

Supporting Information

Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorenes) Prepared Via Nickel Catalyzed Cross-Coupling of Diarylmagnesate Monomers

Jeffrey J. McDowell, Isabel Schick, Alastair Price, Daniel Faulkner, Geoffrey Ozin

Contents:

Section 1: $^1\text{H}/^{13}\text{C}$ NMR of Intermediate Compounds, Monomers (1-7) and Polymer (9-15)

S1.1.0 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) ^1H -NMR

S1.1.1 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) ^{13}C -NMR

S1.2.0 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) ^1H -NMR

S1.2.1 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) ^{13}C -NMR

S1.3.0 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ^1H -NMR

S1.3.1 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ^{13}C -NMR

S1.3.2 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ^{29}Si -NMR

S1.4.0 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) ^1H -NMR

S1.4.1 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) ^{13}C -NMR

S1.4.2 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) ^{29}Si -NMR

S1.5.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) ^1H -NMR

S1.5.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) ^{13}C -NMR

S1.6.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafluorene (2) ^1H -NMR

S1.6.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafluorene (2) ^{13}C -NMR

S1.7.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) ^1H -NMR

S1.7.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) ^{13}C -NMR

- S1.8.0 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafuorene (4) ^1H -NMR
- S1.8.1 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafuorene (4) ^{13}C -NMR
- S1.9.0 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafuorene (5) ^1H -NMR
- S1.9.1 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafuorene (5) ^{13}C -NMR
- S1.10.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafuorene (6) ^1H -NMR
- S1.10.1 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafuorene (6) ^{13}C -NMR
- S1.11.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafuorene (7) ^1H -NMR
- S1.11.1 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafuorene (7) ^{13}C -NMR
- S1.12.0 – Poly(3,6-dimethoxy-9,9-dihexylsilafuorene) (PDHSF) (9) ^1H -NMR
- S1.13.0 – Poly(3,6-dimethoxy-9,9-dioctylsilafuorene) (PDOSF) (10) ^1H -NMR
- S1.14.0 – Poly(3,6-dimethoxy-9,9-dimethylsilafuorene) (PDMSF) (11) ^1H -NMR
- S1.15.0 – Poly(3,6-dimethoxy-9,9-methylvinylsilafuorene) (PMVSF) (12) ^1H -NMR
- S1.16.0 – Poly(3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl] silafuorene)(PMCySF) (13) ^1H - NMR
- S1.17.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafuorene) (PHCySF) (14) ^1H -NMR
- S1.18.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafuorene) (PHNSF) (15) ^1H -NMR
- S1.19.0 – Partial Grignard Metathesis of Monomer (9) (66% Conversion, MeOH Quenched) ^1H -NMR
- S1.19.1 – Grignard Metathesis of Monomer (**9**) (90% Conversion, MeOH Quenched) ^1H -NMR

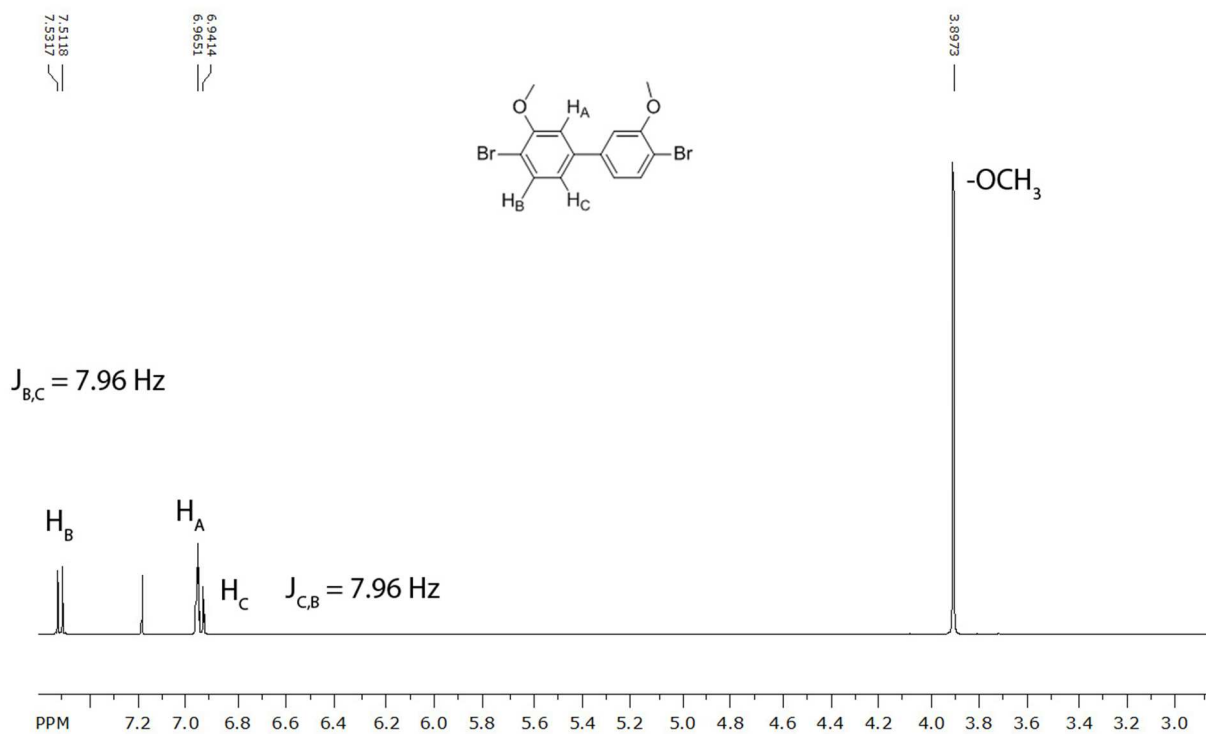
Section 2: Optoelectronic Polymer Properties

S2.1—Complete Solution Phase Absorption and Photoluminescence Spectra (Normalized)

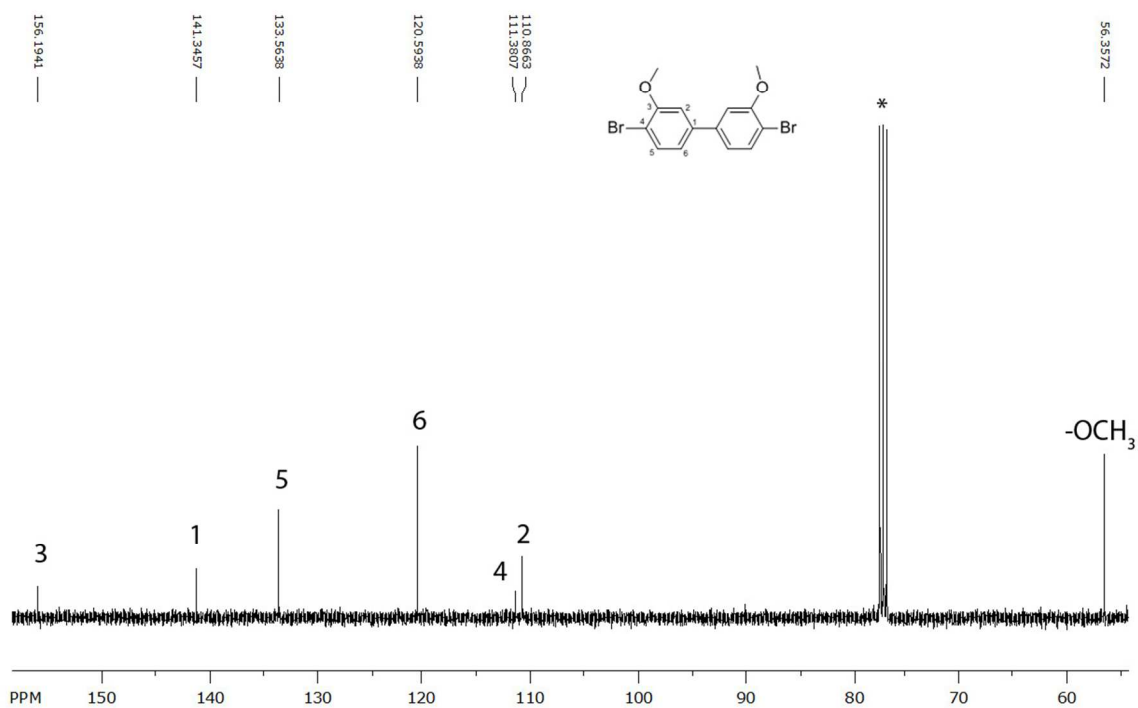
S2.2-- Complete Solid Phase Photoluminescence Spectra (Normalized)

S2.3—Complete Set of Cyclic Voltammograms for polymers (9-15)

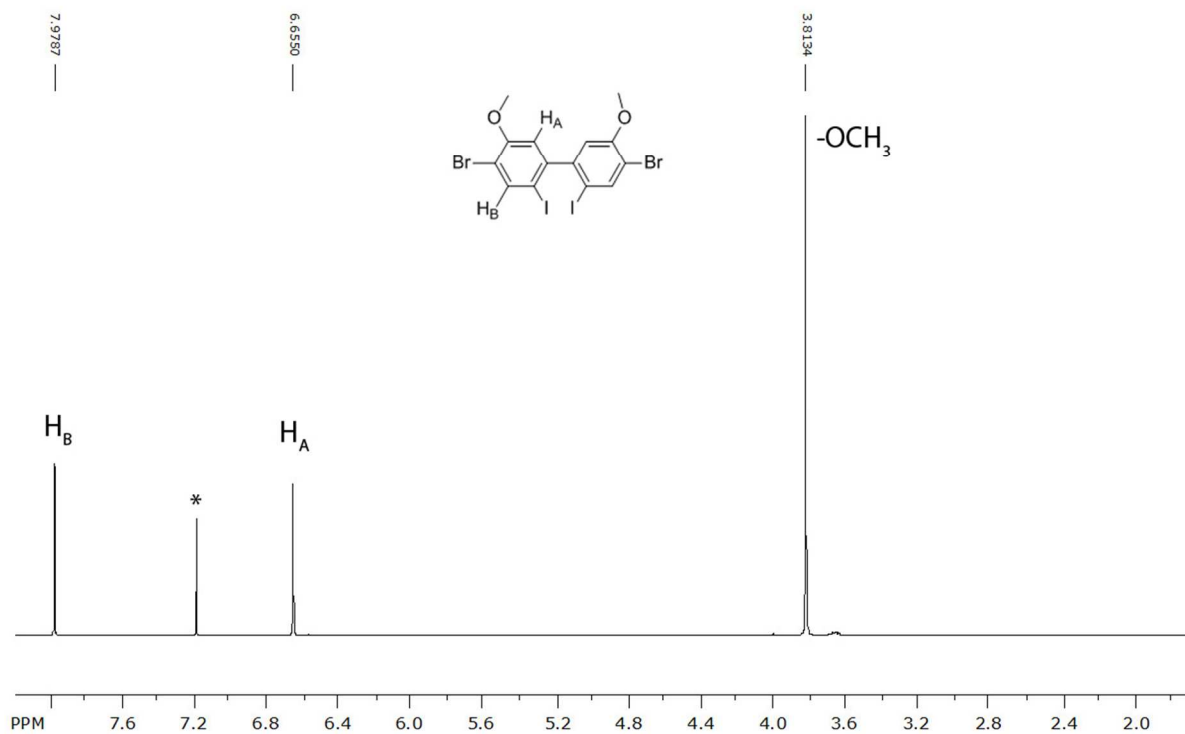
- S2.3.1— PDHSF (9) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.2— (PDOSF) (10) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.3— (PDMSF) (11) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.4— (PMVSF) (12) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.5— (PMCySF) (13) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.6— (PHCySF) (14) (Solutions in DCM with 120mM TBAPF₆)
- S2.3.7— (PHNSF) (15) (Solutions in DCM with 120mM TBAPF₆)
- S2.4— TGA/DSC curves
 - S2.4.1— TGA/DSC (PDOSF) (10)
 - S2.4.2— TGA/DSC (PDMSF) (11)
 - S2.4.3— TGA/DSC (PMVSF) (12)
 - S2.4.4— TGA/DSC (PMCySF) (13)
 - S2.4.5— TGA/DSC (PHCySF) (14)
 - S2.4.6— TGA/DSC (PHNSF) (15)
 - S2.4.7— EI-MS of HNSF (7) showing retro Diels-Alder fracturing of the norbornenyl group



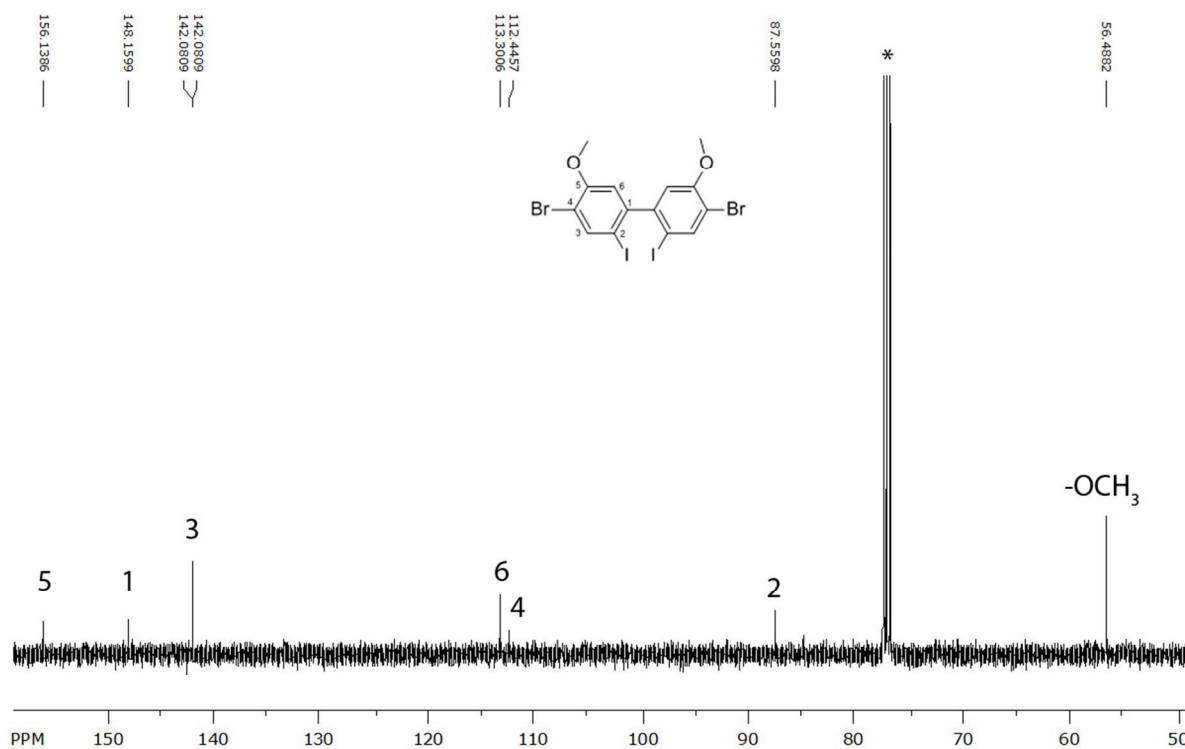
S1.1.0 –4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) ¹H-NMR



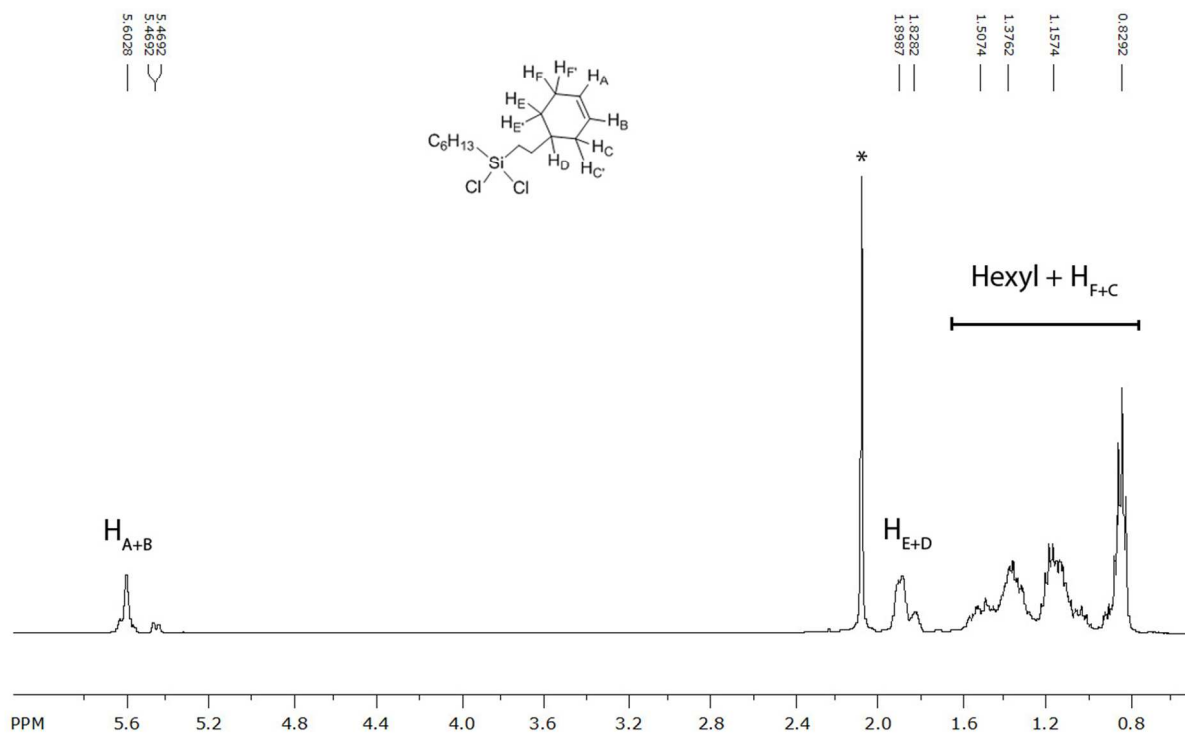
S1.1.1 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) ¹³C-NMR



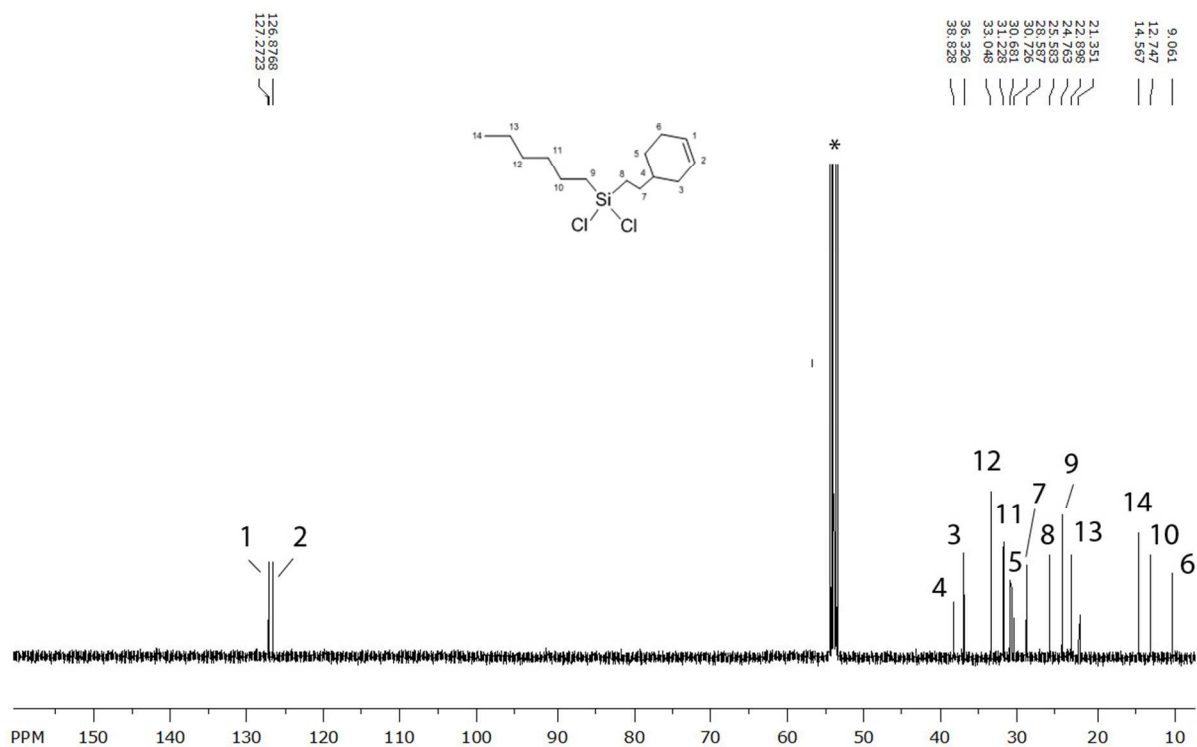
S1.2.0 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) ¹H-NMR



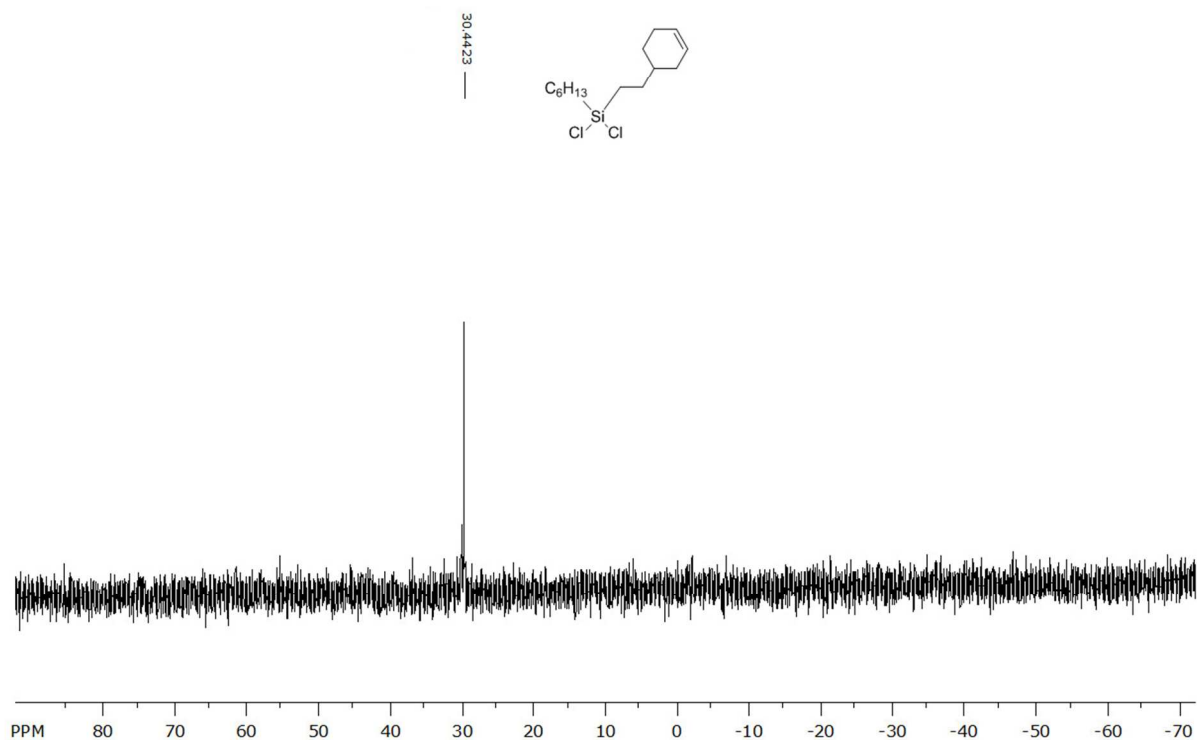
S1.2.1 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) ¹³C-NMR



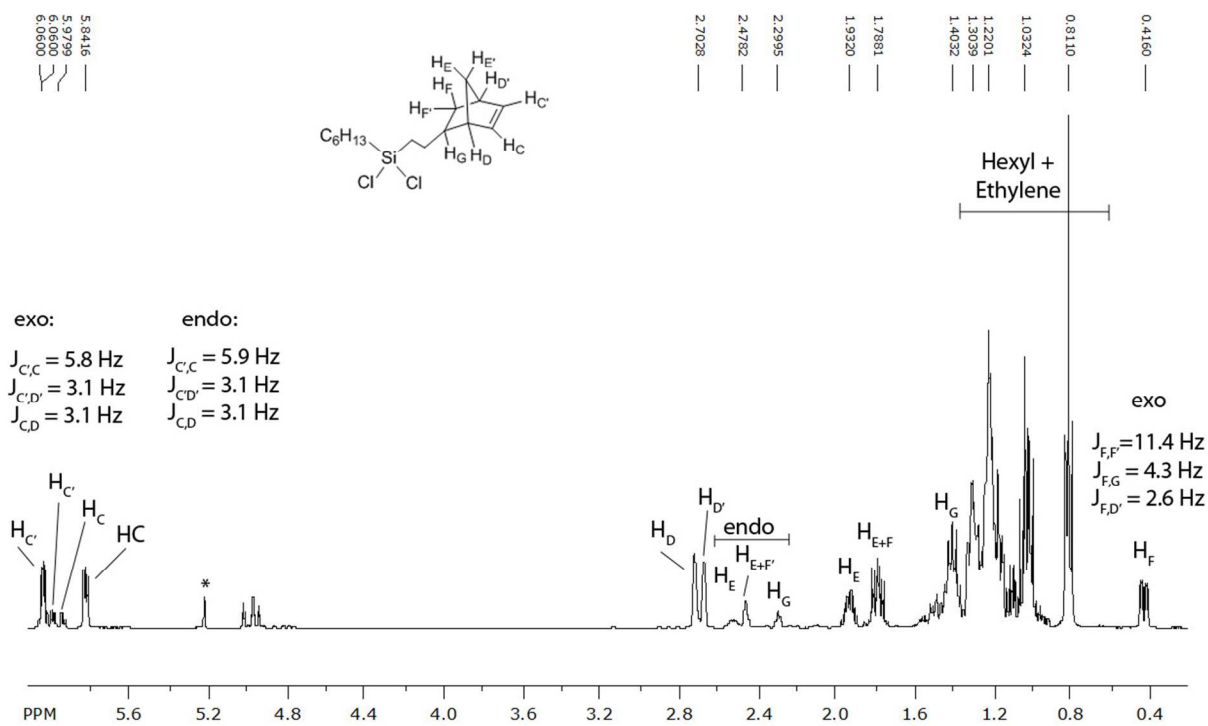
S1.3.0 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ¹H-NMR



S1.3.1 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ¹³C-NMR

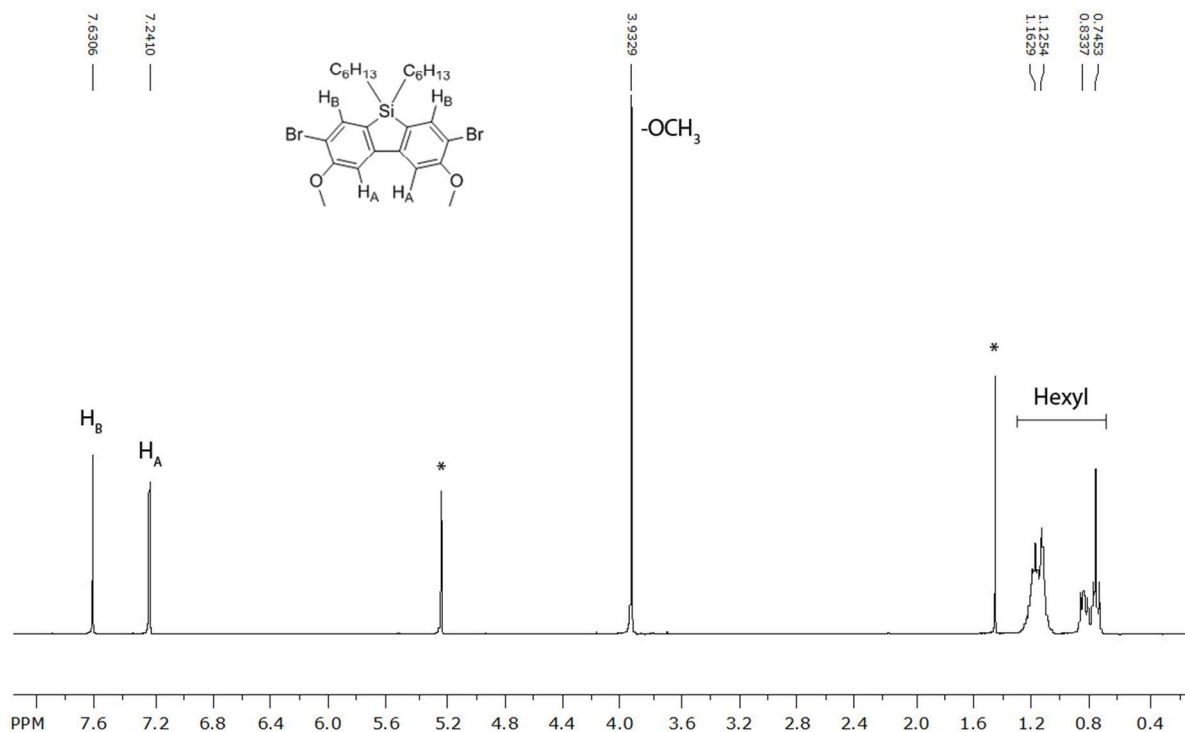


S1.3.2 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) ^{29}Si -NMR

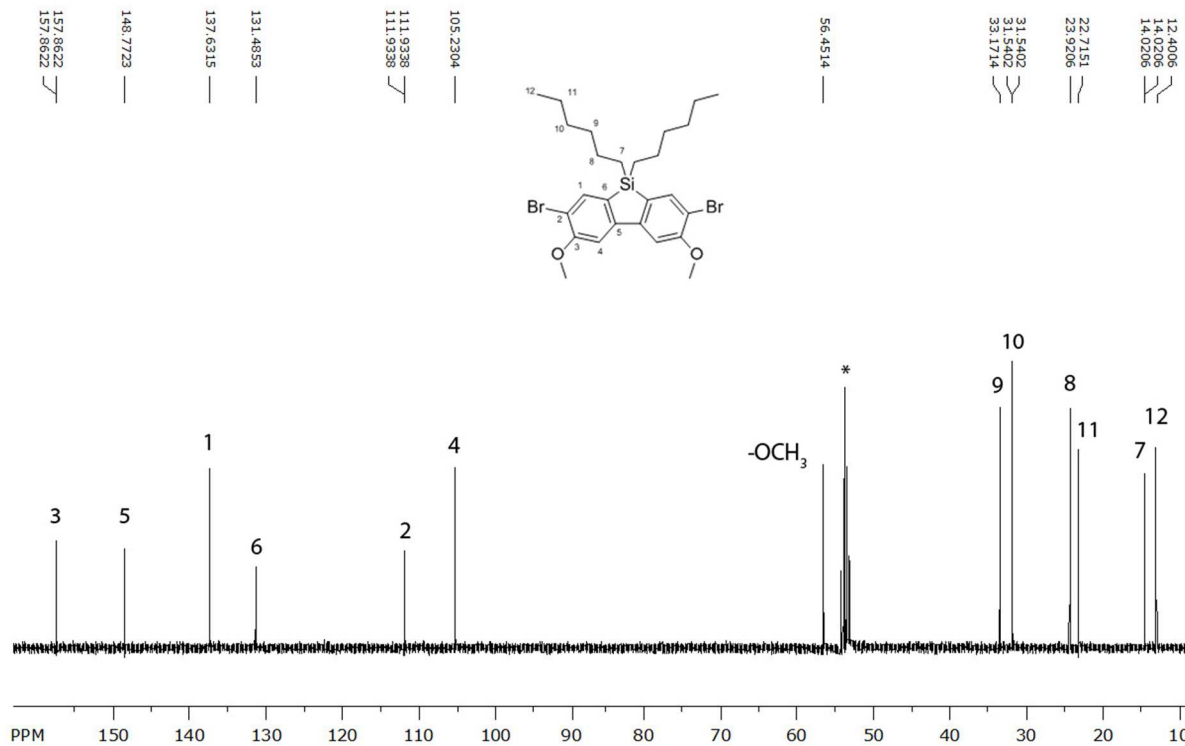


S1.4.0 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) ^1H -NMR

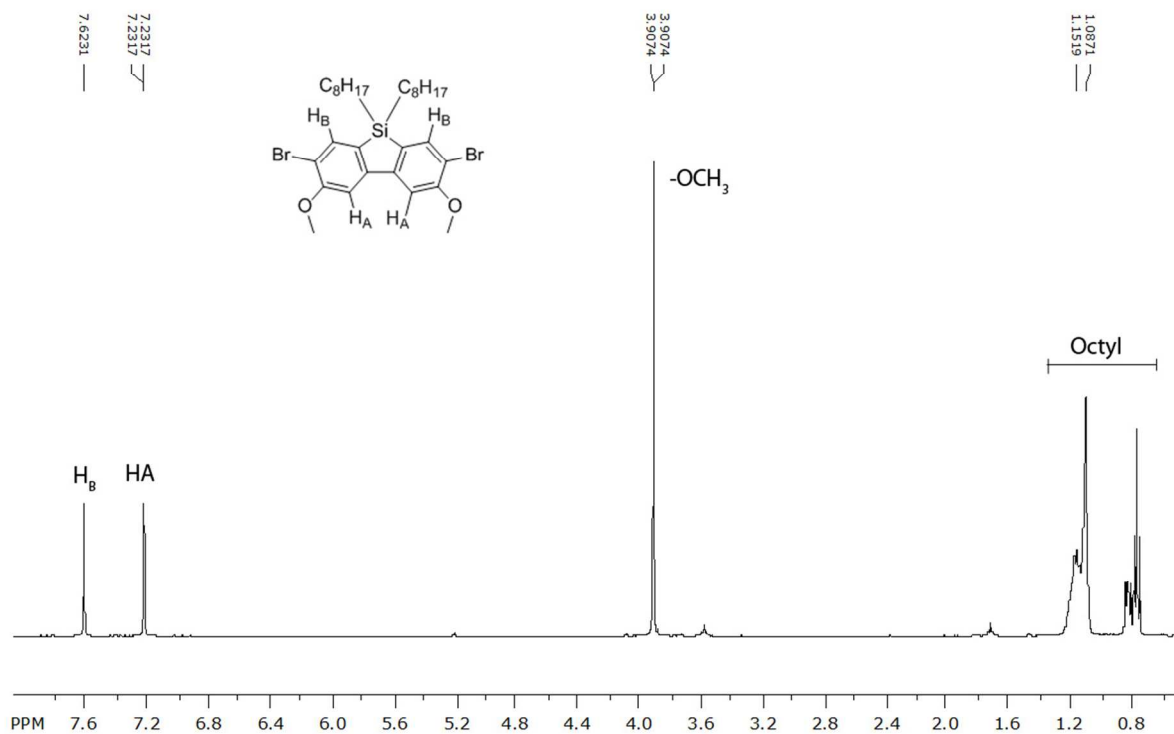




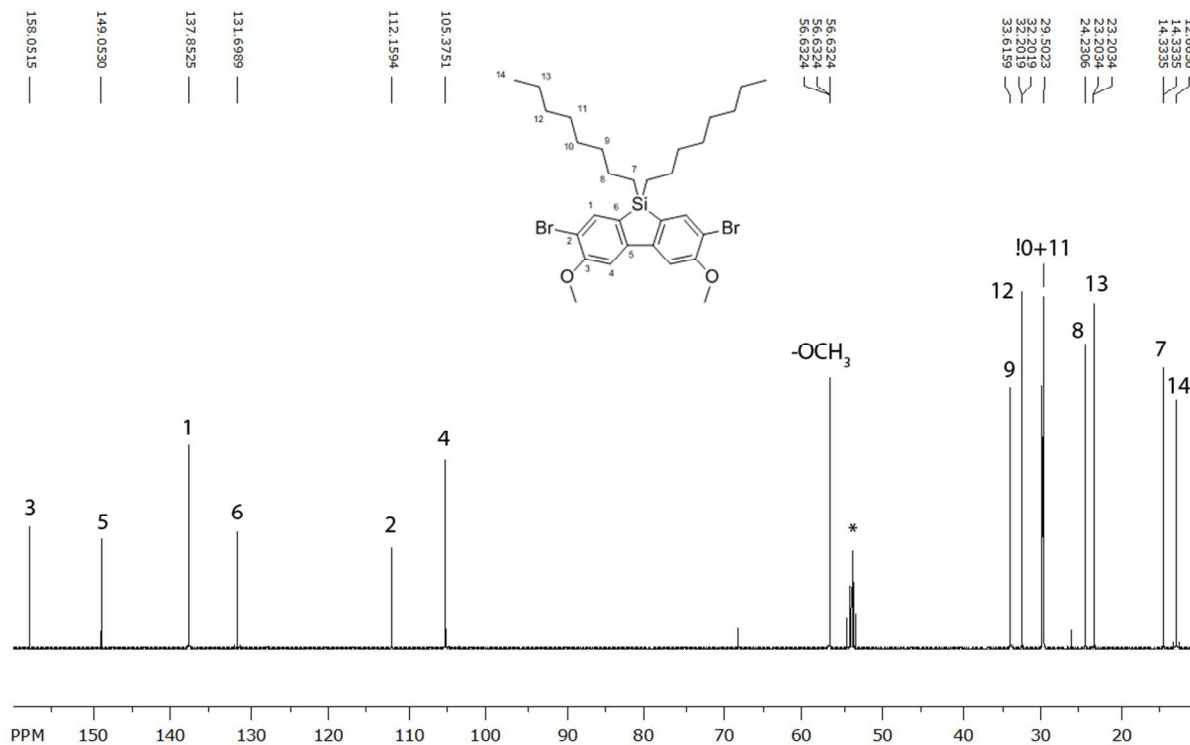
S1.5.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) ¹H-NMR



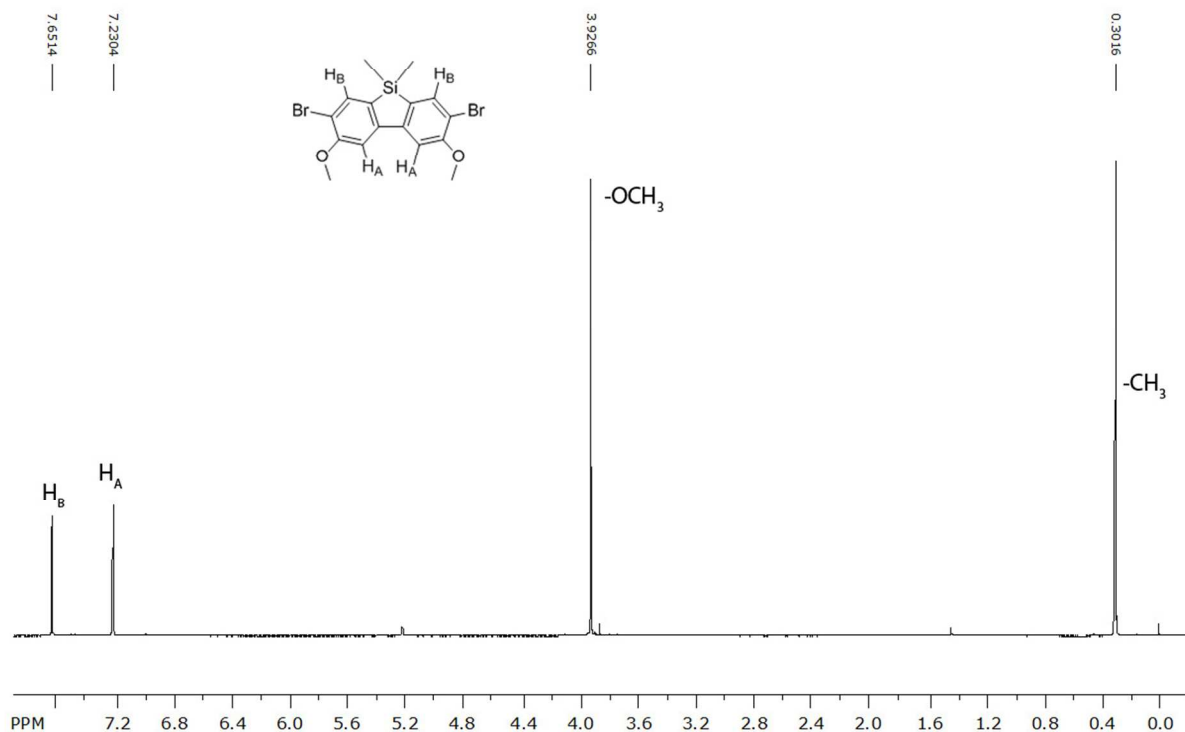
S1.5.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) ¹³C-NMR



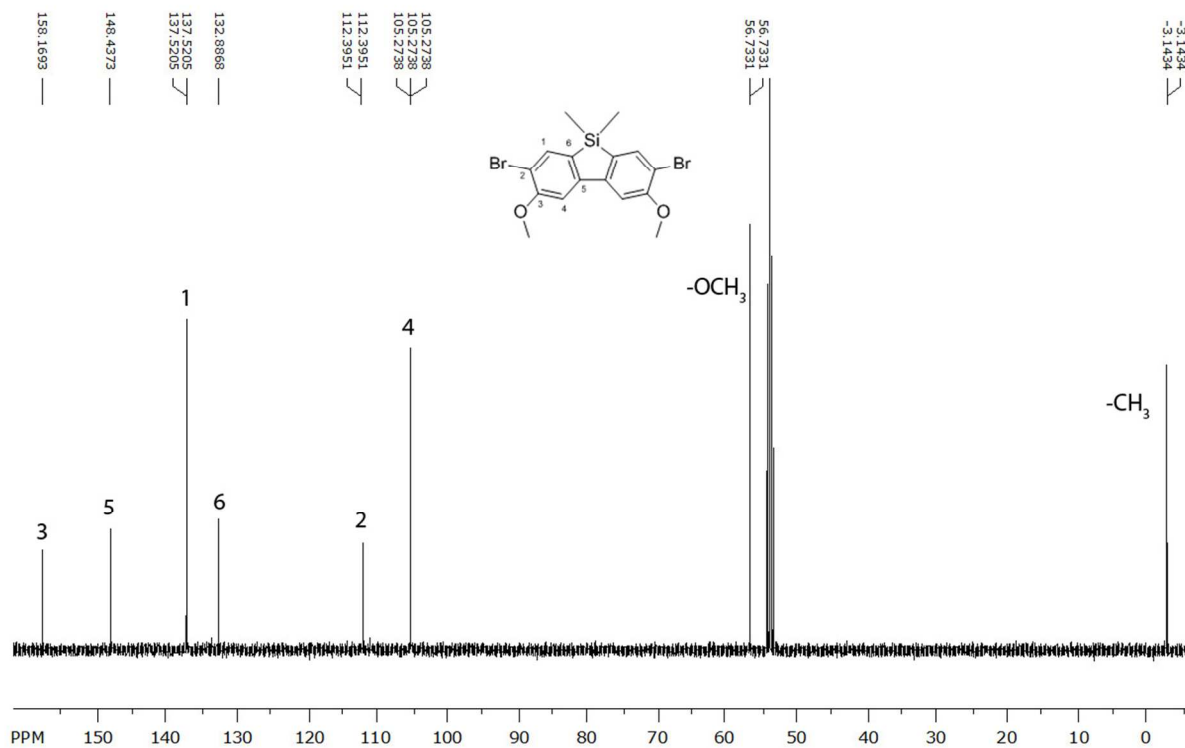
S1.6.0 –2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafluorene (2) ¹H-NMR



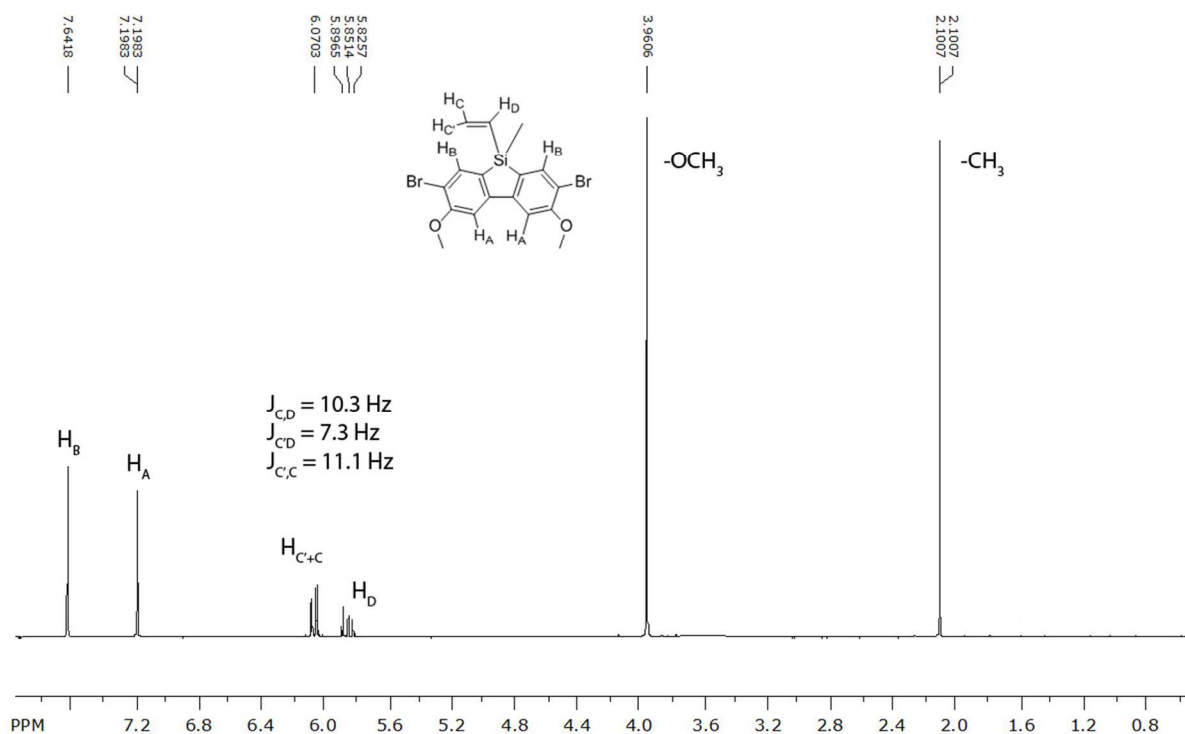
S1.6.1 –2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafluorene (2) ¹³C-NMR



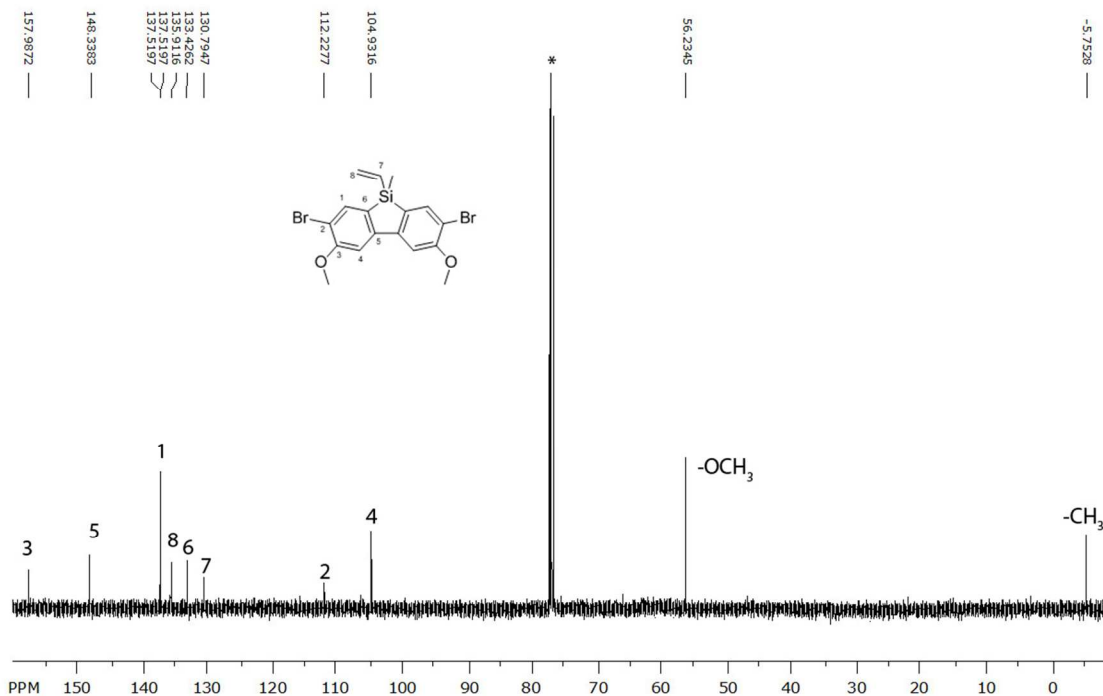
S1.7.0 –2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafuorene (3) ^1H -NMR



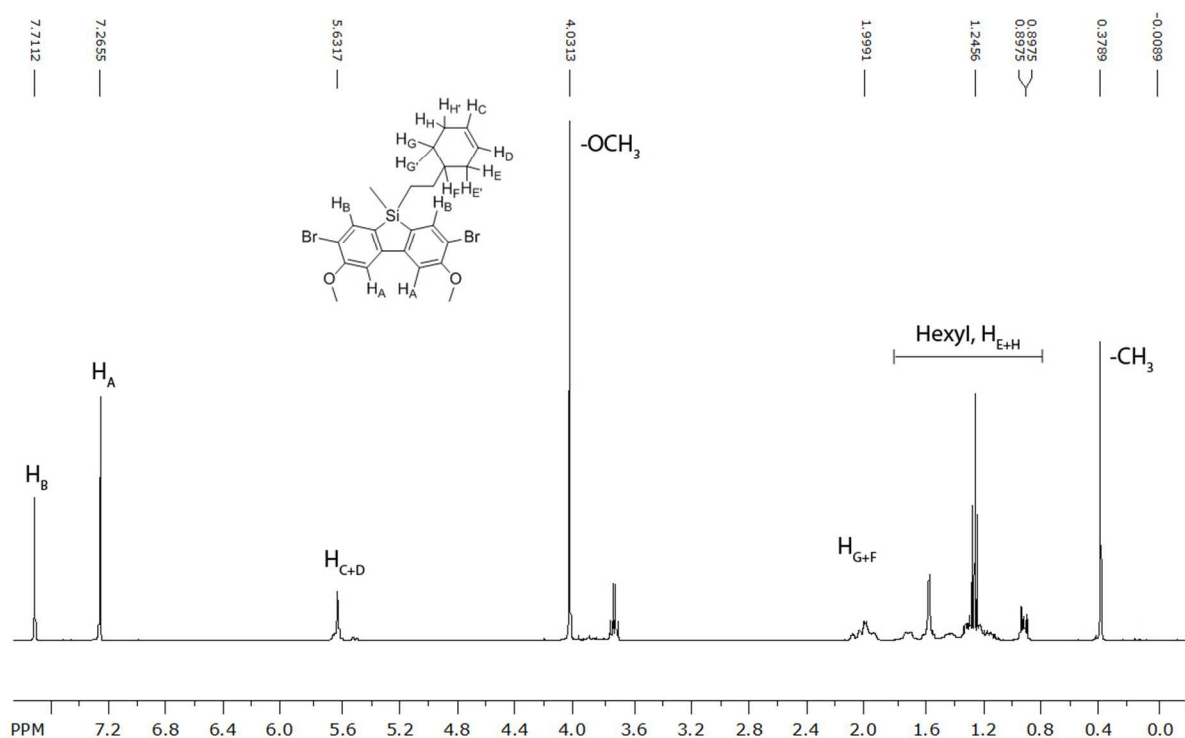
S1.7.1 –2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafuorene (3) ^{13}C -NMR



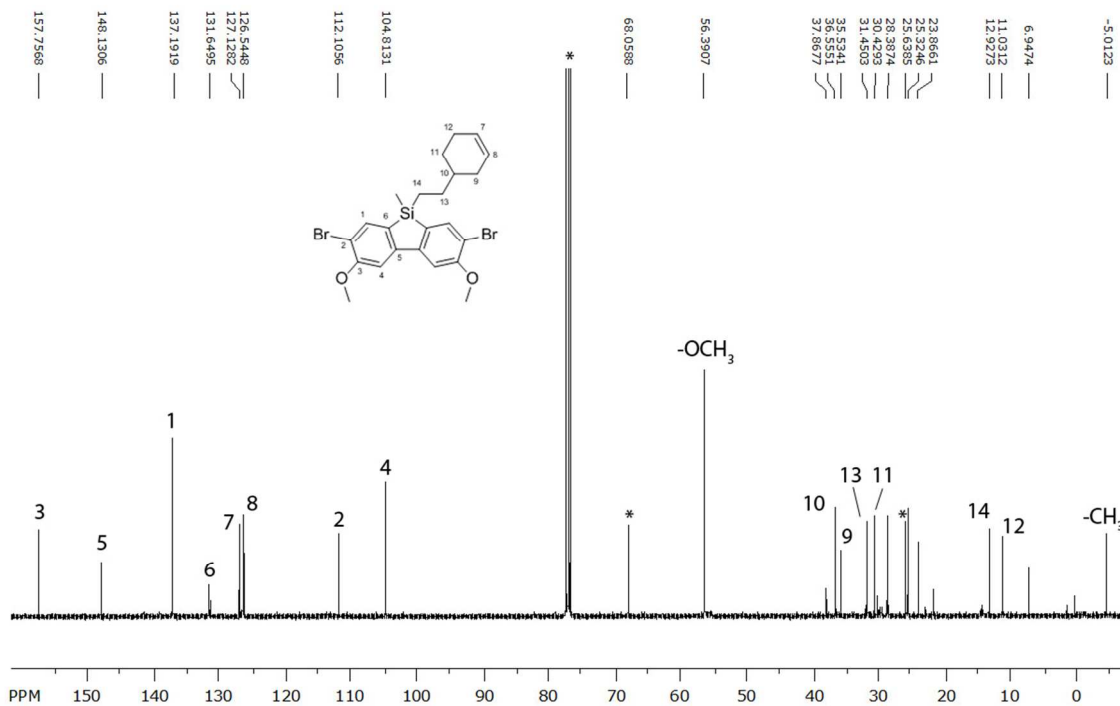
S1.8.0 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafluorene (4) $^1\text{H-NMR}$



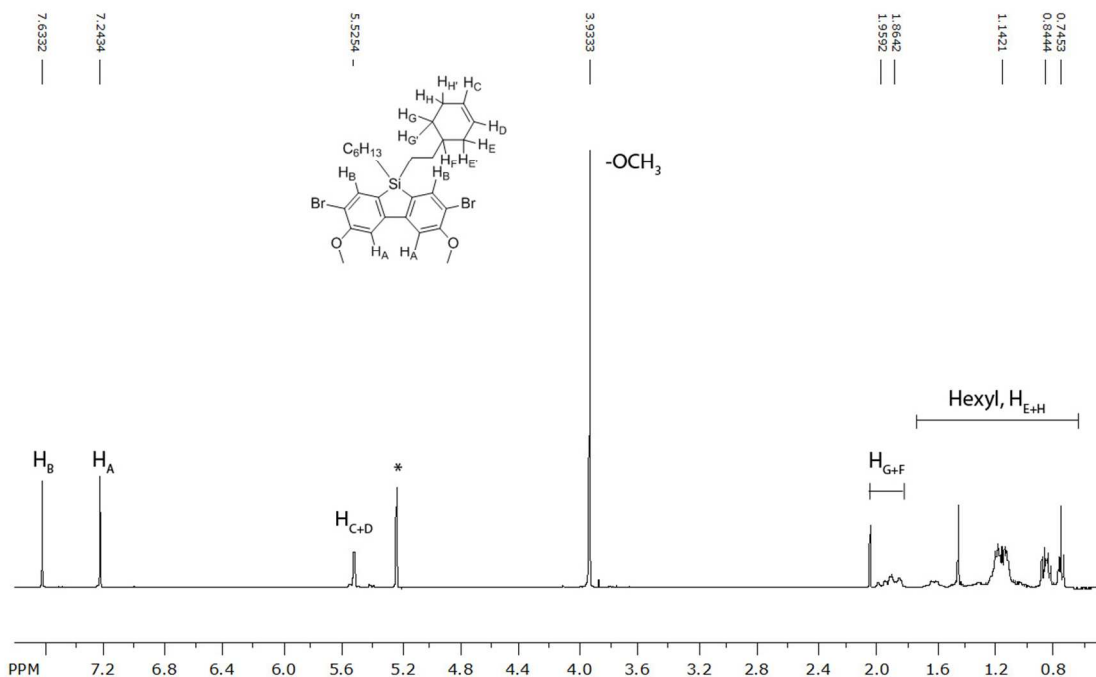
S1.8.1 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafluorene (4) $^{13}\text{C-NMR}$



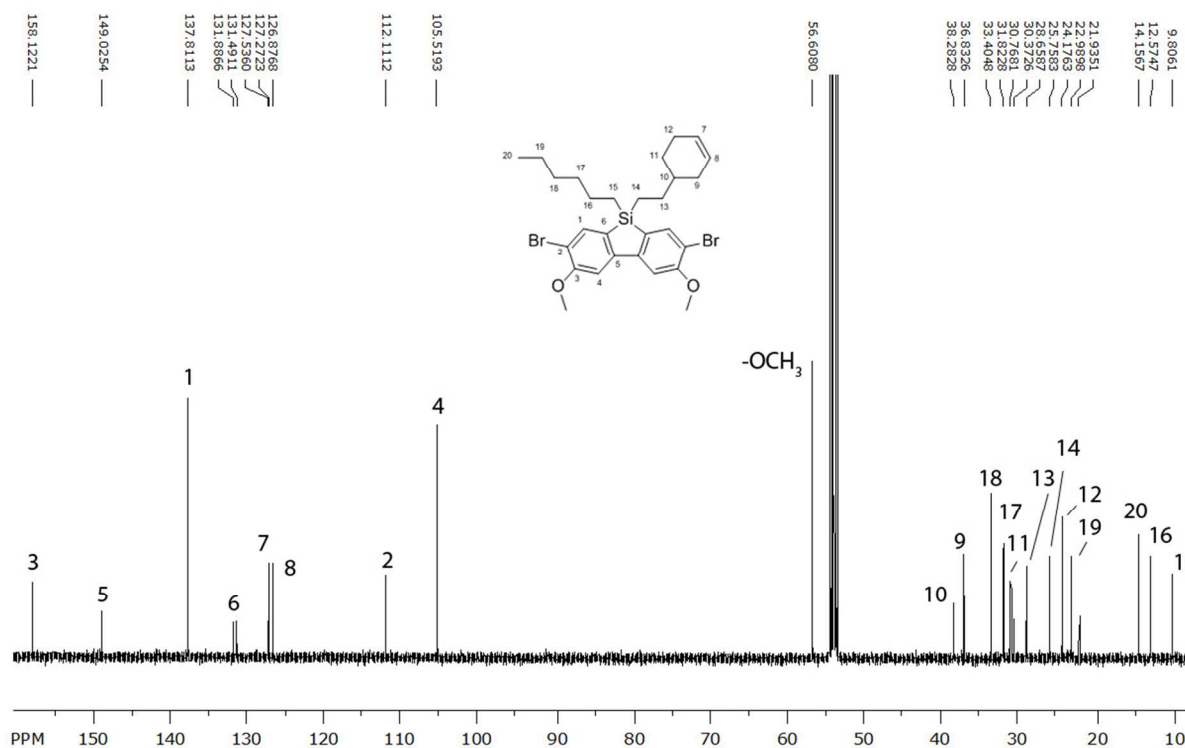
S1.9.0 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5)
¹H-NMR



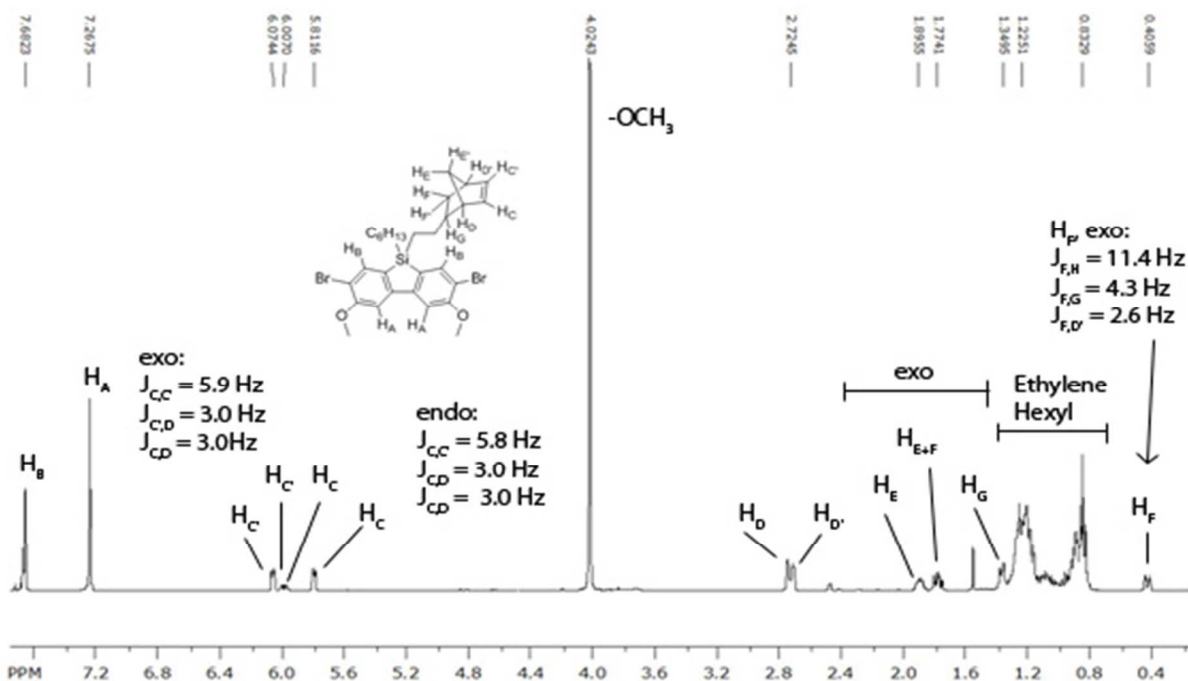
S1.9.1 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5)
¹³C-NMR



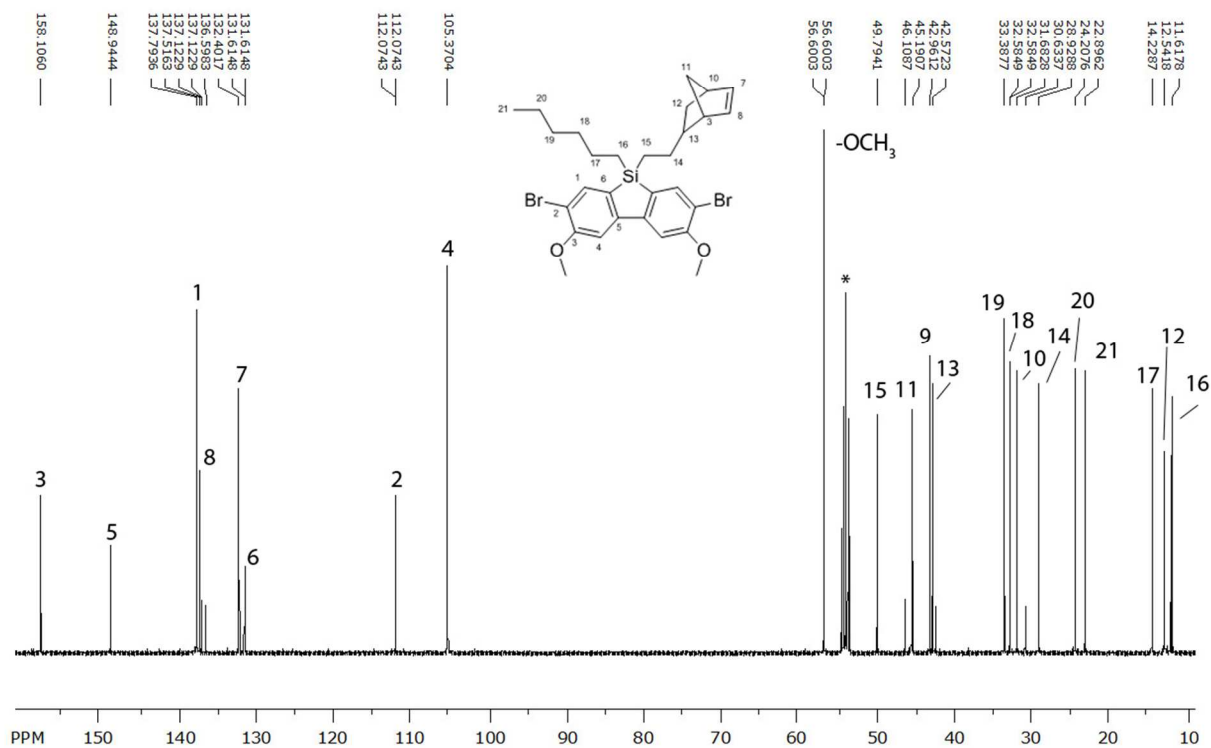
S1.10.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (**6**)
¹H-NMR



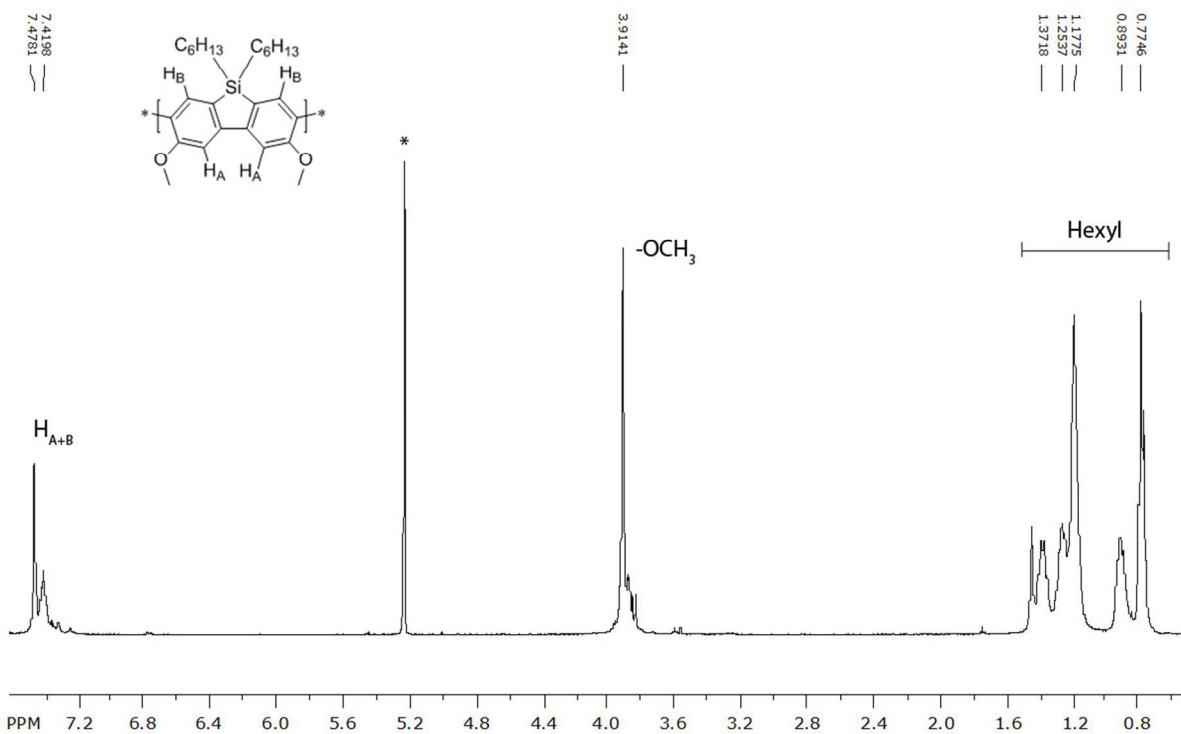
S1.10.1 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (**6**)
¹³C-NMR



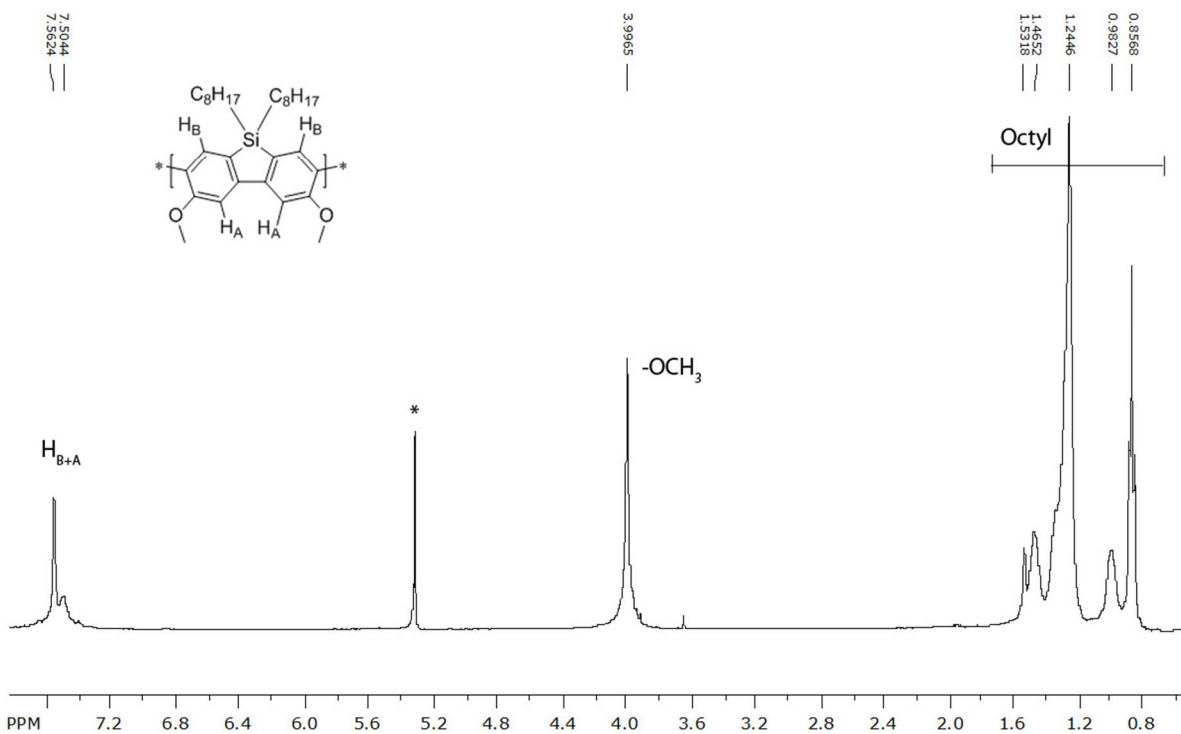
S1.11.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7) ¹H-NMR



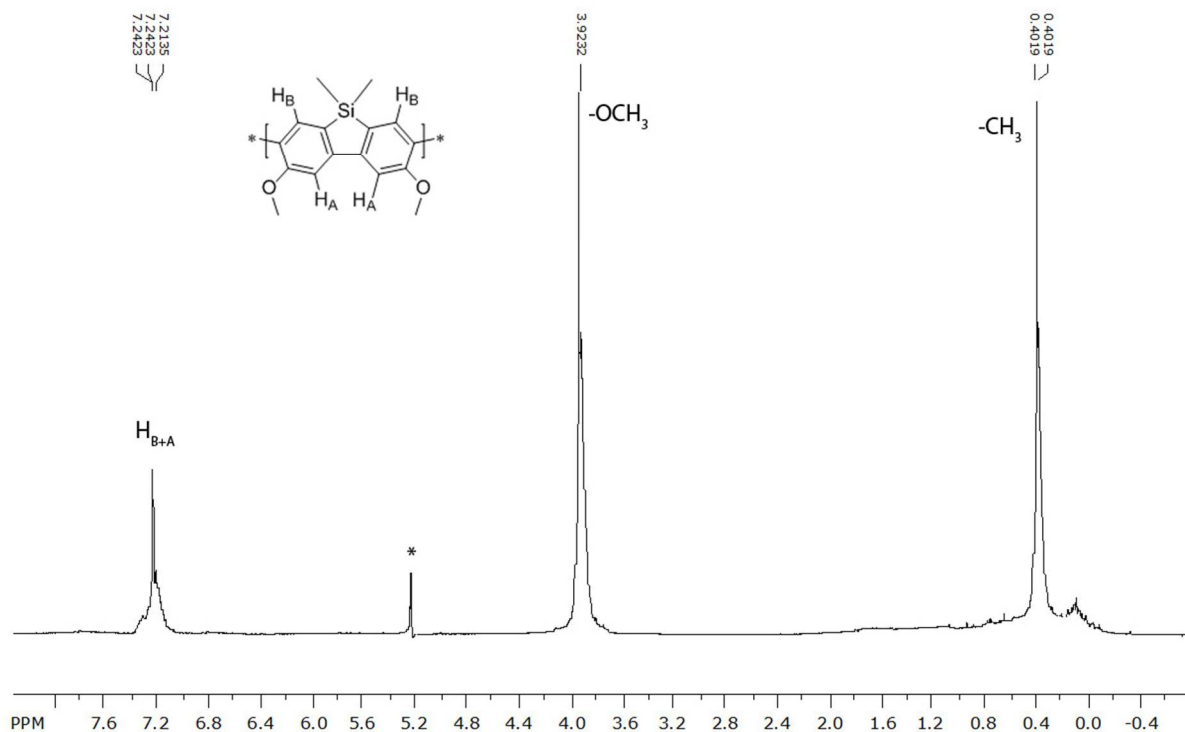
S1.11.1 –,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7) ¹³C-NMR



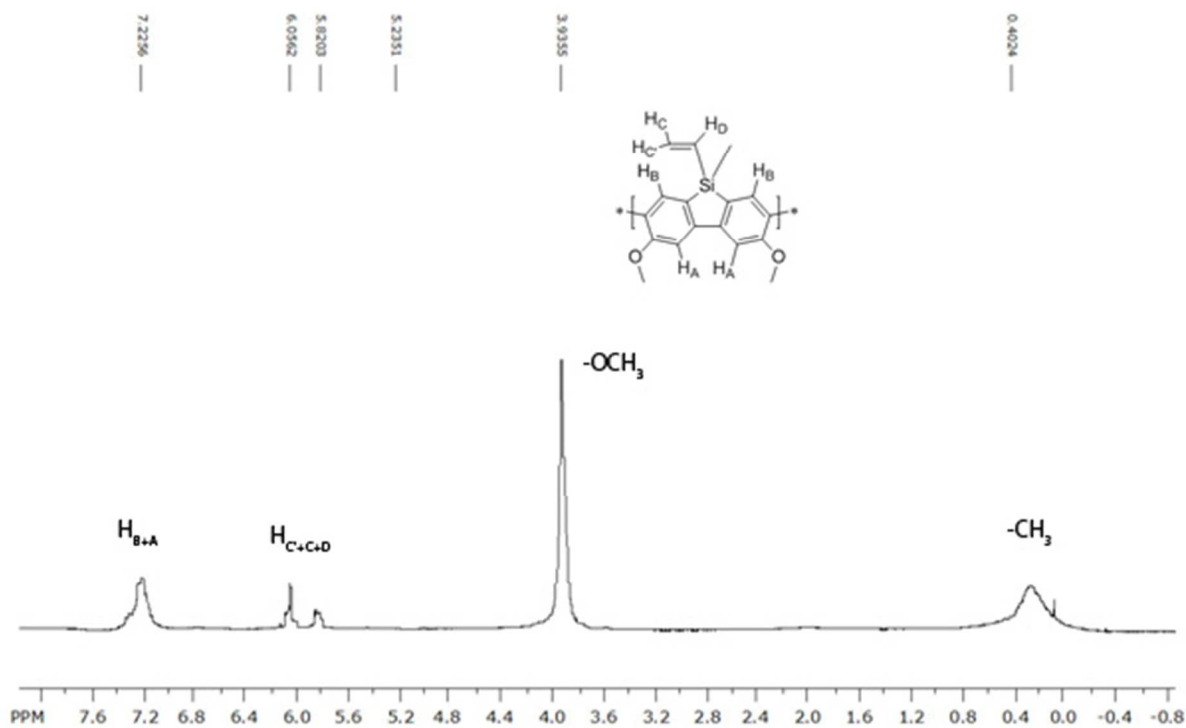
S1.12.0 – Poly(3,6-dimethoxy-9,9-dihexylsilafluorene) (PDHSF) (9) ¹H-NMR



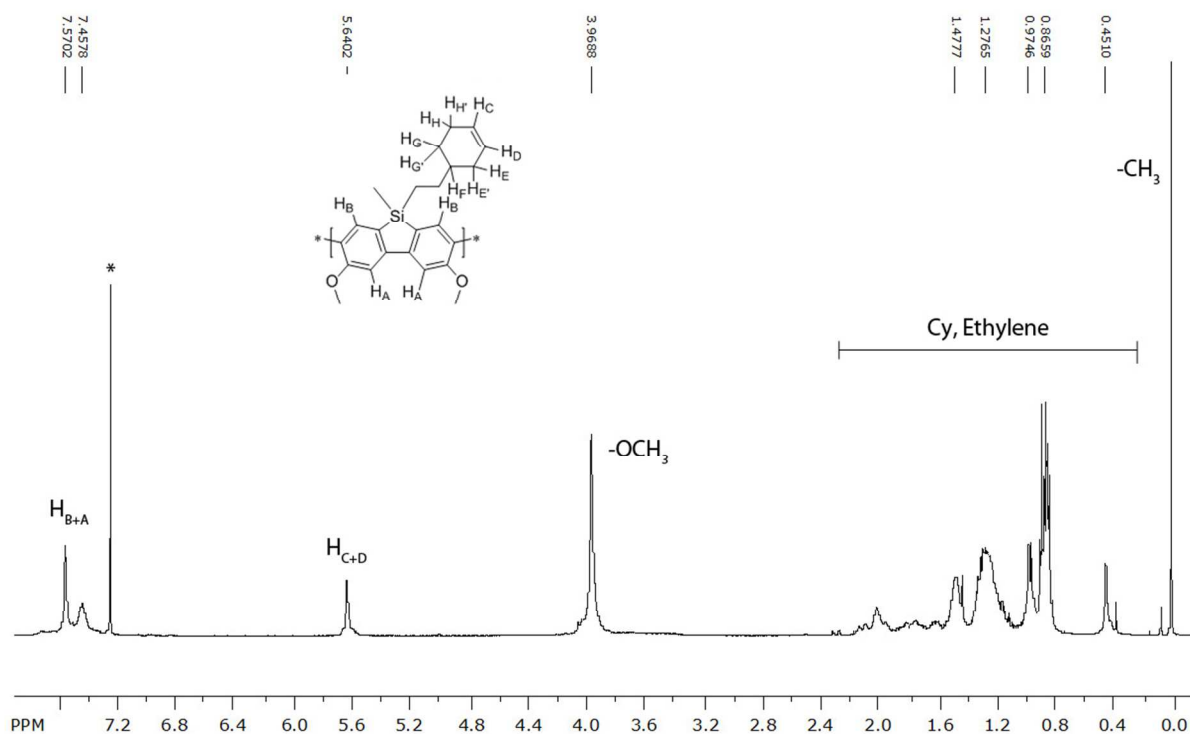
S1.13.0 – Poly(3,6-dimethoxy-9,9-dioctylsilafluorene) (PDOSF) (10) ¹H-NMR



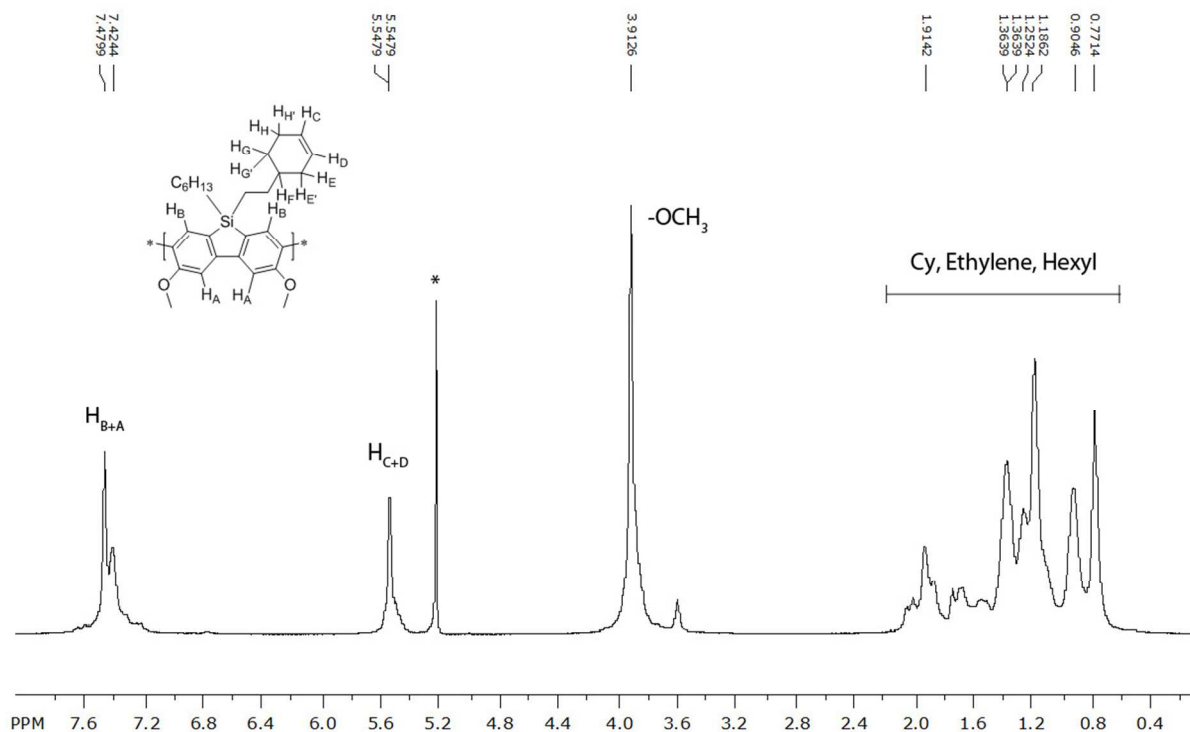
S1.14.0 – Poly(3,6-dimethoxy-9,9-dimethylsilafluorene) (PDMSF) (11) ¹H-NMR



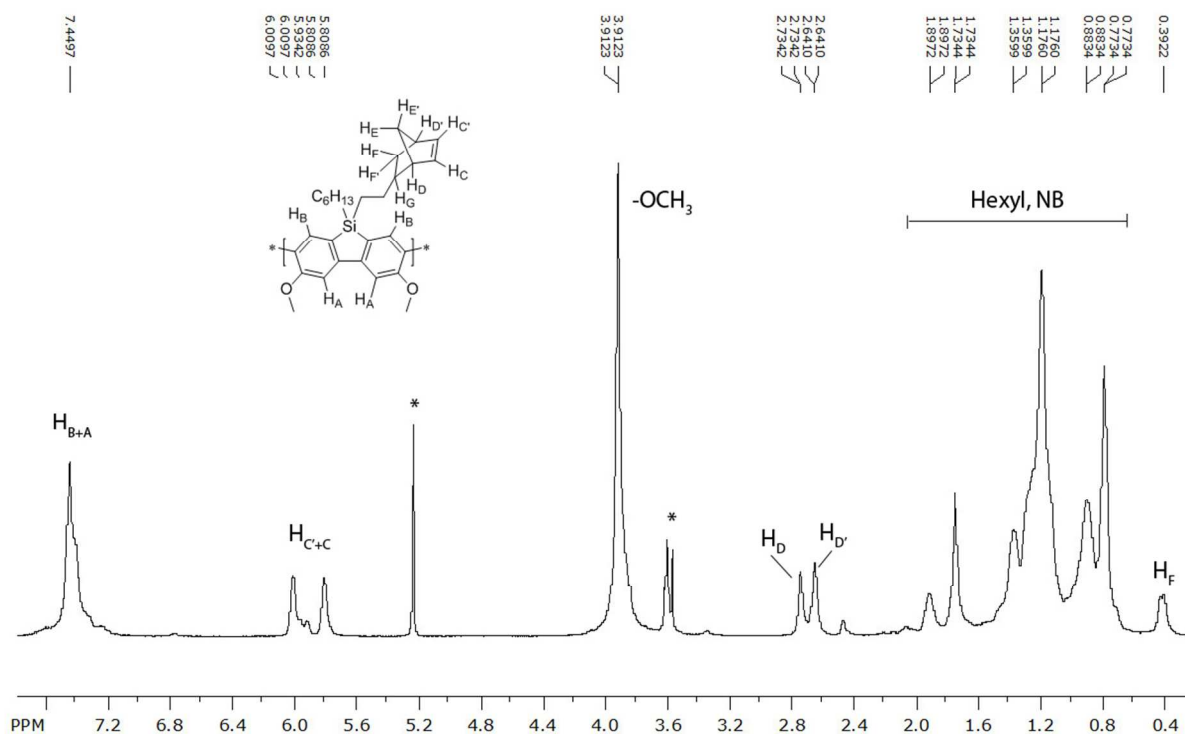
S1.15.0 – Poly(3,6-dimethoxy-9,9-methylvinylsilafluorene) (PMVSF) (12) ¹H-NMR



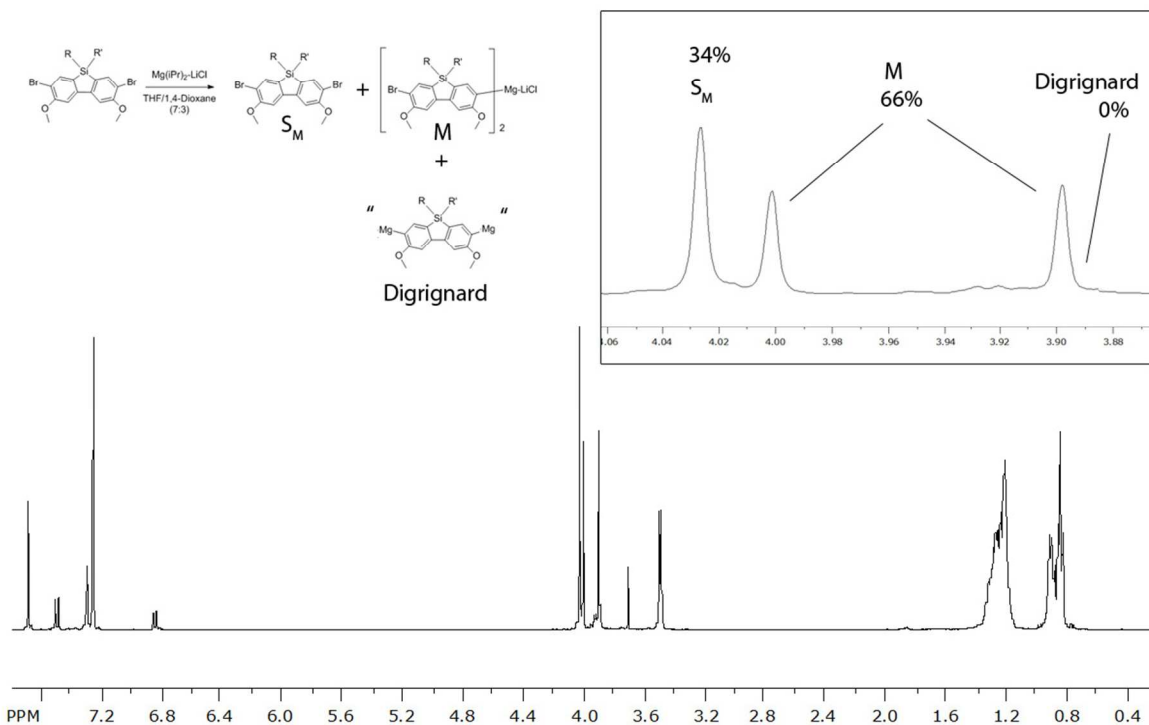
S1.16.0 – Poly(3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene)(PMCySF) (13) ¹H NMR



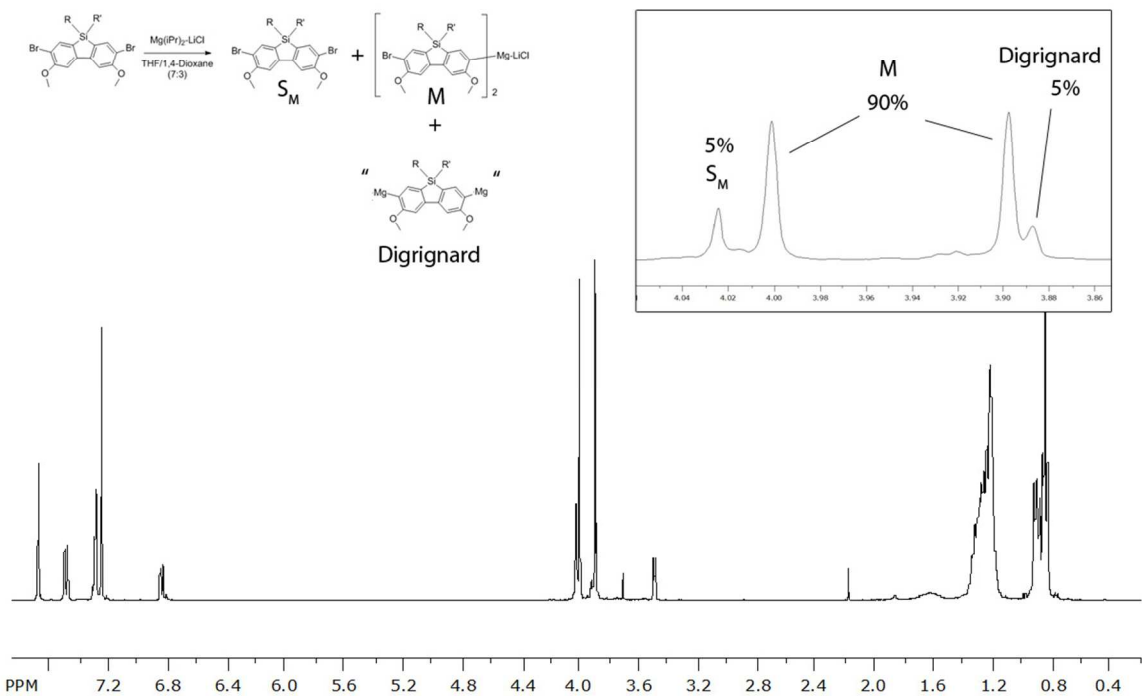
S1.17.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene) (PHCySF) (14) ¹H-NMR



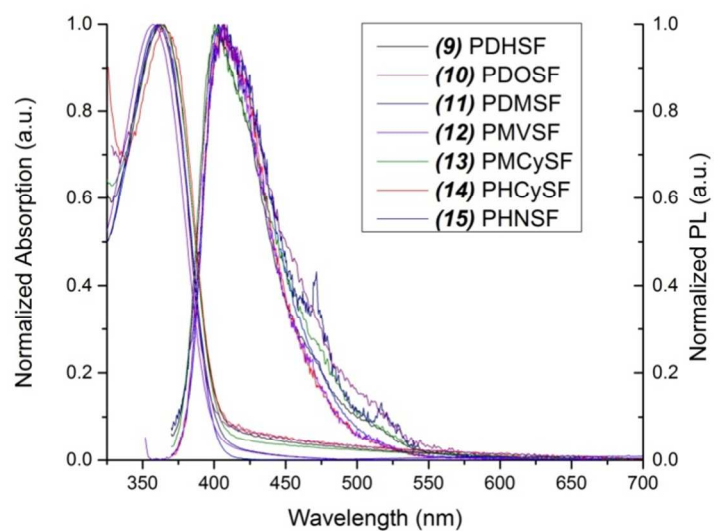
S1.18.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene) (PHNSF) (15) ^1H -NMR



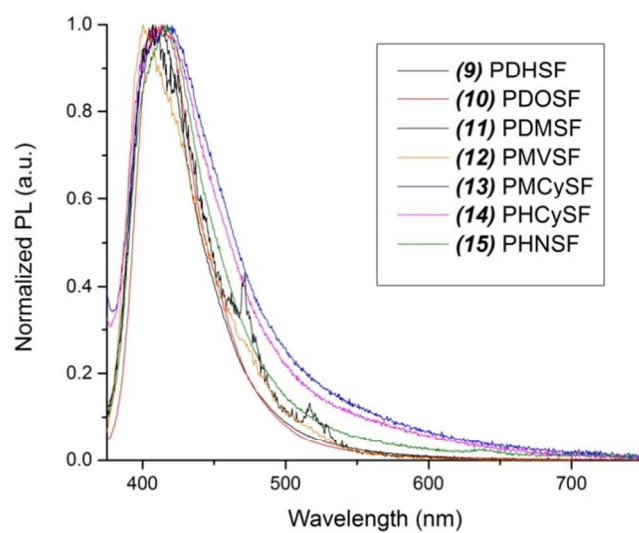
S1.19.0 – Partial Grignard Metathesis of Monomer (9) (66% Conversion, MeOH Quenched) ^1H -NMR



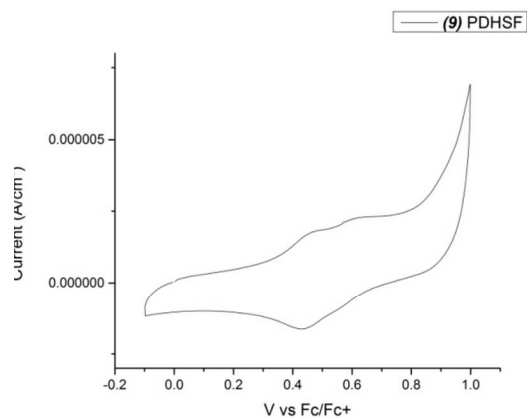
S1.19.1 – Grignard Metathesis of Monomer **(9)** (90% Conversion, MeOH Quenched) ¹H-NMR. Note the presence of both ~5% Starting material and 5% Digrignard by-product.



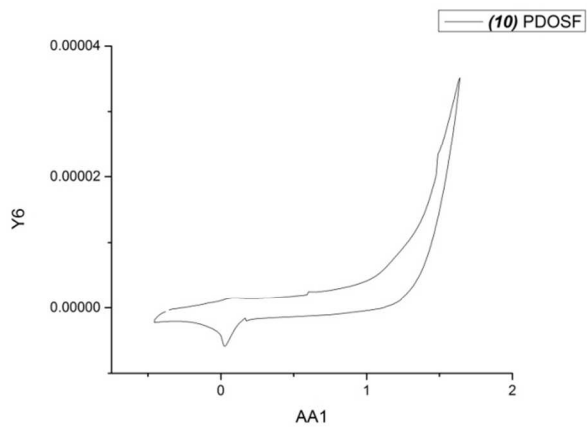
S2.1—Complete Solution Phase Absorption and Photoluminescence Spectra (Normalized)



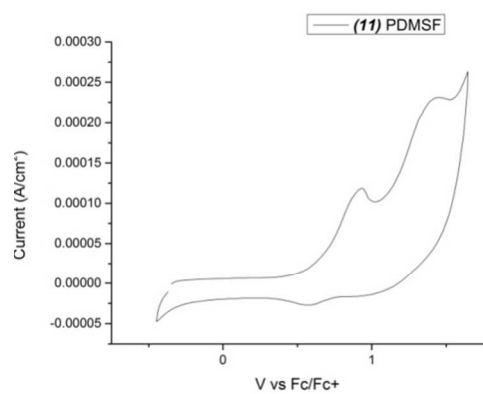
S2.2-- Complete Solid Phase Photoluminescence Spectra (Normalized)



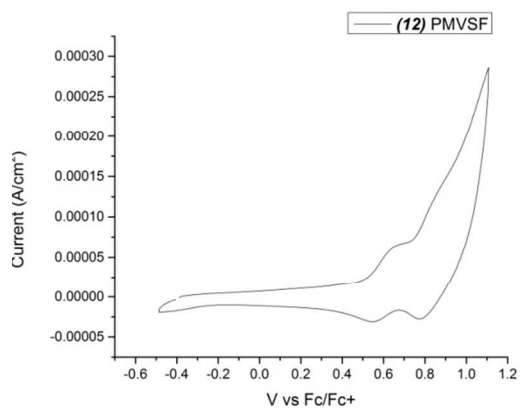
S2.3.1— PDHSF (9)



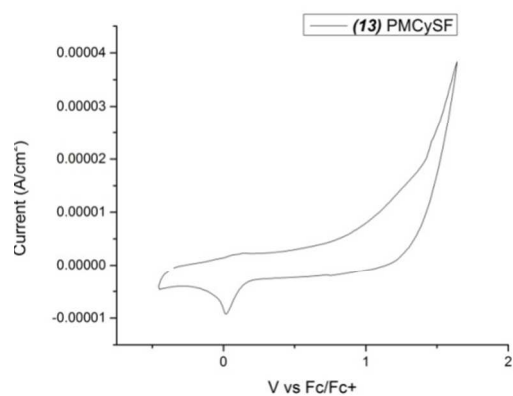
S2.3.2— PDOSF (10)



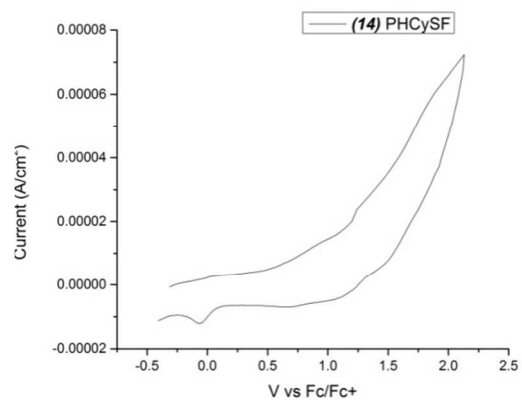
S2.3.3— PDMSF (11)



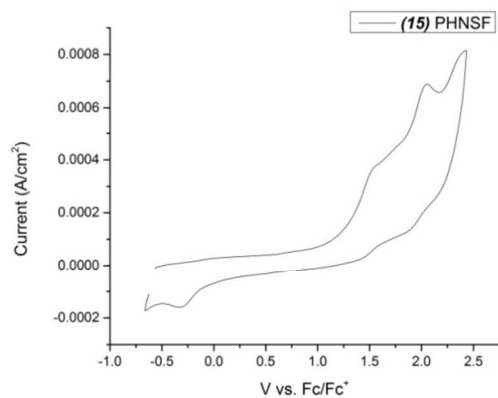
S2.3.4— PMVSF (12)



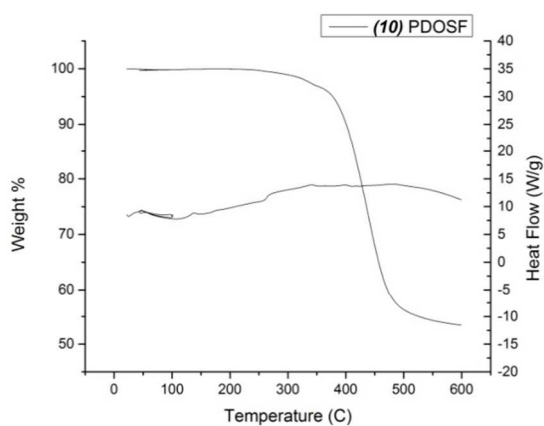
S2.3.5— PMCySF (13)



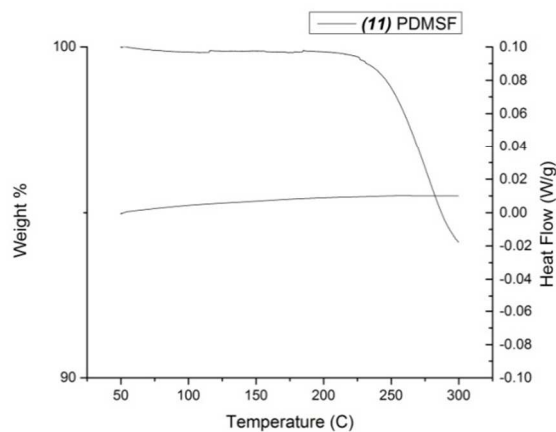
S2.3.6— PHCySF (14)



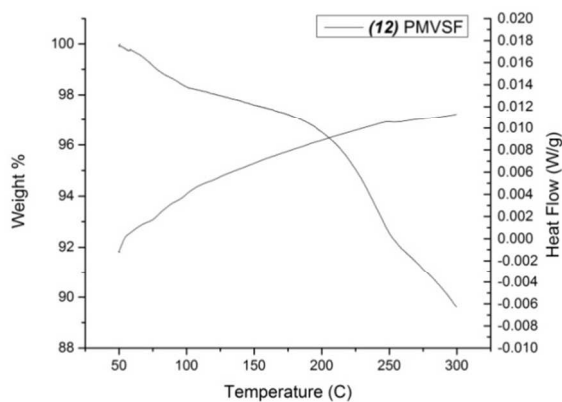
S2.3.7— PHNSF (15)



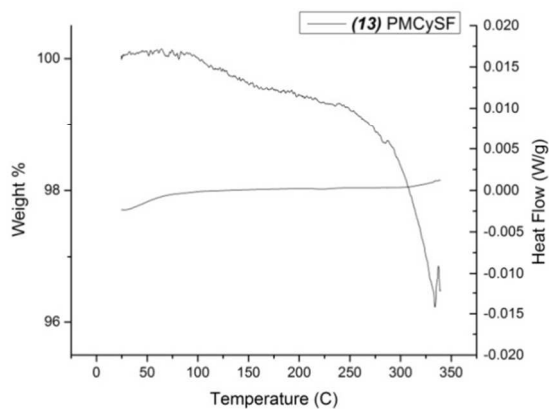
S2.4.1— TGA/DSC (PDOSF) (10)



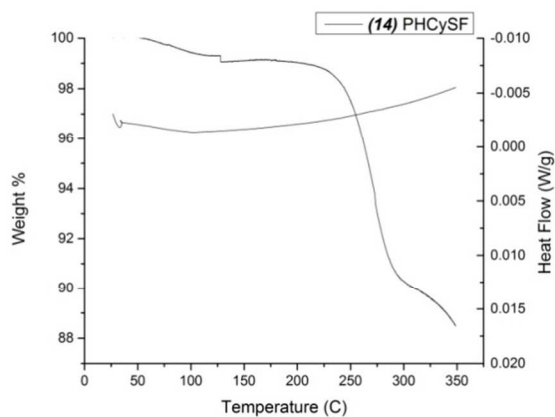
S2.4.2— TGA/DSC (PDMSF) (11)



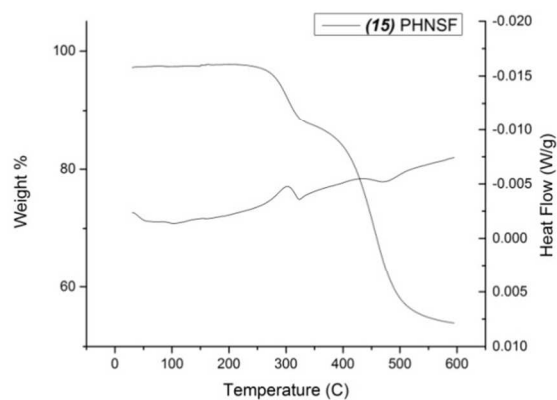
S2.4.3— TGA/DSC (PMVSF) (12)



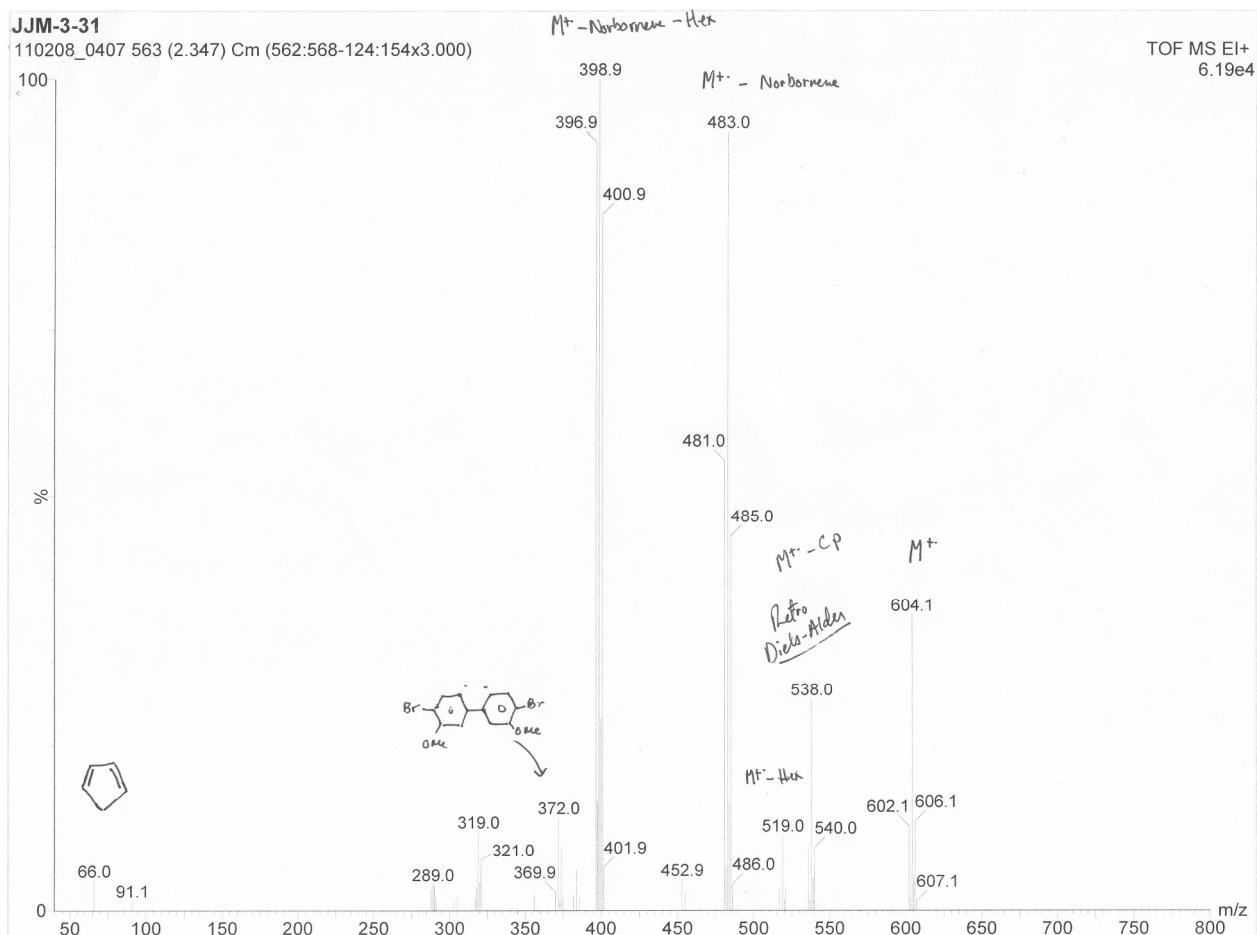
S2.4.4— TGA/DSC (PMCySF) (13)



S2.4.5— TGA/DSC (PHCySF) (14)



S2.4.1— TGA/DSC (PHNSF) (15)



S2.4.7— EI-MS of HNSF (7) showing retro diels alder fracturing of the norbornenyl group