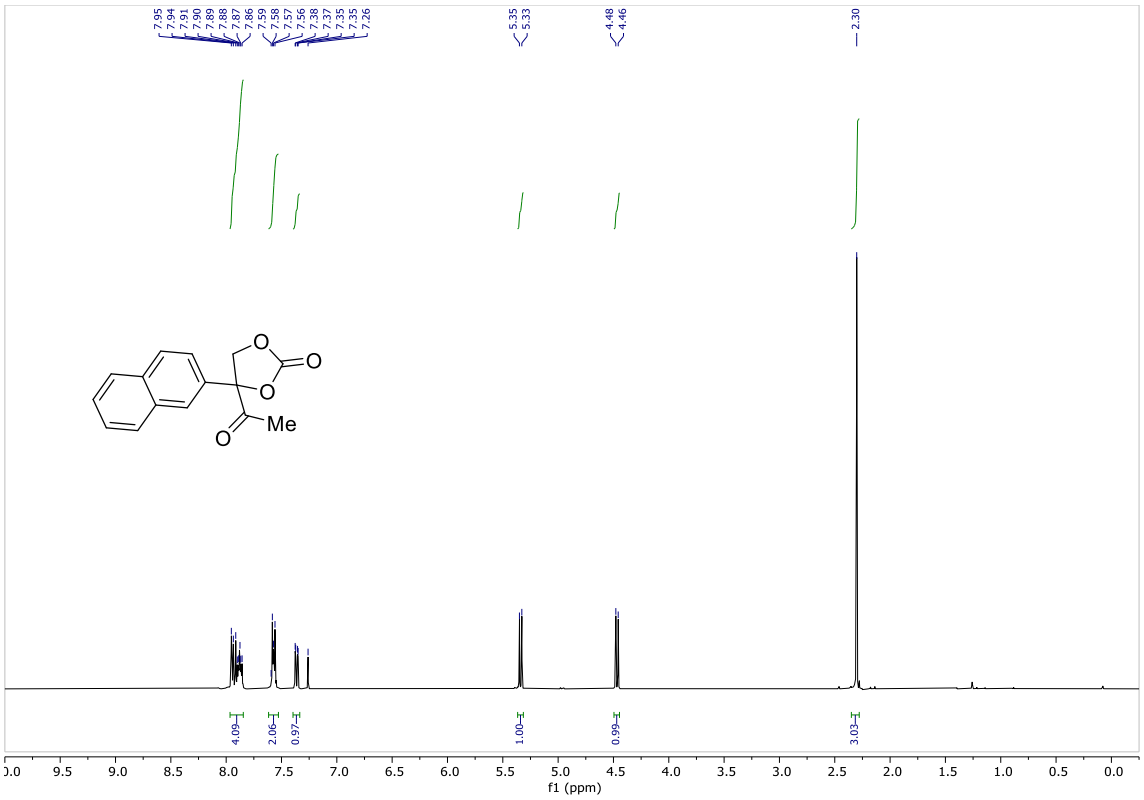
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2k**



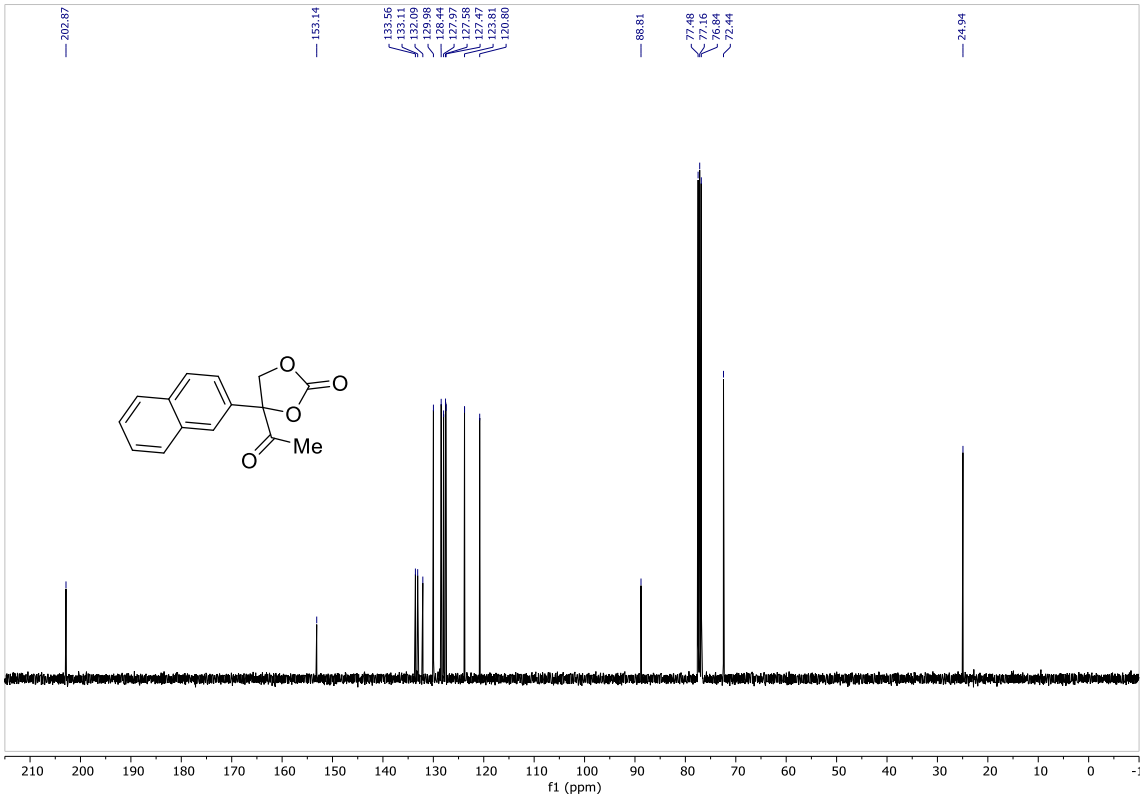
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2k**



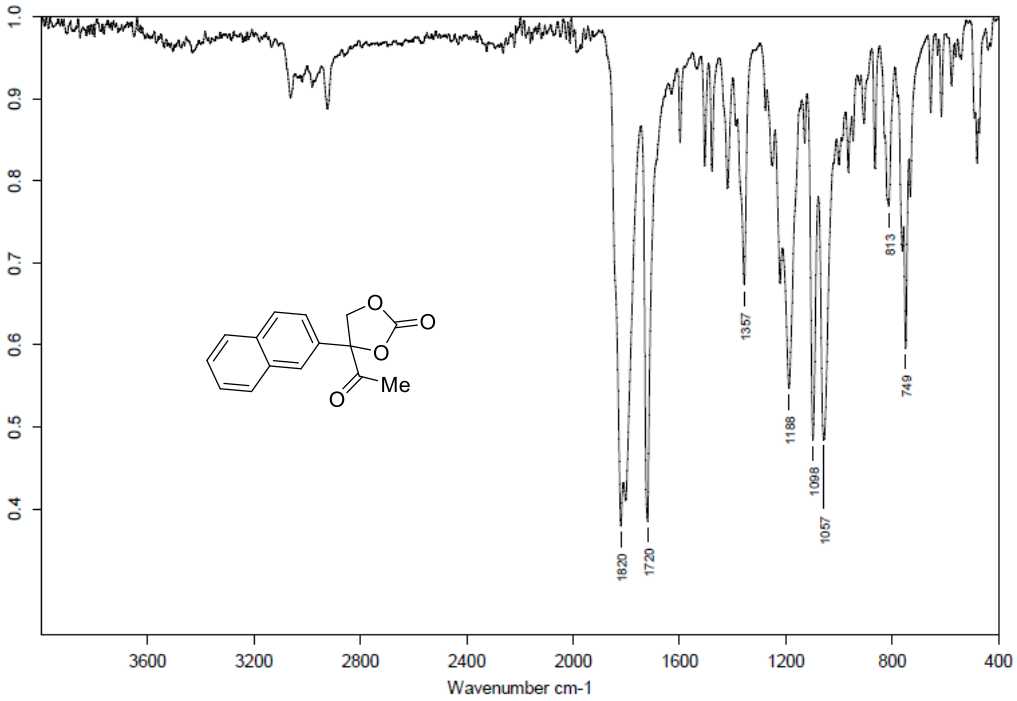
IR (neat) spectrum for **2k**



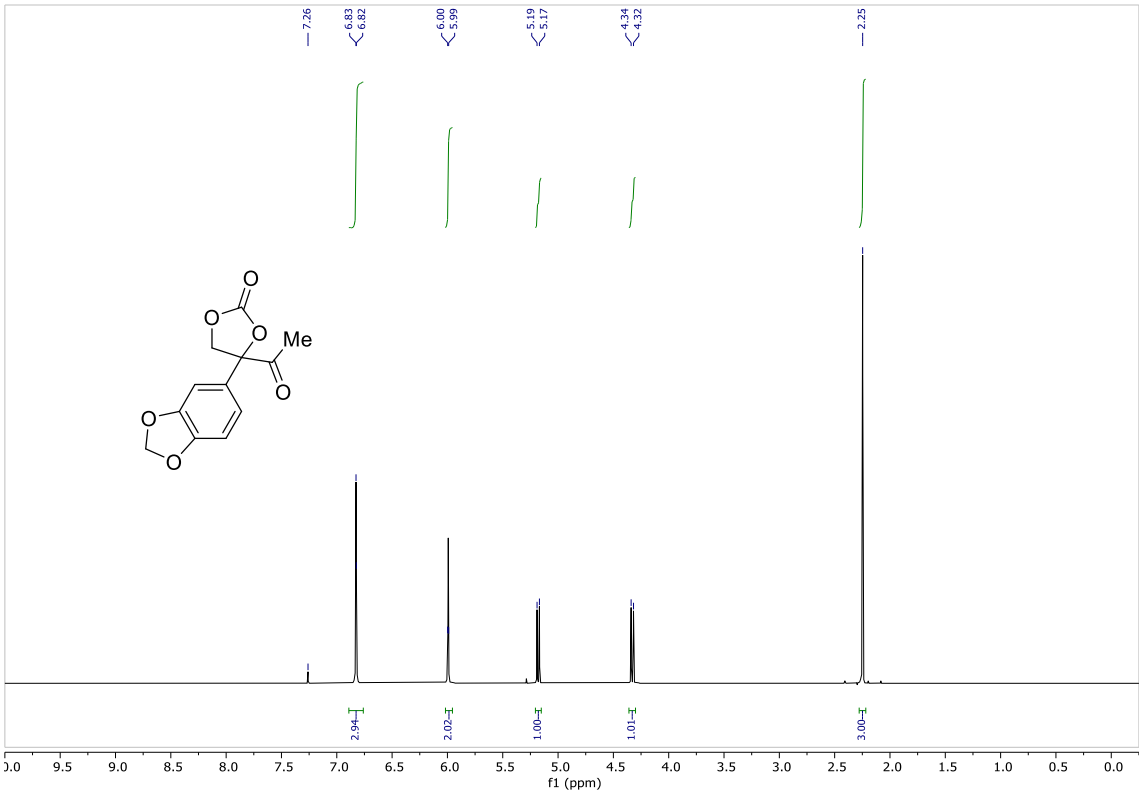
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2l**



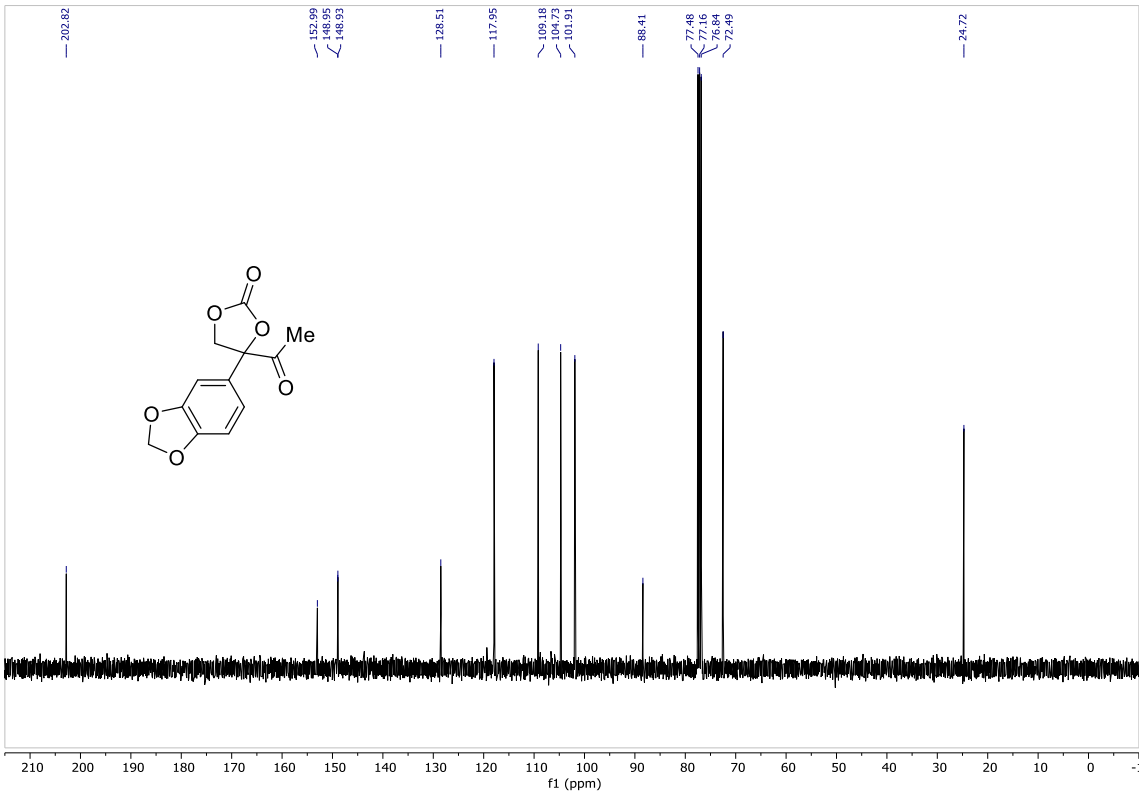
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2l**



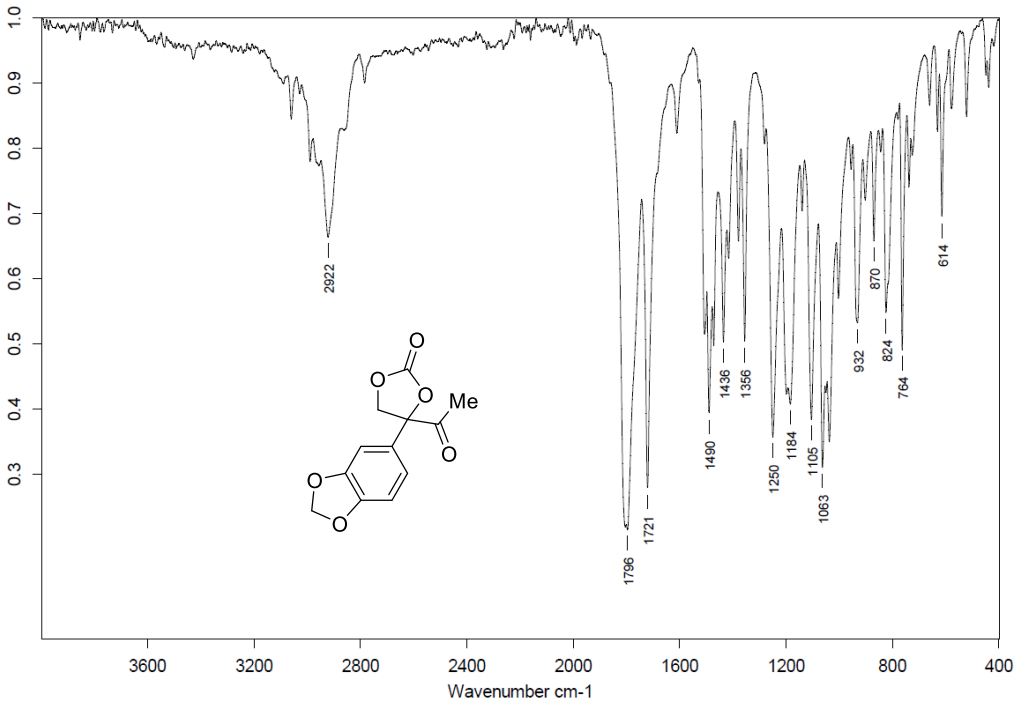
IR (neat) spectrum for **2l**



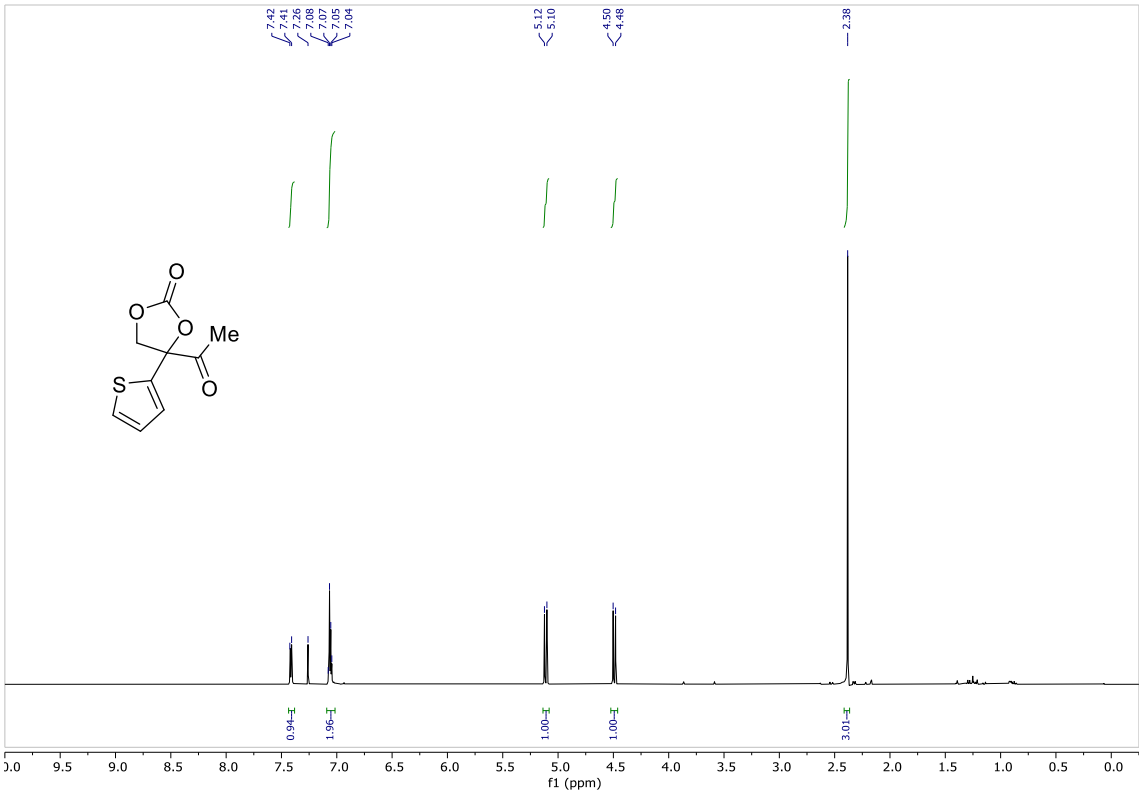
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2m**



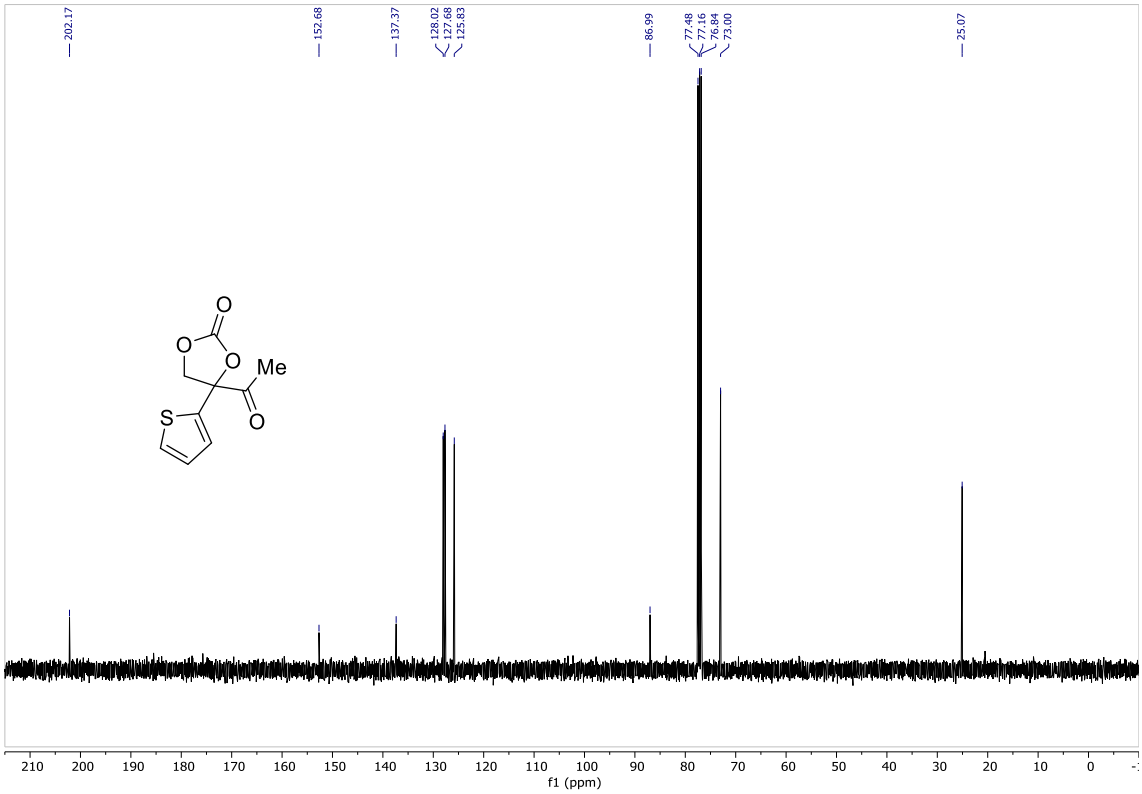
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2m**



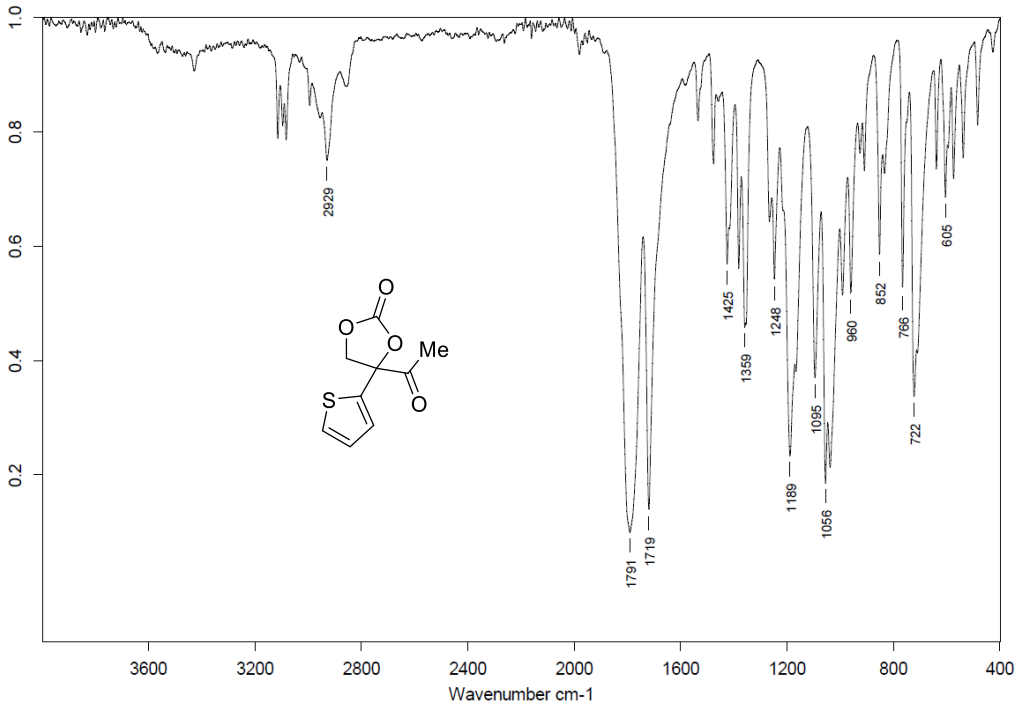
IR (neat) spectrum for **2m**



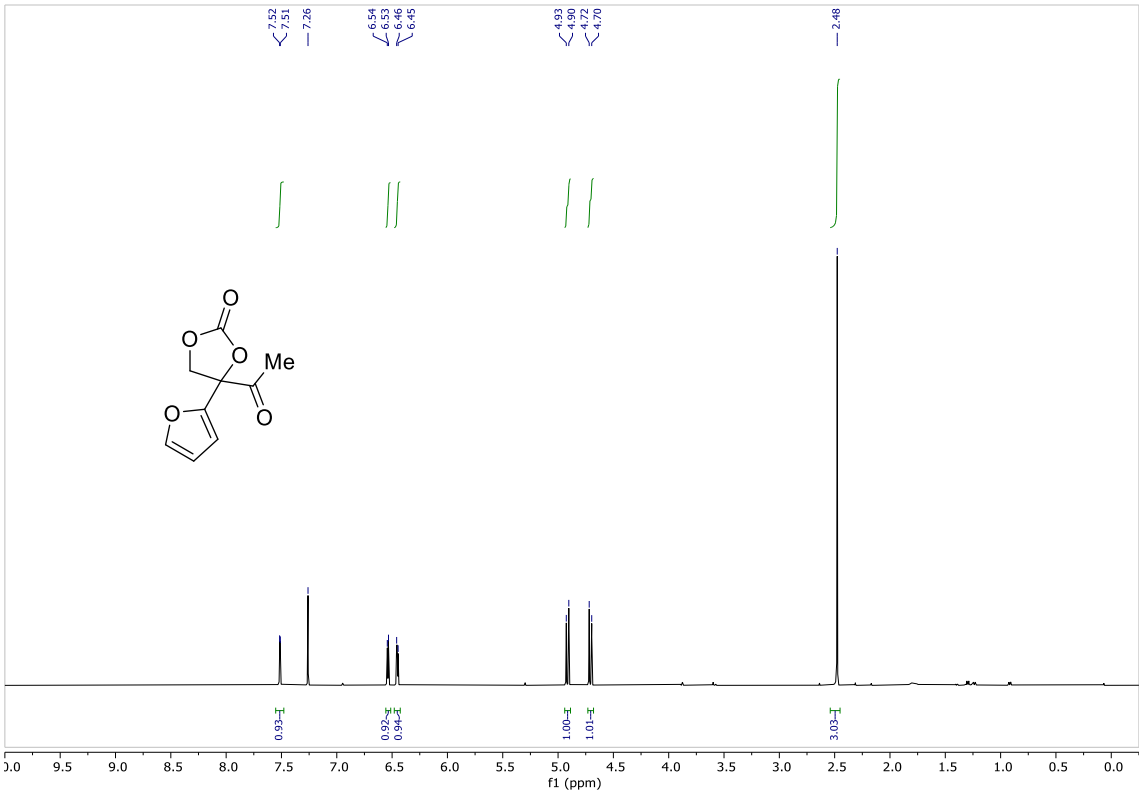
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2n**



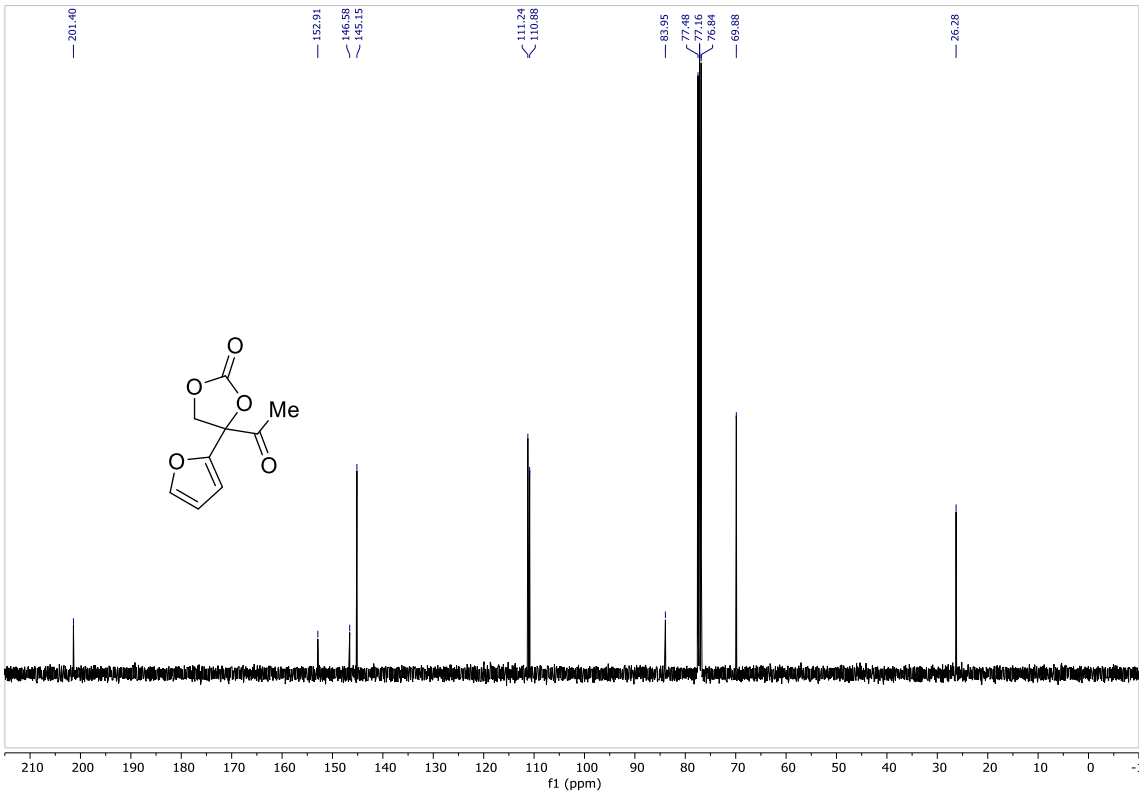
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2n**



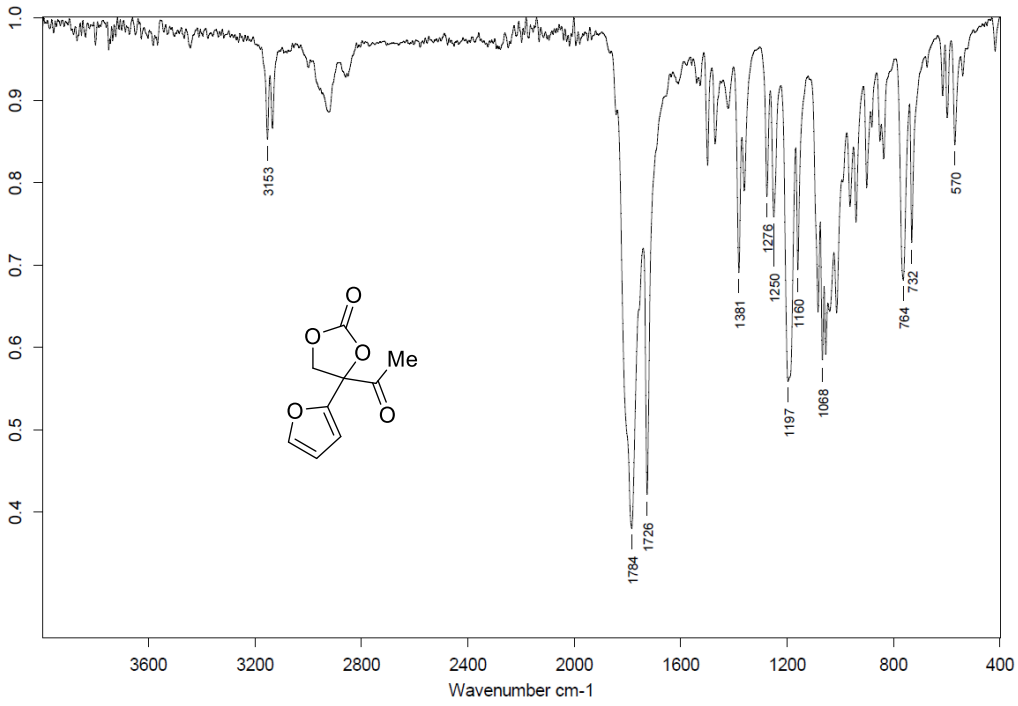
IR (neat) spectrum for **2n**



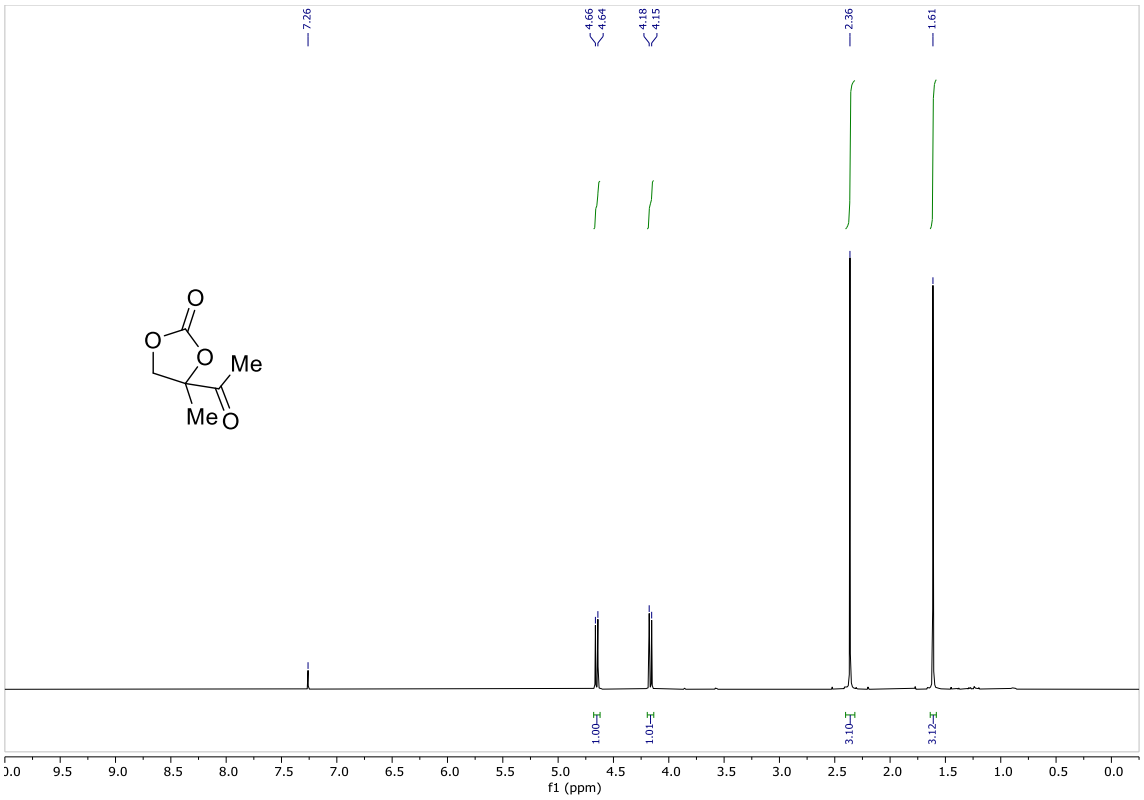
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2o**



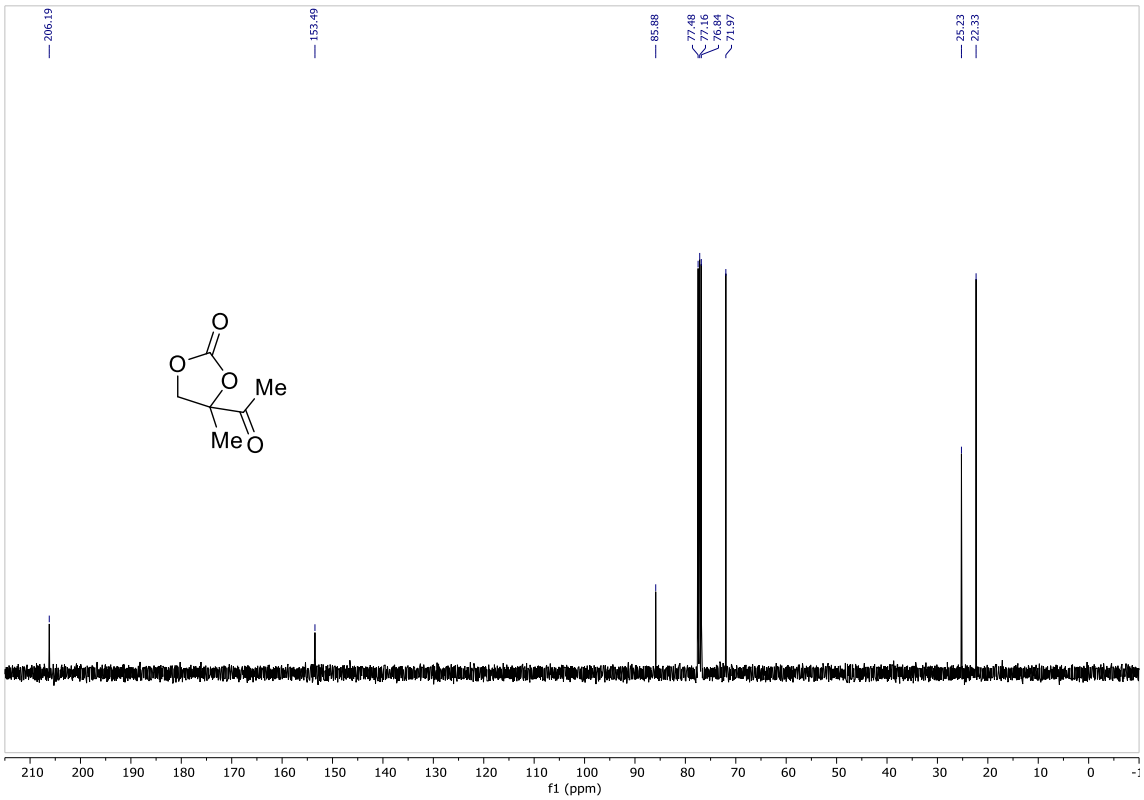
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2o**



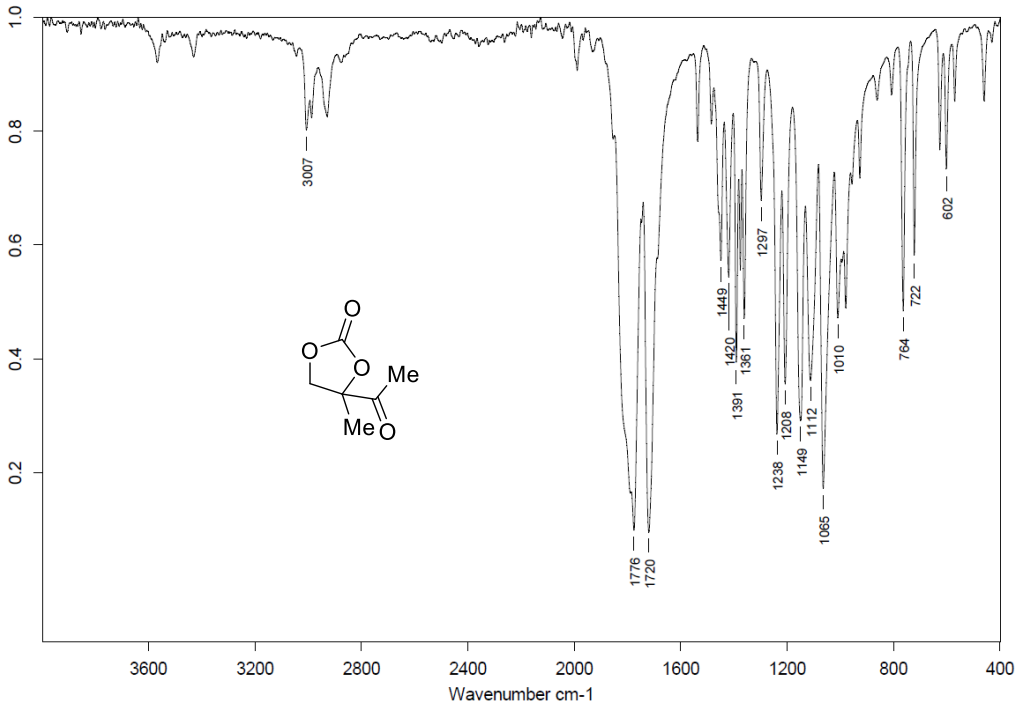
IR (neat) spectrum for **2o**



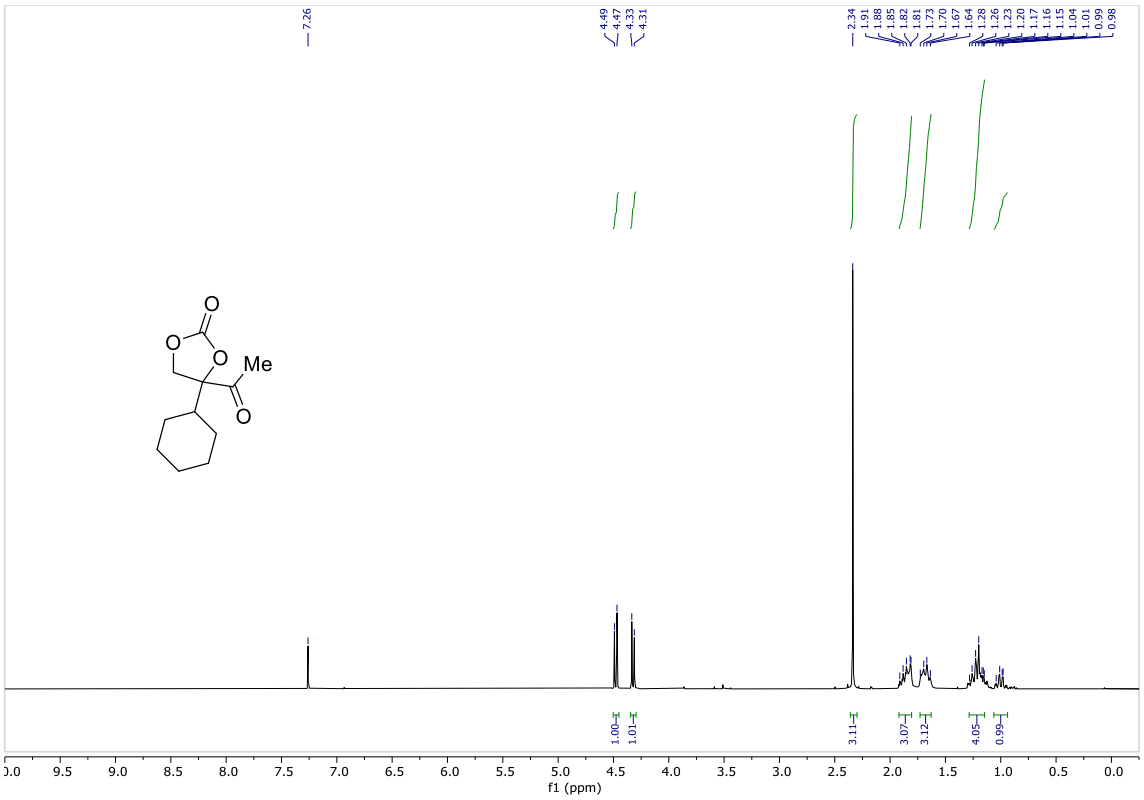
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2p**



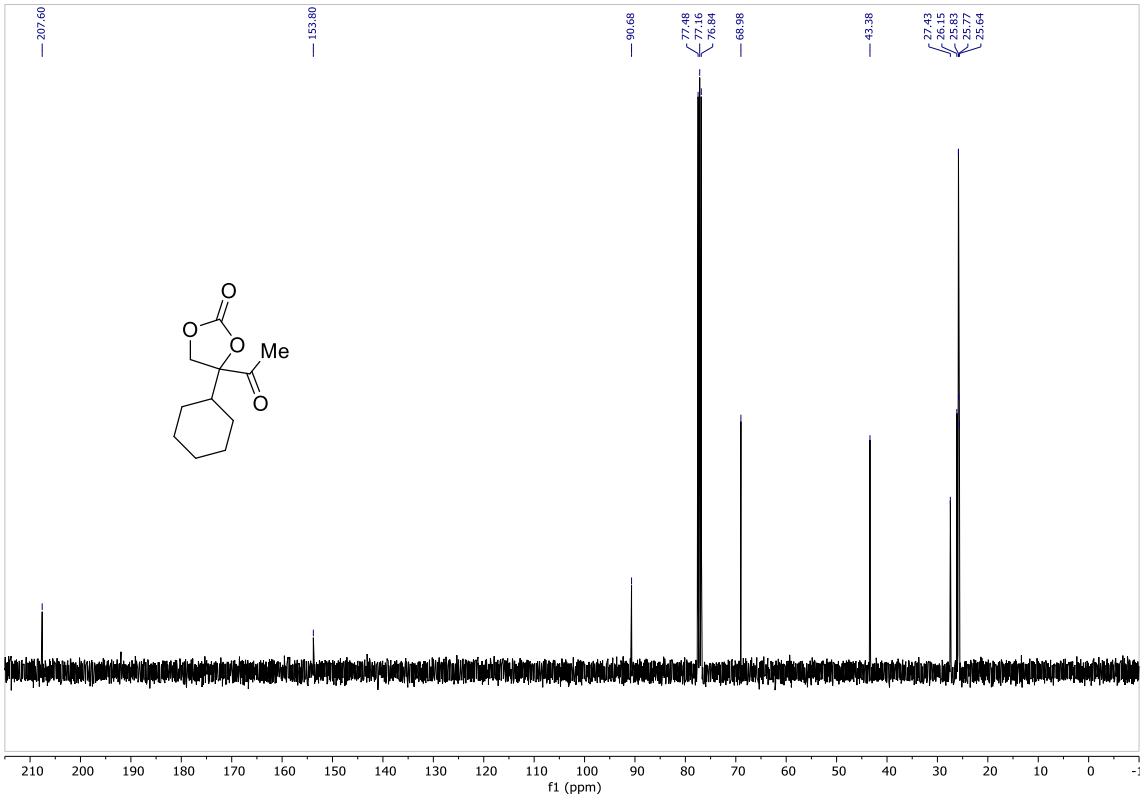
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2p**



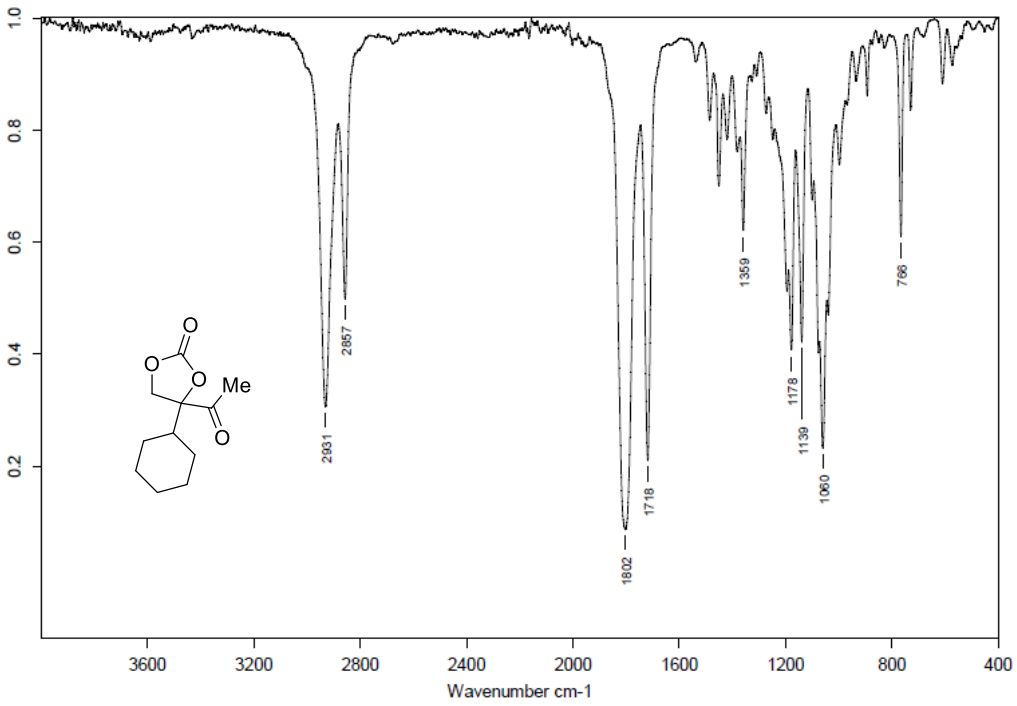
IR (neat) spectrum for **2p**



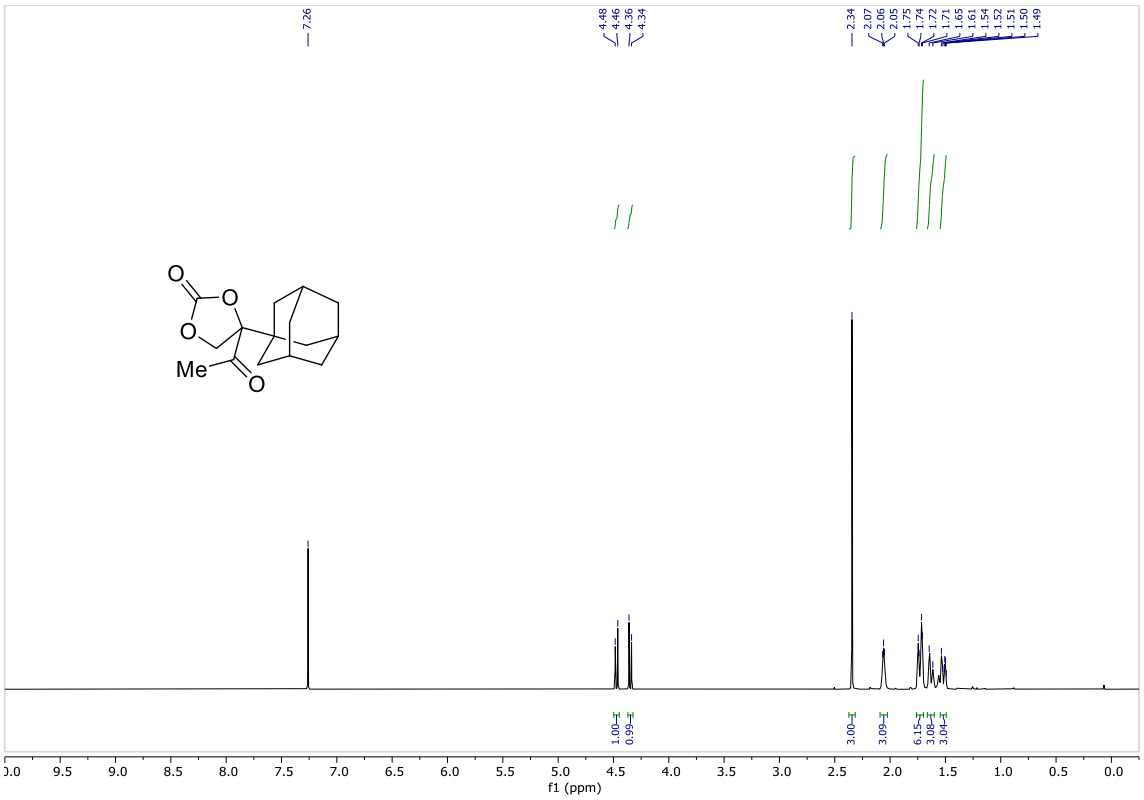
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2q**



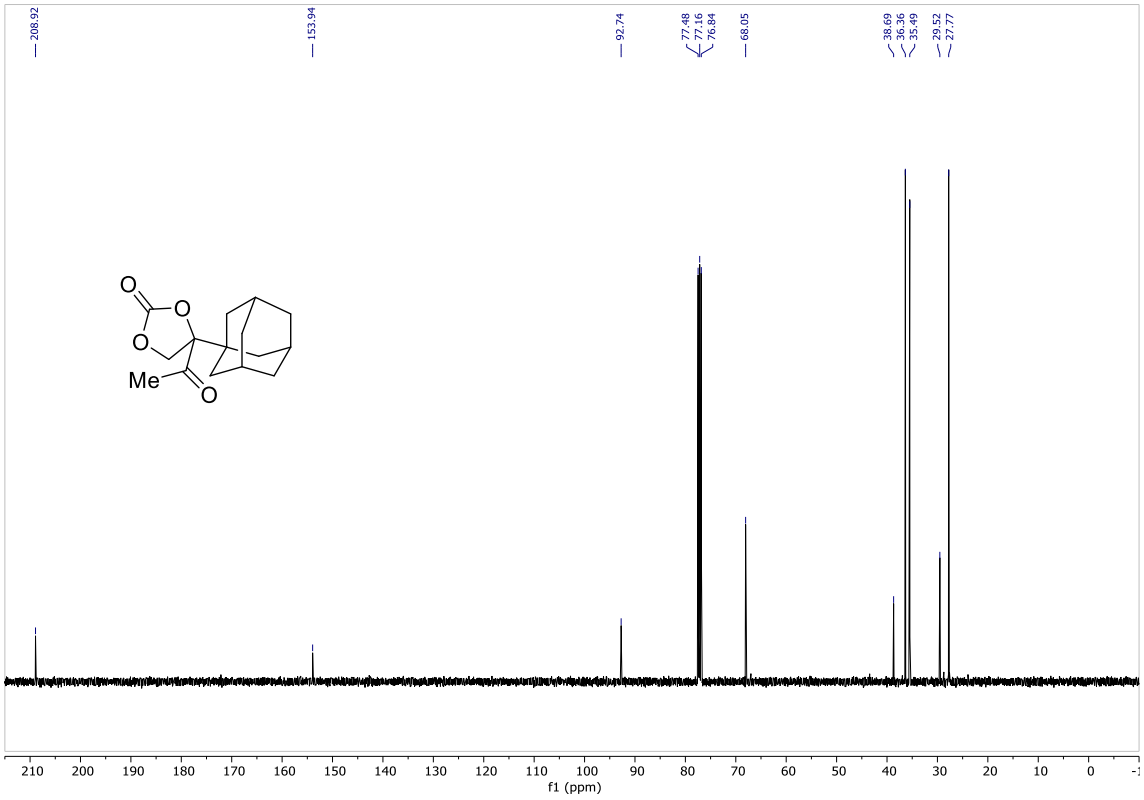
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2q**



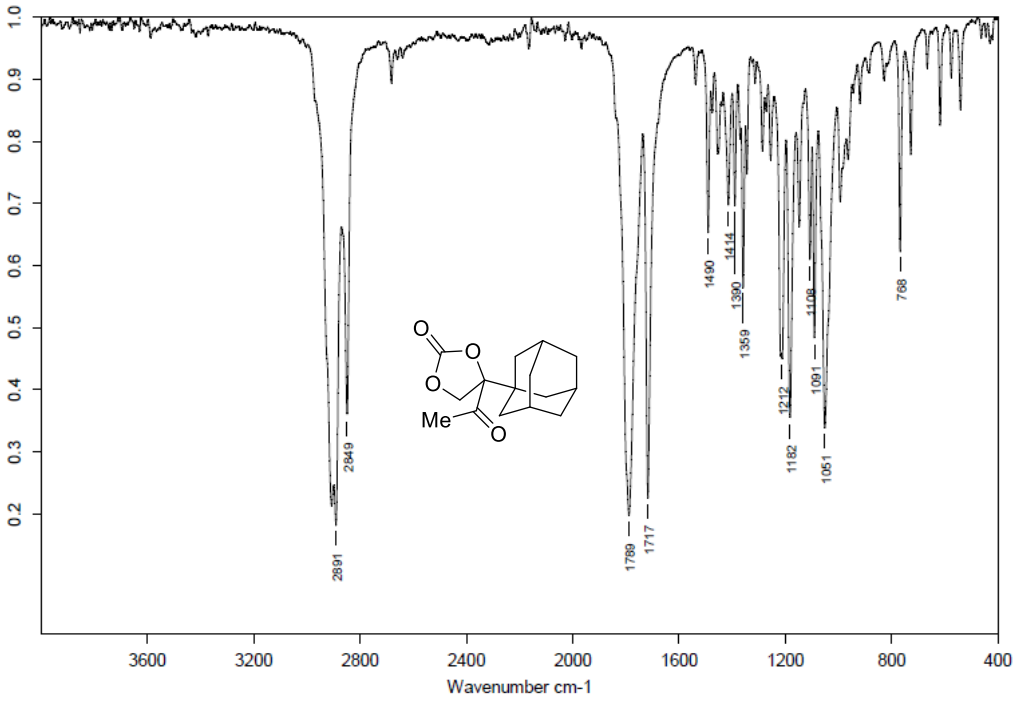
IR (neat) spectrum for **2q**



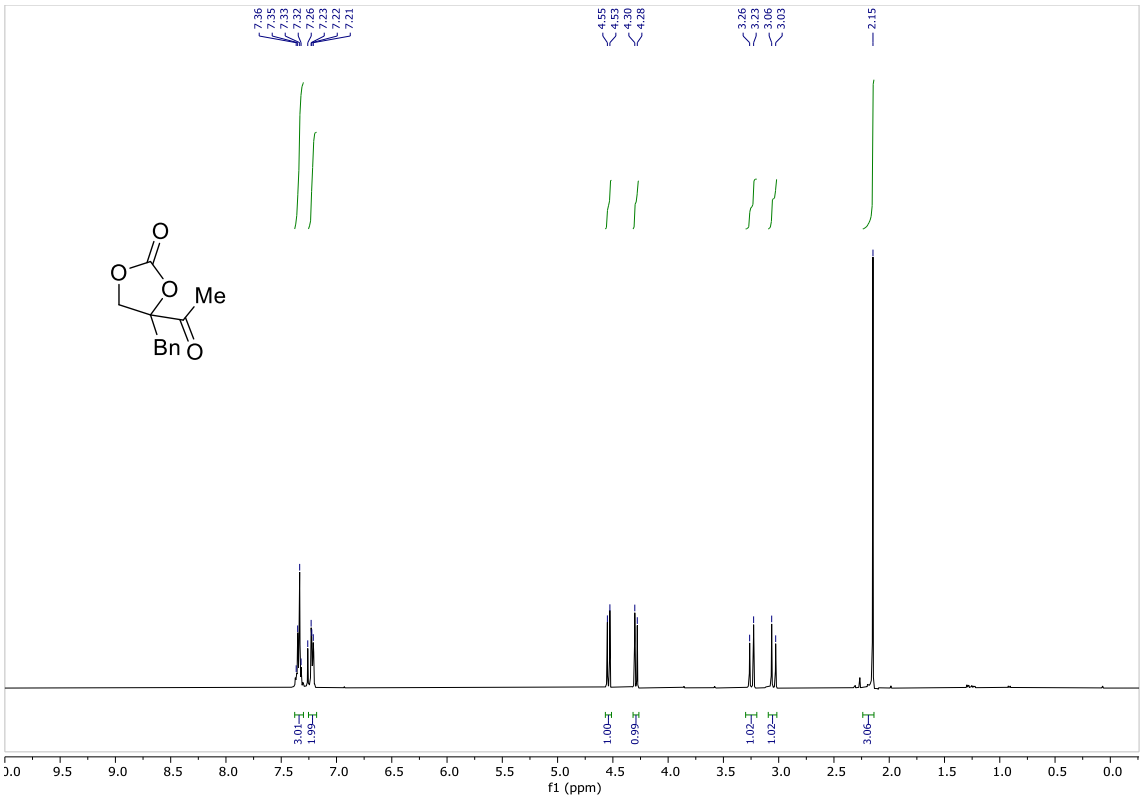
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2r**



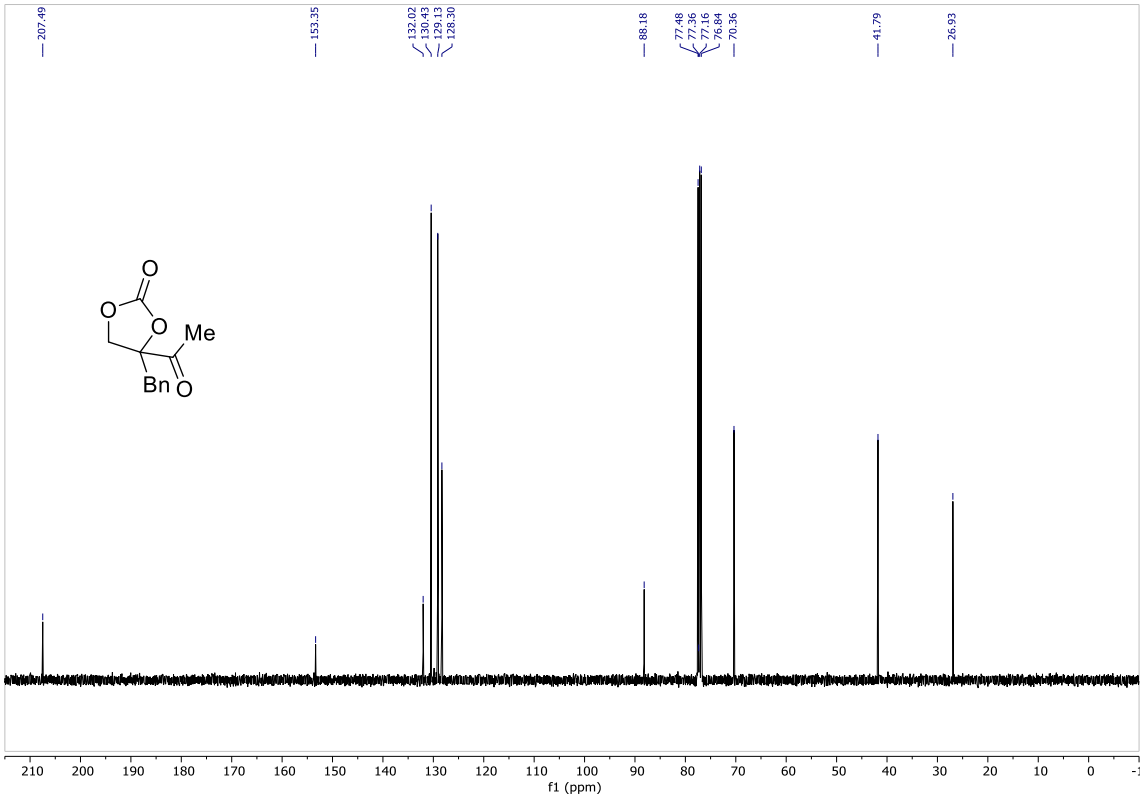
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2r**



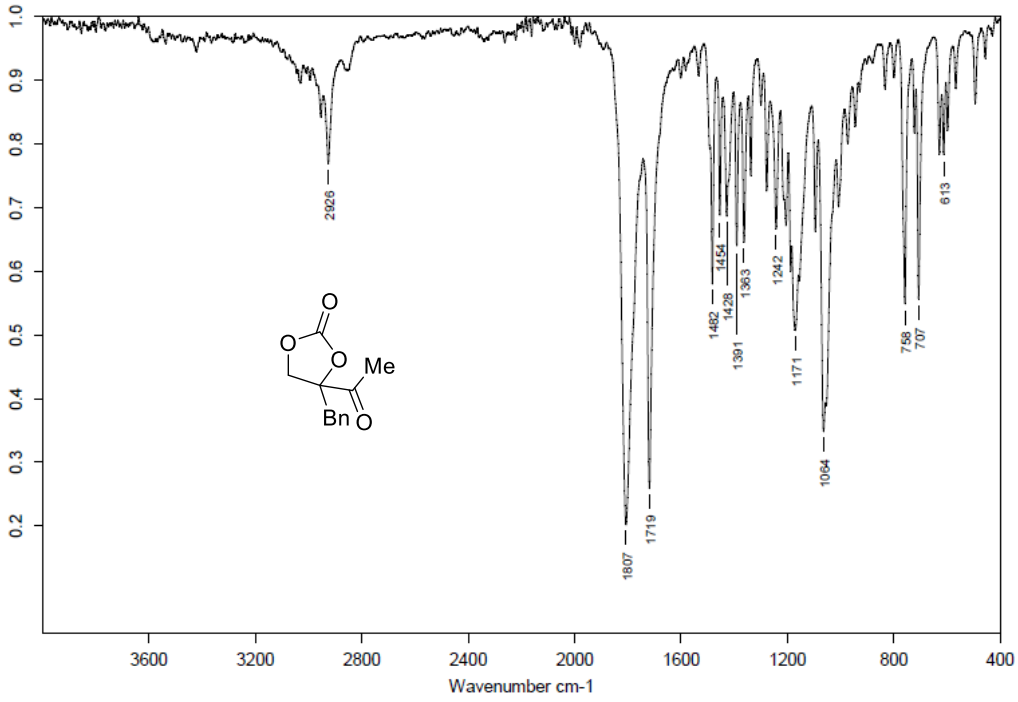
IR (neat) spectrum for **2r**



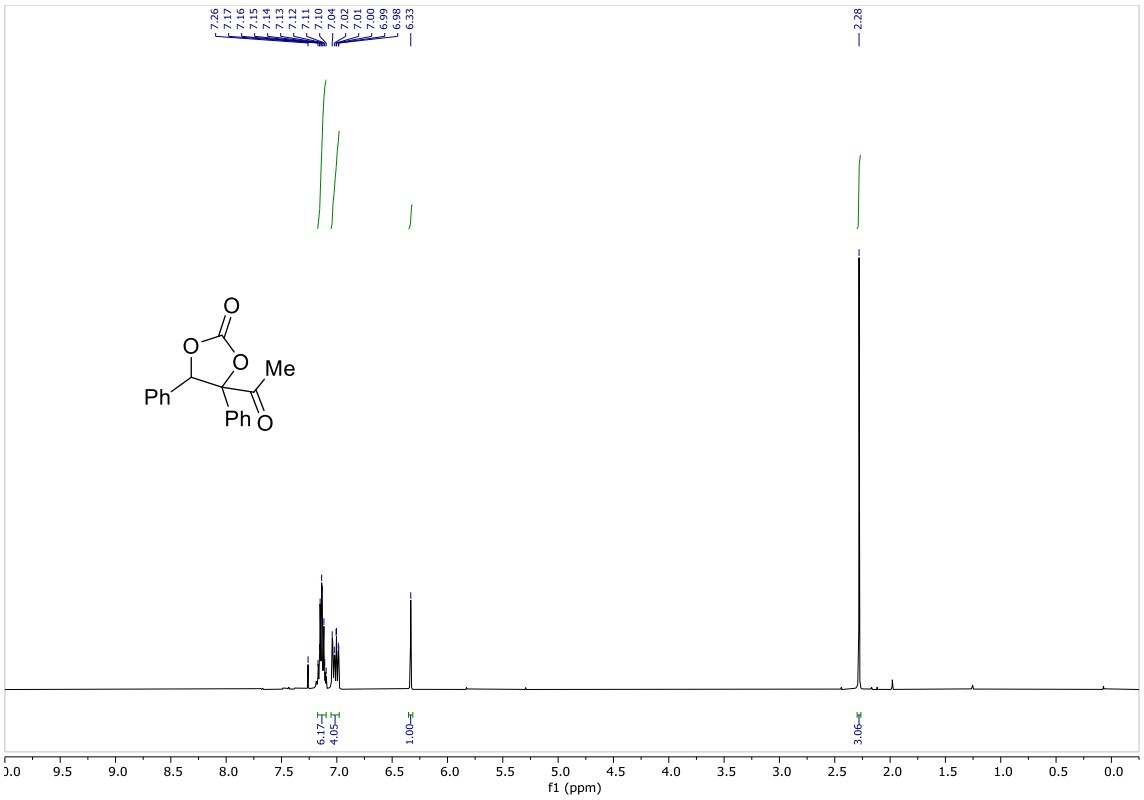
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2s**



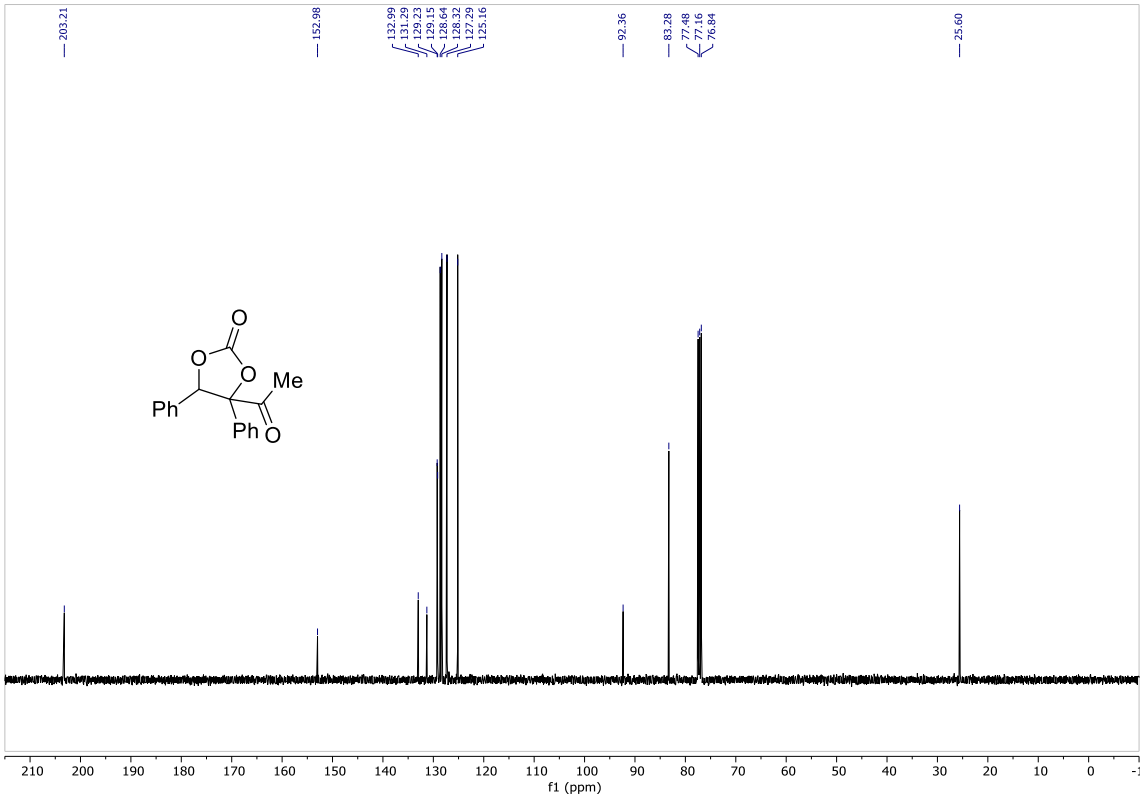
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2s**



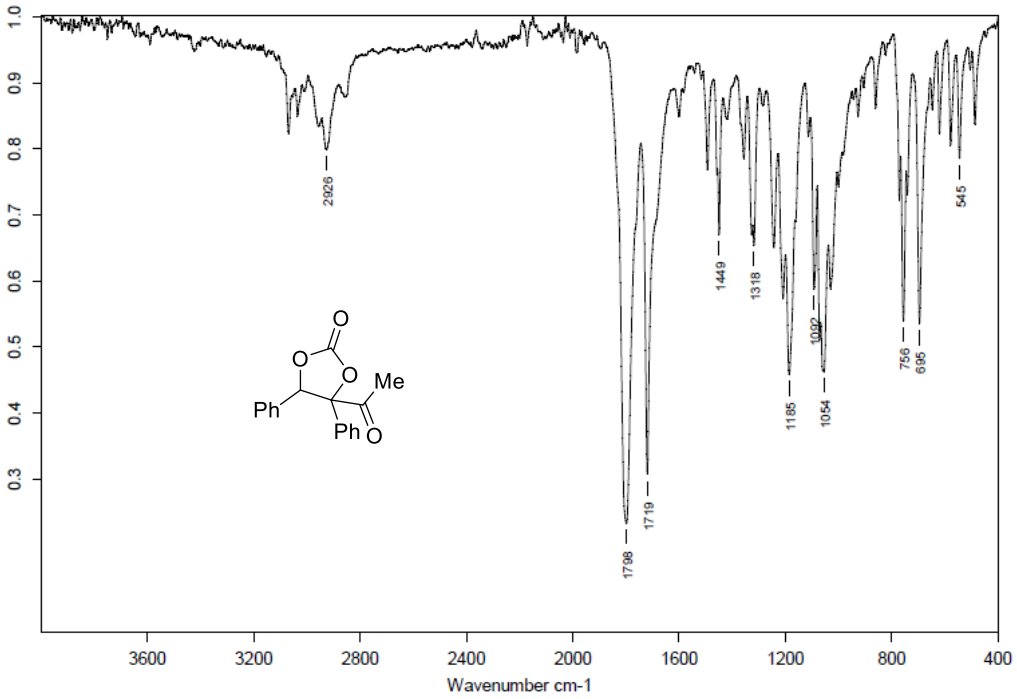
IR (neat) spectrum for **2s**



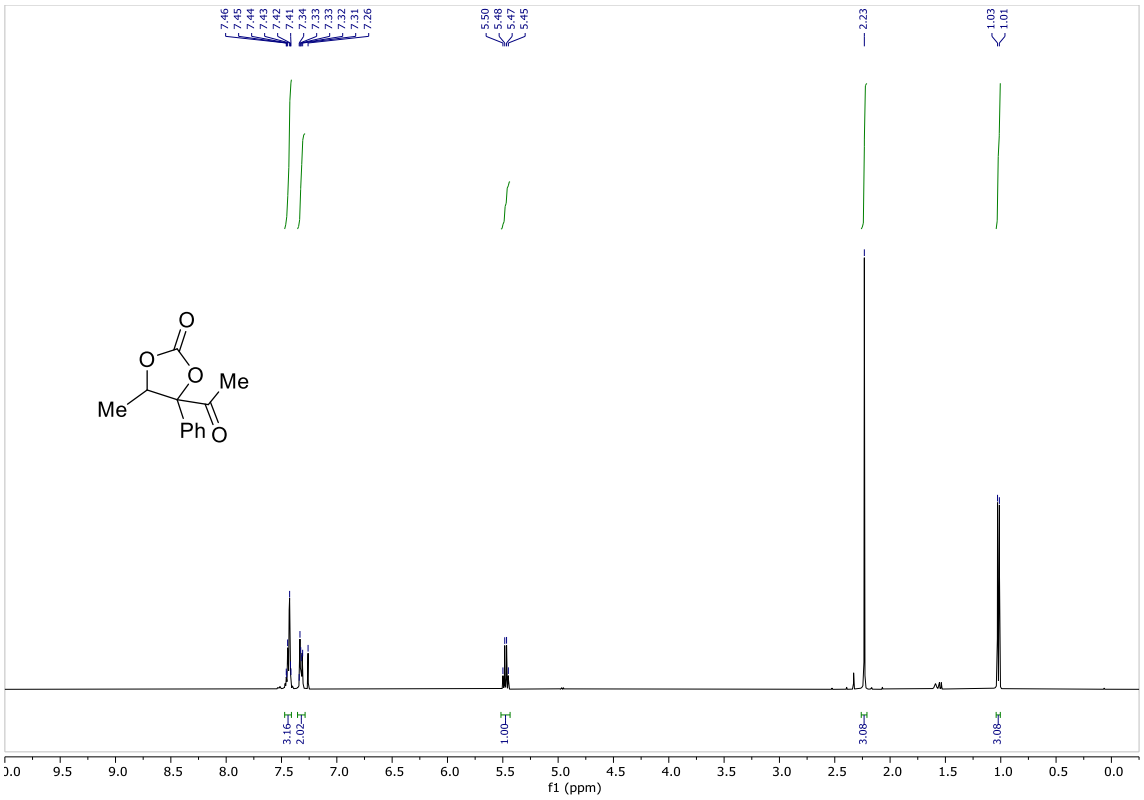
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4a**



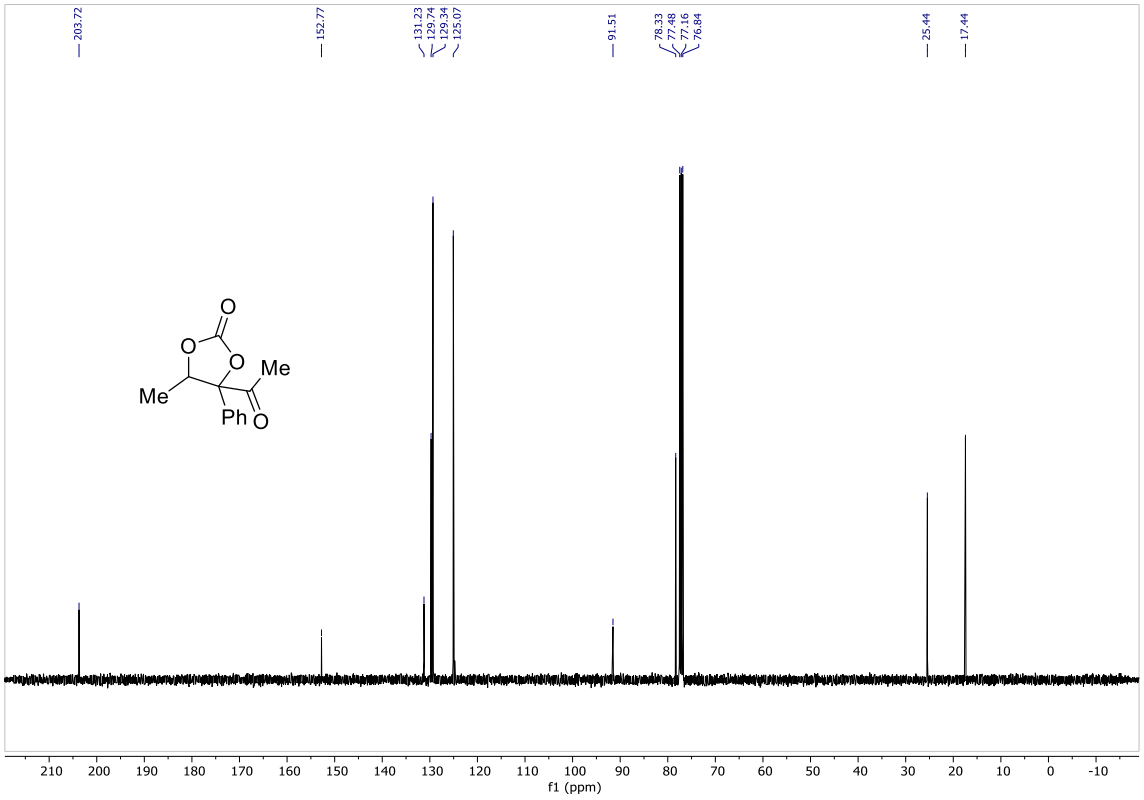
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4a**



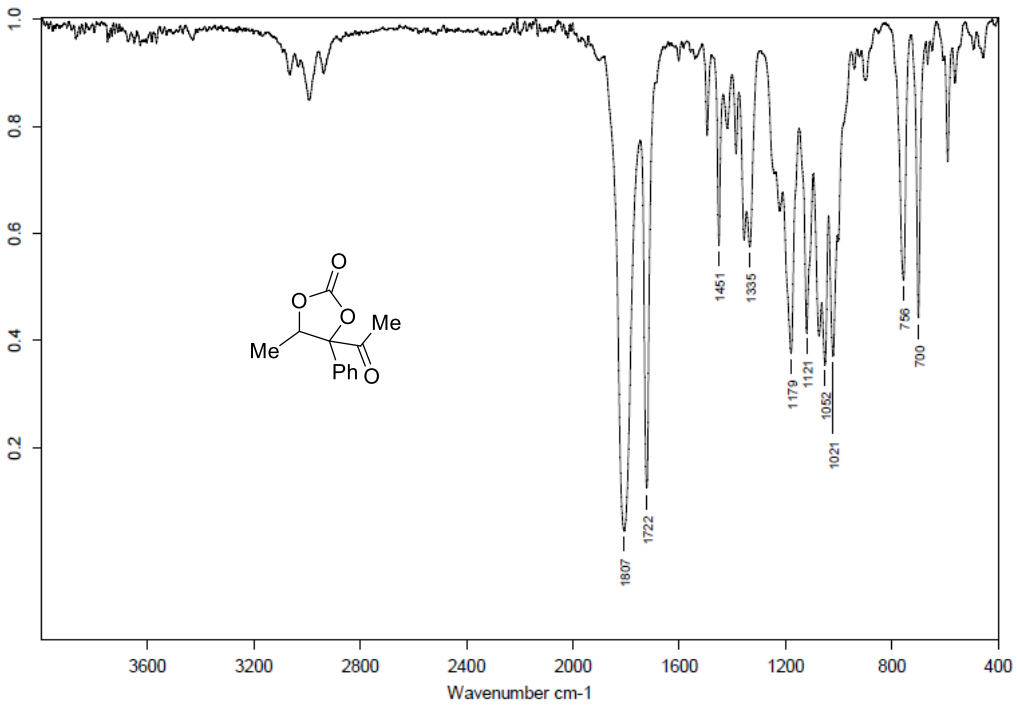
IR (neat) spectrum for **4a**



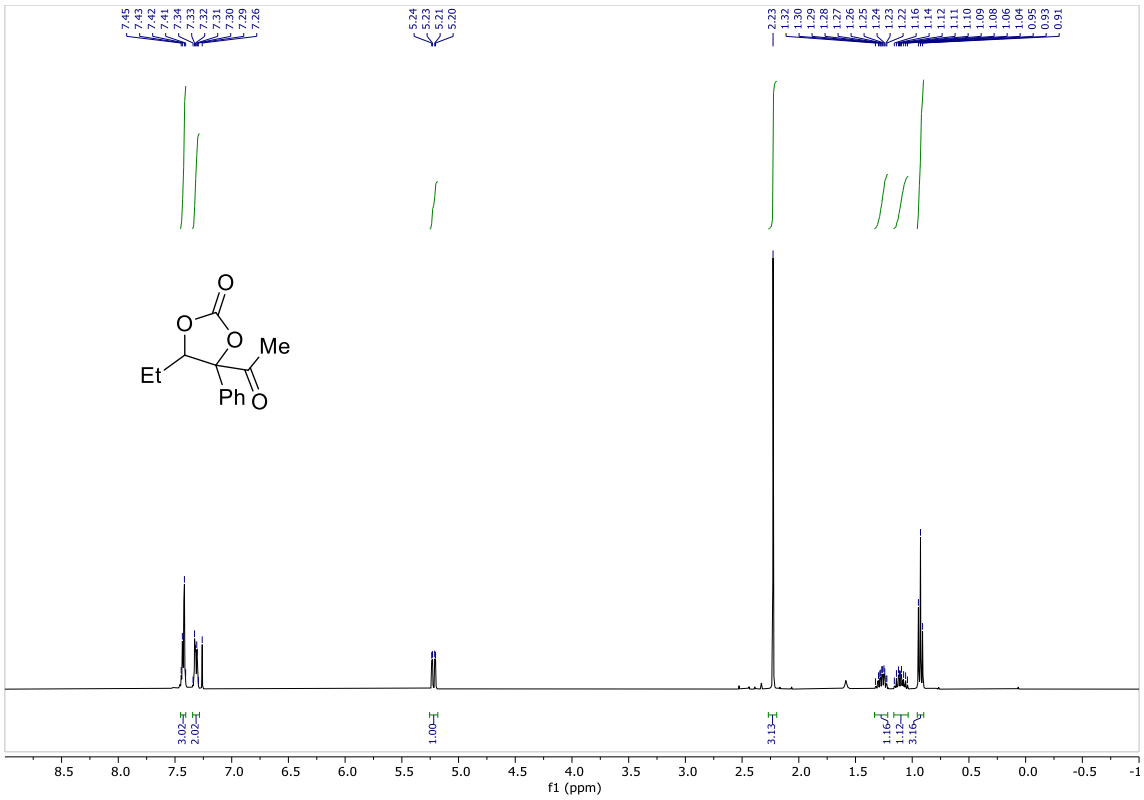
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4b**



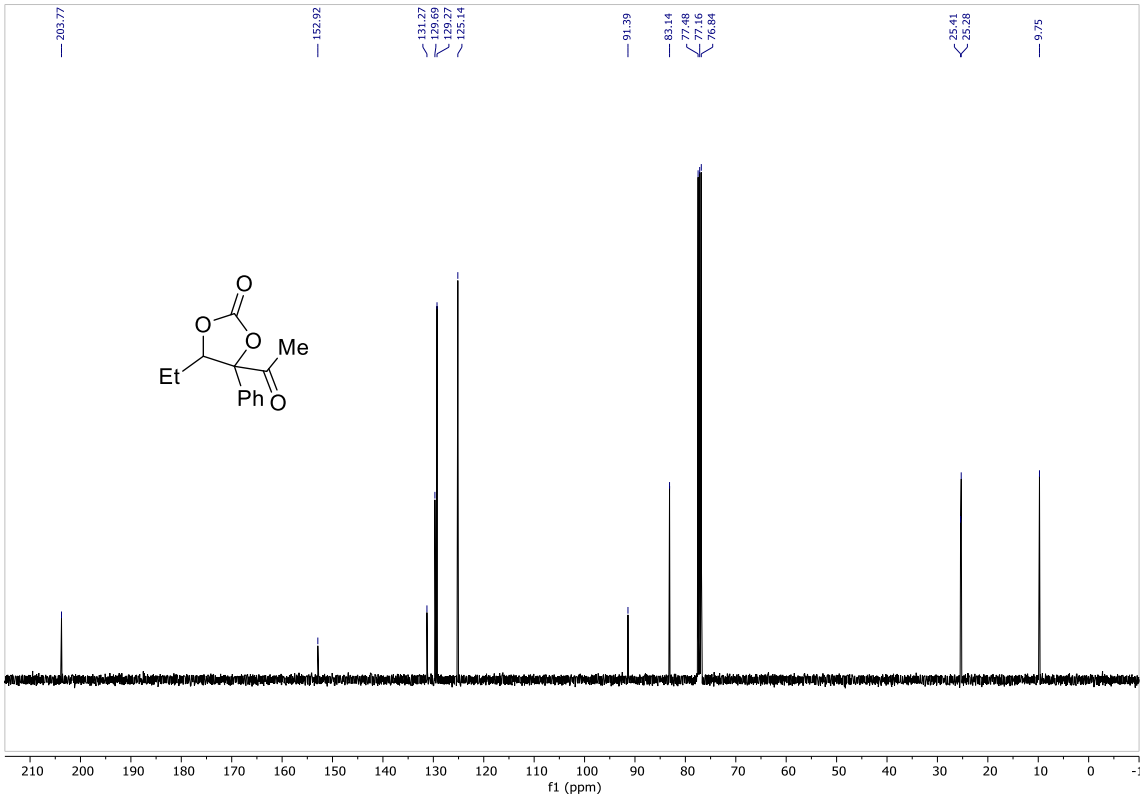
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4b**



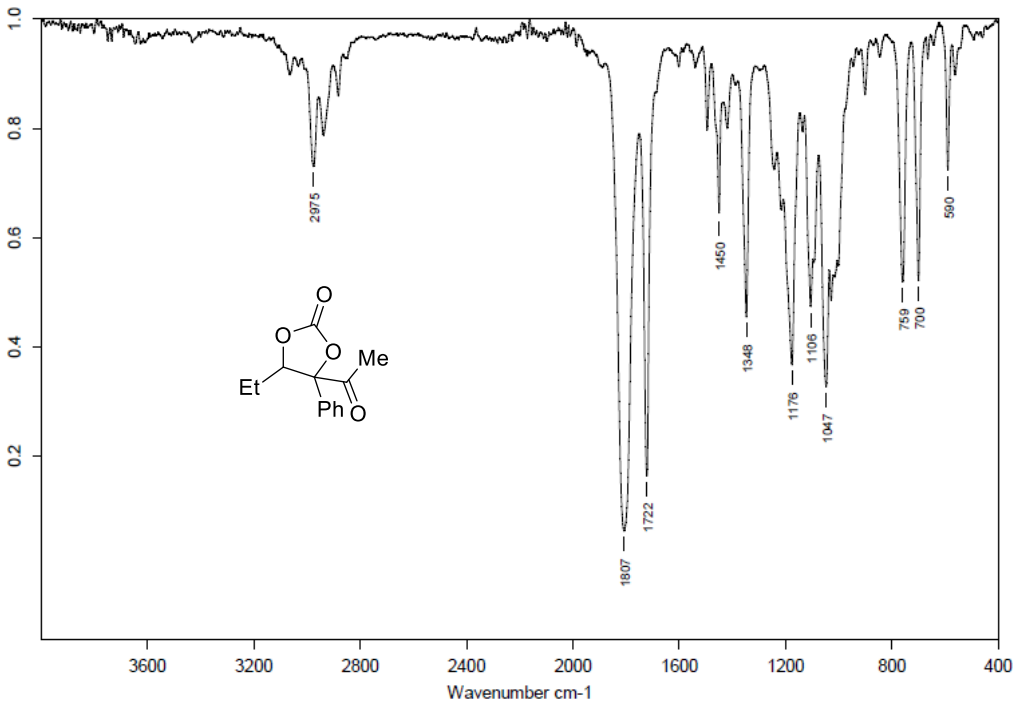
IR (neat) spectrum for **4b**



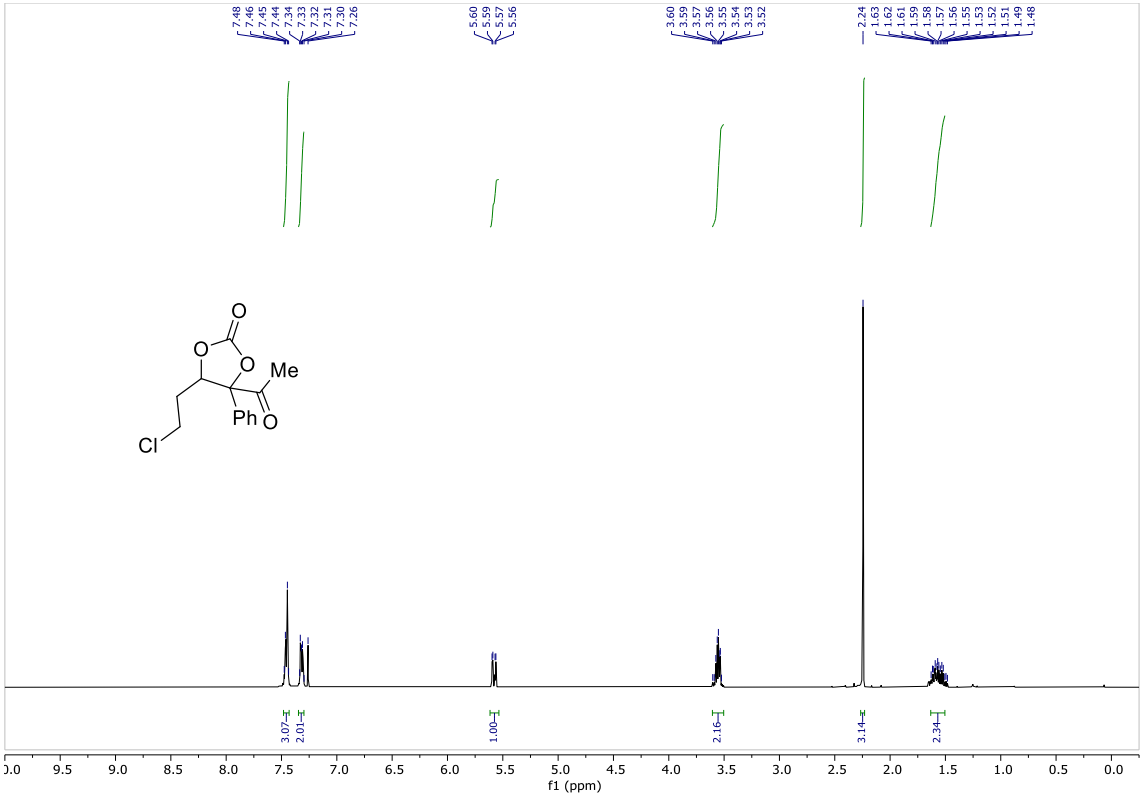
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4c**



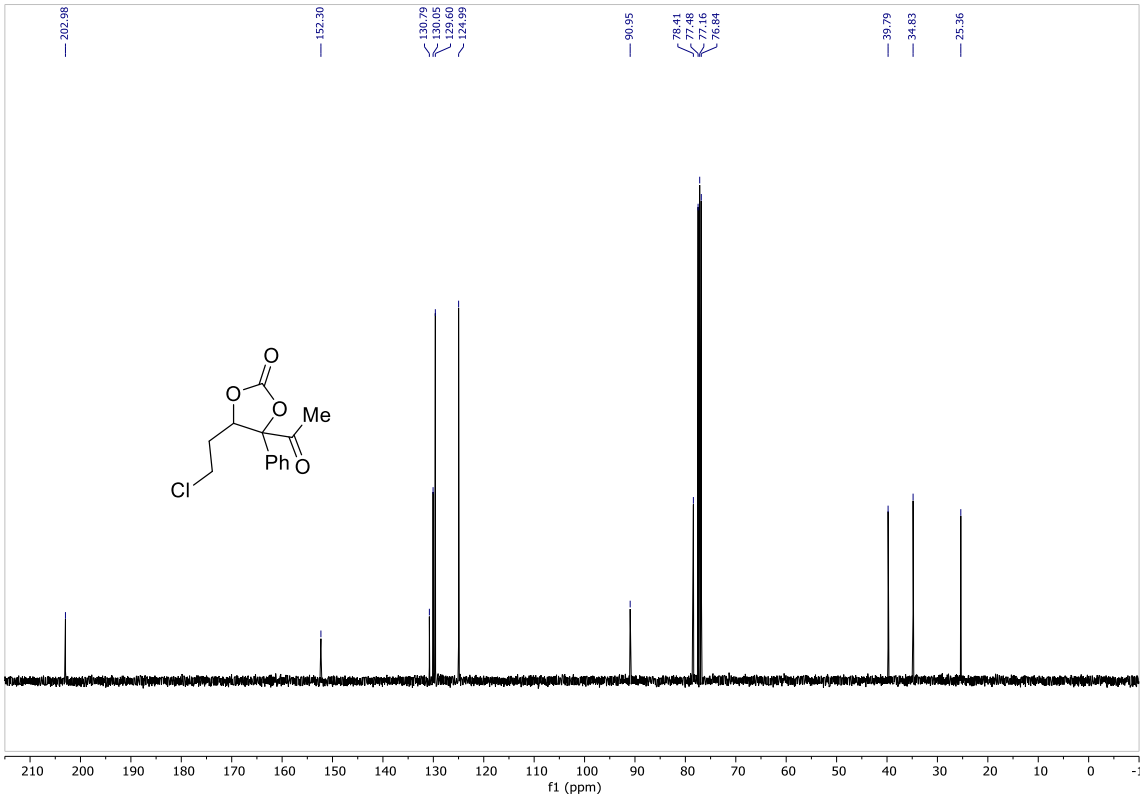
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4c**



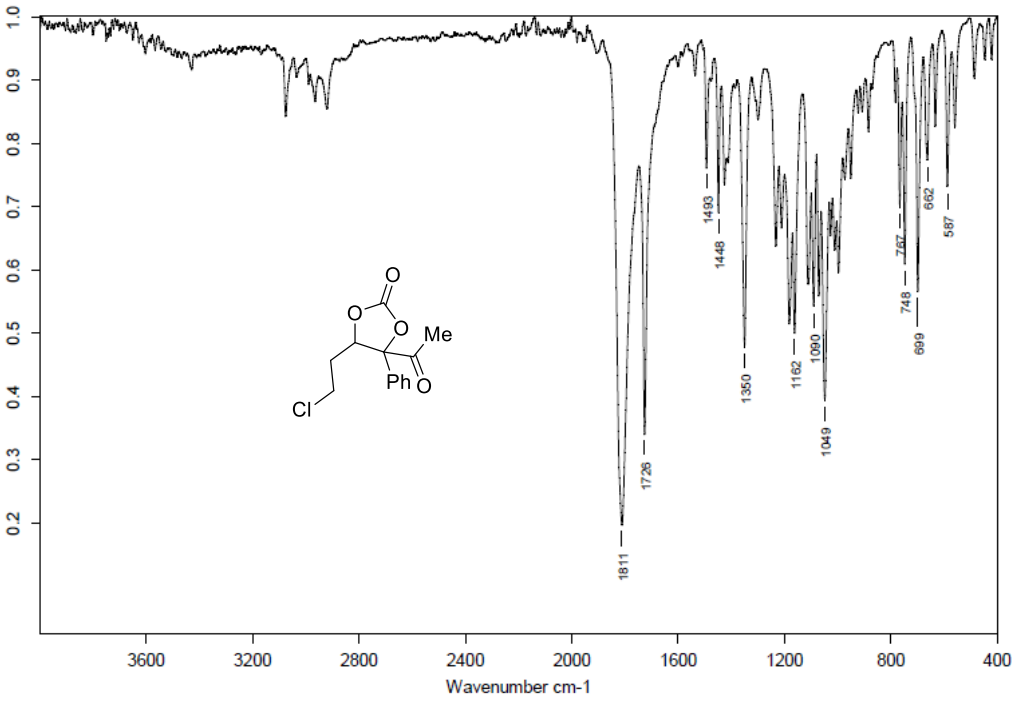
IR (neat) spectrum for **4c**



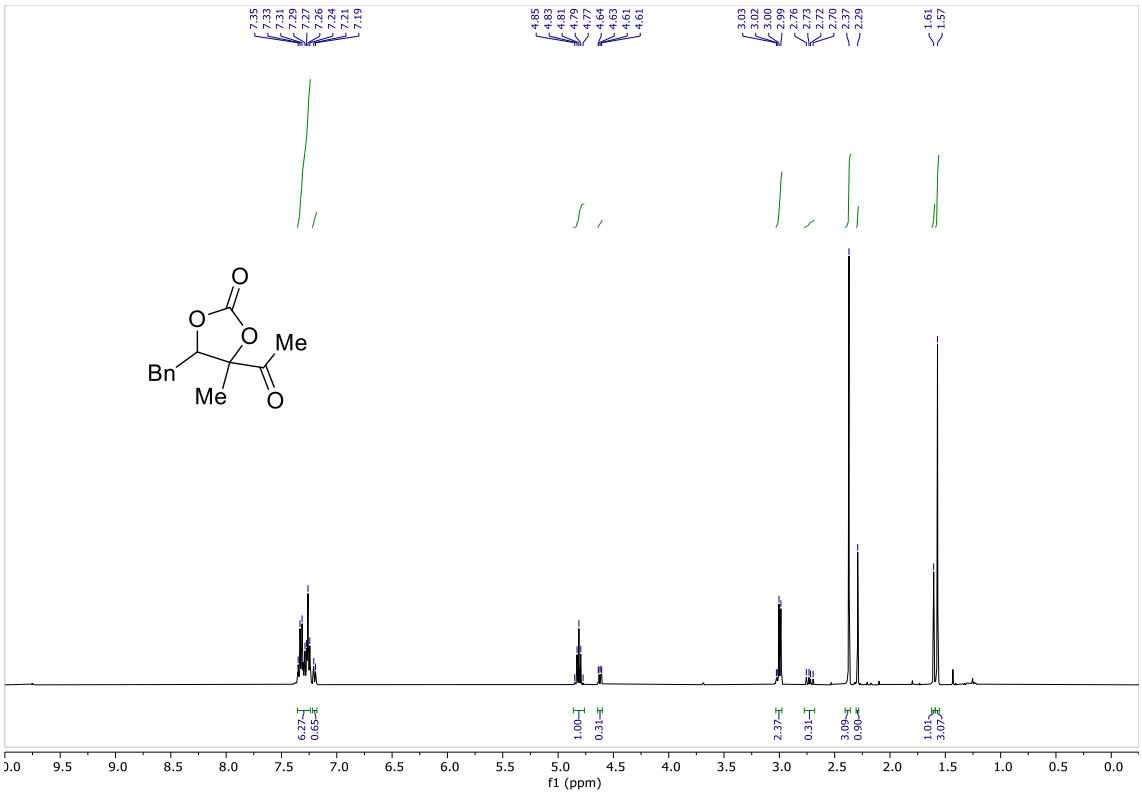
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4d**



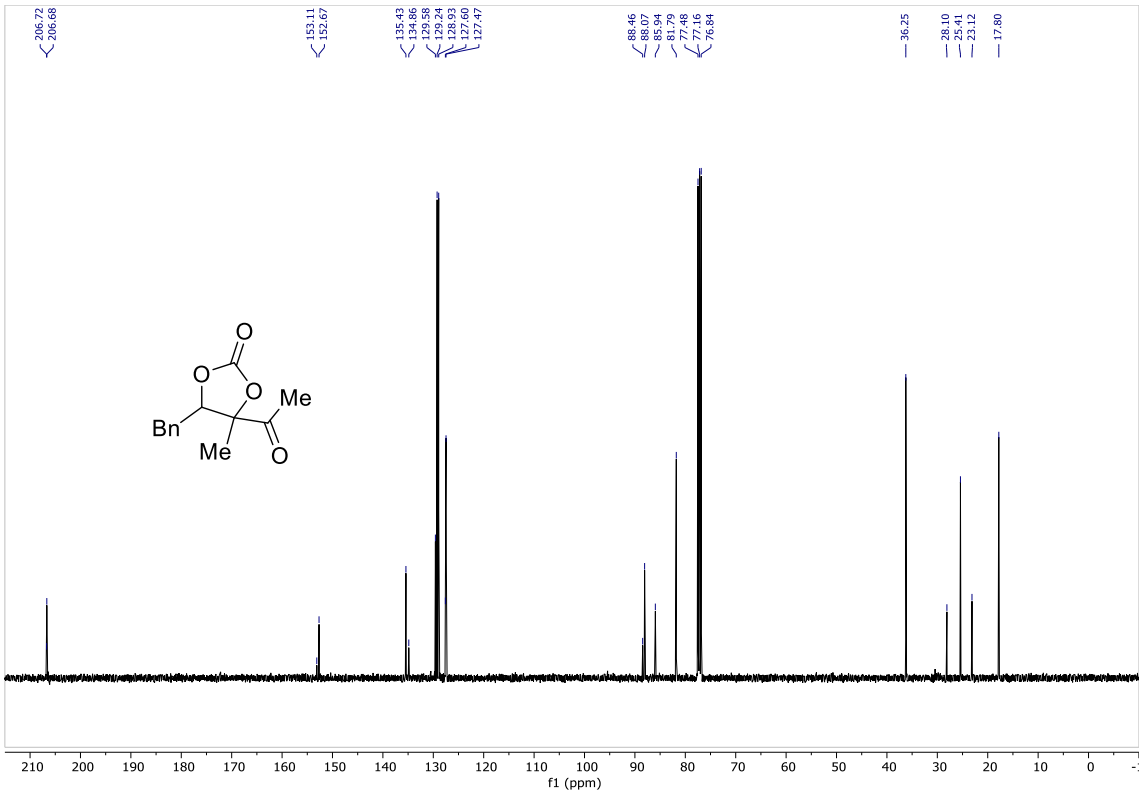
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4d**



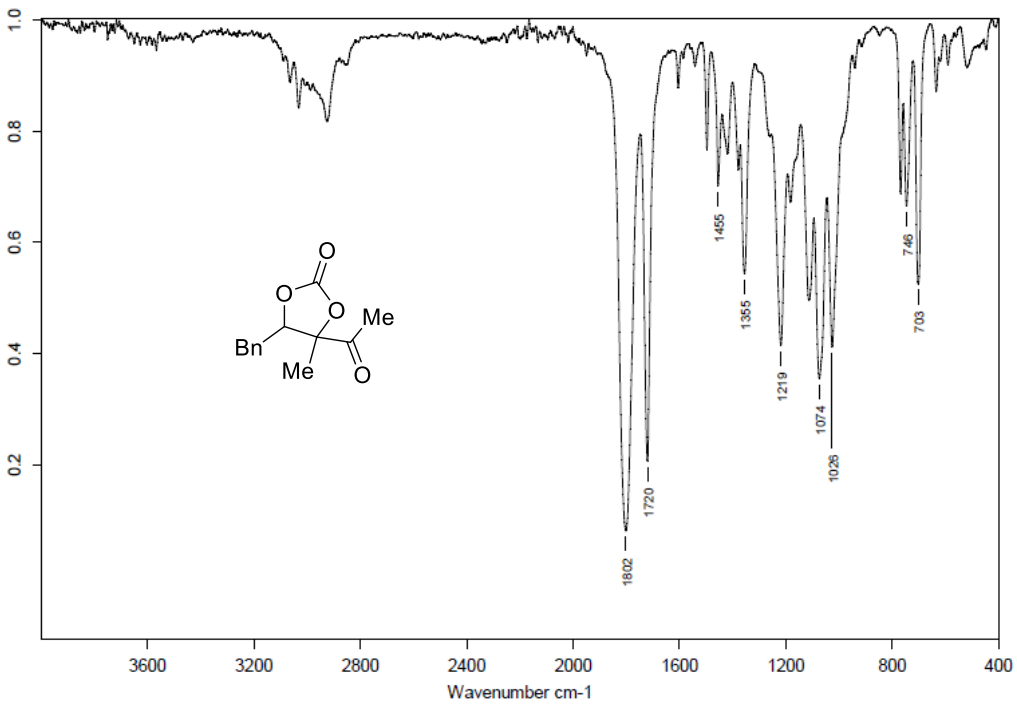
IR (neat) spectrum for **4d**



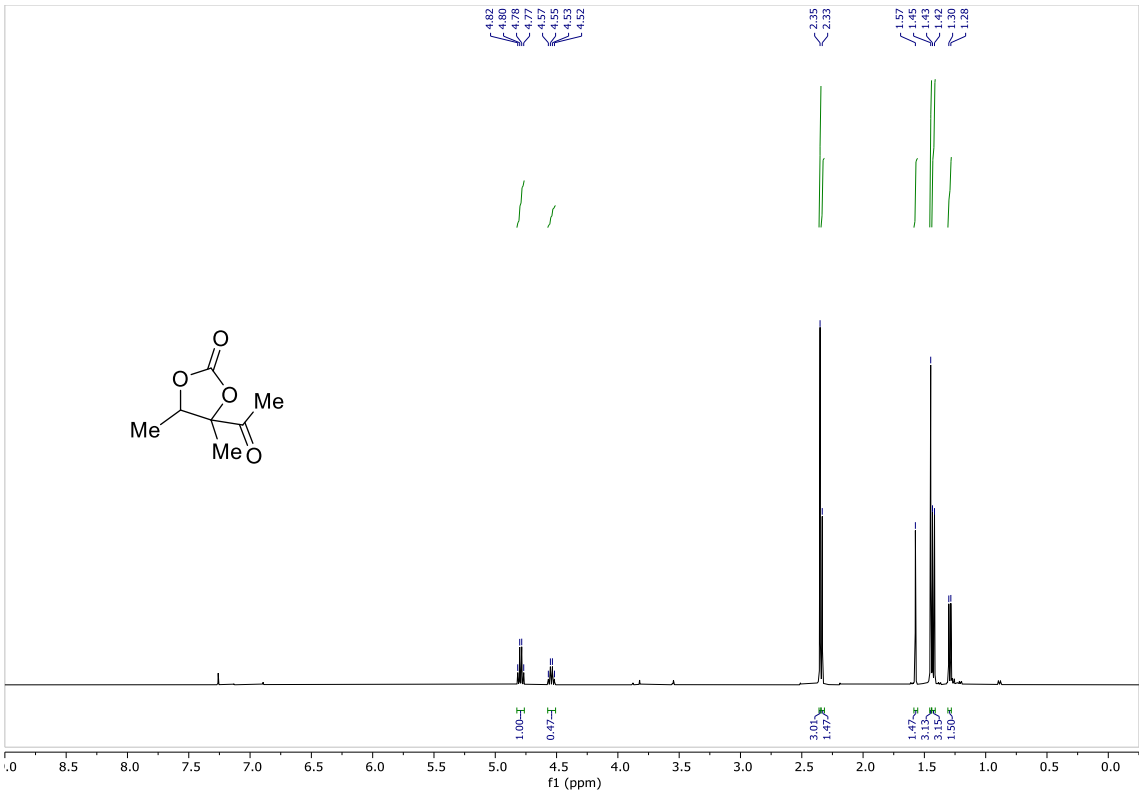
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4e**



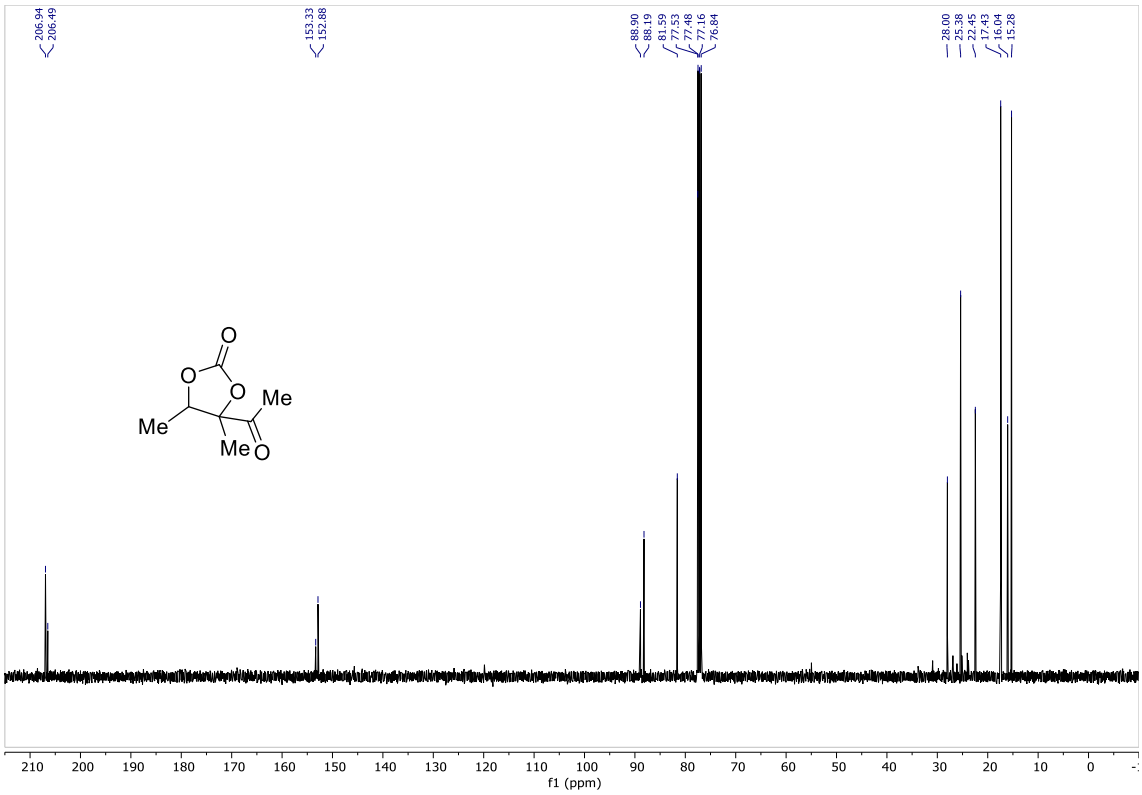
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4e**



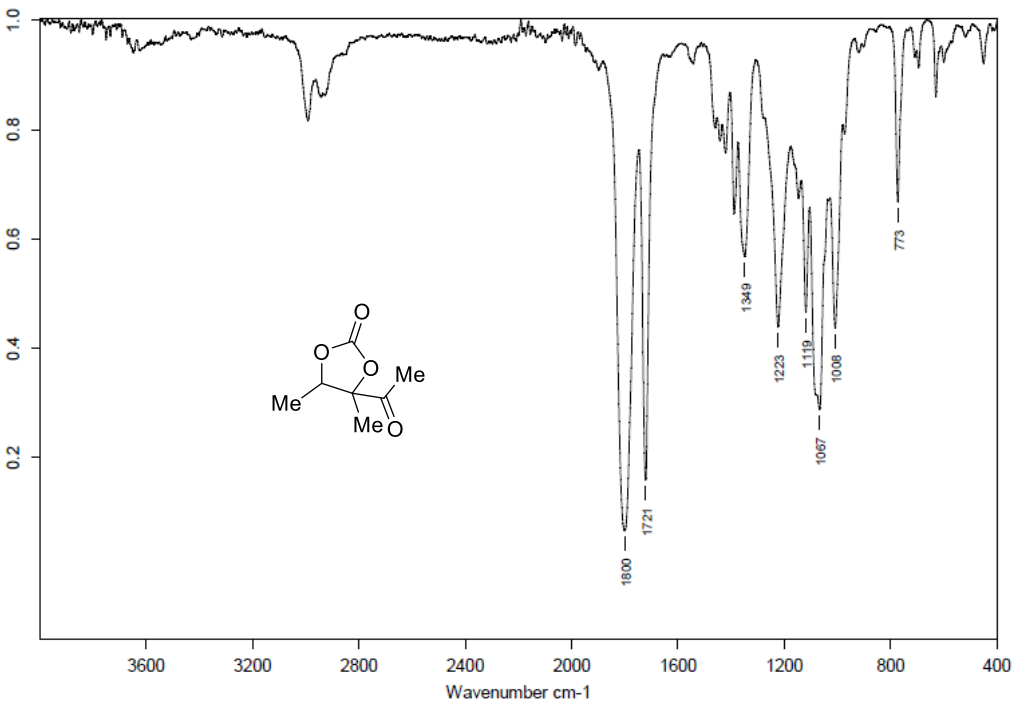
IR (neat) spectrum for **4e**



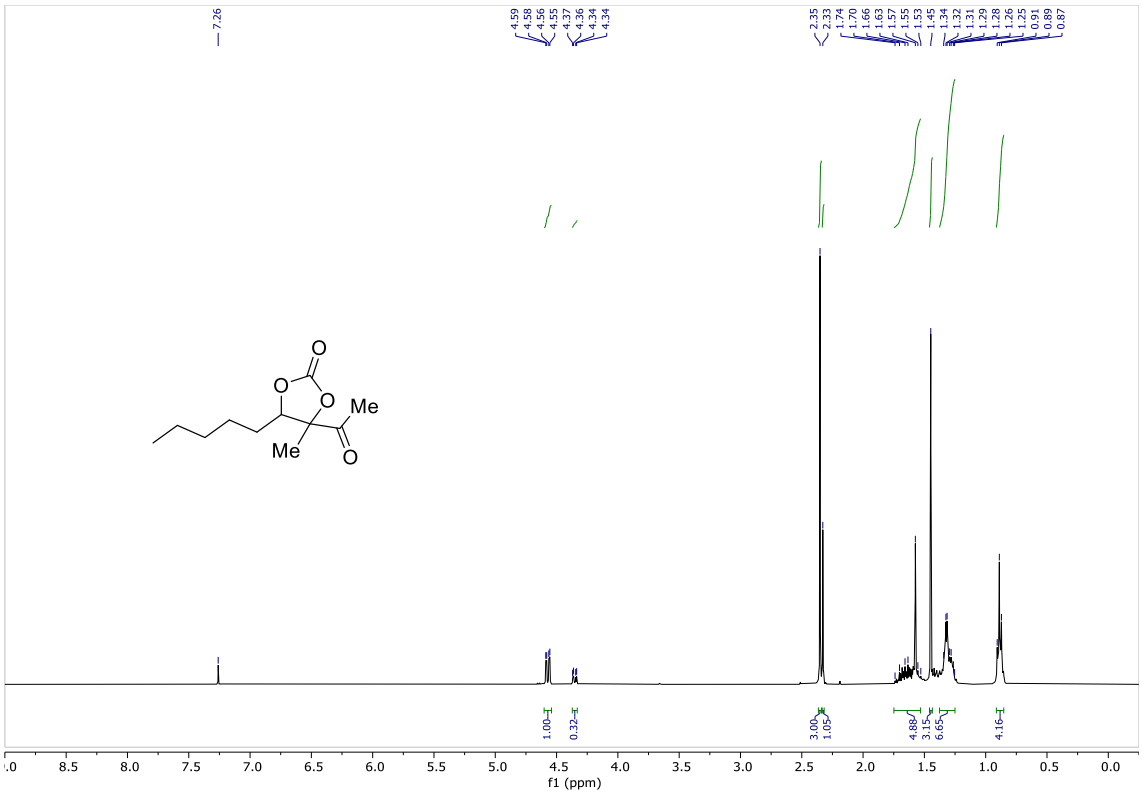
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4f**



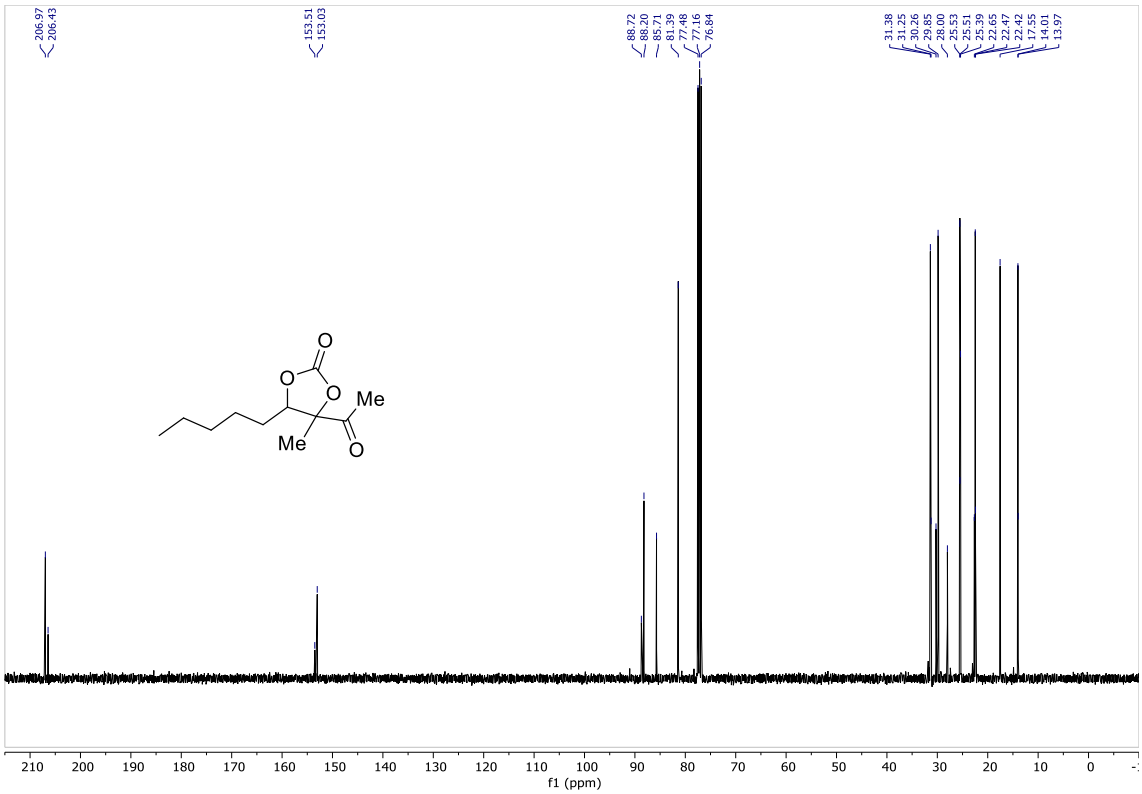
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4f**



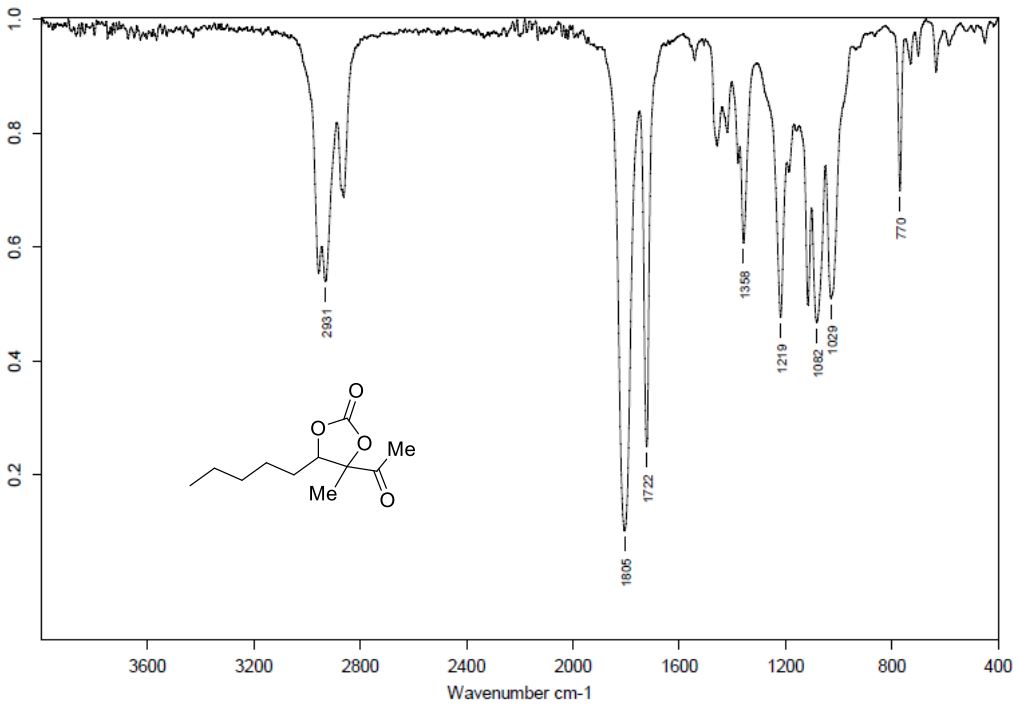
IR (neat) spectrum for **4f**



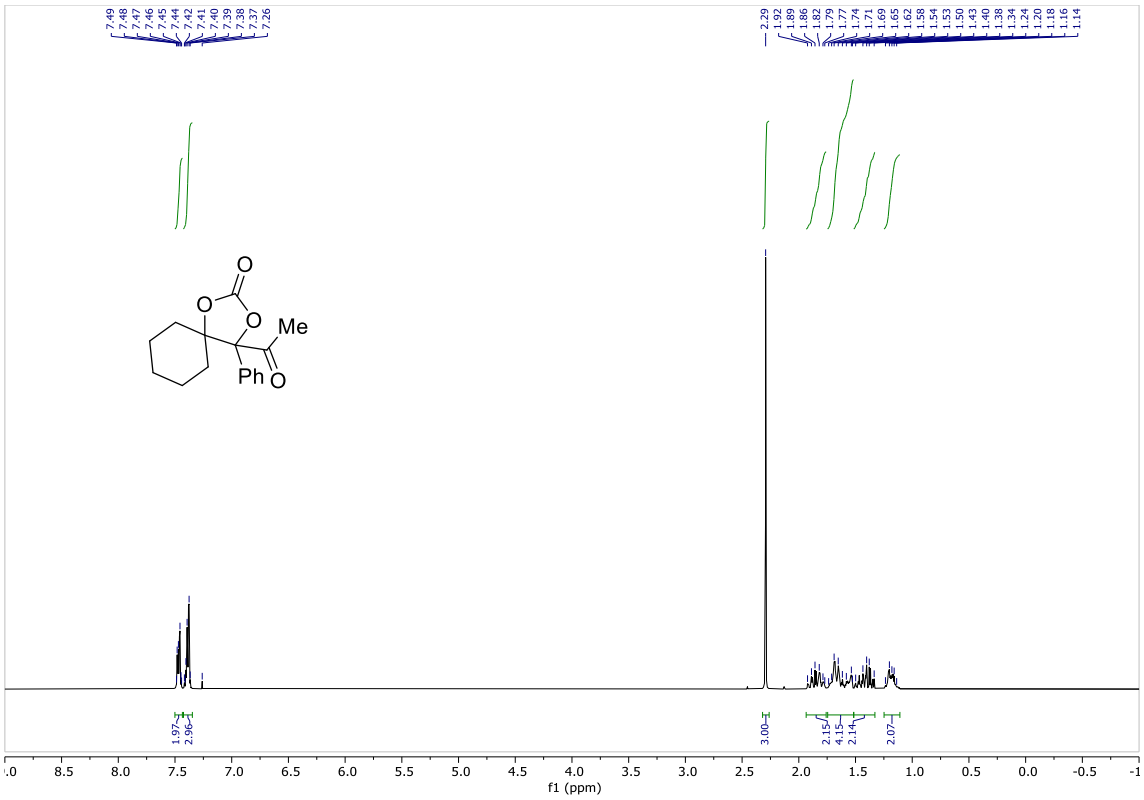
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4g**



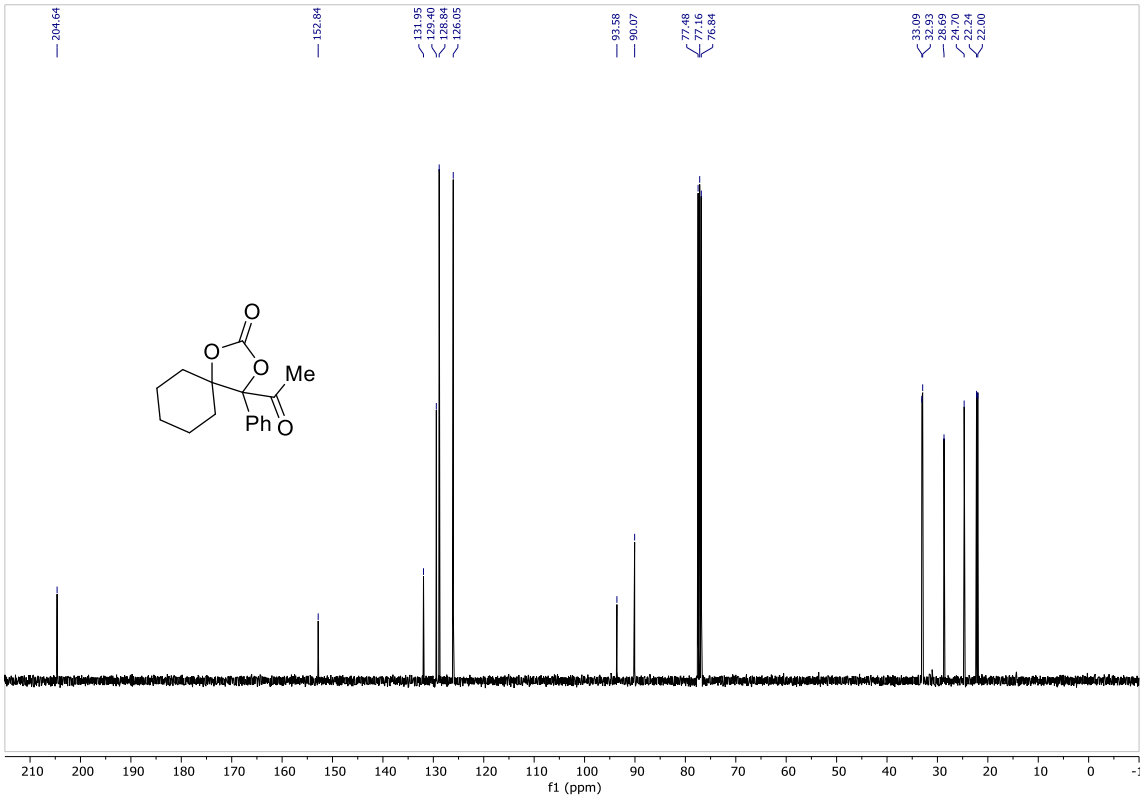
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4g**



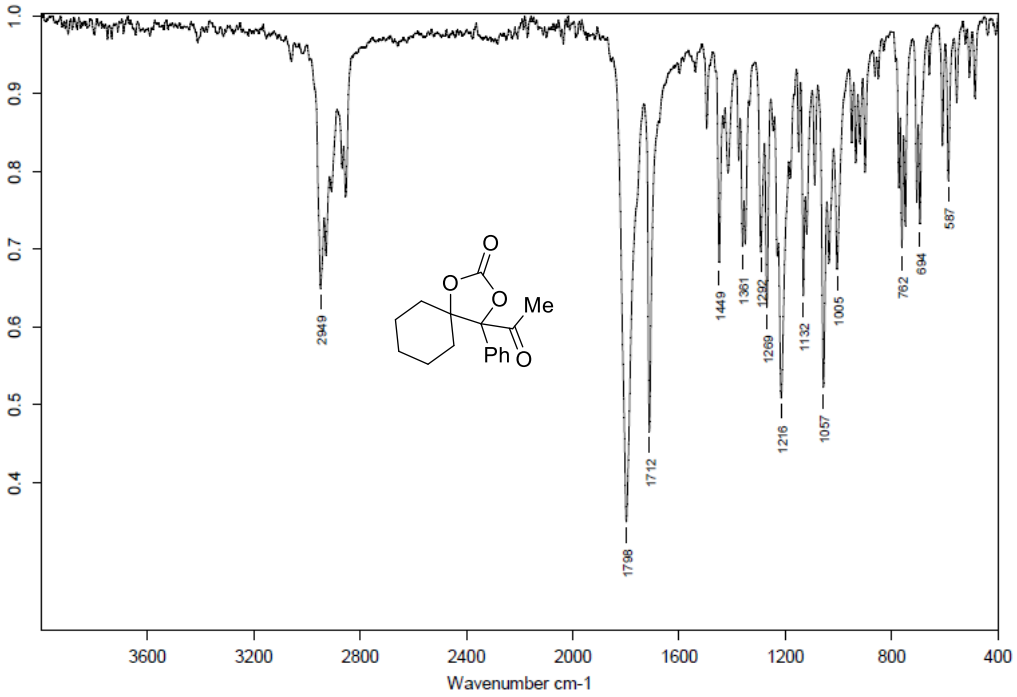
IR (neat) spectrum for **4g**



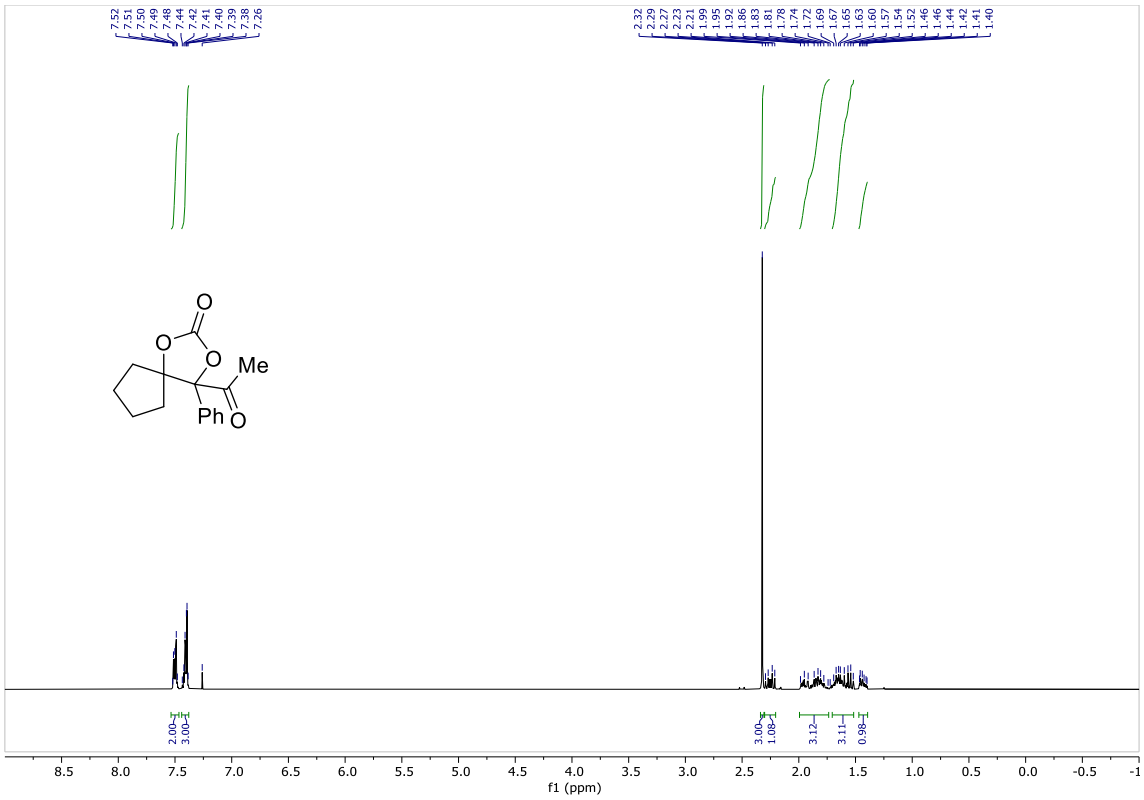
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4h**



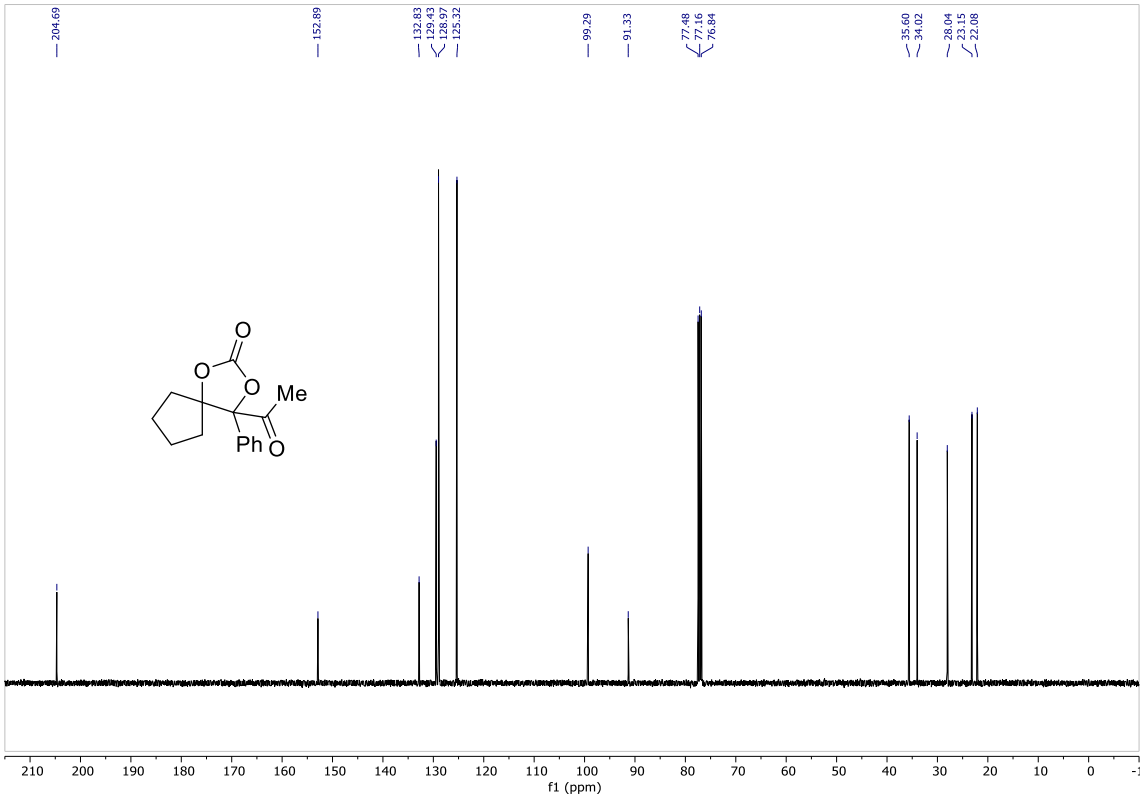
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4h**



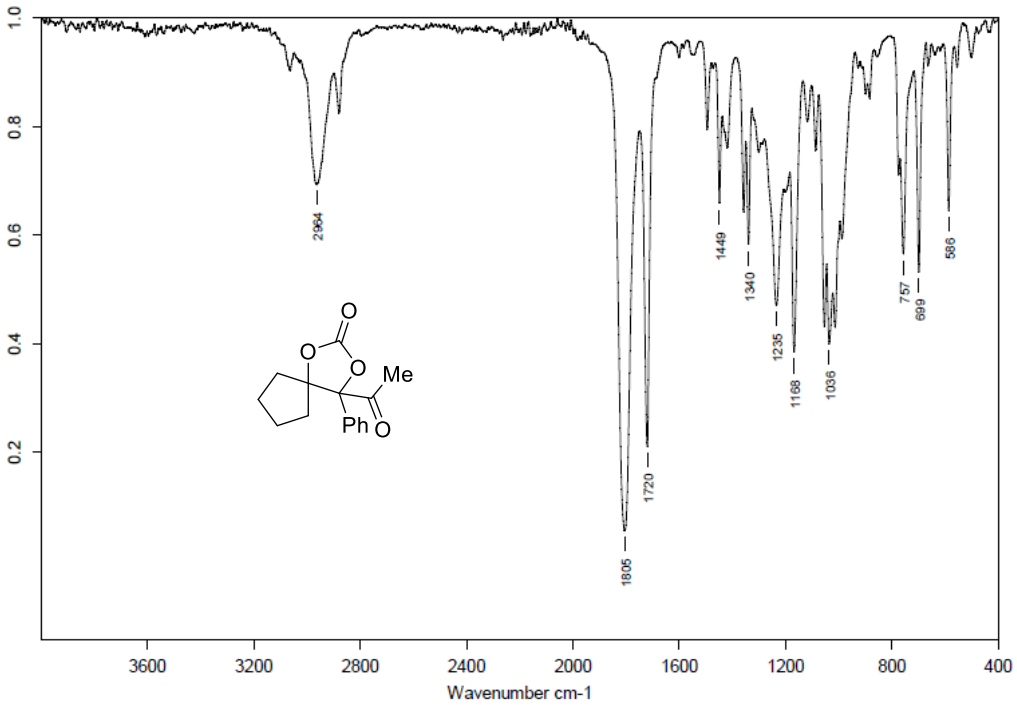
IR (neat) spectrum for **4h**



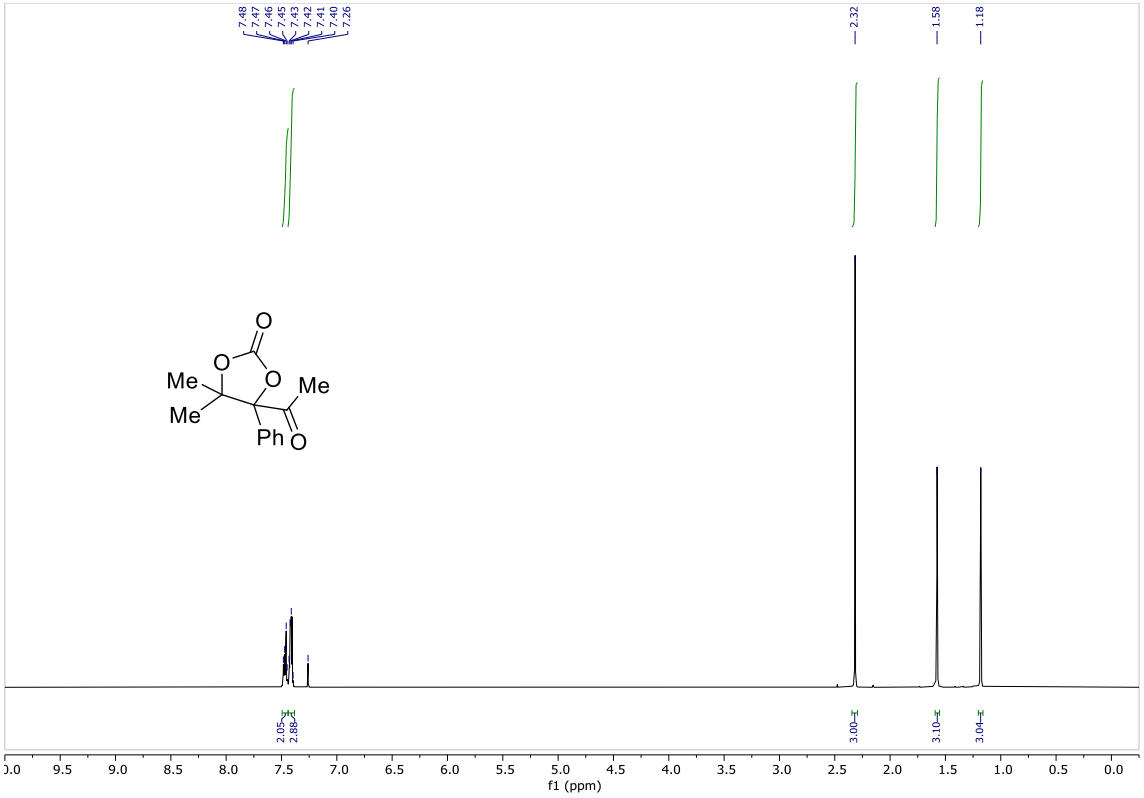
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4i**



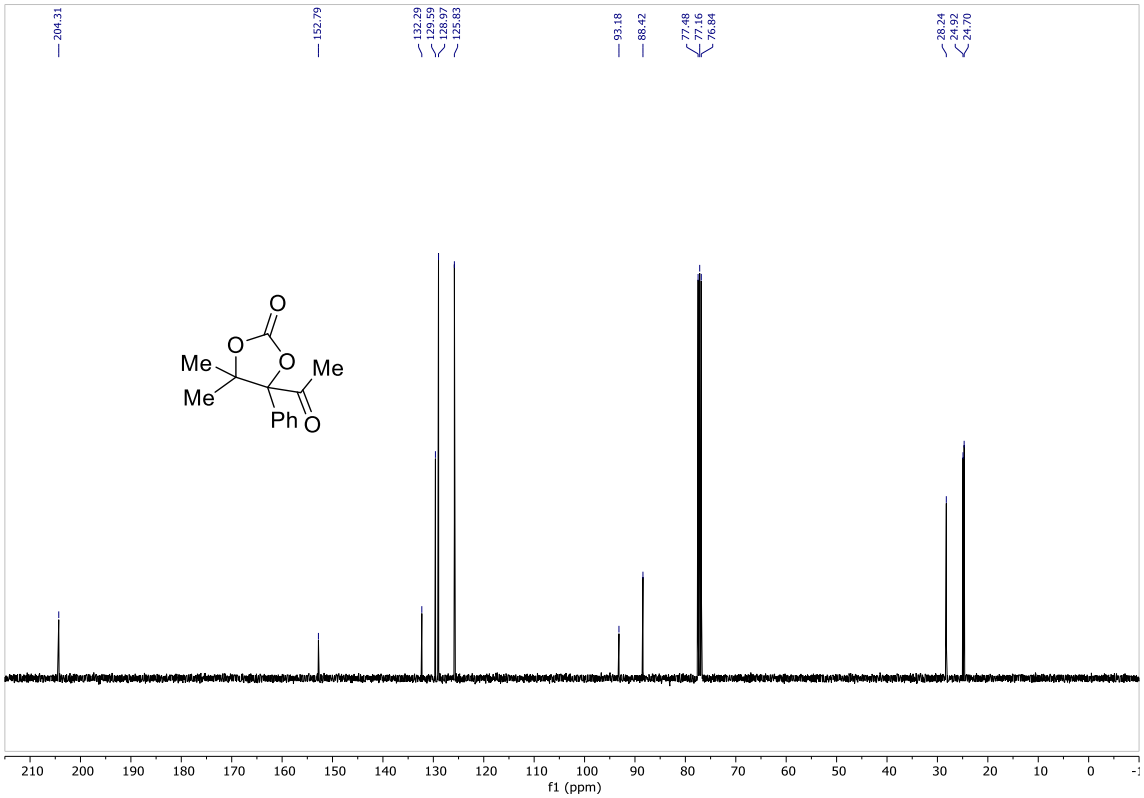
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4i**



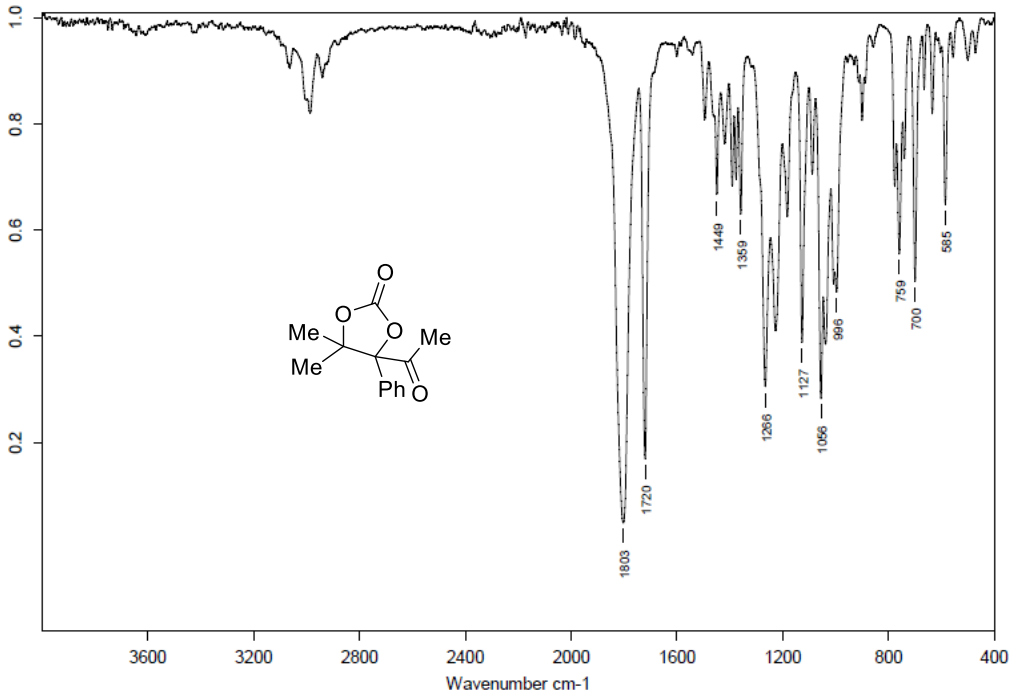
IR (neat) spectrum for **4i**



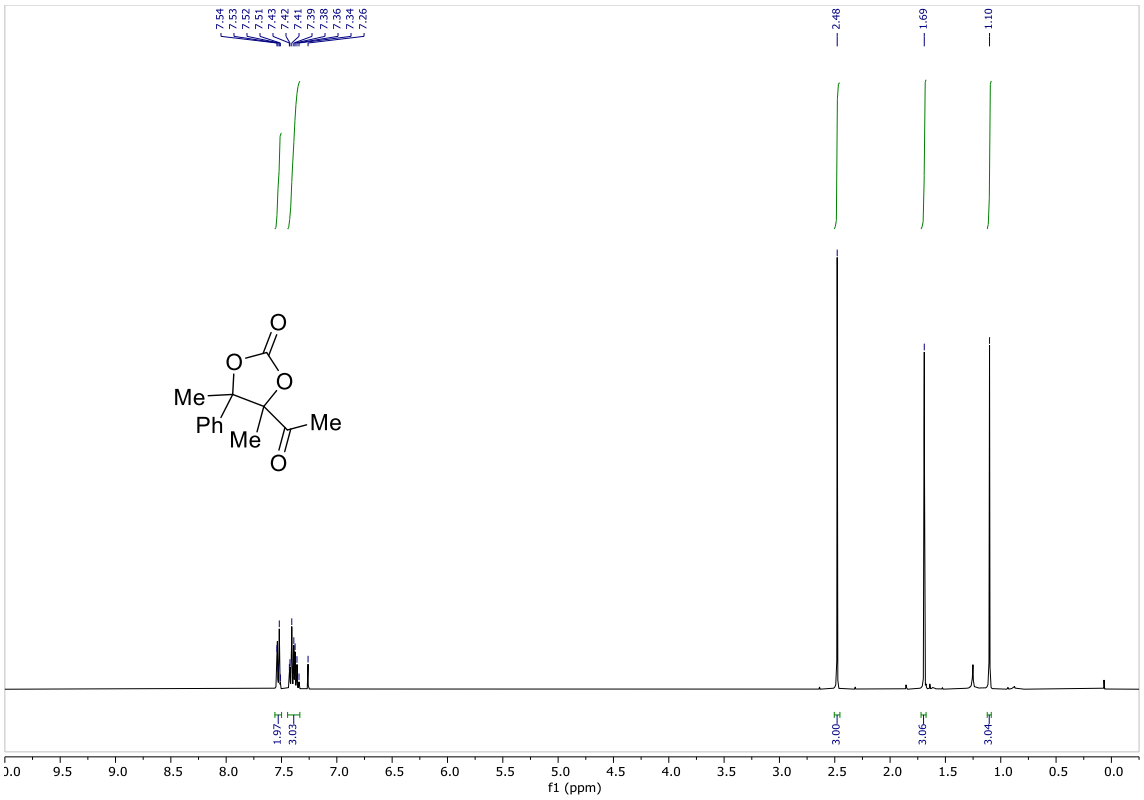
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4j**



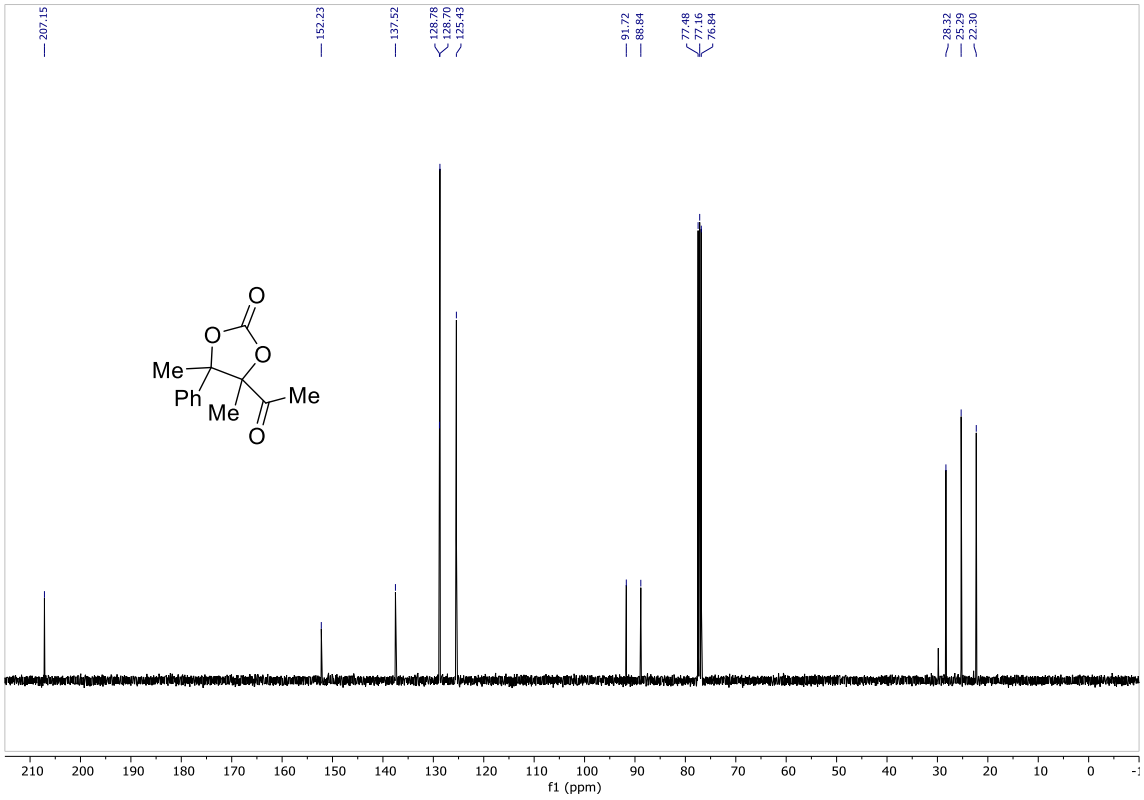
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4j**



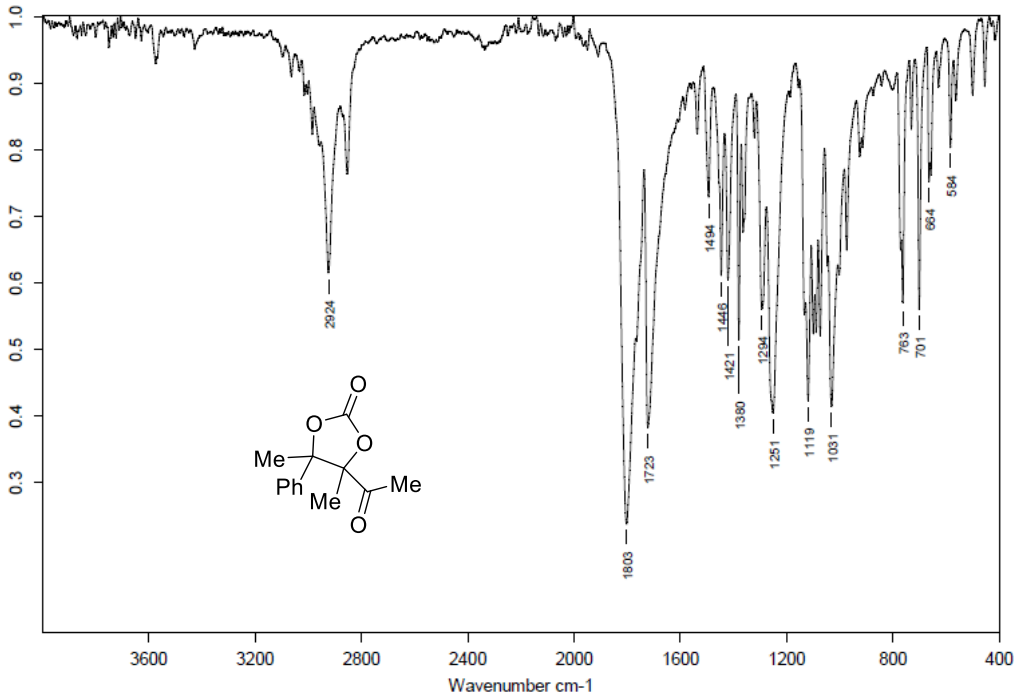
IR (neat) spectrum for **4j**



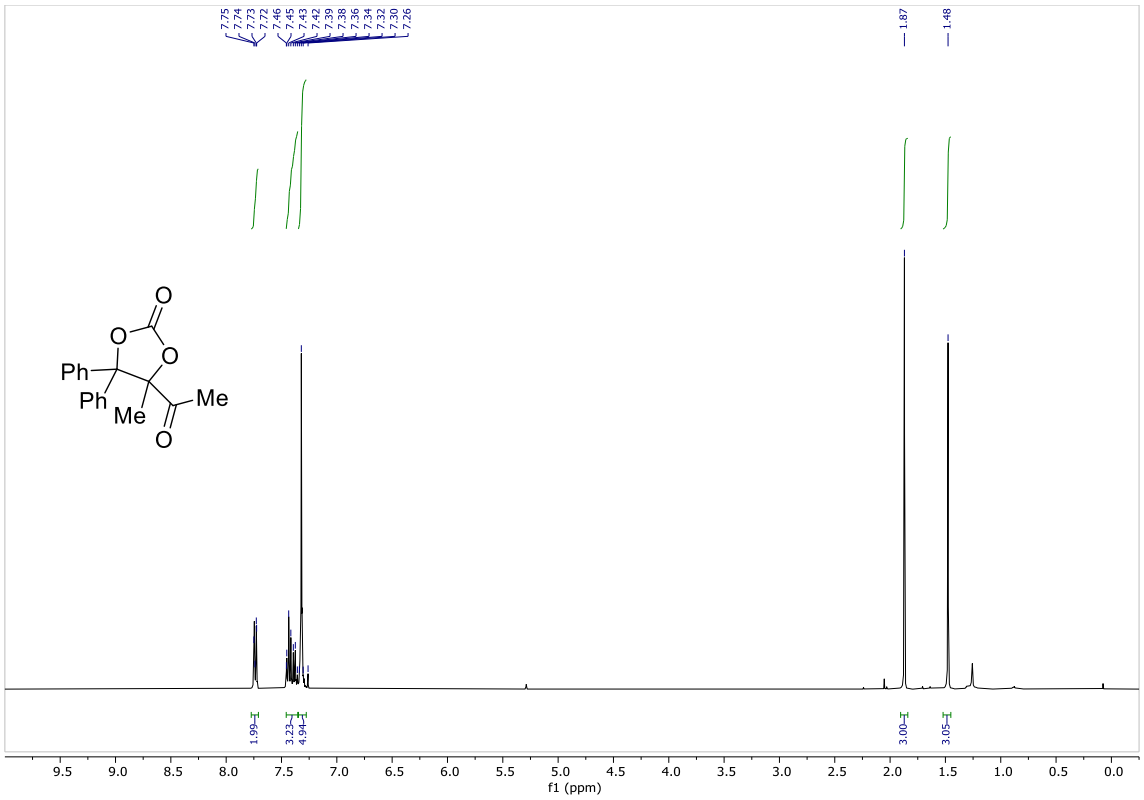
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4k**



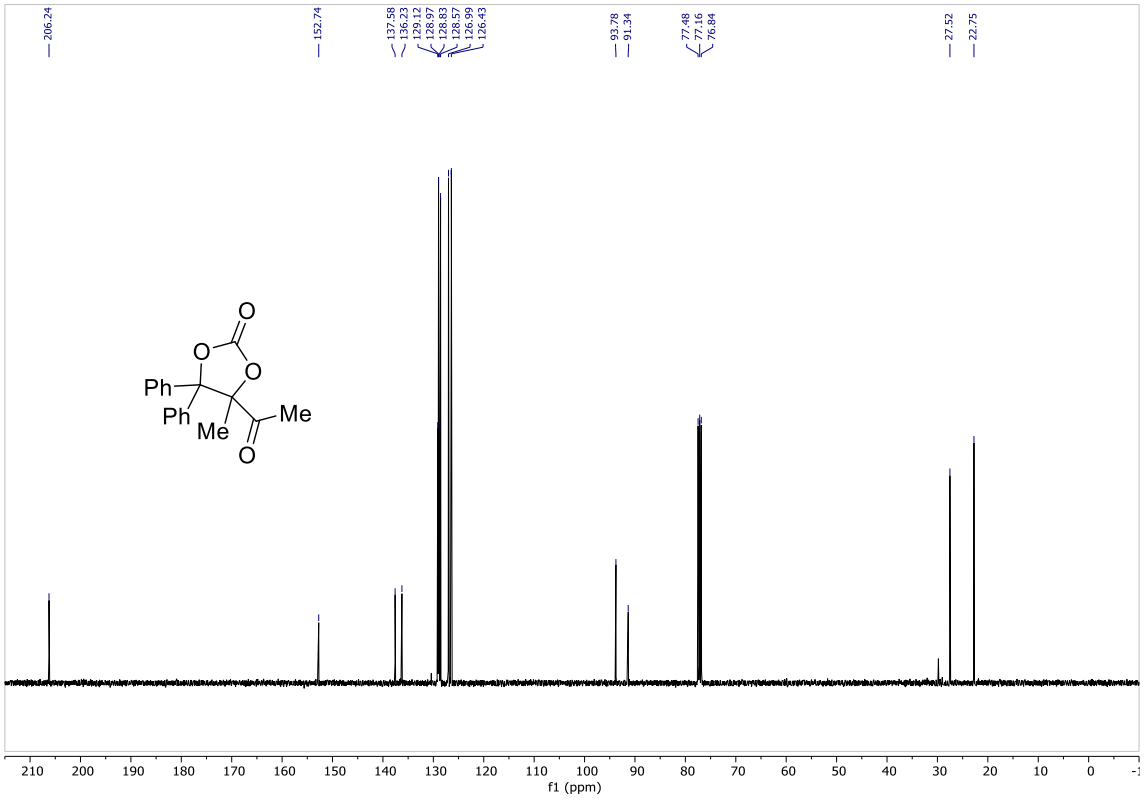
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4k**



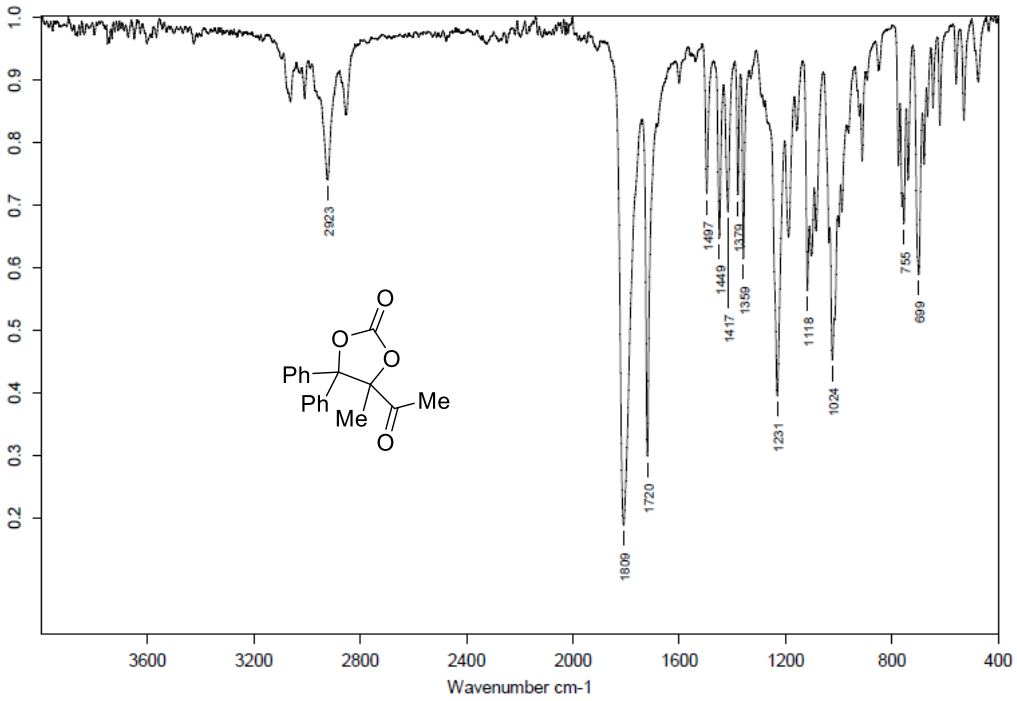
IR (neat) spectrum for **4k**



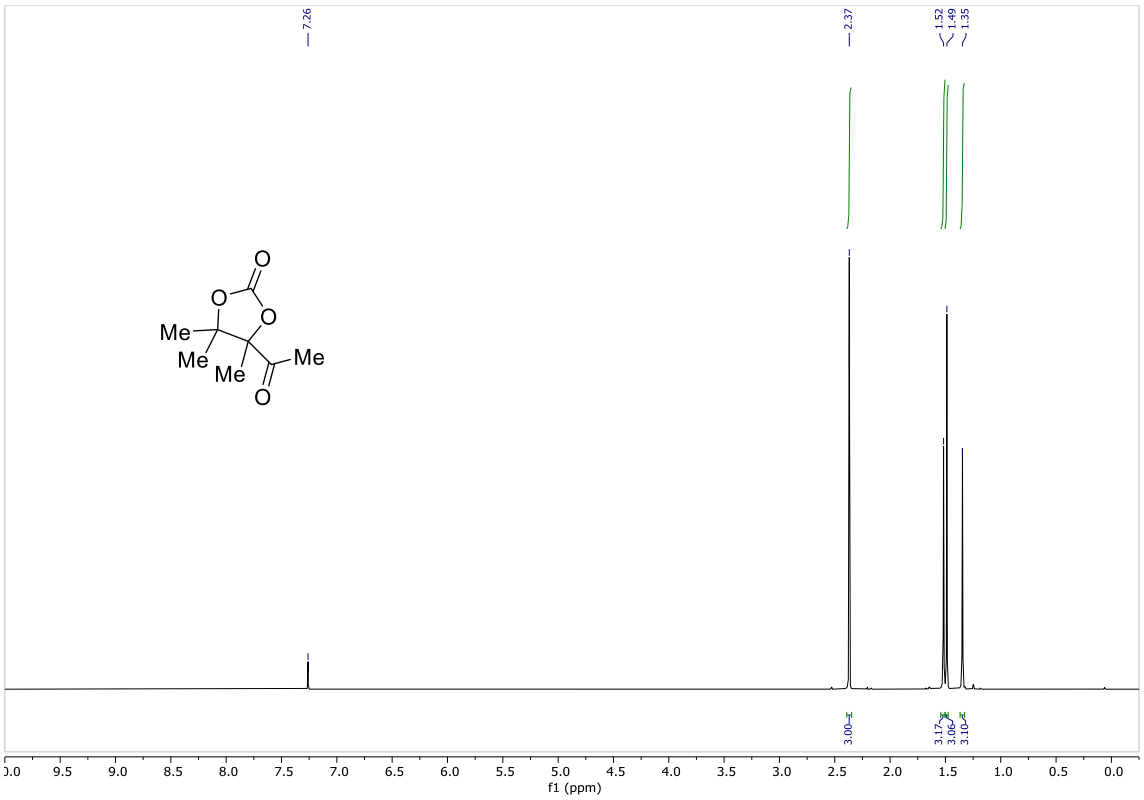
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4l**



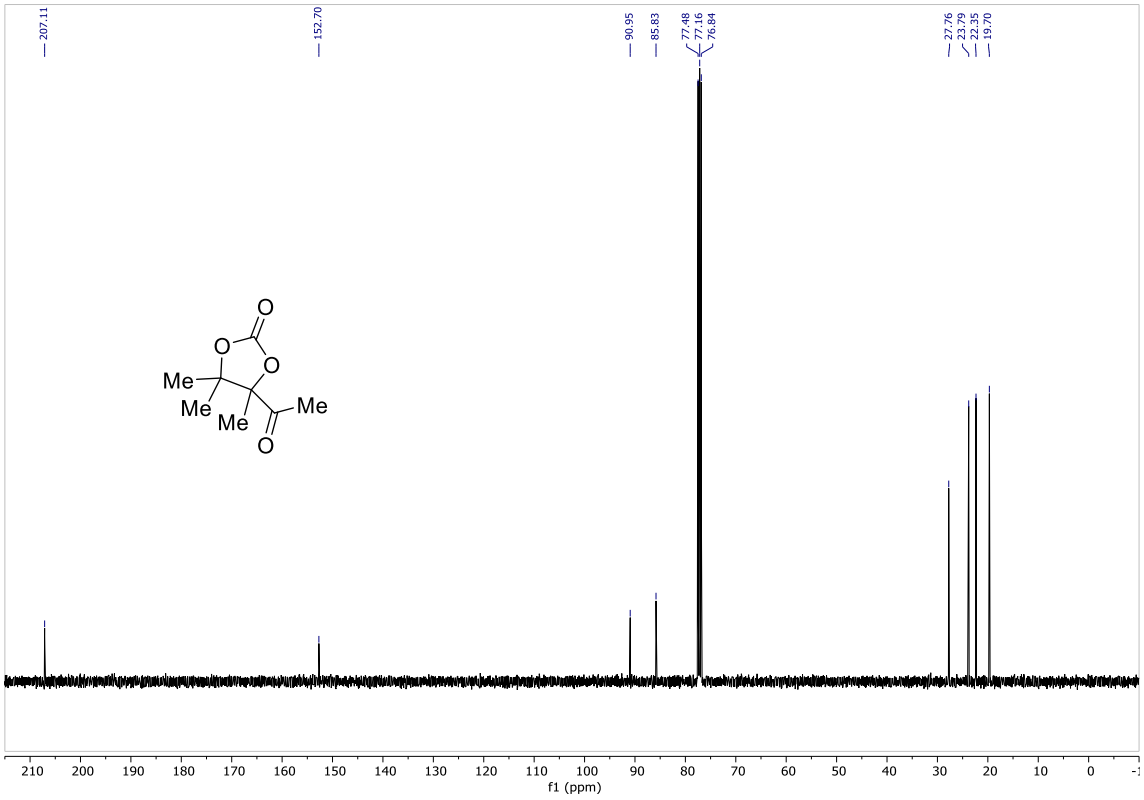
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4l**



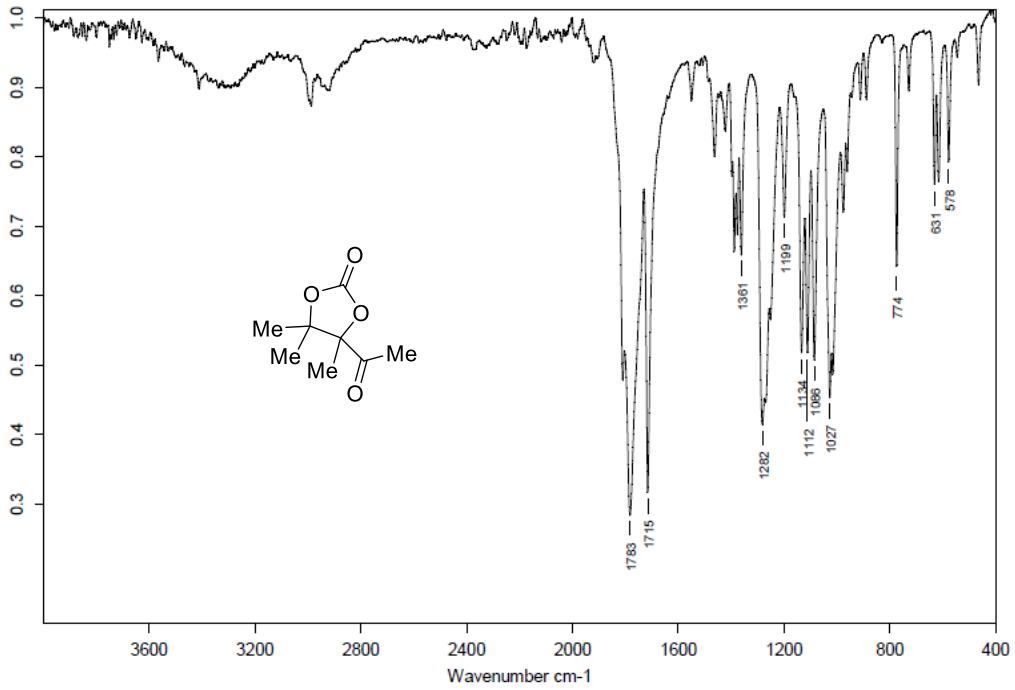
IR (neat) spectrum for **4l**



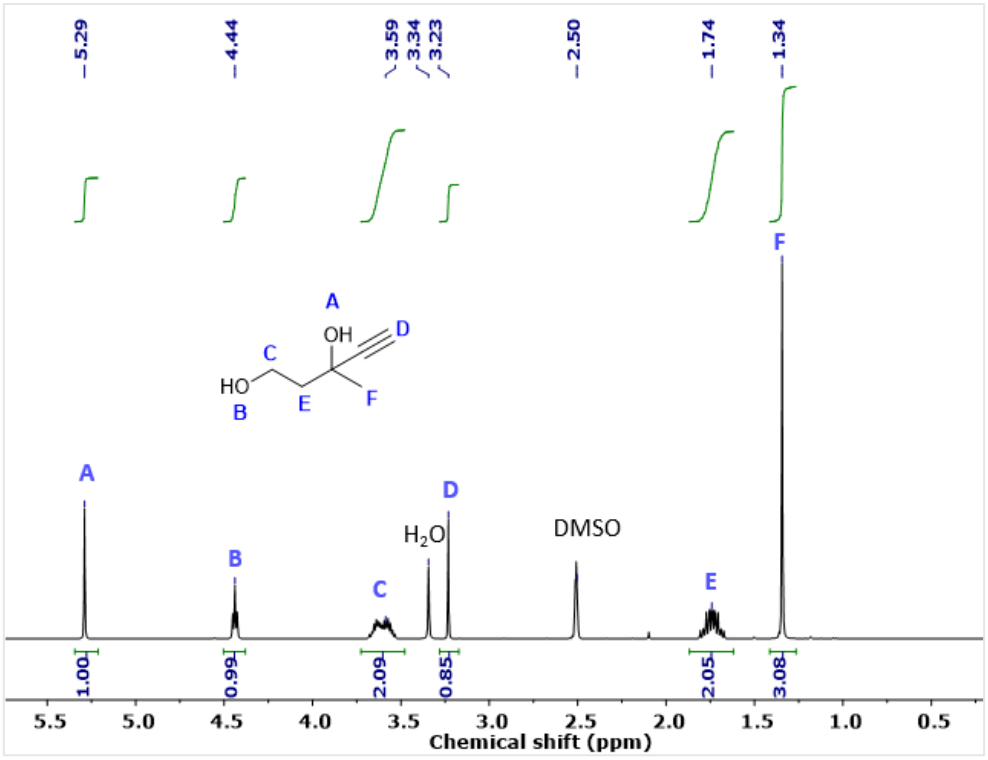
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **4m**



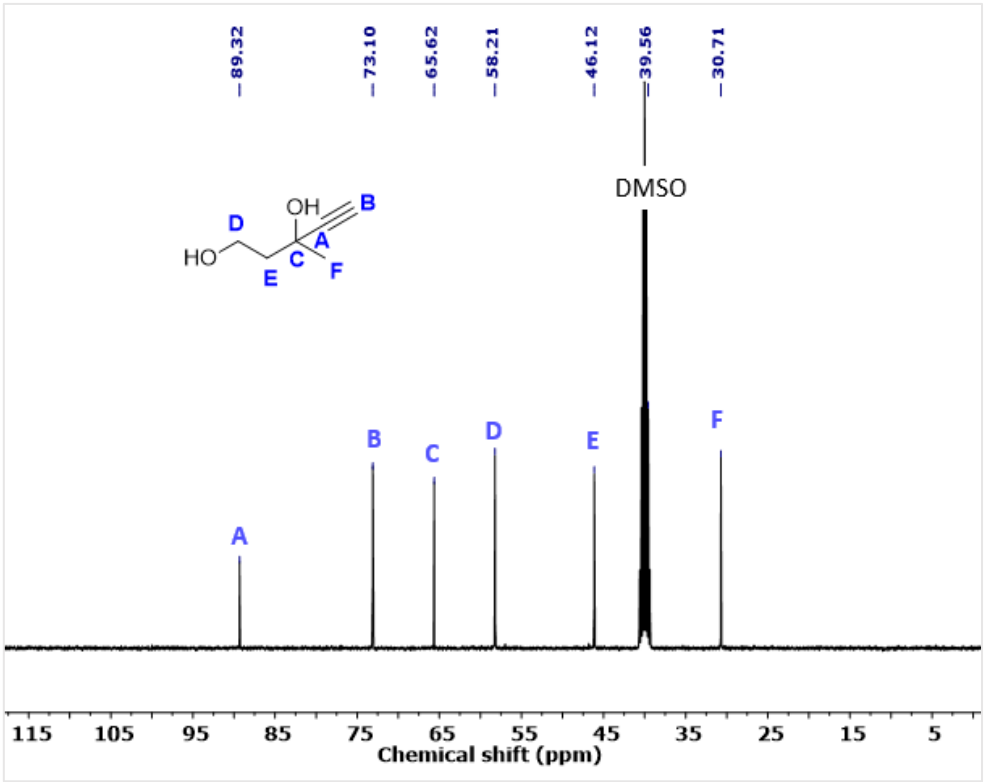
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **4m**



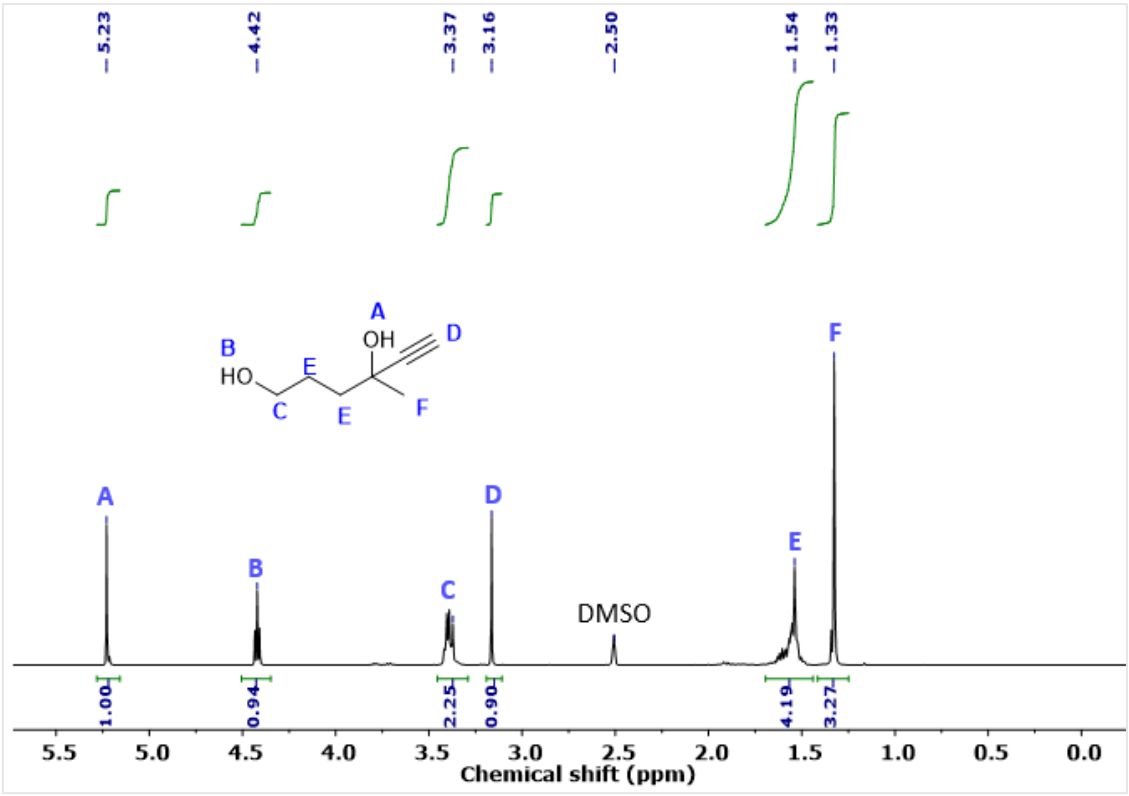
IR (neat) spectrum for **4m**



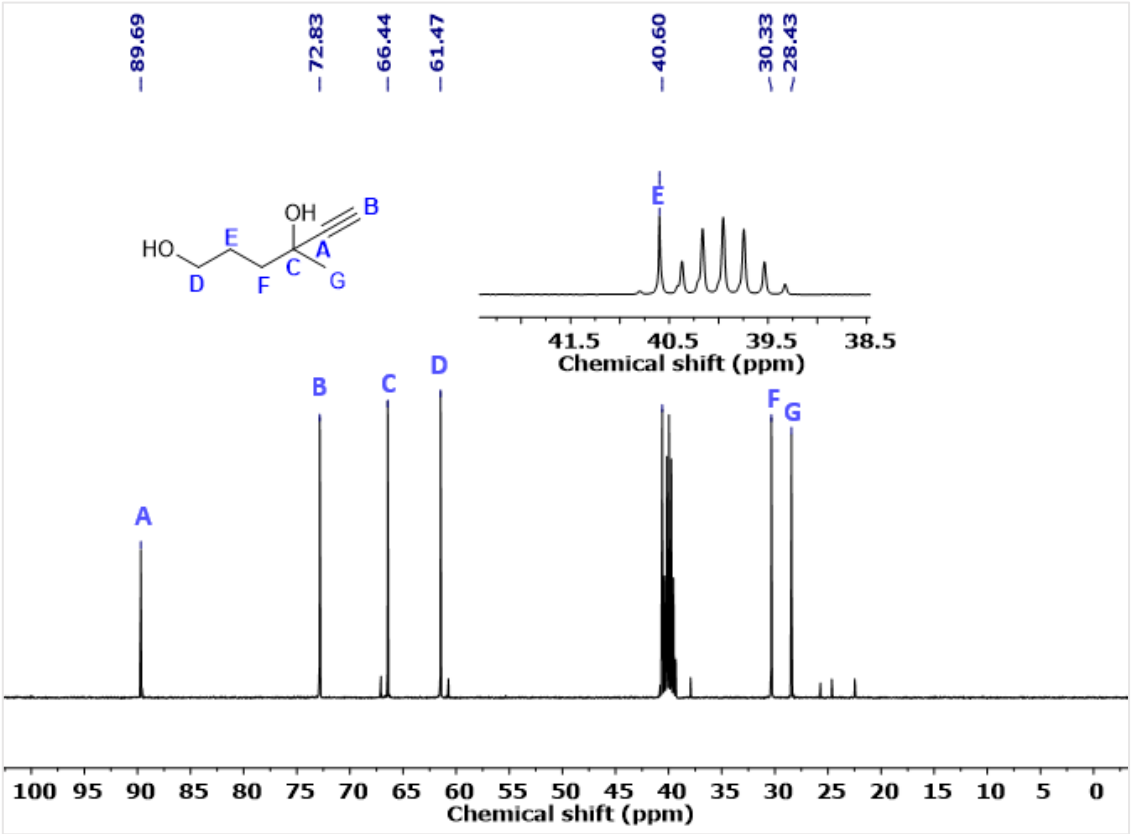
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for **5a**



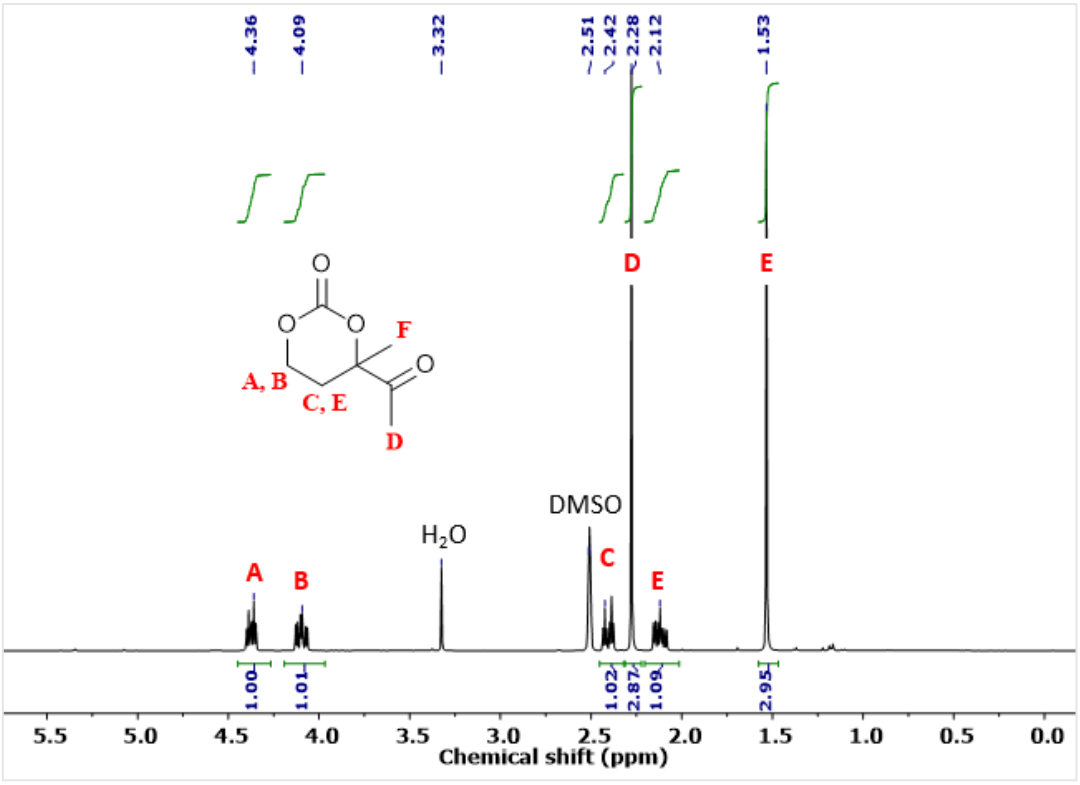
^{13}C NMR (101 MHz, DMSO-d_6) for **5a**



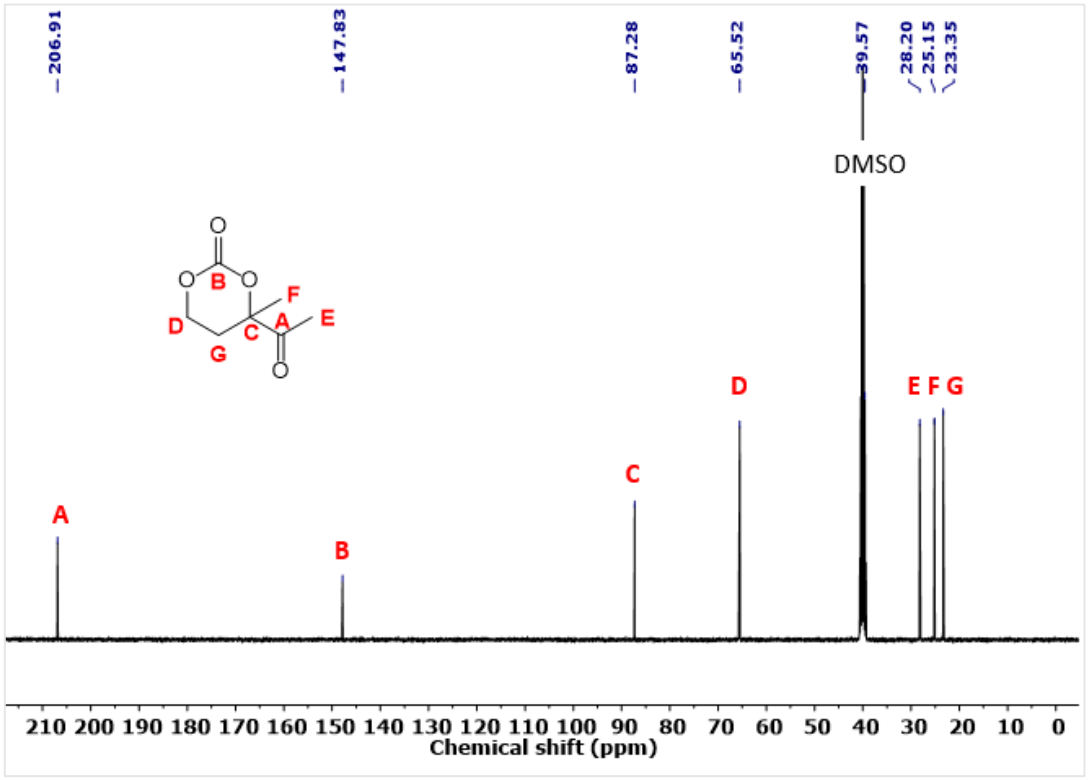
^{1}H NMR (400 MHz, DMSO-d_6) for **5b**



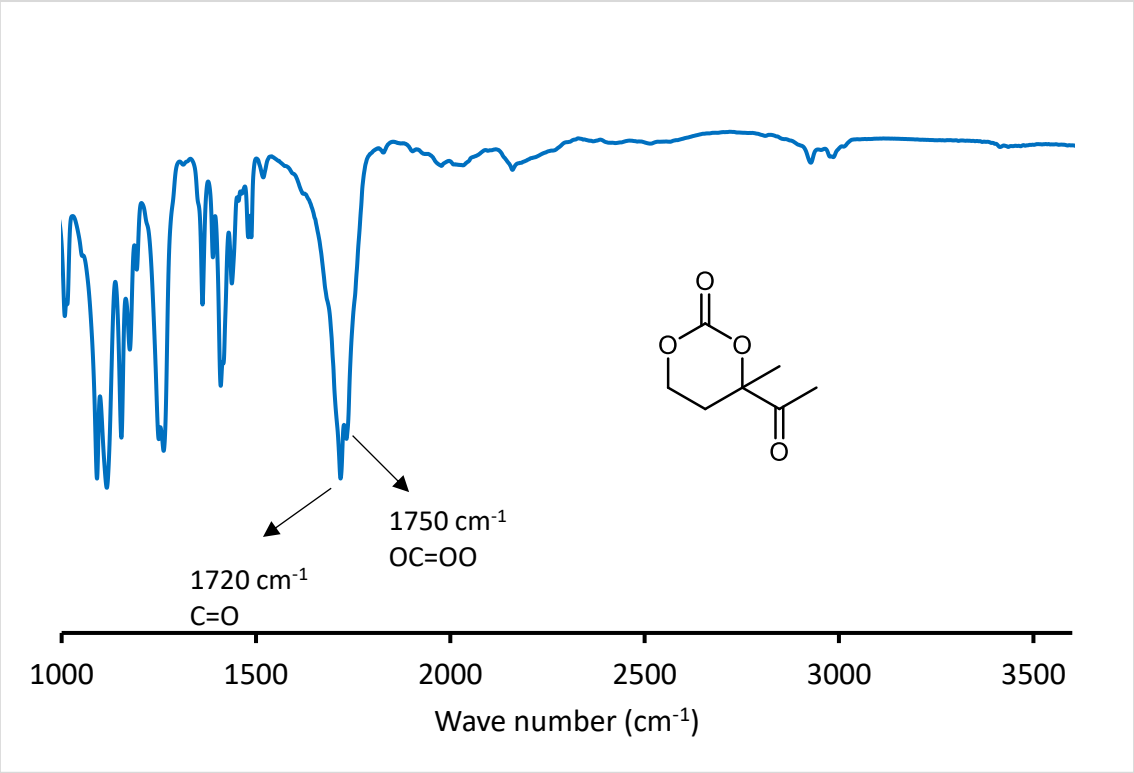
^{13}C NMR (101 MHz, DMSO-d_6) for **5b**



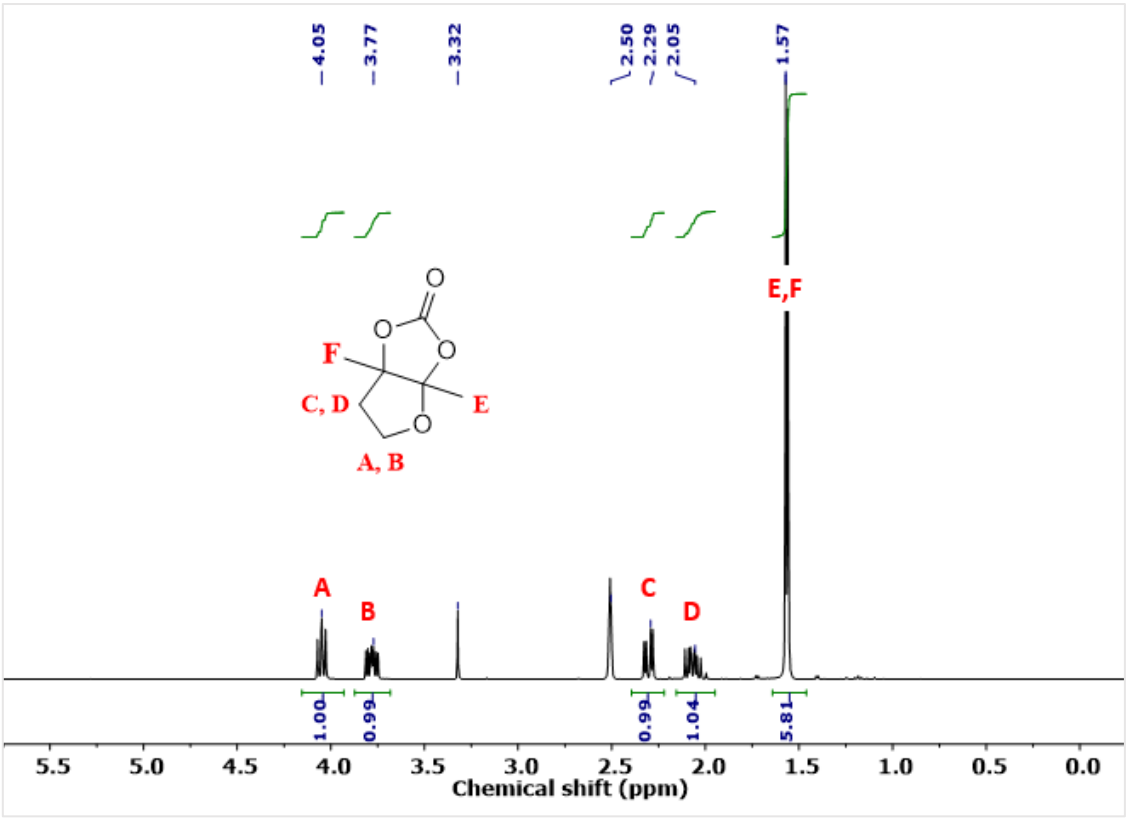
^{1}H NMR (400 MHz, DMSO-d$_6$) for **6**



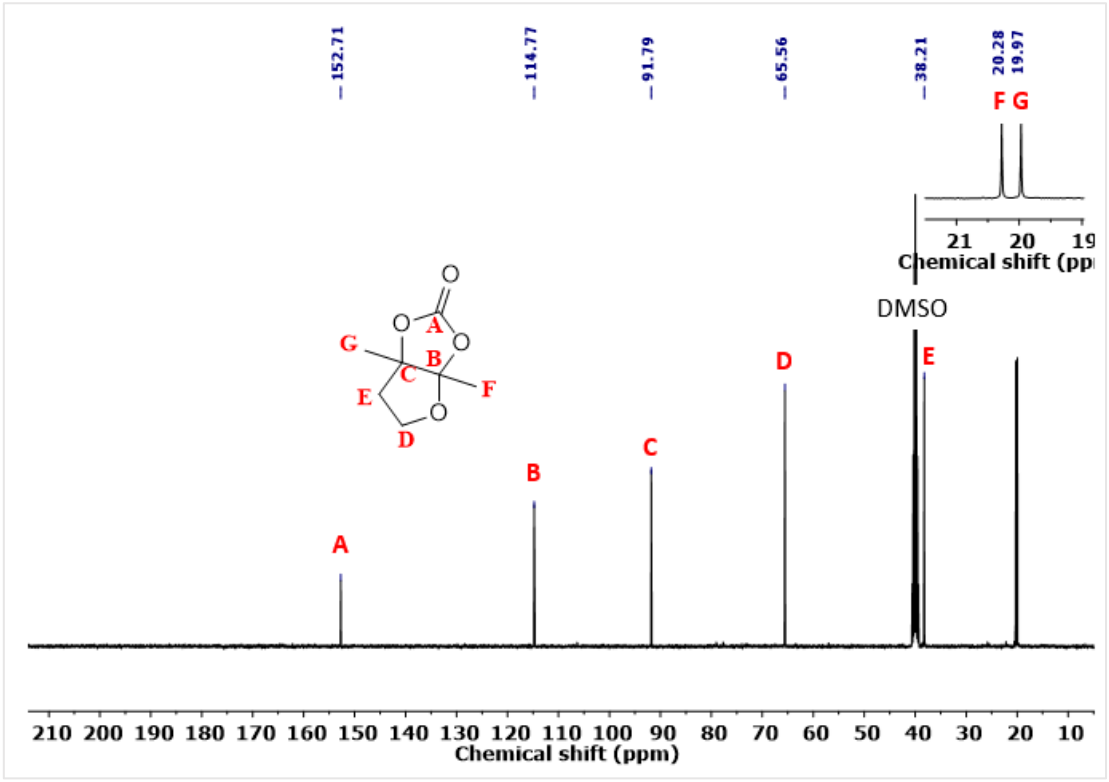
^{13}C NMR (101 MHz, DMSO-d$_6$) for **5b**



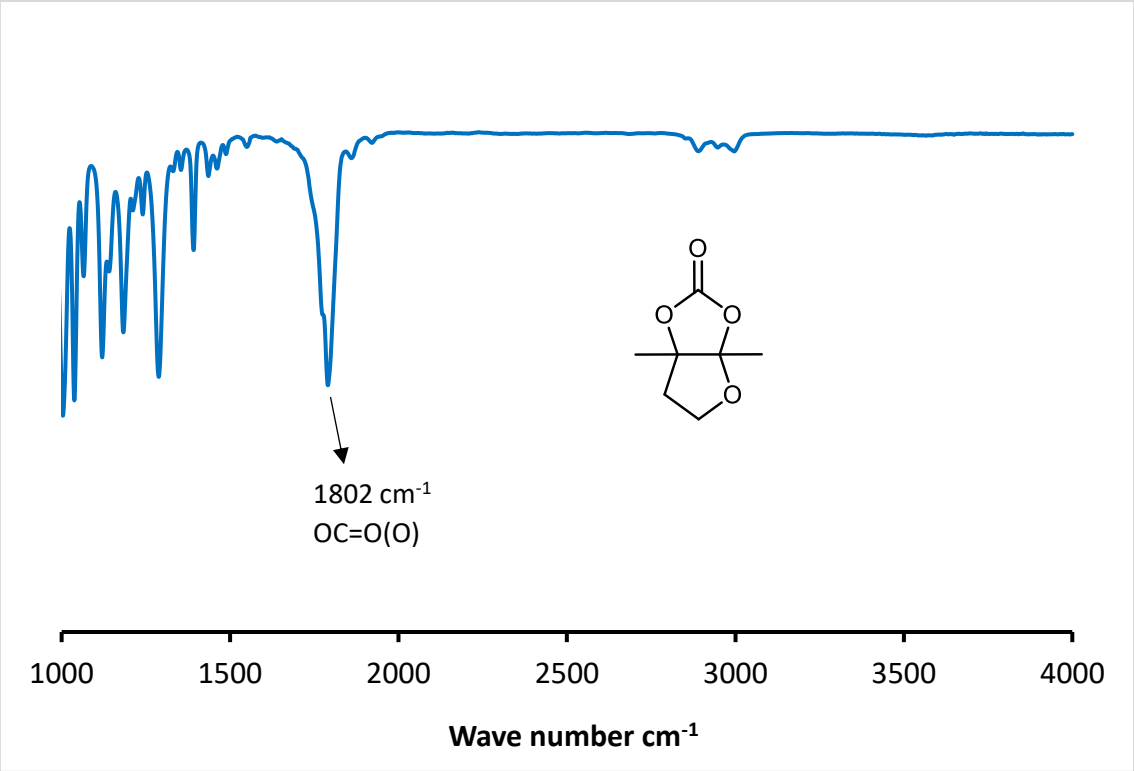
IR (neat) spectrum for **6**



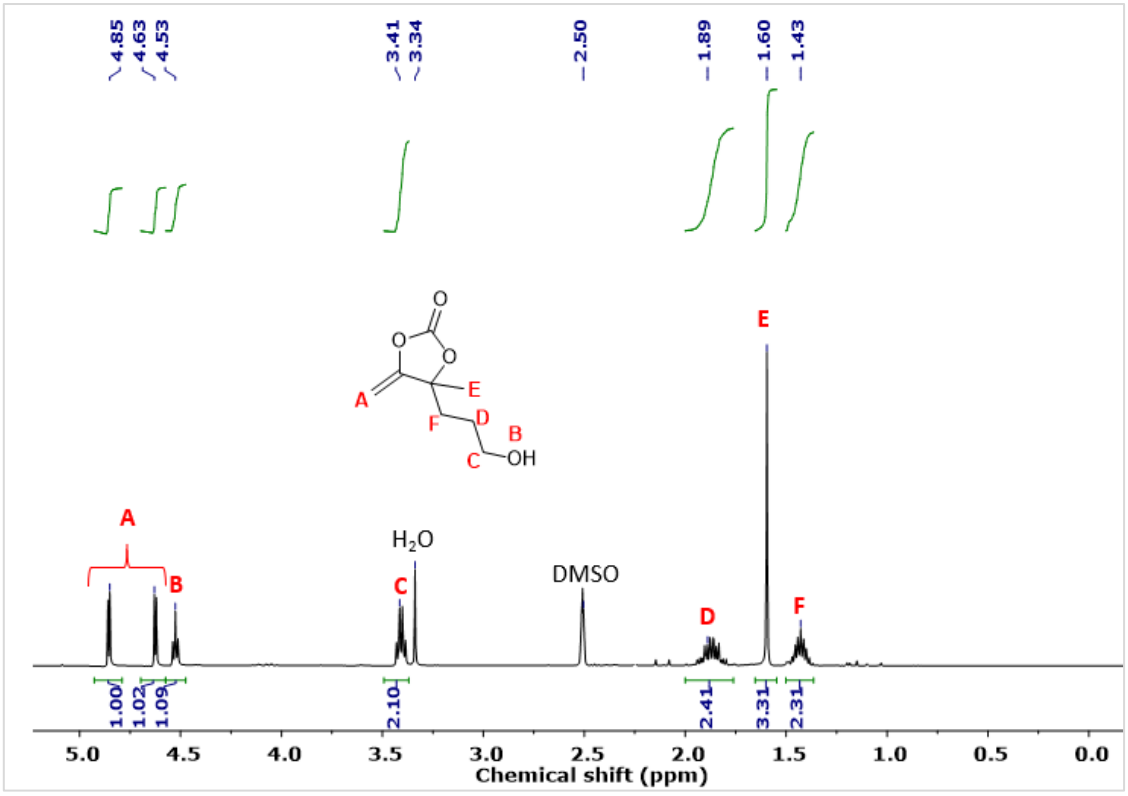
^{1}H NMR (400 MHz, DMSO-d_6) for **7**



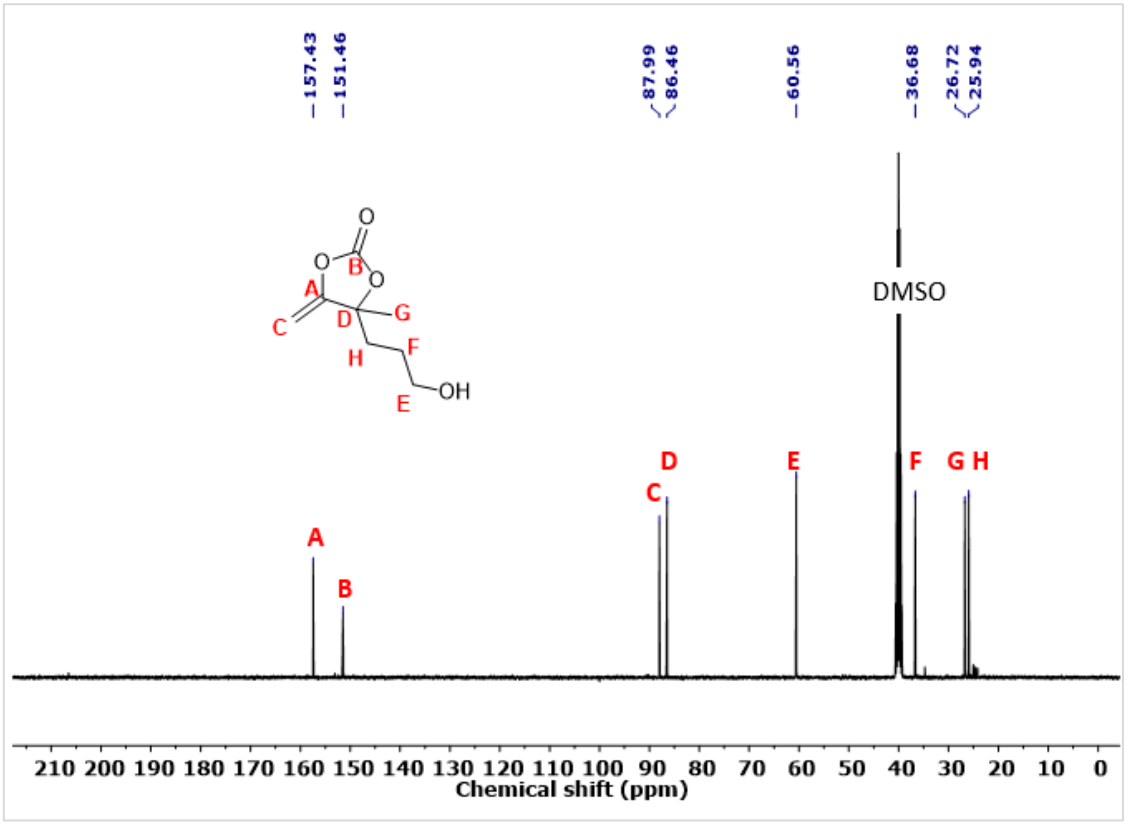
^{13}C NMR (101 MHz, DMSO-d_6) for **7**



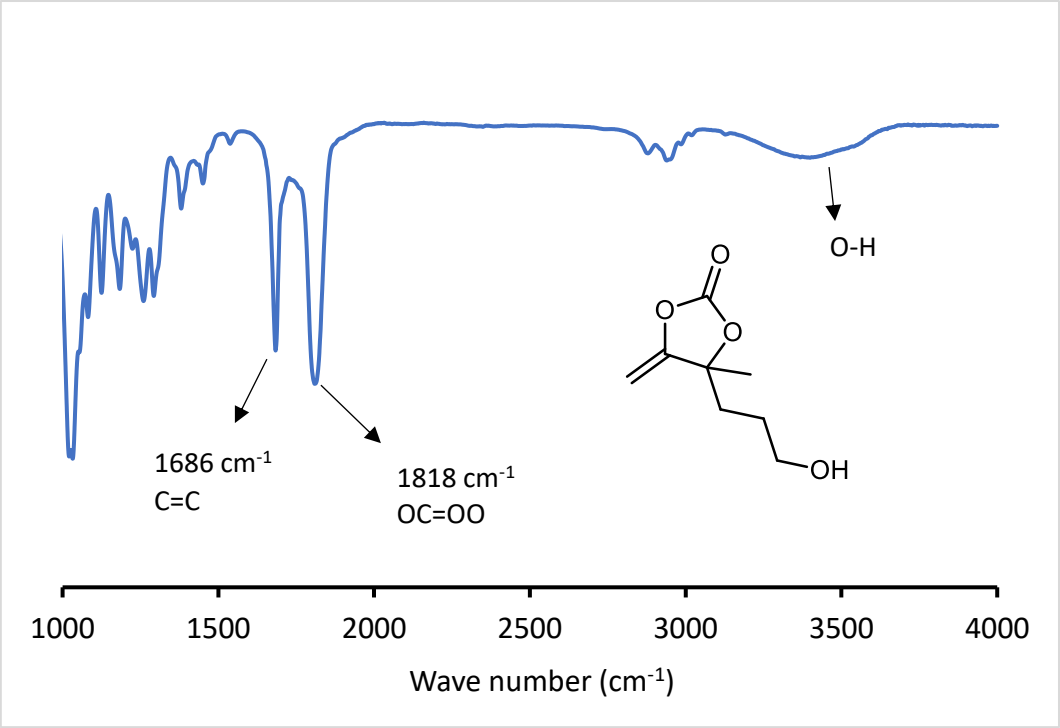
IR (neat) spectrum for **7**



^{1}H NMR (400 MHz, DMSO-d_6) for **8**

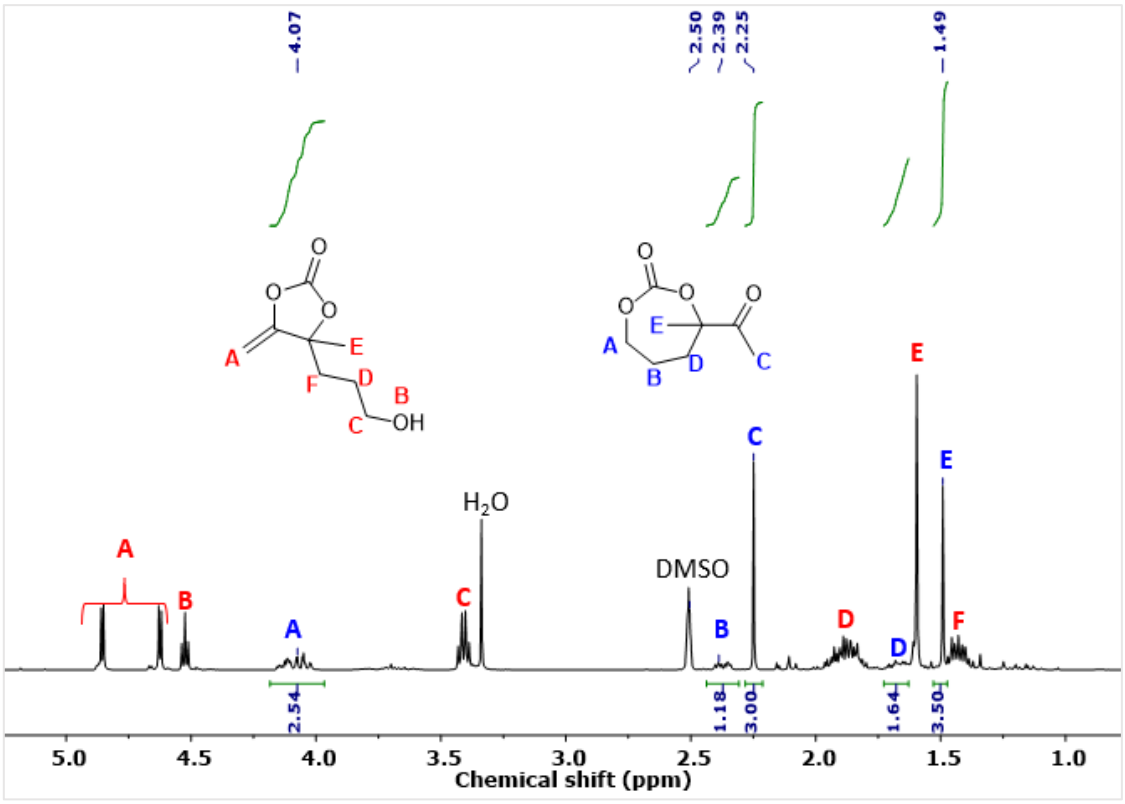


^{13}C NMR (101 MHz, DMSO-d_6) for **8**

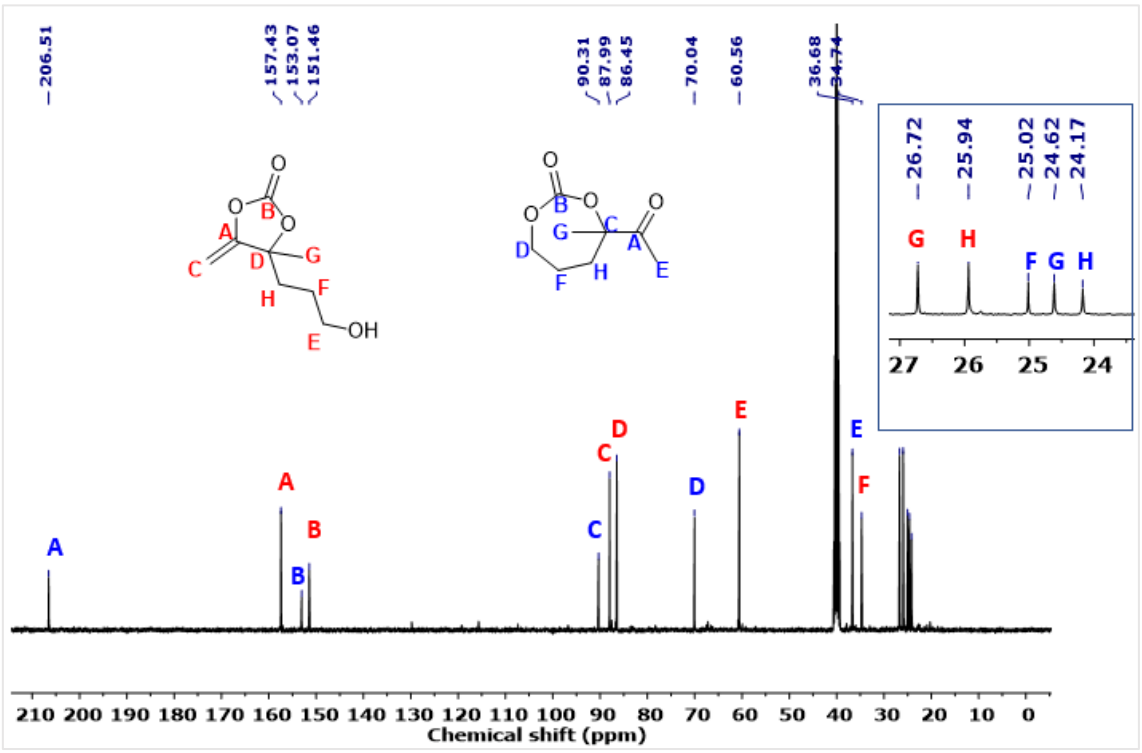


IR (neat) spectrum for **8**

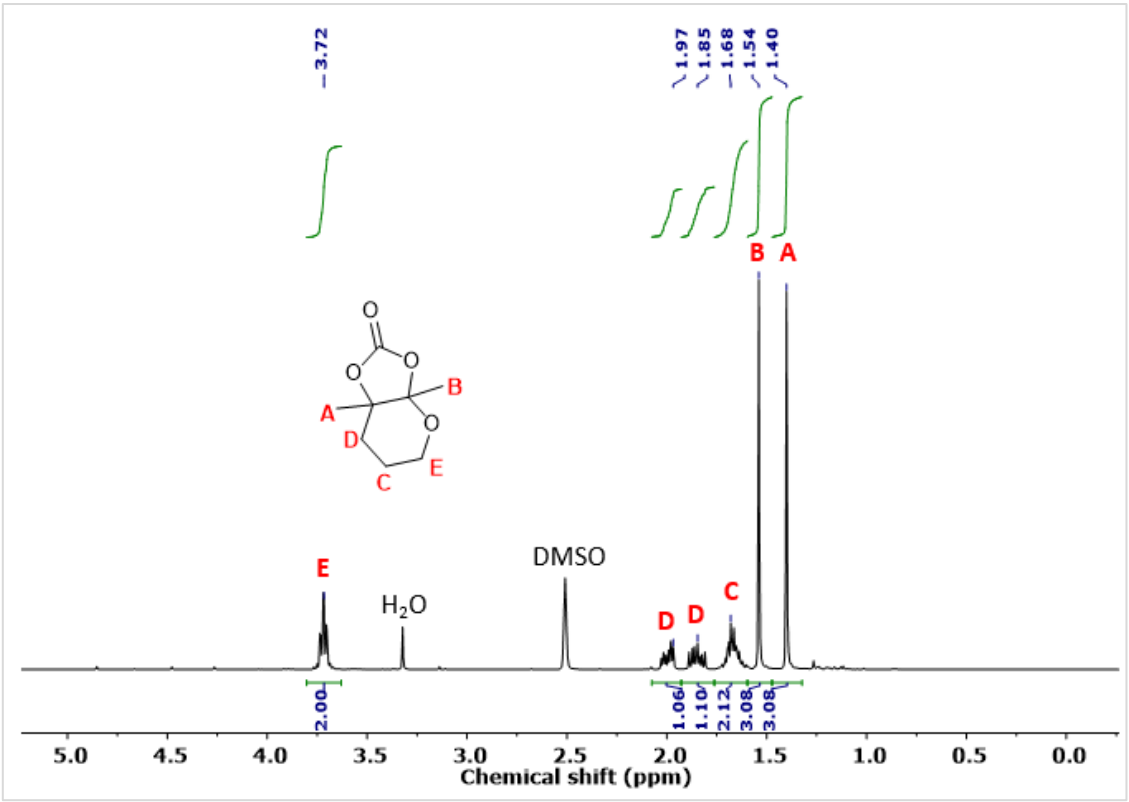
Note: A mixture of both α-alkylidene carbonate **8** and seven-membered carbonate **9**:



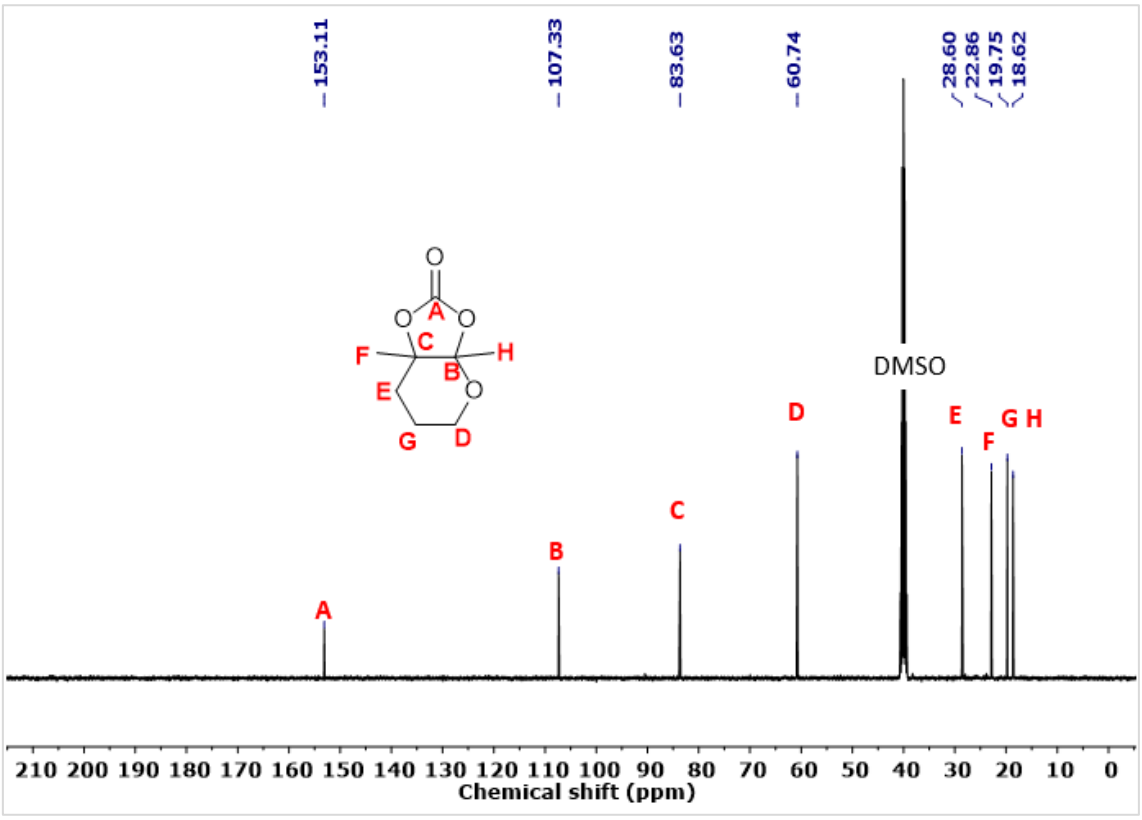
^{1}H NMR (400 MHZ, DMSO-d_6) of a mixture of **8** and **9**



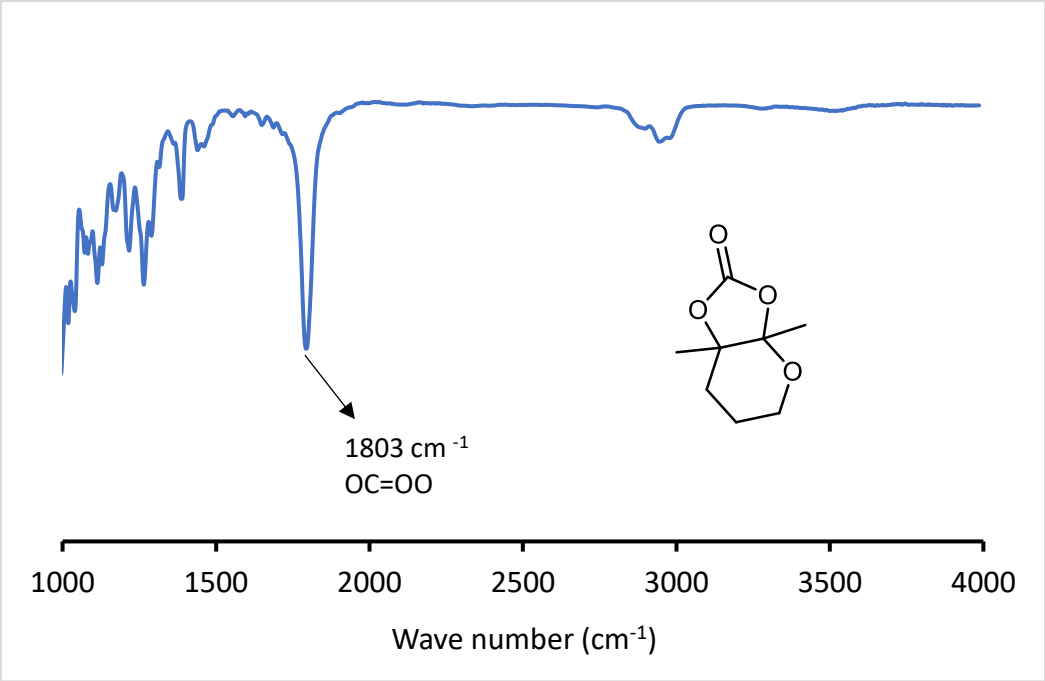
^{13}C NMR (101 MHZ, DMSO-d_6) of a mixture of **8** and **9**



^{1}H NMR (400 MHZ, DMSO-d_6) of **10**



^{13}C NMR (101 MHZ, DMSO-d_6) of **10**

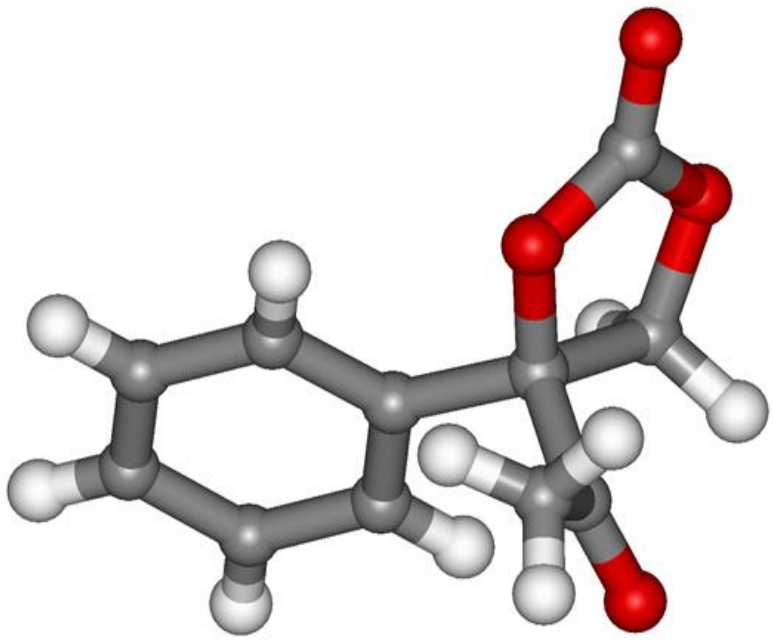


IR (neat) spectrum of **10**

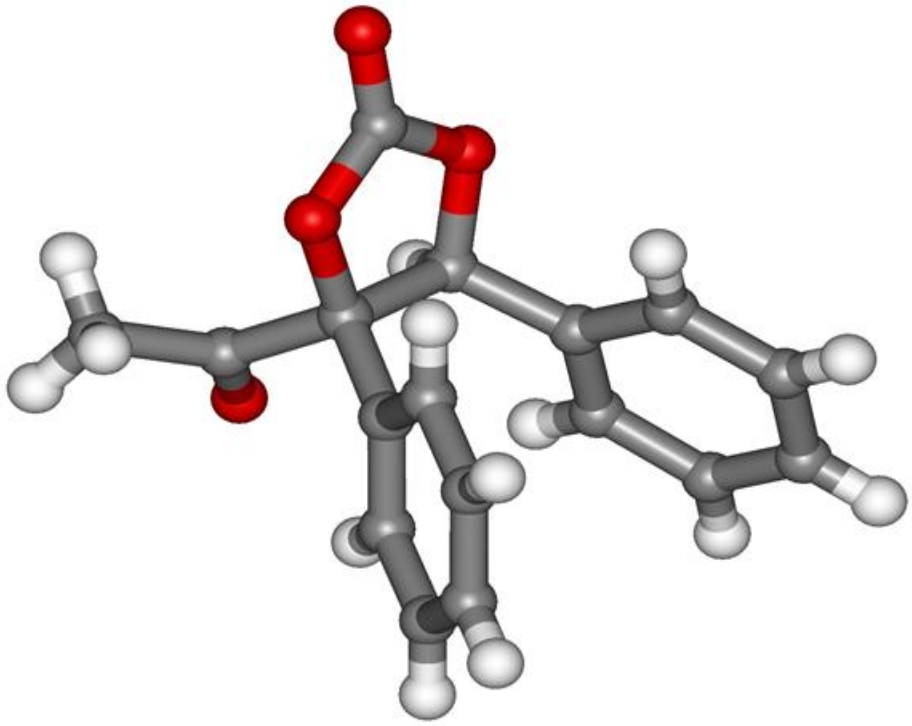
8. X-ray details

Procedure: single crystals of each compound suitable for X-ray diffraction were stable under atmospheric conditions; nevertheless, they were treated under inert conditions immersed in perfluoro-polyether as protecting oil for manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors and a Kryoflex low temperature device (*T* = −173 °C). Full-sphere data collection was used with ω and ϕ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008−1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used (Sheldrick, G. M. SHELXTL Crystallographic System, version 6.10; Bruker AXS, Inc.: Madison, WI, **2000**). Structure Refinement: SHELXTL-97-UNIX VERSION.

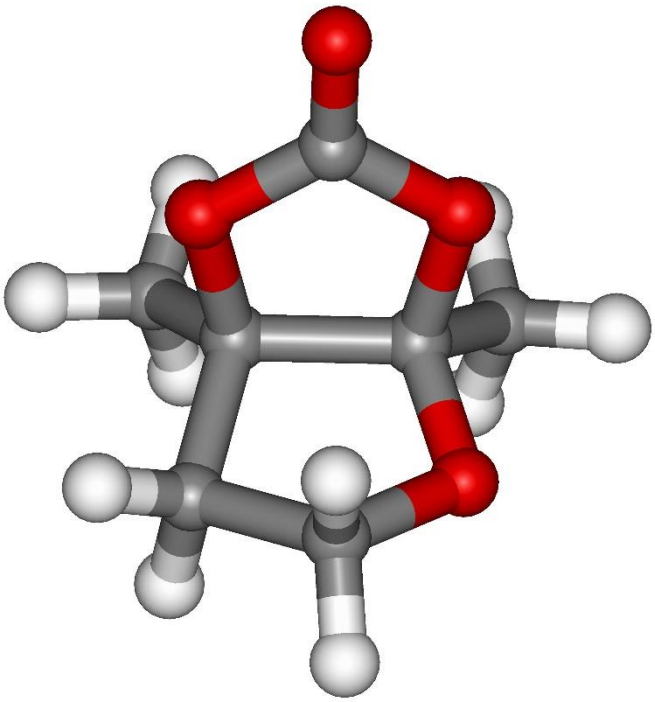
Disubstituted keto-carbonate **2a** (CCDC-2088491):



Trisubstituted keto-carbonate **4a** (CCDC-2088492):

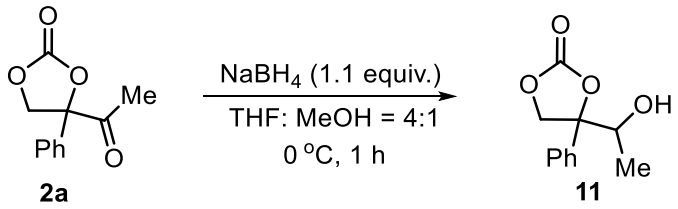


Bicyclic carbonate **7** (CCDC-2112335):



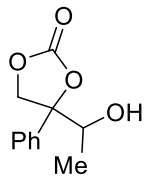
9. Synthetic and analytical details for compound 11 and 12

Procedures for the synthesis of the cyclic carbonates 11 and 12:

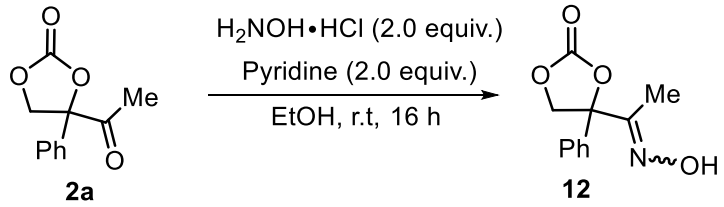


To a solution of 1,3-dioxolan-2-one product **2a** (0.3 mmol, 1.0 equiv) in a 4:1 mixture of tetrahydrofuran and methanol (1.5 mL) was added $NaBH_4$ (0.33 mmol, 1.1 equiv) under an argon atmosphere at 0 ºC. Then, the reaction mixture was stirred for 1 h. When the starting material had disappeared (as followed by TLC), the solvent was removed by evaporation and the residue was quenched by addition of a saturated ammonium chloride (5 mL) solution. Ethyl acetate (5 mL) was added to it and the aqueous layer was separated. Further extraction was carried out of the aqueous layer with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel to obtain the corresponding product.

4-(1-Hydroxyethyl)-4-phenyl-1,3-dioxolan-2-one (11)

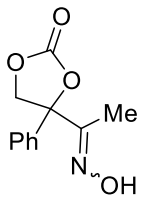


Colorless oil (42.8 mg, 67% yield, 2:1 *dr*). Eluent hexanes/EtOAc = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 7.6H), 4.95 (d, *J* = 8.4 Hz, 0.5H), 4.81 (q, *J* = 6.6 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 0.5H), 4.16 – 4.07 (m, 1.5H), 3.95 (d, *J* = 12.8 Hz, 1H), 2.55 (brs, 1.6 H), 1.78 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 1.6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 154.3, 137.6, 137.0, 129.2, 129.12, 129.07, 128.8, 125.7, 124.2, 88.1, 88.0, 82.0, 71.5, 71.0, 65.4, 17.1, 14.8; **IR (neat)**: *v* = 1770 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{12}NaO_4$ $[M + Na]^+$ 231.0628; Found 231.0620.



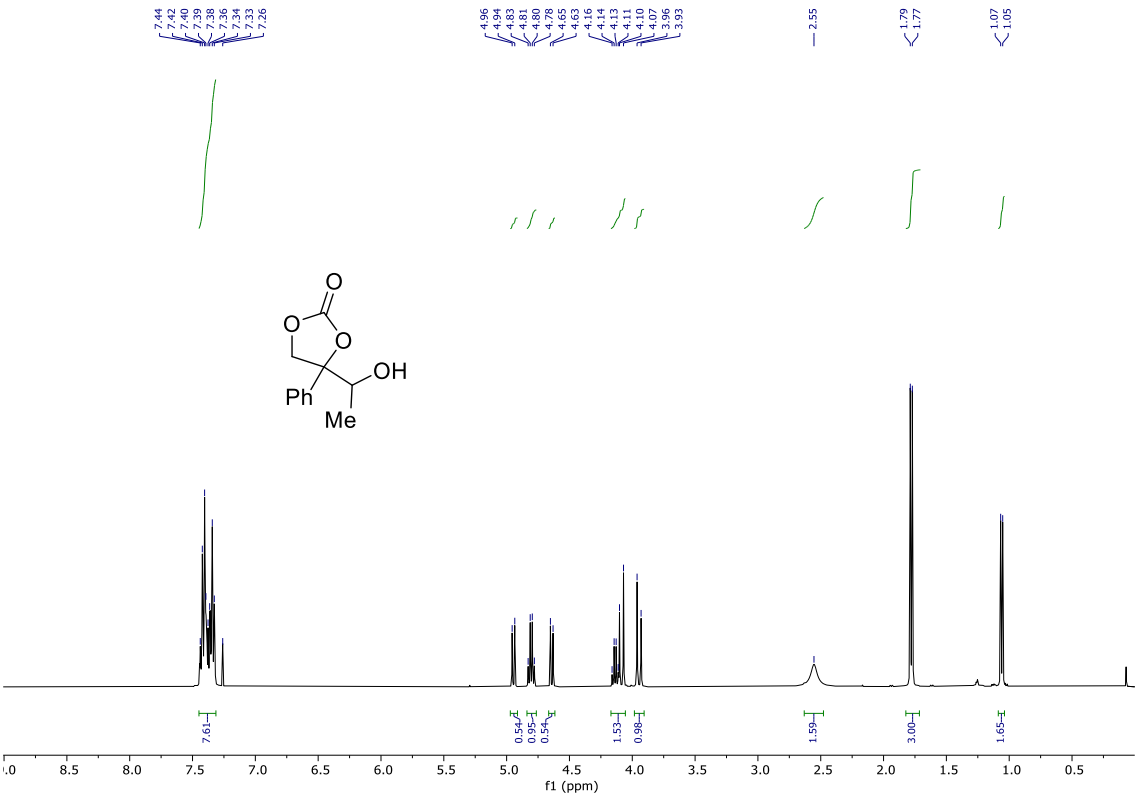
To a stirred solution of hydroxylamine hydrochloride (0.6 mmol, 2.0 equiv), pyridine (0.6 mmol, 2.0 equiv) in ethanol (3 mL) maintained at room temperature was added the 1,3-dioxolan-2-one **2a** (0.3 mmol, 1.0 equiv) dissolved in ethanol (3 mL). After the reaction was complete (followed by TLC), the solvent was removed under reduced pressure. To the residue was added water and the product was extracted twice with methylene chloride (2 × 5 mL) and washed with a 0.1 M HCl solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel to obtain the final product.

4-(1-(Hydroxyimino)ethyl)-4-phenyl-1,3-dioxolan-2-one (12)

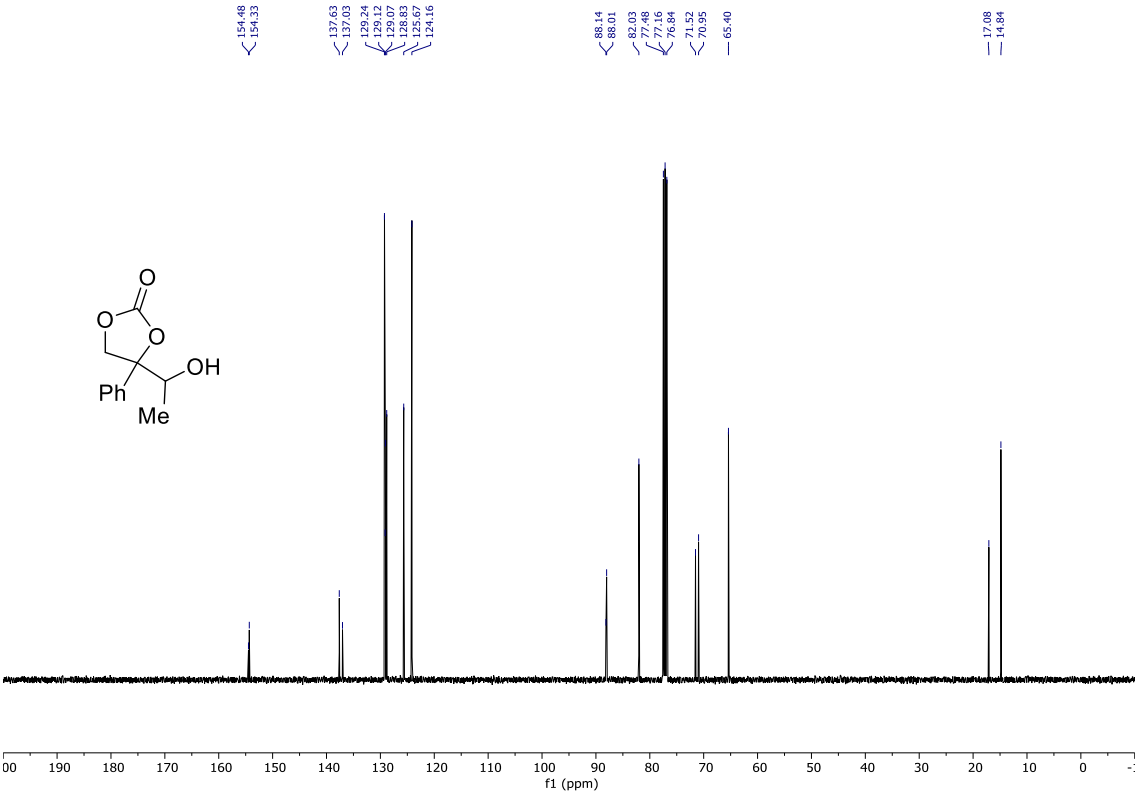


White solid (55.3 mg, 85% yield, *Z/E* = 3:1). Eluent hexanes/EtOAc = 5/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 6.9H), 5.45 (d, *J* = 8.5 Hz, 1H), 4.49 (d, *J* = 10.3 Hz, 0.3H), 4.40 (d, *J* = 10.3 Hz, 0.3H), 4.28 (d, *J* = 8.5 Hz, 1H), 1.85 (s, 1H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 155.0, 154.1, 139.1, 137.8, 129.4, 129.3, 128.9, 128.4, 125.1, 124.4, 89.5, 86.9, 82.6, 72.6, 10.6, 8.7; **IR (neat)**: *v* = 1804 cm^{-1}; **HRMS** (ESI/TOF) *m/z* Calcd for $C_{11}H_{11}NNaO_4$ $[M + Na]^+$ 244.0580; Found 244.0578.

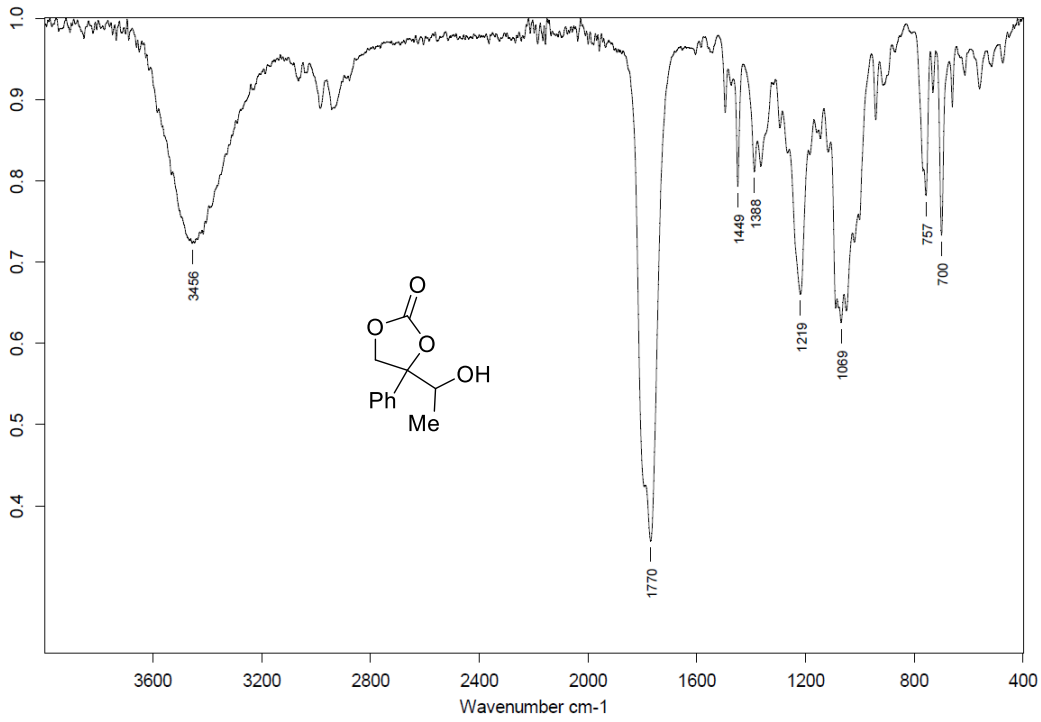
NB. The NMR and IR spectra for compounds **11** and **12** are provided on the following pages



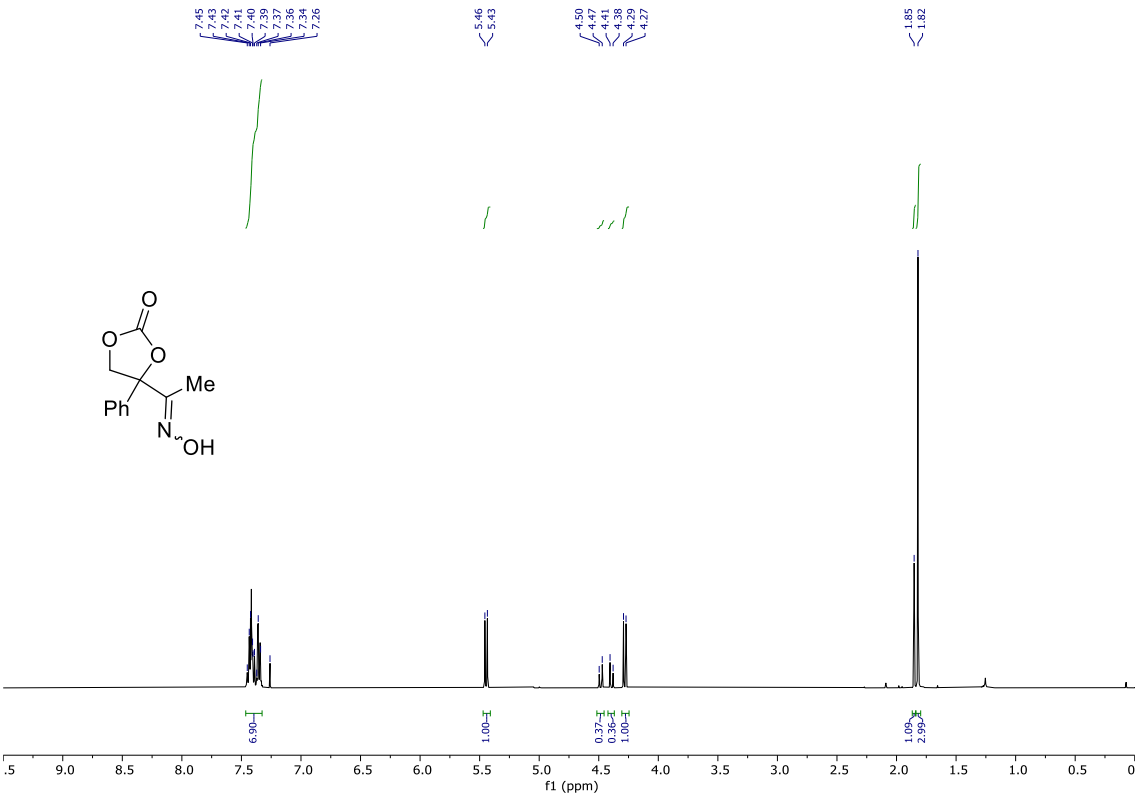
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **11**



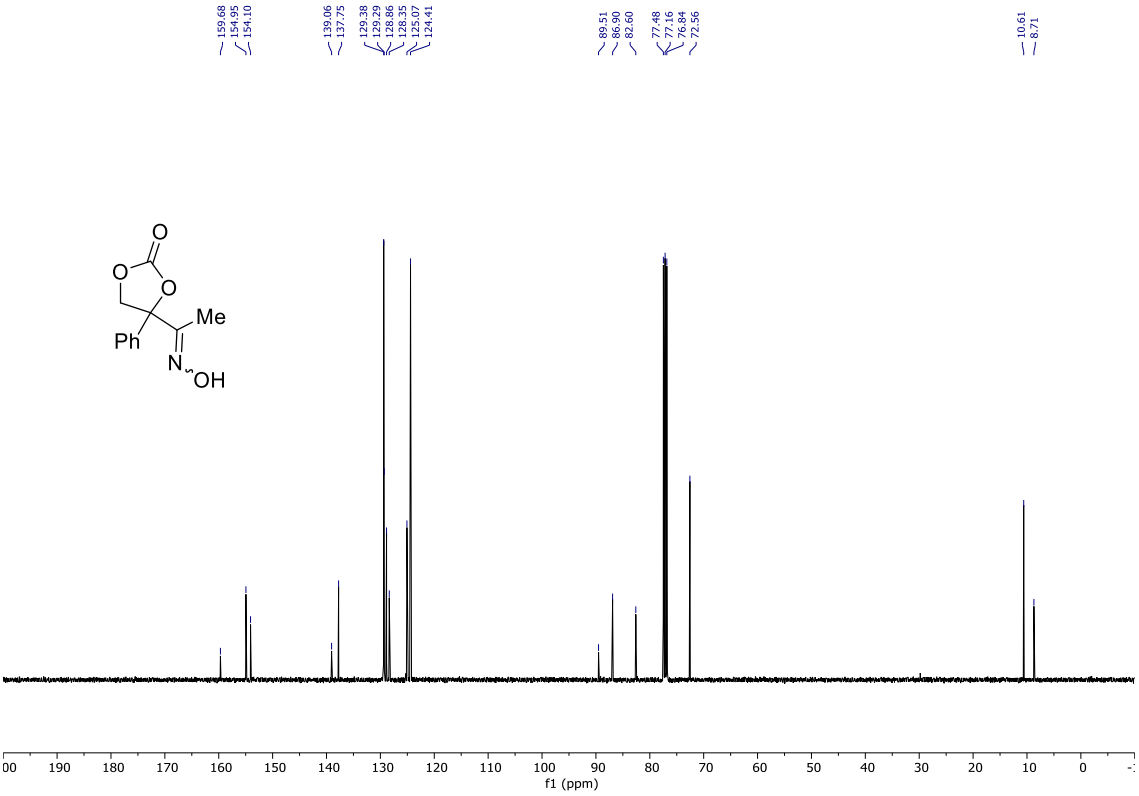
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **11**



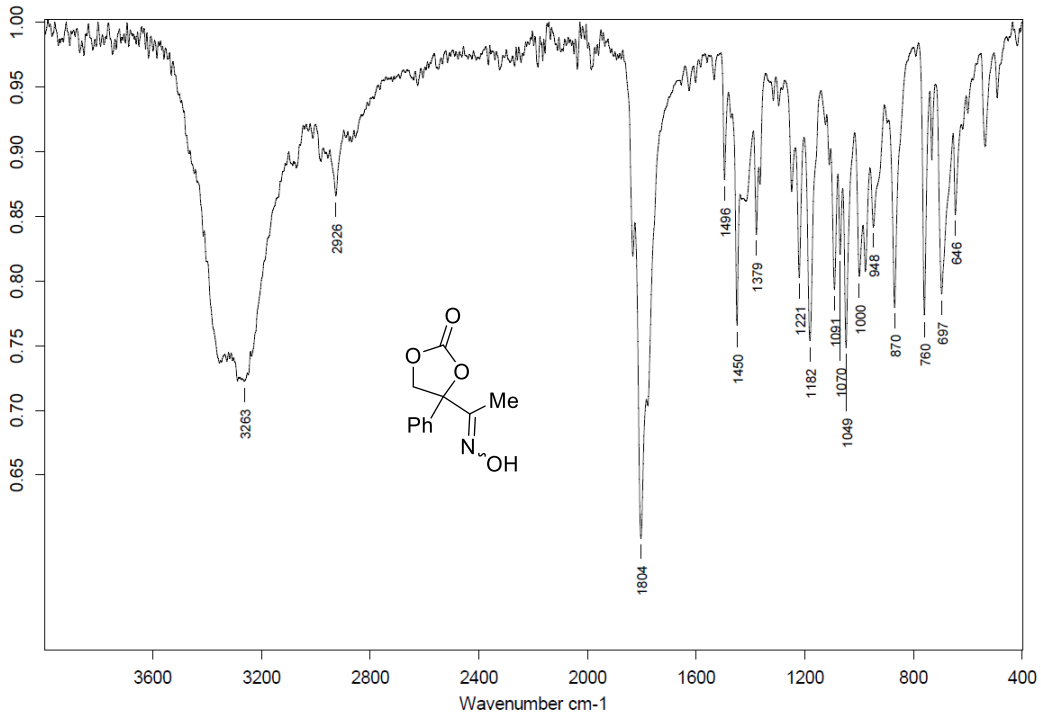
IR (neat) spectrum for carbonate **11**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **12**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **12**



IR spectrum (neat) for carbonate **12**

10. DFT details

As indicated in footnote 17 of the main text, the Gaussian 16[S1] program was used with the implemented functional and basis set PBE0-D3(BJ)/SDD/def2tzv being chosen using dispersion correction with Becke-Johnson damping. All calculations were carried out at 298 K using an acetonitrile implicit solvent model SMD.

Full access to the computational data set is provided through:
http://dx.doi.org/10.19061/iochem-bd-1-214.

Please find below (**Figure S6**, next page) a full description of all energies involved in the conversion of both (*R*)- and (*S*)-**1a** using the selected chiral conformation of **L1** in the Ag(**L1**)OAc (pre)-catalyst. Obviously, upon using the other catalyst enantiomer, the energies for the conversion of (*R*)- and (*S*)-**1a** should be **reversed**.

[S1] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

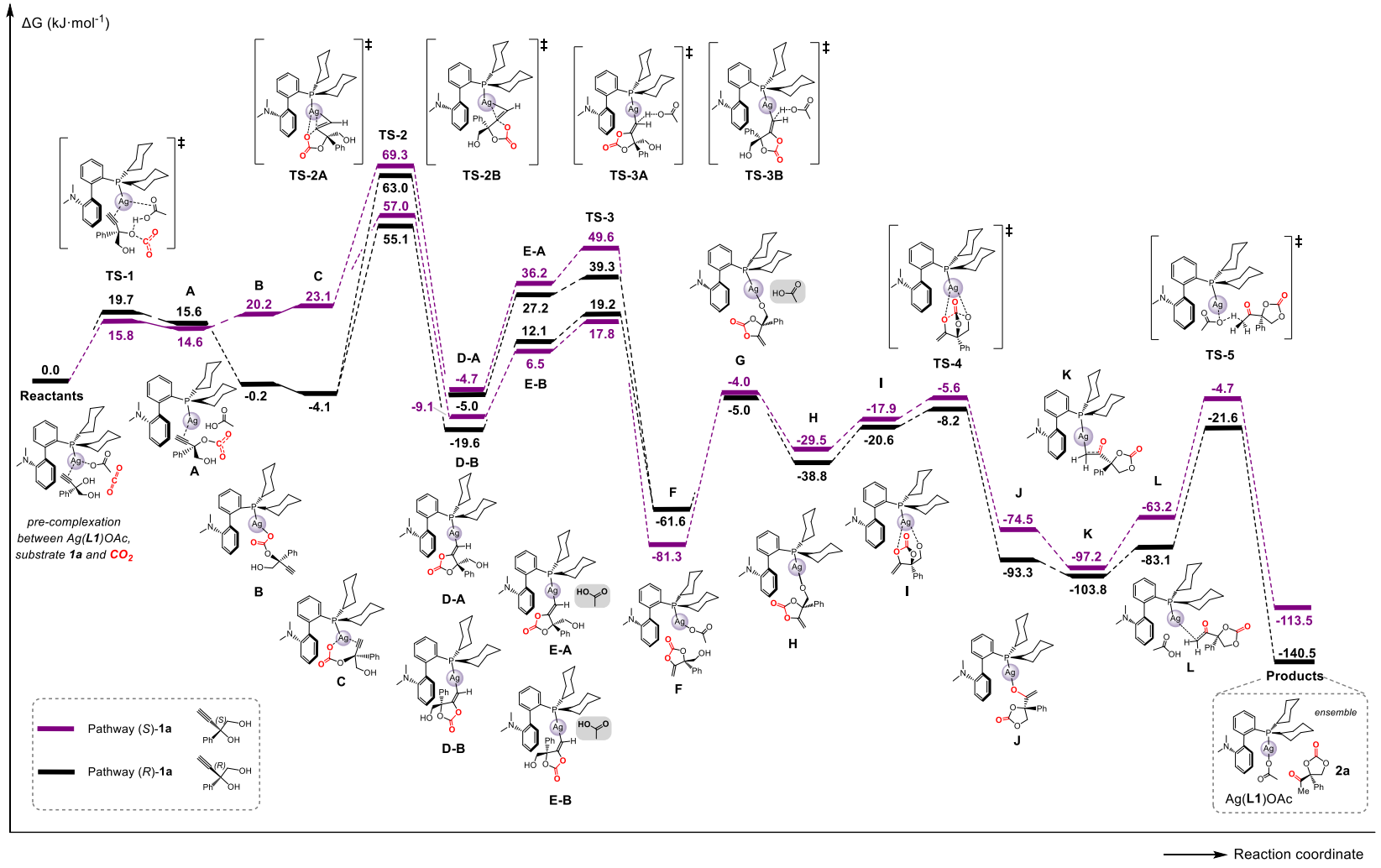


Figure S6. DFT-calculated pathway for the conversion of (*R*)-**1a** and (*S*)-**1a** into keto-carbonate **2a** by catalyst Ag(**L1**)OAc in the presence of carbon dioxide.