Supporting Information

for

Metal-free functionalization of sulfur-functionalized SQs: a case of chemoselectivity and what ball-milling has got to do with it?

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CONTENTS:

1. General considerations

1.1. General methods and reagents

All reagents, except NHC carbene precursor, were commercially available and used as received. NHC salts were prepared according to literature procedures.[1] All syntheses and catalytic tests were carried out under argon atmosphere using standard Schlenk-line and vacuum techniques. THF was dried over sodium benzophenone ketyl and freshly distilled before use. The other solvents were dried over CaH_2 prior to use and stored over 4Å molecular sieves under argon. Dichloromethane was additionally passed through an alumina column and degassed by repeated freeze-pump-thaw cycles.

1.2. Instruments and measurements

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H NMR (402.6 MHz), ^{13}C NMR (101.2 MHz) and ^{29}Si NMR (79 MHz) spectra were recorded at 25̊C on a Varian 400 and 300 MHz spectrometers in CDCl3 solution. Chemical shifts are reported in ppm with reference to the residual solvent peaks for 1H and 13C NMR and to TMS for ^{29}Si NMR.

Thin-layer chromatography (TLC): TLC was conducted on plates coated with 250 µm thick silica gel and column chromatography was performed on silica gel 60 (70-230 mesh) using a mixture of n-hexane or n-heptane/DCM.

Electrospray Ionisation Mass Spectrometry (ESI-MS): Mass spectra were obtained using Synapt Gs-S HDMS (Waters) mass spectrometer with Electrospray ion source and quadrupole-Time-of-flight analyzer with resolving power FWMH 38000. Acetonitrile was utilised as the sample solvent. The Capillary Voltage was set to 4.5 kV, the sampling was set 40 and the source temperature was equal to 120oC. The most abundant ions in ESI-MS spectras were sodiated and potassiated ions of desired products.

Ball milling methods: Solid-state syntheses and tests were carried out by using Retsch MM400 mixer mill (stainless steel milling jars, V = 10, 50 mL; stainless steel milling balls, ϕ = 2 and 7 mm). After each reaction, milling jars were rinsed with small volumes of THF and acetone, was hed with detergent and water by using a sponge, and rinsed again with small amount of acetone. Jars were pre-dried by wiping with a paper towel and then dried in an oven at 50°C for 1 h.

2. Additional optimization tests

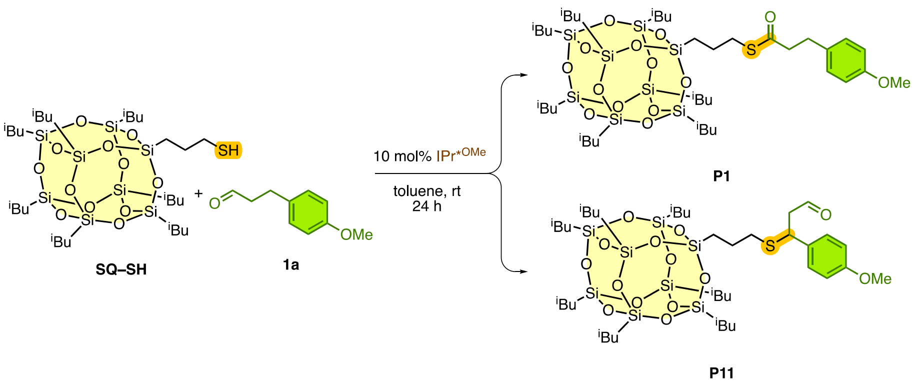


Table S1. Additional optimization tests in solution.

Entry	NHC	[NHC] [%mol]	[SQ-SH]:[1a]	Conv. of SQ-SH[c] [%]	P1:P11[c] [%]
1		10	1:1	70	100:0
2		10	1:1.5	80	100:0
3		**10**	**1:2**	**95**	**100:0**
4	IPr*OMe	7.5	1:2	90	92:8
5		5	1:2	75	80:20
6[a]		-	1:2	2	-
7[b]		10	1:2	45	51:49
8	IMes	7.5	1:1	90	93:7
9		5	1:1	70	85:15

Reaction condition: 0.075 M, Toluene, 60 ^{o}C, 24 h, argon
[a] 96h
[b] Air atmosphere
[c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture

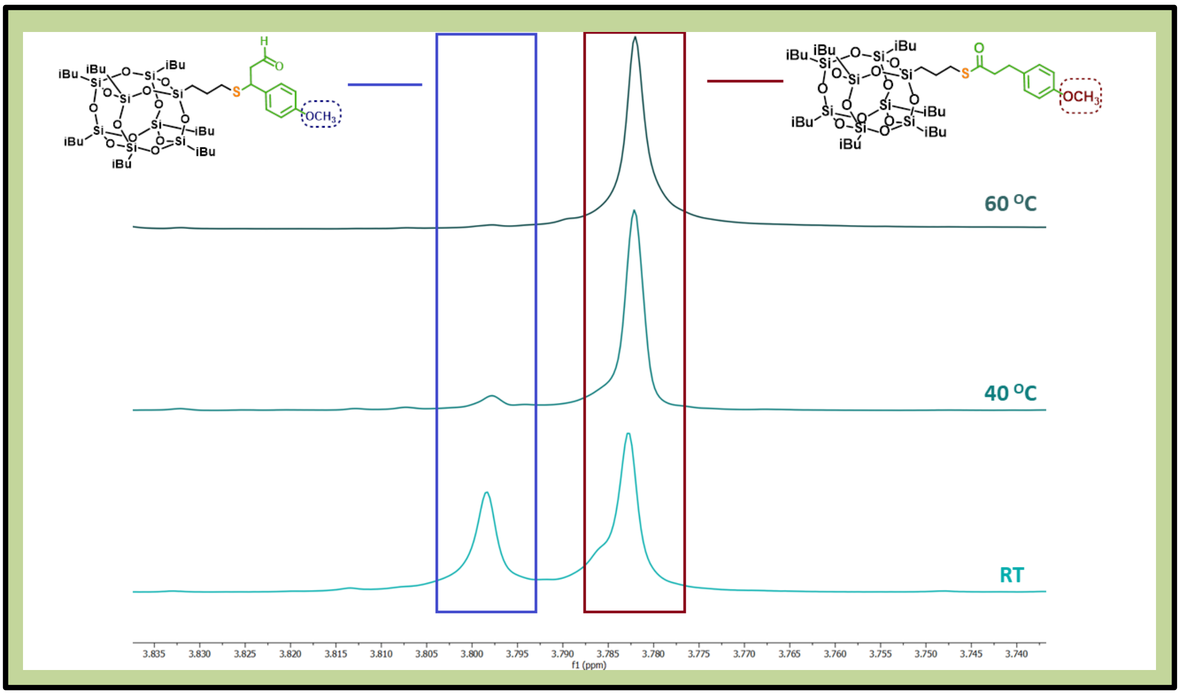


Figure S1. Influence of temperature on process selectivity conducting in solution

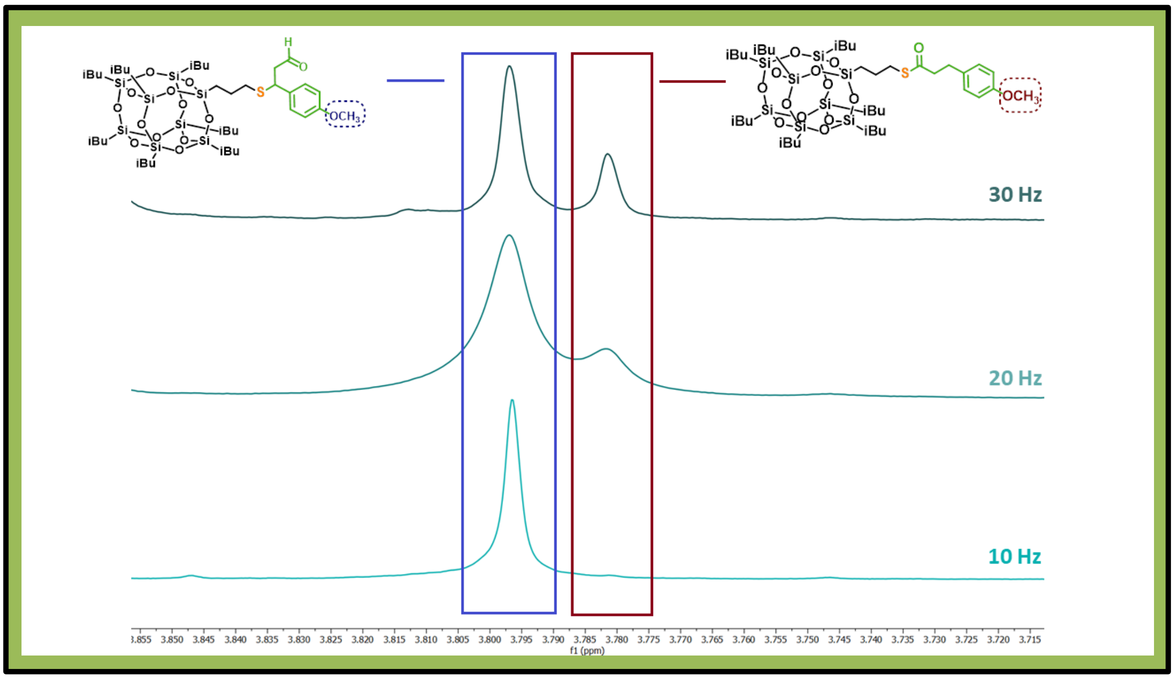


Figure S2. Influence of frequency on process selectivity conducting in solid-sate

3. General procedures for the synthesis of functionalized SQ derivatives

3.1. Procedure for generating free NHC carbene

A flame-dried glass reactor equipped with stirring bar and connected to gas and vacuum line was charged with NHC carbene precursor (11.0 mg, 1.12×10^{-5} mol, 1 equiv.), KHMDS (2.68 mg, 1.34×10^{-5} mol, 1.1 equiv.) and toluene (1.0 mL). After 30 minutes of vigorous stirring at RT the reaction mixture was filtrated under argon into the other flame-dried glass reactor equipped with magnetic stirring bar and connected to gas and vacuum line. The solvent was evaporated and the isolated carbene was washed with *n*-hexane and dried.

3.2. Approach A: Reactions in solution

A) Pathway based on isolated NHC carbene

A flame-dried glass reactor equipped with a magnetic stirring bar was charged with NHC carbene (10.59 mg, 1.12×10^{-5} mol) in the glovebox. Then mercaptopropylisobutyl-POSS (100 mg, 1.12×10^{-4} mol), α,β-unsaturated aldehyde (2.24×10^{-4} mol) and toluene (1.0 mL) were added under argon. The reaction mixture was stirred at 60°C for 24 h. The solvent was evaporated under vacuum and the residue was preliminarily separated from impurities by precipitation with methanol. The alcohol was evaporated under vacuum and the obtained residue was purified by column chromatography on silica gel using 3:1 v/v mixture of *n*-hexane and dichloromethane as eluent. Evaporation of the solvents afforded analytically pure compounds.

B) Pathway based on NHC carbene generated *in situ*

A flame-dried glass reactor equipped with a magnetic stirring bar and connected to gas and vacuum line was charged with NHC carbene precursor (11.0 mg, 1.12×10^{-5} mol), KHMDS (2.68 mg, 1.34×10^{-5} mol) and toluene (1.0 mL) under argon. After 30 minutes of vigorous stirring at RT mercaptopropylisobutyl-POSS (100 mg, 1.12×10^{-4} mol) and α,β-unsaturated aldehyde (2.24×10^{-4} mol) were added. The reaction mixture was then stirred at 60°C for 24 h. The solvent was evaporated under vacuum and the residue was preliminarily separated from the impurities by precipitation with methanol. The alcohol was evaporated under vacuum and the obtained residue was purified by column chromatography on silica gel using 3:1 v/v mixture of *n*-hexane and dichloromethane as eluent. Evaporation of the solvents afforded analytically pure compounds.

3.3. Approach B: Solid-state synthesis

A) Pathway based on isolated NHC carbene

A 10 mL stainless steel milling jar was charged with (3-Mercapto)propyl-heptaisobutyl POSS (100 mg, 1.12×10^{-4} mol), aldehyde (2.24×10^{-4} mol), freshly isolated NHC carbene (2.24×10^{-5} mol) and one stainless steel ball (*Φ* = 2 mm) under inert gas atmosphere in the glove-box. The powders were ball milled for 2 hours at 10 Hz. The solids were dissolved in dichloromethane (5 mL), transferred to the Schlenk vessel and evaporated under vacuum. The residue was washed with methanol and purified by column chromatography on silica gel using 3:1 or 3:2 v/v mixture of *n*-hexane and dichloromethane as eluent. Evaporation of the solvents afforded analytically pure compounds.

B) Pathway based on NHC carbene generated *in situ*

A 10 mL stainless steel milling jar was charged with (3-Mercapto)propyl-heptaisobutyl POSS (100 mg, 1.12×10^{-4} mol), aldehyde (2.24×10^{-4} mol), NHC carbene precursor (2.24×10^{-5} mol), KHMDS (5.36 mg, 2.69×10^{-5} mol) and one stainless steel ball (*Φ* = 5 mm). The powders were ball milled for 2 hours at 10 Hz. The solids were dissolved in dichloromethane (5 mL), transferred to the Schlenk vessel and evaporated under vacuum. The residue was washed with methanol and purified by column chromatography on silica gel using 3:1 or 3:2 v/v mixture of *n*-hexane and dichloromethane as eluent. Evaporation of the solvents afforded analytically pure compounds.

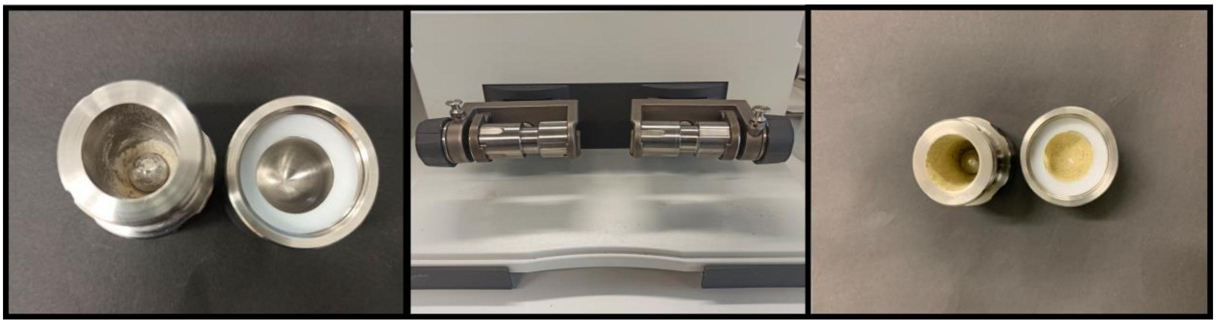
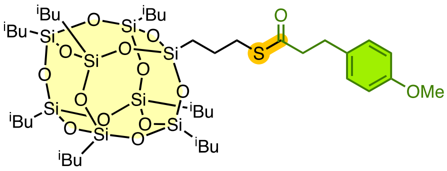


Figure S3. Reaction sequence for the solid-state synthesis of product P1

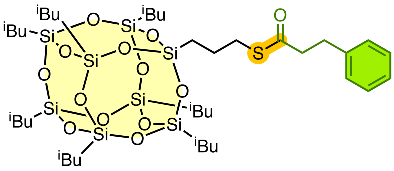
4. Analytical data of isolated products P1-P16

Product P1:



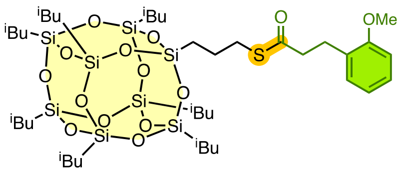
White solid, isolated yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.62 (m, 14H, CH_2), 0.66 – 0.70 (m, 2H, CH_2), 0.93 – 0.97 (m, 42H, CH_3), 1.64 – 1.69 (m, 2H, CH_2), 1.80 – 1.89 (m, 7H, CH), 2.79 – 2.83 (m, 2H, CH_2), 2.88 – 2.93 (m, 4H, CH_2CH_2CO), 3.78 (s, 3H, OCH_3), 6.83 (d, 2H, J_{HH} = 8.7 Hz, C_6H_4-OCH_3), 7.10 (d, 2H, J_{HH} = 8.7 Hz, C_6H_4-OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.58 (CH_2), 22.39 (CH_2), 22.46 (CH_2), 23.15 (CH_2), 23.83 (CH), 23.86 (CH), 25.66 (CH_3), 25.67 (CH_3), 31.63 (CH_2), 31.66 (CH_2), 45.91 (CH_2), 55.22 (OCH_3), 113.88, 129.22, 132.20, 158.05, 198.55 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -68.15, -67.84, -67.58; MS (ESI+): m/z: 1091 $[M + K]^+$.

Product P2:



White solid, isolated yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.63 (m, 14H, CH_2), 0.65 – 0.70 (m, 2H, CH_2), 0.90 – 1.00 (m, 42H, CH_3), 1.63 – 1.70 (m, 2H, CH_2), 1.80 – 1.90 (m, 7H, CH), 2.82 – 2.92 (m, 4H, CH_2), 2.94 – 3.00 (m, 2H, CH_2), 7.16 – 7.23 (m, 3H, C_6H_5), 7.26-7.31 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.55 (CH_2), 22.39 (CH_2), 22.46 (CH_2), 23.15 (CH_2), 23.82 (CH), 23.85 (CH), 25.66 (CH_3), 31.49 (CH_2), 31.64 (CH_2), 45.56 (CH_2), 126.27, 128.27, 128.48, 140.12, 198.42 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.66, -67.91, -68.17; MS (ESI+): m/z: 1061 $[M + K]^+$.

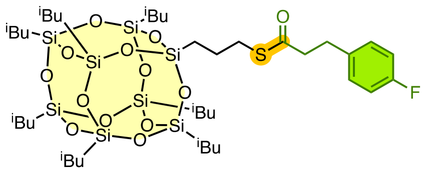
Product P3:



White solid, isolated yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.58 – 0.62 (m, 14H, CH_2), 0.66 – 0.70 (m, 2H, CH_2), 0.94 – 0.98 (m, 42H, CH_3), 1.63 – 1.69 (m, 2H, CH_2), 1.82 – 1.89 (m, 7H, CH), 2.81 – 2.91 (m, 4H, CH_2CH_2CO), 2.94 – 2.99 (m, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.83 – 6.89 (m, 2H, C_6H_4-OCH_3), 7.11 – 7.14 (m, 1H, C_6H_4-OCH_3), 7.17 – 7.22 (m, 1H, C_6H_4-OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.59 (CH_2), 22.40 (CH_2), 22.47 (CH_2), 23.20 (CH_2), 23.83 (CH), 23.87 (CH), 25.67 (CH_3), 25.68 (CH_3), 26.70 (CH_2), 31.58 (CH_2), 43.88 (CH_2), 55.15

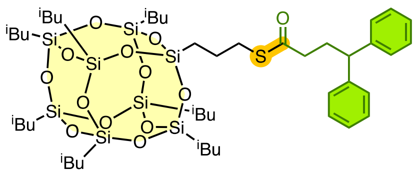
(OCH_3), 110.15, 120.39, 127.62, 128.45, 129.94, 157.41, 198.92 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -68.10, -67.89, -67.62; MS (ESI+): m/z: 1075 [M + Na]$^+$.

Product P4:



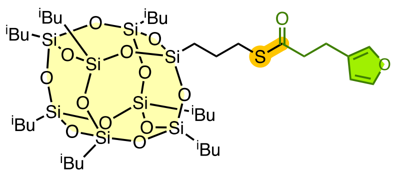
White solid, isolated yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.63 (m, 14H, CH_2), 0.65 – 0.70 (m, 2H, CH_2), 0.92 – 1.00 (m, 42H, CH_3), 1.62 – 1.69 (m, 2H, CH_2), 1.80 – 1.89 (m, 7H, CH), 2.79 – 2.85 (m, 2H, CH_2), 2.87 – 2.98 (m, 4H, CH_2CH_2CO), 6.94 – 6.99 (m, 2H, C_6H_4-F), 7.10 – 7.17 (m, 2H, C_6H_4-F); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.56 (CH_2), 22.40 (CH_2), 22.47 (CH_2), 23.16 (CH_2), 23.83 (CH), 23.87 (CH), 25.66 (CH_3), 25.68 (CH_3), 30.67 (CH_2), 31.66 (CH_2), 45.59 (CH_2), 115.15, 115.37, 129.71 (d, J = 7.9 Hz), 135.73 (d, J = 3.3 Hz), 161.47 (d, J = 244.42 Hz), 198.26 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.05, -67.31, -67.62; MS (ESI+): m/z: 1079 [M + K]$^+$.

Product P5:



White solid, isolated yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.54 – 0.67 (m, 16H, CH_2), 0.82 – 1.06 (m, 42H, CH_3), 1.54 – 1.60 (m, 2H, CH_2), 1.79 – 1.91 (m, 7H, CH), 2.82 (t, 2H, J_{HH} = 7.2 Hz, CH_2), 3.29 (d, 2H, J_{HH} = 7.8 Hz, CH_2), 4.64 (t, 1H, J_{HH} = 7.8 Hz, CH), 7.16 – 7.24 (m, 6H, C_6H_5), 7.26 – 7.32 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.41 (CH_2), 22.40 (CH_2), 22.47 (CH_2), 22.99 (CH_2), 23.83 (CH), 23.86 (CH), 25.67 (CH_3), 25.68 (CH_3), 31.62 (CH_2), 47.19 (CH_2), 49.88 (CH), 126.53, 127.72, 128.51, 143.10, 197.36 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.65, -67.90, -68.15; MS (ESI+): m/z: 1137 [M + K]$^+$.

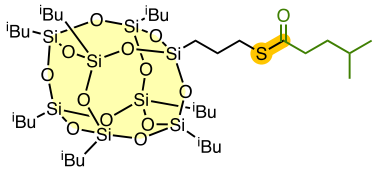
Product P6:



White solid, isolated yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.63 (m, 14H, CH_2), 0.65 – 0.70 (m, 2H, CH_2), 0.92 – 0.99 (m, 42H, CH_3), 1.62 – 1.70 (m, 2H, CH_2), 1.80 – 1.89 (m, 7H, CH), 2.85 – 2.92 (m, 2H, CH_2), 2.96 – 3.01 (m, 4H, CH_2CH_2CO), 6.02 (dd, 1H, J_{HH} = 3.2, 0.9 Hz, CH from furan), 6.27 (dd, 1H, J_{HH} = 3.2, 0.9 Hz, CH from furan), 7.30 (dd, 1H, J_{HH} = 1.9, 0.8 Hz, CH from furan); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.56 (CH_2), 22.42 (CH_2), 22.48 (CH_2), 23.15 (CH_2), 23.83 (CH), 23.87 (CH), 25.66 (CH_3), 25.68 (CH_3), 31.66 (CH_2), 42.18

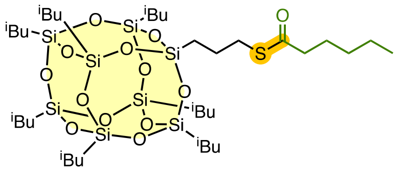
(CH_2), 105.48, 110.17, 141.25, 153.70, 197.95 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.63, -67.88, -68.14; MS (ESI+): m/z: 1051 $[M + K]^+$.

Product P7:



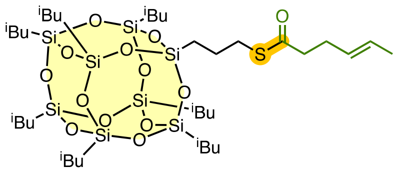
White solid, isolated yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.58 – 0.61 (m, 14H, CH_2), 0.66 – 0.71 (m, 2H, CH_2), 0.93 – 0.97 (m, 48H, CH_3), 1.62 – 1.69 (m, 2H, CH_2), 1.81 – 1.87 (m, 7H, CH), 2.12 – 2.19 (m, 1H, CH), 2.42 (d, 2H, J_{HH} = 7.2 Hz, CH_2), 2.69 – 2.75 (m, 1H, CH), 2.88 (t, 2H, J_{HH} = 7.2 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.59 (CH_2), 22.27 (CH_2), 22.39 (CH_2), 22.47 (CH_2), 23.29 (CH_3), 23.83 (CH), 23.86 (CH), 25.65 (CH_3), 25.68 (CH_3), 26.46 (CH_3), 31.59 (CH_2), 52.93 (CH), 198.86 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.55, -67.81, -68.12; MS (ESI+): m/z: 1013 $[M + K]^+$.

Product P8:



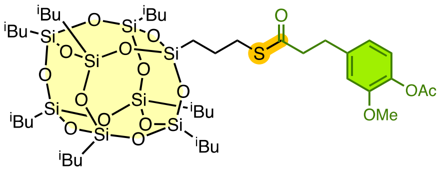
White solid, isolated yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.56 – 0.63 (m, 14H, CH_2), 0.65– 0.71 (m, 2H, CH_2), 0.87 – 0.91 (m, 3H, CH_3), 0.93– 0.99 (m, 42H, CH_3), 1.29 – 1.33 (m, 2H, CH_2), 1.56 – 1.72 (m, 4H, CH_2), 1.75 – 1.95 (m, 9H, CH and CH_2), 2.49 – 2.57 (m, 2H, CH_2), 2.80 – 2.94 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.57 (CH_2), 13.87 (CH_3), 22.31 (CH_2), 22.39 (CH_2), 22.42 (CH_2), 22.46 (CH_2), 23.23 (CH_2), 23.83 (CH), 23.86 (CH), 25.38 (CH_2), 25.68 (CH_3), 31.10 (CH_2), 31.55 (CH_2), 44.11 (CH_2), 199.52 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.64, -67.90, -68.12; MS (ESI+): m/z: 1029 $[M + K]^+$.

Product P9:



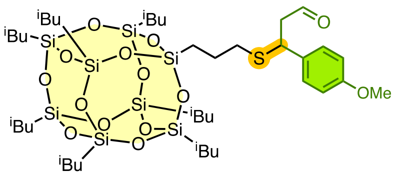
White solid, isolated yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.53 – 0.64 (m, 14H, CH_2), 0.65 – 0.70 (m, 2H, CH_2), 0.86– 1.00 (m, 42H, CH_3), 1.57 – 1.72 (m, 5H, CH_2 and CH_3), 1.79 – 1.89 (m, 7H, CH), 2.29 – 2.42 (m, 2H, CH_2), 2.53 – 2.63 (m, 2H, CH_2), 2.85 – 2.93 (m, 2H, CH_2CO), 5.34 – 5.50 (m, 2H, HC=CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.54 (CH_2), 17.88 (CH_3) 22.38 (CH_2), 22.45 (CH_2), 23.20 (CH_2), 23.83 (CH), 23.86 (CH), 25.66 (CH_2), 25.68 (CH_3), 28.54 (CH_3), 31.57 (CH_2), 43.95 (CH_2), 126.41, 128.72, 198.87 (CO); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.61, -67.86, -68.11; MS (ESI+): m/z: 1025 $[M + K]^+$.

Product P10:



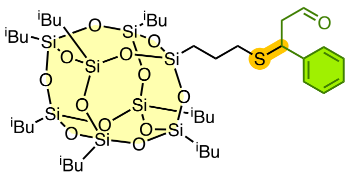
White solid, isolated yield: 88%; ^{1}H NMR (400 MHz, CDCl$_3$, 296K): δ (ppm) 0.59 – 0.62 (m, 14H, CH_2), 0.67 – 0.71 (m, 2H, CH_2), 0.94 – 0.99 (m, 42H, CH_3), 1.64 – 1.70 (m, 2H, CH_2), 1.81 – 1.88 (m, 7H, CH), 2.30 (s, 3H, CH$_3$), 2.83 – 2.95 (m, 6H, CH_2), 3.81 (s, 3H, OCH_3), 6.74 – 6.79 (m, 2H, C$_6H_3$-), 6.94 (d, 1H, J_{HH} = 8.0 Hz, C$_6$H$_3$-); ^{13}C NMR (100 MHz, CDCl$_3$, 296K): δ (ppm) 11.59 (CH$_2$), 20.66 (CH$_3$), 22.39 (CH$_2$), 22.46 (CH$_2$), 23.16 (CH$_2$), 23.82 (CH), 23.86 (CH), 25.67 (CH$_3$), 25.68 (CH$_3$), 30.67 (CH$_2$), 31.66 (CH$_2$), 45.59 (CH$_2$), 31.36 (CH$_2$), 31.68 (CH$_2$), 45.51 (CH$_2$), 55.80 (OCH$_3$), 112.46, 120.33, 122.62, 139.14, 150.87, 169.17, 198.30 (CO); ^{29}Si NMR (79 MHz, CDCl$_3$, 296K): -67.62, -67.89, -68.19; MS (ESI+): m/z: 1149 $[M + K]^+$.

Product P11:



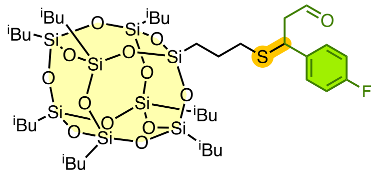
White solid, isolated yield: 70%; ^{1}H NMR (400 MHz, CDCl$_3$, 296K): δ (ppm) 0.58 – 0.61 (m, 14H, CH_2), 0.63 – 0.72 (m, 2H, CH_2), 0.94 – 0.98 (m, 42H, CH_3), 1.57 – 1.66 (m, 2H, CH_2), 1.80 – 1.88 (m, 7H, CH), 2.26 – 2.36 (m, 2H, CH_2), 2.89 – 2.93 (m, 2H, CH_2), 3.80 (s, 3H, OCH_3), 4.28 (t, 1H, J_{HH} = 7.5 Hz, SCH), 6.85 (d, 2H, J_{HH} = 8.7 Hz, C$_6H_4$-OCH$_3$), 7.26 (d, 2H, J_{HH} = 8.7 Hz, C$_6H_4$-OCH$_3$), 9.67 (t, 1H, J_{HH} = 2.0 Hz, CH); ^{13}C NMR (100 MHz, CDCl$_3$, 296K): δ (ppm) 11.70 (CH$_2$), 22.42 (CH$_2$), 22.46 (CH$_2$), 22.65 (CH$_2$), 23.83 (CH), 23.87 (CH), 25.68 (CH$_3$), 33.91 (CH$_2$), 42.28 (CH$_2$), 49.99 (CH$_2$), 55.22 (OCH$_3$), 114.01, 128.67, 133.05, 158.83, 199.66 (CO); ^{29}Si NMR (79 MHz, CDCl$_3$, 296K): δ (ppm) -67.88, -68.14, -68.45; MS (ESI+): m/z: 1091 $[M + K]^+$.

Product P12:



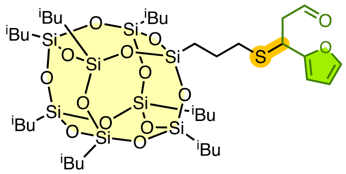
White solid, isolated yield: 71%; ^{1}H NMR (400 MHz, CDCl$_3$, 296K): δ (ppm) 0.58 – 0.60 (m, 14H, CH_2), 0.63 – 0.71 (m, 2H, CH_2), 0.94 – 0.96 (m, 42H, CH_3), 1.55 – 1.65 (m, 2H, CH_2), 1.81 – 1.86 (m, 7H, CH), 2.26 – 2.38 (m, 2H, CH_2), 2.92 – 2.96 (m, 2H, CH_2), 4.31 (t, 1H, J_{HH} = 7.5 Hz, SCH), 7.30 – 7.35 (m, 5H, C$_6H_5$), 9.69 (t, 1H, J_{HH} = 1.8 Hz, CH); ^{13}C NMR (100 MHz, CDCl$_3$, 296K): δ (ppm) 11.69 (CH$_2$), 22.44 (CH$_2$), 22.48 (CH$_2$), 22.69 (CH$_2$), 23.83 (CH), 23.88 (CH), 25.67 (CH$_3$), 25.68 (CH$_3$), 34.00 (CH$_2$), 42.98 (CH$_2$), 49.85 (CH$_2$), 127.52, 127.61, 128.69, 141.24, 199.39 (CO); ^{29}Si NMR (79 MHz, CDCl$_3$, 296K): δ (ppm) -67.68, -67.90, -68.12; MS (ESI+): m/z: 1061 $[M + K]^+$.

Product P13:



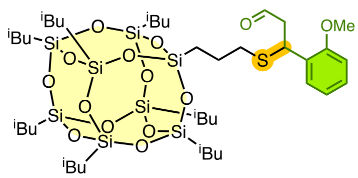
White solid, isolated yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.60 (m, 14H, CH_2), 0.64 – 0.69 (m, 2H, CH_2), 0.94 – 0.97 (m, 42H, CH_3), 1.57 – 1.64 (m, 2H, CH_2), 1.81 – 1.87 (m, 7H, C*H*), 2.26 – 2.36 (m, 2H, CH_2), 2.89 – 2.95 (m, 2H, CH_2), 4.31 (t, 1H, J_{HH} = 7.5 Hz, SC*H*), 6.99 – 7.03 (m, 2H, C_6H_4-F), 7.29 – 7.34 (m, 2H, C_6H_4-F), 9.68 (t, 1H, J_{HH} = 1.7 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.69 (*C*H_2), 22.44 (*C*H_2), 22.48 (*C*H_2), 22.68 (*C*H_2), 23.83 (*C*H), 23.88 (*C*H), 25.68 (br s, *C*H_3), 29.74 (*C*H), 34.00 (*C*H_2), 42.17 (*C*H_2), 50.06 (*C*H_2), 115.56 (d, *J* = 21.6 Hz), 129.19 (d, *J* = 8.3 Hz), 137.09 (d, *J* = 3.6 Hz), 161.93 (d, *J* = 246.40 Hz), 199.04 (*C*O); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.68, -67.94, -68.24; MS (ESI+): m/z: 1079 $[M + K]^+$.

Product P14:



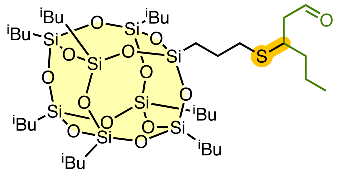
White solid, isolated yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.62 (m, 14H, CH_2), 0.64 – 0.70 (m, 2H, CH_2), 0.94 – 0.97 (m, 42H, CH_3), 1.59 – 1.70 (m, 2H, CH_2), 1.81 – 1.89 (m, 7H, C*H*), 2.42 – 2.51 (m, 2H, CH_2), 2.93 (ddd, 1H, J_{HH} = 17.3, 7.1, 1.9 Hz, CH_2), 3.07 (ddd, 1H, J_{HH} = 17.3, 7.6, 1.5 Hz, CH_2), 4.39 (t, 1H, J_{HH} = 7.5 Hz, SC*H*), 6.19 (d, 1H, J_{HH} = 3.2 Hz, C*H* from furan), 6.30 (dd, 1H, J_{HH} = 3.2, 1.9 Hz, C*H* from furan), 7.36 (dd, 1H, J_{HH} = 1.9, 0.8 Hz, C*H* from furan), 9.74 (t, 1H, J_{HH} = 1.7 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.71 (*C*H_2), 22.41 (*C*H_2), 22.45 (*C*H_2), 22.86 (*C*H_2), 23.82 (*C*H), 23.86 (*C*H), 25.66 (*C*H_3), 33.96 (*C*H_2), 35.78 (*C*H), 46.90 (*C*H_2), 107.08, 110.26, 142.21, 153.13, 199.00 (*C*O); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.64, -67.88, -68.13; MS (ESI+): m/z: 1051 $[M + K]^+$.

Product P15:



White solid, isolated yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 – 0.61 (m, 14H, CH_2), 0.63 – 0.69 (m, 2H, CH_2), 0.93 – 0.97 (m, 42H, CH_3), 1.60 – 1.67 (m, 2H, CH_2), 1.80 – 1.88 (m, 7H, C*H*), 2.36 – 2.44 (m, 2H, CH_2), 2.86 – 2.91 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.80 (t, 1H, J_{HH} = 7.6 Hz, SC*H*), 6.86 – 6.89 (m, 1H, C_6H_4-OCH_3), 6.94 – 6.98 (m, 1H, C_6H_4-OCH_3), 7.21 – 7.25 (m, 1H, C_6H_4-OCH_3), 7.42 – 7.49 (m, 1H, C_6H_4-OCH_3), 9.68 (t, 1H, J_{HH} = 2.2 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.72 (*C*H_2), 22.42 (*C*H_2), 22.46 (*C*H_2), 22.83 (*C*H_2), 23.84 (*C*H), 23.87 (*C*H), 25.68 (*C*H_3), 34.38 (*C*H_2), 36.49 (*C*H), 42.28 (*C*H_2), 49.02 (*C*H_2), 55.44 (O*C*H_3), 110.66, 120.93, 128.30 (d, *J* = 21.7 Hz), 129.21, 156.62, 200.48 (*C*O); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.68, -67.93, -68.19; MS (ESI+): m/z: 1091 $[M + K]^+$.

Product P16:



White solid, isolated yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.53 – 0.61 (m, 14H, C*H_2*), 0.69– 0.72 (m, 2H, C*H_2*), 0.92– 0.98 (m, 45H, C*H_3*), 1.42 – 1.48 (m, 2H, C*H_2*), 1.56 – 1.59 (m, 2H, C*H_2*), 1.65 – 1.70 (m, 2H, C*H_2*), 1.83 – 1.87 (m, 7H, C*H*), 2.52 – 2.55 (m, 2H, C*H_2*), 2.60 – 2.66 (m, 2H, C*H_2*), 3.07 – 3.12 (m, 1H, SC*H*), 9.78 (t, 1H, J_{HH} = 2.1 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 11.81 (*C*H_2), 11.83 (*C*H_3), 20.01 (*C*H_2), 22.45 (*C*H_2), 22.48 (*C*H_2), 23.36 (*C*H_2), 23.84 (*C*H), 23.88 (*C*H), 25.67 (*C*H), 25.68 (*C*H_3), 28.54 (*C*H_3), 33.42 (*C*H_2), 37.50 (*C*H_2), 39.27 (*C*H_2), 48.83 (*C*H_2), 201.02 (*C*O); ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.65, -67.88, -68.04; MS (ESI+): m/z: 1059 $[M + K]^+$.

5. NMR spectra of isolated products P1-P16

Product P1

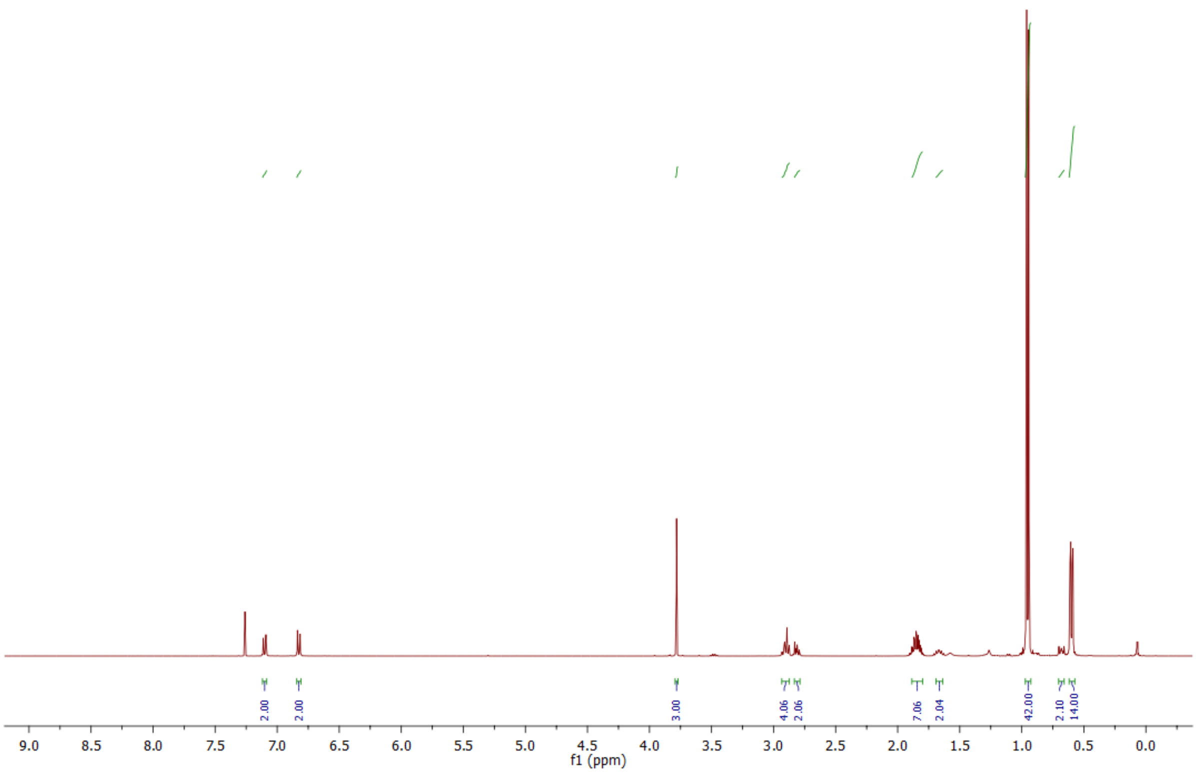


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P1**

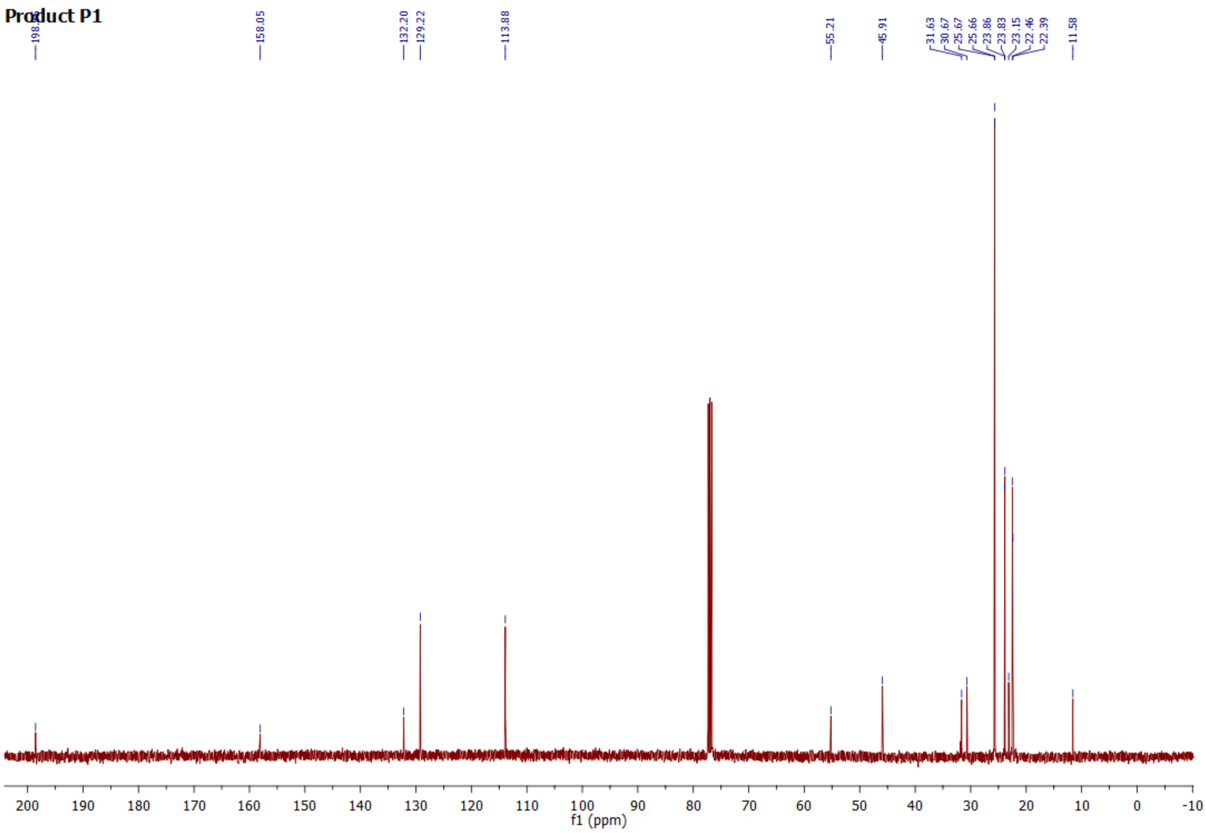


Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P1**

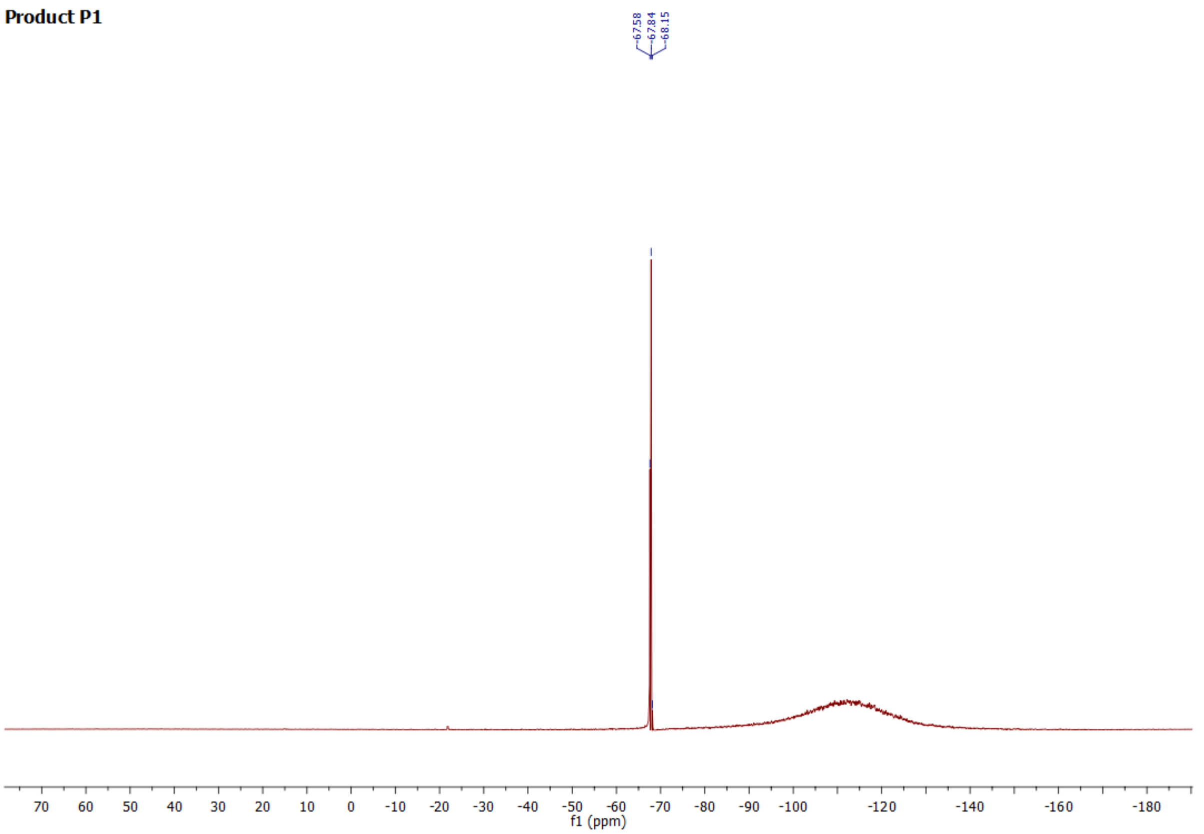


Figure S6. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P1**

Product P2

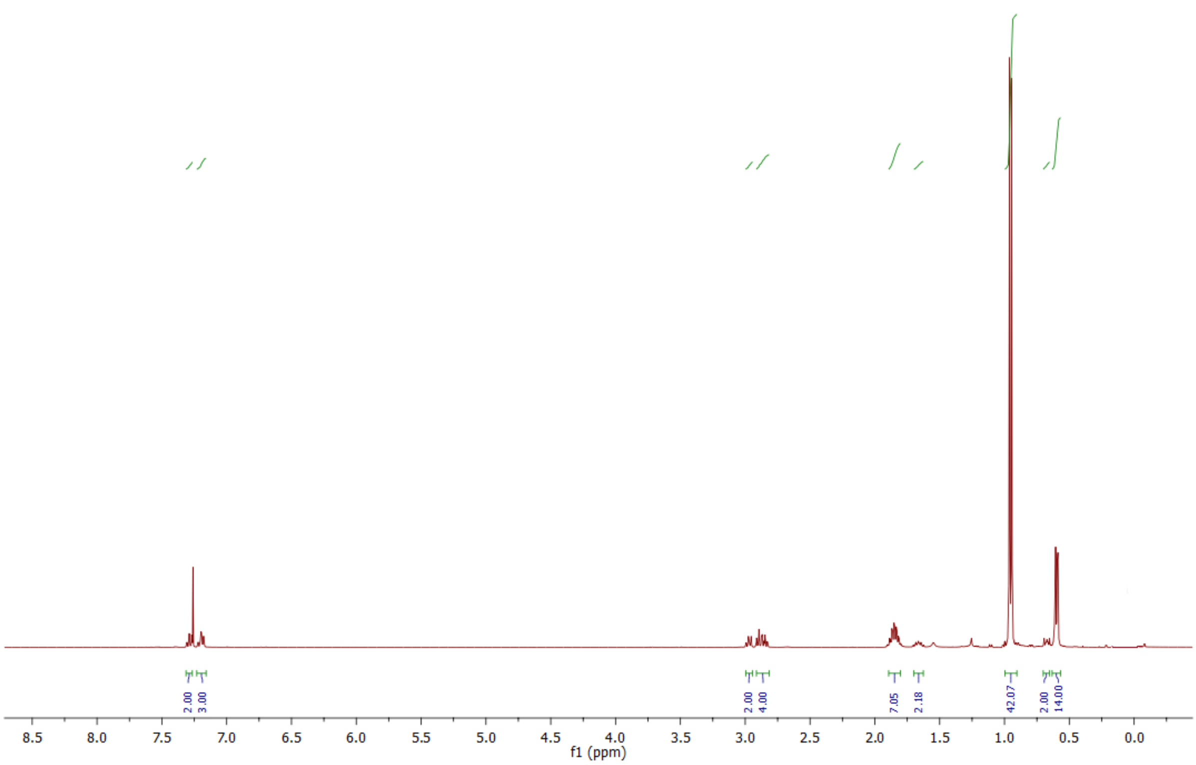


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P2**

Product P2

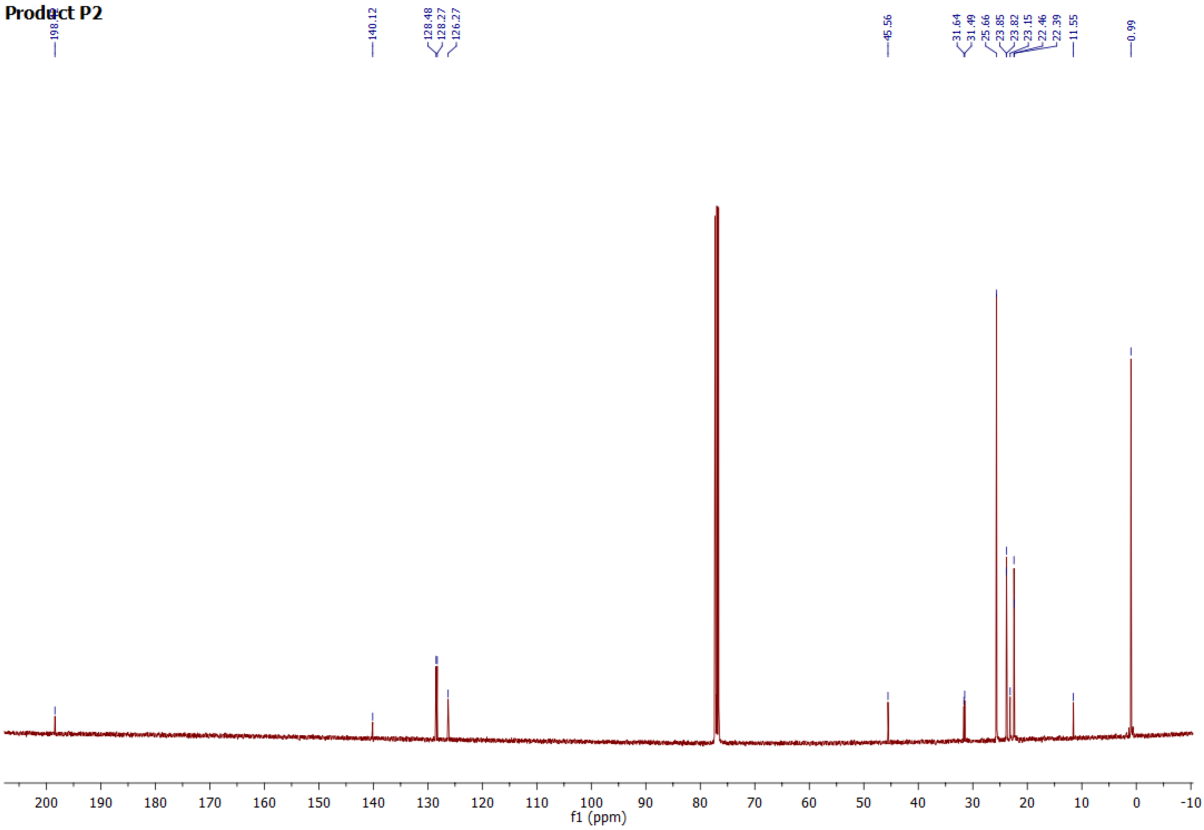


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P2**

Product P2

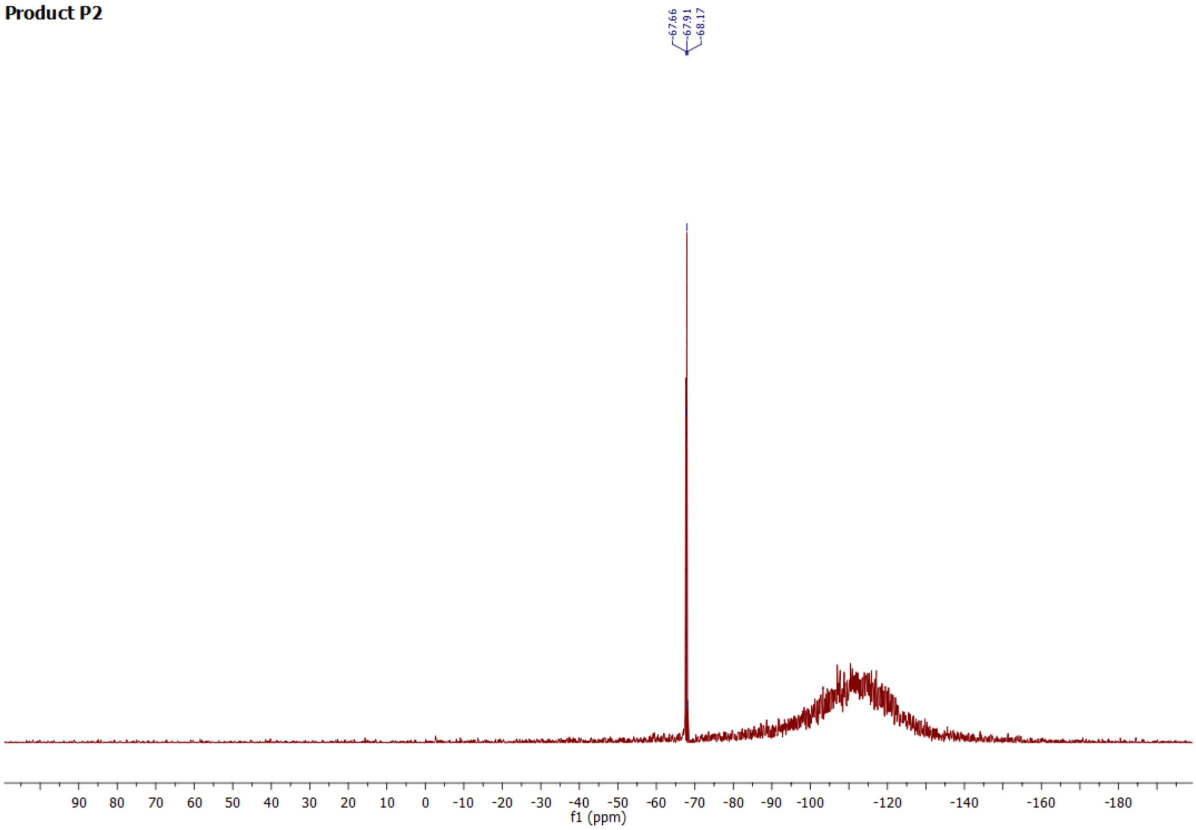


Figure S9. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P2**

Product P3

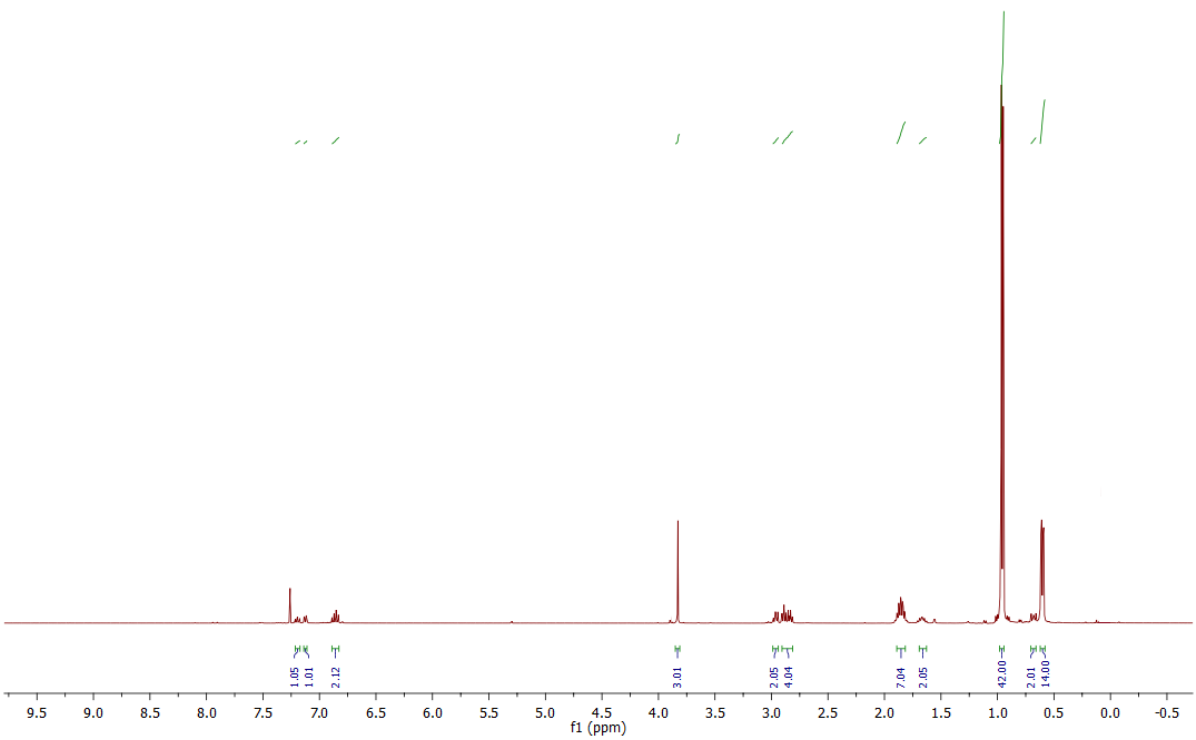


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P3**

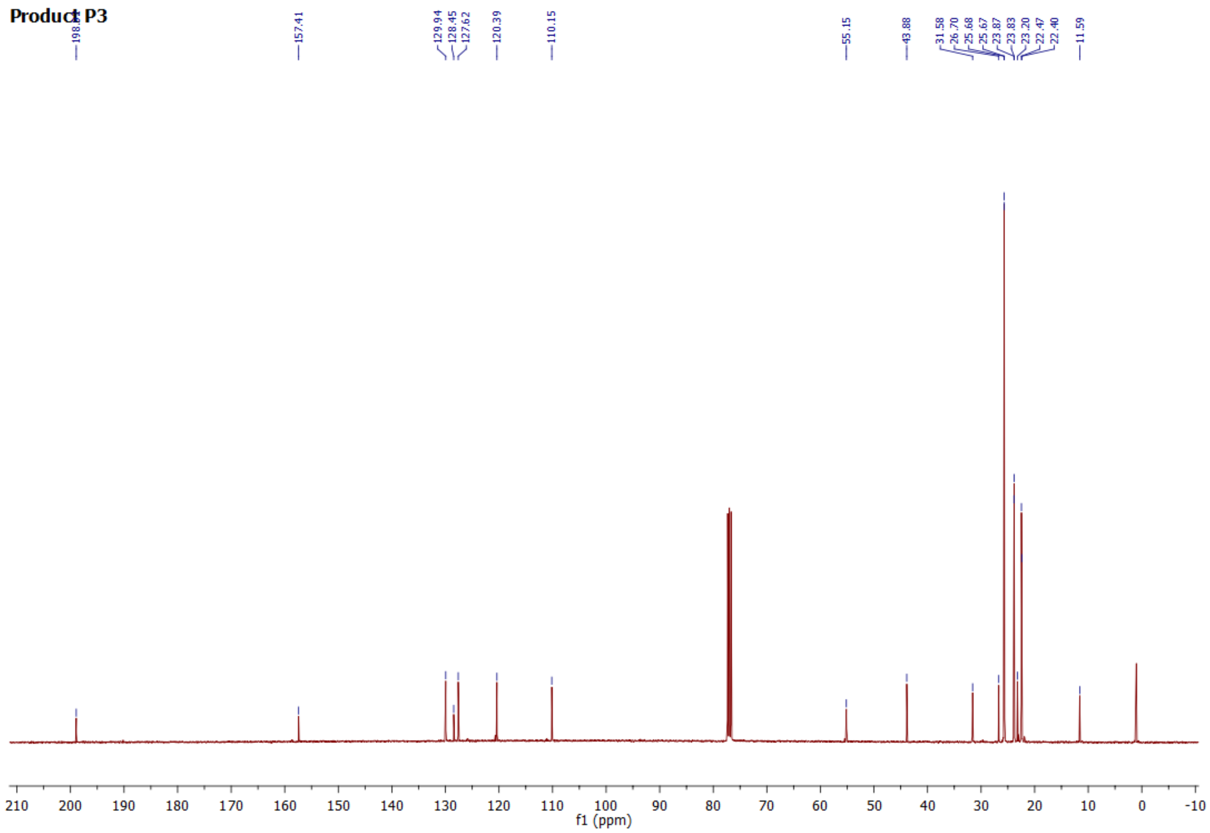


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P3**

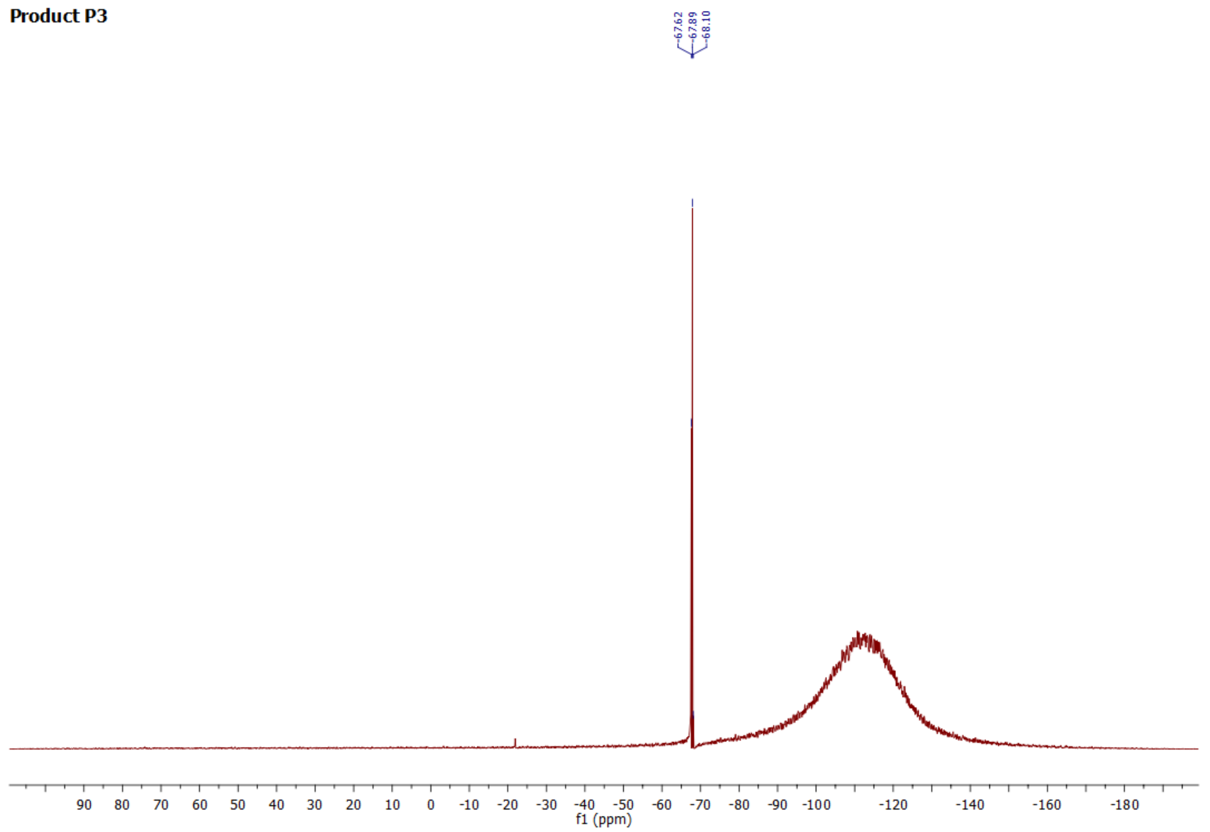


Figure S12. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P3**

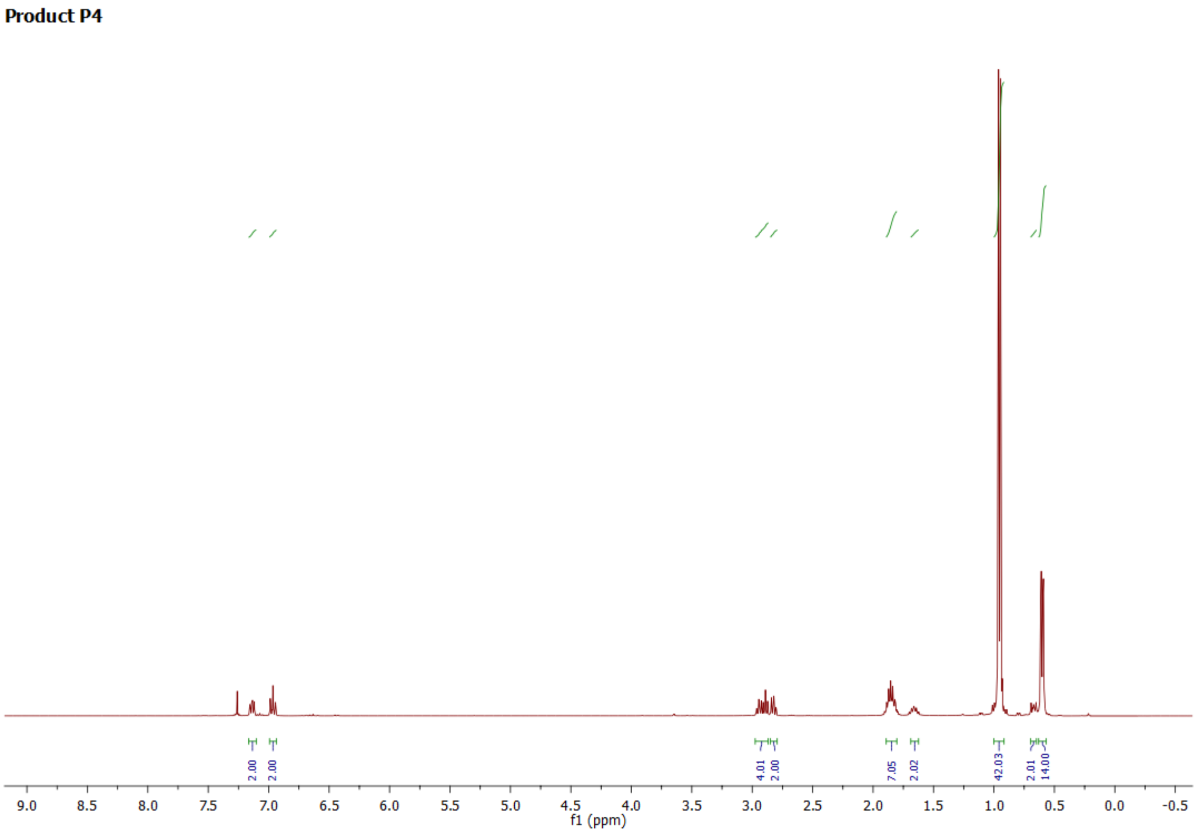


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P4**

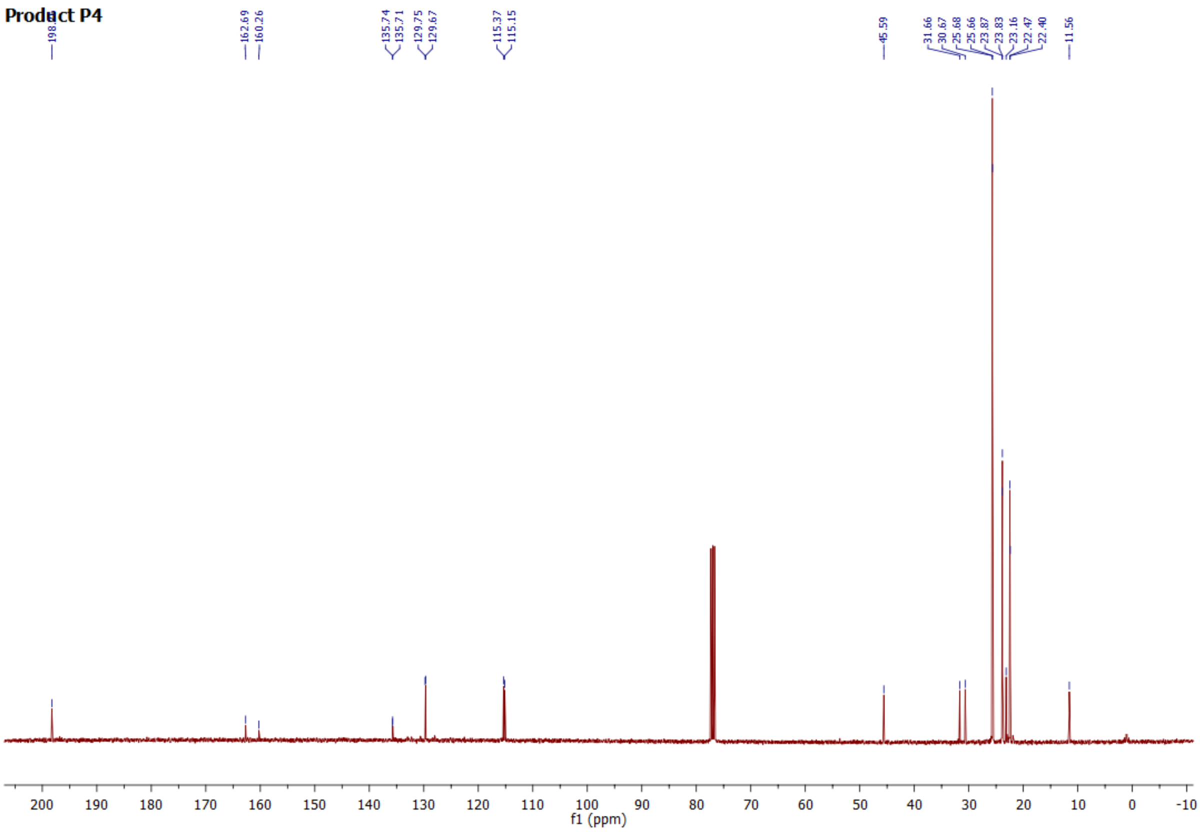


Figure S14. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P4**

Product P4

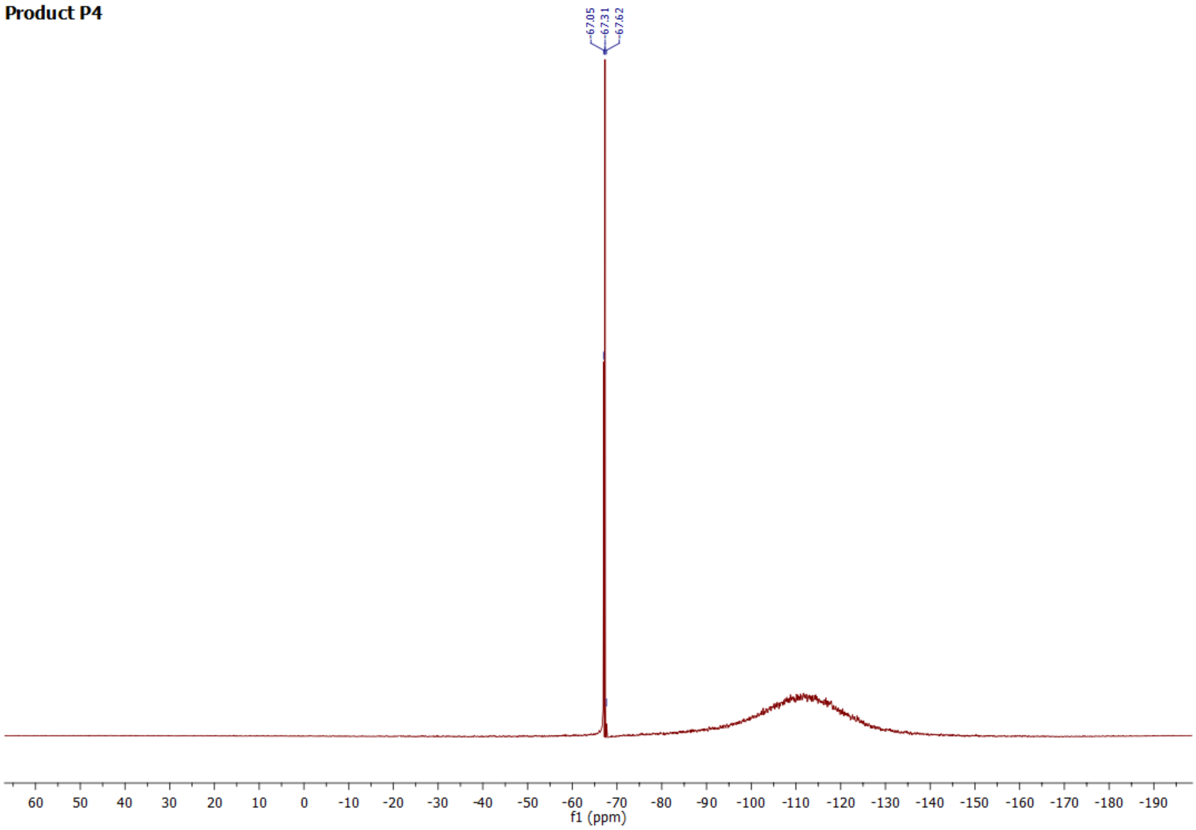


Figure S15. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P4**

Product P5

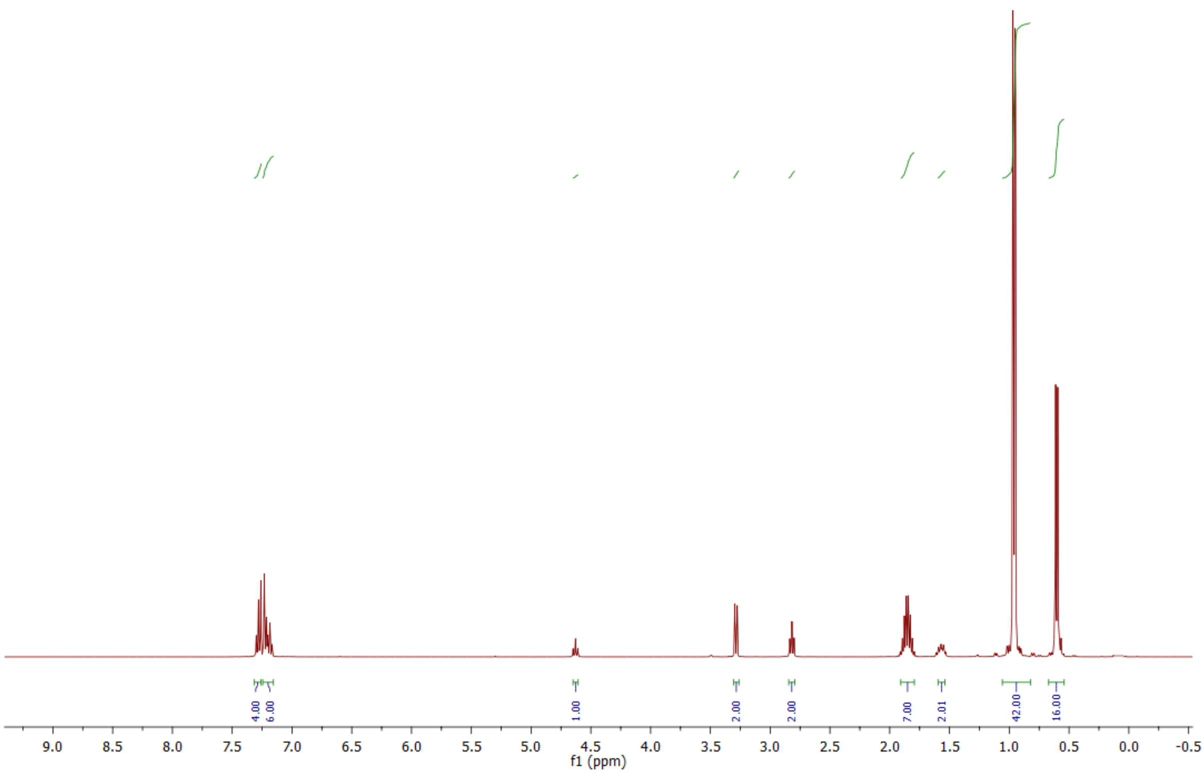


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P5**

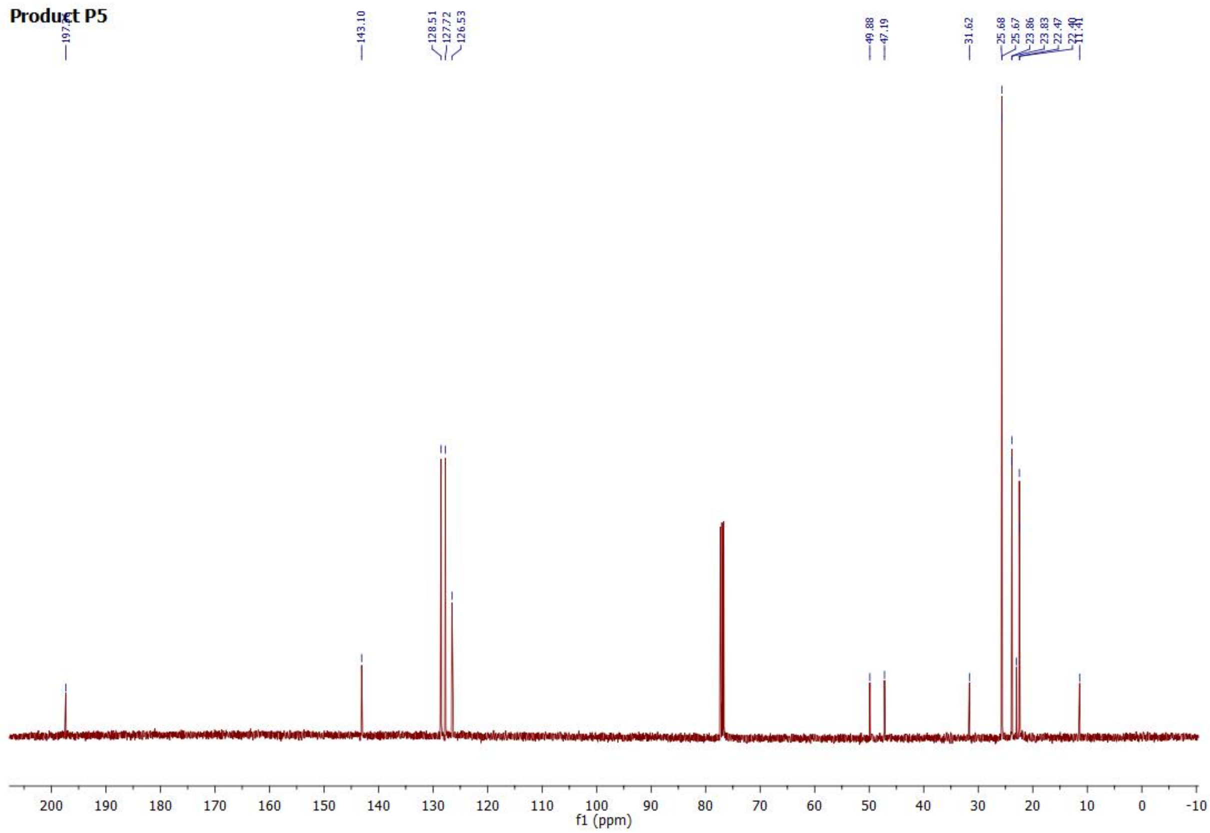


Figure S17. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P5**

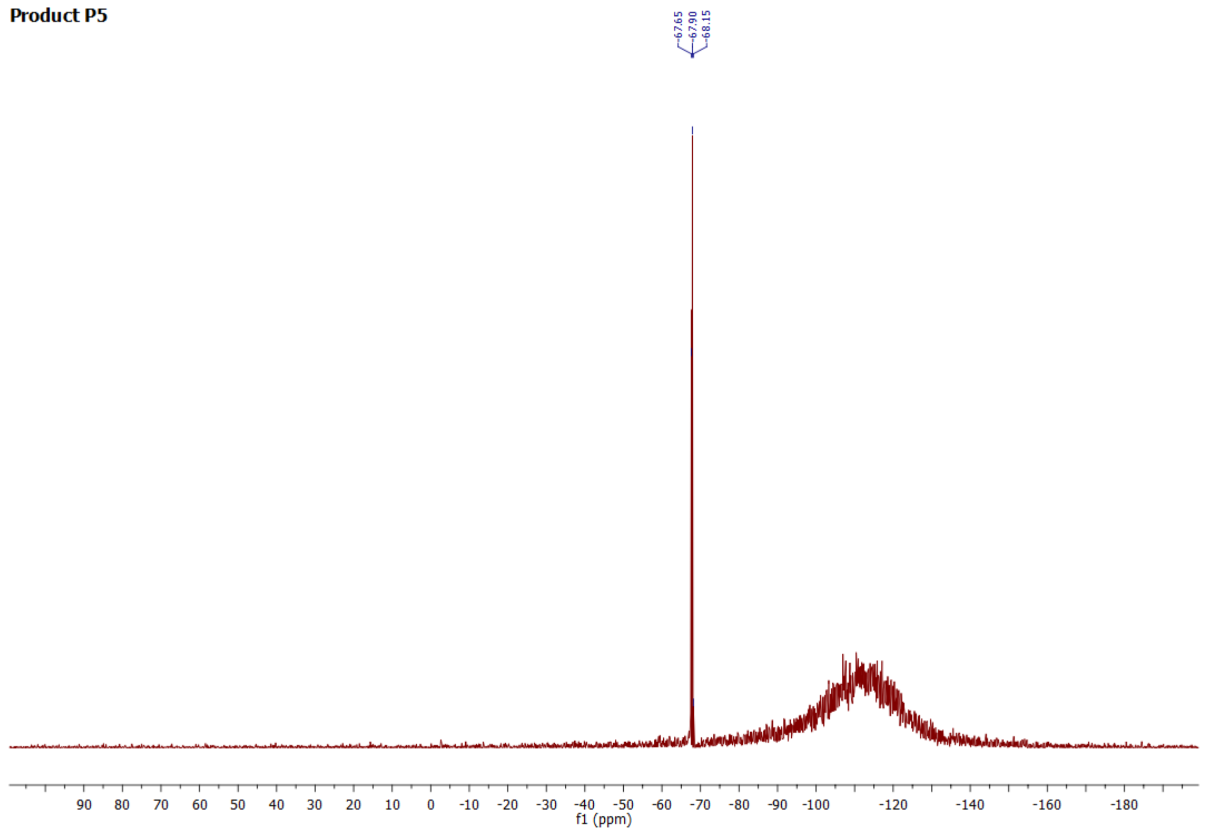


Figure S18. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P5**

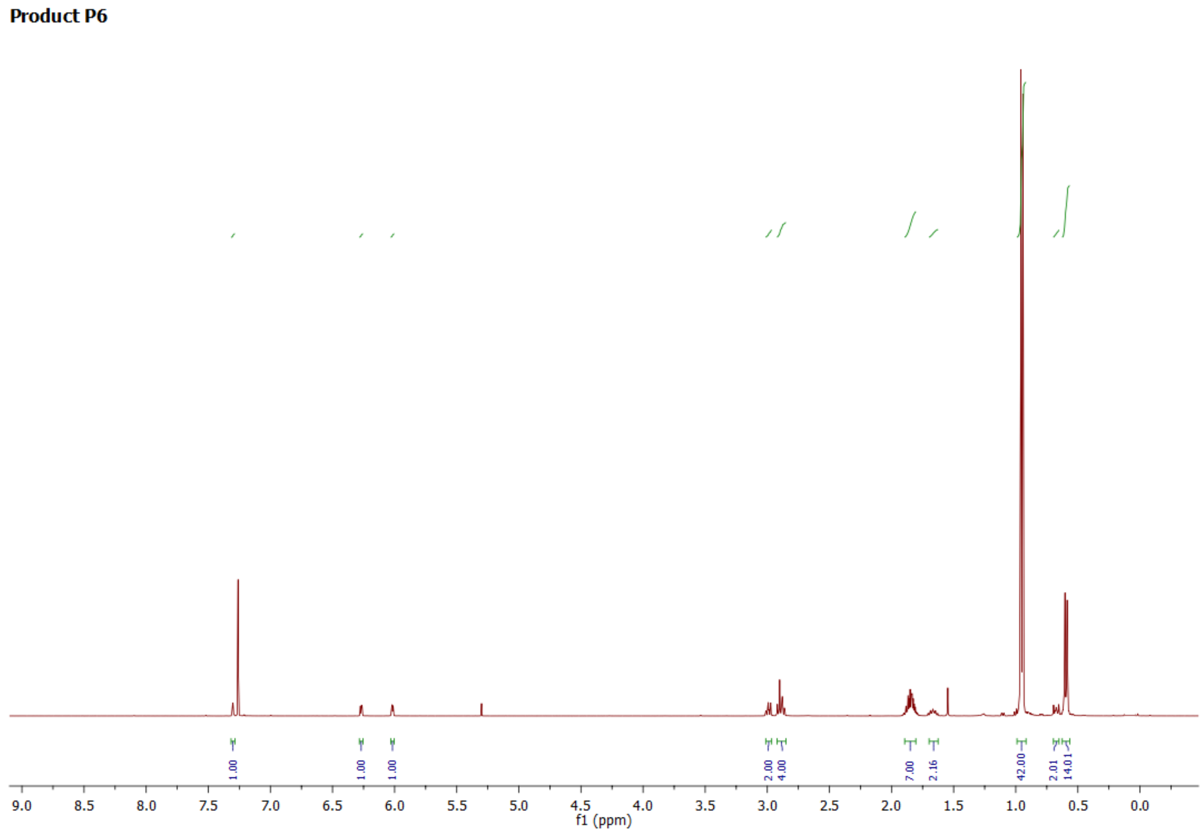


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P6**

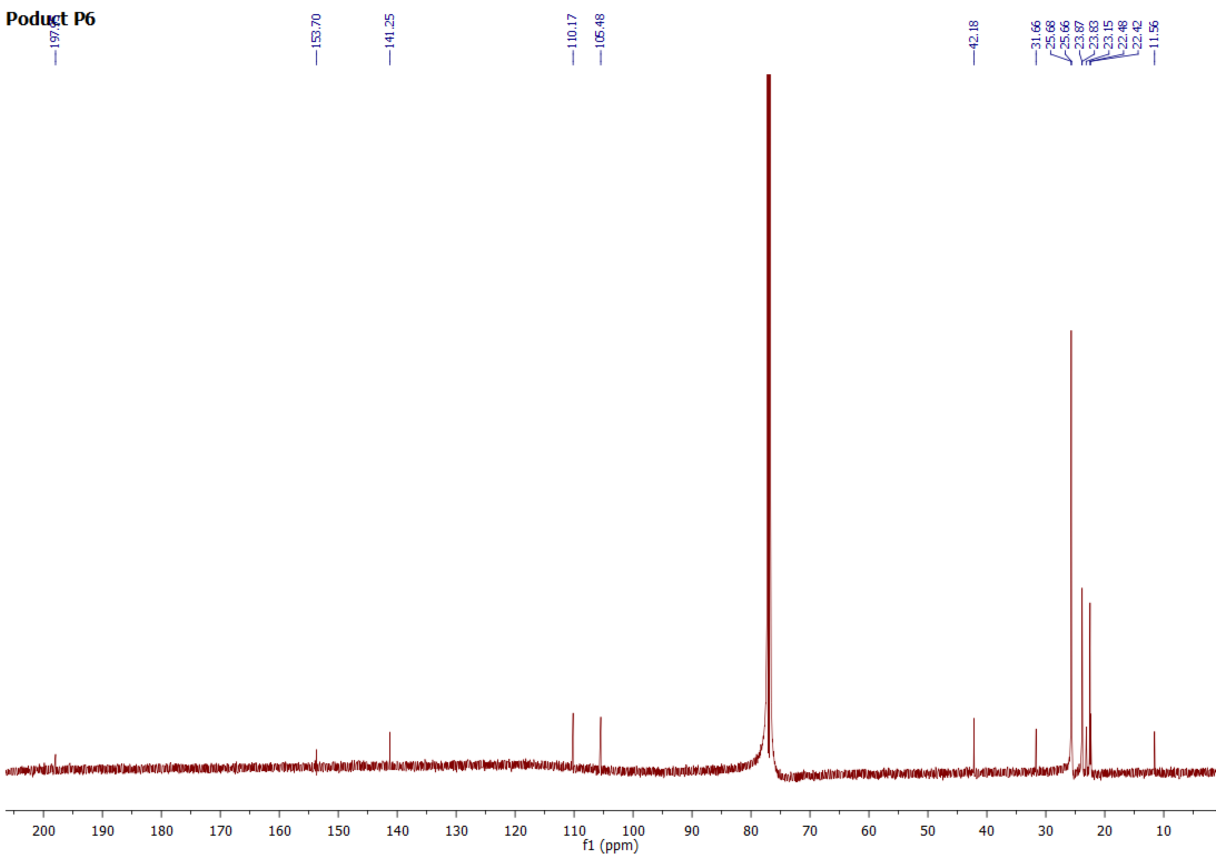


Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P6**

Product P6

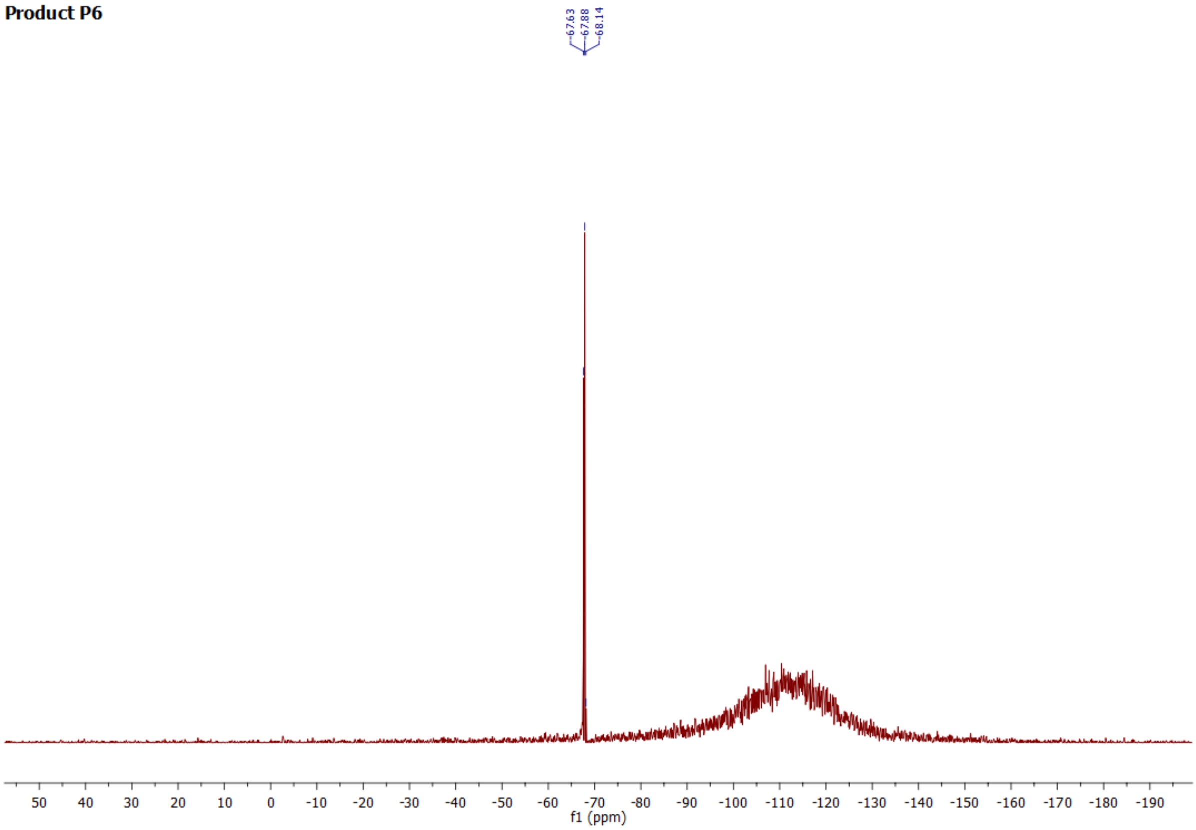


Figure S21. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P6**

Product P7

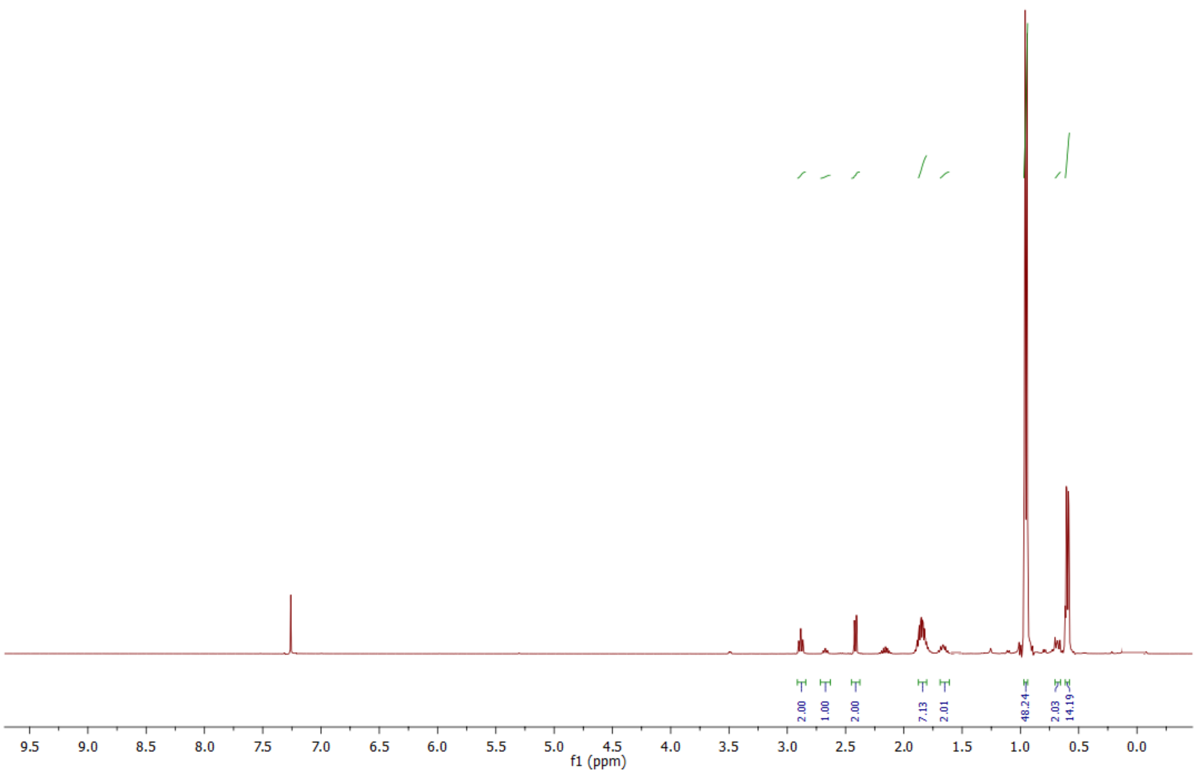


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P7**

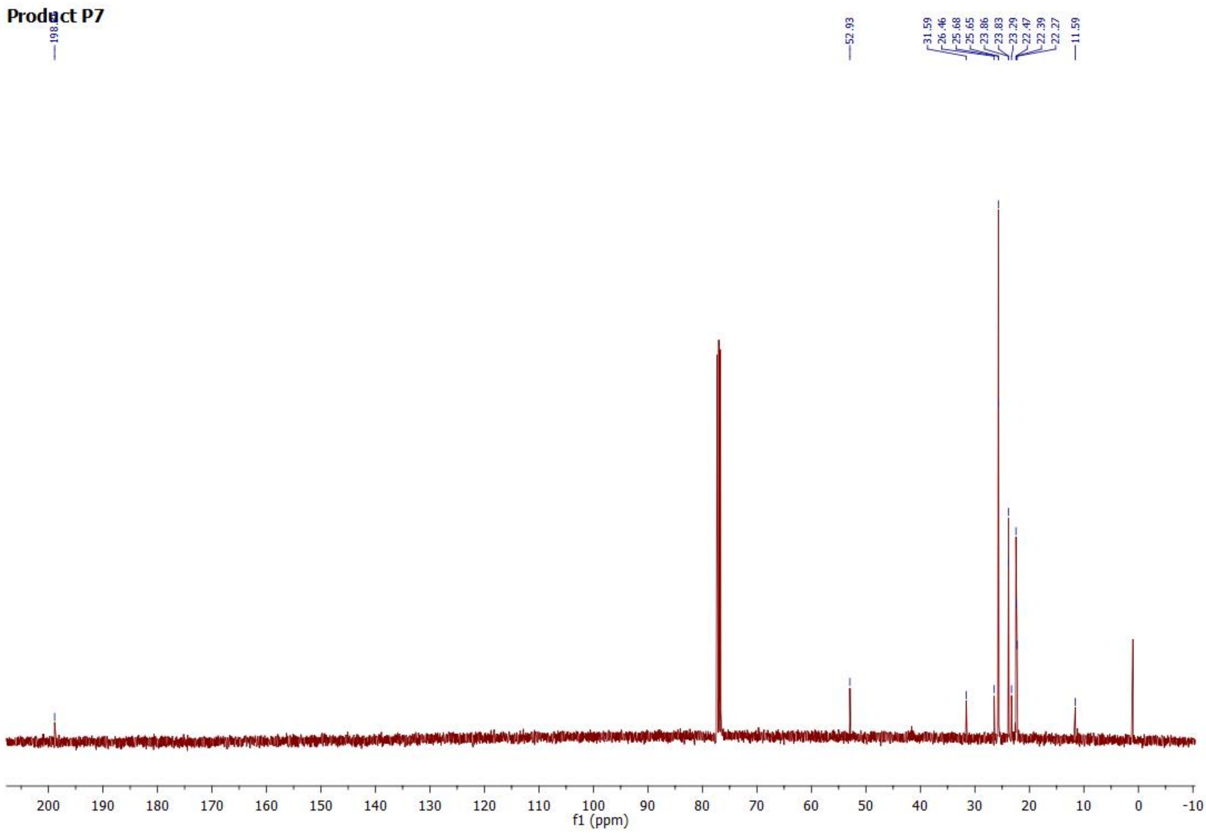


Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P7**

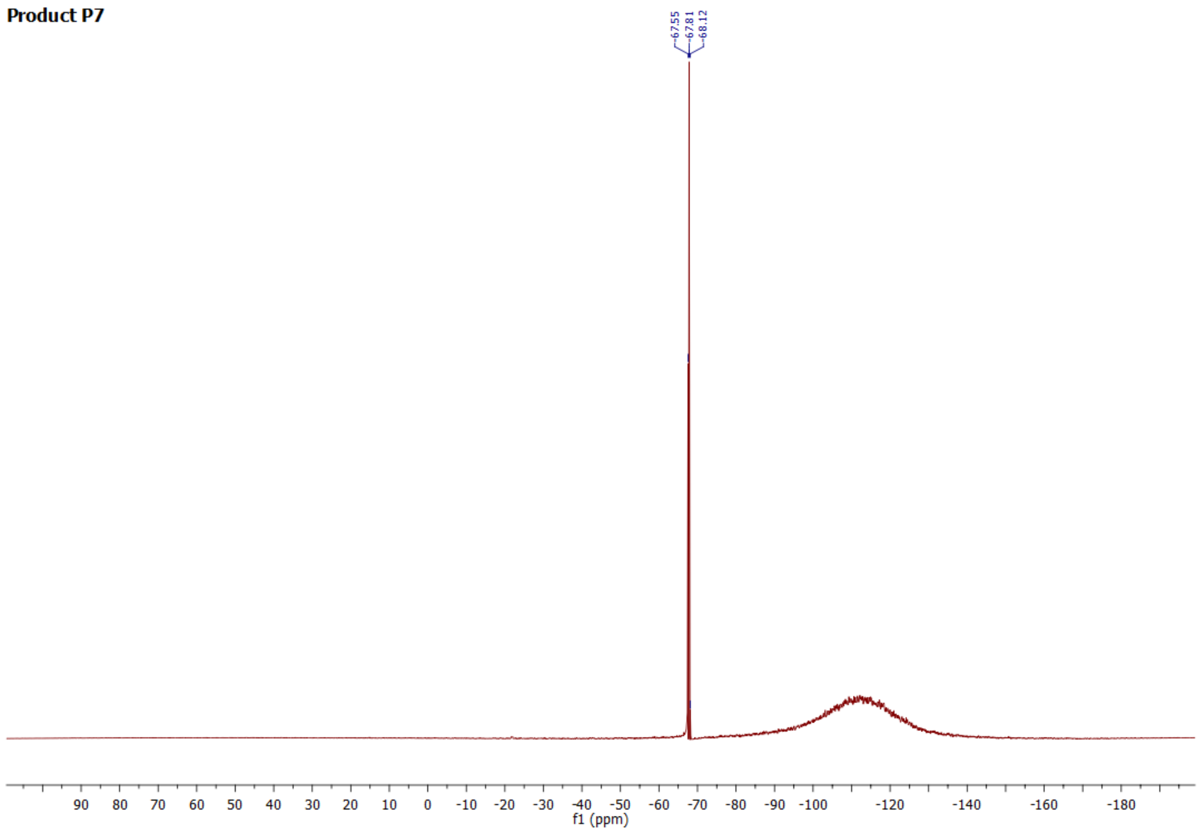


Figure S24. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P7**

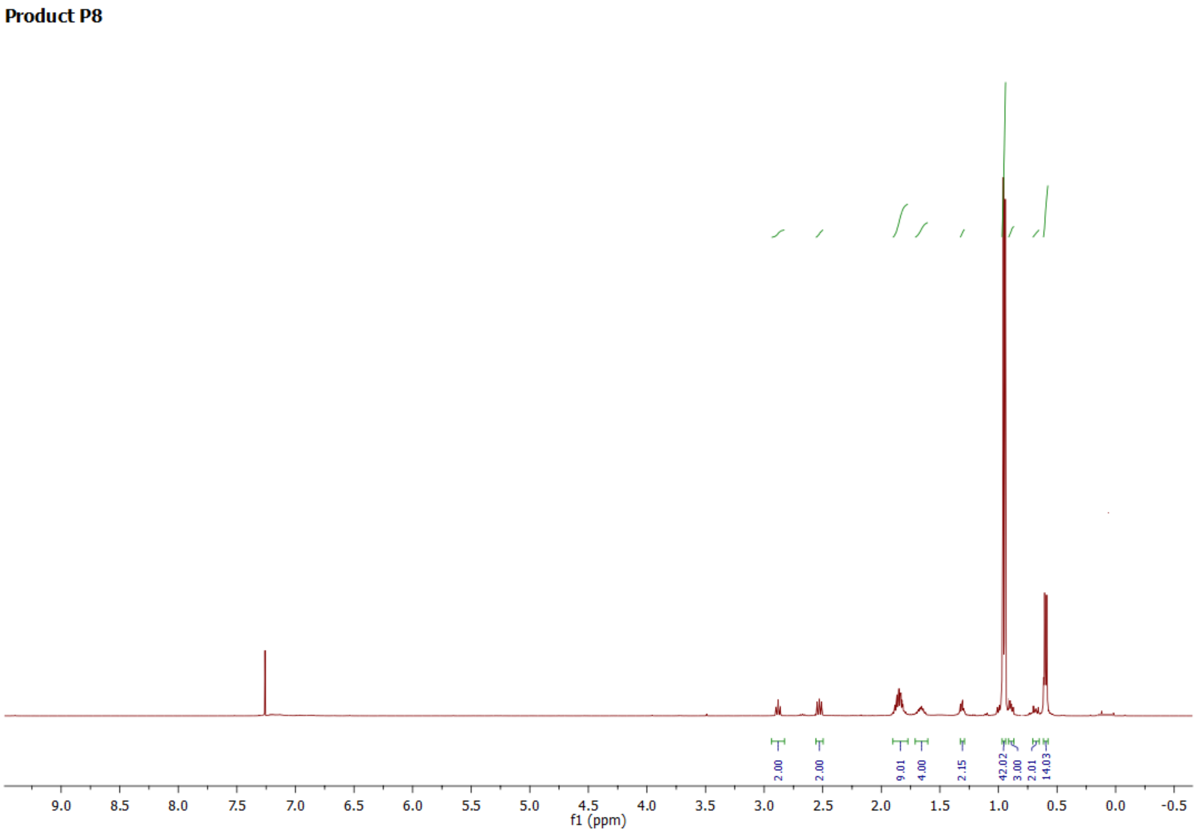


Figure S25. [1]H NMR (400 MHz, $CDCl_3$) of product **P8**

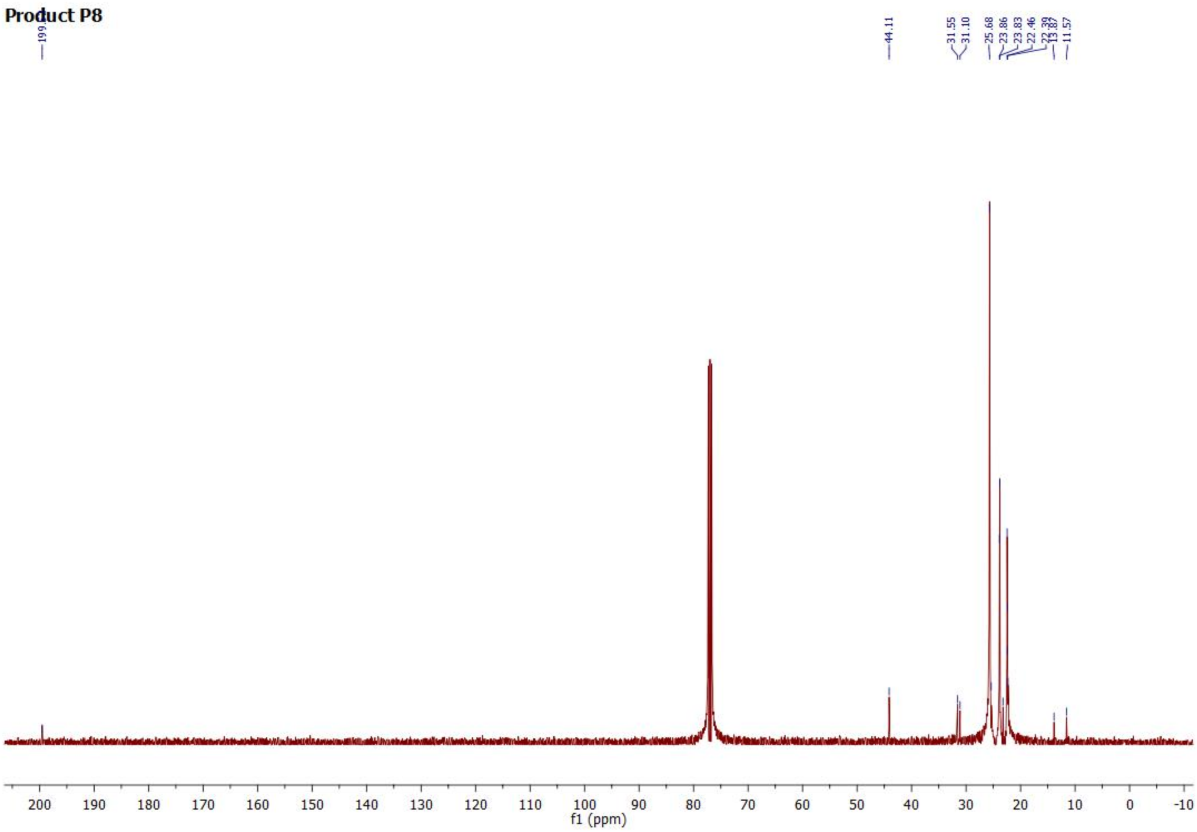


Figure S26. [13]C NMR (101 MHz, $CDCl_3$) of product **P8**

Product P8

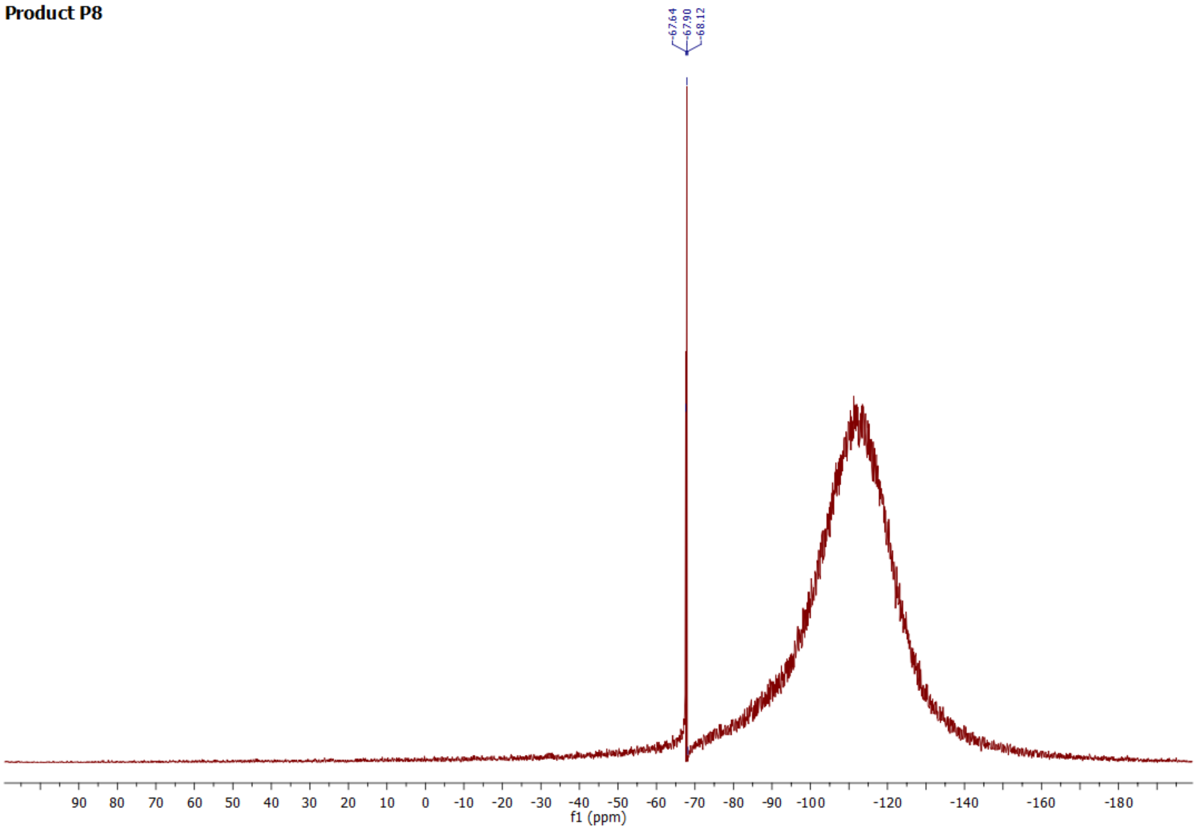


Figure S27. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P8**

Product P9

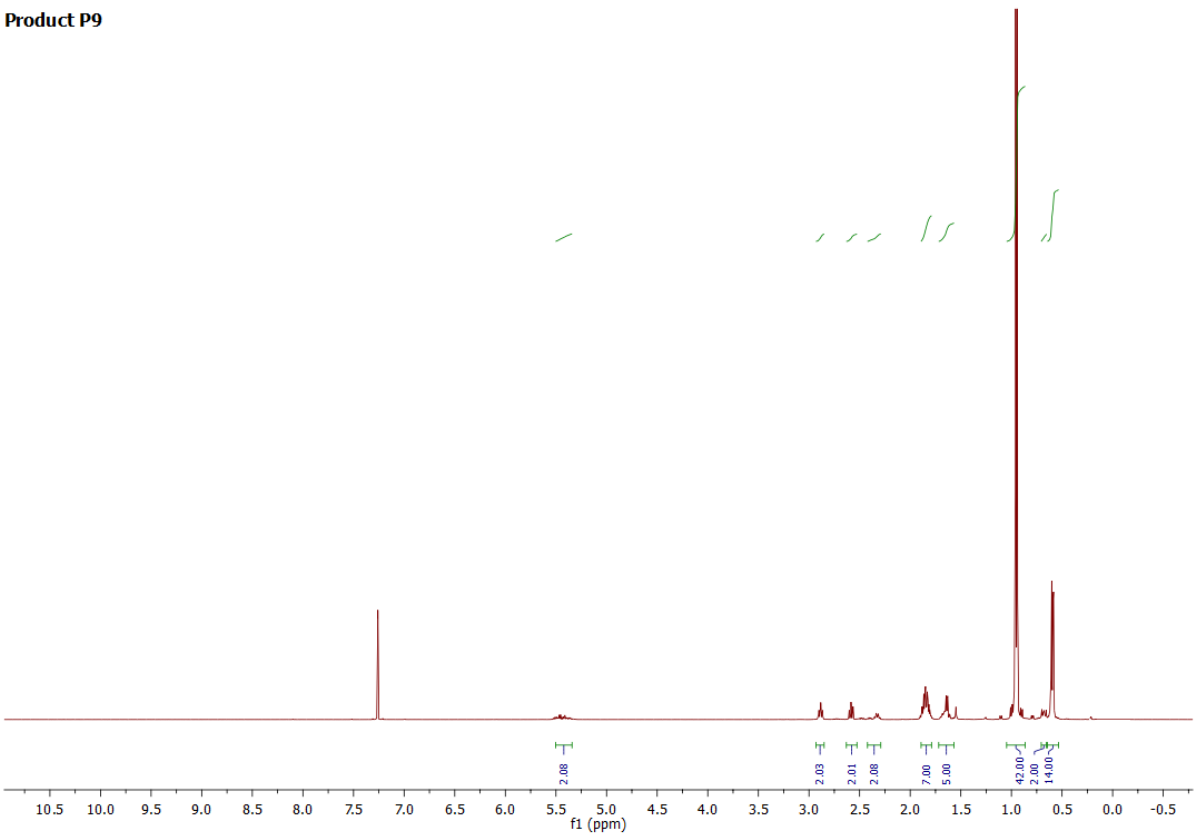


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P9**

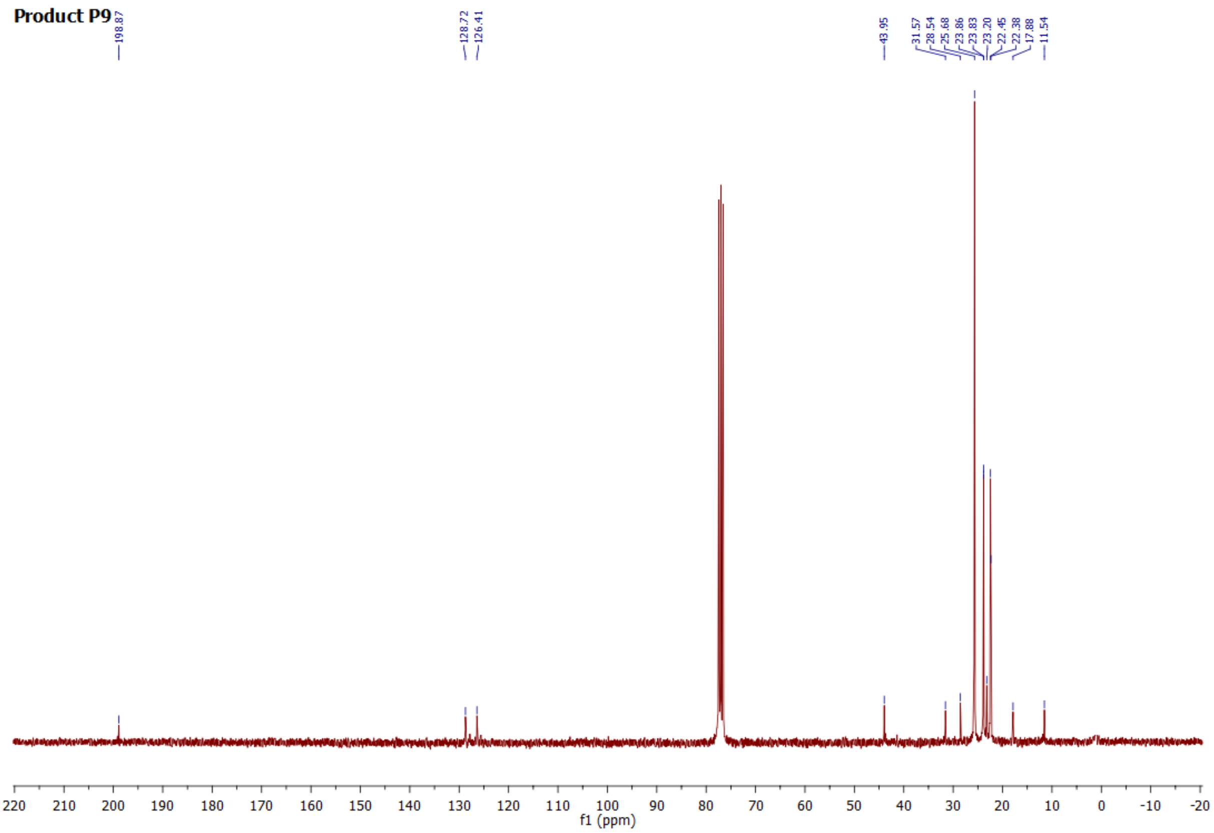


Figure S29. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P9**

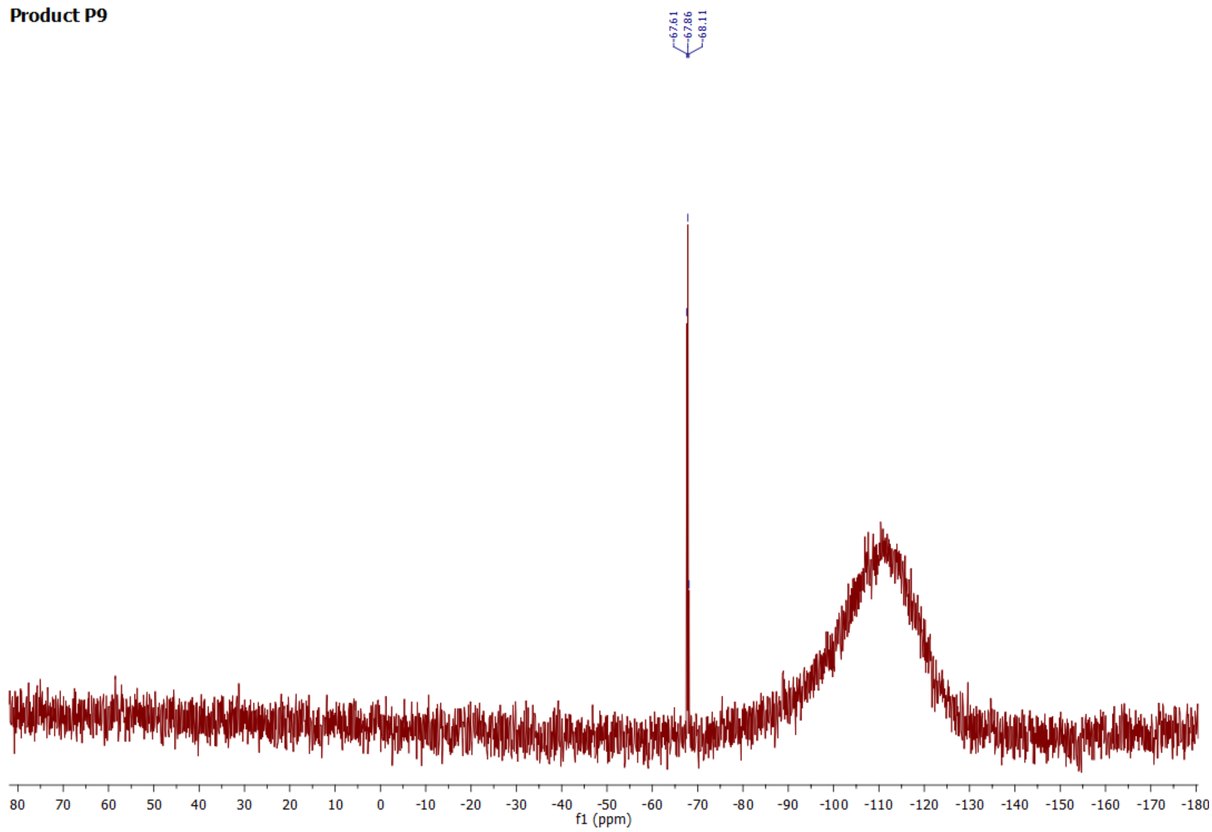


Figure S30. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P9**

Product 10

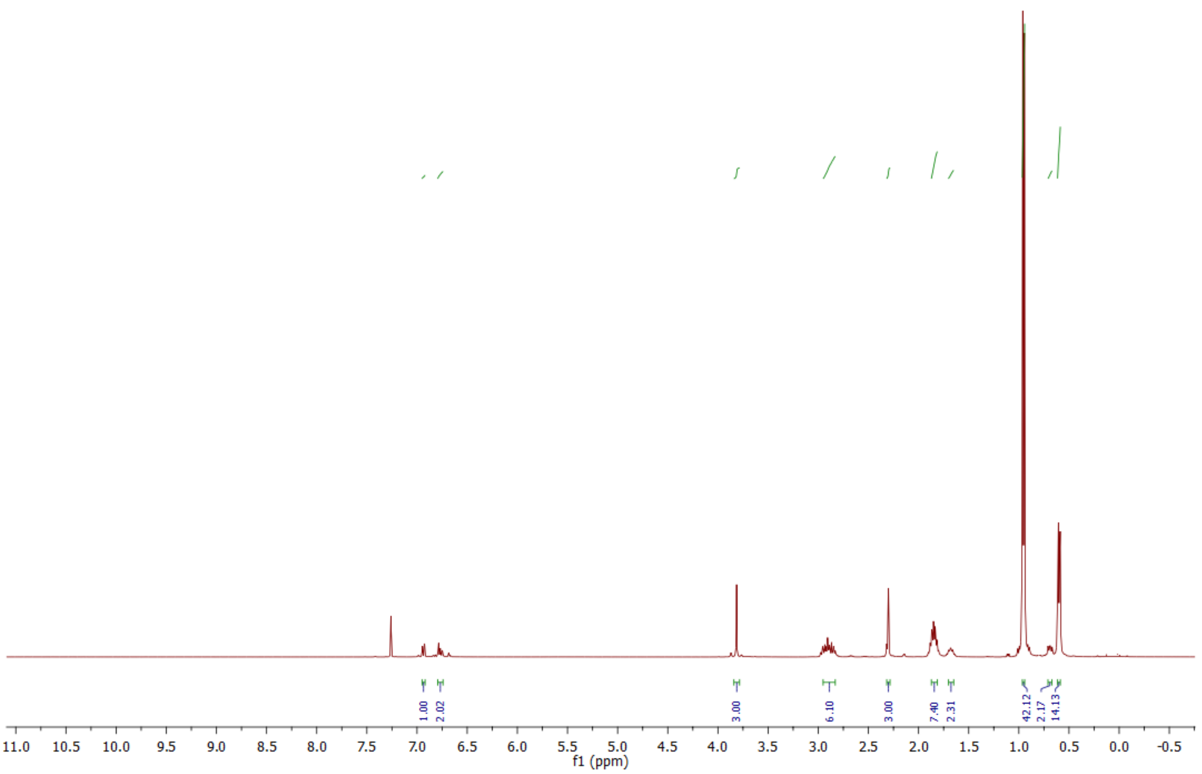


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P10**

Product P10

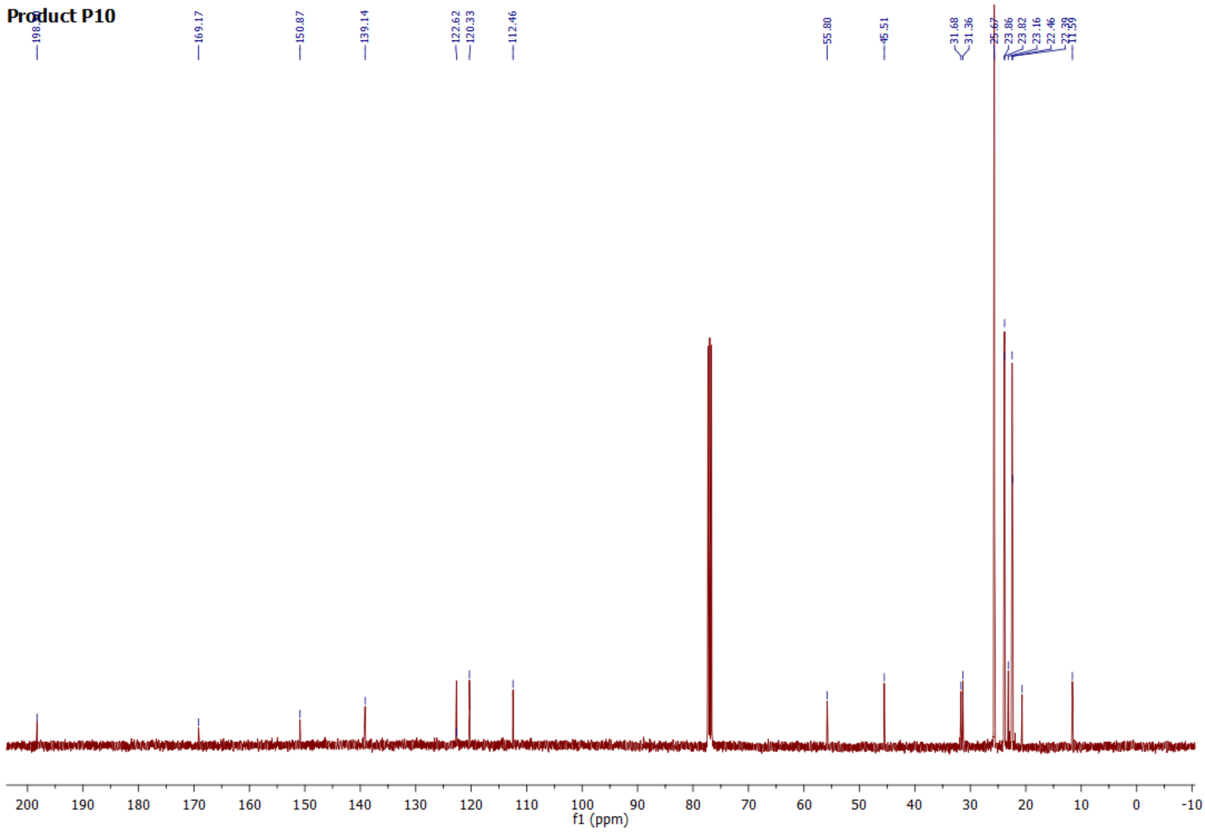


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P10**

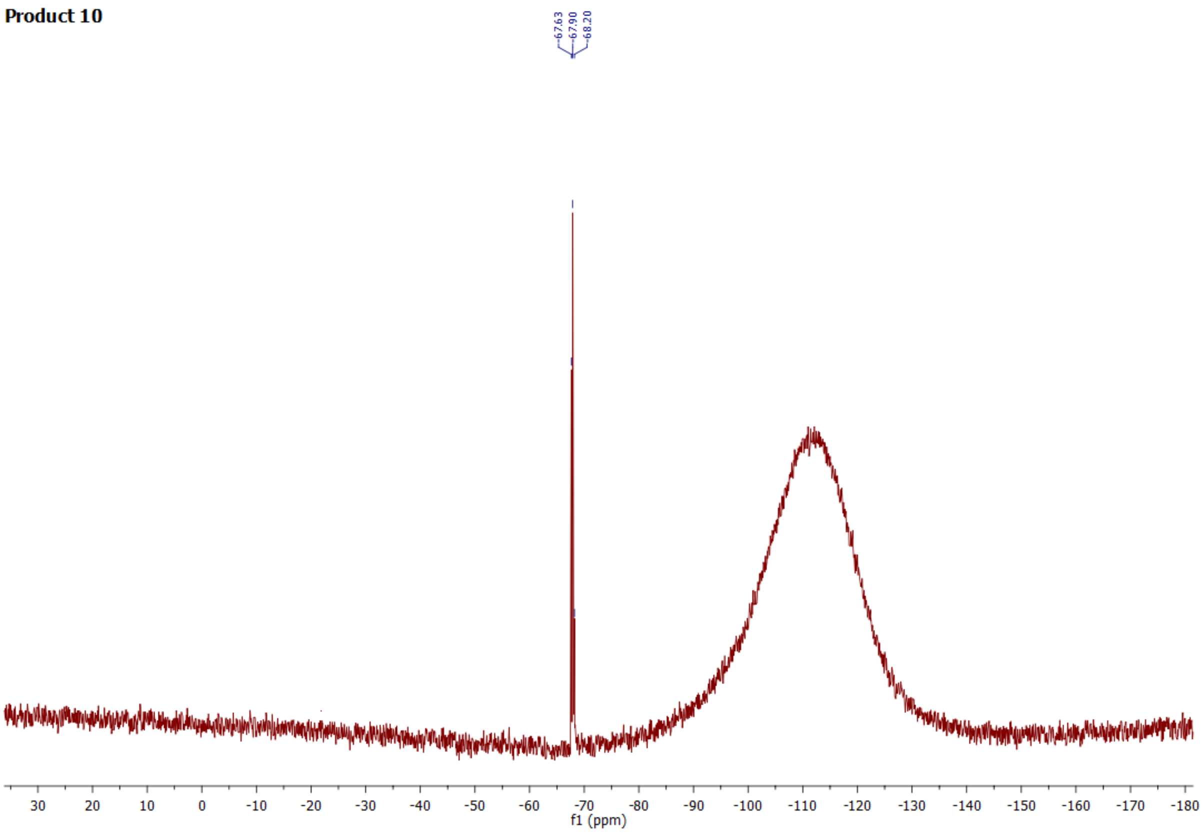


Figure S33. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P10**

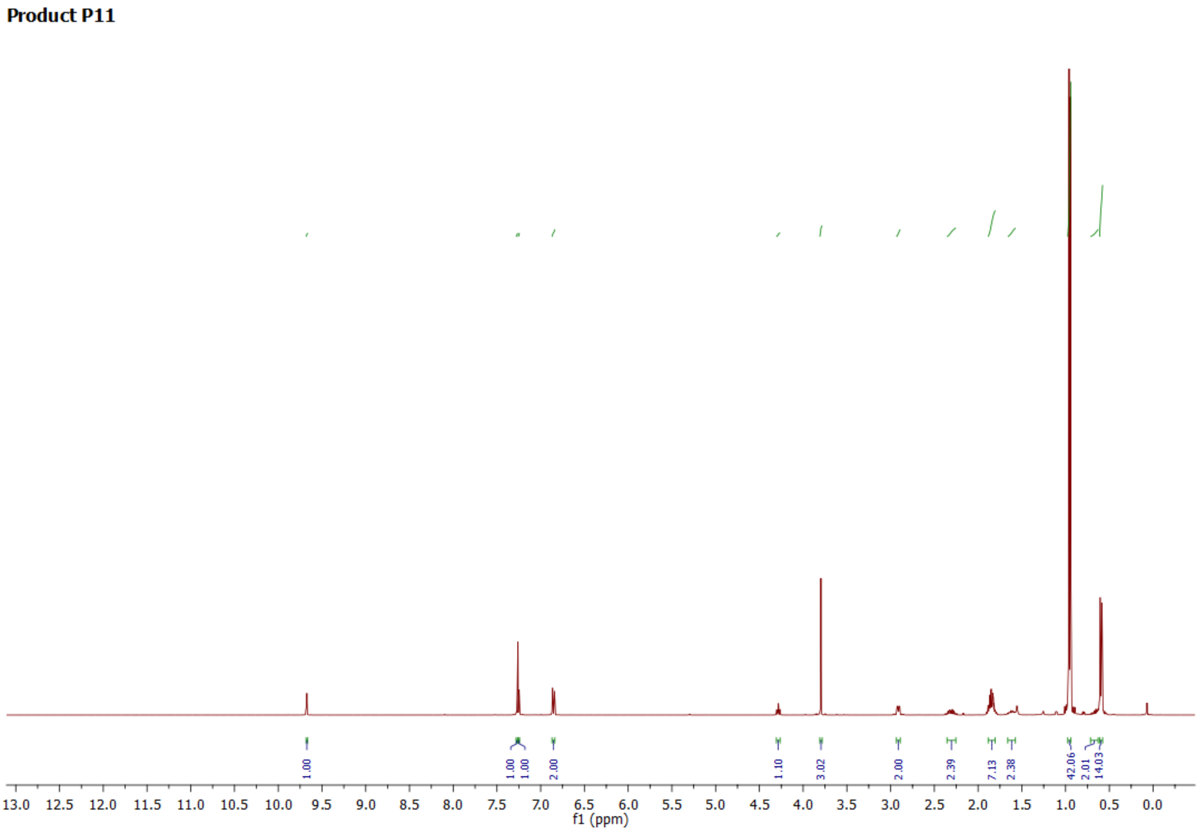


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P11**

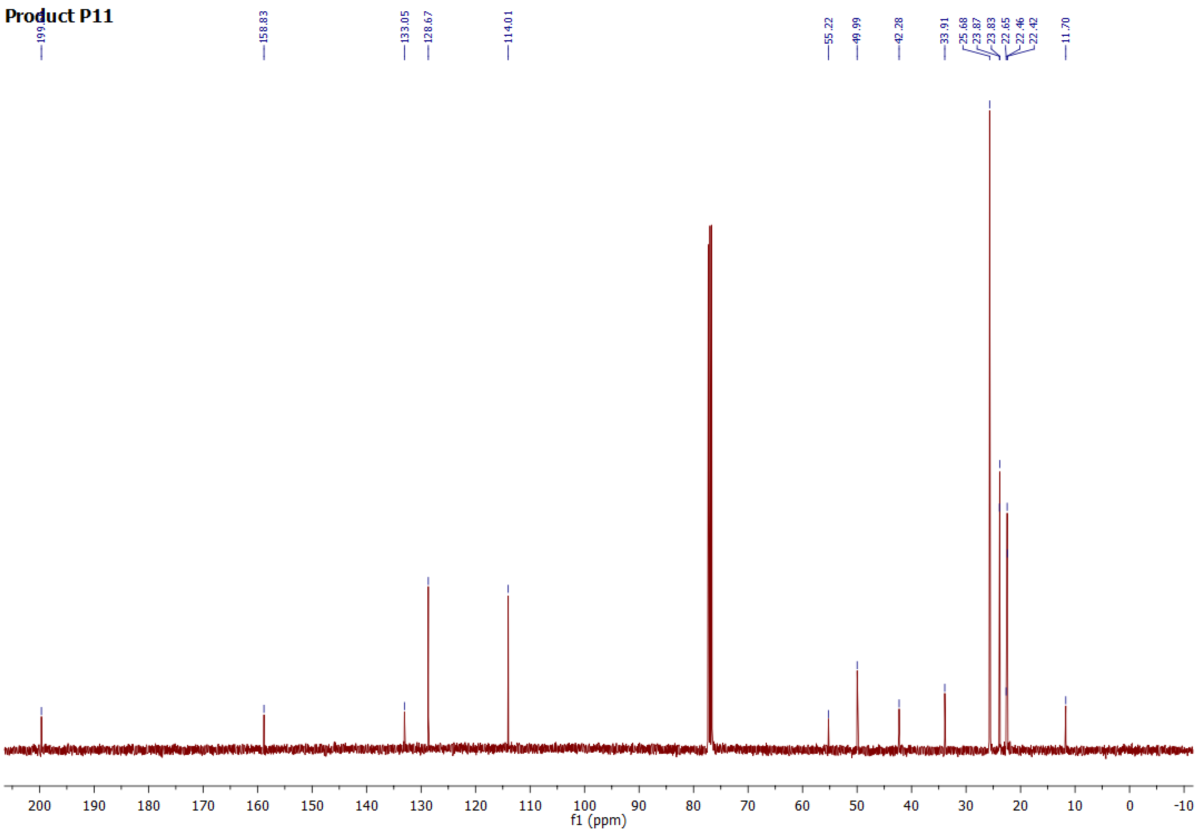


Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P11**

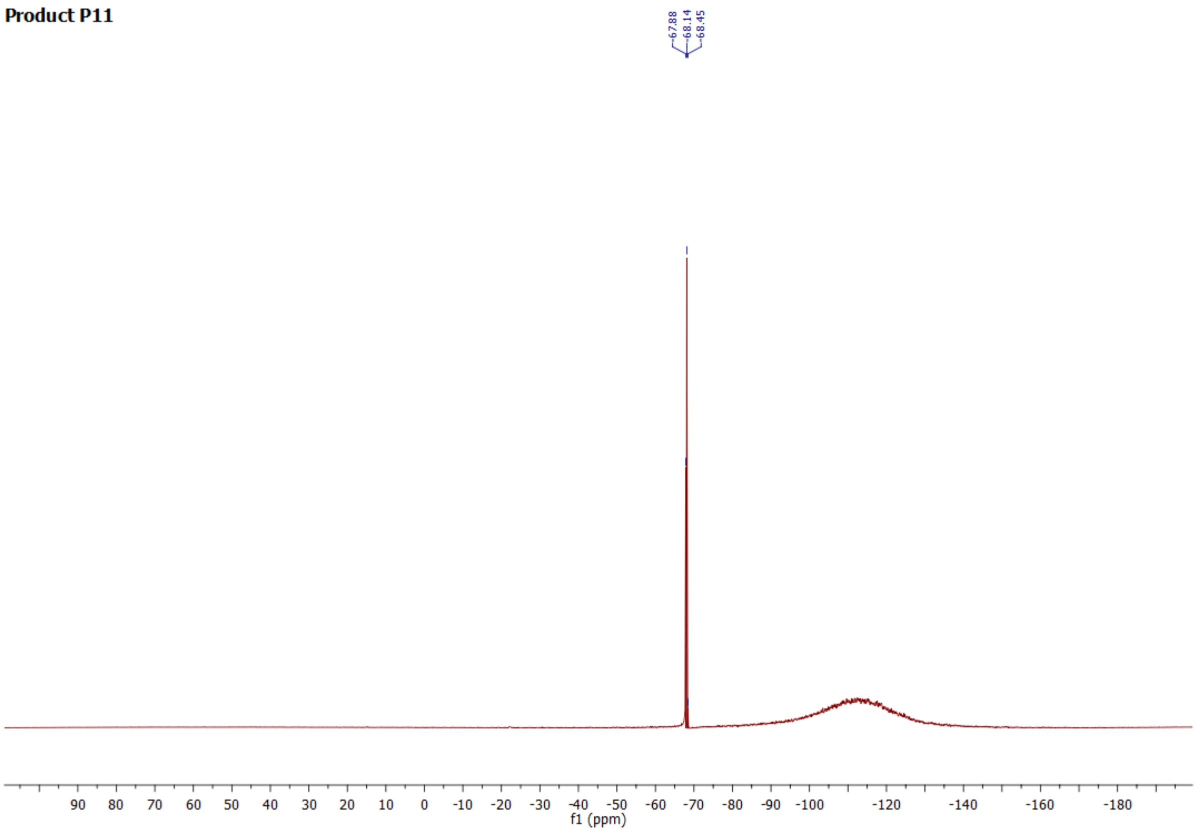


Figure S36. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P11**

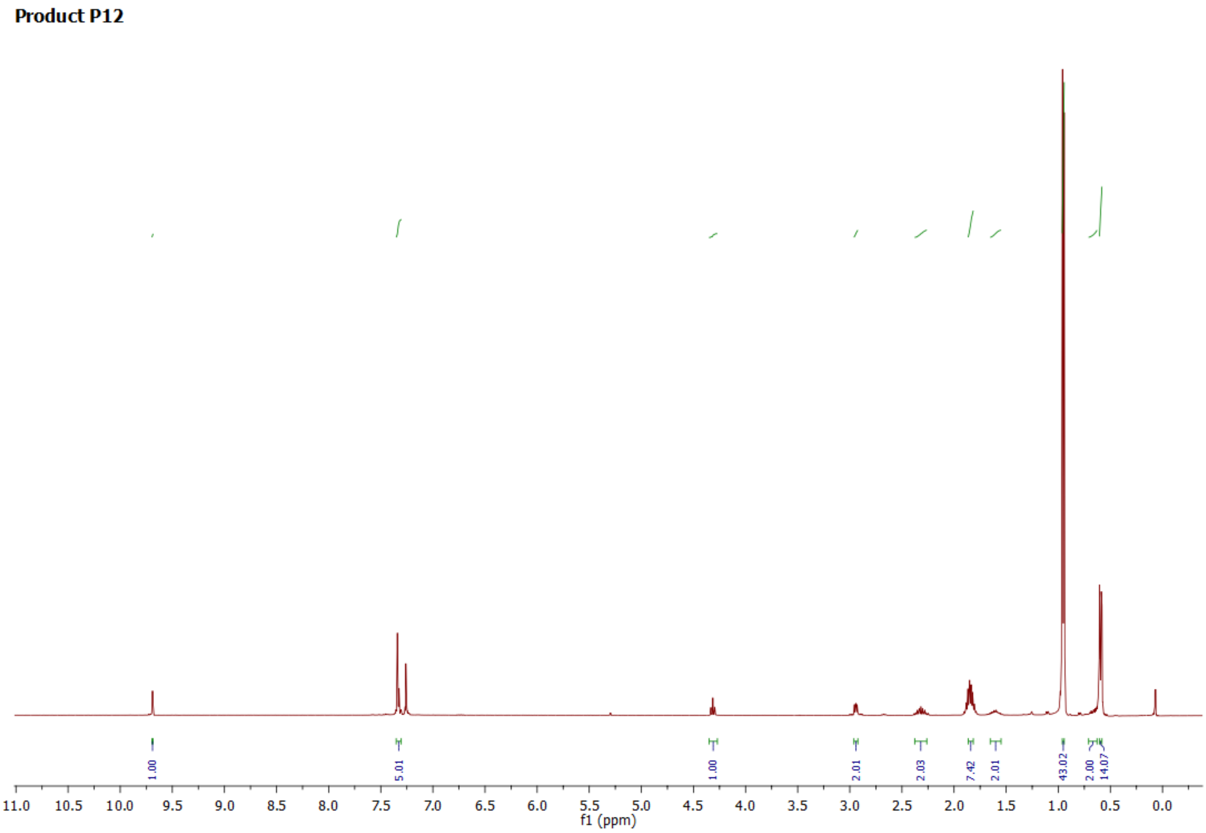


Figure S37. [1]H NMR (400 MHz, $CDCl_3$) of product **P12**

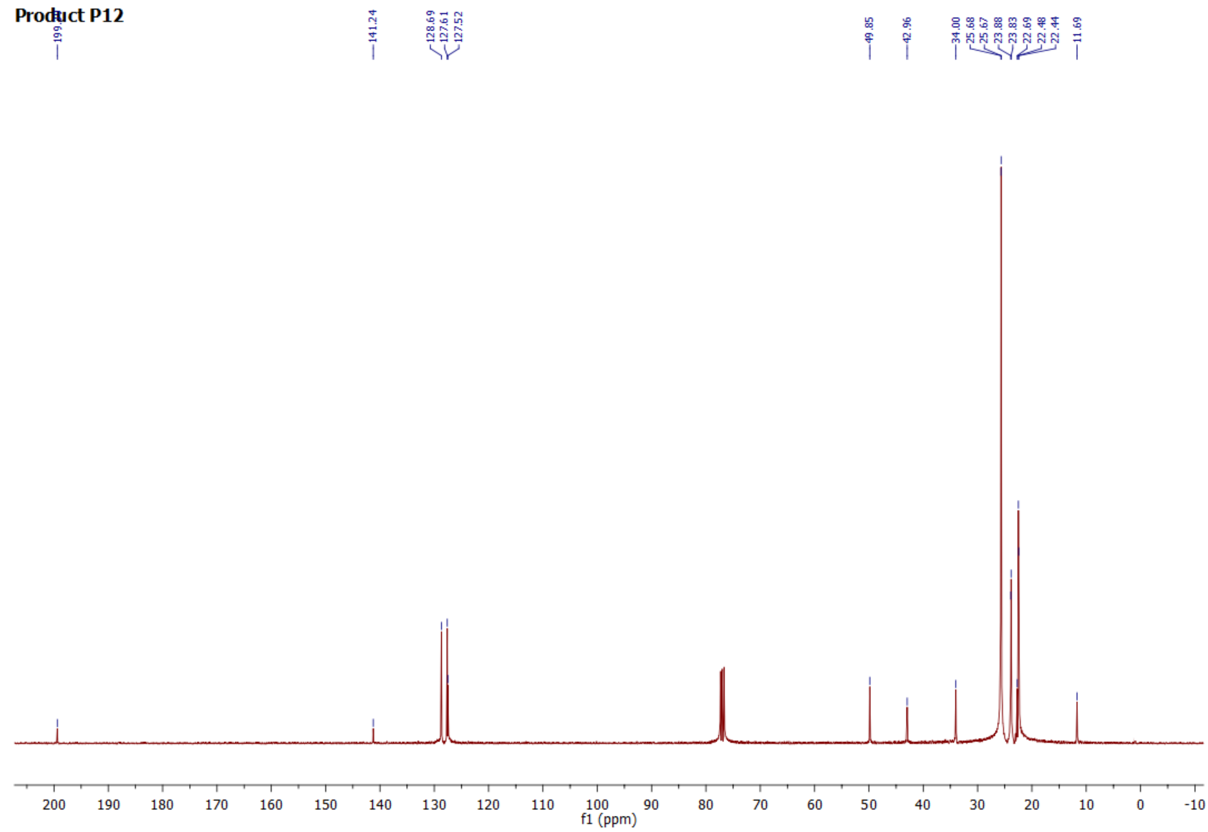


Figure S38. [13]C NMR (101 MHz, $CDCl_3$) of product **P12**

Product P12

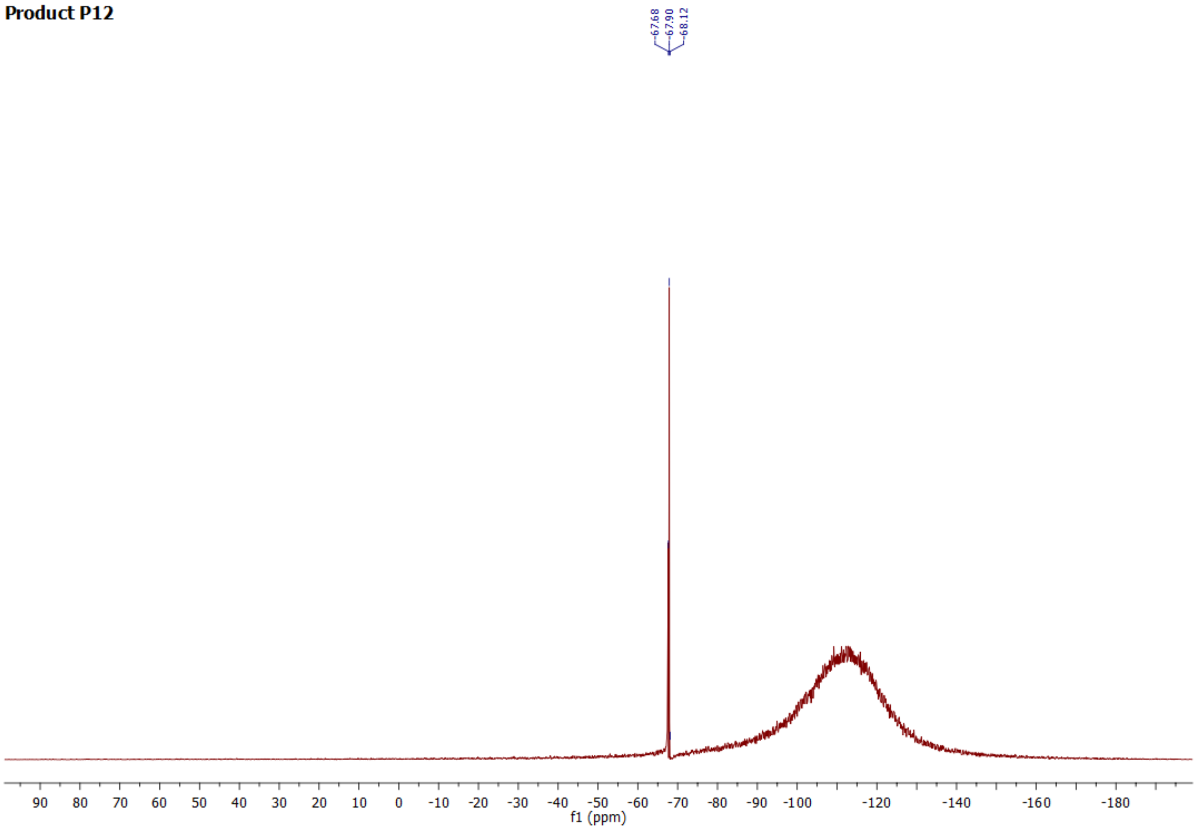


Figure S39. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P12**

Product P13

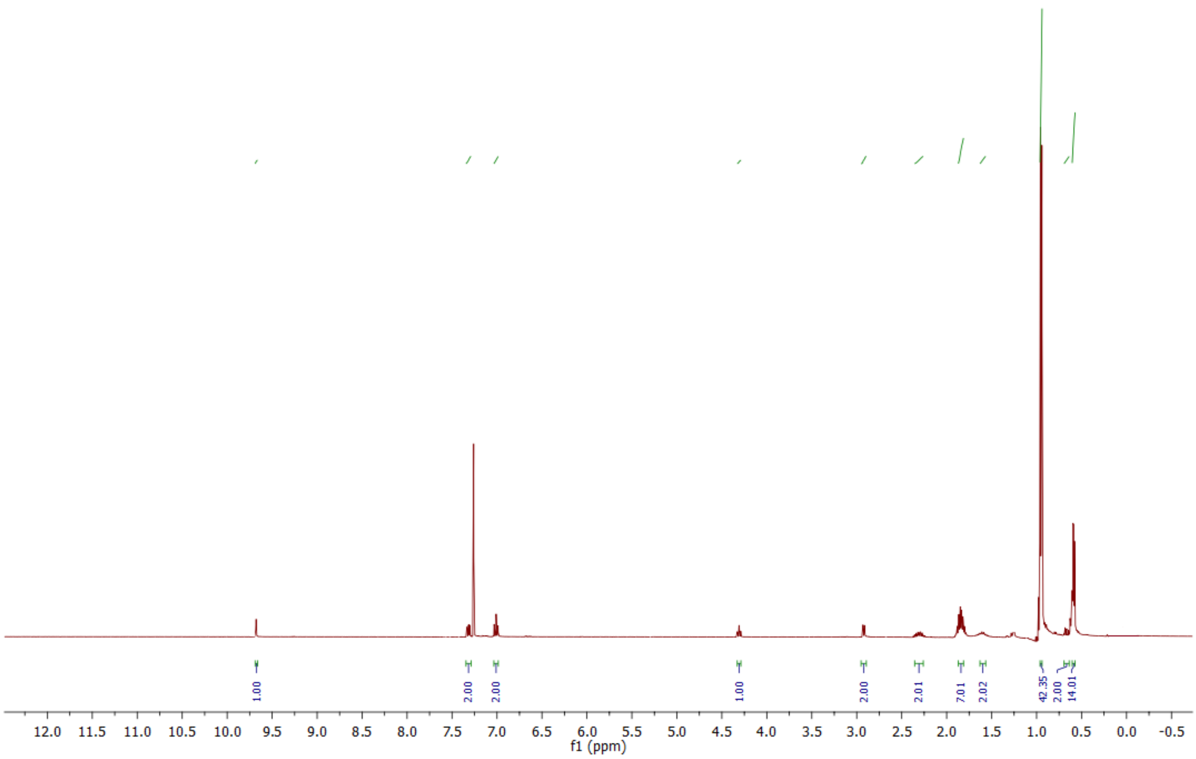


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P13**

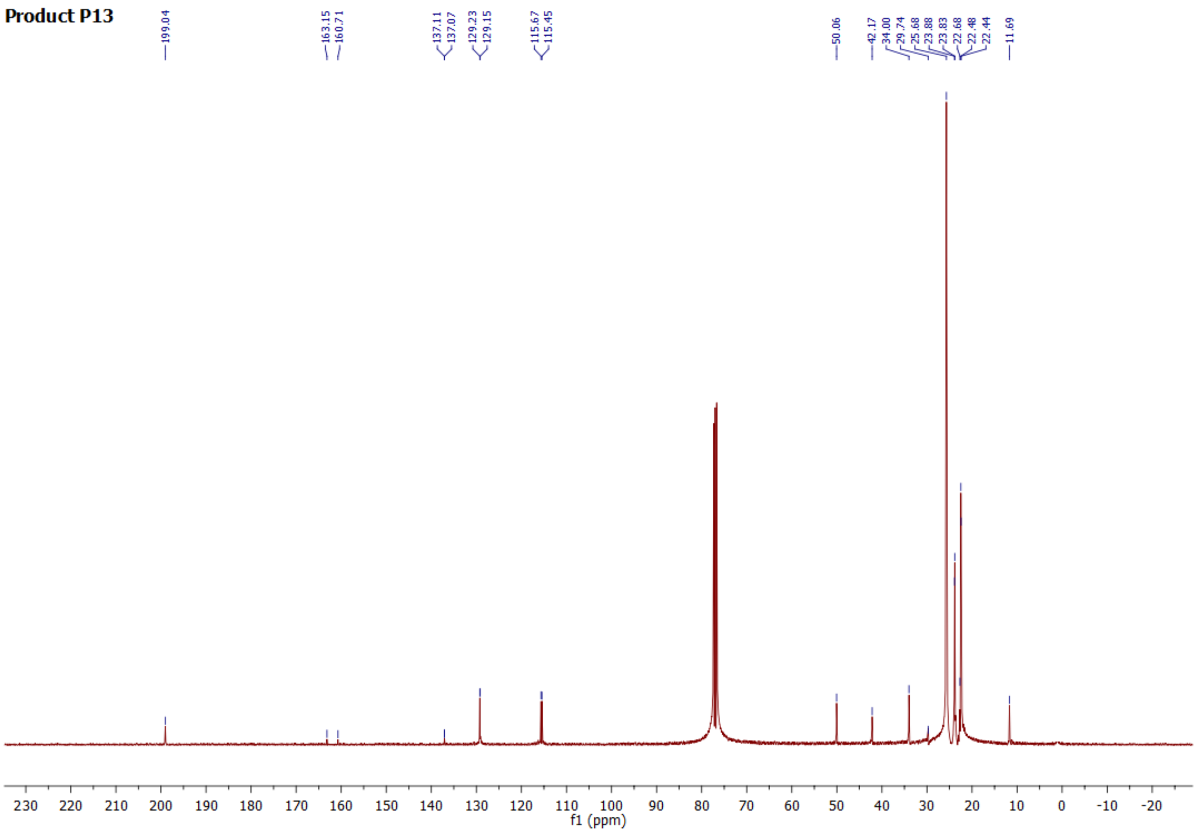


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P13**

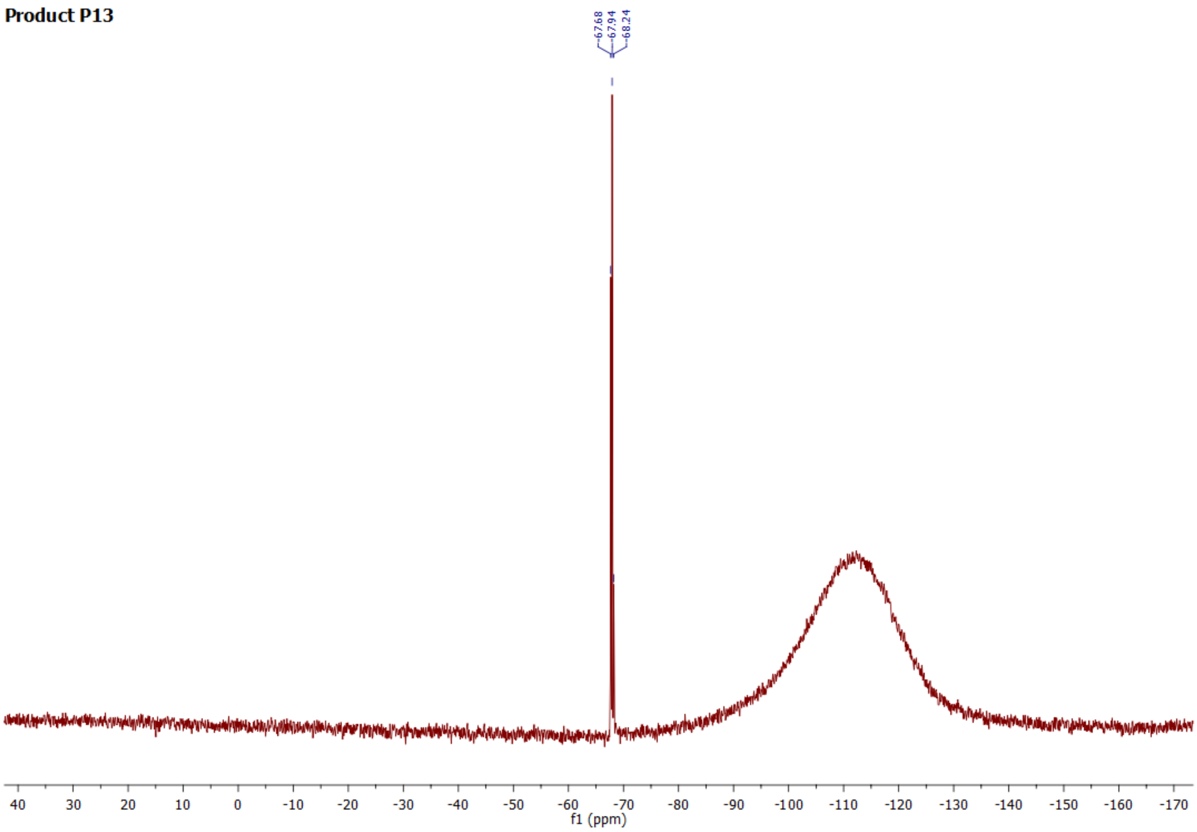


Figure S42. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P13**

Product P14

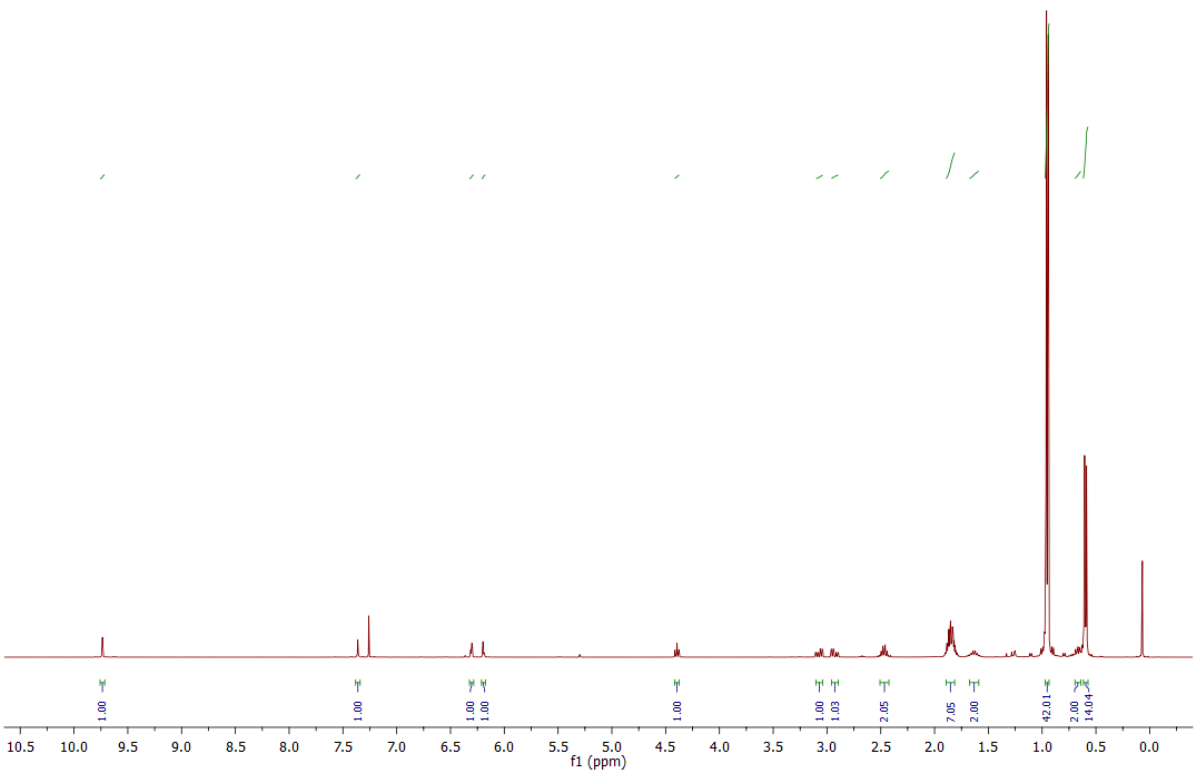


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P14**

Product P14

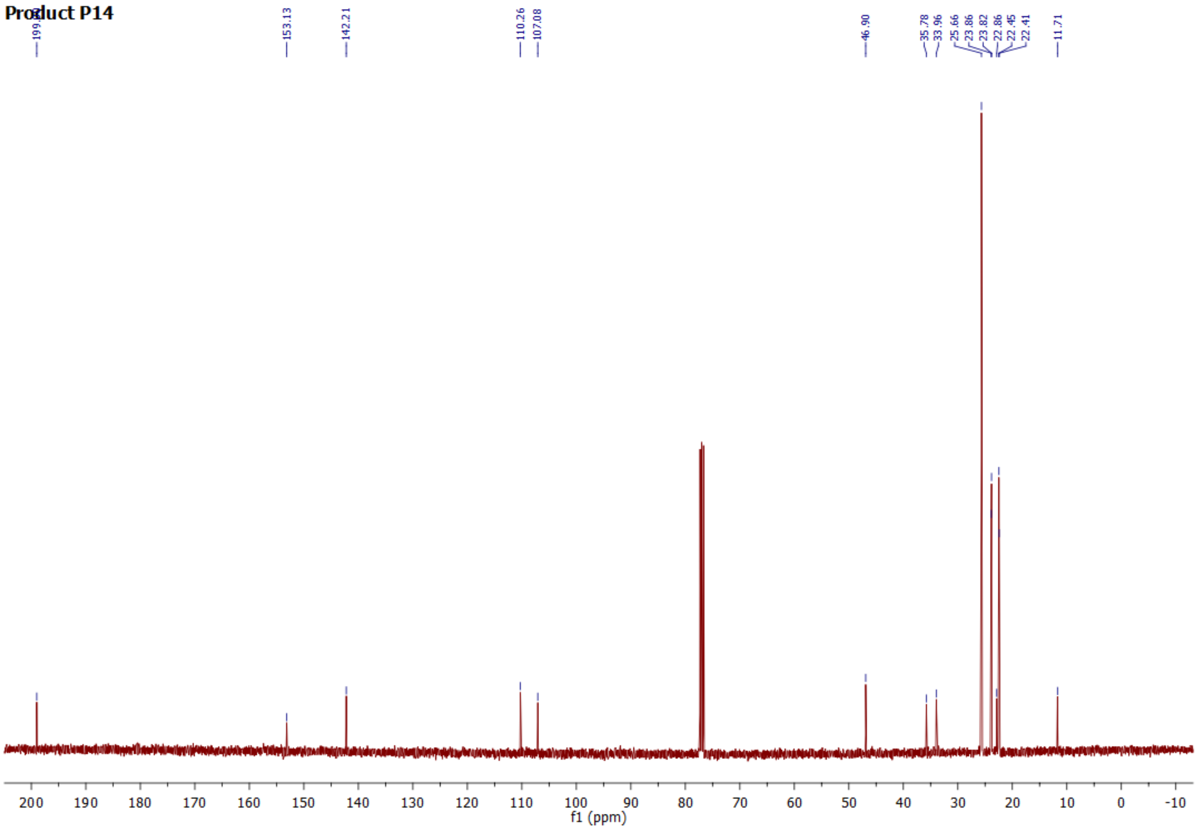


Figure S44. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P14**

Product P14

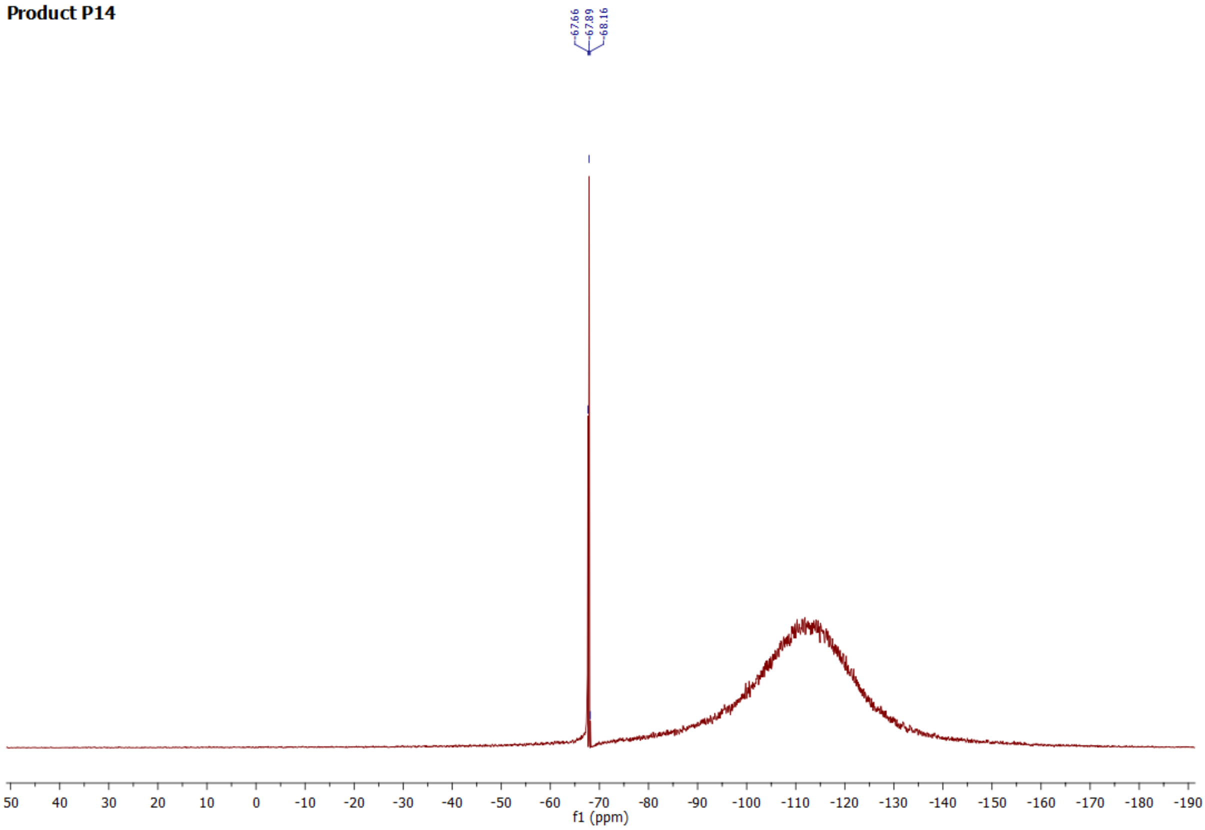


Figure S45. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P14**

Product P15

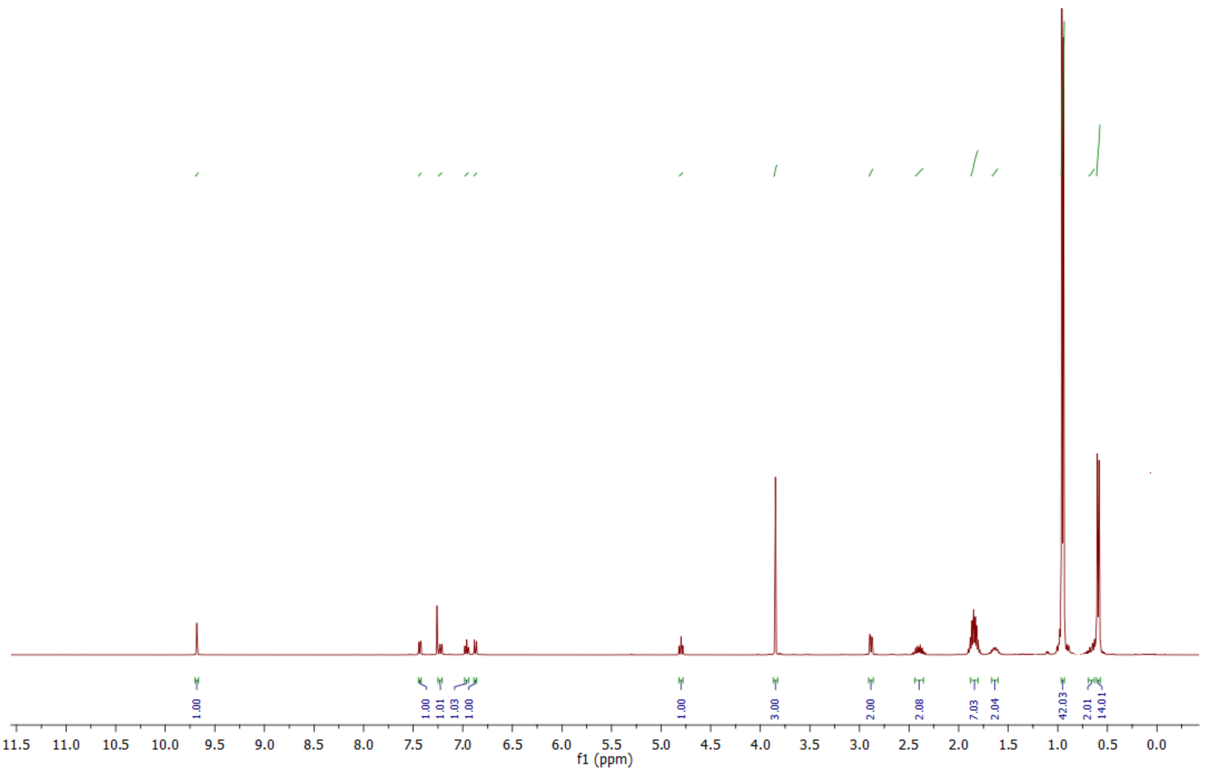


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P15**

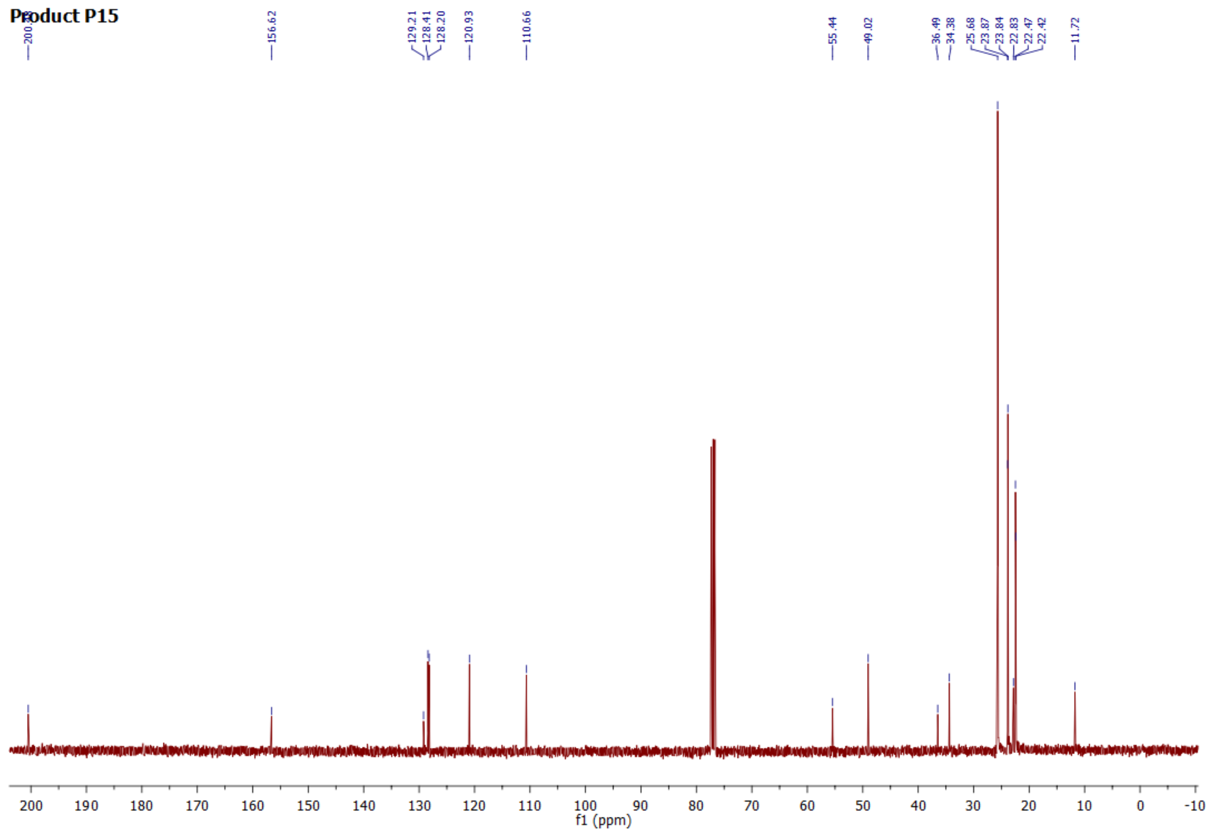


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P15**

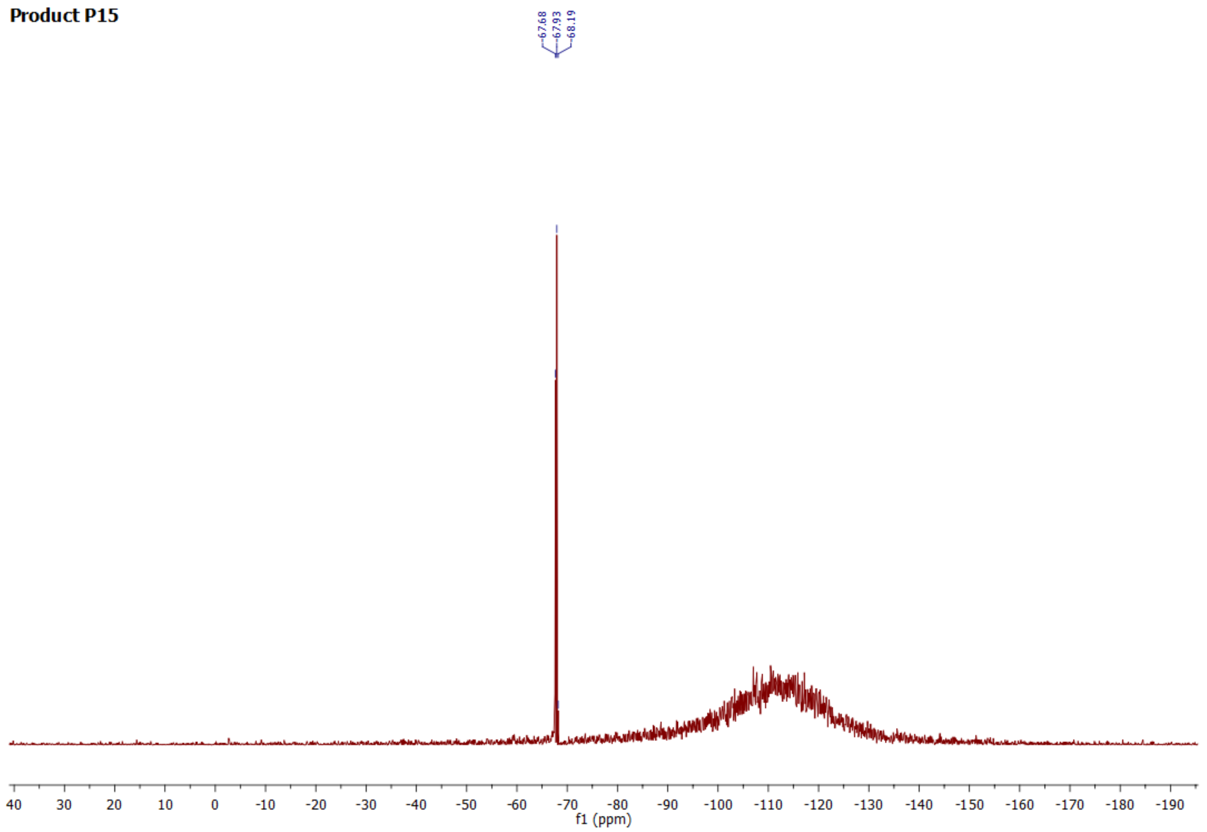


Figure S48. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P15**

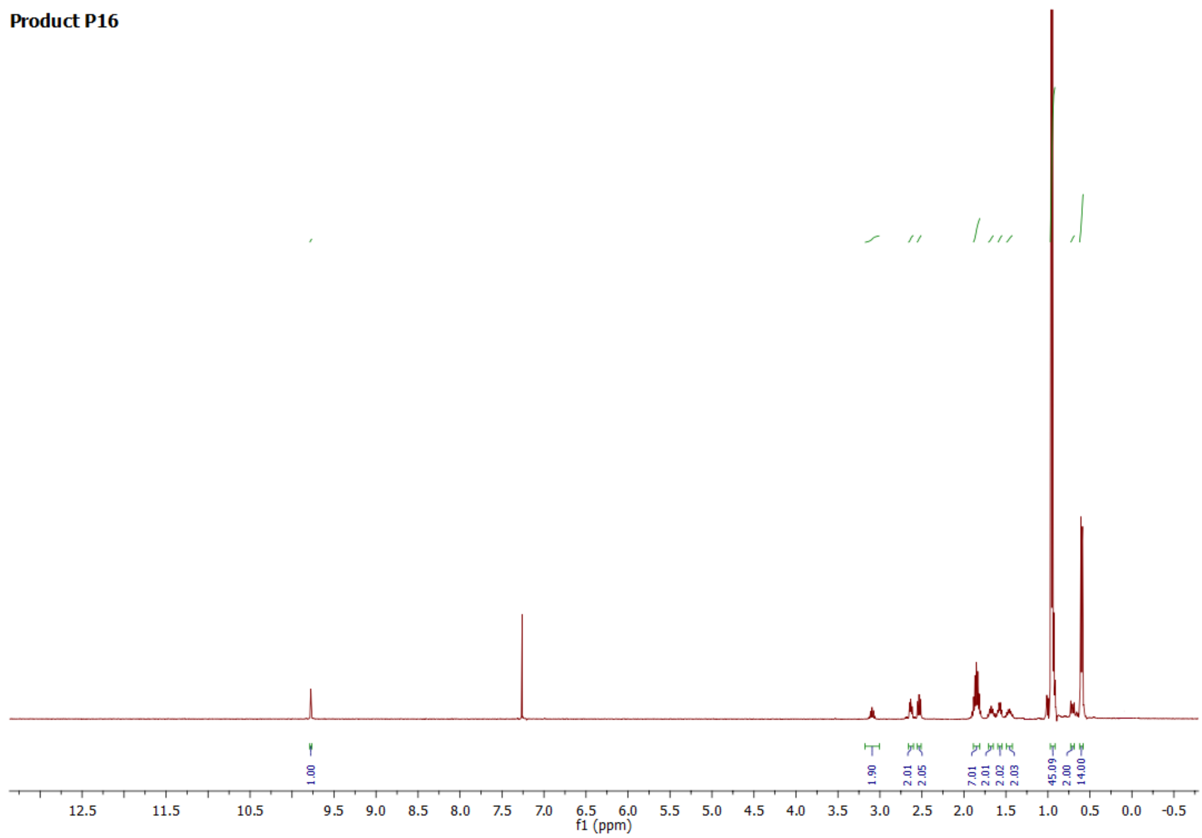


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P16**

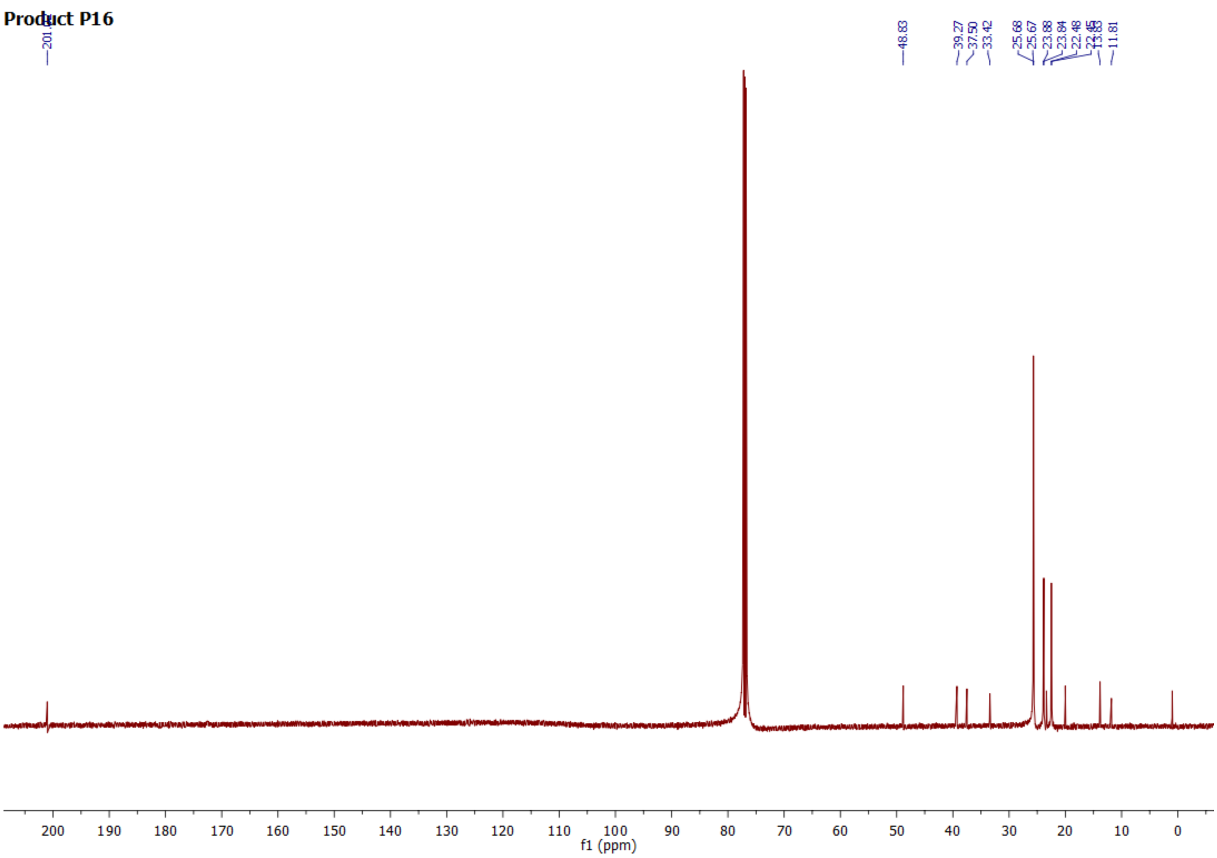


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P16**

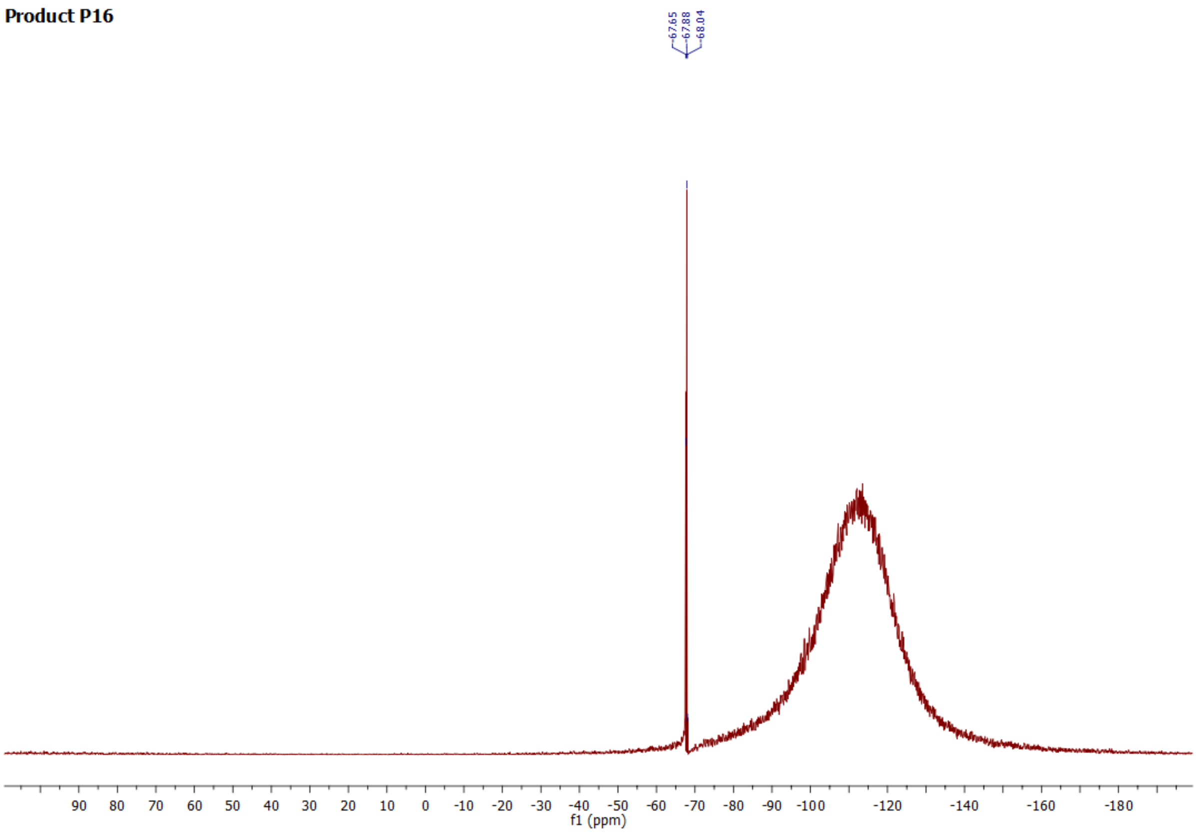


Figure S51. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **P16**

6. References

[1] a) S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, Organometallics, **2013**, *32*, 330; b) M. Hans, J. Lorkowski, A. Demonceau, L. Delaude, *Beilstein J. Org. Chem*., **2015**, *11*, 2318–2325.