SUPPORTING INFORMATION

For

Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

Maciej Skroczki, Violettta Patroniak, Piotr Pawluć

+Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.
+Centre for Advanced Technologies, Adam Mickiewicz University, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland.

CONTENTS:

1. Experimental procedures P2
2. Analytical data of isolated products P4
3. Deuterium labelled experiment P14
4. Spectra of products P15
5. References P55

CONTACT WITH AUTHORS:

M. Skroczki macliej.skroczki@amu.edu.pl
P. Pawluć piotr.pawluc@amu.edu.pl
V. Patroniak violapat@amu.edu.pl
EXPERIMENTAL PROCEDURES

1.1. General remarks:

All reactions were performed in flame-dried glassware under argon atmosphere. THF was purified by distillation over sodium and benzophenone, under argon atmosphere. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 MHz or 400 MHz spectrometer.

FT-IR spectra were recorded on a Nicolet iS50 (Thermo Scientific) Fourier transform spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm⁻¹ were collected, to record the spectra in the range of 4000-400 cm⁻¹.

HRMS Spectra were recorded on a QTOF type mass spectrometer (Impact HD, Bruker) in positive ion mode.

1.2. General procedure of alkyne hydrosilylation:

General procedure for hydrosilylation of alkyne A: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.1 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 40°C with stirring in oil bath. After 10 minutes LiHBEt₃ was added (0.3 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ¹H NMR.

General procedure for hydrosilylation of alkyne B: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.5 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 60°C with stirring in oil bath. After 10 minutes LiHBEt₃ was added (1.5 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ¹H NMR.

General procedure for hydrosilylation of alkyne C: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.05 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 40°C with stirring in oil bath. After 10 minutes LiHBEt₃ was added (0.15 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ¹H NMR.
1.3. Optimization of hydrosilylation of phenylacetylene with phenylsilane\(^a\)

\[
\text{Ph} = \text{Si} + \text{PhCH} = \text{CH}_2 + \text{PhSiH}_3 \xrightarrow{2 \text{M THF}} \text{Ph}_2\text{SiH}_3 + \text{PhCH}_2\text{SiH}_3
\]

| Entry | Catalyst \(1\) loading \([\text{mol} \%]\) | Time \([\text{h}]\) | Temp. \([\text{°C}]\) | Phenyldisilane Conversion\(^b\) [%] | Selectivity\(^c\) \((3a : 3aa)\) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1     | 0.1             | 20              | 40              | >99             | 78:22           |
| 2     | 0.05            | 20              | 40              | >99             | 79:21           |
| 3\(^d\) | 0.05            | 20              | 40              | >99             | 91:9            |
| 4     | 0.05            | 20              | 20              | 91              | 79:21           |
| 5     | 0.025           | 20              | 40              | >99             | 84:16           |
| 6     | 0.01            | 20              | 40              | >99             | 86:14           |
| 7     | 0.01            | 0.166           | 40              | 14              | 94:6            |
| 8     | 0.005           | 20              | 40              | 85              | 89:11           |
| 9     | 0.005           | 0.5             | 40              | 20              | 92:8            |

\(^a\)Conditions: phenylacetylene (1 mmol), phenylsilane (1 mmol).
\(^b\)Calculated by GC with decane as internal standard.
\(^c\)Reaction with 1.5 mmol of phenylsilane.

1.4. Ligand\((L)\) and complex 1 synthesis:

Ligand was synthesized according to reported procedure\([1]\). 2-chlorobenzimidazole (8.00 g 0.05 mol) was placed under argon atmosphere in two-necked round-bottomed flask. Methylhydrazine (11.9 g, 0.25 mol), in five-fold excess, was dissolved in anhydrous ethanol and was added to the reaction mixture, which was heated in heating mantle to 80°C and stirred for 20 h. The white, crystalline product was filtered on Büchner funnel and dried under vacuum. Yield 68.2% (5.8 g, 0.036 mol). Then condensation of 2-imidazolecarboxyaldehyde with 2-(1-methylhydrazine)benzimidazole was performed. At two-necked round-bottomed flask 2-(1-methylhydrazine)benzimidazole (1 g, 6.16 mmol) placed under argon atmosphere. The 4-imidazolecarboxyaldehyde (0.591 g, 6.16 mmol) was dissolved in anhydrous ethanol and was added to the reaction mixture. Reaction mixture was stirred for 24 h at 60°C. Yellow clear solution was cooled to room temperature. Precipitate, was then filtered by vacuum filtration, washed with anhydrous ethanol and dried under vacuum to give 1.24 g (5.16 mmol) of \(L\). The supernatant was concentrated to minimal amount of volume and the next part of precipitate was obtained 0.140 g (0.58 mmol). Total yield is 91% (1.38 g, 5.74 mmol).

Complex 1 was synthesized according to reported procedure\([2]\). To a solution of \(L\) (100.0 mg) in hot MeOH, the methanolic solution of CoCl\(_2\)-6H\(_2\)O (99.1 mg) was added. Mixture was stirred for 24 h at room temperature. Solvents were subsequently evaporated under vacuum to minimal amount. Then, excess of Et\(_2\)O was added. Precipitate was filtered and washed twice with Et\(_2\)O and air dried, affording 153.9 mg (99.8% yield) of complex 1.
2. Analytical data of isolated products

2.1. (2a) Diphenyl(1-phenylvinyl)silane – prepared from phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (colorless oil, 285.9 mg - >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.52 - 7.45 (m, 4H), 7.36 - 7.23 (m, 8H), 7.21 - 7.12 (m, 3H), 6.23 - 6.19 (d, 1H, } J = 1.7 \text{ Hz), 5.63 - 5.59 (d, 1H, } J = 2.4 \text{ Hz), 5.31 (s, 1H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 145.9, 142.9, 135.8, 133.1, 132.2, 129.9, 128.5, 128.1, 127.1, 126.8 \]

Corresponds to previously reported data [3]

2.2. (2b) (1-(4-(tert-butyl)phenyl)vinyl)diphenylsilane - prepared from (4-tert-butyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 340.5 mg - >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.53 - 7.46 (m, 4H), 7.36 - 7.17 (m, 10H), 6.23 - 6.19 (dd, 1H, } J = 2.3 \text{ Hz), 5.58 - 5.53 (d, 1H, } J = 2.4 \text{ Hz), 5.32 (s, 1H), 1.20 (s, 9H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 150.1, 145.1, 139.8, 135.8, 133.3, 131.5, 139.8, 128.1, 126.3, 125.4, 34.5, 31.3 \]

Corresponds to previously reported data [3]

2.3. (2c) (1-(4-bromophenyl)vinyl)diphenylsilane - prepared from (4-bromo)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 365.0 mg - >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.59 - 7.53 (m, 4H), 7.47 - 7.34 (m, 8H), 7.24 - 7.16 (m, 2H), 6.29 - 6.26 (d, 1H, } J = 1.7 \text{ Hz), 5.74 - 5.70 (d, 1H, } J = 2.2 \text{ Hz), 5.38 (s, 1H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 144.9, 141.9, 135.8, 132.7, 132.6, 131.5, 130.0, 128.4, 128.2, 121.1 \]

Corresponds to previously reported data [3]
2.4.(2d) (1-cyclohex-1-enylvinyl)diphenylsilane - prepared from cyclohexylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg • >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.59 - 7.53 \text{ (m, 4H)}, 7.41 - 7.34 \text{ (m, 6H)}, 5.99 \text{ (s, 1H)}, 5.96 - 5.91 \text{ (t, 1H)}, 5.38 - 5.34 \text{ (d, 1H, } J = 2.2 \text{ Hz)}, 5.33 - 5.30 \text{ (s, 1H)}, 2.29 - 2.20 \text{ (m, 2H)}, 2.10 - 2.01 \text{ (m, 2H)}, 1.75 - 1.65 \text{ (m, 2H)}, 1.60 - 1.52 \text{ (m, 2H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 145.9, 138.5, 135.8, 135.5, 133.9, 129.5, 127.9, 127.0, 26.0, 26.0, 22.3, 22.2 \]

Corresponds to previously reported data [4]

2.5.(2e) Diphenyl(3-phenylprop-1-en-2-yl)silane - prepared from 3-phenylprop-1-yne (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 298.0 mg • >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.46 - 7.41 \text{ (m, 4H)}, 7.33 - 7.24 \text{ (m, 6H)}, 7.19 - 7.09 \text{ (m, 3H)}, 7.01 - 6.96 \text{ (d, 2H)}, 5.68 - 5.65 \text{ (d, 1H, } J = 1.1 \text{ Hz)}, 5.49 - 5.46 \text{ (d, 1H, } J = 1.3 \text{ Hz)}, 4.92 \text{ (s, 1H)}, 3.44 \text{ (s, 2H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 145.8, 139.3, 135.7, 132.9, 131.2, 129.75, 129.5, 128.3, 128.0, 126.1, 126.0, 43.0 \]

HRMS (ESI): calculated for [C\text{_{24}H}\text{_{20}SiNa}]^+ requires 323.1226 m/z, found 323.1226 m/z

2.6.(2f) (1-(4-methoxyphenyl)vinyl)diphenylsilane - prepared from 4-ethynylanisole (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 313.8 mg • >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.63 - 7.57 \text{ (m, 4H)}, 7.45 - 7.31 \text{ (m, 8H)}, 6.86 - 6.80 \text{ (d, 2H)}, 6.28 - 6.25 \text{ (d, 1H, } J = 1.8 \text{ Hz)}, 5.64 - 5.61 \text{ (d, 1H, } J = 2.1 \text{ Hz)}, 5.42 \text{ (s, 1H)}, 3.77 \text{ (s, 3H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 158.9, 144.7, 135.8, 133.2, 129.8, 128.1, 127.8, 113.8, 55.3 \]

Corresponds to previously reported data [3]

2.7.(2g) (1-cyclohexylvinyl)diphenylsilane - prepared from cyclohexylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg • >99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.62 - 7.56 \text{ (m, 4H)}, 7.46 - 7.36 \text{ (m, 6H)}, 5.94 - 5.92 \text{ (m, 1H)}, 5.46 - 5.42 \text{ (d, 1H, } J = 2.3 \text{ Hz)}, 5.18 \text{ (s, 1H)}, 2.25-2.15 \text{ (m, 1H)}, 1.81 - 1.71 \text{ (m, 4H)}, 1.31 - 1.17 \text{ (m, 4H)}, 1.20 - 1.09 \text{ (m, 2H)} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 152.0, 135.7, 133.9, 129.5, 128.0, 127.9, 42.9, 33.2, 26.7, 26.2 \]

Corresponds to previously reported data [4]
2.8.(2h) (1-cyclopropylvinyl)diphenylsilane - prepared from cyclopropylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 249.8 mg >99%).

\begin{align*}
\text{H} &\text{ NMR (300 MHz, CDCl}_3\text{): } \delta 7.64 - 7.57 \text{ (m, 4H), } 7.45 - 7.34 \text{ (m, 6H), } 5.65 - 5.62 \text{ (d, 1H, } J = 1.8 \text{ Hz), } 5.28 - 5.25 \text{ (d, 1H, } J = 2.4 \text{ Hz), } 5.01 \text{ (s, 1H), } 1.59 - 1.50 \text{ (m, 1H), } 0.73 - 0.64 \text{ (m, 2H), } 0.57 - 0.51 \text{ (m, 2H)} \\
\text{C} &\text{ NMR (75 MHz, CDCl}_3\text{): } \delta 147.7, 135.5, 133.1, 129.5, 127.5, 127.8, 125.8, 16.4, 7.3
\end{align*}

Corresponds to previously reported data [5]

2.9.(2i) (E)-diphenyl(1-phenylprop-1-en-1-yl)silane (major product) - prepared from 1-phenylprop-1-yn (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg >99%).

\begin{align*}
\text{H} &\text{ NMR (300 MHz, CDCl}_3\text{): } \delta 7.68 - 7.61 \text{ (m, 1H), } 7.59 - 7.50 \text{ (m, 3H), } 7.47 - 7.32 \text{ (m, 7H), } 7.30 - 7.21 \text{ (m, 2H), } 7.21 - 7.12 \text{ (m, 1H), } 7.06 - 7.01 \text{ (m, 1H), } 6.95 \text{ (s, 0.26H minor), } 6.41 - 6.22 \text{ (q, 0.74H major), } 5.32 \text{ (s, 0.28H minor), } 5.22 \text{ (s, 0.72H major), } 2.09 \text{ (s, 0.8H minor), } 1.81 - 1.69 \text{ (d, 2.20H major)} \\
\text{C} &\text{ NMR (75 MHz, CDCl}_3\text{): } \delta 142.8, 142.1, 141.1, 139.04, 137.9, 135.8, 135.8, 133.6, 133.2, 129.8, 129.6, 129.1, 128.5, 128.1, 128.1, 127.9, 127.0, 125.8, 17.5, 16.4
\end{align*}

Corresponds to previously reported data [3]

2.10.(2j) 4-(1-(diphenylsilyl)vinyl)aniline - prepared from (4-ethynyl)aniline (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (brown oil, 300.9 mg >99%).

\begin{align*}
\text{H} &\text{ NMR (300 MHz, CDCl}_3\text{): } \delta 7.62 - 7.55 \text{ (m, 4H), } 7.42 - 7.32 \text{ (m, 6H), } 7.25 - 7.19 \text{ (m, 2H), } 6.62 - 6.56 \text{ (m, 2H), } 6.25 - 6.22 \text{ (dd, 1H, } J = 2.3 \text{ Hz), } 5.55 - 5.52 \text{ (d, 1H, } J = 2.4 \text{ Hz), } 5.39 \text{ (s, 1H), } 3.63 \text{ (s, 2H)} \\
\text{C} &\text{ NMR (75 MHz, CDCl}_3\text{): } \delta 145.7, 144.6, 135.8, 133.4, 133.0, 129.7, 129.2, 128.0, 127.7, 115.0
\end{align*}

Corresponds to previously reported data [3]
2.11.(2k) (E)-oct-4-en-4-ylidiphenylsilane - prepared from oct-4-yne (1.0 mmol) and
diphenylsilane (1.0 mmol) according to general procedure B. Purified by extraction with n-
hexane followed by filtration through silica plug. Volatiles were removed under lower pressure
affording pure product (pale yellow oil, 280.3 mg - 95%).

\[
\begin{align*}
&\text{[Structure image]} \\
&{^1}H\text{ NMR (300 MHz, CDCl}_3\text{): }\delta 7.60 - 7.55 (m, 4H), 7.42 - 7.35 (m, 4H), \\
&5.96 - 5.90 (t, 1H), 6.28 - 6.25 (d, 1H, }J = 1.8\text{ Hz), 5.10 (s, 1H), 2.26-2.14 \\
&(m, 4H), 1.48 - 1.38 (h, 2H), 1.38 - 1.28 (h, 2H), 0.97 - 0.90 (t, 3H), 0.88 \\
&- 0.81 (t, 3H), \\
&{^{13}}C\text{ NMR (75 MHz, CDCl}_3\text{): }\delta 146.7, 135.7, 135.1, 134.3, 129.4, 127.9, \\
&32.6, 30.9, 23.1, 22.6, 14.3, 14.0
\end{align*}
\]

Corresponds to previously reported data [3]

2.12.(2l) Oct-1-en-2-ylidiphenylsilane - prepared from okt-1-yne (0.5 mmol) and diphenylsilane
(0.5 mmol) according to general procedure A. Purified by extraction with n-hexane followed by
filtration through silica plug. Volatiles were removed under lower pressure affording pure product
(pale yellow oil, 146.2 mg - >99%).

\[
\begin{align*}
&\text{[Structure image]} \\
&{^1}H\text{ NMR (300 MHz, CDCl}_3\text{): }\delta 7.61 - 7.51 (m, 4H), 7.45 - 7.31 (m, 6H), \\
&5.93 - 5.80 (b, 1H), 5.50 - 5.43 (d, 1H, }J = 2.8\text{ Hz), 5.07 (s, 1H), 2.28- \\
&2.17 (t, 2H), 1.46 - 1.34 (m, 2H), 1.27 - 1.17 (m, 6H), 0.89 - 0.79 (m, \\
&3H) \\
&{^{13}}C\text{ NMR (75 MHz, CDCl}_3\text{): }\delta 146.6, 135.7, 135.4, 129.6, 129.5, 128.0, \\
&37.0, 31.7, 29.0, 28.8, 22.6, 14.1
\end{align*}
\]

Corresponds to previously reported data [4]

2.13.(2m) ((3-(diphenylsilyl))but-3-en-1-yl)oxydimethyl(phenyl)silane - (but-3-yn-1-yloxy)-
dimethyl(phenyl)silane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general
procedure A. Purified by extraction with n-hexane followed by filtration through silica plug.
Volatiles were removed under lower pressure affording pure product (colorless oil, 140.1 mg –
72%).

\[
\begin{align*}
&\text{[Structure image]} \\
&{^1}H\text{ NMR (300 MHz, CDCl}_3\text{): }\delta 7.58 - 7.50 (m, 5H), 7.45 - 7.33 \\
&(m, 10H), 5.99 - 5.83 (m, 1H), 5.56 (s, 1H), 5.09 (s, 1H), 3.68 - \\
&3.58 (t, 2H), 2.55 - 2.45 (t, 1H), 0.35 - 0.26 (s, 6H) \\
&{^{13}}C\text{ NMR (75 MHz, CDCl}_3\text{): }\delta 146.7, 146.5, 136.8, 136.6, 136.3, 129.5, \\
&128.6, 32.6, 29.0, 22.6, 14.1
\end{align*}
\]

HRMS (ESI): calculated for [C_{24}H_{28}Si_{2}ONa]^+ requires 411.1571 m/z, found 411.1575 m/z
2.14.(2n) Diphenyl(1-(p-tolyl)vinyl)silane - prepared from (4-methyl)phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 142.8 mg - 95%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.59 – 7.53 (m, 4H), 7.41 – 7.31 (m, 7H), $\delta$7.24 – 7.22 (m, 1H), 7.08 – 7.03 (m, 2H), 6.29 – 6.23 (dd, 1H, $J =$ 2.1 Hz), 5.66 – 5.59 (d, 1H, $J =$ 2.2 Hz), 5.37 (s, 1H), 2.29 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 145.5, 139.9, 136.8, 135.8, 133.2, 131.3, 129.8, 129.1, 128.1, 126.6, 21.1

Corresponds to previously reported data [3]

2.15.(2o) Diphenyl(1-(m-tolyl)vinyl)silane - prepared from (3-methyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 281.3 mg - 94%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.65 – 7.60 (m, 4H), 7.48 – 7.38 (m, 6H), $\delta$7.23 – 7.17 (m, 3H), 7.10 – 7.06 (m, 1H), 6.33 – 6.31 (dd, 1H, $J =$ 2.5 Hz), 5.73 – 5.71 (d, 1H, $J =$ 2.5 Hz), 4.74 (s, 1H), 2.24 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 148.0, 143.4, 135.7, 134.6, 133.8, 132.9, 130.1, 129.8, 128.1, 128.0, 126.4, 125.5, 20.4

Corresponds to previously reported data [3]

2.16.(2p) Diphenyl(1-(o-tolyl)vinyl)silane - prepared from (2-methyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 298.5 mg - >99%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.63 – 7.57 (m, 4H), 7.48 – 7.37 (m, 6H), $\delta$7.19 – 7.06 (m, 3H), 6.98 – 6.95 (d, 1H), 6.01 – 5.98 (d, 1H, $J =$ 3.1 Hz), 5.95 – 5.93 (d, 1H, $J =$ 3.1 Hz), 5.26 (s, 1H), 2.24 (s, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 148.0, 143.4, 135.7, 134.5, 133.3, 132.9, 130.1, 129.8, 128.0, 128.0, 126.4, 125.4, 20.4

Corresponds to previously reported data [3]
2.17.(2r) 4-(1-(diphenylsilyl)vinyl)benzonitrile - prepared from 4-ethynylbenzonitrile (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure B at 40°C. Purified by extraction with n-hexane followed by filtration through silica plug. Mixture required further purification by column chromatography on silica gel (hexane:ethyl acetate = 2:1). Volatiles were removed under lower pressure affording pure product (yellow oil, 85.3 mg - 55%).

\[
\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.57 - 7.51 (m, 6H), 7.45 - 7.34 (m, 8H), 6.34 - 6.27 (dd, 1H, } J = 2.0, 0.6 \text{ Hz), 5.84 - 5.79 (d, 1H, } J = 2.1 \text{ Hz), 5.40 - 5.33 (s, 1H)}
\]

\[
\text{C NMR (75 MHz, CDCl}_3\text{): } \delta 147.9, 145.3, 135.7, 134.5, 132.2, 132.0, 130.2, 128.2, 127.4, 118.9, 110.6
\]

Corresponds to previously reported data [3]

2.18.(2s) Diphenyl(1-(thiophen-3-yl)vinyl)silane - prepared from 3-ethynlthiophene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (brown oil, 144.2 mg - 98%).

\[
\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.63 - 7.58 (m, 4H), 7.43 - 7.35 (m, 6H), 7.16 - 7.12 (m, 1H), 6.96 - 6.91 (m, 1H), 6.90 - 6.85 (m, 1H), 6.35 (s, 1H), 5.52 - 5.47 (d, 1H, } J = 1.6 \text{ Hz), 5.42 (s, 1H)}
\]

\[
\text{C NMR (75 MHz, CDCl}_3\text{): } \delta 146.4, 137.9, 135.8, 134.7, 134.3, 132.4, 130.0, 129.6, 128.1, 127.5, 126.0, 124.2
\]

Corresponds to previously reported data [3]

2.19.(2t) (E)-(1,2-diphenyvinyl)diphenylsilane - prepared from diphenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 176.8 mg - 98%).

\[
\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.60 - 7.54 (m, 4H), 7.46 - 7.36 (m, 6H), 7.42 - 7.33 (m, 6H), 7.24 - 7.15 (m, 3H), 7.13 - 7.08 (m, 3H), 7.04 - 6.98 (m, 5H), 5.28 (s, 1H)
\]

\[
\text{C NMR (75 MHz, CDCl}_3\text{): } \delta 142.9, 141.6, 140.2, 136.9, 135.9, 133.0, 129.8, 129.7, 128.6, 128.1, 128.0, 127.9, 127.5, 126.2
\]

Corresponds to previously reported data [3]

2.20.(2u) 3-(diphenylsilyl)but-3-en-1-yl benzoate - prepared from butyn-3-yl benzoate (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure A. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (colourless, 178.2 mg - 99%).

\[
\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 8.02 - 7.95 (m, 2H), 7.61 - 7.51 (m, 5H), 7.45 - 7.32 (m, 8H), 6.07 - 6.01 (d, 1H, } J = 1.4 \text{ Hz), 5.65 - 5.57 (d, 1H, } J = 2.3 \text{ Hz), 5.15 (s, 1H), 4.43 - 4.31 (t, 2H), 2.76 - 2.67 (t, 2H)}
\]

\[
\text{C NMR (75 MHz, CDCl}_3\text{): } \delta 166.4, 142.2, 135.6, 132.8, 132.6, 132.5, 130.3, 129.9, 129.6, 128.3, 128.1, 63.8, 35.8
\]

HRMS (ESI): calculated for [C_{23}H_{22}SiO_2Na]^+ requires 381.1281 m/z, found 381.1289 m/z
2.21. (but-3-y1-1-yloxy)dimethyl(phenyl)silane - But-3-yn-1-ol was silylated with dimethylphenylsilane according to reported procedure[6]. (but-3-yn-1-yloxy)dimethyl(phenyl)silane was purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under reduced pressure.

\[\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta 7.63 – 7.54 (m, 2H), 7.42 – 7.33 (m, 3H), 3.78 – 3.68 (t, 2H), 2.47 – 2.37 (td, 2H), 2.00 – 1.93 (t, 1H), 0.40 (s, 6H)\]

2.22.(3a) Phenyl(1-phenylvinyl)silane – prepared from phenylsilane (1.0 mmol) and phenylacetylene (1.0 mmol) according to general procedure C. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 206.3 mg – 98%).

\[\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta 7.58 – 7.51 (m, 2H), 7.37 – 7.27 (m, 6H), 7.25 – 7.17 (m, 2H), 6.23 – 6.18 (d, 1H, J = 2.4 Hz), 5.81 – 5.77 (d, 1H, J = 2.3 Hz), 4.80 (s, 2H)\]

\[\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta 144.2, 142.3, 135.6, 131.4, 131.2, 129.9, 128.6, 128.2, 127.3, 126.5\]

Corresponds to previously reported data [7]

2.23.(3g) Phenyl(1-(m-tolyl)vinyl)silane – prepared from phenylsilane (1.0 mmol) and 3-ethynyltoluene (1.0 mmol) according to general procedure C. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 210.3 mg – 94%).

\[\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta 7.65 – 7.58 (m, 2H), 7.46 – 7.34 (m, 3H), 7.25 – 7.16 (m, 3H), 7.12 – 7.04 (m, 1H), 6.27 – 6.23 (d, 1H, J = 2.5 Hz), 5.87 – 5.79 (d, 1H, J = 2.4 Hz), 4.86 (s, 2H), 2.40– 2.34 (s, 3H)\]

\[\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta 144.3, 142.3, 138.1, 135.6, 131.1, 129.9, 128.4, 128.1, 127.1, 123.7, 21.5\]

Corresponds to previously reported data [7]

2.24.(3h) Phenyl(1-(o-tolyl)vinyl)silane – prepared from phenylsilane (1.0 mmol) and 2-ethynyltoluene (1.0 mmol) according to general procedure C. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 223.9 mg – 99%).

\[\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta 7.62 – 7.53 (m, 2H), 7.44 – 7.32 (m, 3H), 7.19 – 7.08 (m, 3H), 7.02 – 6.89 (m, 1H), 5.95 – 5.91 (d, 1H, J = 2.0 Hz), 5.90 – 5.86 (d, 1H, J = 1.9 Hz), 4.71 (s, 2H), 2.25 (s, 3H)\]

\[\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta 146.5, 143.1, 135.6, 133.0, 130.1, 129.9, 128.0, 127.9, 126.6, 125.6, 20.3\]

Corresponds to previously reported data [7]
2.25.(4a) Dimethyl(phenyl)(1-phenylvinyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and phenylacetylene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 225.0 mg – 94%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.62 – 7.51 (m, 2H), 7.41 – 7.32 (m, 3H), 7.25 – 7.17 (m, 3H), 7.12 (m, 2H), 6.04 – 5.95 (d, 1H, } J = 2.8 \text{ Hz), 5.72 – 5.63 (d, 1H, } J = 2.9 \text{ Hz), 0.41 (s, 6H) } \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 153.3, 146.5, 140.6, 136.4, 131.5, 131.4, 130.4, 130.1, 129.2, 128.7, 0.0 \]

Corresponds to previously reported data [8]

2.26.(4b) (1-(4-(tert-butyl)phenyl)vinyl)dimethyl(phenyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and 1-(tert-butyl)-4-ethynylbenzene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 291.5 mg – 99%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.67 – 7.54 (m, 2H), 7.46 – 7.35 (m, 3H), 7.32 – 7.24 (m, 2H), 7.17 – 7.02 (m, 2H), 6.11 – 6.00 (d, 1H, } J = 2.8 \text{ Hz), 5.72 – 5.62 (d, 1H, } J = 2.9 \text{ Hz), 1.32 (s, 9H), 0.50 (s, 6H) } \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 152.3, 151.5, 143.0, 140.8, 136.2, 131.2, 130.8, 130.0, 128.6, 127.2, 36.6, 33.5, 0.0 \]

Corresponds to previously reported data [10]

2.27.(4c) (1-(4-bromophenyl)vinyl)dimethyl(phenyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and 1-bromo-4-ethynylbenzene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 251.7 mg – 79%).

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.59 – 7.49 (m, 2H), 7.41 – 7.29 (m, 5H), 7.01 – 6.96 (m, 2H), 6.01 – 5.92 (d, 1H, } J = 2.7, 0.6 \text{ Hz), 5.74 – 5.66 (d, 1H, } J = 2.8 \text{ Hz), 0.40 (s, 6H) } \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta 152.6, 145.6, 140.3, 136.5, 133.7, 132.0, 131.7, 131.0, 130.4, 122.9, 0.0 \]

Corresponds to previously reported data [8]
2.28. (4d) 1-(4-methoxyphenyl)vinyl)dimethyl(phenyl)silane – prepared from dimethyl(phenyl) silane (1.0 mmol) and 4-ethynylanisole (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 251.7 mg – 94%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.61 – 7.54 (m, 2H), 7.40 – 7.33 (m, 3H), 7.13 – 7.05 (m, 2H), 6.82 – 6.75 (m, 2H), 6.03 – 5.96 (d, 1H, $J = 2.8$ Hz), 5.65 – 5.59 (d, 1H, $J = 2.8$ Hz), 3.77 (s, 3H), 0.42 (s, 6H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 160.6, 152.1, 140.7, 138.6, 136.2, 131.2, 130.2, 130.1, 130.0, 115.7, 57.4, 0.0

Corresponds to previously reported data [8]

2.29. (4e) 4-(1-(dimethyl(phenyl)silyl)vinyl)aniline – prepared from dimethyl(phenyl)silane (1.0 mmol) and 4-ethynylniline (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 189.4 mg – 75%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.63 – 7.52 (m, 2H), 7.41 – 7.32 (m, 3H), 7.02 – 6.96 (m, 2H), 5.59 – 5.54 (m, 2H), 6.00 – 5.96 (d, 1H, $J = 2.8$ Hz), 5.58 – 5.55 (d, 1H, $J = 2.8$ Hz), 3.78 – 3.45 (b, 2H), 0.42 (s, 6H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 151.8, 147.1, 140.9, 136.3, 136.1, 131.0, 129.9, 129.9, 129.0, 117.0, 0.0

HRMS (ESI): calculated for [C$_{16}$H$_{20}$SiN]$^+$ requires 254.1360 m/z, found 254.1365 m/z

2.30. (4f) dimethyl(phenyl)(1-(p-tolyl)vinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 4-ethylnyltoluene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 243.4 mg – 96%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.63 – 7.53 (m, 2H), 7.43 – 7.32 (m, 3H), 7.10 – 6.99 (m, 4H), 6.05 – 5.95 (d, 1H, $J = 2.8$ Hz), 5.71 – 5.61 (d, 1H, $J = 2.9$ Hz), 2.31 (s, 3H), 0.44 (s, 6H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 152.8, 143.4, 140.7, 138.3, 136.3, 131.3, 131.1, 130.9, 130.0, 129.0, 23.3, 0.0

Corresponds to previously reported data [9]
2.31.(4g) dimethyl(phenyl)(1-(m-tolyl)vinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 3-ethylnyltoluene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 231.3 mg – 92%).

\[
\begin{align*}
\text{Si} & \quad \text{H} \quad \text{H} \\
& \quad \text{H} \quad \text{H} \\
\end{align*}
\]

\[^1\text{H} \text{ NMR (300 MHz, CDCl}_3\text{): } & \delta 7.61 - 7.53 \text{ (m, 2H), 7.24 - 7.17 \text{ (m, 3H),} \\
& 7.10 - 6.99 \text{ (m, 2H), 6.91 - 6.84 \text{ (m, 2H), 6.02 - 6.98 \text{ (d, 1H, } J = 3.0 \text{ Hz),} \\
& 6.67 - 5.63 \text{ (d, 1H, } J = 3.0 \text{ Hz), 2.07 \text{ (s, 3H), 0.39 \text{ (s, 6H)}}}
\]

\[^13\text{C} \text{ NMR (75 MHz, CDCl}_3\text{): } & \delta 153.3, 146.4, 140.6, 139.9, 136.4, 131.3, \\
& 130.2, 129.1, 129.9, 126.3, 23.8, 0.00
\]

HRMS (ESI): calculated for [C\textsubscript{17}H\textsubscript{20}SiNa\textsuperscript{+}]\textsuperscript{+} requires 275.1226 m/z, found 275.1226 m/z

2.32.(4h) dimethyl(phenyl)(1-(o-tolyl)vinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 2-ethylnyltoluene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (orange oil, 243.3 mg – 96%).

\[
\begin{align*}
\text{Si} & \quad \text{H} \quad \text{H} \\
& \quad \text{H} \quad \text{H} \\
\end{align*}
\]

\[^1\text{H} \text{ NMR (300 MHz, CDCl}_3\text{): } & \delta 7.52 - 7.44 \text{ (m, 2H), 7.24 - 7.18 \text{ (m, 3H),} \\
& 7.08 - 6.99 \text{ (m, 3H), 6.94 - 6.88 \text{ (m, 1H), 5.72 - 5.69 \text{ (d, 1H, } J = 3.4 \text{ Hz),} \\
& 5.67 - 5.63 \text{ (d, 1H, } J = 3.4 \text{ Hz), 2.06 \text{ (s, 3H), 0.32 \text{ (s, 6H)}}}
\]

\[^13\text{C} \text{ NMR (75 MHz, CDCl}_3\text{): } & \delta 152.3, 143.9, 137.7, 134.3, 134.1, 130.0, \\
& 129.6, 129.1, 127.7, 127.7, 125.9, 125.0, 20.2, -3.0
\]

Corresponds to previously reported data [11]

2.33.(4i) (1-cyclopropylvinyl)dimethyl(phenyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and cyclopropylacetylene (1.0 mmol) according to general procedure B. Purified by extraction with n-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 193.1 mg – 95%).

\[
\begin{align*}
\text{Si} & \quad \text{H} \quad \text{H} \\
& \quad \text{H} \quad \text{H} \\
\end{align*}
\]

\[^1\text{H} \text{ NMR (300 MHz, CDCl}_3\text{): } & \delta 7.61 - 7.52 \text{ (m, 2H), 7.28 - 7.20 \text{ (m, 3H), 5.54} \\
& - 5.45 \text{ (m, 1H), 5.35 - 5.26 \text{ (d, 1H, } J = 2.6 \text{ Hz),} 1.35 - 1.22 \text{ (quint, 1H), 0.46} \\
& - 0.41 \text{ (m, 4H), 0.38 \text{ (s, 6H)}}}
\]

\[^13\text{C} \text{ NMR (75 MHz, CDCl}_3\text{): } & \delta 151.8, 138.4, 134.0, 128.9, 127.7, 121.6, 15.4, \\
& 6.9, -2.9
\]

Corresponds to previously reported data [12]
3. Deuterium labelled experiment

3.1 Hydrosilylation of D\textsubscript{1}-phenylacetylene with diphenylsilane.

To a flame-dried Schlenk bomb flask charged with argon, precatalyst (1 mol \%), THF (1.0 mL), diphenylsilane (0.5 mmol), and D\textsubscript{1}-phenylacetylene (0.5 mmol) were placed. Mixture was then heated to 40°C with stirring. After 10 minutes LiHBEt\textsubscript{3} was added (0.3 mol \%), and reaction vessel was then closed. After 1 hour, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by \textsuperscript{1}H NMR.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \delta 7.52 – 7.46 (m, 4H), 7.36 – 7.24 (m, 8H), 7.21 -7.11 (m, 3H), [6.23 – 6.19 Not observed], 5.63 - 5.56 (s, 1H\textsubscript{1}), 5.37 – 5.28 (s, 1H)
2a (300 MHz, CDCl₃):

\[
\begin{align*}
\text{H} & \rightarrow \text{Si} \\
\text{Ph} & \rightarrow \text{Ph}
\end{align*}
\]

2a (75 MHz, CDCl₃):

\[
\begin{align*}
\text{H} & \rightarrow \text{Si} \\
\text{Ph} & \rightarrow \text{Ph}
\end{align*}
\]
2b (300 MHz, CDCl₃):

![NMR spectrum for 2b (300 MHz, CDCl₃)]

2b (75 MHz, CDCl₃):

![NMR spectrum for 2b (75 MHz, CDCl₃)]
2c (300 MHz, CDCl₃):

![NMR spectrum and structure](image1)

2c (75 MHz, CDCl₃):

![NMR spectrum and structure](image2)
2d (300 MHz, CDCl₃): [Chemical Structure Image]

2d (75 MHz, CDCl₃): [Chemical Structure Image]
2e (300 MHz, CDCl₃):
2f (300 MHz, CDCl₃):

---

2f (75 MHz, CDCl₃):

---
2g (300 MHz, CDCl₃):

2g (75 MHz, CDCl₃):
$2h$ (300 MHz, CDCl$_3$):

$2h$ (75 MHz, CDCl$_3$):
2i (300 MHz, CDCl₃):

![Chemical Structure](image1)

2i (75 MHz, CDCl₃):

![Chemical Structure](image2)
$2j$ (300 MHz, CDCl$_3$):

![NMR spectrum for $2j$ (300 MHz, CDCl$_3$)]

$2j$ (75 MHz, CDCl$_3$):

![NMR spectrum for $2j$ (75 MHz, CDCl$_3$)]
2k (300 MHz, CDCl₃):

2k (75 MHz, CDCl₃):
2I (300 MHz, CDCl₃):

2I (75 MHz, CDCl₃):
2m (300 MHz, CDCl₃):

![NMR spectrum of 2m]

2m substrate (300 MHz, CDCl₃):

![NMR spectrum of 2m substrate]
2n (300 MHz, CDCl₃):

![NMR Spectrum of 2n (300 MHz, CDCl₃)]

2n (75 MHz, CDCl₃):

![NMR Spectrum of 2n (75 MHz, CDCl₃)]
2p (300 MHz, CDCl₃):

![NMR Spectrum 300 MHz CDCl₃]

2p (75 MHz, CDCl₃):

![NMR Spectrum 75 MHz CDCl₃]
2s (300 MHz, CDCl₃):

![NMR spectrum of 2s (300 MHz, CDCl₃)]

2s (75 MHz, CDCl₃):

![NMR spectrum of 2s (75 MHz, CDCl₃)]
2t (300 MHz, CDCl₃):

2t (75 MHz, CDCl₃):
2u (300 MHz, CDCl₃):

2u (75 MHz, CDCl₃):
3a (300 MHz, CDCl₃):

3a (75 MHz, CDCl₃):
$3g$ (300 MHz, CDCl$_3$):

$3g$ (75 MHz, CDCl$_3$):
$3h$ (300 MHz, CDCl$_3$): 

![NMR spectrum of 3h (300 MHz, CDCl$_3$)](image1)

$3h$ (75 MHz, CDCl$_3$): 

![NMR spectrum of 3h (75 MHz, CDCl$_3$)](image2)
4a (300 MHz, CDCl₃):

![Chemical structure image]

4a (75 MHz, CDCl₃):

![Chemical structure image]
4b (300 MHz, CDCl₃):

4b (75 MHz, CDCl₃):
4c (300 MHz, CDCl₃):

![NMR spectrum of 4c (300 MHz, CDCl₃)]

4c (75 MHz, CDCl₃):

![NMR spectrum of 4c (75 MHz, CDCl₃)]
4d (300 MHz, CDCl₃):

4d (75 MHz, CDCl₃):
4e (300 MHz, CDCl₃):

4e (75 MHz, CDCl₃):
4f (300 MHz, CDCl₃):

![Chemical structure and NMR spectra for 4f (300 MHz, CDCl₃)]

4f (75 MHz, CDCl₃):

![Chemical structure and NMR spectra for 4f (75 MHz, CDCl₃)]
$4g$ (300 MHz, CDCl$_3$):

$4g$ (75 MHz, CDCl$_3$):
4g
$4h$ (300 MHz, CDCl$_3$):

$4h$ (75 MHz, CDCl$_3$):
4i (300 MHz, CDCl₃):

\[ \text{Diagram of 4i (300 MHz, CDCl₃)} \]

4i (75 MHz, CDCl₃):

\[ \text{Diagram of 4i (75 MHz, CDCl₃)} \]
Deuterium labelled experiment (300 MHz, CDCl₃):
References:

[1] Bocian, A.; Szymańska, M.; Bryczyńska, D.; Kubicki, M.; Wałęsa-Chorab, M.; Roviello, GN.; Fik-Jaskółka, MA.; Gorczyński A.; Patroniak, V., Molecules. 2019, 24(17), 3173.
[2] Bocian, A.; Skrodzki M.; Kubicki, M.; Gorczyński, A.; Pawluć, P.; Patroniak, V. Appl. Catal. A, 2020, 602, 117665.
[3] Guo, J.; Lu, Z., Angew. Chem. Int. Ed. 2016, 55(36), 10835-10838.
[4] Zuo, Z.; Yang, J.; Huang, Z., Angew. Chem. Int. Ed. 2016, 55(36), 10839-10843.
[5] Guo, J.; Shen, X.; Lu, Z., Angew. Chem. Int. Ed. 2017, 56(2), 615-618.
[6] Skrodzki, M.; Zaranek, M.; Witomska, S.; Pawluć, P. Catalysts, 2018, 8, 618.
[7] Zhang, S.; Ibrahim, J. J.; Yang, Y., Org. Lett. 2018, 20, 19, 6265–6269.
[8] Song, L.; Feng, Q.; Wang, Y.; Ding, S.; Wu, Y-D.; Zhang, X.; Chung L. W.; Sun, J., J. Am. Chem. Soc. 2019, 141, 43, 17441–17451
[9] Cassani, M. C.; Brucka M. A.; Femoni, C.; Mancinelli, M.; Mazzanti A.; Mazzoni, R.; Solinas, G., New J. Chem., 2014, 38, 1768-1779
[10] Gee, J. C.; Fuller, B. A.; Locket, H.-M.; Sedghi, G.; Robertson, C. M.; Luzyanin K. V., Chem. Commun., 2018, 54, 9450-9453.
[11] Rivero-Crespo, M. A.; Levya-Perez A.; Corma, A., Chem. Eur. J., 2017, 23(7), 1702-1708.
[12] Wang, P.; Yeo X.-L.; Loh P.-T., J. Am. Chem. Soc. 2011, 133, 5, 1254–1256.