# Creation of highly congested quarternary centers via Cu catalyzed conjugate addition of alkenyl alanates to *β*-substituted cyclic enones

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## SUPPORTING INFORMATION

## Table of Contents

**General**. $^1H$ (400 MHz or 300 MHz) and $^{13}C$ (100 MHz or 75 MHz) NMR spectra were recorded in $CDCl_3$ and chemical shifts are given in ppm relative to residual $CHCl_3$. Evolution of reaction was followed by GC-MS Hewlett Packard (EI mode) HP6890-5973. Flash chromatographies were performed using silica gel 32-63 µm, 60 Å and a pentane-diethylether mixture as eluent. All reactions were carried out under inert atmosphere. All solvents were dried on alumina columns.

## ■ Reagents

***Reagents used for alane and alanate synthesis:***

**Methyllithium:** was purchased from ACROS (1.6 M solution in ether)

***n*-Butyllithium:** was purchased from ACROS (1.6 M solution in hexane)

***tert*-Butyllithium:** was purchased from ACROS (1.9 M solution in pentane)

**2-Bromopropene** was purchased from Sigma-Aldrich (99%) and used as received.

**cis-1-Bromo-1-propene** was purchased from Sigma-Aldrich (97%) and used as received.

**1-Bromo-2-methyl-1-propene** was purchased from Sigma-Aldrich (98%) and used as received.

**2-Bromo-3-methyl-2-butene** was purchased from Sigma-Aldrich (96%) and used as received.

**$Me_3Al$** was purchased from Sigma-Aldrich (2.0 M in heptane) and used as received.

**DIBAL-H** was purchased from ACROS (ACROSEAL, 1.0M solution in heptane) and used as received.

**5-Chloro-1-pentyne** was purchased from ACROS (98%) and used as received.

***Reagents used for Catalysis***

**3-methylcyclohex-2-enone** was purchased from Sigma-Aldrich (98%)

**isophorone**: was purchased from ACROS (98%)

**CuTC** was purchased from Frontier Scientific and used as received.

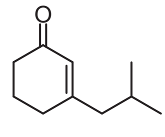
**Copper(II)naphtenate, 77% in mineral spirits (8% Cu)** was purchased from Strem (CAS: 1338-02-9) and used as a solution in pentane (3.2 g of the fir green viscous oil was dissolved in pentane (50 mL)).

**Dichlorobis(triphenylphosphine)nickel(II)** was purchased from Fluka (98%) and used as received. (CAS: 14264-16-5).

## ■ Synthesis of Enones

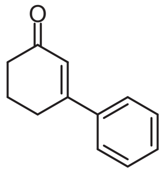
*General Procedure A:*
A flame-dried flask was charged with Grignard or lithium reagent (2.0 eq.), cooled to 0 °C and ethoxycyclohex-2-en-1-one (50 mmol) in THF (40mL) was added dropwise. Once the addition was complete the reaction mixture was left at rt until complete disappearance of the starting material. The reaction mixture poured into 1M aqueous HCl (50 mL). Diethyl ether (50 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (2 × 50 mL). The combined organic fractions were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The oily residue was purified by distillation under reduced pressure or trituration with pentane.

### 3-isobutylcyclohex-2-enone (2)[1]



The crude oil was obtained according to *General Procedure E* and purified by distillation (150 °C at 30 mbar) to afford **2** as a pale yellow oil (53% yield). **$^1$H-NMR** (400.13 MHz, $CDCl_3$): $\delta$ = 5.90 (brs, 1H), 2.44-2.37 (m, 2H), 2.31 (t, $J$ = 5.7 Hz, 2H), 2.13 (d, $J$ = 7.2 Hz, 2H), 2.08-1.99 (m, 2H), 1.98-1.87 (m, 1H), 0.96 (dt, $J$ = 6.4, 3.1 Hz, 6H).

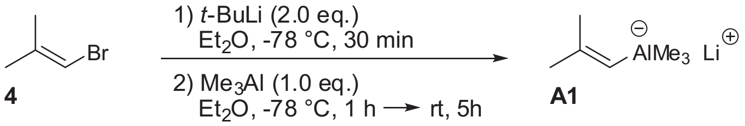
### 3-phenylcyclohex-2-enone (3)[2]



The crude product was obtained according to *General Procedure E* and was triturated in Pentane / $Et_2O$ = 5:1 to afford **3** as beige crystals (72% yield). **$^1$H-NMR** (400.13 MHz, $CDCl_3$): $\delta$ = 7.65-7.51 (m, 2H), 7.45-7.38 (m, 3H), 6.43 (brs, 1H), 2.82-2.75 (m, 1H), 2.52-2.47 (m, 1H), 2.21-2.12 (m, 1H).

## ■ Preparation of alkenylalanates from the corresponding alkenyl bromides; exemplified for 4.103

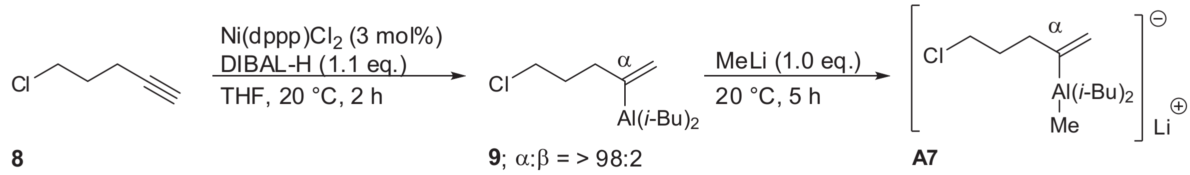
*General Procedure B:*



To a solution of 1-bromo-2-methylprop-1-ene **4** (166 $\mu$L, 243 g, 1.8 mmol, 1.0 eq.) in $Et_2O$ (1.8 mL) was added under inert atmosphere *t*-BuLi (1.9 mL, 3.6 mmol, 1.9 M in pentane, 2.0 eq.) at –78 °C. The reaction was stirred for 30 min at this temperature. Then $Me_3Al$ (0.9 mL, 1.8 mmol, 2.0 M in heptane, 1.0 eq.) was added and the reaction mixture was stirred for 30 min maintaining the temperature at –78 °C. The cooling bath was removed and the reaction vessel was immediately submerged in a water bath (20 °C). The alanate was stirred over 5 h at 20 °C and **A1** was used without purification.

## ■ Preparation of alkenylaluminums by Ni-catalyzed hydroalumination from alkynes[3]

*General Procedure C:*

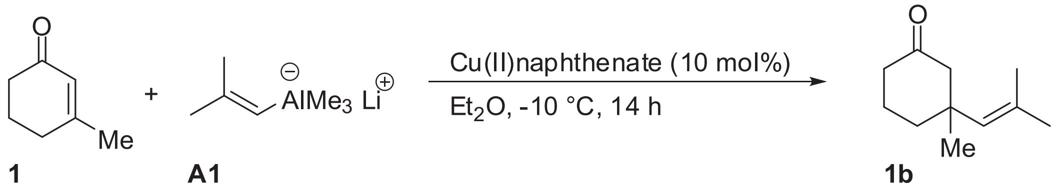


Commercial grade 1,3-bis(diphenylphosphino)propane nickel(II) chloride ($Ni(dppp)Cl_2$, 57 mg, 0.10 mmol, 3 mol %) is placed in an oven-dried round bottom flask equipped with a stir bar. The flask was sealed with a septum and purged with $N_2$. THF (3.5 mL) is added through a syringe, followed by dropwise addition of DIBAL-H (3.8 mL, 3.8 mmol, 1.1 eq. 1.0 M in heptane) at rt. The resulting black solution was allowed to cool to 0 °C before 5-chloropent-1-yne (0.37 mL, 0.36 g, 3.5 mmol, 1.0 eq.) was added slowly over five minutes. The resulting black solution was allowed to warm to 20 °C and stirred for an additional two hours. Then the reaction mixture was cooled to 0 °C and MeLi (2.9 mL, 3.5 mmol, 1.2 M solution in $Et_2O$) was added. The reaction was stirred for another 10 min at 0 °C and then for 5 h at 20 °C.[a]

[a] The reaction was stirred for another 5 h to ensure complete equilibration of alane and alanate species.

## ■ Cu-catalyzed conjugate addition employing alkenylalanates generated from the alkenylbromides; exemplified for the synthesis of 1b

*General Procedure D:*

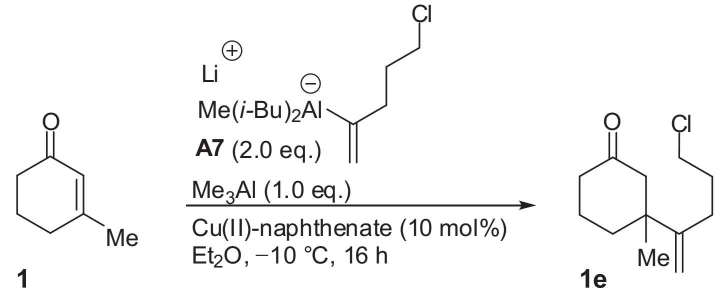


A flame-dried Schlenk tube was charged with Copper(II)naphthenate solution in pentane (1.17 mL, 0.09 mmol Cu(II), 10 mol %) and and ether (3.0 mL).[a] The solution of the Cu-salt was cooled to – 10°C and a solution of the alanate (4.8 mL, 1.8 mmol, 2.0 eq., 0.38 M solution in ether; prepared according to *General Procedure B*) was added slowly. After 5 min neat 3-methylcyclohex-2-enone **1** (102 µl, 99 mg, 0.9 mmol, 1.0 eq.) was added at once and the solution was allowed to stir at –10 °C for another 14 h after which the reaction was quenched by slow addition of MeOH (0.1 mL; CAUTION: gas evolution) at –10°C. When the gas evolution stopped aq. 1 M HCl (3 mL) was added slowly (CAUTION: gas evolution) and stirred vigorously for 30 min at room temperature.[b] The aqueous layer was extracted with $Et_2O$ (3 × 10 mL), the combined organic phases were dried over $Na_2SO_4$ and the solvents removed under reduced pressure to yield the crude product as a brownish oil. Purification by column chromatography over silica gel (Pentane / $Et_2O$ = 10:1) afforded **1b** as a colourless viscous oil (89 mg, 0.54 mmol, 60% yield).

[a] Alternatively the Cu(II)naphthenate solution can be directly added to the cooled suspension of the alante (– 10 °C) without addition of diethyl ether. The neat 3-methylcyclohex-2-enone is then added directly to the black solution.
[b] For reactions on a **larger scale** it is highly recommended to slowly pour the black solution into a mixture of ice and HCl (aq.; 5%) in order to quench the reaction mixture!

- **Cu-catalyzed conjugate addition employing alkenylalalanates generated from the corresponding alkyne via Ni-catalyzed hydroalumination.**

*General Procedure E:*

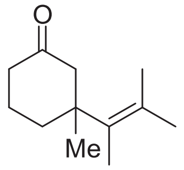


A flame-dried Schlenk tube was charged with Copper(II)naphthenate solution in pentane (2.3 mL, 0.18 mmol Cu(II), 10 mol %) and and ether (6.0 mL).[a] The solution of the Cu-salt was cooled to – 10°C and a solution of the alanate (10.6 mL, 3.5 mmol, 2.0 eq., 0.33 M solution in THF; prepared according to *General Procedure C*) was added slowly. After 5 min neat 3-methylcyclohex-2-enone **5** (198 µl, 193 mg, 1.75 mmol, 1.0 eq.) was added followed by $Me_3Al$ (0.9 mL, 1.75 mmol, 2.0 M in heptane, 1.0 eq.). After 14 h the reaction mixture was slowly poured onto a slush of ice and HCl (aq.; 5%; 30 mL) in an Erlenmeyer flask. Once the gas evolution ceased (careful shaking of the Erlenmeyer flask) the mixture was transferred into a separatory funnel and vigorously shaken for 5 min. Then the organic phase was separated and the aqueous layer was extracted with $Et_2O$ (3 × 20 mL), the combined organic phases were dried over $Na_2SO_4$ and the solvents removed under reduced pressure to yield the crude product as a brownish oil. Purification by column chromatography over silica gel (Pentane / $Et_2O$ = 8:1) afforded **1e** as a brownish viscous oil (250 mg, 1.17 mmol, 67% yield).

[a] Alternatively the Cu(II)naphthenate solution can be directly added to the cooled suspension of the alante (– 10 °C) without addition of diethyl ether. The neat 3-methylcyclohex-2-enone is then added directly to the black solution.

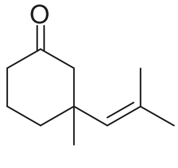
- Analytical Data of Addition Products

**3-methyl-3-(3-methylbut-2-en-2-yl)cyclohexanone (1a)**



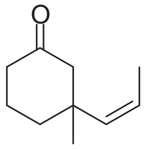
**1a** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1; $R_f$ = 0.23 in pentane / $Et_2O$ = 10:1) gave **1a** in 81% yield as a colourless oil. Product was revealed with anisaldehyde to give brown stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$): δ = 2.72 (d, *J* = 14.1 Hz, 1H), 2.29-2.20 (m, 5H), 1.86-1.81 (m, 1H), 1.78 (d, *J* = 1.1 Hz, 3H), 1.72-1.66 (m, 1H), 1.64 (s, 3H), 1.59 (s, 3H), 1.14 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$): δ =212.7, 132.4, 126.2, 54.6, 44.3, 40.9, 36.4, 26.2, 24.5, 23.5, 22.2, 17.4. **EI-MSHR**: $[M]^+$ calculated for: $C_{12}H_{20}O$: 180.15087, found 180.15099. **IR**: ν [$cm^{-1}$] = 2934, 1707, 1454, 1078.

### 3-methyl-3-(2-methylprop-1-enyl)cyclohexanone (1b)[4]



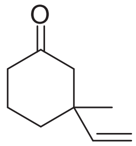
**1b** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1; $R_f$ = 0.33 in pentane / $Et_2O$ = 10:1) gave **1b** in 60% yield as a colourless oil. Product was revealed with anisaldehyde to give purple stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$): δ = 4.99 (s, 1H), 2.42 (d, *J* = 13.4 Hz, 1H), 2.27-2.11 (m, 3H), 1.97-1.75 (m, 3H), 1.66 (d, *J* = 0.8 Hz, 3H), 1.63 (d, *J* = 1.0 Hz, 3H), 1.59-1.51 (m, 1H), 1.12 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$): δ = 211.8, 133.1, 130.3, 55.1, 40.9, 40.4, 37.7, 28.0, 27.3, 22.5, 19.1.

### (*Z*)-3-methyl-3-(prop-1-enyl)cyclohexanone (1c)[5]



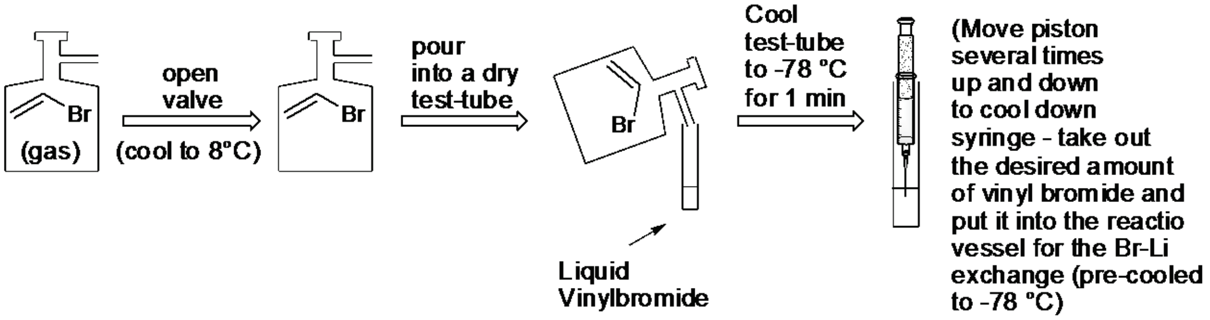
**1c** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1*,* $R_f$ = 0.22 in pentane / $Et_2O$ = 10:1) gave **1c** in 66% yield as colourless viscous oil. Product was revealed with anisaldehyde to give yellow stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$): δ = 5.42 (dq, *J* = 12.0, 7.2 Hz, 1H), 5.23 (dd, *J* = 12.0, 1.6 Hz, 1H), 2.52 (d, *J* = 13.5 Hz, 1H), 2.32-2.20 (m, 3H), 2.01-1.82 (m, 3H), 1.72 (dd, *J* = 7.2, 1.6 Hz, 3H), 1.69-1.59 (m, 1H), 1.20 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$): δ = 211.7, 136.3, 125.2, 54.6, 41.2, 40.9, 37.6, 27.2, 22.5, 14.5. **IR**: ν [$cm^{-1}$] = 2953, 1707, 1454, 1227, 709.

### 3-methyl-3-vinylcyclohexanone (1d)[6]

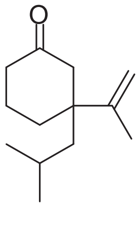


**1d** was prepared according to *General Procedure D*.[a] Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 7:1; $R_f$ = 0.29 in pentane / $Et_2O$ = 7:1) gave **1d** in 83% yield as a colourless oil. Product was revealed with anisaldehyde to give yellow stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$): δ = 5.65 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.01-4.84 (m, 2H), 2.38 (d, *J* = 14.0 Hz, 1H), 2.25-2.03 (m, 3H), 1.84-1.73 (m, 2H), 1.70-1.51 (m, 2H), 1.00 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$, 298 K): δ = 211.2, 145.7, 112.6, 51.6, 41.5, 40.8, 36.5, 27.2, 22.0.

[a] Due to the low boiling point of vinyl bromide (15 °C) the handling of it requires a special technique which is shown in the picture below.



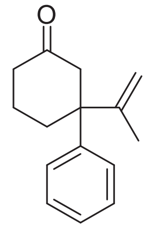
### 3-isobutyl-3-(prop-1-en-2-yl)cyclohexanone (2a)



**2a** was prepared according to *General Procedure K*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1; $R_f$ = 0.29 in Pentane / $Et_2O$ = 10:1) gave **2a** in 65% yield as a pale yellow viscous oil.

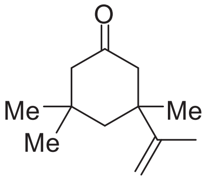
Product was revealed with anisaldehyde to give brown stains. $^1$H-NMR (400.13 MHz, $CDCl_3$): δ = 4.93 (s, 1H), 4.74 (s, 1H), 2.73 (d, *J* = 14.5 Hz, 1H), 2.35-2.09 (m, 3H), 1.90-1.73 (m, 2H), 1.65 (d, *J* = 0.4 Hz, 3H), 1.53 (ddd, *J* = 19.5, 13.5, 5.4 Hz, 3H), 1.25-1.17 (m, 2H), 0.85 (td, *J* = 6.7, 2.8 Hz, 6H). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): δ = 211.8, 147.6, 114.8, 51.3, 48.3, 47.6, 41.0, 34.9, 25.1, 24.7, 24.1, 21.2, 19.3. **EI-MSHR**: $[M-C_3H_7]^+$ calculated for: $C_{13}H_{22}O$: 151.11174, found 151.11183. **IR**: ν [cm$^{-1}$] = 2952, 1710, 1447, 1233, 902.

**3-phenyl-3-(prop-1-en-2-yl)cyclohexanone (3a)**



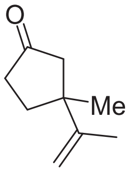
**3a** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1; $R_f$ = 0.21 in pentane / $Et_2O$ = 10:1) gave **3a** in 44% yield as a colourless viscous oil. Product was revealed with anisaldehyde to give brown stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$): δ = 7.35-7.28 (m, 4H), 7.24-7.18 (m, 1H), 5.06 (s, 1H), 4.99 (s, 1H), 2.78 (d, *J* = 15.1 Hz, 1H), 2.62 (d, *J* = 15.1 Hz, 1H), 2.44-2.17 (m, 4H), 1.82-1.73 (m, 2H), 1.44 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$,): δ = 210.9, 148.7, 145.1, 128.5, 126.5, 126.2, 113.5, 52.5, 51.3, 40.8, 32.4, 21.0, 19.6. **EI-MSHR**: $[M]^+$ calculated for: $C_{15}H_{18}O$: 214.13522, found 214.13523. **IR**: ν [cm$^{-1}$] = 2945, 1710, 1447, 1233, 902, 755.

**3,3,5-trimethyl-5-(prop-1-en-2-yl)cyclohexanone (6a)[7]**



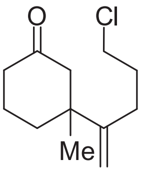
**6a** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 9:1; $R_f$ = 0.38 in Pentane / $Et_2O$ = 7:1) gave **6a** in 77% yield as a colourless oil. Product was revealed with $KMnO_4$ to give yellow stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$, 298 K): δ = 4.85 (s, 1H), 4.76 (s, 1H), 2.74 (d, *J* = 13.7 Hz, 1H), 2.19 (d, *J* = 13.4 Hz, 1H), 2.15-2.12 (m, 2H), 1.97 (d, *J* = 14.3 Hz, 1H), 1.76 (s, 3H), 1.55 (d, *J* = 14.3 Hz, 1H), 1.13 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$): δ = 211.6, 150.9, 111.4, 54.5, 51.3, 47.3, 43.7, 36.1, 33.1, 30.8, 27.5, 19.8.

**3-methyl-3-(prop-1-en-2-yl)cyclopentanone (7a)** [8]



**7a** was prepared according to *General Procedure D*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 10:1; $R_f$ = 0.22 in pentane / $Et_2O$ = 10:1) gave **7a** in 30% yield as a colourless oil. Product was revealed with anisaldehyde to give brown stains. **$^1$H-NMR** (400.13 MHz, $CDCl_3$, 298 K): δ = 4.80-4.75 (m, 1H), 4.73-4.68 (m, 1H), 2.41 (dd, *J* = 17.6, 4.1 Hz, 1H), 2.34-2.24 (m, 2H), 2.17-1.98 (m, 2H), 1.93-1.81 (m, 1H), 1.77 (s, 3H), 1.17 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$, 298 K): δ = 219.0, 150.5, 109.5, 51.2, 44.8, 36.6, 33.7, 25.6, 19.5. **IR**: ν [cm$^{-1}$] = 2923, 1703, 1457, 1164, 893.

**3-(5-chloropent-1-en-2-yl)-3-methylcyclohexanone (1e)[9]**



**1e** was prepared according to *General Procedure E*. Purification of the crude mixture by flash chromatography on silica gel (Pentane / $Et_2O$ = 8:1; $R_f$ = 0162 in pentane / $Et_2O$ = 10:1) gave **1e** in 67% yield as a brownish viscous oil. Product was revealed with anisaldehyde to give brown stains which later on turned pink. **$^1$H-NMR** (400.13 MHz, $CDCl_3$, 298 K): δ = 4.92 (s, 1H), 4.86 (s, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.61 (d, *J* = 14.2 Hz, 1H), 2.36 – 2.22 (m, 3H), 2.18 – 2.10 (m, 2H), 2.02 – 1.80 (m, 4H), 1.77 – 1.58 (m, 2H), 1.10 (s, 3H). **$^{13}$C-NMR** (100.61 MHz, $CDCl_3$, 298 K): δ = 211.4, 152.5, 110.3, 52.6, 44.8, 44.3, 40.7, 34.8, 31.7, 27.6, 26.7, 21.8.

Cyclization of **1e** to yield cis-decaline derivative is described in ref. 9.

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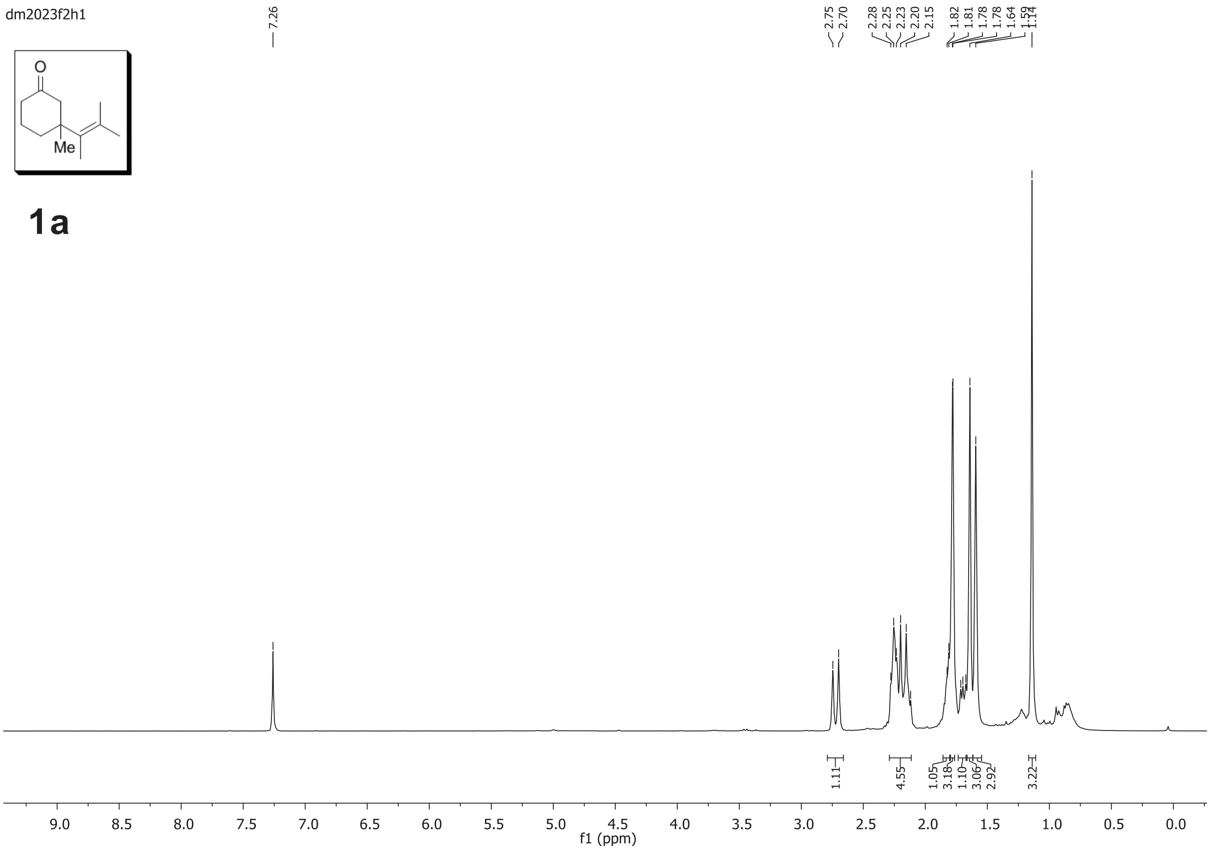
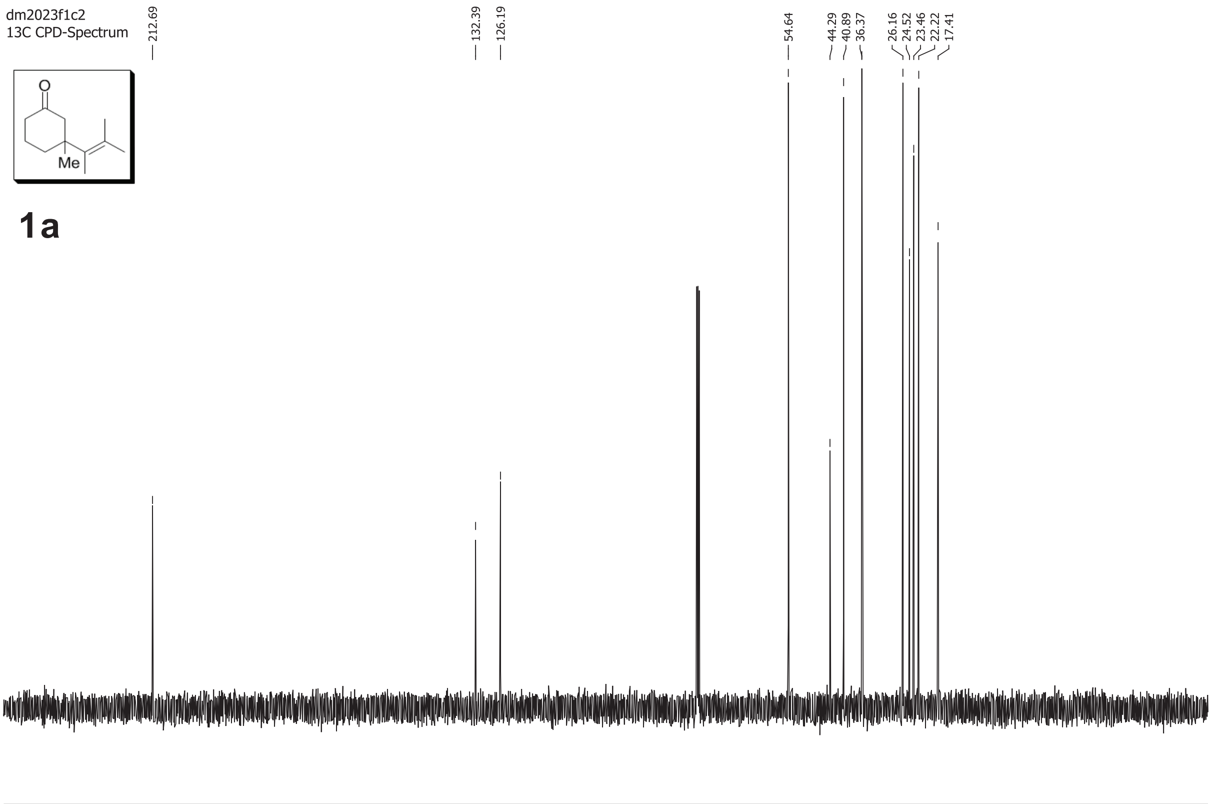
[9] E. Piers, B. W. A. Yeung, F. F. Fleming, *Can. J. Chem.* **1993**, *71*, 280-286.

## ■ NMR-data



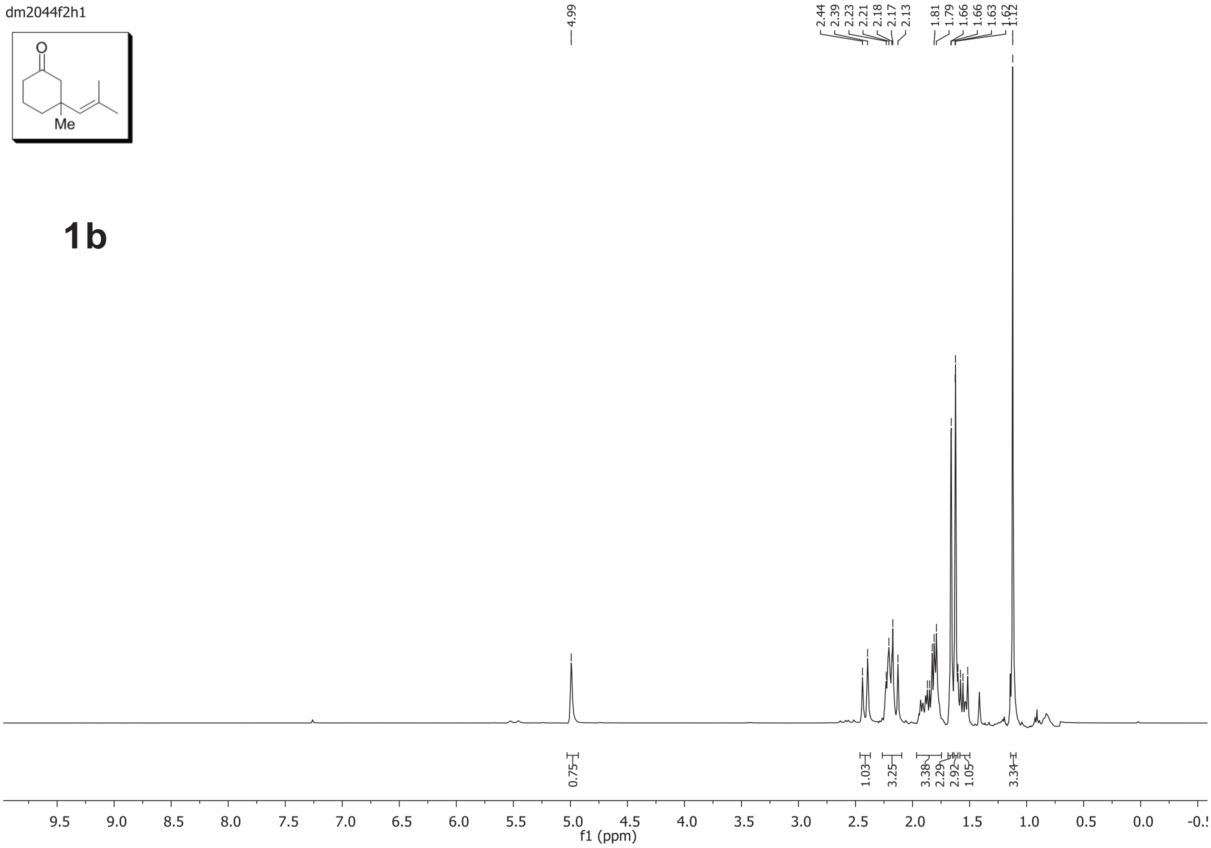
**1a**



**1a**

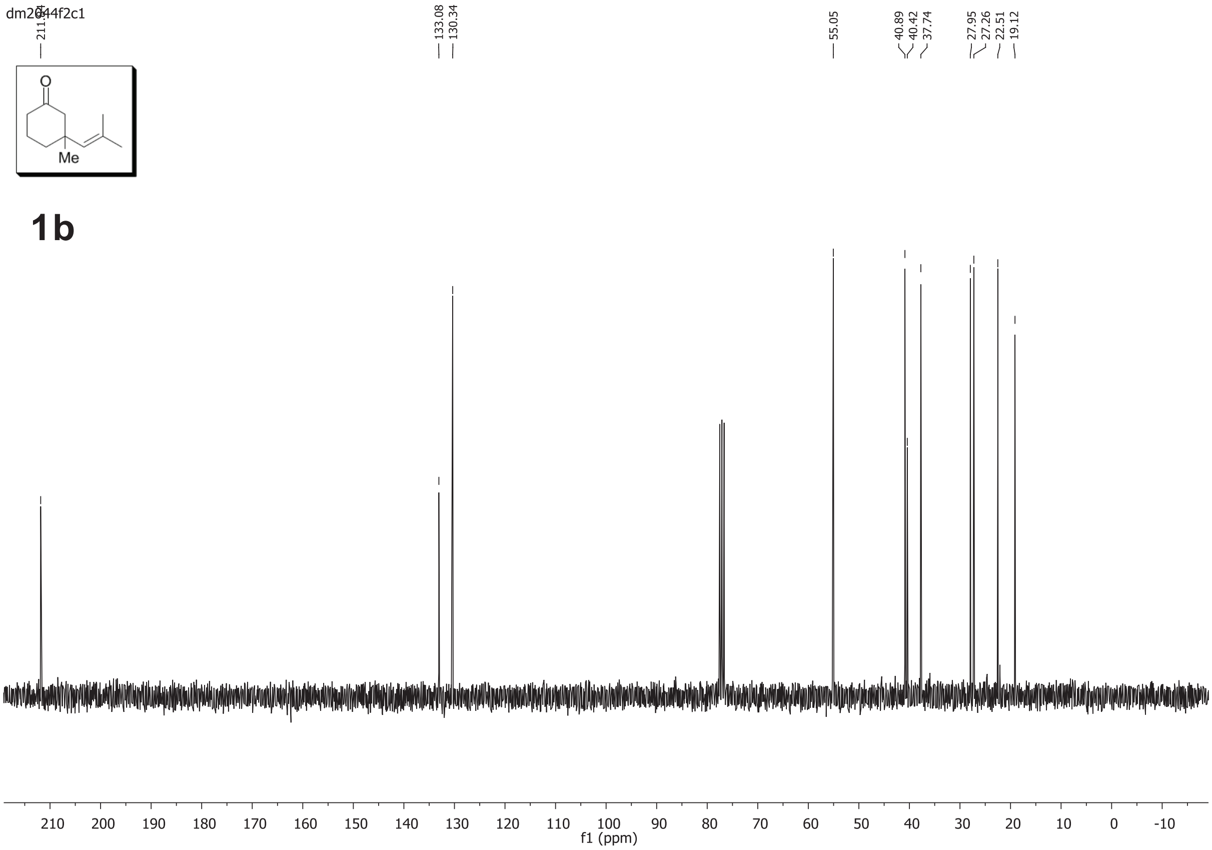
dm2044f2h1

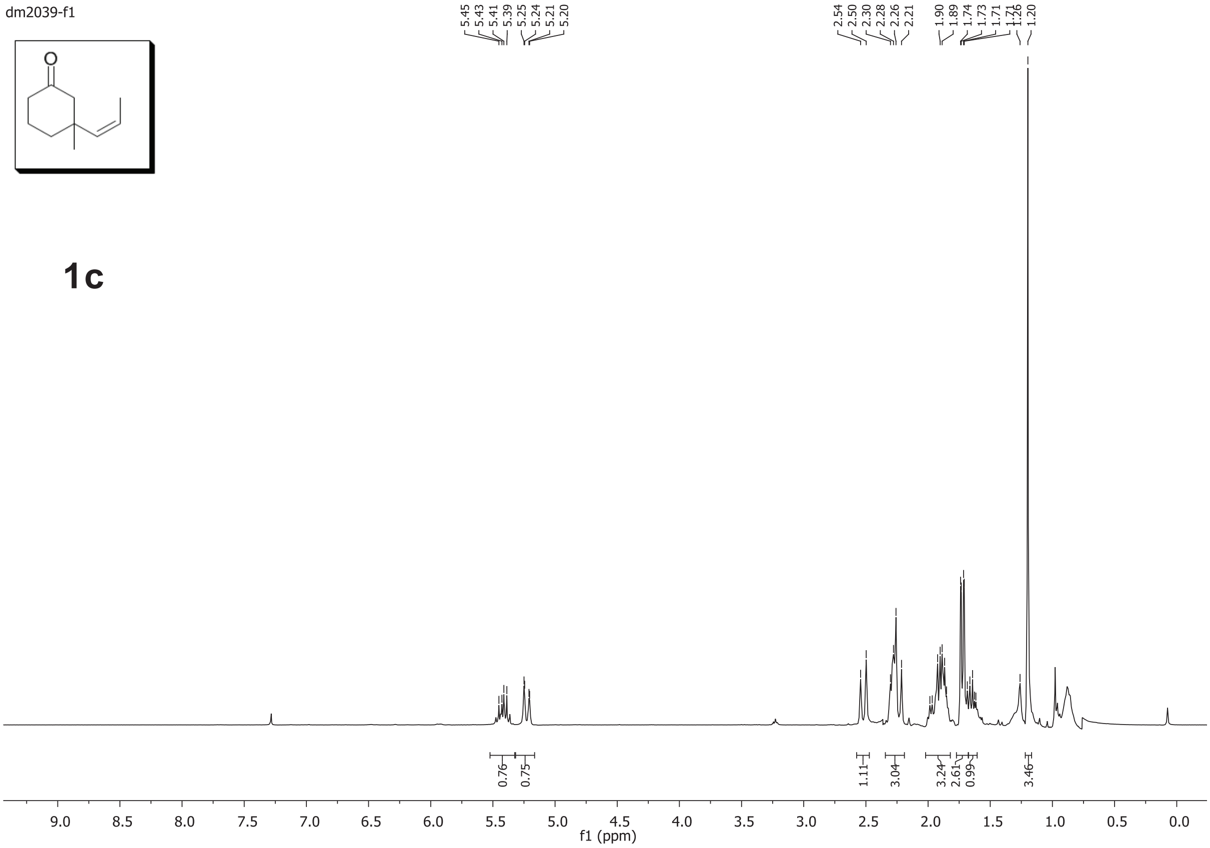
**1b**



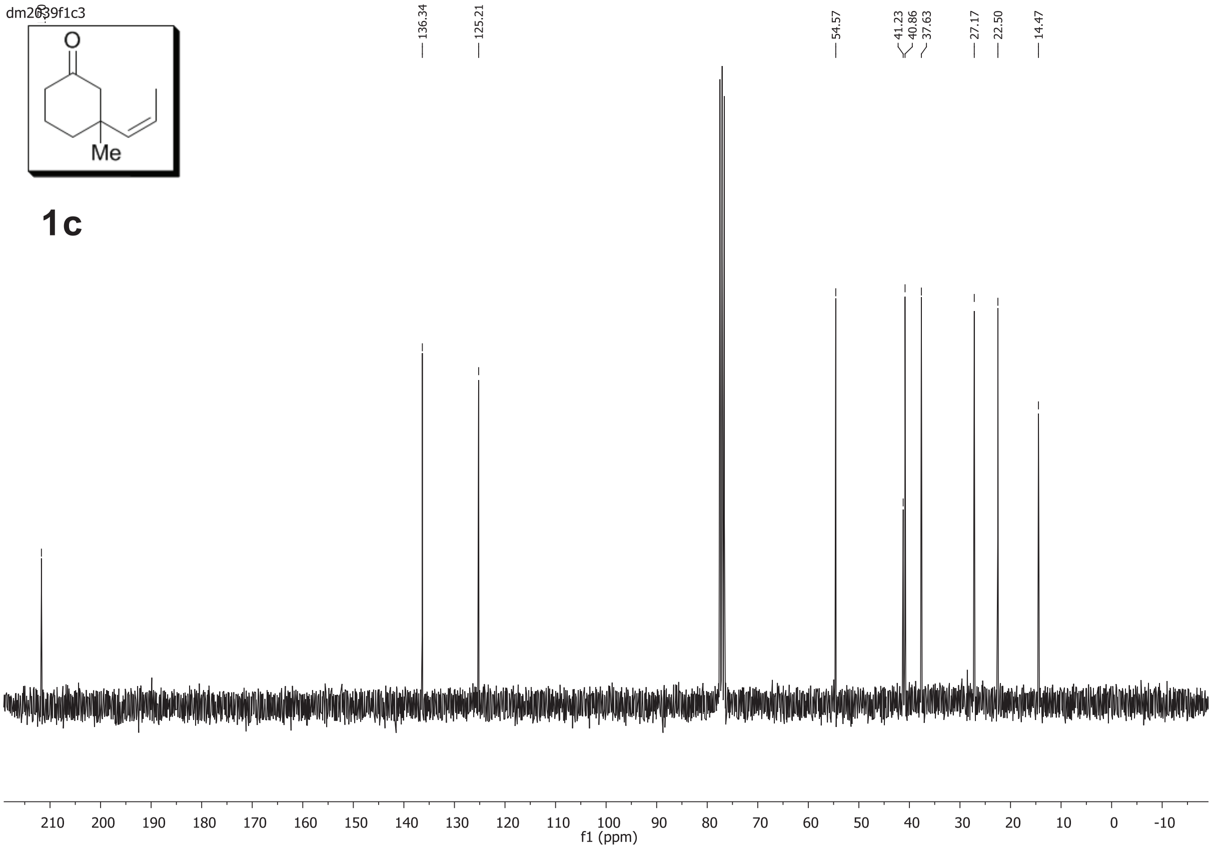
dm2044f2c1

**1b**

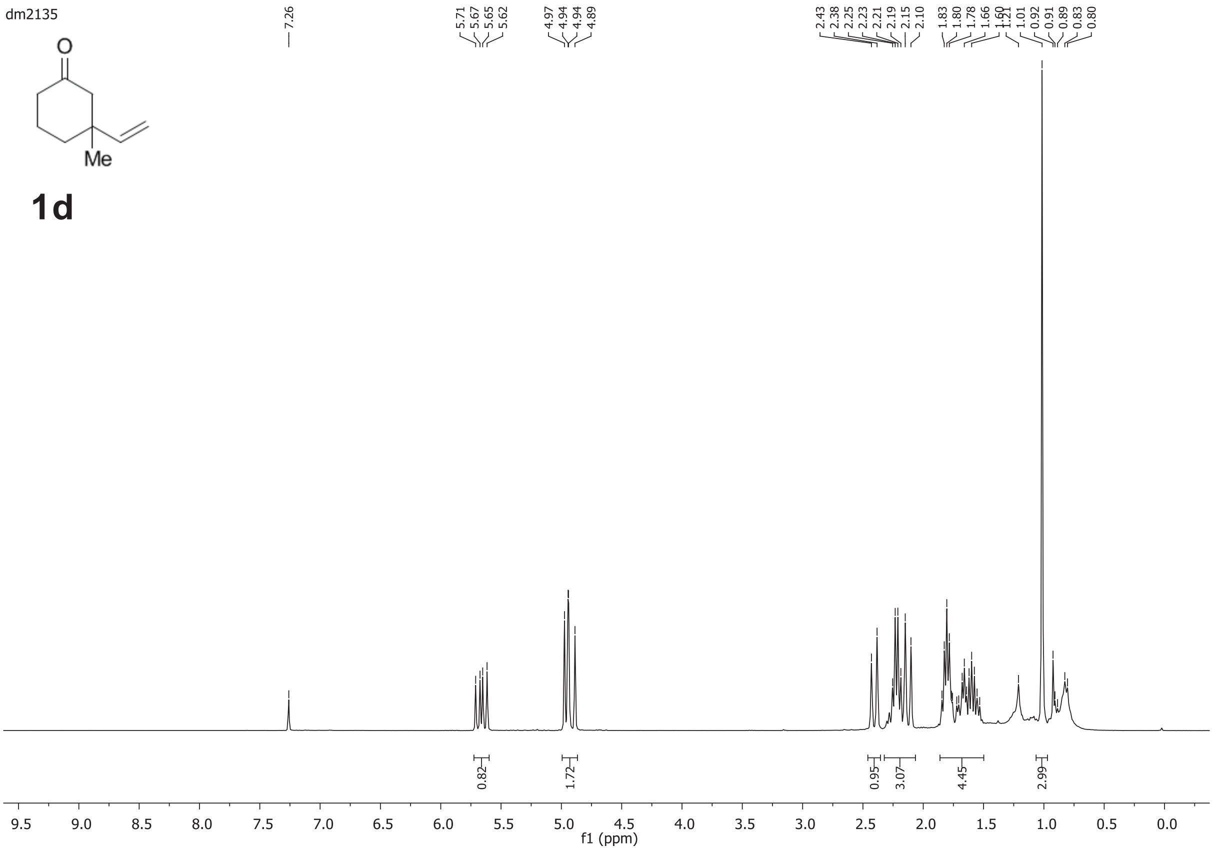



dm2039-f1
5.45
5.43
5.41
5.39
5.25
5.24
5.21
5.20
2.54
2.50
2.30
2.28
2.26
2.21
1.90
1.89
1.74
1.73
1.71
1.71
1.26
1.20
O
0.76
0.75
1.11
3.04
3.24
2.61
0.99
3.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

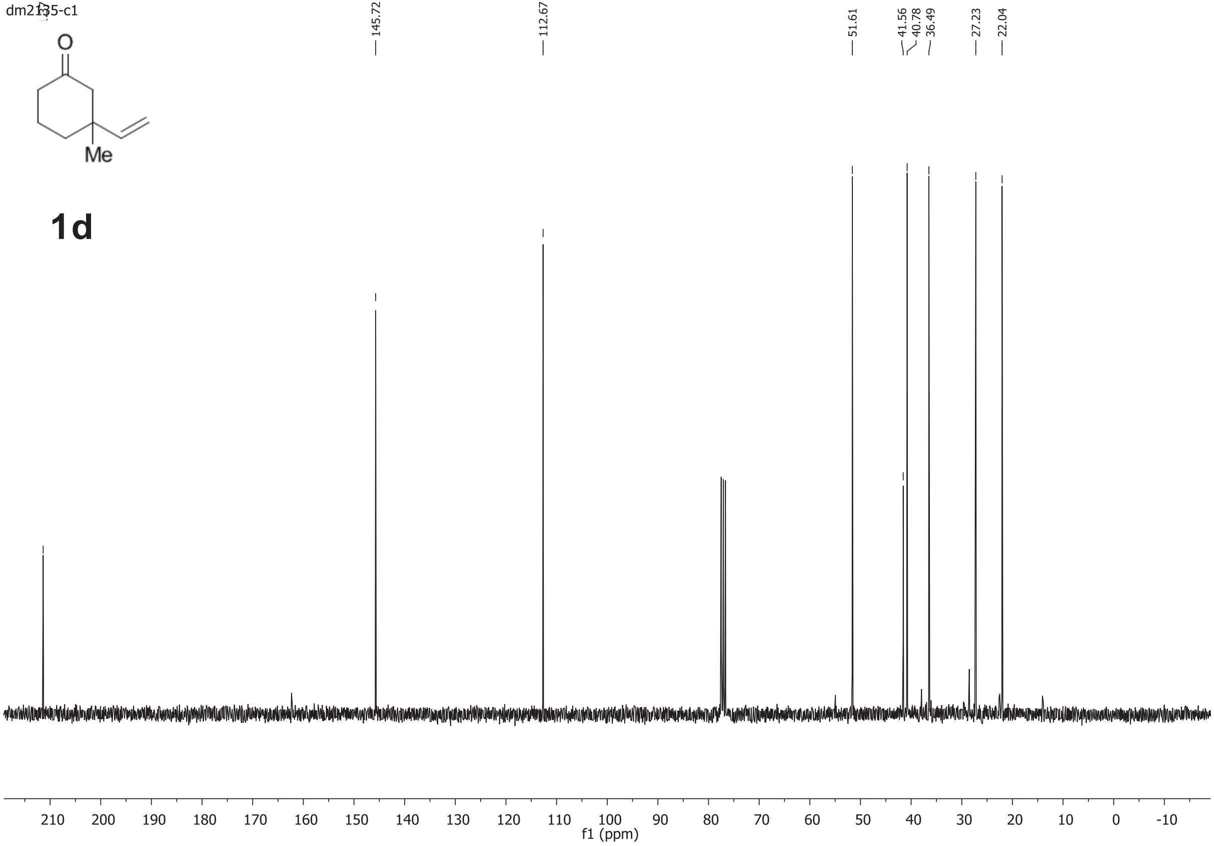
**1c**


dm2039f1c3
136.34
125.21
54.57
41.23
40.86
37.63
27.17
22.50
14.47
O
Me
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)

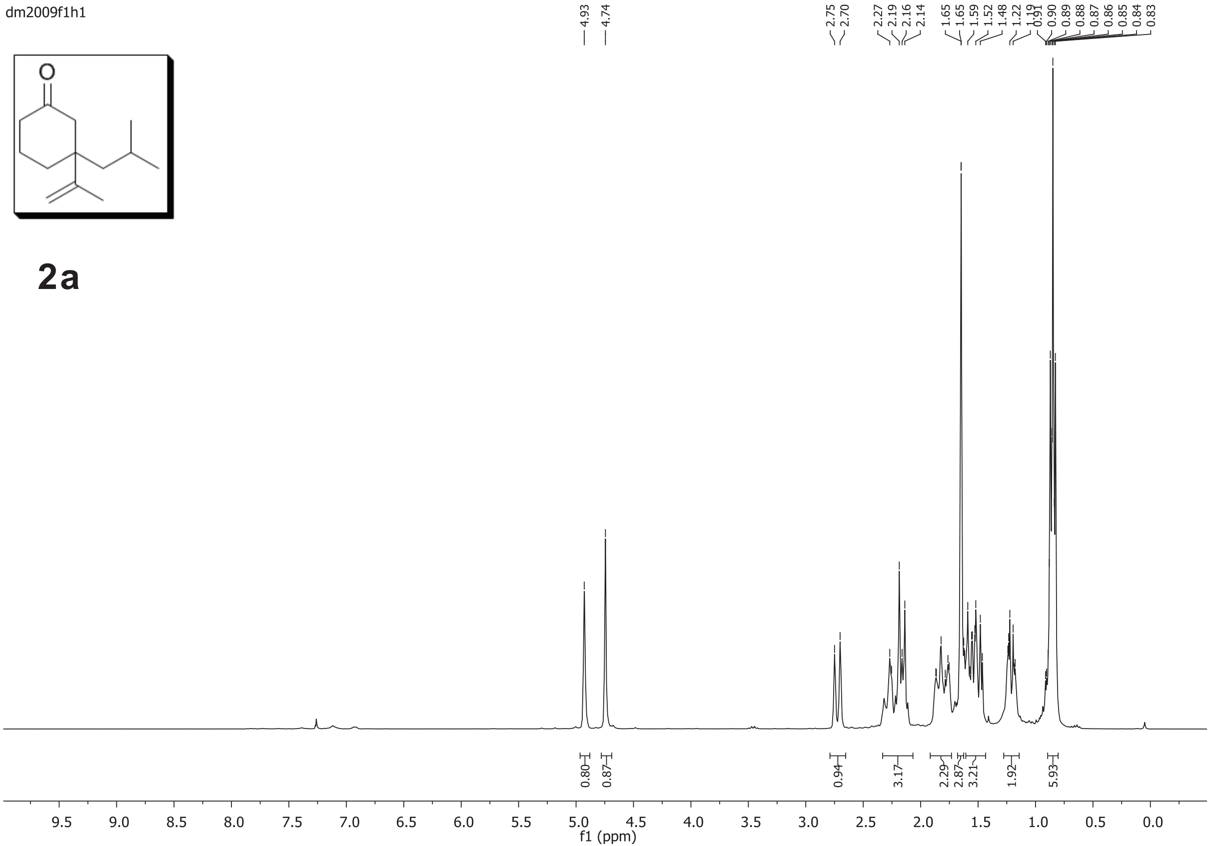
**1c**

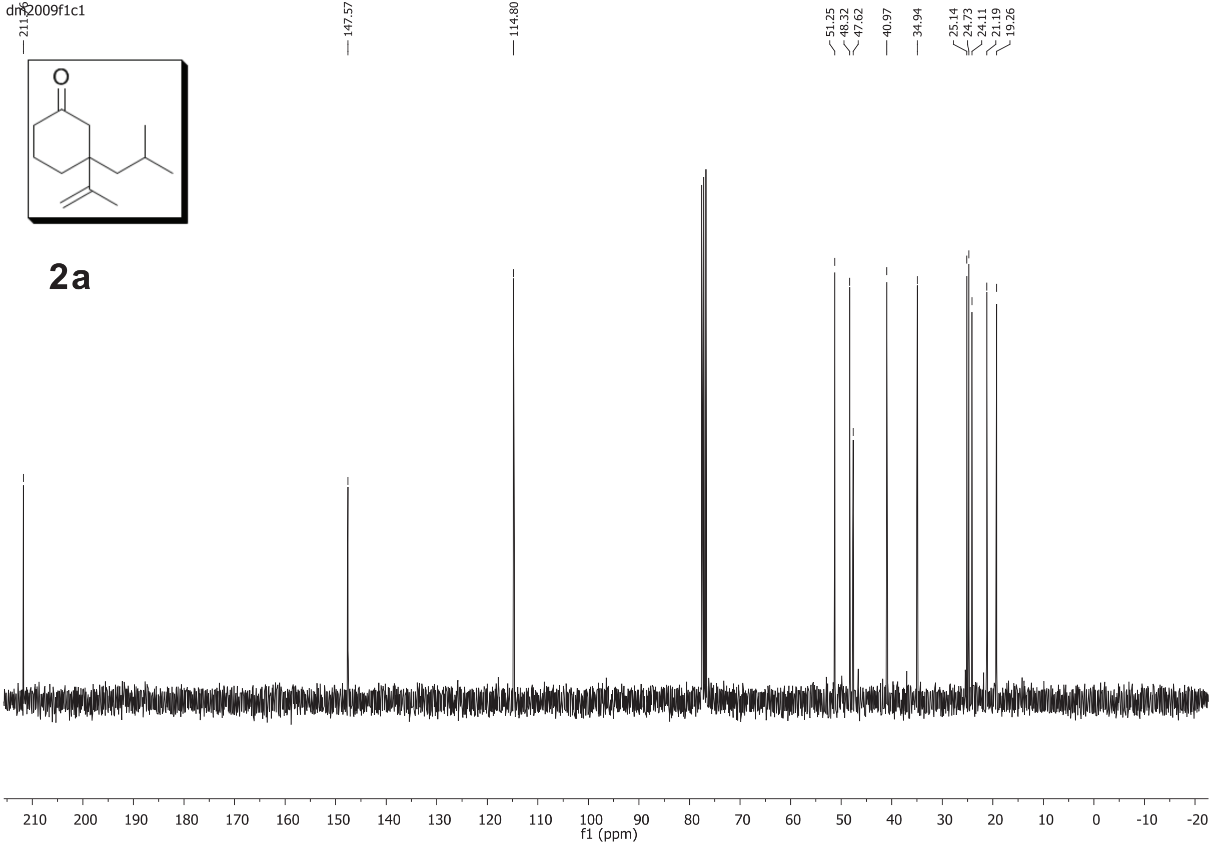

dm2135
O
Me
7.26
5.71
5.67
5.65
5.62
4.97
4.94
4.94
4.89
2.43
2.38
2.25
2.23
2.21
2.19
2.15
2.10
1.83
1.80
1.78
1.66
1.60
1.21
1.01
0.92
0.91
0.89
0.83
0.80
0.82
1.72
0.95
3.07
4.45
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

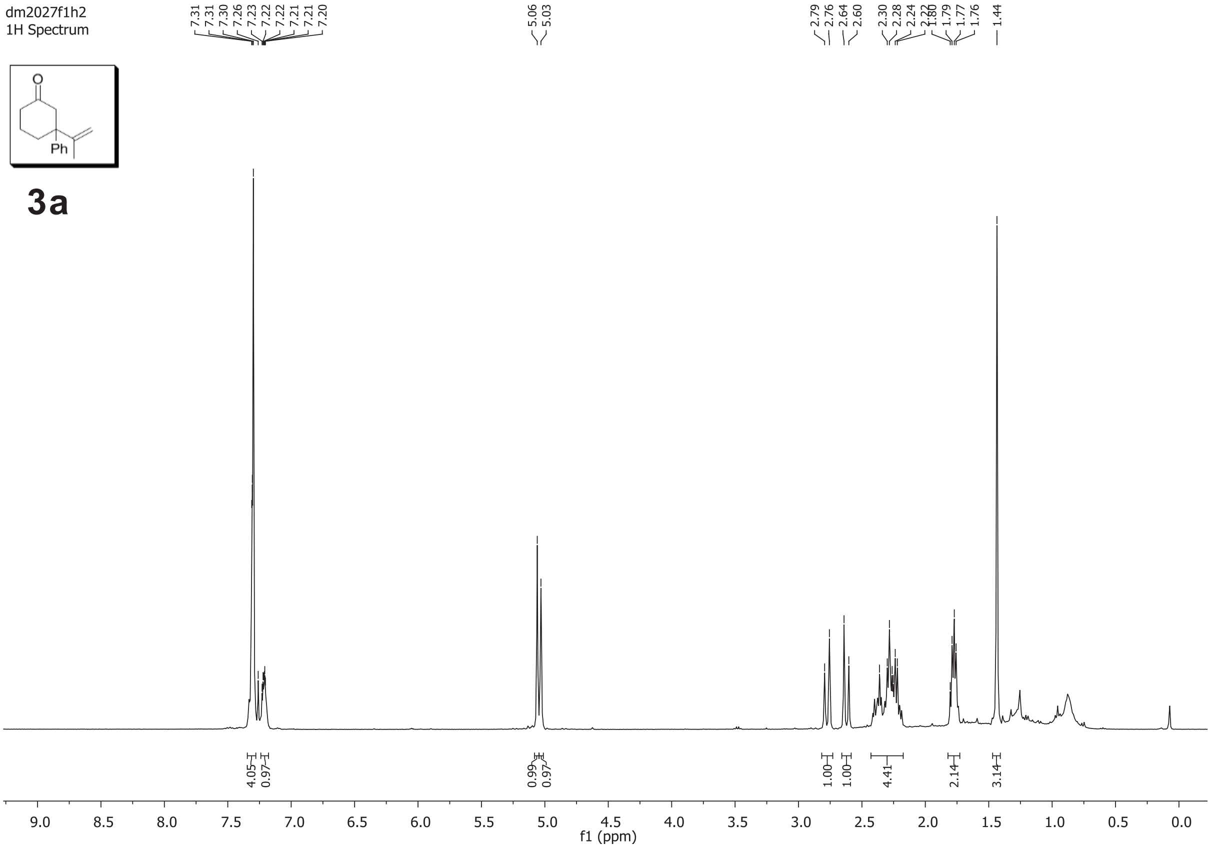
**1d**


dm2135-c1
O
Me
145.72
112.67
51.61
41.56
40.78
36.49
27.23
22.04
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)

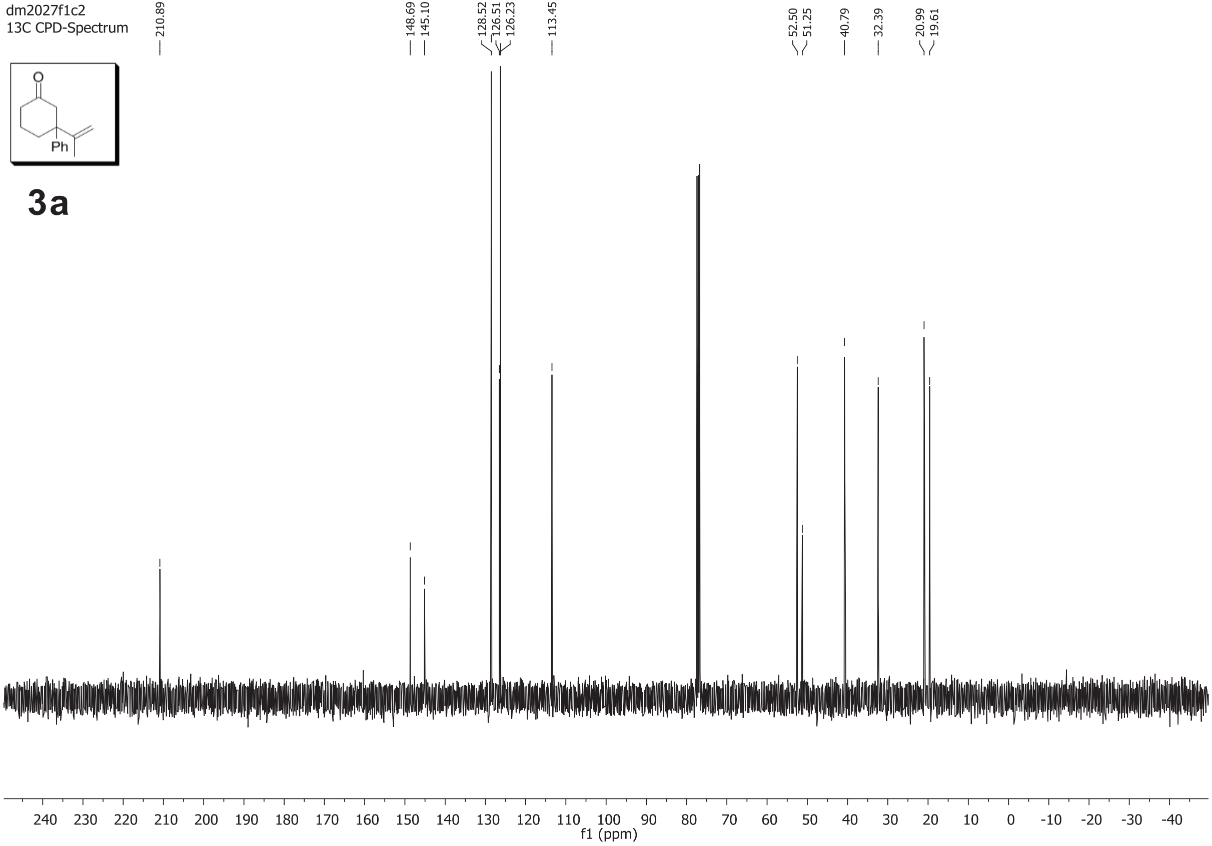
**1d**


dm2009f1h1
2a
4.93
4.74
2.75
2.70
2.27
2.19
2.16
2.14
1.65
1.65
1.59
1.52
1.48
1.22
1.19
0.91
0.90
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.80
0.87
0.94
3.17
2.29
2.87
3.21
1.92
5.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

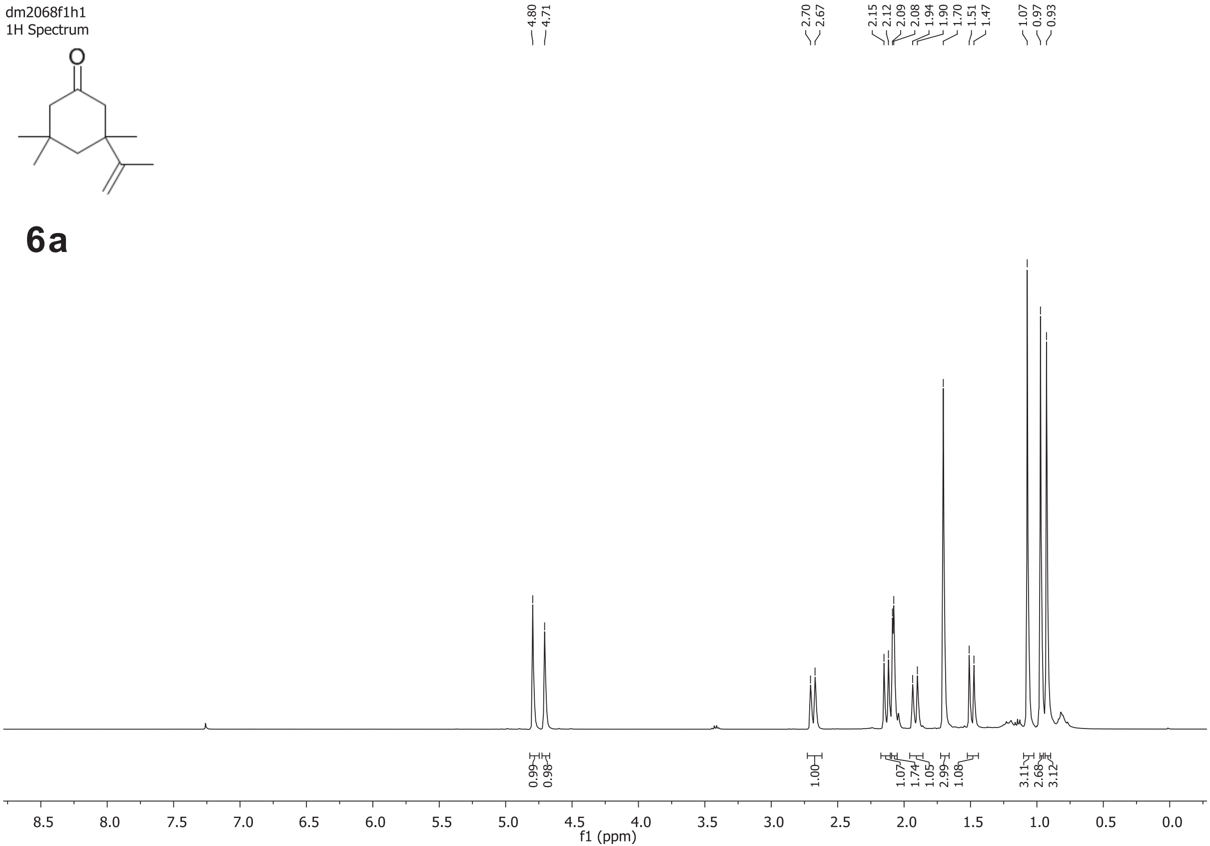

dm2009f1c1
2a
211.[illegible]6
147.57
114.80
51.25
48.32
47.62
40.97
34.94
25.14
24.73
24.11
21.19
19.26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

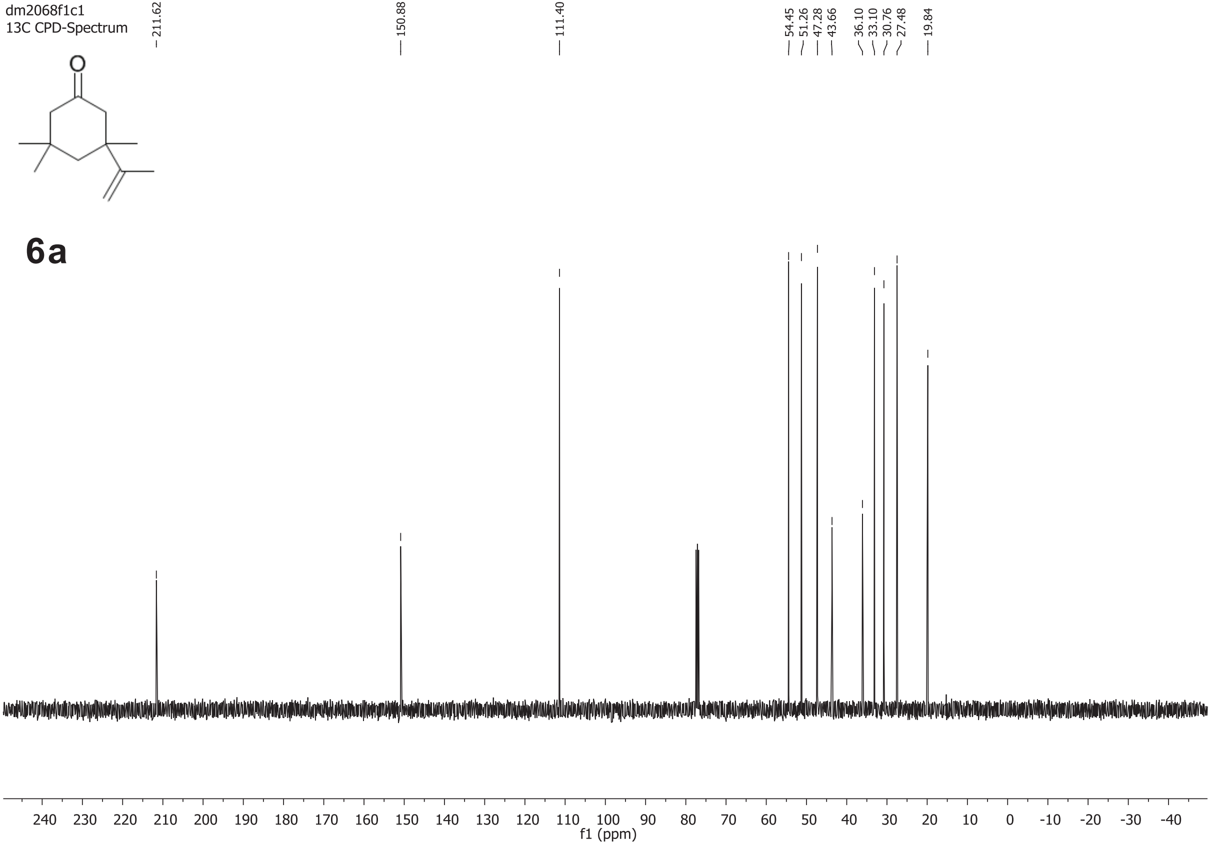

dm2027f1h2
1H Spectrum
O
Ph
7.31
7.31
7.30
7.26
7.23
7.22
7.22
7.21
7.21
7.20
5.06
5.03
2.79
2.76
2.64
2.60
2.30
2.28
2.24
2.22
1.80
1.79
1.77
1.76
1.44
4.05
0.97
0.99
0.97
1.00
1.00
4.41
2.14
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

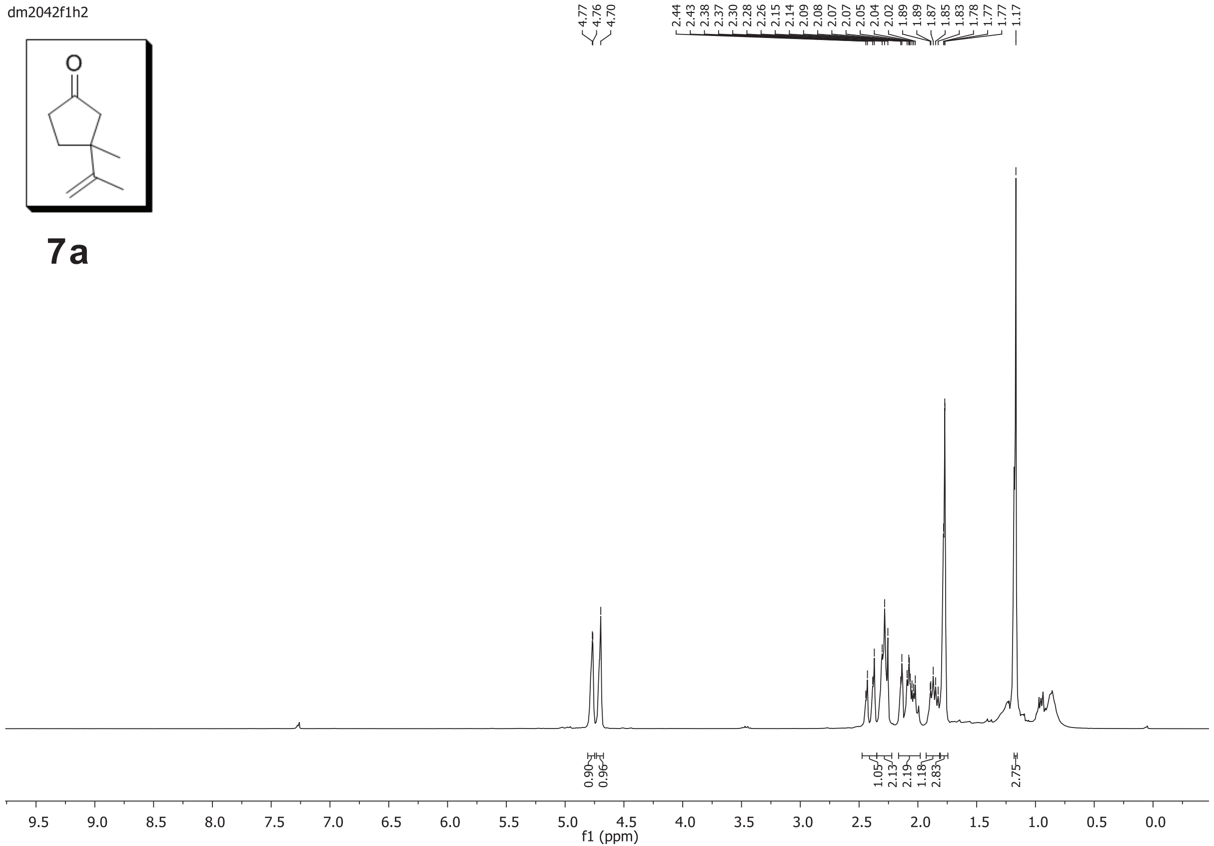
**3a**

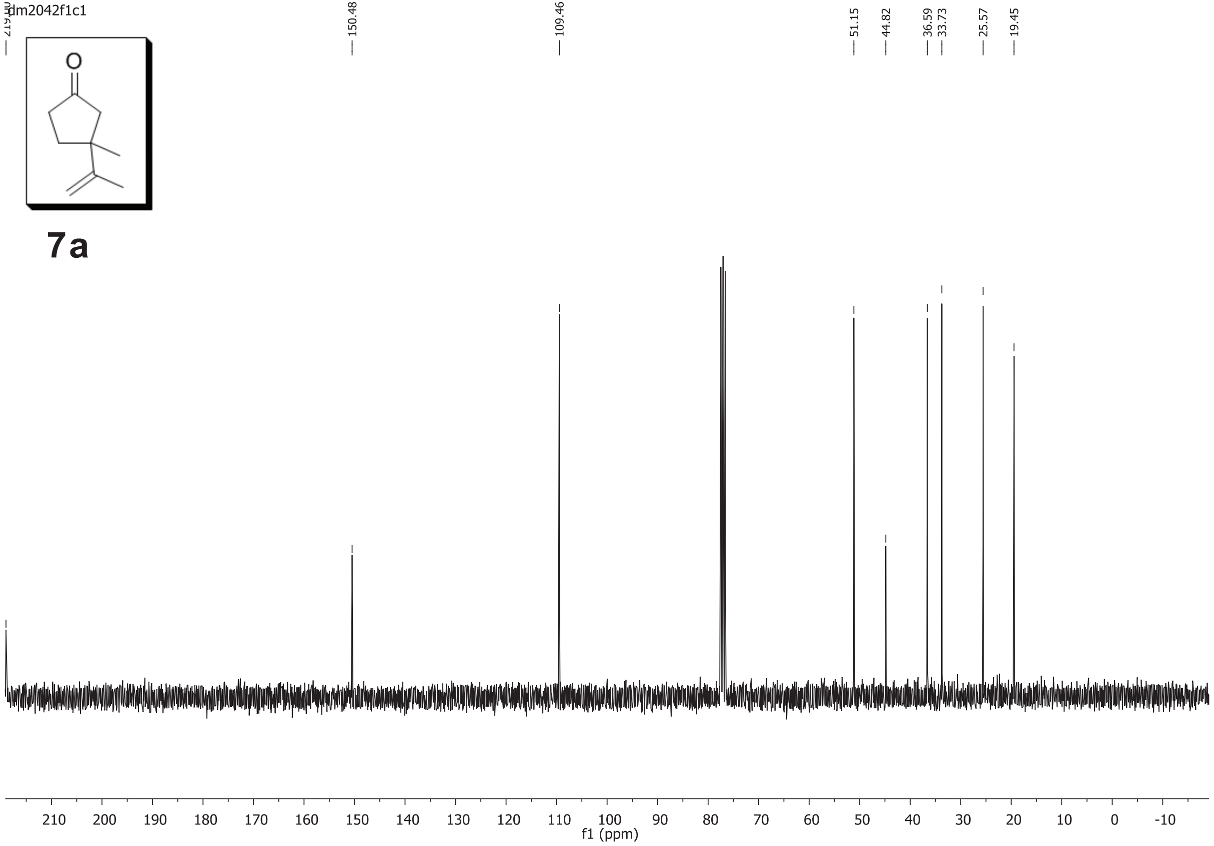

dm2027f1c2
13C CPD-Spectrum
O
Ph
210.89
148.69
145.10
128.52
126.51
126.23
113.45
52.50
51.25
40.79
32.39
20.99
19.61
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

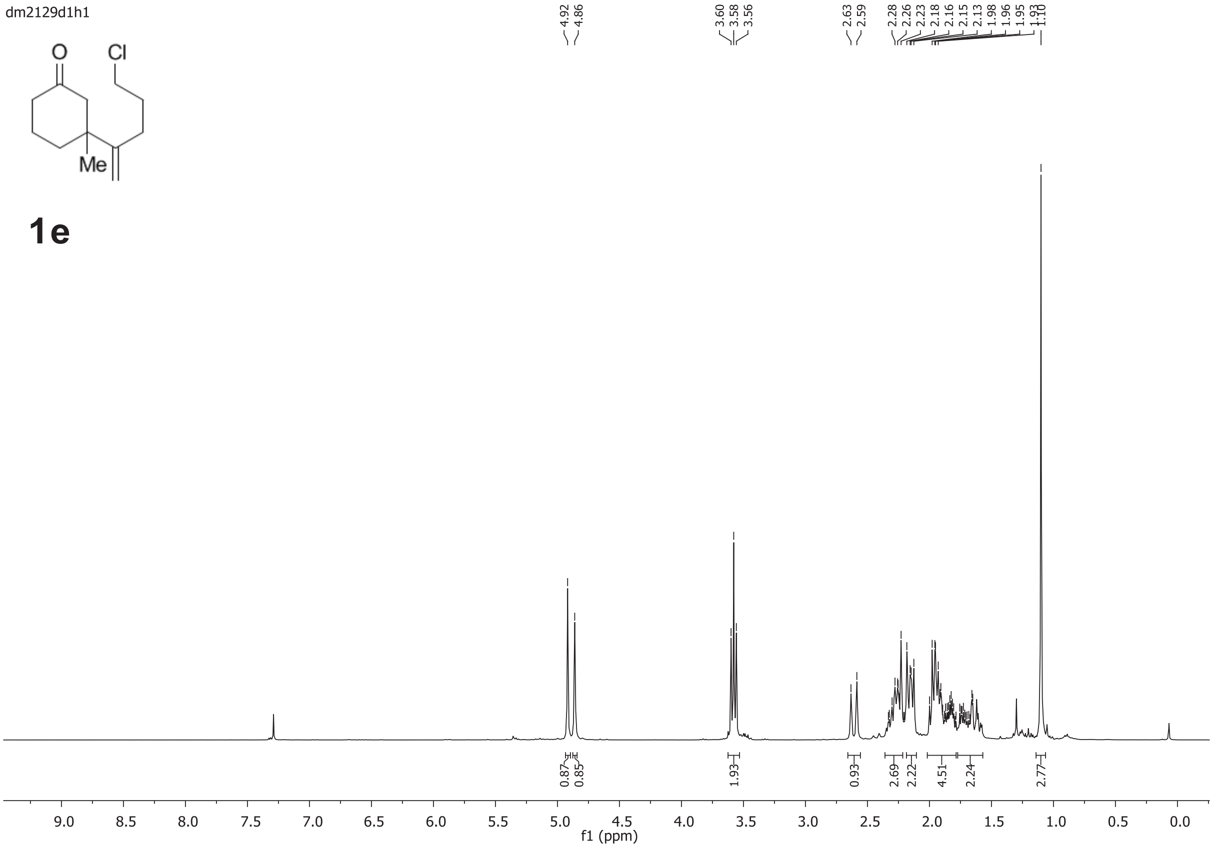
**3a**


dm2068f1h1
1H Spectrum
6a
4.80
4.71
2.70
2.67
2.15
2.12
2.09
2.08
1.94
1.90
1.70
1.51
1.47
1.07
0.97
0.93
0.99
0.98
1.00
1.07
1.74
1.05
2.99
1.08
3.11
2.68
3.12
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)


dm2068f1c1
13C CPD-Spectrum
6a
211.62
150.88
111.40
54.45
51.26
47.28
43.66
36.10
33.10
30.76
27.48
19.84
240
230
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
-40
f1 (ppm)

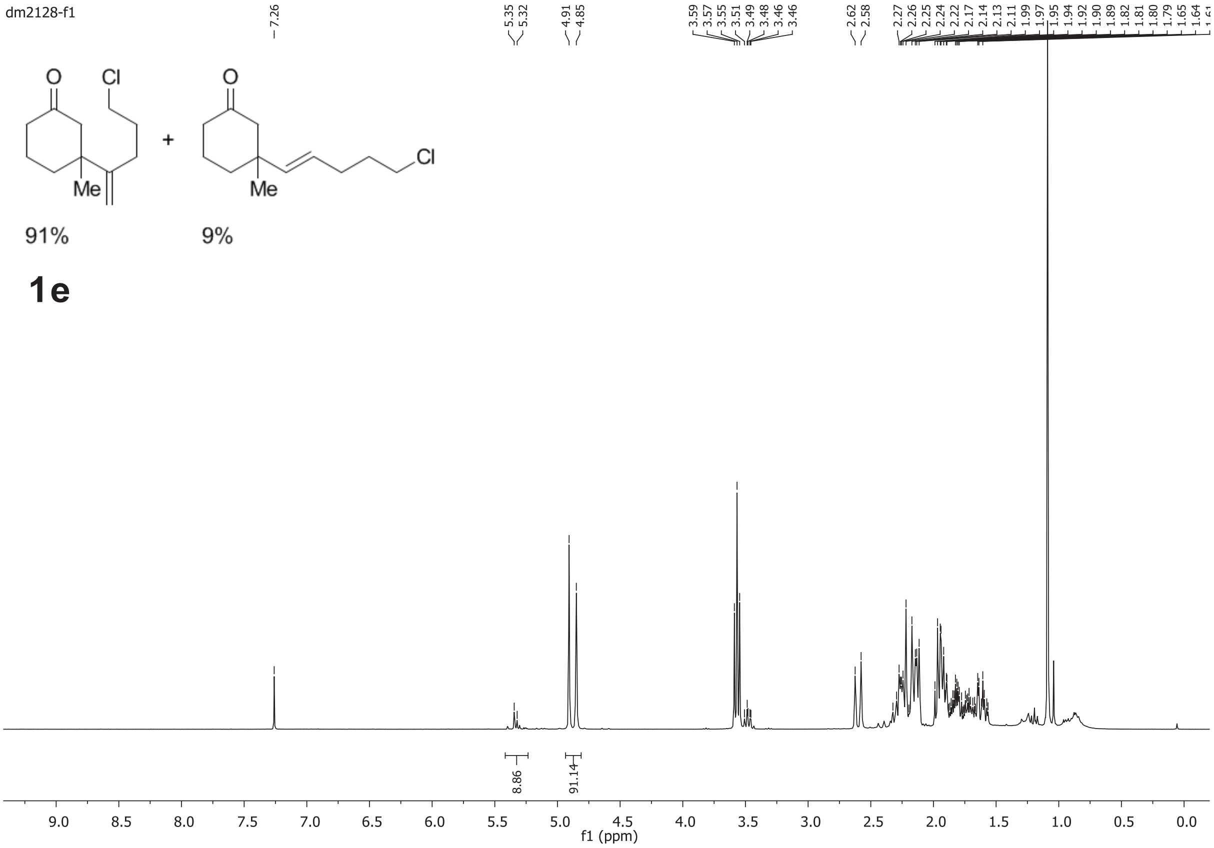

dm2042f1h2
7a
4.77
4.76
4.70
2.44
2.43
2.38
2.37
2.30
2.28
2.26
2.15
2.14
2.09
2.08
2.07
2.07
2.05
2.04
2.02
1.89
1.89
1.87
1.85
1.83
1.78
1.77
1.77
1.17
0.90
0.96
1.05
2.13
2.19
1.18
2.83
2.75
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


dm2042f1c1
7a
219.1
150.48
109.46
51.15
44.82
36.59
33.73
25.57
19.45
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)



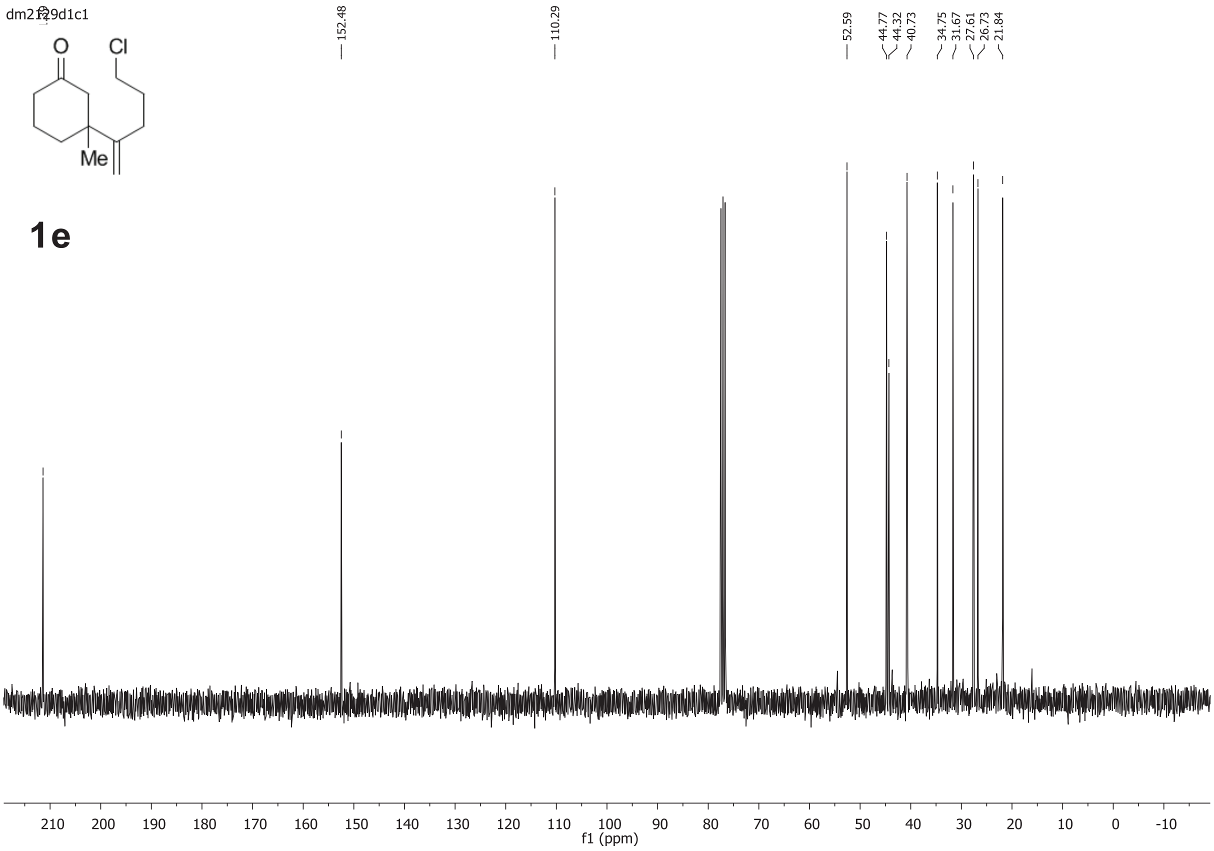
**1e**

(Product obtained according to Weiss conditions with alanate **A8**; Table 4, Entry 10)



**1e**

(Product obtained by Cu-catalyzed conjuagate addition with alanate **A7**; Table 4, Entry 7)


dm2129d1c1
O
Cl
Me
1e
152.48
110.29
52.59
44.77
44.32
40.73
34.75
31.67
27.61
26.73
21.84
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)