Supporting Information for

Probing Solvent Effects on Mixed Aggregates Associating a Chiral Lithium Amide and *n*-BuLi by NMR: From Structure to Reactivity

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1. Instrumental Considerations

NMR spectra were recorded at 195K and 250K on a Bruker AVIII 500 spectrometer operating at 500.13 MHz for ^{1}H, 125.13 MHz for ^{13}C and 73.60 MHz for ^{6}Li. Experiments were run under TopSpin (version 2.1, Bruker Biospin, Karlsruhe) with a BBFO$\{^{1}H,X\}$ probe and a z gradient coil giving a maximum gradient of 50 G cm^{-1}. ^{1}H and ^{13}C chemical shifts were referenced to the solvent residual signals (for Et_2O_{d10} at δ 3.34 ppm (^{1}H) and 14.5 ppm (^{13}C), for THF_{d8} at δ 1.73 (^{1}H) and 25.31 ppm(^{13}C)). Lithium spectra were referenced to external 0.3 M ^{6}LiCl solution in THF_{d8} (δ 0.0).

2. NMR spectra of amine 3a and amide 4a in Et_2O_{d10}

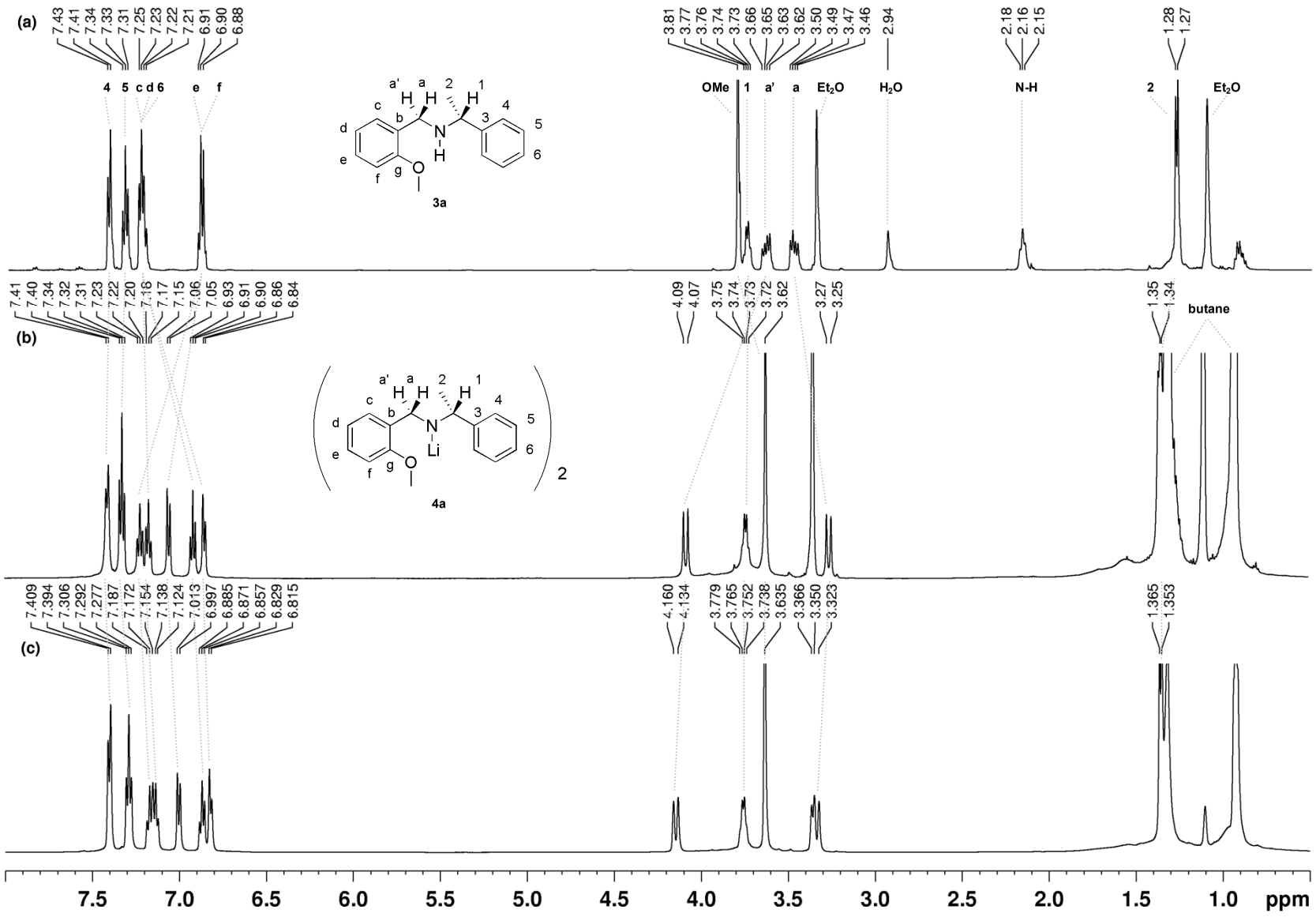


Figure S1. ^{1}H NMR spectra of **3a** at 195K (a) and **4a** at 195K (b) and at 250K (c) in Et_2O_{d10}

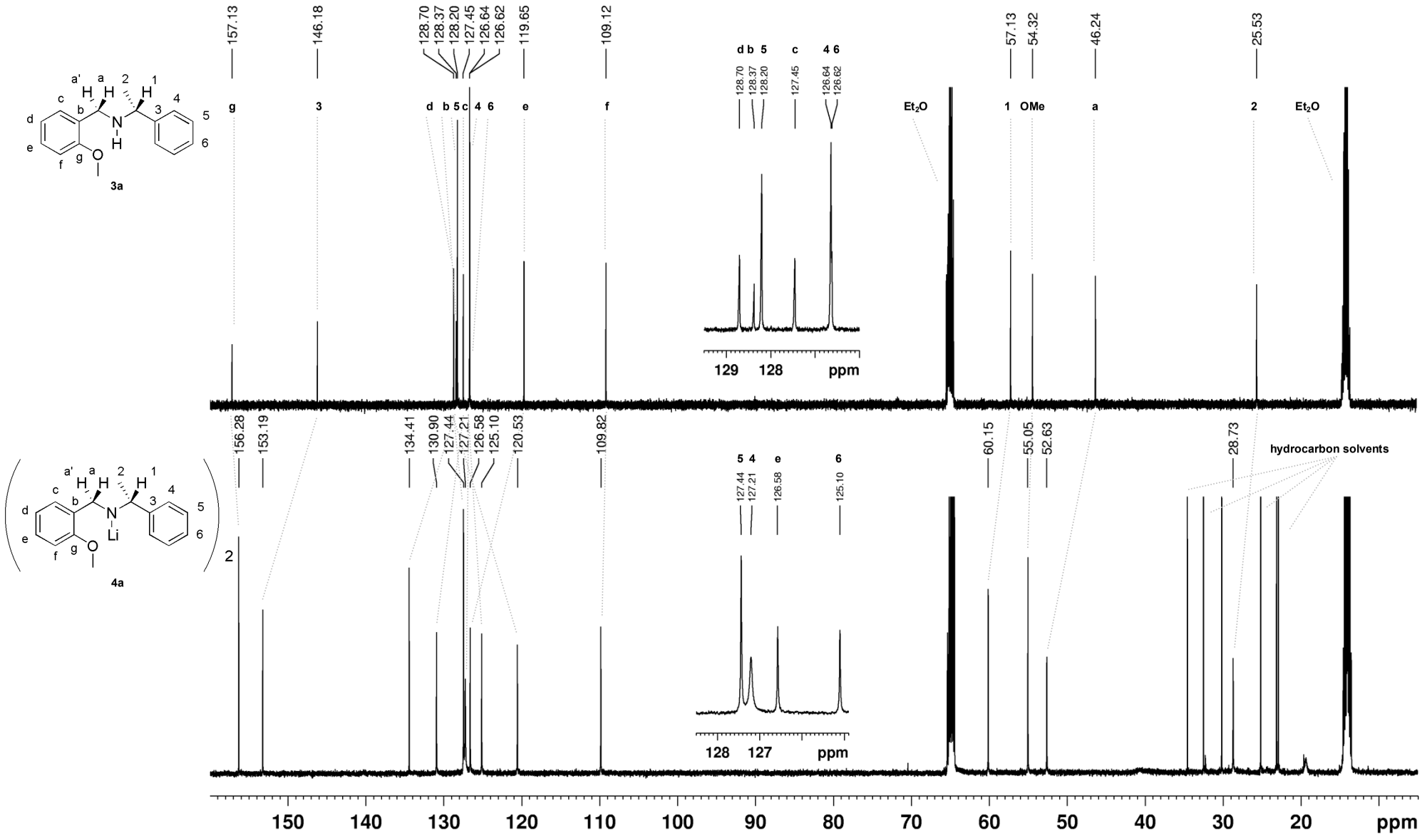


Figure S2. $^{13}C\{^{1}H\}$ NMR spectra of **3a** (top) and **4a** (bottom) in Et_2O_{d10} at 195K

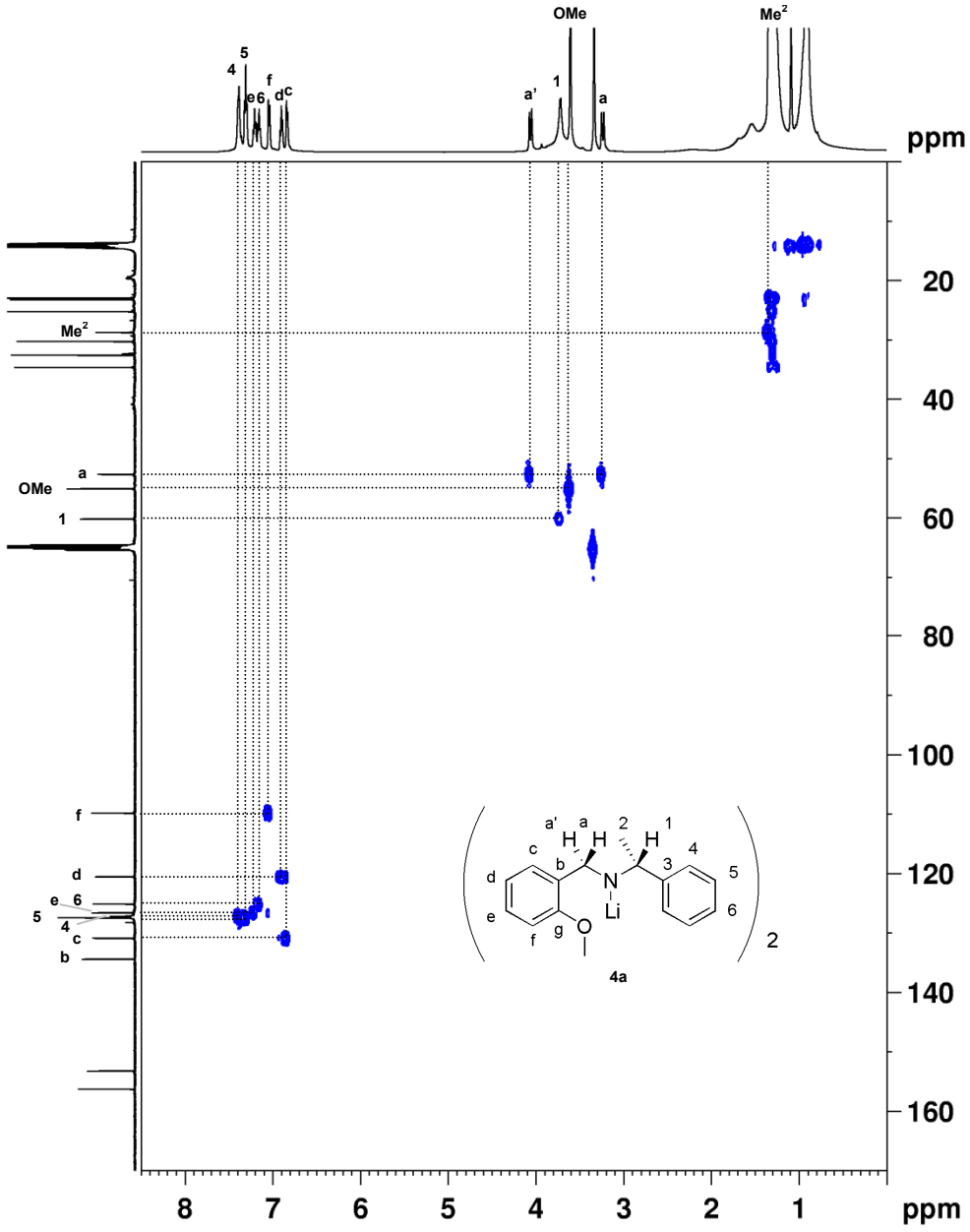


Figure S3. ^{1}H, ^{13}C-HMQC spectrum of **4a** in Et_2O_{d10} at 195K

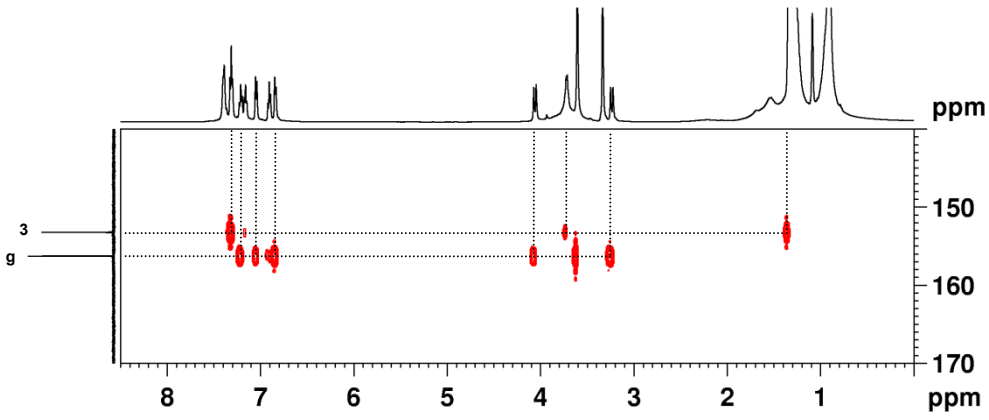


Figure S4. ^{1}H, ^{13}C-HMBC spectrum of **4a** in Et_2O_{d10} at 195K

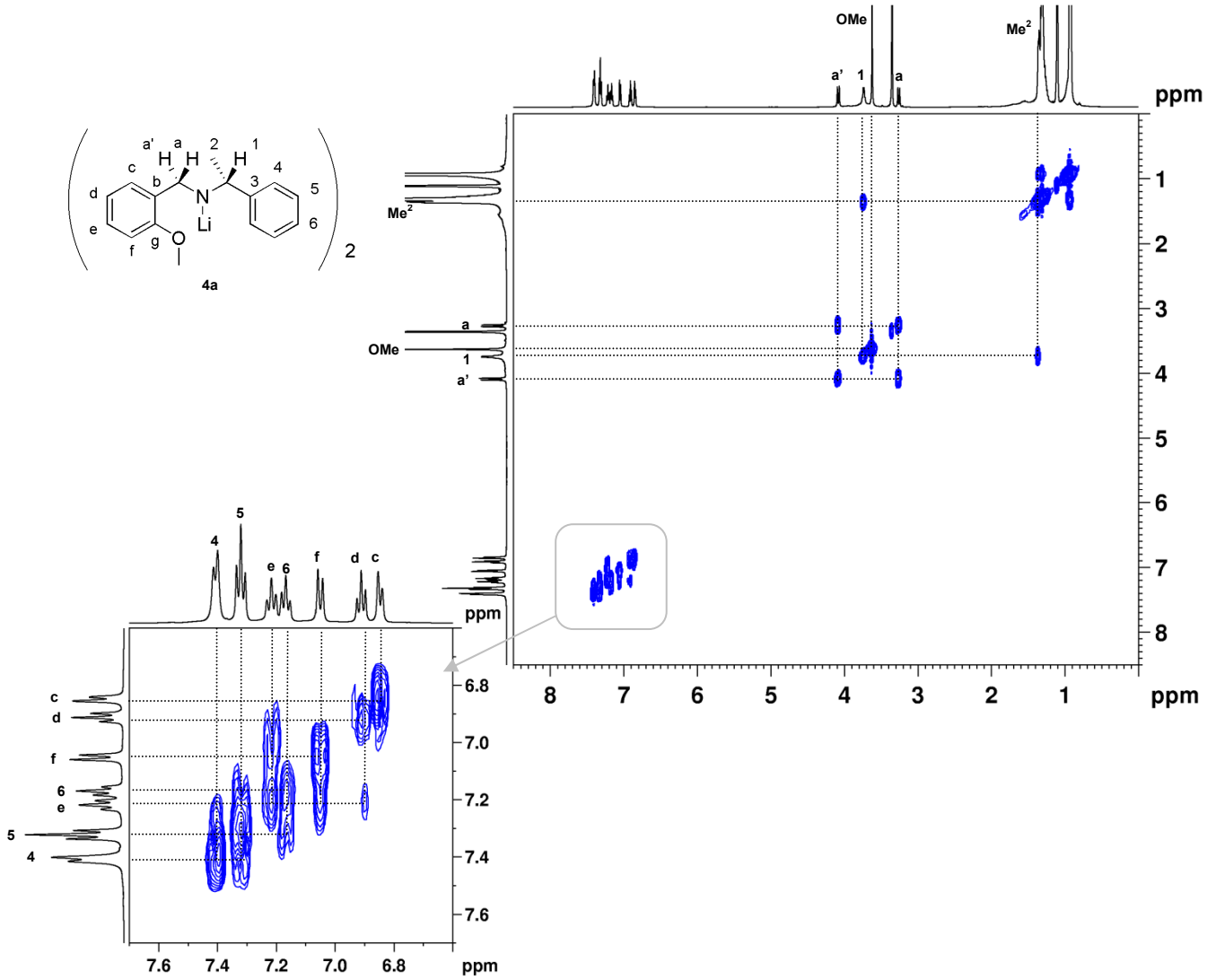


Figure S5. $^{1}H,^{1}H$-COSY spectrum of **4a** in Et_2O_{d10} at 195K

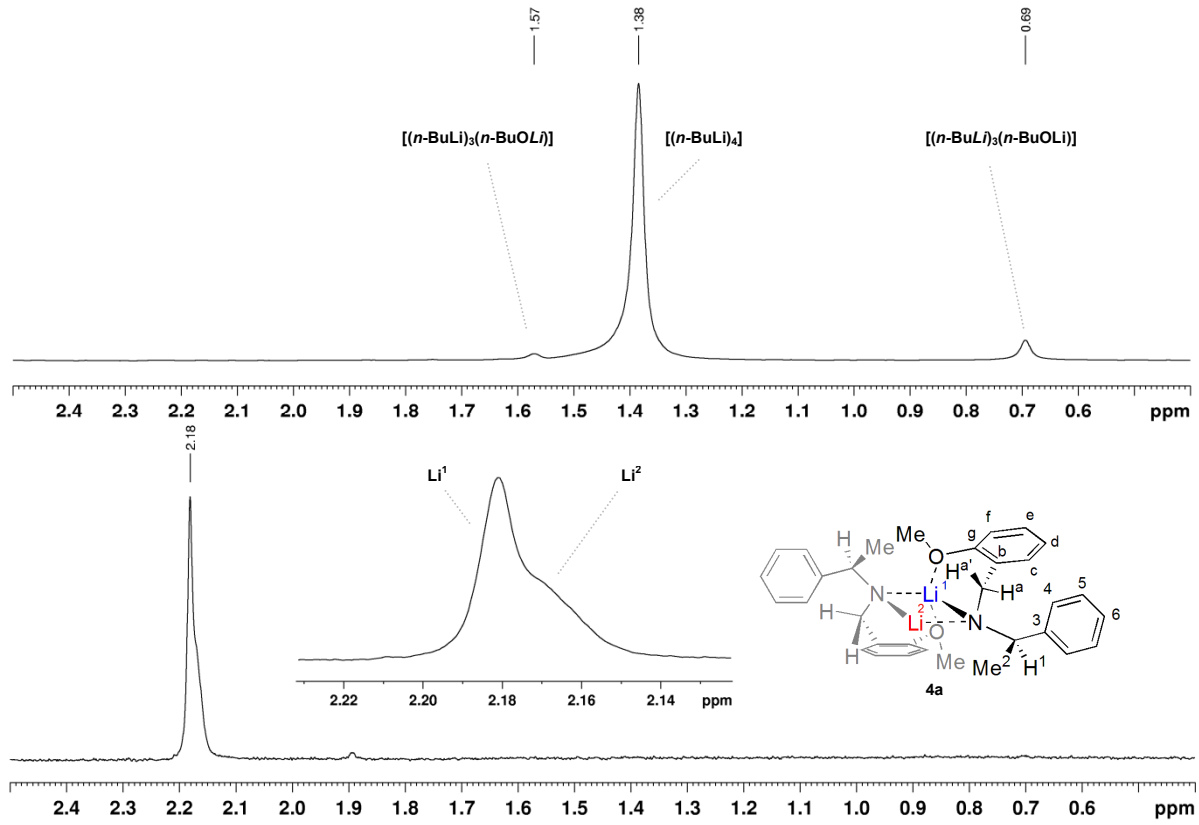


Figure S6. ^{6}Li NMR spectra of *n*-BuLi (top) and **4a** (bottom) in Et_2O_{d10} at 195K

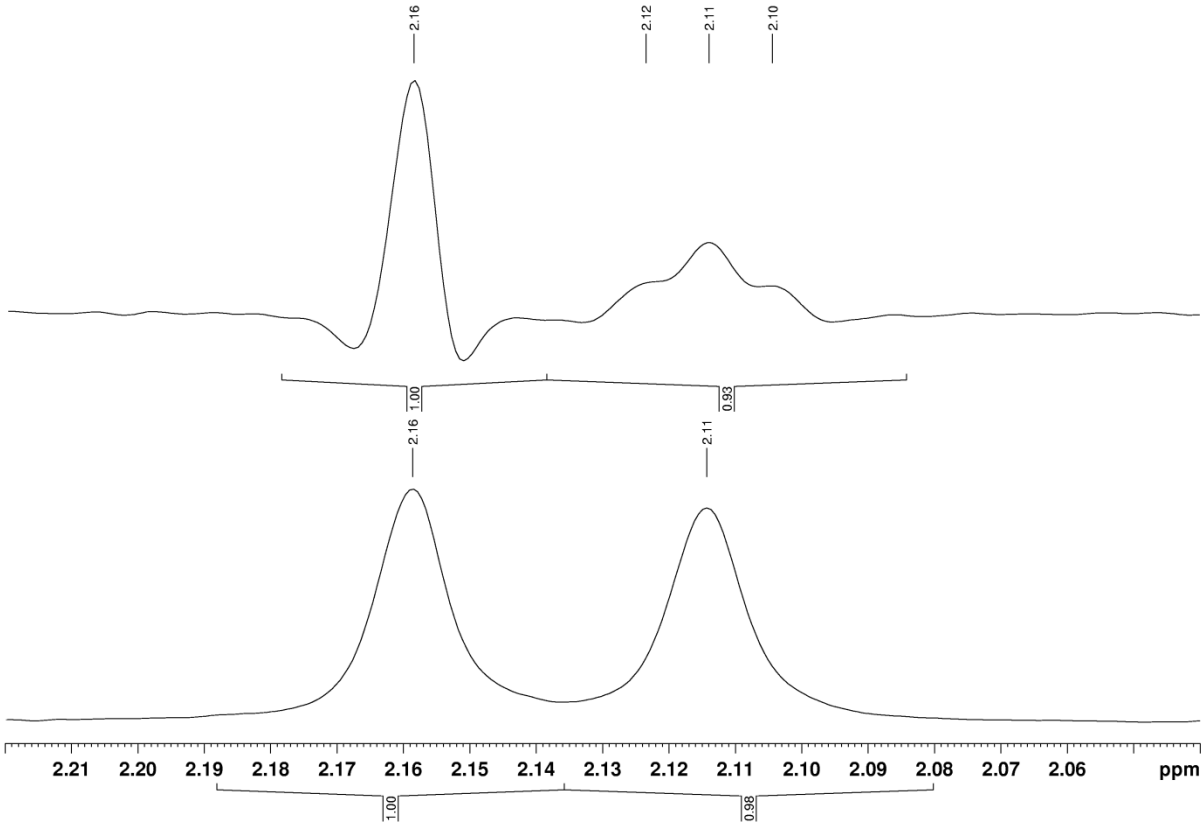


Figure S7. ^{6}Li NMR spectra with resolution enhancement (GB = 0.1, LB = –0.5) (top) and proton H^1 selective decoupling (bottom) of **4a** in Et_2O_{d10} at 250K

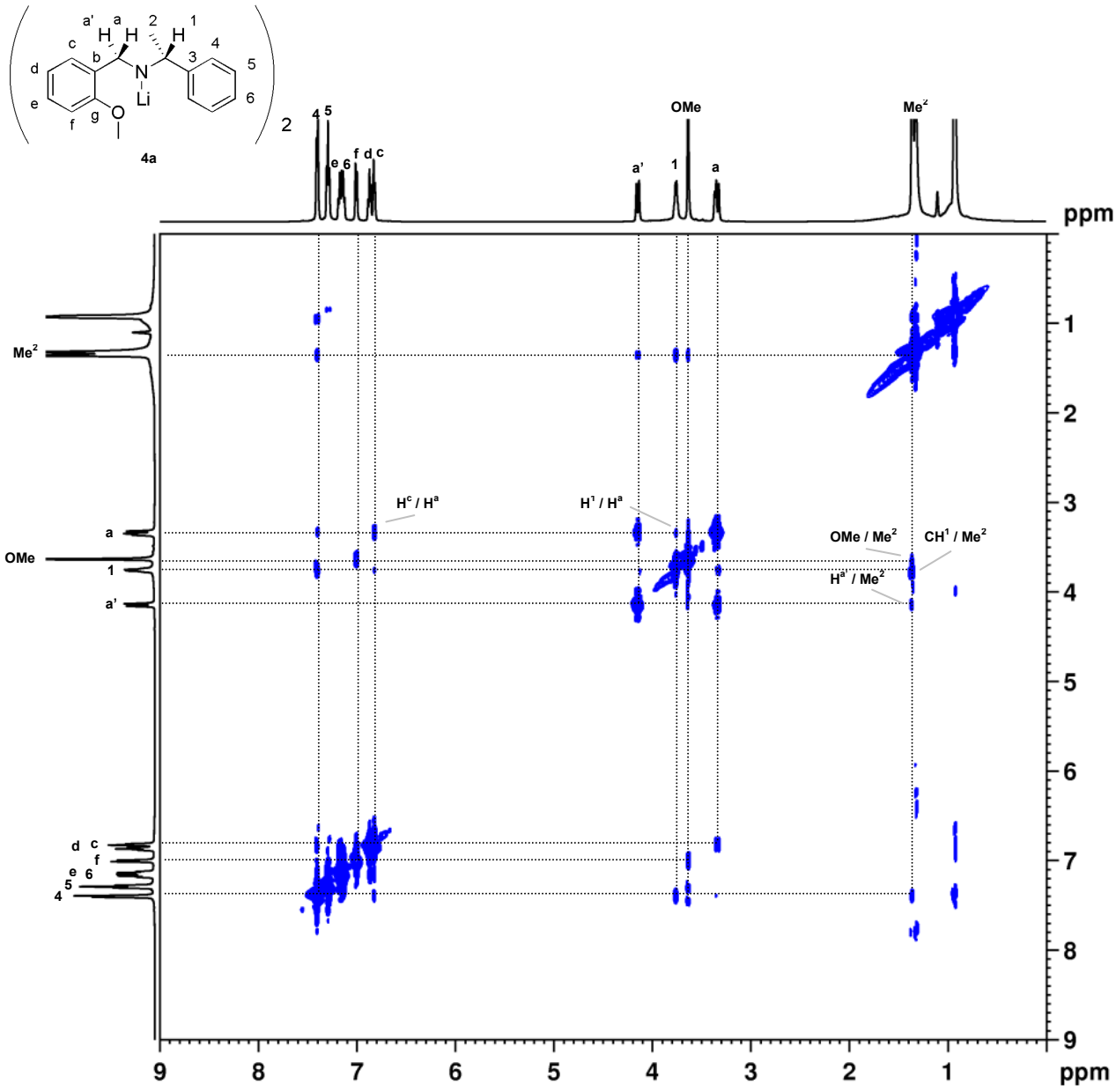


Figure S8. ^{1}H,^{1}H-NOESY (mixing time τ_m = 0.60s) spectrum of **4a** in Et_2O_{d10} at 250K.

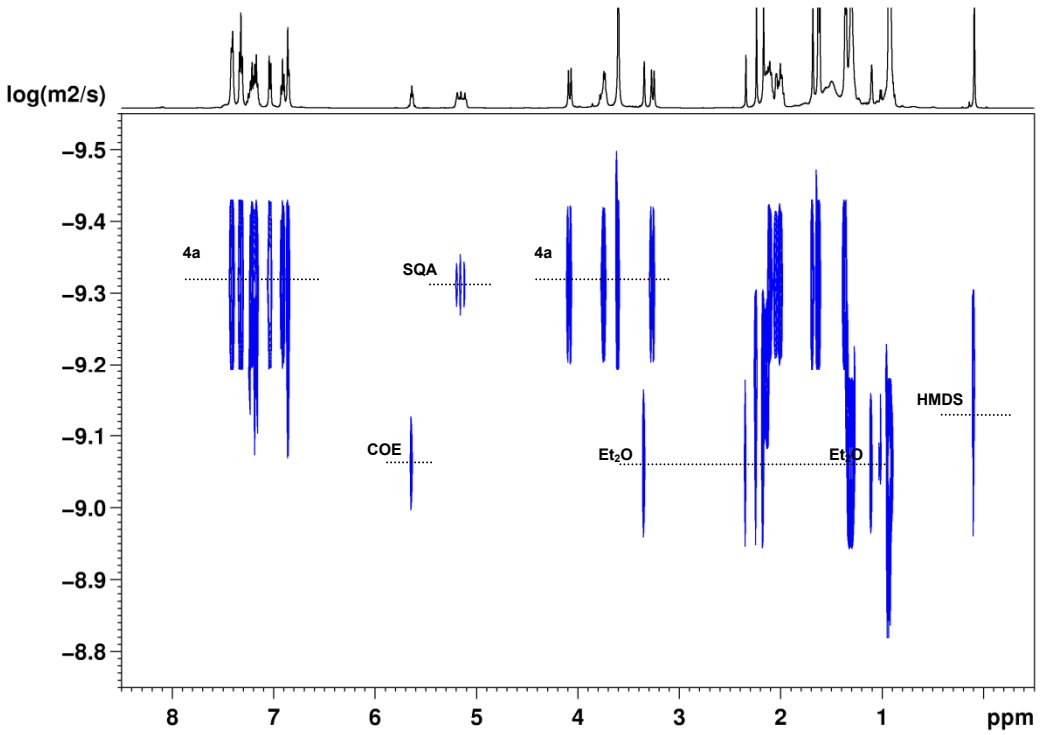
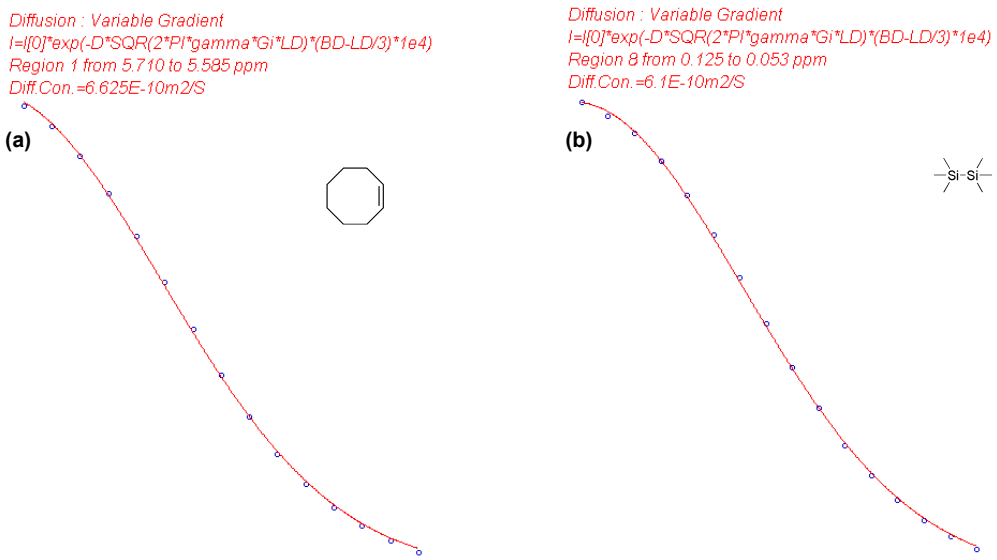


Figure S9. ^{1}H-DOSY spectrum of **4a** in Et_2O_{d10} at 195K

Figure S10. Decay curves of ^{1}H-DOSY for Internal References [COE (a), HMDS (b), SQA (c)] and **4a** (d) in Et_2O_{d10} at 195K



(Figure S10, continued)

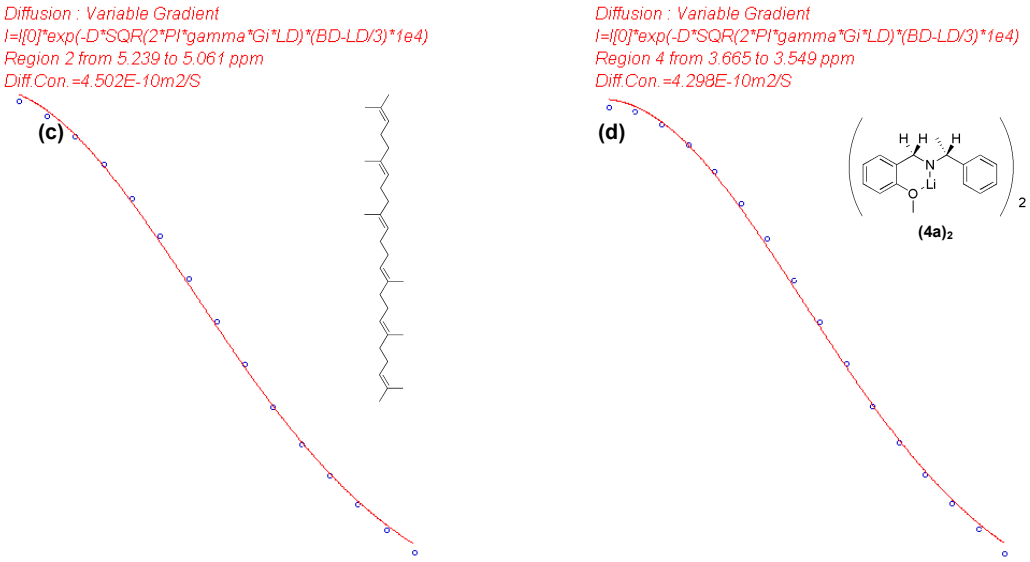
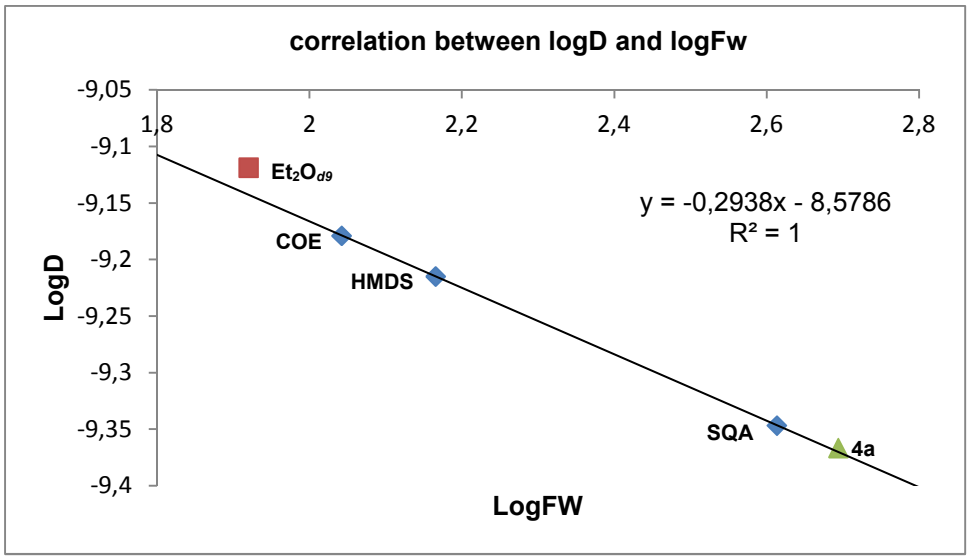


Table S1 D-FW analyses of ^{1}H-DOSY data of **4a** in Et_2O_{d10} at 195K

compound	FW (g mol^{-1})	LogFW	D (m^2 s^{-1})	logD	predicted FW (g mol^{-1})	Error (%)
COE	110,2	2,042	6,63E-10	-9,178	110.2	
HMDS	146,4	2,165	6,10E-10	-9,214	146.4	
SQA	410,7	2,613	4,50E-10	-9,346	410.7	
Et_2O_{d9}	68,7	1,837	7,61E-10	-9,118	83,2	–20.8
4a	479,8	2,681	4,29E-10	-9,367	494.5[a]	–2.5

[a]: the predicted FW is referred to an unsolvated dimer [(**4a**)$_2$].



3. NMR spectra of amine 3a and amide 4a in THF-d_8

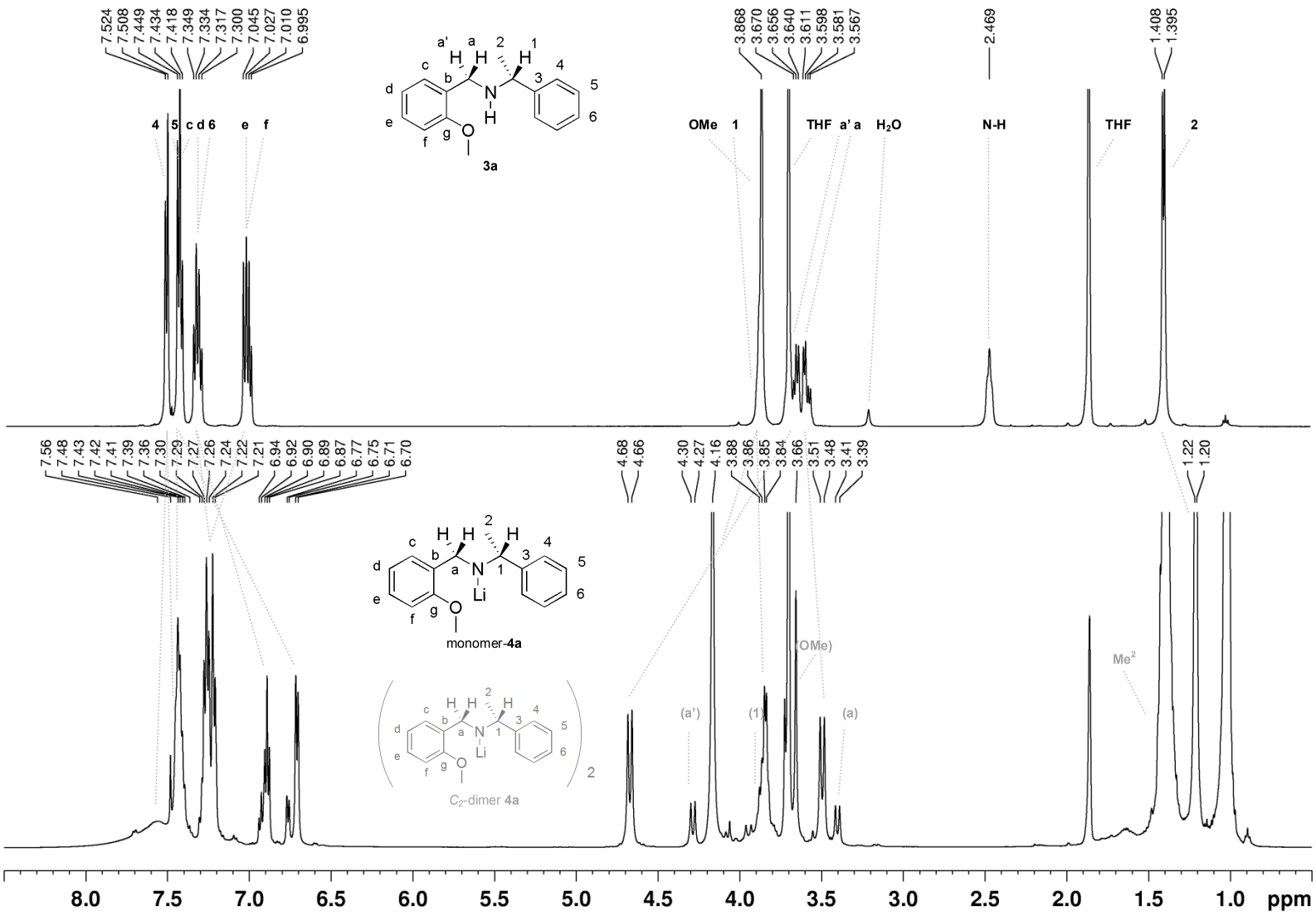


Figure S11. ^{1}H NMR spectra of **3a** (top) and **4a** (bottom) in THF$_{d8}$ at 195K

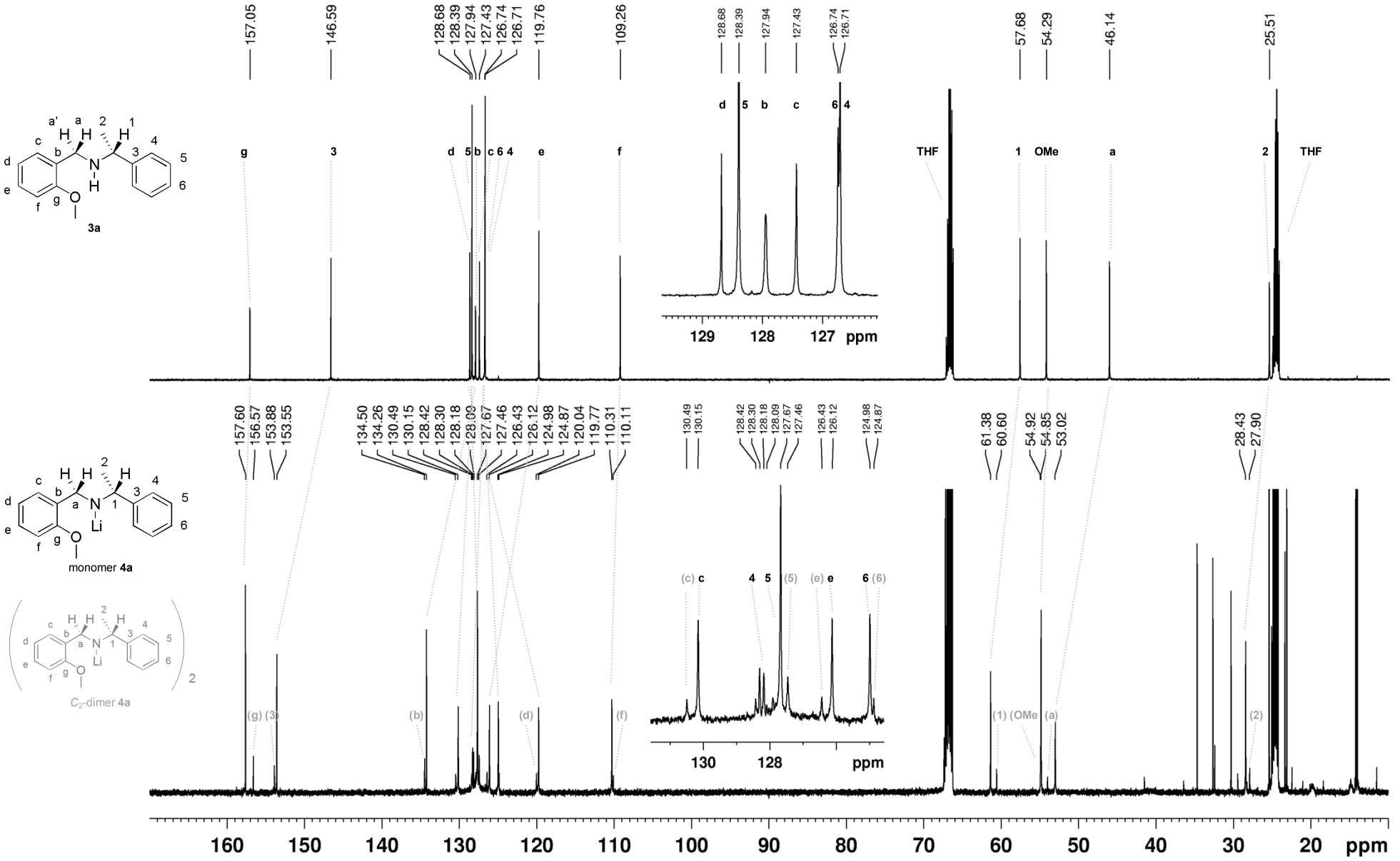


Figure S12. $^{13}C\{^{1}H\}$ NMR spectra of **3a** (top) and **4a** (bottom) in THF_{d8} at 195K

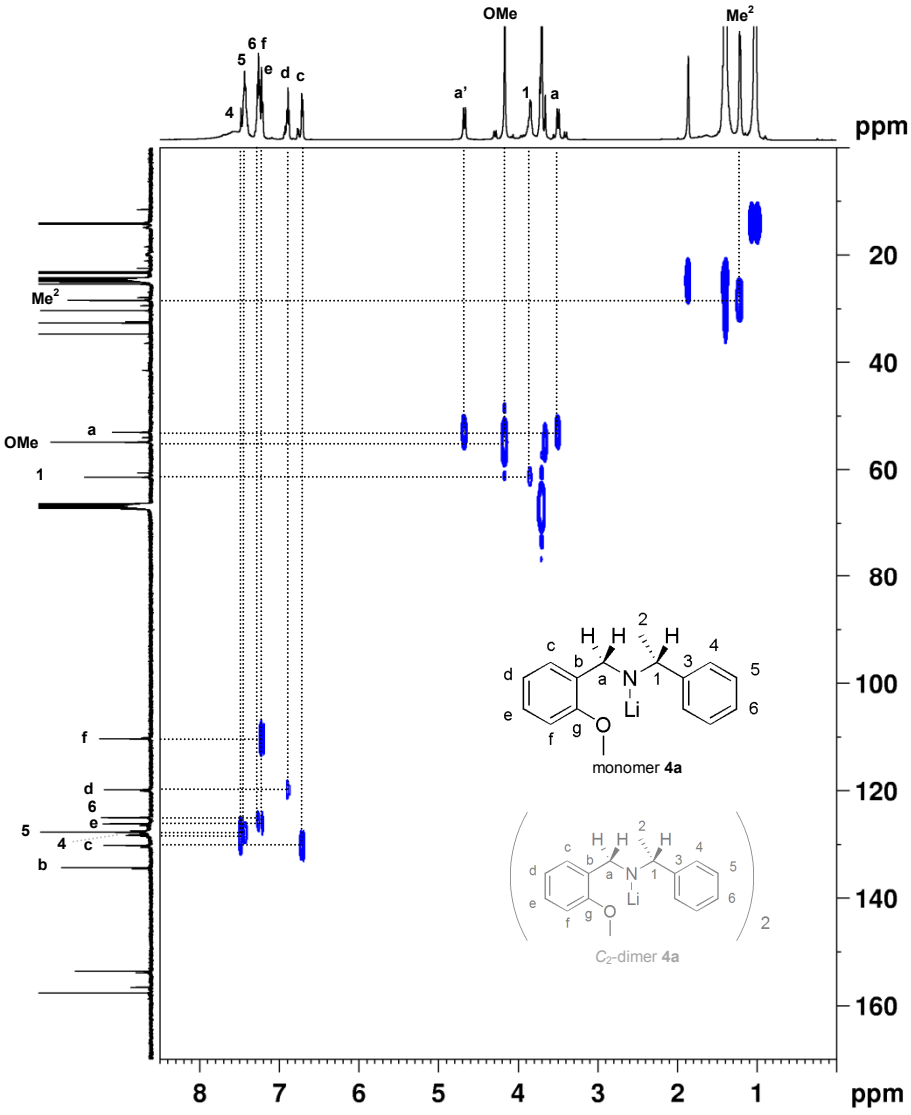


Figure S13. $^{1}H,^{13}C$-HMQC spectrum of **4a** in THF_{d8} at 195K

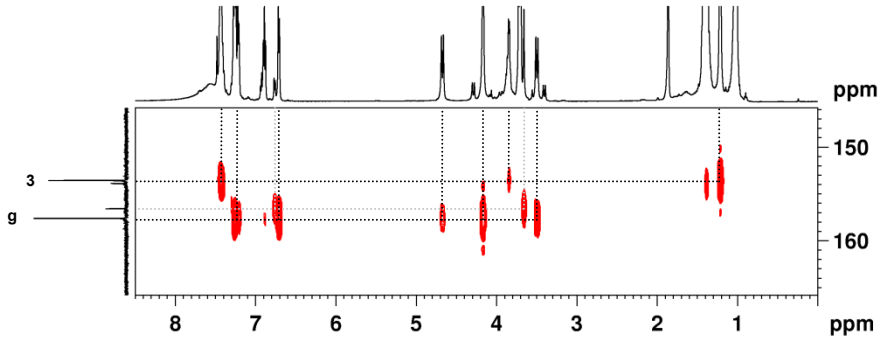


Figure S14. $^{1}H,^{13}C$-HMBC spectrum of **4a** in THF_{d8} at 195K

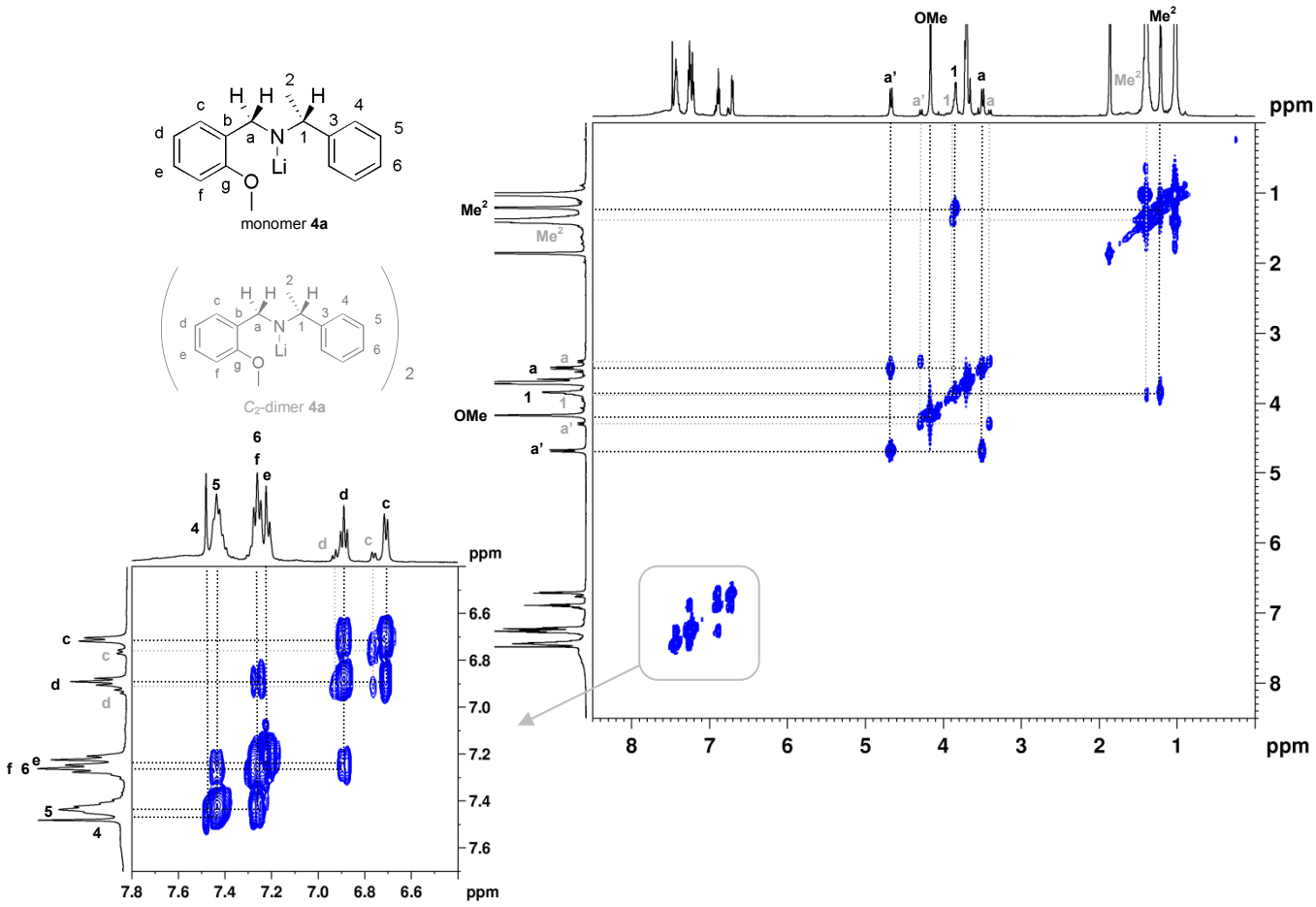


Figure S15. $^{1}H,^{1}H$-COSY spectrum of **4a** in THF_{d8} at 195K

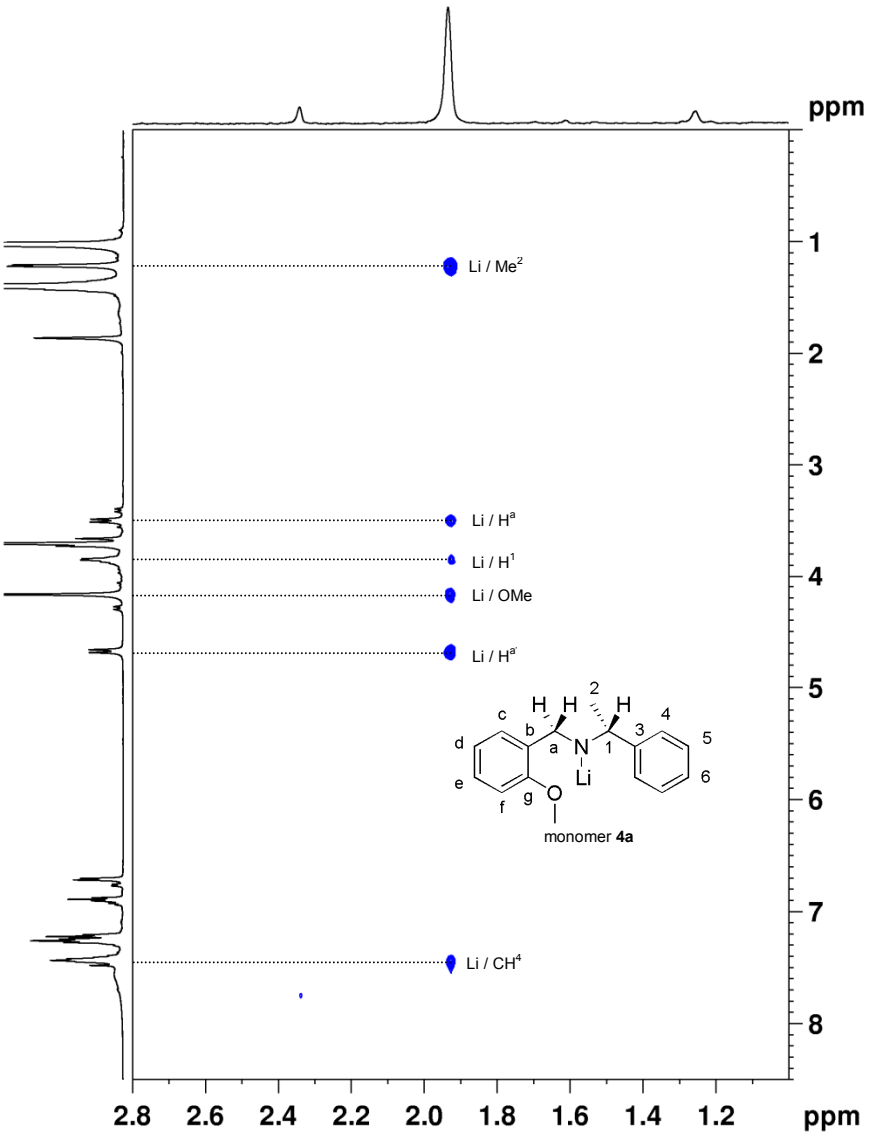


Figure S16. ^{6}Li,^{1}H-HOESY spectrum (mixing time τ_m= 1.44s) of **4a** in THF$_{d8}$ at 195K

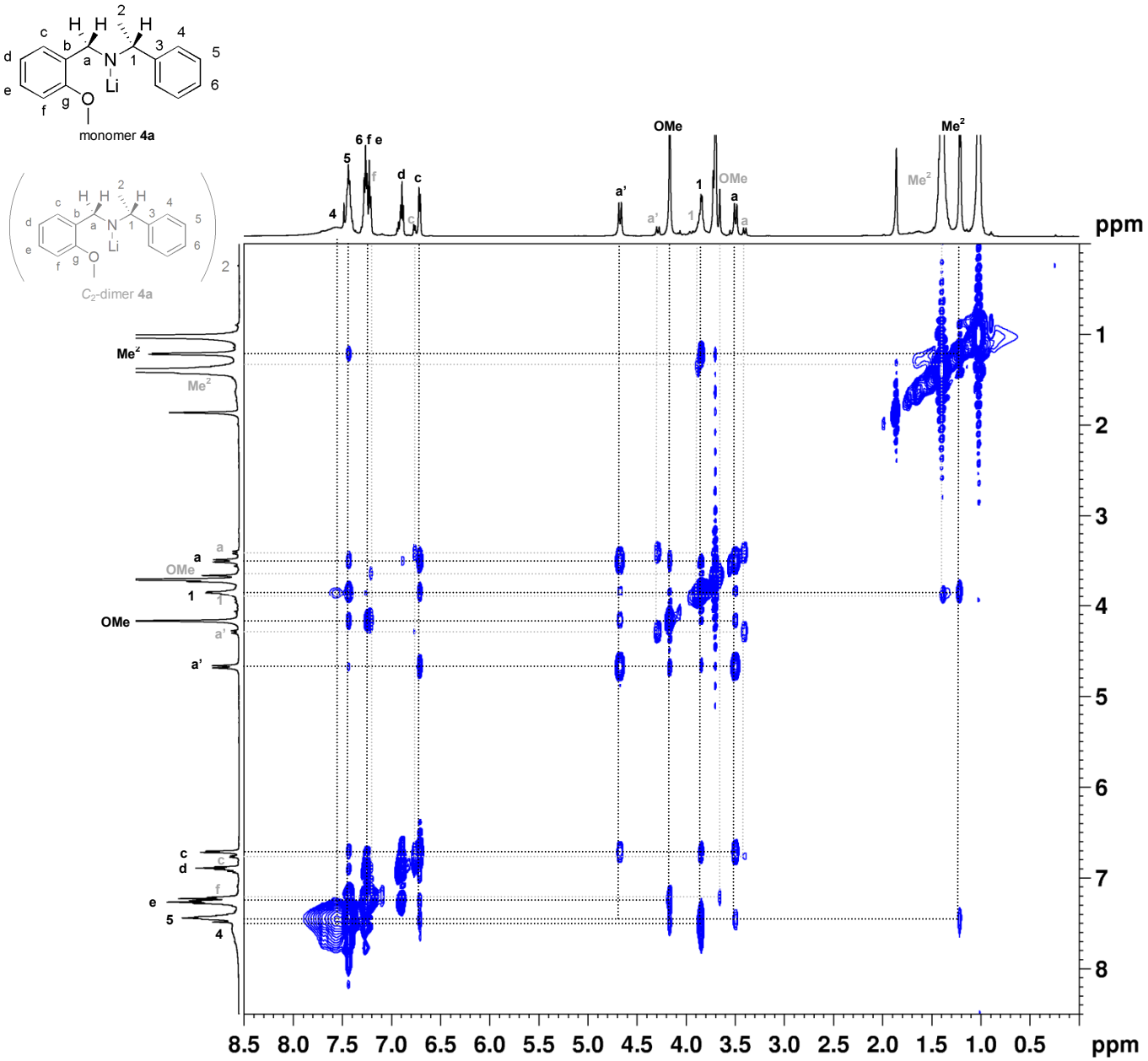


Figure S17. ^{1}H,^{1}H-NOESY spectrum (mixing time τ_m= 0.60s) of **4a** in THF_{d8} at 195K

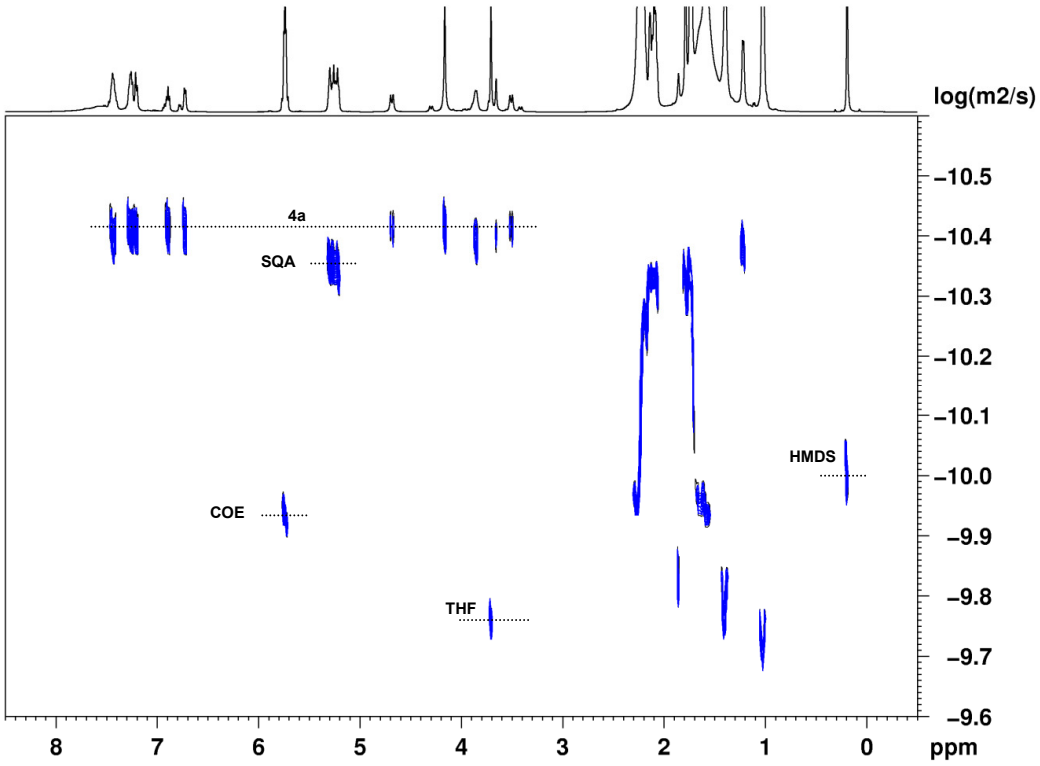
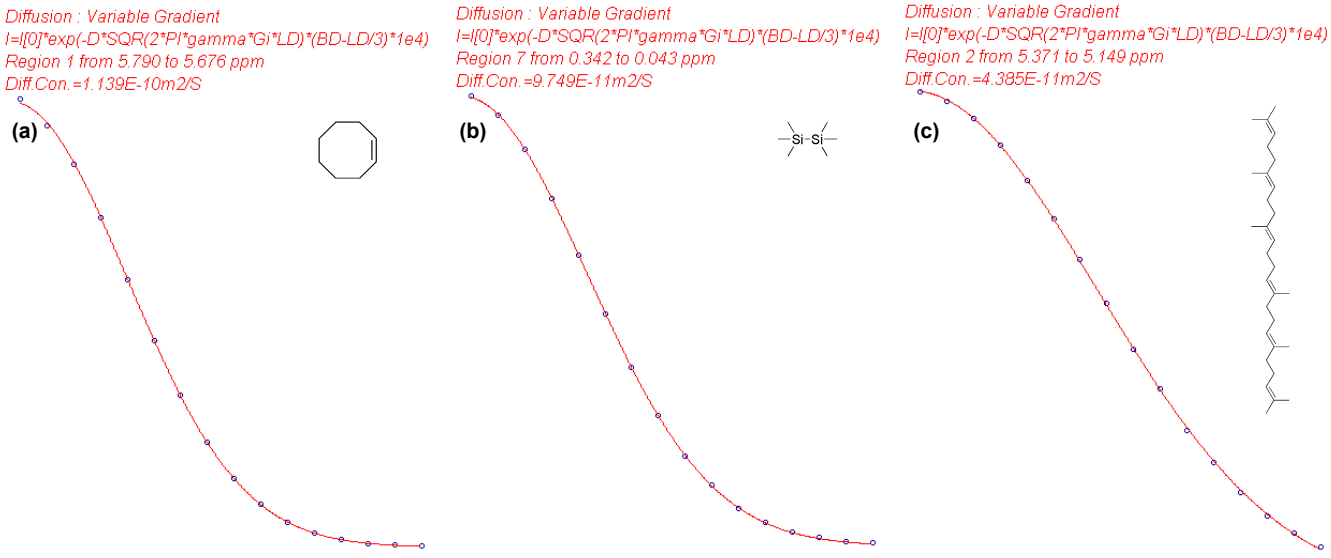


Figure S18. ^{1}H-DOSY spectrum of **4a** in THF_{d8} at 195K

Figure S19. Decay curves of ^{1}H-DOSY for Internal References [COE (a), HMDS (b), SQA (c)], monomer **4a** (d) and C_2-dimer **4a** (e) in THF_{d8} at 195K



(Figure S19, continued)

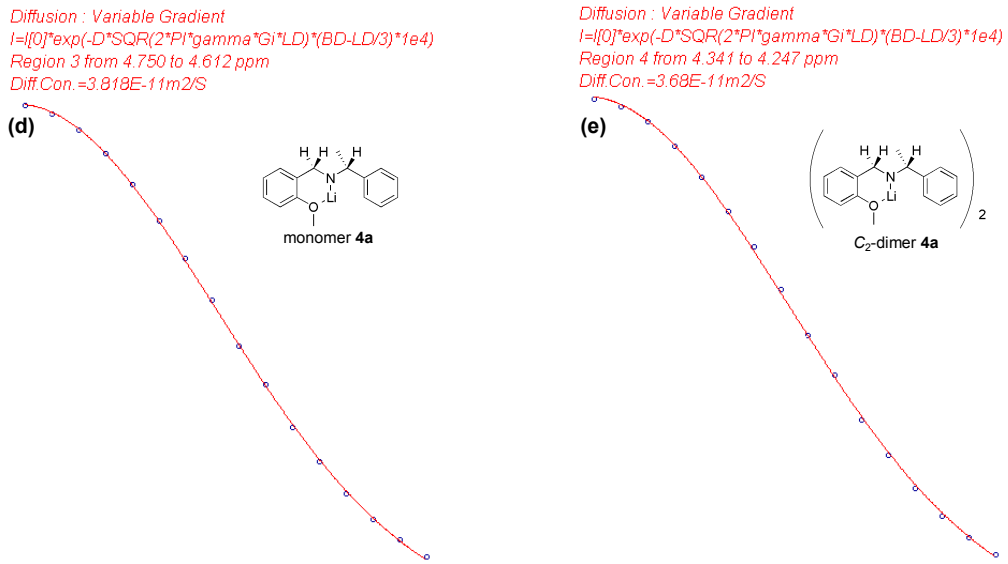
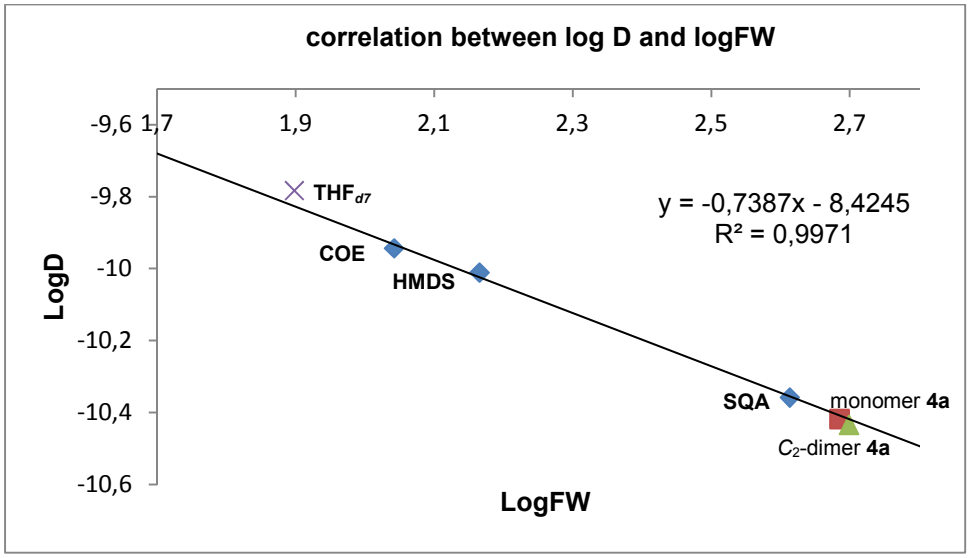


Table S2. D-FW analyses of ^{1}H-DOSY data of **4a** in THF_{d8} at 195K

compound	FW (g mol^{-1})	LogFW	D (m^2 s^{-1})	logD	predicted FW (g mol^{-1})	Error (%)
COE	110,2	2,042	1,14E-10	-9,943	110.2	
HMDS	146,4	2,165	9,75E-11	-10,011	146.4	
SQA	410,7	2,613	4,39E-11	-10,358	410.7	
THF_{d7}	69,040	1,839	1,65E-10	-9,783	79,1	–20.8
monomer **4a**	500, 0	2,699	3,82E-11	-10,418	484,7[a]	3.1
C_2-dimer **4a**	525,4	2,720	3,68E-11	-10,434	494.5[b]	5.9
C_2-dimer **4a**	525,4	2,720	3,68E-11	-10,434	573.7[c]	–9.2

[a]: the predicted FW is referred to a trisolvated monomer [(**4a**)+3THF]. [b]: the predicted FW is referred to an unsolvated dimer [(**4a**)$_2$]. [c]: the predicted FW is referred to a monosolvated dimer [(**4a**)$_2$+THF].



4. NMR spectra of 4a/*n*-BuLi complex in Et_2O_{d10} and THF_{d8}

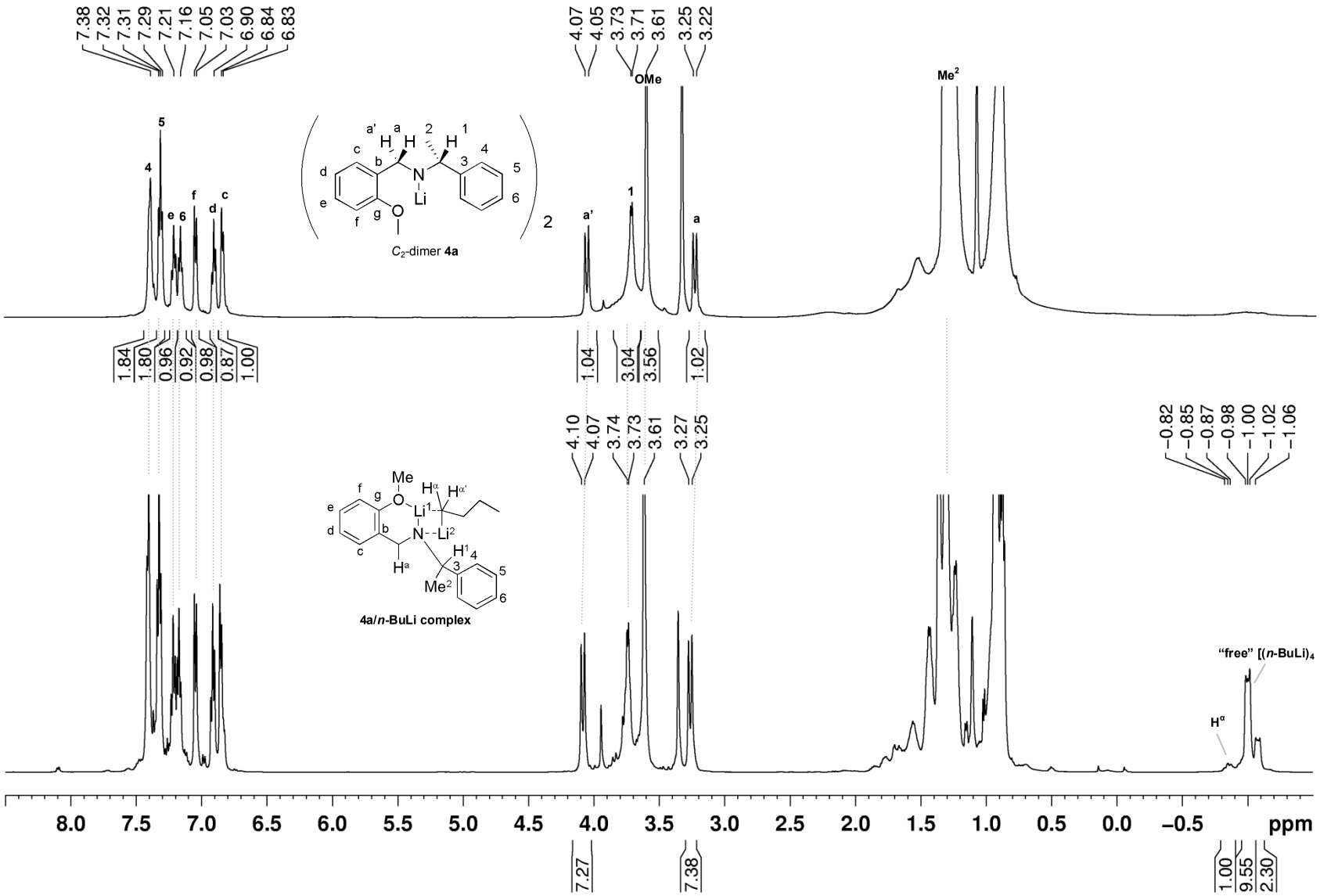


Figure S20. ^{1}H NMR spectra of **4a** (top) and **4a** + *n*-BuLi (bottom) in Et_2O_{d10} at 195K

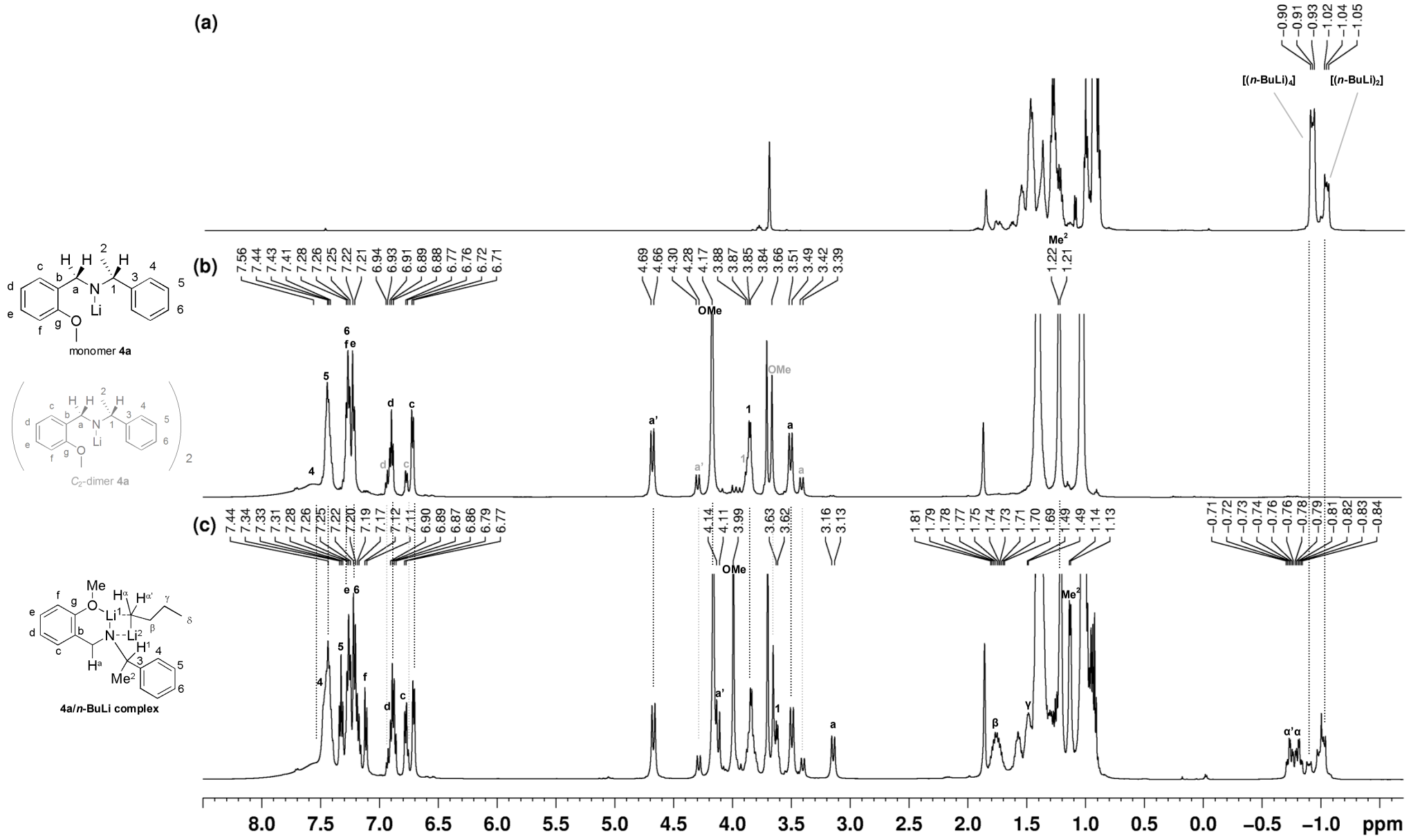


Figure S21. ^{1}H NMR spectra of *n*-BuLi (a), **4a** (b) and **4a** + *n*-BuLi (c) in THF_{d8} at 195K

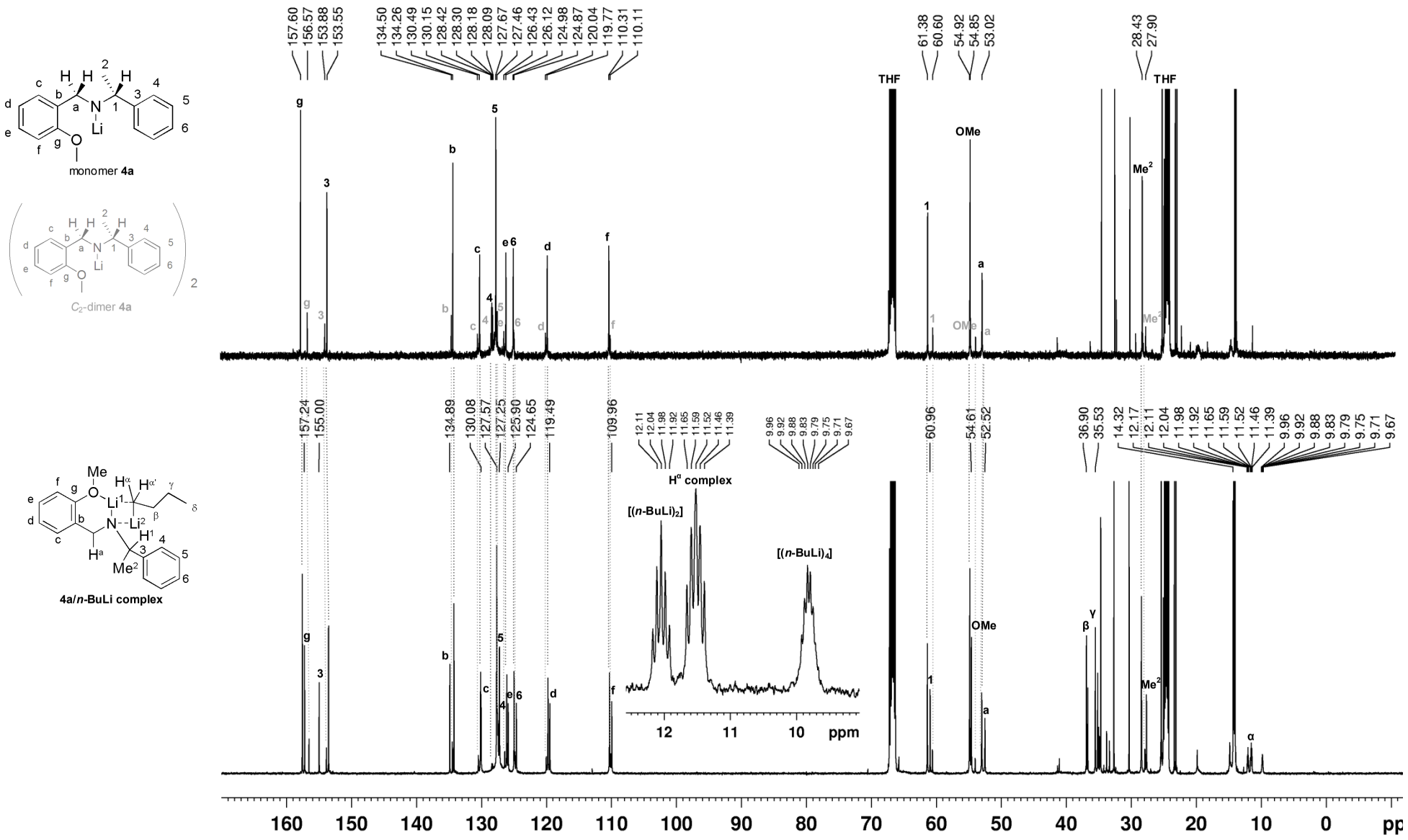


Figure S22. $^{13}C\{^{1}H\}$ NMR spectra of **4a** (top) and **4a** + *n*-BuLi (bottom) in THF_{d8} at 195K

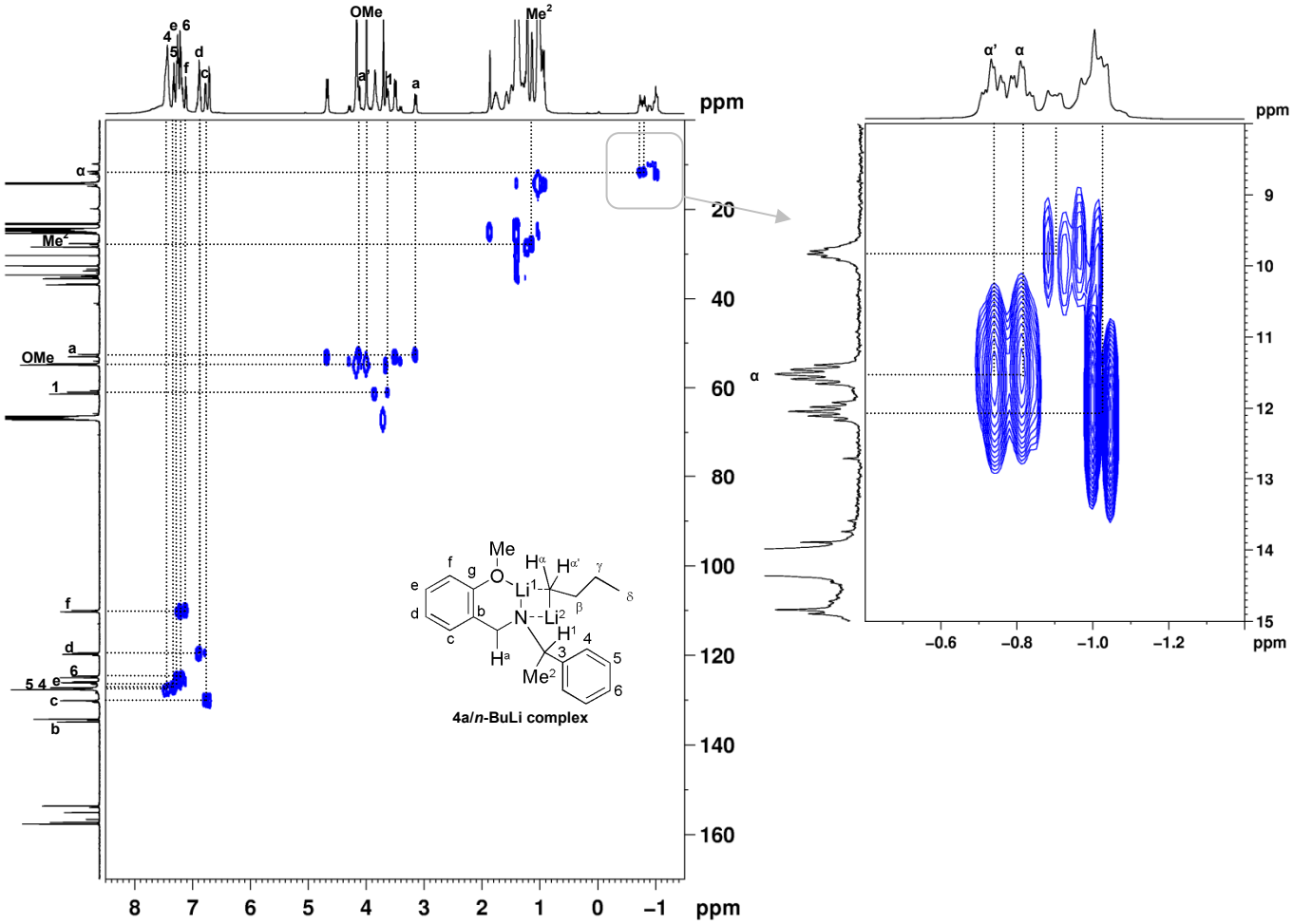


Figure S23. $^{1}H,^{13}C$-HMQC spectrum of **4a** + *n*-BuLi in THF_{d8} at 195K

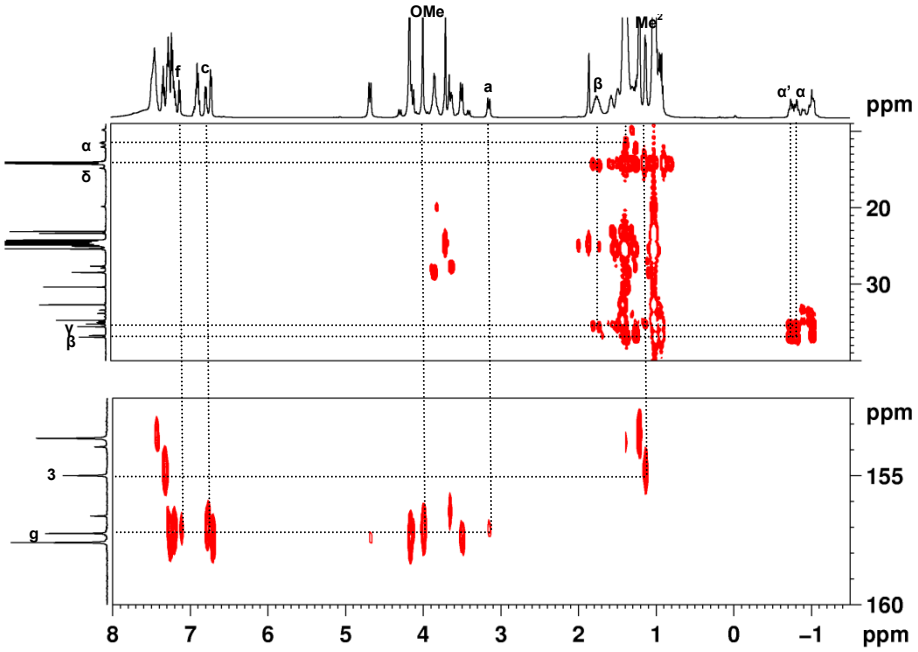


Figure S24. $^{1}H,^{13}C$-HMBC spectrum of **4a** + *n*-BuLi in THF_{d8} at 195K

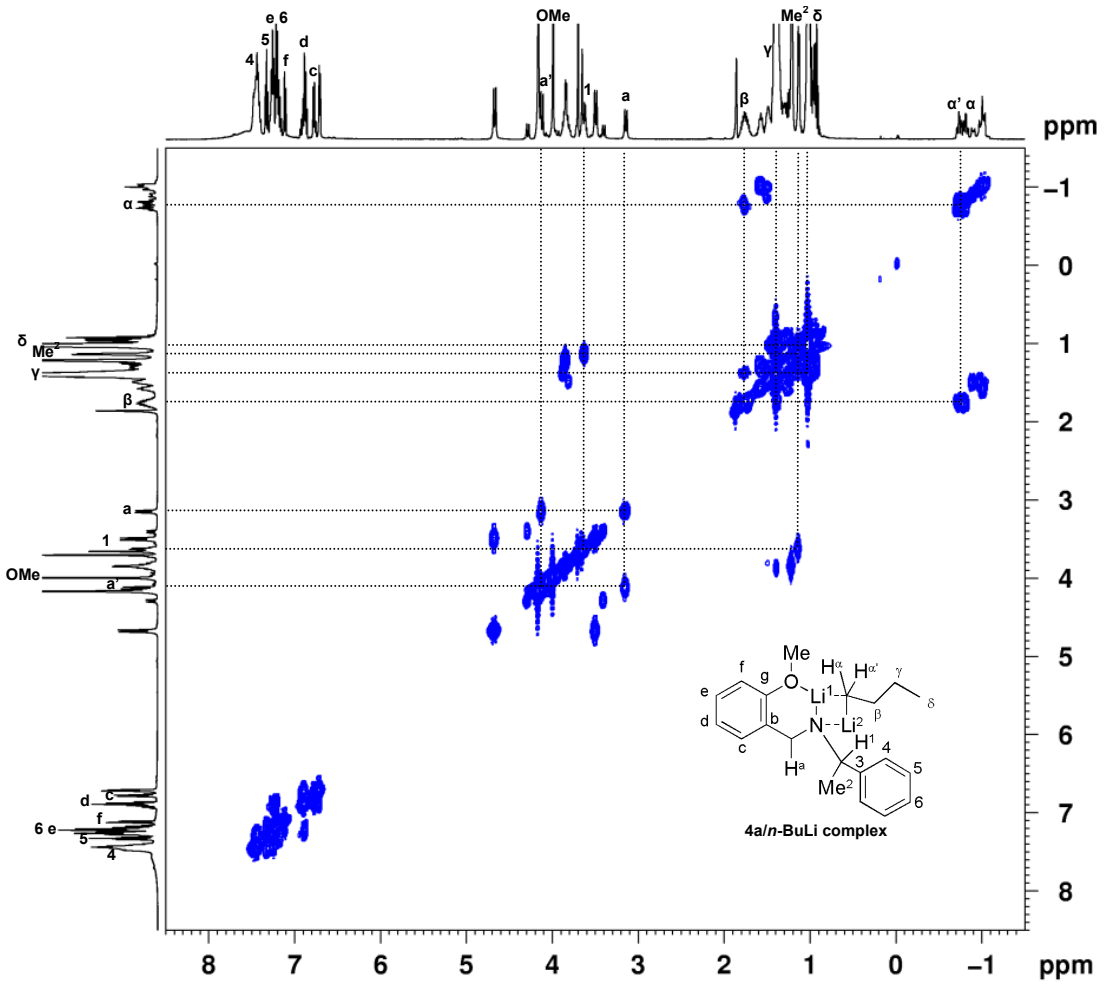


Figure S25. ^{1}H,^{1}H-COSY spectrum of **4a** + *n*-BuLi in THF_{d8} at 195K

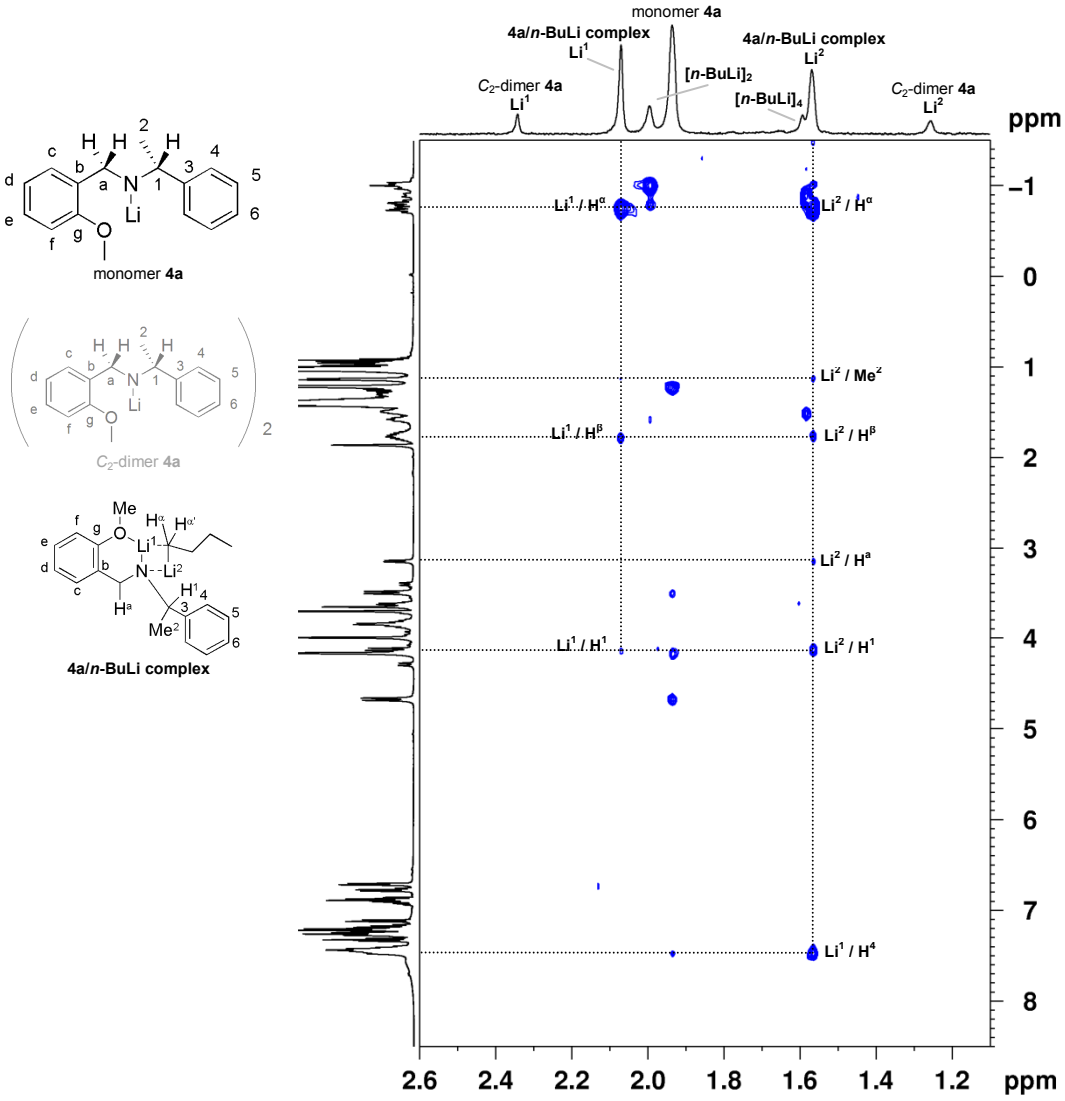


Figure S26. ^{6}Li,^{1}H-HOESY spectrum (mixing time τ_m = 1.44s) of **4a** + *n*-BuLi in THF_{d8} at 195K

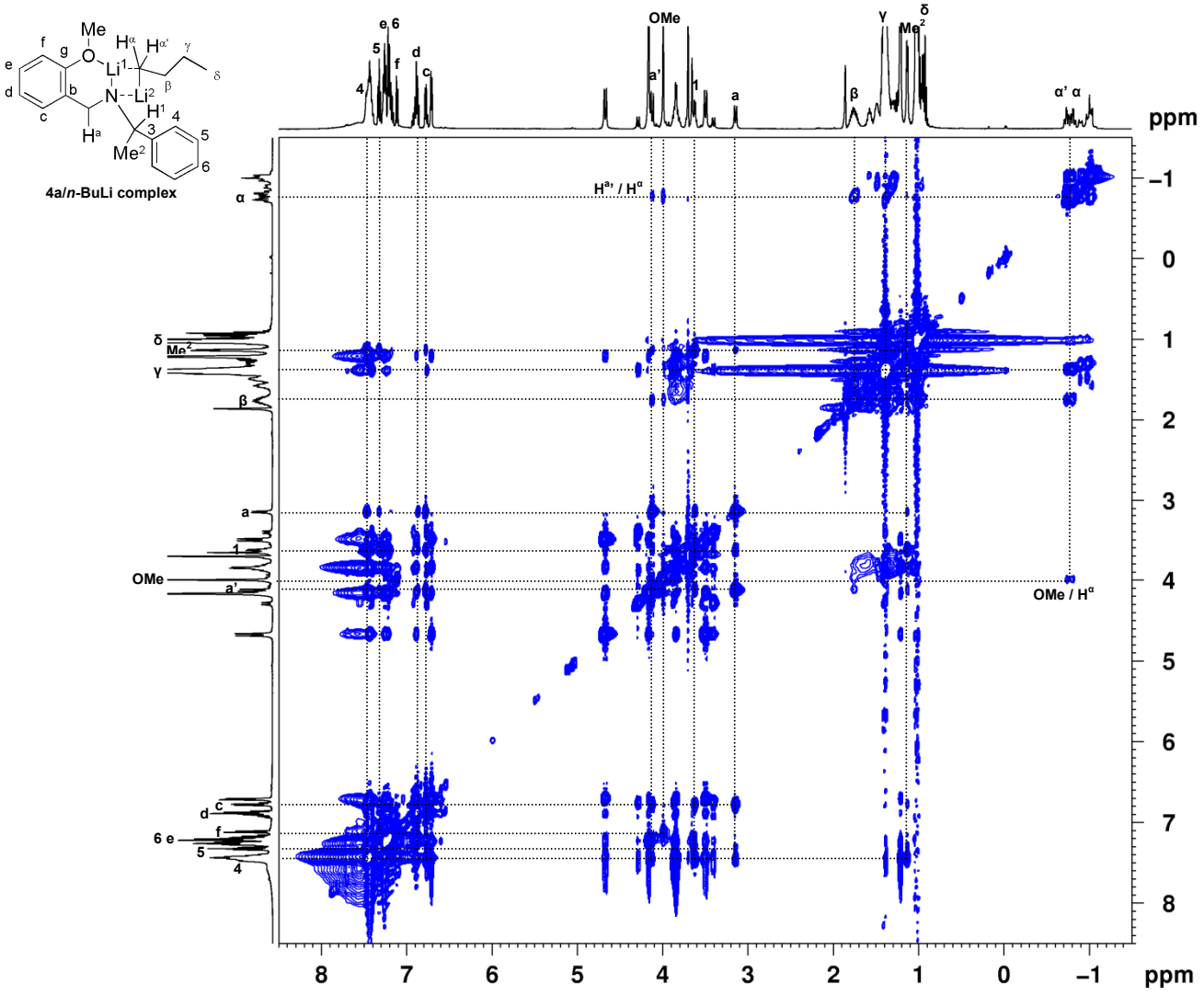


Figure S27. ^{1}H,^{1}H-NOESY spectrum (mixing time τ_m = 0.60s) of **4a** + *n*-BuLi in THF_{d8} at 195K

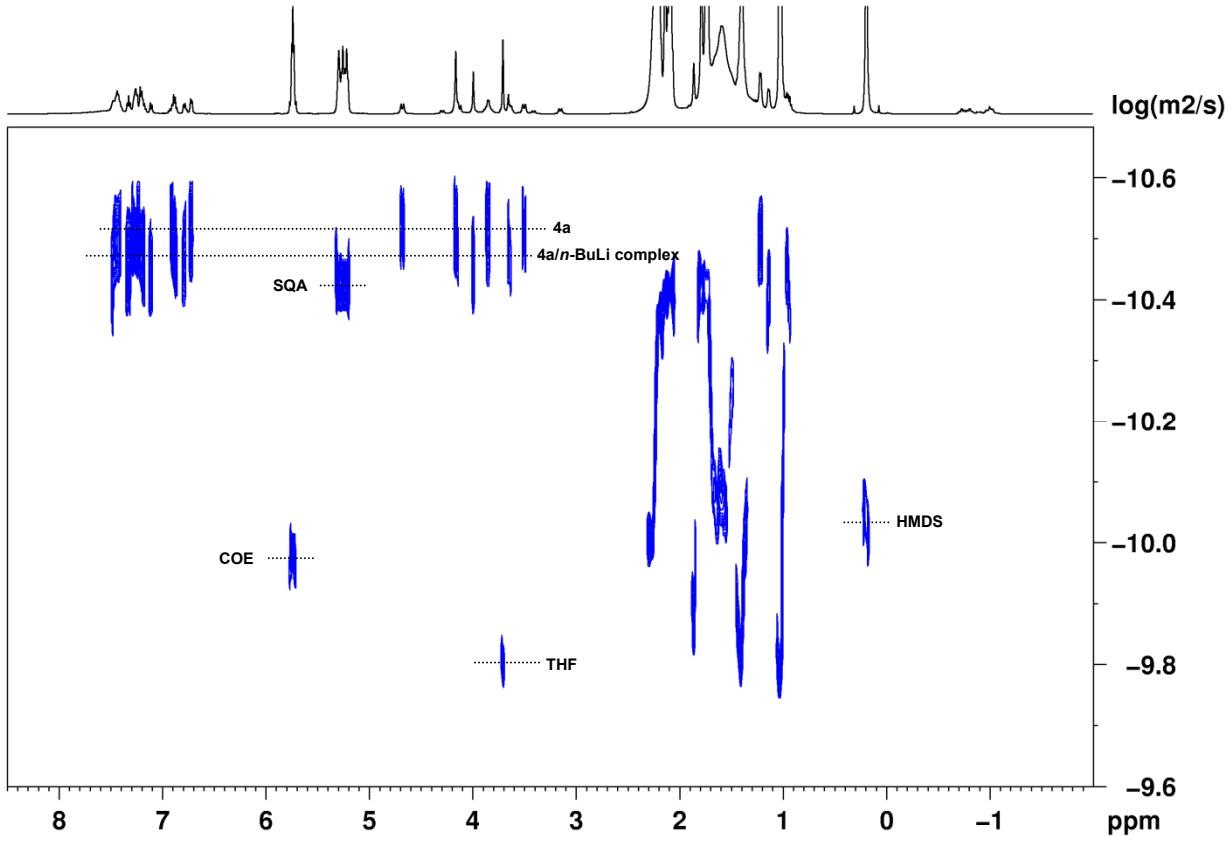
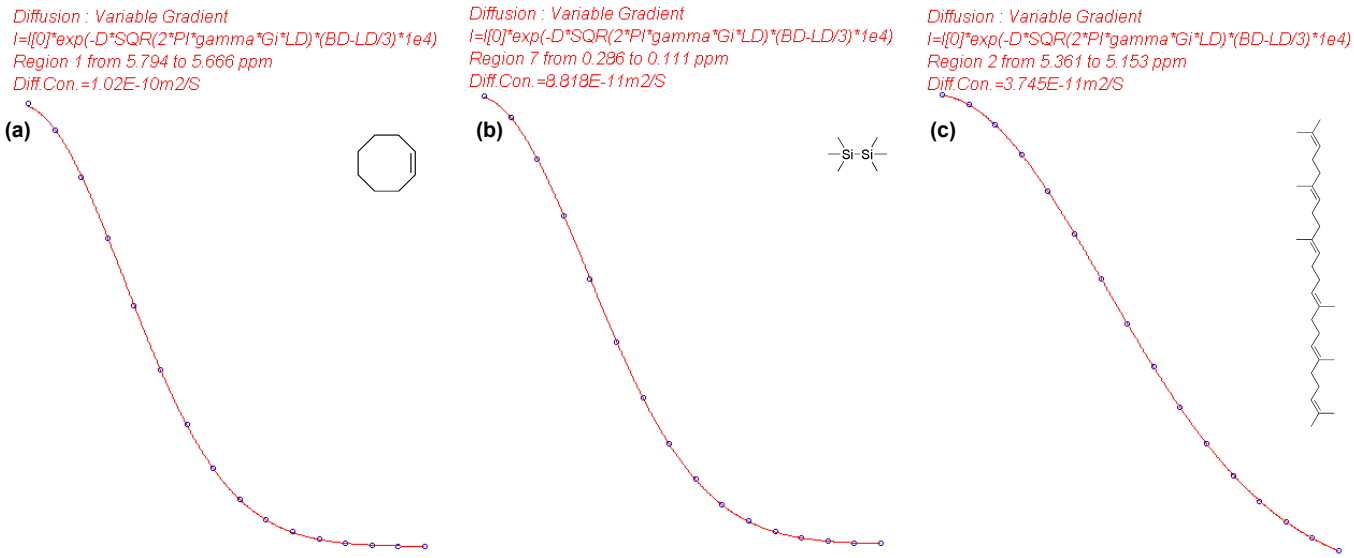


Figure S28. ^{1}H-DOSY spectrum of **4a** / *n*-BuLi complex in THF_{d8} at 195K

Figure S29. Decay curves of ^{1}H-DOSY for Internal References [COE (a), HMDS (b), SQA (c)], monomer **4a** (d), C_2-dimer **4a** (e) and **4a** / *n*-BuLi complex (f) in THF_{d8} at 195K



(Figure S29, continued)

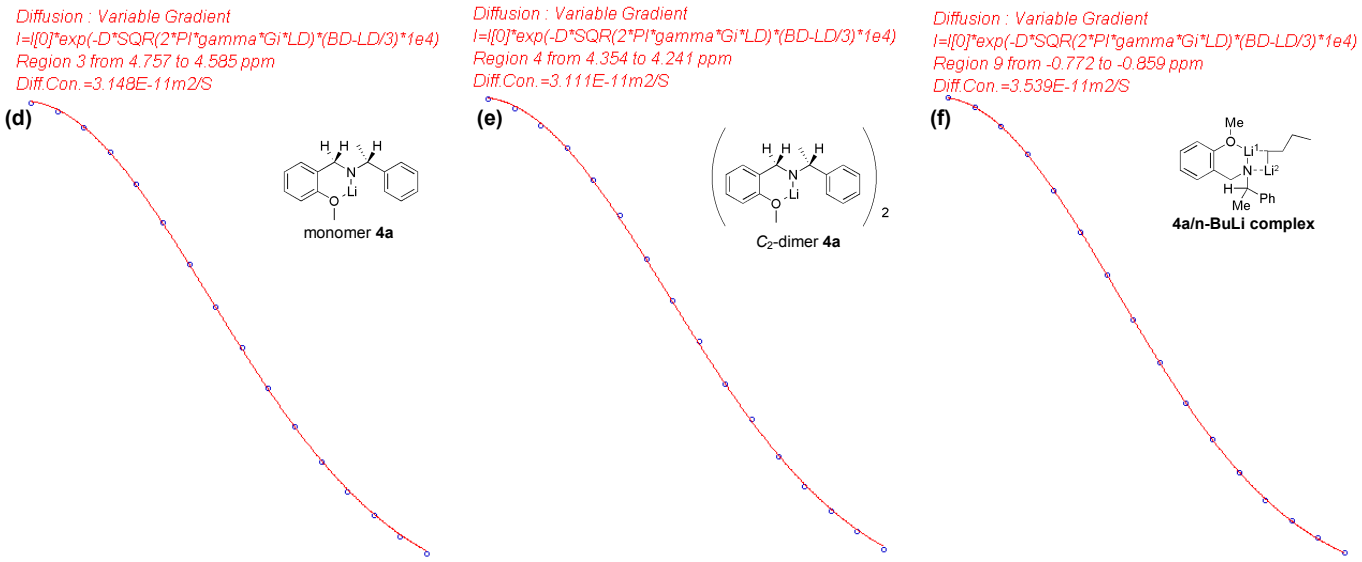


Table S3. D-FW analysis of ^{1}H-DOSY data of **4a**/*n*-BuLi complex in THF_{d8} at 195K

Compound	FW (g mol^{-1})	LogFW	D (m^2 s^{-1})	logD	predicted FW (g mol^{-1})	Error (%)
COE	110,2	2,042	1,02E-10	-9,991	110.2	
HMDS	146,4	2,165	8,82E-11	-10,054	146.4	
SQA	410,7	2,613	3,75E-11	-10,426	410.7	
THF_{d7}	70,8	1,850	1,49E-10	-9,827	79,1	–11.8
monomer **4a**	519,2	2,715	3,15E-11	-10,502	484,7[a]	6.6
C_2-dimer **4a**	527,1	2,722	3,11E-11	-10,507	494.5[b]	6.2
4a/*n*-**BuLi**	446,8	2,650	3,54E-11	-10,451	469.6[c]	–5.1

[a]: the predicted FW is referred to a trisolvated monomer [(**4a**) + 3THF]. [b]: the predicted to FW is referred an unsolvated dimer [(**4a**)$_2$]. [c]: the predicted FW is referred to a disolvated mixed dimer [(**4a**+*n*-BuLi) + 2THF].