Electronic Supporting Information (ESI) for

Synthesis of a dilithiobutadiene bearing extremely bulky silyl substituents and its reactivity toward functionalized silanes

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1. NMR spectroscopy

1.1. 1,4-Dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenyl-buta-1,3-diene (1b)

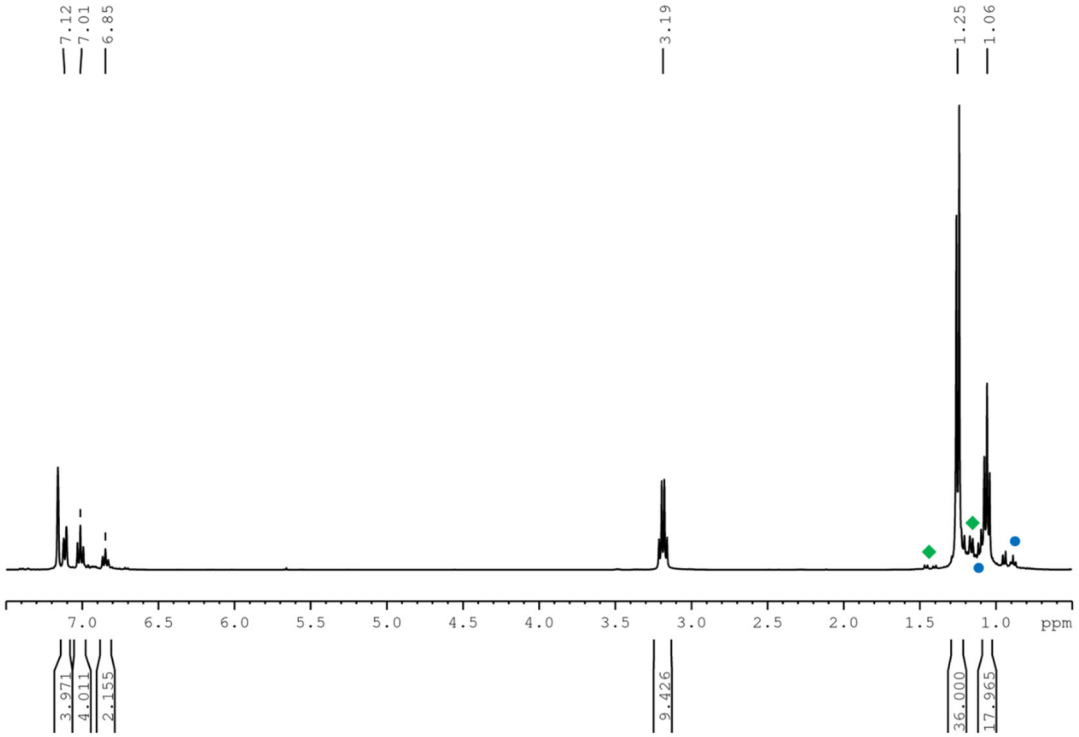

Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dilithiobutadiene **1b**. ◆ Residual dilithiodibenzopentalene **2b**. ● *n*-hexane.

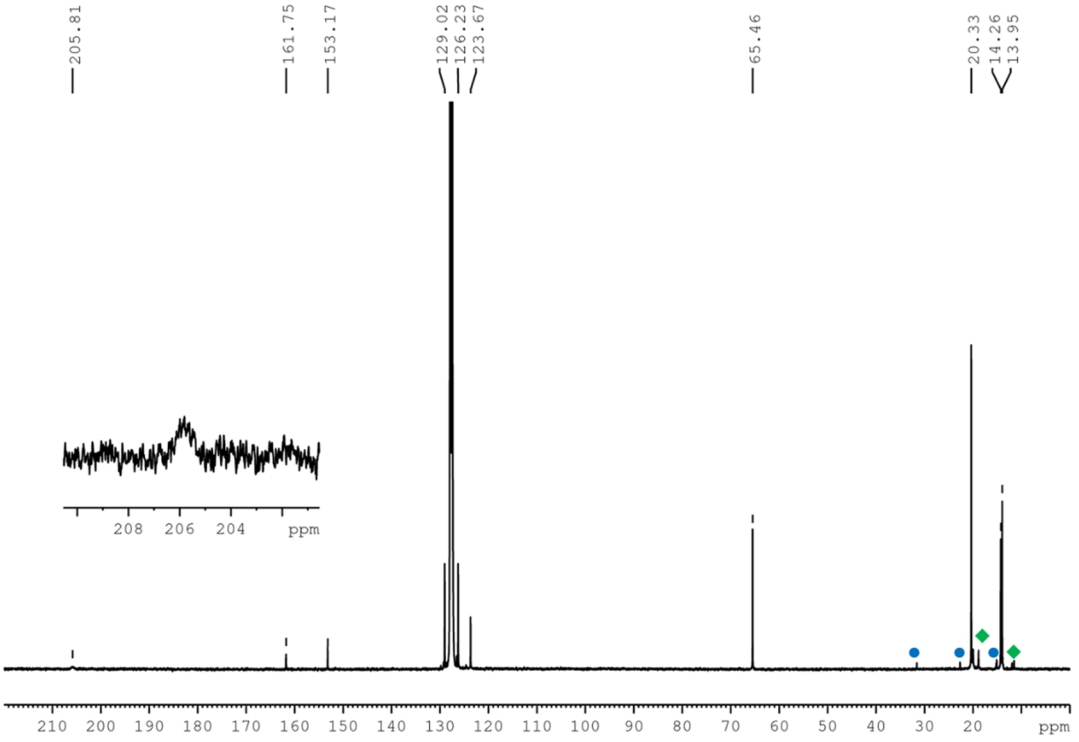

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of dilithiobutadiene **1b**. ◆ Residual dilithiodibenzopentalene **2b**. ● *n*-hexane.

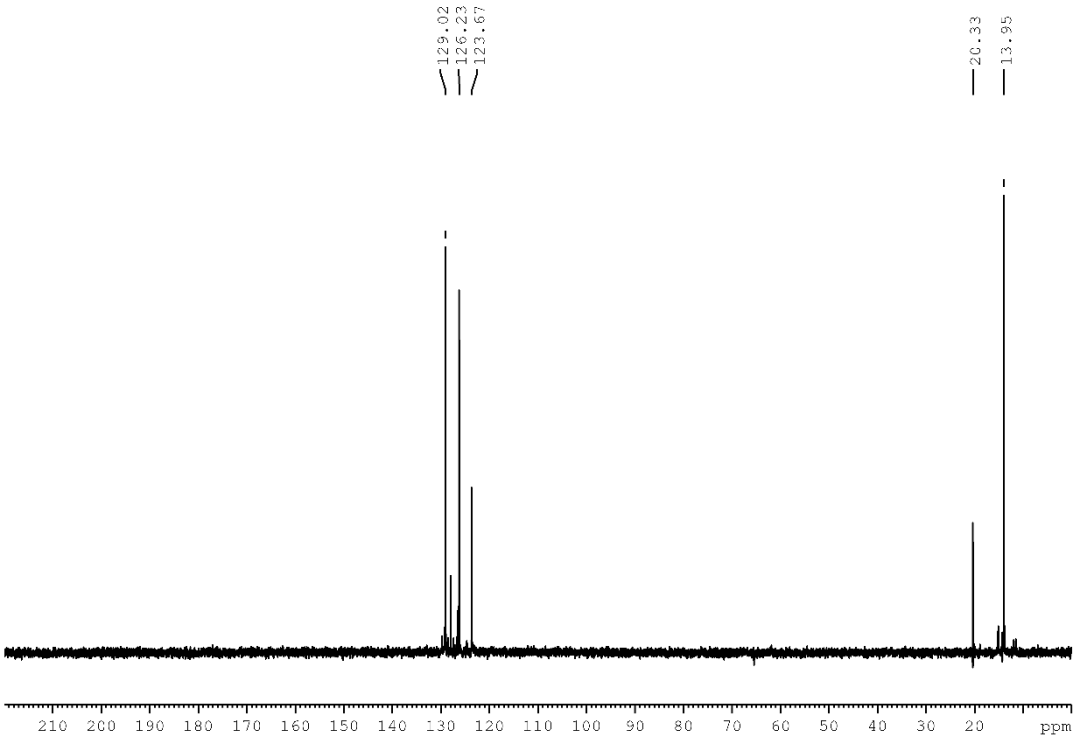

Figure S3. ^{13}C dept135 NMR spectrum (101 MHz, C_6D_6) of dilithiobutadiene **1b**. For impurity assignment, see Figure S2.

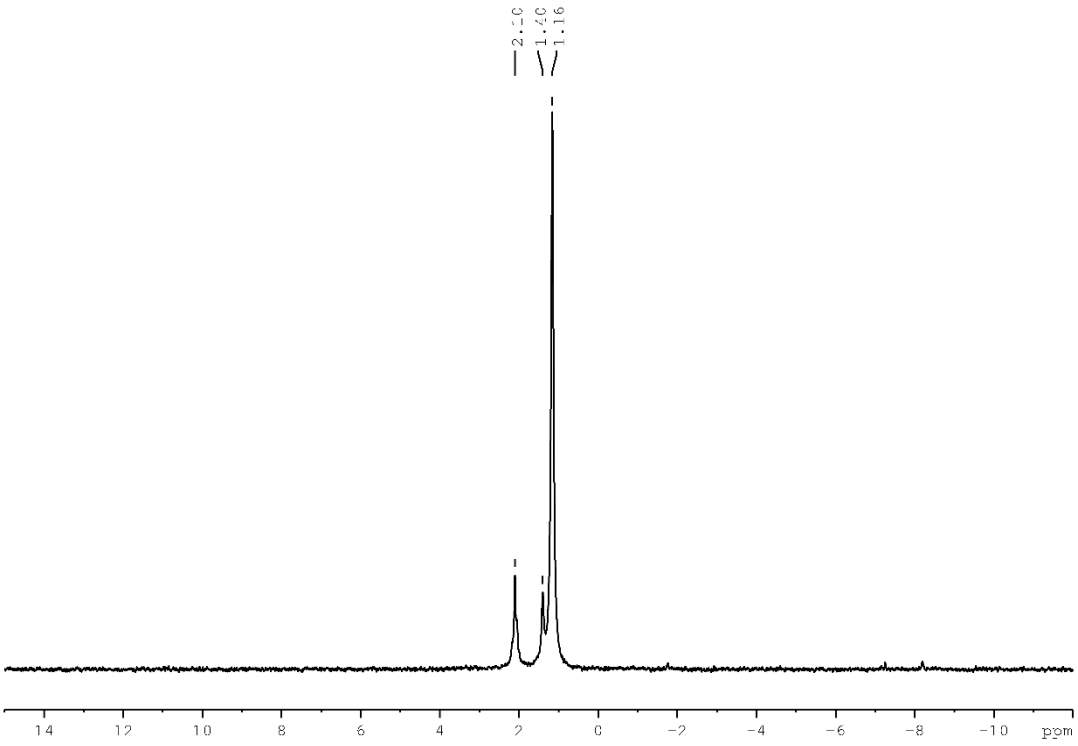

Figure S4. ^{7}Li NMR spectrum (194 MHz, C_6D_6) of dilithiobutadiene **1b**.

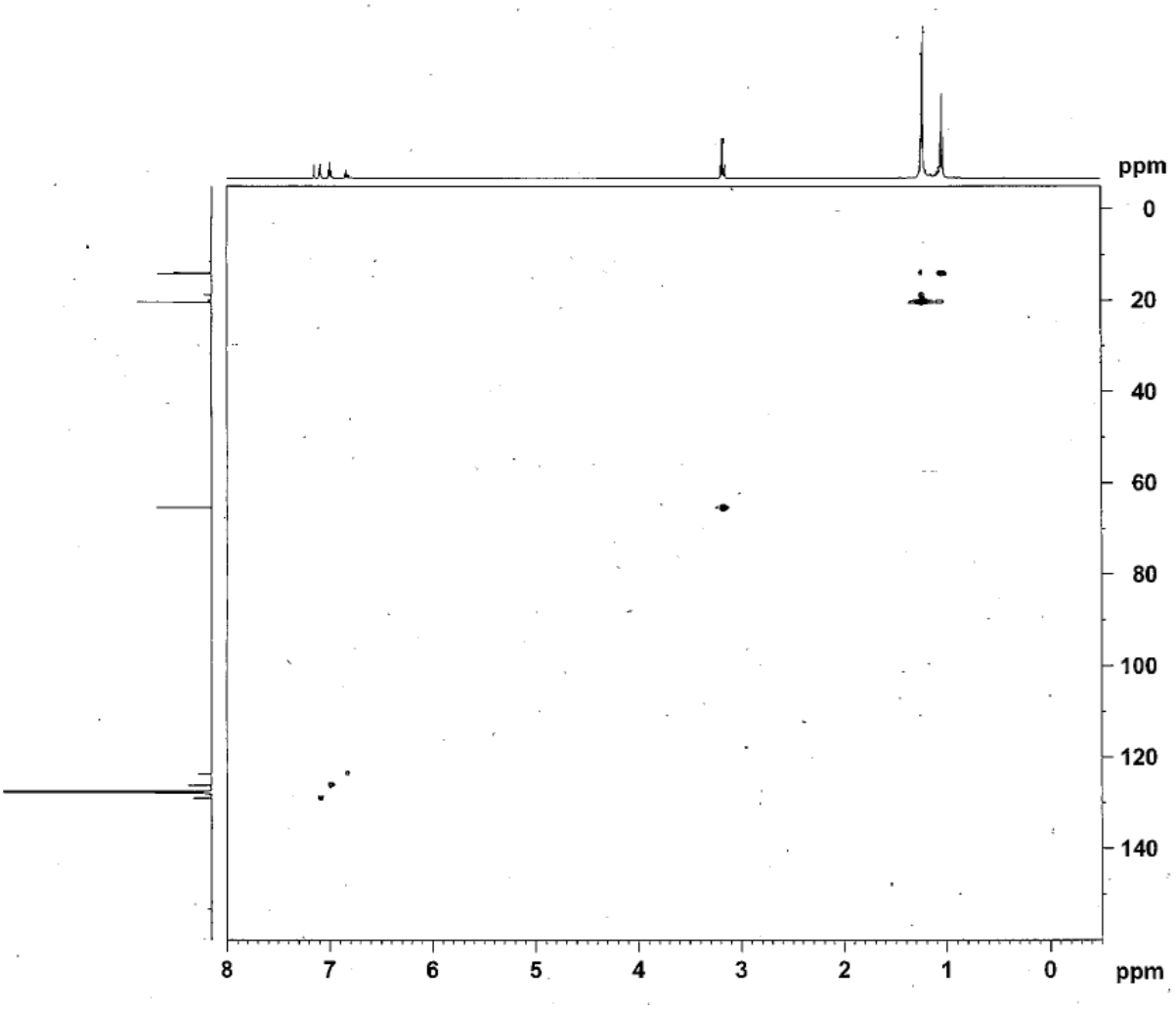

Figure S5. ^{1}H-^{13}C HSQC spectrum of dilithiobutadiene **1b**.

1.2. 1,4-Dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenyl-buta-1,3-diene (1b) after addition of Et_2O to the previous sample

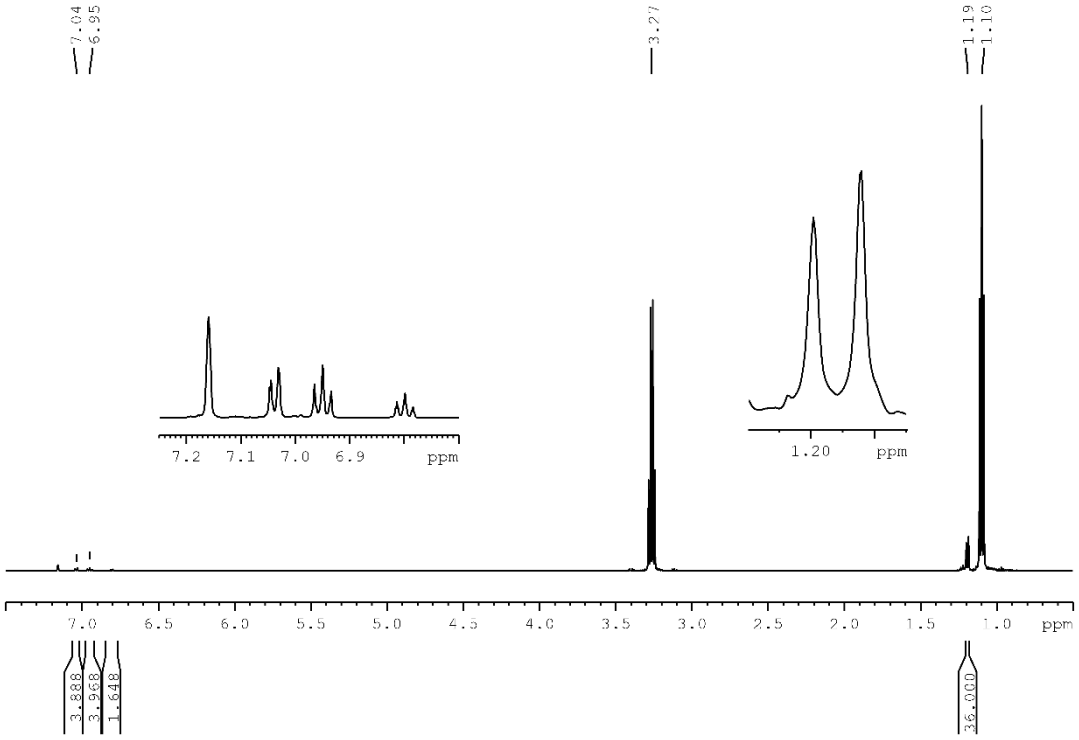

Figure S6. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dilithiobutadiene **1b** with additional Et_2O.

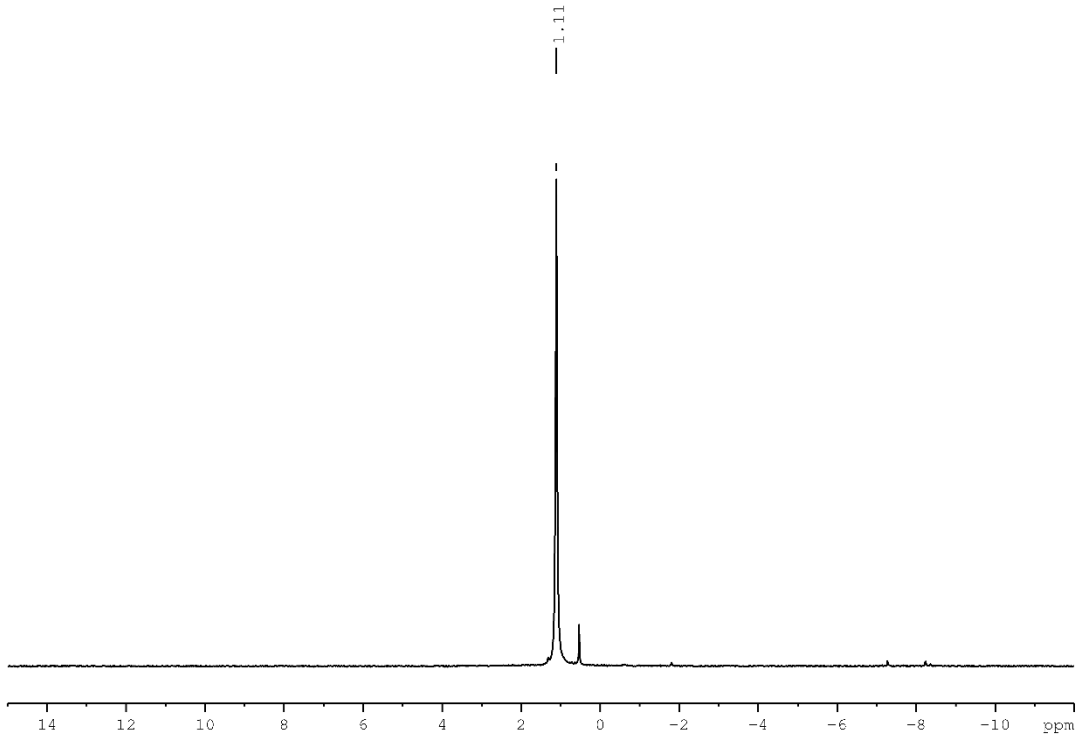

Figure S7. ^{7}Li NMR spectrum (194 MHz, C_6D_6) of dilithiobutadiene **1b** with additional Et_2O.

1.3. Dilithiodibenzopentalene 2b

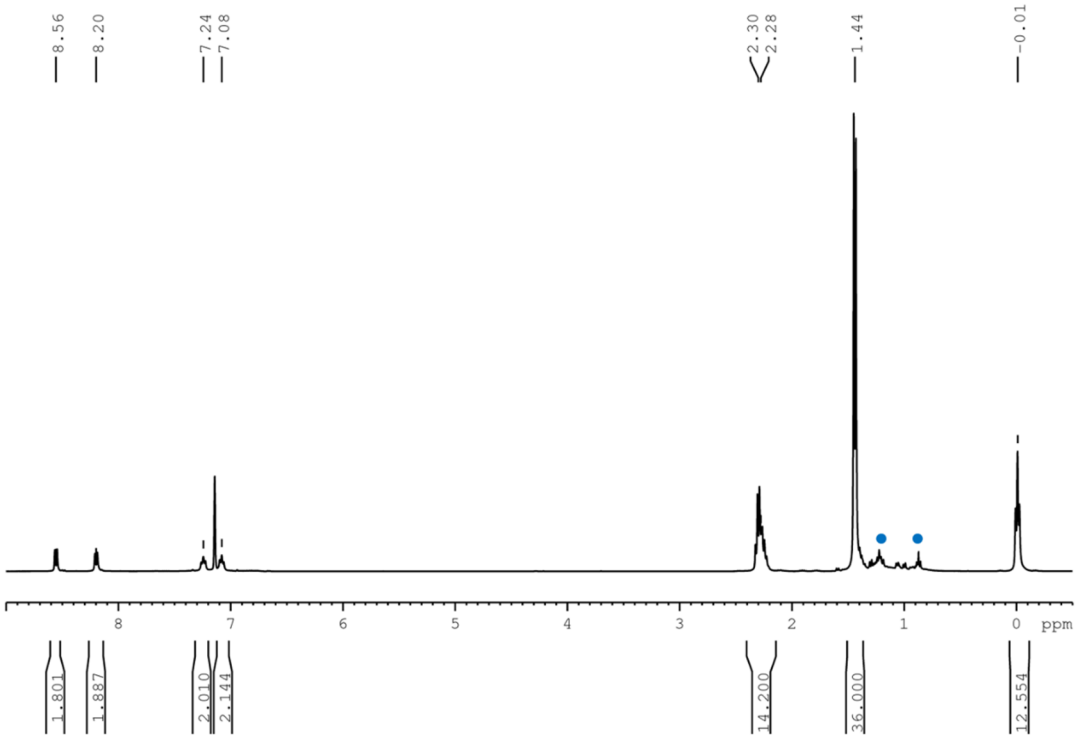

Figure S8. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dilithiodibenzopentalene **2b**. ● *n*-hexane.

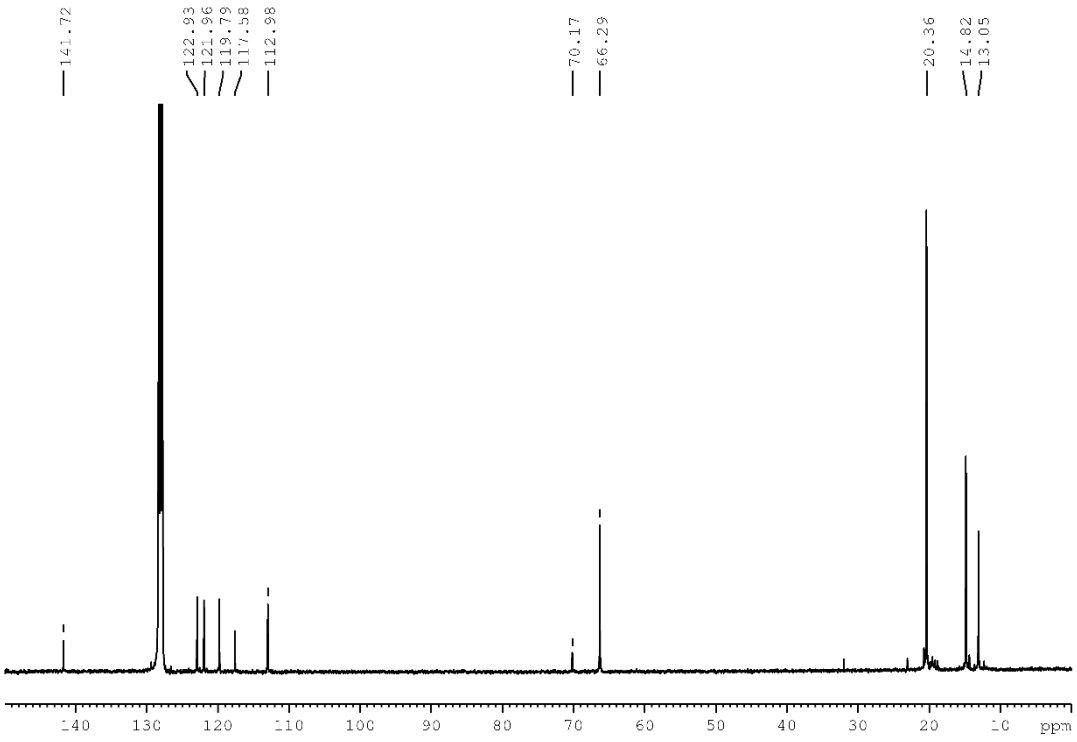

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of dilithiodibenzopentalene **2b**. ● *n*-hexane.

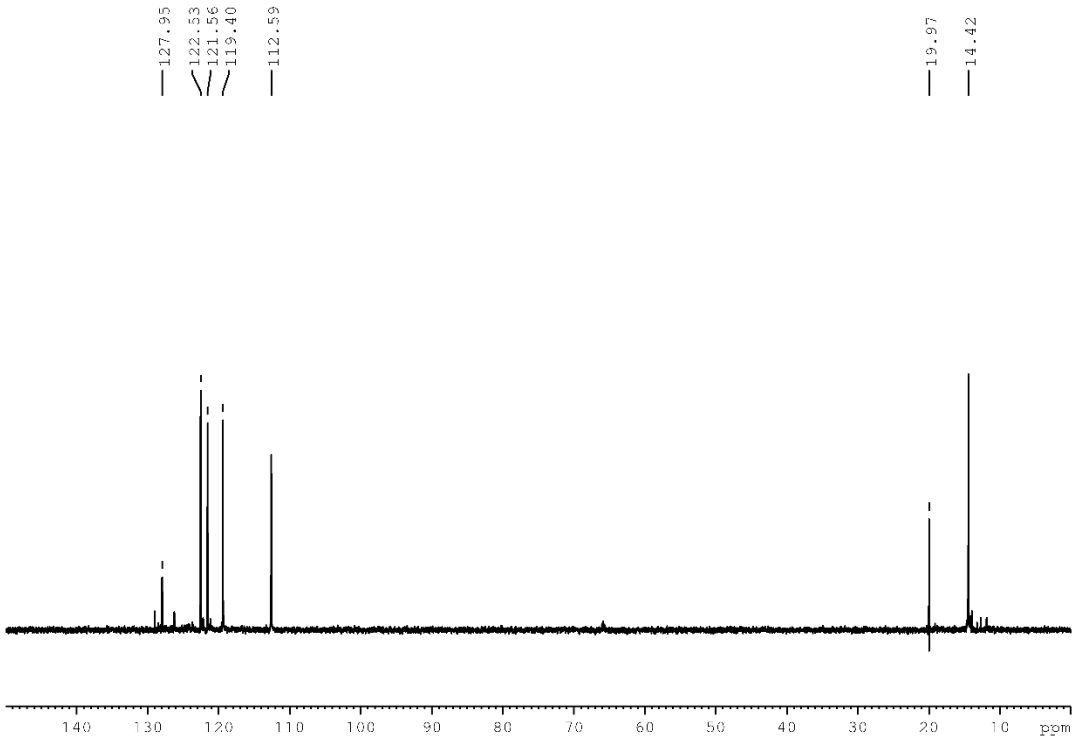

Figure S10. ^{13}C-dept135 NMR spectrum (101 MHz, C_6D_6) of dilithiodibenzopentalene **2b**. For impurity assignment, see Figure S9.

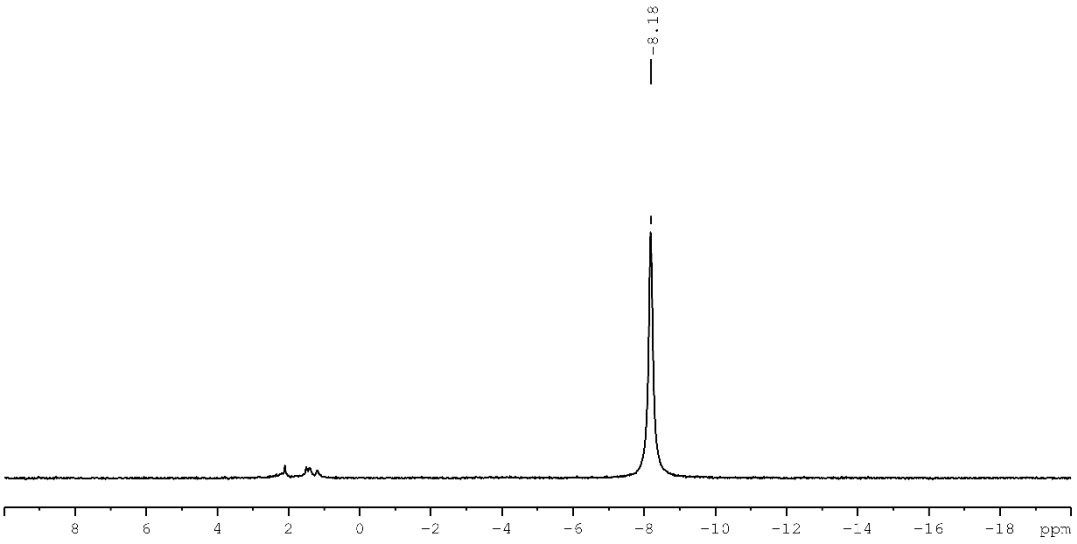

Figure S11. ^{7}Li NMR spectrum (194 MHz, C_6D_6) of dilithiodibenzopentalene **2b**.

1.4. 1,1-Dihydro-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (4)

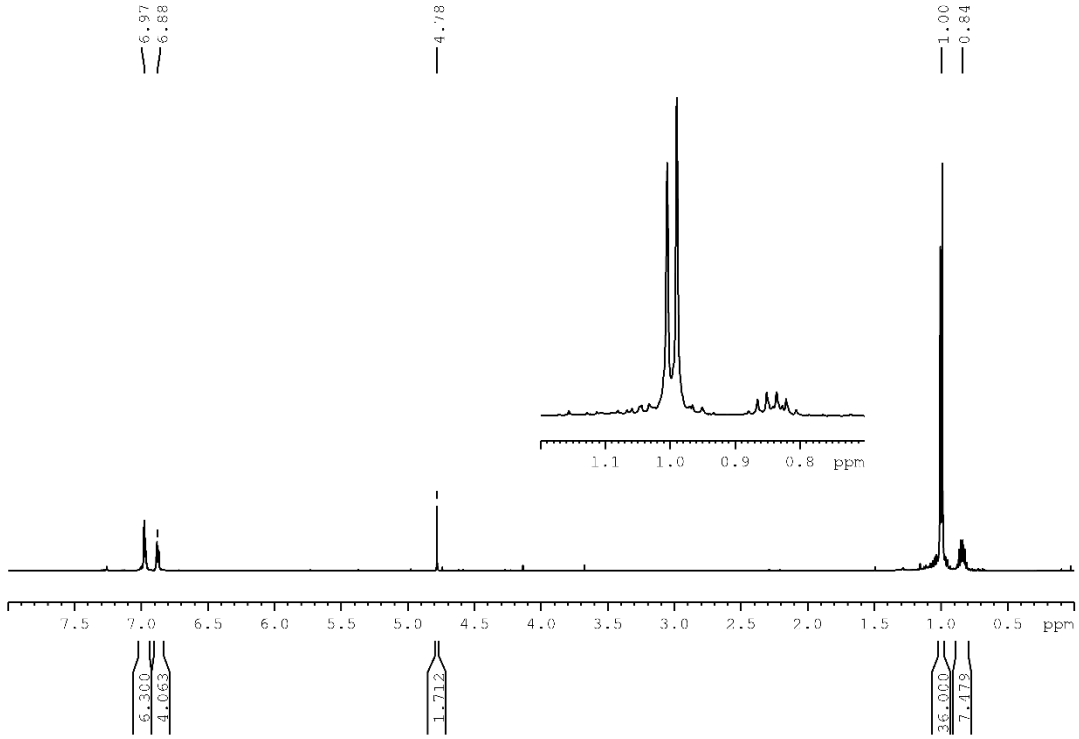

Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of dihydrosilole **4**.

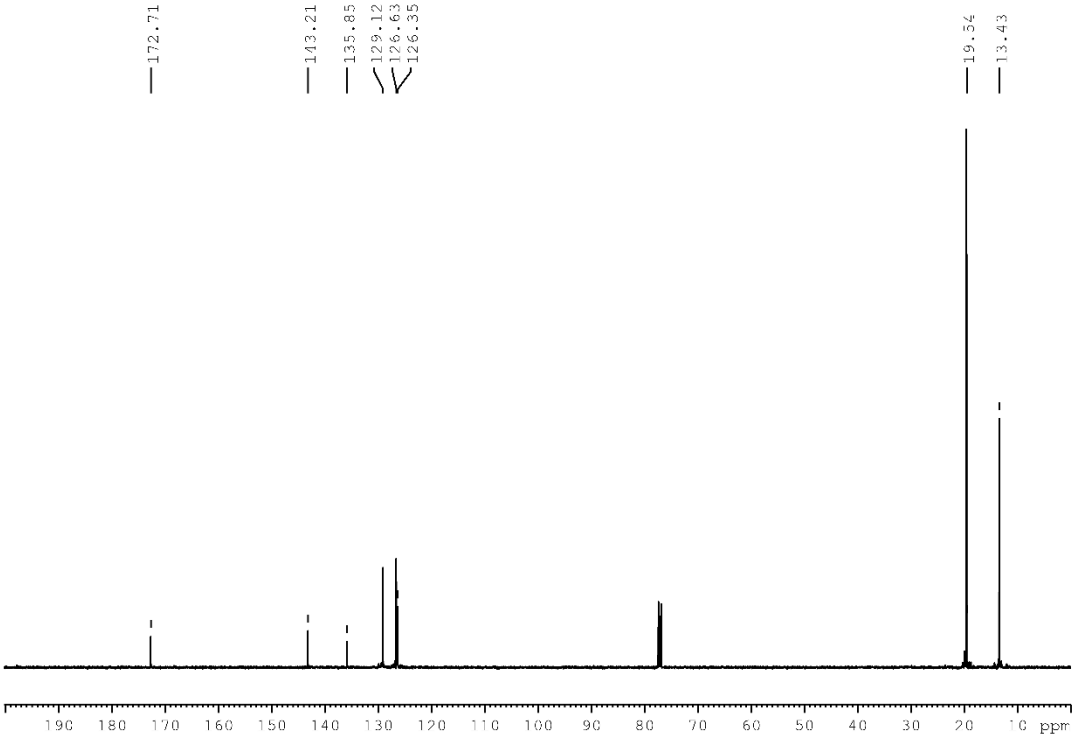

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of dihydrosilole **4**.

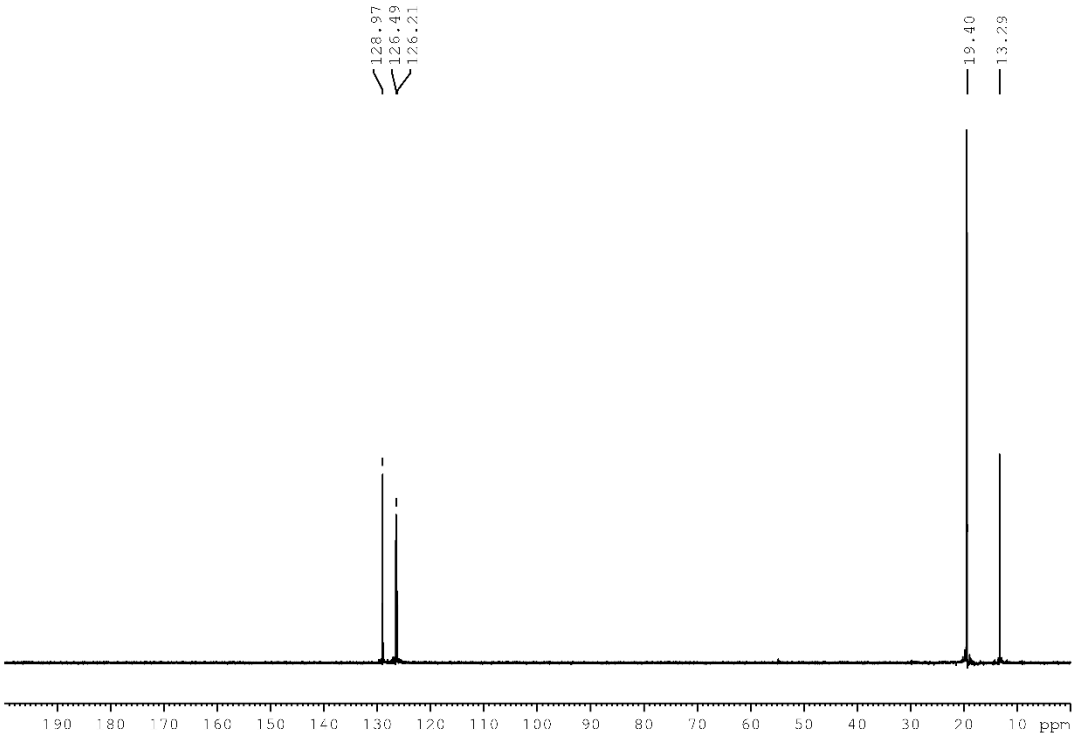

Figure S14. ^{13}C-dept135 NMR spectrum (126 MHz, $CDCl_3$) of dihydrosilole **4**.

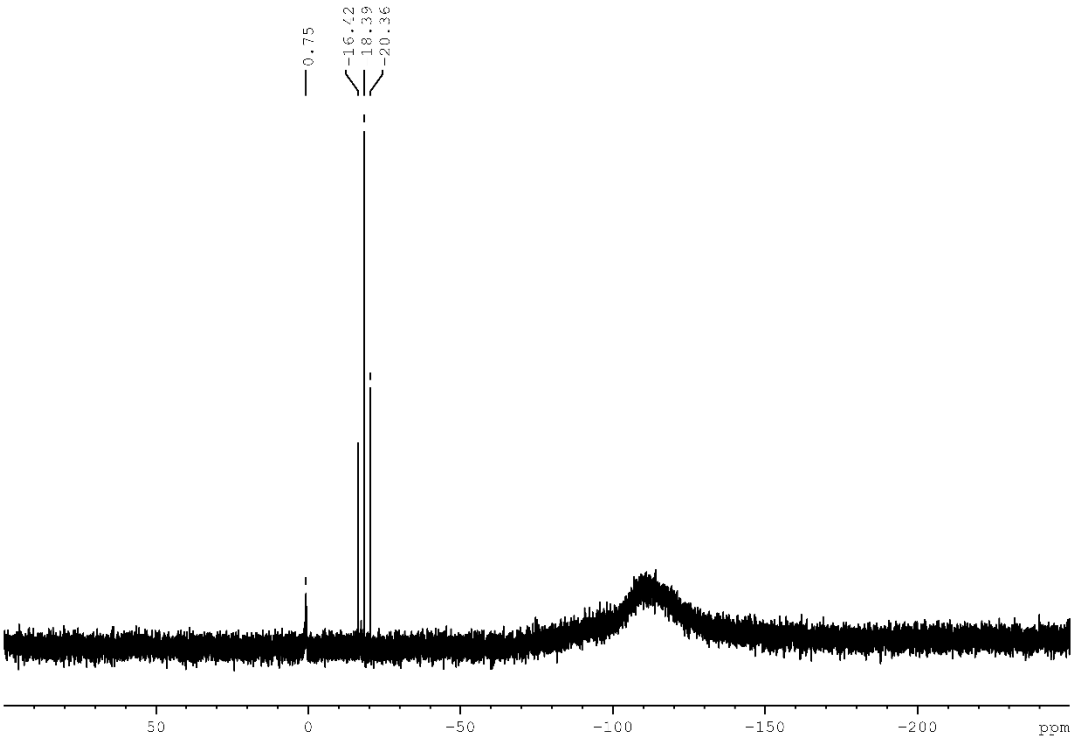

Figure S15. ^{29}Si NMR spectrum (99 MHz, $CDCl_3$) of dihydrosilole **4**.

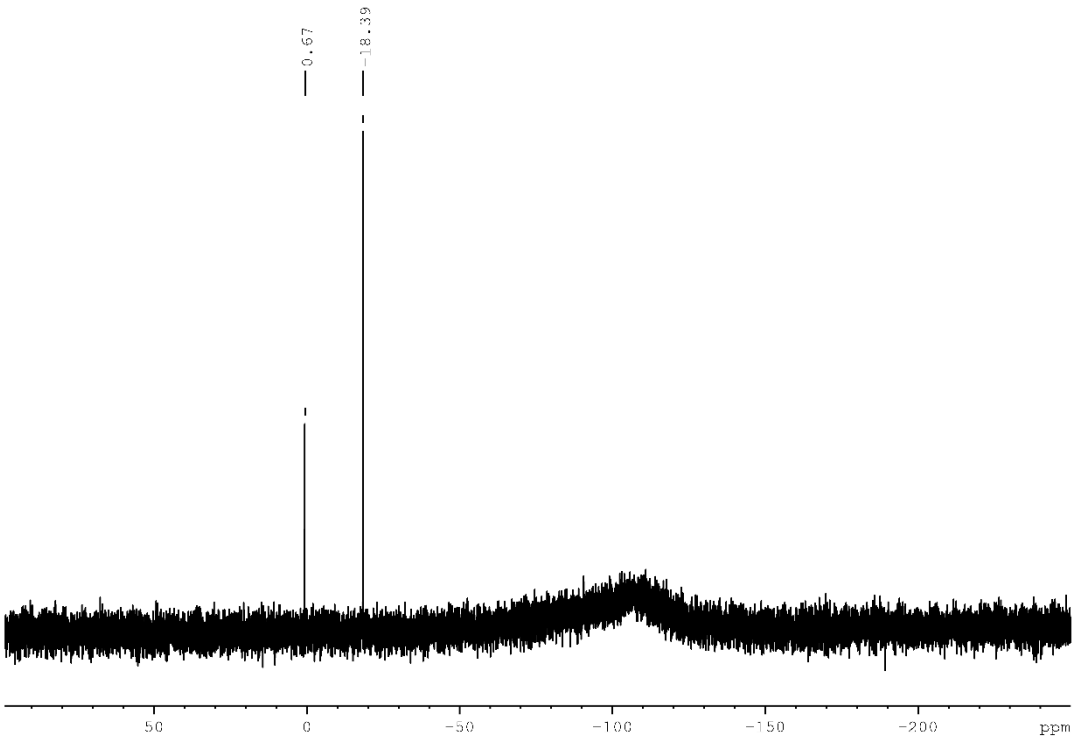

Figure S16. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, $CDCl_3$) of dihydrosilole **4**.

1.5. 1-Hydro-1-methoxy-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (5)

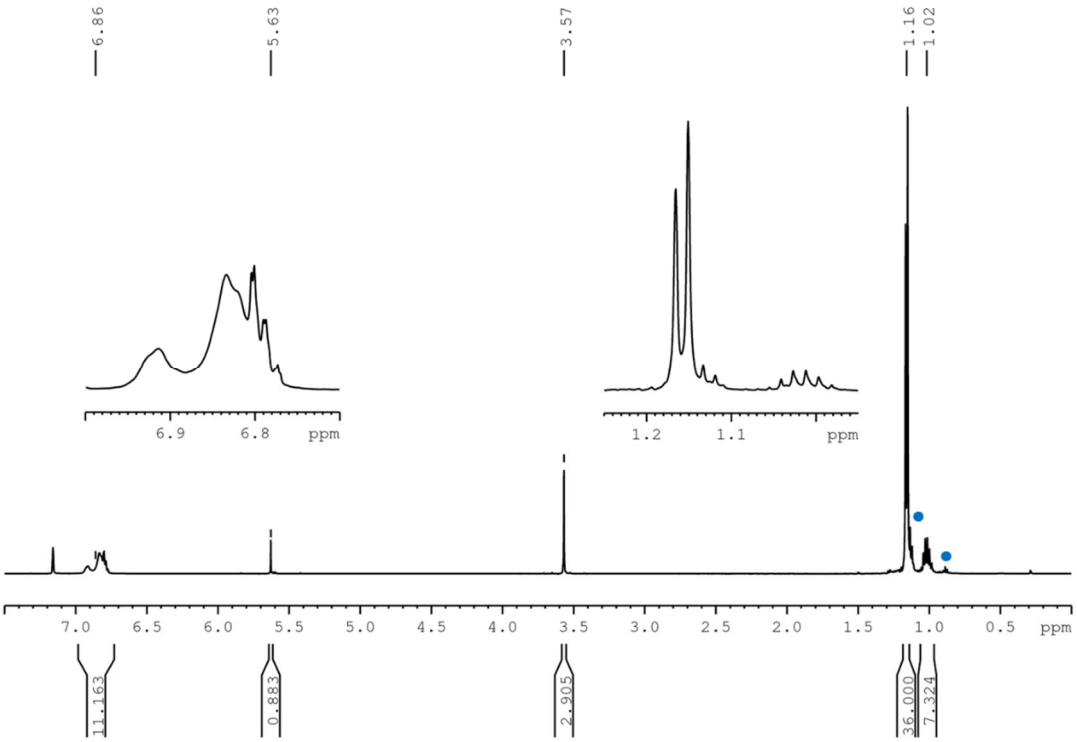

Figure S17. ^{1}H NMR spectrum (500 MHz, C_6D_6) of methoxysilole **5**. ● *n*-hexane.

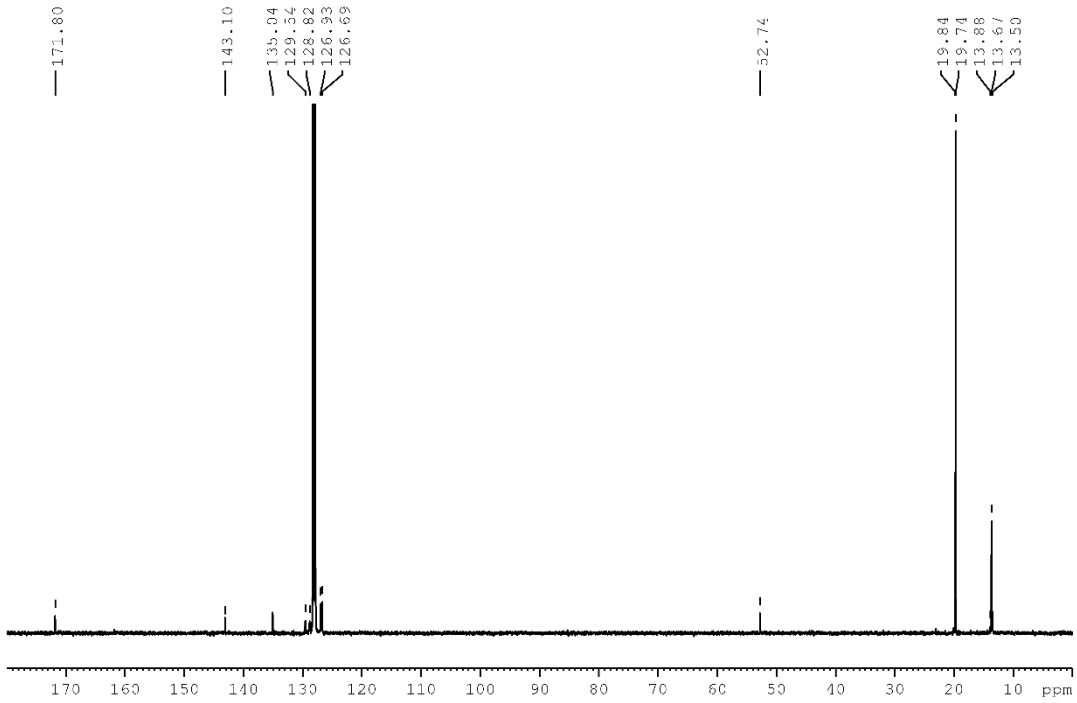

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of methoxysilole **5**. ● *n*-hexane.

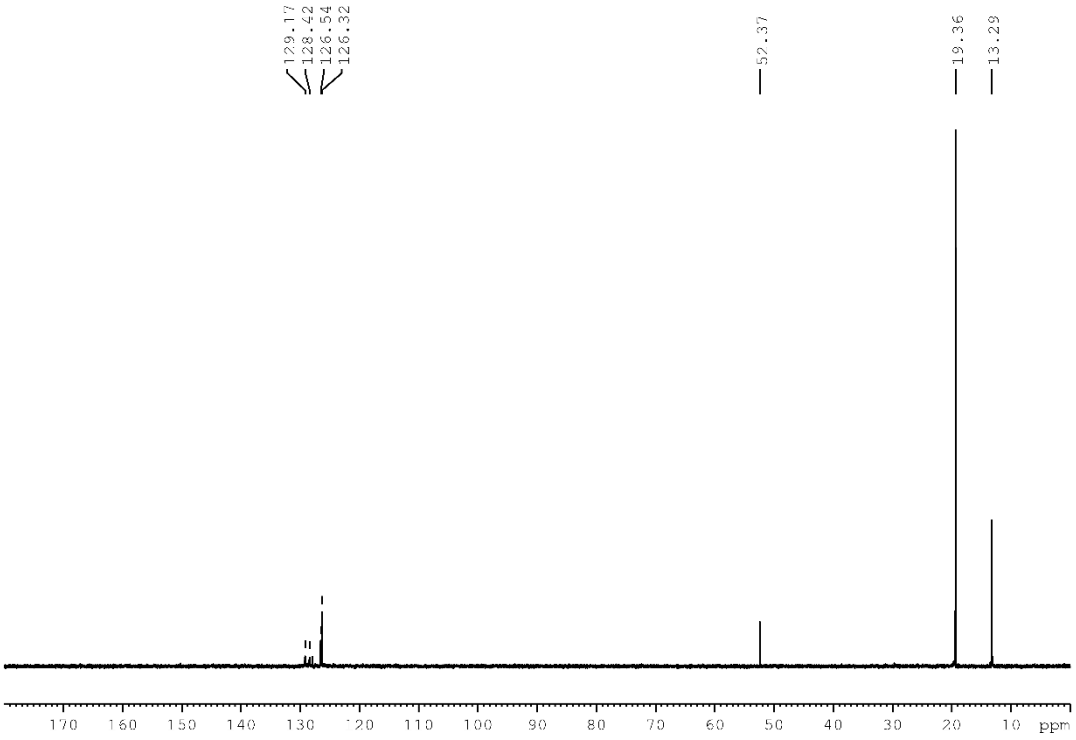

Figure S19. ^{13}C-dept135 NMR spectrum (126 MHz, C_6D_6) of methoxysilole **5**.

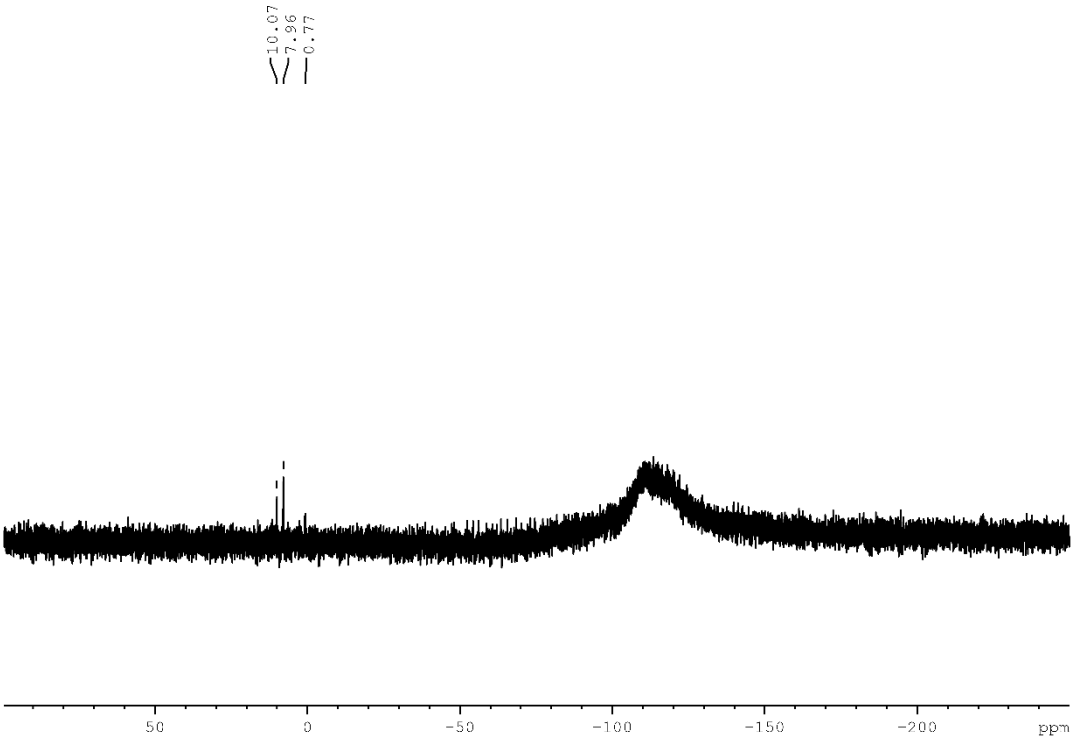

Figure S20. ^{29}Si NMR spectrum (99 MHz, C_6D_6) of methoxysilole **5**.

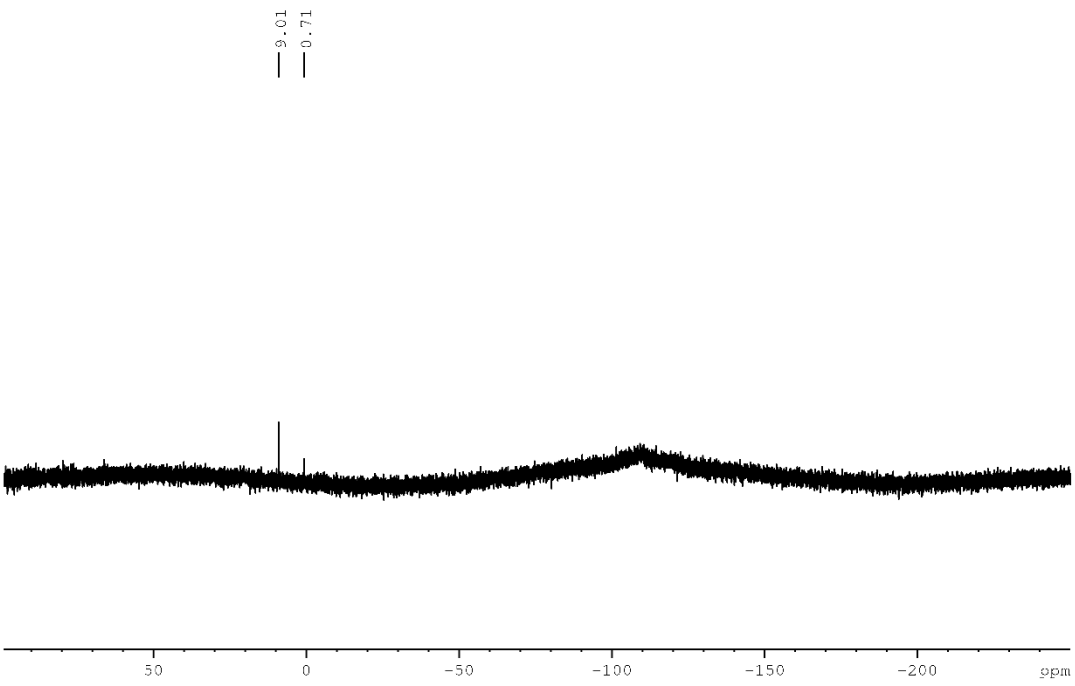

Figure S21. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, C_6D_6) of methoxysilole **5**.

1.6. 1,1-Difluoro-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (6)

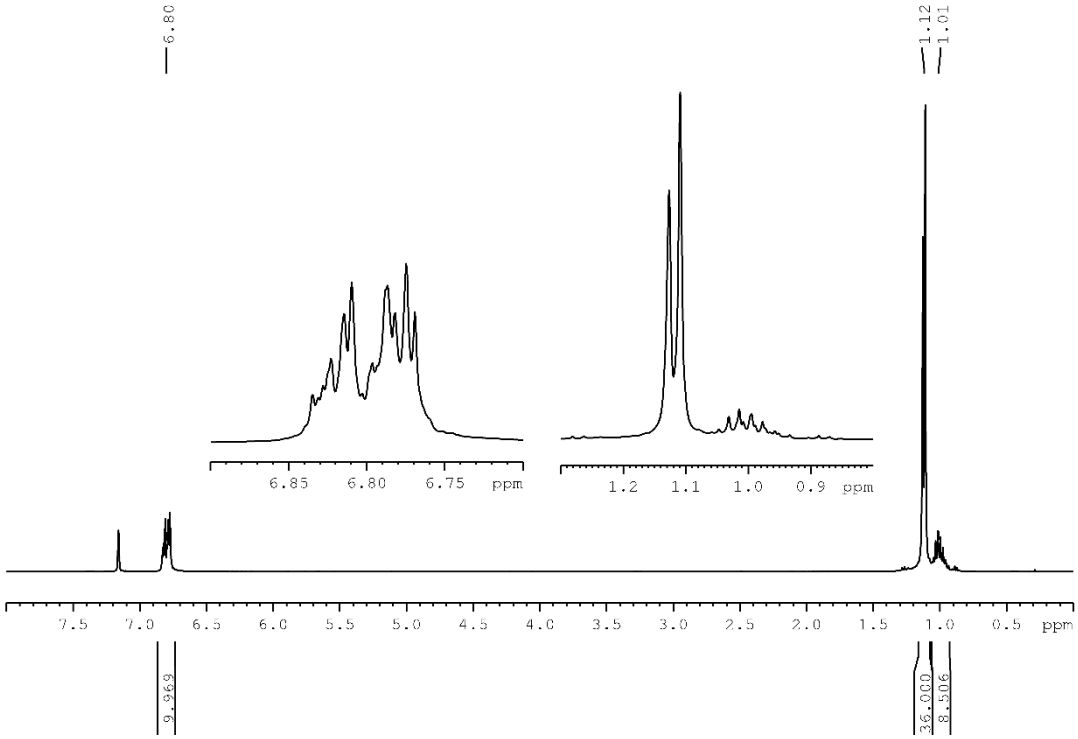

Figure S22. ^{1}H NMR spectrum (400 MHz, C_6D_6) of difluorosilole **6**.

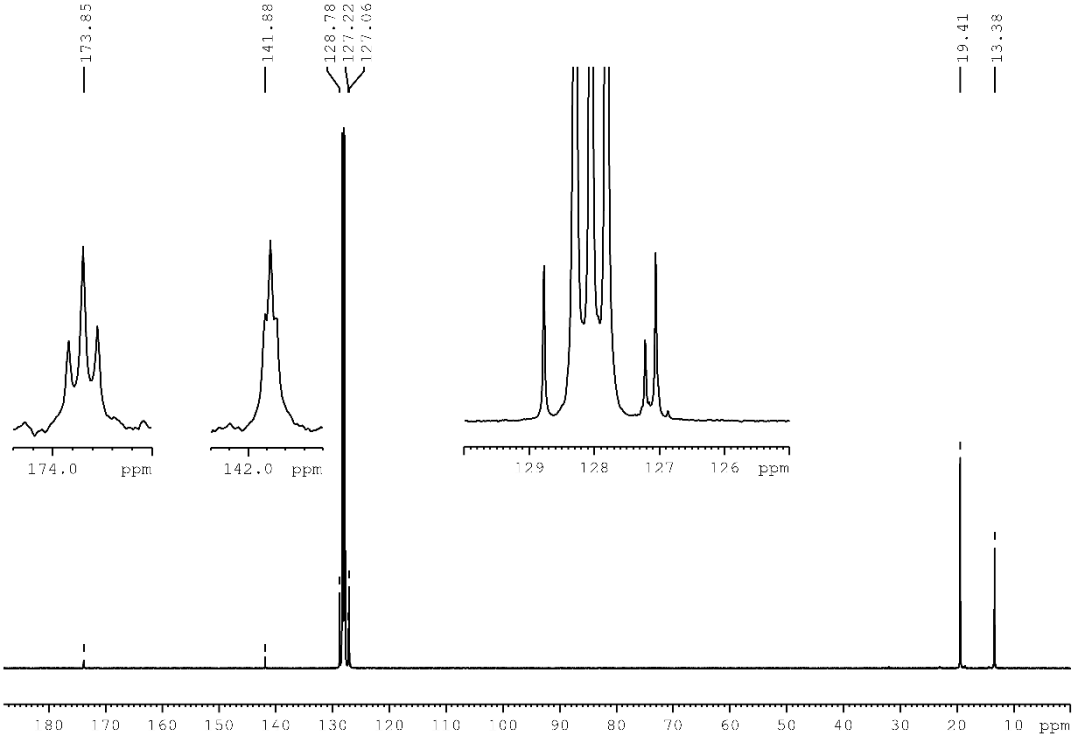

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of difluorosilole **6**.

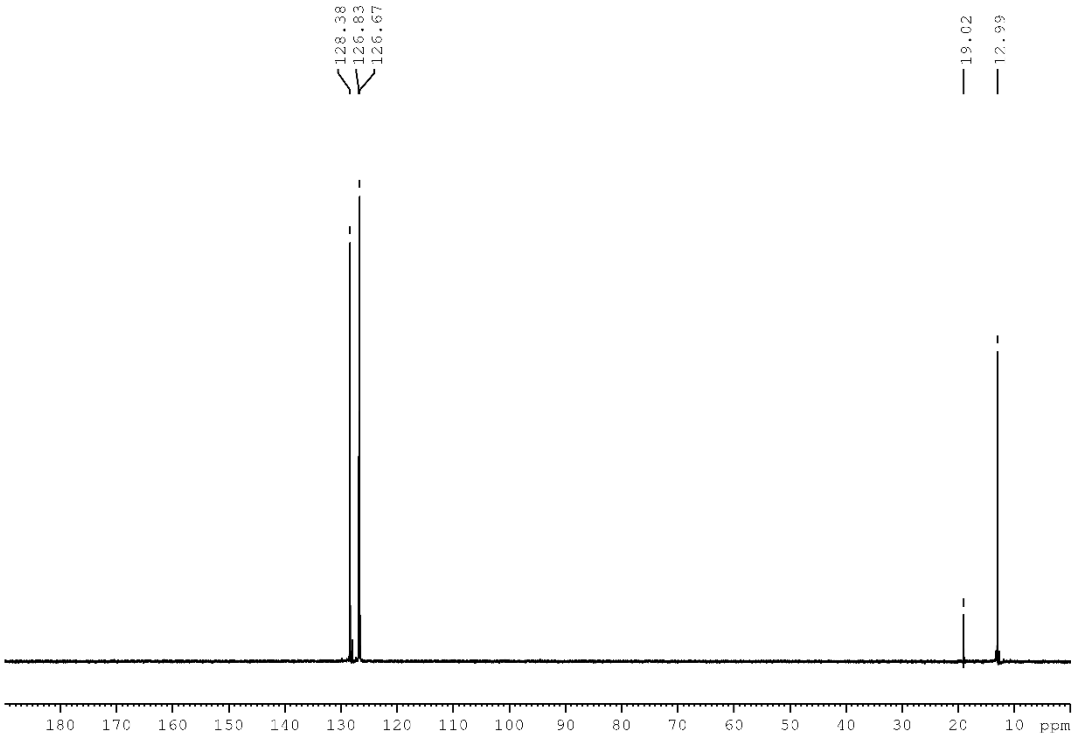

Figure S24. ^{13}C-dept135 NMR spectrum (101 MHz, C_6D_6) of difluorosilole **6**.

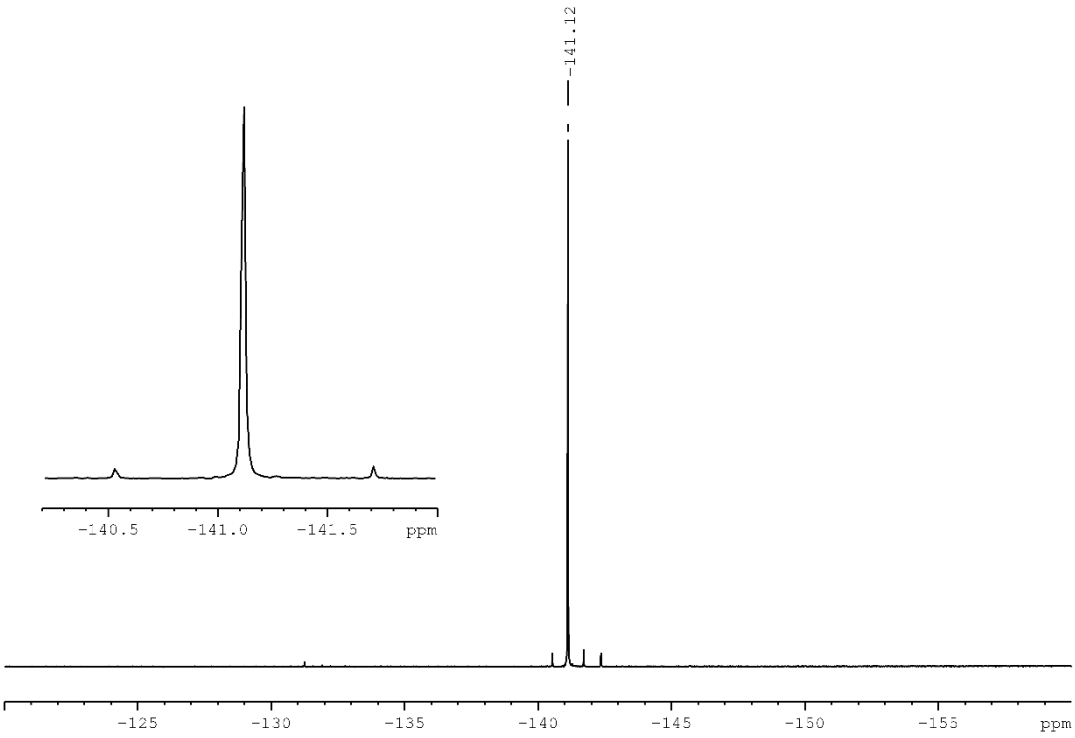

Figure S25. ^{19}F NMR spectrum (282 MHz, C_6D_6) of difluorosilole **6**.

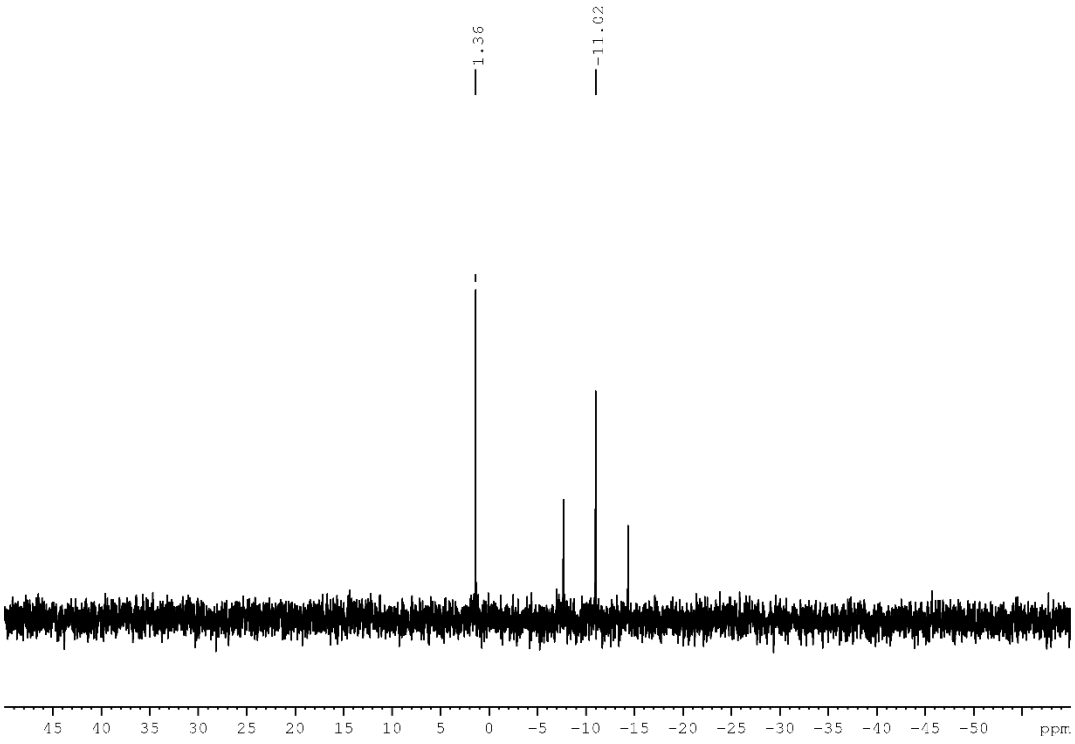

Figure S26. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, C_6D_6) of difluorosilole **6**.

1.7. 1,1-Dibromo-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (7)

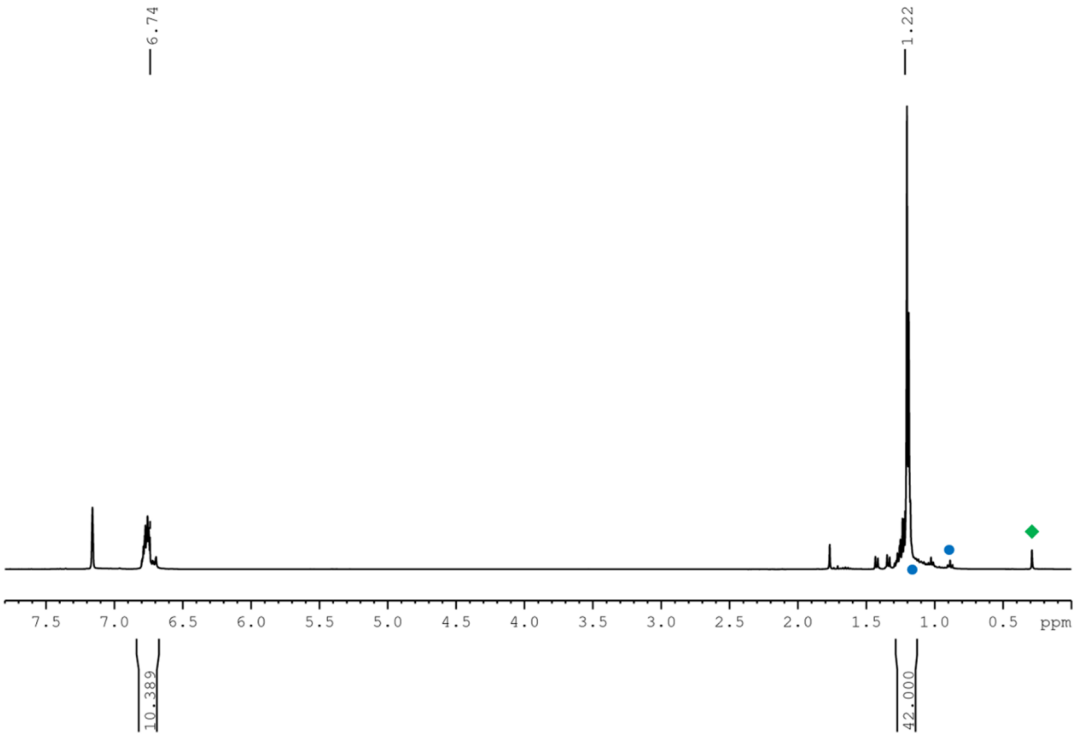

Figure S27. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dibromosilole **7**. ◆ Silicone grease. ● *n*-hexane.

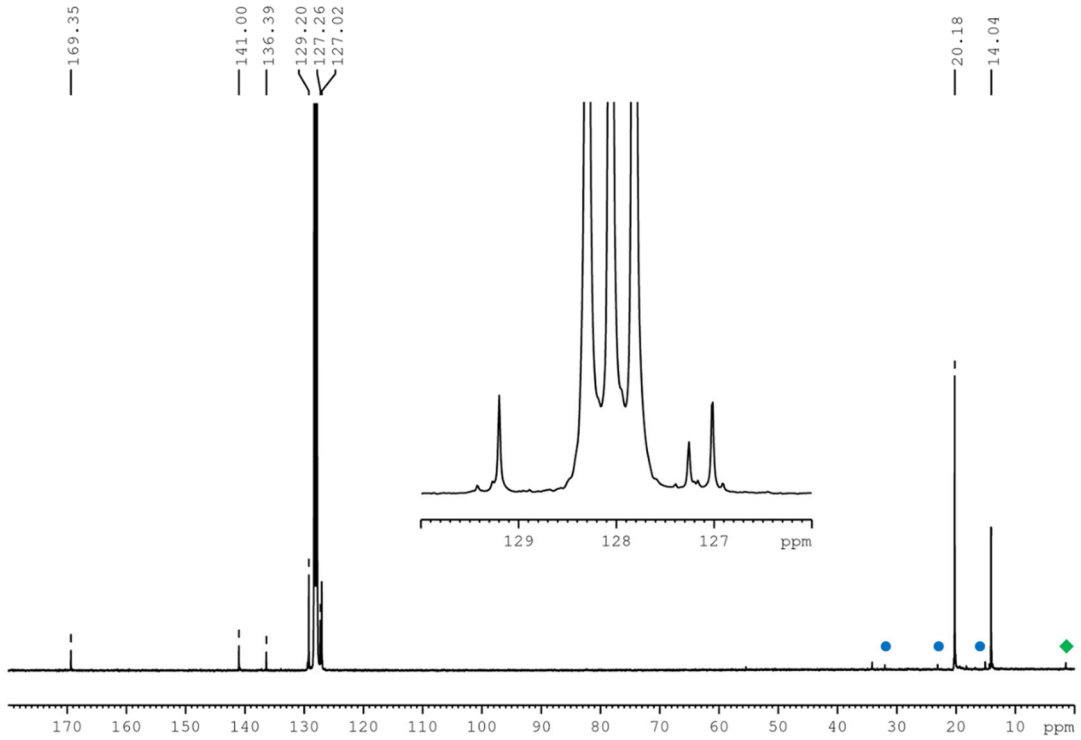

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of dibromosilole **7**. ◆ Silicone grease. ● *n*-hexane.

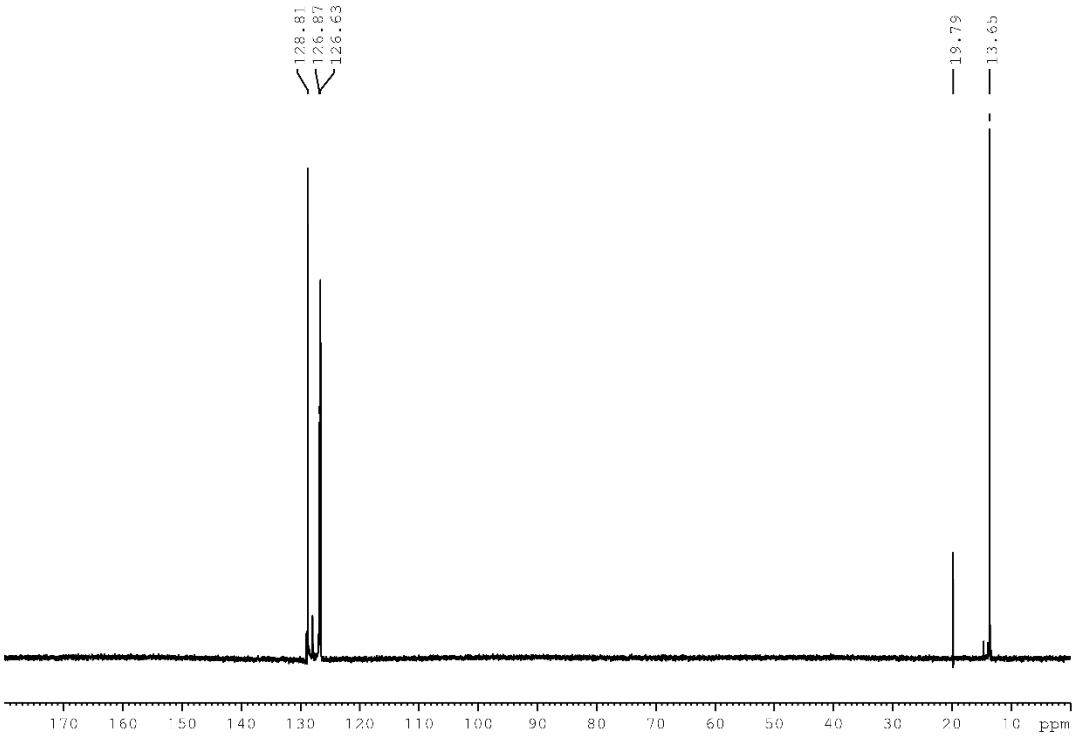

Figure S29. ^{13}C-dept135 NMR spectrum (101 MHz, C_6D_6) of dibromosilole **7**.

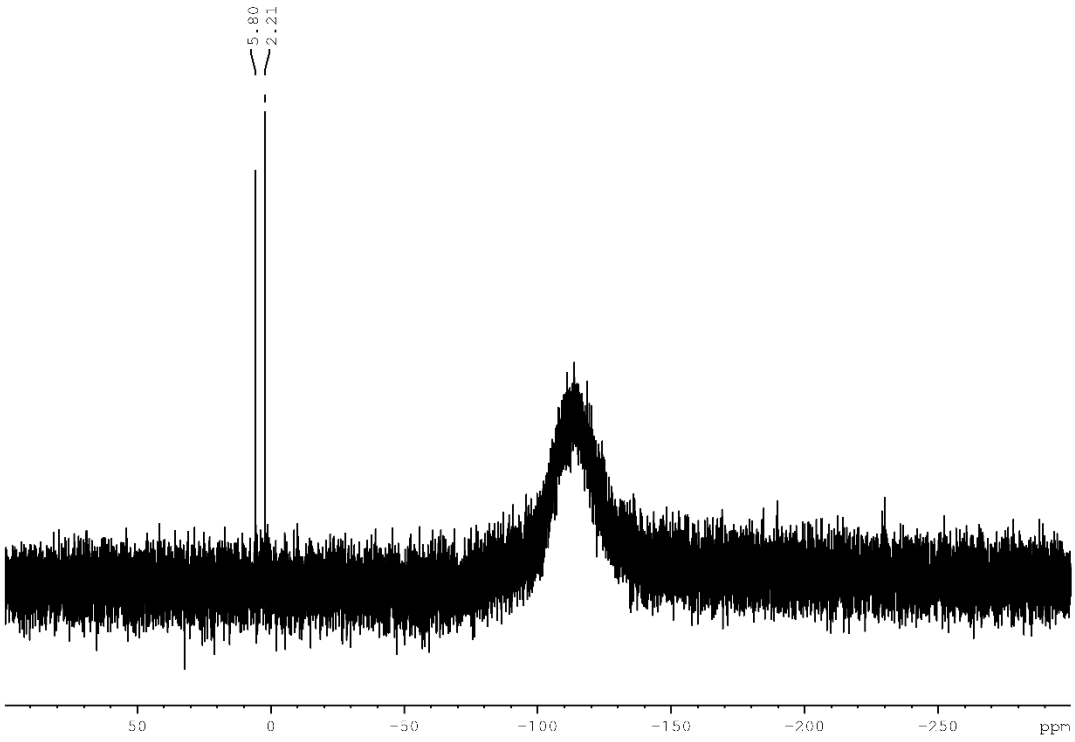

Figure S30. ^{29}Si{^{1}H} NMR spectrum (99 MHz, C_6D_6) of dibromosilole **7**.

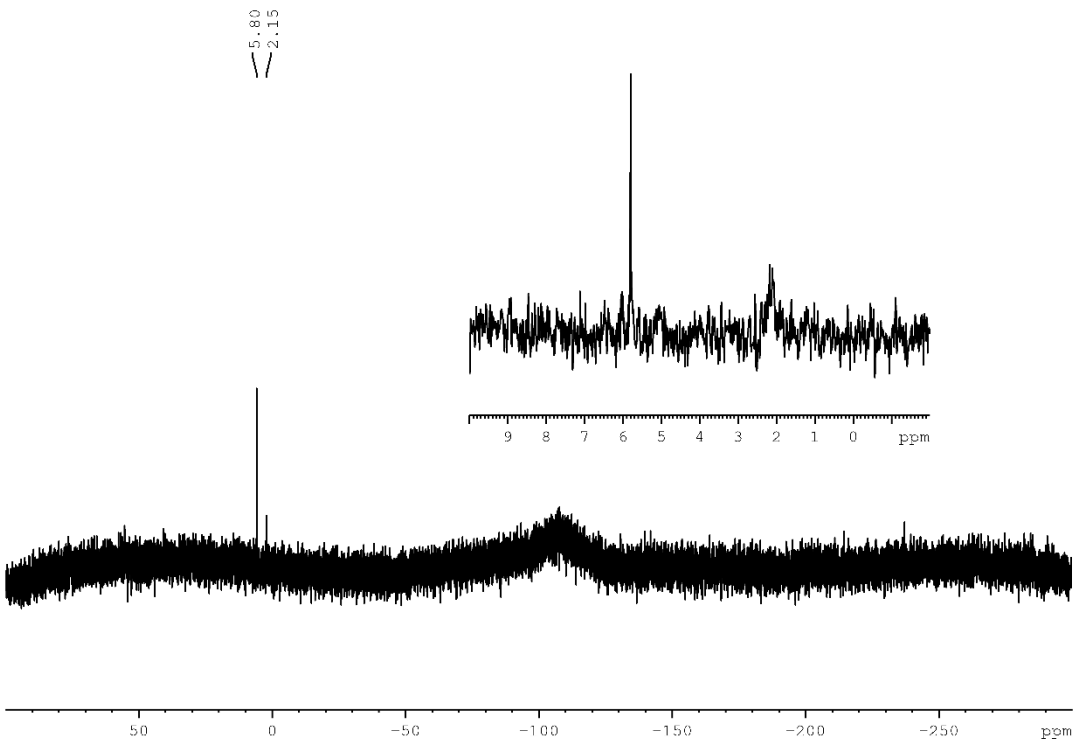

Figure S31. ^{29}Si NMR spectrum (99 MHz, C_6D_6) of dibromosilole **7**.

1.8. 1-Bromo-1-methoxy-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (8)

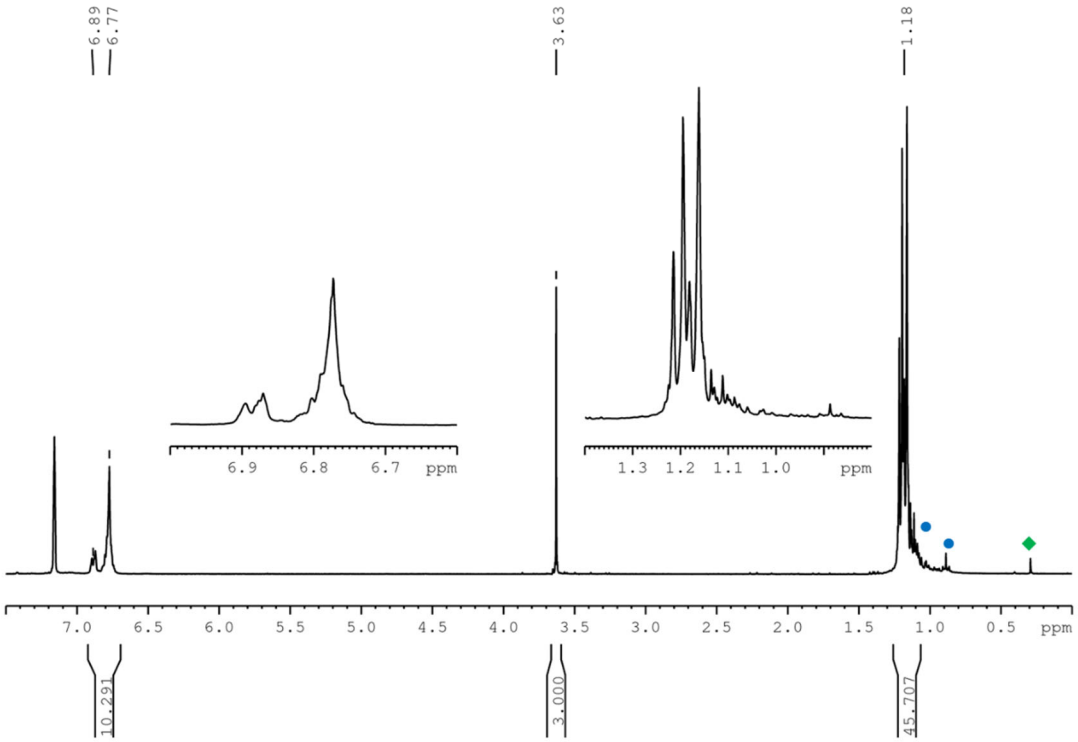

Figure S32. ^{1}H NMR spectrum (300 MHz, C_6D_6) of bromomethoxysilole **8**. ◆ Silicone grease. ● *n*-hexane.

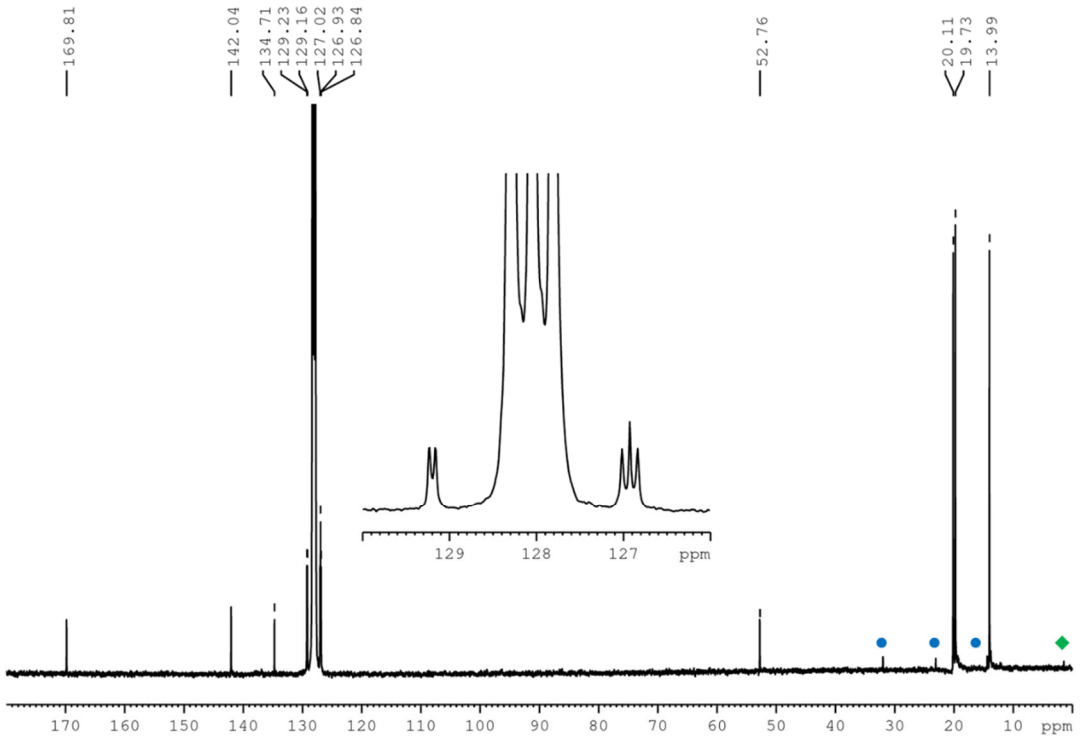

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of bromomethoxysilole **8**. ◆ Silicone grease. ● *n*-hexane.

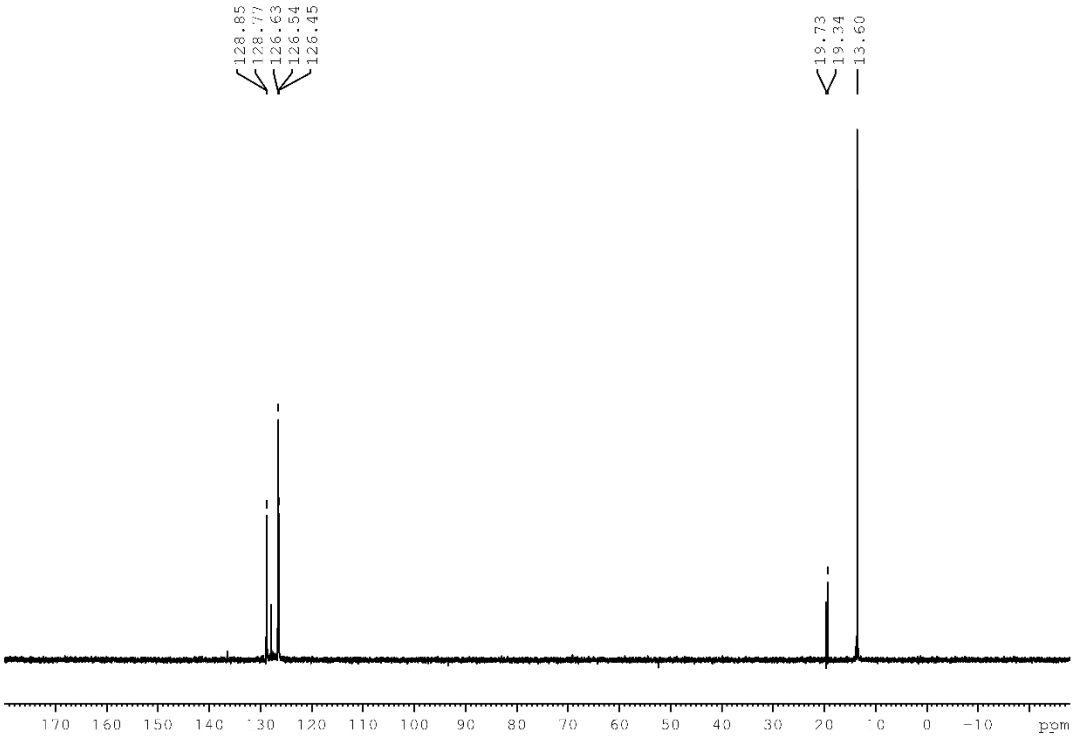

Figure S34. ^{13}C-dept135 NMR spectrum (101 MHz, C_6D_6) of bromomethoxysilole **8**.

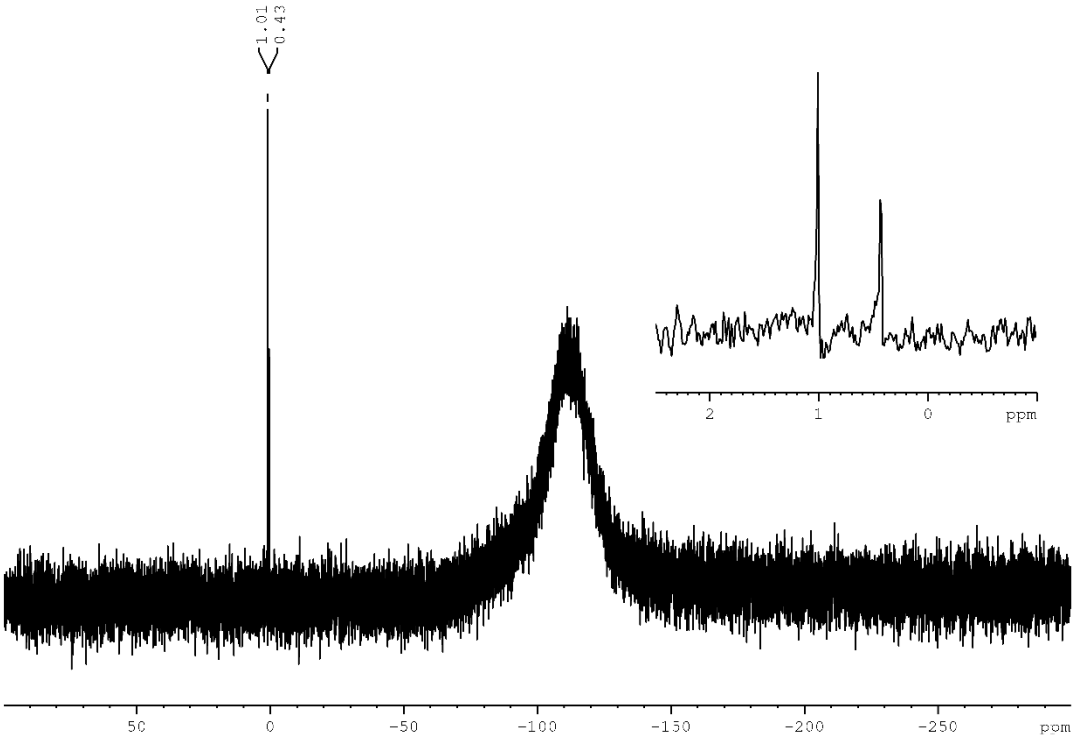

Figure S35. ^{29}Si{^{1}H} NMR spectrum (99 MHz, C_6D_6) of bromomethoxysilole **8**.

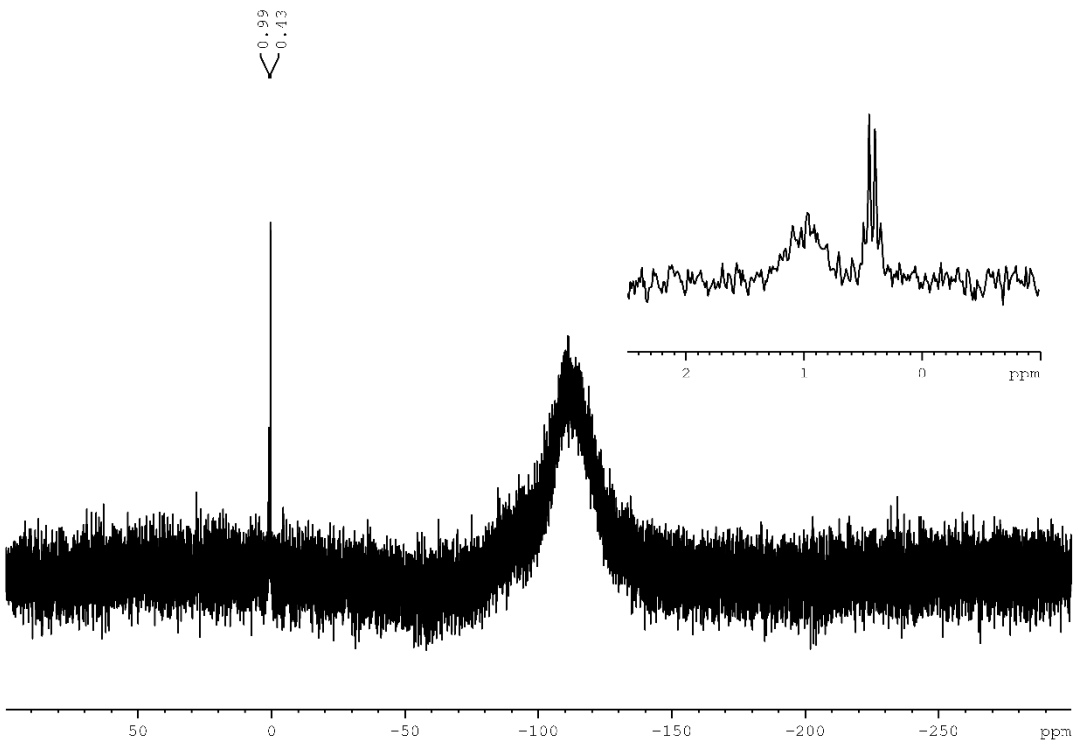

Figure S36. ^{29}Si NMR spectrum (99 MHz, C_6D_6) of bromomethoxysilole **8**.

1.9. 2,5-bis(triisopropylsilyl)-3,4-diphenyldilithiosilole (9)

1.9.1. Obtained from dibromosilole 7

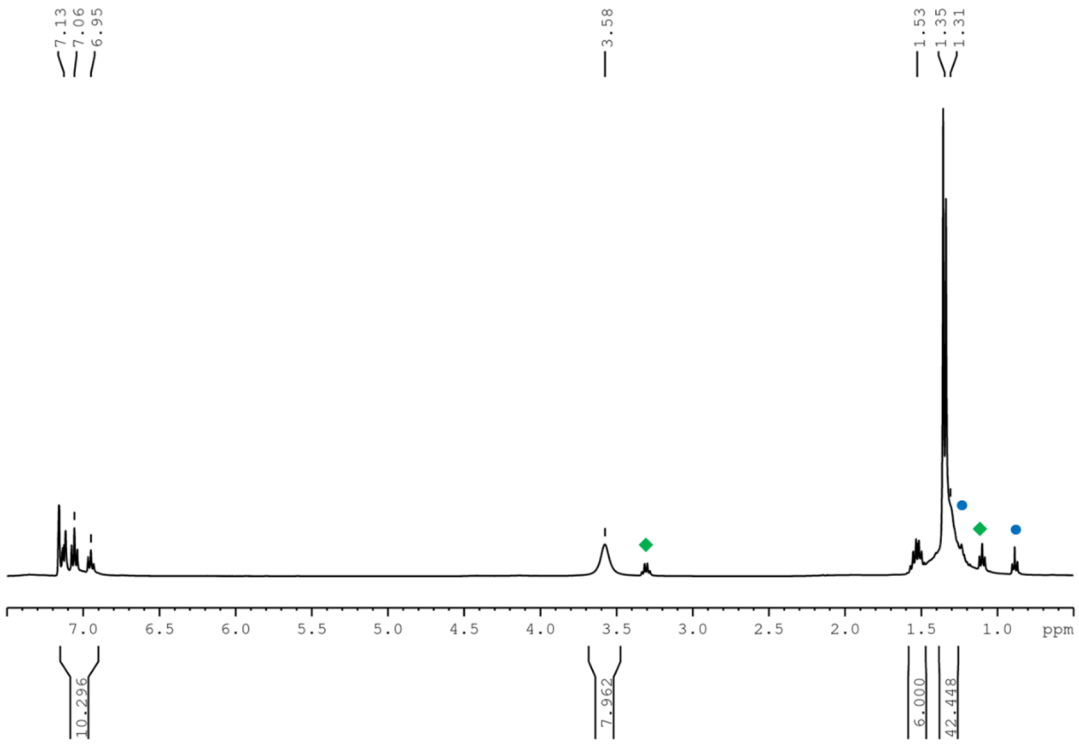

Figure S37. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dilithiosilole **9**. ◆ Et_2O. ● *n*-hexane.

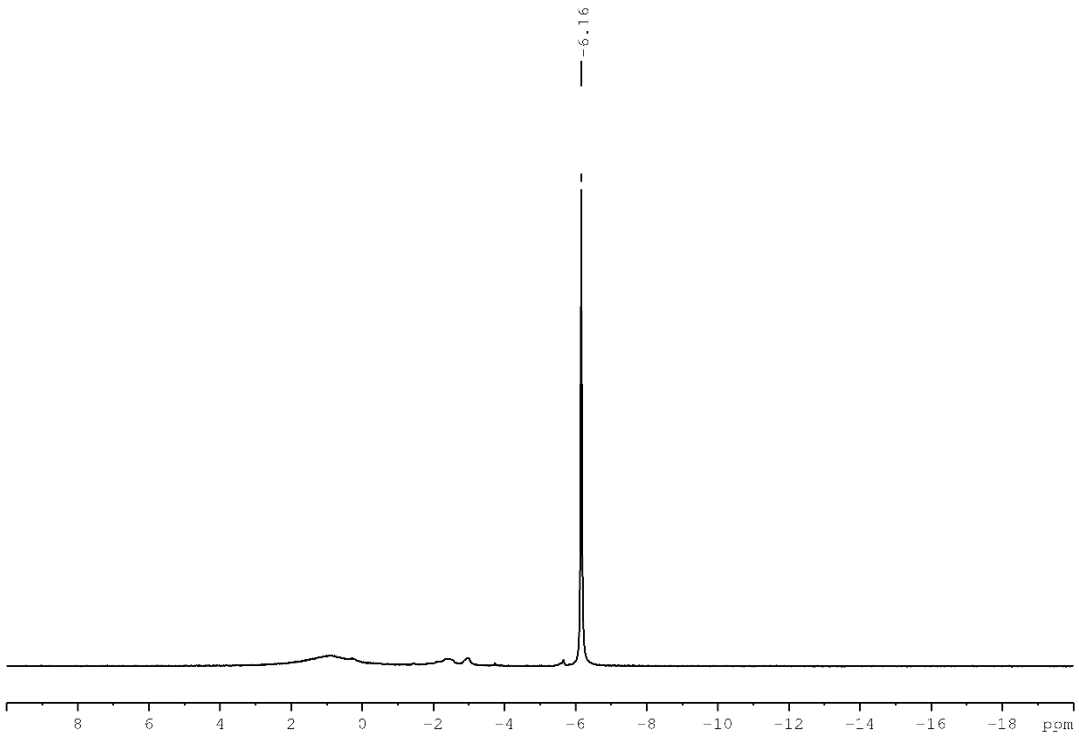

Figure S38. ^{7}Li NMR spectrum (117 MHz, C_6D_6) of dilithiosilole **9**.

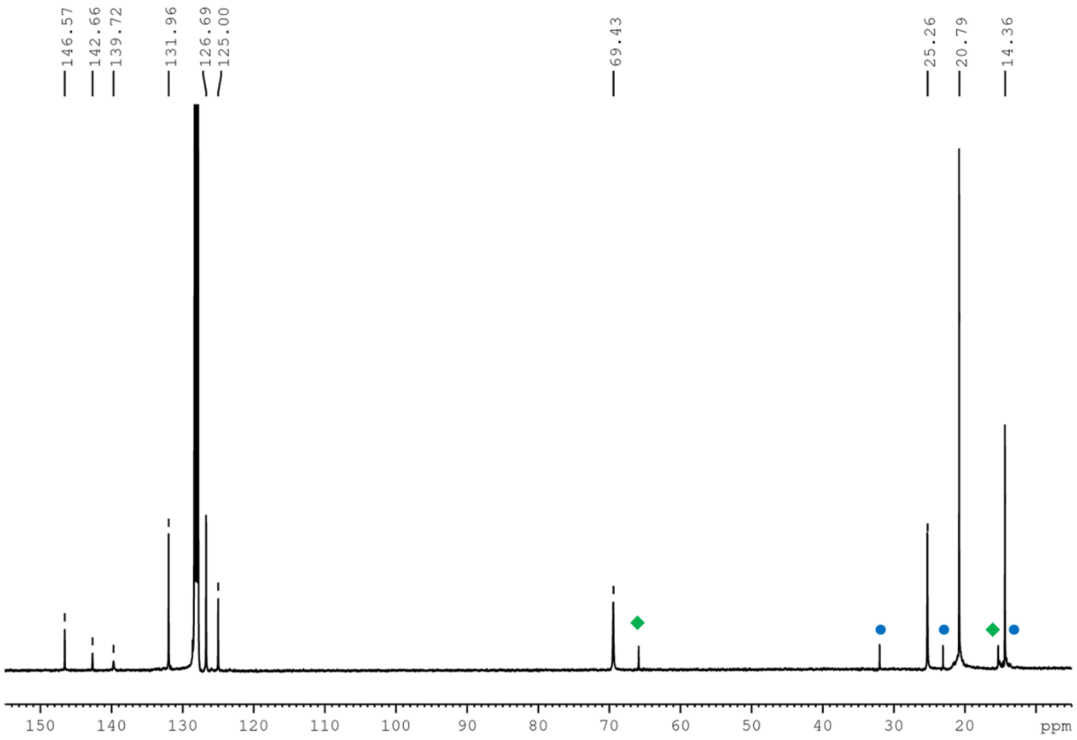

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of dilithiosilole **9**. ◆ Et_2O. ● *n*-hexane.

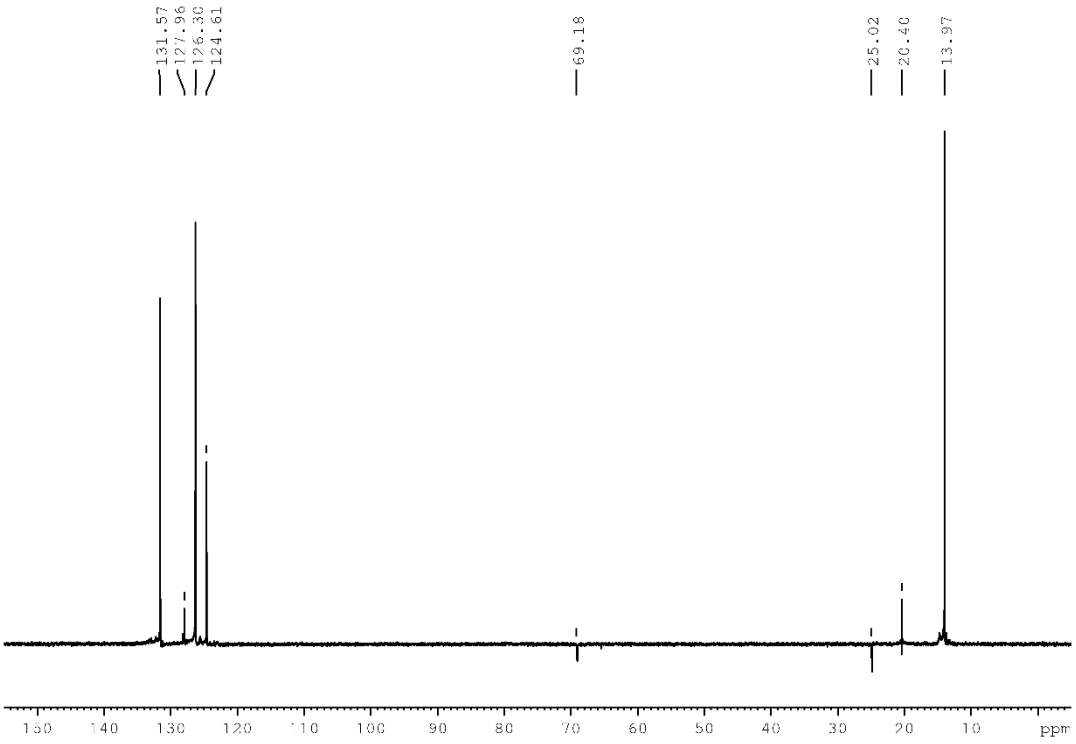

Figure S40. ^{13}C-dept135 NMR spectrum (101 MHz, C_6D_6) of dilithiosilole **9**.

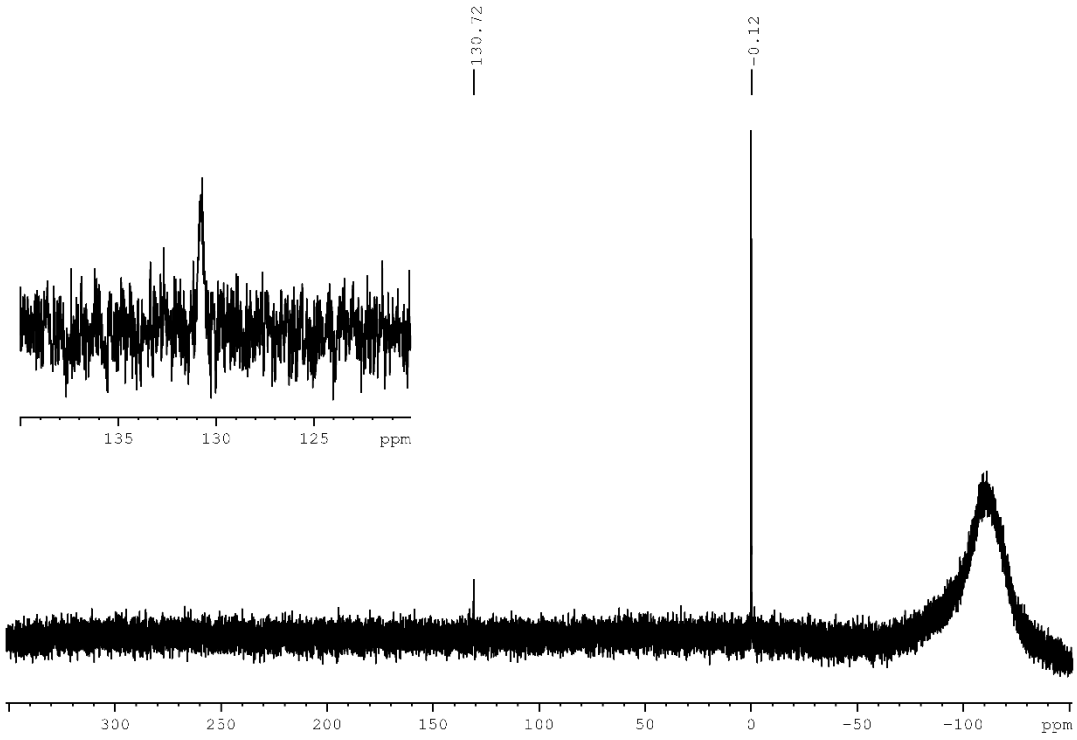

Figure S41. ^{29}Si NMR spectrum (99 MHz, C_6D_6) of dilithiosilole **9**.

1.9.2. Obtained from difluorosilole 7

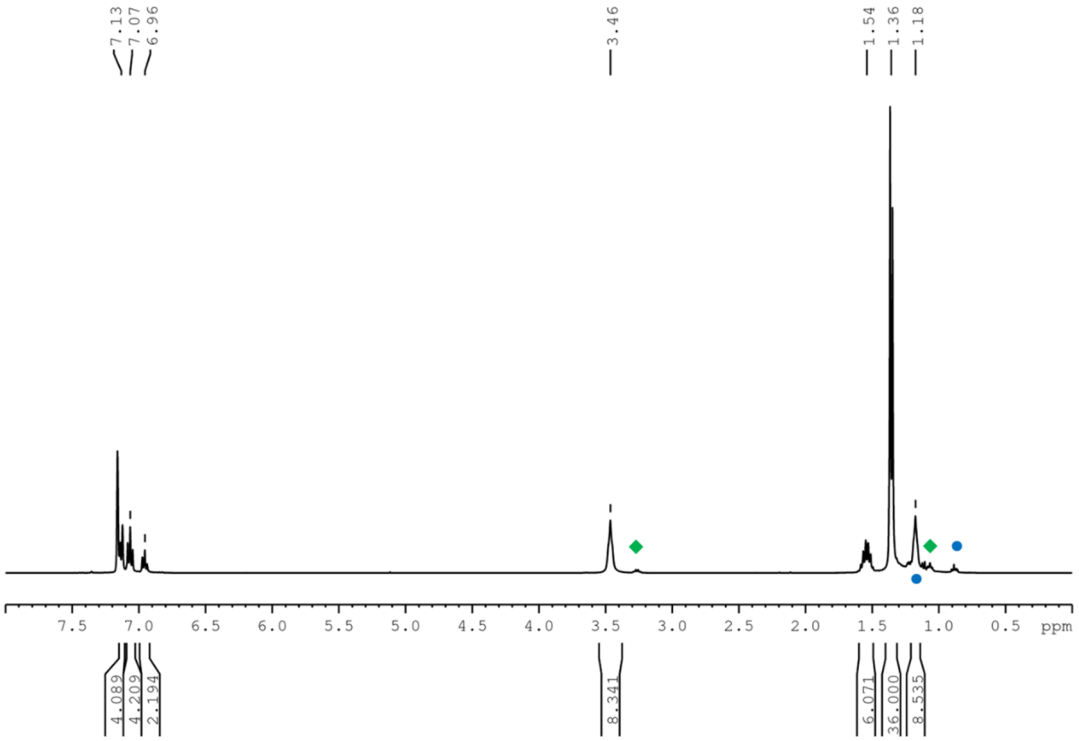

Figure S42. ^{1}H NMR spectrum (400 MHz, C_6D_6) of dilithiosilole **9**. ◆ Et_2O. ● *n*-hexane.

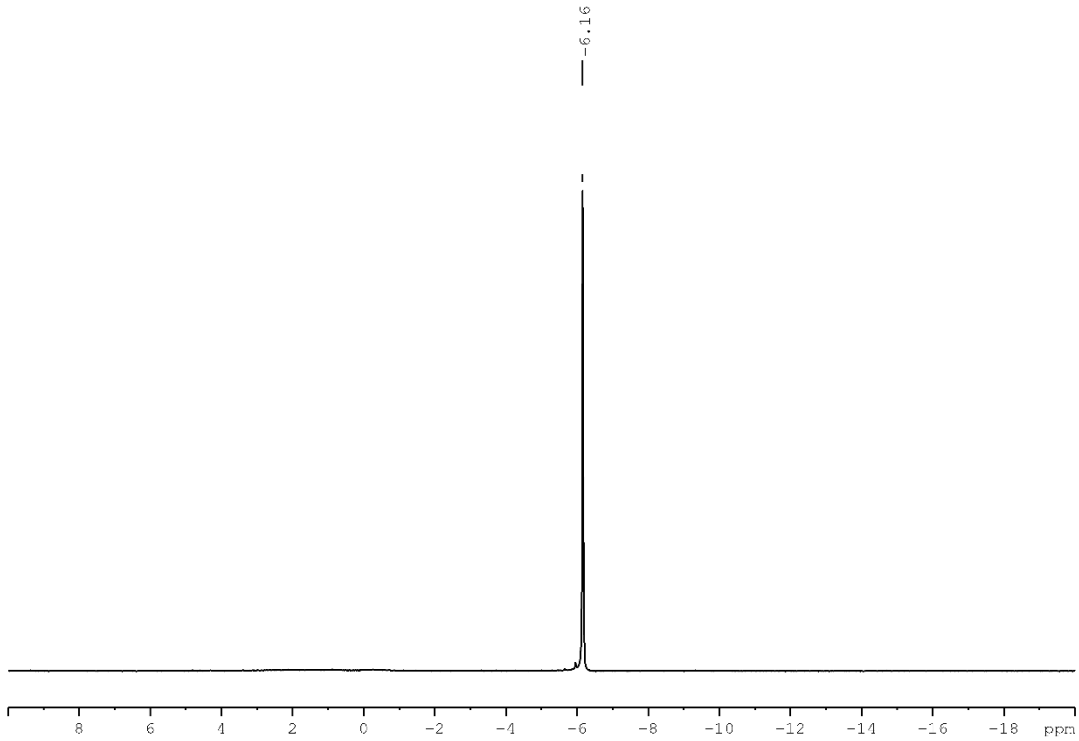

Figure S43. ^{7}Li NMR spectrum (194 MHz, C_6D_6) of dilithiosilole **9**.

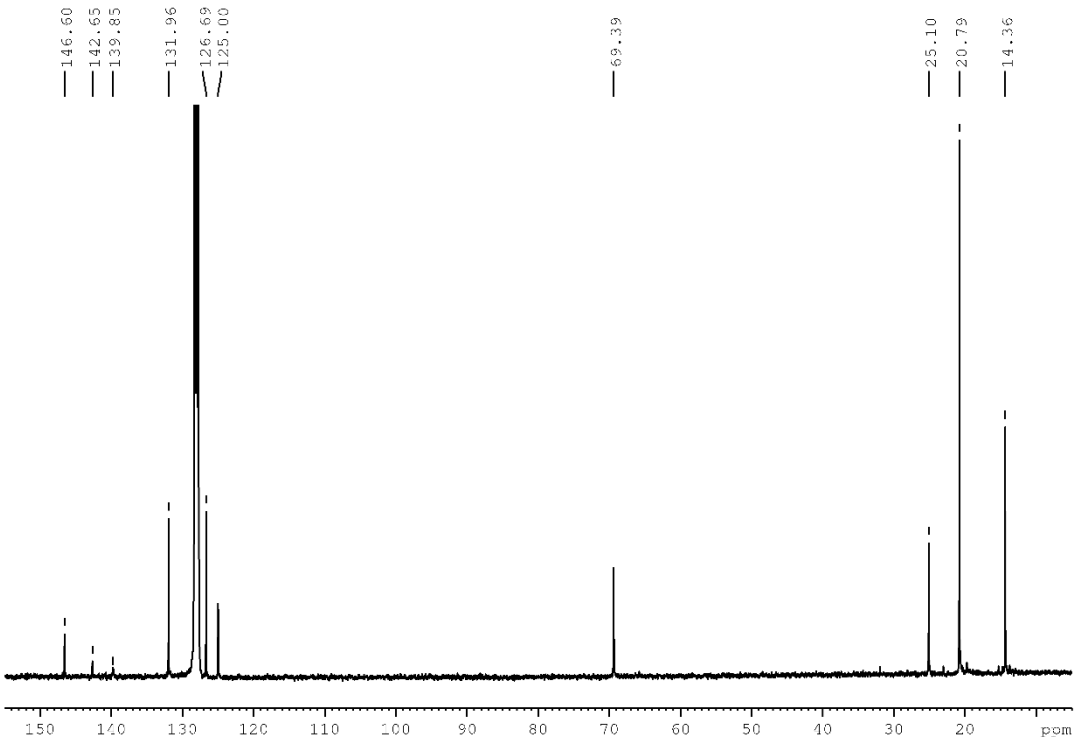

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of dilithiosilole **9**.

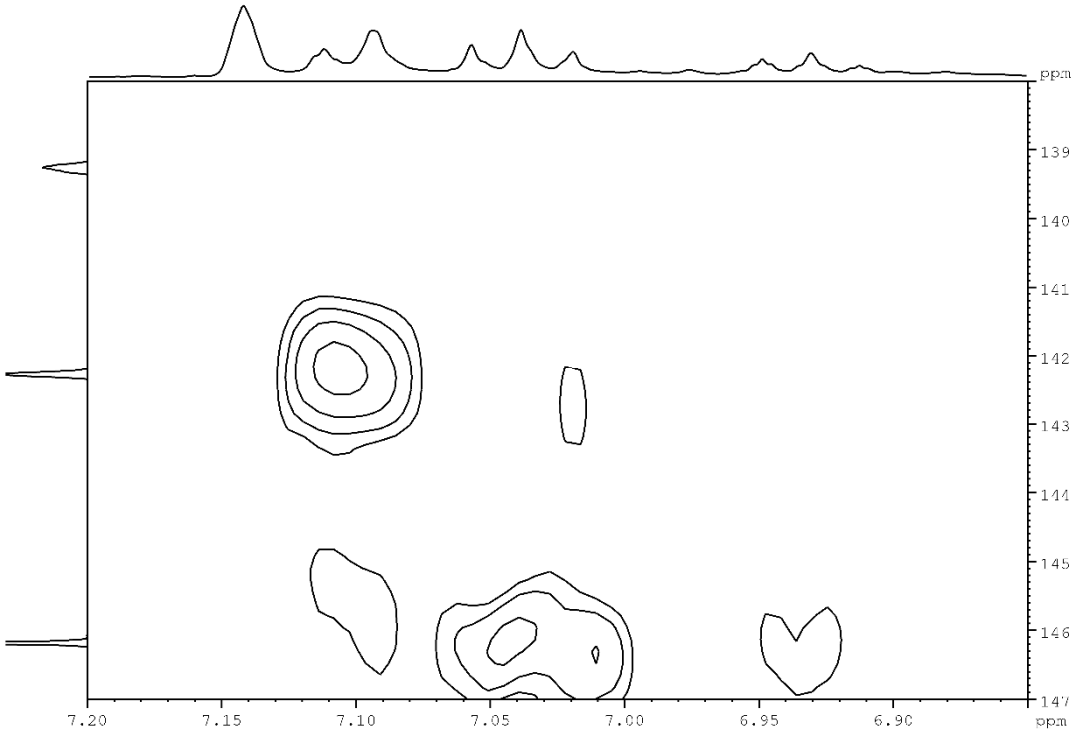

Figure S45. Cutout from the $^{13}C,^{1}H$ HMBC NMR spectrum (C_6D_6) of dilithiosilole **9**.

1.9.3. Products in the reaction of bromo(methoxy)silole 8 and Li

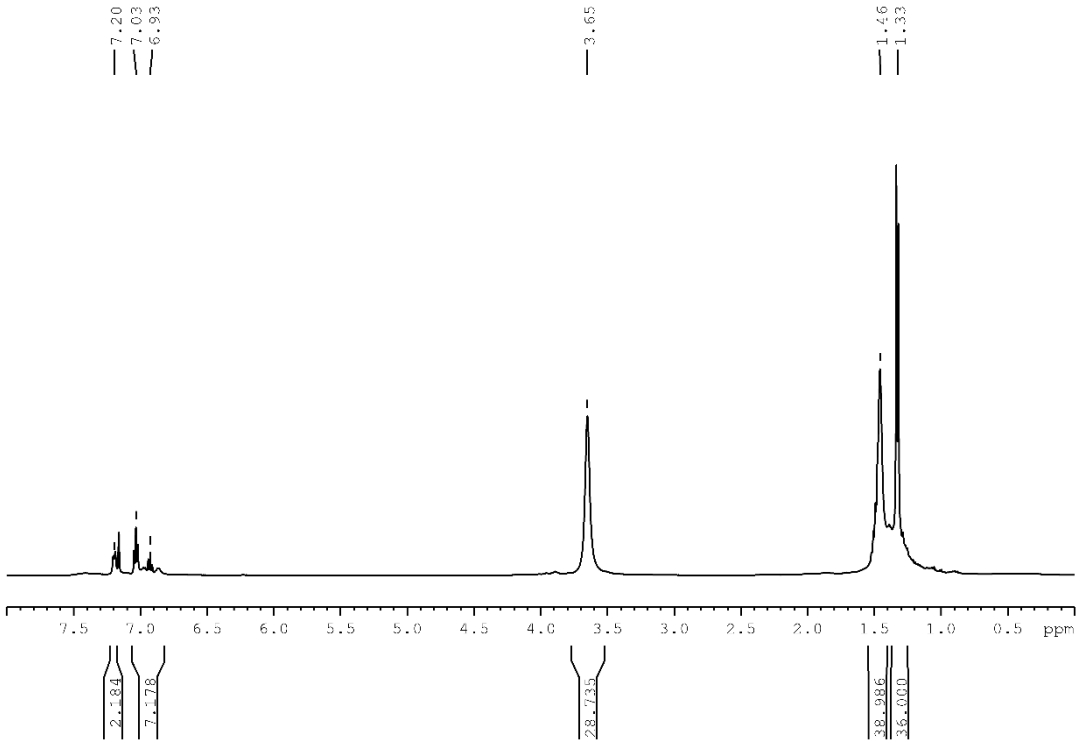

Figure S46. ^{1}H NMR spectrum (500 MHz, C_6D_6).

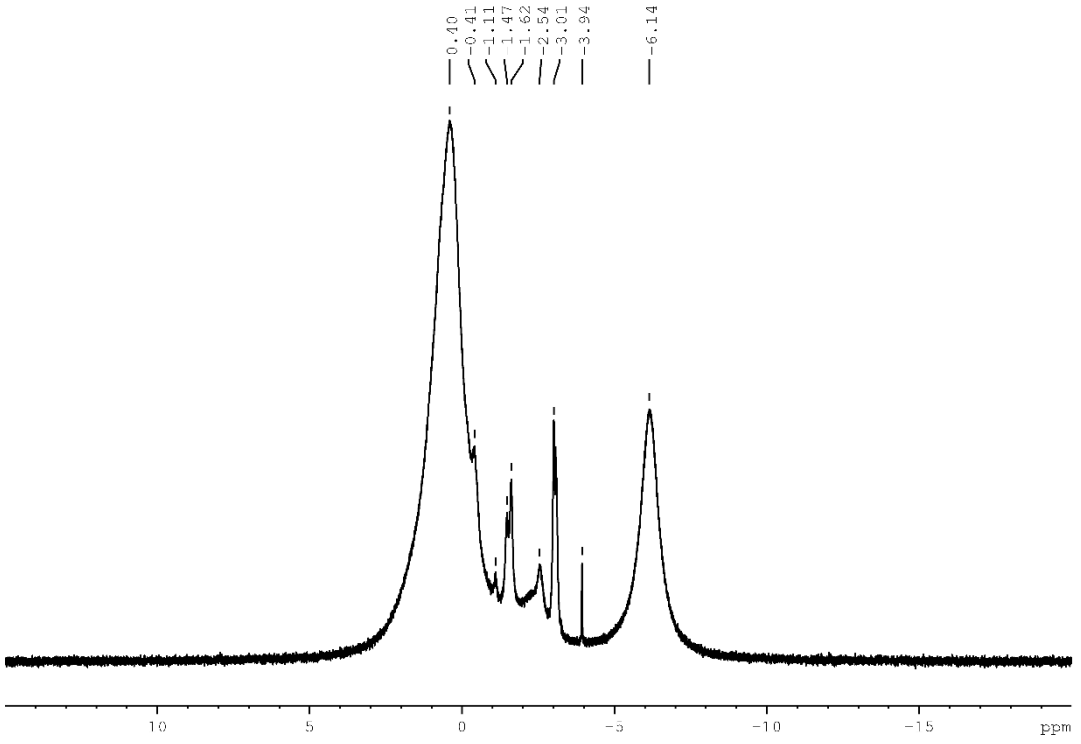

Figure S47. ^{7}Li NMR spectrum (194 MHz, C_6D_6).

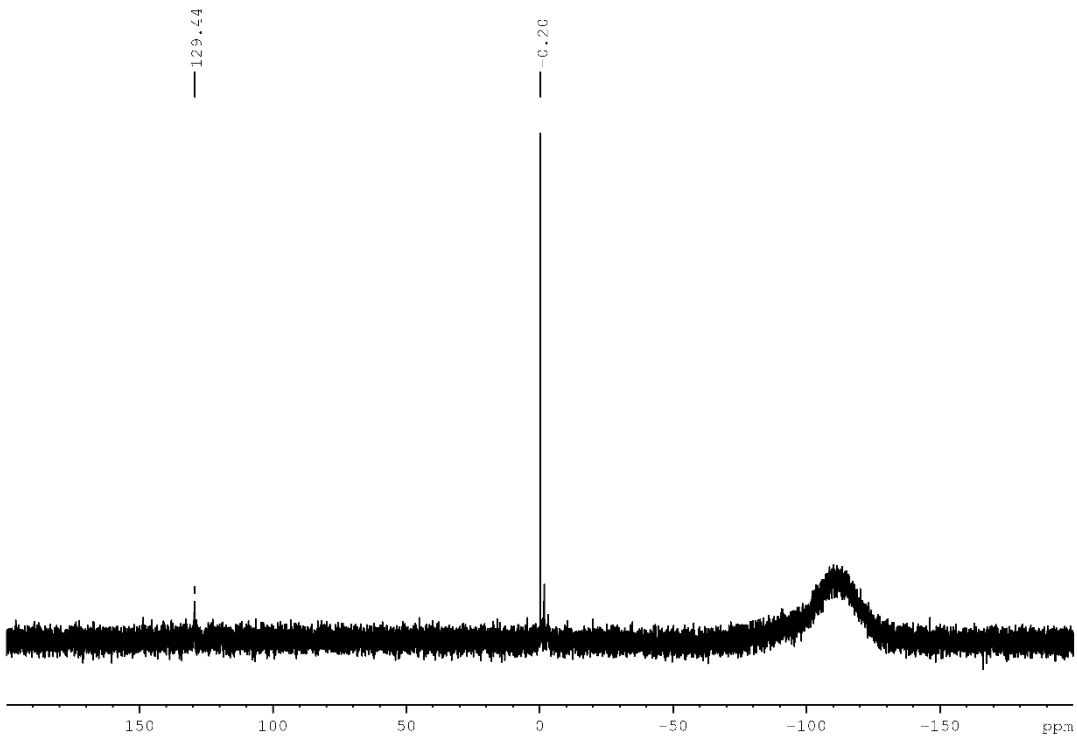

Figure S48. ^{29}Si NMR spectrum (99 MHz, C_6D_6).

2. Single-crystal X-ray diffraction analysis

2.1. 1,4-Dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenyl-buta-1,3-diene (1b)

Table S1. Crystallographic details of dilithiobutadiene **1b**.

Chemical formula	$C_{42}H_{72}O_2Li_2Si_2$
Formula mass	679.05 g/mol
Crystal system	monoclinic
***a*/Å**	18.308(2)
***b*/Å**	11.0924(14)
***c*/Å**	21.176(3)
α/°	90
β/°	95.485(2)
γ/°	90
Unit cell volume/Å^3	4280.6(9)
Temperature/K	120(2)
Space group	$P2_1/n$
No. of formula units per unit cell, *Z*	4
Radiation type	MoKα (λ = 0.71073)
Absorption coefficient, μ/mm^{-1}	0.114
No. of reflections measured	44762
No. of independent reflections	8590
R_{int}	0.1561
Final R_1 value ($I > 2\sigma(I)$)	0.0454
Final $wR(F^2)$ value ($I > 2\sigma(I)$)	0.1266
Final R_1 value (all data)	0.0565
Final $wR(F^2)$ value (all data)	0.1338
Goodness of fit on F^2	1.045
Δρ / e Å^{-3}	0.58/-0.37

2.2. 1,1-Dibromo-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (7)

Table S2. Crystallographic details of dibromosilole **7**.

Chemical formula	$C_{34}H_{52}Si_3Br_2$
Formula mass	704.84 g/mol
Crystal system	monoclinic
***a*/Å**	25.3003(8)
***b*/Å**	8.7240(2)
***c*/Å**	34.4836(11)
***α*/°**	90
***β*/°**	108.683(4)
***γ*/°**	90
Unit cell volume/Å^3	7210.1(4)
Temperature/K	123.15
Space group	*I*121
No. of formula units per unit cell, *Z*	8
Radiation type	MoKα (λ = 0.71073)
Absorption coefficient, μ/mm^{-1}	2.369
No. of reflections measured	24321
No. of independent reflections	13377
R_{int}	0.0240
Final R_1 value ($I > 2\sigma(I)$)	0.0328
Final $wR(F^2)$ value ($I > 2\sigma(I)$)	0.0773
Final R_1 value (all data)	0.0384
Final $wR(F^2)$ value (all data)	0.0792
Goodness of fit on F^2	1.043
Δρ / e Å^{-3}	0.85/-0.25

2.3. Dilithio-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (9)

Table S3. Crystallographic details of dilithiosilole **9**.

Chemical formula	$C_{42}H_{68}O_2Li_2Si_3$
Formula mass	703.11 g/mol
Crystal system	monoclinic
***a*/Å**	15.4817(14)
***b*/Å**	12.5178(12)
***c*/Å**	12.8080(11)
***α*/°**	90
***β*/°**	118.074(4)
***γ*/°**	90
Unit cell volume/Å^3	2190.1(4)
Temperature/K	150(2)
Space group	C2
No. of formula units per unit cell, *Z*	2
Radiation type	MoKα (λ = 0.71073)
Absorption coefficient, μ/mm^{-1}	0.138
No. of reflections measured	13155
No. of independent reflections	3908
R_{int}	0.0411
Final R_1 value ($I > 2\sigma(I)$)	0.0451
Final $wR(F^2)$ value ($I > 2\sigma(I)$)	0.1035
Final R_1 value (all data)	0.0550
Final $wR(F^2)$ value (all data)	0.1082
Goodness of fit on F^2	1.054
Flack parameter	0.5
Δρ / e Å^{-3}	0.24/-0.16