

Supplementary Data for:

Frustrated Lewis Pair catalyzed Hydrosilylation and Hydrosilane mediated Hydrogenation of Fulvenes

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General Information

Synthesis and techniques

All preparations were done in oven dried (140 °C) glassware under an atmosphere of dry, O₂-free Ar employing both Schlenk line techniques and a *MBraun* inert atmosphere glove box. Experiments on NMR scale were carried out in Teflon cap sealed J Young NMR tubes. Solvents were purified with a Grubbs-type column system manufactured by *MBraun* and dispensed into thick-walled glass Schlenk bombs equipped with Young type Teflon valve stop-cocks. All solvents were stored over 4 Å molecular sieves in the glove box. Molecular sieves (4 Å) were dried at 140 °C under vacuum for 24 h prior to use. Deuterated solvents were vacuum transferred from CaH₂ (CD₂Cl₂, CDCl₃) or sodium/benzophenone (C₆D₆), degassed by 3 freeze-pump-thaw cycles and stored over 4 Å molecular sieves for usage in a glove box. Technical grade solvents for extraction were distilled prior to use.

Reagents and materials

All commercially available silanes, fulvenes and phosphines were stored in the glovebox and used as received (*Sigma Aldrich, ABCR*) without further purification unless noted otherwise. Liquid substrates were stored over molecular sieves in the glovebox. Tris(pentafluorophenyl)borane (**1**) was purchased from *Sigma Aldrich* and used as received.

Characterization

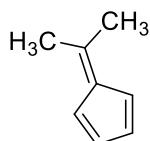
NMR spectra were recorded on a *Bruker* AC 300 (300 MHz) or *Bruker* DRX 600 (600 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to the residual proton signals of CD₂Cl₂ (5.32 ppm, 53.84 ppm), CDCl₃ (7.26 ppm,

77.16 ppm) or C₆D₆ (7.16 ppm, 128.06 ppm) as internal standard. All coupling constants are absolute values and are expressed in Hertz (Hz). The description of ¹H-NMR signals include: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc. The spectra were analyzed according to first order. High resolution mass spectrometry (HRMS) analysis were obtained from the Analytical Facility in the Institute of Organic Chemistry, KIT.

Experimental Details

Synthesis of pentafulvene derivatives

6,6-dimethylfulvene (2)

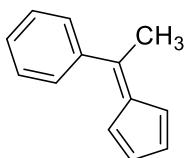


In a 100 ml Schlenk flask acetone (3.47 ml, 2.74 g, 47.2 mmol, 1.00 eq.) and cyclopentadiene (9.75 ml, 7.79 g, 118 mmol, 2.50 eq.) were dissolved in methanol (25 ml). The solution was cooled to 0 °C and pyrrolidine (7.75 ml, 6.71 g, 94.4 mmol, 2.00 eq.) was added slowly. The reaction mixture was stirred for 2 h at 0 °C and subsequently neutralized with glacial acetic acid. Water (25 ml) and pentane (25 ml) were added to the solution and the layers were separated. The aqueous layer was washed with pentane (3 x 25 ml) and the combined organic layers were dried over anhydrous MgSO₄. Removal of the solvent under reduced pressure followed by distillation (1 mbar, 60 °C) yielded the title compound as a yellow oil (95 %).

¹H-NMR (300 MHz, CDCl₃): δ = 6.56 – 6.52 (m, 2H, H_{Cp}), 6.51 – 6.47 (m, 2H, H_{Cp}), 2.21 (s, 6H, CH₃).

NMR data is in agreement with literature reported chemical shifts and signal pattern.¹

6-methyl-6-phenylfulvene (13)

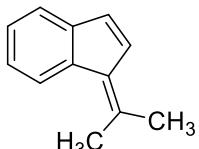


In a Schlenk flask a mixture of sodium (139 mg, 6.07 mmol, 1.02 eq.) and methanol (5 ml) was stirred for 30 min at 0 °C. Subsequently a solution of acetophenone (0.69 ml, 714 mg, 5.95 mmol, 1.00 eq.) and cyclopentadiene (0.49 ml, 393 mg, 5.95 mmol, 1.00 eq.) in methanol was added dropwise at 0 °C. The reaction mixture was allowed to warm up to room temperature over night. Water (10 ml) and pentane (5 ml) were added to the solution and the layers were separated. The aqueous layer was washed with pentane (3 x 10 ml) and the combined organic layers were dried over anhydrous MgSO₄. Removal of the solvent under reduced pressure followed by column chromatography (pentane) yielded the title compound as an orange oil (40%).

¹H-NMR (300 MHz, CDCl₃): δ = 7.44 – 7.33 (m, 5H, H_{Ph}), 6.70 – 6.62 (m, 1H, H_{Cp}), 6.62 – 6.54 (m, 1H, H_{Cp}), 6.54 – 6.43 (m, 1H, H_{Cp}), 6.26 – 6.15 (m, 1H, H_{Cp}), 2.57 (s, 3H, CH₃).

NMR data is in agreement with literature reported chemical shifts and signal pattern.²

6,6-dimethylbenzofulvene (16)



In a Schlenk flask a mixture of sodium (99.0 mg, 4.30 mmol, 1.00 eq.) and ethanol (2.5 ml) was stirred for 1 h. Sequentially acetone (0.31 ml, 250 mg, 4.30 mmol, 1.00 eq.) and indene (0.50 ml, 500 mg, 4.30 mmol, 1.00 eq.) were added dropwise at room temperature. The reaction mixture was refluxed for 24 h at 70° C. Water (3 ml) and pentane (1 ml) were added and the layers were separated. The aqueous layer was extracted with pentane (3 x 5 ml) and the combined organic layers were dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residual yellow oil was purified by distillation (90 °C, 10⁻³ mbar) to give the title compound as a yellow oil (27 %).

¹H-NMR (300 MHz, CD₂Cl₂): δ = 7.79 – 7.69 (m, 1H, H_{Ar}), 7.36 – 7.25 (m, 1H, H_{Ar}), 7.25 – 7.11 (m, 2H, H_{Ar}), 6.86 (d, *J* = 5.5 Hz, 1H, H_{Olefin}), 6.75 (d, *J* = 5.5 Hz, 1H, H_{Olefin}), 2.41 (s, 3H, CH₃), 2.28 (s, 3H, CH₃).

¹H-NMR (300 MHz, C₆D₆): δ = 7.67 – 7.56 (m, 1H, H_{Ar}), 7.29 – 7.23 (m, 1H, H_{Ar}), 7.20 – 7.08 (m, 2H, H_{Ar}), 6.74 – 6.64 (m, 2H, H_{Olefin}), 1.94 (s, 3H, CH₃), 1.81 (s, 3H, CH₃).

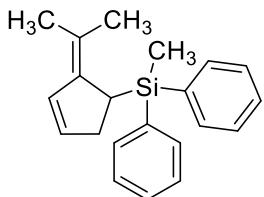
NMR data is in agreement with literature reported chemical shifts and signal pattern.³

Hydrosilylation of pentafulvenes

General procedure for the hydrosilylation of disubstituted fulvenes and benzofulvenes in 0.1 mmol scale (10 mol% catalyst loading)

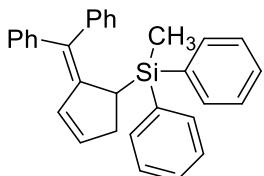
In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (5.10 mg, 0.01 mmol, 0.10 eq.) and trimesitylphosphine (3.90 mg, 0.01 mmol, 0.10 eq.) and dissolved in CD_2Cl_2 (0.6 ml). Sequentially methyl(diphenyl) silane (19.8 mg, 0.10 mmol, 1.00 eq.) and corresponding fulvene (0.1 mmol, 1.00 eq.) were added. The reaction was monitored by NMR spectroscopy. After complete conversion the reaction solution was freeze-pump thawed for 2 cycles, charged with H_2 at 77 K and held at room temperature. After 24 h the solvent was removed under reduced pressure. The residual oil was dried *in vacuo* for 4 h and subsequently extracted with pentane (3 x 1 ml). The organic layers were combined and the solvent was removed under reduced pressure. Drying the residual solid/oil *in vacuo* gave the hydrosilylated product.

Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (5)



> 95 % NMR yield, 79% isolated yield, yellowish solid; **1H -NMR** (300 MHz, CD_2Cl_2): $\delta = 7.62 - 7.52$ (m, 2H, H_{Ph}), $7.49 - 7.41$ (m, 2H, H_{Ph}), $7.39 - 7.20$ (m, 6H, H_{Ph}), $6.46 - 6.34$ (m, 1H, $H_{Olefín}$), $5.83 - 5.72$ (m, 1H, $H_{Olefín}$), $2.98 - 2.75$ (m, 2H, CH_AH_B , $C(H)Si$), 2.42 (d, $J_{AB} = 16.0$ Hz, 1H, CH_AH_B), 1.68 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.45 (s, 3H, $SiCH_3$); **^{13}C -NMR** (151 MHz, CD_2Cl_2): $\delta = 140.30$, 137.72 , 137.05 , 135.61 , 135.54 , 134.20 , 133.17 , 129.61 , 129.50 , 128.19 , 128.02 , 120.06 , 54.00 , 35.89 , 28.53 , 22.40 , 21.14 , -5.84 ; **MS** (EI, 70 mV) m/z: 304 (77) [M]⁺, 241 (22), 212 (25), 197 (100), 178 (23), 106 (28); **HRMS** (EI) exact mass for [M]⁺ ($C_21H_{24}^{28}Si$): calc m/z 304.1642, found 304.1643.

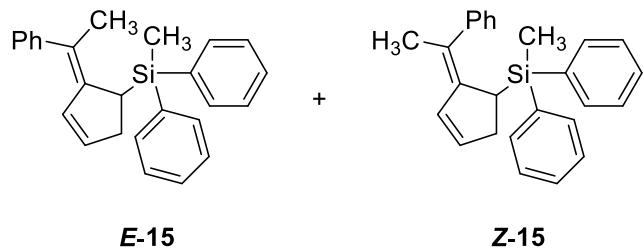
(2-(Diphenylmethylene)cyclopent-3-en-1-yl)dimethyl(phenyl)silane (14)



> 95 % NMR yield, 93 % isolated yield, yellow oil; **1H -NMR** (600 MHz, CD_2Cl_2): $\delta = 7.48 - 7.43$ (m, 2H, H_{Ph}), $7.42 - 7.36$ (m, 1H, H_{Ph}), $7.36 - 7.31$ (m, 4H, H_{Ph}), $7.31 - 7.23$ (m, 3H, H_{Ph}), $7.23 - 7.17$ (m, 3H, H_{Ph}), $7.16 - 7.11$ (m, 2H, H_{Ph}), $7.11 - 7.07$ (m, 1H, H_{Ph}), $7.06 - 6.99$ (m, 4H, H_{Ph}), $6.30 - 6.26$ (m, 1H, $H_{Olefín}$), $6.04 - 5.99$ (m, 1H, $H_{Olefín}$), 3.73 (d, $J = 7.7$ Hz, 1H, $CHSi$), 2.99 (ddt, $J = 18.3$, 7.7 , 2.5 Hz, 1H,

CH_AH_B), 2.61 (d, $J = 18.3$ Hz, 1H, CH_AH_B), 0.21 (s, 3H, $SiCH_3$). **^{13}C -NMR** (151 MHz, CD_2Cl_2): $\delta = 147.83, 144.93, 144.33, 139.26, 137.19, 136.36, 135.52, 135.50, 135.49, 135.25, 135.24, 132.57, 131.36, 130.81, 130.80, 130.80, 130.66, 129.71, 129.40, 128.55, 128.54, 128.40, 128.39, 128.32, 128.30, 128.20, 128.19, 128.18, 128.17, 128.17, 128.09, 128.08, 128.08, 128.07, 128.06, 126.63, 126.52, 36.28, 28.56, -4.34$; **HRMS** (EI) exact mass for $[M]^+$ ($C_{31}H_{28}^{28}Si$): calc m/z 428.1960, found 428.1956.

(E/Z)-Methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (E/Z-15)



93 % NMR yield, E/Z ratio = 1.6:1, 69% isolated yield, yellow oil;

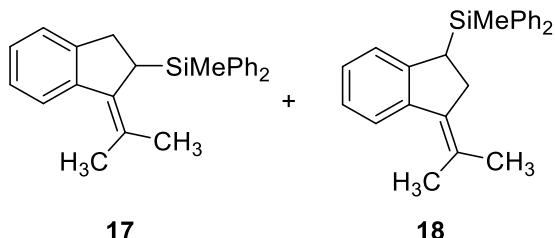
1H -NMR (E-15) (300 MHz, CD_2Cl_2): $\delta = 7.70 - 7.02$ (m, 15H, H_{Ar}), 6.58 – 6.45 (m, 1H, $H_{Olefins}$), 6.05 – 5.95 (m, 1H, $H_{Olefins}$), 3.51 (d, $J = 7.8$ Hz, 1H, $CHSi$), 3.05 – 2.86 (m, 1H, CH_AH_B), 2.60 – 2.46 (m, 1H, CH_AH_B), 2.06 (s, 3H, CH_3), 0.11 (s, 3H, $SiCH_3$).

1H -NMR (Z-15) (300 MHz, CD_2Cl_2): $\delta = 7.71 - 7.63$ (m, 2H, H_{Ar}), 7.59 – 7.53 (m, 2H, H_{Ar}), 7.48 – 7.02 (m, 11H, H_{Ar}), 6.27 (dt, $J = 5.7, 2.1$ Hz, 1H, $H_{Olefins}$), 5.88 (dt, $J = 5.6, 2.7$ Hz, 1H, $H_{Olefins}$), 3.13 (d, $J = 7.8$ Hz, 1H, $CHSi$), 3.04 – 2.89 (m, 1H, CH_AH_B), 2.63 – 2.44 (m, 1H, CH_AH_B), 1.38 (s, 3H, CH_3), 0.56 (s, 3H, $SiCH_3$).

^{13}C -NMR (Mixture) (151 MHz, CD_2Cl_2): $\delta = 145.48, 145.28, 144.39, 143.95, 137.45, 137.33, 137.11, 136.69, 136.56, 135.69, 135.56, 135.42, 135.31, 135.19, 134.47, 134.26, 134.10, 130.08, 129.82, 129.75, 129.43, 129.20, 128.98, 128.78, 128.47, 128.33, 128.18, 128.01, 127.92, 126.38, 126.11, 125.41, 124.15, 36.18, 36.08, 29.65, 27.87, 22.16, 21.88, -4.43, -5.85.$

HRMS (EI) exact mass for $[M]^+$ ($C_{26}H_{26}^{28}Si$): calc m/z 366.1797, found 366.1798.

Methyldiphenyl(1-(propan-2-ylidene)-2,3-dihydro-1H-inden-2-yl)silane (17), methyldiphenyl(3-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-yl)silane (18)



90 % conv. NMR, ratio **17:18** = 1.2:1, products were not isolated;

¹H-NMR (17) (300 MHz, CD₂Cl₂): δ = 7.61 – 7.01 (m, 14H, H_{Ar}) 3.34 (dd, J = 15.7, 8.7 Hz, 1H, CH_AH_B), 3.24 – 3.19 (m, 1H, CHSi), 2.85 (d, J = 15.7 Hz, 1H, CH_AH_B), 1.99 (s, 3H, CH₃), 1.26 (s, 3H, CH₃), 0.13 (s, 3H, SiCH₃).

¹H-NMR (18) (300 MHz, CD₂Cl₂): δ = 7.61 – 7.01 (m, 12H, H_{Ar}), 6.93 (t, J = 7.6 Hz, 1H, H_{Ar}), 6.73 (d, J = 7.6 Hz, 1H, H_{Ar}), 3.34 (dd, J = 15.7, 8.7 Hz, 1H, CH_AH_B), 3.24 – 3.19 (m, 1H, CHSi), 2.85 (d, J = 15.7 Hz, 1H, CH_AH_B), 1.99 (s, 3H, CH₃), 1.26 (s, 3H, CH₃), 0.13 (s, 3H, SiCH₃).

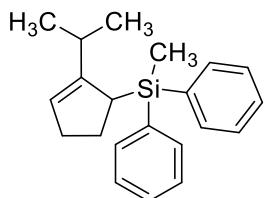
¹³C-NMR (Mixture) (151 MHz, CD₂Cl₂): δ = 149.20, 147.02, 143.53, 142.61, 137.59, 136.98, 136.52, 136.48, 136.29, 135.56, 135.48, 135.47, 135.33, 135.32, 134.50, 130.19, 129.89, 129.79, 129.71, 129.56, 128.70, 128.33, 128.29, 128.28, 128.27, 128.27, 128.26, 128.24, 128.23, 128.00, 128.00, 127.99, 126.63, 126.40, 126.22, 125.56, 125.49, 125.21, 125.19, 125.17, 125.16, 124.90, 124.64, 34.94, 34.09, 32.31, 30.38, 24.35, 24.15, 21.72, 21.63, -6.07, -6.24.

Synthesis of dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**5**) in 1.00 mmol scale (3 mol% catalyst loading).

In a glove box a 20 ml Schlenk flask with J Young Teflon tap was charged with $B(C_6F_5)_3$ (15.4 mg, 0.03 mmol, 3.00 mol%) and trimesitylphosphine (11.6 mg, 0.03 mmol, 3.00 mol%) and dissolved in CH_2Cl_2 (6 ml). methyl(diphenyl) silane (198 mg, 1.00 mmol, 1.00 eq) and 6,6-dimethylfulvene (106 mg, 1.00 mmol, 1.00 eq) were added consecutively. After stirring the solution over night at room temperature all volatiles were removed under reduced pressure and the residuals were dried *in vacuo* for 4 h. The residual oil was redissolved in CH_2Cl_2 (6 ml), the solution was freeze-pump thawed for 2 cycles, charged with H_2 at 77 K and stirred for another 24 h at room temperature. The solvent was removed under reduced pressure and the residual oil was extracted with pentane (3 x 1 ml). The organic solvent layers were combined and the solvent was removed under reduced pressure. Drying *in vacuo* yielded the title compound as a yellowish solid (241 mg, 79 %).

Hydrogenation and protodesilylation experiments

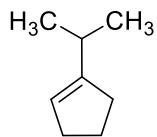
Synthesis of dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (19)



In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (4.80 mg, 9.40 μmol , 0.10 eq) and tris(1-naphthyl)phosphine (3.90 mg, 9.40 μmol , 0.10 eq.) and dissolved in CD_2Cl_2 (0.6 ml). Sequentially methyl(diphenyl) silane (18.6 mg, 0.094 mmol, 1.00 eq.) and 6,6-dimethylfulvene (10 mg, 0.094 mmol, 1.00 eq.) were added. After holding the reaction mixture at room temperature for 24 h the solution was freeze-pump thawed for 2 cycles, charged with H_2 at 77 K and held at 50 °C. The reaction was monitored by NMR spectroscopy. After 24 h approximately over 95 % of starting material were converted to allyl silane **19** (determined by 1H NMR). The product was not isolated.

1H -NMR (600 MHz, CD_2Cl_2): δ = 7.62 – 7.55 (m, 4H, H_{Ph}), 7.41 – 7.33 (m, 6H, H_{Ph}), 5.31 – 5.29 (m, 1H, H_{Olef}), 2.79 – 2.71 (m, 1H, $CHSi$), 2.27 – 2.13 (m, 2H, CH_2), 2.13 – 2.05 (m, 1H, CH_2), 2.03 – 1.97 (m, 1H, CH_2), 1.95 – 1.89 (m, 1H, $CH(CH_3)_2$), 1.00 (d, J = 6.8 Hz, 3H, CH_3), 0.83 (d, J = 6.8 Hz, 3H, CH_3), 0.59 (s, 3H, $SiCH_3$). **^{13}C -NMR** (151 MHz, CD_2Cl_2): δ = 135.19, 135.17, 129.62, 129.52, 128.25, 120.01, 34.15, 32.49, 29.67, 28.33, 22.69, 21.52, -5.15.

Synthesis of 1-*iso*-propylcyclopent-1-ene (20)

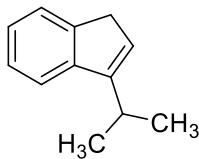


The reaction solution comprising dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**19**), $B(C_6F_5)_3$ (4.80 mg, 9.40 μmol , 0.10 eq) and tris(1-naphthyl)phosphine (3.90 mg, 9.40 μmol , 0.10 eq.) under hydrogen atmosphere was heated to 70 °C. The reaction was monitored by NMR spectroscopy. After 24 h 68% of **20** was obtained as determined by 1H NMR spectroscopy. The reaction mixture was subsequently subjected to trap-to-trap condensation giving a colorless solution of the desired product in CD_2Cl_2 . The title compound (**20**) was characterized by NMR spectroscopy.

1H -NMR (300 MHz, CD_2Cl_2): δ = 5.38 – 5.30 (m, 1H, H_{Olef}), 2.42 – 2.20 (m, 5H, CH_2), 1.93 – 1.77 (m, 2H, $CH(CH_3)_2$, CH_2), 1.05 (d, J = 6.7 Hz, 6H, CH_3); **^{13}C -NMR** (151 MHz, CD_2Cl_2): δ = 151.68, 121.29, 33.56, 32.78, 30.37, 24.01, 21.84.

NMR data is in agreement with literature reported chemical shifts and signal pattern.⁴

Synthesis of 3-isopropyl-1H-indene (21)



The reaction solution comprising methyldiphenyl(1-(propan-2-ylidene)-2,3-dihydro-1H-inden-2-yl)silane (**17**), methyldiphenyl(3-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-yl)silane (**18**), $B(C_6F_5)_3$ (5.10 mg, 0.01 mmol, 10 mol%) and tris(1-naphthyl)phosphine (4.10 mg, 0.01 mmol, 10 mol%) was freeze-pump thawed for 2 cycles, charged with H_2 at 77 K and held at 70 °C. The reaction was monitored by NMR spectroscopy. After 24 h 56 % of the product **21** was obtained (determined by 1H NMR). The product was not isolated. 1H -NMR (300 MHz, CD_2Cl_2): δ = 7.61 – 7.12 (m, 4H, H_{Ar}), 6.25 – 6.22 (m, 1H, H_{Olefin}), 3.33 (s, 2H, CH_2), 2.96 (m, 1H, $CH(CH_3)_2$), 1.31 (d, J = 6.8 Hz, 6H, CH_3).

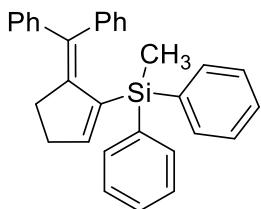
NMR data is in agreement with literature reported chemical shifts and signal pattern.⁵

Hydrosilane/FLP mediated hydrogenation



In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (5.10 mg, 0.01 mmol, 0.10 eq) and tris(1-naphthyl)phosphine (4.10 mg, 0.01 mmol, 0.10 eq.) and dissolved in CD_2Cl_2 (0.6 ml). Sequentially methyl(diphenyl) silane (1.98 mg, 0.01 mmol, 0.10 eq.) and 6,6-dimethylfulvene (10.6 mg, 0.01 mmol, 1.00 eq.) were added. The reaction solution was freeze-pump thawed for 2 cycles, charged with H_2 at 77 K and held at room temperature. The reaction was monitored by NMR spectroscopy. After 7 d approximately 77 % of starting material were converted to 1-*iso*-propylcyclopentene (**20**).

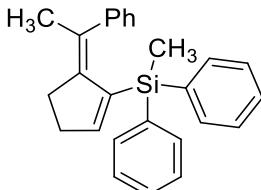
Synthesis of (2-(diphenylmethylene)cyclopent-3-en-1-yl)(methyl)diphenylsilane (22)



In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (2.20 mg, 4.00 μmol , 0.10 eq.) and (2-(diphenylmethylene)cyclopent-3-en-1-yl)dimethyl(phenyl)silane (**14**) (10.0 mg, 0.043 mmol, 1.00 eq.) and dissolved in CD_2Cl_2 (0.6 ml). The reaction mixture was held at 70 °C and monitored by NMR spectroscopy. After 24 h **22** was obtained in 78% yield as determined from the crude 1H NMR. The product was not isolated.

1H -NMR (300 MHz, CD_2Cl_2): δ = 7.59 – 7.49 (m, 4H, H_{Ph}), 7.43 – 7.13 (m, 16H, H_{Ph}), 6.71 (s, 1H, $H_{Olefins}$), 2.83 – 2.71 (m, 2H, CH_2), 2.72 – 2.61 (m, 2H, CH_2), 0.66 (s, 3H, $SiCH_3$).

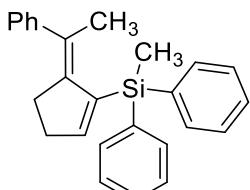
Synthesis of Z-methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (Z-23)



In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (1.80 mg, 3.00 μmol , 0.10 eq.) and (*E/Z*)-methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (*E/Z*-**15**) (12.0 mg, 0.03 mmol, 1.00 eq.) and dissolved in CD_2Cl_2 (0.6 ml). The reaction mixture was held at 40 °C. The reaction was monitored by NMR spectroscopy. As determined by 1H NMR more than 95% of **Z-15** was converted to vinyl silane **Z-23** after 1 h.

1H -NMR (300 MHz, CD_2Cl_2): δ = 7.55 – 7.49 (m, 4H, H_{Ar}), 7.45 – 7.14 (m, 11H, H_{Ar}), 6.67 (s, 1H, $H_{Olefins}$), 2.73 – 2.67 (m, 4H, CH_2CH_2), 2.09 (s, 3H, CH_3), 0.64 (s, 3H, $SiCH_3$).

Synthesis of E-methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (E-23)

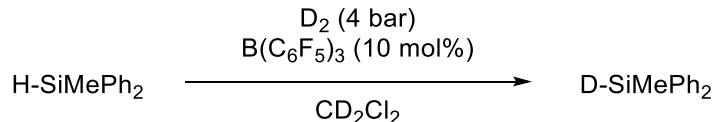


The reaction mixture comprising **Z-15** and **E-23** and $B(C_6F_5)_3$ (1.80 mg, 3.00 μmol , 0.10 eq.) was heated to 70 °C. The reaction was monitored by NMR spectroscopy. As determined by 1H NMR spectroscopy more than 95% of **E-15** was converted to vinyl silane **E-23** after 24 h.

¹H-NMR (300 MHz, CD₂Cl₂): δ = 7.61 – 7.54 (m, 4H, H_{Ar}), 7.45 – 7.15 (m, 11H, H_{Ar}), 6.88 (s, 1H, H_{Olefin}), 2.63 – 2.56 (m, 4H, CH₂CH₂), 2.14 (s, 3H, CH₃), 0.73 (s, 3H, SiCH₃).

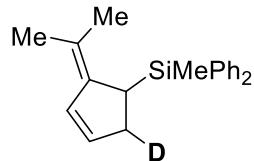
Deuteration experiments

Synthesis of Methyl(diphenyl)silane-d¹ (D-3)



Methyl(diphenyl)silane-*d*¹ was prepared according to NIKONOV et al.⁶ In a glove box a NMR tube with J Young Teflon tap was charged with B(C₆F₅)₃ (4.80 mg, 9.40 μ mol, 0.10 eq.) and methyl(diphenyl)silane (18.6 mg, 0.094 mmol, 1.00 eq.) and dissolved in CD₂Cl₂ (0.6 ml). The solution was freeze-pump thawed for 2 cycles, charged with D₂ at 77 K and held at 70 °C. After 24 h approximately over 90 % conversion to deuterated silane was observed by NMR spectroscopy.

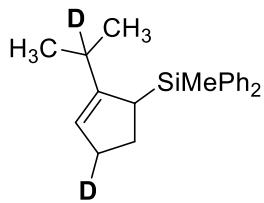
Synthesis of dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane-d¹ (D-5)



To the degassed solution of methyl(diphenyl)silane-*d*¹ (D-3) (18.7 mg, 0.094 mmol, 1.00 eq) and B(C₆F₅)₃ (4.80 mg, 9.40 μ mol, 0.10 eq.) in CD₂Cl₂ (0.6 ml) tris(1-naphthyl)phosphine (3.90 mg, 9.40 μ mol, 0.10 eq.) and 6,6-dimethylfulvene (10.0 mg, 0.094 mmol, 1.00 eq) were added sequentially in a glovebox. The reaction was monitored by NMR spectroscopy. After 5 h approximately 95 % of starting material were converted to deuterated allyl silane D-5.

¹H-NMR (300 MHz, CD₂Cl₂): δ = 7.64 – 7.56 (m, 1H), 7.51 – 7.44 (m, J = 7.4 Hz, 1H), 7.43 – 7.23 (m, 3H), 6.44 (s, 1H), 5.82 (s, 1H), 2.95 (bs, 1H, CH₂), 2.43 (bs, 1H, CH₂), 1.71 (s, 3H, CH₃), 1.06 (s, 3H, CH₃), 0.48 (s, 3H, SiCH₃).

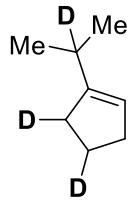
Synthesis of dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane-*d*² (24)



In a glove box a NMR tube with J Young Teflon tap was charged with $B(C_6F_5)_3$ (4.80 mg, 9.40 μ mol, 0.10 eq) and tris(1-naphthyl)phosphine (3.90 mg, 9.40 μ mol, 0.10 eq.) and dissolved in CD_2Cl_2 (0.6 ml). Sequentially methyl(diphenyl) silane (18.6 mg, 0.094 mmol, 1.00 eq.) and 6,6-dimethylfulvene (10 mg, 0.094 mmol, 1.00 eq.) were added. After holding the reaction mixture at room temperature for 24 h the solution was freeze-pump thawed for 2 cycles, charged with D_2 at 77 K and held at 50 °C. The reaction was monitored by NMR spectroscopy. After 24 h approximately 76 % of starting material were converted to deuterated allyl silane **24**. The product was not isolated.

¹H-NMR (300 MHz, CD_2Cl_2): δ = 7.65 – 7.52 (m, 3H), 7.43 – 7.28 (m, 4H), 5.29 (s, 0H), 2.76 – 2.68 (m, 1H), 2.24 – 1.89 (m, 3H, CHD), 0.98 (s, 3H, CH_3), 0.82 (s, 3H, CH_3), 0.58 (s, 3H, $SiCH_3$).

Synthesis of 1-(propan-2-yl-2-d)cyclopent-1-ene-2,3-d₂ (25)



The solution containing **24**, tris(1-naphthyl)phosphine (3.90 mg, 0.0094 mmol, 0.10 eq.) and $B(C_6F_5)_3$ (4.80 mg, 0.0094 mmol, 0.10 eq) under D_2 atmosphere was heated to 70 °C. After 24 h formation of deuterated cyclopentene (**25**) and deutrosilane **D-3** was observed by NMR spectroscopy (48%). The reaction mixture was subsequently subjected to trap-to-trap condensation giving a solution of the desired product in CD_2Cl_2 . The title compound was characterized by NMR spectroscopy.

¹H-NMR (300 MHz, CD_2Cl_2): δ = 5.30 (bs, 1H, H_{Olefin}), 2.28 – 2.19 (m, 3H, CH_2), 1.87 – 1.77 (m, 1H, CH_2), 1.02 – 1.01 (m, 6H, CH_3).

Crystal structure determination:

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and *wR*² values are given for all reflections.

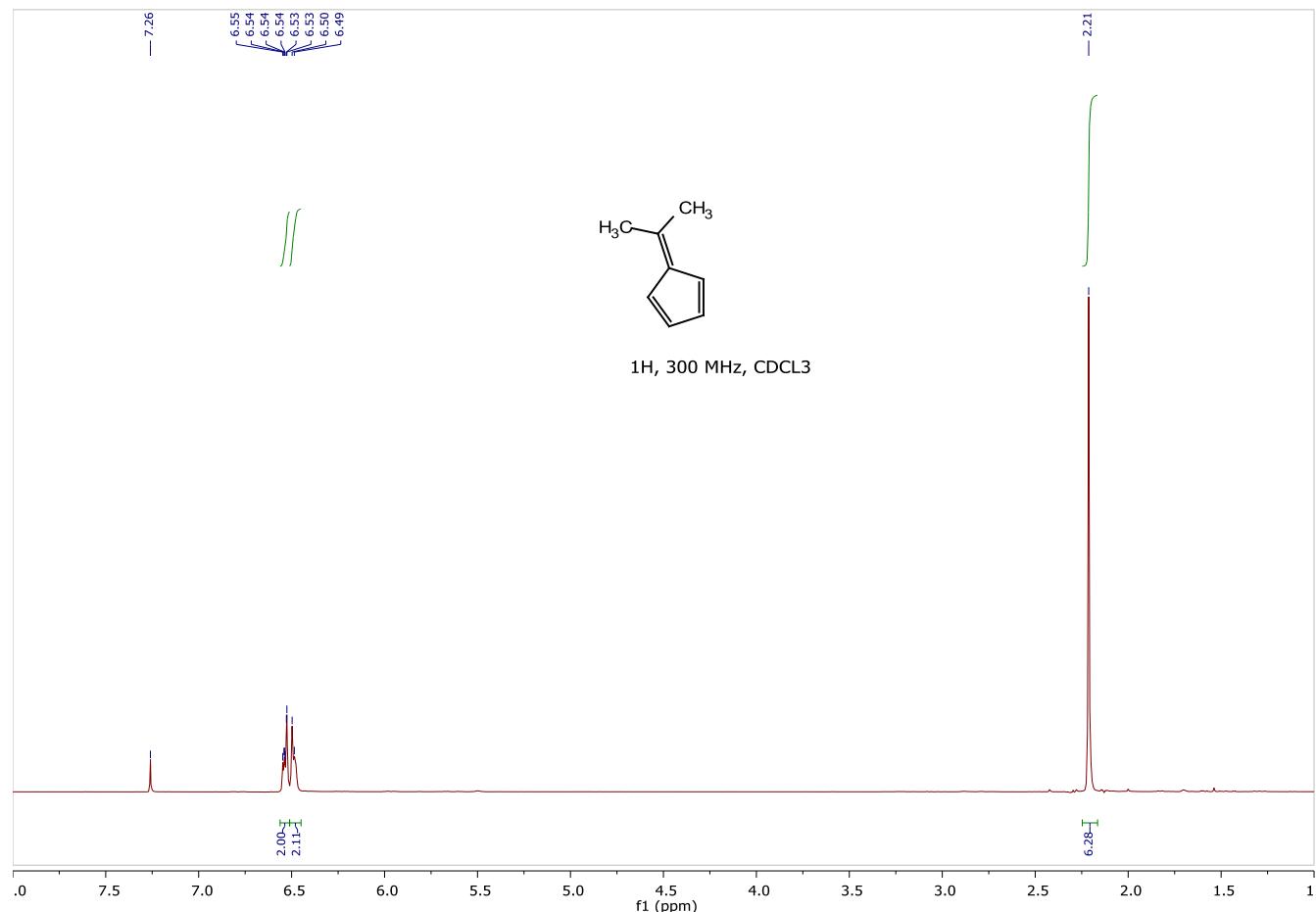
X-ray crystal structure analysis of 5: formula C₂₁H₂₄Si, *M* = 304.49, yellow crystal, 0.20 x 0.10 x 0.04 mm, *a* = 7.5625(6), *b* = 8.5844(6), *c* = 14.9024(15) Å, α = 105.447(4), β = 98.731(5), γ = 99.813(4)°, *V* = 898.84(13) Å³, ρ_{calc} = 1.125 gcm⁻³, μ = 1.084 mm⁻¹, empirical absorption correction (0.812 ≤ *T* ≤ 0.957), *Z* = 2, triclinic, space group *P*̄¹ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 10040 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å⁻¹, 3007 independent (*R*_{int} = 0.057) and 2606 observed reflections [*I*>2σ(*I*)], 202 refined parameters, *R* = 0.056, *wR*² = 0.158, max. (min.) residual electron density 0.22 (-0.34) e.Å⁻³, the hydrogen atoms were calculated and refined as riding atoms.

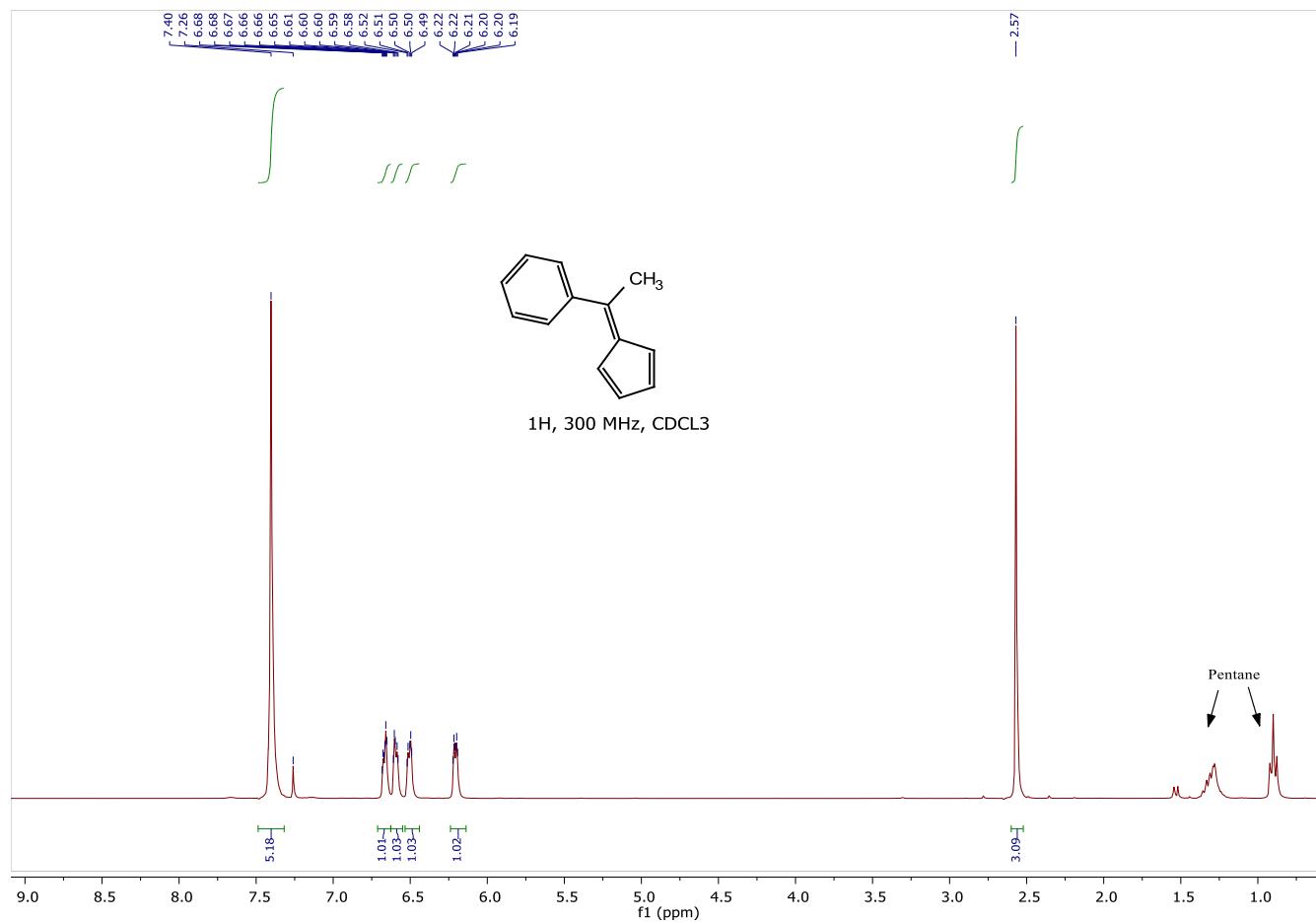
Literature

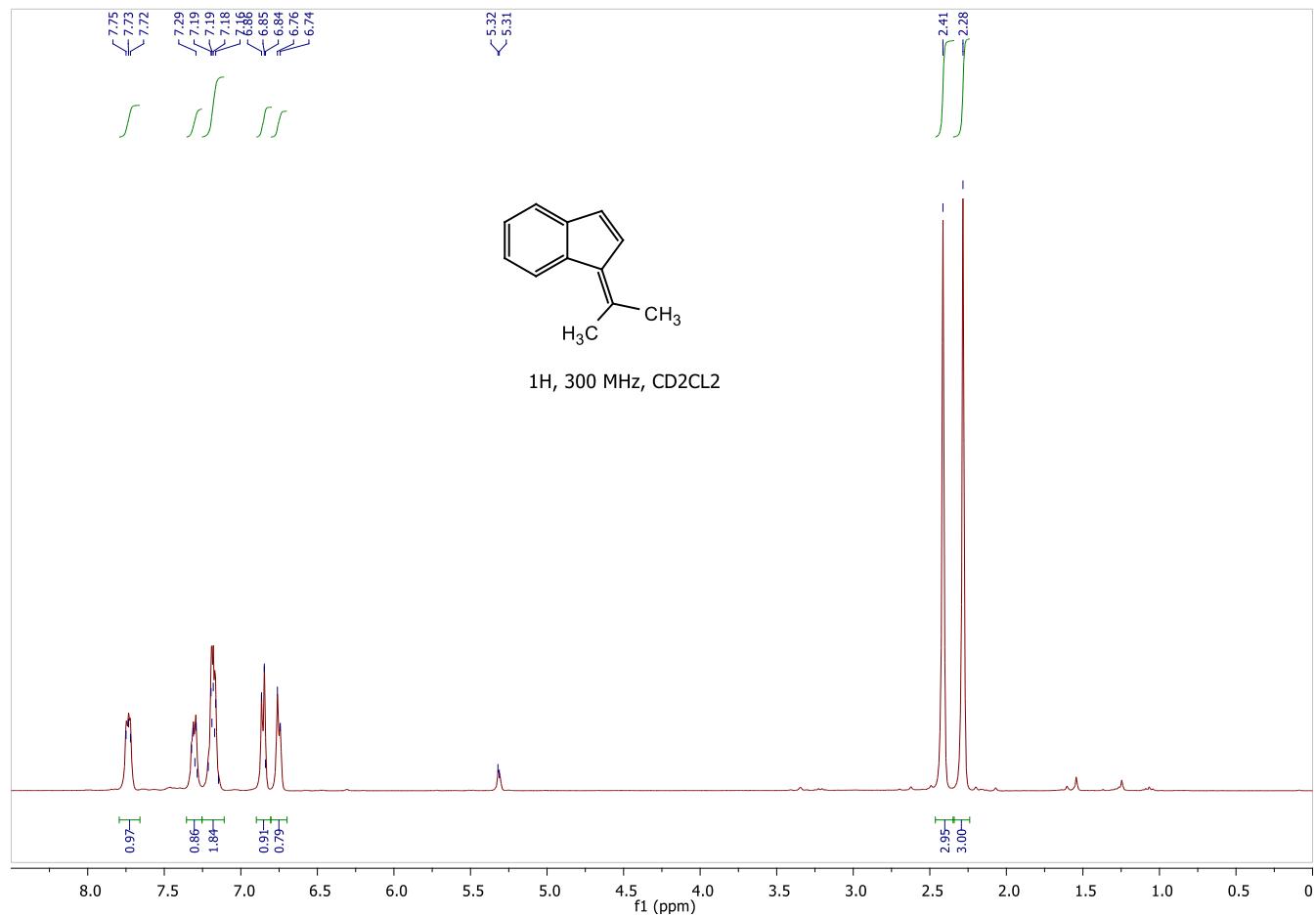
1. N. Coşkun and I. Erden, *Tetrahedron*, 2011, **67**, 8607-8614.
2. H. Alper and D. E. Laycock, *Synthesis*, 1980, **1980**, 799-799.
3. A. C. Möller, R. Blom, R. H. Heyn, O. Swang, C.-H. Görbitz and T. Seraidaris, *Eur. J. Inorg. Chem.*, 2005, **2005**, 1759-1769.
4. M. Nishizawa, Y. Asai and H. Imagawa, *Org. Lett.*, 2006, **8**, 5793-5796.
5. S. P. Liang, Leo A., *Acta Chem. Scand.*, 1992, **46**, 597-605.
6. G. I. Nikonov, S. F. Vyboishchikov and O. G. Shirobokov, *J. Am. Chem. Soc.*, 2012, **134**, 5488-5491.

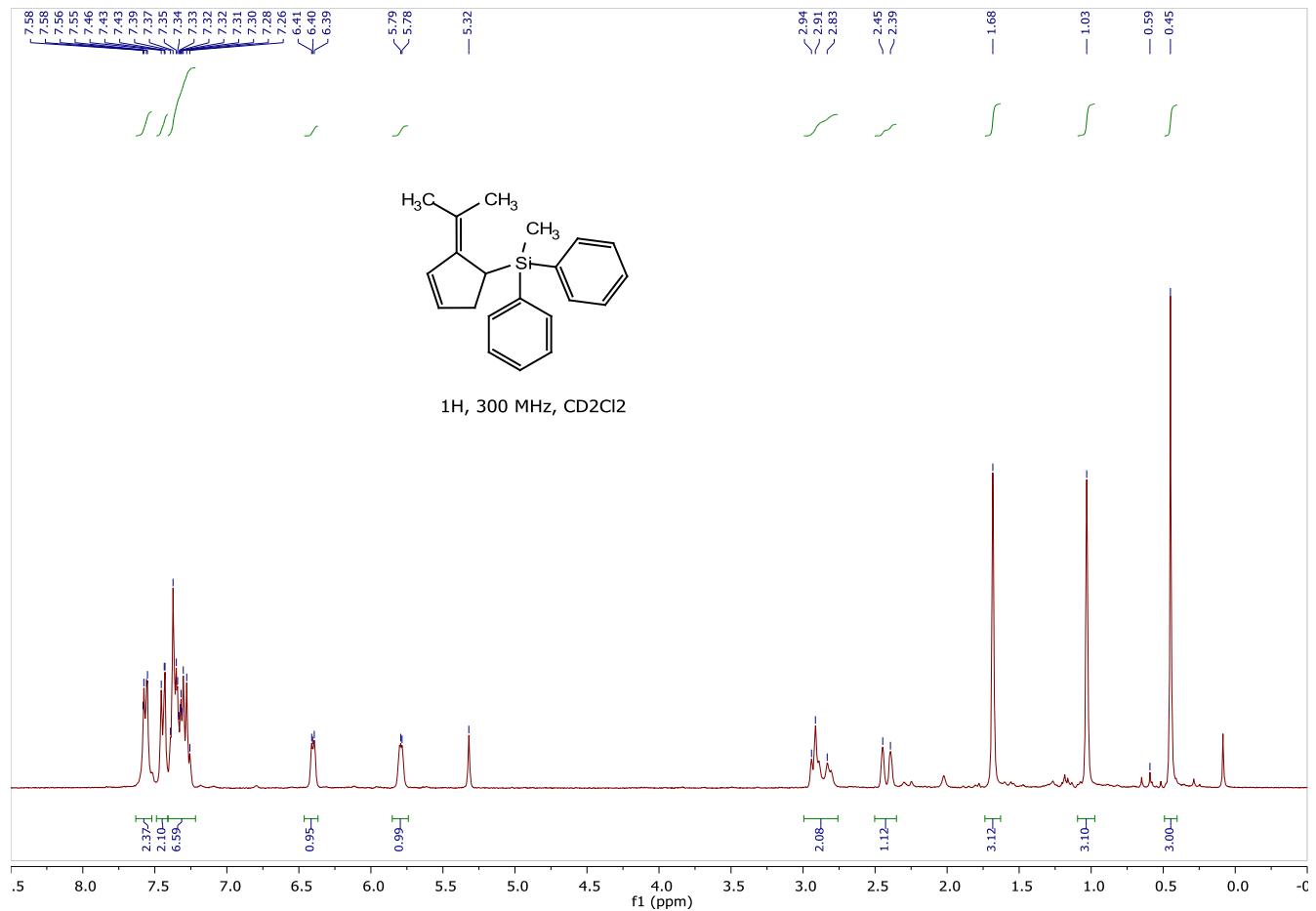
NMR spectra of the synthesized substances

6,6-Dimethylfulvene (2), ^1H -NMR

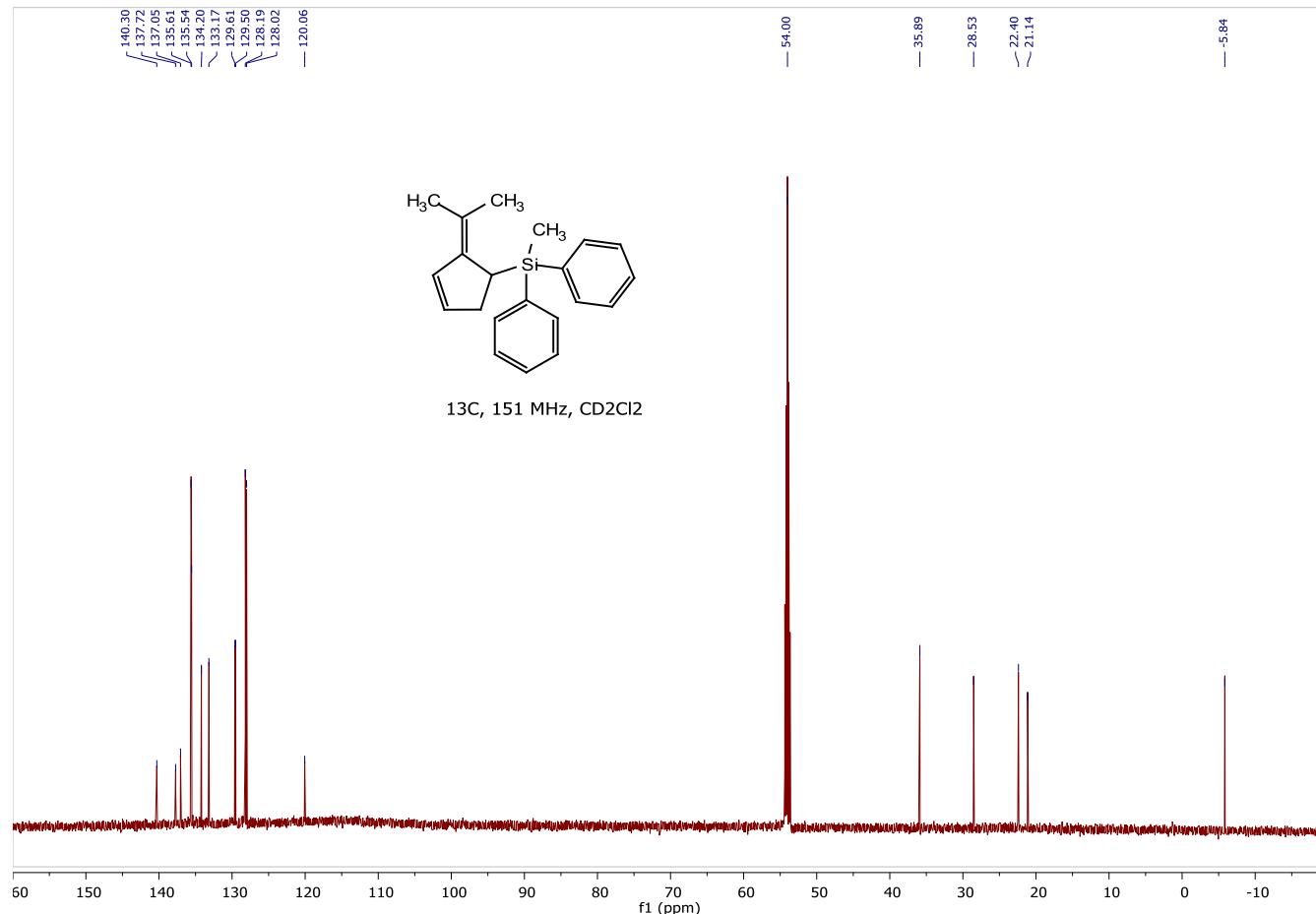


6-Methyl-6-phenylfulvene (**13**), ^1H -NMR

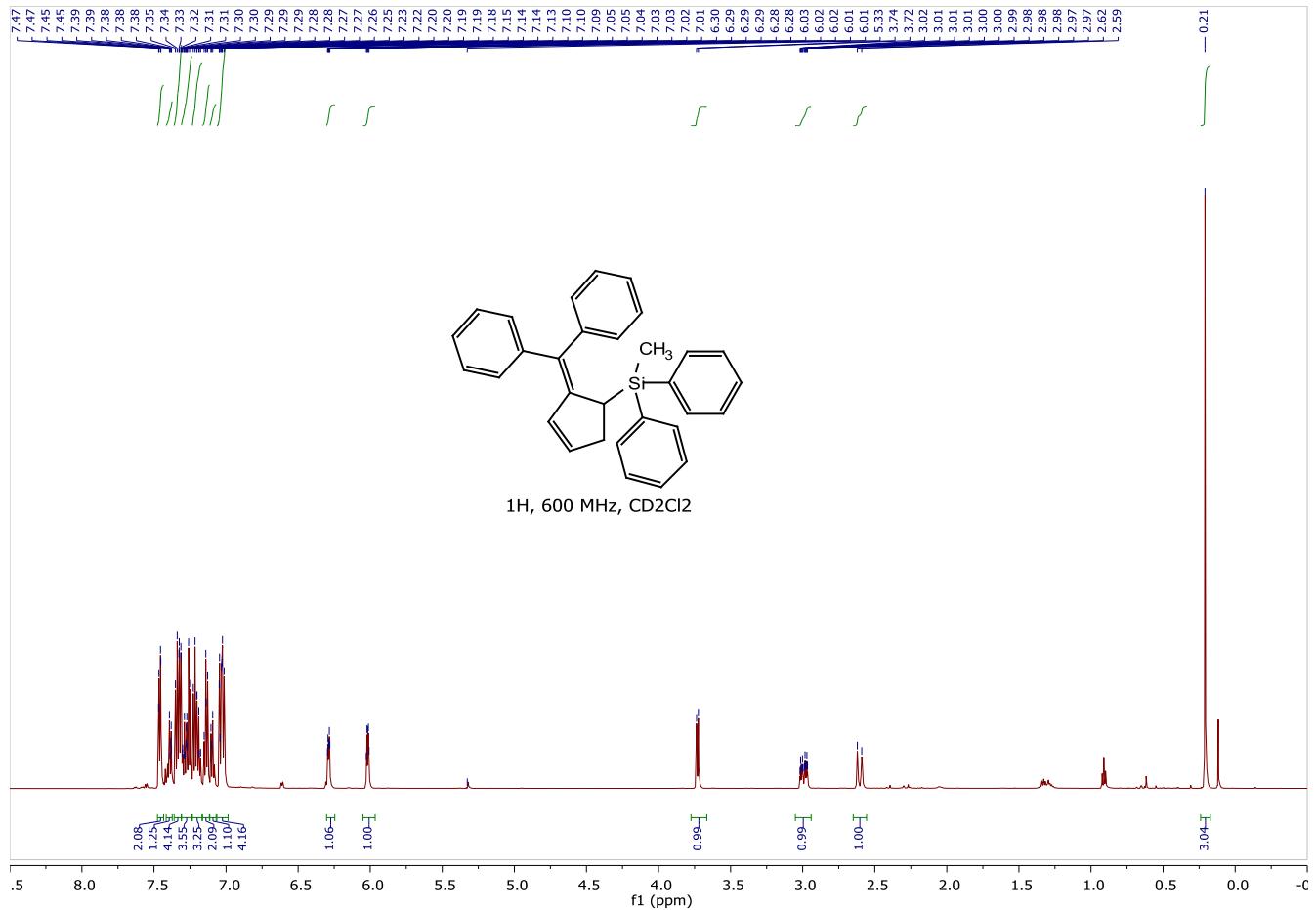
6,6-Dimethylbenzofulven (**16**), ^1H -NMR

Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**5**), ¹H-NMR

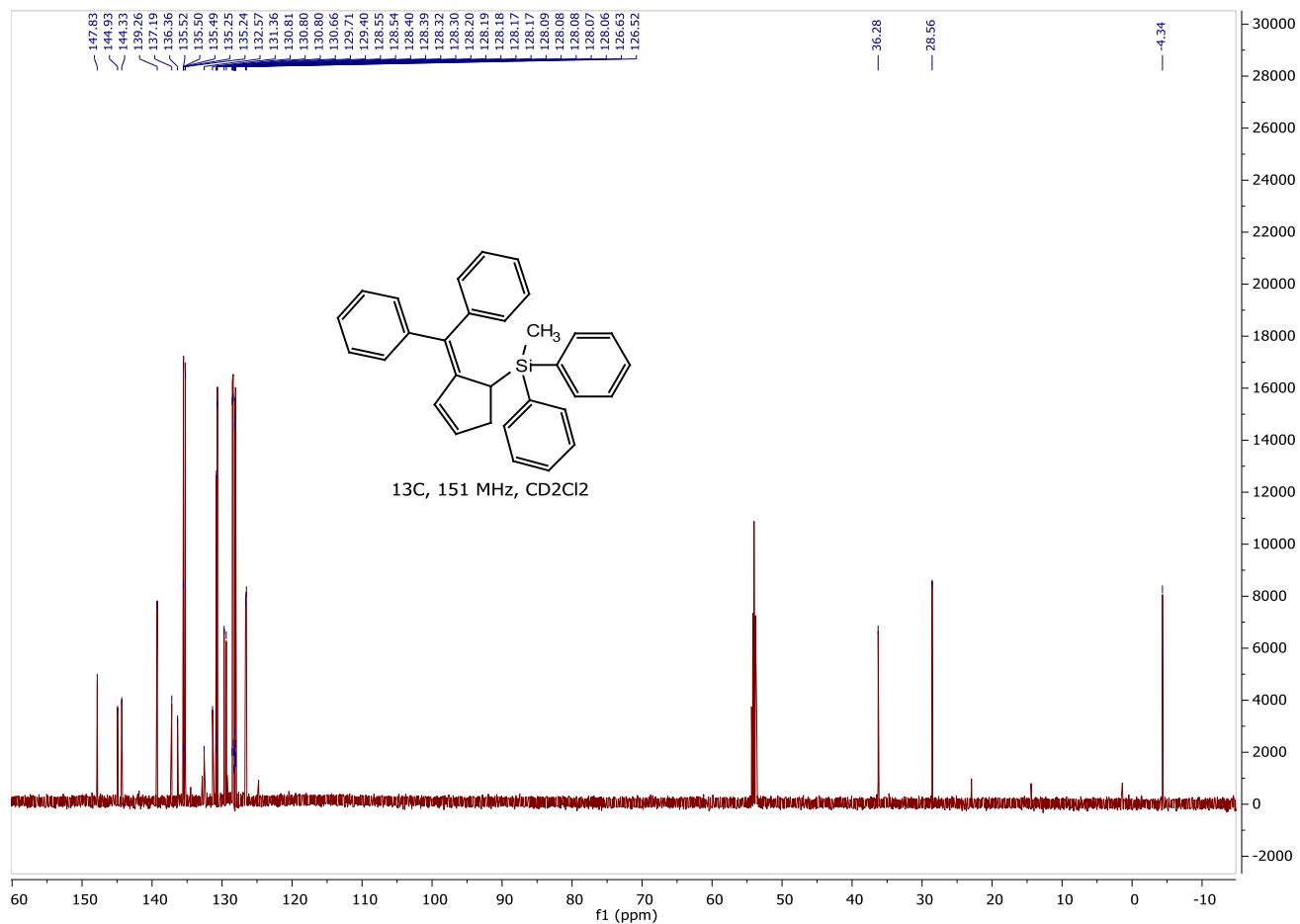
Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**5**), ^{13}C -NMR



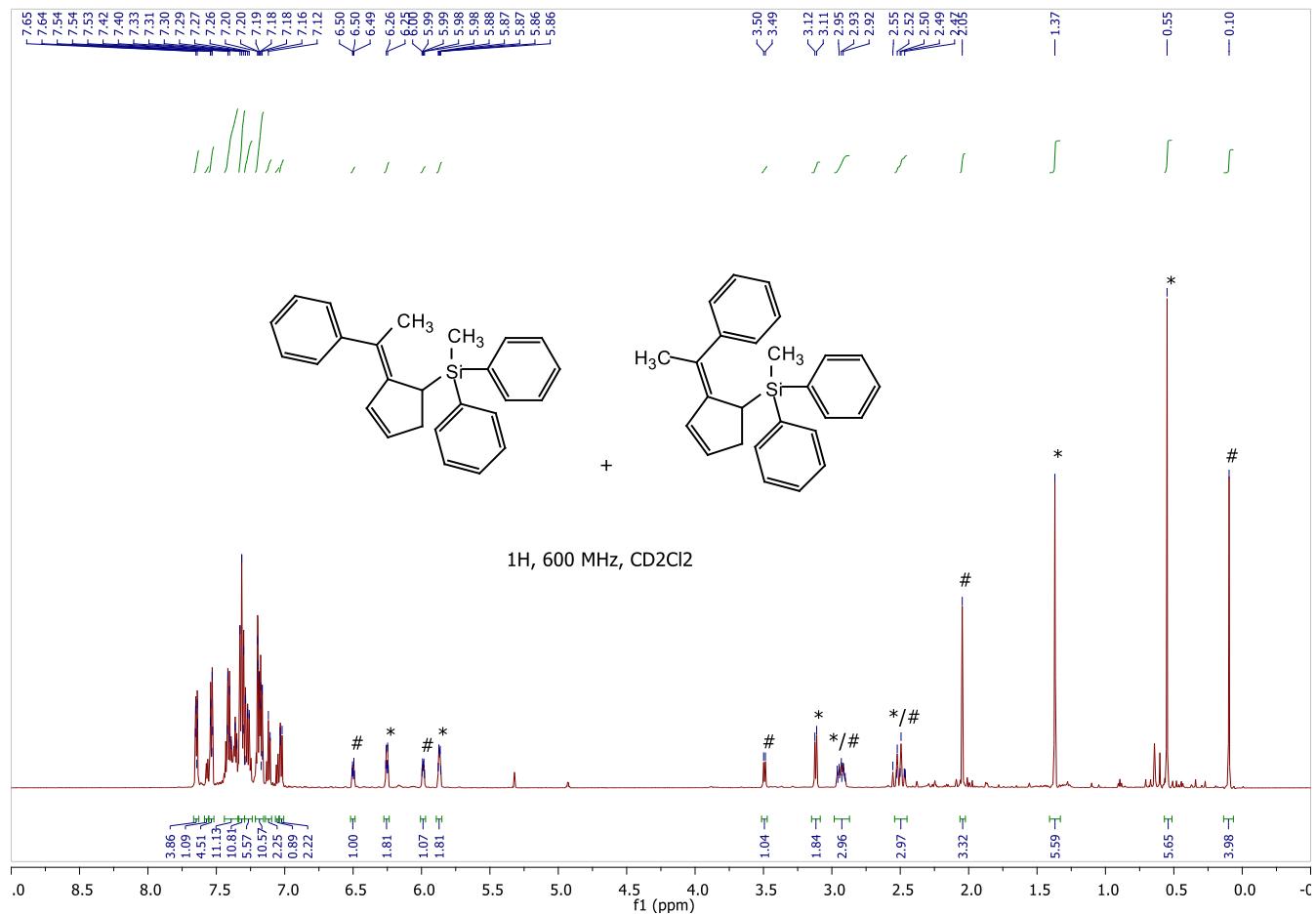
(2-(Diphenylmethylene)cyclopent-3-en-1-yl)dimethyl(phenyl)silane (**14**), $^1\text{H-NMR}$



(2-(Diphenylmethylene)cyclopent-3-en-1-yl)dimethyl(phenyl)silane (**14**), ^{13}C -NMR

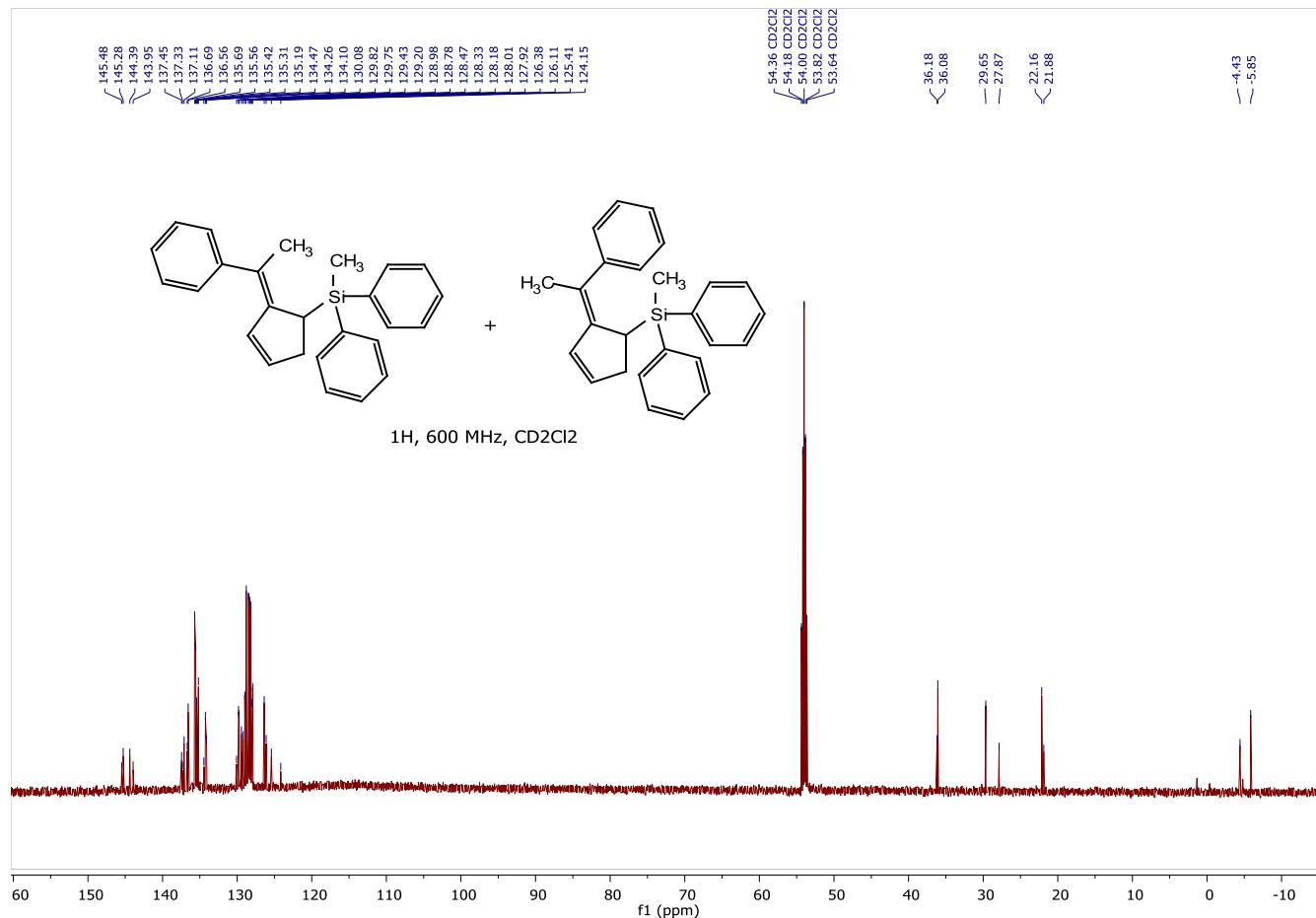


(*E/Z*)-Methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (*E/Z*-15), $^1\text{H-NMR}$

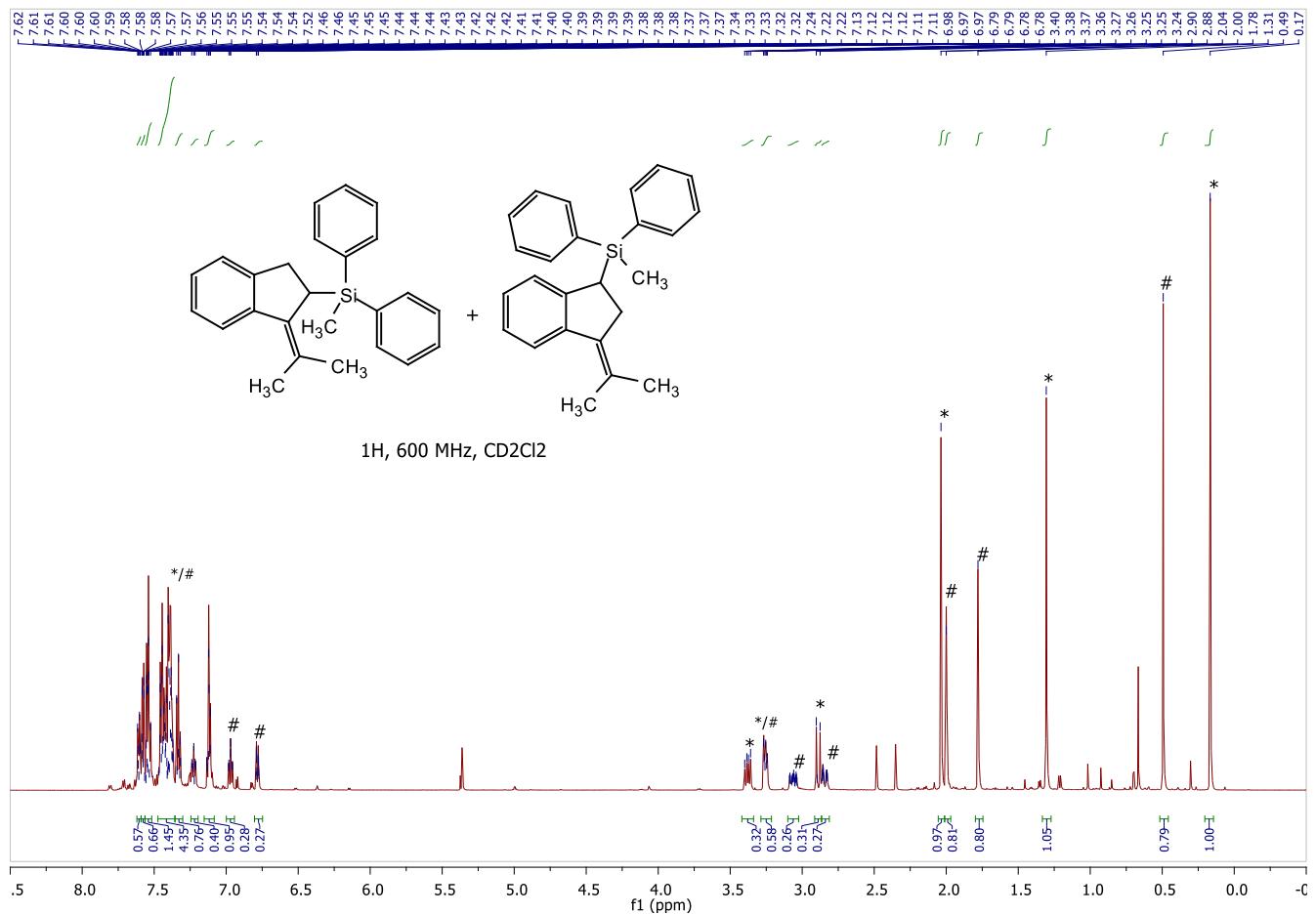


* E-15; # Z-15

(*E/Z*)-Methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (*E/Z*-**15**), ^{13}C -NMR

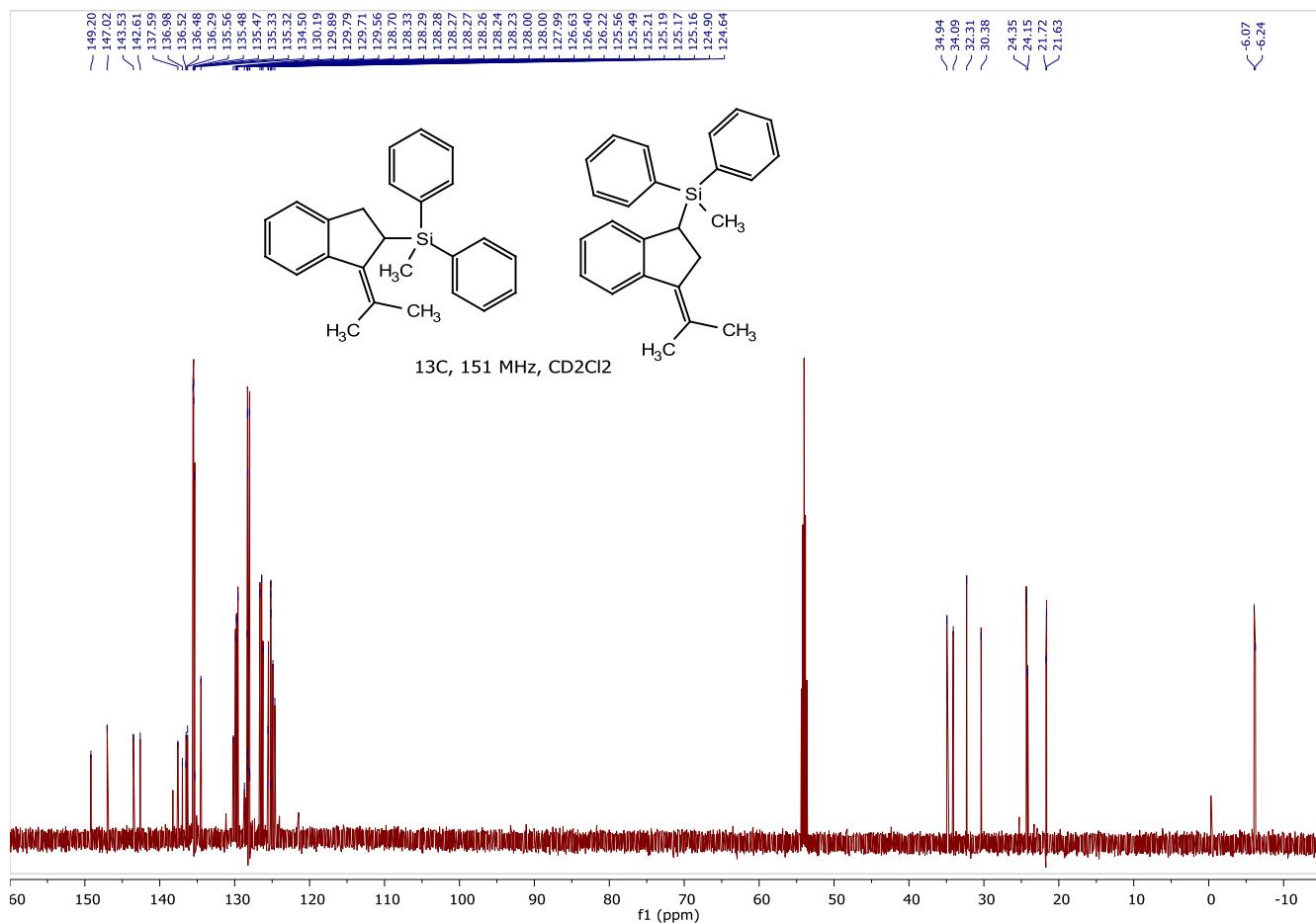


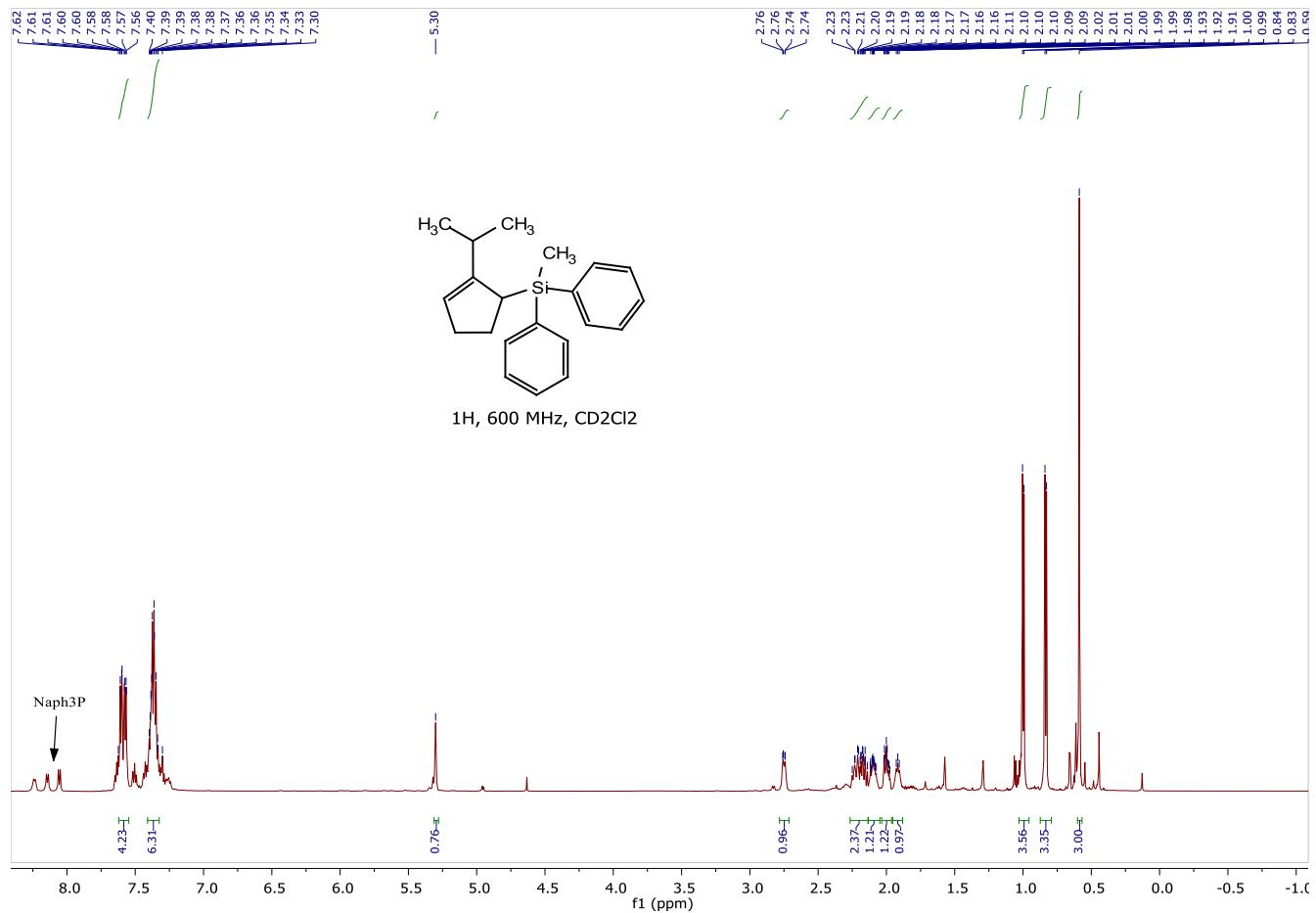
Methyldiphenyl(1-(propan-2-ylidene)-2,3-dihydro-1H-inden-2-yl)silane (**17**), Methyldiphenyl(3-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-yl)silane (**18**), $^1\text{H-NMR}$

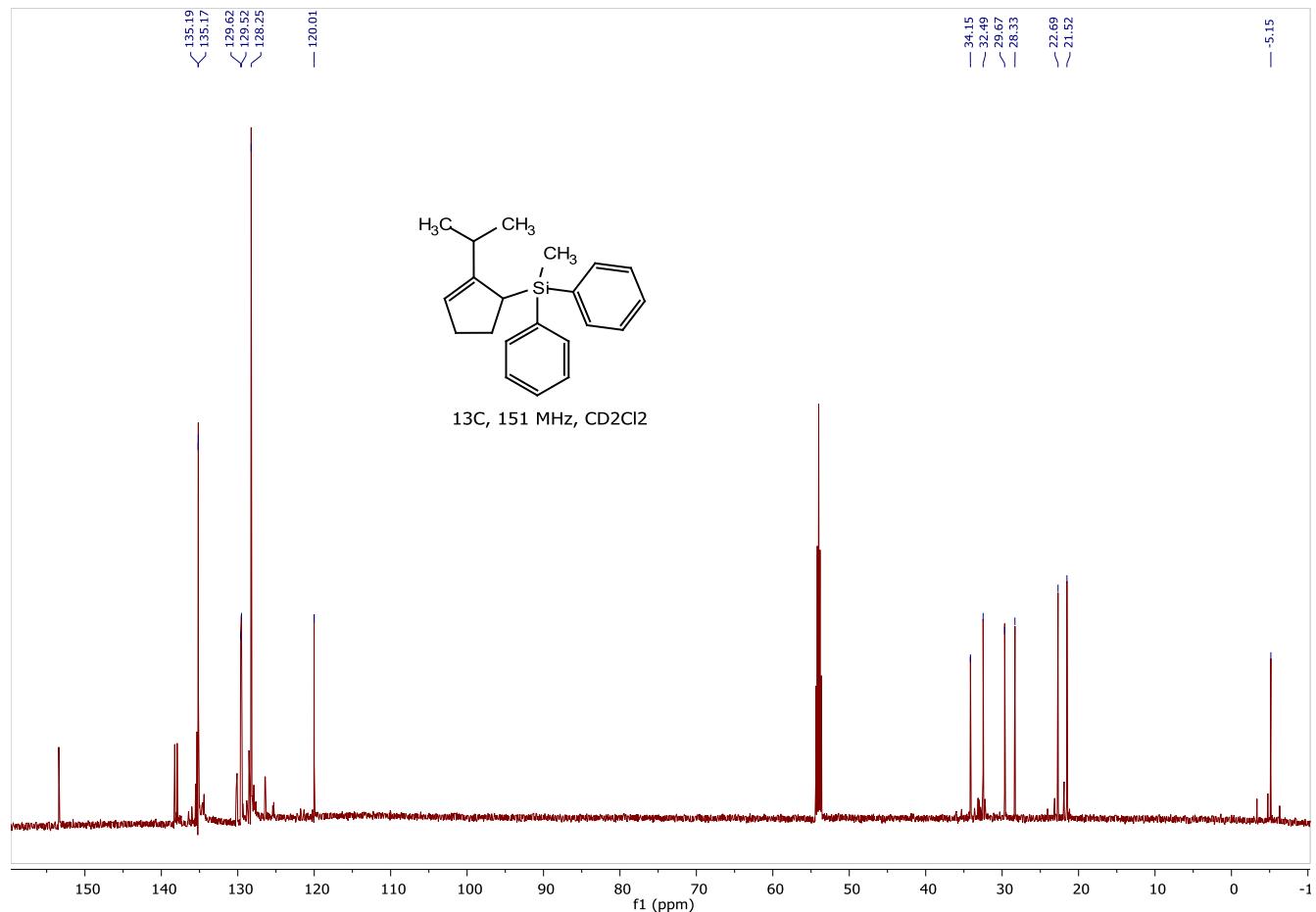


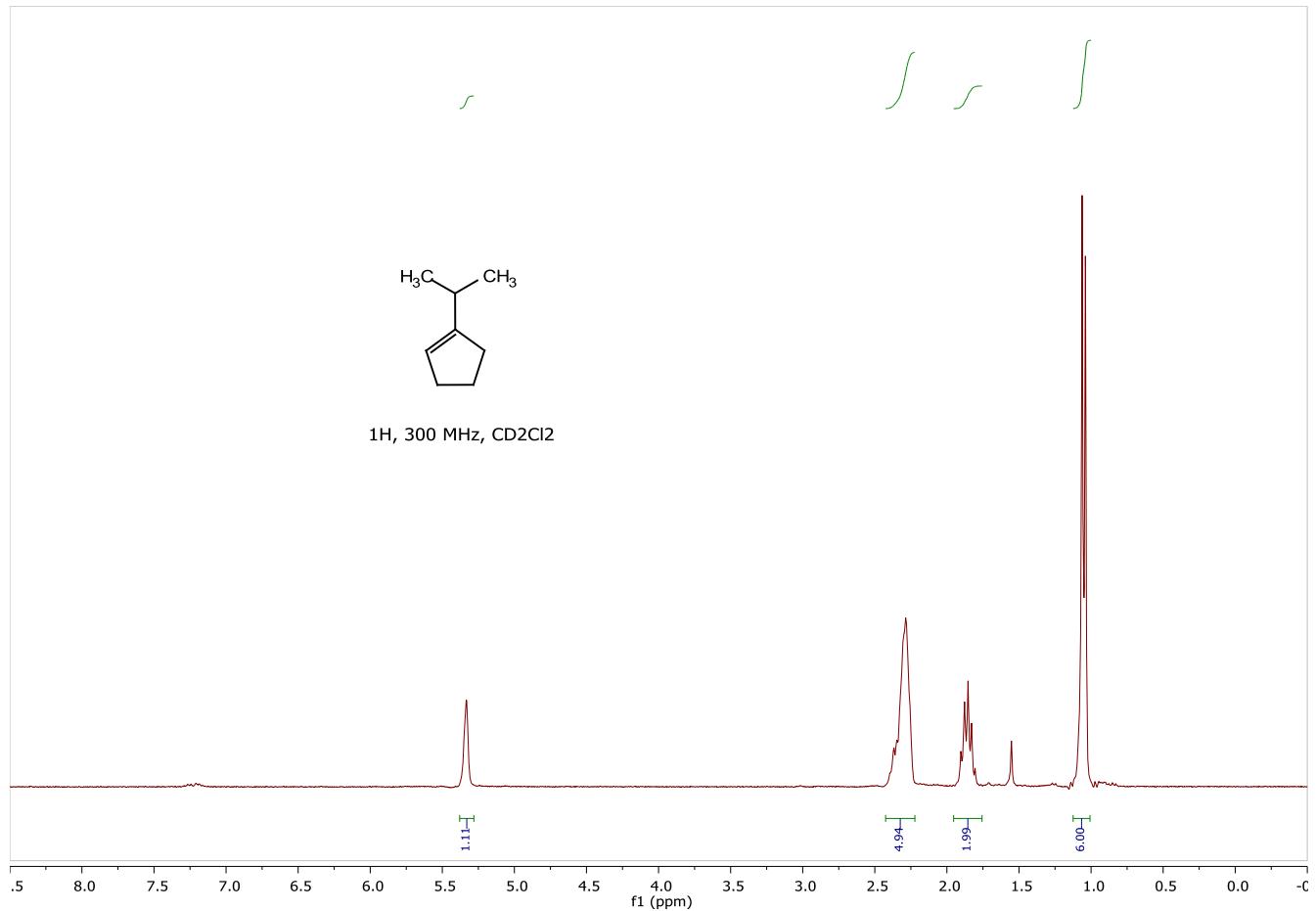
* 17; # 18

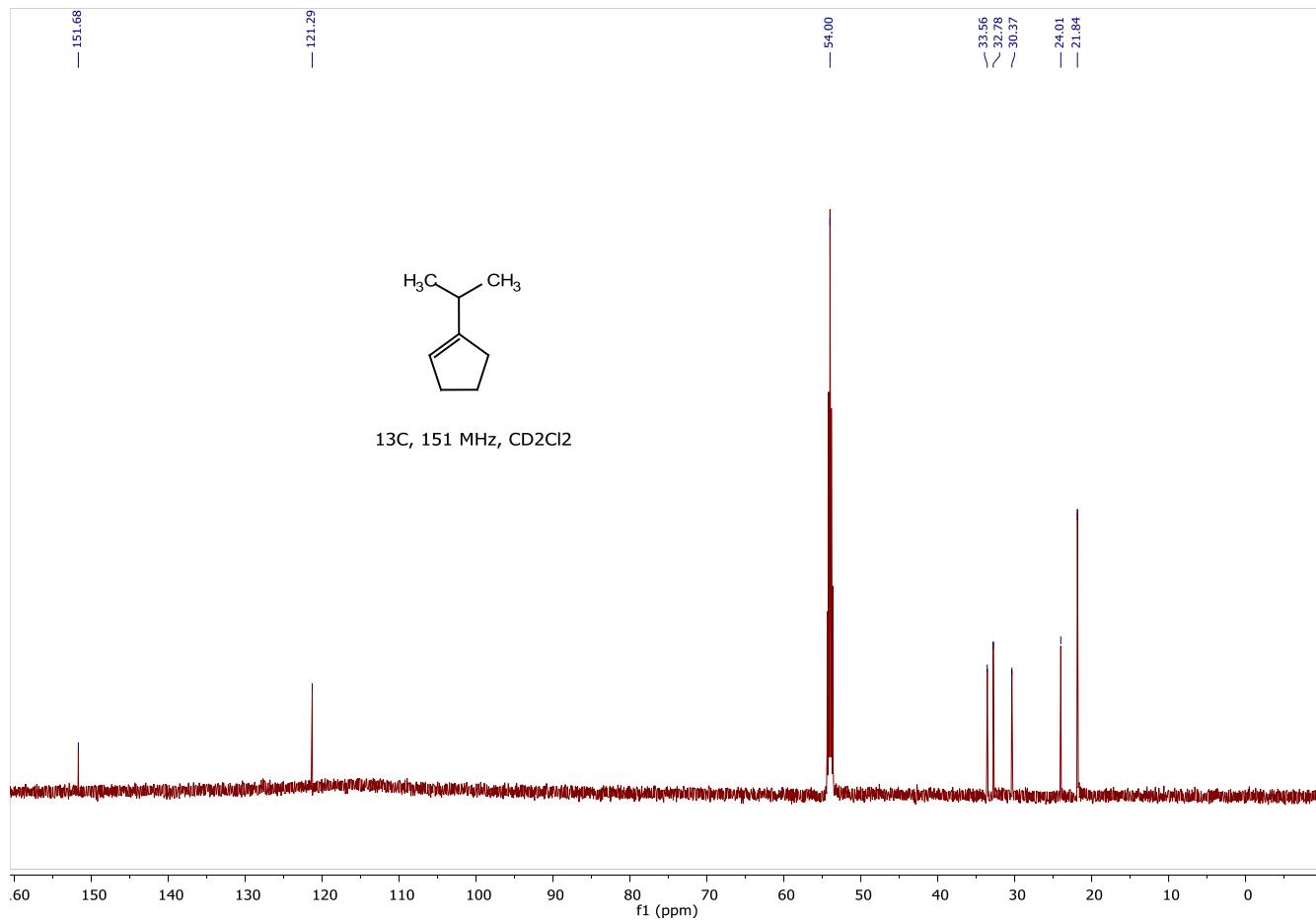
Methyldiphenyl(1-(propan-2-ylidene)-2,3-dihydro-1H-inden-2-yl)silane (**17**), methyldiphenyl(3-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-yl)silane (**18**), ^{13}C -NMR



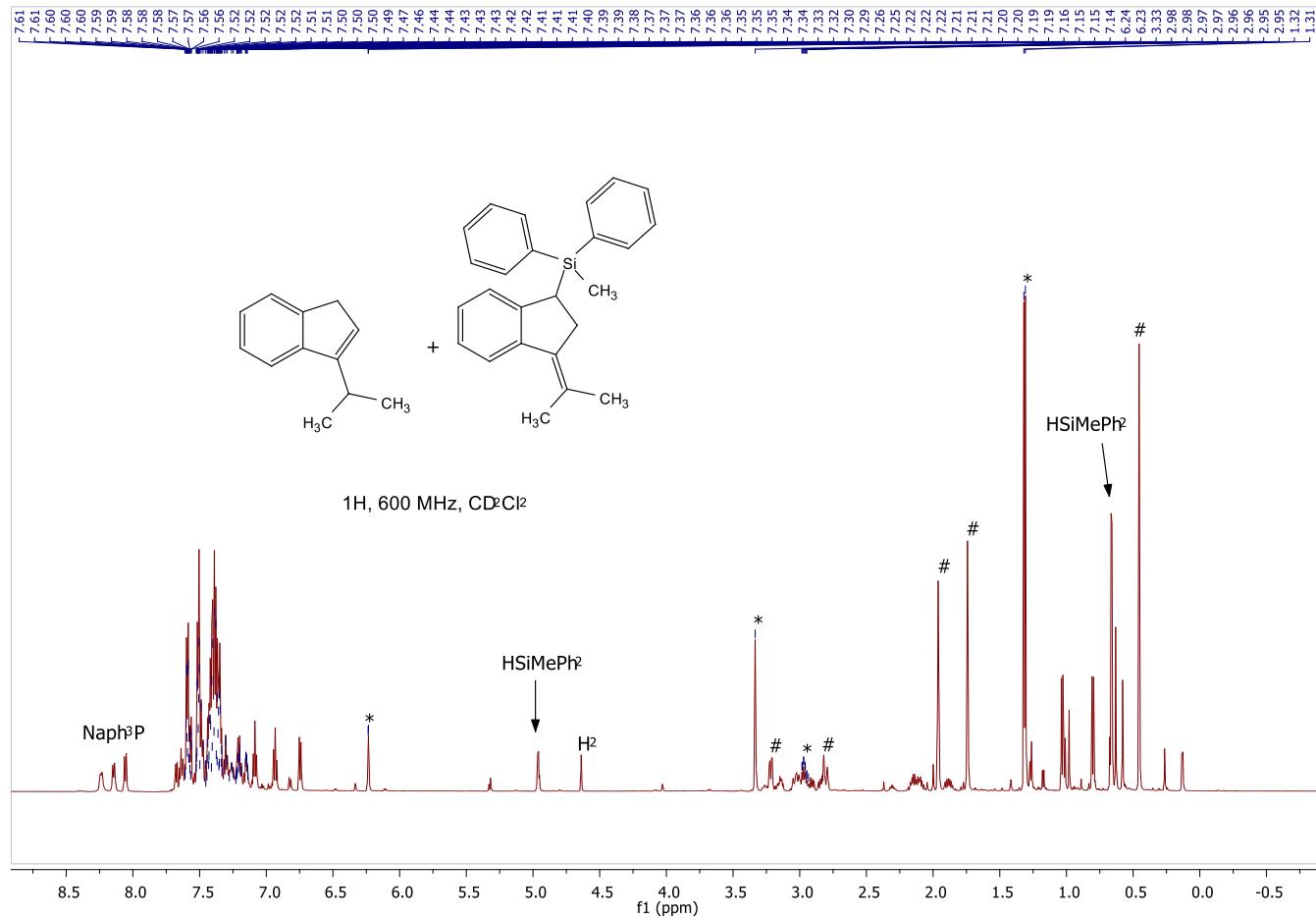
Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**19**), ^1H -NMR

Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane (**19**), ^{13}C -NMR

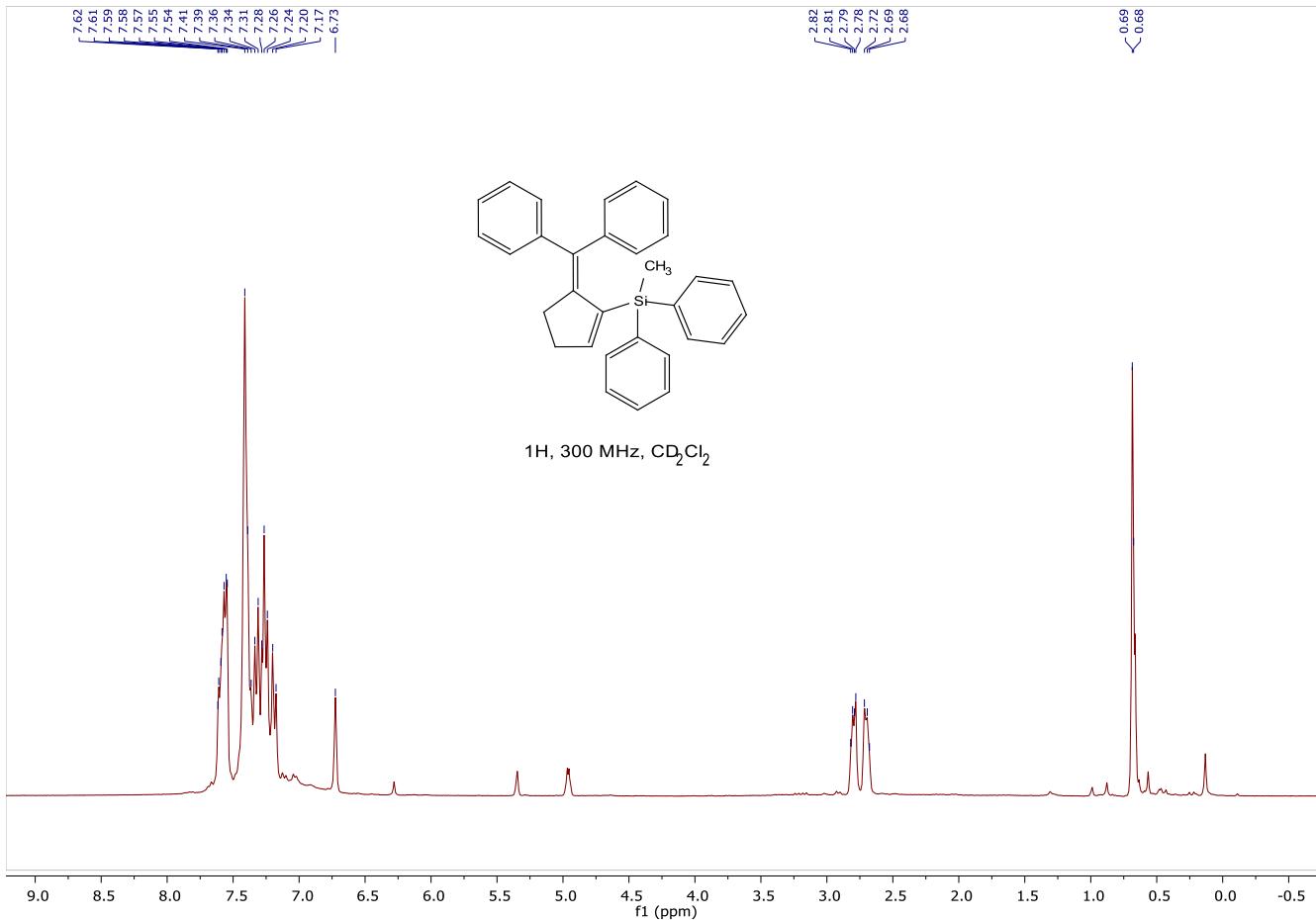
1-*Iso*-propylcyclopent-1-ene (**20**), ^1H -NMR

1-*Iso*-propylcyclopent-1-ene (**20**), ^{13}C -NMR

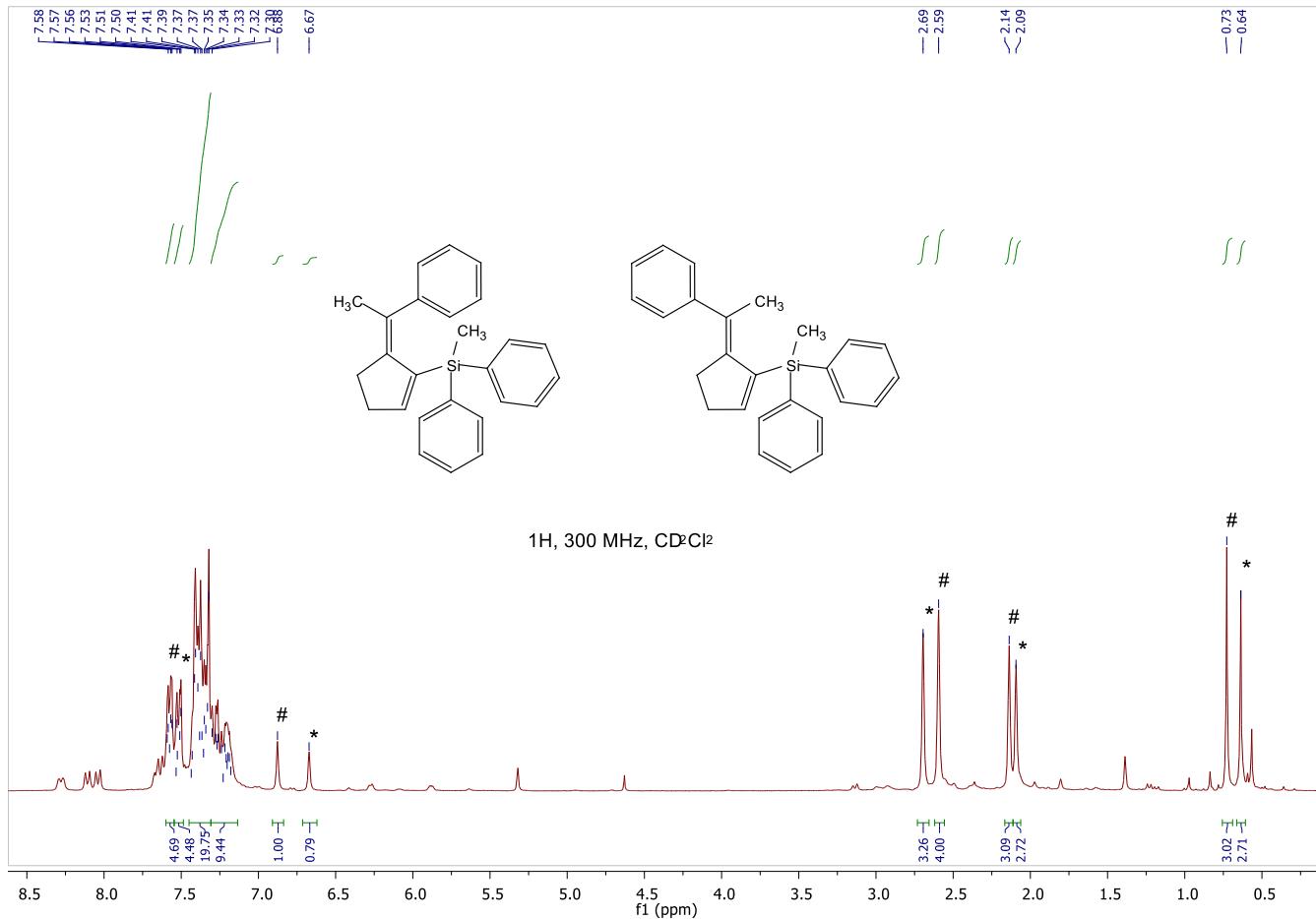
3-*Iso*-propyl-1H-indene (**21**), Methylidiphenyl(3-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-yl)silane (**18**), ^1H -NMR



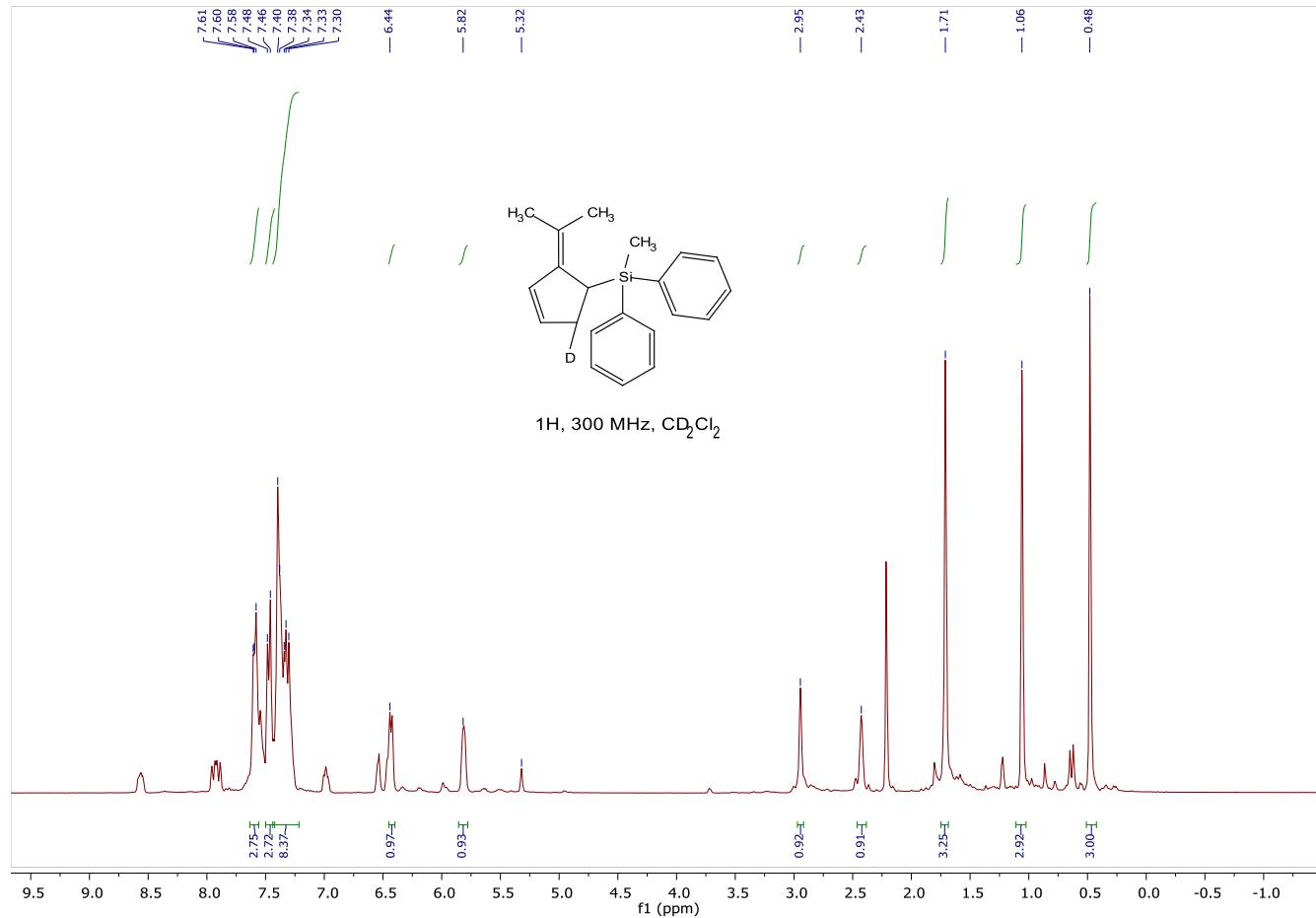
* **21**; # **18**

(2-(Diphenylmethylene)cyclopent-3-en-1-yl)(methyl)diphenylsilane (**22**), ^1H -NMR

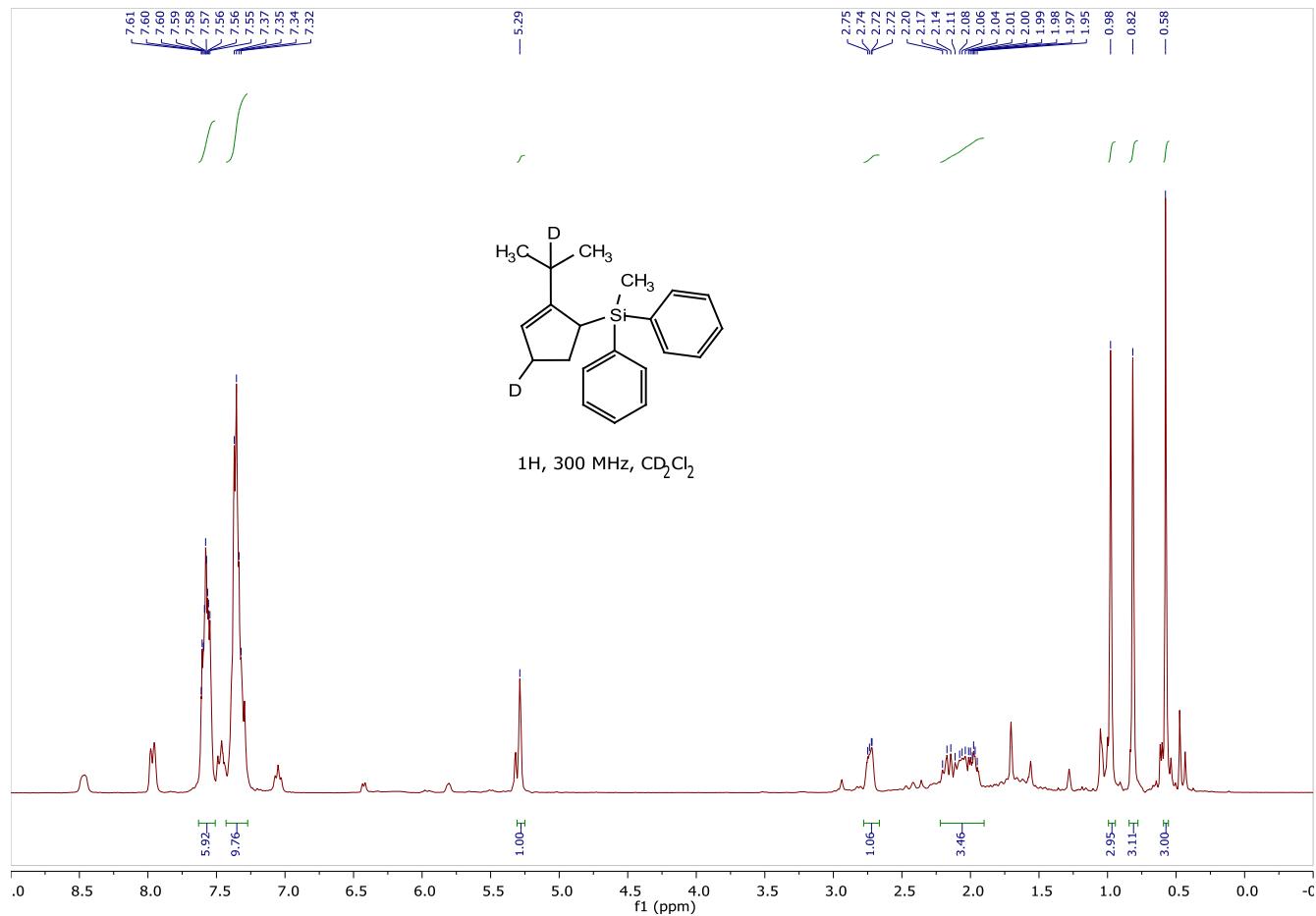
Z-Methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (**Z-23**), *E*-methyldiphenyl(2-(1-phenylethylidene)cyclopent-3-en-1-yl)silane (**E-23**), $^1\text{H-NMR}$



* Z-23; # E-23

Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane-*d*¹ (D-5), ¹H-NMR

Dimethyl(phenyl)(2-(propan-2-ylidene)cyclopent-3-en-1-yl)silane-*d*² (24), ¹H-NMR



1-(Propan-2-yl-2-d)cyclopent-1-ene-2,3-d₂ (**25**), ¹H-NMR