

Supplementary Information of

Introduction of Ferrocene-containing [2]Rotaxanes onto Siloxane, Silsesquioxane and Polysiloxanes via Click Chemistry

Gilbert Yu, Yuji Suzaki, Tomoko Abe and Kohtaro Osakada*

Chemical Resources Laboratory R1-3, Tokyo Institute of Technology

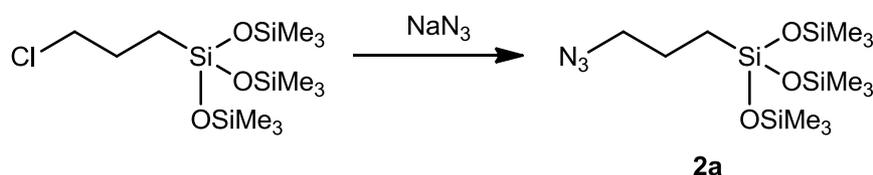
4259 Nagatsuta, Midoriku, Yokohama 226-8503, Japan

Fax/Tel: +81-45-924-5224

e-mail: kosakada@res.titech.ac.jp

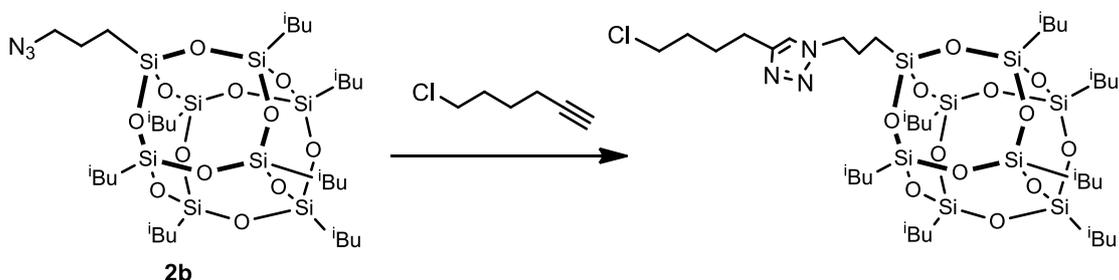
Experimental Section

$\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OSiMe}_3)_3$ (**2a**)



2a was prepared by a similar procedure reported in the literature.¹ The reaction of NaN_3 (870 mg, 13 mmol) and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OSiMe}_3)_3$ (2.0 g, 5.4 mmol) in DMF yield **2a** (1.62 g, 4.3 mmol, 80%).

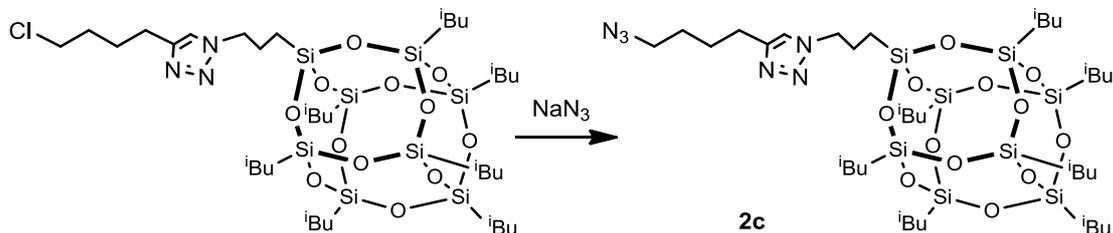
^1H NMR (400 MHz, CDCl_3 , r.t.) δ 0.10 (s, 27H, Me), 0.50 (m, 2H, CH_2Si), 1.63 (2H, $\text{CH}_2\text{CH}_2\text{N}_3$), 3.23 (t, 2H, CH_2N_3 , $J = 7.0$ Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , r.t.) δ 1.8 (Me), 11.7 (SiCH_2), 23.3 (SiCH_2CH_2), 54.1 (N_3CH_2) ppm; IR (KBr disk, r.t.): ν 2097 (N_3) cm^{-1} ; ESI-MS (eluent: acetone); calcd for $\text{C}_{12}\text{H}_{34}\text{N}_3\text{O}_3\text{Si}_4+\text{H}$ 380.2; found, m/z 380.3 $[\text{M}+\text{H}]^+$;



A CHCl_3 solution (30 mL) containing **2b** (1.20 g, 1.33 mmol), $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}$ (164 mg, 1.41 mmol) and $\text{Cu}[\text{Fe}(\text{CN})_4]\text{PF}_6$ (991 mg, 2.66 mmol) was stirred for 48 h at 50 °C. The resulting solution was fractionated between H_2O and CH_2Cl_2 and the separated organic phase was dried over MgSO_4 , filtered and evaporated to yield crude product which was purified by SiO_2 column chromatography (successive eluent; Hexane, Et_2O , and CH_2Cl_2) to $\text{ClCH}_2\text{CH}_2\text{CH}_2(\text{C}_2\text{HN}_3)(\text{CH}_2)_3(\text{C}_{28}\text{H}_{63}\text{O}_{12}\text{Si}_8)$ as a white solid (722 mg, 0.71 mmol, 53%).

^1H NMR (400 MHz, CDCl_3 , r.t.) δ 0.60-0.63 (2H, SiCH_2), 0.598 (d, 6H, SiCH_2 , $J = 7$ Hz), 0.601 (d, 6H, SiCH_2 , $J = 7$ Hz), 0.946 (d, 18H, Me, $J = 8$ Hz), 0.951 (d, 24H, Me, $J = 8$ Hz), 1.78-1.92 (m, 13H), 1.98 (m, 2H), 2.76 (t, 2H, $\text{C}_{\text{triazole}}\text{CH}_2$, $J = 7$ Hz), 3.57 (t, 2H, ClCH_2 , $J = 7$ Hz), 4.30 (t, 2H, NCH_2 , $J = 7$ Hz), 7.25 (s, 1H, C_2HN_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , r.t.) δ 9.4 (SiCH_2), 22.59, 22.63, 23.99, 24.00, 24.3, 25.1, 25.82, 25.83, 26.8, 32.2 ($\text{C}_{\text{triazole}}\text{CH}_2$), 44.9 (ClCH_2), 52.5 (NCH_2), 120.5 (C_2HN_3), 147.7 (C_2HN_3) ppm; Anal. Calcd for $\text{C}_{37}\text{H}_{78}\text{N}_3\text{O}_{12}\text{Si}_8\text{Cl}$: C, 43.69; H, 7.73; N, 4.13%. Found: C, 43.49; H, 7.62; N, 4.05%; HR-ESI-MS (eluent: acetone); calcd for $\text{C}_{37}\text{H}_{78}\text{N}_3\text{O}_{12}\text{Si}_8\text{Cl}+\text{Na}$ 1038.3326; found, m/z 1038.3320 $[\text{M}+\text{Na}]^+$.

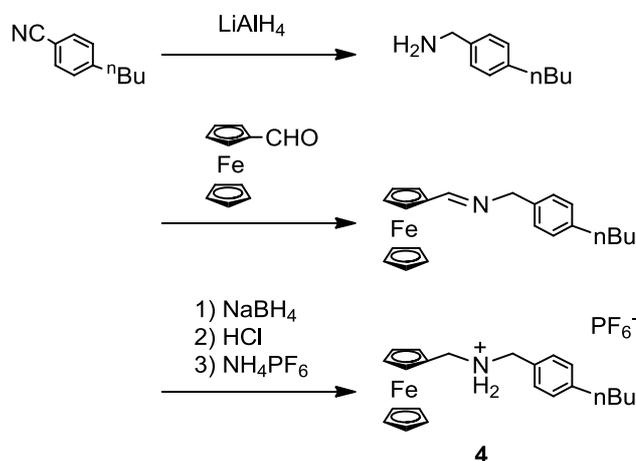
$\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_2\text{HN}_3)(\text{CH}_2)_3(\text{C}_{28}\text{H}_{63}\text{O}_{12}\text{Si}_8)$ (**2c**)



2c was prepared by a similar procedure reported in the literature.¹ The reaction of NaN₃ (319 mg, 4.9 mmol), KI (814 mg, 4.9 mmol) and ClCH₂CH₂CH₂(C₂HN₃)(CH₂)₃(C₂₈H₆₃O₁₂Si₈) (960 mg, 0.94 mmol) in DMF (20 mL) at 80 °C overnight. The resulting solution was fractionated between brine and CH₂Cl₂/Hexane and the separated organic phase was dried over MgSO₄, filtered and evaporated to yield **2c** as a yellow solid (713 mg, 0.70 mmol, 74%).

¹H NMR (400 MHz, CDCl₃, r.t.) δ 0.61-0.63 (2H, SiCH₂), 0.601 (d, 6H, SiCH₂, *J* = 7 Hz), 0.604 (d, 6H, SiCH₂, *J* = 7 Hz), 0.949 (d, 18H, Me, *J* = 7 Hz), 0.954 (d, 24H, Me, *J* = 7 Hz), 1.64-1.72 (m, 2H), 1.75-1.90 (m, 11H), 1.98 (m, 2H), 2.76 (t, 2H, *J* = 7 Hz), 3.31 (t, 2H, N₃CH₂, *J* = 7 Hz), 4.30 (t, 2H, NCH₂, *J* = 8 Hz), 7.24 (s, 1H, C₂HN₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃, r.t.) δ 9.4 (SiCH₂), 22.6, 22.7, 24.0, 24.1, 25.4, 25.8 (2 signals), 26.8, 28.6 (C_{triazole}CH₂), 51.4 (NCH₂), 52.5 (NCH₂), 120.4 (C₂HN₃), 147.7 (C₂HN₃) ppm; Anal. Calcd for C₃₇H₇₈N₆O₁₂Si₈: C, 43.41; H, 7.68; N, 8.21%. Found: C, 43.50; H, 7.98; N, 7.94%; HR-ESI-MS (eluent: acetone); calcd for C₃₇H₇₈N₆O₁₂Si₈+Na 1045.3730; found, *m/z* 1045.3754 [M+Na]⁺.

Synthesis of model compound, $[\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{-4-nBu}]\text{PF}_6$



Scheme S1. Synthesis of model compound **4**

$\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$

$\text{NCC}_6\text{H}_4\text{-4-nBu}$ (3.19 g, 20 mmol) was added dropwise to a suspension of LiAlH_4 (1.55 g, 41 mmol) in THF (150 mL) at room temperature and was refluxed for 15 h. The resulting mixture was cooled to 0 °C, quenched with 1M $\text{KOH}(\text{aq})$ (ca. 40 mL), and fractionated by addition of hexane. The separated organic phase was dried over MgSO_4 and evaporation of the solution gave the crude product which was purified by SiO_2 column chromatography (eluent: $\text{CHCl}_3/\text{methanol} = 10/1$) to give $\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$ as colorless oil (2.22 g, 14 mmol, 70%). The compound was analyzed by ^1H NMR spectroscopy.²

$\text{FcCH}=\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$ ($\text{Fc} = \text{Fe}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)$)

A solution of ferrocenecarboxaldehyde (2.37 g, 11 mmol) and $\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$ (2.16 g, 13 mmol) in EtOH (200 mL) was stirred for 12 h at 65 °C in the presence of MS4A (molecular sieves 4A, 2.0 g). The reaction mixture was filtered and then evaporated to yield the crude product which was purified by washing

with cold hexane to yield $\text{FcCH}=\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$ as a reddish-brown solid (2.35 g, 6.6 mmol, 49%).

^1H NMR (300 MHz, CDCl_3 , r.t.) δ 0.91 (t, 3H, Me, $J = 7$ Hz), 1.34 (m, 2H, CH_2 , $J = 7$ Hz), 1.58 (m, 2H, CH_2 , $J = 7$ Hz), 2.59 (m, 2H, CH_2), 4.17 (s, 5H, C_5H_5), 4.37 (m, 2H, C_5H_4), 4.63 (s, 2H, NCH_2), 4.68 (m, 2H, C_5H_4), 7.15 (d, C_6H_4 , $J = 8$ Hz), 7.21 (d, C_6H_4 , $J = 8$ Hz), 8.23 (s, 1H, NCH) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , r.t.) δ 13.8 (Me), 22.1 (CH_2), 33.5 (CH_2), 35.1 (CH_2), 64.7 (NCH_2), 68.4 (C_5H_4), 68.9 (C_5H_5), 70.2 (C_5H_4), 80.4 (C_5H_4), 127.6 (C_6H_4), 128.3 (C_6H_4), 136.6 (C_6H_4), 141.2 (C_6H_4), 161.7 ($\text{N}=\text{C}$) ppm; IR (KBr disk, r.t.): ν 1636 ($\text{C}=\text{N}$) cm^{-1} ; Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{FeN}+(\text{H}_2\text{O})_{0.25}$: C, 72.63; H, 7.07; N, 3.85%. Found: C, 72.41; H, 7.16; N, 3.73%.

[FcCH₂NH₂CH₂C₆H₄-4-nBu]PF₆ (4)

$\text{FcCH}=\text{NCH}_2\text{C}_6\text{H}_4\text{-4-nBu}$ (1.79 g, 5.0 mmol) was dissolved in MeOH (50 mL) at room temperature. NaBH_4 (2.25 g, 59 mmol) was added to the solution and stirred for 4 h at room temperature and then mixed with 4 M HCl to cause the separation of a solid from the solution. The resulting solid was filtered and washed with hexane and Et_2O to yield $[\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{-4-nBu}]\text{Cl}$ (1.81 g, 4.5 mmol) which was used without further purification. Acetone (50 mL) suspension of $[\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{-4-nBu}]\text{Cl}$ (1.81 g) was poured into an acetone solution (50 mL) of NH_4PF_6 (3.32 g, 20 mmol) and stirred for 1 h at room temperature. The resulting mixture was filtered and the solids were washed with water and CH_2Cl_2 to give $[\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{-4-nBu}]\text{PF}_6$ (**4**) as yellow solid (1.79 g, 3.5 mmol).

^1H NMR (300 MHz, CD_3CN , r.t.) δ 0.91 (t, 3H, Me, $J = 7$ Hz), 1.33 (m, 2H, CH_2 , $J = 7$ Hz), 1.51 (m, 2H, CH_2 , $J = 7$ Hz), 2.62 (m, 2H, CH_2), 4.04 (s, 2H, NCH_2), 4.06 (s, 2H, NCH_2), 4.21 (s, 5H, C_5H_5), 4.27 (m, 2H, C_5H_4), 4.37 (m, 2H, C_5H_4), 7.26 (d, C_6H_4 , $J = 8$ Hz), 7.31 (d, C_6H_4 , $J = 8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_3CN , r.t.) δ

13.9 (Me), 22.7 (CH₂), 33.9 (CH₂), 35.5 (CH₂), 48.2 (NCH₂), 51.4 (NCH₂), 68.9 (C₃H₅), 70.2 (C₅H₄), 71.2 (C₅H₄), 76.3 (C₅H₄), 128.6 (C₆H₄), 129.7 (C₆H₄), 130.6 (C₆H₄), 145.2 (C₆H₄) ppm; Anal. Calcd for C₂₂H₂₈F₆FeNP: C, 52.09; H, 5.56; N, 2.76%. Found: C, 52.05; H, 5.50; N, 2.79%; IR (KBr disk, r.t.) ν 3258 (N–H), 3235 (N–H), 824 (P–F), 559 (P–F) cm⁻¹.

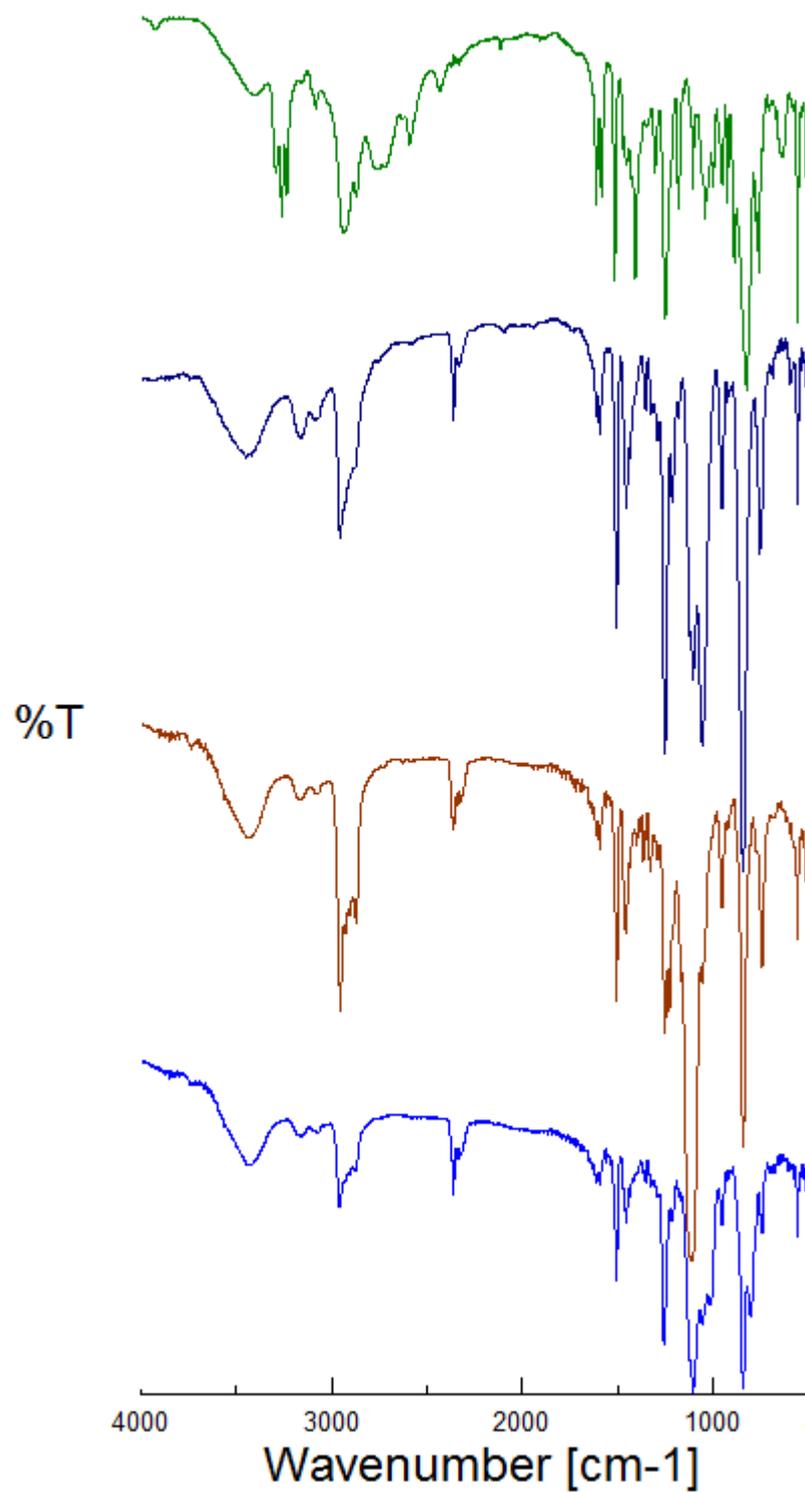


Figure S1, IR spectra of (A) **1**, (B) **3a**, (C) **3b** and (D) **3d** (KBr disk, r.t.).

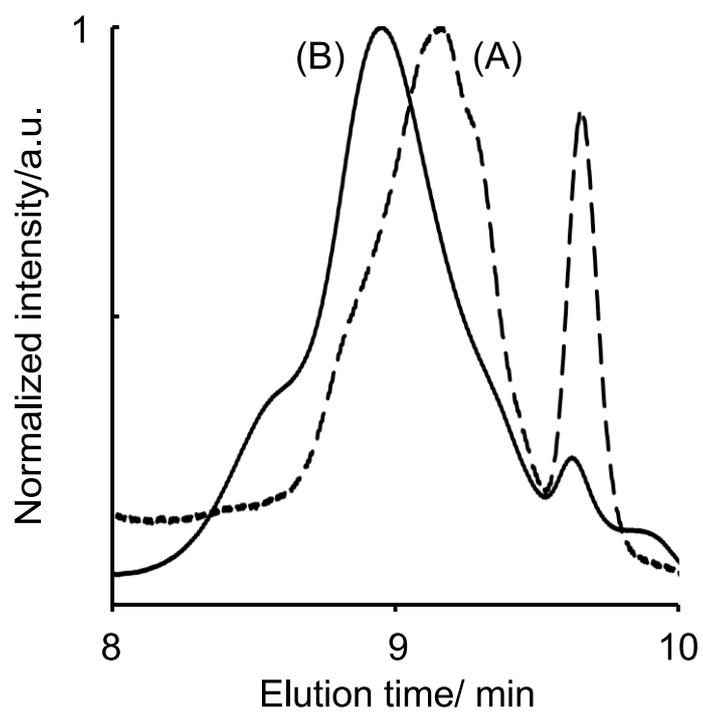


Figure S2, GPC Charts of (A) **2d** and (B) **3d** (eluent; THF).

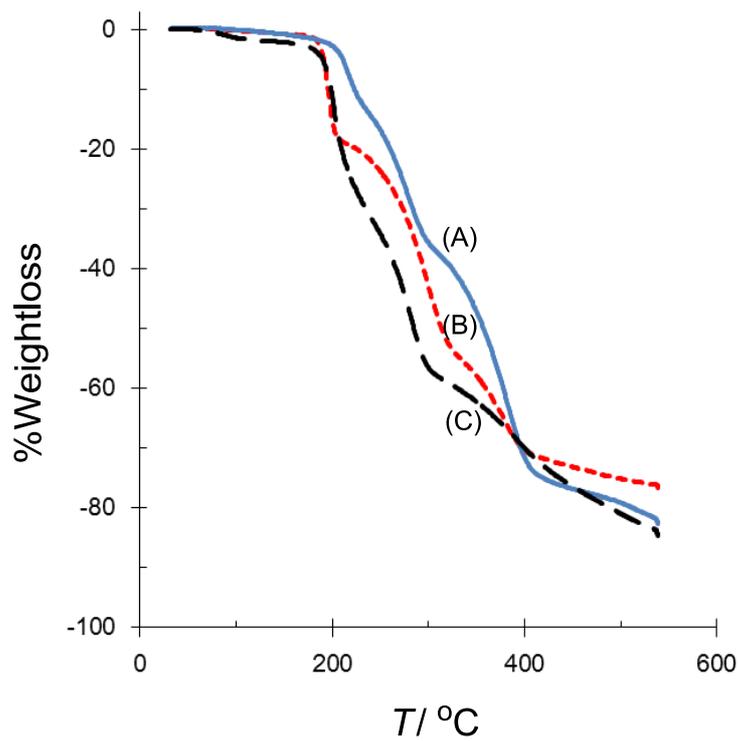


Figure S4, Thermogravimetric (TG) analysis charts of (A) **3a**, (B) **3b** and (C) **3d** (scan rate: 5 °C/min).

Table S1, 5% weight loss temperature, T_{d5} , of the compounds determined by TG analysis (5 °C/min).

Compound	5% weight loss temperature, T_{d5}
1	197 °C
2c	159 °C
3a	193 °C
3b	213 °C
3d	192 °C
chloropropyl-heptaisobutyl substituted silasesquioxane	230 °C

Table S2, Crystallographic data of [(DB24C8)4].

Formula	C ₅₀ H ₆₈ F ₆ FeNO ₁₀ P
<i>F</i> _w	1043.90
size of crystal/ mm	0.50 x 0.30 x 0.35
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (no 14)
<i>a</i> / Å	10.108(4)
<i>b</i> / Å	24.054(9)
<i>c</i> / Å	21.012(8)
<i>β</i> / °	92.146(7)
<i>V</i> / Å ³	5105(4)
<i>Z</i>	4
<i>D</i> _c / g cm ⁻³	1.358
No. of reflections measured	36929
No. of unique reflections	11405
No. of observations (<i>I</i> > 3.0σ(<i>I</i>))	8012
No. of variables	707
<i>GOF</i>	0.966
<i>R</i> , <i>R</i> _w	0.0695, 0.1154

References

- 1) X. Yang, L. Dai and P. W. Carr, *J. Chromatogr. A*, 2003, **996**, 13.
- 2) Pat. US2005/203086 A1, 2005.