Surface Functionalization of Silica by Si-H Activation of Hydrosilanes

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1. Chemicals:

Tris(pentafluorophenyl)borane (denoted as **Cat**, Sigma-Aldrich Co. Ltd. USA), benzyldimethylsilane (**15**, Sigma-Aldrich Co. Ltd. USA), phenyldimethylsilane (**16**, Sigma-Aldrich Co. Ltd. USA), *t*-butyldimetylsilane (**20**, Sigma-Aldrich Co. Ltd. USA), (*N,N*-dimethylamino)dimethylsilane (**21**, Gelest Co. Ltd. USA), allyldimethylsilane (**23**, Gelest Co. Ltd. USA), polymethylhydrosiloxane (**24**, M_n = 1700-3200, trimethylsilyl terminated, Sigma-Aldrich Co. Ltd. USA), *n*-octadecyldimethylsilane (**25**, Gelest Co. Ltd. USA), dimethylchlorosilane (Sigma-Aldrich Co. Ltd. USA) and microscope glass slide were purchased from commercial sources. Mesoporous silica (MCM-41) **1** was purchased from Sigma-Aldrich Co. Ltd. USA, and SBA-15[1],macroporous monolithic silica[2] with 5 μm pore size (specific surface area of 150 $m^2 g^{-1}$) and (3-aminopropyl)dimethylsilane (**5**)[3] were synthesized by published procedures.

2. Characterizations:

Liquid-state ^1H and ^{13}C NMR measurements of synthesized hydrosilanes were performed using an ECX-400 spectrometer (JEOL Ltd. (Japan)). The exact mass of the newly synthesized hydrosilanes were measured by using a high resolution mass spectrometer (Xevo G2-S-Q-Tof, Waters, USA).

Solid-state ^1H-^{13}C/^1H-^{29}Si CPMAS NMR experiments were performed in a magnetic field of 7 T using an OPENCORE NMR spectrometer and a 5 mm MAS probe. The carrier frequencies were 299.52 MHz, 75.323 MHz, and 59.507 MHz for ^1H, ^{13}C and ^{29}Si, respectively. The contact time and the spinning frequency were, respectively, 10 ms and 5 kHz for ^{29}Si, and 1 ms and 8 kHz for ^{13}C.[4]

Elemental analyses of grafted samples were performed at the Center for Organic Elemental Microanalysis in Kyoto University using YANACO MT-3 and MT-6 analyzers.

The FT-IR spectra of the grafted samples were recorded on an FT-IR spectrometer (FT/IR-4100, JASCO Corp. (Japan)) using ground samples that were mixed with KBr.

Contact angle of water droplet on modified and unmodified microscopic glass slide was measured by using a contact angle meter (LSE-ME 1, Nick Corp. (Japan)).

3. General procedure for grafting of hydrosilanes:

Prior to grafting, 0.1 g of mesoporous silica (**1**) was dried under vacuum at 200 °C, for 12 h in order to eliminate adsorbed water. Then it was cooled to room temperature under nitrogen atmosphere, followed by an addition of 3 mL of dichloromethane (DCM) and 0.5 mmol of hydrosilane. This mixture was then stirred gently for 2 min followed by an addition of 2.56 mg (0.005 mmol) of **Cat**. Immediately after the addition of **Cat** hydrogen evolution was observed, which is finished within a few minutes (1-4 min). After reacted for exactly 5 min (after an addition of **Cat**) the resultant mixture was filtered and washed rigorously by DCM and hexane to eliminate physisorbed hydrosilanes. Then the samples were dried under vacuum. After drying, no physisorbed hydrosilanes were detected by FT-IR and solid-state ^{13}C and ^{29}Si NMR measurements. (The nitrogen atmosphere during the grafting is recommended, but not required).

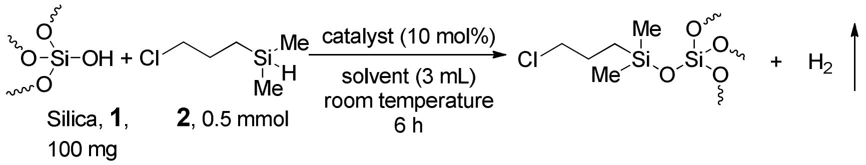
***Grafting on microscopy glass slide*:** Initially the silanols on the glass surface were activated with piranha solution. Then it was washed and dried in air. This dried glass slide was then immersed in DCM solution containing hydrosilane and catalyst **Cat** for 2 min. After that the slide was washed with DCM and hexane in order to eliminate physisorbed and unreacted hydrosilanes, followed by drying in air at room temperature.

***Grafting on 5 μm spherical silica gel beads for chromatographic column packing*:** Silica gel beads were generously supplied by GL Sciences, Inc. According to the product test sheet, silica gels are characterized as ; specific surface area: 414 m^2 g^{-1}, specific pore volume: 1.1 mL g^{-1}, median pore diameter: 10 nm.

A new procedure is given for the reaction of octadecyldimethylsilane with the silica gel (dried at 200 °C for 12 h under vacuum). To a suspension of the dried silica gel (19 g) and octadecyldimethylsilane (14.82 g, 47.5 mmol) in 300 mL of dehydrated dichloromethane was added **Cat**. (243 mg, 0.48 mmol) and stirred at rt. After hydrogen evolution ceased (5 min), the modified silica gel was filtered, thoroughly rinsed with dichloromethane, and dried in vacuo at 100 °C.

4. Catalyst and Si-H*n* optimization:

(a) Catalyst Optimization:



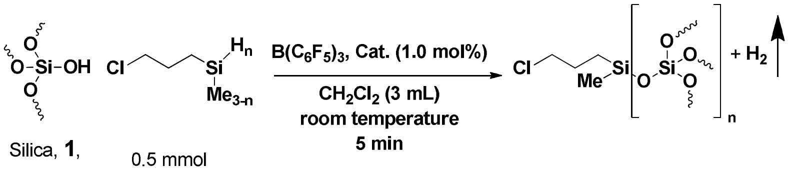
Silica, **1**, 100 mg

2, 0.5 mmol

entry	catalyst	solvent	hydrogen formation	loading /mmol g^{-1}
1	$Zn(OAc)_2$[a]	THF	N. D.	0.00
2	$Zn(EtH)_2$[a]	THF	N. D.	0.00
3	$Sc(OTf)_3$[b]	CH_3CN	N. D.	0.00
4	$Al(OTf)_3$	CH_2Cl_2	N. D.	0.00
5	$Bi(OTf)_3$	CH_2Cl_2	N. D.	0.00
6	$BiCl_3$[c]	CH_3CN	N. D.	0.00
7	$ZrCl_4$	CH_2Cl_2	N. D.	0.00
8	$InBr_3$[d]	THF	N. D.	0.00
9	$[RuCl_2(p\text{-cymene})]_2$[e]	CH_3CN	N. D.	0.00
10	$PdCl_2$	THF	slow	0.00[f]
11	Co_2CO_8	CH_2Cl_2	slow	0.53
12	BF_3	CH_2Cl_2	N. D.	0.00

[a] ref. 5 [b] ref. 6 [c] ref. 7 [d] ref 8 [e] ref. 9 [f] Changed in silica color from white to black due to reduction of $PdCl_2$ to its corresponding nanoparticles by hydrosilanes and as-formed hydrogen.

(b) Si-H$_n$ Optimization:



Silica, **1**, 100 mg

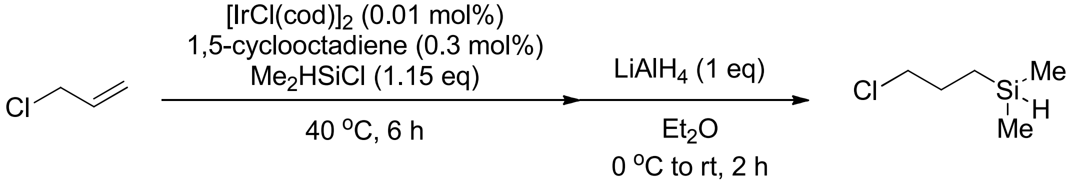
0.5 mmol

n	Loading /mmolg^{-1}
1	1.67
2[a]	1.72

[a] *The hydrosilane was synthesized using published procedure as in,* Missaghi, M. N.; Downing, C. M.; Kung, M. C.; Kung, H. H. *Organometallics*, **2008**, *27*, 6364.

5. Synthesis and characterization of hydrosilanes

(3-chloropropyl)dimethylsilane (2) [CAS Registry Number: 18157-31-8]

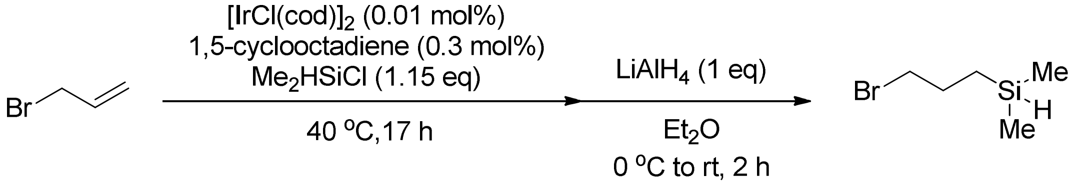


(**2**)

To a mixture of $[IrCl(cod)]_2$ (2.6 mg, 0.003 mmol Ir), allyl chloride (3.25 mL, 40 mmol), and 1,5-cyclooctadiene (10 μL, 0.08 mmol) was added chlorodimethylsilane (5.18 mL, 46 mmol) and the reaction mixture was stirred at 40 °C for 6 h. The resulting solution was distilled under reduced pressure to give chloro(3-chloropropyl)dimethylsilane (6293 mg, 36.8 mmol, yield 92 %). It was then subjected to reduction by $LiAlH_4$ (36.8 mmol).[10] After reduction the resultant mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ in ice cooled bath followed by filtration through a pad of Celite with CH_2Cl_2. The obtained clear solution was distilled under reduced pressure to give (3-chloropropyl)dimethylsiane (**2**) (4484 mg, 32.8 mmol) in 89% yield.

^{1}H NMR ($CDCl_3$) δ = 3.85-3.90 (m, 1H), 3.50-3.54 (t, J = 7.2 Hz, 2H), 1.78-1.85 (m, 2H), 0.68-0.73 (m, 2H), 0.09-0.10 (d, J = 4.0 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.46, 11.92, 28.16, 47.79

(3-bromopropyl)dimethylsilane (3) [CAS Registry Number: 88760-69-4]



(**3**)

To a mixture containing $[IrCl(cod)]_2$ (2.6 mg, 0.003 mmol Ir), allyl bromide (3.49 mL, 40 mmol), and 1,5-cyclooctadiene (10 μL, 0.08 mmol) was added chlorodimethylsilane (5.18 mL, 46 mmol and the reaction mixture was stirred at 40 °C for 6 h. The resulting solution was distilled under reduced pressure to give chloro(3-bromopropyl)dimethylsilane (6443 mg, 35.6 mmol, yield 89 %). It was then subjected to reduction by $LiAlH_4$ (1352 mg, 35.6 mmol). After reduction the resultant mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ in ice cooled bath followed by filtration through a pad of Celite with CH_2Cl_2. The obtained clear solution was distilled under reduced pressure to give (3-bromoropropyl)dimethylsiane (**2**) (6449 mg, 33.5 mmol) in 94% yield.

^{1}H NMR ($CDCl_3$) δ = 3.85-3.90 (m, 1H), 3.39-3.43 (t, J = 6.8 Hz, 2H), 1.86-1.93 (m, 2H), 0.68-0.73 (m, 2H), 0.09-0.10 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.46, 13.48, 28.41, 36.87

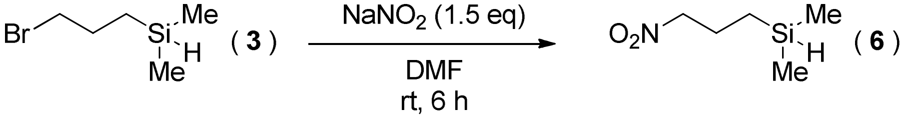
(3-azidepropyl)dimethylsilane (4)

To a solution of sodium azide (1170 mg, 18.0 mmol) in DMF (24 mL) was added (3-bromopropyl)dimethylsilane (**3**) (2172 mg, 12 mmol) and the mixture was stirred at 60 °C for 12 h. After the reaction mixture was cooled to room temperature, distilled water was added and extracted with pentane. The organic layer was washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded almost pure (3-azidepropyl)dimethylsilane (**4**) (1681 mg, 11.7 mmol) in 98% yield. This compound was used next reactions without further purification.

^{1}H NMR ($CDCl_3$) δ = 3.85-3.90 (m, 1H), 3.24-3.28 (t, J = 6.8 Hz, 2H), 1.61-1.69 (m, 2H), 0.62-0.67 (m, 2H), 0.09-0.10 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.44, 11.44, 24.23, 54.25

HRMS (ESI+): *m/z* calcd for $C_5H_{13}N_3Si$ 143.0829, found 143.0879.

(3-nitropropyl)dimethylsilane (6)

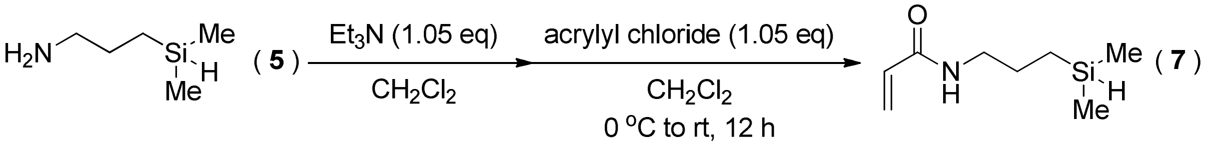


To a solution of sodium nitrite (556 mg, 8.05 mmol) in DMF (28 mL) was added (3-bromopropyl)dimethylsilane (**3**) (1267 mg, 7.0 mmol) and the mixture was stirred at room temperature for 6 h. To the reaction mixture was added distilled water and extracted with Et_2O. The organic layer was washed with brine. After drying over Na_2SO_4, organic solvent was removed under reduced pressure. The residue was purified with silica gel chlomathography (hexane) to give (3-nitropropyl)dimethylsilane (**6**) (649 mg, 4.34 mmol) in 62% yield.

^{1}H NMR ($CDCl_3$) δ = 4.36-4.40 (t, J = 7.2 Hz, 2H), 3.87-3.92 (m, 1H), 2.02-2.10 (m, 2H), 0.62-0.66 (m, 2H), 0.11-0.12 (d, J = 3.6 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.60, 10.93, 23.11, 78.22.

HRMS (APCI+): *m/z* calcd for $C_5H_{13}NO_2NaSi$ $[M+Na]^+$ 170.0613, found 170.0613.

[3-(dimethylsilyl)propyl]acrylamide (7)

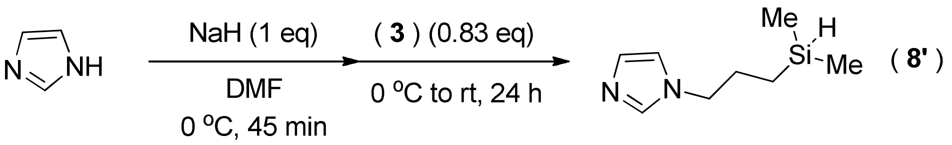


To a solution of (3-aminopropyl)dimethylsilane (**5**) (585 mg, 5.0 mmol) and Et_3N (531 mg, 5.25 mmol) in CH_2Cl_2 (4 mL) was added dropwise acryloyl chloride (475 mg, 5.25 mmol) in CH_2Cl_2 (20 mL) at 0 ^oC. The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was washed with brine and dried over Na_2SO_4. Removal of solvent under reduced pressure afforded [3-(dimethylsilyl)propyl]acrylamide (**7**) (795 mg, 5 mmol) quantitatively.

^{1}H NMR ($CDCl_3$) δ = 6.26-6.30 (dd, J = 2.0, 16.8 Hz, 1H), 6.05-6.12 (m, 1H), 5.66 (bs, 1H), 5.62-5.65 (dd, J = 1.2, 10 Hz, 1H), 3.84-3.89 (m, 1H), 3.31-3.36 (q, J = 7.2 Hz, 2H), 1.55-1.62 (m, 2H), 0.58-0.63 (m, 2H), 0.07-0.08 (d, J = 4.0 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.41, 11.51, 24.79, 42.50, 126.44, 131.05, 165.57

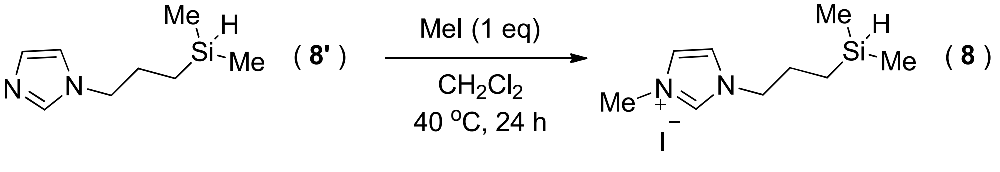
HRMS (ESI+): *m/z* calcd for $C_8H_{16}NOSi$ $[M-H]^+$ 170.1001, found 170.1006.

1-[3-(dimethylsilyl)propyl]-3-methylimidazolium iodide (8)



To a solution of sodium hydride (144 mg, 6.0 mmol) in DMF (24 mL) was slowly added imidazole (408 mg, 6.0 mmol) at 0 ^oC. The mixture was stirred at the same temperature for 45 min before (3-bromopopyl)dimethylsilane (**3**) (905 mg, 5.0 mmol) was added. The mixture was further stirred at room temperature for 24 h. The reaction was quenched with distilled water and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. The organic solvent was removed in vacuum and the resulting mixture was purified with silica gel chromatography (EtOAc/hexane=3/1) to give 1-[3-(dimethylsilyl)propyl]imidazole (**8'**) (781 mg, 4.7 mmol) in 93% yield.

^{1}H NMR ($CDCl_3$) δ = 7.47 (s, 1H), 7.06 (s, 1H), 6.91 (s, 1H), 3.91-3.94 (t, J = 7.6 Hz, 2H), 3.83-3.89 (m, 1H), 1.88 (bs, 1H), 1.77-1.85 (m, 2H), 0.52-0.57 (m, 2H), 0.07-0.08 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.52, 11.18, 26.52, 49.82, 118.84, 129.52, 137.25

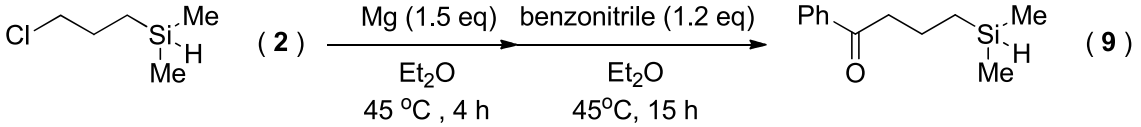


A solution of 1-[3-(dimethylsilyl)propyl]imidazole (**8'**) (504 mg, 3.0 mmol) and iodomethane (426 mg, 3.0 mmol) in CH_2Cl_2 (6 mL) was charged in a sealed tube and stirred at 40 °C for 24 h. Removal of solvent under reduced pressure afforded 1-[3-(dimethylsilyl)propyl]-3-methylimidazolium iodide (**8**) (930 mg, 3.0 mmol) as viscous liquid quantitatively.

^{1}H NMR ($CDCl_3$) δ = 10.17 (s, 1H), 7.47 (s, 1H), 7.37 (s, 1H), 4.32-4.36 (t, J = 7.2 Hz, 2H), 4.14 (s, 3H), 3.83-3.89 (m, 1H), 1.92-2.00 (m, 2H), 0.60-0.65 (m, 2H), 0.10-0.11 (d, J = 3.6 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.42, 10.91, 25.93, 37.23, 52.77, 122.20, 123.85, 137.01.

HRMS (APCI+): m/z calcd for $C_9H_{19}N_2Si$ $[M]^+$ 183.1318, found 183.1318

(3-benzoylpropyl)dimethylsilane (9)

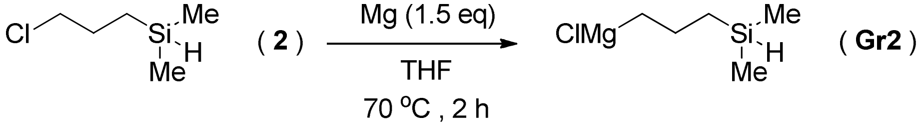


The two neck flask charged with Mg (365 mg, 15 mmol) was heated under vacuum, flushed with N_2 , and added Et_2O (2 mL) and a small amount of iodine. The mixture was heated at 45 °C, then slowly added a solution of (3-chloropropyl)dimethylsilane (**2**) (1365 mg, 10 mmol) in Et_2O (10 mL) and stirred at same temperature for 4 h. To a benzonitrile (1236 mg, 12.0 mmol) in Et_2O (2 mL) at 0 °C was slowly added the supernatant solution and stirred at 45 °C for 15 h. The reaction mixture was quenched with 10% HCl and extracted with Et_2O. The organic layer was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and purified with silica gel chromatography (hexane/EtOAc=20/1) to give (3-benzoylpropyl)dimethylsilane (**9**) (1339 mg, 6.5 mmol) in 65% yield.

^{1}H NMR ($CDCl_3$) δ = 7.95-7.98 (m, 2H), 7.54-7.58 (s, 1H), 7.44-7.49 (m, 2H), 3.86-3.91 (m, 1H), 3.00-3.03 (t, J = 7.2 Hz, 2H), 1.77-1.85 (m, 2H), 0.66-0.71 (m, 2H), 0.09-0.10 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.44, 14.17, 19.55, 41.92, 128.14, 128.67, 133.01, 137.17, 200.54

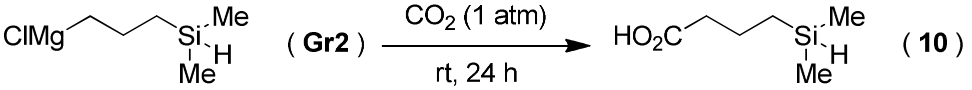
HRMS (APCI+): m/z calcd for $C_{12}H_{18}ONaSi$ $[M+Na]^+$ 229.1025, found 229.1026.

3-(dimethylsilyl)propylmagnesium chloride [11]



The two neck flask charged with Mg (365 mg, 15 mmol) was heated under vacuum, flushed with N_2, and added THF (2 mL) and a small amount of iodine. The mixture was heated at 70 °C, then slowly added a solution of (3-chloropropyl)dimethylsilane (**2**) (1365 mg, 10 mmol) in THF (8 mL) and stirred at same temperature for 2 h. The supernatant solution was obtained as the corresponding Grignard reagent (**Gr2**) (0.94 M).

4-(dimethylsilyl)butyric acid (10)

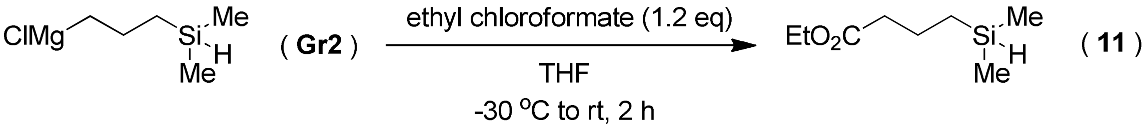


The flame dried Schlenk flask was filled with CO_2 (1 atm). To this flask was added 3-(dimethylsilyl)propylmagnesium chloride (**Gr2**) in THF (9.4 mmol, 10 mL). The resultant solution was stirred at room temperature for 24 h. The reaction mixture was quenched with 10% HCl and extracted with Et_2O. The organic layer was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and purified with silica gel chromatography (hexane/EtOAc=3/1) to give 4-(dimethylsilyl)butyric acid (**10**) (933 mg, 6.4 mmol) in 68% yield.

^{1}H NMR (DMSO) δ = 11.96 (s, 1H), 3.77-3.82 (m, 1H), 2.17-2.21 (t, J = 7.2 Hz, 2H), 1.46-1.54 (m, 2H), 0.52-0.57 (m, 2H), 0.02-0.03 (d, J = 3.6 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.51, 13.93, 20.01, 37.37, 179.98

HRMS (APCI+): *m/z* calcd for $C_6H_{13}O_2Si$ $[M-H]^+$ 145.0687, found 145.0685.

ethyl 4-(dimethylsilyl)butyrate (11)

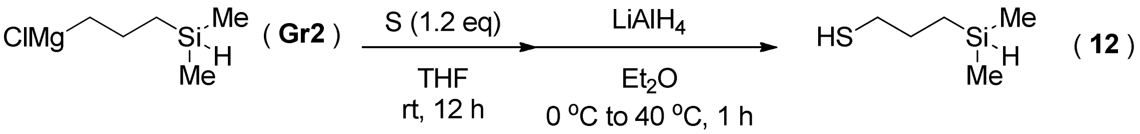


To a solution of ethyl chloroformate (1224 mg, 11.3 mmol) in THF (4 mL) was slowly added 3-(dimethylsilyl)propylmagnesium chloride in THF (**Gr2**) (9.4 mmol, 10 mL) at -30 °C and stirred for 1 h. The cooled bath was removed and the mixture was further stirred at room temperature for 1 h. The reaction mixture was quenched with 10% HCl and extracted with Et_2O. The organic layer was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and purified with silica gel chromatography (hexane/EtOAc=30/1) to give ethyl 4-(dimethylsilyl)butyrate (**11**) (1456 mg, 8.4 mmol) in 89% yield.

^{1}H NMR ($CDCl_3$) δ = 4.11-4.15 (q, J = 6.8 Hz, 2H), 3.84-3.89 (m, 1H), 2.32-2.36 (t, J = 7.2 Hz, 2H), 1.65-1.73 (m, 2H), 1.25-1.29 (t, J = 7.2 Hz, 3H), 0.60-0.65 (m, 2H), 0.08-0.09 (d, J = 4.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.45, 14.02, 14.40, 20.28, 37.73, 60.30, 173.77

HRMS (APCI+): *m/z* calcd for $C_8H_{19}O_2Si$ $[M+H]^+$ 175.1154, found 175.1148.

(3-mercaptopropyl)dimethylsilane (12) [CAS Registry Number: 35847-21-3]

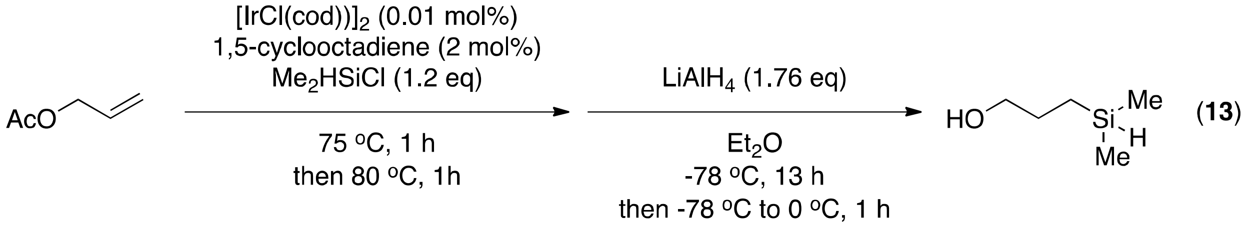


To a suspension of sulfur (346 mg, 10.8 mmol) in THF (4 mL) was added slowly 3-(dimethylsilyl)propylmagnesium chloride in THF (**Gr2**) (9.0 mmol, 10 mL) at 0 °C. The resultant mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with 10% HCl and extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4 and removed under the reduced pressure. The residue was obtained as the mixture of corresponding thiol and disulfide (1073 mg).

To an ice-cold solution of $LiAlH_4$ (304 mg, 8 mmol) in Et_2O (16 mL) was slowly added the mixture of (3-mercaptopropyl)dimethylsilane and bis[3-(dimethylsilyl)propyl]disulfide (1073 mg) at 0 °C, and the reaction mixture was stirred at 40 °C for 1 h. The reaction was quenched with 10% HCl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4 and distilled under reduced pressure to give (3-mercaptopropyl)dimethylsilane (**12**) (820 mg, 6.1 mmol) in 68% yield.

^{1}H NMR ($CDCl_3$) δ = 3.84-3.89 (m, 1H), 2.52-2.57 (q, J = 7.6 Hz, 2H), 1.62-1.70 (m, 2H), 1.33-1.37 (t, J = 7.6 Hz, 1H), 0.66-0.71 (m, 2H), 0.08-0.09 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −4.37, 13.52, 28.05, 29.45

3-(dimethylsilyl)-1-propanol (13) [CAS Registry No. 54655-57-1]

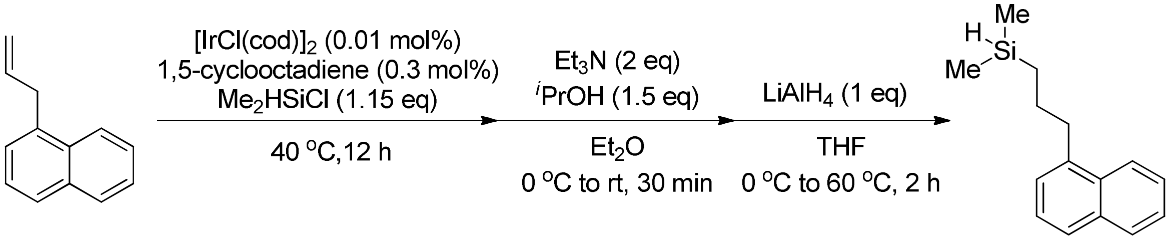


To a mixture of $[IrCl(cod)]_2$ (4.0 mg, 0.006 mmol Ir), allyl acetate (6.48 mL, 60 mmol), and 1,5-cyclooctadiene (0.15 mL, 1.2 mmol) was added slowly chlorodimethylsilane (8.11 mL, 72 mmol) for a period of 1 h at 75 °C. After the addition, the mixture was heated at 80 °C for 1 h. The mixture was distilled under reduced pressure to give chloro(3-acetoxypropyl)dimethylsilane (9029 mg, 56.4 mmol) in 94% yield.

To a suspension of $LiAlH_4$ (3767 mg, 99.2 mmol) in Et_2O (120 mL) was slowly added chloro(3-acetoxypropyl)dimethylsilane (9029 mg, 56.4 mmol) at -78 °C, and the reaction mixture was stirred at same temperature for 13 h. The mixture was slowly warmed to 0 °C for a period of 1 h. The reaction mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ in an ice cooled bath and filtered through a pad of Celite with Et_2O. The obtained clear solution was distilled under reduced pressure to give 3-(dimethylsilyl)-1-propanol (**13**) (6136 mg, 51.9mmol) in 92% yield.

^{1}H NMR ($CDCl_3$) δ 3.87-3.89 (m, 1H), 3.60-3.65 (q, J = 6.0 Hz, 2H), 1.58-1.64 (m, 2H), 1.32-1.35 (t, J = 5.6 Hz, 1 H), 0.58-0.63 (m, 2H), 0.08-0.09 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ-4.40, 9.96, 27.70, 65.57.

1-[(3-dimethylsilyl)propyl]naphtalene (14)



(**14**)

To a mixture of $[IrCl(cod)]_2$ (0.65 mg, 0.75μmol Ir), 1-allylnaphtalene (1682 mL, 10 mmol), and 1,5-cyclooctadiene (2.5 μL, 0.02 mmol) was added chlorodimethylsilane (1.54 mL, 11.5 mmol), and the reaction mixture was stirred at 40 °C for 12 h.

The mixture was diluted with Et_2O (30 mL) and triethylamine (2038 mg, 20 mmol). To the solution was slowly added 2-propanol (900 mg, 15 mmol) at 0 °C and stirred at room temperature for 30 min.

The mixture was filtered through a pad of Celite with Et_2O, and the organic solvent was removed under reduced pressure. The yellow residue was passed through a short silica gel column (hexane) to give 1-[(3-*i*-p-ropyldimet-hylsilyl)propyl]naphtalene (2345 mg, 8.2 mmol) in 82% yield.

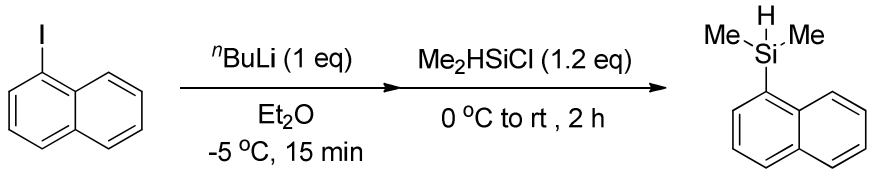
To a suspension of $LiAlH_4$ (312 mg, 8.2 mmol) in THF (20 mL) was slowly added 1-[(3-*i*-propyldimethylsilyl)propyl]naphtalene (2345 mg, 8.2 mmol) at 0 °C, and the reaction mixture was stirred at 60 °C for 2 h. The reaction mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ in ice cooled bath and filtered through a pad of Celite with CH_2Cl_2. The organic solvents were reduced under reduced pressure and the residue was chromatographed on silica gel (hexane) to give 1-[(3-dimethylsilyl)propyl]naphtalene (**14**) (1622 mg, 7.1 mmol) in 87% yield.

^{1}H NMR ($CDCl_3$) δ = 8.03-8.05 (d, J = 8.4 Hz, 1H), 7.84-7.86 (d, J = 8.0 Hz, 1H), 7.70-7.12 (d, J = 7.6 Hz, 1H), 7.45-7.53 (m, 2H), 7.38-7.42 (t, J = 7.5 Hz, 3H), 7.31-7.33 (d, J = 6.8 Hz, 1H), 3.85-3.90 (m, 1H), 3.50-3.54 (t, J = 7.2 Hz, 2H), 1.78-1.85 (m, 2H), 0.68-0.73 (m, 2H), 0.09-

0.10 (d, J = 4.0 Hz, 6H) ; ^{13}C NMR ($CDCl_3$) δ = −4.32, 14.65, 25.98, 36.76, 123.99, 125.47, 125.62, 125.76, 126.13, 126.56, 128.84, 131.98, 133.95, 138.78.

HRMS (APCI+): *m/z* calcd for $C_{15}H_{20}NaSi$ $[M+Na]^+$ 251.1232, found 251.1235.

1-(dimethylsilyl)naphthalene (17) [CAS Registry Number: 38274-80-5]

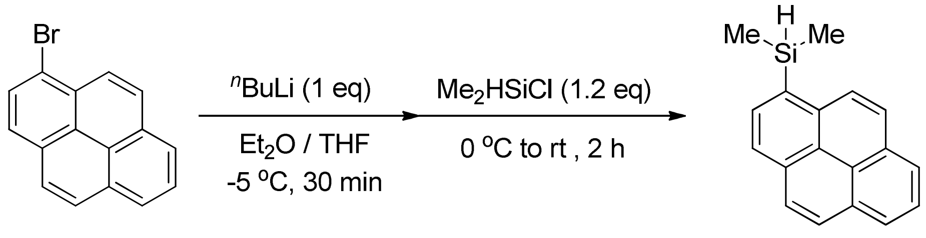


(**17**)

To a solution of 1-iodonaphtalene (2541 mg, 10 mmol) in Et_2O (40 mL) was added dropwise n-BuLi in hexane (6.25 mL, 10 mmol) at -5 °C. The mixture was stirred for 15 min before chlorodimethylsilane (1135 mg, 12 mmol) was added. After the addition, the reaction mixture was warmed to room temperature and further stirred for 2 h. The mixture was quenched with 10 % HCl and extracted with Et_2O. The organic layer was washed with brine. After drying over Na_2SO_4, organic solvent was removed under reduced pressure and the residue was purified with silica gel chromatography (hexane) to give 1-(dimethylsilyl)naphthalene (**17**) (1769 mg, 9.5 mmol) in 95% yield.

^{1}H NMR ($CDCl_3$) δ = 8.11-8.13 (d, J = 8.4 Hz, 1H), 7.86-7.90 (m, 2H), 7.72-7.74 (d, J = 6.6 Hz, 1H), 7.45-7.56 (m, 3H), 4.84-4.90 (m, 1H), 0.50-0.51 (d, J = 3.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ = −3.15, 125.29, 125.65, 126.03, 127.71, 129.05, 130.09, 133.26, 133.72, 135.75, 137.02

1-(dimethylsilyl)pyrene (18)



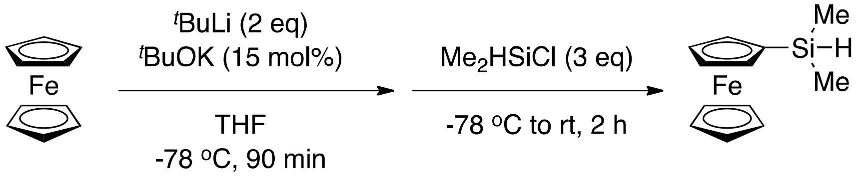
(**18**)

To a solution of 1-bromopyrene (843 mg, 3 mmol) in Et_2O (25 mL) and THF (5 mL) was added dropwise ^{n}BuLi in hexane (1.88 mL, 3 mmol) at -5 °C. The mixture was stirred for 30 min before chlorodimethylsilane (339 mg, 3.6mmol) was added. After the addition, the reaction mixture was warmed to room temperature and further stirred for 2 h. The mixture was quenched with 10 % HCl and extracted with CH_2Cl_2. The organic layer was washed with brine. After drying over Na_2SO_4, organic solvent was removed under reduced pressure and the residue was purified with silica gel chromatography (hexane) to give 1-(dimethylsilyl)pyrene (**18**) (735 mg, 2.82 mmol) in 94% yield.

^{1}H NMR (CDCl$_3$) δ = 8.38-8.40 (d, J = 9.2 Hz, 1H), 8.17-8.22 (t, J = 7.6 Hz, 3H), 8.12-8.17 (t, J = 9.2 Hz, 2H), 8.03-8.10 (dd, J = 6.0, 9.2 Hz, 2H) , 7.99-8.03 (t, J = 7.6 Hz, 1H), 5.05-5.11 (m, 1H), 0.60-0.61 (d, J = 4.0 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ= −2.83, 124.24, 124.49, 124.88, 125.01, 125.22, 125.31, 125.91, 127.17, 127.49, 127.56, 128.05, 130.80, 131.35, 132.34, 132.99, 135.76.

HRMS (APCI+): *m/z* calcd for $C_{18}H_{17}Si$ $[M+H]^+$ 261.1100, found 261.1099.

(dimethylsilyl)ferrocene (19) [CAS Registry Number: 32993-02-5]

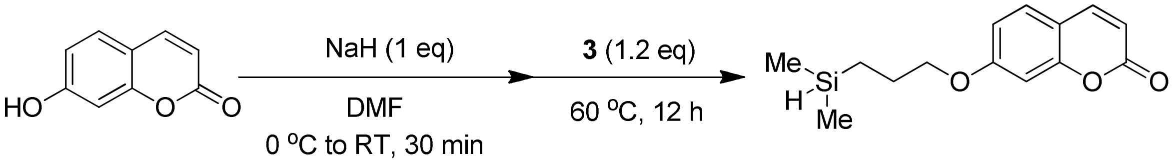


(**19**)

To a solution of ferrocene (1860 mg, 10 mmol) and potassium *tert*-butoxide (168 mg, 1.5 mmol) in THF (20 mL) was stirred at -78 °C for 15 min. The mixture was slowly added ^{t}BuLi in pentane (12.5 mL, 20 mmol) at -70 °C and stirred for 90 min before chlorodimethylsilane (2838 mg, 30 mmol) was added. After the addition, the reaction mixture was warmed to room temperature and further stirred for 2 h. The mixture was quenched with 10 % HCl and extracted with Et_2O. The organic layer was washed with brine. After drying over Na_2SO_4, organic solvent was removed under reduced pressure and the residue was distilled under reduced pressure to give (dimethylsilyl)ferrocene (**19**) (1806 mg, 7.4 mmol) in 74% yield.

^{1}H NMR (CDCl$_3$) δ = 4.38-4.44 (m, 1H), 4.35-4.36 (t, J = 1.6 Hz, 2H), 4.14 (s, 2H), 4.13 (s, 5H), 0.30-0.31 (d, J = 3.6 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ= −3.02, 68.09, 68.42, 71.12, 73.44.

7-[(3-dimethylsilyl)propoxy]coumarin (22)

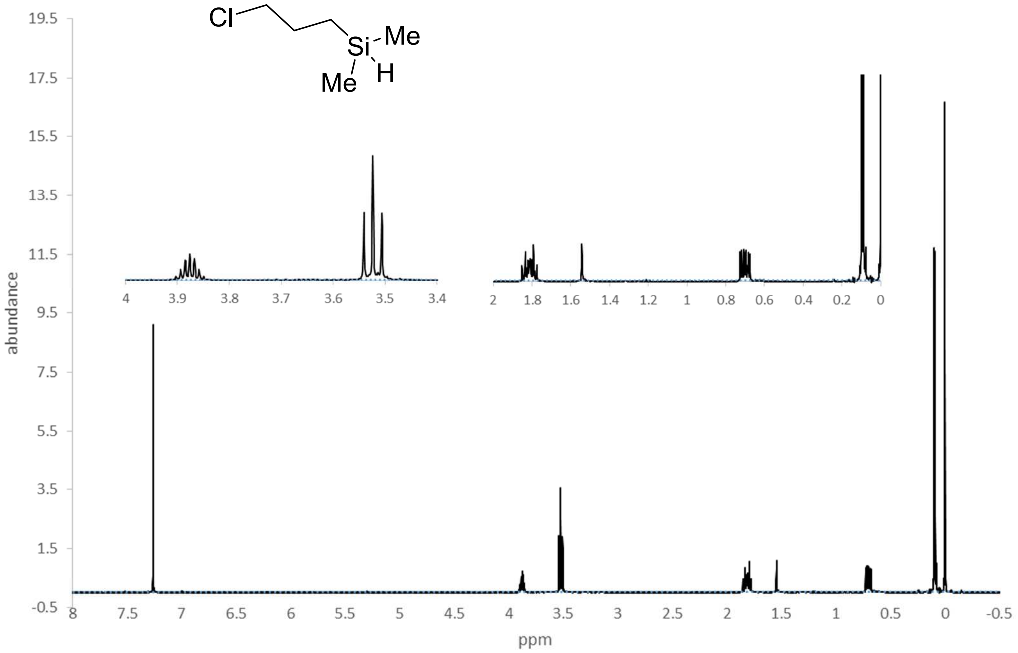


To a solution of sodium hydride (72 mg, 3.0 mmol) in DMF (9 mL) was slowly added umbelliferone (486 mg, 3.0 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min before (3-bromopopyl)dimethylsilane (**3**) (655 mg, 3.6 mmol) was added. The mixture was further stirred at 60 °C for 12 h. The reaction was quenched with distilled water and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. The organic solvent was removed in vacuum and the resulting mixture was purified with silica gel chromatography (hexane/EtOAc=8/1) to give 7-[(3-dimethylsilyl)propoxy]coumarin (**22**) (677 mg, 2.58 mmol) in 86% yield.

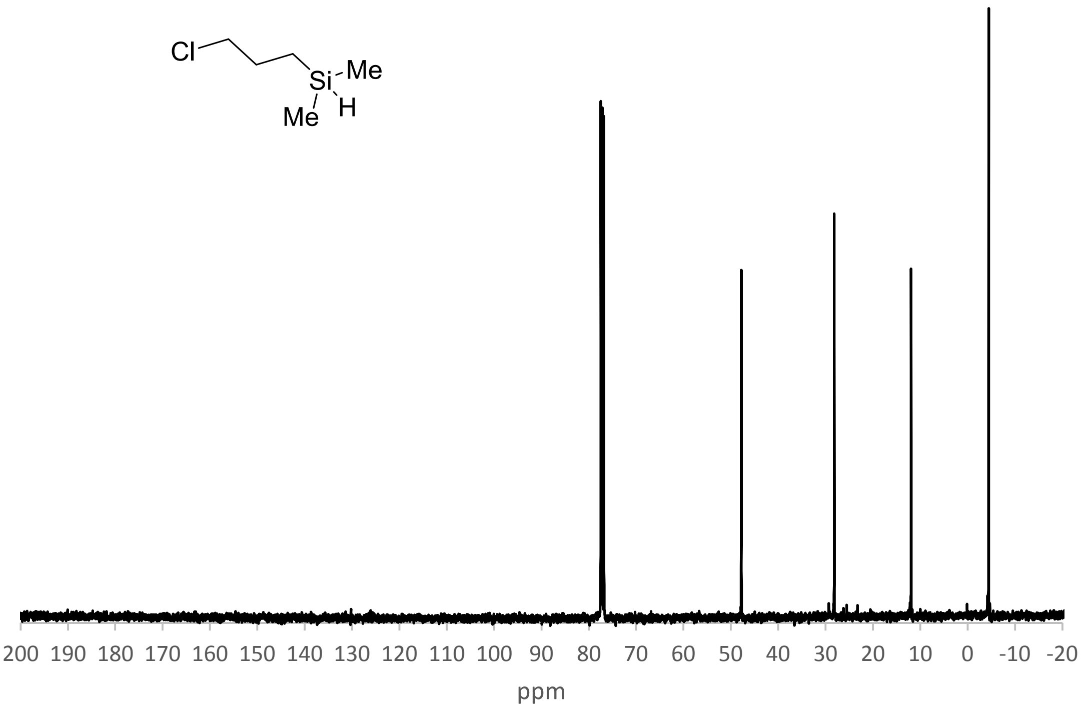
^{1}H NMR (CDCl$_3$) δ = 7.63-7.65 (d, J = 9.6 Hz, 2H), 7.36-7.38 (d, J = 8.8 Hz, 2H) , 6.80-6.85 (m, 2H), 6.24-6.26 (d, J = 9.2 Hz, 1H), 3.98-4.01 (t, J = 6.8 Hz, 2H), 3.89-3.94 (m, 1H), 1.83-1.91 (m, 2H), 0.70-0.75 (m, 2H), 0.11-0.12 (d, J = 3.6 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ = −4.39, 10.34, 24.13, 70.91, 101.39, 112.47, 113.02, 113.09, 128.82, 143.60, 156.01, 161.45, 162.42.

HRMS (APCI+): m/z calcd for $C_{14}H_{18}O_3NaSi$ $[M+Na]^+$ 285.0923, found 285.0929.

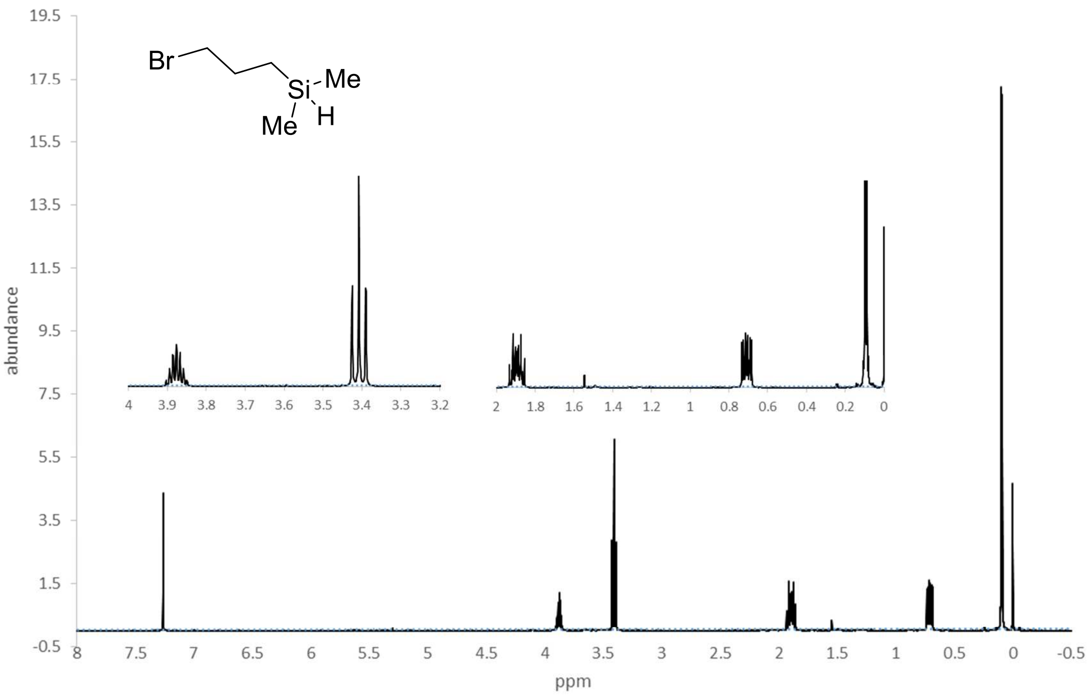
^{1}H NMR, 2



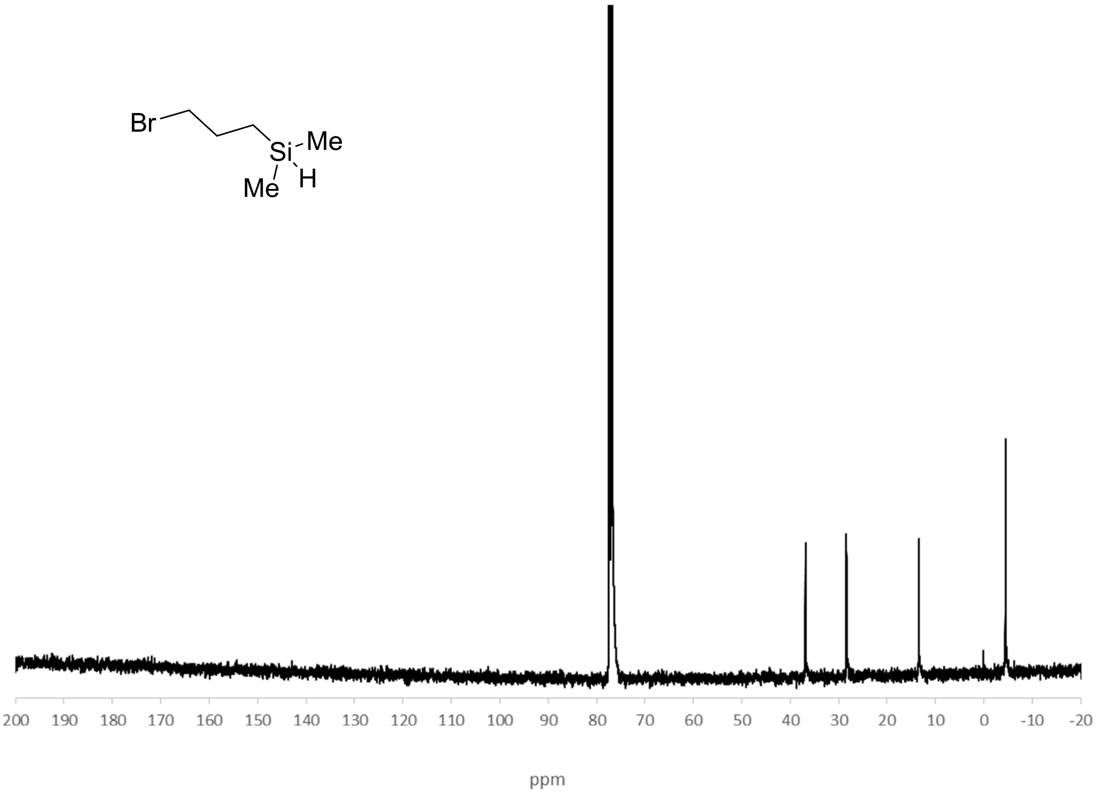
^{13}C NMR, 2



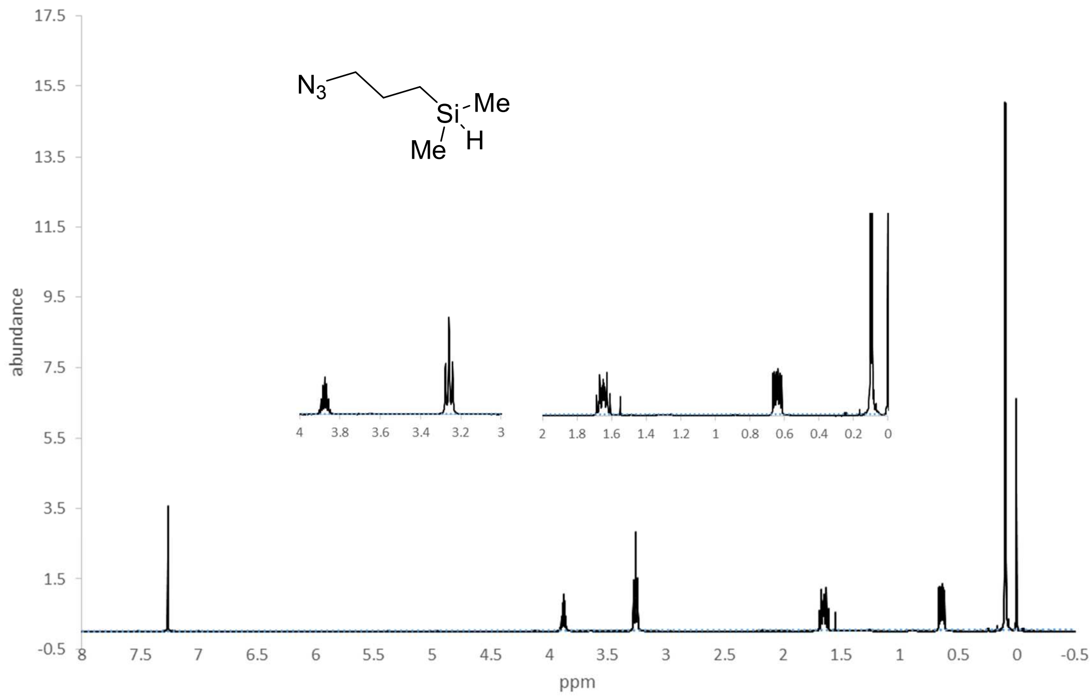
^{1}H NMR, 3



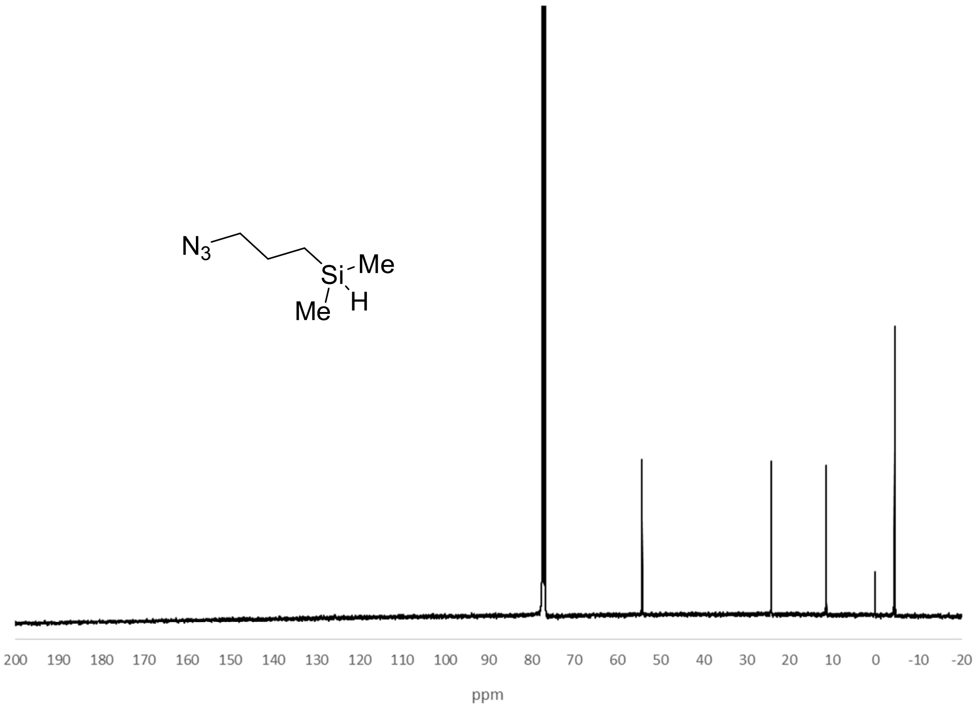
^{13}C NMR, 3



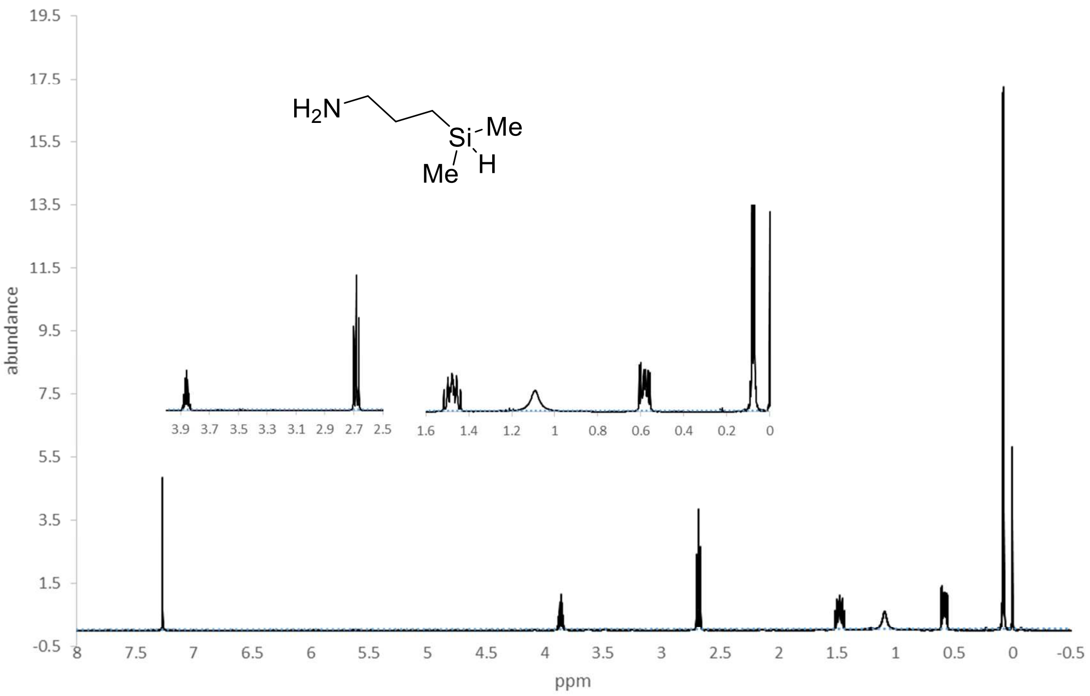
^{1}H NMR, 4



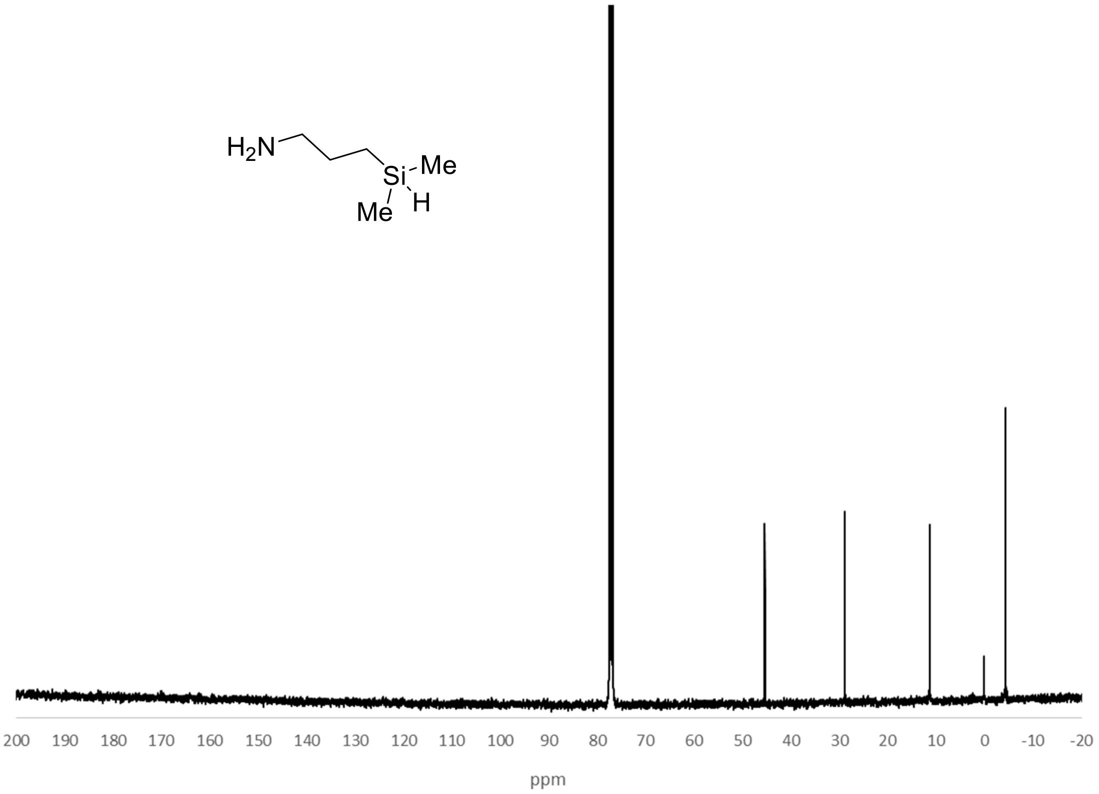
^{13}C NMR, 4



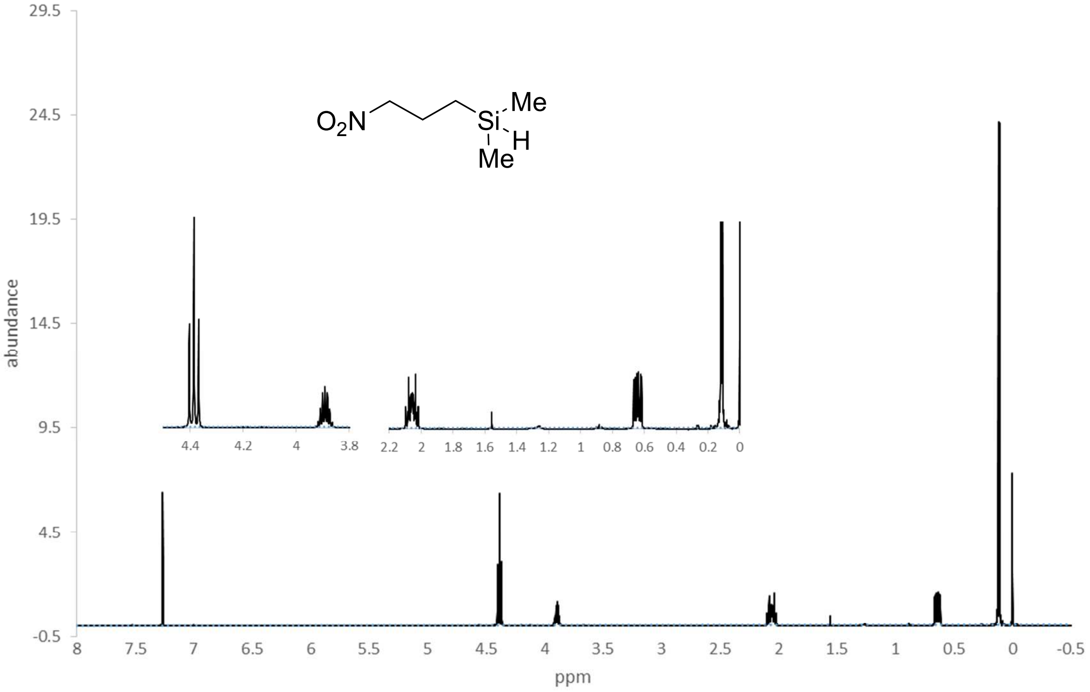
^{1}H NMR, 5



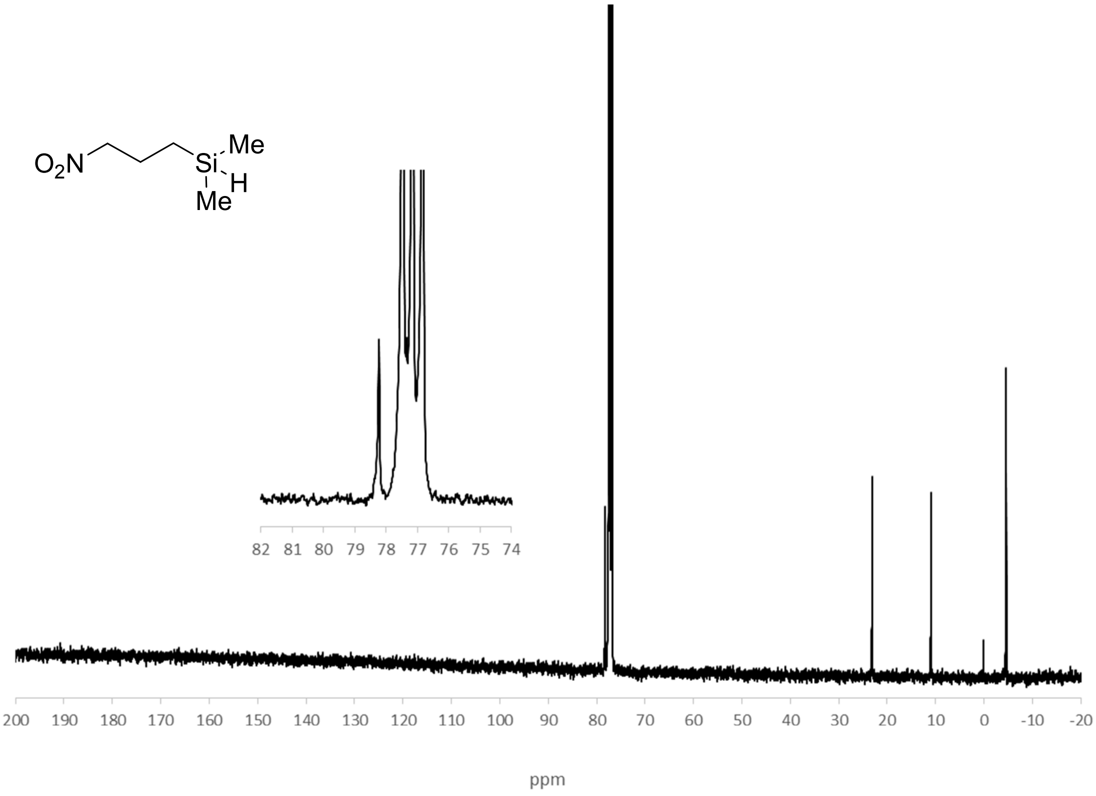
^{13}C NMR, 5



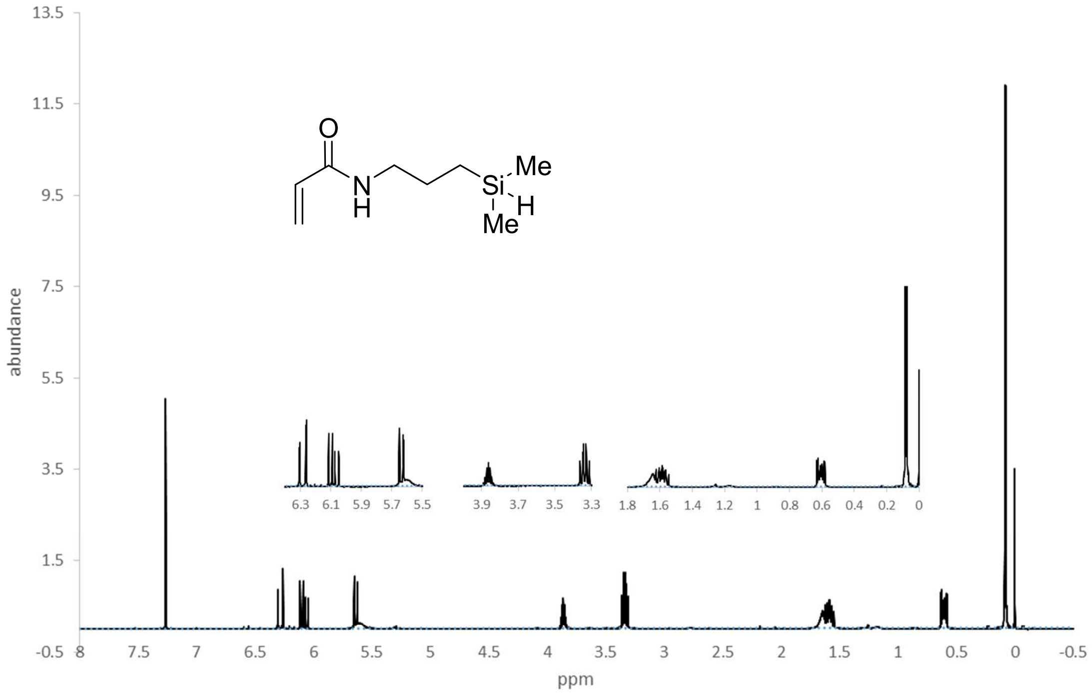
^{1}H NMR, 6



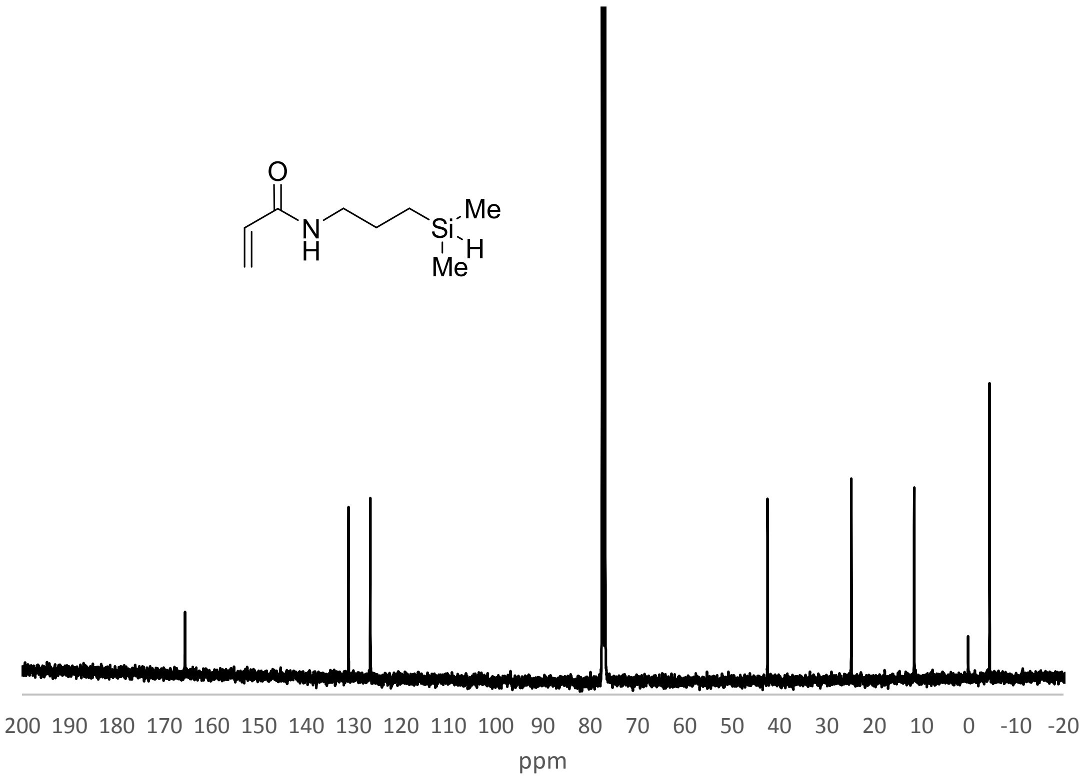
^{13}C NMR, 6



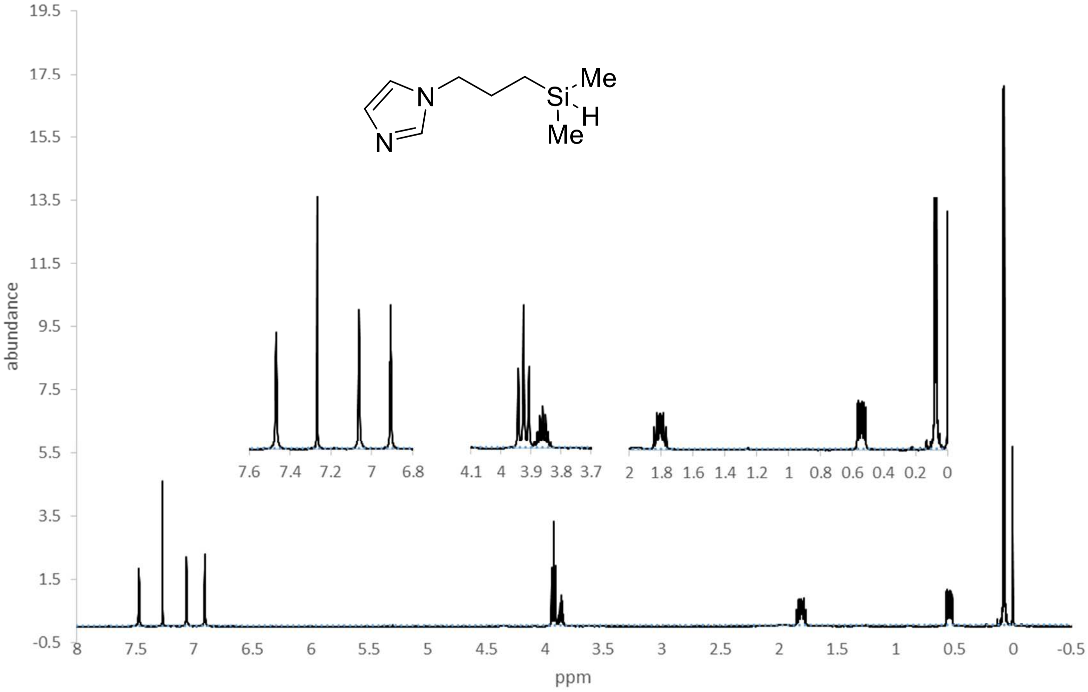
^{1}H NMR, 7



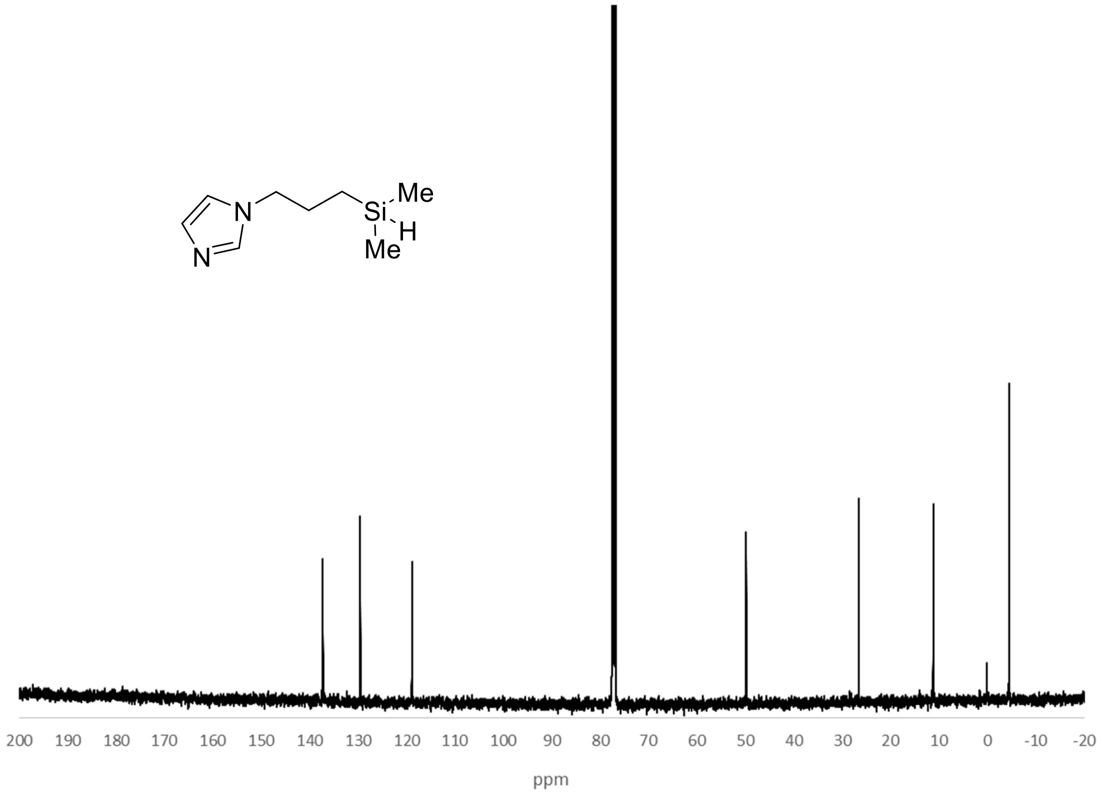
^{13}C NMR, 7



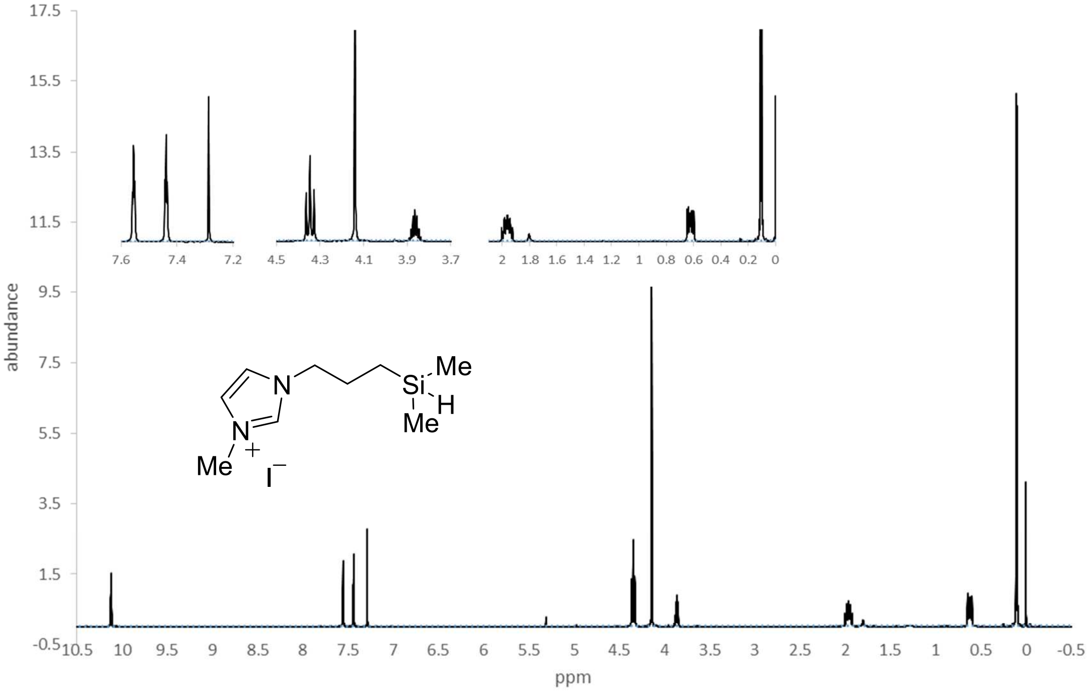
^{1}H NMR, 8’



^{13}C NMR, 8'



^{1}H NMR, 8



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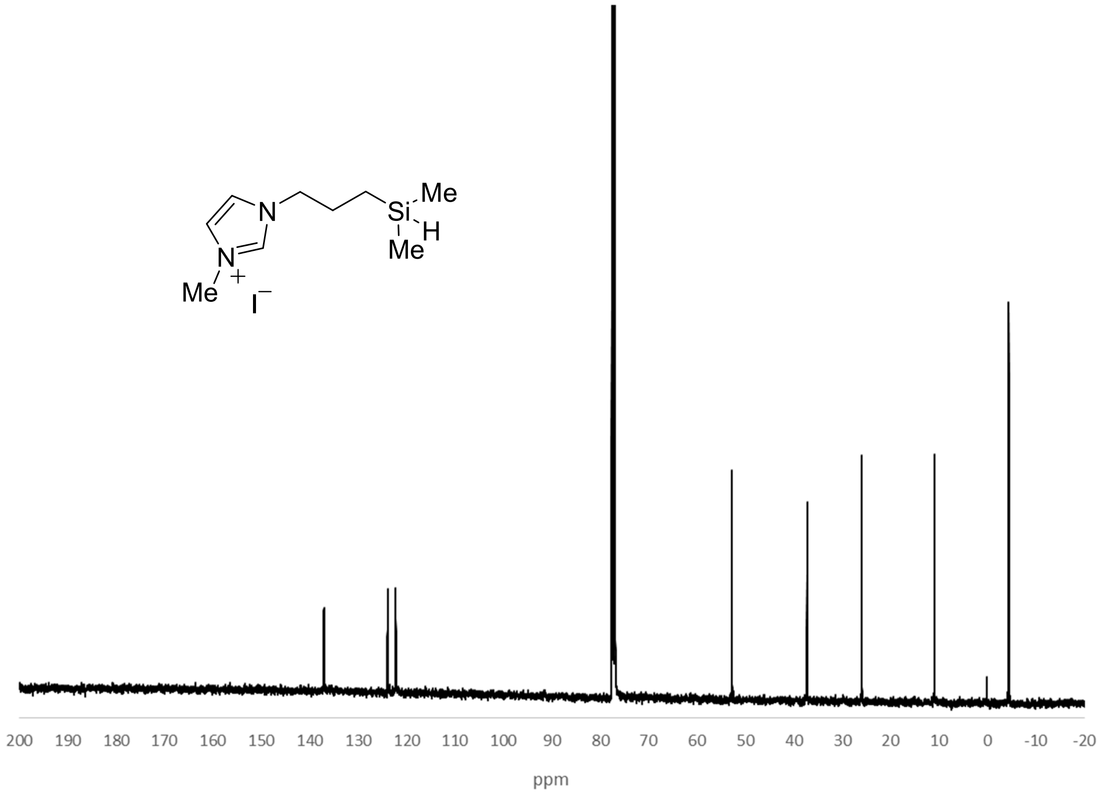
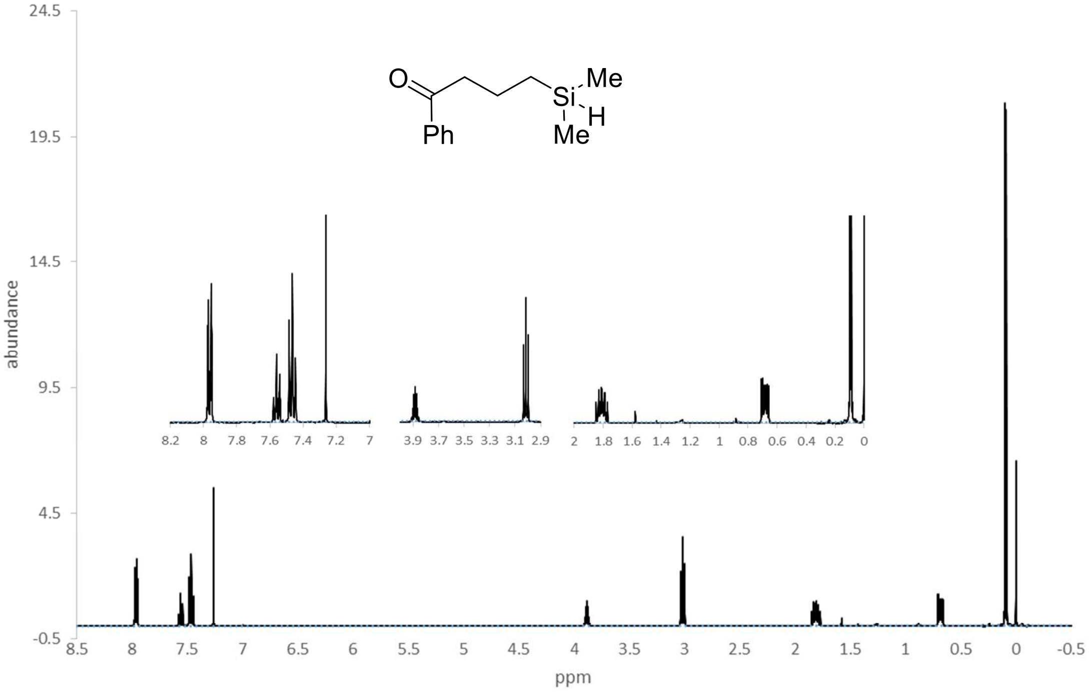


^{1}H NMR, 9



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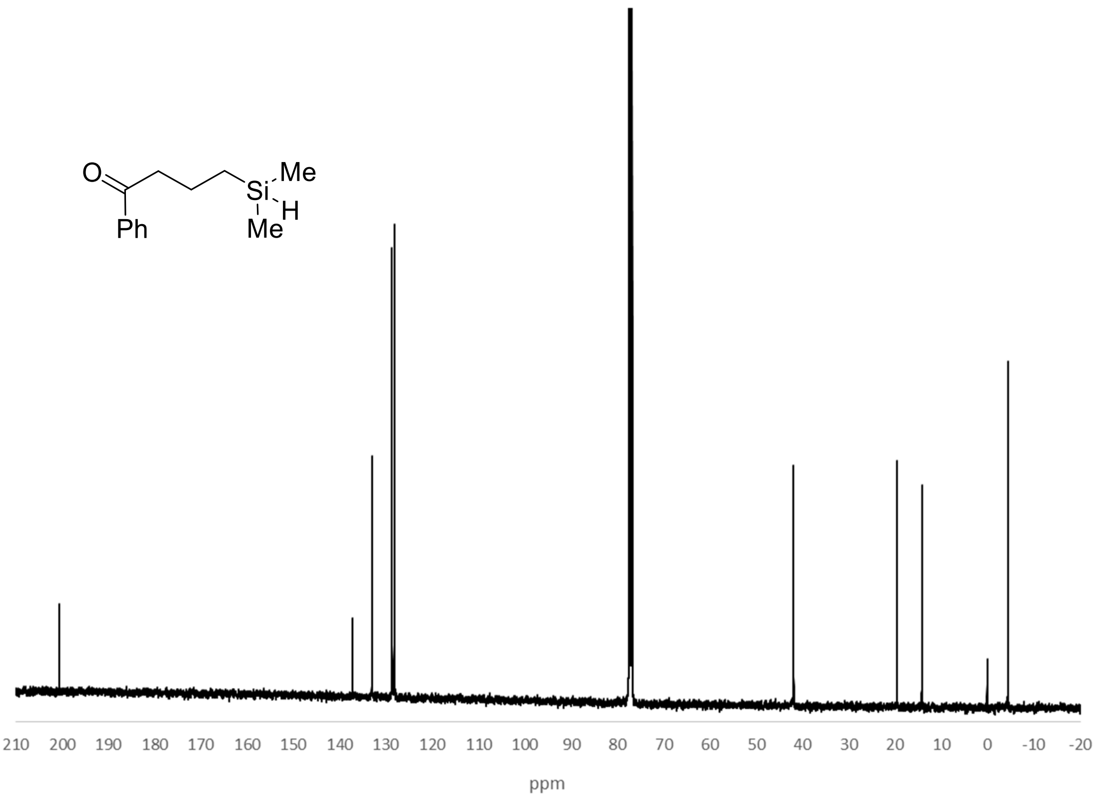

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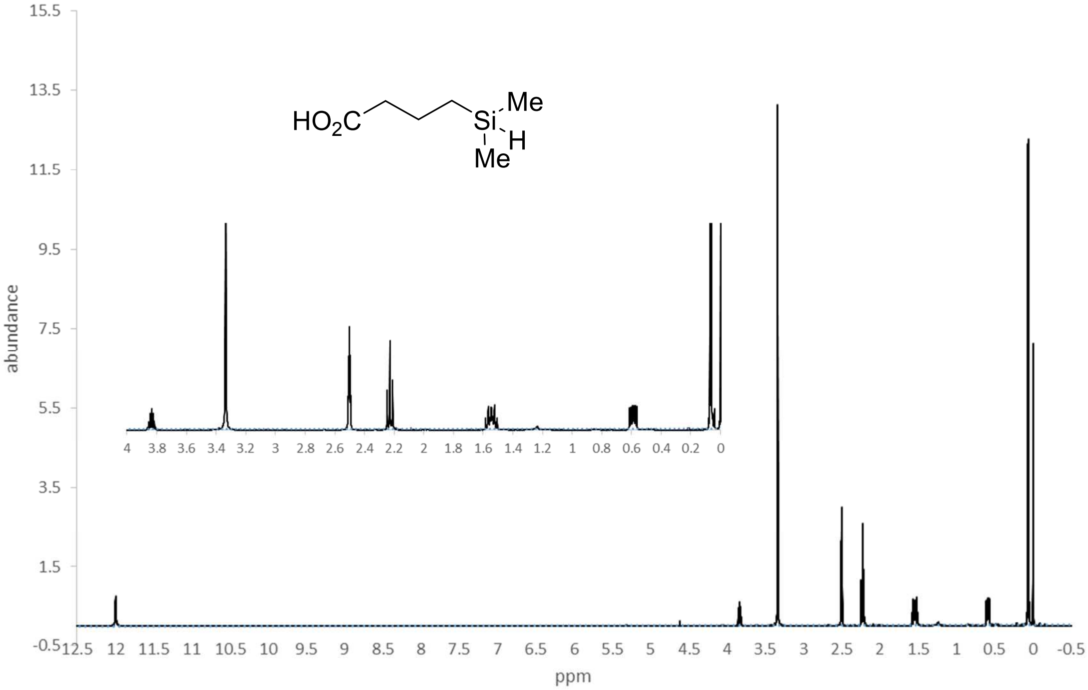

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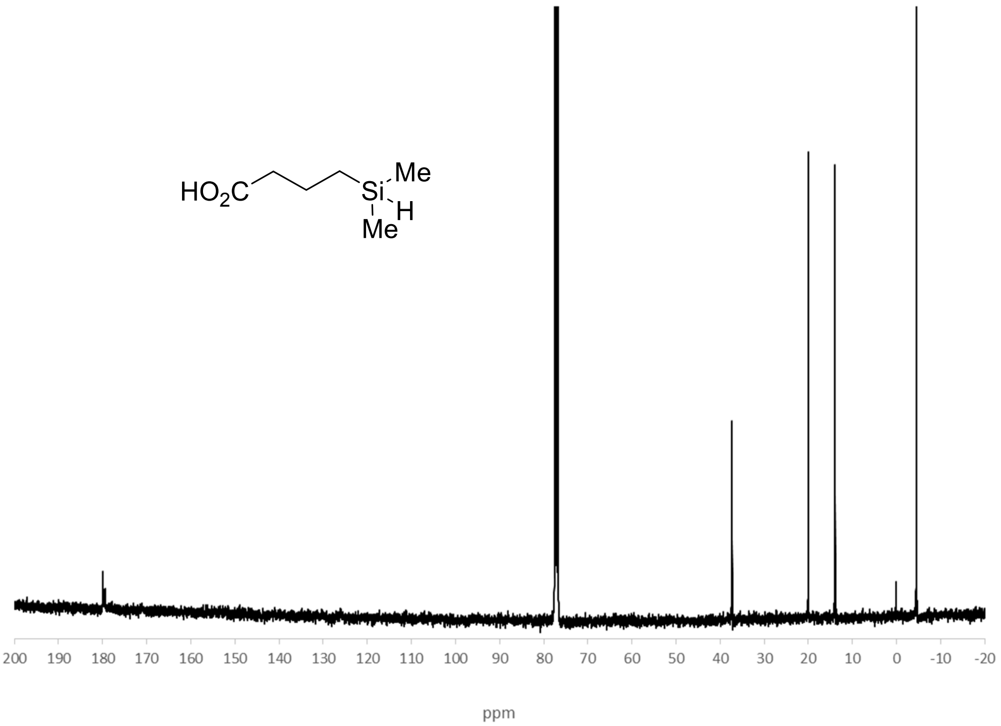

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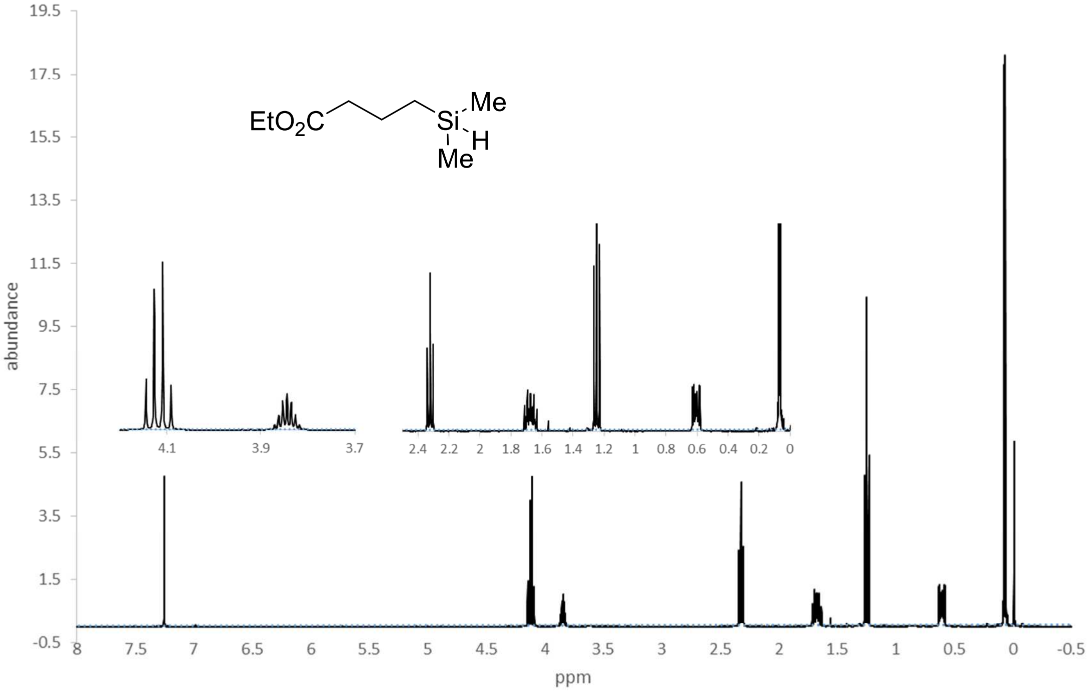

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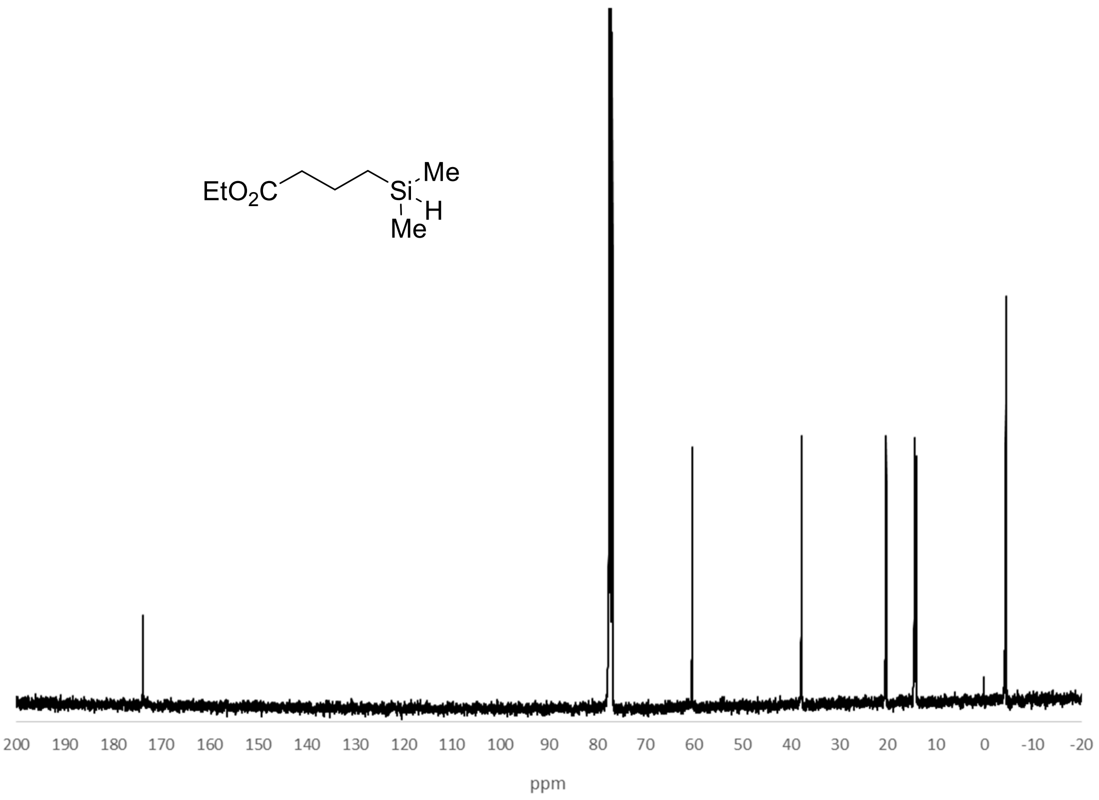

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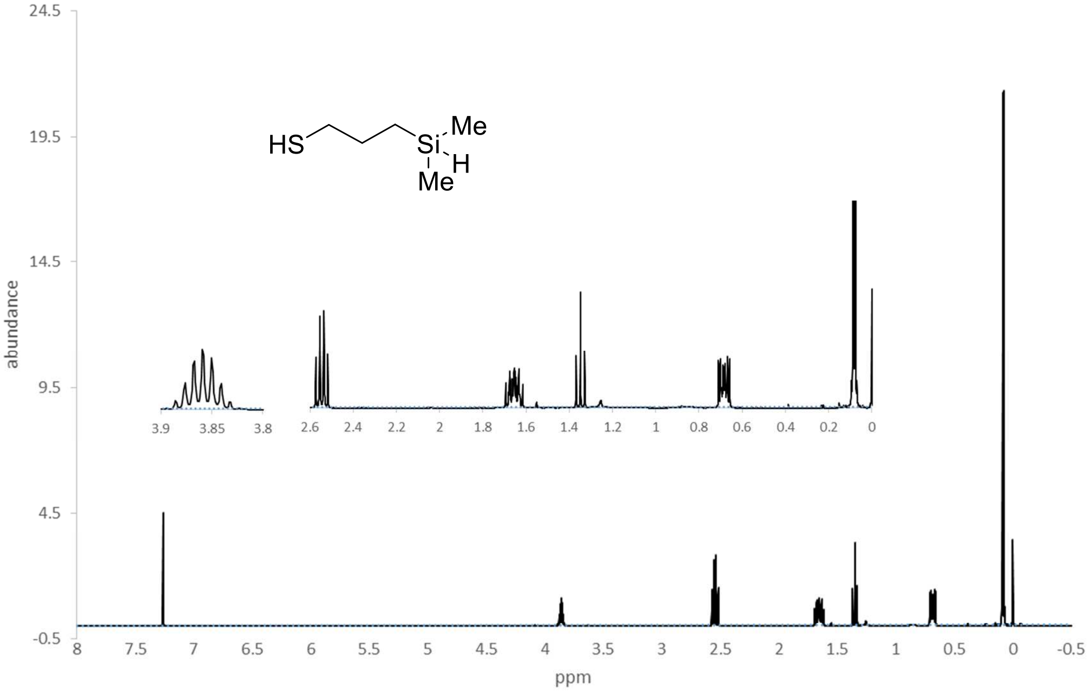

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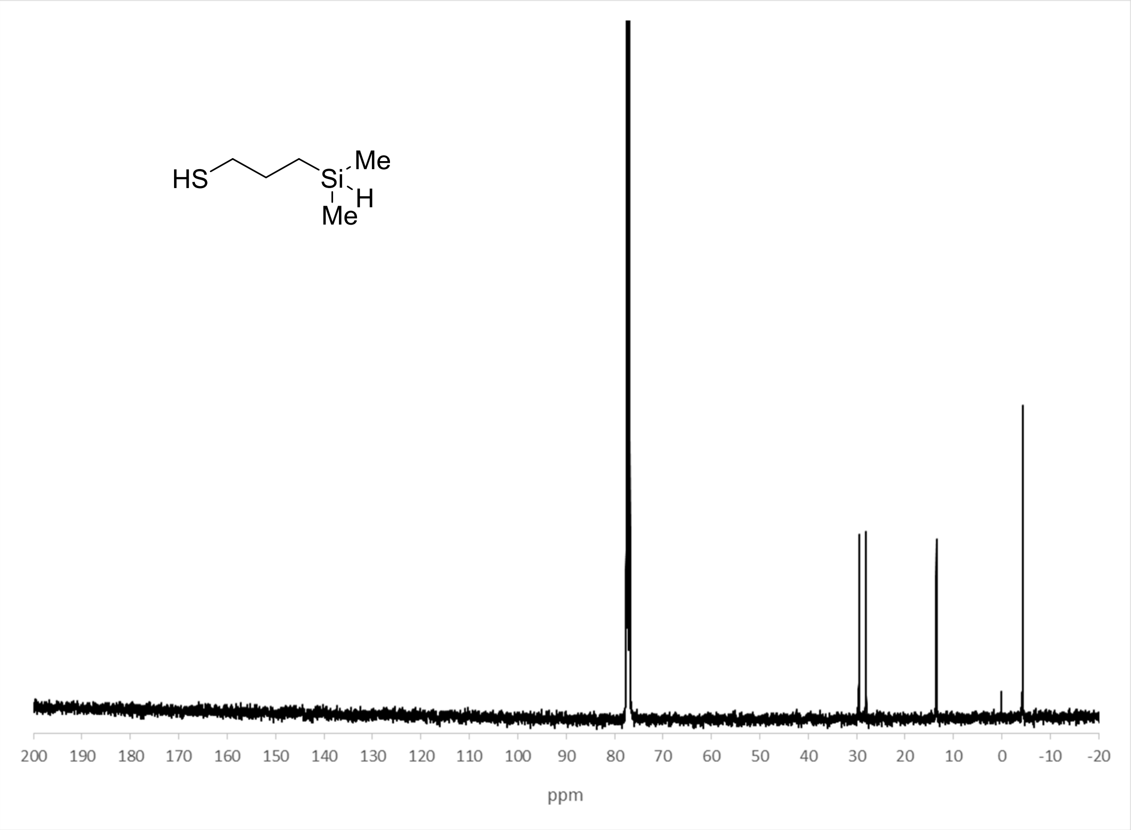

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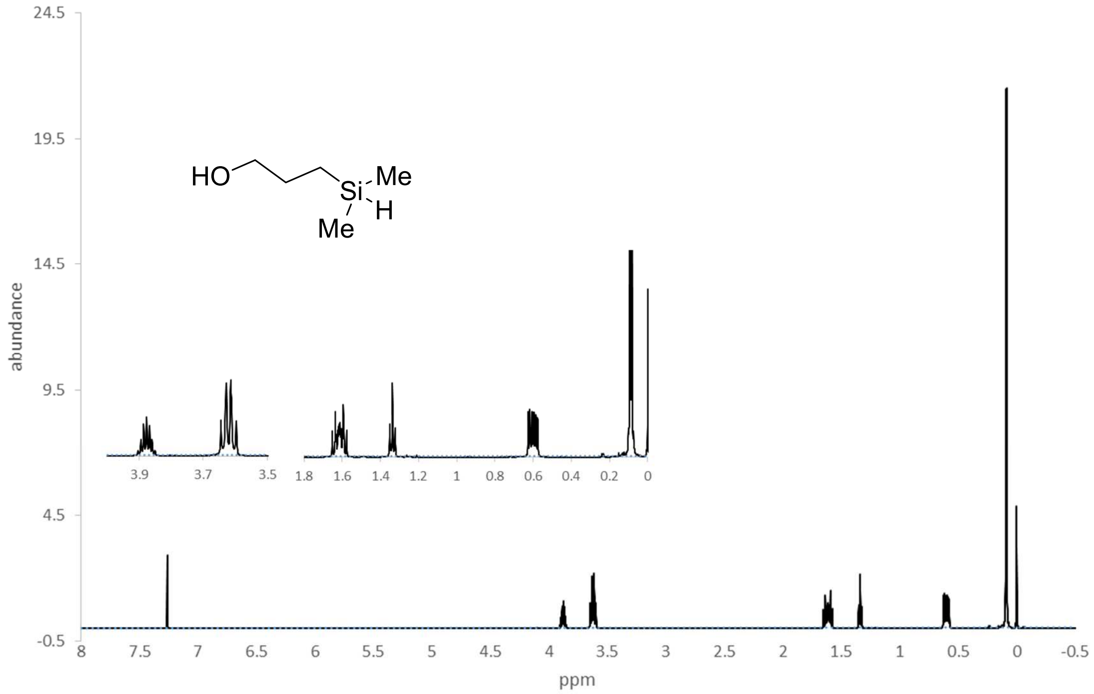
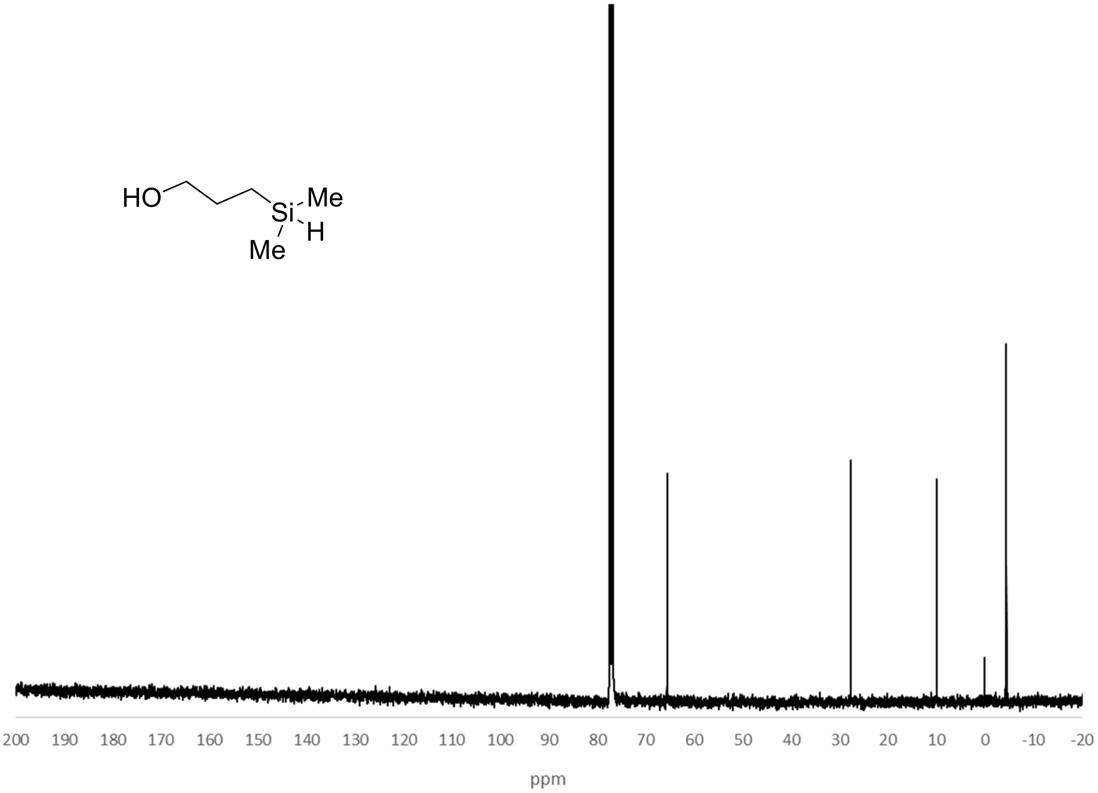


^{13}C NMR, 13



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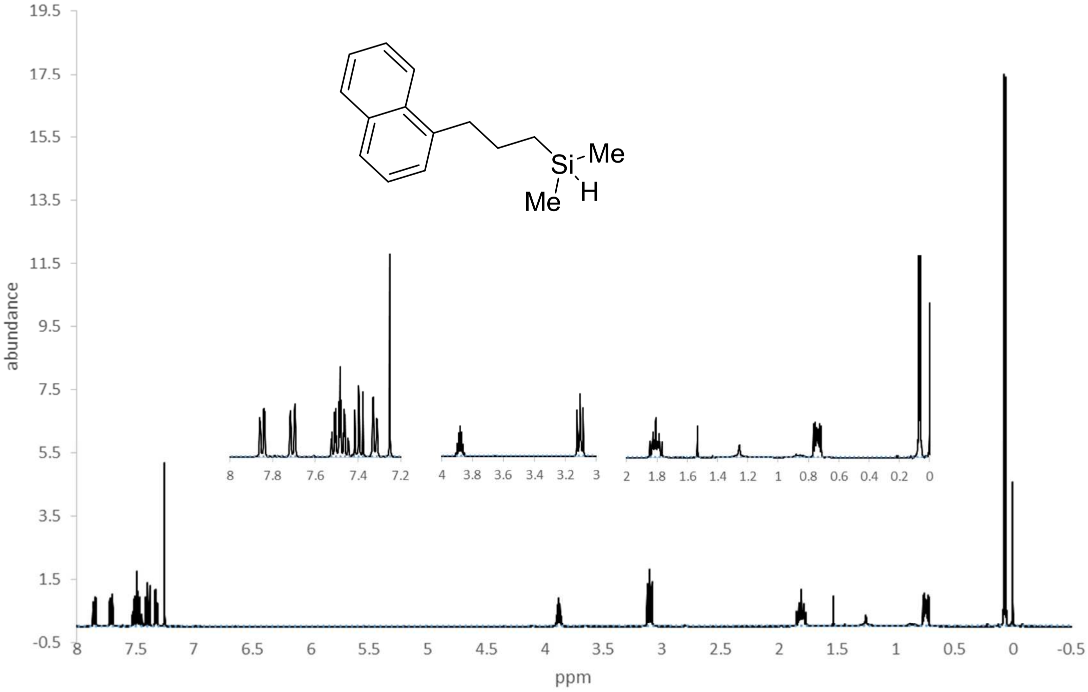
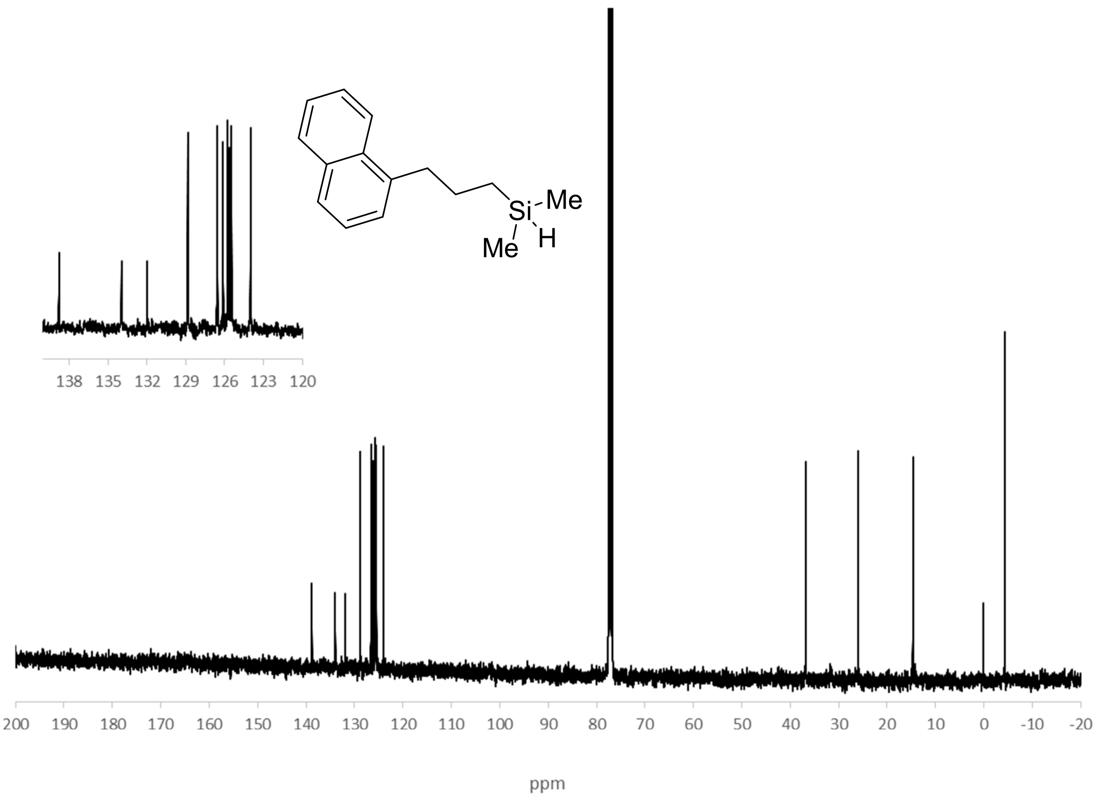
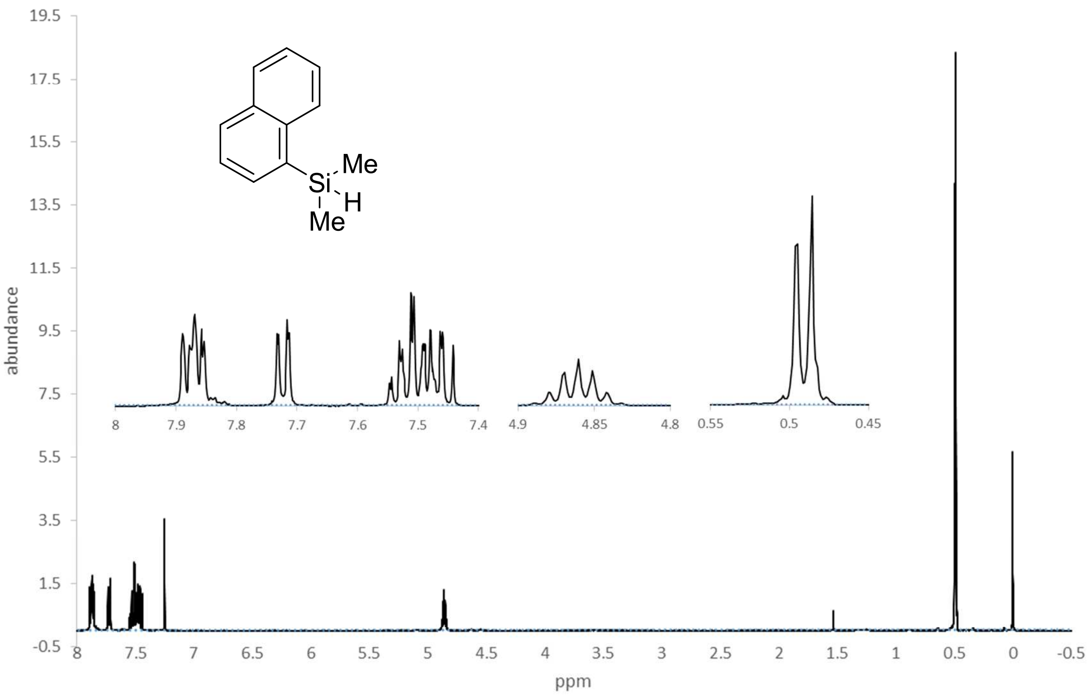


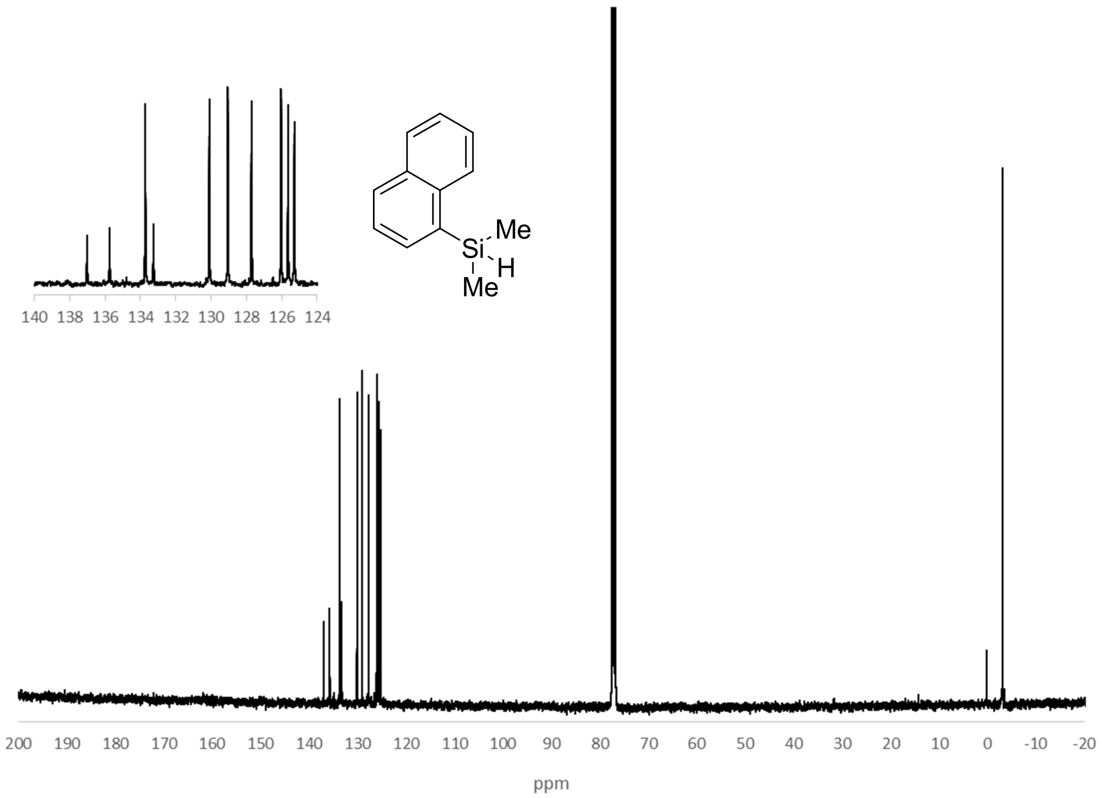
^{13}C NMR, 14



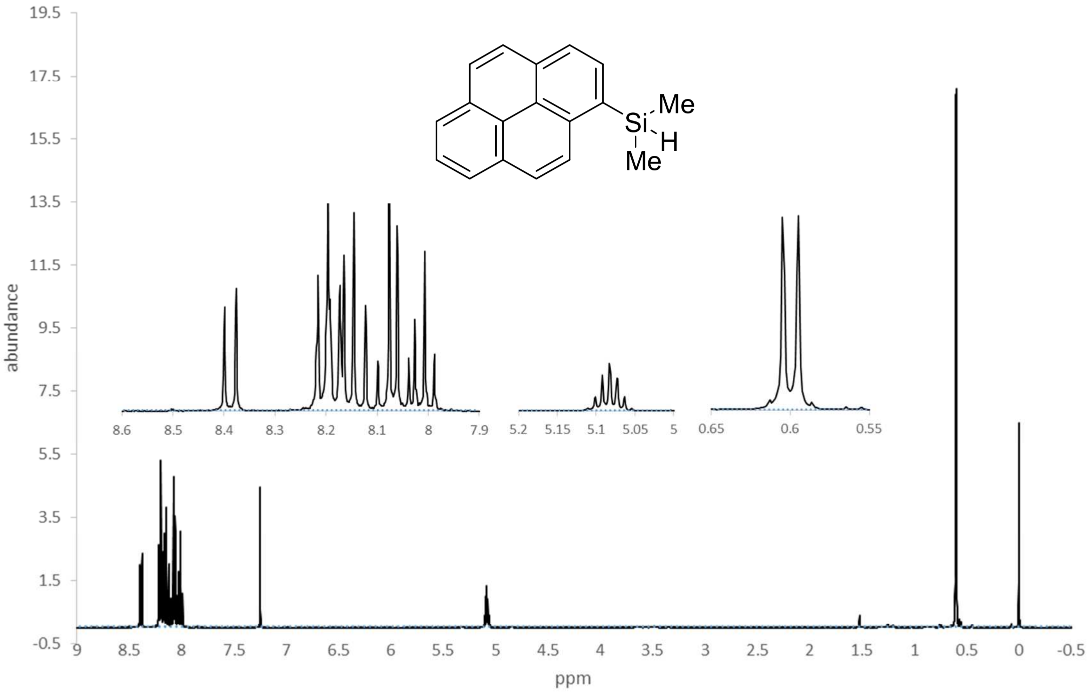
^{1}H NMR, 17



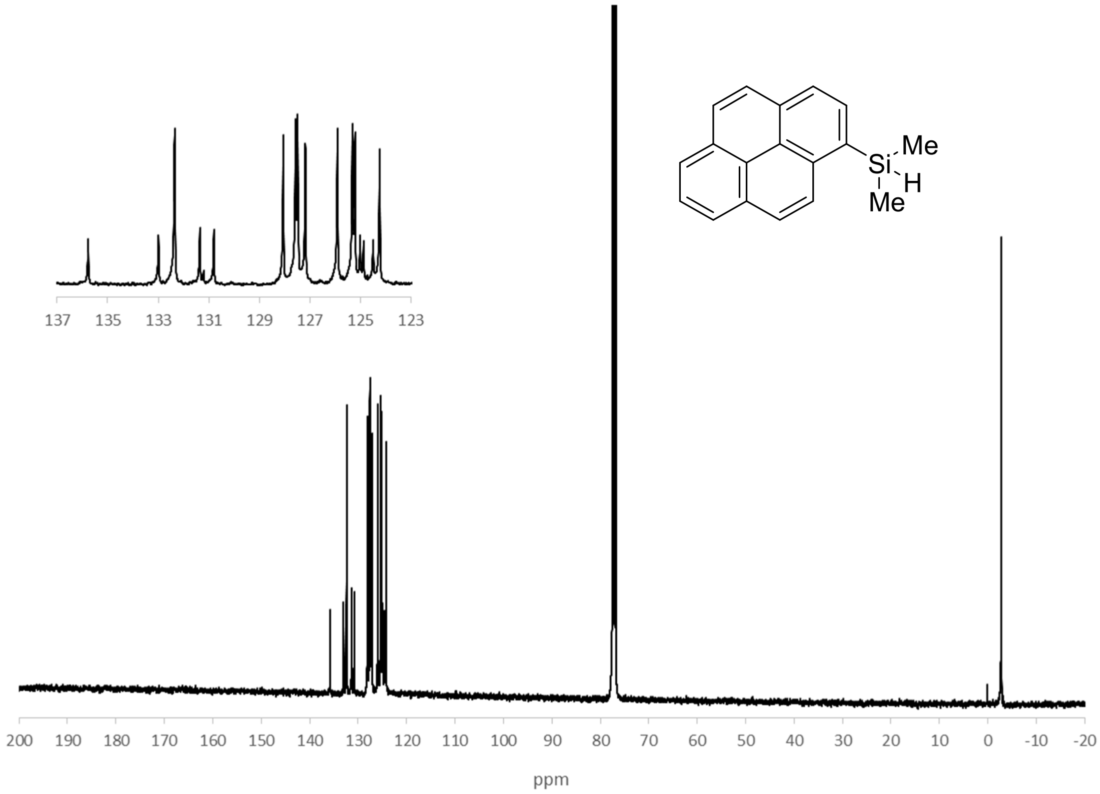
^{13}C NMR, 17



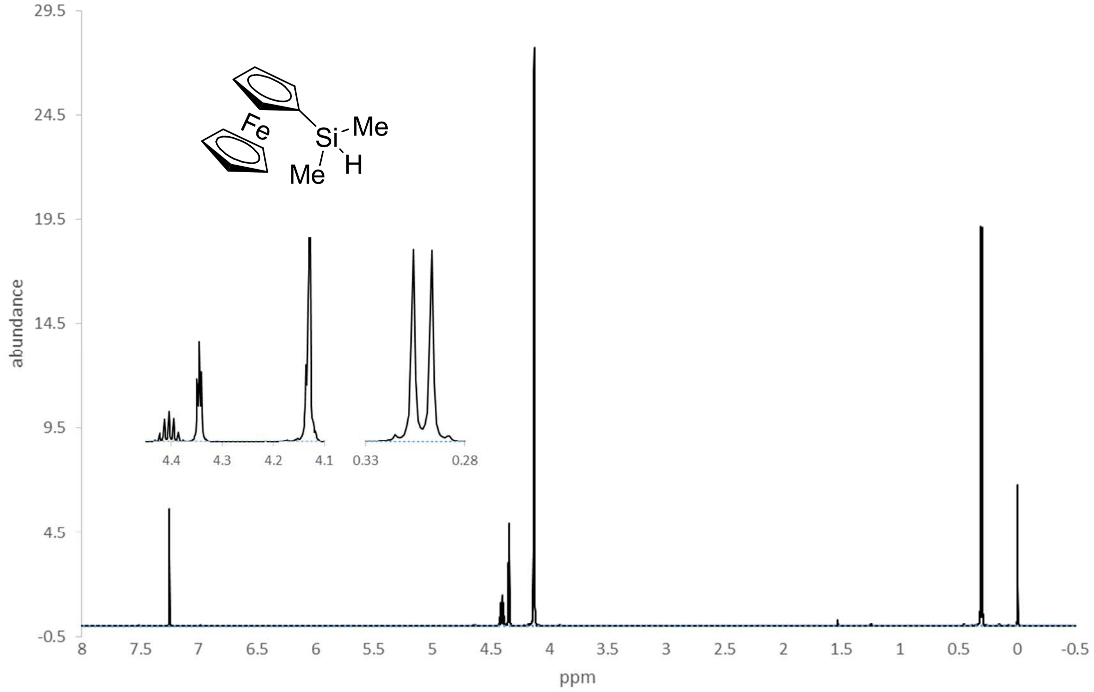
^{1}H NMR, 18



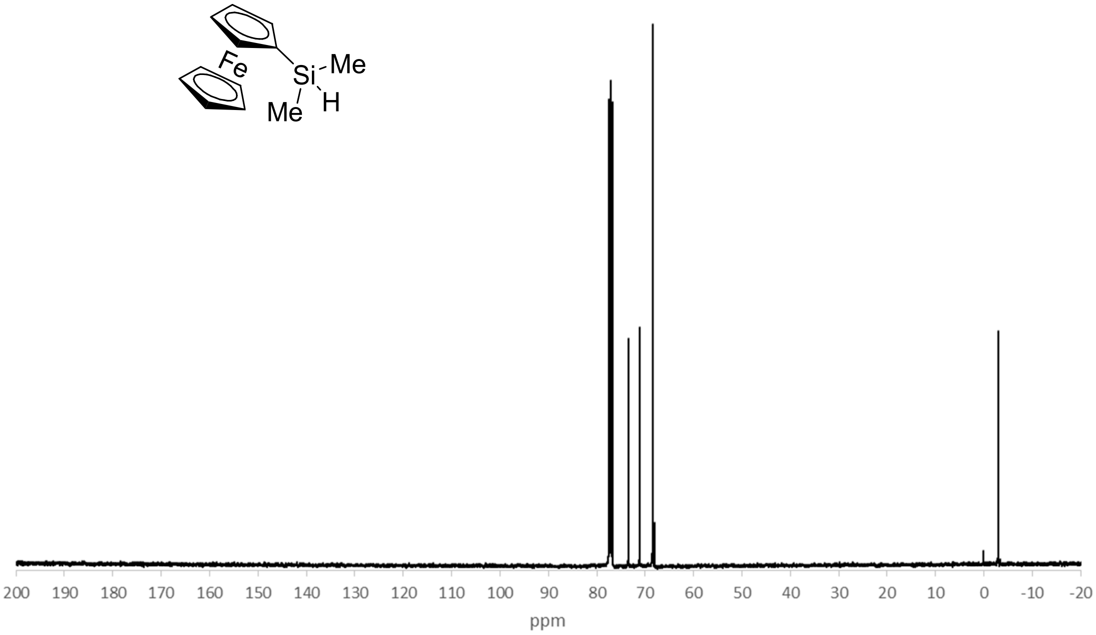
^{13}C NMR, 18



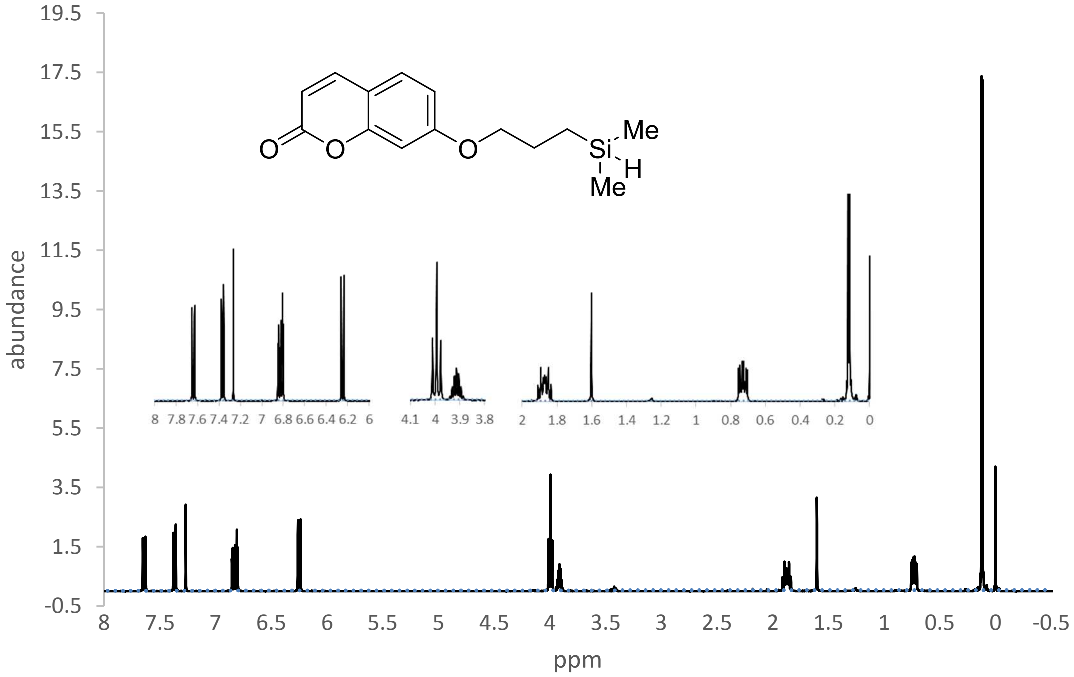
^{1}H NMR, 19



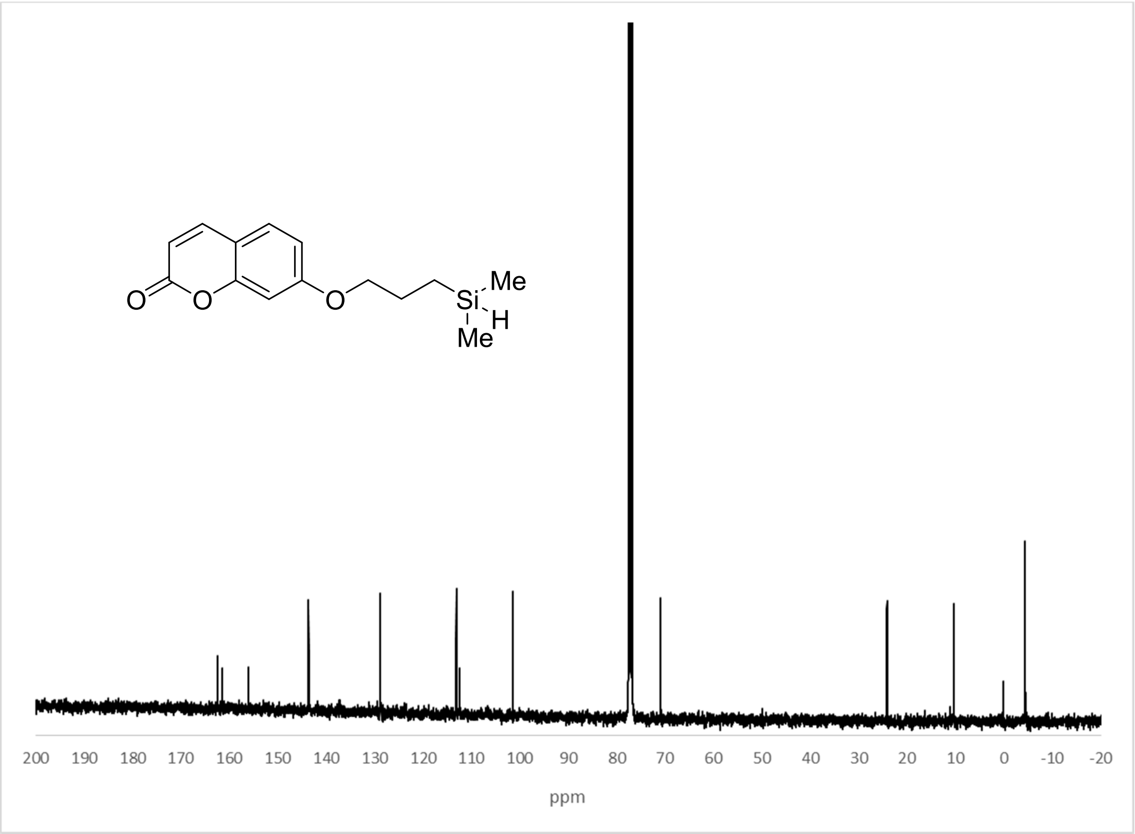
^{13}C NMR, 19



^{1}H NMR, 22

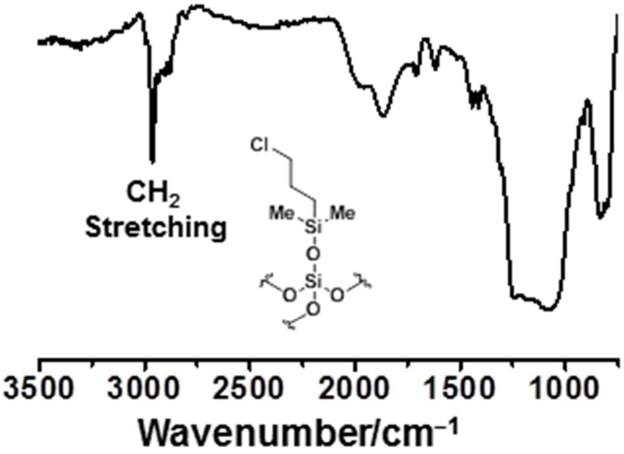


¹³C NMR, 22



6. FT-IR of grafted samples:

G2


CH$_2$
Stretching
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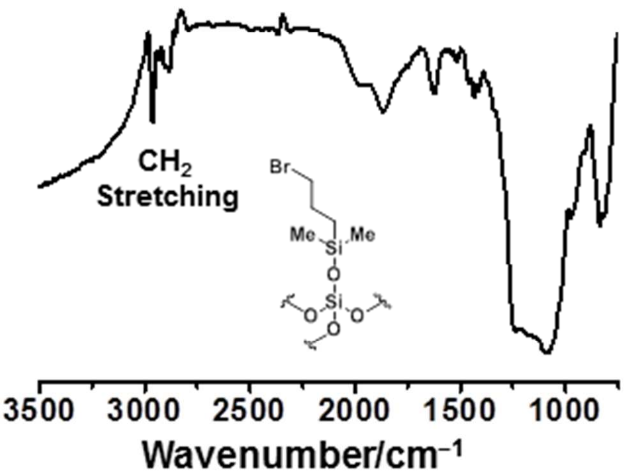
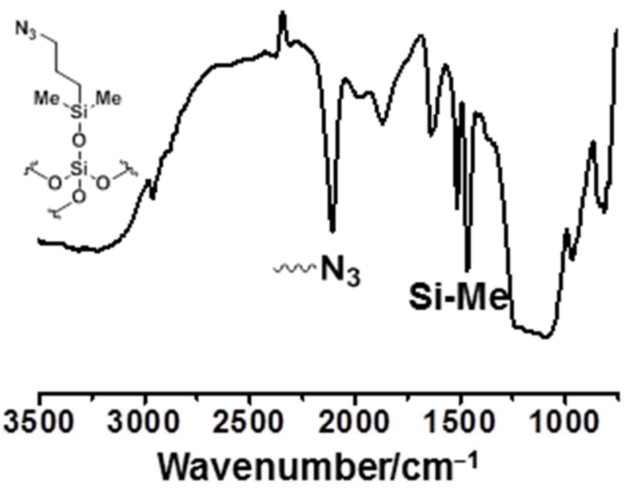
Me
Si
Me
O
Si
O
O
O
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

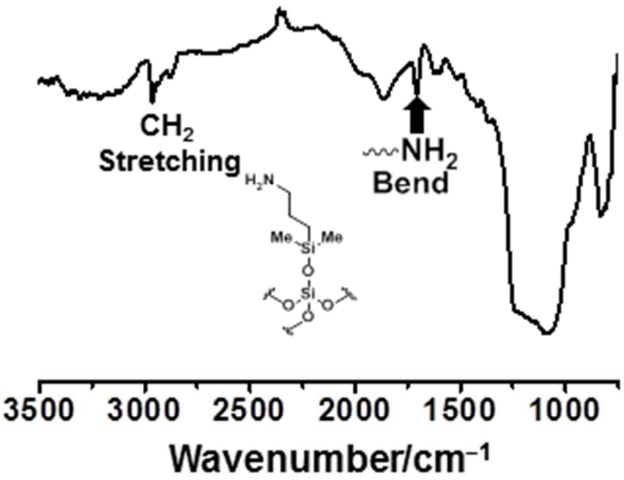
G3

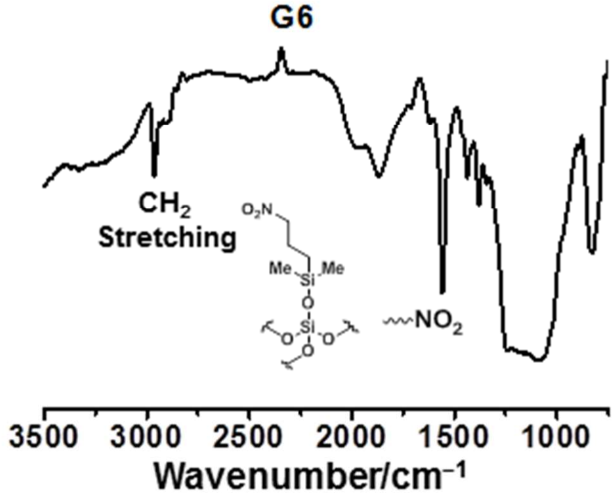

CH$_2$
Stretching
Br
Me
Si
Me
O
Si
O
O
O
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

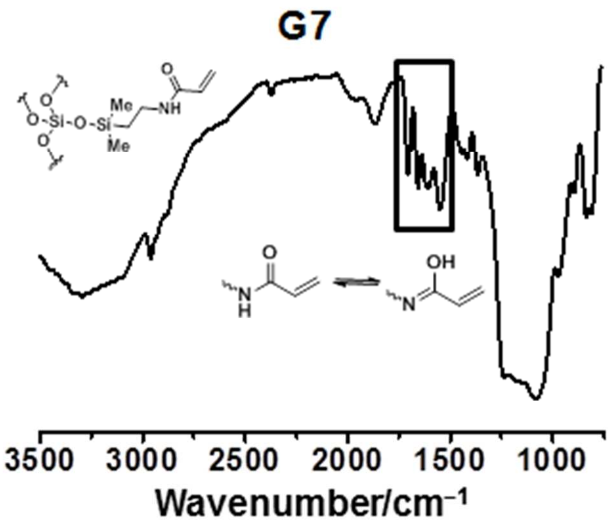
G4

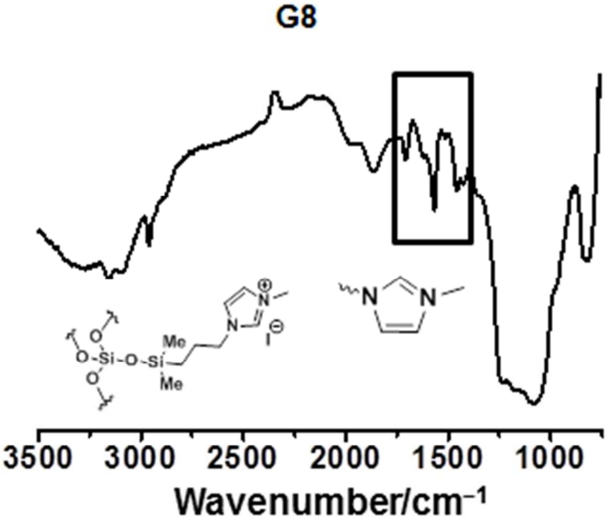

N$_3$
Me
Si
Me
O
Si
O
O
O
N$_3$
Si-Me
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

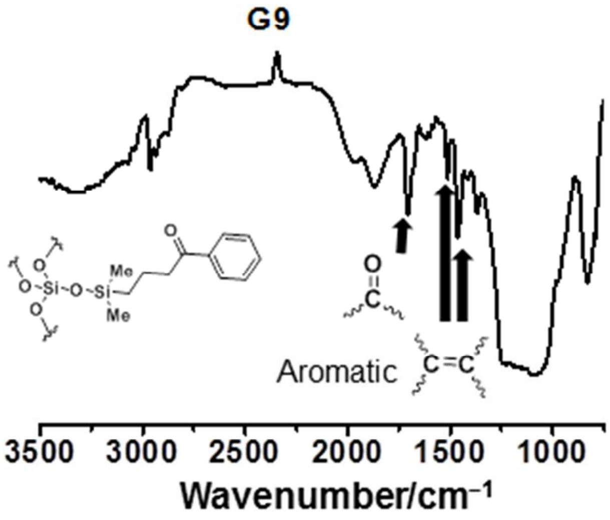
G5


CH$_2$
Stretching
H$_2$N
Me
Si
Me
O
Si
O
O
O
NH$_2$
Bend
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

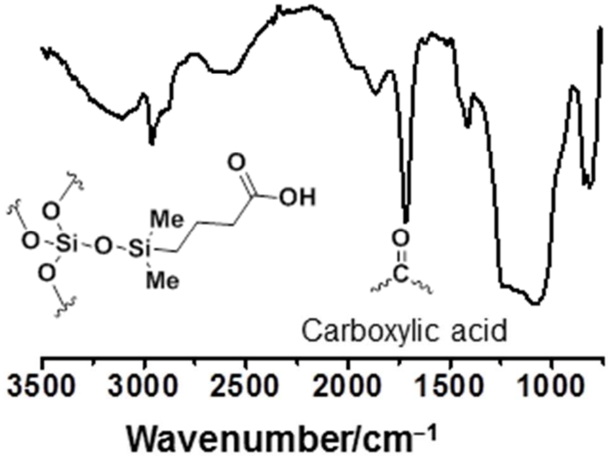

G6
CH$_2$
Stretching
O_2N
Me
Si
Me
O
Si
O
O
O
NO$_2$
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}


G7
O
Si
O
Si
Me
Me
O
NH
O
N
H
OH
N
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

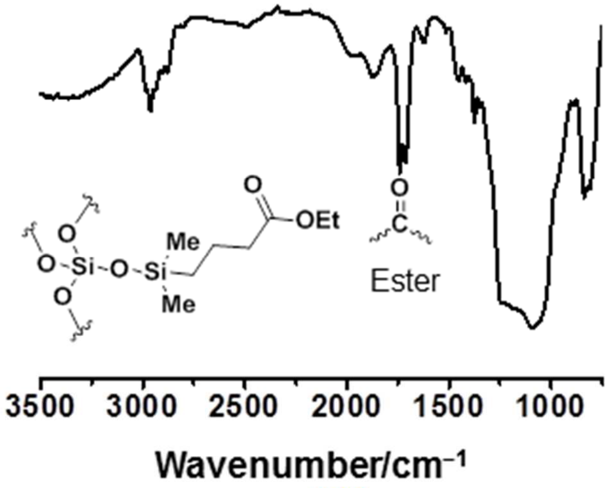

G8
O
Si
O
Si
Me
Me
N
N
⊕
I
⊖
N
N
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}


G9
O
Si
O
Si
Me
Me
O
O
C
Aromatic
C=C
3500
3000
2500
2000
1500
1000
Wavenumber/cm^{-1}

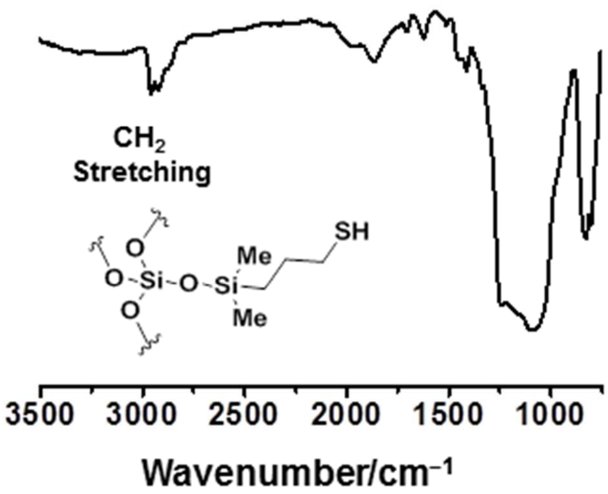
G10



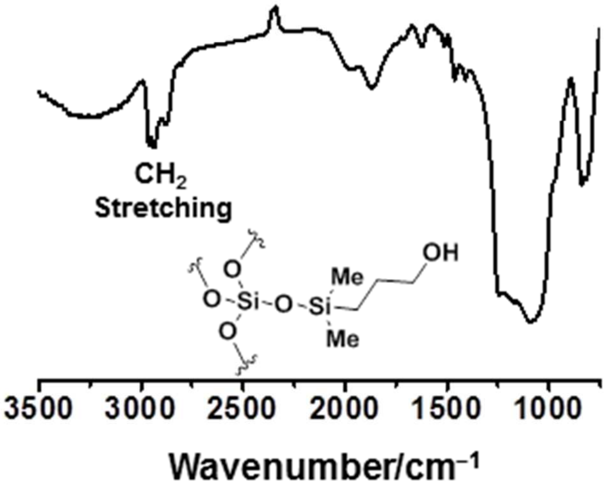
G11



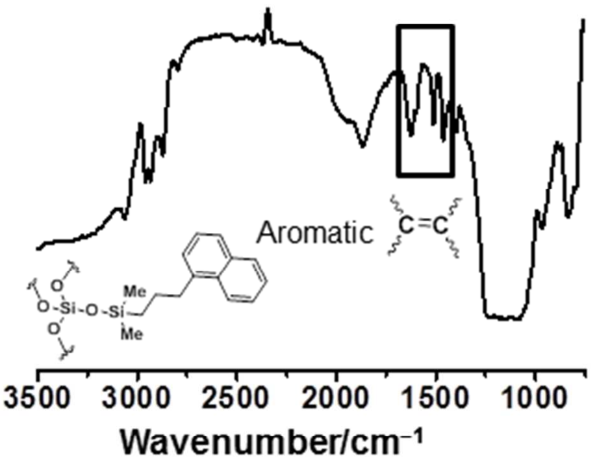
G12



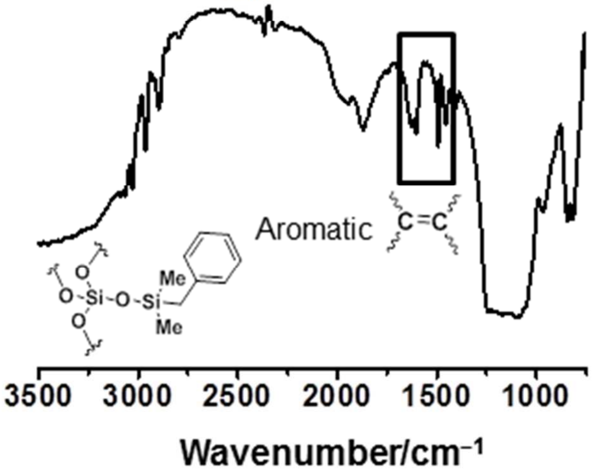
G13



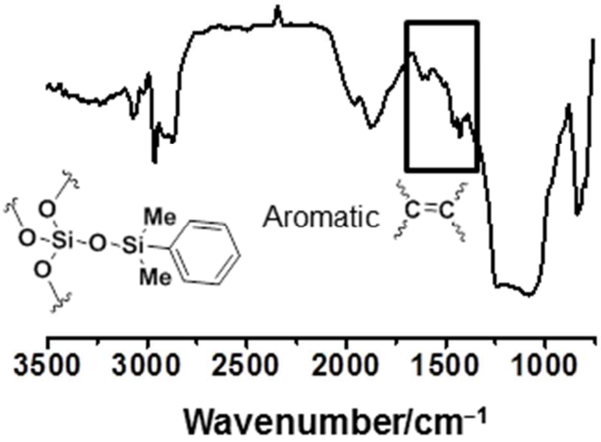
G14



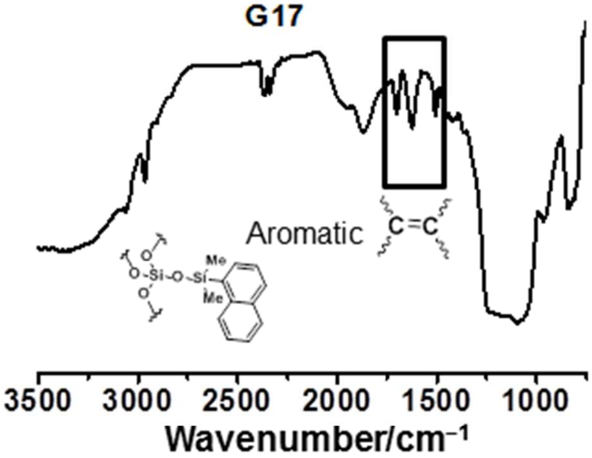
G15



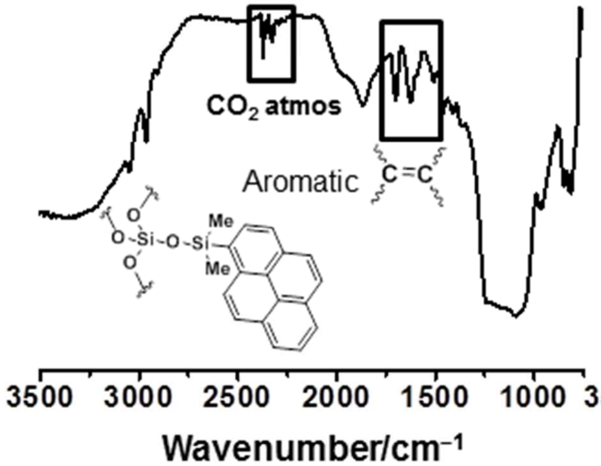
G16



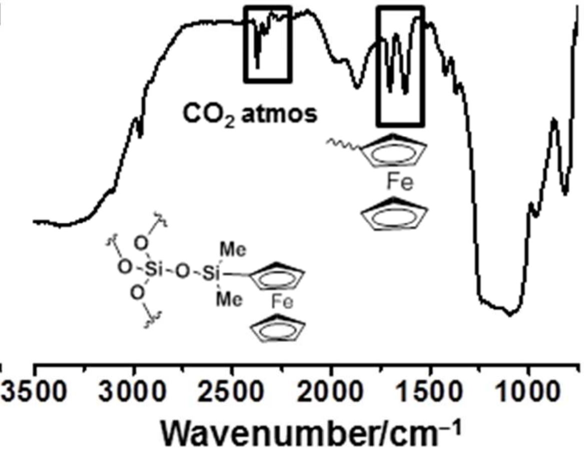
G17



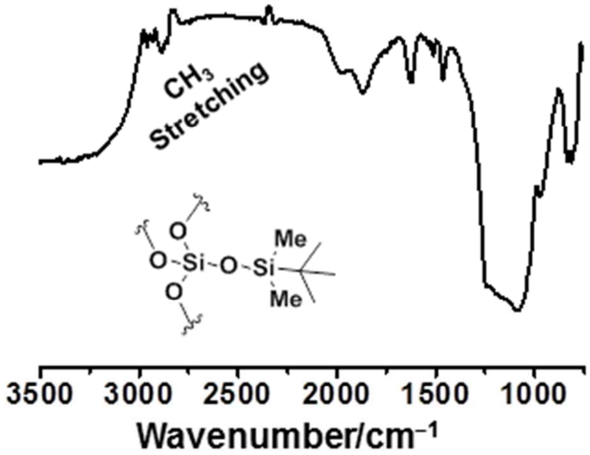
G18



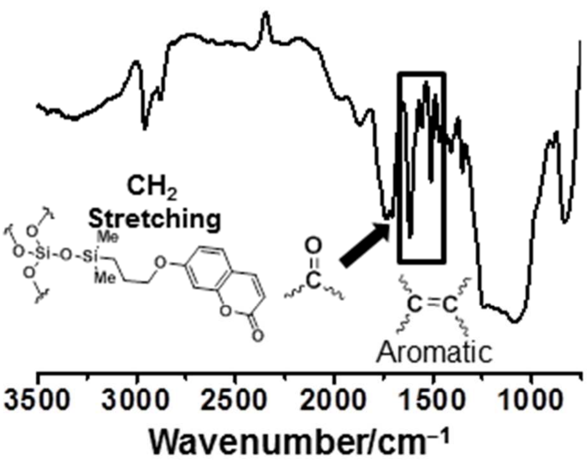
G19



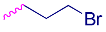
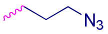
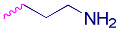
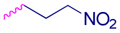
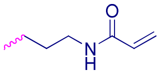
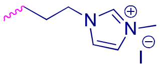
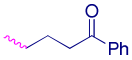
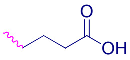
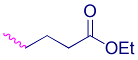
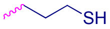
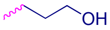
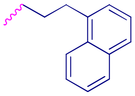
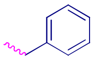
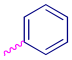
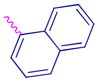
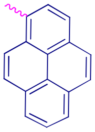
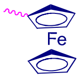
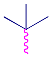
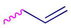
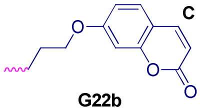
G20



G22b



7. Weight percentage of organics loading and surface coverage:

R	Wt% of organics	Surface Covrage, number/nm^2
 G2	C = 10.02 % Cl = 5.92 %	1.20
 G3	C = 10.12 % Br = 13.74 %	1.21
 G4	C = 10.45 % N = 7.35 %	1.23
 G5	C = 6.82 % N = 1.62 %	0.814
 G6	C = 8.05 % N = 1.80 %	0.94
 G7	C = 13.17 % N = 1.87 %	0.97
 G8	C = 10.57 % N = 2.75 %	0.69
 G9	C = 15.84 %	0.78
 G10	C = 9.02 %	0.89
 G11	C = 14.20 %	1.04
 G12	C = 9.06 % S = 4.81 %	1.06
 G13	C = 9.84 %	1.16
 G14	C = 28.08 %	1.10
 G15	C = 16.30 %	1.06
 G16	C = 13.25 %	0.97
 G17	C = 11.08 %	0.54
 G18	C = 11.45 %	0.37
 G19	C = 7.47 %	0.44
 G20	C = 3.74 %	0.37
 G21b	C = 10.44 %	1.23
 G22b	C = 18.94 %	0.80

8. Surface modification with ODS and confirmation by HPLC

Standard preparation procedure of C18 modified silica using alkoxysilane

Silica gel beads identical to that described in S3 was derivatized to C_{18} phase silica gel. A conventional procedure is given for the reaction of octadecyldimethylmethoxysilane with the silica gel (dried at 120 ^{o}C for 6 h under vacuum at 10^{-5} mmHg). To the dried silica gel was added 10 % solution of octadecyldimethylmethoxysilane in dodecane, and the mixture was stirred at 200 ^{o}C for 10 h. The modified silica gel was thoroughly rinsed with chloroform-acetone and dried in vacuo. The resulting silica gel was treated with 10% solution of trimethylmethoxysilane in hexane at 50 ^{o}C for 10 h, thoroughly rinsed with acetone and dried in vacuo (endcapping of residual silanols with trimethylsiloxy groups).

HPLC Separation Experiments

Modified silica gel beads were packed into stainless steel columns with 4.6 mmID x 250 mm length. The plate number per column (25 000 plates) and peak symmetries fulfilled the standards set to the commercial ODS-4 columns and were equivalent to those obtained with ODS-4 columns.

HPLC separations were performed under the conditions below.
Mobile Phase : CH_3CN / H_2O = 65 / 35
Flow Rate : 1.0 [mL/min]
Pressure : 6.8 [MPa]
Column Temp. : 40 [^{o}C]
Detector UV : 254 [nm]
Sample Size : 1.0 [μL]

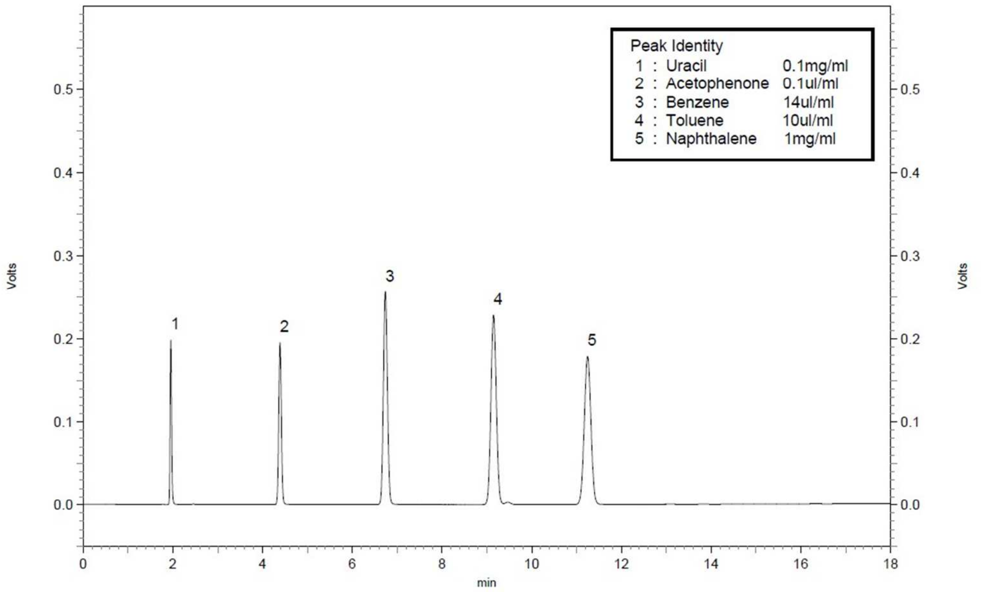


Figure S1. Chromatogram of a mixture of aromatic compounds. Column was packed with C18-modified spherical silica gel beads by hydrosilane modification. Relative retention for naphthalene (5th peak) is k' = 4.6.

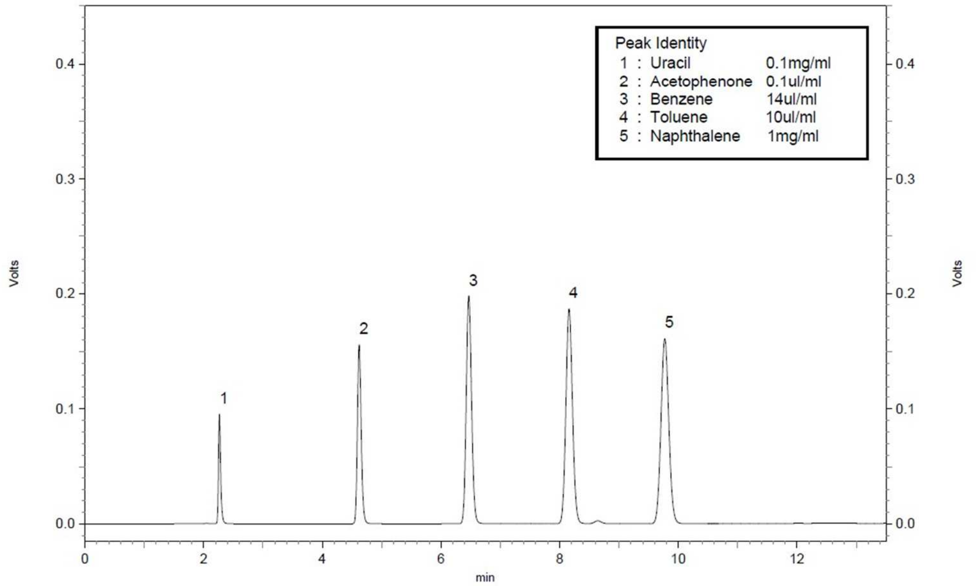


Figure S2. Chromatogram of a mixture of aromatic compounds. Column was packed with C18-modified spherical silica gel beads by alkoxysilane modification. Relative retention for naphthalene (5th peak) is k' = 3.7.

9. REFERENCES:

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