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Supporting Information

Photo-Induced Ruthenium-Catalyzed Double Remote C(sp^2)–H / C(sp^3)–H Functionalizations by Radical Relay

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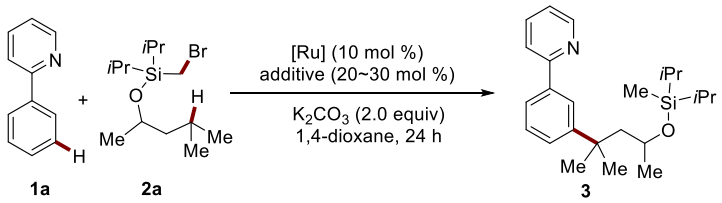
1. General Remarks

Catalytic reactions were performed under a N_2 atmosphere using pre-dried glassware. 1,4-Dioxane was dried over sodium and distilled under N_2. Methanol, dichloromethane, ethyl acetate, *n*-hexane and *n*-pentane were distilled prior to use. The reaction temperature was measured by digital thermometer PCE-T 390, which was in the range of 30 to 35 °C. The substrates were either purchased directly from commercial suppliers or prepared according to previously reported procedures, if not noted otherwise. All other reagents and solvents used in this study were purchased from commercial sources and used as received. Chromatography was carried out on Merck silica gel 60 (40–63 μm). NMR spectra were recorded on a Varian Mercury VX 300 or Bruker Avance III 400 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha-P device. EI-MS spectra were recorded on Jeol AccuTOF at 70eV, ESI-MS spectra on Bruker MicrOTOF and maXis. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected. Absorption spectra were measured on a Jasco V-770 spectrophotometer.

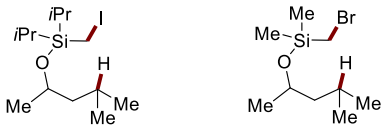
2. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions[a].



1a **2a** **3**

Entry	Catalyst	Additive	Solvent	Temperature	Yield (%)[b]
1	$Ru(OAc)_2$(*p*-cymene)	/	1,4-dioxane	80 °C	trace
2	$Ru(OAc)_2$(*p*-cymene)	Ph_3P	1,4-dioxane	80 °C	28
3	$Ru(OAc)_2$(*p*-cymene)	$(p\text{-}CF_3C_6H_4)_3P$	1,4-dioxane	80 °C	36
4	$[RuCl_2(p\text{-cymene})]_2$	$MesCO_2H$	1,4-dioxane	Blue LEDs, RT	trace
5	$[RuCl_2(p\text{-cymene})]_2$	$(n\text{-BuO})_2PO_2H$	1,4-dioxane	Blue LEDs, RT	34
6	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	73
7	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	DCE	Blue LEDs, RT	0
8	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	DMA	Blue LEDs, RT	16
9	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	DMF	Blue LEDs, RT	16
10[c]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
11[d]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
12[e]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	82
13	$[RuCl_2(benzene)]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	77
14	$Ru(OAc)_2$(*p*-cymene)	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	13
15	$RuCl_3{\cdot}3H_2O$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
16	$Ru_3(CO)_{12}$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
17[f]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
18[g]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	0
19	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	No light, RT	0
20	$[RuCl_2(benzene)]_2$	$(PhO)_2PO_2H$	1,4-dioxane	No light, RT	0
21	$[RuCl_2(benzene)]_2$	$(PhO)_2PO_2H$	1,4-dioxane	No light, 60 °C	trace
22	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	No light, 100 °C	22
23[h]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	30
24[i]	$[RuCl_2(p\text{-cymene})]_2$	$(PhO)_2PO_2H$	1,4-dioxane	Blue LEDs, RT	< 20% (mixture)

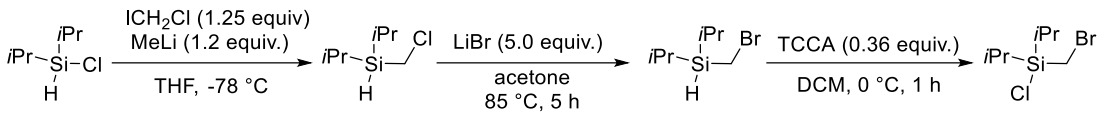


4 **4'**

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), [Ru] (0.05 mmol), additive (0.1 mmol for PPh_3 and $(p\text{-}CF_3C_6H_4)_3P$, 0.15 mmol for the others), K_2CO_3 (1.0 mmol), 1,4-dioxane (2.0 mL), RT = 30-35 °C. [b] Yield of isolated products. [c] Using KOAc as base. [d] No base. [e] **2a** (1.0 mmol). [f] Under air. [g] H_2O (1.0 mmol) was added into the solution. [h] Using **4** instead of **2a**. [i] Using **4'** instead of **2a**.

3. Syntheses of Starting Materials.

Synthesis of chloro(bromomethyl)diisopropylsilane:



At -78 °C, MeLi (1.6 M in ether, 60 mL, 96 mmol, 1.20 equiv,) was added dropwise into a solution of dichlorodiisopropylsilane (80 mmol, 12.06 g) and chloroiodomethane (100 mmol, 17.64 g, 1.25 equiv) in THF (100 mL). The reaction mixture was stirred at -78 °C for 2 h and then allowed to warm to room temperature before quenching with saturated NH_4Cl solution. The aqueous layer was extracted with *n*-hexane. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane) to afford (chloromethyl)diisopropylsilane (9.62 g, 73%).

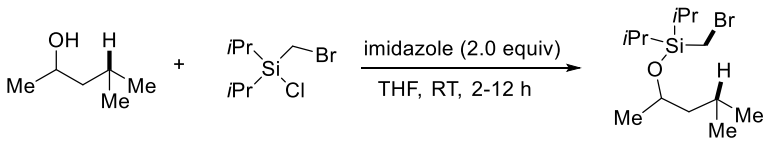
(Chloromethyl)diisopropylsilane (58 mmol, 9.62 g) was added into a stirred solution of LiBr (290 mmol, 25.2 g, 5 equiv) in acetone (200 mL). The mixture was refluxed at 85 °C for 5 h. The reaction was allowed to cool to room temperature before quenching with saturated solution of $Na_2S_2O_3$.The aqueous layer was extracted with *n*-hexane. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product (bromomethyl)diisopropylsilane (11.5 g, 95% yield) was used for the next step without further purification.

Under N_2, (bromomethyl)diisopropylsilane (55 mmol in 10 mL DCM) was added dropwise into a solution of TCCA (20.0 mmol, 4.64 g, 0.36 equiv) in dry DCM (100 mL) at 0 °C for 1.0 h. The mixture was allowed to warm to r.t. and filtered through celite and concentrated. The residue was then dissolved in *n*-hexane and re-filtered through celite and then concentrated to yield chloro(bromomethyl)diisopropylsilane (12.6 g, 94%, >95% purity) as a colorless oil, which was used for the next step without further purification.

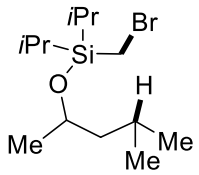
(Bromomethyl)chlorodiisopropylsilane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.68 (s, 2H), 1.46 – 1.34 (m, 2H), 1.18 – 1.12 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 17.3 (CH_3), 16.9 (CH_3), 13.1 (CH_2), 11.6 (CH). **IR** (ATR): 2955, 2868, 1463, 1390, 1068, 998, 882,

734 cm^{-1}. **MS** (EI) *m*/*z* (relative intensity): 201 $[M\text{-}i\text{Pr}]^+$ (100) ($^{81}Br^{35}Cl$), 199 $[M]^+$ (97) ($^{79}Br^{35}Cl$). **HR-MS** (EI) *m*/*z* calcd for $C_4H_9{}^{81}Br^{35}ClSi$ $[M\text{-}i\text{Pr}]^+$: 200.9319, found: 200.9319.

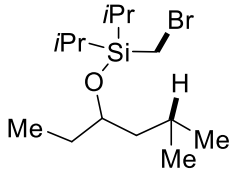
Synthesis of Si-tethered alcohols.



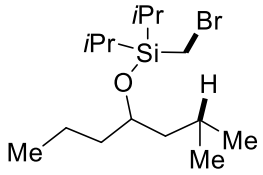
General procedure: Under N_2 atmosphere, chloro(bromomethyl)diisopropylsilane (1.0 equiv.) was added into a solution of alcohol (1.1 equiv.) and imidazole (2.0 equiv.) in THF (5.0 mL/mmol of alcohol) at room temperature. After being stirred for 2-12 h, the reaction mixture was diluted with *n*-hexane and then filtered. Then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane or *n*-hexane/EtOAc) to afford the corresponding products.



(Bromomethyl)diisopropyl((4-methylpentan-2-yl)oxy)silane (**2a**). The product was obtained following the general procedure using alcohol (22 mmol) and chloro(bromomethyl)diisopropylsilane (20 mmol) for 6 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2a** (4.70 g, 76%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.10 – 4.00 (m, 1H), 2.58 (s, 2H), 1.73 – 1.64 (m, 1H), 1.47 – 1.38 (m, 1H), 1.29 – 1.13 (m, 6H), 1.10 – 1.07 (m, 12H), 0.95 – 0.84 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 67.9 (CH), 49.3 (CH_2), 24.9 (CH_3), 24.2 (CH), 23.2 (CH_3), 23.0 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.4 (CH), 12.4 (CH_2), 12.4 (CH). **IR** (ATR): 2957, 2867, 1463, 1376, 1127, 1071, 996, 960, 885 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 331 $[M+Na]^+$ (97) (^{79}Br), 333 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{13}H_{29}O^{81}BrSiNa$ $[M+Na]^+$: 333.1043, found: 333.1036.

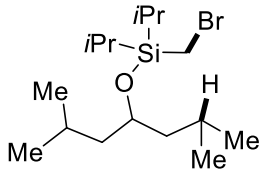


(Bromomethyl)diisopropyl((5-methylhexan-3-yl)oxy)silane (**2b**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2b** (820 mg, 63%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.91 – 3.85 (m, 1H), 2.58 (s, 2H), 1.73 – 1.61 (m, 1H), 1.59 – 1.42 (m, 2H), 1.40 – 1.27 (m, 2H), 1.24 – 1.13 (m, 2H), 1.11 – 1.06 (m, 12H), 0.92 – 0.85 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 72.6 (CH), 45.8 (CH_2), 29.9 (CH_2), 24.7 (CH), 23.2 (CH_3), 23.2 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 12.6 (CH_2), 12.5 (CH), 12.5 (CH), 9.1 (CH_3). **IR** (ATR): 2958, 2868, 1463, 1379, 1125, 1081, 883, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 345 $[M+Na]^+$ (97) (^{79}Br), 347 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{14}H_{31}O^{79}BrSiNa$ $[M+Na]^+$: 345.1220, found: 345.1216.

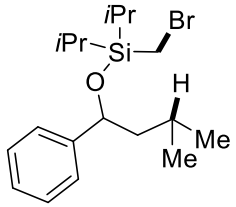


(Bromomethyl)diisopropyl((2-methylheptan-4-yl)oxy)silane (**2c**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 10 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2c** (500 mg, 37%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.97 – 3.88 (m, 1H), 2.58 (s, 2H), 1.72 – 1.62 (m, 1H), 1.52 – 1.40 (m, 2H), 1.39 – 1.25 (m, 4H), 1.24 – 1.13 (m, 2H), 1.12 – 1.03 (m, 12H), 0.94 – 0.86 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 71.5 (CH), 46.5 (CH_2), 39.7 (CH_2), 24.7 (CH), 23.2 (CH_3), 23.2 (CH_3), 18.2 (CH_2), 17.9 (CH_3), 17.9 (CH_3),

17.7(CH_3), 17.7 (CH_3), 14.5 (CH_3), 12.6 (CH_2), 12.6 (CH), 12.5 (CH). **IR** (ATR): 2957, 2867, 1462, 1378, 1131, 1087, 1041, 883, 880, 731 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 359 $[M+H]^+$ (100) (^{79}Br), 361 $[M+Na]^+$ (80) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{15}H_{33}O^{79}BrSiNa$ $[M+Na]^+$: 359.1376, found: 359.1370.

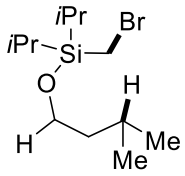


(Bromomethyl)((2,6-dimethylheptan-4-yl)oxy)diisopropylsilane (**2d**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 10 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2d** (818 mg, 59%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.97 (p, *J* = 6.3 Hz, 1H), 2.58 (s, 2H), 1.76 – 1.62 (m, 2H), 1.41 – 1.26 (m, 4H), 1.23 – 1.13 (m, 2H), 1.13 – 1.04 (m, 12H), 0.93 – 0.86 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 70.3 (CH), 47.1 (CH_2), 24.7 (CH), 23.2 (CH_3), 23.2 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 12.6 (CH), 12.6 (CH_2). **IR** (ATR): 2955, 2867, 1463, 1377, 1249, 1142, 1089, 1049, 994, 880, 733 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 373 $[M+H]^+$ (100) (^{79}Br), 375 $[M+Na]^+$ (97) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{16}H_{35}O^{79}BrSiNa$ $[M+Na]^+$: 373.1533, found: 373.1522.

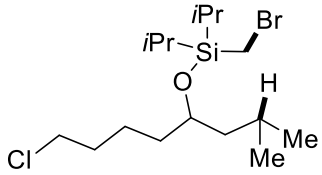


(Bromomethyl)diisopropyl(3-methyl-1-phenylbutoxy)silane (**2e**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2e** (841 mg, 57%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.21 (m, 5H), 4.86 (dd, *J* = 7.4, 6.1 Hz, 1H),

2.37 (s, 2H), 1.79 – 1.67 (m, 1H), 1.64 – 1.53 (m, 1H), 1.51 – 1.42 (m, 1H), 1.26 – 1.15 (m, 1H), 1.13 – 1.04 (m, 7H), 1.01 – 0.96 (m, 3H), 0.95 – 0.86 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.5 (C_q), 128.3 (CH), 127.4 (CH), 126.2 (CH), 74.5 (CH), 50.4 (CH_2), 24.6 (CH), 23.2 (CH_3), 22.9 (CH_3), 17.9 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 17.4 (CH_3), 12.3 (CH), 12.3 (CH_2), 12.2 (CH). **IR** (ATR): 2955, 2866, 1461, 1377, 1089, 1059, 1002, 886, 732, 696, 555 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 393 $[M+Na]^+$ (90) (^{79}Br), 395 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{18}H_{31}O^{79}BrSiNa$ $[M+Na]^+$: 393.1220, found: 393.1213.

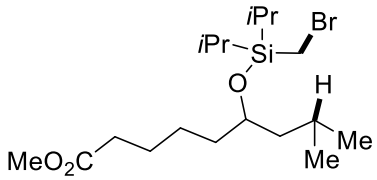


(Bromomethyl)(isopentyloxy)diisopropylsilane (**2f**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 2 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2f** (898 mg, 76%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.77 (t, *J* = 6.8 Hz, 2H), 2.58 (s, 2H), 1.78 – 1.65 (m, 1H), 1.49 – 1.41 (m, 2H), 1.24 – 1.14 (m, 2H), 1.10 – 1.07 (m, 12H), 0.90 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 62.5 (CH_2), 41.9 (CH_2), 24.8 (CH_3), 22.8 (CH), 17.7 (CH_3), 17.5 (CH_3), 12.1 (CH), 11.7 (CH_2). **IR** (ATR): 2956, 2867, 1464, 1389, 1245, 1096, 995, 884, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 317 $[M+Na]^+$ (96) (^{79}Br), 319 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{12}H_{27}O^{79}BrSiNa$ $[M+Na]^+$: 317.0907, found: 317.0909.

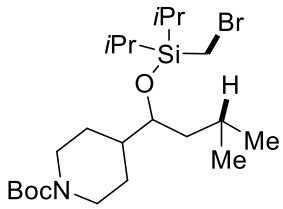


(Bromomethyl)((8-chloro-2-methyloctan-4-yl)oxy)diisopropylsilane (**2g**). The product was obtained following the general procedure using alcohol (4.4 mmol) and

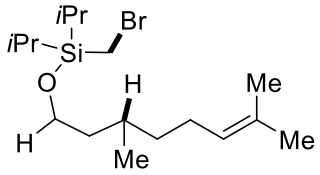
chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2g** (1.18g, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.00 – 3.89 (m, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.57 (s, 2H), 1.84 – 1.73 (m, 2H), 1.66 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.56 – 1.45 (m, 4H), 1.43 – 1.27 (m, *J* = 6.8 Hz, 2H), 1.24 – 1.12 (m, 2H), 1.11 – 1.03 (m, 12H), 0.92 – 0.86 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 71.3 (CH), 46.3 (CH_2), 45.2 (CH_2), 36.5 (CH_2), 33.0 (CH_2), 24.8 (CH), 23.3 (CH_3), 23.1 (CH_3), 22.2 (CH_2), 17.8 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 12.6 (CH), 12.5 (CH_2), 12.5 (CH). **IR** (ATR): 2955, 2866, 1463, 1378, 1071, 997, 882, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 407 $[M+Na]^+$ (70) (^{79}Br, ^{35}Cl), 409 $[M+Na]^+$ (100) (^{81}Br/^{35}Cl or ^{79}Br/^{81}Cl) . **HR-MS** (ESI) *m*/*z* calcd for $C_{16}H_{34}O^{79}Br^{35}ClSiNa$ $[M+Na]^+$: 407.1143, found: 407.1138.



Methyl 6-(((bromomethyl)diisopropylsilyl)oxy)-8-methylnonanoate (**2h**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane/EA: 50/1) yielded **2h** (689 mg, 42%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.00 – 3.85 (m, 1H), 3.65 (s, 3H), 2.55 (s, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.72 – 1.56 (m, 3H), 1.54 – 1.41 (m, 2H), 1.41 – 1.25 (m, 4H), 1.21 – 1.10 (m, 2H), 1.09 – 1.04 (m, 12H), 0.88 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 174.2 (C_q), 71.4 (CH), 51.6 (CH_3), 46.3 (CH_2), 36.9 (CH_2), 34.2 (CH_2), 25.4 (CH_2), 24.7 (CH), 24.3 (CH_2), 23.2 (CH_3), 23.0 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.5 (CH), 12.5 (CH_2), 12.5 (CH). **IR** (ATR): 2954, 2866, 1741, 1463, 1374, 1166, 1076, 999, 881, 733 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 431 $[M+Na]^+$ (100) (^{79}Br), 433 $[M+Na]^+$ (97) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{18}H_{37}O_3{}^{79}BrSiNa$ $[M+Na]^+$: 431.1588, found: 431.1580.

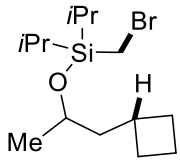


***Tert*-butyl 4-(1-(((bromomethyl)diisopropylsilyl)oxy)-3-methylbutyl)piperidine-1-carboxylate** (**2i**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane/EA: 60/1) yielded **2i** (1.16 g, 60%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.13 (d, *J* = 12.7 Hz, 2H), 3.83 (td, *J* = 6.5, 2.8 Hz, 1H), 2.59 (t, *J* = 13.0 Hz, 2H), 2.53 (s, 2H), 1.67 – 1.44 (m, 4H), 1.42 (s, 9H), 1.37 – 1.22 (m, 4H), 1.14 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.08 – 1.01 (m, 12H), 0.89 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 154.9 (C_q), 79.2 (C_q), 74.6 (CH), 44.4 (CH_2), 44.3 (CH_2), 43.0 (CH_2), 42.0 (CH), 28.5 (CH_3), 28.5 (CH_3), 28.5 (CH_3), 28.0 (CH_2), 26.3 (CH_2), 24.7 (CH), 23.1 (CH_3), 23.1 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 12.6 (CH), 12.6 (CH), 12.5 (CH_2). **IR** (ATR): 2954, 2865, 1694, 1461, 1419, 1171, 1138, 1090, 1054, 877, 733 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 500 $[M+Na]^+$ (97) (^{79}Br), 502 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{22}H_{44}NO_3{}^{79}BrSiNa$ $[M+Na]^+$: 500.2166, found: 500.2164.

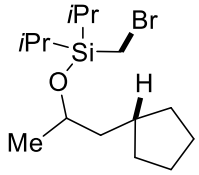


(Bromomethyl)((3,7-dimethyloct-6-en-1-yl)oxy)diisopropylsilane (**2j**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 2 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2j** (1.05 g, 72%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* = 5.14 – 5.04 (m, 1H), 3.84 – 3.70 (m, 2H), 2.58 (s, 2H), 2.07 – 1.90 (m, 2H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.63 – 1.55 (m, 5H), 1.41 – 1.28 (m, 2H), 1.27 – 1.13 (m, 3H), 1.10 – 1.06 (m, 12H), 0.89 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ = 131.2 (C_q), 125.0 (CH), 62.3 (CH_2), 40.0 (CH_2), 37.3 (CH_2), 29.2 (CH), 25.9 (CH_3), 25.6 (CH_2), 19.8 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 17. (CH_3), 12.1 (CH_3), 11.7 (CH_2). **IR** (ATR): 2921, 2866, 1461, 1384, 1247, 1095, 993, 885, 733 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 385 $[M+Na]^+$ (98) (^{79}Br), 387 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{17}H_{35}O^{79}BrSiNa$ $[M+Na]^+$: 385.1533, found: 385.1522.

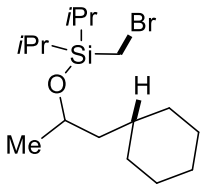


(Bromomethyl)((1-cyclobutylpropan-2-yl)oxy)diisopropylsilane (**2k**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2k** (765 mg, 60%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.95 – 3.87 (m, 1H), 2.56 (s, 2H), 2.43 – 2.31 (m, 1H), 2.09 – 1.99 (m, 2H), 1.91 – 1.75 (m, 2H), 1.71 – 1.57 (m, 3H), 1.55 – 1.45 (m, 1H), 1.20 – 1.06 (m, 17H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 68.3 (CH), 47.3 (CH_2), 32.9 (CH_3), 29.2 (CH_2), 28.9 (CH_2), 24.0 (CH), 19.0 (CH_2), 17.8 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.4 (CH), 12.4 (CH), 12.3 (CH_2). **IR** (ATR): 2934, 2865, 1465, 1379, 1136, 1101, 1048, 992, 883, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 343 $[M+Na]^+$ (97) (^{79}Br), 345 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{14}H_{29}O^{79}BrSiNa$ $[M+Na]^+$: 343.1063, found: 343.1054.

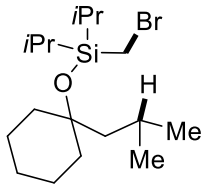


(Bromomethyl)((1-cyclopentylpropan-2-yl)oxy)diisopropylsilane (**2l**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2l** (1.05 g, 78%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.05 – 3.93 (m, 1H), 2.57 (s, 2H), 1.91 – 1.67 (m, 4H),

1.64 – 1.47 (m, 5H), 1.45 – 1.37 (m, 1H), 1.24 – 1.13 (m, 6H), 1.10 – 1.06 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 69.0 (CH), 46.5 (CH_2), 36.8 (CH_3), 33.3 (CH_2), 32.9 (CH_2), 25.2 (CH_2), 25.1(CH_2), 24.10 (CH), 17.8 (CH_3), 17.8 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.4 (CH), 12.4 (CH), 12.3 (CH_2). **IR** (ATR): 2946, 2865, 1461, 1380, 1141, 1072, 1005, 885, 734 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 357 $[M+Na]^+$ (97) (^{79}Br), 359 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{31}O^{79}BrSiNa$ $[M+Na]^+$: 357.1220, found: 357.1210.

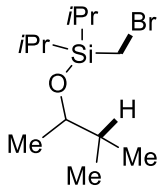


(Bromomethyl)((1-cyclohexylpropan-2-yl)oxy)diisopropylsilane (**2m**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 12 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2m** (1.01 g, 72%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.12 – 4.02 (m, 1H), 2.57 (s, 2H), 1.77 – 1.59 (m, 5H), 1.46 – 1.29 (m, 2H), 1.28 – 1.12 (m, 9H), 1.11 – 1.03 (m, 12H), 0.96 – 0.83 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 67.3 (CH), 47.9 (CH_2), 34.5 (CH_3), 33.9 (CH_2), 33.8 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 24.3 (CH), 17.83 (CH_3), 17.8 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.4 (CH), 12.4 (CH_2), 12.4(CH). **IR** (ATR): 2922, 2860, 1455, 1379, 1135, 995, 881, 733 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 371 $[M+Na]^+$ (100) (^{79}Br), 373 $[M+Na]^+$ (97) (^{81}Br). **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{33}O^{79}BrSiNa$ $[M+Na]^+$: 371.1376, found: 371.1369.



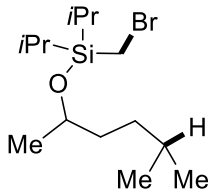
(Bromomethyl)((1-isobutylcyclohexyl)oxy)diisopropylsilane. (**2n**). Under N_2 atmosphere, MeLi (2.7 mL, 1.5 M, 1.0 equiv.) was added dropwise to a stirred mixture

of alcohol (625 mg, 1.0 equiv., 4.0 mmol) in THF (20 mL) at 0 °C. To this mixture, HMPA (0.70 mL, 4.0 mmol, 1.0 equiv.) was added, followed by chloro(bromomethyl)diisopropylsilane (1.07 g, 1.1 equiv., 4.4 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 h before quenching with saturated NH_4Cl solution. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane) yielded **2n** (720 mg, 49%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.59 (s, 2H), 1.79 – 1.63 (m, 5H), 1.48 – 1.34 (m, 8H), 1.20 – 1.12 (m, 2H), 1.10 – 1.07 (m, 12H), 0.96 – 0.93 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 77.0 (C_q), 49.3 (CH_2), 38.9 (CH_2), 25.8 (CH_2), 25.4 (CH_3), 24.0 (CH_3), 23.4 (CH_2), 18.2 (CH_3), 17.9 (CH_3), 14.6 (CH_2), 13.5 (CH). **IR** (ATR): 2933, 2863, 1464, 1361, 1138, 1058, 1002, 882, 731 cm^{-1}. **MS** (EI) *m*/*z* (relative intensity): 305 $[M\text{-}i\text{Pr-Me}]^+$ (100) (^{79}Br), 307 $[M\text{-}i\text{Pr-Me}]^+$ (97) (^{81}Br). **HR-MS** (EI) *m*/*z* calcd for $C_{13}H_{26}O^{79}BrSi$ $[M\text{-}i\text{Pr-Me}]^+$: 305.0931, found: 305.0930.

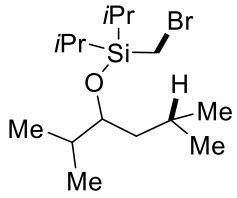


(Bromomethyl)diisopropyl((3-methylbutan-2-yl)oxy)silane (**2o**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 6 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2o** (886 mg, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.87 – 3.78 (m, 1H), 2.58 (s, 2H), 1.72 – 1.62 (m, 1H), 1.23 – 1.05 (m, 17H), 0.90 – 0.84 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ= 73.8 (CH), 35.4 (CH), 19.8 (CH_3), 18.1 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.5 (CH_2), 12.4 (CH). **IR** (ATR): 2966, 2867, 1466, 1380, 1107, 1053, 995, 963, 882, 796 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 317 $[M+H]^+$ (98) (^{79}Br), 419 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{12}H_{27}BrOSiNa$ $[M+Na]^+$: 317.0907, found:

317.0902.

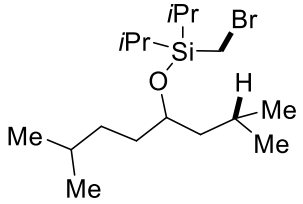


(Bromomethyl)diisopropyl((5-methylhexan-2-yl)oxy)silane (**2p**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 6 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2p** (880 mg, 68%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.99 – 3.90 (m, 1H), 2.58 (s, 2H), 1.57 – 1.36 (m, 3H), 1.27 – 1.04 (m, 19H), 0.90 – 0.86 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ= 69.9 (CH), 37.7 (CH_2), 34.8 (CH_2), 28.3 (CH), 23.8 (CH_3), 22.8 (CH_3), 22.8 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 12.4 (CH), 12.4 (CH_2). **IR** (ATR): 2959, 2867, 1463, 1377, 1128, 1085, 1057, 999, 882, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 345 $[M+H]^+$ (100) (^{79}Br), 347 $[M+Na]^+$ (98) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{14}H_{31}{}^{79}BrOSiNa$ $[M+Na]^+$: 345.1220, found: 345.1213.

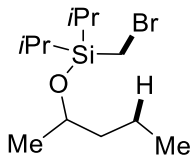


(Bromomethyl)((2,5-dimethylhexan-3-yl)oxy)diisopropylsilane (**2q**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 10 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2q** (878 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.84 – 3.79 (m, 1H), 2.58 (s, 2H), 1.82 – 1.73 (m, 1H), 1.71 – 1.60 (m, 1H), 1.33 – 1.15 (m, 4H), 1.10 – 1.05 (m, 12H), 0.93 – 0.88 (m, 9H), 0.84 – 0.80 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 75.8 (CH), 42.4(CH_2), 33.0 (CH), 24.7 (CH), 23.4 (CH_3), 22.9 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 16.9 (CH_3), 12.7 (CH_2), 12.7 (CH), 12.7 (CH). **IR** (ATR): 2958, 2867, 1462,

1380, 1051, 997, 886, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 359 $[M+Na]^+$ (97) (^{79}Br), 361 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{15}H_{33}O^{79}BrSiNa$ $[M+Na]^+$: 359.1376, found: 359.1370.

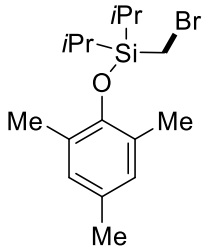


(Bromomethyl)((2,7-dimethyloctan-4-yl)oxy)diisopropylsilane (**2r**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 10 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2r** (804 mg, 55%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.95 – 3.86 (m, 1H), 2.58 (s, 2H), 1.74 – 1.62 (m, 1H), 1.56 – 1.41 (m, 3H), 1.40 – 1.26 (m, 2H), 1.25 – 1.13 (m, 4H), 1.12 – 1.03 (m, 12H), 0.94 – 0.84 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 71.9 (CH), 46.4 (CH_2), 35.2 (CH_2), 34.0 (CH_2), 28.5 (CH), 24.7 (CH), 23.2 (CH_3), 23.2 (CH_3), 22.9 (CH_3), 22.8 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 12.6 (CH_2), 12.6 (CH), 12.5 (CH). **IR** (ATR): 2956, 2867, 1462, 1138, 1088, 1051, 997, 881, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 387 $[M+Na]^+$ (97) (^{79}Br), 389 $[M+Na]^+$ (100) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{17}H_{37}O^{79}BrSiNa$ $[M+Na]^+$: 387.1689, found: 387.1681.

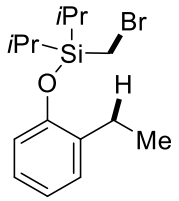


(Bromomethyl)diisopropyl(pentan-2-yloxy)silane (**2s**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 10 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2s** (883 mg, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.02 – 3.94 (m, 1H), 2.57 (s, 2H), 1.52 – 1.44 (m, 1H),

1.43 – 1.27 (m, 3H), 1.23 – 1.13 (m, 5H), 1.11 – 1.04 (m, 12H), 0.90 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 69.4 (CH), 42.2 (CH_2), 23.8 (CH_3), 18.9 (CH_2), 17.8 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 14.4 (CH_3), 12.4 (CH), 12.4 (CH), 12.3 (CH_2). **IR** (ATR): 2964, 2867, 1462, 1379, 1113, 1071, 1043, 1004, 881, 732 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 317 $[M+Na]^+$ (100) (^{79}Br), 319 $[M+Na]^+$ (97) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{12}H_{27}O^{79}BrSiNa$ $[M+Na]^+$: 317.0907, found: 317.0910.



(Bromomethyl)diisopropyl(mesityloxy)silane (**2t**). The product was obtained following the general procedure using alcohol (4.4 mmol) and chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 8 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2t** (823 mg, 60%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.78 (d, J = 0.7 Hz, 2H), 2.78 (s, 2H), 2.22 (s, 9H), 1.49 – 1.29 (m, 2H), 1.19 – 1.06 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.2 (C_q), 130.7 (C_q), 129.5 (CH), 127.5 (C_q), 20.6 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.5 (CH_3), 13.3 (CH), 11.9 (CH_2). **IR** (ATR): 2950, 2866, 1485, 1313, 1228, 1157, 1003, 962, 909, 853, 740 cm^{-1}. **HR-MS** (ESI) *m*/*z* calcd for $C_{16}H_{27}BrOSi$ $[M+Na]^+$: 365.0907, found: 365.0900. **MS** (ESI) *m*/*z* (relative intensity): 365 $[M+Na]^+$ (100) (^{79}Br), 367 $[M+Na]^+$ (97) (^{81}Br). **HR-MS** (ESI) *m*/*z* calcd for $C_{16}H_{27}O^{79}BrSiNa$ $[M+Na]^+$: 365.0907, found: 365.0900.



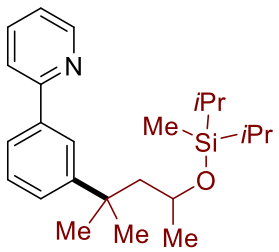
(Bromomethyl)(2-ethylphenoxy)diisopropylsilane (**2u**). The product was obtained following the general procedure using alcohol (4.4 mmol) and

chloro(bromomethyl)diisopropylsilane (4.0 mmol) for 8 h. Purification by column chromatography on silica gel (*n*-hexane) yielded **2u** (834 mg, 63%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.00 – 6.94 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 2.81 (s, 2H), 2.77 – 2.64 (m, 2H), 1.55 – 1.42 (m, 2H), 1.33 – 1.24 (m, 3H), 1.24 – 1.16 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 152.9 (C_q), 134.5 (C_q), 129.5 (CH), 126.8 (CH), 121.7 (CH), 118.2 (CH), 23.7 (CH_2), 17.7 (CH_3), 17.7 (CH_3), 17.5 (CH_3), 17.5 (CH_3), 14.4 (CH_3), 12.6 (CH), 12.6 (CH), 11.5 (CH_2). **IR** (ATR): 2937, 2867, 1590, 1490, 1456, 1257, 1120, 924, 881, 750 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 351 $[M+Na]^+$ (100), 353 $[M+Na]^+$ (97). **HR-MS** (ESI) *m*/*z* calcd for $C_{15}H_{25}O^{79}BrSiNa$ $[M+Na]^+$: 351.0750, found: 351.0740.

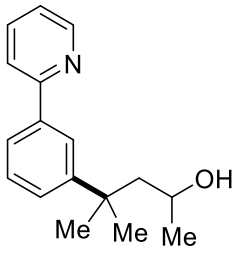
3. General Procedure and Product Characterization.

General procedure: In an N_2 filled glovebox, $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), diphenyl phosphate (38 mg, 30 mol %), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), 1,4-dioxane (2.0 mL), arene **1** (0.5 mmol, 1.0 equiv) and alcohol derivative **2** (1.0 mmol, 2.0 equiv) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred for 24-48 h under visible light irradiation (2 x Kessil A360N, the temperature was maintained between 30~35 °C). After the indicated reaction time, the mixture was filtered through a pad of celite (Et_2O), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford the corresponding products.

Characterization data of products

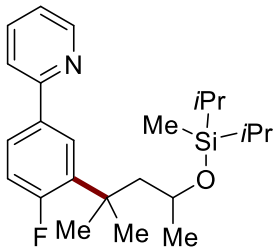


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)pyridine (**3**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **3** (157 mg, 82%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (dt, *J* = 4.8, 1.5 Hz, 1H), 8.02 – 7.96 (m, 1H), 7.81 – 7.69 (m, 3H), 7.43 – 7.39 (m, 2H), 7.22 (ddd, *J* = 6.6, 4.8, 1.9 Hz, 1H), 3.82 – 3.70 (m, 1H), 1.99 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.90 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 0.96 – 0.90 (m, 15H), 0.85 – 0.76 (m, 2H), -0.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 150.1 (C_q), 149.7 (CH), 139.3 (C_q), 136.7 (CH), 128.5 (CH), 126.9 (CH), 124.7 (CH), 124.3 (CH), 122.0 (CH), 120.8 (CH), 66.9 (CH), 54.5 (CH_2), 37.3 (C_q), 31.3 (CH_3), 28.8 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2963, 2864, 1589, 1466, 1249, 1128, 1058, 990, 883, 777 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 384 $[M+H]^+$ (100), 406 $[M+Na]^+$ (35). **HR-MS** (ESI) *m*/*z* calcd for $C_{24}H_{38}ONSi$ $[M+H]^+$: 384.2717, found: 384.2713.

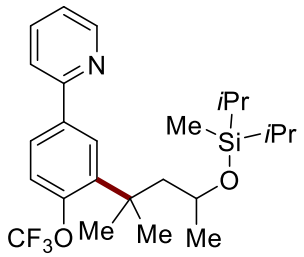


4-Methyl-4-(3-(pyridin-2-yl)phenyl)pentan-2-ol (**7**). The product was obtained following the general procedure for 24 h. Then TBAF (1.0 M in THF, 4.0 mmol, 4.0 mL) was injected into the solution, and the mixture was stirred for another 12 h. The resulting mixture was quenched with brine (10 mL), and extracted with EtOAc (20 mL × 3), dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1→3/1) yielded **7** (99 mg, 77%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.68 (ddd, *J* = 4.8, 1.7, 1.1 Hz, 1H), 8.03 (td, *J* = 1.8, 0.7 Hz, 1H), 7.78 (dt, *J* = 6.9, 1.9 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.47 – 7.41 (m, 2H), 7.22 (ddd, *J* = 6.7, 4.8, 1.8 Hz, 1H), 3.74 – 3.84 (m, 1H), 1.95 (dd, *J* = 14.5, 8.0 Hz, 1H), 1.80 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.31 (s,

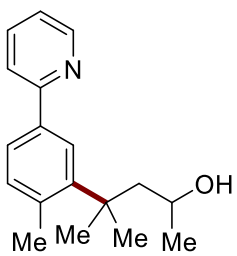
1H), 1.06 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.9 (C_q), 149.7 (CH), 149.6 (C_q), 139.5 (C_q), 136.8 (CH), 128.8 (CH), 126.8 (CH), 124.8 (CH), 124.7 (CH), 122.2 (CH), 120.9 (CH), 65.9 (CH), 53.7 (CH_2), 37.5 (C_q), 30.2 (CH_3), 29.3 (CH_3), 25.3 (CH_3). **IR** (ATR): 3382, 2962, 1589, 1468, 1364, 1266, 1122, 1044, 893, 775 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 256 $[M+H]^+$ (40), 278 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{17}H_{22}ON$ $[M+H]^+$: 256.1696, found: 256.1697.



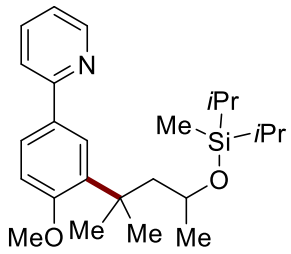
2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4-fluorophenyl)pyridine (**8**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **8** (143 mg, 71%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.68 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 7.93 (dd, J = 8.0, 2.3 Hz, 1H), 7.79 (ddd, J = 8.4, 4.5, 2.3 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.69 – 7.64 (m, 1H), 7.21 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H), 7.07 (dd, J = 12.2, 8.4 Hz, 1H), 3.80 – 3.70 (m, 1H), 2.12 – 1.98 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 0.96 (d, J = 6.1 Hz, 3H), 0.93 – 0.86 (m, 12H), 0.81 – 0.73 (m, 2H), -0.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 162.7 (d, $^{1}J_{C–F}$ = 250.5 Hz, C_q), 157.2 (C_q), 149.7 (CH), 136.9 (CH), 135.9 (d, $^{2}J_{C–F}$ = 12.0 Hz, C_q), 135.2 (d, $^{4}J_{C–F}$ = 2.9 Hz, C_q), 127.2 (d, $^{3}J_{C–F}$ = 6.4 Hz, CH), 126.4 (d, $^{3}J_{C–F}$ = 9.4 Hz, CH), 122.0 (CH), 120.4 (CH), 116.7 (d, $^{2}J_{C–F}$ = 25.1 Hz, CH), 67.2 (CH), 51.4 (d, $^{4}J_{C–F}$ = 4.2 Hz, CH_2), 37.1 (d, $^{3}J_{C–F}$ = 3.1 Hz, C_q), 30.1 (d, $^{4}J_{C–F}$ = 2.9 Hz, CH_3), 28.9 (d, $^{4}J_{C–F}$ = 2.0 Hz, CH_3), 25.5 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.6 (CH), -7.4 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -108.7. **IR** (ATR): 2963, 2864, 1589, 1463, 1435, 1256, 1219, 1087, 991, 882 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 402 $[M+H]^+$ (100), 424 $[M+Na]^+$ (70). **HR-MS** (ESI) *m*/*z* calcd for $C_{24}H_{37}FNOSi$ $[M+H]^+$: 402.2623, found: 402.2627.



2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4-(trifluoromethoxy)phenyl)pyridine (**9**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 40/1→20/1) yielded **9** (163 mg, 70%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.84 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.72 – 7.64 (m, 1H), 7.34 – 7.28 (m, 1H), 7.23 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 3.77 – 3.69 (m, 1H), 2.11 (dd, *J* = 14.3, 5.7 Hz, 1H), 1.97 (dd, *J* = 14.3, 6.2 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 0.95 (d, *J* = 6.1 Hz, 3H), 0.91 – 0.86 (m, 12H), 0.82 – 0.73 (m, 2H), -0.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 156.8 (C_q), 149.9 (CH), 149.5 (C_q), 139.2 (C_q), 136.9 (CH), 136.8 (C_q), 127.8 (CH), 126.0 (CH), 122.3 (CH), 120.5 (CH), 119.8 (q, $^1J_{C–F}$ = 259.6 Hz, C_q), 118.6 (d, $^2J_{C–F}$ = 2.3 Hz, C_q), 67.2 (CH), 51.1 (CH_2), 37.8 (C_q), 30.3 (CH_3), 29.6 (CH_3), 25.3 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.6 (CH), -7.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -54.1 (s, 3F). **IR** (ATR): 2965, 2866, 1589, 1464, 1246, 1210, 1162, 1089, 780 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 468 $[M+H]^+$ (100), 490 $[M+Na]^+$ (60). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{37}F_3NO_2Si$ $[M+H]^+$: 468.2540, found: 468.2542.

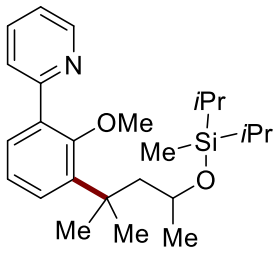


4-Methyl-4-(2-methyl-5-(pyridin-2-yl)phenyl)pentan-2-ol (**10**). The product was obtained following the general procedure for 48 h. Then TBAF (1.0 M in THF, 4.0 mmol, 4.0 mL) was injected into the solution, and the mixture was stirred for another 12 h. The resulting mixture was quenched with brine (10 mL), and extracted with EtOAc (20 mL × 3), dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1→3/1) yielded **10** (83 mg, 62%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 4.9 Hz, 1H), 8.06 (d, *J* = 1.9 Hz, 1H), 7.75 – 7.66 (m, 3H), 7.26 – 7.15 (m, 2H), 3.84 – 3.74 (m, 1H), 2.59 (s, 3H), 2.15 (dd, *J* = 14.6, 8.3 Hz, 1H), 1.86 (dd, *J* = 14.8, 2.8 Hz, 1H), 1.54 (s, 3H), 1.53 (s, 3H), 1.37 (s, 1H), 1.07 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.8 (C_q), 149.7 (CH), 146.0 (C_q), 137.8 (C_q), 137.2 (C_q), 136.8 (CH), 133.6 (CH), 126.0 (CH), 124.9 (CH), 121.9 (CH), 120.6 (CH), 66.0 (CH), 50.3 (CH_2), 38.9 (C_q), 30.7 (CH_3), 30.4 (CH_3), 24.9 (CH_3), 23.5 (CH_3). **IR** (ATR): 3381, 2963, 2924, 1586, 1464, 1432, 1390, 1151, 1040, 781 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 270 $[M+H]^+$ (30), 292 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{18}H_{24}ON$ $[M+H]^+$: 270.1852, found: 270.1855.

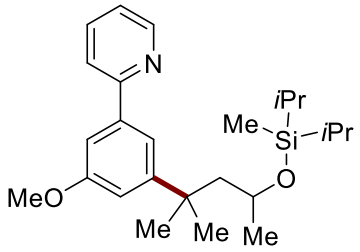


2-(3-(4-((diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4-methoxyphenyl)pyridine (**11**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→8/1) yielded **11** (141 mg, 68%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.66 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.15 (ddd, *J* = 7.1, 4.8, 1.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 3.73 – 3.63 (m, 1H), 2.27 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.99 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 0.96 – 0.86 (m, 15H), 0.84 –

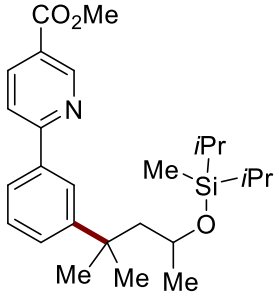
0.74 (m, 2H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.5 (C_q), 157.9 (C_q), 149.6 (CH), 136.7 (CH), 136.6 (C_q), 131.5 (C_q), 126.6 (CH), 126.0 (CH), 121.3 (CH), 120.0 (CH), 111.4 (CH), 67.5 (CH), 55.1 (CH_3), 50.4 (CH_2), 37.5 (C_q), 30.0 (CH_3), 29.4 (CH_3), 25.3 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH), -7.6 (CH_3). **IR** (ATR): 2961, 2864, 1740, 1586, 1463, 1240, 1089, 991, 881cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (100), 436 $[M+Na]^+$ (80). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}O_2NSi$ $[M+H]^+$: 414.2823, found: 414.2827.



2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-2-methoxyphenyl)pyridine (**12**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→10/1) yielded **12** (134 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.73 (s, 1H), 7.72 (s, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 3.85 – 3.73 (m, 1H), 3.33 (s, 3H), 2.23 (dd, *J* = 14.0, 6.5 Hz, 1H), 1.96 (dd, *J* = 14.0, 5.4 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 0.98 – 0.92 (m, 15H), 0.88 – 0.79 (m, 2H), -0.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ= 157.9 (C_q), 149.9 (CH), 141.1 (C_q), 136.2 (CH), 133.9 (C_q), 130.1 (CH), 128.4 (CH), 124.7 (CH), 123.5 (CH), 121.9 (CH), 67.4 (CH), 61.4 (CH_3), 51.7 (CH_2), 37.7 (C_q), 30.9 (CH_3), 29.8 (CH_3), 25.4 (CH_3), 17.7 (CH_3, overlapped, 3C), 17.6 (CH_3), 13.6 (CH), 13.6 (CH), -7.35 (CH_3). **IR** (ATR): 2864, 1591, 1456, 1410, 1224, 1089, 992, 730, 644 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (100), 436 $[M+Na]^+$ (25). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NO_2Si$ $[M+H]^+$: 414.2823, found: 414.2826.

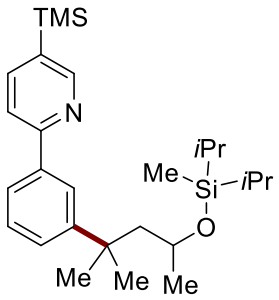


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-5-methoxyphenyl)pyridine (**13**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→8/1) yielded **13** (68 mg, 33%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.53 (t, *J* = 1.6 Hz, 1H), 7.40 (dd, *J* = 2.5, 1.4 Hz, 1H), 7.23 (ddd, *J* = 7.1, 4.8, 1.5 Hz, 1H), 6.97 (t, *J* = 2.1 Hz, 1H), 3.90 (s, 3H), 3.79 – 3.70 (m, 1H), 1.96 (dd, *J* = 14.1, 5.0 Hz, 1H), 1.88 (dd, *J* = 14.1, 6.5 Hz, 1H), 1.42 (s, 3H), 1.36 (s, 3H), 0.97 – 0.88 (m, 15H), 0.88 – 0.78 (m, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.1 (C_q), 157.9 (C_q), 151.7 (C_q), 149.5 (CH), 140.3 (C_q), 136.9 (CH), 122.2 (CH), 121.0 (CH), 117.6 (CH), 114.2 (CH), 108.7 (CH), 66.9 (CH), 55.5 (CH_3), 54.4 (CH_2), 37.4 (C_q), 31.3 (CH_3), 28.7 (CH_3), 25.7 (CH_3), 17.9 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2962, 2864, 1590, 1465, 1420, 1335, 1217, 1058, 1016, 879, 781, 741 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (80), 436 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NO_2Si$ $[M+H]^+$: 414.2823, found: 414.2824.



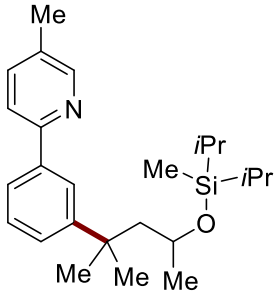
Methyl 6-(3-(4-((diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-nicotinate (**14**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→10/1)

yielded **14** (159 mg, 72%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.28 (dd, J = 2.2, 0.9 Hz, 1H), 8.33 (dd, J = 8.3, 2.2 Hz, 1H), 8.06 (t, J = 1.9 Hz, 1H), 7.84 (dt, J = 7.5, 1.5 Hz, 1H), 7.80 (dd, J = 8.3, 0.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 3.97 (s, 3H), 3.75 (dd, J = 11.3, 6.3 Hz, 1H), 1.99 (dd, J = 14.2, 5.0 Hz, 1H), 1.89 (dd, J = 14.2, 6.5 Hz, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 0.94 – 0.88 (m, 15H), 0.82 – 0.76 (m, 2H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 166.1 (C_q), 161.5 (C_q), 151.1 (CH), 150.4 (C_q), 138.1 (C_q), 137.9 (CH), 128.7 (CH), 127.9 (CH), 125.2 (CH), 124.8 (CH), 124.1 (C_q), 120.0 (CH), 66.9 (CH), 54.4 (CH_2), 52.5 (CH_3), 37.4 (C_q), 31.2 (CH_3), 28.8 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2961, 2865, 1726, 1594, 1469, 1290, 1119, 1056, 1018, 883 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 442 $[M+H]^+$ (100), 464 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{26}H_{40}O_3NSi$ $[M+H]^+$: 442.2772, found: 442.2762.

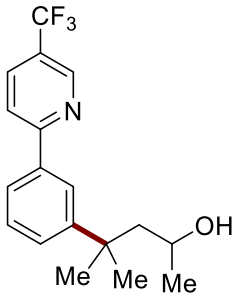


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-5-(trimethylsilyl)pyridine (**15**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→10/1) yielded **15** (127 mg, 56%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (s, 1H), 8.03 (s, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 6.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.45 – 7.37 (m, 2H), 3.82 – 3.72 (m, 1H), 2.00 (dd, J = 14.1, 4.9 Hz, 1H), 1.91 (dd, J = 14.2, 6.5 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.97 – 0.88 (m, 15H), 0.87 – 0.76 (m, 2H), 0.34 (s, 9H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.0 (C_q), 153.8 (CH), 150.1 (C_q), 142.0 (CH), 139.1 (C_q), 133.0 (C_q), 128.5 (CH), 127.0 (CH), 124.7 (CH), 124.3 (CH), 120.1 (CH), 66.9 (CH), 54.5 (CH_2), 37.3 (C_q), 31.3 (CH_3), 28.7 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7

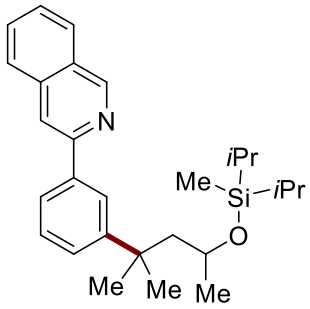
(CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH), -1.16 (CH_3), -7.4 (CH_3). **IR** (ATR): 2956, 2864, 1580, 1462, 1250, 1128, 995, 832, 701 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 456 $[M+H]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{27}H_{46}ONSi_2$ $[M+H]^+$: 456.3112, found: 456.3109.



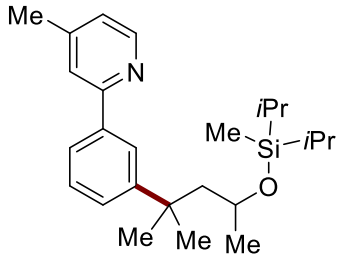
2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-5-methylpyridine (**16**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **16** (105 mg, 53%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.53 (dt, *J* = 2.0, 0.9 Hz, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 7.76 (td, *J* = 4.3, 1.7 Hz, 1H), 7.61 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.54 (ddd, *J* = 8.1, 2.3, 0.8 Hz, 1H), 7.41 – 7.37 (m, 2H), 3.84 – 3.70 (m, 1H), 2.37 (s, 3H), 1.99 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.91 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 0.95 – 0.91 (m, 15H), 0.86 – 0.78 (m, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 155.4 (C_q), 150.1 (CH), 150.0 (C_q), 139.2 (C_q), 137.3 (CH), 131.5 (C_q), 128.5 (CH) 126.5 (CH), 124.5 (CH), 124.1 (CH), 120.2 (CH), 66.9 (CH), 54.5 (CH_2), 37.3 (C_q), 31.3 (CH_3), 28.7 (CH_3), 25.7 (CH_3), 18.3 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.5 (CH_3). **IR** (ATR): 2962, 2864, 1598, 1563, 1471, 1377, 1250, 1057, 789 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 398 $[M+H]^+$ (70), 420 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NOSi$ $[M+H]^+$: 398.2874, found: 398.2875.



4-Methyl-4-(3-(5-(trifluoromethyl)pyridin-2-yl)phenyl)pentan-2-ol (**17**). The product was obtained following the general procedure for 48 h. Then TBAF (1.0 M in THF, 4.0 mmol, 4.0 mL) was injected into the solution, and the mixture was stirred for another 12 h. The resulting mixture was quenched with brine (10 mL), and extracted with EtOAc (20 mL × 3), dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1→2/1) yielded **17** (129 mg, 80%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.95 (dt, *J* = 2.4, 0.9 Hz, 1H), 8.10 (td, *J* = 1.9, 0.5 Hz, 1H), 7.98 (ddd, *J* = 8.4, 2.4, 0.7 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.52 (ddd, *J* = 7.9, 2.0, 1.3 Hz, 1H), 7.50 – 7.43 (m, 1H), 3.94 – 3.65 (m, 1H), 1.96 (dd, *J* = 14.6, 8.1 Hz, 1H), 1.82 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.47 (s, 3H), 1.46 (s, 3H), 1.08 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.0 (C_q), 150.1 (C_q), 146.6 (q, $^3J_{C\text{-}F}$ = 4.0 Hz, CH), 138.0 (C_q), 134.2 (q, $^3J_{C\text{-}F}$ = 4.9 Hz, CH), 129.1 (CH), 128.0 (CH), 125.2 (CH), 125.0 (CH), 125.0 (q, $^2J_{C\text{-}F}$ = 26.3 Hz, C_q), 123.9 (q, $^1J_{C\text{-}F}$ = 274.0 Hz, C_q), 120.4 (CH), 66.0 (CH), 53.7 (CH_2), 37.6 (C_q), 30.1 (CH_3), 29.4 (CH_3), 25.4 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ= - 66.2 (s, 3F). **IR** (ATR): 3404, 2966, 2925, 1605, 1568, 1477, 1381, 1329, 1132, 1168, 1086 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 324 $[M+H]^+$ (40), 346 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{18}H_{21}F_3NO$ $[M+H]^+$: 324.1570, found: 324.1573.

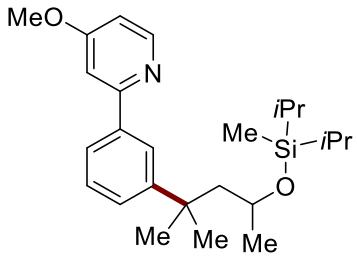


3-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)isoquinoline (**18**). The product was obtained following the general procedure for 36 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **18** (100 mg, 46%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.35 (t, *J* = 0.9 Hz, 1H), 8.12 (td, *J* = 1.8, 0.7 Hz, 1H), 8.07 – 8.04 (m, 1H), 7.99 (dq, *J* = 8.2, 1.0 Hz, 1H), 7.93 (dt, *J* = 7.1, 1.7 Hz, 1H), 7.88 (dq, *J* = 8.4, 1.0 Hz, 1H), 7.70 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 3.78 – 3.72 (m, 1H), 2.02 (dd, 1H), 1.94 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.48 (s, 3H), 1.42 (s, 3H), 0.96 – 0.89 (m, 15H), 0.87 – 0.80 (m, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 152.5 (CH), 152.0 (C_q), 150.1 (C_q), 139.5 (C_q), 136.8 (C_q), 130.6 (CH), 128.6 (CH), 127.9 (C_q), 127.7 (CH), 127.1 (CH), 127.0 (CH), 126.5 (CH), 124.8 (CH), 124.5 (CH), 116.6 (CH), 67.0 (CH), 54.6 (CH_2), 37.4 (C_q), 31.4 (CH_3) , 28.8 (CH_3), 25.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.6 (CH), -7.4 (CH_3). **IR** (ATR): 2961, 2863, 1626, 1578, 1460, 1250, 1130, 1058, 1012, 881, 785, 745, 702 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 434 $[M+H]^+$ (100), 456 $[M+Na]^+$ (98). **HR-MS** (ESI) *m*/*z* calcd for $C_{28}H_{40}NOSi$ $[M+H]^+$: 434.2874, found: 434.2874.

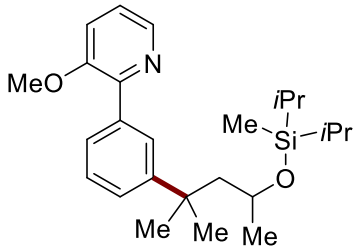


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-4-methylpyridine (**19**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **19** (151 mg, 76%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* = 8.55 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.97 – 7.95 (m, 1H), 7.77 (ddd, *J* = 5.0, 3.4, 1.7 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.43 – 7.36 (m, 2H), 7.04 (ddd, *J* = 5.0, 1.6, 0.8 Hz, 1H), 3.81 – 3.73 (m, 1H), 2.42 (s, 3H), 2.00 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.91 (dd, *J* = 14.1, 6.7 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 0.98 – 0.88 (m, 15H), 0.88 – 0.76 (m, 2H), -0.09 (s, 3H). **^{13}C NMR**

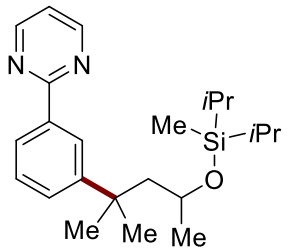
(101 MHz, $CDCl_3$) δ = 158.0 (C_q), 150.0 (C_q), 149.5 (CH), 147.7 (C_q), 139.4 (C_q), 128.5 (CH), 126.7 (CH), 124.7 (CH), 124.4 (CH), 123.1 (CH), 121.7 (CH), 66.9 (CH), 54.5 (CH_2), 37.3 (C_q), 31.4 (CH_3), 28.8 (CH_3), 25.7 (CH_3), 21.4 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2961, 2863, 1600, 1464, 1378, 1249, 1128, 1057, 993, 882 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 398 $[M+H]^+$ (100), 420 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}ONSi$ $[M+H]^+$: 398.2874, found: 398.2875.



2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-4-methoxypyridine (**20**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→ 20/1) yielded **20** (144 mg, 74%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.52 (d, J = 5.7 Hz, 1H), 7.95 (t, 1H), 7.74 (dt, J = 6.5, 2.0 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.21 (d, J = 2.4 Hz, 1H), 6.76 (dd, J = 5.7, 2.4 Hz, 1H), 3.90 (s, 3H), 3.81 – 3.69 (m, 1H), 1.99 (dd, J = 14.1, 5.0 Hz, 1H), 1.90 (dd, J = 14.1, 6.6 Hz, 1H), 1.44 (s, 3H), 1.38 (s, 3H), 0.99 – 0.88 (m, 15H), 0.85 – 0.76 (m, 2H), -0.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 166.4 (C_q), 159.8 (C_q), 150.9 (CH), 150.0 (C_q), 139.2 (C_q), 128.4 (CH), 126.9 (CH), 124.7 (CH), 124.4 (CH), 107.9 (CH), 107.2 (CH), 66.9 (CH), 55.3 (CH_3), 54.5 (CH_2), 37.3 (C_q), 31.3 (CH_3), 28.7 (CH_3), 25.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH), -7.5 (CH_3). **IR** (ATR): 2964, 2864, 1591, 1561, 1469, 1214, 1038, 777 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (90), 436 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NO_2Si$ $[M+H]^+$: 414.2823, found: 414.2823.

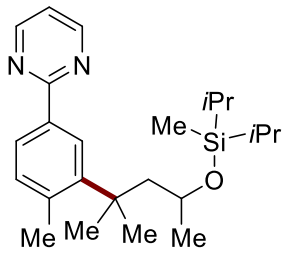


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-3-methoxypyridine (**21**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **21** (155mg, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.29 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.86 (td, *J* = 1.7, 1.0 Hz, 1H), 7.72 – 7.57 (m, 1H), 7.39 – 7.32 (m, 2H), 7.25 – 7.23 (m, 1H), 7.19 (dd, *J* = 8.3, 4.6 Hz, 1H), 3.82 (s, 3H), 3.79 – 3.68 (m, 1H), 1.99 – 1.82 (m, 2H), 1.40 (s, 3H), 1.33 (s, 3H), 0.94 – 0.88 (m, 15H), 0.84 – 0.77 (m, 2H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 153.67 (C_q), 148.9 (C_q), 148.9 (C_q), 141.4 (CH), 137.4(C_q), 127.7 (CH), 127.3 (CH), 126.7 (CH), 126.1 (CH), 122.8 (CH), 118.6 (CH), 67.0 (CH), 55.6 (CH_3), 54.5 (CH_2), 37.2 (C_q), 31.5 (CH_3), 28.5 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2962, 2864, 1577, 1455, 1272, 1127, 1068, 1016, 882, 768, 705 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (70), 406 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NO_2Si$ $[M+H]^+$: 414.2824, found: 414.2823.

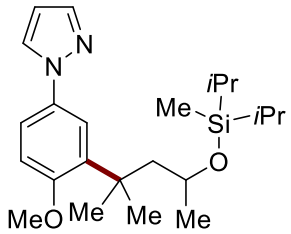


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)pyrimidine (**22**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1→10/1) yielded **22** (103 mg, 53%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 4.8 Hz,

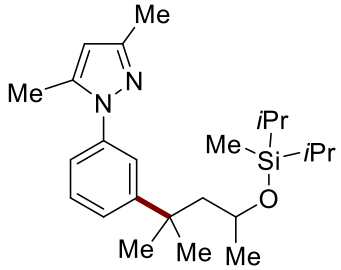
2H), 8.47 (t, *J* = 1.8 Hz, 1H), 8.25 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.48 (ddd, *J* = 7.8, 2.1, 1.3 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 3.78 – 3.72 (m, 1H), 2.00 (dd, *J* = 14.1, 5.0 Hz, 1H), 1.92 (dd, *J* = 14.1, 6.7 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.94 – 0.89 (m, 15H), 0.85 – 0.80 (m, 2H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.2 (C_q), 157.3 (CH), 157.3 (CH), 150.0 (C_q), 137.4 (C_q), 128.7 (CH), 128.5 (CH), 125.9 (CH), 125.6 (CH), 119.1 (CH), 66.9 (CH), 54.5 (CH_2), 37.3 (C_q), 31.4 (CH_3), 28.8 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.5 (CH_3). **IR** (ATR): 2963, 2864, 1562, 1460, 1413, 1058, 990, 881, 782, 705 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 385 $[M+H]^+$ (40), 407 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{23}H_{37}N_2OSi$ $[M+H]^+$: 385.2670, found: 385.2672.



2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4-methylphenyl)pyrimidine (**23**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1→10/1) yielded **23** (82 mg, 41%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 4.8 Hz, 2H), 8.47 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.17 – 7.10 (m, 1H), 3.82 – 3.72 (m, 1H), 2.59 (s, 3H), 2.10 (dd, *J* = 14.5, 6.4 Hz, 1H), 2.02 (dd, *J* = 14.4, 5.3 Hz, 1H), 1.57 (s, 3H), 1.49 (s, 3H), 0.94 – 0.87 (m, 15H), 0.83 – 0.76 (m, 2H), -0.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.3 (C_q), 157.3 (CH), 146.6 (C_q), 139.8 (C_q), 135.1 (C_q), 133.4 (CH), 127.2 (CH), 125.8 (CH), 118.8 (CH), 67.2 (CH), 51.2 (CH_2), 38.7 (CH_q), 30.8 (CH_3), 30.6 (CH_3), 25.3 (CH_3), 23.6 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2864, 1568, 1548, 1416, 1251, 1052, 799, 731, 636 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 399 $[M+H]^+$ (97), 421 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{24}H_{39}N_2OSi$ $[M+H]^+$: 399.2826, found: 399.2820.

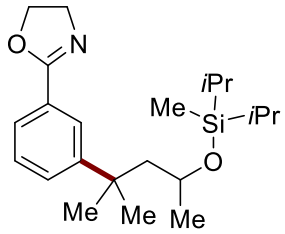


1-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4-methoxyphenyl)-*1H*-pyrazole (**24**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **24** (114 mg, 57%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.81 (d, J = 2.3 Hz, 1H), 7.70 (d, J = 1.7 Hz, 1H), 7.56 (d, J = 2.7 Hz, 1H), 7.44 (dd, J = 8.7, 2.7 Hz, 1H), 6.88 (d, J = 8.7 Hz, 1H), 6.43 (s, 1H), 3.84 (s, 3H), 3.71 – 3.63 (m, 1H), 2.25 (dd, J = 13.9, 7.0 Hz, 1H), 1.98 (dd, J = 13.9, 5.0 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.95 – 0.87 (m, 15H), 0.83 – 0.77 (m, 2H), -0.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.2 (C_q), 140.6 (CH), 137.7 (C_q), 133.8 (C_q), 127.0 (CH), 120.0 (CH), 118.4 (CH), 111.6 (CH), 107.1 (CH), 67.3 (CH), 55.3 (CH_3), 50.2 (CH_2), 37.6 (C_q), 29.8 (CH_3), 29.2 (CH_3), 25.3 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.6 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH), -7.5 (CH_3). **IR** (ATR): 2960, 1495, 1465, 1238, 1045, 1029, 785, 743 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 403 $[M+H]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{23}H_{39}O_2N_2Si$ $[M+H]^+$: 403.2775, found: 403.2773.



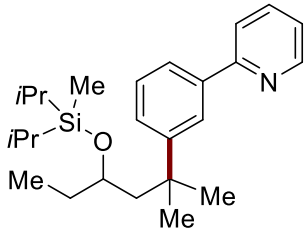
1-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-3,5-dimethyl-1H-pyrazole (**25**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **25** (114 mg, 57%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.30 (m, 3H), 7.22 (dt, J = 7.4, 1.9 Hz, 1H), 5.99 (s, 1H),

3.81 – 3.70 (m, 1H), 2.34 – 2.24 (m, 6H), 1.94 (dd, J = 14.2, 5.0 Hz, 1H), 1.84 (dd, J = 14.2, 6.5 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 0.98 – 0.88 (m, 15H), 0.87 – 0.77 (m, 2H), -0.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.9 (C_q), 148.8 (C_q), 139.8 (C_q), 139.4 (C_q), 128.7 (CH), 125.2 (CH), 122.8 (CH), 122.3 (CH), 106.8 (CH), 66.8 (CH), 54.4 (CH_2), 37.3 (C_q), 31.4 (CH_3), 28.4 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.7 (CH_3), 13.6 (CH), 13.5 (CH), 12.5 (CH_3), -7.4 (CH_3). **IR** (ATR): 2960, 2863, 1555, 1496, 1462, 1368, 1249, 1126, 1076, 884 cm^{-1}. **MS** (ESI) m/z (relative intensity): 401 $[M+H]^+$ (100), 423 $[M+Na]^+$ (20). **HR-MS** (ESI) m/z calcd for $C_{24}H_{41}ON_2Si$ $[M+H]^+$: 401.2983, found: 401.2970.

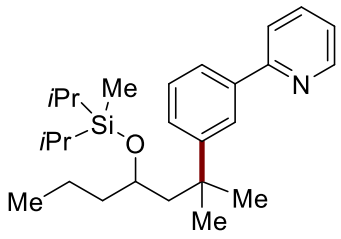


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-4,5-dihydrooxazole (**26**). A 10 mL sealed tube was charged with $Ru(OAc)_2$(p-cymene) (10 mol %), K_2CO_3 (1.0 mmol, 138 mg, 2.0 equiv), (p-$CF_3C_6H_4)_3P$ (47 mg, 0.1 mmol, 20 mol %), 1,4-dioxane (2.0 mL), phenyloxazoline (74 mg, 0.5 mmol), **2a** (309 mg, 1.0 mmol, 2.0 equiv). The tube was sealed with a Teflon plug and moved out of the glovebox and stirred at 90 °C for 24 h. Then the mixture was cooled to room temperature. After removal of the solvent in vacuum, the residue was purified by chromatography on silica gel (n-hexane/EtOAc = 20/1→3/1) yielded **26** (69 mg, 37%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.93 (t, J = 1.8 Hz, 1H), 7.75 (dt, J = 7.6, 1.4 Hz, 1H), 7.46 (ddd, J = 7.9, 2.1, 1.2 Hz, 1H), 7.36 – 7.31 (m, 1H), 4.43 (t, J = 9.7 Hz, 2H), 4.06 (t, J = 9.7 Hz, 2H), 3.75 – 3.64 (m, 1H), 1.94 (dd, J = 14.1, 5.0 Hz, 1H), 1.84 (dd, J = 14.2, 6.5 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 0.95 – 0.86 (m, 15H), 0.82 – 0.77 (m, 2H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.2 (C_q), 149.9 (C_q), 129.3 (CH), 128.2 (CH), 127.5 (C_q), 125.9 (CH), 125.6 (CH), 67.7 (CH_2), 66.8 (CH), 55.0 (CH_2), 54.3 (CH_2), 37.2 (C_q), 31.2 (CH_3), 28.7 (CH_3), 25.7 (CH_3), 17.7 (CH_3, overlapped, 2C), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR):

2963, 2867, 1647, 1462, 1359, 1255, 882, 847 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 376 $[M+H]^+$ (100), 398 $[M+Na]^+$ (10). **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{38}O_2NSi$ $[M+H]^+$: 376.2666, found: 376.2663.



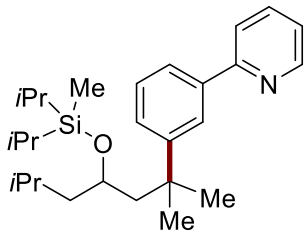
2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylhexan-2-yl)phenyl)pyridine (28). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **28** (154 mg, 78%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.76 – 8.60 (m, 1H), 7.98 (dt, *J* = 1.8, 1.1 Hz, 1H), 7.85 – 7.65 (m, 3H), 7.45 – 7.39 (m, 2H), 7.22 (ddd, *J* = 6.6, 4.8, 1.9 Hz, 1H), 3.70 – 3.58 (m, 1H), 1.99 (dd, *J* = 14.3, 5.9 Hz, 1H), 1.84 (dd, *J* = 14.3, 5.3 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 1.35 – 1.12 (m, 2H), 0.96 – 0.91 (m, 12H), 0.85 – 0.80 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H), -0.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 150.2 (C_q), 149.7 (CH), 139.2 (C_q), 136.7 (CH), 128.5 (CH), 126.9 (CH), 124.7 (CH), 124.3 (CH), 122.0 (CH), 120.7 (CH), 71.4 (CH), 50.8 (CH_2), 37.3 (C_q), 31.4 (CH_3), 30.9 (CH_2), 28.7 (CH_3), 17.9 (CH_3), 17.8 (CH_3, overlapped, 2C) 17.7 (CH_3), 13.8 (CH), 13.8 (CH), 8.9 (CH_3), -6.9 (CH_3). **IR** (ATR): 2963, 2864, 1589, 1465, 1250, 1034, 882, 773, 738, 701 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 398 $[M+H]^+$ (100), 420 $[M+Na]^+$ (95). **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{40}NOSi$ $[M+H]^+$: 398.2874, found: 398.2876.



2-(3-(4-((diisopropyl(methyl)silyl)oxy)-2-methylheptan-2-yl)phenyl)pyridine (29)

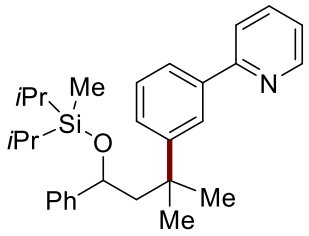
The product was obtained following the general procedure for 24 h. Purification by

column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **29** (152 mg, 74%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.98 (q, *J* = 1.6 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.76 – 7.69 (m, 2H), 7.43 – 7.38 (m, 2H), 7.22 (ddd, *J* = 6.7, 4.9, 1.7 Hz, 1H), 3.70 – 3.65 (m, 1H), 1.99 (dd, *J* = 14.3, 5.9 Hz, 1H), 1.84 (dd, *J* = 14.3, 5.3 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 1.30 – 1.13 (m, 4H), 0.96 – 0.90 (m, 12H), 0.85 – 0.79 (m, 2H), 0.74 – 0.66 (m, 3H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 150.2 (C_q), 149.7 (CH), 139.2 (C_q), 136.8 (CH), 128.5 (CH), 126.9 (CH), 124.8 (CH), 124.3 (CH), 122.0 (CH), 120.8 (CH), 70.3 (CH), 51.3 (CH_2), 40.7 (CH_2), 37.4 (C_q), 31.4 (CH_3), 28.6 (CH_3), 17.9 (CH_3, overlapped, 2C), 17.8 (CH_3), 17.8 (CH_3), 17.7 (CH_2), 14.3 (CH_3), 13.8 (CH), 13.8 (CH), -6.9 (CH_3). **IR** (ATR): 2960, 2865, 1589, 1465, 1248, 1067, 1036, 884, 778, 736 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 412 $[M+H]^+$ (100), 434 $[M+Na]^+$ (85). **HR-MS** (ESI) *m*/*z* calcd for $C_{26}H_{42}N_2OSi$ $[M+H]^+$: 412.3030, found: 412.3031.

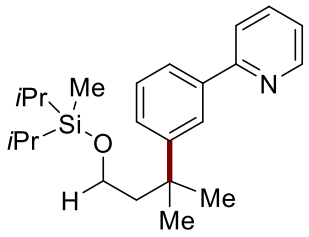


2-(3-(4-((diisopropyl(methyl)silyl)oxy)-2,6-dimethylheptan-2-yl)phenyl)pyridine (**30**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **30** (138 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.81 – 7.77 (m, 1H), 7.77 – 7.69 (m, 2H), 7.42 – 7.39 (m, 2H), 7.22 (ddd, *J* = 7.0, 4.8, 1.6 Hz, 1H), 3.68 (p, *J* = 6.0 Hz, 1H), 1.95 (dd, *J* = 14.3, 5.5 Hz, 1H), 1.83 (dd, *J* = 14.3, 5.4 Hz, 1H), 1.54 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.20 – 1.03 (m, 2H), 0.99 – 0.89 (m, 12H), 0.86 – 0.81 (m, 2H), 0.74 (d, *J* = 6.6 Hz, 3H), 0.64 (d, *J* = 6.6 Hz, 3H), -0.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 150.2 (C_q), 149.7 (CH), 139.2 (C_q), 136.8 (CH), 128.5 (CH), 126.9 (CH), 124.9 (CH), 124.4 (CH), 122.0 (CH), 120.7 (CH), 69.2 (CH), 52.3 (CH_2), 48.5 (CH_2), 37.5 (C_q), 31.3 (CH_3), 28.7 (CH_3), 24.7 (CH), 23.1 (CH_3), 22.9

(CH_3), 17.9 (CH_3, overlapped, 2C), 17.9 (CH_3), 17.8 (CH_3), 14.0 (CH), 13.9 (CH), -6.6 (CH_3). **IR** (ATR): 2957, 2864, 1589, 1465, 1049, 775, 739, 699 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 426 $[M+H]^+$ (100), 448 $[M+Na]^+$ (90). **HR-MS** (ESI) *m*/*z* calcd for $C_{27}H_{44}NOSi$ $[M+H]^+$: 426.3187, found: 426.3188.

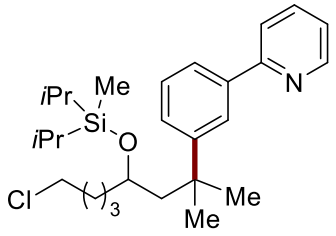


2-(3-(4-((diisopropyl(methyl)silyl)oxy)-2-methyl-4-phenylbutan-2-yl)phenyl)pyridine (**31**). The product was obtained following the general procedure for 36 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1 →20/1) yielded **31** (94 mg, 44%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.71 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 7.98 – 7.90 (m, 1H), 7.81 (dt, J = 7.2, 1.6 Hz, 1H), 7.78 – 7.67 (m, 2H), 7.44 – 7.34 (m, 2H), 7.25 – 7.11 (m, 6H), 4.47 (t, J = 6.0 Hz, 1H), 2.31 (dd, J = 14.3, 6.3 Hz, 1H), 2.15 (dd, J = 14.3, 5.8 Hz, 1H), 1.46 (s, 3H), 1.22 (s, 3H), 0.88 – 0.66 (m, 14H), -0.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 149.7 (C_q), 149.7 (CH), 146.5 (C_q), 139.1 (C_q), 136.8 (CH), 128.6 (CH), 128.0 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 124.9 (CH), 124.4 (CH), 122.0 (CH), 120.8 (CH), 73.9 (CH), 55.0 (CH_2), 37.7 (C_q), 30.2 (CH_3), 30.0 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.5 (CH_3), 17.4 (CH_3), 13.5 (CH), 13.3 (CH), -7.5 (CH_3). **IR** (ATR): 2961, 2864, 1589, 1464, 1254, 1095, 883, 779, 745, 702 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 446 $[M+H]^+$ (100), 468 $[M+Na]^+$ (20). **HR-MS** (ESI) *m*/*z* calcd for $C_{29}H_{40}NOSi$ $[M+H]^+$: 446.2874, found: 446.2865.



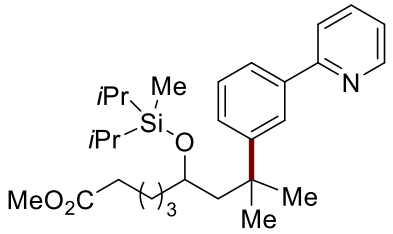
2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylbutan-2-yl)phenyl)pyridine (**32**).

The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **32** (85 mg, 46%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 4.7 Hz, 1H), 7.98 (s, 1H), 7.81 – 7.69 (m, 3H), 7.41 (d, *J* = 5.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 3.49 (d, *J* = 7.7 Hz, 2H), 2.00 (d, *J* = 7.7 Hz,, 2H), 1.40 (s, 6H), 0.93 (dd, *J* = 13.0, 7.2 Hz, 12H), 0.88 – 0.82 (m, 2H), -0.09 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 149.7 (C_q), 149.7 (CH), 139.3 (C_q), 136.8 (CH), 128.7 (CH), 126.6 (CH), 124.5 (CH), 124.5 (CH), 122.1 (CH), 120.9 (CH), 60.6 (CH), 47.0 (CH_2), 37.0 (C_q), 29.6 (CH_3), 17.5 (CH_3), 17.5 (CH_3), 13.0 (CH), -8.5 (CH_3). **IR** (ATR): 2962, 2864, 1589, 1468, 1254, 1023, 888, 774 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 370 $[M+H]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{23}H_{36}NOSi$ $[M+H]^+$: 370.2561, found: 370.2554.

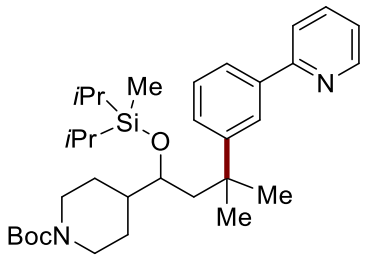


2-(3-(8-Chloro-4-((diisopropyl(methyl)silyl)oxy)-2-methyloctan-2-yl)phenyl)pyridine (**33**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1 →20/1) yielded **33** (150 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.00 (dt, *J* = 2.5, 1.1 Hz, 1H), 7.88 – 7.61 (m, 3H), 7.51 – 7.35 (m, 2H), 7.23 (ddd, *J* = 6.7, 4.8, 1.6 Hz, 1H), 3.76 – 3.62 (m, 1H), 3.33 (t, *J* = 6.7 Hz, 2H), 2.03 (dd, *J* = 14.3, 6.7 Hz, 1H), 1.83 (dd, *J* = 14.3, 4.8 Hz, 1H), 1.57 – 1.47 (m, 2H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36 – 1.03 (m, 4H), 0.98 – 0.89 (m, 12H), 0.89 – 0.78 (m, 2H), -0.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.9 (C_q), 149.9 (C_q), 149.7 (CH), 139.2 (C_q), 136.9 (CH), 128.6 (CH), 126.9 (CH), 124.8 (CH), 124.4 (CH), 122.1 (CH), 120.8 (CH), 70.1 (CH), 51.2 (CH_2), 45.1 (CH_2) 37.3 (C_q), 37.2 (CH_2), 32.9 (CH_2), 31.9 (CH_3), 28.3 (CH_3), 21.8 (CH_2), 17.8 (CH_3, overlapped, 2C), 17.8 (CH_3), 17.7 (CH_3), 13.8 (CH), 13.7 (CH), -7.0 (CH_3). **IR** (ATR): 2960, 2864, 1589, 1466, 1250, 883, 778, 736 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 460 $[M+H]^+$ (100),

482 $[M+Na]^+$ (20). **HR-MS** (ESI) *m*/*z* calcd for $C_{27}H_{43}ClNOSi$ $[M+H]^+$: 460.2797, found: 460.2798.

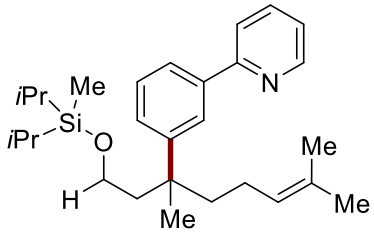


Methyl 6-((diisopropyl(methyl)silyl)oxy)-8-methyl-8-(3-(pyridin-2-yl)phenyl)nonanoate (**34**). The product was obtained following the general procedure for 36 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1 →10/1) yielded **34** (181 mg, 73%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.71 – 8.68 (m, 1H), 7.98 (q, *J* = 1.5 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.41 – 7.37 (m, 2H), 7.22 (ddd, *J* = 6.7, 4.8, 1.6 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 1H), 3.61 (s, 3H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.99 (dd, *J* = 14.3, 6.4 Hz, 1H), 1.82 (dd, *J* = 14.3, 5.0 Hz, 1H), 1.44 (s, 3H), 1.38 (s, 3H), 1.36 – 1.05 (m, 6H), 0.95 – 0.90 (m, 12H), 0.81 (d, *J* = 2.8 Hz, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 174.3 (C_q), 158.0 (C_q), 150.0 (C_q), 149.7 (CH), 139.1 (C_q), 136.8 (CH), 128.6 (CH), 126.9 (CH), 124.8 (CH), 124.4 (CH), 122.1 (CH), 120.8 (CH), 70.1 (CH), 51.5 (CH_3), 51.2 (CH_2), 37.8 (CH_2), 37.3 (C_q), 34.2 (CH_2), 31.6 (CH_3), 28.4 (CH_3), 25.2 (CH_2), 23.9 (CH_2), 17.8 (CH_3, overlapped, 2C), 17.8 (CH_3), 17.7 (CH_3), 13.8 (CH), 13.7 (CH), -7.0 (CH_3). **IR** (ATR): 2953, 2864, 1738, 1589, 1465, 1247, 1161, 1036, 998, 882, 776, 737, 701 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 484 $[M+H]^+$ (100), 506 $[M+Na]^+$ (30). **HR-MS** (ESI) *m*/*z* calcd for $C_{29}H_{46}NO_3Si$ $[M+H]^+$: 484.3241, found: 484.3241.



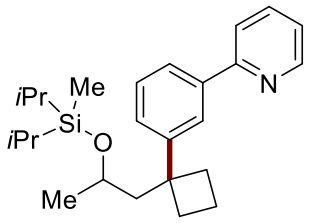
***Tert*-butyl 4-(1-((diisopropyl(methyl)silyl)oxy)-3-methyl-3-(3-(pyridin-2-**

yl)phenyl)butyl)piperidine-1-carboxylate (**35**). The product was obtained following the general procedure for 36 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→10/1) yielded **35** (182mg, 66%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.98 (dt, *J* = 2.5, 1.1 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.75 – 7.64 (m, 2H), 7.42 – 7.35 (m, 2H), 7.24 – 7.19 (m, 1H), 4.00 (s, 2H), 3.59 (ddd, *J* = 6.7, 5.2, 2.1 Hz, 1H), 2.33 (s, 1H), 2.15 (t, *J* = 12.0 Hz, 1H), 2.04 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.67 (dd, *J* = 14.4, 5.1 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 9H), 1.37 (s, 3H), 1.36 – 0.99 (m, 5H), 0.97 – 0.89 (m, 12H), 0.86 – 0.79 (m, 2H), -0.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.8 (C_q), 154.9 (C_q), 149.7 (C_q) , 149.7 (CH), 139.1 (C_q), 136.8 (CH), 128.5 (CH), 126.8 (CH), 124.8 (CH), 124.4 (CH), 122.1 (CH), 120.6 (CH), 79.13 (C_q), 73.47 (CH) , 47.8 (CH_2), 42.1 (CH), 37.2 (C_q), 32.3 (CH_3), 28.5 (CH_3), 28.1 (CH_2), 27.6 (CH_3), 25.9 (CH_2), 17.9 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 13.9 (CH), 13.8 (CH), -6.6 (CH_3). **IR** (ATR): 2941, 2863, 1691, 1586, 1469, 1421, 1362, 1237, 1171, 1088, 1057, 777, 706 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 553 $[M+H]^+$ (100), 575 $[M+Na]^+$ (70). **HR-MS** (ESI) *m*/*z* calcd for $C_{33}H_{53}N_2O_3Si$ $[M+H]^+$: 553.3820, found: 553.3811.

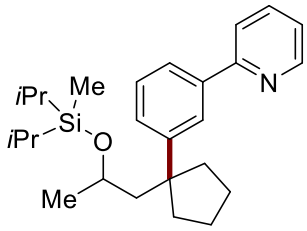


2-(3-(1-((Diisopropyl(methyl)silyl)oxy)-3,7-dimethyloct-6-en-3-yl)phenyl)pyridine (**36**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **36** (116 mg, 45%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.93 (t, *J* = 1.9 Hz, 1H), 7.80 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.45 – 7.35 (m, 2H), 7.22 (ddd, *J* = 7.1, 4.8, 1.4 Hz, 1H), 5.08 – 4.99 (m, 1H), 3.56 (td, *J* = 10.1, 5.7 Hz, 1H), 3.41 (td, *J* = 10.1, 5.1 Hz, 1H), 2.14 – 2.03 (m, 1H), 1.96 – 1.81 (m, 2H), 1.76 (td, *J* = 12.7, 12.1, 3.2 Hz, 1H), 1.71 – 1.58 (m, 5H), 1.47 (d, *J* = 1.5 Hz, 3H), 1.42 (s, 3H), 0.95 – 0.89 (m, 12H), 0.88 – 0.82 (m, 2H), -0.09 (s, 3H). **^{13}C**

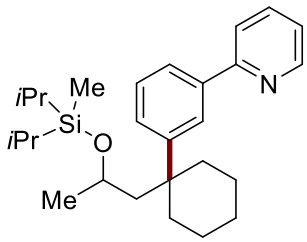
NMR (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 149.7 (CH), 148.0 (C_q), 139.2 (C_q), 136.8 (CH), 131.4 (C_q), 128.7 (CH), 127.1 (CH), 125.0 (CH), 124.8 (CH), 124.4 (CH), 122.1 (CH), 120.8 (CH), 60.3 (CH), 45.8 (CH_2), 44.0 (CH_2), 40.1 (C_q), 25.8 (CH_3), 24.4 (CH_3), 23.0 (CH_2), 17.7 (CH_3), 17.5 (CH_3), 17.5 (CH_3), 13.0 (CH), 13.0 (CH), -8.5 (CH_3). **IR** (ATR): 2941, 2862, 1589, 1465, 1381, 1249, 1091, 995, 885, 777 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 438 $[M+H]^+$ (100), 460 $[M+Na]^+$ (30). **HR-MS** (ESI) *m*/*z* calcd for $C_{28}H_{44}NOSi$ $[M+H]^+$: 438.3187, found: 438.3179.



2-(3-(1-(2-((Diisopropyl(methyl)silyl)oxy)propyl)cyclobutyl)phenyl)pyridine (**37**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **37** (99 mg, 50%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.87 – 7.68 (m, 4H), 7.45 – 7.37 (m, 1H), 7.26 – 7.21 (m, 2H), 3.48 – 3.38 (m, 1H), 2.53 – 2.39 (m, 2H), 2.37 – 2.31 (m, 1H), 2.27 – 2.17 (m, 2H), 2.12 – 1.93 (m, 2H), 1.91 – 1.79 (m, 1H), 0.95 (d, 3H), 0.93 – 0.85 (m, 12H), 0.84 – 0.72 (m, 2H), -0.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.9 (C_q), 150.1 (C_q), 149.6 (CH), 139.1 (C_q), 136.9 (CH), 128.6 (CH), 126.8 (CH), 124.6 (CH), 124.2 (CH), 122.1 (CH), 120.8 (CH), 67.0 (CH), 52.8 (CH_2), 45.7 (C_q), 34.5 (CH_2), 34.1 (CH_2), 24.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 16.4 (CH_2), 13.5 (CH), 13.5 (CH), -7.6 (CH_3). **IR** (ATR): 2932, 2863, 1589, 1466, 1249, 1144, 1094, 1043, 882, 776, 742 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 396 $[M+H]^+$ (100), 418 $[M+Na]^+$ (90). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{38}NOSi$ $[M+H]^+$: 396.2717, found: 396.2720.

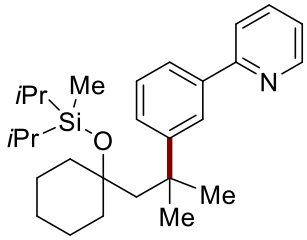


2-(3-(1-(2-((Diisopropyl(methyl)silyl)oxy)propyl)cyclopentyl)phenyl)pyridine (**38**). The product was obtained following the general procedure for 38 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **38** (108 mg, 53%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.7, 1.1 Hz, 1H), 7.93 (t, *J* = 1.8 Hz, 1H), 7.87 – 7.65 (m, 3H), 7.43 – 7.32 (m, 2H), 7.21 (ddd, *J* = 6.7, 4.8, 1.8 Hz, 1H), 3.61 – 3.52 (m, 1H), 2.15 – 1.91 (m, 4H), 1.89 – 1.81 (m, 2H), 1.80 – 1.70 (m, 2H), 1.69 – 1.58 (m, 2H), 0.94 – 0.87 (m, 15H), 0.82 – 0.74 (m, 2H), -0.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.0 (C_q), 149.8 (CH), 148.6 (C_q), 139.2 (C_q), 136.7 (CH), 128.5 (CH), 127.7 (CH), 125.6 (CH), 124.3 (CH), 122.0 (CH), 120.7 (CH), 67.2 (CH), 52.1 (CH_2), 50.2 (C_q), 39.6 (CH_2), 38.2 (CH_2), 25.4 (CH_3), 23.1 (CH_2), 23.0 (CH_2), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH), -7.6 (CH_3). **IR** (ATR): 2959, 2864, 1589, 1464, 1249, 1145, 1060, 997, 884, 777, 741 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 410 $[M+H]^+$ (100), 432 $[M+Na]^+$ (80). **HR-MS** (ESI) *m*/*z* calcd for $C_{26}H_{40}NOSi$ $[M+H]^+$: 410.2874, found: 410.2875.

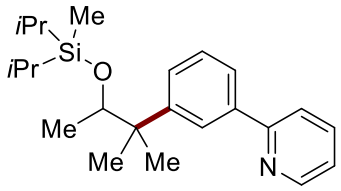


2-(3-(1-(2-((Diisopropyl(methyl)silyl)oxy)propyl)cyclohexyl)phenyl)pyridine (**39**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **39** (131 mg, 62%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.98 (td, *J* = 1.8, 0.7 Hz, 1H), 7.81 (dt, *J* = 7.1, 1.8 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.47 – 7.37 (m, 2H), 7.22 (ddd, *J* = 6.6, 4.8, 1.6 Hz, 1H), 3.68 – 3.53 (m, 1H), 1.98 (dd, *J* = 14.1, 4.5 Hz, 1H), 1.79 – 1.72 (m, 2H), 1.68 – 1.54 (m, 3H), 1.48 – 1.38

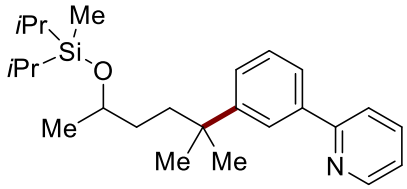
(m, 4H), 0.98 – 0.84 (m, 17H), 0.80 – 0.71 (m, 2H), -0.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.0 (C_q), 149.6 (CH), 147.8 (C_q), 139.2 (C_q), 136.9 (CH), 128.7 (CH), 128.0 (CH), 125.8 (CH), 124.2 (CH), 122.0 (CH), 120.8 (CH), 66.2 (CH), 40.9 (C_q), 38.1 (CH_2), 36.3 (CH_2), 26.6 (CH_2), 25.9 (CH_3), 22.6 (CH_2), 22.5 (CH_2), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.5 (CH) , -7.5 (CH_3). **IR** (ATR): 2928, 2860, 1589, 1464, 1249, 1134, 1089, 1050, 996, 883, 776, 743 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 424 $[M+H]^+$ (100), 446 $[M+Na]^+$ (30). **HR-MS** (ESI) *m*/*z* calcd for $C_{27}H_{42}NOSi$ $[M+H]^+$: 424.3030, found: 424.4028.



2-(3-(1-(1-((Diisopropyl(methyl)silyl)oxy)cyclohexyl)-2-methylpropan-2-yl)phenyl)pyridine (**40**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1 →20/1) yielded **40** (136 mg, 62%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.7, 1.1 Hz, 1H), 8.03 (t, *J* = 1.8 Hz, 1H), 7.85 – 7.66 (m, 3H), 7.47 (ddd, *J* = 7.9, 2.0, 1.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.22 (ddd, *J* = 6.7, 4.9, 1.8 Hz, 1H), 2.08 (s, 2H), 1.49 (s, 6H), 1.45 – 1.36 (m, 4H), 1.29 – 1.11 (m, 6H), 1.05 – 0.95 (m, 12H), 0.92 – 0.84 (m, 2H), 0.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2(C_q), 151.0 (C_q), 149.7(CH), 138.9(C_q), 136.8(CH), 128.3(CH), 127.1(CH), 124.9(CH), 124.2(CH), 122.0(CH), 120.7 (CH), 53.9 (CH_2), 40.0 (CH_2), 38.0 (C_q), 31.5 (CH_3), 25.7 (CH_2), 23.3 (CH_2), 18.2 (CH_3), 18.0 (CH_3), 14.9 (CH), -3.8 (CH_3). **IR** (ATR): 2931, 2861, 1589, 1466, 1248, 1051, 1018, 881, 769, 710 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 438 $[M+H]^+$ (100), 460 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{28}H_{44}NOSi$ $[M+H]^+$: 438.3187, found: 438.3183.

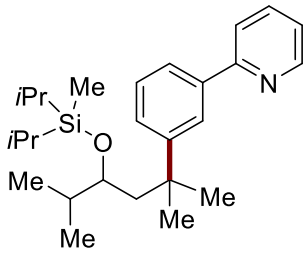


2-(3-(3-((Diisopropyl(methyl)silyl)oxy)-2-methylbutan-2-yl)phenyl)pyridine (**41**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **41** (94 mg, 51%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.99 (t, *J* = 1.9 Hz, 1H), 7.80 (ddd, *J* = 7.5, 1.8, 1.2 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.45 – 7.37 (m, 2H), 7.22 (ddd, *J* = 7.2, 4.8, 1.5 Hz, 1H), 3.99 (q, *J* = 6.2 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 1.00 – 0.90 (m, 15H), 0.88 – 0.83 (m, 2H), -0.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 149.7 (CH), 148.8 (C_q), 139.0 (C_q), 136.8 (CH), 128.3 (CH), 127.7 (CH), 125.6 (CH), 124.5 (CH), 122.0 (CH), 120.8 (CH), 76.3 (CH), 43.6 (C_q), 26.0 (CH_3), 23.1 (CH_3), 19.3 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 13.9 (CH), 13.6 (CH), -7.2 (CH_3). **IR** (ATR): 2864, 1589, 1466, 1377, 1246, 1118, 999, 883, 773 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 370 $[M+H]^+$ (100), 392 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{23}H_{36}NOSi$ $[M+H]^+$: 370.2561, found: 370.2554.

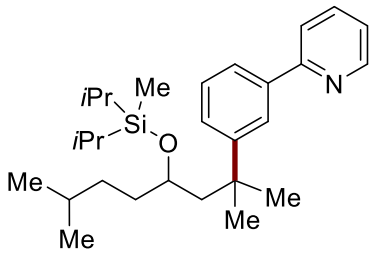


2-(3-(5-((Diisopropyl(methyl)silyl)oxy)-2-methylhexan-2-yl)phenyl)pyridine (**42**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **42** (107 mg, 54%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.79 – 7.70 (m, 3H), 7.41 – 7.37 (m, 2H), 7.22 (ddd, *J* = 7.1, 4.8, 1.4 Hz, 1H), 3.74 – 3.68 (m, 1H), 1.77 (ddd, *J* = 13.5, 12.3, 4.4 Hz, 1H), 1.64 (ddd, *J* = 13.4, 12.3, 4.9 Hz, 1H), 1.37 (s, 3H), 1.37 (s, 3H), 1.32 – 1.18 (m, 2H), 1.07 (d, *J* = 6.0 Hz, 3H), 0.97 – 0.90 (m, 12H), 0.88 – 0.81 (m, 2H), -0.05 (s, 3H). **^{13}C**

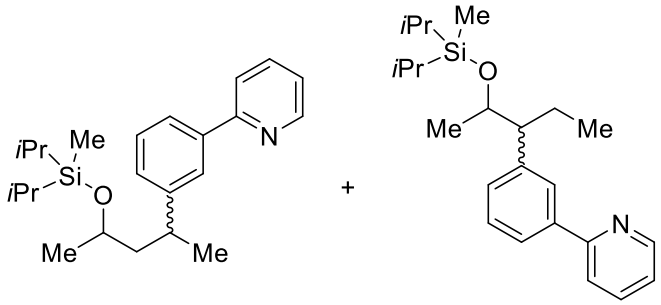
NMR (101 MHz, $CDCl_3$) δ = 158.2 (C_q), 150.2 (C_q), 149.7 (CH), 139.2 (C_q), 136.8 (CH), 128.6 (CH), 126.8 (CH), 124.7 (CH), 124.3 (CH), 122.0 (CH), 120.9 (CH), 69.2 (CH), 40.2 (CH_2), 37.8 (C_q), 35.0 (CH_2), 29.3 (CH_3), 29.2 (CH_3), 23.7 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 13.5 (CH), 13.4 (CH), -7.8 (CH_3). **IR** (ATR): 2964, 2864, 1589, 1466, 1375, 1249, 1129, 882, 774 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 398 $[M+H]^+$ (100), 420 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NOSi$ $[M+H]^+$: 398.2874, found: 398.2869.



2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2,5-dimethylhexan-2-yl)phenyl)pyridine (**43**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **43** (129 mg, 63%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.71 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.98 (td, *J* = 1.7, 1.0 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.78 – 7.69 (m, 2H), 7.44 – 7.37 (m, 2H), 7.23 (ddd, *J* = 6.7, 4.9, 1.7 Hz, 1H), 3.55 (ddd, *J* = 6.8, 4.2, 2.7 Hz, 1H), 1.90 (dd, *J* = 14.4, 4.2 Hz, 1H), 1.68 (dd, *J* = 14.5, 6.3 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.06 – 0.87 (m, 12H), 0.86 – 0.77 (m, 6H), 0.65 (d, *J* = 6.9 Hz, 3H), -0.07 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = δ = 158.0 (C_q), 150.3 (C_q), 149.6 (CH), 138.9 (C_q), 136.9 (CH), 128.5 (CH), 127.1 (CH), 124.9 (CH), 124.4 (CH), 122.0 (CH), 120.8 (CH), 74.6 (CH), 46.6 (CH_2), 37.4 (C_q), 33.9 (CH_3), 31.5 (CH_3), 28.4 (CH), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.4 (CH_3), 17.0 (CH_3), 14.0 (CH), 14.0 (CH), -6.5 (CH_3). **IR** (ATR): 2961, 2865, 1589, 1466, 1377, 1249, 1048, 778, 703 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 412 $[M+H]^+$ (100), 434 $[M+Na]^+$ (70). **HR-MS** (ESI) *m*/*z* calcd for $C_{26}H_{42}NOSi$ $[M+H]^+$: 412.3030, found: 412.3033.

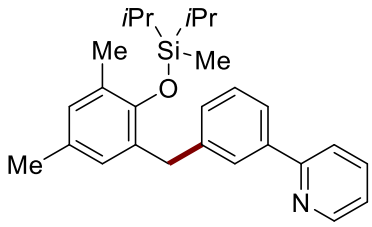


2-(3-(4-((Diisopropyl(methyl)silyl)oxy)-2,6-dimethylheptan-2-yl)phenyl)pyridine (**44**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **44** (157mg, 74%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.72 – 8.69 (m, 1H), 8.00 (dt, *J* = 1.7, 1.0 Hz, 1H), 7.79 (ddd, *J* = 5.0, 3.5, 1.8 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.42 – 7.39 (m, 2H), 7.25 – 7.17 (m, 1H), 3.66 (p, *J* = 5.5 Hz, 1H), 2.02 (dd, *J* = 14.3, 6.0 Hz, 1H), 1.84 (dd, *J* = 14.3, 5.3 Hz, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.19 – 1.01 (m, 3H), 0.94 (ddd, *J* = 7.0, 3.9, 3.0 Hz, 12H), 0.88 – 0.80 (m, 4H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H), -0.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 150.1 (C_q), 149.7 (CH), 139.2 (C_q), 136.7 (CH), 128.5 (CH), 126.9 (CH), 124.8 (CH), 124.3 (CH), 122.0 (CH), 120.7 (CH), 70.7 (CH), 51.3 (CH_2), 37.4 (C_q), 36.2 (CH_2), 33.6 (CH_2), 31.6 (CH), 28.4 (CH_3), 28.3 (CH_3), 22.7 (CH_3), 22.6 (CH_3), 18.0 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 17.7 (CH_3), 13.8 (CH), 13.8 (CH), -6.9 (CH_3). **IR** (ATR): 2957, 2865, 1589, 1465, 1373, 1250, 1048, 776, 737 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 440 $[M+H]^+$ (100), 462 $[M+Na]^+$ (80). **HR-MS** (ESI) *m*/*z* calcd for $C_{28}H_{46}NOSi$ $[M+H]^+$: 440.3343, found: 440.3346.

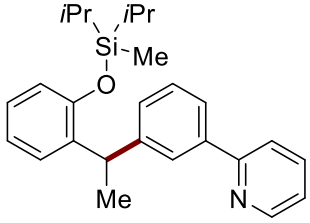


(**45**). The product was obtained following the general procedure for 48 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **45** as a colorless oil in 40% overall yield (74 mg). Analytical sample was failed to be obtained

via GPC (eluent: hexane). **IR** (ATR): 2963, 2930, 2864, 1589, 1465, 1249, 1149, 1045, 994, 882, 776, 741 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 370 $[M+H]^+$ (100), 392 $[M+Na]^+$ (80). **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{36}NOSi$ $[M+H]^+$: 370.2561, found: 370.2562



2-(3-(2-((Diisopropyl(methyl)silyl)oxy)-3,5-dimethylbenzyl)phenyl)pyridine (**46**). The product was obtained following the general procedure for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **46** (109 mg, 52%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 – 7.17 (m, 2H), 6.74 (d, *J* = 2.6 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 4.01 (s, 2H), 2.18 (s, 3H), 2.12 (s, 3H), 1.02 – 0.96 (m, 2H), 0.94 – 0.90 (m, 12H), 0.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.9 (C_q), 150.3 (C_q), 149.3 (CH), 141.0 (C_q), 138.5 (C_q), 136.1 (CH), 131.2 (C_q), 131.0 (CH), 130.2 (C_q), 129.9 (CH), 129.5 (CH), 128.5 (CH), 128.5 (CH), 127.5 (C_q), 126.3 (CH), 124.1 (CH), 121.7 (CH), 33.8 (CH_2), 20.8 (CH_3), 18.0 (CH_3), 17.6 (CH_3), 17.6 (CH_3), 14.1 (CH), -6.3 (CH_3). **IR** (ATR): 2945, 2865, 1585, 1471, 1253, 1228, 1151, 885, 780, 754, 723 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 418 $[M+H]^+$ (100), 440 $[M+Na]^+$ (40). **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{36}NOSi$ $[M+H]^+$: 418.2561, found: 418.2562.

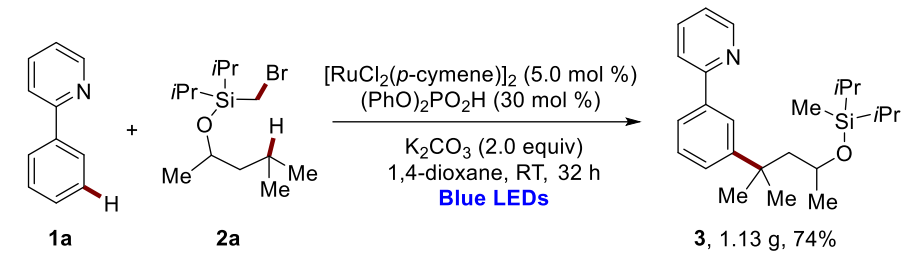


2-(3-(1-(2-((Diisopropyl(methyl)silyl)oxy)phenyl)ethyl)phenyl)pyridine (**47**). The product was obtained following the general procedure for 24 h. Purification by column

chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **47** (95mg, 47%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.68 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.87 (t, *J* = 1.8 Hz, 1H), 7.80 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.66 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.21 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.06 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.66 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.13 – 1.07 (m, 2H), 1.02 – 0.99 (m, 6H), 0.98 – 0.96 (m, 6H), 0.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.0 (C_q), 153.4 (C_q), 149.7 (CH), 147.0 (C_q), 139.3 (C_q), 136.8 (CH), 136.5 (C_q), 128.7 (CH), 128.7 (CH), 128.4 (CH), 126.9 (CH), 126.5 (CH), 124.6 (CH), 122.0 (CH), 120.9 (CH), 120.8 (CH), 118.0 (CH), 38.1 (CH), 21.2 (CH_3), 17.6 (CH_3), 17.5 (CH_3), 17.5 (CH_3), 17.5 (CH_3), 13.7 (CH), 13.6 (CH), -6.6 (CH_3). **IR** (ATR): 2965, 2865, 1589, 1485, 1457, 1254, 919, 882, 784, 752, 695 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 404 $[M+H]^+$ (100), 426 $[M+Na]^+$ (50). **HR-MS** (ESI) *m*/*z* calcd for $C_{26}H_{34}NOSi$ $[M+H]^+$: 404.2404, found: 404.2400.

5. Gram-Scale Synthesis and Late-Stage Derivatization

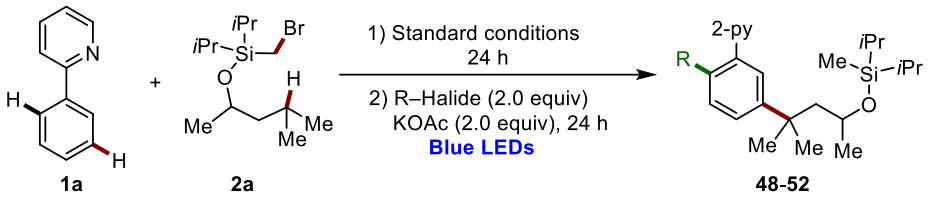
Gram-scale synthesis



1a **2a** **3**, 1.13 g, 74%

In an N_2 filled glovebox, $[RuCl_2(p\text{-cymene})]_2$ (122 mg, 5.0 mol %), diphenyl phosphate (38 mg, 30 mol %), K_2CO_3 (1.10 g, 8.0 mmol, 2.0 equiv), 1,4-dioxane (16 mL), **1a** (621 mg, 4.0 mmol, 1.0 equiv) and **2a** (1.86 g, 6.0 mmol, 1.5 equiv) were added into an oven-dried 100 mL round bottomed flask. The flask was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred under visible light irradiation (2 x Kessil A360N, the temperature was maintained between 30~35 °C). After 32 h, the mixture was filtered through a pad of celite (Et_2O), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford the corresponding product **3** in 74% (1.13 g) yield.

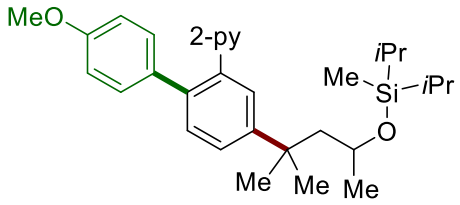
Sequential one-pot threefold C(sp^2)−H/C(sp^3)−H/C(sp^2)−H functionalizations



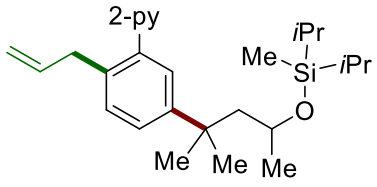
1a **2a** **48-52**

In an N_2 filled glovebox, $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 5.0 mol %), diphenyl phosphate (19.0 mg, 30.0 mol %), K_2CO_3 (69 mg, 0.5 mmol, 2.0 equiv), 1,4-dioxane (1.0 mL), **1a** (39 mg, 0.25 mmol, 1.0 equiv) and **2a** (155 mg, 0.5 mmol, 2.0 equiv) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred under visible light irradiation (2 x Kessil A360N, the temperature was maintained between 30~35 °C). After 24 h, the vial was taken into the glovebox, and to the mixture was added KOAc

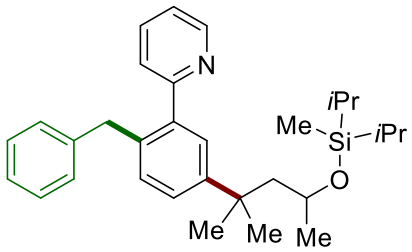
(49 mg, 0.5 mmol) and RX (2.0 equiv). Then the vial was re-sealed, moved out of the glovebox, stirred under visible light irradiation. After another 24 h, the mixture was filtered through a pad of celite (Et_2O), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford the corresponding products.



2-(4-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (**48**). The product was obtained following the general procedure with 4-iodoanisole (117 mg, 0.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→5/1) yielded **48** (103 mg, 84%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.65 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.46 – 7.32 (m, 3H), 7.13 – 7.03 (m, 3H), 6.90 (dt, *J* = 8.0, 1.1 Hz, 1H), 6.79 – 6.73 (m, 2H), 3.87 – 3.77 (m, 1H), 3.78 (s, 3H), 2.00 (dd, *J* = 14.1, 5.0 Hz, 1H), 1.87 (dd, *J* = 14.1, 6.4 Hz, 1H), 1.43 (s, 3H), 1.40 (s, 3H), 1.00 (d, *J* = 6.0 Hz, 3H), 0.97 – 0.88 (m, 12H), 0.86 – 0.75 (m, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.1 (C_q), 158.5 (C_q), 149.5 (CH), 148.8 (C_q), 139.0 (C_q), 137.5 (C_q), 135.3 (CH), 133.9 (C_q), 130.9 (CH), 130.2 (CH), 128.1 (CH), 126.5 (CH), 125.7 (CH), 121.3 (CH), 113.6 (CH), 66.9 (CH), 55.3 (CH_3), 54.5 (CH_2), 37.1 (C_q), 30.8 (CH_3), 29.1 (CH_3), 25.9 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2962, 2864, 1585, 1464, 1246, 1063, 991, 881, 784 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 490 $[M+H]^+$ (100), 512 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{31}H_{44}NO_2Si$ $[M+H]^+$: 490.3136, found: 490.3128.

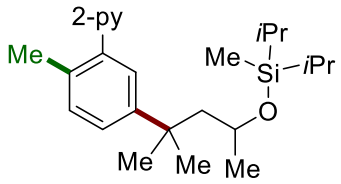


2-(2-Allyl-5-(4-((diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)pyridine (**49**). The product was obtained following the general procedure with allyl bromide (61 mg, 0.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→30/1) yielded **49** (54 mg, 51%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.26 – 7.20 (m, 2H), 5.94 – 5.79 (m, 1H), 4.99 – 4.80 (m, 2H), 3.77 (td, *J* = 6.3, 5.0 Hz, 1H), 3.52 – 3.37 (m, 2H), 1.94 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.84 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 1.01 – 0.88 (m, 15H), 0.88 – 0.73 (m, 2H), -0.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.5 (C_q), 149.1 (CH), 147.6 (C_q), 140.0 (C_q), 137.9 (CH), 136.2 (CH), 134.8 (C_q), 129.8 (CH), 127.5 (CH), 126.3 (CH), 124.3 (CH), 121.7 (CH), 115.4 (C_q), 66.9 (CH), 54.4 (CH_2), 37.1 (CH_2), 36.9 (C_q), 31.2 (CH_3), 28.6 (CH_3), 25.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2964, 2864, 1589, 1466, 1375, 1249, 1129, 882, 774 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 424 $[M+H]^+$ (100), 446 $[M+Na]^+$ (10). **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{42}NOSi$ $[M+H]^+$: 424.3030, found: 424.3023.

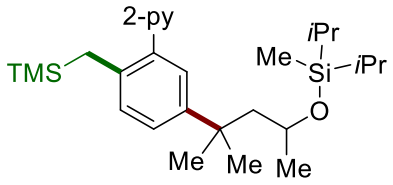


2-(2-Benzyl-5-(4-((diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)pyridine (**50**). The product was obtained following the general procedure with benzoyl chloride (70 mg, 0.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→30/1) yielded **50** (92 mg, 78%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.25 – 7.06 (m, 6H), 7.01 – 6.94 (m, 2H), 4.09 (s, 2H), 3.82 – 3.72 (m, 1H), 1.93 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.84 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 1.00 – 0.89 (m, 15H), 0.89 – 0.74 (m, 2H), -0.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.6 (C_q), 149.1 (CH), 147.6 (C_q), 141.7 (C_q), 140.2 (C_q), 136.3 (CH), 136.0 (C_q), 130.4 (CH), 129.0 (CH), 128.2 (CH), 127.6 (CH), 126.3 (CH), 125.7 (CH), 124.4 (CH), 121.7 (CH), 66.9 (CH), 54.5 (CH_2), 38.5 (CH_2), 36.9 (C_q), 31.2 (CH_3), 28.7 (CH_3), 25.8 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2963, 2864, 1589, 1466, 1250, 1127, 1060, 989, 882 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 474 $[M+H]^+$ (100), 496 $[M+Na]^+$ (40). **HR-MS** (ESI) *m*/*z* calcd for $C_{31}H_{44}NOSi$ $[M+H]^+$: 474.3187, found: 474.3183.

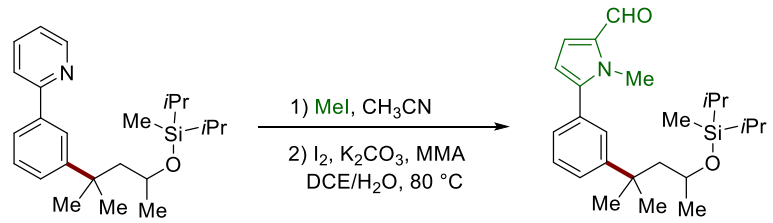


2-(4-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (**51**). The product was obtained following the general procedure with iodomethane (71 mg, 0.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→30/1) yielded **51** (65 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.37 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.34 (d, *J* = 2.2 Hz, 1H), 7.29 – 7.19 (m, 3H), 3.84 – 3.69 (m, 1H), 2.32 (s, 3H), 1.93 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.84 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 0.99 – 0.88 (m, 15H), 0.86 – 0.78 (m, 2H), -0.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.8 (C_q), 149.3 (CH), 147.2 (C_q), 140.1 (C_q), 136.1 (CH), 132.9 (C_q), 130.6 (CH), 127.3 (CH), 126.1 (CH), 124.2 (CH), 121.6 (CH), 67.0 (CH), 54.4 (CH_2), 36.9 (C_q), 31.4 (CH_3), 28.6 (CH_3), 25.7 (CH_3), 19.8 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2962, 2864, 1589, 1467, 1250, 1060, 990, 881, 783 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 398 $[M+H]^+$ (100), 420 $[M+Na]^+$ (30). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NOSi$ $[M+H]^+$: 398.2874, found: 398.2877.



2-(4-(4-((Diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)-4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (**52**). The product was obtained following the general procedure with (iodomethyl)trimethylsilane (107 mg, 0.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1→20/1) yielded **52** (90 mg, 77%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.68 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.72 (td, *J* = 7.7, 1.9 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.83 – 3.67 (m, 1H), 2.44 – 2.33 (m, 2H), 1.91 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.84 (dd, *J* = 14.0, 6.9 Hz, 1H), 1.36 (s, 3H), 1.31 (s, 3H), 0.97 – 0.88 (m, 15H), 0.89 – 0.77 (m, 2H), -0.08 (s, 3H), -0.23 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 161.6 (C_q), 149.0 (CH), 145.2 (C_q), 138.5 (C_q), 136.2 (CH), 135.9 (C_q), 129.7 (CH), 127.8 (CH), 125.9 (CH), 124.7 (CH), 121.4 (CH), 67.0 (CH), 54.6 (CH_2), 36.7 (C_q), 31.6 (CH_3), 28.5 (CH_3), 25.6 (CH_3), 23.0 (CH_2), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -1.3 (CH_3), -7.4 (CH_3). **IR** (ATR): 2960, 2864, 1590, 1467, 1250, 1061, 1016, 850 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 470 $[M+H]^+$ (100), 492 $[M+Na]^+$ (15). **HR-MS** (ESI) *m/z* calcd for $C_{28}H_{48}NOSi_2$ $[M+H]^+$: 470.3269, found: 470.3268.

Conversion of pyridine ring to 2-formylpyrrole

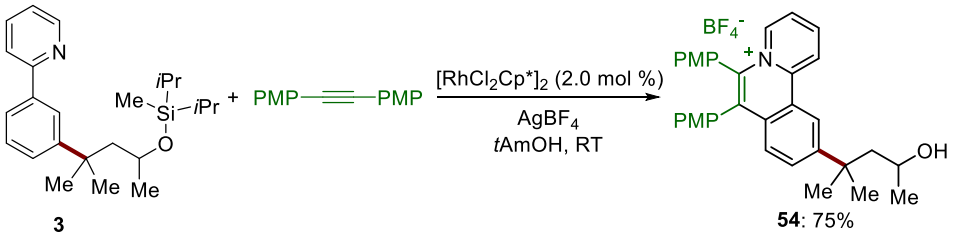


3 **53**: 53%

To a solution of **3** (115 mg, 0.3 mmol) in acetonitrile (0.3 mL) was added CH_3I (67 μL, 0.96 mmol) under N_2 in a sealed tube. The mixture was stirred at 80 °C for 15 h, and then cooled to room temperature. The solvent was removed under reduced pressure The residue was washed with EtOAc to afford a pale-yellow solid, which was

used for the next step without further purification. A 15 mL Schlenk tube was charged with the pale-yellow solid, I_2 (0.2 mmol, 51 mg), K_2CO_3 (1.2 mmol, 166 mg), methyl methacrylate (0.3 mmol, 34 μL), H_2O (0.6 mL) and DCE (0.6 mL) under air. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, water (10 mL) was added into the solution, and the mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc: 30/1→10/1) to afford the corresponding product **53** (66 mg, 53%) as a yellow liquid. **5-(3-(4-((diisopropyl(methyl)silyl)oxy)-2-methylpentan-2-yl)phenyl)-1-methyl-1H-pyrrole-2-carbaldehyde** (**53**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.58 (s, 1H), 7.44 – 7.34 (m, 3H), 7.22 (dt, J = 6.6, 1.8 Hz, 1H), 6.98 (d, J = 4.0 Hz, 1H), 6.30 (d, J = 4.1 Hz, 1H), 3.92 (s, 3H), 3.79 – 3.70 (m, 1H), 1.95 (dd, J = 14.2, 5.1 Hz, 1H), 1.84 (dd, J = 14.2, 6.3 Hz, 1H), 1.40 (s, 3H), 1.35 (s, 3H), 0.97 – 0.88 (m, 15H), 0.85 – 0.74 (m, 3H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.6 (CH), 150.3 (C_q), 145.0 (C_q), 133.1 (C_q), 130.8 (C_q), 128.4 (CH), 127.1 (CH), 126.6 (CH), 126.5 (CH), 124.6 (CH), 110.8 (CH), 66.8 (CH), 54.4 (CH_2), 37.3 (C_q), 34.5 (CH_3), 31.1 (CH_3), 28.8 (CH_3), 25.7 (CH_3), 17.7 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.6 (CH), 13.5 (CH), -7.4 (CH_3). **IR** (ATR): 2963, 2864, 1660, 1357, 1250, 1057, 990, 883, 778 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 414 $[M+H]^+$ (30), 436 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{25}H_{40}NO_2Si$ $[M+H]^+$: 414.2823, found: 414.2817.

Conversion of pyridine ring to polycyclic pyridinium salt

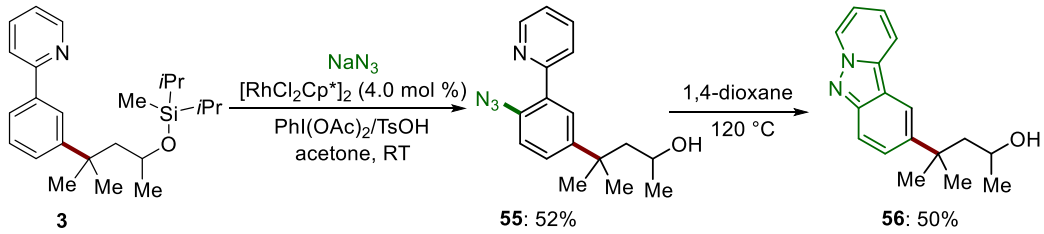


A 15 mL Schlenk tube was charged with alkyne (48 mg, 0.2 mmol), $[RhCl_2Cp^*]_2$ (2.5 mg, 2.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), *t*AmOH (1 mL) and **3** (92 mg, 0.24 mmol, 1.2 equiv). The mixture was stirred at RT for 24 h. The mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of celite, and washed with CH_2Cl_2

(50 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel (CH_2Cl_2/MeOH, 95:5) to afford the corresponding product **54** (74 mg, 75%) as a white solid.

10-(4-Hydroxy-2-methylpentan-2-yl)-6,7-bis(4-methoxyphenyl)pyrido[2,1-a]isoquinolin-5-ium tetrafluoroborate (**54**). **M.p.**: 112 – 116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.56 (d, J = 8.8 Hz, 1H), 9.00 (d, J = 1.8 Hz, 1H), 8.73 (dd, J = 7.2, 1.1 Hz, 1H), 8.54 (ddd, J = 8.7, 7.2, 1.3 Hz, 1H), 7.93 (dd, J = 8.7, 1.7 Hz, 1H), 7.86 (td, J = 7.1, 1.4 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.08 – 7.01 (m, 2H), 6.98 – 6.87 (m, 2H), 6.83 – 6.76 (m, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.74 – 3.69 (m, 1H), 2.14 – 2.01 (m, 2H), 1.79 (dd, J = 14.6, 3.0 Hz, 1H), 1.52 (s, 6H), 1.02 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.8 (C_q), 159.4 (C_q), 153.8 (C_q), 143.8 (C_q), 139.7 (CH), 137.6 (C_q), 137.1 (C_q), 135.6 (CH), 133.1 (CH), 132.4 (CH), 132.3 (CH), 131.3 (CH), 130.9 (C_q), 127.4 (CH), 126.3 (C_q), 124.6 (C_q), 124.4 (CH), 124.2 (CH), 122.7 (C_q), 122.7 (CH), 115.5 (CH), 114.0 (CH), 114.0 (CH), 65.3 (CH), 55.5 (CH_3), 55.4 (CH_3), 52.8 (CH_2), 38.6 (C_q), 30.0 (CH_3), 29.2 (CH_3), 25.7 (CH_3). **IR** (ATR): 3542, 2965, 2931, 1611, 1518, 1460, 1251, 1059, 911 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 492 [M(BF_4^-)]$^+$ (100). **HR-MS** (ESI) *m/z* calcd for $C_{33}H_{34}NO_3$ [M-(BF_4^-)]$^+$: 492.2533, found: 492.2532.

Conversion of pyridine ring to indazole



To a solution of **3** (0.3 mmol) in acetone (2 mL) was added $[Cp^*RhCl_2]_2$ (4 mol%), $PhI(OAc)_2$ (1.5 equiv) and *p*-TsOH•H_2O (1.5 equiv) in a pressure tube under air. After stirring at room temperature for 15 min, NaN_3 was added (0.9 mmol). The reaction mixture was stirred at 50 °C for 16 h. After cooling down to room temperature, the mixture was filtered over Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (*n*-

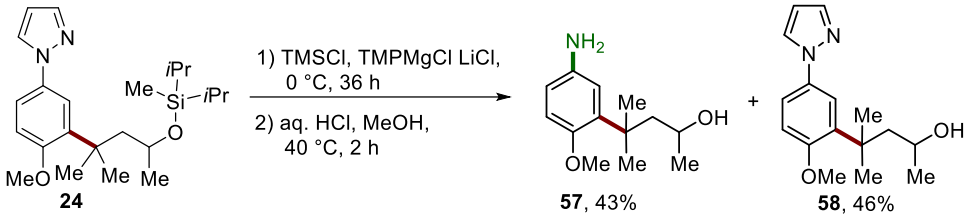
hexane/EtOAc: 5/1→1/1) to afford the corresponding azidation product **55** as a yellow liquid.

4-(4-azido-3-(pyridin-2-yl)phenyl)-4-methylpentan-2-ol (55). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.77 (td, *J* = 7.7, 1.9 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.47 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.28 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 3.78 (ddp, *J* = 12.4, 6.2, 3.1 Hz, 1H), 1.91 (dd, *J* = 14.6, 8.1 Hz, 1H), 1.76 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.44 – 1.35 (m, 6H), 1.08 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 156.0 (C_q), 149.4 (CH), 146.4 (C_q), 136.3 (CH), 135.0 (C_q), 131.5 (C_q), 129.2 (CH), 128.0 (CH), 125.3 (CH), 122.4 (CH), 119.0 (CH), 65.8 (CH), 53.5 (CH_2), 37.3 (C_q), 30.0 (CH_3), 29.4 (CH_3), 25.5 (CH_3). **IR** (ATR): 3354，2963, 2922, 2114, 1589, 1468, 1295 cm^{-1}.**MS** (ESI) *m*/*z* (relative intensity): 297 $[M+H]^+$ (20), 319 $[M+H]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{17}H_{21}N_4O$ $[M+H]^+$: 297.1710, found: 297.1715.

Azidation product **55** (0.11 mmol) and dry dioxane (4 mL) were added into a pressure tube under nitrogen. The tube was stirred at 125 °C for 24 h. After cooling down to room temperature, the volatiles were removed under reduced pressure, and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc: 2/1) to afford the corresponding product **56** as a red liquid.

4-Methyl-4-(pyrido[1,2-b]indazol-2-yl)pentan-2-ol (56). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 (dt, *J* = 6.9, 1.0 Hz, 1H), 8.11 (dt, *J* = 8.6, 1.3 Hz, 1H), 8.02 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.81 (dd, *J* = 9.1, 0.8 Hz, 1H), 7.65 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.33 (ddd, *J* = 8.6, 6.9, 1.0 Hz, 1H), 7.15 (td, *J* = 6.9, 1.5 Hz, 1H), 3.86 – 3.77 (m, 1H), 2.00 (dd, *J* = 14.6, 8.3 Hz, 1H), 1.84 (dd, *J* = 14.6, 2.8 Hz, 1H), 1.50 (d, *J* = 2.1 Hz, 6H), 1.05 (d, *J* = 6.2 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 148.5 (C_q), 140.2 (C_q), 135.6 (C_q), 128.2 (CH), 128.0 (CH), 121.7 (CH), 118.1 (CH), 116.2 (CH), 115.9 (CH), 115.8 (CH), 115.2 (C_q), 66.0 (CH), 53.6 (CH_2), 37.5 (C_q), 30.7 (CH_3), 29.3 (CH_3), 25.1 (CH_3). **IR** (ATR): 3379, 2962, 2924, 1646, 1510, 1216, 1118, 744 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 269 $[M+H]^+$ (50), 291 $[M+H]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$: 269.1648, found: 269.1654.

Removal of pyrazole group



24 **57**, 43% **58**, 46%

To a solution of **24** (201 mg, 0.5 mmol) and TMSCl (163 mg, 1.5 mmol) in THF (2.5 mL), TMPMgCl·LiCl in THF (1.0 M, 3.0 mmol) was added dropwise, and the mixture was stirred at 0 ºC for 36 h. Then, water (15 mL) was added, and the mixture was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude material was dissolved in MeOH (15 mL), mixed with aq. HCl (2 M, 8 mL) and stirred for 2.0 h at 40 ºC. After this period, the mixture was neutralized with saturated aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by chromatography on silica gel (n-hexane/EtOAc: 15/1→3/1) to afford the corresponding product **57** (48 mg, 43%) as a yellow liquid. Meanwhile, compound **58** was obtained in 46% (63 mg) yield as a yellow liquid.

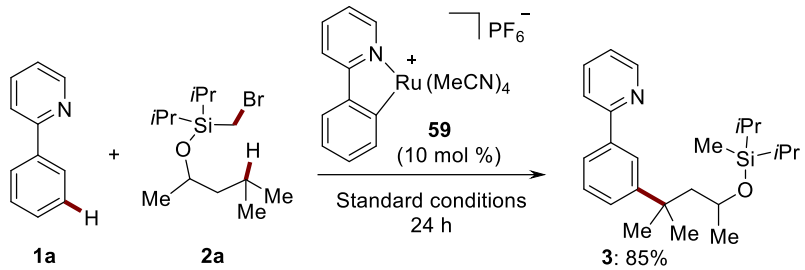
4-(5-Amino-2-methoxyphenyl)-4-methylpentan-2-ol (**57**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.71 (d, J = 8.5 Hz, 1H), 6.66 (d, J = 2.8 Hz, 1H), 6.54 (dd, J = 8.5, 2.8 Hz, 1H), 3.76 (s, 3H), 3.73 – 3.66 (m, 1H), 3.41 (bs, 2H), 2.13 (dd, J = 14.3, 8.4 Hz, 1H), 1.83 (dd, J = 14.3, 2.8 Hz, 1H), 1.38 (s, 3H), 1.34 (s, 3H), 1.03 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 151.7 (C_q), 139.8 (C_q), 136.9 (C_q), 115.8 (CH), 113.9 (CH), 113.3 (CH), 66.3 (CH), 55.7 (CH_3), 49.9 (CH_2), 37.4 (C_q), 29.6 (CH_3), 29.1 (CH_3), 24.8 (CH_3). **IR** (ATR): 3342, 2961, 2914, 1616, 1495, 1232, 1091, 1029, 810 cm^{-1}. **MS** (ESI) *m*/*z* (relative intensity): 224 $[M+H]^+$ (10), 246 $[M+Na]^+$ (100). **HR-MS** (ESI) *m*/*z* calcd for $C_{13}H_{21}NO_2Na$ $[M+Na]^+$: 246.1465, found: 246.1467.

4-(2-Methoxy-5-(*1H*-pyrazol-1-yl)phenyl)-4-methylpentan-2-ol (**58**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, J = 2.4 Hz, 1H), 7.69 (s, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.44 (dd, J = 8.8, 2.7 Hz, 1H), 6.92 (d, J = 8.7 Hz, 1H), 6.43 (t, J = 2.1 Hz, 1H), 3.87 (s, 3H), 3.74 – 3.61 (m, 1H), 2.11 (dd, J = 14.4, 7.9 Hz, 1H), 1.98 (dd, J = 14.4, 3.4 Hz, 1H),

1.46 (s, 3H), 1.42 (s, 3H), 1.04 (d, J = 6.3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.1 (C_q), 140.6 (CH), 137.4 (C_q), 133.9 (C_q), 127.1 (CH), 120.0 (CH), 118.7 (CH), 112.0 (CH), 107.2 (CH), 66.3 (CH), 55.5 (CH_3), 49.6 (CH_2), 37.9 (C_q), 29.4 (CH_3), 29.1 (CH_3), 25.1 (CH_3). **IR** (ATR): 3293, 3030, 2926, 2110, 1604, 1498, 1308, 1075 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 275 $[M+H]^+$ (20), 297 $[M+Na]^+$ (100). **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{22}N_2O_2Na$ $[M+Na]^+$: 297.1573, found: 297.1577.

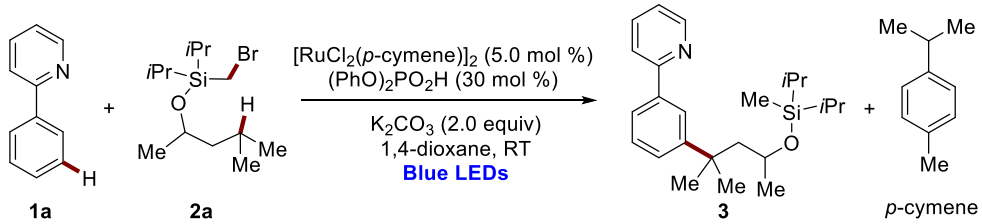
6. Mechanistic Studies

p-Cymene-free ruthenium complex as catalyst



In an N_2 filled glovebox, ruthenium complex **59** (28.2 mg, 10 mol %), diphenyl phosphate (38 mg, 30 mol %), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), 1,4-dioxane (2.0 mL), **1a** (0.5 mmol, 1.0 equiv) and **2a** (1.0 mmol, 2.0 equiv) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred for 24 h under visible light irradiation (2 x Kessil A360N, the temperature was maintained between 30~35 °C). Then the mixture was filtered through a pad of celite (Et_2O), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford product **3** in 85% yield.

Detection of free *p*-cymene



In an N_2 filled glovebox, $[RuCl_2(p\text{-cymene})]_2$ (30.6 mg, 5.0 mol %), diphenyl phosphate (76 mg, 30 mol %), K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv), 1,4-dioxane (4.0 mL), **1a**

(155 mg, 1.0 mmol, 1.0 equiv), **2a** (718 mg, 2.0 mmol, 2.0 equiv) and n-dodecane (100 μL) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred with a N_2 balloon under visible light irradiation (2 x Kessil A360N, the temperature was maintained between 30~35 °C). During the course of the reaction aliquots of 25 μL were removed via syringe after 30 min, 60 min, 100 min, 140 min, 3 h, 4 h, 6 h, 9.5 h and 17 h. The sample was diluted with EtOAc, filtered through a short plug of silica gel and analyzed by gas chromatography.

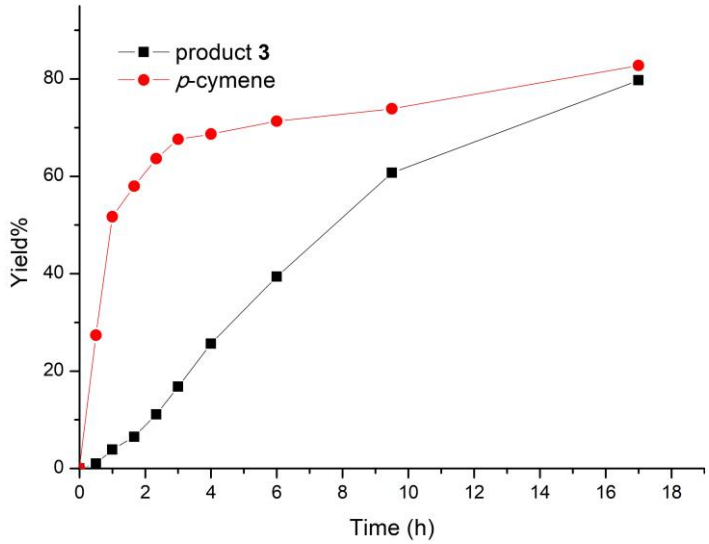


Figure S1. Release of *p*-cymene in the reaction of **1a** and **2a**.

In addition, we have detected the *p*-cymene dissociation of a mixture of [$RuCl_2$(*p*-cymene)] (0.025 mmol) with different components in dioxane (2 mL). In all cases, *p*-cymene dissociation were observed after 1.0 h under the blue-light irradiation. [$RuCl_2$(*p*-cymene)] (0.0125 M), 36%; [$RuCl_2$(*p*-cymene)] + **1a** (0.50 mmol) + K_2CO_3 (1.0 mmol), 57%; [$RuCl_2$(*p*-cymene)] + $(PhO)_2PO_2H$ (0.15 mmol) + K_2CO_3 (1.0 mmol), 38%; [$RuCl_2$(*p*-cymene)] + **1a** (0.50 mmol) + $(PhO)_2PO_2H$ (0.15 mmol) + K_2CO_3 (1.0 mmol), 39%.

UV/Vis absorption spectra

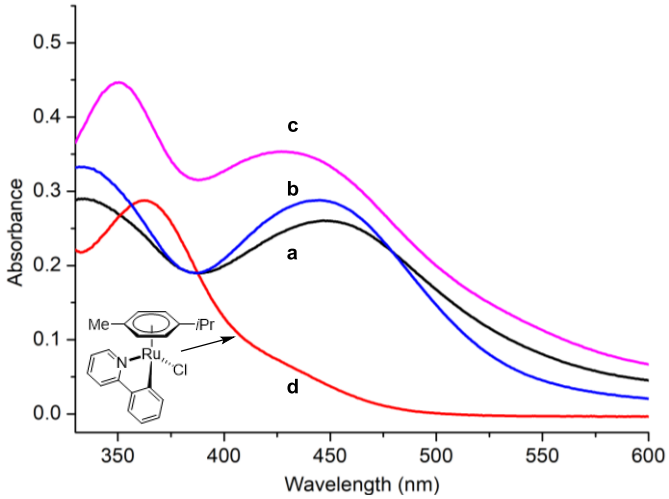
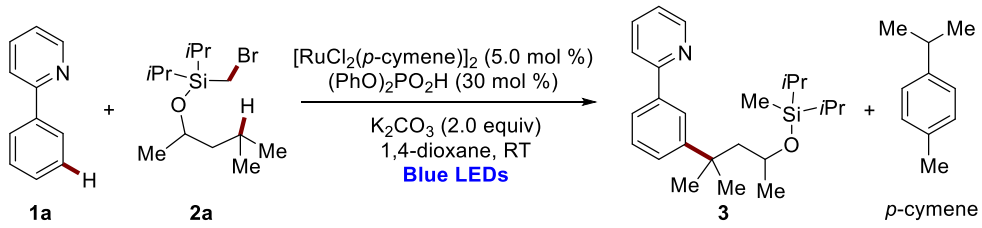


Figure S2. UV-Vis Absorption Spectroscopy. a) $[RuCl_2(p\text{-cymene})]_2$ (0.15mM) in 1,4-dioxane; b) $[RuCl_2(p\text{-cymene})]_2$ (0.15 mM), **1a** (3.0 mM) and $(PhO)_2PO_2H$ (0.9 mM) in 1,4-dioxane; c) $[RuCl_2(p\text{-cymene})]_2$ (0.15 mM), **1a** (3.0 mM), $(PhO)_2PO_2H$ (0.9 mM) and K_2CO_3 (2.0 equiv related to **1a**) in 1,4-dioxane; the mixture was maintained under ultrasonic conditions for 5 min before the UV/Vis absorption spectra detection; d) Cycloruthenated complex (0.05 mM) in 1,4-dioxane.

Switch on-off experiment



In an N_2 filled glovebox, $[RuCl_2(p\text{-cymene})]_2$ (23 mg, 5.0 mol %), diphenyl phosphate (57 mg, 30 mol %), K_2CO_3 (207 mg, 1.5 mmol, 2.0 equiv), 1,4-dioxane (3.0 mL), **1a** (116 mg, 0.75 mmol, 1.0 equiv), **2a** (464 mg, 1.5 mmol, 2.0 equiv) and *n*-dodecane (75 μL) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred with a N_2 balloon sequentially under visible light irradiation (2 × Kessil A360N, the temperature was maintained between 30~35 °C) and in the absence of light. Every two hours, an aliquot of 25 μL was removed via syringe, diluted with EtOAc, filtered

through a short plug of silica gel and analyzed by gas chromatography.

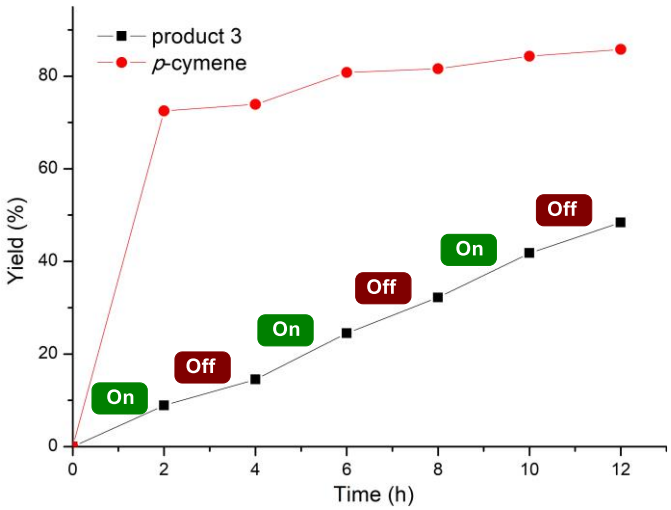
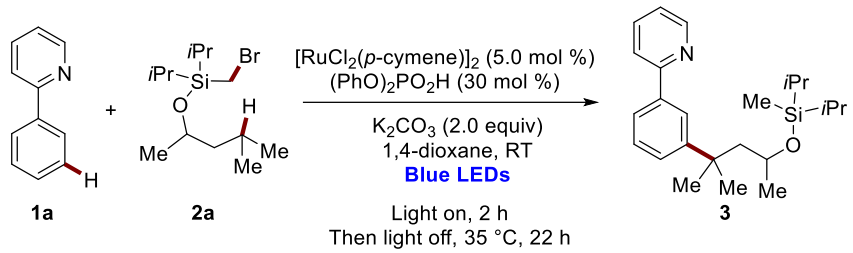


Figure S3. Switch on-off experiment.

On-off experiment



In an N_2 filled glovebox, [$RuCl_2$(*p*-cymene)]$_2$ (15.3 mg, 5.0 mol %), diphenyl phosphate (38 mg, 30 mol %), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), 1,4-dioxane (2.0 mL), **1a** (78 mg, 0.5 mmol, 1.0 equiv) and **2a** (309 mg, 1.0 mmol, 2.0 equiv) were added into an oven-dried 10 mL vial. The vial was capped with a septum, sealed with electrical tape, and moved out of the glovebox. The reaction mixture was stirred under visible light irradiation (2 × Kessil A360N, the temperature was maintained between 30~35 °C) for 2 h and then stirred at 35 °C in the absence of light. After 22 h, the mixture was filtered through a pad of celite (Et_2O), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford product **3** in 65% yield.

7. Computational studies

Computational Methods

All DFT calculations were carried out with Gaussian 16 program.[1] The geometry optimizations were conducted using B3LYP functional[2] including Grimme's dispersion corrections[3] with Becke-Johnson damping, LANL2DZ basis set[4] for ruthenium as well as bromine and 6-31G(d) basis set for other atoms. To confirm whether each optimized stationary point is an energy minimum or a transition state as well as evaluate the zero-point vibrational energy and thermal corrections at 298 K, the vibrational frequencies were computed at the same level of theory as for the geometry optimizations. On the basis of the gas-phase optimized structures, the single-point energies and solvent effects were evaluated with the PBE0 functional[5] SDD basis set[6] for ruthenium and bromine and 6-311+G(d, p) for other atoms. The solvation energies were calculated using the self-consistent reaction field with the SMD implicit solvent model.[7]

Table of Energies

Zero-point correction (*ZPE*) thermal correction to enthalpy (*TCH*) thermal correction to Gibbs free energy (*TCG*) energies (*E*) enthalpies (*H*) and Gibbs free energy (*G*) (in Hartree) of the structures calculated at the PBE0-D3(BJ)/6-311+G(d,p)-SDD-SMD(1,4-Dioxane)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Table S3. Energies in **Figure 1**

Structures	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
radical A	0.398603	0.421724	0.346350	−876.896855	−876.475131	−876.550505	
radical B	0.397802	0.421241	0.345999	−876.907491	−876.48625	−876.561492	
int1(singlet)	0.536277	0.572204	0.467789	−2156.994527	−2156.545148	−2156.649563	
int2(singlet)	0.941291	1.002706	0.836868	−3047.528425	−3046.525719	−3046.691557	
int2* (singlet)	0.941291	1.002706	0.836868	−3047.45753	−3046.454824	−3046.620662	
int2' (triplet)	0.940134	1.002045	1.001101	−3047.516829	−3046.514784	−3046.681424	

TS1 (triplet)	0.938079	0.999505	0.833762	−3047.494436	−3046.494931	−3046.660674	197.20*i*
int3 (doublet)	0.538410	0.576690	0.465127	−2170.536318	−2169.959628	−2170.071191	
TS2 (triplet)	0.935997	0.997561	0.831349	−3047.479096	−3046.481535	−3046.647747	453.46*i*
int4(singlet)	0.940330	1.001222	0.842459	−3047.542718	−3046.541496	−3046.700259	
int4' (triplet)	0.937782	0.999047	0.836654	−3047.501845	−3046.502798	−3046.665191	

Cartesian coordinates of the structures

radical A

C	0.95014200	-2.15298000	1.62065300
H	1.72669200	-2.38248500	2.35939000
H	0.86227800	-3.00223700	0.93378200
H	-0.00195100	-2.03584800	2.14732700
C	1.30090300	-0.88414000	0.84520300
H	1.38261700	-0.04795700	1.55488900
C	2.61990000	-1.04842400	0.08680500
H	2.46539100	-1.84587300	-0.65231800
H	3.38741900	-1.40873600	0.78695800
C	3.63618600	1.26592800	0.37412700
H	3.95862200	2.17664600	-0.14387500
H	2.86502600	1.55358600	1.09609300
H	4.49582600	0.88222900	0.93921900
C	4.24314700	-0.14772300	-1.61961100
H	3.88459600	-0.85918400	-2.37243200
H	4.61162900	0.74207800	-2.14352500
H	5.09736200	-0.60741300	-1.10513600
O	0.28693700	-0.58921700	-0.11833300
Si	-1.24682000	0.04794400	0.11649500
C	-1.82632300	-0.15893900	1.87390900
H	-1.62566800	0.56920000	2.65894400
H	-2.39279500	-1.02238600	2.21958400
C	-2.32962200	-0.96101300	-1.06618600
H	-1.84061000	-0.87254600	-2.04856000
C	-1.22169300	1.90558600	-0.29011800
H	-1.19013700	1.98381000	-1.38800600
C	-2.48050600	2.63898100	0.20741200
H	-2.45535400	3.69724300	-0.08514900

H	-3.40494300	2.20797000	-0.18885600
H	-2.54841700	2.60520300	1.30135900
C	0.04194400	2.58430400	0.26538100
H	0.95183200	2.14793900	-0.15291800
H	0.04522000	3.65846500	0.03645400
H	0.09797800	2.48928900	1.35835300
C	-3.76912500	-0.43875400	-1.19922200
H	-4.27788000	-0.41267600	-0.22720100
H	-3.80126900	0.57255200	-1.61798800
H	-4.36120400	-1.08683300	-1.85913800
C	-2.31719100	-2.44858300	-0.67315800
H	-2.87065200	-3.05284200	-1.40419700
H	-1.29660300	-2.83952100	-0.61410000
H	-2.79394600	-2.60638800	0.30278200
C	3.13474900	0.21316500	-0.62303100
H	2.29386600	0.63478400	-1.18898500

radical B

C	1.32535200	-2.32762100	-1.78681000
H	2.09259800	-3.09508300	-1.63339800
H	1.47986100	-1.86985700	-2.76993900
H	0.34363400	-2.81223000	-1.78903600
C	1.39230800	-1.25931900	-0.70046600
H	1.23000300	-1.73190800	0.27974900
C	2.75957900	-0.54594300	-0.66389500
H	2.88829900	-0.04210300	-1.63034200
H	3.53692500	-1.32408200	-0.59726800
C	2.88898000	0.42843800	0.46623200
C	3.26082600	-0.07061400	1.82617300
H	2.76678300	0.50395500	2.62110800
H	2.99595300	-1.12654300	1.96174100
H	4.34728400	0.00928200	2.01535300
C	2.85836800	1.89985700	0.21404000
H	2.32236600	2.13631600	-0.71014700
H	2.37280800	2.44309100	1.03748600
H	3.87315100	2.33056800	0.12320800
O	0.38064600	-0.28683700	-0.95065400
Si	-0.93654900	0.06646100	0.02050500
C	-0.38589100	0.42302200	1.78952900
H	0.21551100	1.33713400	1.83458300
H	-1.25044700	0.55564300	2.45094700
H	0.22201100	-0.39088000	2.19817600
C	-2.15079600	-1.40195200	0.00845200
H	-2.23659500	-1.69954800	-1.04815700

C	-1.71553600	1.60587600	-0.77329600
H	-2.38541100	1.24090900	-1.56736700
C	-2.56024300	2.41483400	0.22887200
H	-3.04385100	3.26653100	-0.26743200
H	-3.34789800	1.81729200	0.69939100
H	-1.93227800	2.82126200	1.03094400
C	-0.65902500	2.51243700	-1.42788600
H	-0.06193200	1.96938300	-2.16543500
H	-1.13392900	3.36878600	-1.92547800
H	0.03166900	2.91442500	-0.67644900
C	-3.55634100	-1.01670600	0.50262700
H	-3.53171300	-0.64819400	1.53638300
H	-4.01088100	-0.23710200	-0.11754600
H	-4.22880700	-1.88499900	0.48709400
C	-1.62483100	-2.61218800	0.80076100
H	-2.33124300	-3.45181300	0.75088700
H	-0.66252600	-2.97265700	0.42213600
H	-1.49132400	-2.36406200	1.86097800

int1(singlet)

Ru	-0.01326300	-0.70337600	-0.02474600
C	2.63729300	-1.77298200	-0.53655200
C	3.99817400	-2.04813500	-0.47939900
C	4.74453300	-1.52814200	0.58074300
C	4.10594600	-0.74227300	1.53863200
C	2.74369400	-0.49168800	1.41204000
H	4.45422200	-2.66498800	-1.24664700
H	5.80910400	-1.72815500	0.65166100
H	4.65603900	-0.30282100	2.36222400
H	2.19120200	0.13640000	2.10066100
C	1.68865800	-2.22853100	-1.59279100
C	0.58483300	-3.03692700	-1.22851300
C	-0.42075500	-3.30084200	-2.16959400
H	0.53754100	-3.47834500	-0.23930800
C	0.81351300	-2.07182000	-3.84652500
C	-0.31140000	-2.81476300	-3.47108300
H	-1.27904400	-3.89610100	-1.87359400
H	0.90153300	-1.69812000	-4.86244000
H	-1.09497300	-3.01723200	-4.19481200
N	2.02510500	-1.00296600	0.39744000
P	0.21324400	2.17832800	0.03743300
O	0.27730700	1.58750900	-1.35002900
O	1.49207200	3.12524700	0.40415400
O	-0.87665300	3.37458400	0.20001800

C	2.80102900	2.68746200	0.27795400
C	3.67198400	3.01413500	1.31780100
C	3.25778500	2.00592400	-0.85439300
C	5.01916900	2.66545700	1.22023700
H	3.28145600	3.54504600	2.17955700
C	4.60572700	1.65710500	-0.93218400
H	2.55801500	1.75987400	-1.64330200
C	5.49139800	1.98497800	0.09615800
H	5.69887200	2.92796900	2.02628600
H	4.96453500	1.12377500	-1.80809200
H	6.54042800	1.71330600	0.02220100
C	-2.24336900	3.10790400	0.19476000
C	-2.82145200	2.25941600	1.14125000
C	-3.02050900	3.76859800	-0.75434800
C	-4.20421600	2.08166800	1.12859300
H	-2.18821300	1.74261000	1.85153600
C	-4.40399100	3.58555700	-0.75023300
H	-2.53271600	4.41871900	-1.47283700
C	-4.99914500	2.74227100	0.18958200
H	-4.65849200	1.41442400	1.85482100
H	-5.01453200	4.10323500	-1.48492400
H	-6.07573900	2.59816800	0.18865400
O	0.01576600	1.11902300	1.14430800
C	-2.56828400	0.13772100	-1.49692400
C	-3.92440900	0.13402600	-1.79446300
C	-4.77702600	-0.63659200	-1.00203700
C	-4.24927600	-1.36802800	0.05548200
C	-2.87338700	-1.33088900	0.31292900
H	-1.84806600	0.73171600	-2.04841100
H	-4.29965700	0.73915400	-2.61146300
H	-5.84474900	-0.65838900	-1.20009000
H	-4.89746400	-1.96854100	0.68363800
C	-2.17006900	-2.05009100	1.37800800
C	-0.75086100	-1.88989300	1.40164100
C	-2.82135600	-2.85131000	2.32782700
C	-0.04443300	-2.56850800	2.41038700
C	-2.09254200	-3.50910400	3.31381900
H	-3.90273100	-2.96258400	2.30353700
C	-0.70131000	-3.36424000	3.35070500
H	1.03661400	-2.47043300	2.46502200
H	-2.60141400	-4.12693800	4.04803500
H	-0.12651600	-3.87452100	4.12071000
N	-2.05584800	-0.57959200	-0.48195000
C	1.80414000	-1.77135400	-2.91500500

H	2.64641600	-1.14323500	-3.18836900

int2(singlet)

Ru	-0.74630500	1.17823600	0.39024900
C	-0.32023800	-1.74159000	0.70790900
C	-0.30373500	-3.10739500	0.40661900
C	-0.70782300	-3.54645100	-0.84954500
C	-1.12422200	-2.61009500	-1.79418300
C	-1.10810000	-1.26506300	-1.44695500
H	0.00132900	-3.82095800	1.16323800
H	-0.72633100	-4.60703300	-1.07796400
H	-1.47926600	-2.91022500	-2.77268400
H	-1.44547300	-0.49382000	-2.12593000
C	0.07743300	-1.12804900	1.97571200
C	0.61346800	-1.85813300	3.04644300
C	-0.02992500	0.29551900	2.03071400
C	1.07274700	-1.20434300	4.18613300
H	0.69168000	-2.94051900	2.98701700
C	0.46979400	0.92425700	3.18573200
C	1.00889500	0.19171300	4.24486500
H	1.49122200	-1.77326300	5.01092800
H	0.47100700	2.00775200	3.25012000
H	1.38928000	0.71300900	5.12050500
N	-0.70788400	-0.83713200	-0.23797500
P	-3.78416800	0.25608300	0.16547800
O	-2.79168800	1.04717500	1.02109100
O	-3.74039800	0.35403100	-1.32649200
O	-5.23832900	0.69445400	0.78846200
O	-3.65665700	-1.29258500	0.71448200
C	-6.36053000	-0.01032200	0.36624600
C	-6.92407400	0.25100700	-0.88263400
C	-6.90238900	-0.97441000	1.21457700
C	-8.05232700	-0.46660000	-1.28080500
H	-6.46031800	0.99028400	-1.52519100
C	-8.03094600	-1.68518800	0.80598800
H	-6.42444100	-1.16132600	2.17003400
C	-8.60741200	-1.43487500	-0.44100800
H	-8.49525600	-0.27075800	-2.25346600
H	-8.45401300	-2.44183600	1.46065100
H	-9.48355900	-1.99329000	-0.75784200
C	-3.94944300	-2.47302400	0.07051200
C	-4.46710600	-2.56277700	-1.22449600
C	-3.67663200	-3.62856100	0.80717100
C	-4.68953200	-3.82542400	-1.77578600

H	-4.66918200	-1.66046100	-1.78538600
C	-3.90194300	-4.88108500	0.24160100
H	-3.27622700	-3.51976100	1.80959700
C	-4.40508300	-4.98783900	-1.05743500
H	-5.09264100	-3.89473900	-2.78280700
H	-3.68401700	-5.77556600	0.81931300
H	-4.58338200	-5.96418700	-1.49884700
Si	4.04931800	-0.93901200	-0.19847200
C	3.64016100	-1.00098400	-2.04706700
C	2.23805600	-1.59615400	-2.26347900
C	4.68715000	-1.74732900	-2.89334800
H	3.61245800	0.04331400	-2.39173100
H	1.47158700	-1.04706200	-1.71434100
H	1.96335000	-1.56914500	-3.32594900
H	2.18959100	-2.64235100	-1.94055000
H	5.67951500	-1.29152200	-2.82747600
H	4.78665900	-2.79370500	-2.58711600
H	4.39221000	-1.74483100	-3.95107800
C	3.70082900	-2.54039900	0.74391600
C	4.12655800	-2.40120400	2.21767900
C	4.36232500	-3.77232300	0.10428900
H	2.60929500	-2.67600100	0.71446700
H	3.60822800	-1.58017300	2.72336700
H	3.89610700	-3.31989800	2.77336500
H	5.20491000	-2.22363400	2.29549600
H	3.96890200	-3.97772300	-0.89669500
H	5.44740400	-3.63896400	0.01827900
H	4.18846800	-4.66733300	0.71657800
O	5.66166400	-0.62022700	0.08633500
C	6.53382900	0.33025500	-0.52504800
H	6.62712700	0.08274400	-1.59095500
C	5.99316800	1.75482000	-0.41076700
H	6.69226400	2.46394700	-0.86790700
H	5.02858600	1.86234800	-0.91925100
H	5.86242800	2.03239400	0.64120600
C	7.90424600	0.18906000	0.13939400
H	8.60998900	0.84638000	-0.38928600
H	7.82696500	0.56828100	1.16783100
C	8.46555200	-1.24185900	0.17759400
C	9.81949500	-1.25546100	0.89783000
C	8.58584500	-1.86136000	-1.22028400
H	7.76018700	-1.85065300	0.75653600
H	9.73980800	-0.83237500	1.90629600
H	10.20789100	-2.27636800	0.99056300

H	10.56350900	-0.66550400	0.34640500
H	7.60772500	-1.97641400	-1.69763900
H	9.21392600	-1.24174400	-1.87445500
H	9.04470900	-2.85543000	-1.16609000
C	3.01994800	0.39104200	0.71448000
H	2.28721000	-0.04321800	1.39111100
H	3.64055100	1.08734900	1.27733500
Br	1.86413000	1.62107100	-0.44816900
C	-1.32644400	3.59113300	2.22863800
C	-1.44941700	4.92221000	2.61008500
C	-1.21769600	5.91887000	1.66215600
C	-0.92922600	5.54213800	0.35279200
C	-0.84696700	4.18617900	0.03065200
H	-1.50341100	2.77626600	2.91845300
H	-1.72323100	5.16486400	3.63117500
H	-1.29437300	6.96851900	1.92901800
H	-0.80794100	6.28000500	-0.43299000
C	-0.69112700	3.70968200	-1.36440700
C	-1.58867100	2.74361200	-1.85819900
C	0.32888600	4.18689600	-2.19889200
C	-1.43971200	2.23866400	-3.14968700
H	-2.42455700	2.39720900	-1.25635400
C	0.47022100	3.67972800	-3.49077100
H	1.03190700	4.92280100	-1.81949800
C	-0.40693900	2.70109600	-3.96681800
H	-2.14767200	1.49287900	-3.49749600
H	1.27595200	4.04095800	-4.12346300
H	-0.28572500	2.30687100	-4.97162600
N	-0.97788500	3.22546800	0.98153500

int2*(singlet)

Ru	-0.74630500	1.17823600	0.39024900
C	-0.32023800	-1.74159000	0.70790900
C	-0.30373500	-3.10739500	0.40661900
C	-0.70782300	-3.54645100	-0.84954500
C	-1.12422200	-2.61009500	-1.79418300
C	-1.10810000	-1.26506300	-1.44695500
H	0.00132900	-3.82095800	1.16323800
H	-0.72633100	-4.60703300	-1.07796400
H	-1.47926600	-2.91022500	-2.77268400
H	-1.44547300	-0.49382000	-2.12593000
C	0.07743300	-1.12804900	1.97571200
C	0.61346800	-1.85813300	3.04644300
C	-0.02992500	0.29551900	2.03071400

C	1.07274700	-1.20434300	4.18613300
H	0.69168000	-2.94051900	2.98701700
C	0.46979400	0.92425700	3.18573200
C	1.00889500	0.19171300	4.24486500
H	1.49122200	-1.77326300	5.01092800
H	0.47100700	2.00775200	3.25012000
H	1.38928000	0.71300900	5.12050500
N	-0.70788400	-0.83713200	-0.23797500
P	-3.78416800	0.25608300	0.16547800
O	-2.79168800	1.04717500	1.02109100
O	-3.74039800	0.35403100	-1.32649200
O	-5.23832900	0.69445400	0.78846200
O	-3.65665700	-1.29258500	0.71448200
C	-6.36053000	-0.01032200	0.36624600
C	-6.92407400	0.25100700	-0.88263400
C	-6.90238900	-0.97441000	1.21457700
C	-8.05232700	-0.46660000	-1.28080500
H	-6.46031800	0.99028400	-1.52519100
C	-8.03094600	-1.68518800	0.80598800
H	-6.42444100	-1.16132600	2.17003400
C	-8.60741200	-1.43487500	-0.44100800
H	-8.49525600	-0.27075800	-2.25346600
H	-8.45401300	-2.44183600	1.46065100
H	-9.48355900	-1.99329000	-0.75784200
C	-3.94944300	-2.47302400	0.07051200
C	-4.46710600	-2.56277700	-1.22449600
C	-3.67663200	-3.62856100	0.80717100
C	-4.68953200	-3.82542400	-1.77578600
H	-4.66918200	-1.66046100	-1.78538600
C	-3.90194300	-4.88108500	0.24160100
H	-3.27622700	-3.51976100	1.80959700
C	-4.40508300	-4.98783900	-1.05743500
H	-5.09264100	-3.89473900	-2.78280700
H	-3.68401700	-5.77556600	0.81931300
H	-4.58338200	-5.96418700	-1.49884700
Si	4.04931800	-0.93901200	-0.19847200
C	3.64016100	-1.00098400	-2.04706700
C	2.23805600	-1.59615400	-2.26347900
C	4.68715000	-1.74732900	-2.89334800
H	3.61245800	0.04331400	-2.39173100
H	1.47158700	-1.04706200	-1.71434100
H	1.96335000	-1.56914500	-3.32594900
H	2.18959100	-2.64235100	-1.94055000
H	5.67951500	-1.29152200	-2.82747600

H	4.78665900	-2.79370500	-2.58711600
H	4.39221000	-1.74483100	-3.95107800
C	3.70082900	-2.54039900	0.74391600
C	4.12655800	-2.40120400	2.21767900
C	4.36232500	-3.77232300	0.10428900
H	2.60929500	-2.67600100	0.71446700
H	3.60822800	-1.58017300	2.72336700
H	3.89610700	-3.31989800	2.77336500
H	5.20491000	-2.22363400	2.29549600
H	3.96890200	-3.97772300	-0.89669500
H	5.44740400	-3.63896400	0.01827900
H	4.18846800	-4.66733300	0.71657800
O	5.66166400	-0.62022700	0.08633500
C	6.53382900	0.33025500	-0.52504800
H	6.62712700	0.08274400	-1.59095500
C	5.99316800	1.75482000	-0.41076700
H	6.69226400	2.46394700	-0.86790700
H	5.02858600	1.86234800	-0.91925100
H	5.86242800	2.03239400	0.64120600
C	7.90424600	0.18906000	0.13939400
H	8.60998900	0.84638000	-0.38928600
H	7.82696500	0.56828100	1.16783100
C	8.46555200	-1.24185900	0.17759400
C	9.81949500	-1.25546100	0.89783000
C	8.58584500	-1.86136000	-1.22028400
H	7.76018700	-1.85065300	0.75653600
H	9.73980800	-0.83237500	1.90629600
H	10.20789100	-2.27636800	0.99056300
H	10.56350900	-0.66550400	0.34640500
H	7.60772500	-1.97641400	-1.69763900
H	9.21392600	-1.24174400	-1.87445500
H	9.04470900	-2.85543000	-1.16609000
C	3.01994800	0.39104200	0.71448000
H	2.28721000	-0.04321800	1.39111100
H	3.64055100	1.08734900	1.27733500
Br	1.86413000	1.62107100	-0.44816900
C	-1.32644400	3.59113300	2.22863800
C	-1.44941700	4.92221000	2.61008500
C	-1.21769600	5.91887000	1.66215600
C	-0.92922600	5.54213800	0.35279200
C	-0.84696700	4.18617900	0.03065200
H	-1.50341100	2.77626600	2.91845300
H	-1.72323100	5.16486400	3.63117500
H	-1.29437300	6.96851900	1.92901800

H	-0.80794100	6.28000500	-0.43299000
C	-0.69112700	3.70968200	-1.36440700
C	-1.58867100	2.74361200	-1.85819900
C	0.32888600	4.18689600	-2.19889200
C	-1.43971200	2.23866400	-3.14968700
H	-2.42455700	2.39720900	-1.25635400
C	0.47022100	3.67972800	-3.49077100
H	1.03190700	4.92280100	-1.81949800
C	-0.40693900	2.70109600	-3.96681800
H	-2.14767200	1.49287900	-3.49749600
H	1.27595200	4.04095800	-4.12346300
H	-0.28572500	2.30687100	-4.97162600
N	-0.97788500	3.22546800	0.98153500

int2'(triplet)

Ru	-1.09161700	0.95295500	0.63525000
C	-0.39442500	-1.86075600	1.31363300
C	-0.20427700	-3.23646600	1.15395300
C	-0.73586800	-3.88416700	0.04385800
C	-1.44927400	-3.14049900	-0.89307900
C	-1.62461000	-1.77944100	-0.67637200
H	0.37714000	-3.78658000	1.88480100
H	-0.59395200	-4.95253200	-0.08643900
H	-1.90070300	-3.60235100	-1.76276200
H	-2.21153400	-1.16966600	-1.35391300
C	0.20566700	-1.03800700	2.36322600
C	0.90812400	-1.56589200	3.45568700
C	0.08194400	0.36804400	2.18203000
C	1.49946200	-0.71275900	4.38437500
H	0.99648200	-2.64036300	3.58949500
C	0.69914000	1.20114800	3.13116300
C	1.39672600	0.67267500	4.21907300
H	2.04127500	-1.12540400	5.23038800
H	0.66749900	2.27799100	3.00731500
H	1.87254100	1.33972200	4.93354900
N	-1.11858100	-1.14931400	0.40040500
P	-4.21722300	0.48660400	-0.31043900
O	-3.21934500	1.43913800	0.34664300
O	-3.94831200	-0.02753200	-1.68901500
O	-5.65205000	1.27122200	-0.19528300
O	-4.45885700	-0.72211700	0.78763700
C	-6.79586100	0.58109300	-0.58183000
C	-7.10478700	0.43965400	-1.93486300
C	-7.61799300	0.04126800	0.40587500

C	-8.26431700	-0.24688700	-2.29771300
H	-6.42793000	0.84939800	-2.67534700
C	-8.77568500	-0.64136700	0.03117000
H	-7.33318100	0.15533100	1.44599300
C	-9.10150700	-0.78761500	-1.31893600
H	-8.51100500	-0.36167400	-3.34960200
H	-9.41917700	-1.06575500	0.79664600
H	-10.00195200	-1.32239700	-1.60708200
C	-4.47240400	-2.07716500	0.54959300
C	-5.03020700	-2.64674000	-0.59817400
C	-3.92577700	-2.88178400	1.55197700
C	-5.01244200	-4.03489200	-0.73924000
H	-5.45135500	-2.01070900	-1.36572800
C	-3.92050700	-4.26624400	1.39917700
H	-3.49874000	-2.40313900	2.42692200
C	-4.45830700	-4.85034400	0.24991800
H	-5.44354200	-4.47997500	-1.63204400
H	-3.48692200	-4.88807700	2.17759500
H	-4.45227300	-5.92991300	0.12958900
Si	4.04698100	-0.65952600	0.04074800
C	3.06904600	-0.31374200	-1.54070900
C	1.58059000	-0.54220600	-1.23183500
C	3.49710300	-1.10892600	-2.78422300
H	3.19774400	0.75415600	-1.76233100
H	1.24923500	0.06530800	-0.38229400
H	0.95410400	-0.27393200	-2.08696800
H	1.37558500	-1.58994600	-0.98746100
H	4.52772800	-0.89196100	-3.08195100
H	3.42126200	-2.18996800	-2.62652300
H	2.84715200	-0.85792400	-3.63323000
C	3.55499500	-2.27204700	0.90472500
C	4.32060900	-2.44073400	2.22929900
C	3.73451000	-3.50638000	0.00635800
H	2.48816600	-2.17342700	1.14365500
H	4.11689500	-1.61963600	2.92559500
H	4.02865600	-3.37379900	2.73049000
H	5.40216600	-2.47972300	2.05729900
H	3.07626400	-3.47352100	-0.86815500
H	4.76696200	-3.59150400	-0.35251500
H	3.49985500	-4.42661000	0.55898800
O	5.69181900	-0.79898300	-0.18248600
C	6.59089600	-0.07706200	-1.02363900
H	6.21572900	-0.11687100	-2.05525000
C	6.69293500	1.38556000	-0.59885800

H	7.41618700	1.91751000	-1.22768900
H	5.72881400	1.89660900	-0.68280700
H	7.02608700	1.45433100	0.44295600
C	7.94707700	-0.78272200	-0.95730200
H	8.62225500	-0.29340500	-1.67447400
H	8.37066900	-0.61277200	0.04229300
C	7.91520900	-2.29497500	-1.23158600
C	9.32330100	-2.88533500	-1.08618000
C	7.32445300	-2.62958900	-2.60657500
H	7.27092200	-2.74838100	-0.46803600
H	9.74670300	-2.66987600	-0.09789500
H	9.31178900	-3.97363100	-1.21805700
H	10.00414500	-2.46651300	-1.83900000
H	6.27621400	-2.32533600	-2.68157800
H	7.88294600	-2.12840700	-3.40860600
H	7.36903900	-3.70838000	-2.79673400
C	3.68243200	0.68743600	1.34426200
H	2.83587000	0.42660400	1.97710000
H	4.54849300	0.88244500	1.97781800
Br	3.16370400	2.53106600	0.63585600
C	-0.95307900	3.78865700	1.78919300
C	-0.56795400	5.11913800	1.88263500
C	0.06452900	5.70932300	0.78756700
C	0.24185600	4.95816000	-0.36911000
C	-0.18940600	3.62850000	-0.40793000
H	-1.43245900	3.27557500	2.61502400
H	-0.75701900	5.67272800	2.79574800
H	0.39172100	6.74369400	0.82698700
H	0.68449600	5.39345000	-1.25793000
C	-0.10544400	2.81878200	-1.64405900
C	-1.21239200	2.04450800	-2.03981500
C	1.04238500	2.83076100	-2.44959200
C	-1.16289700	1.27901600	-3.20593300
H	-2.13547100	2.08434000	-1.47155400
C	1.08309800	2.07514200	-3.62021100
H	1.91178400	3.40106400	-2.13962000
C	-0.01504700	1.29555100	-3.99930500
H	-2.03390800	0.68836800	-3.47138500
H	1.98169600	2.08093500	-4.23043200
H	0.02934500	0.70372900	-4.90916400
N	-0.74058200	3.04443800	0.68794400

TS1(triplet)

Ru	-0.95800200	1.21245900	0.29009400

C	-0.61119600	-1.70456900	-0.07914300
C	-0.64382700	-2.96151200	-0.69094300
C	-1.03867200	-3.07091100	-2.01627600
C	-1.39566400	-1.91721200	-2.71650100
C	-1.36628500	-0.69912400	-2.05458600
H	-0.36820600	-3.84265000	-0.12596500
H	-1.08232700	-4.04443000	-2.49307300
H	-1.71782300	-1.95768300	-3.75068100
H	-1.66522800	0.22074700	-2.53518600
C	-0.15852100	-1.41629100	1.27436300
C	0.30490500	-2.39241200	2.16729500
C	-0.14353600	-0.04119000	1.63261100
C	0.81321300	-2.01880300	3.40798900
H	0.27866700	-3.44311000	1.89310500
C	0.41766200	0.31151900	2.86688300
C	0.88356000	-0.66453900	3.74952400
H	1.17435100	-2.77623200	4.09711100
H	0.53014700	1.35555000	3.13591800
H	1.31576300	-0.36838200	4.70182700
N	-0.98642600	-0.59292200	-0.76938300
P	-4.03341400	0.27174700	0.04030800
O	-3.09205500	1.25433600	0.74385000
O	-4.10398000	0.25835600	-1.45112300
O	-5.48870400	0.55834200	0.74485600
O	-3.64689900	-1.18598500	0.70297700
C	-6.52431500	-0.32984100	0.47130200
C	-7.19282100	-0.27617800	-0.75171700
C	-6.87157900	-1.26723000	1.44263000
C	-8.22886400	-1.17767100	-0.99767500
H	-6.87867600	0.44973600	-1.49249500
C	-7.90970400	-2.16283000	1.18576400
H	-6.31589300	-1.28883500	2.37381300
C	-8.58927300	-2.12171600	-0.03343200
H	-8.75250500	-1.14401600	-1.94911500
H	-8.18088300	-2.89907600	1.93708500
H	-9.39425500	-2.82338500	-0.23209100
C	-3.81258700	-2.45194500	0.19018200
C	-4.36970000	-2.73137000	-1.05935600
C	-3.35445400	-3.48506600	1.01349300
C	-4.44779300	-4.05995700	-1.47887400
H	-4.70990700	-1.92028200	-1.68877400
C	-3.43989600	-4.80563200	0.57918900
H	-2.92235300	-3.22743300	1.97500500
C	-3.98275400	-5.10118900	-0.67374500

H	-4.88053100	-4.27844300	-2.45162700
H	-3.08006200	-5.60451600	1.22233100
H	-4.05144500	-6.13068200	-1.01324200
Si	4.48460500	-0.31679400	-0.28285900
C	4.04817400	-1.70016500	-1.51395200
C	2.54209900	-2.01795600	-1.48965700
C	4.86922200	-2.98518600	-1.31173400
H	4.29224500	-1.30185600	-2.51202600
H	1.92501500	-1.13909000	-1.69604300
H	2.29045000	-2.78885800	-2.23016700
H	2.24106000	-2.40010400	-0.50784000
H	5.94596500	-2.80078400	-1.34312500
H	4.64867300	-3.45075100	-0.34497800
H	4.63139100	-3.72342300	-2.08965100
C	3.75468400	-0.54279600	1.44406600
C	4.05176100	0.68591100	2.32094900
C	4.25055000	-1.82898400	2.12504900
H	2.66743700	-0.61378300	1.32563800
H	3.61556200	1.59672900	1.89713400
H	3.62437400	0.55222900	3.32323300
H	5.13146000	0.84028400	2.43367900
H	3.92516600	-2.72654800	1.58798900
H	5.34477400	-1.85186000	2.18864600
H	3.85103200	-1.89924000	3.14500000
O	6.13800000	-0.26476200	-0.00128700
C	7.21354200	-0.13233000	-0.92766900
H	7.03296800	-0.79033100	-1.79152200
C	7.33004800	1.30776900	-1.42620100
H	8.17706700	1.41156000	-2.11409600
H	6.42147800	1.61793000	-1.95222200
H	7.48281100	1.98666800	-0.57977700
C	8.48490100	-0.57734200	-0.19936100
H	9.36042900	-0.34337500	-0.82171800
H	8.56152800	0.04079800	0.70494400
C	8.51418000	-2.06574600	0.18725600
C	9.53924200	-2.31681700	1.29984900
C	8.81265100	-2.95886600	-1.02454100
H	7.52022300	-2.32108800	0.57650000
H	9.30022000	-1.73428300	2.19707400
H	9.56866100	-3.37603000	1.58188800
H	10.54855200	-2.03176300	0.97429400
H	8.11495600	-2.78339400	-1.85070900
H	9.82623100	-2.76936400	-1.40202700
H	8.74866500	-4.02036000	-0.75857000

C	3.93457000	1.32435800	-1.03700200
H	4.30817400	2.23762800	-0.57675100
H	3.89311800	1.41204300	-2.12229200
Br	1.69351400	1.57834600	-0.54902900
C	-1.05988200	3.34454200	2.55514600
C	-0.96606500	4.61036000	3.12187700
C	-0.74691000	5.70420500	2.28526200
C	-0.68842700	5.49562600	0.90987000
C	-0.81988600	4.20108000	0.40399500
H	-1.22950900	2.46202800	3.15836700
H	-1.06202300	4.72751400	4.19569500
H	-0.65453000	6.70573500	2.69406500
H	-0.57982600	6.32356100	0.21791800
C	-0.90492700	3.91939600	-1.04683200
C	-1.95750800	3.11436800	-1.52119000
C	0.03061600	4.43323900	-1.95463500
C	-2.04940200	2.80220600	-2.88037900
H	-2.73149400	2.77168900	-0.84126700
C	-0.06848400	4.12088800	-3.30778900
H	0.85736600	5.03489500	-1.59018400
C	-1.10151500	3.29954600	-3.77337400
H	-2.87181300	2.17562900	-3.21243000
H	0.67273200	4.50525900	-4.00241500
H	-1.16549600	3.05657700	-4.83009100
N	-0.94154200	3.13394500	1.23354100

int3(doublet)

Ru	0.34675600	-0.46150200	-0.67654900
C	2.11869100	-2.65633100	0.10121300
C	2.50687200	-3.90592400	0.59639900
C	1.54477300	-4.85555600	0.91438700
C	0.19630300	-4.55141500	0.71751900
C	-0.13858700	-3.29622600	0.23149100
H	3.56159000	-4.12418400	0.71767300
H	1.84214100	-5.82608300	1.30000000
H	-0.59111100	-5.26198600	0.93858100
H	-1.16485900	-3.00840000	0.06060700
C	3.00274600	-1.58704200	-0.33873100
C	4.40348300	-1.64709800	-0.35369500
C	2.33361300	-0.43995100	-0.82577100
C	5.12956900	-0.57929300	-0.87123800
H	4.92624100	-2.52278500	0.02157900
C	3.07700100	0.62747600	-1.34226000
C	4.46810400	0.55076000	-1.37046500

H	6.21469500	-0.62271200	-0.88756600
H	2.56379400	1.51043900	-1.70760500
H	5.04514700	1.38190800	-1.76376400
N	0.78851400	-2.36305200	-0.04186200
P	0.22454600	1.97980600	0.74296600
O	0.13223100	1.98600900	-0.77327500
O	0.48328300	0.55248700	1.27518900
O	-1.07260800	2.61130700	1.47934200
O	1.31193100	3.01131700	1.35333400
C	-2.25490500	2.96502400	0.83885600
C	-3.43616200	2.42129600	1.33768900
C	-2.26424000	3.87570700	-0.21623900
C	-4.65167100	2.80193300	0.77063600
H	-3.38619700	1.70772300	2.15300500
C	-3.48739900	4.24454200	-0.77671500
H	-1.32999000	4.27491300	-0.59239400
C	-4.68187000	3.71372400	-0.28622500
H	-5.57470700	2.37595100	1.15233900
H	-3.50252300	4.95300500	-1.59995600
H	-5.63031400	4.00705100	-0.72645300
C	2.68715300	2.76623600	1.29677900
C	3.24838200	1.66863300	1.94826700
C	3.47546900	3.69666400	0.62605300
C	4.63297900	1.51030800	1.92173800
H	2.60318900	0.95247100	2.44087000
C	4.86089000	3.52846500	0.61391300
H	2.99816400	4.53604500	0.13185100
C	5.44203800	2.43686200	1.26118100
H	5.07860400	0.65069100	2.41292400
H	5.48333700	4.25240000	0.09580200
H	6.51994800	2.30531700	1.24591400
Br	0.01906100	-1.36128300	-3.02967100
C	-3.24308200	-0.81283300	0.04088000
C	-2.56305600	0.67387400	-1.60018100
C	-3.86137600	0.83879400	-2.07179500
C	-4.88600000	0.12691200	-1.45435900
C	-4.57479100	-0.70071300	-0.38135600
H	-1.73297100	1.21033200	-2.04197400
H	-4.05452800	1.51640900	-2.89536200
H	-5.91467300	0.23063700	-1.78740200
H	-5.35128500	-1.23658700	0.15345200
C	-2.89145600	-1.66174000	1.20198700
C	-3.50662900	-2.91016100	1.38657600
C	-1.91907700	-1.23690400	2.11905300

C	-3.14052900	-3.72687500	2.45597500
H	-4.24418800	-3.25693500	0.66846900
C	-1.55765400	-2.05510800	3.18726400
H	-1.42609600	-0.28417300	1.97783600
C	-2.16215200	-3.30208600	3.35812600
H	-3.61343700	-4.69717800	2.57967000
H	-0.79488100	-1.71580100	3.88179600
H	-1.87261600	-3.94087800	4.18770700
N	-2.24970400	-0.14185600	-0.58012000

TS2(triplet)

Ru	-1.41676900	-1.51994200	-0.55331800
C	1.06135300	-2.29868800	0.78780200
C	1.92048500	-3.02619300	1.62414200
C	1.47170900	-4.18964000	2.23099500
C	0.17082200	-4.63911300	1.97513900
C	-0.64209600	-3.87386500	1.15425700
H	2.93703900	-2.67933500	1.76888200
H	2.13295200	-4.75864300	2.87768500
H	-0.20465600	-5.56525100	2.39542100
H	-1.65297700	-4.16962700	0.90044300
C	1.41963400	-1.14730000	-0.02496300
C	2.69253700	-0.58489300	-0.06129800
C	0.37498700	-0.66305100	-0.85158400
H	3.48467400	-0.92039300	0.59672300
C	0.63955000	0.41845100	-1.71034000
C	1.90684200	0.96660100	-1.77987700
H	-0.16432500	0.83961600	-2.30434500
H	2.08687100	1.82451300	-2.42218400
N	-0.22708600	-2.71344900	0.61468500
P	-2.58985300	0.91221200	-0.40648000
O	-1.81748300	0.21148000	0.71640400
O	-4.09697300	1.35201100	0.02092400
O	-1.85288900	2.32906800	-0.67871600
C	-4.36510600	2.45143000	0.83211800
C	-5.50320600	3.19075300	0.52068600
C	-3.55125900	2.79001400	1.91359700
C	-5.83144900	4.29699700	1.30394200
H	-6.10090600	2.89939200	-0.33622500
C	-3.88756100	3.90485900	2.68255500
H	-2.68250800	2.18693600	2.14990800
C	-5.02318700	4.66084200	2.38322100
H	-6.71537000	4.87982800	1.06188800
H	-3.25675100	4.17719000	3.52395200

H	-5.27741400	5.52625600	2.98788500
C	-2.36647900	3.27367900	-1.57170500
C	-2.53564100	4.57141500	-1.09514900
C	-2.66184600	2.93382900	-2.89103100
C	-3.00830700	5.55410200	-1.96406200
H	-2.31283700	4.78651200	-0.05617600
C	-3.13957200	3.92827500	-3.74677100
H	-2.52989900	1.91119500	-3.22599900
C	-3.31202600	5.23614400	-3.29005600
H	-3.14557300	6.56808100	-1.59970300
H	-3.37501900	3.67428100	-4.77624300
H	-3.68248800	6.00376900	-3.96308600
C	7.54481500	-1.45696200	-0.74511600
H	7.29061900	-2.35382500	-0.16910300
H	8.28936600	-0.88822500	-0.17880000
H	7.99900600	-1.76943500	-1.69202900
C	6.29100400	-0.61705100	-0.99047200
H	6.57135500	0.26230800	-1.58461100
C	5.22325500	-1.41735900	-1.74738900
H	4.78921900	-2.14032900	-1.04514000
H	5.74641800	-2.01875800	-2.51130100
C	4.11101700	-0.67150700	-2.47086600
C	4.57731600	0.40765800	-3.42314900
H	3.72681800	0.87707300	-3.92756300
H	5.14887500	1.19826000	-2.92273500
H	5.22719900	-0.01712700	-4.20543000
C	3.10834600	-1.62381400	-3.08102700
H	2.70120500	-2.31468100	-2.33614300
H	2.26726600	-1.09067500	-3.53170700
H	3.58378700	-2.22808700	-3.87025800
O	5.74910200	-0.19196400	0.26096600
Si	6.11501000	1.19533300	1.13082000
C	4.61855500	1.45368900	2.24041700
H	4.44200900	0.56562600	2.85789400
H	4.75476900	2.30723800	2.91374600
H	3.71202200	1.62561500	1.65074700
C	6.35792100	2.65499700	-0.07320000
H	5.69403200	2.44284300	-0.92587500
C	7.66558100	0.90337000	2.19165900
H	8.51010500	0.77664400	1.49748800
C	7.98289800	2.10192300	3.10370500
H	8.88282700	1.91276000	3.70406200
H	8.15518200	3.02260800	2.53521600
H	7.16165500	2.29555500	3.80492600

C	7.53358500	-0.38886800	3.01617200
H	7.32987800	-1.25598400	2.37969300
H	8.45144400	-0.59137700	3.58430400
H	6.71383000	-0.31088300	3.74160900
C	7.79485900	2.76009200	-0.61576200
H	8.50501800	2.99889000	0.18457700
H	8.13459000	1.82905800	-1.08407900
H	7.87358500	3.55577600	-1.36831400
C	5.90390600	3.99714600	0.52977600
H	6.02429500	4.81217100	-0.19624900
H	4.85131700	3.97249200	0.83062300
H	6.49444600	4.26322600	1.41490600
C	3.01778900	0.38558800	-1.06388100
H	3.86653800	1.03060100	-0.86136400
Br	-0.99185100	-3.15865900	-2.45812100
C	-4.26553400	-2.80768400	-1.09090900
C	-5.63948400	-2.88439200	-1.29078400
C	-6.48180200	-2.41863100	-0.28443600
C	-5.91227900	-1.91222700	0.87688200
C	-4.51649600	-1.86286100	1.01180600
H	-3.57351900	-3.14039500	-1.85646400
H	-6.02712300	-3.29366100	-2.21747600
H	-7.56167300	-2.45884700	-0.39530200
H	-6.53363900	-1.57190600	1.69723200
C	-3.92929800	-1.33302300	2.26421100
C	-4.50812200	-0.22717400	2.90151100
C	-2.26370200	-1.43491300	4.02612700
C	-3.96388200	0.27608900	4.08147600
H	-5.35672300	0.27257600	2.44712500
C	-2.83658400	-0.32220000	4.64568700
H	-1.39042500	-1.91504400	4.45870700
H	-4.40989300	1.15134200	4.54411100
H	-2.40797600	0.07469100	5.56161600
N	-3.70148900	-2.30739900	0.02412200
O	-2.68351900	0.00084700	-1.62164000
C	-2.81027700	-1.93619300	2.84933500
H	-2.37553700	-2.80742800	2.38301100

int4(singlet)

Ru	-1.38390100	-0.08253700	-1.18873600
C	0.79023100	-1.88921800	-1.78483700
C	1.49773200	-3.07316700	-1.98897100
C	0.81294800	-4.28558300	-2.00106000
C	-0.57332000	-4.28063400	-1.84782200

C	-1.22341000	-3.06890600	-1.64945500
H	2.56930600	-3.03680500	-2.14987500
H	1.35133600	-5.21658900	-2.14931100
H	-1.15164000	-5.19661200	-1.87531700
H	-2.29486400	-3.00039000	-1.53860700
C	1.33643700	-0.52716900	-1.79675100
C	2.65028500	-0.22339100	-1.72133700
C	0.30644000	0.51116000	-1.75291200
H	3.38714400	-1.00906200	-1.62952500
C	0.75058800	1.86981200	-1.93384000
C	2.06137800	2.19100400	-1.85450300
H	-0.00231500	2.63879100	-2.06372000
H	2.35356900	3.23281600	-1.91121600
N	-0.55408600	-1.90859700	-1.56973900
P	-1.60119700	1.63332700	0.95312900
O	-0.70751200	0.39611200	0.93675400
O	-2.10375000	1.99193400	-0.43679700
O	-0.89392000	2.89680600	1.69965400
O	-2.76464700	1.35820900	2.04880300
C	0.16212300	3.58926100	1.11668400
C	-0.08797600	4.53118100	0.12026900
C	1.44925000	3.37502300	1.60402000
C	0.97508400	5.28126600	-0.38406600
H	-1.09948000	4.65913300	-0.24752700
C	2.50468000	4.13144400	1.09321900
H	1.60137800	2.63316500	2.37958400
C	2.27064600	5.08762000	0.10216000
H	0.78755100	6.02023100	-1.15773300
H	3.50771300	3.97940300	1.47933700
H	3.09361100	5.67951700	-0.28771800
C	-4.07469300	1.80247800	2.03046100
C	-4.51956200	2.87141300	1.25118600
C	-4.95177600	1.10364300	2.85926800
C	-5.86889200	3.22517500	1.30193000
H	-3.83417800	3.39371700	0.59630100
C	-6.29489100	1.47001900	2.90015400
H	-4.56881500	0.27316600	3.44213700
C	-6.76132900	2.53001300	2.11918700
H	-6.22016400	4.05234200	0.69153300
H	-6.97846400	0.92085900	3.54150400
H	-7.80912600	2.81359300	2.15018600
C	7.06854000	-0.74105600	-0.08122500
H	7.96884700	-0.22743800	-0.43639500
H	6.96242800	-1.68006600	-0.63593200

H	7.21120900	-0.98524200	0.97652800
C	5.82596300	0.12977700	-0.27456100
H	5.97167300	1.07377700	0.27000200
C	5.59423800	0.42426900	-1.76460700
H	5.37036800	-0.53158000	-2.25398600
H	6.54876500	0.75997200	-2.19042700
C	4.53188000	1.48624800	-2.16311100
C	5.01834600	2.86980700	-1.69076700
H	4.39215000	3.67882200	-2.07702400
H	5.01919700	2.94875400	-0.59789000
H	6.03967100	3.05205500	-2.04414700
C	4.41432300	1.48114600	-3.69699600
H	4.06414200	0.50785500	-4.05934400
H	3.70001200	2.23830100	-4.03774500
H	5.38244300	1.69115000	-4.16657400
O	4.67252900	-0.52943200	0.22870300
Si	4.15096500	-0.95534400	1.76533900
C	2.29741200	-0.65017400	1.78884700
H	1.76652900	-1.34541100	1.13053300
H	1.88274900	-0.77717300	2.79626800
H	2.02673700	0.35405500	1.45069300
C	5.05564600	0.13487500	3.03494200
H	6.12513000	0.09376400	2.77719200
C	4.48950100	-2.81308000	1.99994600
H	5.54917400	-2.92597000	2.27769000
C	3.62849700	-3.43091000	3.11761300
H	3.86550700	-4.49470300	3.25132000
H	3.77011800	-2.93717800	4.08423600
H	2.56239200	-3.36592000	2.86821500
C	4.25830400	-3.57497900	0.68148900
H	4.89320800	-3.19487000	-0.12477600
H	4.46622500	-4.64625300	0.80535700
H	3.21545400	-3.48253600	0.35185400
C	4.90708800	-0.35909600	4.48372600
H	3.85277800	-0.40811500	4.78410500
H	5.33965100	-1.35563200	4.62145200
H	5.41116100	0.32023200	5.18401100
C	4.59798000	1.59947100	2.91455100
H	5.19336500	2.25806900	3.56055500
H	4.68050700	1.97475200	1.88803000
H	3.54993400	1.70503600	3.21743700
C	3.12780000	1.18281600	-1.53989100
H	3.27999100	1.26637500	-0.44846300
Br	-2.48434400	-0.21778100	-3.51869600

C	-4.47291000	0.08467900	-0.65287100
C	-5.82743800	-0.05409900	-0.36911500
C	-6.23129300	-1.12404100	0.42158400
C	-5.26605200	-2.01249100	0.88293700
C	-3.91829000	-1.82043500	0.54589200
H	-4.11180800	0.91046800	-1.25084400
H	-6.53217600	0.68151300	-0.73849300
H	-7.27537600	-1.25772100	0.68905500
H	-5.53600300	-2.84640200	1.52143800
C	-2.90773800	-2.80723200	1.00523800
C	-1.66535600	-2.40469500	1.51311000
C	-3.19270300	-4.17976500	0.91113200
C	-0.72056700	-3.35827900	1.88972800
H	-1.43406800	-1.35094300	1.59717700
C	-2.24430400	-5.12947700	1.28711100
H	-4.14679300	-4.50163200	0.50296100
C	-0.99996600	-4.72031300	1.77222600
H	0.23973200	-3.02771900	2.27519100
H	-2.47326700	-6.18738100	1.19179000
H	-0.25594900	-5.45865600	2.05841700
N	-3.52978200	-0.77087800	-0.21724000

int4’(triplet)

Ru	-1.11352500	-1.66397000	-0.89073400
C	1.59797600	-2.70486100	-0.67730500
C	2.64375800	-3.53463800	-0.25273700
C	2.35671800	-4.76958500	0.31218500
C	1.02348000	-5.17680500	0.43576400
C	0.02621600	-4.30123800	0.03396300
H	3.66806200	-3.20745300	-0.38711300
H	3.16251700	-5.42155900	0.63599900
H	0.76019100	-6.14916200	0.83649400
H	-1.02682700	-4.54516500	0.10385700
C	1.72546100	-1.44127800	-1.39316400
C	2.92104700	-0.81522600	-1.66651600
C	0.48187700	-0.89545900	-1.81772500
H	3.85759700	-1.23384500	-1.32372300
C	0.49485300	0.19315600	-2.72631800
C	1.65671900	0.85436000	-3.00635600
H	-0.43737100	0.50635800	-3.18753900
H	1.63757000	1.69578000	-3.69094400
N	0.30459800	-3.08493300	-0.46440700
P	-1.66422800	0.83172900	0.00239300
O	-0.64669500	-0.12809500	0.60804100

O	-2.41377400	0.15809200	-1.14709000
O	-0.86322700	2.17084900	-0.44076700
O	-2.66665700	1.34401500	1.17672200
C	-1.51080300	3.33295600	-0.86134800
C	-2.51394100	3.29563400	-1.82901800
C	-1.10330500	4.52982300	-0.27799200
C	-3.14318200	4.48799300	-2.18635700
H	-2.80385900	2.34772100	-2.26752300
C	-1.73247200	5.71570300	-0.65706800
H	-0.31290500	4.51314800	0.46441000
C	-2.75957800	5.69716800	-1.60305900
H	-3.93892700	4.46683400	-2.92497100
H	-1.42312800	6.65368800	-0.20478200
H	-3.25493900	6.62065900	-1.88759300
C	-3.85601900	2.03559700	0.92003700
C	-4.87587900	1.44861600	0.17478700
C	-3.98867300	3.31000800	1.46383800
C	-6.04877700	2.17334600	-0.04006800
H	-4.73293000	0.46164500	-0.24390300
C	-5.16640300	4.02203500	1.24068300
H	-3.16363100	3.73577300	2.02361900
C	-6.19810500	3.45748400	0.48725800
H	-6.84704300	1.72896700	-0.62785800
H	-5.27163100	5.02266700	1.64933500
H	-7.11215800	4.01666400	0.31065100
C	6.87844800	1.65398200	-0.16880500
H	7.45937800	2.32343200	-0.81331500
H	7.40298700	0.69416400	-0.10382900
H	6.84296800	2.09134900	0.83499800
C	5.46723400	1.45282400	-0.72268300
H	4.99060300	2.43876100	-0.81679300
C	5.49687400	0.76202800	-2.09547900
H	5.70367200	-0.29912000	-1.91132900
H	6.35965000	1.14306100	-2.65743300
C	4.25277500	0.92435500	-3.01177600
C	4.20028300	2.38536400	-3.50096600
H	3.45909200	2.52354600	-4.29324100
H	3.95183600	3.07994400	-2.68995900
H	5.17198500	2.68319600	-3.91206400
C	4.41794900	-0.00527900	-4.22454400
H	4.47418100	-1.05362400	-3.91031600
H	3.56388300	0.08957600	-4.90417900
H	5.33039400	0.23385500	-4.78424200
O	4.69916800	0.64180100	0.16080400

Si	3.97184500	1.02434600	1.62581200
C	2.40132800	0.01346500	1.72779200
H	2.61492800	-1.06166600	1.72378200
H	1.84994400	0.22468900	2.64984400
H	1.71712400	0.20909800	0.90020200
C	3.58093300	2.88956100	1.67685600
H	4.50097700	3.42344000	1.39117800
C	5.14821500	0.49381900	3.03252000
H	5.88717100	1.29732700	3.17948800
C	4.40794900	0.27293800	4.36548000
H	5.11003900	-0.00871500	5.16193400
H	3.86583200	1.16219300	4.70201900
H	3.67742200	-0.53997500	4.27244600
C	5.90918600	-0.78771300	2.64593700
H	6.49495000	-0.65611300	1.73237800
H	6.58943800	-1.10015200	3.45001300
H	5.21157800	-1.61739900	2.46970800
C	3.19182800	3.36426100	3.08839400
H	2.31520100	2.82153700	3.46460300
H	4.00524800	3.22578500	3.80840000
H	2.93290200	4.43186300	3.08354900
C	2.47775400	3.26515500	0.67004700
H	2.25382200	4.34020900	0.71954400
H	2.76116900	3.04056600	-0.36351200
H	1.54729800	2.72180300	0.86838800
C	2.93469300	0.57011100	-2.25077600
H	2.92353200	1.25771100	-1.38184900
Br	-1.85871700	-3.04508000	-2.88355300
C	-4.08431500	-2.45799400	-0.10897700
C	-5.36352100	-2.20274100	0.37418400
C	-5.49613000	-1.71358800	1.67276800
C	-4.35050300	-1.53668500	2.43895900
C	-3.09293400	-1.83692100	1.89606200
H	-3.92599200	-2.80068200	-1.12632800
H	-6.22519500	-2.36902500	-0.26356700
H	-6.47381000	-1.48135200	2.08457700
H	-4.41264600	-1.18988100	3.46418900
C	-1.87990200	-1.71432700	2.73676200
C	-1.69286700	-0.60490000	3.57267900
C	-0.91487500	-2.72679800	2.72831400
C	-0.55080800	-0.50603200	4.36360500
H	-2.41574700	0.20342500	3.55700700
C	0.23010400	-2.62669700	3.51406600
H	-1.07584100	-3.60071400	2.11246800

C	0.41600900	-1.51384900	4.33528300
H	-0.40660900	0.36781900	4.99277200
H	0.97341100	-3.41841000	3.48370700
H	1.31009500	-1.42866600	4.94646600
N	-2.96749100	-2.27334400	0.61904400

7. References

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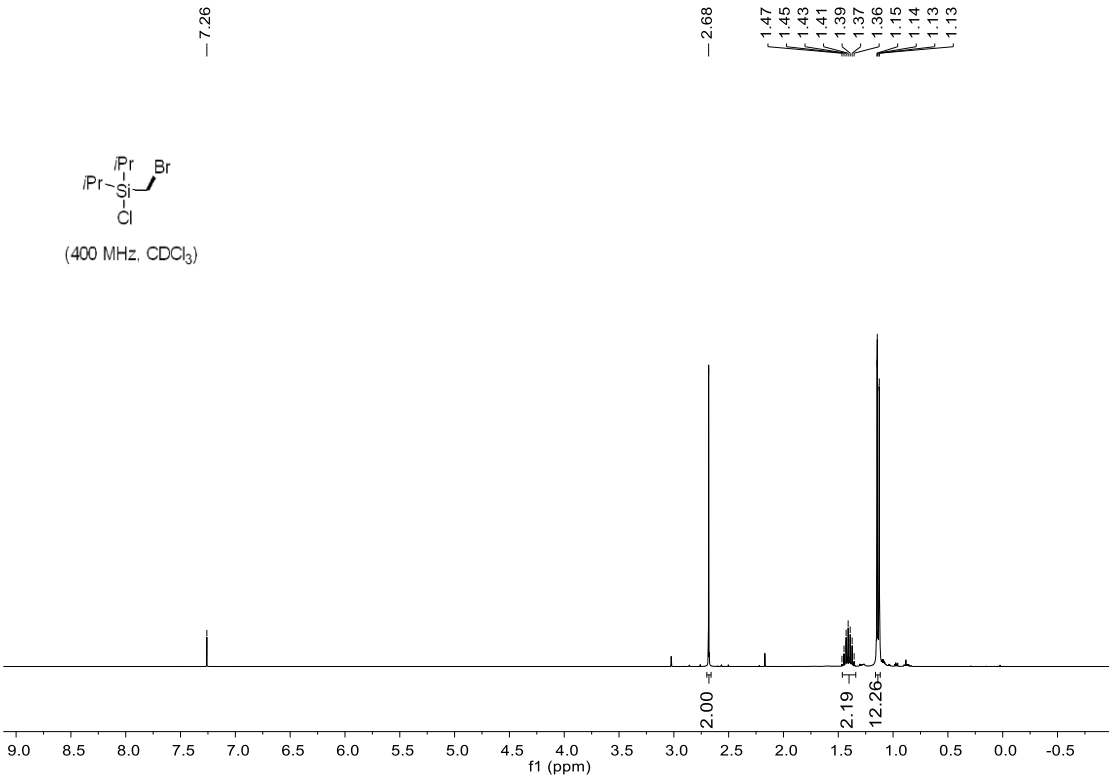
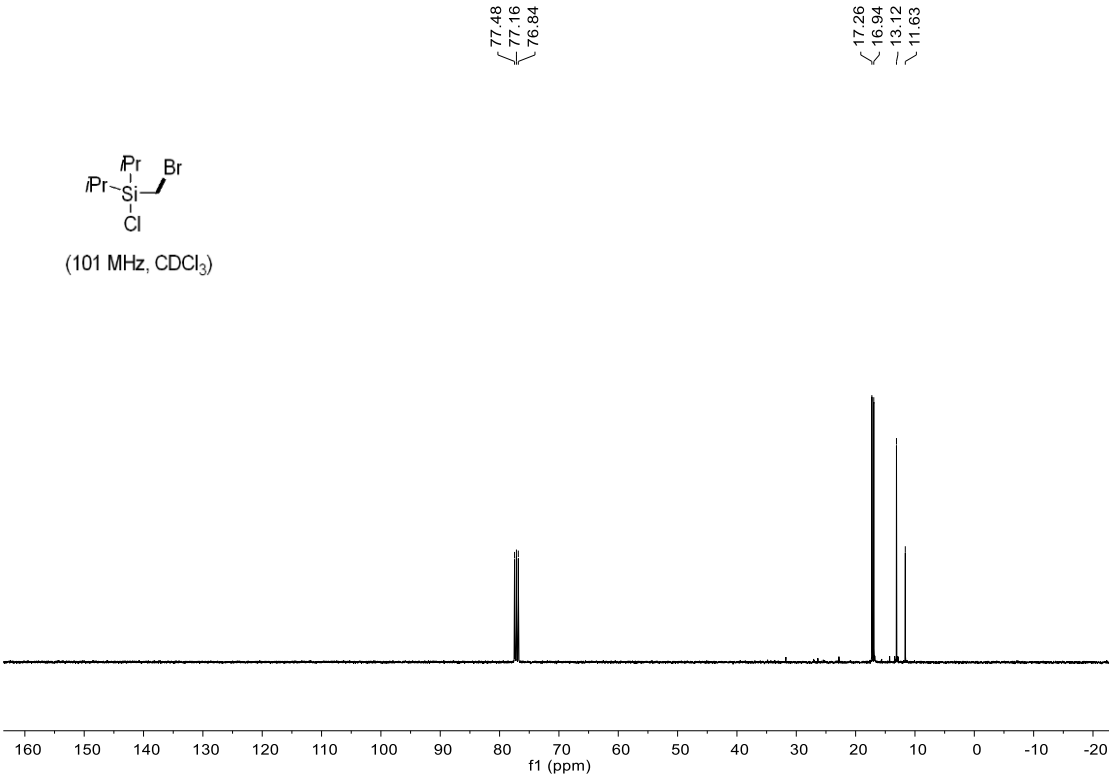
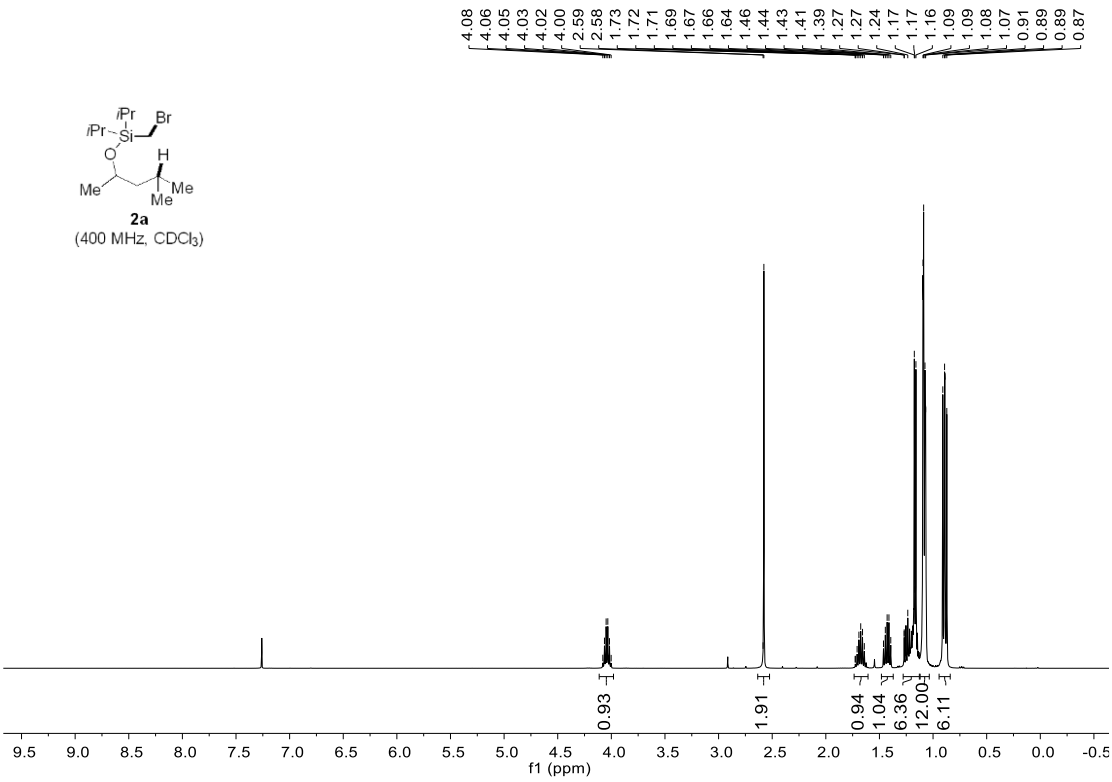
8. NMR Spectra.



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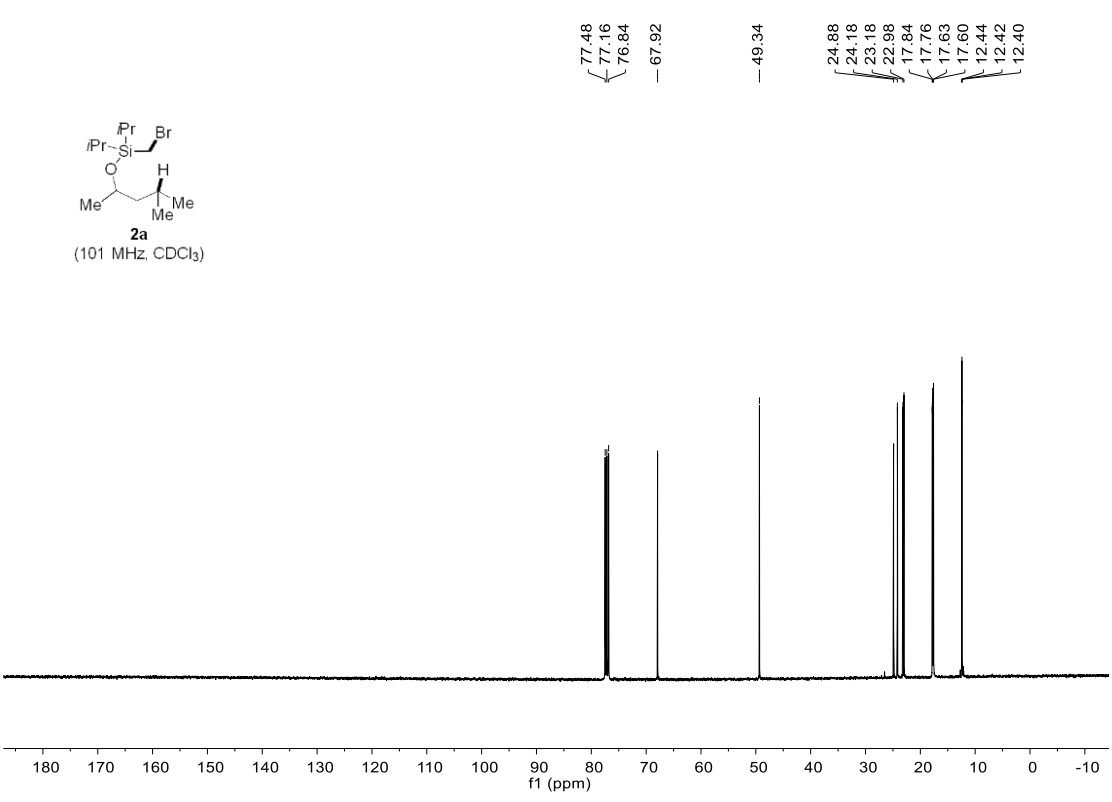
4.06
4.05
4.03
4.02
4.00
2.59
2.58
1.73
1.72
1.71
1.69
1.67
1.66
1.64
1.46
1.44
1.43
1.41
1.39
1.27
1.24
1.17
1.17
1.16
1.09
1.09
1.08
1.07
0.91
0.89
0.89
0.87
iPr
iPr
Si
Br
O
H
Me
Me
Me
2a
(400 MHz, CDCl3)
0.93
1.91
0.94
1.04
6.36
12.00
6.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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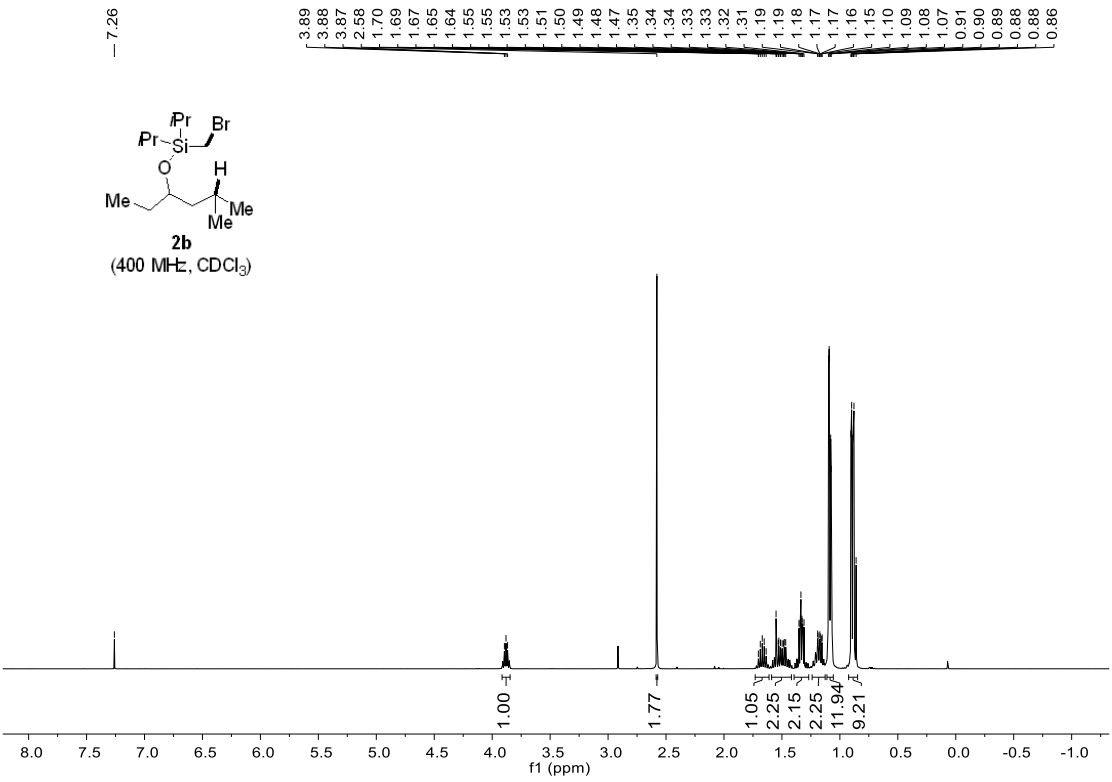
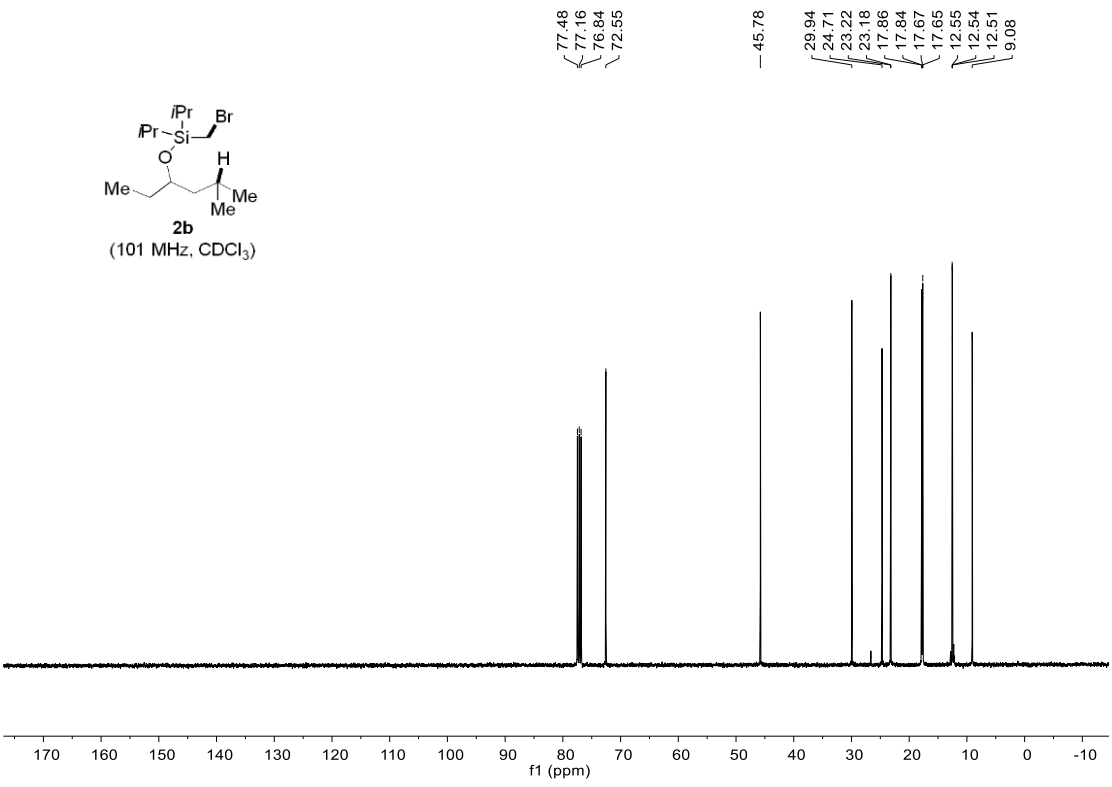
77.16
76.84
67.92
49.34
24.88
24.18
23.18
22.98
17.84
17.76
17.63
17.60
12.44
12.42
12.40
iPr
iPr
Si
Br
O
H
Me
Me
Me
2a
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
3.89
3.88
3.87
2.58
1.70
1.69
1.67
1.65
1.64
1.55
1.55
1.53
1.53
1.51
1.50
1.49
1.48
1.47
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.19
1.19
1.18
1.17
1.17
1.16
1.15
1.10
1.09
1.08
1.07
0.91
0.90
0.89
0.88
0.88
0.86
iPr
iPr
Si
Br
O
H
Me
Me
Me
2b
(400 MHz, CDCl3)
1.00
1.77
1.05
2.25
2.15
2.25
11.94
9.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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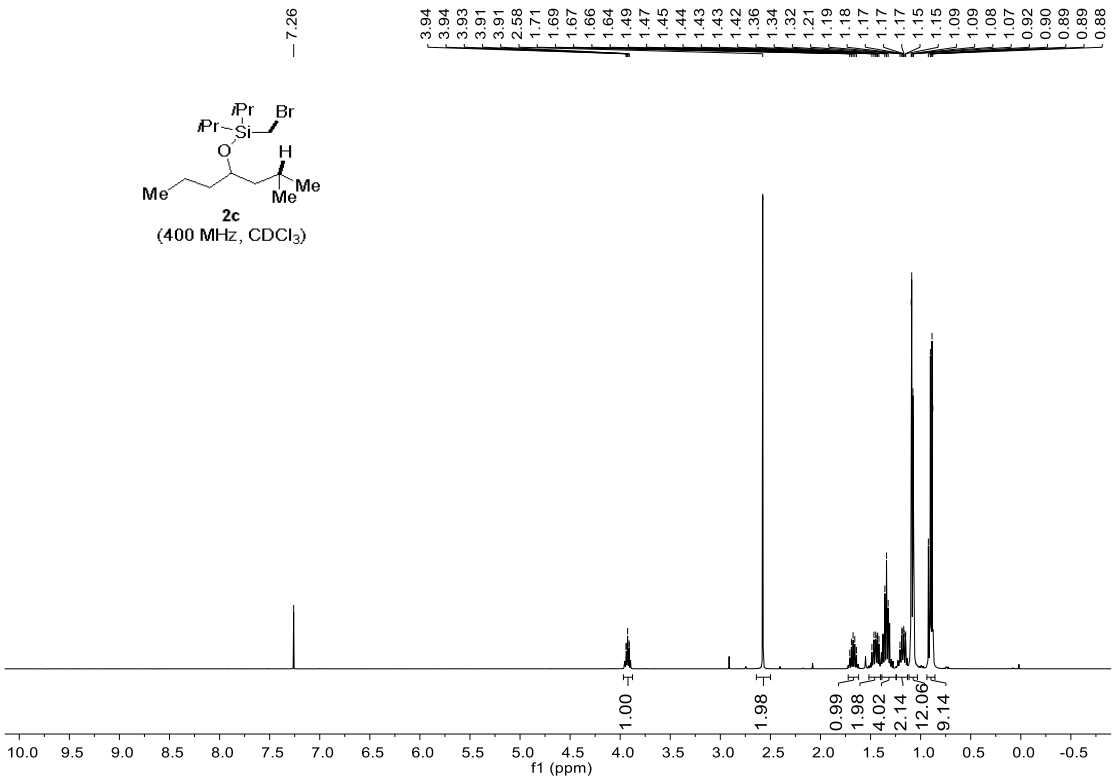
77.16
76.84
72.55
45.78
29.94
24.71
23.22
23.18
17.86
17.84
17.67
17.65
12.55
12.54
12.51
9.08
iPr
iPr
Si
Br
O
H
Me
Me
Me
2b
(101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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3.94
3.94
3.93
3.91
3.91
2.58
1.71
1.69
1.67
1.66
1.64
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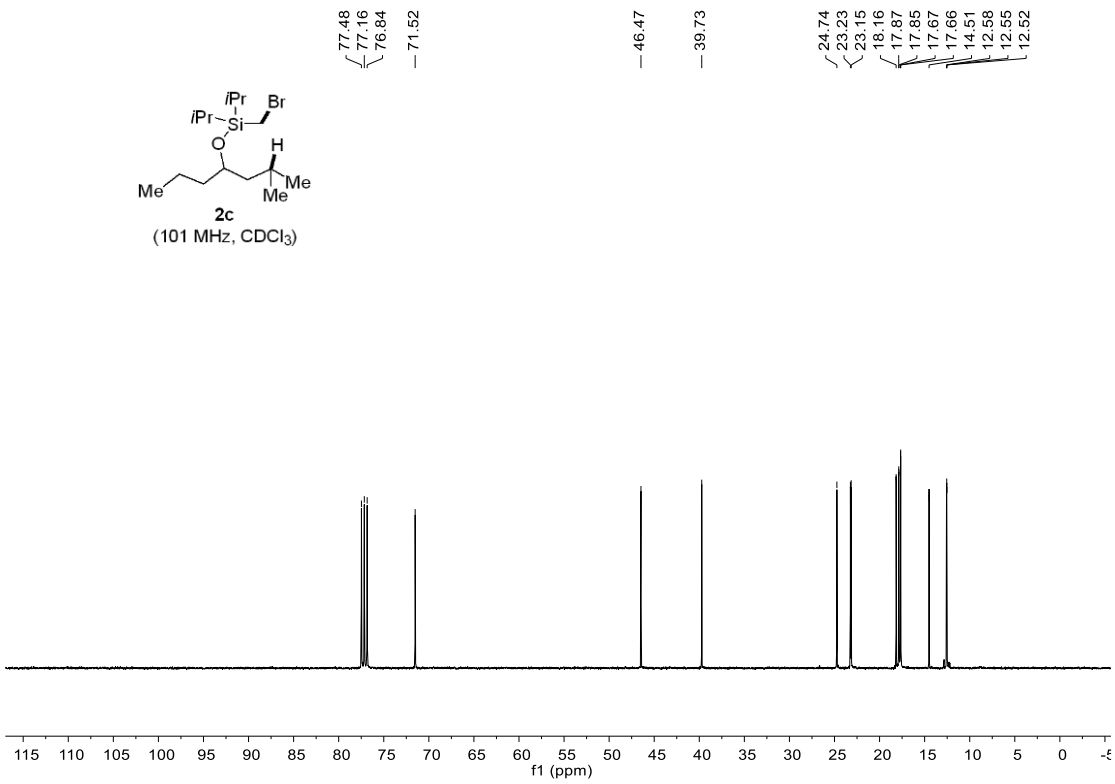
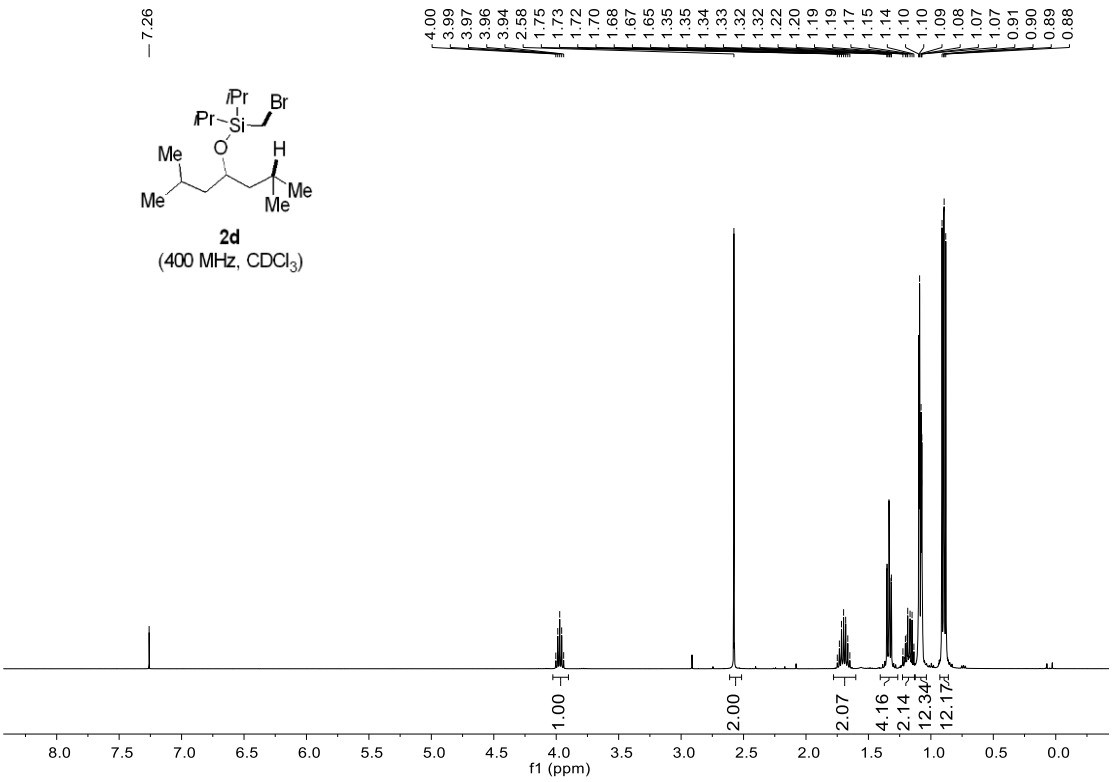
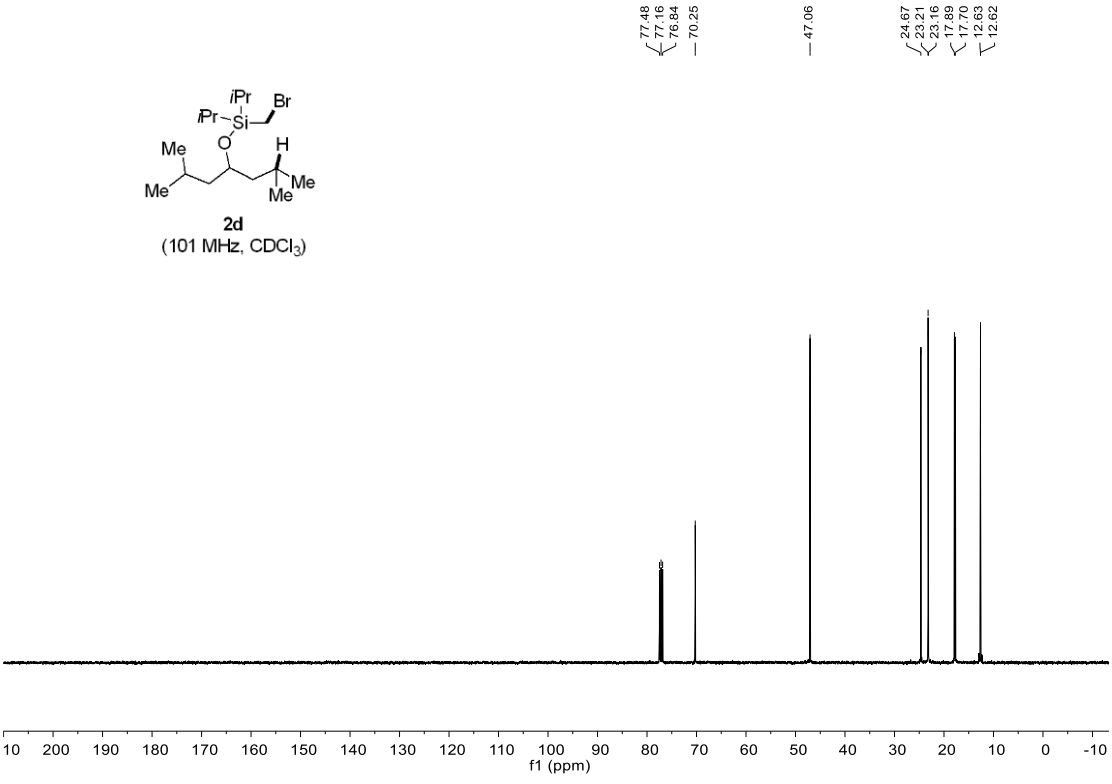
1.47
1.45
1.44
1.43
1.43
1.42
1.36
1.34
1.32
1.21
1.19
1.18
1.17
1.17
1.17
1.15
1.15
1.09
1.09
1.08
1.07
0.92
0.90
0.89
0.89
0.88
iPr
iPr
Si
Br
O
H
Me
Me
Me
2c
(400 MHz, CDCl3)
1.00
1.98
0.99
1.98
4.02
2.14
12.06
9.14
f1 (ppm)

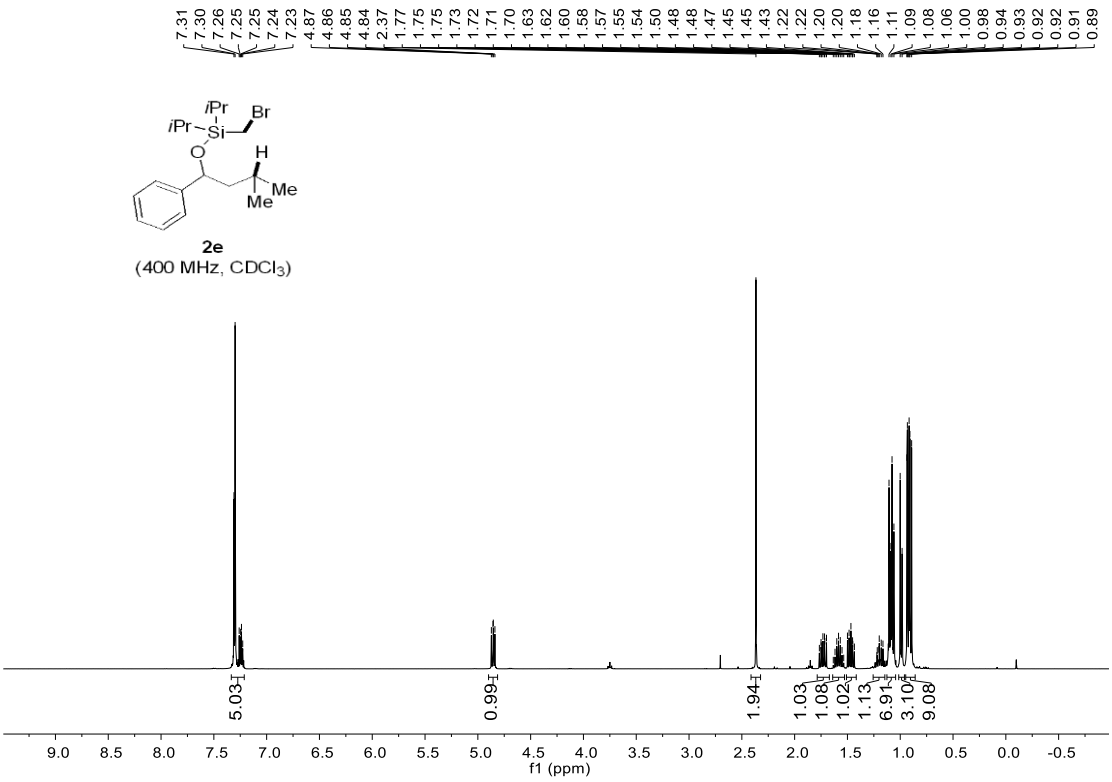

77.48
77.16
76.84
71.52
46.47
39.73
24.74
23.23
23.15
18.16
17.87
17.85
17.67
17.66
14.51
12.58
12.55
12.52
iPr
iPr
Si
Br
O
H
Me
Me
Me
2c
(101 MHz, CDCl3)
f1 (ppm)



2d
(400 MHz, $CDCl_3$)



2d
(101 MHz, $CDCl_3$)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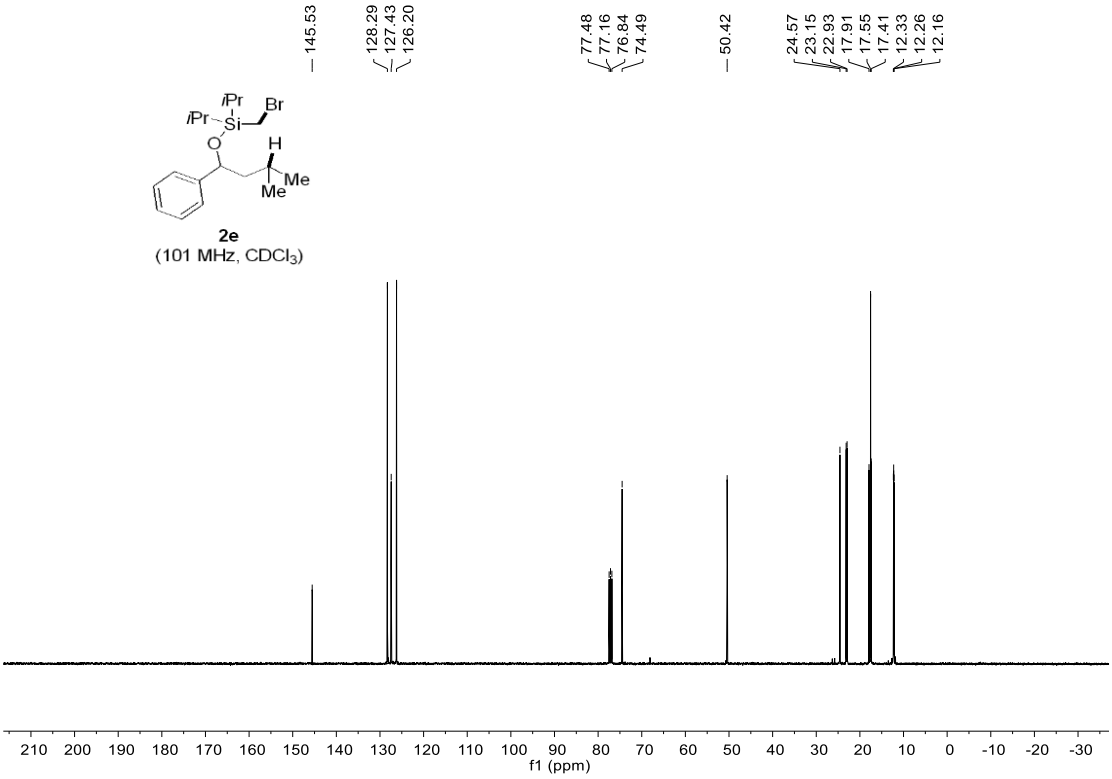
iPr
iPr
Si
Br
O
H
Me
Me
2e
(400 MHz, CDCl3)
5.03
0.99
1.94
1.03
1.08
1.02
1.13
6.91
3.10
9.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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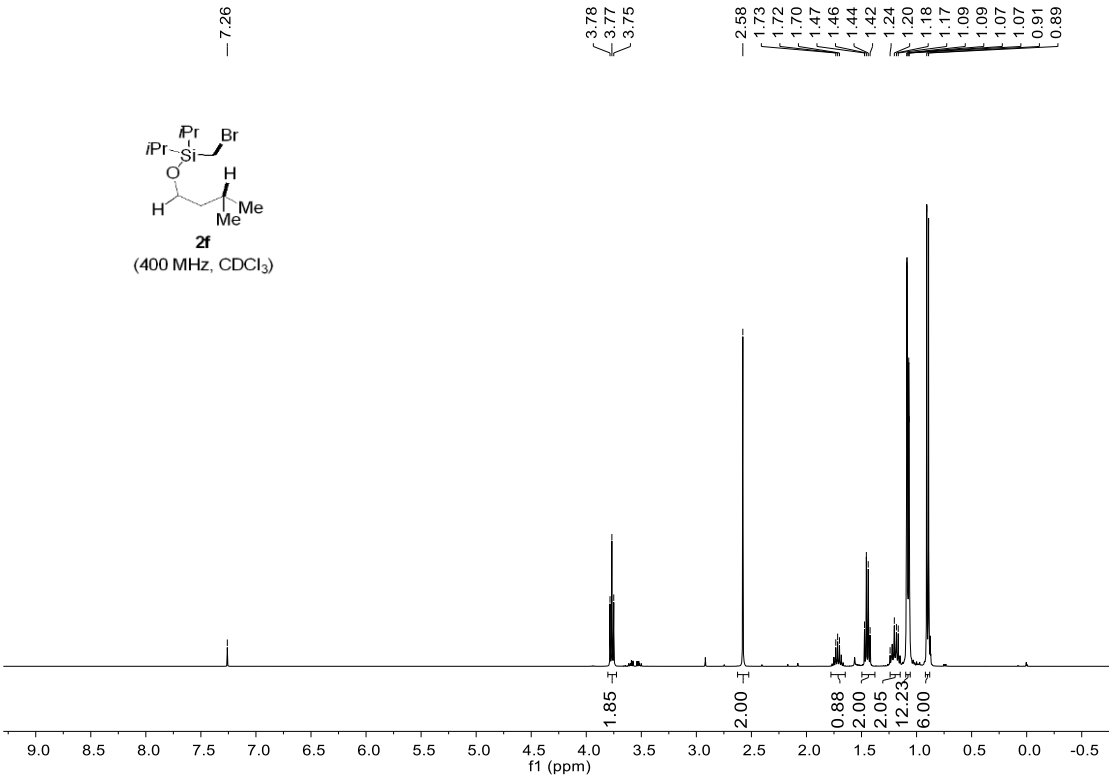
127.43
126.20
77.48
77.16
76.84
74.49
50.42
24.57
23.15
22.93
17.91
17.55
17.41
12.33
12.26
12.16
iPr
iPr
Si
Br
O
H
Me
Me
2e
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)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2.58
1.73
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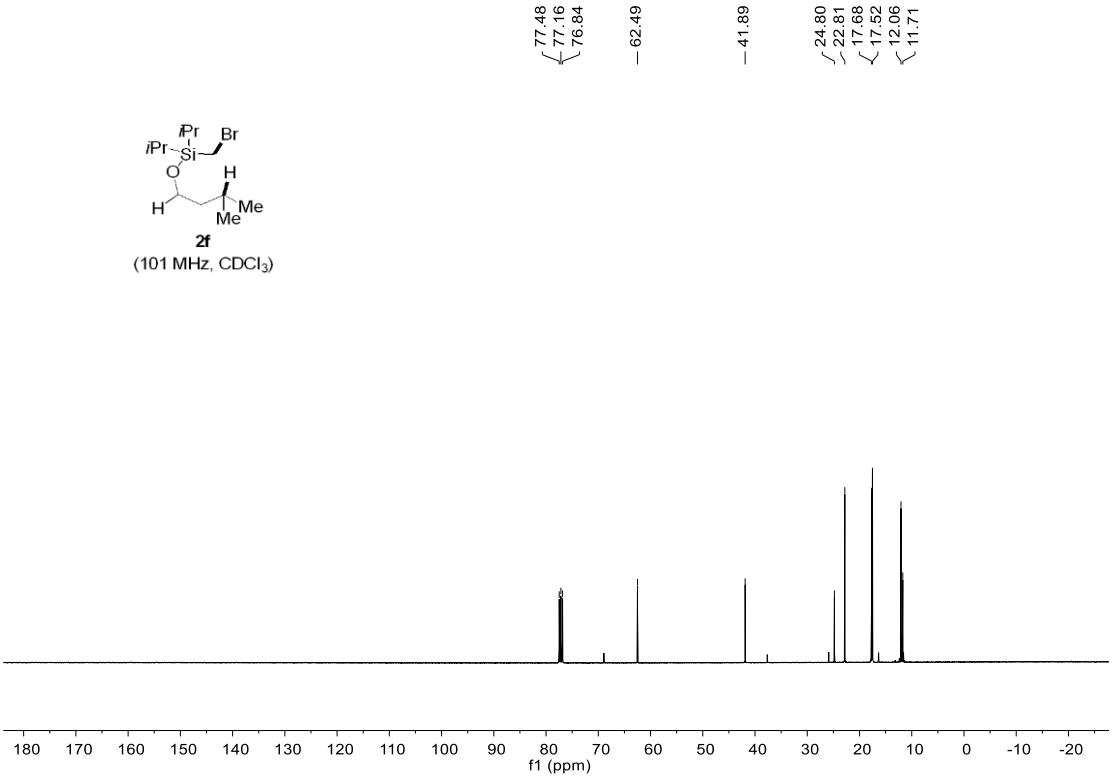
1.70
1.47
1.46
1.44
1.42
1.24
1.20
1.18
1.17
1.09
1.09
1.07
1.07
0.91
0.89
iPr
Br
iPr
Si
O
H
H
Me
Me
2f
(400 MHz, CDCl3)
1.85
2.00
0.88
2.00
2.05
12.23
6.00
f1 (ppm)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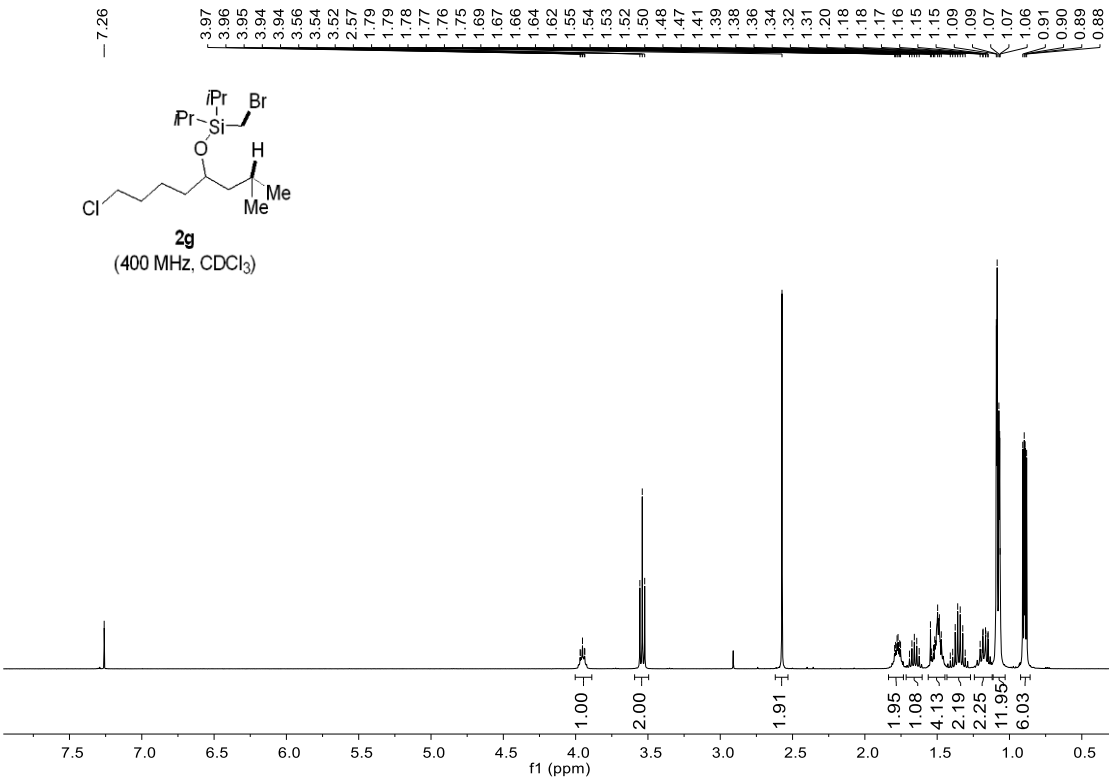
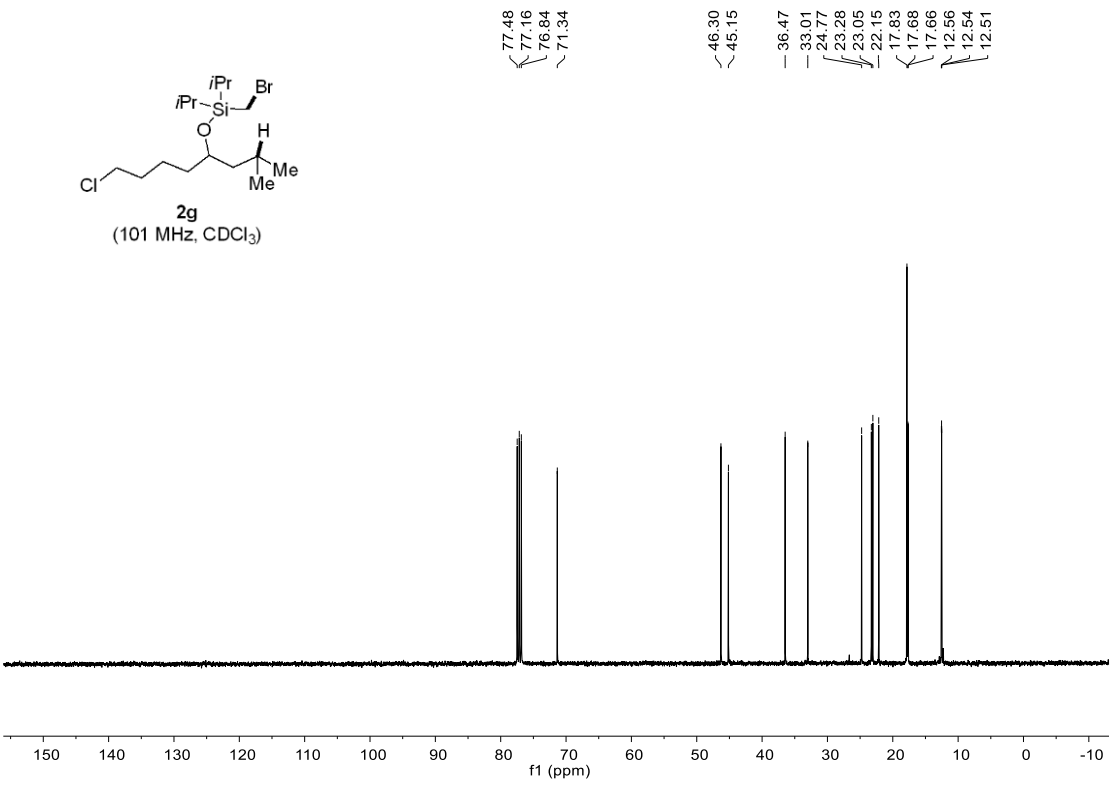
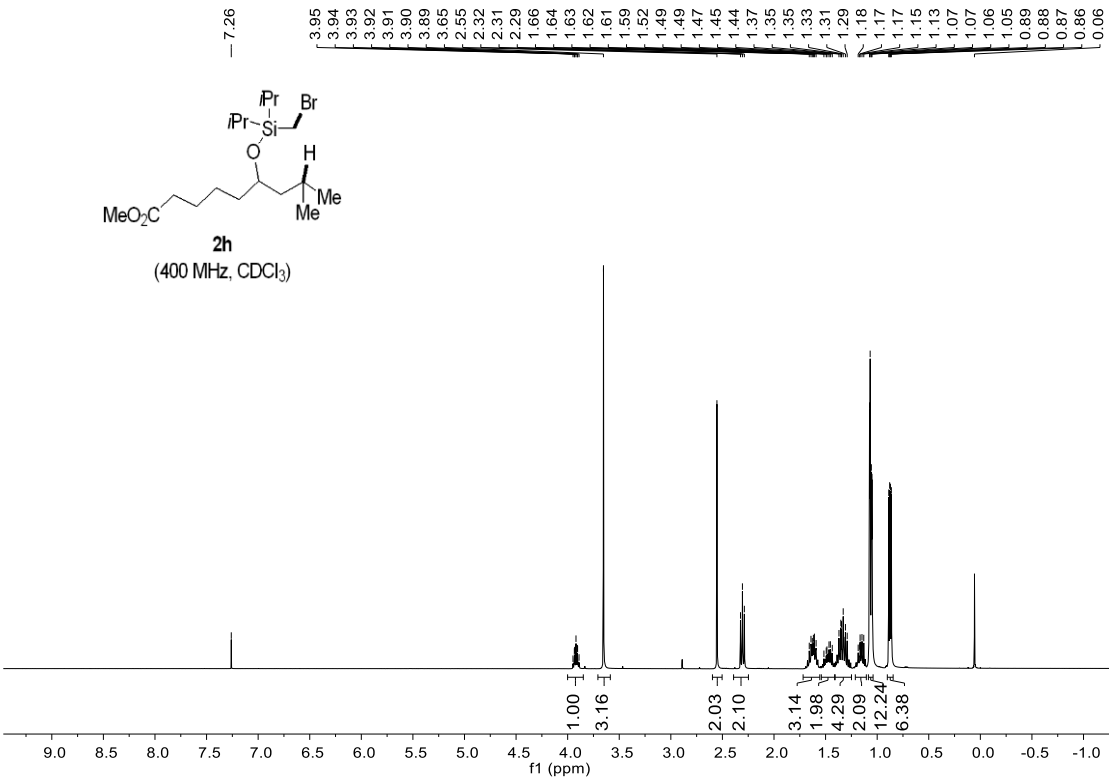
17.52
12.06
11.71
iPr
Br
iPr
Si
O
H
H
Me
Me
2f
(101 MHz, CDCl3)
f1 (ppm)

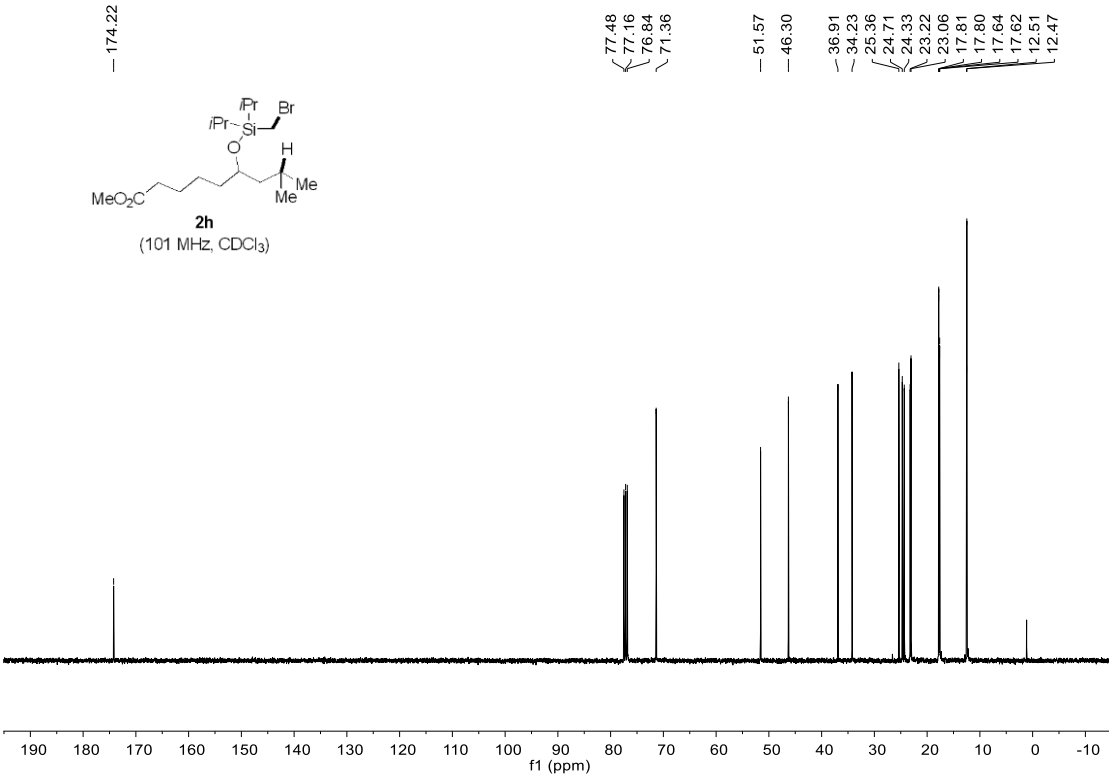


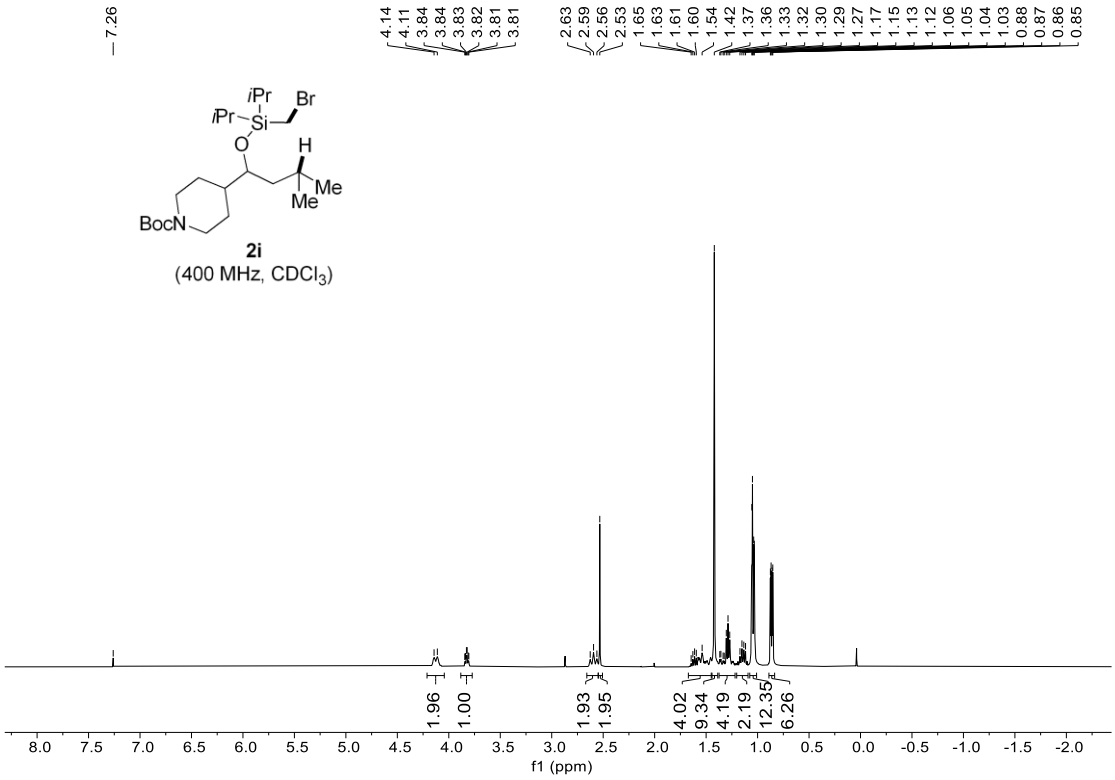
2g
(400 MHz, $CDCl_3$)



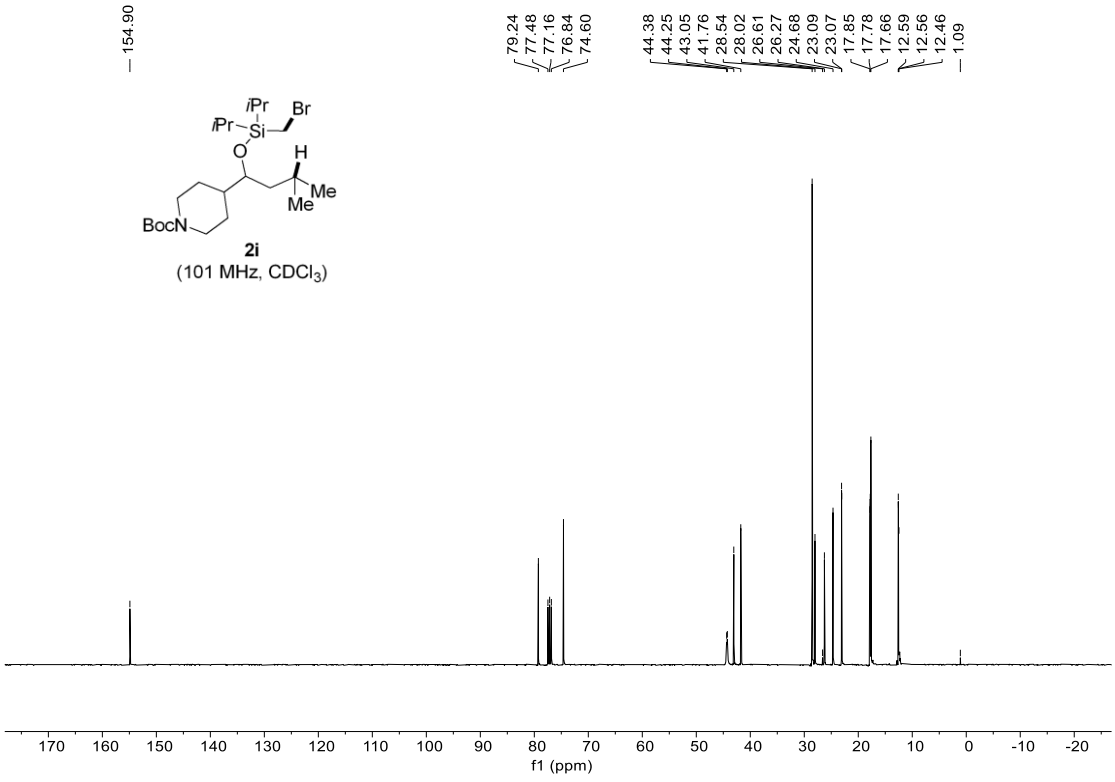
2g
(101 MHz, $CDCl_3$)


7.26
3.95
3.94
3.93
3.92
3.91
3.90
3.89
3.65
2.55
2.32
2.31
2.29
1.66
1.64
1.63
1.62
1.61
1.59
1.52
1.49
1.49
1.47
1.45
1.44
1.37
1.35
1.35
1.33
1.31
1.29
1.18
1.17
1.17
1.15
1.13
1.07
1.07
1.06
1.05
0.89
0.88
0.87
0.86
0.06
iPr
Br
iPr
Si
O
H
Me
Me
MeO2C
2h
(400 MHz, CDCl3)
1.00
3.16
2.03
2.10
3.14
1.98
4.29
2.09
12.24
6.38
f1 (ppm)

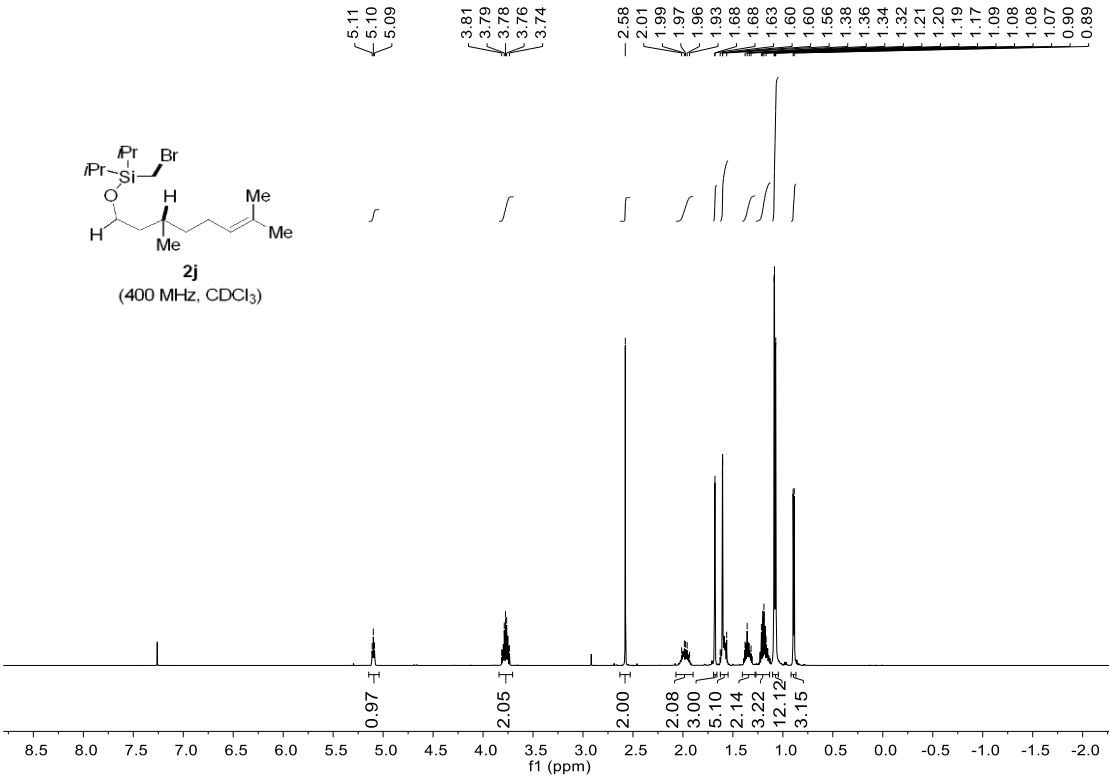

174.22
77.48
77.16
76.84
71.36
51.57
46.30
36.91
34.23
25.36
24.71
24.33
23.22
23.06
17.81
17.80
17.64
17.62
12.51
12.47
iPr
Br
iPr
Si
O
H
Me
Me
MeO2C
2h
(101 MHz, CDCl3)
f1 (ppm)



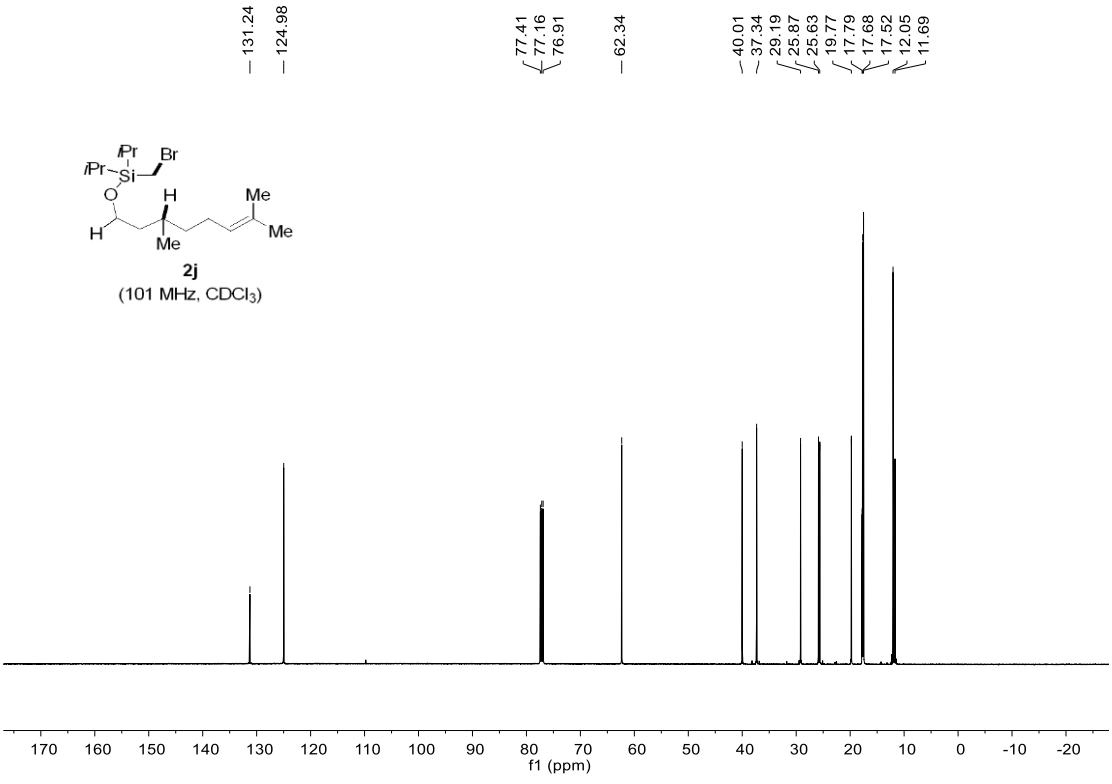
2i
(400 MHz, $CDCl_3$)



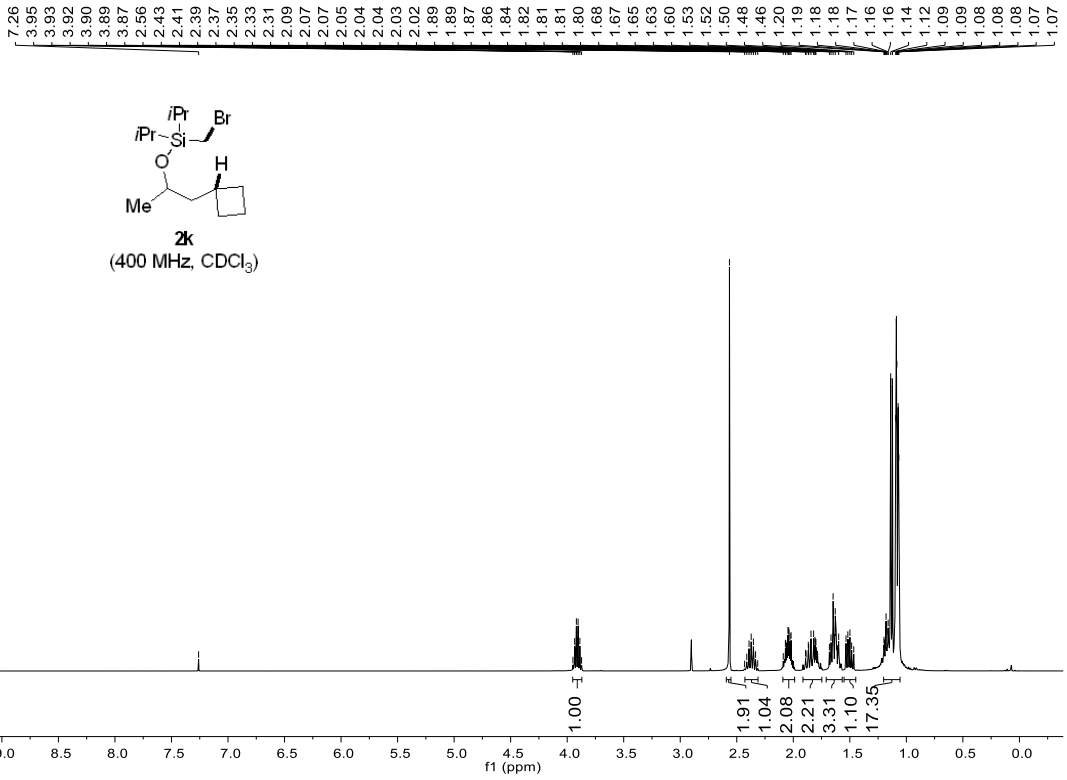
2i
(101 MHz, $CDCl_3$)

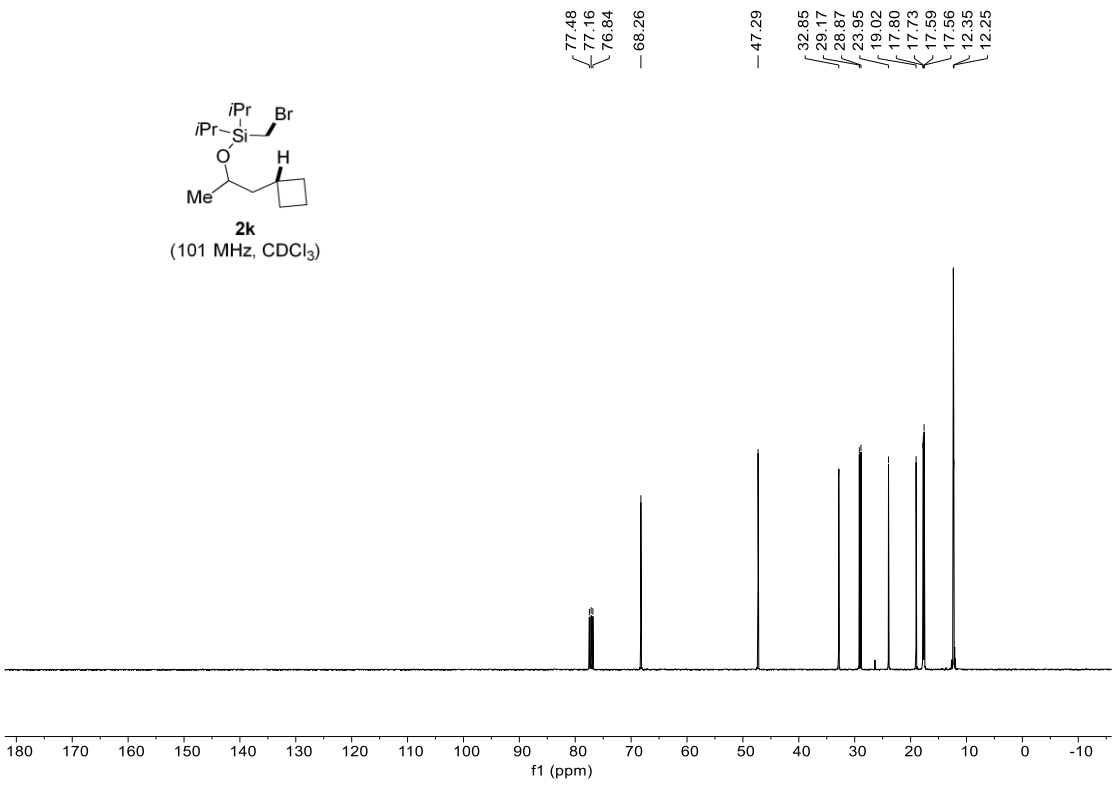


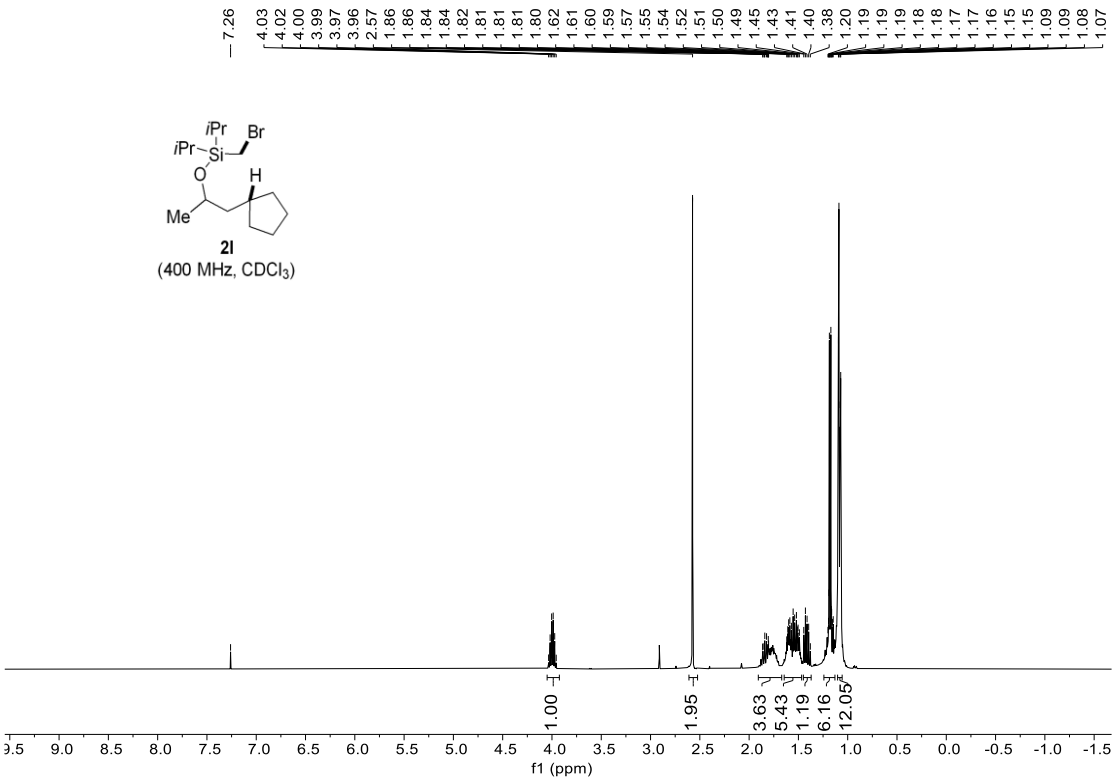
2j
(400 MHz, $CDCl_3$)

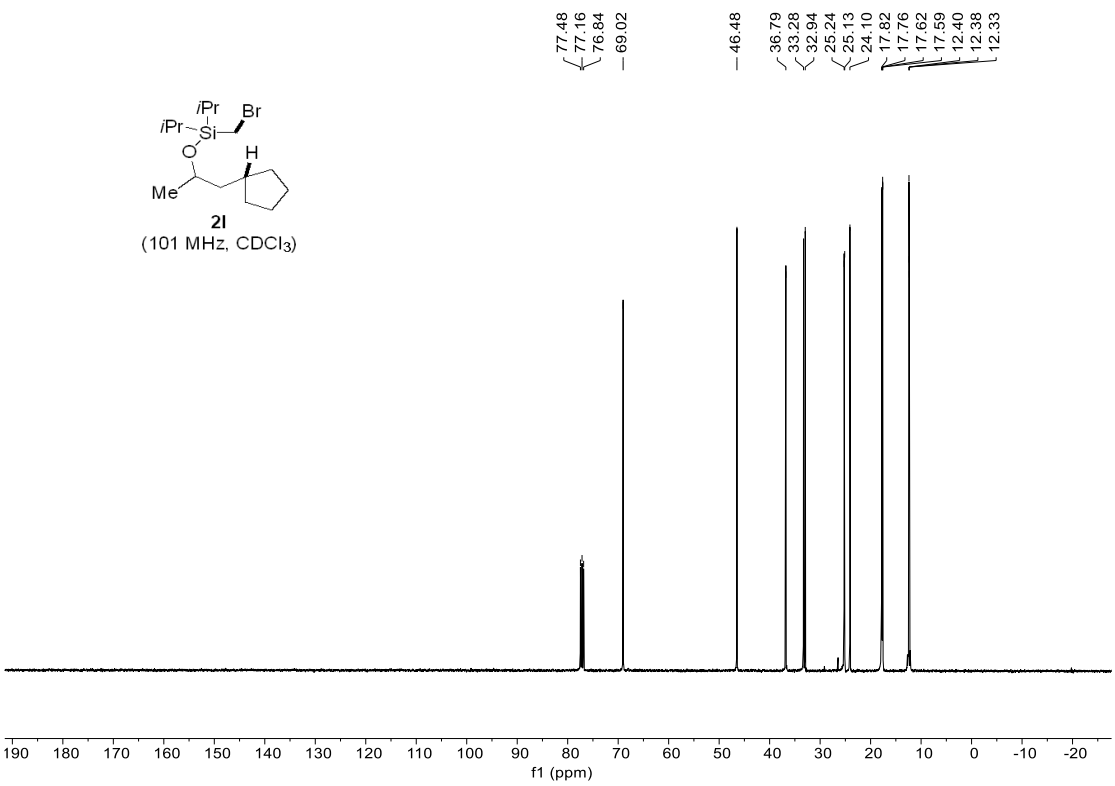


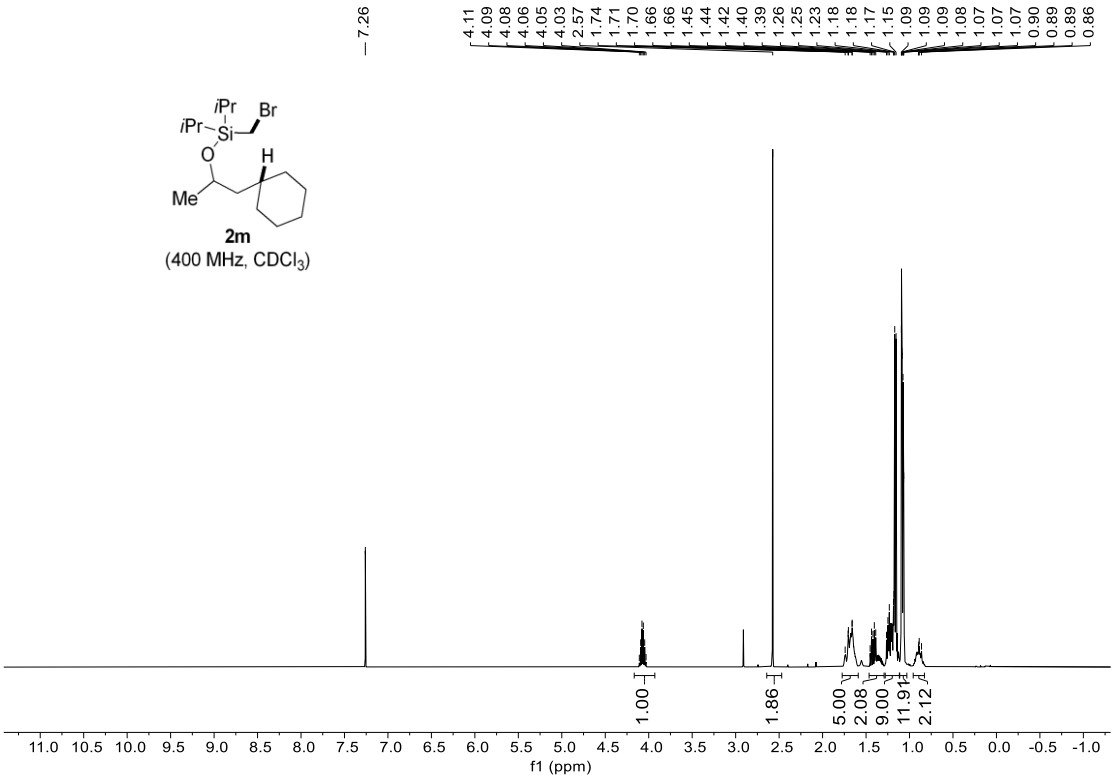
2j
(101 MHz, $CDCl_3$)

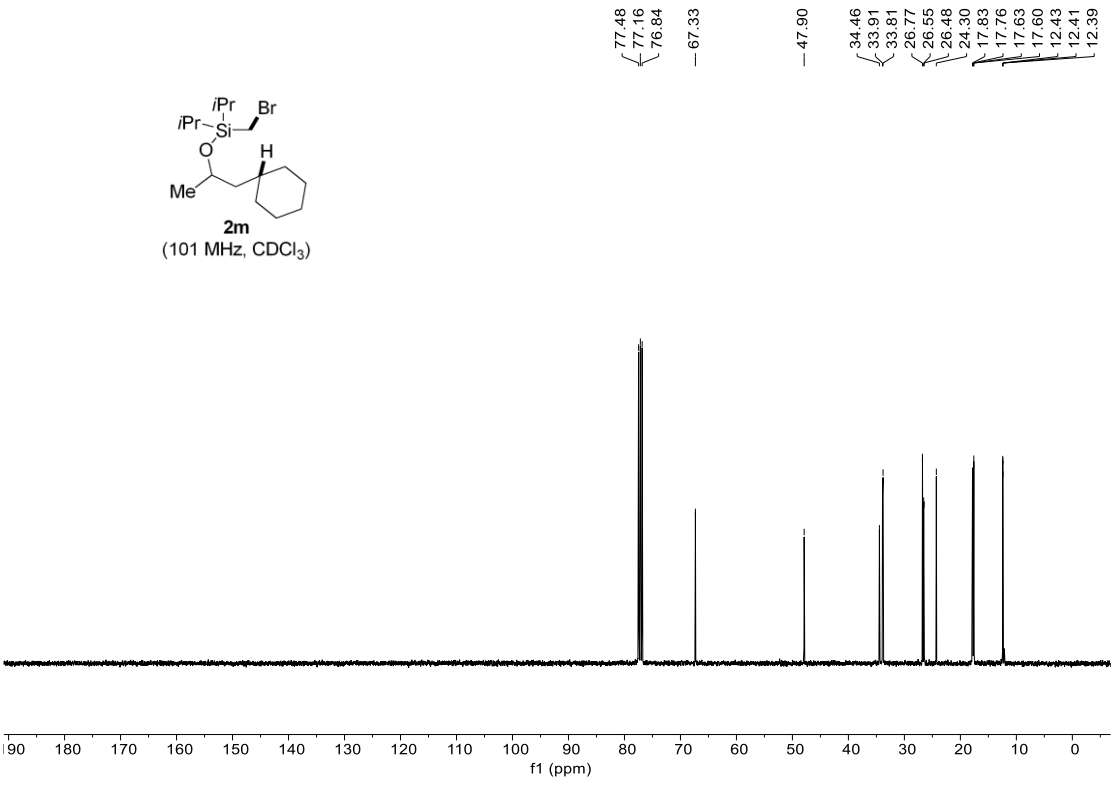

7.26 3.95 3.93 3.92 3.90 3.89 3.87 2.56 2.43 2.41 2.39 2.37 2.35 2.33 2.31 2.09 2.07 2.07 2.05 2.04 2.04 2.03 2.02 1.89 1.89 1.87 1.86 1.84 1.82 1.81 1.81 1.80 1.68 1.67 1.65 1.63 1.60 1.53 1.52 1.50 1.48 1.46 1.20 1.19 1.18 1.18 1.17 1.16 1.16 1.14 1.12 1.09 1.09 1.08 1.08 1.08 1.07 1.07
iPr
iPr
Si
Br
O
H
Me
2k
(400 MHz, CDCl3)
1.00
1.91
1.04
2.08
2.21
3.31
1.10
17.35
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

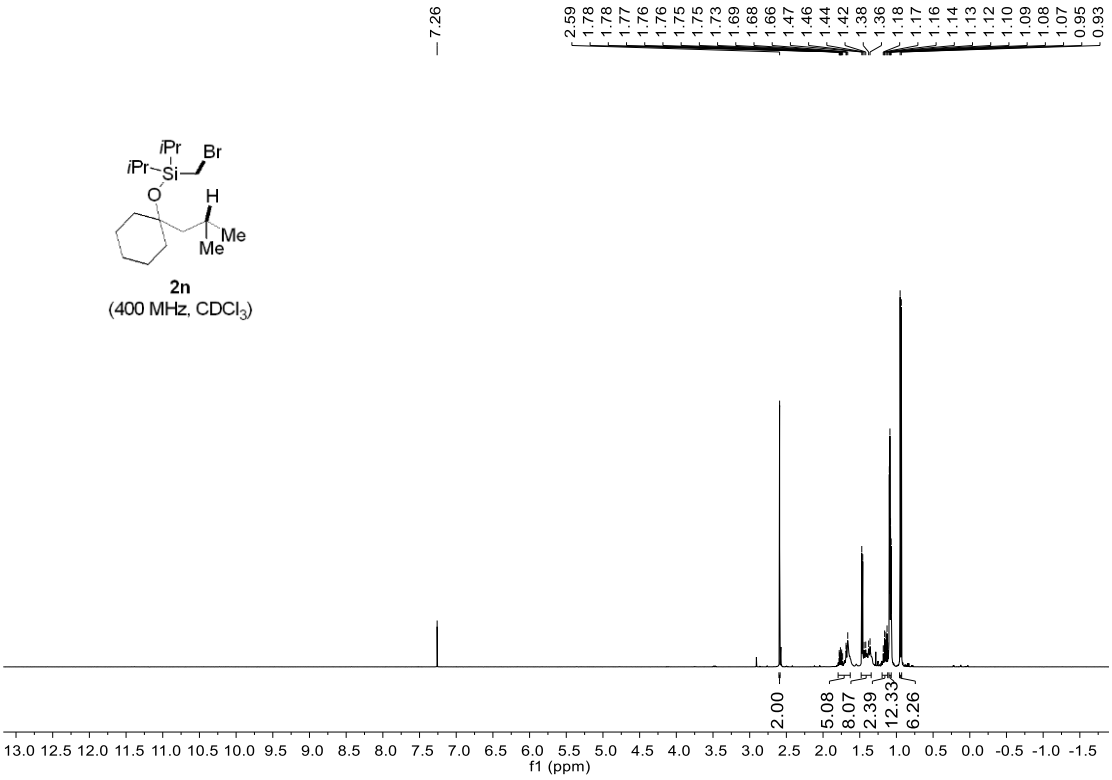

77.48
77.16
76.84
68.26
47.29
32.85
29.17
28.87
23.95
19.02
17.80
17.73
17.59
17.56
12.35
12.25
iPr
iPr
Si
Br
O
H
Me
2k
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

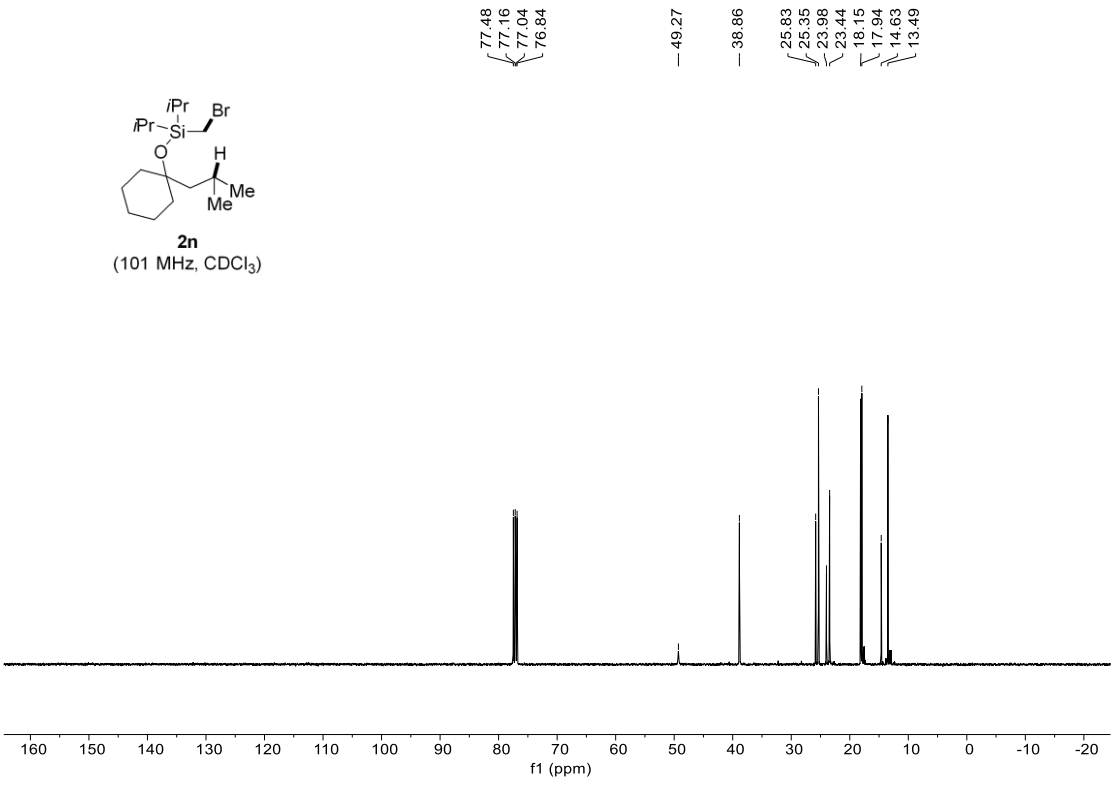

7.26
4.03 4.02 4.00 3.99 3.97 3.96 2.57 1.86 1.86 1.84 1.84 1.82 1.81 1.81 1.81 1.80 1.62 1.61 1.60 1.59 1.57 1.55 1.54 1.52 1.51 1.50 1.49 1.45 1.43 1.41 1.40 1.38 1.20 1.19 1.19 1.19 1.18 1.18 1.17 1.17 1.16 1.15 1.15 1.09 1.09 1.08 1.07
iPr
iPr
Si
Br
O
H
Me
2l
(400 MHz, CDCl3)
1.00
1.95
3.63
5.43
1.19
6.16
12.05
f1 (ppm)

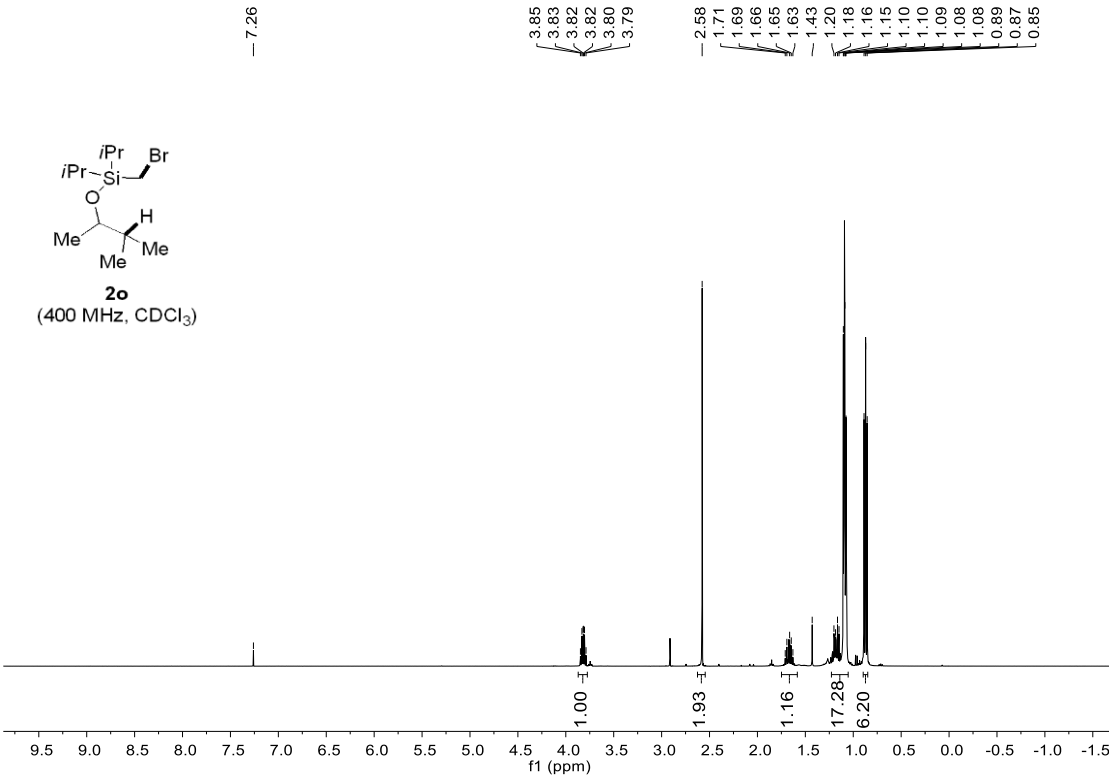

77.48
77.16
76.84
69.02
46.48
36.79
33.28
32.94
25.24
25.13
24.10
17.82
17.76
17.62
17.59
12.40
12.38
12.33
iPr
iPr
Si
Br
O
H
Me
2l
(101 MHz, CDCl3)
f1 (ppm)


7.26
4.11
4.09
4.08
4.06
4.05
4.03
2.57
1.74
1.71
1.70
1.66
1.66
1.45
1.44
1.42
1.40
1.39
1.26
1.25
1.23
1.18
1.18
1.17
1.15
1.09
1.09
1.09
1.08
1.07
1.07
1.07
0.90
0.89
0.89
0.86
iPr
iPr
Si
Br
O
H
Me
2m
(400 MHz, CDCl3)
1.00
1.86
5.00
2.08
9.00
11.91
2.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

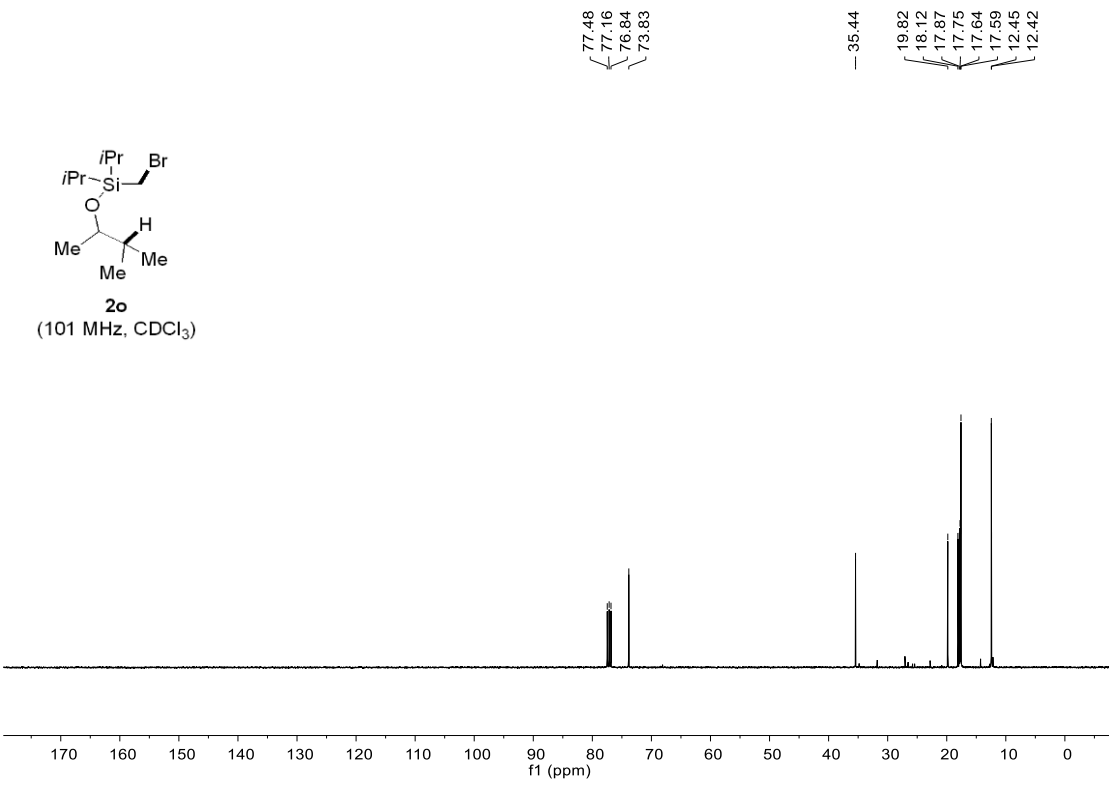

77.48
77.16
76.84
67.33
47.90
34.46
33.91
33.81
26.77
26.55
26.48
24.30
17.83
17.76
17.63
17.60
12.43
12.41
12.39
iPr
iPr
Si
Br
O
H
Me
2m
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
2.59
1.78
1.78
1.77
1.76
1.76
1.75
1.75
1.73
1.69
1.68
1.66
1.47
1.46
1.44
1.42
1.38
1.36
1.18
1.17
1.16
1.14
1.13
1.12
1.10
1.09
1.08
1.07
0.95
0.93
iPr
iPr
Si
Br
O
H
Me
Me
2n
(400 MHz, CDCl3)
2.00
5.08
8.07
2.39
12.33
6.26
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

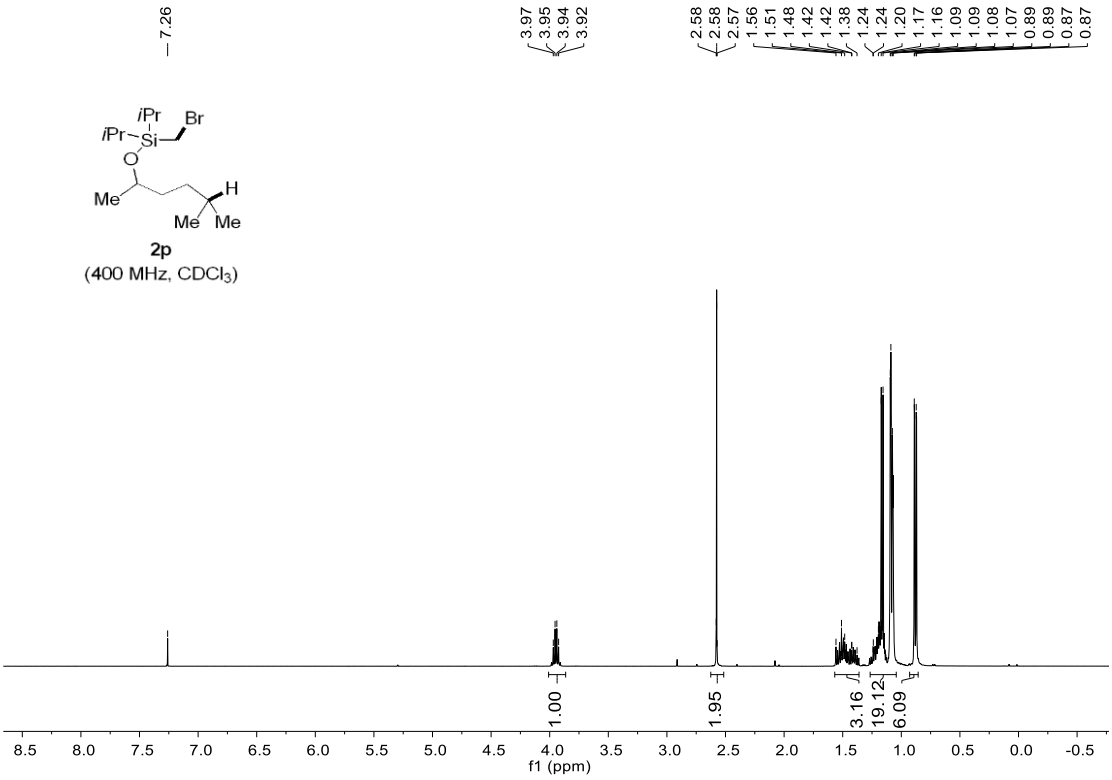

77.48
77.16
77.04
76.84
49.27
38.86
25.83
25.35
23.98
23.44
18.15
17.94
14.63
13.49
iPr
iPr
Si
Br
O
H
Me
Me
2n
(101 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



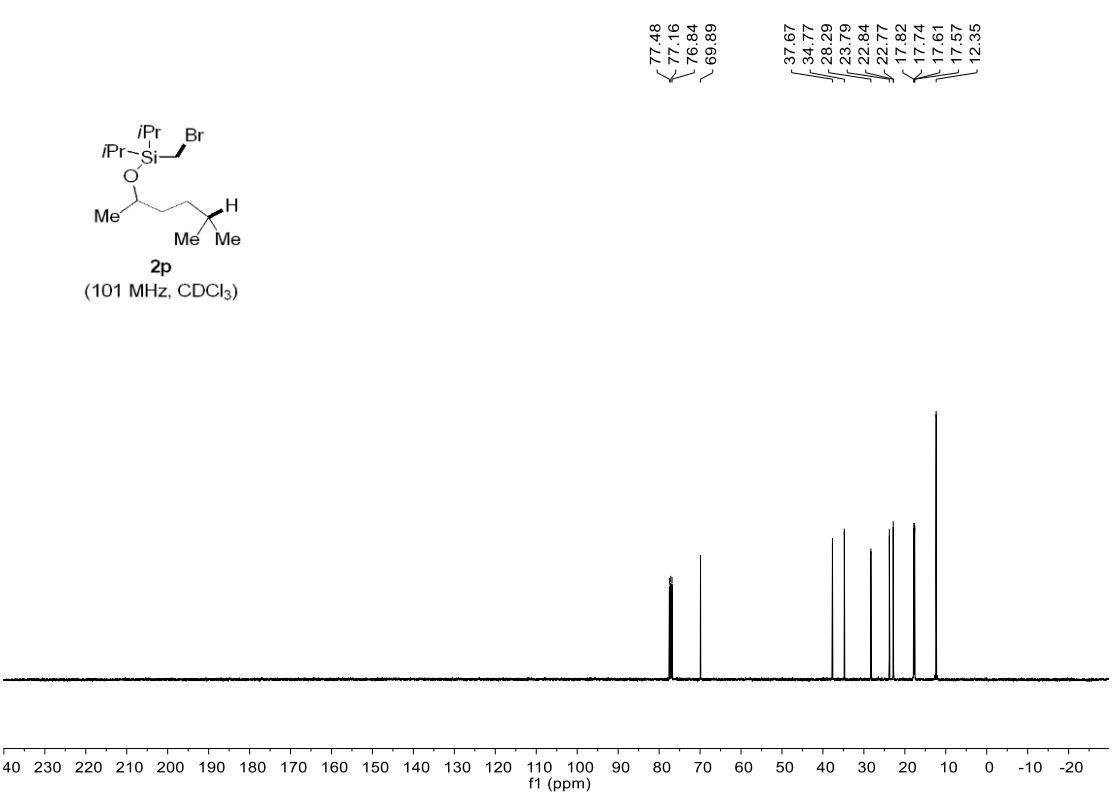
2o
(400 MHz, $CDCl_3$)



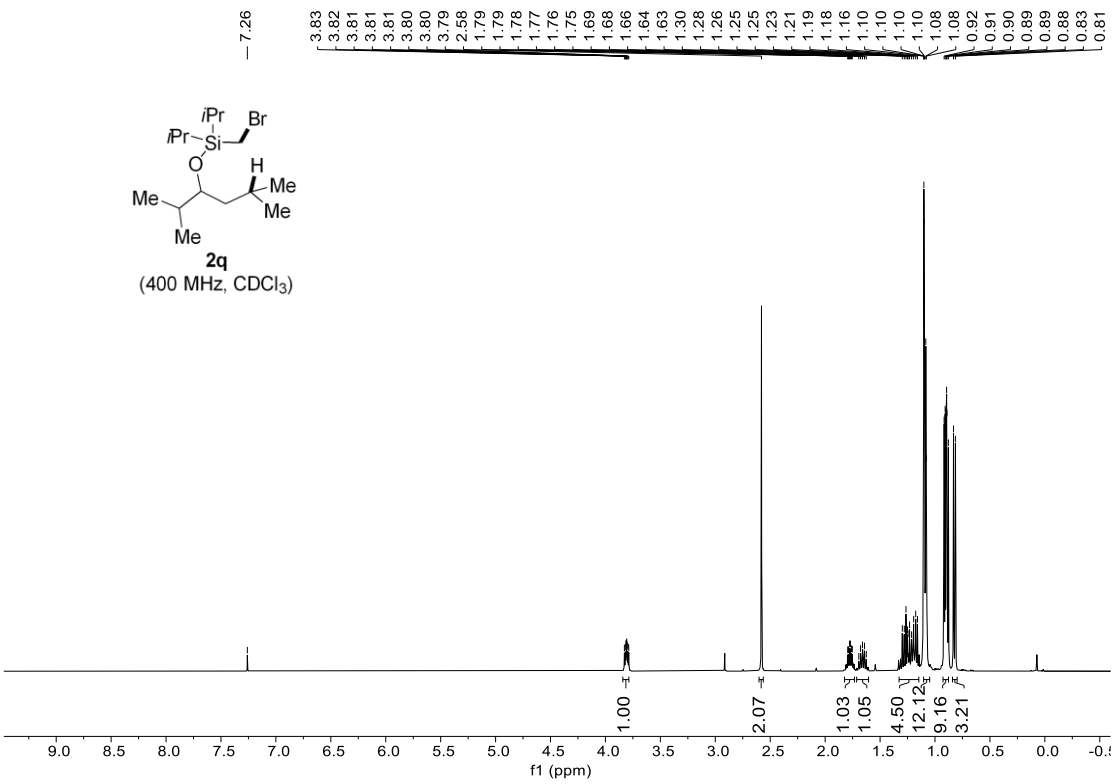
2o
(101 MHz, $CDCl_3$)

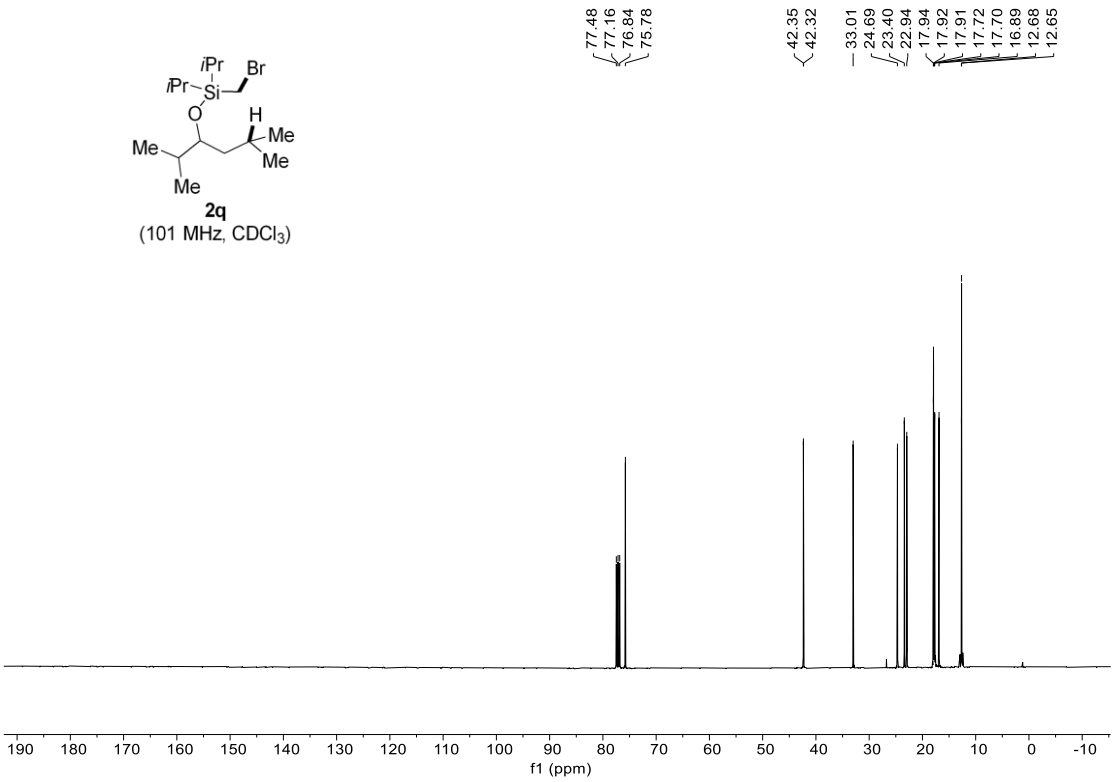


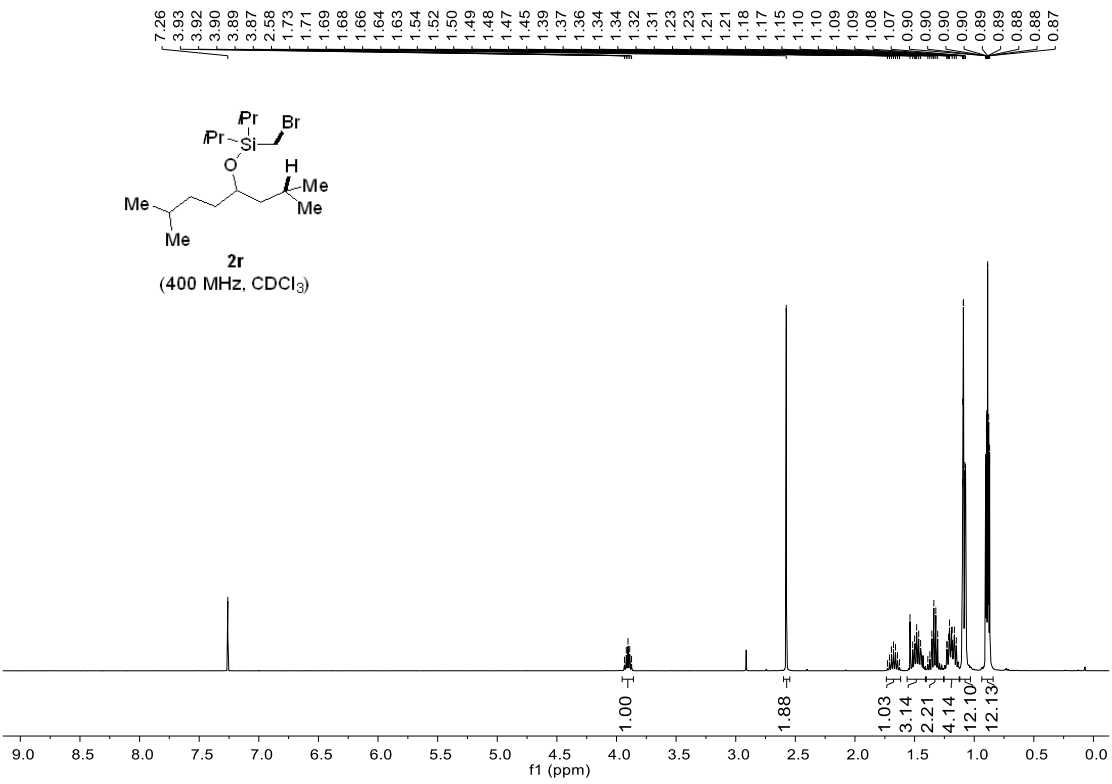
2p
(400 MHz, $CDCl_3$)

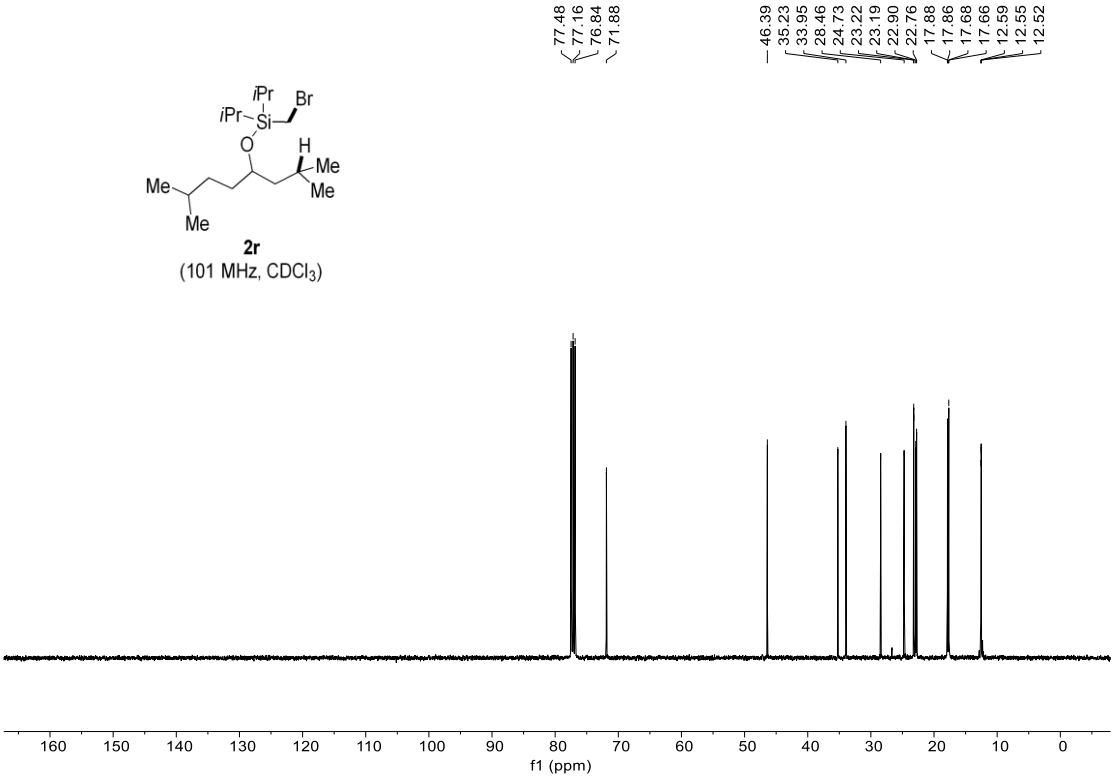


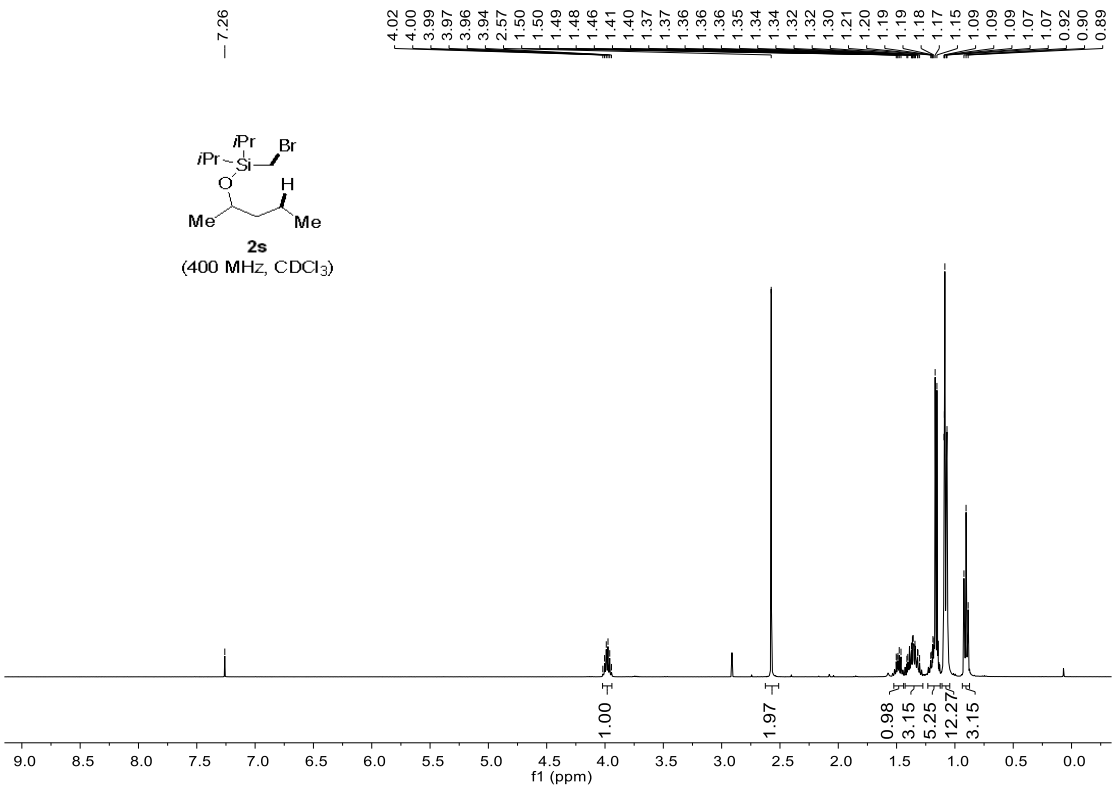
2p
(101 MHz, $CDCl_3$)

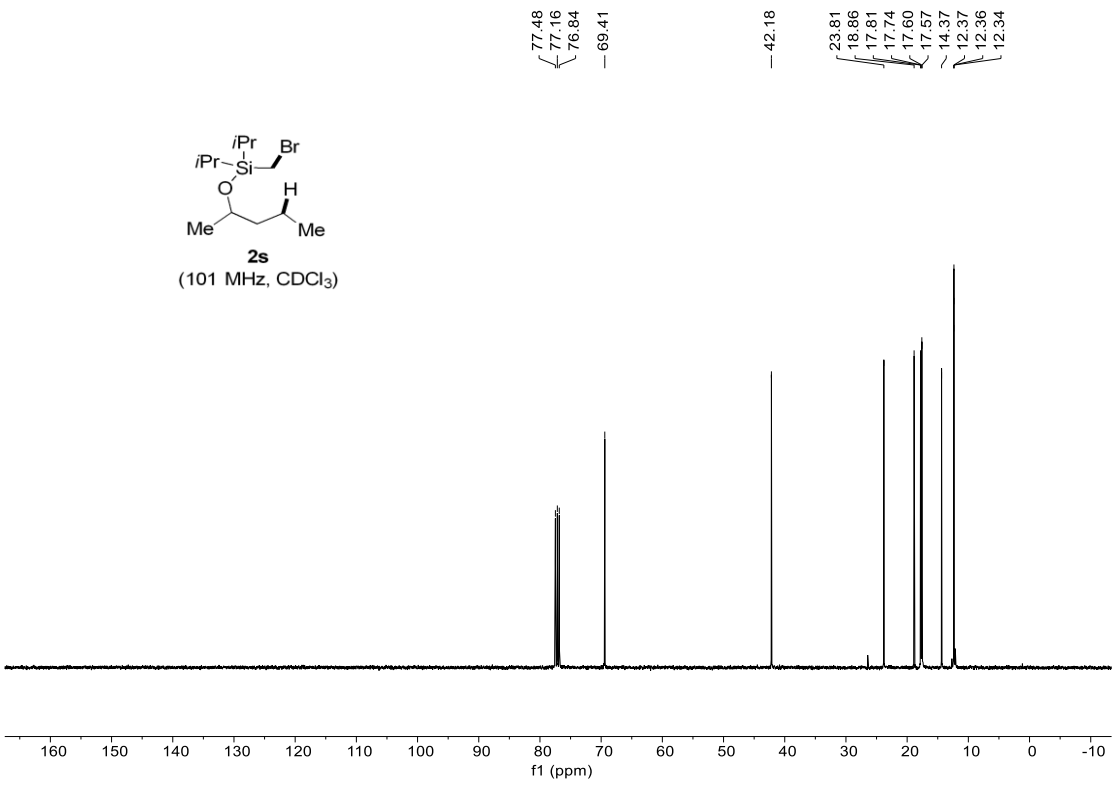

7.26
3.83 3.82 3.81 3.81 3.81 3.80 3.80 3.79 2.58 1.79 1.79 1.78 1.77 1.76 1.75 1.69 1.68 1.66 1.64 1.63 1.30 1.28 1.26 1.25 1.25 1.23 1.21 1.19 1.18 1.16 1.10 1.10 1.10 1.10 1.08 1.08 0.92 0.91 0.90 0.89 0.89 0.88 0.83 0.81
iPr
Br
iPr
Si
O
H
Me
Me
Me
Me
2q
(400 MHz, CDCl3)
1.00
2.07
1.03
1.05
4.50
12.12
9.16
3.21
f1 (ppm)

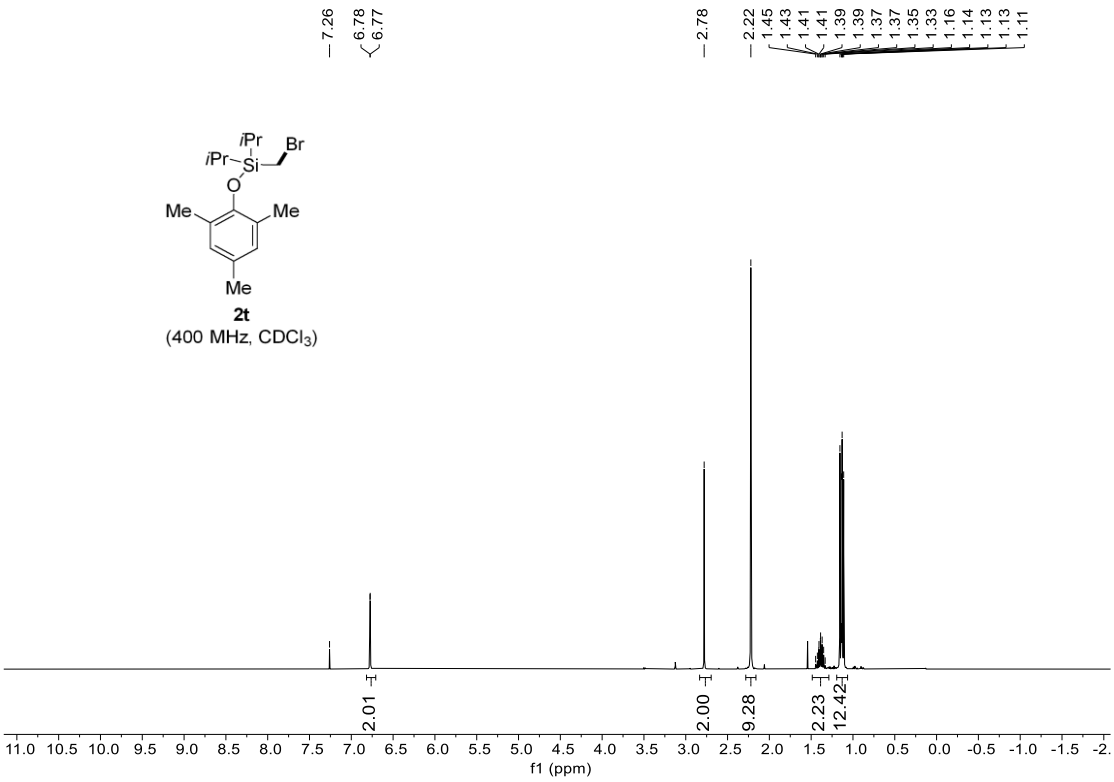

77.48
77.16
76.84
75.78
42.35
42.32
33.01
24.69
23.40
22.94
17.94
17.92
17.91
17.72
17.70
16.89
12.68
12.65
iPr
Br
iPr
Si
O
H
Me
Me
Me
Me
2q
(101 MHz, CDCl3)
f1 (ppm)

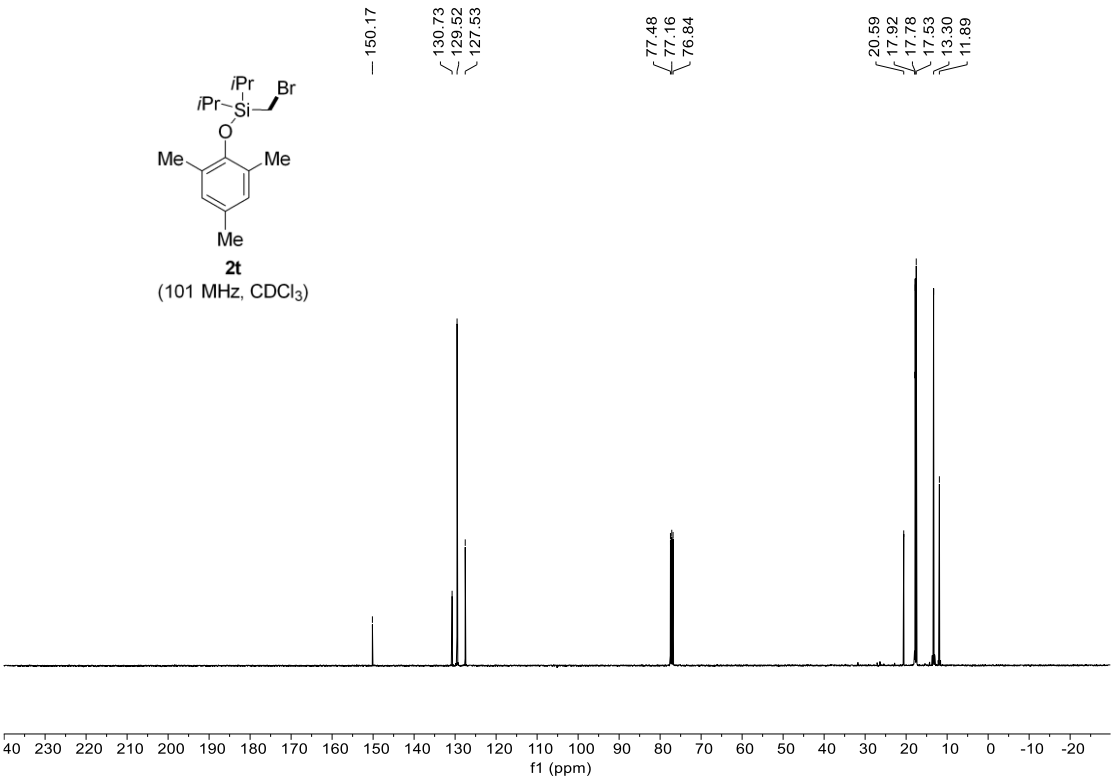

7.26 3.93 3.92 3.90 3.89 3.87 2.58 1.73 1.71 1.69 1.68 1.66 1.64 1.63 1.54 1.52 1.50 1.49 1.48 1.47 1.45 1.39 1.37 1.36 1.34 1.34 1.32 1.31 1.23 1.23 1.21 1.21 1.18 1.17 1.15 1.10 1.10 1.09 1.09 1.08 1.07 0.90 0.90 0.90 0.89 0.89 0.88 0.88 0.87
iPr
iPr
Si
Br
O
H
Me
Me
Me
Me
2r
(400 MHz, CDCl3)
1.00
1.88
1.03
3.14
2.21
4.14
12.10
12.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

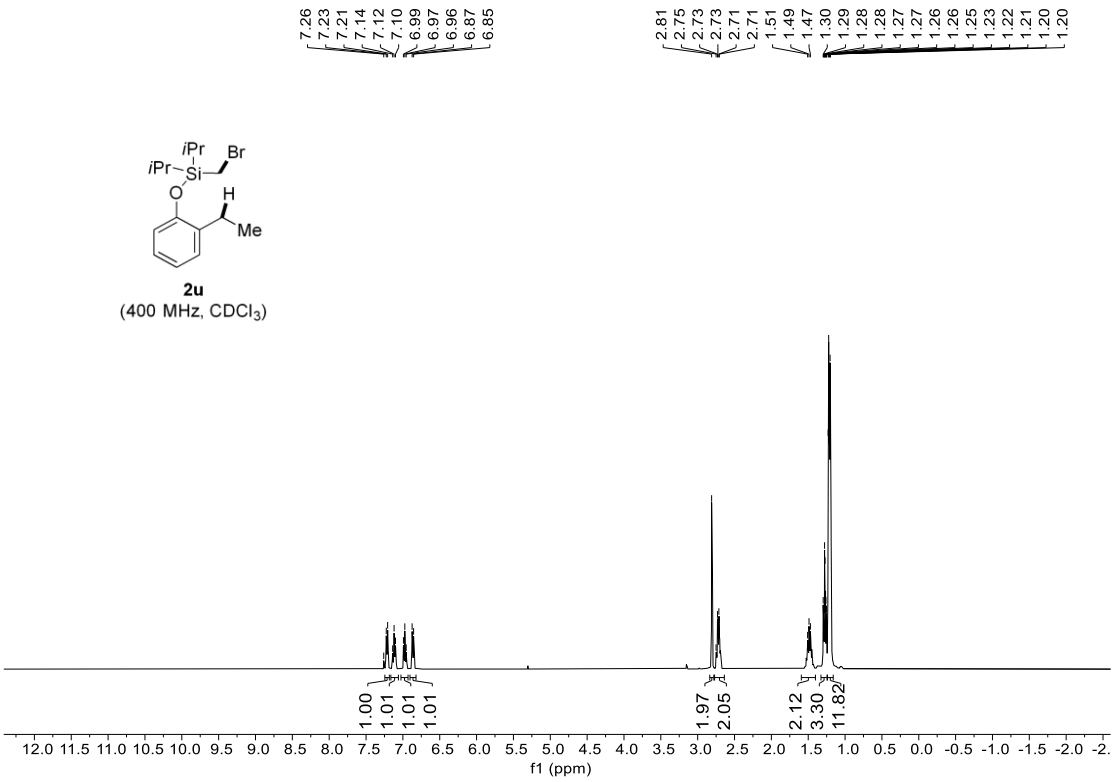

77.48 77.16 76.84 71.88
46.39 35.23 33.95 28.46 24.73 23.22 23.19 22.90 22.76 17.88 17.86 17.68 17.66 12.59 12.55 12.52
iPr
iPr
Si
Br
O
H
Me
Me
Me
Me
2r
(101 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

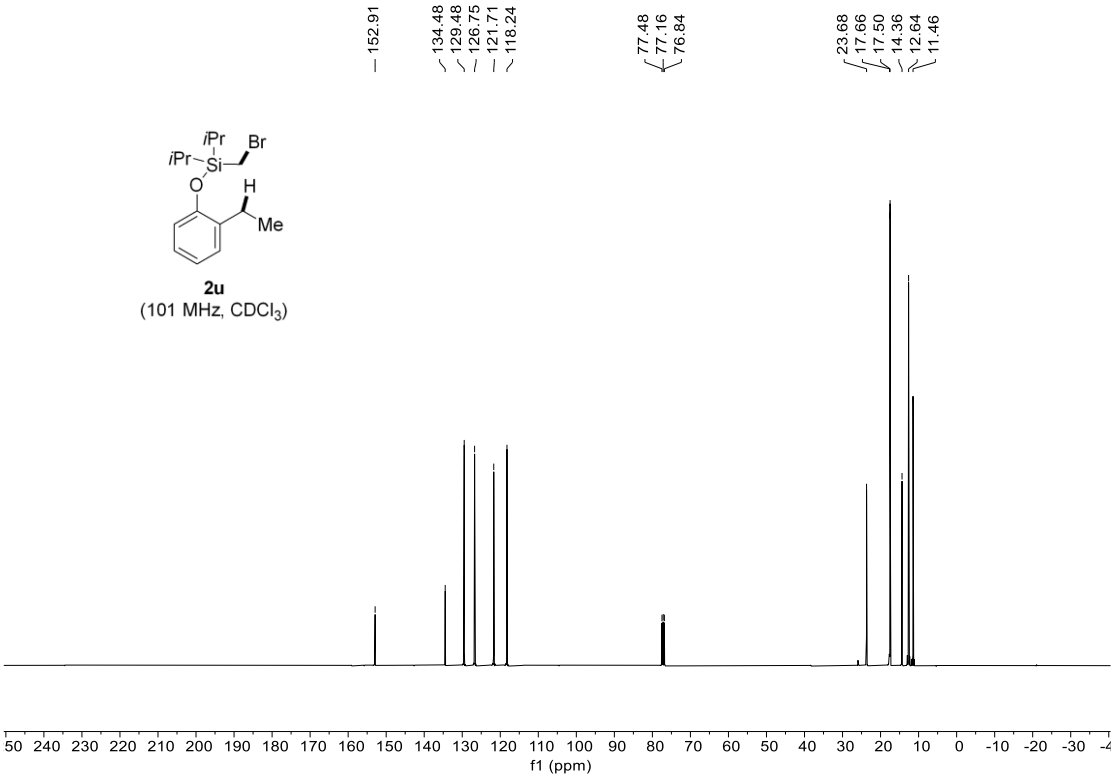

7.26
4.02
4.00
3.99
3.97
3.96
3.94
2.57
1.50
1.50
1.49
1.48
1.46
1.41
1.40
1.37
1.37
1.36
1.36
1.36
1.35
1.34
1.34
1.32
1.32
1.30
1.21
1.20
1.19
1.19
1.18
1.17
1.15
1.09
1.09
1.09
1.07
1.07
0.92
0.90
0.89
iPr
iPr
Si
Br
O
H
Me
Me
2s
(400 MHz, CDCl3)
1.00
1.97
0.98
3.15
5.25
12.27
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

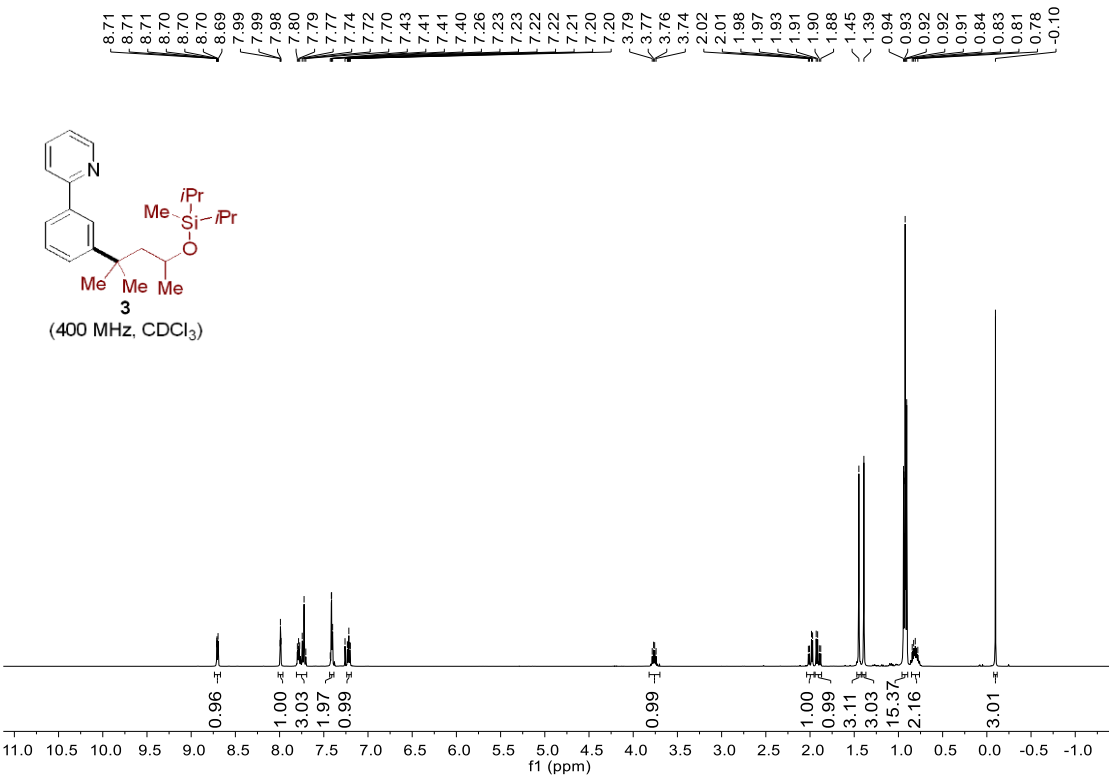

77.48
77.16
76.84
69.41
42.18
23.81
18.86
17.81
17.74
17.60
17.57
14.37
12.37
12.36
12.34
iPr
iPr
Si
Br
O
H
Me
Me
2s
(101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

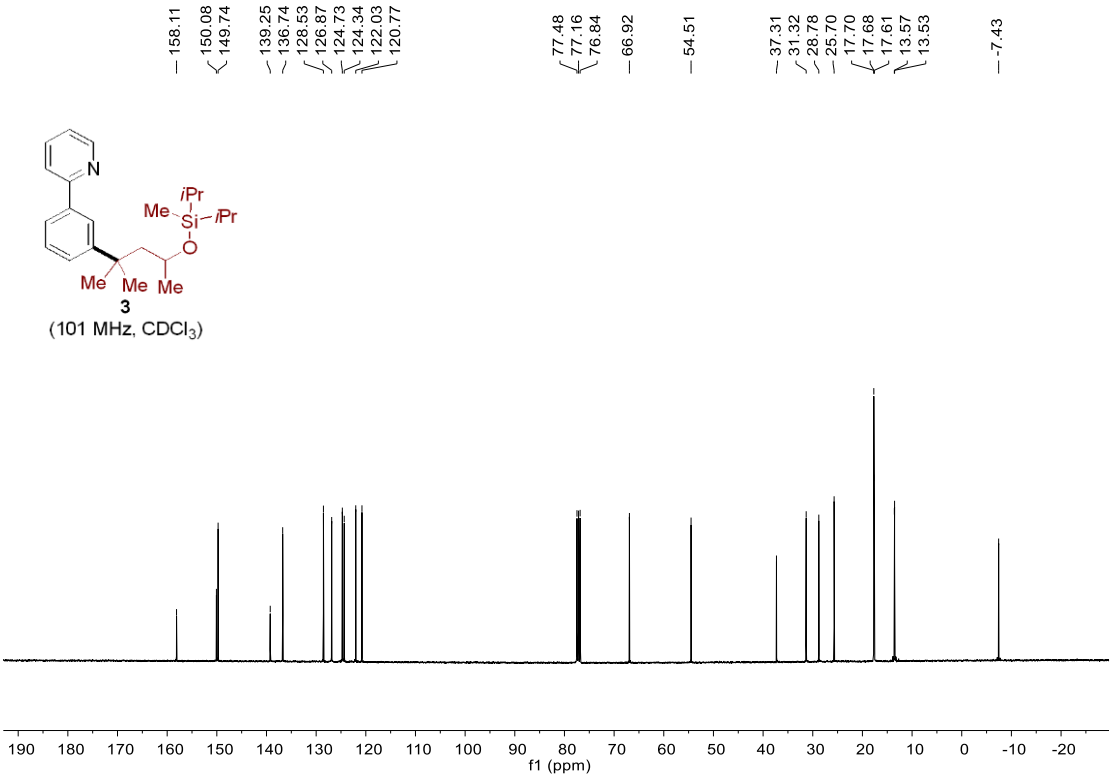

7.26
6.78
6.77
2.78
2.22
1.45
1.43
1.41
1.41
1.39
1.39
1.37
1.37
1.35
1.33
1.16
1.14
1.13
1.13
1.11
iPr
iPr
Si
Br
O
Me
Me
Me
2t
(400 MHz, CDCl3)
2.01
2.00
9.28
2.23
12.42
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)

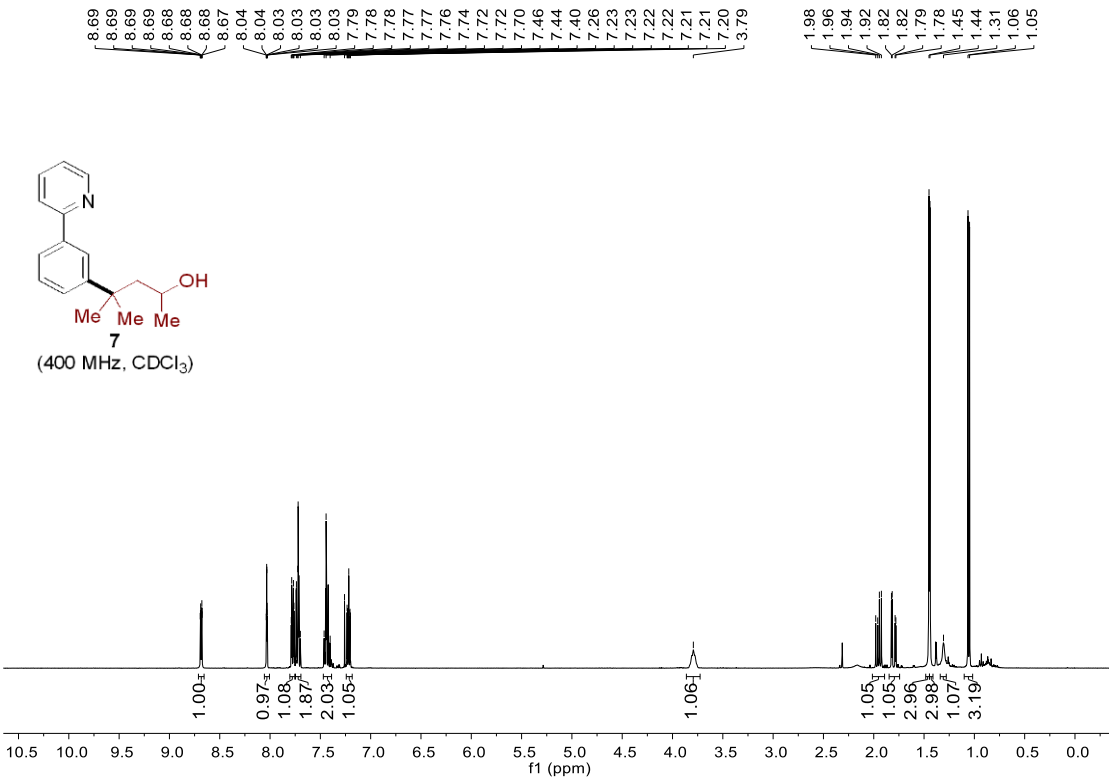

150.17
130.73
129.52
127.53
77.48
77.16
76.84
20.59
17.92
17.78
17.53
13.30
11.89
iPr
iPr
Si
Br
O
Me
Me
Me
2t
(101 MHz, CDCl3)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

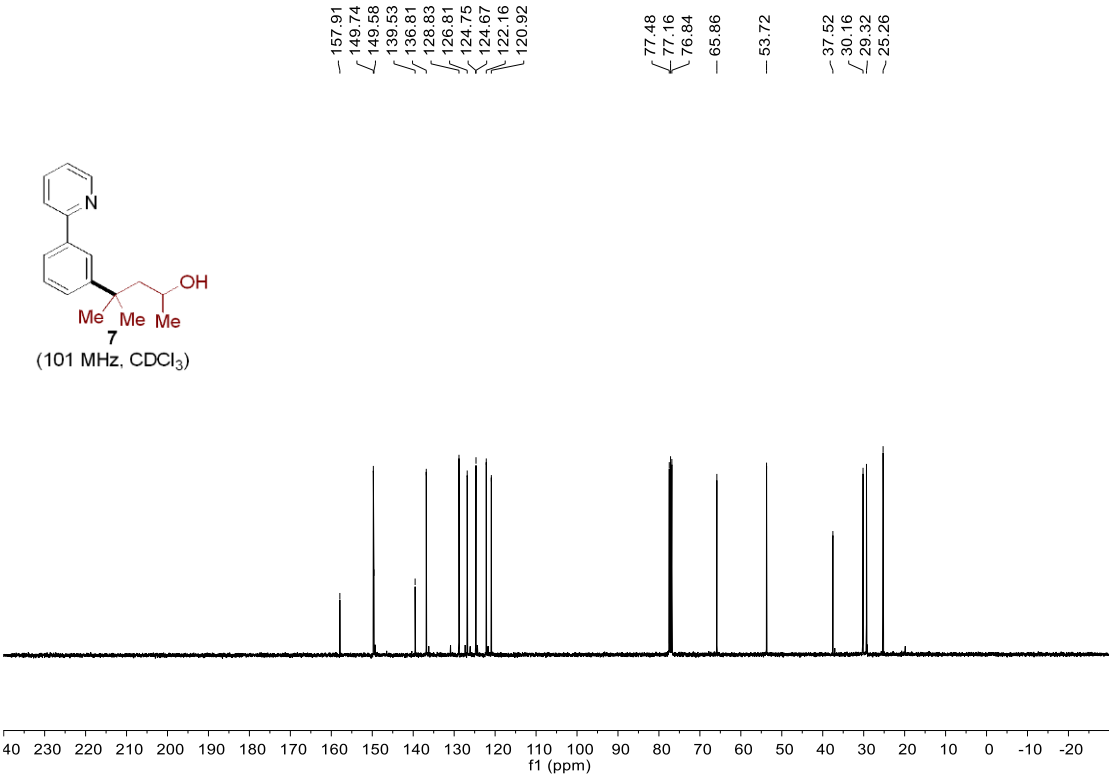

7.26
7.23
7.21
7.14
7.12
7.10
6.99
6.97
6.96
6.87
6.85
2.81
2.75
2.73
2.73
2.71
2.71
1.51
1.49
1.47
1.30
1.29
1.28
1.28
1.27
1.27
1.26
1.26
1.25
1.23
1.22
1.21
1.20
1.20
iPr
iPr
Si
Br
O
H
Me
2u
(400 MHz, CDCl3)
1.00
1.01
1.01
1.01
1.97
2.05
2.12
3.30
11.82
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.
f1 (ppm)

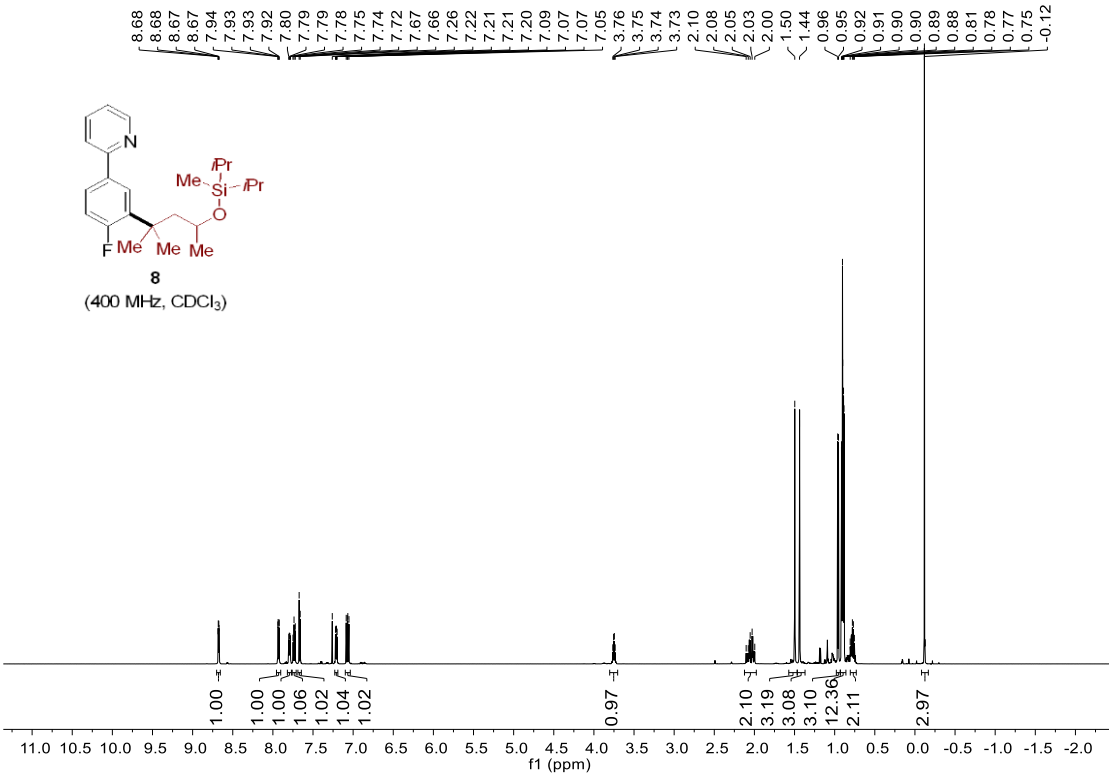

152.91
134.48
129.48
126.75
121.71
118.24
77.48
77.16
76.84
23.68
17.66
17.50
14.36
12.64
11.46
iPr
iPr
Si
Br
O
H
Me
2u
(101 MHz, CDCl3)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4
f1 (ppm)


8.71 8.71 8.71 8.70 8.70 8.70 8.69 7.99 7.99 7.98 7.80 7.79 7.77 7.74 7.72 7.70 7.43 7.41 7.41 7.40 7.26 7.23 7.23 7.22 7.22 7.21 7.20 7.20 3.79 3.77 3.76 3.74 2.02 2.01 1.98 1.97 1.93 1.91 1.90 1.88 1.45 1.39 0.94 0.93 0.92 0.92 0.91 0.84 0.83 0.81 0.78 -0.10
N
iPr
Me
Si
iPr
O
Me
Me
Me
3
(400 MHz, CDCl3)
0.96 1.00 3.03 1.97 0.99 0.99 1.00 0.99 3.11 3.03 15.37 2.16 3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.11 150.08 149.74 139.25 136.74 128.53 126.87 124.73 124.34 122.03 120.77 77.48 77.16 76.84 66.92 54.51 37.31 31.32 28.78 25.70 17.70 17.68 17.61 13.57 13.53 -7.43
N
iPr
Me
Si
iPr
O
Me
Me
Me
3
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

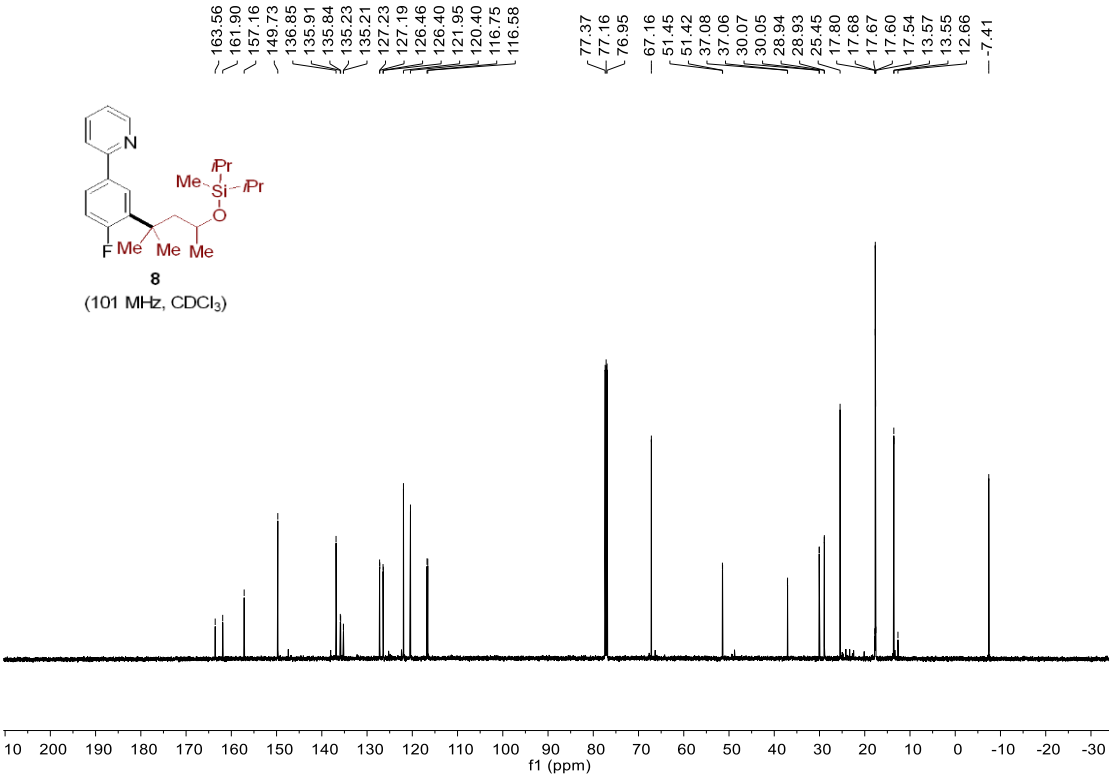

8.69 8.69 8.69 8.69 8.68 8.68 8.68 8.67 8.04 8.04 8.03 8.03 8.03 8.03 7.79 7.78 7.78 7.77 7.77 7.76 7.74 7.72 7.72 7.70 7.46 7.44 7.40 7.26 7.23 7.23 7.22 7.22 7.21 7.21 7.20 3.79
1.98 1.96 1.94 1.92 1.82 1.82 1.79 1.78 1.45 1.44 1.31 1.06 1.05
N
OH
Me Me Me
7
(400 MHz, CDCl3)
1.00 0.97 1.08 1.87 2.03 1.05 1.06 1.05 1.05 2.96 2.98 1.07 3.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.91 149.74 149.58 139.53 136.81 128.83 126.81 124.75 124.67 122.16 120.92
77.48 77.16 76.84 65.86 53.72 37.52 30.16 29.32 25.26
N
OH
Me Me Me
7
(101 MHz, CDCl3)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



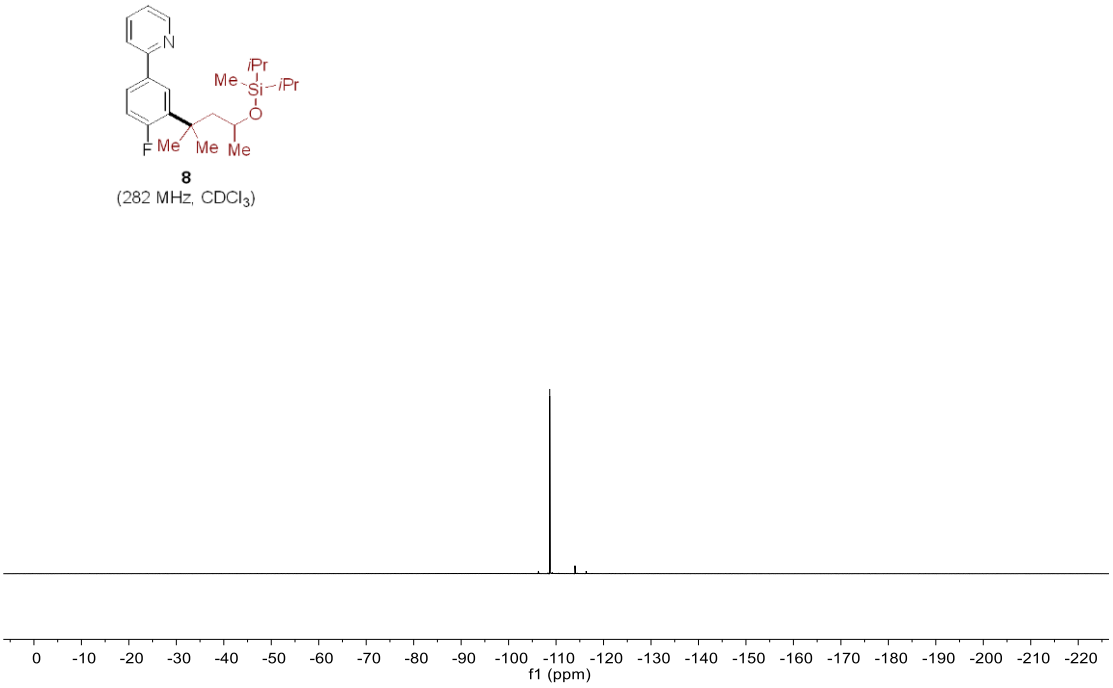
8

(400 MHz, $CDCl_3$)

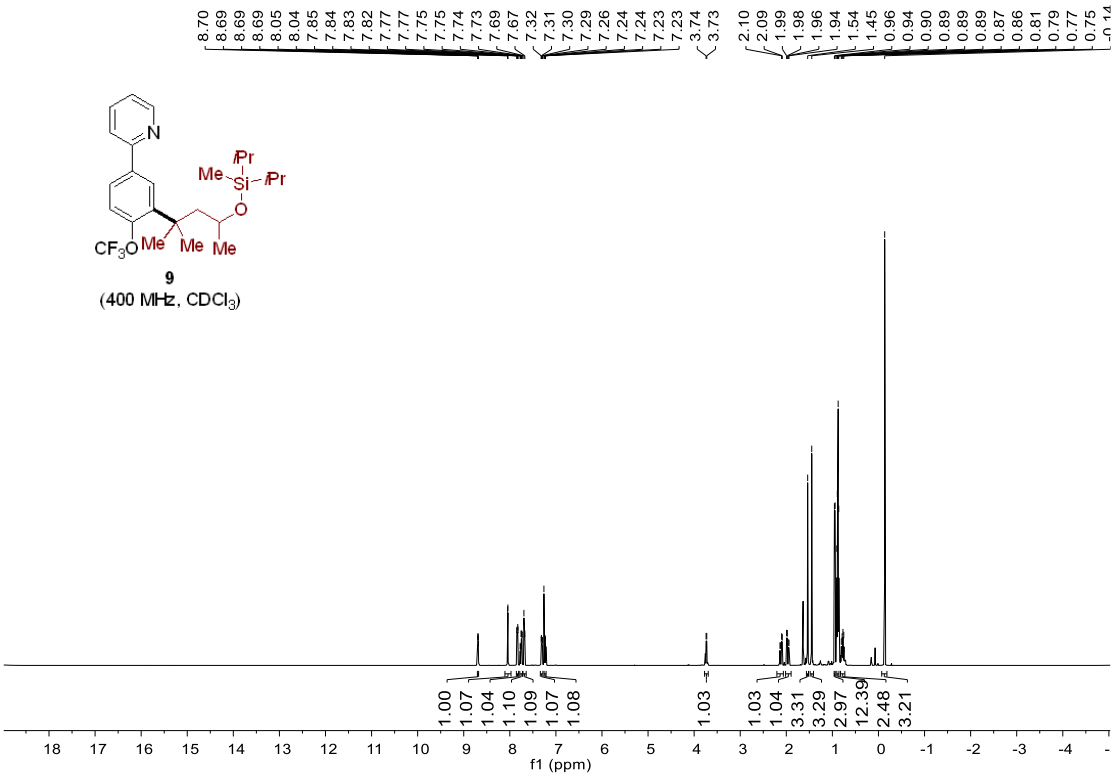


8

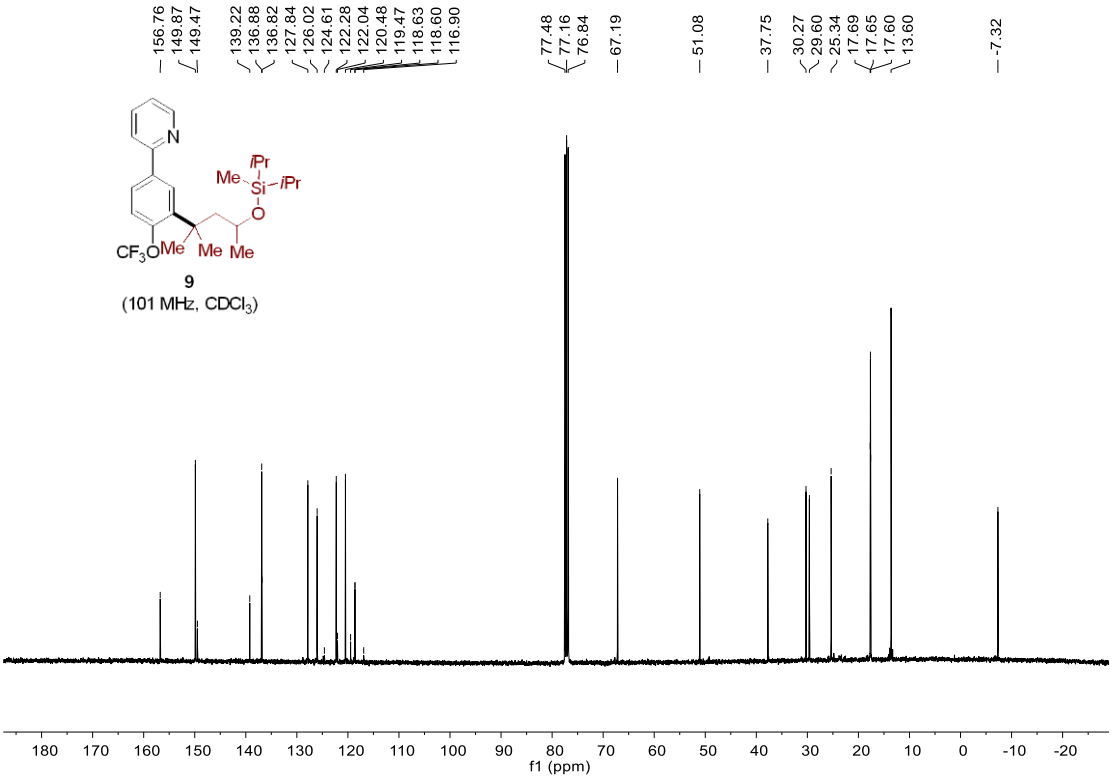
(101 MHz, $CDCl_3$)

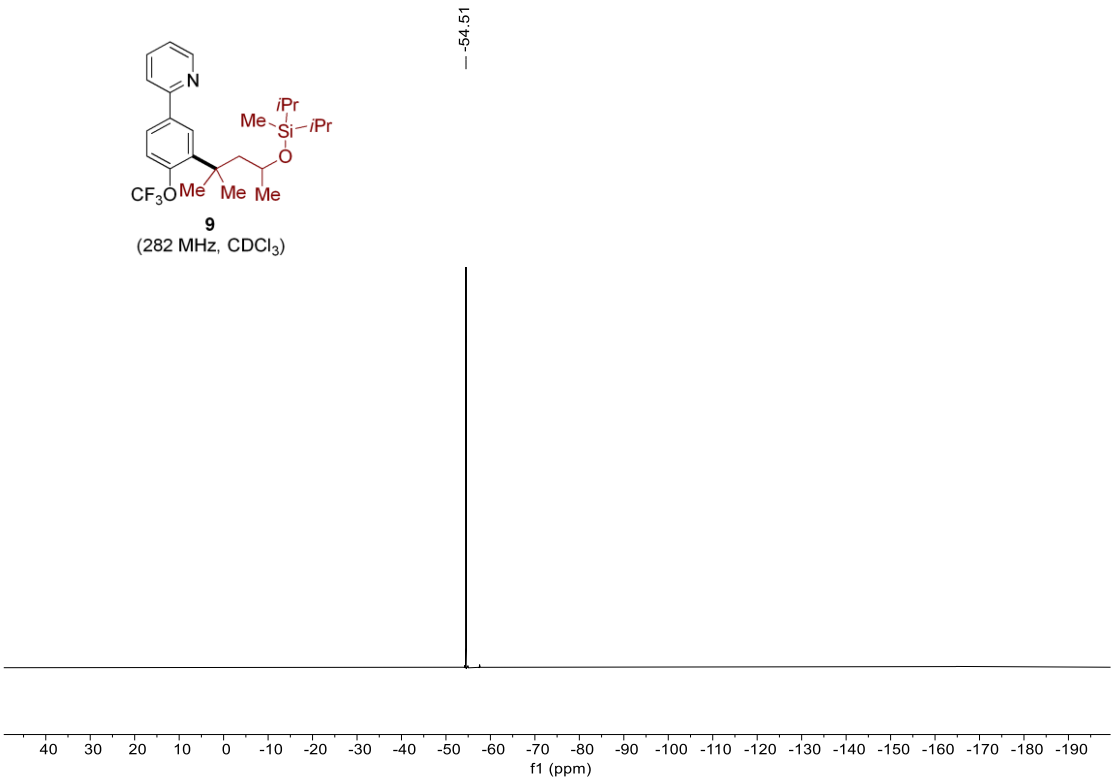


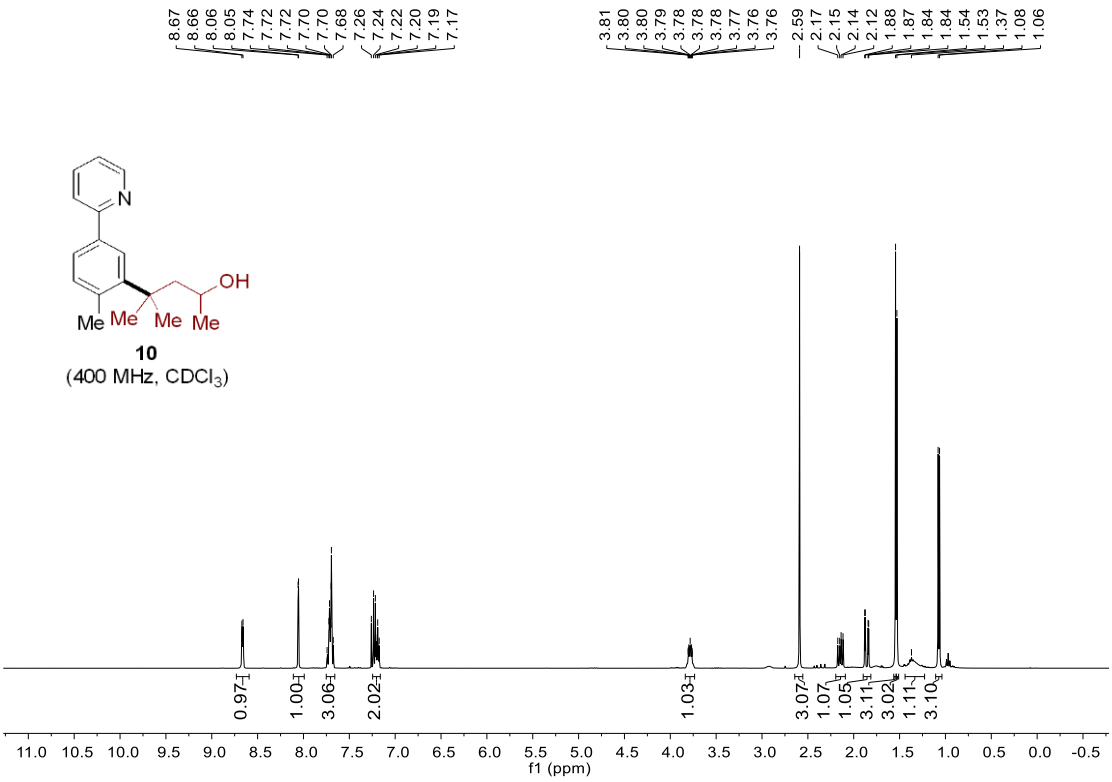
8
(282 MHz, $CDCl_3$)

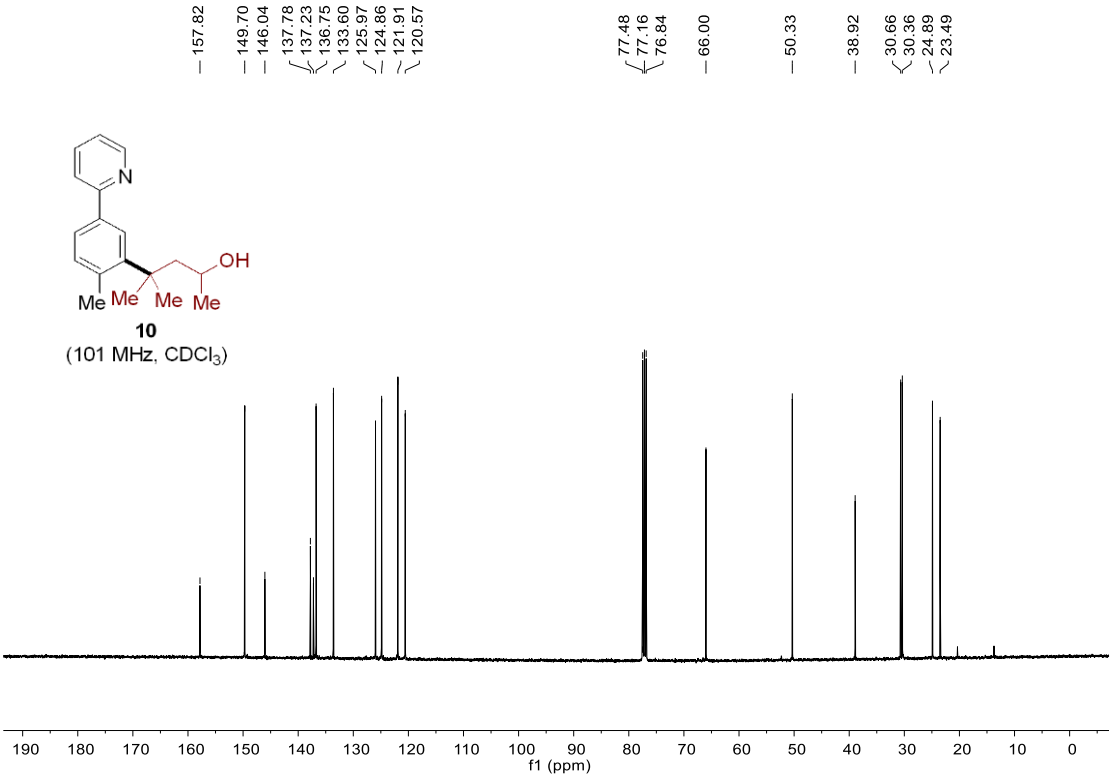


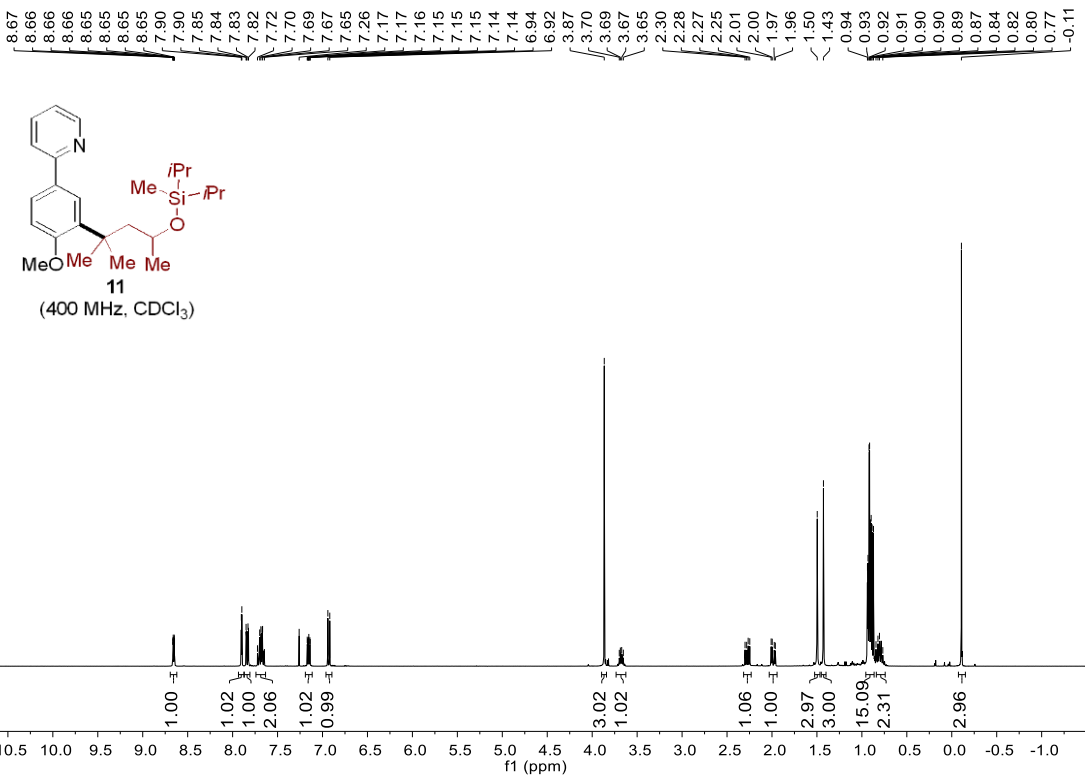
9
(400 MHz, $CDCl_3$)

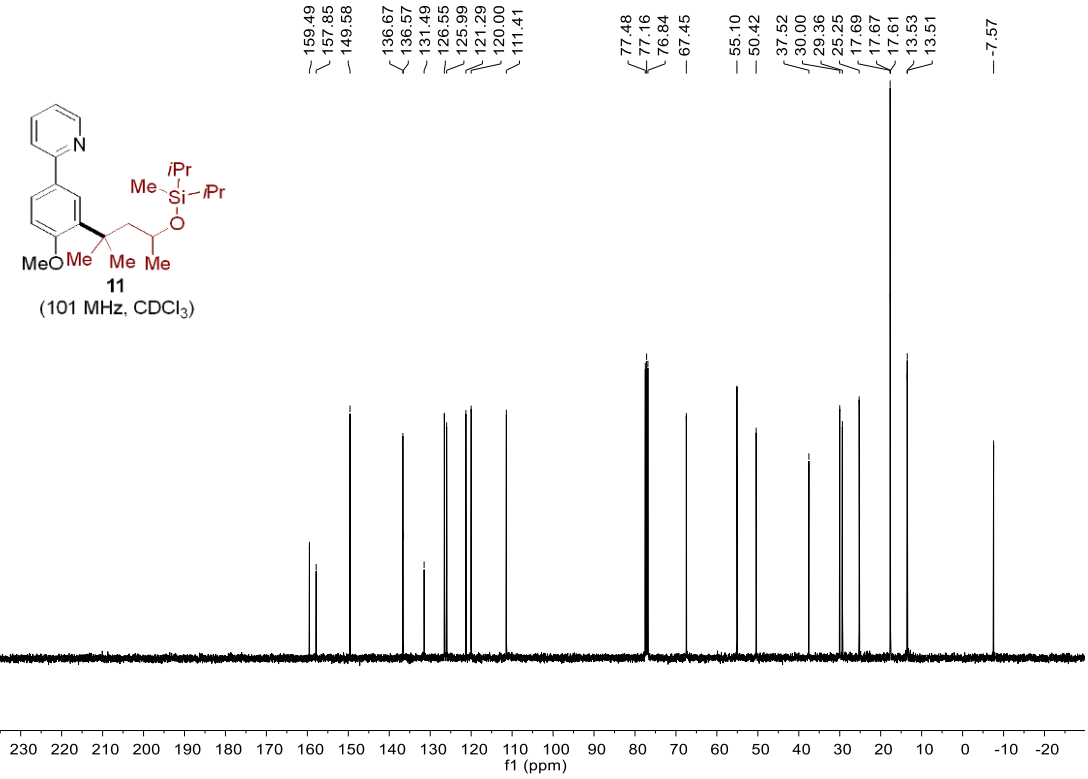

156.76
149.87
149.47
139.22
136.88
136.82
127.84
126.02
124.61
122.28
122.04
120.48
119.47
118.63
118.60
116.90
77.48
77.16
76.84
67.19
51.08
37.75
30.27
29.60
25.34
17.69
17.65
17.60
13.60
-7.32
N
iPr
Me
Si
iPr
O
CF3O
Me
Me
Me
9
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

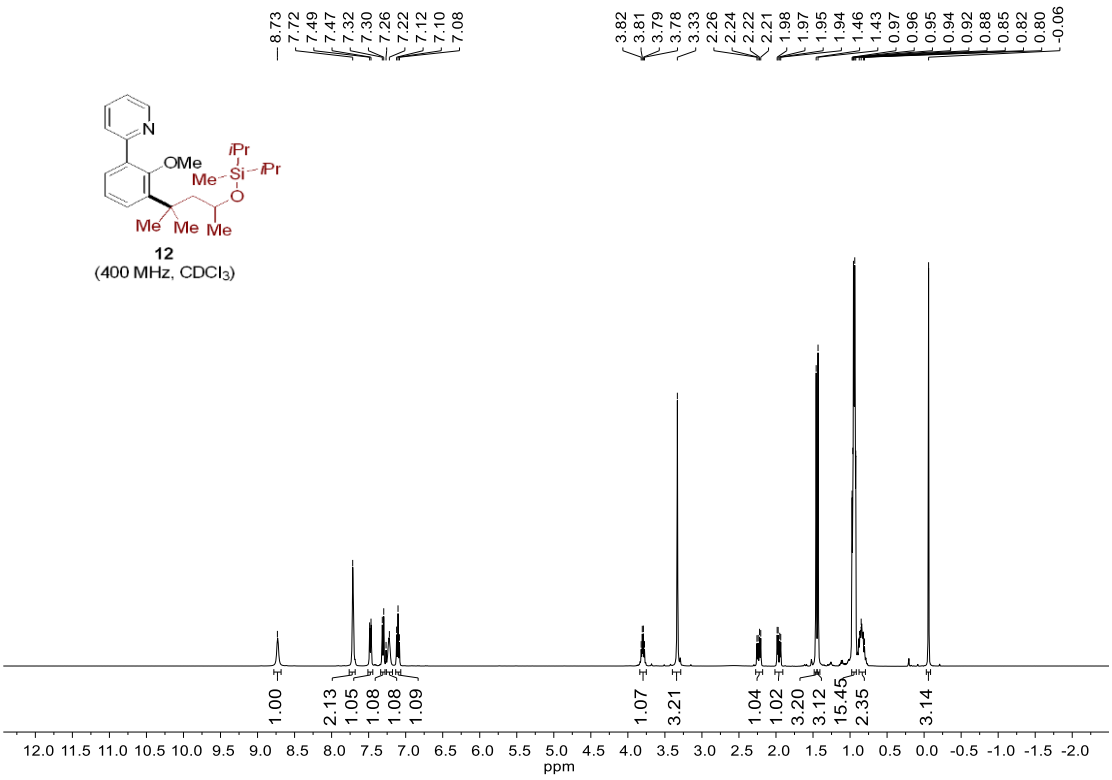

-54.51
N
iPr
Me
Si
iPr
O
CF3O
Me
Me
Me
9
(282 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

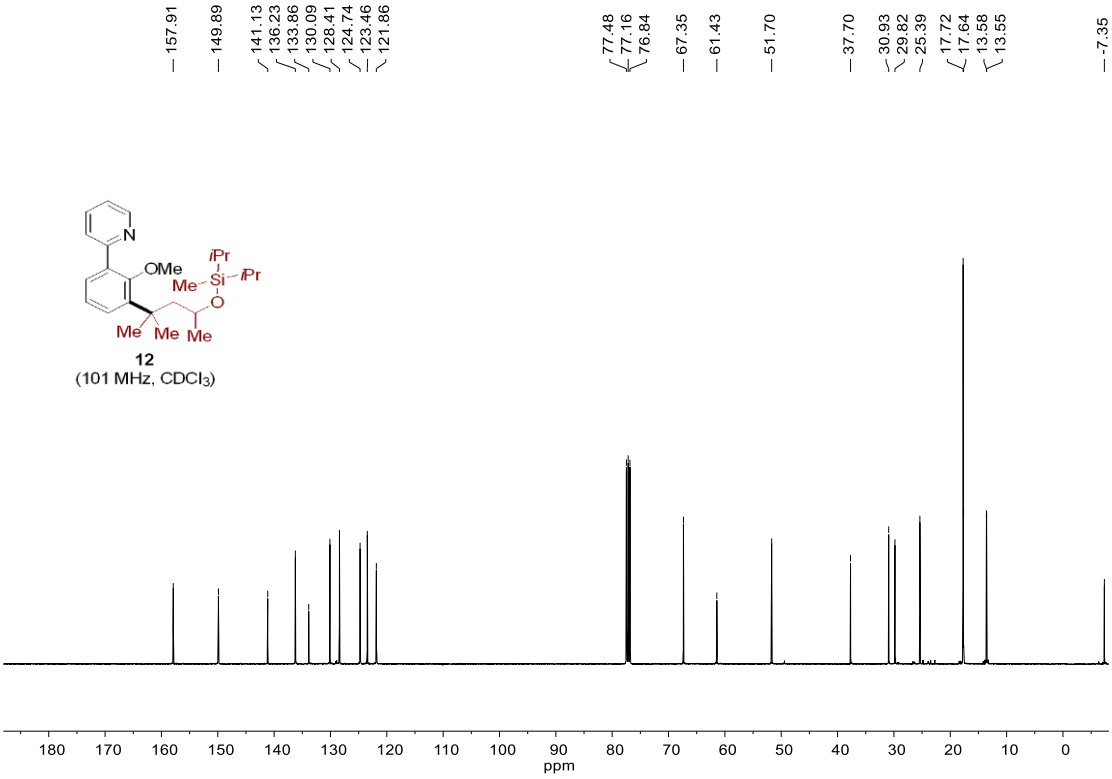

8.67
8.66
8.06
8.05
7.74
7.72
7.72
7.70
7.70
7.68
7.26
7.24
7.22
7.20
7.19
7.17
3.81
3.80
3.80
3.79
3.78
3.78
3.78
3.77
3.76
3.76
2.59
2.17
2.15
2.14
2.12
1.88
1.87
1.84
1.84
1.54
1.53
1.37
1.08
1.06
N
OH
Me
Me
Me
Me
10
(400 MHz, CDCl3)
0.97
1.00
3.06
2.02
1.03
3.07
1.07
1.05
3.11
3.02
1.11
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

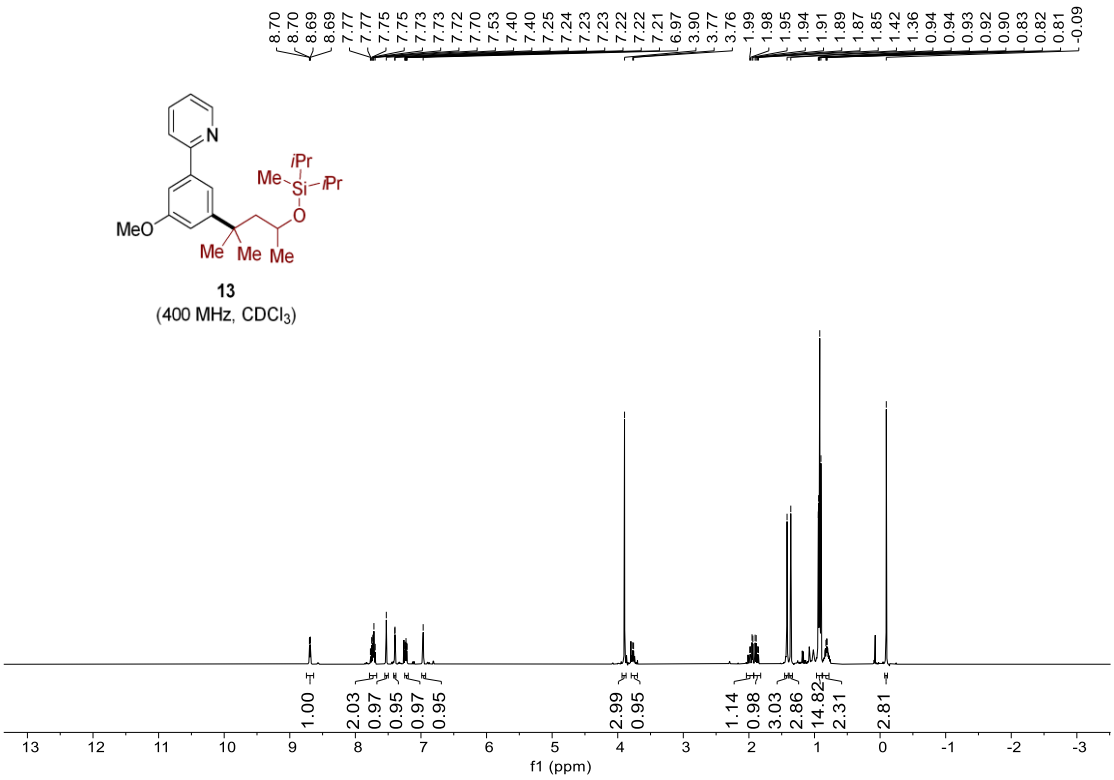

157.82
149.70
146.04
137.78
137.23
136.75
133.60
125.97
124.86
121.91
120.57
77.48
77.16
76.84
66.00
50.33
38.92
30.66
30.36
24.89
23.49
N
OH
Me
Me
Me
Me
10
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11
(400 MHz, CDCl3)
f1 (ppm)

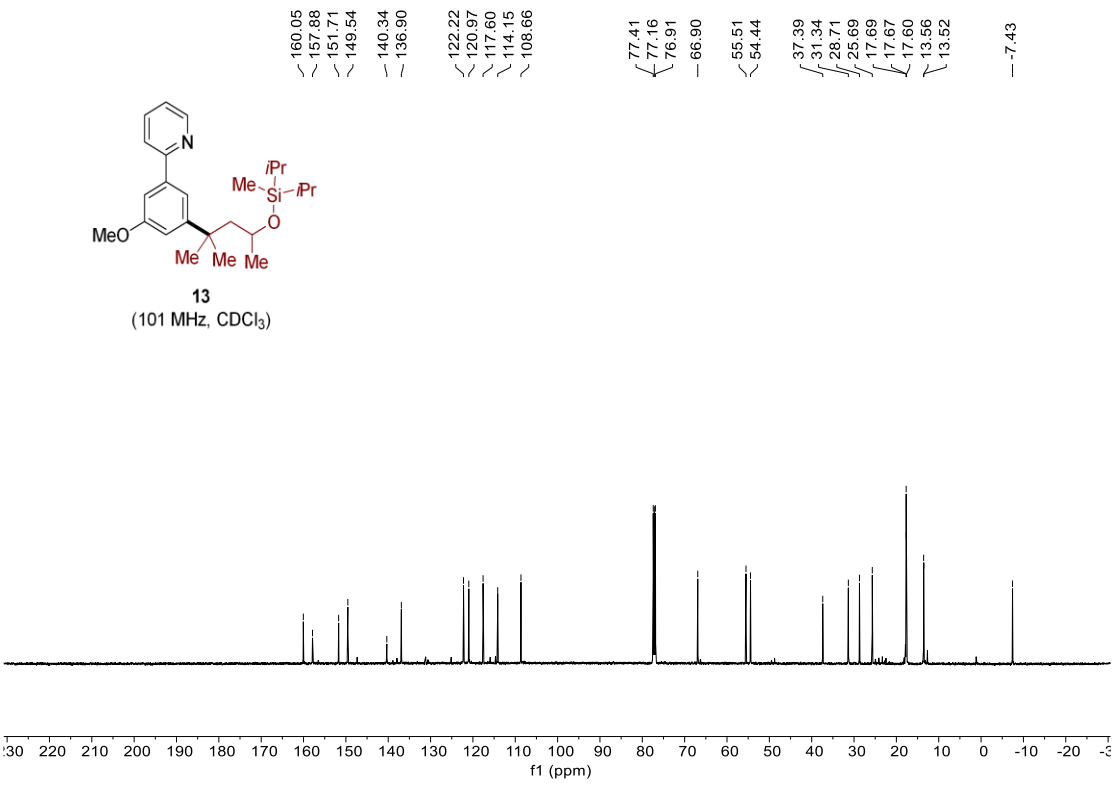

11
(101 MHz, CDCl3)
f1 (ppm)


8.73
7.72
7.49
7.47
7.32
7.30
7.26
7.22
7.12
7.10
7.08
3.82
3.81
3.79
3.78
3.33
2.26
2.24
2.22
2.21
1.98
1.97
1.95
1.94
1.46
1.43
0.97
0.96
0.95
0.94
0.92
0.88
0.85
0.82
0.80
-0.06
N
OMe
iPr
Me
Si
iPr
O
Me
Me
Me
12
(400 MHz, CDCl3)
1.00
2.13
1.05
1.08
1.08
1.09
1.07
3.21
1.04
1.02
3.20
3.12
15.45
2.35
3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
ppm

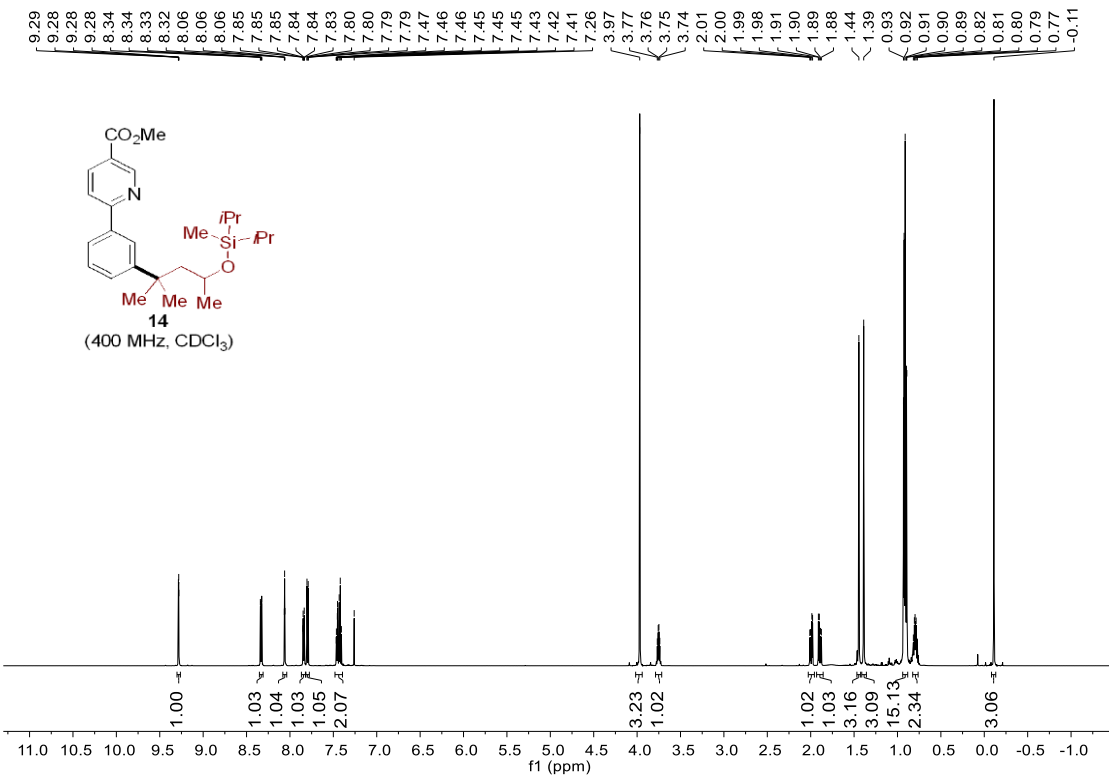

157.91
149.89
141.13
136.23
133.86
130.09
128.41
124.74
123.46
121.86
77.48
77.16
76.84
67.35
61.43
51.70
37.70
30.93
29.82
25.39
17.72
17.64
13.58
13.55
-7.35
N
OMe
iPr
Me
Si
iPr
O
Me
Me
Me
12
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

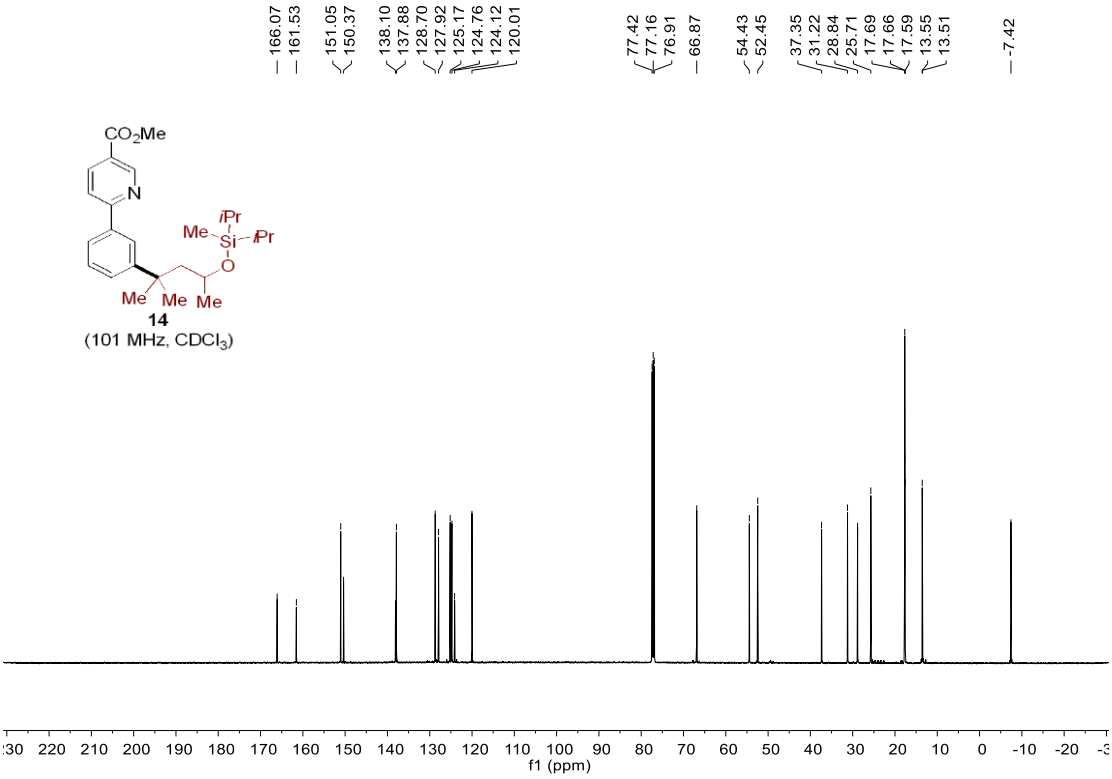


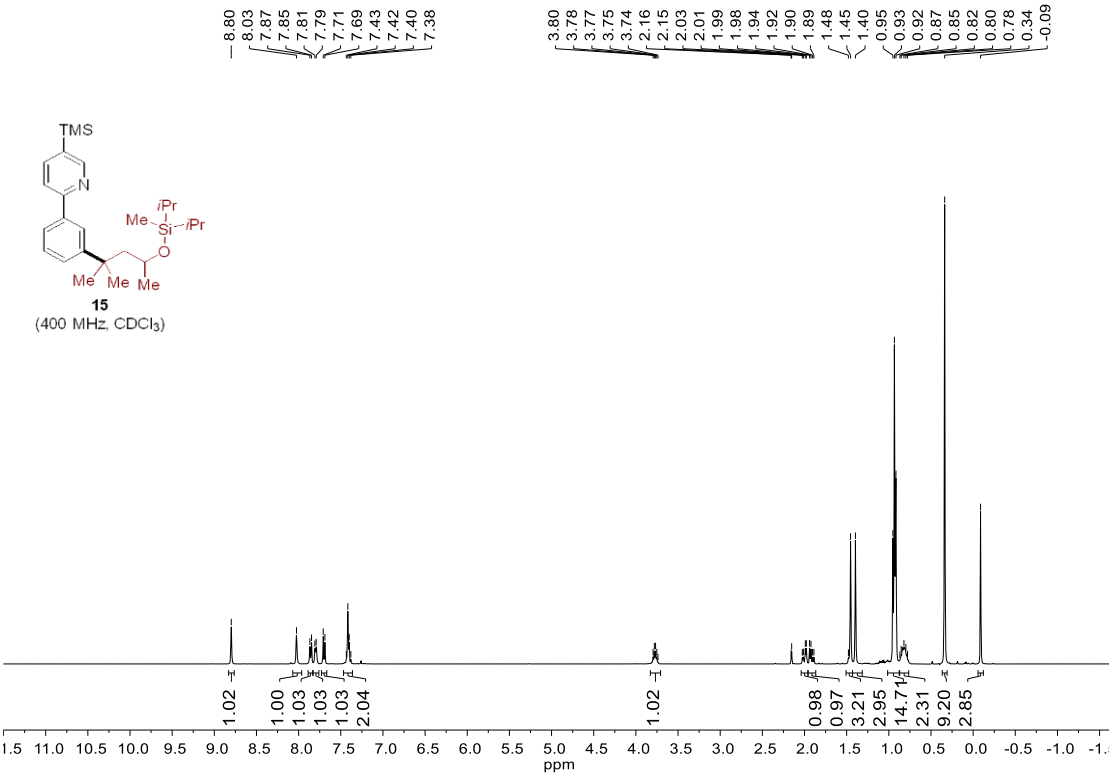
13
(400 MHz, $CDCl_3$)

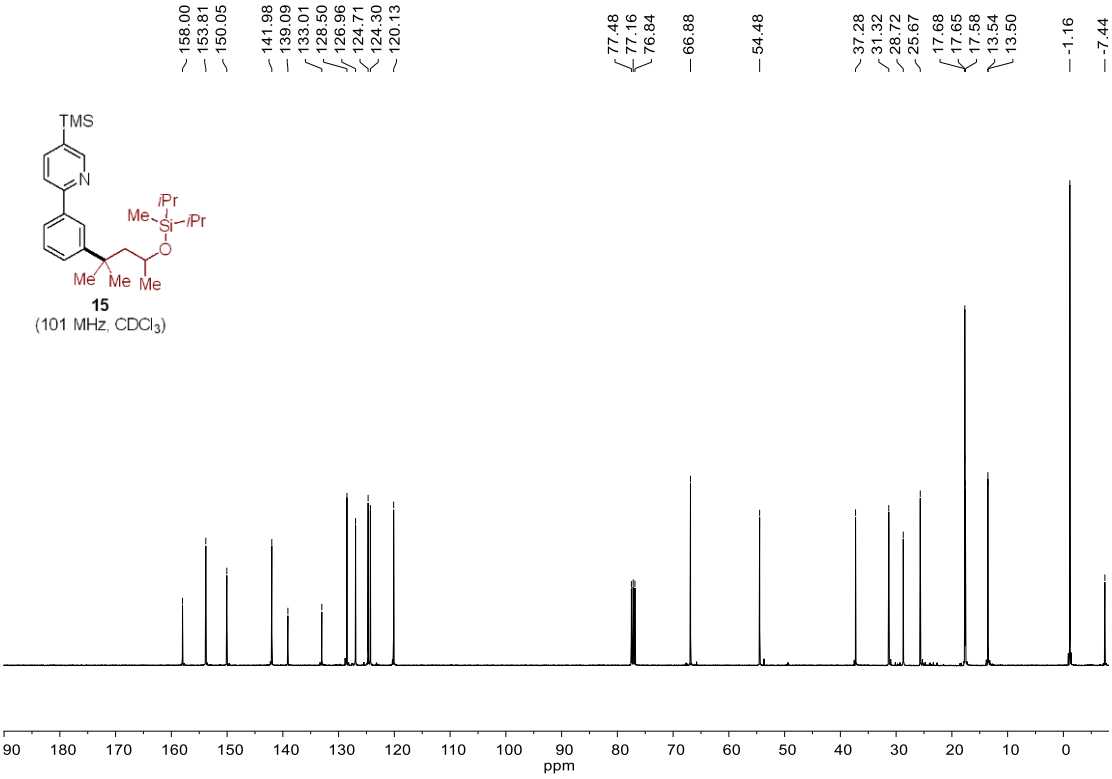


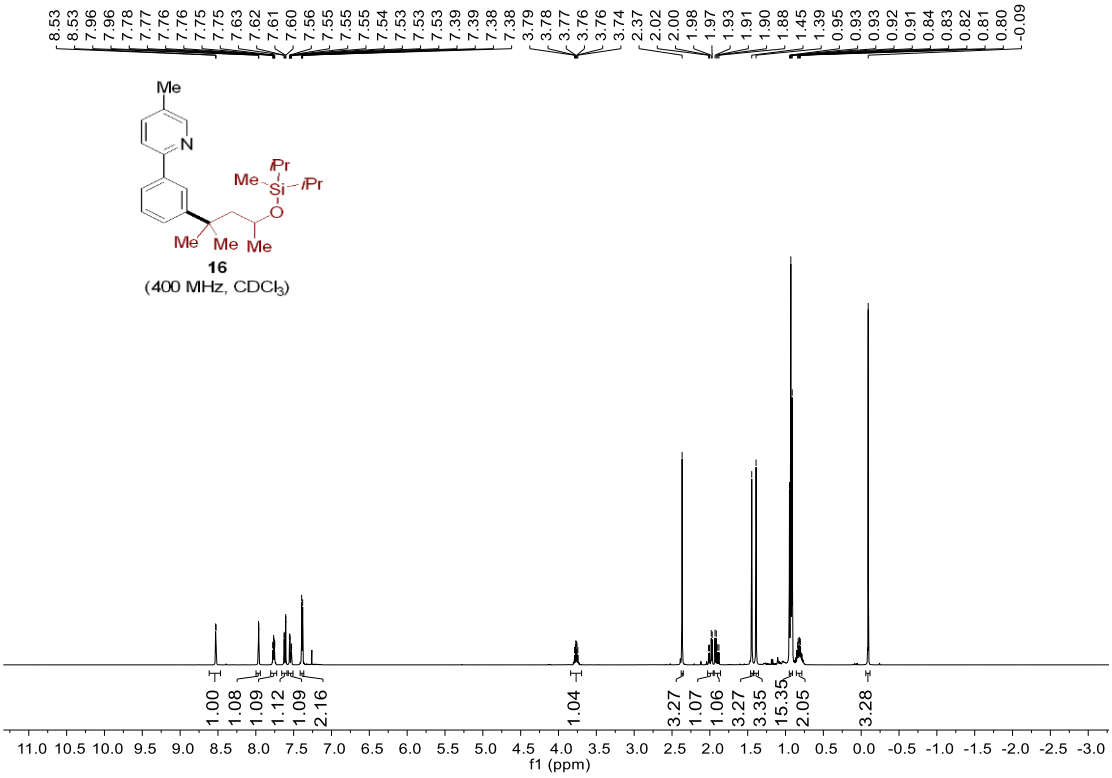
13
(101 MHz, $CDCl_3$)

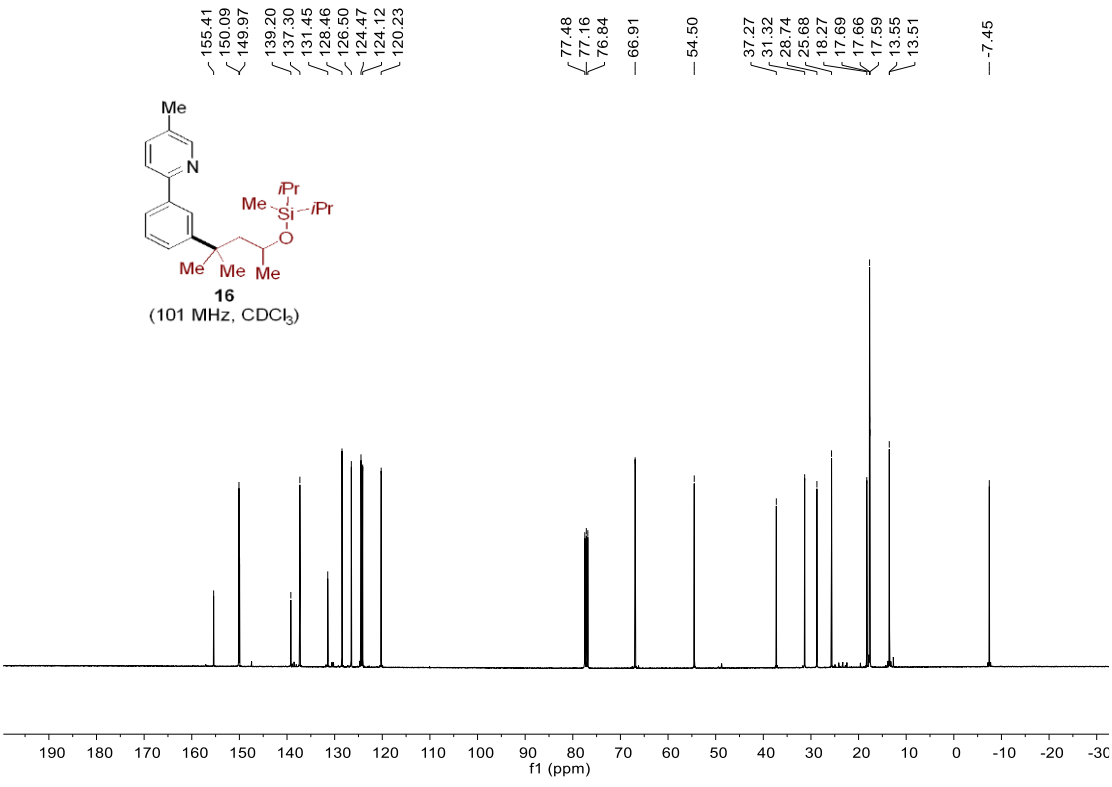

9.29 9.28 9.28 9.28 8.34 8.34 8.33 8.32 8.06 8.06 8.06 7.85 7.85 7.84 7.84 7.83 7.80 7.80 7.79 7.79 7.47 7.46 7.46 7.45 7.45 7.45 7.43 7.42 7.41 7.26 3.97 3.77 3.76 3.75 3.74 2.01 2.00 1.99 1.98 1.91 1.90 1.89 1.88 1.44 1.39 0.93 0.92 0.91 0.90 0.89 0.82 0.81 0.80 0.79 0.77 -0.11
CO2Me
N
Me
iPr
Si
iPr
O
Me Me Me
14
(400 MHz, CDCl3)
1.00 1.03 1.04 1.03 1.05 2.07 3.23 1.02 1.02 1.03 3.16 3.09 15.13 2.34 3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

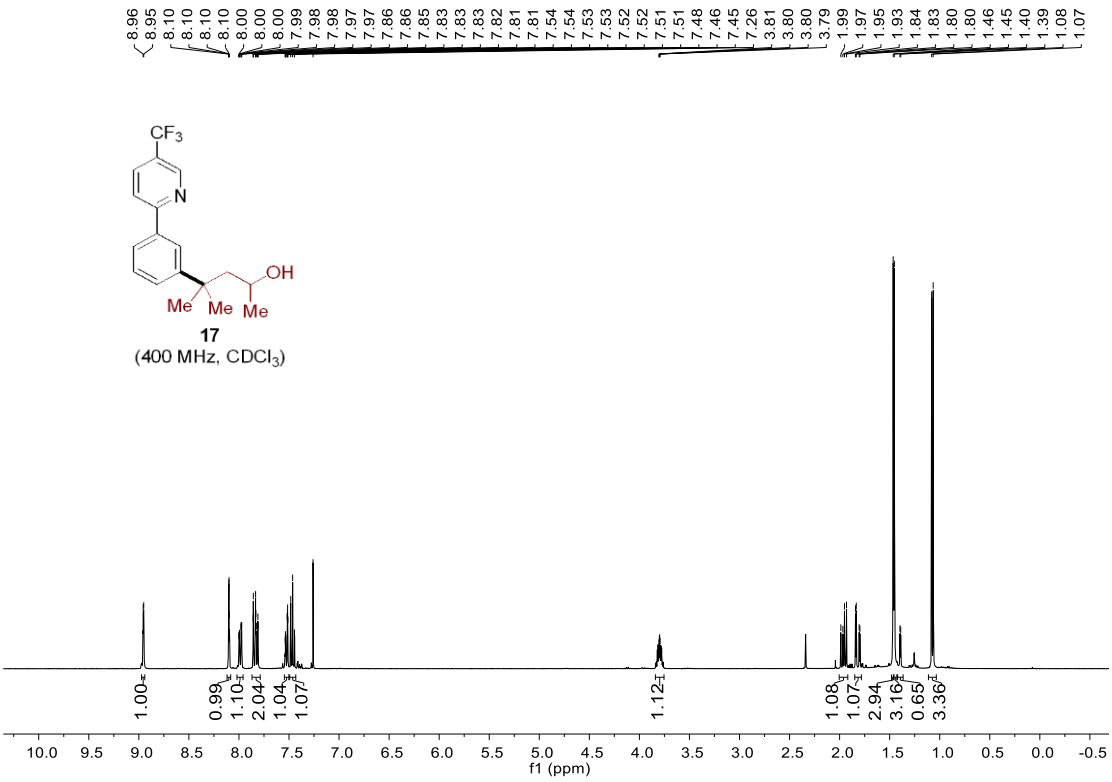

166.07 161.53 151.05 150.37 138.10 137.88 128.70 127.92 125.17 124.76 124.12 120.01 77.42 77.16 76.91 66.87 54.43 52.45 37.35 31.22 28.84 25.71 17.69 17.66 17.59 13.55 13.51 -7.42
CO2Me
N
Me
iPr
Si
iPr
O
Me Me Me
14
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

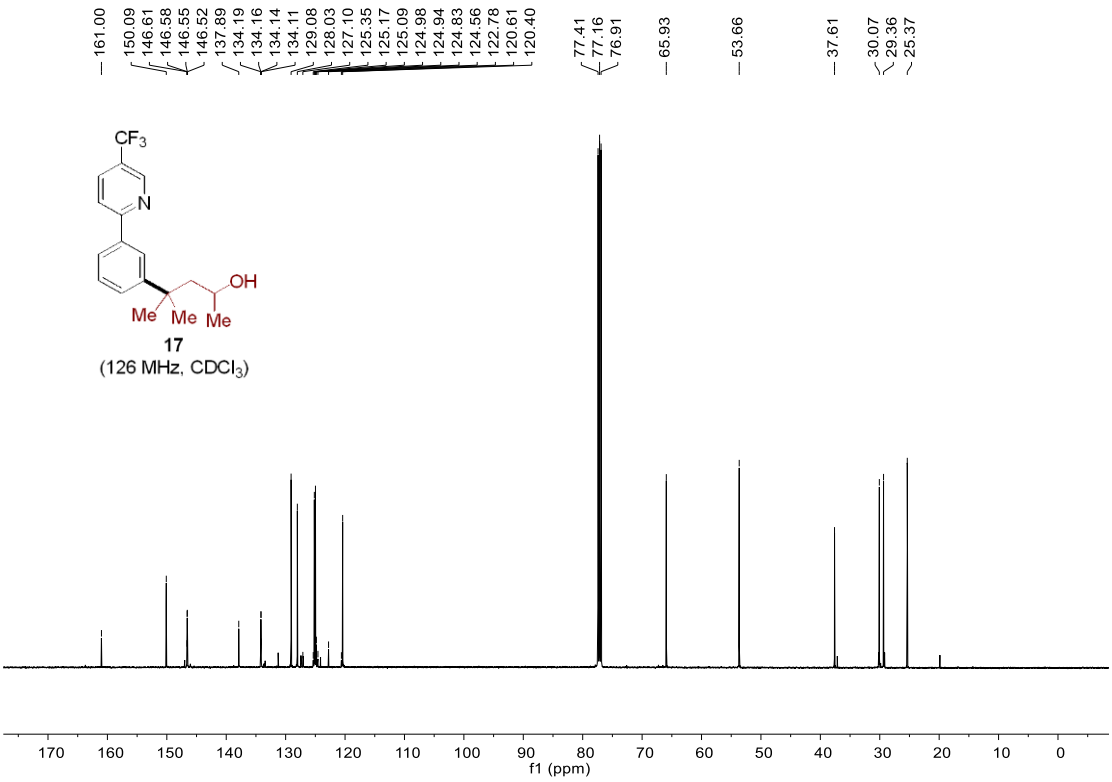

8.80
8.03
7.87
7.85
7.81
7.79
7.71
7.69
7.43
7.42
7.40
7.38
3.80
3.78
3.77
3.75
3.74
2.16
2.15
2.03
2.01
1.99
1.98
1.94
1.92
1.90
1.89
1.48
1.45
1.40
0.95
0.93
0.92
0.87
0.85
0.82
0.80
0.78
0.34
-0.09
TMS
N
iPr
Me
Si
iPr
O
Me
Me
Me
15
(400 MHz, CDCl3)
1.02
1.00
1.03
1.03
1.03
2.04
1.02
0.98
0.97
3.21
2.95
14.74
2.31
9.20
2.85
ppm

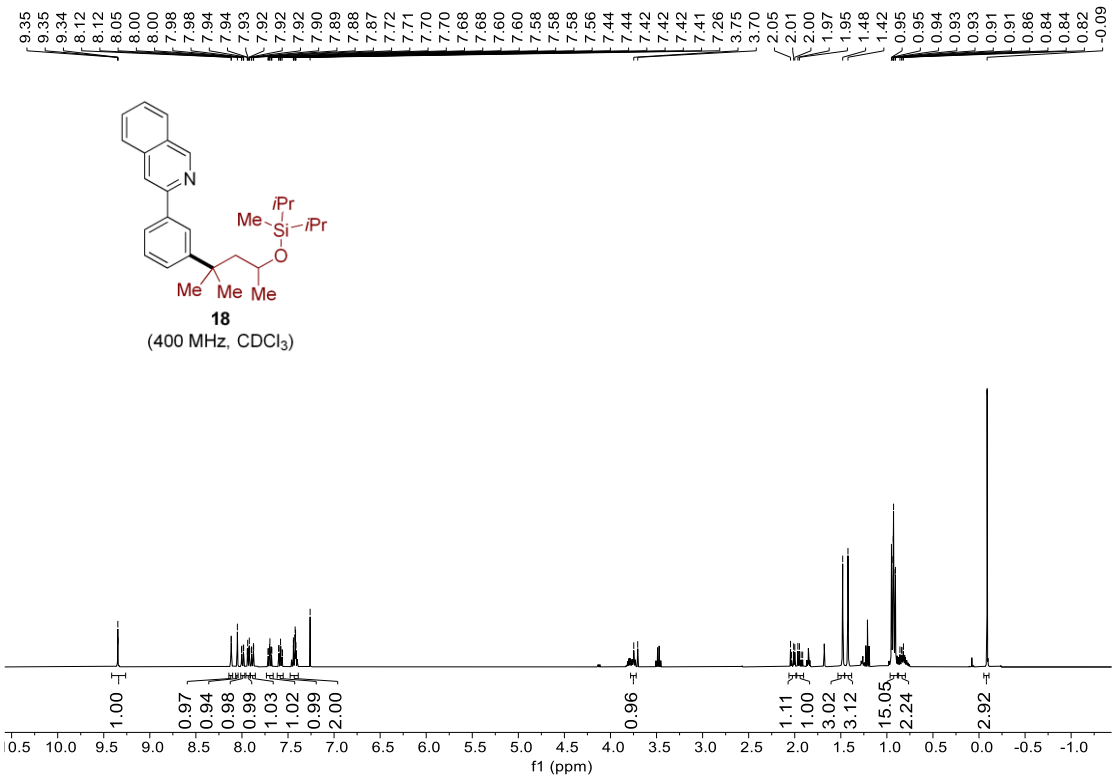

158.00
153.81
150.05
141.98
139.09
133.01
128.50
126.96
124.71
124.30
120.13
77.48
77.16
76.84
66.88
54.48
37.28
31.32
28.72
25.67
17.68
17.65
17.58
13.54
13.50
-1.16
-7.44
TMS
N
iPr
Me
Si
iPr
O
Me
Me
Me
15
(101 MHz, CDCl3)
ppm

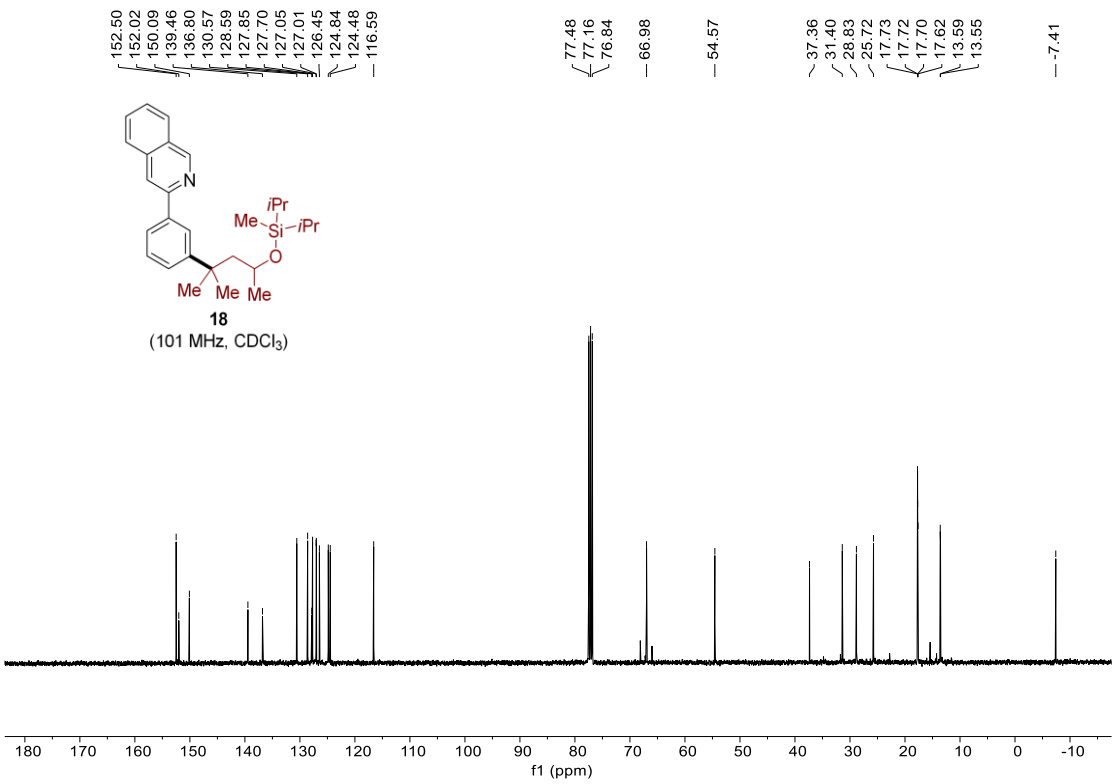

8.53 8.53 7.96 7.96 7.78 7.77 7.76 7.76 7.75 7.75 7.63 7.62 7.61 7.60 7.56 7.55 7.55 7.55 7.54 7.53 7.53 7.53 7.39 7.39 7.38 7.38 3.79 3.78 3.77 3.76 3.76 3.74 2.37 2.02 2.00 1.98 1.97 1.93 1.91 1.90 1.88 1.45 1.39 0.95 0.93 0.93 0.92 0.91 0.84 0.83 0.82 0.81 0.80 -0.09
Me
N
Me
iPr
Si
iPr
O
Me
Me
Me
16
(400 MHz, CDCl3)
1.00 1.08 1.09 1.12 1.09 2.16 1.04 3.27 1.07 1.06 3.27 3.35 15.35 2.05 3.28
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)

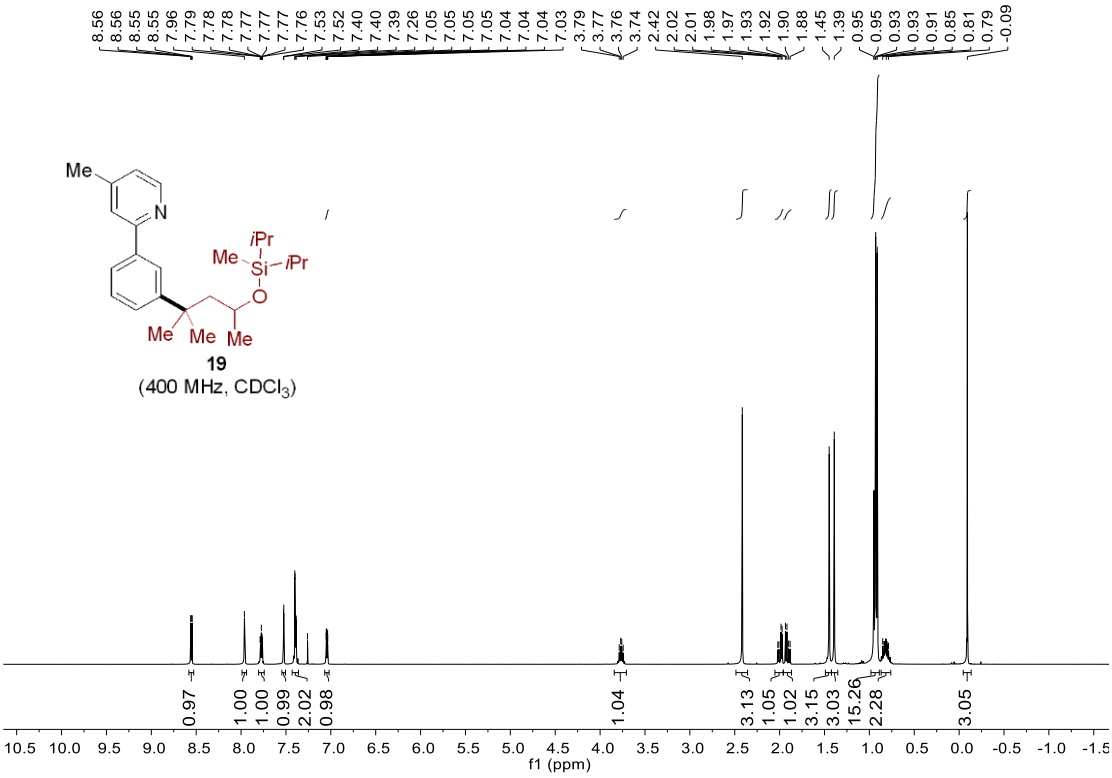

155.41 150.09 149.97 139.20 137.30 131.45 128.46 126.50 124.47 124.12 120.23
77.48 77.16 76.84 66.91 54.50 37.27 31.32 28.74 25.68 18.27 17.69 17.66 17.59 13.55 13.51 -7.45
Me
N
Me
iPr
Si
iPr
O
Me
Me
Me
16
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

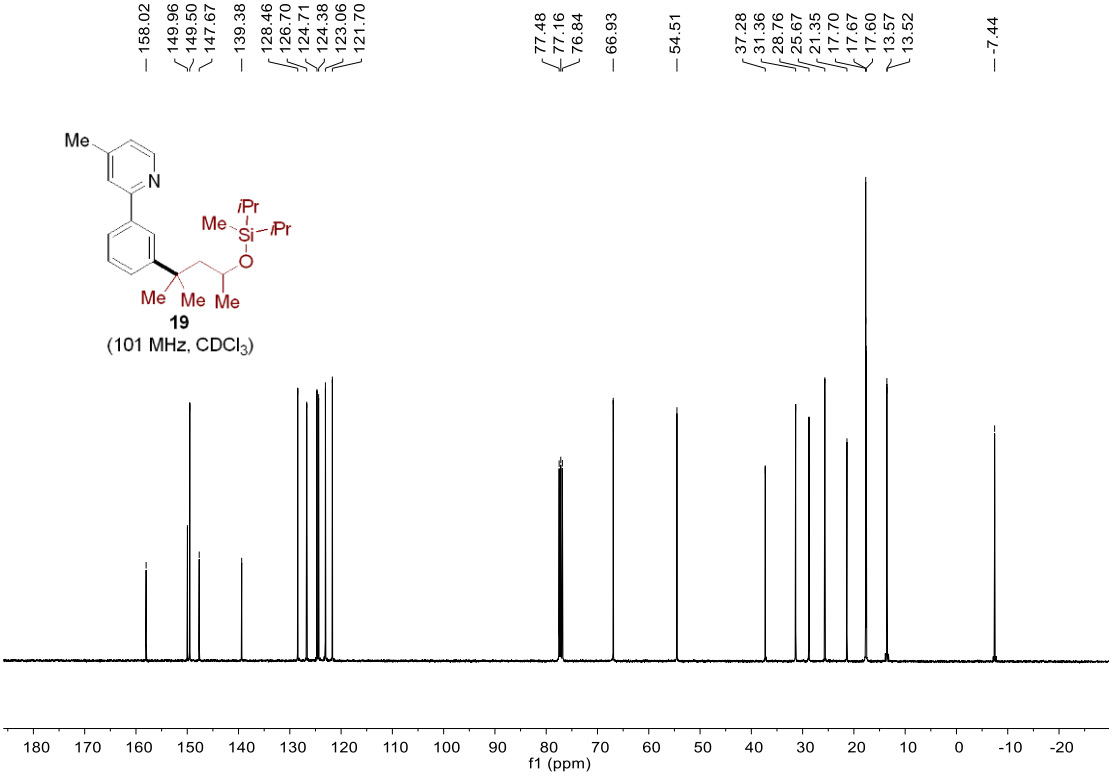

8.96 8.95 8.10 8.10 8.10 8.00 8.00 8.00 7.99 7.98 7.98 7.97 7.97 7.86 7.86 7.85 7.83 7.83 7.83 7.82 7.81 7.81 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.48 7.46 7.45 7.26 3.81 3.80 3.80 3.79 1.99 1.97 1.95 1.93 1.84 1.83 1.80 1.80 1.46 1.45 1.40 1.39 1.08 1.07
CF3
N
OH
Me Me Me
17
(400 MHz, CDCl3)
1.00 0.99 1.10 2.04 1.04 1.07 1.12 1.08 1.07 2.94 3.16 0.65 3.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

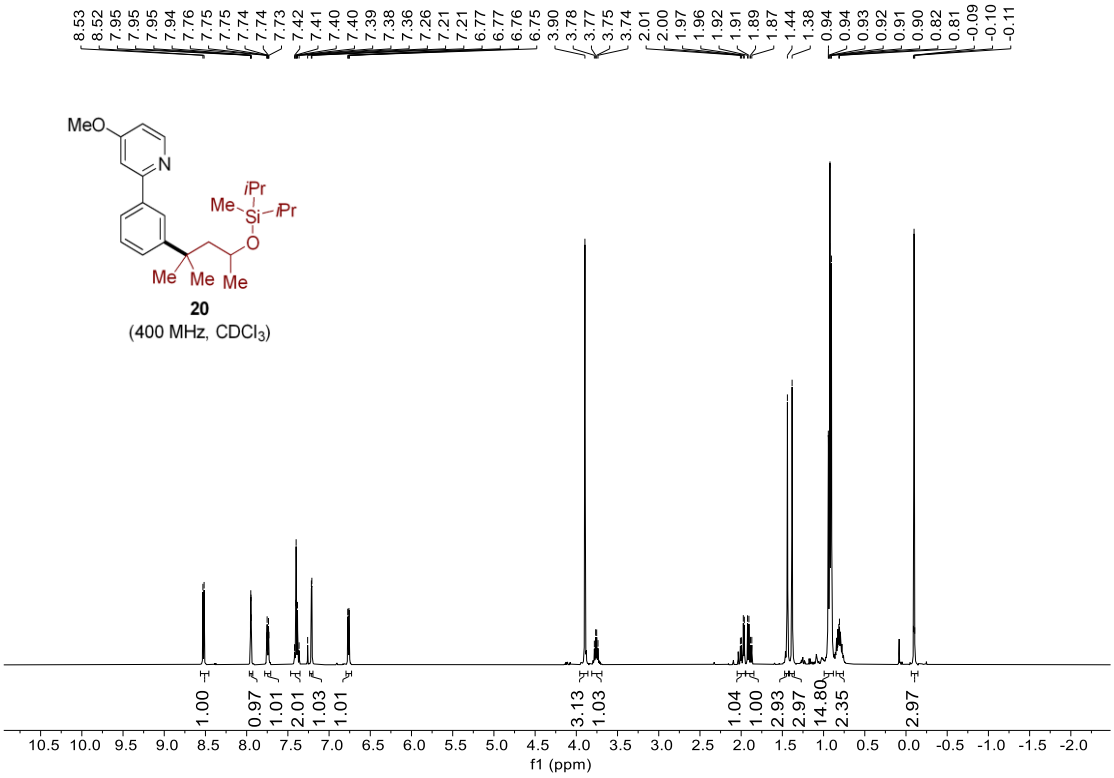

161.00 150.09 146.61 146.58 146.55 146.52 137.89 134.19 134.16 134.14 134.11 129.08 128.03 127.10 125.35 125.17 125.09 124.98 124.94 124.83 124.56 122.78 120.61 120.40 77.41 77.16 76.91 65.93 53.66 37.61 30.07 29.36 25.37
CF3
N
OH
Me Me Me
17
(126 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

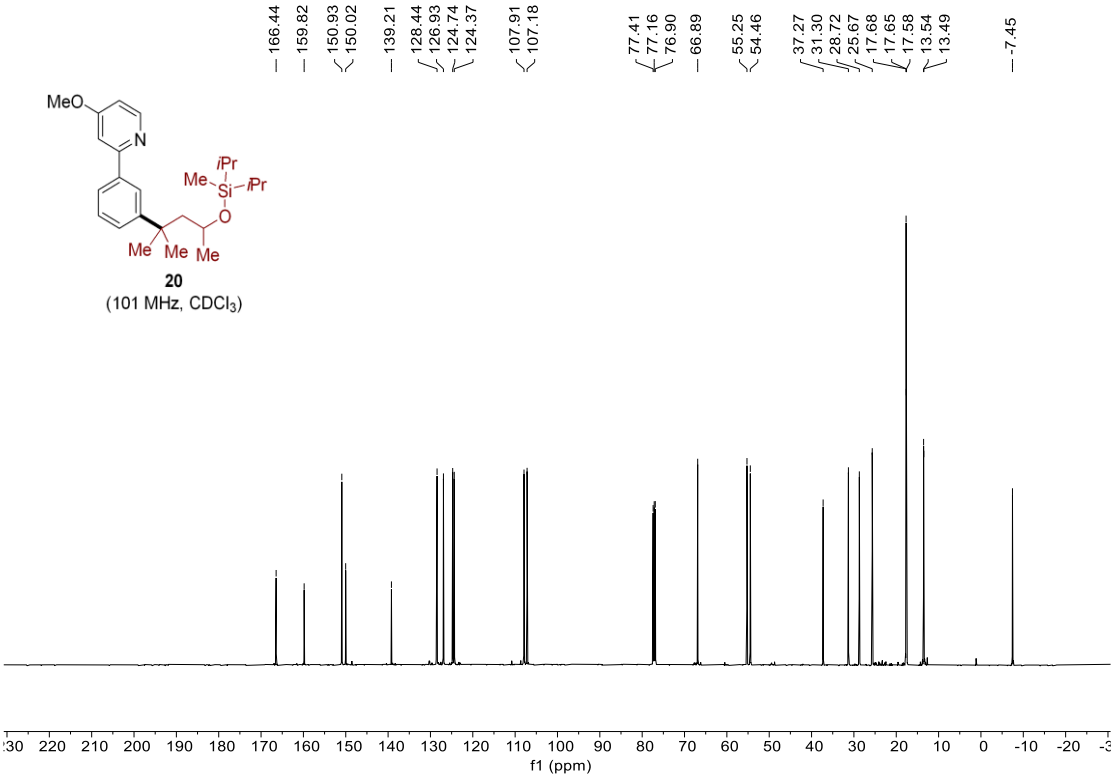

9.35 9.35 9.34 8.12 8.12 8.05 8.00 8.00 7.98 7.98 7.94 7.94 7.93 7.92 7.92 7.92 7.90 7.89 7.88 7.87 7.72 7.71 7.70 7.70 7.68 7.68 7.60 7.60 7.58 7.58 7.58 7.56 7.44 7.44 7.42 7.42 7.42 7.41 7.26 3.75 3.70 2.05 2.01 2.00 1.97 1.95 1.48 1.42 0.95 0.95 0.94 0.93 0.93 0.91 0.91 0.86 0.84 0.84 0.82 -0.09
N
iPr
Me
Si
iPr
O
Me Me Me
18
(400 MHz, CDCl3)
1.00 0.97 0.94 0.98 0.99 1.03 1.02 0.99 2.00 0.96 1.11 1.00 3.02 3.12 15.05 2.24 2.92
f1 (ppm)

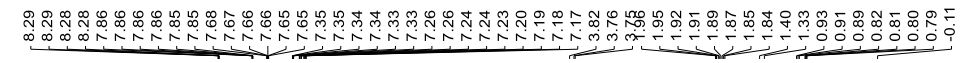

152.50 152.02 150.09 139.46 136.80 130.57 128.59 127.85 127.70 127.05 127.01 126.45 124.84 124.48 116.59
77.48 77.16 76.84 66.98 54.57 37.36 31.40 28.83 25.72 17.73 17.72 17.70 17.62 13.59 13.55 -7.41
N
iPr
Me
Si
iPr
O
Me Me Me
18
(101 MHz, CDCl3)
f1 (ppm)

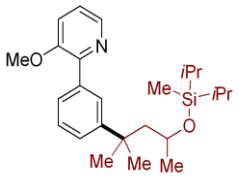

Me
N
iPr
Me
Si
iPr
O
Me
Me
Me
19
(400 MHz, CDCl3)
f1 (ppm)


Me
N
iPr
Me
Si
iPr
O
Me
Me
Me
19
(101 MHz, CDCl3)
f1 (ppm)

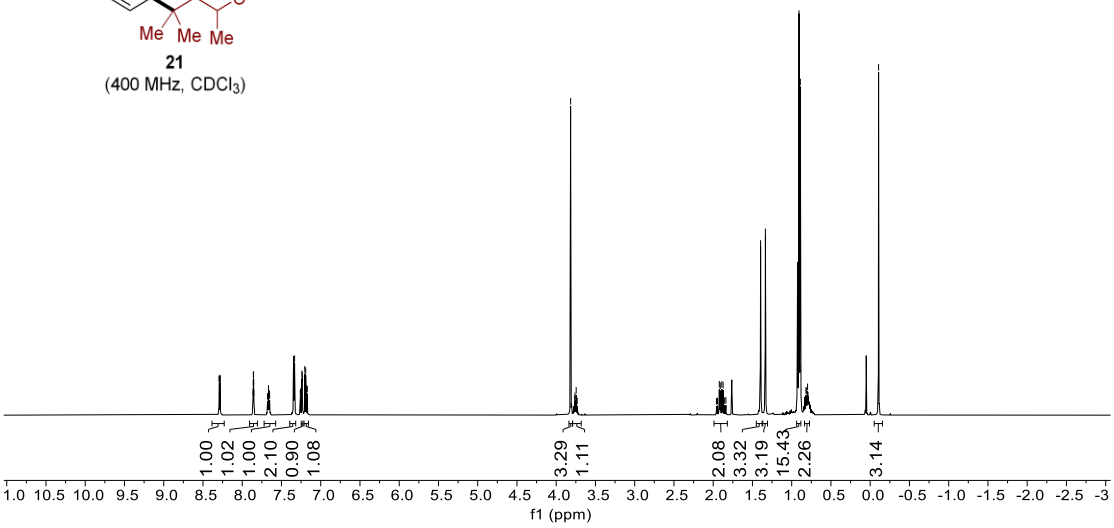

8.53 8.52 7.95 7.95 7.95 7.94 7.76 7.75 7.75 7.74 7.74 7.73 7.42 7.41 7.40 7.40 7.39 7.38 7.36 7.26 7.21 7.21 6.77 6.76 6.75 3.90 3.78 3.77 3.75 3.74 2.01 2.00 1.97 1.96 1.92 1.91 1.89 1.87 1.44 1.38 0.94 0.94 0.93 0.92 0.91 0.90 0.82 0.81 -0.09 -0.10 -0.11
MeO
N
iPr
Me
Si
iPr
O
Me Me Me
20
(400 MHz, CDCl3)
1.00 0.97 1.01 2.01 1.03 1.01 3.13 1.03 1.04 1.00 2.93 2.97 14.80 2.35 2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

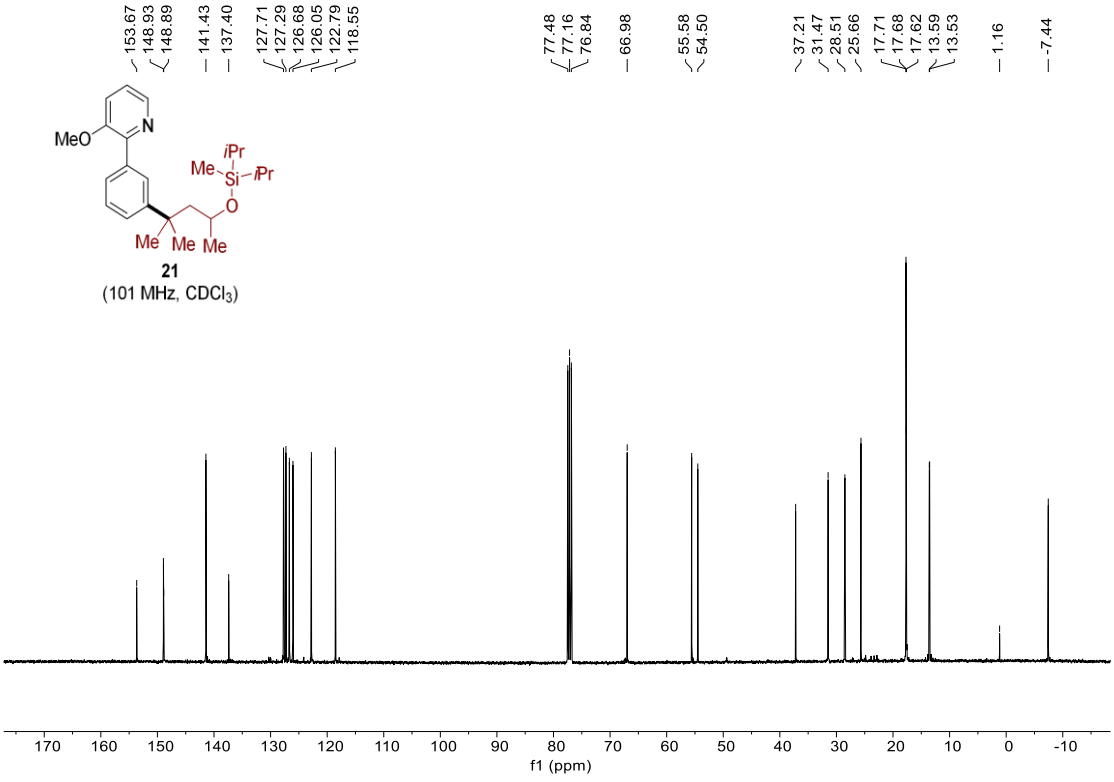

166.44 159.82 150.93 150.02 139.21 128.44 126.93 124.74 124.37 107.91 107.18 77.41 77.16 76.90 66.89 55.25 54.46 37.27 31.30 28.72 25.67 17.68 17.65 17.58 13.54 13.49 -7.45
MeO
N
iPr
Me
Si
iPr
O
Me Me Me
20
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



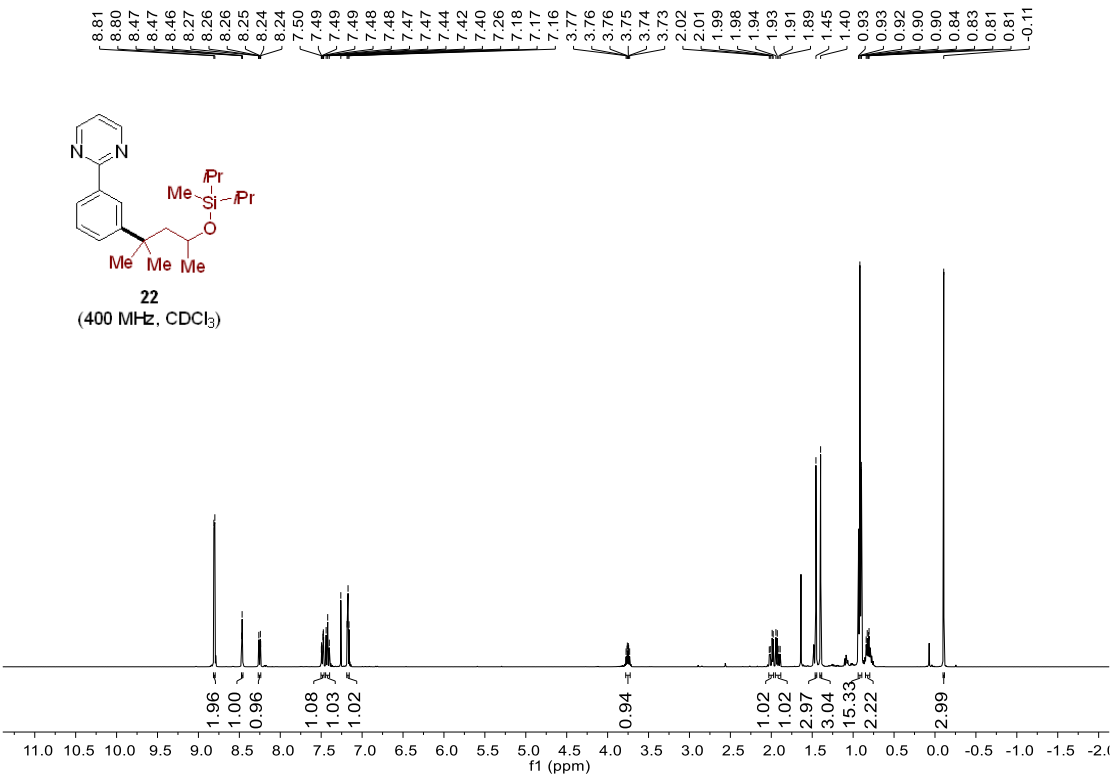


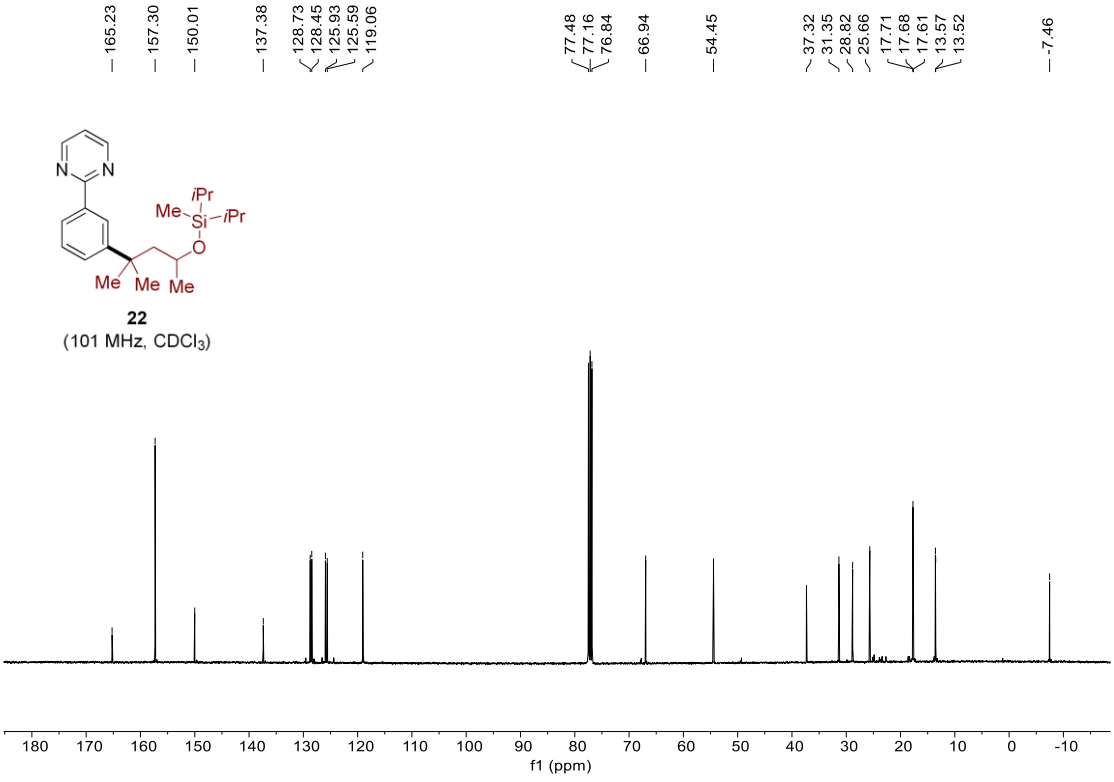
21
(400 MHz, $CDCl_3$)

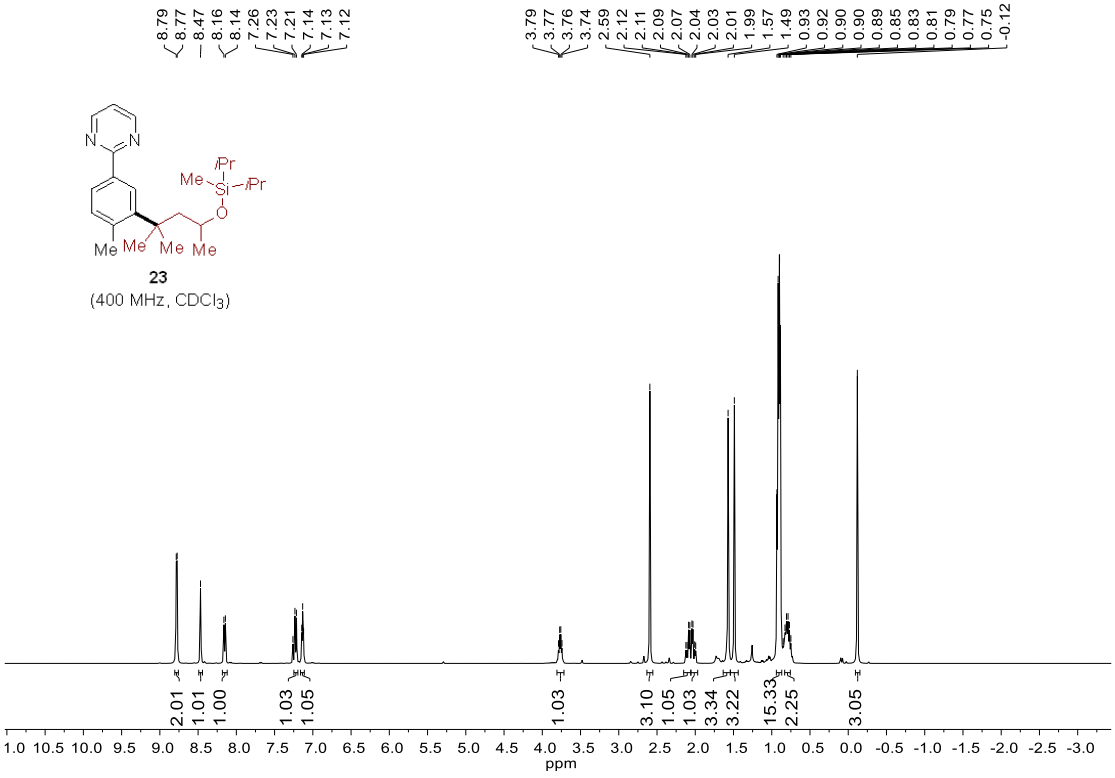


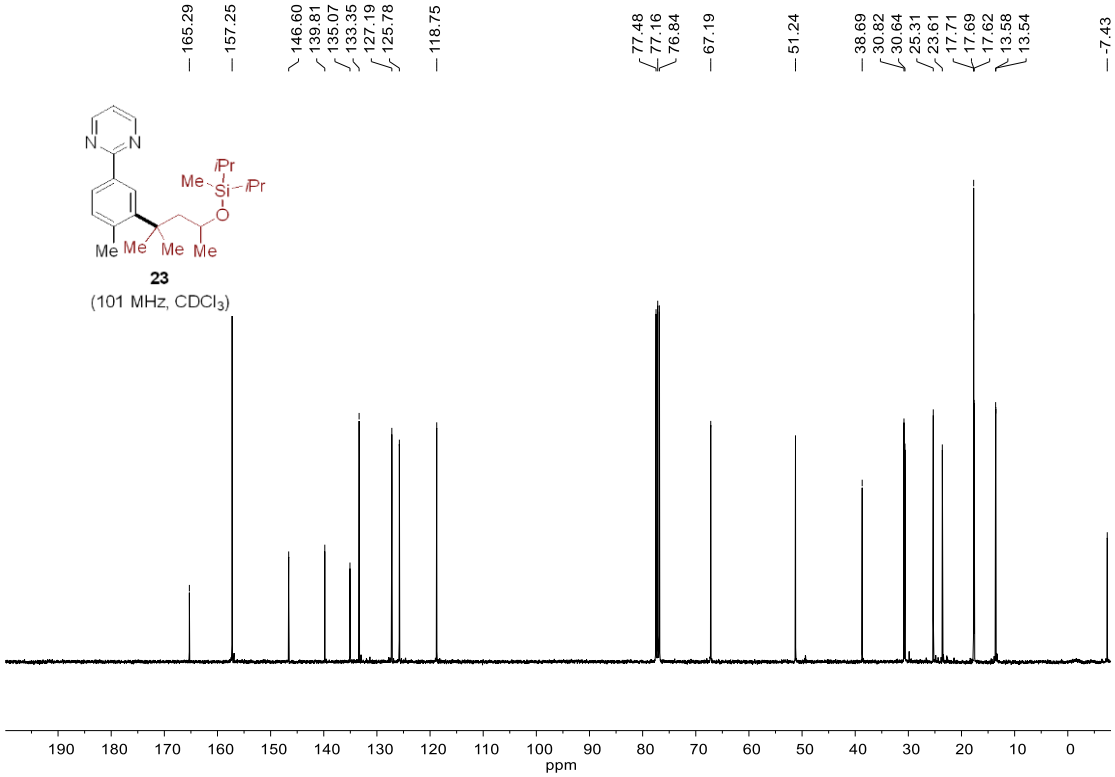


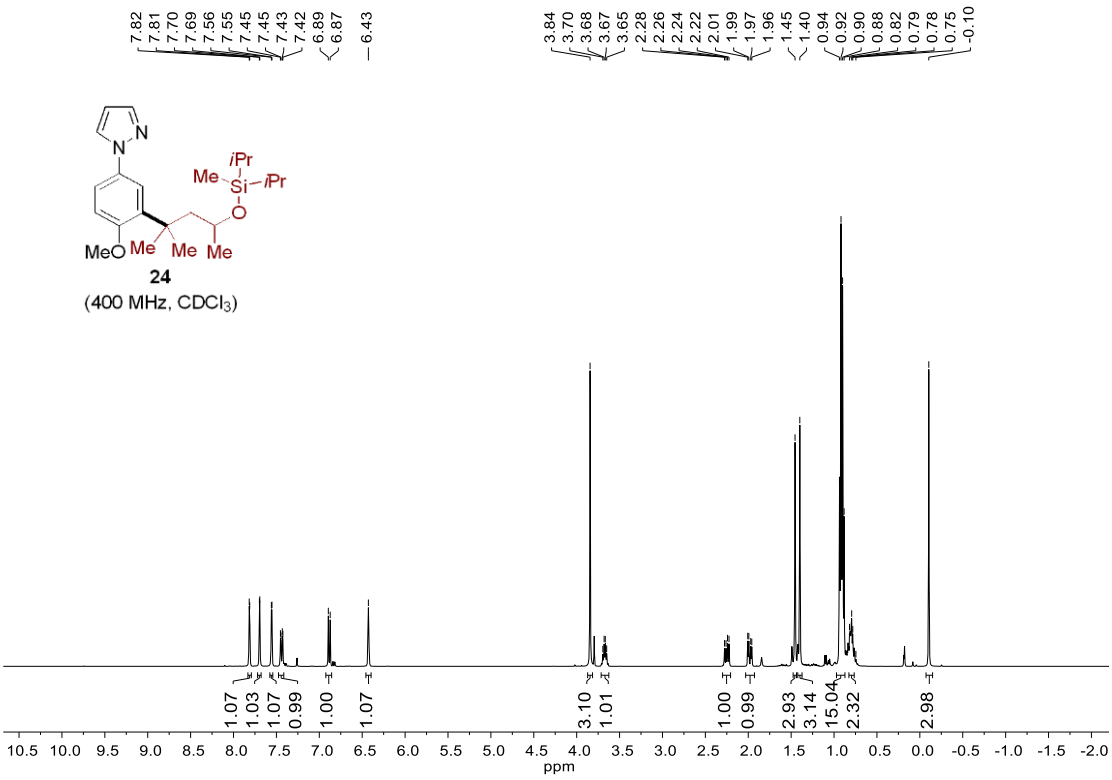
21
(101 MHz, $CDCl_3$)

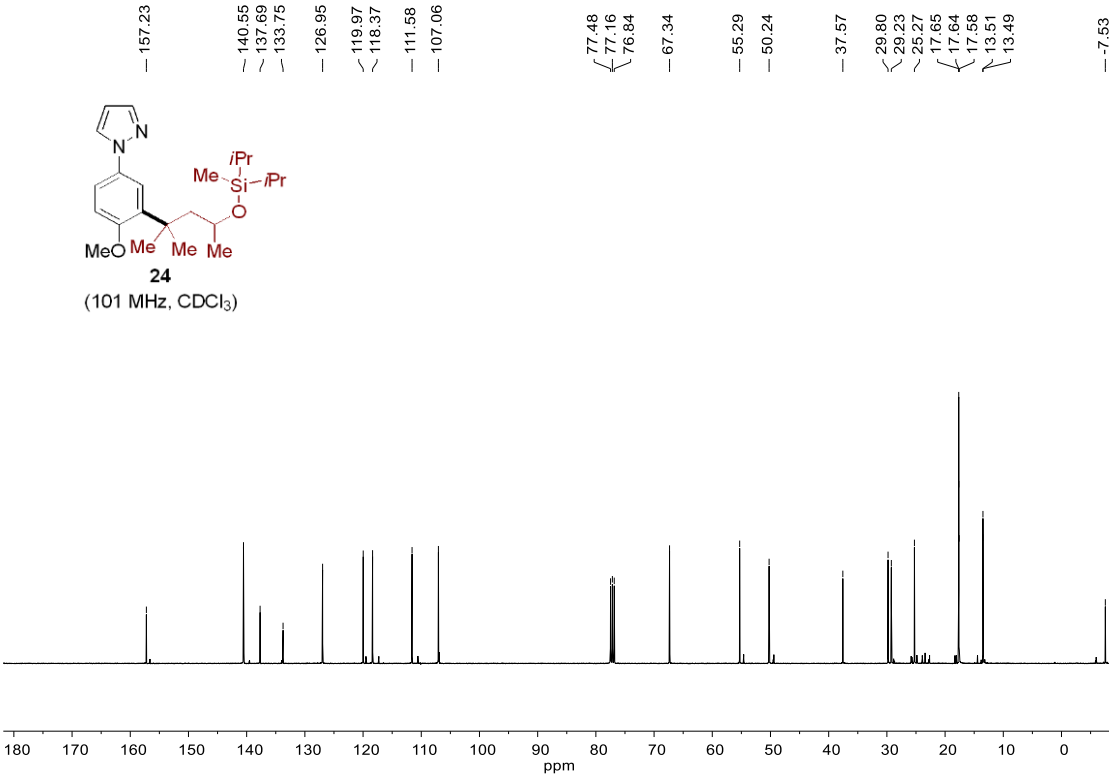

8.81 8.80 8.47 8.47 8.46 8.27 8.26 8.26 8.25 8.24 8.24 7.50 7.49 7.49 7.49 7.48 7.48 7.47 7.47 7.44 7.42 7.40 7.26 7.18 7.17 7.16 3.77 3.76 3.76 3.75 3.74 3.73 2.02 2.01 1.99 1.98 1.94 1.93 1.91 1.89 1.45 1.40 0.93 0.93 0.92 0.90 0.90 0.84 0.83 0.81 0.81 -0.11
N N
Me iPr Si iPr O
Me Me Me
22
(400 MHz, CDCl3)
1.96 1.00 0.96 1.08 1.03 1.02 0.94 1.02 1.02 2.97 3.04 15.33 2.22 2.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

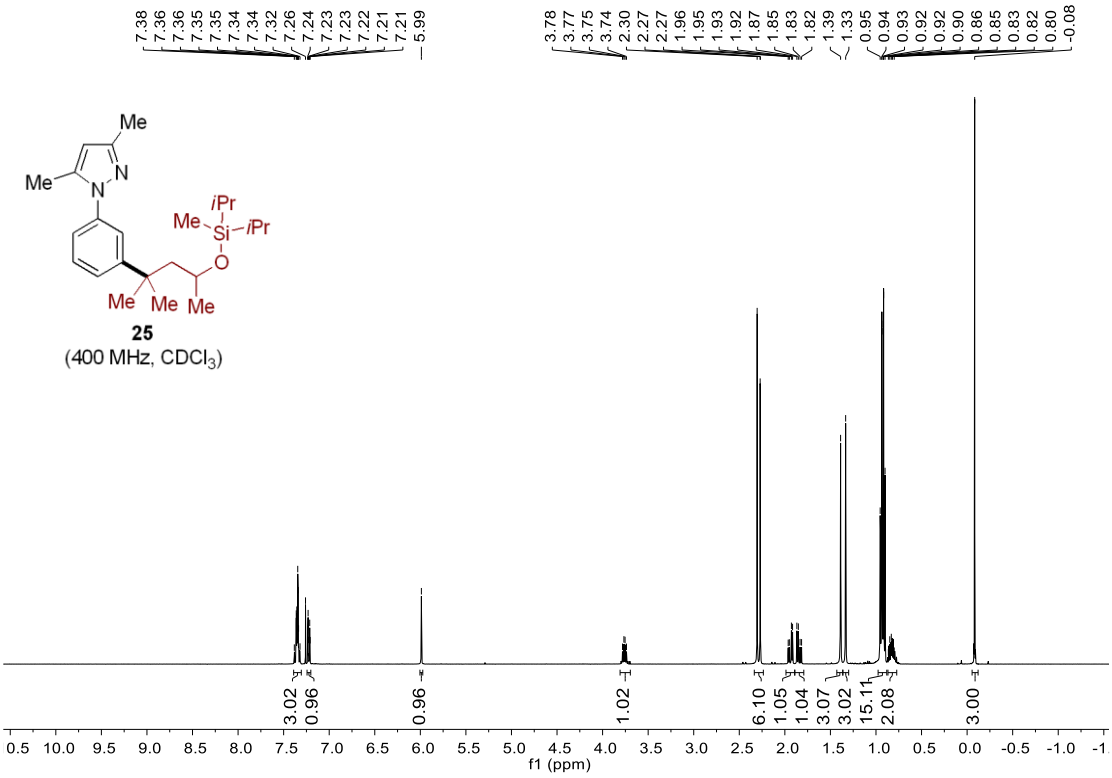

165.23 157.30 150.01 137.38 128.73 128.45 125.93 125.59 119.06 77.48 77.16 76.84 66.94 54.45 37.32 31.35 28.82 25.66 17.71 17.68 17.61 13.57 13.52 -7.46
N N
Me iPr Si iPr O
Me Me Me
22
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

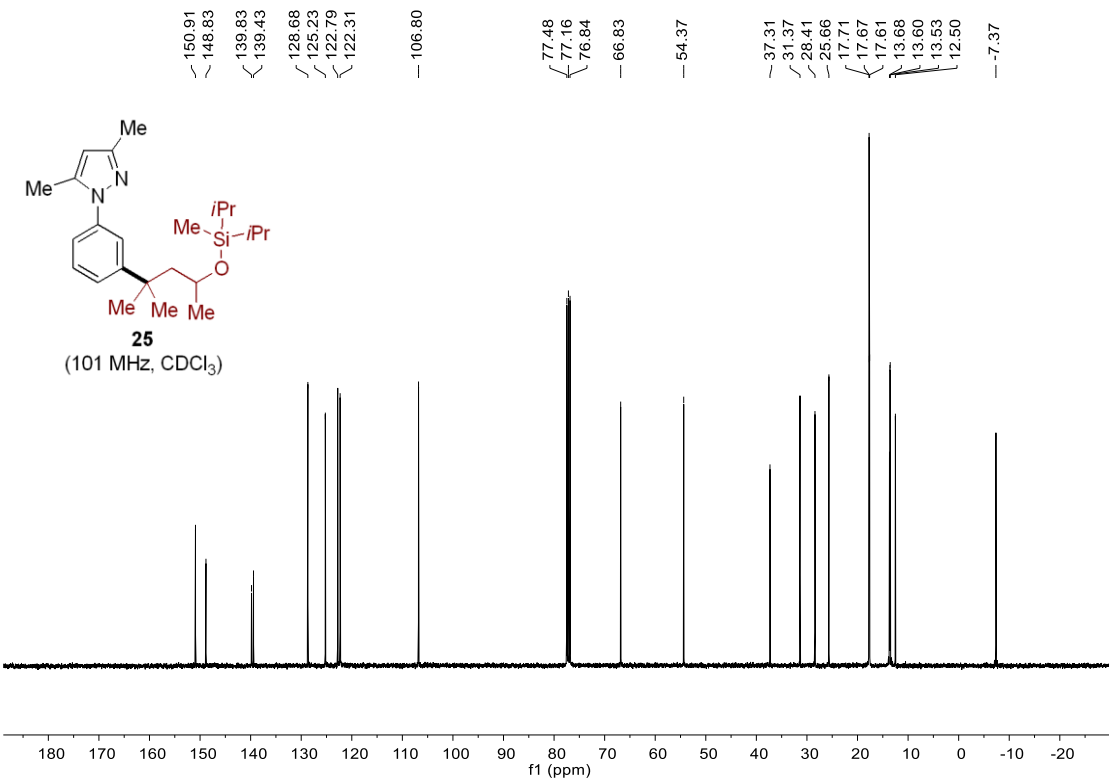

8.79
8.77
8.47
8.16
8.14
7.26
7.23
7.21
7.14
7.13
7.12
3.79
3.77
3.76
3.74
2.59
2.12
2.11
2.09
2.07
2.04
2.03
2.01
1.99
1.57
1.49
0.93
0.92
0.90
0.90
0.89
0.85
0.83
0.81
0.79
0.77
0.75
-0.12
iPr
Me
Si
iPr
O
Me
Me
Me
Me
23
(400 MHz, CDCl3)
2.01
1.01
1.00
1.03
1.05
1.03
3.10
1.05
1.03
3.34
3.22
15.33
2.25
3.05
ppm

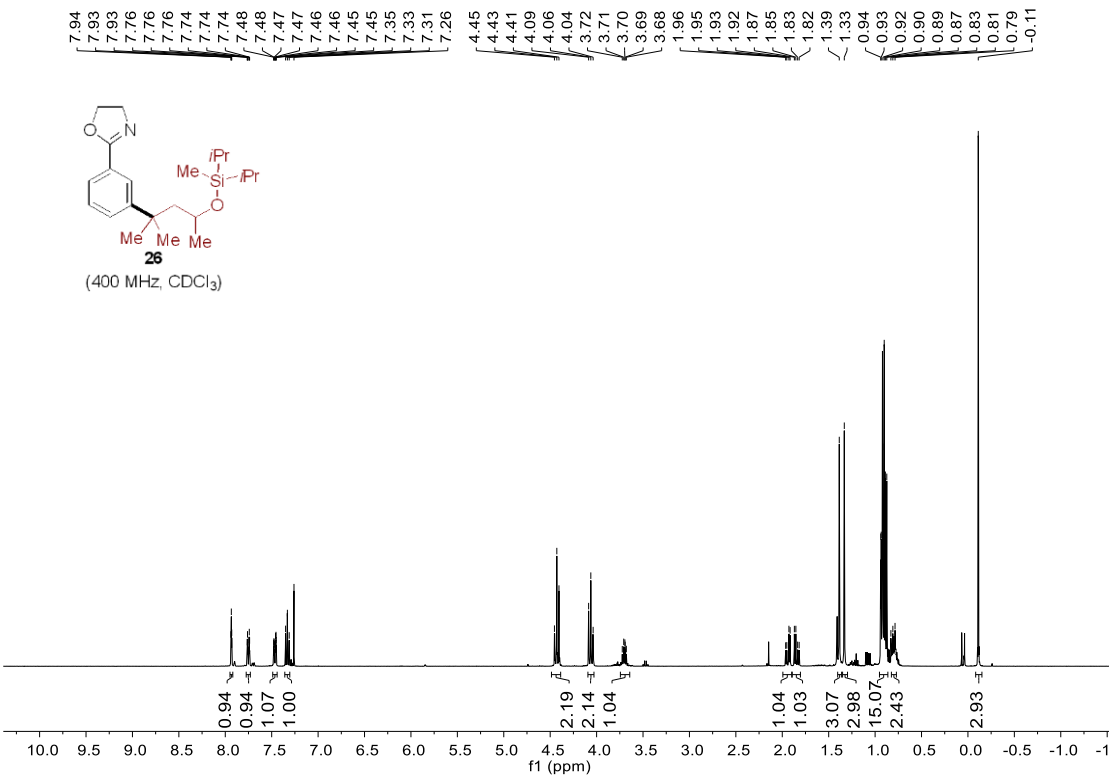

165.29
157.25
146.60
139.81
135.07
133.35
127.19
125.78
118.75
77.48
77.16
76.84
67.19
51.24
38.69
30.82
30.64
25.31
23.61
17.71
17.69
17.62
13.58
13.54
-7.43
iPr
Me
Si
iPr
O
Me
Me
Me
Me
23
(101 MHz, CDCl3)
ppm

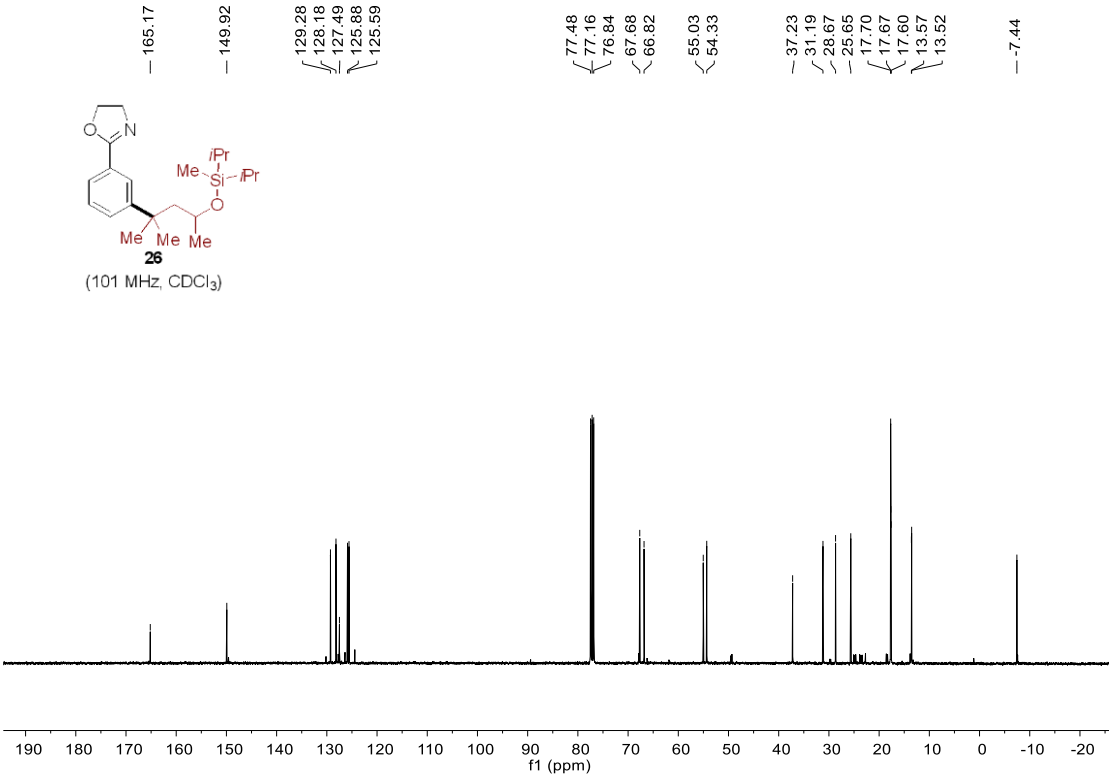

7.82 7.81 7.70 7.69 7.56 7.55 7.45 7.45 7.43 7.42 6.89 6.87 6.43
3.84 3.70 3.68 3.67 3.65 2.28 2.26 2.24 2.22 2.01 1.99 1.97 1.96 1.45 1.40 0.94 0.92 0.90 0.88 0.82 0.79 0.78 0.75 -0.10
iPr
Me
Si
iPr
O
MeO
Me
Me
Me
24
(400 MHz, CDCl3)
1.07 1.03 1.07 0.99 1.00 1.07 3.10 1.01 1.00 0.99 2.93 3.14 15.04 2.32 2.98
ppm

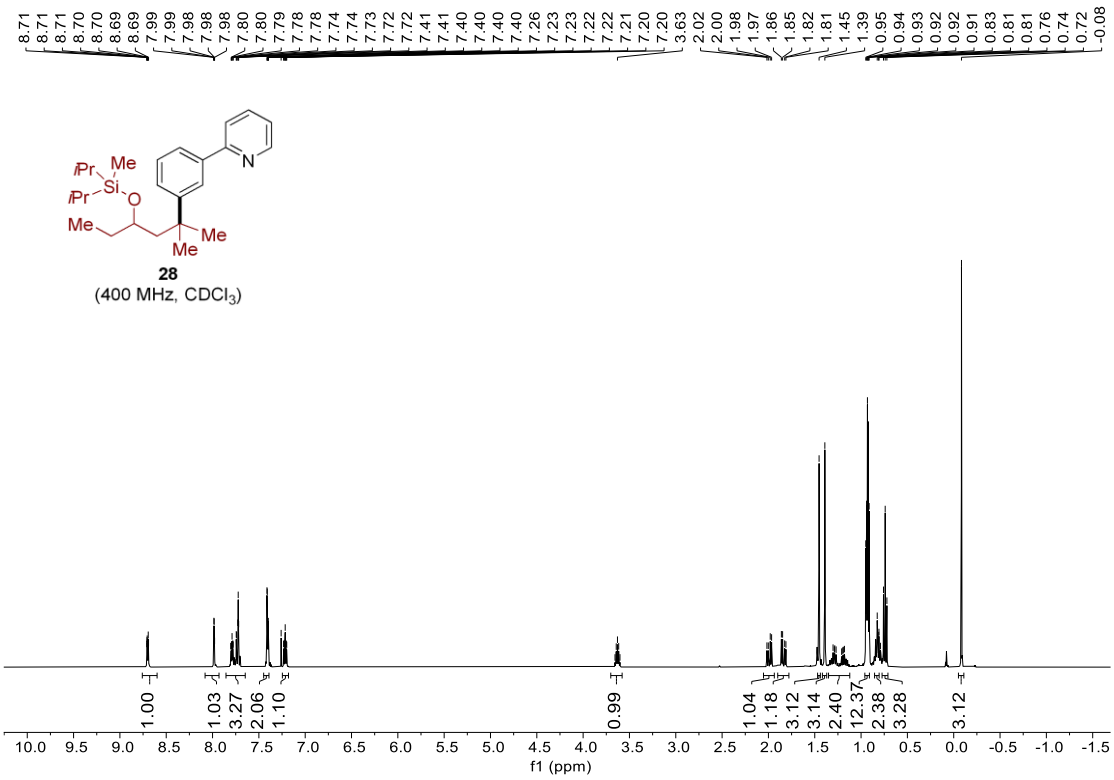

157.23 140.55 137.69 133.75 126.95 119.97 118.37 111.58 107.06
77.48 77.16 76.84 67.34 55.29 50.24 37.57 29.80 29.23 25.27 17.65 17.64 17.58 13.51 13.49 -7.53
iPr
Me
Si
iPr
O
MeO
Me
Me
Me
24
(101 MHz, CDCl3)
ppm

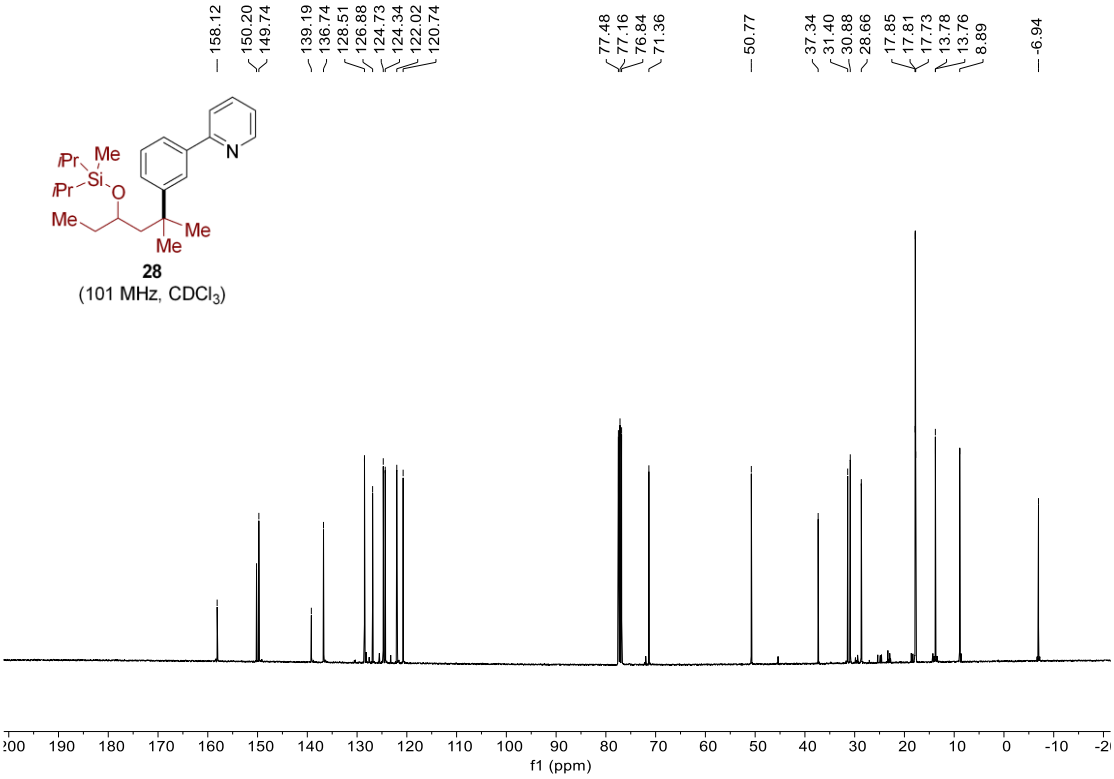

7.38 7.36 7.36 7.35 7.35 7.34 7.34 7.32 7.26 7.24 7.23 7.23 7.22 7.21 7.21 5.99
3.78 3.77 3.75 3.74 2.30 2.27 2.27 1.96 1.95 1.93 1.92 1.87 1.85 1.83 1.82 1.39 1.33 0.95 0.94 0.93 0.92 0.92 0.90 0.86 0.85 0.83 0.82 0.80 -0.08
Me
Me
N
N
iPr
Me
Si
iPr
O
Me
Me
Me
25
(400 MHz, CDCl3)
3.02 0.96 0.96 1.02 6.10 1.05 1.04 3.07 3.02 15.11 2.08 3.00
f1 (ppm)

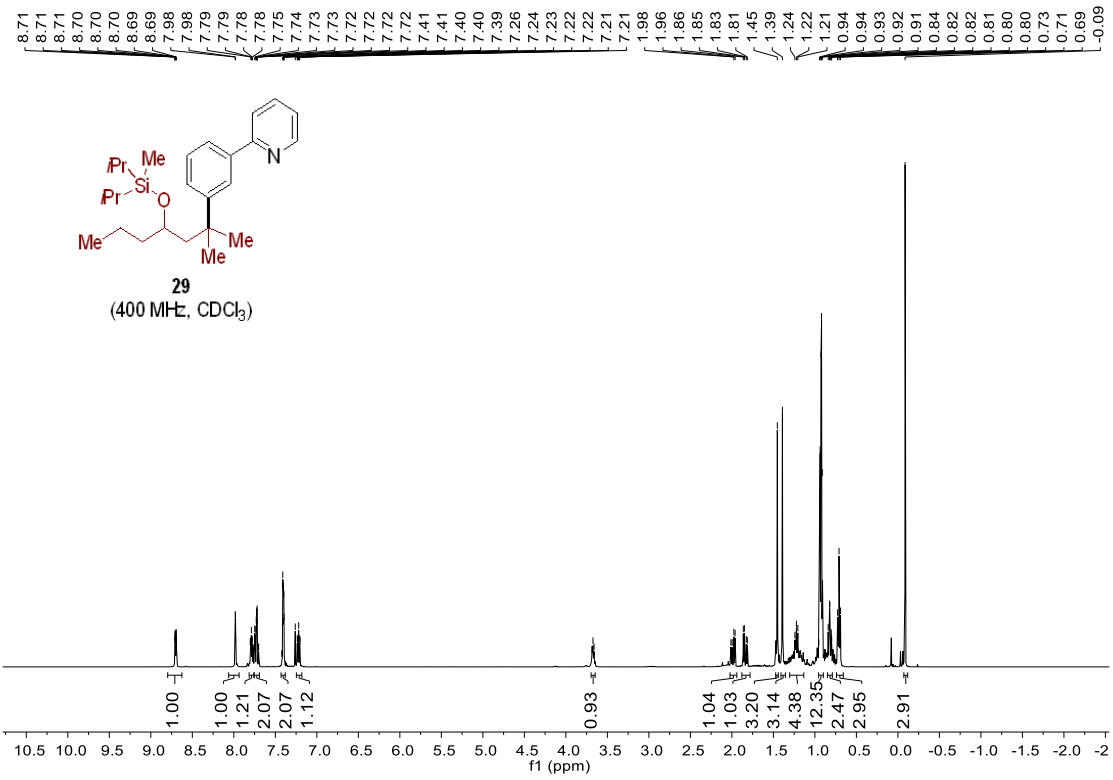

150.91 148.83 139.83 139.43 128.68 125.23 122.79 122.31 106.80 77.48 77.16 76.84 66.83 54.37 37.31 31.37 28.41 25.66 17.71 17.67 17.61 13.68 13.60 13.53 12.50 -7.37
Me
Me
N
N
iPr
Me
Si
iPr
O
Me
Me
Me
25
(101 MHz, CDCl3)
f1 (ppm)

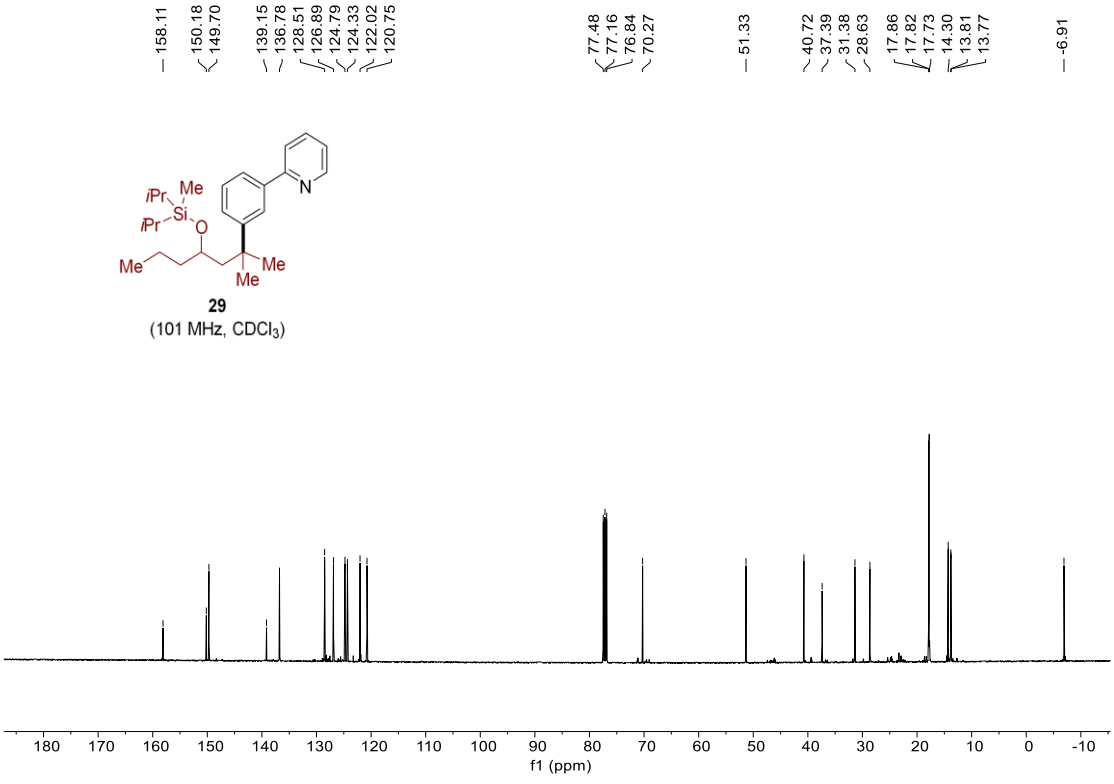

7.94 7.93 7.93 7.76 7.76 7.76 7.74 7.74 7.74 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.35 7.33 7.31 7.26
4.45 4.43 4.41 4.09 4.06 4.04 3.72 3.71 3.70 3.69 3.68
1.96 1.95 1.93 1.92 1.87 1.85 1.83 1.82 1.39 1.33 0.94 0.93 0.92 0.90 0.89 0.87 0.83 0.81 0.79 -0.11
O
N
iPr
Me
Si
iPr
O
Me Me Me
26
(400 MHz, CDCl3)
0.94 0.94 1.07 1.00 2.19 2.14 1.04 1.04 1.03 3.07 2.98 15.07 2.43 2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

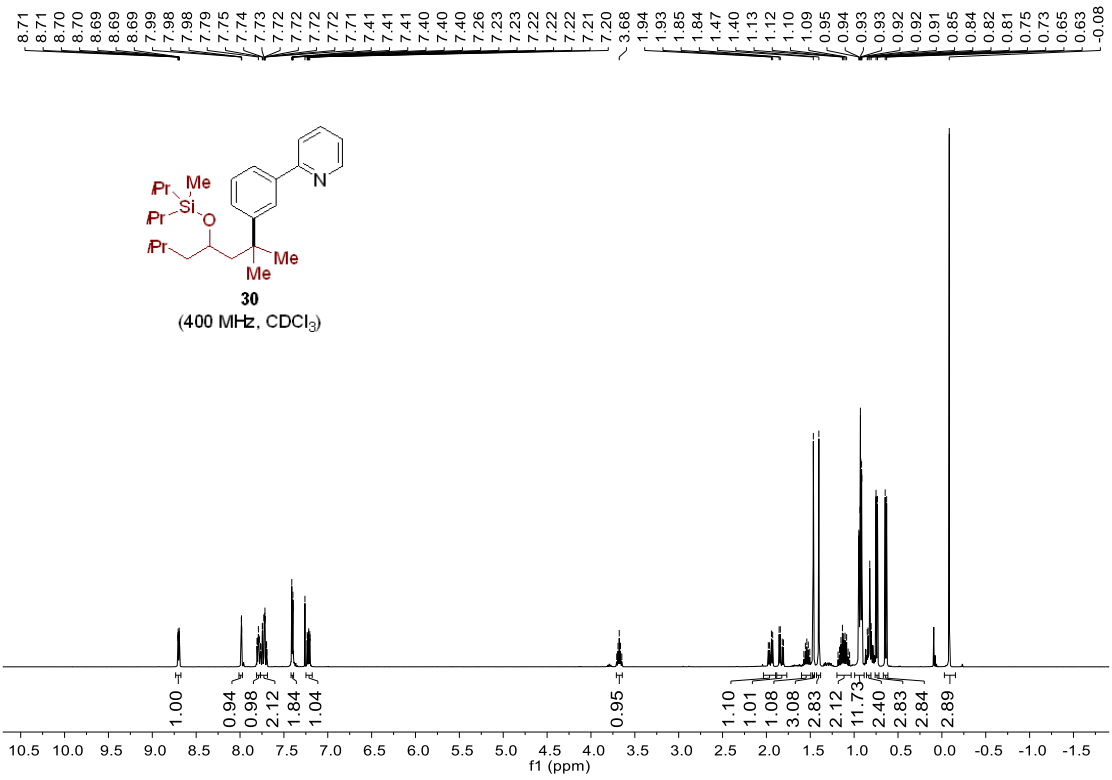

165.17 149.92 129.28 128.18 127.49 125.88 125.59
77.48 77.16 76.84 67.68 66.82 55.03 54.33
37.23 31.19 28.67 25.65 17.70 17.67 17.60 13.57 13.52 -7.44
O
N
iPr
Me
Si
iPr
O
Me Me Me
26
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

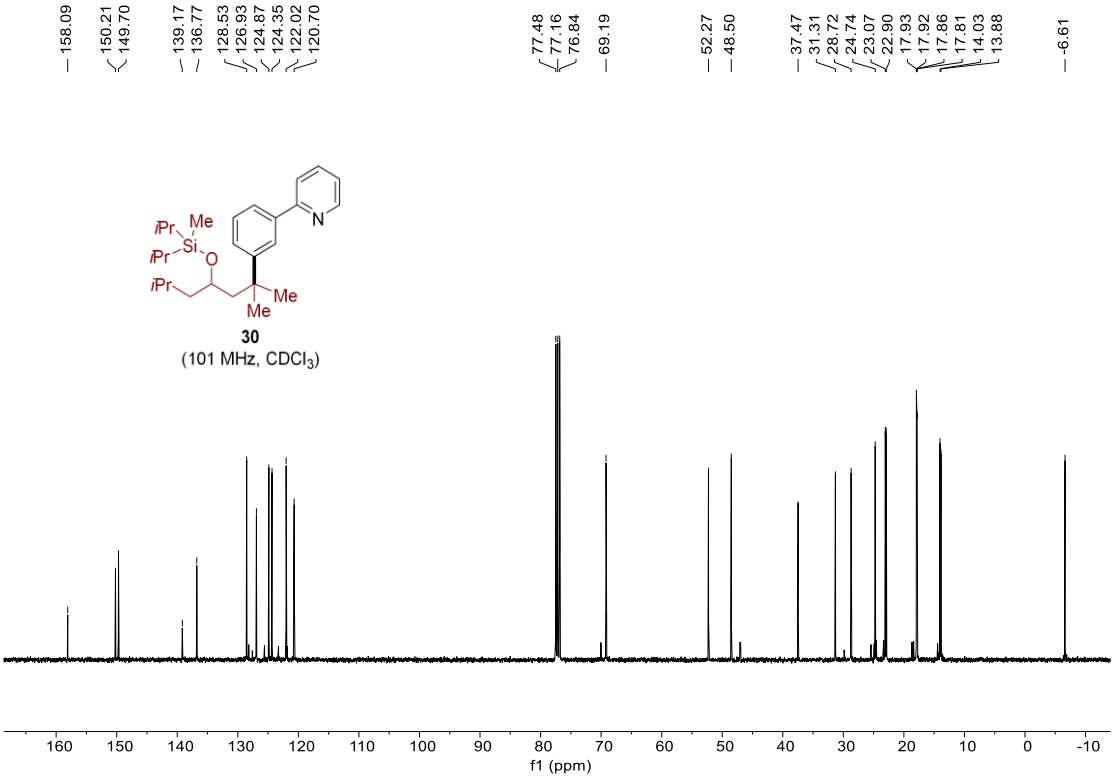

8.71 8.71 8.71 8.70 8.70 8.69 8.69 7.99 7.99 7.98 7.98 7.98 7.80 7.80 7.79 7.78 7.78 7.74 7.74 7.73 7.72 7.72 7.41 7.41 7.40 7.40 7.40 7.40 7.26 7.23 7.23 7.22 7.22 7.21 7.20 7.20 3.63 2.02 2.00 1.98 1.97 1.86 1.85 1.82 1.81 1.45 1.39 0.95 0.94 0.93 0.92 0.92 0.91 0.83 0.81 0.81 0.76 0.74 0.72 -0.08
iPr Me
iPr Si O
Me
Me
Me
N
28
(400 MHz, CDCl3)
1.00 1.03 3.27 2.06 1.10 0.99 1.04 1.18 3.12 3.14 2.40 12.37 2.38 3.28 3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

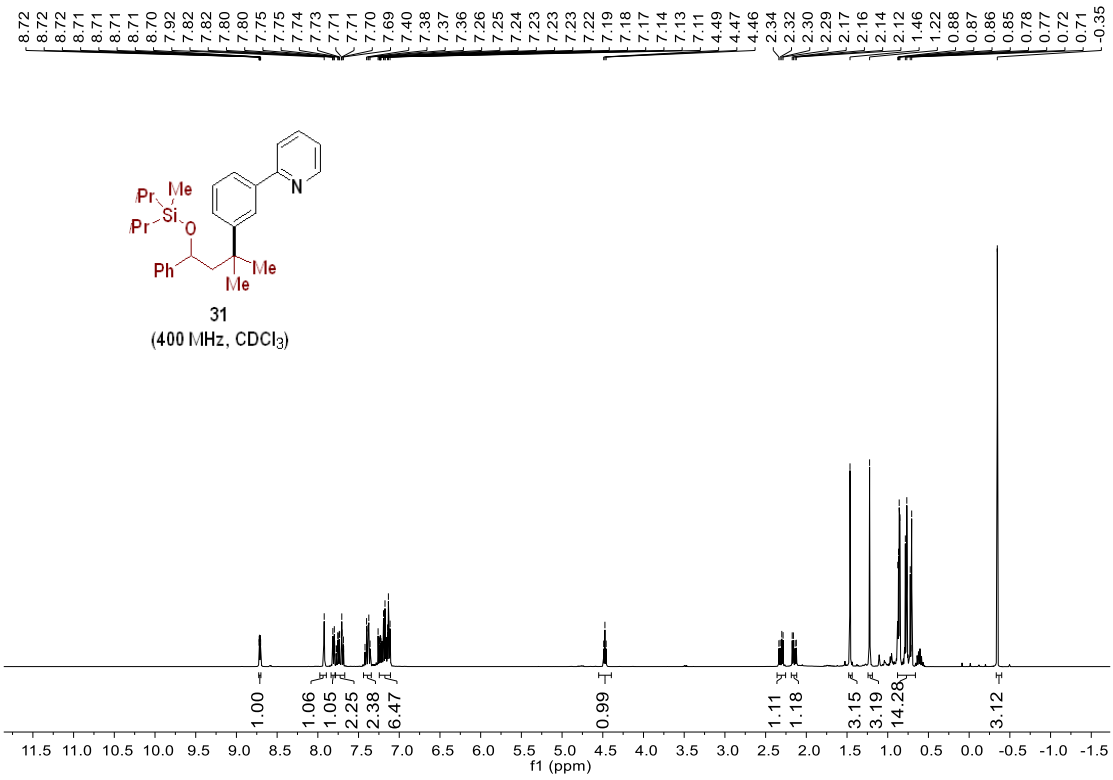

158.12 150.20 149.74 139.19 136.74 128.51 126.88 124.73 124.34 122.02 120.74
77.48 77.16 76.84 71.36 50.77 37.34 31.40 30.88 28.66 17.85 17.81 17.73 13.78 13.76 8.89 -6.94
iPr Me
iPr Si O
Me
Me
Me
N
28
(101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

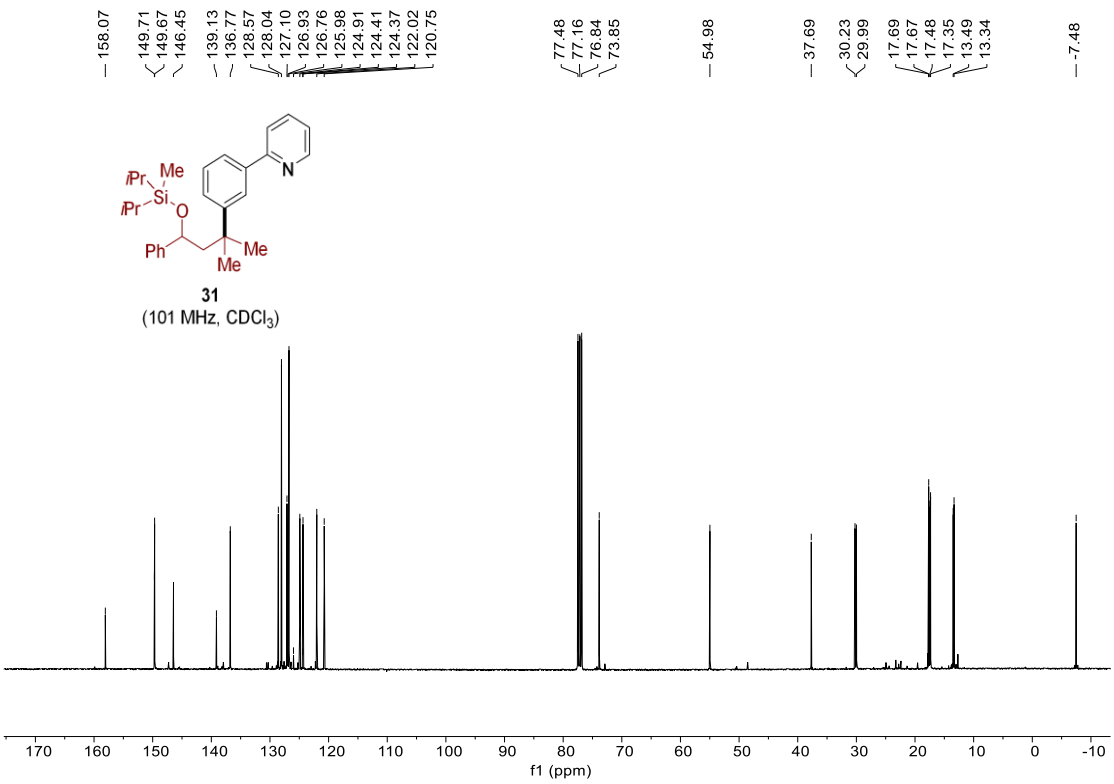

8.71 8.71 8.71 8.70 8.70 8.70 8.69 8.69 7.98 7.98 7.79 7.79 7.78 7.78 7.75 7.74 7.73 7.73 7.72 7.72 7.72 7.72 7.41 7.41 7.40 7.40 7.39 7.26 7.24 7.23 7.22 7.22 7.21 7.21 1.98 1.96 1.86 1.85 1.83 1.81 1.45 1.39 1.24 1.22 1.21 0.94 0.94 0.93 0.92 0.91 0.84 0.82 0.82 0.81 0.80 0.80 0.73 0.71 0.69 -0.09
iPr
Me
Si
iPr
O
Me
Me
Me
N
29
(400 MHz, CDCl3)
1.00 1.00 1.21 2.07 2.07 1.12 0.93 1.04 1.03 3.20 3.14 4.38 12.35 2.47 2.95 2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2
f1 (ppm)

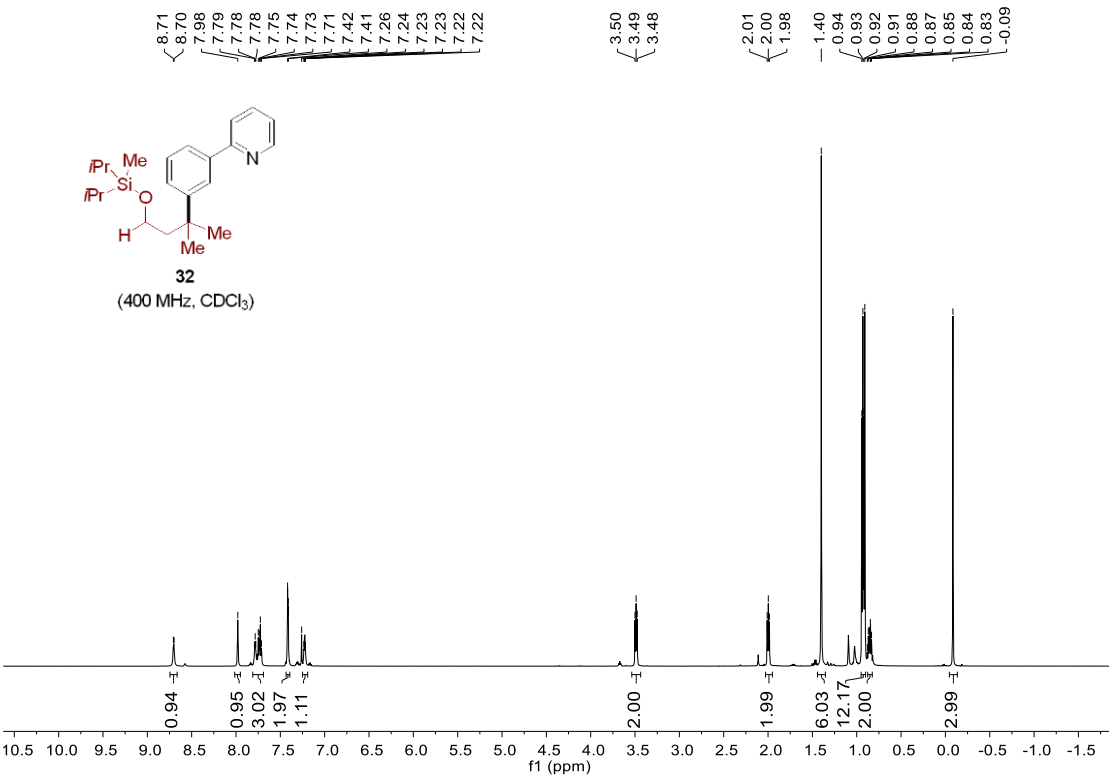

158.11 150.18 149.70 139.15 136.78 128.51 126.89 124.79 124.33 122.02 120.75 77.48 77.16 76.84 70.27 51.33 40.72 37.39 31.38 28.63 17.86 17.82 17.73 14.30 13.81 13.77 -6.91
iPr
Me
Si
iPr
O
Me
Me
Me
N
29
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

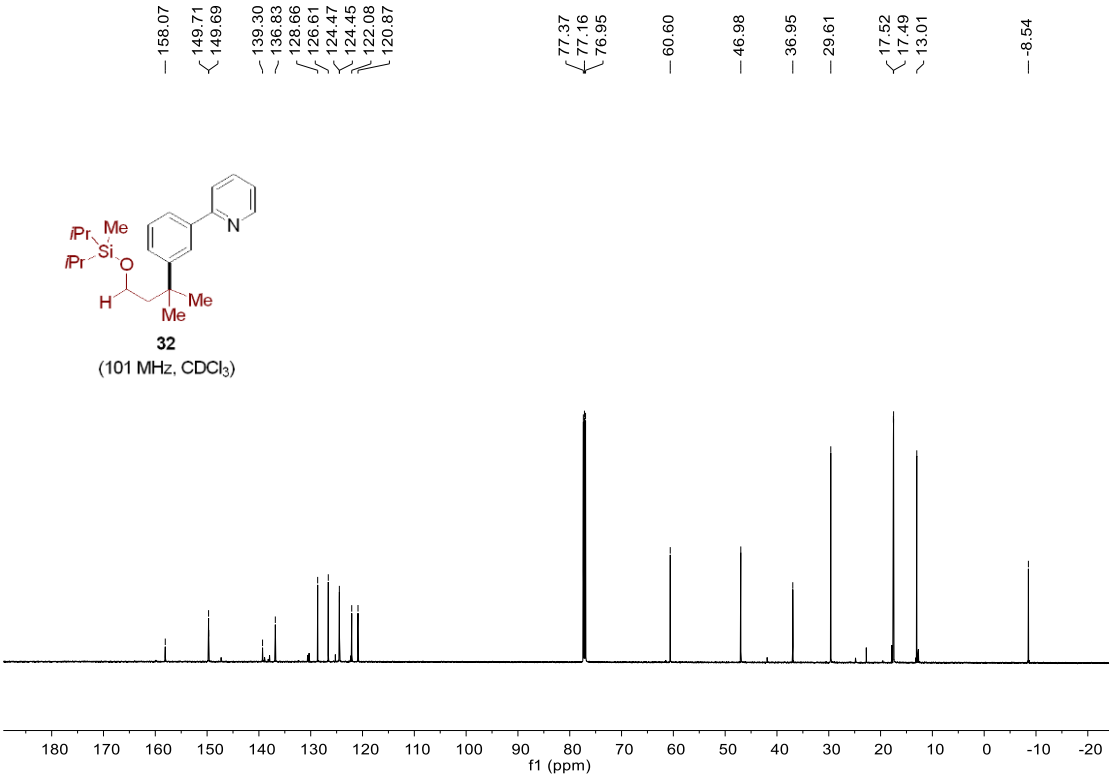

8.71 8.71 8.70 8.70 8.69 8.69 8.69 7.99 7.98 7.98 7.79 7.75 7.74 7.73 7.72 7.72 7.72 7.72 7.71 7.41 7.41 7.41 7.40 7.40 7.40 7.26 7.23 7.23 7.22 7.22 7.22 7.21 7.20 3.68 1.94 1.93 1.85 1.84 1.47 1.40 1.13 1.12 1.10 1.09 0.95 0.94 0.93 0.93 0.92 0.92 0.91 0.85 0.84 0.82 0.81 0.75 0.73 0.65 0.63 -0.08
iPr Me
iPr Si O
iPr
Me
Me
N
30
(400 MHz, CDCl3)
1.00 0.94 0.98 2.12 1.84 1.04 0.95 1.10 1.01 1.08 3.08 2.83 2.12 11.73 2.40 2.83 2.84 2.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

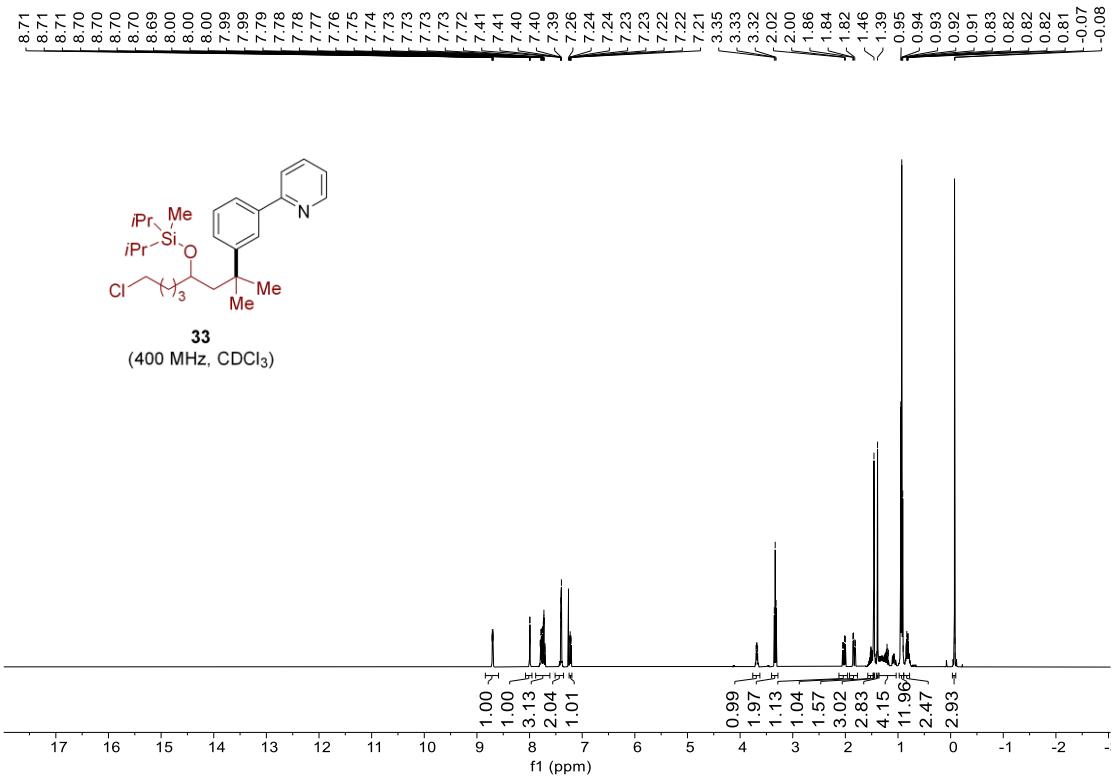

158.09 150.21 149.70 139.17 136.77 128.53 126.93 124.87 124.35 122.02 120.70 77.48 77.16 76.84 69.19 52.27 48.50 37.47 31.31 28.72 24.74 23.07 22.90 17.93 17.92 17.86 17.81 14.03 13.88 -6.61
iPr Me
iPr Si O
iPr
Me
Me
N
30
(101 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

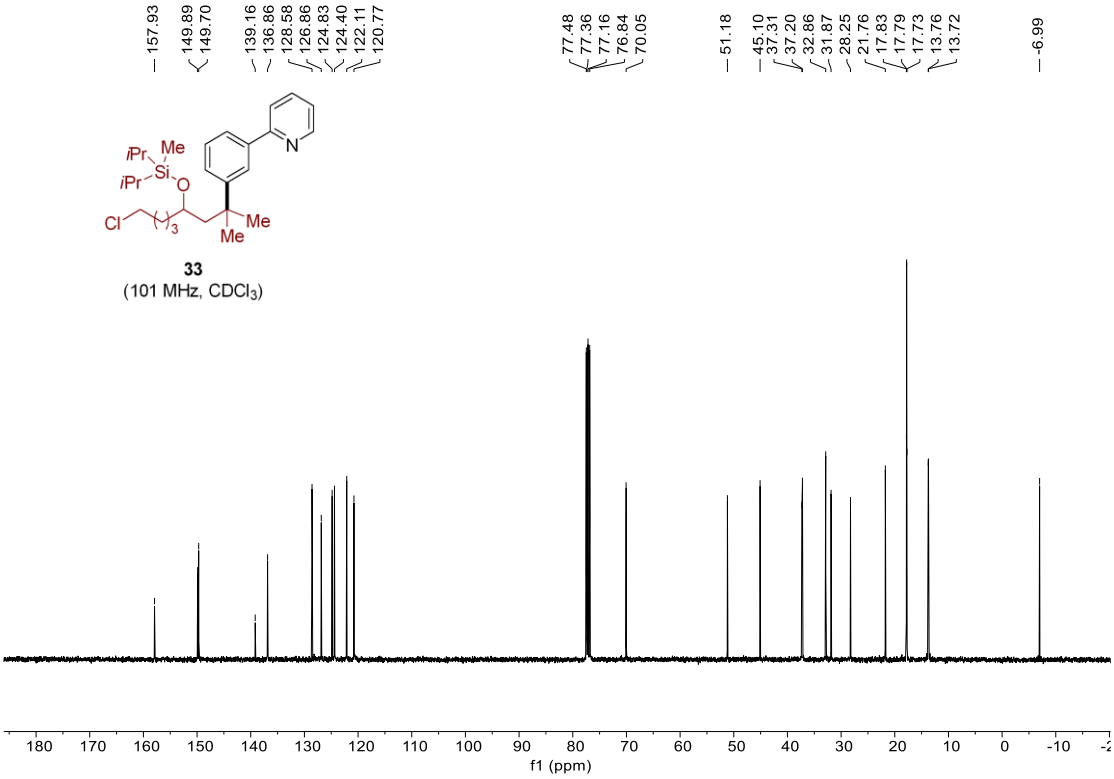

8.72 8.72 8.72 8.71 8.71 8.71 8.71 8.70 7.92 7.82 7.82 7.80 7.80 7.75 7.75 7.74 7.73 7.71 7.71 7.70 7.69 7.40 7.38 7.37 7.36 7.26 7.25 7.24 7.23 7.23 7.23 7.22 7.19 7.18 7.17 7.14 7.13 7.11 4.49 4.47 4.46 2.34 2.32 2.30 2.29 2.17 2.16 2.14 2.12 1.46 1.22 0.88 0.87 0.86 0.85 0.78 0.77 0.72 0.71 -0.35
iPr Me
iPr Si O
Ph Me
Me
N
31
(400 MHz, CDCl3)
1.00 1.06 1.05 2.25 2.38 6.47 0.99 1.11 1.18 3.15 3.19 14.28 3.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

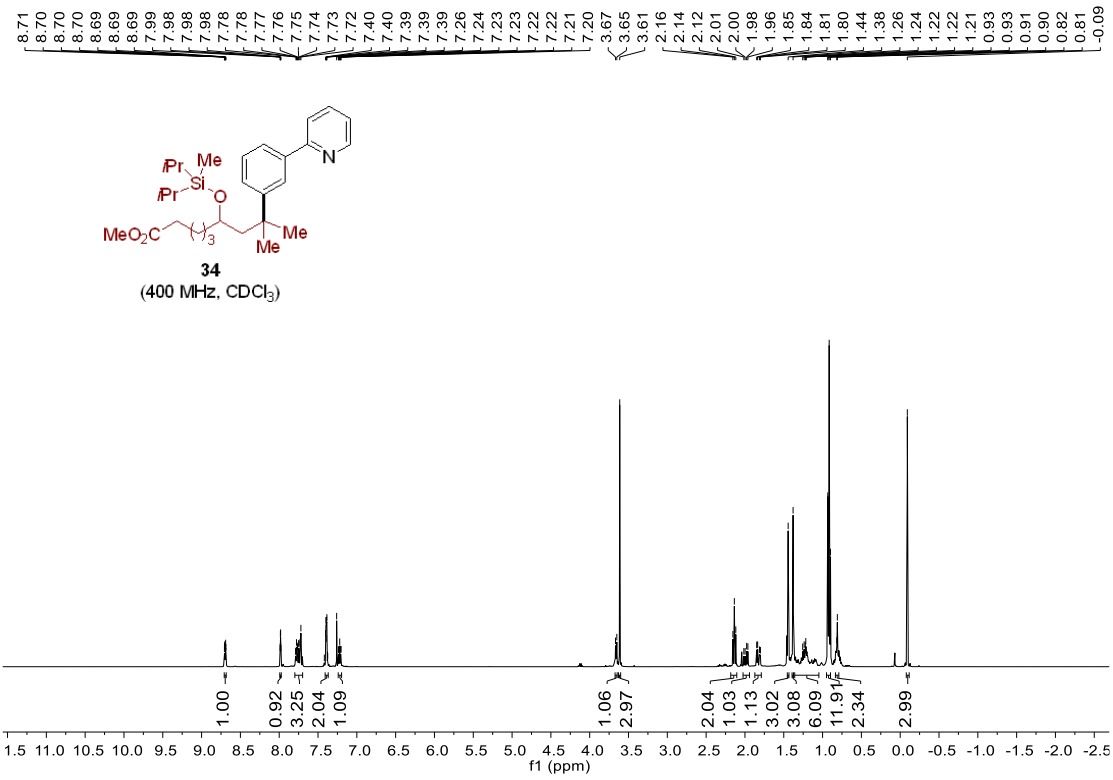

158.07 149.71 149.67 146.45 139.13 136.77 128.57 128.04 127.10 126.93 126.76 125.98 124.91 124.41 124.37 122.02 120.75
77.48 77.16 76.84 73.85 54.98 37.69 30.23 29.99 17.69 17.67 17.48 17.35 13.49 13.34 -7.48
iPr Me
iPr Si O
Ph Me
Me
N
31
(101 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

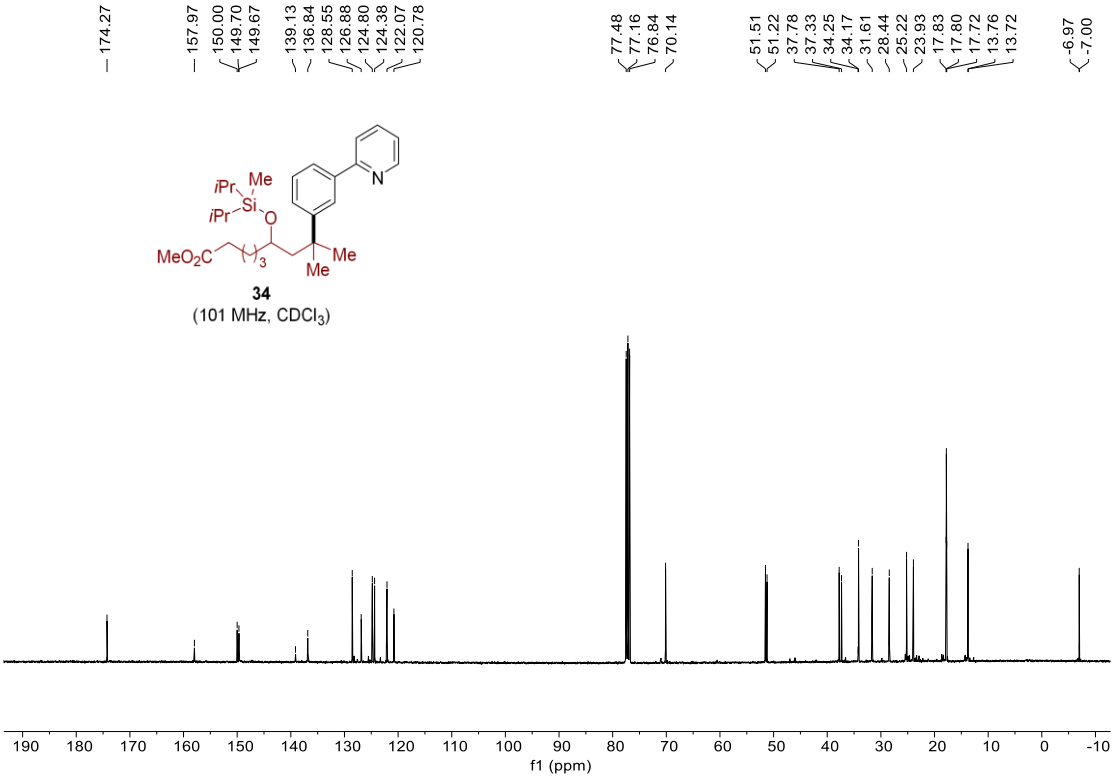

8.71
8.70
7.98
7.79
7.78
7.78
7.75
7.74
7.73
7.71
7.42
7.41
7.26
7.24
7.23
7.23
7.22
7.22
3.50
3.49
3.48
2.01
2.00
1.98
1.40
0.94
0.93
0.92
0.91
0.88
0.87
0.85
0.84
0.83
-0.09
iPr
Me
Si
iPr
O
H
N
Me
Me
32
(400 MHz, CDCl3)
0.94
0.95
3.02
1.97
1.11
2.00
1.99
6.03
12.17
2.00
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

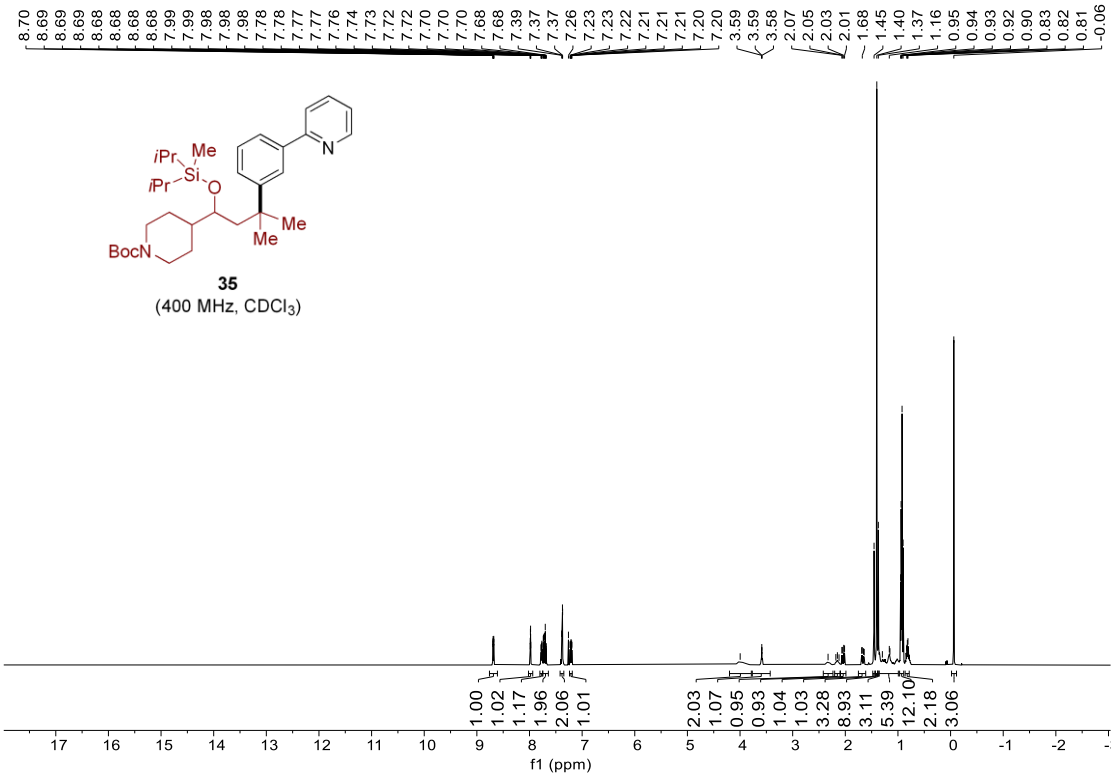

158.07
149.71
149.69
139.30
136.83
128.66
126.61
124.47
124.45
122.08
120.87
77.37
77.16
76.95
60.60
46.98
36.95
29.61
17.52
17.49
13.01
-8.54
iPr
Me
Si
iPr
O
H
N
Me
Me
32
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

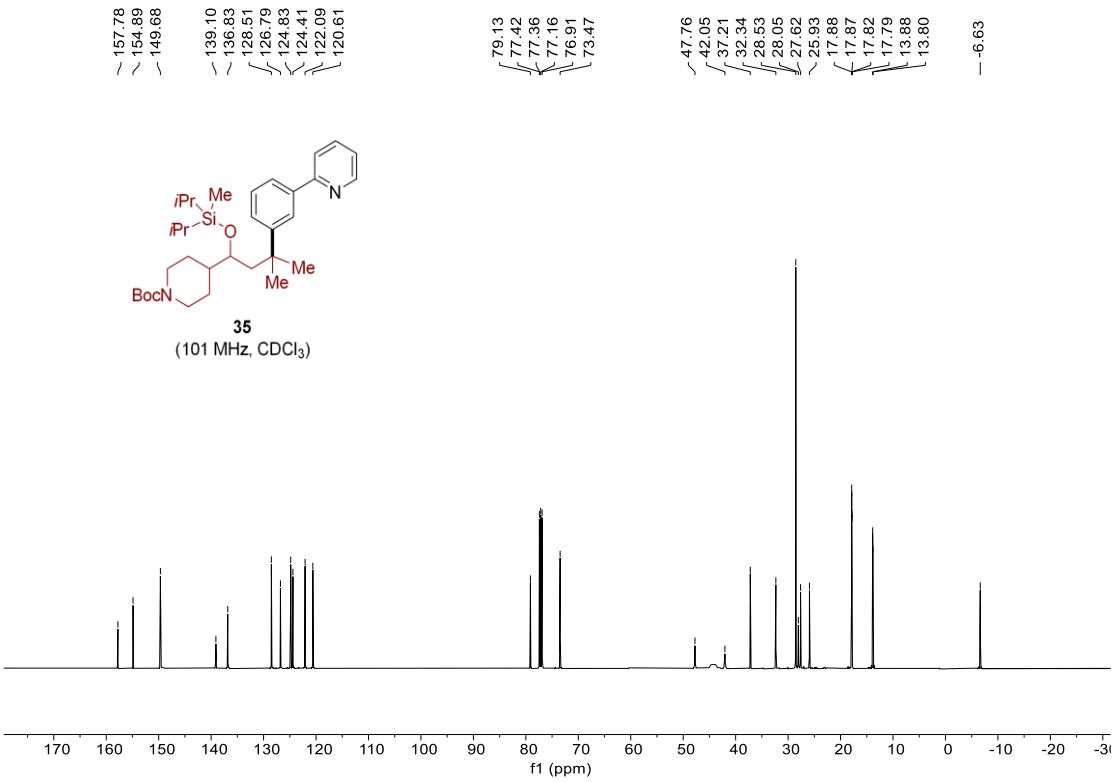

8.71 8.71 8.71 8.70 8.70 8.70 8.70 8.69 8.00 8.00 8.00 7.99 7.99 7.79 7.78 7.78 7.77 7.76 7.75 7.74 7.73 7.73 7.73 7.72 7.41 7.41 7.40 7.40 7.39 7.26 7.24 7.24 7.23 7.23 7.22 7.22 7.21 3.35 3.33 3.32 2.02 2.00 1.86 1.84 1.82 1.46 1.39 0.95 0.94 0.93 0.92 0.91 0.83 0.82 0.82 0.82 0.81 -0.07 -0.08
iPr Me iPr Si O Cl 3 Me Me N
33
(400 MHz, CDCl3)
1.00 1.00 3.13 2.04 1.01 0.99 1.97 1.13 1.04 1.57 3.02 2.83 4.15 11.96 2.47 2.93
f1 (ppm)

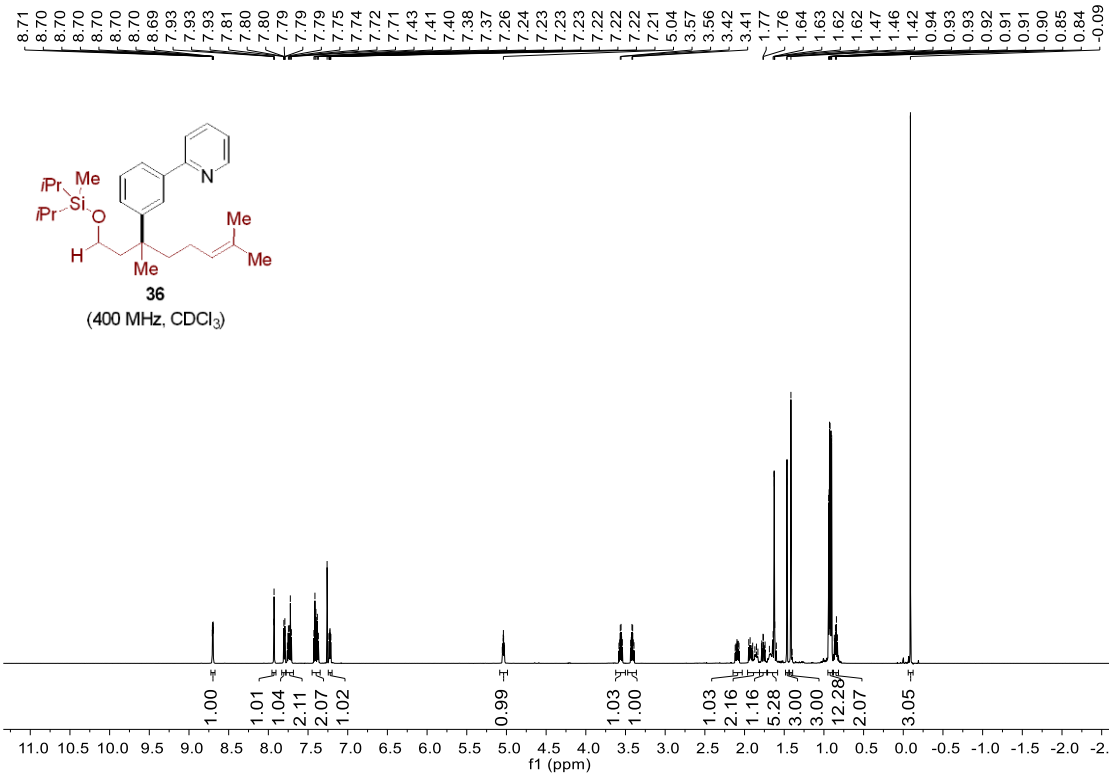

157.93 149.89 149.70 139.16 136.86 128.58 126.86 124.83 124.40 122.11 120.77 77.48 77.36 77.16 76.84 70.05 51.18 45.10 37.31 37.20 32.86 31.87 28.25 21.76 17.83 17.79 17.73 13.76 13.72 -6.99
iPr Me iPr Si O Cl 3 Me Me N
33
(101 MHz, CDCl3)
f1 (ppm)

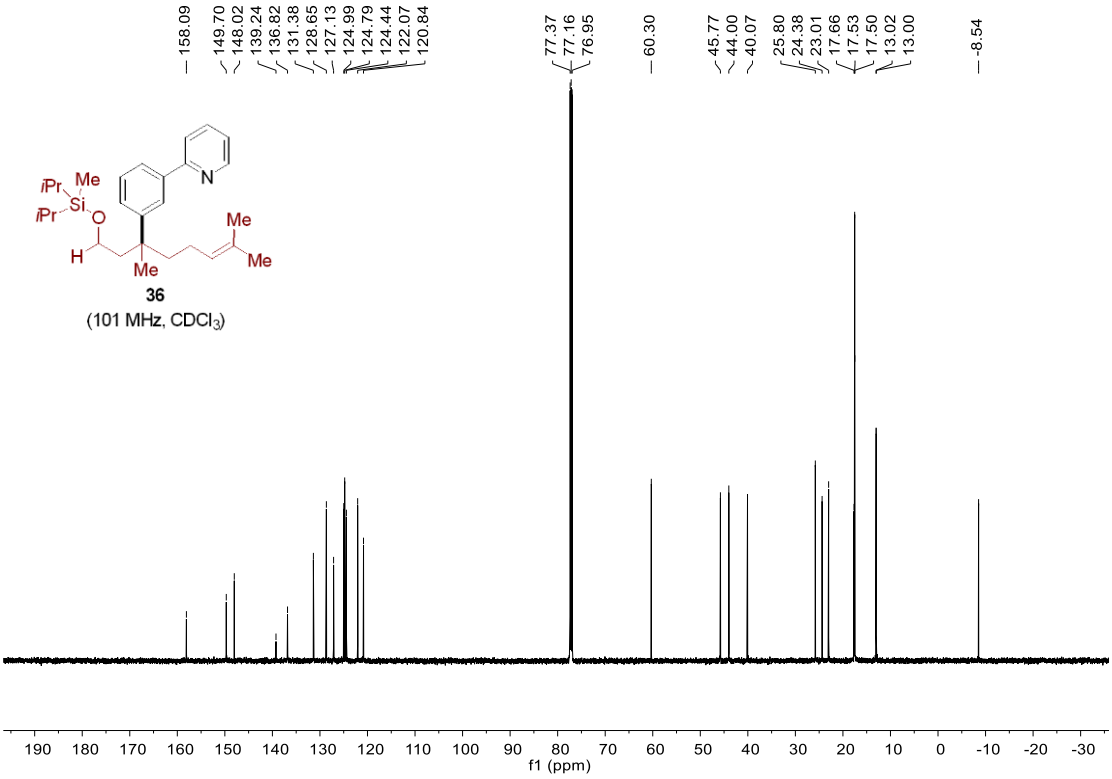

8.71 8.70 8.70 8.70 8.69 8.69 8.69 7.99 7.98 7.98 7.98 7.78 7.78 7.77 7.76 7.75 7.74 7.73 7.72 7.40 7.40 7.39 7.39 7.39 7.26 7.24 7.23 7.23 7.22 7.22 7.21 7.20 3.67 3.65 3.61 2.16 2.14 2.12 2.01 2.00 1.98 1.96 1.85 1.84 1.81 1.80 1.44 1.38 1.26 1.24 1.22 1.22 1.21 0.93 0.93 0.91 0.90 0.82 0.81 -0.09
iPr
Me
Si
iPr
O
MeO2C
3
Me
Me
N
34
(400 MHz, CDCl3)
1.00 0.92 3.25 2.04 1.09 1.06 2.97 2.04 1.03 1.13 3.02 3.08 6.09 11.91 2.34 2.99
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)

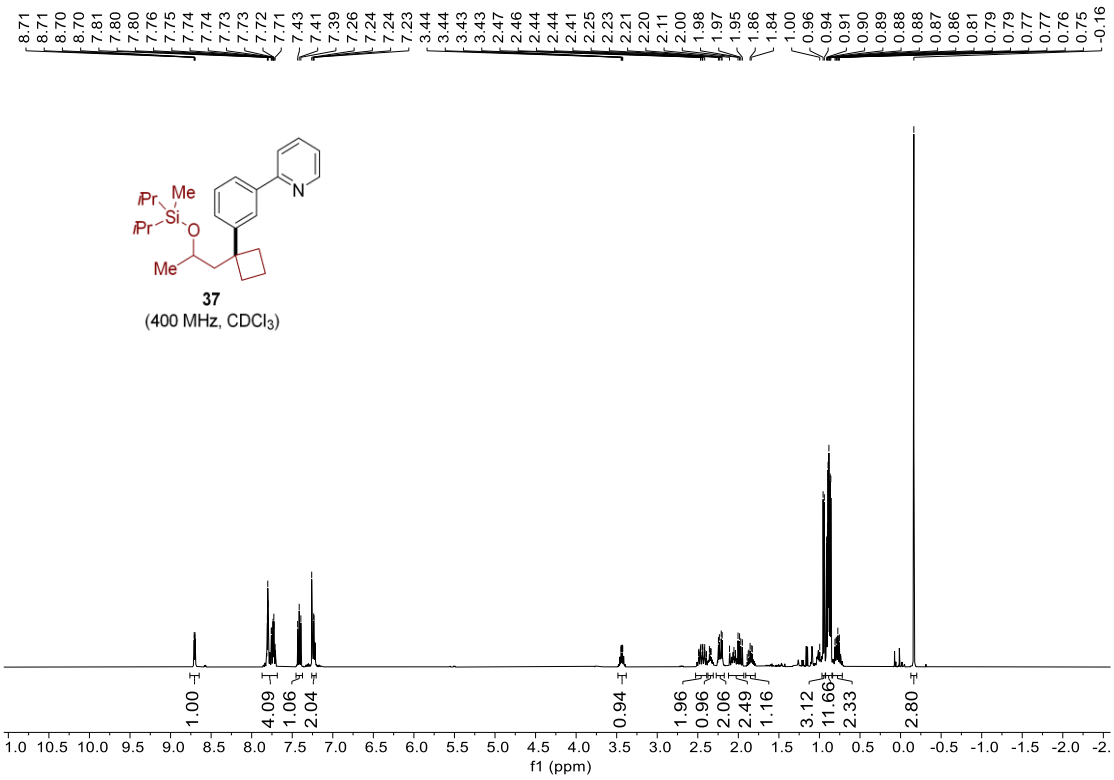

174.27
157.97
150.00
149.70
149.67
139.13
136.84
128.55
126.88
124.80
124.38
122.07
120.78
77.48
77.16
76.84
70.14
51.51
51.22
37.78
37.33
34.25
34.17
31.61
28.44
25.22
23.93
17.83
17.80
17.72
13.76
13.72
-6.97
-7.00
iPr
Me
Si
iPr
O
MeO2C
3
Me
Me
N
34
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

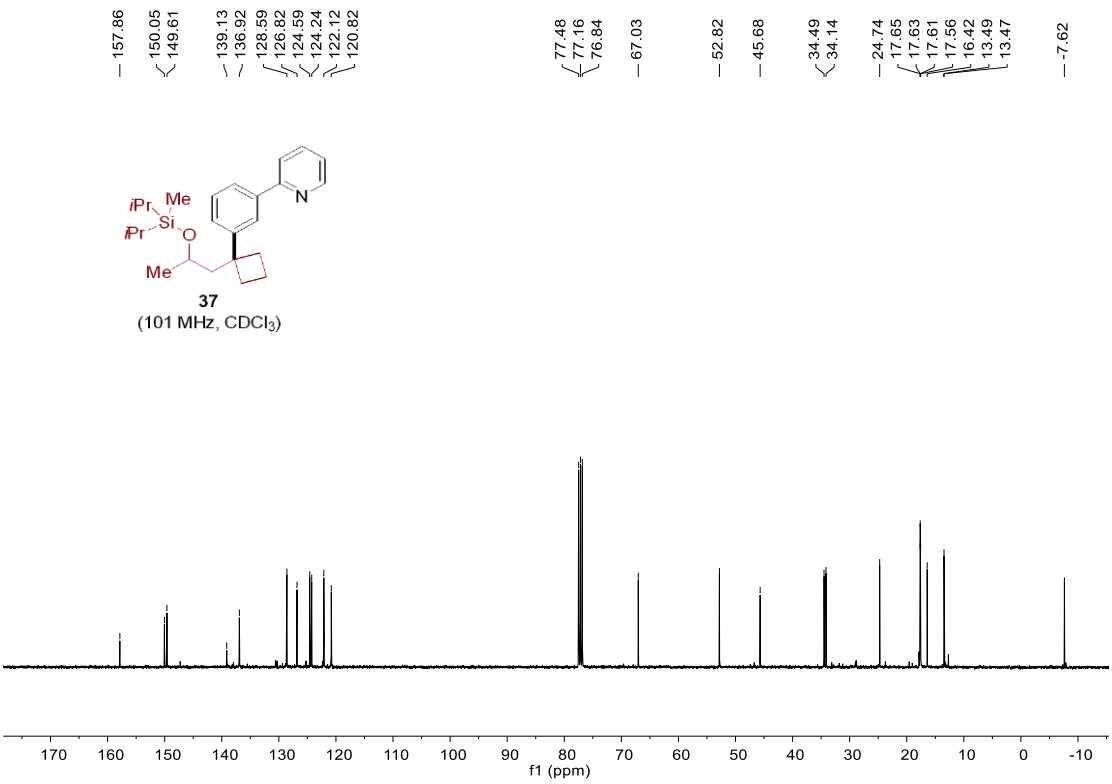

8.70 8.69 8.69 8.69 8.68 8.68 8.68 8.68 8.68 7.99 7.99 7.98 7.98 7.98 7.78 7.78 7.77 7.77 7.77 7.76 7.74 7.73 7.72 7.72 7.70 7.70 7.70 7.68 7.68 7.39 7.37 7.37 7.26 7.23 7.23 7.22 7.21 7.21 7.21 7.20 7.20 3.59 3.59 3.58 2.07 2.05 2.03 2.01 1.68 1.45 1.40 1.37 1.16 0.95 0.94 0.93 0.92 0.90 0.83 0.82 0.81 -0.06
iPr
Me
iPr
Si
O
N
Me
Me
BocN
35
(400 MHz, CDCl3)
1.00 1.02 1.17 1.96 2.06 1.01 2.03 1.07 0.95 0.93 1.04 1.03 3.28 8.93 3.11 5.39 12.10 2.18 3.06
f1 (ppm)

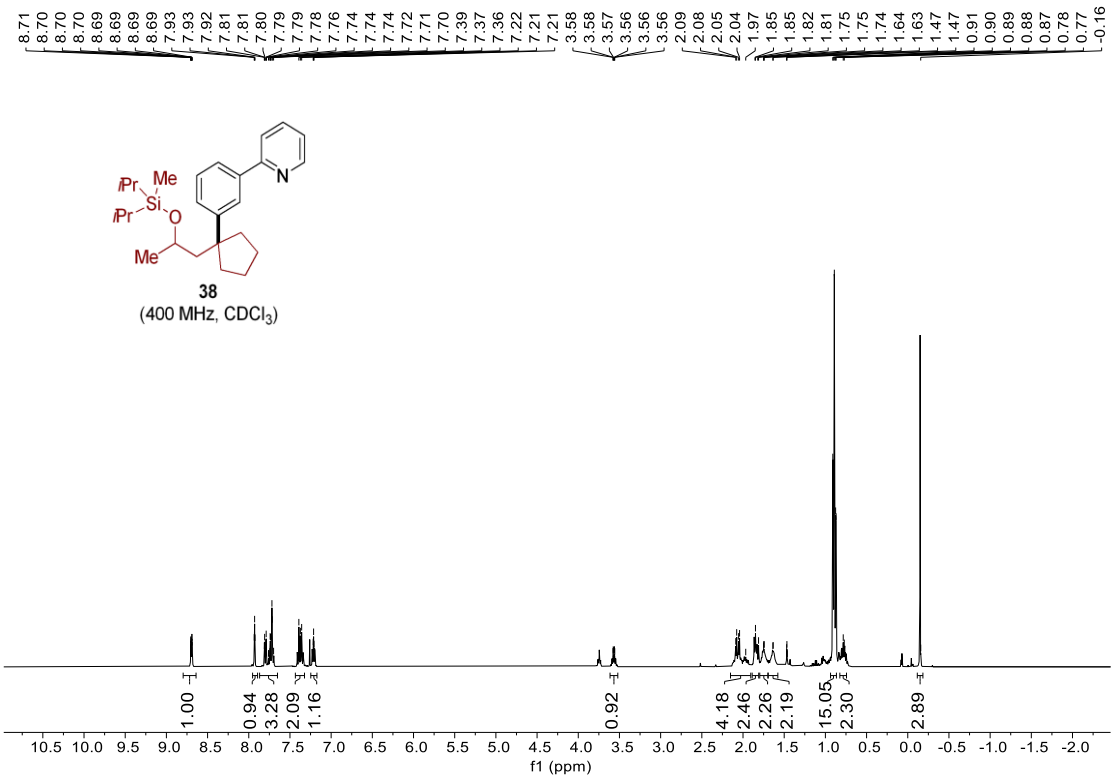

157.78 154.89 149.68 139.10 136.83 128.51 126.79 124.83 124.41 122.09 120.61 79.13 77.42 77.36 77.16 76.91 73.47 47.76 42.05 37.21 32.34 28.53 28.05 27.62 25.93 17.88 17.87 17.82 17.79 13.88 13.80 -6.63
iPr
Me
iPr
Si
O
N
Me
Me
BocN
35
(101 MHz, CDCl3)
f1 (ppm)

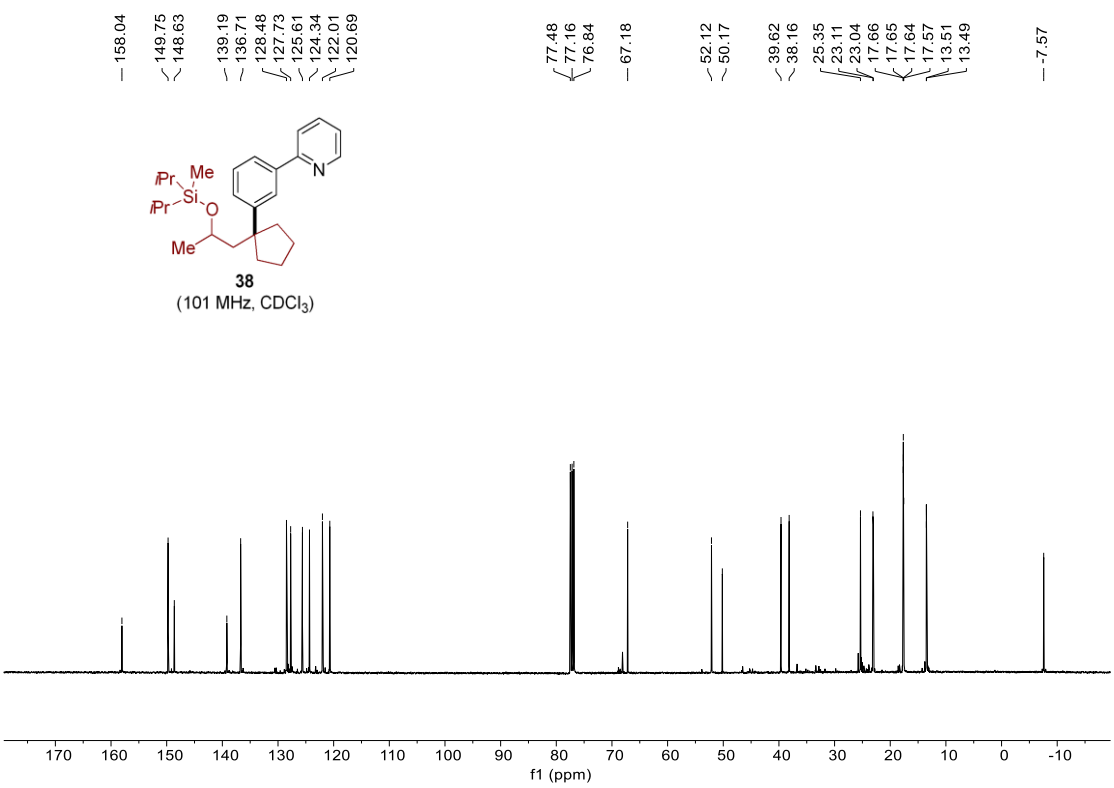

8.71 8.70 8.70 8.70 8.70 8.70 8.69 7.93 7.93 7.93 7.81 7.80 7.80 7.79 7.79 7.79 7.75 7.74 7.72 7.71 7.43 7.41 7.40 7.38 7.37 7.26 7.24 7.23 7.23 7.22 7.22 7.22 7.21 5.04 3.57 3.56 3.42 3.41 1.77 1.76 1.64 1.63 1.62 1.62 1.47 1.46 1.42 0.94 0.93 0.93 0.92 0.91 0.91 0.90 0.85 0.84 -0.09
iPr Me iPr Si O H Me N Me Me
36
(400 MHz, CDCl3)
1.00 1.01 1.04 2.11 2.07 1.02 0.99 1.03 1.00 1.03 2.16 1.16 5.28 3.00 3.00 12.28 2.07 3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.
f1 (ppm)

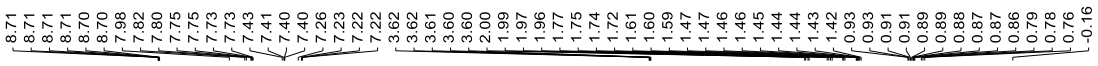

158.09 149.70 148.02 139.24 136.82 131.38 128.65 127.13 124.99 124.79 124.44 122.07 120.84
77.37 77.16 76.95 60.30 45.77 44.00 40.07 25.80 24.38 23.01 17.66 17.53 17.50 13.02 13.00 -8.54
iPr Me iPr Si O H Me N Me Me
36
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

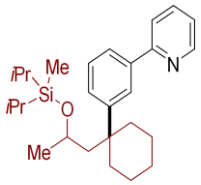

8.71 8.71 8.70 8.70 7.81 7.80 7.80 7.76 7.75 7.74 7.74 7.73 7.73 7.72 7.71 7.43 7.41 7.39 7.26 7.24 7.24 7.23 3.44 3.44 3.43 3.43 2.47 2.46 2.44 2.44 2.41 2.25 2.23 2.21 2.20 2.11 2.00 1.98 1.97 1.95 1.86 1.84 1.00 0.96 0.94 0.91 0.90 0.89 0.88 0.88 0.87 0.86 0.81 0.79 0.79 0.77 0.77 0.76 0.75 -0.16
iPr Me iPr Si O Me N
37
(400 MHz, CDCl3)
1.00 4.09 1.06 2.04 0.94 1.96 0.96 2.06 2.49 1.16 3.12 11.66 2.33 2.80
f1 (ppm)


157.86 150.05 149.61 139.13 136.92 128.59 126.82 124.59 124.24 122.12 120.82 77.48 77.16 76.84 67.03 52.82 45.68 34.49 34.14 24.74 17.65 17.63 17.61 17.56 16.42 13.49 13.47 -7.62
iPr Me iPr Si O Me N
37
(101 MHz, CDCl3)
f1 (ppm)

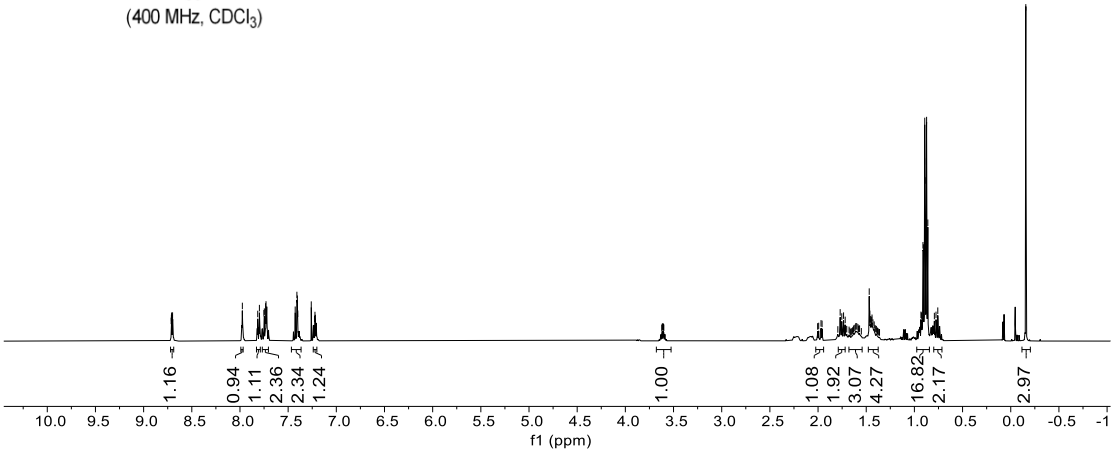

8.71 8.70 8.70 8.70 8.69 8.69 8.69 8.69 7.93 7.93 7.92 7.81 7.81 7.80 7.79 7.79 7.78 7.76 7.74 7.74 7.74 7.72 7.71 7.70 7.39 7.37 7.36 7.22 7.21 7.21 3.58 3.58 3.57 3.56 3.56 3.56 2.09 2.08 2.05 2.04 1.97 1.85 1.85 1.82 1.81 1.75 1.75 1.74 1.64 1.63 1.47 1.47 0.91 0.90 0.89 0.88 0.87 0.78 0.77 -0.16
iPr Me iPr Si O Me N
38
(400 MHz, CDCl3)
1.00 0.94 3.28 2.09 1.16 0.92 4.18 2.46 2.26 2.19 15.05 2.30 2.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

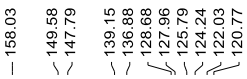

158.04 149.75 148.63 139.19 136.71 128.48 127.73 125.61 124.34 122.01 120.69
77.48 77.16 76.84 67.18 52.12 50.17 39.62 38.16 25.35 23.11 23.04 17.66 17.65 17.64 17.57 13.51 13.49 -7.57
iPr Me iPr Si O Me N
38
(101 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

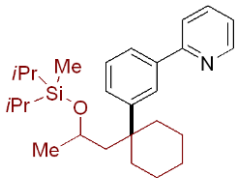




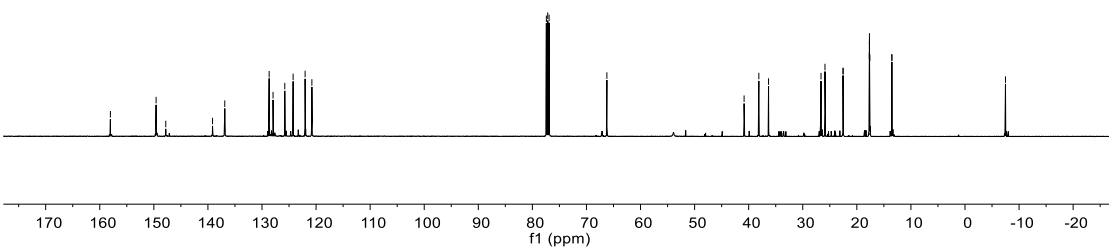
39
(400 MHz, $CDCl_3$)

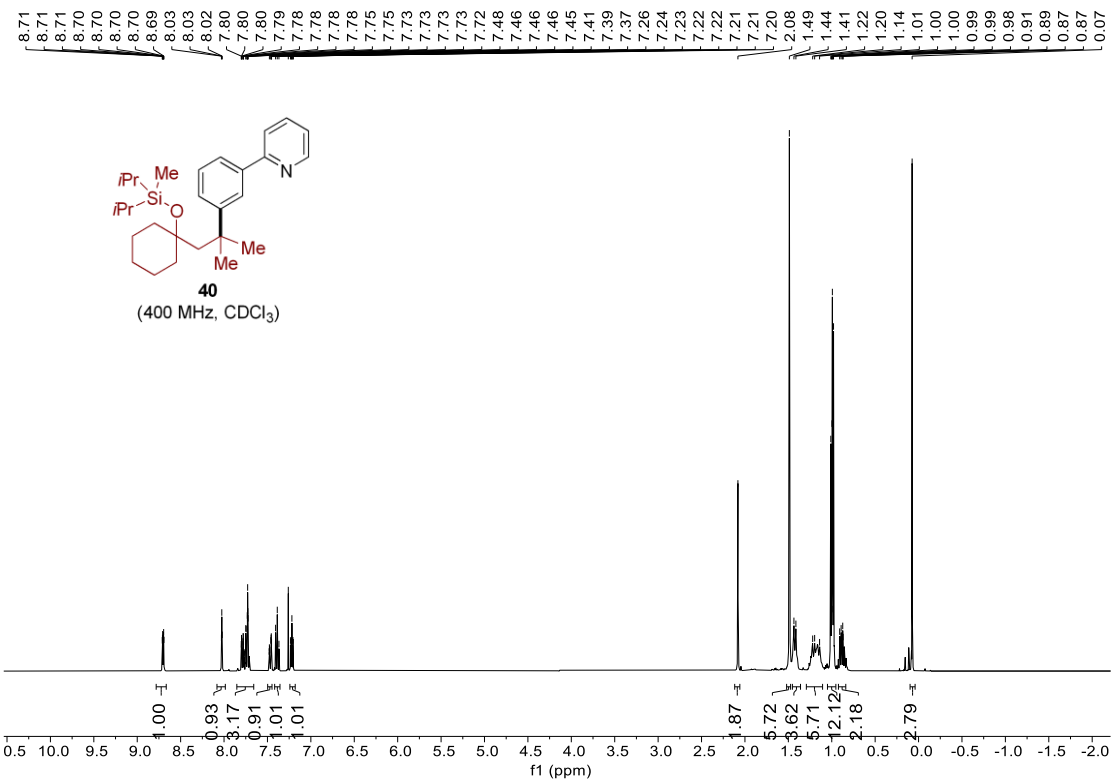


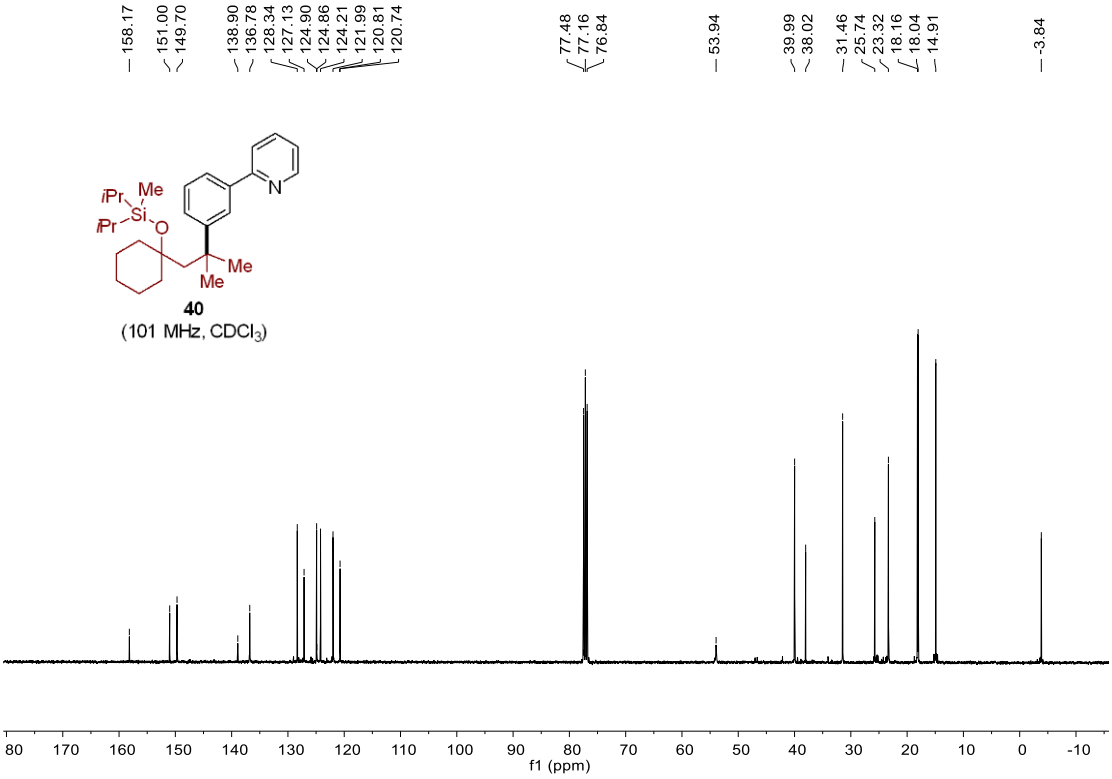


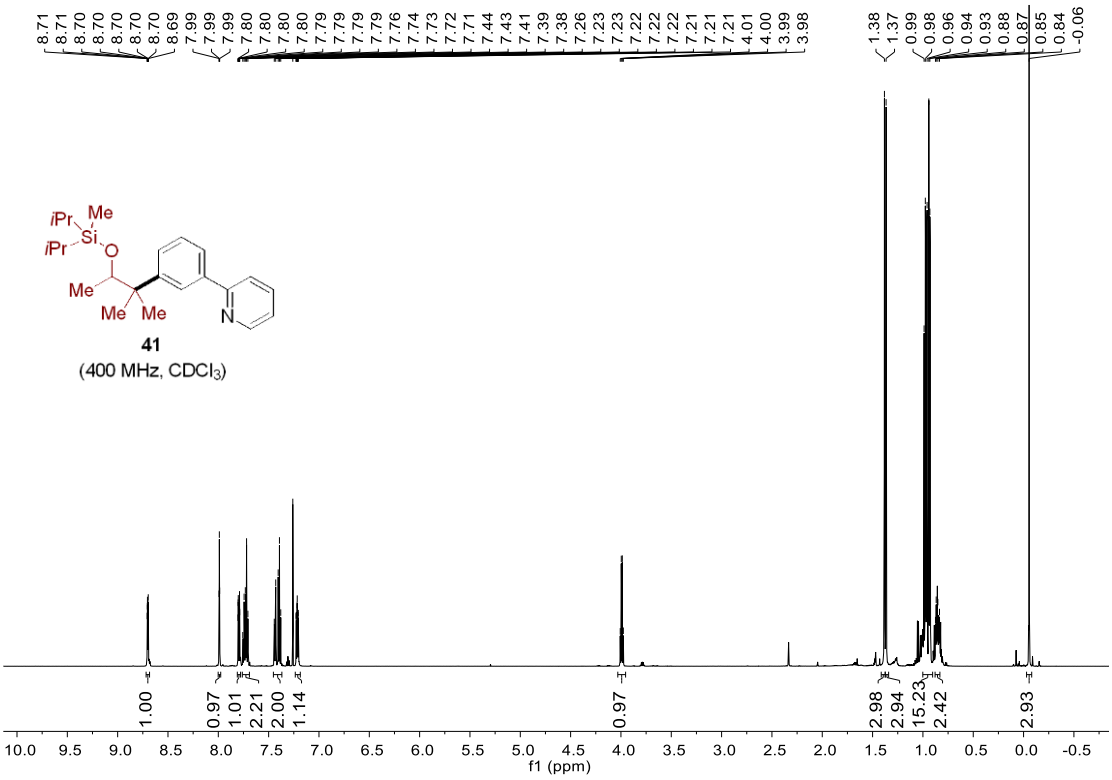


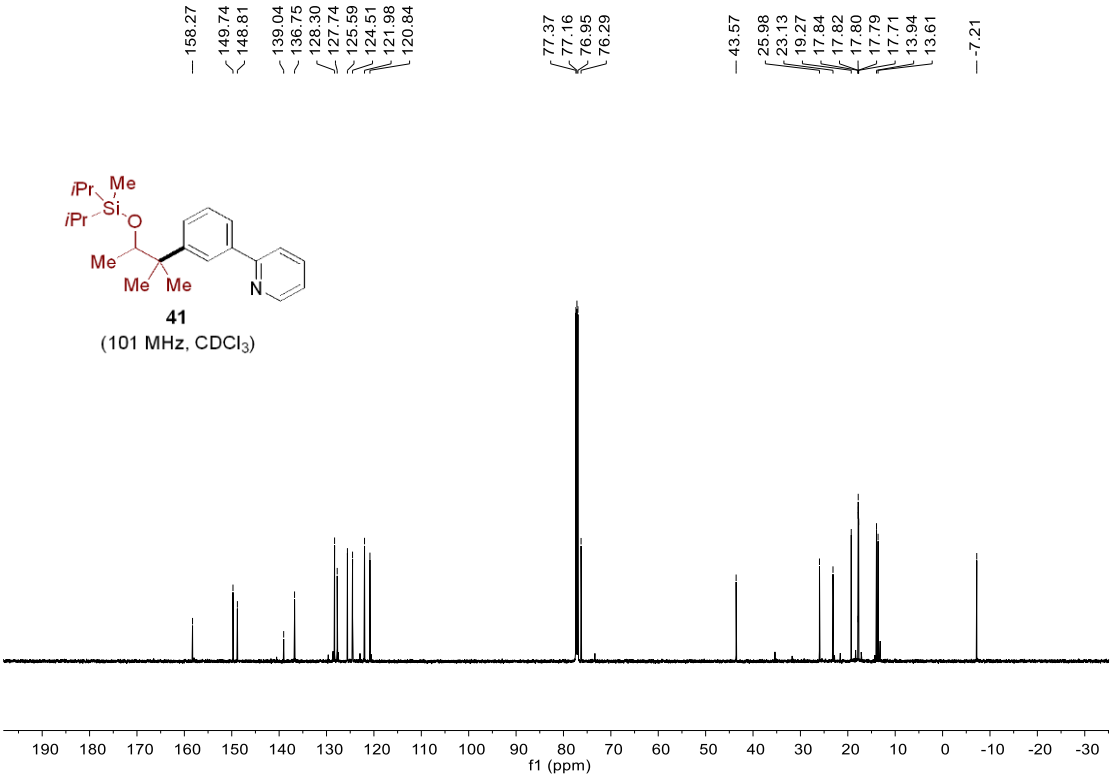
39
(101 MHz, $CDCl_3$)

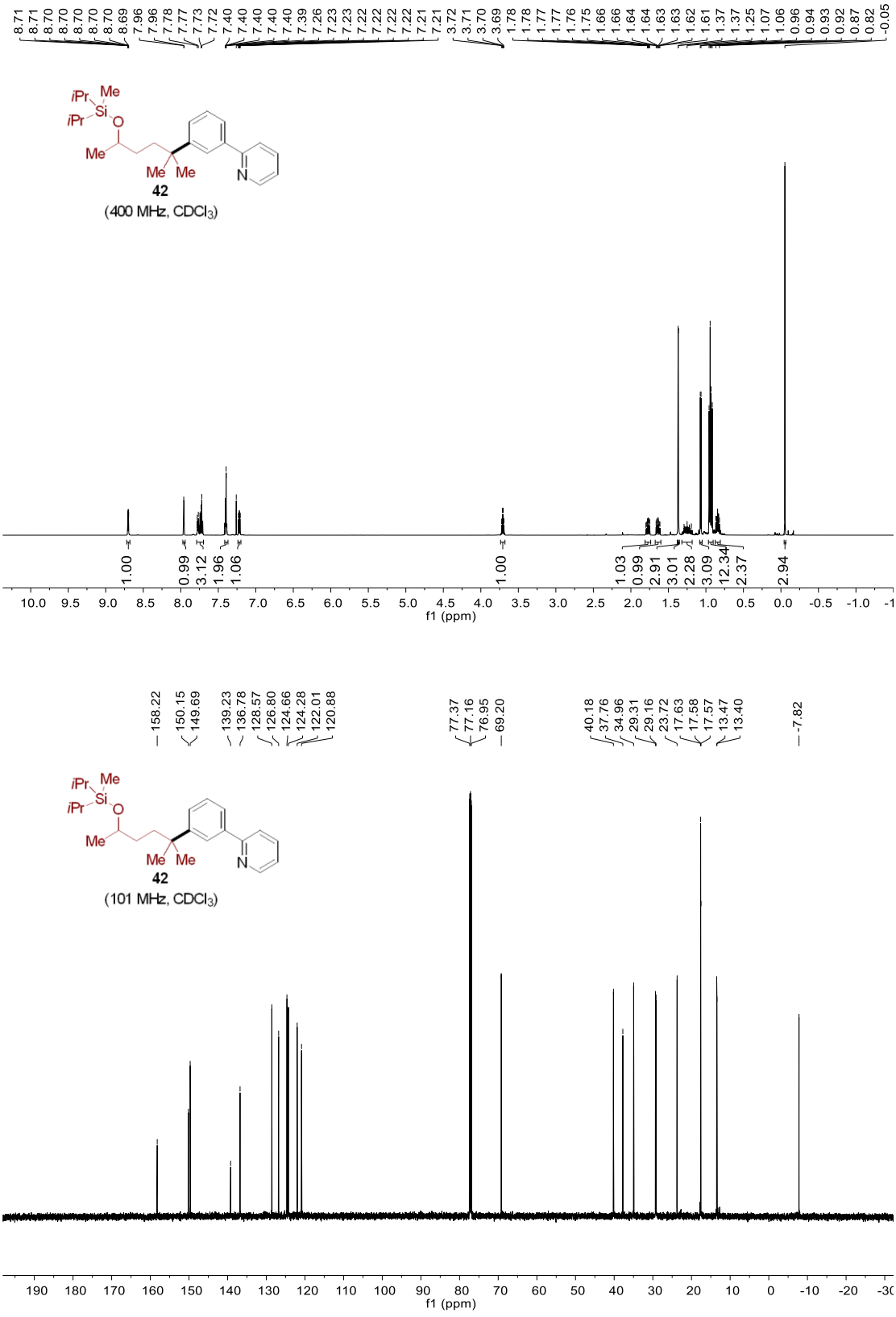


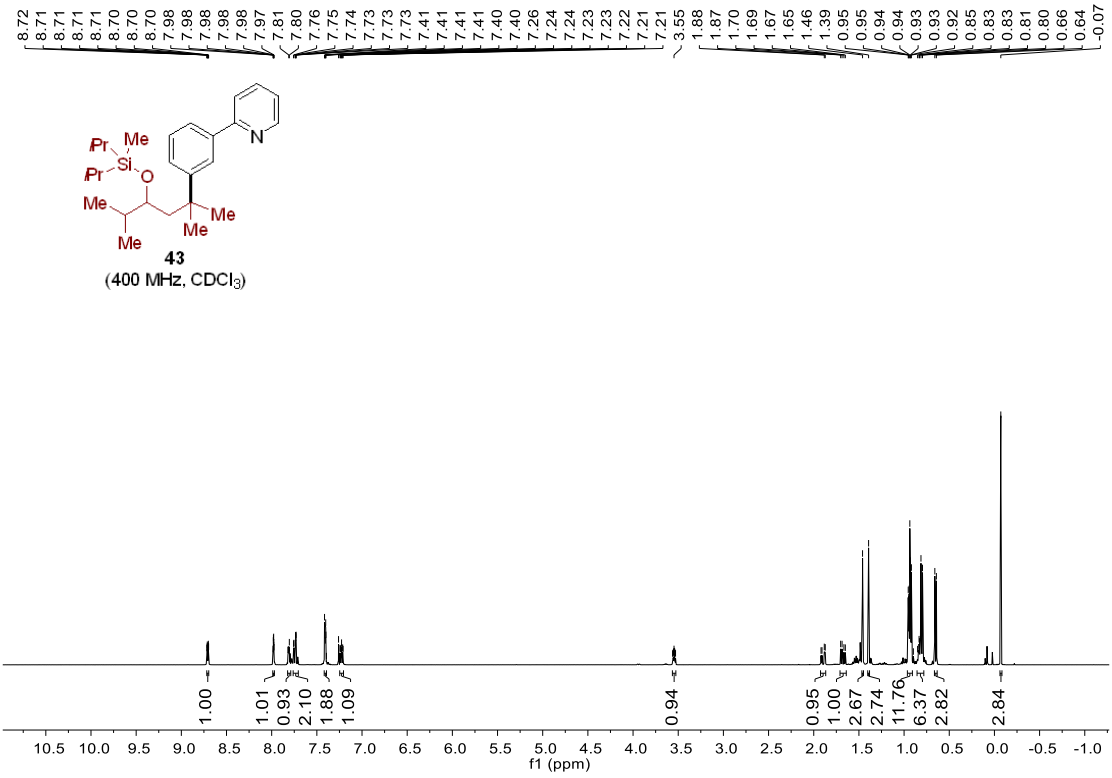

8.71 8.71 8.71 8.70 8.70 8.70 8.70 8.69 8.03 8.03 8.02 7.80 7.80 7.80 7.79 7.78 7.78 7.78 7.78 7.75 7.75 7.73 7.73 7.73 7.73 7.72 7.48 7.46 7.46 7.46 7.45 7.41 7.39 7.37 7.26 7.24 7.23 7.22 7.22 7.21 7.21 7.20 2.08 1.49 1.44 1.41 1.22 1.20 1.14 1.01 1.00 1.00 0.99 0.99 0.98 0.91 0.89 0.87 0.87 0.07
iPr Me iPr Si O N Me Me
40
(400 MHz, CDCl3)
1.00 0.93 3.17 0.91 1.01 1.01 1.87 5.72 3.62 5.71 12.12 2.18 2.79
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

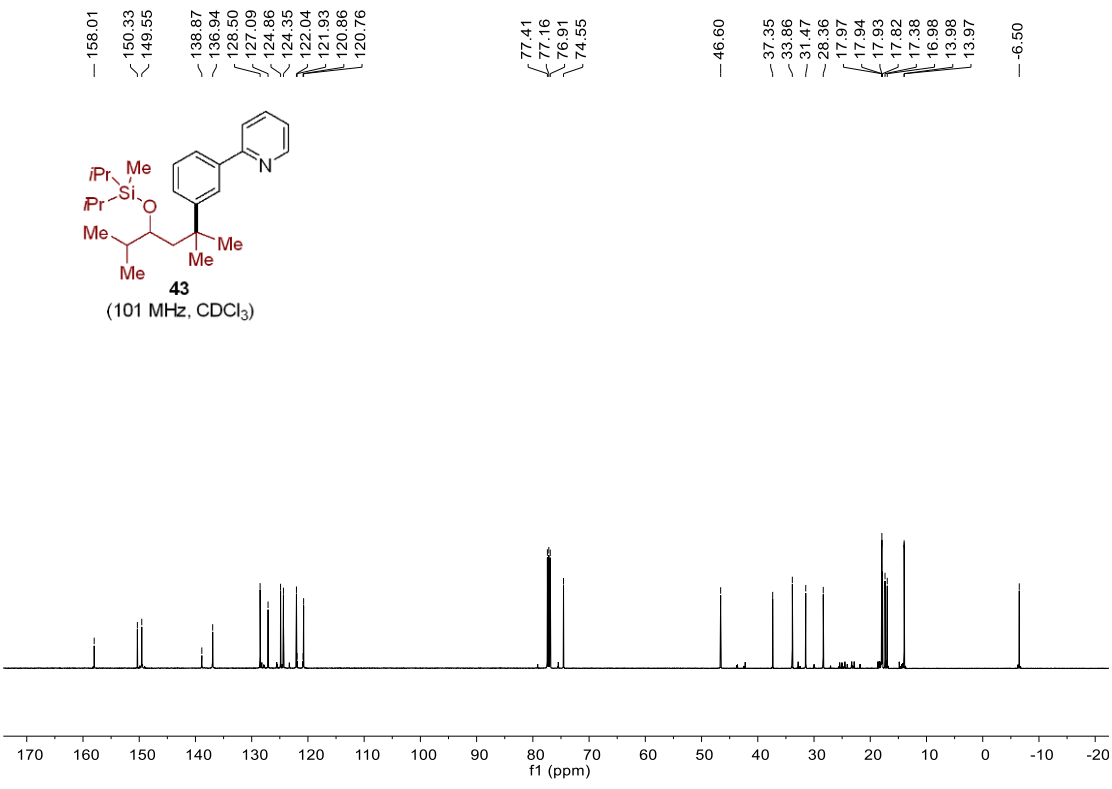

158.17 151.00 149.70 138.90 136.78 128.34 127.13 124.90 124.86 124.21 121.99 120.81 120.74 77.48 77.16 76.84 53.94 39.99 38.02 31.46 25.74 23.32 18.16 18.04 14.91 -3.84
iPr Me iPr Si O N Me Me
40
(101 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

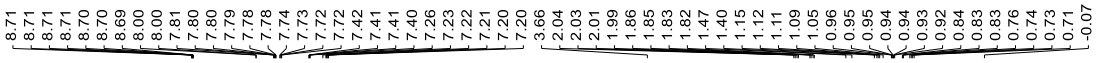

8.71 8.71 8.70 8.70 8.70 8.70 8.69 7.99 7.99 7.99 7.80 7.80 7.80 7.79 7.79 7.79 7.79 7.76 7.74 7.73 7.72 7.71 7.44 7.43 7.41 7.39 7.38 7.26 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 4.01 4.00 3.99 3.98
1.38 1.37 0.99 0.98 0.96 0.94 0.93 0.88 0.87 0.85 0.84 -0.06
iPr Me
iPr Si O
Me
Me Me
N
41
(400 MHz, CDCl3)
1.00 0.97 1.01 2.21 2.00 1.14 0.97 2.98 2.94 15.23 2.42 2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

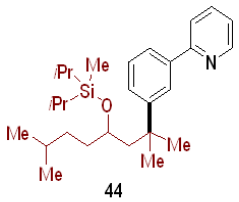

158.27 149.74 148.81 139.04 136.75 128.30 127.74 125.59 124.51 121.98 120.84
77.37 77.16 76.95 76.29
43.57 25.98 23.13 19.27 17.84 17.82 17.80 17.79 17.71 13.94 13.61 -7.21
iPr Me
iPr Si O
Me
Me Me
N
41
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


8.71 8.71 8.70 8.70 8.70 8.70 8.69 7.96 7.96 7.78 7.77 7.73 7.72 7.40 7.40 7.40 7.40 7.39 7.26 7.23 7.22 7.22 7.22 7.21 7.21 3.72 3.71 3.70 3.69 1.78 1.78 1.77 1.77 1.76 1.75 1.66 1.66 1.64 1.63 1.63 1.62 1.61 1.37 1.37 1.25 1.07 1.06 0.96 0.94 0.93 0.92 0.87 0.82 -0.05
iPr Me
iPr Si O
Me
Me Me
N
42
(400 MHz, CDCl3)
1.00 0.99 3.12 1.96 1.06 1.00 1.03 0.99 2.91 3.01 2.28 3.09 12.34 2.37 2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
158.22 150.15 149.69 139.23 136.78 128.57 126.80 124.66 124.28 122.01 120.88 77.37 77.16 76.95 69.20 40.18 37.76 34.96 29.31 29.16 23.72 17.63 17.58 17.57 13.47 13.40 -7.82
iPr Me
iPr Si O
Me
Me Me
N
42
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


8.72 8.71 8.71 8.71 8.71 8.70 8.70 8.70 7.98 7.98 7.98 7.98 7.98 7.97 7.81 7.80 7.76 7.75 7.74 7.73 7.73 7.73 7.41 7.41 7.41 7.41 7.40 7.40 7.26 7.24 7.24 7.23 7.22 7.21 7.21 3.55 1.88 1.87 1.70 1.69 1.67 1.65 1.46 1.39 0.95 0.95 0.94 0.94 0.93 0.93 0.92 0.85 0.83 0.83 0.81 0.80 0.66 0.64 -0.07
N
iPr
Me
Si
iPr
O
Me
Me
Me
Me
43
(400 MHz, CDCl3)
1.00 1.01 0.93 2.10 1.88 1.09 0.94 0.95 1.00 2.67 2.74 11.76 6.37 2.82 2.84
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

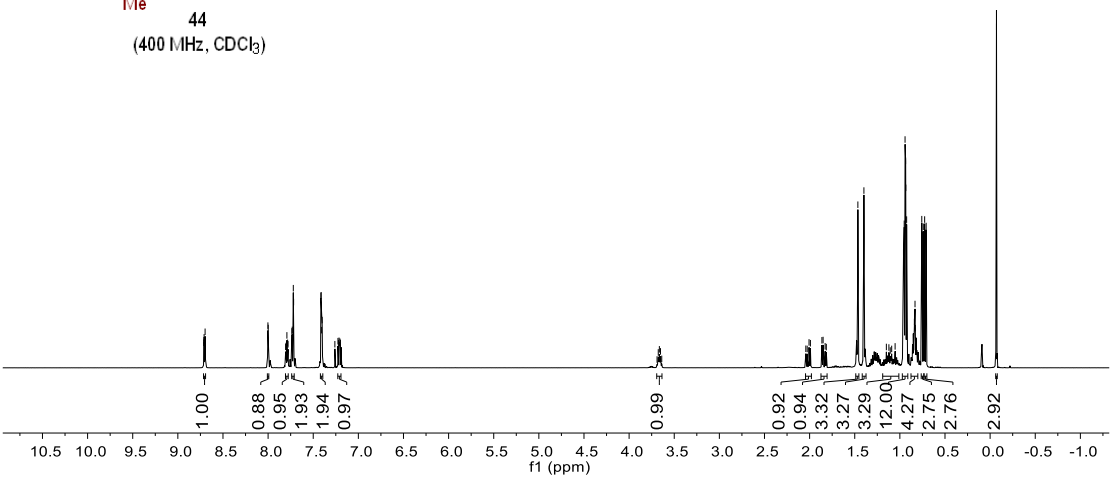

158.01 150.33 149.55 138.87 136.94 128.50 127.09 124.86 124.35 122.04 121.93 120.86 120.76 77.41 77.16 76.91 74.55 46.60 37.35 33.86 31.47 28.36 17.97 17.94 17.93 17.82 17.38 16.98 13.98 13.97 -6.50
N
iPr
Me
Si
iPr
O
Me
Me
Me
Me
43
(101 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

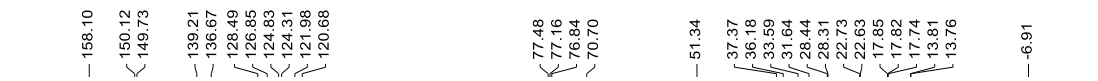


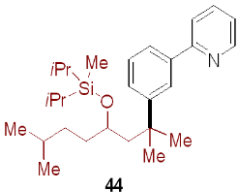


44

(400 MHz, $CDCl_3$)

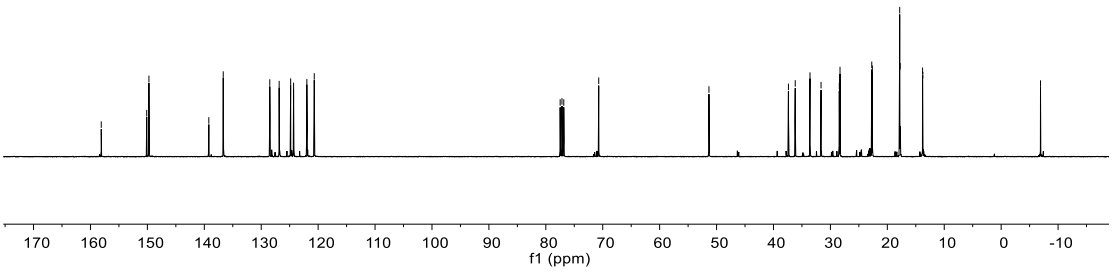


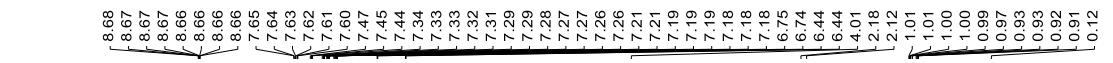


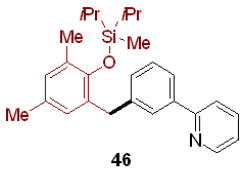


44

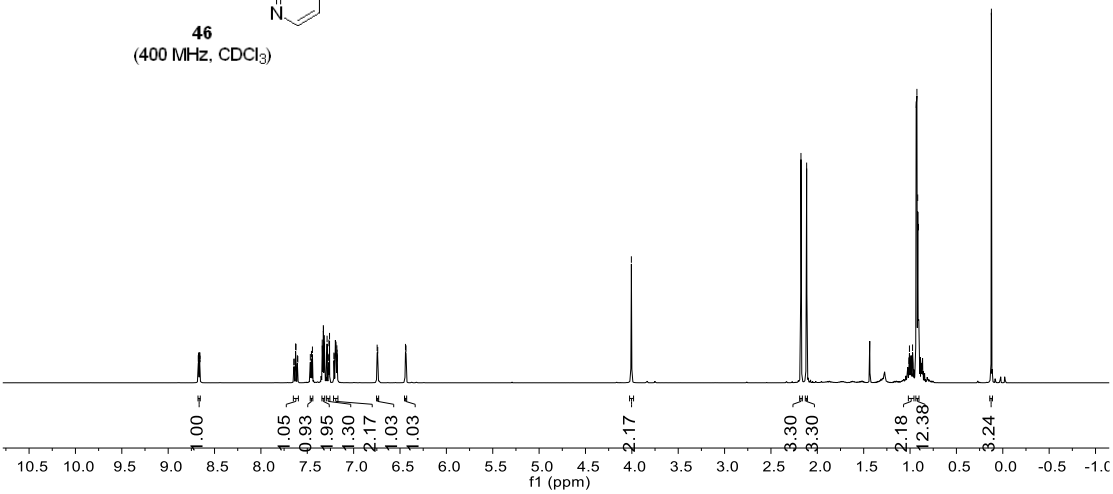
(101 MHz, $CDCl_3$)

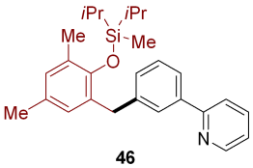




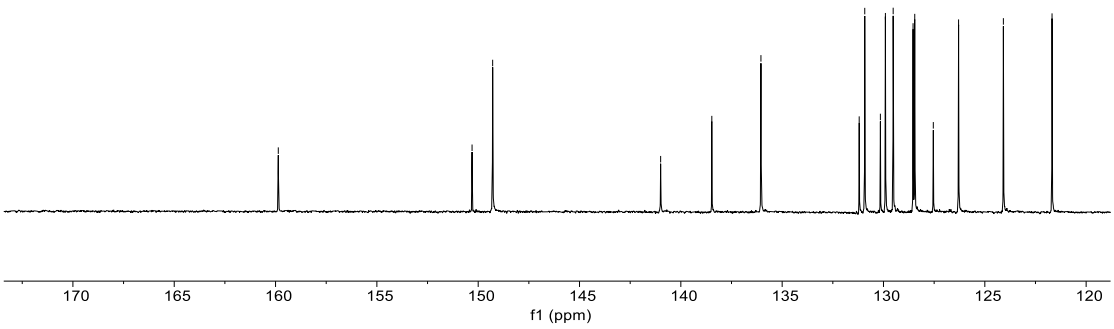


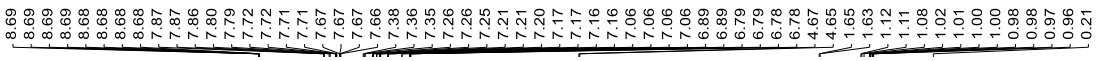
46
(400 MHz, $CDCl_3$)

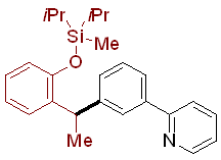




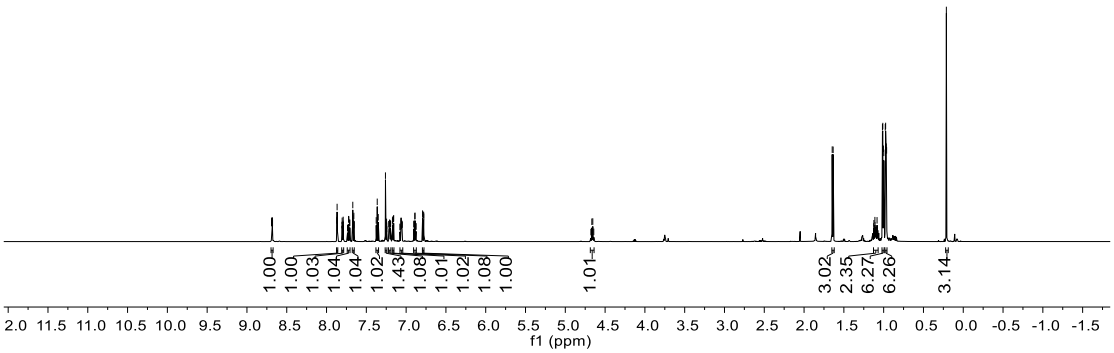
46
(101 MHz, $CDCl_3$)

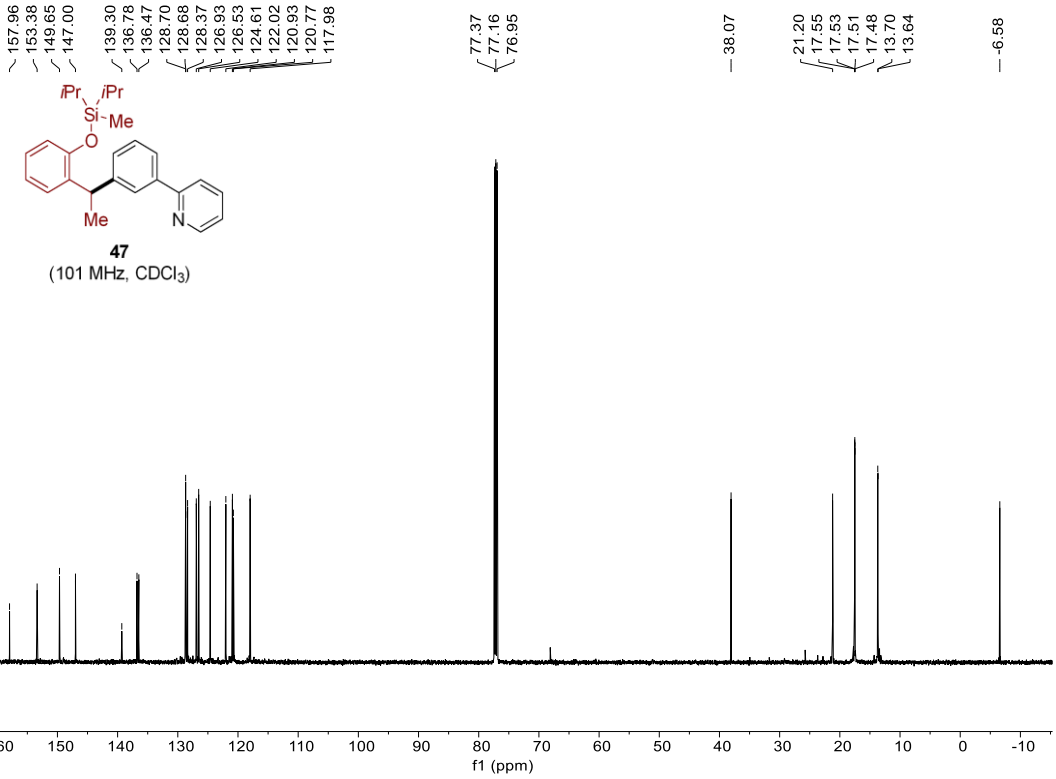




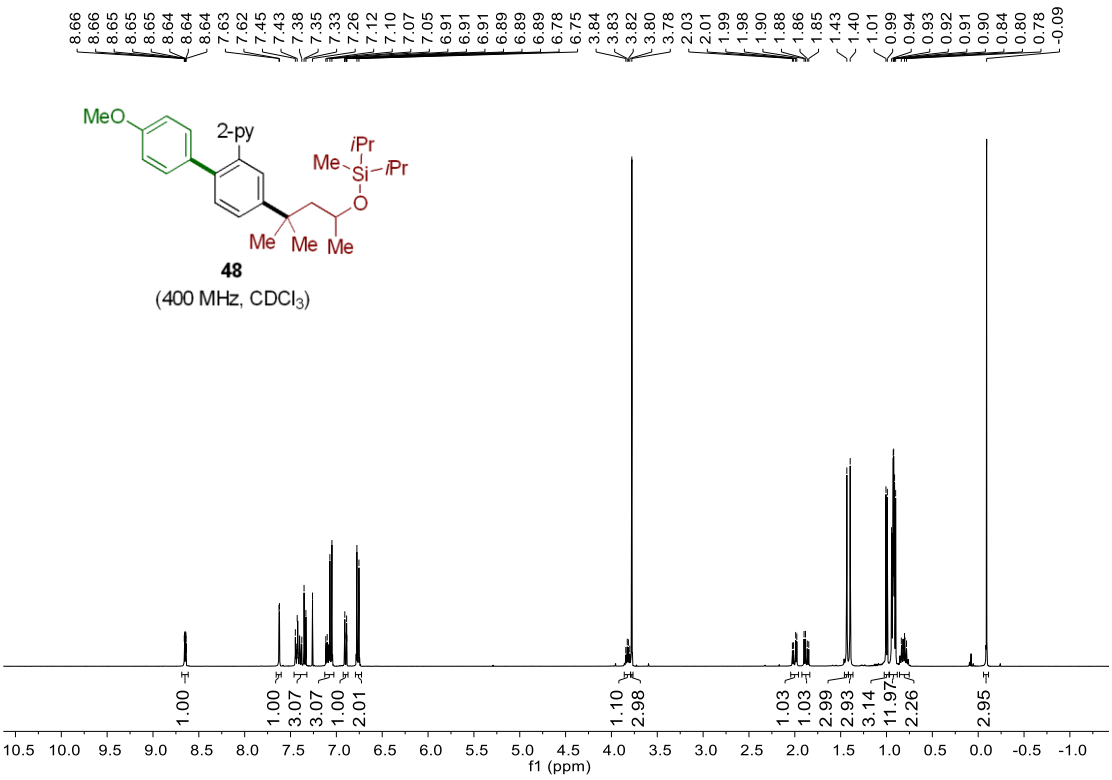


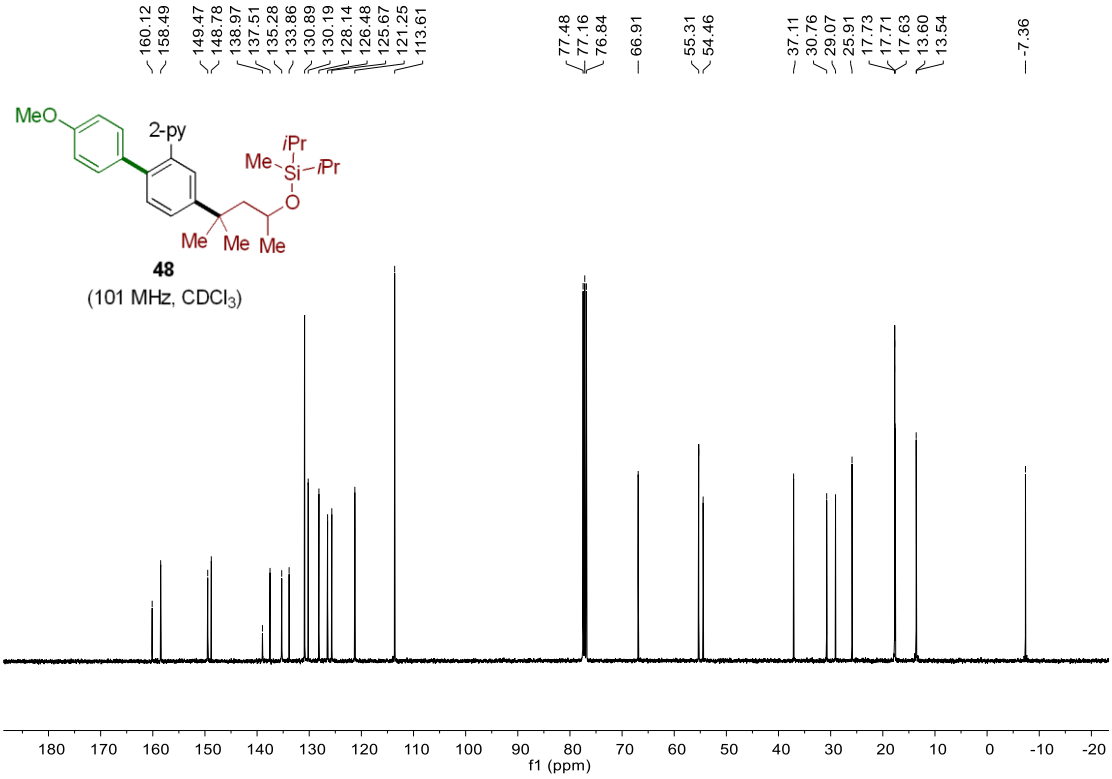
47
(600 MHz, $CDCl_3$)

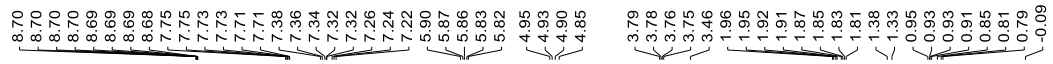


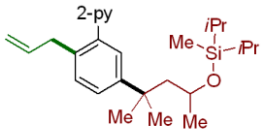


47
(101 MHz, $CDCl_3$)


MeO
2-py
iPr
Me
Si
iPr
O
Me
Me
Me
48
(400 MHz, CDCl3)
f1 (ppm)

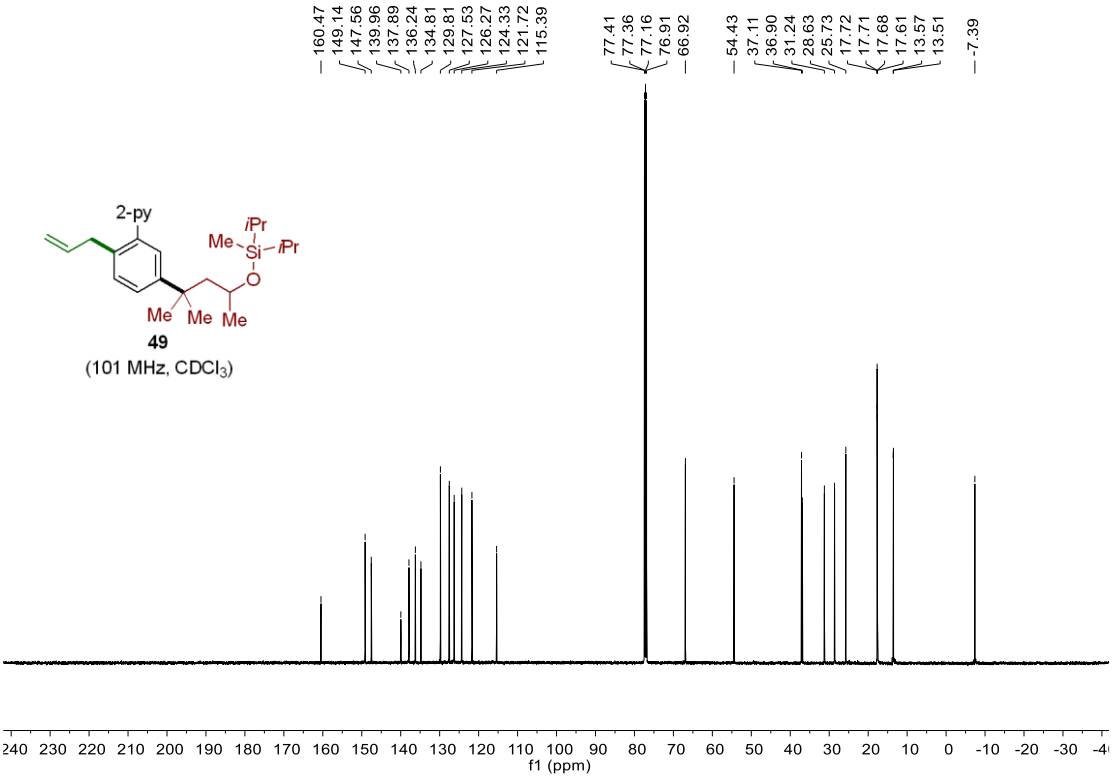

MeO
2-py
iPr
Me
Si
iPr
O
Me
Me
Me
48
(101 MHz, CDCl3)
f1 (ppm)





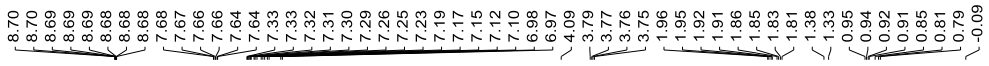
49

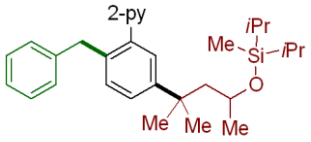
(400 MHz, $CDCl_3$)



49

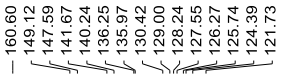
(101 MHz, $CDCl_3$)

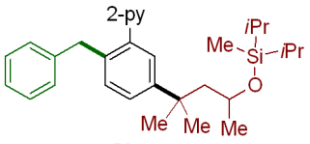




50

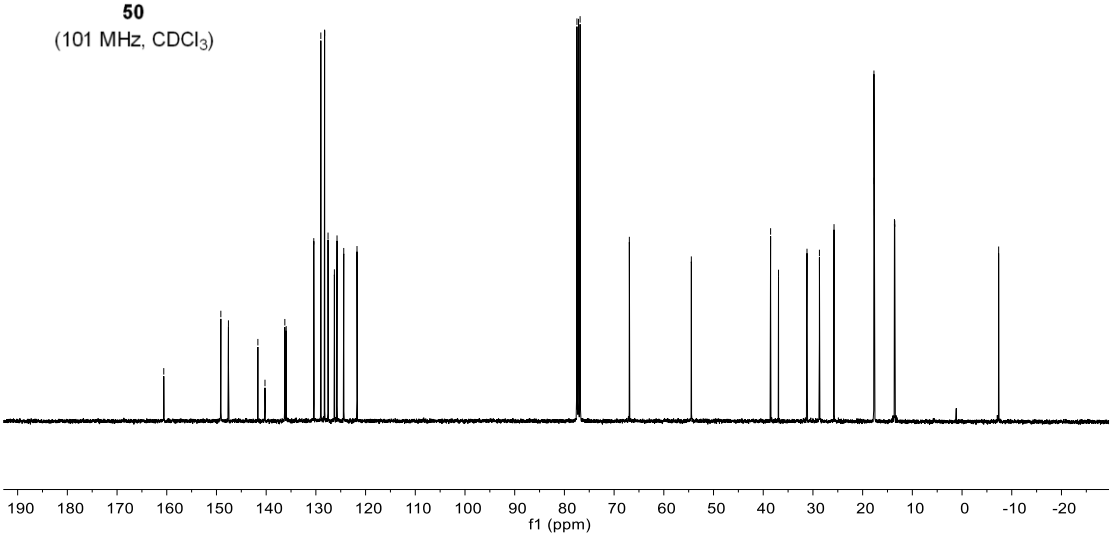
(400 MHz, $CDCl_3$)

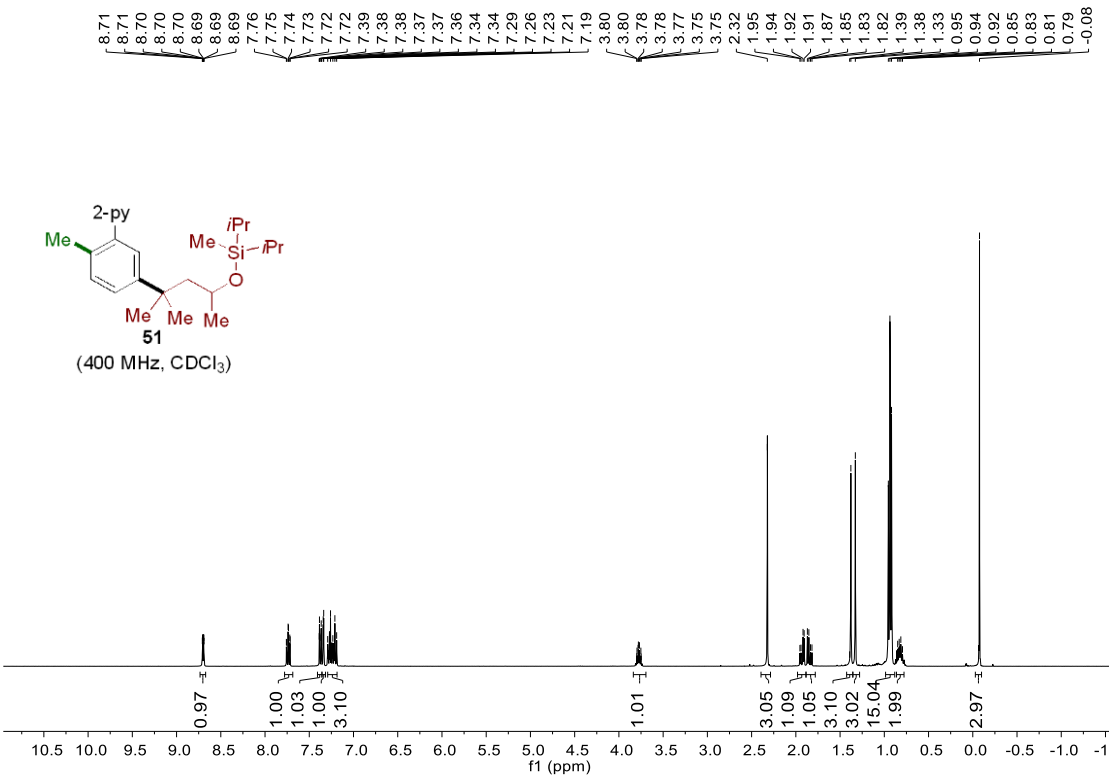


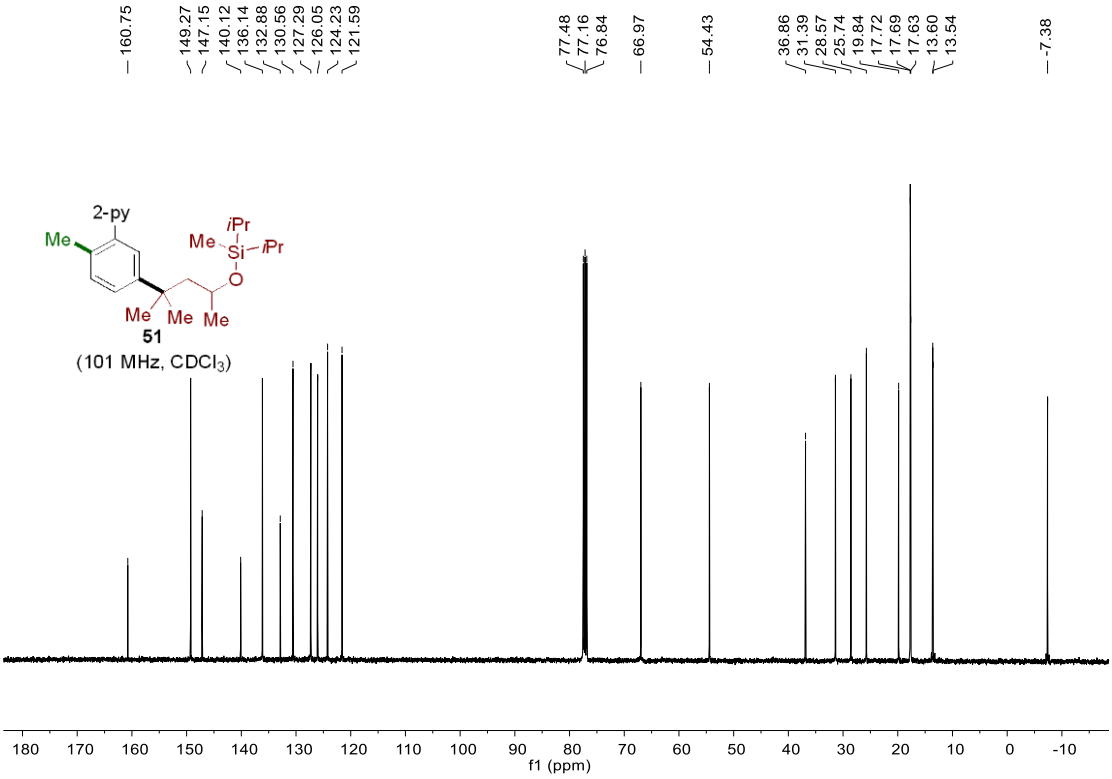


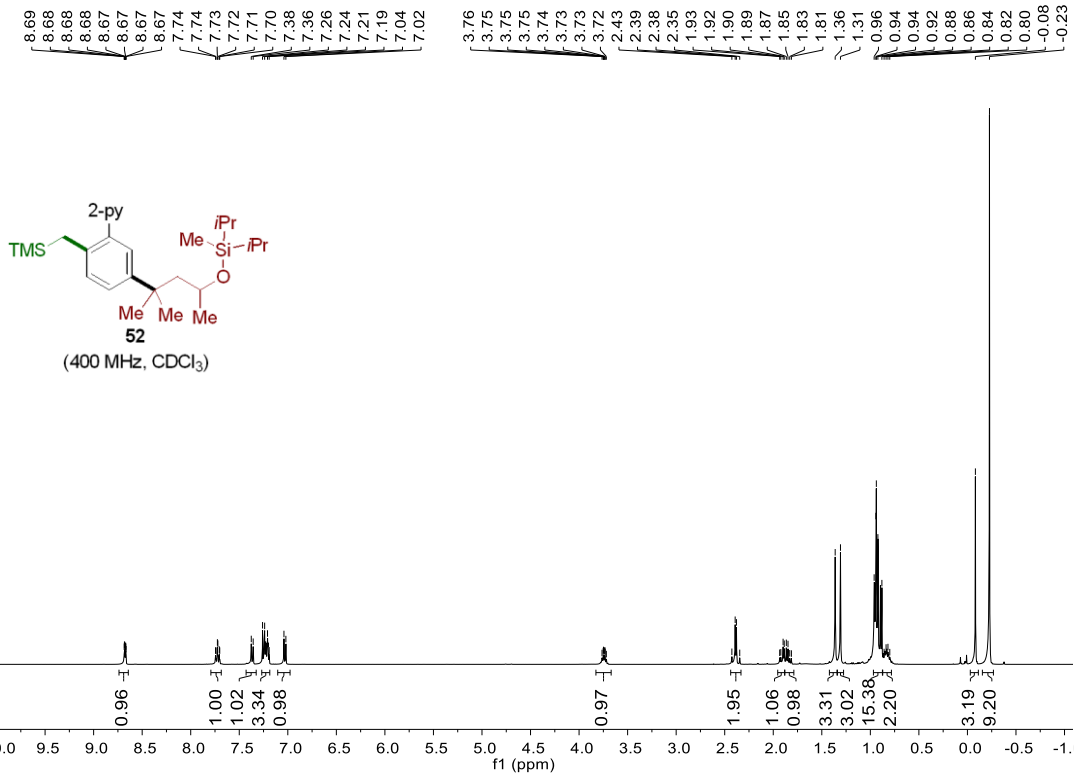
50

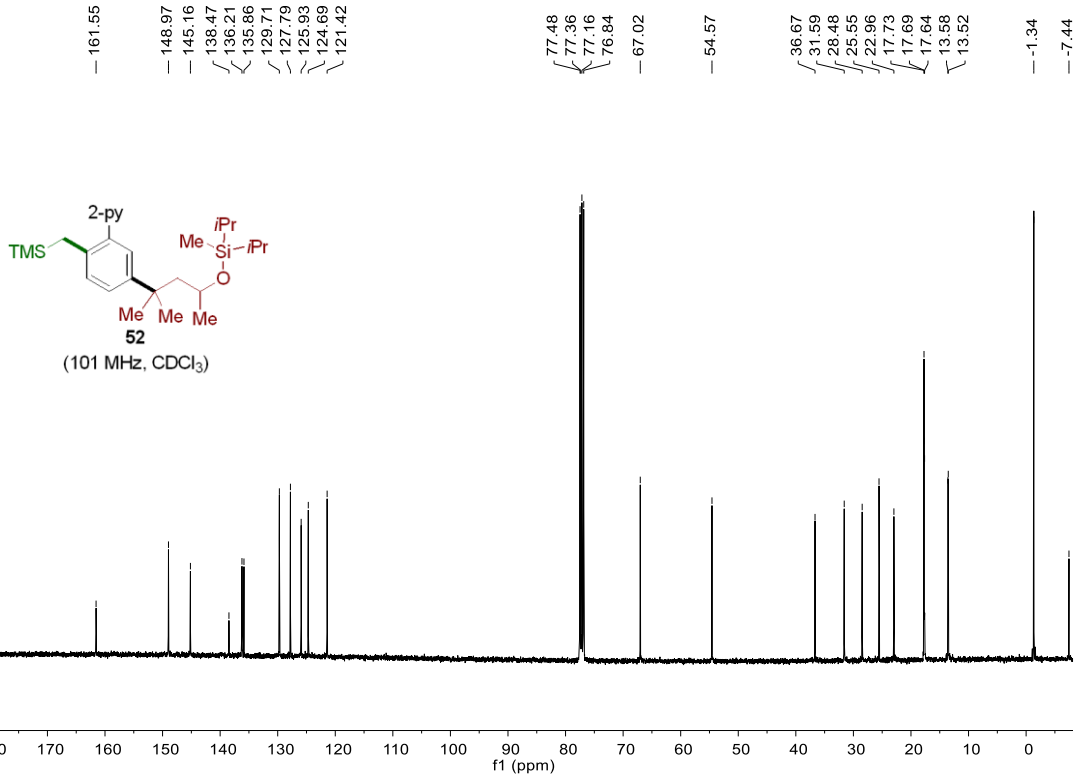
(101 MHz, $CDCl_3$)

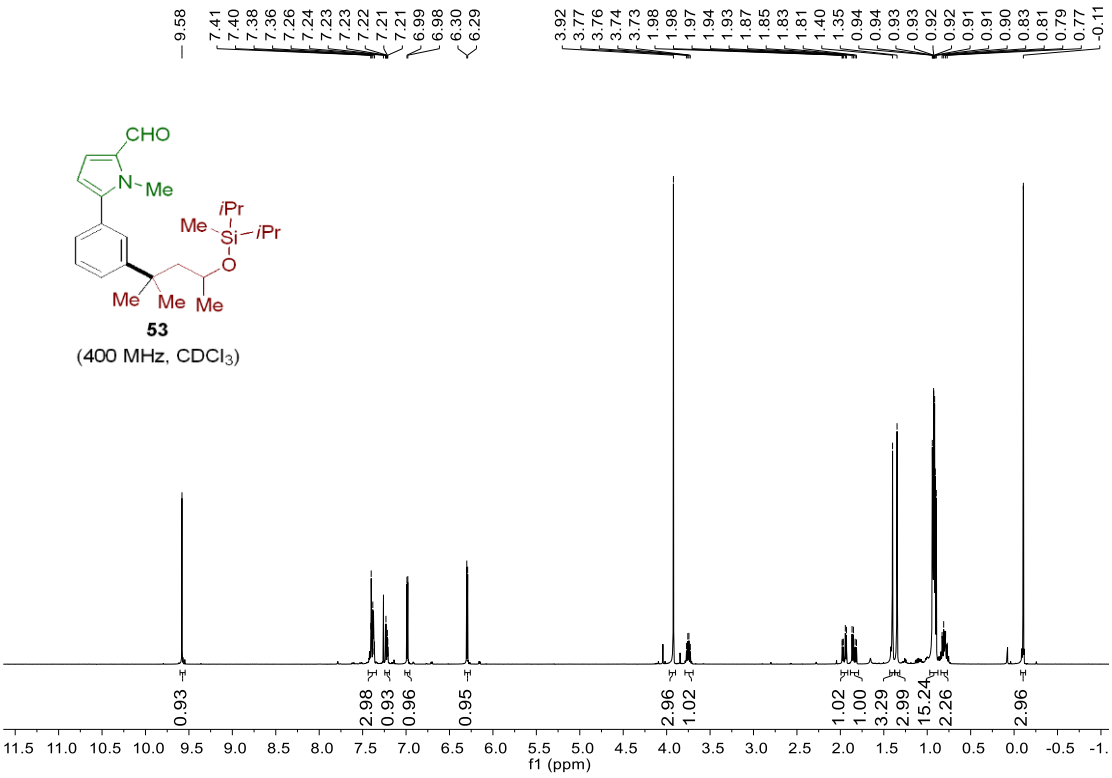


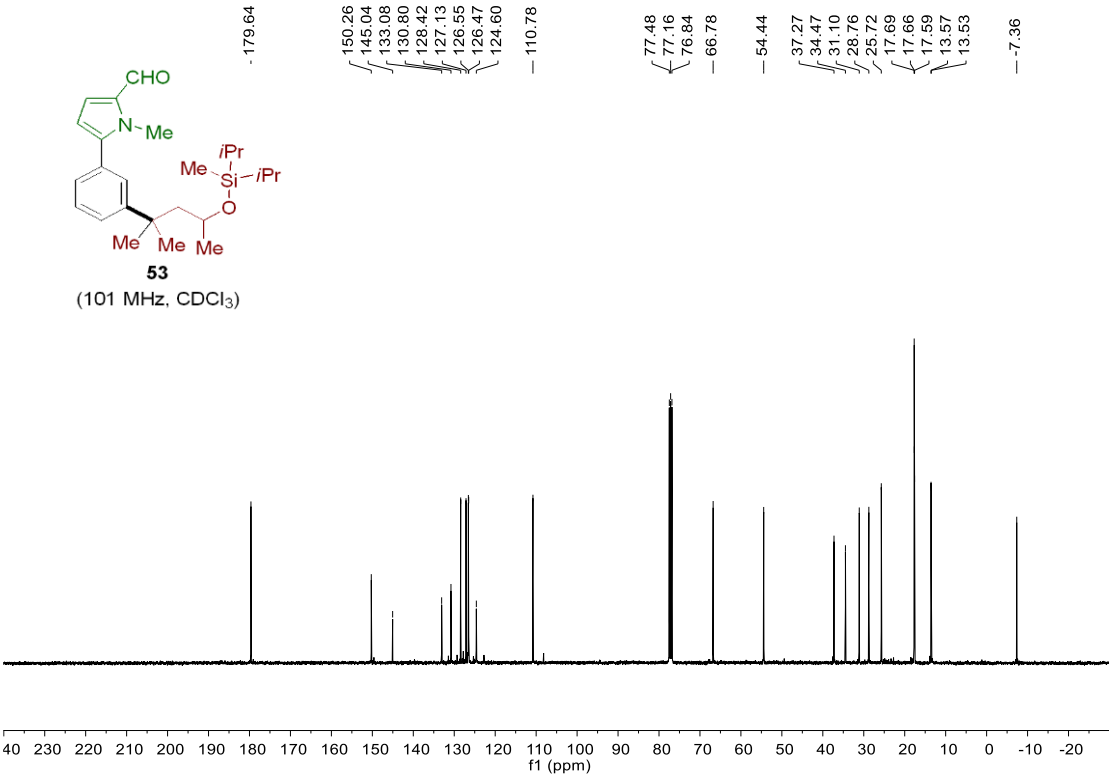

8.71 8.71 8.70 8.70 8.70 8.69 8.69 8.69 7.76 7.75 7.74 7.73 7.72 7.72 7.39 7.38 7.38 7.37 7.37 7.36 7.34 7.34 7.29 7.26 7.23 7.21 7.19 3.80 3.80 3.78 3.78 3.77 3.75 3.75 2.32 1.95 1.94 1.92 1.91 1.87 1.85 1.83 1.82 1.39 1.38 1.33 0.95 0.94 0.92 0.85 0.83 0.81 0.79 -0.08
2-py
Me
iPr
Me
Si
iPr
O
Me Me Me
51
(400 MHz, CDCl3)
0.97 1.00 1.03 1.00 3.10 1.01 3.05 1.09 1.05 3.10 3.02 15.04 1.99 2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

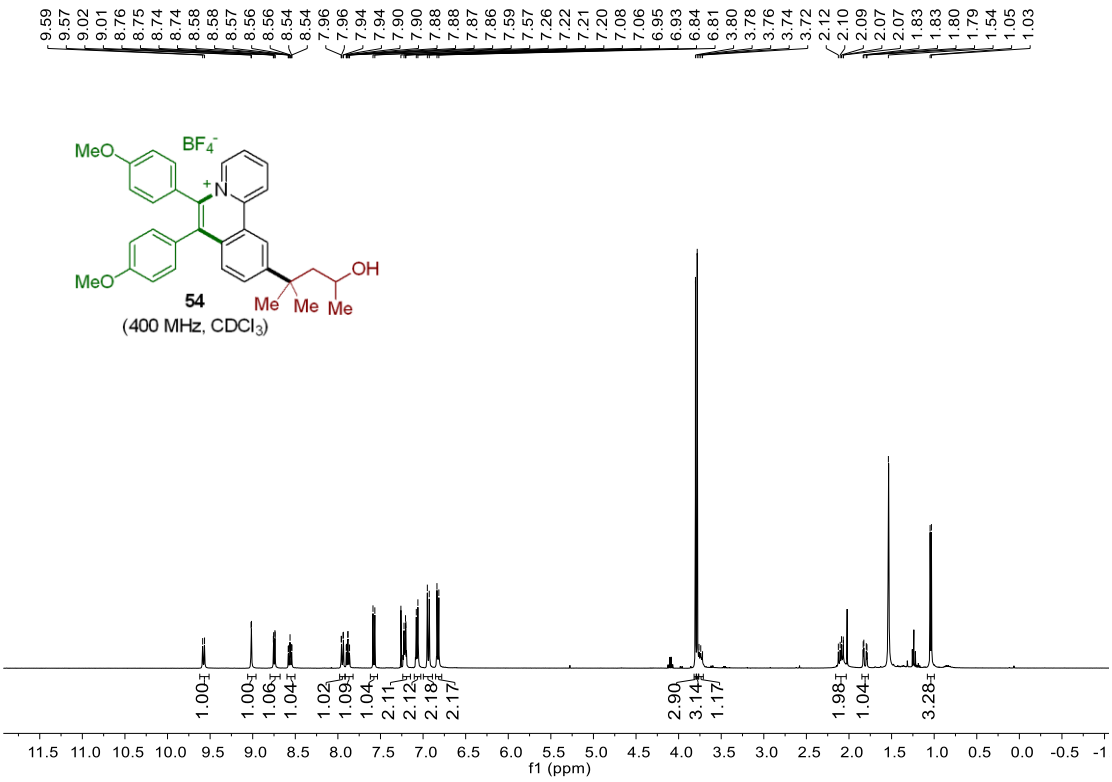

160.75 149.27 147.15 140.12 136.14 132.88 130.56 127.29 126.05 124.23 121.59 77.48 77.16 76.84 66.97 54.43 36.86 31.39 28.57 25.74 19.84 17.72 17.69 17.63 13.60 13.54 -7.38
2-py
Me
iPr
Me
Si
iPr
O
Me Me Me
51
(101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

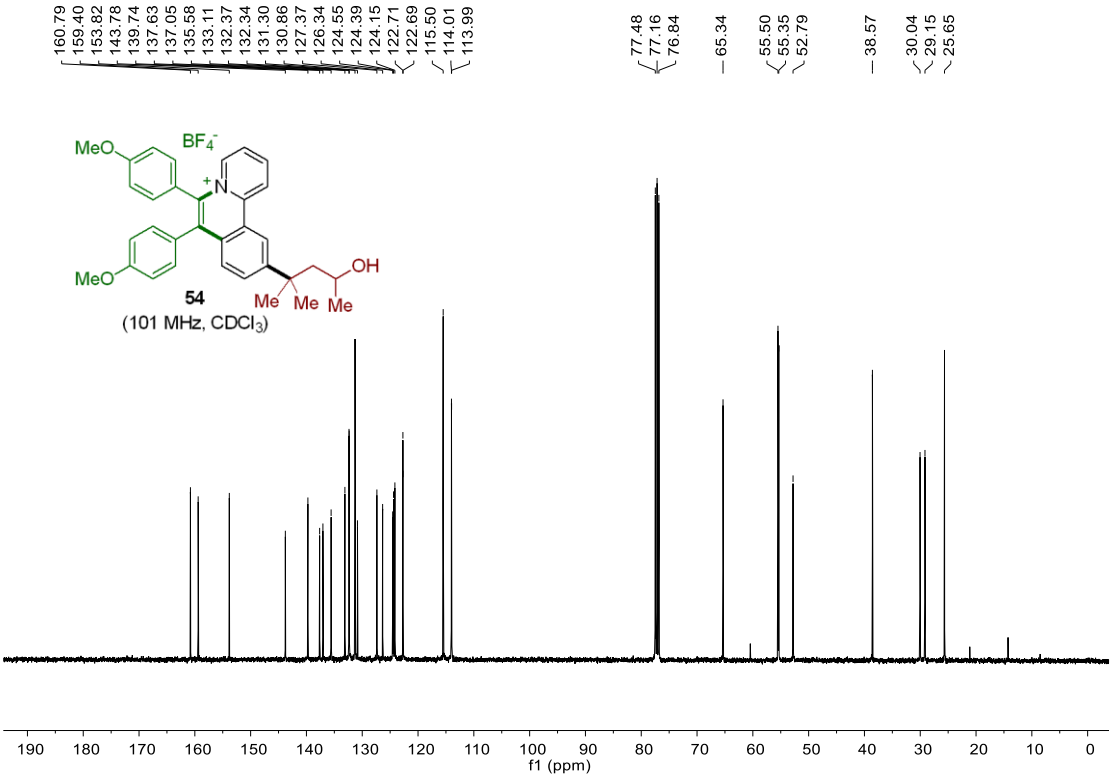

8.69 8.68 8.68 8.68 8.67 8.67 8.67 8.67 7.74 7.74 7.73 7.72 7.71 7.70 7.38 7.36 7.26 7.24 7.21 7.19 7.04 7.02
3.76 3.75 3.75 3.75 3.74 3.73 3.73 3.72 2.43 2.39 2.38 2.35 1.93 1.92 1.90 1.89 1.87 1.85 1.83 1.81 1.36 1.31 0.96 0.94 0.94 0.92 0.88 0.86 0.84 0.82 0.80 -0.08 -0.23
2-py
TMS
iPr
Me
Si
iPr
O
Me Me Me
52
(400 MHz, CDCl3)
0.96 1.00 1.02 3.34 0.98 0.97 1.95 1.06 0.98 3.31 3.02 15.38 2.20 3.19 9.20
f1 (ppm)

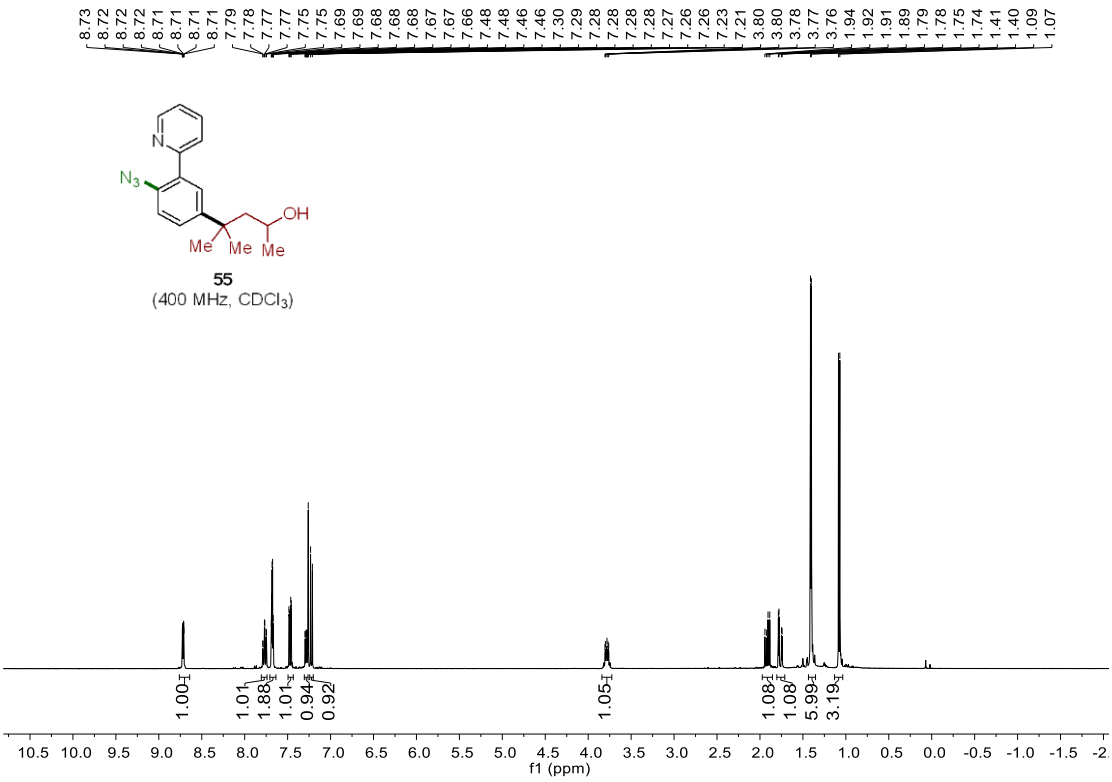

161.55 148.97 145.16 138.47 136.21 135.86 129.71 127.79 125.93 124.69 121.42
77.48 77.36 77.16 76.84 67.02 54.57 36.67 31.59 28.48 25.55 22.96 17.73 17.69 17.64 13.58 13.52 -1.34 -7.44
2-py
TMS
iPr
Me
Si
iPr
O
Me Me Me
52
(101 MHz, CDCl3)
f1 (ppm)

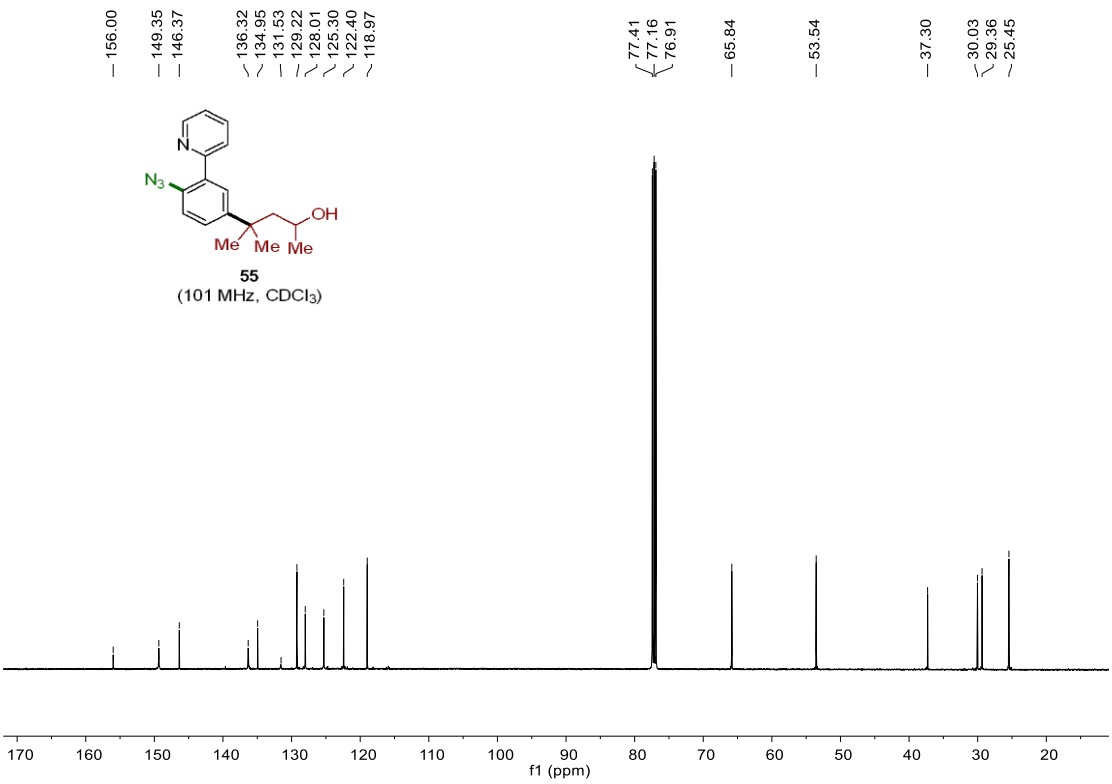

9.58
7.41
7.40
7.38
7.36
7.26
7.24
7.23
7.23
7.22
7.21
7.21
6.99
6.98
6.30
6.29
3.92
3.77
3.76
3.74
3.73
1.98
1.98
1.97
1.94
1.93
1.87
1.85
1.83
1.81
1.40
1.35
0.94
0.94
0.93
0.93
0.92
0.92
0.91
0.91
0.90
0.83
0.81
0.79
0.77
-0.11
CHO
N
Me
iPr
Me
Si
iPr
O
Me
Me
Me
53
(400 MHz, CDCl3)
0.93
2.98
0.93
0.96
0.95
2.96
1.02
1.02
1.00
3.29
2.99
15.24
2.26
2.96
f1 (ppm)

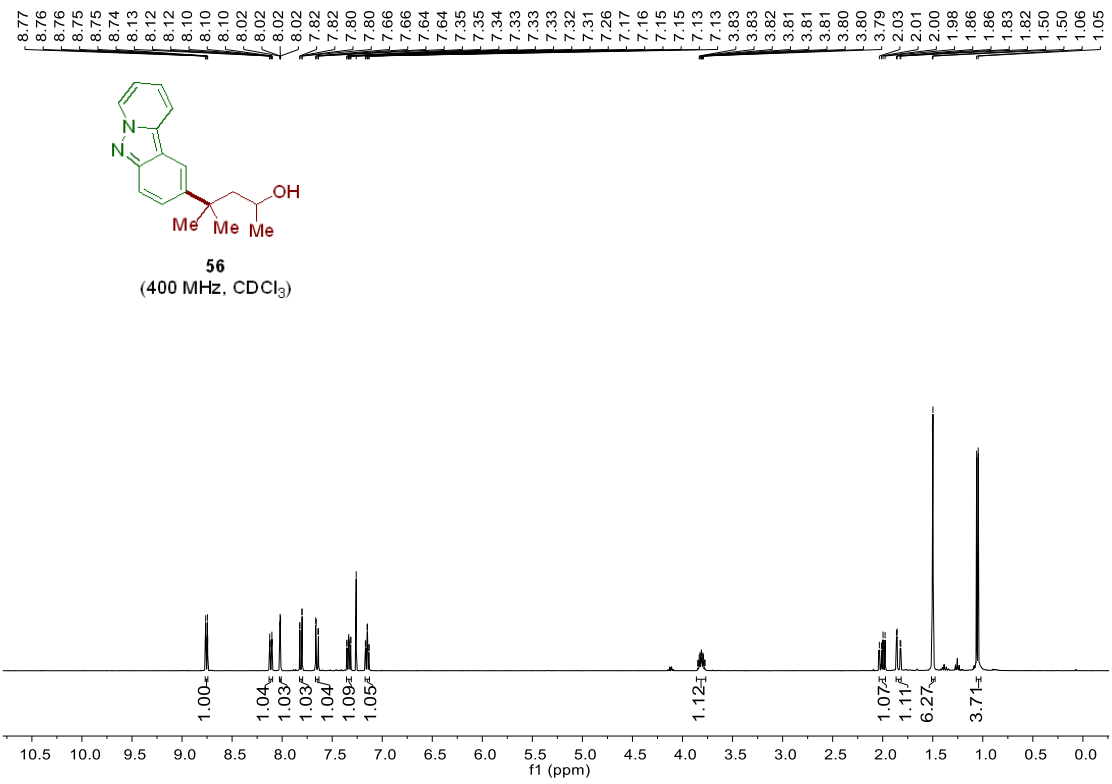

179.64
150.26
145.04
133.08
130.80
128.42
127.13
126.55
126.47
124.60
110.78
77.48
77.16
76.84
66.78
54.44
37.27
34.47
31.10
28.76
25.72
17.69
17.66
17.59
13.57
13.53
7.36
CHO
N
Me
iPr
Me
Si
iPr
O
Me
Me
Me
53
(101 MHz, CDCl3)
f1 (ppm)


9.59 9.57 9.02 9.01 8.76 8.75 8.74 8.74 8.58 8.58 8.57 8.56 8.56 8.54 8.54 7.96 7.96 7.94 7.94 7.90 7.90 7.88 7.88 7.87 7.86 7.59 7.57 7.26 7.22 7.21 7.20 7.08 7.06 6.95 6.93 6.84 6.81 3.80 3.78 3.76 3.74 3.72 2.12 2.10 2.09 2.07 2.07 1.83 1.83 1.80 1.79 1.54 1.05 1.03
MeO
BF4-
N+
MeO
OH
Me Me Me
54
(400 MHz, CDCl3)
1.00 1.00 1.06 1.04 1.02 1.09 1.04 2.11 2.12 2.18 2.17 2.90 3.14 1.17 1.98 1.04 3.28
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

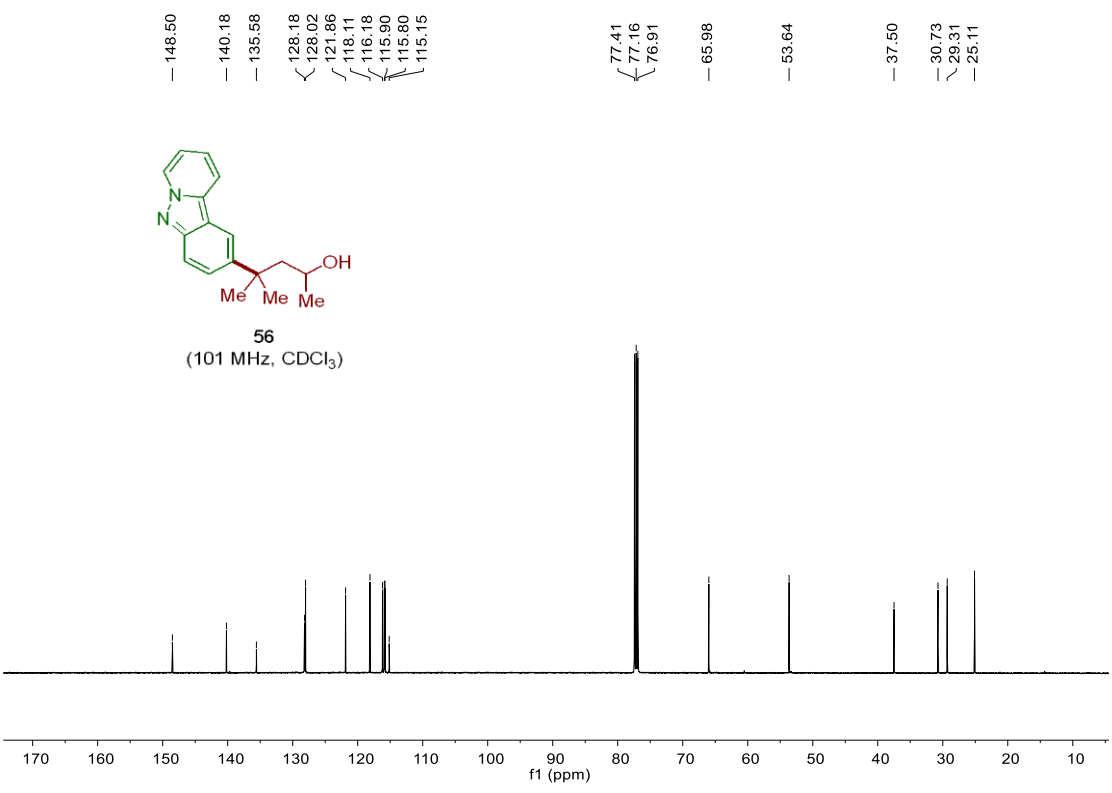

160.79 159.40 153.82 143.78 139.74 137.63 137.05 135.58 133.11 132.37 132.34 131.30 130.86 127.37 126.34 124.55 124.39 124.15 122.71 122.69 115.50 114.01 113.99
77.48 77.16 76.84 65.34 55.50 55.35 52.79 38.57 30.04 29.15 25.65
MeO
BF4-
N+
MeO
OH
Me Me Me
54
(101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.73 8.72 8.72 8.72 8.71 8.71 8.71 8.71 7.79 7.78 7.77 7.77 7.75 7.75 7.69 7.69 7.68 7.68 7.68 7.67 7.67 7.66 7.48 7.48 7.46 7.46 7.30 7.29 7.28 7.28 7.28 7.28 7.27 7.26 7.26 7.23 7.21 3.80 3.80 3.78 3.77 3.76 1.94 1.92 1.91 1.89 1.79 1.78 1.75 1.74 1.41 1.40 1.09 1.07
N
N3
OH
Me Me Me
55
(400 MHz, CDCl3)
1.00 1.01 1.88 1.01 0.94 0.92 1.05 1.08 1.08 5.99 3.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

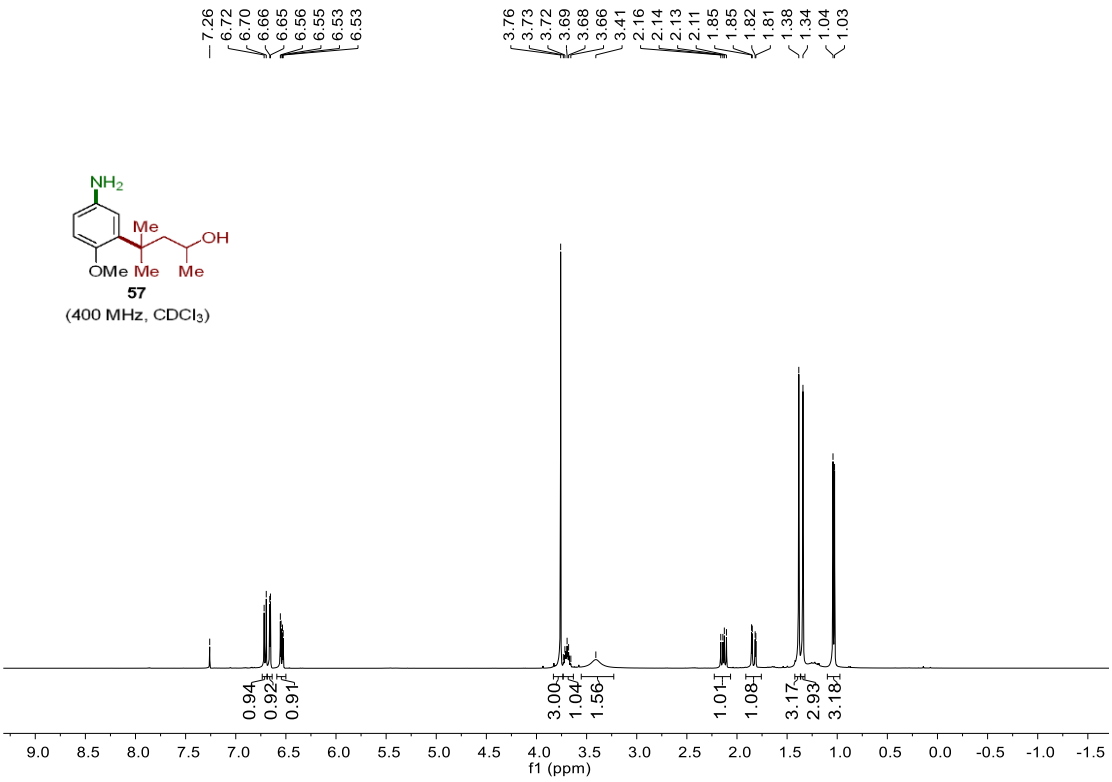

156.00 149.35 146.37 136.32 134.95 131.53 129.22 128.01 125.30 122.40 118.97 77.41 77.16 76.91 65.84 53.54 37.30 30.03 29.36 25.45
N
N3
OH
Me Me Me
55
(101 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

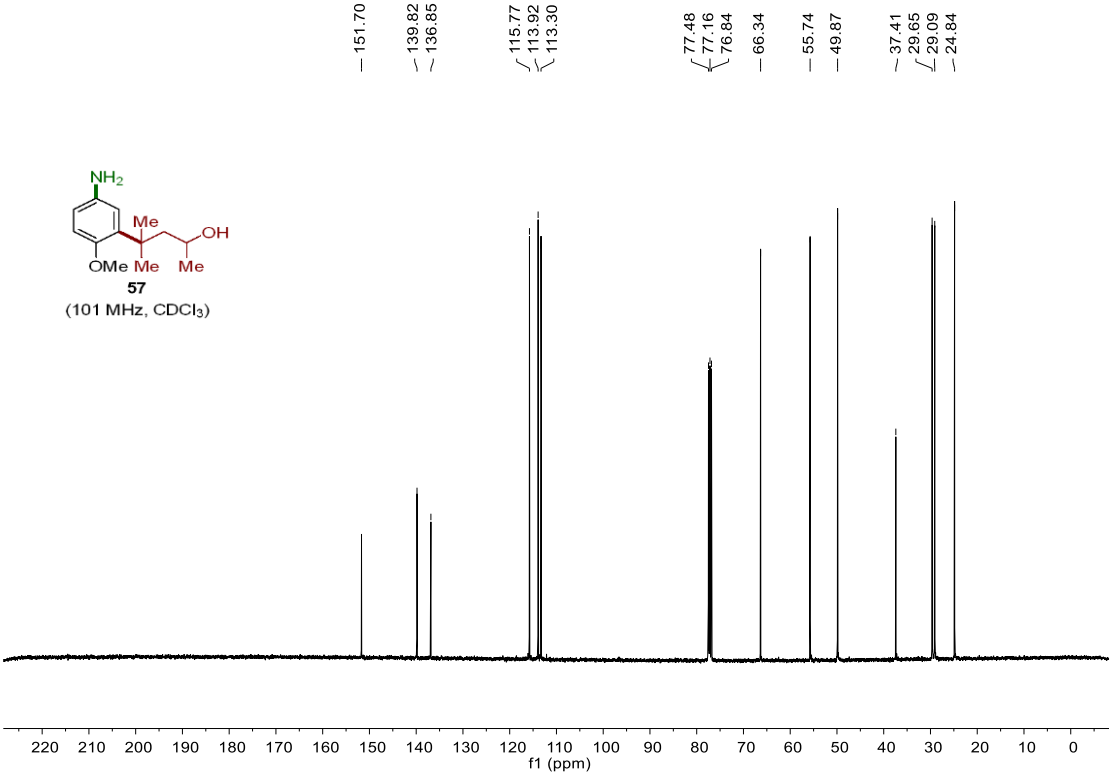


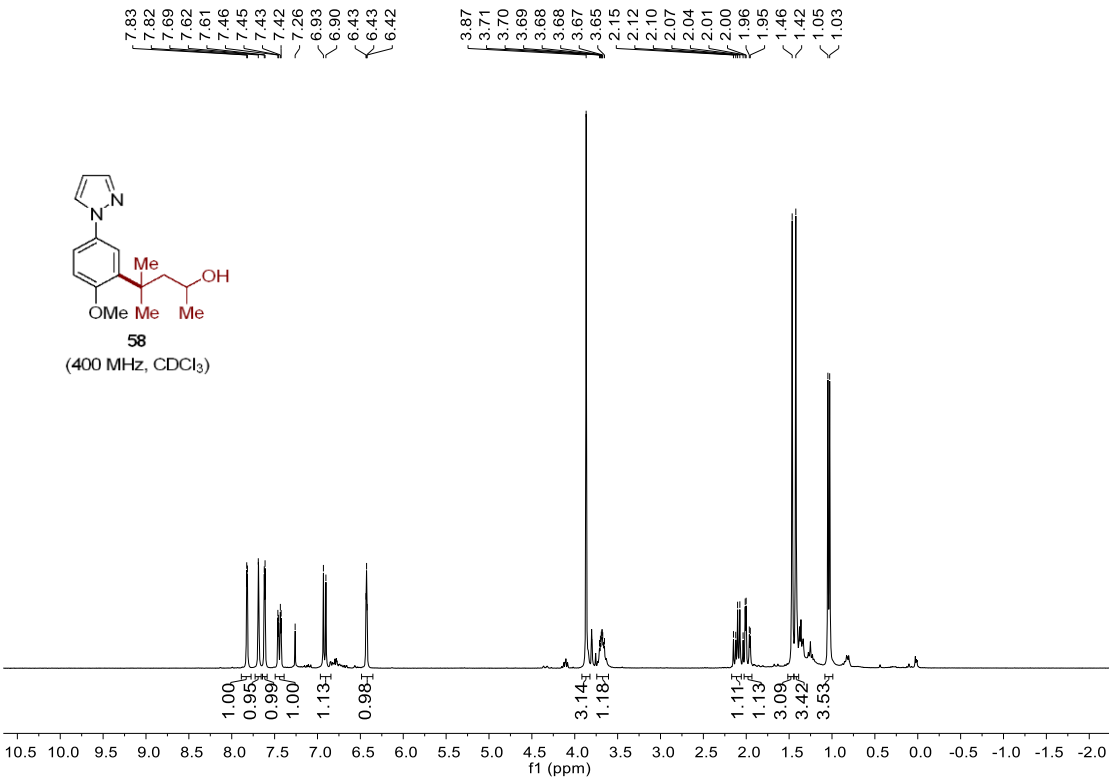
56
(400 MHz, $CDCl_3$)

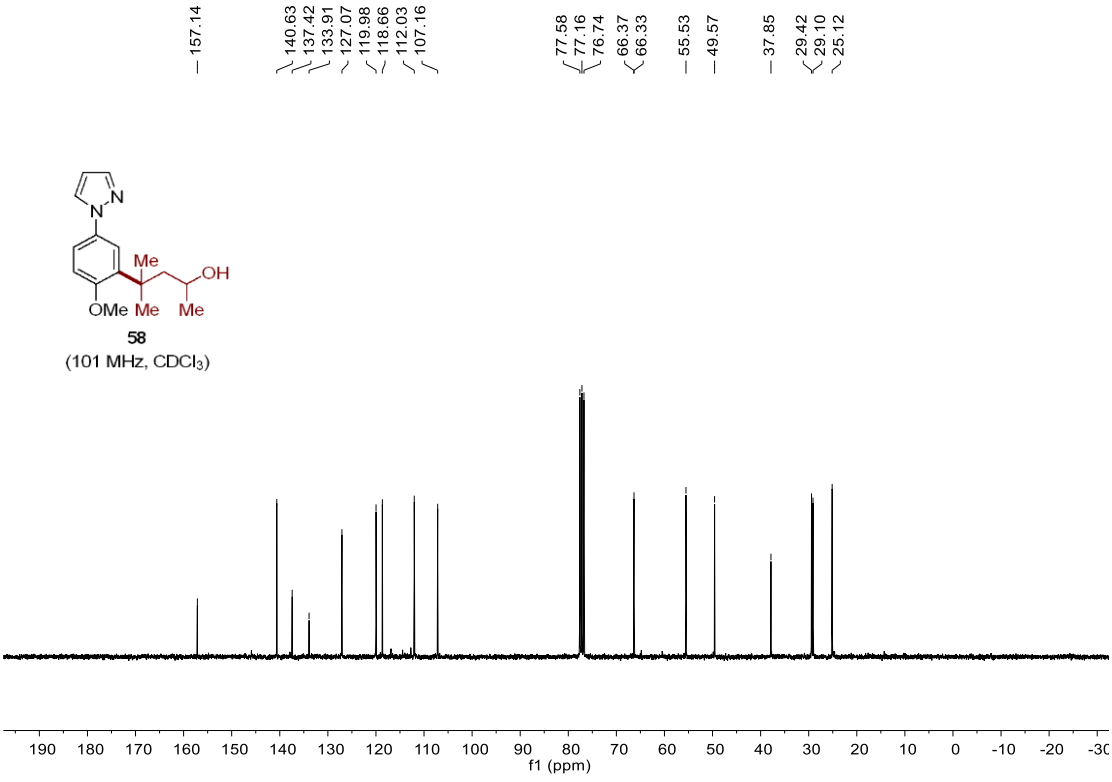


56
(101 MHz, $CDCl_3$)


7.26
6.72
6.70
6.66
6.65
6.56
6.55
6.53
6.53
3.76
3.73
3.72
3.69
3.68
3.66
3.41
2.16
2.14
2.13
2.11
1.85
1.85
1.82
1.81
1.38
1.34
1.04
1.03
NH2
Me
OH
OMe Me Me
57
(400 MHz, CDCl3)
0.94
0.92
0.91
3.00
1.04
1.56
1.01
1.08
3.17
2.93
3.18
f1 (ppm)


151.70
139.82
136.85
115.77
113.92
113.30
77.48
77.16
76.84
66.34
55.74
49.87
37.41
29.65
29.09
24.84
NH2
Me
OH
OMe Me Me
57
(101 MHz, CDCl3)
f1 (ppm)


7.83
7.82
7.69
7.62
7.61
7.46
7.45
7.43
7.42
7.26
6.93
6.90
6.43
6.43
6.42
3.87
3.71
3.70
3.69
3.68
3.68
3.67
3.65
2.15
2.12
2.10
2.07
2.04
2.01
2.00
1.96
1.95
1.46
1.42
1.05
1.03
Me
OH
OMe Me Me
58
(400 MHz, CDCl3)
1.00
0.95
0.99
1.00
1.13
0.98
3.14
1.18
1.11
1.13
3.09
3.42
3.53
f1 (ppm)


157.14
140.63
137.42
133.91
127.07
119.98
118.66
112.03
107.16
77.58
77.16
76.74
66.37
66.33
55.53
49.57
37.85
29.42
29.10
25.12
Me
OH
OMe Me Me
58
(101 MHz, CDCl3)
f1 (ppm)