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Supporting Information

Titanocene-Catalyzed [2+2] Cycloaddition of Bisenones and Comparison with Photoredox Catalysis and Established Methods

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1. General Information

All reactions involving air or moisture sensitive compounds were carried out in oven-dried glassware under argon using standard Schlenk and vacuum line technique. All solvents were either dried and deoxygenated by distillation (THF over K) before use or purified inside an M-Braun MB-SPS-800 solvent purification system. All reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 plates using UV light as visualizing agent (if applicable), or a solution of ammoniummolybdate tetrahydrate (12.5 g) and $Ce(SO_4)_2 \bullet 4H_2O$ (5 g) and conc. H_2SO_4 (16 mL) in distilled water (450 mL) or a solution of ammonium molybdate (12 g), ceric ammonium molybdate (0.5 g) and conc. sulfuric acid (15 mL) in distilled water (235 mL) followed by heating as developing agents. Products were purified by flash column chromatography on Merck silica gel 50 or Macherey-Nagel silica gel 60. ^1H NMR and ^{13}C NMR spectra were measured on Bruker AMX 300 MHz or Bruker 400 MHz or 500 MHz spectrometers. ^1H NMR chemical shift were given in ppm, and calibrated by using the residual undeuterated solvent as internal reference ($CHCl_3$ (7.26 ppm), CD_2Cl_2 (5.32 ppm)). ^{13}C NMR chemical shift were recorded in ppm and the solvent peak was employed as internal reference ($CDCl_3$ (77.00 ppm), CD_2Cl_2 (54.00 ppm)). IR spectra were measured on an ATR-IR-Spectrometer Nicolet TM 380 instrument as neat film. High-resolution mass spectra analysis data were obtained on a Thermoquest MAT 95 XL instrument. COSY, NOESY, HSQC, HMBC were used to identify the relative configuration.

2. General Procedure for the [2+2]-Cycloaddition of Bisenones (GP 1).

To a heat-dried Schlenk tube bisenone (0.25 mmol, 1 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zinc (5.0 mg, 0.075 mmol, 15 mol%) and 5 mL dioxane are added under argon atmosphere. The mixture is then stirred rapidly at 65 or 80 °C for 8-24h. After TCL indicates the substrate was completely consumed, the solvent of the resulting mixture is concentrated under vacuum and the residue is purified by flash column chromatography on silica gel affording pure product. Alternatively, the mixture is directly filtered through a silica plug and flushed with ethyl acetate or dichloromethane. After removal of solvent, the residue is washed with pentane and diethyl ether to afford pure product.

3. Synthesis of Ti Catalysts.

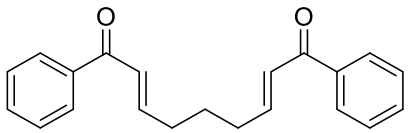
$Cp_2Ti(OMs)_2$, $Cp_2Ti(OTs)_2$, $Cp_2Ti(TFA)_2$ are synthesized according to the procedure described in the literature.[1]

Cp_2TiCl_2, Cp^*TiCl_3 methyl glycolate, *n*-octyl glycolate and 2-decyloxirane are commercially available and directly used without further purification.

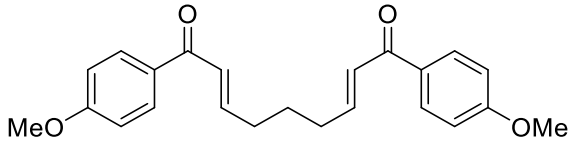
4. Synthesis of Triphenyl Phosphonium Ylide.

All triphenyl phosphonium ylides used in this paper are synthesized according to the procedures described in the literature.[2]

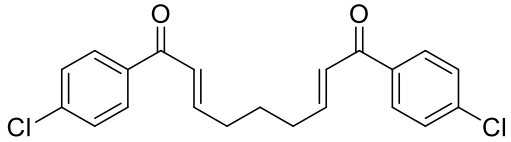
5. Synthesis of Substrates.



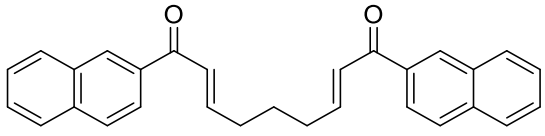
(2*E*,7*E*)-1,9-diphenylnona-2,7-diene-1,9-dione (1a) is synthesized according to the procedure described in the literature.[3]



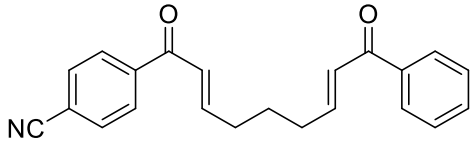
(2*E*,7*E*)-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione (1b) is synthesized according to the procedure described in the literature.[4]



(2*E*,7*E*)-1,9-bis(4-chlorophenyl)nona-2,7-diene-1,9-dione (1c) is synthesized according to the procedure described in the literature.[3]



(2*E*,7*E*)-1,9-di(naphthalen-2-yl)nona-2,7-diene-1,9-dione (1d) is synthesized according to the procedure described in the literature.[5]



4-((2*E*,7*E*)-9-oxo-9-phenylnona-2,7-dienoyl)benzonitrile (1e).

(*E*)-4-(7-oxohept-2-enoyl)benzonitrile (680 mg, 3.00 mmol, 1.00 eq.) was dissolved in CH_2Cl_2

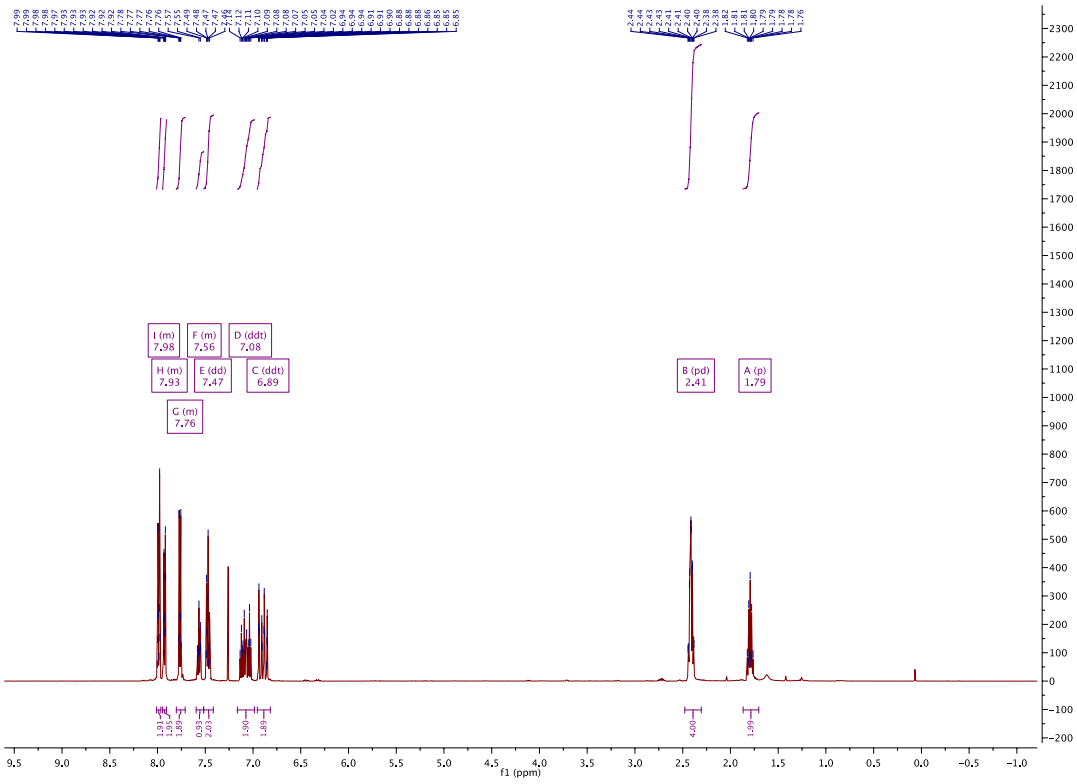
(5 mL) and treated with 1-phenyl-2-(triphenylphosphaneylidene)ethan-1-one (1.71 g, 4.50 mmol, 1.50 eq.). The reaction was stirred at room temperature for 2 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1e** as colorless liquid (542 mg, 1.65 mmol, 55%).

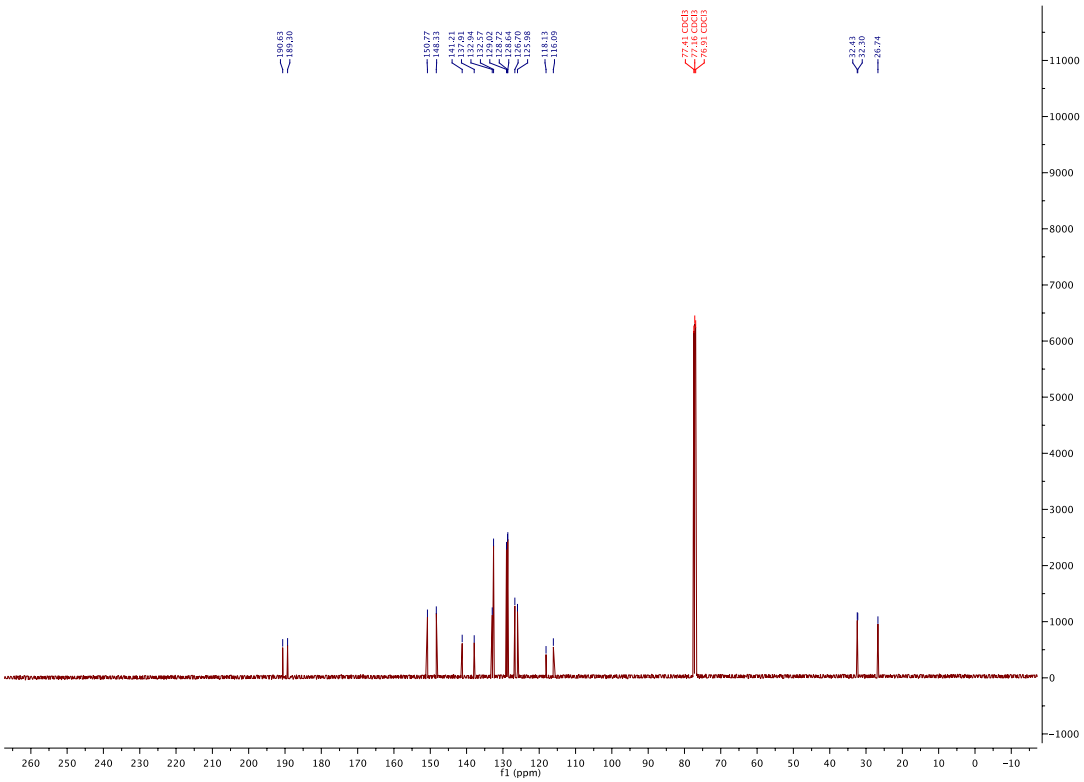
IR 2933, 2229, 1733, 1668, 1617, 1446, 1291, 1219, 1043, 968, 828, 693, 660, 543.

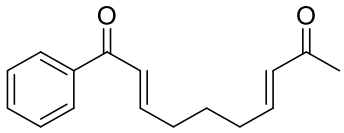
^{1}H NMR (499 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.95 – 7.91 (m, 2H), 7.80 – 7.71 (m, 2H), 7.60 – 7.52 (m, 1H), 7.47 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.08 (ddt, *J* = 27.0, 15.4, 6.9 Hz, 2H), 6.89 (ddt, *J* = 28.2, 15.4, 1.5 Hz, 2H), 2.41 (pd, *J* = 7.3, 1.5 Hz, 4H), 1.79 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.63, 189.30, 150.77, 148.33, 141.21, 137.91, 132.94, 132.57, 129.02, 128.72, 128.64, 126.70, 125.98, 118.13, 116.09, 32.43, 32.30, 26.74.

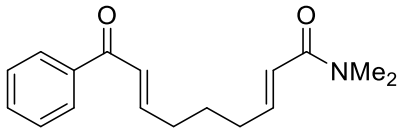
HRMS (ESI) calculated for $C_{22}H_{19}NO_2H$ $[M+H]^+$:330.1416, found 330.1489.







(2*E*,7*E*)-1-phenyldeca-2,7-diene-1,9-dione (1g) is synthesized according to the procedure described in the literature.[6]



(2*E*,7*E*)-*N*,*N*-dimethyl-9-oxo-9-phenylnona-2,7-dienamide (1h) is synthesized according to the procedure in the literature.[10]

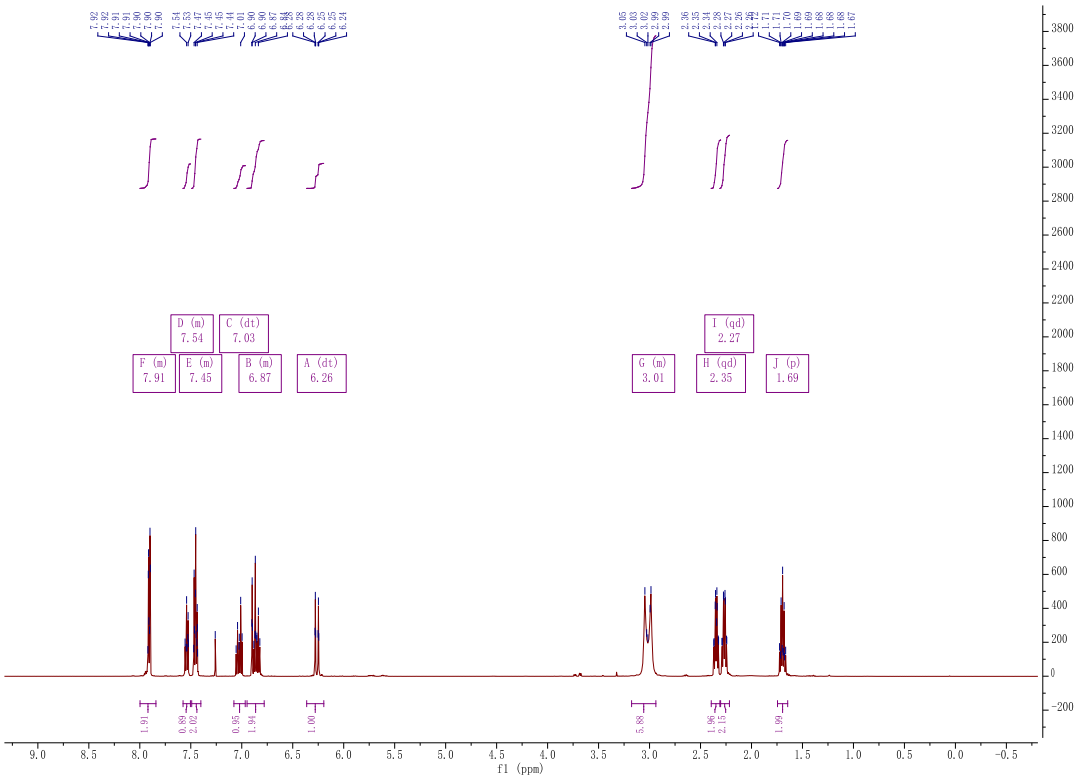
(*E*)-7-*oxo*-7-phenylhept-5-enal (242 mg, 1.20 mmol, 1.00 eq.) was dissolved in $CHCl_3$ (1.7 mL) and treated with [(dimethylcarbamoyl)methyl]triphenylphosphonium chloride (540 mg, 1.40 mmol, 1.20 eq.). Sodium hydroxide (1.0 M in water, 1.7 mL, 1.7 mmol, 1.4 eq.) was added dropwise to the stirring solution. After 20 min, the organic layer was separated, dried over $NaSO_4$, and concentrated by rotary evaporation. The residue was purified by chromatography (2:1 EtOAc:hexanes eluent) to afford **1h** (0.18 g, 0.95 mmol, 56%) as yellow liquid.

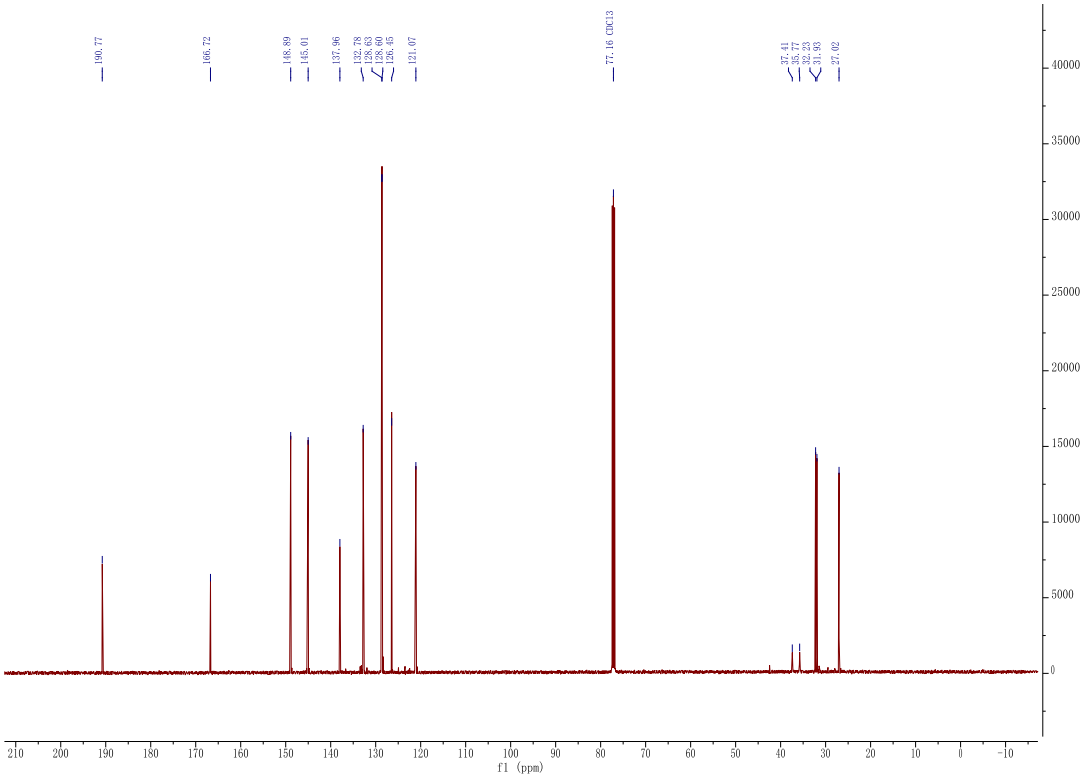
IR 2930, 1660, 1615, 1393, 1225, 1141, 976, 693, 540.

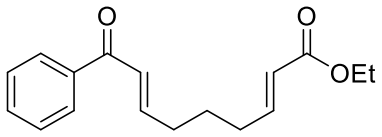
^{1}H NMR (499 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.40 (m, 2H), 7.03 (dt, *J* = 15.4, 6.9 Hz, 1H), 6.95 – 6.78 (m, 2H), 6.26 (dt, *J* = 15.1, 1.5 Hz, 1H), 3.18 – 2.94 (m, 6H), 2.35 (qd, *J* = 7.0, 1.4 Hz, 2H), 2.27 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.69 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.77, 166.72, 148.89, 145.01, 137.96, 132.78, 128.63, 128.60, 126.45, 121.07, 37.41, 35.77, 32.23, 31.93, 27.02.

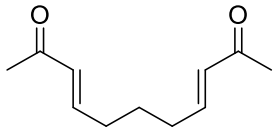
HRMS (ESI) calculated for $C_{17}H_{21}NO_2H$ $[M+H]^+$:272.1572, found 272.1645



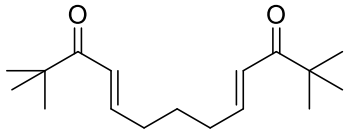




Ethyl (2*E*,7*E*)-9-oxo-9-phenylnona-2,7-dienoate (1i) is synthesized according to the procedure described in the literature.[6]



(3*E*,8*E*)-undeca-3,8-diene-2,10-dione (1j) is synthesized according to the procedure in the literature.[7]



(4*E*,9*E*)-2,2,12,12-tetramethyltrideca-4,9-diene-3,11-dione (1k).

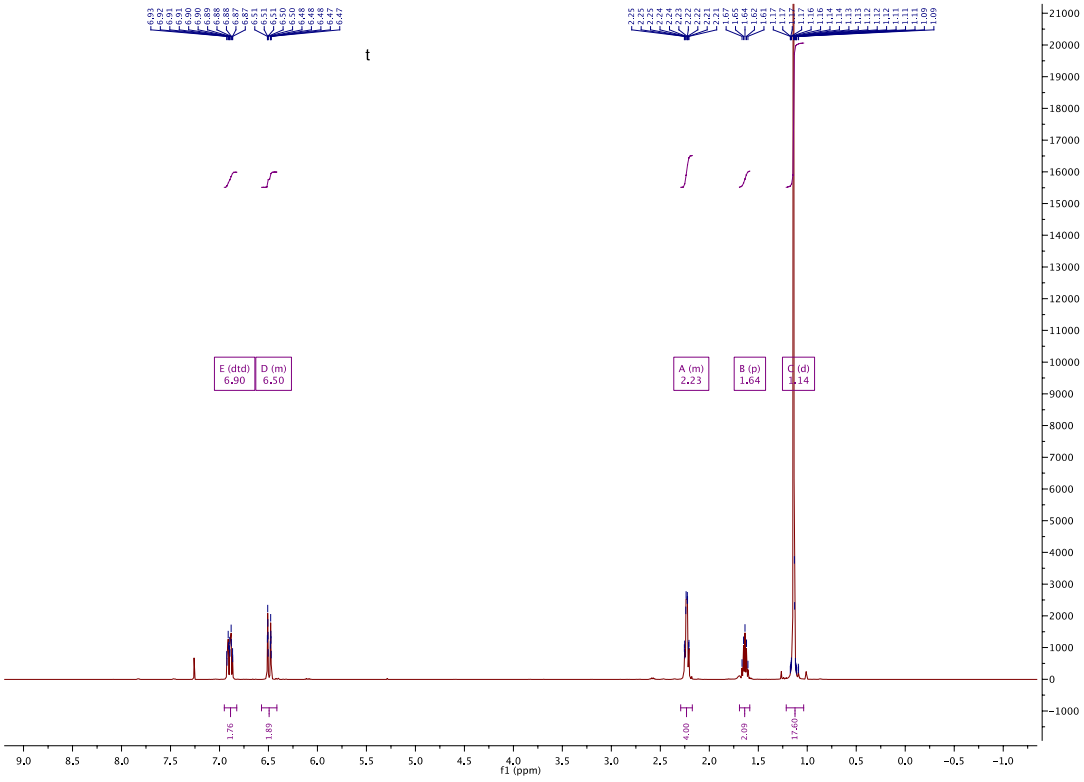
Glutaric dialdehyde (50 wt. % in H_2O, 0.90 mL, 5.0 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 and treated with 1- 1-adamantan-1-yl)-2-(triphenyl-l5-phosphaneylidene)ethan-1-one (5.50 g, 12.5 mmol, 2.50 eq.). The reaction is stirred at room temperature for 2 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1k** as colorless liquid (0.26 g, 1.0 mmol, 20%).

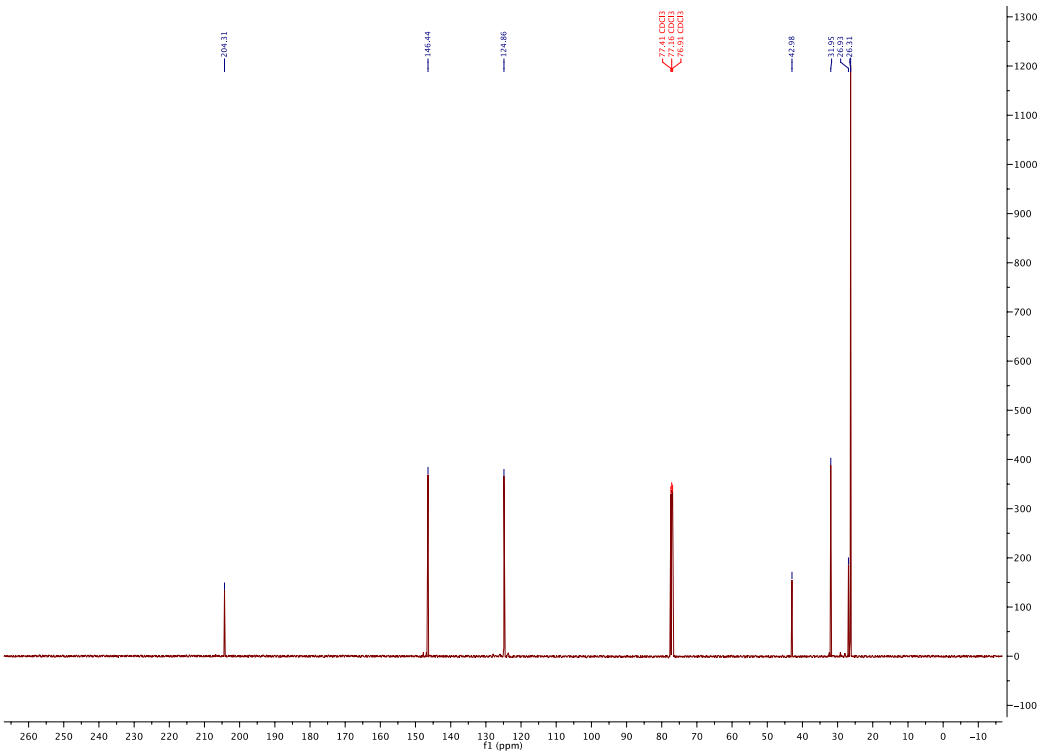
IR 2967, 2359, 1687, 1622, 1477, 1365, 1329, 1294, 1075, 972, 860, 564.

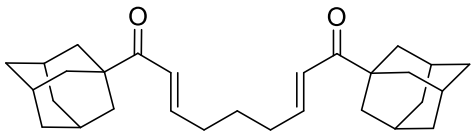
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (dtd, *J* = 15.1, 7.0, 1.1 Hz, 2H), 6.57 – 6.41 (m, 2H), 2.29 – 2.17 (m, 4H), 1.64 (p, *J* = 7.5 Hz, 2H), 1.14 (d, *J* = 1.0 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.31, 146.44, 124.86, 42.98, 31.95, 26.93, 26.31.

HRMS (EI) calculated for $C_{17}H_{28}O_2$ $[M]^+$:264.2089, found 264.2094.







(2*E*,7*E*)-1,9-diadamantyl-nona-2,7-diene-1,9-dione (1l).

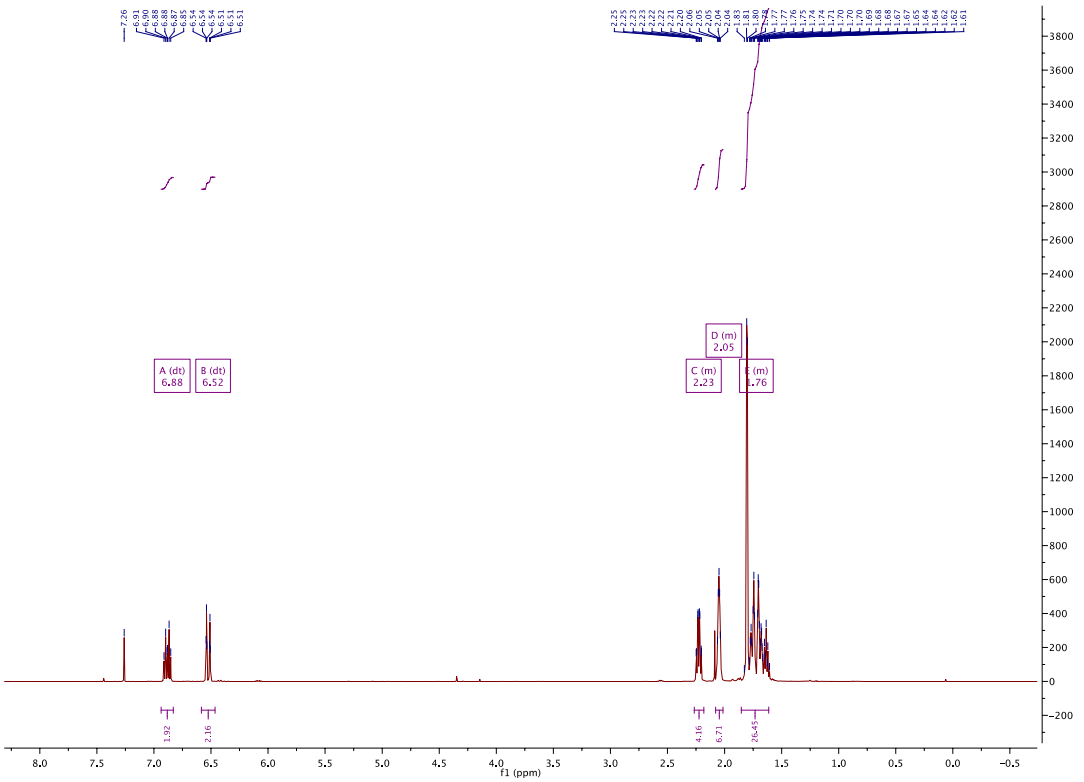
Glutaric dialdehyde (50 wt. % in H_2O, 0.90 mL, 5.0 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 and treated with 1- 1-adamantan-1-yl)-2-(triphenyl-l5-phosphaneylidene)ethan-1-one (5.50 g, 12.5 mmol, 2.50 eq.). The reaction is stirred at room temperature for 2 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1l** as colorless liquid (0.46 g, 1.1 mmol, 22%).

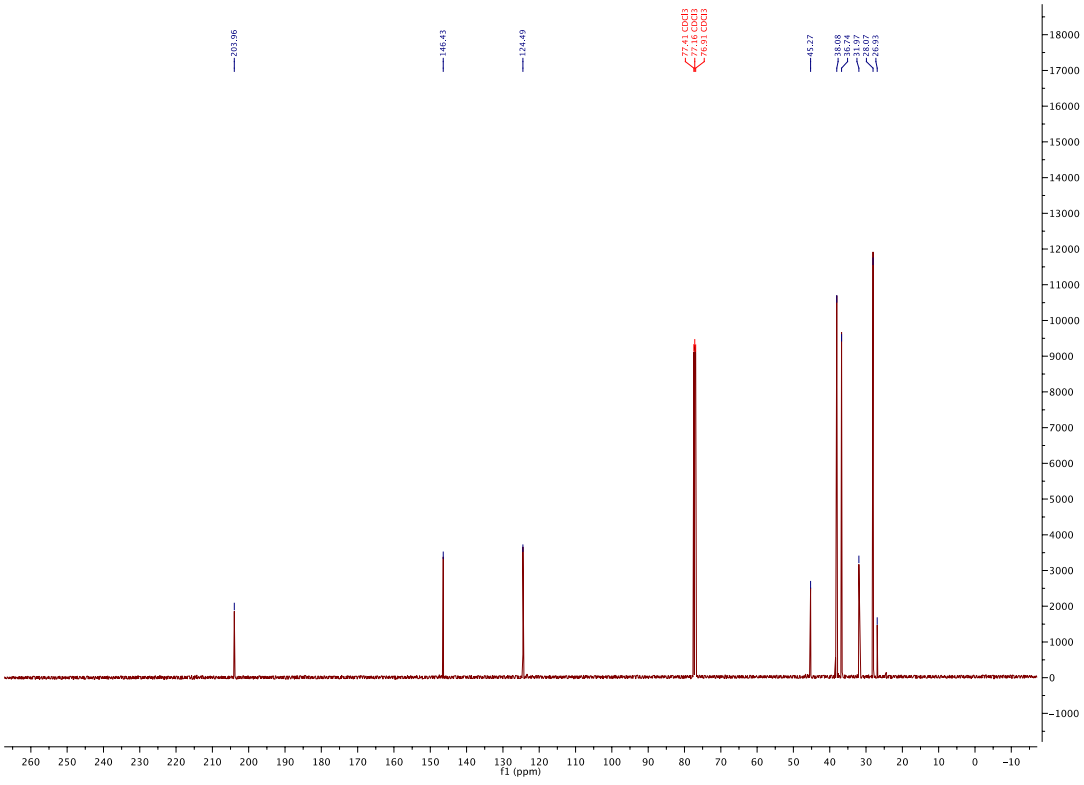
IR 2902, 2849, 1738, 1683, 1620, 1451, 1237, 1046, 972, 669.

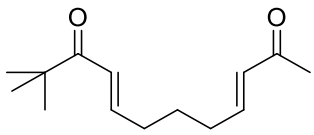
^{1}H NMR (499 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 15.3, 7.0 Hz, 2H), 6.52 (dt, *J* = 15.2, 1.5 Hz, 2H), 2.25 – 2.20 (m, 4H), 2.08 – 2.01 (m, 7H), 1.85 – 1.61 (m, 26H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.96, 146.43, 124.49, 45.27, 38.08, 36.74, 31.97, 28.07, 26.93.

HRMS (ESI) calculated for $C_{29}H_{40}O_2H$ $[M+H]^+$:301.1725, found 301.1798.







(3*E*,8*E*)-11,11-dimethyldodeca-3,8-diene-2,10-dione (1m).

(*E*)-8,8-dimethyl-7-oxonon-5-enal[8] (625 mg, 3.43 mmol, 1.00 eq.) was dissolved in dry

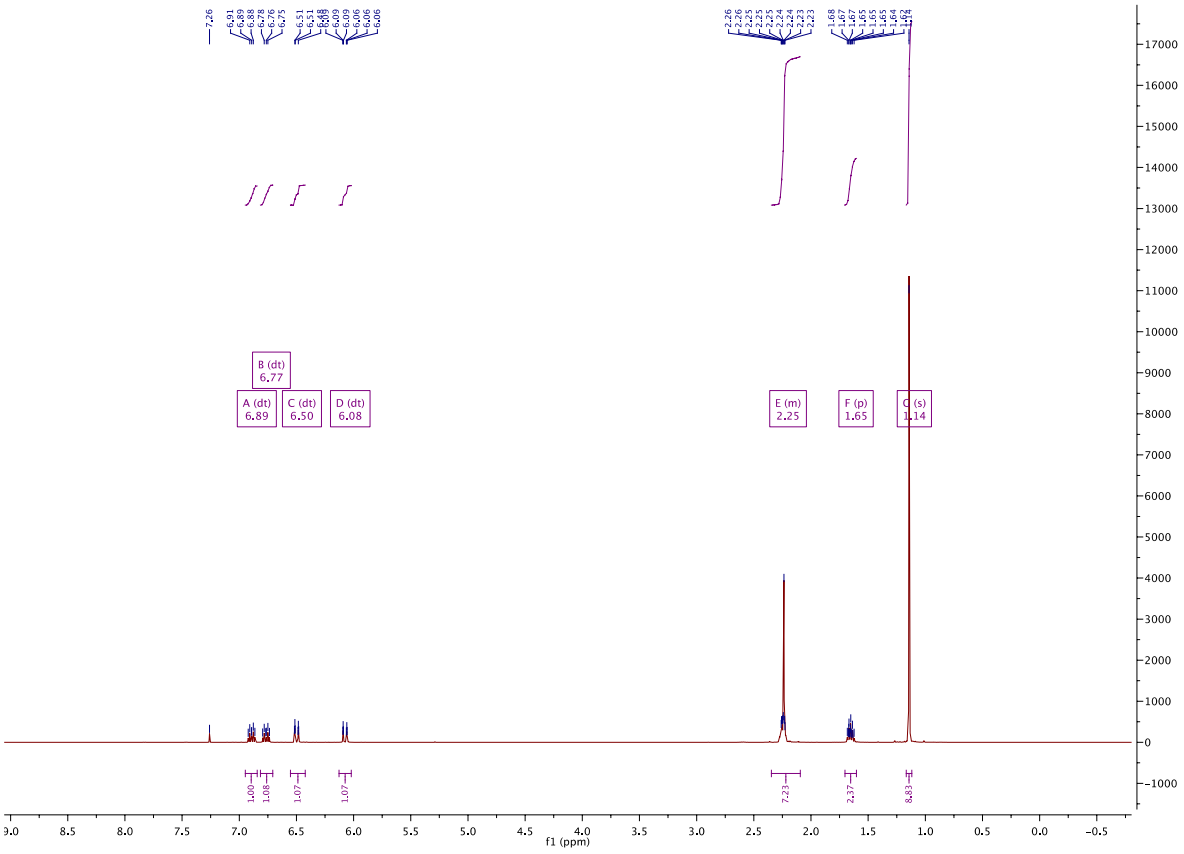
CH_2Cl_2 and treated with 1-(triphenylphosphaneylidene)propan-2-one (1.42, 4.43 mmol, 1.30 eq.). The reaction was stirred at room temperature for 3 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1m** as colorless liquid (457 mg, 2.06 mmol, 60%).

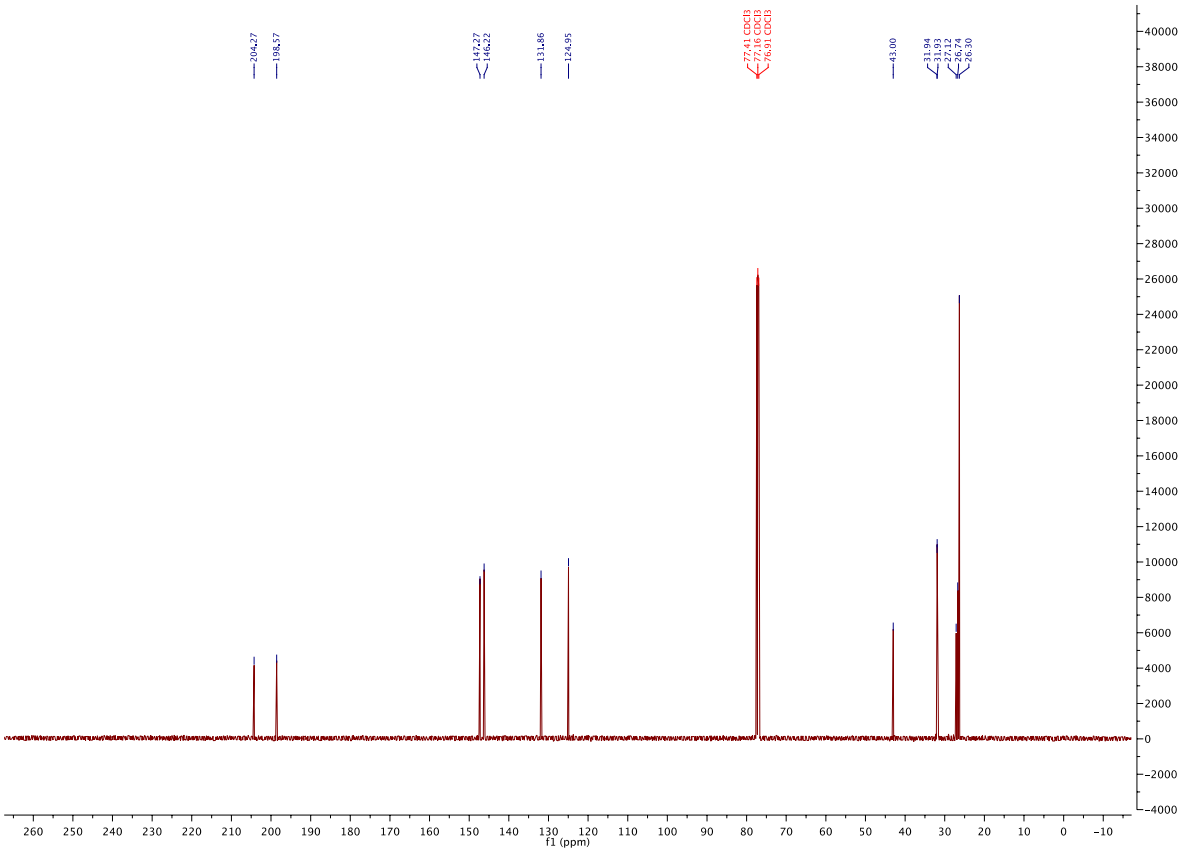
IR 2967, 1686, 1622, 1363, 1252, 1082, 974, 544.

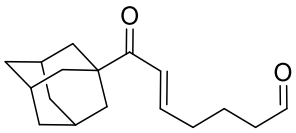
^{1}H NMR (499 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.3, 7.0 Hz, 1H), 6.77 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.50 (dt, *J* = 15.2, 1.5 Hz, 1H), 6.08 (dt, *J* = 15.9, 1.6 Hz, 1H), 2.35 – 2.09 (m, 7H), 1.65 (p, *J* = 7.5 Hz, 2H), 1.14 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.27, 198.57, 147.27, 146.22, 131.86, 124.95, 43.00, 31.94, 31.93, 27.12, 26.74, 26.30.

HRMS (ESI) calculated for $C_{14}H_{22}O_2H$ $[M+H]^+$:223.1620, found 223.1693.







(*E*)- adamantan-1-yl)-7-oxohept-5-enal

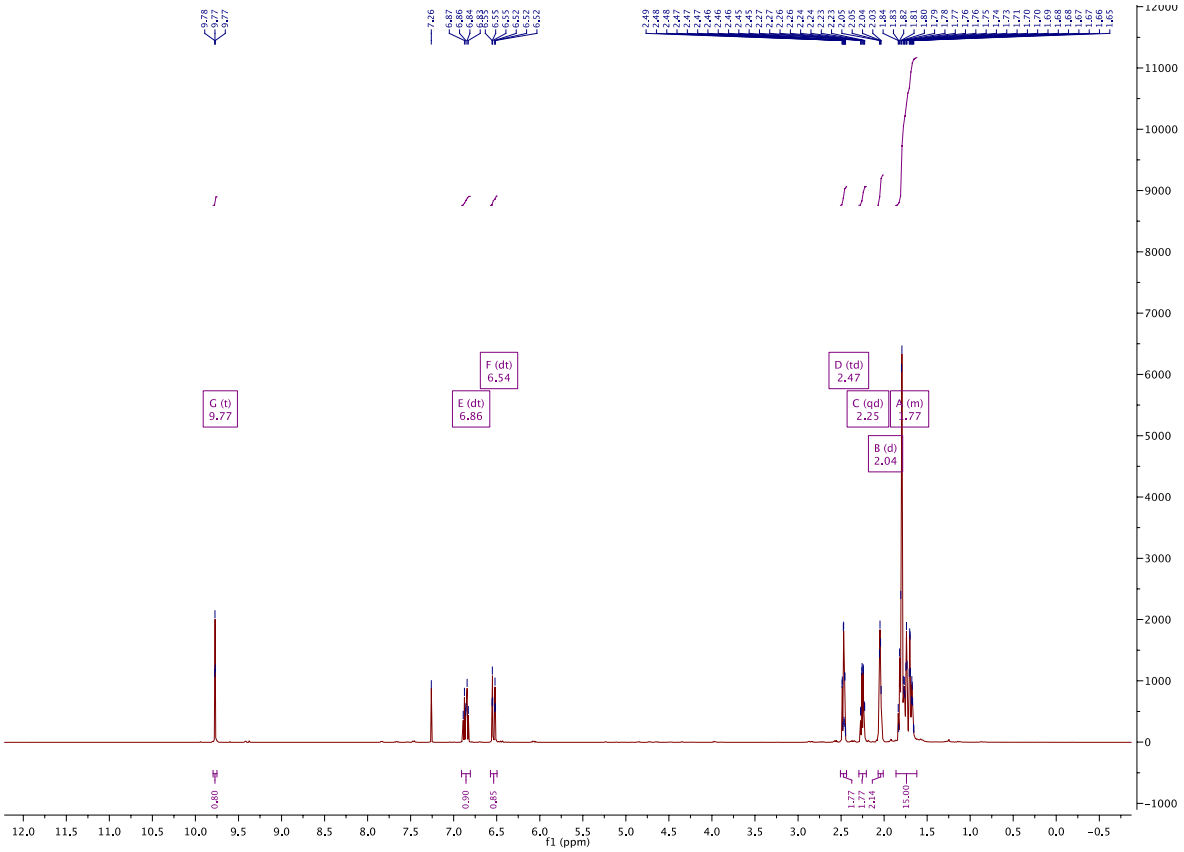
Glutaric dialdehyde (50 wt. % in H_2O, 0.90 mL, 5.0 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 and treated with 1- 1-adamantan-1-yl)-2-(triphenyl-l5-phosphaneylidene)ethan-1-one (5.50 g, 12.5 mmol, 2.50 eq.). The reaction is stirred at room temperature for 1 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **(*E*)- adamantan-1-yl)-7-oxohept-5-enal** as colorless liquid (0.41 g, 1.6 mmol, 31%).

IR 2901, 2849, 1722, 1681, 1619, 1451, 1344, 1285, 1200, 972, 668.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.5 Hz, 1H), 6.86 (dt, *J* = 15.3, 6.9 Hz, 1H), 6.54 (dt, *J* = 15.3, 1.6 Hz, 1H), 2.47 (td, *J* = 7.3, 1.5 Hz, 2H), 2.25 (qd, *J* = 7.2, 1.5 Hz, 2H), 2.04 (d, *J* = 3.1 Hz, 2H), 1.86 – 1.62 (m, 15H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.90, 201.89, 145.73, 124.75, 45.27, 43.19, 38.03, 36.71, 31.74, 28.04, 20.69.

HRMS (ESI) calculated for $C_{17}H_{24}O_2H$ $[M+H]^+$:261.1776, found 261.1849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A (m)
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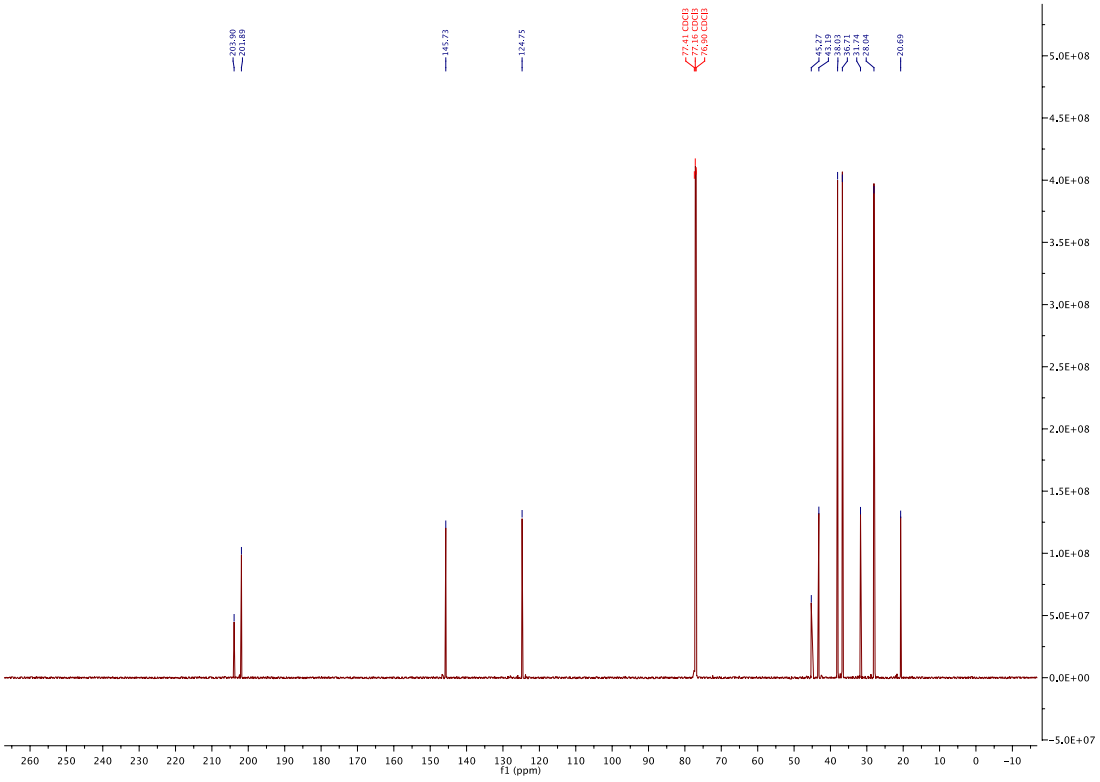
B (d)
2.04
f1 (ppm)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201.89
145.73
124.75
77.41 CDCl3
77.16 CDCl3
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43.03
38.03
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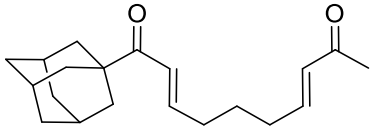
31.24
28.04
20.69
f1 (ppm)


O
O

(2*E*,7*E*)-1-adamantan-1-yl)deca-2,7-diene-1,9-dione (1n)

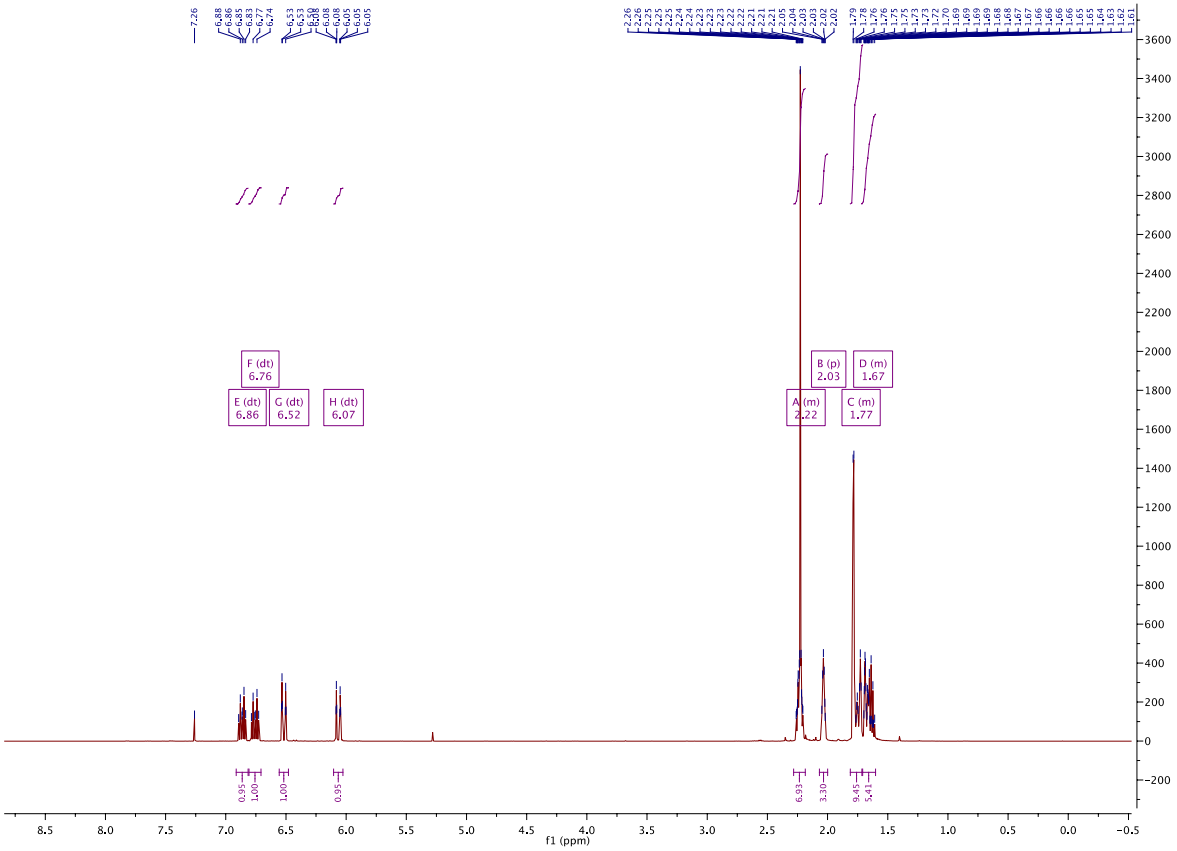
(*E*)- adamantan-1-yl)-7-oxohept-5-enal (400 mg, 1.54 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 and treated with 1-(triphenylphosphaneylidene)propan-2-one (640 mg, 2.00 mmol, 1.30 eq.). The reaction was stirred at room temperature for 3 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1n** as colorless liquid (0.18 g, 0.62 mmol, 40%).

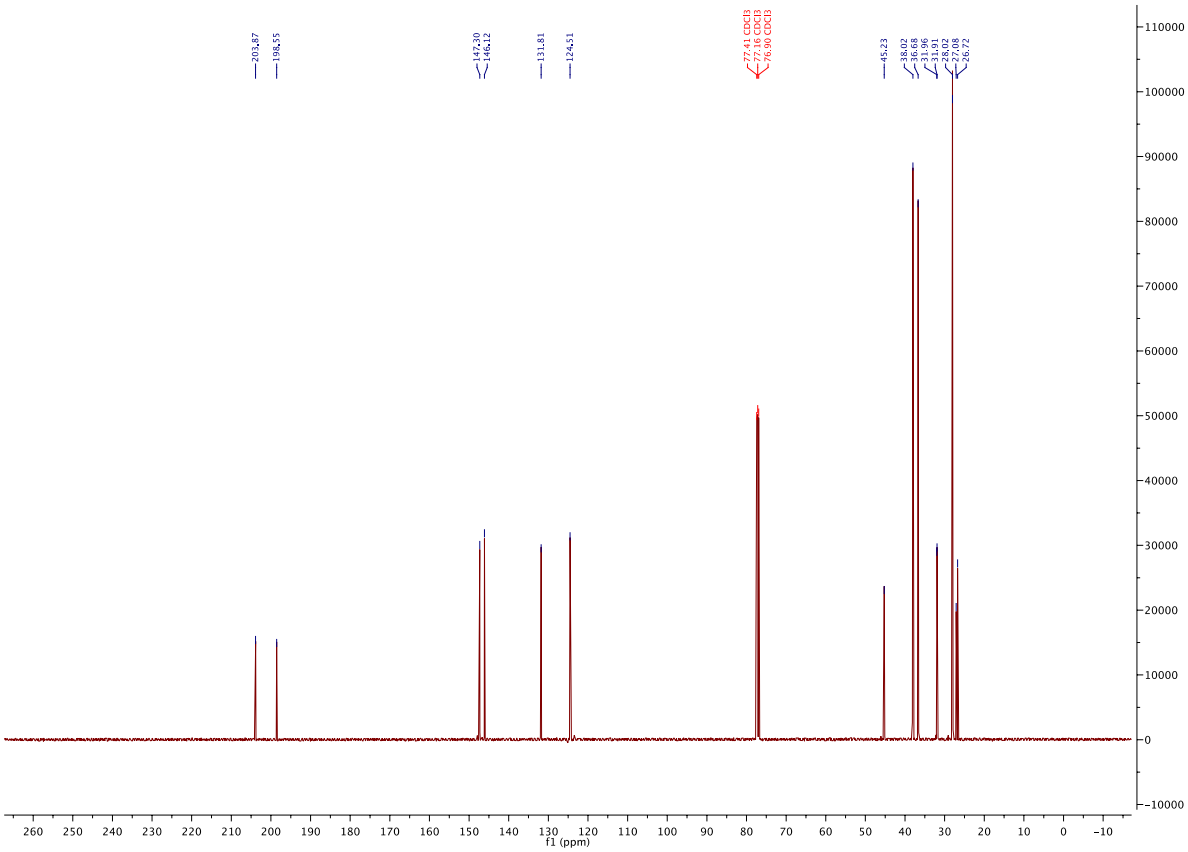
IR 2902, 2849, 1674, 1619, 1451, 1359, 1252, 972, 669.

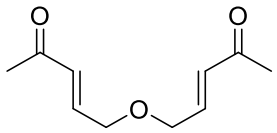
^{1}H NMR (499 MHz, $CDCl_3$) δ 6.86 (dt, *J* = 15.3, 7.0 Hz, 1H), 6.76 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.52 (dt, *J* = 15.3, 1.5 Hz, 1H), 6.07 (dt, *J* = 15.9, 1.5 Hz, 1H), 2.28 – 2.19 (m, 7H), 2.03 (p, *J* = 3.0 Hz, 3H), 1.81 – 1.71 (m, 9H), 1.71 – 1.60 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.87, 198.55, 147.30, 146.12, 131.81, 124.51, 45.23, 38.02, 36.68, 31.96, 31.91, 28.02, 27.08, 26.72.

HRMS (ESI) calculated for $C_{20}H_{28}O_2H$ $[M+H]^+$:301.2089, found 301.2162.







(3*E*,3'*E*)-5,5'-oxybis(pent-3-en-2-one) (1o)

Diglycolaldehyde (100 mg, 1.00 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 and treated with 1-(triphenylphosphaneylidene)propan-2-one (800 mg, 2.50 mmol, 2.50 eq.). The reaction was stirred at room temperature for 1 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1o** as white solid (0.11 g, 0.60 mmol, 40%).

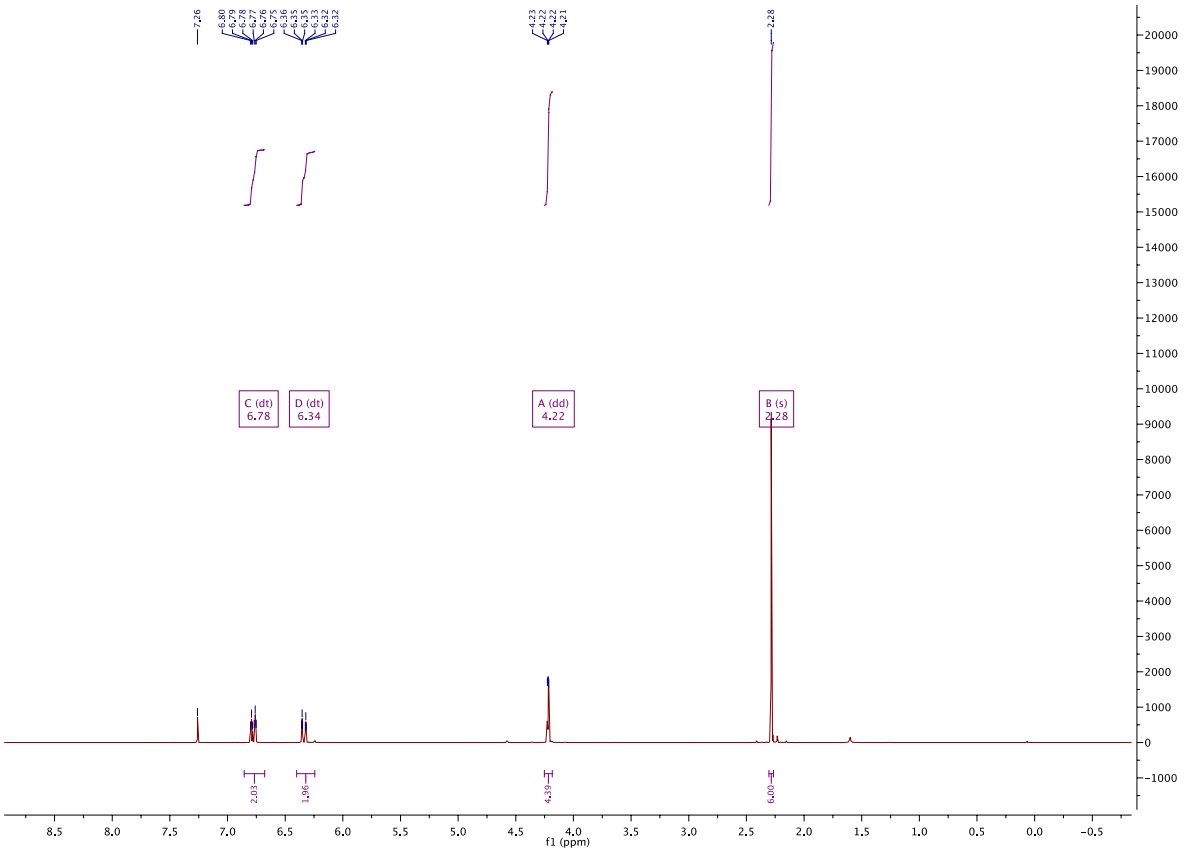
IR 2847, 1671, 1633, 1425, 1357, 1252, 1132, 970, 543, 508.

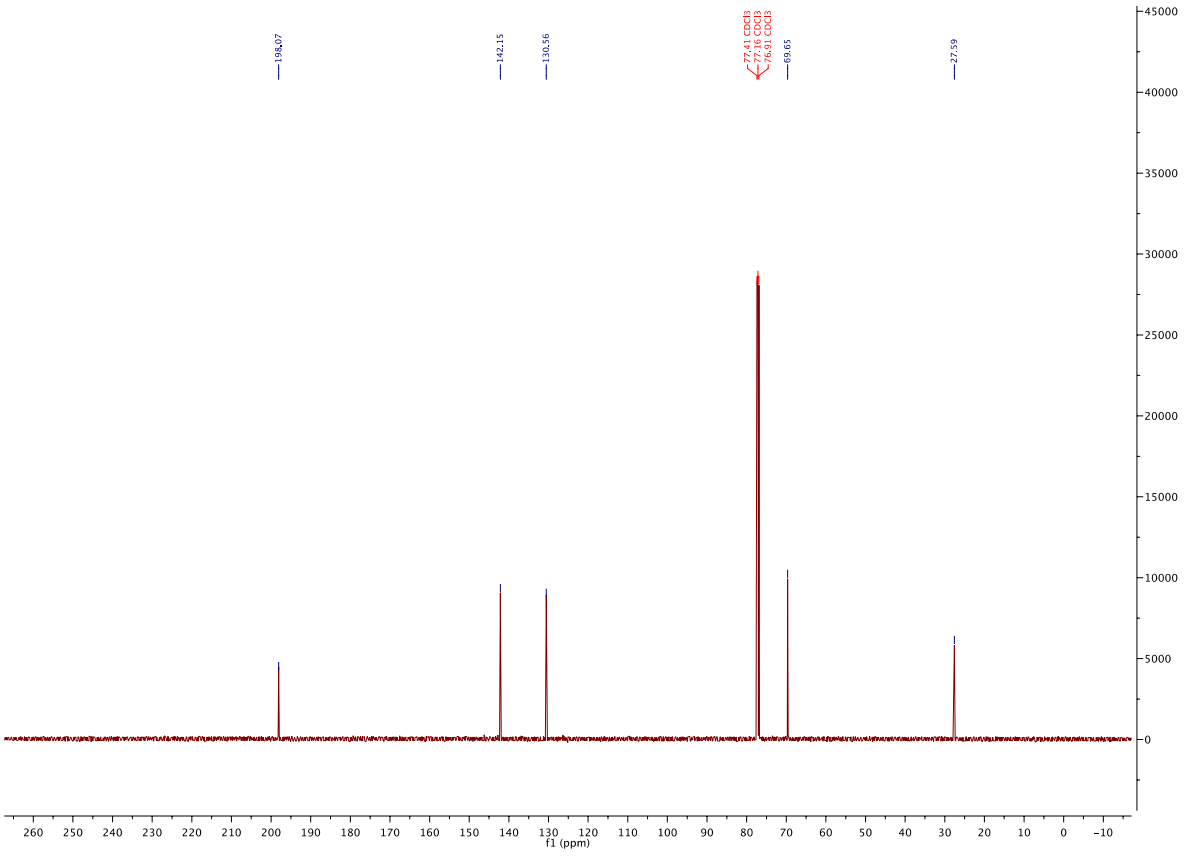
^{1}H NMR (499 MHz, $CDCl_3$) δ 6.78 (dt, *J* = 16.1, 4.4 Hz, 2H), 6.34 (dt, *J* = 16.1, 2.0 Hz, 2H), 4.22 (dd, *J* = 4.4, 2.0 Hz, 4H), 2.28 (s, 6H).

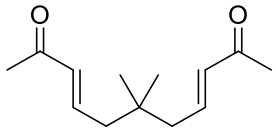
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.07, 142.15, 130.56, 69.65, 27.59.

HRMS (ESI) calculated for $C_{10}H_{14}O_3H$ $[M+H]^+$:183.1943, found 183.1016.

m.p. 33 ℃


7.26
6.80
6.79
6.78
6.77
6.77
6.76
6.75
6.36
6.35
6.35
6.33
6.32
6.32
4.23
4.22
4.22
4.22
4.21
2.28
C (dt)
6.78
D (dt)
6.34
A (dd)
4.22
B (s)
2.28
2.03
1.96
4.39
6.00
f1 (ppm)


198.07
142.15
130.56
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.65
27.59
f1 (ppm)



(3*E*,8*E*)-6,6-dimethylundeca-3,8-diene-2,10-dione (1p)

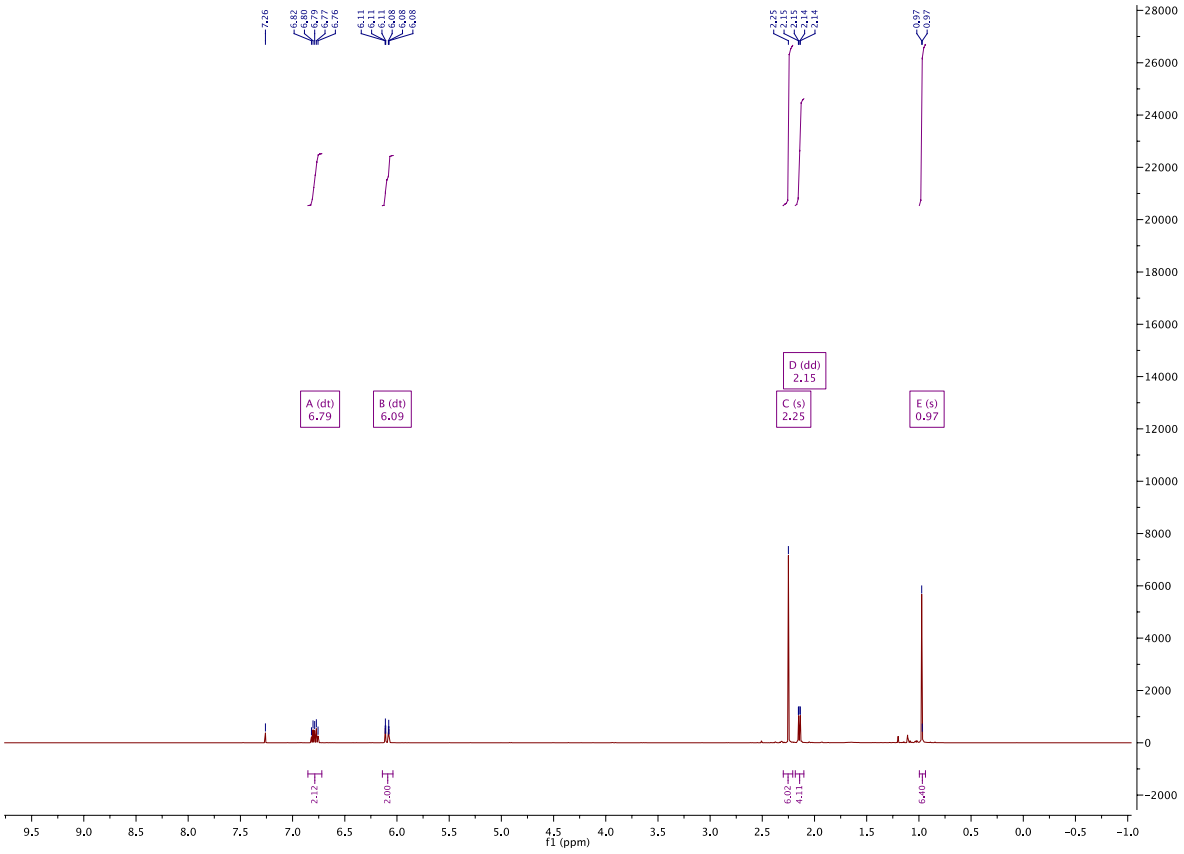
Dimethylpentanedial (128 mg, 1.00 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 and treated with 1-(triphenylphosphaneylidene)propan-2-one (800 mg, 2.50 mmol, 2.50 eq.). The reaction was stirred at room temperature for 1 days. The solvent was then removed by rotary evaporation, and the residue as purified by chromatography on a silica gel column to afford **1p** as colorless liquid (0.12 g, 0.60 mmol, 40%).

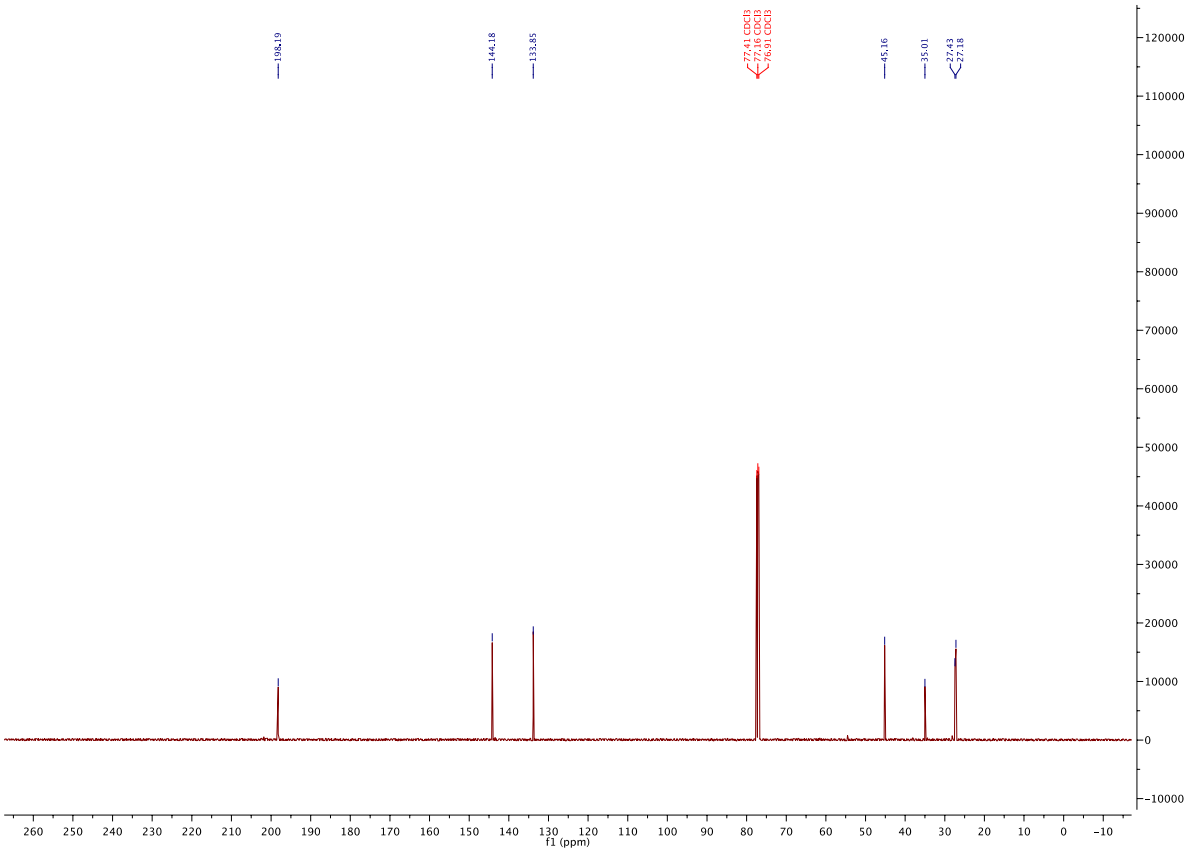
IR 2959, 1737, 1669, 1626, 1360, 1250, 1182, 980, 543.

^{1}H NMR (499 MHz, $CDCl_3$) δ 6.79 (dt, *J* = 15.6, 7.7 Hz, 2H), 6.09 (dt, *J* = 15.8, 1.3 Hz, 2H), 2.25 (s, 6H), 2.15 (dd, *J* = 7.8, 1.4 Hz, 4H), 0.97 (s, 6H).

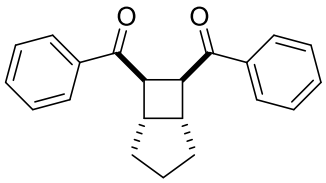
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.19, 144.18, 133.85, 45.16, 35.01, 27.43, 27.18.

HRMS (ESI) calculated for $C_{13}H_2O_2H$ $[M+H]^+$:209.1463, found 209.1536.





6. Synthesis of Products.

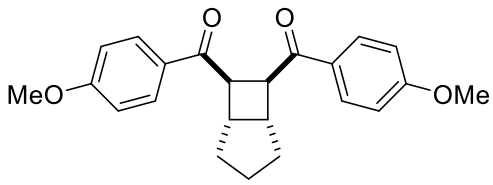


Bicyclo[3.2.0]heptane-6,7-diyl)bis(phenylmethanone) (2a)

According to GP 1, **1a** (76 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5.0 mg, 0.075 mmol, 30 mol%) in THF (5 mL) was stirred at 65°C for 12 h. The mixture was directly filtered through a silica plug and flushed with dichloromethane. Solvent is removed under reduced pressure and the residue was washed with pentane : diethyl ether = 20 : 1 to afford the pure product **2a** as white solid(65 mg, 0.21 mmol, 85%).

The NMR data is in agreement with the literature.[9]

The relative configuration is assigned according to previous literature report.[9]



Bicyclo[3.2.0]heptane-6,7-diyl)bis((4-methoxyphenyl)methanone) (2b)

According to GP 1, **1b** (91 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 12 h. Chromatography on silica (dichloromethane : cyclohexane : ethyl acetate = 40 : 60 : 3 to 40 : 60 : 5) yielded the product **2b** as white solid (73 mg, 0.20 mmol, 80%).

IR 2960, 1669, 1597, 1575, 1509, 1422, 1343, 1315, 1256, 1236, 1167, 1146, 1109, 1022, 925, 835, 803, 584, 517.

^{1}H NMR (499 MHz, CD_2Cl_2) δ 7.74 – 7.65 (m, 4H), 6.90 – 6.77 (m, 3H), 3.80 (s, 8H), 3.12 (tt, *J* = 4.4, 2.4 Hz, 2H), 2.13 – 1.95 (m, 2H), 1.82 (ddd, *J* = 13.6, 6.0, 1.6 Hz, 2H), 1.68 (dddd, *J* = 13.6, 12.0, 6.0, 3.5 Hz, 2H).

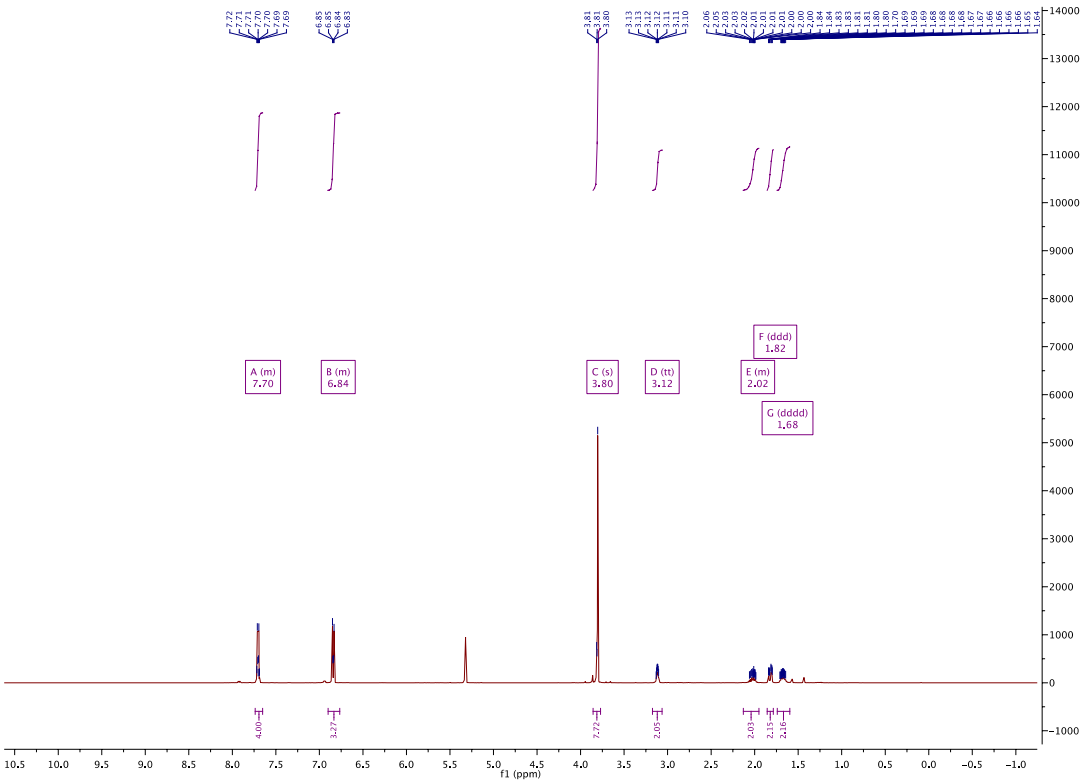
^{13}C NMR (126 MHz, CD_2Cl_2) δ 197.62, 163.59, 130.38, 130.09, 114.11, 55.96, 48.52, 39.69, 32.94, 25.79.

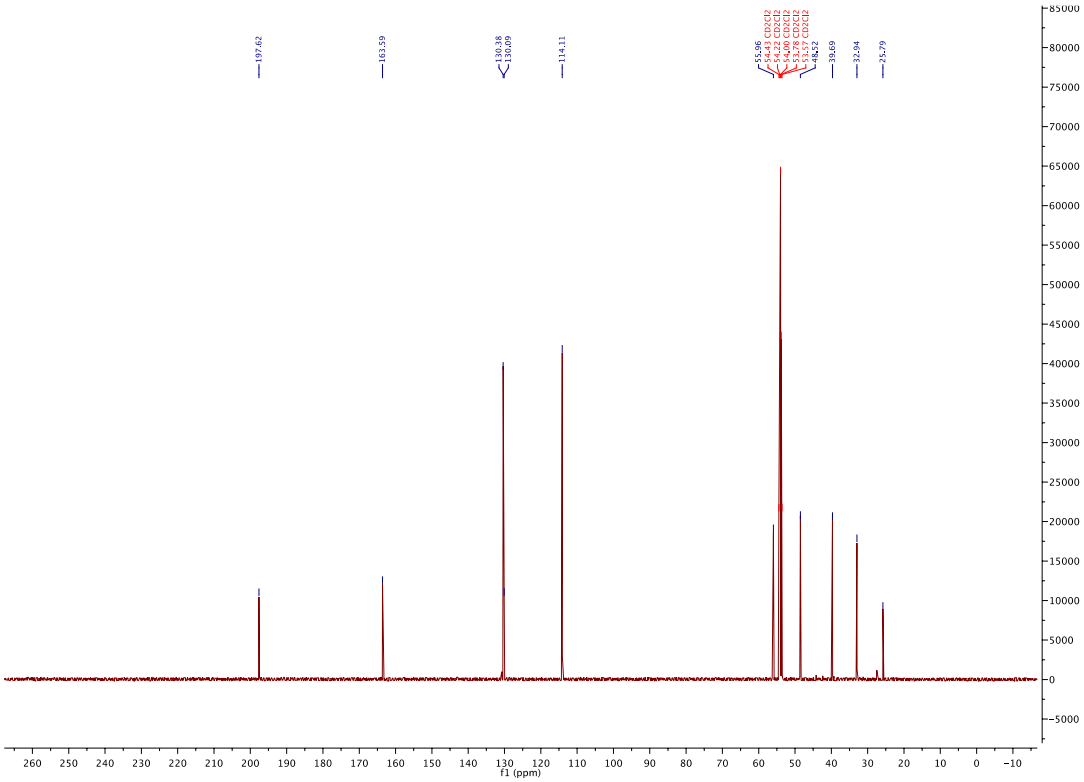
HRMS (ESI) calculated for $C_{23}H_{24}O_4H$ $[M+H]^+$:365.1675, found 365.1747.

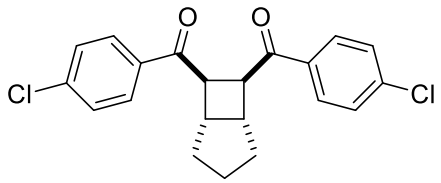
m.p. 148 °C

The NMR data is in agreement with the literature.[10]

The relative configuration is assigned according to previous literature report.[10]





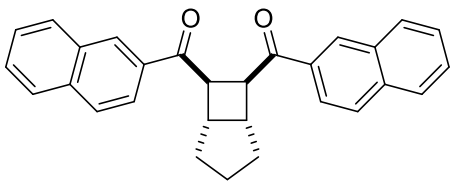


Bicyclo[3.2.0]heptane-6,7-diyl)bis((4-chlorophenyl)methanone) (2c)

According to GP 1, **1c** (94 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 12 h. The mixture was directly filtered through a silica plug and flushed with dichloromethane. Solvent is removed under reduced pressure and the residue was washed with pentane to afford the pure product **2c** as white solid with (81 mg, 0.22 mmol, 86%).

NMR data is in agreement with the literature.[11]

The relative configuration is assigned according to previous literature report.[11]



Bicyclo[3.2.0]heptane-6,7-diyl)bis(naphthalen-2-ylmethanone) (2d)

According to GP 1, **1d** (100 mg, 0.250 mmol, 1.00 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 12 h. The

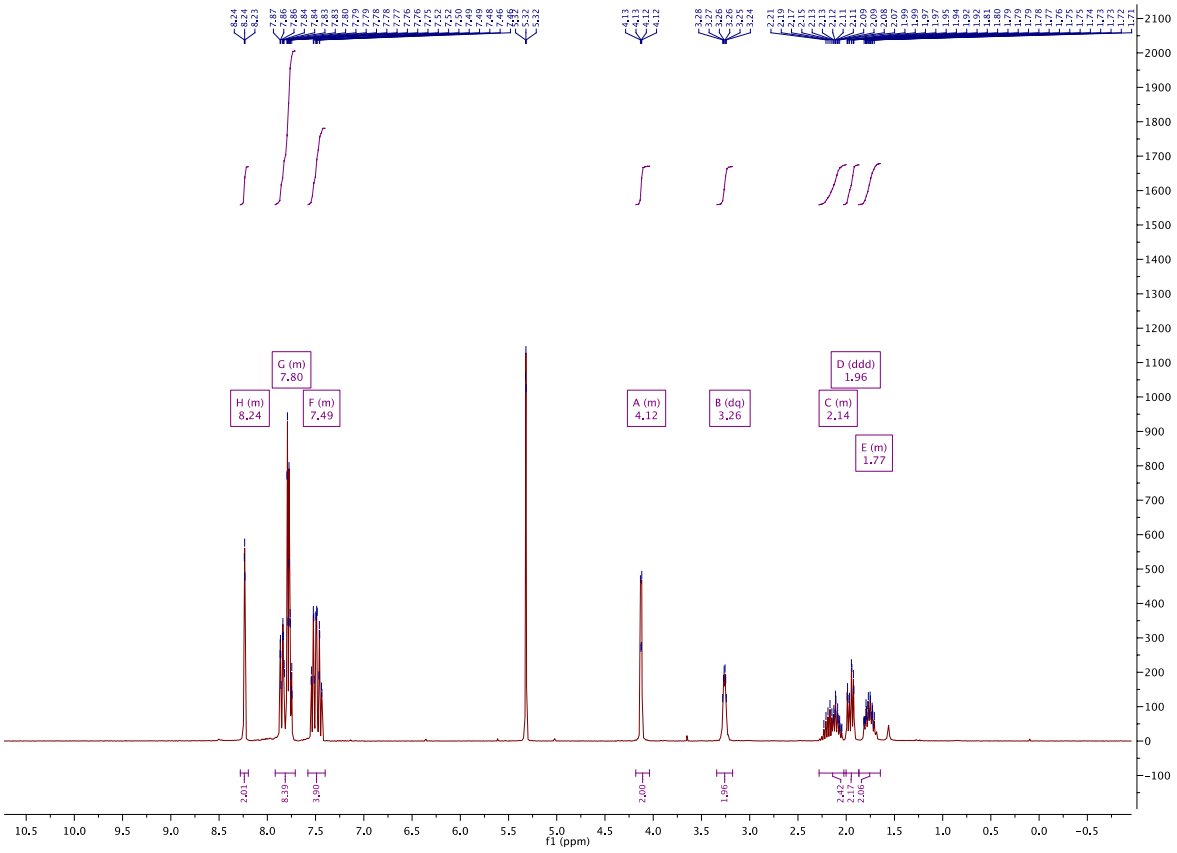
mixture was directly filtered through a silica plug and flushed with dichloromethane. Solvent is removed under reduced pressure and the residue was washed with pentane : diethyl ether = 20 : 1 to afford the pure product **2d** as white solid (90 mg, 0.23 mmol, 90%).

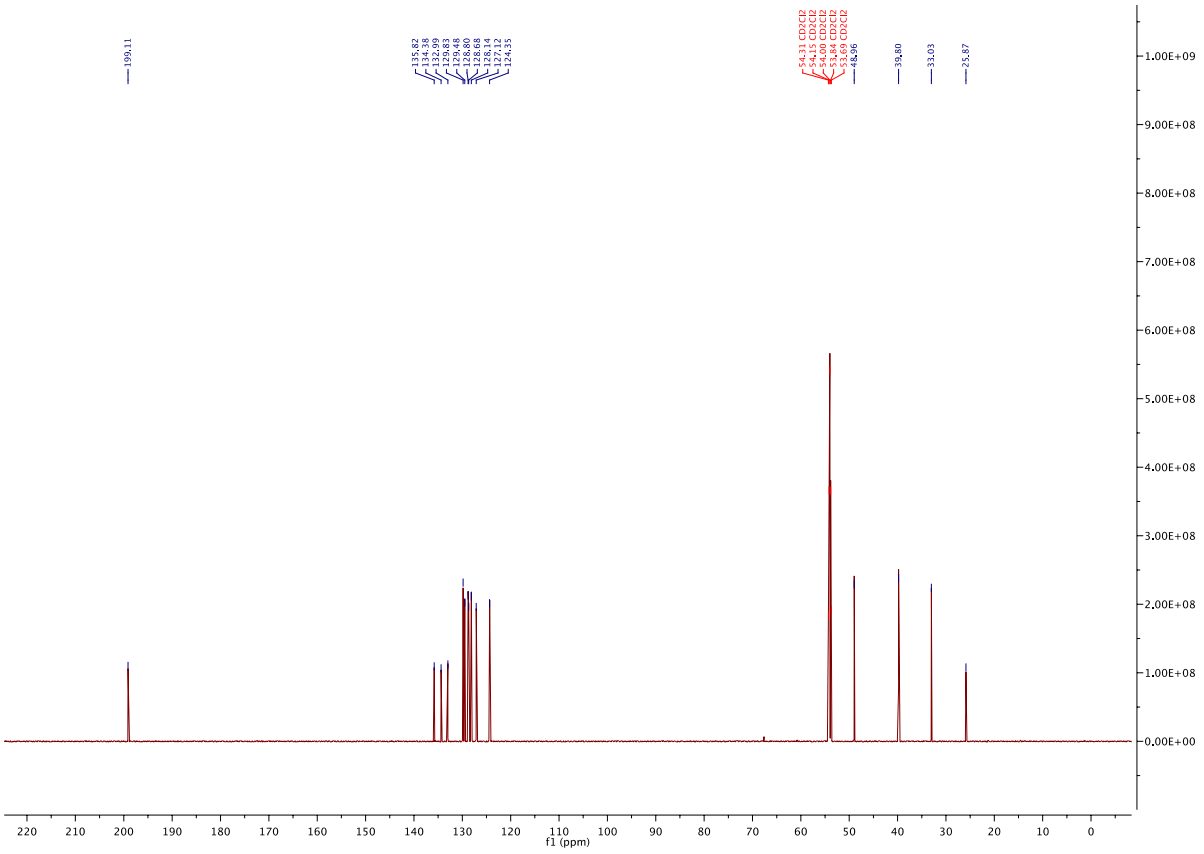
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.28 – 8.20 (m, 2H), 7.92 – 7.71 (m, 8H), 7.57 – 7.42 (m, 4H), 4.18 – 4.04 (m, 2H), 3.26 (dq, *J* = 4.4, 2.3 Hz, 2H), 2.28 – 2.00 (m, 2H), 1.96 (ddd, *J* = 13.7, 6.2, 1.4 Hz, 2H), 1.87 – 1.65 (m, 2H).

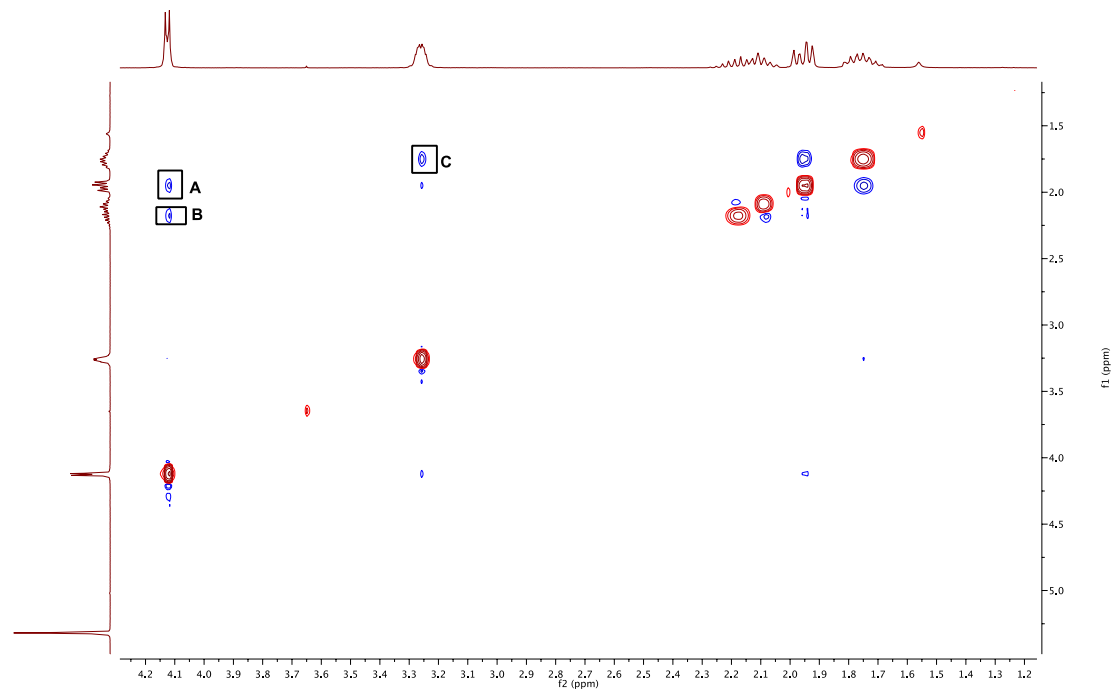
^{13}C NMR (176 MHz, CD_2Cl_2) δ 199.11, 135.82, 134.38, 132.99, 129.83, 129.48, 128.80, 128.68, 128.14, 127.12, 124.35, 48.96, 39.80, 33.03, 25.87.

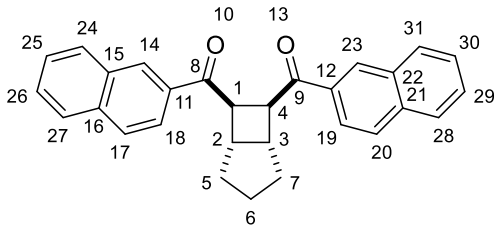
HRMS (ESI) calculated for $C_{29}H_{24}O_2H$ $[M+H]^+$:405.1776, found 405.1849.

m.p. 170 ℃

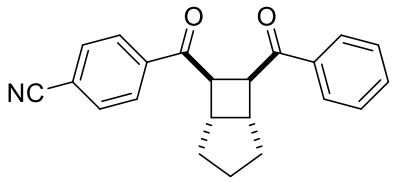



199.11
135.82
134.38
132.99
129.83
129.48
128.80
128.65
128.14
127.12
124.35
54.31 CD2Cl2
54.15 CD2Cl2
54.00 CD2Cl2
53.84 CD2Cl2
53.69 CD2Cl2
48.96
39.80
33.03
25.87
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
f1 (ppm)


A
B
C
f2 (ppm)
f1 (ppm)



Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A**) of H1 and H5 (bottom) or H4 and H7 (bottom), the cross peak (**B**) of H1 and H6 (bottom) or H4 and H6 (bottom), the cross peak (**C**) of H2 and H5 (top) or H3 and H7 (top).



4-(7-benzoylbicyclo[3.2.0]heptane-6-carbonyl)benzonitrile (2e).

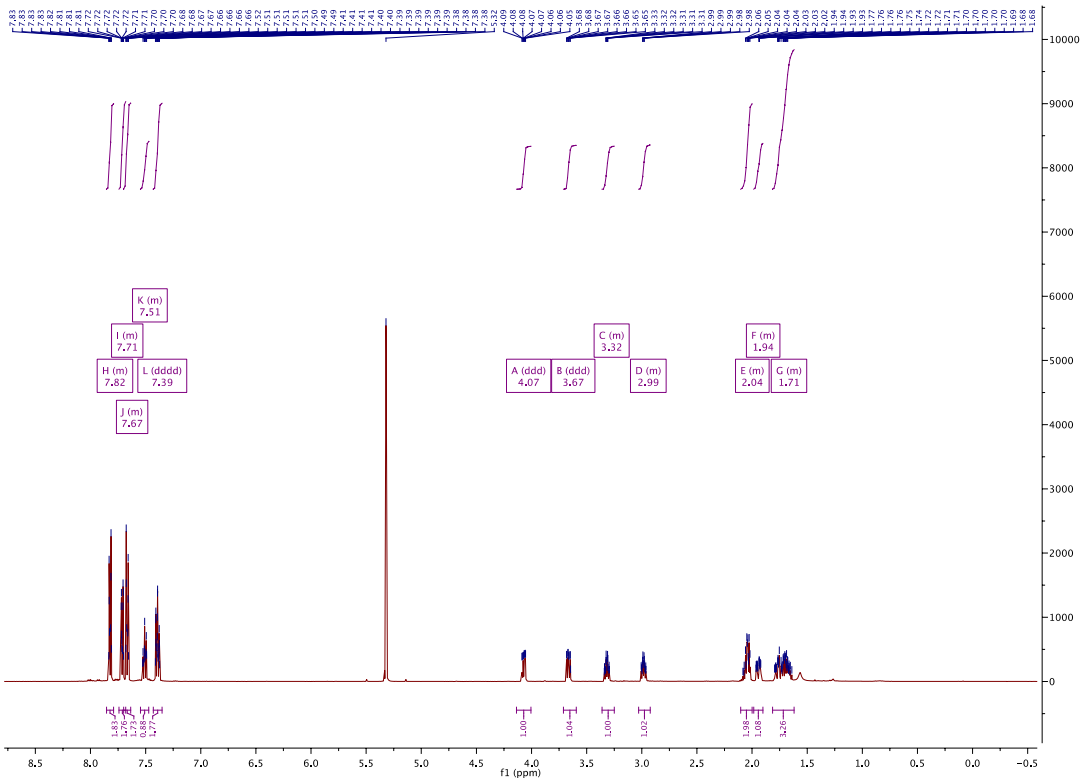
According to GP 1, **1e** (83 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 12 h. The mixture was directly filtered through a silica plug and flushed with ethyl acetate. Solvent is removed under reduced pressure and the residue was washed with pentane : diethyl ether = 4 : 1 to afford the pure product **2e** as white solid (71 mg, 0.22 mmol, 86%).

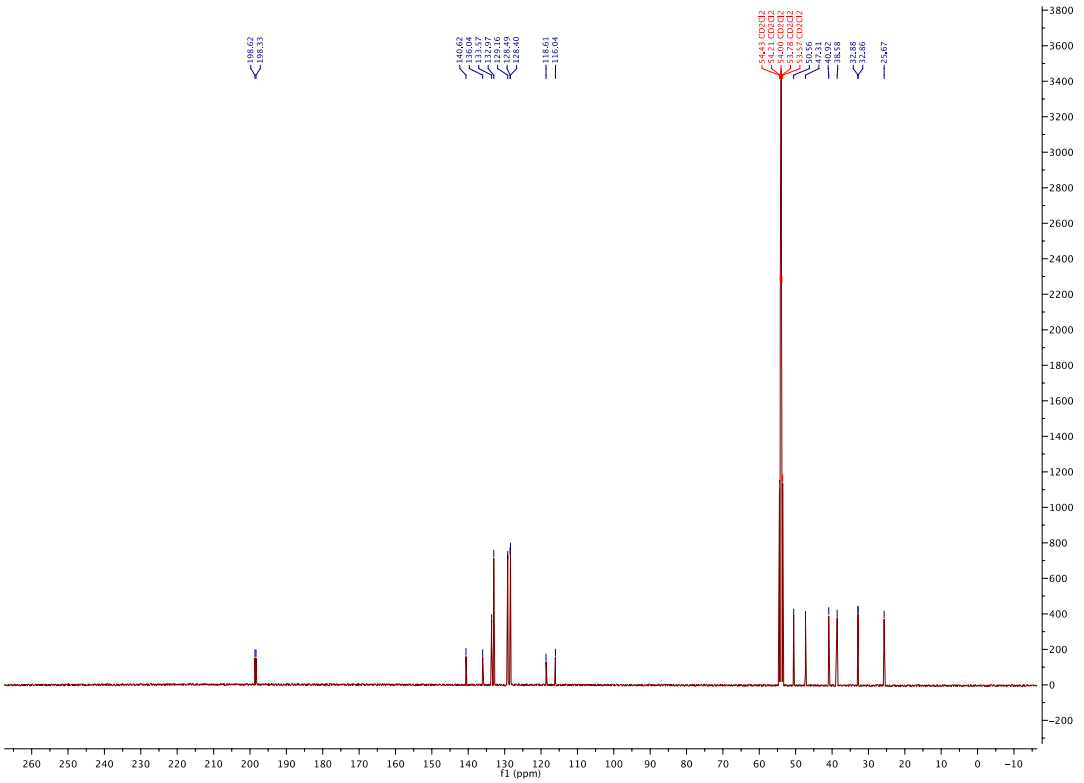
IR 2948, 2923, 2231, 1682, 1669, 1447, 1347, 1210, 1181, 1016, 881, 839, 750, 689, 600, 556.

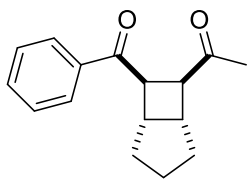
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.84 – 7.80 (m, 2H), 7.73 – 7.69 (m, 2H), 7.68 – 7.64 (m, 2H), 7.54 – 7.48 (m, 1H), 7.39 (dddd, *J* = 7.9, 6.7, 1.5, 0.9 Hz, 2H), 4.07 (ddd, *J* = 9.7, 5.0, 1.2 Hz, 1H), 3.67 (ddd, *J* = 9.7, 5.7, 1.3 Hz, 1H), 3.36 – 3.25 (m, 1H), 3.03 – 2.92 (m, 1H), 2.10 – 2.00 (m, 2H), 1.97 – 1.91 (m, 1H), 1.80 – 1.63 (m, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 198.62, 198.33, 140.62, 136.04, 133.57, 132.97, 129.16, 128.49, 128.40, 118.61, 116.04, 50.56, 47.31, 40.92, 38.58, 32.88, 32.86, 25.67.

HRMS (ESI) calculated for $C_{22}H_{19}NO_2H$ $[M+H]^+$:330.1416, found 330.1489.





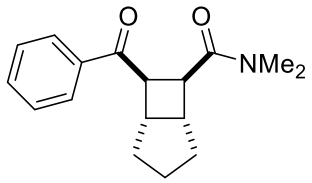


7-Benzoylbicyclo[3.2.0]heptan-6-yl)ethan-1-one (2g)

According to GP 1, **1g** (61 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 12 h. Chromatography on silica (cyclohexane to ethyl acetate = 2 : 1) yielded the product **2g** as white solid (50 mg, 0.21 mmol, 82%).

The NMR data is in agreement with the literature.[9]

The relative configuration is assigned according to previous literature report.[9]



7-Benzoyl-*N*,*N*-dimethylbicyclo[3.2.0]heptane-6-carboxamide (2h)

According to GP 1, **1h** (84 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in THF (5 mL) was stirred at 65°C for 12 h. Chromatography on silica (dichloromethane : ethyl acetate = 3 : 1) yielded the product **2h** as white solid (71 mg, 0.21 mmol, 85%).

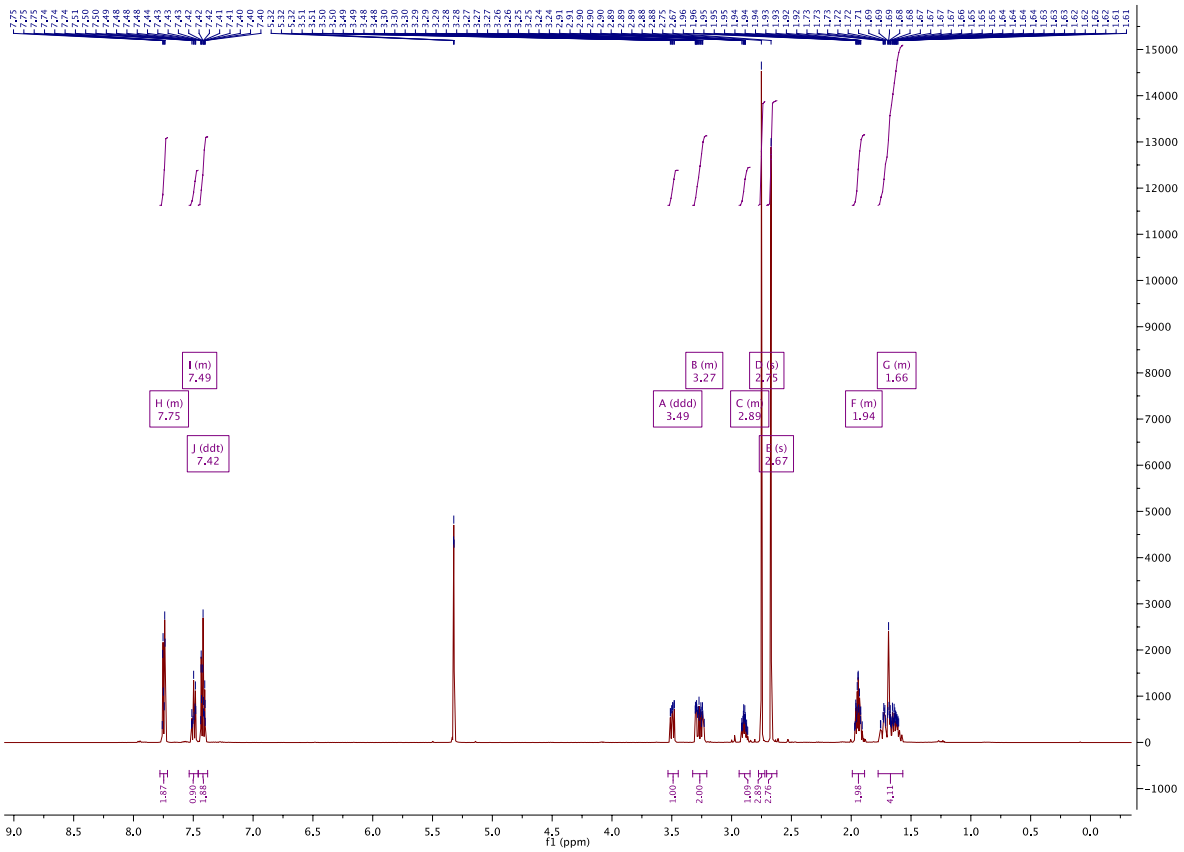
IR 2927 2849, 1676, 1626, 1495, 1448, 1397, 1351, 1236, 1139, 1064, 1021, 728, 692.

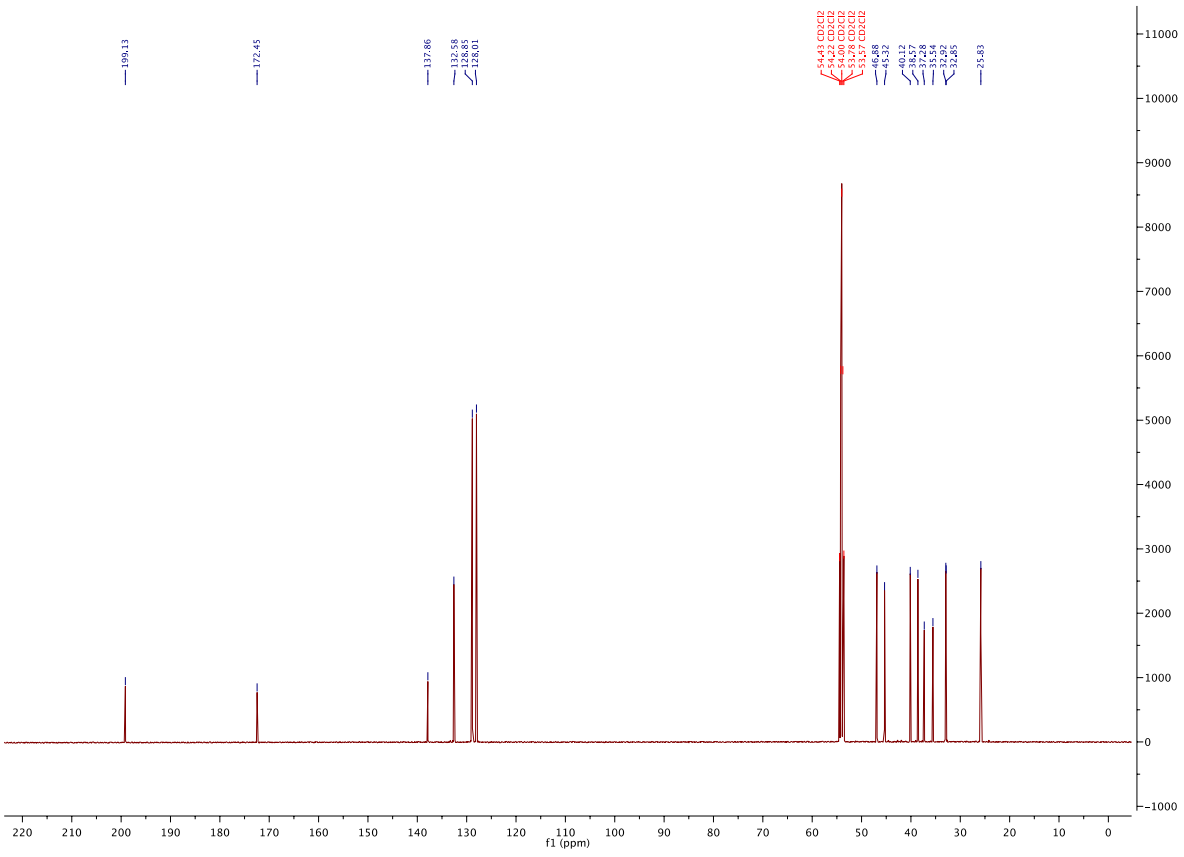
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.76 – 7.72 (m, 2H), 7.52 – 7.46 (m, 1H), 7.42 (ddt, *J* = 8.2, 6.8, 1.1 Hz, 2H), 3.49 (ddd, *J* = 9.7, 5.7, 1.3 Hz, 1H), 3.33 – 3.21 (m, 2H), 2.93 – 2.86 (m, 1H), 2.75 (s, 3H), 2.67 (s, 3H), 1.98 – 1.89 (m, 2H), 1.77 – 1.57 (m, 4H).

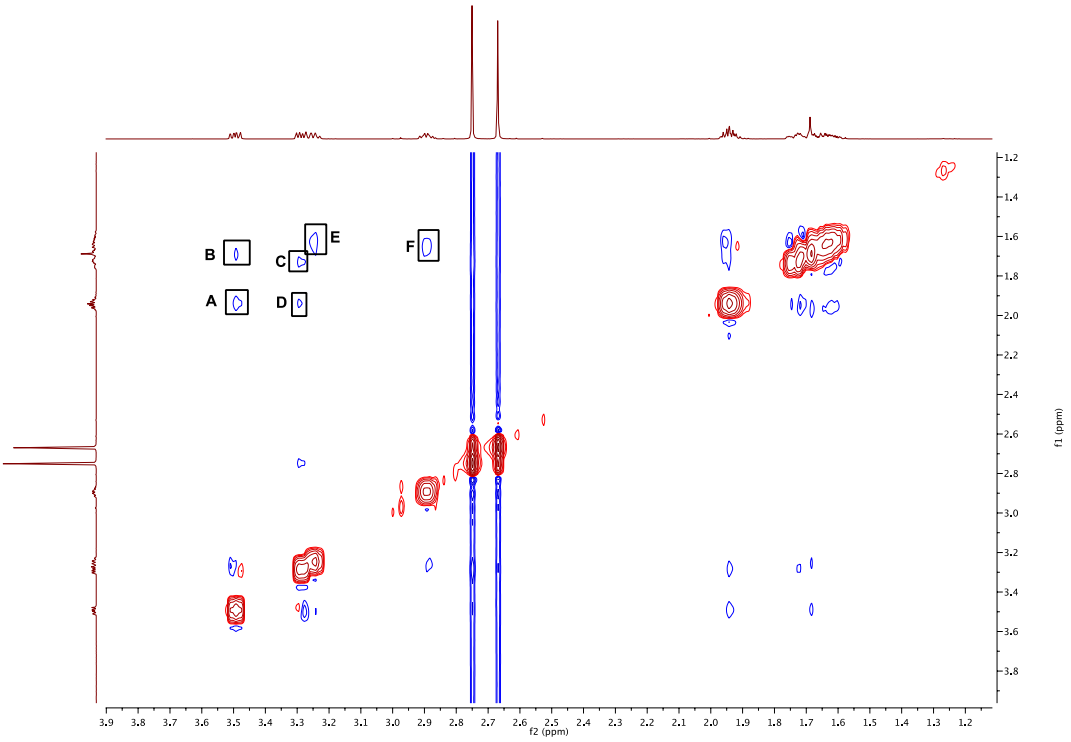
^{13}C NMR (126 MHz, CD_2Cl_2) δ 199.13, 172.45, 137.86, 132.58, 128.85, 128.01, 46.88, 45.32, 40.12, 38.57, 37.28, 35.54, 32.92, 32.85, 25.83.

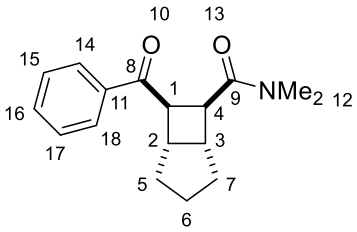
HRMS (ESI) calculated for $C_{17}H_{21}NO_2H$ $[M+H]^+$:272.1572, found 272.1645

m.p. 120 °C

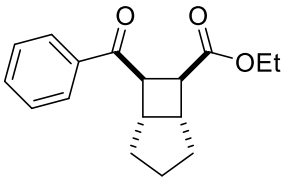

I (m)
7.49
H (m)
7.75
J (ddt)
7.42
B (m)
3.27
D (s)
2.75
A (ddd)
3.49
C (m)
2.89
E (s)
2.67
G (m)
1.66
F (m)
1.94
f1 (ppm)


199.13
172.45
137.86
132.58
128.85
128.01
54.43 CD2Cl2
54.22 CD2Cl2
54.00 CD2Cl2
53.78 CD2Cl2
53.57 CD2Cl2
46.68
45.32
40.12
38.17
37.28
35.54
32.22
32.05
25.83
f1 (ppm)





Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H1 and H6 (bottom), the cross peak (**B)** of H1 and H5 (bottom), the cross peak (**C)** of H4 and H7 (bottom), the cross peak (**D**) of H4 and H6 (bottom), the cross peak (**E)** of H3 and H7 (top), the cross peak (**F)** of H2 and H5 (top).

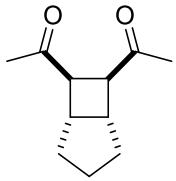


Ethyl-7-benzoylbicyclo[3.2.0]heptane-6-carboxylate (2i)

According to GP 1, **1i** (68 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (10 mg, 0.025 mmol, 10 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in THF (5 mL) was stirred at 80°C for 12 h. Additional $Cp_2Ti(TFA)_2$ (10 mg, 0.025 mmol, 10 mol%) was added and the mixture was stirred at 80°C for additional 12 h. Chromatography on silica (cyclohexane : ethyl acetate = 3 : 1) yielded the product **2i** (50 mg, 0.19 mmol, 74%).

The NMR data is in agreement with the literature.[9]

The relative configuration is assigned according to previous literature report.[9]



Bicyclo[3.2.0]heptane-6,7-diyl)bis(ethan-1-one) (2j)

According to GP 1, **1j** (72 mg, 0.40 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (24 mg, 0.060 mmol, 15 mol%), Zn (7.8 mg, 0.12 mmol, 30 mol%) in dioxane (8 mL) was stirred at 80°C for 18 h. Chromatography on silica (cyclohexane to ethyl acetate = 5 : 1 to 3 : 1) yielded the product **2j** as white solid (58 mg, 0.32 mmol, 80%).

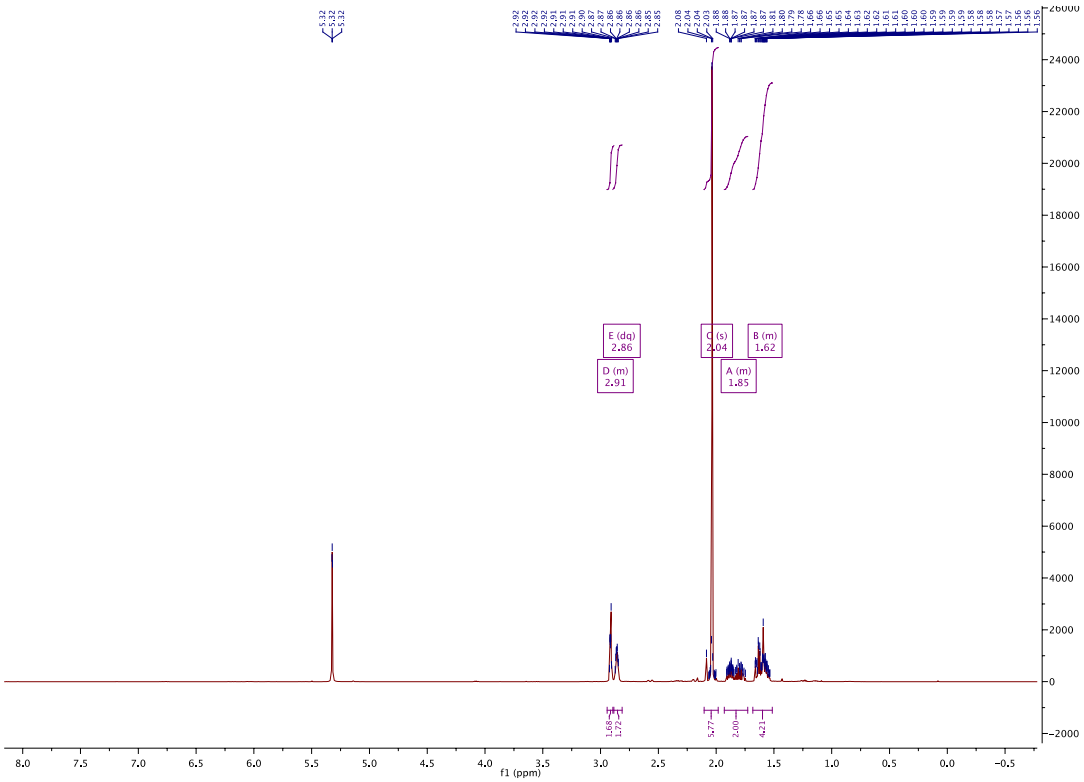
IR 2948, 1697, 1427, 1352, 1196, 1168, 595, 546, 448.

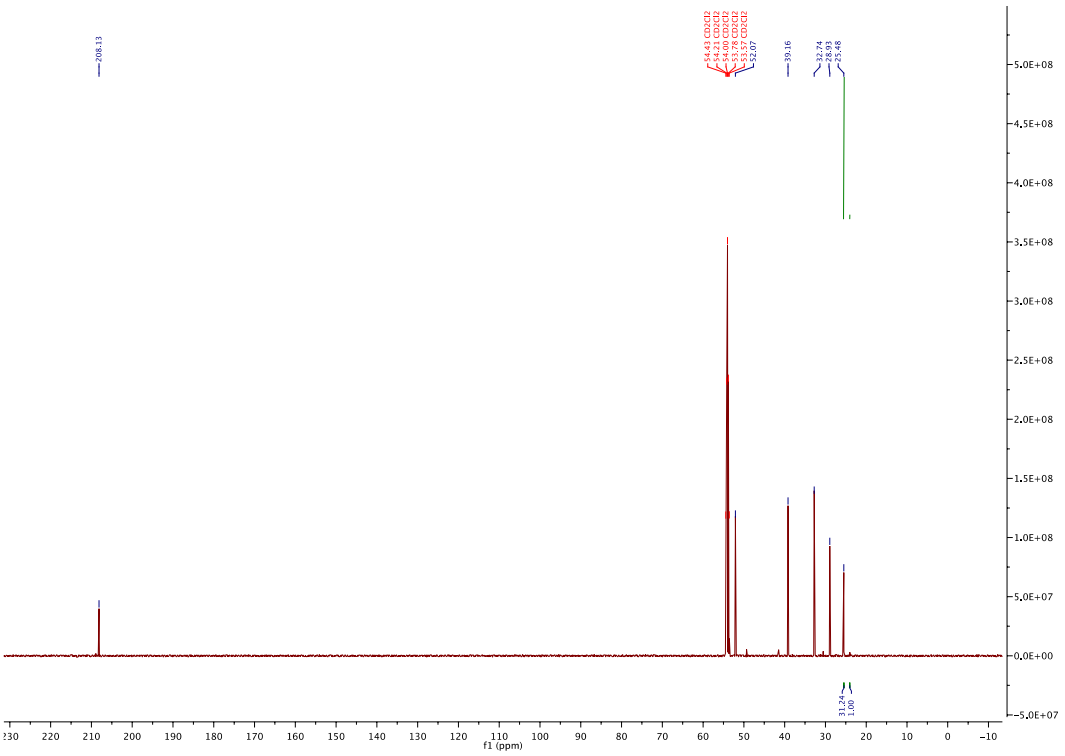
^{1}H NMR (500 MHz, CD_2Cl_2) δ 2.93 – 2.89 (m, 2H), 2.86 (dq, *J* = 4.5, 2.2 Hz, 2H), 2.04 (s, 6H), 1.92 – 1.74 (m, 2H), 1.68 – 1.52 (m, 4H).

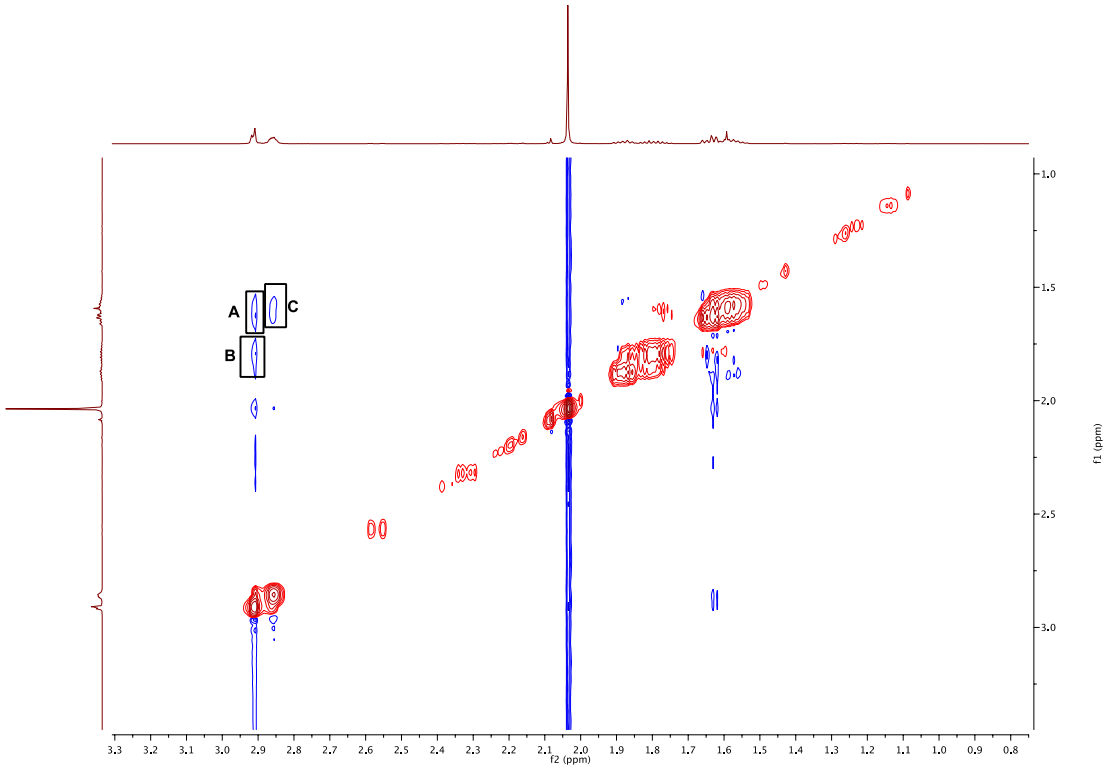
^{13}C NMR (126 MHz, CD_2Cl_2) δ 208.13, 52.07, 39.16, 32.74, 28.93, 25.48.

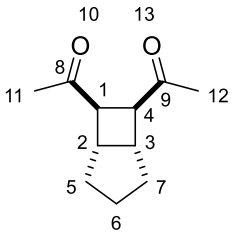
HRMS (ESI) calculated for $C_{17}H_{24}O_2H$ $[M+H]^+$:181.1150, found 181.1223

m.p. 60 °C




208.13
54.43 CD2Cl2
54.21 CD2Cl2
53.99 CD2Cl2
53.76 CD2Cl2
53.57 CD2Cl2
52.07
39.16
32.74
28.93
25.48
31.24
1.00
f1 (ppm)


A
B
C
f2 (ppm)
f1 (ppm)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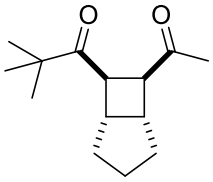
Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H1 and H5 (bottom) or H4 and H7 (bottom), the cross peak (**B)** of H1 and H6 (bottom) or H4 and H6 (bottom), the cross peak (**C)** of H3 and H7 (top) or H2 and H5 (top).



7-Acetylbicyclo[3.2.0]heptan-6-yl)-2,2-dimethylpropan-1-one (2m)

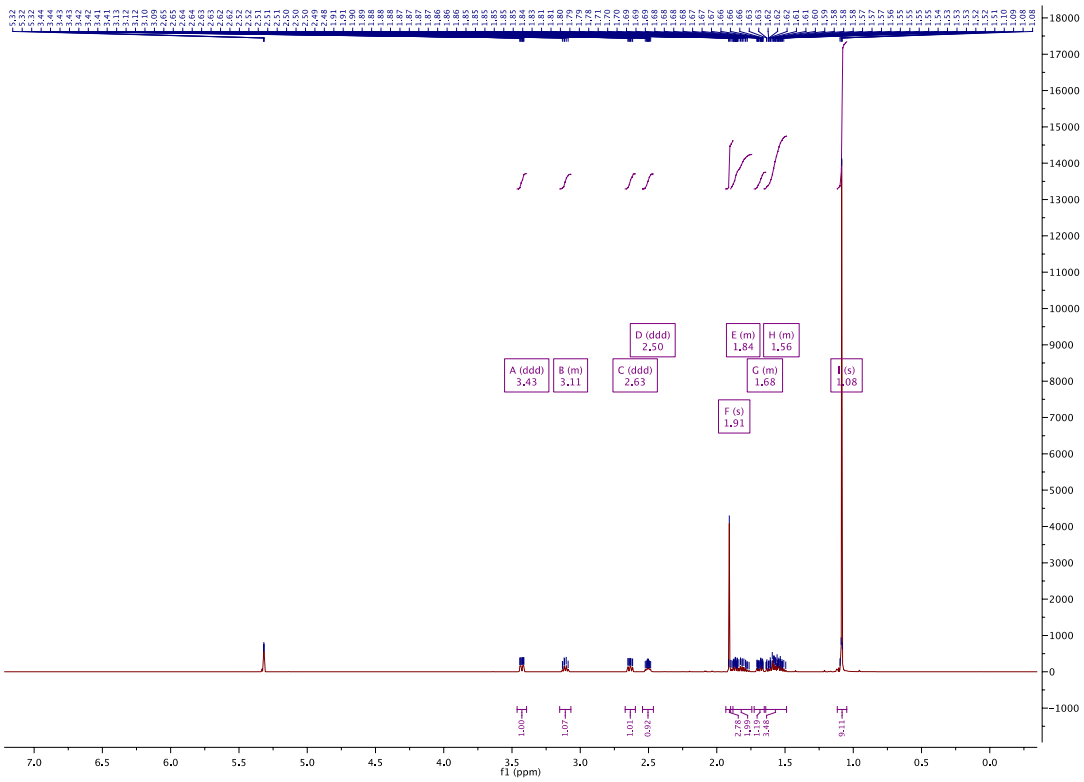
According to GP 1, **1m** (56 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 24 h. Chromatography on silica (cyclohexane : ethyl acetate = 8 : 1 to 4 : 1) yielded the product **2m** as liquid (44 mg, 0.20 mmol, 78%).

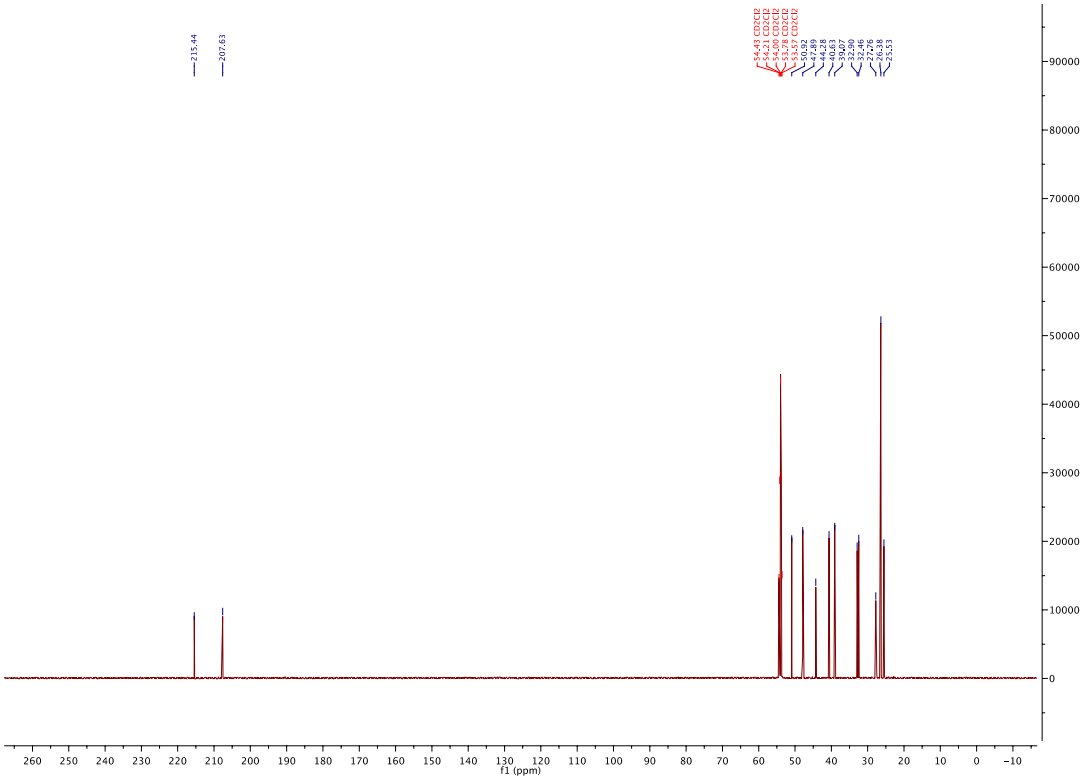
IR 2950, 1704, 1692, 1477, 1353, 1231, 1181, 1072, 1010, 565.

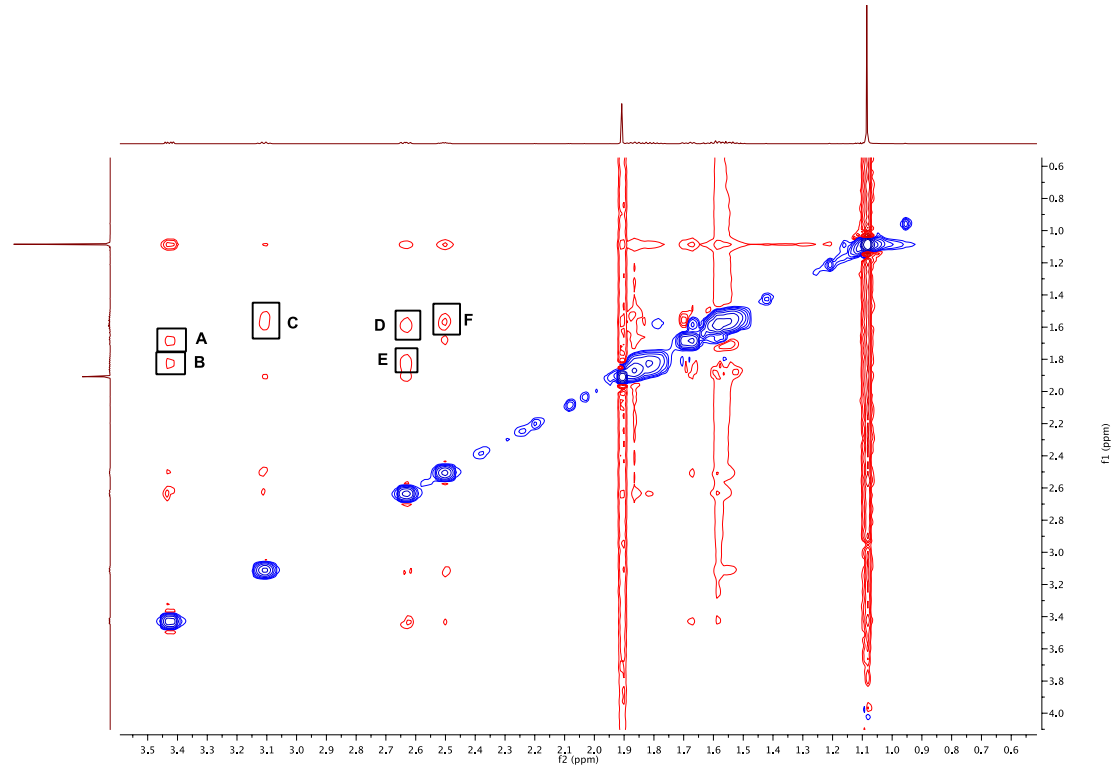
^{1}H NMR (499 MHz, CD_2Cl_2) δ 3.43 (ddd, *J* = 9.5, 4.1, 1.0 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.63 (ddd, *J* = 9.6, 6.4, 1.3 Hz, 1H), 2.50 (ddd, *J* = 9.0, 7.2, 4.2 Hz, 1H), 1.91 (s, 3H), 1.88 – 1.76 (m, 2H), 1.72 – 1.65 (m, 1H), 1.64 – 1.49 (m, 3H), 1.08 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 215.44, 207.63, 50.92, 47.89, 44.28, 40.63, 39.07, 32.90, 32.46, 27.76, 26.38, 25.53.

HRMS (ESI) calculated for $C_{14}H_{22}O_2H$ $[M+H]^+$:223.1620, found 223.1693.




215.44
207.63
54.93 CD2Cl2
54.21 CD2Cl2
53.90 CD2Cl2
53.59 CD2Cl2
51.57 CD2Cl2
50.92
44.88
44.28
40.83
39.07
32.90
32.46
27.25
26.38
25.53
f1 (ppm)


A
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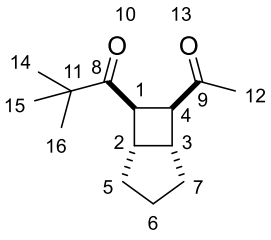
f2 (ppm)
f1 (ppm)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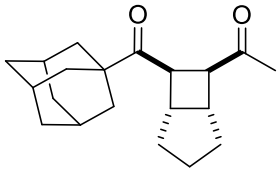
Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H1 and H5 (bottom), the cross peak (**B)** of H1 and H6 (bottom), the cross peak (**C)** of H3 and H7 (top), the cross peak (**D**) of H4 and H7 (bottom), the cross peak (**E)** of H4 and H6 (bottom), the cross peak (**F)** of H2 and H5 (top).



(Adamantane-1-carbonyl)bicyclo[3.2.0]heptan-6-yl)ethan-1-one (2n)

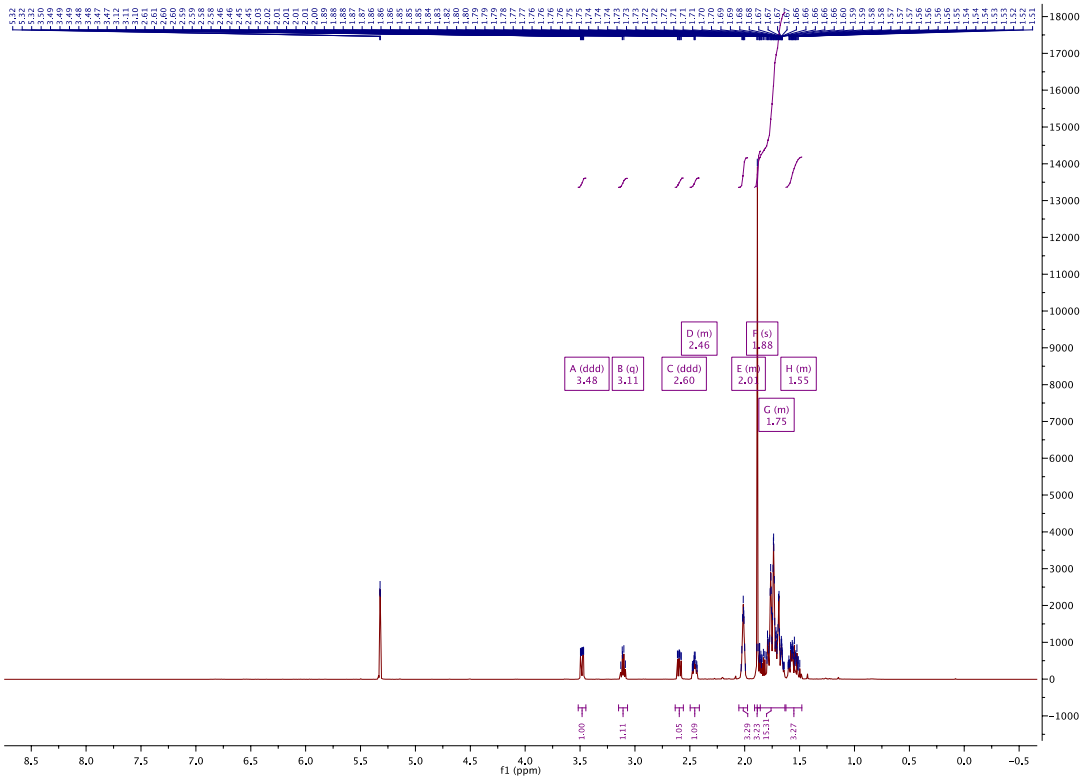
According to GP 1, **1n** (76 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 24 h. Chromatography on silica yielded the product **2n** as liquid (61 mg, 0.20 mmol, 80%).

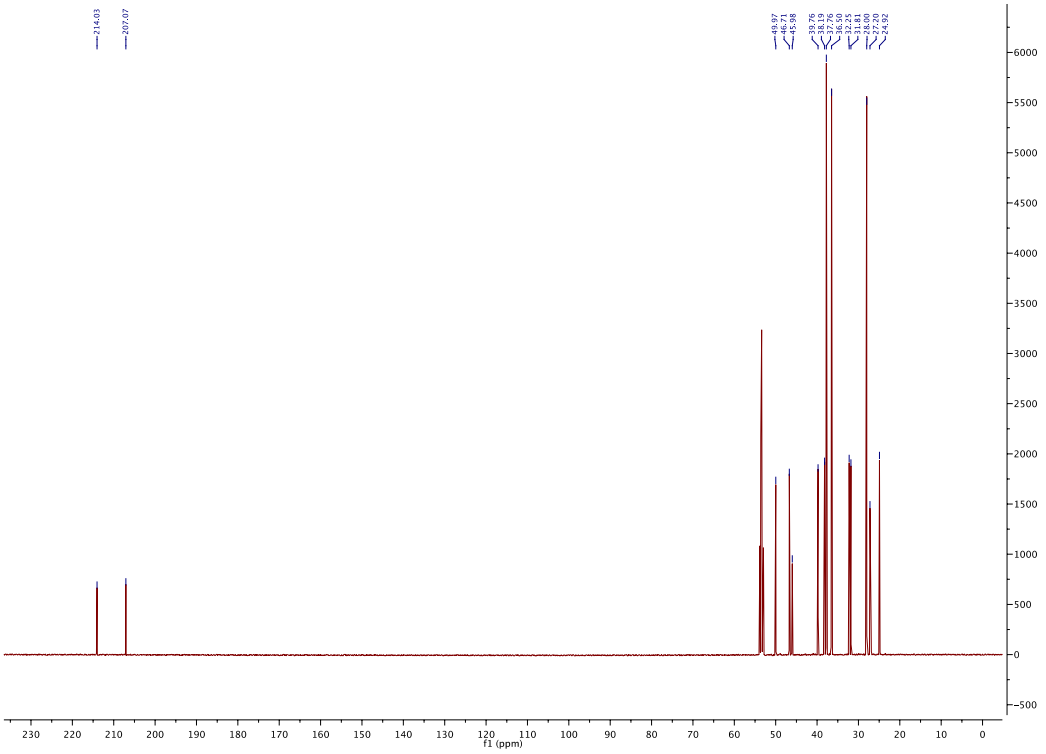
IR 2903, 2849, 1707, 1688, 1449, 1348, 1307, 1160, 1023, 569.

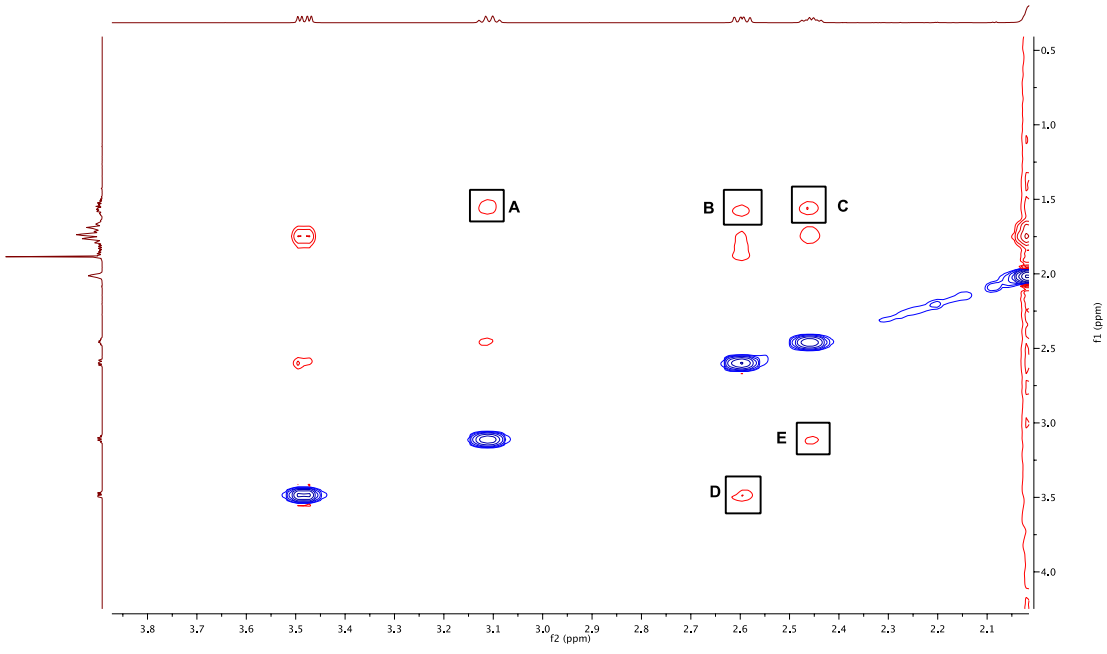
^{1}H NMR (500 MHz, , CD_2Cl_2) δ 3.48 (ddd, *J* = 9.5, 4.1, 1.0 Hz, 1H), 3.11 (q, *J* = 6.8 Hz, 1H), 2.60 (ddd, *J* = 9.7, 6.4, 1.3 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.05 – 1.98 (m, 3H), 1.88 (s, 3H), 1.87 – 1.63 (m, 15H), 1.62 – 1.48 (m, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 214.03, 207.07, 49.97, 46.71, 45.98, 39.76, 38.19, 37.76, 36.50, 32.25, 31.81, 28.00, 27.20, 24.92.

HRMS (ESI) calculated for $C_{20}H_{28}OH$ $[M+H]^+$:301.2089, found 301.2162.




214.03
207.07
49.97
46.71
43.98
39.78
38.13
37.76
36.50
34.23
31.81
25.80
25.00
24.92
f1 (ppm)


A
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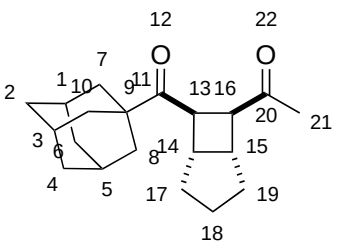
f2 (ppm)
f1 (ppm)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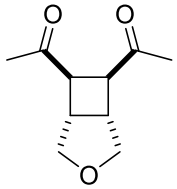
18

Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H15 and H19 (TOP), the cross peak (**B)** of H16 and H19 (bottom), the cross peak (**C)** of H14 and H17 (top), the cross peak (**D**) of H13 and H16, the cross peak (**E)** of H14 and H15.



3-Oxabicyclo[3.2.0]heptane-6,7-diyl)bis(ethan-1-one) (2o)

According to GP 1, **1o** (55 mg, 0.30 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (18 mg, 0.045 mmol, 15 mol%), Zn (5.9 mg, 0.070 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 18 h. Chromatography on silica (cyclohexane : ethyl acetate = 4 : 1 to 1 : 1) yielded the product **2o** as white solid (39 mg, 0.21 mmol, 70%).

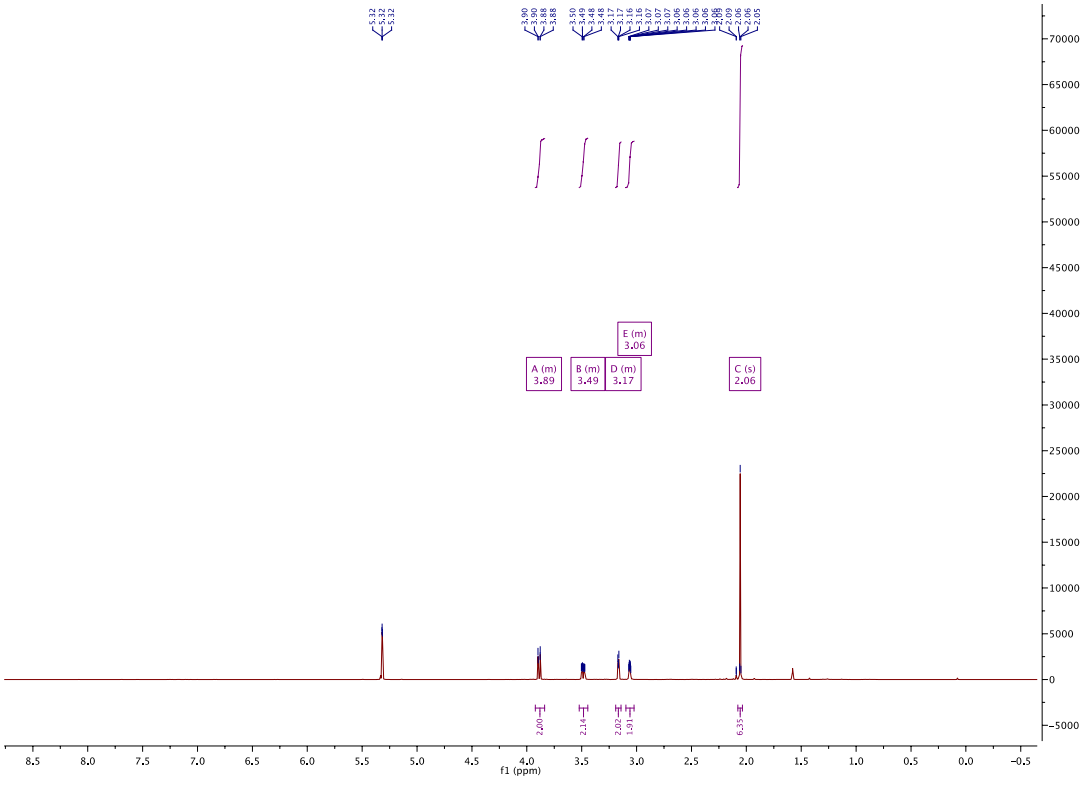
IR 2921, 2851, 2360, 2342, 1697, 1423, 1357, 1245, 1182, 1061, 1022, 996, 909, 872, 742, 659, 579, 552.

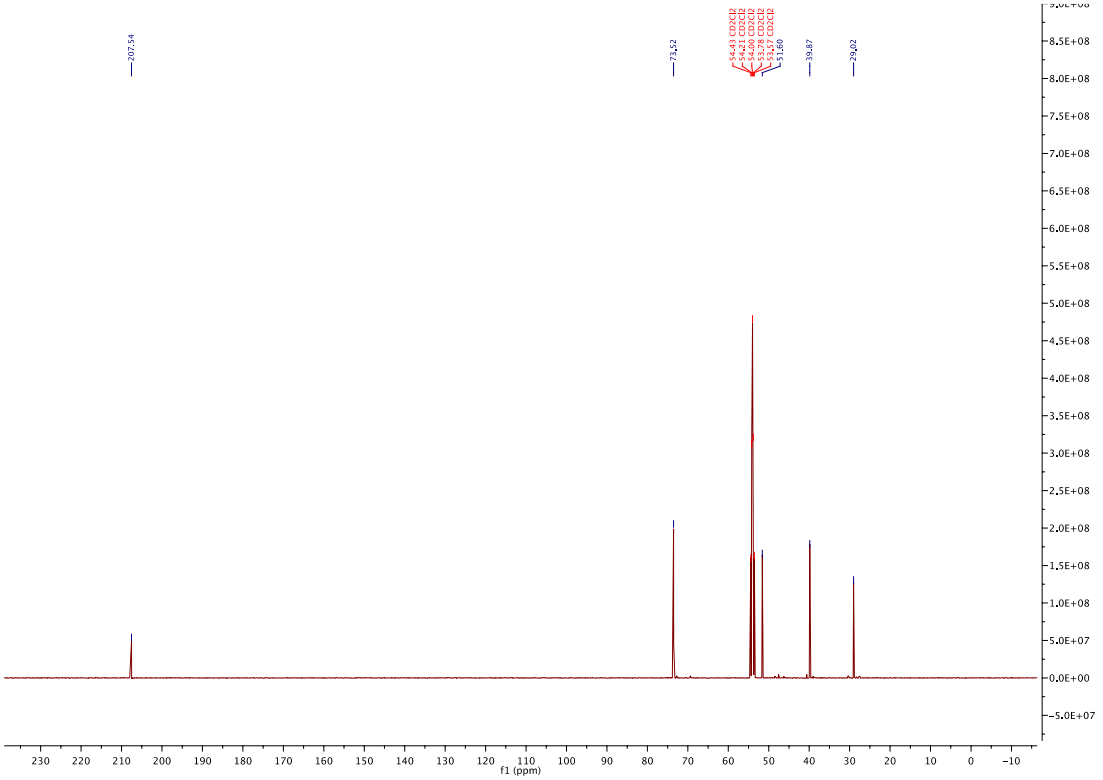
^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.92 – 3.84 (m, 2H), 3.52 – 3.44 (m, 2H), 3.19 – 3.15 (m, 2H), 3.10 – 3.02 (m, 2H), 2.06 (s, 6H).

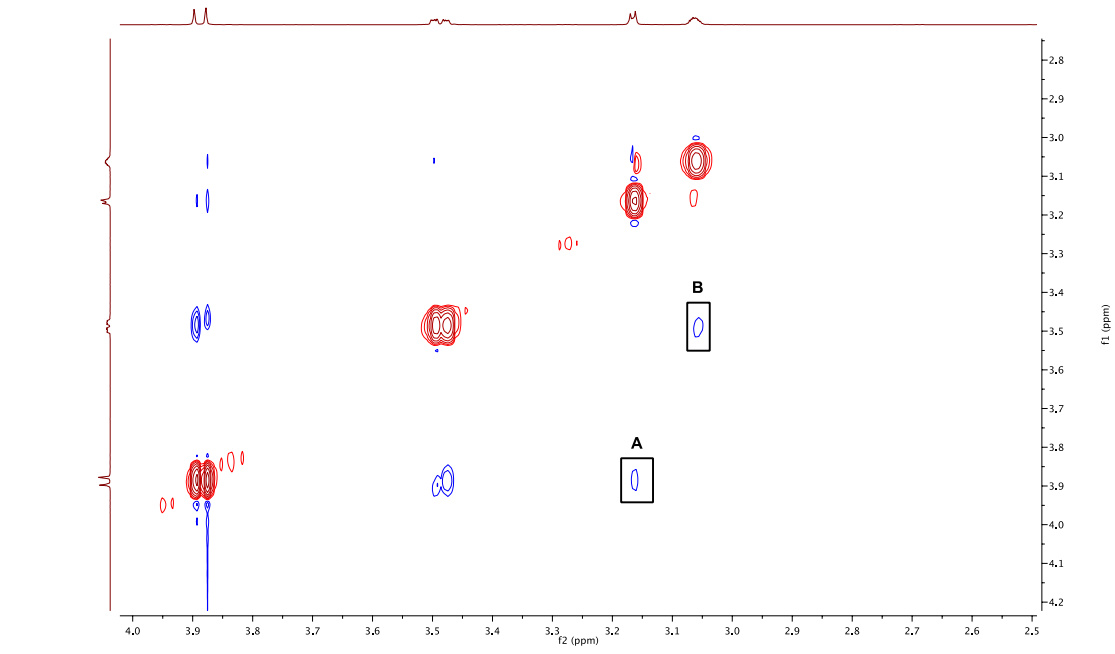
^{13}C NMR (126 MHz, CD_2Cl_2) δ 207.54, 73.52, 51.60, 39.87, 29.02.

HRMS (ESI) calculated for $C_{10}H_{14}O_3H$ $[M+H]^+$:183.0943, found 183.1016.

m.p. 50 ℃




207.54
73.52
54.41 CD2Cl2
54.21 CD2Cl2
54.00 CD2Cl2
53.79 CD2Cl2
53.58 CD2Cl2
51.60
39.87
29.02
f1 (ppm)


A
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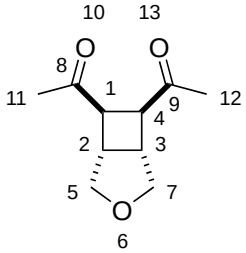
f2 (ppm)
f1 (ppm)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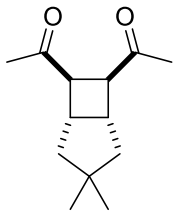
Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H1 and H5 (bottom) or H4 and H7 (bottom), the cross peak (**B)** of H3 and H7 (top) or H2 and H5 (top).



3,3-Dimethylbicyclo[3.2.0]heptane-6,7-diyl)bis(ethan-1-one) (2p)

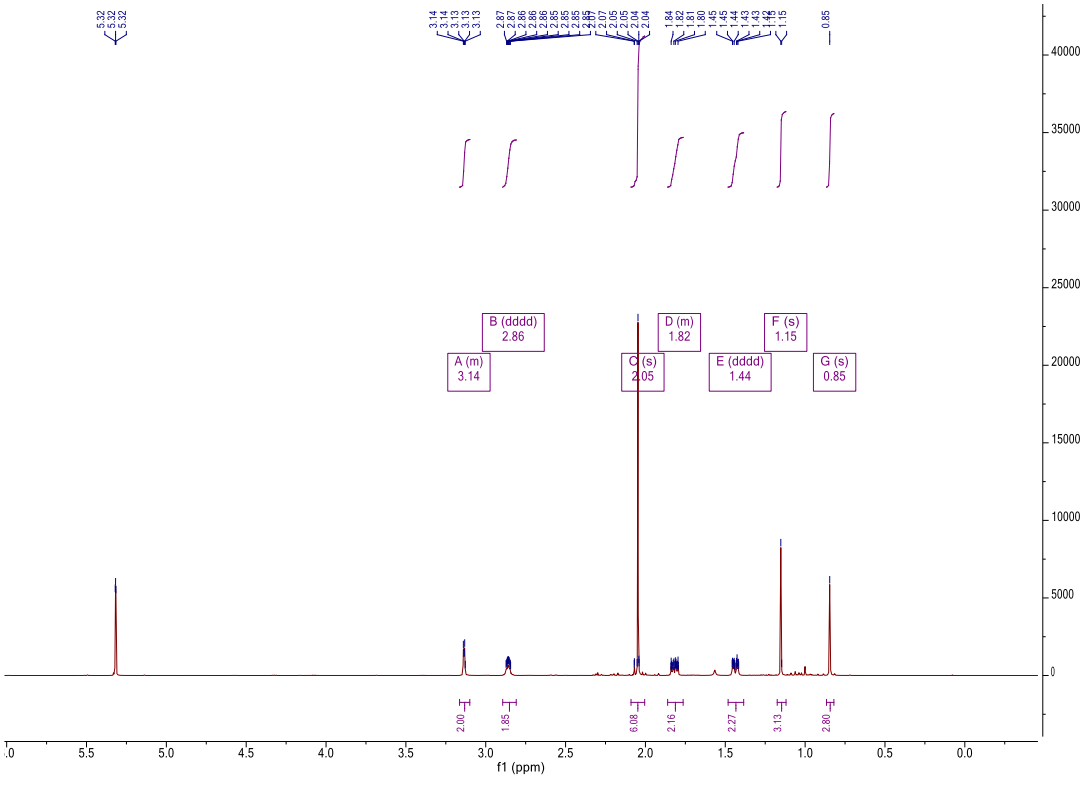
According to GP 1, **1p** (52 mg, 0.25 mmol, 1.0 eq.), $Cp_2Ti(TFA)_2$ (15 mg, 0.038 mmol, 15 mol%), Zn (5 mg, 0.075 mmol, 30 mol%) in dioxane (5 mL) was stirred at 80°C for 18 h. Chromatography on silica yielded the product **2p** as liquid (46 mg, 0.22 mmol, 88%).

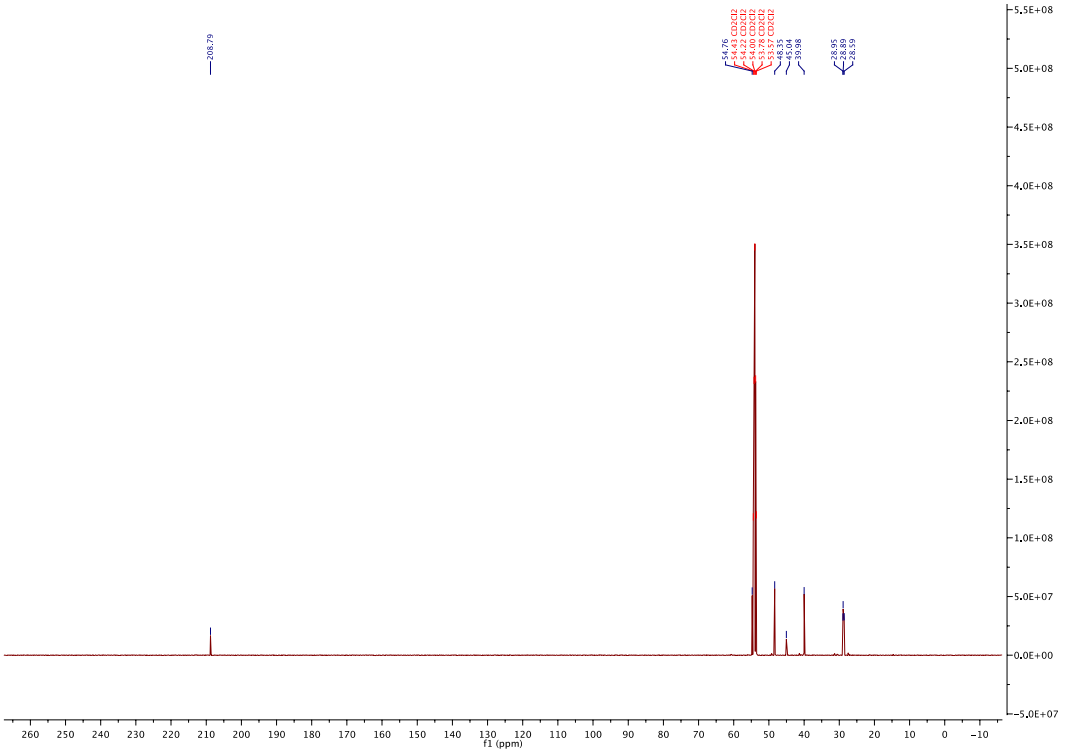
IR 2952, 2864, 1703, 1463, 1357, 1184, 561.

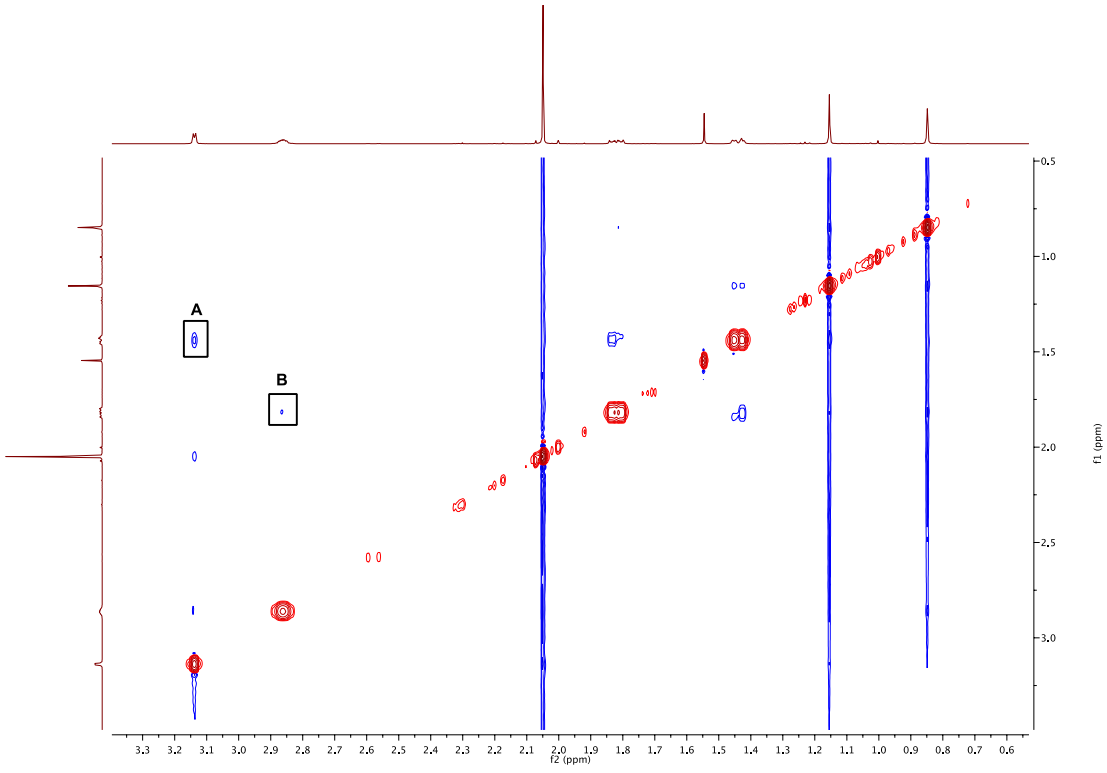
^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.16 – 3.10 (m, 2H), 2.86 (dddd, *J* = 5.3, 4.3, 2.9, 1.2 Hz, 2H), 2.05 (s, 6H), 1.85 – 1.76 (m, 2H), 1.44 (dddd, *J* = 12.9, 5.0, 2.0, 1.0 Hz, 2H), 1.15 (s, 3H), 0.85 (s, 3H).

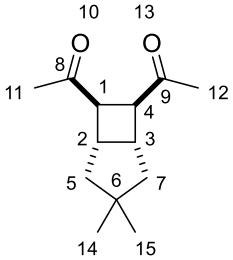
^{13}C NMR (126 MHz, CD_2Cl_2) δ 208.79, 54.76, 48.35, 45.04, 39.98, 28.95, 28.89, 28.59.

HRMS (ESI) calculated for $C_{14}H_{22}O_2H$ $[M+H]^+$:223.1620, found 223.1693.




208.79
54.76
54.43 CDCl2
54.22 CDCl2
54.00 CDCl2
53.78 CDCl2
53.57 CDCl2
45.35
45.04
39.98
28.95
28.89
28.59
f1 (ppm)


A
B
f2 (ppm)
f1 (ppm)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Assignment was based on COSY, HSQC, HMBC. The relative configuration was assigned according to NOESY. We observed the cross peak (**A)** of H1 and H5 (bottom) or H4 and H7 (bottom), the cross peak (**B)** of H3 and H7 (top) or H2 and H5 (top).

7. Additional Computational and Technical Details

After using the CREST 2.11 program[1] for the generation of conformers for every compound of interest with X=TFA, the resulting conformational ensembles were refined in a multi-level approach using the CENSO 1.0.0 program[2] in conjunction with the TURBOMOLE 7.5.1 program package. The refinement started with the default low-level pre-screening in part 0 with a free energy threshold of 4 kcal mol^{-1} followed by a screening (part 1) on the r^{2}SCAN-3c level of theory and free energy contributions calculated with GFN2-xTB at 353.15 K. All conformers below the threshold of 2.5 kcal mol^{-1} above the lowest one were taken into account for the final optimization (part 2) on the r^{2}SCAN-3c + COSMO-RS[1,4-dioxane] + G_{mRRHO}(GFN2-xTB(ALPB[1,4-dioxane])) // r^{2}SCAN-3c(DCOSMO-RS[1,4-dioxane])[12] level of theory.

All further geometry optimizations and single-point calculations were performed with the TURBOMOLE 7.4.1 program package (version 7.5.1 for all r^{2}SCAN-3c calculations). The resolution of the identity (RI) approximation was generally applied using the default auxiliary basis sets.[13] The energy convergence threshold for all single-point SCF calculations with TURBOMOLE 7.4.1/7.5.1 was set to the default value of 10^{-7} E_{h} and the energy and gradient convergence thresholds for geometry optimizations using the STATPT optimizer were set to $5 \cdot 10^{-7}$ E_{h} and 10^{-3} E_{h} Bohr^{-1}, respectively (10^{-6} E_{h} and $2 \cdot 10^{-3}$ E_{h} Bohr^{-1} for transition state optimizations). All calculations applied the m5 numerical grid. The conformer lowest in free energy of each compound was re-optimized with r^{2}SCAN-3c(COSMO[1,4-dioxane]) followed by a frequency calculation used to obtain the modified rigid rotor harmonic oscillator free energy contribution (G_{mRRHO}) at 353.15 K (without scaling of the vibrational frequencies). On these structures, PW6B95-D4/def2-QZVP single-point energies as well as solvation free energy contributions (δG_{solv}) were calculated within the conductor-like screening model for real solvents (COSMO-RS[1,4-dioxane], 353.15 K). For the latter ones, the COSMOtherm program with the BP_TZVP_19 parametrization of 2019 was used. The total Gibbs free energy G_{c} of a compound is the sum of the single-point energy E_{c} and the two free energy contributions:

$$G_{\mathrm{c}} = E_{\mathrm{c}} + G_{\mathrm{mRRHO}} + \delta G_{\mathrm{solv}}$$

Transition state structures obtained from the GSM reaction path searches at the GFN2-xTB(ALPB[1,4-dioxane]) level of theory were pre-optimized on the r^{2}SCAN-3c(COSMO[1,4-dioxane]) level of theory with the atoms most affected by the reaction remaining fixed in order to facilitate the convergence towards the desired saddle point on the potential energy surface. Afterwards a full optimization and frequency calculation was performed on the same level and it was verified that the corresponding imaginary vibrational mode was present. All subsequent single-point and free energy contribution calculations mentioned above were performed in the same way for the

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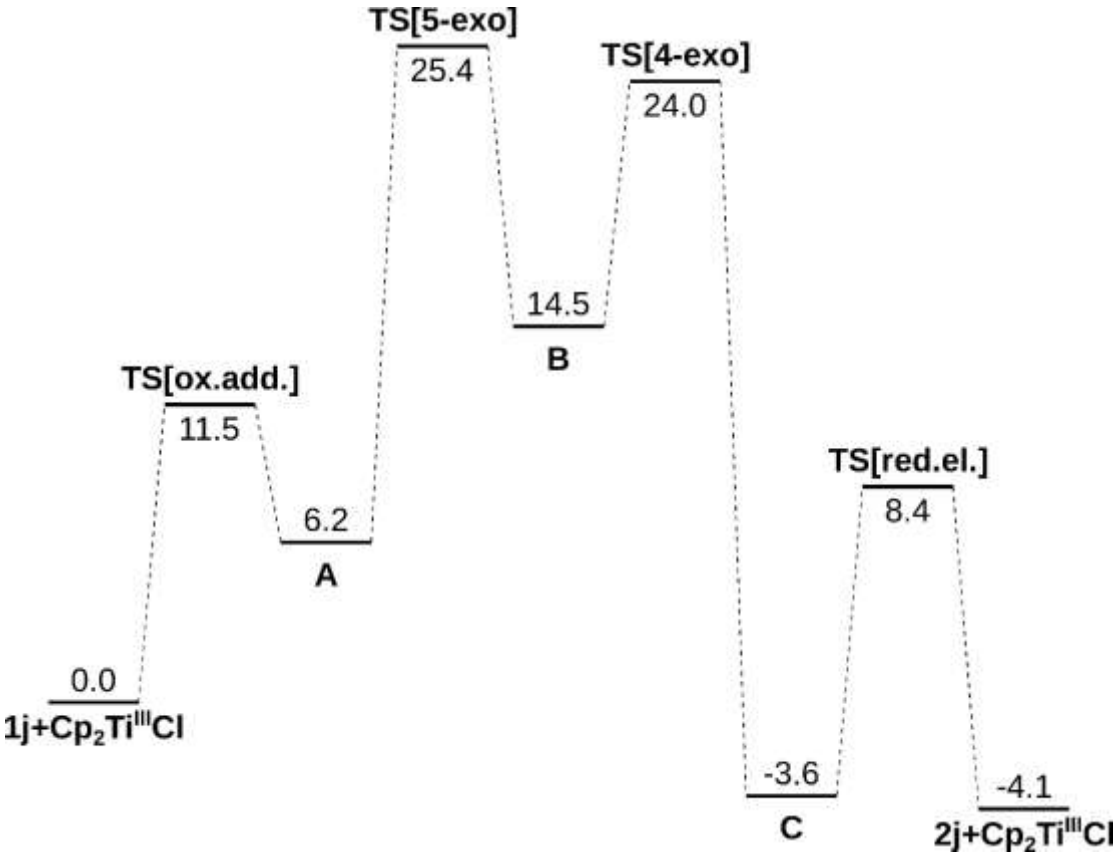
[1] Program available at https://github.com/grimme-lab/crest/releases.

[2] Program available at https://github.com/grimme-lab/CENSO/releases upon personal request.

optimized transition state structures. No CREST or CENSO treatment was done for the transition states.

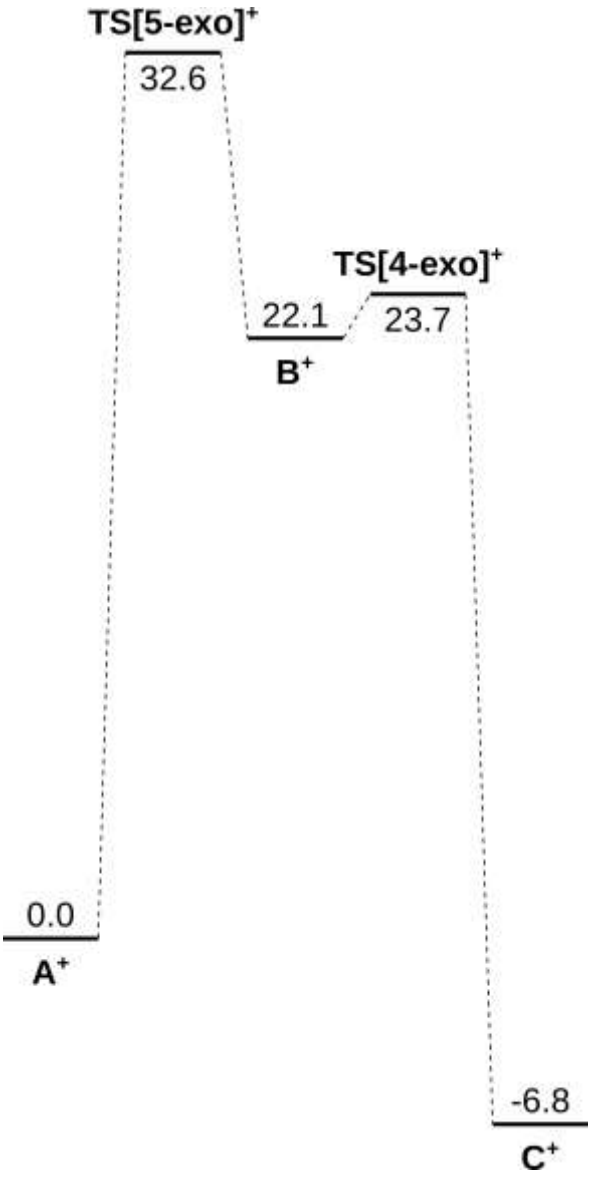
All optimized minimum and transition state structures containing the titanium catalyst with the TFA ligand were used to create input structures for the chlorine analogues with a Cl ligand instead of TFA. The structures were optimized directly (no further CREST or CENSO treatment) and all subsequent calculations were done in the same way as mentioned above. The resulting energy profile analogous to Scheme 3 is shown in Scheme S1.



Scheme S1: Energy profile of the conversion of **1j** to **2j** in the presence of Cp_2TiCl in 1,4-dioxane at 353.15 K. All Gibbs free energies are shown in kcal mol^{-1}. The complexes' labels refer to the ones given in Scheme 3. All structures were investigated at the PW6B95-D4/def2-QZVP+COMSO-RS[1,4-dioxane]//r^2SCAN-3c(COSMO[1,4-dioxane]) level of theory.

In order to generate structures of the chelated cationic analogues of **A**, **B** and **C** (denoted as $\mathbf{A}^+$, $\mathbf{B}^+$ and $\mathbf{C}^+$, respectively) as well as the corresponding transition states (**TS[5-exo]**$^+$, **TS[4-exo]**$^+$), new conformational investigations were performed with CREST and CENSO in the same way as mentioned above. Again, the same subsequent calculations were done to yield the free energies on the PW6B95-D4/def2-QZVP+COSMO-RS[1,4-dioxane]//r^2SCAN-3c(COSMO[1,4-dioxane]) level of theory. The energy profile of this part of the reaction (normed to $\mathbf{A}^+$) is shown in Scheme S2

and is analogous to the inner part of Schemes 3 and S1.



Scheme S2: Energy profile for the 5-exo and 4-exo cyclisation steps of the chelated cationic reaction path without TFA or Cl. This path is analogous to the one shown in Schemes 3 and S1 (but normed to $\mathbf{A}^+$) and is also investigated in 1,4-dioxane at 353.15 K. All Gibbs free energies are shown in kcal mol^{-1}. All structures were investigated at the PW6B95-D4/def2-QZVP+COMSO-RS[1,4-dioxane]//r^2SCAN-3c(COSMO[1,4-dioxane]) level of theory.

8. Molecular Structures

In the following, all molecular structures optimized on the r^{2}SCAN-3c level of theory are listed in xyz format.

```
14
1,4-dioxane
C    -3.8705629    1.7819015   -0.2006863
O    -4.6943078    0.7179380    0.2865020
C    -2.4241189    1.5639286    0.2019602
H    -4.2598061    2.7081144    0.2353381
H    -3.9484207    1.8407243   -1.2997441
O    -1.9476222    0.3087344   -0.2934021
H    -2.3336091    1.5897713    1.3013146
H    -1.7802146    2.3385112   -0.2280477
C    -2.7712523   -0.7554594    0.1935052
C    -4.2179008   -0.5375105   -0.2083194
H    -2.6929434   -0.8149106    1.2924970
H    -2.3821532   -1.6814201   -0.2431819
H    -4.8615340   -1.3118531    0.2225251
H    -4.3090741   -0.5640601   -1.3076010

29
Compound 1j
C     1.8727338   -4.6987541   -0.5678553
C     0.7990189   -4.6550714    0.4961974
O     0.7147747   -5.5376123    1.3418834
C    -0.1598286   -3.5345208    0.5199409
C    -0.1642308   -2.5109524   -0.3431698
C    -1.1208220   -1.3674850   -0.2980148
C    -0.3944225   -0.0336986   -0.0601499
C    -1.3660073    1.1575145   -0.0689663
C    -0.6618289    2.4402332    0.2197666
C    -0.5815944    3.4729180   -0.6286516
C     0.1339547    4.7341255   -0.3583956
O     0.1479945    5.6132587   -1.2116978
C     0.8412682    4.9243804    0.9646485
H     1.3069694    5.9104996    0.9806783
H     1.6091119    4.1560933    1.1073316
H     0.1345988    4.8407488    1.7975331
H    -1.0629796    3.4268654   -1.6049808
H    -0.1698234    2.5024031    1.1916182
H    -2.1330623    0.9879063    0.7013292
H    -1.8799596    1.2158260   -1.0359175
H     0.3688074    0.1169165   -0.8345243
```

```
H     0.1324820   -0.0760800    0.9018492
H    -1.6548536   -1.3078035   -1.2580521
H    -1.8711401   -1.5310389    0.4848164
H     0.5860235   -2.4705652   -1.1343053
H    -0.8986518   -3.5890316    1.3188288
H     2.4778297   -5.5950685   -0.4262829
H     2.5140933   -3.8126212   -0.5072868
H     1.4268585   -4.7134320   -1.5683695

29
Compound 2j
C     0.0344958   -0.7061936    0.6288178
C     1.2061832   -1.5202209    0.1613326
O     2.1285704   -1.0261717   -0.4633969
C     1.1390718   -2.9977777    0.4560472
H     1.8228432   -3.5496777   -0.1911301
H     1.4352564   -3.1523114    1.5015417
H     0.1170214   -3.3773121    0.3526582
H    -0.2966244   -1.0416634    1.6194231
C    -1.1091982   -0.7665194   -0.4540121
C    -2.5279755   -0.9626441    0.0874308
H    -2.5929707   -1.7661236    0.8302951
C    -2.9269510    0.4157265    0.6403460
H    -4.0108727    0.5368117    0.7333408
C    -2.2951511    1.3974419   -0.3612939
C    -0.9400683    0.7716118   -0.6965595
H    -0.5343685    1.0728688   -1.6652866
C     0.1131650    0.8348398    0.4290267
C     1.4499661    1.4757510    0.1137845
O     1.6194031    2.1296954   -0.8978171
C     2.5005582    1.4114505    1.1985874
H     3.4901397    1.3210753    0.7460914
H     2.3320470    0.5889573    1.8989549
H     2.4645285    2.3552620    1.7573990
H    -0.2547250    1.3509317    1.3289176
H    -2.1977201    2.4154972    0.0330700
H    -2.9129938    1.4483659   -1.2669583
H    -2.4978678    0.5622817    1.6405206
H    -3.1910555   -1.2280182   -0.7458349
H    -0.8765783   -1.4238940   -1.2981030

42
Cp2Ti(TFA)*(1,4-dioxane)
C    -0.1276200    3.1687471   -1.1289889
```

```
C    -1.2403326    2.4492740   -1.6362967
C    -0.7341742    1.2954464   -2.2908495
C     0.6691369    1.2976821   -2.1717966
C     1.0534320    2.4445626   -1.4385807
H     2.0650495    2.7022686   -1.1571552
Ti   -0.2290892    1.1557582    0.0814270
O     0.9360833   -0.5585587   -0.0289905
C     2.2115338   -0.6426676   -0.0736589
O     3.0563555    0.2393600   -0.0861683
C     2.6623631   -2.1300653   -0.1163169
F     2.1341785   -2.7639901   -1.1931836
F     3.9926966   -2.2648548   -0.1808875
F     2.2359282   -2.7946718    0.9852944
C    -0.2648696    0.5841192    2.3743965
C    -1.4017942    1.4047277    2.1618259
C    -0.9494526    2.6902521    1.8003266
C     0.4722589    2.6715780    1.8078406
C     0.8942682    1.3768329    2.1689623
H     1.9200667    1.0383815    2.2199546
H     1.1220700    3.4983478    1.5541054
H    -1.5742349    3.5368164    1.5473961
H    -2.4341713    1.0936351    2.2479360
H    -0.2768320   -0.4712087    2.6121480
O    -1.8203590   -0.4413294   -0.1549410
C    -3.1859050   -0.0198331   -0.3651678
C    -4.1305024   -0.9628184    0.3519548
H    -5.1679728   -0.6764973    0.1511293
H    -3.9503009   -0.9167220    1.4398438
O    -3.9655362   -2.2995009   -0.1142431
C    -2.6104978   -2.7169811    0.0739027
C    -1.6494603   -1.7979894   -0.6463649
H    -0.6111928   -2.0695177   -0.4537636
H    -1.8412435   -1.8030745   -1.7298971
H    -2.5298286   -3.7309946   -0.3300448
H    -2.3707253   -2.7403072    1.1501739
H    -3.2698947    0.9974947    0.0265062
H    -3.3951678   -0.0105023   -1.4455415
H     1.3365021    0.5230695   -2.5239272
H    -1.3234953    0.5256455   -2.7720902
H    -2.2776639    2.7510496   -1.5749142
H    -0.1733285    4.1060200   -0.5928414

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Complex A in Scheme 3 (TFA)
```

C	1.5475762	2.6533693	2.2774842
C	2.7419287	1.8922747	2.1671412
C	2.4179844	0.5425911	2.4273990
C	1.0315619	0.4594657	2.6750240
C	0.4894703	1.7673075	2.5834219
H	-0.5514803	2.0350209	2.7072792
Ti	1.2640774	1.2006063	0.4025025
O	-0.4582834	0.1491803	0.3248933
C	-1.1738387	-0.6852652	-0.3053902
C	-2.2904605	-1.2515514	0.3984210
C	-3.2244852	-2.0632976	-0.1418727
H	-3.1393513	-2.3634758	-1.1861700
C	-4.4127652	-2.5927674	0.5878450
H	-4.4261071	-2.2168662	1.6185784
H	-4.3234084	-3.6881088	0.6460606
C	-5.7462266	-2.2691569	-0.1129607
H	-5.6830746	-2.5678729	-1.1680562
H	-6.5411508	-2.8731923	0.3391167
C	-6.1518321	-0.7859848	-0.0237757
H	-7.1193367	-0.6735885	-0.5360696
H	-6.3061550	-0.4993537	1.0239452
C	-5.1631587	0.1217009	-0.6669905
C	-4.5996091	1.1936094	-0.0939641
C	-3.5305080	1.9503069	-0.7698441
O	-3.1424149	1.6751631	-1.9025883
C	-2.8643824	3.0440800	0.0286778
H	-3.5582016	3.5388401	0.7143522
H	-2.0694650	2.5802017	0.6309029
H	-2.4033604	3.7710709	-0.6431611
H	-4.8578471	1.4788150	0.9248725
H	-4.8546458	-0.1216351	-1.6857455
H	-2.3893224	-0.9304504	1.4346212
C	-0.8716759	-1.0311140	-1.7293173
H	-1.3957625	-0.3291215	-2.3919460
H	0.2001324	-0.9440852	-1.9085585
H	-1.1939664	-2.0428565	-1.9823892
O	2.1926876	-0.5530598	-0.2089826
C	2.0102432	-1.7610509	0.1754385
O	1.3280578	-2.2146084	1.0816153
C	2.8174251	-2.7442928	-0.7213488
F	2.3941069	-2.6703477	-2.0094153
F	2.6861624	-4.0202081	-0.3305741
F	4.1371549	-2.4497171	-0.7154127
C	2.1718823	3.1889799	-0.5862180

C 2.6131744 2.0946447 -1.3583089
C 1.4733634 1.5188103 -1.9790067
C 0.3334505 2.2467591 -1.5793297
C 0.7585919 3.2703479 -0.6990313
H 0.1229606 3.9936506 -0.2059061
H -0.6939870 2.0389238 -1.8539541
H 1.4881643 0.6501138 -2.6206534
H 3.6313940 1.7402740 -1.4479486
H 2.7990317 3.8364407 0.0105021
H 0.4805566 -0.4570564 2.8240561
H 3.1010054 -0.2944417 2.3822687
H 3.7229839 2.2737333 1.9164978
H 1.4596435 3.7220857 2.1392752

57
Complex B in Scheme 3 (TFA)
C 0.1133043 -1.9787898 1.1032077
C -0.9760422 -2.8799653 1.0252861
C -2.1351647 -2.2042079 1.4973215
C -1.7705672 -0.8838599 1.8111774
C -0.3766555 -0.7429079 1.5627994
H 0.1904298 0.1727387 1.6599994
Ti -1.4387445 -1.1702090 -0.5563136
O 0.1490407 -1.0603182 -1.5515539
C 1.4459474 -0.7215621 -1.4012066
C 1.7965526 0.4840515 -0.9163969
C 3.1951136 1.0131766 -0.7937432
H 3.8742140 0.4538497 -1.4449762
C 3.2754983 2.5229885 -1.0798473
H 2.6821845 2.8044478 -1.9559729
H 4.3198574 2.7900906 -1.2824129
C 2.7929427 3.2073871 0.2159836
H 3.3161080 4.1533463 0.3845747
H 1.7255539 3.4424104 0.1548934
C 3.0529567 2.1851256 1.3538275
H 3.6764608 2.5923952 2.1555338
H 2.1063762 1.8780398 1.8140830
C 3.7271940 0.9653708 0.6910497
C 3.4524790 -0.3292949 1.3511098
C 4.2093289 -1.5405287 1.1750237
O 3.7470374 -2.6179351 1.5856048
C 5.5596060 -1.4912093 0.4942674
H 6.2710808 -0.9360137 1.1175757
H 5.9296520 -2.5070986 0.3471299

```
H     5.5094368   -0.9741004   -0.4697230
H     2.5386706   -0.4415534    1.9310024
H     4.8122024    1.1352647    0.6287890
H     0.9840929    1.1449974   -0.6154905
C     2.3684711   -1.7980123   -1.8928842
H     2.2619351   -2.6964650   -1.2722771
H     2.0946072   -2.0774409   -2.9165038
H     3.4171899   -1.4983964   -1.8770333
O    -1.6135872    0.8401030   -0.4506781
C    -2.5149885    1.6305250    0.0048121
O    -3.6381259    1.3784906    0.4069755
C    -1.9877191    3.0912290    0.0436714
F    -2.9469687    3.9675988    0.3624495
F    -1.4582072    3.4667938   -1.1385655
F    -1.0074873    3.1946864    0.9780030
C    -2.3004591   -1.2617116   -2.8186672
C    -2.0836309   -2.5882229   -2.3748848
C    -2.9728053   -2.8396152   -1.3040644
C    -3.7316498   -1.6619015   -1.0771555
C    -3.3211146   -0.6982786   -2.0251578
H    -3.6957515    0.3132573   -2.0906775
H    -4.4764051   -1.5082487   -0.3085149
H    -3.0561880   -3.7663492   -0.7539170
H    -1.3345748   -3.2704102   -2.7539529
H    -1.7330439   -0.7470315   -3.5813931
H    -2.4435787   -0.1060830    2.1455756
H    -3.1294223   -2.6212737    1.5738598
H    -0.9234608   -3.9092102    0.6962528
H     1.1348038   -2.1915725    0.8180231

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Complex C in Scheme 3 (TFA)
C    -2.0732987    3.2763165   -0.9321721
C    -3.1113365    2.3605346   -1.2590703
C    -2.5340448    1.2910193   -1.9724802
C    -1.1420238    1.5238748   -2.0696827
C    -0.8574346    2.7600579   -1.4299459
H     0.1199723    3.2093606   -1.3162257
Ti   -1.5837190    1.2551101    0.2475016
O     0.4408794    0.6270810    0.1340573
C     1.2080219   -0.3050292    0.3966477
C     2.4574376   -0.4184898   -0.4163106
H     2.1002375   -0.8075811   -1.3814418
C     3.3008707    0.8614958   -0.6198420
```

C	3.1774841	1.8466536	0.5123873
O	2.7853102	1.4936280	1.6130661
C	3.6398760	3.2499964	0.2353456
H	2.9182483	3.7285252	-0.4390612
H	4.6009431	3.2406780	-0.2917149
H	3.7144835	3.8255310	1.1591569
H	3.2462309	1.3505932	-1.5977754
C	4.5983965	0.0007729	-0.3686185
C	5.3549122	-0.4814608	-1.6143173
C	4.6028850	-1.7344135	-2.0981438
H	5.2378834	-2.4017197	-2.6889671
C	4.1033235	-2.3876484	-0.7977199
H	3.2769819	-3.0892318	-0.9622399
C	3.6996545	-1.2018496	0.0770033
H	3.6956322	-1.4094664	1.1498919
H	4.9219006	-2.9391572	-0.3179381
H	3.7554767	-1.4526722	-2.7352050
H	5.4425978	0.2937535	-2.3834531
H	6.3722660	-0.7611398	-1.3140389
H	5.2655029	0.4254511	0.3878329
C	0.9127209	-1.3612149	1.4069380
H	1.5049816	-1.1487415	2.3065529
H	-0.1446469	-1.3785271	1.6649401
H	1.2318919	-2.3411219	1.0365293
O	-1.9791376	-0.7854051	-0.0608719
C	-1.4393225	-1.6628123	-0.8104978
O	-0.5134131	-1.5770816	-1.6115529
C	-2.1021373	-3.0548082	-0.5958131
F	-3.4361047	-3.0099042	-0.8095260
F	-1.9126627	-3.4772166	0.6814298
F	-1.5957366	-3.9983527	-1.4052088
C	-1.4122600	2.6364443	2.1924225
C	-2.7858541	2.5084717	1.8551917
C	-3.1599499	1.1516291	2.0153755
C	-2.0206781	0.4498034	2.4855478
C	-0.9506580	1.3616952	2.5962320
H	0.0670695	1.1266940	2.8792649
H	-1.9817710	-0.6138372	2.6745385
H	-4.1345224	0.7246931	1.8195495
H	-3.4356009	3.3058331	1.5232883
H	-0.8229898	3.5431036	2.1518347
H	-0.4226985	0.8396020	-2.4960472
H	-3.0537738	0.4089336	-2.3215929
H	-4.1551851	2.4562356	-0.9896682

```
H    -2.1901335    4.2004015   -0.3828311

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TS[oxidative addition] (TFA)
C     2.1855196    1.5320609    2.9208788
C     3.3517158    0.7384297    2.7389123
C     2.9425222   -0.5183975    2.2468928
C     1.5393420   -0.4965764    2.0915128
C     1.0615588    0.7762546    2.5076901
H     0.0322981    1.1077138    2.5141862
Ti    2.3894804    1.1637232    0.6063133
O    -0.1441698    0.4208583   -0.6413396
C    -0.4984833   -0.7529372   -0.4789869
C    -1.4381460   -1.0500911    0.6100486
C    -2.1664989   -2.1695704    0.7137266
H    -2.0000779   -2.9884421    0.0124394
C    -3.2794334   -2.3567335    1.6893029
H    -3.2993364   -1.5240366    2.4032391
H    -3.1000873   -3.2777810    2.2615831
C    -4.6567626   -2.4873134    1.0056756
H    -4.6205851   -3.2920154    0.2589749
H    -5.3849016   -2.7954967    1.7645024
C    -5.1653885   -1.1960192    0.3399355
H    -6.2012783   -1.3817678    0.0165758
H    -5.2049485   -0.3785042    1.0710754
C    -4.3769996   -0.7872533   -0.8579059
C    -3.9396457    0.4461654   -1.1334465
C    -3.0870796    0.7097676   -2.3165606
O    -2.7750249   -0.1749722   -3.1040506
C    -2.5897824    2.1237183   -2.4744889
H    -3.4368468    2.8175465   -2.5367881
H    -2.0099723    2.4006035   -1.5857549
H    -1.9656181    2.2109866   -3.3647737
H    -4.1383649    1.2752712   -0.4550594
H    -4.1287988   -1.5732190   -1.5750264
H    -1.6383801   -0.2107638    1.2748309
C    -0.0991675   -1.8402507   -1.4369702
H    -0.9586239   -2.0546473   -2.0851502
H     0.7297229   -1.5114747   -2.0607018
H     0.1723053   -2.7640659   -0.9168940
O     5.2220569   -0.5144660   -0.1918762
C     4.1855564   -0.8091057   -0.7646590
O     3.0176451   -0.2958961   -0.6417383
C     4.1789499   -1.9886617   -1.7747649
```

```
F     5.4156350   -2.3808623   -2.1079924
F     3.5268324   -1.6744937   -2.9150013
F     3.5433795   -3.0564111   -1.2277317
C     3.3084744    3.3447832    0.7770613
C     3.9480962    2.6824759   -0.2967398
C     2.9659496    2.4356113   -1.2911222
C     1.7278810    2.9400849   -0.8263642
C     1.9336817    3.4979076    0.4534859
H     1.1739332    3.9388660    1.0853843
H     0.7824909    2.8401371   -1.3348754
H     3.1209769    1.9017624   -2.2186365
H     4.9878558    2.3870097   -0.3398116
H     3.7852518    3.6595775    1.6954822
H     0.9401434   -1.3082945    1.7010171
H     3.6020349   -1.3290739    1.9679706
H     4.3721119    1.0418935    2.9325543
H     2.1610002    2.5463860    3.2939587

57
TS[5-exo cyclization] (TFA)
C     2.5428549    2.3047208    2.2923967
C     3.7329780    1.5475591    2.1421304
C     3.4183242    0.1954826    2.4164069
C     2.0441925    0.1101586    2.7156191
C     1.4989933    1.4136330    2.6355284
H     0.4580276    1.6765167    2.7706883
Ti    2.2117555    0.8578346    0.4096391
O     0.5920786   -0.0977336    0.3543455
C    -0.3089261   -0.8275471   -0.2795859
C    -1.4546921   -1.1503343    0.3992772
C    -2.5959764   -1.7989455   -0.1494588
H    -2.4522987   -2.2507812   -1.1306360
C    -3.5322147   -2.5837343    0.7332402
H    -3.5974771   -2.1128060    1.7233394
H    -3.1373240   -3.5988548    0.8790536
C    -4.9033186   -2.6020711    0.0620742
H    -4.8424926   -3.1676995   -0.8774838
H    -5.6691792   -3.0775288    0.6839750
C    -5.2303130   -1.1337258   -0.2266908
H    -6.0613556   -1.0392100   -0.9371742
H    -5.5404595   -0.6419855    0.7042378
C    -4.0003402   -0.4386899   -0.7692955
C    -3.6565164    0.8320212   -0.2896068
C    -2.6185020    1.6211292   -0.8927777
```

O -2.0601443 1.2868025 -1.9533480
C -2.1503557 2.8582244 -0.1529151
H -2.9419119 3.3102272 0.4516286
H -1.3381265 2.5632204 0.5267471
H -1.7518675 3.5909784 -0.8594180
H -4.0698834 1.1725966 0.6585671
H -3.7671362 -0.6047971 -1.8212531
H -1.5253114 -0.7768949 1.4207072
C 0.0122971 -1.2577781 -1.6780403
H -0.1916906 -0.4439362 -2.3824455
H 1.0716283 -1.5206765 -1.7481253
H -0.5800706 -2.1214997 -1.9836318
O 3.2915984 -0.7388561 -0.2369692
C 3.1539628 -1.9733227 0.1086145
O 2.4571558 -2.4762071 0.9690902
C 4.0450779 -2.8805458 -0.7862348
F 3.6615216 -2.7881881 -2.0825886
F 3.9694739 -4.1692940 -0.4318852
F 5.3430516 -2.5102374 -0.7196937
C 3.1275028 2.8633983 -0.5735460
C 3.4990403 1.7935733 -1.4054081
C 2.3149752 1.2440478 -1.9683139
C 1.2141346 1.9747043 -1.4815025
C 1.7080951 2.9578242 -0.5884543
H 1.1108473 3.6738607 -0.0393178
H 0.1679385 1.7888355 -1.6993047
H 2.2745178 0.3862942 -2.6240994
H 4.5028188 1.4195998 -1.5565651
H 3.7999413 3.4815954 0.0044377
H 1.4955926 -0.8059549 2.8774974
H 4.1040416 -0.6382037 2.3586480
H 4.7060726 1.9294153 1.8636694
H 2.4473937 3.3737856 2.1642110

57
TS[4-exo cyclization] (TFA)
C -2.8692837 2.6420938 -1.1194792
C -3.9673847 1.7432703 -1.1727012
C -3.5589071 0.6097640 -1.9123441
C -2.2156071 0.7936575 -2.3010376
C -1.7878585 2.0507112 -1.8111126
H -0.7934743 2.4656561 -1.9095426
Ti -2.2361867 0.6928113 0.1184594
O -0.4799430 0.0354996 -0.2599393

C	0.5148047	-0.7477226	0.0795274
C	1.6847411	-0.6619164	-0.6671900
H	1.5937438	-0.1469726	-1.6220846
C	3.0973831	0.7541185	0.1581517
C	2.4378338	1.3415666	1.2950471
O	2.3665343	0.7729838	2.3941818
C	1.7521709	2.6751807	1.0630080
H	0.9468385	2.5463608	0.3284697
H	2.4524437	3.4107554	0.6526211
H	1.3344495	3.0498437	1.9996847
H	3.2322544	1.3931456	-0.7132585
C	3.8987625	-0.5253244	0.2241160
C	5.1447059	-0.5015114	-0.6761328
C	4.6059587	-0.8711209	-2.0657009
H	5.3896527	-1.1920164	-2.7595343
C	3.5897515	-1.9799328	-1.7561593
H	2.8664427	-2.1489022	-2.5617965
C	2.9114259	-1.5327011	-0.4460429
H	2.6820067	-2.3877543	0.1944125
H	4.1217678	-2.9237044	-1.5854492
H	4.1015350	-0.0081821	-2.5210520
H	5.6606280	0.4653157	-0.6503997
H	5.8548080	-1.2682245	-0.3417186
H	4.1206724	-0.7712621	1.2670202
C	0.3588102	-1.6558407	1.2614372
H	0.8145923	-1.2127512	2.1566412
H	-0.6992852	-1.8370446	1.4534032
H	0.8489512	-2.6171805	1.0888882
O	-2.9909887	-1.1977159	0.1846969
C	-2.7240617	-2.1943301	-0.5865930
O	-2.0652373	-2.2458628	-1.6083125
C	-3.3777594	-3.4906064	-0.0292992
F	-4.7157668	-3.3476283	0.0981831
F	-2.8813478	-3.7809836	1.1978498
F	-3.1540262	-4.5494758	-0.8175815
C	-1.8531070	2.3247848	1.8120104
C	-3.2581515	2.1196767	1.7737094
C	-3.5163694	0.7918145	2.1603362
C	-2.2740652	0.1842769	2.4875759
C	-1.2528393	1.1303948	2.2855331
H	-0.1911185	0.9689815	2.4235839
H	-2.1460944	-0.8415436	2.8008825
H	-4.4824780	0.3050899	2.1786258
H	-3.9971959	2.8456829	1.4659084

H -1.3353779 3.2386649 1.5522395
H -1.6045907 0.0582046 -2.8027580
H -4.1565736 -0.2708792 -2.1029407
H -4.9400244 1.8912045 -0.7228601
H -2.8585655 3.6075799 -0.6331831

57
TS[reductive elimination] (TFA)
C -2.5029536 2.9144053 -0.8578646
C -3.8207968 2.3994751 -1.0237583
C -3.7230360 1.2230101 -1.7992133
C -2.3594436 0.9838490 -2.0746930
C -1.6004151 2.0392607 -1.5033785
H -0.5240214 2.1266117 -1.5255058
Ti -2.5801853 0.8648849 0.3021733
O -0.0966374 -0.1070883 -0.1947985
C 0.7014182 -0.9817980 0.1109484
C 2.0768307 -0.9456190 -0.5065752
H 1.9373157 -1.3467719 -1.5209683
C 2.7770253 0.4360449 -0.5655850
C 2.3330414 1.3862763 0.5182772
O 1.9595189 0.9688228 1.6027127
C 2.4526625 2.8560668 0.2260793
H 1.7229244 3.1222754 -0.5492613
H 3.4422971 3.0840797 -0.1872386
H 2.2698655 3.4475411 1.1247579
H 2.8224764 0.9262635 -1.5434301
C 4.1106918 -0.2646803 -0.1020665
C 5.1241182 -0.6025248 -1.2034240
C 4.6295536 -1.9172344 -1.8321672
H 5.4328652 -2.4773756 -2.3207759
C 4.0096180 -2.6774163 -0.6465486
H 3.3205450 -3.4711574 -0.9592156
C 3.3169753 -1.5864124 0.1691539
H 3.1679995 -1.8348521 1.2226656
H 4.8027213 -3.1411210 -0.0461648
H 3.8697540 -1.7139307 -2.5971970
H 5.2436908 0.2068601 -1.9321636
H 6.1024507 -0.7689390 -0.7357719
H 4.5752293 0.2157611 0.7638739
C 0.3698858 -2.1188955 1.0283846
H 0.8874053 -1.9565665 1.9824502
H -0.7059328 -2.1808379 1.1875551
H 0.7496950 -3.0623784 0.6198989

```
O    -4.1648458   -0.6132766    0.2621878
C    -3.5809372   -1.6487233   -0.1704366
O    -2.3812746   -1.7302129   -0.4579097
C    -4.4975195   -2.8838726   -0.3381692
F    -5.4913603   -2.6245924   -1.2172703
F    -5.0712010   -3.2185606    0.8389125
F    -3.8287028   -3.9580353   -0.7848240
C    -1.4794433    2.0958662    2.0618637
C    -2.8674364    2.4106183    2.0846069
C    -3.5828345    1.2340992    2.3912549
C    -2.6337790    0.1857221    2.5597047
C    -1.3404161    0.7319572    2.3803190
H    -0.4027071    0.1989057    2.4233119
H    -2.8676463   -0.8486487    2.7752558
H    -4.6580697    1.1323045    2.4471003
H    -3.3045041    3.3792016    1.8835118
H    -0.6689651    2.7742562    1.8298271
H    -1.9579172    0.1186834   -2.5847060
H    -4.5458527    0.5717841   -2.0601955
H    -4.7326292    2.8306798   -0.6319247
H    -2.2371109    3.8159555   -0.3235860

36
Cp2TiCl*(1,4-dioxane)
C    -0.1331459    3.1414690   -1.1213109
C    -1.2298284    2.3954107   -1.6194062
C    -0.7008872    1.2574124   -2.2847831
C     0.7015691    1.2942609   -2.1810535
C     1.0627259    2.4466980   -1.4428789
H     2.0695555    2.7442357   -1.1810226
Ti   -0.1730877    1.1161091    0.0925739
Cl    1.3775929   -0.7971973    0.0060519
C    -0.2127208    0.5974347    2.4041435
C    -1.3876474    1.3510591    2.1647655
C    -1.0043804    2.6495862    1.7743496
C     0.4168542    2.7097571    1.8004125
C     0.9044142    1.4486706    2.1935962
H     1.9431135    1.1597898    2.2682040
H     1.0218404    3.5677374    1.5394615
H    -1.6718470    3.4533629    1.4922431
H    -2.4016797    0.9843992    2.2472528
H    -0.1682937   -0.4498403    2.6677968
O    -1.8194186   -0.4598368   -0.1544232
C    -3.1739032    0.0060488   -0.3403006
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C    -4.1402231   -0.9192344    0.3718134
H    -5.1702139   -0.5956755    0.1890794
H    -3.9456977   -0.8977721    1.4580791
O    -4.0256782   -2.2526696   -0.1177385
C    -2.6797021   -2.7131843    0.0392080
C    -1.7033151   -1.8095474   -0.6784775
H    -0.6706279   -2.1187018   -0.5111496
H    -1.9151287   -1.7841350   -1.7581125
H    -2.6366787   -3.7211310   -0.3852462
H    -2.4225612   -2.7638922    1.1104562
H    -3.2251075    1.0180975    0.0694937
H    -3.3955426    0.0411890   -1.4179026
H     1.3820369    0.5356232   -2.5379606
H    -1.2751611    0.4736031   -2.7612567
H    -2.2733334    2.6718019   -1.5460828
H    -0.1992314    4.0772117   -0.5850151

51
Complex A in Scheme S1 (Cl)
C     1.4042973    2.6295183    2.2849716
C     2.6728681    1.9947891    2.2081904
C     2.4858635    0.6210636    2.4701865
C     1.1089666    0.3958011    2.6797388
C     0.4377264    1.6414803    2.5706894
H    -0.6290000    1.7987066    2.6575947
Ti    1.3123621    1.1416414    0.3977660
O    -0.3755515    0.0756874    0.3225980
C    -1.1381450   -0.7179551   -0.3214501
C    -2.2626651   -1.2525295    0.3860711
C    -3.2327684   -2.0377049   -0.1408794
H    -3.1743304   -2.3384880   -1.1865445
C    -4.4152330   -2.5463736    0.6149652
H    -4.4185425   -2.1405351    1.6347872
H    -4.3270053   -3.6398719    0.7072182
C    -5.7559776   -2.2443494   -0.0795268
H    -5.7023297   -2.5715748   -1.1266975
H    -6.5473005   -2.8354520    0.3958987
C    -6.1587283   -0.7591927   -0.0277385
H    -7.1245669   -0.6556859   -0.5451246
H    -6.3150826   -0.4469050    1.0124060
C    -5.1654909    0.1307106   -0.6883978
C    -4.6001429    1.2117989   -0.1336583
C    -3.5361676    1.9612944   -0.8230057
O    -3.1535076    1.6766306   -1.9552656
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C    -2.8719045    3.0666632   -0.0378563
H    -3.5770167    3.5904462    0.6142662
H    -2.1023593    2.6095665    0.6013266
H    -2.3826048    3.7679578   -0.7168287
H    -4.8576800    1.5126834    0.8809488
H    -4.8608119   -0.1296936   -1.7038451
H    -2.3416814   -0.9344481    1.4256555
C    -0.8587007   -1.0396277   -1.7548005
H    -1.2935544   -0.2648172   -2.4001440
H     0.2220418   -1.0662931   -1.9070830
H    -1.2846922   -2.0006224   -2.0485496
Cl    2.5182367   -0.8884367   -0.2163536
C     2.1621794    3.1707660   -0.5803920
C     2.6071520    2.1013030   -1.3801090
C     1.4643838    1.5049447   -1.9802325
C     0.3207667    2.2053376   -1.5464204
C     0.7438919    3.2205258   -0.6572746
H     0.1043350    3.9241984   -0.1421830
H    -0.7075920    1.9839267   -1.8046424
H     1.4814372    0.6469485   -2.6349865
H     3.6291395    1.7681597   -1.4969498
H     2.7866242    3.8228112    0.0142612
H     0.6432785   -0.5677169    2.8323367
H     3.2539642   -0.1374961    2.4455456
H     3.6163890    2.4734580    1.9829366
H     1.2113299    3.6828706    2.1370207

51
Complex B in Scheme S1 (Cl)
C     0.0946607   -1.9010195    1.1103987
C    -0.9906102   -2.8041330    1.0450667
C    -2.1525107   -2.1244581    1.5080597
C    -1.7900081   -0.7995845    1.8031747
C    -0.3968198   -0.6584278    1.5494341
H     0.1675434    0.2585849    1.6377441
Ti   -1.4647237   -1.1054781   -0.5648039
O     0.1384796   -1.0305070   -1.5444926
C     1.4374587   -0.7034200   -1.4044319
C     1.8059300    0.4889867   -0.9012113
C     3.2072024    1.0095647   -0.7836782
H     3.8806679    0.4596523   -1.4488567
C     3.2830490    2.5238485   -1.0451675
H     2.6954942    2.8167795   -1.9214817
H     4.3278687    2.8018017   -1.2310630
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C     2.7823743    3.1777158    0.2576188
H     3.2619668    4.1456934    0.4308101
H     1.7045059    3.3626123    0.2032865
C     3.0941803    2.1571105    1.3841919
H     3.7497698    2.5692327    2.1573717
H     2.1705997    1.8463855    1.8860160
C     3.7509228    0.9396114    0.6966548
C     3.4696283   -0.3602925    1.3433046
C     4.2216981   -1.5724559    1.1567839
O     3.7626000   -2.6502924    1.5699629
C     5.5647092   -1.5233192    0.4611153
H     6.2833724   -0.9660682    1.0741639
H     5.9335980   -2.5392488    0.3115482
H     5.5018041   -1.0086018   -0.5034581
H     2.5559898   -0.4722438    1.9236860
H     4.8367631    1.0997152    0.6275985
H     1.0011280    1.1478399   -0.5785326
C     2.3462030   -1.7813641   -1.9199254
H     2.2340412   -2.6872569   -1.3109591
H     2.0629617   -2.0437107   -2.9455440
H     3.3980122   -1.4919488   -1.9067603
Cl   -1.8038823    1.2670417   -0.4958127
C    -2.3067672   -1.3058959   -2.8418153
C    -2.0173937   -2.6080323   -2.3679367
C    -2.8984223   -2.8893019   -1.3007207
C    -3.7289205   -1.7539034   -1.1064043
C    -3.3687623   -0.7878989   -2.0722964
H    -3.7961506    0.1989708   -2.1668064
H    -4.4993059   -1.6424388   -0.3553656
H    -2.9343403   -3.8076645   -0.7321149
H    -1.2226393   -3.2509319   -2.7211749
H    -1.7623896   -0.7733450   -3.6089085
H    -2.4560329   -0.0119740    2.1258601
H    -3.1446297   -2.5458017    1.5904092
H    -0.9338651   -3.8369283    0.7294032
H     1.1146008   -2.1167801    0.8223190

51
Complex C in Scheme S1 (Cl)
C    -1.8202738    3.2723504   -0.9638089
C    -3.0654219    2.6013225   -1.1166808
C    -2.8391975    1.4291757   -1.8629198
C    -1.4554418    1.3533830   -2.1524746
C    -0.8286814    2.5056715   -1.6069919
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H	0.2293039	2.7278312	-1.6371872
Ti	-1.6220224	1.1746130	0.2098344
O	0.3088889	0.3562471	-0.1032053
C	1.1307892	-0.5009132	0.2487550
C	2.4417325	-0.5185639	-0.4829021
H	2.2094396	-0.9220562	-1.4794475
C	3.1931444	0.8315863	-0.6241308
C	2.9032470	1.8113359	0.4815668
O	2.4927061	1.4292491	1.5657243
C	3.2335425	3.2530189	0.2118128
H	2.5154168	3.6497451	-0.5170607
H	4.2249558	3.3395059	-0.2480442
H	3.1854644	3.8403733	1.1300668
H	3.1791440	1.3086600	-1.6095224
C	4.5322391	0.0825224	-0.2599178
C	5.4362378	-0.3189496	-1.4329029
C	4.8359608	-1.6219258	-1.9898164
H	5.5723376	-2.2261858	-2.5285785
C	4.2827854	-2.3319175	-0.7415573
H	3.5373863	-3.0998749	-0.9801413
C	3.7059183	-1.1968145	0.1036029
H	3.6330393	-1.4187003	1.1709848
H	5.1016605	-2.8185010	-0.1966466
H	4.0261662	-1.3997002	-2.6959759
H	5.5294158	0.4711362	-2.1861621
H	6.4417386	-0.5192224	-1.0426687
H	5.0887077	0.5563684	0.5543896
C	0.8503590	-1.5373659	1.2821983
H	1.3620457	-1.2600646	2.2132947
H	-0.2230510	-1.6222770	1.4526156
H	1.2629982	-2.5028379	0.9688516
Cl	-2.4280459	-1.1397737	-0.1183041
C	-1.0497249	2.5716140	2.0685193
C	-2.4572104	2.6266745	1.8914101
C	-2.9881673	1.3392111	2.1429459
C	-1.9060603	0.4973594	2.5153669
C	-0.7213976	1.2578154	2.4768855
H	0.2814802	0.9024533	2.6656915
H	-1.9841207	-0.5560368	2.7410340
H	-4.0256212	1.0432530	2.0642252
H	-3.0251137	3.4975968	1.5959624
H	-0.3504501	3.3855059	1.9282977
H	-0.9614358	0.5367648	-2.6603834
H	-3.5775054	0.6795306	-2.1073024

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H    -4.0169061    2.9220583   -0.7133419
H    -1.6575124    4.1963384   -0.4257705

51
TS[oxidative addition] (Cl)
C     2.4586265    1.4902901    2.8322568
C     3.7373179    0.8991061    2.6448934
C     3.5361230   -0.3979078    2.1210861
C     2.1466649   -0.5968466    1.9563220
C     1.4738543    0.5719172    2.3947088
H     0.4063954    0.7412671    2.3751153
Ti    2.7417788    1.1942010    0.5037946
O    -0.2535894    0.2822694   -0.1893539
C    -0.6781313   -0.8718650   -0.1064418
C    -1.7411000   -1.1601690    0.8665329
C    -2.5257040   -2.2450764    0.8377063
H    -2.3135674   -3.0412867    0.1225719
C    -3.7551140   -2.4207239    1.6645899
H    -3.8340911   -1.6127214    2.4023352
H    -3.6817545   -3.3673885    2.2183759
C    -5.0387371   -2.4742956    0.8102939
H    -4.9414025   -3.2654667    0.0545129
H    -5.8716536   -2.7626985    1.4616379
C    -5.3990886   -1.1483552    0.1166199
H    -6.3977770   -1.2734936   -0.3297532
H    -5.4833403   -0.3412244    0.8555295
C    -4.4567979   -0.7594007   -0.9722123
C    -3.9422844    0.4591263   -1.1700773
C    -2.9540854    0.7114007   -2.2443714
O    -2.5904649   -0.1676586   -3.0159640
C    -2.3939332    2.1091552   -2.3132450
H    -3.2045630    2.8329256   -2.4617562
H    -1.9162397    2.3521754   -1.3563872
H    -1.6669856    2.1891400   -3.1226996
H    -4.1849088    1.2835059   -0.5002919
H    -4.1594130   -1.5443084   -1.6714269
H    -1.9733043   -0.3366882    1.5416538
C    -0.1752556   -1.9473783   -1.0314879
H    -0.8431538   -1.9903400   -1.9015922
H     0.8225127   -1.6742619   -1.3796250
H    -0.1562867   -2.9345322   -0.5620898
Cl    3.3956912   -0.4482716   -1.0694452
C     3.1749692    3.5252519    0.6923330
C     3.8893071    3.0400664   -0.4281608
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C 2.9371372 2.6062157 -1.3874441
C 1.6423516 2.8143606 -0.8543428
C 1.7870989 3.3785782 0.4321900
H 0.9828048 3.6236806 1.1133428
H 0.7120482 2.5263313 -1.3227151
H 3.1628692 2.1496382 -2.3398511
H 4.9655740 3.0018237 -0.5340919
H 3.6158592 3.9144719 1.6003613
H 1.6868471 -1.4702512 1.5128377
H 4.3138150 -1.0871114 1.8221150
H 4.6927907 1.3558682 2.8682557
H 2.2694599 2.4807653 3.2219341

51
TS[5-exo cyclization] (Cl)
C 2.4852178 2.2406215 2.3193148
C 3.7325441 1.5805746 2.1656084
C 3.5256248 0.2059893 2.4219549
C 2.1591559 0.0089948 2.7032299
C 1.5134290 1.2678592 2.6407632
H 0.4538176 1.4459237 2.7663969
Ti 2.2746967 0.8035562 0.3998304
O 0.6481695 -0.1693942 0.3667979
C -0.2841414 -0.8501608 -0.2743394
C -1.4428342 -1.1355476 0.4046746
C -2.5963893 -1.7710967 -0.1329007
H -2.4620371 -2.2394246 -1.1075586
C -3.5375647 -2.5312142 0.7670146
H -3.6027003 -2.0349737 1.7449130
H -3.1470406 -3.5439499 0.9401125
C -4.9080633 -2.5633049 0.0965320
H -4.8474830 -3.1491181 -0.8306010
H -5.6741638 -3.0250049 0.7286470
C -5.2354303 -1.1016609 -0.2238589
H -6.0664166 -1.0237960 -0.9365895
H -5.5472914 -0.5903611 0.6959574
C -4.0067392 -0.4166663 -0.7805734
C -3.6667371 0.8647730 -0.3312956
C -2.6354650 1.6435690 -0.9562314
O -2.0614443 1.2750720 -1.9973102
C -2.2010249 2.9213174 -0.2652998
H -3.0256826 3.4087742 0.2631992
H -1.4336310 2.6692288 0.4800178
H -1.7601616 3.6100549 -0.9903431

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H    -4.0864604    1.2308385    0.6046358
H    -3.7699678   -0.6087796   -1.8271208
H    -1.5021888   -0.7566612    1.4251225
C     0.0246387   -1.2879632   -1.6732082
H    -0.1595217   -0.4681196   -2.3761321
H     1.0786785   -1.5747238   -1.7342996
H    -0.5937024   -2.1329132   -1.9808793
Cl    3.5973979   -1.0528355   -0.3322939
C     3.0675315    2.8812875   -0.5310054
C     3.4673468    1.8622325   -1.4110581
C     2.2947434    1.2767578   -1.9656143
C     1.1757154    1.9413863   -1.4309948
C     1.6444257    2.9101075   -0.5117421
H     1.0276898    3.5788927    0.0734575
H     0.1343767    1.7207711   -1.6373747
H     2.2762531    0.4428456   -2.6517635
H     4.4832668    1.5480139   -1.6056599
H     3.7241775    3.5106589    0.0530243
H     1.6767184   -0.9453125    2.8620800
H     4.2761400   -0.5673275    2.3569137
H     4.6749720    2.0410415    1.9015700
H     2.3080551    3.3007975    2.2067394

51
TS[4-exo cyclization] (Cl)
C    -2.7521141    2.6344191   -1.1342332
C    -3.9188097    1.8257618   -1.1907056
C    -3.6025172    0.6646723   -1.9294756
C    -2.2449943    0.7358818   -2.3048270
C    -1.7194847    1.9577717   -1.8176568
H    -0.6936373    2.2888605   -1.9074234
Ti   -2.2733259    0.6387500    0.1207469
O    -0.5130354   -0.0385761   -0.2509740
C     0.4996243   -0.7912750    0.1031266
C     1.6746457   -0.6729004   -0.6405079
H     1.5615758   -0.1697154   -1.5999565
C     3.0490870    0.7484027    0.1564043
C     2.4216780    1.3434043    1.3075243
O     2.3664599    0.7753236    2.4078218
C     1.7529261    2.6888113    1.0920317
H     0.9691205    2.5931271    0.3299030
H     2.4749534    3.4263586    0.7242518
H     1.3139887    3.0444313    2.0264158
H     3.1731931    1.3912358   -0.7141511
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C     3.8868855   -0.5100918    0.2222212
C     5.1271490   -0.4558680   -0.6833299
C     4.5859514   -0.8216541   -2.0731346
H     5.3705104   -1.1232010   -2.7747387
C     3.5895133   -1.9502716   -1.7682361
H     2.8622806   -2.1194405   -2.5704909
C     2.9163087   -1.5322025   -0.4453173
H     2.7093612   -2.4000169    0.1853977
H     4.1383203   -2.8875968   -1.6158302
H     4.0651604    0.0373959   -2.5171149
H     5.6260417    0.5197287   -0.6517507
H     5.8528227   -1.2131293   -0.3605414
H     4.1174868   -0.7499979    1.2646009
C     0.3506283   -1.6877404    1.2933878
H     0.6541597   -1.1707840    2.2126444
H    -0.6938451   -1.9950493    1.3820372
H     0.9761671   -2.5783778    1.2062423
Cl   -3.2535266   -1.5536750    0.1164478
C    -1.8345164    2.3131876    1.7607745
C    -3.2425483    2.1135552    1.7636269
C    -3.4949883    0.7997218    2.1942005
C    -2.2448776    0.1919432    2.4985042
C    -1.2283295    1.1320733    2.2522141
H    -0.1645296    0.9726102    2.3696762
H    -2.1089193   -0.8256318    2.8329382
H    -4.4619779    0.3198081    2.2547195
H    -3.9857049    2.8357888    1.4566916
H    -1.3190460    3.2181746    1.4691962
H    -1.6883672   -0.0384052   -2.8139980
H    -4.2695652   -0.1620349   -2.1224365
H    -4.8797331    2.0528190   -0.7492751
H    -2.6675361    3.5965272   -0.6488919

51
TS[reductive elimination] (Cl)
C    -2.8722031    2.7886245   -0.9628411
C    -4.0406773    1.9855844   -1.0885089
C    -3.6760410    0.8086832   -1.7795668
C    -2.2900050    0.8527037   -2.0285893
C    -1.7882832    2.0879225   -1.5319214
H    -0.7591710    2.4155637   -1.5622994
Ti   -2.5049433    0.8543079    0.3680530
O     0.0986279    0.3669017   -0.2181020
C     0.7098711   -0.6963521   -0.1495032
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C     2.1333329   -0.7654973   -0.6193318
H     2.0569902   -1.0213410   -1.6874395
C     3.0318738    0.4890872   -0.4215736
C     2.5507197    1.3815459    0.7022008
O     2.2605236    0.8982448    1.7845743
C     2.4730548    2.8570215    0.4373286
H     1.6739022    3.0285638   -0.2955552
H     3.4021405    3.2190878   -0.0173844
H     2.2553854    3.4048655    1.3557661
H     3.2532805    1.0610957   -1.3282153
C     4.1734477   -0.4661554    0.0768240
C     5.2589489   -0.8238864   -0.9465387
C     4.6652624   -1.9564070   -1.8028484
H     5.4344773   -2.5709115   -2.2807746
C     3.8028189   -2.7513423   -0.8070155
H     3.0533263   -3.3843893   -1.2972461
C     3.1797189   -1.6748964    0.0801666
H     2.8685684   -2.0220351    1.0684846
H     4.4422011   -3.4033343   -0.1984916
H     4.0420754   -1.5429205   -2.6062046
H     5.5846149    0.0390236   -1.5379398
H     6.1364435   -1.1996789   -0.4060125
H     4.5813952   -0.1719657    1.0468873
C     0.0738140   -1.9514378    0.3582360
H     0.3620911   -2.0678627    1.4121521
H    -1.0176012   -1.8925058    0.3034558
H     0.4437253   -2.8345844   -0.1725262
Cl   -3.8612815   -1.1032264    0.5688577
C    -1.5144274    2.4748487    1.8626968
C    -2.9294165    2.5421453    1.9981031
C    -3.3830456    1.3116885    2.5176010
C    -2.2445915    0.4795821    2.7079204
C    -1.0970859    1.2101240    2.3239904
H    -0.0764435    0.8534803    2.3331311
H    -2.2631521   -0.5402166    3.0656896
H    -4.4105685    1.0340983    2.7059483
H    -3.5564312    3.3845404    1.7400378
H    -0.8732571    3.2482041    1.4604507
H    -1.7052879    0.0694254   -2.4941119
H    -4.3308364   -0.0212041   -1.9987725
H    -5.0314344    2.2318358   -0.7295447
H    -2.8184845    3.7649193   -0.5025824
```

Complex A+ in Scheme S2 (chelated cationic)

C	2.5048768	-1.4351047	-1.2497571
C	1.4156601	-1.9940163	-0.5335728
C	1.7084796	-1.9270774	0.8420365
C	2.9838954	-1.3293123	0.9929724
C	3.4862271	-1.0555871	-0.3035843
H	4.4494756	-0.6228486	-0.5325023
Ti	1.5981180	0.3571429	0.0239715
O	-0.0118628	0.3393723	-1.2439329
C	-1.1950289	0.6985519	-1.4903460
C	-2.1071735	-0.3180058	-1.9502780
C	-3.4375860	-0.2642906	-1.7351589
H	-3.8870117	0.6525944	-1.3527442
C	-4.3403769	-1.4386742	-1.8510323
H	-3.8380487	-2.2544809	-2.3836574
H	-5.2344976	-1.1621511	-2.4255905
C	-4.8096096	-1.9461374	-0.4666011
H	-5.3797948	-1.1610909	0.0461215
H	-5.5016768	-2.7772502	-0.6374750
C	-3.6576630	-2.4375979	0.4410106
H	-4.0902933	-3.1374533	1.1711361
H	-2.9271499	-3.0033307	-0.1503271
C	-2.9793661	-1.3611807	1.2172952
C	-1.6662565	-1.0601662	1.1265258
C	-1.0226874	0.0191306	1.8324878
H	-1.0483418	-1.5900091	0.4081889
H	-3.6159701	-0.7951906	1.8987247
H	-1.6471943	-1.2509714	-2.2733099
C	-1.6406647	2.1018973	-1.2151112
H	-2.5660645	2.3546439	-1.7334213
H	-1.7931510	2.2356637	-0.1363166
H	-0.8592354	2.8010853	-1.5205599
C	2.3485534	2.2357279	1.2873336
C	3.4658455	1.7582429	0.5764754
C	3.2101341	1.9208188	-0.8128596
C	1.9433705	2.5255938	-0.9514065
C	1.4001834	2.7076204	0.3421939
H	0.4314209	3.1223718	0.5802114
H	1.4665019	2.7635378	-1.8926935
H	3.8695104	1.6382927	-1.6226540
H	4.3566888	1.3284136	1.0130810
H	2.2208633	2.2169540	2.3611269
H	3.4878273	-1.1340908	1.9304060
H	1.0631436	-2.2433677	1.6508959

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H     0.5057690   -2.3700659   -0.9794245
H     2.5802700   -1.3376988   -2.3248642
O     0.1190050    0.4312850    1.4943860
C    -1.7009932    0.7176424    2.9741238
H    -2.5728540    1.2762625    2.6111473
H    -1.0079795    1.4181628    3.4413047
H    -2.0628220    0.0016030    3.7181871

50
Complex B+ in Scheme S2 (chelated cationic)
C     0.9027381    2.2606195    0.9706025
C     0.4523284    2.3279197   -0.3582662
C     1.5842707    2.3123443   -1.2142286
C     2.7369854    2.2728257   -0.4043488
C     2.3220224    2.1954533    0.9495515
H     2.9678384    2.1315161    1.8155855
Ti    1.5723773    0.1894805   -0.0727655
O     0.4274353   -0.5290820    1.3269536
C    -0.8383750   -0.8066919    1.5659023
C    -1.8451879   -0.0513589    1.0132581
C    -3.2841794   -0.4266122    0.8021636
H    -3.5164683   -1.3724904    1.2979820
C    -4.2646704    0.6919363    1.2307719
H    -3.8636541    1.2935289    2.0532396
H    -5.2025884    0.2418399    1.5754506
C    -4.5232246    1.4999759   -0.0458995
H    -5.4150279    2.1298430    0.0215759
H    -3.6724829    2.1628378   -0.2588528
C    -4.6358011    0.4124278   -1.1175703
H    -5.6028117   -0.0946883   -1.0245723
H    -4.5591373    0.7921803   -2.1420734
C    -3.5025162   -0.5725751   -0.7779289
C    -2.2046747   -0.1938997   -1.4287258
C    -1.0108479   -0.9206071   -1.2622194
H    -2.0962820    0.8217658   -1.8069762
H    -3.7787421   -1.6026591   -1.0283097
H    -1.5517537    0.9259804    0.6400359
C    -1.0531417   -2.0216603    2.4135067
H    -0.4704113   -1.9113245    3.3342439
H    -2.1005715   -2.1694766    2.6782086
H    -0.6803731   -2.9200307    1.9062998
C     3.9067091   -0.3238501    0.1403000
C     3.2170051   -1.2427554    0.9576728
C     2.4373415   -2.0745853    0.1172109
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C     2.6314635   -1.6595283   -1.2148902
C     3.5250958   -0.5601008   -1.2075482
H     3.8693866   -0.0149410   -2.0764717
H     2.1456119   -2.0692393   -2.0897741
H     1.7875353   -2.8682172    0.4557323
H     3.2570162   -1.2901351    2.0379596
H     4.6003624    0.4291381    0.4859149
H     3.7572543    2.2779347   -0.7598151
H     1.5632087    2.3267593   -2.2963056
H    -0.5754297    2.3531529   -0.6901145
H     0.2851903    2.2149921    1.8576286
O     0.1187802   -0.2935192   -1.3559777
C    -0.9949141   -2.4082717   -1.1039011
H    -0.2037651   -2.7182437   -0.4201220
H    -0.7709850   -2.8459778   -2.0859237
H    -1.9522034   -2.8082161   -0.7671421

50
Complex C+ in Scheme S2 (chelated cationic)
C     0.6578959   -0.5588458   -2.1711430
C     1.8365341   -1.3464831   -2.0620731
C     2.9380260   -0.4595615   -2.0667307
C     2.4436830    0.8702921   -2.1465976
C     1.0364238    0.7992998   -2.2321575
H     0.3694493    1.6486680   -2.3002638
Ti    1.7216682   -0.0814935   -0.0788651
O     0.3215212    1.3898763    0.5083396
C    -0.8684932    1.7162445    0.4304459
C    -1.9548157    0.8549492   -0.1362552
C    -3.3551375    0.9828806    0.5472106
H    -3.3375224    1.5566108    1.4765978
C    -4.5192689    1.3537511   -0.3760863
H    -4.2896910    2.2021859   -1.0304312
H    -5.3856921    1.6325481    0.2352487
C    -4.8253724    0.0568832   -1.1430809
H    -5.8273713    0.0496653   -1.5809030
H    -4.1150384   -0.0772686   -1.9706729
C    -4.6309372   -1.0389823   -0.0821283
H    -5.5070436   -1.0753555    0.5762164
H    -4.4969625   -2.0388911   -0.5102705
C    -3.4172740   -0.5673724    0.7220897
C    -2.0394843   -0.7009218   -0.0005423
C    -1.0159747   -1.5853103    0.6371343
H    -2.1976197   -1.1609642   -0.9902936
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H    -3.4058849   -0.9215003    1.7558918
H    -2.0125153    1.1619455   -1.1949112
C    -1.2559017    3.0969654    0.8627464
H    -0.4032786    3.7705465    0.7591314
H    -2.1193335    3.4705003    0.3050231
H    -1.5411091    3.0735558    1.9229859
C     3.0495736    1.1130451    1.4647649
C     2.2938860    0.1541248    2.1939545
C     2.7479724   -1.1358604    1.8229820
C     3.7515494   -0.9827878    0.8486070
C     3.9458586    0.4106106    0.6341497
H     4.6507925    0.8543550   -0.0557711
H     4.2783643   -1.7848447    0.3487352
H     2.3497307   -2.0761232    2.1786054
H     1.5060746    0.3712904    2.9028435
H     2.9360156    2.1874825    1.5159778
H     3.0378969    1.7744070   -2.1575787
H     3.9793179   -0.7441356   -2.0126070
H     1.8830636   -2.4262320   -2.0092739
H    -0.3517185   -0.9416796   -2.2179094
O     0.2019690   -1.3770856    0.6211696
C    -1.5197116   -2.8414483    1.2777218
H    -0.7446810   -3.6095643    1.2550967
H    -2.4384550   -3.1989278    0.8044554
H    -1.7590415   -2.6305383    2.3286606

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TS[5-exo cyclization]+ (chelated cationic)
C     1.4775357    2.3539486    1.0117538
C     1.0101746    2.4665138   -0.3063867
C     2.1294810    2.4309109   -1.1824511
C     3.2909139    2.3353058   -0.3920850
C     2.8929941    2.2353438    0.9656279
H     3.5492099    2.1270212    1.8195129
Ti    2.0559283    0.2842713   -0.0933002
O     0.9609928   -0.4332929    1.3147564
C    -0.3062865   -0.6658396    1.6195296
C    -1.2984721    0.1848322    1.2117127
C    -2.6849126   -0.1205611    1.0245636
H    -3.0134395   -1.0793715    1.4242990
C    -3.7141151    1.0007492    1.1330462
H    -3.3004653    1.8263220    1.7216949
H    -4.5876966    0.6160288    1.6710133
C    -4.1500488    1.4727077   -0.2584721
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H -5.0873450 2.0361555 -0.2229603
H -3.3877806 2.1388046 -0.6834555
C -4.2633593 0.2049793 -1.1025573
H -5.1088926 -0.3986218 -0.7547885
H -4.4287050 0.4308910 -2.1622498
C -2.9740038 -0.5695367 -0.9153002
C -1.8117651 -0.1054793 -1.5514841
C -0.5649935 -0.7747616 -1.4113043
H -1.7575406 0.9344864 -1.8713092
H -3.0558949 -1.6474291 -0.7799168
H -0.9627524 1.1232069 0.7787025
C -0.5142885 -1.9107693 2.4264347
H -0.0220040 -1.7825962 3.3977662
H -1.5692272 -2.1219622 2.6087011
H -0.0423685 -2.7745104 1.9453253
C 4.3628409 -0.3413853 0.0554256
C 3.6349302 -1.3049227 0.7864854
C 2.8150174 -2.0150024 -0.1206923
C 3.0342589 -1.4884970 -1.4131135
C 3.9821973 -0.4446654 -1.3090180
H 4.3546897 0.1567794 -2.1271818
H 2.5422029 -1.7943947 -2.3265441
H 2.1189806 -2.7962821 0.1485633
H 3.6660362 -1.4467238 1.8585598
H 5.0866233 0.3479474 0.4668263
H 4.3065456 2.3116234 -0.7598113
H 2.0923129 2.4750995 -2.2632686
H -0.0213685 2.5278946 -0.6220114
H 0.8727627 2.3055270 1.9072467
O 0.5004963 -0.0657921 -1.3902376
C -0.5131484 -2.2643692 -1.2635666
H -0.8406723 -2.5666600 -0.2620254
H 0.4988058 -2.6331822 -1.4212311
H -1.1888845 -2.7401893 -1.9807532

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TS[4-exo cyclization]+ (chelated cationic)
C 1.7911460 0.3091454 -2.3656814
C 1.1874050 -0.9536886 -2.2340352
C 2.1883743 -1.8902390 -1.8684064
C 3.4153903 -1.2033540 -1.7936223
C 3.1700035 0.1695949 -2.0642822
H 3.9058292 0.9626427 -2.0776379
Ti 2.0394490 -0.3112056 -0.0413923

O	0.9038476	1.2716908	0.1695808
C	-0.3240086	1.6801143	0.2571293
C	-1.3218266	1.0864617	-0.5324745
C	-2.8092290	1.1630766	-0.2341580
H	-3.0359666	1.9494163	0.4906348
C	-3.7114737	1.2441056	-1.4785708
H	-3.2662835	1.8458205	-2.2783979
H	-4.6618021	1.7146719	-1.2025556
C	-3.9598712	-0.2180210	-1.8792615
H	-4.8448102	-0.3391526	-2.5104693
H	-3.1065269	-0.6131543	-2.4470692
C	-4.0889832	-0.9364885	-0.5280383
H	-5.0761538	-0.7351709	-0.0960133
H	-3.9695032	-2.0233179	-0.5975468
C	-3.0075055	-0.2848978	0.3472926
C	-1.6200424	-0.8535485	0.0833547
C	-0.6071162	-1.1903090	0.9939972
H	-1.4760171	-1.2975936	-0.8990943
H	-3.2617802	-0.2864325	1.4103859
H	-1.0118637	0.7779665	-1.5286398
C	-0.6226169	2.6773869	1.3342178
H	0.3007769	3.1728464	1.6401721
H	-1.3498052	3.4253066	1.0064660
H	-1.0480186	2.1739091	2.2136187
C	4.2954773	-0.0541225	0.7480442
C	3.5304450	0.9651399	1.3464471
C	2.5940237	0.3527996	2.2206295
C	2.7802472	-1.0405907	2.1545833
C	3.8104946	-1.3037891	1.2215936
H	4.1790905	-2.2818880	0.9422536
H	2.1998087	-1.7900083	2.6726341
H	1.8537954	0.8756710	2.8097282
H	3.6209354	2.0260399	1.1532573
H	5.1023297	0.0910941	0.0439436
H	4.3733854	-1.6437794	-1.5572314
H	2.0297487	-2.9404528	-1.6620071
H	0.1398027	-1.1809017	-2.3663465
H	1.2931484	1.2393479	-2.6044917
O	0.5448894	-1.5774347	0.5180682
C	-0.7555348	-1.0744046	2.4769851
H	-0.1796414	-0.2214827	2.8566802
H	-0.3398611	-1.9723761	2.9456980
H	-1.7936023	-0.9564442	2.7900278

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