Silylium Ion-Catalyzed Challenging Diels-Alder Reactions: The Danger of Hidden Proton Catalysis with Strong Lewis Acids

Ruth K. Schmidt,[a,b] Kristine Müther,[a,b] Christian Mück-Lichtenfeld,[b] Stefan Grimme,[b,c] and Martin Oestreich*[a,b]

[a] *Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 115, D-10623 Berlin, Germany*
martin.oestreich@tu-berlin.de

[b] *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany*

[c] *Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Beringstrasse 4, D-53115 Bonn, Germany*

Supporting Information

Table of Contents

1 General Information

All reactions were performed in flame-dried glassware using an *MBraun* glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon. Liquids and solutions were transferred with syringes. Solvents (THF and CH_2Cl_2) were purified and dried following standard procedures. Technical grade solvents for extraction or chromatography (cyclohexane, *tert*-butyl methyl ether, and ethyl acetate) were distilled prior to use. 1,2-$Cl_2C_6D_4$ (purchased from *Amar* Chemicals) and 1,2-$Cl_2C_6H_4$ (purchased from *Acros)* were dried over CaH_2 prior to use. $CDCl_3$ and C_6D_6 (purchased from *Eurisotop*) were used without further purification. Dienophiles were obtained from commercial suppliers and distilled (for liquids) or recrystallized and dried under vacuum (for solids) prior to use. Cyclohexa-1,3-diene and 2,3-dimethyl-1,3-butadiene (purchased from *Alfa Aesar*) were dried over $NaBH_4$ prior to use. Cyclopentadiene was obtained by cracking of the dimer (purchased from *Acros Organics*) at 180°C directly prior to use. Triflic anhydride (purchased from *Alfa Aesar*) was dissolved in CH_2Cl_2 under Argon using only glass pipettes. $[Ph_3C]^+[B(C_6F_5)_4]^-$[S1], *tert*-butylferrocenylmethylsilane[S2], *tert*-butylmethyl-silylchloride[S2] and ferrocene-d10[S3] were prepared according to reported procedures. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Merck* using the indicated solvents. ^1H, ^2H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were recorded in $CDCl_3$, C_6D_6, 1,2-$Cl_2C_6H_4$ or 1,2-$Cl_2C_6D_4$ on *Bruker* AV300, *Bruker* AV400, and *Varian* INOVA 500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.1 ppm for ^{13}C NMR; C_6H_6: δ = 7.16 ppm for ^1H NMR and C_6D_6: δ =128.1 ppm for ^{13}C NMR; 1,2-$Cl_2C_6H_4$: δ = 6.94 and 7.20 ppm for ^1H NMR and 1,2-$Cl_2C_6D_4$: δ =127.1, 130.1 and 132.5 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad), coupling constants (Hz) and integration. Gas liquid chromatography (GLC) was performed on a *Shimadzu* GC-2010 gas chromatograph equipped with a FS-Supreme-5ms capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 250°C, detector temperature 310°C; temperature program: start temperature 50°C, heating rate 10°C/min, end temperature 300°C for 5 min. Infrared (IR) spectra were recorded on a Varian 3100 FT-IR spectrophotometer equipped with an ATR unit and are reported in wavenumbers (cm^{-1}). Melting points (mp) were determined with a *Thompson Scientific* apparatus and are not corrected. Mass spectrometry (MS) was obtained from the Analytical Facility at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.

2 General Procedures (GPs)

2.1 General Procedure for NMR Experiments (GP 1)

In a glove box, a solution of *tert*-butylferrocenylmethylsilane (**S1**, 1.00 equiv) or *tert*-butylferrocenylmethylsilane-d9 (d9-**S1**, 1.00 equiv) in *o*-$Cl_2C_6D_4$ or *o*-$Cl_2C_6H_4$ (0.3 mL) is added to a suspension of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**S2**, 1.00 equiv) in *o*-$Cl_2C_6D_4$ or *o*-$Cl_2C_6H_4$ (0.2 mL) in an 8 mL vial equipped with a magnetic stir bar. The resulting red-brown solution is stirred for 1 min and then added to a solution of the proton scavenger (1.00 equiv) in *o*-$Cl_2C_6D_4$ or *o*-$Cl_2C_6H_4$ (0.2 mL). The solution is transferred to an NMR tube and directly subjected to NMR spectroscopic analysis.

2.2 General Procedure for Silylium Ion-Catalyzed Diels-Alder Reactions (GP 2)

In a glove box, a flame-dried 10-mL Schlenk tube equipped with a magnetic stir bar is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**S2**, 0.0500 equiv). The Schlenk tube is transferred to a fume hood and connected to an argon-vacuum manifold. Addition of dry CH_2Cl_2 results in a yellow solution, which is subsequently cooled to –78°C, followed by addition of *tert*-butylferrocenylmethylsilane (**S1**, 0.0550 equiv). The solution is maintained at –78°C for 10 min whereupon the color changes to deep red. To the thus obtained catalyst solution, a solution of the diene (2.00 equiv) and dienophile (1.00 equiv) in dry CH_2Cl_2 (0.5 mL) is added dropwise. The reaction mixture is stirred at the temperature and for the time indicated in Tables 2 or 3 and subsequently quenched by the addition of saturated aqueous $NaHCO_3$ solution (2 mL). The phases are separated, and the aqueous phase is extracted with *tert*-butyl methyl ether. The combined organic phases are washed with brine and dried over anhydrous $MgSO_4$. After evaporation of solvents under reduced pressure, the resulting residue is purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate mixtures affording analytically pure Diels-Alder products. The *endo*:*exo* ratio is determined by GLC analysis of the reaction mixture prior to workup.

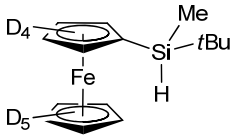
2.3 General Procedure for Triflic Acid-Catalyzed Diels-Alder Reactions (GP 3)

To a solution of triflic anhydride (0.1M in CH_2Cl_2, 0.0275 equiv) and CH_2Cl_2, a solution of H_2O (0.5M in CH_2Cl_2) is added. The solution is cooled to the temperature indicated in Tables 4–6 and a solution of the diene (2.00 equiv) and dienophile (1.00 equiv) in CH_2Cl_2 is added dropwise. The reaction mixture is stirred at the same temperature for the indicated time (cf. Tables 4–6) and subsequently quenched by the addition of saturated aqueous $NaHCO_3$ solution (2 mL). The phases are separated and the

aqueous phase is extracted with *tert*-butyl methyl ether. The combined organic phases are washed with brine and dried over anhydrous $MgSO_4$. After evaporation of solvents under reduced pressure, the resulting residue is purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate mixtures affording analytically pure Diels-Alder products. Unless stated otherwise, the *endo*:*exo* ratio is determined by GLC analysis of the reaction mixture prior to workup.

3 Experimental Details for the Preparation of *tert*-Butylferrocenylmethylsilane-d9 (d9-S1)

tert-Butylferrocenylmethylsilane-d9 (d9-S1)



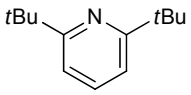
S1
$C_{15}H_{13}D_9FeSi$
M =295.32 g/mol

Ferrocene-d10 (960 mg, 4.92 mmol, 1.01 equiv, 90% deuteration grade determined by HRMS) and potassium *tert*-butoxide (54.0 mg, 0.490 mmol, 0.100 equiv) were dissolved in THF (20 mL) and cooled to −78°C. *tert*-Butyllithium (1.00M in pentane, 4.90 mL, 4.90 mmol, 1.00 equiv) was added dropwise and the reaction mixture was stirred at −78°C for 30 min, slowly warmed to room temperature and stirred for an additional 30 min. At −20°C, a solution of *tert*-butylmethylsilylchloride (670 mg, 4.90 mmol, 1.00 equiv) in THF (10 mL) was added via canula and the reaction mixture was slowly warmed to room temperature overnight. After the addition of water (10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and the solvents were evaporated under reduced pressure. Purification of the crude product by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure deuterated silane d9-**S1** (653 mg, 46%, 93% deuteration grade determined by HRMS). $\mathbf{R_f}$: 0.44 (CH). **GLC** (FS-Supreme): t_R = 18.0 min. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.29 (d, *J* = 3.7 Hz, 3H), 0.97 (s, 9H), 4.36 (q, *J* = 3.6 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = −8.1, 17.2, 27.1, 64.9–65.2 (m), 68.2–68.8 (m), 70.8−71.8 (m, 2C), 73.4−73.9 (m), 74.3−74.8 (m) ppm.[S4] **^{29}Si NMR** (60 MHz, C_6D_6): δ = −2.5 ppm. **IR** (ATR): $\tilde{\nu}$ = 2102 (s, Si−H) cm^{-1}. **HRMS** (ESI) calculated for $C_{15}H_{13}D_9FeSi$ $[M]^{\bullet+}$: 295.1400; Found: 295.1391.

4 Details for NMR Experiments Using Different Proton Scavengers

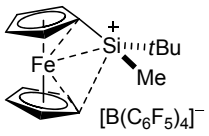
4.1 NMR Experiment Using 2,6-Di-*tert*-butylpyridine (S3)

According to GP 1, silylium ion **7** was prepared from *tert*-butylferrocenylmethylsilane (**S1**, 26.2 mg, 91.6 µmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**S2**, 84.5 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.5 mL) and added to a solution of 2,6-di-*tert*-butylpyridine (**S3**, 17.5 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.2 mL). The mixture was transferred to an NMR tube and directly subjected to NMR analysis.



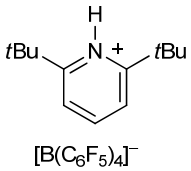
S3
$C_{13}H_{21}N$
M = 191.31 g/mol

^{1}H NMR (300 MHz, *o*-$Cl_2C_6D_4$): δ = 1.33 (s, 18H), 6.98 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H) ppm.



7
$C_{39}H_{21}BF_{20}FeSi$
M = 964.29 g/mol

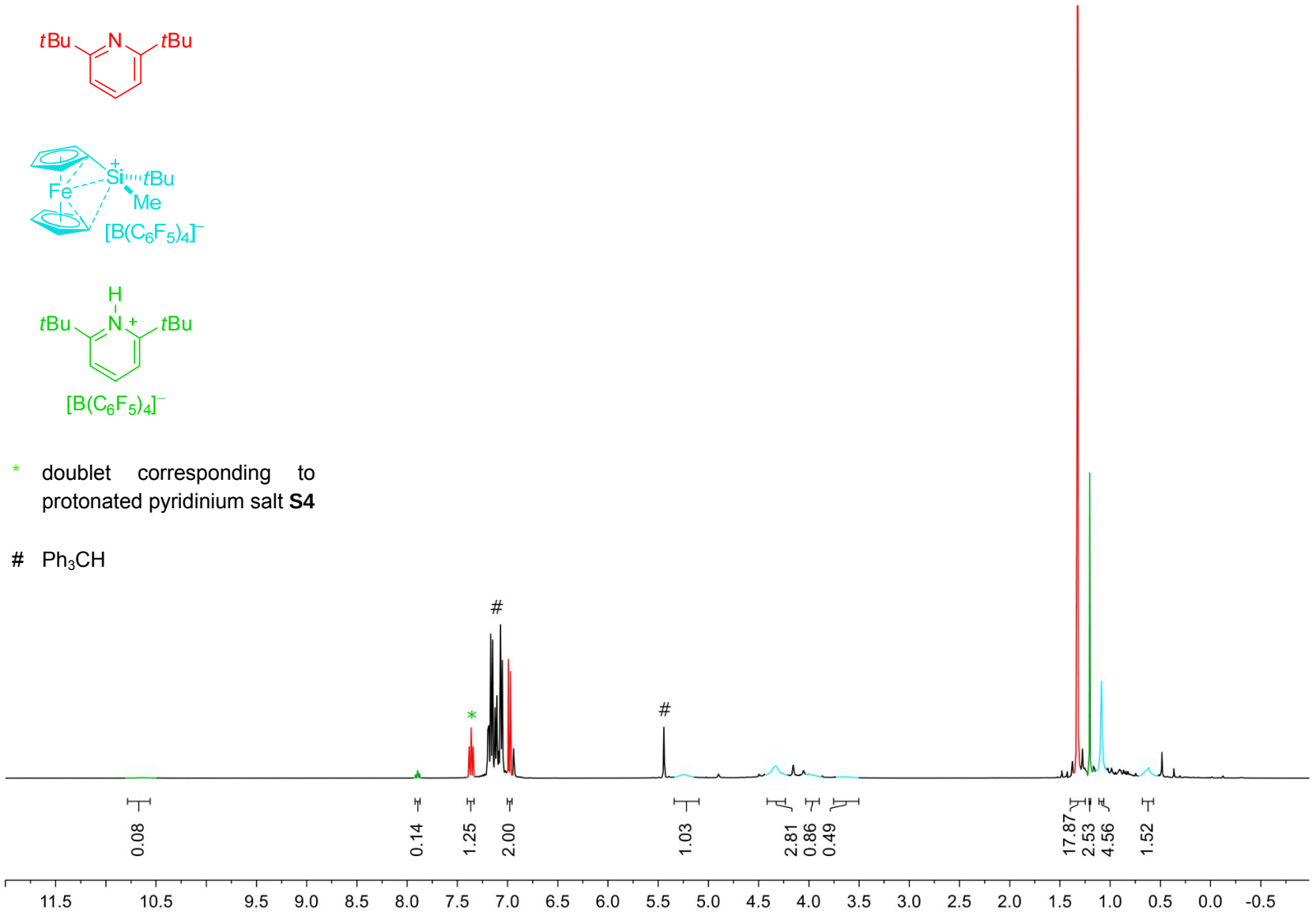
^{1}H NMR (300 MHz, *o*-$Cl_2C_6D_4$): δ = 0.63 (bs, 3H), 1.09 (s, 9H), 3.65 (bs, 1H), 3.98 (bs, 1H), 4.33 (bs, 5H), 5.24 (bs, 2H) ppm.



S4
$C_{37}H_{22}BF_{20}N$
M = 871.36 g/mol

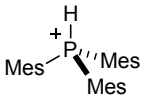
^{1}H NMR (300 MHz, *o*-$Cl_2C_6D_4$): δ = 1.20 (s, 18H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.90 (t, *J* = 8.1 Hz, 1H), 10.64 (bs, 1H).

^{1}H NMR (300 MHz, *o*-$Cl_2C_6D_4$):



4.2 NMR Experiment Using Trimesitylphosphine (S5)

According to GP 1, silylium ion **7** was prepared from *tert*-butylferrocenylmethylsilane (**S1**, 26.8 mg, 91.6 µmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**S2**, 84.5 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.5 mL) and added to a solution of trimesitylphosphine (**S5**, 35.6 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.2 mL). The mixture was transferred to an NMR tube and directly subjected to NMR analysis.



$[B(C_6F_5)_4]^-$

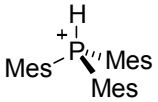
12

$C_{51}H_{34}BF_{20}P$

M = 1068.57 g/mol

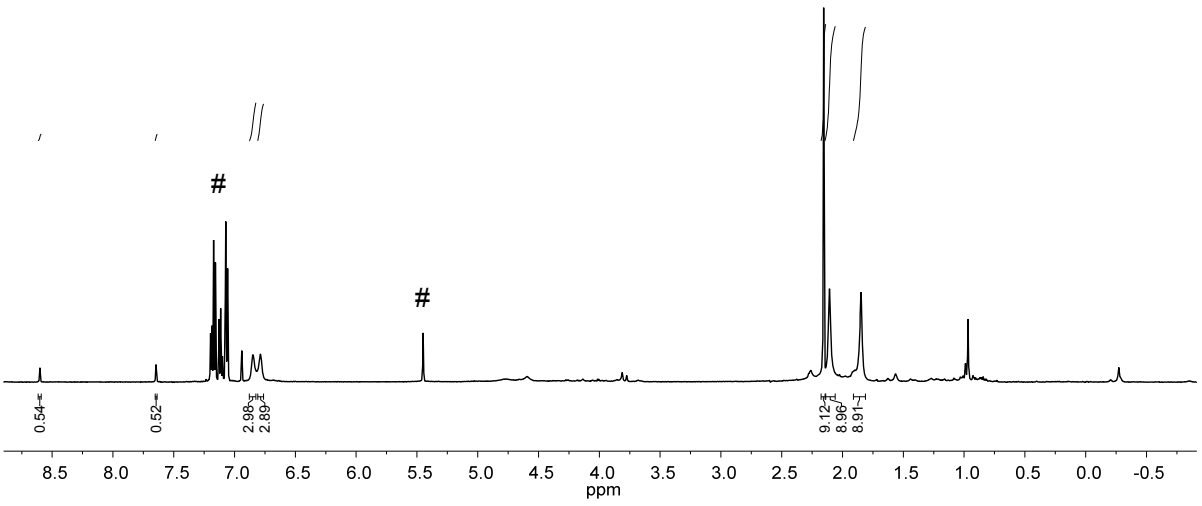
^{1}H NMR (500 MHz, *o*-$Cl_2C_6D_4$): δ = 1.85 (bs, 9H), 2.11 (bs, 9H), 2.15 (s, 9H), 6.79 (bs, 3H), 6.85 (bs, 3H), 8.12 (d, $J_{H,P}$ = 477 Hz, 1H) ppm. **^{31}P NMR** (202 MHz, *o*-$Cl_2C_6D_4$): δ = −27.7 (d, $J_{P,H}$ = 477 Hz) ppm. **^{11}B NMR** (96 MHz, *o*-$Cl_2C_6D_4$): δ = −16.0 ppm. **^{19}F NMR** (282 MHz, *o*-$Cl_2C_6D_4$): δ = −165.9, −162.1, −131.6 ppm.

^{1}H NMR (500 MHz, *o*-$Cl_2C_6D_4$):

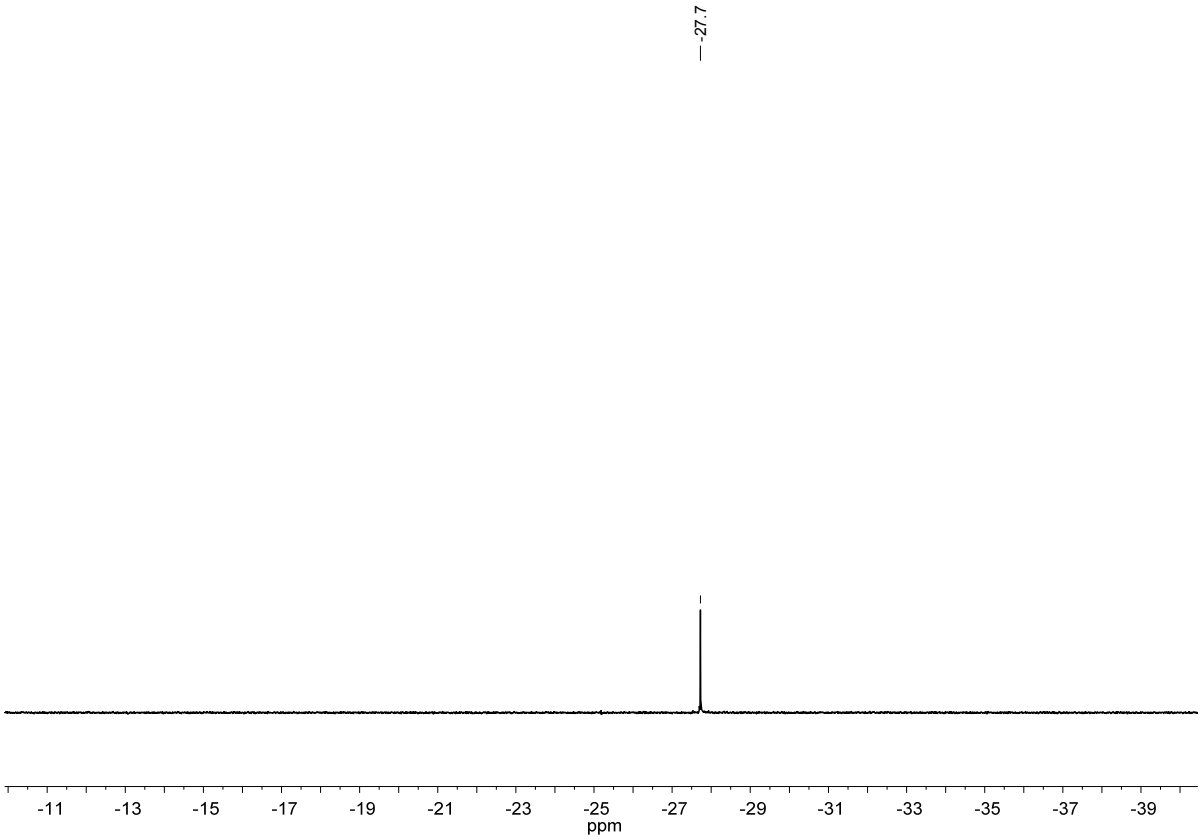


$[B(C_6F_5)_4]^-$

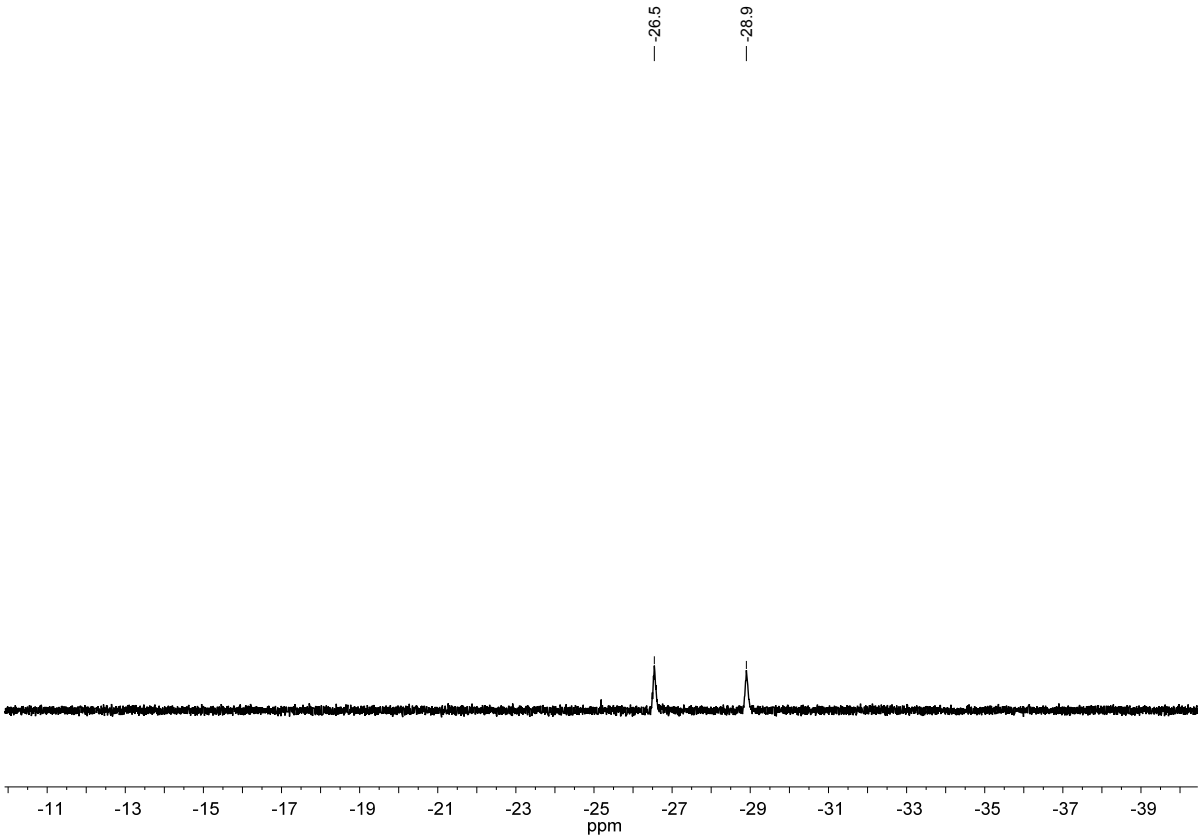
\# Ph_3CH



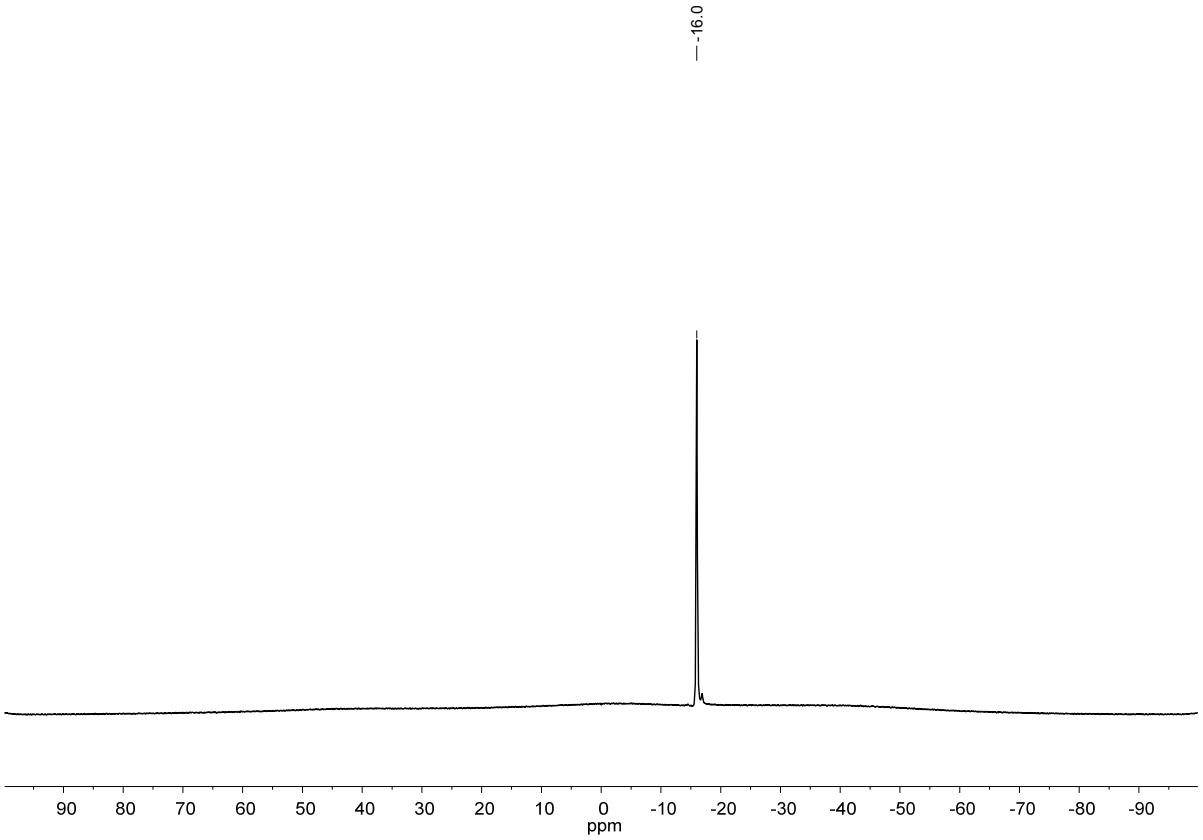
$^{31}P\{^{1}H\}$ NMR (202 MHz, *o*-$Cl_2C_6D_4$):



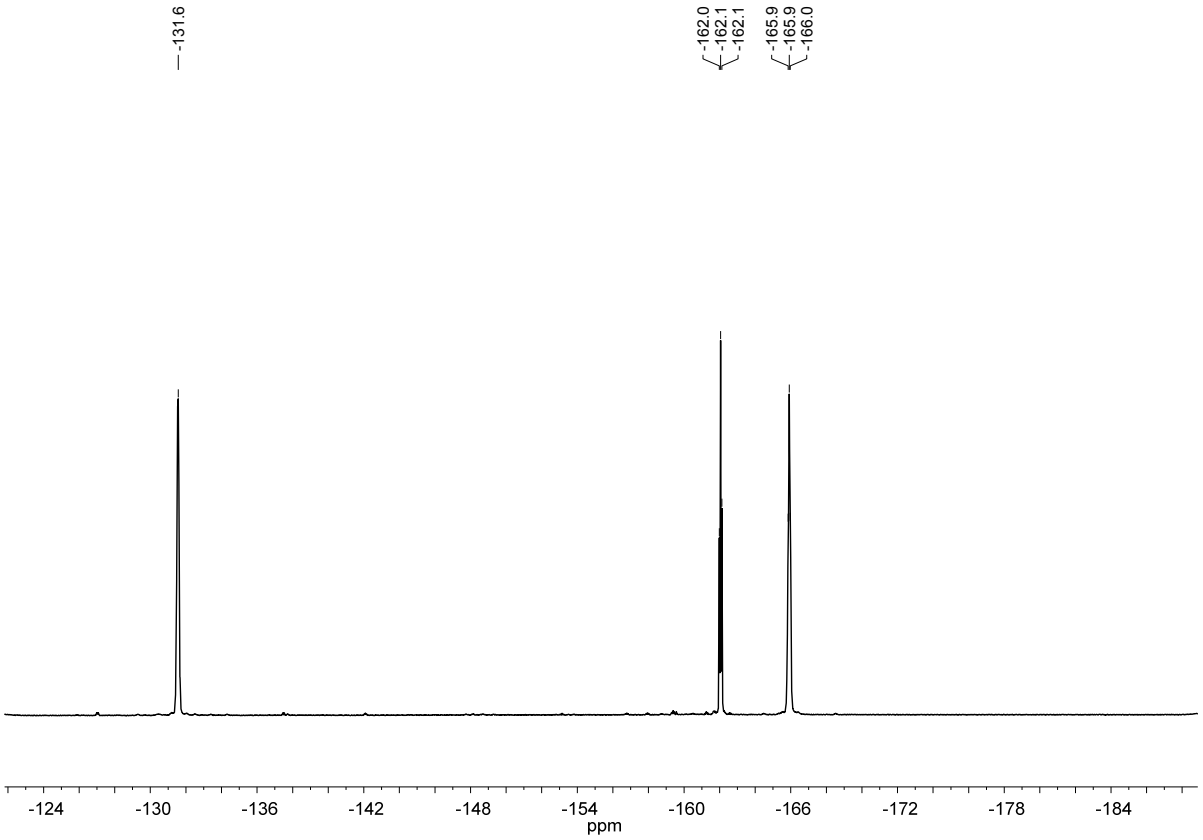
^{31}P NMR (202 MHz, *o*-$Cl_2C_6D_4$):



^{11}B NMR (96 MHz, *o*-$Cl_2C_6D_4$):

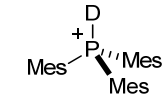


^{19}F NMR (282 MHz, *o*-$Cl_2C_6D_4$):



4.3 NMR Experiment Using Trimesitylphosphine (S5) and Deuterated Silylium Ion d9-S1

According to GP 1, silylium ion d9-**7** was prepared from *tert*-butylferrocenylmethylsilane-d9 (d9-**S1**, 26.8 mg, 92.7 µmol, 1.01 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**S2**, 84.5 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.5 mL) and added to a solution of trimesitylphosphine (**S5**, 35.6 mg, 91.6 µmol, 1.00 equiv) in *o*-$Cl_2C_6D_4$ (0.2 mL). The mixture was transferred to an NMR tube and directly subjected to NMR analysis. Another sample was prepared in *o*-$Cl_2C_6H_4$ accordingly.

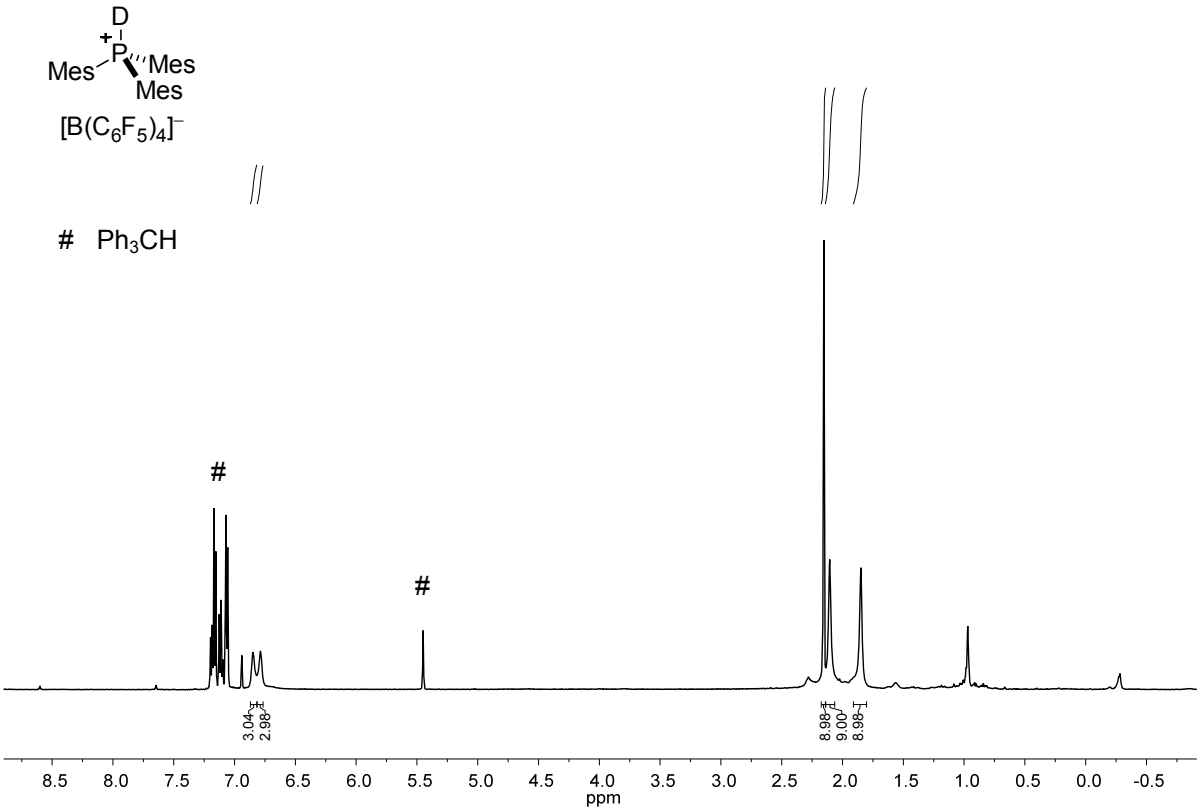


$[B(C_6F_5)_4]^-$

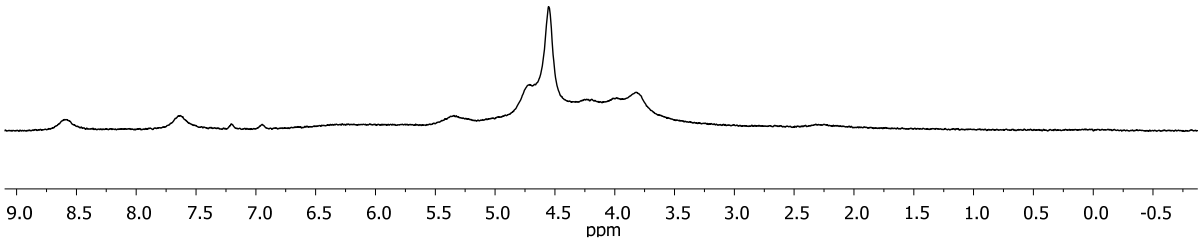
d1-**12**
$C_{51}H_{33}DBF_{20}P$
M = 1069.57 g/mol

^{1}H NMR (500 MHz, *o*-$Cl_2C_6D_4$): δ = 1.85 (bs, 9H), 2.11 (bs, 9H), 2.15 (s, 9H), 6.79 (bs, 3H), 6.85 (bs, 3H) ppm. **^{2}H NMR** (77 MHz, *o*-$Cl_2C_6H_4$): δ = 8.11 (d, $J_{D,P}$ = 74 Hz, 1H) ppm. **^{31}P NMR** (202 MHz, *o*-$Cl_2C_6D_4$): δ = 28.1 (t, $J_{P,D}$ = 74 Hz) ppm.

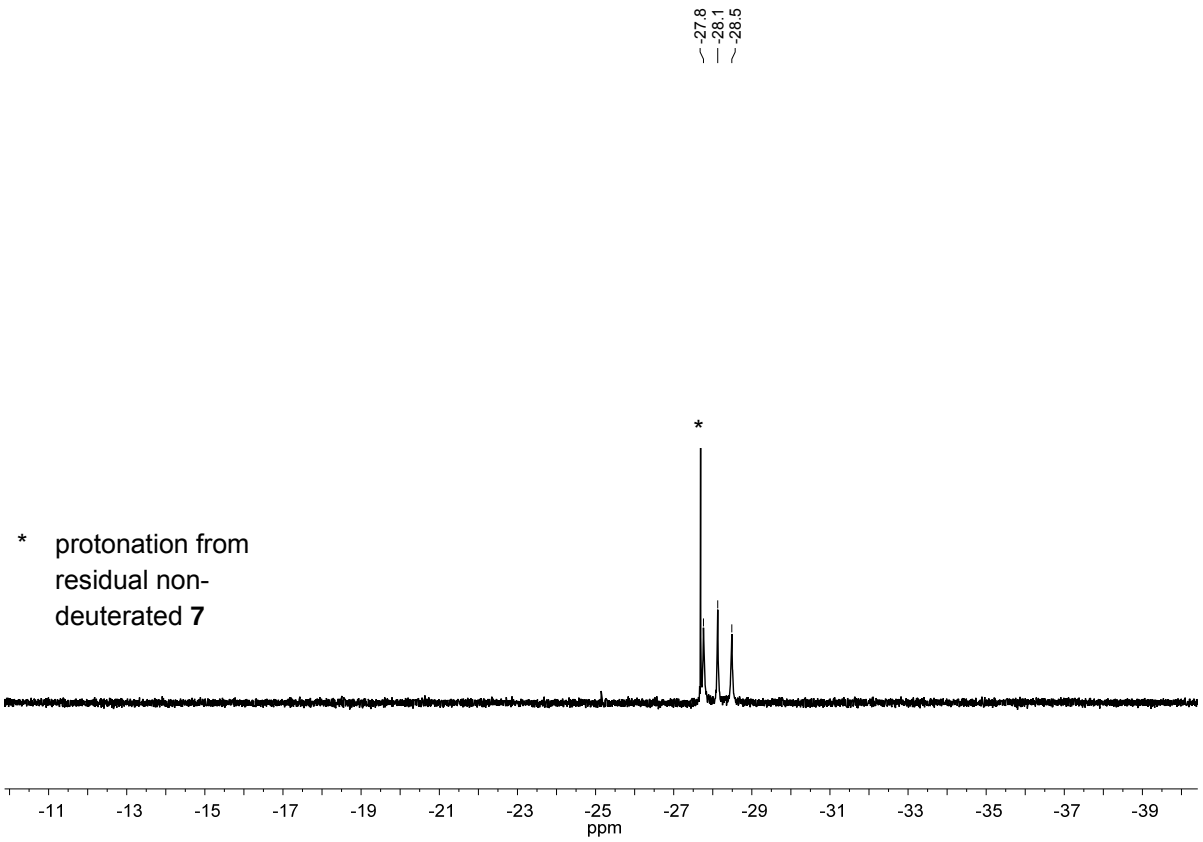
^{1}H NMR (500 MHz, *o*-$Cl_2C_6D_4$):



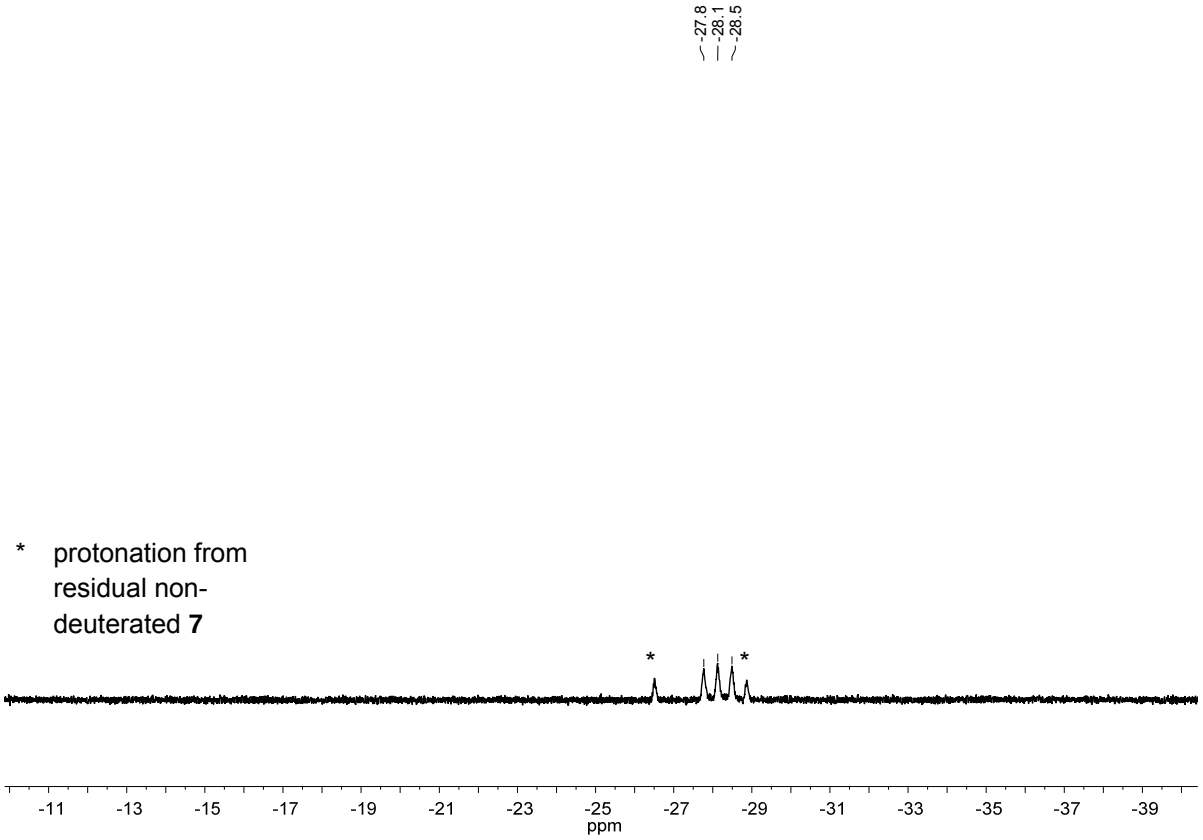
^{2}H NMR (77 MHz, *o*-$Cl_2C_6H_4$):



$^{31}P\{^{1}H\}$ NMR (203 MHz, *o*-$Cl_2C_6D_4$):

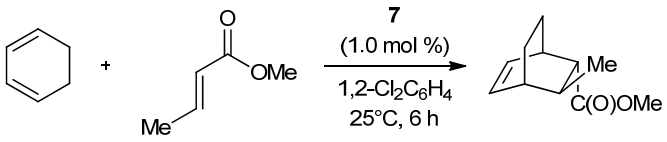


^{31}P NMR (203 MHz, *o*-$Cl_2C_6D_4$):



5 Experimental Details for Silylium Ion-and Triflic Acid-Catalyzed Diels-Alder Reactions

5.1 Silylium Ion-Catalyzed Diels-Alder Reaction of Methyl Crotonate (S6) and Cyclohexa-1,3-diene (1)



1 **S6** **S7**

85%, 91% *endo*

$C_{11}H_{16}O_2$

M = 180.24 g/mol

Prepared according to GP 2 from methyl crotonate (**S5**, 103 mg, 1.03 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.20 mL, 2.06 mmol, 2.00 equiv) with silylium ion catalyst **7** (0.0100 equiv) in 1,2-$Cl_2C_6H_4$ (not CH_2Cl_2) at 25°C for 6 h in 85% (157 mg, *endo*:*exo* = 95.5:4.5). The product **S7** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 98:2) as a colourless oil. $\mathbf{R_f}$: 0.21 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 10.2 min (*exo*), 10.6 min (*endo*). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.04–1.10 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.28 (dddd, *J* = 12.3 Hz, *J* = 12.3 Hz, *J* = 3.8 Hz, *J* = 3.8 Hz, 1H), 1.47–1.52 (m, 1H), 1.70–1.76 (m, 1H), 1.82–1.89 (m, 1H), 2.25–2.26 (m, 1H), 2.81–2.83 (m, 1H), 3.63 (s, 3H), 6.14 (t, *J* = 7.3 Hz, 1H), 6.41 (t, *J* = 7.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 17.9, 19.9, 26.0, 33.1, 35.8, 35.9, 51.6, 51.7, 131.1, 136.9, 176.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 1732 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223; Found: 181.1216. The analytical and spectroscopic data are in accordance with those reported.[S5]

5.2 Silylium Ion- and Triflic Acid-Catalyzed Diels-Alder Reactions of Ketones

endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)ethanone (16)

16
$C_{10}H_{14}O$
M = 150.22 g/mol

Prepared according to GP 2 from methyl vinyl ketone (**14**, 70.0 mg, 1.00 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.190 mL, 2.00 mmol, 2.00 equiv) in 93% yield (140 mg, *endo*:*exo* = 99:1). Prepared according to GP 3 from methyl vinyl ketone (**14**, 71.6 mg, 1.02 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.194 mL, 2.04 mmol, 2.00 equiv) in 82% yield (126 mg, *endo*:*exo* = 99:1). The product **16** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a slightly yellow oil. $\mathbf{R_f}$: 0.18 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 9.0 min (*exo*), 9.5 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.19–1.37 (m, 2H), 1.44–1.54 (m, 1H), 1.56–1.61 (m, 1H), 1.61–1.68 (m, 2H), 2.11 (s, 3H), 2.50–2.63 (m, 1H), 2.66 (ddd, *J* = 8.7 Hz, *J* = 6.9 Hz, *J* = 2.1 Hz, 1H), 2.86–2.92 (m, 1H), 6.10 (ddd, *J* = 8.3 Hz, *J* = 6.5 Hz, *J* = 1.1 Hz, 1H), 6.27 (ddd, *J* = 8.5 Hz, *J* = 6.8 Hz, *J* = 1.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 24.6, 26.0, 28.4, 28.8, 29.7, 32.2, 51.7, 131.2, 135.3, 209.9 ppm. **IR** (ATR): $\tilde{\nu}$ = 1706 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_{14}ONa$ $[M+Na]^+$: 173.0937; Found: 173.0940. The analytical and spectroscopic data are in accordance with those reported.[S2]

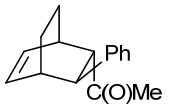
endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)propan-1-one (22)

22
$C_{11}H_{16}O$
M = 164.24 g/mol

Prepared according to GP 2 from ethyl vinyl ketone (**17**, 74.6 mg, 0.887 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.169 mL, 1.77 mmol, 2.00 equiv) in 73% yield (106 mg, *endo*:*exo* = 99:1). Prepared according to GP 3 from ethyl vinyl ketone (**17**, 80.4 mg, 0.956 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.182 mL, 1.91 mmol, 2.00 equiv) in 45% yield (70.7 mg, *endo*:*exo* = 99:1). The product **22** was

obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. $\mathbf{R_f}$: 0.29 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 12.3 min (*exo*), 12.7 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.3 Hz, 3H), 1.20–1.35 (m, 2H), 1.45–1.53 (m, 1H), 1.53–1.62 (m, 1H), 1.62–1.68 (m, 2H), 2.32–2.51 (m, 2H), 2.56–2.61 (m, 1H), 2.67 (dt, *J* = 7.7 Hz, *J* = 2.1 Hz, 1H), 2.83–2.89 (m, 1H), 6.09 (ddd, *J* = 7.9 Hz, *J* = 6.5 Hz, *J* = 1.0 Hz, 1H), 6.26 (ddd, *J* = 8.0 Hz, *J* = 6.7 Hz, *J* = 1.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 8.2, 24.6, 26.1, 29.0, 29.7, 32.3, 34.0, 50.6, 131.3, 135.1, 212.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 1718 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{16}ONa$ $[M+Na]^+$: 187.1093; Found: 187.1094. The analytical and spectroscopic data are in accordance with those reported.[S6]

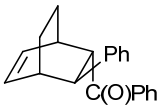
endo-1-(3-Phenylbicyclo[2.2.2]oct-5-en-2-yl)ethanone (23)



23
$C_{16}H_{18}O$
M = 226.31 g/mol

Prepared according to GP 2 from 4-phenyl-3-buten-2-one (**18**, 75.1 mg, 0.514 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.098 mL, 1.03 mmol, 2.00 equiv) in 65% yield (75.3 mg, *endo*:*exo* > 99:1). Prepared according to GP 3 from 4-phenyl-3-buten-2-one (**18**, 132 mg, 0.901 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.172 mL, 1.80 mmol, 2.00 equiv) in 44% yield (89.6 mg, *endo*:*exo* > 99:1). The product **23** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a slightly yellow oil. $\mathbf{R_f}$: 0.28 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 19.0 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.97–1.09 (m, 1H), 1.42–1.49 (m, 1H), 1.65–1.79 (m, 2H), 2.03 (s, 3H), 2.49–2.56 (m, 1H), 2.94 (dd, *J* = 6.8 Hz, *J* = 1.8 Hz, 1H), 2.99–3.04 (m, 1H), 3.12 (ddd, *J* = 6.7 Hz. *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 6.12 (ddd, *J* = 7.6 Hz, *J* = 6.8 Hz, *J* = 0.9 Hz, 1H), 6.47 (ddd, *J* = 8.0 Hz, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.21–7.40 (m, 5H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.5, 26.1, 28.5, 32.7, 37.3, 45.6, 56.6, 126.5, 128.2, 128.6, 131.6, 136.1, 142.8, 209.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 1707 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{18}ONa$ $[M+Na]^+$: 249.1250; Found: 249.1256. The analytical and spectroscopic data are in accordance with those reported.[S7]

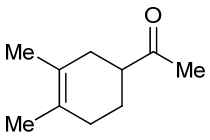
endo-Phenyl-(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (24)



24
$C_{21}H_{20}O$
M = 288.38 g/mol

Prepared according to GP 2 from *trans*-chalcone (**19**, 101 mg, 0.486 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**, 0.093 mL, 0.973 mmol, 2.00 equiv) in 71% yield (98.9 mg, *endo*:*exo* = 99:1). The product **24** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 98:2) as a white solid. **R_f**: 0.35 (CH:EtOAc = 98:2). **Mp**: 118.9°C. **GLC** (FS-Supreme): t_R = 24.1 min (*exo*), 24.5 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.07–1.18 (m, 1H), 1.48 (dddd, *J* = 11.3 Hz, *J* = 11.3 Hz, *J* = 3.4 Hz, *J* = 3.4 Hz, 1H), 1.79–1.95 (m, 2H), 2.54–2.71 (m, 1H), 2.94–3.01 (m, 1H), 3.49 (ddd, *J* = 6.5 Hz, *J* = 4.0 Hz, *J* = 2.0 Hz, 1H), 3.81 (dd, *J* = 6.5 Hz, *J* = 1.6 Hz, 1H), 6.12 (ddd, *J* = 8.9 Hz, *J* = 7.7 Hz, *J* = 0.8 Hz, 1H), 6.57 (ddd, *J* = 9.1 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.18–7.24 (m, 1H), 7.27–7.35 (m, 4H), 7.36–7.42 (m, 2H), 7.47–7.53 (m, 1H), 7.84–7.90 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.6, 26.6, 34.7, 36.6, 44.8, 51.1, 126.3, 128.3, 128.6, 128.6, 130.8, 132.8, 136.4, 136.6, 143.0, 200.9 ppm. **IR** (ATR): $\tilde{\nu}$ = 1674 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{21}H_{20}ONa$ $[M+Na]^+$: 311.1406; Found: 311.1403. The analytical and spectroscopic data are in accordance with those reported.[S7]

1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone (28)

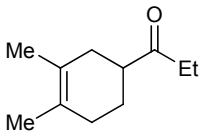


28
$C_{10}H_{16}O$
M = 152.23 g/mol

Prepared according to GP 2 from methyl vinyl ketone (**14**, 83.0 mg, 1.18 mmol, 1.00 equiv) and 2,3-dimethyl-1,3-butadiene (**27**, 0.269 mL, 2.36 mmol, 2.00 equiv) in 62% yield (111 mg). Prepared according to GP 3 from methyl vinyl ketone (**14**, 58.7 mg, 0.838 mmol, 1.00 equiv) and 2,3-dimethyl-1,3-butadiene (**27**, 0.190 mL, 1.68 mmol, 2.00 equiv) in 45% yield (57.0 mg). The product **28** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil.

R_f: 0.31 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 11.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.46–1.59 (m, 1H), 1.60 (s, 3H), 1.62 (s, 3H), 1.89–1.92 (m, 1H), 1.96–2.12 (m, 4H), 2.16 (s, 3H), 2.51–2.57 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.9, 19.2, 25.5, 28.1, 31.4, 33.2, 48.4, 124.1, 125.5, 212.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 1714 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_{16}ONa$ [*M*+Na]$^+$: 175.1093; Found: 175.1098. The analytical and spectroscopic data are in accordance with those reported.[S8]

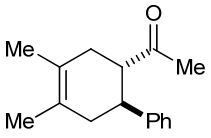
1-(3,4-Dimethylcyclohex-3-en-1-yl)propan-1-one (29)



29
$C_{11}H_{18}O$
M = 166.26 g/mol

Prepared according to GP 2 from ethyl vinyl ketone (**17**, 89.6 mg, 1.07 mmol, 1.00 equiv) and 2,3-dimethyl-1,3-butadiene (**27**, 0.242 mL, 2.14 mmol, 2.00 equiv) in 64% yield (113 mg). Prepared according to GP 3 from ethyl vinyl ketone (**17**, 79.6 mg, 0.946 mmol, 1.00 equiv), and 2,3-dimethyl-1,3-butadiene (**27**, 0.214 mL, 1.89 mmol, 2.00 equiv) in 62% yield (98.0 mg). The product **29** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. **R_f**: 0.38 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 12.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.3 Hz, 3H), 1.46–1.57 (m, 1H), 1.59 (s, 3H), 1.61 (s, 3H), 1.83–1.91 (m, 1H), 1.94–2.18 (m, 4H), 2.48 (dq, *J* = 7.2 Hz, *J* = 4.0 Hz, 2H), 2.53–2.60 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 7.9, 18.9, 19.2, 25.7, 31.4, 33.5, 33.9, 47.5, 124.2, 125.5, 214.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 1717 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{18}ONa$ [*M*+Na]$^+$: 189.1250; Found: 189.1256. The analytical and spectroscopic data are in accordance with those reported.[S6, S8]

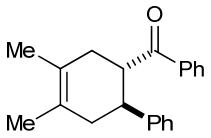
1-(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)ethanone (30)



30
$C_{16}H_{20}O$
M = 228.33 g/mol

Prepared according to GP 2 from 4-phenyl-3-buten-2-one (**18**, 72.8 mg, 0.498 mmol, 1.00 equiv) and 2,3-dimethyl-1,3-butadiene (**27**, 0.113 mL, 0.996 mmol, 2.00 equiv) in 72% yield (81.6 mg). Prepared according to GP 3 from 4-phenyl-3-buten-2-one (**18**, 125 mg, 0.852 mmol, 1.00 equiv), and 2,3-dimethyl-1,3-butadiene (**27**, 0.193 mL, 1.71 mmol, 2.00 equiv) in 57% yield (110 mg). The product **30** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a slightly yellow oil. **R_f**: 0.37 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 18.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.60 (s, 3H), 1.63 (s, 3H), 1.80 (s, 3H), 2.02–2.11 (m, 1H), 2.13–2.20 (m, 2H), 2.21–2.30 (m, 1H), 2.88–3.00 (m, 2H), 7.11–7.17 (m, 3H), 7.20–7.26 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.8, 18.8, 29.7, 35.1, 40.5, 43.6, 54.1, 123.9, 125.6, 126.7, 127.5, 128.7, 144.3, 212.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 1714 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{20}ONa$ [*M*+Na]$^+$: 251.1406; Found: 251.1407.

(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)phenylmethanone (31)

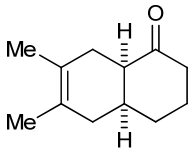


31
$C_{21}H_{22}O$
M = 290.40 g/mol

Prepared according to GP 2 from *trans*-chalcone (**19**, 91.0 mg, 0.437 mmol, 1.00 equiv) and 2,3-dimethyl-1,3-butadiene (**27**, 0.0990 mL, 0.874 mmol, 2.00 equiv) in 71% yield (89.8 mg). Prepared according to GP 3 from *trans*-chalcone (**19**, 92.2 mg, 0.443 mmol, 1.00 equiv), and 2,3-dimethyl-1,3-butadiene (**27**, 0.100 mL, 0.886 mmol, 2.00 equiv) in 44% yield (55.9 mg). The product **31** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 98:2) as a white solid. **R_f**: 0.37 (CH:EtOAc = 98:2). **Mp**: 79.6°C. **GLC** (FS-Supreme): t_R = 23.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.69 (bs, 6H), 2.23–2.39 (m, 4H), 3.30 (ddd, *J* = 14.4 Hz, *J* = 9.6 Hz, *J* = 7.1 Hz, 1H), 4.01 (dt, *J* = 10.7 Hz, *J* = 5.6 Hz, 1H), 7.03–7.09 (m, 1H), 7.12–7.23 (m, 4H), 7.34–7.41 (m, 2H), 7.45–7.52 (m, 1H), 7.80–7.86 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.8, 18.9, 37.1, 40.8, 43.2, 47.5, 124.2, 125.8, 126.3, 127.5, 128.2, 128.4, 128.6, 132.8, 137.5, 144.8, 203.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 1670 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{21}H_{22}ONa$ [*M*+Na]$^+$: 313.1563;

Found: 313.1562. The analytical and spectroscopic data are in accordance with those reported.[S9]

6,7-Dimethyl-3,4,4a,5,8,8a-hexahydro-2H-naphthalen-1-one (33)



33

$C_{12}H_{18}O$

M = 178.27 g/mol

Prepared according to GP 2 from 2-cyclohexene-1-one (**21**, 87.9 mg, 0.914 mmol, 1.00 equiv), and 2,3-dimethyl-1,3-butadiene (**27**, 0.207 mL, 1.83 mmol, 2.00 equiv) in 45% yield (74.0 mg). The product **33** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. **R_f**: 0.24 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 15.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.58 (bd, *J* = 1.6 Hz, 3H), 1.63 (bd, *J* = 0.7 Hz, 3H), 1.67–1.79 (m, 2H), 1.80–1.95 (m, 4H), 1.96–2.05 (m, 1H), 2.21–2.20 (m, 1H), 2.30–2.45 (m, 3H), 2.67 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.9, 19.3, 24.2, 28.4, 30.2, 34.1, 36.6, 39.9, 49.3, 122.9, 123.6, 213.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 1709 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{12}H_{18}ONa$ $[M+Na]^+$: 201.1250; Found: 201.1255. The analytical and spectroscopic data are in accordance with those reported.[S10]

***endo*-1-(Bicyclo[2.2.1]hept-5-en-2-yl)ethanone (35)**

35

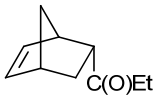
$C_9H_{12}O$

M = 136.19 g/mol

Prepared according to GP 3 from methyl vinyl ketone (**14**, 76.2 mg, 1.09 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.180 mL, 2.18 mmol, 2.00 equiv) in 62% yield (92.2 mg, *endo:exo* = 99:1). The product **35** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. **R_f**: 0.18 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 8.95 min (*exo*), 9.34 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 8.0 Hz, 1H), 1.43–1.50 (m, 2H), 1.74 (ddd, *J* = 11.7 Hz, *J* = 8.9 Hz, *J* = 3.7 Hz, 1H), 2.12 (s, 3H), 2.89 (bs, 1H), 3.00

(ddd, *J* = 9.0 Hz, *J* = 3.9 Hz, *J* = 3.9 Hz, 1H), 3.23 (bs, 1H), 5.85 (dd, *J* = 5.7 Hz, *J* = 2.8 Hz, 1H), 6.15 (dd, *J* = 5.7 Hz, *J* = 3.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 27.5, 29.3, 42.8, 46.0, 50.1, 52.5, 131.4, 138.0, 209.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 1706 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_9H_{12}ONa$ [*M*+Na]$^+$: 159.0780; Found: 159.0778. The analytical and spectroscopic data are in accordance with those reported.[S8]

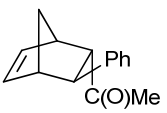
endo-1-(Bicyclo[2.2.1]hept-5-en-2-yl)propan-1-one (36)



36
$C_{10}H_{14}O$
M = 150.22 g/mol

Prepared according to GP 3 from ethyl vinyl ketone (**17**, 61.6 mg, 0.732 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.121 mL, 1.47 mmol, 2.00 equiv) in 76% yield (84.0 mg, *endo:exo* = 99:1). The product **36** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. **R_f**: 0.21 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 10.4 min (*exo*), 10.7 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.3 Hz, 3H), 1.31 (d, *J* = 8.1 Hz, 1H), 1.41–1.46 (m, 1H), 1.49 (ddd, *J* = 11.5 Hz, *J* = 4.2 Hz, *J* = 2.7 Hz, 1H), 1.74 (ddd, *J* = 11.7 Hz, *J* = 9.0 Hz, *J* = 3.8 Hz, 1H), 2.35–2.51 (m, 2H), 2.89 (bs, 1H), 3.00 (ddd, *J* = 8.1 Hz, *J* = 4.0 Hz, *J* = 4.0 Hz, 1H), 3.22 (bs, 1H), 5.81 (dd, *J* = 5.7 Hz, *J* = 2.8 Hz, 1H), 6.14 (dd, *J* = 5.7 Hz, *J* = 3.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 8.0, 27.6, 35.0, 42.8, 46.1, 50.1, 51.4, 131.5, 137.8, 211.7 ppm. **IR** (ATR): $\tilde{\nu}$ = 1717 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_{14}ONa$ [*M*+Na]$^+$: 173.0937; Found: 173.0940. The analytical and spectroscopic data are in accordance with those reported.[S8]

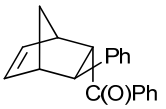
endo-1-(3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)ethanone (37)



37
$C_{15}H_{16}O$
M = 212.29 g/mol

Prepared according to GP 3 from 4-phenyl-3-buten-2-one (**18**, 73.3 mg, 0.501 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.0830 mL, 1.00 mmol, 2.00 equiv) in 77% yield (81.5 mg, *endo:exo* > 95:5 determined by ^{1}H NMR analysis of the crude product). The product **37** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a white solid. **R_f**: 0.26 (CH:EtOAc = 95:5). **Mp**: 58.2°C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.61 (ddd, *J* = 8.6 Hz, *J* = 3.5 Hz, *J* = 1.7 Hz, 1H), 1.87 (bd, *J* = 8.6 Hz, 1H), 2.16 (s, 3H), 3.02 (bs, 1H), 3.07 (dd, *J* = 5.0 Hz, *J* = 3.5 Hz, 1H), 3.20 (dd, *J* = 5.0 Hz, *J* = 1.6 Hz, 1H), 3.34 (bs, 1H), 6.03 (dd, *J* = 5.7 Hz, *J* = 2.8 Hz, 1H), 6.41 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 7.17–7.22 (m, 1H), 7.25–7.33 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 29.3, 45.4, 46.6, 47.7, 48.6, 61.2, 126.1, 127.6, 128.6, 133.3, 139.5, 144.5, 208.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 1693 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{15}H_{16}ONa$ [*M*+Na]$^{+}$: 235.1093; Found: 235.1088. The analytical and spectroscopic data are in accordance with those reported.[S11]

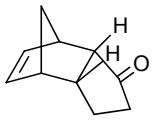
endo-Phenyl-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (38)



38
$C_{20}H_{18}O$
M = 274.36 g/mol

Prepared according to GP 3 from *trans*-chalcone (**19**, 99.7 mg, 0.479 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.079 mL, 0.958 mmol, 2.00 equiv) in 73% yield (96.0 mg, *endo:exo* > 95:5 determined by 1H NMR analysis of the crude mixture). The product **38** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 98:2) as a white solid. **R_f**: 0.27 (CH:EtOAc = 95:5). **Mp**: 78.4°C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.64–1.69 (m, 1H), 2.03 (bd, *J* = 8.5 Hz, 1H), 3.14 (bs, 1H), 3.36 (bs, 1H), 3.50 (dd, *J* = 4.8 Hz, *J* = 1.3 Hz, 1H), 3.93 (dd, *J* = 4.9 Hz, *J* = 3.5 Hz, 1H), 5.89 (dd, *J* = 5.6 Hz, *J* = 2.8 Hz, 1H), 6.48 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 1H), 7.17–7.23 (m, 1H), 7.28–7.33 (m, 4H), 7.42–7.48 (m, 2H), 7.52–7.58 (m, 1H), 7.93–7.98 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 45.9, 48.1, 48.6, 48.7, 56.3, 126.1, 127.6, 128.5, 128.6, 126.8, 126.8, 132.9, 133.0, 137.3, 139.3, 144.8, 200.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 1673 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{20}H_{18}ONa$ [*M*+Na]$^{+}$: 297.1250; Found: 297.1262.

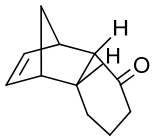
endo-Tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (39)



39
$C_{10}H_{12}O$
M = 148.20 g/mol

Prepared according to GP 3 from 2-cyclopentene-1-one (**20**, 76.8 mg, 0.937 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.155 mL, 1.87 mmol, 2.00 equiv) in 68% yield (94.8 mg, *endo:exo* = 95:5). The product **39** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a white solid. **R_f**: 0.15 (CH:EtOAc = 95:5). **Mp**: 94.6°C. **GLC** (FS-Supreme): t_R = 11.9 min (*exo*), 12.1 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.38–1.43 (m, 1H), 1.46–1.56 (m, 2H), 1.92–2.04 (m, 2H), 2.06–2.19 (m, 1H), 2.84 (ddd, *J* = 8.9 Hz, *J* = 4.6 Hz, *J* = 1.4 Hz, 1H), 2.92–2.98 (m, 1H), 2.98–3.02 (m, 1H), 3.16–3.21 (m, 1H), 6.10 (dd, *J* = 5.7 Hz, *J* = 2.9 Hz, 1H), 6.21 (dd, *J* = 5.7 Hz, *J* = 2.9 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 22.8, 40.7, 41.4, 47.2, 47.6, 52.4, 54.5, 134.9, 136.3, 222.5 ppm. **IR** (ATR): $\tilde{\nu}$ = 1726 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_{12}ONa$ $[M+Na]^+$: 171.0780; Found:171.0783. The analytical and spectroscopic data are in accordance with those reported.[S12]

endo-Tricyclo[5.2.1.0^{2,7}]undec-9-en-3-one (40)



40
$C_{11}H_{14}O$
M = 162.23 g/mol

Prepared according to GP 3 from 2-cyclohexene-1-one (**21**, 91.2 mg, 0.949 mmol, 1.00 equiv), and cyclopentadiene (**34**, 0.157 mL, 1.90 mmol, 2.00 equiv) in 68% yield (104 mg, *endo:exo* = 95:5). The product **40** was obtained after flash column chromatography on silica gel (cyclohexane:ethyl acetate = 95:5) as a colourless oil. **R_f**: 0.16 (CH:EtOAc = 95:5). **GLC** (FS-Supreme): t_R = 13.4 min (*exo*), 13.6 min (*endo*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.70–0.81 (m, 1H), 1.30 (ddd, *J* = 8.3 Hz, *J* = 1.4 Hz, *J* = 1.4 Hz, 1H), 1.44 (ddd, *J* = 8.3 Hz, *J* = 1.9 Hz, *J* = 1.9 Hz, 1H), 1.62–1.82 (m, 2H), 1.86–2.00 (m, 2H), 2.26–2.36 (m, 1H), 2.62–2.68 (m, 1H), 2.68–2.74 (m,

1H), 2.87 (bs, 1H), 3.25 (bs, 1H), 6.00 (dd, *J* = 5.7 Hz, *J* = 3.0 Hz, 1H), 6.17 (dd, *J* = 5.7 Hz, *J* = 2.9 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.9, 28.1, 39.5, 41.5, 45.3, 46.7, 48.5, 51.8, 135.1, 137.8, 215.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 1698 (s, C=O) cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{14}ONa$ $[M+Na]^+$: 185.0937; Found: 185.0941. The analytical and spectroscopic data are in accordance with those reported.[S13]

6 Details for DFT Calculations

All DFT calculations have been performed with the Turbomole program[S14]. We have used the TPSS meta-GGA functional[S15] and a basis set with triple zeta quality and additional polarization functions (def2-TZVPP).[S16] The resolution of the identity (RI)[S17] approximation was used in the SCF procedures. An atom pair-wise dispersion correction has been applied in all calculations (-D3)[S18] with a Becke-Johnson type damping function.[S19] In all calculations, the COSMO[S20] solvation model was applied with a dielectric constant of ε = 9.80.

Transition structure optimizations were performed in three steps: after preoptimizing the complexes with fixed C'_{ipso}, H and P/N coordinates in reasonable distances, second derivatives of the energy were calculated numerically with SNF.[S21] Then, a full geometry optimization was performed, following the largest negative eigenvalue of the Hessian matrix. The nature of the TS was verified by numerical calculation of the harmonical vibration frequencies at the optimized geometry with SNF. For the transition structures, the number of negative eigenvalues and the one imaginary frequency obtained in that calculation is also given in the following.

6.1 DFT Energies (TPSS-D3/def2-TZVPP) and Optimized Geometries of the Structures

Electronic energies (E) in hartree, Cartesian coordinates in Å

Silylium Ion (**7**) E = -2137.868361663 h

FE	-1.40348813	-0.88422047	0.24368552
C	-3.13201122	-0.08267659	-0.57311395
C	-2.19221753	0.58594474	1.43094633
C	-1.37995964	1.14286798	0.35827605
C	-2.00166396	0.71722334	-0.88711061
C	-3.24911363	-0.16433380	0.85018778
C	-0.50419462	-2.29704616	1.43927747
C	-1.66048773	-2.83819537	0.81149593
C	-1.48798270	-2.74963686	-0.60884302
C	-0.22301319	-2.15464689	-0.87000356
C	0.39938383	-1.87545846	0.40095750
SI	0.39018891	0.74164164	0.54497742
C	1.07231978	0.80888781	2.27710561
C	1.63632583	1.20710296	-0.79662780
C	2.14172674	2.61002267	-0.36109020
C	2.83056263	0.23143479	-0.81920956
C	1.02523472	1.31059169	-2.20412923
H	-3.77076058	-0.58241756	-1.28761276
H	-1.99242637	0.68169204	2.48857750
H	-1.64000275	0.92695640	-1.88150963
H	-3.99141991	-0.73504730	1.39003229
H	-0.33298985	-2.21094306	2.50241176
H	-2.53730873	-3.21271118	1.31969342
H	-2.21258270	-3.04484626	-1.35390455
H	0.19839515	-1.95057875	-1.84334457
H	1.43148748	-1.57935332	0.54983620
H	1.24705677	1.85098991	2.56581896
H	0.38046195	0.36450445	2.99662345
H	2.02736833	0.27828949	2.34146797
H	2.65707473	2.57901906	0.60357797
H	2.85624617	2.97063135	-1.11130919
H	1.32514579	3.33769855	-0.29840517
H	3.26369594	0.07979023	0.17558680
H	2.55197140	-0.74291654	-1.23167190
H	3.61704437	0.64777958	-1.46029594
H	0.24070512	2.07172742	-2.24821821
H	1.81047962	1.60318665	-2.91197456
H	0.60874799	0.35704581	-2.54216153

Sila[1]ferrocenophane (**11**) E = -2137.421177292 h

FE	-2.00533006	-0.32026742	0.00000000
C	-2.78164965	0.41357744	1.77658399
C	-1.47573550	-1.48187462	1.56193928
C	-0.57729524	-0.34413556	1.40983246
C	-1.42953666	0.82735245	1.55155547
C	-2.81165934	-1.01594390	1.77627978
C	-1.47573550	-1.48187462	-1.56193928
C	-2.81165934	-1.01594390	-1.77627978
C	-2.78164965	0.41357744	-1.77658399
C	-1.42953666	0.82735245	-1.55155547
C	-0.57729524	-0.34413556	-1.40983246
SI	0.69074091	-0.46896605	0.00000000
C	2.05186641	0.85987278	0.00000000
C	2.92142990	0.66739478	1.26066620
C	2.92142990	0.66739478	-1.26066620
C	1.49783742	2.29720196	0.00000000
H	-3.63376683	1.07144727	1.88569924
H	-1.18808370	-2.52054495	1.46717470
H	-1.10806318	1.85517216	1.45823788
H	-3.68935558	-1.63788189	1.89179385
H	-1.18808370	-2.52054495	-1.46717470
H	-3.68935558	-1.63788189	-1.89179385
H	-3.63376683	1.07144727	-1.88569924
H	-1.10806318	1.85517216	-1.45823788
H	3.39181699	-0.32138657	1.28516445
H	3.72276600	1.41883002	1.27744964
H	2.33017289	0.78564544	2.17576918
H	3.39181699	-0.32138657	-1.28516445
H	2.33017289	0.78564544	-2.17576918
H	3.72276600	1.41883002	-1.27744964
H	0.89113398	2.50043813	0.88755070
H	2.33335916	3.01110212	0.00000000
H	0.89113398	2.50043813	-0.88755070
C	1.45651033	-2.18462680	0.00000000
H	2.08165435	-2.33361055	0.88691041
H	2.08165435	-2.33361055	-0.88691041
H	0.68735897	-2.96327593	0.00000000

$(Mes)_3P$ (**S5**) E = -1390.846136309 h

P	-0.06698377	-0.86068860	0.18187911
C	1.55425962	0.97449848	1.75031282
C	1.44782651	-0.20177607	0.96958815
C	2.57861406	-1.05508030	0.85765299
C	3.76183155	-0.73309352	1.52523704
C	3.87031721	0.40650017	2.32654854
C	2.75663290	1.24358192	2.41528018
C	-0.86465142	-1.47052815	-2.36510037
C	0.02642722	-0.64061218	-1.63254249
C	0.95435290	0.15924391	-2.34222640
C	0.99127966	0.08112306	-3.73969510
C	0.13305779	-0.74182070	-4.47122010
C	-0.80159459	-1.49851351	-3.75955162
C	-1.94261492	-0.44213112	2.13175928
C	-1.54110432	-0.00023126	0.84208151
C	-2.35148512	0.93790480	0.15851331
C	-3.53974284	1.37456391	0.75680622
C	-3.95413753	0.93717512	2.01600011
C	-3.12679195	0.03794594	2.69404802
H	4.61954231	-1.39378740	1.41435003
H	2.82691274	2.15601660	3.00475655
H	1.70455586	0.70739972	-4.27254633
H	-1.50288617	-2.13082263	-4.30078414
H	-4.14854611	2.10217283	0.22315889
H	-3.40761327	-0.30319820	3.68870123
C	-1.98199298	1.55194189	-1.16927318
H	-0.93118444	1.85330000	-1.19109704
H	-2.60042139	2.43508131	-1.35120426
H	-2.12645308	0.85737573	-2.00280873
C	-1.09581865	-1.39547123	2.93868894
H	-0.14635819	-0.93295284	3.23411346
H	-0.83819142	-2.28474912	2.35138341
H	-1.62285048	-1.70298093	3.84560863
C	0.45699362	2.00361334	1.86637236
H	0.00860114	2.22037908	0.89306910
H	0.86479152	2.93198701	2.27546021
H	-0.35633069	1.67186946	2.51932479
C	2.55166262	-2.29261589	-0.00523039
H	3.46693355	-2.87466139	0.13026464
H	2.46300259	-2.03561070	-1.06764645
H	1.68535249	-2.91997053	0.23551990
C	1.88089531	1.15054322	-1.68241918
H	2.72304548	0.66281065	-1.18161372
H	1.36028284	1.73703158	-0.92064659
H	2.28242079	1.83562850	-2.43408134
C	-1.91761758	-2.30156721	-1.67397014
H	-1.47542330	-2.91225107	-0.87792035
H	-2.42259774	-2.95446132	-2.39058789
H	-2.67405265	-1.66816949	-1.19510524
C	0.21850448	-0.81913221	-5.97522228
H	-0.76836011	-0.97736489	-6.42063326
H	0.85584796	-1.65693552	-6.28514290
H	0.64933816	0.09497250	-6.39394305
C	-5.25337136	1.41004174	2.61914593
H	-6.05787861	0.69056707	2.42093467
H	-5.55852714	2.37131184	2.19585875
H	-5.17088935	1.51582267	3.70523052
C	5.14162314	0.71573858	3.07718784
H	5.23223712	1.78761509	3.27578454
H	6.02240740	0.38744800	2.51702526
H	5.15692060	0.19797221	4.04456561

$[(Mes)_3P\text{-}H]^+$ (**12**) E = -1391.303949031 h

P	0.00023553	0.00077825	-0.59327615
C	1.53778716	-1.89715413	0.83862879
C	1.48058312	-0.93820781	-0.19889004
C	2.61028013	-0.67898079	-1.01671813
C	3.77914025	-1.40189495	-0.78246967
C	3.86158093	-2.36715306	0.22560074
C	2.73491088	-2.59081243	1.02253572
C	-0.71680817	2.60040915	-1.01841968
C	0.07252410	1.75252738	-0.19974634
C	0.87323931	2.28226759	0.83824315
C	0.87385457	3.66578780	1.02223962
C	0.11624418	4.52888596	0.22497924
C	-0.67693225	3.97414364	-0.78391247
C	-1.89287146	-1.91986251	-1.01829420
C	-1.55309712	-0.81213591	-0.19984203
C	-2.41180983	-0.38386456	0.83871010
C	-3.61010847	-1.07536697	1.02310745
C	-3.97871510	-2.16345413	0.22634984
C	-3.10210545	-2.57272238	-0.78303833
H	4.64949296	-1.19668521	-1.40041559
H	2.78920655	-3.32111838	1.82575956
H	1.47826826	4.07858169	1.82585095
H	-1.28989724	4.62464426	-1.40242099
H	-4.26987658	-0.75814094	1.82662683
H	-3.35878756	-3.42910129	-1.40119717
H	0.00070012	0.00072324	-1.99064807
C	1.71130650	1.44100314	1.76835702
H	1.15999828	0.58152701	2.16019288
H	2.03595082	2.04584372	2.61735839
H	2.60291017	1.05261861	1.26668903
C	-1.59928294	2.07178972	-2.12240793
H	-1.00388144	1.66896848	-2.95121733
H	-2.22006502	2.87516224	-2.52260268
H	-2.26248085	1.27325503	-1.77266943
C	0.16320224	6.01824243	0.43912620
H	-0.78355968	6.48771885	0.15934559
H	0.94977078	6.46366590	-0.18233250
H	0.38805717	6.26069421	1.48094305
C	2.59543867	0.35114719	-2.11930682
H	3.60181868	0.48604712	-2.51930805
H	2.23694913	1.32482768	-1.76816490
H	1.94833026	0.03943889	-2.94858494
C	0.38993896	-2.20176968	1.76846810
H	-0.07736744	-1.29432886	2.16134315
H	0.75061742	-2.78677237	2.61681505
H	-0.39294613	-2.77826790	1.26613483
C	5.12688835	-3.15434263	0.43911637
H	5.22293073	-3.47324641	1.48017750
H	6.00766953	-2.56922328	0.16187511
H	5.11922019	-4.05653946	-0.18485102
C	-5.29129136	-2.86843695	0.44174614
H	-6.07067297	-2.41213795	-0.18086153
H	-5.61400108	-2.79317642	1.48336610
H	-5.22315540	-3.92356531	0.16418341
C	-2.10153847	0.76162850	1.76959435
H	-1.08139501	0.71315656	2.16073590
H	-2.78720722	0.73996610	2.61901320
H	-2.21110853	1.72839569	1.26878271
C	-0.99419239	-2.41955586	-2.12269341
H	-0.94383303	-1.70270442	-2.95166878
H	-1.37933537	-3.35916140	-2.52243237
H	0.02927764	-2.59396166	-1.77360552

Di-*tert*-butylpyridine (**S3**) E = -563.1557160059

N	0.00000000	0.00000000	-0.06536694
C	0.00000000	-1.16563149	0.60180714
C	0.00000000	-1.20404761	2.00096817
C	0.00000000	0.00000000	2.70202299
C	0.00000000	1.20404761	2.00096817
C	0.00000000	1.16563149	0.60180714
C	0.00000000	-2.41346642	-0.28218919
C	0.00000000	2.41346642	-0.28218919
C	0.00000000	-3.71221738	0.53592682
C	1.25477402	-2.36796397	-1.18025503
C	-1.25477402	-2.36796397	-1.18025503
C	0.00000000	3.71221738	0.53592682
C	1.25477402	2.36796397	-1.18025503
C	-1.25477402	2.36796397	-1.18025503
H	0.00000000	-2.14742000	2.53417463
H	0.00000000	0.00000000	3.78852976
H	0.00000000	2.14742000	2.53417463
H	0.88851713	-3.78693280	1.17220765
H	0.00000000	-4.57041893	-0.14394878
H	-0.88851713	-3.78693280	1.17220765
H	2.16885425	-2.40068551	-0.57720681
H	1.25594897	-1.44505547	-1.76616994
H	1.25949400	-3.22512696	-1.86250446
H	-2.16885425	-2.40068551	-0.57720681
H	-1.25949400	-3.22512696	-1.86250446
H	-1.25594897	-1.44505547	-1.76616994
H	0.88851713	3.78693280	1.17220765
H	-0.88851713	3.78693280	1.17220765
H	0.00000000	4.57041893	-0.14394878
H	2.16885425	2.40068551	-0.57720681
H	1.25949400	3.22512696	-1.86250446
H	1.25594897	1.44505547	-1.76616994
H	-2.16885425	2.40068551	-0.57720681
H	-1.25594897	1.44505547	-1.76616994
H	-1.25949400	3.22512696	-1.86250446

Di-*tert*-butylpyridine-H^+ (**S4**) E = -563.6073692282 h

N	-0.01240097	-0.02165835	0.00000000
C	0.32908581	-1.34140815	0.00000000
C	1.68196166	-1.63576521	0.00000000
C	2.61671287	-0.59661788	0.00000000
C	2.20294897	0.72985290	0.00000000
C	0.84315551	1.02654611	0.00000000
C	-0.81433061	-2.33862285	0.00000000
C	0.28189425	2.43634094	0.00000000
C	-0.28001979	-3.77833504	0.00000000
C	-1.67446566	-2.11338075	-1.26631350
C	-1.67446566	-2.11338075	1.26631350
C	0.79732278	3.16233867	-1.26512943
C	-1.25475300	2.44210044	0.00000000
C	0.79732278	3.16233867	1.26512943
H	2.00759212	-2.66675788	0.00000000
H	3.67607222	-0.82968517	0.00000000
H	2.92527942	1.53589424	0.00000000
H	0.32264021	-3.98225684	-0.89014349
H	-1.12838021	-4.46749047	0.00000000
H	0.32264021	-3.98225684	0.89014349
H	-1.07973726	-2.26006347	-2.17223657
H	-2.10959046	-1.10857398	-1.29803887
H	-2.49941135	-2.83076973	-1.26872082
H	-1.07973726	-2.26006347	2.17223657
H	-2.49941135	-2.83076973	1.26872082
H	-2.10959046	-1.10857398	1.29803887
H	0.45012134	2.65997673	-2.17263383
H	1.88958255	3.20179138	-1.28289176
H	0.41675479	4.18757120	-1.26482132
H	-1.66865463	1.96266242	-0.89527296
H	-1.60427236	3.47702086	0.00000000
H	-1.66865463	1.96266242	0.89527296
H	1.88958255	3.20179138	1.28289176
H	0.45012134	2.65997673	2.17263383
H	0.41675479	4.18757120	1.26482132
H	-1.00692565	0.19994721	0.00000000

$(Mes)_3P$ (**S5**) + **7,** transition structure (**TS-P)** E = -3528.693137653 h

NIMAG = 1 (-1180.72 cm^{-1})

FE	4.09698771	0.09698128	0.61638785
C	6.11859493	0.15695232	0.19807313
C	5.04464710	-1.53644937	1.34875468
C	4.68606496	-1.68349855	-0.05596511
C	5.39738573	-0.62687565	-0.75320144
C	5.90127519	-0.40507483	1.49523306
C	2.32816718	0.17483765	1.57358330
C	2.97907642	1.42534603	1.73085245
C	3.25547088	1.95628229	0.43079816
C	2.78556196	1.02952970	-0.53930798
C	2.10289207	-0.11328205	0.13051046
SI	2.84500070	-1.92709012	-0.37032423
C	2.41409519	-2.40346908	-2.15585394
C	3.43162059	-3.47257479	-2.61183808
C	1.00144820	-3.02730784	-2.15342799
C	2.46002556	-1.21678350	-3.13321817
H	6.70658029	1.03739443	-0.02177820
H	4.66673204	-2.14323353	2.15979841
H	5.33212205	-0.41487908	-1.81141198
H	6.30227809	-0.02674449	2.42542470
H	2.03105302	-0.47473764	2.38118139
H	3.24517179	1.88308501	2.67339451
H	3.76852191	2.88411022	0.21847049
H	2.88787519	1.14251420	-1.60690568
H	0.73452420	-0.01301940	-0.14302804
H	3.45535423	-4.32764046	-1.92706895
H	3.14983565	-3.84768092	-3.60442935
H	4.44378379	-3.06191531	-2.67701187
H	0.99584905	-3.99024344	-1.63463212
H	0.26073416	-2.38456194	-1.66717156
H	0.66618813	-3.19728765	-3.18426583
H	3.45250658	-0.75696349	-3.17229262
H	2.21145856	-1.56159549	-4.14512641
H	1.73712921	-0.44021481	-2.86607769
P	-1.01371404	0.51820458	0.08558432
C	2.26975414	-3.24681299	0.82846135
H	2.88071474	-4.13825897	0.64321912
H	1.22304709	-3.52519285	0.69661654
H	2.42106950	-2.95212614	1.87009551
C	-0.80451807	0.79771083	1.87651474
C	-0.73345349	2.08220928	2.47417481
C	-0.51497789	-0.34697554	2.66470377
C	-0.28186164	-0.20495593	4.03192814
C	-0.49054027	2.16504960	3.84940156
C	-0.28971256	1.04317036	4.65519161
H	-0.06426713	-1.09699753	4.61491054
H	-0.43806860	3.15384989	4.29865562
C	-1.70573606	1.99333944	-0.78078915
C	-0.94625209	2.69160609	-1.74805195
C	-3.04656453	2.38688235	-0.54840499
C	-3.59060537	3.43154997	-1.30163027
C	-1.53790783	3.72093784	-2.48168247
C	-2.86501322	4.10661813	-2.28253991
H	-4.61709721	3.72845046	-1.09965786
H	-0.93457716	4.23647741	-3.22513034
C	-2.24677810	-0.78925555	-0.32933308
C	-3.20154963	-1.40239887	0.52155341
C	-2.19643294	-1.18797555	-1.69760272
C	-3.02213939	-2.21179830	-2.15594741
C	-4.00326780	-2.42936958	0.00249876
C	-3.92757609	-2.86517509	-1.31651622
H	-2.95436944	-2.49934978	-3.20251383
H	-4.72708141	-2.89115833	0.67085715
C	-4.79046503	-3.99026340	-1.82555108
H	-5.57689351	-4.23991088	-1.10906807

H	-4.18815908	-4.89036483	-1.99658147
H	-5.25651799	-3.72627467	-2.78029855
C	-3.48075957	5.22251962	-3.08571129
H	-2.93131109	6.15837826	-2.93518012
H	-4.52307425	5.38486747	-2.80123308
H	-3.44525014	4.99574677	-4.15688387
C	-0.06873232	1.17543595	6.13900795
H	0.60785623	0.39920935	6.50786370
H	-1.01848650	1.06620605	6.67693560
H	0.34444292	2.15545689	6.39203624
C	-1.32111830	-0.50720083	-2.71774596
H	-1.76282543	0.44152192	-3.03898299
H	-1.19620280	-1.14302111	-3.59626819
H	-0.32690127	-0.28322700	-2.32342204
C	0.50714996	2.41376035	-1.98911423
H	0.83607006	2.84532968	-2.93693820
H	0.71715829	1.34380245	-2.00770389
H	1.11728364	2.84887524	-1.19110214
C	-3.52342036	-1.03034239	1.95399204
H	-3.46941797	-1.91599833	2.59496619
H	-4.55443726	-0.66528264	2.00312109
H	-2.87762841	-0.26576398	2.37207670
C	-0.84117640	3.39212554	1.72999759
H	-1.85529150	3.58937079	1.37395618
H	-0.18211140	3.42044102	0.85877569
H	-0.55369192	4.20640639	2.39883515
C	-3.92336165	1.77345816	0.50695028
H	-4.72134434	2.46826443	0.77871260
H	-3.35884475	1.53209204	1.40979823
H	-4.38779162	0.85104697	0.14630178
C	-0.40706254	-1.73139896	2.08239034
H	0.27547285	-2.33082724	2.68727666
H	-0.03240550	-1.71561333	1.05598922
H	-1.36728688	-2.25099067	2.06010982

Di-*tert*-butylpyridine (**S3**)+ **7** Transition Structure **(TS-N)**

E = -2700.994450641 h

NIMAG = 1 (-1433.97 cm^{-1})

C	-4.00355339	0.06652169	-1.40726311
C	-3.71050126	-0.50719730	-0.10587864
C	-3.79026185	-1.95066012	-0.28706713
C	-4.06836140	-2.23342596	-1.65699825
C	-4.20126415	-0.98873765	-2.34788331
SI	-2.19525320	0.04872968	0.86860775
C	-2.06502903	-1.09740879	2.34855308
FE	-2.35208202	-1.10143872	-1.43506309
C	-0.84574888	-0.78975853	-2.80190884
C	-0.90735743	0.21818916	-1.80429062
C	-0.71175867	-0.38017621	-0.45597737
C	-0.61869674	-1.83772785	-0.75645682
C	-0.66257838	-2.05327214	-2.15573932
C	-2.25529867	1.87242542	1.39062193
C	-2.43190799	2.85311428	0.21717130
C	-3.49231972	1.98593488	2.31515030
C	-0.99883767	2.25535013	2.19610356
N	1.93243924	-0.18750945	-0.12327272
C	2.42871430	0.23713156	-1.31783827
C	3.21112228	-0.62307910	-2.08751256
C	3.52736897	-1.88770117	-1.60377949
C	3.16177319	-2.22356505	-0.30417592
C	2.37716491	-1.34491783	0.43885002
C	2.29103375	1.70926081	-1.70775923
C	3.73092732	2.28932932	-1.62031073
C	2.12742862	-1.59024083	1.92687634
C	1.36350407	-2.90545296	2.17677852
C	1.78870492	1.89107019	-3.15319152
C	1.42189343	2.49987537	-0.72356717
C	1.39989281	-0.40715218	2.57301092
C	3.52430290	-1.70679646	2.59279249
H	-4.39138912	-0.86709860	-3.40527096
H	-3.59443114	-2.69041384	0.47668966
H	-3.99343662	1.11836878	-1.65284932
H	-4.14436669	-3.21649886	-2.10059478
H	-0.49249499	-2.60951419	-0.01214340
H	-0.60192331	-3.01377103	-2.64838952
H	-0.95154133	-0.63148033	-3.86615911
H	-1.06775553	1.26913327	-1.99249027
H	0.53673352	-0.03205857	-0.00506030
H	-3.40017098	1.34616447	3.19900217
H	-3.58726644	3.02271873	2.66246167
H	-4.41486078	1.71818766	1.78972015
H	-0.08698466	2.16839038	1.60023579
H	-1.08431479	3.29839675	2.52706395
H	-3.35439873	2.66223770	-0.33766427
H	-2.48921293	3.87681714	0.60916037
H	-1.59397319	2.81911820	-0.48429511
H	3.58757981	-0.29319026	-3.04851026
H	3.49542420	-3.15483955	0.13836918
H	4.10598253	-2.57859091	-2.20825733
H	0.43181625	-0.22605262	2.10769811
H	1.98955578	0.50979033	2.48997034
H	1.23126694	-0.61811368	3.63293349
H	0.77116124	1.51826480	-3.27833325
H	2.43325938	1.37071492	-3.86719413
H	1.79989971	2.95598716	-3.40450902
H	4.14174538	2.16208200	-0.61405217
H	3.69584365	3.35917562	-1.84995725
H	4.40023461	1.80275345	-2.33498108
H	0.39450675	2.13773961	-0.69651451
H	1.39951045	3.55004746	-1.02782251
H	1.82935560	2.44380989	0.28942557
H	4.07771373	-2.57365231	2.22207916

H	3.39155939	-1.82085400	3.67346770
H	4.11957399	-0.80737999	2.40836810
H	0.33537789	-2.85031680	1.81381938
H	1.32788688	-3.10512716	3.25200239
H	1.85677282	-3.75045479	1.68808634
H	-0.88480152	1.63236374	3.08866730
H	-3.06286287	-1.17927604	2.79354633
H	-1.38454393	-0.73012317	3.11885681
H	-1.74749120	-2.10416956	2.06484249

7 References

[S1] a) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24*, 4760–4773; b) Lambert, J.B.; Lin, L.; Keinan, S. *Org. Biomol. Chem.* **2003**, *1*, 2559–2565.

[S2] Klare, H. F. T.; Bergander, K.; Oestreich, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 9077–9079.

[S3] Evchenko, S.V.; Kamounah, F.S.; Schaumburg, K.; *J. Labelled Compd. Radiopharm.* **2005**, *48*, 209–218.

[S4] The assignment of $^{2}H,^{13}C$ coupling constants was not possible due to the incomplete degree of deuteration.

[S5] Hara, K.; Akiyama, R.; Sawamura, M. *Org. Lett.* **2005**, *7*, 5621–5623.

[S6] Nakashima, D.; Yamamoto, H. *Org. Lett.* **2005**, *7*, 1251–1253.

[S7] Kinsman, A. C.; Kerr, M. A. *Org. Lett.* **2000**, *2*, 3517–3520.

[S8] Rickerby, J.; Vallet, M.; Bernardinelli, G.; Viton, F.; Kündig, E. P. *Chem. Eur. J.* **2007**, *13*, 3354–3368.

[S9] Cong, H.; Ledbetter, D.; Rowe, G. T.; Caradonna, J.P.; Porco, Jr., J. A. *J. Am. Chem. Soc.* **2008**, *130*, 9214–9215.

[S10] Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388–6390.

[S11] Singh, R. S.; Harada, T. *Eur. J. Org. Chem.* **2005**, 3433–3435.

[S12] Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 2458–2460.

[S13] Angell, E. C.; Fringuelli, F.; Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4325–4328.

[S14] TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[S15] Tao, J.; Perdew, J.P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

[S16] Weigend; F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[S17] Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5119–5121.

[S18] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

[S19] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

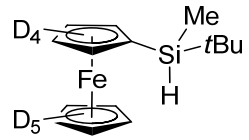
[S20] Klamt, A.; Schüürmann, G. *J. Chem. Soc. Perkin Trans. 2* **1993**, 799.

[S21] Neugebauer, J.; Reiher, M.; Kind, C.; Hess, B.A. *J. Comput. Chem.* **2002**, *23*, 895–910.

8 NMR Spectra of New Compounds

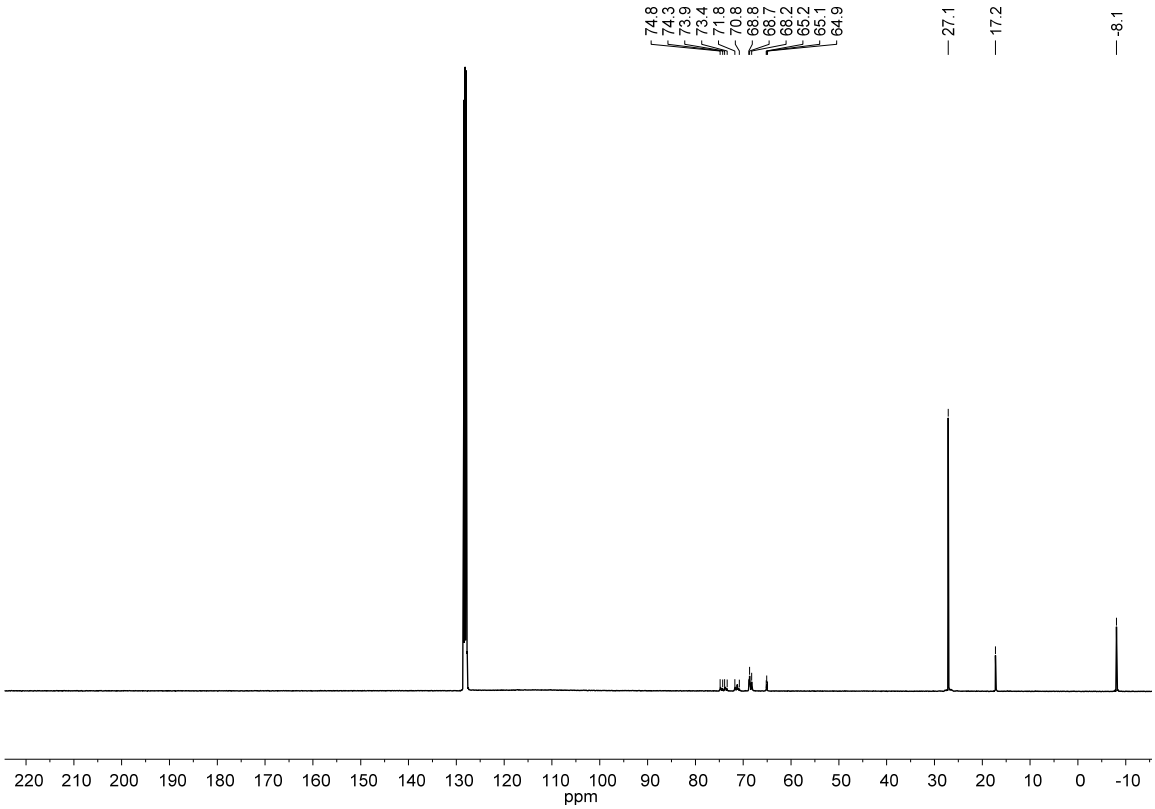
tert-Butylferrocenylmethylsilane-d9 (d9-S1)

^{1}H NMR (400 MHz, C_6D_6):

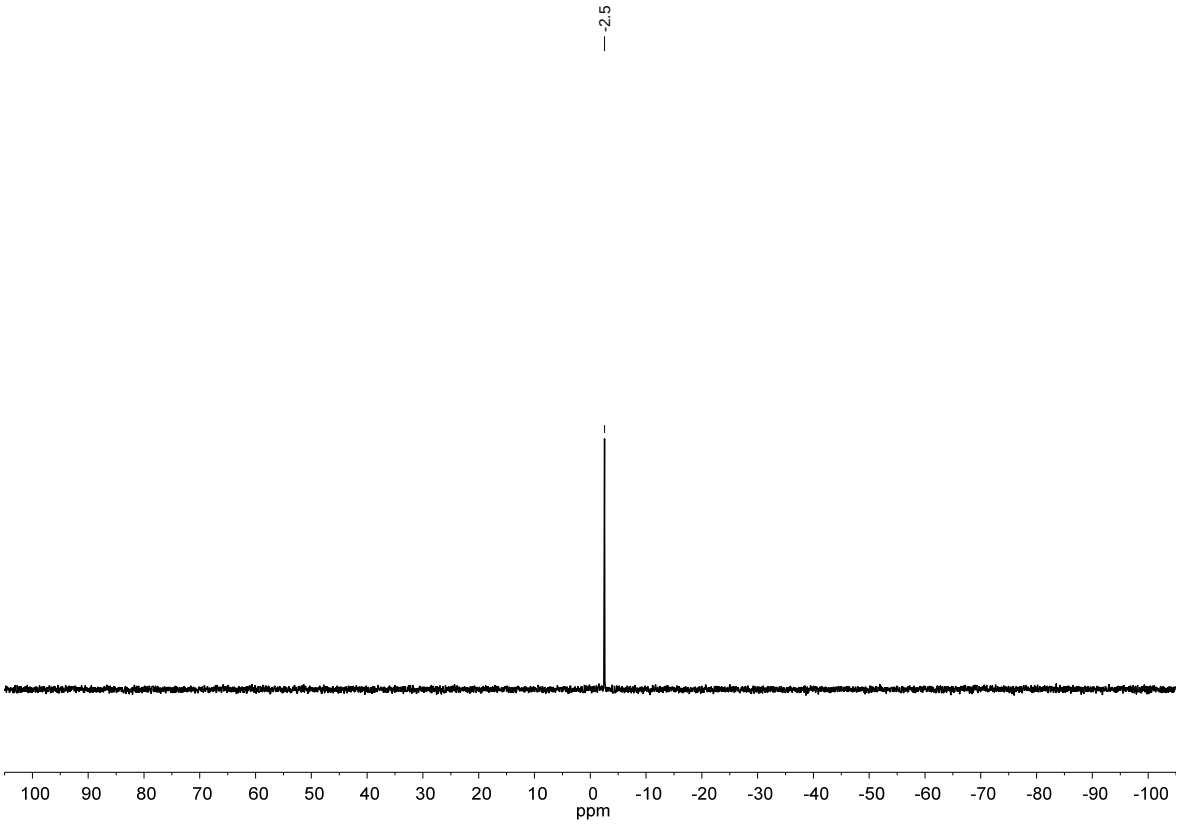


* residual non-deuterated ferrocene backbone

^{13}C NMR (100 MHz, C_6D_6):

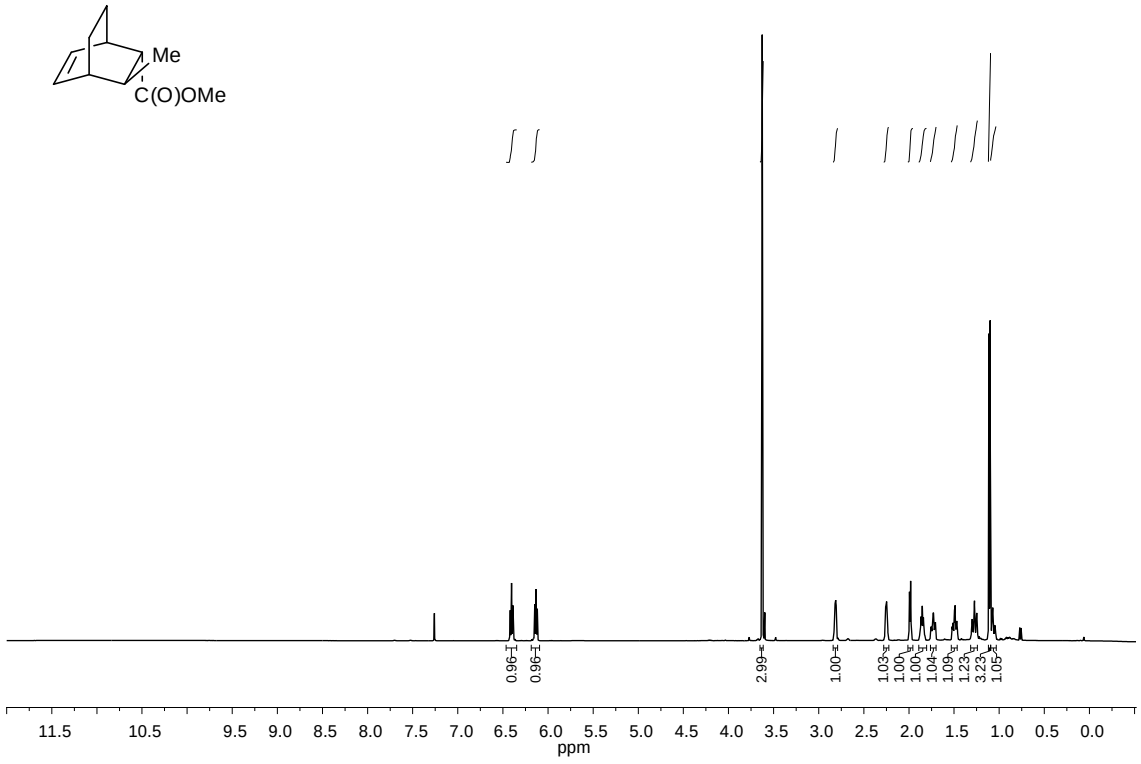


^{29}Si NMR (60 MHz, C_6D_6):

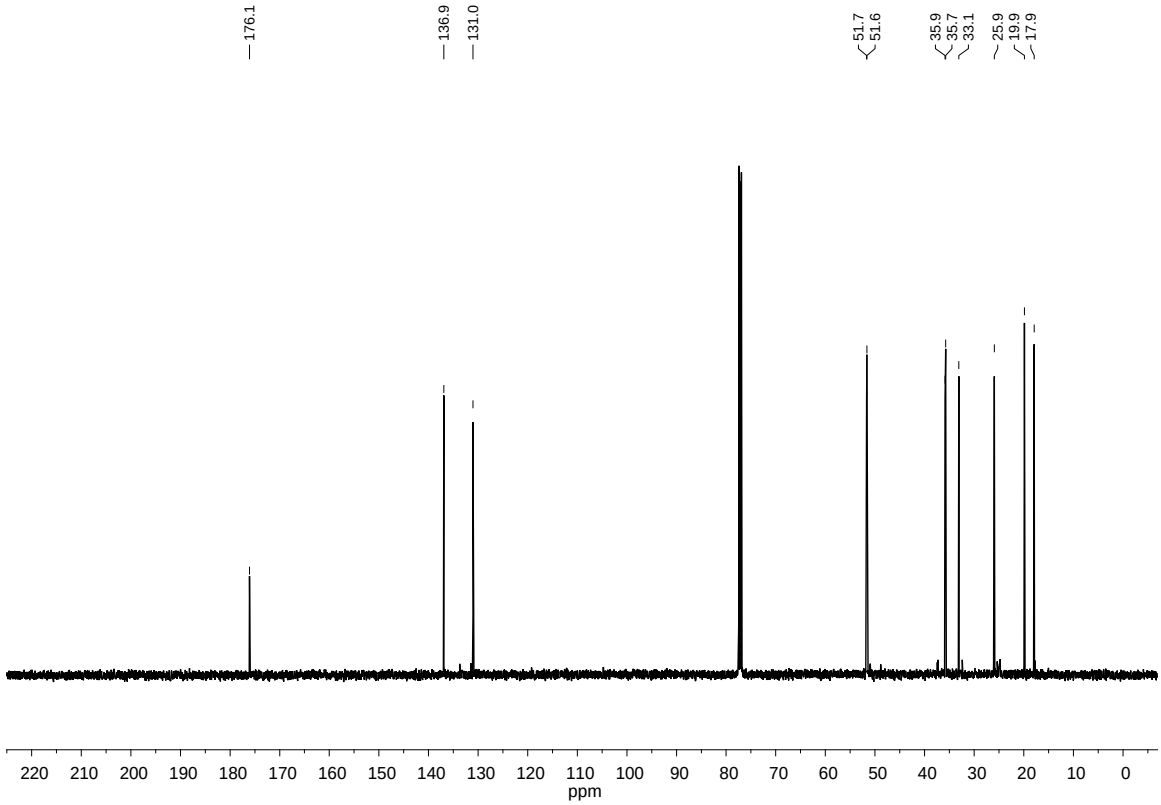


endo-1-(3-Methylbicyclo[2.2.2]oct-5-en-2-yl)carboxylic acid methyl ester (S7)

^{1}H NMR (500 MHz, $CDCl_3$):

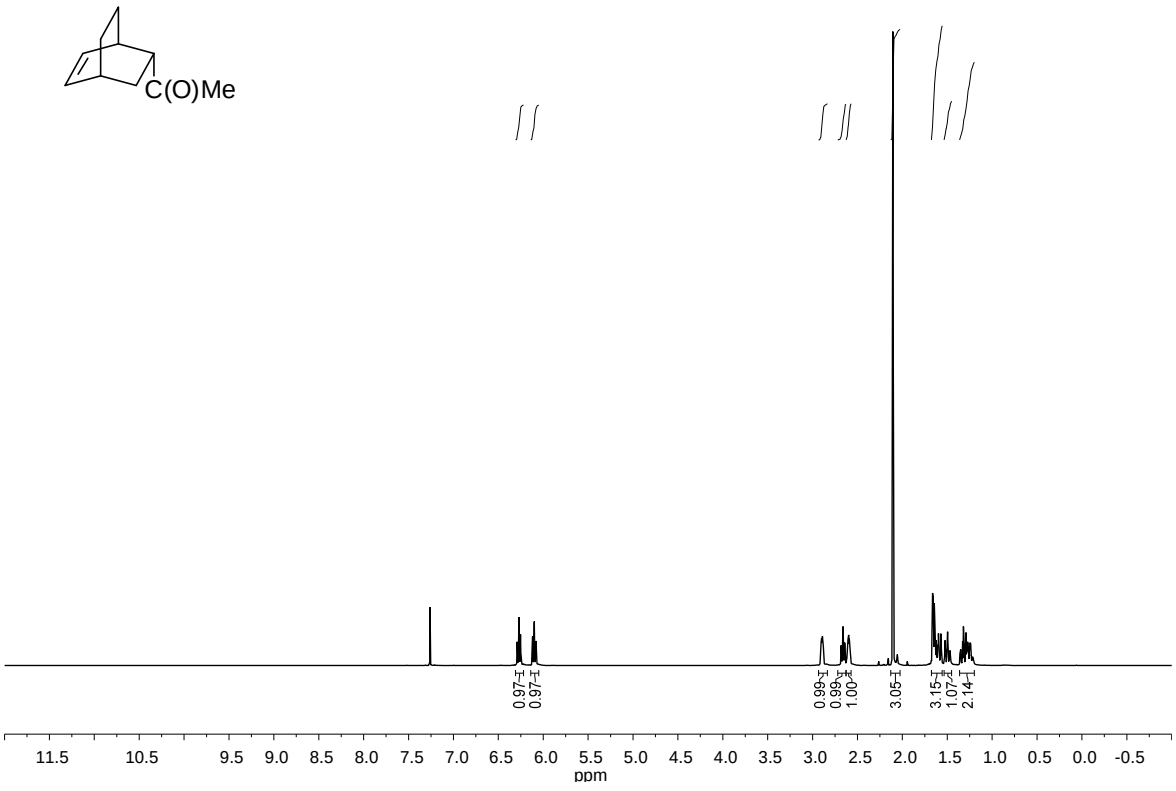


^{13}C NMR (125 MHz, $CDCl_3$):

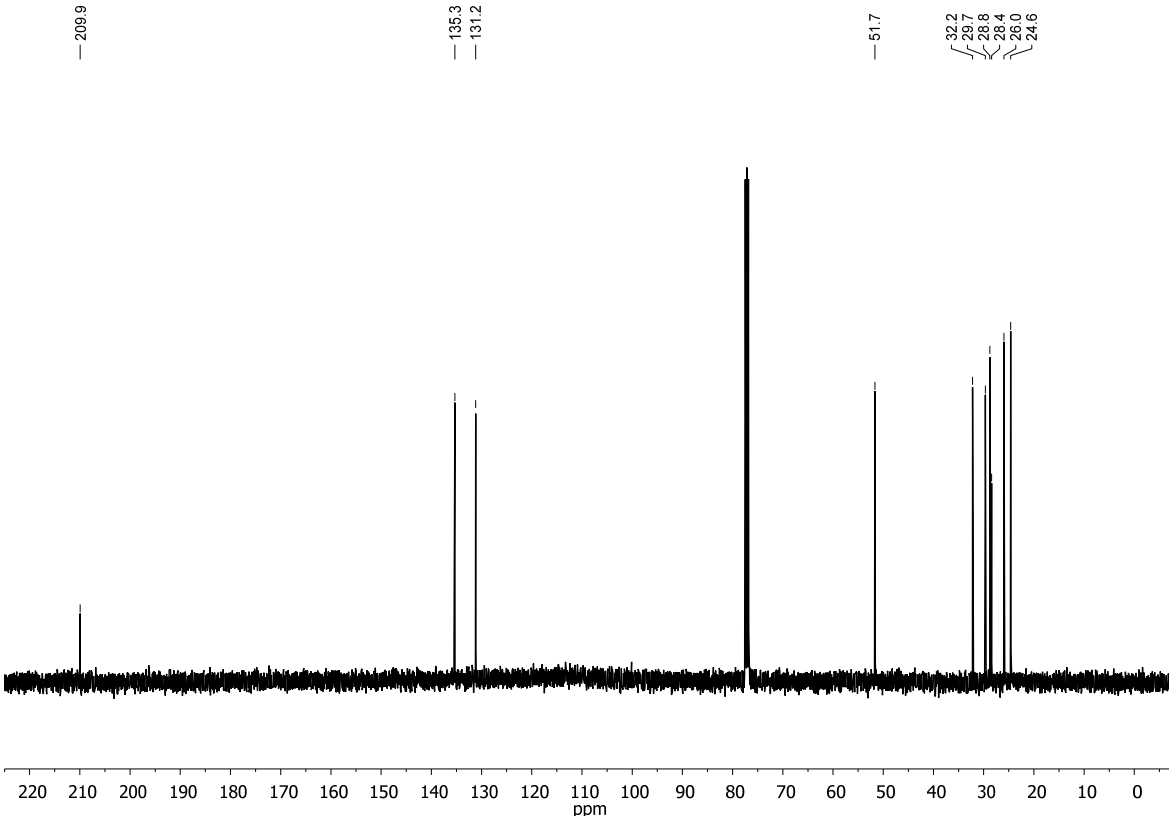


endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)ethanone (16)

^{1}H NMR (400 MHz, $CDCl_3$):

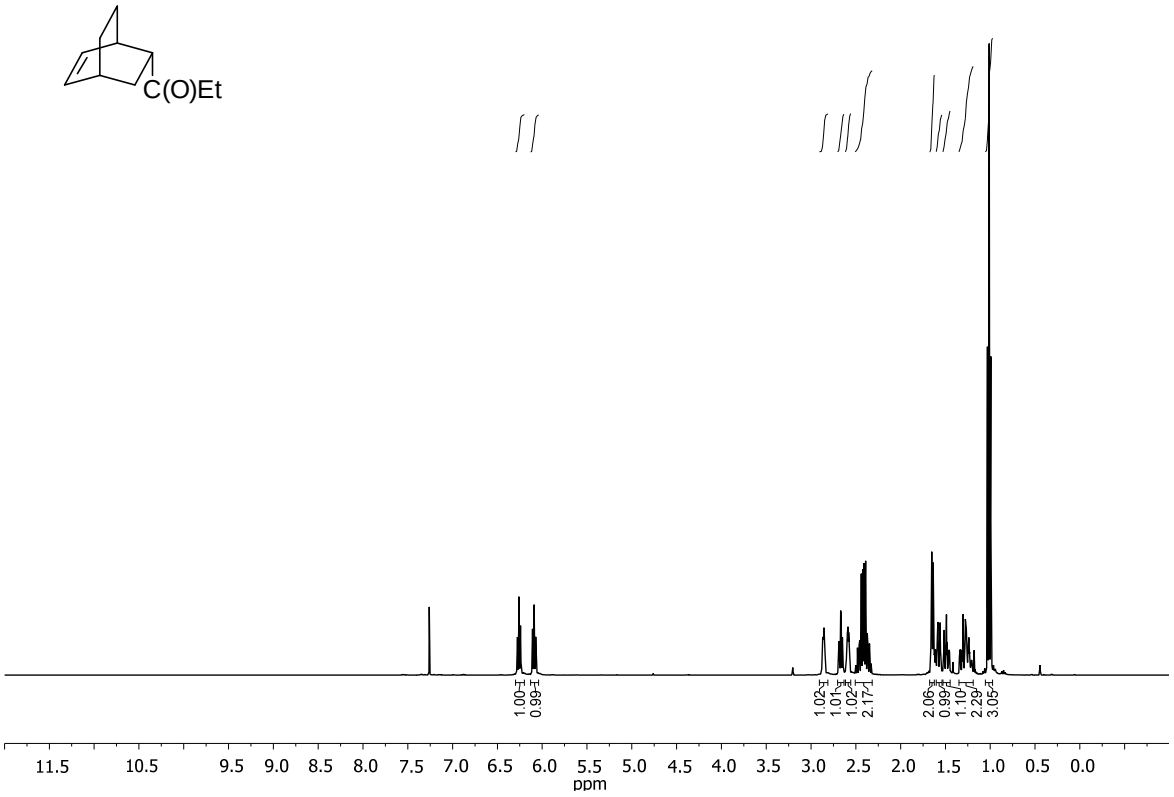


^{13}C NMR (100 MHz, $CDCl_3$):

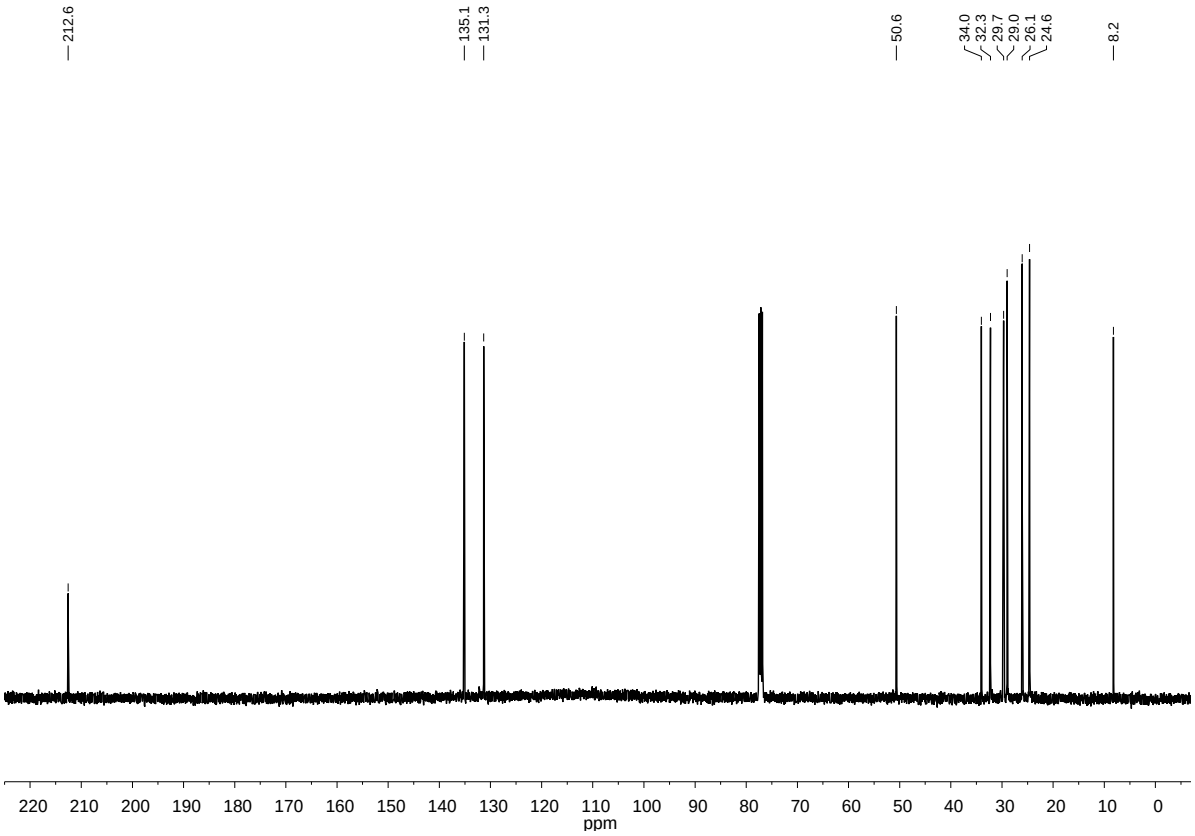


endo-1-(Bicyclo[2.2.2]oct-5-en-2-yl)propan-1-one (22)

^{1}H NMR (400 MHz, $CDCl_3$):

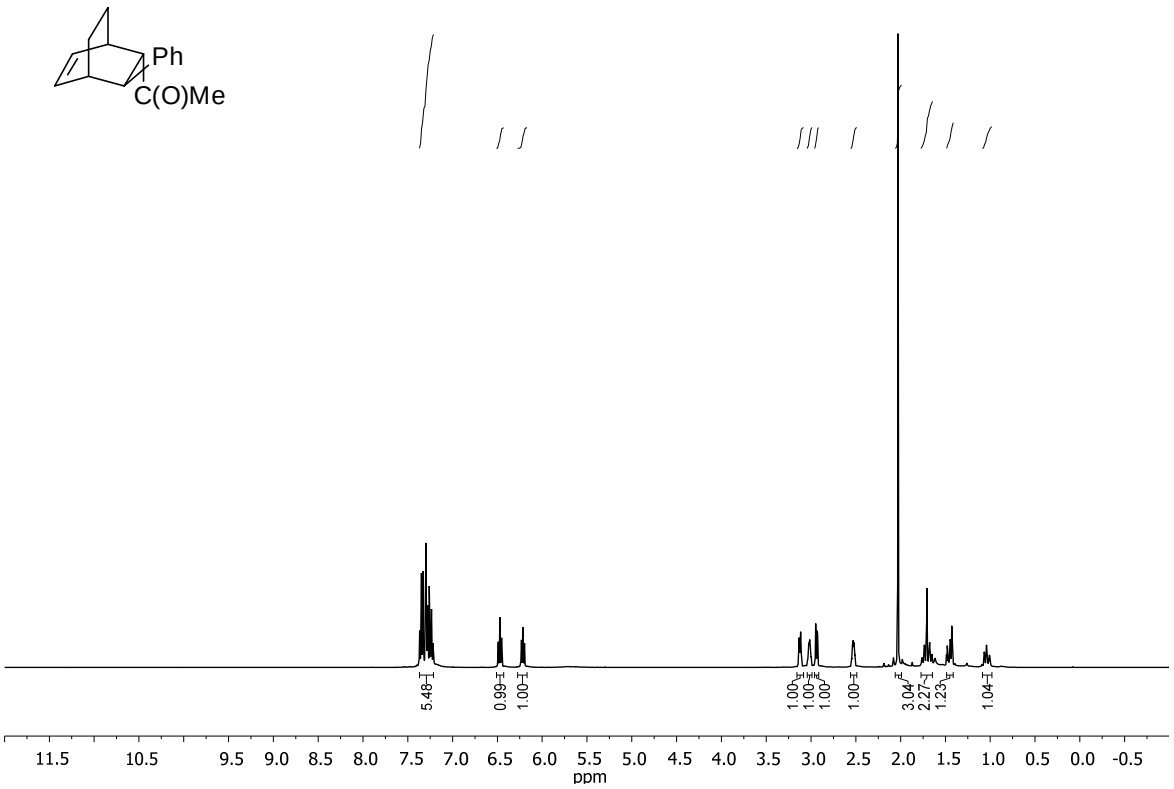


^{13}C NMR (100 MHz, $CDCl_3$):

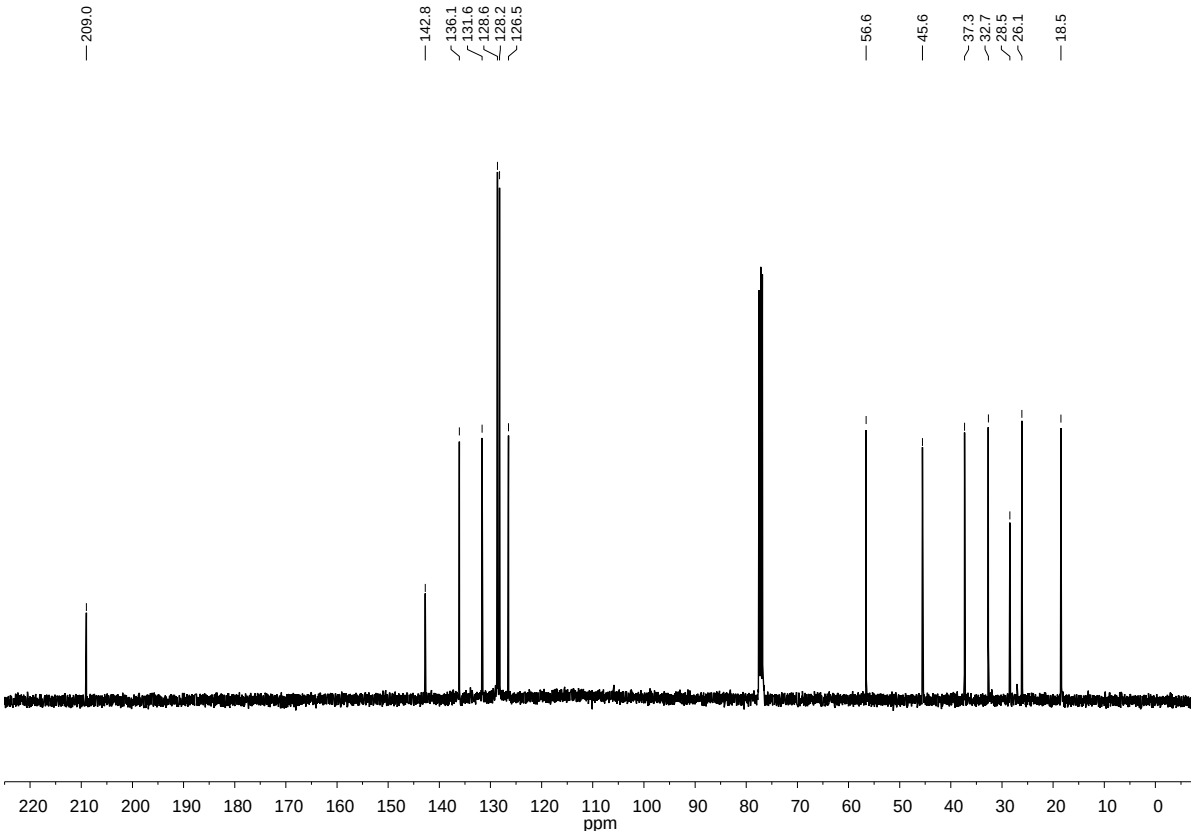


endo-1-(3-Phenylbicyclo[2.2.2]oct-5-en-2-yl)ethanone (23)

^{1}H NMR (400 MHz, $CDCl_3$):

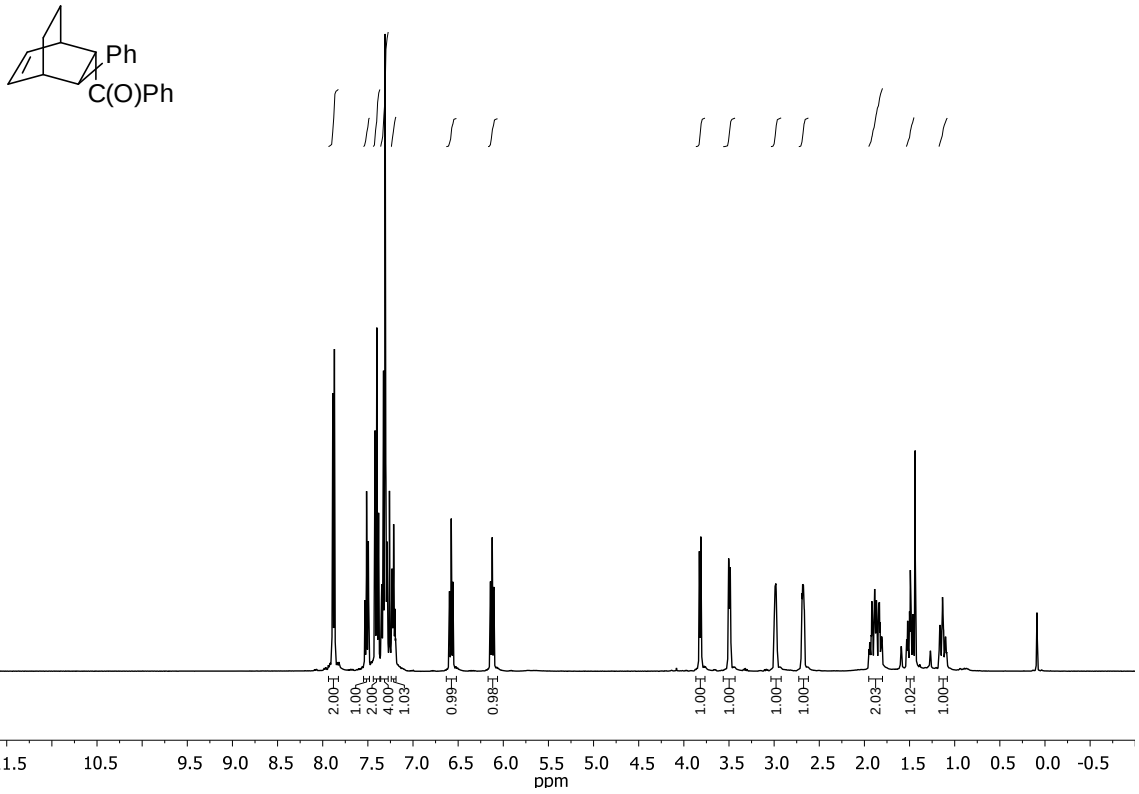


^{13}C NMR (100 MHz, $CDCl_3$):

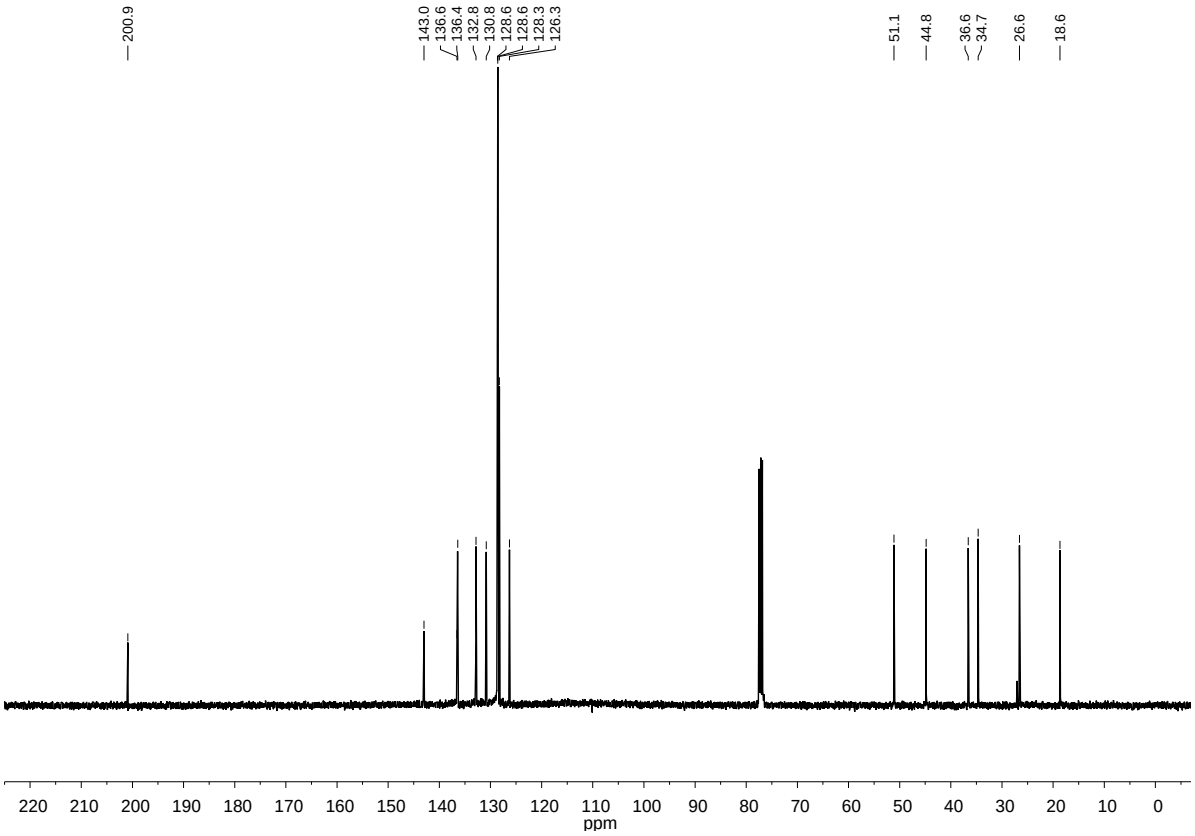


endo-Phenyl-(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (24)

^{1}H NMR (400 MHz, $CDCl_3$):

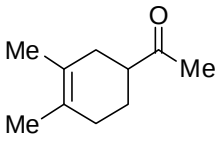


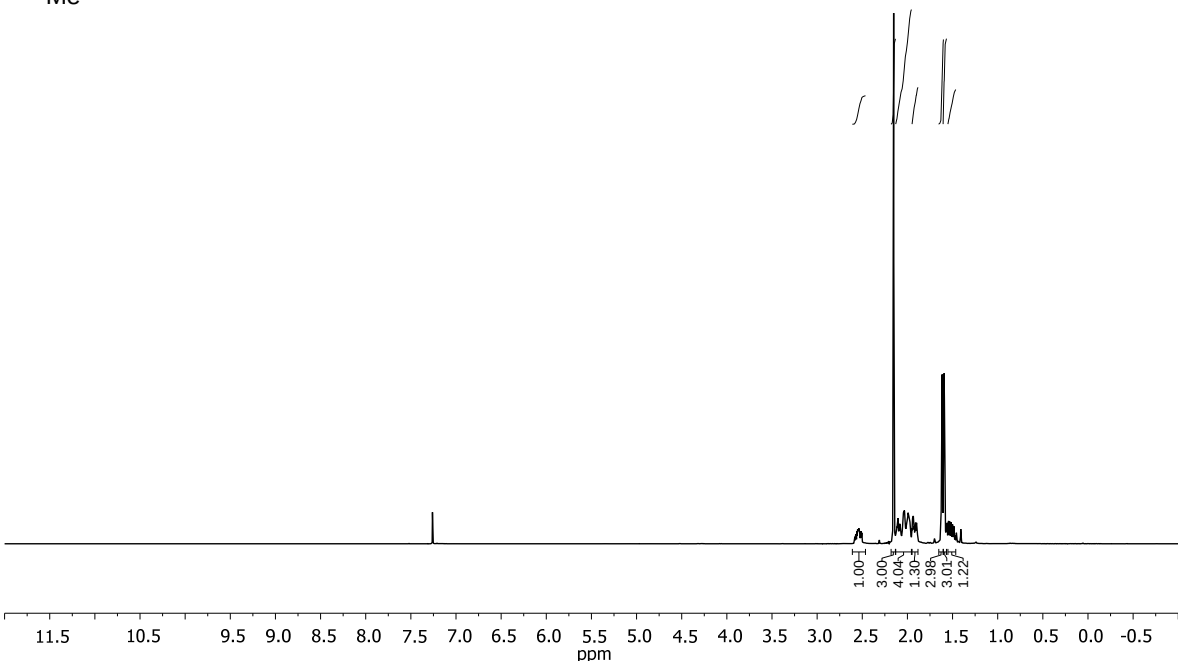
^{13}C NMR (100 MHz, $CDCl_3$):



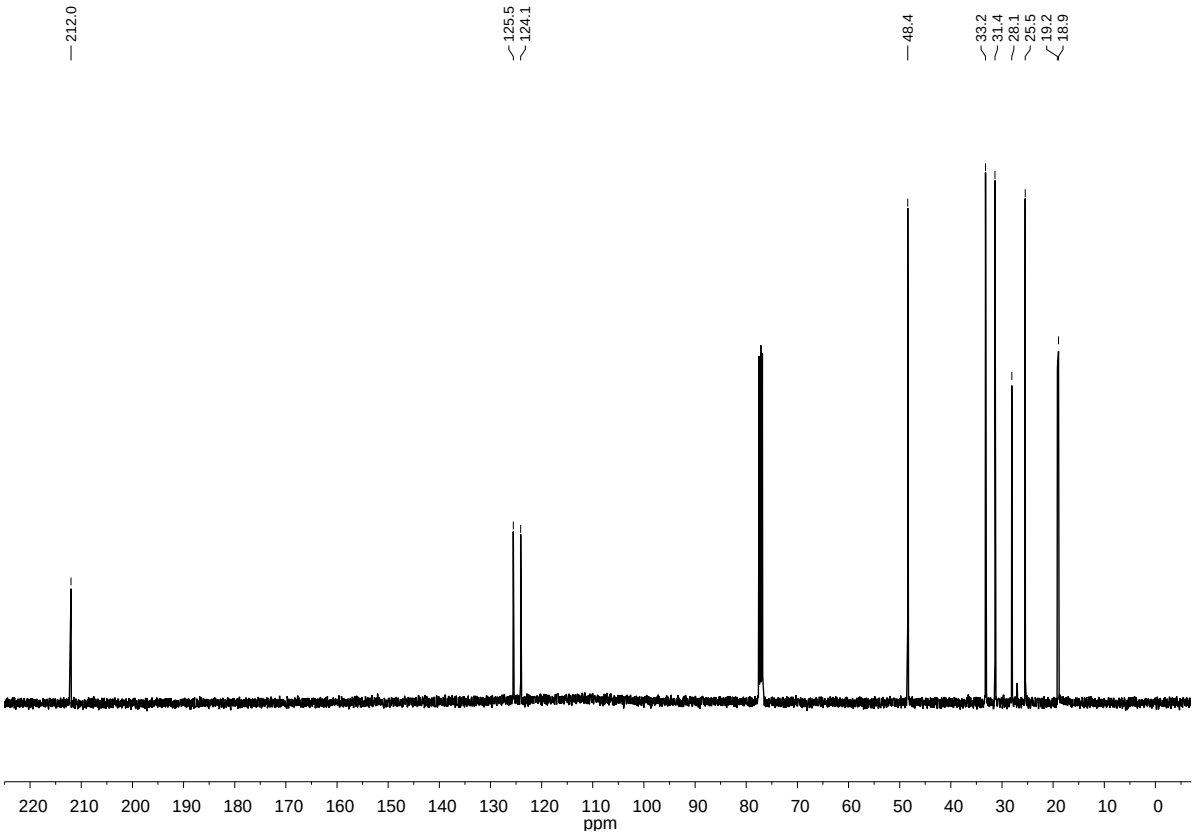
1-(3,4-Dimethylcyclohex-3-en-1-yl)ethanone (28)

^{1}H NMR (400 MHz, $CDCl_3$):



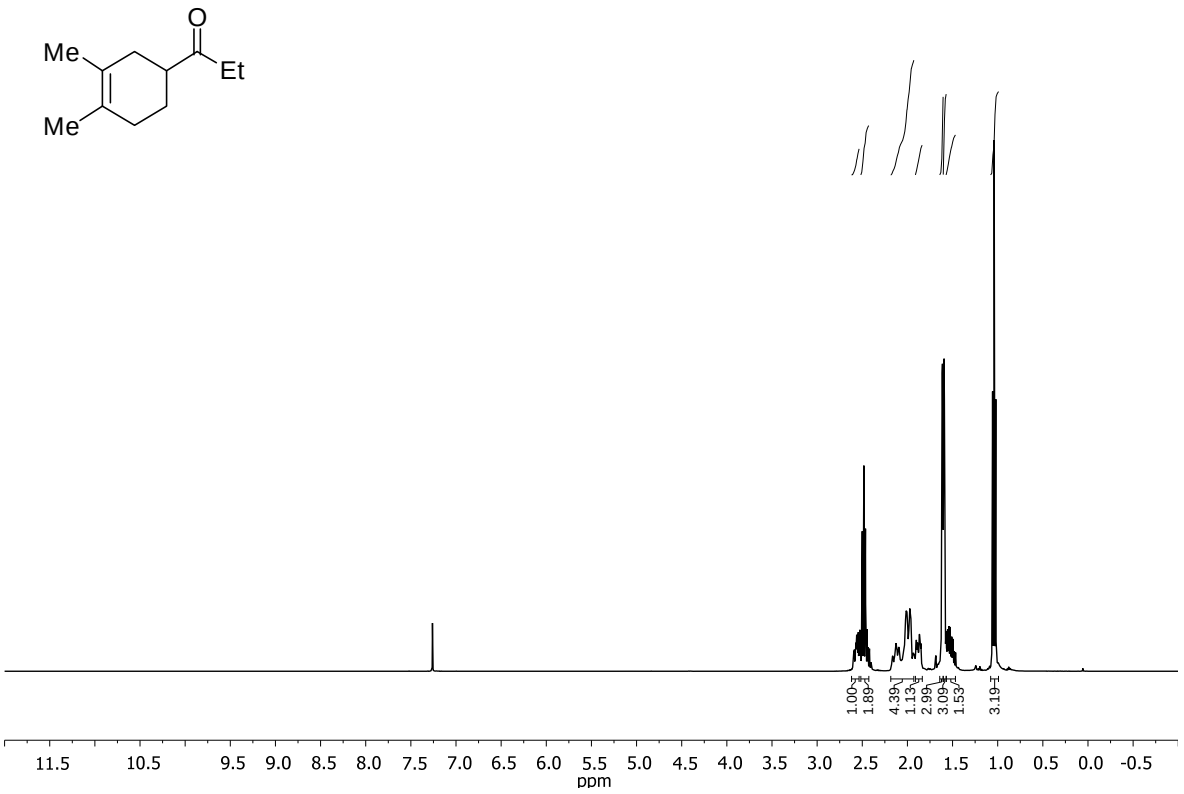


^{13}C NMR (100 MHz, $CDCl_3$):

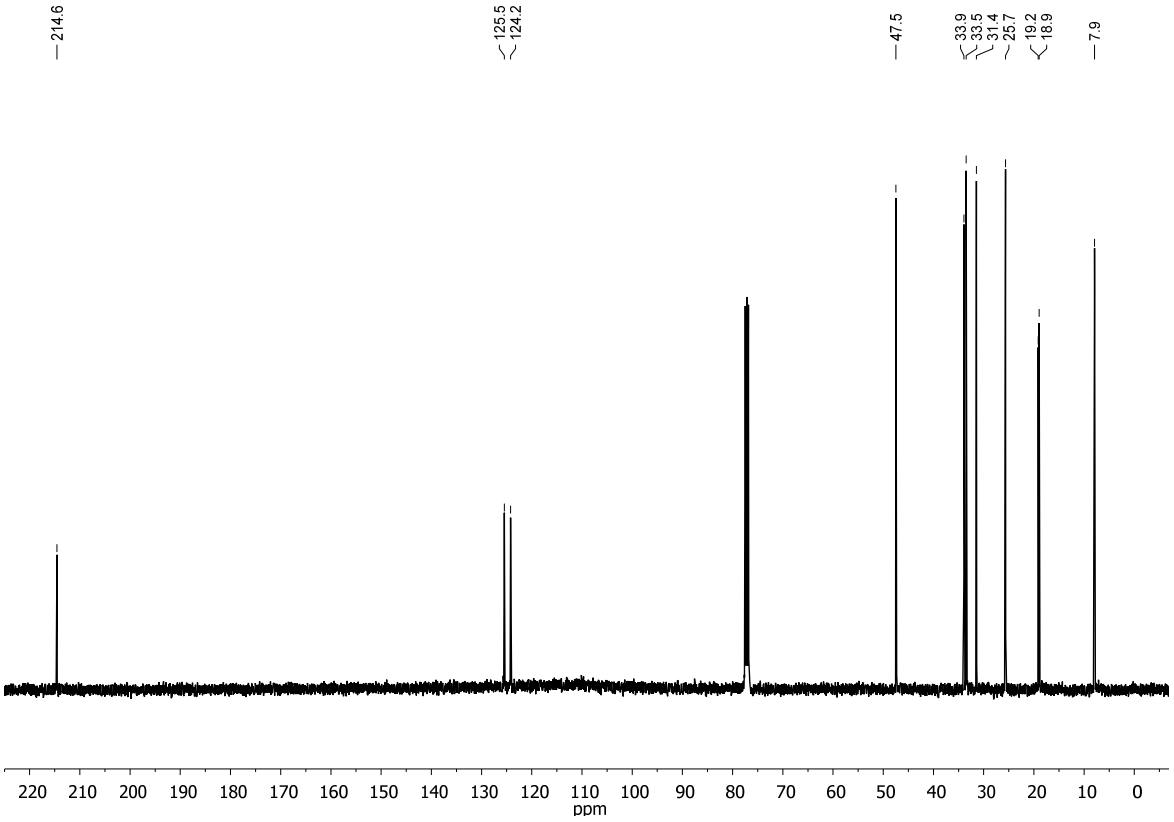


1-(3,4-Dimethylcyclohex-3-en-1-yl)propan-1-one (29)

^{1}H NMR (400 MHz, $CDCl_3$):

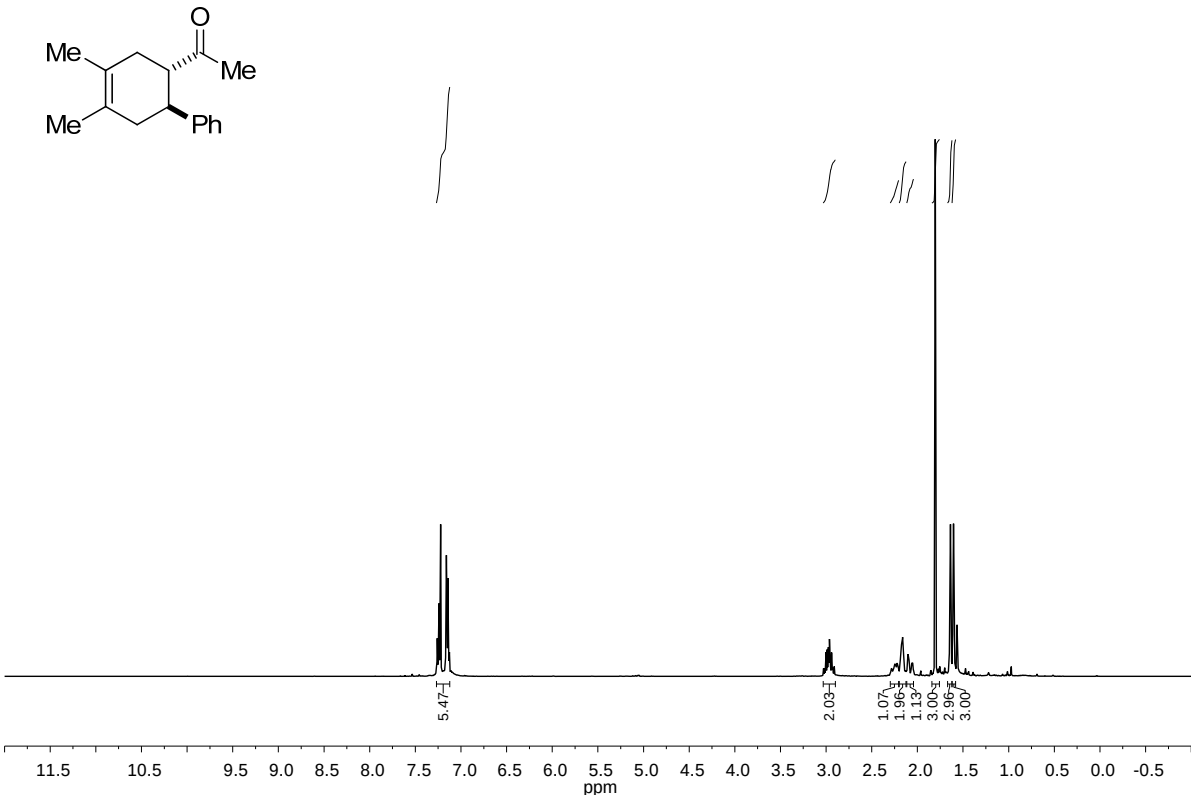


^{13}C NMR (100 MHz, $CDCl_3$):

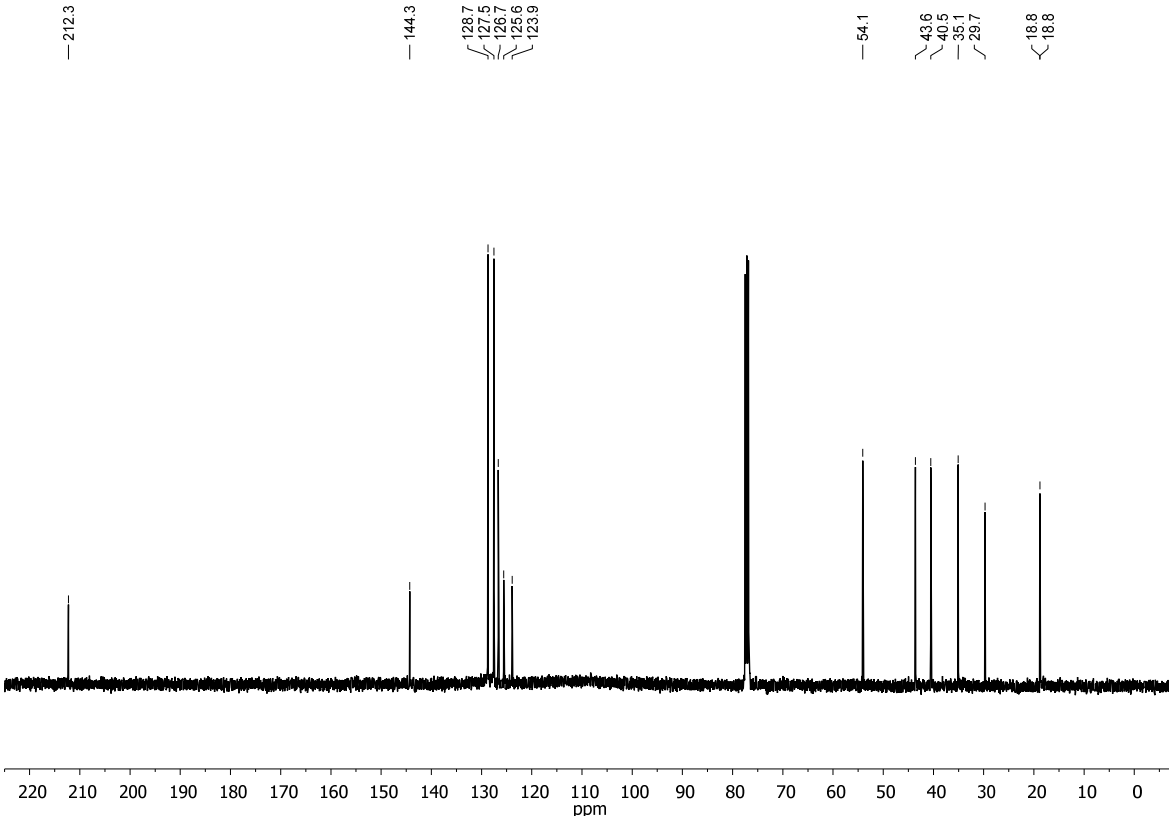


1-(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)ethanone (30)

^{1}H NMR (400 MHz, $CDCl_3$):

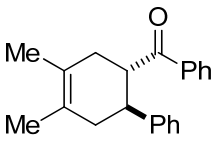


^{13}C NMR (100 MHz, $CDCl_3$):

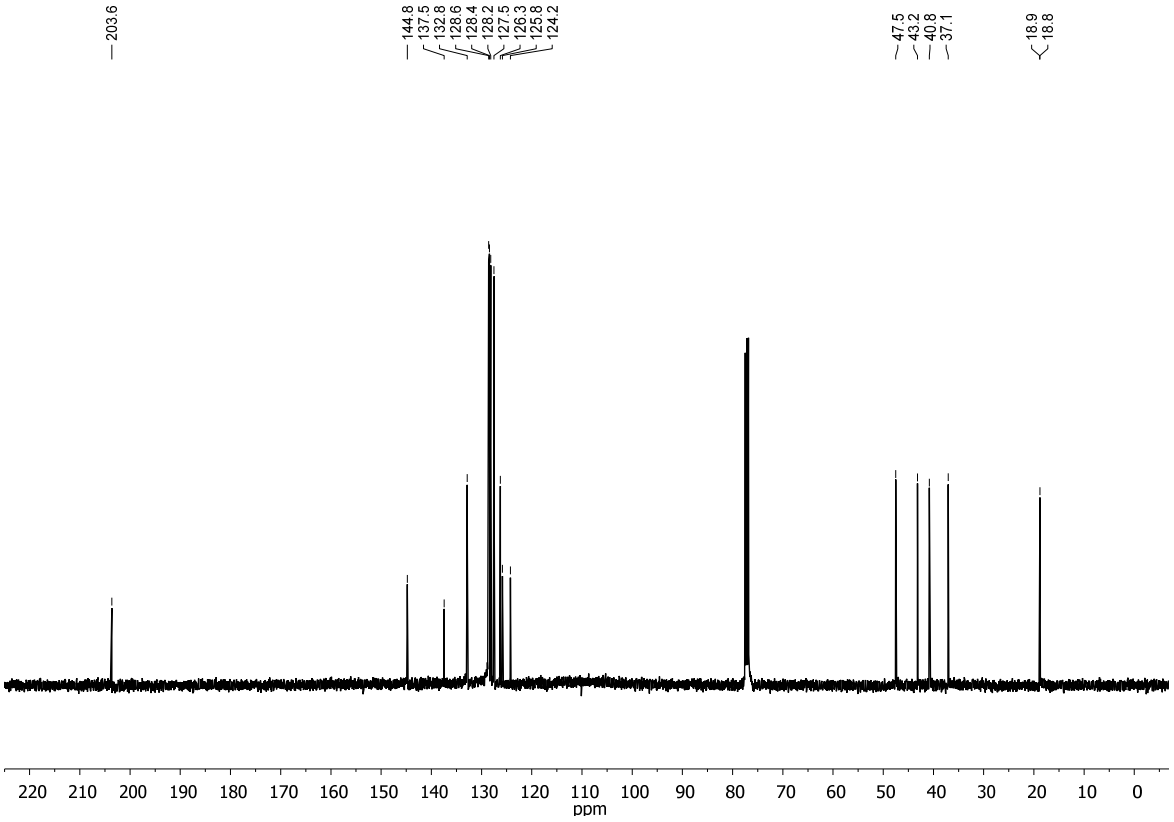


(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)phenylmethanone (31)

^{1}H (400 MHz, $CDCl_3$):

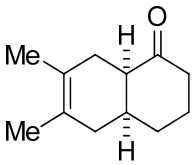


^{13}C NMR (100 MHz, $CDCl_3$):

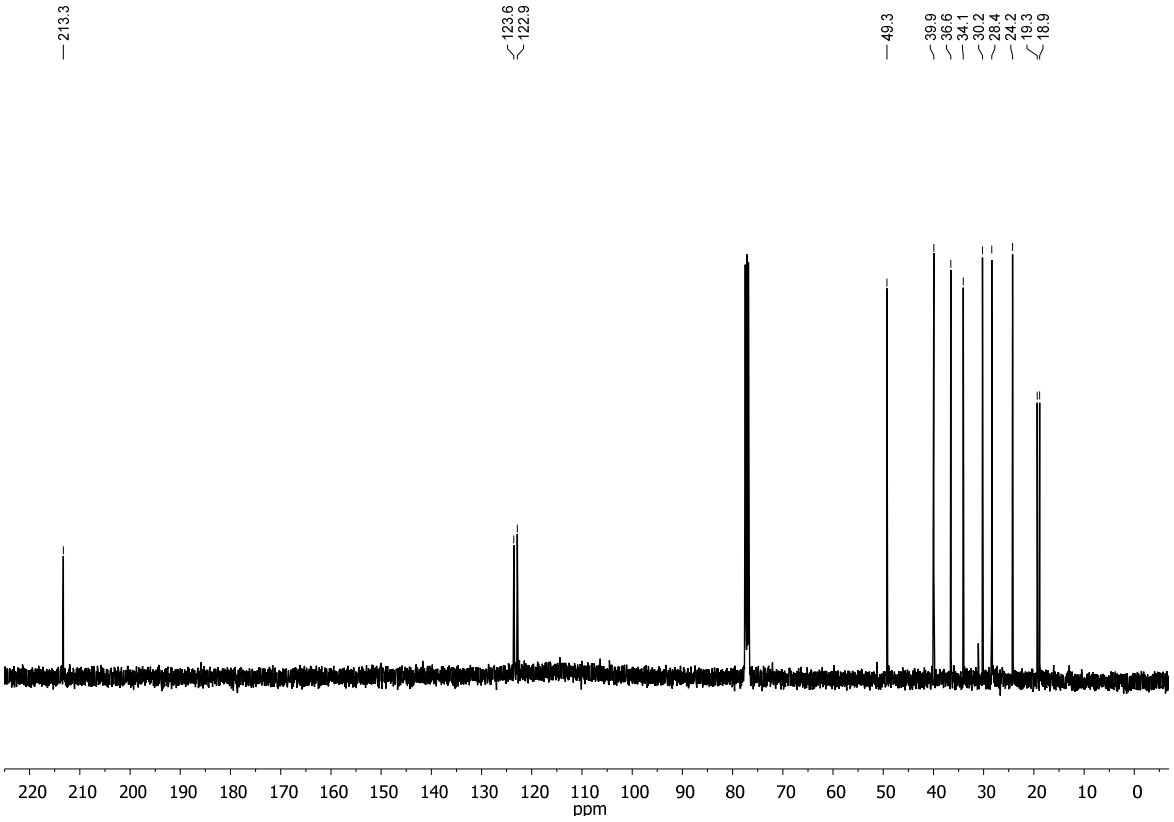


6,7-Dimethyl-3,4,4a,5,8,8a-hexahydro-2H-naphthalen-1-one (33)

^{1}H NMR (400 MHz, $CDCl_3$):

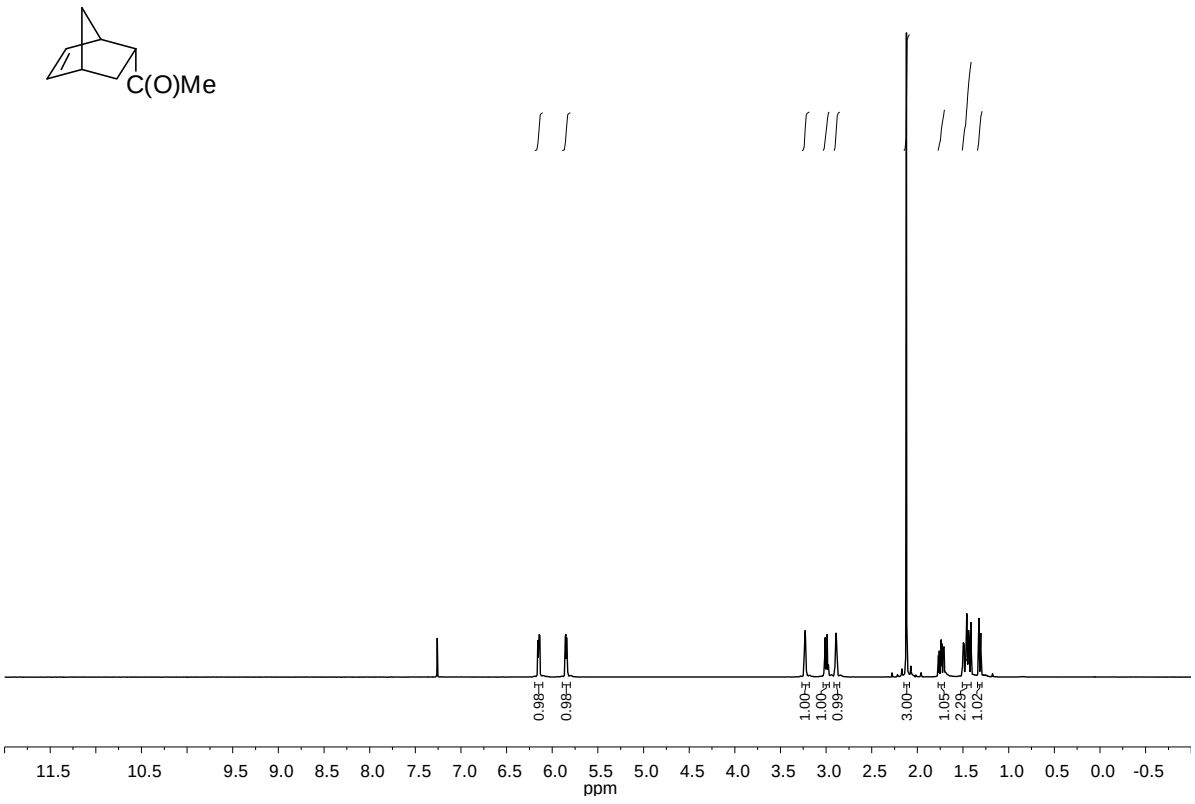


^{13}C NMR (100 MHz, $CDCl_3$):

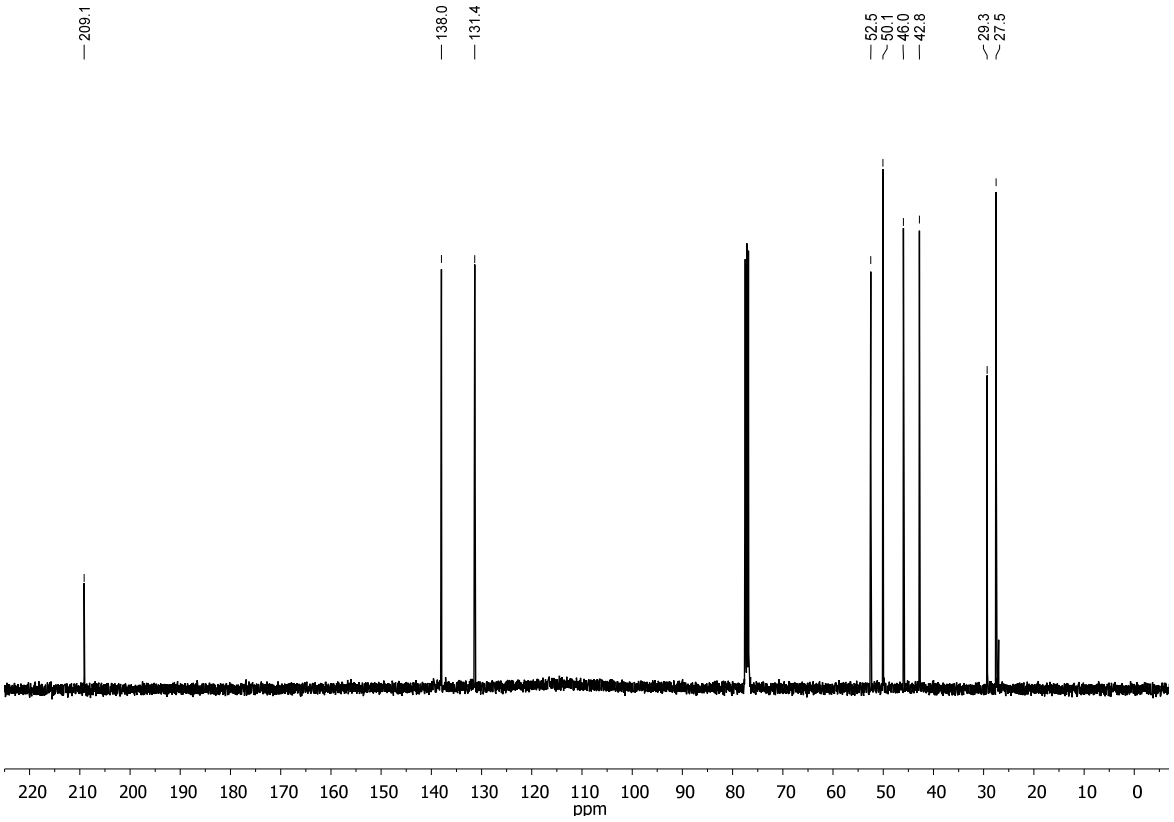


endo-1-(Bicyclo[2.2.1]hept-5-en-2-yl)ethanone (35)

^{1}H NMR (400 MHz, $CDCl_3$):

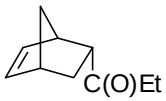


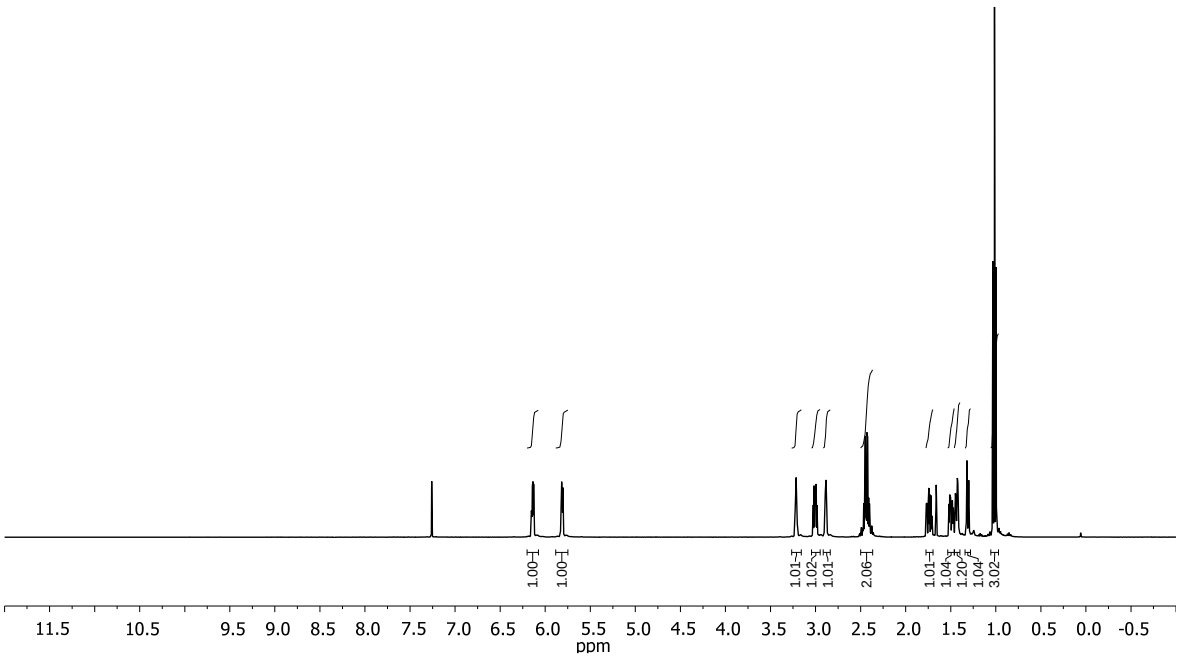
^{13}C NMR (100 MHz, CDC_3):



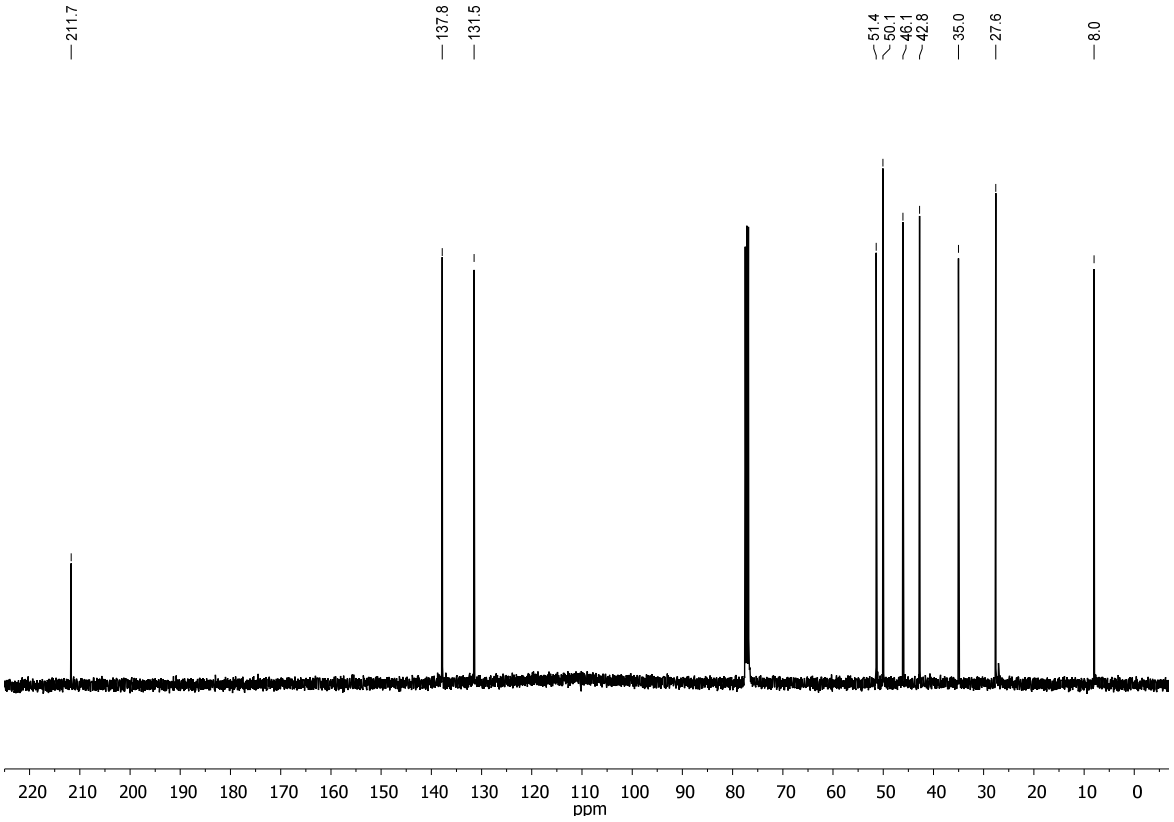
endo-1-(Bicyclo[2.2.1]hept-5-en-2-yl)propan-1-one (36)

^{1}H (400 MHz, $CDCl_3$):



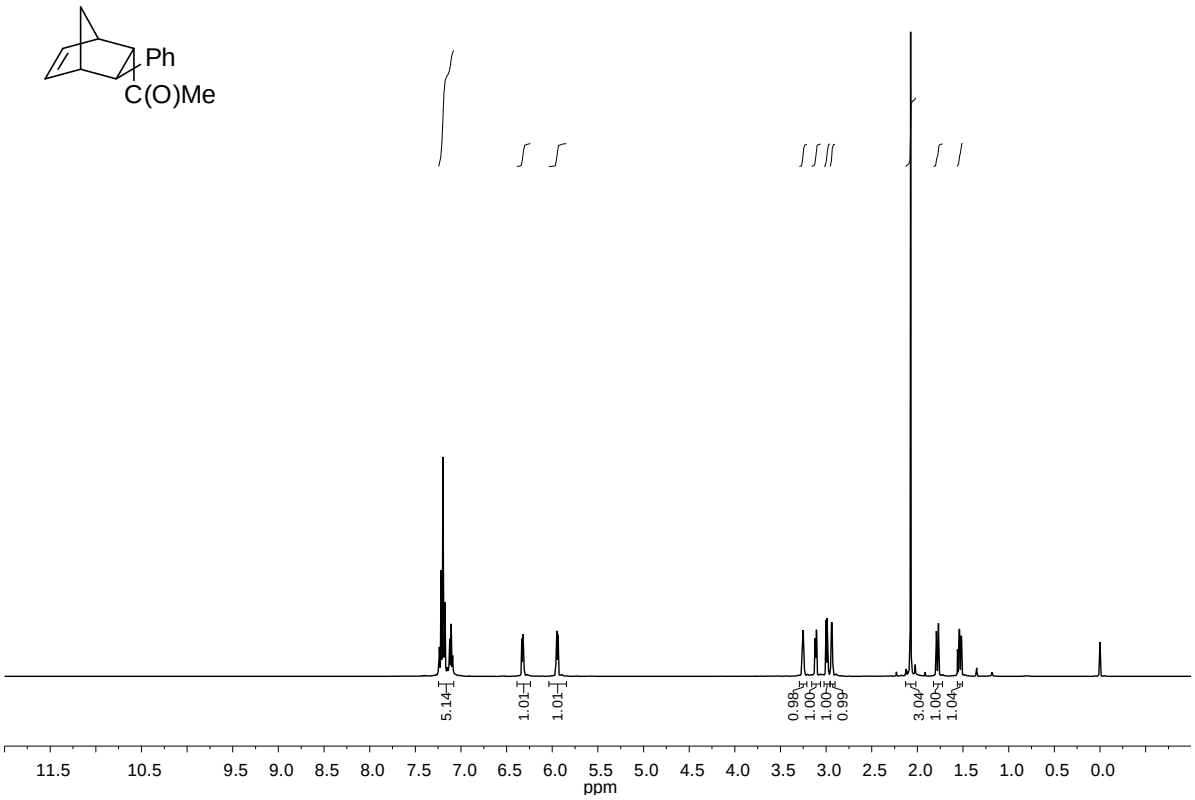


^{13}C NMR (100 MHz, $CDCl_3$):

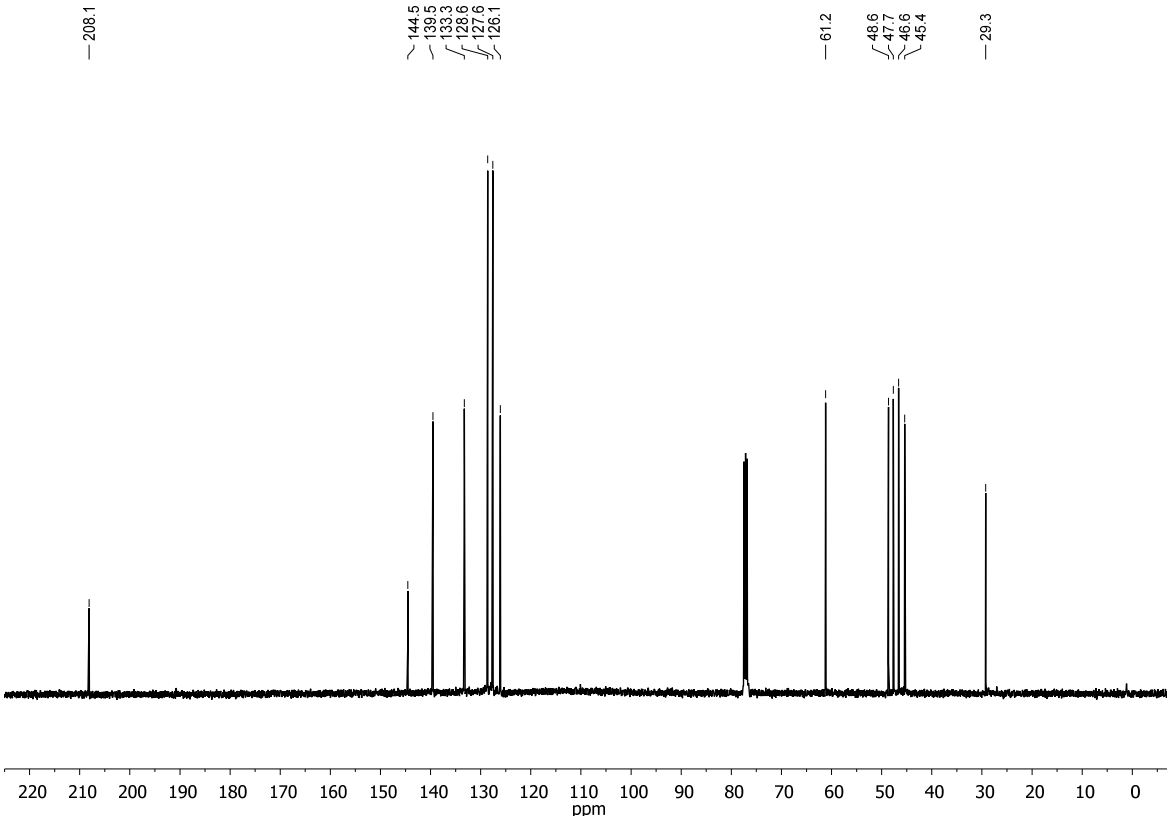


endo-1-(3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)ethanone (37)

^{1}H NMR (400 MHz, $CDCl_3$):

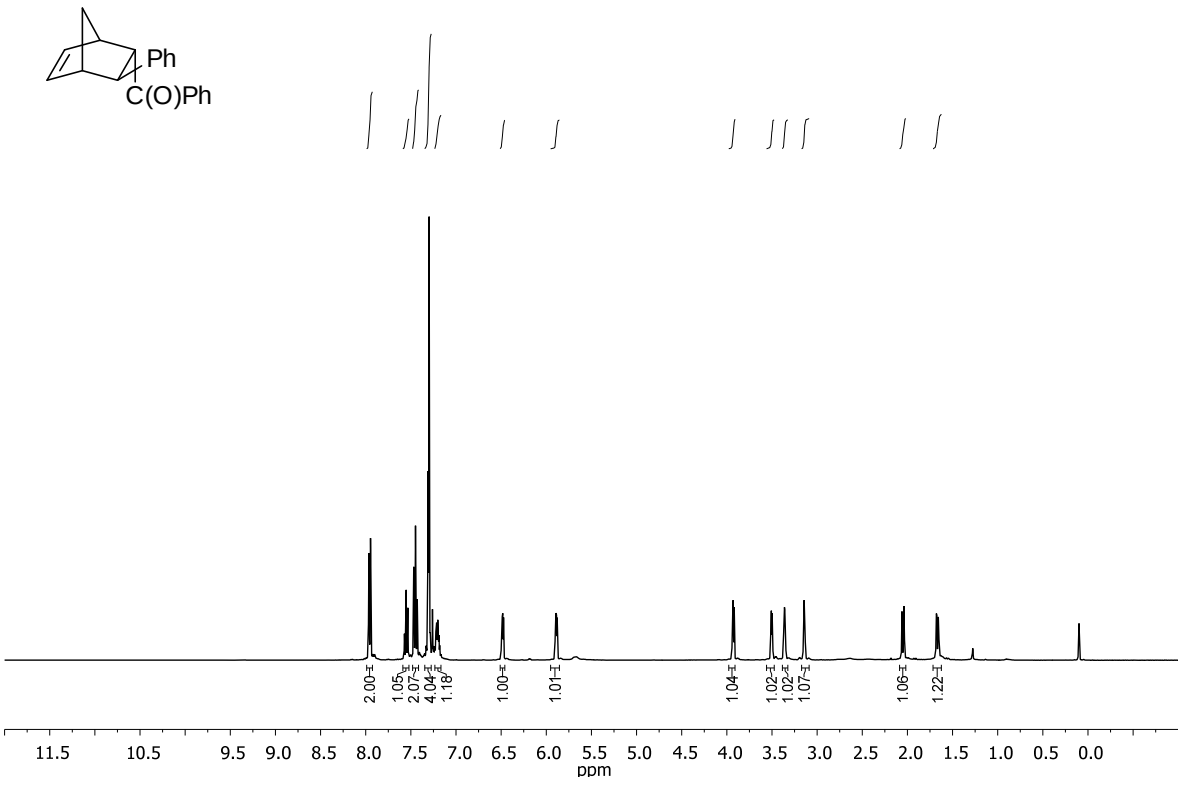


^{13}C NMR (100 MHz, $CDCl_3$):

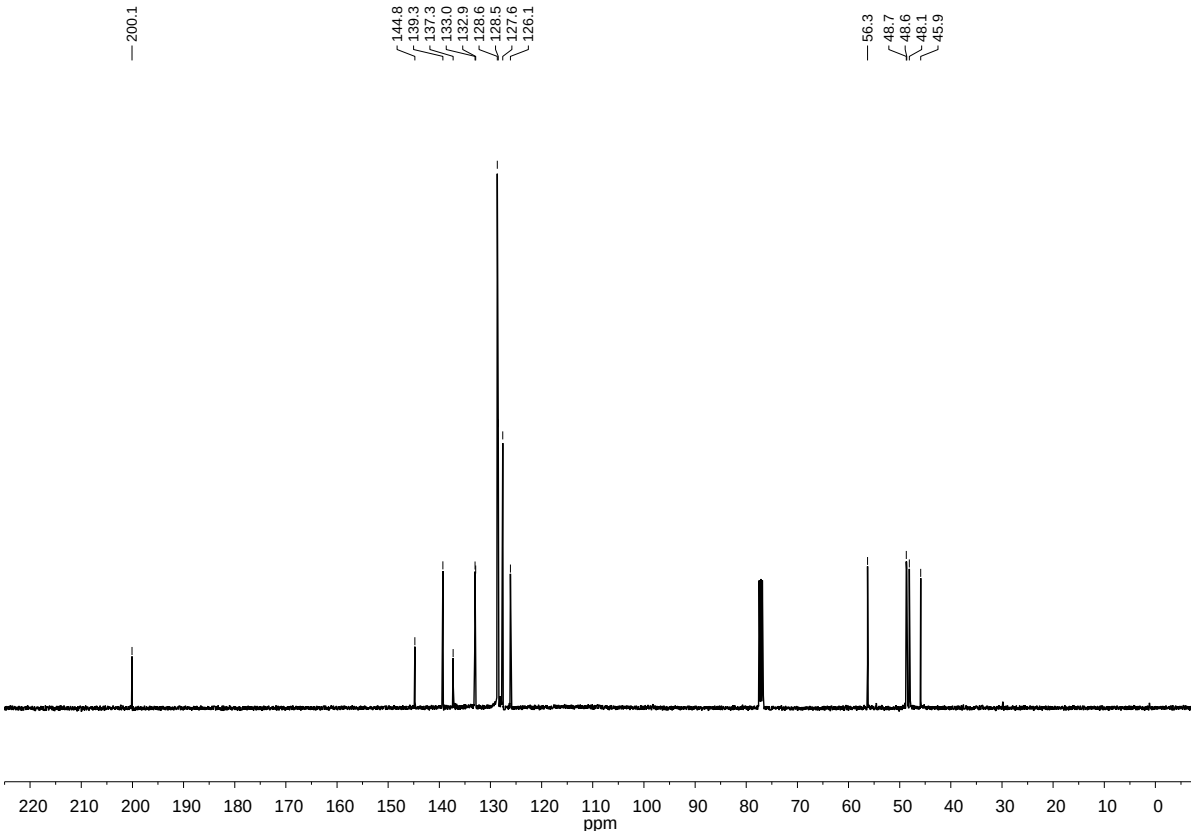


endo-Phenyl-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (38)

^{1}H NMR (400 MHz, $CDCl_3$):

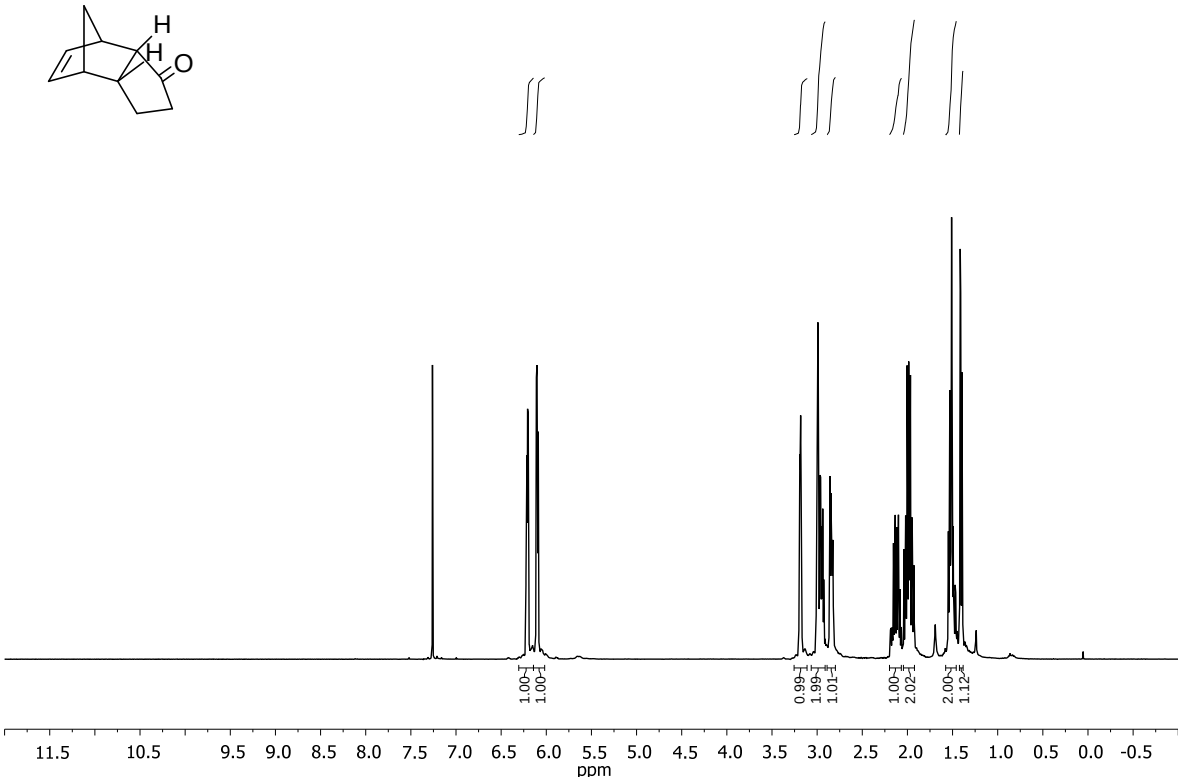


^{13}C NMR (100 MHz, $CDCl_3$):

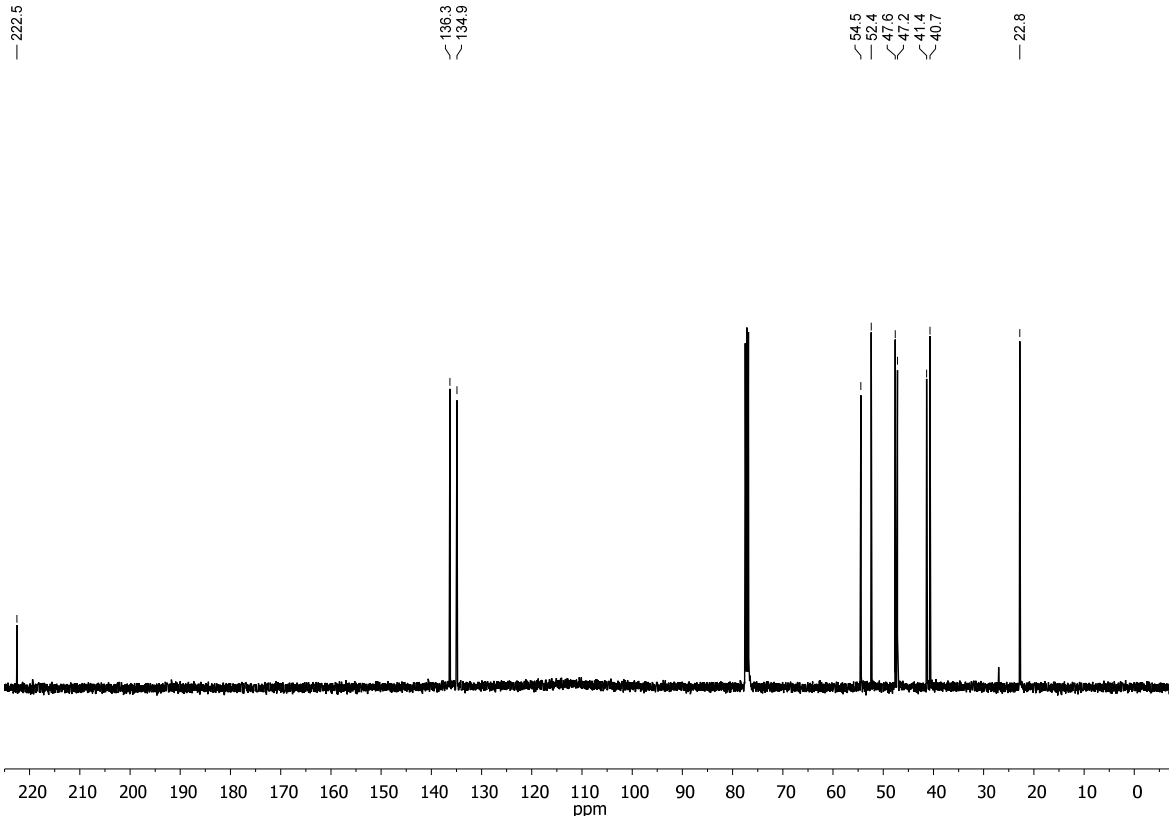


endo-Tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (39)

^{1}H NMR (400 MHz, $CDCl_3$):

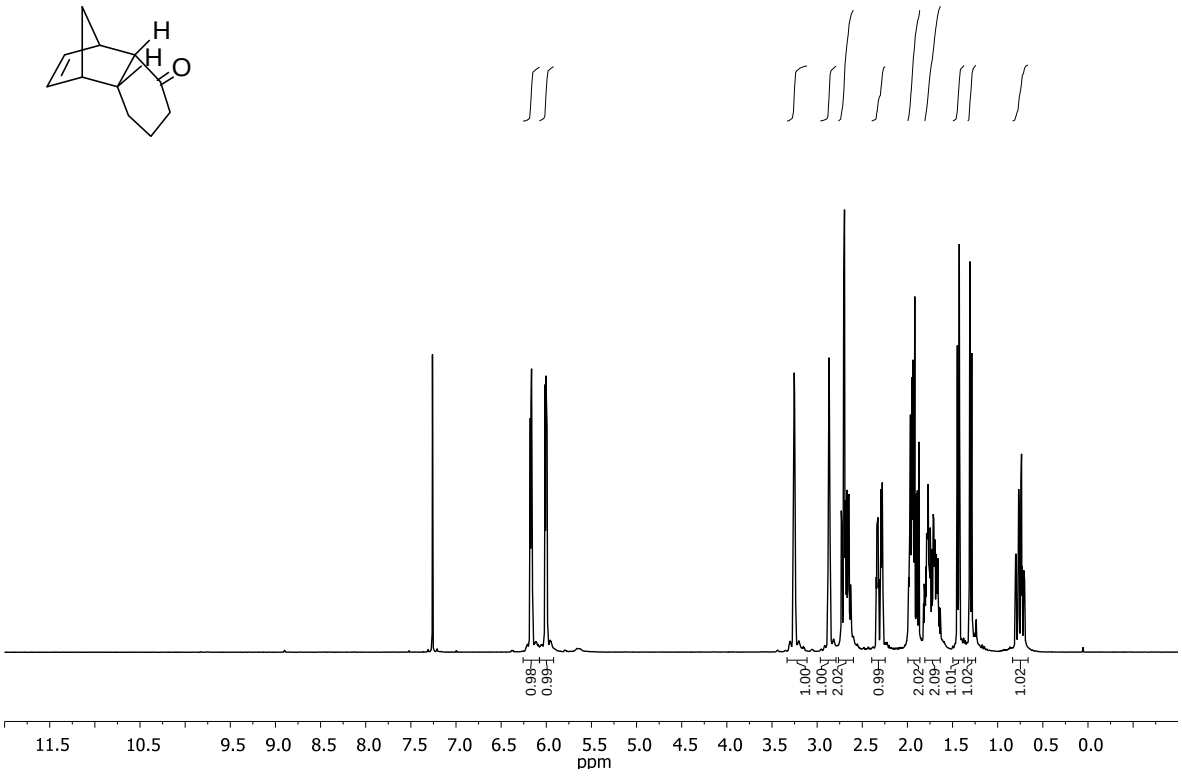


^{13}C NMR (100 MHz, $CDCl_3$):



endo-Tricyclo[5.2.1.0^{2,7}]undec-9-en-3-one (40)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):