Supporting Information

For

Base-catalyzed pathway towards isocyanate derivatives of silsesquioxanes

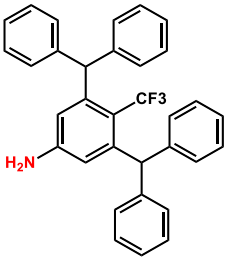
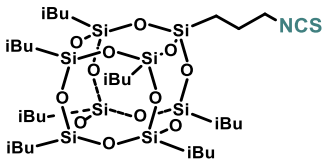
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Faculty of Chemistry, Adam Mickiewicz University in Poznan, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland. E-mail: pkw@amu.edu.pl

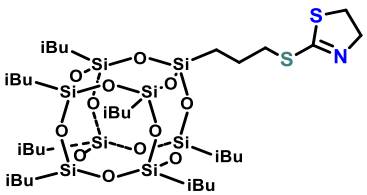
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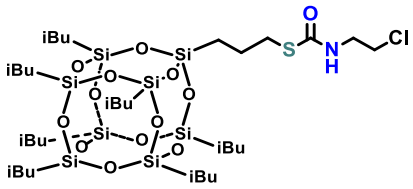
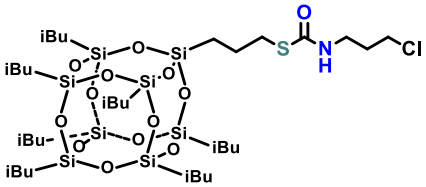
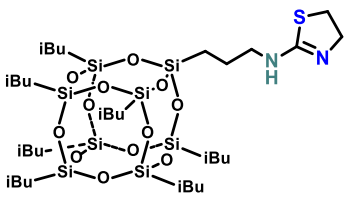
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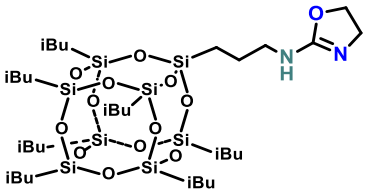
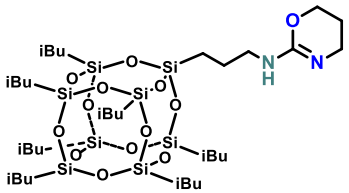
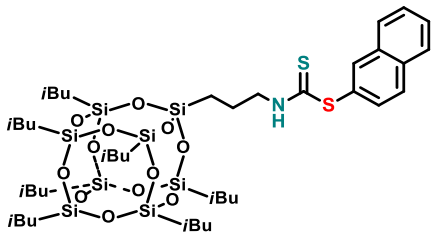
1. Analytical data of substrates 2c and SQ-NCS

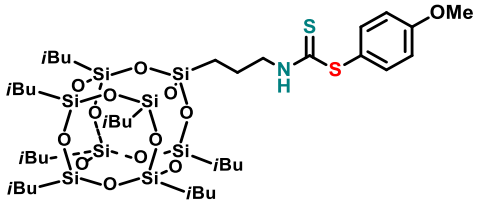
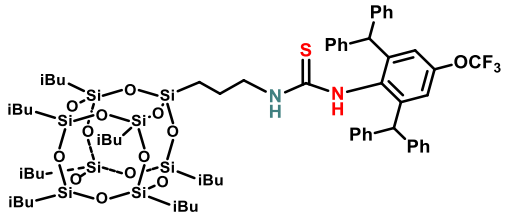
 **2c**	White solid, isolated yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 3.75 (s, 2H, NH_2), 5.40 (s, 2H, CHPh$_2$), 6.83 (s, 2H, m-CH$_{Ar}$), 7.03-7.10 (m, 8H, C$_6H_5$), 7.20-7.25 (m, 4H, C$_6H_5$), 7.27-7.34 (m, 8H, C$_6H_5$); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 52.54 (*C*HPh$_2$), 119.22 (q, J = 32.1 Hz), 123.50, 125.49 (q, J = 3.8 Hz), 126.20, 128.69, 128.77, 129.36, 141.58, 145.21; MS (ESI+): m/z 494 [M+H]$^+$.
 **SQ-NCS**	White solid, isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.54 (dd, 14H, J_{HH} = 7.0, 3.2 Hz, CH_2), 0.59 – 0.66 (m, 2H, CH_2), 0.89 (dd, 42H, J_{HH} = 6.6, 1.9 Hz, CH_3), 1.70-1.86 (m, 9H, CH_2 and CH), 3.43 (t, 2H, J_{HH} = 6.7 Hz, NCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 9.37 (*C*H$_2$), 22.44 (*C*H$_2$), 22.48 (*C*H$_2$), 23.83 (*C*H), 23.89 (*C*H), 24.03 (*C*H$_2$), 25.66 (*C*H$_3$), 25.67 (*C*H$_3$), 47.22 (N*C*H$_2$), 164.65 (N*C*S); MS (ESI+): m/z 938 [M+Na]$^+$. These NMR data matched those reported in the literature.[S1]

2. Analytical data of products P1-P12

 **Product P1**	White solid, isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.60 (dd, 14H, J_{HH} = 7.1, 2.0 Hz, CH_2), 0.70 – 0.75 (m, 2H, CH_2), 0.88 – 0.92 (m, 42H, CH_3), 1.78 – 1.90 (m, 9H, CH_2 and CH), 3.10 (t, 2H, J_{HH} = 7.3 Hz, CH_2), 3.36 (t, 2H, J_{HH} = 8.0 Hz, SCH_2), 4.20 (t, 2H, J_{HH} = 8.0 Hz, SCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.57 (*C*H$_2$), 22.44 (*C*H$_2$), 22.51 (*C*H$_2$), 23.00 (*C*H$_2$), 23.83 (*C*H$_2$), 23.87 (*C*H), 23.88 (*C*H), 25.67 (*C*H$_3$), 25.69 (*C*H$_3$), 34.27 (*C*H$_2$), 35.50 (N*C*H$_2$), 64.35 (S*C*H$_2$), 165.60 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.63, -67.90, -68.20; MS (ESI+): m/z 976 [M+H]$^+$.

 **Product P2**	White solid, isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.55 – 0.64 (m, 14H, CH_2), 0.68 – 0.73 (m, 2H, CH_2), 0.89 – 1.01 (m, 42H, CH_3), 1.67 – 1.74 (m, 2H, CH_2), 1.80 – 1.90 (m, 7H, CH_2), 2.48– 2.57 (m, 1H, CH_2), 2.93 (t, 2H, J_{HH} = 7.1 Hz, CH_2), 3.61 – 3.63 (m, 2H, CH_2), 5.73 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.45 (*C*H_2), 22.40 (*C*H_2), 22.47 (*C*H_2), 23.83 (*C*H), 23.86 (*C*H), 25.67 (br s, *C*H_3), 27.37 (*C*H_2), 27.65 (*C*H_2), 32.83 (*C*H_2), 43.67 (S*C*H_2), 167.83 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.64, -67.90, -68.09; MS (ESI+): m/z 1020 $[M+K]^+$.
 **Product P3**	White solid, isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.53 – 0.65 (m, 14H, CH_2), 0.67 – 0.73 (m, 2H, CH_2), 0.88 – 1.03 (m, 42H, CH_3), 1.66 – 1.74 (m, 2H, CH_2), 1.79 – 1.89 (m, 7H, CH_2), 1.96 – 2.04 (m, 2H, CH_2), 2.48 – 2.56 (m, 1H, CH_2), 2.92 (t, 1H, J_{HH} = 7.1 Hz, CH_2), 3.35 (dd, 1H, J_{HH} = 12.6, 6.4 Hz, SCH_2), 3.45 (dd, 1H, J_{HH} = 12.6, 6.4 Hz, SCH_2), 3.55 – 3.63 (m, 2H, CH_2), 5.48 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.49 (*C*H_2), 22.44 (*C*H_2), 22.51 (*C*H_2), 23.84 (*C*H), 23.87 (*C*H), 25.66 (*C*H_3), 25.68 (*C*H_3), 32.23 (*C*H_2), 32.76 (*C*H_2), 37.84 (*C*H_2), 42.15 (*C*H_2), 42.55 (*C*H_2), 158.08 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.65, -67.90, -68.06; MS (ESI+): m/z 1034 $[M+Na]^+$.
 **Product P4**	White solid, isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.56 – 0.65 (m, 16H, CH_2), 0.90 – 0.99 (m, 42H, CH_3), 1.67 – 1.74 (m, 2H, CH_2), 1.80 – 1.89 (m, 7H, CH_2), 3.27 (t, 2H, J_{HH} = 7.3 Hz, CH_2), 3.38 (t, 2H, J_{HH} = 7.4 Hz, CH_2), 3.98 (t, 2H, J_{HH} = 7.4 Hz, CH_2), 5.67 (br s, 1H, NH); ^{13}C NMR (100 MHz, CD_2Cl_2, 296K): δ (ppm) 10.08 (*C*H_2), 22.50 (*C*H_2), 22.54 (*C*H_2), 23.83 (*C*H), 23.87 (*C*H), 24.30 (*C*H_2), 25.68 (*C*H_3), 26.59 (*C*H_2), 33.60 (*C*H_2), 50.57 (N*C*H_2), 57.56 (S*C*H_2), 158.26 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.62, -67.89 (br s); MS (ESI+): m/z 959 $[M+Na]^+$.

 **Product P5**	White solid, isolated yield: 96%; ^{1}H NMR (400 MHz, CD_2Cl_2, 296K): δ (ppm) 0.58 – 0.61 (m, 16H, CH_2), 0.94 – 0.96 (m, 42H, CH_3), 1.56 – 1.65 (m, 2H, CH_2), 1.82 – 1.88 (m, 7H, CH_2), 3.13 (t, 2H, J_{HH} = 7.0 Hz, CH_2), 3.69 (t, 2H, J_{HH} = 8.5 Hz, CH_2), 4.18 (t, 2H, J_{HH} = 8.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 9.37 (*C*H_2), 22.42 (*C*H_2), 22.45 (*C*H_2), 23.51 (*C*H_2), 23.47 (*C*H_2), 23.83 (*C*H), 23.87 (*C*H), 25.68 (*C*H_3), 42.13 (*C*H_2), 42.96 (*C*H_2), 45.15 (*C*H_2), 157.56 (N*C*N); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.62, -67.86 (br s); MS (ESI+): m/z 943 $[M+H]^+$.
 **Product P6**	White solid, isolated yield: 96%; ^{1}H NMR (400 MHz, CD_2Cl_2, 296K): δ (ppm) 0.58 – 0.62 (m, 16H, CH_2), 0.94 – 0.96 (m, 42H, CH_3), 1.50 – 1.61 (m, 2H, CH_2), 1.82 – 1.88 (m, 7H, CH_2), 1.94 (t, 2H, J_{HH} = 6.5 Hz, CH_2), 3.06 – 3.13 (m, 2H, CH_2), 3.26 – 3.30 (m, 2H, CH_2), 3.59 (t, 2H, J_{HH} = 6.5 Hz, CH_2), 4.53 – 4.64 (m, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 9.40 (*C*H_2), 22.43 (*C*H_2), 22.46 (*C*H_2), 23.51 (*C*H_2), 23.83 (*C*H), 23.87 (*C*H), 25.66 (*C*H_3), 32.78 (*C*H_2), 32.62 (*C*H_2), 42.59 (*C*H_2), 65.60 (*C*H_2), 157.97 (N*C*N); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.63, -67.86, -67.91; MS (ESI+): m/z 957 $[M+H]^+$.
 **Product P7**	White solid, isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57–0.66 (m, 14H, CH_2), 0.68 – 0.74 (m, 2H, CH_2), 0.95–1.00 (m, 42H, CH_3), 1.80–1.90 (m, 9H, CH_2), 3.50 (t, 2H, J_{HH} = 6.7 Hz, CH_2), 7.14–7.24 (m, 1H, N*H*), 7.43–7.48 (m, 2H, Ph), 7.63 (dd, 1H, J_{HH} = 8.7, 1.9 Hz, Ph), 7.72–7.75 (m, 1H, Ph), 7.78-7.81 (m, 2H, Ph), 7.99 (d, 1H, J_{HH} = 1.9 Hz, Ph); ^{13}C NMR (100 MHz, CD_2Cl_2, 296K): δ (ppm) 9.37 (*C*H_2), 22.44 (*C*H_2), 22.49 (*C*H_2), 23.84 (*C*H), 23.90 (*C*H), 24.05 (*C*H_2), 25.66 (*C*H_3), 25.58 (*C*H_2), 47.21 (N*C*H_2), 125.69, 126.22, 126.60, 126.71, 127.45, 127.75, 128.95, 132.52, 133.49, 134.29, 164.65 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.50, -67.83. -68.55.

 **Product P8**	White solid, isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.59–0.63 (m, 14H, CH_2), 0.68 – 0.72 (m, 2H, CH_2), 0.94–0.98 (m, 42H, CH_3), 1.79–1.88 (m, 9H, CH_2), 3.80 (t, 2H, J_{HH} = 8.9 Hz, CH_2), 5.23 (s, 1H, N*H*), 6.83 (d, 2H, J_{HH} = 8.9 Hz, C_6H_4-OCH_3), 7.39 (d, 2H, J_{HH} = 8.9 Hz, C_6H_4- OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 9.36 (*C*H_2), 22.43 (*C*H_2), 22.48 (*C*H_2), 23.83 (*C*H), 23.89 (*C*H), 24.03 (*C*H_2), 25.65 (*C*H_3), 25.68 (*C*H_2), 47.21 (N*C*H_2), 55.34 (O*C*H_3), 114.61, 128.46, 129.94, 132.64, 159.92 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.52, -67.85, -68.57.
 **Product P9**	White solid, isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.59–0.67 (m, 14H, CH_2), 0.70 – 0.74 (m, 2H, CH_2), 0.93–1.03 (m, 42H, CH_3), 1.80–1.92 (m, 9H, CH_2), 3.51 (t, 2H, J_{HH} = 6.7 Hz, CH_2), 5.42 (s, 2H, C*H*Ph), 6.84 (s, 2H, m-CH_{Ar}), 7.00-7.12 (m, 9H, Ph + N*H*), 7.13-7.25 (m, 5H, Ph + N*H*), 7.27-7.35 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 9.36 (*C*H_2), 22.43 (*C*H_2), 22.48 (*C*H_2), 23.83 (*C*H), 23.89 (*C*H), 24.04 (*C*H_2), 25.65 (*C*H_3), 25.68 (*C*H_2), 47.20 (N*C*H_2), 52.41 (*C*HPh_2), 125.48, 127.02, 127.86, 128.36, 128.71, 129.31, 141.56, 145.18, 173.20 (N*C*S); ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.50, -67.76, -67.95.

3. NMR spectra of substrates 2c and SQ-NCS

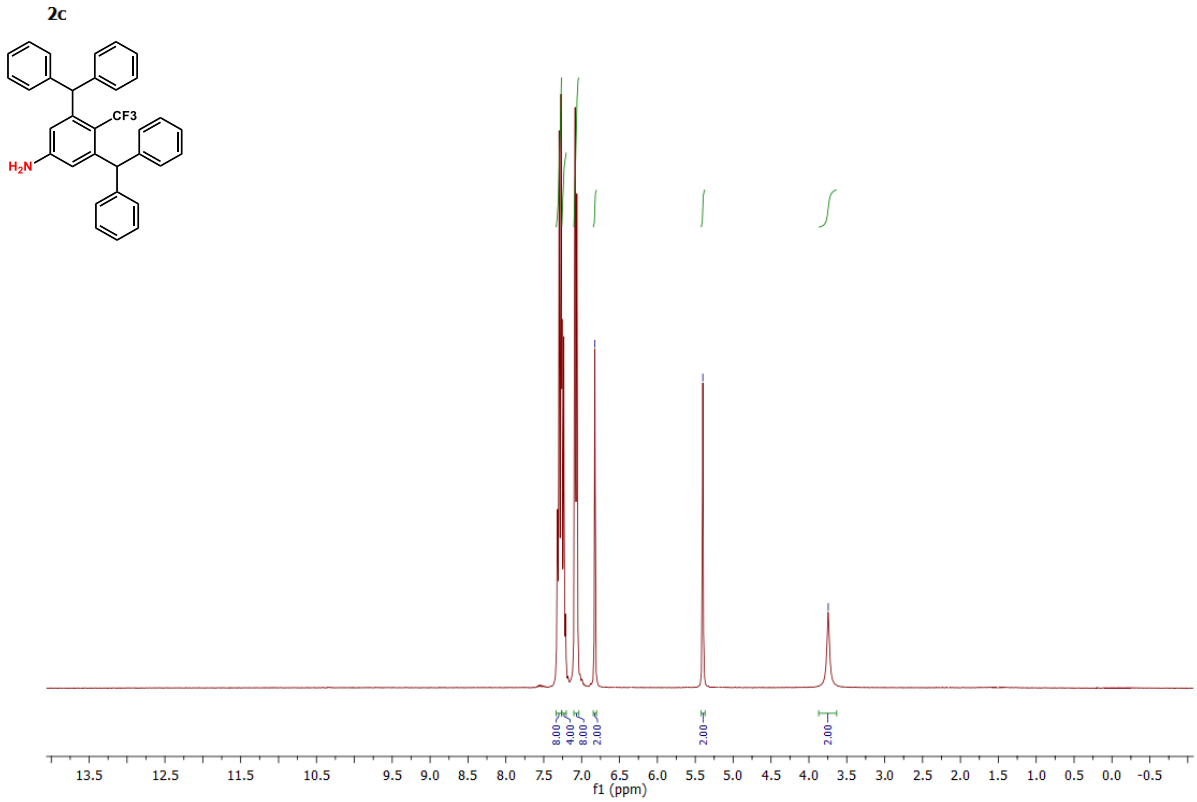


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of substrate **2c**

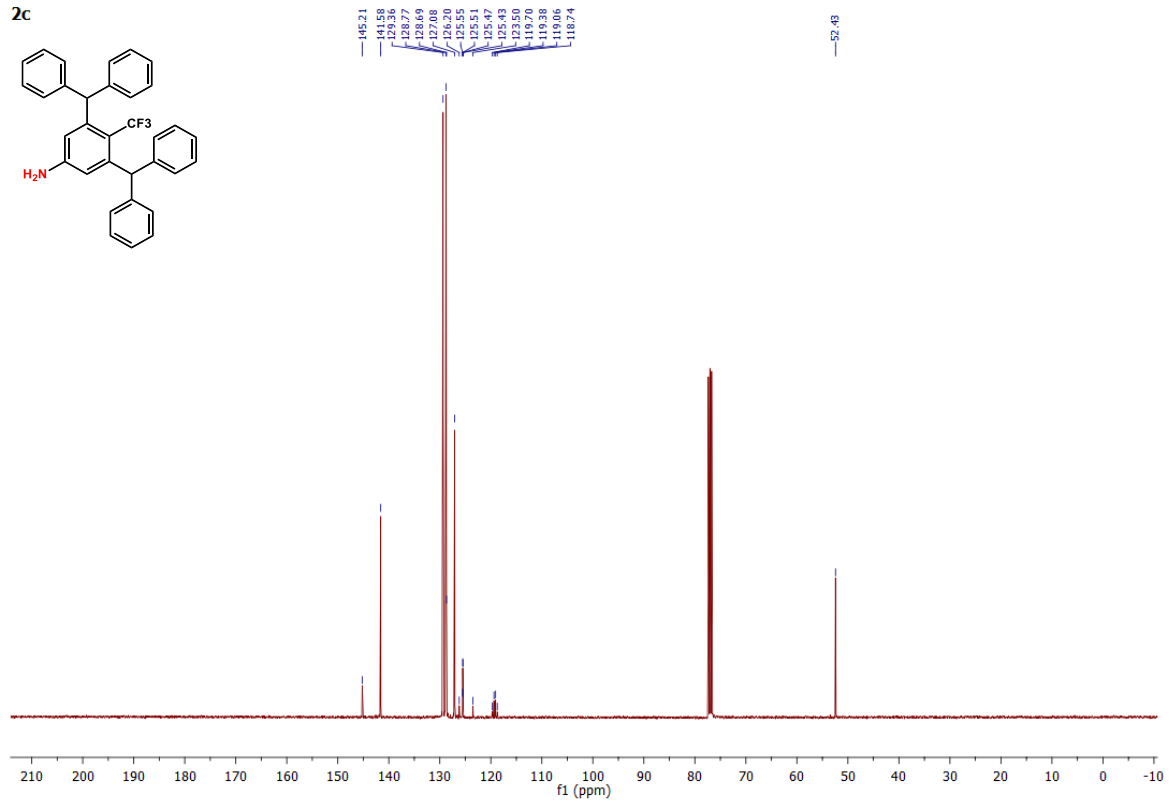


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) of substrate **2c**

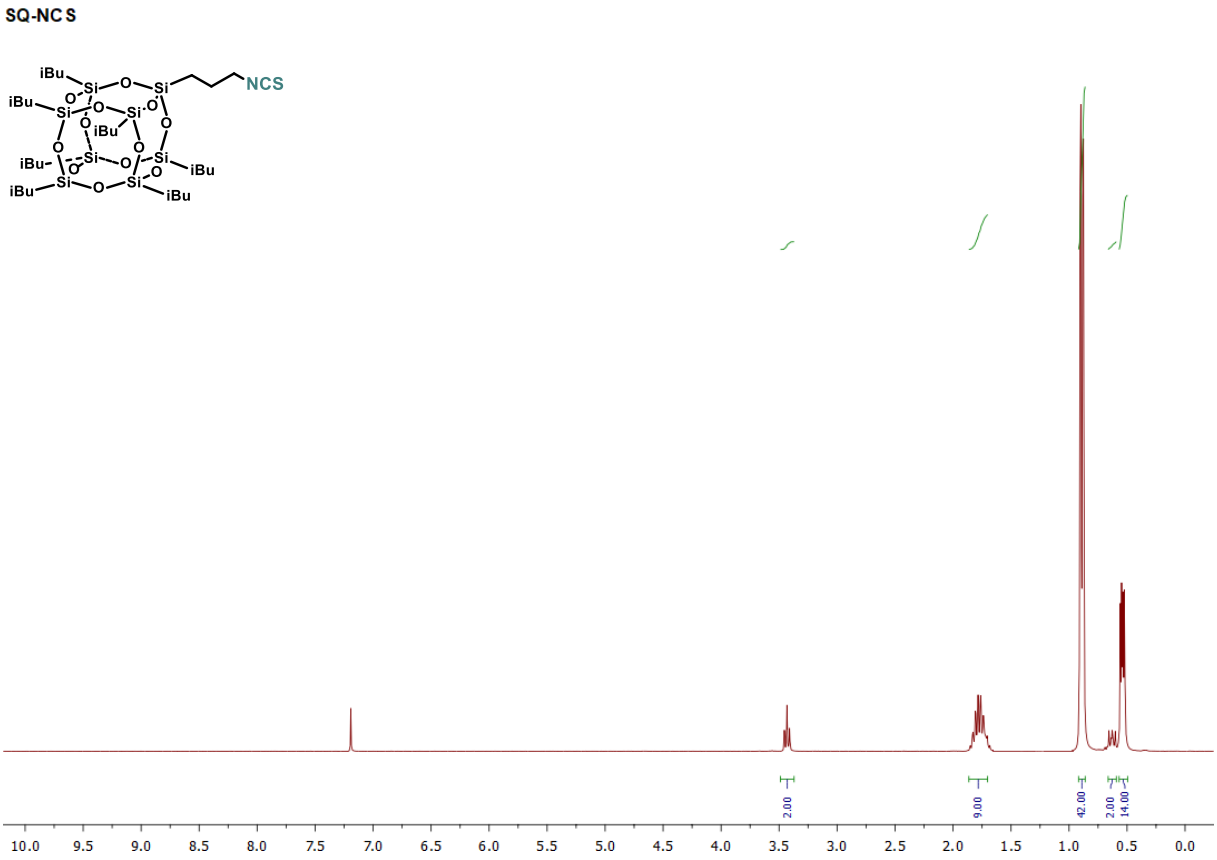


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of substrate **SQ-NCS**

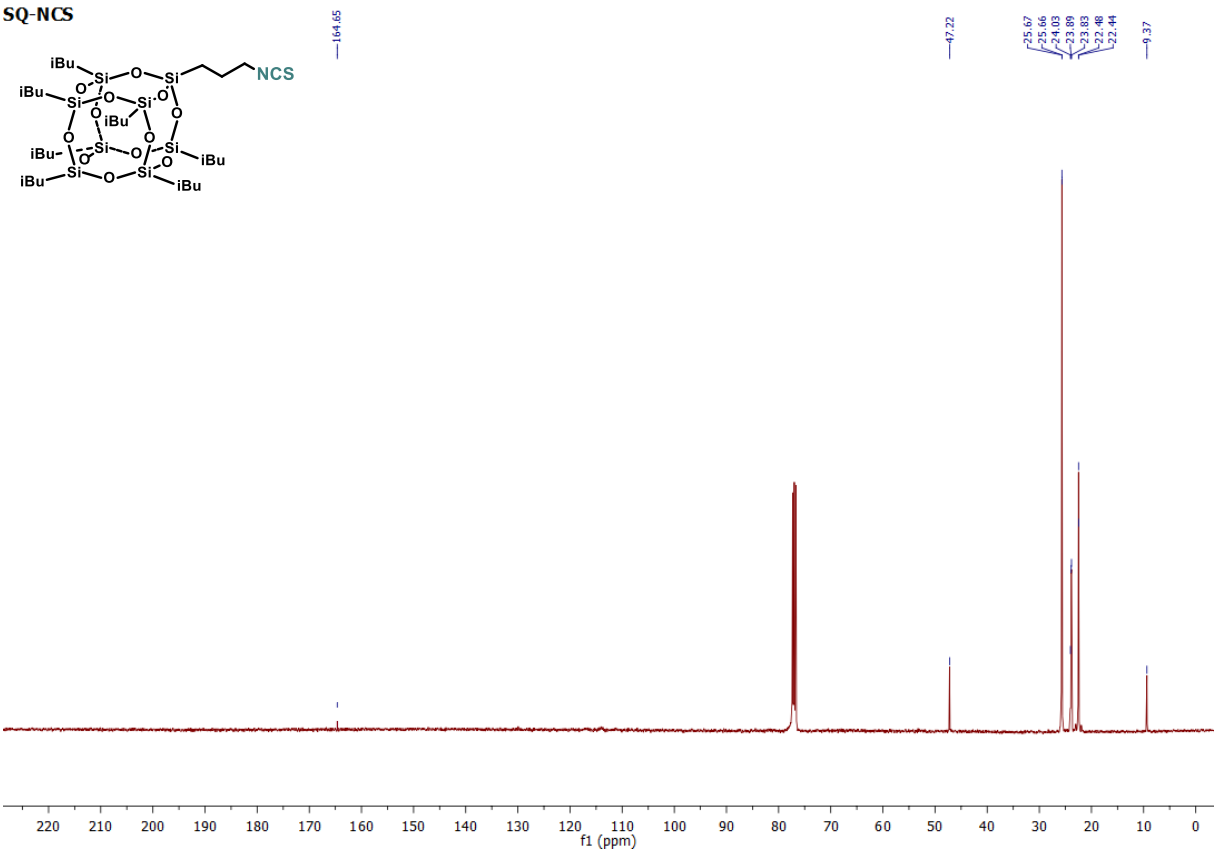


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) of substrate **SQ-NCS**

4. NMR spectra of products P1-P9

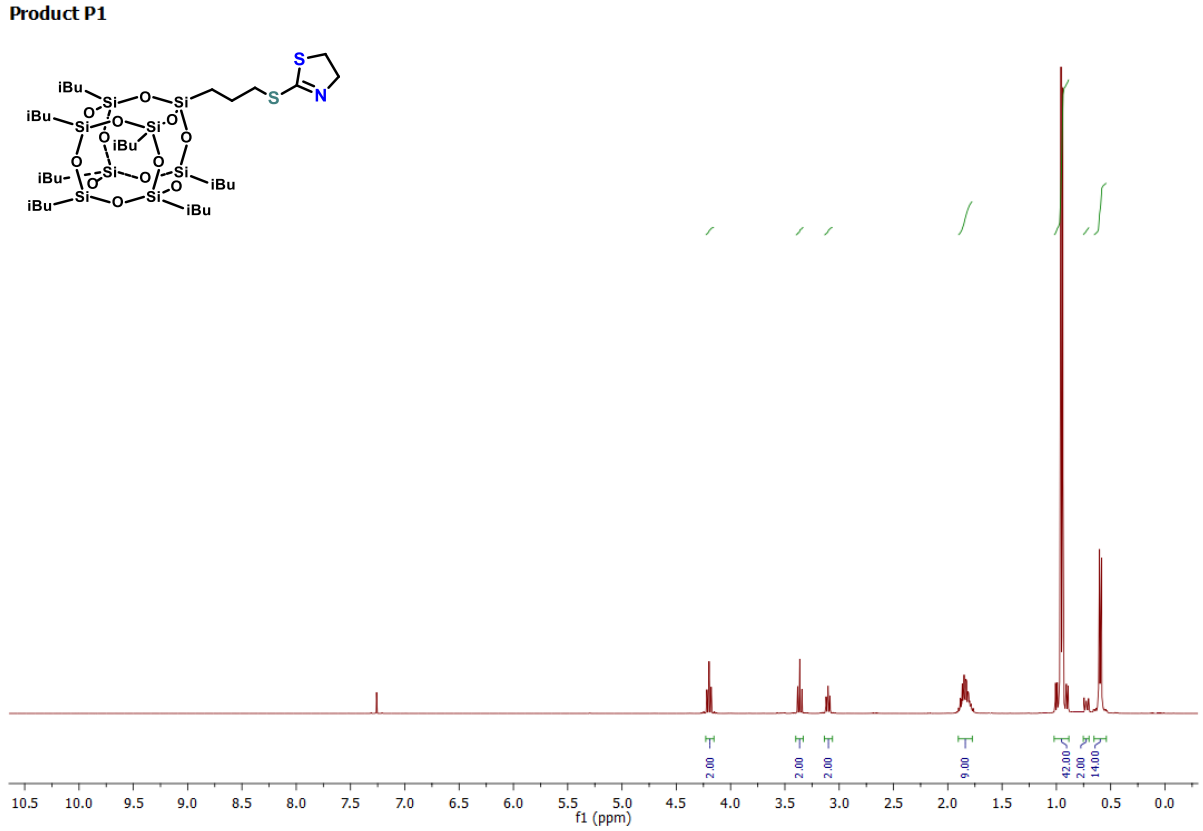


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P1**

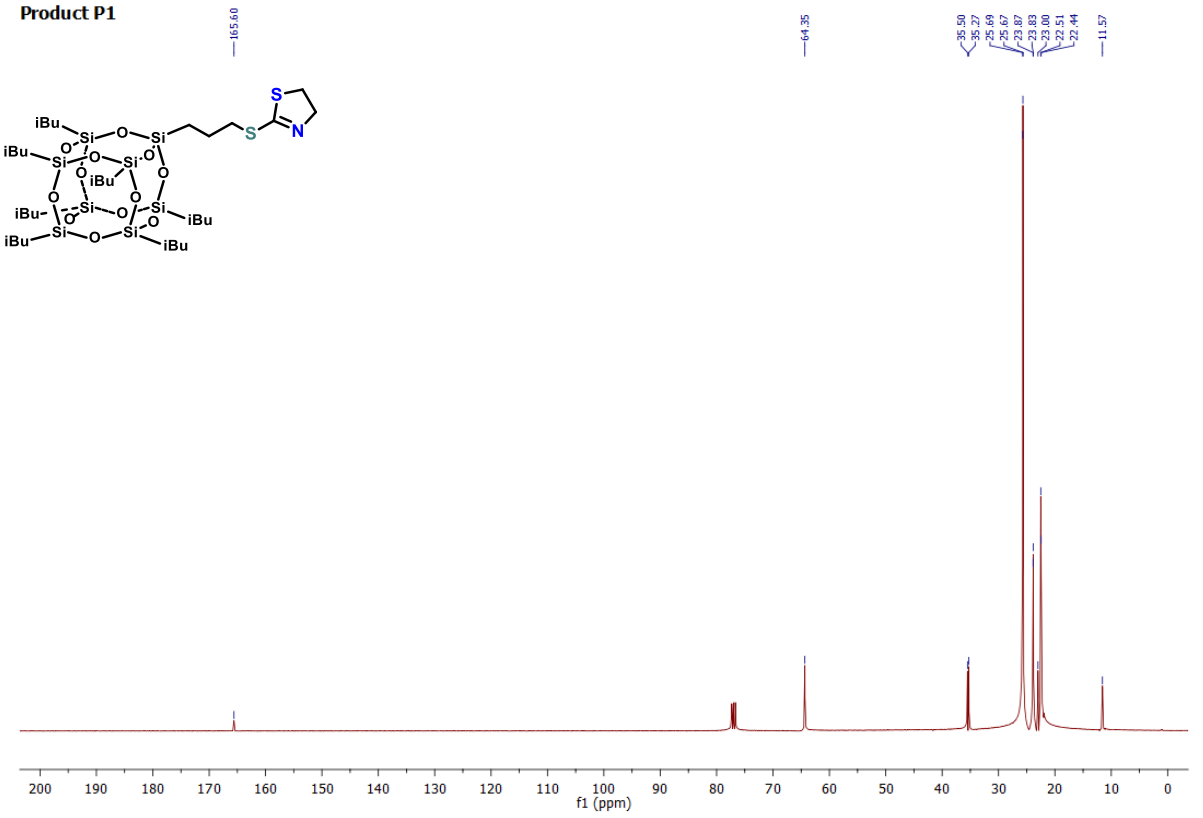


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P1**

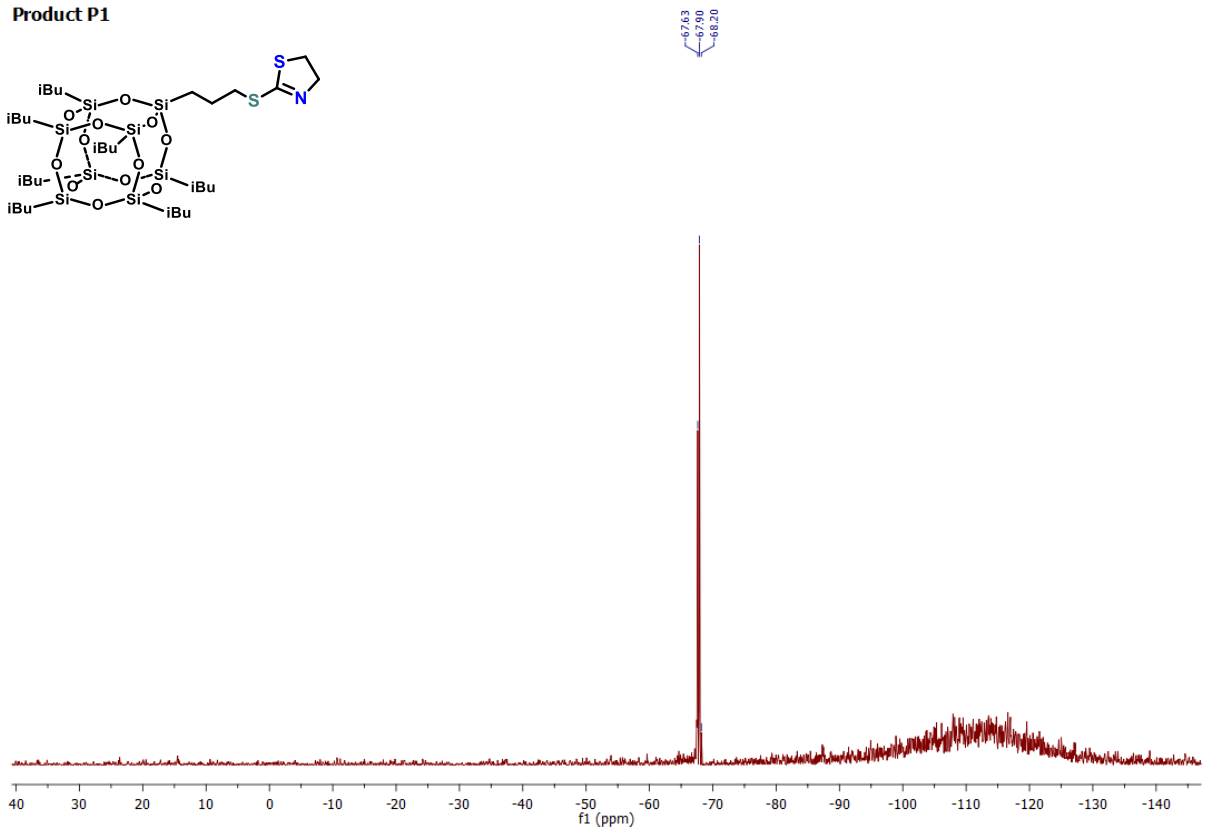


Figure S7. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P1**

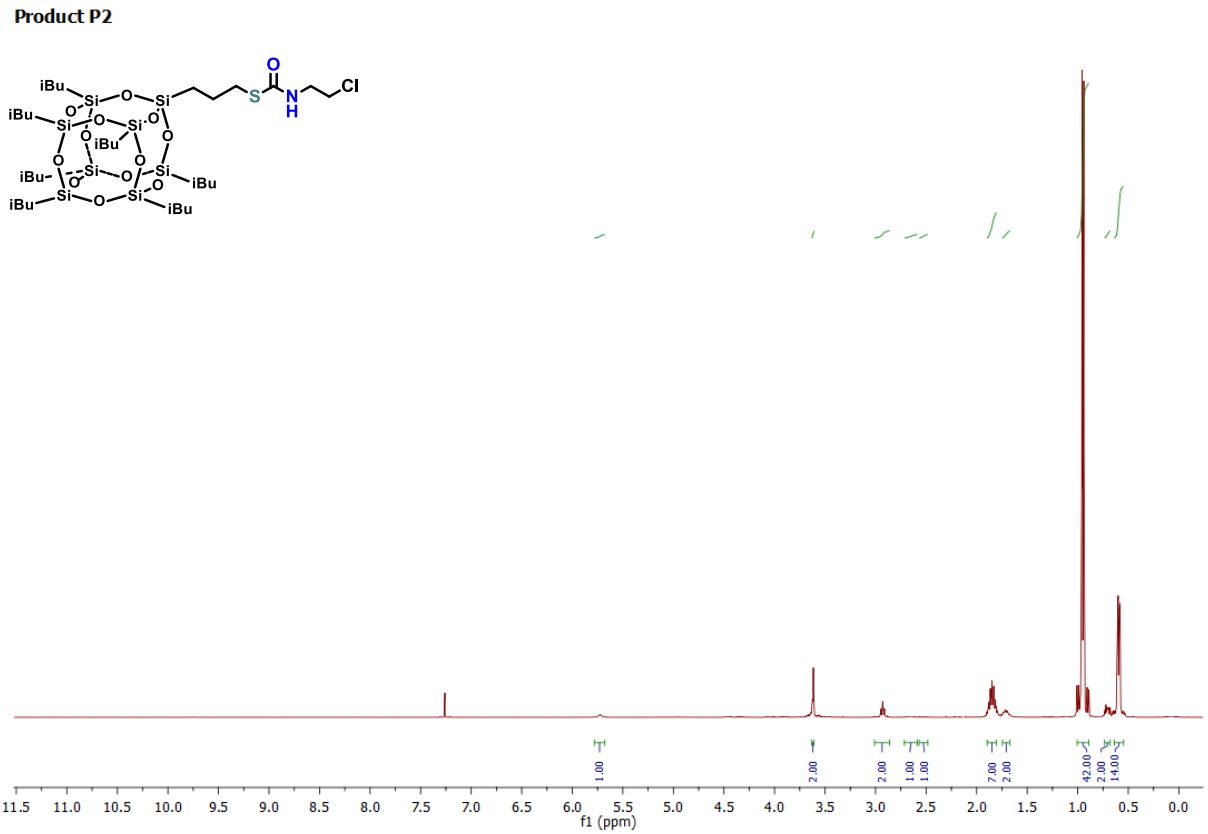


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P2**

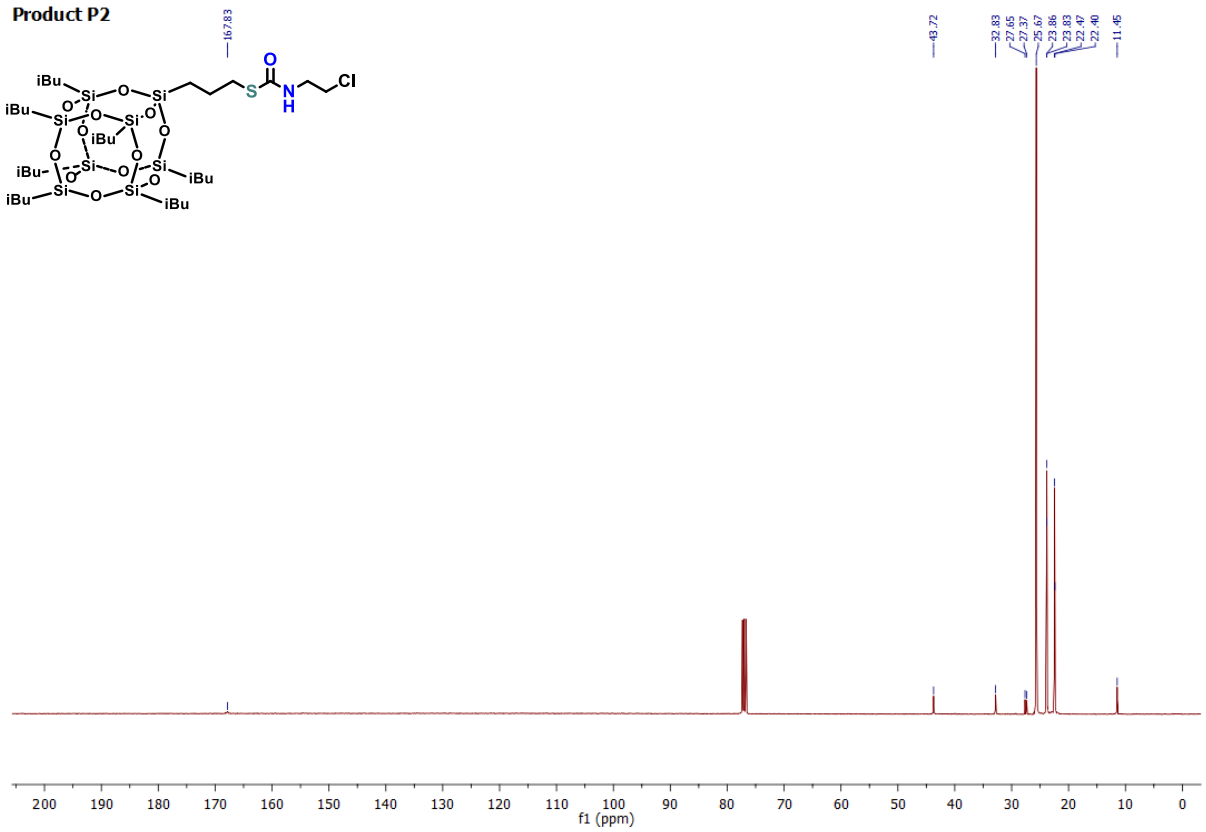


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P2**

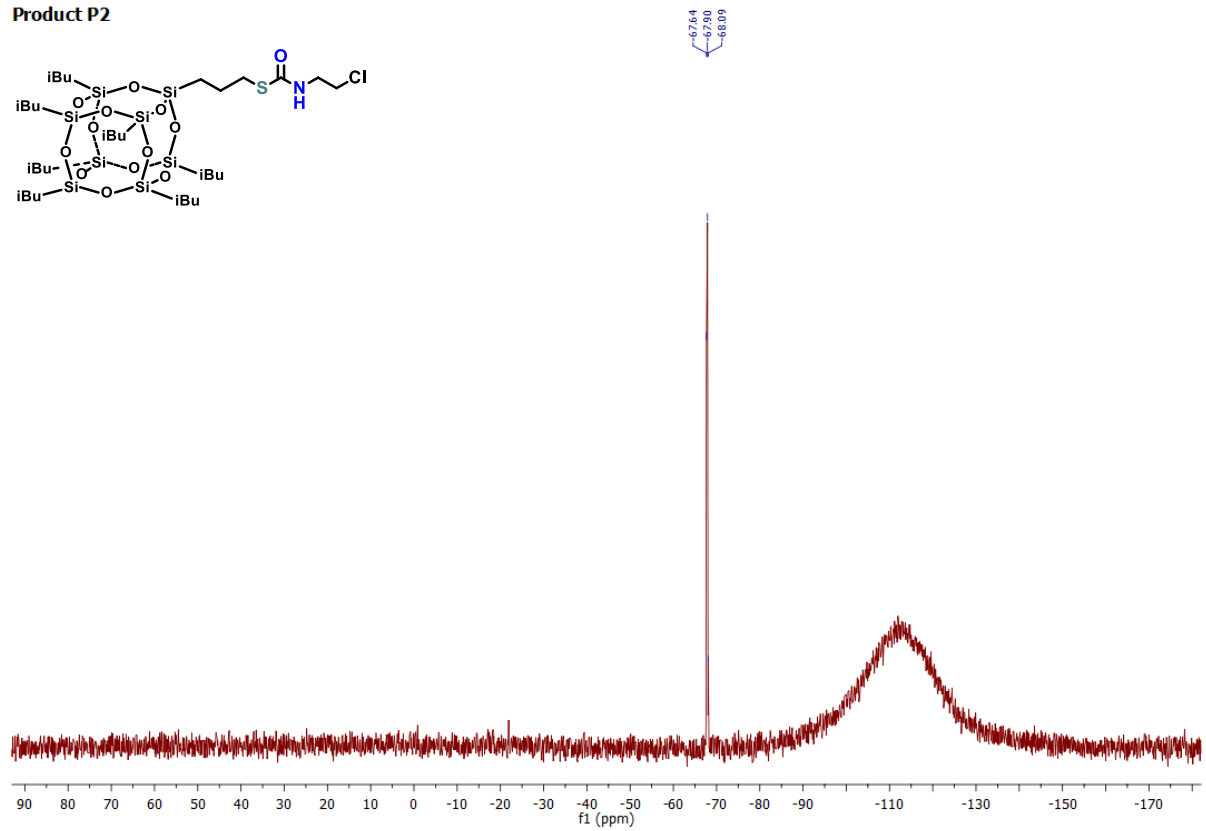


Figure S10. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P2**

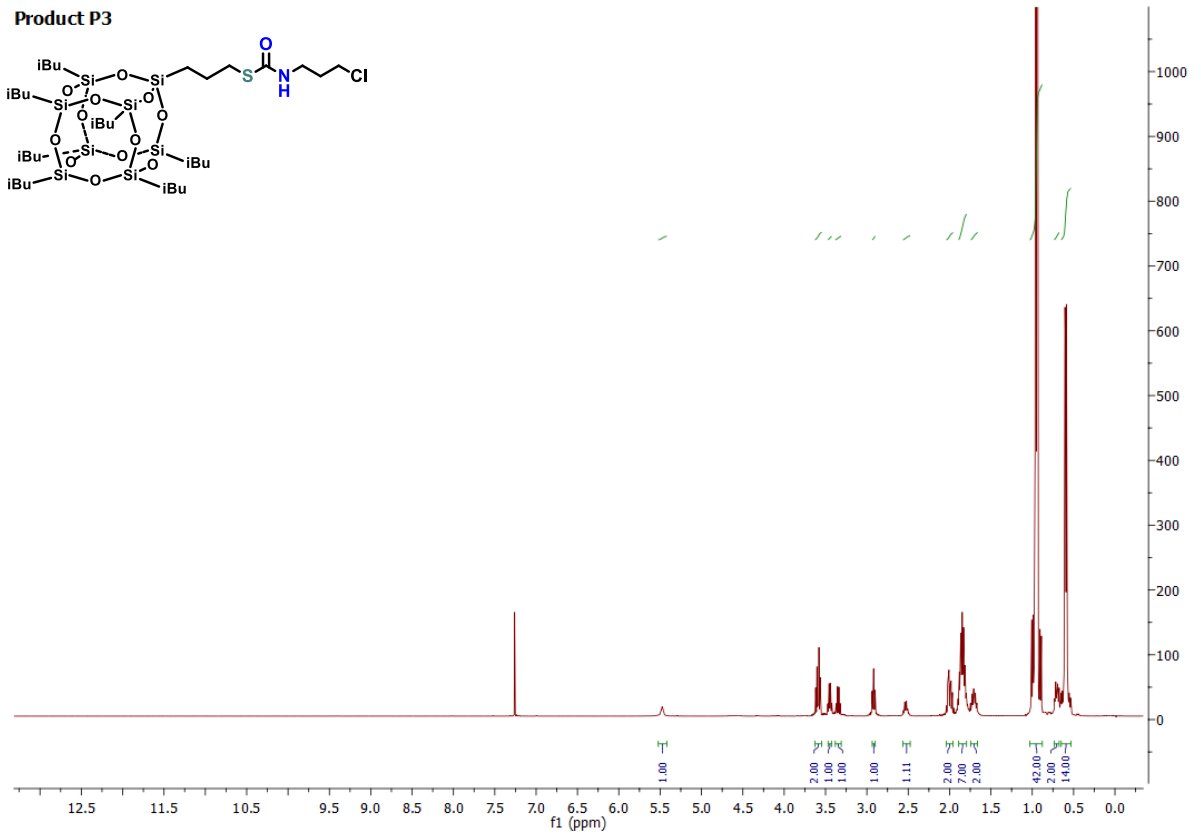


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P3**

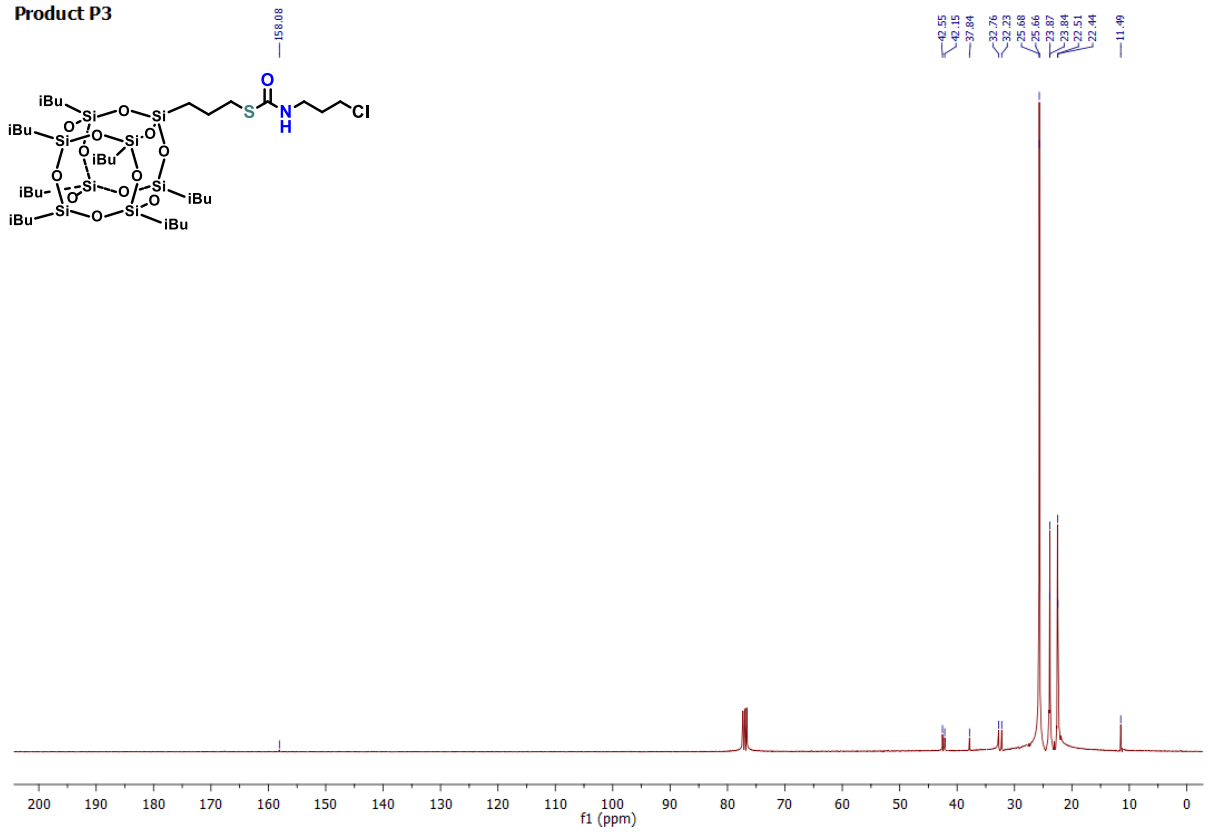


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P3**

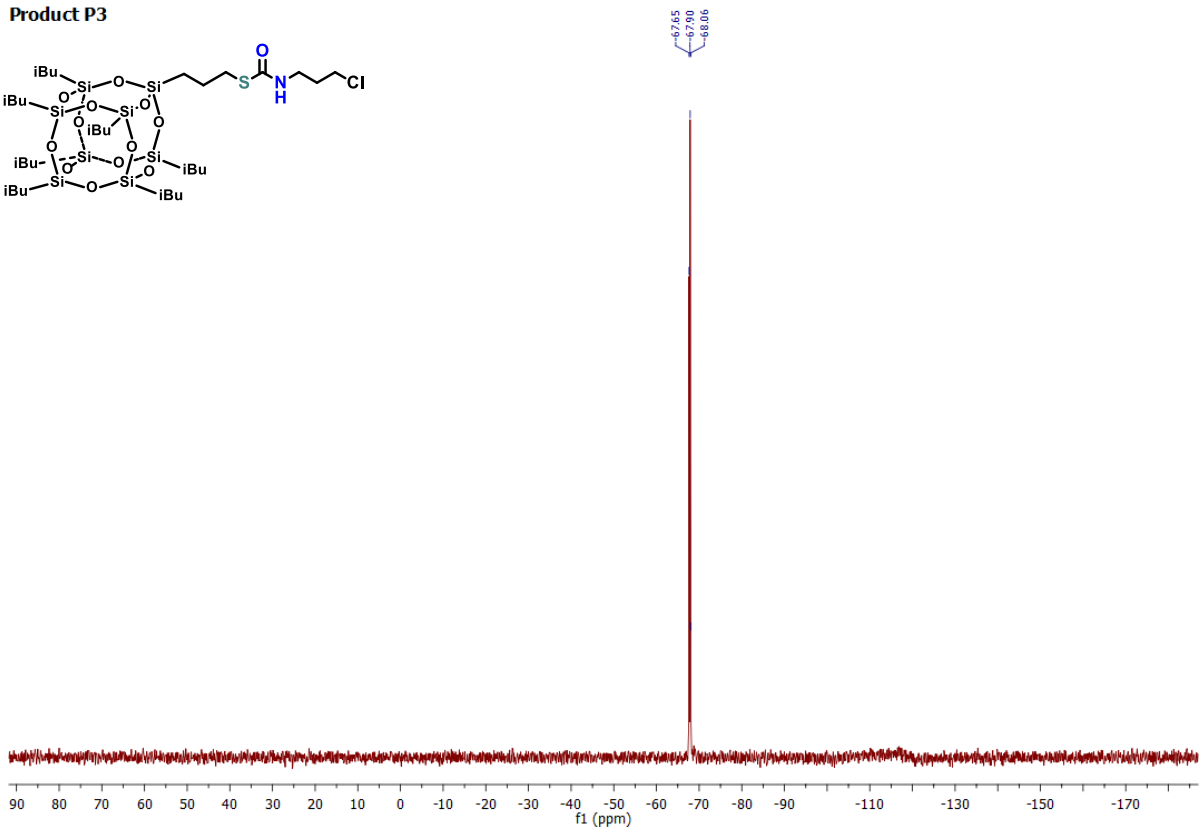


Figure S13. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P3**

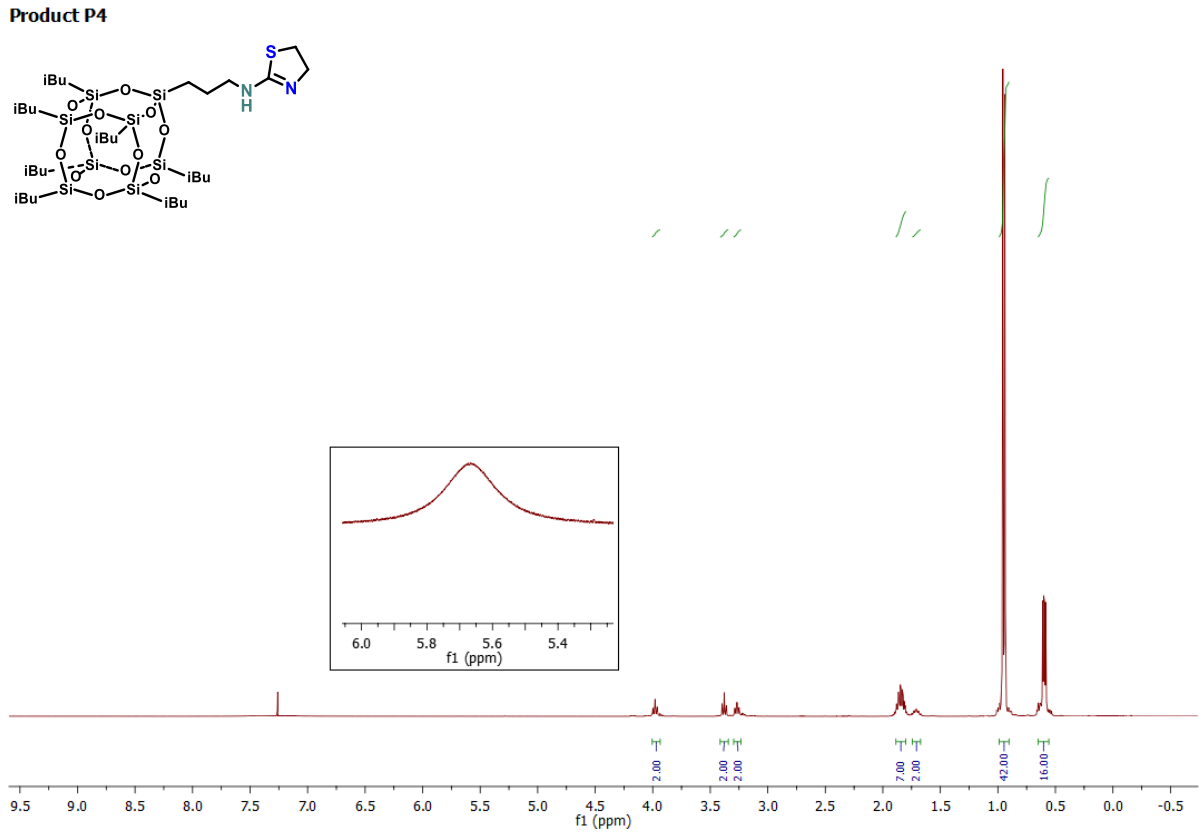


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P4.** The N*H* signal visible after lifting the baseline.

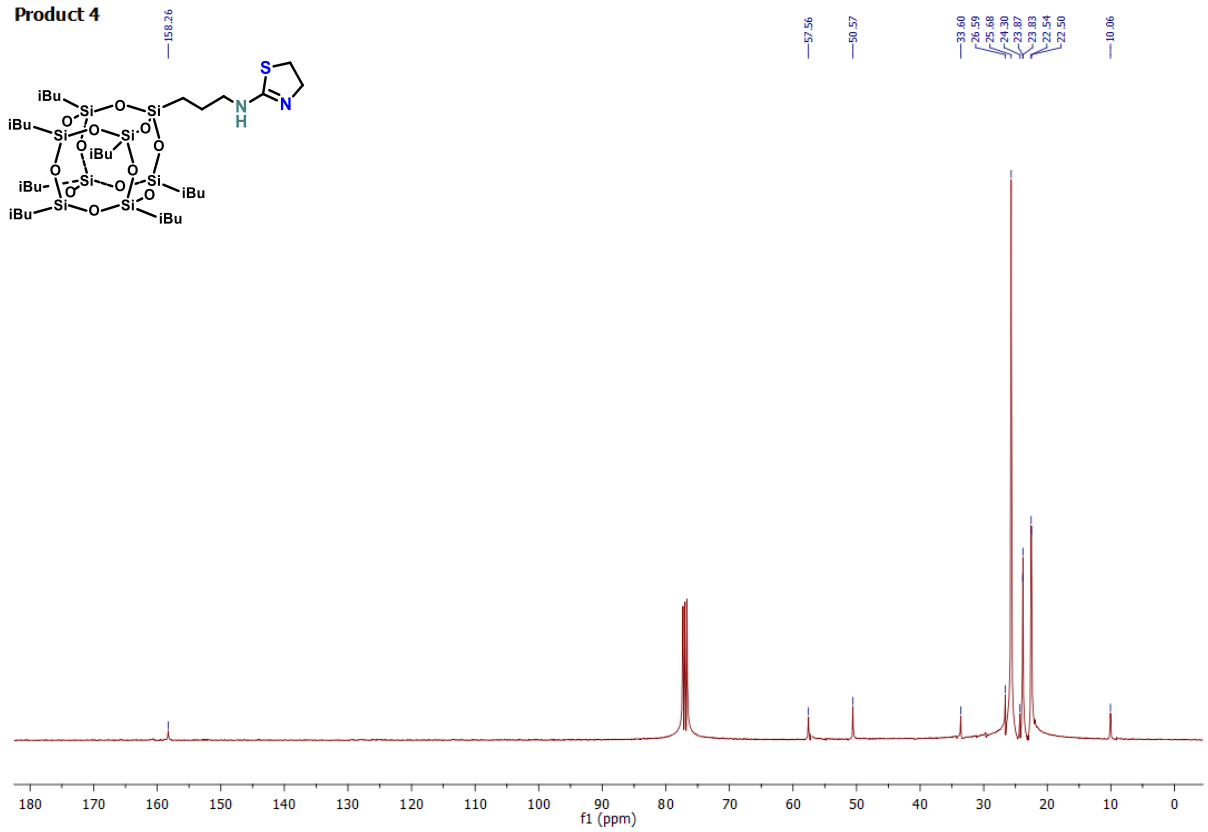


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P4**

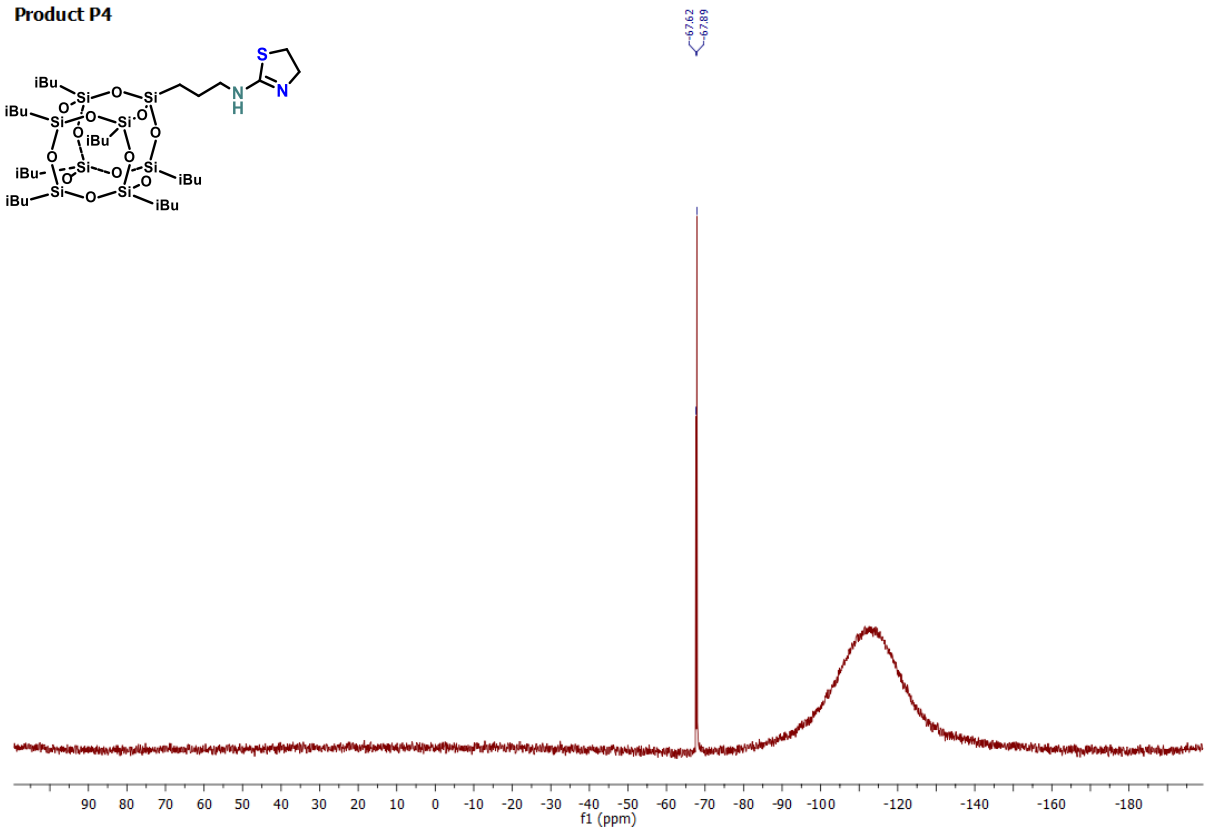


Figure S16. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P4**

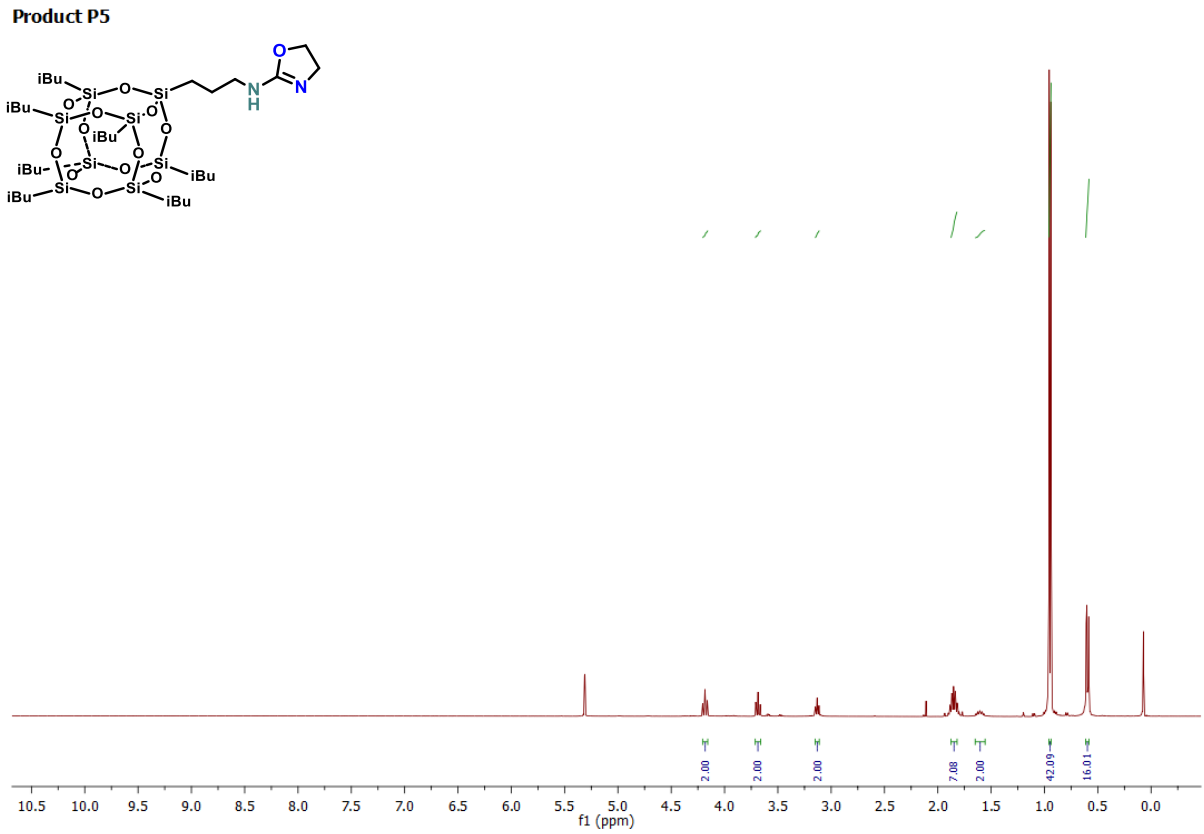


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P5**

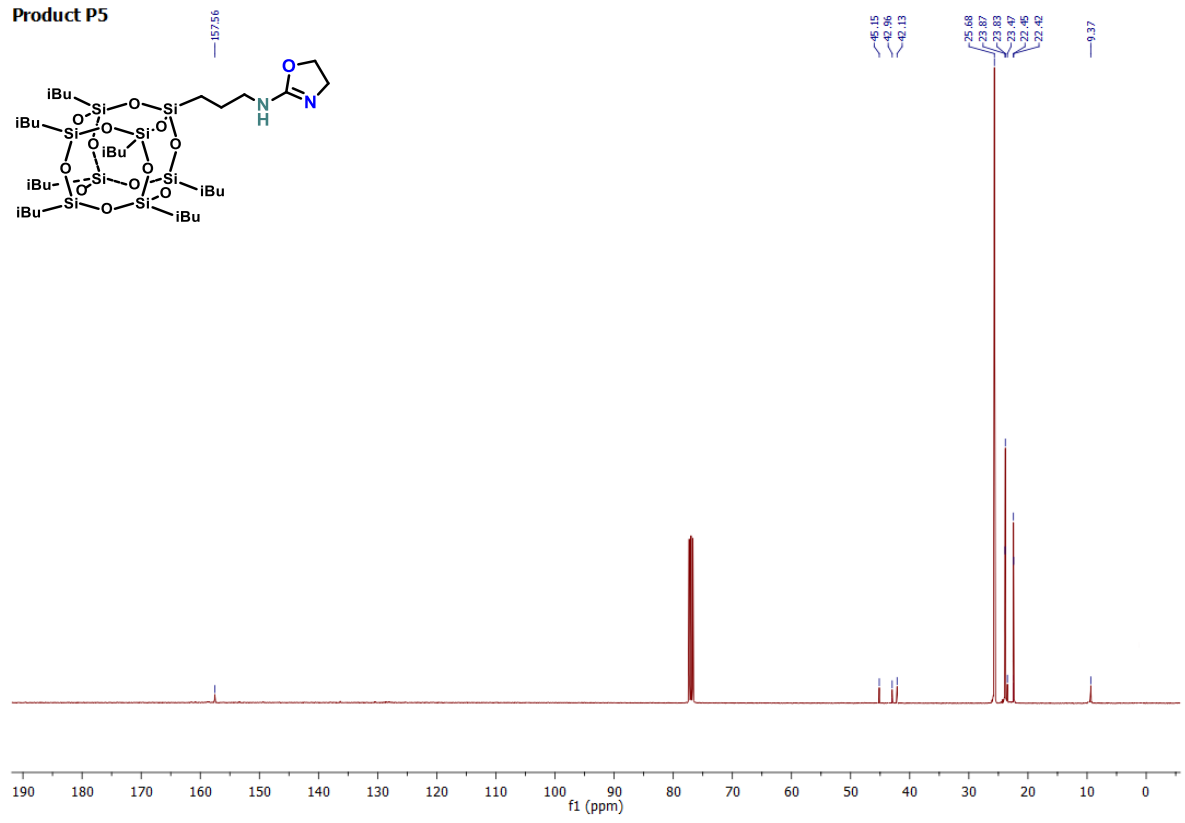


Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P5**

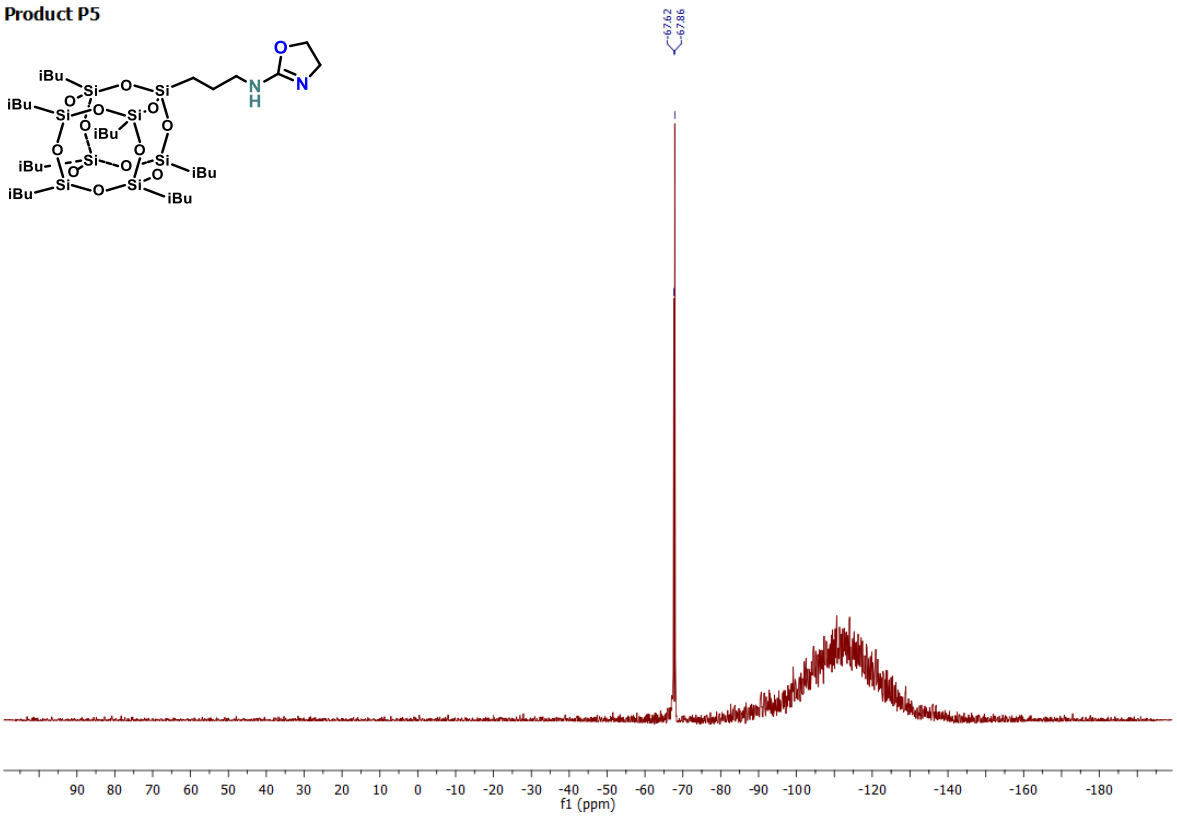


Figure S19. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P5**

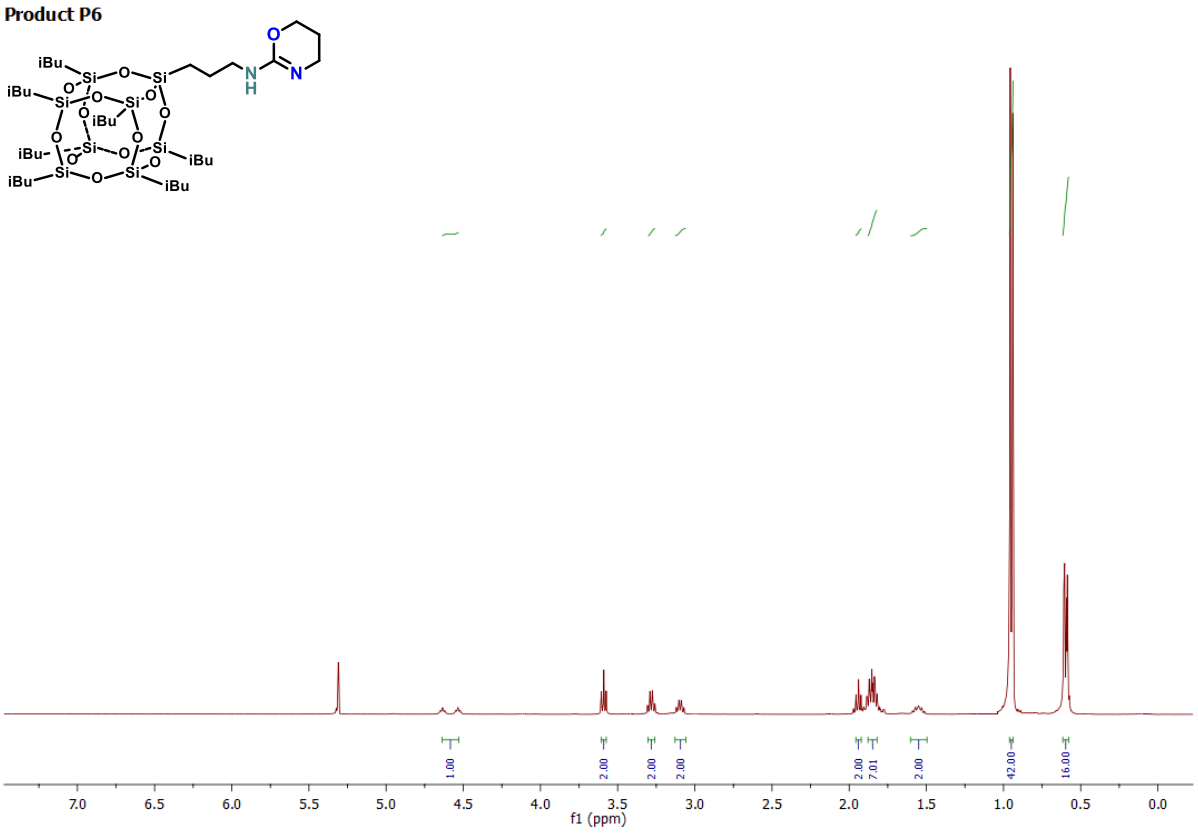


Figure S20. ^{1}H NMR (400 MHz, CD_2Cl_2) of product **P6**

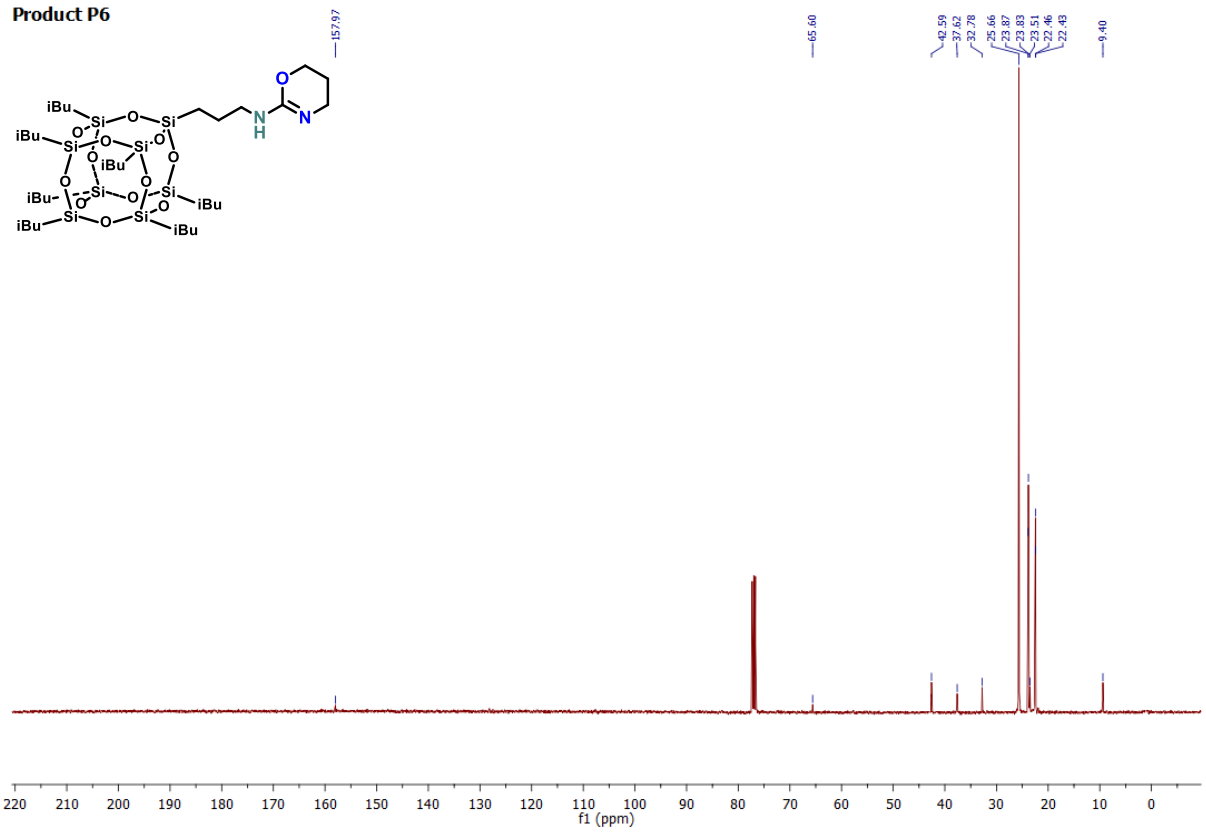


Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P6**

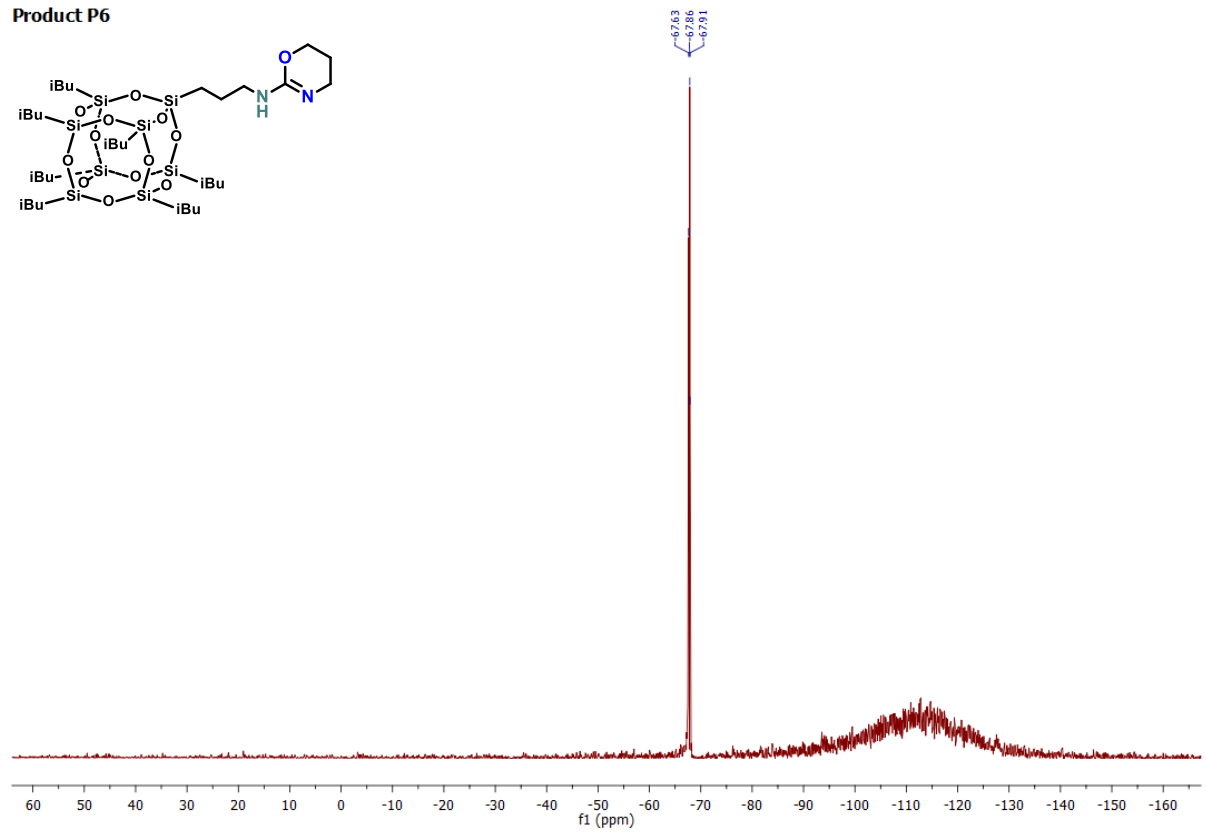


Figure S22. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P6**

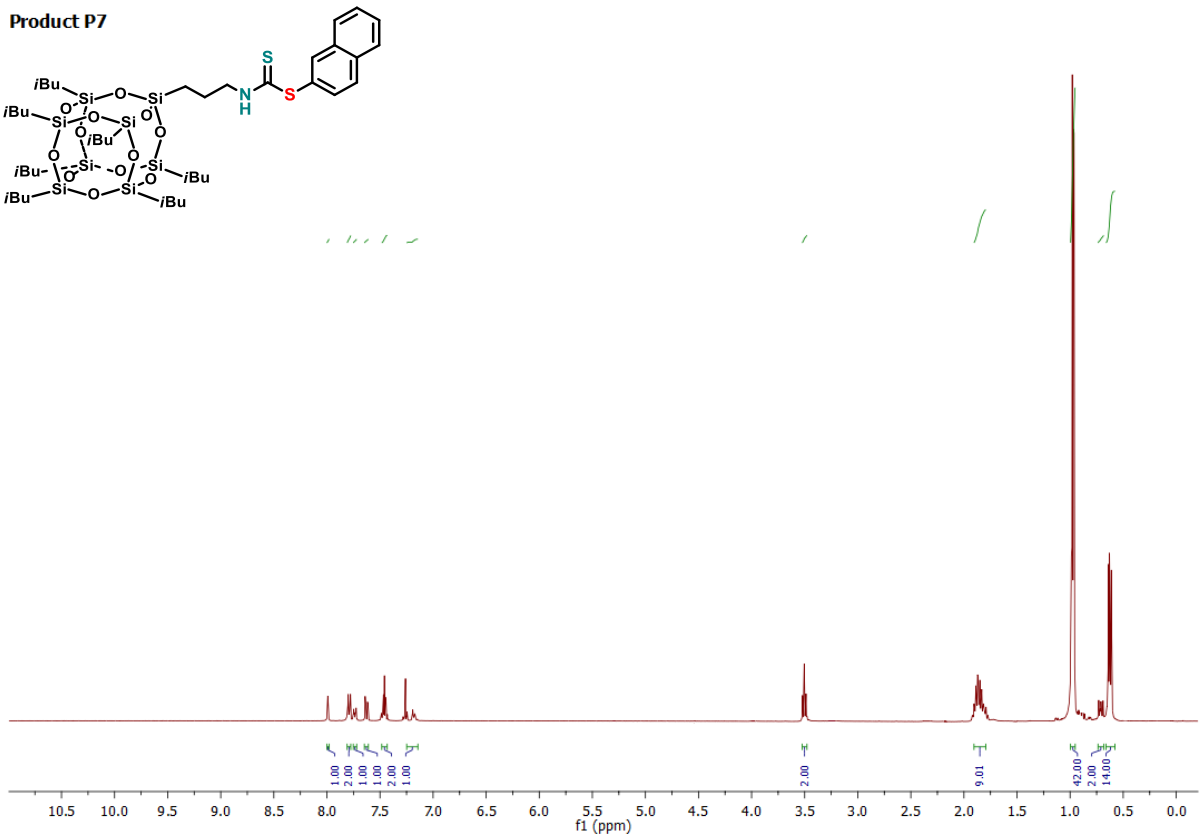


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P7**

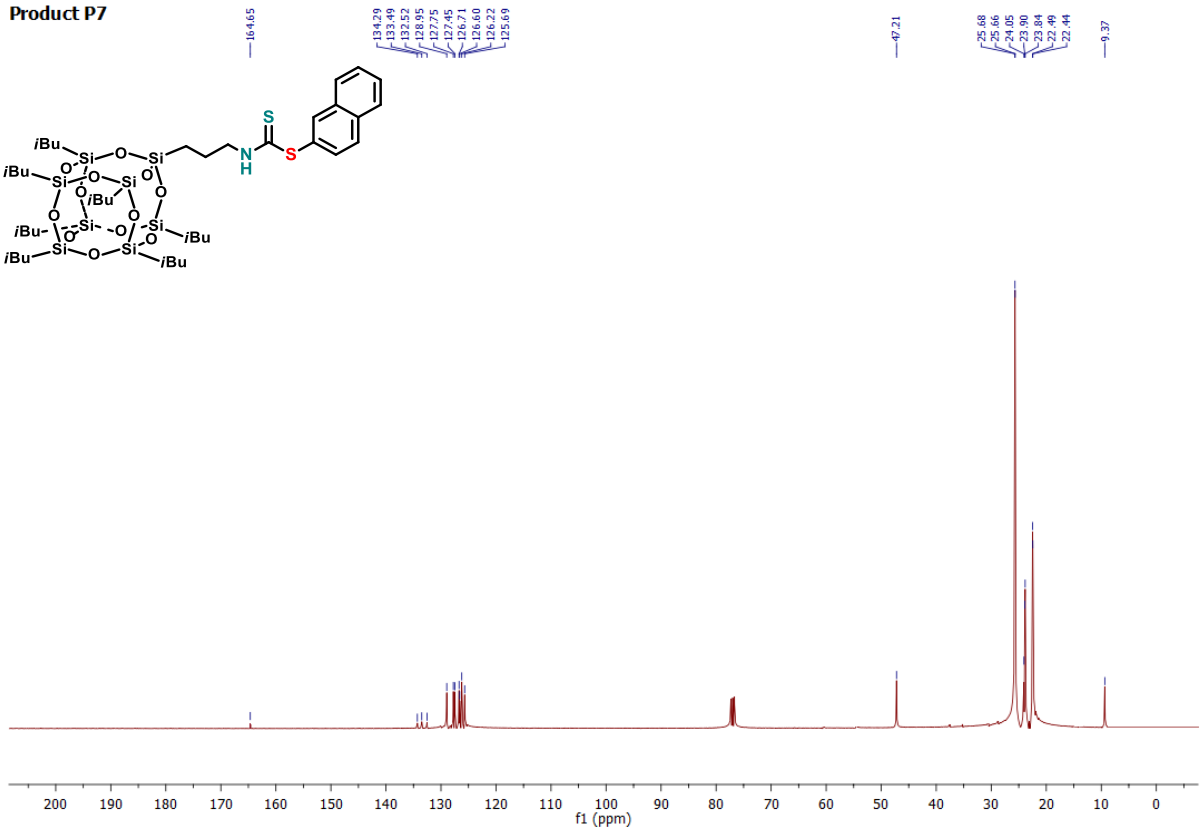


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P7**

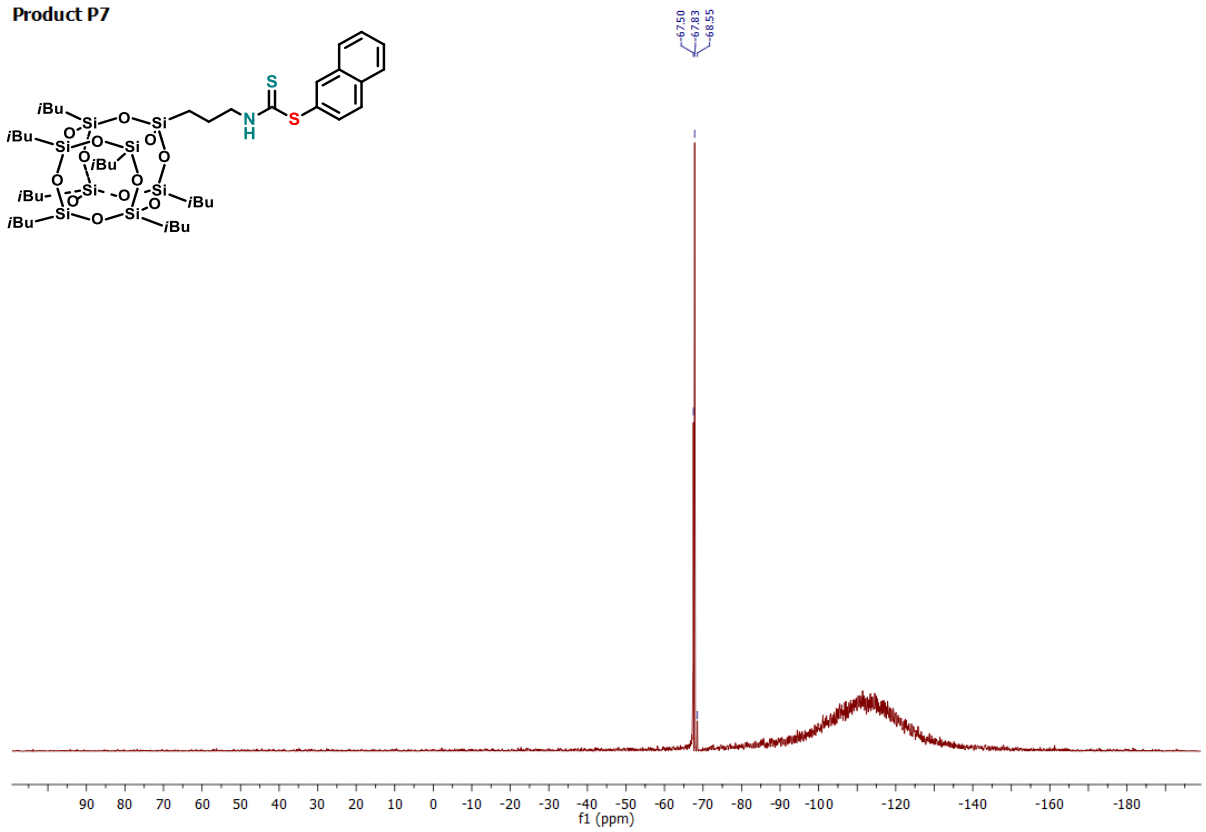


Figure S25. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P7**

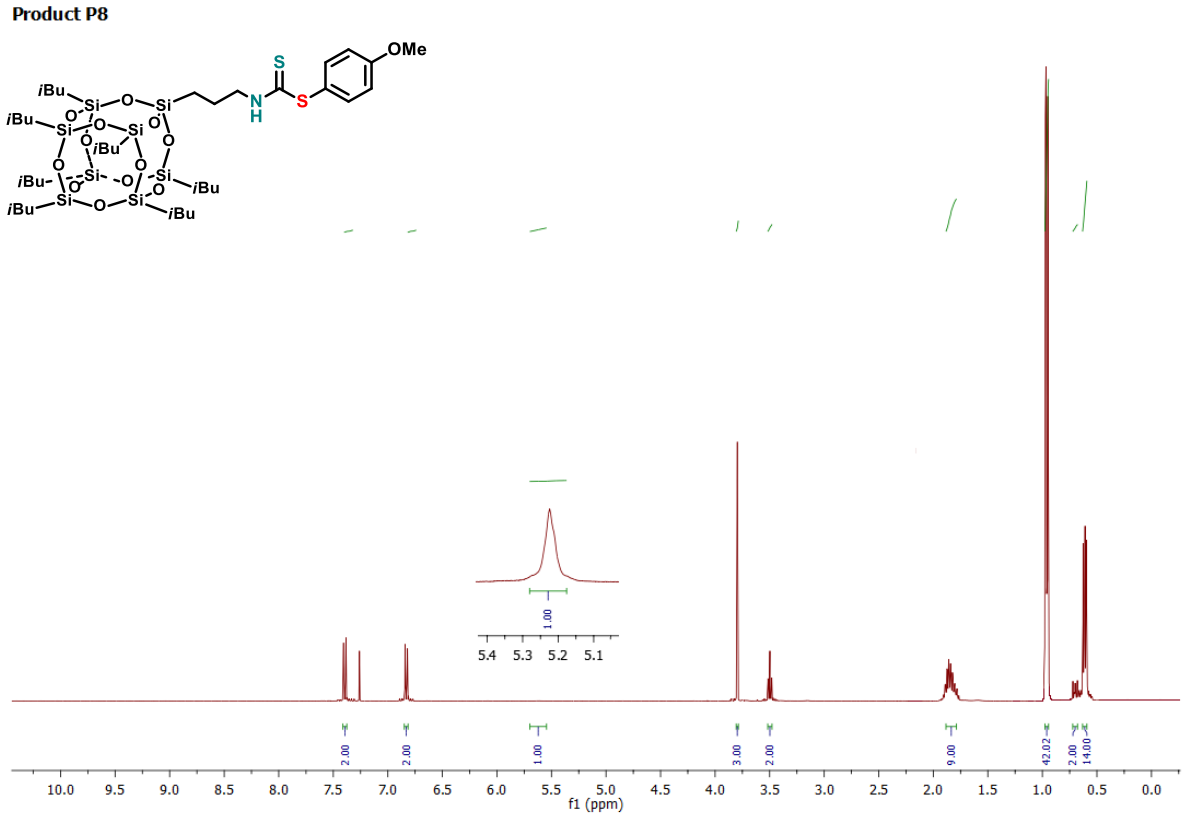


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P8.** The N*H* signal visible after lifting the baseline.

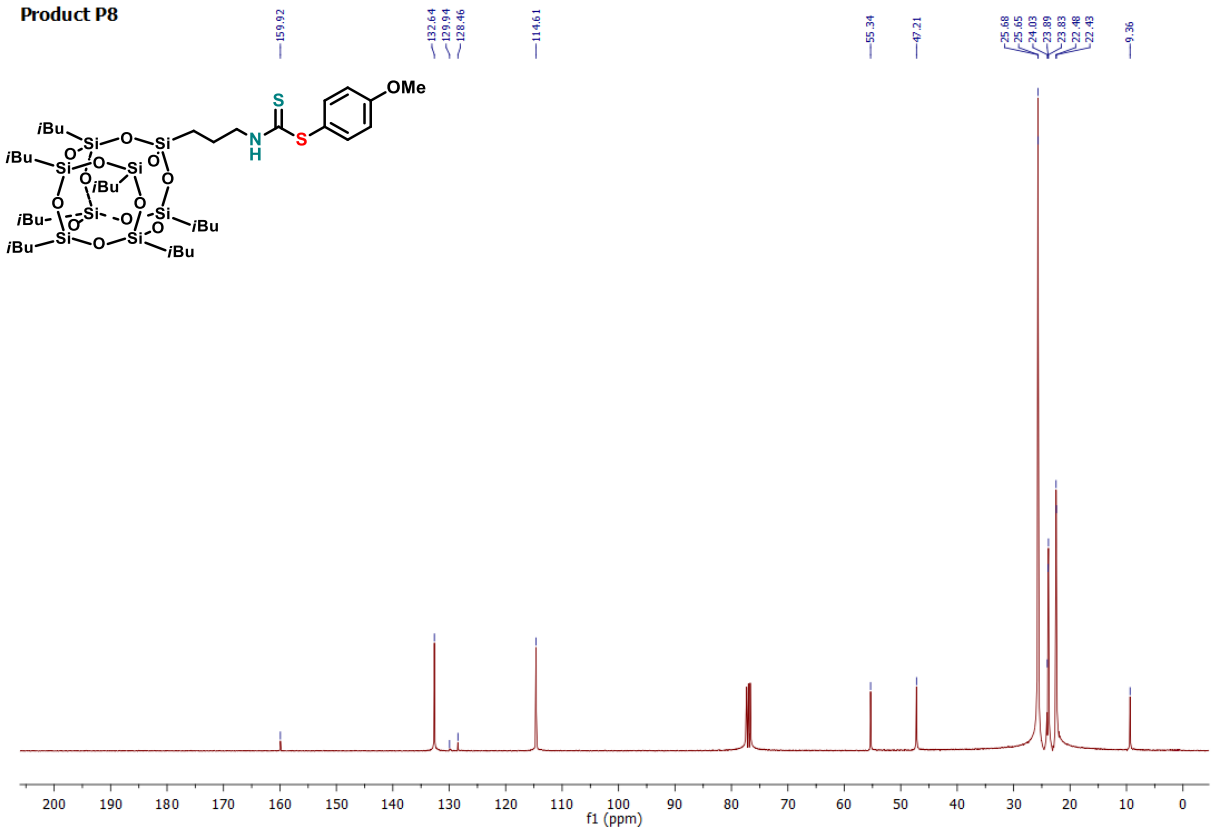


Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P8**

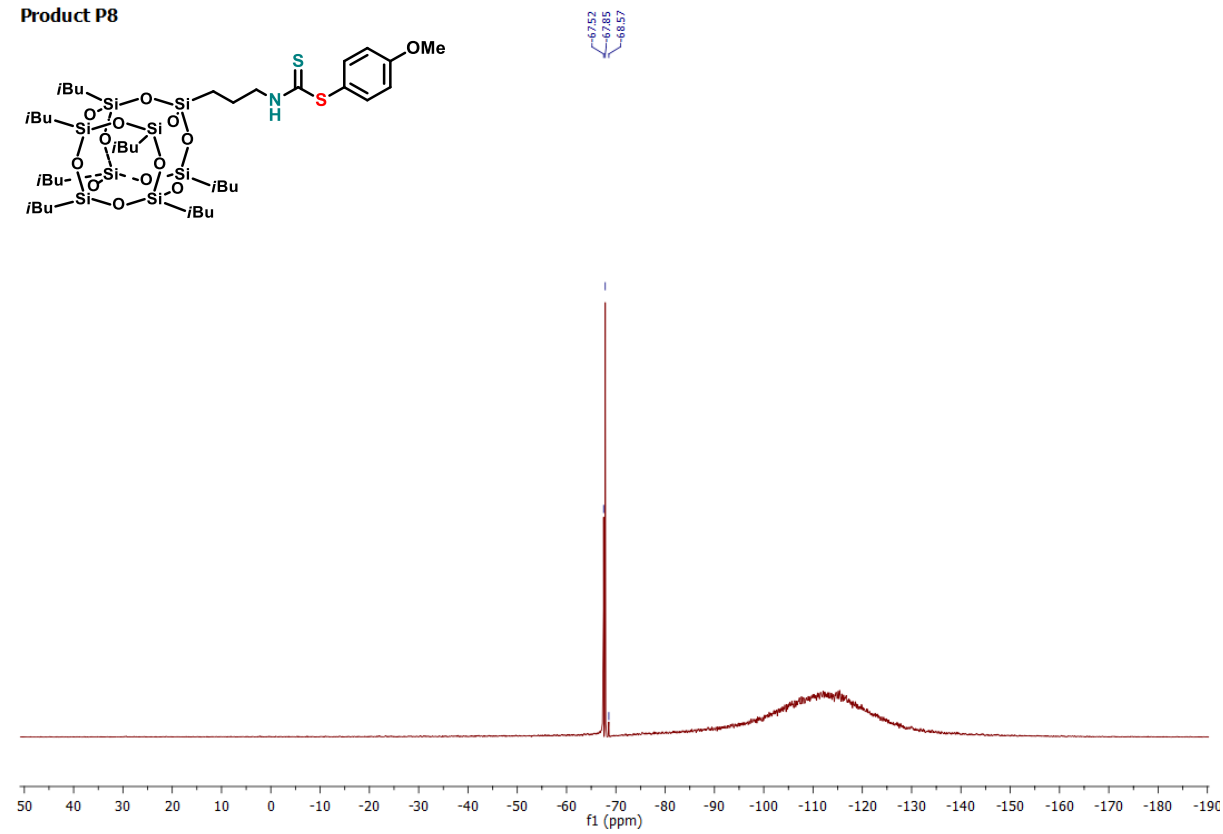


Figure S28. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P8**

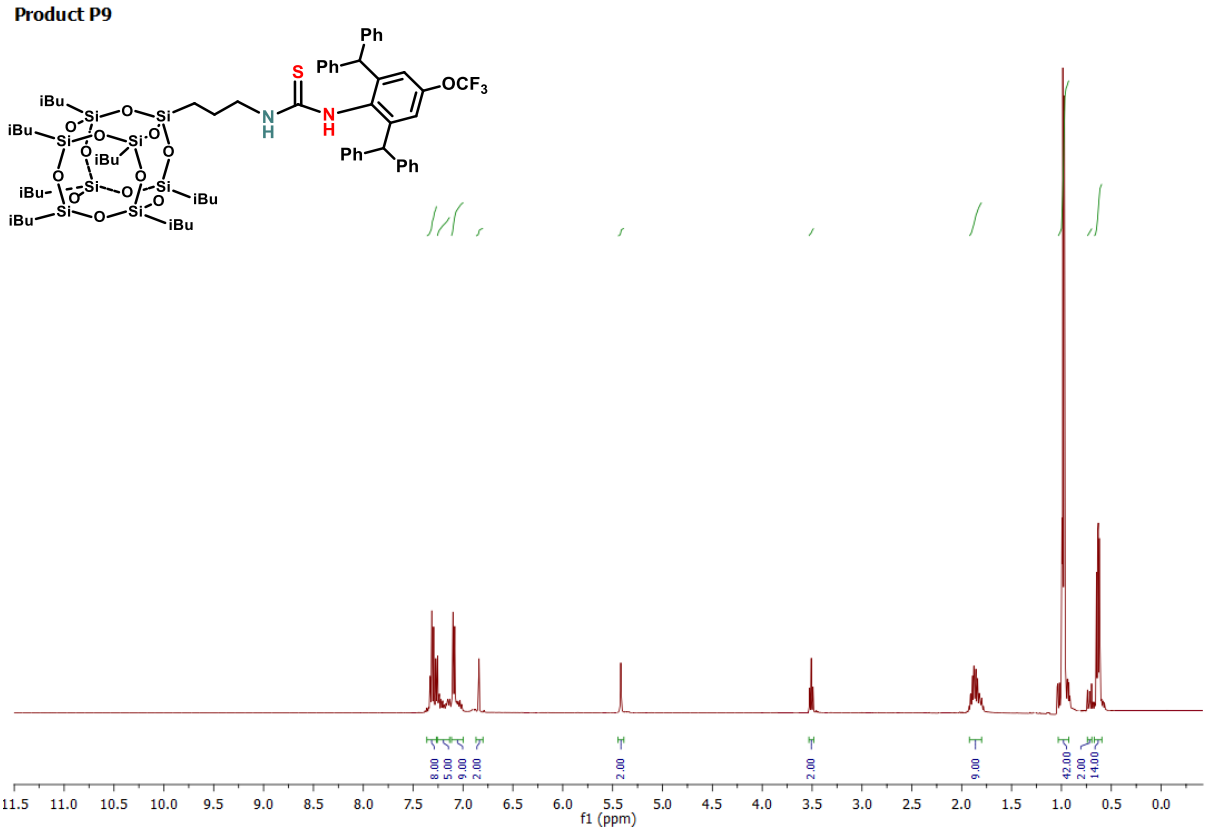


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P9**

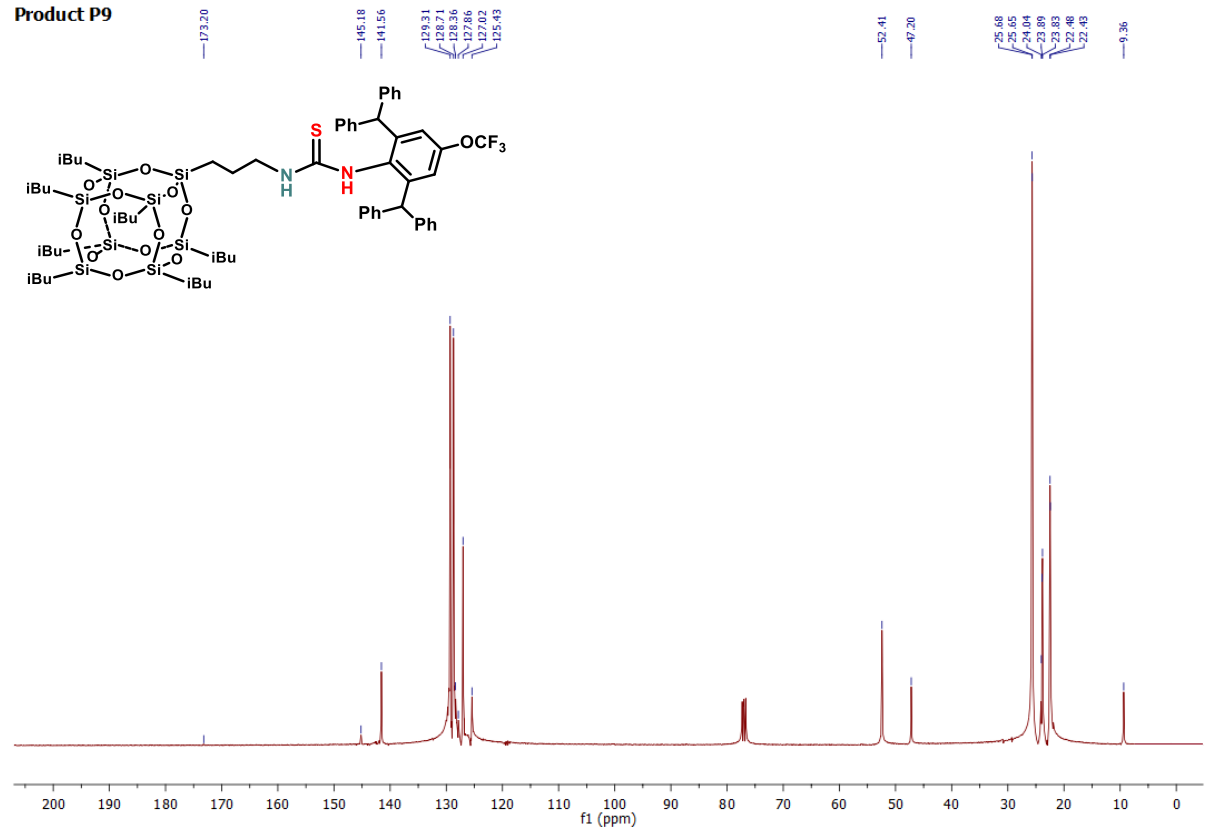


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P9**

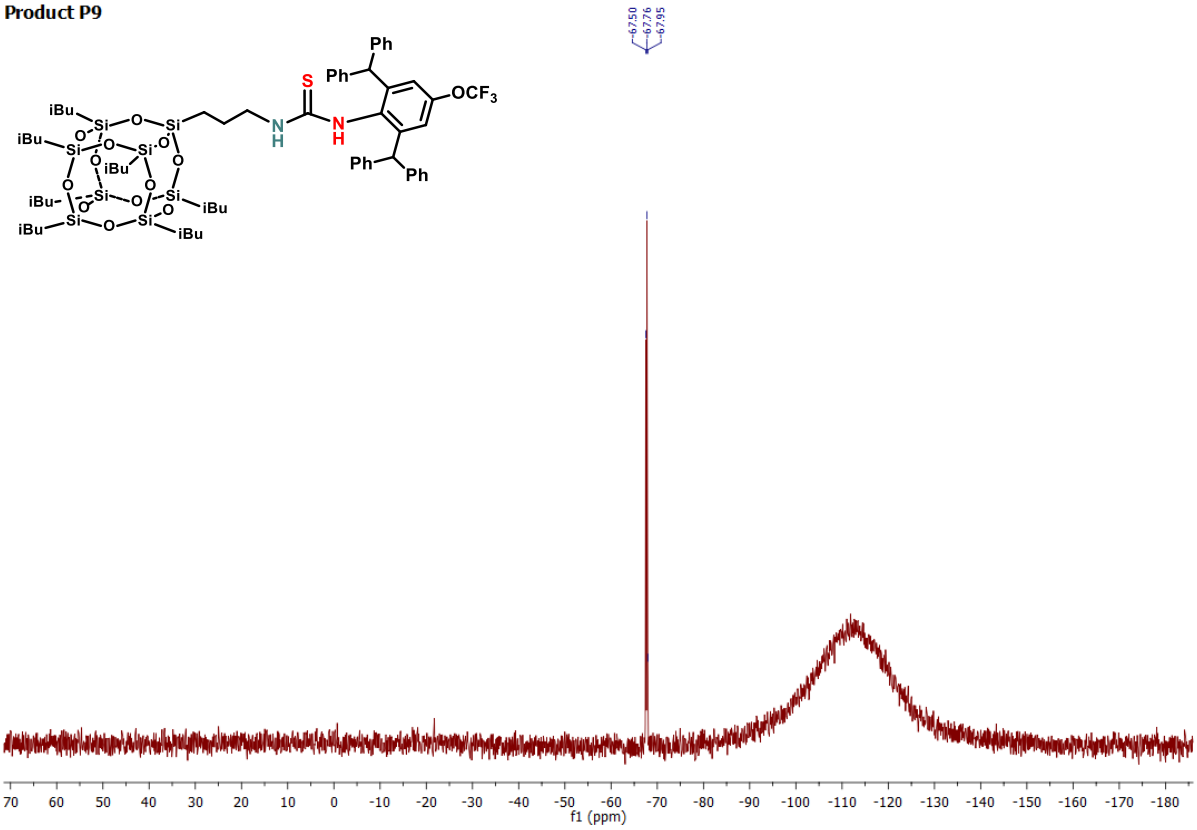


Figure S31. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P9**

5. Thermogravimetric analyses

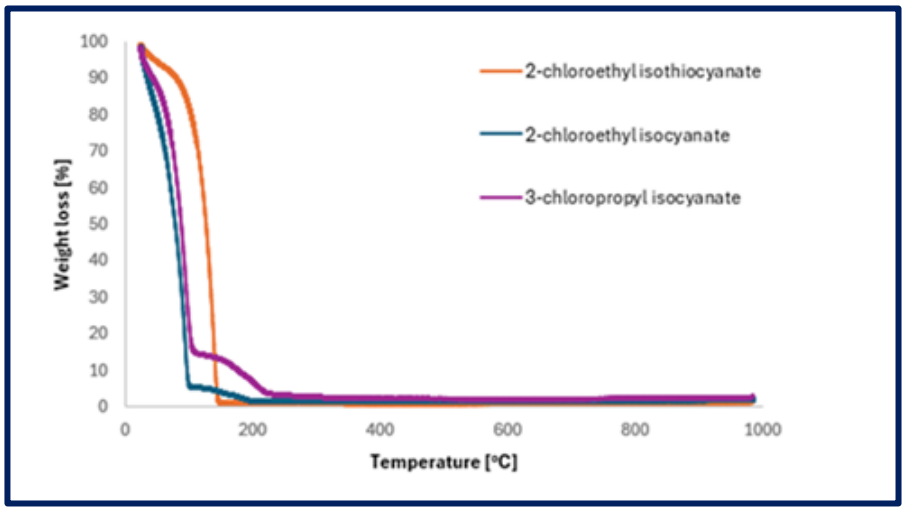


Figure S32. TGA curves of substrates

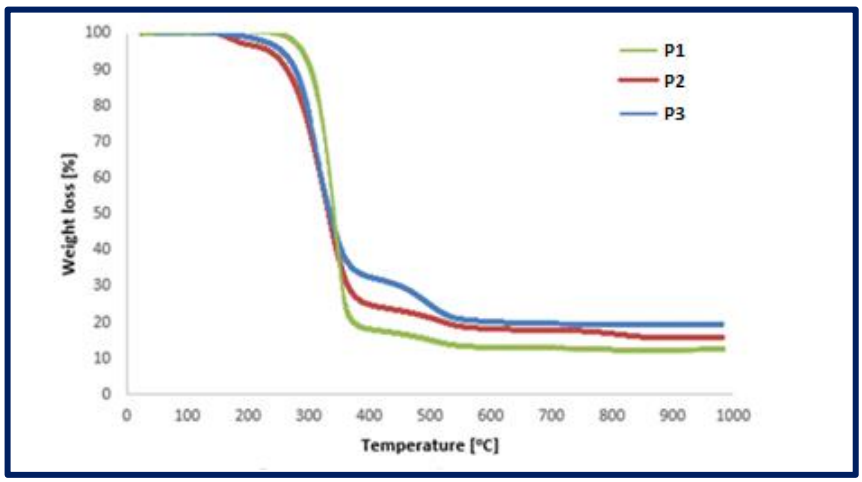


Figure S33. TGA curves of products **P1**-**P3**.

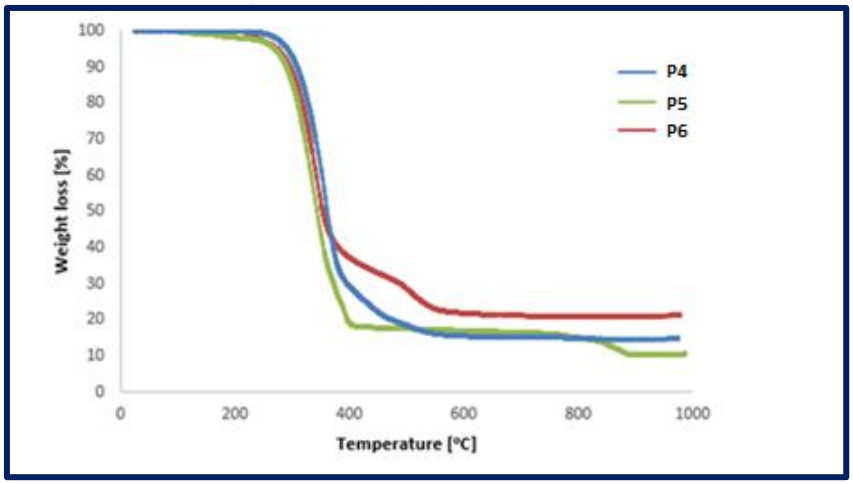


Figure S34. TGA curves of products **P4**-**P6**.

6. UV-VIS analyses of substrates

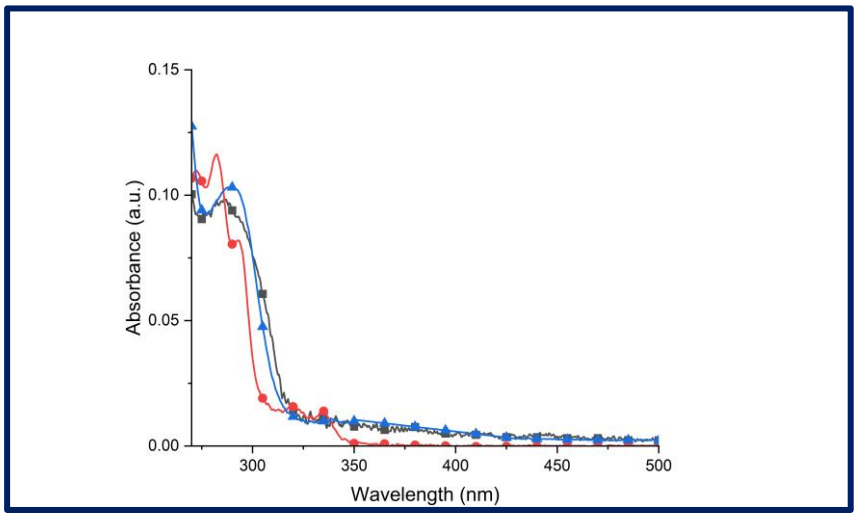


Figure S35. The UV-Vis absorption spectra of **2b** (■), **2a** (●) and **2c** (▲) measured in dichloromethane solutions at room temperature.

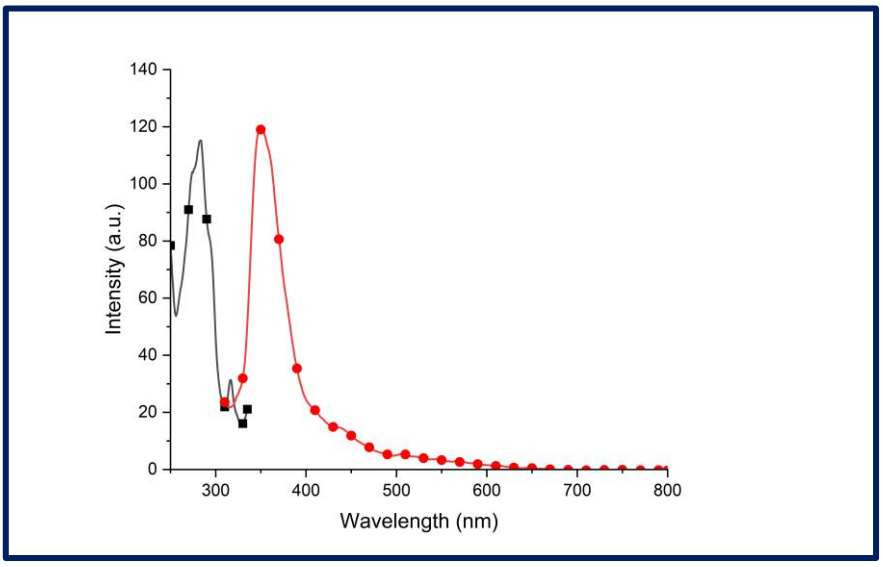


Figure S36. Excitation ($\lambda_{em.}$ = 348 nm ■) and emission ($\lambda_{ex.}$ = 282 nm ●) spectra of **2a** in dichloromethane.

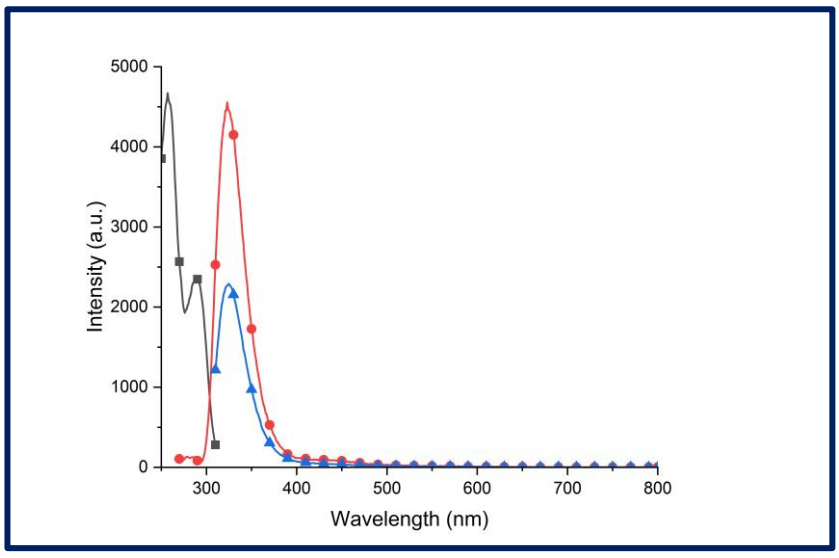


Figure S37. Excitation ($\lambda_{em.}$ = 325 nm; ■) and emission ($\lambda_{ex.}$ = 257 nm ● and $\lambda_{ex.}$ = 290 nm ▲) spectra of **2c** in dichloromethane.

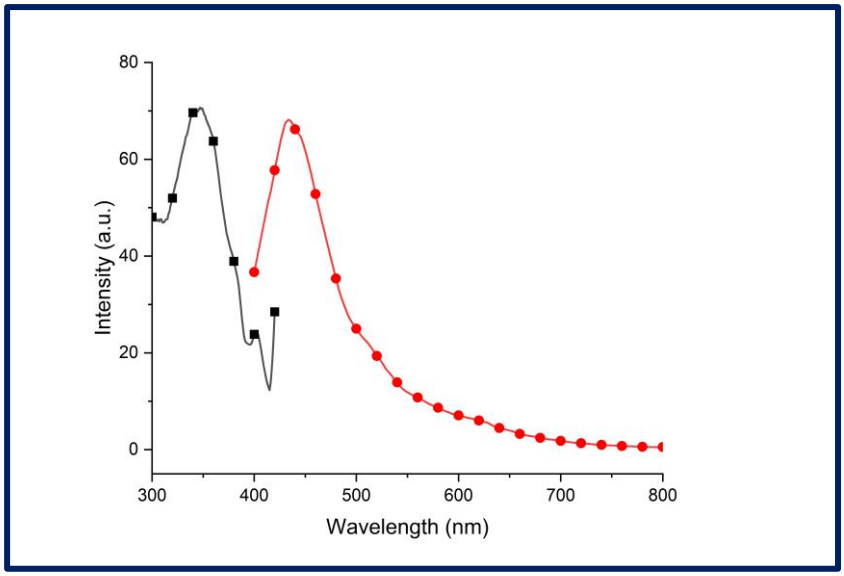


Figure S38. Excitation ($\lambda_{em.}$ = 435 nm; ■) and emission ($\lambda_{ex.}$ = 347 nm ●) spectra of **2c** in dichloromethane.

7. References

[S1] C. H. Wanke, J. L. Feijó, L. G. Barbosa, L. F. Campo, R. V. B. Oliveira, F. Horowitz, *Polymer*, **2011**, *52*, 1797-1802.