Electronic Supporting Information (ESI)

Mono-substituted amine-oligosilsesquioxanes as functional tools in the Pd(II) coordination chemistry: synthesis and properties

Kamila Piec, Sylwia Kostera, Dawid Jędrzkiewicz, Jolanta Ejfler and Łukasz John*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

**Corresponding Author: Łukasz John, e-mail: lukasz.john@chem.uni.wroc.pl*

Table of Contents

Table S1. X-ray experimental data and refinement for palladium complexes **9** and **10**.

	9	**10**
Empirical formula	$C_{78}H_{156}N_2O_{28}PdSi_{16}$	$C_{80}H_{156}N_2O_{32}PdSi_{16}$
Formula weight	2125.88	2213.90
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.895(7)	9.910(3)
b (Å)	10.696(8)	10.779(4)
c (Å)	26.93(2)	26.361(9)
α (°)	88.13(6)	89.83(4)
β (°)	85.08(6)	81.99(3)
γ (°)	76.48(5)	88.94(4)
V (Å^3)	2761(4)	2787.9(17)
Z	1	1
Crystal description	Block, yellow	Needle, yellow
Crystal size (mm)	0.48 × 0.27 × 0.17	0.37 × 0.11 × 0.08
d_{calc} (g/cm^3)	1.279	1.319
μ (mm^{-1})	0.408	0.409
F(000)	1132	1176
Diffractometer	Kuma KM-4 CCD	Xcalibur, CCD Ruby
λ (Å)	0.71073 (Mo)	0.71073 (Mo)
T (K)	100	100
Θ min/max (°)	3.0/25.5	1.6/26.5
h, k, l min/max	-9/11, -12/12, -32/32	-12/11, -13/11, -24/33
Reflections collected	20719	19647
Independent reflections	10182	11534
Reflections [I>2σ(I)]	5001	7437
R (int.)	0.1023	0.0335
data/restraints/params	10182/36/610	11534/1221/977
R[$F^2 > 2\sigma(F^2)$]	0.0854	0.0585
wR(F^2)	0.2419	0.1517
GooF	0.948	1.018
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	1.31/-0.79	0.82/-0.33

Table S2. Selected bond distances (Å) and angles (°) for **9** and **10**.

Atoms	9	Atoms	10	Atoms	10
Distances (Å)					
Pd1-O13	2.003(6)	Pd1A-O15A	1.980(11)	Pd1B-O15B	1.99(3)
		Pd1A-O15C	2.060(11)	Pd1B-O15D	2.12(3)
Pd1-N1	2.082(7)	Pd1A-N1A	2.072(13)	Pd1B-N1B	2.02(3)
		Pd1A-N1C	2.098(11)	Pd1B-N1D	2.00(4)
Angles (°)					
O13-Pd1-O13^{i}	180.0	O15A-Pd1A-O15C	178.6(5)	O15B-Pd1B-O15D	174.5(10)
O13-Pd1-N1	93.5(3)	O15A-Pd1A-N1A	92.8(5)	O15B-Pd1B-N1B	94.9(13)
O13-Pd1-N1^{i}	93.5(3)	O15A-Pd1A-N1C	86.5(5)	O15B-Pd1B-N1D	83.1(14)
O13^{i}-Pd1-N1	86.5(3)	O15C-Pd1A-N1A	88.1(5)	O15D-Pd1B-N1B	88.9(12)
O13^{i}-Pd1-N1^{i}	86.5(3)	O15C-Pd1A-N1C	92.7(4)	O15D-Pd1B-N1D	93.0(12)
N1-Pd1-N1^{i}	180.0	N1A-Pd1A-N1C	175.9(5)	N1B-Pd1B-N1D	177.8(15)

^{i} 1-X,1-Y,1-Z for 9

ALERT B EXPLANATION

B Alert explanation for **9**:

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 17 Note

RESPONSE: Theta min = 3.0 deg. The missing reflections have a theta value in the range 0.8 – 2.9 deg. and therefore they either are masked by the beamstop or their intensities have overflown.

Table S3. Energies and relative energies of isomers corresponding to **9** optimized in *vacuo*.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
9_RS_A	-1394.872770	323.58	0.00	0.00	0.00
9_RS_B	-1394.855381	323.03	10.91	10.36	43.36
9_RR/SS_A	-1394.863788	323.90	5.64	5.96	24.93
9_RR/SS_B	-1394.840228	324.00	20.42	20.84	87.19

Table S4. Energies and relative energies of isomers corresponding to **9** optimized in chloroform.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
9_RS_A	-1394.872770	323.58	0.00	0.00	0.00
9_RS_B	-1394.855369	323.71	10.92	11.05	46.24
9_RR/SS_A	-1394.872362	323.50	0.26	0.17	0.72
9_RR/SS_B	-1394.852759	323.52	12.56	12.50	52.29

Table S5. Energies and relative energies of isomers corresponding to **10** optimized in *vacuo*.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
10_RS_A	-1771.913828	343.45	0.00	0.00	0.00
10_RS_B	-1771.891082	343.36	14.27	14.18	59.34
10_RR/SS_A	-1771.913639	343.47	0.12	0.14	0.59
10_RR/SS_B	-1771.890010	343.60	14.95	15.10	63.17

Table S6. Energies and relative energies of isomers corresponding to **10** optimized in chloroform.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
10_RS_A	-1771.924923	343.45	0.00	0.00	0.00
10_RS_B	-1771.905876	343.36	11.95	11.86	49.63
10_RR/SS_A	-1771.924737	343.47	0.12	0.14	0.58
10_RR/SS_B	-1771.904993	343.60	12.51	12.66	52.96

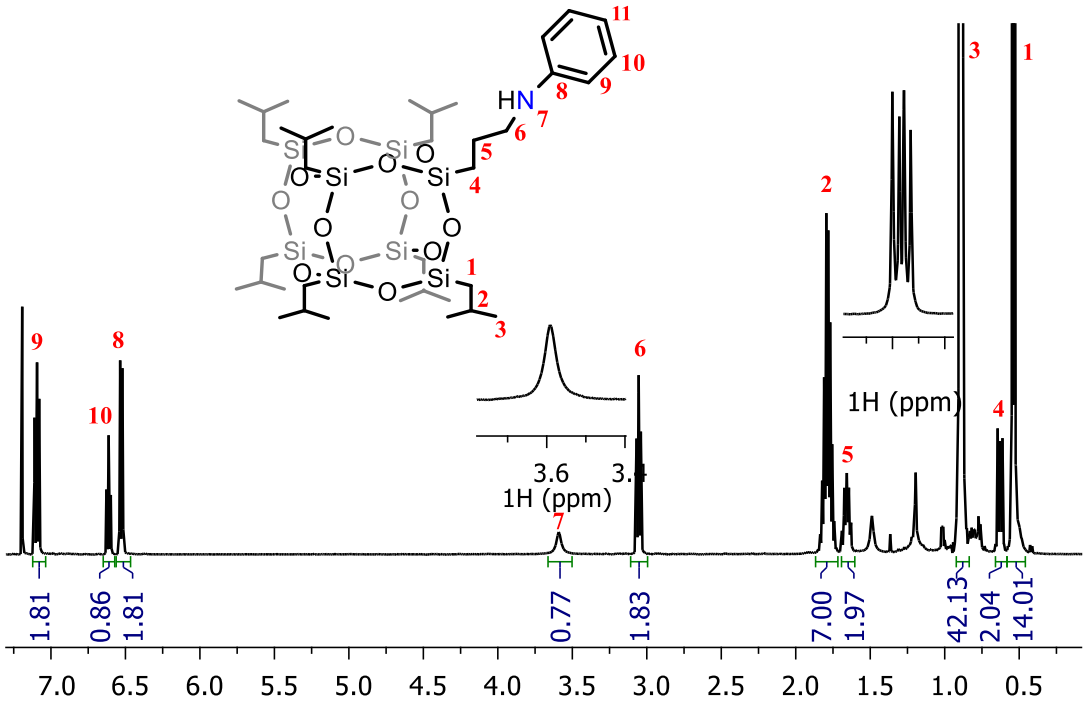

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **1**.

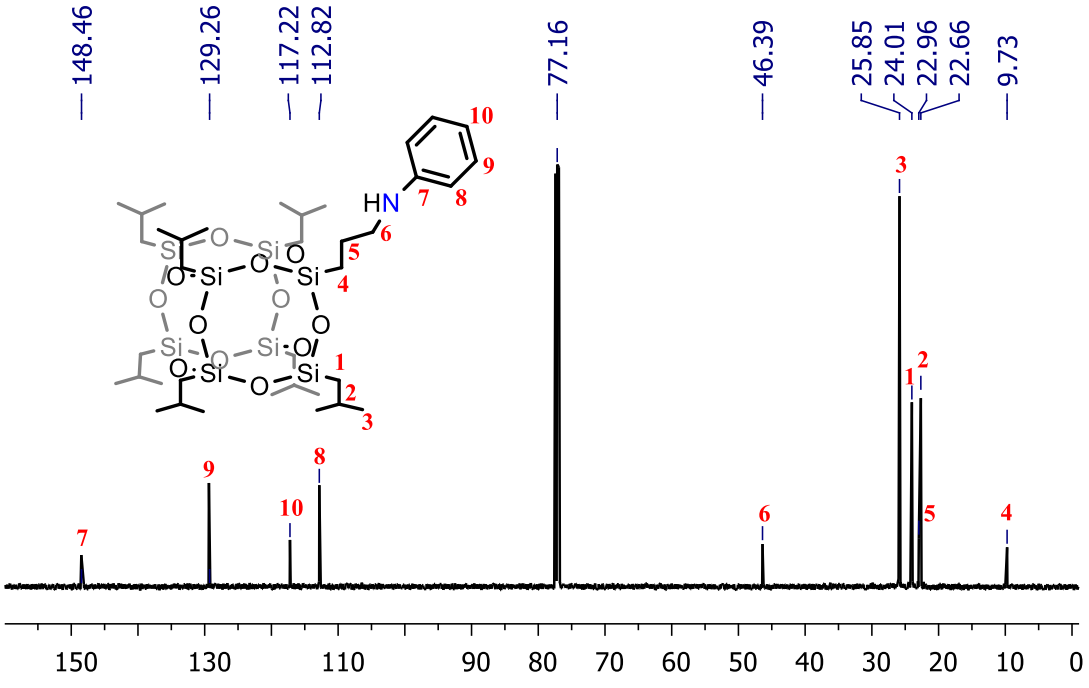

Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **1**.

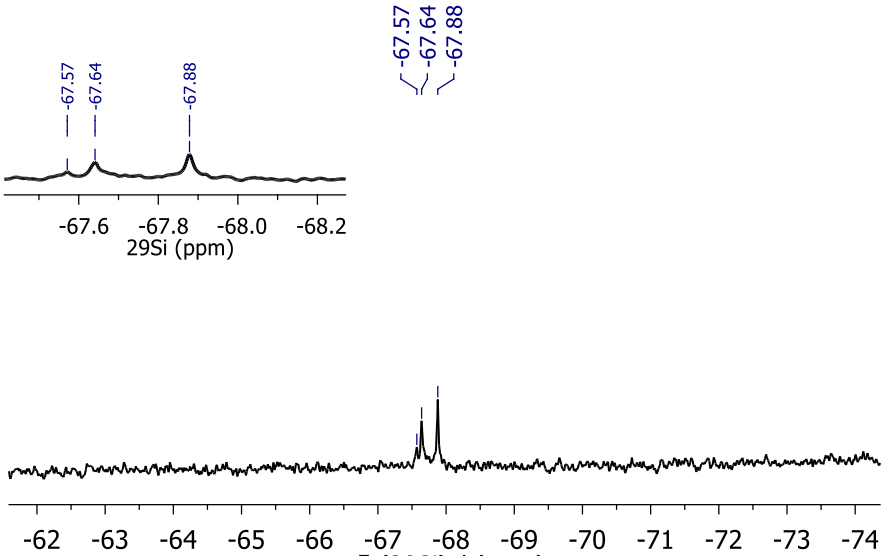

Figure S3. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **1**.

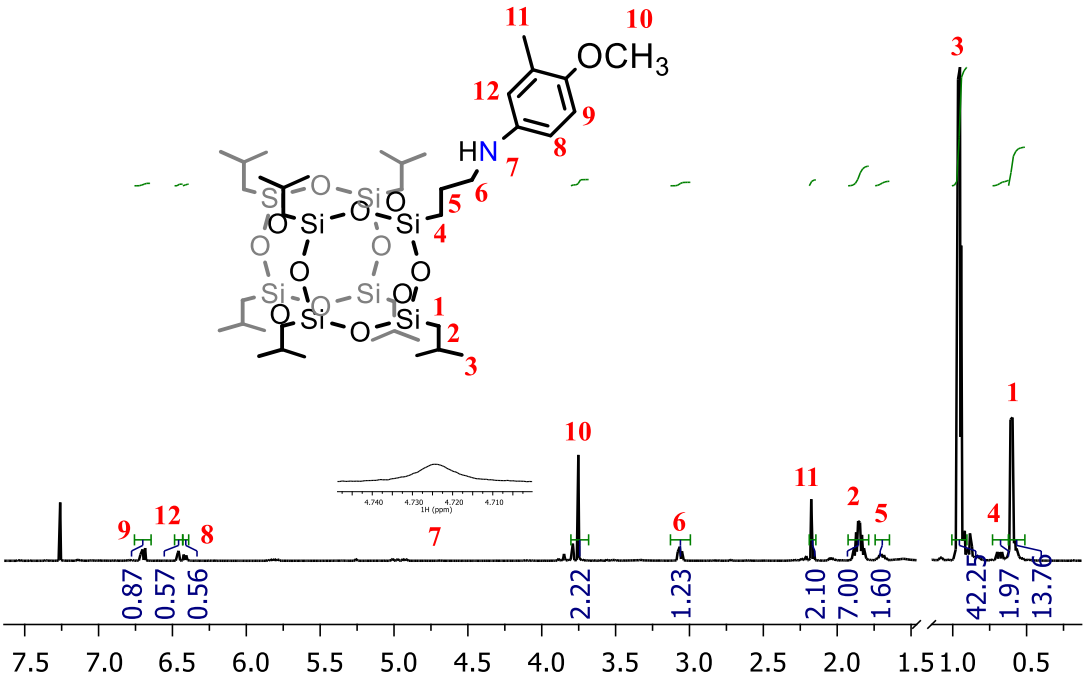

Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **2**.

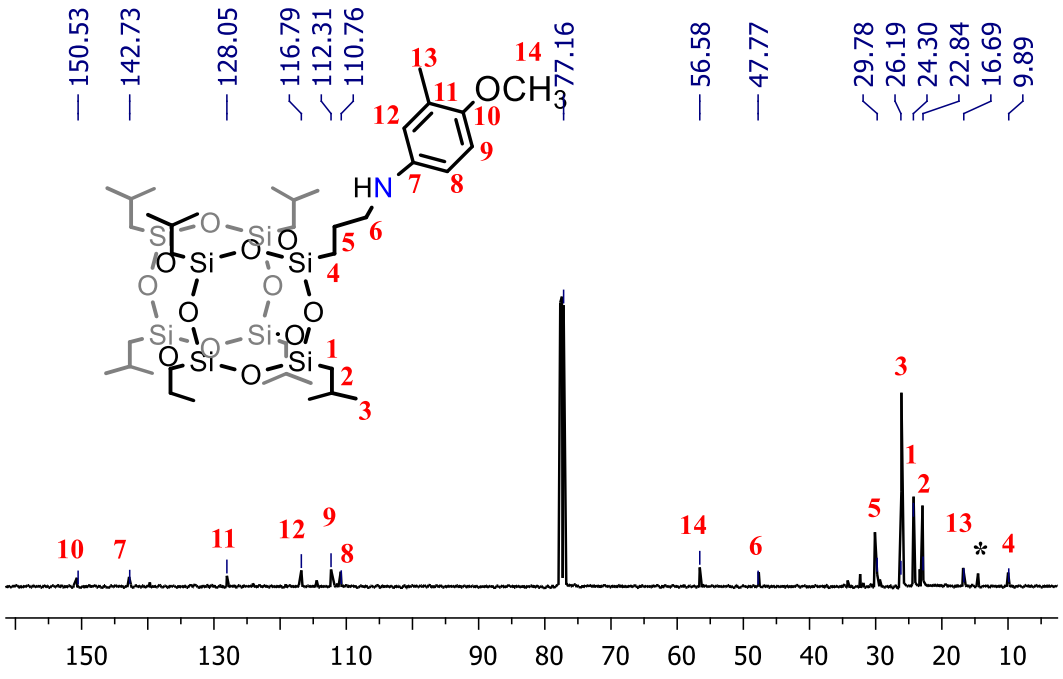

Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **2**.

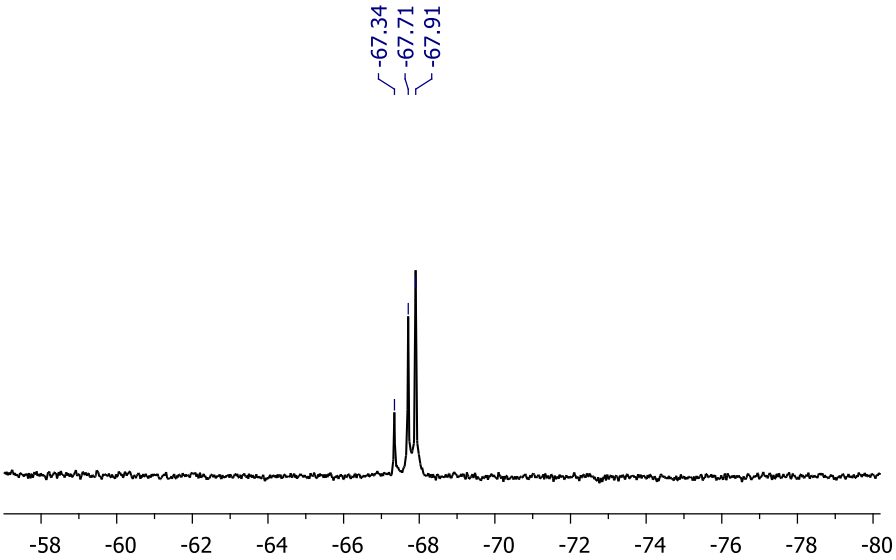

Figure S6. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **2**.

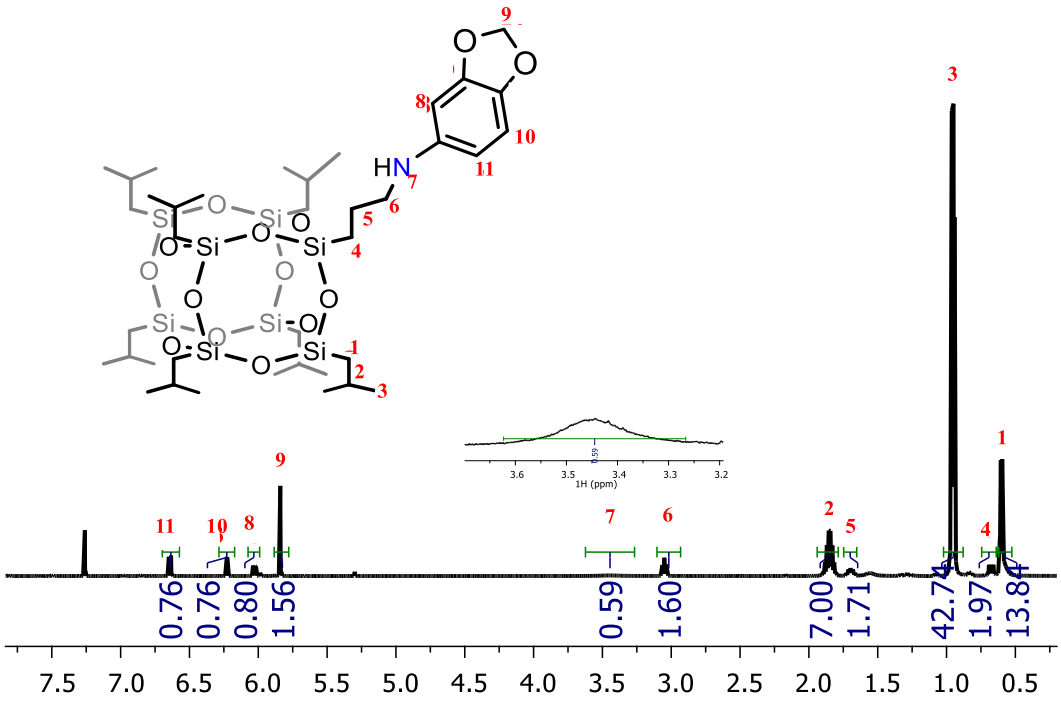

Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **3**.

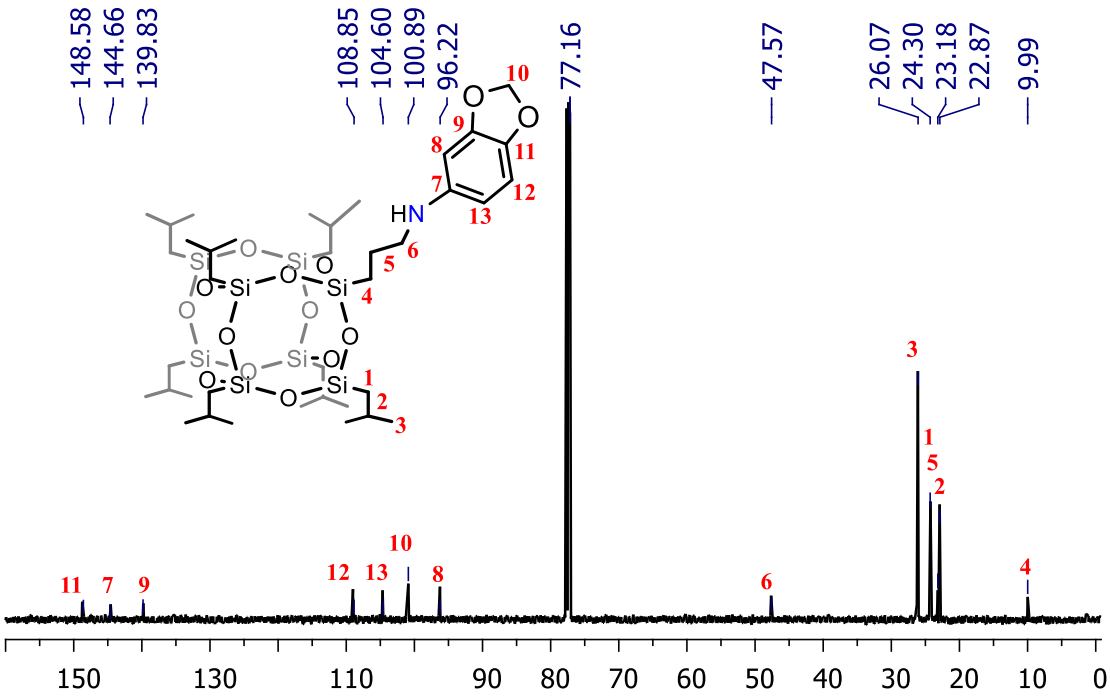

Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **3**.

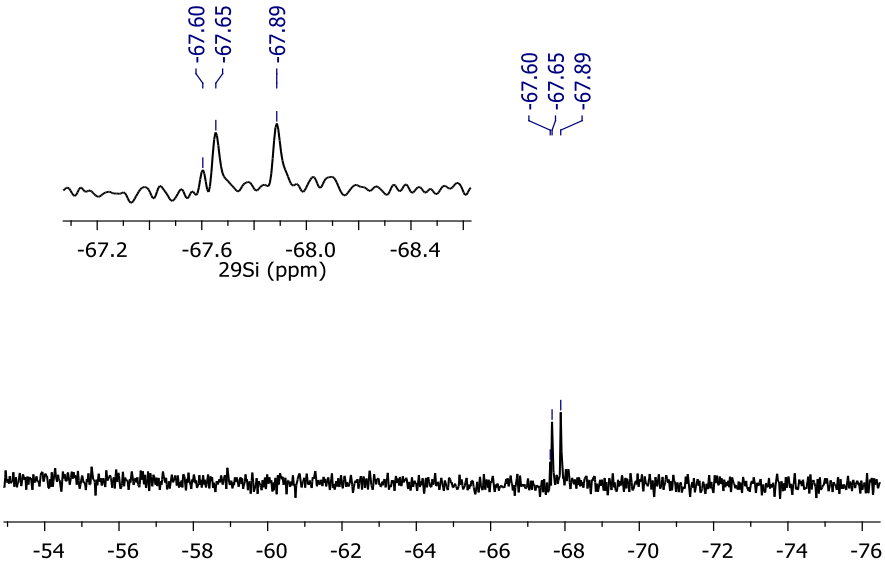

Figure S9. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **3**.

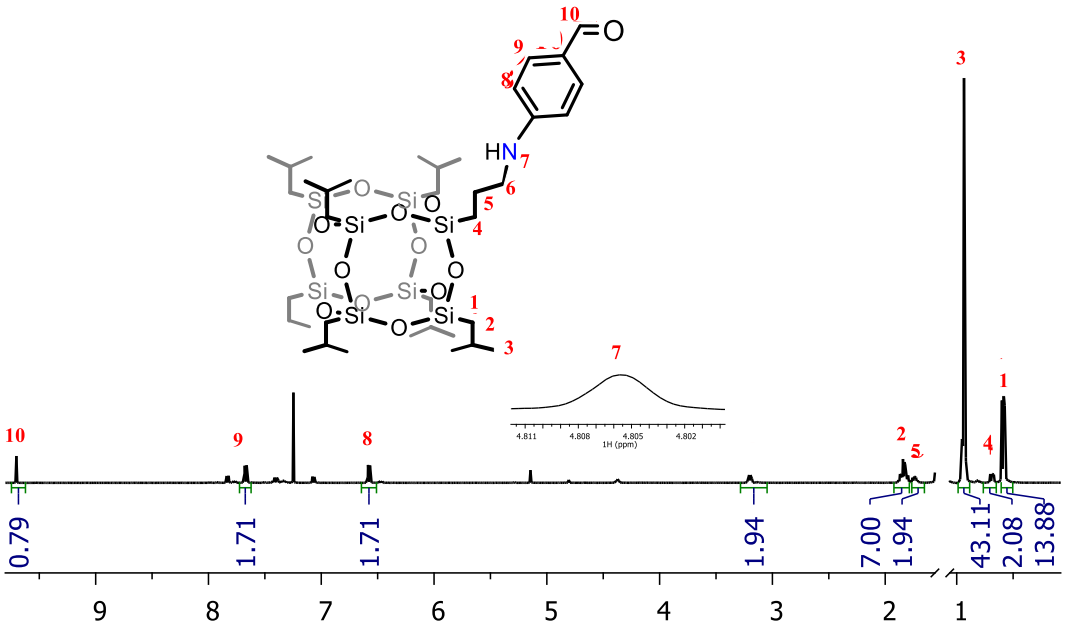

Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **4**.

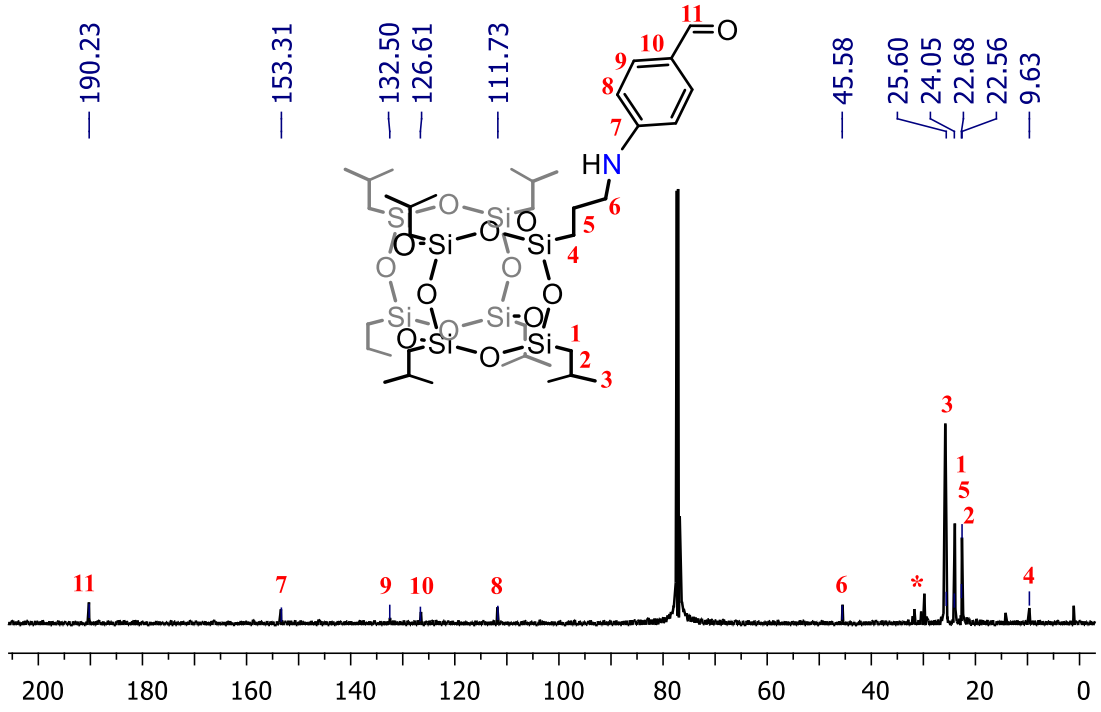

Figure S11. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **4**.

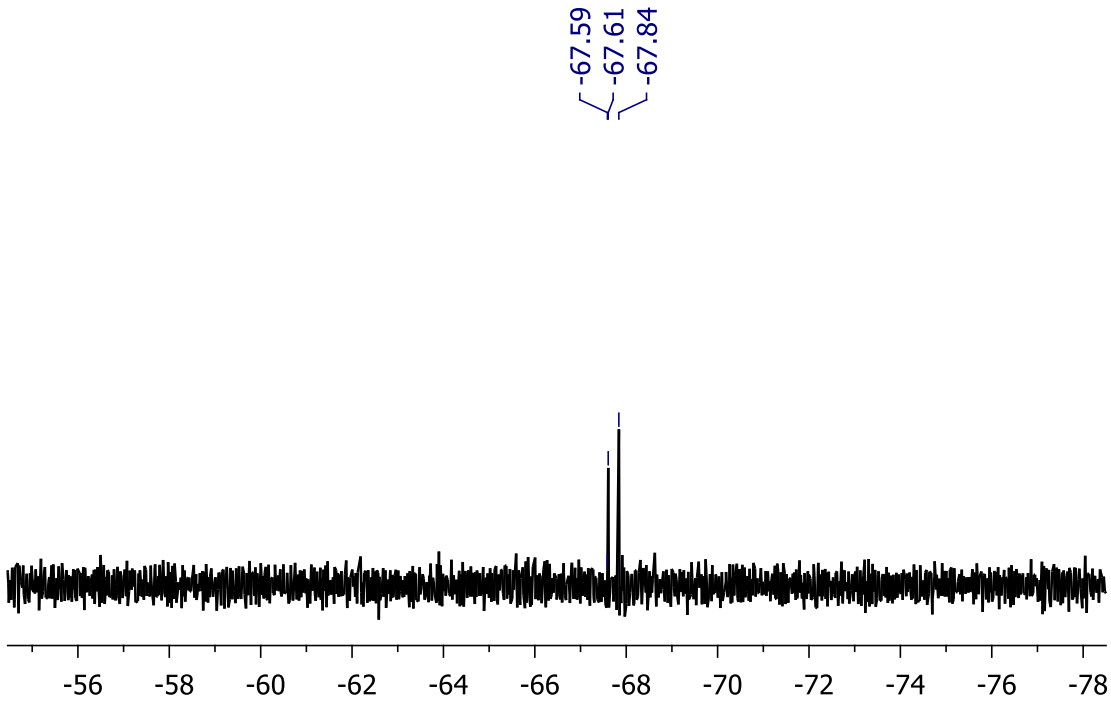

Figure S12. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **4**.

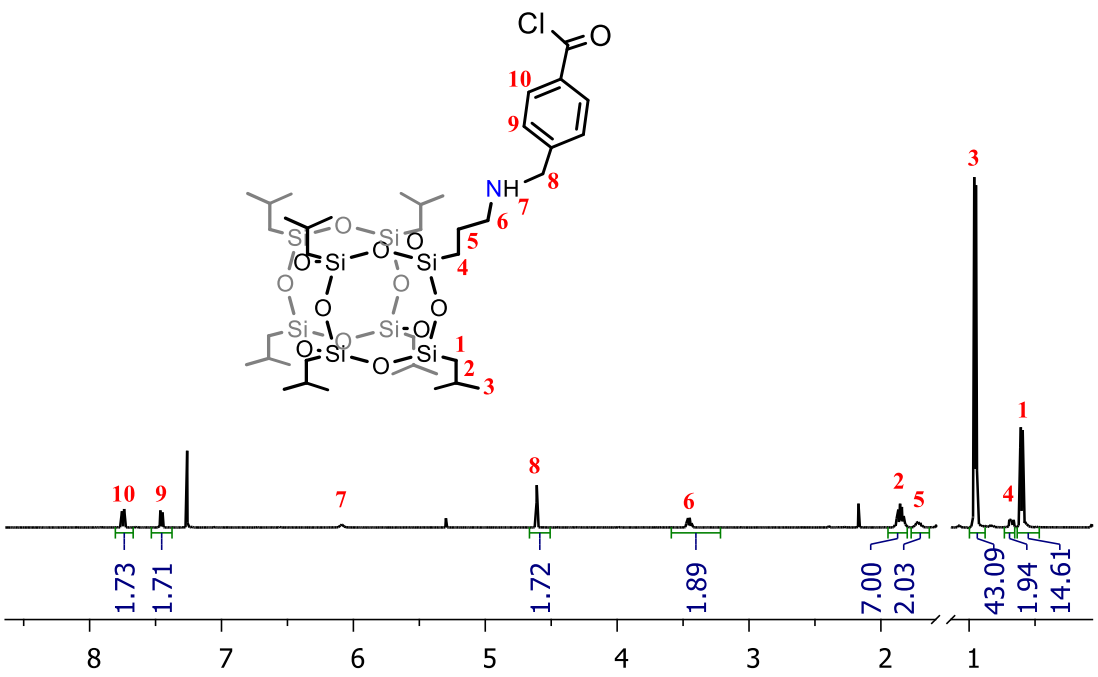

Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **5**.

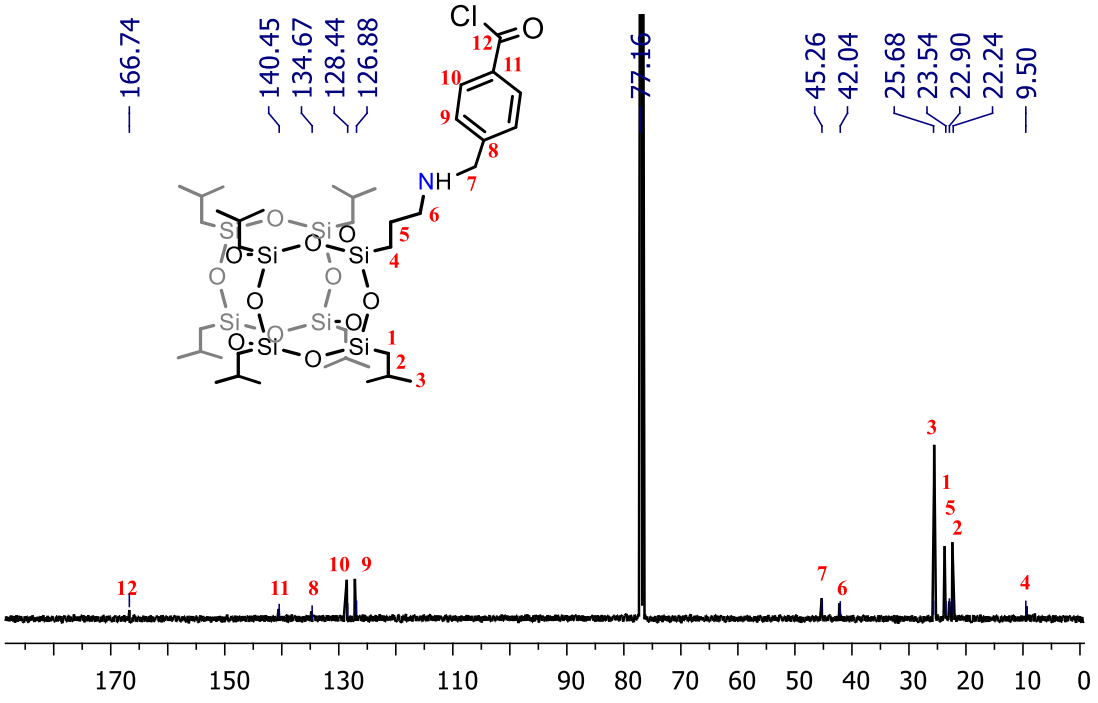

Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **5**.

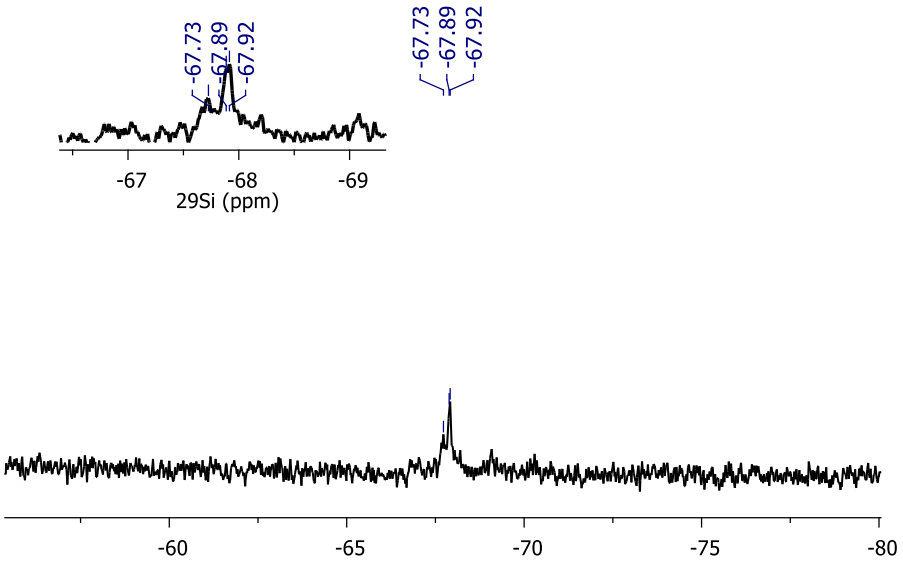

Figure S15. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **5**.

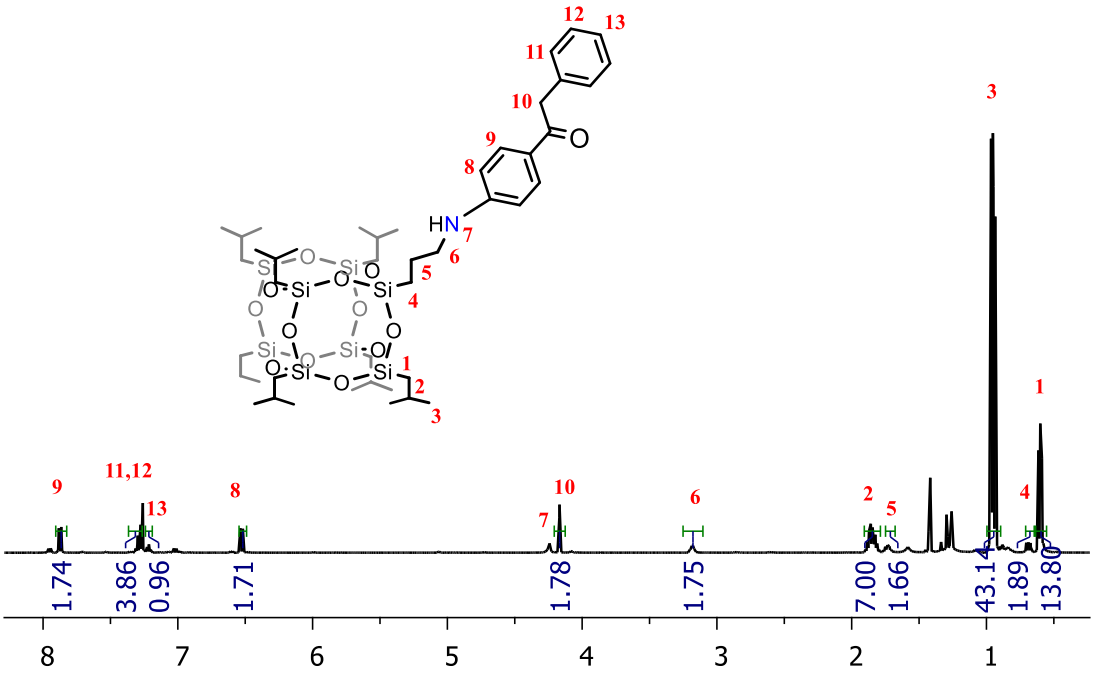

Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **6**.

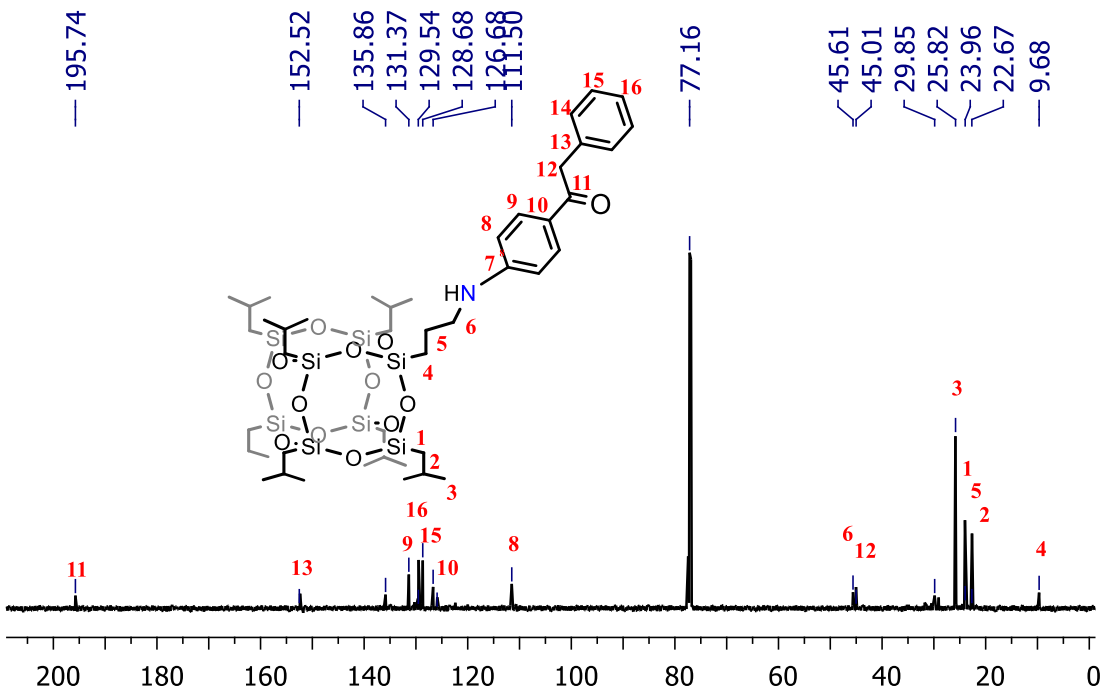

Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **6**.

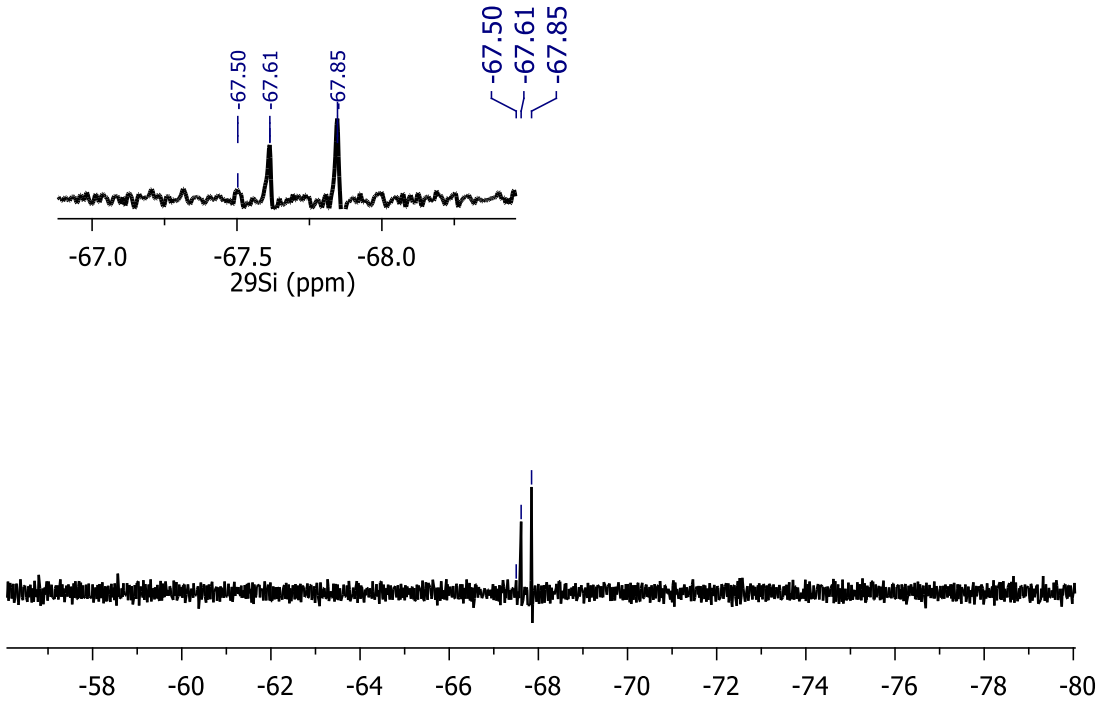

Figure S18. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **6**.

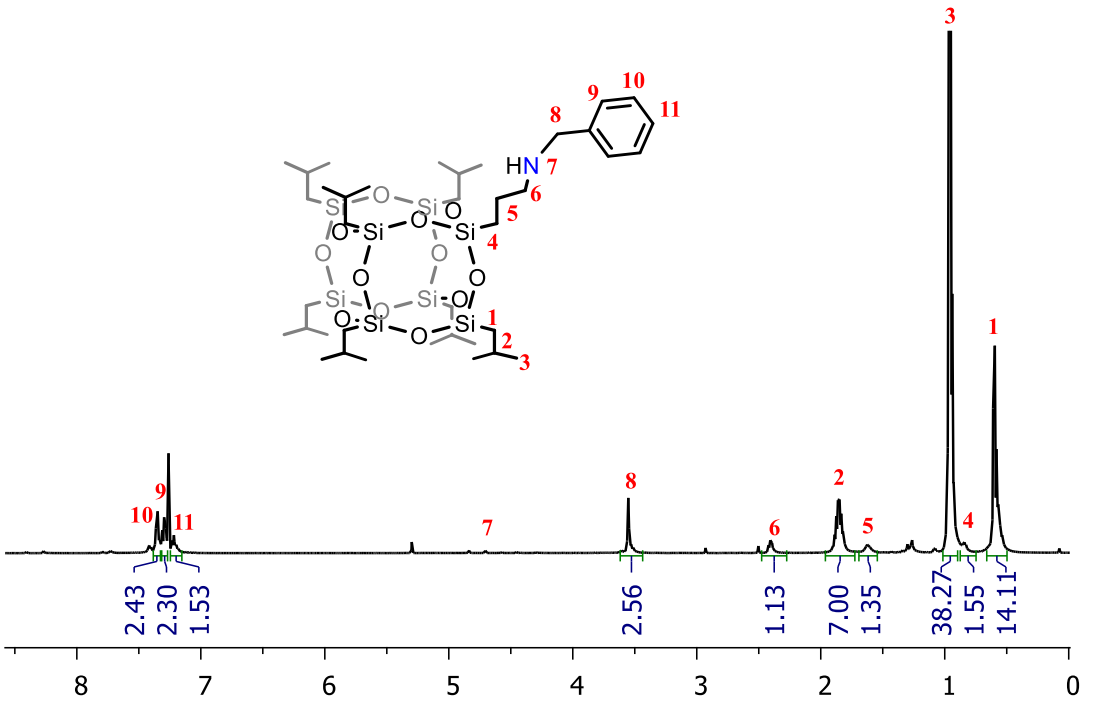

Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **7**.

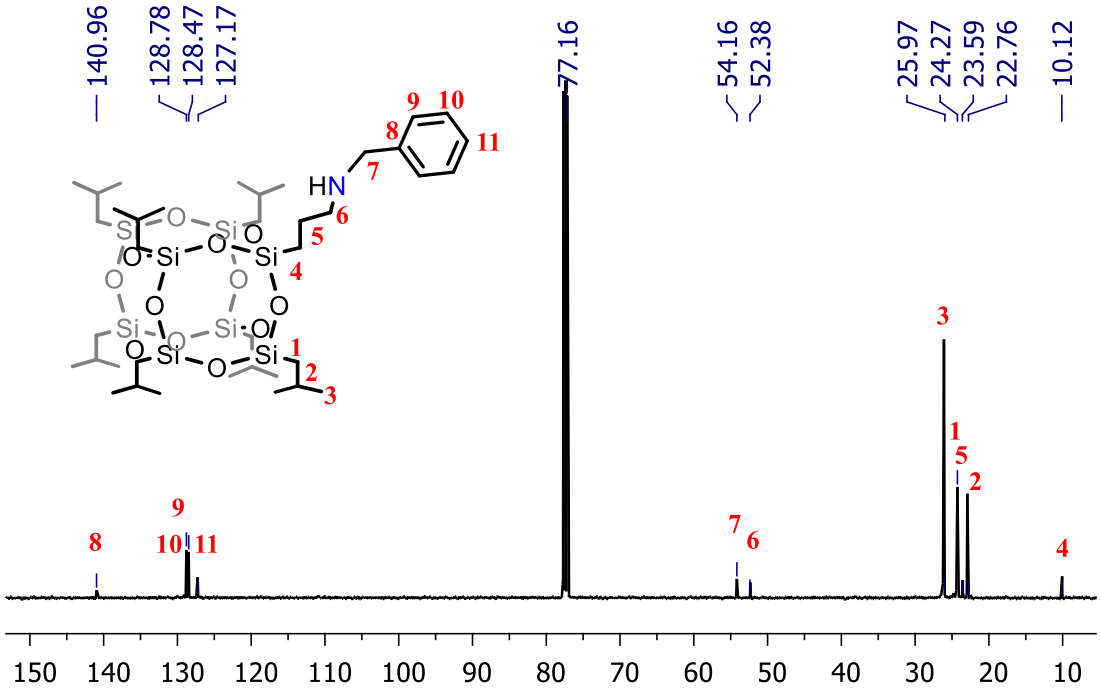

Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **7**.

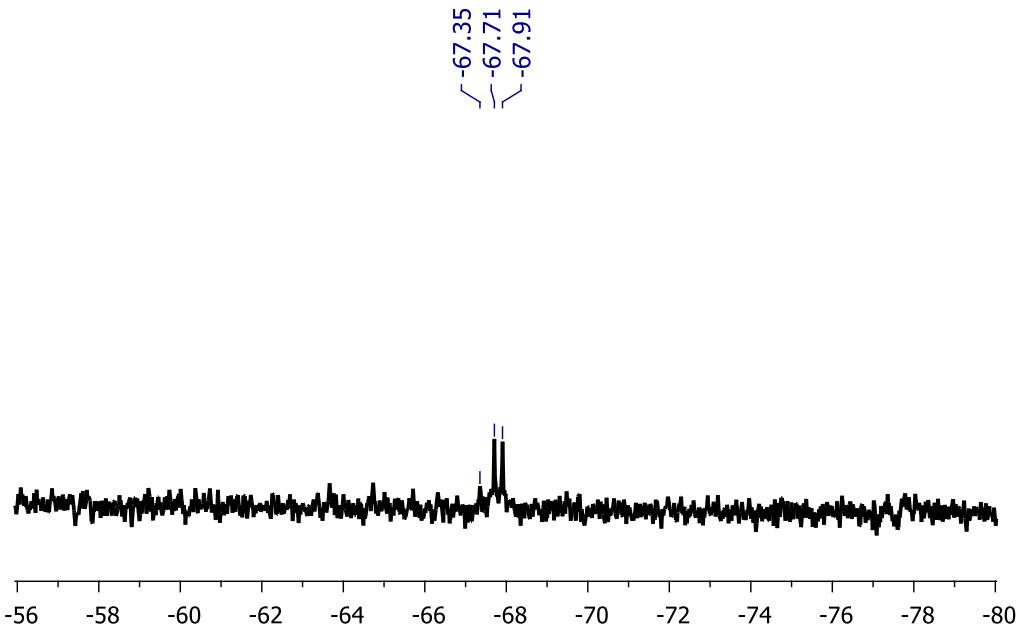

Figure S21. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **7**.

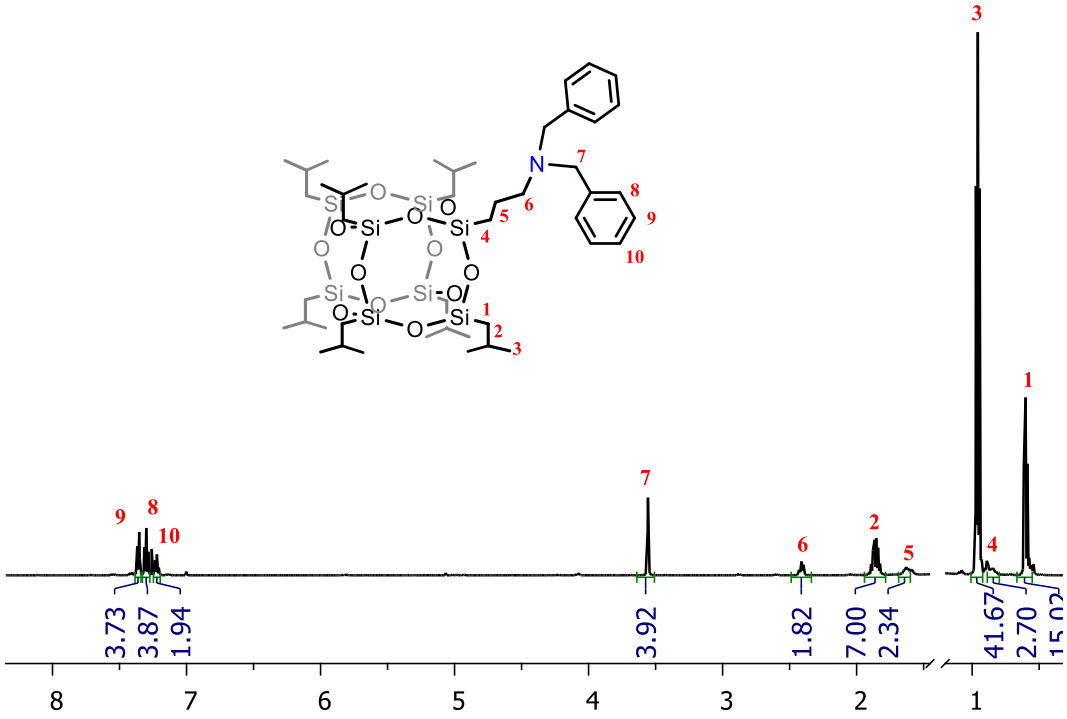

Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **8**.

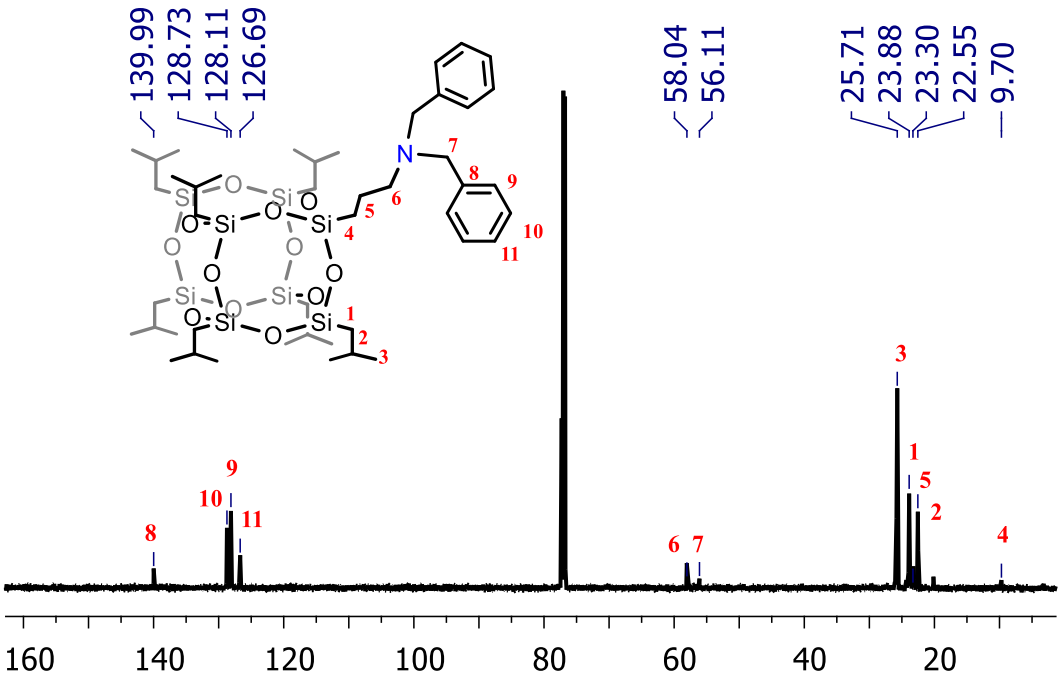

Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **8**.

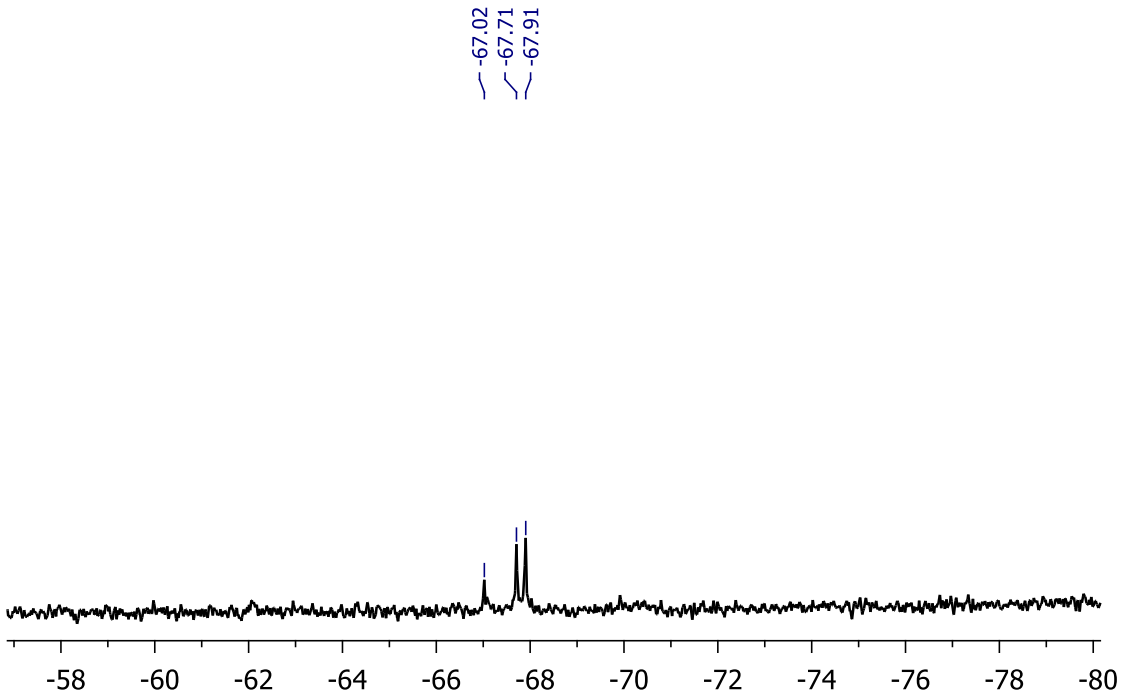

Figure S24. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **8**.

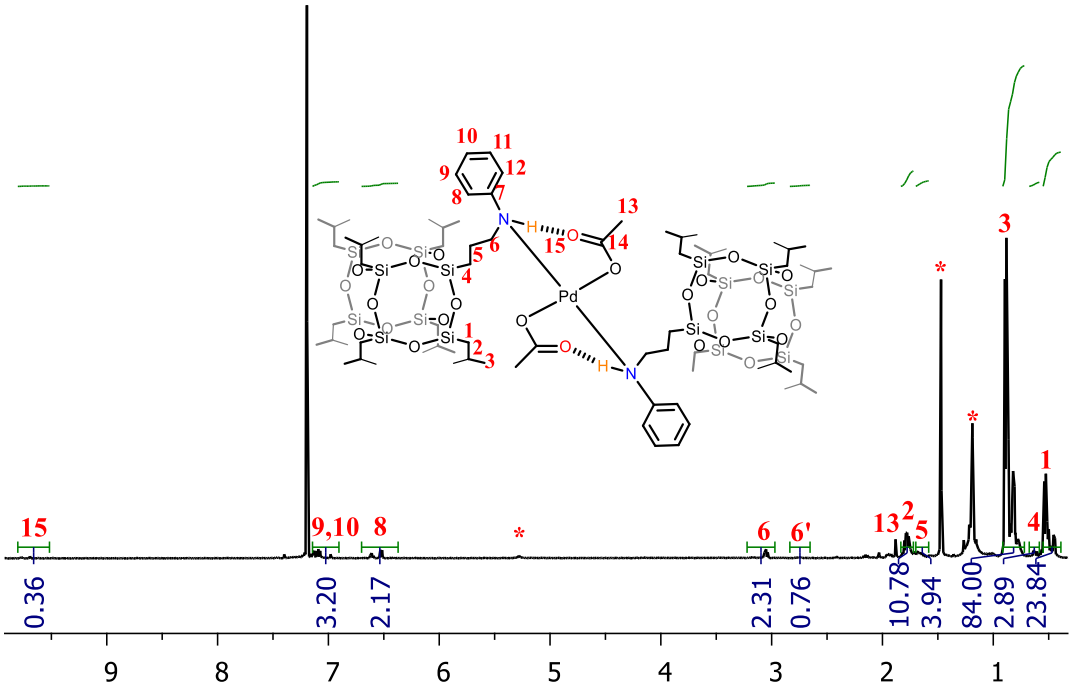

Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **9**.

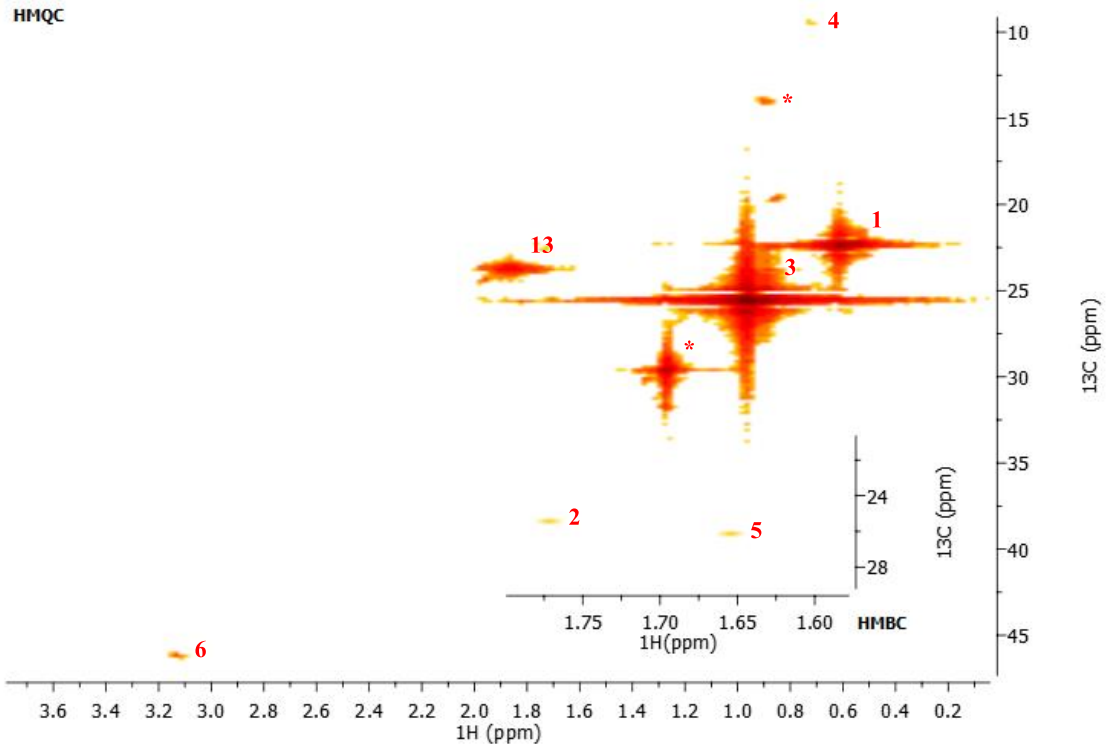

Figure S26. ^{1}H-^{13}C HMQC NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **9**.

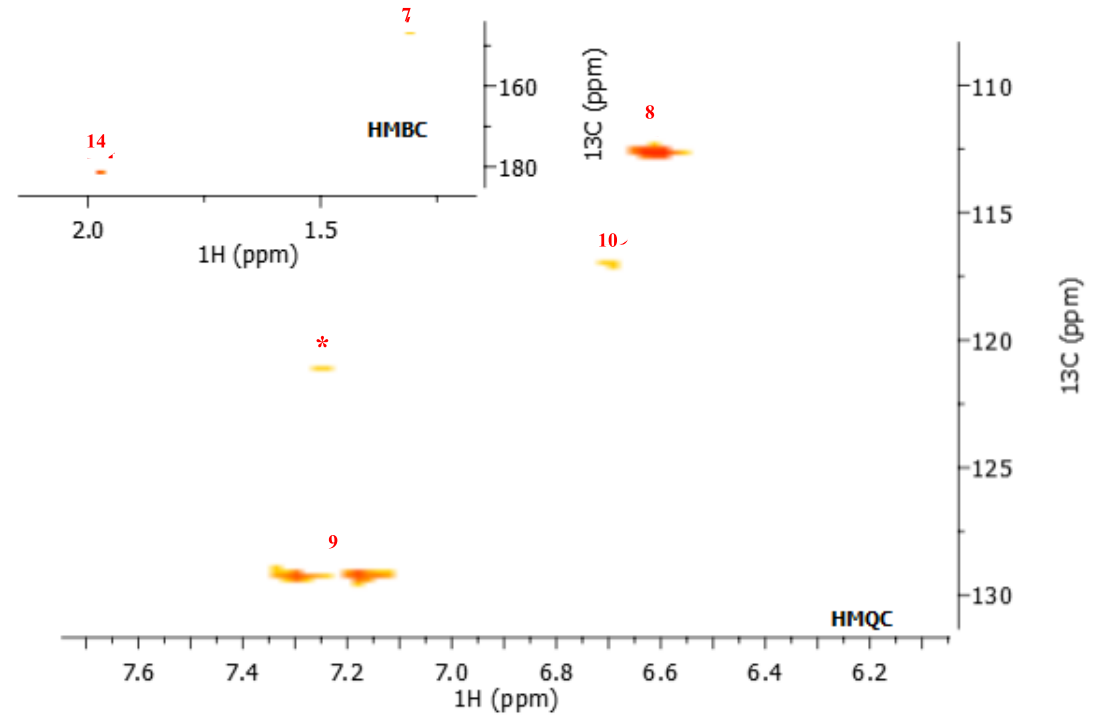

Figure S27. ^{1}H-^{13}C HMQC NMR (500 MHz, $CDCl_3$, 20 °C) spectrum of **9**.

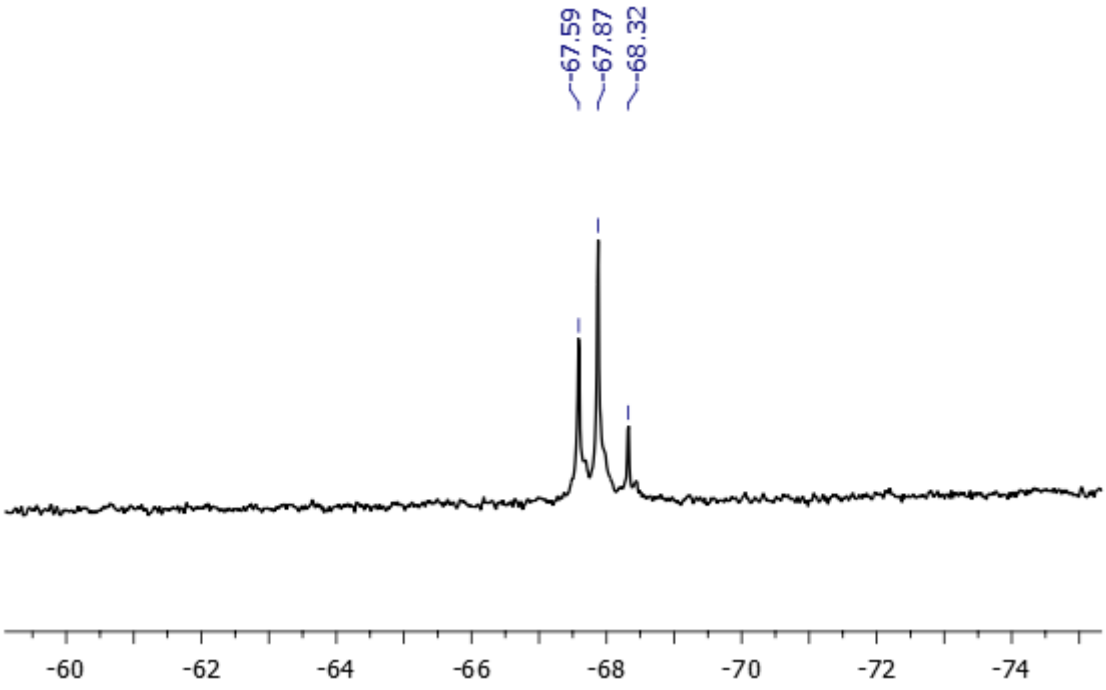

Figure S28. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **9**.

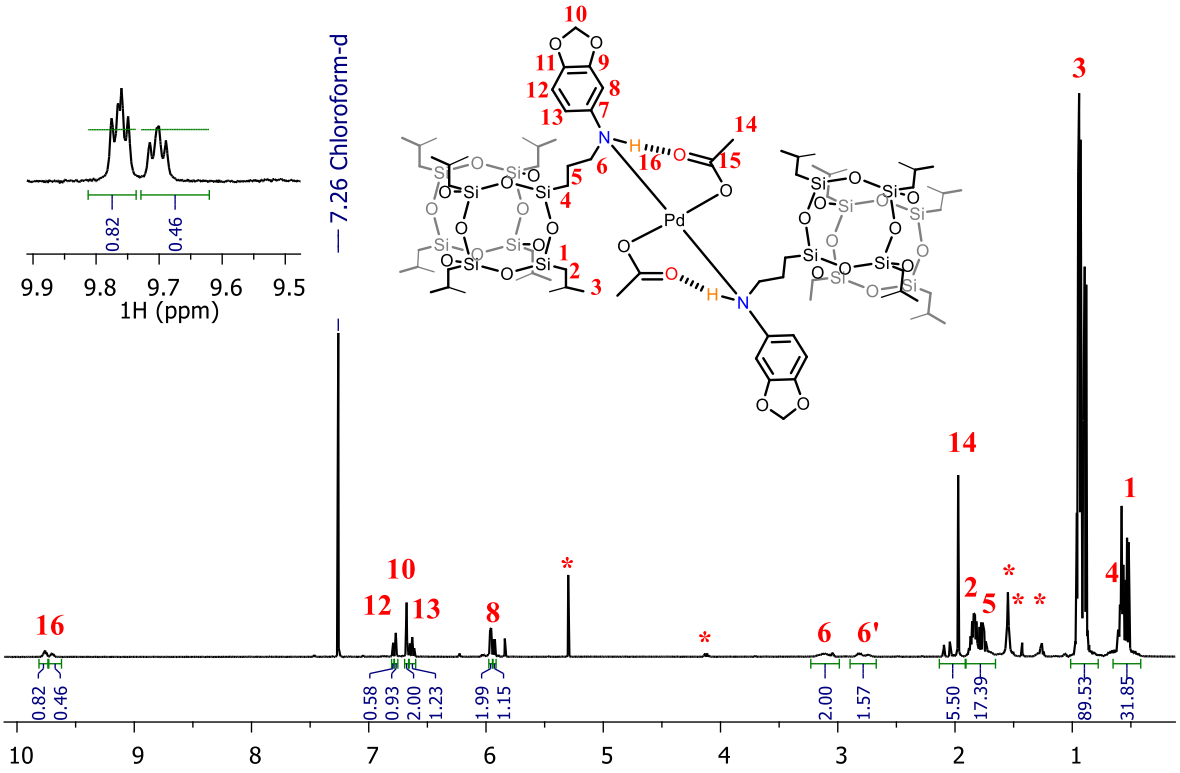

Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **10**.

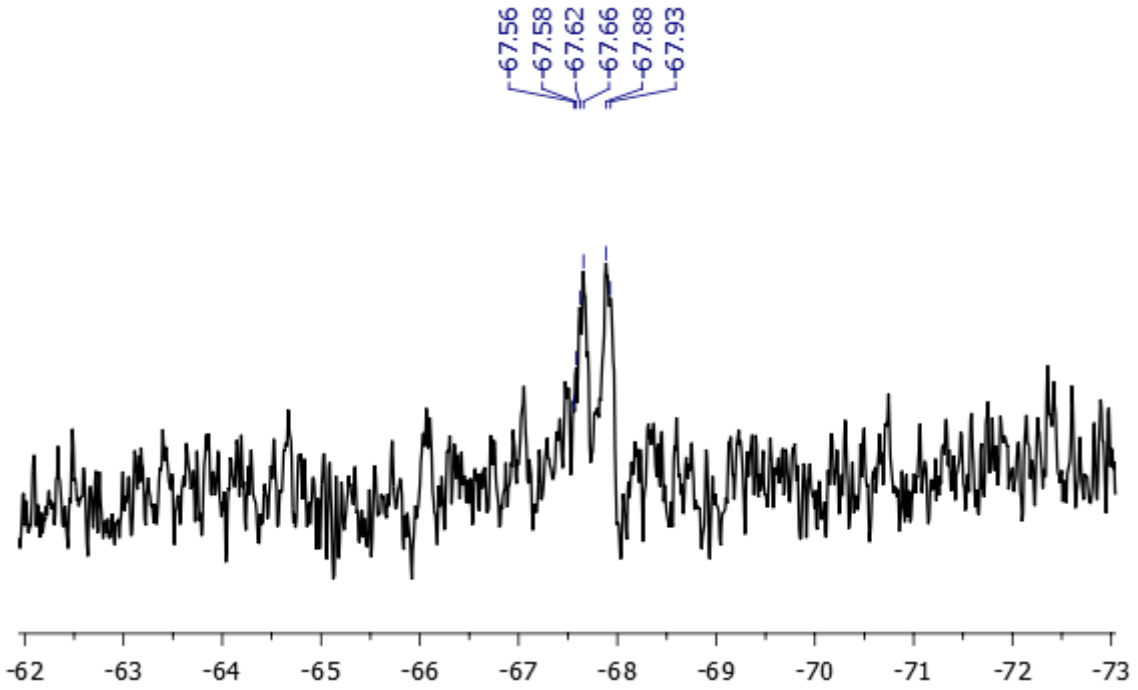

Figure S30. ^{29}Si NMR (59.6 MHz, $CDCl_3$, 300 K) spectrum of **10**.

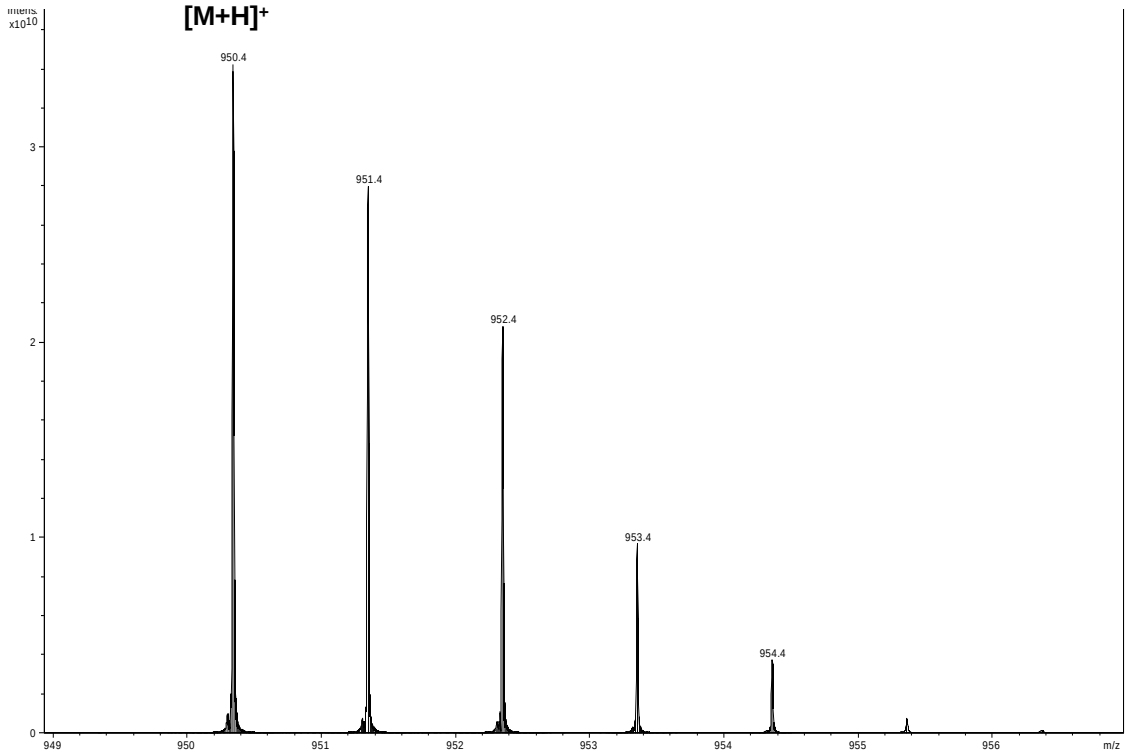

Figure S31. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **1**.

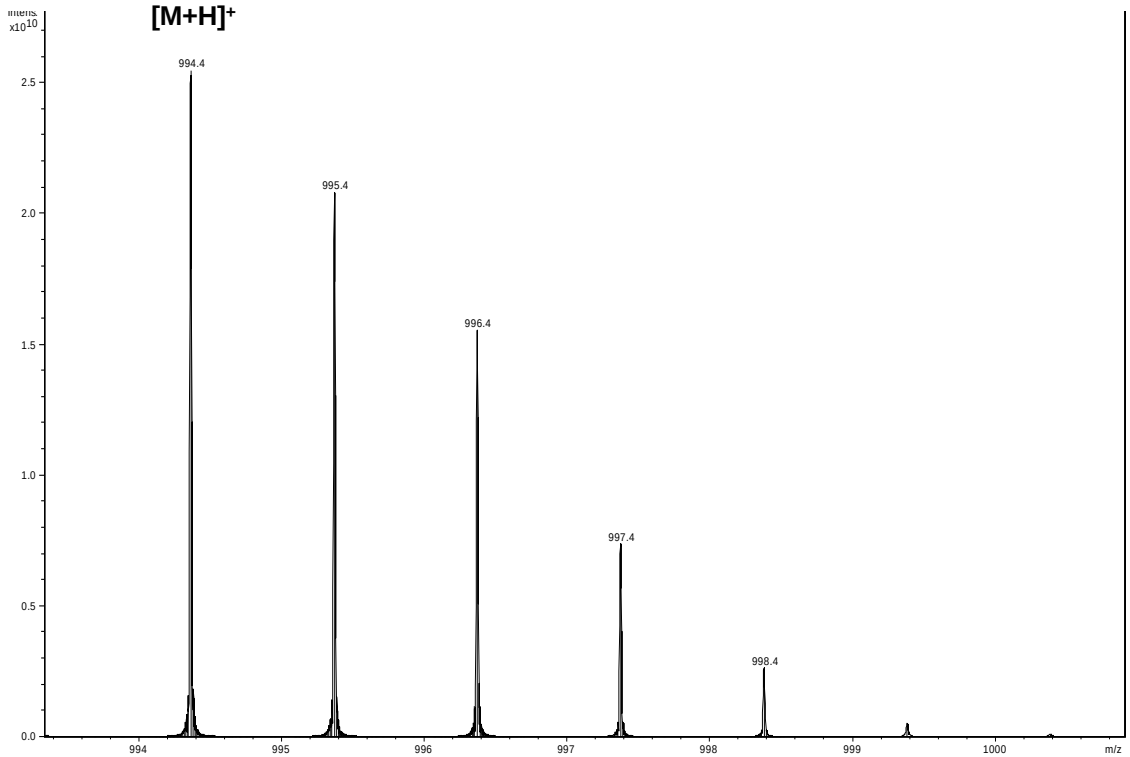

Figure S32. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **2**.

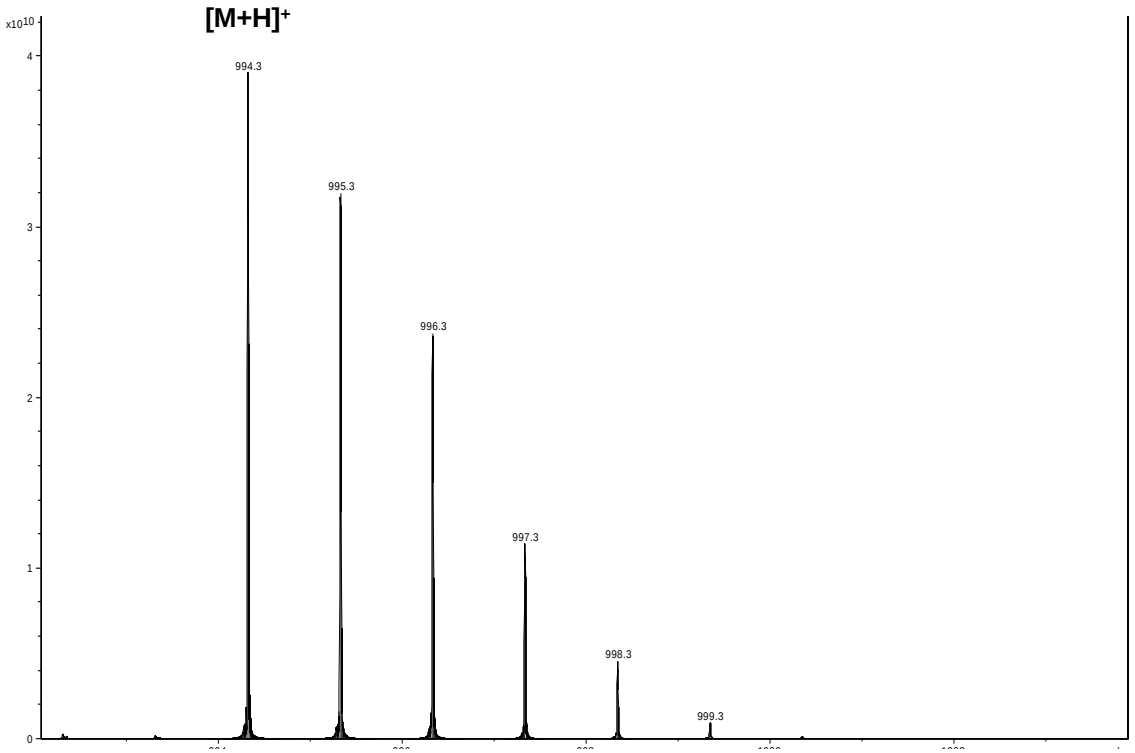

Figure S33. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **3**.

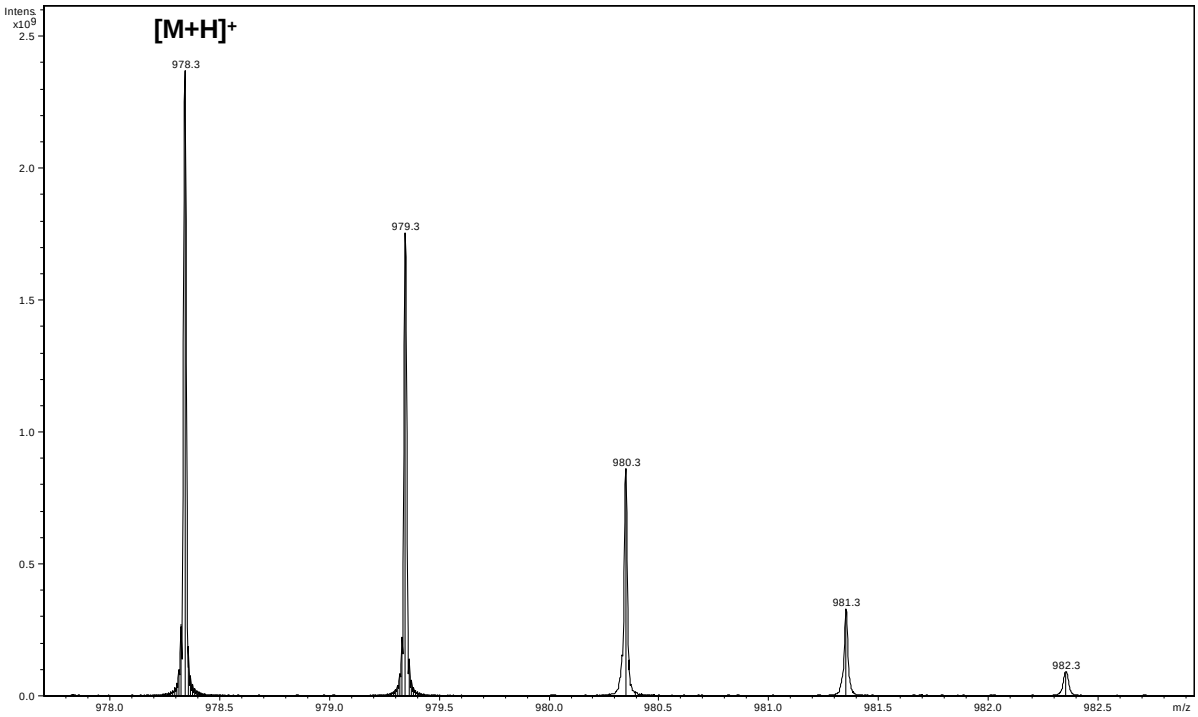

Figure S34. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **4**.

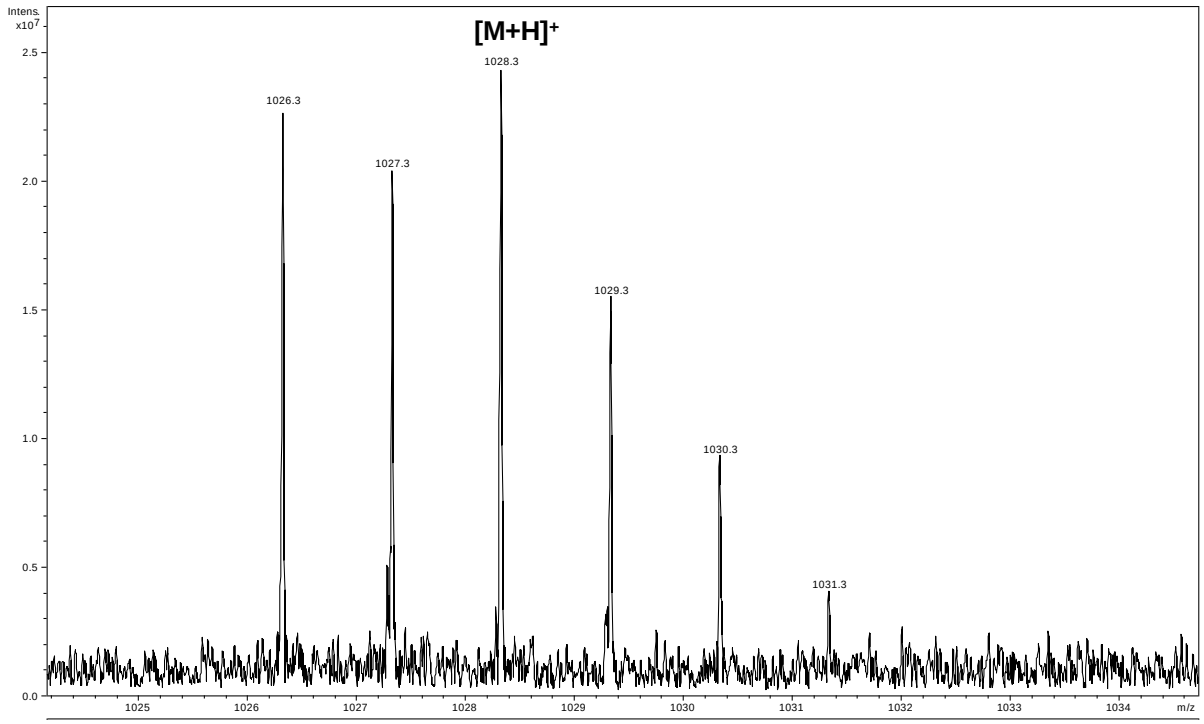

Figure S35. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **5**.

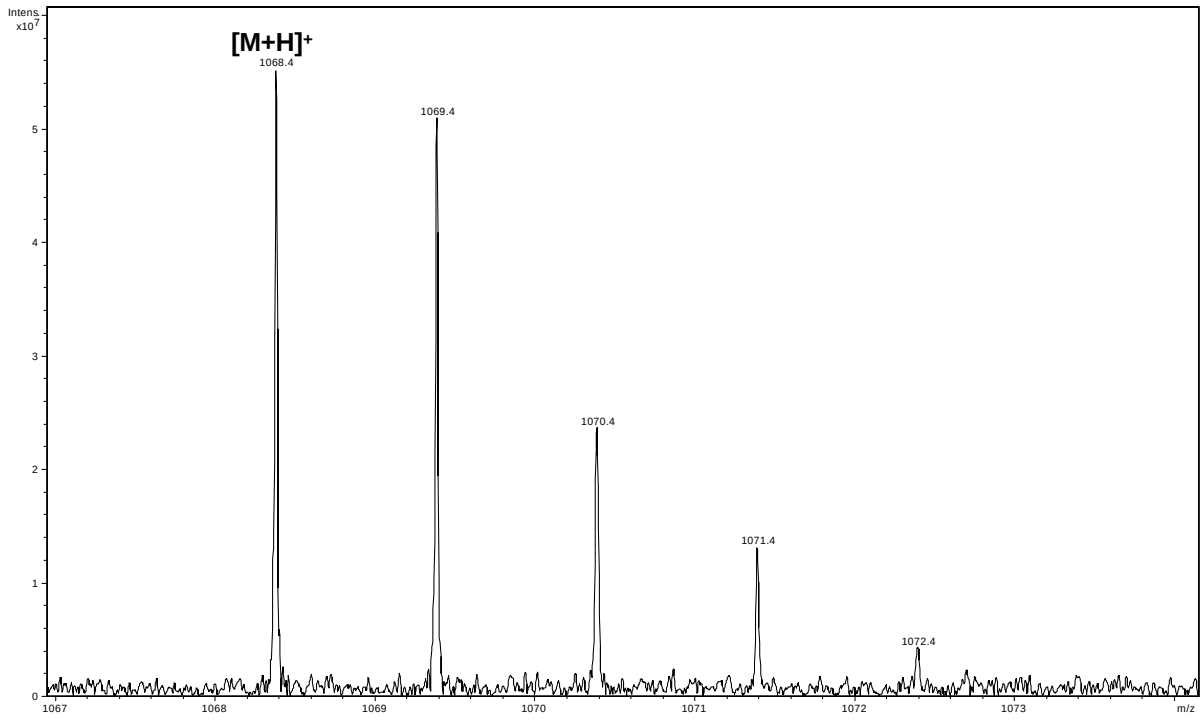

Figure S36. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **6**.

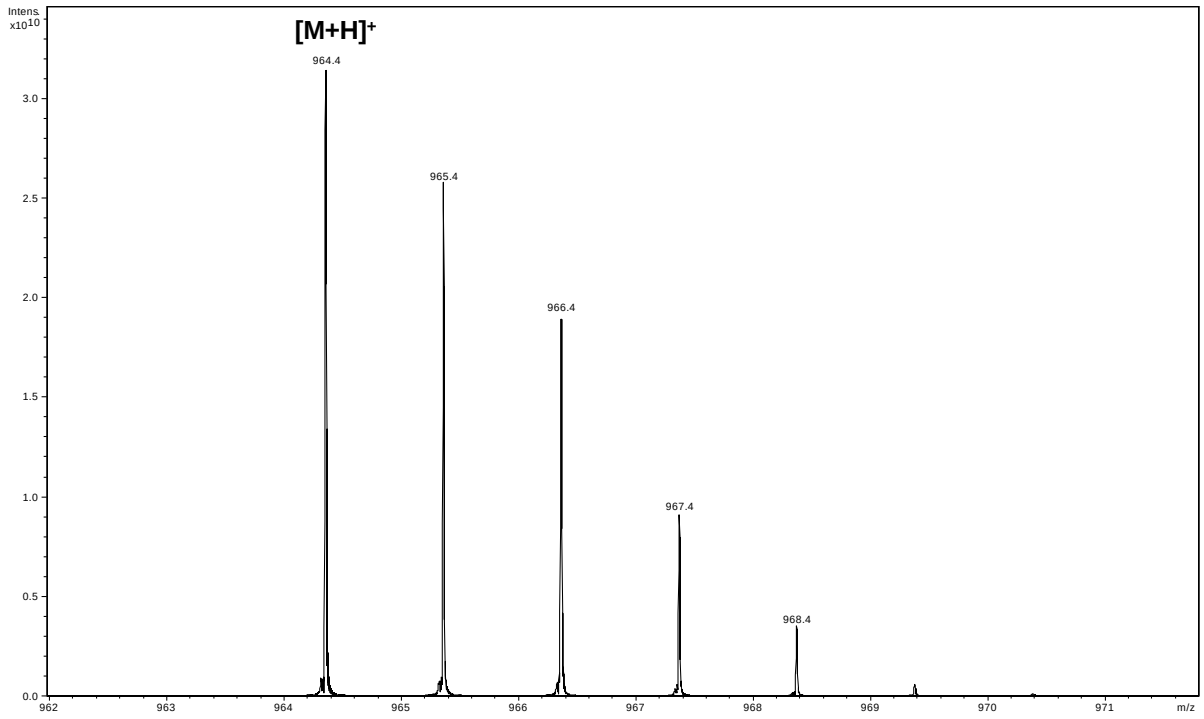

Figure S37. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **7**.

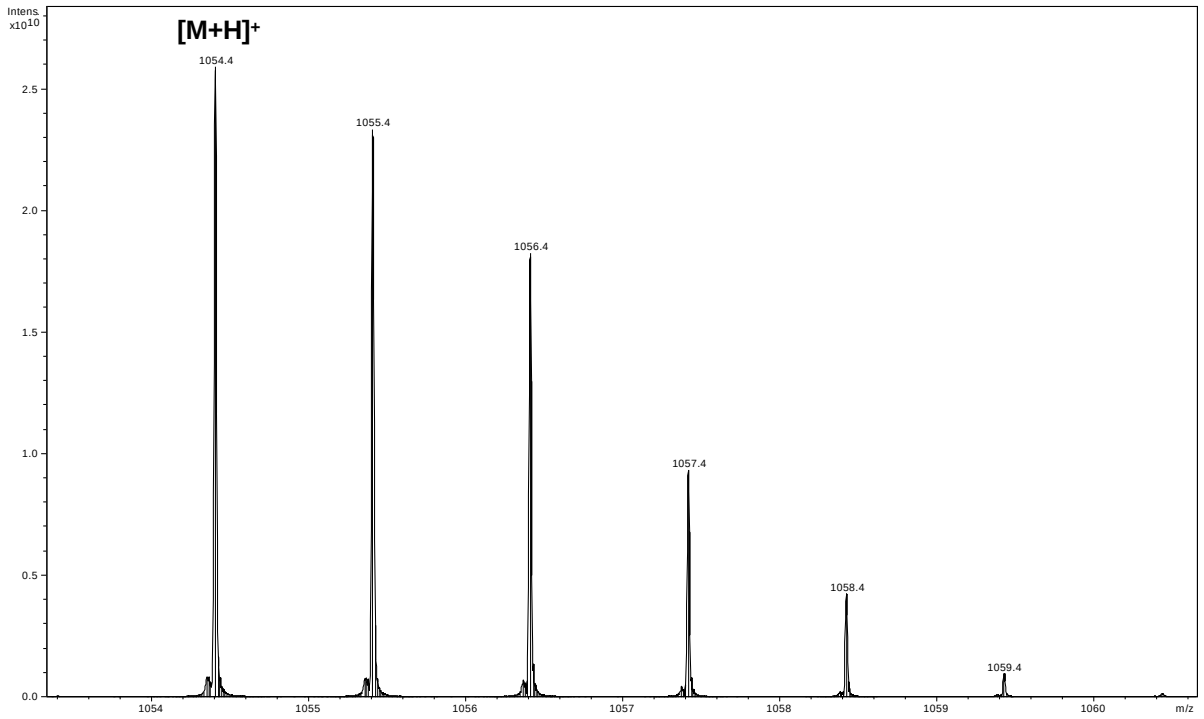

Figure S38. HR-MS (ESI+, TOF, $CHCl_3$) spectrum of **8**.

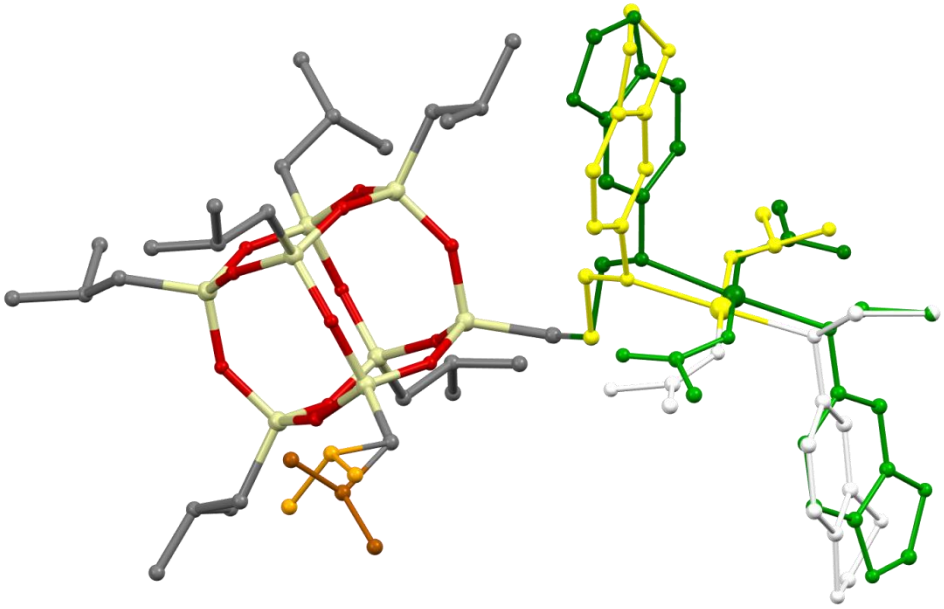

Figure S39. The asymmetric unit of **10** crystal structure.

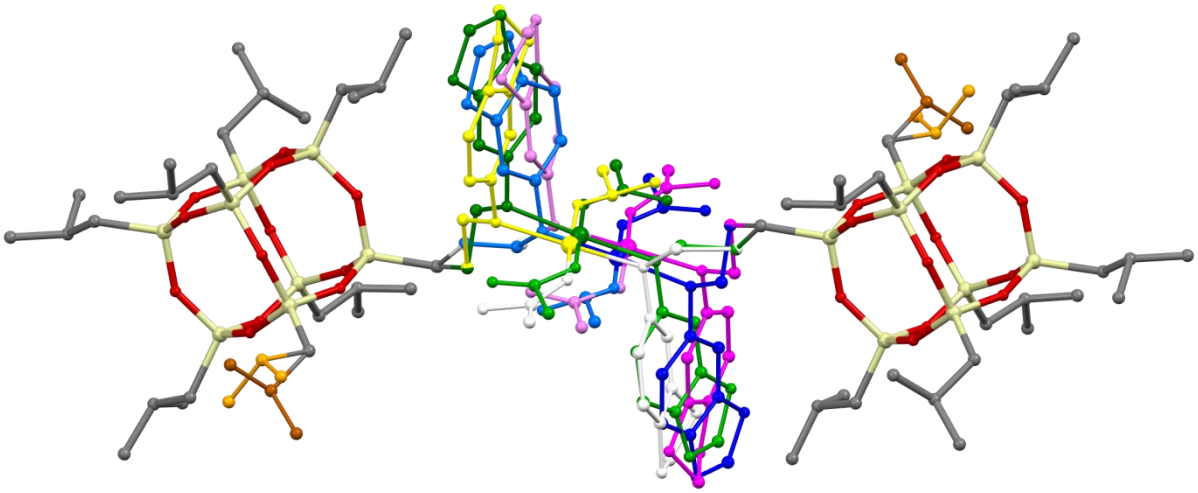

Figure S40. Structure disordering present in **10**.