Electronic Supplementary Information for

Ni-catalyzed undirected and regioselective acceptorless dehydrogenative silylation of primary benzylic C(sp^3)–H bonds

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Supplementary Experimental Methods

Instrumental and Reagents: GC analyses were performed on Shimadzu GC-2014 equipped with a flame ionization detector (FID) and an InertCap-5 using Shimadzu C-R8A Chromatopac Data Processor for area calculations. GC-MS spectra were recorded on Shimadzu GCMS-QP2020 equipped with an InertCap-5 capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on JEOL JNM-ECA-500. ^{1}H, ^{2}H, and ^{13}C NMR spectra were measured at 500.16, 76.78, and 125.76 MHz, respectively. ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS) signal (0 ppm). ^{13}C NMR chemical shifts were referenced to residual solvent peaks. Column chromatography on silica gel was performed by using Biotage Isolera. ICP-AES analyses were performed on Shimadzu ICPS-8100. STEM observations were performed on a JEOL JEM-ARM200F. XRD patterns were recorded on a Rigaku SmartLab diffractometer (Cu Kα, λ = 1.5405 Å, 45 kV, 20 mA). The XPS spectra were measured on an Ulvac-Phi PHI5000 VersaProbe at the Advanced Characterization Nanotechnology Platform of the University of Tokyo. The samples were embedded in In foil and brought in the introduction chamber without exposing them to air by using the transfer vessel. The binding energies were calibrated by using the C 1s signal at 284.8 eV. Ni K-edge X-ray absorption spectroscopy (XAS) was carried out at the BL14B2 beamline of SPring-8 (Proposal No. 2022A1803, 2021A1620, and 2019B1820). XAFS measurements were conducted in fluorescence mode using a Si (111) crystal monochromator. Each sample was formed into a pellet, doubly wrapped in an Al laminate pack, and heat-sealed in an Ar-filled glovebox. XANES and EXAFS data were analyzed using Athena and Artemis software (Demeter, ver. 0.9.025; Bruce Ravel). The k^3-weighed EXAFS spectra were Fourier-transformed into R-space at 3–12 Å^{-1}. Ni foil and Ni(OH)$_2$ were used as standard samples. IFFEFIT (Athena and Artemis) programs were used for data analysis, treatment, and modeling. FEFF6 was used to generate Feff.inp files for analysis by Artemis using the atomic coordinates of the relevant theoretical references calculated using X-ray crystallographic methods available in the literature: Ni and Ni(OH)$_2$. IR-ATR spectra were measured on Jasco FT/IR-4100. DRIFTS was performed using Jasco FT/IR-6700. BET surface areas were measured on micromeritics ASAP 2010 and calculated from the N$_2$ adsorption isotherm with the BET equation. CeO$_2$ (BET: 50 m^2 g^{-1} after calcination at 550 °C for 3 h, Cat. No. 544841-25G, Aldrich), Al$_2$O$_3$ (BET: 160 m^2 g^{-1} after calcination at 550 °C for 3 h, Cat. No. KHS-24, Sumitomo Chemical), TiO$_2$ (BET: 316 m^2 g^{-1}, Cat. No. ST-01, Ishihara Sangyo Kaisya), ZrO$_2$ (Cat. No. 37022-35, Nacalai Tesque), Co$_3$O$_4$ (Cat. No. 039-08792, FUJIFILM Wako Pure Chemical), and hydroxyapatite (HAP, BET surface area: 11 m^2 g^{-1}, Cat. No. 011-14882, FUJIFILM Wako Pure Chemical) were acquired from commercial sources. Solvents and substrates were obtained from Tokyo Chemical Industry, Aldrich, Kanto Chemical, or FUJIFILM Wako Pure Chemical (reagent grade), and purified prior to being used, if necessary.

Preparation of Ni(OH)$_x$/CeO$_2$: The aqueous solution of NiCl$_2$·6H$_2$O (118.8 mg, 8.3 mM) was mixed with CeO$_2$ (2.0 g). The mixture was vigorously stirred at room temperature for 15 min, then the pH of the mixture was adjusted to 10.0 by dropping the aqueous solution of NaOH (1.0 M). The resulting slurry was continuously stirred for 24 h. The precipitation was filtered off and washed by water (3 L) then dried in vacuo to obtain Ni(OH)$_x$/CeO$_2$ as pale yellow powder. The Ni(OH)$_x$ supported on other supports such as Ni(OH)$_x$/TiO$_2$, Ni(OH)$_x$/ZrO$_2$, Ni(OH)$_x$/Al$_2$O$_3$, Ni(OH)$_x$/Co$_3$O$_4$ and Ni(OH)$_x$/HAP was prepared in the same method using TiO$_2$, ZrO$_2$, Al$_2$O$_3$,

Co_3O_4, and HAP instead of CeO_2. In the same way, various metal hydroxide supported on CeO_2 such as $Mn(OH)_x/CeO_2$, $Fe(OH)_x/CeO_2$, $Co(OH)_x/CeO_2$, $Cu(OH)_x/CeO_2$ and $Zn(OH)_x/CeO_2$ were prepared using $MnCl_2\cdot 4H_2O$, $FeCl_3\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$ and $ZnCl_2$ as the metal source respectively.

Preparation of Ni/CeO$_2$-HBpin: By modifying the method reported in our previous report,[S1] Ni/CeO$_2$-HBpin was prepared as follows. $Ni(OH)_x/CeO_2$ was dried in vacuo for 15 min at 150 °C and moved into an Ar-filled glovebox. The $Ni(OH)_x/CeO_2$ (1.0 g) was mixed with pinacolborane (HBpin) (8.0 mmol) and cyclopentyl methyl ether (CPME) (10 mL) in a Pyrex glass reactor (volume: ~100 mL), and a Teflon-coated magnetic stir bar was placed in the reactor. The mixture was vigorously stirred at 100 °C for 30 min under an Ar atmosphere, then moved into the glovebox after cooled down to room temperature. The solid was filtered off and washed by diethyl ether (30 mL), then dried in vacuo for 30 min. Ni/CeO$_2$-HBpin (Ni content: 1.4 wt%) was obtained as dark gray or black powder. The $Ni(OH)_x$ supported on other supports and other metal hydroxide supported on CeO_2 reduced by HBpin was treated in the same method.

Preparation of Ni/CeO$_2$-NaNaph: According to our previous report,[S2] Ni/CeO$_2$-NaNaph was prepared as follows. In an Ar-filled glovebox, $Ni(OH)_x/CeO_2$ (500 mg) was mixed with the THF solution (3.0 mL, 0.17 M) of sodium naphthalenide and vigorously stirred at room temperature for 12 h. Methanol (2 mL) was dropped into the reaction system to quench the reduction, and then the solid was filtered off and washed by methanol (30 mL) and diethyl ether (30 mL), then dried in vacuo for 30 min. Ni/CeO$_2$-NaNaph was obtained as black powder.

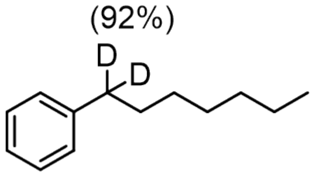
Preparation of Ni/CeO$_2$-NaBH$_4$: In an Ar-filled glovebox, $Ni(OH)_x/CeO_2$ (500 mg) was mixed with the isopropanol solution (10.0 mL, 0.15 M) of sodium borohydride and vigorously stirred at 80 °C for 90 min. The solid was filtered off and washed by ethanol (30 mL), then dried in vacuo for 30 min. Ni/CeO$_2$-NaNaph was obtained as black powder.

Preparation of Ni/CeO$_2$-HSi(OEt)$_3$: In an Ar-filled glovebox, $Ni(OH)_x/CeO_2$ (1.0 g) was mixed with cyclopentyl methyl ether (CPME) solution of triethoxysilane ($HSi(OEt)_3$) (5.0 mL, 0.4 M) and vigorously stirred at 100 °C for 30 min. The solid was filtered off and washed by diethyl ether (30 mL), then dried in vacuo for 30 min. Ni/CeO$_2$-HSi(OEt)$_3$ was obtained as gray powder.

Preparation of Ni/CeO$_2$-H$_2$: According to our previous report,[S1] Ni/CeO$_2$-H$_2$ was prepared as follows. $Ni(OH)_x/CeO_2$ (575 mg) was dried in vacuo at 400 °C for 30 min in a Schlenk flask (volume: ~30 mL). The dried $Ni(OH)_x/CeO_2$ was heated at 400 °C for 1 h with an H_2 balloon, and it was dried in vacuo for 30 min while the reactor was cooled down to 150 °C. Ni/CeO$_2$-H$_2$ was obtained as black powder and stored in an Ar-filled glovebox.

A Typical Procedure for the Dehydrogenative Benzylic Silylation of Alkylarenes: In an Ar-filled glovebox, Ni/CeO$_2$-HBpin (Ni: 1.8 mol%, 32 mg), alkylarene (2 mmol), *n*-hexadecane (0.1 mmol, internal standard), triethoxysilane (0.4 mmol), methylcyclohexane (1 mL) were mixed in a in a Pyrex glass reactor (volume: ~20 mL), and a Teflon-coated magnetic stir bar was placed in the reactor. The mixture was vigorously stirred at 120 °C for 24 h. Product yields were determined by GC analysis with *n*-hexadecane as the internal standard based on the initial amount of triethoxysilane. *n*-Hexadecane was not added for the product isolation. The catalyst was removed by filtration after the reaction. The filtrate was moved into an eggplant flask (volume: ~10 mL) and washed by dichloromethane. The filtrate was concentrated by rotary evaporation, then purified by silica-gel column chromatography. The solvent of the pure products was finally removed by rotary evaporation at 50 °C, 6 mbar for 30 min. The isolated products were identified by GC-MS and NMR (^{1}H and ^{13}C).

Synthesis of Heptylbenzene-1,1-*d*$_2$: By referring to previous reports,[S1,S3] heptylbenzene-1,1-*d*$_2$ was synthesized as follows. Pd/C (N.E. CHEMCAT K-type, 5 wt%, 350 mg) was placed in a Schlenk flask (volume: ~ 50 mL) with a Teflon-coated magnetic stir bar and dried in vacuo. Then, the atmosphere was filled in an H_2 gas with a balloon. Heptylbenzene (10 mmol) and D_2O (10 mL) were then added by syringe. The mixture was stirred at room temperature for 4.5 days. After the reaction, the catalyst was removed by filtration. The filtrate was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, then concentrated with the rotary evaporator at 45 °C, 6 mbar for 30 min to give the product (deuteration ratio: 92%, determined by ^{1}H NMR).



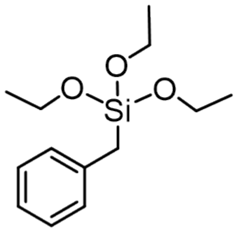
heptylbenzene-1,1-*d*$_2$ (CAS number: 2596115-67-0): GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 8.3 min. Rotary evaporator (45 °C, 6 mbar, 30 min) yielded 1.19 g (67% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 179 (5), 178 (36) [M^+], 177 (6), 135 (8), 107 (8), 106 (5), 95 (8), 94 (100), 93 (99), 92 (29), 91 (9), 78 (8), 67 (5), 66 (7). ^{1}H NMR (500 MHz, CD_3OD): δ 7.19–7.22 (m, 2H), 7.09–7.13 (m, 3H), 2.52–2.56 (m, 0.16H), 1.55–1.58 (m, 2H), 1.27–1.31 (m, 8H), 0.86–0.89 (m, 3H). The NMR spectral data accord with the previous report.[S1]

A Procedure for the Dehydrogenative Benzylic Silylation of 1a in a Gram-Scale: In an Ar-filled glovebox, Ni/CeO_2-HBpin (Ni: 1.8 mol%, 463.8 mg), toluene (**1a**) (29 mmol), *n*-hexadecane (1.45 mmol, internal standard), triethoxysilane (5.8 mmol), methylcyclohexane (7 mL) were added into a 40 mL pressure tube possessing a valve, and a Teflon-coated magnetic stir bar was placed in the reactor. The mixture was vigorously stirred at 120 °C for 24 h with the cooling to room temperature and degassing by immediate open/close a valve per 1 h till 3 h after the reaction started. The product yields were determined by GC analysis with *n*-hexadecane as the internal standard based on the initial amount of triethoxysilane.

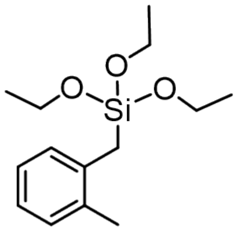
Leaching Test: A magnetic stir bar, *n*-hexadecane (0.1 mmol), $HSi(OEt)_3$ (0.4 mmol), toluene (2 mmol), methylcyclohexane (1 mL) and Ni/CeO_2-HBpin (32 mg, 1.8 mol%) were added to a Pyrex glass reactor (volume: ~ 20 mL), and the reaction was carried out at 120 °C in an Ar-filled glovebox. The catalyst was removed by hot filtration after the reaction started for 7.5 min, when the yield of **2a** reached 55%. The solution was moved to another reactor which had been heated to 120 °C with a magnetic stir bar, and then the reaction solution was stirred at 120 °C continuously. As a result, the reaction immediately stopped after the hot filtration (Fig. S11). To determine the leaching amount of Ni species into the reaction solution, the solution after 1 h reaction was filtered by a disposable syringe and concentrated by a rotary evaporator. Next, aqua regia (1 mL) was added into the concentrated mixture, and the amount of Ni species leached into the reaction solution was measured by ICP-AES. Ni species in the solution after the reaction were hardly observed by ICP-AES (0.7% of the Ni species used for the reaction). Therefore, this Ni/CeO_2-HBpin-catalyzed reaction was confirmed to be truly heterogeneous.

Reuse Test: After the dehydrogenative benzylic silylation of **1a** for 1 h under the optimized conditions, the Ni/CeO_2-HBpin catalyst was filtered off in an Ar-filled glovebox, washed by methanol (30 mL), and dried in vacuo for 30 min. Then, the retrieved catalyst was applied to the dehydrogenative benzylic silylation of **2a** again for 1 h.

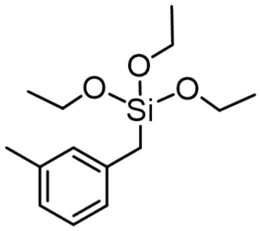
Spectral Data of Products



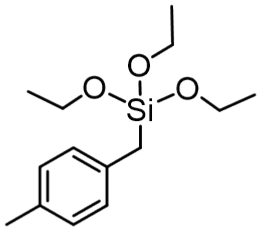
Benzyltriethoxysilane (**2a**) (CAS number: 2549-99-7): 93% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL·min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C·min^{-1} (1 min), 10 °C·min^{-1} (20 min), 0 °C·min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 9.2 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by calibration curve using an isolated substance). Rotary evaporator (60 °C, 6 mBar, 30 min) yielded 79.5 mg (79% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 254 (16) [M^{+}], 165 (9), 164 (12), 163 (100), 135 (14), 121 (6), 120 (6), 119 (55), 107 (15), 91 (33), 79 (20), 65 (5), 63 (7), 45 (7). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.16–7.23 (m, 4H), 7.07–7.10 (m, 1H), 3.75 (q, J = 7.0 Hz, 6H), 2.20 (s, 2H), 1.16 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 137.68, 128.99, 128.31, 124.69, 58.81, 20.50, 18.30. The NMR spectral data accord with the previous report.[S4]



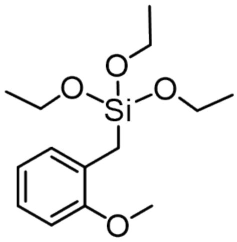
Triethoxy(2-methylbenzyl)silane (**2b**) (CAS number: 1428345-75-8): 74% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL·min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C·min^{-1} (1 min), 10 °C·min^{-1} (20 min), 0 °C·min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 10.2 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.810 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.33) yielded 49.6 mg (45% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 163 (100), 268 (24) [M^{+}], 164 (12), 135 (13), 119 (47), 107 (11), 105 (11), 91 (7), 79 (16). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.00–7.15 (m, 4H), 3.73 (q, J = 7.5 Hz, 6H), 2.32 (s, 3H), 2.18 (s, 2H), 1.16 (t, J = 7.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 136.28, 135.81, 130.05, 129.42, 125.77, 124,85, 58.75, 20.32, 18.28, 18.05. The NMR spectral data accord with the previous report.[S4]



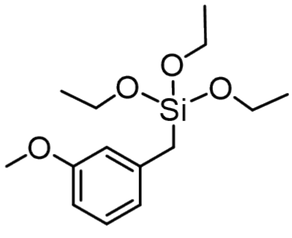
Triethoxy(3-methylbenzyl)silane (**2c**) (CAS number: 1443303-79-4): 85% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 10.0 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.810 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 9/1, Rf = 0.44) yielded 54.9 mg (50% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 268 (24) [M^+], 164 (12), 163 (100), 135 (15), 120 (5), 119 (50), 107 (12), 105 (14), 91 (9), 79 (17). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.10 (t, J = 7.5 Hz, 1H), 6.96–7.00 (m, 2H), 6.90 (d, J = 7.5 Hz, 1H), 3.75 (q, J = 7.0 Hz, 6H), 2.29 (s, 3H), 2.17 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 137.70, 137.46, 129.84, 128.17, 125.99, 125.41, 58.77, 21.46, 20.29, 18.28.



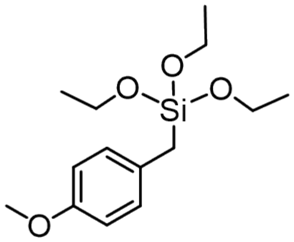
Triethoxy(4-methylbenzyl)silane (**2d**) (CAS number: 1443341-91-0): 77% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 10.2 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.810 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.25) yielded 65.5 mg (61% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 268 (21) [M^+], 164 (12), 163 (100), 135 (12), 119 (47), 107 (11), 105 (12), 91 (8), 79 (20), 77 (5), 63 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.00–7.08 (m, 4H), 3.75 (q, J = 7.0 Hz, 6H), 2.28 (s, 3H), 2.16 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 134.29, 133.94, 128.99, 128.83, 58.74, 21.02, 19.82, 18.29.



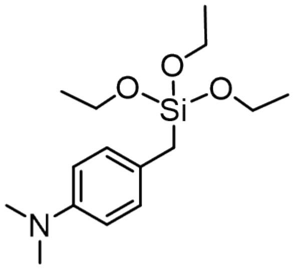
Triethoxy(2-methoxybenzyl)silane (**2e**) (CAS number: 1443323-43-0): 63% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 11.3 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.20) yielded 22.9 mg (56% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 286 (6), 285 (21), 284 (100) [M^+], 270 (9), 269 (48), 241 (5), 240 (6), 239 (22), 225 (21), 223 (15), 197 (8), 196 (6), 195 (28), 183 (13), 182 (6), 181 (22), 179 (11), 169 (6), 168 (8), 167 (22), 165 (7), 163 (10), 153 (7), 151 (16), 150 (28), 149 (75), 148 (21), 147 (95), 137 (6), 136 (7), 135 (50), 134 (7), 133 (18), 131 (8), 123 (5), 122 (27), 121 (15), 120 (8), 119 (58), 118 (64), 117 (17), 107 (25), 106 (7), 105 (50), 104 (6), 103 (27), 99 (11), 93 (14), 92 (13), 91 (53), 90 (9), 89 (9), 84 (12), 79 (29), 78 (13), 77 (14), 73 (6), 63 (13), 62 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.16–7.18 (m, 1H), 7.07–7.10 (m, 1H), 6.79–6.85 (m, 2H), 3.81 (s, 3H), 3.75 (q, J = 7.0 Hz, 6H), 2.23 (s, 2H), 1.15 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 156.90, 130.36, 126.36, 125.87, 120.44, 110.15, 58.61, 55.32, 18.28, 13.26.



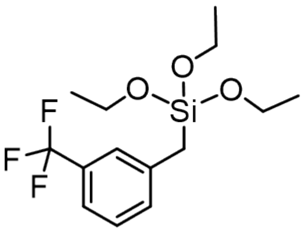
Triethoxy(3-methoxybenzyl)silane (**2f**) (CAS number: 1443302-78-0): 62% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 11.7 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.30) yielded 11.2 mg (37% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 285 (9), 284 (43) [M^+], 165 (5), 164 (12), 163 (100), 135 (14), 121 (11), 120 (6), 119 (57), 107 (14), 91 (19), 79 (18), 63 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.13 (t, J = 7.8 Hz, 1H), 6.75–6.77 (m, 2H), 6.64–6.67 (m, 1H), 3.78 (s, 3H), 3.76 (q, J = 7.0 Hz, 6H), 2.19 (s, 2H), 1.18 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 159.65, 139.28, 129.20, 121.56, 114.56, 110.39, 58.83, 55.21, 20.66, 18.34.



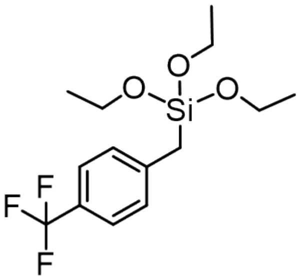
Triethoxy(4-methoxybenzyl)silane (**2g**) (CAS number: 1443324-33-1): 77% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 12.0 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.25) yielded 58.4 mg (52% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 285 (6), 284 (30) [M^+], 271 (6), 270 (19), 269 (100), 195 (6), 181 (5), 164 (8), 163 (66), 135 (15), 121 (45), 120 (6), 119 (64), 107 (18), 91 (22), 79 (26), 77 (9), 63 (8), 45 (6), 78 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.08–7.11 (m, 2H), 6.76–6.79 (m, 2H), 3.75 (q, J = 7.0 Hz, 6H), 3.76 (s, 3H), 2.14 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 157.08, 129.79, 129.39, 113.80, 58.74, 55.31, 19.10, 18.30. The NMR spectral data accord with the previous report.[S5]



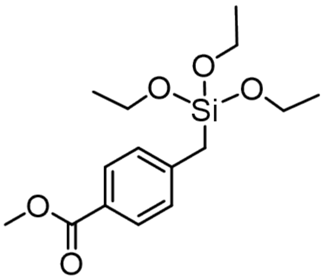
***N*,*N*-dimethyl-4-((triethoxysilyl)methyl)aniline** (**2h**): 49% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 13.6 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.856 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 13/1, Rf = 0.15) yielded 41.9 mg (35% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 298 (14), 297 (66) [M^+], 282 (22), 251 (6), 163 (22), 135 (15), 134 (100), 133 (9), 119 (26), 118 (13), 107 (6), 98 (7), 91 (11), 79 (12). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.04–7.06 (m, 2H), 6.66–6.68 (m, 2H), 3.76 (q, J = 7.0 Hz, 6H), 2.88 (s, 6H), 2.11 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 148.45, 129.55, 125.54, 113.46, 58.71, 41.19, 18.68, 18.34.



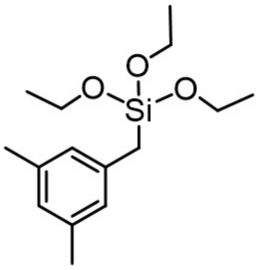
Triethoxy(3-(trifluoromethyl)benzyl)silane (**2i**): 46% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 8.9 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.30) yielded 41.9 mg (35% yield) of a colorless oil. MS (EI, 70 eV): *m/z* (%): 322 (1) [M^+], 164 (6), 163 (48), 141 (12), 140 (100), 135 (9), 120 (5), 119 (42), 107 (11), 91 (9), 79 (16), 63 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.45 (s, 1H), 7.31–7.37 (m, 3H), 3.76 (q, J = 7.0 Hz, 6H), 2.25 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 139.02, 132.29, 130.56 (q, J = 32.4 Hz), 128.61, 125.69 (q, J = 3.6 Hz), 124.48 (q, J = 272.3 Hz), 121.53 (q, J = 3.6 Hz), 58.93, 20.76, 18.26.



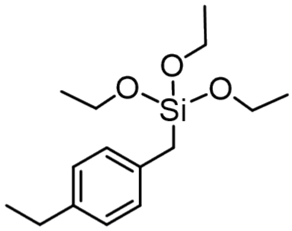
Triethoxy(4-(trifluoromethyl)benzyl)silane (**2j**): 41% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 9.1 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.3) yielded 7.4 mg (11% yield) of a colorless oil. MS (EI, 70 eV): m/z (%): 322 (1), 277 (5), 233 (6), 164 (7), 163 (56), 159 (9), 141 (12), 140 (100), 135 (9), 120 (5), 119 (45), 109 (6), 107 (12), 91 (9), 79 (18), 63 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.46–7.48 (m, 2H), 7.26–7.28 (m, 2H), 3.76 (q, J = 7.0 Hz, 6H), 2.25 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 142.49, 129.13, 127.06 (q, J = 32.4 Hz), 125.19 (q, J = 3.6 Hz), 124.68 (q, J = 272.3 Hz), 58.94, 21.05, 18.31.



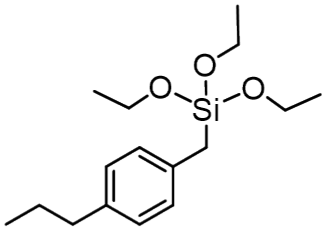
methyl 4-((triethoxysilyl)methyl)benzoate (**2k**): 60% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 14.1 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.747 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.14) yielded 53.1 mg (43% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 312 (13) [M^+], 163 (28), 135 (8), 119 (42), 118 (100), 107 (9), 91 (10), 90 (19), 79 (15), 63 (5). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.89–7.92 (m, 2H), 7.22–7.25 (m, 2H), 3.89 (s, 3H), 3.75 (q, J = 7.0 Hz, 6H), 2.26 (s, 2H), 1.16 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 167.42, 144.05, 129.66, 128.89, 126.66, 58.89, 51.99, 21.39, 18.27.



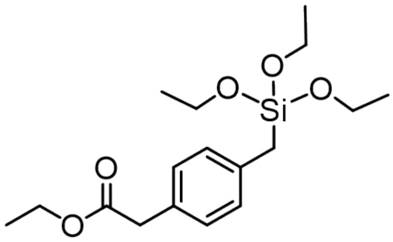
(3,5-dimethylbenzyl)triethoxysilane (**2l**) (CAS number: 1443323-10-1): 80% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 10.8 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.872 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.28) yielded 17.0 mg (45% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 282 (19) [M^+], 165 (5), 164 (12), 163 (100), 135 (11), 120 (7), 119 (53), 107 (10), 91 (13), 79 (17), 63 (6), 45 (5). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 6.79 (s, 2H), 6.73 (s, 1H), 3.76 (q, J = 7.0 Hz, 6H), 2.25 (s, 6H), 2.13 (s, 2H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 137.61, 137.29, 126.89, 126.35, 58.78, 21.38, 20.09, 18.28.



Triethoxy(4-ethylbenzyl)silane (**2m**) (CAS number: 1443323-41-8): 55% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 11.2 min; relative sensitivity for quantification (vs biphenyl, internal standard), 0.872 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.36) yielded 21.3 mg (19% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 283 (10), 282 (43) [M^+], 253 (9), 238 (17), 237 (10), 236 (25), 223 (6), 210 (10), 209 (53), 207 (9), 192 (7), 191 (21), 190 (11), 165 (7), 164 (14), 163 (100), 147 (9), 146 (5), 136 (6), 137 (6), 135 (58), 120 (6), 119 (61), 118 (32), 117 (18), 115 (6), 107 (21), 105 (14), 103 (7), 91 (31), 90 (5), 79 (31), 77 (8), 63 (16), 45 (9). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.08–7.10 (m, 2H), 7.04–7.06 (m, 2H), 3.76 (q, J = 6.8 Hz, 6H), 2.59 (q, J = 7.5 Hz, 2H), 2.17 (s, 2H), 1.20 (t, J = 7.8 Hz, 3H), 1.17 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 140.52, 134.55, 128.92, 127.82, 58.78, 28.51, 19.83, 18.32, 15.85.



Triethoxy(4-propylbenzyl)silane (**2n**) : 70% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 12.2 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.935 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 19/1, Rf = 0.35) yielded 66.3 mg (sum of 4 runs, 56% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 296 (15) [M^+], 164 (12), 163 (100), 135 (9), 133 (6), 119 (39), 107 (9), 104 (6), 91 (13), 79 (15). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.07–7.09 (m, 2H), 7.02–7.03 (m, 2H), 3.75 (q, J = 7.0 Hz, 6H), 2.52 (t, J = 7.8 Hz, 2H), 2.17 (s, 2H), 1.60 (sext, J = 7.4 Hz, 2H), 1.16 (t, J = 7.3 Hz, 9H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 138.89, 134.56, 128.81, 128.43, 58.75, 37.70, 24.75, 19.84, 18.29, 13.88.



Ethyl 2-(4-((triethoxysilyl)methyl)phenyl)acetate (**2o**): 30% GC yield. GC conditions and analysis: InertCap-5 capillary column, 0.25 mm × 30 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.6 mL· min^{-1}; initial column temp., 80 °C; final column temp., 280 °C; progress rate, 0 °C· min^{-1} (1 min), 10 °C· min^{-1} (20 min), 0 °C· min^{-1} (9 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 15.0 min; relative sensitivity for quantification (vs *n*-hexadecane, internal standard), 0.872 (calculated by the relative sensitivity of **2a** and the effective carbon number concept). Silica gel column chromatography (eluent, hexane/ethyl acetate = 24/1, Rf = 0.08) yielded 30.8 mg (sum of 2 runs, 23% yield) of a colorless oil. MS (EI, 70 eV): *m*/*z* (%): 341 (7), 340 (31) [M^+], 294 (6), 268 (7), 267 (27), 266 (67), 265 (25),209 (12), 165 (6), 164 (12), 163 (100), 135 (21), 133 (6), 132 (25), 120 (6), 119 (66), 107 (20), 104 (72), 103 (9), 105 (15), 91 (19), 79 (35), 78 (7), 77 (6), 63 (10), 45 (6). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.11–7.15 (m, 4H), 4.13 (q, J = 7.3 Hz, 2H), 3.75 (q, J = 6.8 Hz, 6H), 3.55 (s, 2H), 2.18 (s, 2H), 1.23 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 171.99, 136.41, 130.43, 129.16, 129.13, 60.82, 58.79, 41.16, 20.08, 18.29, 14.27.

Supplementary Figures

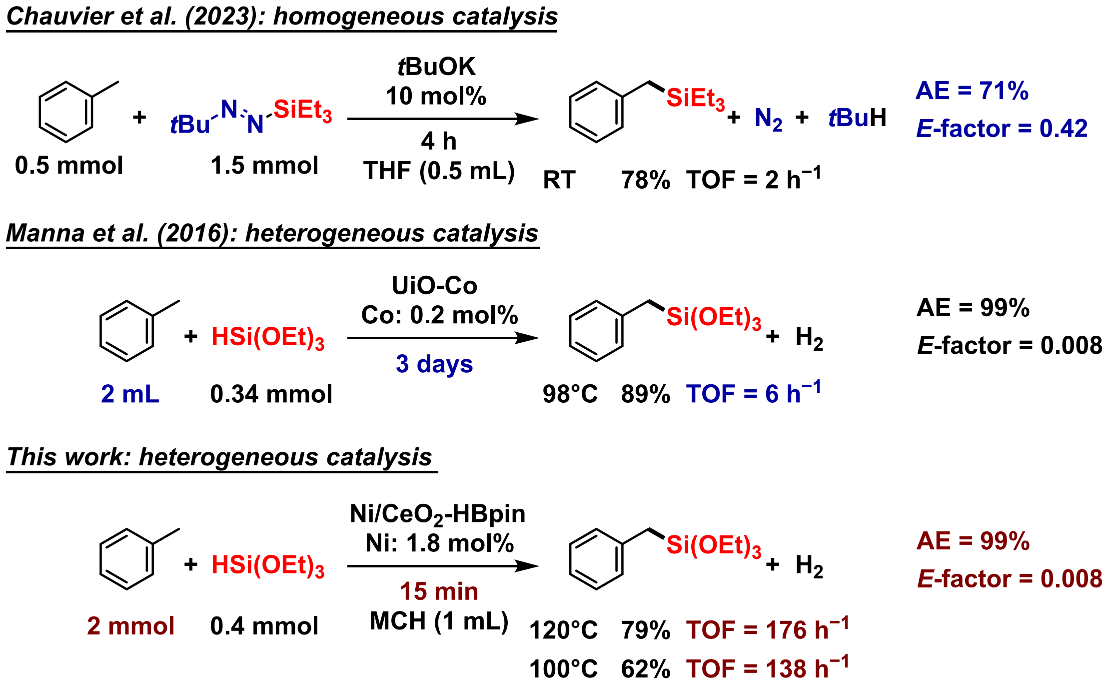


Fig. S1 Comparison of the present Ni-catalyzed undirected dehydrogenative benzylic silylation system in terms of green chemistry indicators such as atom economy (AE), *E*-factor, and turnover frequency (TOF) with the previously reported efficient systems showing comparatively broad substrate scopes[S5,S6] by utilizing the cases of dehydrogenative benzylic silylation of toluene. The catalytic system using a *tert*-butyl-substituted silyldiazene[S5] shows worse AE and *E*-factor than those of the present catalytic system due to the silylating reagent. The UiO-Co-catalyzed system using hydrosilane as the same silylating reagent[S6] showed much lower TOF than that of the present catalytic system even when comparing them at almost the same temperature. Also, much longer reaction time and solvent amount of alkylarenes were required in the UiO-Co-catalyzed system. Overall, all of the indicators were tremendously improved in this study.

AE: molecular weight (MW) of desired product divided by total MW of reactants. *E*-factor: weight of waste divided by weight of desired product (in this case, MW of byproducts were divided by MW of desired product). TOF was calculated using demonstrated yields, amounts of metal catalysts used for the reactions, and reaction times. THF = tetrahydrofuran. MCH = methylcyclohexane.

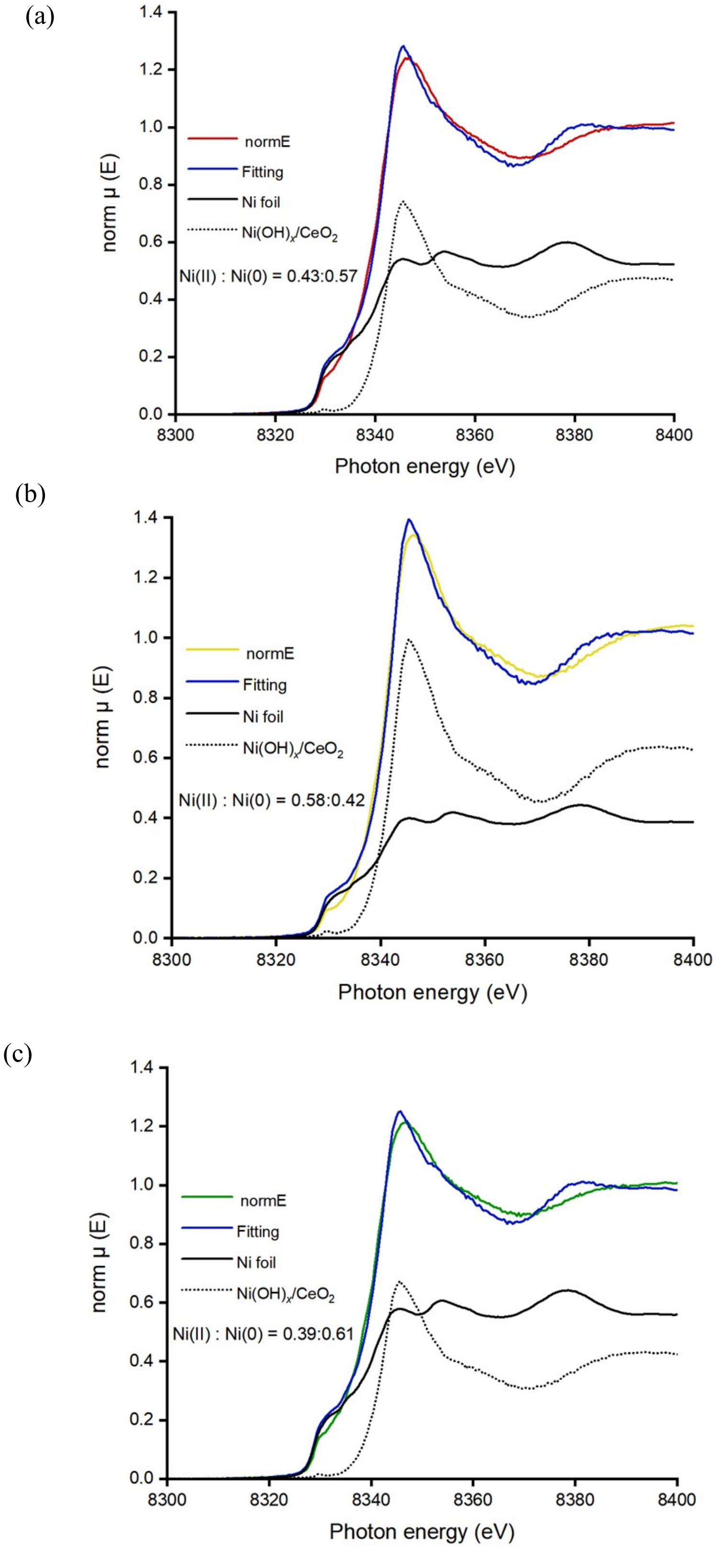
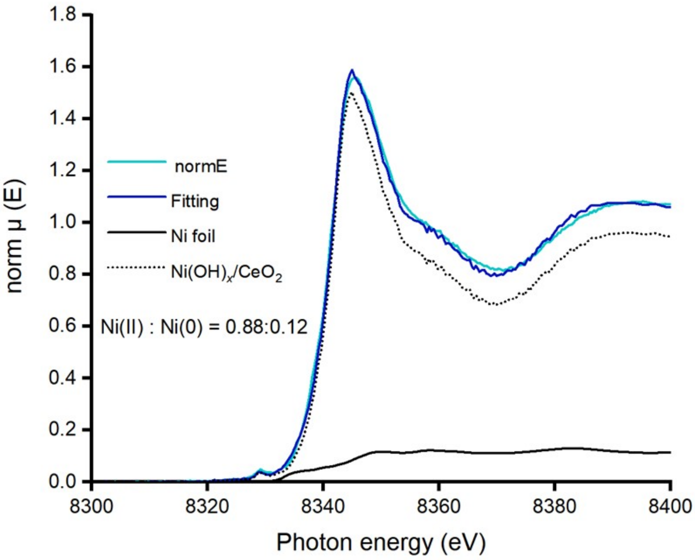


Fig. S2 Linear combination fittings of Ni K-edge XANES spectra of (a) Ni/CeO$_2$-HBpin, (b) Ni/CeO$_2$-HBpin-used, (c) Ni/CeO$_2$-4HBpin.

(d)



(e)

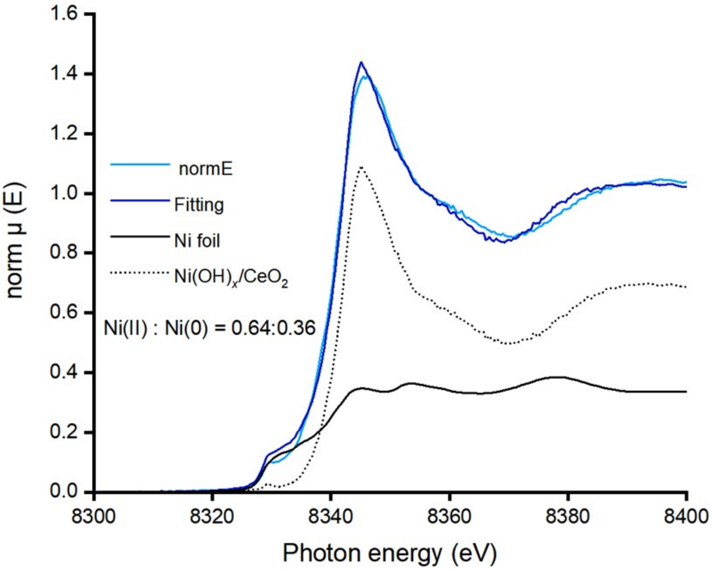


Fig. S2 (continued) Linear combination fittings of Ni K-edge XANES spectra of (d) Ni/CeO$_2$-HSi(OEt)$_3$ and (e) Ni/CeO$_2$-NaBH$_4$.

(i)

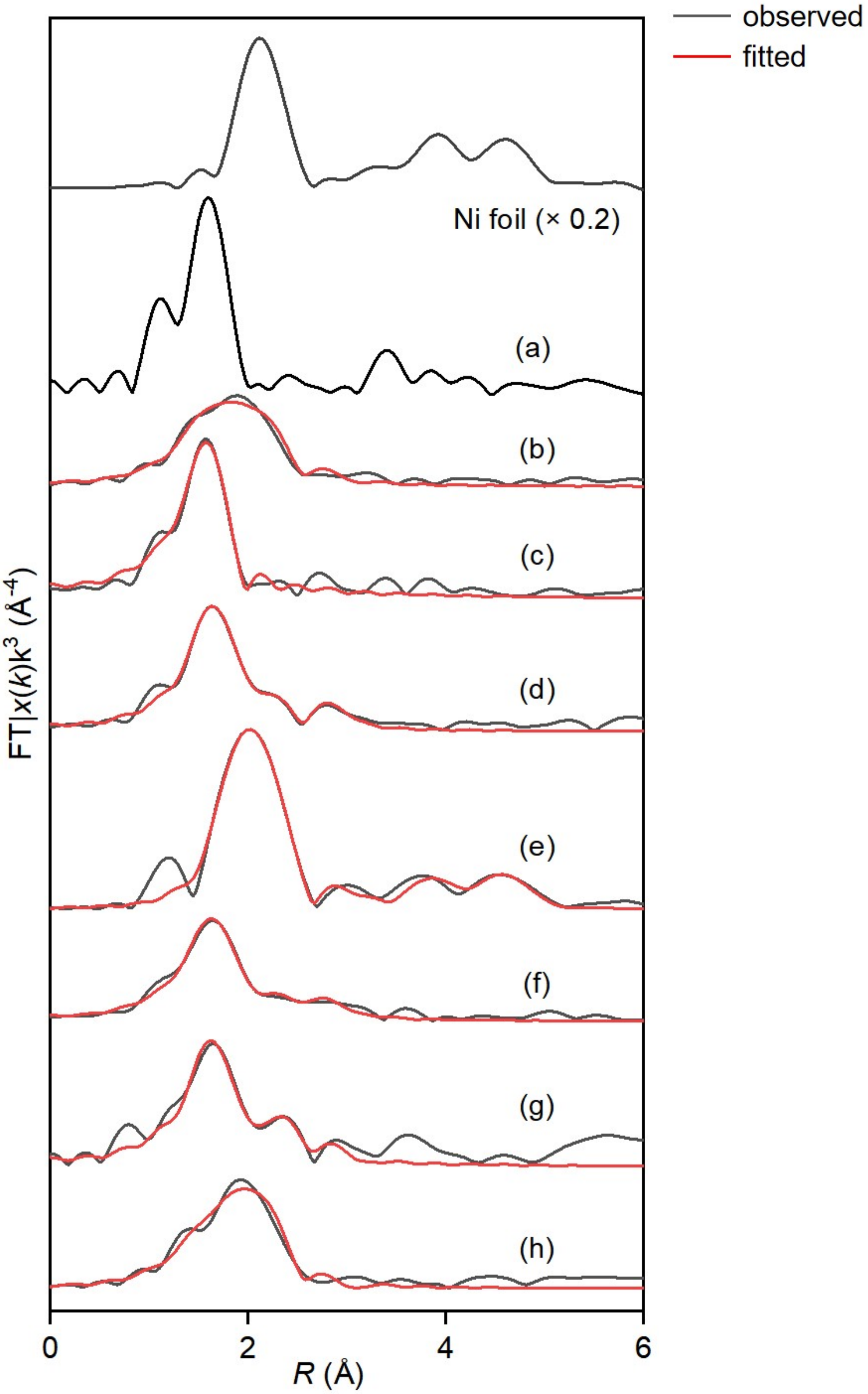


Fig. S3 (i) k^3-weighted Fourier-transformed Ni K-edge EXAFS spectra of Ni-foil, (a) $Ni(OH)_x/CeO_2$, (b) Ni/CeO_2-HBpin, (c) Ni/CeO_2-$HSi(OEt)_3$, (d) Ni/CeO_2-$NaBH_4$, (e) Ni/CeO_2-NaNaph, (f) Ni/CeO_2-HBpin-used, (g) Ni/CeO_2-0.5HBpin, and (h) Ni/CeO_2-4HBpin. Experimental data and fitted data are shown. FFT parameters, *k*-range: 3–12, window: Hanning. All *R*-space spectra are shown without phase correction.

(ii)

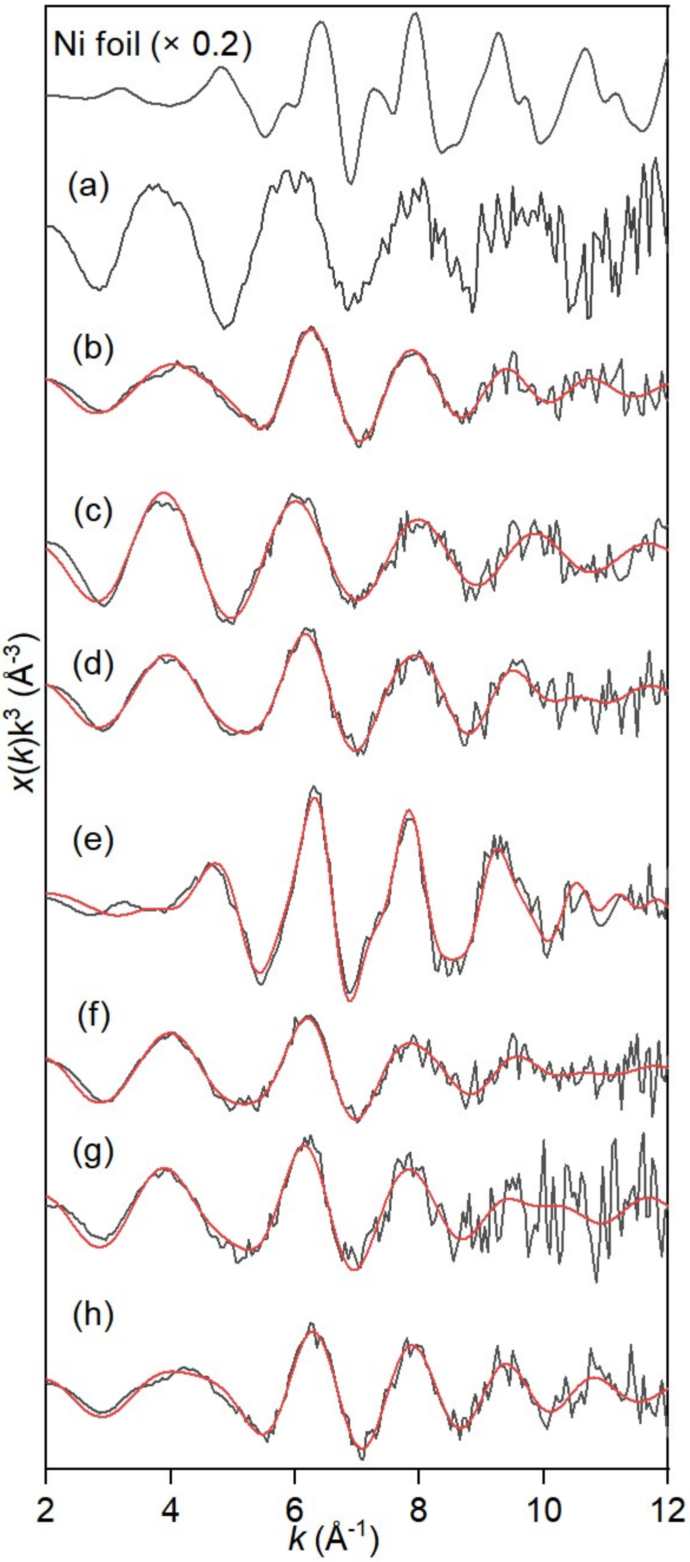


Fig. S3 (continued) (ii) Raw k^3-weighted Ni K-edge EXAFS spectra of Ni-foil, (a) Ni(OH)$_x$/CeO$_2$, (b) Ni/CeO$_2$-HBpin, (c) Ni/CeO$_2$-HSi(OEt)$_3$, (d) Ni/CeO$_2$-NaBH$_4$, (e) Ni/CeO$_2$-NaNaph, (f) Ni/CeO$_2$-HBpin-used, (g) Ni/CeO$_2$-0.5HBpin, and (h) Ni/CeO$_2$-4HBpin. Experimental data and fitted data are shown. FFT parameters, *k*-range: 3–12, window: Hanning. All *R*-space spectra are shown without phase correction.

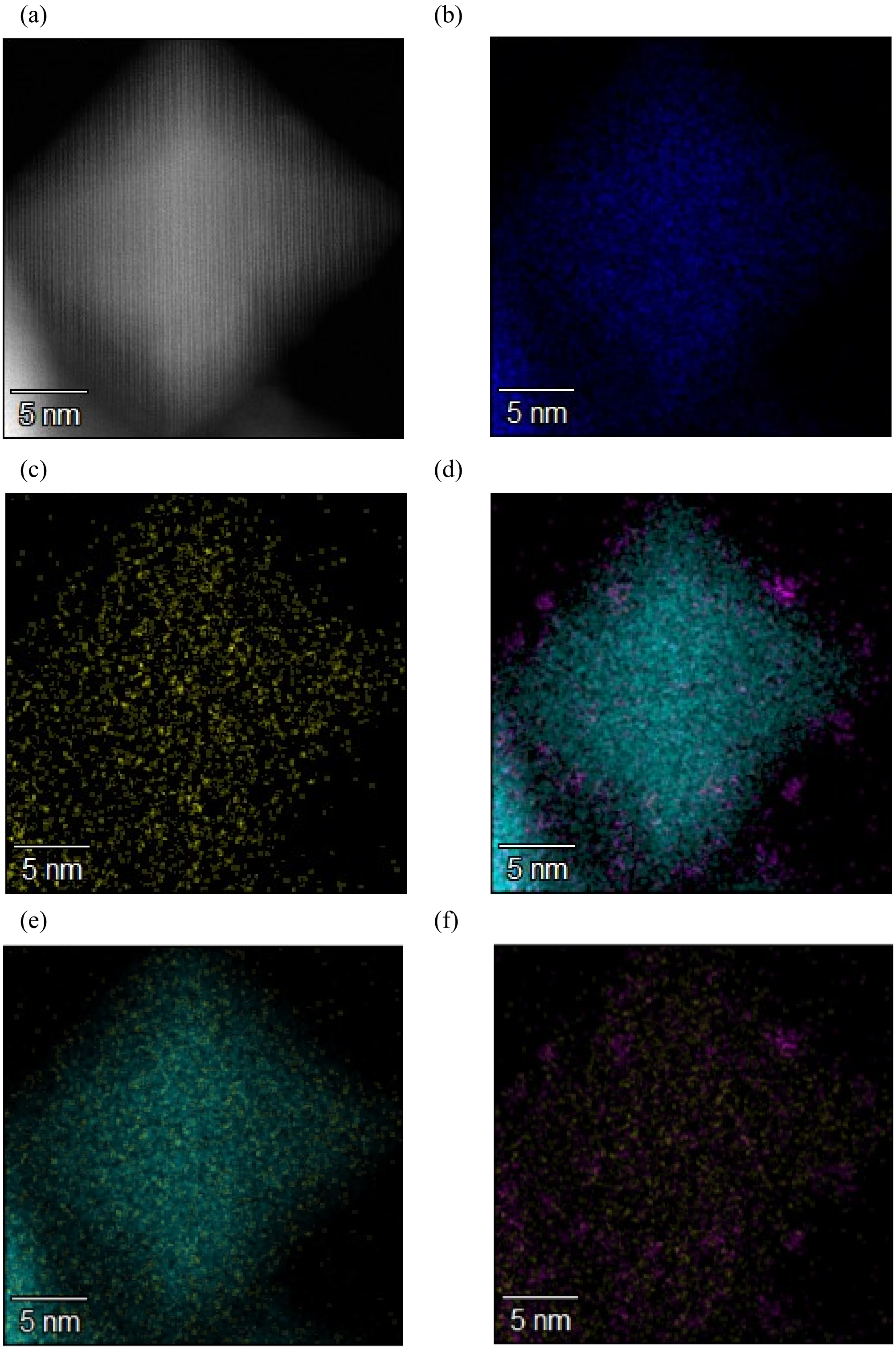


Fig. S4 (a) HAADF-STEM image of Ni/CeO$_2$-HBpin; (b, c) STEM-EDS mapping of Ni/CeO$_2$-HBpin, showing the distribution of O in blue (panel (b)), and the distribution of B in yellow (panel (c)); (d) Overlap of the STEM-EDS mapping of Ni/CeO$_2$-HBpin, showing the distributions of Ni in magenta and Ce in cyan; (e) Overlap of the STEM-EDS mapping of Ni/CeO$_2$-HBpin, showing the distributions of Ce in cyan and B in yellow; (f) Overlap of the STEM-EDS mapping of Ni/CeO$_2$-HBpin, showing the distributions of B in yellow and Ni in magenta

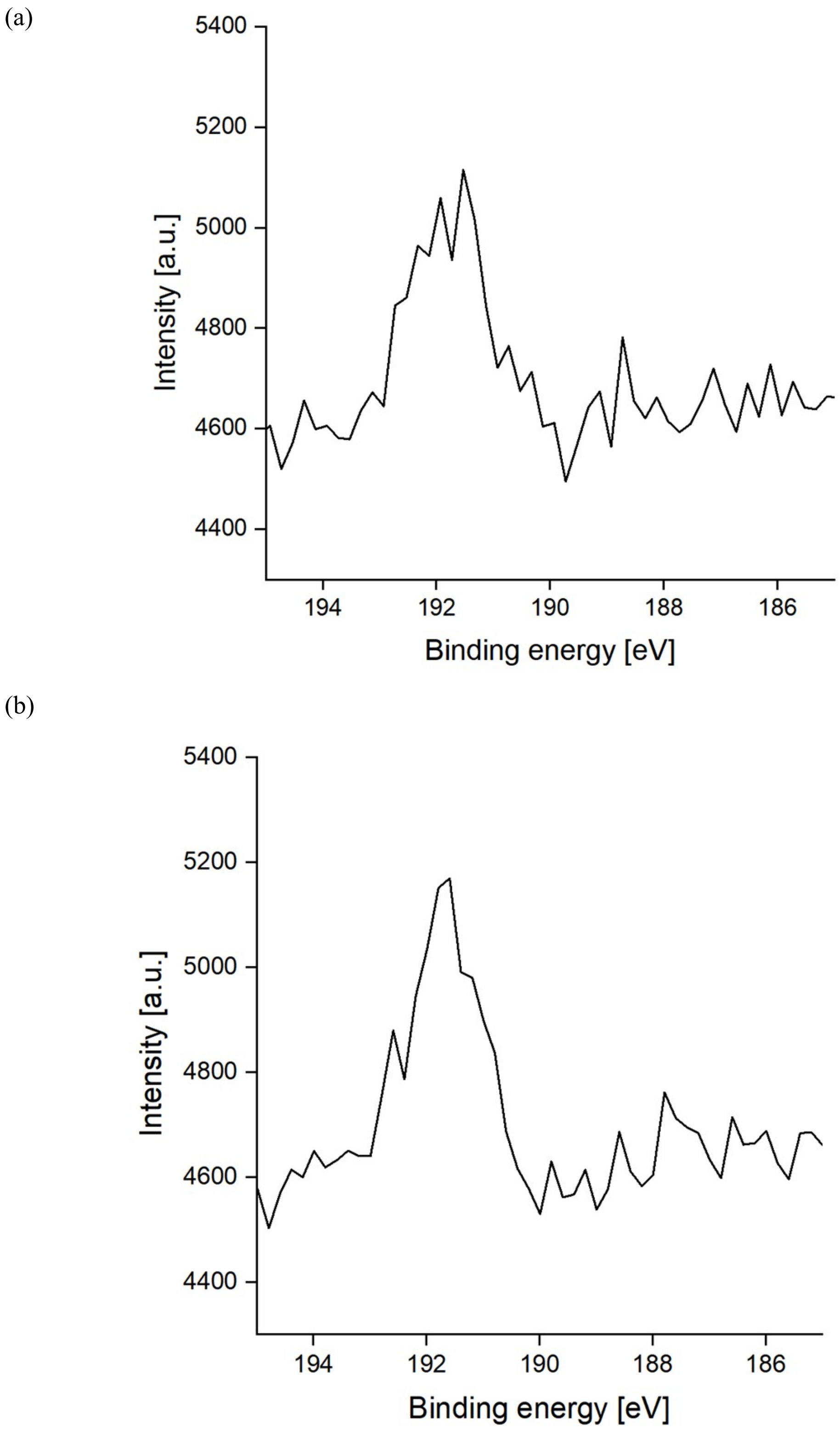
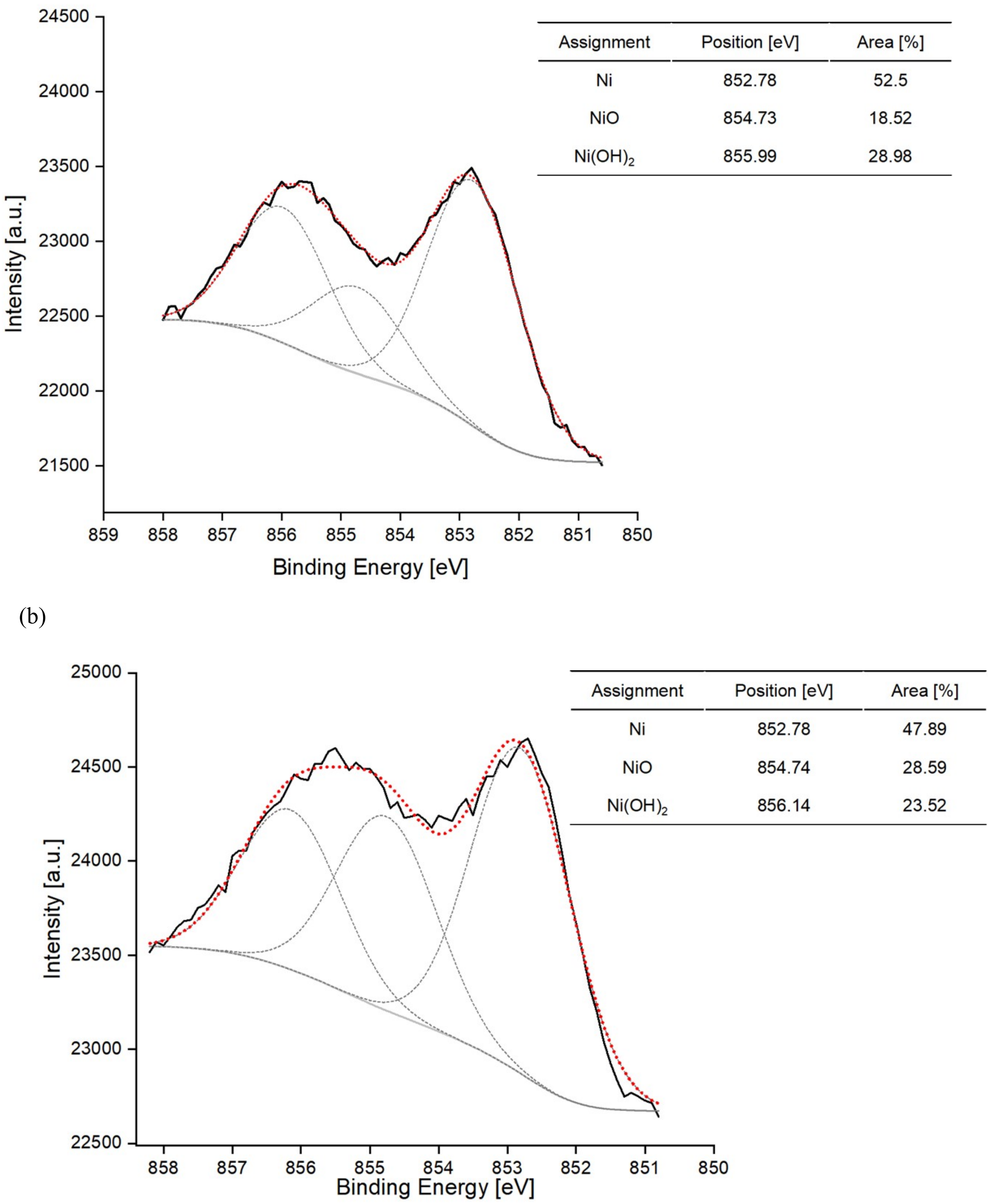


Fig. S5 X-ray photoelectron spectra of (a) Ni/CeO_2-HBpin and (b) Ni/CeO_2-$NaBH_4$ around the B 1s region. The binding energies were calibrated by using the C 1s signal at 284.8 eV.

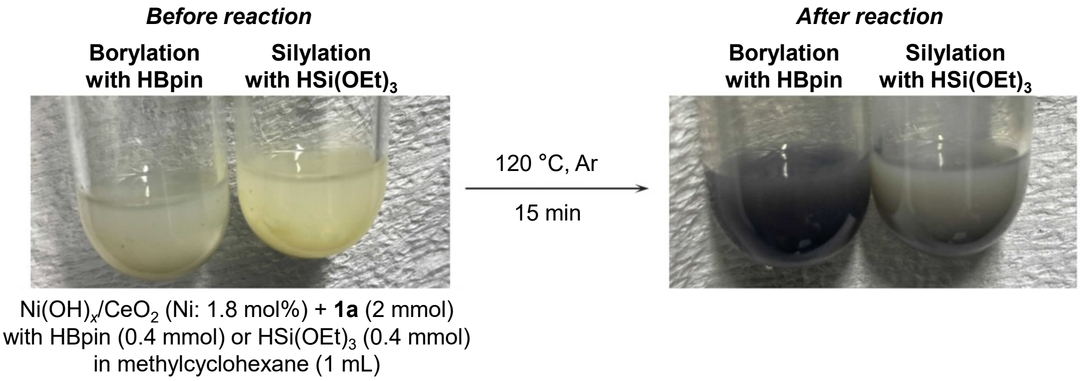

(a)

Assignment	Position [eV]	Area [%]
Ni	852.78	52.5
NiO	854.73	18.52
$Ni(OH)_2$	855.99	28.98

(b)

Assignment	Position [eV]	Area [%]
Ni	852.78	47.89
NiO	854.74	28.59
$Ni(OH)_2$	856.14	23.52

Fig. S6 X-ray photoelectron spectra of (a) Ni/CeO_2-HBpin, (b) Ni/CeO_2-NaNaph around the Ni 2p region. Black lines indicate the data plots. The gray dotted lines indicate the deconvoluted signals. The red dotted lines indicate the sum of the lines of the deconvoluted signals. The binding energies were calibrated by using the C 1s signal at 284.8 eV.



Ni(OH)$_x$/CeO$_2$ (Ni: 1.8 mol%) + **1a** (2 mmol)
with HBpin (0.4 mmol) or HSi(OEt)$_3$ (0.4 mmol)
in methylcyclohexane (1 mL)

Fig. S7 The images of Ni(OH)$_x$/CeO$_2$ before/after the reaction of borylation or silylation of **1a** using HBpin or HSi(OEt)$_3$, respectively. Reaction conditions: **1a** (2 mmol), HBpin or HSi(OEt)$_3$ (0.4 mmol), catalyst (Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 15 min.

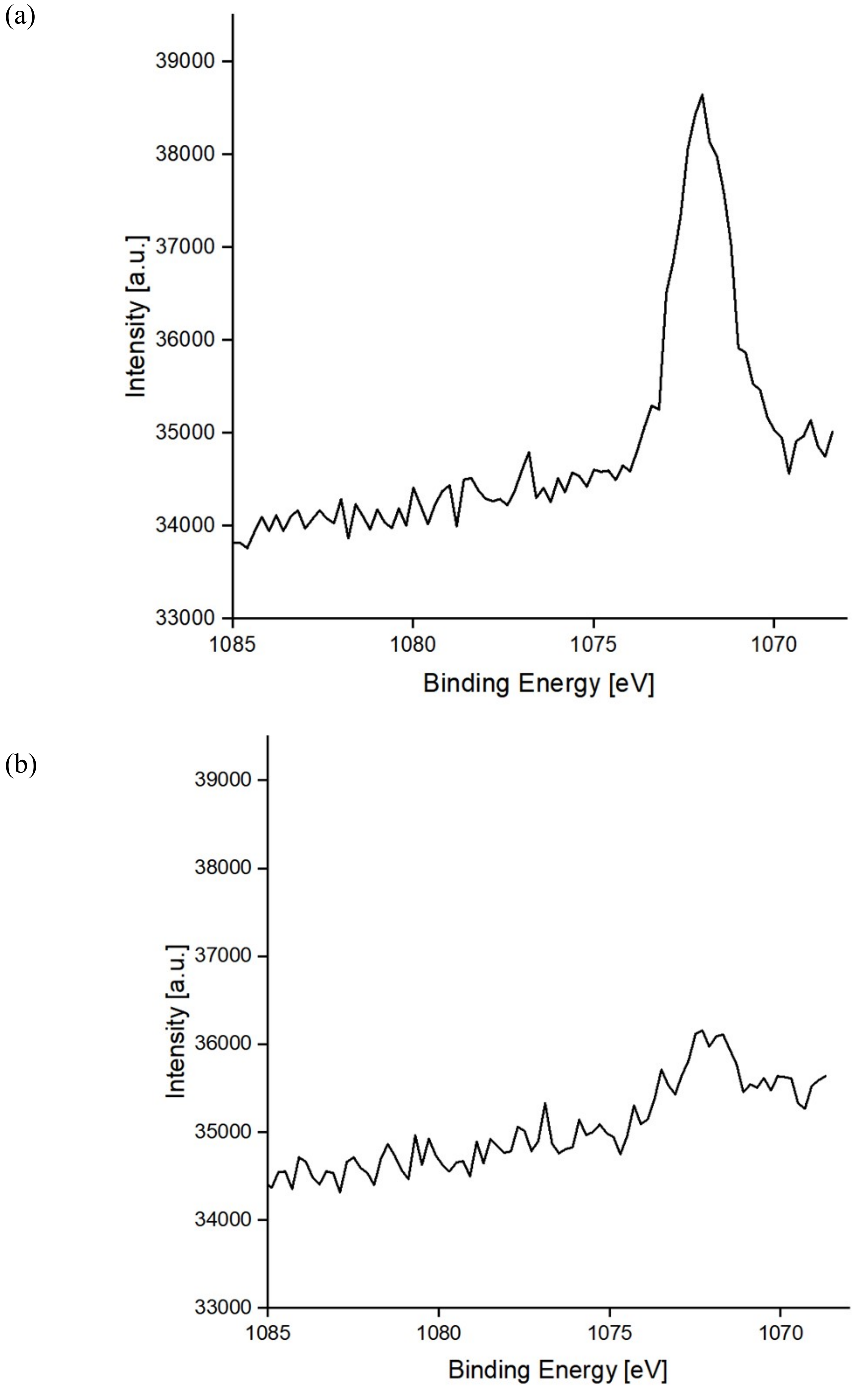
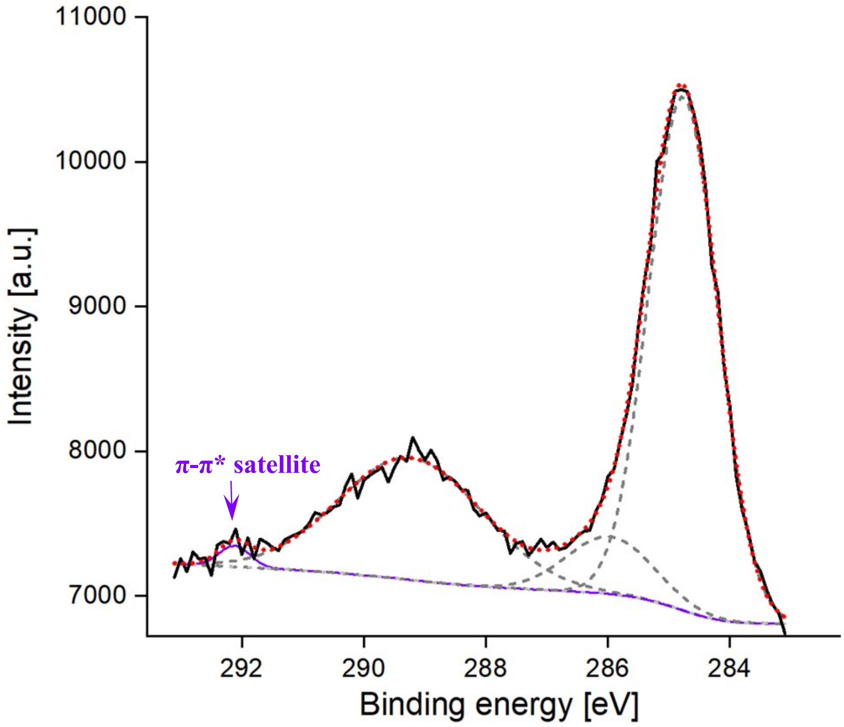


Fig. S8 X-ray photoelectron spectra of (a) Ni/CeO_2-$NaBH_4$ and (b) Ni/CeO_2-NaNaph around the Na 1s region. The binding energies were calibrated by using the C 1s signal at 284.8 eV.

(a)



(b)

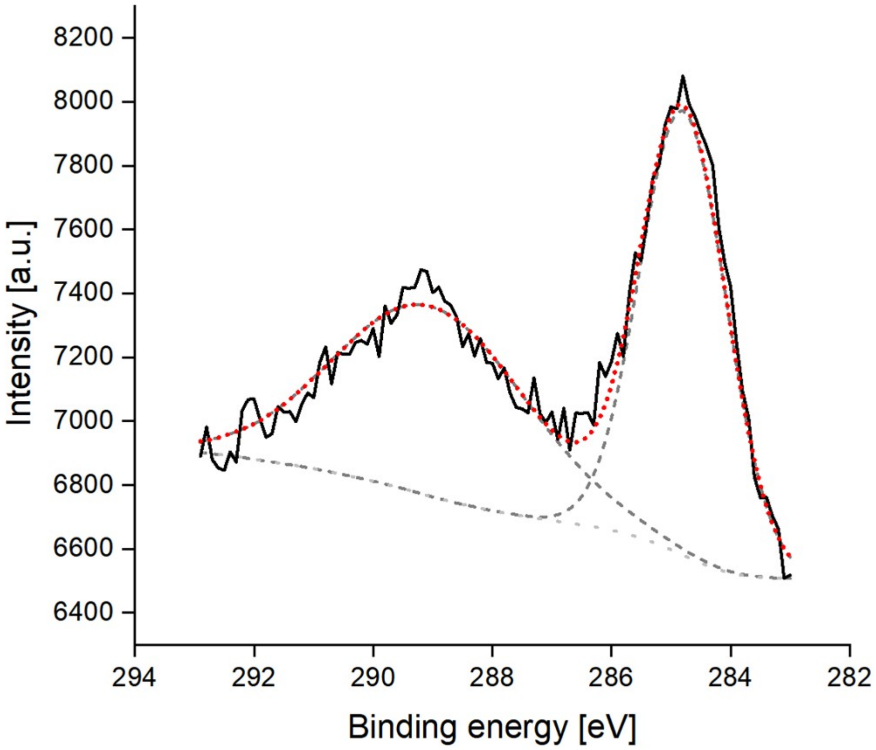


Fig. S9 X-ray photoelectron spectra of (a) Ni/CeO_2-NaNaph and (b) Ni/CeO_2-HBpin around the C 1s region. Black lines indicate the data plots. The gray dotted lines indicate the deconvoluted signals. The red dotted lines indicate the sum of the lines of the deconvoluted signals. The π-π* satellite in (a) is highlighted in violet line.[S7] The binding energies were calibrated by using the C 1s signal at 284.8 eV.

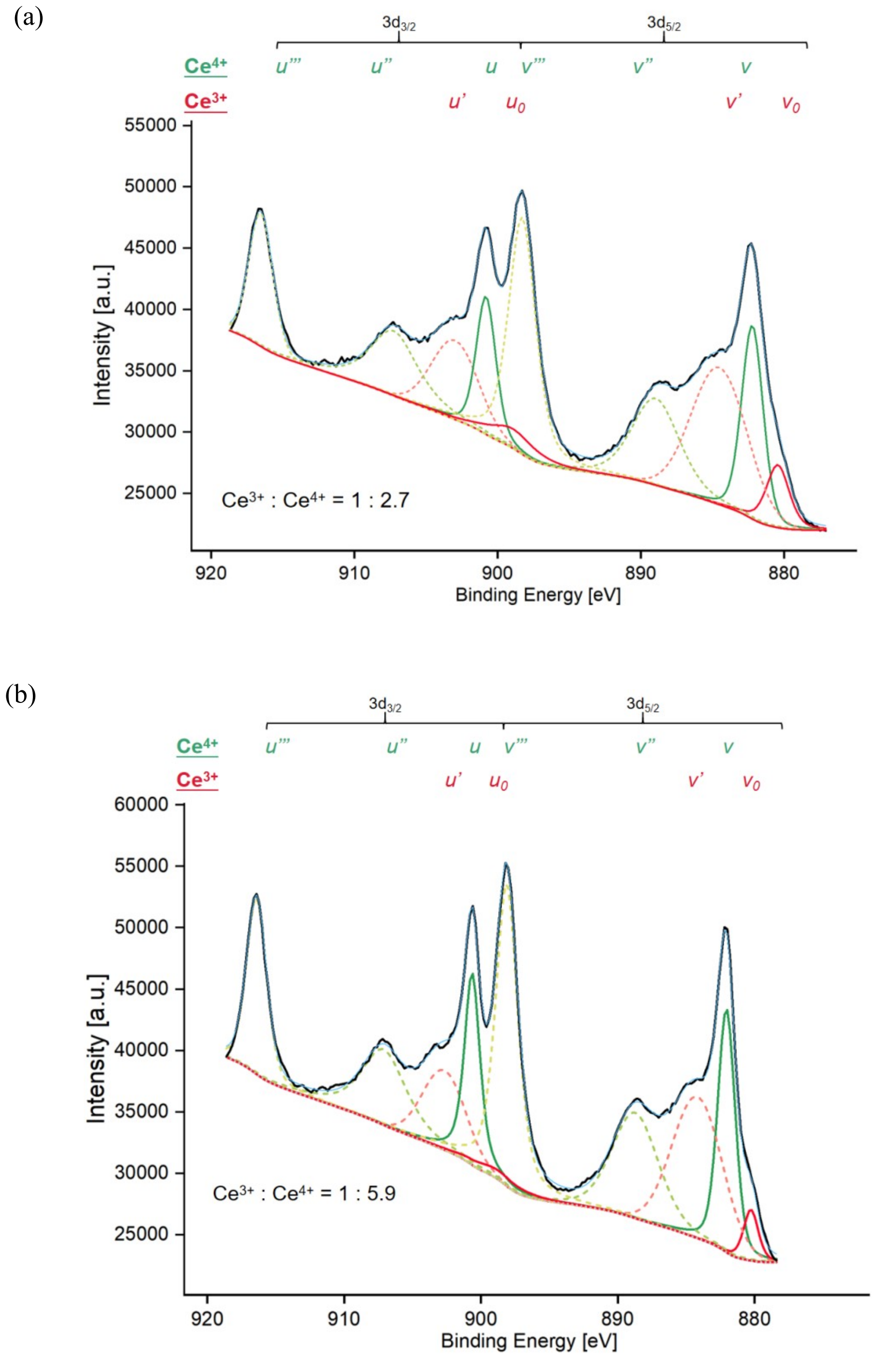


Fig. S10 X-ray photoelectron spectra of (a) Ni/CeO_2-HBpin, (b) Ni/CeO_2-$NaBH_4$ around the Ce 3d region. Black lines indicate the data plots. The green lines indicate the deconvoluted signals of Ce^{4+} species, including the satellite peaks u''', u'', v''', v'', and the main peaks u, v. The red lines indicate the deconvoluted signals of Ce^{3+} species, including the satellite peaks u', v', and the main peaks u_0, v_0. Blue lines indicate the sum of the lines of the deconvoluted signals. The ratios of Ce^{3+}/Ce^{4+} was calculated based on the area of Ce $3d_{5/2}$ region (~875–895 eV). The equation to calculate the percentages of Ce^{3+} species was as follows: $\frac{Area(Ce^{3+}) \times 100}{Area(Ce^{3+}) + Area(Ce^{4+})}$.[S8] The binding energies were calibrated by using the C 1s signal at 284.8 eV.

(c)

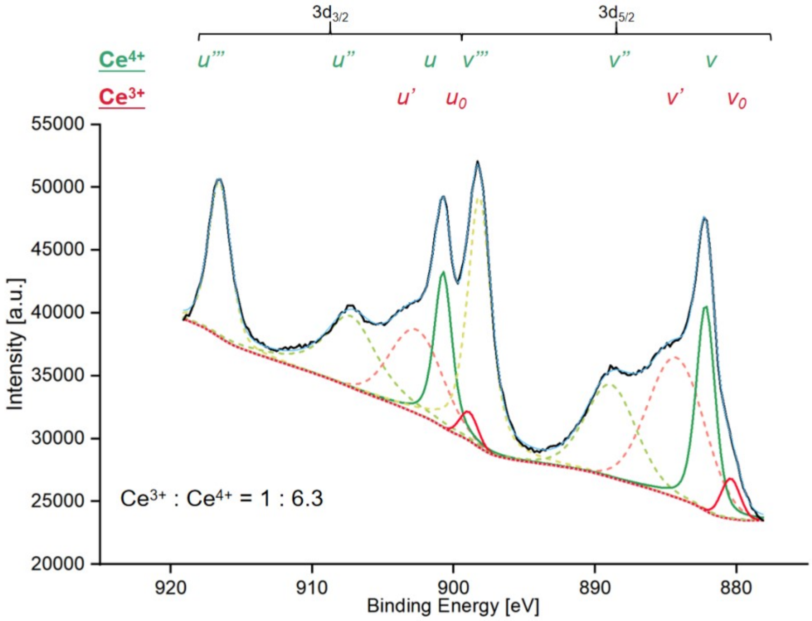


Fig. S10 (continued) X-ray photoelectron spectra of (c) Ni/CeO_2-NaNaph around the Ce 3d region. Black lines indicate the data plots. The green lines indicate the deconvoluted signals of Ce^{4+} species, including the satellite peaks u''', u'', v''', v'', and the main peaks u, v. The red lines indicate the deconvoluted signals of Ce^{3+} species, including the satellite peaks u', v', and the main peaks u_0, v_0. Blue lines indicate the sum of the lines of the deconvoluted signals. The ratios of Ce^{3+}/Ce^{4+} was calculated based on the area of Ce $3d_{5/2}$ region (~875–895 eV). The equation to calculate the percentages of Ce^{3+} species was as follows: $\frac{Area(Ce^{3+}) \times 100}{Area(Ce^{3+}) + Area(Ce^{4+})}$.[S8] The binding energies were calibrated by using the C 1s signal at 284.8 eV.

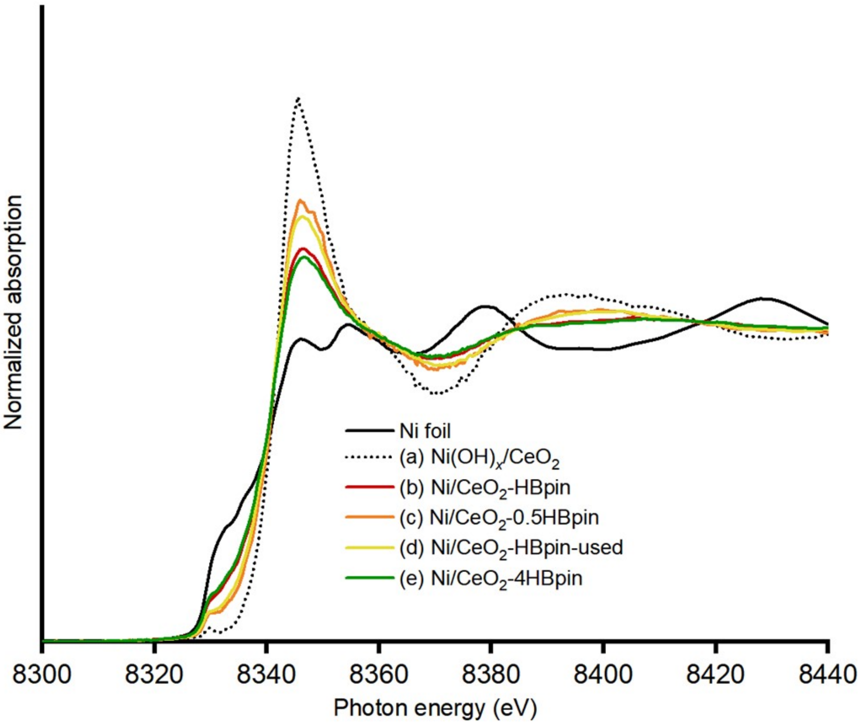


Fig. S11 Ni K-edge XANES spectra of Ni-foil, (a) $Ni(OH)_x/CeO_2$, (b) Ni/CeO_2-HBpin, (c) Ni/CeO_2-0.5HBpin, (d) Ni/CeO_2-HBpin-used, (e) Ni/CeO_2-4HBpin.

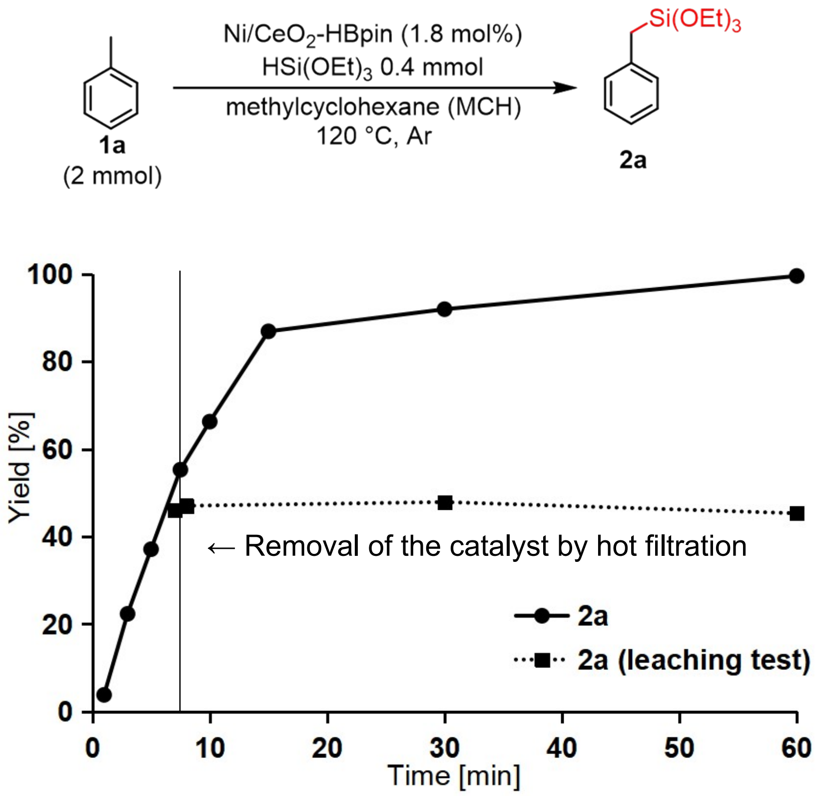


Fig. S12 Effect of removal of Ni/CeO$_2$-HBpin catalyst on the dehydrogenative benzylic silylation of toluene (**1a**). Reaction conditions: **1a** (2 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 1.8 mol%), HSi(OEt)$_3$ (0.4 mmol), methylcyclohexane (1 mL), 120 °C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

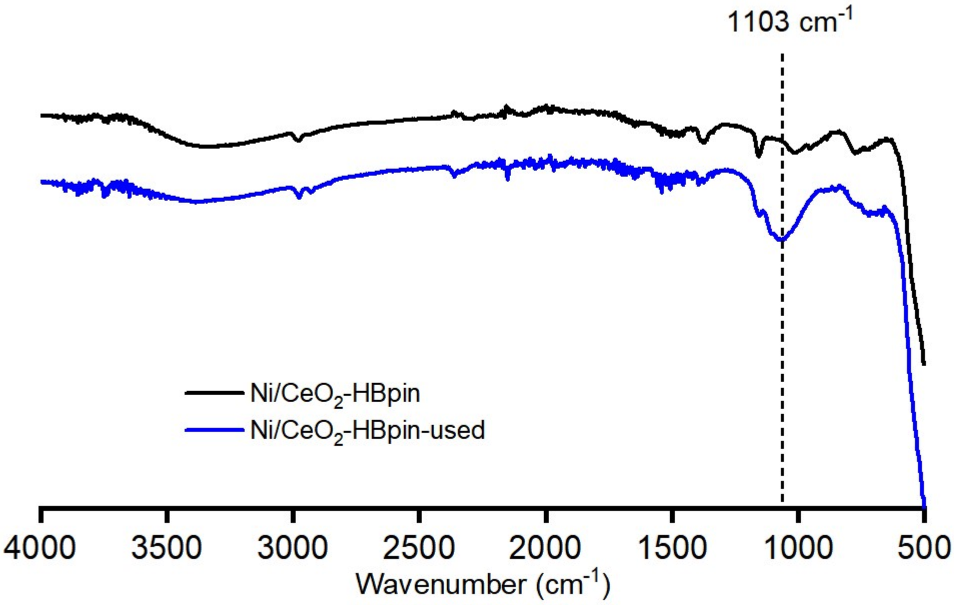


Fig. S13 IR-ATR spectra of fresh (marked in black) and used Ni/CeO$_2$-HBpin (marked in blue). The used catalyst was obtained under the conditions in Table 1, entry 11.

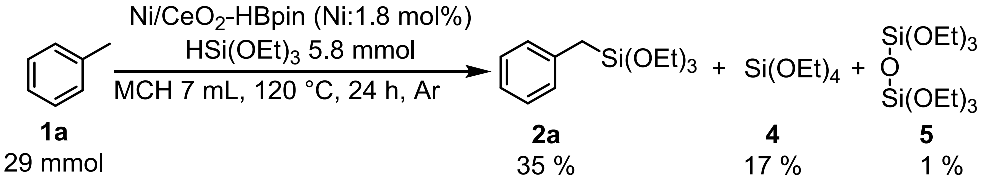


Fig. S14 Ni/CeO$_2$-HBpin-catalyzed benzylic C(sp^3)–H dehydrogenative of **1a** in a gram-scale. Reaction conditions: **1a** (29 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 1.8 mol%), HSi(OEt)$_3$ (5.8 mmol), methylcyclohexane (7 mL), 120 °C, 24 h, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

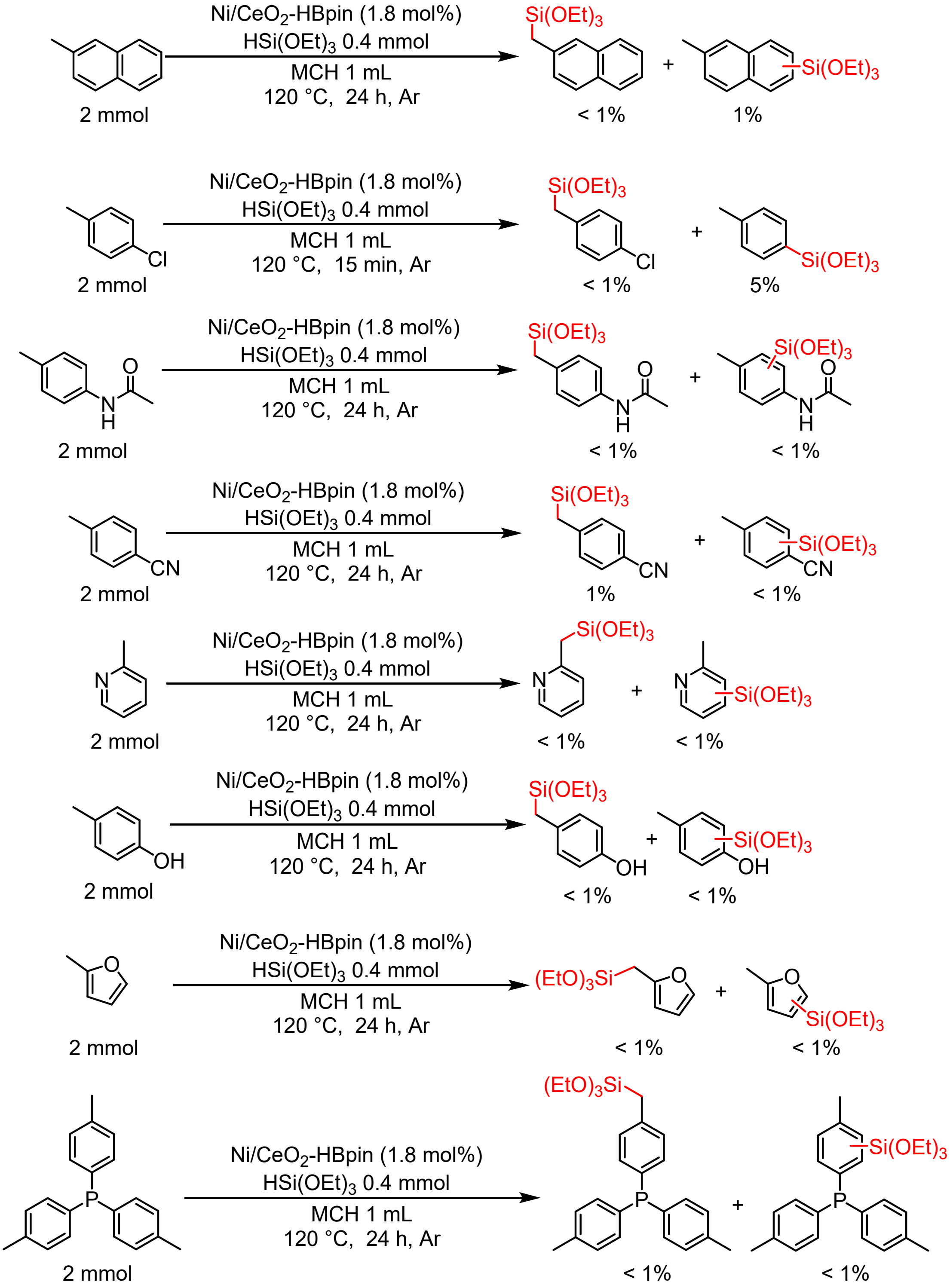


Fig. S15 Limitation of substrates. Reaction conditions are indicated in the figure.

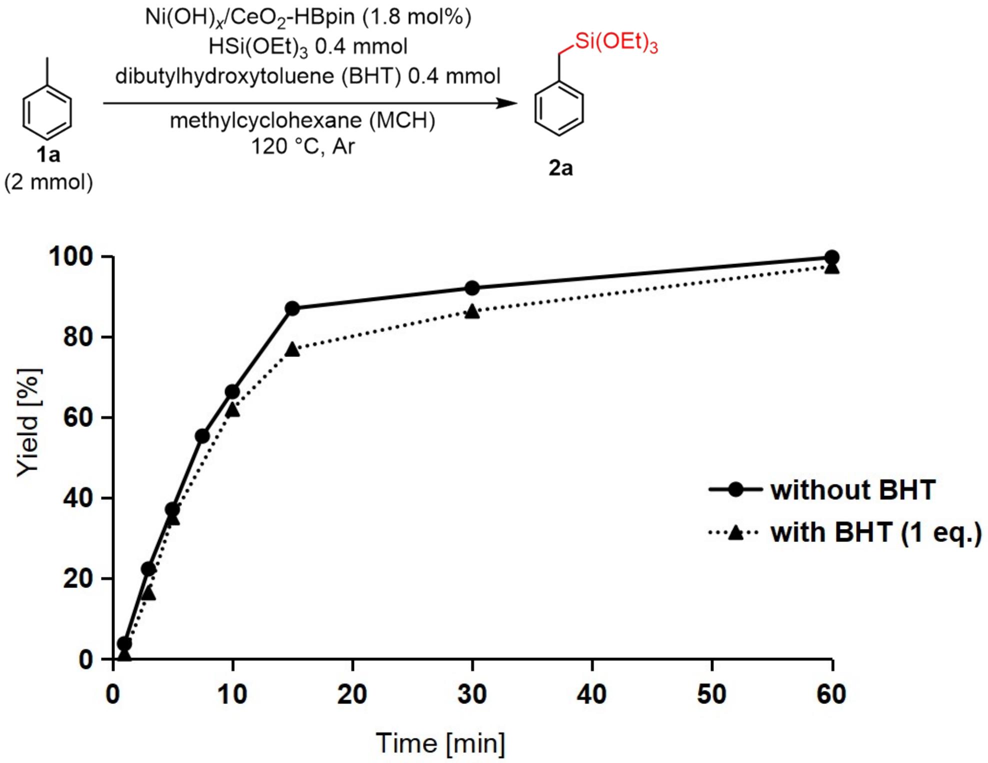


Fig. S16 The reaction profile of the dehydrogenative benzylic silylation of toluene (**1a**) with or without 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT). Reaction conditions: **1a** (2 mmol), Ni/CeO_2-HBpin (Ni: 1.5 wt%, 1.8 mol%), $HSi(OEt)_3$ (0.4 mmol), BHT (0 or 0.4 mmol), methylcyclohexane (1 mL), 120 °C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

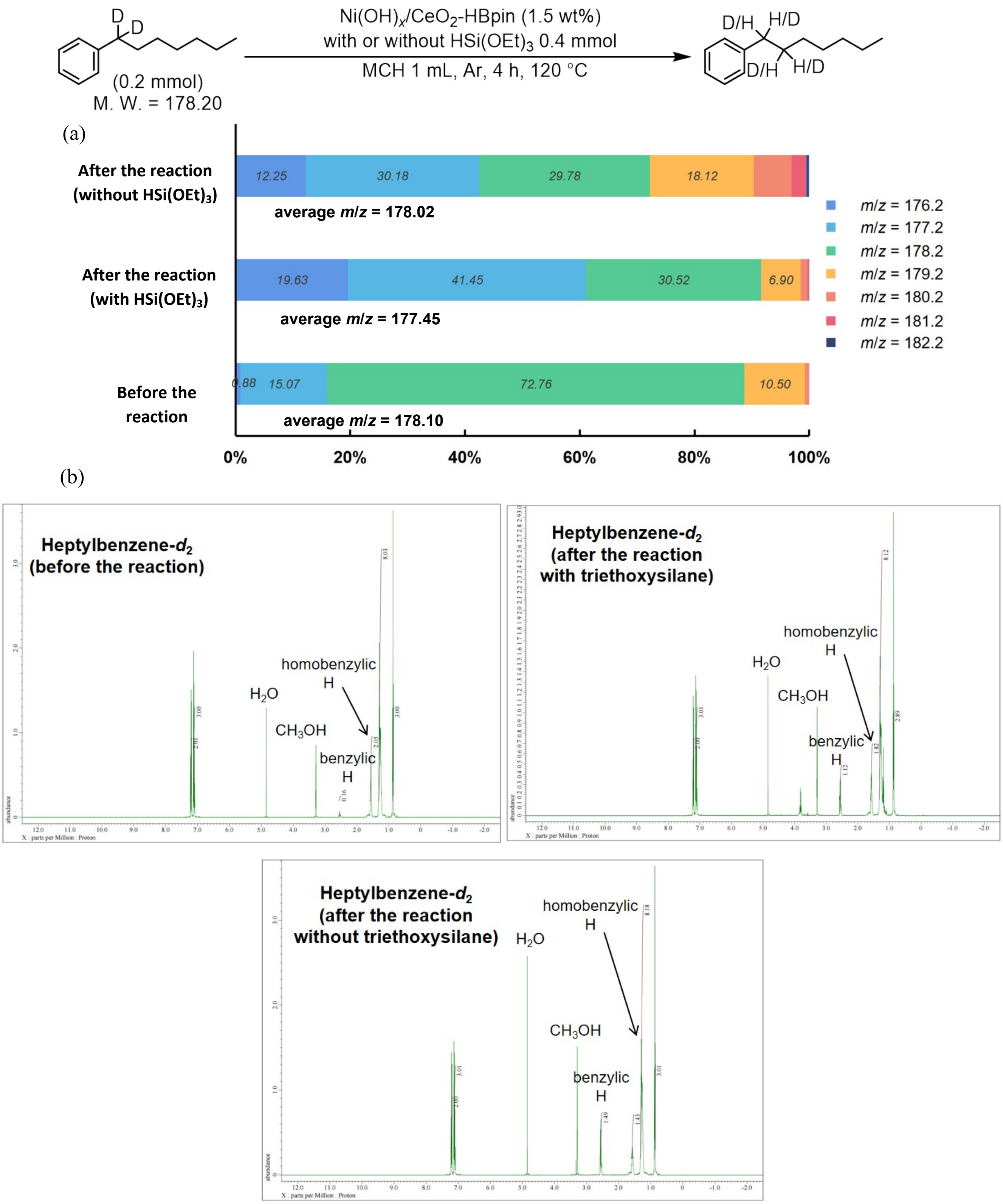


Fig. S17 (a) m/z distribution of heptylbenzenes between m/z = 176.2 and m/z = 182.2 and (b) ^{1}H NMR spectra (500 MHz, CD_3OD) of heptylbenzenes before/after the reaction. Reaction conditions: hepylbenzene-d_2 (0.2 mmol), $HSi(OEt)_3$ (0 or 0.4 mmol), Ni/CeO$_2$-HBpin (Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 4 h.

(c)

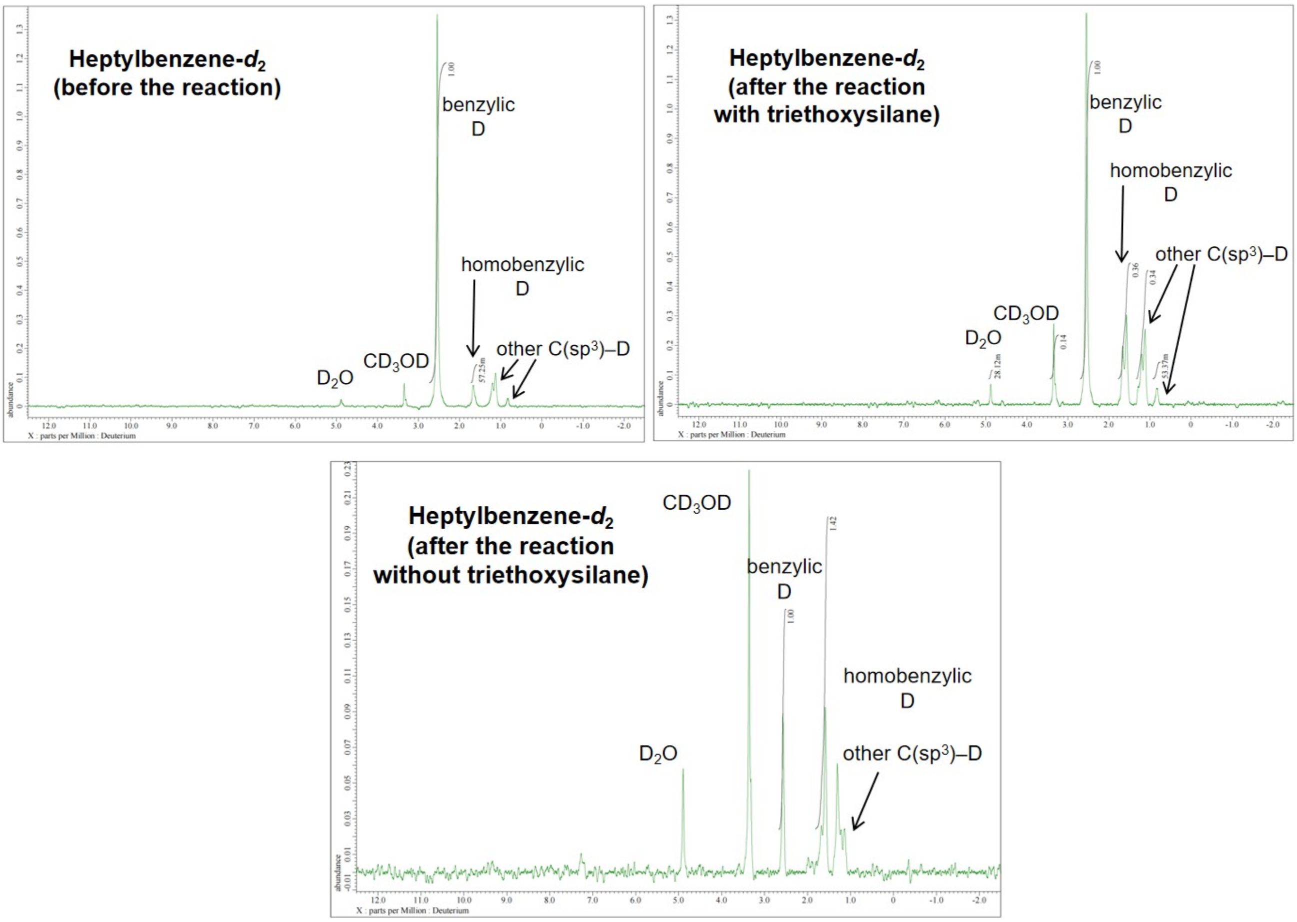


Fig. S17 (continued) (c) ^{2}H NMR spectra (77 MHz, CH_3OH) of the heptylbenzene-d_2 during the reaction catalyzed by Ni/CeO_2-HBpin with or without $HSi(OEt)_3$. Reaction conditions: hepylbenzene-1,1-d_2 (0.2 mmol), $HSi(OEt)_3$ (0.4 mmol), Ni/CeO_2-HBpin (Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 4 h.

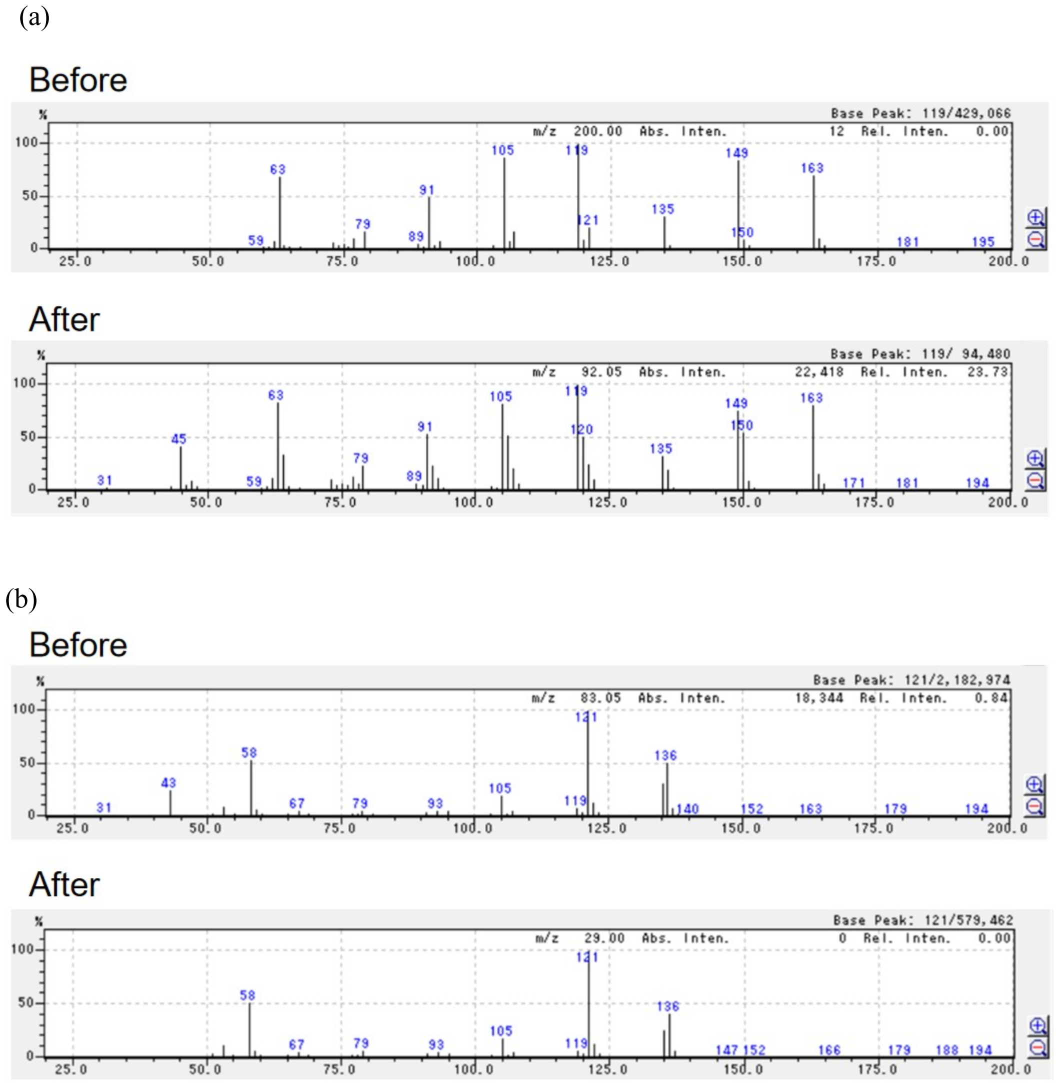


Fig. S18 GC-MS spectra of (a) $HSi(OEt)_3$ and (b) $HSiMe_2Ph$ before/after the reactions with toluene-d_8 in the presence of Ni/CeO_2-HBpin. Reaction conditions: $HSi(OEt)_3$ or $HSiMe_2Ph$ (0.4 mmol), toluene-d_8 (0.2 mmol), Ni/CeO_2-HBpin (Ni: 1.5 wt%, 3.6 mol%), methylcyclohexane (1 mL), 120 °C, 4 h, Ar (1 atm).

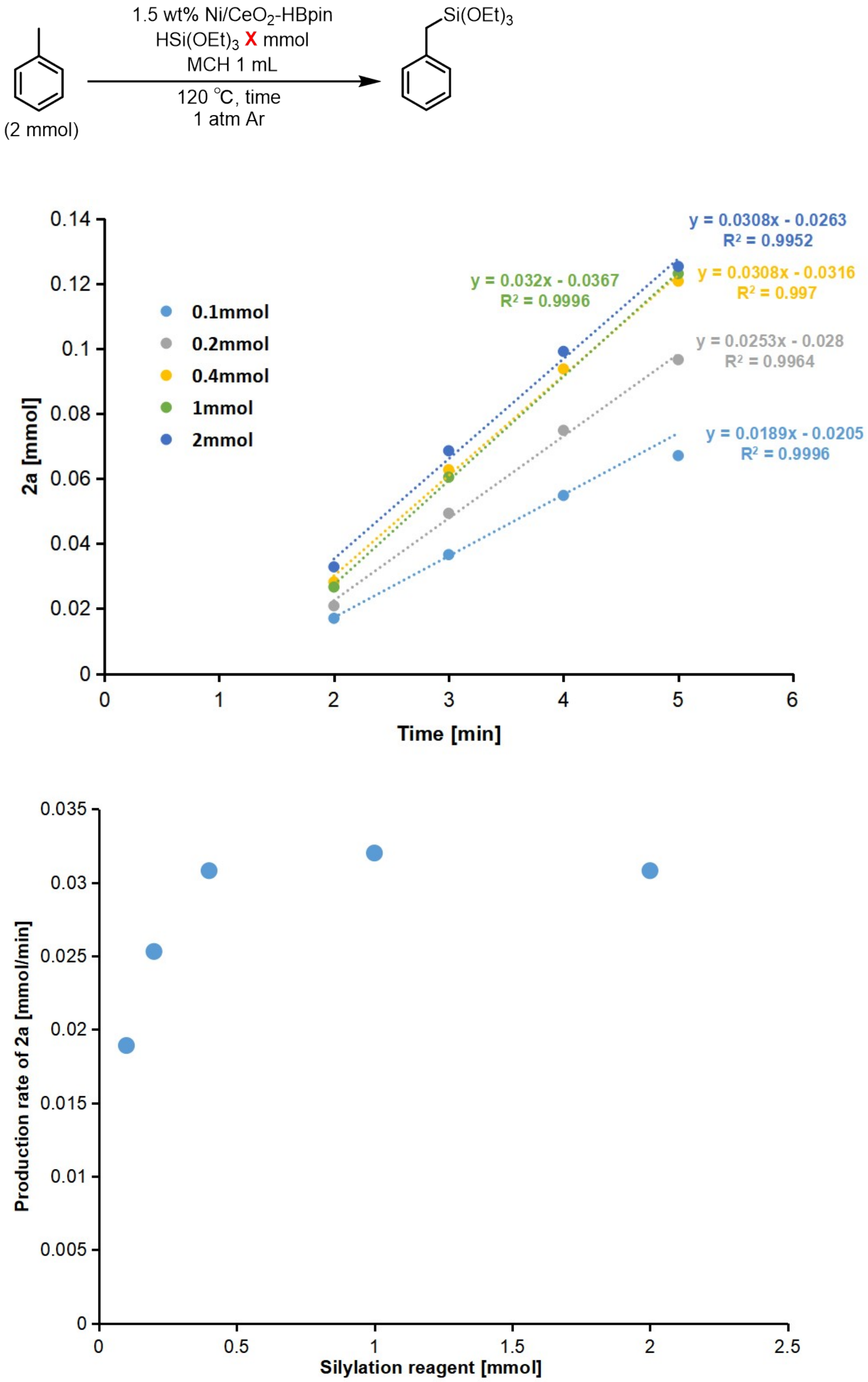


Fig. S19 Dependence of the amount of $HSi(OEt)_3$ on the production rate. Reaction conditions: **1a** (2 mmol), Ni/CeO_2-HBpin (Ni: 1.5 wt%, 1.8 mol%), $HSi(OEt)_3$ (0.1, 0.2, 0.4, 1, or 2 mmol), methylcyclohexane (1 mL), 120 °C, Ar (1 atm).

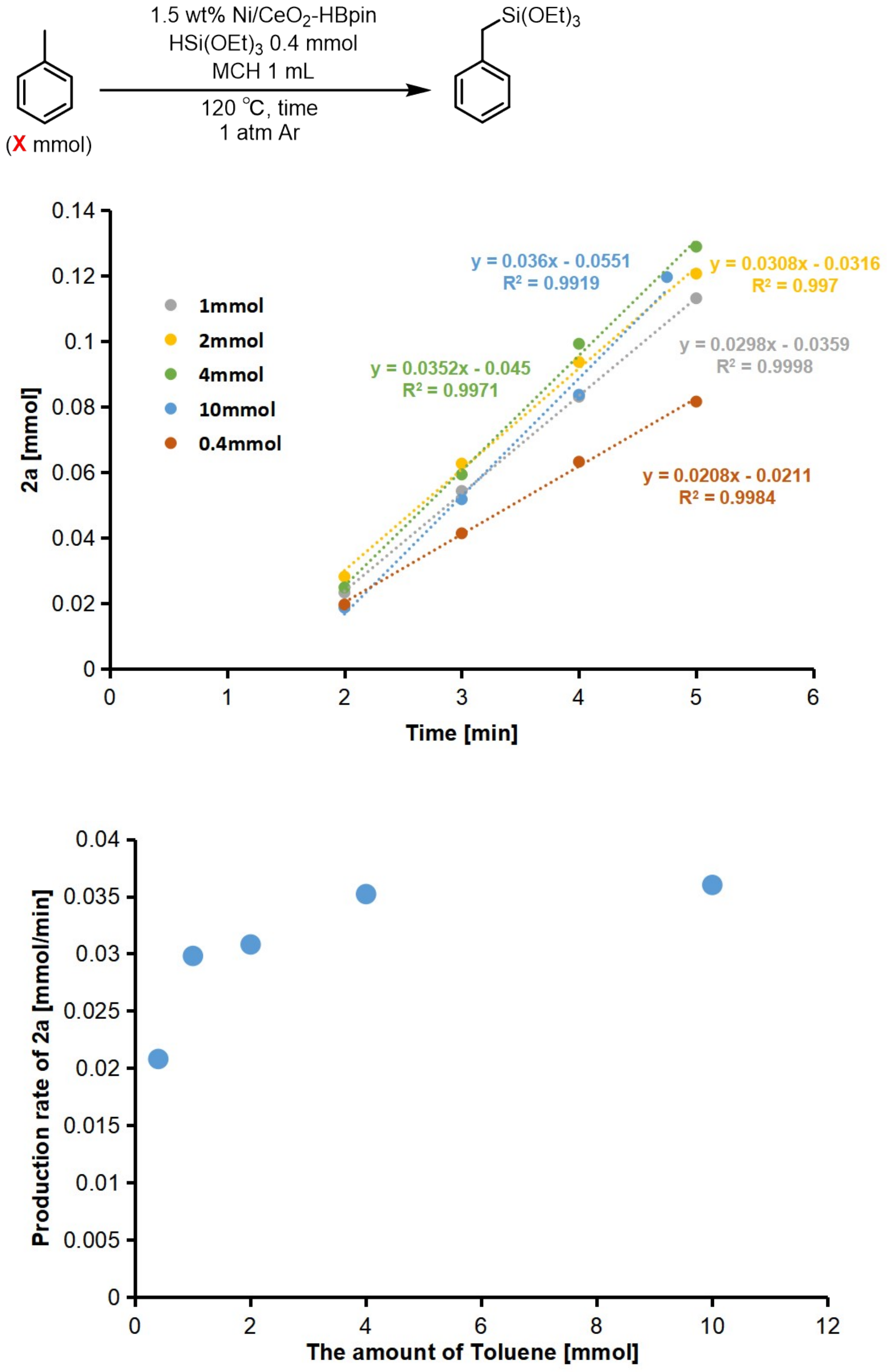


Fig. S20 Dependence of the amount of toluene (**1a**) on the production rate. Reaction conditions: **1a** (0.4, 1, 2, 4, or 10 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 1.8 mol%), HSi(OEt)$_3$ (0.4 mmol), methylcyclohexane (1 mL), 120 °C, Ar (1 atm).

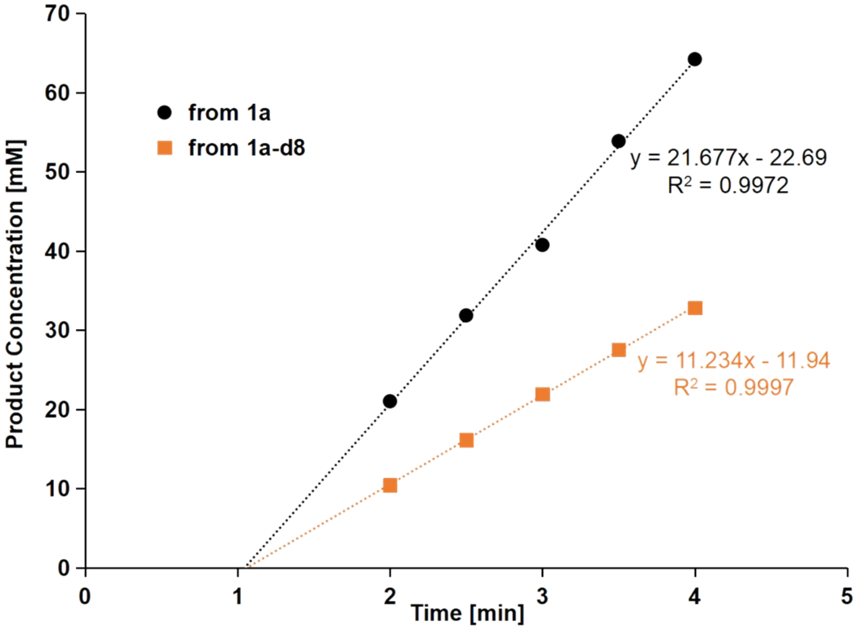


Fig. S21 Initial production rates of the dehydrogenative benzylic silylation of toluene (**1a**, marked in black) and toluene-*d*$_8$ (**1a-*d*$_8$**, marked in orange). Reaction conditions: **1a** or **1a-*d*$_8$** (2 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 1.8 mol%), HSi(OEt)$_3$ (0.4 mmol), methylcyclohexane (1 mL), 120 °C, Ar (1 atm). The product concentrations were calculated by GC analysis.

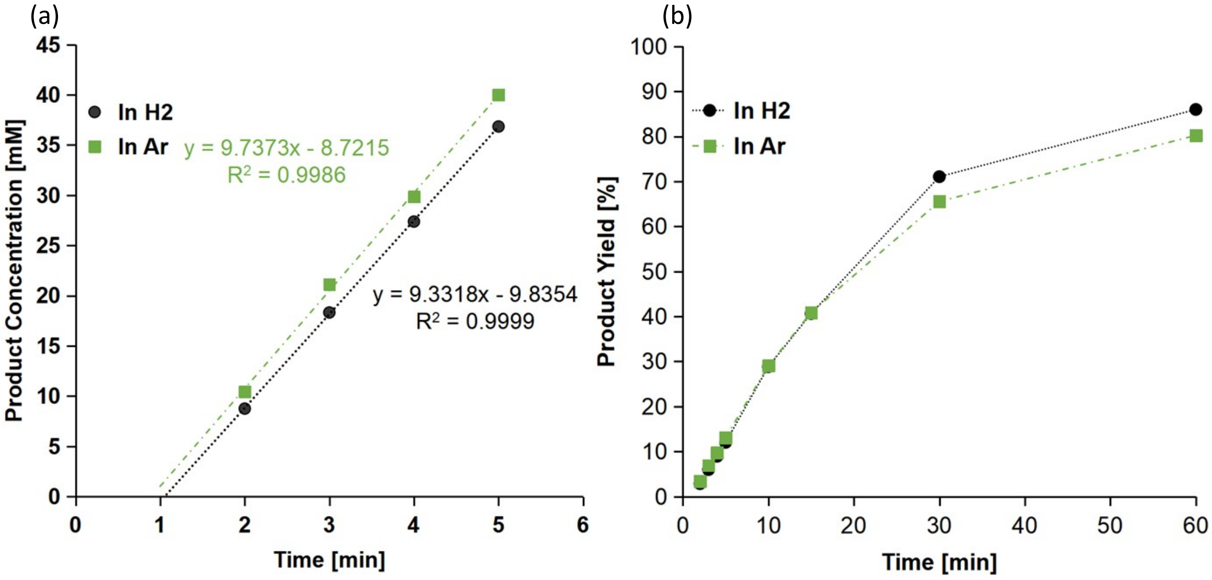


Fig. S22 (a) Initial production rates and (b) reaction profiles of the dehydrogenative benzylic silylation of toluene (**1a**) in an Ar atmosphere (marked in black) or in an H$_2$ atmosphere (marked in green). Reaction conditions: **1a** (2 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 1.8 mol%), HSi(OEt)$_3$ (0.4 mmol), methylcyclohexane (1 mL), 120 °C, Ar or H$_2$ (1 atm). The product concentrations and yields were calculated by GC analysis.

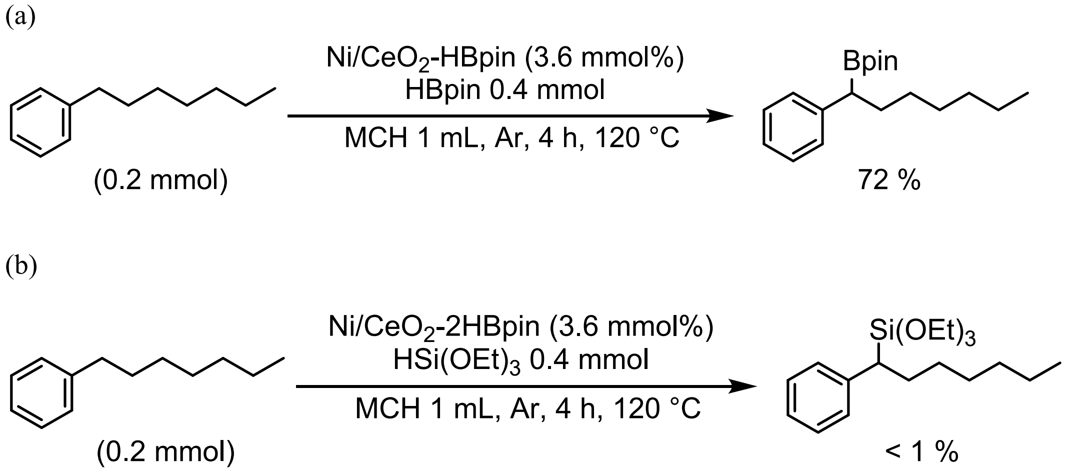


Fig. S23 Ni/CeO$_2$-HBpin-catalyzed benzylic C(sp^3)–H dehydrogenative (a) borylation or (b) silylation of heptylbenzene. Reaction conditions: heptylbenzene (0.2 mmol), Ni/CeO$_2$-HBpin (Ni: 1.5 wt%, 3.6 mol%), pinacolborane or HSi(OEt)$_3$ (0.4 mmol), methylcyclohexane (1 mL), 120 °C, 4 h, Ar (1 atm).

Supplementary Tables

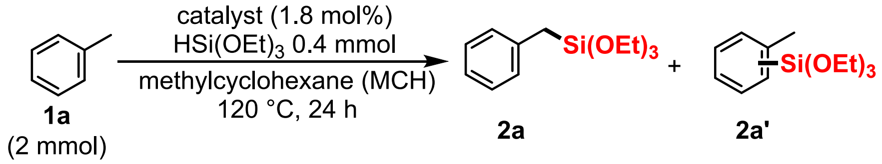
Table S1. Comparison of this work with previous reports on undirected C(sp^3)–H silylation.

Reference	Silylating reagent	Scope of Substrates (Number of examples)	Reaction time	Regioselectivity
This work	**$HSi(OEt)_3$**	**alkylarenes (15)**	**1–24 h**	**primary benzylic**
S9	$HSiMe_3$	$HSiMe_3$ (1)	425 h	—
S10	$HSiEt_3$, $Me_3SiSiMe_3$	toluene (1) (trace)	16.5 h	aryl C(sp^2)–H
S11	1,2-benzenedisilane	mesitylene (1)	30 h	benzylic
S12	$HSiEt_3$	$HSiEt_3$ (1)	12 h	—
S13	H_3SiMes, H_2SiPh_2	CH_4, cyclopropane (2)	168–480 h	—
S5	$HSiEt_3$, $HSi(OEt)_3$	alkylarenes (9)	48–144 h	benzylic
S14	H_2SiEt_2	toluene, ethylbenzene (2)	20 h	benzylic
S15	$HSiEt_3$	alkylarenes (4)	96–120 h	benzylic
S6	*t*Bu–N=N–SiR$_3$	alkylarenes (>30)	1.5–18 h	benzylic

Table S2. Fitted parameters from Ni K-edge EXAFS.

Sample	Shell	C.N.	*R* (Å)	ΔE_{j0} (eV)	$\sigma^2\times10^2$ (Å^2)	*R*-factor (%)
Ni/CeO$_2$-HBpin	Ni−O	2.6±0.7	2.02	−4.72	1.15	1.40
	Ni−Ni (in Ni)	2.0±0.6	2.45	−10.0	1.03	
	Ni−Ni (in Ni(OH)$_2$)	1.1±1.1	3.12	−10.0	1.88	
Ni/CeO$_2$-4HBpin	Ni−O	2.9±0.9	2.03	−2.34	1.47	2.48
	Ni−Ni (in Ni)	2.5±0.8	2.45	−9.33	1.05	
	Ni−Ni (in Ni(OH)$_2$)	0.5±0.3	3.13	10.0	1.50	
Ni/CeO$_2$-HSi(OEt)$_3$	Ni−O	4.5±0.4	2.02	−6.44	0.76	0.88
Ni/CeO$_2$-NaBH$_4$	Ni−O	3.0±0.4	2.03	−3.95	0.66	0.74
	Ni−Ni (in Ni)	1.2±0.5	2.46	−10.0	10.0	
	Ni−Ni (in Ni(OH)$_2$)	0.7±0.4	3.16	10.0	0.86	
Ni/CeO$_2$-HBpin (used)	Ni−O	3.0±0.2	2.03	−4.03	0.088	0.79
	Ni−Ni (in Ni)	1.3±0.6	2.46	−10.0	1.27	
	Ni−Ni (in Ni(OH)$_2$)	1.0±0.4	3.11	−10.0	1.41	
Ni/CeO$_2$-0.5HBpin	Ni−O	3.2±0.6	2.04	−3.45	0.69	1.94
	Ni−Ni (in Ni)	1.8±0.9	2.54	−0.22	1.27	
	Ni−Ni (in Ni(OH)$_2$)	0.7±0.4	3.18	10	1.22	
Ni/CeO$_2$-NaNaph[S2]	Ni−O	1.4	2.04	0.27	0.63	1.01
	Ni−Ni (in Ni)	3.1	2.48	−7.88	0.81	
	Ni−Ni (in Ni(OH)$_2$)	0.4	3.17	10.66	0.59	
	Ni−Ni (in Ni)	3.3	4.39	−4.89	1.07	
	Ni−Ni (in Ni)	2.5	5.04	−9.16	0.93	

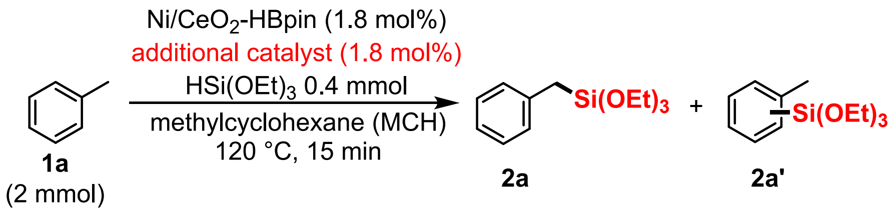
Table S3. Effect of catalysts on dehydrogenative benzylic silylation of toluene (**1a**) for 24 h.



entry	catalyst	yield [%]	
		2a	**2a'**
1	Ni/CeO$_2$-HBpin	80	<1
2	Ni/CeO$_2$-HSi(OEt)$_3$	16	<1
3	Ni/CeO$_2$-NaBH$_4$	<1	<1
4	Ni/CeO$_2$-NaNaph	<1	<1

Reaction conditions: **1a** (2 mmol), HSi(OEt)$_3$ (0.4 mmol), catalyst (Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 24 h. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

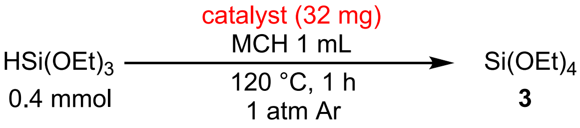
Table S4. Effect of the additional catalysts on Ni/CeO_2-HBpin-catalyzed **1a** silylation with $HSi(OEt)_3$.



entry	additional catalyst	yield [%]	
		2a	**2a'**
1	-	79	<1
2	CeO_2 (32 mg)	77	3
3	CeO_2-HBpin (32 mg)	65	<1
4	Ni/CeO_2-$NaBH_4$	7	<1
5	Ni/CeO_2-NaNaph	18	<1

Reaction conditions: **1a** (2 mmol), $HSi(OEt)_3$ (0.4 mmol), Ni/CeO_2-HBpin (Ni: 1.8 mol%), additive (Ni: 1.8 mol% or 32 mg), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 15 min. Conversions and yields were determined by GC analysis using *n*-hexadecane as an internal standard.

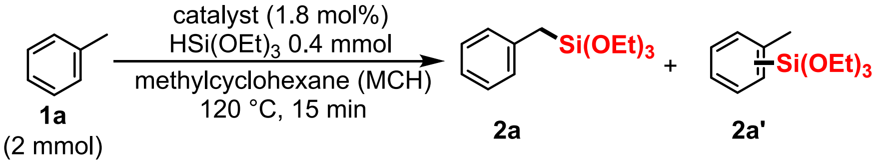
Table S5. Effect of the pretreated CeO_2 supports on the conversion of $HSi(OEt)_3$ without **1a** or Ni catalysts.



entry	catalyst	conv. [%]	yield of **3** [%]
1	CeO_2-HBpin	18	2
2	CeO_2-$NaBH_4$	56	30
3	CeO_2-3NaNaph	>99	34

Reaction conditions: $HSi(OEt)_3$ (0.4 mmol), catalyst (32 mg), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 1 h. Conversions and yields were determined by GC analysis using *n*-hexadecane as an internal standard.

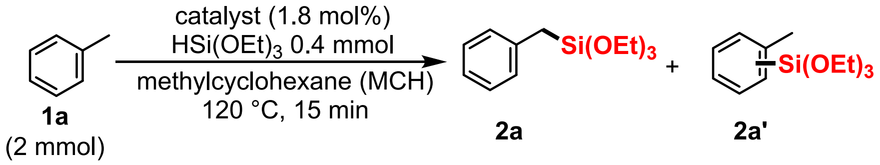
Table S6. Optimization of the amount of reducing agent used in the catalyst pretreatment for silylation of toluene (**1a**).



entry	catalyst	yield [%]	
		2a	**2a'**
1	Ni/CeO$_2$-4HBpin	44	<1
2	Ni/CeO$_2$-HBpin	79	<1
3	Ni/CeO$_2$-0.5HBpin	46	<1

Reaction conditions: **1a** (2 mmol), HSi(OEt)$_3$ (0.4 mmol), catalyst (Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 15 min. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

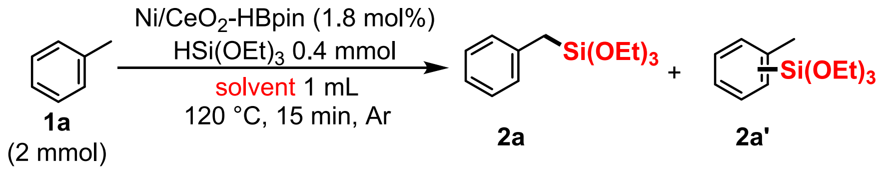
Table S7. Effect of metals on dehydrogenative benzylic silylation of toluene (**1a**).



entry	catalyst	yield [%]	
		2a	**2a'**
1	Ni/CeO$_2$-0.5HBpin	46	<1
2	Mn/CeO$_2$-0.5HBpin	<1	<1
3	Fe/CeO$_2$-0.5HBpin	<1	<1
4	Co/CeO$_2$-0.5HBpin	<1	<1
5	Cu/CeO$_2$-0.5HBpin	<1	<1
6	Zn/CeO$_2$-0.5HBpin	<1	<1

Reaction conditions: **1a** (2 mmol), HSi(OEt)$_3$ (0.4 mmol), catalyst (metal: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 15 min. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

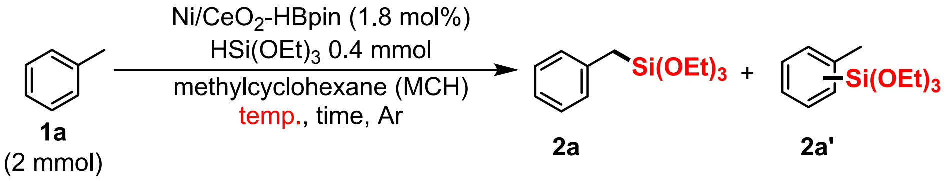
Table S8. Effect of solvents on dehydrogenative benzylic silylation of toluene (**1a**).



entry	solvent	yield [%]	
		2a	**2a'**
1	heptane	81	<1
2	methylcyclohexane (MCH)	79	<1
3	cyclopentyl methyl ether (CPME)	73	<1
4	1,4-dioxane	77	1
5	*N*,*N*-dimethylacetamide (DMA)	53	<1
6	*N*-methylpyrrolidone (NMP)	56	<1

Reaction conditions: **1a** (2 mmol), HSi(OEt)$_3$ (0.4 mmol), Ni/CeO$_2$-HBpin (Ni: 1.8 mol%), solvent (1 mL), Ar (1 atm), 120 °C, 15 min. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

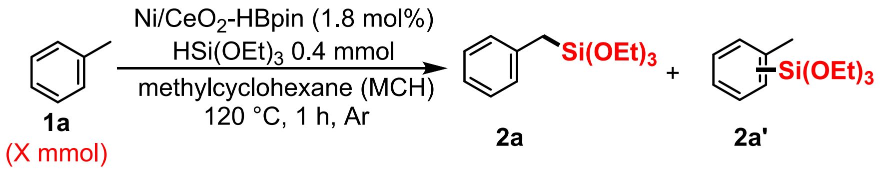
Table S9. Effect of temperature on dehydrogenative benzylic silylation of toluene (**1a**).



entry	temp. [°C]	time [min]	yield [%]	
			2a	**2a'**
1	80	15	15	<1
2	100		62	<1
3	120		79	<1
4	140		81	<1
5	80	60	41	<1
6	100		86	<1
7	120		93	<1
8	140		91	<1

Reaction conditions: **1a** (2 mmol), HSi(OEt)$_3$ (0.4 mmol), Ni/CeO$_2$-HBpin (Ni: 1.8 mol%, 1.5 wt%), methylcyclohexane (1 mL), Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

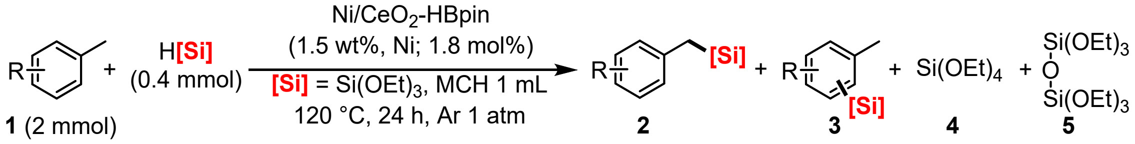
Table S10. Effect of the amount of **1a** on dehydrogenative benzylic silylation of **1a**.



entry	amount of **1a** [mmol]	yield [%]	
		2a	**2a'**
1[a]	0.2	58	<1
2	0.4	57	<1
3	1	87	<1
4	2	93	<1

Reaction conditions: **1a** (0.2, 0.4, 1, or 2 mmol), $HSi(OEt)_3$ (0.4 mmol), Ni/CeO_2-HBpin (Ni: 1.8 mol%, based on the silylating reagents), methylcyclohexane (1 mL), Ar (1 atm), 120 °C. Yields were determined by GC analysis using *n*-hexadecane as an internal standard (based on $HSi(OEt)_3$). [a]24 h. The yields were calculated based on **1a**.

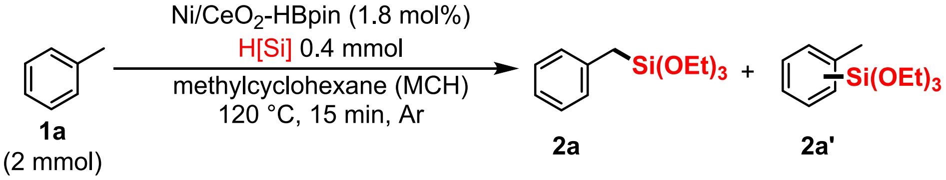
Table S11. The details about of the investigation of the substrate scope of the present regioselective dehydrogenative silylation.[a]



Entry	Substrate	Conv. of $HSi(OEt)_3$ [%]	Yield [%]				
			2	**3**	**4**	**5**	**disilylated product**
1[b]	**1a**	>99	93	1	1	<1	<1
2[c]	**1b**	99	74	1	10	<1	5
3[d]	**1c**	99	85	<1	4	<1	2
4	**1d**	99	77	<1	4	6	5
5[e]	**1e**	96	63	<1	8	<1	<1
6[f]	**1f**	96	62	<1	5	1	<1
7[d]	**1g**	98	77	5	8	<1	1
8[d]	**1h**	>99	49	<1	13	1	<1
9	**1i**	>99	46	2	8	<1	2
10[g]	**1j**	91	41	2	20	1	3
11	**1k**	99	60	<1	4	6	1
12[f]	**1l**	95	80	<1	<1	<1	4
13[h]	**1m**	77	55 (1)	<1	<1	1	<1
14[e]	**1n**	95	70 (1)	<1	<1	<1	<1
15[g]	**1o**	90	30 (< 1)	<1	<1	<1	<1

[a]Reaction conditions: **1** (2 mmol), $HSi(OEt)_3$ (0.4 mmol), Ni/CeO_2-HBpin (32 mg, Ni: 1.8 mol%), methylcyclohexane (1 mL), Ar (1 atm), 120°C, 24 h. Yields were determined via GC using *n*-hexadecane as an internal standard. The regioisomer yields (secondary $C(sp^3)$–H silylation) determined via GC are shown in parentheses. [b]1 h. [c]6 h. [d]8 h. [e]$HSi(OEt)_3$ (0.1 mmol), 140°C. [f]$HSi(OEt)_3$ (0.1 mmol). [g]$HSi(OEt)_3$ (0.2 mmol). [h]Using biphenyl as an internal standard.

Table S12. Effect of different kinds of silylating reagents on dehydrogenative benzylic silylation of toluene (**1a**).



entry	silylating reagent	yield [%]	
		2a	**2a'**
1	$HSi(OEt)_3$	79	<1
2	$HSi(OMe)_3$	8	<1
3	$HSiEt_3$	<1	<1
4	$HSiMe_2Ph$	<1	<1
5	$HSiPh_3$	<1	<1

Reaction conditions: **1a** (2 mmol), Ni/CeO_2-HBpin (Ni: 1.5 wt%, 1.8 mol%), silylating reagent (0.4 mmol), methylcyclohexane (1 mL), Ar (1 atm), 120 °C, 15 min. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

Supplementary References

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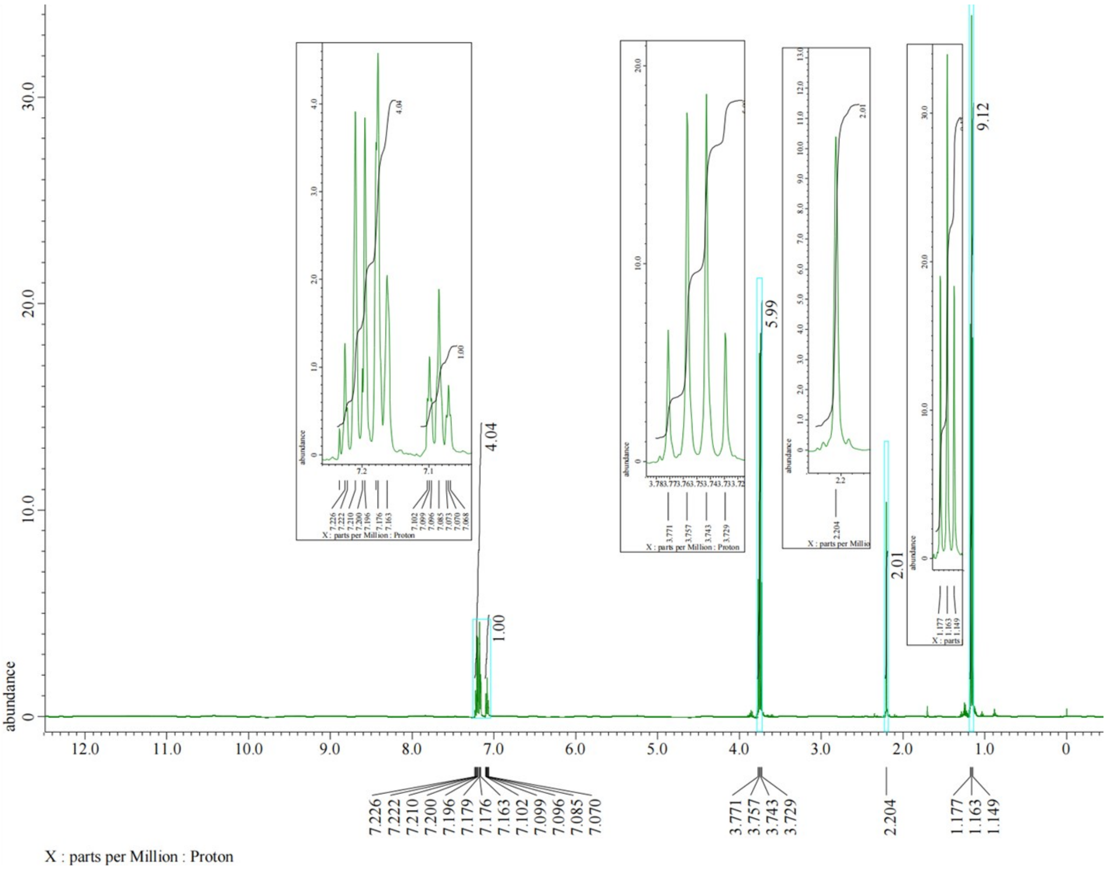
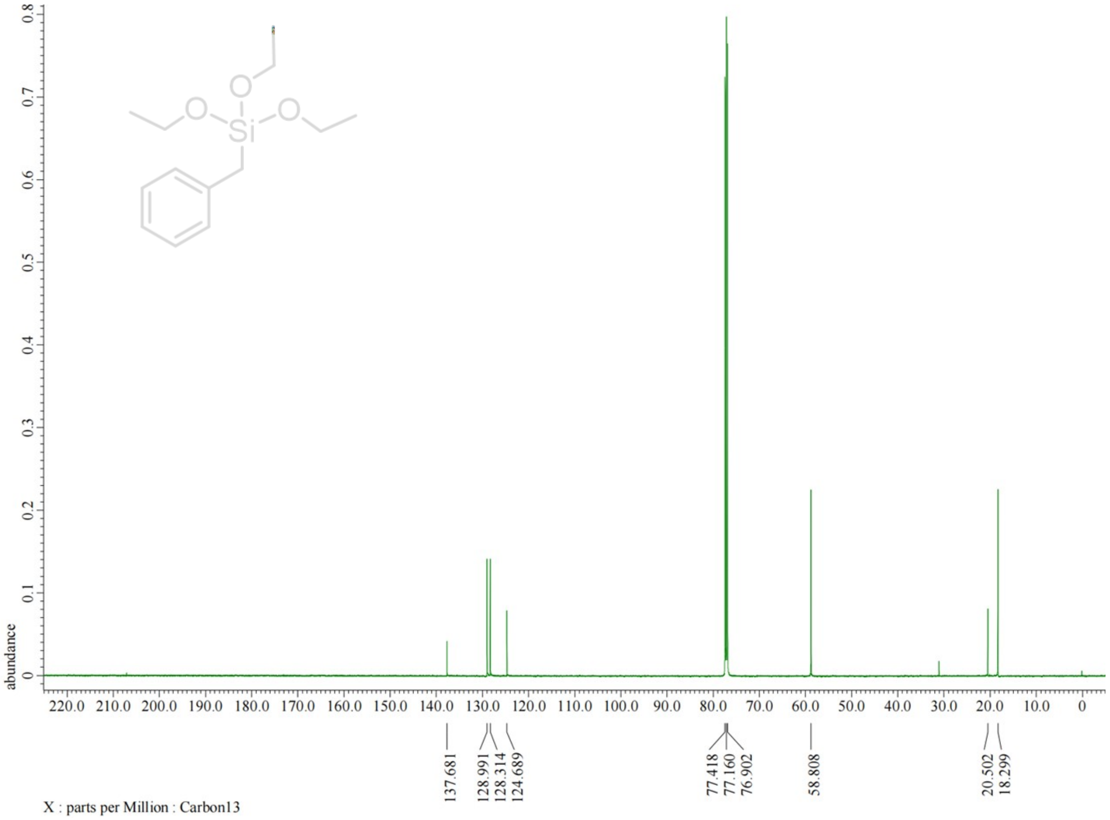
NMR Spectra

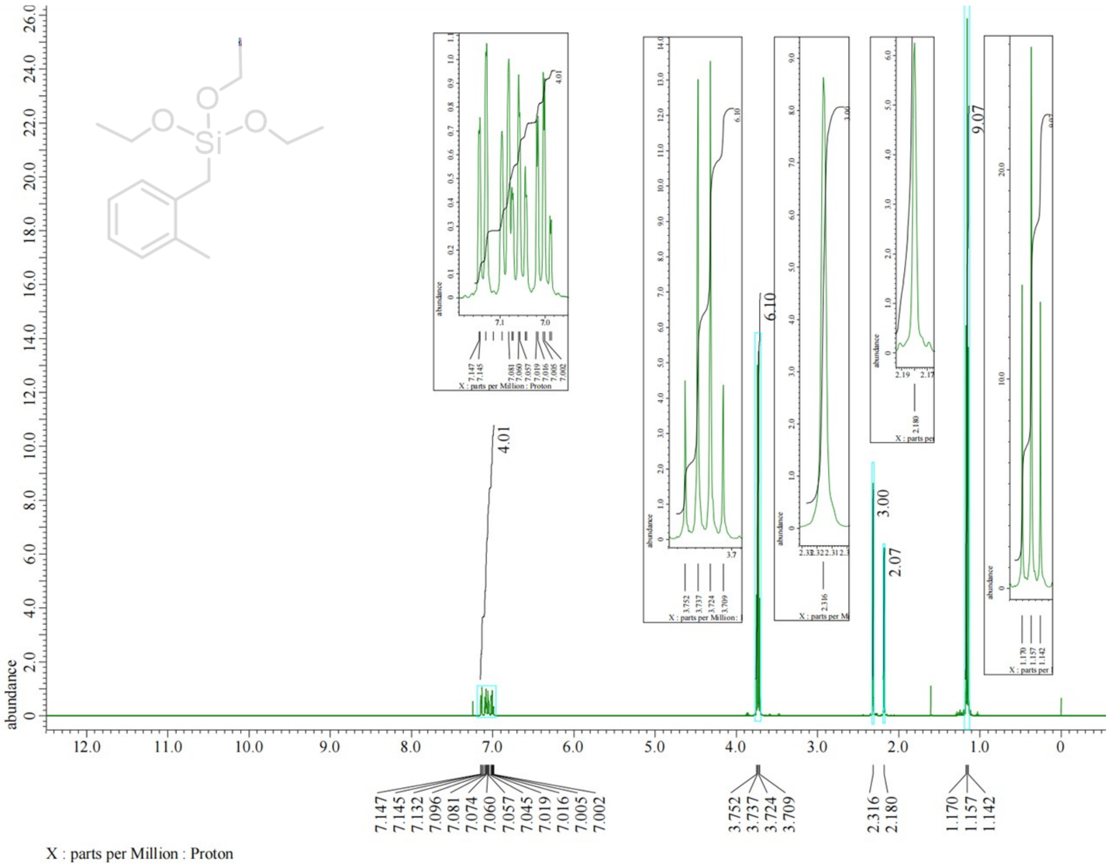
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2a**



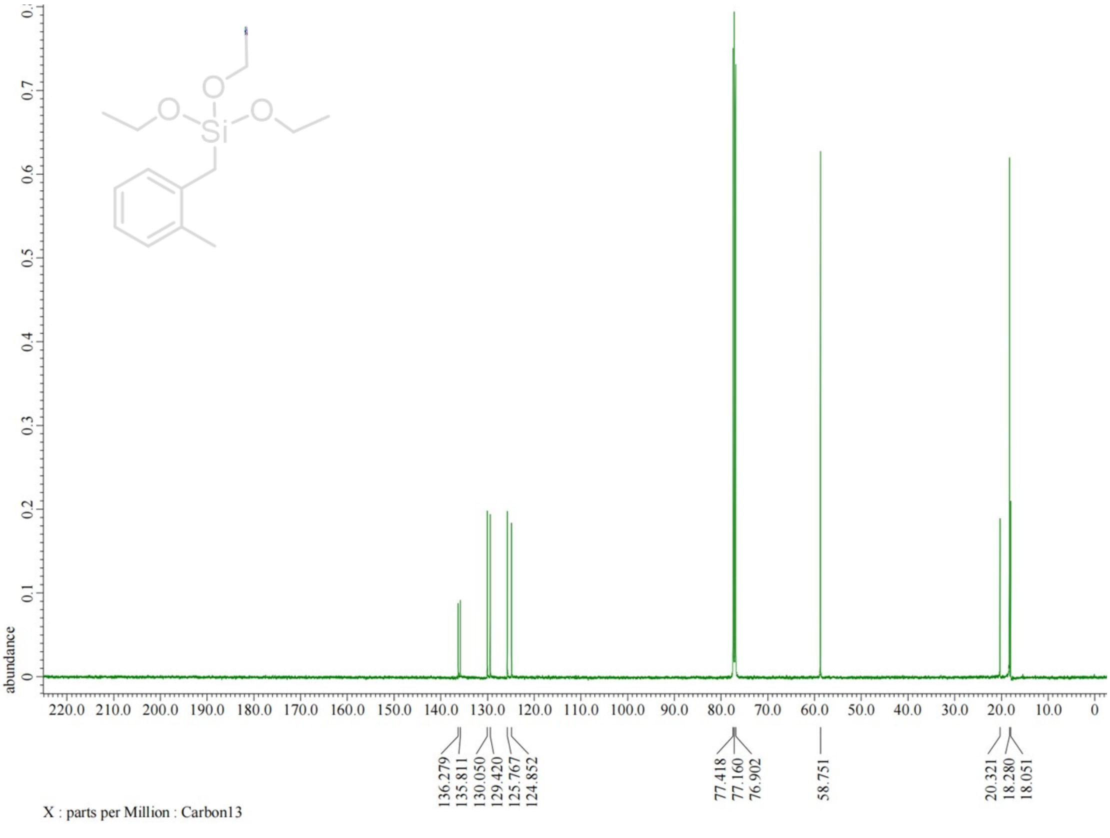
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2a**



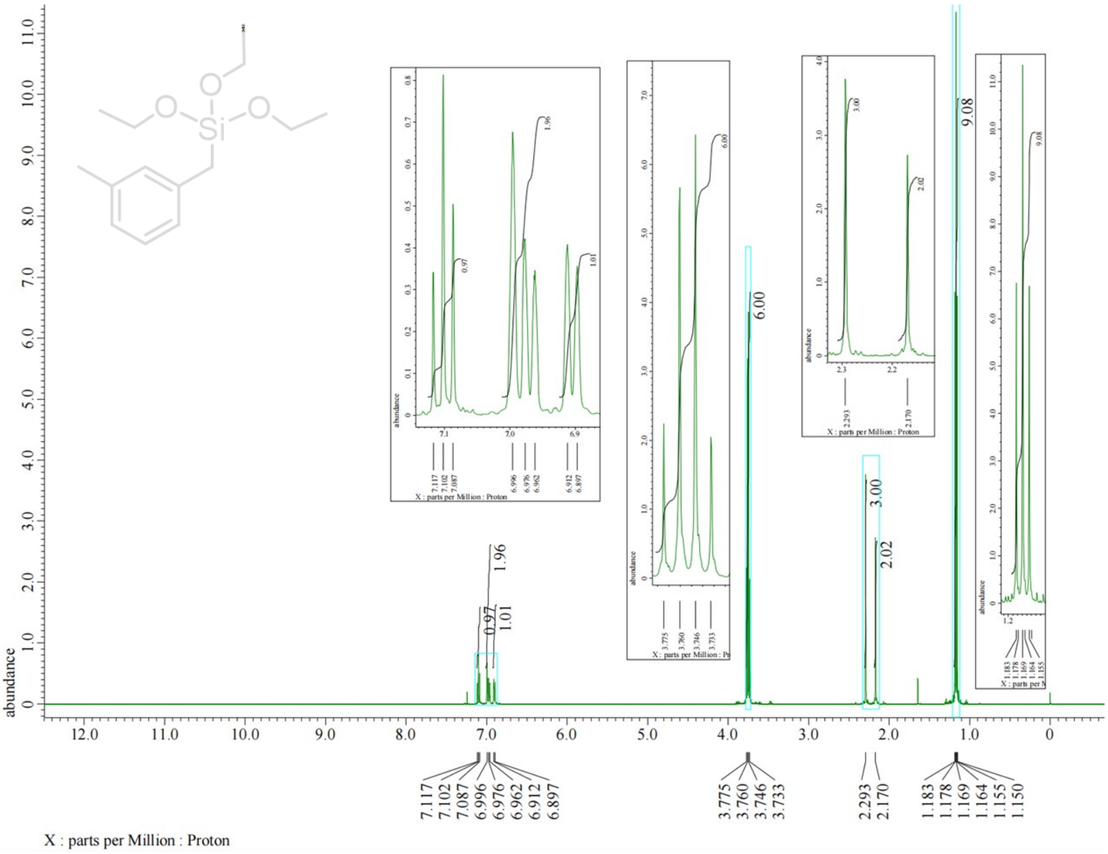
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2b**



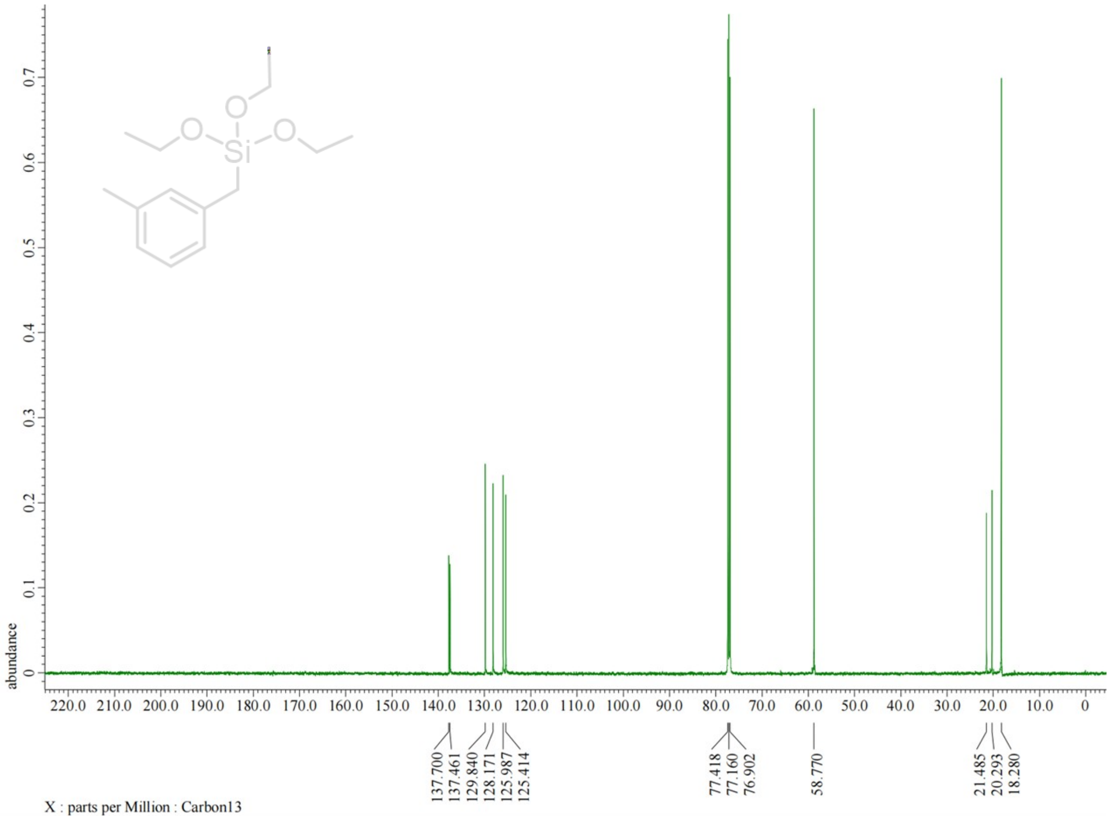
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2b**



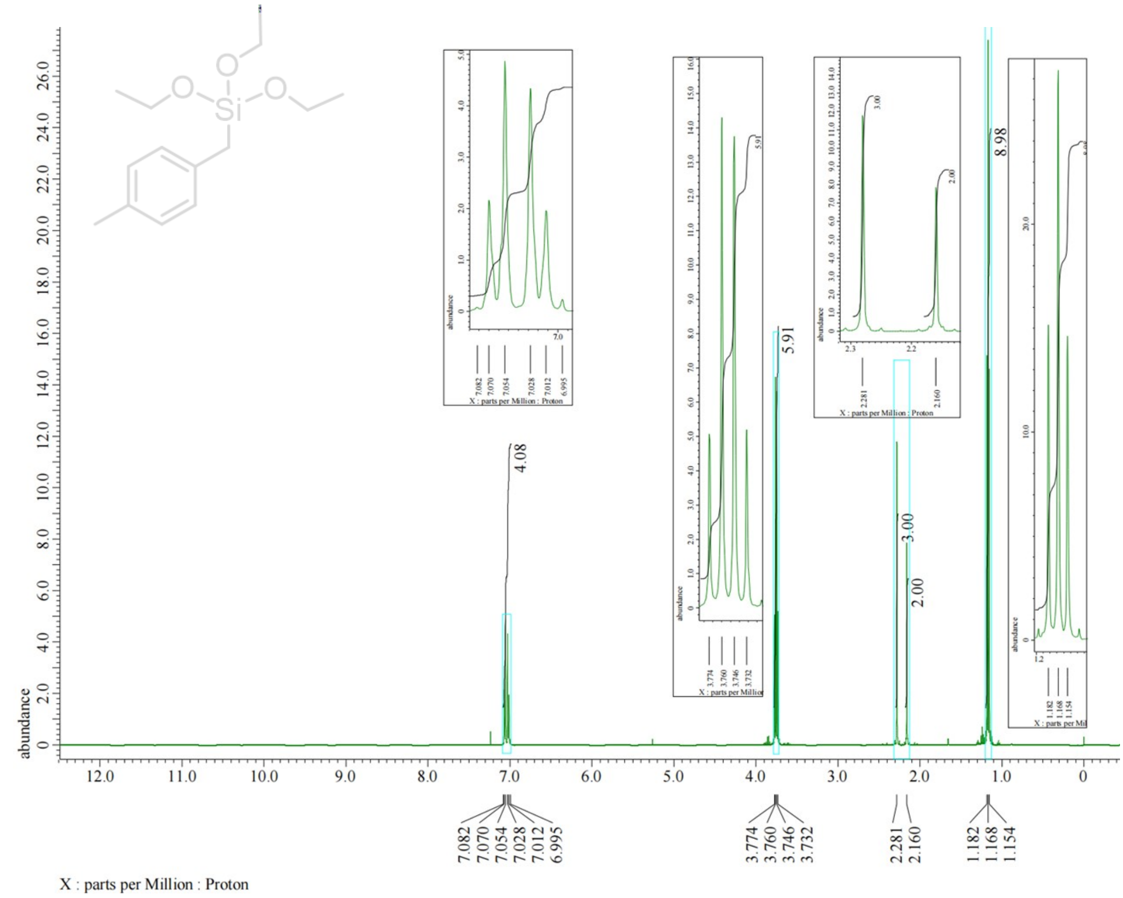
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2c**



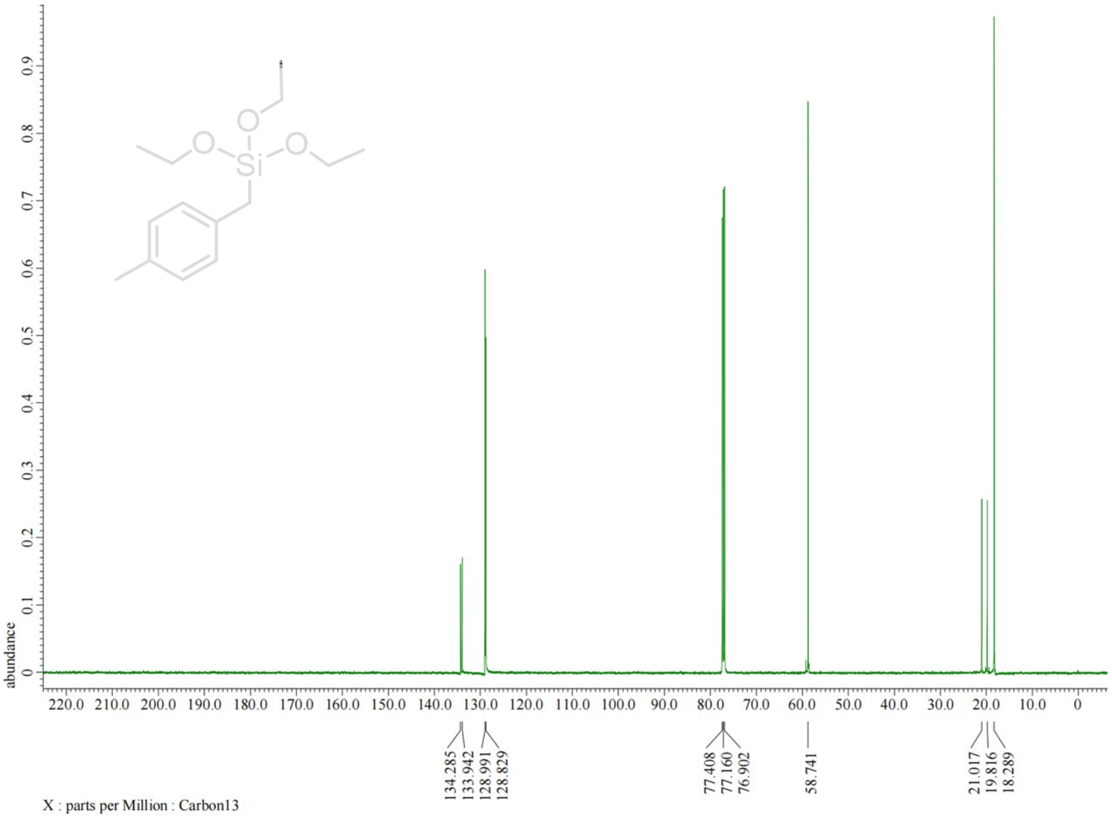
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2c**



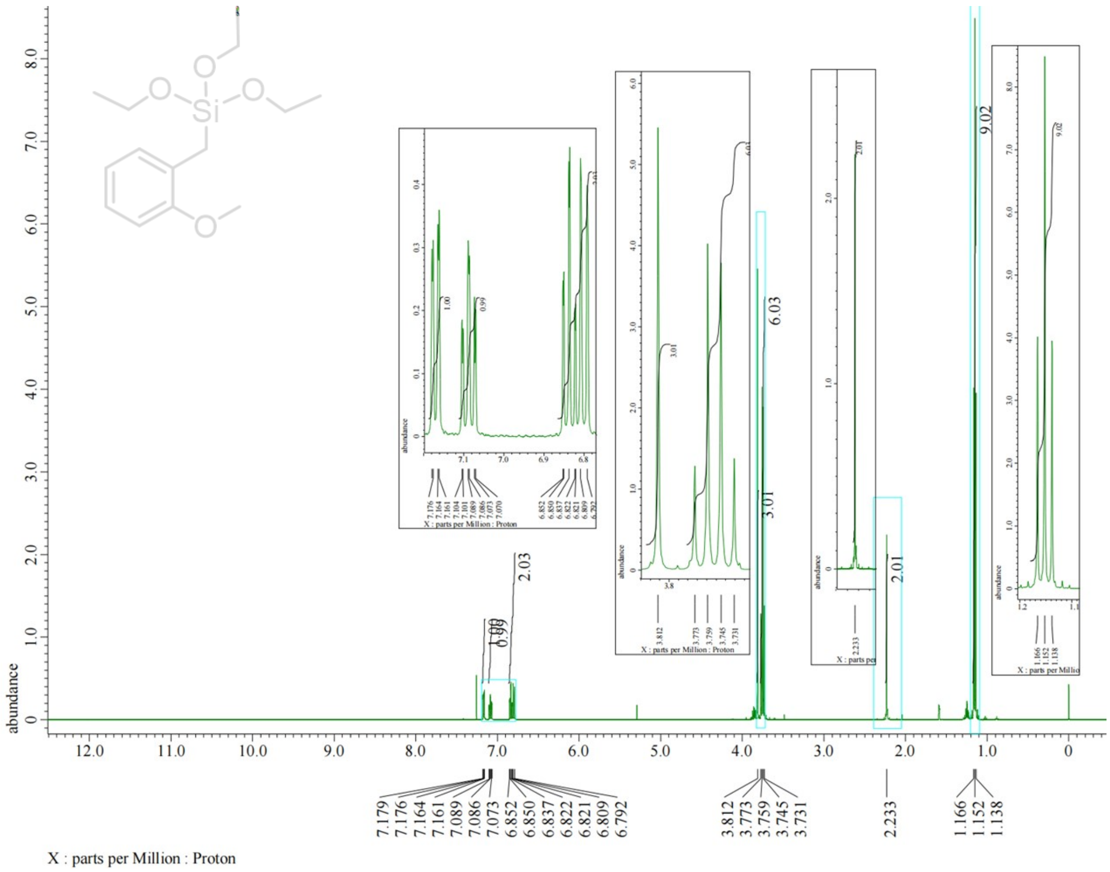
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2d**



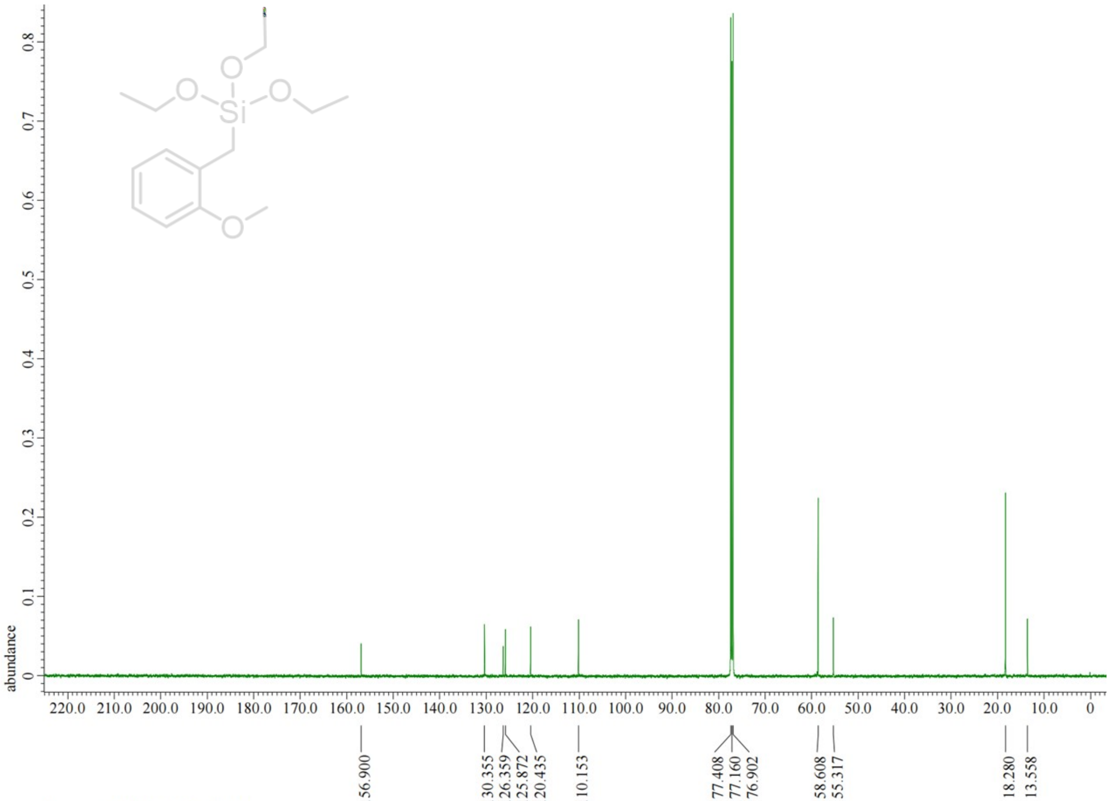
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2d**



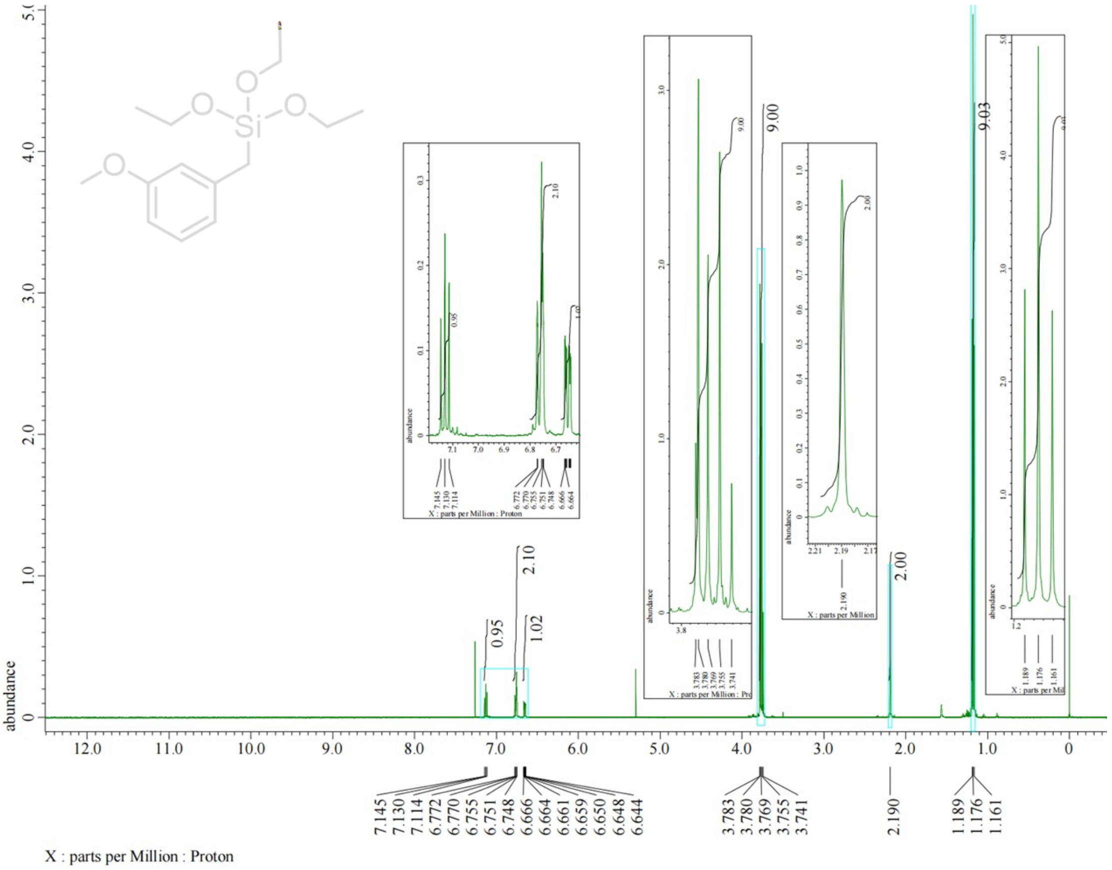
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2e**



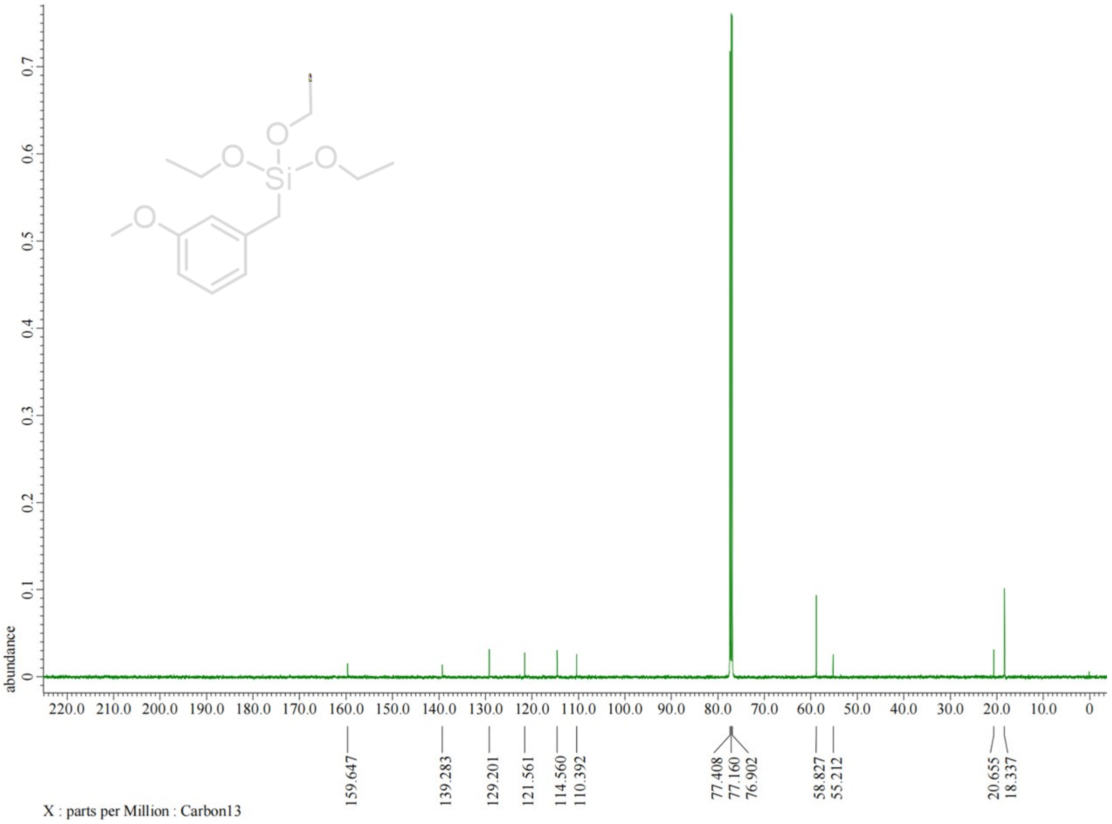
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2e**



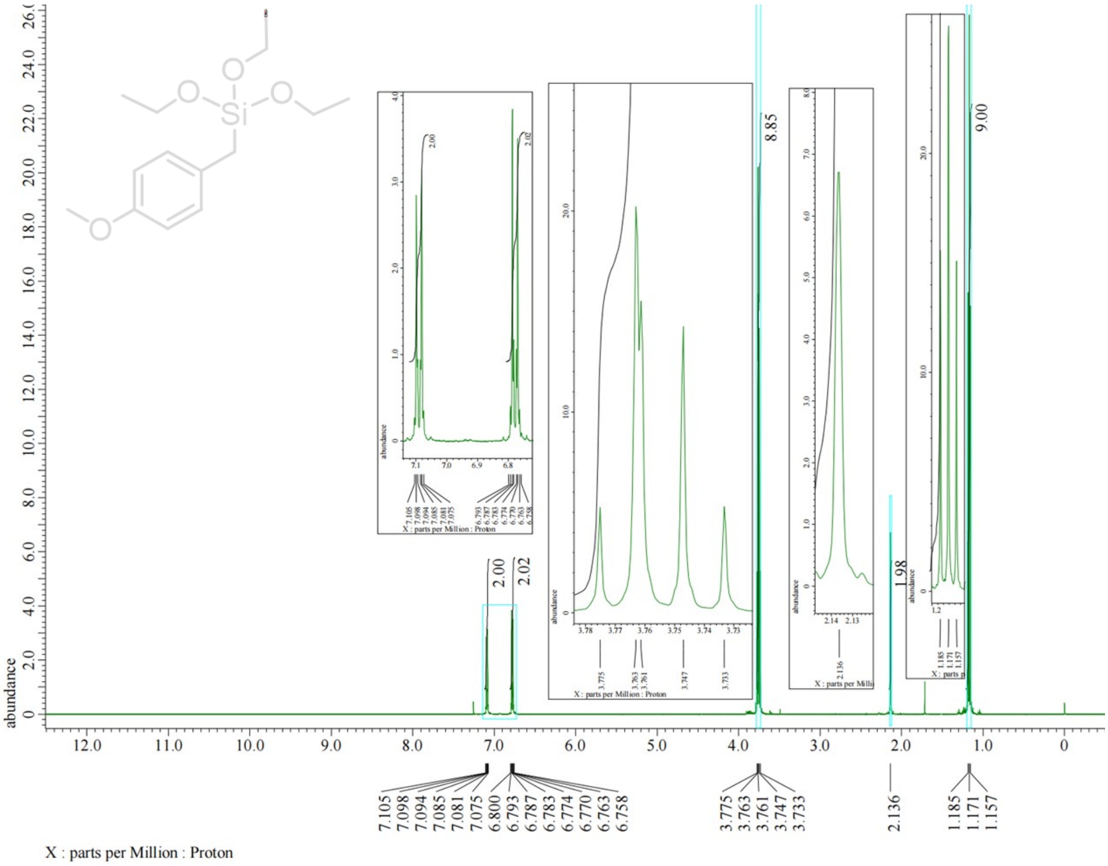
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2f**



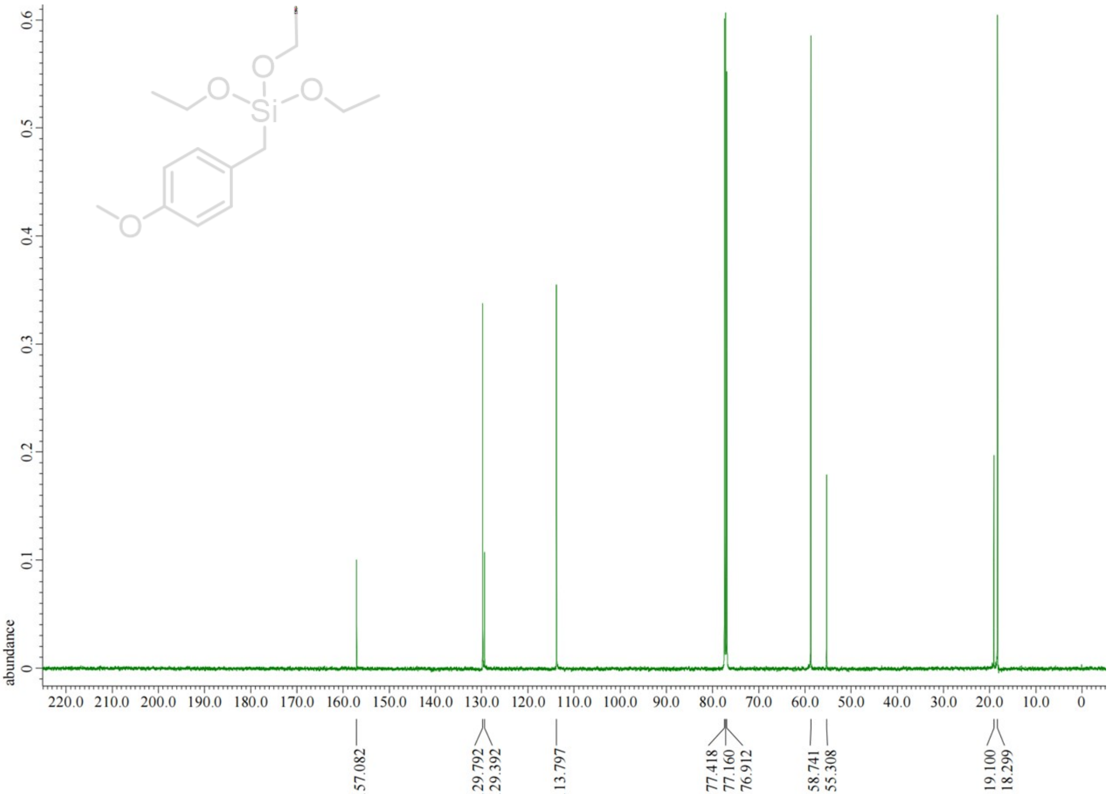
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2f**



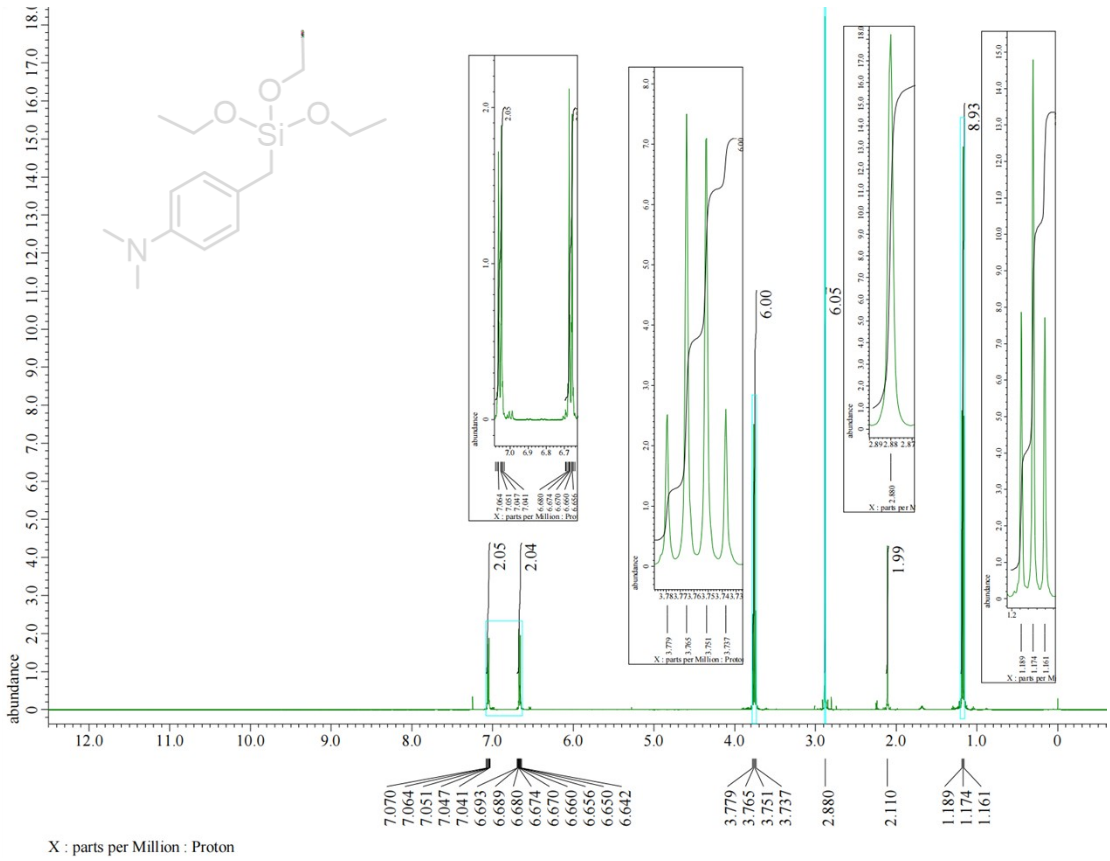
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2g**



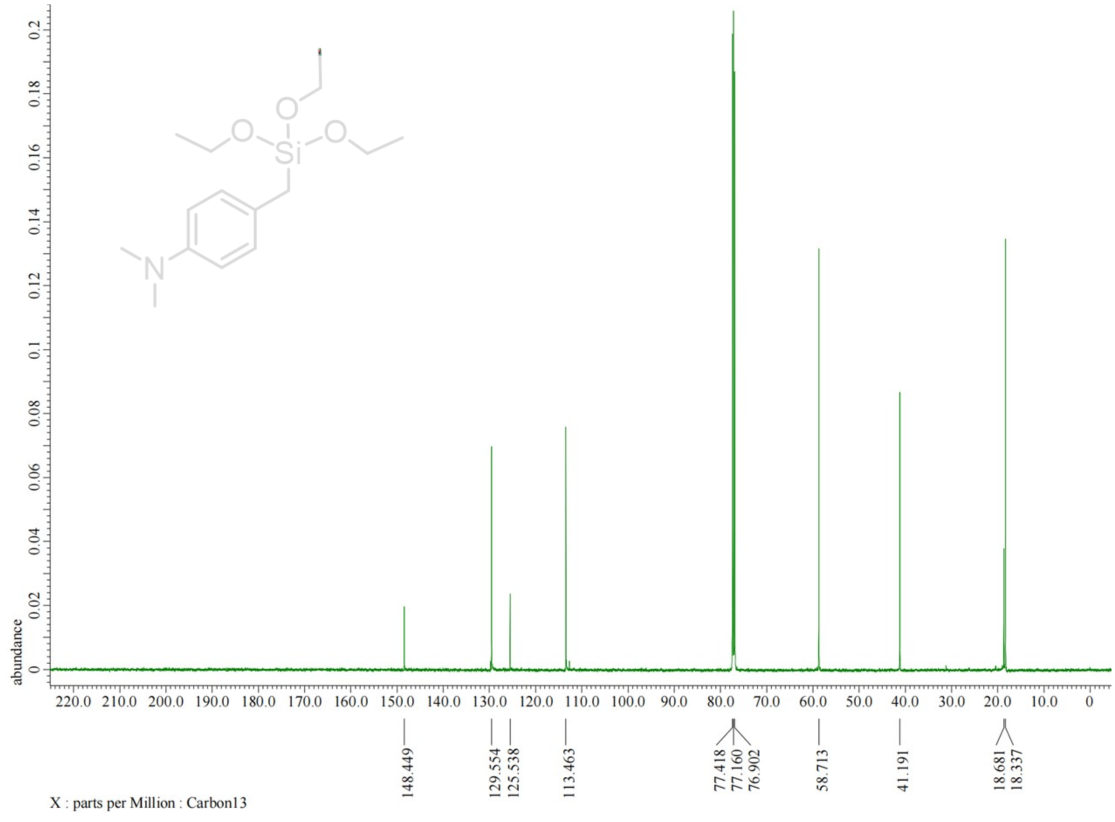
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2g**



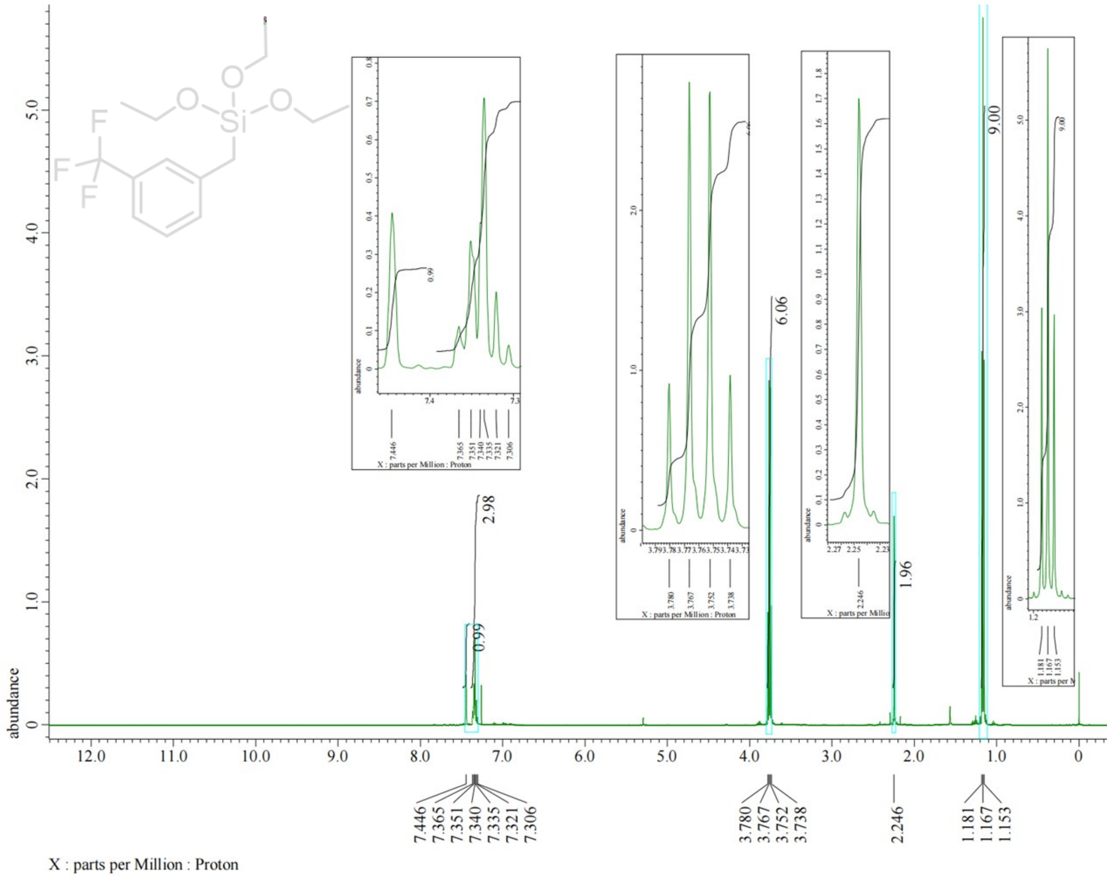
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2h**



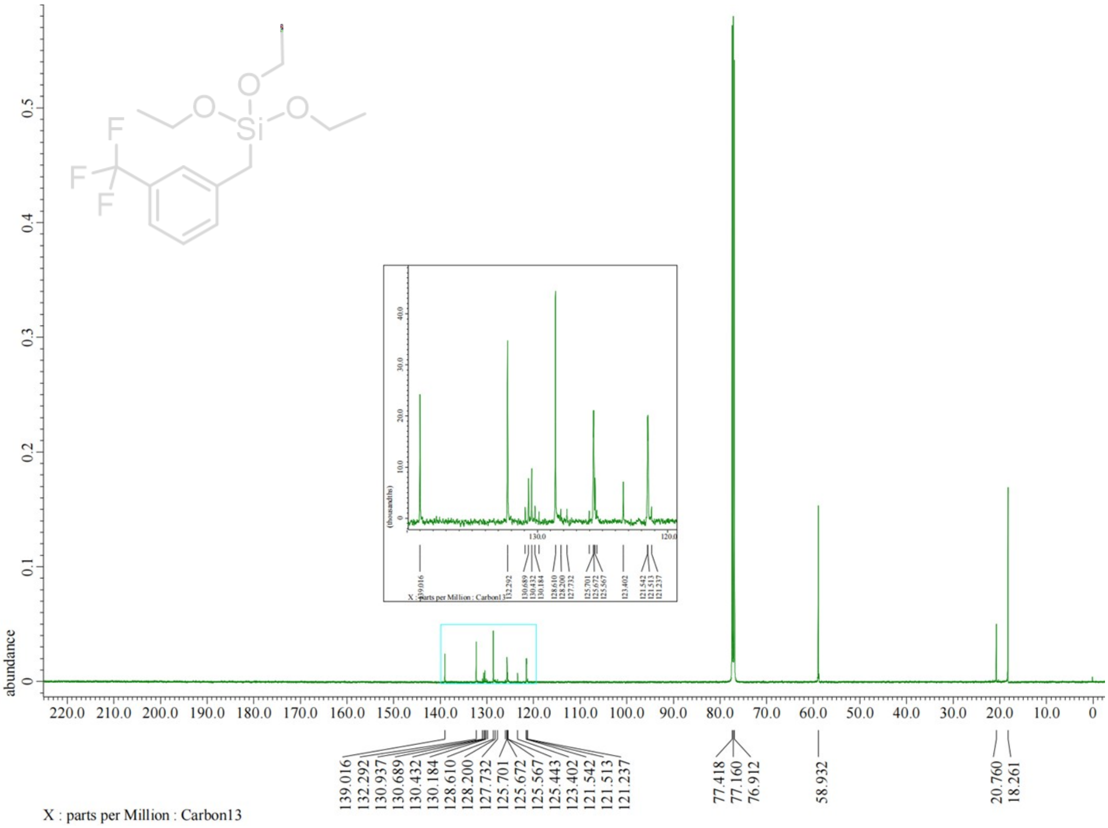
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2h**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2i**



^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2i**



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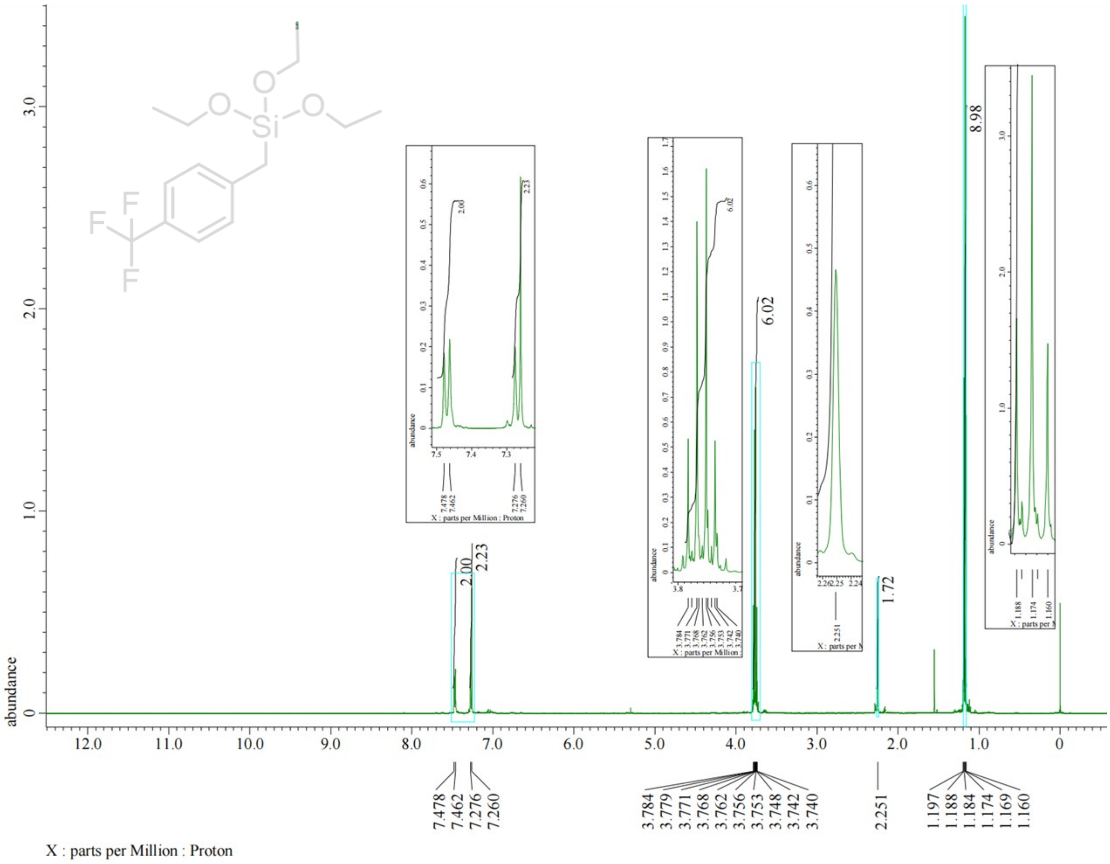

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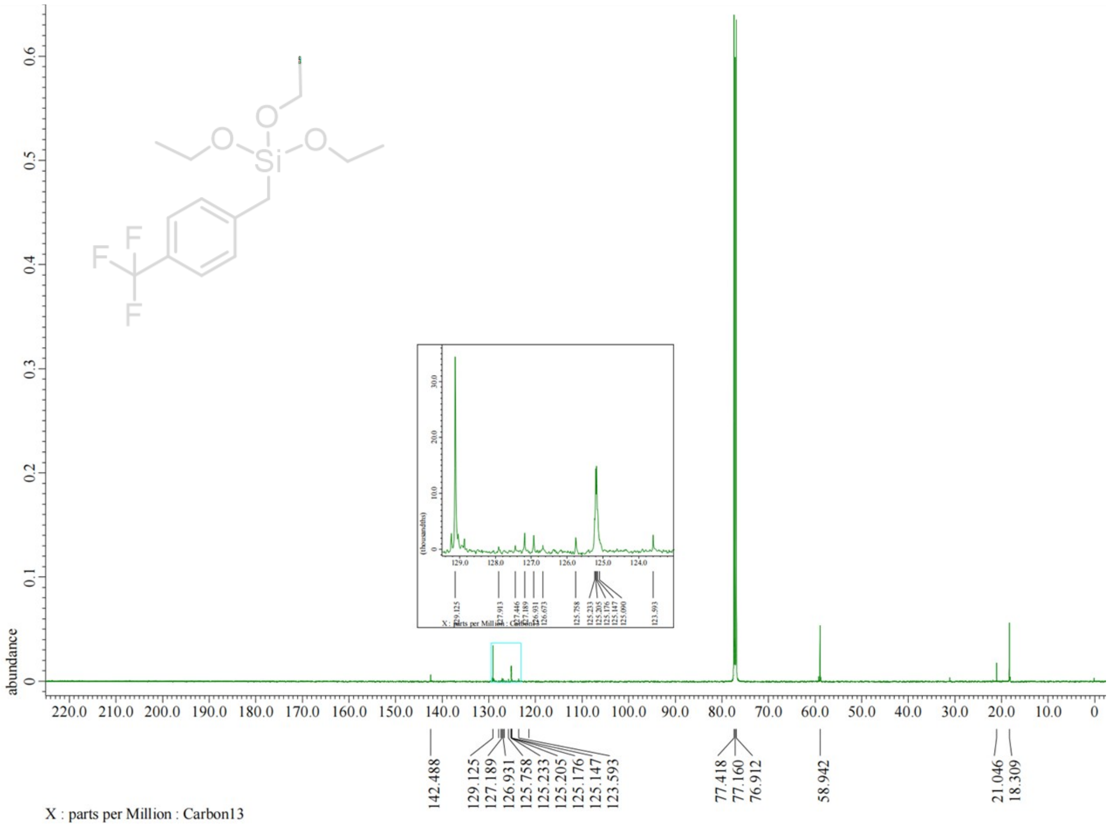
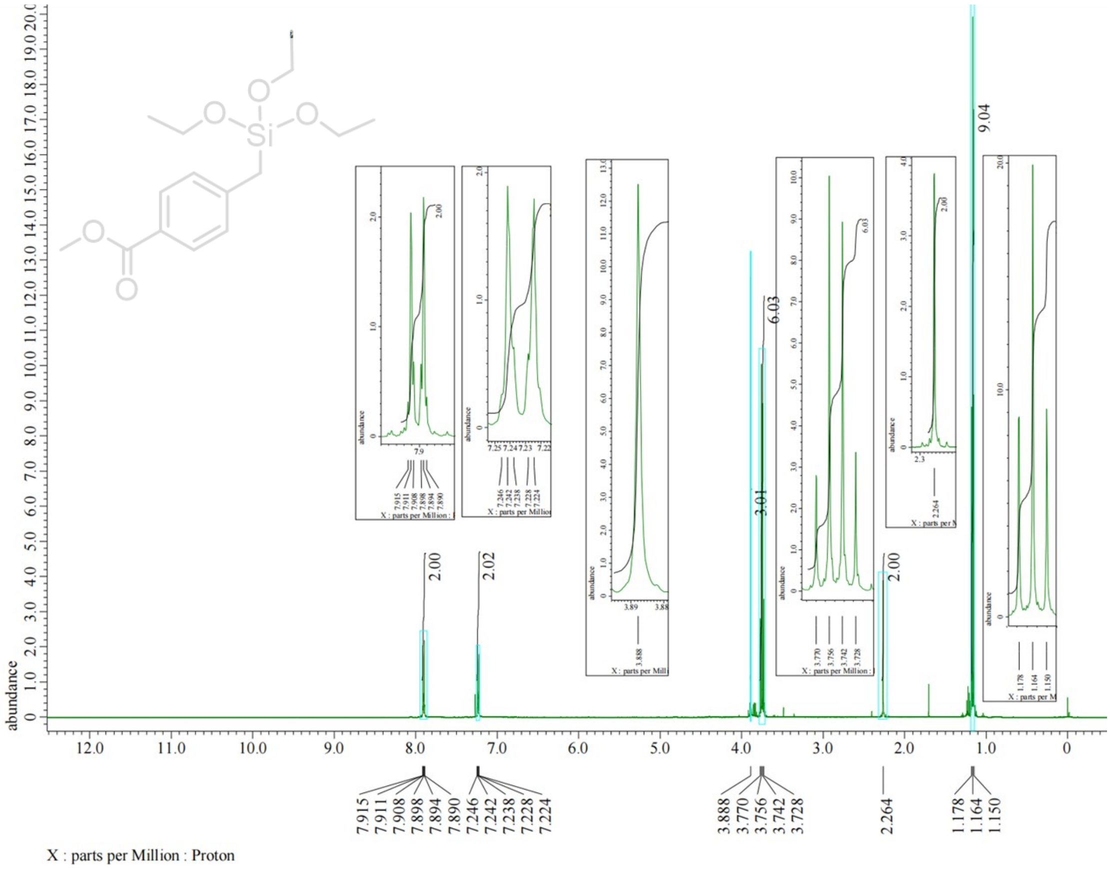
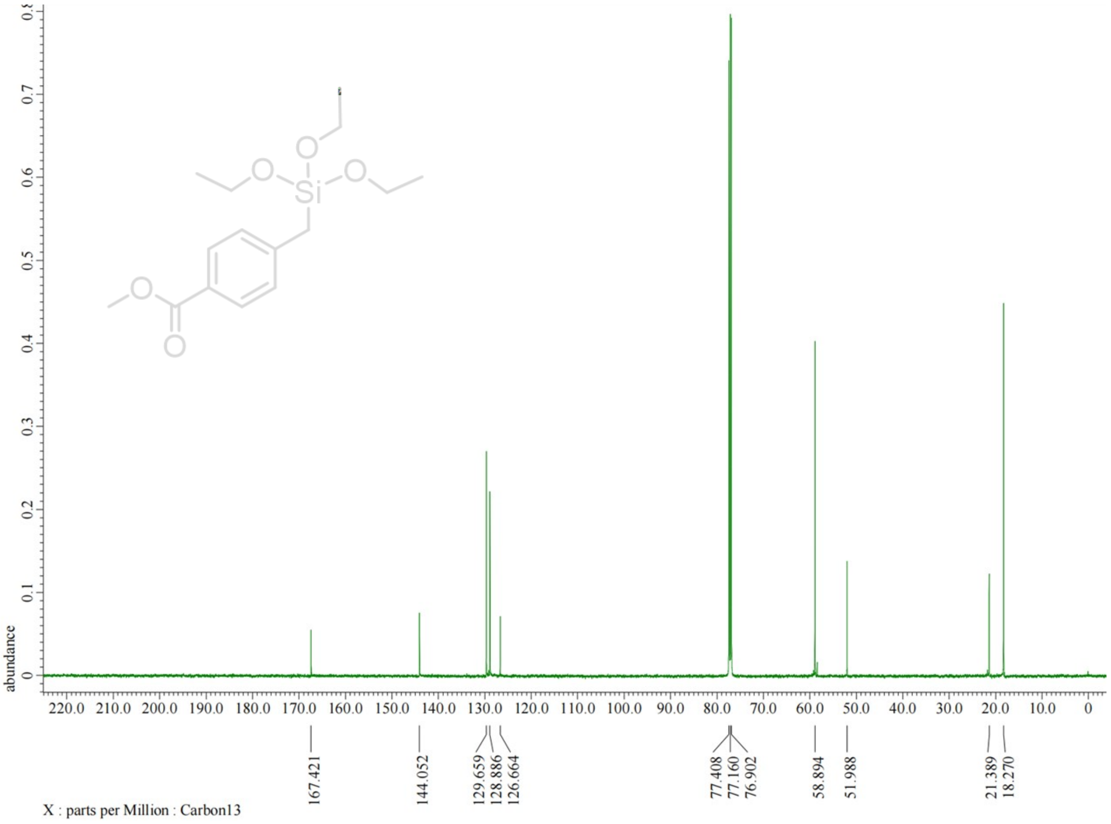


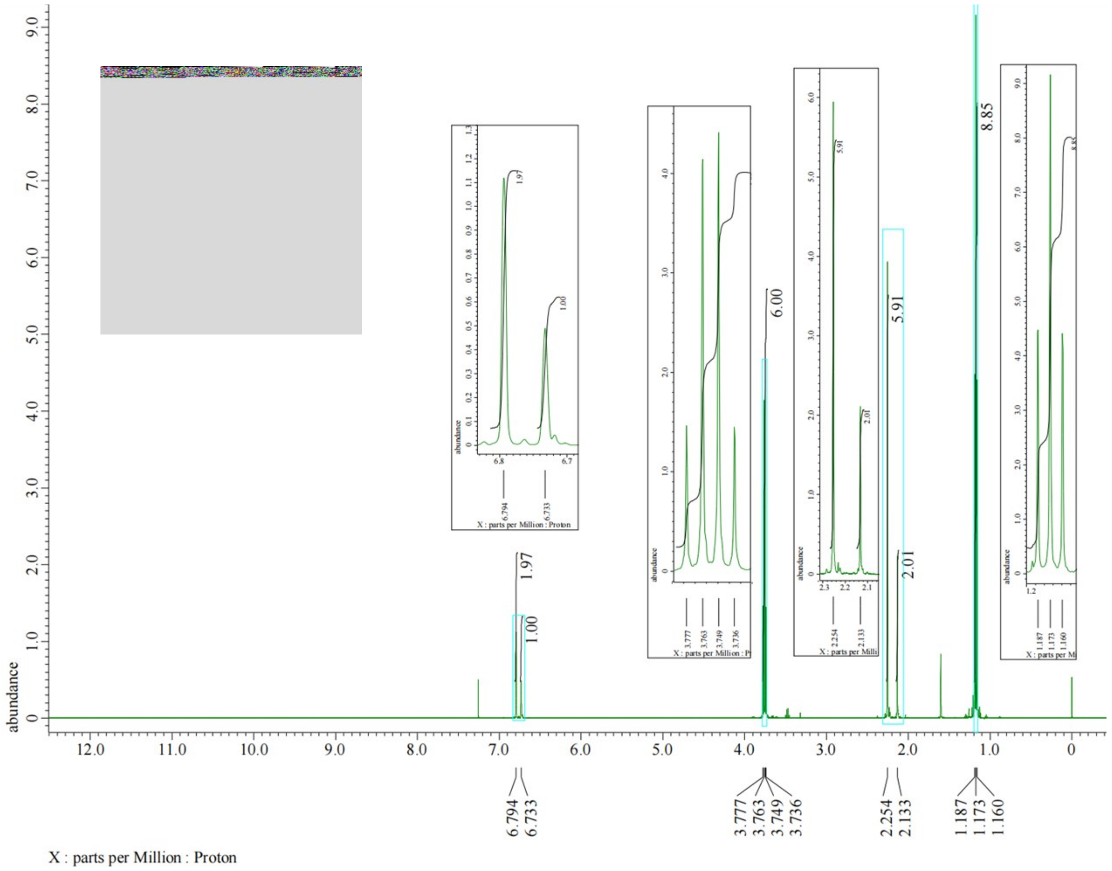
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2k**



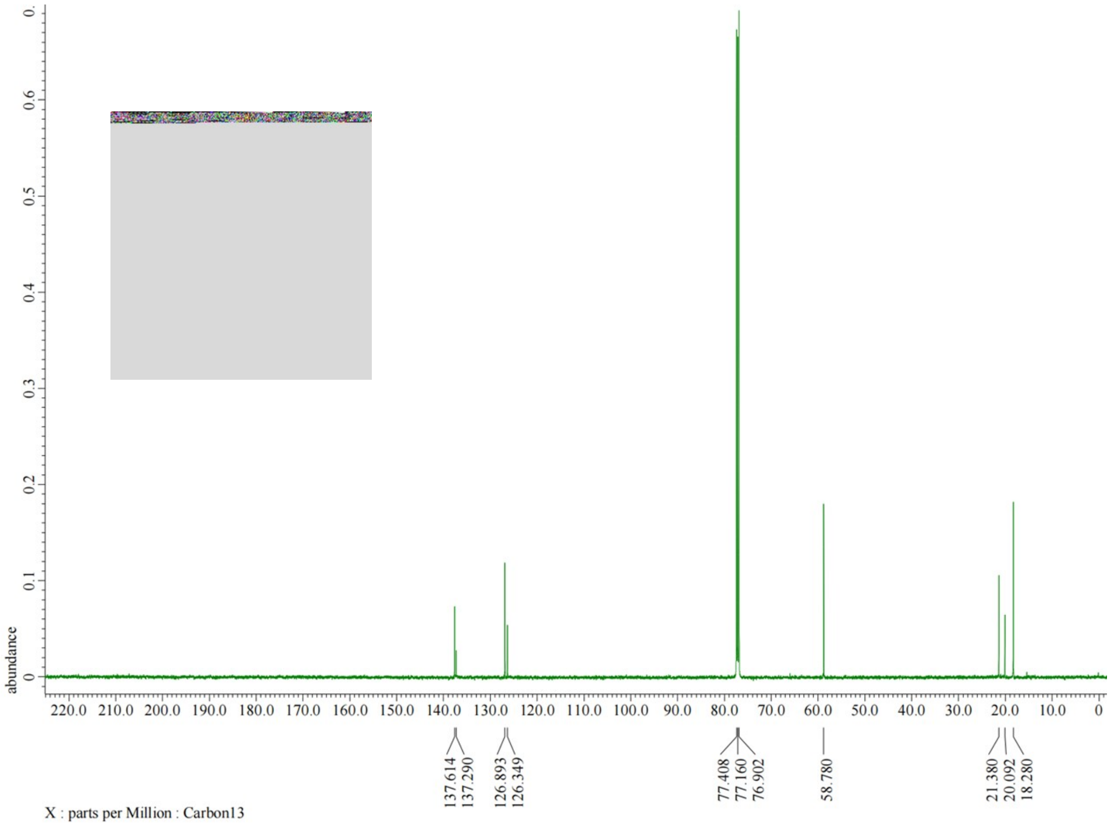
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2k**



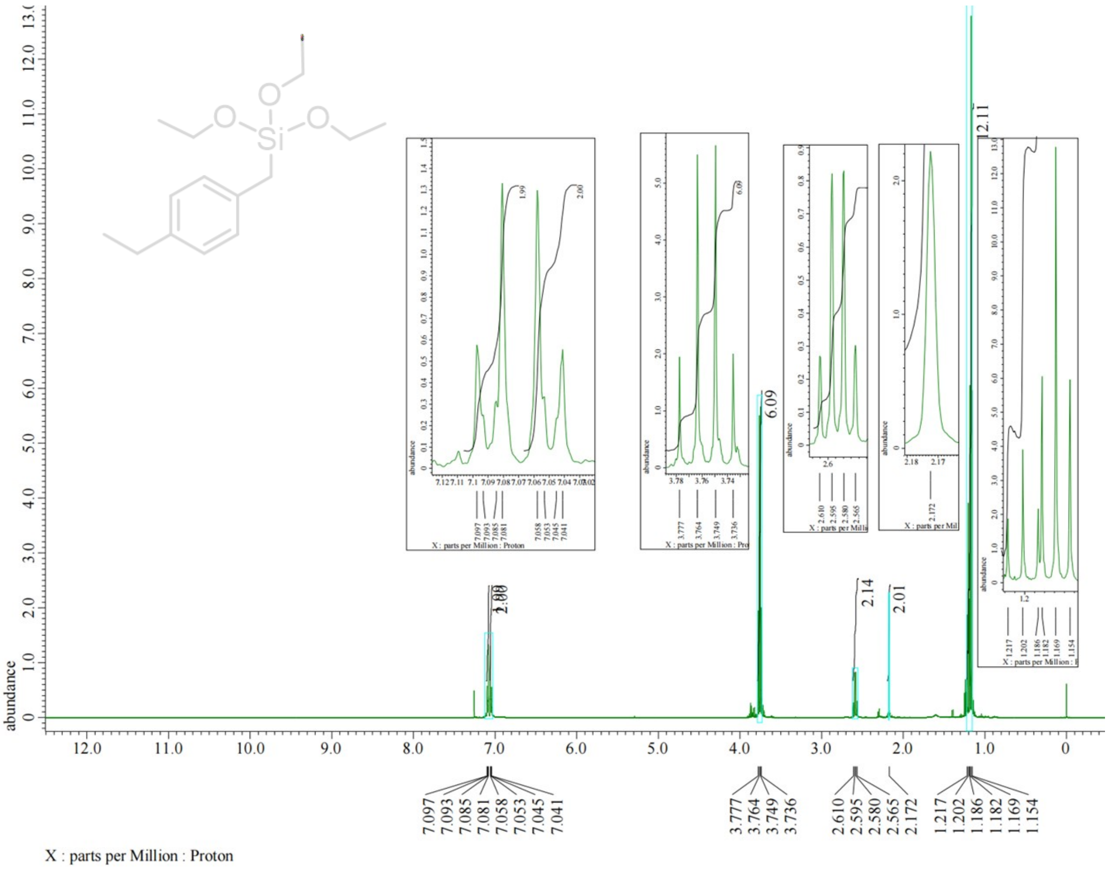
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2l**



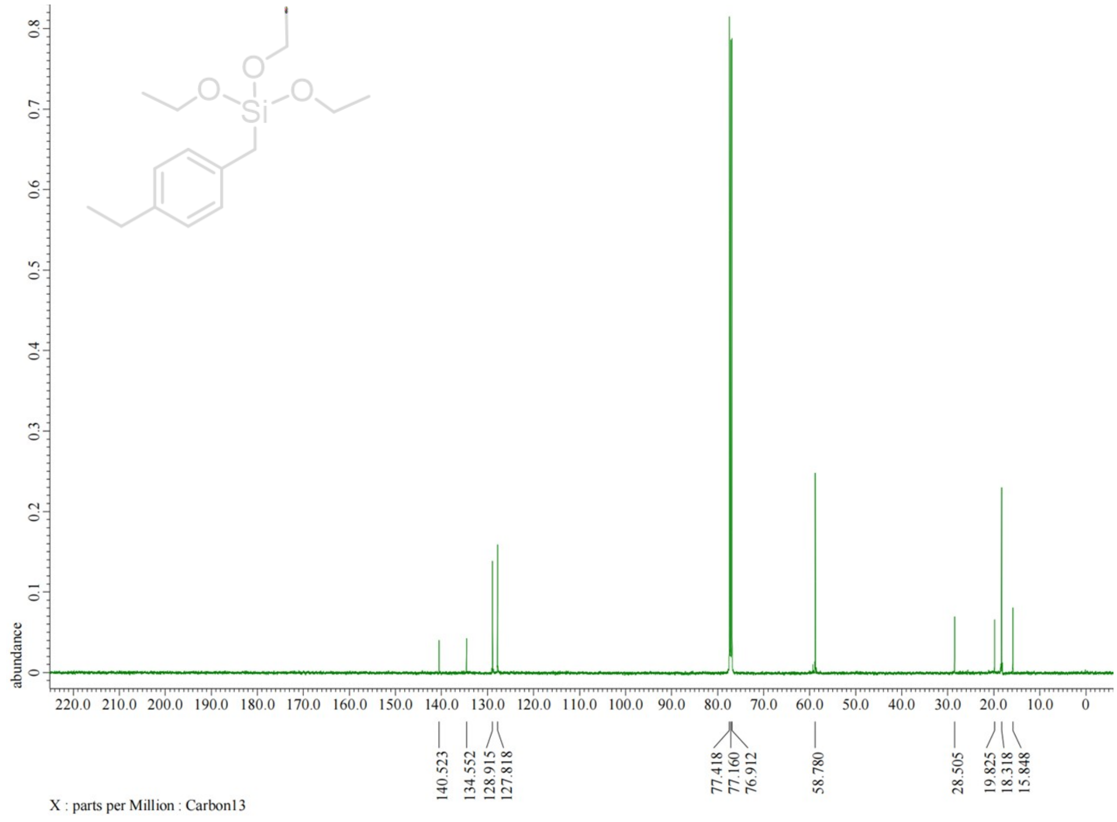
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2l**



^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2m**



^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2m**



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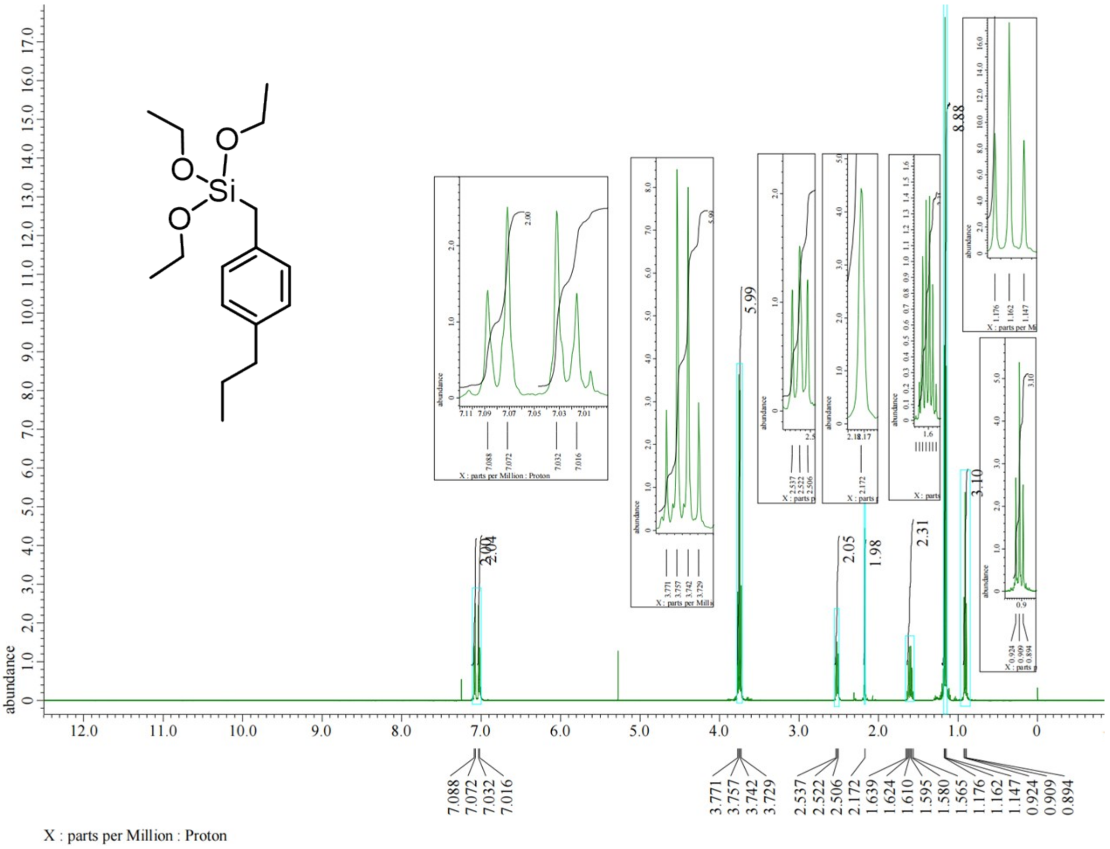
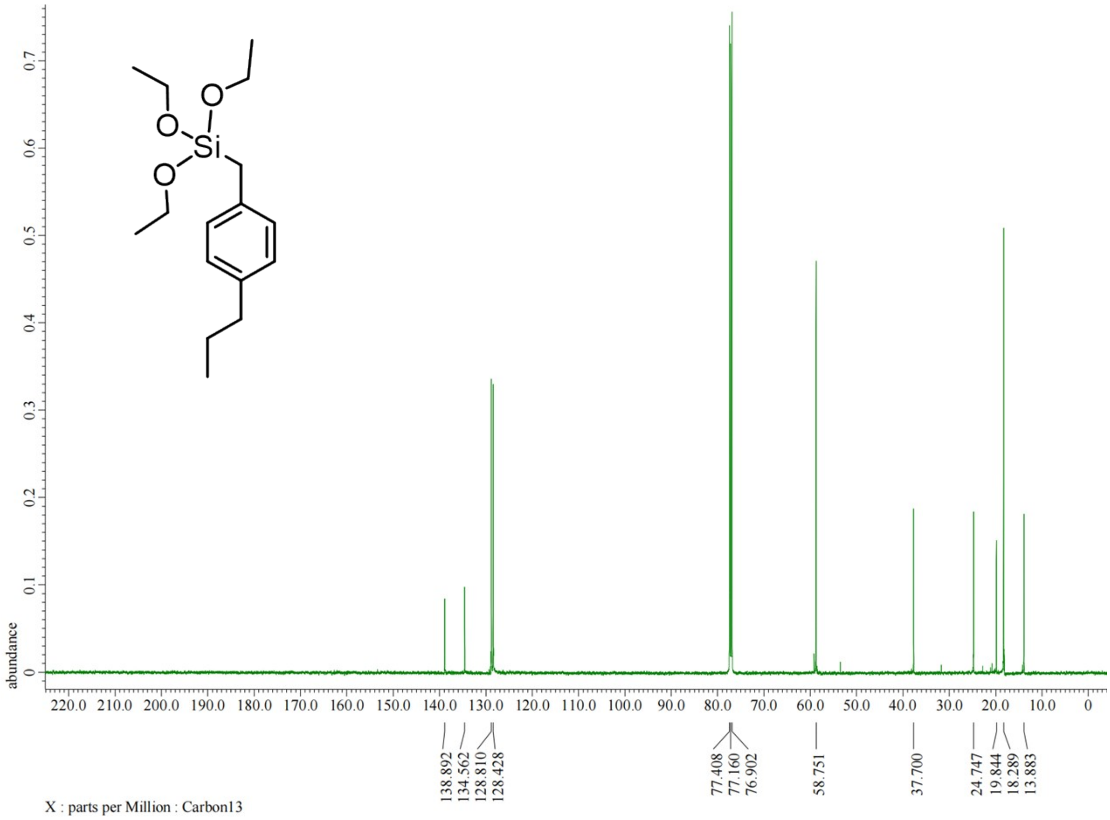
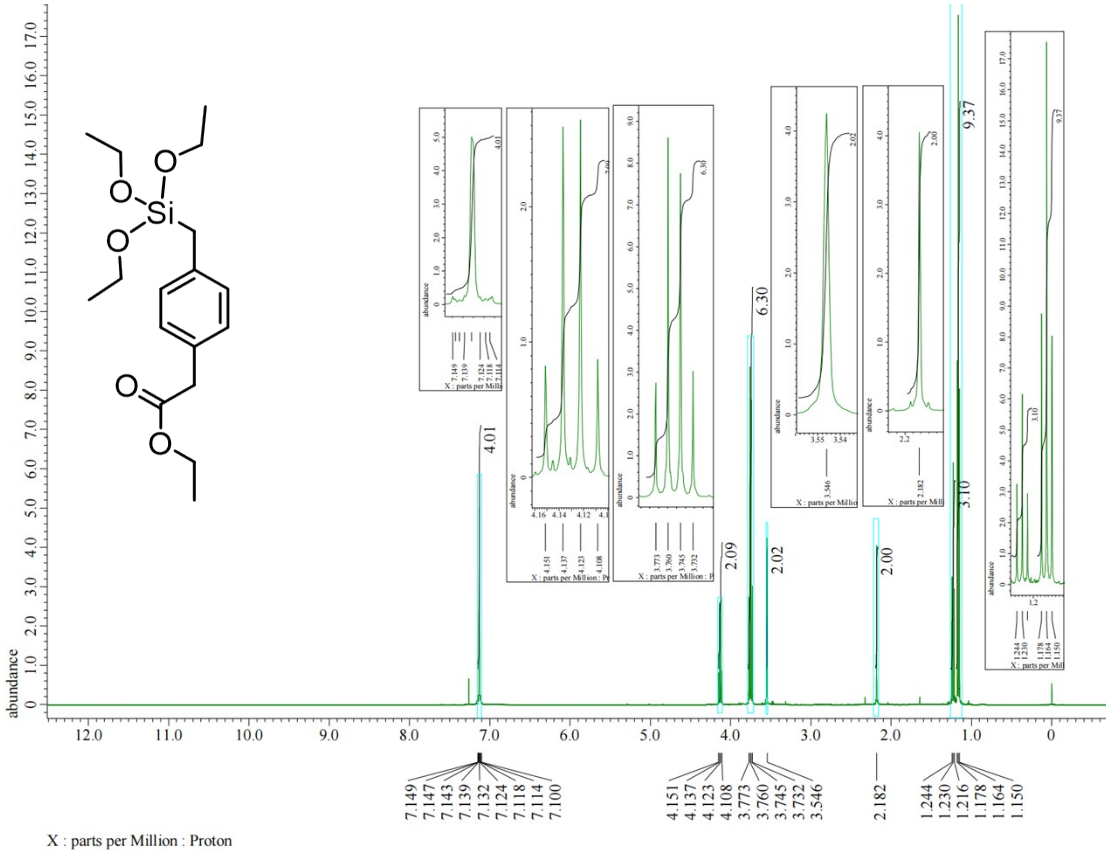


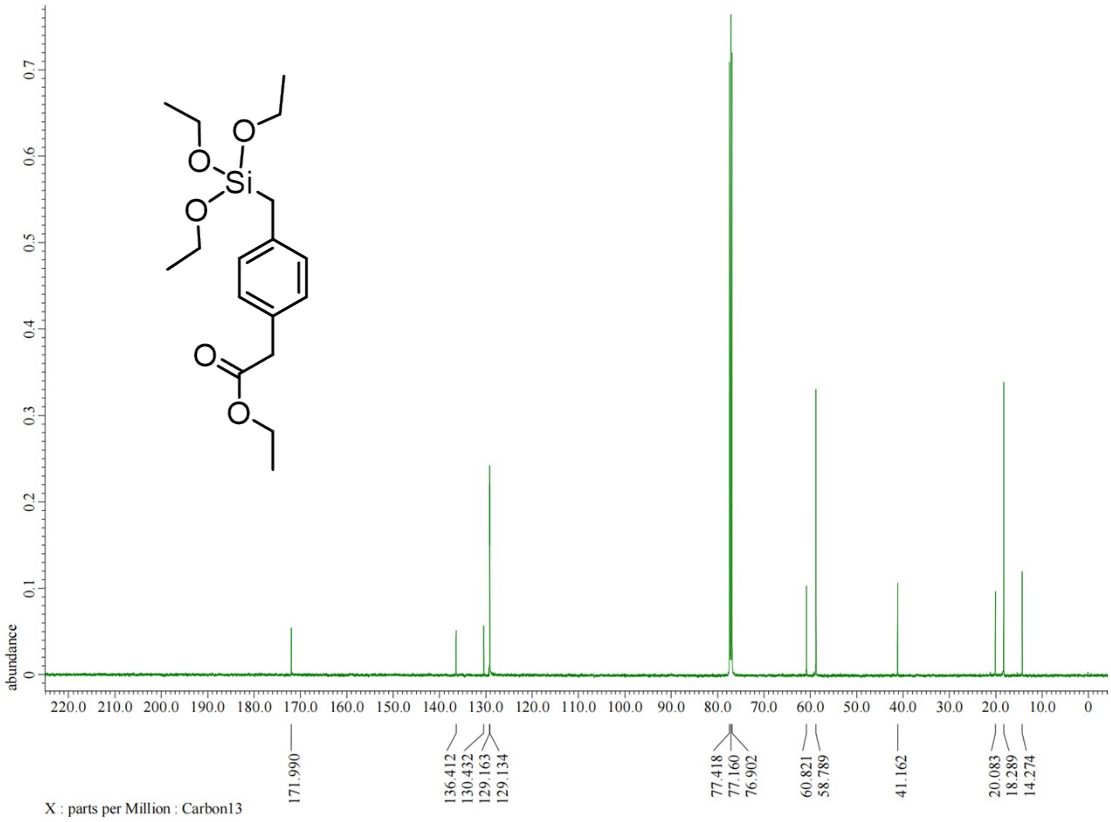
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2n**



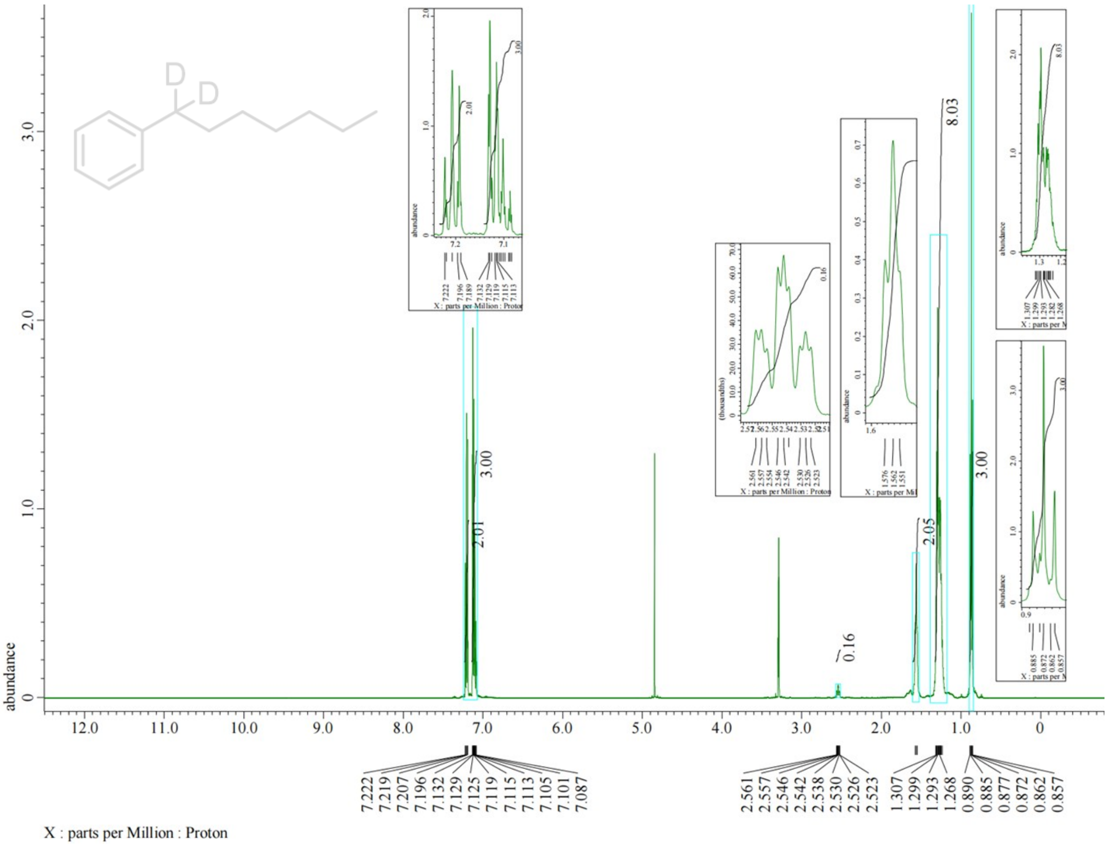
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **2o**



^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **2o**



^{1}H NMR spectrum (500 MHz, CD_3OD) of heptylbenzene-1,1-d_2



^{2}H NMR spectrum (77 MHz, CH_3OH) of heptylbenzene-1,1-d_2