Supporting Information

for

(*Z*)-*γ*-Alkylidenebutenolide Synthesis through Au(I)-Catalyzed 1,3-Acyloxy Migration and the Carbonyl-Ene Reaction

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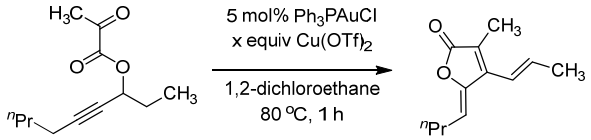
Content

1. General Information

^{1}H NMR and 2D NMR spectra were obtained at 400 MHz and ^{13}C NMR spectra were obtained at 101 MHz. Spectra were recorded in a $CDCl_3$, CD_2Cl_2, CD_3OD and DMSO-d_6 solution using the residual protonated solvent as the internal standard, *J* values are given in hertz. IR spectra were recorded on Fourier Transform infrared spectrometer and listed in cm^{-1}. High-resolution mass spectral analyses (HRMS) were performed on a Q-TOF-MS spectrometer. All air moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry and degassed solvents. Flash column chromatography was performed over silica gel (300-400 mesh). All commercially available reagents were used without further purification.

2. Optimization of the 1,3-acyloxy migration/carbonyl-ene reaction of 1a

Table S1. The copper effect in Au-catalyzed 1,3-acyloxy migration/carbonyl-ene reaction of **1a**[a]



1a **2a**

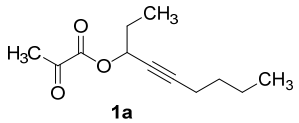
entry	*x*	yield (%)[b]
1	0.1	60
2	0.4	70
3	1.0	82
4	1.2	80

[a]Reaction conditions: a solution of **1a** (0.142 mmol), Ph_3PAuCl (0.0071 mmol), metal additive (*x* equiv) in DCE (1.5 mL) was heated and stirred at 80 °C. [b]Isolated yield after column chromatography.

3. General procedure for the preparation of propargylic α-ketoesters (Procedure A)[1]

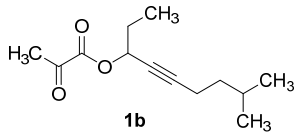
To a stirred solution of propargylic alcohol (1.0 equiv), α-keto acid (2.0 equiv) and pyridine (5.0 equiv) in dry THF was added MsCl (2.4 equiv) dropwise at 0 °C and stirred for 24 h at room temperature. The reaction mixture was quenched by 10% citric acid aqueous solution and extracted with Et_2O. The combined organic layers were washed with brine and dried by anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and the obtained residue was purified by flash column chromatography to get the desired propargylic α-ketoester.

4. Characterization data of propargyl α-ketoesters



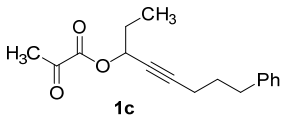
1a

Non-4-yn-3-yl 2-oxopropanoate (1a). According to Procedure A, **1a** was obtained from non-4-yn-3-ol (1.0 g, 7.1 mmol) and 2-oxopropanoic acid (1.26 g, 14.2 mmol) as a yellow oil (0.9 g, 4.28 mmol, 60% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 - 5.35 (m, 1H), 2.36 - 2.45 (m, 3H), 2.14 (dt, *J* = 2.01, 7.03 Hz, 2H), 1.72 - 1.84 (m, 2H), 1.27 - 1.46 (m, 4H), 0.96 (t, *J* = 7.40 Hz, 3H), 0.79 - 0.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 87.8, 76.7, 68.3, 30.4, 28.3, 26.8, 21.9, 18.4, 13.5, 9.4. IR (film) ν_{max} 2935, 1828, 1730, 1288, 1133 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}NaO_3$ 233.1148 $[M+Na]^+$, found 233.1150.



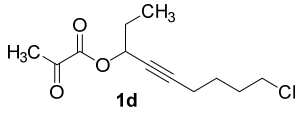
1b

8-Methylnon-4-yn-3-yl 2-oxopropanoate (1b). According to Procedure A, **1b** was obtained from 8-methylnon-4-yn-3-ol (1.0 g, 6.49 mmol) and 2-oxopropanoic acid (1.14 g, 12.98 mmol) as a yellow oil (0.82 g, 3.66 mmol, 56% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 - 5.38 (m, 1H), 2.41 (s, 3H), 2.14 (dt, *J* = 1.96, 7.46 Hz, 2H), 1.79 (q, *J* = 7.15 Hz, 2H), 1.55 - 1.62 (m, 1H), 1.33 (q, *J* = 7.21 Hz, 2H), 0.96 (t, *J* = 7.40 Hz, 3H), 0.82 (d, *J* = 6.72 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 87.9, 75.9, 68.3, 37.3, 28.2, 27.2, 26.8, 22.1, 16.7, 9.3. IR (film) ν_{max} 2957, 1730, 1284, 1133 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}NaO_3$ 247.1305 $[M+Na]^+$, found 247.1301.



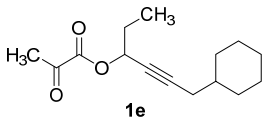
1c

8-Phenyloct-4-yn-3-yl 2-oxopropanoate (1c). According to Procedure A, **1c** was obtained from 8-phenyloct-4-yn-3-ol (1.0 g, 4.9 mmol) and 2-oxopropanoic acid (0.85 g, 9.8 mmol) as a yellow oil (0.91 g, 3.35 mmol, 68% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.23 (m, 2H), 7.08 - 7.13 (m, 3H), 5.32 (tt, *J* = 1.82, 6.43 Hz, 1H), 2.63 (t, *J* = 7.58 Hz, 2H), 2.40 (s, 3H), 2.15 (dt, *J* = 1.90, 7.06 Hz, 2H), 1.73 - 1.83 (m, 4H), 0.98 (t, *J* = 7.46 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 159.9, 141.4, 128.5, 128.4, 126.0, 87.3, 76.7, 68.2, 34.7, 30.0, 28.2, 26.8, 18.1, 9.4. IR (film) ν_{max} 2976, 1728, 1262, 1196, 1134, 1080, 1049, 1001, 886 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NaO_3$ 295.1305 $[M+Na]^+$, found 295.1302.



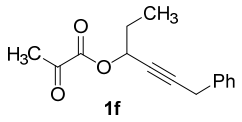
1d

9-Chlorononn-4-yn-3-yl 2-oxopropanoate (1d). According to Procedure A, **1d** was obtained from 9-chlorononn-4-yn-3-ol (1.0 g, 5.7 mmol) and 2-oxopropanoic acid (1.02 g, 11.4 mmol) as a yellow oil (0.92 g, 3.77 mmol, 66% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 - 5.42 (m, 1H), 3.57 (t, *J* = 6.48 Hz, 2H), 2.44 - 2.52 (m, 3H), 2.28 (dt, *J* = 1.96, 6.97 Hz, 2H), 1.83 - 1.91 (m, 4H), 1.63 - 1.72 (m, 2H), 1.04 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 159.9, 86.7, 76.8, 68.1, 44.4, 31.5, 28.2, 26.8, 25.5, 18.0, 9.4. IR (film) ν_{max} 2960, 1731, 1287, 1132 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}ClO_3$ 245.0939 $[M+H]^+$, found 245.0938.



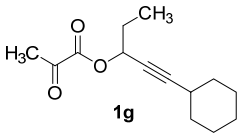
1e

6-Cyclohexylhex-4-yn-3-yl 2-oxopropanoate (1e). According to Procedure A, **1e** was obtained from 6-cyclohexylhex-4-yn-3-ol (1.0 g, 5.5 mmol) and 2-oxopropanoic acid (0.97 g, 11.0 mmol) as a yellow oil (0. 59 g, 2.36 mmol, 43% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (tt, *J* = 1.97, 6.46 Hz, 1H), 2.39 - 2.43 (m, 3H), 2.03 (dd, *J* = 2.02, 6.66 Hz, 2H), 1.76 - 1.83 (m, 2H), 1.55 - 1.73 (m, 6H), 1.34 - 1.43 (m, 1H), 1.03 - 1.22 (m, 4H), 0.95 - 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 86.7, 76.9, 68.3, 37.1, 32.7, 32.6, 28.3, 26.8, 26.5, 26.2, 26.1, 26.1, 9.4. IR (film) ν_{max} 2922, 1728, 1132, 978 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{23}O_3$ 251.1642 $[M+H]^+$, found 251.1637.



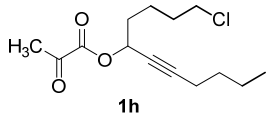
1f

6-Phenylhex-4-yn-3-yl 2-oxopropanoate (1f). According to Procedure A, **1f** was obtained from 6-phenylhex-4-yn-3-ol (1.0 g, 5.7 mmol) and 2-oxopropanoic acid (1.02 g, 11.4 mmol) as a yellow oil (0. 82 g, 3.36 mmol, 58% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.34 (m, 4H), 7.21 - 7.27 (m, 1H), 5.41 - 5.48 (m, 1H), 3.64 (d, *J* = 1.83 Hz, 2H), 2.48 (s, 3H), 1.87 - 1.96 (m, 2H), 1.06 (t, *J* = 7.46 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6,159.9, 136.0, 128.6, 127.8, 126.7, 85.1, 78.3, 68.1, 28.2, 26.8, 25.0, 9.4. IR (film) ν_{max} 2959, 1828, 1732, 1289, 1131 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}NaO_3$ 267.0992 $[M+Na]^+$, found 267.0987.



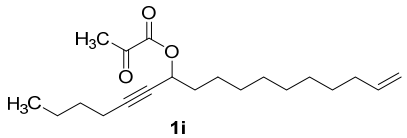
1g

1-Cyclohexylpent-1-yn-3-yl 2-oxopropanoate (1g). According to Procedure A, **1g** was obtained from 1-cyclohexylpent-1-yn-3-ol (1.0 g, 6.0 mmol) and 2-oxopropanoic acid (1.06 g, 12.0 mmol) as a yellow oil (1.3 g, 5.50 mmol, 91% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (dt, *J* = 1.71, 6.48 Hz, 1H), 2.39 - 2.45 (m, 3H), 2.29 - 2.37 (m, 1H), 1.79 (q, *J* = 7.21 Hz, 2H), 1.66 - 1.73 (m, 2H), 1.56 - 1.64 (m, 2H), 1.31 - 1.48 (m, 4H), 1.24 (d, *J* = 8.80 Hz, 2H), 0.96 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 91.8, 76.0, 68.3, 32.3, 28.9, 28.3, 26.8, 25.8, 24.7, 9.4. IR (film) ν_{max} 2930, 1728, 1283, 1133, 899 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{20}NaO_3$ 259.1305 $[M+Na]^+$, found 259.1303.



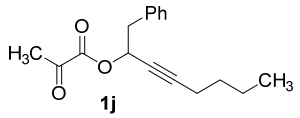
1h

1-Chloroundec-6-yn-5-yl 2-oxopropanoate (1h). According to Procedure A, **1h** was obtained from 1-chloroundec-6-yn-5-ol (1.0 g, 4.9 mmol) and 2-oxopropanoic acid (0.85 g, 12.0 mmol) as a yellow oil (0.85 g, 3.13 mmol, 63% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (t, *J* = 6.30 Hz, 1H), 3.56 (t, *J* = 6.48 Hz, 2H), 2.46 - 2.51 (m, 3H), 2.22 (t, *J* = 6.97 Hz, 2H), 1.80 - 1.90 (m, 4H), 1.61 - 1.68 (m, 2H), 1.36 - 1.53 (m, 4H), 0.91 (t, *J* = 7.21 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 159.8, 88.1, 75.9, 66.8, 44.6, 34.1, 31.9, 30.4, 26.8, 22.4, 21.9, 18.4, 13.5. IR (film) ν_{max} 2958, 1731, 1285, 1131, 978 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}ClNaO_3$ 295.1071 $[M+Na]^+$, found 295.1068.



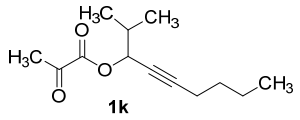
1i

Heptadec-16-en-5-yn-7-yl 2-oxopropanoate (1i). According to Procedure A, **1i** was obtained from heptadec-16-en-5-yn-7-ol (1.0 g, 4.0 mmol) and 2-oxopropanoic acid (0.70 g, 8.0 mmol) as a yellow oil (0.72 g, 2.25 mmol, 56% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 - 5.83 (m, 1H), 5.26 - 5.40 (m, 1H), 4.82 - 4.95 (m, 2H), 2.35 - 2.44 (m, 3H), 2.14 (dt, *J* = 1.96, 7.03 Hz, 2H), 1.92 - 2.00 (m, 2H), 1.71 - 1.80 (m, 2H), 1.27 - 1.44 (m, 8H), 1.20 - 1.24 (m, 8H), 0.81 - 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 159.9, 139.2, 114.1, 87.7, 76.3, 67.2, 34.9, 33.8, 30.4, 29.3, 29.3, 29.1, 29.0, 28.9, 26.8, 25.0, 21.9, 18.4, 13.5. IR (film) ν_{max} 2925, 1728, 1289, 1135, 908 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{32}NaO_3$ 343.2244 $[M+Na]^+$, found 343.2241.



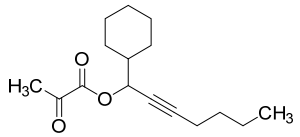
1j

1-Phenyloct-3-yn-2-yl 2-oxopropanoate (1j). According to Procedure A, **1j** was obtained from 1-phenyloct-3-yn-2-ol (1.0 g, 4.9 mmol) and 2-oxopropanoic acid (0.86 g, 8.0 mmol) as a yellow oil (0.85 g, 3.01 mmol, 61% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.32 (m, 5H), 5.58 (tt, *J* = 1.90, 6.82 Hz, 1H), 3.08 - 3.17 (m, 2H), 2.39 (s, 3H), 2.18 (dt, *J* = 1.94, 7.00 Hz, 2H), 1.30 - 1.47 (m, 4H), 0.86 - 0.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 159.5, 129.7, 128.5, 128.4, 127.1, 88.7, 75.9, 67.5, 41.5, 30.3, 26.7, 21.8, 18.4, 13.6. IR (film) ν_{max} 2933, 1730, 1131, 977 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NaO_3$ 295.1305 $[M+Na]^+$, found 295.1303.



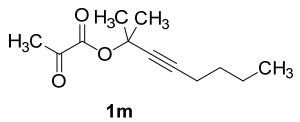
1k

2-Methylnon-4-yn-3-yl 2-oxopropanoate (1k). According to Procedure A, **1k** was obtained from 2-methylnon-4-yn-3-ol (1.0 g, 6.49 mmol) and 2-oxopropanoic acid (1.14 g, 12.9 mmol) as a yellow oil (0.65 g, 2.90 mmol, 45% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (td, *J* = 1.99, 5.69 Hz, 1H), 2.42 - 2.54 (m, 3H), 2.22 (dt, *J* = 1.96, 6.97 Hz, 2H), 2.03 - 2.09 (m, 1H), 1.36 - 1.53 (m, 4H), 1.03 (dd, *J* = 6.72, 13.57 Hz, 6H), 0.88 - 0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 159.9, 88.2, 74.8, 71.9, 32.6, 30.5, 26.8, 21.9, 18.3, 18.2, 17.5, 13.5. IR (film) ν_{max} 2962, 1729, 1291, 1132, 980 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}NaO_3$ 247.1305 $[M+Na]^+$, found 247.1304.



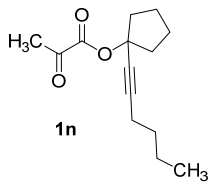
1l

1-Cyclohexylhept-2-ynyl 2-oxopropanoate (1l). According to Procedure A, **1l** was obtained from 1-cyclohexylhept-2-yn-1-ol (1.0 g, 5.14 mmol) and 2-oxopropanoic acid (1.14 g, 12.9 mmol) as a yellow oil (0.67 g, 2.53 mmol, 49% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (td, *J* = 1.91, 6.08 Hz, 1H), 2.46 - 2.50 (m, 3H), 2.22 (dt, *J* = 1.96, 6.97 Hz, 2H), 1.87 (d, *J* = 12.72 Hz, 1H), 1.72 - 1.82 (m, 4H), 1.35 - 1.53 (m, 4H), 1.07 - 1.32 (m, 6H), 0.91 (t, *J* = 7.27 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 160.0, 88.3, 75.2, 71.3, 41.9, 30.5, 28.5, 28.1, 26.9, 26.1, 25.7, 25.6, 21.9, 18.4, 13.5. IR (film) ν_{max} 2929, 1763, 1730, 1278, 1132, 976 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NaO_3$ 287.1618 $[M+Na]^+$, found 287.1616.



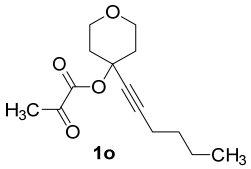
1m

2-Methyloct-3-yn-2-yl 2-oxopropanoate (1m). According to Procedure A, **1m** was obtained from 2-methyloct-3-yn-2-ol (1.0 g, 7.14 mmol) and 2-oxopropanoic acid (1.24 g, 14.28 mmol) as a yellow oil (0.6 g, 2.86 mmol, 40% yield, eluent: EtOAc/petroleum ether = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (d, *J* = 0.98 Hz, 3H), 2.21 (t, *J* = 6.97 Hz, 2H), 1.73 (s, 6H), 1.36 - 1.52 (m, 4H), 0.88 - 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 159.2, 86.3, 79.9, 75.6, 30.4, 29.0, 26.5, 21.8, 18.3, 13.5. IR (film) ν_{max} 2932, 1731, 1265, 1138, 1116, 971 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{19}O_3$ 211.1329 $[M+H]^+$, found 211.1326.



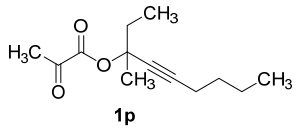
1n

1-(Hex-1-ynyl)cyclopentyl 2-oxopropanoate (1n). According to Procedure A, **1n** was obtained from 1-(hex-1-ynyl)cyclopentanol (1.0 g, 6.57 mmol) and 2-oxopropanoic acid (1.15 g, 13.15 mmol) as a yellow oil (0.6 g, 2.54 mmol, 39% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.11 - 2.33 (m, 6H), 1.74 - 1.79 (m, 4H), 1.34 - 1.52 (m, 4H), 0.88 - 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 159.5, 87.0, 84.0, 79.0, 40.4, 30.5, 26.6, 23.2, 21.9, 18.4, 13.6. IR (film) ν_{max} 2957, 1763, 1732, 1262, 1134, 919 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}O_3$ 237.1485 $[M+H]^+$, found 237.1484.



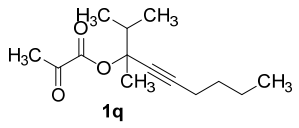
1o

4-(Hex-1-ynyl)tetrahydro-2*H*-pyran-4-yl 2-oxopropanoate (1o). According to Procedure A, **1o** was obtained from 4-(hex-1-ynyl)tetrahydro-2*H*-pyran-4-ol (1.0 g, 5.49 mmol) and 2-oxopropanoic acid (0.96 g, 10.9 mmol) as a yellow oil (0.62 g, 2.46 mmol, 45% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (td, *J* = 4.25, 11.92 Hz, 2H), 3.67 - 3.75 (m, 2H), 2.45 (s, 3H), 2.22 - 2.28 (m, 4H), 2.06 (ddd, *J* = 4.03, 9.48, 13.14 Hz, 2H), 1.36 - 1.55 (m, 4H), 0.90 (t, *J* = 7.27 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 158.9, 89.6, 77.3, 76.1, 64.5, 37.6, 30.5, 26.5, 21.9, 18.4, 13.5. IR (film) ν_{max} 2959, 1731, 1288, 1131, 977 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}O_4$ 253.1434 $[M+H]^+$, found 253.1436.



1p

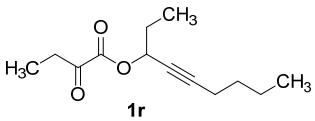
3-Methylnon-4-yn-3-yl 2-oxopropanoate (1p). According to Procedure A, **1p** was obtained from 3-methylnon-4-yn-3-ol (1.0 g, 6.49 mmol) and 2-oxopropanoic acid (1.14 g, 12.9 mmol) as a yellow oil (0.62 g, 2.76 mmol, 42% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.15 (t, *J* = 7.03 Hz, 2H), 1.92 - 2.02 (m, 1H), 1.76 - 1.86 (m, 1H), 1.63 (s, 3H), 1.29 - 1.45 (m, 4H), 0.97 (t, *J* = 7.40 Hz, 3H), 0.81 - 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 159.2, 87.5, 79.5, 78.8, 34.7, 30.6, 26.6, 26.1, 21.9, 18.4, 13.5, 8.6. IR (film) ν_{max} 2935, 1731, 1294, 1142, 1114, 974 cm^{-1}. HRMS (ESI) m/z calcd for $C_{13}H_{21}O_3$ 225.1485 $[M+H]^+$, found 225.1487.



1q

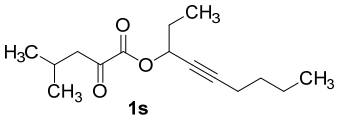
2,3-Dimethylnon-4-yn-3-yl 2-oxopropanoate (1q). According to Procedure A, **1q** was obtained from 2,3-dimethylnon-4-yn-3-ol (1.0 g, 5.95 mmol) and 2-oxopropanoic acid (1.05 g, 11.9 mmol) as a yellow oil (0.62 g, 2.60 mmol, 44% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.17 - 2.26 (m, 3H), 1.68 (s, 3H), 1.37 - 1.54 (m, 4H), 1.07 (d, *J* = 6.65 Hz, 3H), 1.02 (d, *J* = 6.78 Hz, 3H), 0.88 - 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 159.1, 88.0, 82.6, 77.7, 37.7, 30.6, 26.7, 23.3, 21.9, 18.4, 17.5, 17.2, 13.5. IR (film) ν_{max} 2961, 1758, 1731, 1297, 1138, 1119, 973 cm^{-1}. HRMS (ESI) *m/z* calcd for$C_{14}H_{23}O_3$ 239.1641 $[M+H]^+$,

found 239.1635.



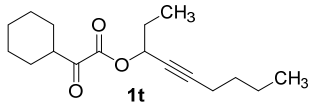
1r

Non-4-yn-3-yl 2-oxobutanoate (1r). According to Procedure A, **1r** was obtained from non-4-yn-3-ol (1.0 g, 7.1 mmol) and 2-oxobutanoic acid (1.44 g, 14.2 mmol) as a yellow oil (1.3 g, 5.8 mmol, 81% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (tt, *J* = 1.96, 6.42 Hz, 1H), 2.76 - 2.81 (m, 2H), 2.14 (dt, *J* = 1.96, 7.03 Hz, 2H), 1.74 - 1.82 (m, 2H), 1.29 - 1.44 (m, 4H), 1.07 (t, *J* = 7.21 Hz, 3H), 0.96 (t, *J* = 7.46 Hz, 3H), 0.81 - 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 160.3, 87.7, 76.1, 68.0, 33.0, 30.4, 28.2, 21.9, 18.3, 13.5, 9.3, 6.9. IR (film) ν_{max} 2937, 1727, 1459, 1266, 1098 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}NaO_3$ 247.1305 $[M+Na]^+$, found 247.1305.



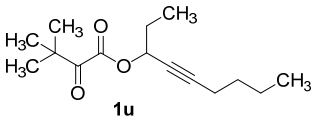
1s

Non-4-yn-3-yl 4-methyl-2-oxopentanoate (1s). According to Procedure A, **1s** was obtained from non-4-yn-3-ol (1.0 g, 7.1 mmol) and 4-methyl-2-oxopentanoic acid (1.84 g, 14.2 mmol) as a yellow oil (1.5 g, 5.95 mmol, 83% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 - 5.46 (m, 1H), 2.71 (dd, *J* = 0.67, 6.79 Hz, 2H), 2.16 - 2.25 (m, 3H), 1.85 (q, *J* = 7.15 Hz, 2H), 1.34 - 1.52 (m, 4H), 1.03 (t, *J* = 7.46 Hz, 3H), 0.97 (d, *J* = 6.72 Hz, 6H), 0.89 - 0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 160.6, 87.7, 76.1, 68.0, 48.0, 30.4, 28.2, 24.2, 22.4, 21.9, 18.3, 13.5, 9.4. IR (film) ν_{max} 2959, 1725, 1253, 1150, 1042 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NaO_3$ 275.1618 $[M+Na]^+$, found 275.1614.



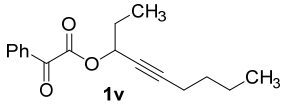
1t

Non-4-yn-3-yl 2-cyclohexyl-2-oxoacetate (1t). According to Procedure A, **1t** was obtained from non-4-yn-3-ol (0.598 g, 4.2 mmol) and 2-cyclohexyl-2-oxoacetic acid (1 g, 6.41 mmol) as a yellow oil (0.8 g, 2.88 mmol, 68% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (tt, *J* = 1.96, 6.42 Hz, 1H), 2.93 (ddd, *J* = 3.67, 7.24, 10.73 Hz, 1H), 2.14 (dt, *J* = 1.96, 6.97 Hz, 2H), 1.70 - 1.87 (m, 6H), 1.51 - 1.65 (m, 2H), 1.25 - 1.46 (m, 8H), 0.96 (t, *J* = 7.46 Hz, 3H), 0.81 - 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 161.3, 87.6, 76.2, 67.8, 46.5, 30.4, 28.2, 27.4, 27.3, 25.7, 25.3, 21.8, 18.3, 13.5, 9.4. IR (film) ν_{max} 2925, 1728, 1000 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{26}NaO_3$ 301.1774 $[M+Na]^+$, found 301.1773.



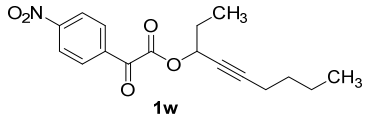
1u

Non-4-yn-3-yl 3,3-dimethyl-2-oxobutanoate (1u). According to Procedure A, **1u** was obtained from non-4-yn-3-ol (1.0 g, 7.1 mmol) and 3,3-dimethyl-2-oxobutanoic acid (1.84 g, 14.2 mmol) as a yellow oil (1.6 g, 6.34 mmol, 89% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 - 5.41 (m, 1H), 2.15 (dt, *J* = 1.96, 6.97 Hz, 2H), 1.77 (q, *J* = 7.15 Hz, 2H), 1.30 - 1.44 (m, 4H), 1.19 (s, 9H), 0.96 (t, *J* = 7.40 Hz, 3H), 0.81 - 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 163.3, 87.6, 76.2, 67.4, 30.4, 28.2, 25.7, 25.6, 23.2, 21.8, 18.3, 13.5, 9.3. IR (film) ν_{max} 2969, 1735, 1282, 1235, 1049, 1001, 892 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}NaO_3$ 275.1618 $[M+H]^+$, found 275.1614.



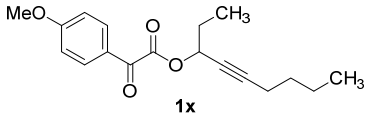
1v

Non-4-yn-3-yl 2-oxo-2-phenylacetate (1v). According to Procedure A, **1v** was obtained from non-4-yn-3-ol (1.04 g, 7.41 mmol) and 2-oxo-2-phenylacetic acid (2.22 g, 14.82 mmol) as a yellow oil (1.6 g, 5.88 mmol, 79% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 1.22, 8.44 Hz, 2H), 7.66 - 7.71 (m, 1H), 7.51 - 7.56 (m, 2H), 5.55 - 5.61 (m, 1H), 2.28 (dt, *J* = 2.02, 7.00 Hz, 2H), 1.93 (q, *J* = 7.15 Hz, 2H), 1.40 - 1.59 (m, 4H), 1.08 (t, *J* = 7.46 Hz, 3H), 0.92 - 0.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1, 163.3, 134.9, 130.2, 130.0, 128.9, 87.9, 76.3, 68.0, 30.5, 28.3, 21.9, 18.4, 13.6, 9.4. IR (film) ν_{max} 2931, 1730, 1281, 1134 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{21}O_3$ 273.1485 $[M+H]^+$, found 273.1482.



1w

Non-4-yn-3-yl 2-(4-nitrophenyl)-2-oxoacetate (1w). According to Procedure A, **1w** was obtained from non-4-yn-3-ol (0.478 g, 3.41 mmol) and 2-(4-nitrophenyl)-2-oxoacetic acid (1 g, 5.12 mmol) as a yellow oil (0.6 g, 1.89 mmol, 55% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 - 8.41 (m, 2H), 8.18 - 8.29 (m, 2H), 5.58 (tt, *J* = 1.86, 6.39 Hz, 1H), 2.27 (dt, *J* = 1.90, 7.00 Hz, 2H), 1.93 (q, *J* = 7.15 Hz, 2H), 1.36 - 1.60 (m, 4H), 1.08 (t, *J* = 7.40 Hz, 3H), 0.93 (t, *J* = 7.21 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 161.7, 151.2, 137.0, 131.2, 124.0, 88.4, 75.9, 68.8, 30.4, 28.3, 21.9, 18.4, 13.5, 9.3. IR (film) ν_{max} 2934, 1734, 1701, 1528, 1345, 1190, 986 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NNaO_5$ 340.1161 $[M+Na]^+$, found 340.1155.



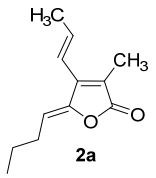
1x

Non-4-yn-3-yl 2-(4-methoxyphenyl)-2-oxoacetate (1x). According to Procedure A, **1x** was obtained from non-4-yn-3-ol (1.1 g, 7.85 mmol) and 2-(4-methoxyphenyl)-2-oxoacetic acid (2.89 g, 15.7 mmol) as a yellow oil (1.9 g, 1.89 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 8.10 (m, 2H), 6.87 - 7.04 (m, 2H), 5.39 - 5.63 (m, 1H), 3.90 (s, 3H), 2.25 (dt, *J* = 1.90, 7.00 Hz, 2H), 1.90 (q, *J* = 7.18 Hz, 2H), 1.39 - 1.57 (m, 4H), 1.06 (t, *J* = 7.40 Hz, 3H), 0.92 (t, *J* = 7.21 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 165.0, 163.6, 132.6, 125.6, 114.2, 87.7, 76.4, 67.8, 55.7, 30.5, 28.3, 21.9, 18.4, 13.6, 9.4. IR (film) ν_{max} 2935, 1735, 1675, 1596, 1264, 1156 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{22}NaO_4$ 325.1410 $[M+Na]^+$, found 325.1415.

5. General procedure for the Au-catalyzed cycloisomerization of propargyl *α*-ketoesters (Procedure B)

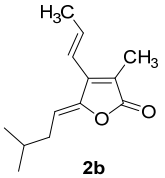
To a solution of propargyl *α*-ketoester (1.0 equiv) and dry 1,2-dichloroethane (the concentration of the substrate is 0.1 M) in a vial was added Ph_3PAuCl (0.05 equiv) and $Cu(OTf)_2$ (1.0 equiv). The solution was stirred at 80 ºC on a heating mantle for 1 h. After cooling, the solution was concentrated under reduced pressure. The obtained residue was purified by column chromatography to give (*Z*)-*γ*-alkylidenebutenolide product.

6. Characterization data of (*Z*)-*γ*-alkylidenebutenolides



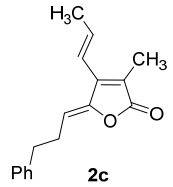
2a

(*Z*)-5-Butylidene-3-methyl-4-((*E*)-prop-1-enyl)furan-2(5*H*)-one (2a). According to Procedure B, to a solution of non-4-yn-3-yl 2-oxopropanoate **1a** (500 mg, 2.38 mmol) and dry 1,2-dichloroethane (8 mL) in a vial was added Ph_3PAuCl (Innochem, 59 mg, 0.119 mg) and $Cu(OTf)_2$ (Aladdin, 860 mg, 2.38 mmol). The solution was stirred at 80 °C on a heating mantle for 1 h. After cooling, the solution was concentrated under reduced pressure. The obtained residue was purified by column chromatography to give **2a** as a yellow oil (375 mg, 1.95 mmol, 82% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 - 6.32 (m, 2H), 5.28 (t, *J* = 7.89 Hz, 1H), 2.29 (q, *J* = 7.58 Hz, 2H), 1.92 (s, 3H), 1.89 (d, *J* = 5.62 Hz, 3H), 1.42 (m, 2H), 0.88 (t, *J* = 7.34 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 147.6, 144.3, 136.3, 120.9, 118.8, 111.0, 76.3, 76.0, 75.7, 27.1, 21.5, 18.5, 12.8, 8.6. IR (film) ν_{max} 2961, 1735, 1228, 1019 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{17}O_2$ 193.1223 $[M+H]^+$, found 193.1224.



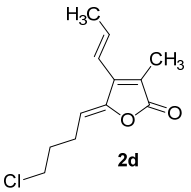
2b

(*Z*)-3-Methyl-5-(3-methylbutylidene)-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2b). According to Procedure B, **2b** was obtained from 8-methylnon-4-yn-3-yl 2-oxopropanoate **1b** (80 mg, 0.357 mmol) as a yellow oil (59 mg, 0.286 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.15 - 6.45 (m, 2H), 5.41 (t, *J* = 7.95 Hz, 1H), 2.30 (t, *J* = 7.46 Hz, 2H), 1.97 - 2.00 (m, 6H), 1.80 (td, *J* = 6.68, 13.42 Hz, 1H), 0.98 (d, *J* = 6.60 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.7, 149.0, 145.1, 137.4, 121.8, 119.6, 110.5, 35.0, 28.7, 22.1, 19.2, 9.4. IR (film) ν_{max} 2939, 1730, 1135, 745 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NaO_2$ 229.1199 $[M+Na]^+$, found 229.1198.



2c

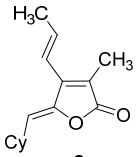
(*Z*)-3-Methyl-5-(3-phenylpropylidene)-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2c). According to Procedure B, **2c** was obtained from 8-phenyloct-4-yn-3-yl 2-oxopropanoate **1c** (80 mg, 0.294 mmol) as a yellow oil (53 mg, 0.208 mmol, 71% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.13 - 7.36 (m, 5H), 6.28 - 6.46 (m, 2H), 5.63 (t, *J* = 7.64 Hz, 1H), 2.73 - 2.79 (m, 2H), 2.60 (q, *J* = 7.50 Hz, 2H), 1.84 - 2.00 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.3, 148.4, 145.2, 141.5, 138.8, 128.8, 128.7, 126.5, 121.6, 119.9, 111.6, 34.9, 28.1, 19.8, 9.9. IR (film) ν_{max} 3026, 1760, 1496, 1043 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}O_2$ 255.1380 $[M+H]^+$, found 255.1380.



2d

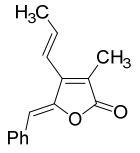
(*Z*)-5-(4-Chlorobutylidene)-3-methyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2d). According to Procedure B, **2d** was

obtained from 9-chlorononon-4-yn-3-yl 2-oxopropanoate **1d** (80 mg, 0.327 mmol) as a yellow oil (57 mg, 0.251 mmol, 77% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 - 6.40 (m, 2H), 5.27 (t, *J* = 7.89 Hz, 1H), 3.29 - 3.67 (m, 2H), 2.46 (q, *J* = 7.66 Hz, 2H), 1.79 - 1.96 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 149.3, 145.2, 137.7, 122.3, 119.6, 109.6, 44.2, 32.0, 23.6, 19.6, 9.6. IR (film) ν_{max} 2958, 1751, 1274, 1043 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}ClNaO_2$ 249.0653 $[M+Na]^+$, found 249.0655.



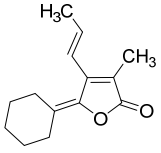
2e

(*Z*)-5-(Cyclohexylmethylene)-3-methyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2e). According to Procedure B, **2e** was obtained from 6-cyclohexylhex-4-yn-3-yl 2-oxopropanoate **1e** (80 mg, 0.32 mmol) as a yellow oil (58 mg, 0.249 mmol, 78% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 - 6.48 (m, 2H), 5.20 (d, *J* = 9.66 Hz, 1H), 2.61 - 2.85 (m, 1H), 1.99 (s, 3H), 1.94 - 1.98 (m, 3H), 1.70 - 1.78 (m, 4H), 1.10 - 1.41 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 147.1, 145.5, 137.3, 121.8, 119.8, 117.6, 35.6, 32.8, 25.9, 25.6, 19.6, 9.7. IR (film) ν_{max} 2936, 1764, 1050, 964 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{21}O_2$ 233.1536 $[M+H]^+$, found 233.1531.



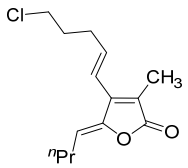
2f

(*Z*)-5-Benzylidene-3-methyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2f). According to Procedure B, **2f** was obtained from 6-phenylhex-4-yn-3-yl 2-oxopropanoate **1f** (80 mg, 0.327 mmol) yellow solid (59 mg, 0.260 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). Mp 134-136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.72 (m, 2H), 7.26 - 7.32 (m, 2H), 7.17 - 7.23 (m, 1H), 6.16 - 6.29 (m, 2H), 6.01 (s, 1H), 1.95 (s, 3H), 1.91 - 1.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 147.7, 147.0, 137.9, 133.4, 130.4, 128.7, 128.5, 121.5, 119.5, 109.1, 19.6, 9.9. IR (film) ν_{max} 2916, 1758, 1644, 1033 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{14}NaO_2$ 249.0886 $[M+Na]^+$, found 249.0887.



2g

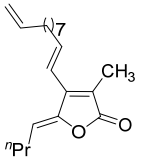
(*E*)-5-Cyclohexylidene-3-methyl-4-(prop-1-enyl) furan-2(5*H*)-one (2g). According to Procedure B, **2g** was obtained from 1-cyclohexylpent-1-yn-3-yl 2-oxopropanoate **1g** (80 mg, 0.338 mmol) as a yellow oil (59 mg, 0.270 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, DMSO-d_6) 6.34 (d, *J* = 16.02 Hz, 1H), 6.00 (dd, *J* = 6.60, 15.89 Hz, 1H), 2.38 - 2.49 (m, 4H), 1.91 (dd, *J* = 1.71, 6.60 Hz, 3H), 1.85 (s, 3H), 1.58 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) 169.9, 147.4, 141.5, 136.0, 129.6, 124.4, 122.4, 29.7, 28.8, 28.0, 27.6, 26.1, 19.1, 9.8. IR (film) ν_{max} 2935, 1763, 1271, 1121, 912 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NaO_2$ 241.1199 $[M+Na]^+$, found 241.1197.



2h

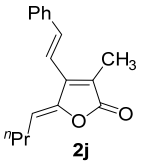
(*Z*)-5-Butylidene-4-((*E*)-5-chloropent-1-enyl)-3-methylfuran-2(5*H*)-one (2h). According to Procedure B, **2h** was

obtained from 1-chloroundec-6-yn-5-yl 2-oxopropanoate **1h** (80 mg, 0.293 mmol) as a yellow oil (59 mg, 0.233 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 - 6.36 (m, 2H), 5.35 (t, *J* = 7.91 Hz, 1H), 3.59 (t, *J* = 6.40 Hz, 2H), 2.42 - 2.49 (m, 2H), 2.36 (q, *J* = 7.61 Hz, 2H), 1.94 - 2.02 (m, 5H), 1.44 - 1.55 (m, 2H), 0.95 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 148.5, 144.9, 140.1, 122.4, 119.7, 112.2, 44.1, 31.4, 30.9, 28.2, 22.5, 13.8, 9.7. IR (film) ν_{max} 2969, 1764, 1267, 911 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}ClO_2$ 254.1079 $[M]^+$, found 254.1082.



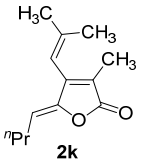
2i

(*Z*)-5-Butylidene-3-methyl-4-((*E*)-undeca-1,10-dienyl) furan-2(5*H*)-one (2i). According to Procedure B, **2i** was obtained from heptadec-16-en-5-yn-7-yl 2-oxopropanoate **1i** (80 mg, 0.229 mmol) as a yellow oil (52 mg, 0.171 mmol, 75% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.34 - 6.39 (m, 2H), 5.73 - 5.83 (m, 1H), 5.60 (t, *J* = 7.84 Hz, 1H), 4.89 - 5.03 (m, 2H), 2.26 (quin, *J* = 7.43 Hz, 4H), 2.01 (q, *J* = 6.90 Hz, 2H), 1.93 (s, 3H), 1.41 - 1.49 (m, 4H), 1.23 - 1.35 (m, 8H), 0.90 (t, *J* = 7.34 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.9, 147.9, 144.8, 143.2, 138.77, 121.0, 118.2, 114.6, 111.7, 33.2, 33.1, 28.6, 28.5, 28.4, 28.2, 28.1, 27.7, 21.8, 13.6, 9.4. IR (film) ν_{max} 2924, 1761, 1667, 1023 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}NaO_2$ 325.2138 $[M+Na]^+$, found 325.2141.



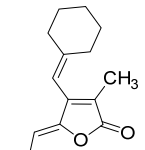
2j

(*Z*)-5-Butylidene-3-methyl-4-styrylfuran-2(5*H*)-one (2j). According to Procedure B, **2j** was obtained from 1-phenyloct-3-yn-2-yl 2-oxopropanoate **1j** (80 mg, 0.293 mmol) as yellow solid (68 mg, 0.267 mmol, 91% yield, eluent: EtOAc/petroleum ether = 1/20). Mp 134-136 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.52 - 7.58 (m, 2H), 7.35 - 7.43 (m, 2H), 7.04 - 7.17 (m, 1H), 6.90 (d, *J* = 16.51 Hz, 1H), 5.50 (t, *J* = 7.82 Hz, 1H), 2.39 (q, *J* = 7.58 Hz, 2H), 2.09 (s, 3H), 1.53 (m, 2H), 0.97 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.5, 148.6, 144.7, 138.5, 136.1, 129.2, 128.9, 127.0, 122.8, 116.5, 111.9, 28.2, 22.5, 13.6, 9.7. IR (film) ν_{max} 2958, 1753, 1042, 758 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NaO_2$ 277.1199 $[M+Na]^+$, found 277.1199.



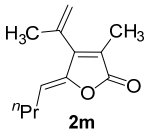
2k

(*Z*)-5-Butylidene-3-methyl-4-(2-methylprop-1-enyl) furan-2(5*H*)-one (2k). According to Procedure B, **2k** was obtained from 2-methylnon-4-yn-3-yl 2-oxopropanoate **1k** (75 mg, 0.334 mmol) as yellow oil (54 mg, 0.261 mmol, 78% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dd, *J* = 1.28, 2.51 Hz, 1H), 5.14 (t, *J* = 7.89 Hz, 1H), 2.33 (q, *J* = 7.62 Hz, 2H), 1.94 (d, *J* = 1.34 Hz, 3H), 1.84 (s, 3H), 1.65 (d, *J* = 1.10 Hz, 3H), 1.43 - 1.53 (m, 2H), 0.94 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 149.2, 147.9, 143.4, 123.8, 113.1, 112.2, 28.0, 26.0, 22.5, 20.7, 13.8, 10.0. IR (film) ν_{max} 2960, 1762, 1263, 1136, 904 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}O_2$ 207.1380 $[M+H]^+$, found 207.1375.



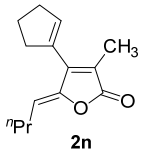
2l

(*Z*)-5-Butylidene-4-(cyclohexylidenemethyl)-3-methylfuran-2(5*H*)-one (2l). According to Procedure B, **2l** was obtained from 1-cyclohexylhept-2-ynyl 2-oxopropanoate **1l** (45 mg, 0.17 mmol) as yellow oil (20 mg, 0.081 mmol, 47% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 1H), 5.17 (t, *J* = 7.91 Hz, 1H), 2.27 - 2.36 (m, 4H), 2.04 (t, *J* = 5.83 Hz, 2H), 1.84 (s, 3H), 1.53 - 1.66 (m, 6H), 1.45 - 1.51 (m, 2H), 0.91 - 0.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 151.0, 149.4, 147.7, 123.7, 112.1, 109.6, 37.1, 31.1, 28.5, 28.1, 27.7, 26.2, 22.5, 13.8, 9.9. IR (film) ν_{max} 2932, 1733, 1244, 1133, 1016 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{16}H_{22}NaO_2$ 269.1512 $[M+Na]^+$, found 269.1513.



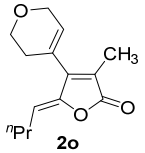
2m

(*Z*)-5-Butylidene-3-methyl-4-(prop-1-en-2-yl) furan-2(5*H*)-one (2m). According to Procedure B, **2m** was obtained from 2-methyloct-3-yn-2-yl 2-oxopropanoate **1m** (70 mg, 0.333 mmol) as yellow oil (44 mg, 0.228 mmol, 69% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.24 - 6.42 (m, 1H), 5.74 - 5.92 (m, 1H), 5.21 - 5.36 (m, 1H), 2.32 (d, *J* = 7.58 Hz, 2H), 1.88 (dd, *J* = 1.83, 6.60 Hz, 3H), 1.48 (d, *J* = 7.46 Hz, 2H), 1.30 (s, 9H), 0.94 (t, *J* = 7.34 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 152.0, 148.5, 135.1, 123.1, 119.2, 113.3, 28.1, 22.6, 22.4, 13.8, 9.2. IR (film) ν_{max} 2960, 1759, 1120, 915 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{16}NaO_2$ 215.1043 $[M+Na]^+$, found 215.1041.



2n

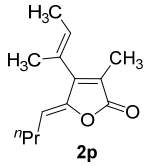
(*Z*)-5-Butylidene-4-cyclopentenyl-3-methylfuran-2(5*H*)-one (2n). According to Procedure B, **2n** was obtained from 1-(hex-1-ynyl)cyclopentyl 2-oxopropanoate **1n** (80 mg, 0.338 mmol) as yellow oil (50 mg, 0.229 mmol, 68% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 - 6.16 (m, 1H), 5.34 (t, *J* = 7.89 Hz, 1H), 2.66 (ddd, *J* = 2.20, 5.14, 9.78 Hz, 2H), 2.51 - 2.56 (m, 2H), 2.36 (q, *J* = 7.58 Hz, 2H), 1.98 - 2.05 (m, 2H), 1.96 (s, 3H),1.51-1.44 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 148.7, 146.7, 136.3, 134.0, 122.8, 113.4, 35.5, 33.4, 28.2, 23.7, 22.5, 13.8, 9.9. IR (film) ν_{max} 2957, 1764, 1741, 1270, 1040, 915 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NaO_2$ 241.1199 $[M+Na]^+$, found 241.1199.



2o

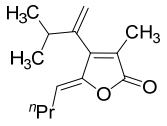
(*Z*)-5-Butylidene-4-(3,6-dihydro-2*H*-pyran-4-yl)-3-methylfuran-2(5*H*)-one (2o). According to Procedure B, **2o** was obtained from 4-(hex-1-ynyl)tetrahydro-2H-pyran-4-yl 2-oxopropanoate **1o** (80 mg, 0.317 mmol) as yellow oil (54 mg, 0.230 mmol, 77% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_3OD) δ 5.91 (qd, *J* = 1.40, 2.89 Hz, 1H), 5.39 (t, *J* = 7.95 Hz, 1H), 4.28 (q, *J* = 2.81 Hz, 2H), 3.88 (t, *J* = 5.38 Hz, 2H), 2.31 - 2.37 (m, 4H), 1.91

(s, 3H), 1.48 - 1.54 (m, 2H), 0.95 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 170.8, 150.6, 148.5, 129.8, 126.4, 123.0, 113.4, 64.7, 63.5, 27.9, 27.8, 22.0, 12.7, 7.9. IR (film) ν_{max} 2966, 2831, 1759, 1723, 1268, 1128 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NaO_3$ 257.1148 $[M+Na]^+$, found 257.1148.



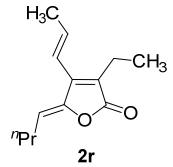
2p

(*Z*)-4-((*E*)-But-2-en-2-yl)-5-butylidene-3-methylfuran-2(5*H*)-one (2p). According to Procedure B, **2p** was obtained from 3-methylnon-4-yn-3-yl 2-oxopropanoate **1p** (80 mg, 0.315 mmol) as yellow oil (48 mg, 0.232 mmol, 65% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (dd, *J* = 1.47, 6.85 Hz, 1H), 5.12 (t, *J* = 7.89 Hz, 1H), 2.27 (q, *J* = 7.58 Hz, 2H), 1.80 - 1.82 (m, 6H), 1.72 (dd, *J* = 0.98, 6.85 Hz, 3H), 1.38 - 1.44 (m, 2H), 0.86 (t, *J* = 7.34 Hz, 3H) (m, 2H), 0.91 - 0.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 153.7, 148.9, 129.0, 126.4, 122.4, 113.1, 28.2, 22.5, 16.3, 13.8, 13.8, 9.3. IR (film) ν_{max} 2959, 1762, 1040, 759 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}O_2$ 207.1380 $[M+H]^+$, found 207.1379.



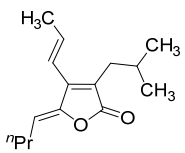
2q

(*Z*)-5-Butylidene-3-methyl-4-(3-methylbut-1-en-2-yl) furan-2(5*H*)-one (2q). According to Procedure B, **2q** was obtained from 2,3-dimethylnon-4-yn-3-yl 2-oxopropanoate **1q** (80 mg, 0.336 mmol) as yellow oil (48 mg, 0.217 mmol, 65% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (t, *J* = 1.34 Hz, 1H), 5.16 (t, *J* = 7.95 Hz, 1H), 4.98 (t, *J* = 0.98 Hz, 1H), 2.45 - 2.59 (m, 1H), 2.34 (q, *J* = 7.58 Hz, 2H), 1.89 (s, 3H), 1.44 - 1.53 (m, 2H), 1.07 (d, *J* = 6.85 Hz, 6H), 0.93 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 152.5, 149.5, 145.9, 123.7, 114.9, 113.4, 33.5, 28.1, 22.4, 21.3, 13.7, 9.3. IR (film) ν_{max} 2931, 1763, 1731, 1257, 1133, 914 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}O_2$ 221.1536 $[M+H]^+$, found 221.1533.



2r

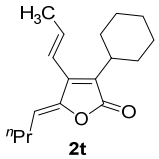
(*Z*)-5-Butylidene-3-ethyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2r). According to Procedure B, **2r** was obtained from non-4-yn-3-yl 2-oxobutanoate **1r** (80 mg, 0.357 mmol) as yellow oil (57 mg, 0.276 mmol, 77% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.07 - 6.42 (m, 2H), 5.37 (t, *J* = 7.89 Hz, 1H), 2.31 - 2.43 (m, 4H), 1.94 (d, *J* = 5.14 Hz, 3H), 1.45 - 1.55 (m, 2H), 1.11 (t, *J* = 7.58 Hz, 3H), 0.95 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.1, 148.6, 145.0, 136.8, 127.6, 119.4, 112.0, 28.2, 22.5, 19.2, 17.3, 13.5, 12.3. IR (film) ν_{max} 2967, 1751, 1651, 956 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NaO_2$ 229.1199 $[M+Na]^+$, found 229.1201.



2s

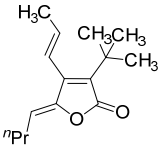
(*Z*)-5-Butylidene-3-isobutyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2s). According to Procedure B, **2s** was obtained from non-4-yn-3-yl 4-methyl-2-oxopentanoate **1s** (80 mg, 0.317 mmol) as yellow oil (53 mg, 0.226 mmol, 72% yield,

eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.06 - 6.47 (m, 2H), 5.40 (t, *J* = 7.82 Hz, 1H), 2.35 (q, *J* = 7.58 Hz, 2H), 2.25 (d, *J* = 7.34 Hz, 2H), 1.92 - 2.00 (m, 4H), 1.47-1.51 (m, 2H), 0.93 - 0.98 (m, 3H), 0.91 (d, *J* = 6.60 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.4, 148.4, 146.1, 136.6, 125.8, 119.9, 112.3, 32.8, 28.2, 27.9, 22.5, 22.3, 19.2, 13.6. IR (film) ν_{max} 2957, 1754, 1049, 1030 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{22}NaO_2$ 257.1512 $[M+Na]^+$, found 257.1515.



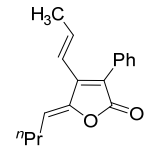
2t

(*Z*)-5-Butylidene-3-cyclohexyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2t). According to Procedure B, **2t** was obtained from non-4-yn-3-yl 2-cyclohexyl-2-oxoacetate **1t** (80 mg, 0.287 mmol) as yellow oil (55 mg, 0.211 mmol, 73% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.95 - 6.46 (m, 2H), 5.12 - 5.47 (m, 1H), 2.50 - 2.60 (m, 1H), 2.33 (q, *J* = 7.58 Hz, 2H), 1.93 (dd, *J* = 1.47, 6.36 Hz, 3H), 1.79 (d, *J* = 10.03 Hz, 4H), 1.56 (d, *J* = 10.39 Hz, 2H), 1.45 - 1.52 (m, 2H), 1.26 - 1.32 (m, 4H), 0.95 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) 169.1, 148.3, 145.1, 136.4, 130.3, 119.5, 112.2, 35.5, 30.0, 28.2, 26.4, 25.7, 22.5, 19.1, 13.6. IR (film) ν_{max} 2928, 1759, 1273, 959 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}O_2$ 261.1849 $[M+H]^+$, found 261.1845.



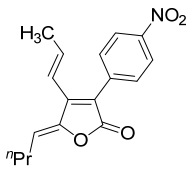
2u

(*Z*)-3-tert-Butyl-5-butylidene-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2u). According to Procedure B, **2u** was obtained from non-4-yn-3-yl 3,3-dimethyl-2-oxobutanoate **1u** (80 mg, 0.317 mmol) as yellow oil (54 mg, 0.230 mmol, 74% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.37 - 5.38 (m, 1H), 5.27 (t, *J* = 7.97 Hz, 1H), 5.03 (dd, *J* = 1.00, 1.51 Hz, 1H), 2.35 (q, *J* = 7.57 Hz, 2H), 1.99 - 2.01 (m, 3H), 1.93 (s, 3H), 1.45-1.49 (m, 2H), 0.92 - 0.96 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.8, 149.1, 145.5, 134.7, 132.5, 121.2, 113.0, 33.2, 29.3, 28.2, 22.5, 18.6, 13.6. IR (film) ν_{max} 2960, 1750, 1027, 989 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{22}NaO_2$ 257.1512 $[M+Na]^+$, found 257.1513.



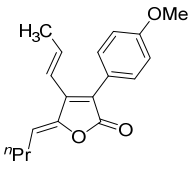
2v

(*Z*)-5-Butylidene-3-phenyl-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2v). According to Procedure B, **2v** was obtained from non-4-yn-3-yl 2-oxo-2-phenylacetate **1v** (67 mg, 0.246 mmol) as gummy solid (51 mg, 0.200 mmol, 81% yield, eluent: EtOAc/petroleum ether = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.48 – 7.42 (m, 2H), 7.39 (ddd, *J* = 7.4, 3.8, 1.3 Hz, 1H), 6.42 – 6.19 (m, 2H), 5.59 (t, *J* = 7.9 Hz, 1H), 2.47 (dd, *J* = 15.1, 7.7 Hz, 2H), 1.95 (d, *J* = 5.0 Hz, 3H), 1.61 – 1.53 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 148.2, 145.2, 137.5, 130.2, 129.3, 128.5, 124.0, 120.6, 115.3, 28.6, 22.5, 19.5, 13.9. IR (film) ν_{max} 2958, 1760, 1265, 1176, 932 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NaO_2$ 277.1199 $[M+Na]^+$, found 277.1202.



2w

(*Z*)-5-Butylidene-3-(4-nitrophenyl)-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2w). According to Procedure B, **2w** was obtained from non-4-yn-3-yl 2-(4-nitrophenyl)-2-oxoacetate **1w** (80 mg, 0.252 mmol) as yellow solid (59 mg, 0.197 mmol, 79% yield, eluent: EtOAc/petroleum ether = 1:20). Mp 90-92 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.08 - 8.40 (m, 2H), 7.65 - 7.91 (m, 2H), 6.21 - 6.46 (m, 2H), 5.70 (t, *J* = 7.95 Hz, 1H), 2.46 (q, *J* = 7.66 Hz, 2H), 1.84 - 2.02 (m, 3H), 1.47 - 1.66 (m, 2H), 0.99 (t, *J* = 7.34 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.9, 148.1, 147.8, 147.3, 139.6, 137.0, 130.1, 123.5, 121.3, 119.6, 117.5, 28.7, 22.3, 19.3, 13.6. IR (film) ν_{max} 3060, 1638, 1231, 712 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NNaO_4$ 322.1050 $[M+Na]^+$, found 322.1047.



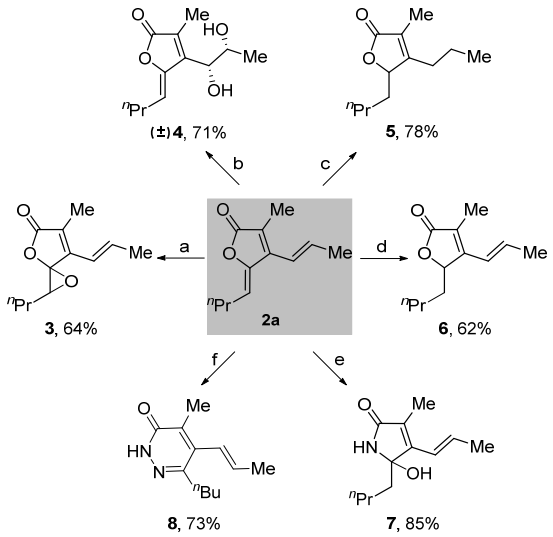
2x

(*Z*)-5-Butylidene-3-(4-methoxyphenyl)-4-((*E*)-prop-1-enyl) furan-2(5*H*)-one (2x). According to Procedure B, **2x** was obtained from non-4-yn-3-yl 2-(4-methoxyphenyl)-2-oxoacetate **1x** (80mg, 0.264 mmol) as yellow solid (60 mg, 0.211 mmol, 80% yield, eluent: EtOAc/petroleum ether = 1/20). Mp 85-87 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 - 7.61 (m, 2H), 6.85 - 7.04 (m, 2H), 6.22 - 6.37 (m, 2H), 5.54 (t, *J* = 7.89 Hz, 1H), 3.82 (s, 3H), 2.42 (q, *J* = 7.66 Hz, 2H), 1.91 (d, *J* = 4.89 Hz, 3H), 1.46 - 1.62 (m, 2H), 0.98 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.9, 159.9, 148.3, 144.0, 137.2, 130.6, 123.3, 122.7, 120.6, 114.4, 113.8, 55.3, 28.5, 22.5, 19.2, 13.6. IR (film) ν_{max} 2958, 1748, 1604, 1508, 1249, 1167 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NaO_3$ 307.1305 $[M+Na]^+$, found 307.1309.

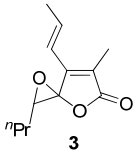
7. Synthetic transformations of 2a [2-3]

To demonstrate the synthetic utilities of this bimetallic cycloisomerization, we attempted diverse site-selective chemical transformations of (Z)-γ-alkylidenebutenolide **2a**. Epoxidation of the enol ester gave epoxide **3**. Dihydroxylation of the olefin on the β-position afforded diol **4**. Reductive hydrogenation of the olefin on the β-position and the enol ester delivered 5, in which unsaturated lactone was kept intact. A formal reduction of the enol ester using triphenylphosphine and iodine furnished **6**. Amination using ammonia and hydrazine afforded heterocycles γ-hydroxy-γ-lactam **7** and pyridazin-3(2*H*)-one **8**, respectively.

Scheme S1. Chemoselective transformations of 2a[a]

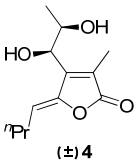


[a](a) MCPBA, DCM, rt, 24 h. (b) K_2OsO_4:2H_2O, NMO, K_2CO_3, ^{t}BuOH/H_2O, rt, 5 h. (c) 5% Pd/C, H_2, EtOH, rt, 4 h. (d) Ph_3P, I_2, $CHCl_3$/H_2O, rt, 24 h. (e) NH_3 (aq.), MeOH, rt, 3 days. (f) NH_2NH_2·H_2O, MeOH, reflux, 12 h. MCPBA = 3-chloroperoxybenzoic acid. NMO = 4-methylmorpholine *N*-oxide.



3

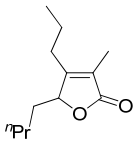
(*E*)-6-Methyl-7-(prop-1-enyl)-2-propyl-1,4-dioxaspiro[2.4]hept-6-en-5-one (3). To a solution of butenolide **2a** (80 mg, 0.42 mmol) in anhydrous DCM (6 mL) was added meta-chloroperoxybenzoic acid (141 mg, 0.82 mmol), and the solution was stirred at room temperature for 24 h. Ice water (20 mL) was added to the solution, and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo, and the obtained residue was purified by column chromatography (EtOAc/petroleum ether = 1/20) to give **3** (55 mg, 64%) as a colorless liquid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.30 (qd, *J* = 6.72, 16.14 Hz, 1H), 6.02 - 6.20 (m, 1H), 3.43 (dd, *J* = 5.81, 6.42 Hz, 1H), 1.96 (s, 3H), 1.90 (dd, *J* = 0.98, 6.72 Hz, 3H), 1.74 - 1.89 (m, 2H), 1.47 - 1.62 (m, 2H), 0.98 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.5, 148.9, 138.0, 126.0, 119.5, 89.8, 62.3, 30.0, 19.5, 19.3, 13.5, 8.9. IR (film) ν_{max} 2956, 1736, 1333, 1092 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{17}O_3$ 209.1172 $[M+H]^+$, found 209.1169.



(±) 4

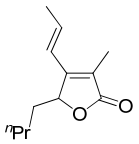
(*Z*)-5-Butylidene-4-(1,2-dihydroxypropyl)-3-methylfuran-2(5*H*)-one (±4). A solution of butenolide **2a** (60 mg, 0.31 mmol) dissolved in ^{t}BuOH and H_2O (1:1 ratio, 3 mL) were added K_2CO_3 (86 mg, 0.62 mmol), K_2OsO_4·2H_2O (6 mg, 0.015 mmol) and NMO (73 mg, 0.62 mmol) under nitrogen atmosphere, and the reaction was stirred for 5 hours at room temperature. The reaction mixture was quenched with saturated aqueous solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 2/3) to obtain **4** as a colorless oil (50 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (t, *J* =

7.95 Hz, 1H), 4.48 (d, *J* = 8.07 Hz, 1H), 3.90 - 4.04 (m, 1H), 3.15 (s, 1H), 2.76 (s, 1H), 2.36 (q, *J* = 7.54 Hz, 2H), 2.00 (s, 3H), 1.48 – 1.52 (m, 2H), 1.09 - 1.18 (m, 3H), 0.94 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 148.0, 147.4, 126.4, 115.2, 77.4, 77.0, 76.7, 72.5, 70.5, 28.3, 22.4, 18.9, 13.8, 9.4. IR (film) ν_{max} 3787, 3723, 3623, 2360, 1508 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}NaO_4$ $[M+ Na]^+$ 249.1097, found 249.1098.



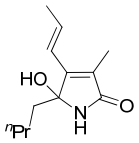
5

(*Z*)-5-Butylidene-3-methyl-4-propyldihydrofuran-2(3*H*)-one (5). To a solution of butenolide **2a** (80 mg, 0.42 mmol) in ethanol (8 mL) was added 5% Pd/C (25 mg). The mixture was hydrogenated under an atmosphere of hydrogen for 4 hours at room temperature. The catalyst was filtered off using a pad of Celite and the filtrate was evaporated in vacuo. A colourless semi-solid was obtained, which was purified by column chromatography (EtOAc/petroleum ether = 1/4) to give **5** (64 mg, 78%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (dd, *J* = 1.53, 6.05 Hz, 1H), 2.42 (ddd, *J* = 7.52, 8.71, 14.09 Hz, 1H), 2.21 (ddd, *J* = 5.93, 8.50, 14.06 Hz, 1H), 1.85 - 1.92 (m, 1H), 1.82 (s, 3H), 1.53 - 1.64 (m, 1H), 1.34 - 1.53 (m, 6H), 0.97 (t, *J* = 7.40 Hz, 3H), 0.87 - 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 163.1, 123.4, 82.1, 31.9, 28.6, 26.7, 22.4, 21.1, 14.0, 13.9, 8.6. IR (film) ν_{max} 2958, 1746, 1331, 1092 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NaO_2$ 219.1356 $[M+Na]^+$, found 219.1358.



6

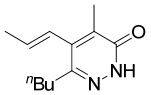
(*E*)-5-Butyl-3-methyl-4-(prop-1-enyl) furan-2(5*H*)-one (6). To a 10 mL round bottom flask, triphenylphosphine (217 mg, 0.83 mmol), iodine (210 mg, 0.83 mmol), water (15 mg, 0.83 mmol), and butenolide **2a** (80 mg, 0.42 mmol) in $CHCl_3$ (2 mL) was added under an inert atmosphere. The mixture was stirred for 24 hours at room temperature. The reaction was quenched with methanol (0.5 mL) and the resulting mixture was concentrated in vacuo and purified by column chromatography (EtOAc/petroleum ether = 1/10) to give **6** (50 mg, 62%) as a colorless liquid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.34 (d, *J* = 16.14 Hz, 1H), 6.07 (qd, *J* = 6.72, 16.14 Hz, 1H), 5.01 (d, *J* = 7.70 Hz, 1H), 1.95 - 2.02 (m, 1H), 1.91 - 1.95 (m, 3H), 1.84 (s, 3H), 1.46 - 1.57 (m, 1H), 1.29 - 1.37 (m, 4H), 0.87 - 0.92 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 174.4, 156.5, 135.2, 121.8, 121.7, 80.6, 33.7, 26.5, 22.4, 19.0, 13.7, 8.4. IR (film) ν_{max} 2956, 1736, 1333, 1092 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{19}O_2$ 195.1380 $[M+H]^+$, found 195.1379.



7

(*E*)-5-Butyl-5-hydroxy-3-methyl-4-(prop-1-enyl)-1*H*-pyrrol-2(5*H*)-one (7). To a vial containing butenolide **2a** (80 mg, 0.42 mmol) in MeOH (2 mL) was added 24% aqueous solution of NH_3 (2 mL), and the mixture was stirred at room temperature for 3 days. The mixture was then concentrated in vacuo and purified by column chromatography (EtOAc/petroleum ether = 1/1) to give γ-hydroxy pyrrolone **7** (74 mg, 85%) as a yellow solid. mp:124-126 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 12.96 (s, 1H), 6.19 (dd, *J* = 0.61, 16.02 Hz, 1H), 5.87 (qd, *J* = 6.56, 16.02 Hz, 1H), 2.54 - 2.59 (m, 2H), 2.18 (s, 3H), 1.94 (dd, *J* = 1.65, 6.54 Hz, 3H), 1.54 - 1.63 (m, 2H), 1.33 - 1.41 (m, 2H), 0.90 - 0.95 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 173.1, 151.4, 135.0, 126.7, 126.6, 121.3, 89.1, 37.6, 25.5, 22.6, 19.4, 13.7, 8.0.

IR (film) ν_{max} 2956, 1685, 1395, 1030 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{20}NO_2$ 210.1489 $[M+H]^+$, found 210.1485.



8

(*E*)-6-Butyl-4-methyl-5-(prop-1-enyl) pyridazin-3(2*H*)-one (8). In a 10 mL round bottom flask equipped with condenser was added butenolide **2a** (80 mg, 0.42 mmol) and MeOH (2 mL) and 80% aqueous solution of hydrazine hydrate (37 mg, 0.92 mmol). The mixture was then refluxed on oil bath for 12 hours. The mixture was concentrated in vacuo. The residue was diluted in toluene (2 mL) and further stirred at 100 °C for 16 hours. It was then concentrated in vacuo and purified by column chromatography (MeOH/DCM = 1.5/98.5) to give pyridazin-3(2*H*)-one **8** (62 mg, 73%) as a yellow solid. mp:74-76 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.98 - 7.39 (m, 1H), 6.44 (qd, *J* = 6.74, 15.97 Hz, 1H), 6.21 (dd, *J* = 1.22, 16.02 Hz, 1H), 4.07 - 4.49 (m, 1H), 1.68 - 2.08 (m, 8H), 1.22 - 1.36 (m, 2H), 0.92 - 1.21 (m, 2H), 0.81 - 0.88 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 163.4, 148.3, 140.6, 135.4, 135.3, 124.2, 32.9, 29.6, 22.3, 18.6, 13.6, 13.1. IR (film) ν_{max} 2955, 1638, 1377, 1197 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{19}N_2O$ 207.1492 $[M+H]^+$, found 207.1495.

8. DFT calculations

Computational methods:

All calculations were performed with the Gaussian 09 program[4]. Geometry optimizations of all minima and transition states involved were carried out using the B3LYP functional[5] and SMD[6] solvation model in DCE solvent. For geometry optimizations, the SDD[7] basis set and pseudopotential (Stuttgart/Dresden ECP) were used for Au, Cu and the 6-31G(d)[8] basis set for the other atoms. We labelled this basis set as SDD-6-31G(d). For single point energy calculations, the M06 functional[9] and def2-TZVP[10] basis set with the D3 version of Grimme's dispersion[11] were used (M06-D3), based on the optimized structures from the SMD/B3LYP/SDD-6-31G(d) method. The keyword "5D" was used to specify that five d type orbitals were used for all elements in the calculations. Frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K.

Computed energies of all of the stationary points

Thermal correction to Gibbs Free Energy ***CG***, Single point energy ***E***, Gibbs free energy ***G***, delta Gibbs free energy ***ΔG***. SMD(DCE)/M06-D3/def2-TZVP//SMD(DCE)/B3LYP/SDD-6-31G(d) level:

	TCG	*E*	*G*	*ΔG*
INT1	0.279553	-1211.691676	-1211.412123	**0.0**
TS1	0.280676	-1211.665528	-1211.384852	**17.1**
INT2	0.282977	-1211.674198	-1211.391221	**13.1**

TS2	0.280158	-1211.668153	-1211.387995	**15.1**
INT3	0.278808	-1211.685321	-1211.406513	**3.5**
TS3-Au	0.281915	-1211.66224	-1211.380325	**20.0**
INT4-Au	0.285638	-1211.694245	-1211.408607	**2.2**
TS4-Au	0.281936	-1211.66919	-1211.387254	**15.6**
INT5-Au	0.286022	-1211.720115	-1211.434093	**-13.8**
INT6-Au	0.259395	-1135.292729	-1135.033334	**-28.3**
H_2O	0.002554	-76.4294463	-76.4268923	
INT6-0	0.157578	-538.5678947	-538.4103167	
INT0	0.176723	-614.961227	-614.784504	
INT3-0	0.176388	-614.9544748	-614.7780868	**3.4**
TS3-0	0.17955	-614.9222377	-614.7426877	**25.6**
INT4-0	0.179514	-614.9300534	-614.7505394	**20.7**
TS4-0	0.179299	-614.9225664	-614.7432674	**25.2**
INT3-Cu	0.206017	-4178.533558	-4178.327541	**4.8**
TS3-Cu	0.209838	-4178.524117	-4178.314279	**13.1**
INT4-Cu	0.212819	-4178.565304	-4178.352485	**-10.9**
TS4-Cu	0.210381	-4178.535719	-4178.325338	**6.2**
INT5-Cu	0.214239	-4178.579216	-4178.364977	**-18.7**
INT6-Cu	0.188952	-4102.15531	-4101.966358	**-34.5**

9. References

(1) Wang, C.; Cui, Q.; Zhang, Z.; Yao, Z.-J.; Wang, S.; Yu, Z.-X. *Chem. Eur. J.* **2019**, *25*, 9821-9826.

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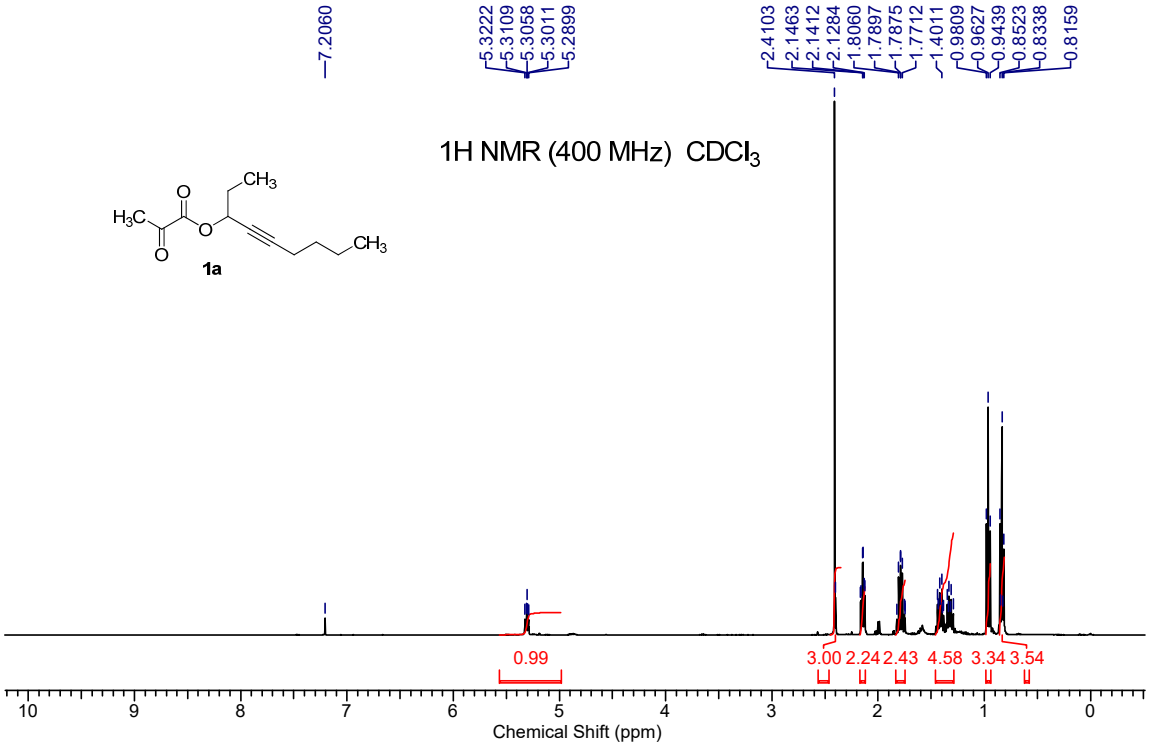
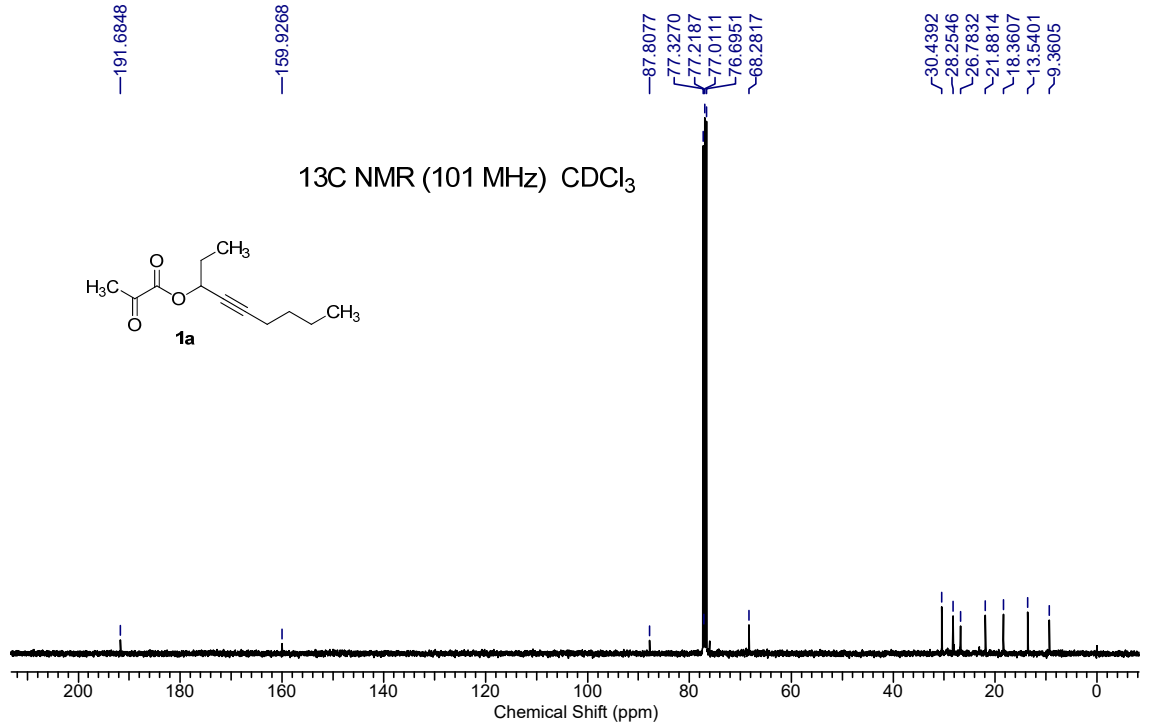
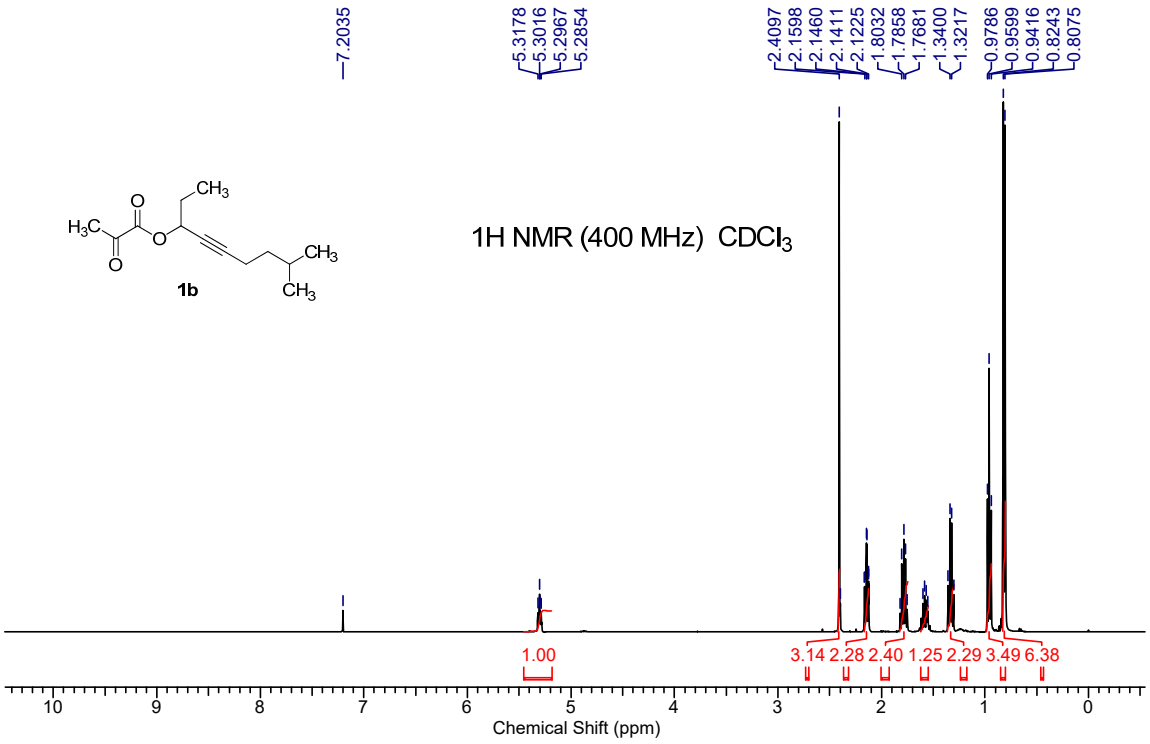
10. Copies of NMR spectra



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0.9416
0.8243
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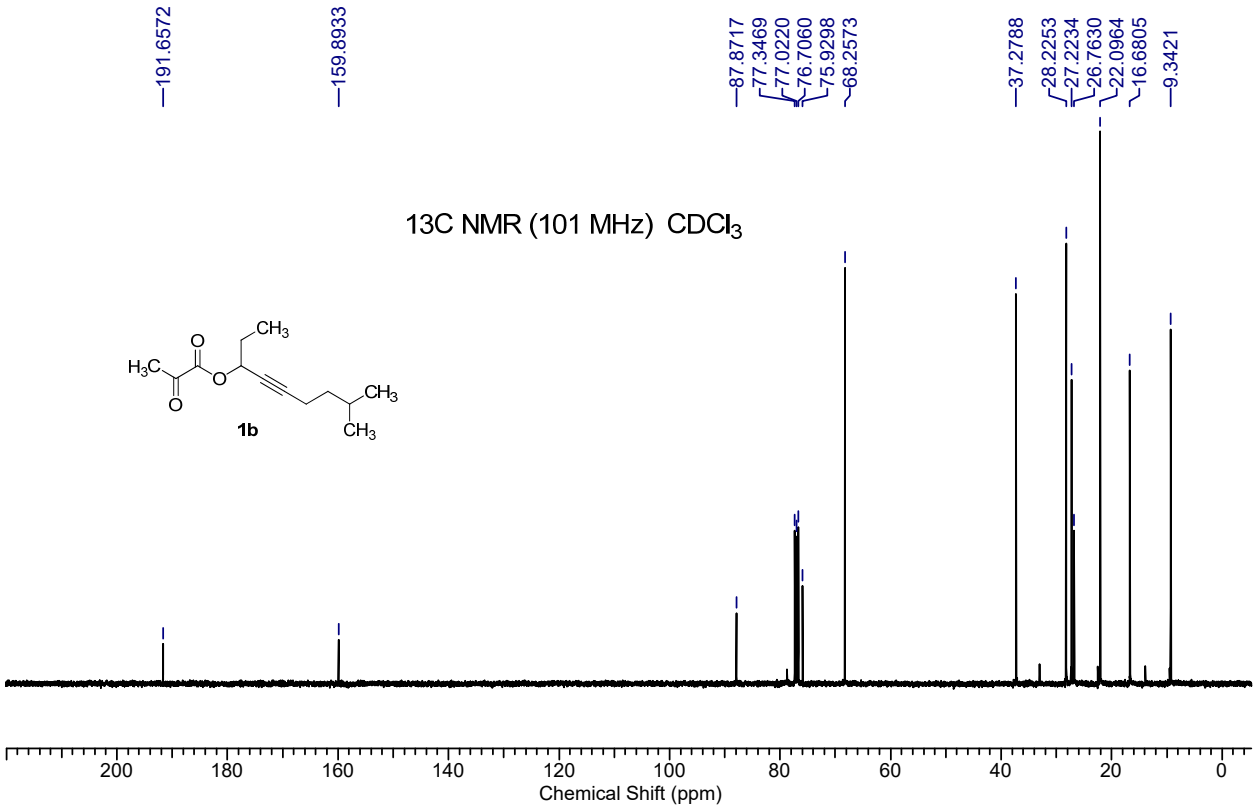
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13C NMR (101 MHz) CDCl3
1b
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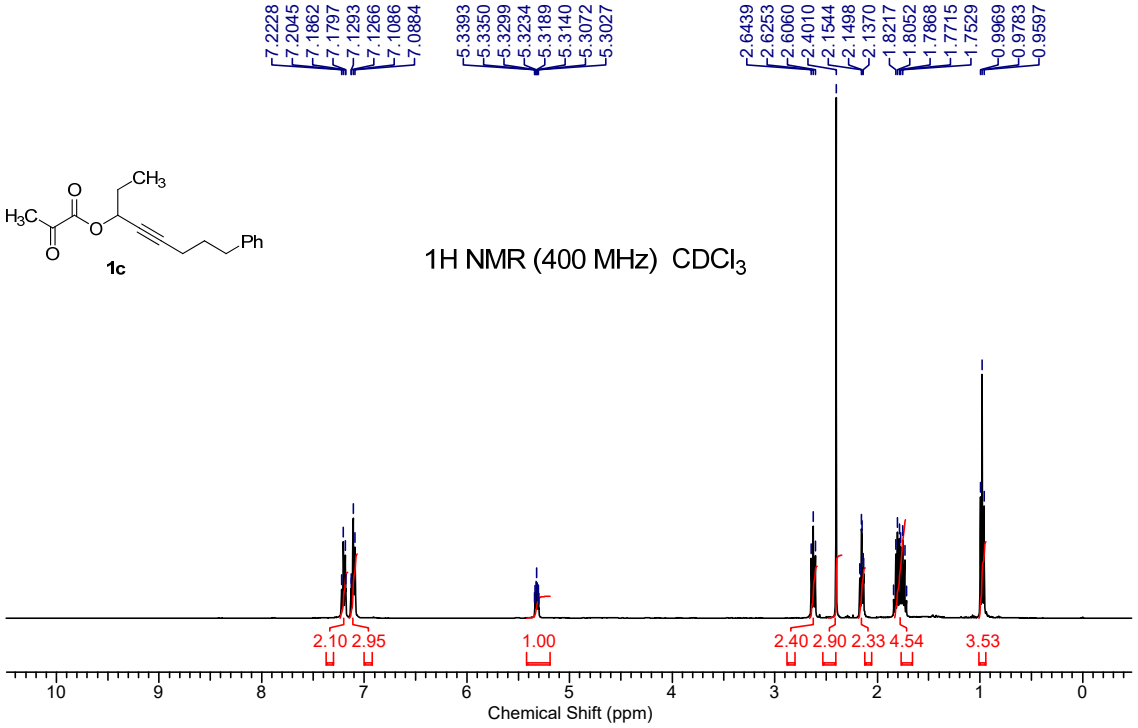
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5.3027
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2.6060
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2.1370
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1.7715
1.7529
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CH3
O
H3C
O
O
Ph
1c
1H NMR (400 MHz) CDCl3
2.10 2.95
1.00
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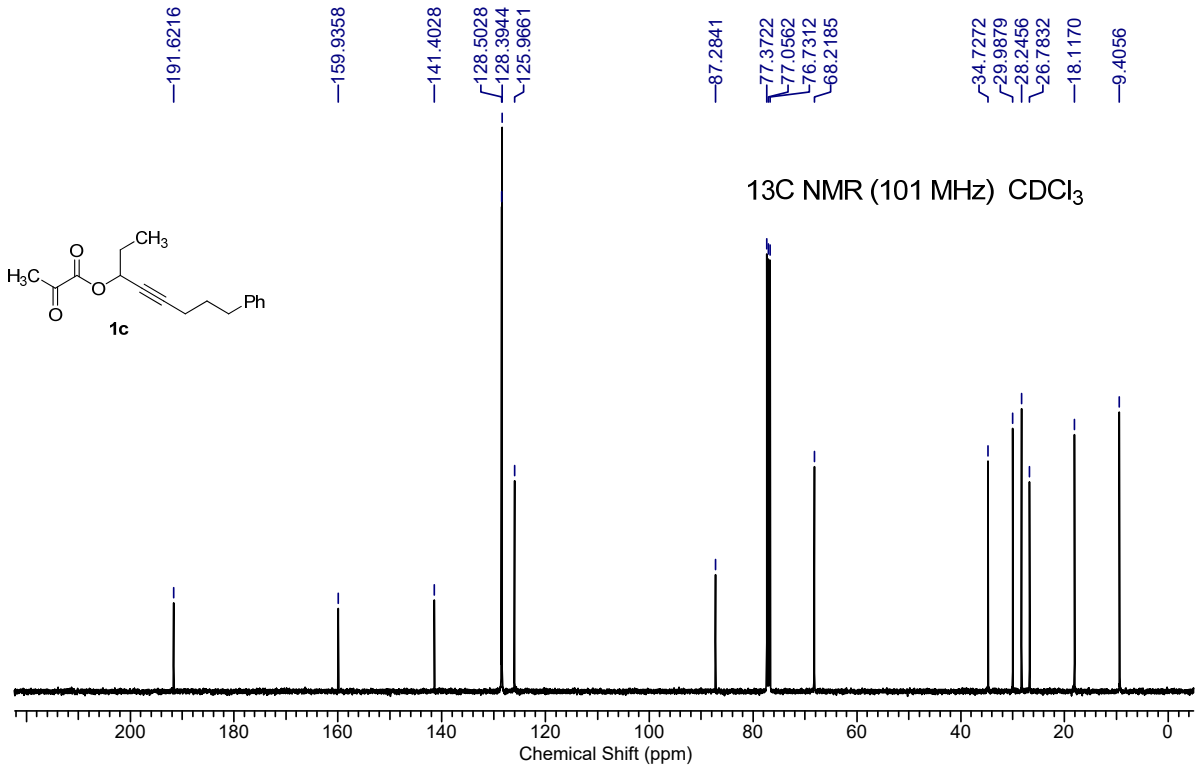
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13C NMR (101 MHz) CDCl3
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20
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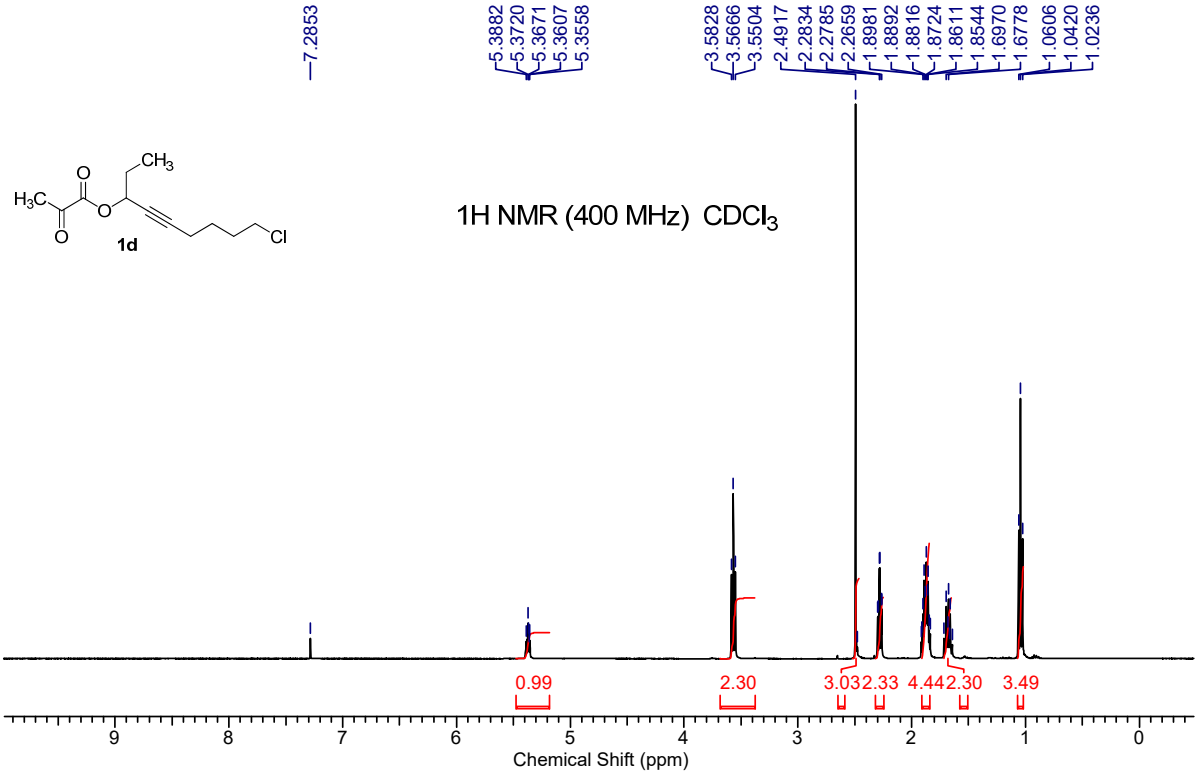
Chemical Shift (ppm)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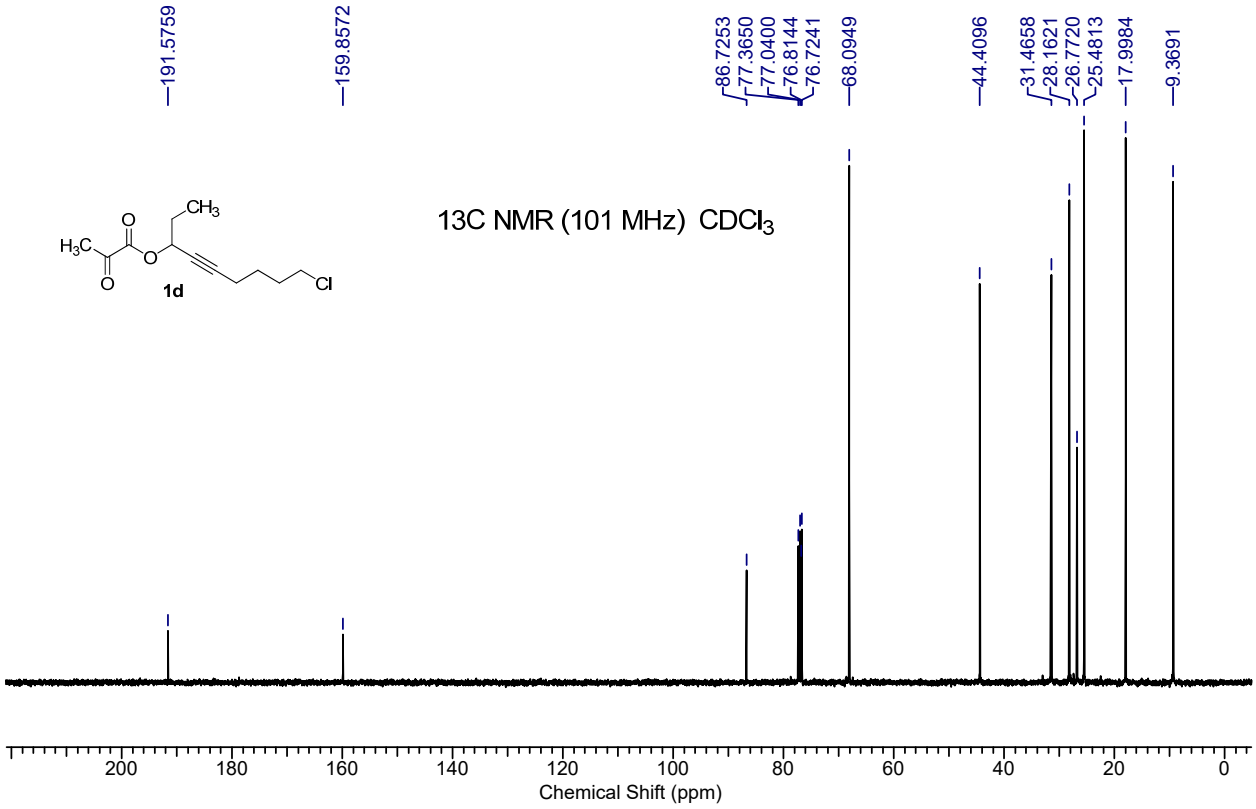
Chemical Shift (ppm)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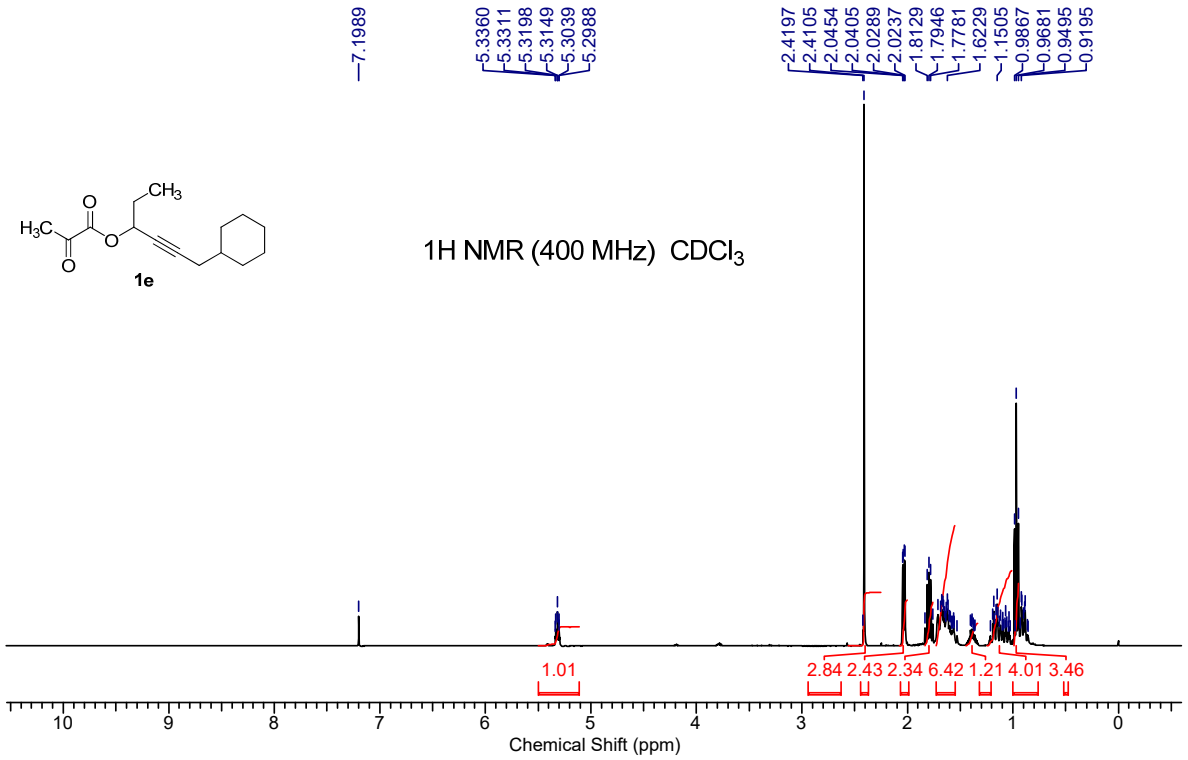
13C NMR (101 MHz) CDCl3
1d
Chemical Shift (ppm)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1.1505
0.9867
0.9681
0.9495
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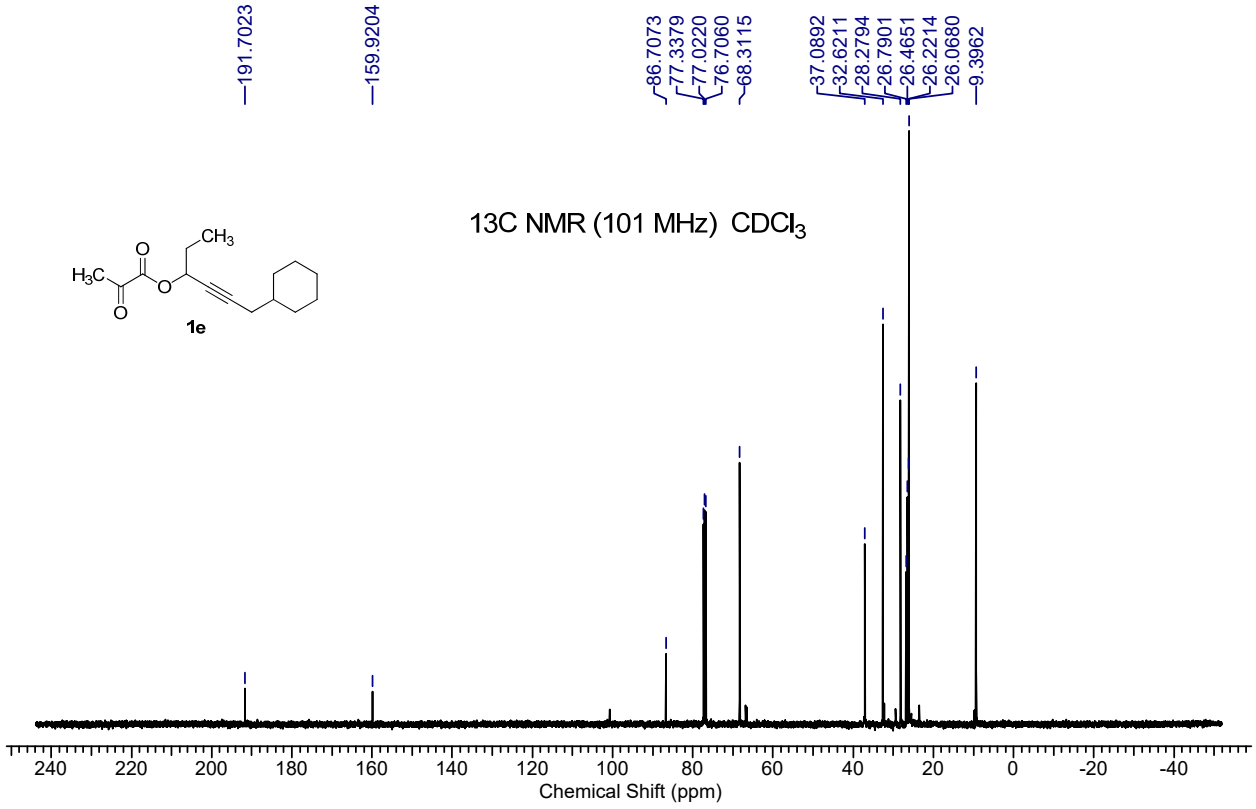
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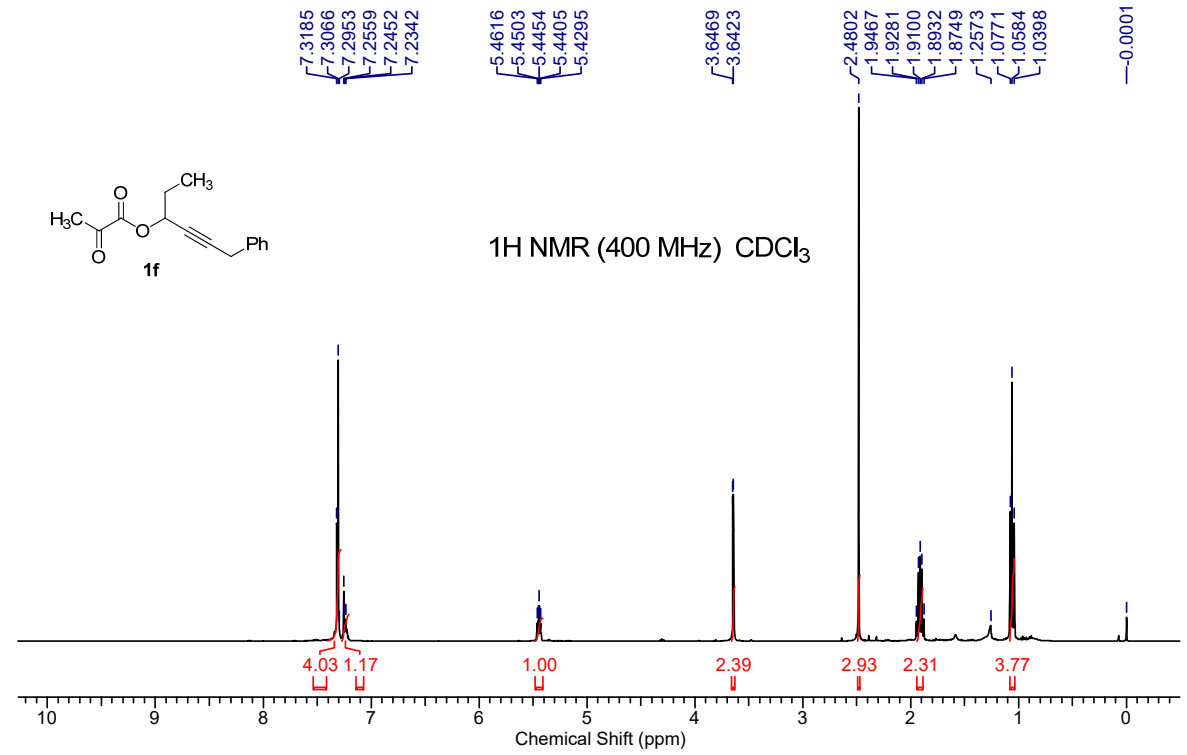
13C NMR (101 MHz) CDCl3
1e
Chemical Shift (ppm)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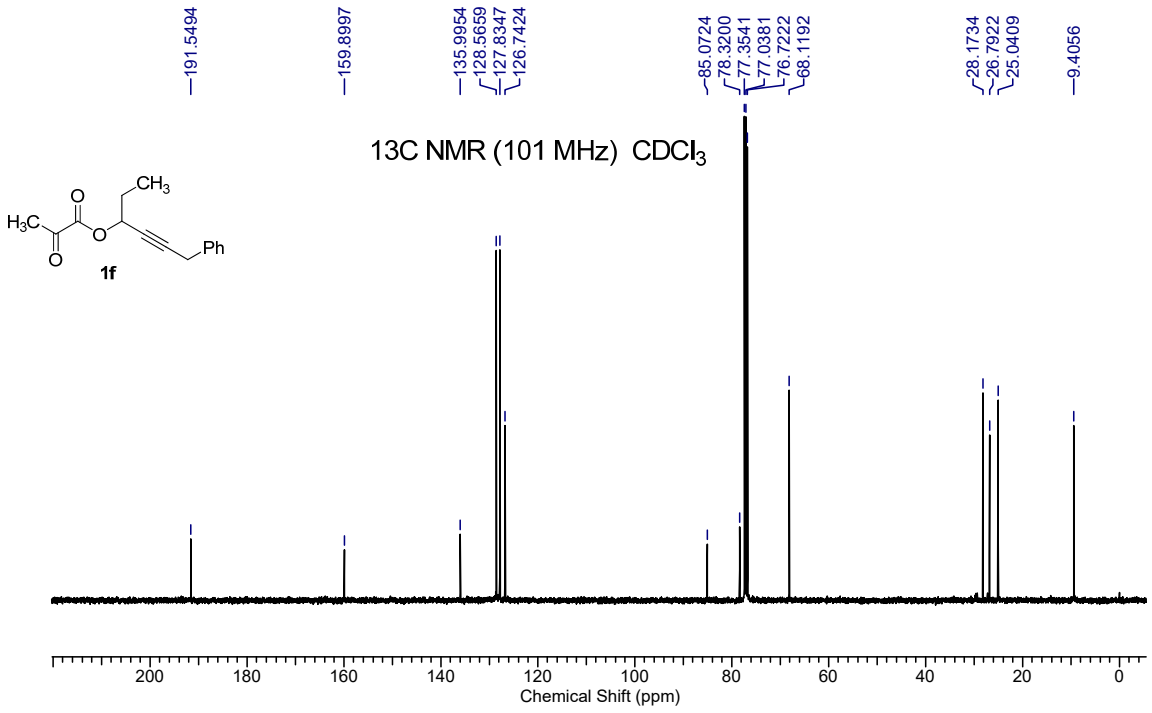
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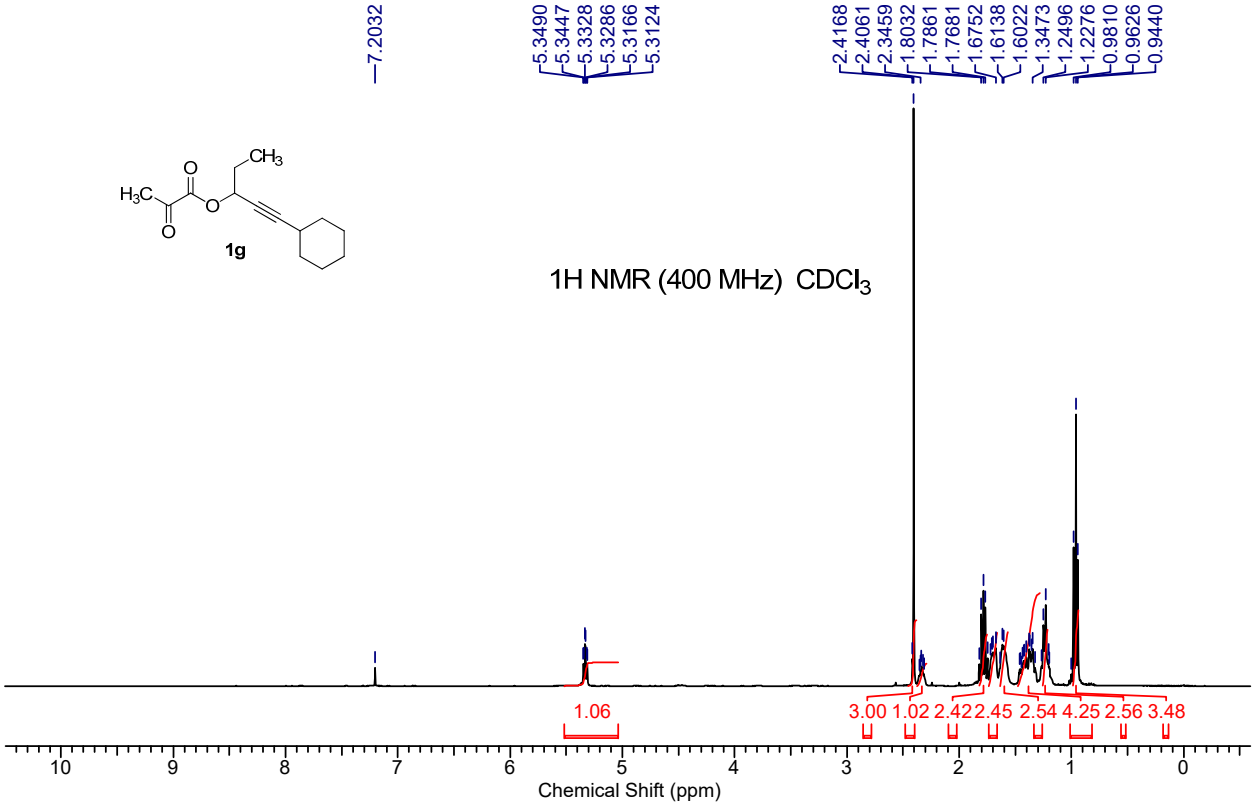
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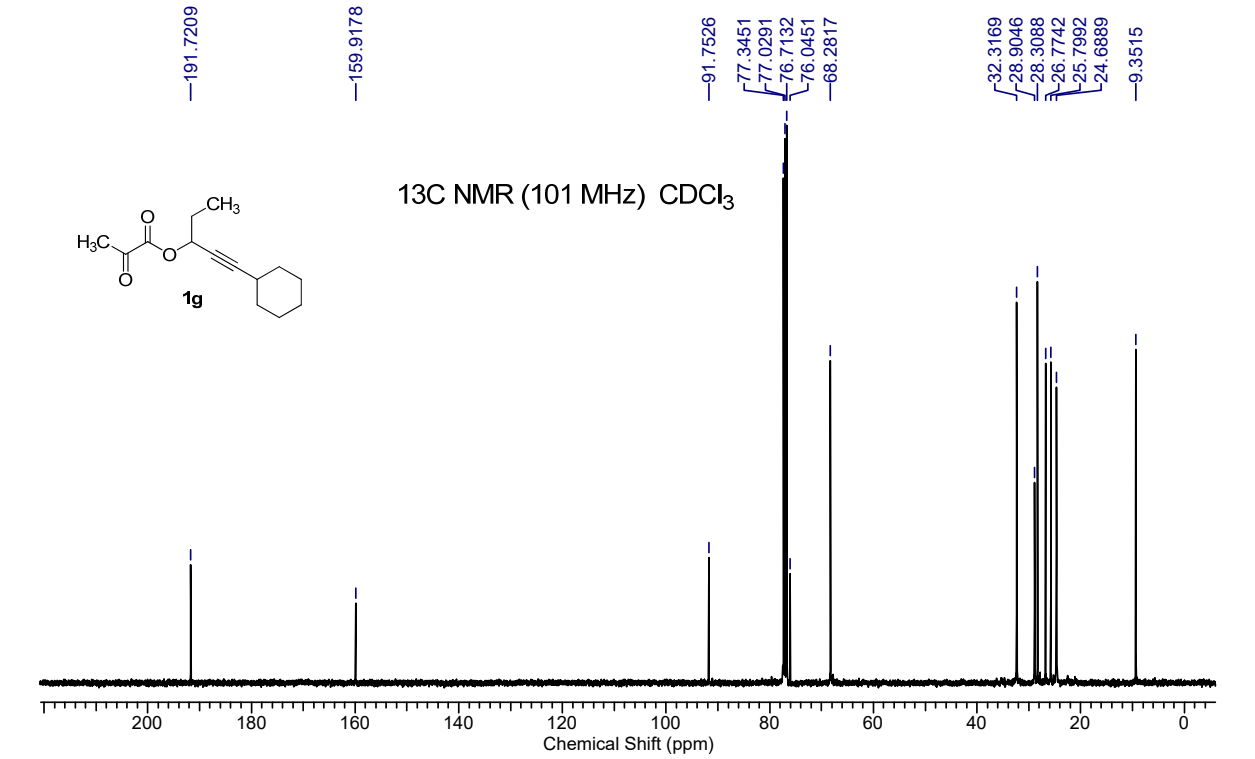
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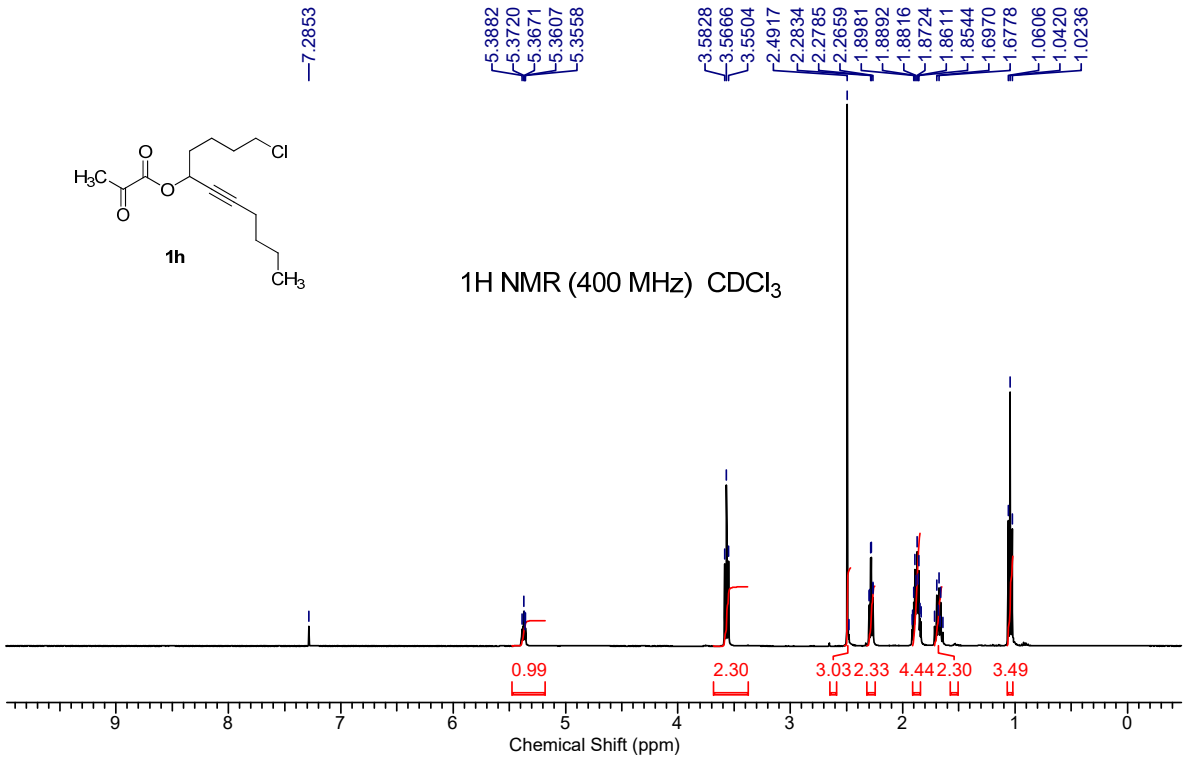
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1.8892
1.8816
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Cl
H3C
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1H NMR (400 MHz) CDCl3
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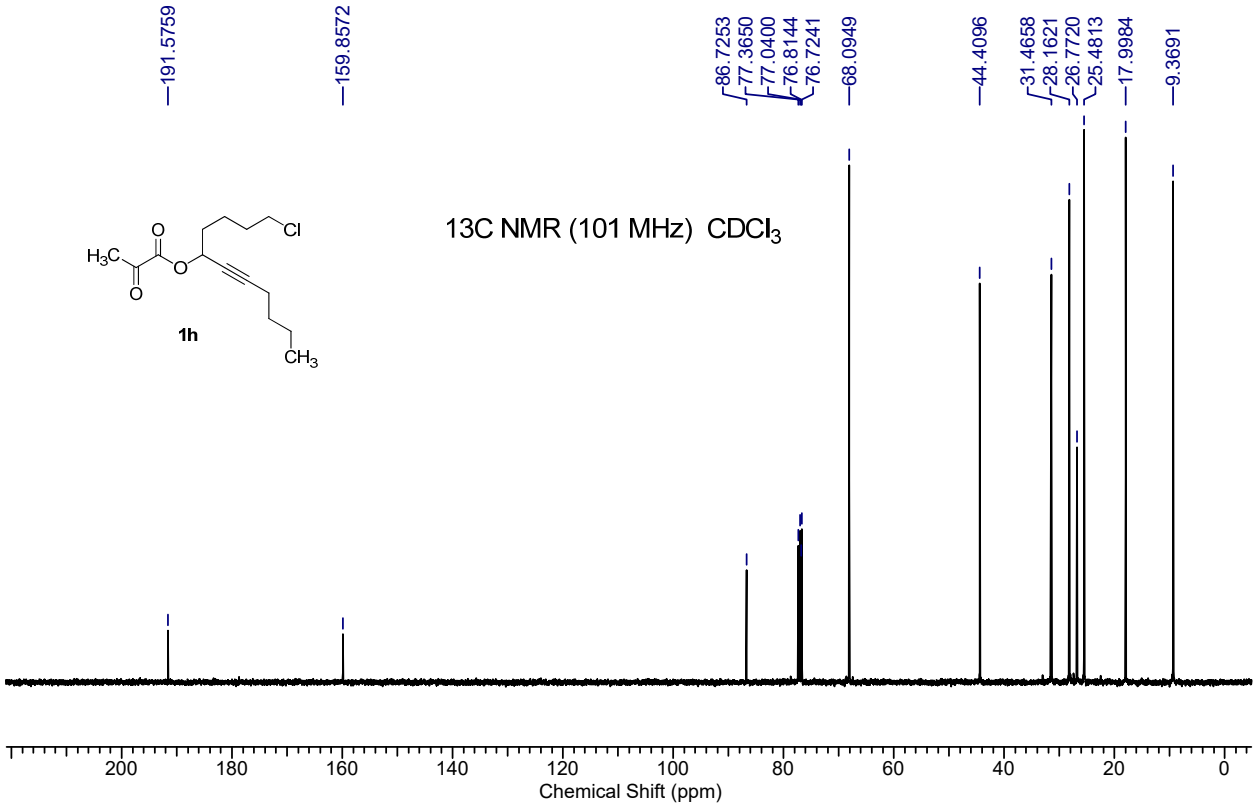
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Cl
H3C
O
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O
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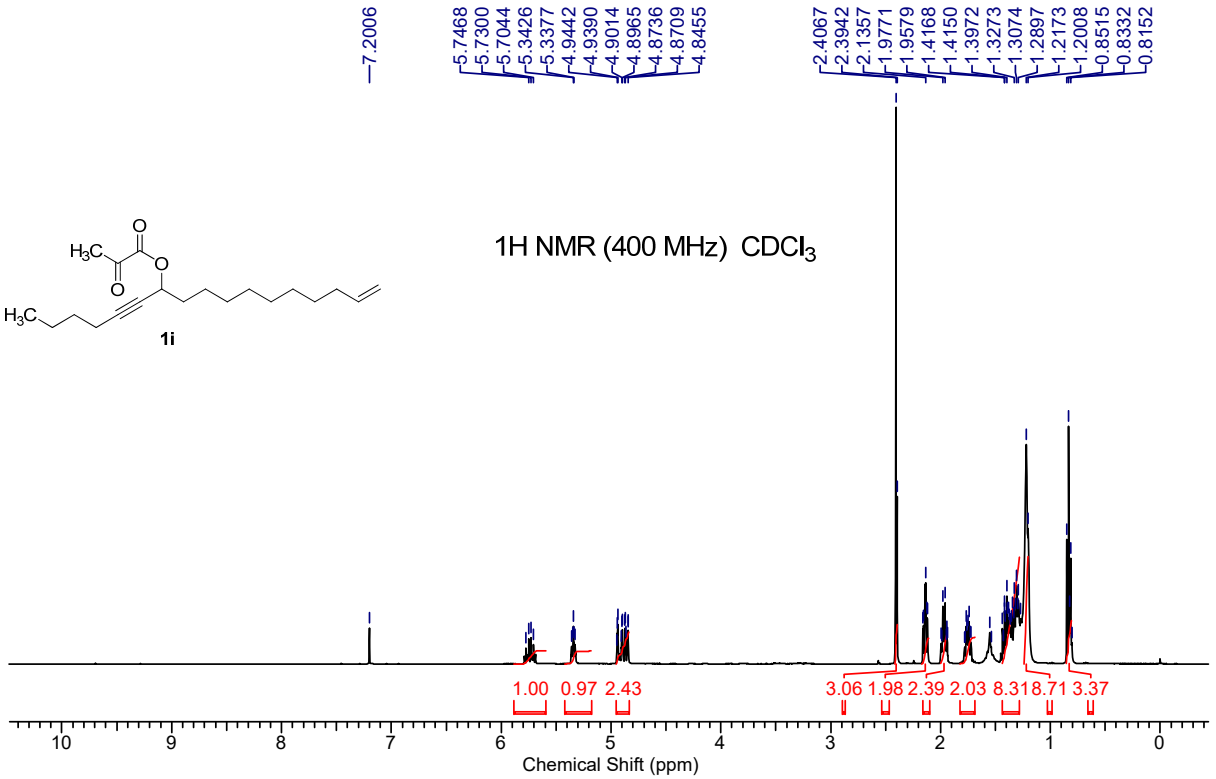
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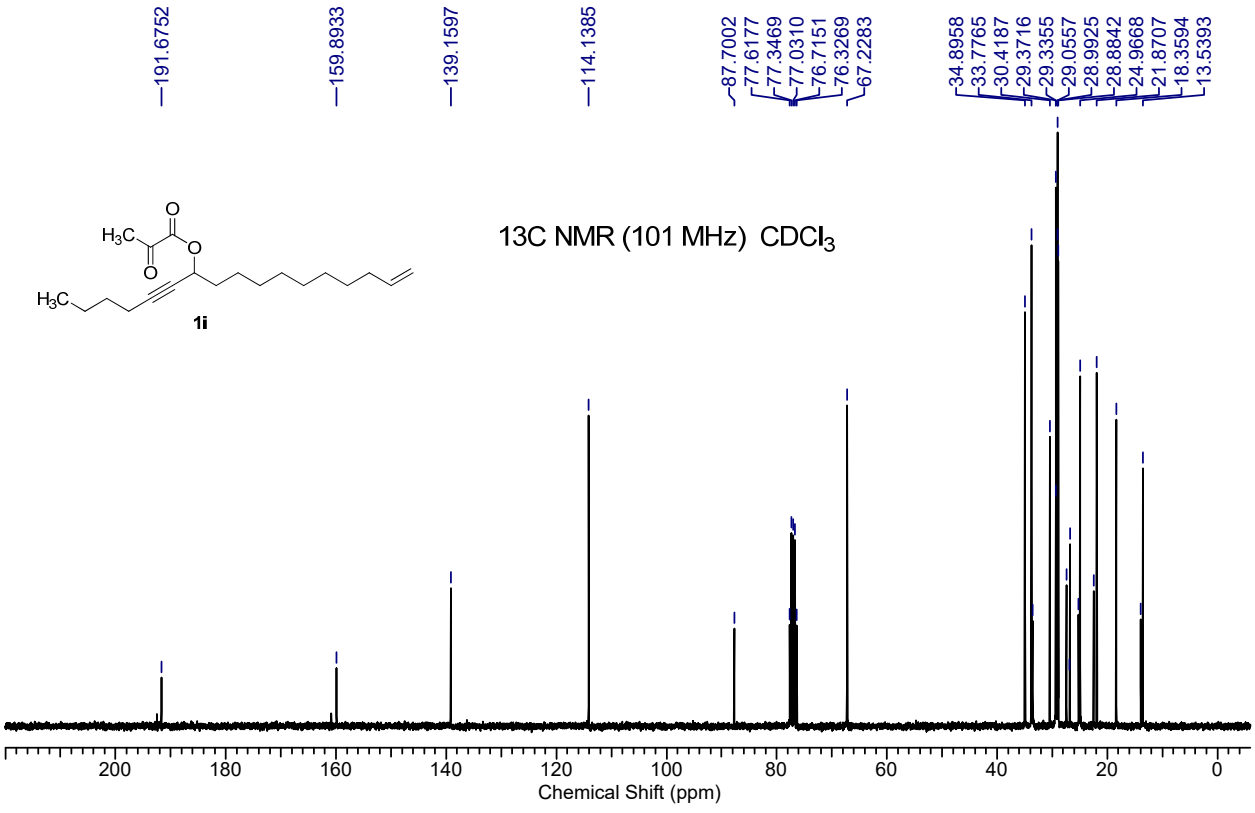
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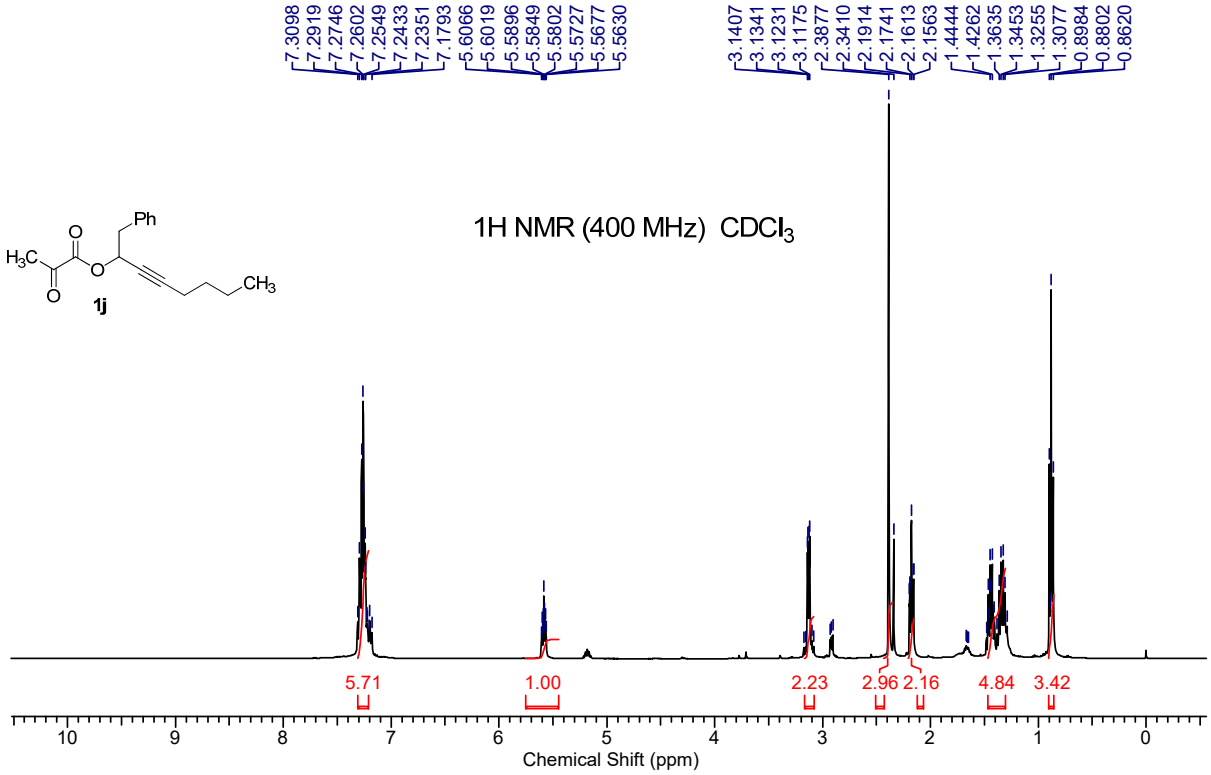
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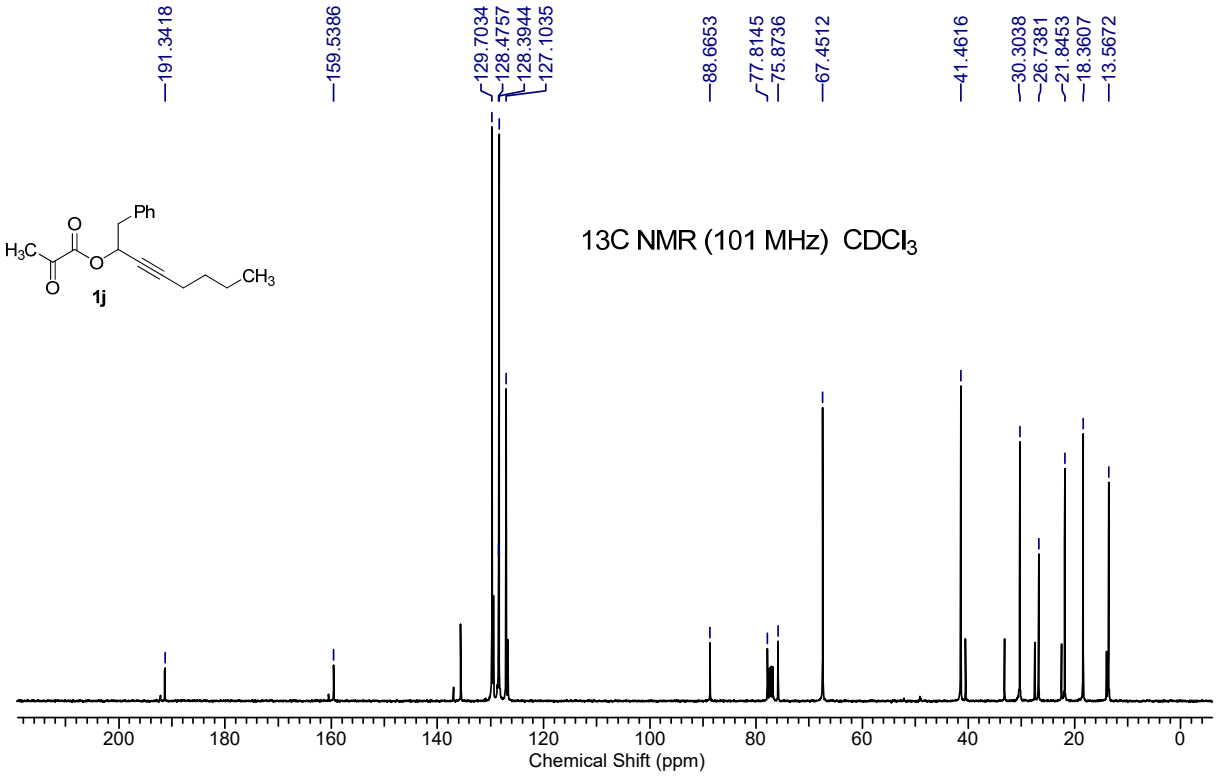
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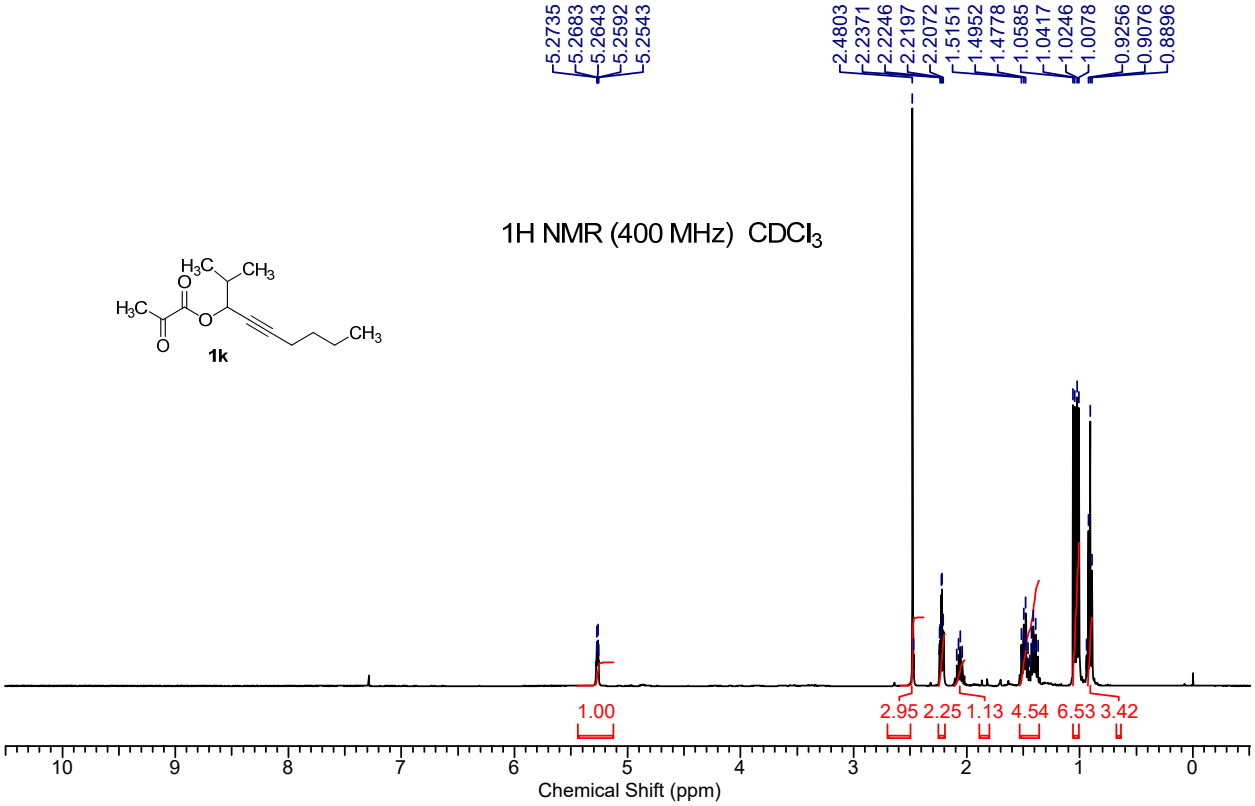
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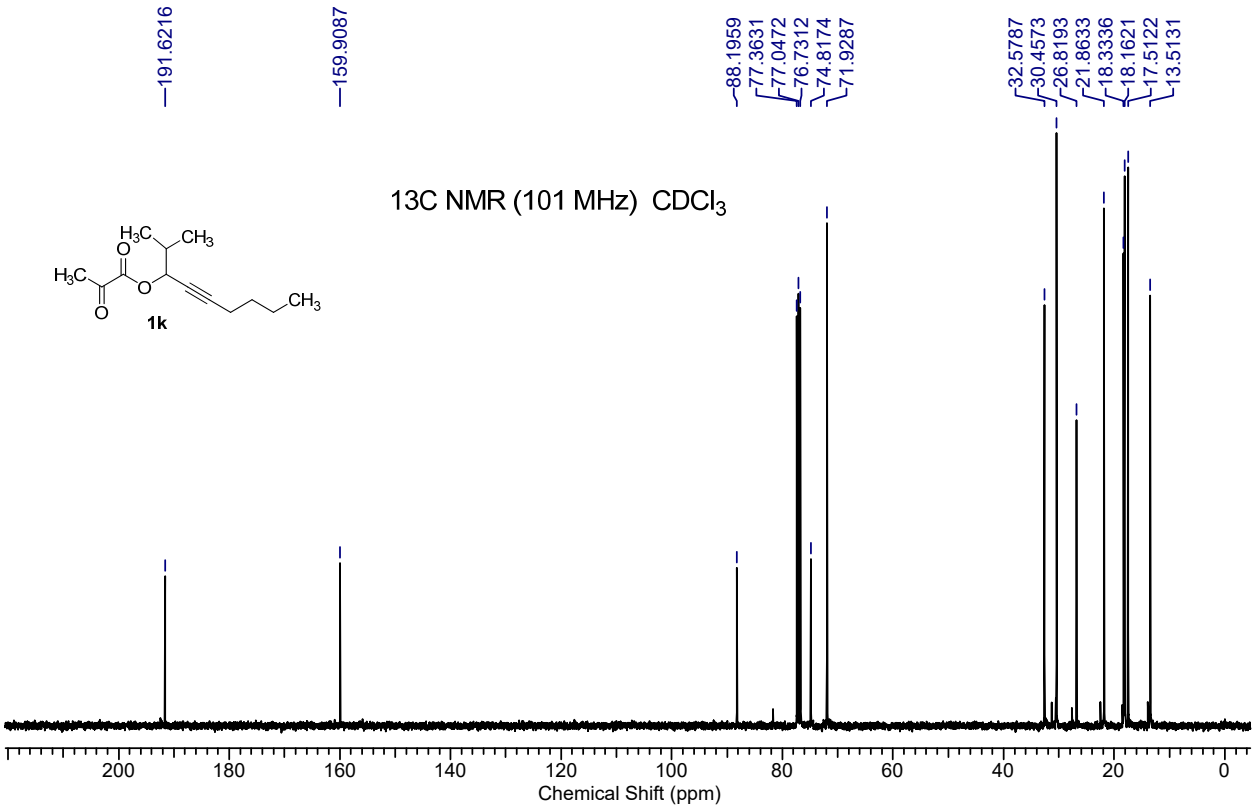
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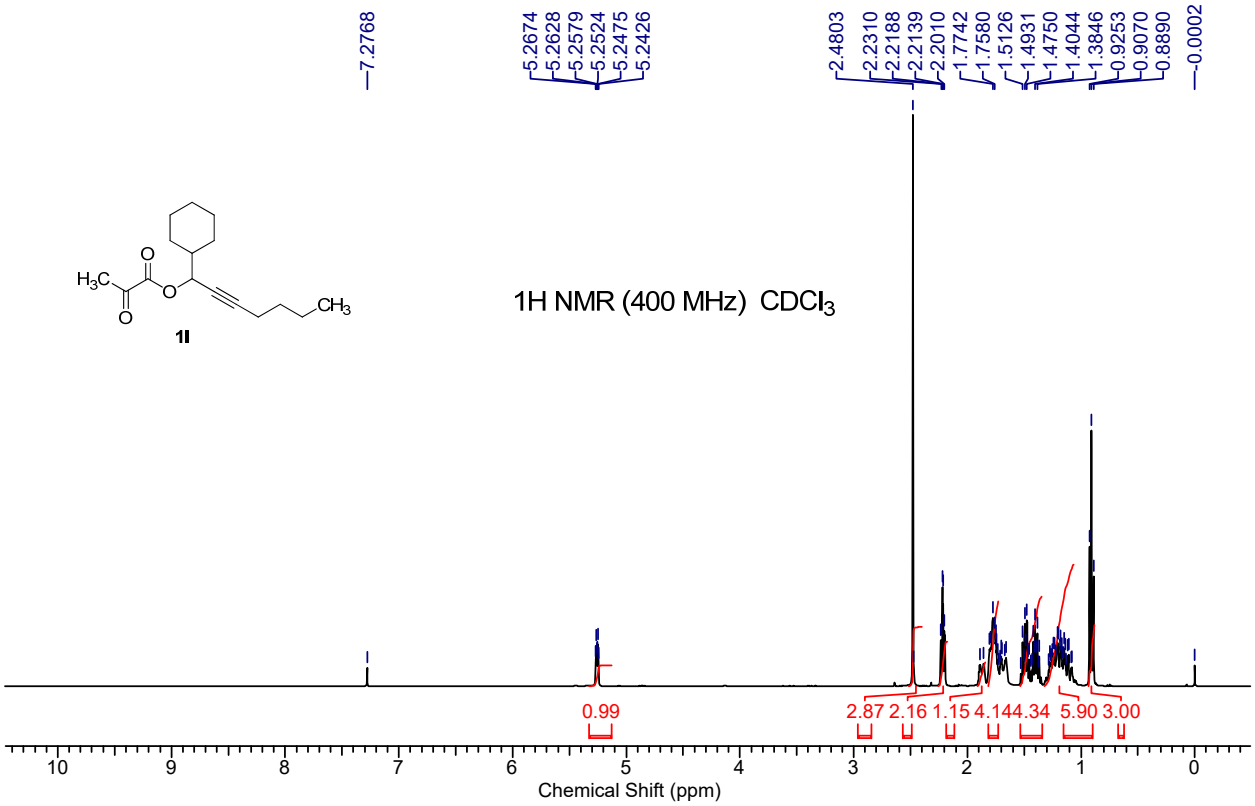
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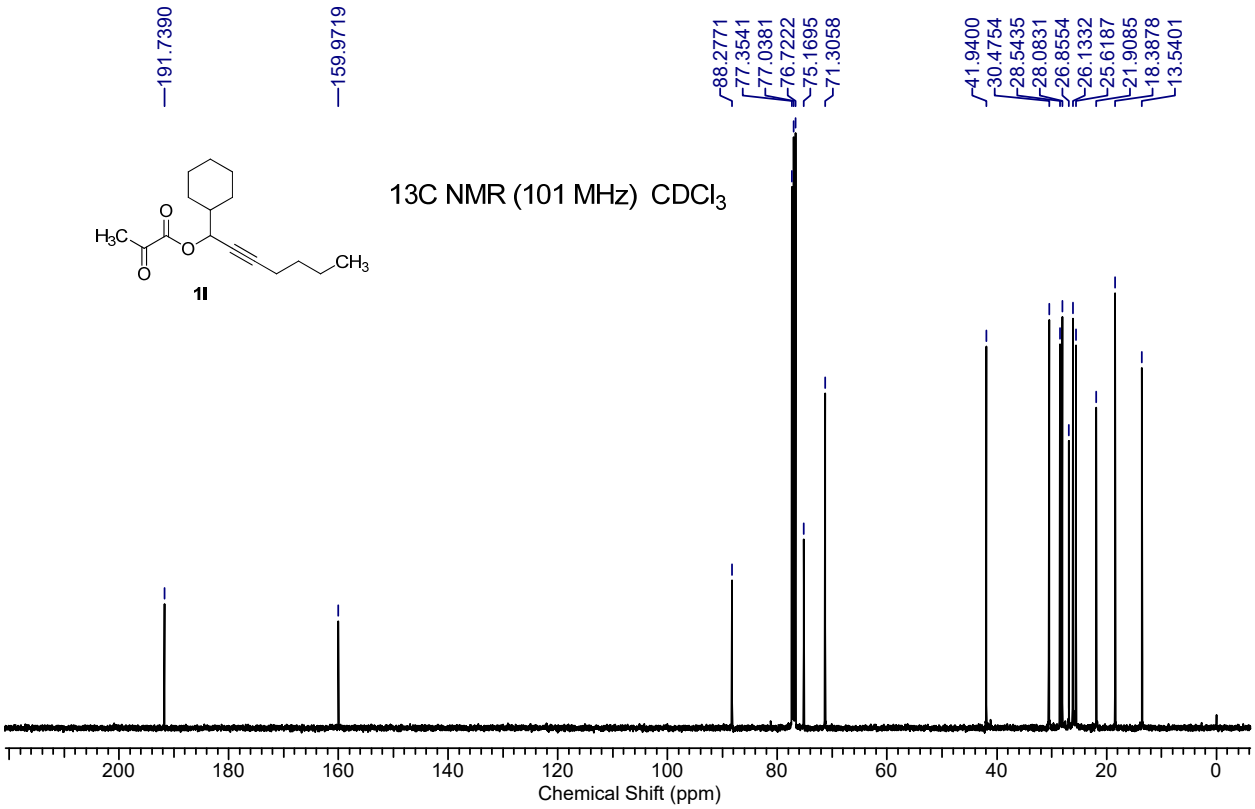
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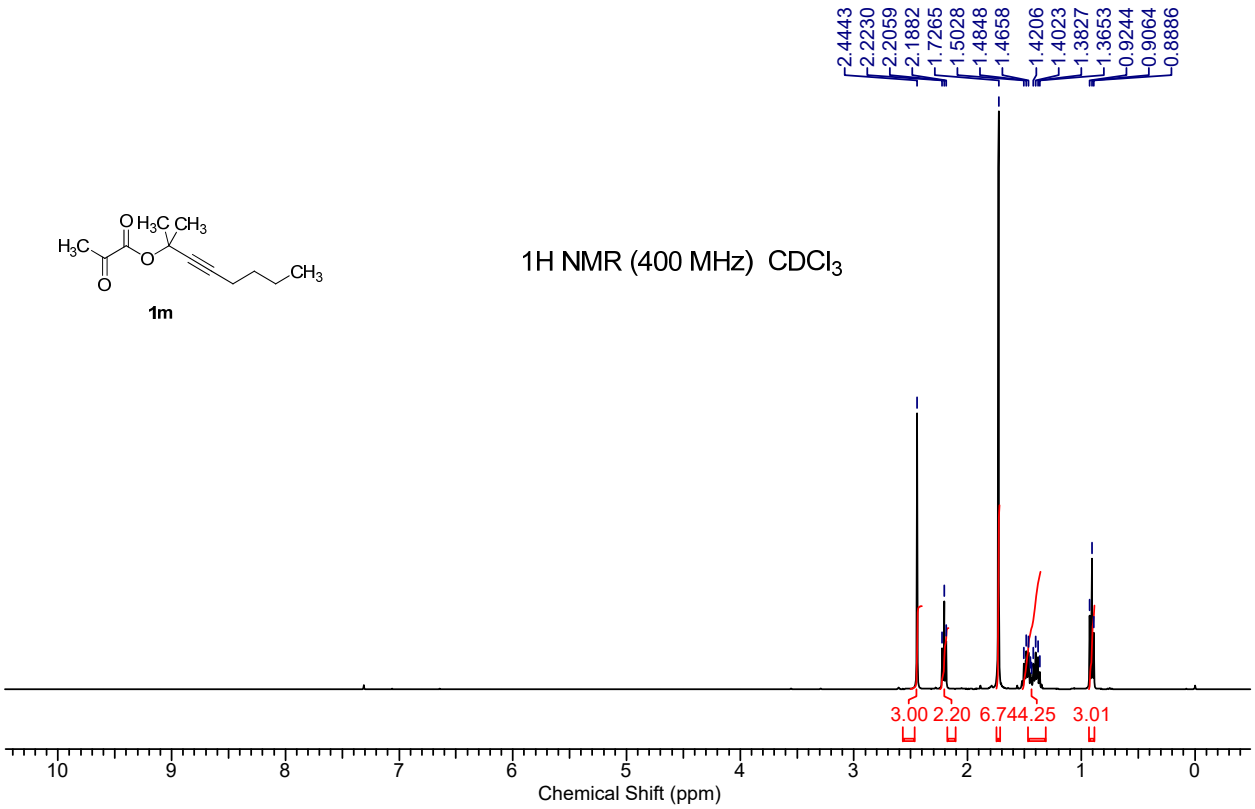
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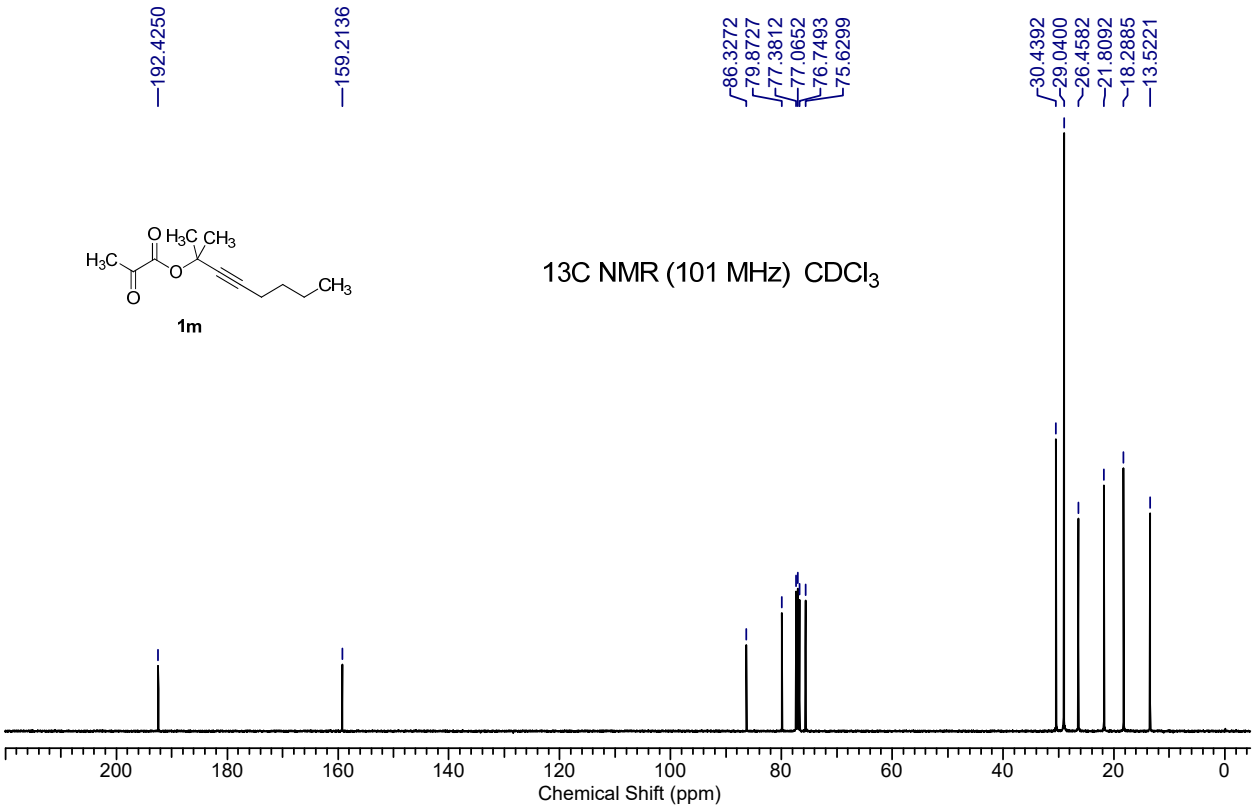
2.2230
2.2059
2.1882
1.7265
1.5028
1.4848
1.4658
1.4206
1.4023
1.3827
1.3653
0.9244
0.9064
0.8886
1H NMR (400 MHz) CDCl3
1m
3.00 2.20 6.744.25 3.01
Chemical Shift (ppm)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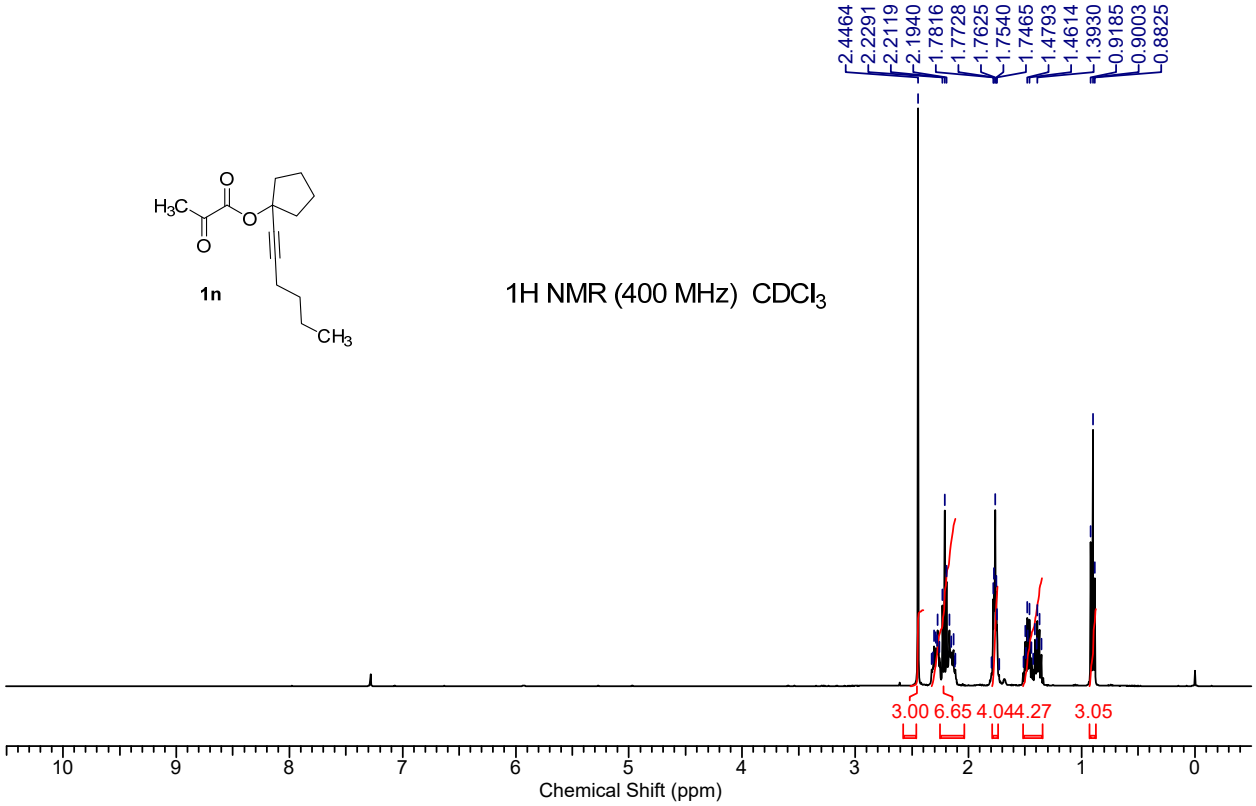
159.2136
86.3272
79.8727
77.3812
77.0652
76.7493
75.6299
30.4392
29.0400
26.4582
21.8092
18.2885
13.5221
13C NMR (101 MHz) CDCl3
1m
Chemical Shift (ppm)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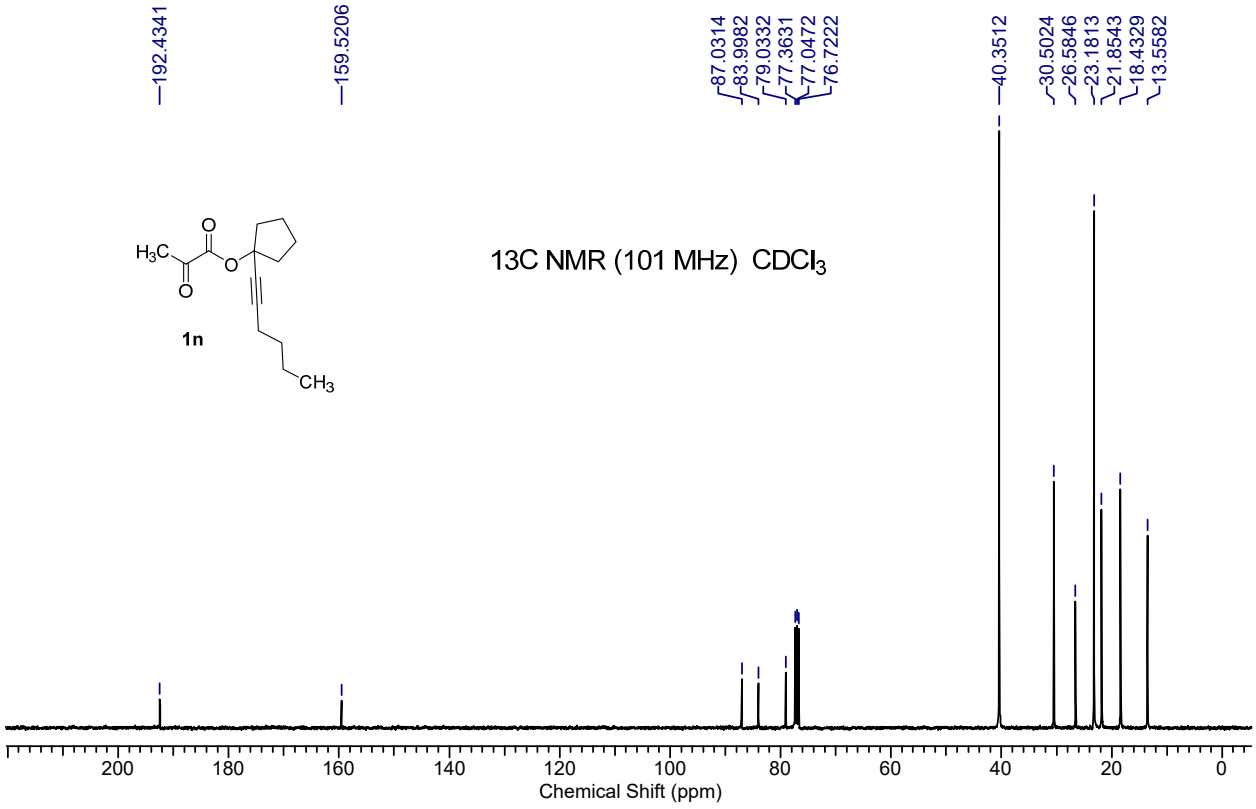
2.2291
2.2119
2.1940
1.7816
1.7728
1.7625
1.7540
1.7465
1.4793
1.4614
1.3930
0.9185
0.9003
0.8825
1n
1H NMR (400 MHz) CDCl3
3.00 6.65 4.044.27 3.05
Chemical Shift (ppm)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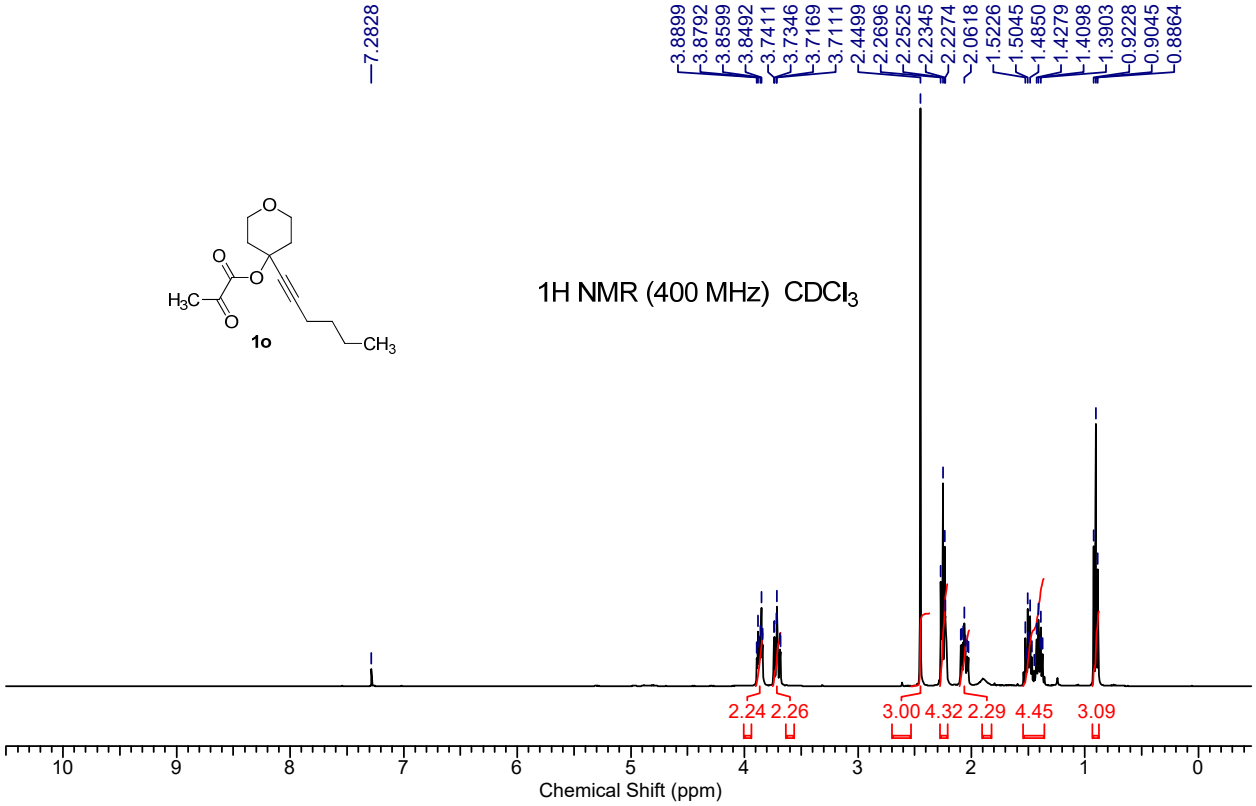
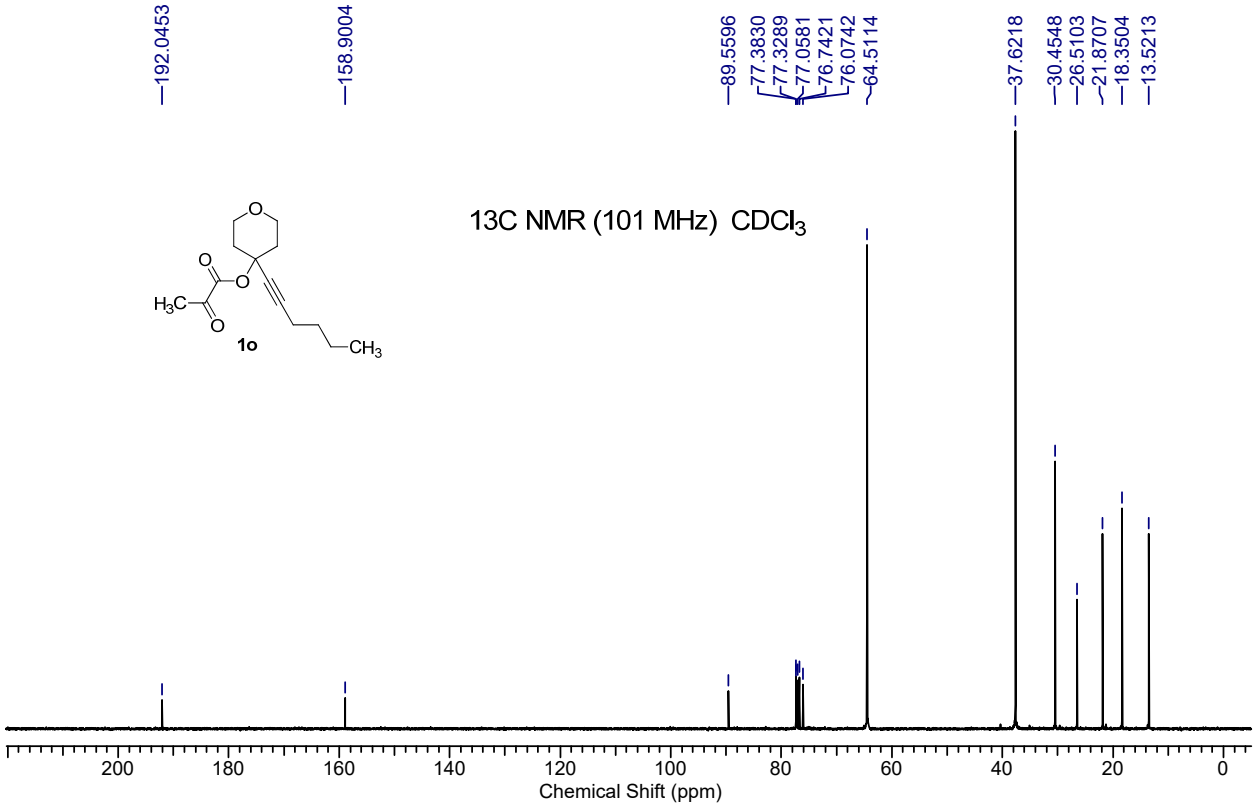
87.0314
83.9982
79.0332
77.3631
77.0472
76.7222
40.3512
30.5024
26.5846
23.1813
21.8543
18.4329
13.5582
1n
13C NMR (101 MHz) CDCl3
Chemical Shift (ppm)


7.2828
3.8899
3.8792
3.8599
3.8492
3.7411
3.7346
3.7169
3.7111
2.4499
2.2696
2.2525
2.2345
2.2274
2.0618
1.5226
1.5045
1.4850
1.4279
1.4098
1.3903
0.9228
0.9045
0.8864
1H NMR (400 MHz) CDCl3
1o
2.24 2.26
3.00 4.32 2.29 4.45
3.09
Chemical Shift (ppm)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89.5596
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77.3289
77.0581
76.7421
76.0742
64.5114
37.6218
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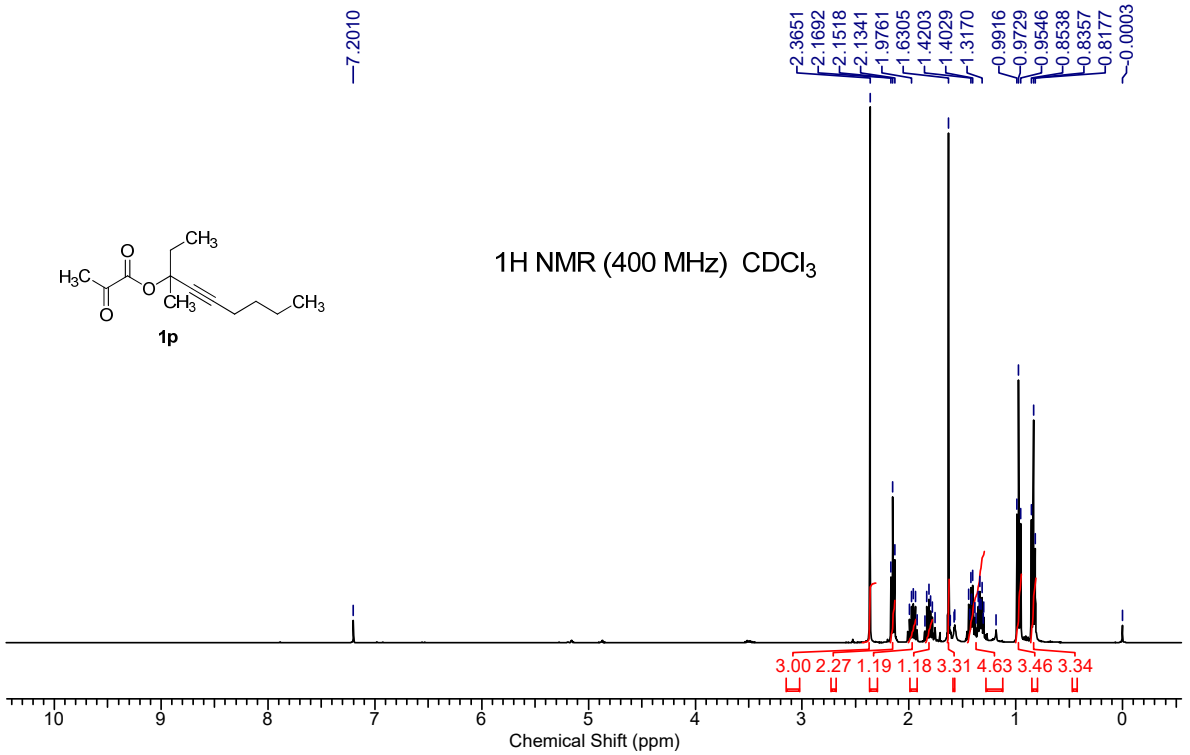
26.5103
21.8707
18.3504
13.5213
13C NMR (101 MHz) CDCl3
1o
Chemical Shift (ppm)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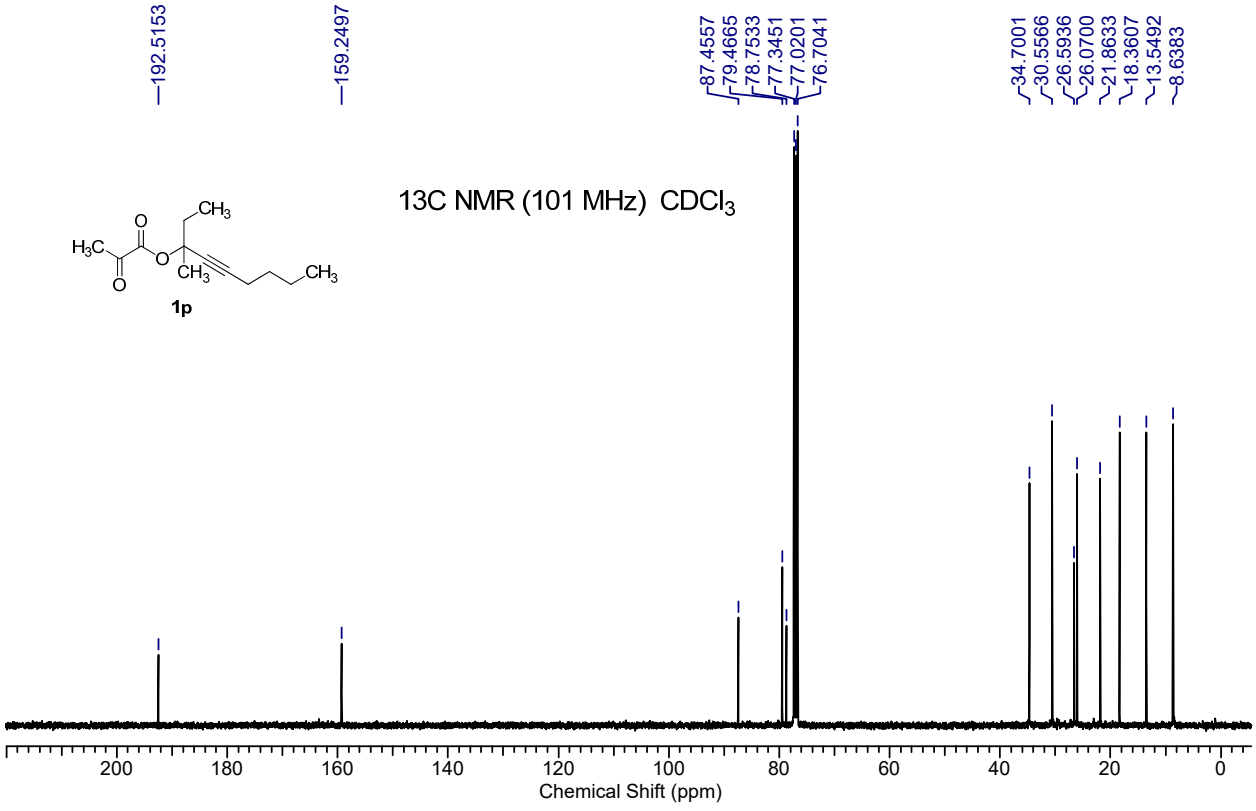
2.1692
2.1518
2.1341
1.9761
1.6305
1.4203
1.4029
1.3170
0.9916
0.9729
0.9546
0.8538
0.8357
0.8177
0.0003
1H NMR (400 MHz) CDCl3
3.00 2.27 1.19 1.18 3.31 4.63 3.46 3.34
Chemical Shift (ppm)
1p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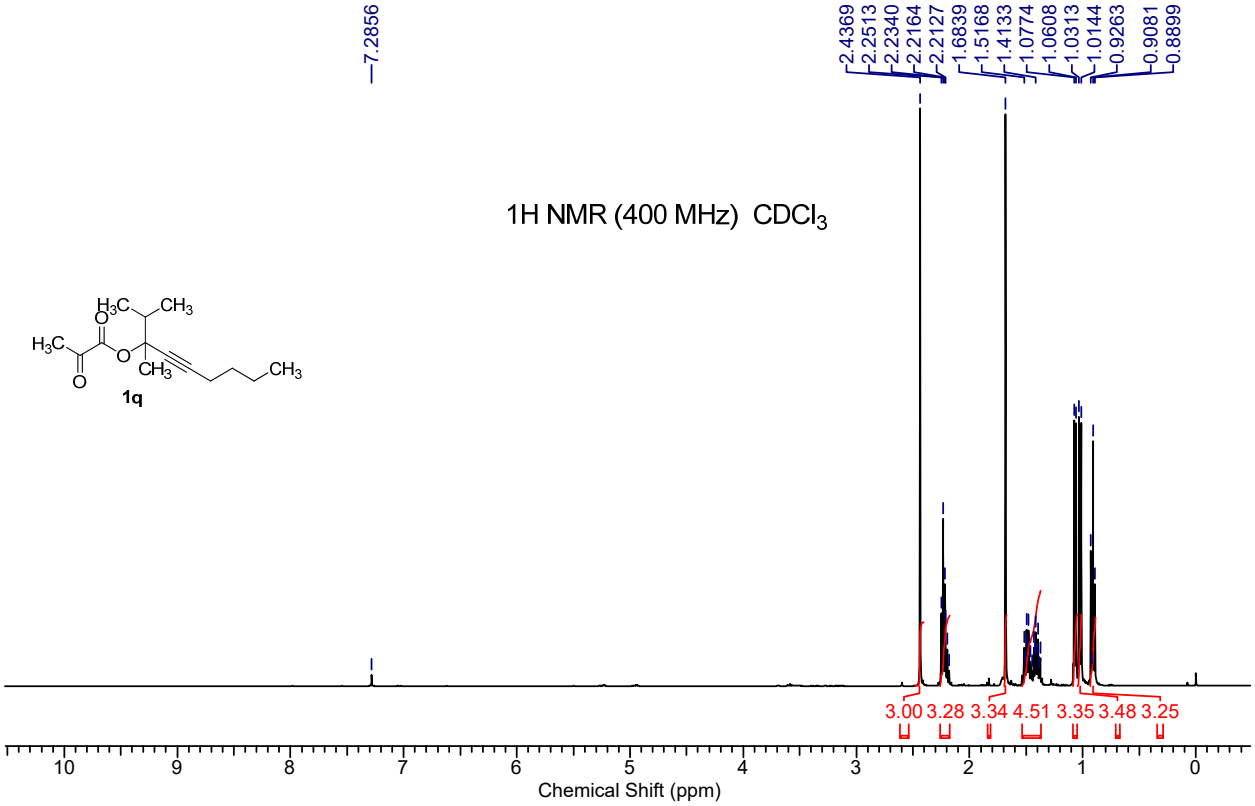
87.4557
79.4665
78.7533
77.3451
77.0201
76.7041
34.7001
30.5566
26.5936
26.0700
21.8633
18.3607
13.5492
8.6383
13C NMR (101 MHz) CDCl3
Chemical Shift (ppm)
1p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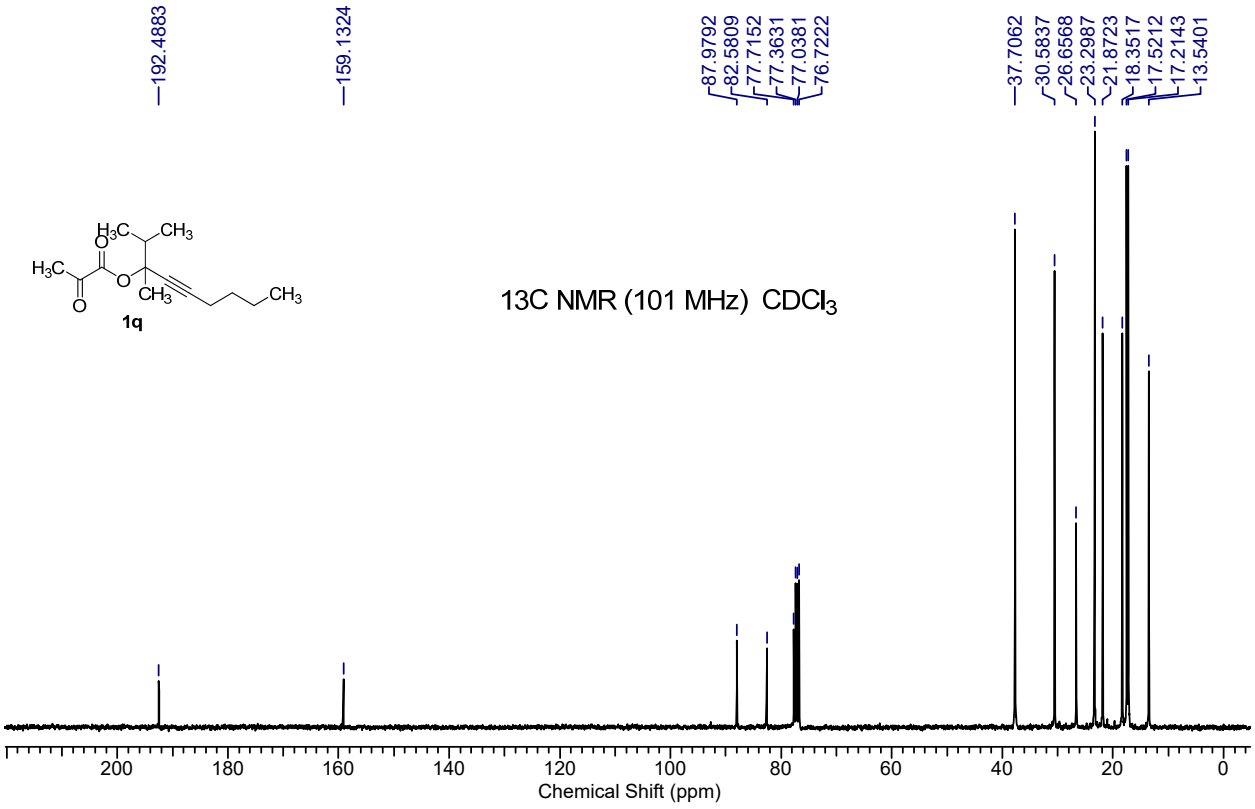
2.2513
2.2340
2.2164
2.2127
1.6839
1.5168
1.4133
1.0774
1.0608
1.0313
1.0144
0.9263
0.9081
0.8899
1H NMR (400 MHz) CDCl3
1q
3.00 3.28 3.34 4.51 3.35 3.48 3.25
Chemical Shift (ppm)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77.0381
76.7222
37.7062
30.5837
26.6568
23.2987
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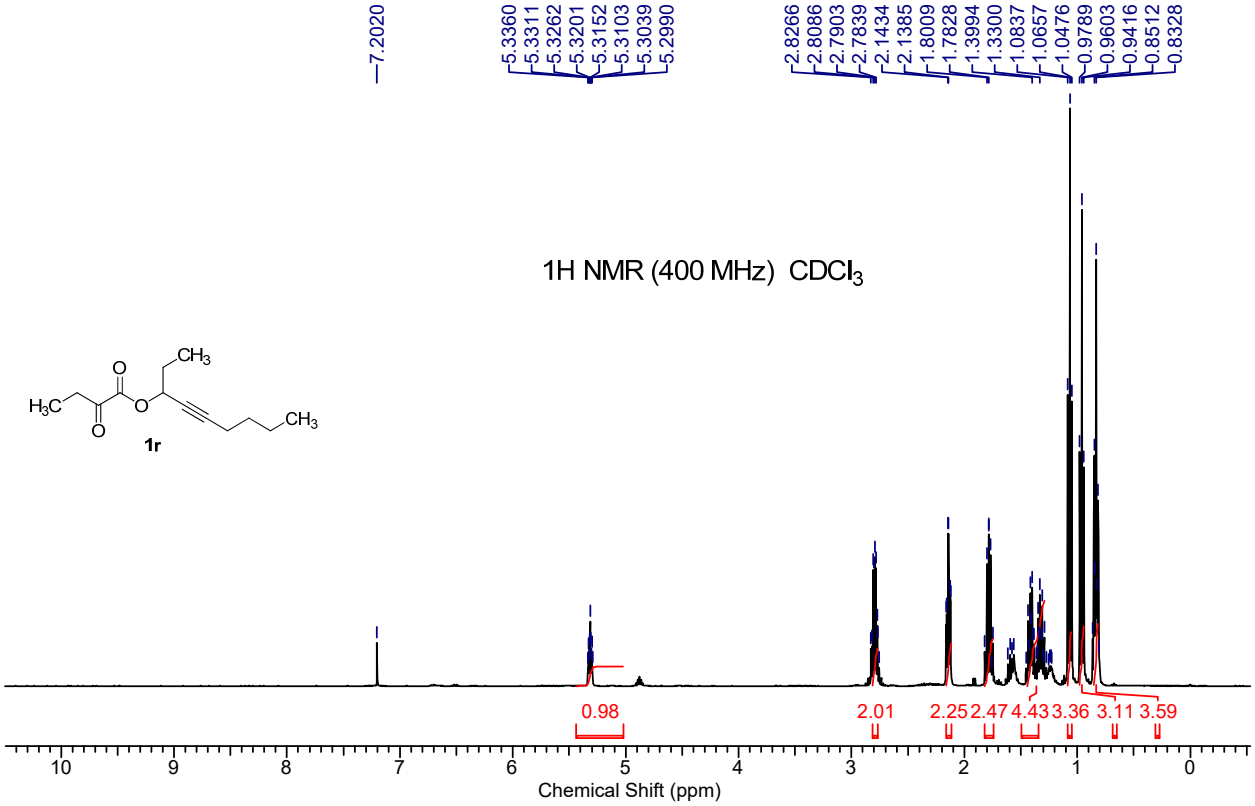
18.3517
17.5212
17.2143
13.5401
13C NMR (101 MHz) CDCl3
1q
Chemical Shift (ppm)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5.3360
5.3311
5.3262
5.3201
5.3152
5.3103
5.3039
5.2990
2.8266
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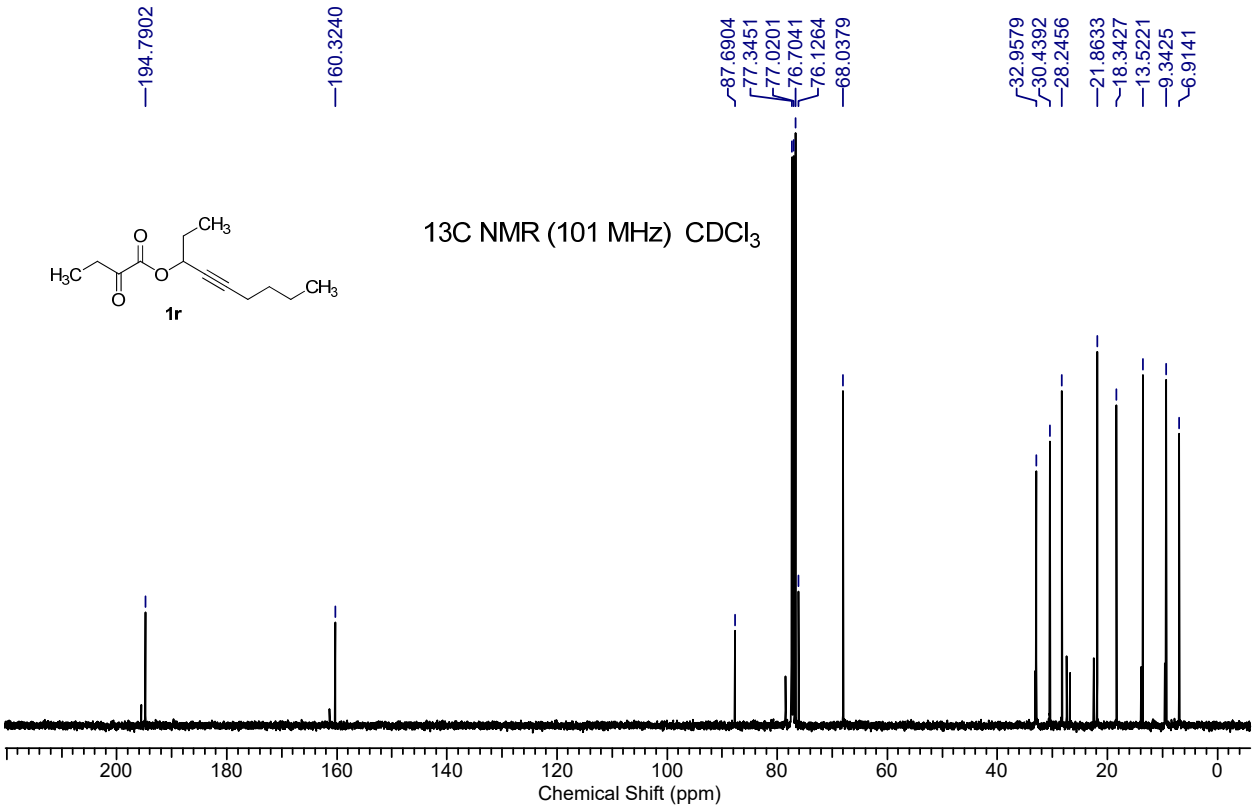
2.7903
2.7839
2.1434
2.1385
1.8009
1.7828
1.3994
1.3300
1.0837
1.0657
1.0476
0.9789
0.9603
0.9416
0.8512
0.8328
1H NMR (400 MHz) CDCl3
1r
0.98
2.01
2.25
2.47
4.43
3.36
3.11
3.59
Chemical Shift (ppm)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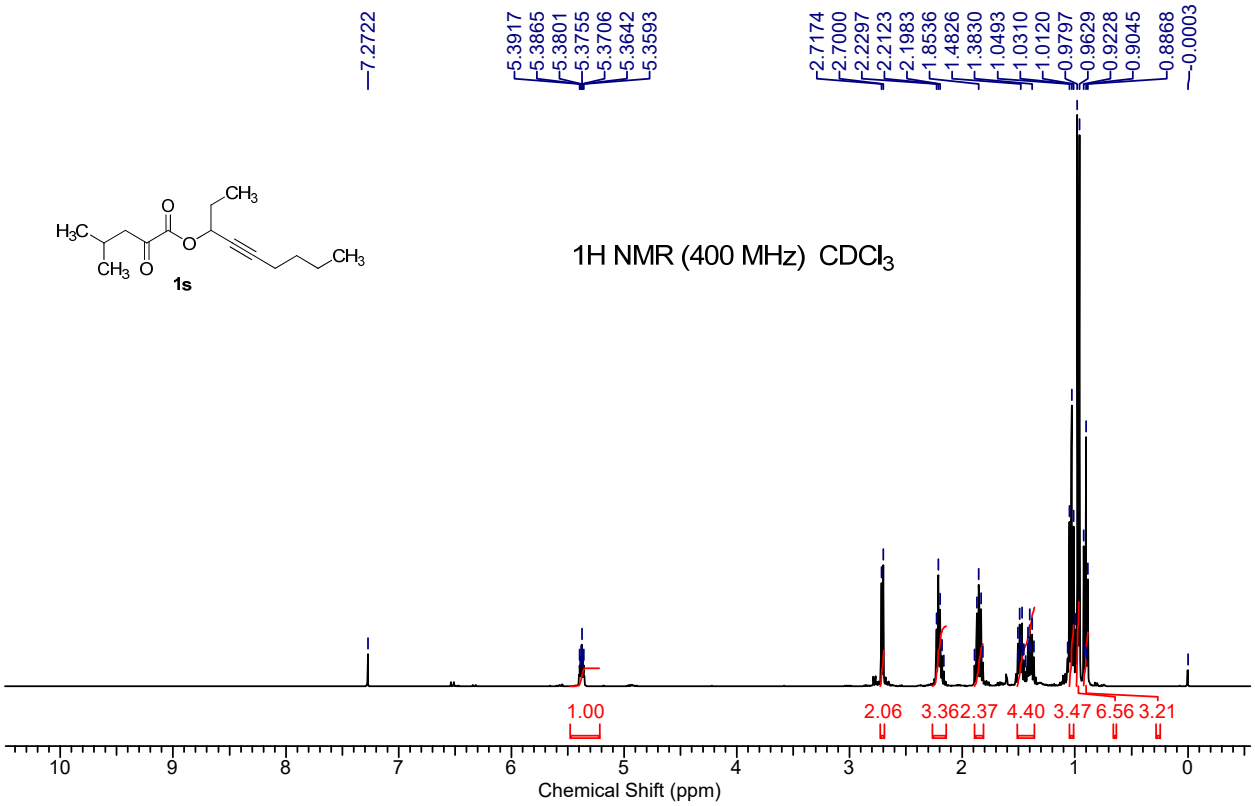
87.6904
77.3451
77.0201
76.7041
76.1264
68.0379
32.9579
30.4392
28.2456
21.8633
18.3427
13.5221
9.3425
6.9141
13C NMR (101 MHz) CDCl3
1r
Chemical Shift (ppm)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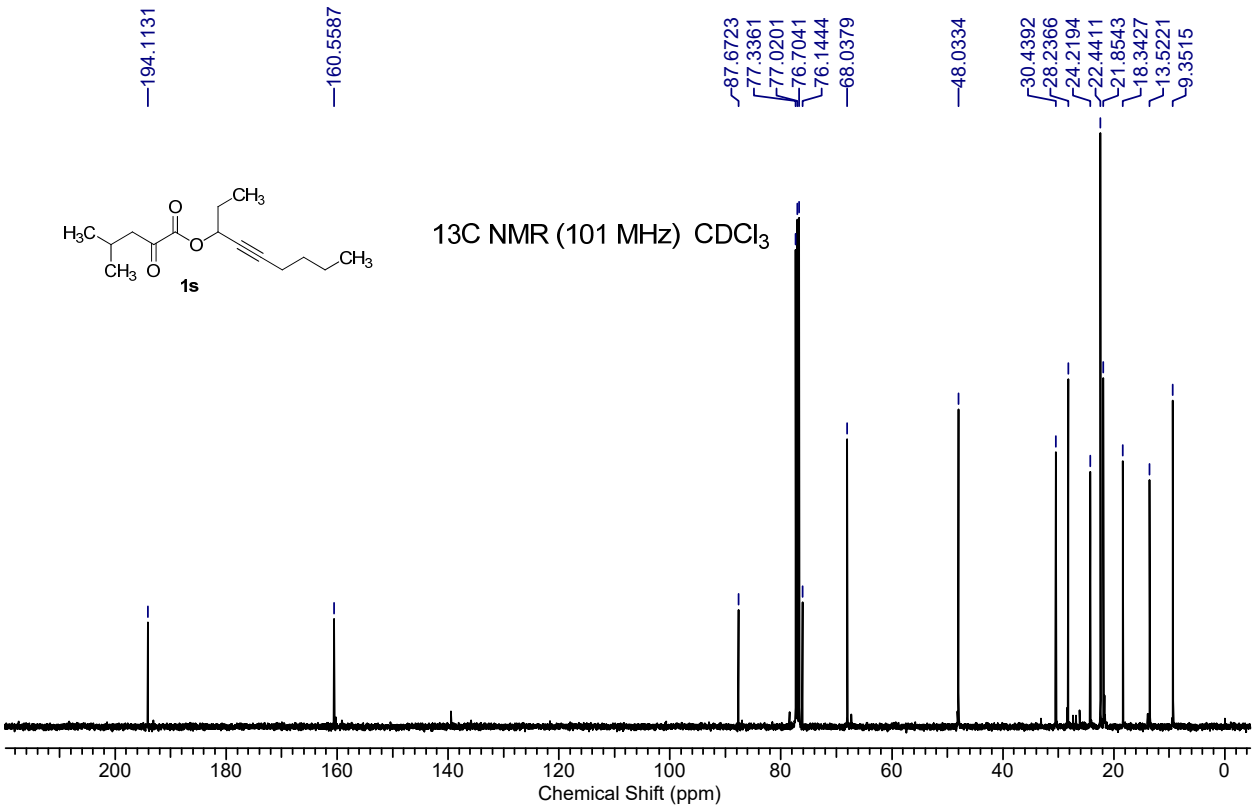
5.3917
5.3865
5.3801
5.3755
5.3706
5.3642
5.3593
2.7174
2.7000
2.2297
2.2123
2.1983
1.8536
1.4826
1.3830
1.0493
1.0310
1.0120
0.9797
0.9629
0.9228
0.9045
0.8868
0.0003
1H NMR (400 MHz) CDCl3
1s
1.00
2.06
3.36
2.37
4.40
3.47
6.56
3.21
Chemical Shift (ppm)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87.6723
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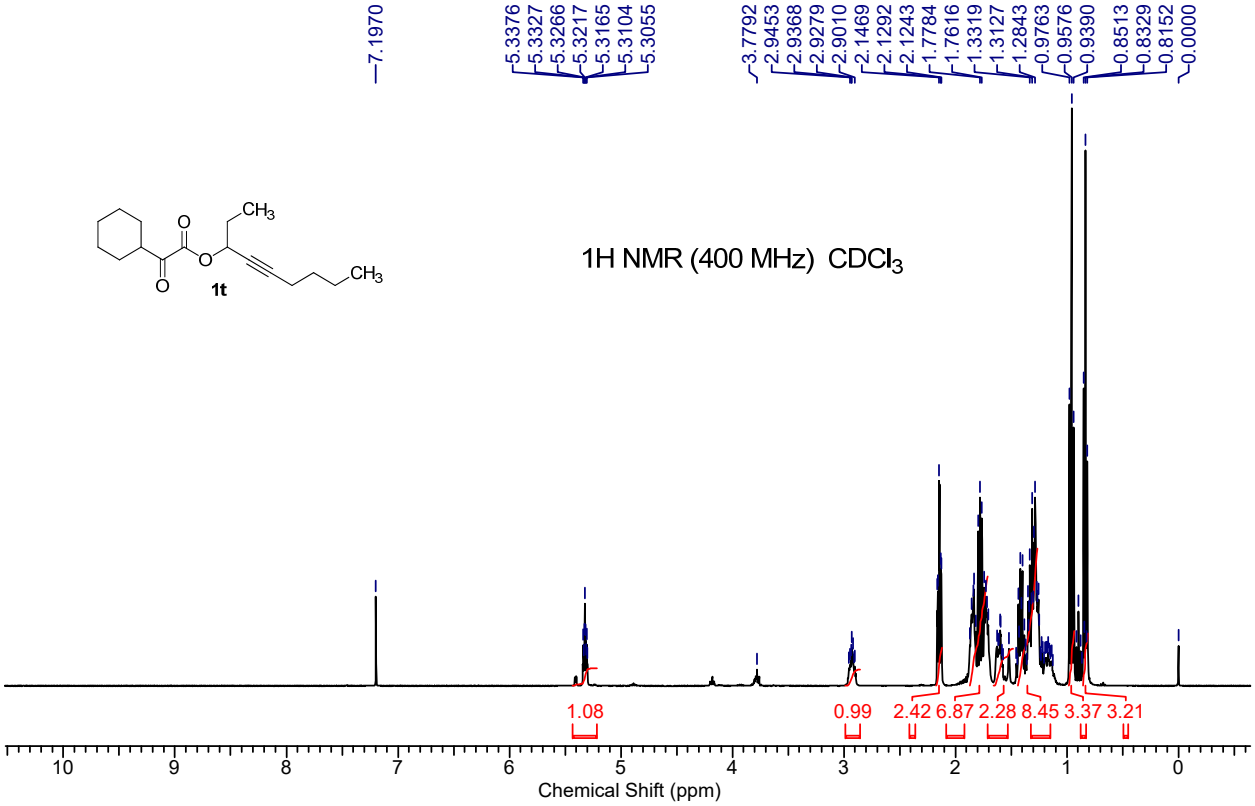
77.0201
76.7041
76.1444
68.0379
48.0334
30.4392
28.2366
24.2194
22.4411
21.8543
18.3427
13.5221
9.3515
13C NMR (101 MHz) CDCl3
1s
Chemical Shift (ppm)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5.3327
5.3266
5.3217
5.3165
5.3104
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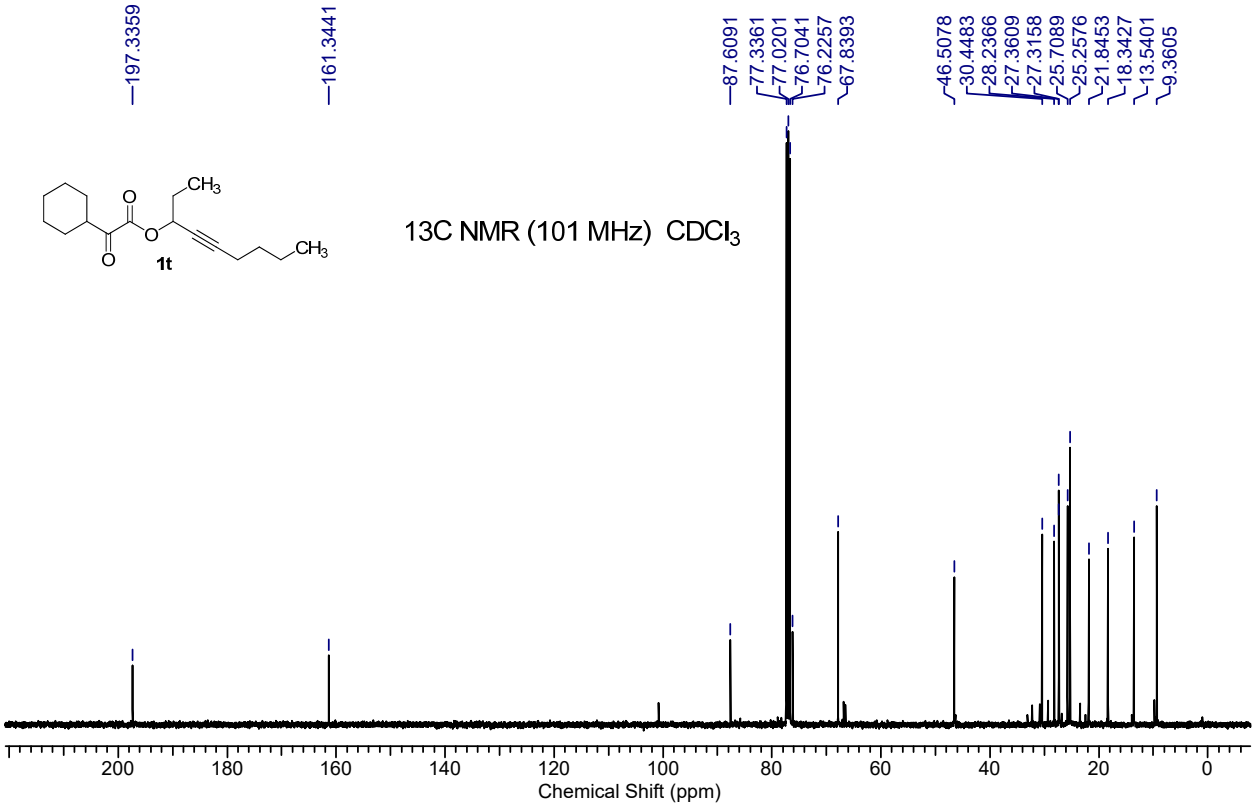
3.7792
2.9453
2.9368
2.9279
2.9010
2.1469
2.1292
2.1243
1.7784
1.7616
1.3319
1.3127
1.2843
0.9763
0.9576
0.9390
0.8513
0.8329
0.8152
0.0000
1t
1H NMR (400 MHz) CDCl3
1.08
0.99
2.42
6.87
2.28
8.45
3.37
3.21
Chemical Shift (ppm)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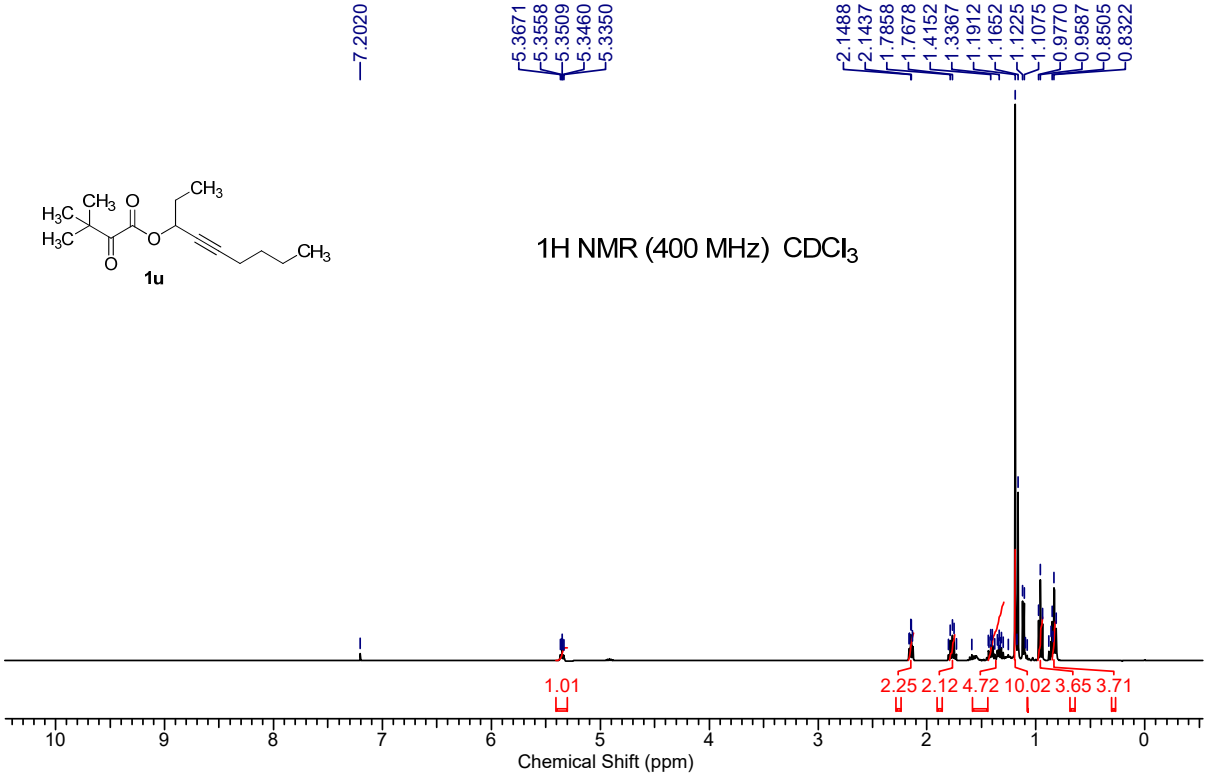
87.6091
77.3361
77.0201
76.7041
76.2257
67.8393
46.5078
30.4483
28.2366
27.3609
27.3158
25.7089
25.2576
21.8453
18.3427
13.5401
9.3605
1t
13C NMR (101 MHz) CDCl3
Chemical Shift (ppm)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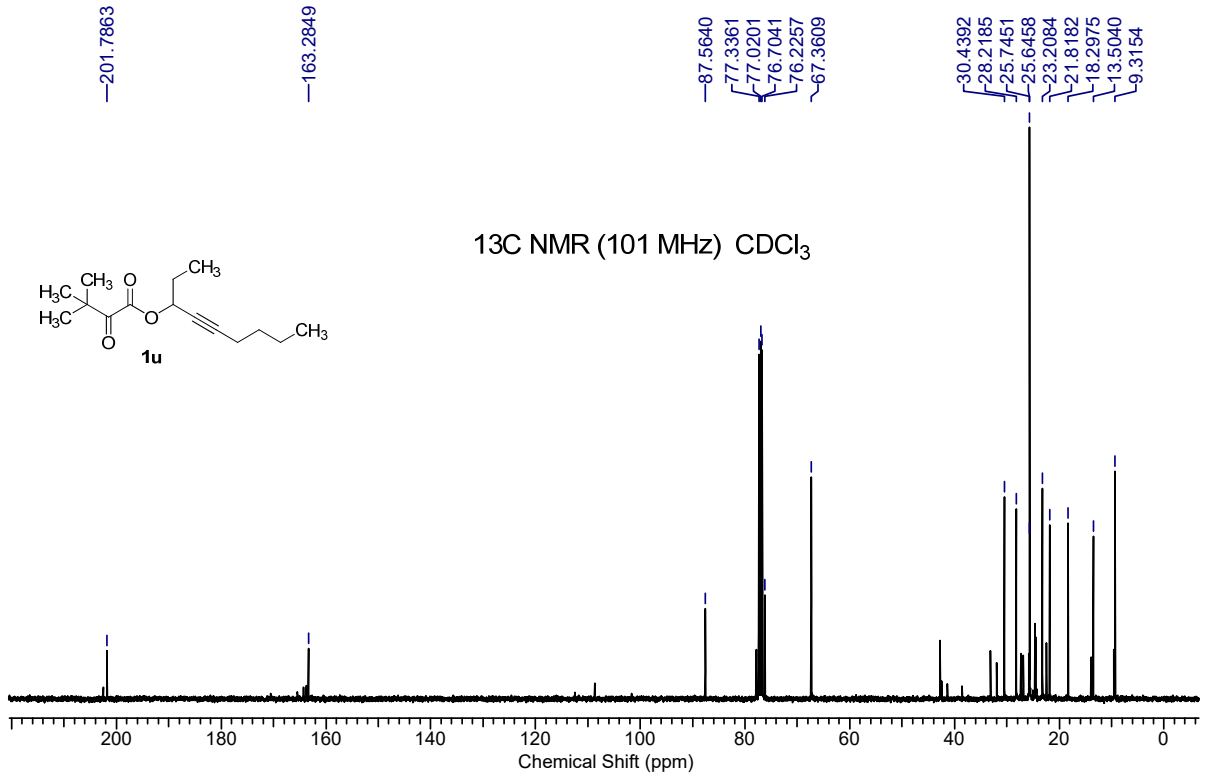
5.3509
5.3460
5.3350
2.1488
2.1437
1.7858
1.7678
1.4152
1.3367
1.1912
1.1652
1.1225
1.1075
0.9770
0.9587
0.8505
0.8322
1H NMR (400 MHz) CDCl3
1u
1.01
2.25 2.12 4.72 10.02 3.65 3.71
Chemical Shift (ppm)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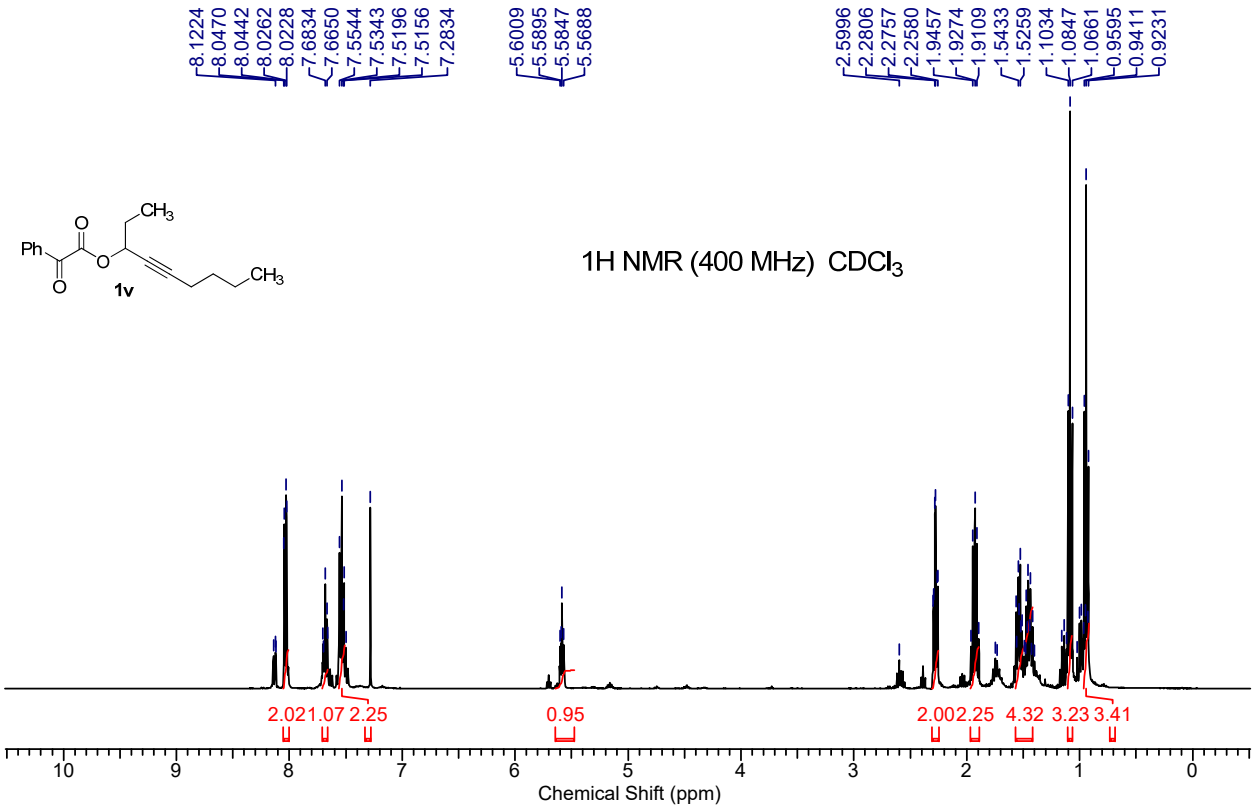
76.7041
76.2257
67.3609
30.4392
28.2185
25.7451
25.6458
23.2084
21.8182
18.2975
13.5040
9.3154
13C NMR (101 MHz) CDCl3
1u
Chemical Shift (ppm)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8.0442
8.0262
8.0228
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7.5343
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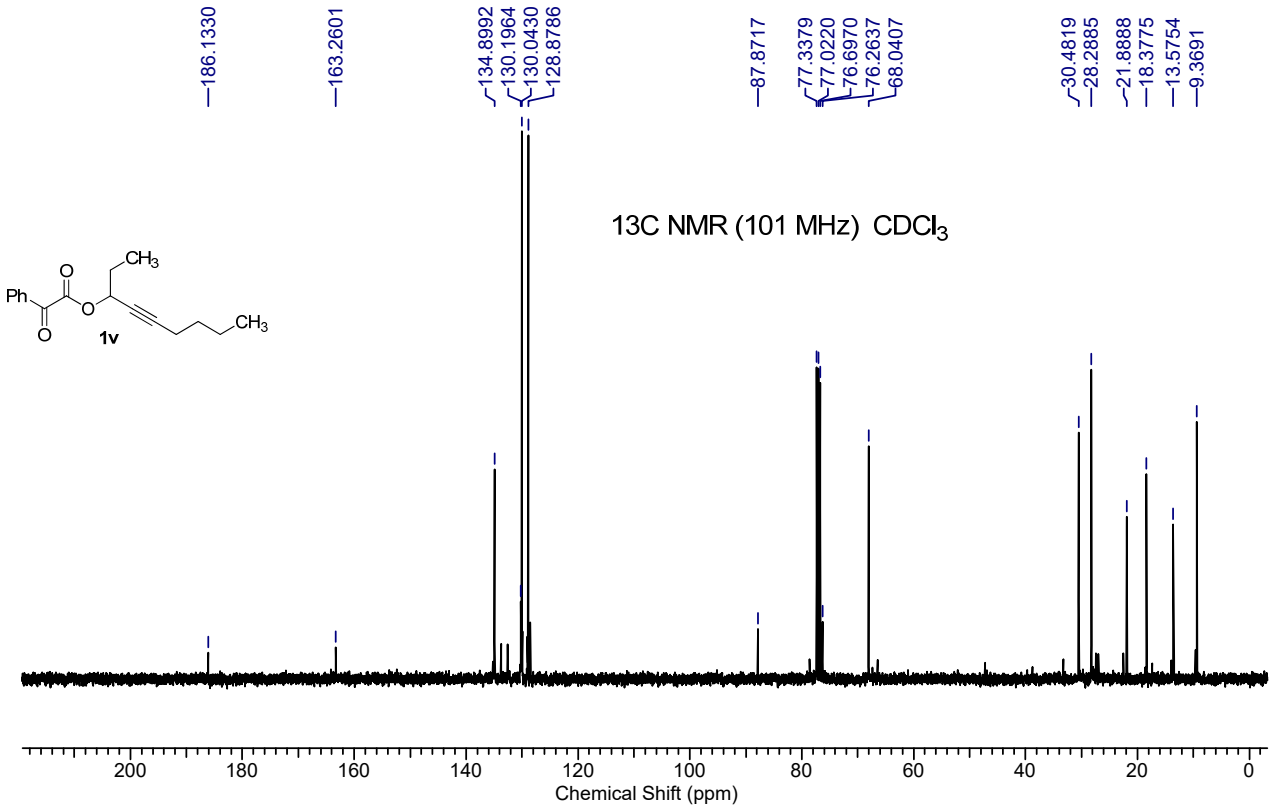
7.5156
7.2834
5.6009
5.5895
5.5847
5.5688
2.5996
2.2806
2.2757
2.2580
1.9457
1.9274
1.9109
1.5433
1.5259
1.1034
1.0847
1.0661
0.9595
0.9411
0.9231
Ph
O
O
O
CH3
CH3
1v
1H NMR (400 MHz) CDCl3
2.02 1.07 2.25
0.95
2.00 2.25 4.32 3.23 3.41
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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130.1964
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128.8786
87.8717
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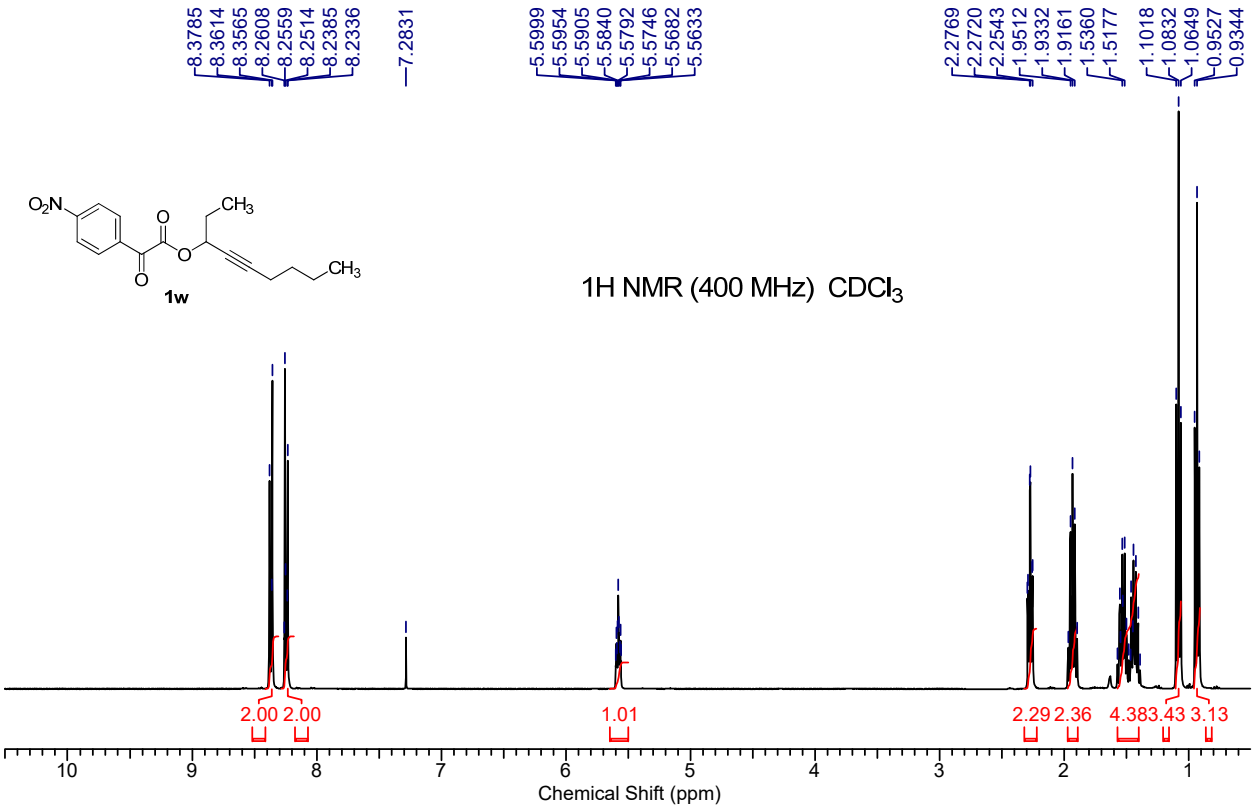
77.0220
76.6970
76.2637
68.0407
30.4819
28.2885
21.8888
18.3775
13.5754
9.3691
Ph
O
O
O
CH3
CH3
1v
13C NMR (101 MHz) CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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8.3565
8.2608
8.2559
8.2514
8.2385
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5.5905
5.5840
5.5792
5.5746
5.5682
5.5633
2.2769
2.2720
2.2543
1.9512
1.9332
1.9161
1.5360
1.5177
1.1018
1.0832
1.0649
0.9527
0.9344
1w
1H NMR (400 MHz) CDCl3
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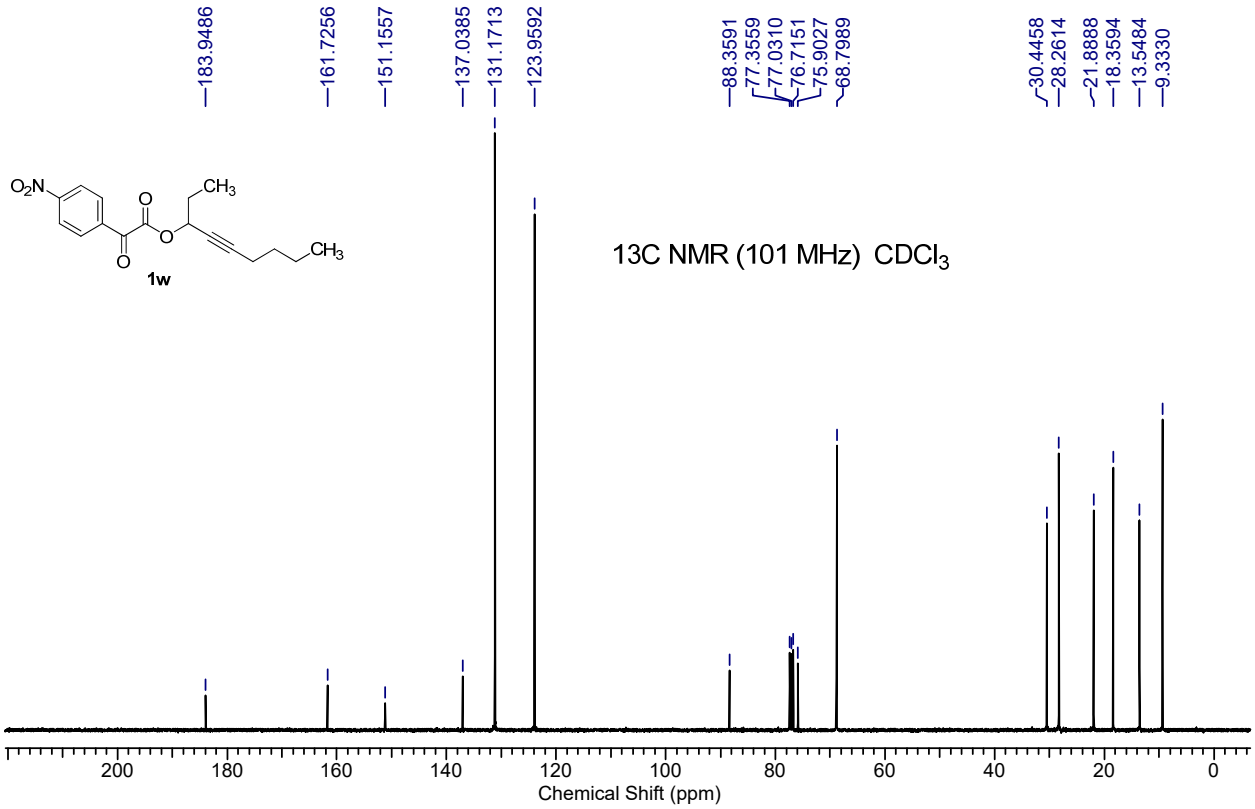
1.01
2.29 2.36
4.38 3.43
3.13
Chemical Shift (ppm)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137.0385
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77.0310
76.7151
75.9027
68.7989
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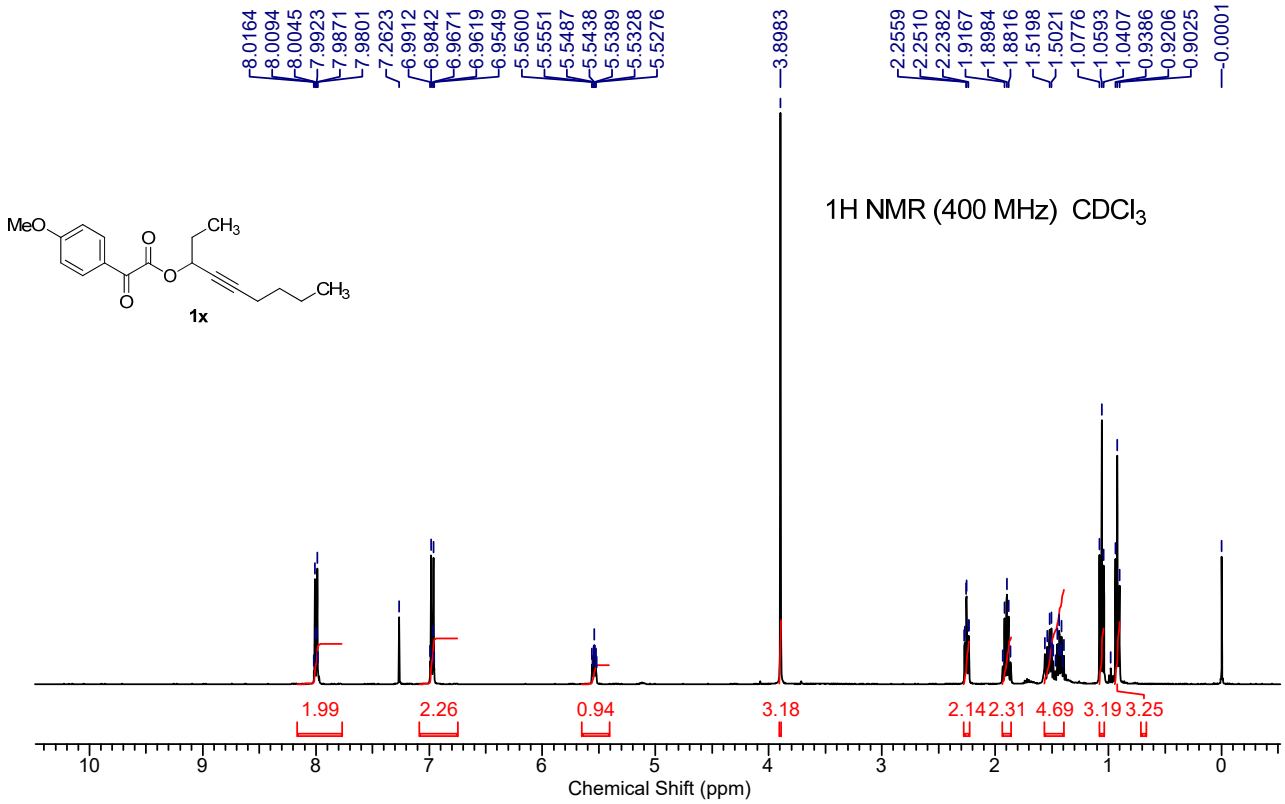
21.8888
18.3594
13.5484
9.3330
1w
13C NMR (101 MHz) CDCl3
Chemical Shift (ppm)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7.2623
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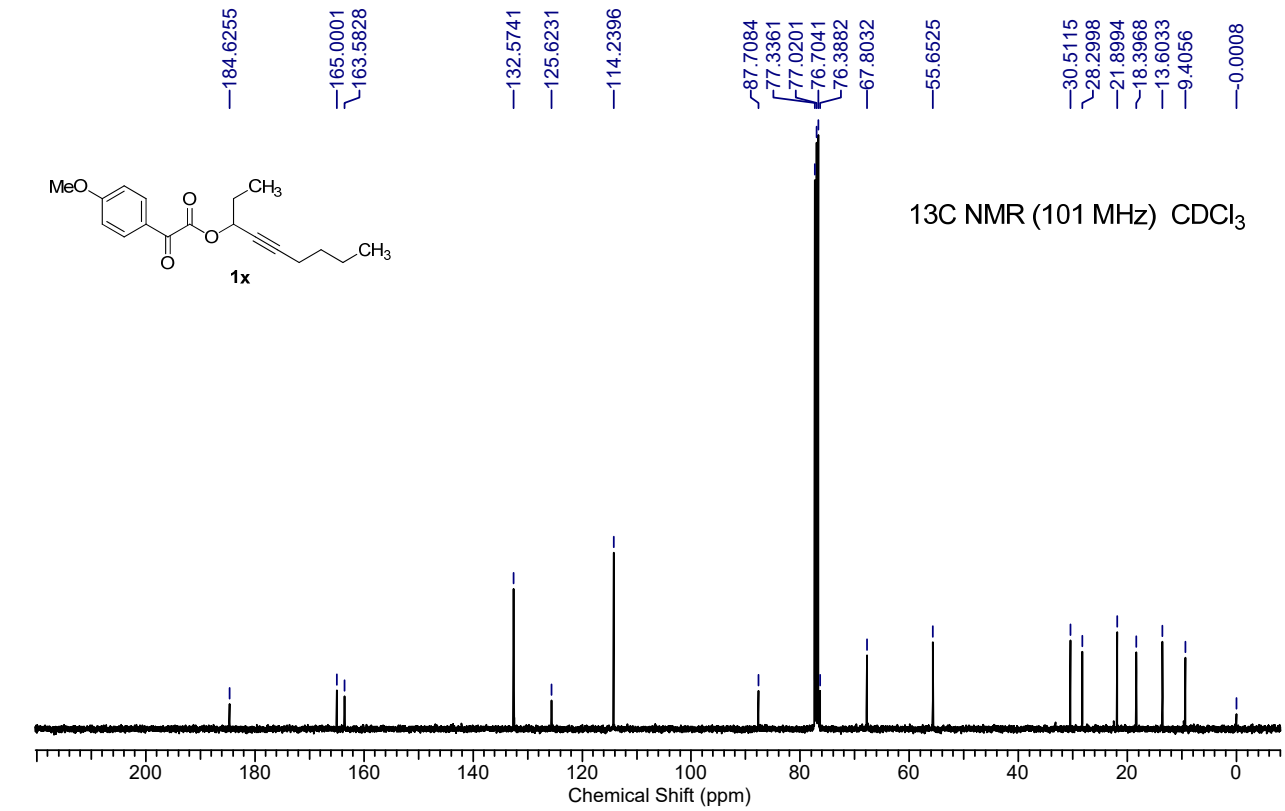
6.9619
6.9549
5.5600
5.5551
5.5487
5.5438
5.5389
5.5328
5.5276
3.8983
2.2559
2.2510
2.2382
1.9167
1.8984
1.8816
1.5198
1.5021
1.0776
1.0593
1.0407
0.9386
0.9206
0.9025
0.0001
MeO
CH3
O
O
O
CH3
1x
1H NMR (400 MHz) CDCl3
1.99
2.26
0.94
3.18
2.14
2.31
4.69
3.19
3.25
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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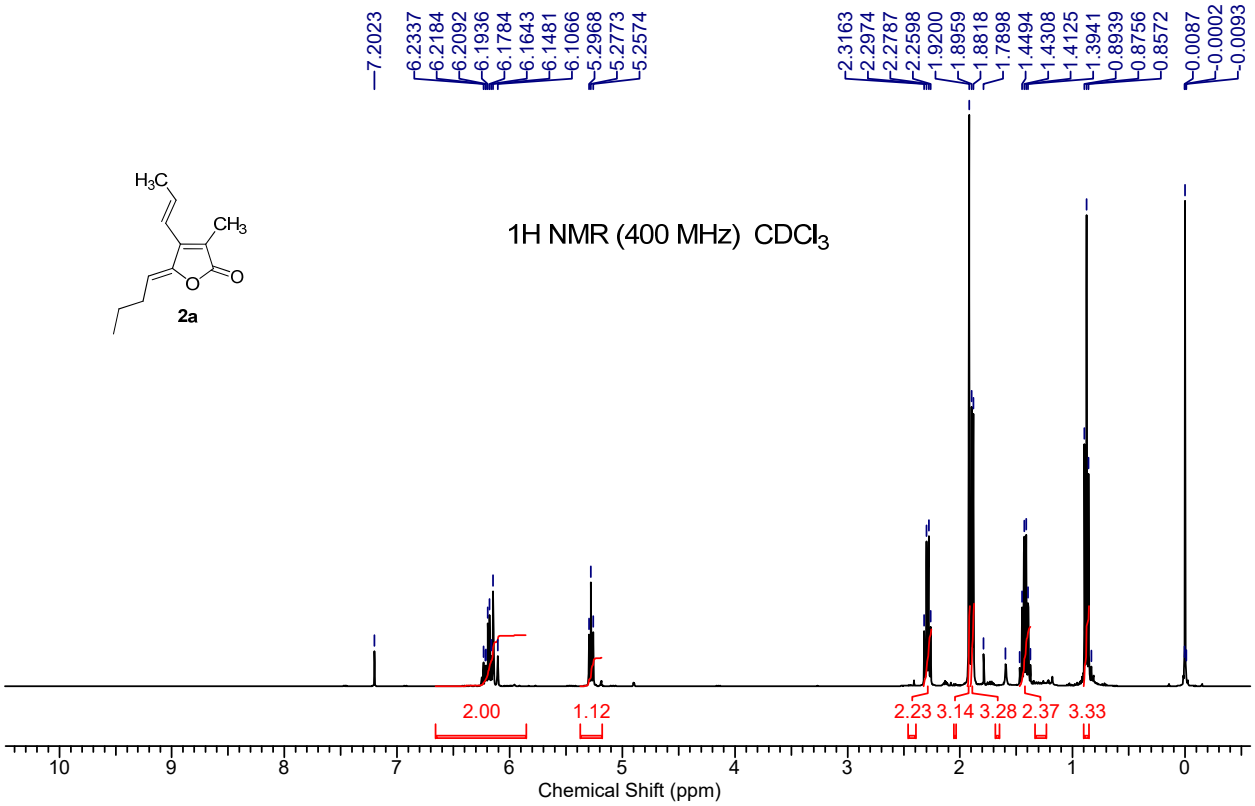
87.7084
77.3361
77.0201
76.7041
76.3882
67.8032
55.6525
30.5115
28.2998
21.8994
18.3968
13.6033
9.4056
0.0008
MeO
CH3
O
O
O
CH3
1x
13C NMR (101 MHz) CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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6.1936
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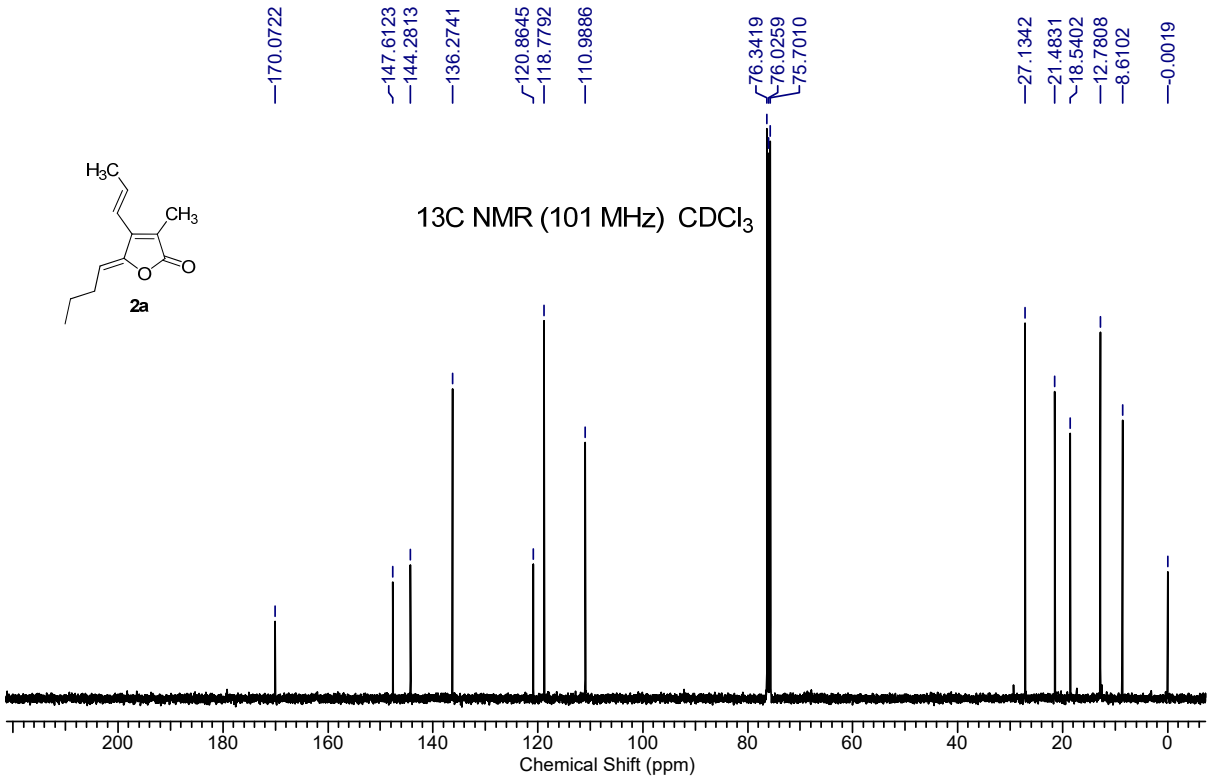
5.2773
5.2574
2.3163
2.2974
2.2787
2.2598
1.9200
1.8959
1.8818
1.7898
1.4494
1.4308
1.4125
1.3941
0.8939
0.8756
0.8572
0.0087
0.0002
0.0093
H3C
CH3
O
O
2a
1H NMR (400 MHz) CDCl3
2.00
1.12
2.23
3.14
3.28
2.37
3.33
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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144.2813
136.2741
120.8645
118.7792
110.9886
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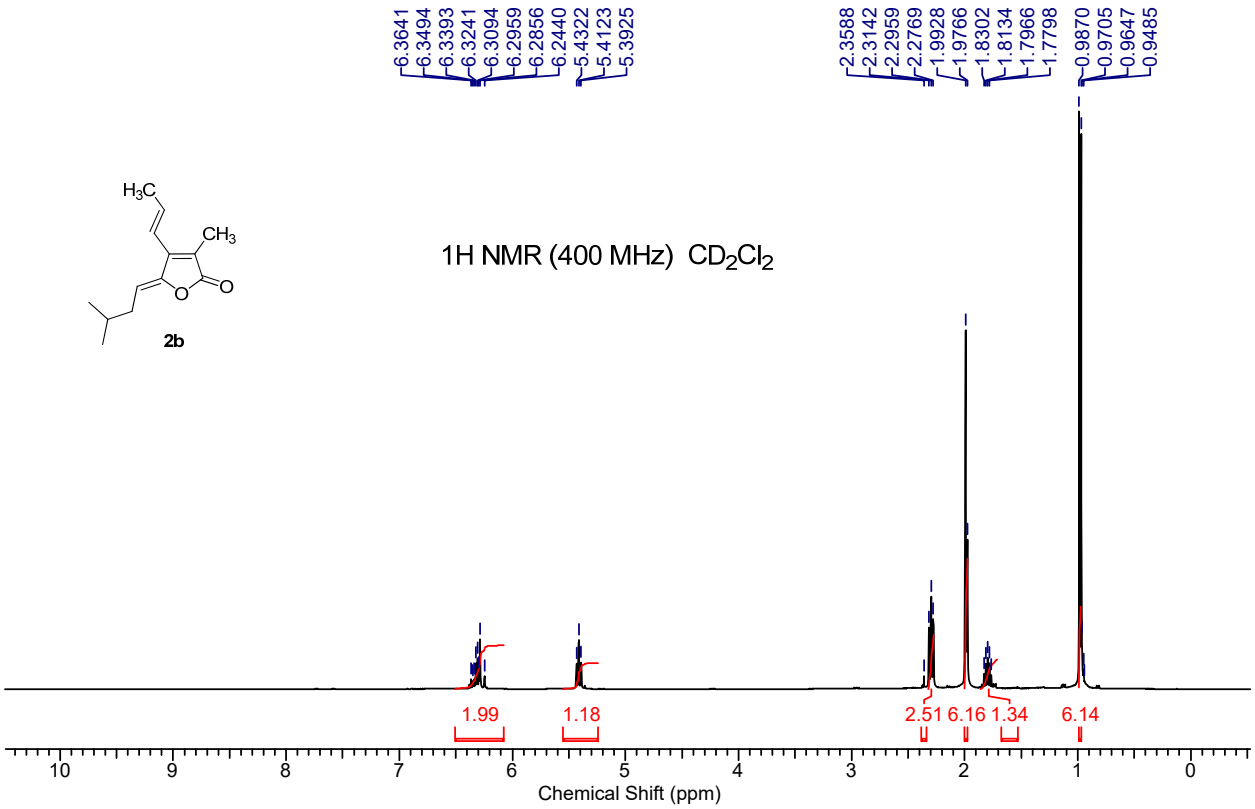
76.0259
75.7010
27.1342
21.4831
18.5402
12.7808
8.6102
0.0019
H3C
CH3
O
O
2a
13C NMR (101 MHz) CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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6.3393
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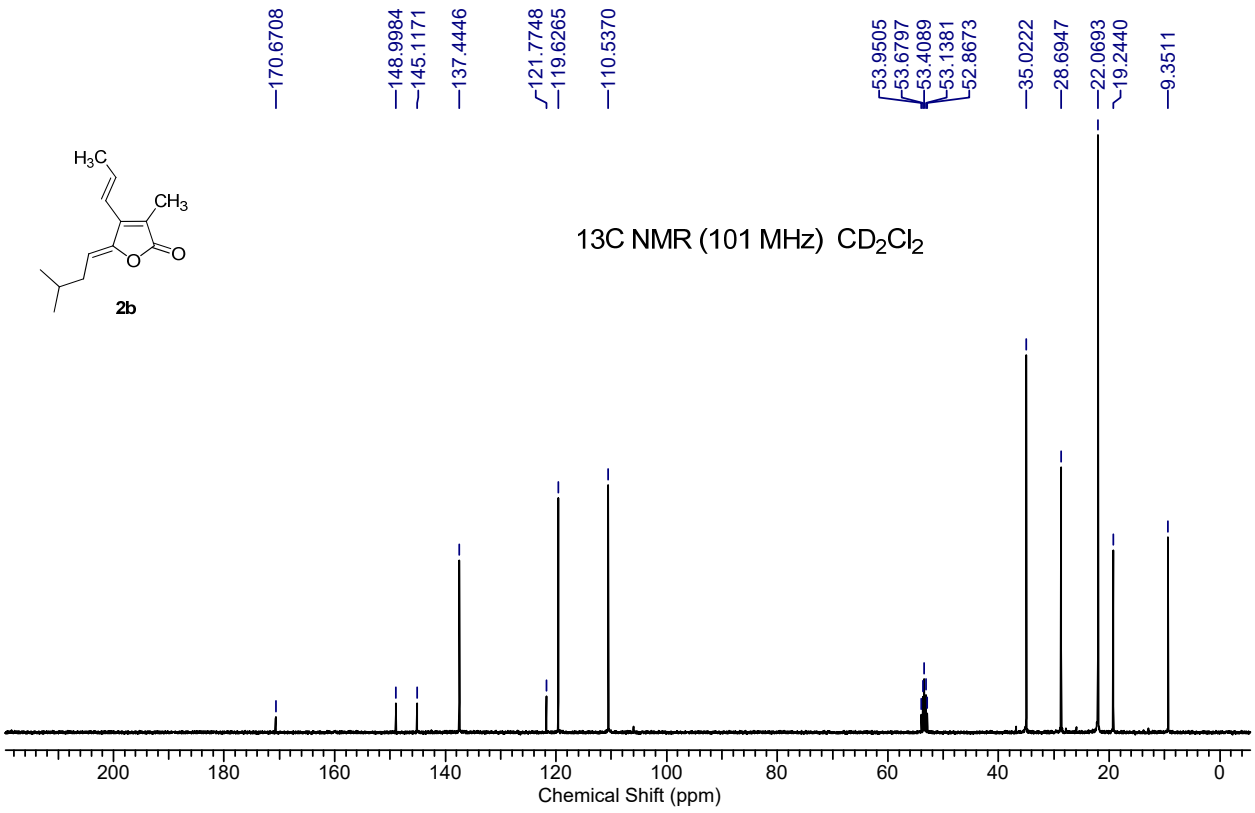
6.3094
6.2959
6.2856
6.2440
5.4322
5.4123
5.3925
2.3588
2.3142
2.2959
2.2769
1.9928
1.9766
1.8302
1.8134
1.7966
1.7798
0.9870
0.9705
0.9647
0.9485
H3C
CH3
O
O
2b
1H NMR (400 MHz) CD2Cl2
1.99
1.18
2.51
6.16
1.34
6.14
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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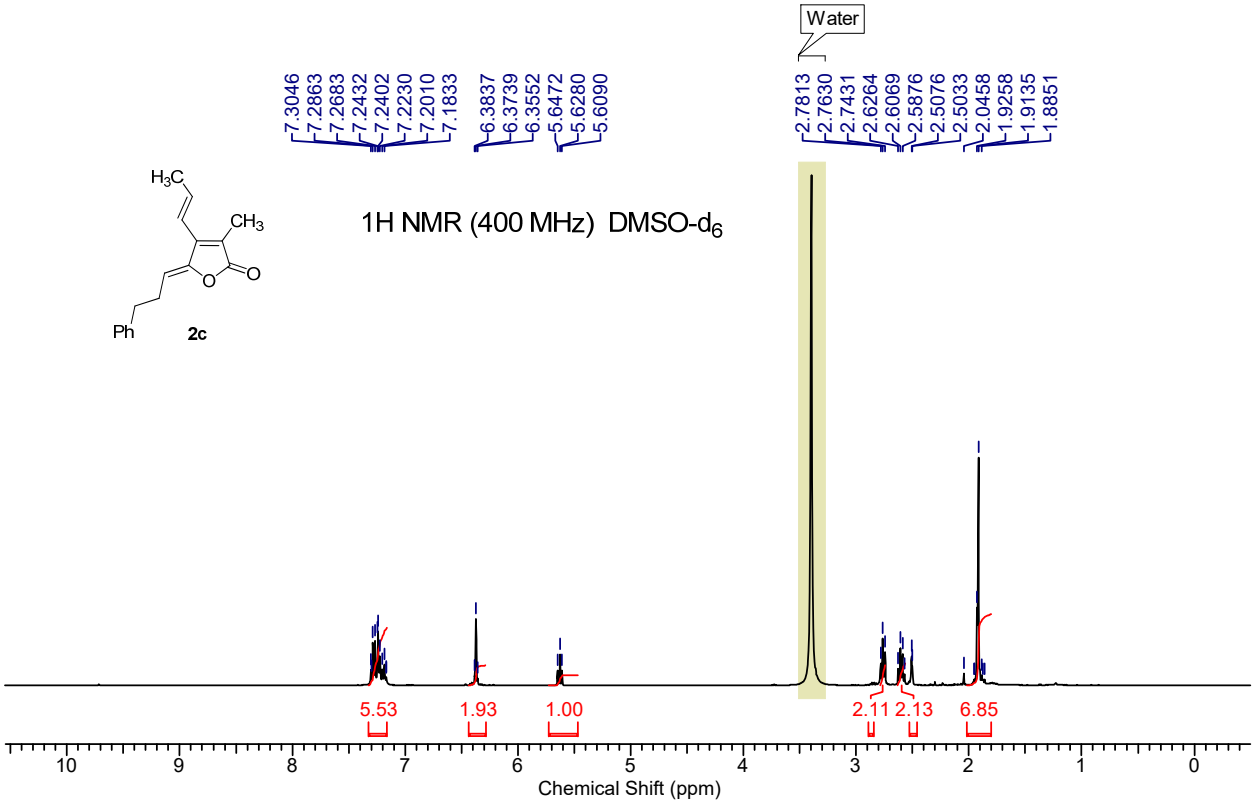
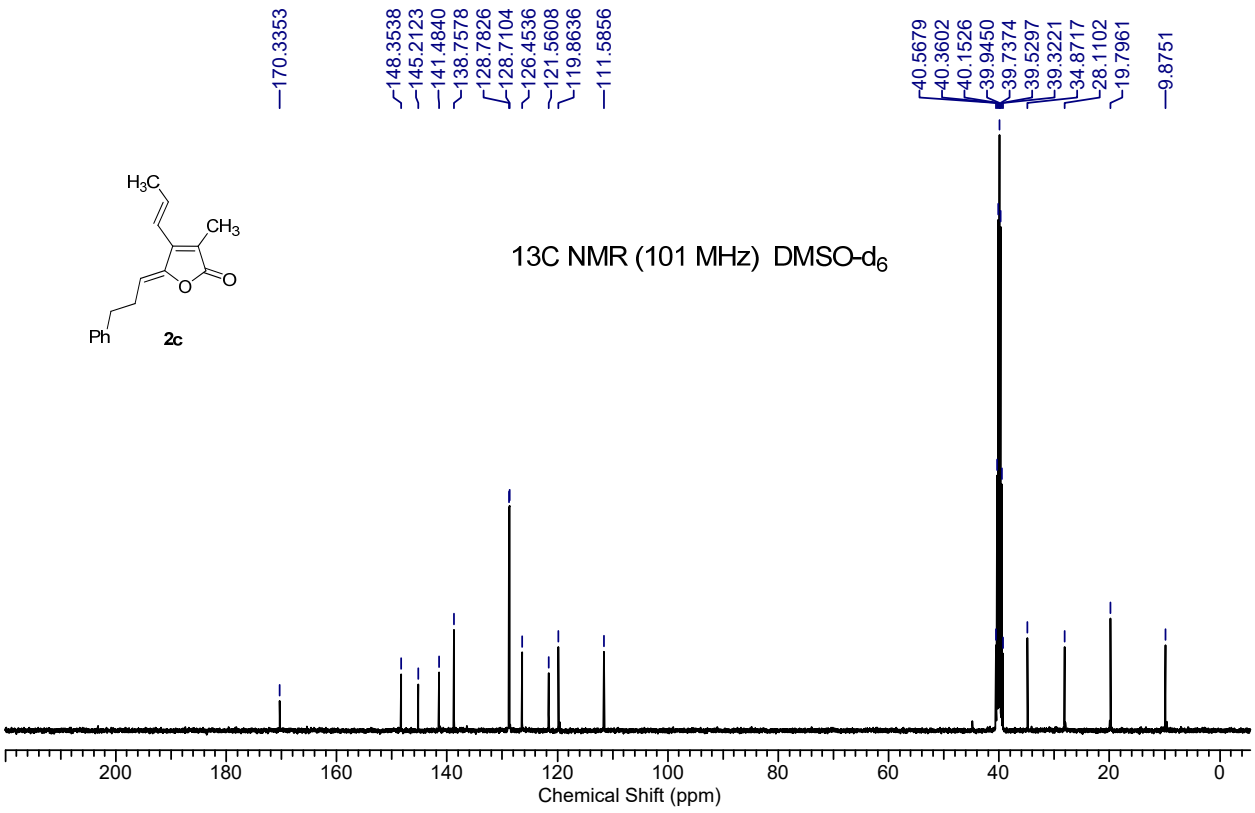
145.1171
137.4446
121.7748
119.6265
110.5370
53.9505
53.6797
53.4089
53.1381
52.8673
35.0222
28.6947
22.0693
19.2440
9.3511
H3C
CH3
O
O
2b
13C NMR (101 MHz) CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Water
7.3046
7.2863
7.2683
7.2432
7.2402
7.2230
7.2010
7.1833
6.3837
6.3739
6.3552
5.6472
5.6280
5.6090
2.7813
2.7630
2.7431
2.6264
2.6069
2.5876
2.5076
2.5033
2.0458
1.9258
1.9135
1.8851
1H NMR (400 MHz) DMSO-d6
H3C
CH3
O
O
Ph
2c
5.53
1.93
1.00
2.11
2.13
6.85
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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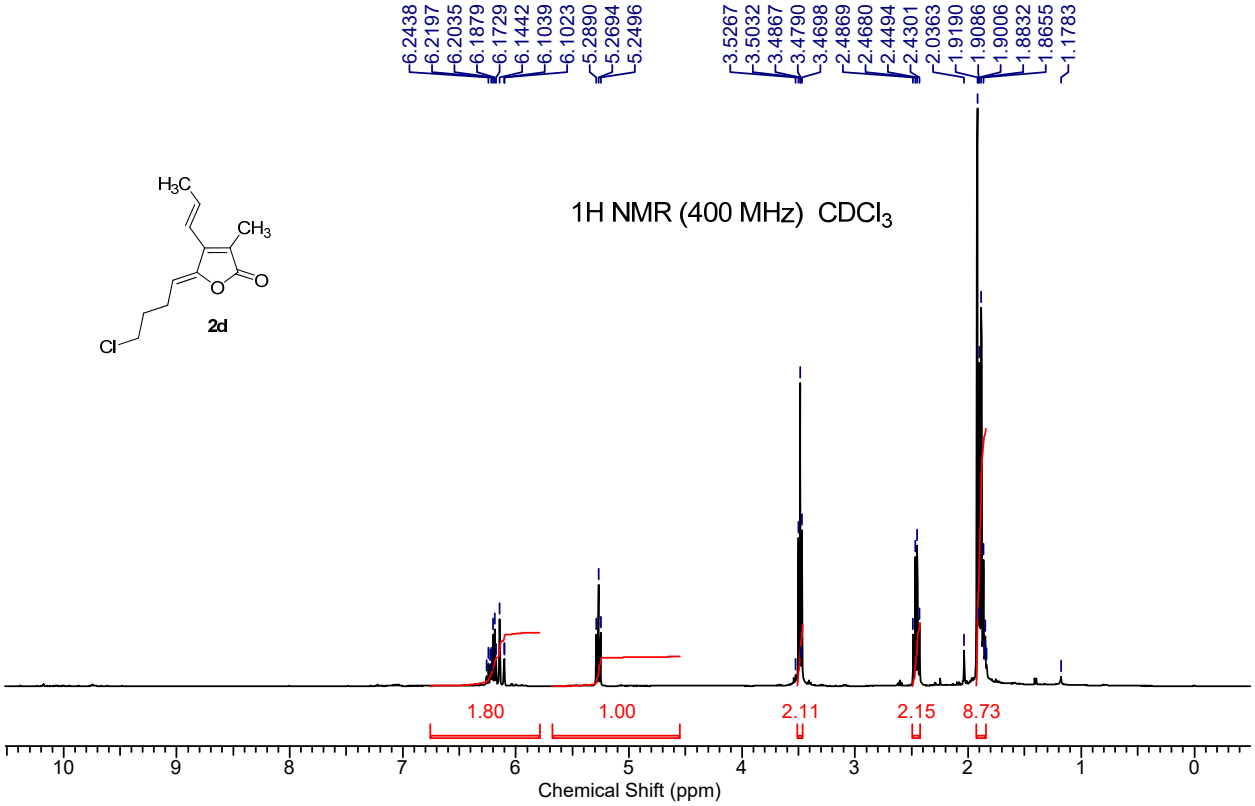
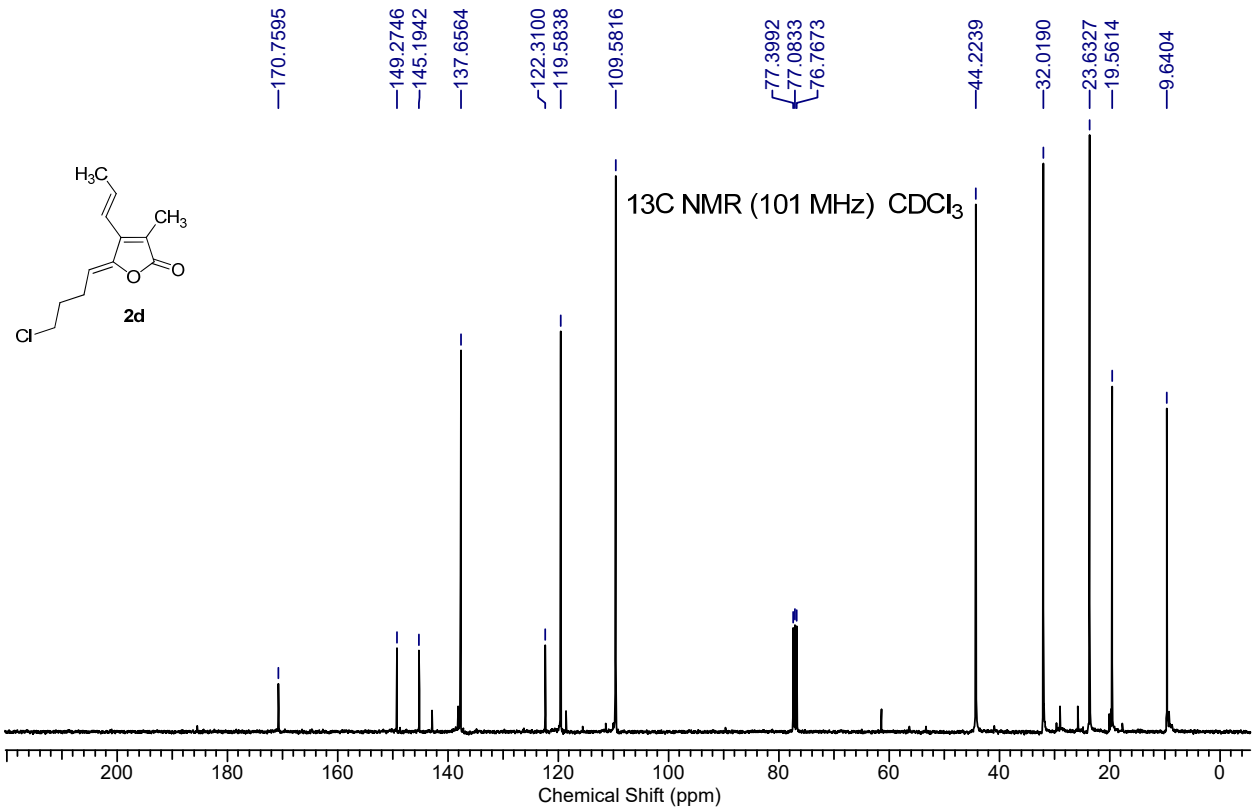
148.3538
145.2123
141.4840
138.7578
128.7826
128.7104
126.4536
121.5608
119.8636
111.5856
40.5679
40.3602
40.1526
39.9450
39.7374
39.5297
39.3221
34.8717
28.1102
19.7961
9.8751
13C NMR (101 MHz) DMSO-d6
H3C
CH3
O
O
Ph
2c
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


6.2438
6.2197
6.2035
6.1879
6.1729
6.1442
6.1039
6.1023
5.2890
5.2694
5.2496
3.5267
3.5032
3.4867
3.4790
3.4698
2.4869
2.4680
2.4494
2.4301
2.0363
1.9190
1.9086
1.9006
1.8832
1.8655
1.1783
1H NMR (400 MHz) CDCl3
H3C
CH3
O
O
Cl
2d
1.80
1.00
2.11
2.15
8.73
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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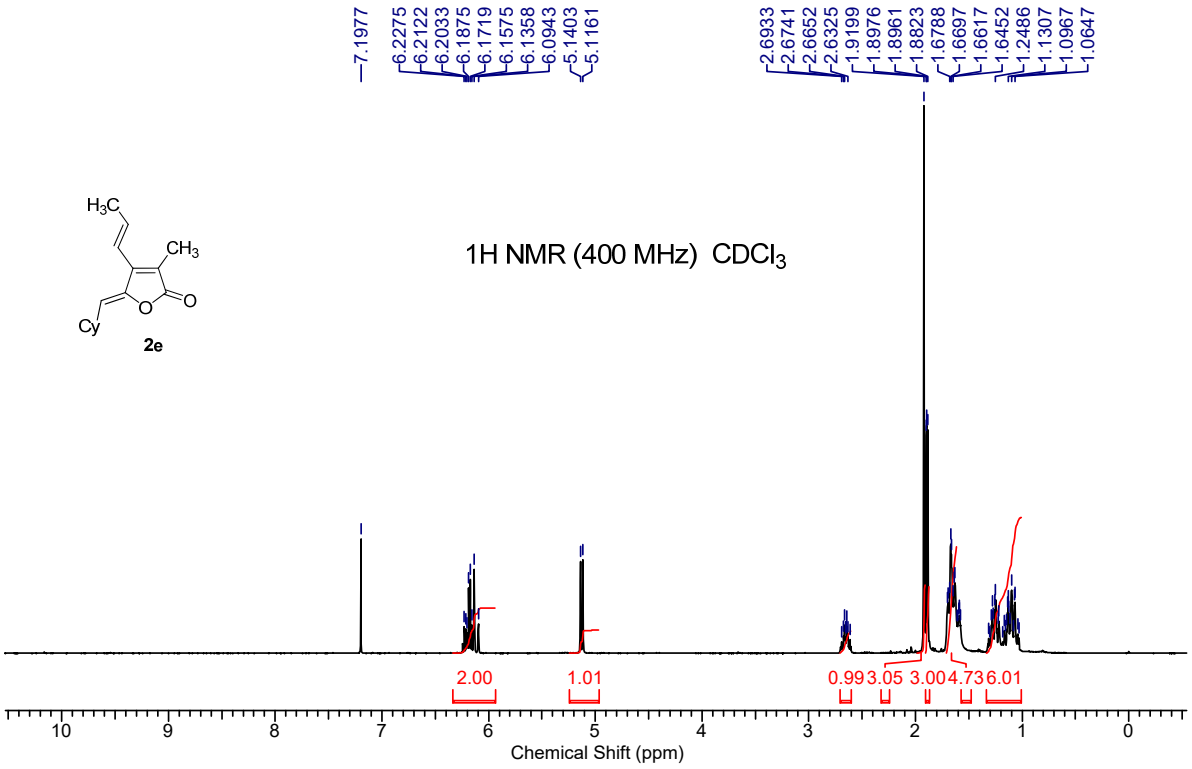
149.2746
145.1942
137.6564
122.3100
119.5838
109.5816
77.3992
77.0833
76.7673
44.2239
32.0190
23.6327
19.5614
9.6404
13C NMR (101 MHz) CDCl3
H3C
CH3
O
O
Cl
2d
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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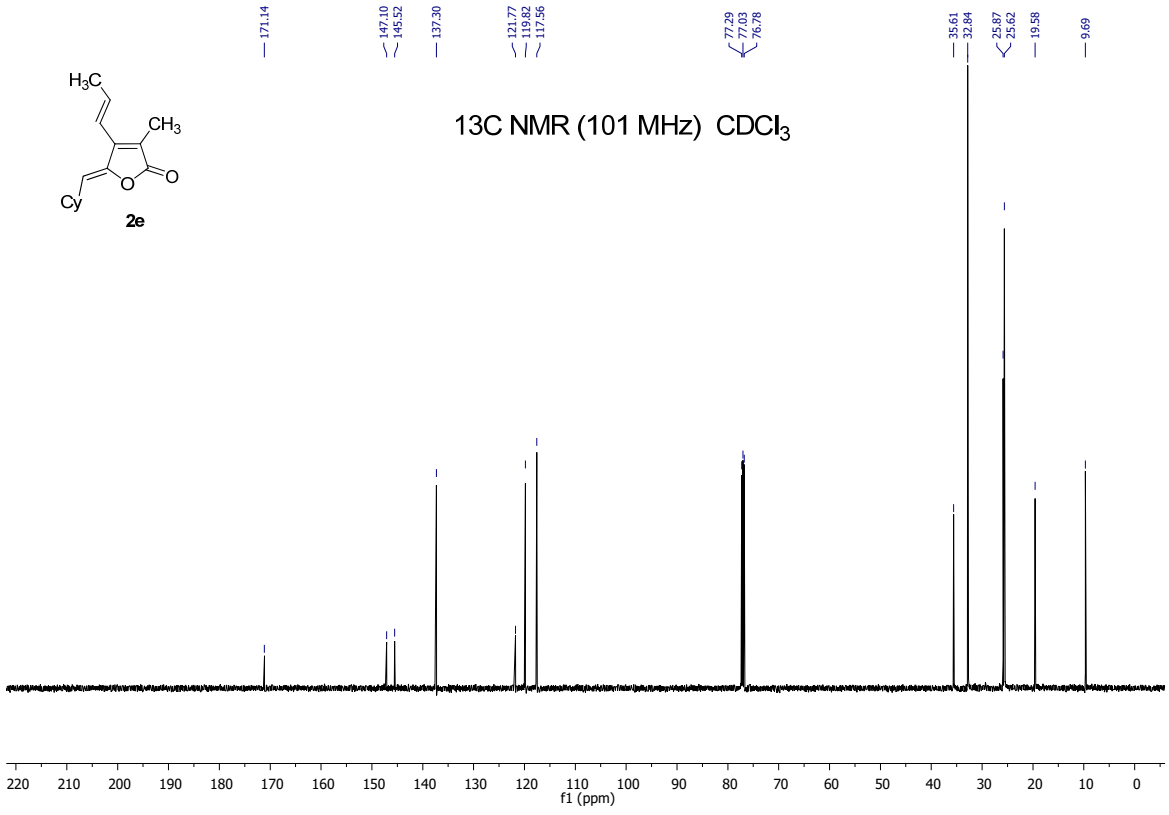
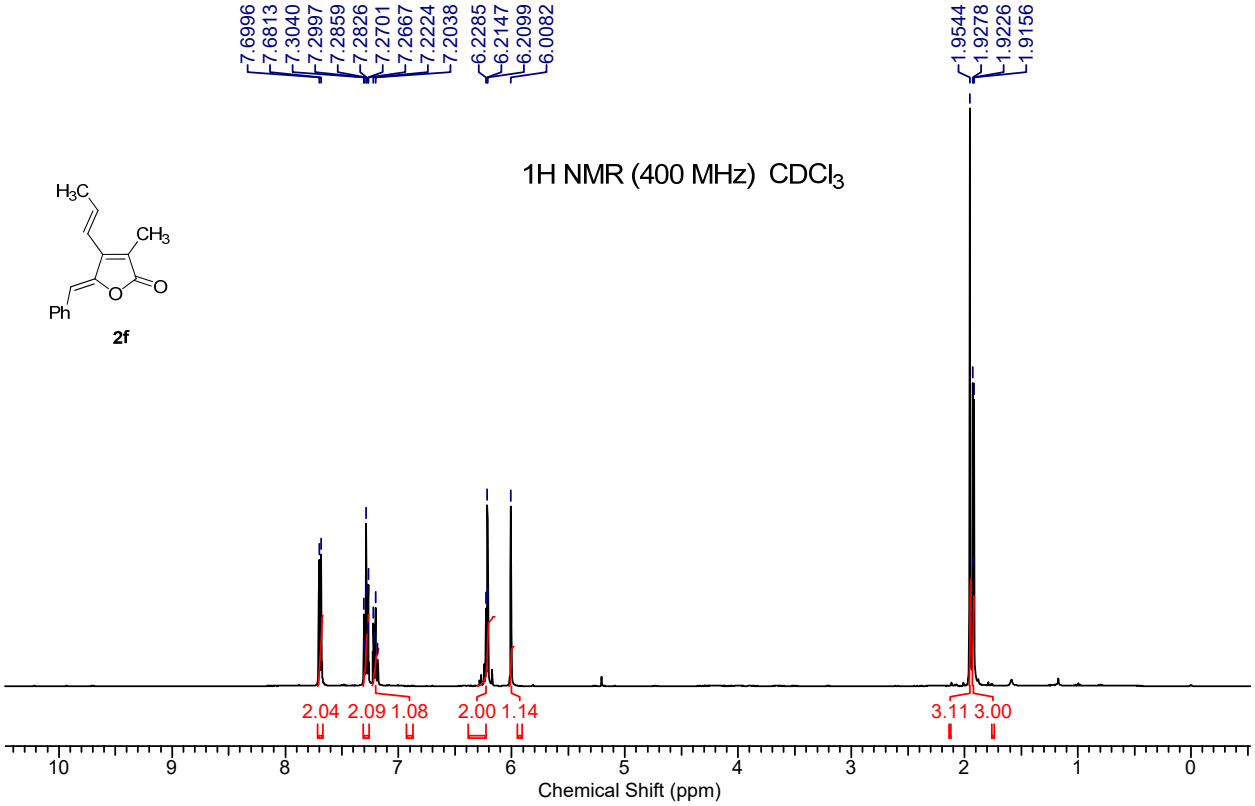
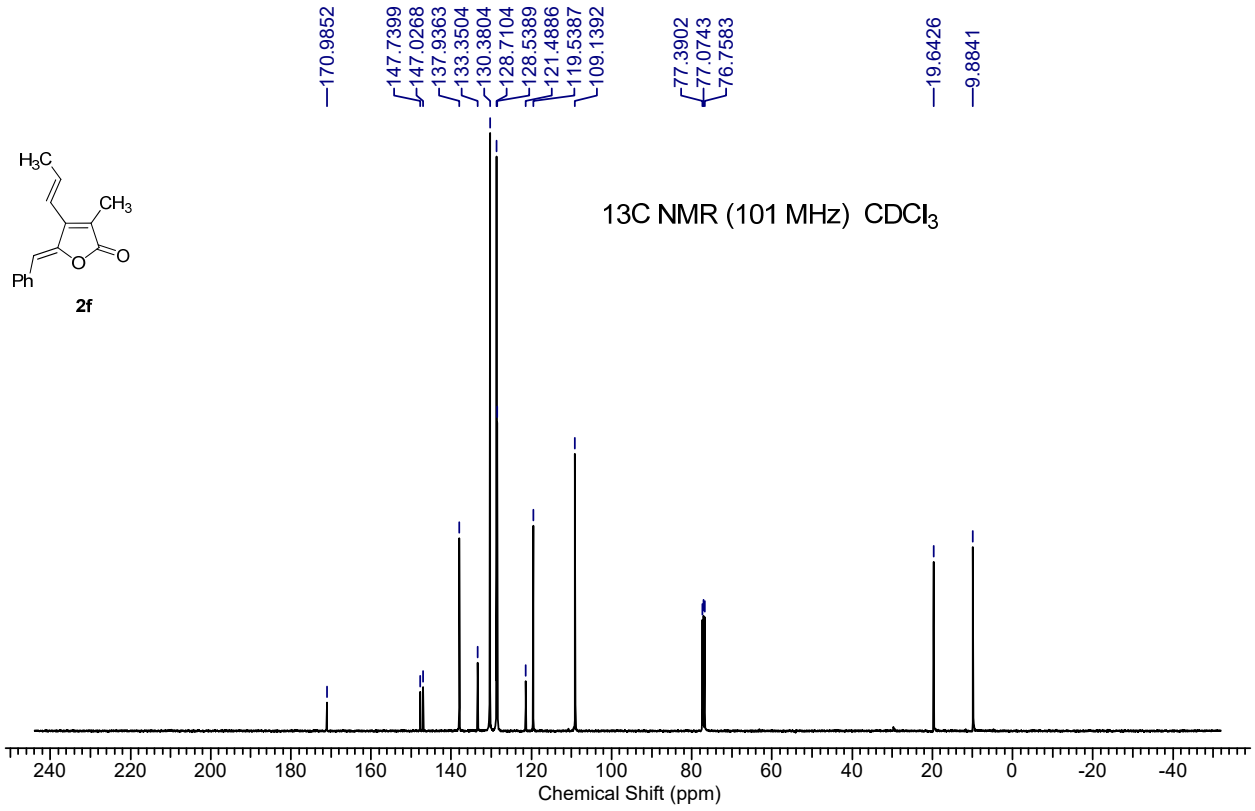
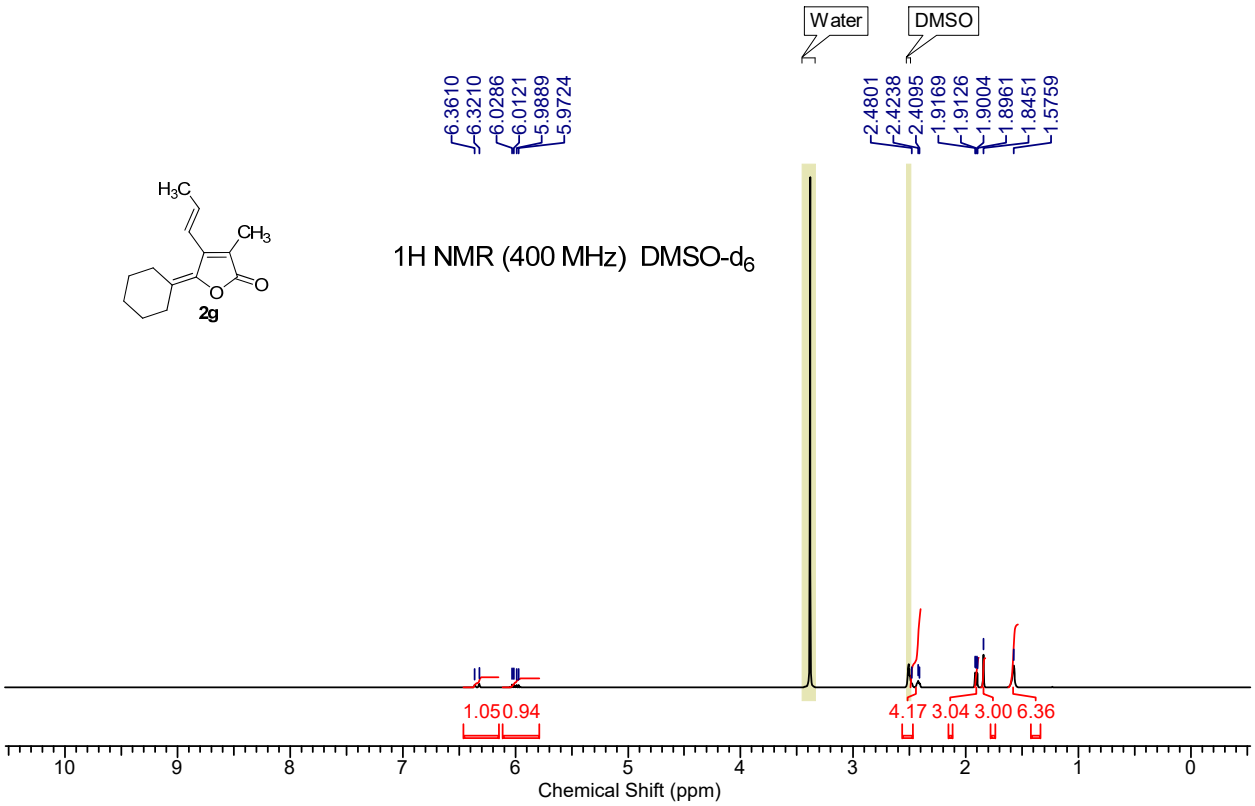
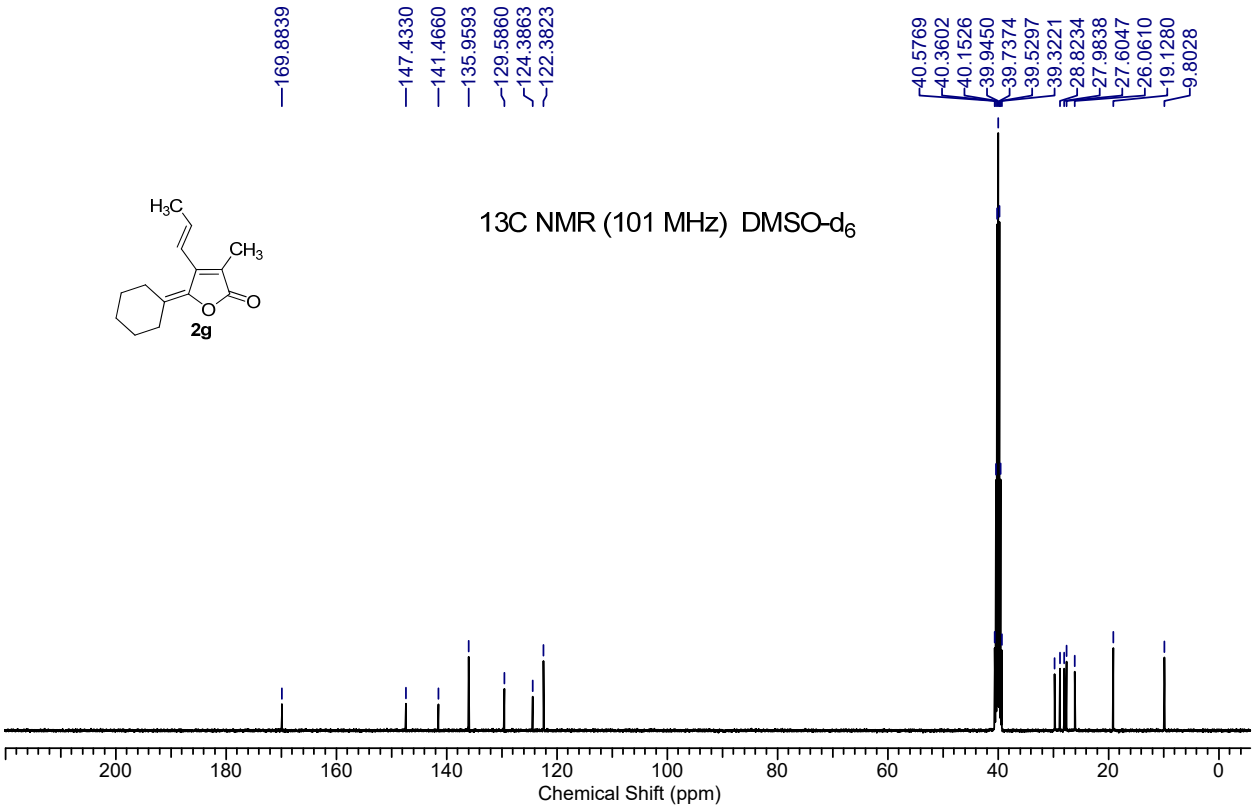
6.2275
6.2122
6.2033
6.1875
6.1719
6.1575
6.1358
6.0943
5.1403
5.1161
2.6933
2.6741
2.6652
2.6325
1.9199
1.8976
1.8961
1.8823
1.6788
1.6697
1.6617
1.6452
1.2486
1.1307
1.0967
1.0647
H3C
CH3
O
O
Cy
2e
1H NMR (400 MHz) CDCl3
2.00
1.01
0.99
3.05
3.00
4.73
6.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


171.14
147.10
145.52
137.30
121.77
119.82
117.56
77.29
77.03
76.78
35.61
32.84
25.87
25.62
19.58
9.69
H3C
CH3
O
O
Cy
2e
13C NMR (101 MHz) CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.6996
7.6813
7.3040
7.2997
7.2859
7.2826
7.2701
7.2667
7.2224
7.2038
6.2285
6.2147
6.2099
6.0082
1.9544
1.9278
1.9226
1.9156
1H NMR (400 MHz) CDCl3
H3C
CH3
O
O
Ph
2f
2.04 2.09 1.08 2.00 1.14
3.11 3.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


170.9852
147.7399
147.0268
137.9363
133.3504
130.3804
128.7104
128.5389
121.4886
119.5387
109.1392
77.3902
77.0743
76.7583
19.6426
9.8841
13C NMR (101 MHz) CDCl3
H3C
CH3
O
O
Ph
2f
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40
Chemical Shift (ppm)


Water
DMSO
6.3610
6.3210
6.0286
6.0121
5.9889
5.9724
2.4801
2.4238
2.4095
1.9169
1.9126
1.9004
1.8961
1.8451
1.5759
H3C
CH3
O
O
2g
1H NMR (400 MHz) DMSO-d6
1.05 0.94
4.17 3.04 3.00 6.36
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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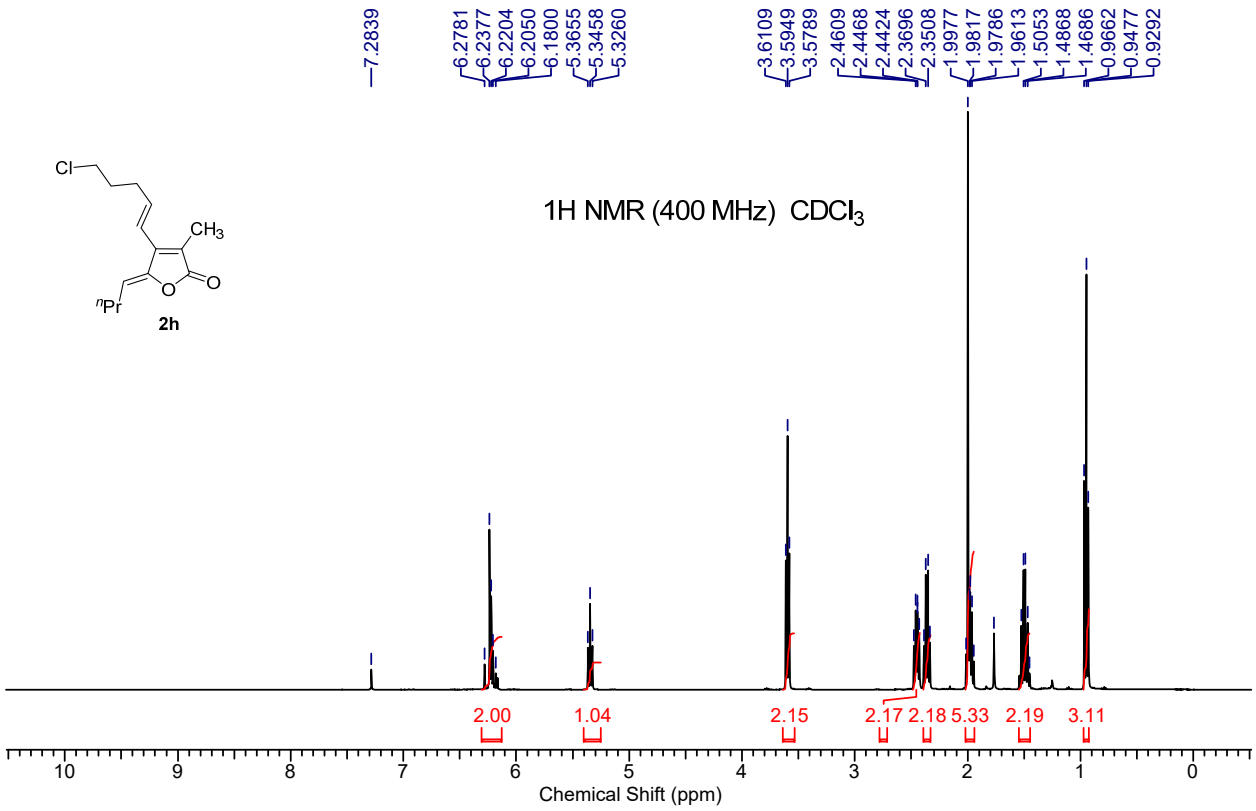
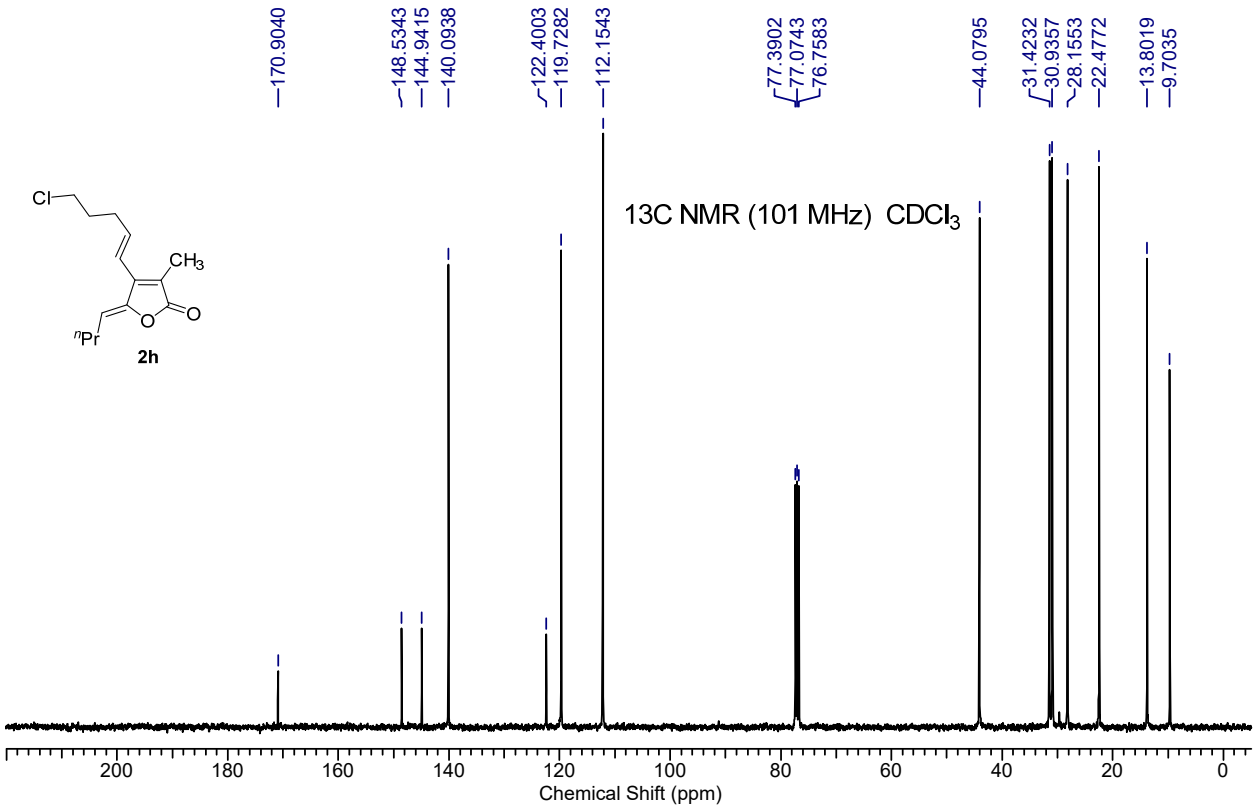
147.4330
141.4660
135.9593
129.5860
124.3863
122.3823
40.5769
40.3602
40.1526
39.9450
39.7374
39.5297
39.3221
28.8234
27.9838
27.6047
26.0610
19.1280
9.8028
H3C
CH3
O
O
2g
13C NMR (101 MHz) DMSO-d6
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)


7.2839
6.2781
6.2377
6.2204
6.2050
6.1800
5.3655
5.3458
5.3260
3.6109
3.5949
3.5789
2.4609
2.4468
2.4424
2.3696
2.3508
1.9977
1.9817
1.9786
1.9613
1.5053
1.4868
1.4686
0.9662
0.9477
0.9292
1H NMR (400 MHz) CDCl3
Cl
CH3
O
O
nPr
2h
2.00
1.04
2.15
2.17
2.18
5.33
2.19
3.11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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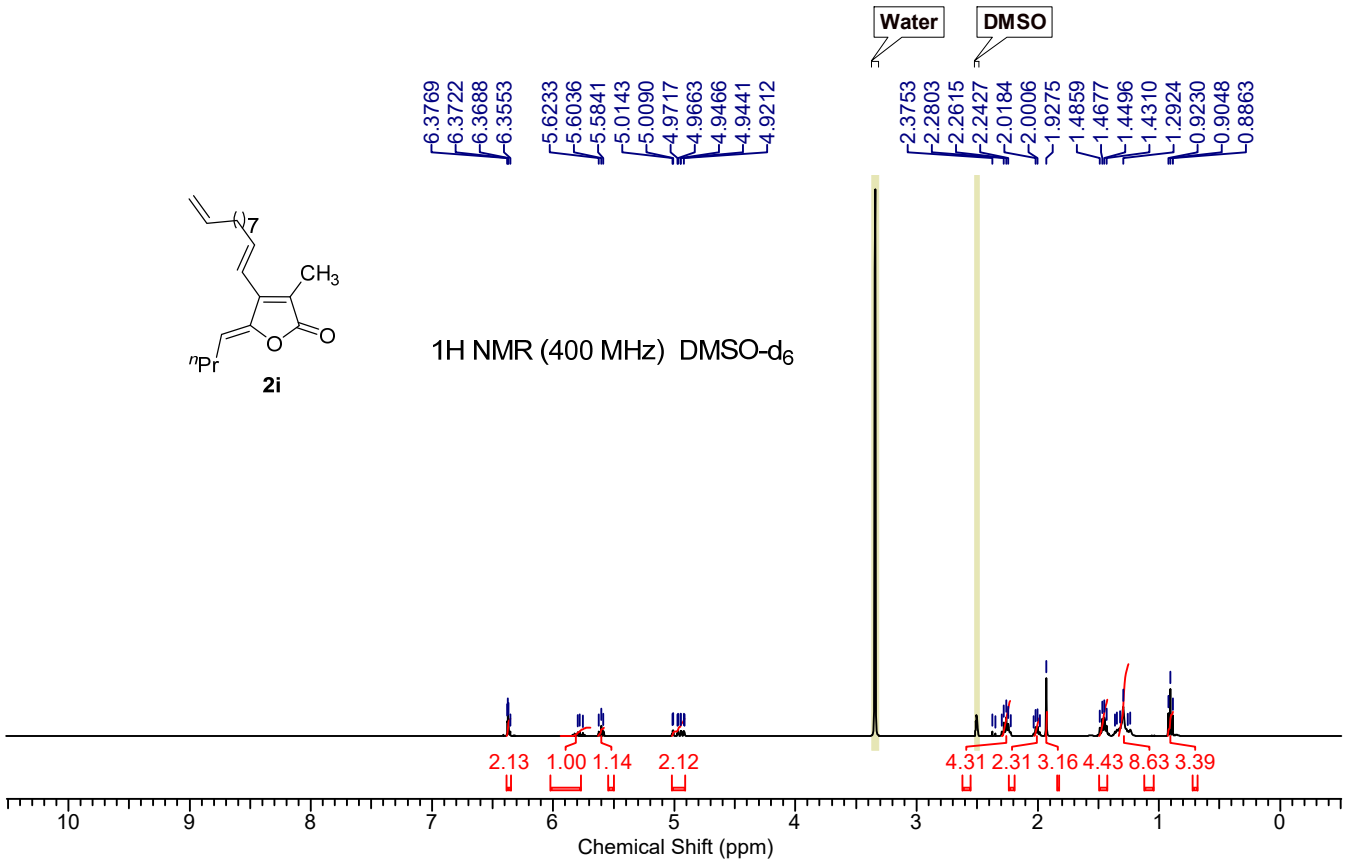
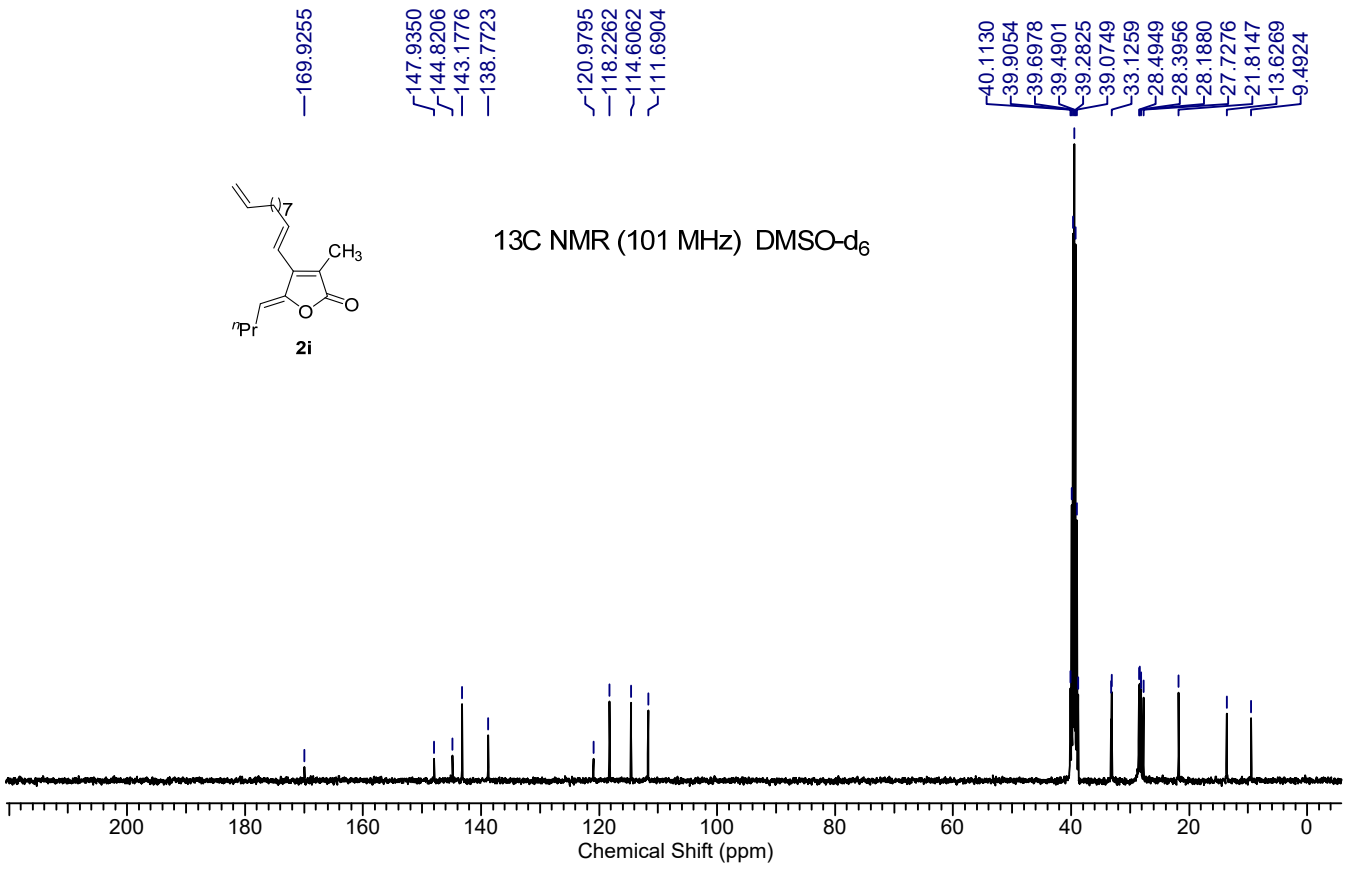
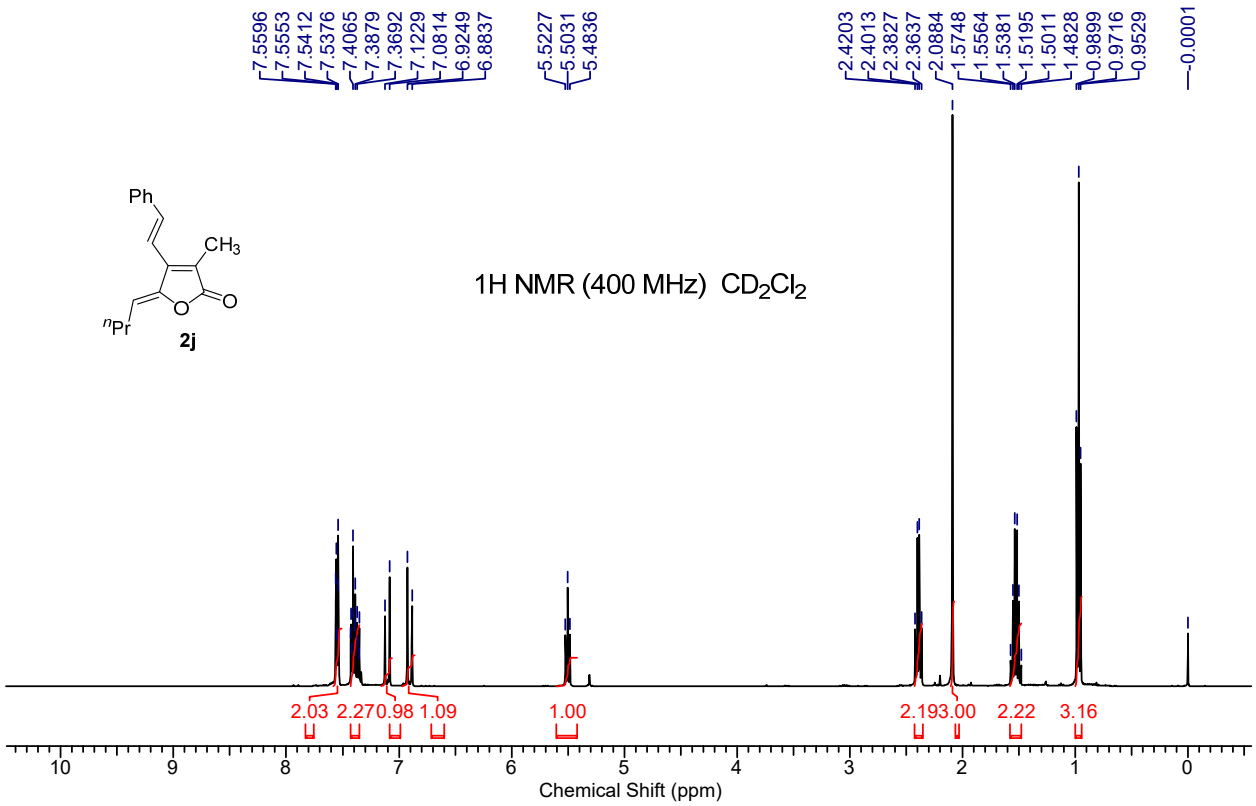
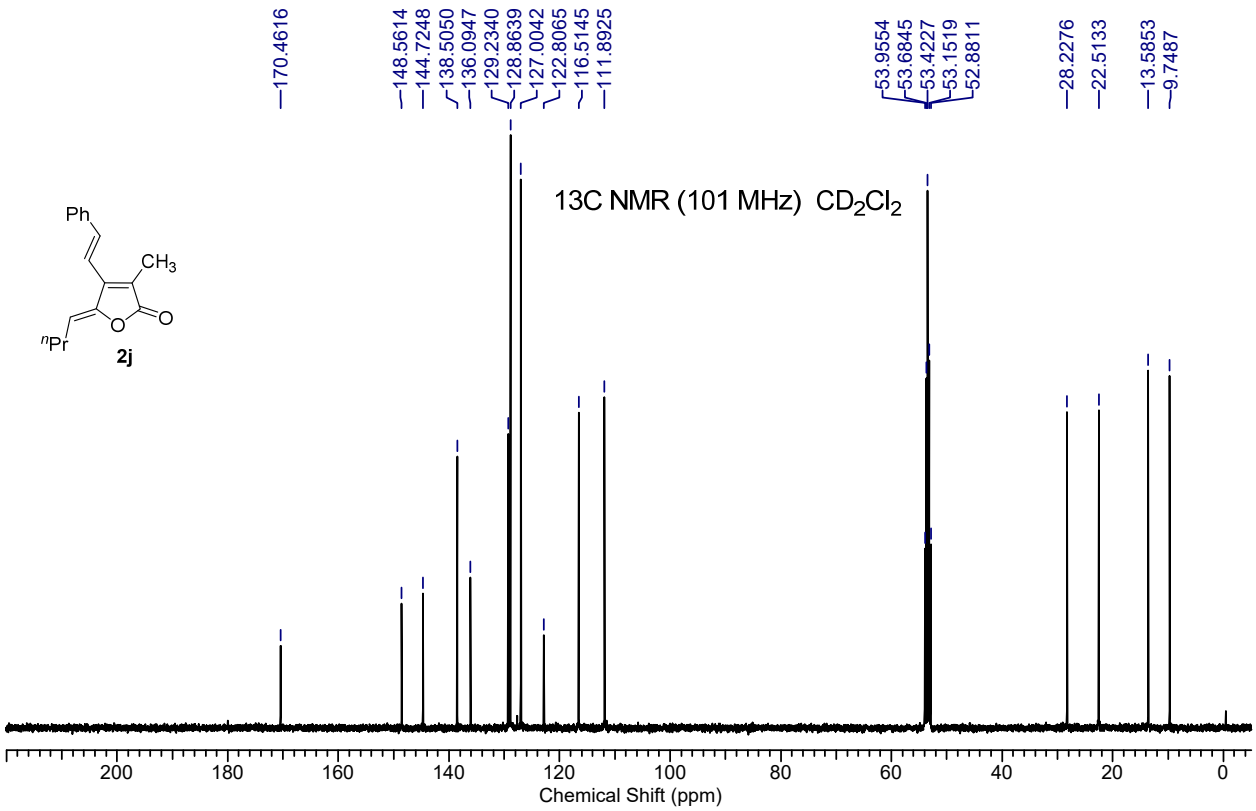
148.5343
144.9415
140.0938
122.4003
119.7282
112.1543
77.3902
77.0743
76.7583
44.0795
31.4232
30.9357
28.1553
22.4772
13.8019
9.7035
13C NMR (101 MHz) CDCl3
Cl
CH3
O
O
nPr
2h
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


Water
DMSO
6.3769
6.3722
6.3688
6.3553
5.6233
5.6036
5.5841
5.0143
5.0090
4.9717
4.9663
4.9466
4.9441
4.9212
2.3753
2.2803
2.2615
2.2427
2.0184
2.0006
1.9275
1.4859
1.4677
1.4496
1.4310
1.2924
0.9230
0.9048
0.8863
CH3
O
O
nPr
2i
1H NMR (400 MHz) DMSO-d6
2.13
1.00
1.14
2.12
4.31
2.31
3.16
4.43
8.63
3.39
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


169.9255
147.9350
144.8206
143.1776
138.7723
120.9795
118.2262
114.6062
111.6904
40.1130
39.9054
39.6978
39.4901
39.2825
39.0749
33.1259
28.4949
28.3956
28.1880
27.7276
21.8147
13.6269
9.4924
CH3
O
O
nPr
2i
13C NMR (101 MHz) DMSO-d6
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.5596
7.5553
7.5412
7.5376
7.4065
7.3879
7.3692
7.1229
7.0814
6.9249
6.8837
5.5227
5.5031
5.4836
2.4203
2.4013
2.3827
2.3637
2.0884
1.5748
1.5564
1.5381
1.5195
1.5011
1.4828
0.9899
0.9716
0.9529
0.0001
Ph
CH3
O
O
nPr
2j
1H NMR (400 MHz) CD2Cl2
2.03
2.27
0.98
1.09
1.00
2.19
3.00
2.22
3.16
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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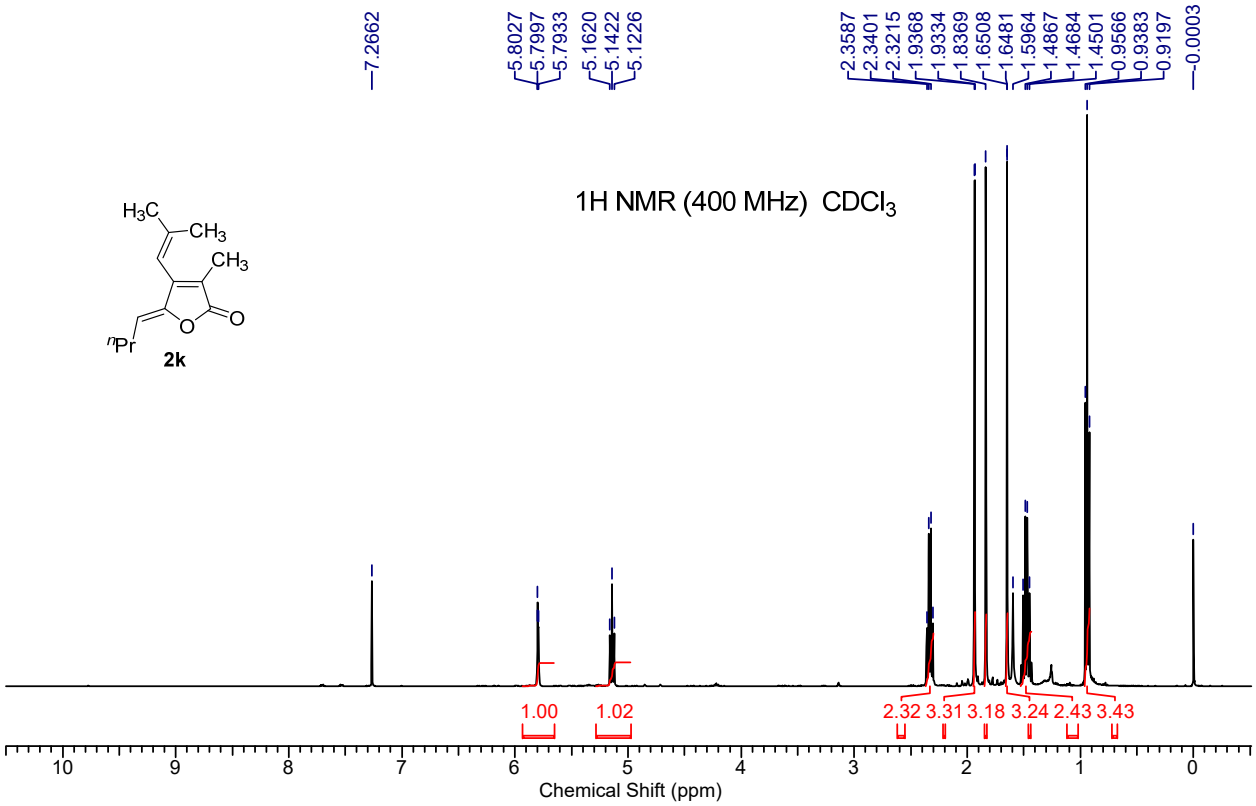
148.5614
144.7248
138.5050
136.0947
129.2340
128.8639
127.0042
122.8065
116.5145
111.8925
53.9554
53.6845
53.4227
53.1519
52.8811
28.2276
22.5133
13.5853
9.7487
Ph
CH3
O
O
nPr
2j
13C NMR (101 MHz) CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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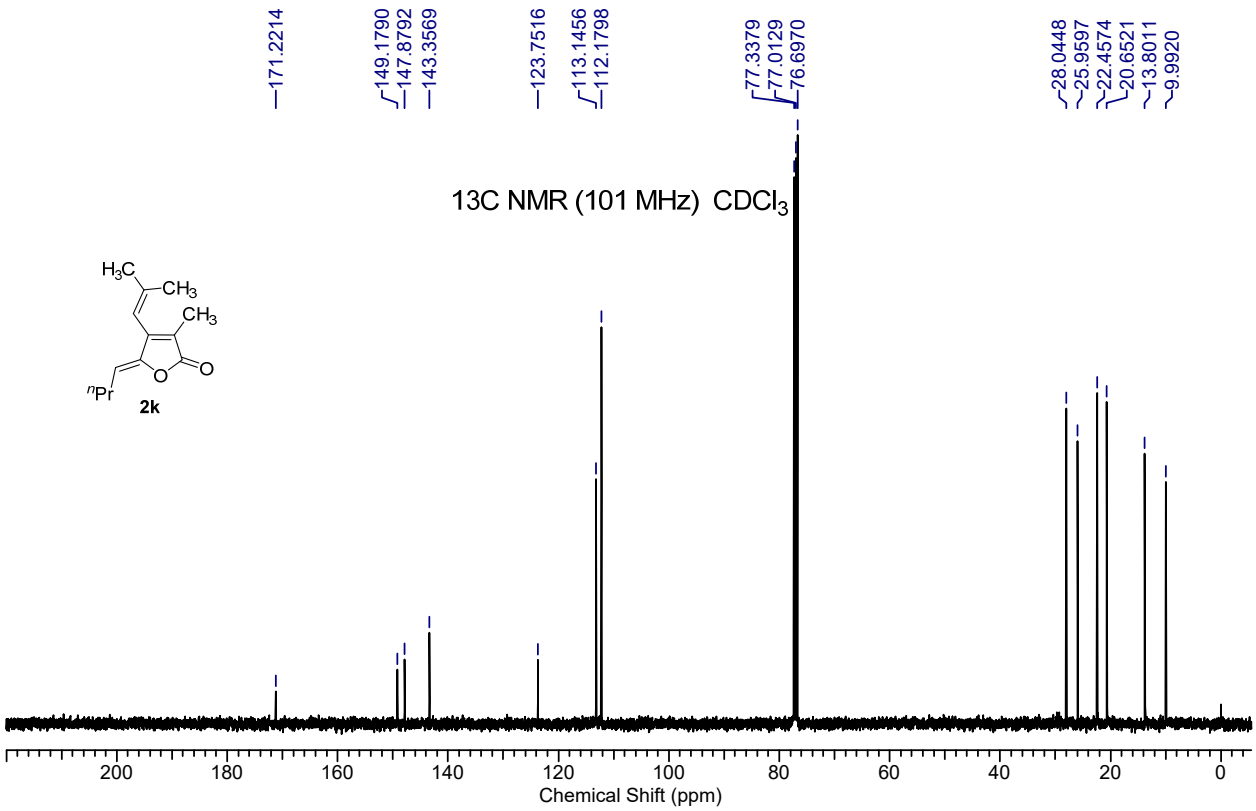
5.8027
5.7997
5.7933
5.1620
5.1422
5.1226
2.3587
2.3401
2.3215
1.9368
1.9334
1.8369
1.6508
1.6481
1.5964
1.4867
1.4684
1.4501
0.9566
0.9383
0.9197
0.0003
1H NMR (400 MHz) CDCl3
H3C
CH3
CH3
O
O
nPr
2k
1.00
1.02
2.32 3.31 3.18 3.24 2.43 3.43
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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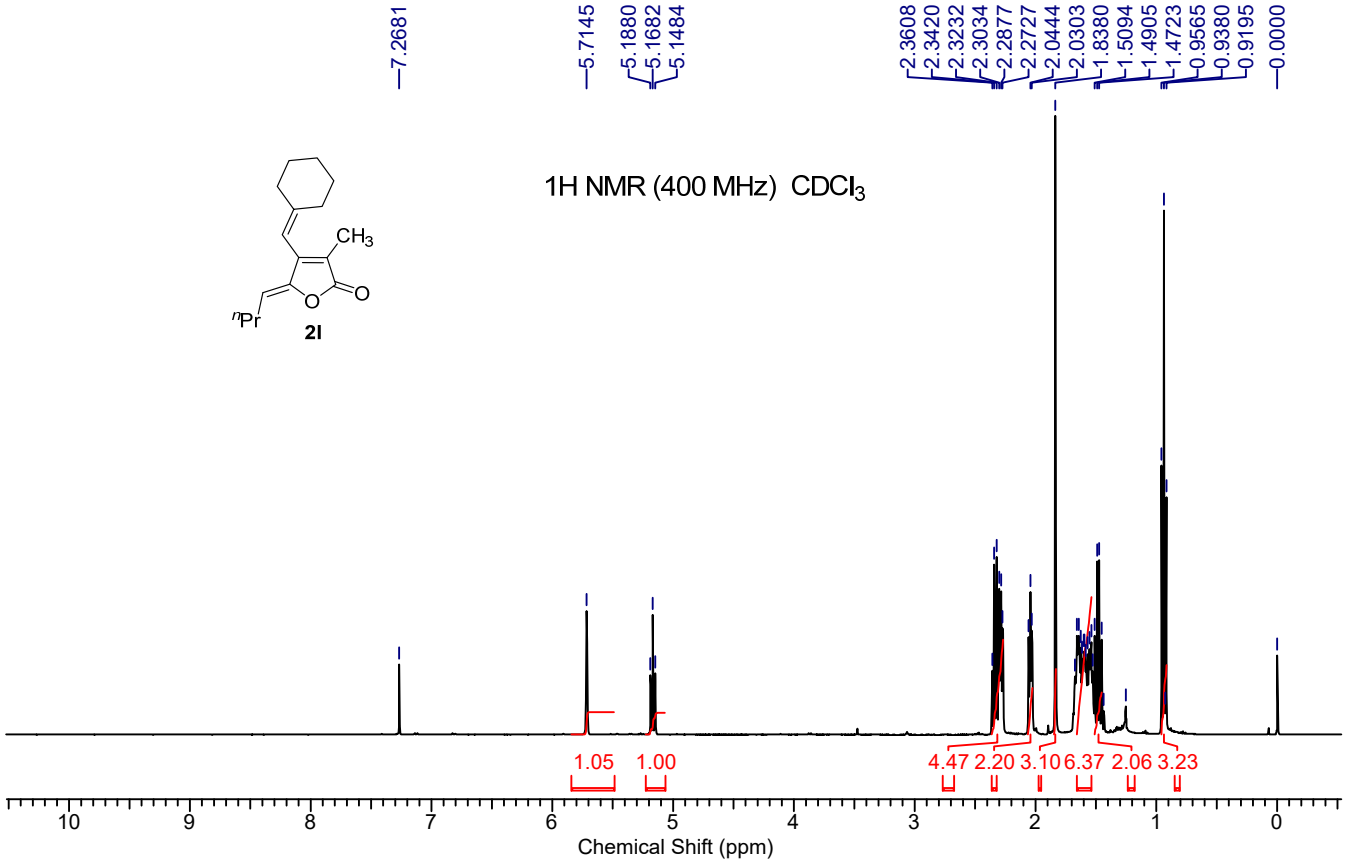
147.8792
143.3569
123.7516
113.1456
112.1798
77.3379
77.0129
76.6970
28.0448
25.9597
22.4574
20.6521
13.8011
9.9920
13C NMR (101 MHz) CDCl3
H3C
CH3
CH3
O
O
nPr
2k
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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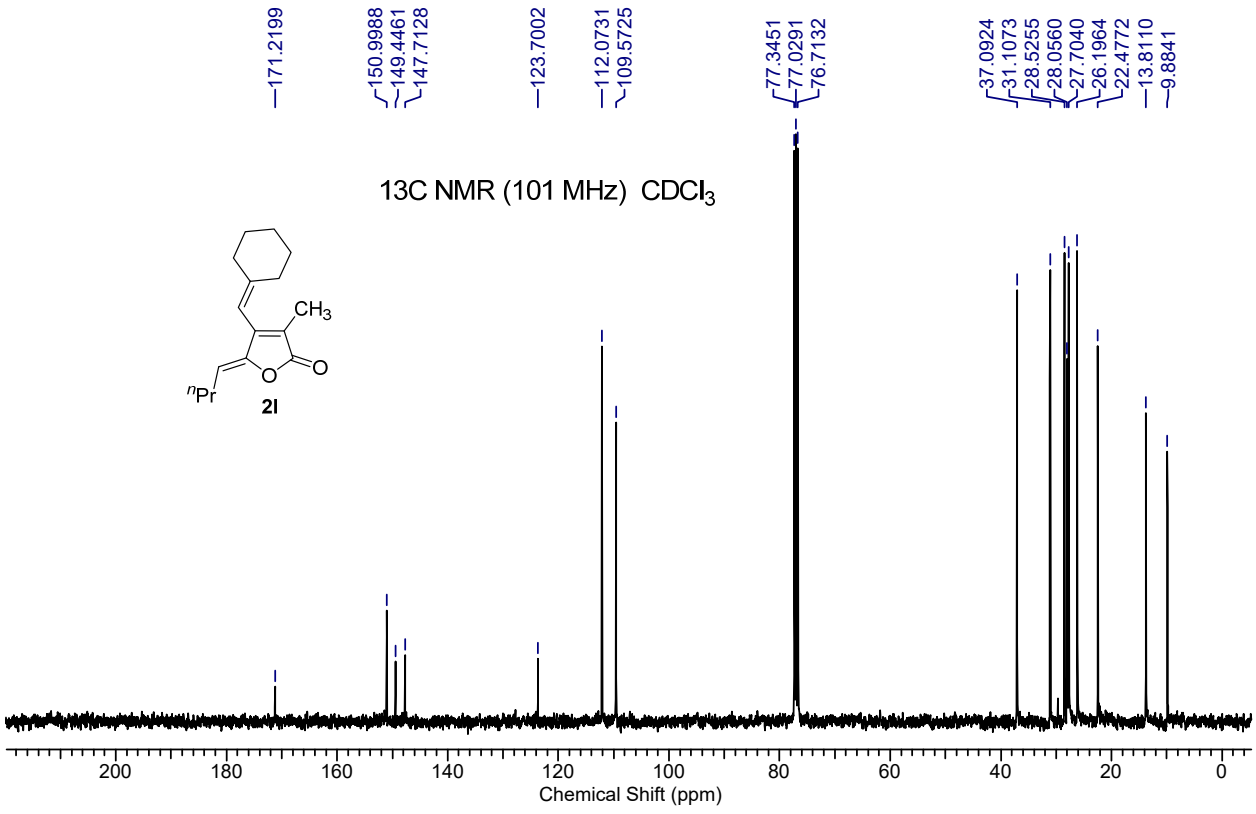
5.1880
5.1682
5.1484
2.3608
2.3420
2.3232
2.3034
2.2877
2.2727
2.0444
2.0303
1.8380
1.5094
1.4905
1.4723
0.9565
0.9380
0.9195
0.0000
1H NMR (400 MHz) CDCl3
CH3
O
O
nPr
2l
1.05
1.00
4.47
2.20
3.10
6.37
2.06
3.23
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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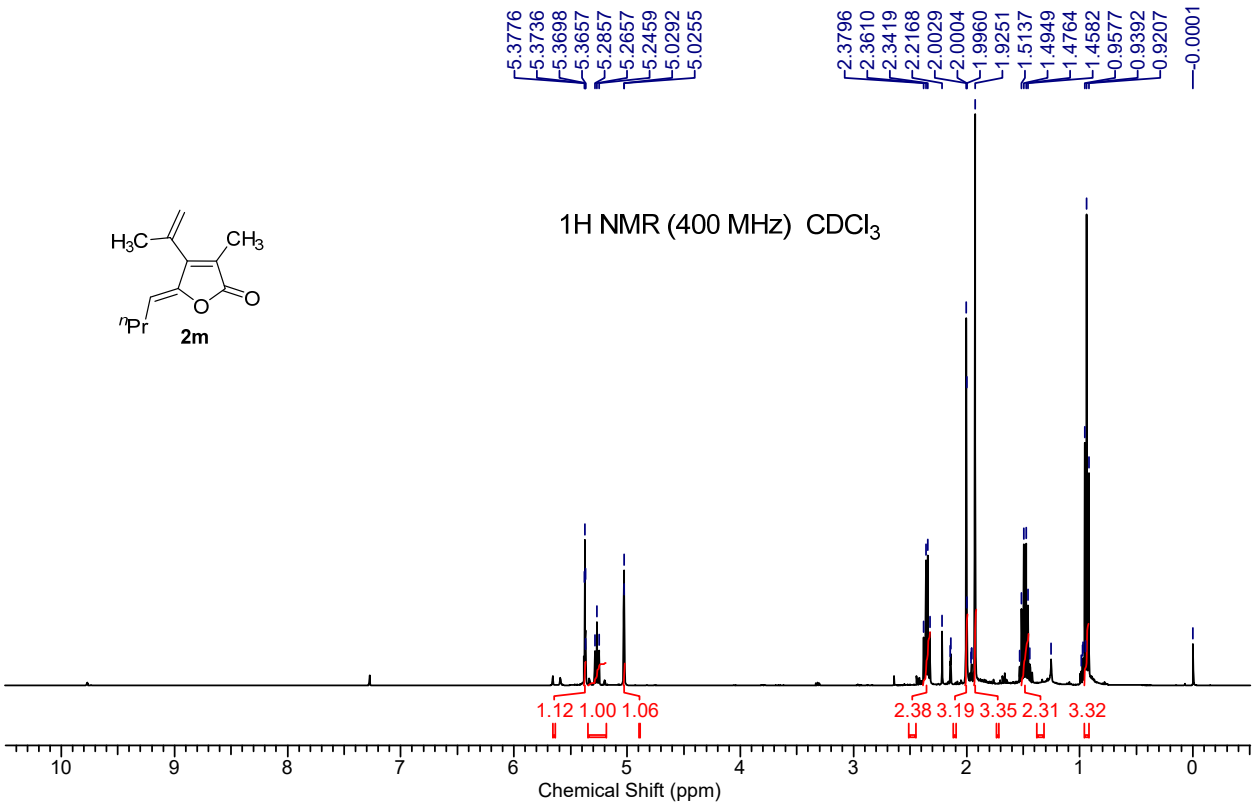
149.4461
147.7128
123.7002
112.0731
109.5725
77.3451
77.0291
76.7132
37.0924
31.1073
28.5255
28.0560
27.7040
26.1964
22.4772
13.8110
9.8841
13C NMR (101 MHz) CDCl3
CH3
O
O
nPr
2l
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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5.3657
5.2857
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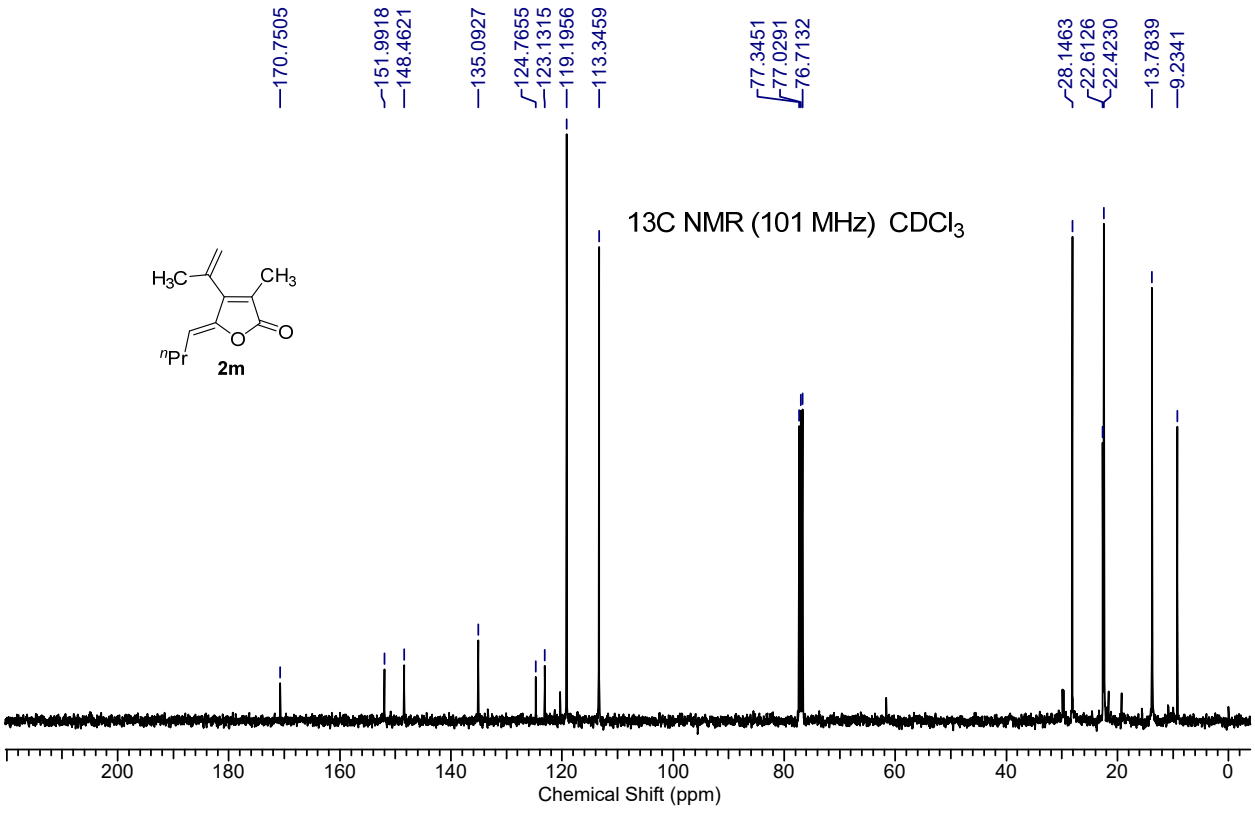
5.2459
5.0292
5.0255
2.3796
2.3610
2.3419
2.2168
2.0029
2.0004
1.9960
1.9251
1.5137
1.4949
1.4764
1.4582
0.9577
0.9392
0.9207
0.0001
1H NMR (400 MHz) CDCl3
H3C
CH3
O
O
nPr
2m
1.12 1.00 1.06
2.38 3.19 3.35 2.31 3.32
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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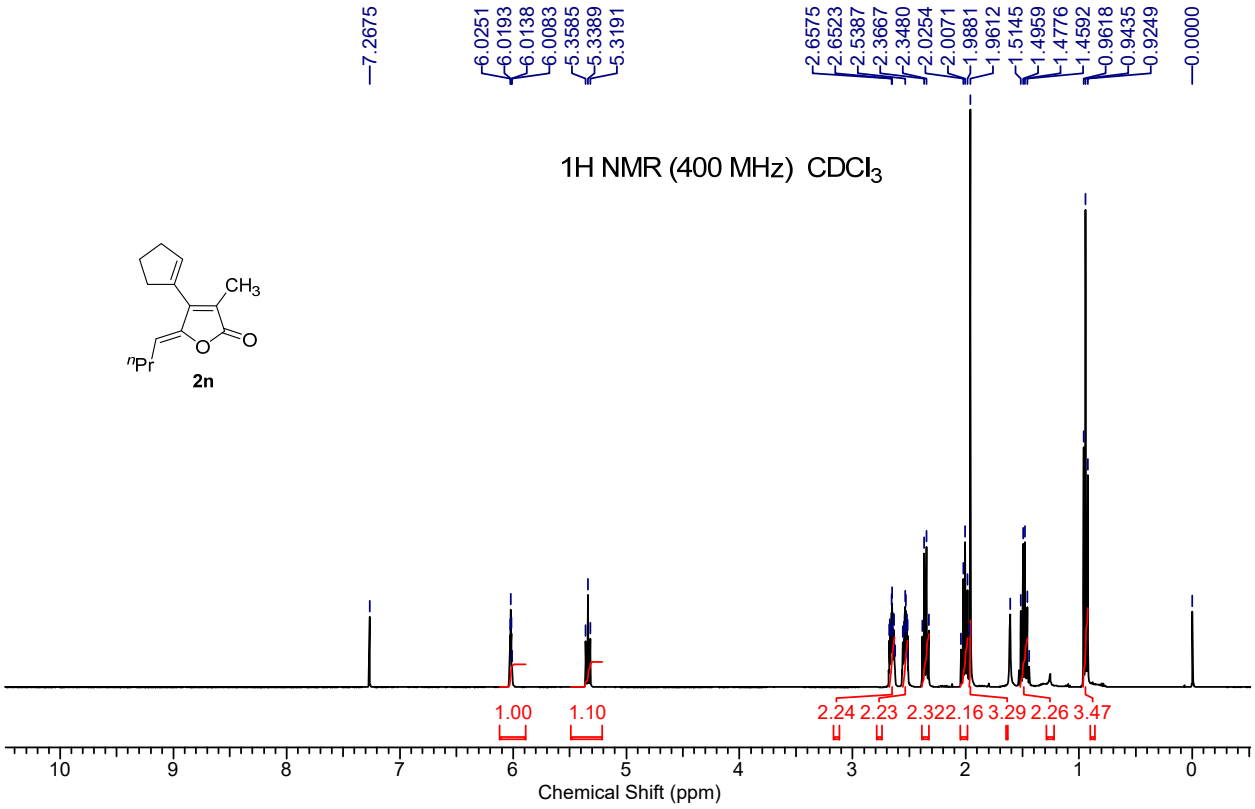
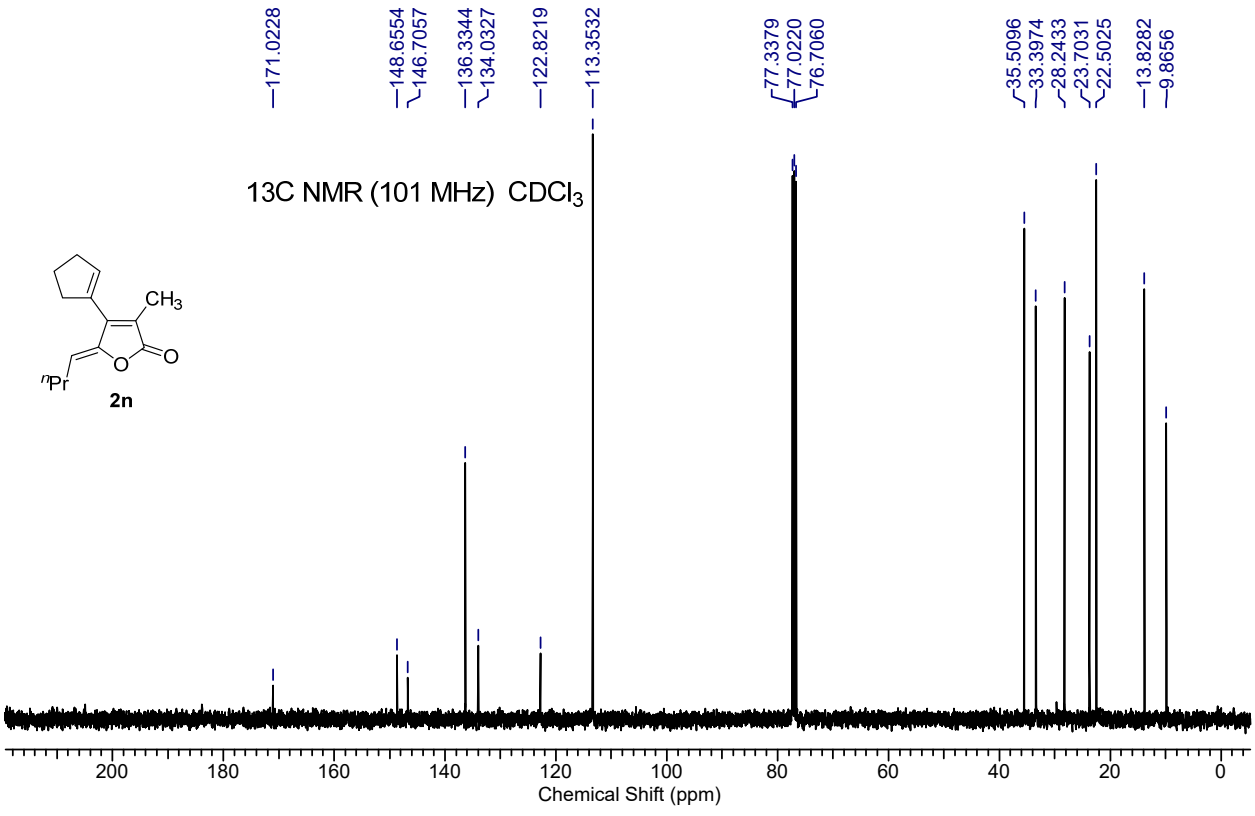
148.4621
135.0927
124.7655
123.1315
119.1956
113.3459
77.3451
77.0291
76.7132
28.1463
22.6126
22.4230
13.7839
9.2341
13C NMR (101 MHz) CDCl3
H3C
CH3
O
O
nPr
2m
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.2675
6.0251
6.0193
6.0138
6.0083
5.3585
5.3389
5.3191
2.6575
2.6523
2.5387
2.3667
2.3480
2.0254
2.0071
1.9881
1.9612
1.5145
1.4959
1.4776
1.4592
0.9618
0.9435
0.9249
0.0000
1H NMR (400 MHz) CDCl3
CH3
O
O
nPr
2n
1.00
1.10
2.24
2.23
2.32
2.16
3.29
2.26
3.47
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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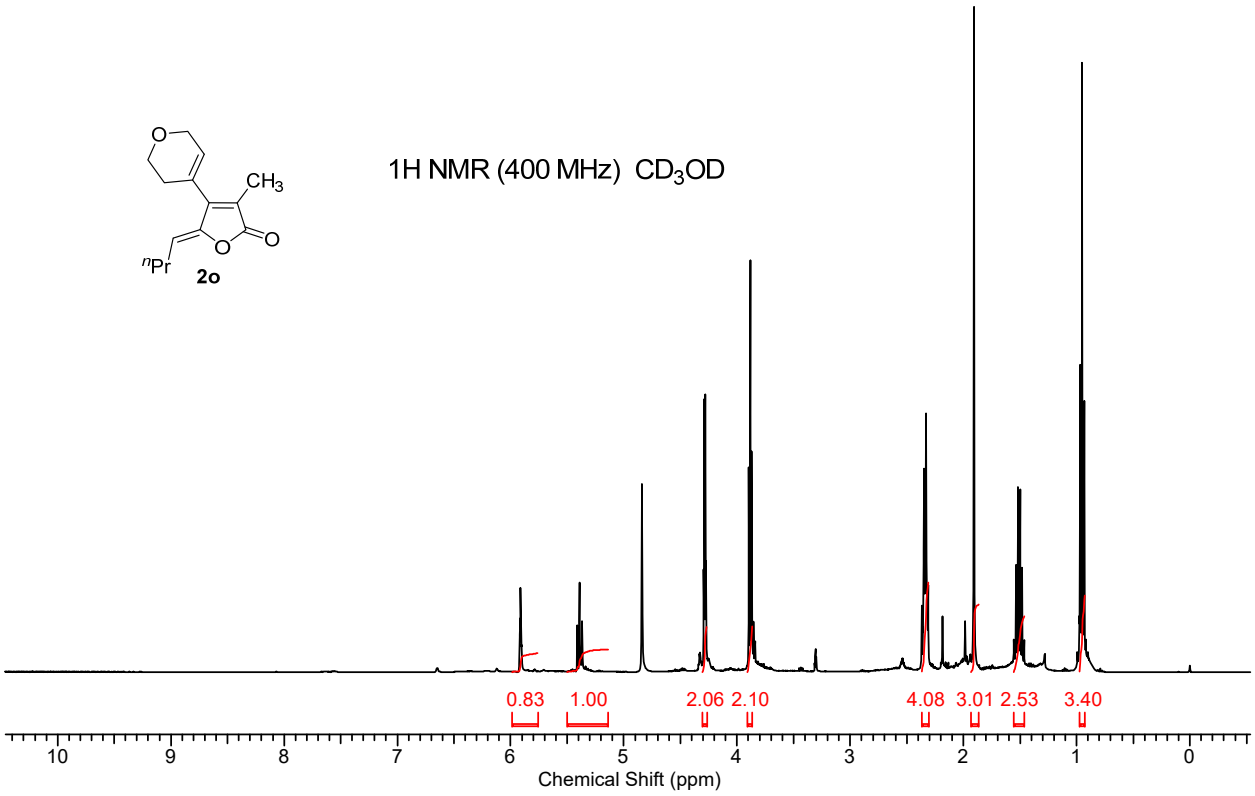
148.6554
146.7057
136.3344
134.0327
122.8219
113.3532
77.3379
77.0220
76.7060
35.5096
33.3974
28.2433
23.7031
22.5025
13.8282
9.8656
13C NMR (101 MHz) CDCl3
CH3
O
O
nPr
2n
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


1H NMR (400 MHz) CD3OD
2o
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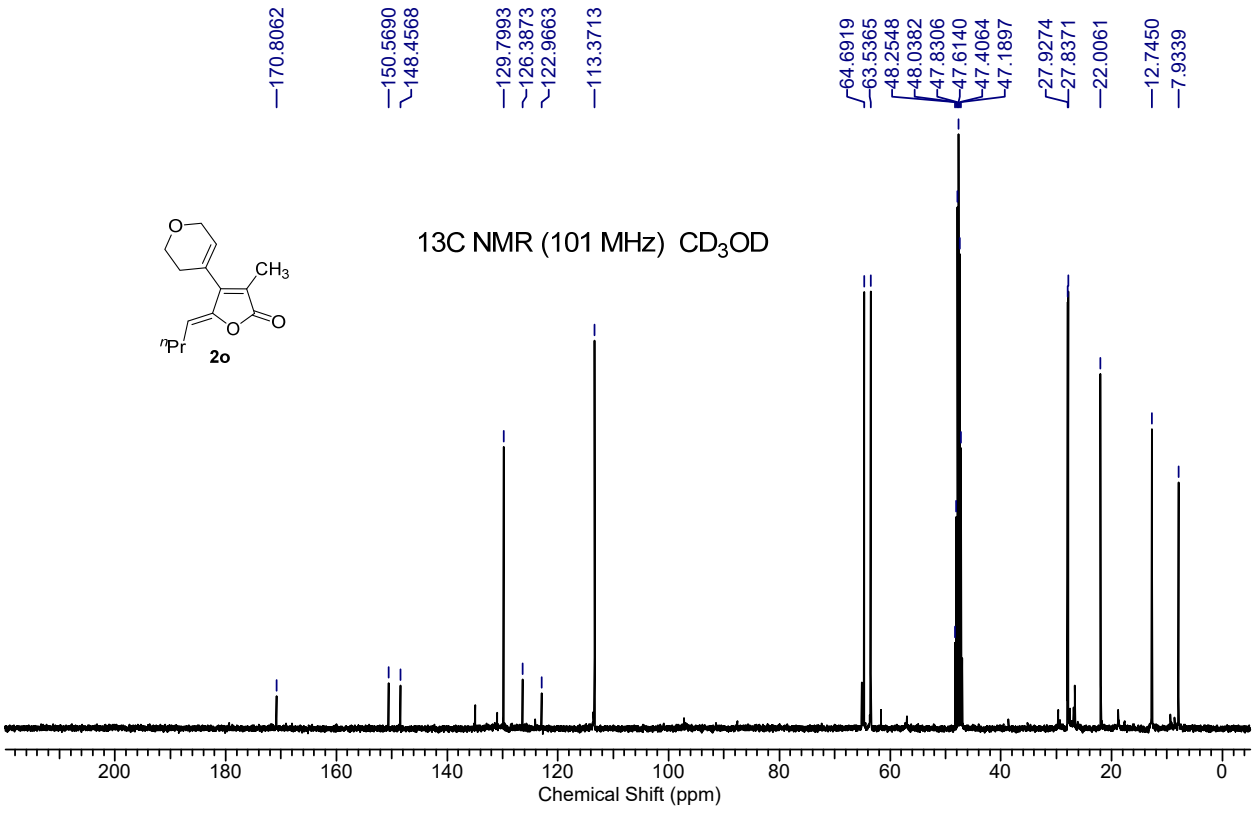
1.00
2.06
2.10
4.08
3.01
2.53
3.40
Chemical Shift (ppm)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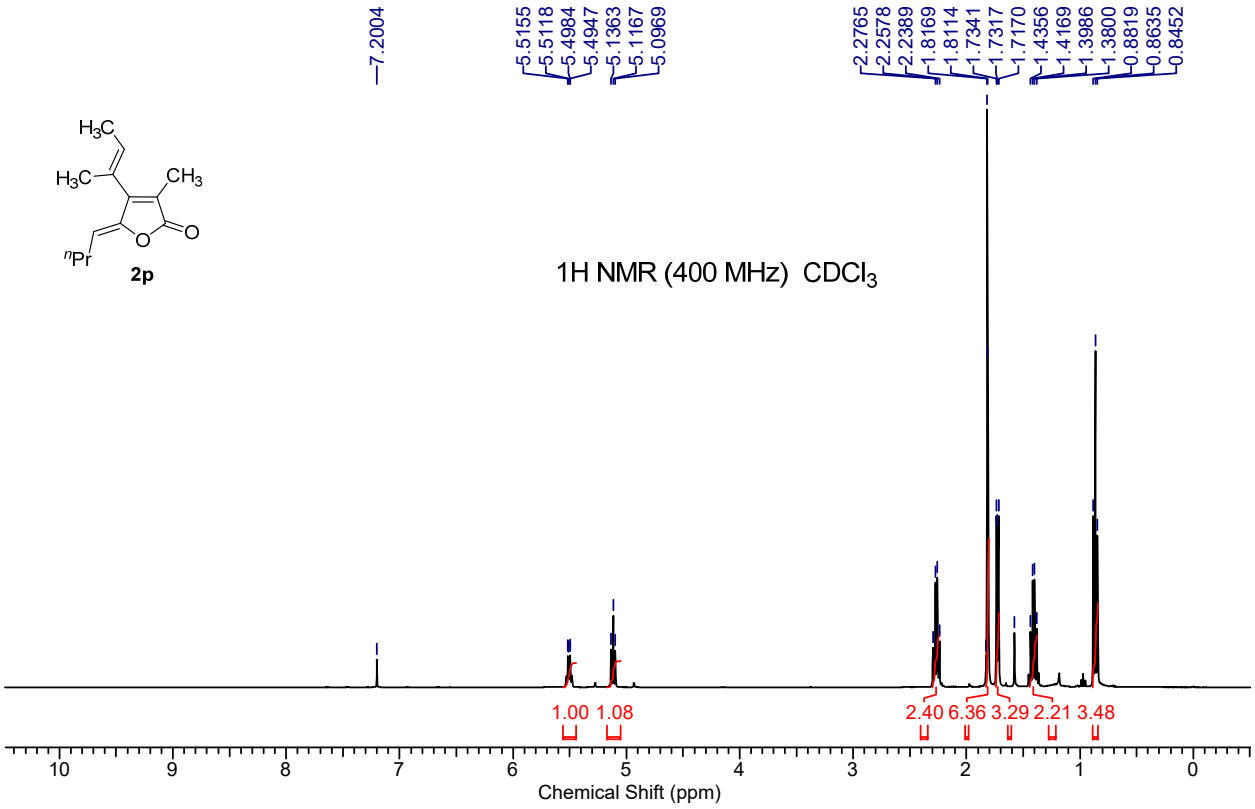
150.5690
148.4568
129.7993
126.3873
122.9663
113.3713
64.6919
63.5365
48.2548
48.0382
47.8306
47.6140
47.4064
47.1897
27.9274
27.8371
22.0061
12.7450
7.9339
13C NMR (101 MHz) CD3OD
2o
Chemical Shift (ppm)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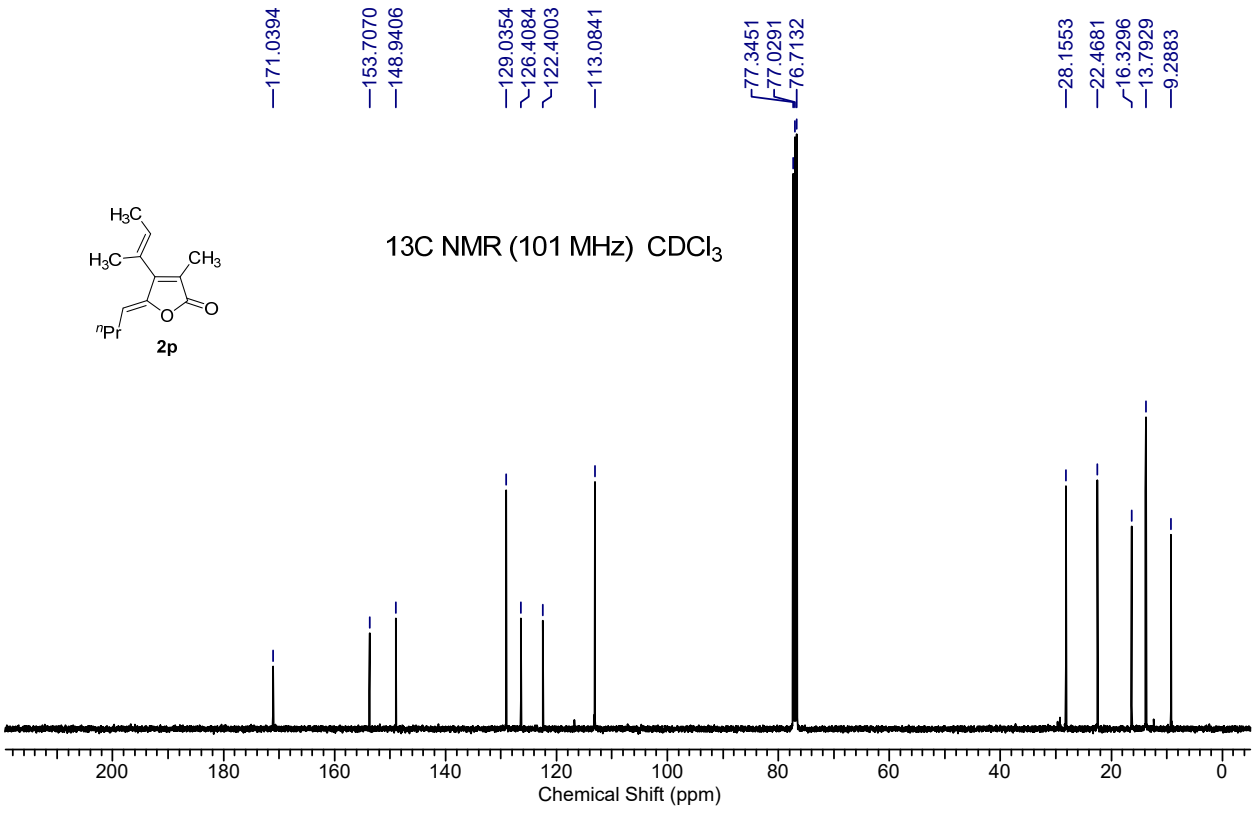
5.5155
5.5118
5.4984
5.4947
5.1363
5.1167
5.0969
2.2765
2.2578
2.2389
1.8169
1.8114
1.7341
1.7317
1.7170
1.4356
1.4169
1.3986
1.3800
0.8819
0.8635
0.8452
1H NMR (400 MHz) CDCl3
2p
1.00 1.08
2.40 6.36 3.29 2.21 3.48
Chemical Shift (ppm)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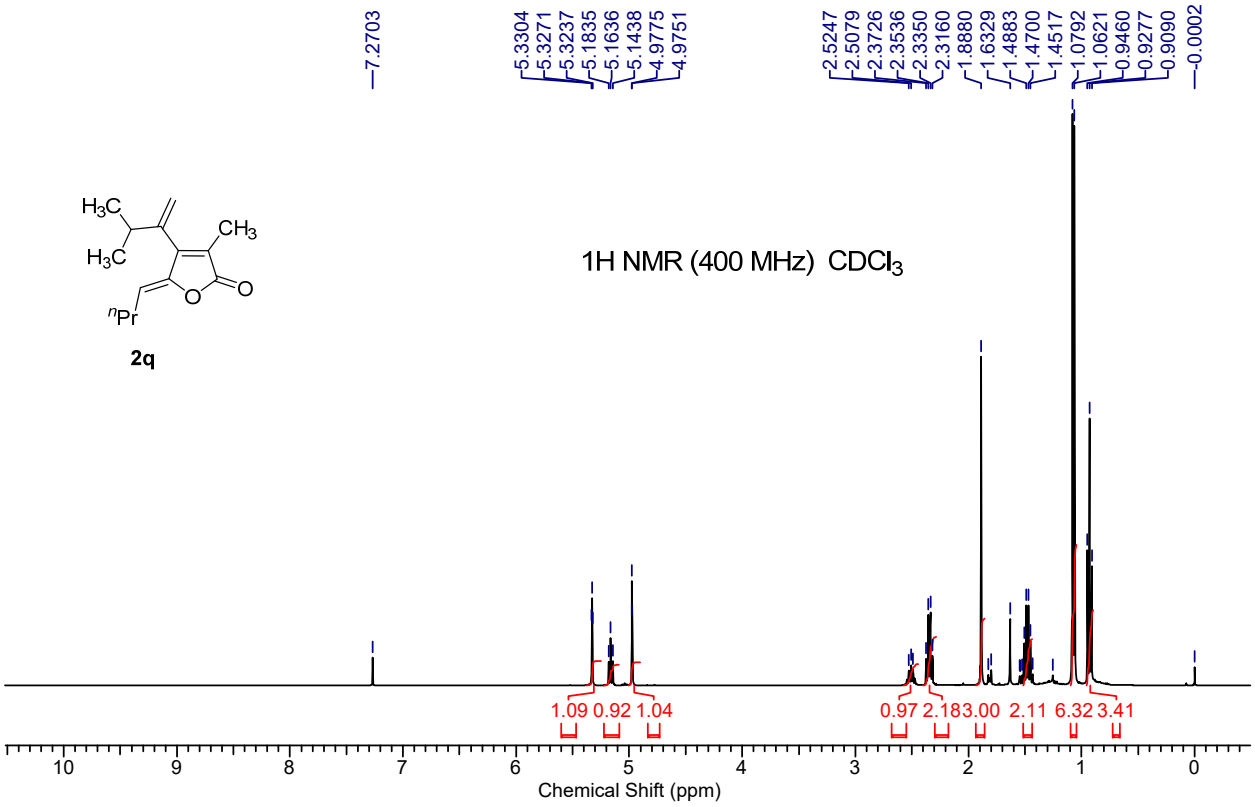
153.7070
148.9406
129.0354
126.4084
122.4003
113.0841
77.3451
77.0291
76.7132
28.1553
22.4681
16.3296
13.7929
9.2883
13C NMR (101 MHz) CDCl3
2p
Chemical Shift (ppm)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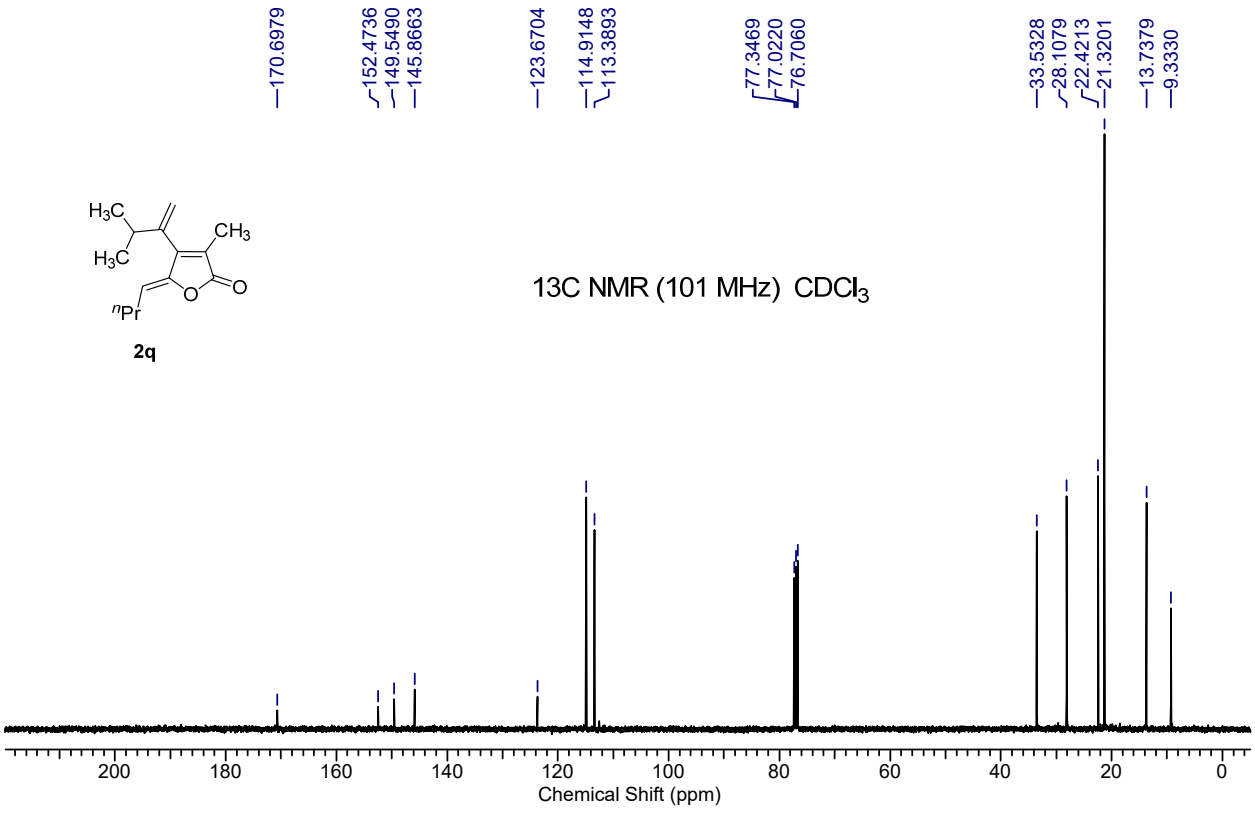
5.3304
5.3271
5.3237
5.1835
5.1636
5.1438
4.9775
4.9751
2.5247
2.5079
2.3726
2.3536
2.3350
2.3160
1.8880
1.6329
1.4883
1.4700
1.4517
1.0792
1.0621
0.9460
0.9277
0.9090
0.0002
1H NMR (400 MHz) CDCl3
2q
1.09 0.92 1.04
0.97 2.18 3.00 2.11 6.32 3.41
Chemical Shift (ppm)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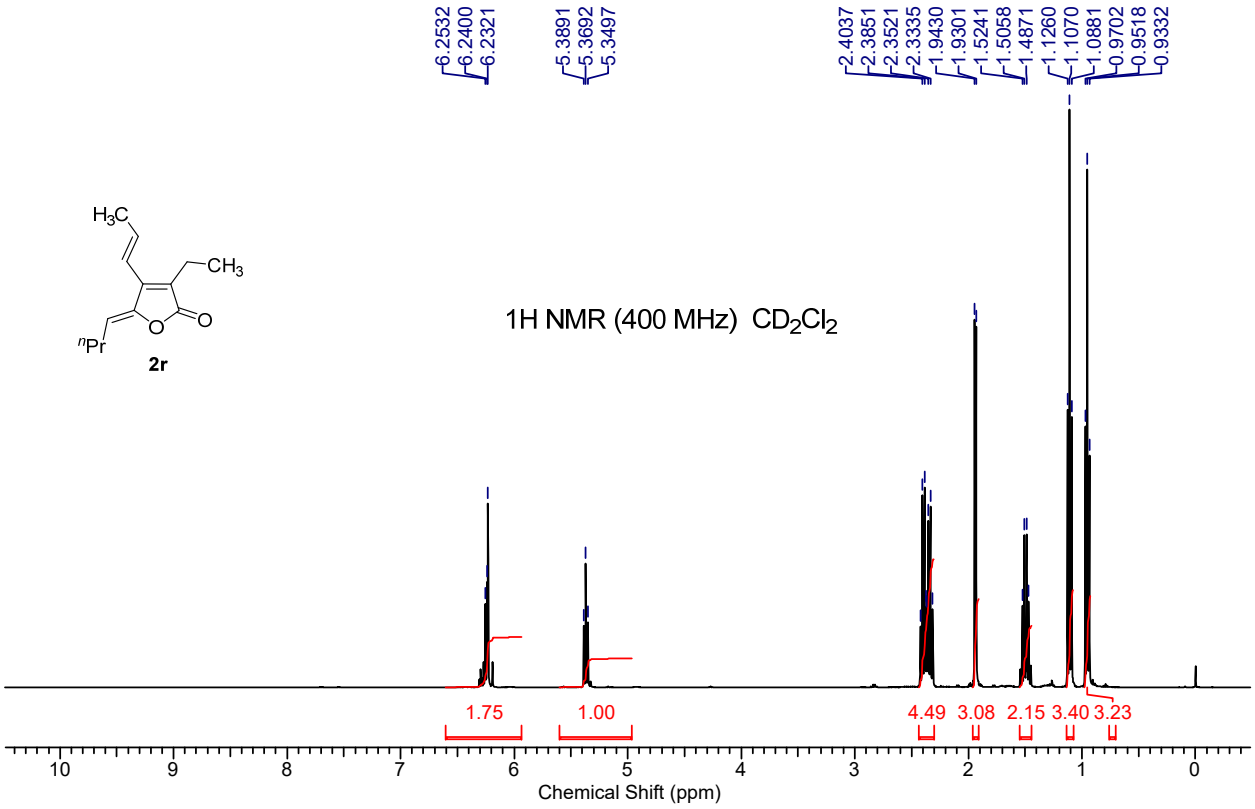
152.4736
149.5490
145.8663
123.6704
114.9148
113.3893
77.3469
77.0220
76.7060
33.5328
28.1079
22.4213
21.3201
13.7379
9.3330
13C NMR (101 MHz) CDCl3
2q
Chemical Shift (ppm)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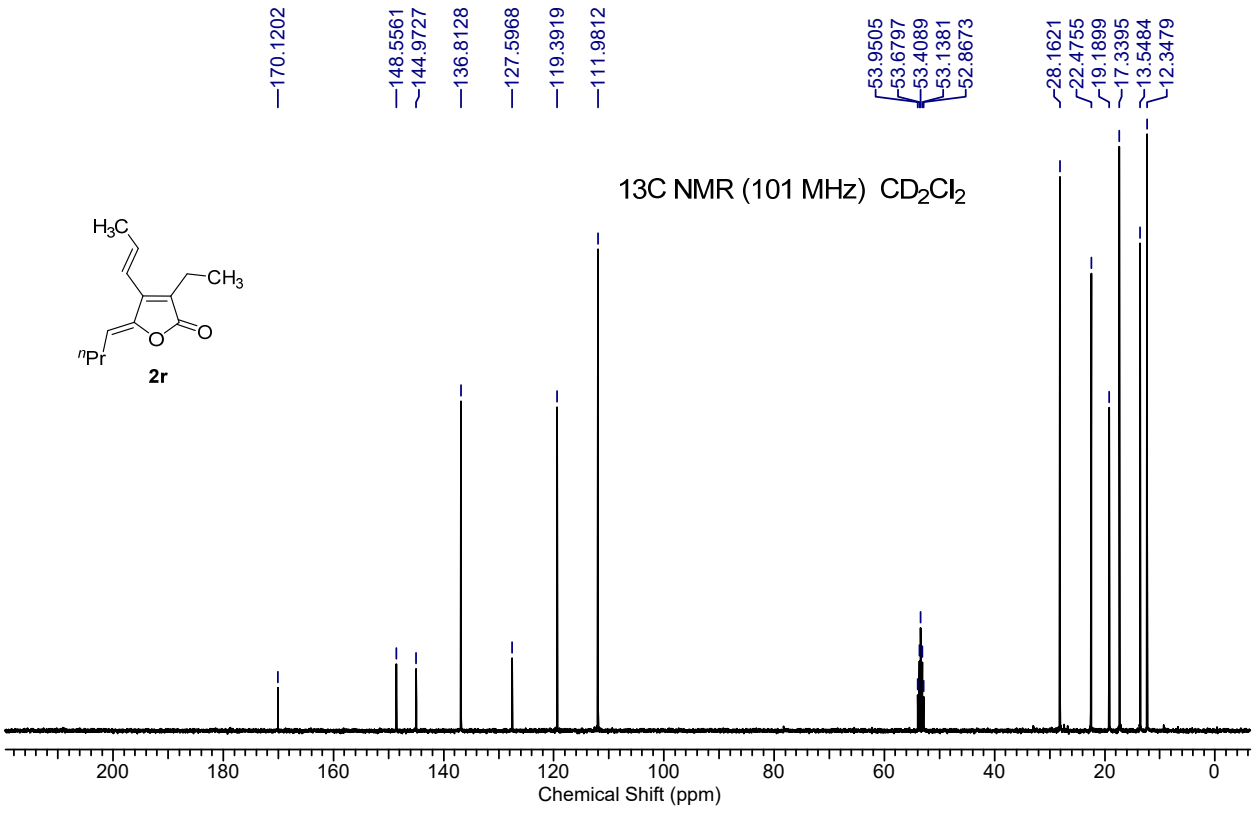
6.2400
6.2321
5.3891
5.3692
5.3497
2.4037
2.3851
2.3521
2.3335
1.9430
1.9301
1.5241
1.5058
1.4871
1.1260
1.1070
1.0881
0.9702
0.9518
0.9332
H3C
CH3
O
O
nPr
2r
1H NMR (400 MHz) CD2Cl2
1.75
1.00
4.49
3.08
2.15
3.40
3.23
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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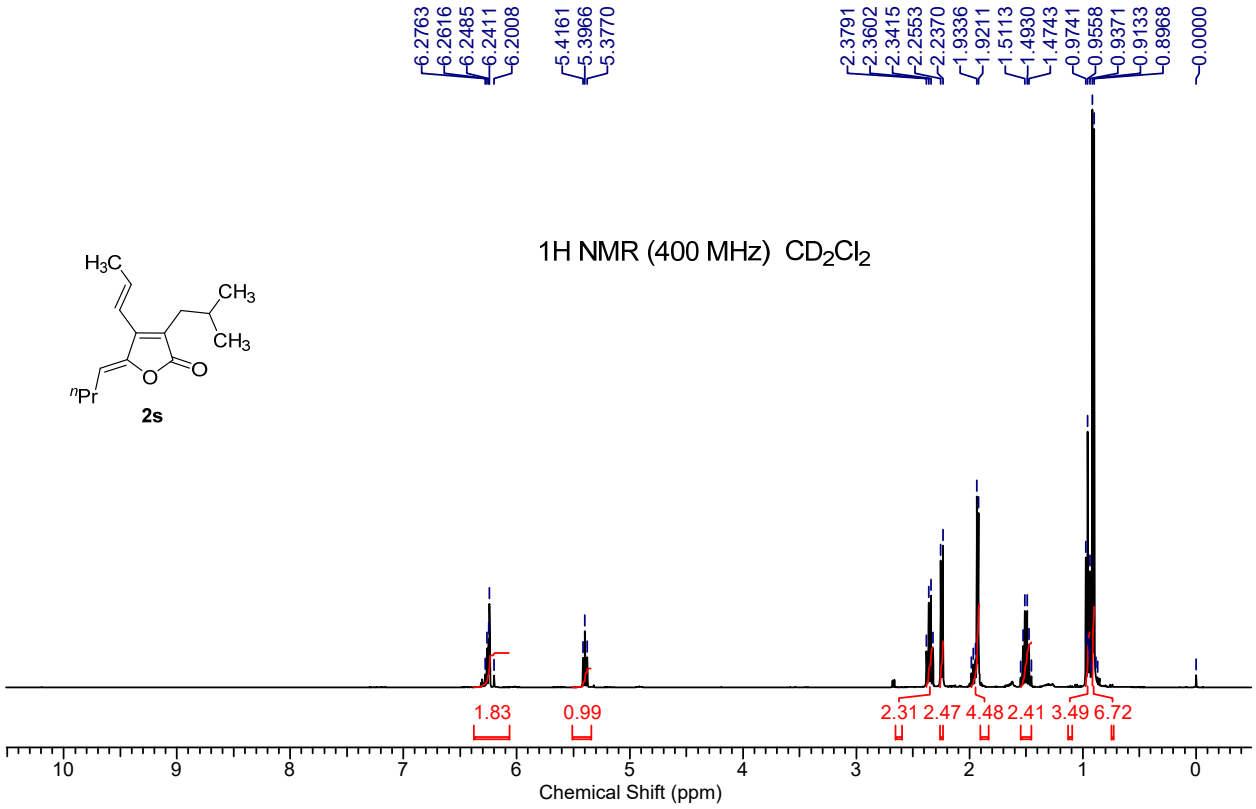
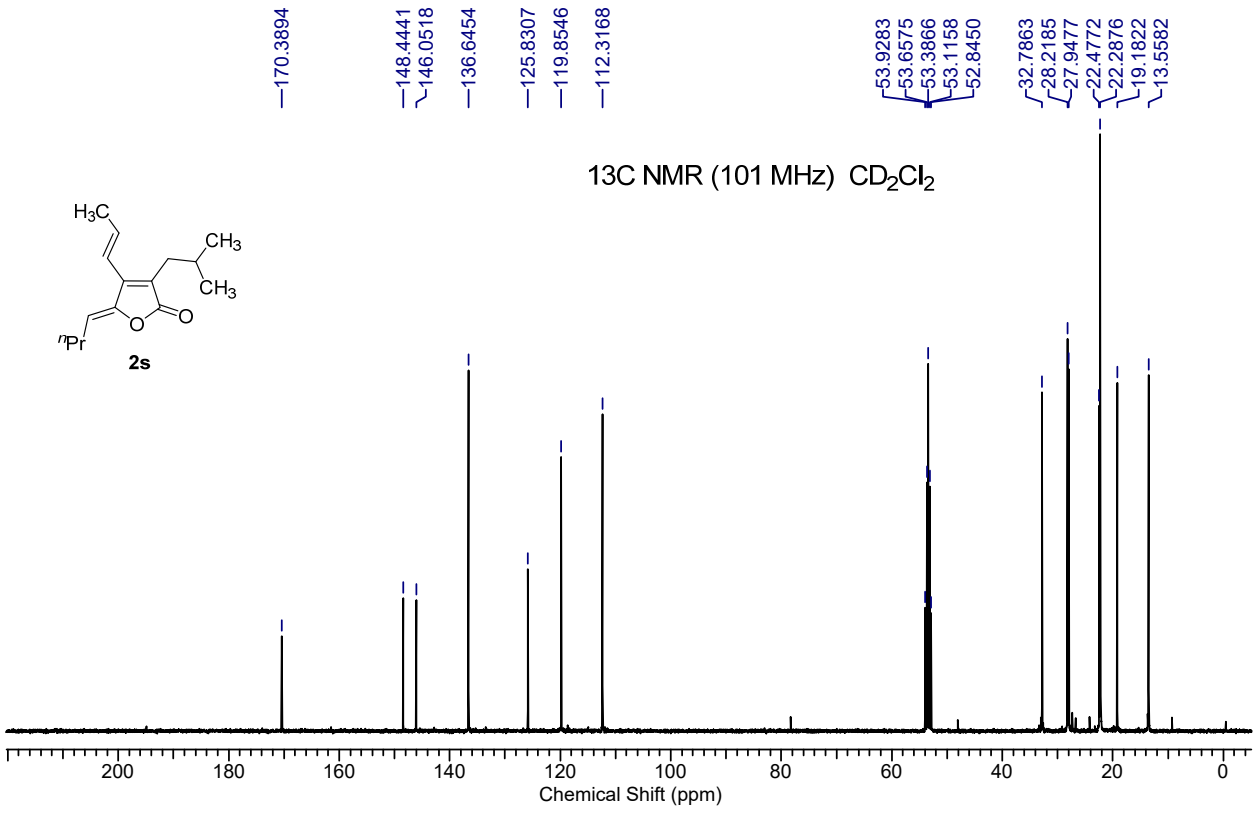
148.5561
144.9727
136.8128
127.5968
119.3919
111.9812
53.9505
53.6797
53.4089
53.1381
52.8673
28.1621
22.4755
19.1899
17.3395
13.5484
12.3479
H3C
CH3
O
O
nPr
2r
13C NMR (101 MHz) CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


6.2763
6.2616
6.2485
6.2411
6.2008
5.4161
5.3966
5.3770
2.3791
2.3602
2.3415
2.2553
2.2370
1.9336
1.9211
1.5113
1.4930
1.4743
0.9741
0.9558
0.9371
0.9133
0.8968
0.0000
1H NMR (400 MHz) CD2Cl2
H3C
CH3
CH3
O
O
nPr
2s
1.83
0.99
2.31 2.47 4.48 2.41 3.49 6.72
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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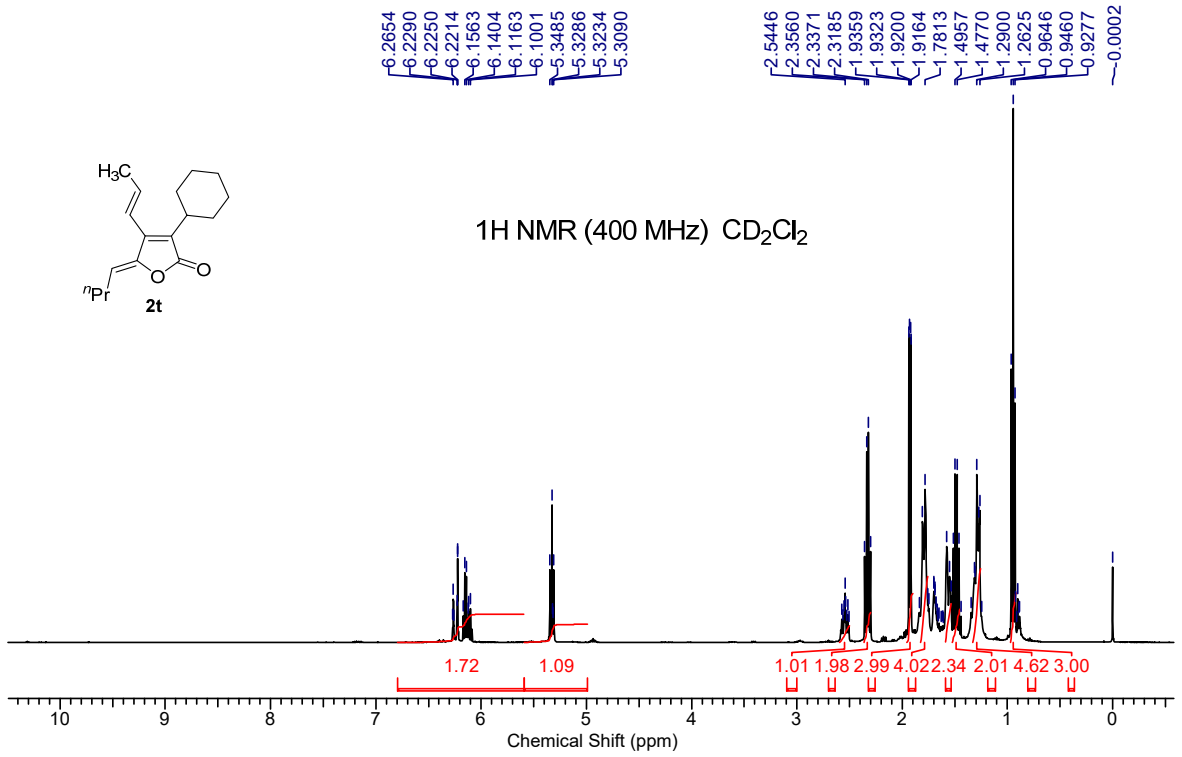
146.0518
136.6454
125.8307
119.8546
112.3168
53.9283
53.6575
53.3866
53.1158
52.8450
32.7863
28.2185
27.9477
22.4772
22.2876
19.1822
13.5582
13C NMR (101 MHz) CD2Cl2
H3C
CH3
CH3
O
O
nPr
2s
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)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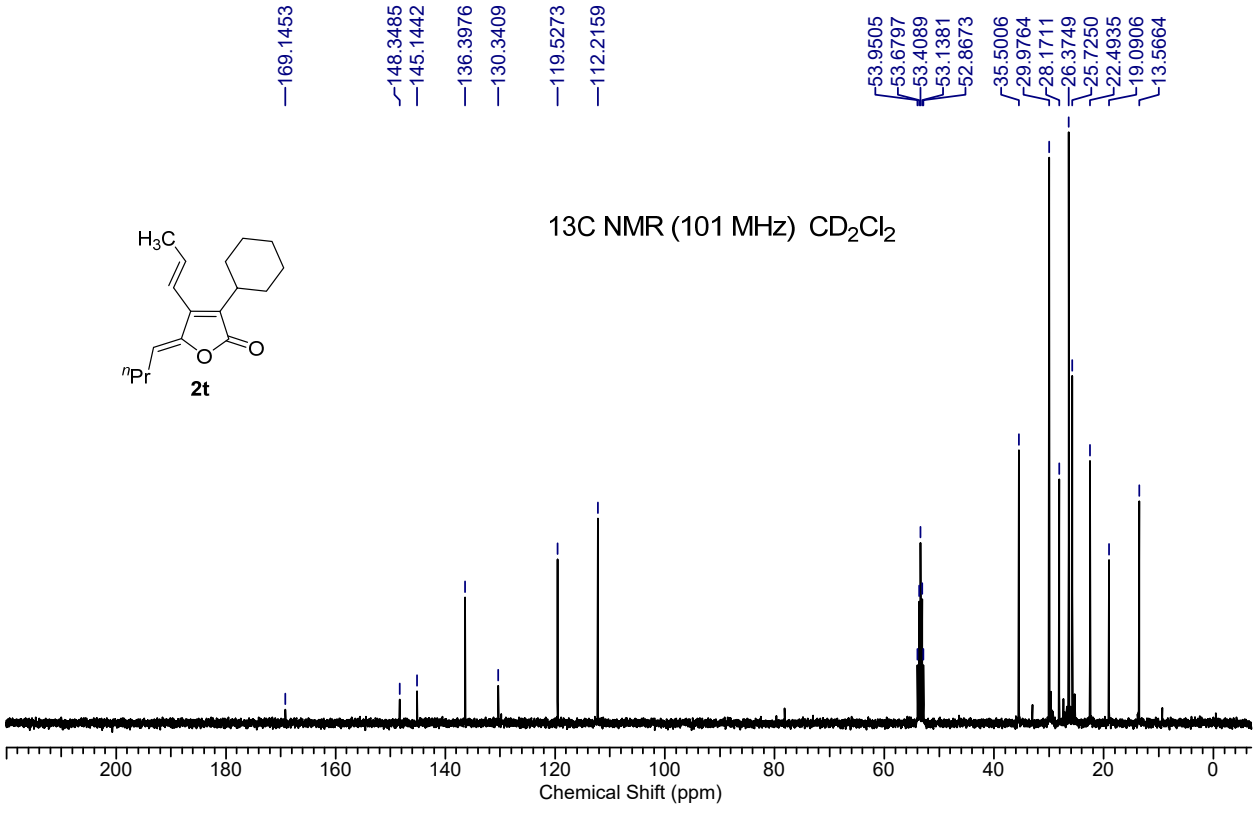
6.2290
6.2250
6.2214
6.1563
6.1404
6.1163
6.1001
5.3485
5.3286
5.3234
5.3090
2.5446
2.3560
2.3371
2.3185
1.9359
1.9323
1.9200
1.9164
1.7813
1.4957
1.4770
1.2900
1.2625
0.9646
0.9460
0.9277
0.0002
H3C
nPr
O
O
2t
1H NMR (400 MHz) CD2Cl2
1.72
1.09
1.01 1.98 2.99 4.02 2.34 2.01 4.62 3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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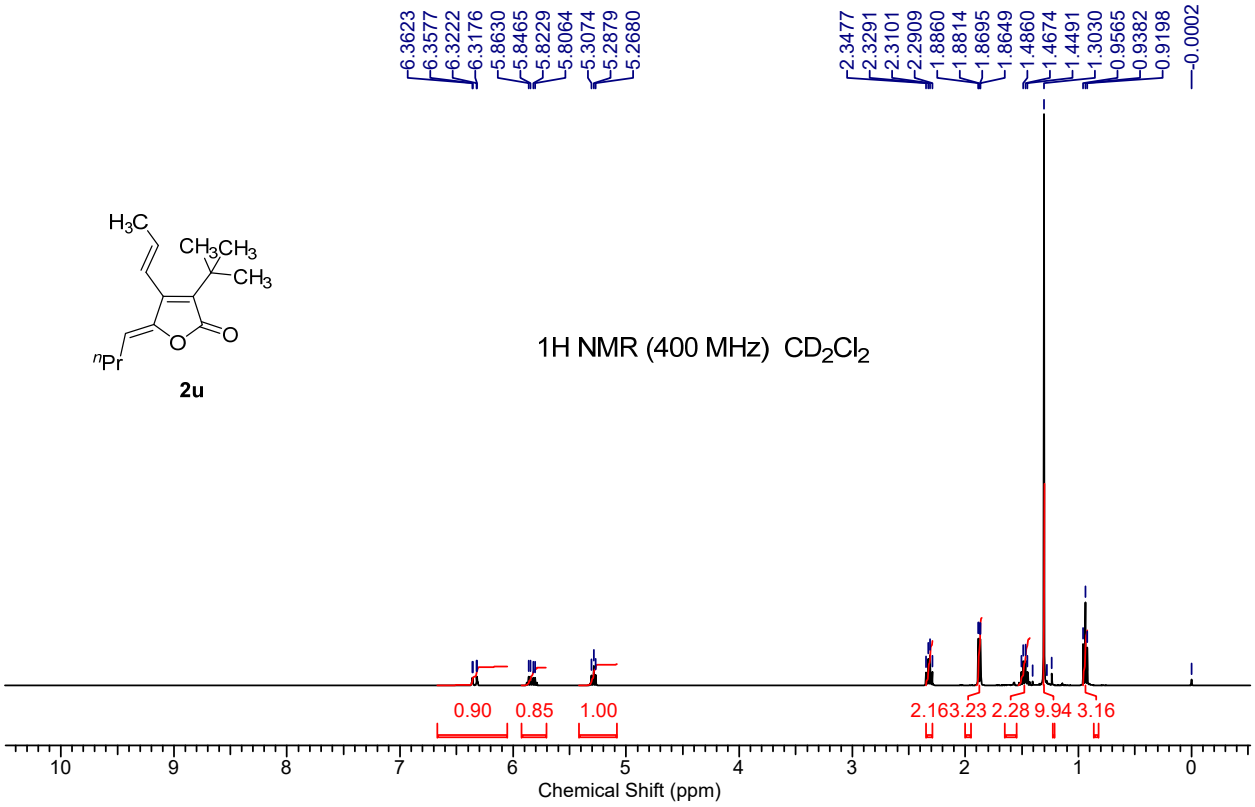
148.3485
145.1442
136.3976
130.3409
119.5273
112.2159
53.9505
53.6797
53.4089
53.1381
52.8673
35.5006
29.9764
28.1711
26.3749
25.7250
22.4935
19.0906
13.5664
H3C
nPr
O
O
2t
13C NMR (101 MHz) CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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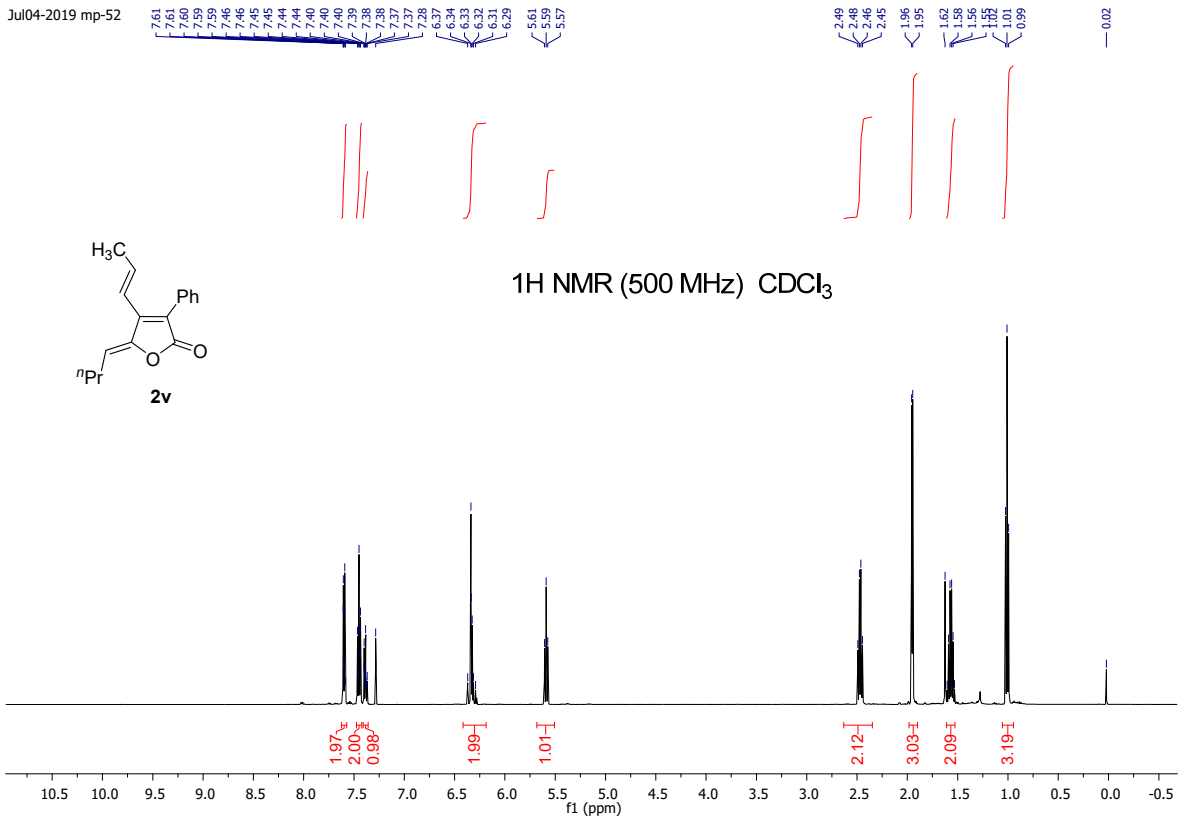
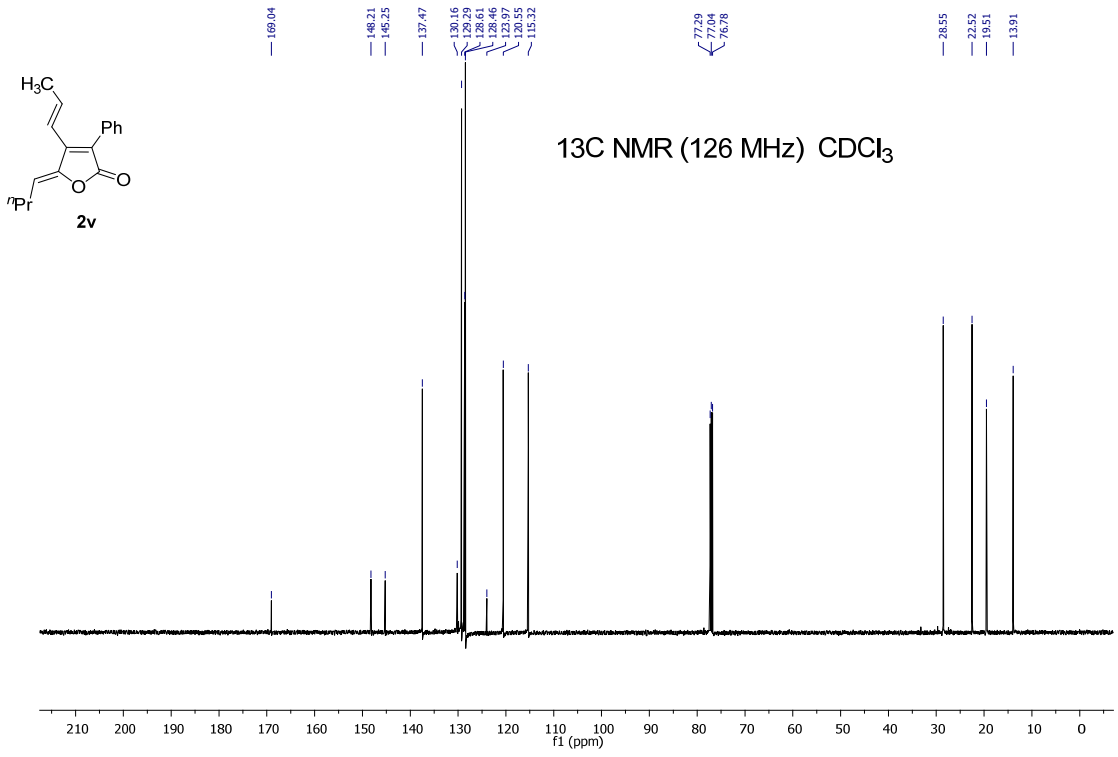
6.3577
6.3222
6.3176
5.8630
5.8465
5.8229
5.8064
5.3074
5.2879
5.2680
2.3477
2.3291
2.3101
2.2909
1.8860
1.8814
1.8695
1.8649
1.4860
1.4674
1.4491
1.3030
0.9565
0.9382
0.9198
0.0002
1H NMR (400 MHz) CD2Cl2
0.90
0.85
1.00
2.16
3.23
2.28
9.94
3.16
Chemical Shift (ppm)

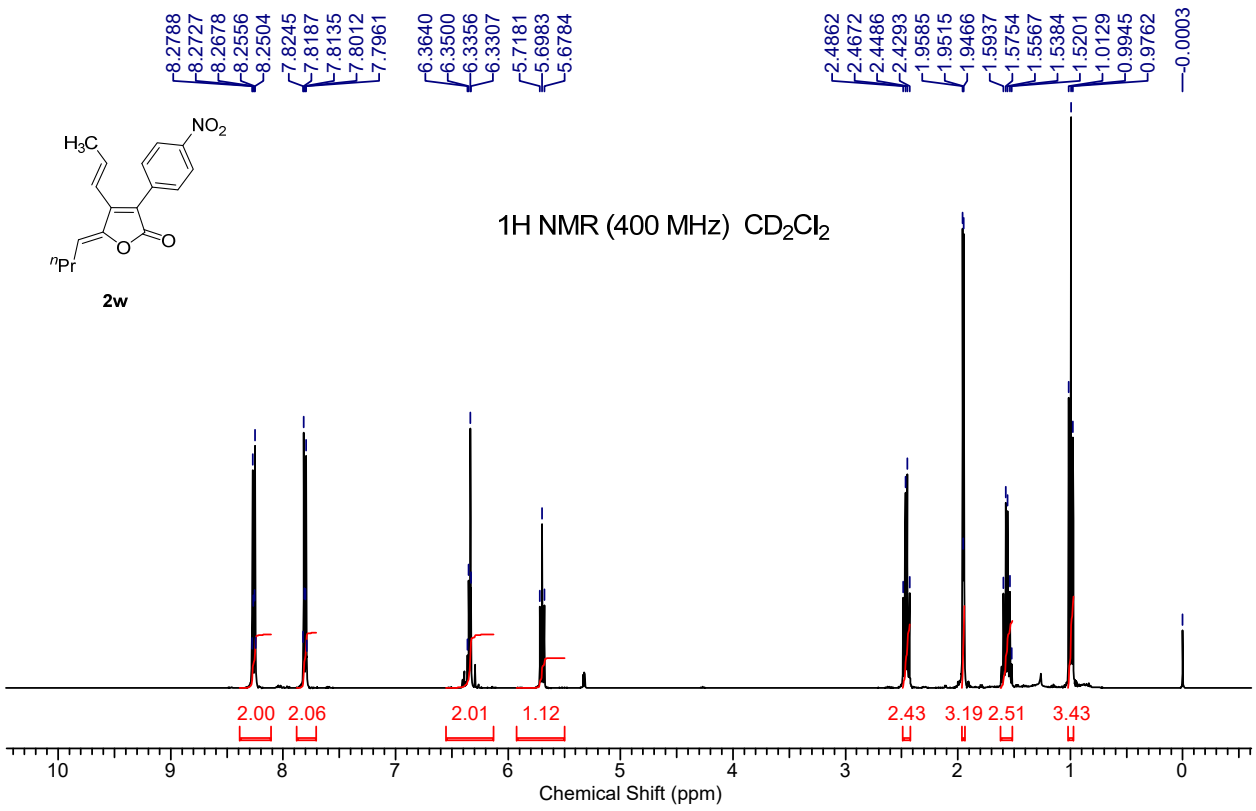
2u

168.8367
149.0850
145.4650
134.7045
132.5199
121.1726
112.9668
53.9373
53.6665
53.3957
53.1248
52.8540
33.2287
29.3289
28.2095
22.4862
18.5684
13.5672
13C NMR (101 MHz) CD2Cl2
Chemical Shift (ppm)

2u


Jul04-2019 mp-52
1H NMR (500 MHz) CDCl3
2v
f1 (ppm)


13C NMR (126 MHz) CDCl3
2v
f1 (ppm)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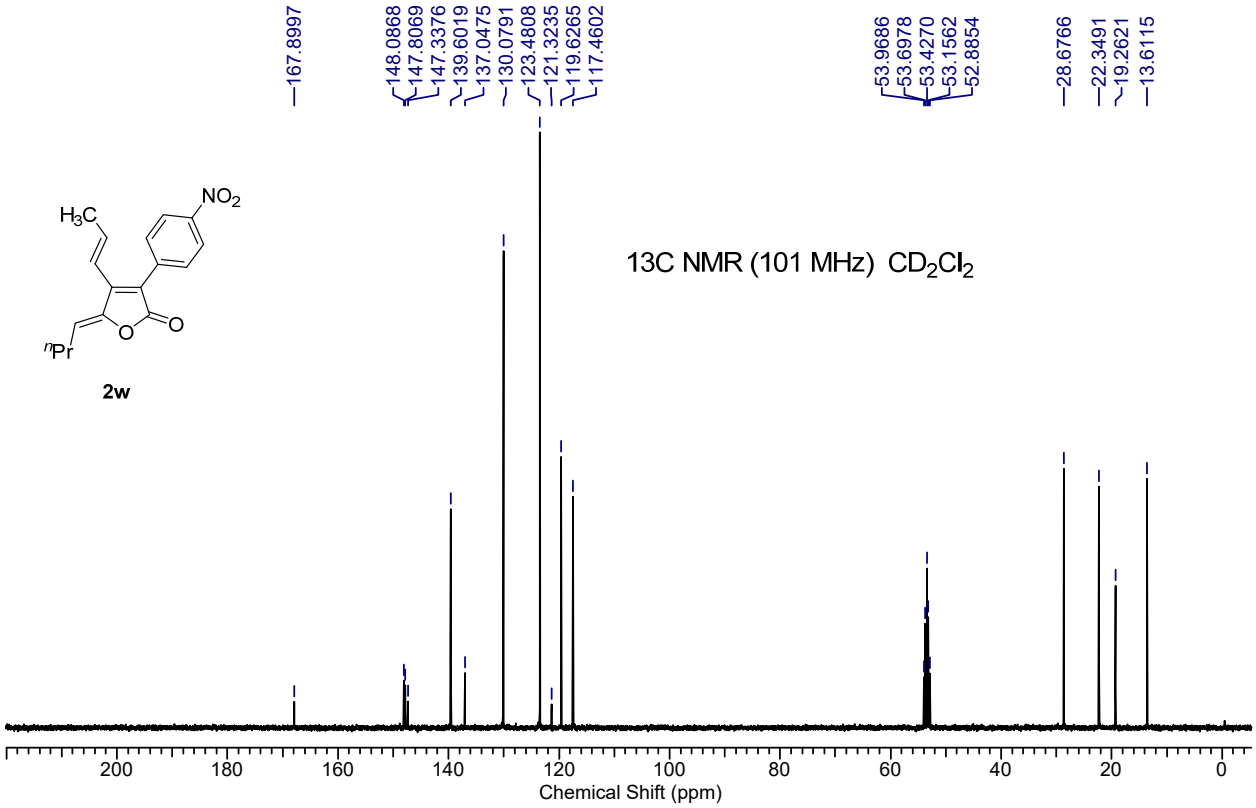
8.2678
8.2556
8.2504
7.8245
7.8187
7.8135
7.8012
7.7961
6.3640
6.3500
6.3356
6.3307
5.7181
5.6983
5.6784
2.4862
2.4672
2.4486
2.4293
1.9585
1.9515
1.9466
1.5937
1.5754
1.5567
1.5384
1.5201
1.0129
0.9945
0.9762
0.0003
1H NMR (400 MHz) CD2Cl2
2w
2.00
2.06
2.01
1.12
2.43
3.19
2.51
3.43
Chemical Shift (ppm)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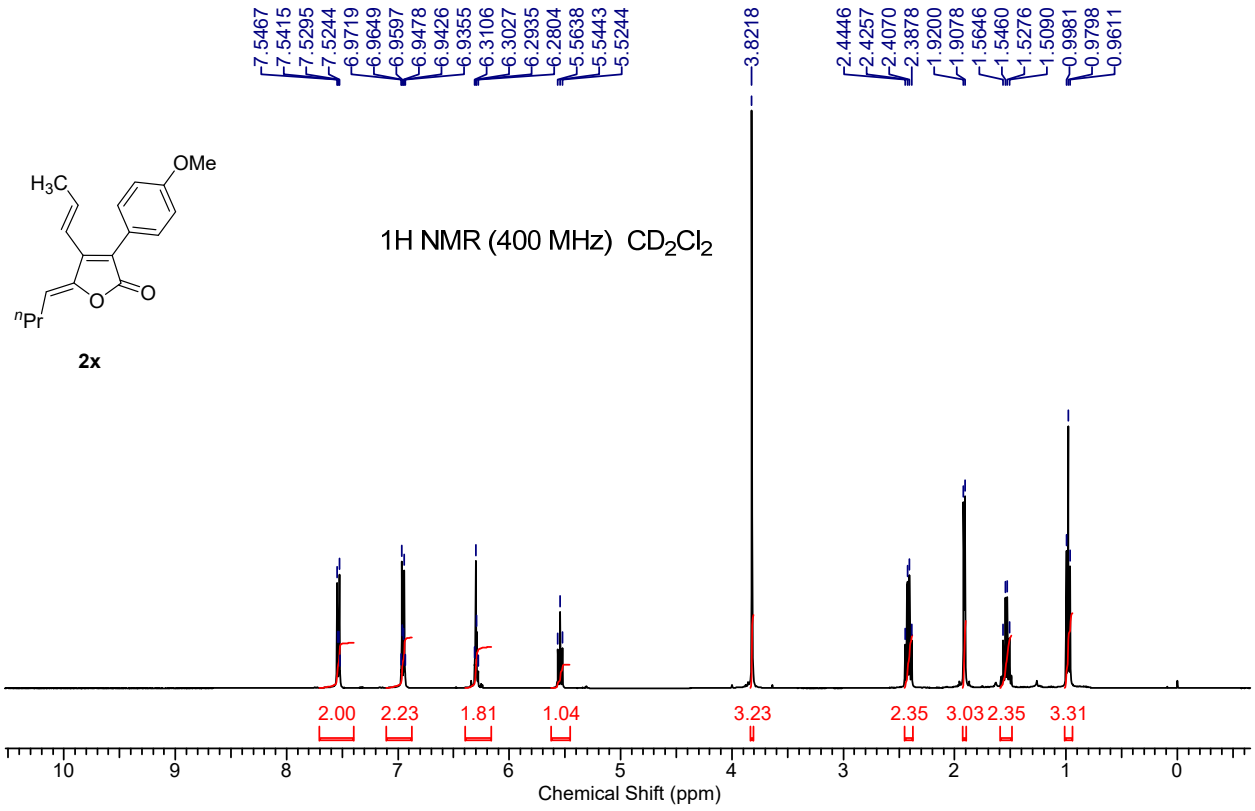
148.0868
147.8069
147.3376
139.6019
137.0475
130.0791
123.4808
121.3235
119.6265
117.4602
53.9686
53.6978
53.4270
53.1562
52.8854
28.6766
22.3491
19.2621
13.6115
13C NMR (101 MHz) CD2Cl2
2w
Chemical Shift (ppm)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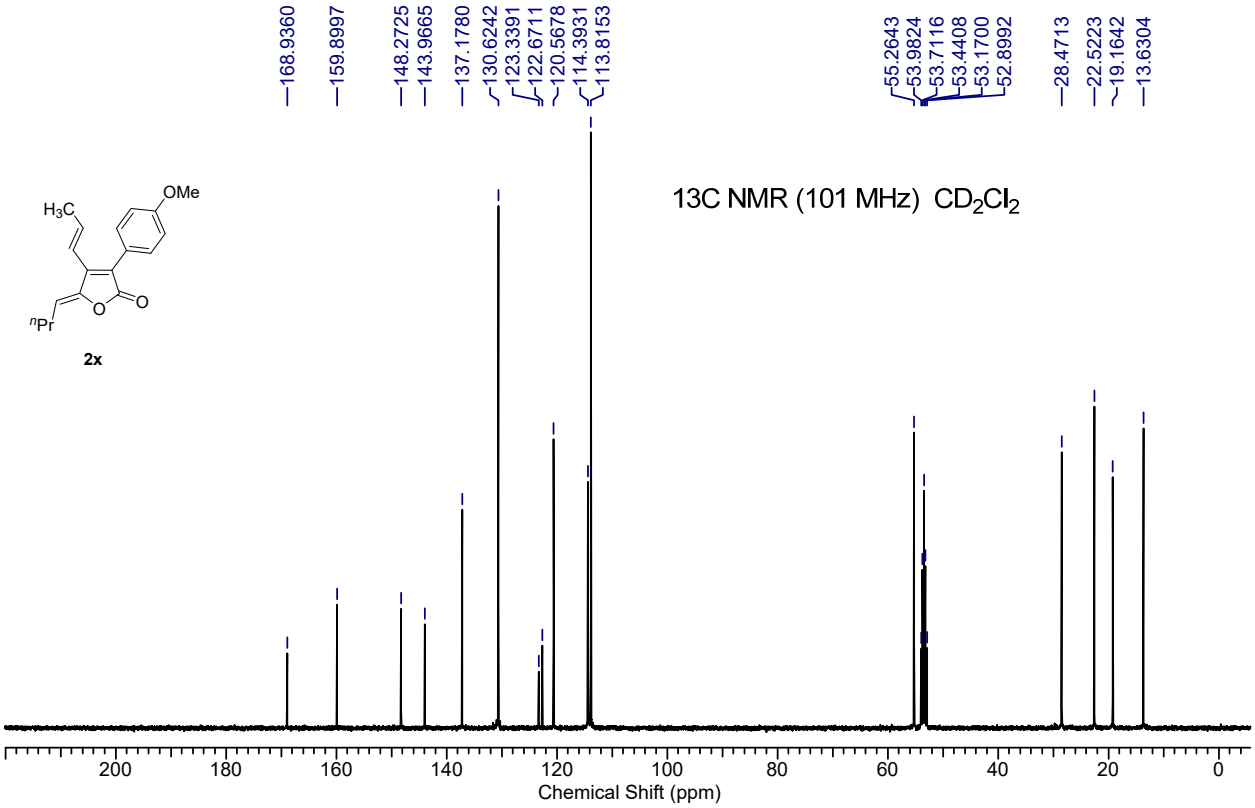
7.5415
7.5295
7.5244
6.9719
6.9649
6.9597
6.9478
6.9426
6.9355
6.3106
6.3027
6.2935
6.2804
5.5638
5.5443
5.5244
3.8218
2.4446
2.4257
2.4070
2.3878
1.9200
1.9078
1.5646
1.5460
1.5276
1.5090
0.9981
0.9798
0.9611
OMe
H3C
O
O
nPr
2x
1H NMR (400 MHz) CD2Cl2
2.00
2.23
1.81
1.04
3.23
2.35
3.03
2.35
3.31
Chemical Shift (ppm)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137.1780
130.6242
123.3391
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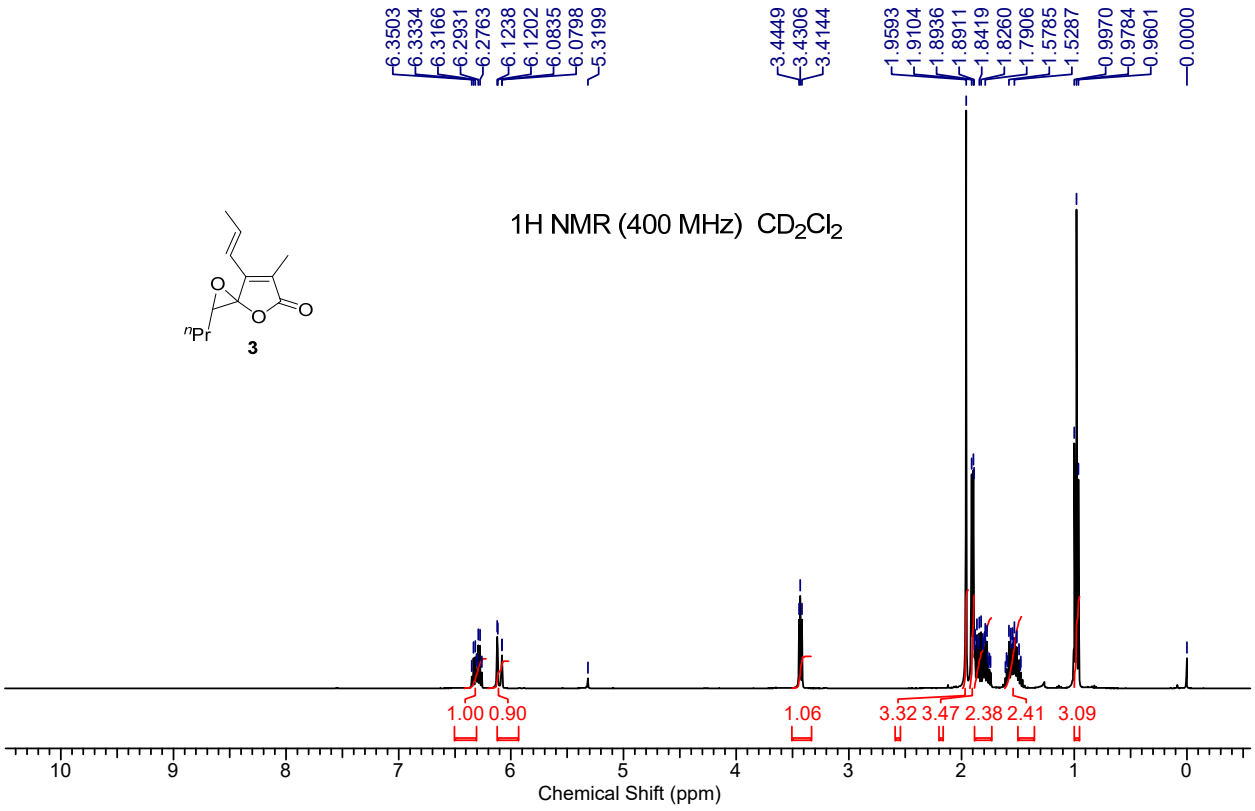
114.3931
113.8153
55.2643
53.9824
53.7116
53.4408
53.1700
52.8992
28.4713
22.5223
19.1642
13.6304
OMe
H3C
O
O
nPr
2x
13C NMR (101 MHz) CD2Cl2
Chemical Shift (ppm)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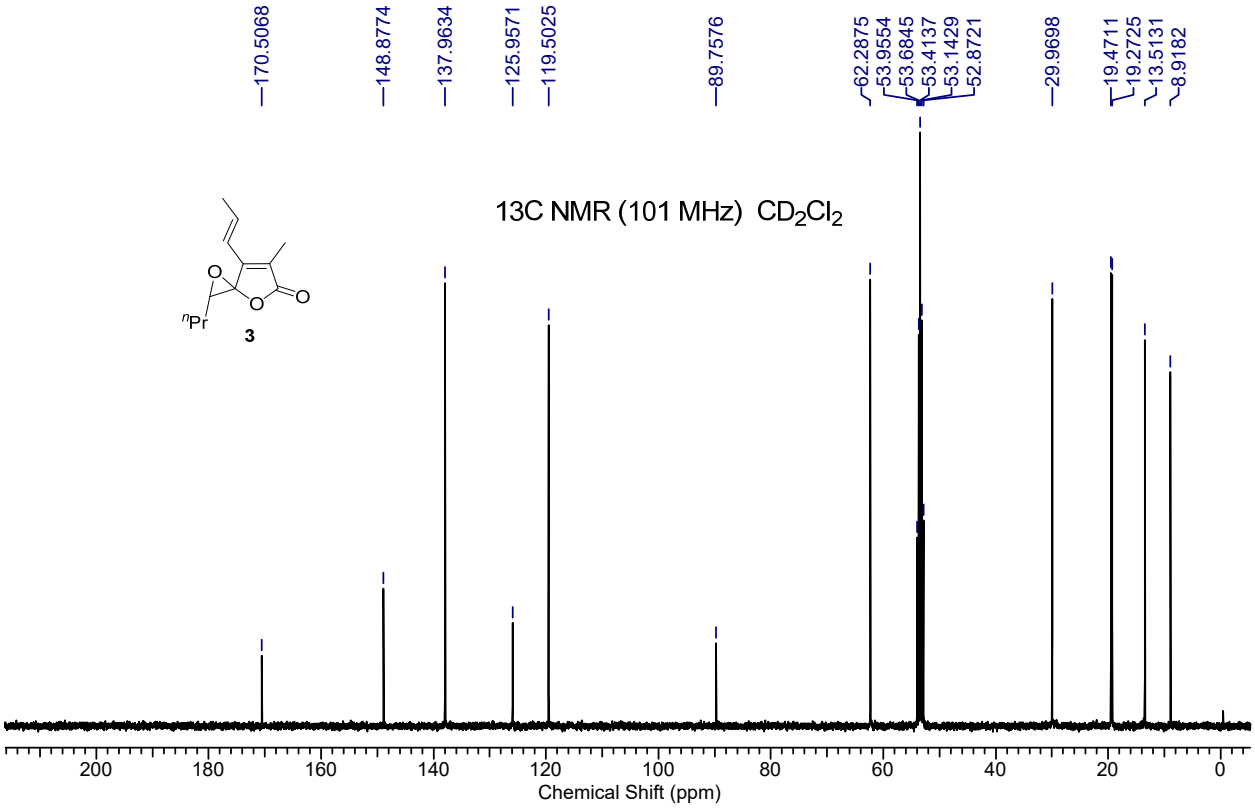
6.3334
6.3166
6.2931
6.2763
6.1238
6.1202
6.0835
6.0798
5.3199
3.4449
3.4306
3.4144
1.9593
1.9104
1.8936
1.8911
1.8419
1.8260
1.7906
1.5785
1.5287
0.9970
0.9784
0.9601
0.0000
1H NMR (400 MHz) CD2Cl2
nPr
3
1.00 0.90
1.06
3.32 3.47 2.38 2.41 3.09
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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119.5025
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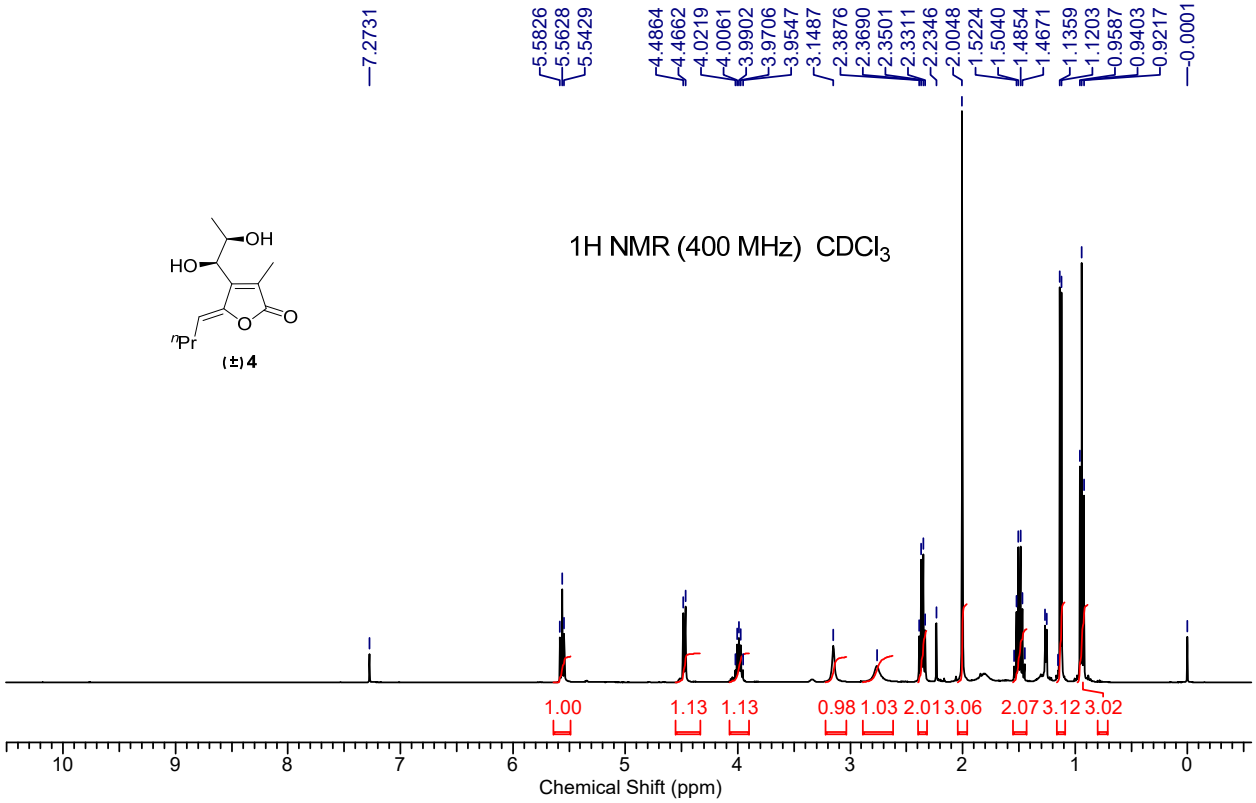
62.2875
53.9554
53.6845
53.4137
53.1429
52.8721
29.9698
19.4711
19.2725
13.5131
8.9182
13C NMR (101 MHz) CD2Cl2
nPr
3
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)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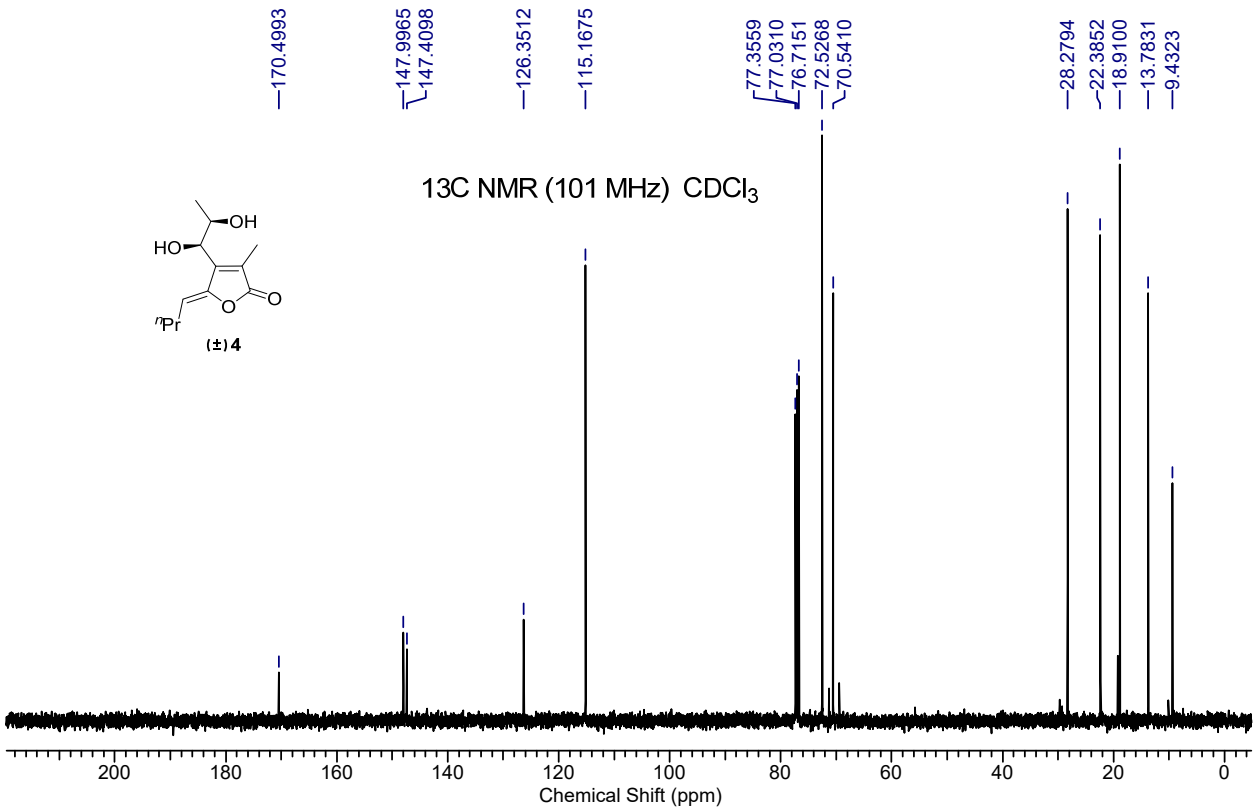
5.5628
5.5429
4.4864
4.4662
4.0219
4.0061
3.9902
3.9706
3.9547
3.1487
2.3876
2.3690
2.3501
2.3311
2.2346
2.0048
1.5224
1.5040
1.4854
1.4671
1.1359
1.1203
0.9587
0.9403
0.9217
0.0001
1H NMR (400 MHz) CDCl3
OH
HO
O
O
nPr
(±)4
1.00
1.13
1.13
0.98
1.03
2.01
3.06
2.07
3.12
3.02
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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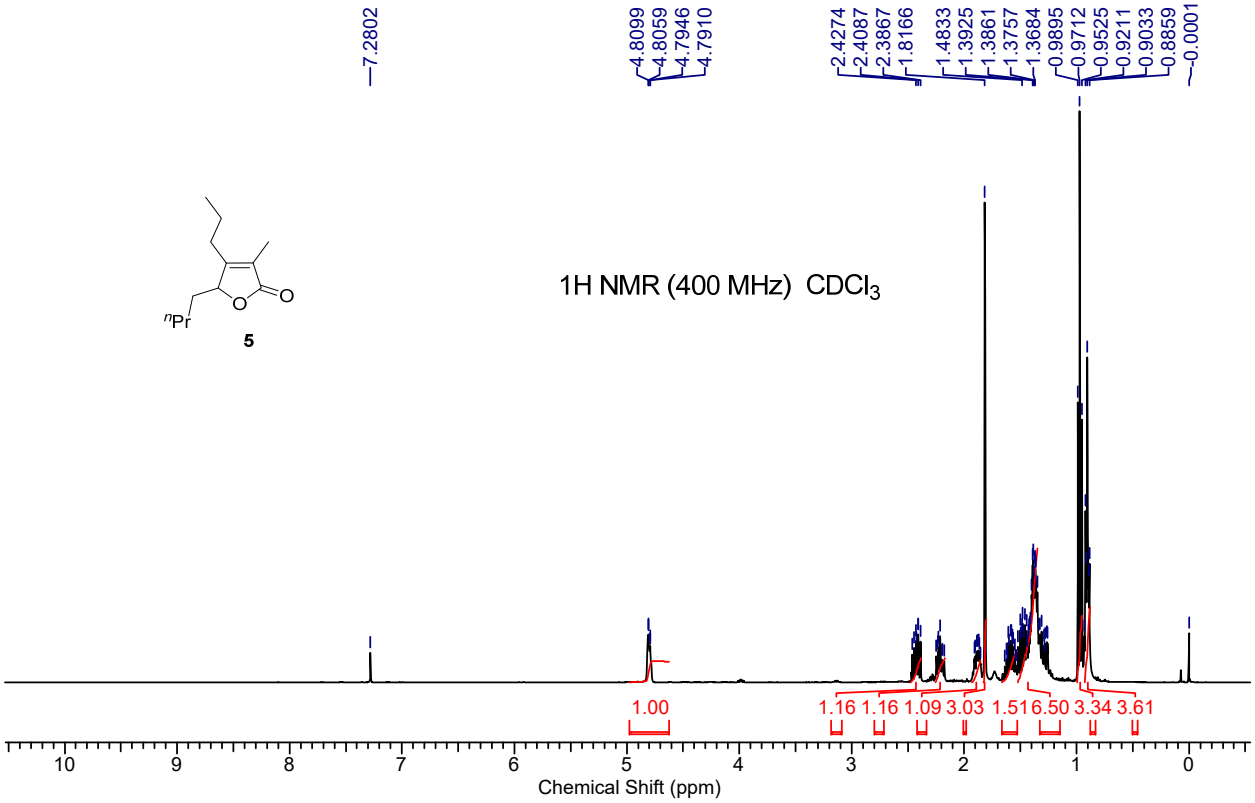
126.3512
115.1675
77.3559
77.0310
76.7151
72.5268
70.5410
28.2794
22.3852
18.9100
13.7831
9.4323
13C NMR (101 MHz) CDCl3
OH
HO
O
O
nPr
(±)4
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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4.8059
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4.7910
2.4274
2.4087
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2.1866
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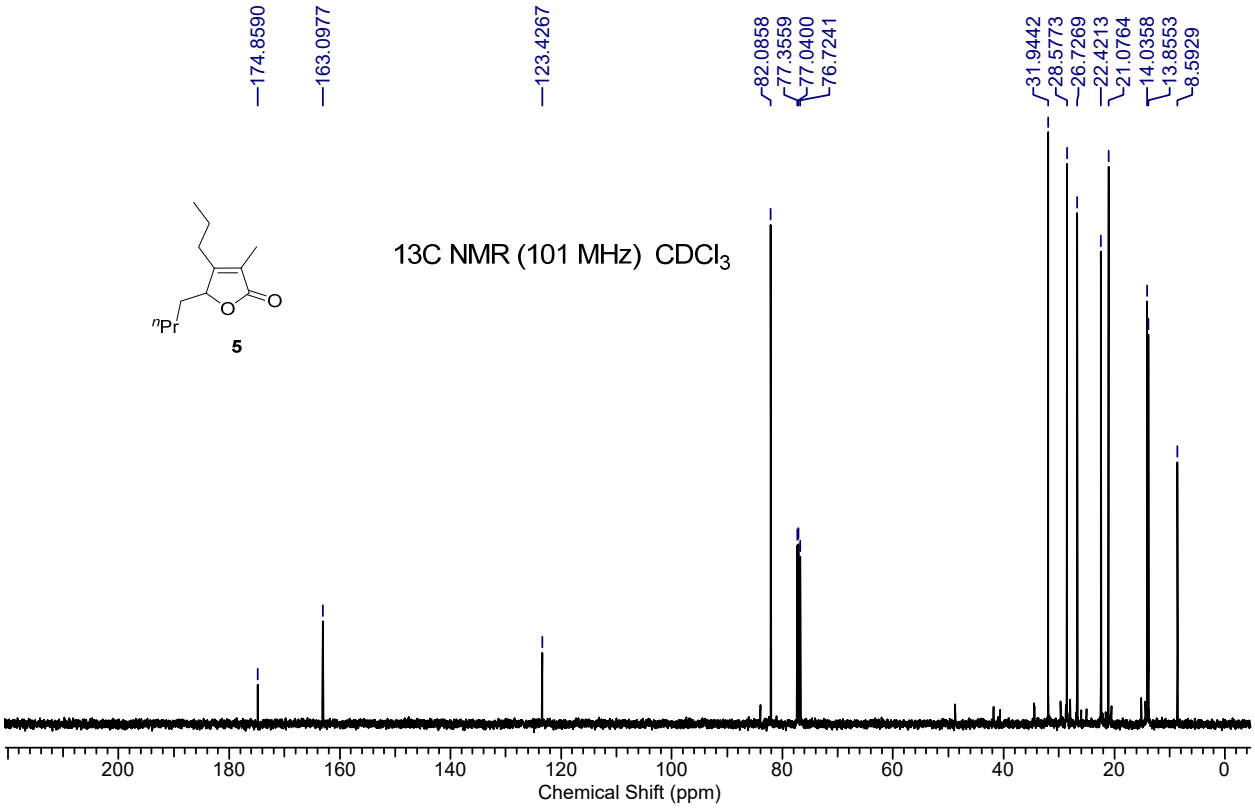
1.3925
1.3861
1.3757
1.3684
0.9895
0.9712
0.9525
0.9211
0.9033
0.8859
0.0001
1H NMR (400 MHz) CDCl3
nPr
O
O
5
1.00
1.16 1.16 1.09 3.03 1.51 6.50 3.34 3.61
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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77.0400
76.7241
31.9442
28.5773
26.7269
22.4213
21.0764
14.0358
13.8553
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13C NMR (101 MHz) CDCl3
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O
O
5
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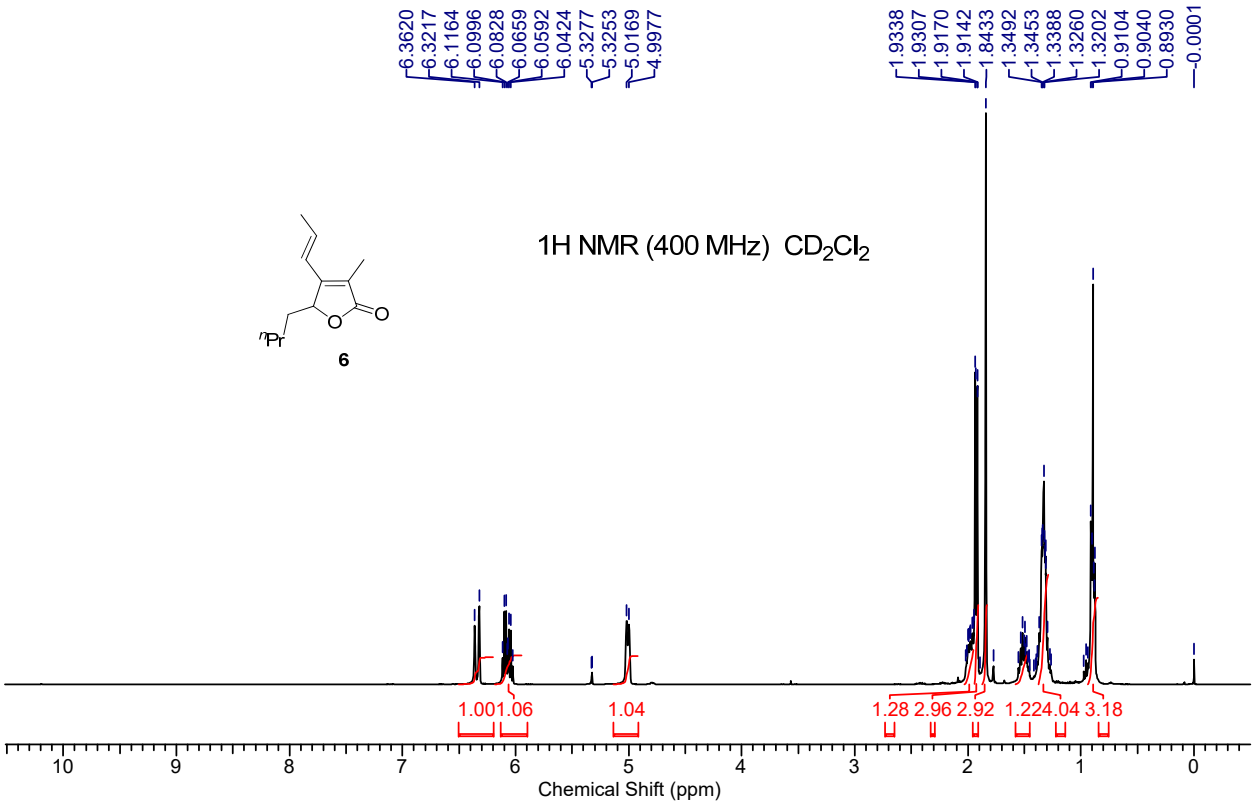
Chemical Shift (ppm)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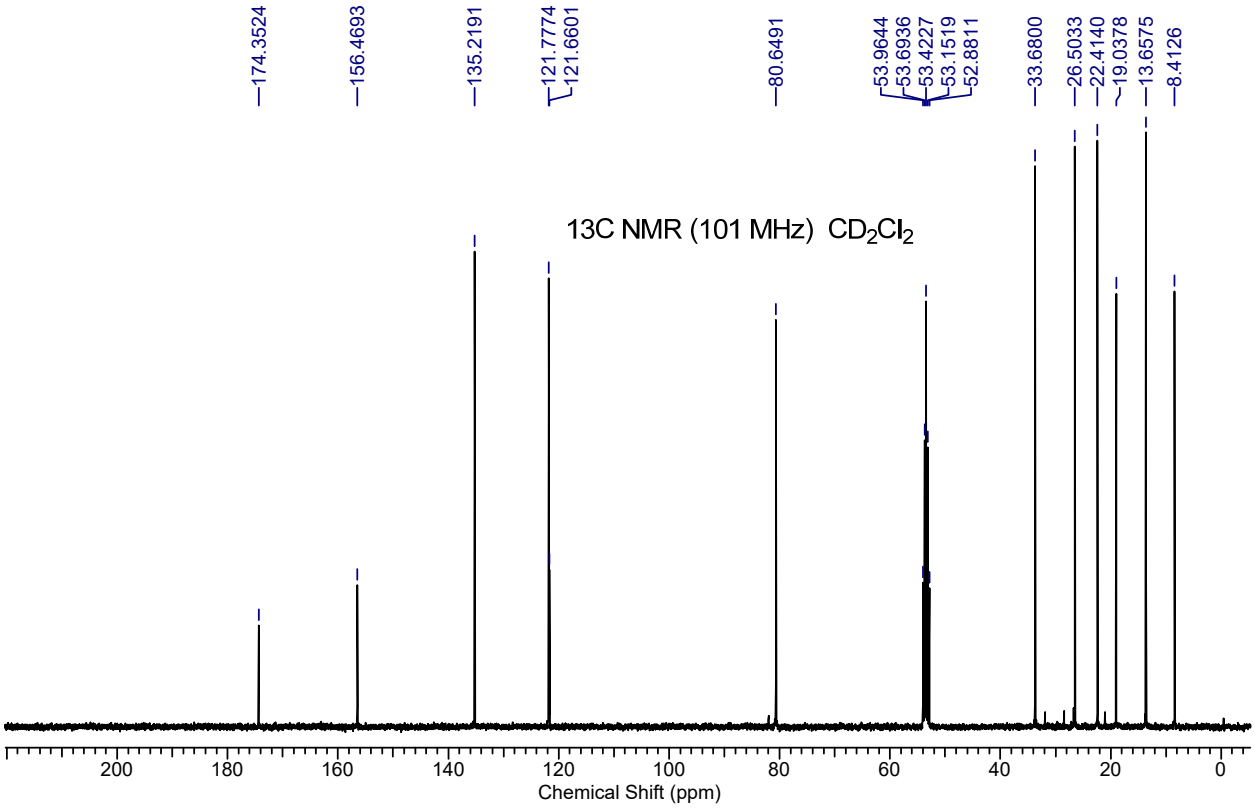
5.3277
5.3253
5.0169
4.9977
1.9338
1.9307
1.9170
1.9142
1.8433
1.3492
1.3453
1.3388
1.3260
1.3202
0.9104
0.9040
0.8930
0.0001
1H NMR (400 MHz) CD2Cl2
nPr
O
O
6
1.00 1.06
1.04
1.28 2.96 2.92 1.22 4.04 3.18
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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121.6601
80.6491
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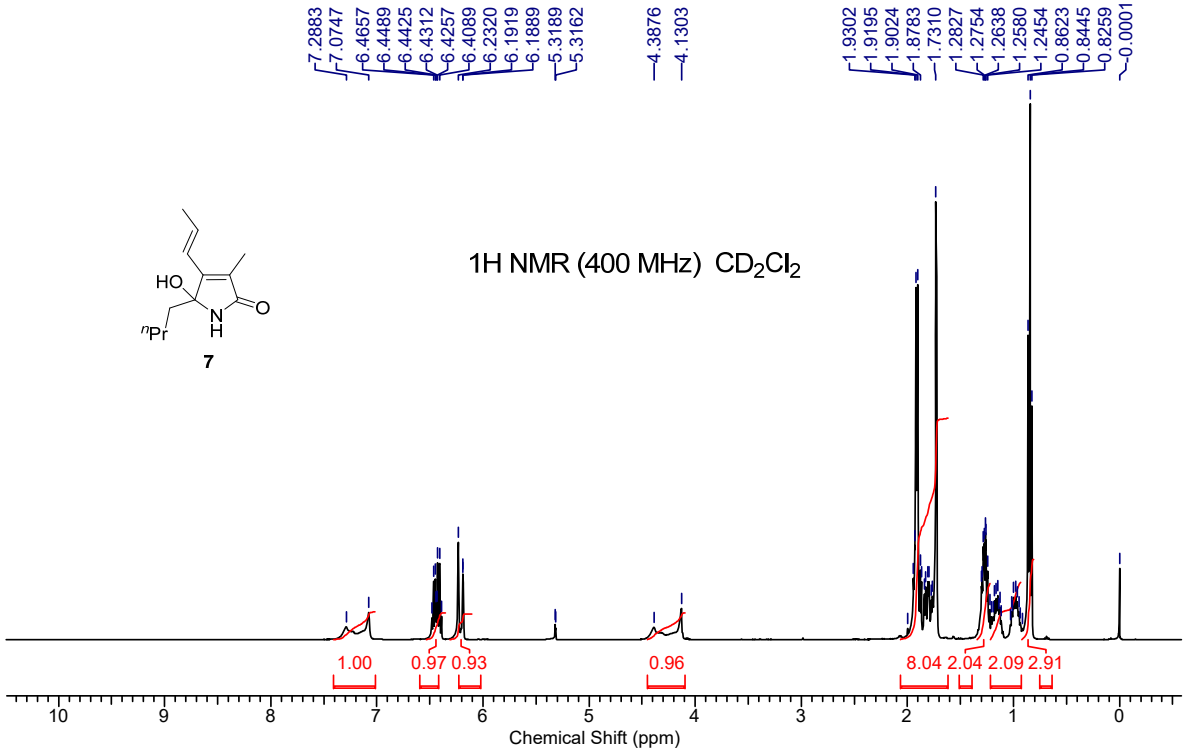
53.6936
53.4227
53.1519
52.8811
33.6800
26.5033
22.4140
19.0378
13.6575
8.4126
13C NMR (101 MHz) CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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6.4657
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6.4425
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6.2320
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6.1889
5.3189
5.3162
4.3876
4.1303
1.9302
1.9195
1.9024
1.8783
1.7310
1.2827
1.2754
1.2638
1.2580
1.2454
0.8623
0.8445
0.8259
0.0001
1H NMR (400 MHz) CD2Cl2
HO
N
H
O
nPr
7
1.00
0.97
0.93
0.96
8.04
2.04
2.09
2.91
10
9
8
7
6
5
4
3
2
1
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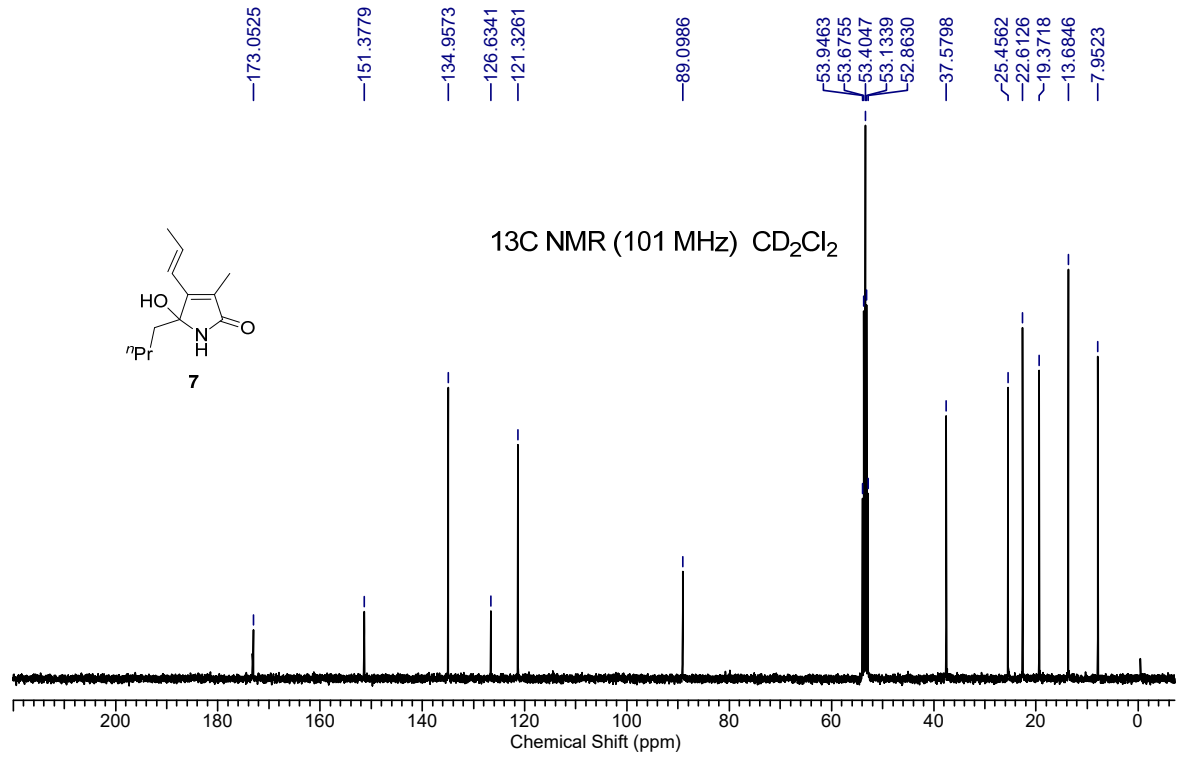
Chemical Shift (ppm)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134.9573
126.6341
121.3261
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37.5798
25.4562
22.6126
19.3718
13.6846
7.9523
13C NMR (101 MHz) CD2Cl2
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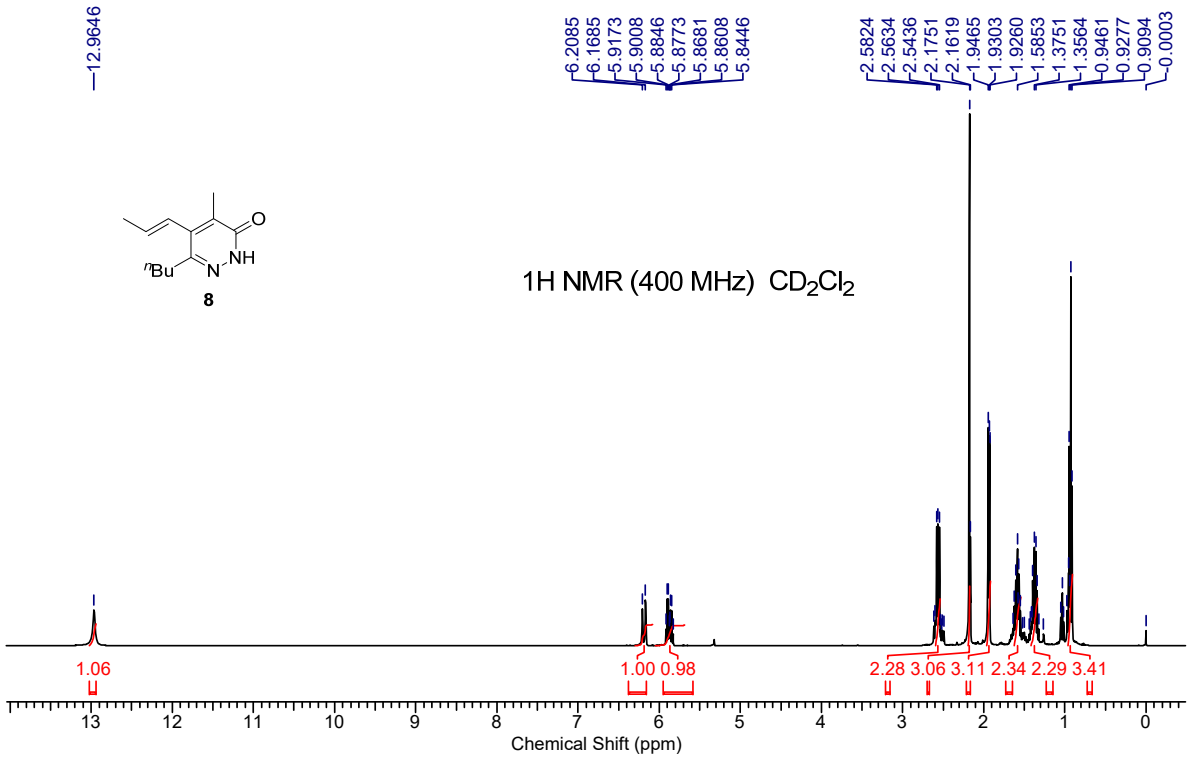
N
H
O
nPr
7
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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6.1685
5.9173
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5.8846
5.8773
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5.8608
5.8446
2.5824
2.5634
2.5436
2.1751
2.1619
1.9465
1.9303
1.9260
1.5853
1.3751
1.3564
0.9461
0.9277
0.9094
0.0003
O
NH
nBu
N
8
1H NMR (400 MHz) CD2Cl2
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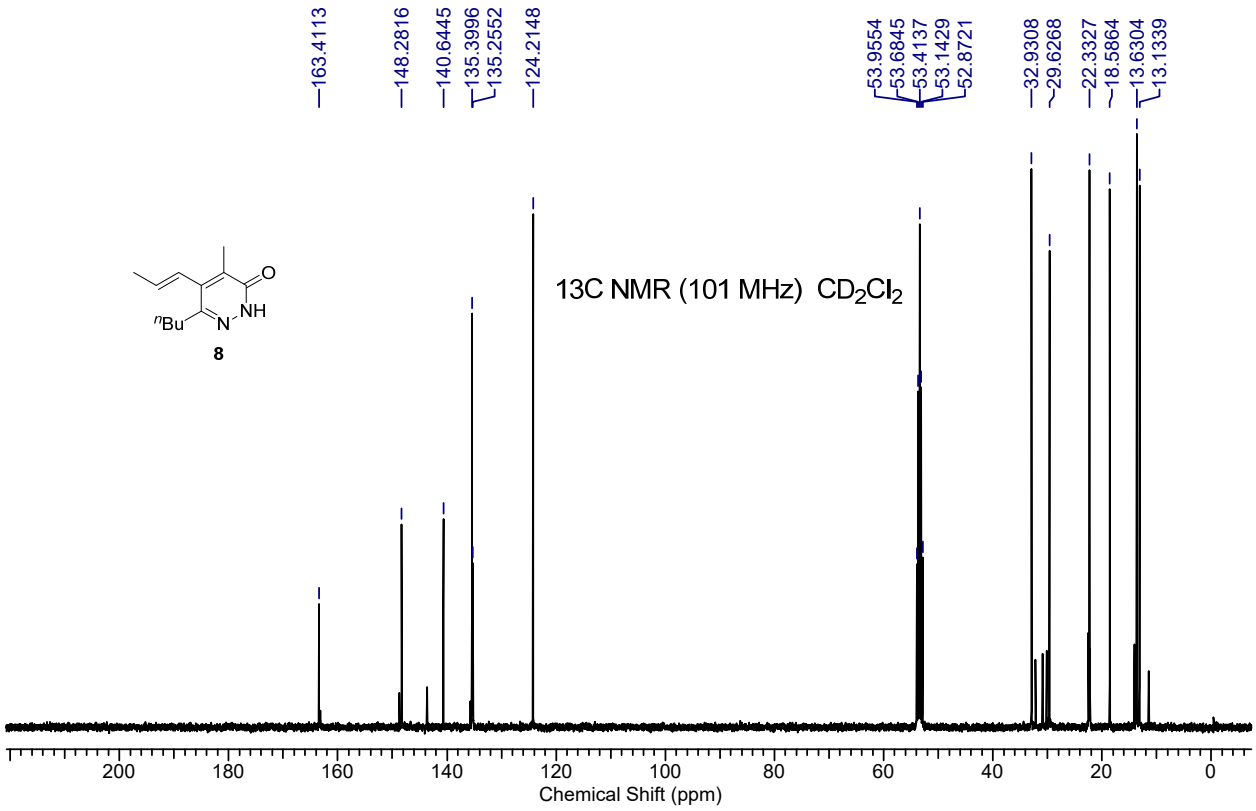
1.00 0.98
2.28 3.06 3.11 2.34 2.29 3.41
13 12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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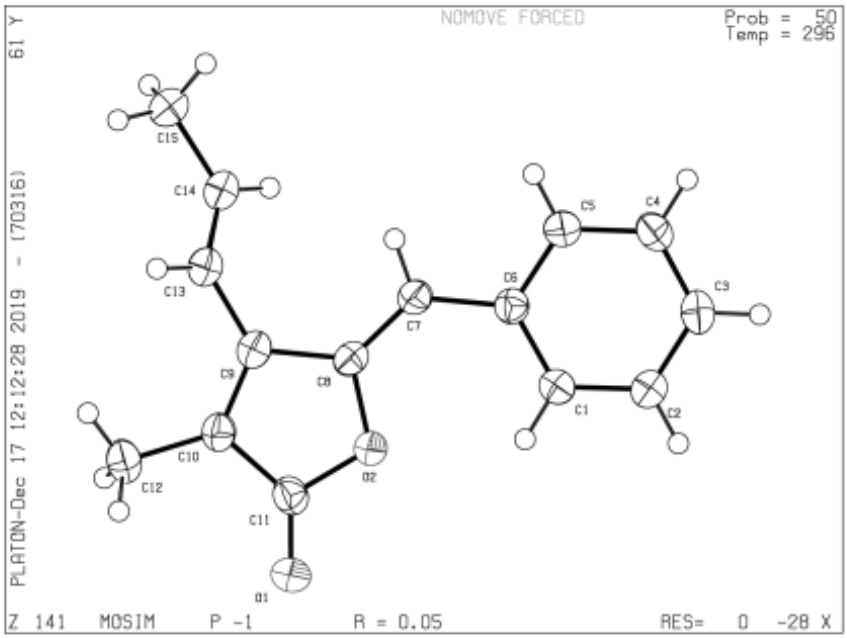
140.6445
135.3996
135.2552
124.2148
53.9554
53.6845
53.4137
53.1429
52.8721
32.9308
29.6268
22.3327
18.5864
13.6304
13.1339
O
NH
nBu
N
8
13C NMR (101 MHz) CD2Cl2
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

11. Single crystal data of 2f

Solvent system and method for crystal generation: To the compound **2f** was added DCM till it is completely soluble. To the solution was then added a drop of *n*-hexane. And solution was left for the slow evaporation to give crystals. The single crystal analysis was carried out using Bruker Smart instrument.




```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:          a=7.7363(12)      b=8.7603(13)      c=9.8228(14)
               alpha=66.327(4)   beta=76.023(4)    gamma=76.865(4)
Temperature:   296 K

                Calculated                Reported
Volume          585.25(15)                585.25(15)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C15 H14 O2                C15 H14 O2
Sum formula     C15 H14 O2                C15 H14 O2
Mr              226.26                    226.26
Dx,g cm-3       1.284                     1.284
Z               2                         2
Mu (mm-1)       0.084                     0.084
F000            240.0                     240.0
F000'           240.11
h,k,lmax        10,11,13                  10,11,13
Nref            2907                      2849
Tmin,Tmax       0.984,0.992               0.191,0.263
Tmin'           0.980

Correction method= # Reported T Limits: Tmin=0.191 Tmax=0.263
AbsCorr = MULTI-SCAN

Data completeness= 0.980          Theta(max)= 28.246

R(reflections)= 0.0544( 1835)     wR2(reflections)= 0.1456( 2849)

S = 1.038                 Npar= 156
```

12. Cartesian coordinates of all computed structures

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H -0.57355800 4.23098300 -0.99013400
H -0.97010000 4.06316200 0.73102500
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O 0.66852900 0.51478600 -0.29705200
H 1.76704700 2.59487200 0.73514700
C 2.94538500 3.90751200 -0.55464600
H 2.46110300 4.82082800 -0.19549600
H 3.99558700 4.13574300 -0.76766300
H 2.46025400 3.60478500 -1.48835900
H 4.56935900 1.71609400 -0.19608700
C 5.20693500 -0.92560200 -0.78327500
H 5.22604900 -1.42231700 -1.76154400
H 5.65589300 0.06251500 -0.89206700
C 6.00667400 -1.77364400 0.23566000
H 5.59313000 -2.78212800 0.32323100
H 7.04007300 -1.84979500 -0.11378900
H 6.00706800 -1.30226600 1.22313900
Au -1.36781200 0.13520900 -0.11245900
P -3.62667900 -0.17327400 -0.01553800
C -4.56983800 0.91338800 -1.15235500
H -4.25858000 0.72417100 -2.18452600
H -5.64383400 0.71830600 -1.05607400
H -4.36927200 1.96206500 -0.91139000
C -4.34140100 0.14358800 1.64308800
H -5.42423900 -0.02261000 1.62724300

H -3.88286700 -0.52799000 2.37583200
H -4.13829100 1.17770600 1.93885300
C -4.15808800 -1.87548800 -0.44196900
H -5.24853700 -1.95902900 -0.37547900
H -3.83757200 -2.11573200 -1.46058700
H -3.69715700 -2.58902700 0.24837200
TS4-Au
O 3.27368900 -1.83113700 -0.42727400
C 3.92095700 -0.62819800 -0.33157100
C 3.09940000 0.36641600 0.12276400
C 1.72623100 -0.23795900 0.43447000
C 1.90966800 -1.64318000 -0.16339900
C 3.23442700 1.75657300 -0.07610200
C 2.18394700 2.63159300 0.25320700
O 1.11665100 -2.51553600 -0.36905200
H 1.73703600 2.49426400 1.24424900
C 1.44346400 -0.41564000 1.93808800
H 0.48124500 -0.92318400 2.06761300
H 2.22570600 -1.01497000 2.41769500
H 1.40072400 0.55873300 2.43249200
O 0.74155900 0.50471800 -0.24775500
H 1.27935500 1.75690800 -0.22115200
C 2.18520300 4.06336500 -0.23763000
H 1.16135900 4.44369600 -0.32533900
H 2.71833200 4.72297300 0.45938200
H 2.66232900 4.14994300 -1.21965900
H 4.04164800 2.10066300 -0.72371800
C 5.35706500 -0.63723800 -0.70109200
H 5.45914800 -1.14705600 -1.66699200
H 5.69177300 0.39730400 -0.82273200
C 6.22553600 -1.35511300 0.35475800
H 5.91447700 -2.39692100 0.48055400
H 7.27019900 -1.34504800 0.02935300
H 6.15934300 -0.85113200 1.32438900
Au -1.33975200 0.10919500 -0.09130400
P -3.58543900 -0.25800000 -0.00667700
C -4.57776500 1.28032300 -0.07486600
H -4.36312500 1.81730200 -1.00395700
H -5.64564000 1.03840900 -0.03396500
H -4.31866400 1.92270500 0.77252900
C -4.19911000 -1.29792400 -1.38411100
H -3.69283700 -2.26802300 -1.36564000
H -5.27981600 -1.45000700 -1.28672200
H -3.98589400 -0.80676700 -2.33865400
C -4.12079300 -1.11119200 1.52322000
H -5.20547600 -1.26487000 1.50484200
H -3.61906800 -2.08083500 1.59951000
H -3.85471500 -0.50582200 2.39534700
INT5-Au
O 1.76095400 -2.07852700 0.19078200
C 1.45433200 -0.95925500 0.95000700
C 1.69336500 0.23287000 0.27054700
C 2.38903600 -0.14334400 -1.05533100
C 2.26648500 -1.68159300 -1.03170000
C 1.80088300 1.54030200 0.93782800
C 2.12800400 2.71239100 0.36230900
O 2.54382600 -2.47392000 -1.88548400
H 2.29843600 2.77426800 -0.71138000
C 1.83355800 0.40939800 -2.36643900
H 2.34767800 -0.07846700 -3.20011200
H 0.75746600 0.22270000 -2.45057500
H 2.00155300 1.48835200 -2.43539600
Au -0.62616400 0.01223600 0.05480000
P -2.90734900 0.19569500 -0.36216200
C -3.31879500 1.64836300 -1.39934500
H -2.80565900 1.57109800 -2.36299900
H -4.40072200 1.69151600 -1.56684000
H -2.99258600 2.56390500 -0.89617900
C -3.90363200 0.38099600 1.16321300
H -4.96393000 0.47806100 0.90451400
H -3.76594800 -0.49591800 1.80331500
H -3.57977700 1.27278400 1.70865700
C -3.60656200 -1.25108900 -1.23975500
H -3.45755500 -2.15409000 -0.63972800
H -4.67859100 -1.09996800 -1.40894600
H -3.10154300 -1.37781200 -2.20245500
O 3.79300000 0.08202400 -0.93582800
H 3.94106400 1.04463200 -0.98172600
C 2.28622600 3.99561600 1.11776100
H 3.30578800 4.38954200 1.00598500
H 1.61145500 4.76700600 0.72202700
H 2.08137100 3.86760000 2.18582600
H 1.62435400 1.53056700 2.01223000
C 1.22677400 -1.25723200 2.39967700
H 2.21434400 -1.51674400 2.81111100
H 0.90117600 -0.34430100 2.90370500
C 0.24436500 -2.40419400 2.67332800
H 0.57642000 -3.33628400 2.20644200
H 0.17172900 -2.57145800 3.75256600
H -0.75580600 -2.16509400 2.29484400
INT6-Au
O -1.76417500 -2.01837000 0.11864000
C -1.53681200 -0.92052100 -0.66975200
C -2.34466600 0.21857400 -0.16635100
C -3.03788300 -0.24130300 0.91567200
C -2.67298200 -1.64880900 1.12512700
C -2.35500600 1.51975200 -0.81923800
C -2.71521700 2.68235200 -0.24045200
O -3.02949600 -2.44996000 1.95152000
H -3.00040400 2.69830500 0.80936500
C -4.04505500 0.42437400 1.79120200
H -4.67299500 -0.32596000 2.28056300
H -3.56206600 1.01652900 2.57995500
H -4.68195200 1.10351000 1.21414000
Au 0.83652900 -0.21619600 -0.34398000
P 2.79617500 0.47647700 0.69530600
C 2.64104500 2.09527200 1.53744500
H 1.86863000 2.03602500 2.31042200
H 3.59674200 2.36709400 1.99954800
H 2.35790900 2.86284400 0.81054500
C 4.18654100 0.66133300 -0.48189700
H 5.08812900 0.97743400 0.05454800
H 4.37683000 -0.29422700 -0.98015100
H 3.93235300 1.41111300 -1.23742800
C 3.38264300 -0.69659700 1.97341200
H 3.56026000 -1.67644900 1.51942000
H 4.31368200 -0.32781300 2.41811400
H 2.62339900 -0.80090600 2.75458100
C -2.73425500 4.00073900 -0.94521600
H -3.74219300 4.43731900 -0.91469000
H -2.07300600 4.71922500 -0.44170700
H -2.42492200 3.91272400 -1.99182800
H -2.03872000 1.53809400 -1.86086400
C -0.77149300 -1.03587200 -1.81036800
H -0.78226100 -0.18225800 -2.48465700
C -0.30266200 -2.34949900 -2.37977100
H -1.05085700 -2.71318400 -3.09866900
H 0.63774500 -2.22393400 -2.92442900
H -0.17055200 -3.11527300 -1.61207500
H2O
O 0.00000000 0.12060100 0.00000000
H 0.76172200 -0.48240000 0.00000000
H -0.76172200 -0.48240800 0.00000000
INT6-0
O -1.98924700 0.22498700 0.03458600
C -0.98700800 -0.73343300 -0.02261800
C 0.31123600 -0.04837500 -0.06701700
C 0.06018900 1.29626200 -0.03514100
C -1.39358000 1.47698200 0.02984400
C 1.57111400 -0.77506200 -0.15703300
C 2.78810000 -0.29209900 0.15705500
O -2.06349000 2.48898600 0.06469500
H 2.88626800 0.72287100 0.53594600
C 0.97921700 2.47223500 -0.09040500
H 0.42342400 3.36531500 -0.39283400
H 1.43282600 2.68339100 0.88752100
H 1.79794000 2.30809100 -0.80058100
C 4.05815900 -1.07605700 0.04874600

H 4.77109700 -0.57103400 -0.61796000
H 4.55310000 -1.15305900 1.02696800
H 3.88420000 -2.08765900 -0.33272500
H 1.50229600 -1.80699300 -0.49801100
C -1.28241300 -2.04248600 -0.01648800
H -0.44887200 -2.73843000 -0.05138800
C -2.66015200 -2.62161400 0.03634100
H -2.84732700 -3.25268900 -0.84341000
H -2.77159100 -3.27195200 0.91477900
H -3.43063100 -1.84775200 0.07774600
INT0
C -2.58661100 -1.11794000 0.38599800
O -2.97903600 -0.59712900 1.40932200
C -3.21994700 -2.31587000 -0.26264300
H -4.07766100 -2.64455000 0.32750700
H -3.53858400 -2.06807300 -1.28217200
H -2.48938000 -3.12877400 -0.34918800
C -1.34702500 -0.55366400 -0.35375400
O -0.91458600 -1.04905700 -1.37448700
O -0.85123600 0.51733800 0.26912700
C 0.31720000 1.16760200 -0.34393600
H 0.18377800 1.11060100 -1.42923900
C 0.29136400 2.62908200 0.11845300
H 0.36710400 2.65073600 1.21198600
H 1.19828300 3.10334100 -0.27454700
C -0.94991000 3.38785600 -0.35394900
H -1.86640200 2.94636400 0.05099000
H -0.90553200 4.43189700 -0.02473800
H -1.02476900 3.38415000 -1.44846900
C 1.53776300 0.46128400 0.04678700
C 2.56526900 -0.09098500 0.37390300
C 3.80350200 -0.77945200 0.74710800
H 4.56646000 -0.03182000 1.00223700
H 3.62568000 -1.35718300 1.66406500
C 4.33755300 -1.70995700 -0.35606800
H 5.25965500 -2.19678300 -0.02016100
H 3.60683900 -2.48800100 -0.60103600
H 4.55845200 -1.14885800 -1.27031100
INT3-0
C -2.92952900 -0.63780300 -0.11951200
O -3.55399700 0.17517000 -0.76887600
C -3.53052200 -1.83894500 0.55460300
H -4.60911300 -1.85498300 0.38557200
H -3.07602800 -2.75692200 0.16324100
H -3.31867800 -1.81532400 1.63017100
C -1.39806500 -0.49086700 0.06191900
O -0.95734000 0.63735300 -0.51940000
O -0.73069300 -1.30662400 0.65771500
C 2.38729400 -0.67164700 -0.85858300
H 2.74833100 -0.84060300 -1.87685600
C 3.11702200 -1.41942800 0.23557600
H 2.63229400 -1.22881500 1.19879000
H 3.02742700 -2.49673500 0.03580700
C 4.60511900 -1.04434400 0.30247900
H 4.73369700 0.01782300 0.54147800
H 5.11622600 -1.63126000 1.07459100
H 5.10655600 -1.23718000 -0.65383100
C 1.38177800 0.14635400 -0.67296600
C 0.41378400 1.00733500 -0.47869800
C 0.55847000 2.48938000 -0.24986400
H 1.61162900 2.75272200 -0.38999900
H -0.01399400 3.02004400 -1.02336200
C 0.07869000 2.93668200 1.13940200
H 0.19022300 4.02143600 1.24854200
H -0.97775000 2.69052100 1.29289200
H 0.66118200 2.45178300 1.93131200
TS3-0
O -1.80885100 0.25202100 -0.77628800
C -0.98755400 -0.79608800 -0.52609000
C 0.30526600 -0.45025700 -0.24782700
C 0.07486900 1.28229200 0.41180100
C -1.14800400 1.47852000 -0.53363800
C 1.53970000 -0.95662000 -0.42787500
C 2.75542200 -0.45305200 0.27651100
O -1.56894000 2.48671200 -1.02027400
H 2.70064500 -0.73192000 1.33972700
C -0.40133200 1.06156700 1.86737600
H -0.67107000 2.04110800 2.28072700
H -1.26217800 0.39092400 1.95897800
H 0.42753300 0.65873400 2.45728100
O 1.06398800 2.04826900 0.23208300
H 2.67617700 0.65077300 0.28018000
C 4.07370600 -0.93321600 -0.33283200
H 4.92693800 -0.52154800 0.21721300
H 4.15318000 -2.02693100 -0.30502400
H 4.16523800 -0.61570000 -1.37839900
H 1.68866300 -1.68305400 -1.23085200
C -1.66931600 -2.11793400 -0.40302500
H -2.23541800 -2.27517400 -1.33143600
H -0.90225100 -2.89459800 -0.34163200
C -2.63186700 -2.20952900 0.79688100
H -3.39985300 -1.43114500 0.74751000
H -3.13147600 -3.18362700 0.79047500
H -2.09104300 -2.10796400 1.74339900
INT4-0
O 1.92965400 -0.01490300 -0.63755300
C 0.95849200 0.84265800 -0.42688800
C -0.26573200 0.23206600 -0.07492900
C -0.02023700 -1.29788600 0.23524900
C 1.40155200 -1.41916200 -0.41485700
C -1.47524900 0.85607700 -0.12915600
C -2.74978600 0.18194000 0.23001200
O 2.08977500 -2.31110900 -0.77781400
H -2.86259600 0.22928200 1.32624800
C 0.24572900 -1.43290900 1.77648600
H 0.55482100 -2.46405800 1.98020600
H 1.00838400 -0.74654600 2.16955800
H -0.69814500 -1.24527900 2.29970100
O -0.88009300 -2.16025900 -0.25480900
H -2.60409800 -0.89090100 0.00970900
C -3.98587800 0.78040800 -0.44552300
H -4.89114900 0.25396600 -0.12469500
H -4.10692800 1.84147600 -0.19457000
H -3.91996700 0.69716100 -1.53657400
H -1.53031700 1.87031700 -0.52781400
C 1.32693400 2.28227200 -0.48070600
H 1.99755900 2.42874000 -1.33451300
H 0.42865900 2.88557700 -0.63384400
C 2.04053700 2.72465400 0.81807000
H 2.95518100 2.14659300 0.98092800
H 2.30911100 3.78187900 0.73354000
H 1.38661500 2.60125600 1.68698200
TS4-0
O -1.87778500 0.41222700 -0.54456700
C -1.12409900 -0.69416800 -0.34081800
C 0.17440500 -0.39755900 -0.00059100
C 0.29681800 1.15394600 0.22273800
C -1.04695300 1.57208200 -0.42482000
C 1.31651000 -1.17640300 -0.14950900
C 2.59011700 -0.59429700 0.16712400
O -1.46910900 2.63149900 -0.77966100
H 2.66013400 -0.25044300 1.20767300
C 0.14284200 1.48928400 1.73823900
H 0.12577300 2.57898900 1.85121900
H -0.76718400 1.07066700 2.18705400
H 1.01063200 1.09726300 2.27816800
O 1.37715500 1.71540600 -0.34763300
H 2.34820300 0.51961300 -0.28333500
C 3.85182100 -1.29340400 -0.31278200
H 4.06595500 -2.19470800 0.27641900
H 3.76743400 -1.59164600 -1.36420300
H 4.71909200 -0.62981100 -0.22436400
H 1.26298800 -2.08844100 -0.74656400
C -1.83471700 -1.99507800 -0.44424300
H -2.38200300 -2.01026600 -1.39516800
H -1.08967200 -2.79611300 -0.46455500
C -2.82456000 -2.21960400 0.71819200
H -3.58446600 -1.43230600 0.74573000

H -3.33008000 -3.18124800 0.58530800
H -2.30199100 -2.23339300 1.68033500
INT3-Cu
C -1.18722000 -0.15952600 1.44657800
O -0.30589100 -0.32752800 0.59931800
C -0.96461900 0.30607600 2.83689800
H 0.09574800 0.30158500 3.09760000
H -1.36010000 1.32855100 2.92411000
H -1.53839300 -0.31112800 3.53560500
C -2.64802200 -0.43192700 1.03392700
O -2.71906800 -0.73269700 -0.25985600
O -3.54868600 -0.35854100 1.83760200
C -6.32174100 -0.22307700 -0.16805300
H -6.69349700 0.72988000 -0.55412000
C -7.26950500 -0.99305500 0.72419400
H -6.77970700 -1.90328200 1.08608400
H -7.49114000 -0.37308800 1.60453700
C -8.58432500 -1.33986300 0.01004000
H -8.40497200 -1.99156000 -0.85296900
H -9.26671900 -1.85921400 0.69277200
H -9.09079400 -0.43598300 -0.34965000
C -5.11368000 -0.60491500 -0.49620400
C -3.94748500 -1.03150500 -0.91550100
C -3.67572900 -1.84662800 -2.15288000
H -4.61301000 -1.92551200 -2.71197200
H -2.96670700 -1.29472300 -2.78527400
C -3.11672500 -3.24539300 -1.85141900
H -2.93080500 -3.78616900 -2.78611600
H -2.17014700 -3.18684200 -1.30293100
H -3.82411300 -3.83076900 -1.25281700
Cu 1.64496400 0.04951900 0.75422800
O 1.51254200 1.96887800 0.78541700
O 3.73321400 -0.15579700 0.73206600
O 2.11910800 -1.91090100 0.85988200
O 1.87702800 2.10545300 -1.68965900
S 1.57138900 2.86311900 -0.46992700
O 2.29545100 4.10475100 -0.19793900
C -0.21903000 3.34912700 -0.61622300
S 3.62392700 -1.66846800 0.75768900
O 4.48020000 -2.40365000 1.67452900
C 4.06125700 -2.21651200 -0.97328100
F 3.26283900 -1.59710100 -1.84276800
F 5.32863300 -1.90019900 -1.21870300
F 3.89234400 -3.53223400 -1.06502200
F -0.37821900 4.15981000 -1.66491200
F -0.97700200 2.25707400 -0.79184500
F -0.62025000 3.97834300 0.49202800
TS3-Cu
O -4.24356600 -2.28905400 -0.10164300
C -4.75206700 -1.01614900 -0.13935700
C -3.99630100 -0.05295800 0.42870400
C -2.17519800 -1.02634800 -0.20529500
C -2.90329100 -2.31536600 0.21029900
C -3.93544400 1.03725900 1.18870200
C -2.86152800 2.07938300 1.20851100
O -2.38221100 -3.27589600 0.70167200
H -3.32288400 3.01136900 0.84662000
C -2.13146700 -0.72267300 -1.68834600
H -1.30155200 -1.30072300 -2.11742700
H -3.04857300 -0.99815500 -2.21219500
H -1.93039600 0.34102000 -1.84487800
H -2.05692600 1.83233600 0.51520300
C -2.30357700 2.32201300 2.62024900
H -1.57094700 3.13471600 2.59651700
H -3.10140000 2.60041000 3.31896800
H -1.80760000 1.42576400 3.00862200
H -4.72698400 1.16626700 1.93242200
C -5.98196900 -0.89501600 -0.98107300
H -5.70964300 -1.15216700 -2.01534500
H -6.66263900 -1.69229400 -0.65037400
C -6.67096300 0.46660100 -0.91810400
H -6.01733100 1.26464500 -1.28504300
H -7.56904900 0.44977400 -1.54344000
H -6.97628800 0.71322400 0.10407300
O -1.19965300 -0.69714000 0.53763300
Cu 0.63237500 -0.26638100 0.00543300
O 1.03349400 -2.18727900 -0.59618200
O 0.87610600 2.20955800 -1.86771800
O 0.63680200 1.59578100 0.53971500
O 2.69203100 -0.47724300 -0.38253400
S 2.53350100 -1.94864800 -0.71097000
O 3.20498700 -2.46294100 -1.89505400
C 3.25416500 -2.84020500 0.76089100
S 0.80462700 2.72387500 -0.49193700
O -0.08643300 3.85148000 -0.20660500
C 2.51336700 3.33980400 -0.08518100
F 3.41660200 2.37553300 -0.27727800
F 2.80504200 4.37560200 -0.87929200
F 2.56351000 3.73782200 1.18989100
F 4.55480000 -2.57016100 0.83782200
F 2.64227500 -2.42180100 1.87083900
F 3.06959900 -4.14932400 0.61368200
INT4-Cu
O 3.54186000 -0.36741500 -1.30844800
C 3.81732500 -1.18091200 -0.31063800
C 2.67220100 -1.86644100 0.17033900
C 1.45760200 -1.45991200 -0.67266200
C 2.11088000 -0.42732300 -1.61809500
C 2.70373800 -2.66291500 1.27785900
C 1.54977600 -3.32765300 1.92797900
O 1.69243800 0.25895000 -2.48873700
H 1.71426500 -4.41293600 1.82518400
C 0.94055400 -2.61631500 -1.55535100
H 0.16825700 -2.24133000 -2.23485200
H 1.74329900 -3.06417600 -2.15280700
H 0.50248000 -3.38746400 -0.91585900
O 0.49620700 -0.87529600 0.12884300
H 0.61236900 -3.07351000 1.43162100
C 1.48151300 -2.99206200 3.43338100
H 0.66316200 -3.55511600 3.89257500
H 2.41295500 -3.25770000 3.94543800
H 1.29283200 -1.92444100 3.58554600
H 3.66587400 -2.81787400 1.76492700
C 5.22881400 -1.21041100 0.14260500
H 5.37181900 -0.29276000 0.73531700
H 5.37938900 -2.05418800 0.81829300
C 6.24469100 -1.23536700 -1.01363300
H 6.14606600 -0.35398100 -1.65252900
H 7.25393800 -1.24528500 -0.59273000
H 6.11870800 -2.13209700 -1.62852600
Cu -1.00924300 0.03340500 -0.51889400
O -0.30943400 1.86430600 -0.68850500
O -2.93867700 0.63766100 -1.11435900
O -2.35514200 -1.60991600 -0.50822400
O -0.46241800 2.18753000 1.79243100
S -0.05050900 2.77625600 0.50940400
O -0.42765800 4.16545700 0.22865700
C 1.81017300 2.79969100 0.54556500
S -3.52643400 -0.74293100 -0.91552100
O -4.41784100 -1.25280700 -1.95122300
C -4.54856600 -0.58860100 0.63472600
F -3.77875500 -0.15637300 1.63756400
F -5.53754600 0.28006800 0.42880700
F -5.05657800 -1.78045200 0.94981100
F 2.23125200 3.57931900 1.54845200
F 2.30345000 1.56350900 0.73444100
F 2.29227100 3.27531600 -0.60704400
TS4-Cu
O 2.87007700 -2.50885800 -1.23642500
C 3.65260500 -1.87753000 -0.30107400
C 2.91108400 -1.35126200 0.71821400
C 1.43845300 -1.71397800 0.48863500
C 1.52706100 -2.27613100 -0.93840800
C 3.25106700 -0.27857100 1.57328700
C 2.29306000 0.29550200 2.42188400
O 0.66123300 -2.54373400 -1.72190100
H 1.67515400 -0.40184100 2.99754000
C 0.91624800 -2.84373600 1.39741300

H -0.10192900 -3.10998900 1.09990300
H 1.55299000 -3.73240100 1.32307900
H 0.90658800 -2.50785900 2.43798000
O 0.66024800 -0.54213700 0.57602600
H 1.36291200 0.21622800 1.44178000
C 2.54262300 1.62769500 3.09201700
H 1.59463000 2.11785900 3.33440400
H 3.10022900 1.50375200 4.02963900
H 3.11122000 2.29996100 2.44140700
H 4.17571400 0.26037500 1.36368500
C 5.11143500 -1.89919100 -0.56877500
H 5.27767300 -1.47506300 -1.56773500
H 5.61014400 -1.25553500 0.16159200
C 5.70066500 -3.32432900 -0.51441000
H 5.22751800 -3.97655700 -1.25494900
H 6.77226100 -3.27938100 -0.73137600
H 5.56651600 -3.76734400 0.47778900
O -0.35453000 1.53432900 -1.23997000
O -2.82534100 -0.06049500 -1.30731300
O -2.10370000 -1.71103100 0.26427200
O -0.28922700 2.48204800 1.06679700
S -0.15801600 2.78220700 -0.36857000
O -0.85557400 3.95223000 -0.90691000
C 1.65061800 3.12746800 -0.64355900
S -3.32017200 -1.26466800 -0.52977200
O -4.06656700 -2.28380700 -1.25269500
C -4.47147500 -0.55363700 0.75472900
F -3.82007400 0.36694400 1.46950200
F -5.51373900 0.00716500 0.14700300
F -4.88666400 -1.53023800 1.55869000
F 2.04229700 4.11514200 0.16894600
F 2.38561600 2.03783000 -0.37757100
F 1.86469200 3.48979800 -1.91080700
Cu -0.94977100 -0.12740600 -0.39647900

INT5-Cu

O 2.38163100 -0.46466700 1.88439400
C 3.63443900 -1.02855600 1.45378900
C 3.62727300 -1.29262300 0.13506800
C 2.30582300 -0.79413500 -0.44547200
C 1.56923300 -0.39881900 0.84753000
C 4.72203300 -1.87404800 -0.62625400
C 4.67471400 -2.25839900 -1.91491100
H 3.74707600 -2.15537600 -2.47415800
C 2.49351100 0.45922900 -1.31911800
H 1.52352300 0.84294900 -1.65078300
H 3.01120600 1.25019600 -0.76971700
H 3.09647600 0.19359900 -2.19202100
O 1.56147900 -1.80329500 -1.10930100
H 1.30028600 -1.47112100 -1.98705700
C 5.83101300 -2.84917500 -2.66104000
H 5.58163300 -3.84888000 -3.04347800
H 6.08538400 -2.23813300 -3.53864600
H 6.72325400 -2.93380900 -2.03123100
H 5.65306400 -2.01209100 -0.07766400
C 4.61445500 -1.18186300 2.55973500
H 4.15607500 -1.79435000 3.34841100
H 5.47254900 -1.74355900 2.17876500
C 5.07921000 0.15938300 3.15638600
H 4.23641400 0.72815800 3.56309500
H 5.78834700 -0.02343700 3.97061400
H 3.62371400 -0.12517900 4.02363400
H 5.57654200 0.77518900 2.39903500
O 0.39353300 -0.05961000 1.01260200
Cu -1.15533100 -0.11745300 -0.21159800
O -0.93366700 1.58438600 -1.09341500
O -2.92290000 -0.60132400 -1.16205100
O -1.72714300 -1.98799100 0.36693100
O -1.72643800 2.72059100 0.98355900
S -1.23672700 2.91951500 -0.38600800
O -1.94372100 3.84277500 -1.27401100
C 0.47587300 3.62843700 -0.20685900
S -3.00369100 -1.94974300 -0.46397300
O -3.31645200 -3.11759000 -1.27219900
C -4.37732900 -1.75694100 0.78557200
F -4.11926500 -0.70414000 1.56105800
F -5.52436400 -1.57104900 0.13957200
F -4.44416200 -2.85826000 1.52785400
F 0.39101000 4.85691200 0.30995200
F 1.21467700 2.86572400 0.61095400
F 1.07848300 3.69295700 -1.39802900

INT6-Cu

O 2.41111300 -0.51804700 1.84809100
C 3.69063800 -0.90047200 1.44007400
C 3.61081600 -1.31918300 0.04518000
C 2.29320000 -1.17860000 -0.34910500
C 1.57966300 -0.67882100 0.79894200
C 4.77584900 -1.76430600 -0.69657000
C 4.76366200 -2.48975300 -1.83351700
H 3.81913100 -2.81354500 -2.26308300
C 5.99449000 -2.92625400 -2.55885600
H 6.02959500 -4.02185900 -2.63491300
H 5.98527300 -2.54730800 -3.59038500
H 6.90850800 -2.57885700 -2.06691400
H 5.74111700 -1.49869600 -0.26999100
C 4.71420600 -0.85735300 2.30764000
O 0.37543300 -0.39055800 0.98918000
Cu -1.13925400 -0.18576900 -0.20064500
O -0.57630500 1.41607900 -1.13279700
O -2.92456400 -0.39404200 -1.20422200
O -2.09037200 -1.89494900 0.45712600
O -1.15611100 2.75834400 0.89700200
S -0.64062600 2.80792400 -0.47766700
O -1.17431900 3.81016000 -1.40194500
C 1.16995100 3.20809900 -0.31863000
S -3.29461400 -1.65541300 -0.44016400
O -3.80409200 -2.78417800 -1.20413700
C -4.65105200 -1.12351100 0.72599900
F -4.22836600 -0.08619900 1.44978200
F -5.72001300 -0.77171800 0.01737000
F -4.95175300 -2.13985400 1.53036000
F 1.30734100 4.44169400 0.17674500
F 1.77075200 2.34259000 0.50910800
F 1.76505000 3.14667500 -1.51350900
C 1.66608100 -1.44442300 -1.67956500
H 2.33240900 -1.13483900 -2.49204500
H 1.44321700 -2.51014800 -1.81882200
H 0.72807000 -0.89400400 -1.80154900
H 5.68589600 -1.17127100 1.93697000
C 4.63341000 -0.42054300 3.73060400
H 4.97184400 -1.23124700 4.38992700
H 5.31456400 0.42365800 3.90290800