Supporting Information for Publication

Ynol ethers as ketene equivalents in rhodium-catalyzed intermolecular [5+2] cycloaddition reactions

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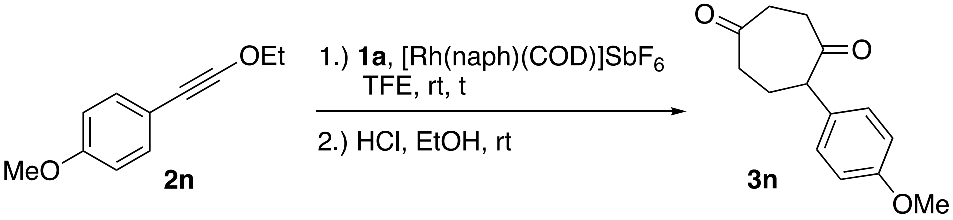
Additional Tables

Table SI-1

Table SI-1. *Optimization of reaction conditions for highly electron-rich* ***2n****.*

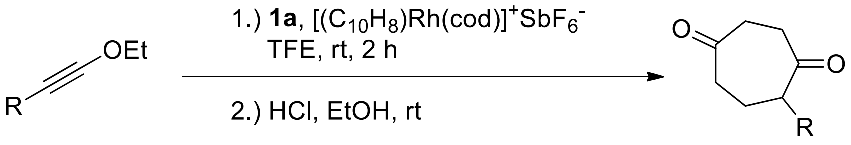


entry	time of alkyne addition [h]	reaction time after addition [h]	yield [%]
1	0.25	3.75	<50[a]
2	2	2	55
3	4	0	80

[a] *Mechanistic yields were obtained on product mixtures by qNMR to avoid loss during purification*

Table SI-2

Table SI-2. *Comparison between results upon use of purified or non-purified alkoxy alkynes.*



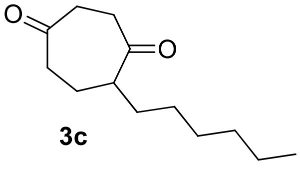
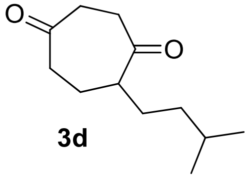
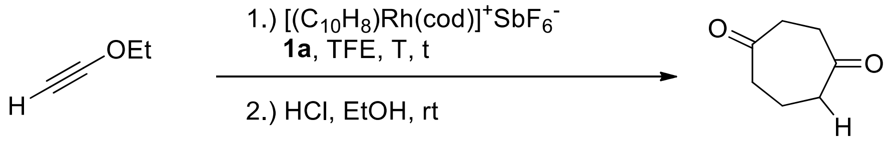
entry	cycloaddition product	yield using purified substrate [%]	yield using crude substrate [%]
1	 **3c**	91	90
2	 **3d**	90	90

Table SI-3

Table SI-3. *Reaction scale-up and reduction of catalyst loading.*



entry	scale [mmol]	conc. [M]	cat.-loading [mol%]	temp. [°C]	time [h]	yield [%]
1	0.15	0.15	5	25	2	87
2	0.15	0.15	2	25	2	86
3	0.3	0.15	1	25	2	86
4	0.3	0.15	0.5	25	3	61
5	0.6	0.3	0.5	25	3	40
6	0.3	0.15	0.5	40	2	30
7	1.0	0.15	1	25	2	87

General methods

All reactions were carried out in flame- or oven-dried glassware cooled under a dry nitrogen stream. Reagents were purchased from common vendors and used as received. Tetrahydrofuran (THF) was passed through *Solv-Tek*® alumina drying columns. 1,2-dichloroethane (DCE) was distilled over calcium hydride under a dry nitrogen atmosphere. 2,2,2-trifluoroethanol (TFE) was stored over activated 4Å molecular sieves after being stirred with anhydrous potassium carbonate overnight followed by distillation from potassium carbonate under dry nitrogen. Column chromatography was performed with Silia*Flash*® silica gel purchased from SiliCycle, Inc. (60 Å, 40-63 µm, 230-400 mesh, R10030B). For TLC analyses, precoated glass-backed plates purchased from EMD Chemicals, Inc. (silica gel 60 F254, 250 µm, 5715-7) were used and the compounds were visualized with *p*-anisaldehyde or potassium permanganate stains followed by gentle heating on a hot plate. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian INOVA 600 (600 MHz), Varian INOVA 500 (500 MHz), Varian 400 (400 MHz) or Mercury 400 (400 MHz) magnetic resonance spectrometer. All spectra were obtained at room temperature in the indicated solvent and referenced relative to tetramethylsilane ($\delta = 0$ ppm) using the solvent residual peaks for ^{1}H-NMR ($CDCl_3$ 7.26 ppm, CD_2Cl_2 5.32 ppm, C_6D_6 7.16 ppm) and the signals of the deuterated solvents for ^{13}C-NMR ($CDCl_3$ 77.16 ppm, CD_2Cl_2 53.5 ppm, C_6D_6 128.1 ppm), respectively as internal standards. Multiplets are assigned as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), and m (multiplet). The index br stand for broad. IR spectra were collected on a Perkin Elmer 1600 series FTIR spectrometer as thin films on a sodium chloride plate. The absorption bands are given in wavenumbers (cm^{-1}). High-resolution mass spectroscopy (HRMS) was recorded at the Vincent Coates foundation mass spectrometry laboratory at Stanford University, California.

Analytical Data

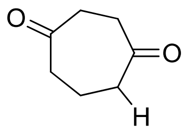
Cycloaddition Products

General method A (Alkyl Substituted [5+2] Procedure)

A solution of ethoxy alkyne **2** (165 µmol, 1.10 eq.) in TFE (0.5 mL) was added dropwise to a solution of vinylcyclopropane **1** (150 µmol, 1.00 eq.) and [Rh(naph)(COD)]SbF_6 (4.3 mg, 7.5 µmol, 5 mol%) in TFE (0.5 mL) over the course of 2 h. After this HCl (0.1 mL, 1% in EtOH) was added to quench the reaction and the mixture was stirred for 1 h. The solution was filtered over a short plug of SiO_2 and eluted with Et_2O (10 mL). After removal of the solvent under reduced pressure, pure product was obtained upon column chromatography (SiO_2, Hexane/EtOAc gradient 0 to 40% EtOAc).

General method B (Aryl Substituted [5+2] Procedure)

A solution of ethoxy alkyne (165 µmol, 1.10 eq.) in DCE (0.5 mL) was added dropwise to a solution of vinylcyclopropane (150 µmol, 1.00 eq.) and [Rh(naph)(COD)]SbF_6 (4.3 mg, 7.5 µmol, 5 mol%) in TFE (0.5 mL) over the course of 2 h. After the addition was completed the reaction mixture was stirred for additional 2 h. Then HCl (0.1 mL, 1% in EtOH) was added to quench the reaction and the mixture was stirred for 1 h. The solution was filtered over a short plug of SiO_2 and eluted with Et_2O. After removal of the solvent under reduced pressure, pure product was obtained upon column chromatography (SiO_2, Hexane/EtOAc gradient 0 to 40% EtOAc).



Cycloheptane-1,4-dione (3a)

3a (16.4 mg, 0.130 mmol, 87%) was obtained as a clear colorless oil from reaction of VCP **1a** with alkyne **2a** according to general method A.

$C_7H_{10}O_2$ (126.15 g mol^{-1})

^{1}H-NMR (500 MHz, $CDCl_3$): δ= 2.68-2.66 (m, 4H, $\mathrm{C(O)C}\mathit{H}_2\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{C(O)}$), 2.63 (s, 4 H, $\mathrm{C(O)C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C(O)}$), 1.99-1.94 (m, 2H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ= 210.7 ($\mathit{C}\mathrm{(O)CH}_2\mathrm{CH}_2\mathit{C}\mathrm{(O)}$), 43.7 ($\mathrm{C(O)}\mathit{C}\mathrm{H}_2\mathrm{CH}_2\mathit{C}\mathrm{H}_2\mathrm{C(O)}$), 28.0 ($\mathrm{C(O)}\mathit{C}\mathrm{H}_2\mathit{C}\mathrm{H}_2\mathrm{C(O)}$), 20.2 ($\mathrm{CH}_2\mathit{C}\mathrm{H}_2\mathrm{CH}_2$) ppm.

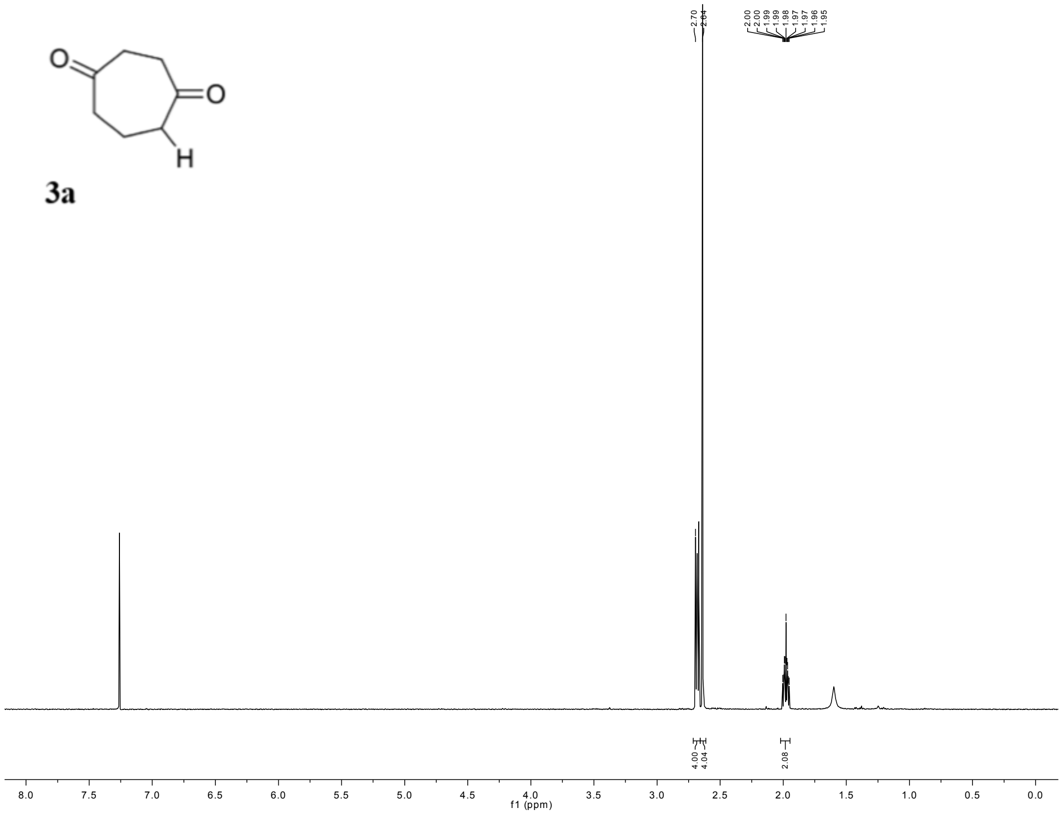
IR (NaCl): = 3505, 2958, 2928, 2875, 1704, 1456, 1433, 1377, 1350, 1322, 1276, 1190, 1170, 1142, 969, 912, 893, 780, 759 cm^{-1}.

HRMS (ESI-MS) calc. (*m*/*z*) for $C_7H_{11}O_2$: 127.0759 $(M+H)^+$; found: 127.0758.

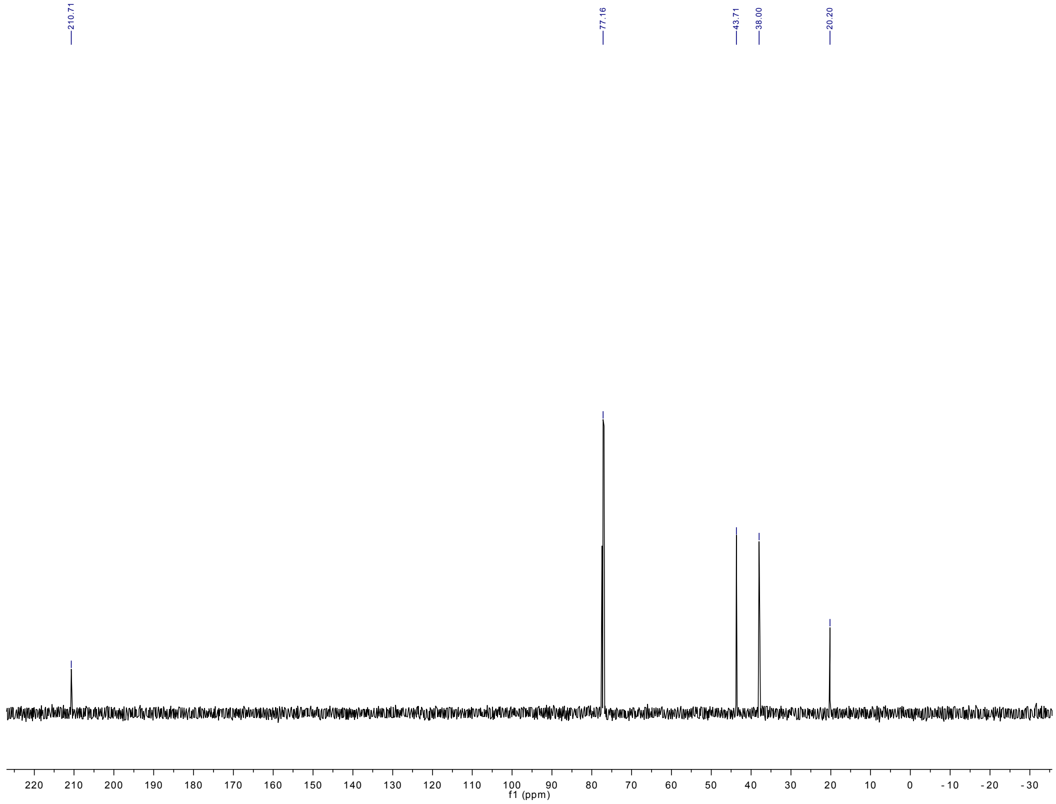
R$_f$ = 0.10 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).

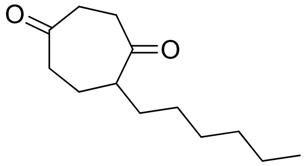
Synthesis at a 1 mmol scale

A solution of ethoxy alkyne **2a** (77.0 mg, 1.1 mmol, 1.10 eq.) in TFE (3.3 mL) was added dropwise to a solution of vinylcyclopropane **1a** (142 mg, 1.0 mmol, 1.00 eq.) and [Rh(naph)(COD)]SbF_6 (5.7 mg, 10 µmol, 1 mol%) in TFE (3.3 mL) over the course of 2 h. After this HCl (0.7 mL, 1% in EtOH) was added to quench the reaction and the mixture was stirred for 1 h. The solution was filtered over a short plug of SiO_2 and eluted with Et_2O (70 mL). After removal of the solvent under reduced pressure, pure product **3a** (109 mg, 0.87 mmol, 87%) was obtained upon column chromatography (SiO_2, Hexane/EtOAc gradient 0 to 40% EtOAc).



3a
2.70
2.64
2.00
2.00
1.99
1.98
1.97
1.97
1.96
1.95
4.00
4.04
2.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.71
77.16
43.71
38.00
20.20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)



5-Hexylcycloheptane-1,4-dione (3c)

3c (28.7 mg, 0.137 mmol, 91%) was obtained as a clear colorless oil from reaction of VCP **1a** with alkyne **2c** according to general method A.

$C_{13}H_{22}O_2$ (210.31 g mol^{-1})

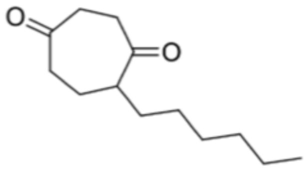
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.69-2.52 (m, 7H, C*H*$_2$C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 2.06-2.00 (m, 1H, C(O)CH$_2$C*H*H'CHCHH'), 1.78-1.71 (m, 1H, C(O)CH$_2$CHH'CHC*H*H'), 1.65-1.57 (m, 1H, C(O)CH$_2$CH*H'*CHCHH'), 1.37-1.31 (m, 1H, C(O)CH$_2$CHH'CHCH*H'*), 1.29-1.23 (m, 8H, CH$_2$(C*H*$_2$)$_4$CH$_3$), 0.86 (t, *J* = 7.1 Hz, 3H, (CH$_2$)$_5$C*H*$_3$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 212.6 (*C*(O)), 210.7 (*C*(O)), 52.5 (C(O)*C*H), 41.9 (*C*H$_2$), 38.2 (*C*H$_2$), 37.4 (*C*H$_2$), 31.8 (*C*H$_2$), 30.9 (*C*H$_2$), 29.4 (*C*H$_2$), 27.4 (*C*H$_2$), 27.0 (*C*H$_2$), 22.7 (*C*H$_2$), 14.2 (*C*H$_3$) ppm.

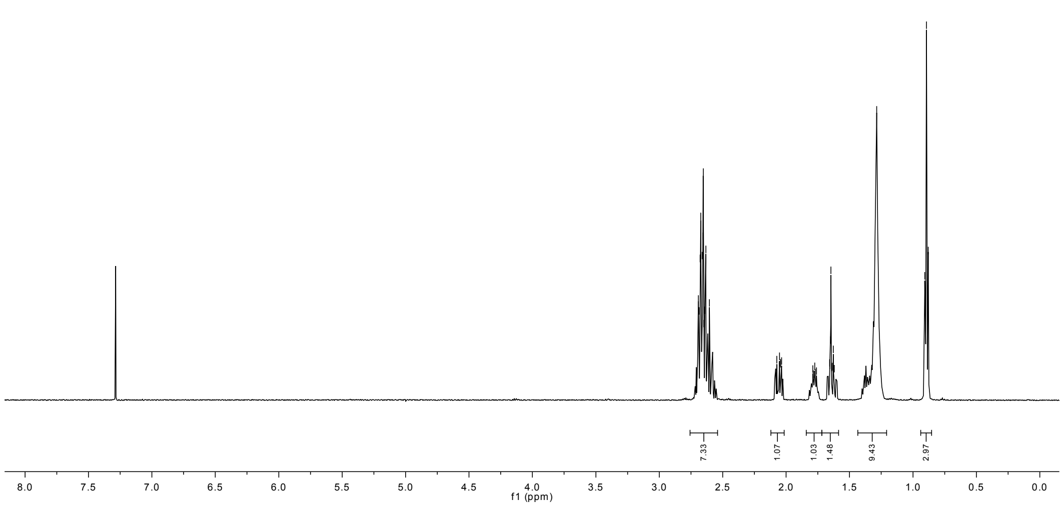
IR (NaCl): 홃=3397, 2955, 2929, 2858, 1707, 1456, 1412, 1378, 1321, 1262, 1189, 1150, 1087, 962, 921, 905, 804, 725 cm^{-1}.

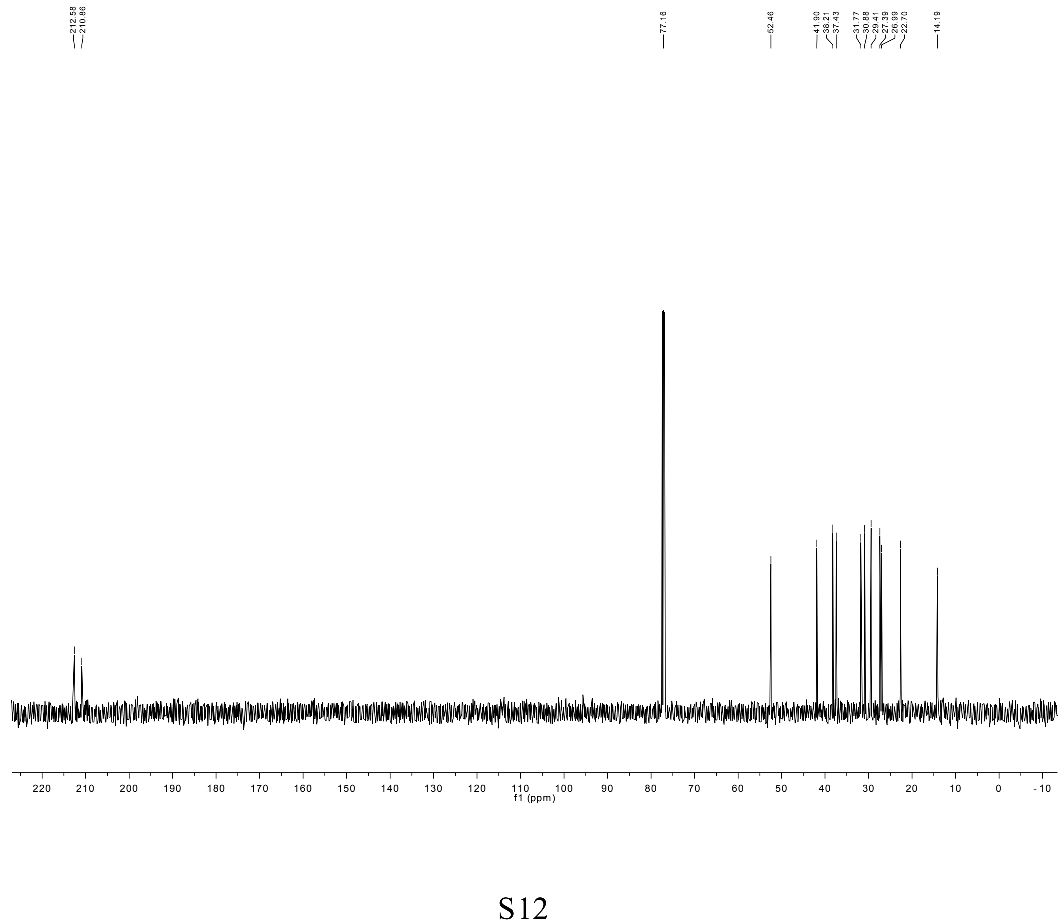
HRMS (ESI-MS) calc. (*m*/*z*) for $C_{13}H_{23}O_2$: 211.1698 (M+H)$^+$; found: 211.1693.

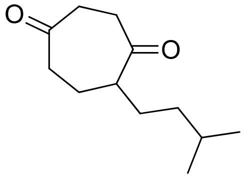
R$_f$ = 0.14 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).



3c


2.69
2.69
2.68
2.68
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.64
2.63
2.60
2.07
2.05
2.04
2.04
2.04
1.79
1.79
1.77
1.77
1.76
1.66
1.66
1.65
1.65
1.64
1.64
1.63
1.62
1.29
0.91
0.89
0.88
7.33
1.07
1.03
1.48
9.43
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.58
210.86
77.16
52.46
41.90
38.21
37.43
31.77
30.88
29.41
27.39
26.99
22.70
14.19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5-*iso*-Pentylcycloheptane-1,4-dione (3d)

3d (26.5 mg, 0.135 mmol, 90%)was obtained as a clear colorless oil from reaction of VCP **1a** with alkyne **2d** according to general method A.

$C_{12}H_{20}O_2$ (196.29 g mol^{-1})

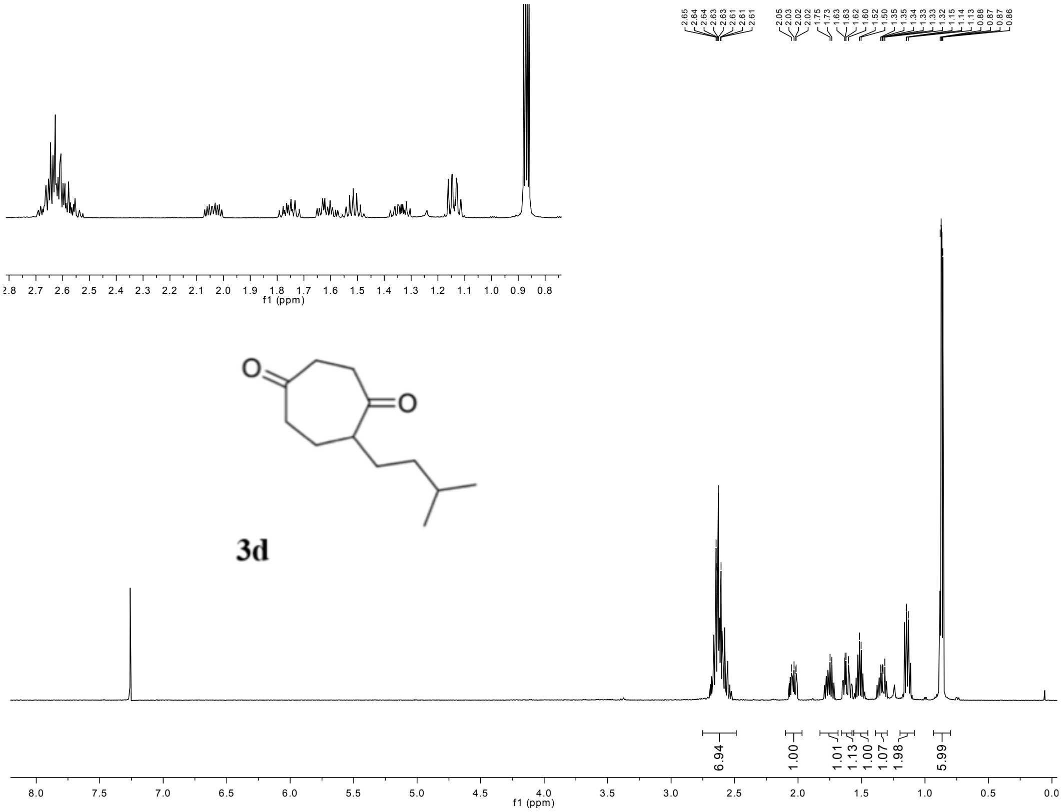
^{1}H-NMR (500 MHz, CDCl$_3$): δ= 2.69-2.53 (m, 7H, C*H*$_2$C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 2.04 (ddt, *J* = 14.6 Hz, 8.3 Hz, 4.2 Hz, 1H, C(O)CH$_2$C*H*H'CHCHH'), 1.79-1.72 (m, 1H, C(O)CH$_2$CHH'CHC*H*H'), 1.61 (ddt, *J* = 14.6 Hz, 10.2 Hz, 4.2 Hz, 1H, C(O)CH$_2$CH*H'*CHCHH'), 1.52 (sept, *J* = 6.7 Hz, 1H, CH$_2$C*H*(CH$_3$)$_2$), 1.38-1.30 (m, 1H, C(O)CH$_2$CHH'CHCH*H'*), 1.18-1.16 (m, 2H, C*H*$_2$CH(CH$_3$)$_2$), 0.87 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)(CH$_3$)), 0.87 (d, *J* = 6.6 Hz, 3H, CH(CH$_3$)(C*H*$_3$)) ppm.

^{13}C{^{1}H}-NMR (126 MHz, CDCl$_3$): δ= 212.6 (*C*(O)), 210.9 (*C*(O)), 52.7 (C(O)*C*H), 41.9 (*C*H$_2$), 38.2 (*C*H$_2$), 37.5 (*C*H$_2$), 36.6 (*C*H$_2$), 28.7 (*C*H$_2$), 28.2 (*C*H$_2$), 27.0 (*C*H$_2$), 22.7 (*C*H$_3$), 22.6 (*C*H$_3$) ppm.

IR (NaCl): 훯= 3396, 2955, 2870, 1706, 1459, 1412, 1385, 1367, 1320, 1261, 1189, 1172, 1152, 1087, 1043, 986, 950, 907, 808 cm^{-1}.

HRMS (ESI-MS) calc. (*m*/*z*) for $C_{12}H_{21}O_2$: 197.1541 (M+H)$^+$; found: 197.1536.

R$_f$ = 0.13 (SiO$_2$, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).


3d

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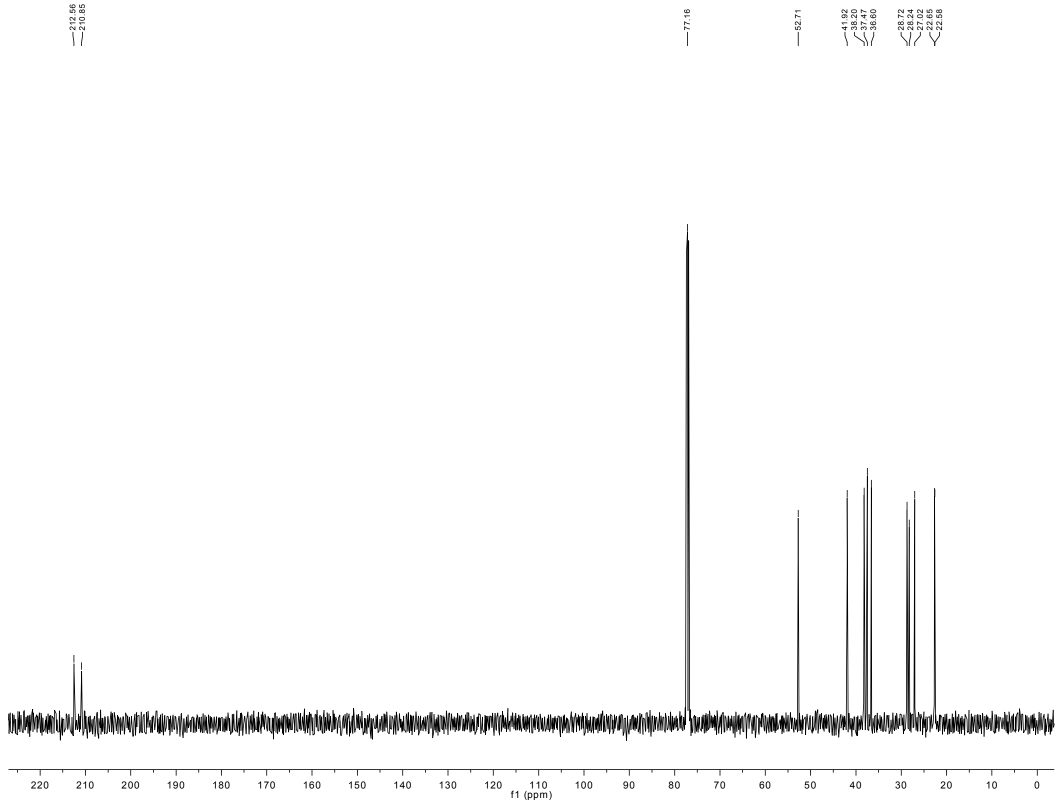
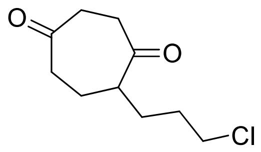
2.64
2.64
2.63
2.63
2.61
2.61
2.61
2.05
2.03
2.02
2.02
1.75
1.73
1.63
1.63
1.62
1.60
1.52
1.50
1.35
1.35
1.34
1.33
1.33
1.32
1.15
1.14
1.13
0.88
0.87
0.87
0.86
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8
f1 (ppm)
O
O
6.94
1.00
1.01
1.13
1.00
1.07
1.98
5.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



212.56
210.85
77.16
52.71
41.92
38.20
37.47
36.60
28.72
28.24
27.02
22.65
22.58
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)



5-(3-Chloropropyl)cycloheptane-1,4-dione (3e)

3e (28.9 mg, 0.143 mmol, 95%) was obtained as a clear colorless oil from reaction of VCP **1a** with alkyne **2e** according to general method A.

$C_{10}H_{15}ClO_2$ (202.68 g mol^{-1})

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.57-3.45 (m, 2H, C*H*$_2$Cl), 2.74-2.52 (m, 7H, C*H*$_2$C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 2.08-2.01 (m, 1H, C(O)CH$_2$C*H*H'CHCHH'), 1.93-1.85 (m, 1H, C(O)CH$_2$CHH'CHC*H*H'), 1.84-1.69 (m, 2H, CH$_2$C*H*$_2$CH$_2$Cl), 1.65-1.60 (m, 1H, C(O)CH$_2$CH*H'*CHCHH'), 1.57-1.50 (m, 1H, C(O)CH$_2$CHH'CHCH*H'*) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 211.7 (*C*(O)), 210.5 (*C*(O)), 51.7 (C(O)*C*H), 44.9 (*C*H$_2$), 42.0 (*C*H$_2$), 38.0 (*C*H$_2$), 37.8 (*C*H$_2$), 30.4 (*C*H$_2$), 28.3 (*C*H$_2$), 27.3 (*C*H$_2$) ppm.

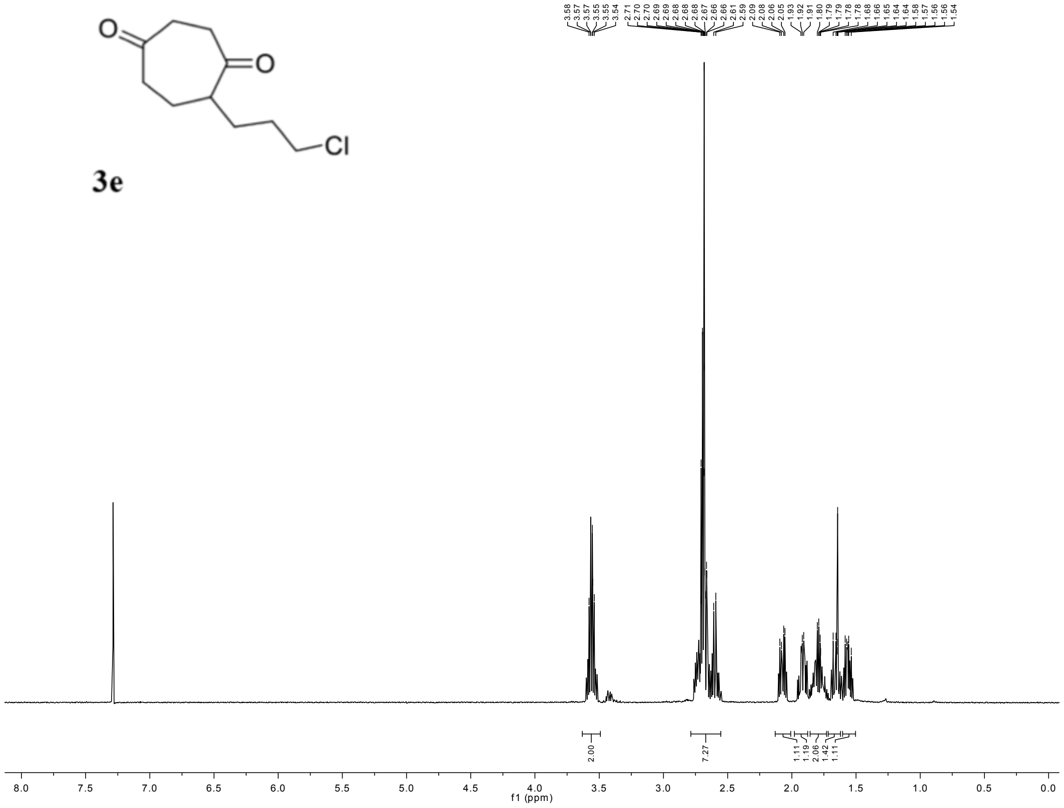
IR (NaCl): 횮= 3394, 2925, 2855, 1704, 1450, 1412, 1379, 1319, 1262, 1194, 1162, 1111, 1087, 1059, 1025, 912, 802, 722, 668, 647 cm^{-1}.

HRMS (ESI-MS) calc. (*m*/*z*) for $C_{10}H_{16}ClO_2$: 203.0839 $(M+H)^+$; found: 203.0837.

R$_f$ = 0.17 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).

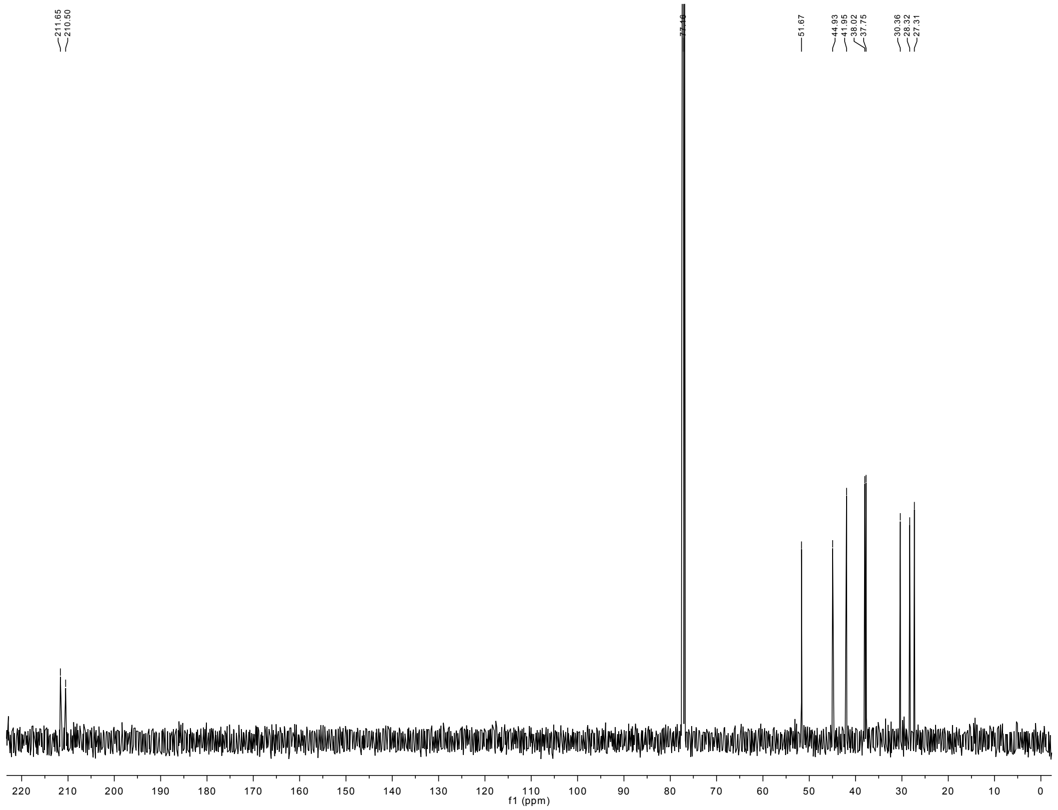
Synthesis at a 1 mmol scale

A solution of ethoxy alkyne **2e** (161 mg, 1.1 mmol, 1.10 eq.) in TFE (3.3 mL) was added dropwise to a solution of vinylcyclopropane **1a** (142 mg, 1.0 mmol, 1.00 eq.) and $[Rh(naph)(COD)]SbF_6$ (5.7 mg, 10 µmol, 1 mol%) in TFE (3.3 mL) over the course of 2 h. After this HCl (0.7 mL, 1% in EtOH) was added to quench the reaction and the mixture was stirred for 1 h. The solution was filtered over a short plug of SiO_2 and eluted with Et_2O (70 mL). After removal of the solvent under reduced pressure, pure product **3e** (188 mg, 0.93 mmol, 93%) was obtained upon column chromatography (SiO_2, Hexane/EtOAc gradient 0 to 40% EtOAc).

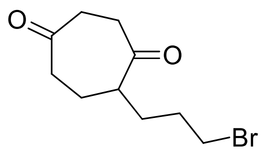


3e

O
O
Cl
3.58
3.57
3.57
3.55
3.55
3.54
2.71
2.70
2.70
2.69
2.69
2.68
2.68
2.68
2.67
2.66
2.66
2.61
2.59
2.09
2.08
2.06
2.05
1.93
1.92
1.91
1.80
1.79
1.79
1.78
1.78
1.68
1.66
1.65
1.64
1.64
1.58
1.57
1.56
1.56
1.54
2.00
7.27
1.11
1.19
2.06
1.42
1.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



211.65
210.50
77.16
51.67
44.93
41.95
38.02
37.75
30.36
28.32
27.31
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)



5-(3-Bromopropyl)cycloheptane-1,4-dione (3f)

3f (36.7 mg, 0.149 mmol, 99%) was obtained as clear colorless oil from reaction of VCP **1a** with alkyne **2f** according to general method A.

$C_{10}H_{15}BrO_2$ (247.13 g mol^{-1})

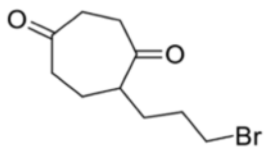
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.44-3.34 (m, 2H, C*H*$_2$Cl), 2.73-2.50 (m, 7H, C*H*$_2$C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 2.08-2.00 (m, 1H, C(O)CH$_2$C*H*H'CHCHH'), 1.93-1.75 (m, 3H, C(O)CH$_2$CHH'CHC*H*H', CH$_2$C*H*$_2$CH$_2$Cl), 1.66-1.48 (m, 2H, C(O)CH$_2$CH*H'*CHCHH', C(O)CH$_2$CHH'CHCH*H'*) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 211.7 (*C*(O)), 210.6 (*C*(O)), 51.7 (C(O)*C*H), 42.0 (*C*H$_2$), 38.1 (*C*H$_2$), 37.8 (*C*H$_2$), 33.6 (*C*H$_2$), 30.6 (*C*H$_2$), 29.7 (*C*H$_2$), 27.4 (*C*H$_2$) ppm.

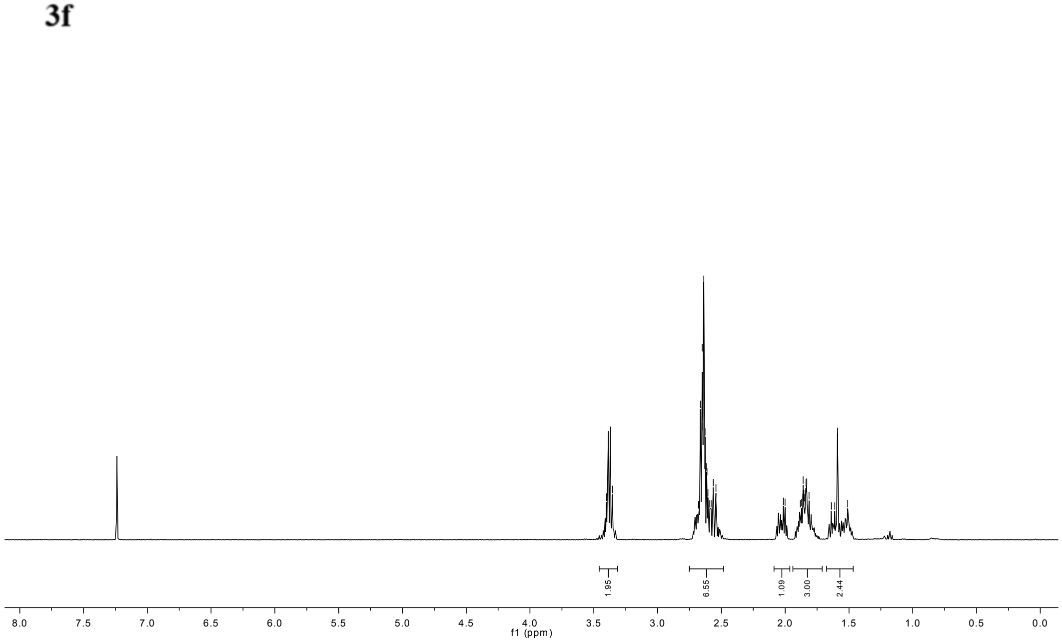
IR (NaCl): 휽= 3392, 2931, 2870, 1704, 1451, 1380, 1336, 1253, 1208, 1114, 1086, 1035, 999, 914, 856, 798, 736, 650 cm^{-1}.

HRMS (ESI-MS) calc. (*m*/*z*) for $C_{10}H_{16}BrO_2$: 247.0334 (M+H)$^+$; found: 247.0338.

R$_f$ = 0.16 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).


O
O
Br

3f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1.51
1.95
6.55
1.09
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2.44
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7.0
6.5
6.0
5.5
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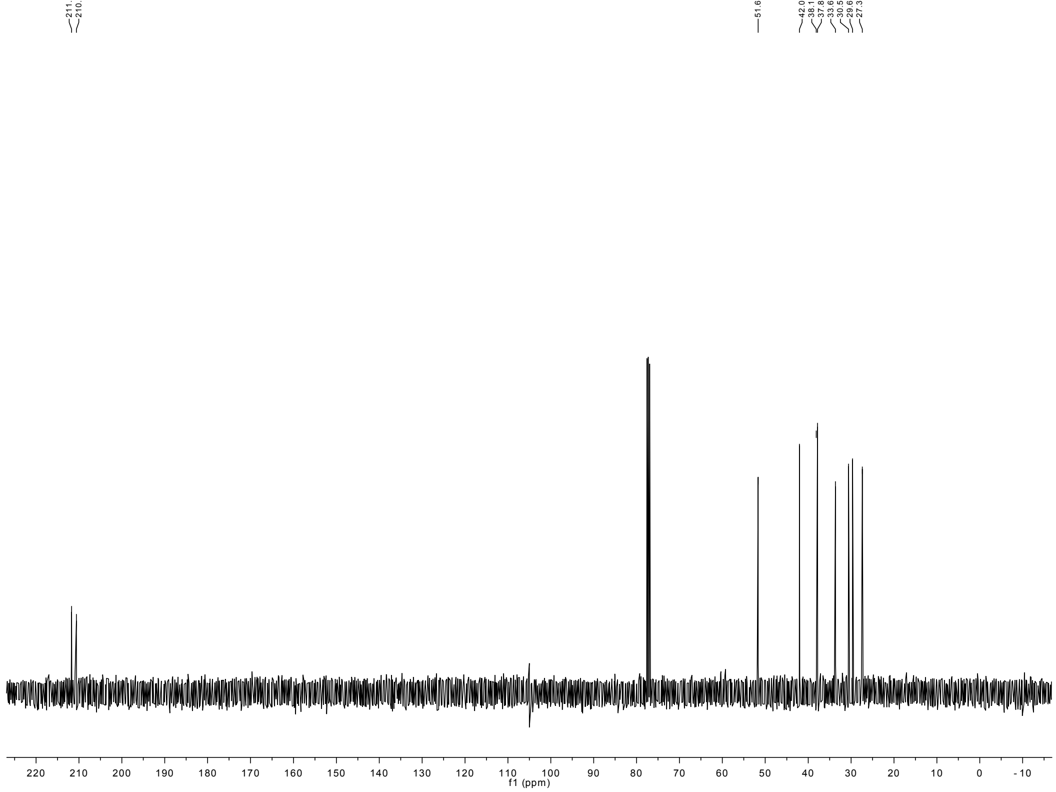
0.0
f1 (ppm)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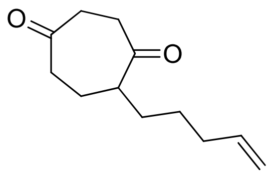
-10
f1 (ppm)



5-(Pent-4-en-1-yl)cycloheptane-1,4-dione (3g)

3g (24.4 mg, 0.126 mmol, 84%) was obtained from reaction of VCP **1a** with alkyne **2g** as a clear colorless oil according to general method A.

$C_{12}H_{18}O_2$ (194.27 g mol^{-1})

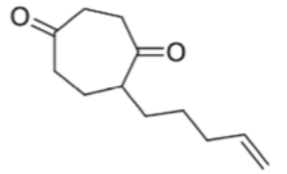
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, J = 17.0 Hz, 10.3 Hz, 6.7 Hz, 1H, $C(O)CH(CH_2)_3C\mathit{H}CH_2$), 5.00 (dq, J = 17.1 Hz, 1.9 Hz, 1H, $C(O)CH(CH_2)_3CHC\mathit{H}H$), 4.95 (brd, J = 10.2 Hz, 1H, $C(O)CH(CH_2)_3CHCH\mathit{H}$), 2.69-2.59 (m, 7H, $C\mathit{H}_2C(O)C\mathit{H}_2C\mathit{H}_2C(O)C\mathit{H}$), 2.07-2.01 (m, 3H, $C(O)CH_2C\mathit{H}H'CHCHH'$, $C(O)CH(CH_2)_2C\mathit{H}_2CHCH_2$), 1.80-1.73 (m, 1H, $C(O)CH_2CHH'CHC\mathit{H}H'$), 1.67-1.56 (m, 2H, $C(O)CH_2CH\mathit{H'}CHCHH'$, $C(O)CH_2CHH'CHCH\mathit{H'}$), 1.38-1.34 (m, 2H, $C(O)CHCH_2C\mathit{H}_2CH_2CHCH_2$) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 212.3 ($\mathit{C}(O)$), 210.8 ($\mathit{C}(O)$), 138.4 ($C(O)CH(CH_2)_3\mathit{C}HCH_2$), 115.0 ($C(O)CH(CH_2)_3CH\mathit{C}H_2$), 52.3 ($C(O)\mathit{C}H$), 41.9 ($\mathit{C}H_2$), 38.2 ($\mathit{C}H_2$), 37.5 ($\mathit{C}H_2$), 33.8 ($\mathit{C}H_2$), 30.3 ($\mathit{C}H_2$), 27.1 ($\mathit{C}H_2$), 26.7 ($\mathit{C}H_2$) ppm.

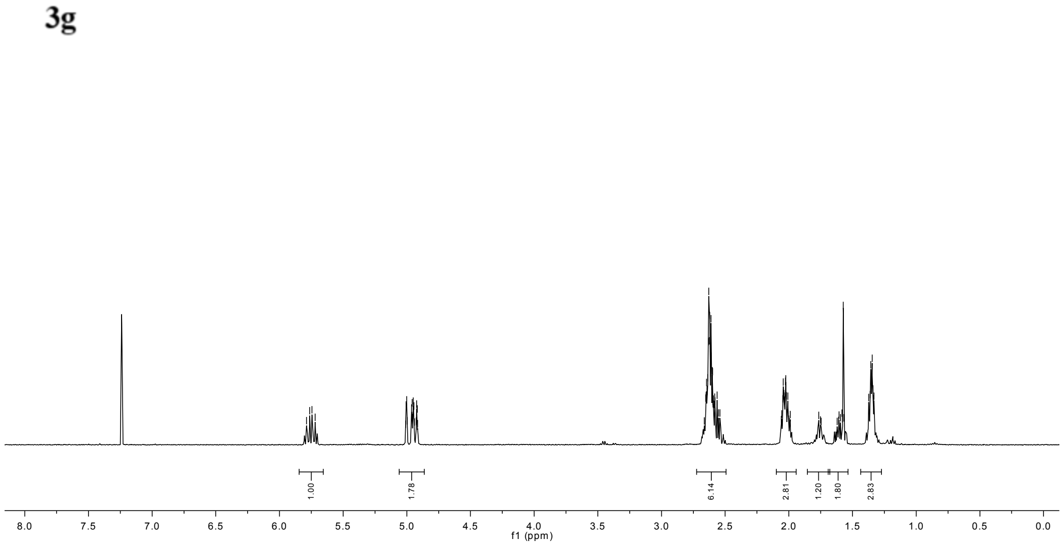
IR (NaCl): 홄= 3395, 3076, 3013, 2933, 2860, 1706, 1640, 1452, 1412, 1377, 1321, 1260, 1188, 1170, 1149, 993, 969, 916, 800, 710 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{12}H_{18}O_2$: 195.1385 $(M+H)^+$; found: 195.1380.

R_f = 0.18 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).



3g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6.5
6.0
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2.5
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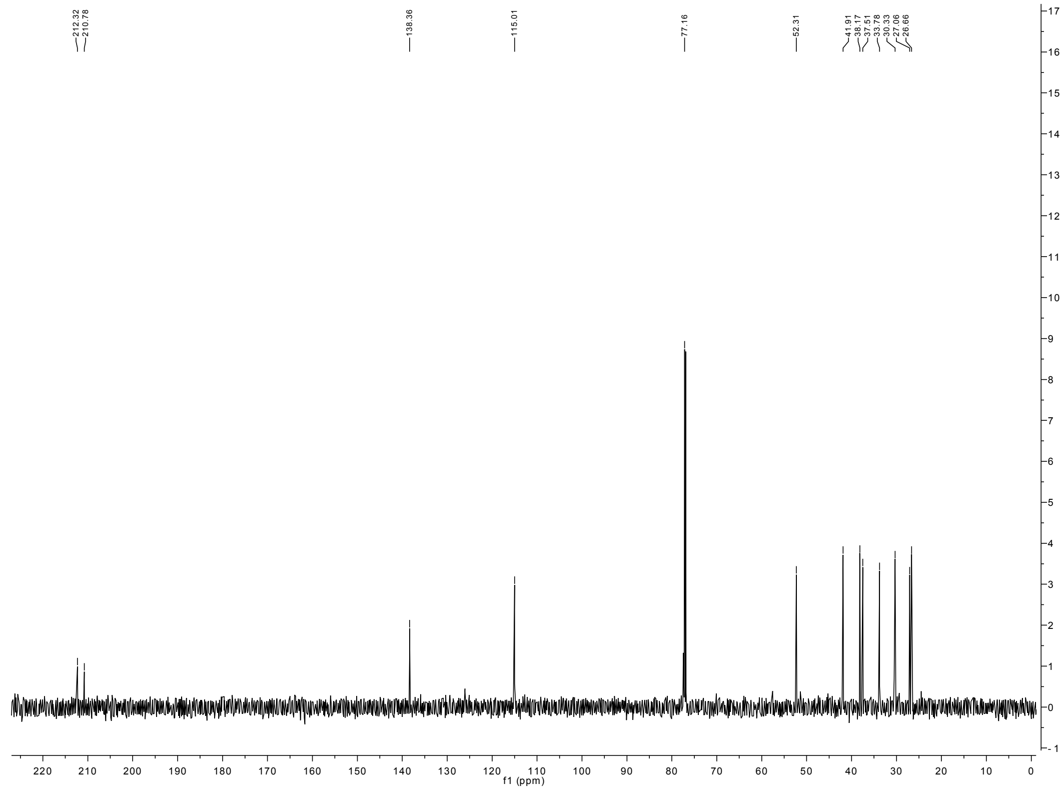
0.0
f1 (ppm)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26.66
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
220
210
200
190
180
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50
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30
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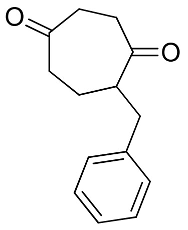
10
0
f1 (ppm)



5-Benzylcycloheptane-1,4-dione (3i)

3i (20.7 mg, 0.096 mmol, 64%) was obtained from reaction of VCP **1a** with alkyne **2i** as a clear colorless oil according to general method B (here no additional reaction time after alkyne addition was necessary).

$C_{14}H_{16}O_2$ (216.28 g mol^{-1})

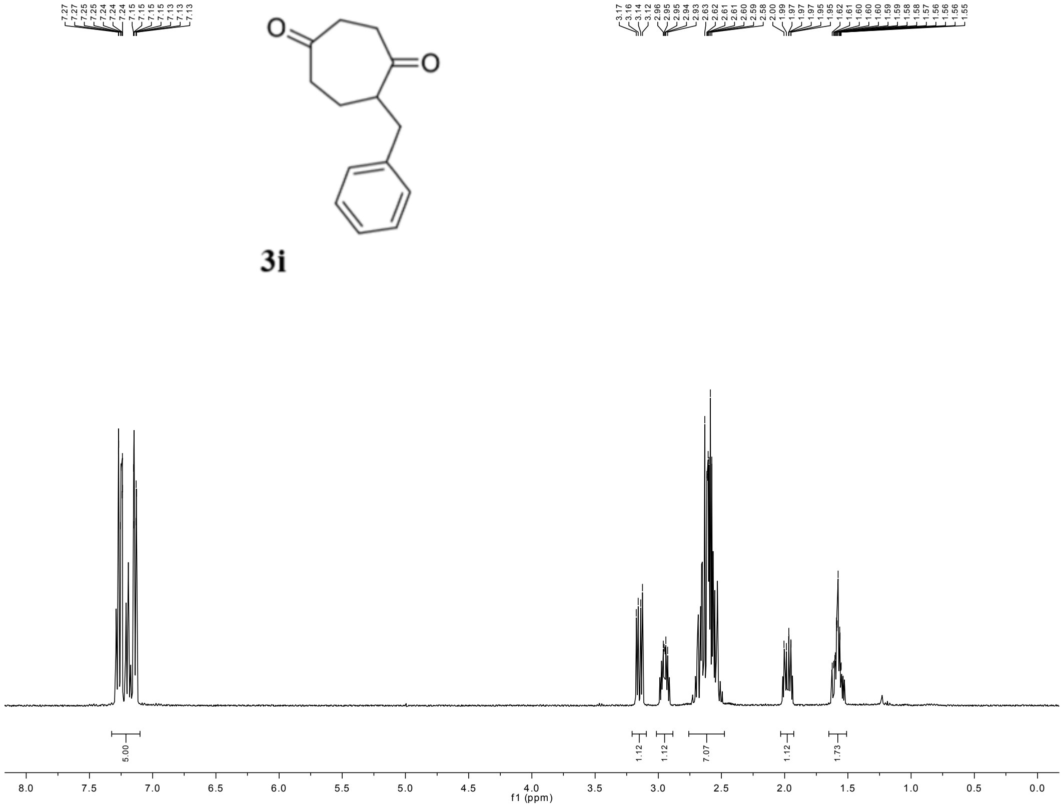
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, J = 7.5 Hz, 2H, aryl-CCHC*H*CHC*H*), 7.21 (t, J = 7.4 Hz, 1H, aryl-CCHCHC*H*), 7.16 (d, J = 7.5 Hz, 2H, aryl-C*H*CC*H*), 3.17 (dd, J = 14.0 Hz, J = 5.7 Hz, 1H, CHC*H*H'Ph), 3.00-2.94 (m, 1H, CHCH*H'*Ph), 2.74-2.52 (m, 7H, CH_2C(O)CH_2CH_2C(O)C*H*), 2.03-1.96 (m, 1H, C(O)CH_2C*H*H'CHC(O)), 1.63-1.55 (m, 1H, C(O)CH_2CH*H'*CHC(O)) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 211.6 (*C*(O)), 210.7 (*C*(O)), 139.3 (aryl-*C*), 129.2 (aryl-CCH*C*HCH*C*H), 128.7 (aryl-*C*HC*C*H), 126.6 (aryl-CCHCHC*H*), 54.0 (C(O)*C*H), 42.1 (*C*H_2), 38.0 (*C*H_2), 38.0 (*C*H_2), 36.6 (*C*H_2), 26.3 (*C*H_2) ppm.

IR (NaCl): 훯= 3394, 3085, 3062, 3028, 2928, 2863, 1704, 1604, 1496, 1454, 1410, 1376, 1322, 1260, 1187, 1170, 1116, 1074, 1031, 944, 911, 809, 746, 702, 668 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{14}H_{16}NaO_2$: 239.1048 $(M+Na)^+$; found: 239.1047.

R$_f$ = 0.19 (SiO_2, hexane/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).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7.15
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7.15
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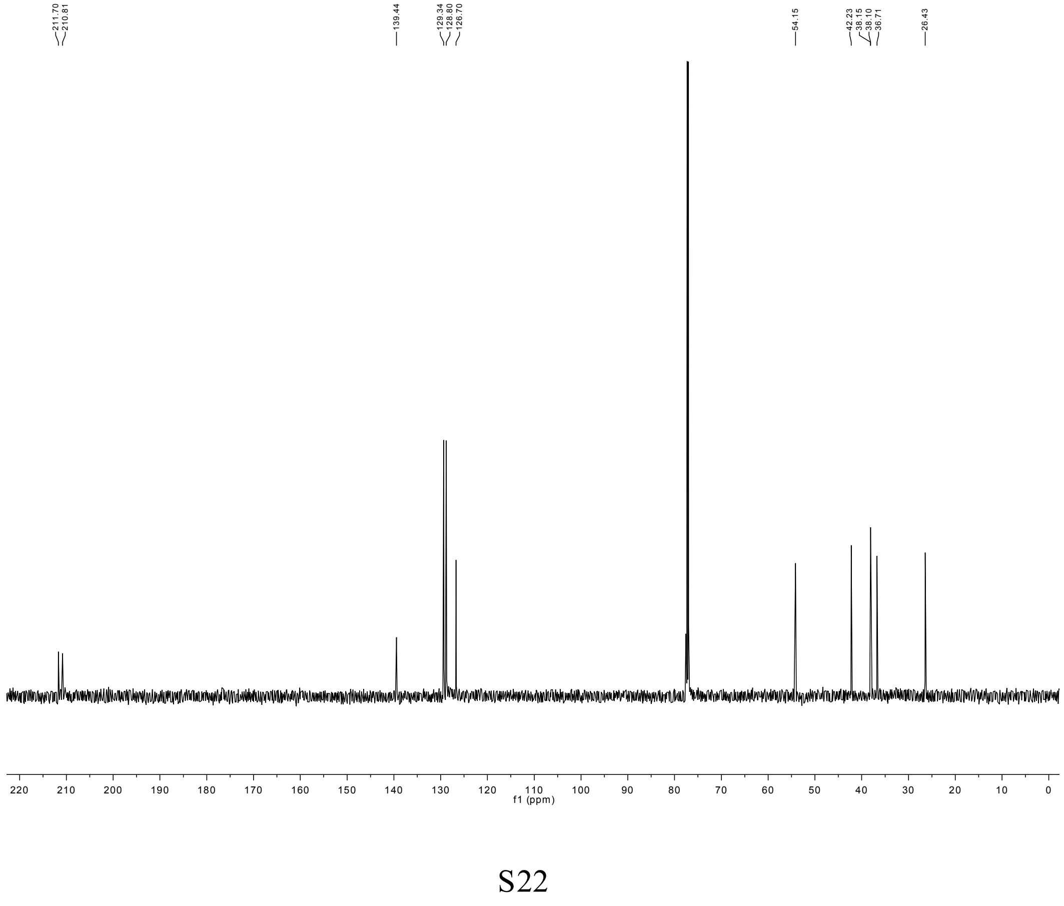
0.0
f1 (ppm)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190
180
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50
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30
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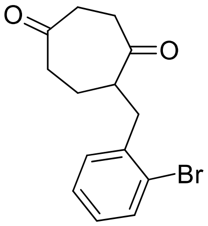
10
0
f1 (ppm)



5-(2-Bromobenzyl)cycloheptane-1,4-dione (3j)

3j (30.5 mg, 0.104 mmol, 69%) was obtained from reaction of VCP **1a** with alkyne **2j** as a clear colorless oil according to general method B (here no additional reaction time after alkyne addition was necessary).

$C_{14}H_{15}BrO_2$ (295.17 g mol^{-1})

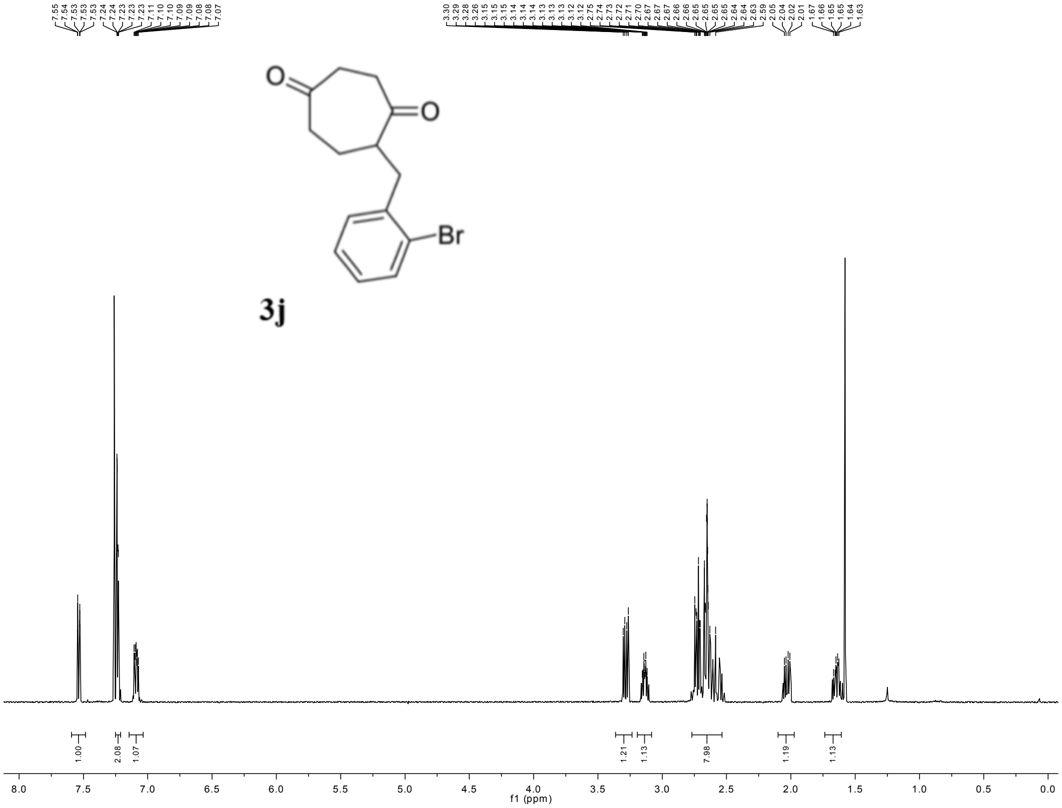
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.54 – 7.49 (m, 1H, C(Br)C*H*), 7.23 – 7.18 (m, 2H, C(Br)CHCHC*H*), 7.10 – 7.03 (m, 1H, C(Br)CHC*H*CHC*H*), 3.26 (dd, *J* = 13.9, 6.2 Hz, 1H, ArC*H*$_2$), 3.17 – 3.06 (m, 1H, ArCH$_2$C*H*C(O)), 2.77 – 2.49 (m, 7H, ArC*H*$_2$ and COC*H*$_2$), 2.07 – 1.95 (m, 1H, CHC*H*$_2$CH$_2$CO), 1.67 – 1.57 (m, 1H, CHC*H*$_2$CH$_2$CO) ppm.

^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$): δ = 211.0 (C=O), 210.7 (C=O), 138.9 (*Ar*-Br), 133.2 (*Ar*-H), 132.1 (*Ar*-H), 128.5 (*Ar*-H), 127.7 (*Ar*-H), 125.0 (*Ar*-C), 52.2 (C(O)*C*H), 42.2 (*C*H$_2$), 38.2 (*C*H$_2$), 38.0 (*C*H$_2$), 36.8 (*C*H$_2$), 26.7 (*C*H$_2$) ppm.

IR (NaCl): 훑 3394, 3058, 2930, 1706, 1566, 1472, 1441, 1319, 1270, 1191, 1127, 1025, 939, 895, 754, 659 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{14}H_{15}BrNaO_2$: 317.0153 (M+Na)$^+$; found 317.0155.

R$_f$ = 0.40 (SiO$_2$, hexane/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).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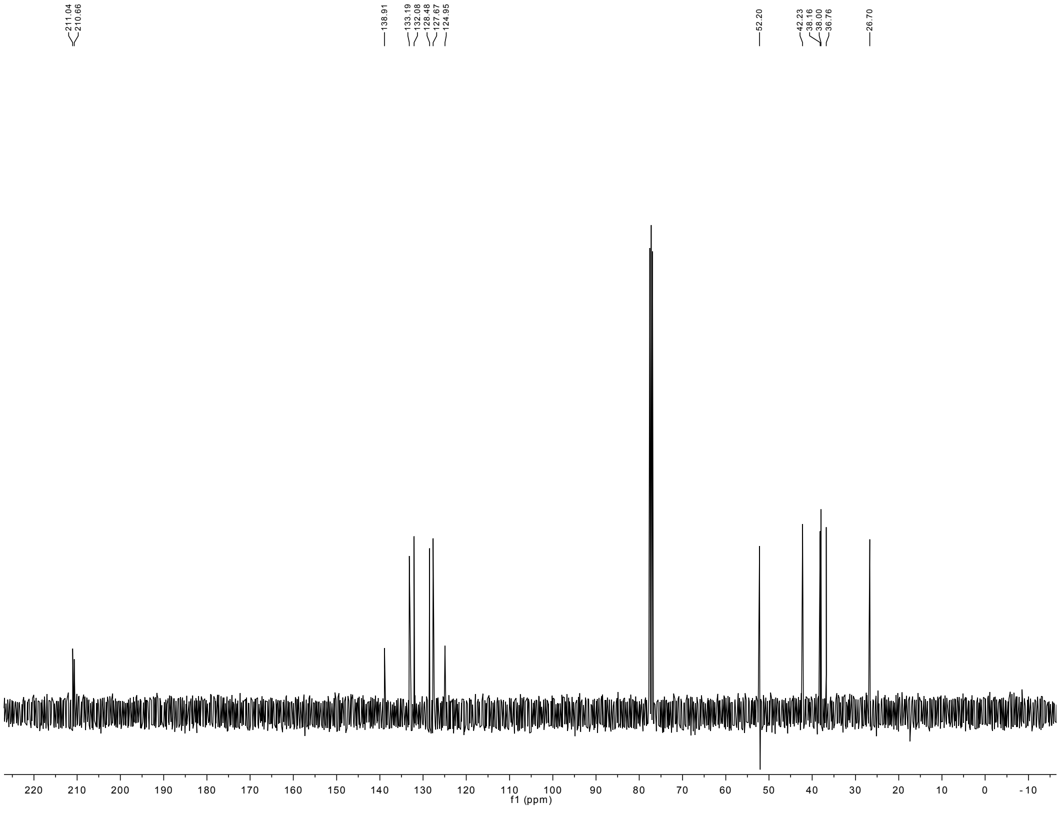
f1 (ppm)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200
190
180
170
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40
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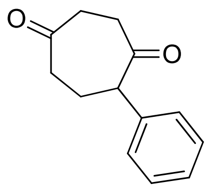
-10
f1 (ppm)



5-Phenylcycloheptane-1,4-dione (3k)

3k (28.5 mg, 0.141 mmol, 94%) was obtained from reaction of VCP **1a** with alkyne **2k** as a while solid according to general method B.

$C_{13}H_{14}O_2$ (202.25 g mol^{-1})

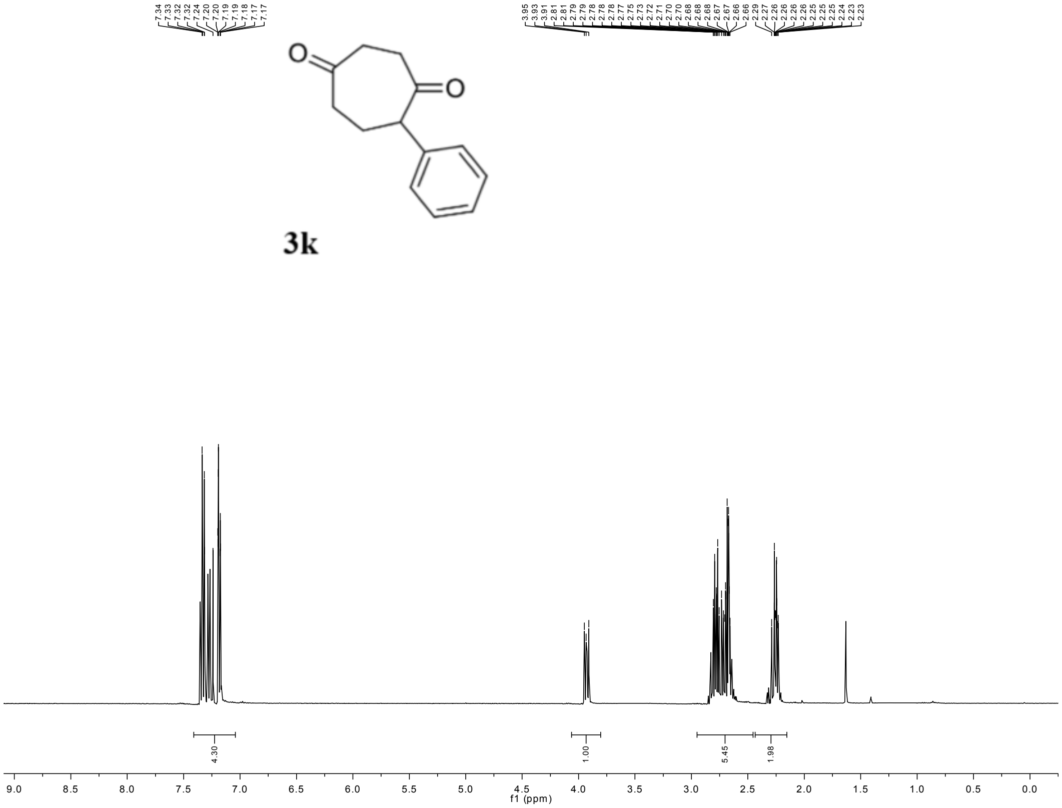
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.46 – 7.14 (m, 5H, *Ph*), 3.95 (dd, *J* = 10.1, 5.8 Hz, 1H, CO*C**H***(Ph)CH_2), 2.96 – 2.55 (m, 6H, COC*H_2*), 2.39 – 2.19 (m, 2H, CHC*H_2*CH_2CO) ppm.

^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$): δ = 210.1 (C=O), 209.9 (C=O), 138.1 (*Ar*-CC), 128.9 (*Ar*-H), 128.2 (*Ar*-H), 127.7 (*Ar*-C), 58.9 (*C*H), 42.4 (*C*H_2), 38.7 (*C*H_2), 37.3 (*C*H_2), 27.7 (*C*H_2) ppm.

IR (NaCl): 휣= 3062, 2946, 1705, 1603, 1497, 1452, 1411, 1318, 1260, 1186, 1168, 1142, 1101, 937, 910, 751, 727, 701, 666 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{13}H_{15}O_2$: 203.1072 (M+H)$^+$; found: 203.1067.

R$_f$ = 0.48 (SiO_2, pentane/Et_2O = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).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1.98
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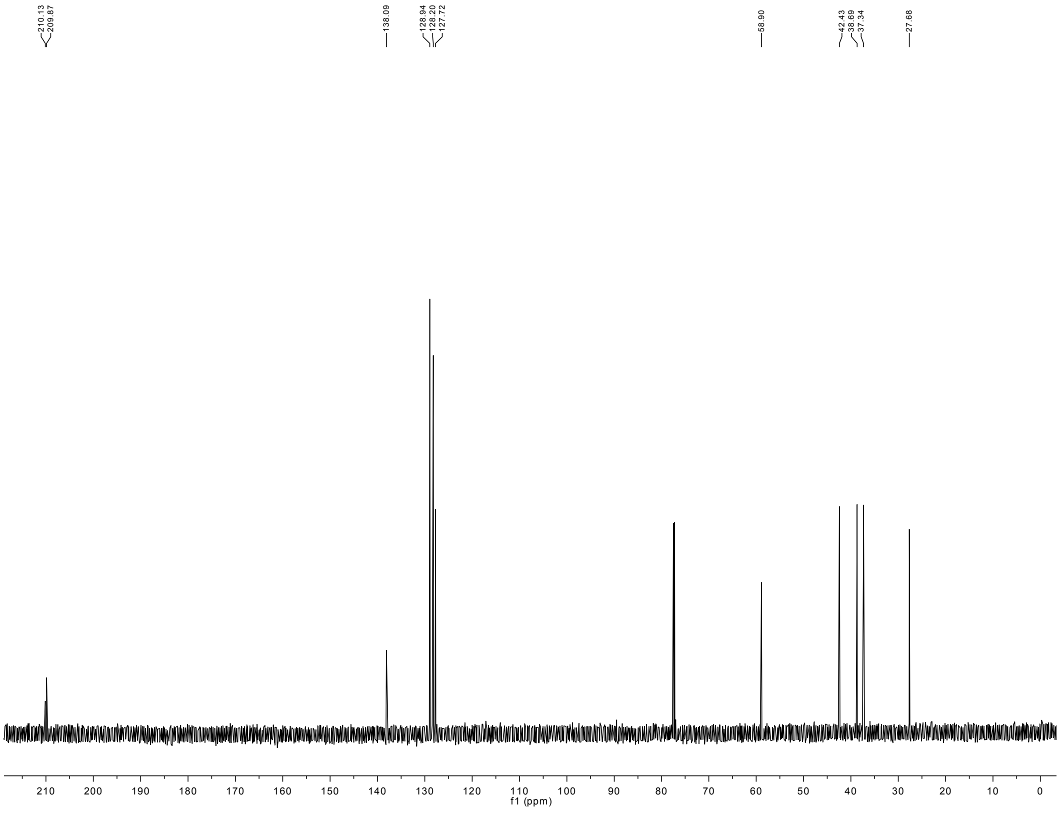
f1 (ppm)

3k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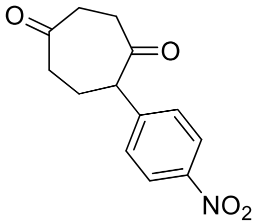
f1 (ppm)



5-(4-Nitrophenyl)cycloheptane-1,4-dione (3l)

3l (24.1 mg, 0.098 mmol, 65%) was obtained from reaction of VCP **1a** with alkyne **2l** as white solid according to general method B.

$C_{13}H_{13}NO_4$ (247.25 g mol^{-1})

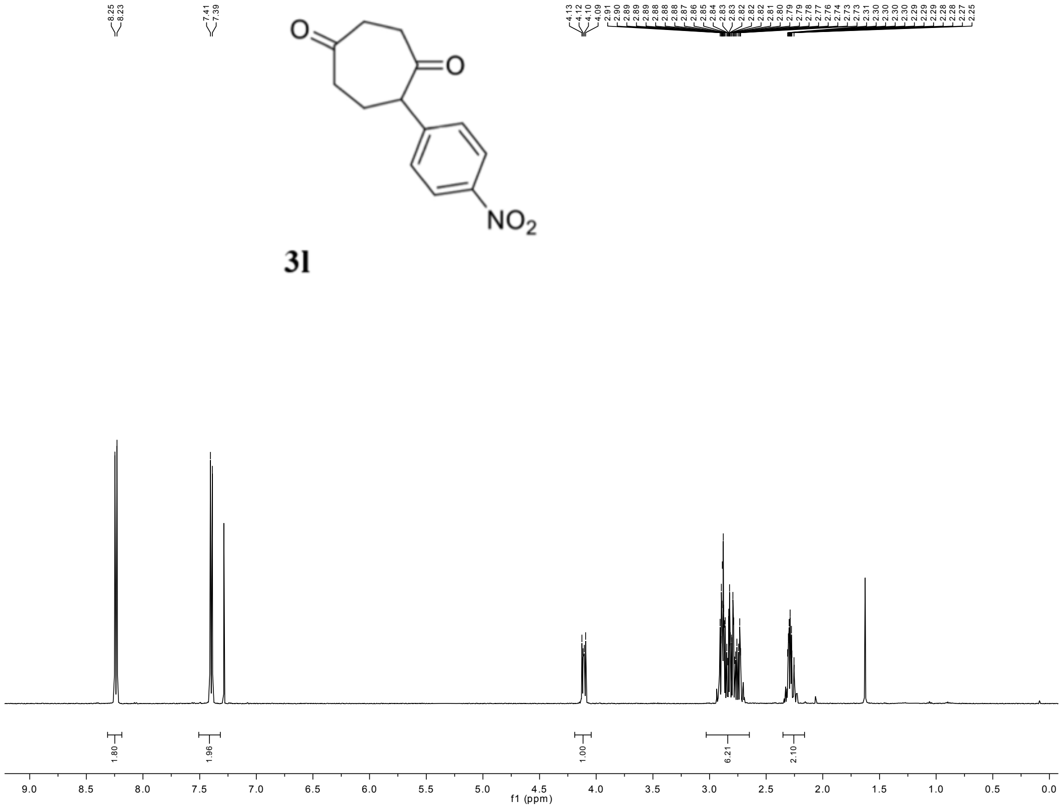
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.19 (d, *J* = 8.2 Hz, 2H, C*H*C(NO$_2$)C*H*), 7.35 (d, *J* = 9.0 Hz, 2H, C*H*C(cycloheptadione)C*H*), 4.10 – 3.98 (m, 1H. COC*H*(Ar)CH$_2$), 3.17 – 2.44 (m, 6H, COC*H*$_2$), 2.37 – 2.11 (m, 2H, CHC*H*$_2$CH$_2$CO) ppm.

^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$): δ = 209.6 (C=O), 207.9 (C=O), 147.5 (*Ar*-NO$_2$), 145.7 (*Ar*-H), 129.6 (*Ar*-H), 123.9 (*Ar*-C), 58.5 (*C*H), 42.5 (*C*H$_2$), 38.2 (*C*H$_2$), 38.1 (*C*H$_2$), 28.4 (*C*H$_2$) ppm.

IR (NaCl): 홄= 3110, 3079, 2929, 2855, 2359, 1705, 1604, 1518, 1453, 1346, 1184, 1110, 580 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{13}H_{14}NO_4$: 248.0923 (M+H)$^+$; found: 248.0921.

R$_f$ = 0.25 (SiO$_2$, hexane/EtOAc = 1:1, obtained as a single spot that stains red with *p*-anisaldehyde).


8.25
8.23
7.41
7.39
4.13
4.12
4.10
4.09
2.91
2.90
2.89
2.89
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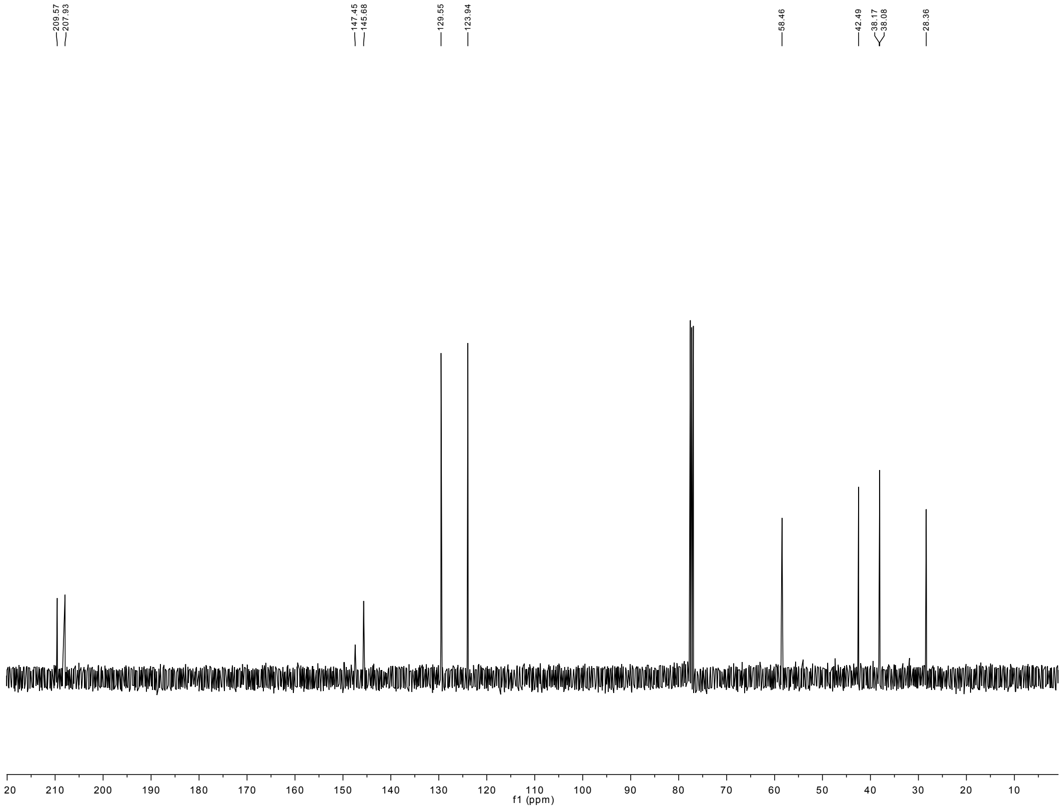
2.88
2.88
2.87
2.86
2.85
2.84
2.83
2.83
2.83
2.82
2.82
2.81
2.80
2.79
2.79
2.78
2.77
2.76
2.74
2.73
2.73
2.31
2.30
2.30
2.30
2.29
2.29
2.28
2.28
2.27
2.25
O
O
NO2
1.80
1.96
1.00
6.21
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3l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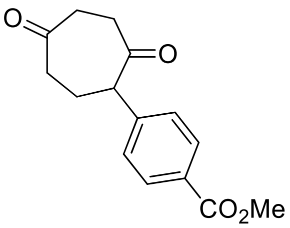
207.93
147.45
145.68
129.55
123.94
58.46
42.49
38.17
38.08
28.36
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



Methyl 4-(2,5-dioxocycloheptyl)benzoate (3m)

3m (27.7 mg, 0.107 mmol, 71%) was obtained from reaction of VCP **1a** with alkyne **2m** as a white solid according to general method B.

$C_{15}H_{16}O_4$ (260.29 g mol^{-1})

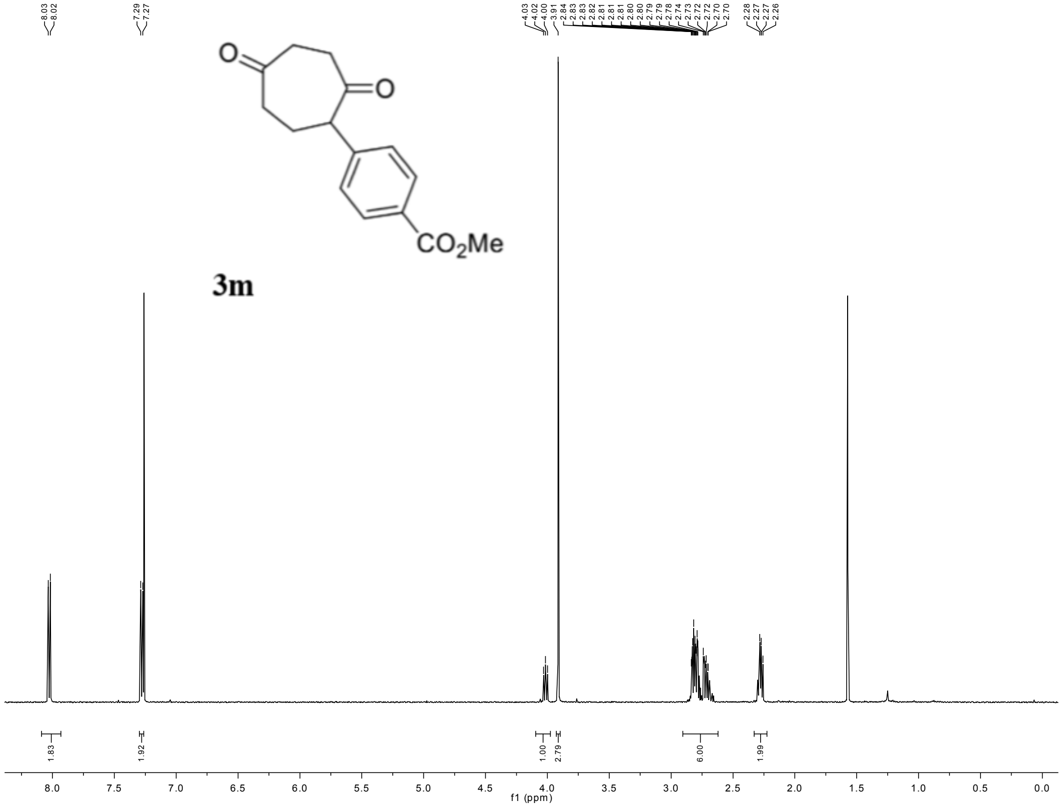
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.06 – 7.95 (m, 2H, C*H*C(COOMe)C*H*), 7.29 – 7.20 (m, 2H, C*H*C(cycloheptadione)C*H*), 3.99 (dd, *J* = 8.7, 7.3 Hz, 1H, COC*H*(Ar)CH_2), 3.89 (s, 3H, COOCH_3), 2.86 – 2.59 (m, 6H, COCH_2), 2.30 – 2.20 (m, 2H, CHCH_2CH_2CO) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 209.9 (C=O), 208.9 (C=O), 167.0 (C(O)O), 143.3 (*Ar*COOCH_3), 130.1 (*Ar*-H), 129.5 (*Ar*-H), 128.5 (*Ar*-C), 58.8 (*C*H), 52.4 (OCH_3), 42.5 (*C*H_2), 38.4 (*C*H_2), 37.8 (*C*H_2), 27.9 (*C*H_2) ppm.

IR (NaCl): 홠⊨ 2954, 1715, 1611, 1436, 1283, 1184, 1112, 1020, 965, 912, 585, 772, 706 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{15}H_{16}NaO_4$: 283.0946 $(M+Na)^+$; found: 283.0942.

R_f = 0.29 (SiO_2, hexane/EtOAc = 1:1, obtained as a single spot that stains red with *p*-anisaldehyde).


8.03
8.02
7.29
7.27
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4.02
4.00
3.91
2.84
2.83
2.83
2.82
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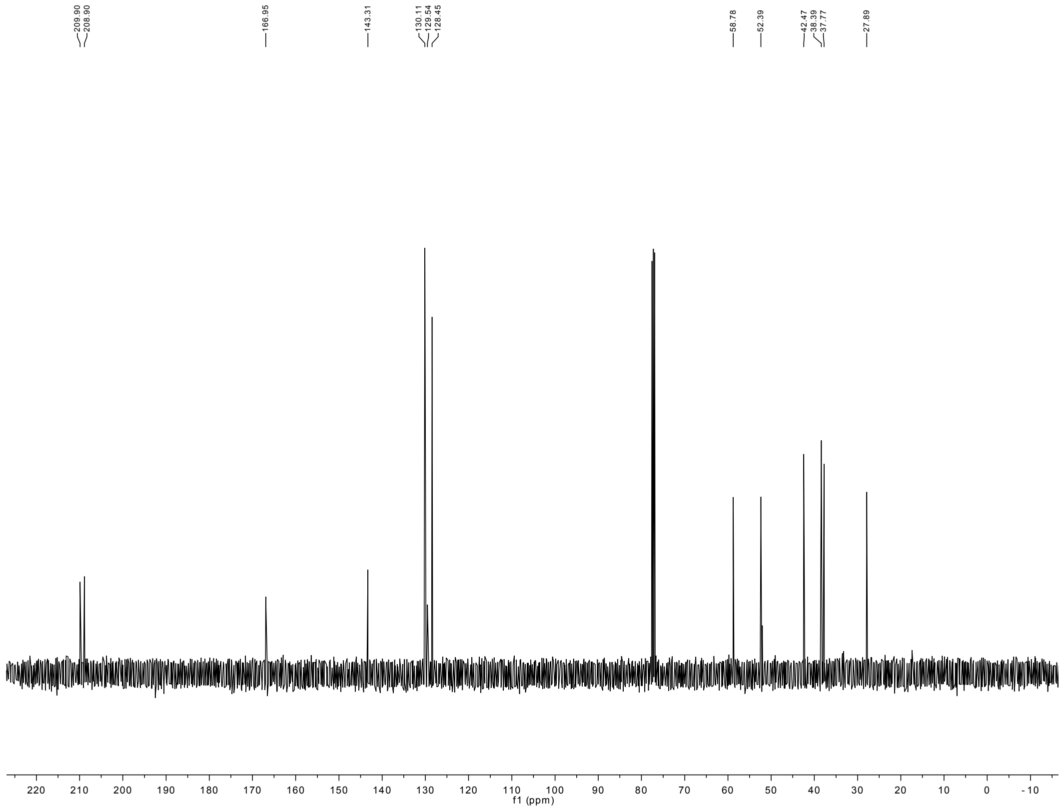
2.81
2.80
2.80
2.79
2.79
2.78
2.74
2.73
2.72
2.72
2.70
2.70
2.28
2.27
2.27
2.26
O
O
CO2Me
1.83
1.92
1.00
2.79
6.00
1.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3m


209.90
208.90
166.95
143.31
130.11
129.54
128.45
58.78
52.39
42.47
38.39
37.77
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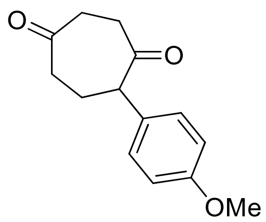
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5-(4-Methoxyphenyl)cycloheptane-1,4-dione (3n)

3n (27.8 mg, 0.120 mmol, 80%) was obtained from reaction of VCP **1a** with alkyne **2n** as a white solid according to general method B.

$C_{14}H_{16}O_3$ (232.28 g mol^{-1})

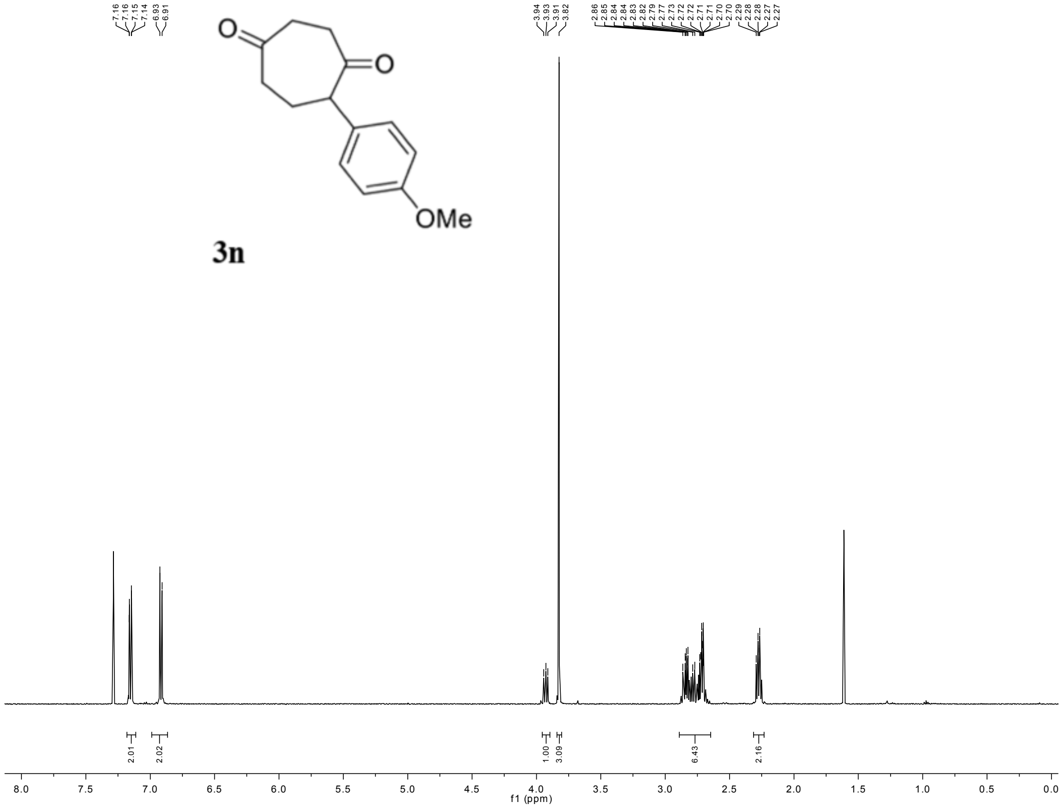
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 8.5 Hz, 2H, C*H*C(cycloheptadione)C*H*), 6.91 (d, *J* = 8.7 Hz, 2H, C*H*C(OMe)C*H*), 3.93 (t, *J* = 8.1 Hz, 1H, COC*H*(Ph)CH_2), 3.82 (s, 3H, OCH_3), 2.91 – 2.61 (m, 6H, COCH_2), 2.34 – 2.18 (m, 2H, CHC$H_2$$CH_2$CO) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 210.3 (C=O), 210.3 (C=O), 159.1 (*Ar*-OCH_3), 130.1 (*Ar*-H), 129.2 (*Ar*-H), 114.4 (*Ar*-C), 58.1 (*C*H), 55.5 (*C*H_3), 42.5 (*C*H_2), 38.8 (*C*H_2), 37.2 (*C*H_2), 27.8 (*C*H_2) ppm.

IR (NaCl): 횷= 3395, 2928, 2855, 1706, 1611, 1584, 1514, 1460, 1305, 1249, 1182, 1033, 910, 833 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{14}H_{17}O_3$: 233.1178 $(M+H)^+$; found: 233.1179.

R_f = 0.37 (SiO_2, hexane/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).


7.16
7.16
7.15
7.14
6.93
6.91
O
O
OMe
3n
3.94
3.93
3.91
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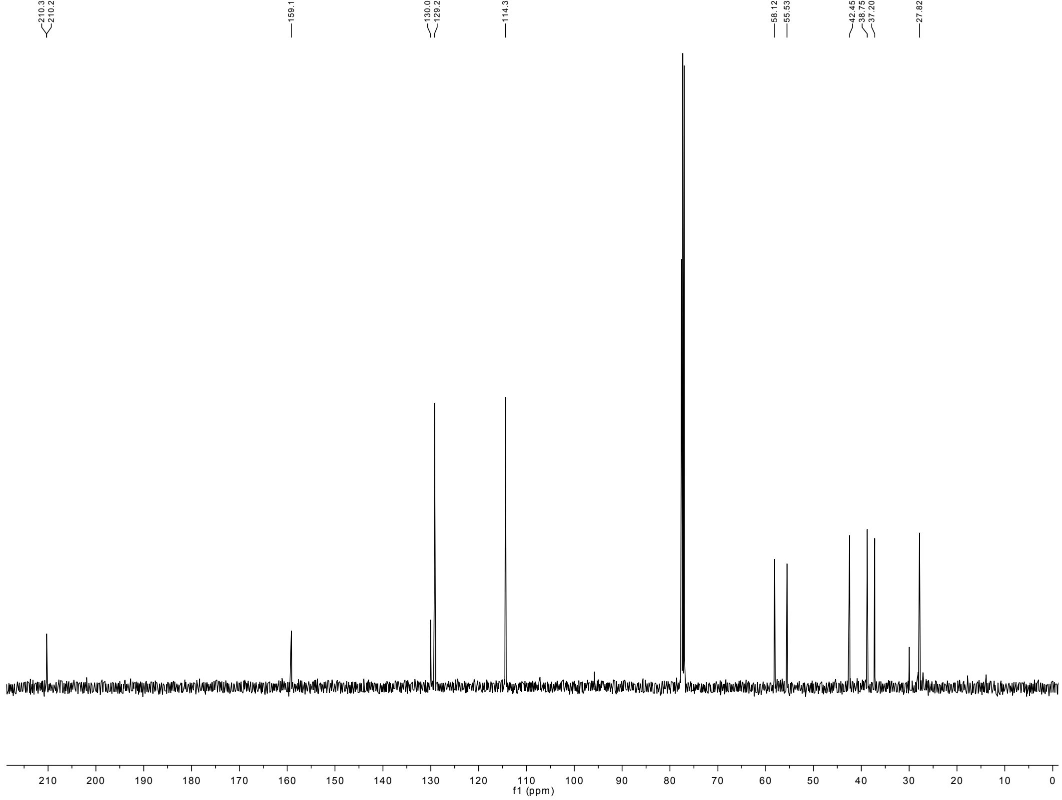
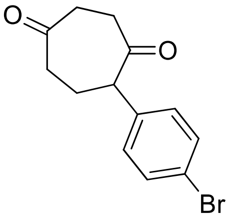
2.86
2.85
2.84
2.84
2.83
2.82
2.79
2.77
2.73
2.72
2.72
2.71
2.71
2.70
2.70
2.29
2.28
2.28
2.27
2.27
2.01
2.02
1.00
3.09
6.43
2.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.32
210.29
159.12
130.07
129.23
114.36
58.12
55.53
42.45
38.75
37.20
27.82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5-(4-Bromophenyl)cycloheptane-1,4-dione (3o)

3o (28.2 mg, 0.101 mmol, 67%) was obtained from reaction of VCP **1a** with alkyne **2o** as a clear colorless oil according to general method B.

$C_{13}H_{13}BrO_2$ (281.15 g mol^{-1})

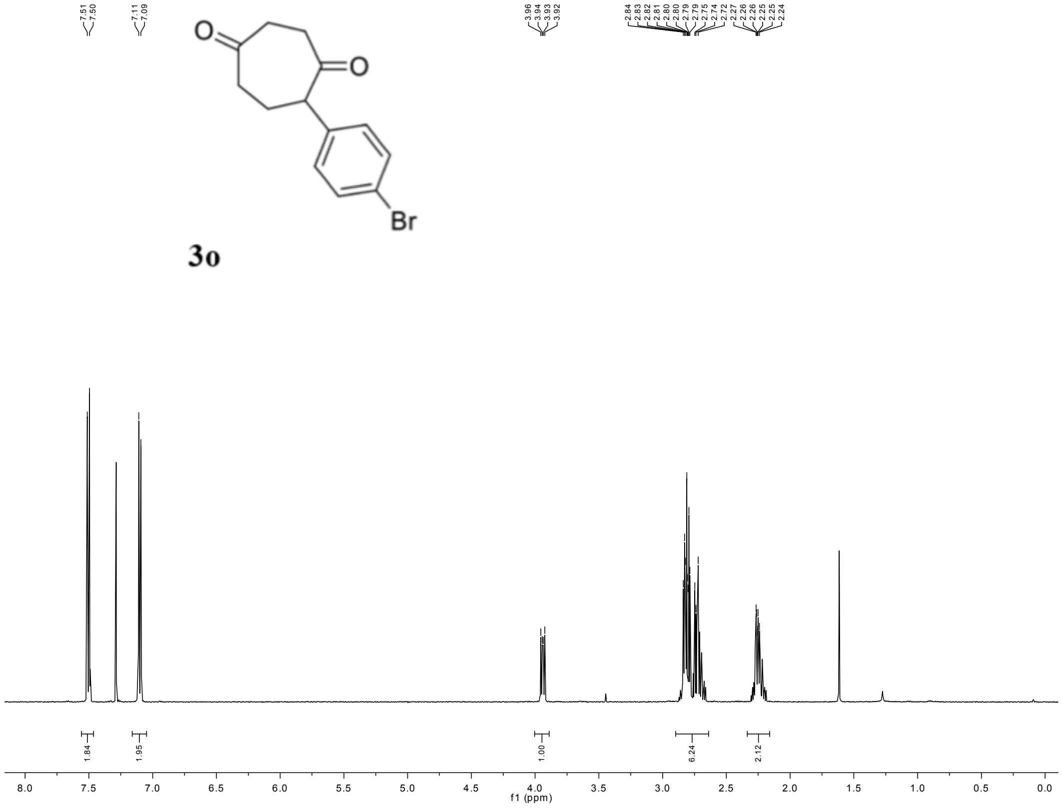
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.55 – 7.47 (m, 2H, Ar), 7.13 – 7.06 (m, 2H, Ar), 3.94 (dd, *J* = 10.4, 5.7 Hz, 1H, COC*H*(Ar)CH_2), 2.88 – 2.64 (m, 6H, COC*H_2*), 2.32 – 2.16 (m, 2H, CHC*H_2*CH_2CO) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 209.99 (C=O), 209.13 (C=O), 137.21 (*Ar*-Br), 132.01 (*Ar*-H), 130.09 (*Ar*-H), 121.75 (*Ar*-C), 58.26 (*C*H), 42.47 (*C*H_2), 38.44 (*C*H_2), 37.68 (*C*H_2), 28.03 (*C*H_2) ppm.

IR (NaCl): 횮= 2360, 1706, 1489, 1407, 1318, 1073, 1011, 910, 827 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{13}H_{14}BrO_2$ 281.0177 (M+H)$^+$; found 281.0156.

R$_f$ = 0.35 (SiO_2, hexane/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).



3o

7.51
7.50
7.11
7.09
3.96
3.94
3.93
3.92
2.84
2.83
2.82
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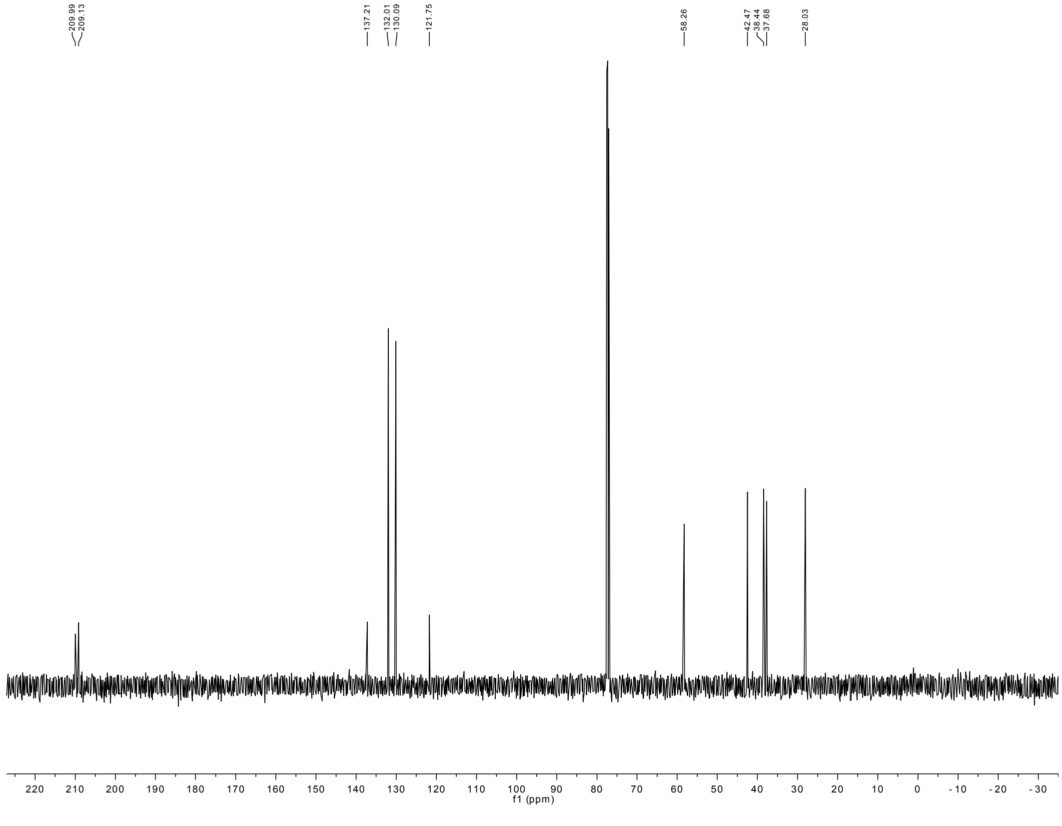
2.80
2.80
2.79
2.79
2.75
2.74
2.72
2.27
2.26
2.26
2.25
2.25
2.24
O
O
Br
1.84
1.95
1.00
6.24
2.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



209.99
209.13
137.21
132.01
130.09
121.75
58.26
42.47
38.44
37.68
28.03
220
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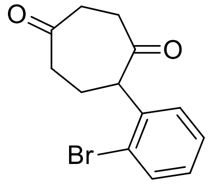
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)



5-(2-Bromophenyl)cycloheptane-1,4-dione (3p)

3p (36.2 mg, 0.129 mmol, 86%) was obtained from reaction of VCP **1a** with alkyne **2p** as a clear colorless oil according to general method B.

$C_{13}H_{13}BrO_2$ (281.15 g mol^{-1})

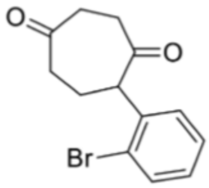
^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H, Ar), 7.31 – 7.23 (m, 1H, Ar), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H, Ar), 4.53 (dd, *J* = 11.6, 4.3 Hz, 1H, C*H*), 3.06 – 2.65 (m, 6H, C*H*$_2$(CO)), 2.35 – 2.16 (m, 2H, C*H*$_2$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, CDCl$_3$): δ = 210.5 (C=O), 208.7 (C=O), 138.7 (*Ar*-Br), 133.0 (*Ar*-H), 129.6 (*Ar*-H), 129.1 (*Ar*-H), 127.9 (*Ar*-H), 125.0 (*Ar*-C), 57.5 (*C*H), 42.9 (*C*H$_2$), 38.9 (*C*H$_2$), 38.0 (*C*H$_2$), 27.4 (*C*H$_2$) ppm.

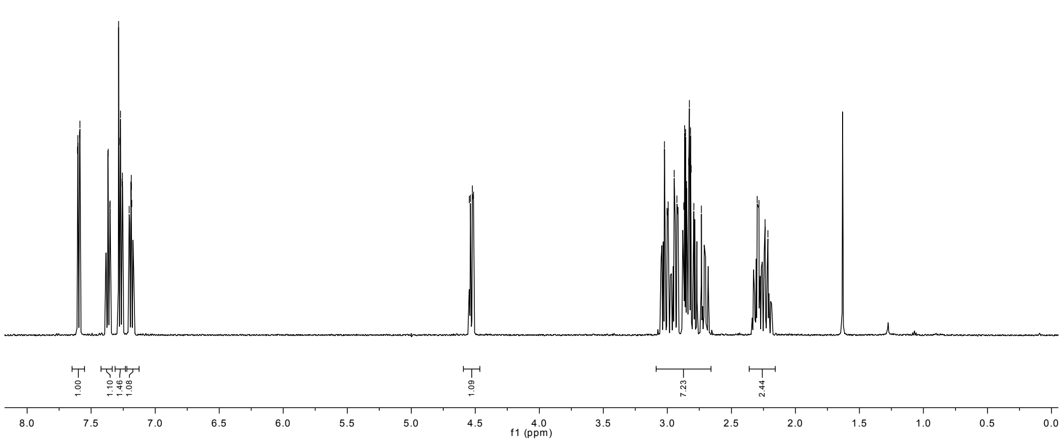
IR (NaCl): 횳= 2933, 1706, 1471, 1439, 1320, 1096, 1024, 932, 749 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{13}H_{14}BrO_2$ 281.0177 (M+H)$^+$; found 281.0157.

R$_f$ = 0.32 (SiO$_2$, hexane/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).



3p


7.61
7.60
7.59
7.59
7.37
7.37
7.35
7.35
7.29
7.27
7.27
7.26
7.26
7.20
7.19
7.19
7.19
7.18
4.55
4.54
4.52
4.51
3.02
3.00
2.99
2.95
2.93
2.92
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2.73
2.30
2.28
2.24
2.21
1.00
1.10
1.46
1.08
1.09
7.23
2.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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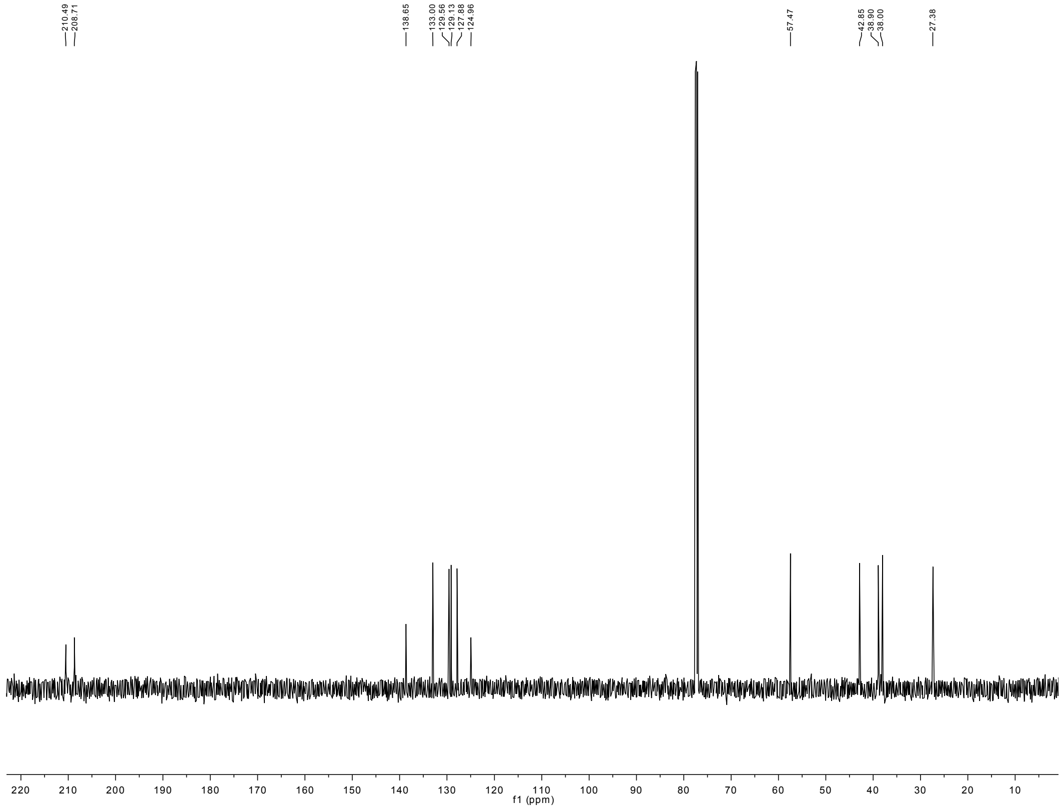
1.5
1.0
0.5
0.0
f1 (ppm)


210.49
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129.56
129.13
127.88
124.96
57.47
42.85
38.90
38.00
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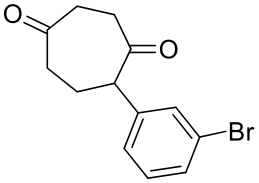
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



5-(3-Bromophenyl)cycloheptane-1,4-dione (3q)

3q (39.2 mg, 0.140 mmol, 93%) was obtained from reaction of VCP **1a** with alkyne **2q** as a clear colorless oil according to general method B.

$C_{13}H_{13}BrO_2$ (281.15 g mol^{-1})

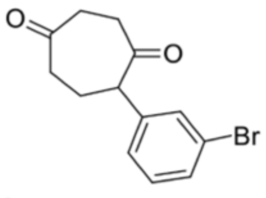
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.45 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, C(Br)C*H*C(cycloheptadione)), 7.37 (t, *J* = 1.8 Hz, 1H, C(Br)C*H*CH), 7.25 (t, *J* = 7.8 Hz, 1H, CHC*H*C(cycloheptadione)), 7.15 (dt, *J* = 7.8, 1.3 Hz, 1H, CHC*H*CH), 3.94 (dd, *J* = 10.1, 6.0 Hz, 1H, COC*H*(Ar)CH_2), 2.90 – 2.65 (m, 6H, COCH_2), 2.34 – 2.19 (m, 2H, CHC$H_2$$CH_2$CO) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 209.9 (C=O), 209.0 (C=O), 140.4 (*Ar*-Br), 131.5 (*Ar*-H), 130.9 (*Ar*-H), 130.4 (*Ar*-H), 127.1 (*Ar*-H), 122.9 (*Ar*-C), 58.4 (*C*H), 42.5 (*C*H_2), 38.5 (*C*H_2), 37.7 (*C*H_2), 28.0 (*C*H_2) ppm.

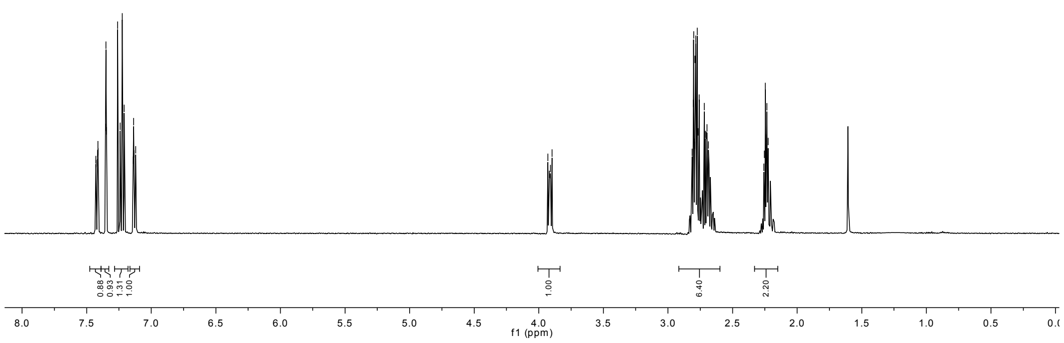
IR (NaCl): 훐= 2926, 1704, 1470, 1440, 1024, 750, 666 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{13}H_{13}BrNaO_2$: 302.9997 $(M+Na)^+$; found: 302.9991.

R$_f$ = 0.30 (SiO_2, hexane/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).


O
O
Br

3q


7.43
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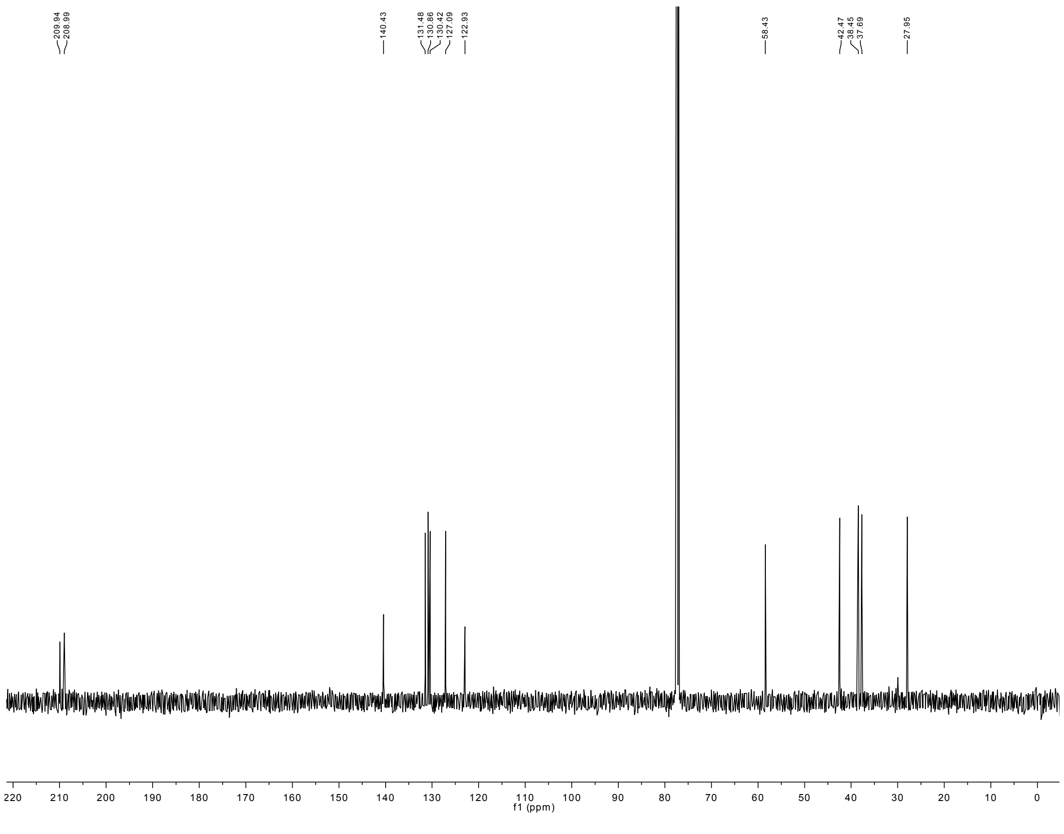
2.72
2.71
2.70
2.70
2.69
2.26
2.25
2.25
2.24
2.24
2.23
2.23
2.22
0.88
0.93
1.31
1.00
1.00
6.40
2.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.94
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122.93
58.43
42.47
38.45
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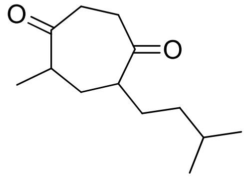
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5-*iso*-Pentyl-7-methylcycloheptane-1,4-dione (4d)

4d (18.9 mg, 0.090 mmol, 60%) was obtained from reaction of VCP **1b** (2 eq) with alkyne **2d** as a clear colorless oil according to general method A as a mixture of two diastereoisomers with a ratio of 1:1.

$C_{13}H_{22}O_2$ (210.31 g mol^{-1})

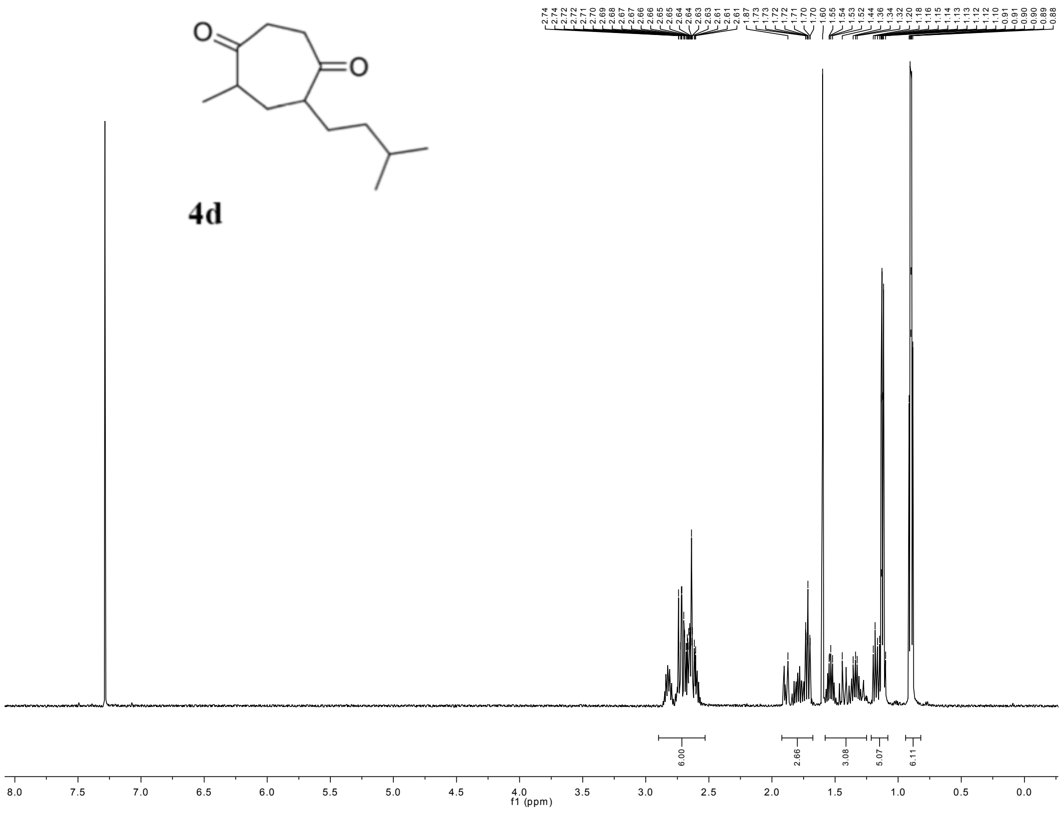
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 2.83-2.52 (m, 6H, MeC*H*C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 1.88-1.56 (m, 3H, MeCHC*H*$_2$CH, CH$_2$C*H*Me$_2$), 1.56-1.06 (m, 7H, C(O)CHC*H*$_3$, C(O)CHC*H*$_2$C*H*$_2$CH), 0.88-0.85 (m, 6H, CH(C*H*$_3$)$_2$) ppm.

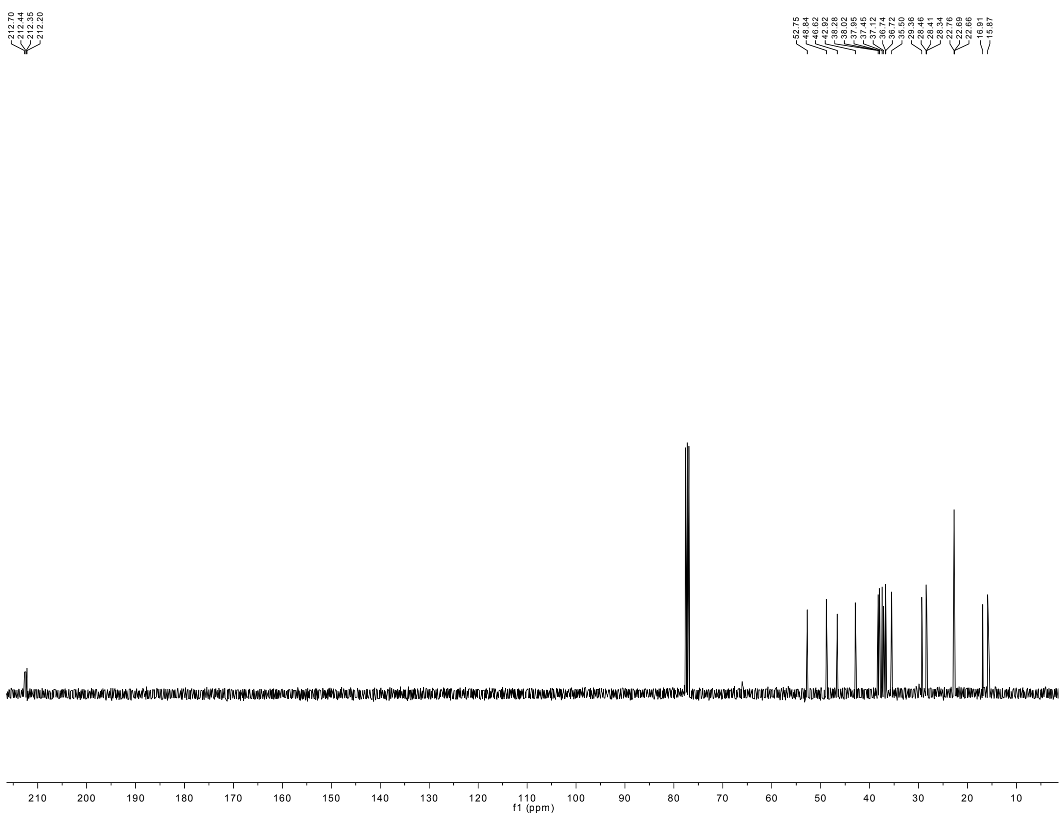
^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$): δ = 212.6, 212.3, 212.3, 212.1 (C=O), 52.7, 48.7, 46.5, 42.8, 38.2, 37.9, 37.9, 37.4, 37.0, 36.6, 36.6, 35.4, 29.3, 28.4, 28.3, 28.2, 22.7, 22.6, 22.6, 16.8, 15.8 (alk-*C*H, alk-CH$_2$, alk-CH$_3$) ppm.

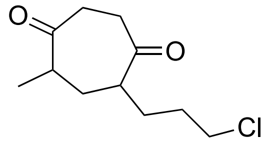
IR (NaCl): 흸= 2954, 2933, 2870, 1708, 1455, 1409, 1366, 1337, 1256, 1224, 1169, 1112, 1064, 972, 951, 927, 890, 820 cm^{-1}.

HRMS (ESI-MS) calc. (*m*/*z*) for $C_{13}H_{23}O_2$: 211.1698 (M+H)$^+$; found: 211.1693.

R$_f$ = 0.33 (SiO$_2$, Hex/EtOAc = 5:1, obtained as a single spot that stains red with *p*-anisaldehyde).


4d
2.74
2.74
2.72
2.72
2.71
2.70
2.69
2.68
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.64
2.63
2.63
2.61
2.61
2.61
1.87
1.73
1.73
1.72
1.72
1.71
1.70
1.70
1.60
1.55
1.54
1.53
1.52
1.44
1.36
1.34
1.32
1.20
1.18
1.16
1.15
1.14
1.13
1.13
1.12
1.12
1.10
0.91
0.91
0.90
0.90
0.89
0.88
6.00
2.66
3.08
5.07
6.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.70
212.44
212.35
212.20
52.75
48.84
46.62
42.92
38.28
38.02
37.95
37.45
37.12
36.74
36.72
35.50
29.36
28.46
28.41
28.34
22.76
22.69
22.66
16.91
15.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



5-(3-Chloropropyl)-7-methylcycloheptane-1,4-dione (4e)

4e (27.3 mg, 0.126 mmol, 84%) was obtained from reaction of VCP **1b** (2 eq.) with alkyne **2e** as a clear colorless oil according to general method B as a mixture of two diastereoisomers with an ratio of 1:1.

$C_{11}H_{17}ClO_2$ (216.70 g mol^{-1})

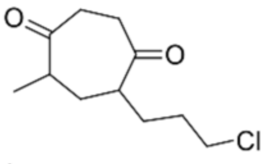
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 3.57-3.54 (m, 2H, C*H*$_2$Cl), 2.89-2.50 (m, 6H, MeC*H*C(O)C*H*$_2$C*H*$_2$C(O)C*H*), 1.93-1.65 (m, 4H, MeCHC*H*$_2$CHCH$_2$C*H*$_2$CH$_2$Cl), 1.53-1.35 (m, 2H, CHC*H*$_2$CH$_2$CH$_2$Cl), 1.10-1.07 (m, 3H, C*H*$_3$CHC(O)) ppm.

^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$): δ = 212.0, 211.9, 211.7, 211.3 (C=O), 51.5, 47.6, 46.4, 45.0, 44.9, 42.7, 38.0, 38.0, 37.9, 37.3, 37.1, 35.4, 30.4, 30.3, 28.7, 28.0, 16.7, 15.6 (alk-*C*H, alk-CH$_2$, alk-CH$_3$) ppm.

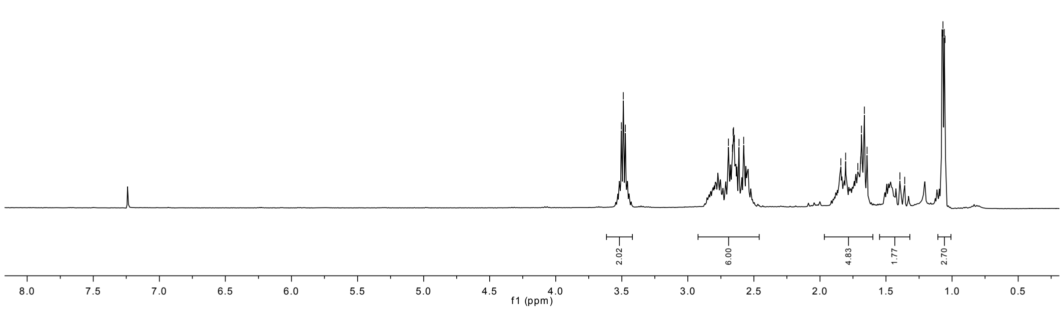
IR (NaCl): 홄= 2962, 2932, 2871, 1704, 1454, 1409, 1376, 1314, 1277, 1220, 1193, 1165, 1117, 1066, 1031, 989, 952, 920, 900, 868, 817, 794, 728, 647 cm^{-1}.

HRMS (ESI-MS) calc. (*m/z*) for $C_{11}H_{18}ClO_2$: 217.0995 (M+H)$^+$; found: 217.0990.

R$_f$ = 0.42 (SiO$_2$, Hex/EtOAc = 2:1, obtained as a single spot that stains red with *p*-anisaldehyde).


O
O
Cl

4e


3.50
3.49
3.47
2.69
2.68
2.66
2.65
2.65
2.61
2.58
1.84
1.81
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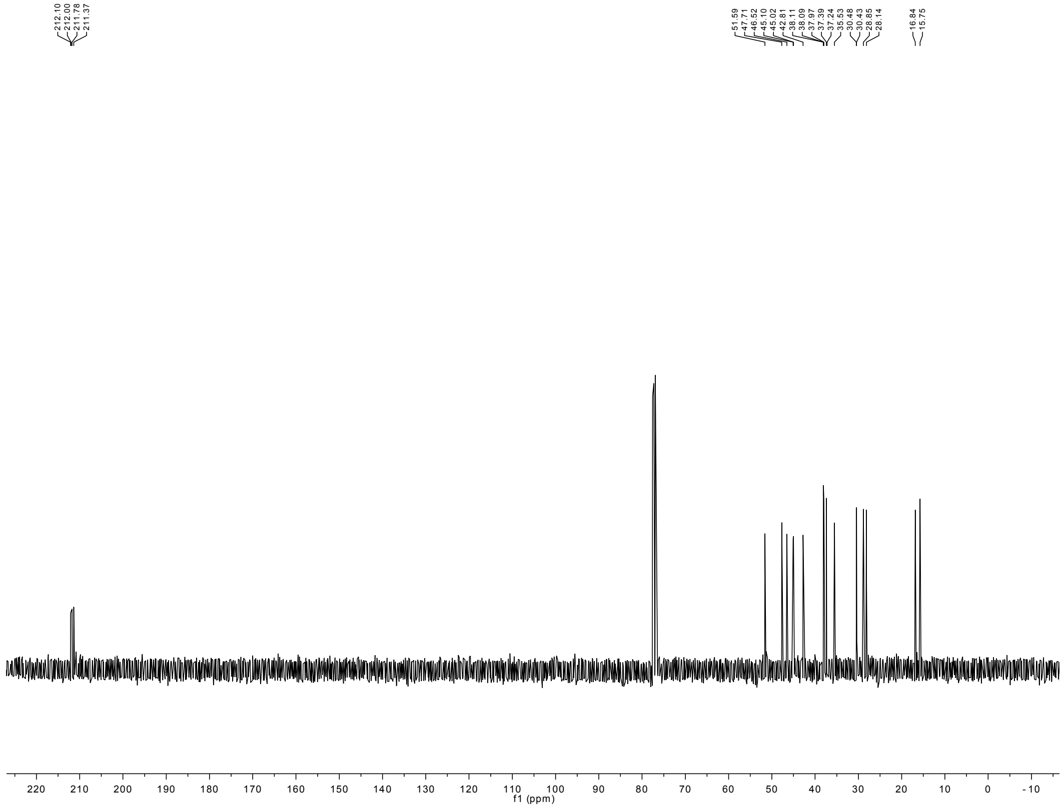
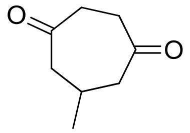
1.69
1.69
1.68
1.66
1.64
1.40
1.36
1.08
1.07
1.06
1.05
2.02
6.00
4.83
1.77
2.70
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


212.10
212.00
211.78
211.37
51.59
47.71
46.52
45.10
45.02
42.81
38.11
38.09
37.97
37.39
37.24
35.53
30.48
30.43
28.85
28.14
16.84
15.75
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



6-methylcycloheptane-1,4-dione (5a)

5a (16.0 mg, 0.114 mmol, 76%) was obtained from reaction of VCP **1c** with alkyne **2a** as a clear colorless oil according to general method A. The ^{1}H-NMR shows residual solvent (diethyl ether) peaks that could not be removed fully due to the volatility of the compound. The yield was adjusted to account for this.

$C_8H_{12}O_2$ (140.18 g mol^{-1})

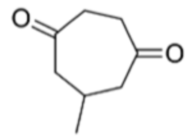
^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (dd, $J = 13.7$ Hz, $J = 3.8$ Hz, 2H, C(O)C*H*H'C*H*H'C(O)), 2.67-2.58 (m, 4H, C(O)CH_2CHCH_2C(O)), 2.53 (dd, $J = 13.6$ Hz, 9.5 Hz, 2H, C(O)CH*H'*CH*H'*C(O)), 2.29-2.19 (m, 1H, CH_3C*H*), 1.07 (d, $J = 6.8$ Hz, 3H, CH_3) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): $\delta = 210.0$ (*C*(O)CH_2CH_2*C*(O)), 51.3 (C(O)*C*H_2CH*C*H_2C(O)), 38.4 (C(O)*C*H_2*C*H_2C(O)), 27.8 (CH_2*C*HCH_2), 22.6 (*C*H_3) ppm.

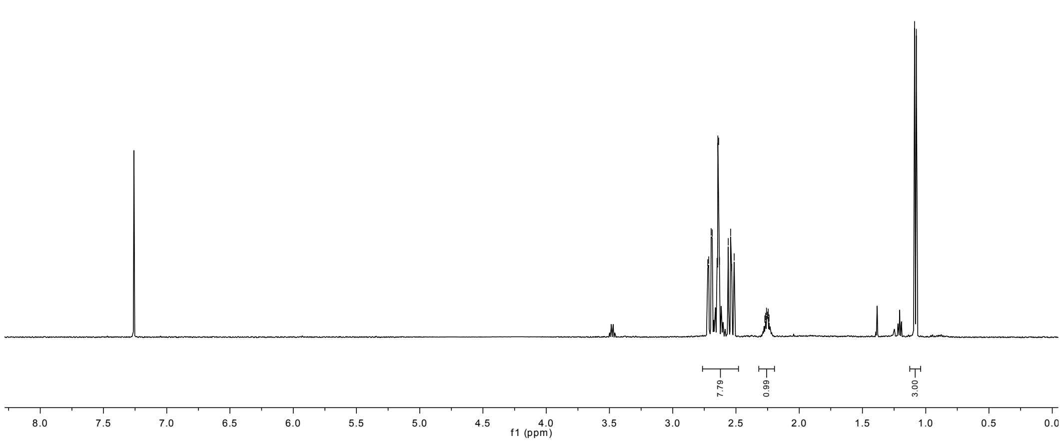
IR (NaCl): 훑= 3394, 2962, 2930, 2876, 1704s, 1456, 1434, 1413, 1381, 1320, 1288, 1260, 1184, 1260, 1184, 1148, 1061, 970, 928, 802 cm^{-1}.

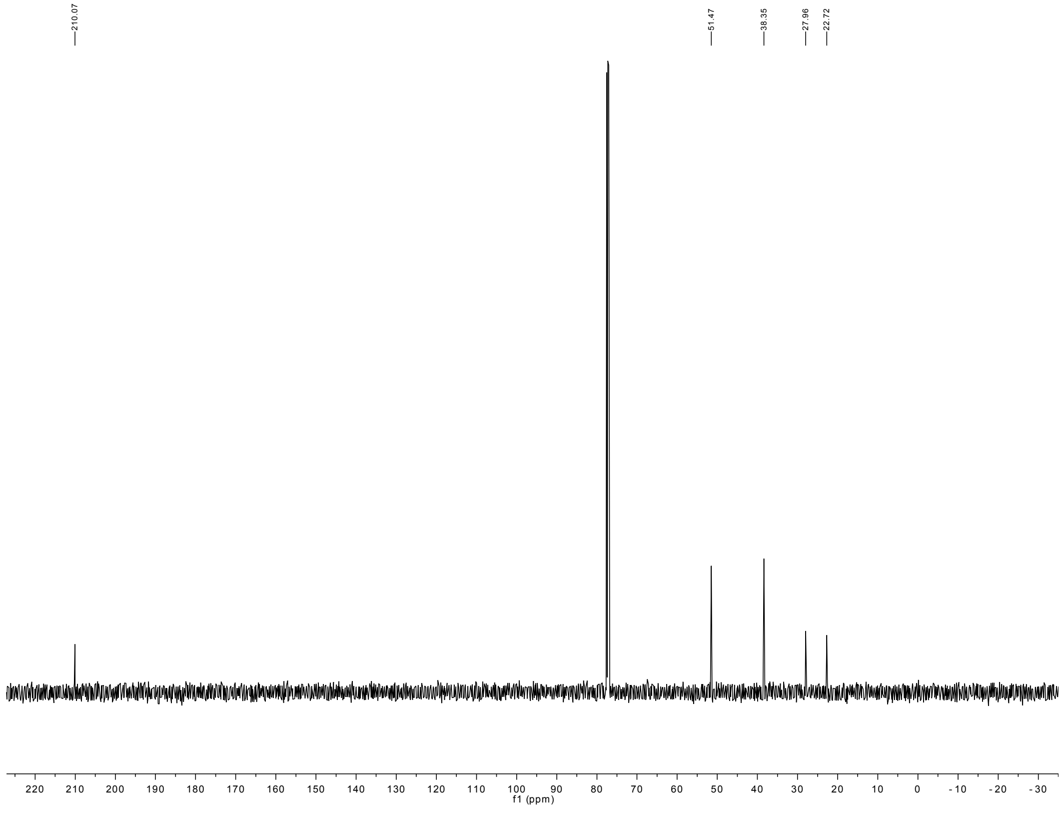
HRMS (ESI-MS) calc. (*m*/*z*) for $C_8H_{13}O_2$: 141.0916 $(M+H)^+$; found: 141.0913.

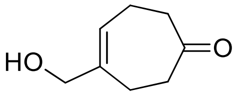
R_f = 0.21 (SiO_2, hexane/EtOAc = 3:1, obtained as a single spot that stains red with *p*-anisaldehyde).



5a


2.72
2.72
2.70
2.69
2.65
2.64
2.64
2.63
2.56
2.54
2.53
2.51
2.27
2.26
2.26
2.25
2.24
2.24
1.09
1.07
7.79
0.99
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.07
51.47
38.35
27.96
22.72
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)



4-(hydroxymethyl)cyclohept-4-enone (6a)

6a (15.3 mg, 0.110 mmol, 73%) was obtained from reaction of VCP **1d** with alkyne **2a** as a clear colorless oil according to general method A with a 4 h addition.

$C_8H_{12}O_2$ (140.18 g mol^{-1})

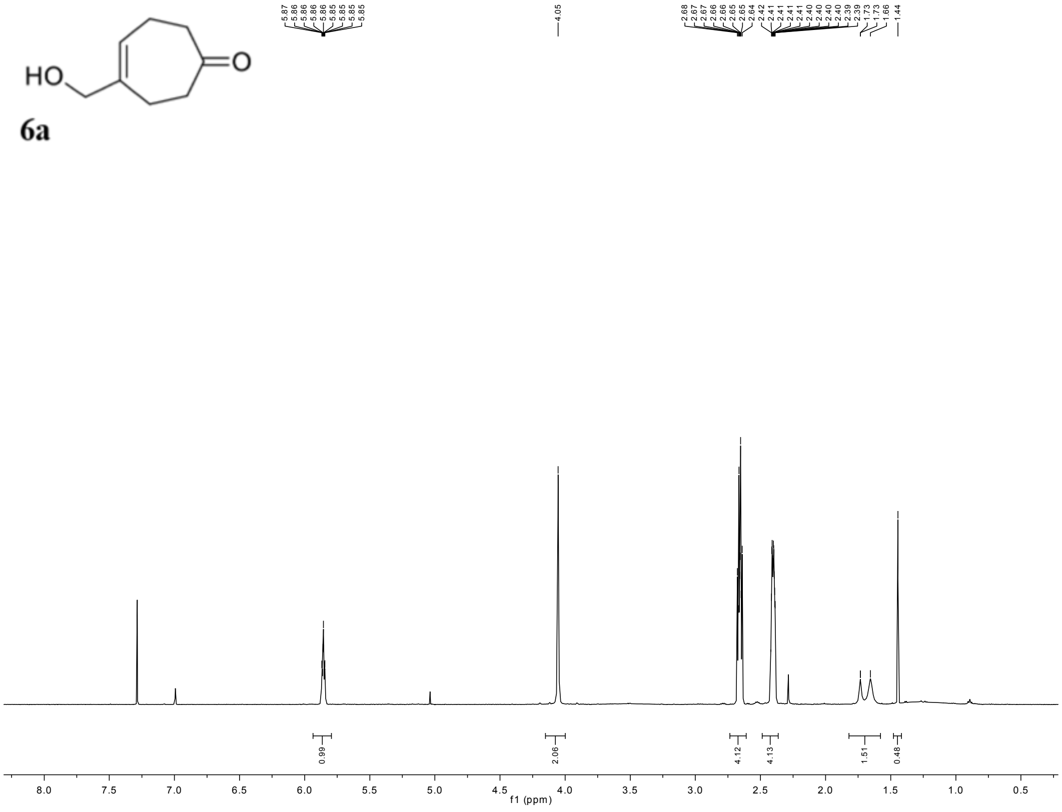
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.84-5.82 (m, 1H, $HOCH_2CC\mathit{H}CH_2$), 4.03 (s, 2H, $HOC\mathit{H}_2CCH$), 2.65-2.61 (m, 4H, $CH_2C\mathit{H}_2C(O)C\mathit{H}_2CH_2$), 2.41-2.35 (m, 4H, $C\mathit{H}_2CH_2C(O)CH_2C\mathit{H}_2$), 1.42 (s, 1H, $O\mathit{H}$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 213.6 ($CH_2\mathit{C}(O)CH_2$), 141.0 ($HOCH_2\mathit{C}CH$), 125.2 ($HOCH_2C\mathit{C}H$), 68.7 ($HO\mathit{C}H_2C$), 42.4 ($CH_2\mathit{C}H_2C(O)CH_2CH_2$), 42.4 ($CH_2CH_2C(O)\mathit{C}H_2CH_2$), 25.0 ($\mathit{C}H_2CH_2C(O)CH_2CH_2$), 23.9 ($CH_2CH_2C(O)CH_2\mathit{C}H_2$) ppm.

IR (NaCl): 훯= 3389, 3004, 2918, 2849, 1694, 1440, 1349, 1322, 1260, 1209, 1175, 1105, 1059, 1018, 930, 884, 829, 801cm^{-1}.

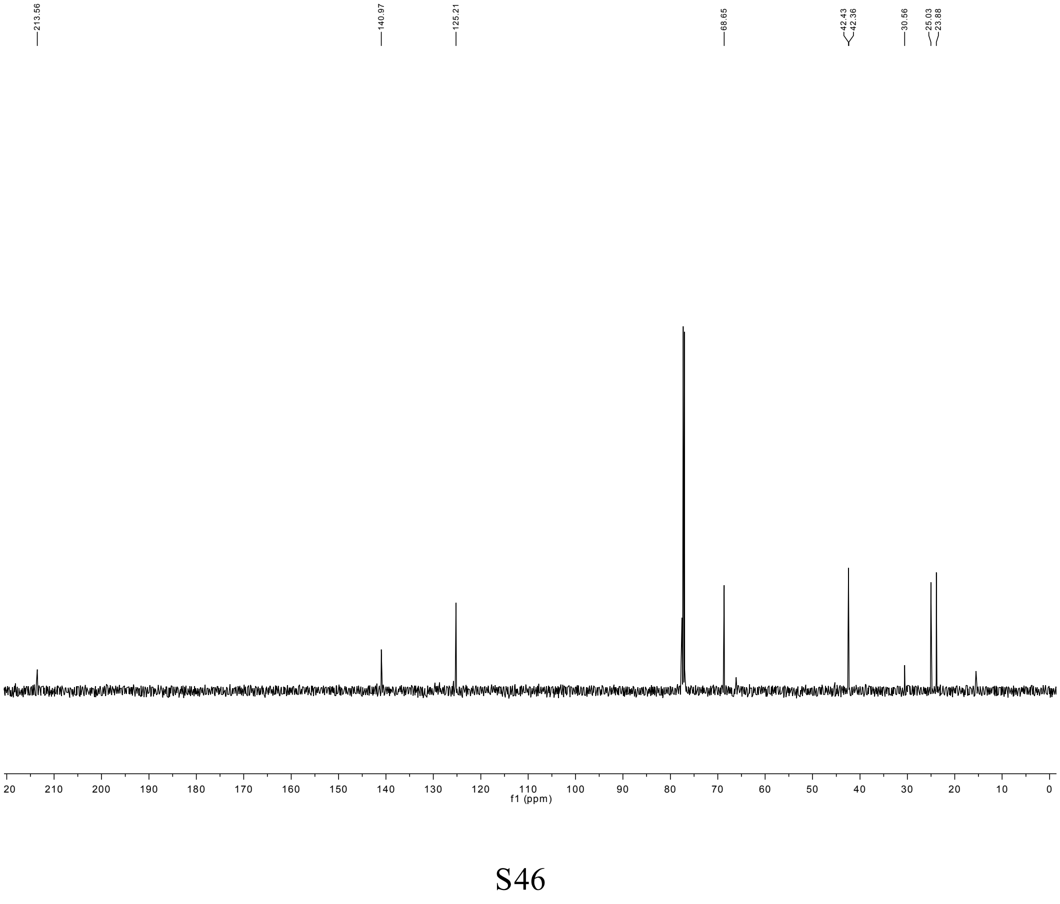
HRMS (ESI-MS) calc. (m/z) for $C_8H_{13}O_2$: 141.0916 $(M+H)^+$; found: 141.0916.

R$_f$ = 0.31 (SiO_2, Et_2O, obtained as a single spot that stains with *p*-anisaldehyde).



6a

HO
O
5.87
5.86
5.86
5.86
5.86
5.85
5.85
5.85
5.85
4.05
2.68
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.42
2.41
2.41
2.41
2.41
2.40
2.40
2.40
2.40
2.39
2.39
1.73
1.73
1.66
1.44
0.99
2.06
4.12
4.13
1.51
0.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

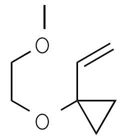


213.56
140.97
125.21
68.65
42.43
42.36
30.56
25.03
23.88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

General method C (Acetone as Solvent)

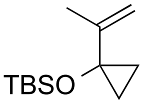
A solution of ethoxy alkyne (165 µmol, 1.10 eq.) in dry acetone (0.5 mL) was added to a solution of vinylcyclopropane **1a** (150 µmol, 1.00 eq.) and [Rh(naph)(COD)]SbF_6 (4.31 mg, 7.5 µmol, 5 mol%) in dry acetone (0.5 mL) in one portion. After the addition was completed the reaction mixture was stirred for additional 30 minutes. Reaction completion was checked via TLC. Then HCl (0.1 mL, 1% in EtOH) was added to quench the reaction and the mixture was stirred for 1 h. The solution was filtered over a short plug of SiO_2 and eluted with Et_2O. After removal of the solvent under reduced pressure, pure product was obtained upon column chromatography (SiO_2).

Vinylcyclopropanes



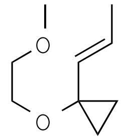
1-(2-methoxyethoxy)-1-vinylcyclopropane (1a)

1a was purchased from Sigma Aldrich (#666246).



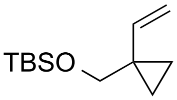
***tert*-butyldimethyl(1-(prop-1-en-2-yl)cyclopropoxy)silane (1b)**

1b was prepared and purified using a previously reported procedure.[1]



(*E*)-1-(2-methoxyethoxy)-1-(prop-1-en-1-yl)cyclopropane (1c)

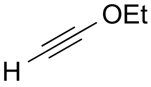
1c was prepared and purified using a previously reported procedure.[2]



***tert*-butyldimethyl((1-vinylcyclopropyl)methoxy)silane (1d)**

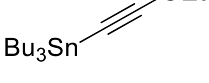
1d was prepared and purified using a previously reported procedure.[3]

Alkoxy alkynes



Ethoxyacetylene (2a)

2a was purchased from Sigma Aldrich (#271365).



Tributyl(ethoxyethynyl)stannane

$C_{16}H_{32}OSn$ (359.13 g mol^{-1})

Diethylamine (7.34 mL, 71.0 mmol, 3.5 eq, freshly distilled from CaH), was dissolved in abs. THF (200 mL) and cooled to 0 °C under nitrogen atmosphere. To this, *n*-BuLi (25.2 mL, 2.5 M in hexane, 3.1 eq.) was added dropwise. The reaction turned slightly yellow. After stirring for 1h, chloroacetaldehyde diethylacetal (3.05 mL, 20.3 mmol, 1 eq.) was added rapidly. The reaction slowly turned darker yellow. After 2 additional hours, tributyltin chloride (5.30 mL, 19.3 mmol, 0.95 eq.) was added over 1 minute. The reaction was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure to give an oily orange/yellow solid. Diethyl ether (150 mL) and sat. aqueous NH_4Cl (150 mL) were added and swirled for 1 minute to produce a yellow/orange organic layer with all solids dissolving. The aqueous layer was extracted with diethyl ether (3 x 75 mL). The combined organic layer was washed with brine (2 x 200 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a dark red oil (6.89 g) that was advanced crude. The approximate weight of the oil should be ~105% of the theoretical yield. Via crude ^{1}H NMR (400 MHz, $CDCl_3$), the following key peaks were observed: δ = 4.07 (q, 2H, OCH_2CH_3), 1.55 – 1.24 (m, CH_2s), 0.89 (t, CH_3) ppm. Residual THF or ether peaks were common. Formation of the lithium ethoxyacetylide was adapted from work by Raucher and Bray.[4]

General method D (Alkyl-Substituted Ynol Ethers)

In a flame- or oven-dried two-necked flask ethoxyethyne (**2a**) (40% in hexane, 1.25 eq.) was diluted in abs. THF (1 M) and the solution was cooled to −78 °C. To this *n*-BuLi (1.6 M in hexane, 1.50 eq.) was added dropwise. After stirring for 1 h, HMPA (2.75 eq.) was added and the reaction mixture was stirred at −78 °C for 30 min. To this a solution of the alkyl bromide species (1.00 eq.) in THF (7 M) was added. The dark brown solution was allowed to warm to room temperature over night and was then diluted with Et_2O and quenched with H_2O. The organic layer was washed with H_2O (3 ×) and brine (1 ×), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material could be applied in the subsequent [5+2] cycloaddition reaction without further purification. As noted in the text, a purified sample could be obtained by filtration over Al_2O_3 (eluted with hexane) with some loss of product due to decomposition. Column chromatography on SiO_2 or distillation led to complete decomposition.

General method E (Alkyl-Substituted Ynol Ethers, alternative method)

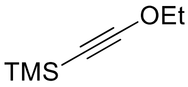
In a flame- or oven-dried two-necked flask ethoxyethyne (**2a**) (40% in hexane, 1.25 eq.) was diluted in abs. THF (1 M) and the solution was cooled to −78 °C. To this *n*-BuLi (1.6 M in hexane, 1.50 eq.) was added dropwise. After stirring for 1 h a solution of the alkyl bromide species (1.00 eq.) in THF (7 M) was added. The reaction mixture was allowed to warm to room temperature over night and then diluted with Et_2O and quenched with H_2O. The organic layer was washed with H_2O (3 ×) and brine (1 ×), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material could be applied in the subsequent [5+2] cycloaddition reaction without further purification.

General method F (Aryl-Substituted Ynol Ethers)

In a flame- or oven-dried two-necked flask under nitrogen atmosphere, crude tributyl(ethoxyethynyl)stannane (1.25 eq) was added followed by anhydrous DMF (0.2 M for aryl-iodide species). Next, the necessary aryl-iodide (1.0 eq) was added followed by tetrabutylammonium chloride (1.0 eq) and bis(triphenylphosphine)palladium(II) dichloride (5 mol %). This was allowed to stir for between 1 h and 4 h (see substrate). The work up and purification are given individually below for each compound. This procedure was adapted from work by Sakamoto et al.[5]

Note on Alkyl-Substituted Ynol Ethers

Due to the volatility of the alkyl substituted ynol ethers, not all of the residual solvent could be removed without substantial or complete loss of the product. As a result, the purity of the prepared sample is reported for each product, accounting for the residual solvent present in each sample. If the sample was used crude (indicated below), other impurities were factored into the reported purity value.

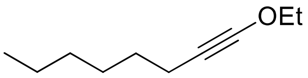


(Ethoxyethynyl)trimethylsilane (2b)

Crude **2b** (541 mg, 50% purity) was obtained according to general method E by reaction of chlorotrimethylsilane (545 mg, 5.00 mmol, 1.00 eq.) with **2a** (438 mg, 6.26 mmol, 1.25 eq.). Purification by filtration over Al_2O_3 led to complete decomposition of the material. The spectroscopic data match the literature values.[6]

$C_7H_{14}OSi$ (142.27 g mol^{-1})

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.13 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 1.37 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 0.13 (s, 9H, $Si(CH_3)_3$) ppm.



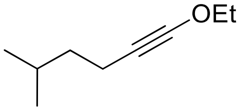
1-Ethoxyoct-1-yne (2c)

Crude **2c** (982 mg, 75% purity) was obtained according to general method D by reaction of 1-bromohexane (1.07 g, 6.49 mmol, 1.00 eq.) with **2a** (568 mg, 8.11 mmol, 1.25 eq.). The spectroscopic data match the literature values.[7]

$\mathrm{C_{10}H_{18}O}$ (154.25 g $\mathrm{mol^{-1}}$).

$^{\mathbf{1}}$**H-NMR** (500 MHz, $\mathrm{CDCl_3}$): $\delta = 4.01$ (q, *J* = 7.1 Hz, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 2.10 (t, *J* = 7.1 Hz, 2H, $\mathrm{OCCC}\mathit{H}_2$), 1.47-1.41 (m, 2H, $\mathrm{C}\mathit{H}_2$), 1.39-1.24 (m, 6H, 3 x $\mathrm{C}\mathit{H}_2$), 1.34 (t, *J* = 7.1 Hz, 3H, $\mathrm{OCH_2C}\mathit{H}_3$), 0.88 (t, *J* = 7.1 Hz, 3H, $\mathrm{(CH_2)_5C}\mathit{H}_3$) ppm.

$^{\mathbf{13}}$**C{$^{\mathbf{1}}$H}-NMR** (126 MHz, $\mathrm{CDCl_3}$): $\delta = 89.4$ ($\mathrm{CH_3CH_2O}\mathit{C}\mathrm{C}$), 74.0 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2OCC}$), 37.6 ($\mathrm{CH_3CH_2OC}\mathit{C}$), 31.6 ($\mathit{C}\mathrm{H_2}$), 29.9 (s, $\mathit{C}\mathrm{H_2}$), 28.7 ($\mathit{C}\mathrm{H_2}$), 22.8 ($\mathit{C}\mathrm{H_2}$), 17.4 ($\mathrm{OCC}\mathit{C}\mathrm{H_2}$), 14.5 ($\mathit{C}\mathrm{H_3CH_2OCCCH_2}$), 14.2 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$) ppm.



1-Ethoxy-5-methylhex-1-yne (2d)

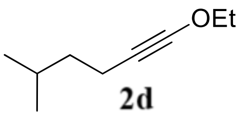
Crude **2d** (835 mg, 80% purity) was obtained according to general method D by reaction of 1-bromo-3-methylbutane (1.62 g, 6.49 mmol, 1.00 eq.) with **2a** (938 mg, 13.5 mmol, 1.25 eq.). The ^{1}H-NMR shows residual solvent (diethyl ether) peaks that could not be removed fully due to the volatility of the compound. The purity was adjusted to account for this.

$C_9H_{16}O$ (140.22 g mol^{-1})

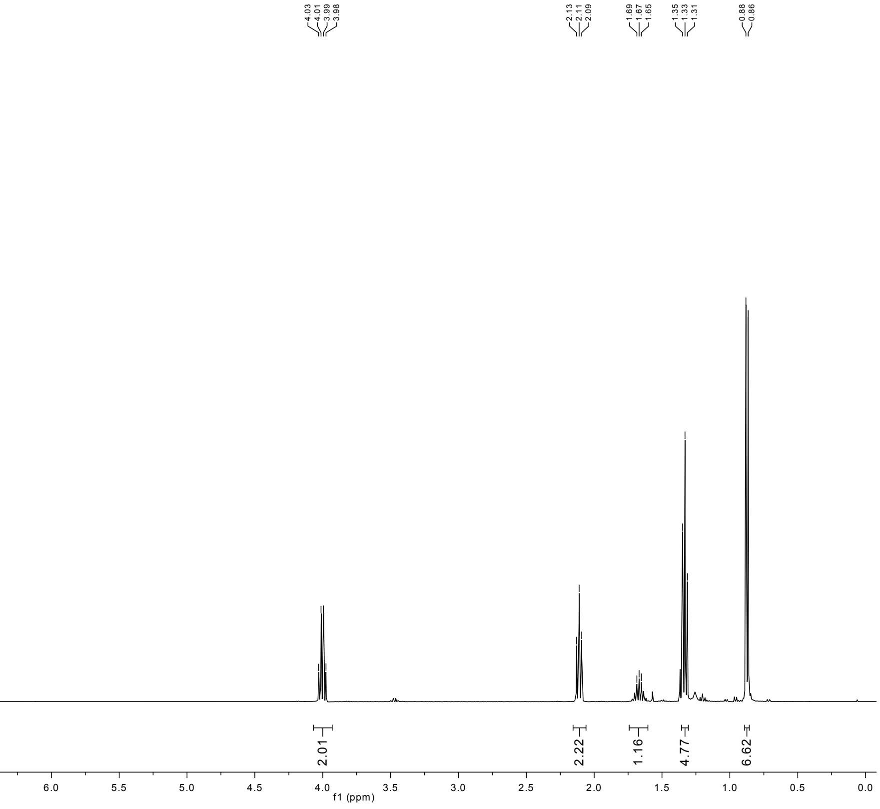
^{1}H-NMR (400 MHz, CDCl$_3$): δ = 4.00 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 2.11 (t, J = 7.4 Hz, 2H, OCCCH_2), 1.67 (sept, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 1.37-1.31 (m, 5H, CH$_2$CH_2CH, OCH$_2$CH_3), 0.87 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) ppm.

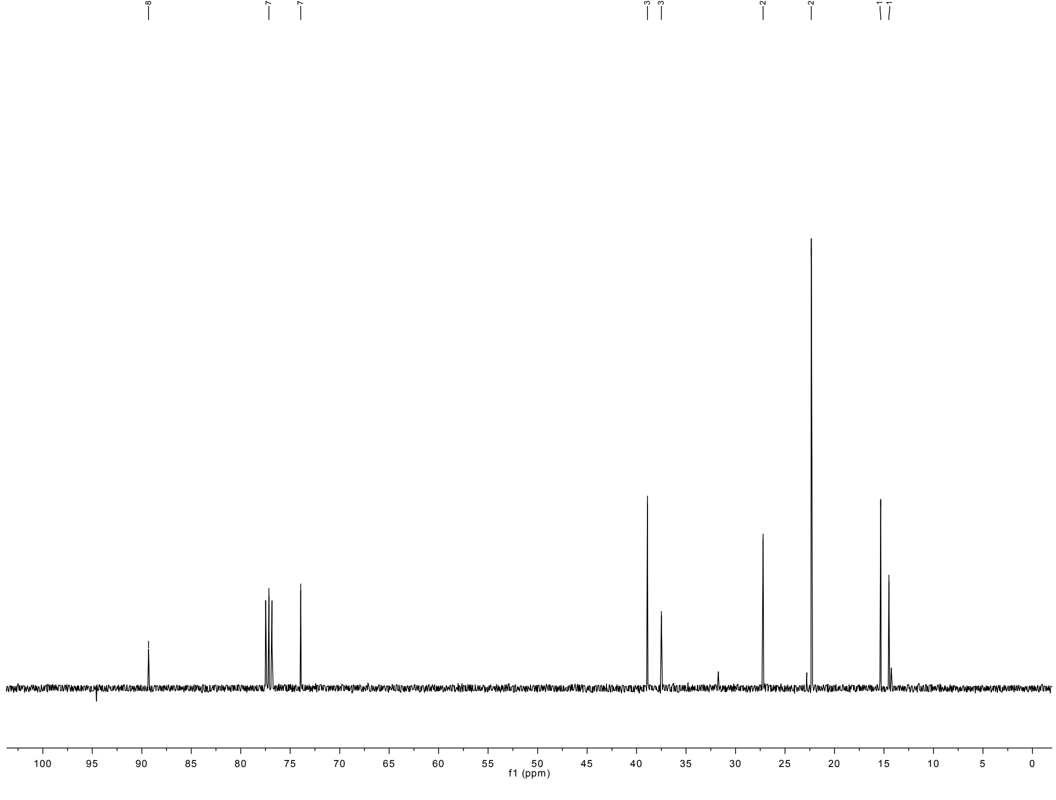
^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$): δ = 89.3 (CH$_3$CH$_2$OCC), 74.0 (CH$_3$$CH_2$OCC), 38.9 (OCCCH$_2$$CH_2$), 37.5 (CH$_3CH_2OCC$), 27.2 ($C$H(CH$_3$)$_2$), 22.4 (CH($CH_3$)$_2$), 15.3 (OCC$CH_2$), 14.5 ($CH_3CH_2$OCCCH$_2$) ppm.

HRMS: m/z calculated for $C_9H_{17}O$ 141.1279 (M+H)$^+$; found 141.1277.


OEt

2d


4.03
4.01
3.99
3.98
2.13
2.11
2.09
1.69
1.67
1.65
1.35
1.33
1.31
0.88
0.86
2.01
2.22
1.16
4.77
6.62
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


89.31
77.16
73.94
38.91
37.50
27.22
22.35
15.32
14.50
100
95
90
85
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60
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50
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40
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20
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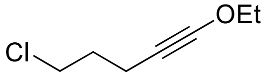
10
5
0
f1 (ppm)



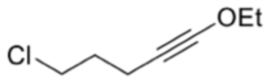
5-Chloro-1-ethoxypent-1-yne (2e)

Crude **2e** (936 mg, 80% purity) was obtained according to general method D by reaction of 1-bromo-3-chloropropane (1.08 g, 6.85 mmol, 1.00 eq.) with **2a** (606 mg, 8.56 mmol, 1.25 eq.). The ^{1}H-NMR shows residual solvent (diethyl ether) peaks that could not be removed fully due to the volatility of the compound. The purity was adjusted to account for this. The analytical data matches the literature values.[8]

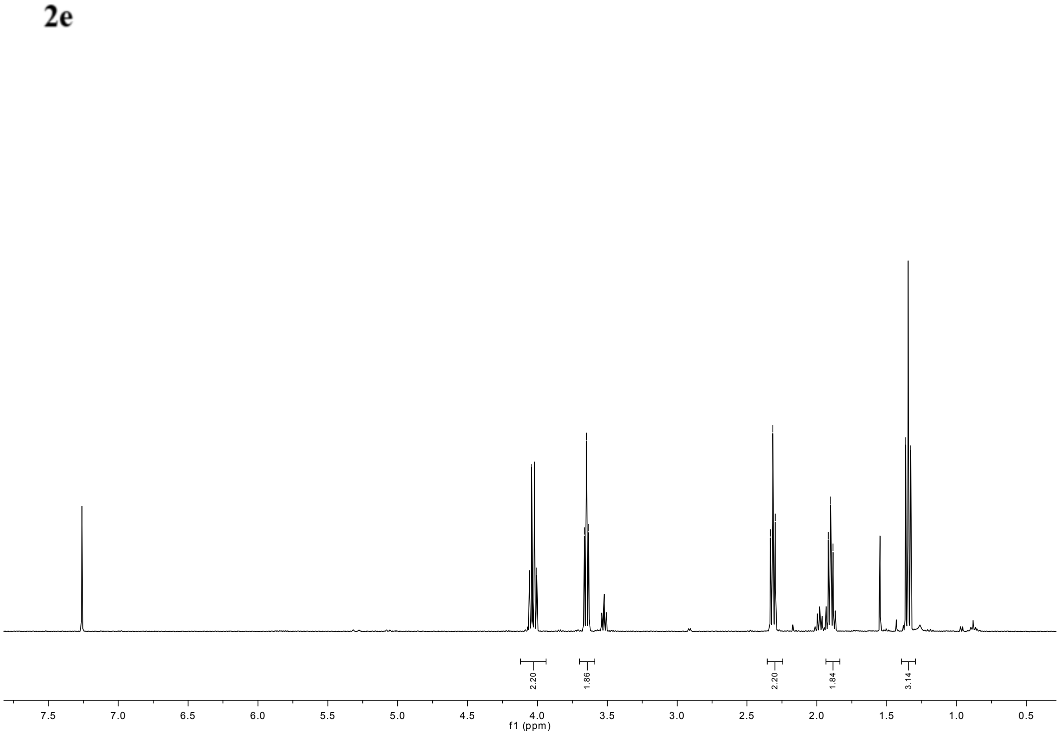
$C_7H_{11}ClO$ (146.61 g mol^{-1})

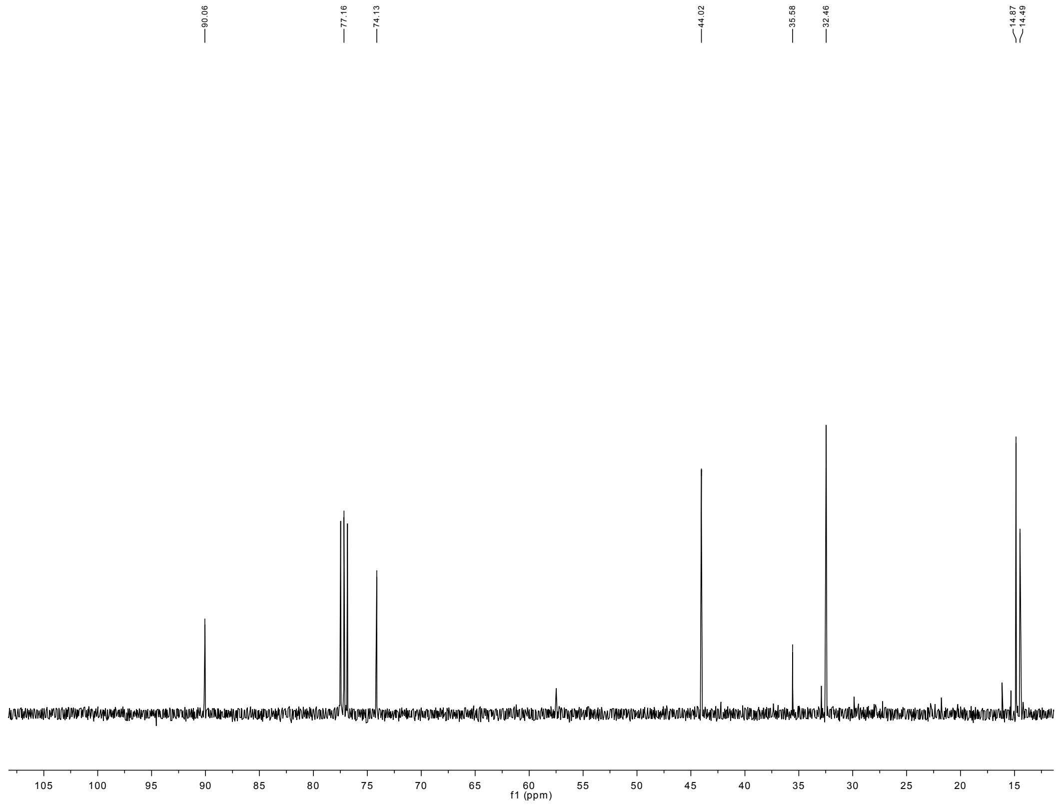
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.02 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 3.64 (t, J = 6.4 Hz, 2H, CH_2CH_2Cl), 2.31 (t, J = 6.7 Hz, 2H, $OCCCH_2$), 1.89 (quint, J = 6.6 Hz, 2H, $CH_2CH_2CH_2$), 1.34 (t, J = 7.1 Hz, 3H, OCH_2CH_3) ppm.

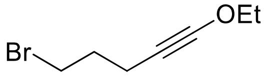
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 90.1 (CH_3CH_2OCC), 74.1 (CH_3CH_2OCC), 44.0 (CH_2CH_2Cl), 35.6 (CH_3CH_2OCC), 32.5 ($CH_2CH_2CH_2$), 14.9 ($OCCCH_2$), 14.5 ($CH_3CH_2OCCCH_2$) ppm.


OEt
Cl

2e


4.06
4.04
4.02
4.00
3.67
3.65
3.63
2.33
2.32
2.30
1.92
1.90
1.88
1.36
1.35
1.33
2.20
1.86
2.20
1.84
3.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


90.06
77.16
74.13
44.02
35.58
32.46
14.87
14.49
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)



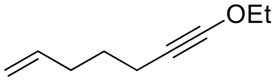
5-Bromo-1-ethoxypent-1-yne (2f)

Crude **2f** (968 mg, 50% purity) was obtained according to general method D by reaction of 1,3-dibromopropane (1.75 g, 8.64 mmol, 1.00 eq.) with **2a** (550 mg, 7.85 mmol, 1.25 eq.). Purification by filtration over Al_2O_3 led to complete decomposition of the material. The analytical data matches the literature values.[9]

$C_7H_{11}BrO$ (191.07 g mol^{-1})

^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 4.02$ (q, $J = 7.1$ Hz, 2H, OCH_2CH_3), 3.51 (t, $J = 6.5$ Hz, 2H, CH_2CH_2Cl), 2.30 (t, $J = 6.7$ Hz, 2H, $OCCCH_2$), 1.97 (quint, $J = 6.7$ Hz, 2H, $CH_2CH_2CH_2$), 1.33 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3) ppm.

The crude product was used without further purification to prevent loss due to decomposition.



7-Ethoxyhept-1-en-6-yne (2g)

Crude **2g** (1.63 g, 80% purity) was obtained according to general method D by reaction of 5-bromopent-1-ene (1.59 g, 10.7 mmol, 1.00 eq.) with **2a** (938 mg, 13.4 mmol, 1.25 eq.).

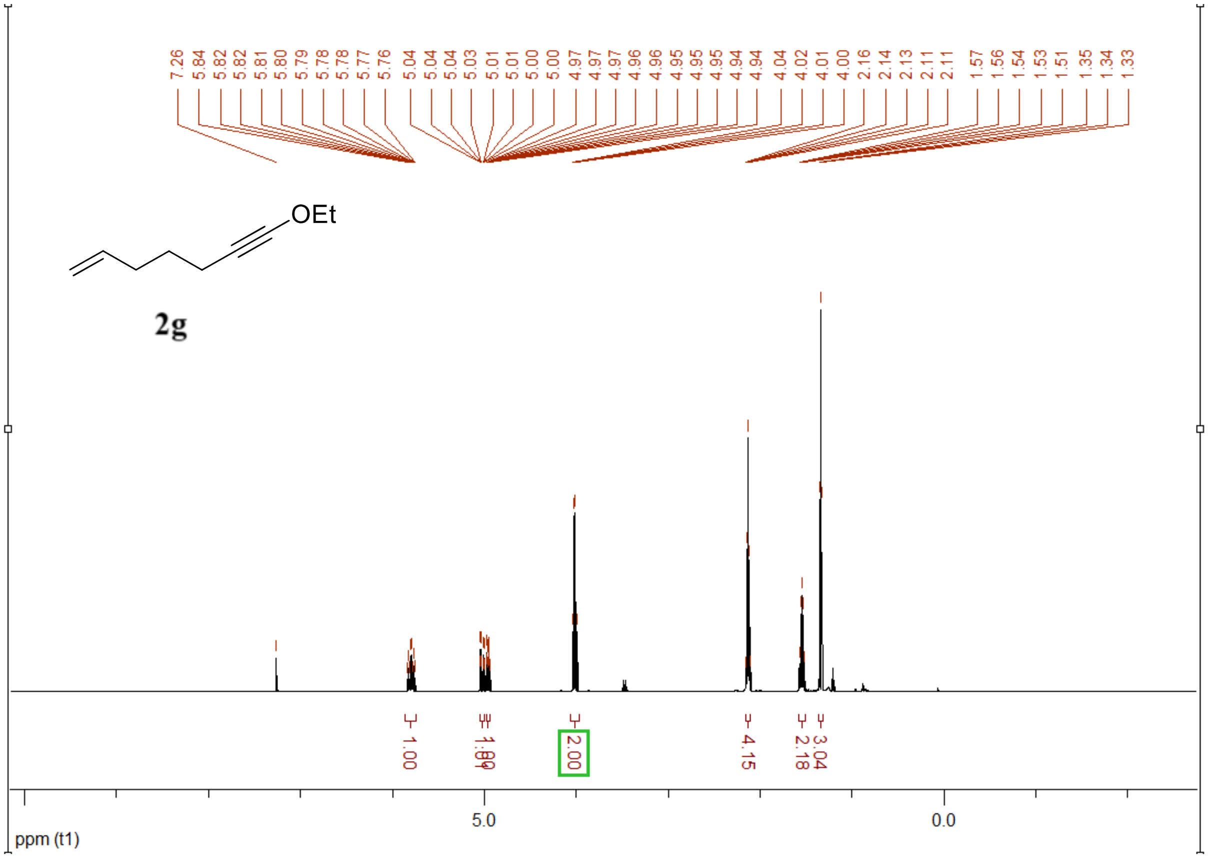
$C_9H_{14}O$ (138.21 g mol^{-1})

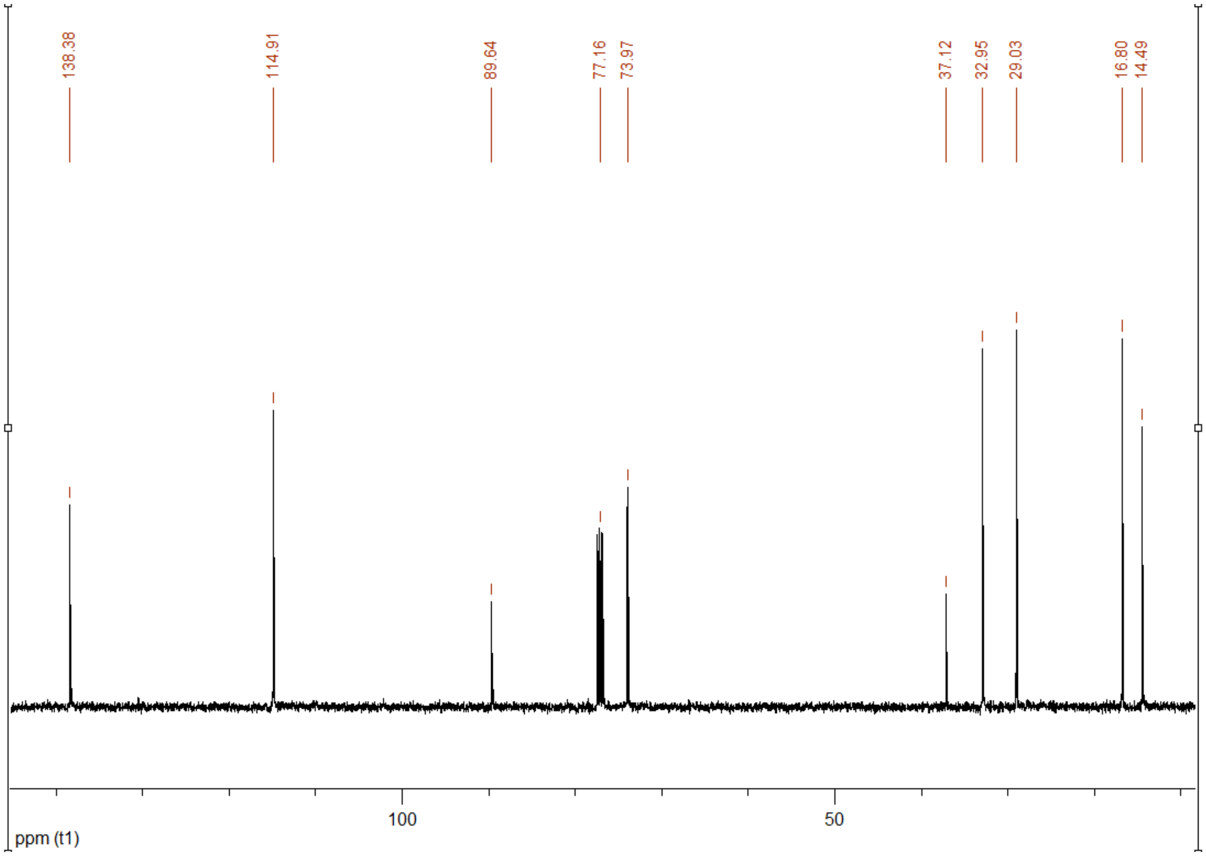
^{1}H-NMR (500 MHz, $CDCl_3$): δ= 5.80 (ddt, J = 17.1 Hz, 10.3 Hz, 6.7 Hz, 1H, $CH_2CH(CH_2)_3$), 5.02 (dq, J = 17.1 Hz, 1.7 Hz, 1H, $(CH_2)_3CHCHH$), 4.96 (dquint, J = 10.2 Hz, J = 1.0 Hz, 1H, $(CH_2)_3CHCHH$), 4.01 (q, J = 6.9 Hz, 2H, OCH_2CH_3), 2.16-2.11 (m, 4H, $CCCH_2CH_2CH_2$), 1.57-1.51 (m, 2H, $CCCH_2CH_2CH_2$), 1.34 (t, J = 6.9 Hz, 3H, OCH_2CH_3) ppm.

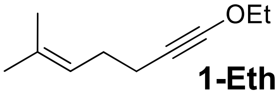
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ= 144.9 ($CH_2CH(CH_2)_3$), 138.4 ($CH_2CH(CH_2)_3$), 89.6 (CH_3CH_2OCC),74.0 (CH_3CH_2OCC), 37.1 (CH_3CH_2OCC), 33.0 ($CH_2CHCH_2(CH_2)_2$), 29.0 ($CHCH_2CH_2CH_2$), 16.8 ($OCCCH_2$), 14.5 ($CH_3CH_2OCCCH_2$) ppm.

HRMS: Due to the instability of this compound, HRMS data could not be obtained. Spectroscopic characterization was consistent with the other ynol ether substrates for which HRMS data was obtained and the resulting cycloheptadione (**3g**) was consistent with the proposed structure of this substrate.

The crude product was used without further purification to prevent loss due to decomposition.


7.26
5.84
5.82
5.82
5.81
5.80
5.79
5.78
5.78
5.77
5.76
5.04
5.04
5.04
5.03
5.01
5.01
5.00
5.00
4.97
4.97
4.97
4.96
4.96
4.95
4.95
4.95
4.94
4.94
4.04
4.02
4.01
4.00
2.16
2.14
2.13
2.11
2.11
1.57
1.56
1.54
1.53
1.51
1.35
1.34
1.33
OEt
2g
1.00
1.00
2.00
4.15
2.18
3.04
5.0
0.0
ppm (t1)


138.38
114.91
89.64
77.16
73.97
37.12
32.95
29.03
16.80
14.49
100
50
ppm (t1)



1-Ethoxy-6-methylhept-5-en-1-yne (2h)

Crude **2h** (347 mg, 70% purity) was obtained according to general method D by reaction of 5-bromo-2-methylpent-2-ene (815 mg, 5.00 mmol, 1.00 eq.) with **2a** (1.45 mL, 6.25 mmol, 1.25 eq.).

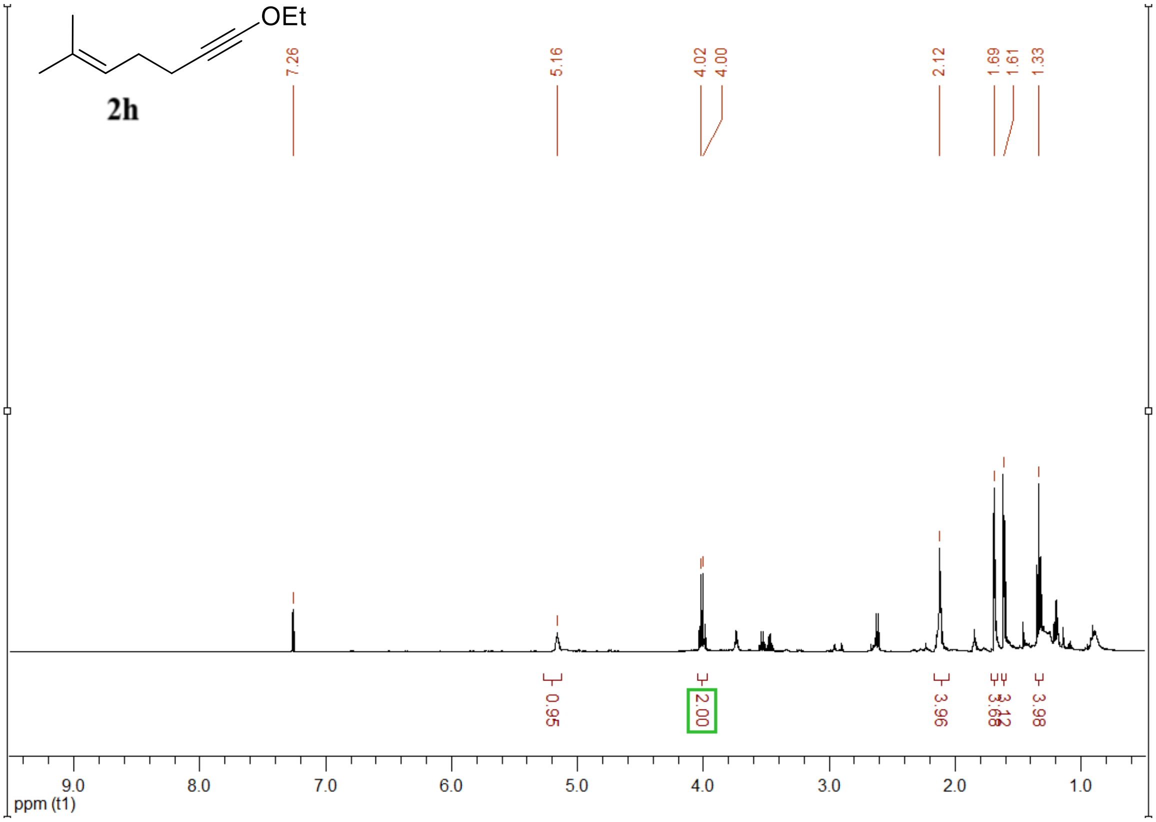
$C_{10}H_{16}O$ (152.23 g mol^{-1})

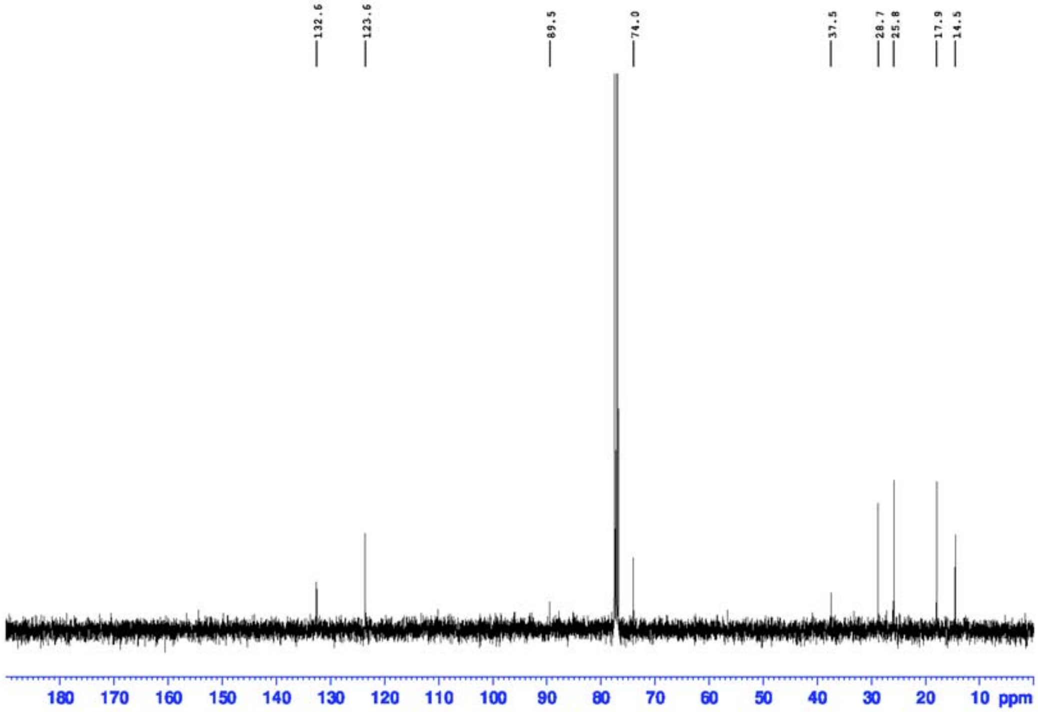
^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.16 (m, 1H, $(CH_3)_2CC\mathit{H}$), 4.01 (q, J = 7.1 Hz, 2H, $OC\mathit{H}_2CH_3$), 2.16-2.06 (m, 4H, $CCC\mathit{H}_2C\mathit{H}_2CH$), 1.69 (s, 3H, $(C\mathit{H}_3)(CH_3)CCH$), 1.61 (s, 3H, $(CH_3)(C\mathit{H}_3)CCH$), 1.33 (t, J = 7.1 Hz, 3H, $OCH_2C\mathit{H}_3$) ppm.

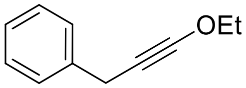
^{13}C{^{1}H}-NMR (126 MHz, CDCl$_3$): δ = 132.6 ($(CH_3)_2\mathit{C}=CHCH_2$), 123.6 ($(CH_3)_2C=\underline{C}HCH_2$), 89.5 ($CH_2CH_2C\mathit{C}OCH_2CH_3$), 74.0 ($CH_2CH_2CCO\mathit{C}H_2CH_3$), 37.5 ($CH_2CH_2\mathit{C}COCH_2CH_3$), 28.7 ($=CH\mathit{C}H_2CH_2CC$), 25.8 ($=CHCH_2\mathit{C}H_2CC$), 17.9 ($(\mathit{C}H_3)_2C=CHCH_2$), 14.5 ($CCOCH_2\mathit{C}H_3$) ppm.

HRMS: Due to the instability of this compound, HRMS data could not be obtained.

The crude product was used without further purification to prevent loss due to decomposition.


2h
OEt
7.26
5.16
4.02
4.00
2.12
1.69
1.61
1.33
0.95
2.00
3.96
3.66
3.12
3.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


132.6
123.6
89.5
74.0
37.5
28.7
25.8
17.9
14.5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



(3-Ethoxyprop-2-yn-1-yl)benzene (2i)

Crude **2i** (900 mg, 60% purity) was obtained according to general method E by reaction of (bromomethyl)benzene (732 mg, 4.28 mmol, 1.00 eq.) with **2a** (300 mg, 4.28 mmol, 1.00 eq.).

$C_{11}H_{12}O$ (160.21 g mol^{-1})

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41-7.29 (m, 4 H, aryl-C*H*), 7.24-7.20 (m, 1 H, aryl-C*H*), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.56 (s, 2 H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm.

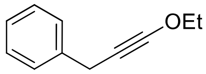
^{13}C-NMR (101 MHz; CDCl3): δ = 138.7, 129.2, 129.0, 128.6, 128.5, 126.5, 91.4, 74.3, 33.8, 23.7, 14.7 ppm.

IR (NaCl): 횟 = 3905-3568, 2920, 2361, 2343, 1734, 1686-1637, 1578-1542, 1508, 1458, 1273, 1121, 1071 cm^{-1}.

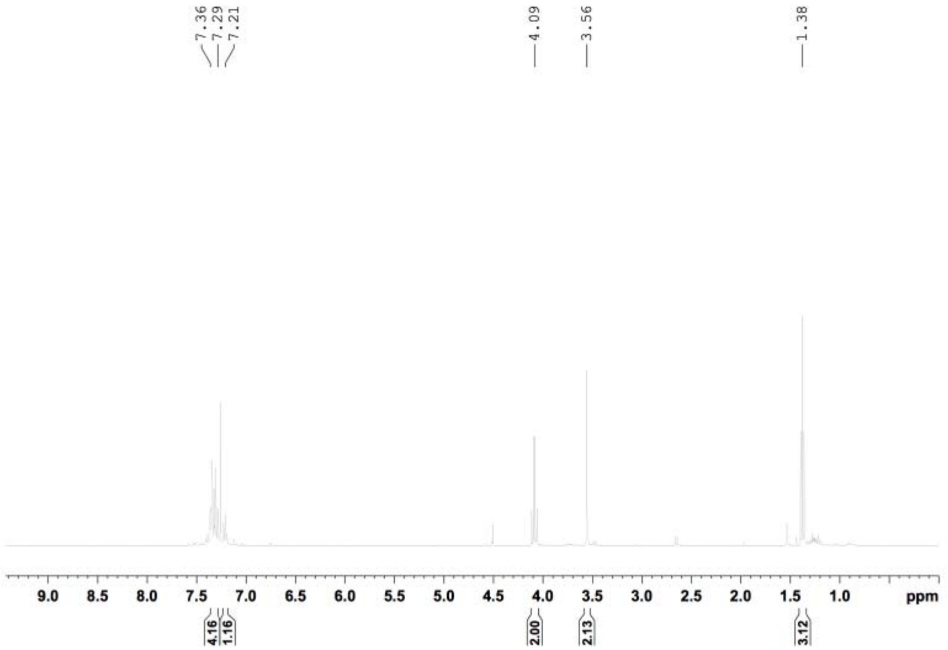
R$_f$ = 0.62 (EtOAc/hexane= 1:10), UV-active, single spot.

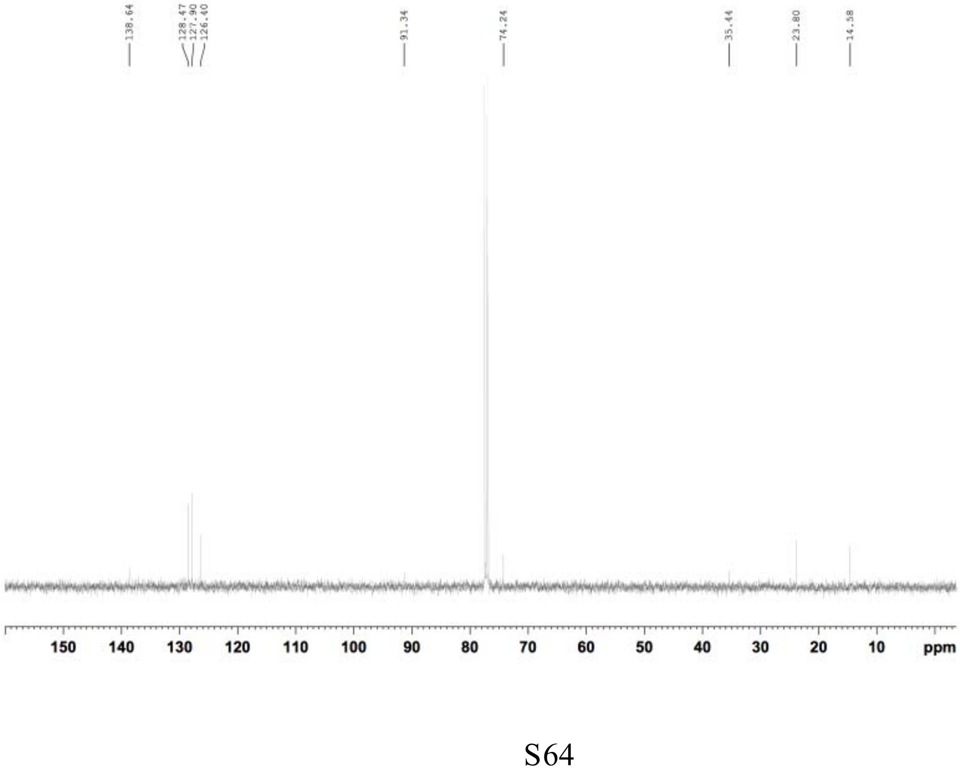
HRMS: m/z calculated for $C_{11}H_{13}O$ 161.0966 (M+H)$^{+;}$ found 161.0969.

The crude product was used without further purification to prevent loss due to decomposition.


OEt

2i


7.36
7.29
7.21
4.09
3.56
1.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.16
1.16
2.00
2.13
3.12


138.64
128.47
127.90
126.40
91.34
74.24
35.44
23.80
14.58
150
140
130
120
110
100
90
80
70
60
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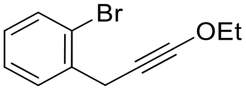
40
30
20
10
ppm



1-bromo-2-(3-ethoxyprop-2-yn-1-yl)benzene (2j)

Crude **2j** (922 mg, 90% purity) was obtained according to general method E by reaction of 1-bromo-2-(bromomethyl)benzene (1.01 g, 4.28 mmol, 1.00 eq.) with **2a** (300 mg, 4.28 mmol, 1.00 eq.).

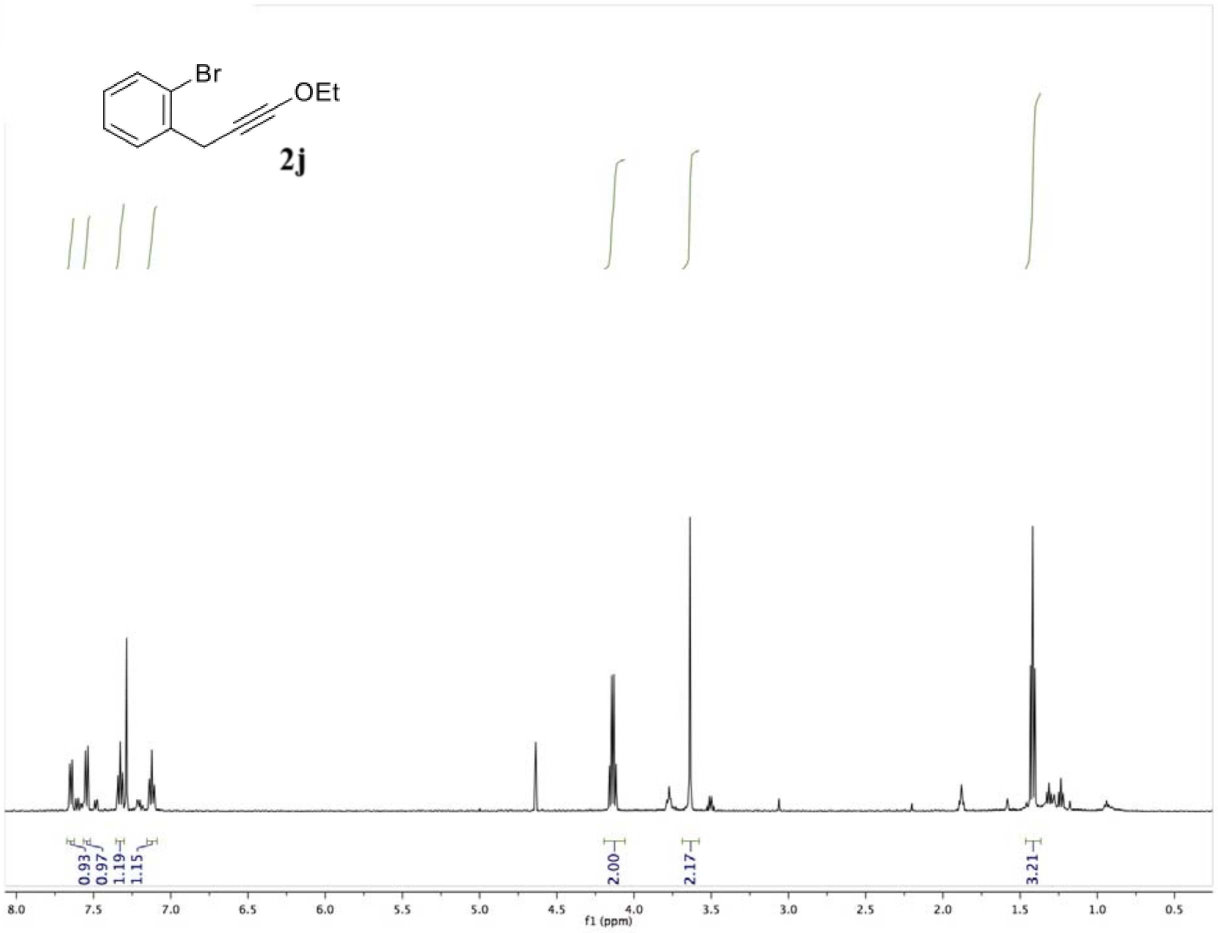
$C_{11}H_{11}BrO$ (239.11 g mol^{-1})

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.64 (d, *J* = 7.7 Hz 1H, C(Br)C*H*), 7.54 (d, *J* = 8.2 Hz, 1H, C(CCOEt)C*H*), 7.33 (t, *J* = 7.6 Hz, 1H, C(Br)CHCHC*H*), 7.12 (t, 1H, C(Br)CHC*H*CH), 4.14 (q, *J* = 7.1, 0.9 Hz, 2H, CH_2CH$_3$), 3.64 (s, 2H, ArCH_2), 1.42 (t, *J* = 7.1, 0.9 Hz, 3H, CH$_2$CH_3) ppm.

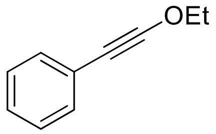
HRMS: m/z calculated for $C_{10}H_{10}BrO$ 224.9915 (M+H)$^+$; found 224.9918.

R$_f$ = 0.38 (SiO$_2$, pentane, obtained as single spot that is UV active)

The crude product was used without further purification to prevent loss due to decomposition.


Br
OEt
0.93
0.97
1.19
1.15
2.00
2.17
3.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

2j



(Ethoxyethynyl)benzene (2k)

2k (72 mg, 44% yield) was obtained as a clear colorless oil according to general method F by reaction of iodobenzene (0.125 mL, 1.11 mmol, 1.0 eq.) with tributyl(ethoxyethynyl)stannane (500 mg, 1.39 mmol, 1.25 eq.). After 2h reaction time, pentane (50 mL) was used to extract the product from the DMF layer. The solvent was removed under reduced pressure to give a red/brown oil. The crude reaction was purified via flash chromatography (silica, pentane, 1.5% triethylamine). The spectroscopic data match the literature values.[5, 10]

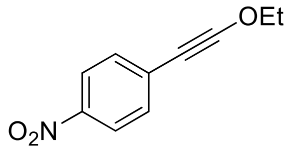
$C_{10}H_{10}O$ (146.19 g mol^{-1})

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.11 (m, 5H, Ph), 4.20 (q, *J* = 7.1, 0.3 Hz, 2H, $\mathit{CH_2}CH_3$), 1.43 (t, 3H, $CH_2\mathit{CH_3}$) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 131.7 (*Ar*-H), 128.4 (*Ar*-H), 126.8 (*Ar*-Br), 124.2 (*Ar*-C), 98.8 (C*C*OEt), 75.1 (*C*H_2), 40.1 (*C*C*O*Et), 14.7 (*C*H_3) ppm.

IR (NaCl): 휧늩 2983, 2259, 1599, 1442, 1321, 1166, 1062, 1024, 830, 754, 962 cm^{-1}.

R$_f$ = 0.37 (SiO_2, pentane, obtained as a single spot that stains with $KMnO_4$).



1-(Ethoxyethynyl)-4-nitrobenzene (2l)

2l (201 mg, 47% yield) was obtained as an orange amorphous solid according to general method F by reaction of 1-iodo-4-nitrobenzene (555 mg, 2.22 mmol, 1.00 eq.) with tributyl(ethoxyethynyl)stannane (1.2 g, 3.34 mmol, 1.50 eq.). After 4h reaction time, water was added to the reaction (20 mL) and ether (3 x 50 mL) was used to extract the product from the aqueous layer. The organic layer was washed with water (3 x 75 mL) and brine (3 x 75 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a red/brown oil. The crude product was purified via flash chromatography (silica, gradient, 2% EtOAc to 20% EtOAc: hexanes). The spectroscopic data match the literature values.[5]

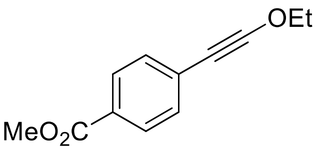
$C_{10}H_9NO_3$ (191.18 g mol^{-1})

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 9.0 Hz, 2H, C*H*C(NO_2)C*H*), 7.42 (d, *J* = 9.0 Hz, 2H, C*H*C(CCOEt)C*H*), 4.29 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 1.48 (t, *J* = 7.1 Hz, 3H, CH_2CH_3) ppm.

^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$): δ = 132.1 (*Ar*-NO_2), 131.9 (*Ar*-H), 123.7 (*Ar*-H), 104.1 (Ar-C), 89.5 (C*C*OEt), 76.0 (*C*H_2), 40.1 (*C*C*O*Et), 14.7 (*C*H_3) ppm.

IR (NaCl): 흜= 3111, 3080, 2990, 2872, 2261, 1923, 1595, 1510, 1376, 1345, 1284, 1108, 1054, 999, 850, 748, 687, 585 cm^{-1}.

R_f = 0.30 (SiO_2, hexane/DCM = 10:1, 2.5% Et_3N, obtained as a single spot that is UV active).



Methyl 4-(ethoxyethynyl)benzoate (2m)

2m (213 mg, 45% yield) was obtained as an amorphous white solid according to general method F by reaction of methyl 4-iodobenzoate (584 mg, 2.23 mmol, 1.00 eq.) with tributyl(ethoxyethynyl)stannane (1.20 g, 3.34 mmol, 1.50 eq.). After 4h reaction time, water was added to the reaction (20 mL) and ether (3 x 50 mL) was used to extract the product from the aqueous layer. The organic layer was washed with water (3 x 75 mL) and brine (3 x 75 mL) and dried with anhydrous $MgSO_4$. The crude product was purified via flash chromatography (silica, 5% Et_2O in pentane). Minor impurities remained in product that could not be removed without total degradation during repeated purification.

$C_{12}H_{12}O_3$ (204.22 g mol^{-1})

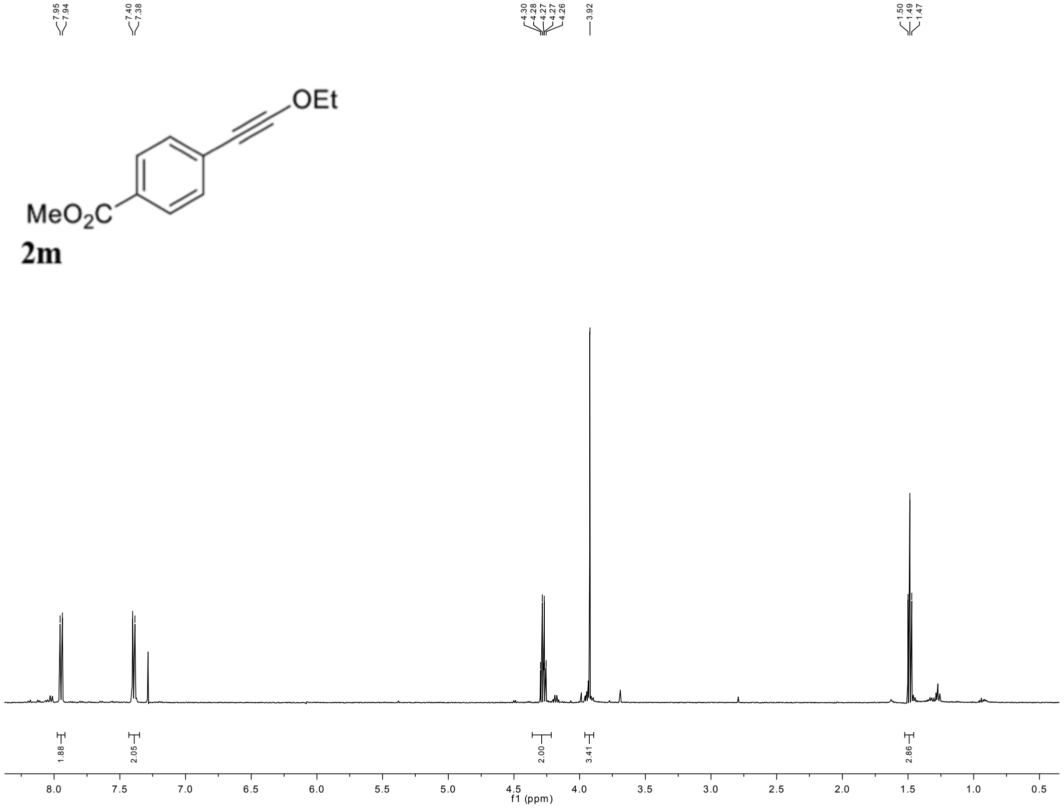
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.7 Hz, 2H, C*H*C(COOMe)C*H*), 7.35 (d, *J* = 8.7 Hz, 2H, C*H*C(CCOEt)C*H*), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 3.88 (s, 3H, COOCH_3), 1.45 (t, *J* = 7.1 Hz, 3H, CH_2CH_3) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 167.1 (*C*=O), 131.4 (*Ar*-H), 129.6 (*Ar*-H), 129.6 (*Ar*-CC), 128.0 (*Ar*-C(O)OCH$_3$), 101.9 (C*C*OEt), 75.6 (CCO*C*H$_2$CH$_3$), 52.3 (Ar-(CO)O*C*H$_3$), 40.3 (*C*COEt), 14.8 (CCOCH$_2$*C*H$_3$) ppm.

IR (NaCl): 훫= 3432, 2985.01m, 2955, 2256, 1725, 1610, 1436, 1281, 1194, 1110, 1019, 967, 860, 770, 730, 579 cm^{-1}.

HRMS: Due to the instability of this compound, HRMS data could not be obtained. Spectroscopic characterization was consistent with the other ynol ether substrates for which HRMS data was obtained and the resulting cycloheptadione (**3m**) was consistent with the proposed structure of this substrate.

R$_f$ = 0.58 (SiO_2, hexane/EtOAc = 5:1, obtained as single spot that is UV active).



OEt
MeO$_2$C
7.95
7.94
7.40
7.38
4.30
4.28
4.27
4.27
4.26
3.92
1.50
1.49
1.47
1.88
2.05
2.00
3.41
2.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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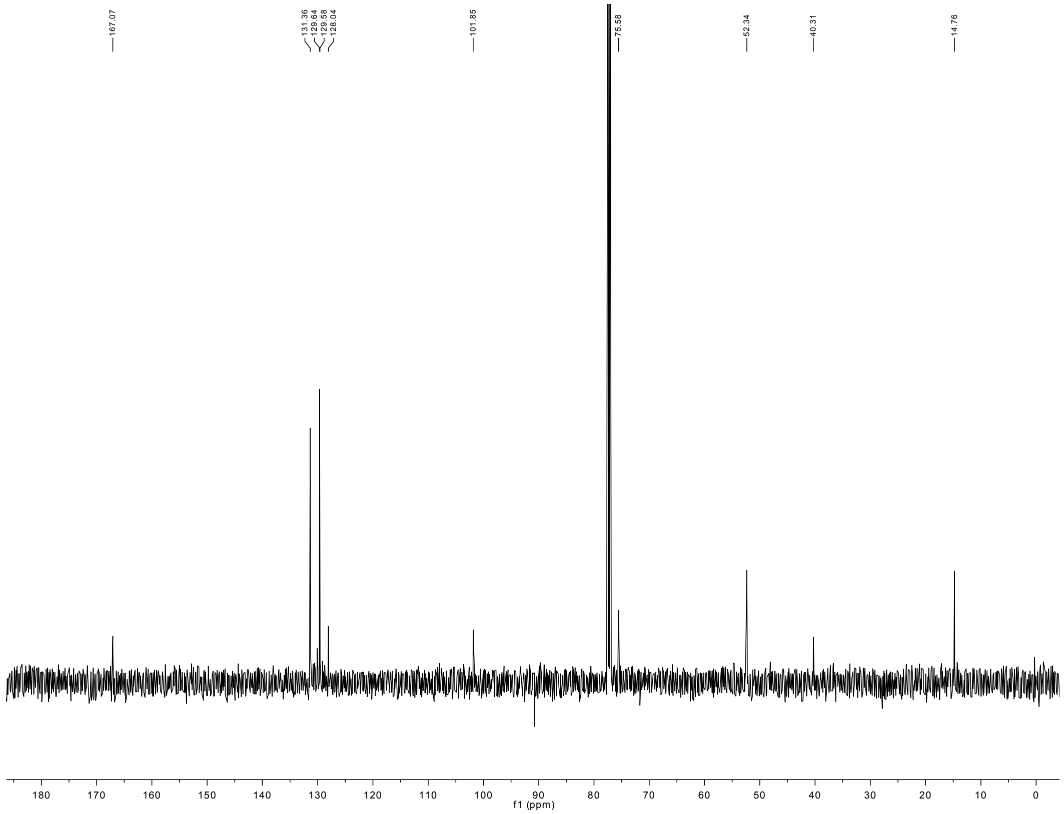
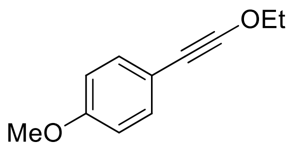
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

2m



167.07
131.36
129.64
129.58
128.04
101.85
75.58
52.34
40.31
14.76
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1-(Ethoxyethynyl)-4-methoxybenzene (2n)

2n (158 mg, 23% yield) was obtained as a slightly yellow oil according to general method F by reaction of 1-methoxy-4-iodobenzene (931mg, 3.98 mmol, 1.40 eq.) with tributyl(ethoxyethynyl)stannane (2.00 g, 5.57 mmol, 1.40 eq.). After 2h reaction time, pentane (50 mL) was used to extract the product from the DMF layer. The solvent was removed under reduced pressure to give a red/brown oil. The crude reaction was purified via flash chromatography (silica, pentane, 1.5% triethylamine). The spectroscopic data match the literature values.[5]

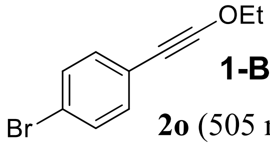
$C_{11}H_{12}O_2$ (176.21 g mol^{-1})

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.9, 0.7 Hz, 2H, C*H*C(CCOEt)C*H*), 6.78 (dd, *J* = 8.9, 0.7 Hz, 2H, C*H*C(OMe)C*H*), 4.17 (q, *J* = 7.1, 0.7 Hz, 2H, CH_2CH_3), 3.77 (s, 3H), 1.42 (td, *J* = 7.1, 0.7 Hz, 3H, CH_2CH_3) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 158.6 (*Ar*-OCH_3), 133.1 (*Ar*-H), 116.2 (*Ar*-H), 114.0 (*Ar*-CC), 97.5 (C*C*OEt), 75.0 (CCOCH_2CH_3), 55.5 (Ar-OCH_3), 39.5 (*C*COEt), 14.7 (CCOCH$_2$CH$_3$) ppm.

IR (NaCl): 훯= 2956, 2935, 2837, 2258, 1607, 1513, 1464, 1442, 1366, 1317, 1284, 1245, 1173, 1061, 1029, 831 cm^{-1}.

R_f = 0.55 (SiO_2, hexane/DCM = 1:1, obtained as a single spot that is UV active).



1-Bromo-4-(ethoxyethynyl)benzene (2o)

2o (505 mg, 50% yield) was obtained according to general method F by reaction of 1-bromo-4-iodobenzene (1.26 g, 4.46 mmol, 1.00 eq.) with tributyl(ethoxyethynyl)stannane (2.00 g, 5.57 mmol, 1.25 eq.). After 2h reaction time, pentane (50 mL) was used to extract the product from the DMF layer. The solvent was removed under reduced pressure to give a red/brown oil. The crude reaction was purified via flash chromatography (silica, pentane, 1.5% triethylamine). The analytical data matches the literature values.[11]

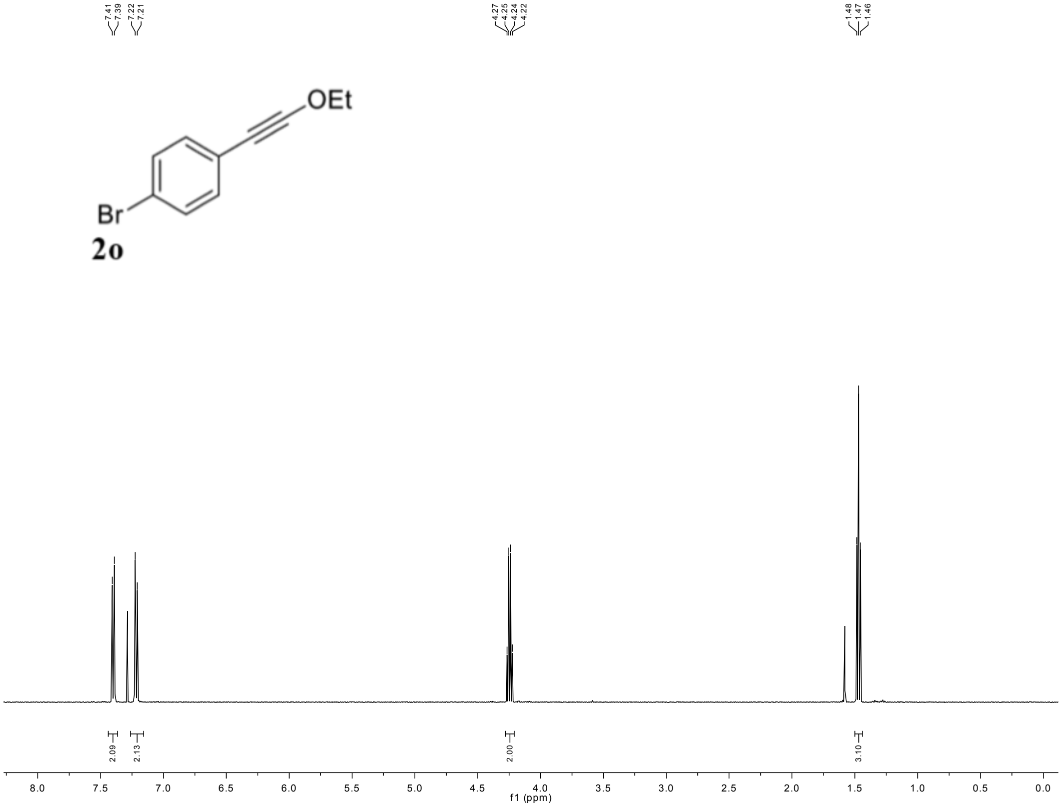
$C_{10}H_9BrO$ (225.08 g mol^{-1})

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.42 – 7.38 (m, 2H, Ar), 7.24 – 7.19 (m, 2H, Ar), 4.24 (q, *J* = 7.1 Hz, 2H, $C\mathit{H}_2CH_3$), 1.47 (t, *J* = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 133.2 (*Ar*-Br), 131.6 (*Ar*-H), 123.4 (*Ar*-H), 120.7 (*Ar*-CC), 99.7 (C*C*OEt), 75.3 (*C*H_2), 39.4 (*C*COEt), 14.8 (*C*H_3) ppm.

IR (NaCl): 홄= 2980, 2255, 1488, 1392, 1317, 1166, 1071, 1009, 820 cm^{-1}.

R$_f$ = 0.32 (SiO_2, pentane, obtained as a singles spot that is UV active).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7.21
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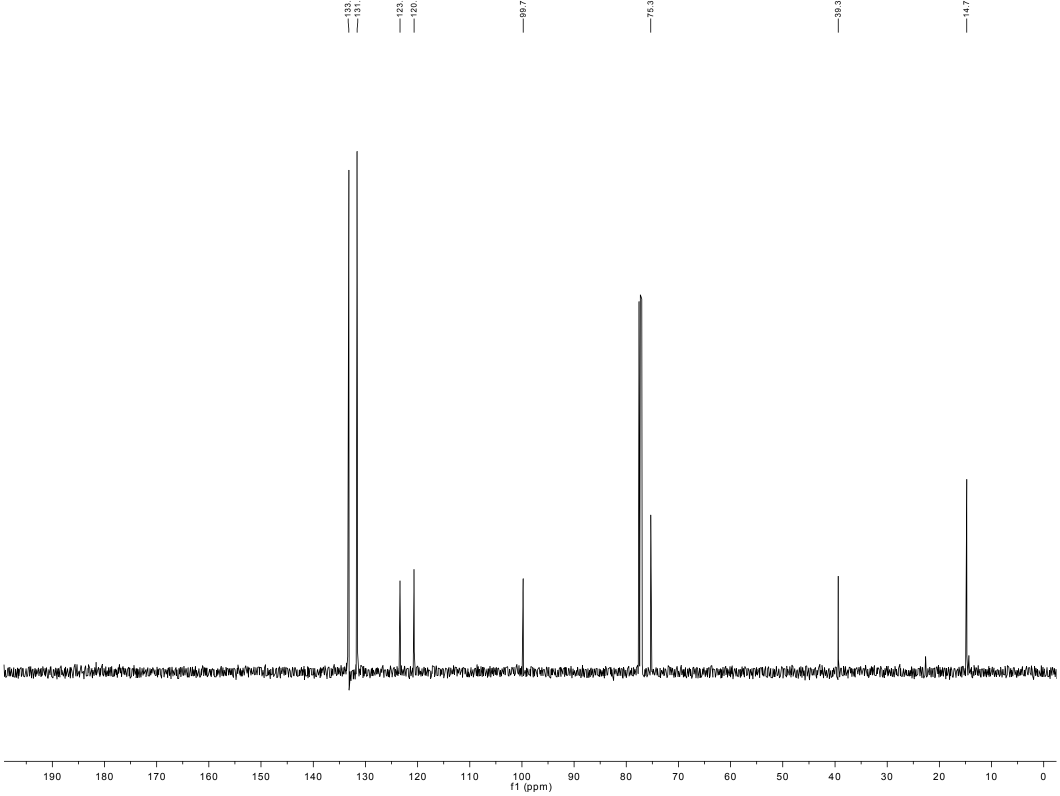
4.25
4.24
4.22
1.48
1.47
1.46
OEt
Br
2o
2.09
2.13
2.00
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


133.19
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120.66
99.74
75.31
39.37
14.76
190
180
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150
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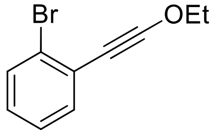
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1-Bromo-2-(ethoxyethynyl)benzene (2p)

2p (302 mg, 20% yield) was obtained according to general method F by reaction of 1-bromo-2-iodobenzene (1.89 g, 6.69 mmol, 1.00 eq.) with tributyl(ethoxyethynyl)stannane (3.00 g, 8.35 mmol, 1.50 eq.). After 2h reaction time, pentane (50 mL) was used to extract the product from the DMF layer. The solvent was removed under reduced pressure to give a red/brown oil. The crude reaction was purified via flash chromatography (silica, pentane, 1.5% triethylamine).

$C_{10}H_{9}BrO$ (225.08 g mol^{-1})

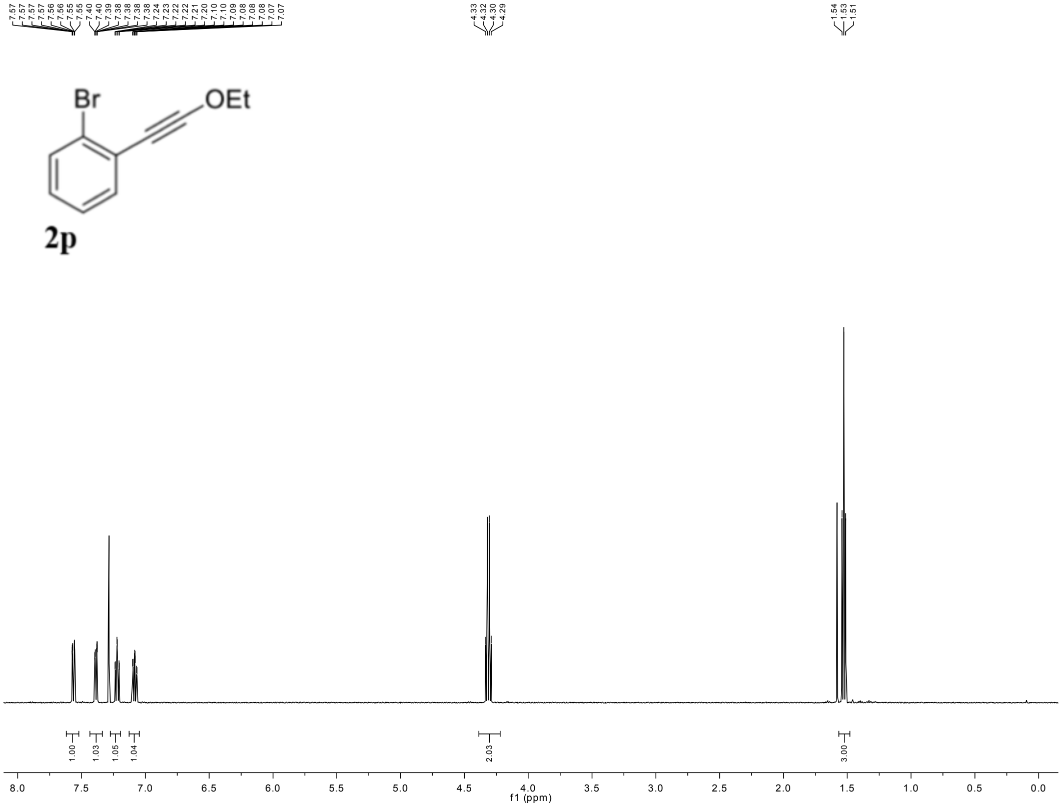
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar), 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar), 7.32 – 7.25 (m, 1H, Ar), 7.07 (ddd, *J* = 7.8, 7.3, 1.7 Hz, 1H, Ar), 4.18 (q, *J* = 7.1 Hz, 2H, $OC\mathit{H}_2CH_3$), 1.35 (t, *J* = 7.1 Hz, 3H, $OCH_2C\mathit{H}_3$) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 145.7 (*Ar*-Br), 134.2 (*Ar*-H), 132.9 (*Ar*-H), 129.8 (*Ar*-H), 128.1 (*Ar*-H), 127.4 (*Ar*-H), 123.2 (C*C*OEt), 109.2 (*C*H_2), 68.0 (*C*COEt), 14.8 (*C*H_3) ppm.

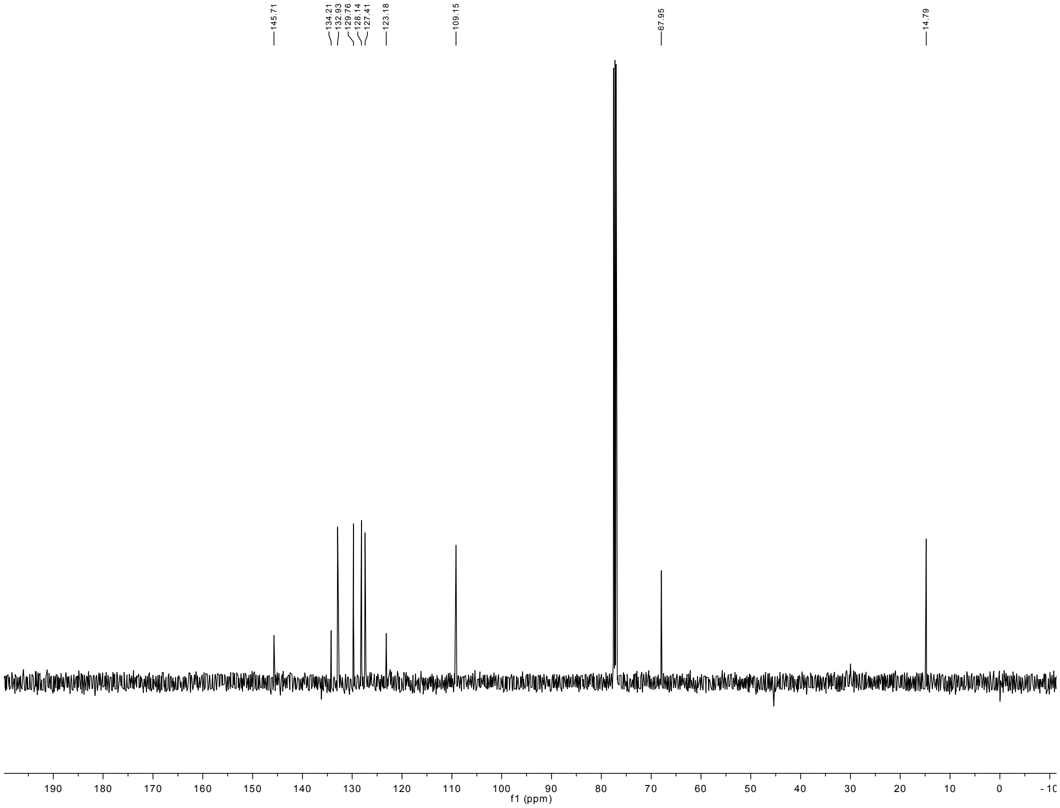
IR (NaCl): 횙는 2927, 2250 1631, 1465, 1435, 1373, 1333, 1070, 1024, 903, 831, 745 cm^{-1}.

R$_{f}$ = 0.35 (SiO_2, pentane, obtained as a single spot that is UV active).

HRMS: m/z calculated for $C_{10}H_{10}BrO$ 224.9915 $(M+H)^+$; found 224.9918.


7.57
7.57
7.57
7.56
7.56
7.55
7.55
7.40
7.39
7.38
7.38
7.38
7.38
7.24
7.23
7.22
7.22
7.21
7.20
7.10
7.10
7.09
7.08
7.08
7.07
7.07
4.33
4.32
4.30
4.29
1.54
1.53
1.51
Br
OEt
1.00
1.03
1.05
1.04
2.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2p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14.79
190
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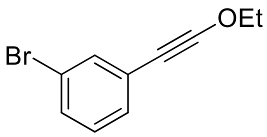
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



1-Bromo-3-(ethoxyethynyl)benzene (2q)

2q (98 mg, 26%) was obtained according to general method F by reaction of 1-bromo-3-iodobenzene (465 mg, 1.65 mmol, 1.00 eq.) with tributyl(ethoxyethynyl)stannane (1.00 g, 1.81 mmol, 1.10 eq.). After 2h reaction time, pentane (50 mL) was used to extract the product from the DMF layer. The solvent was removed under reduced pressure to give a red/brown oil. The crude reaction was purified via flash chromatography (silica, pentane, 1.5% triethylamine).

$C_{10}H_9BrO$ (225.08 g mol^{-1})

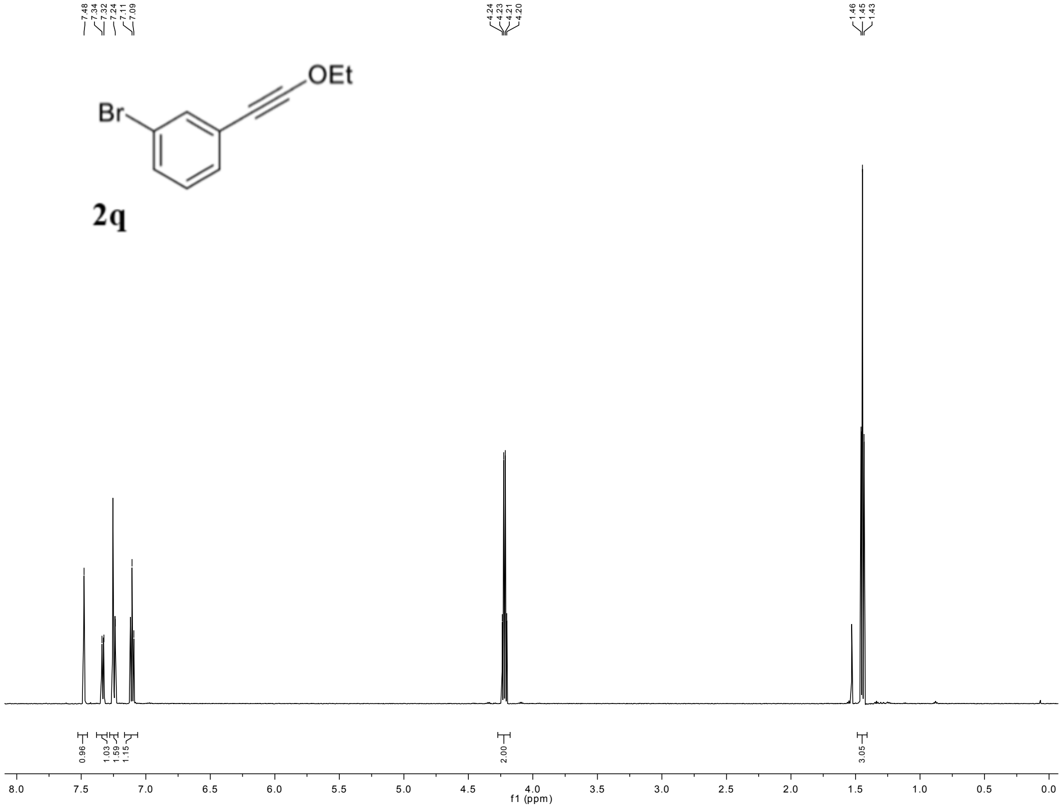
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (t, *J* = 1.8 Hz, 1H, Aryl C(Br)C*H*C(CCOEt)), 7.32 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H, C(Br)C*H*CH), 7.25 – 7.21 (m, 1H, CHC*H*C(CCOEt)), 7.09 (t, *J* = 7.9 Hz, 1H, CHC*H*CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2CH$_3$), 1.43 (d, *J* = 14.1 Hz, 3H, CH$_2$CH_3) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 134.4 (*Ar*-Br), 130.2 (*Ar*-H), 129.9 (*Ar*-H), 129.8 (*Ar*-H), 126.4 (*Ar*-H), 122.2 (*Ar*-CC), 99.9 (C*C*OEt), 75.4 (*C*H$_2$), 39.1 (*C*COEt), 14.7 (*C*H$_3$) ppm.

IR (NaCl): 횘= 2958, 2259, 1592, 1553, 1319, 1058, 834, 780, 682 cm^{-1}.

R$_f$ = 0.34 (SiO_2, pentane, obtained as a single spot that is UV active).

HRMS: m/z calculated for $C_{10}H_{10}BrO$ 224.9915 (M+H)$^+$; found 224.9912.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7.24
7.11
7.09
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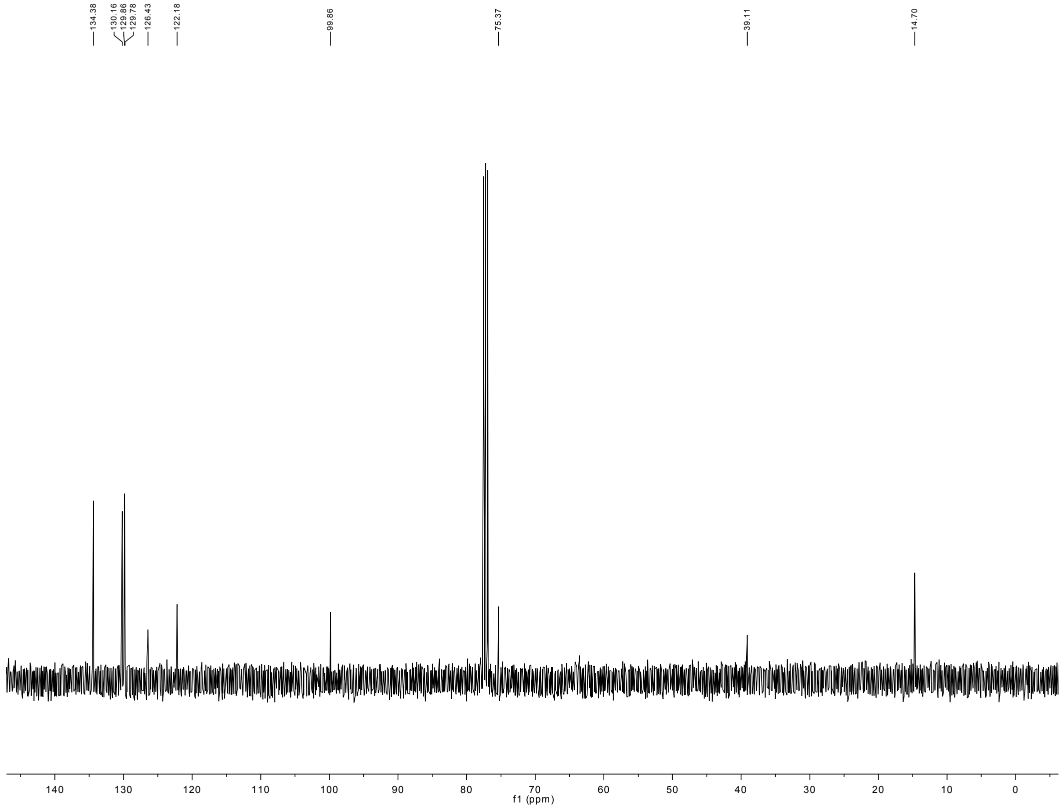
4.23
4.21
4.20
1.46
1.45
1.43
Br
OEt
0.96
1.03
1.59
1.15
2.00
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2q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39.11
14.70
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Literature

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