SUPPORTING INFORMATION

Preferential Geminal Bis-silylation of 3,4-Benzothiophane is Caused by the Dominance of Electron Withdrawal by R_3Si Over Steric Shielding Effects

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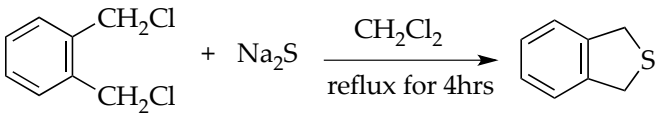
Experimental Section

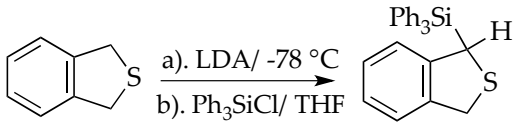
Reagents and Solvents. THF, THF-d_8, *N,N,N',N'*-tetramethyethylenediamine (TMEDA) and hexanes were distilled from blue or purple solutions containing sodium benzophenone ketyl. The hexanes contained 1% tetraglyme to dissolve the ketyl. [^{6}Li]*n*-BuLi used for the spectroscopic studies was prepared and recrystallized as described previously [Hoffmann, D.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 5810.

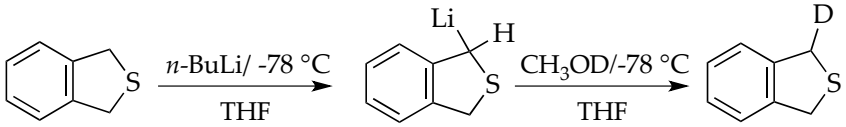
]. 1,3-dihydrobenzo[*c*]thiophene was prepared according to a literature procedure [Kawabata, K. Goto, H. *J. Mater. Chem.* **2012**, *22*, 23514.] Solutions of *n*-BuLi were titrated using a literature method [Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879].

NMR Spectroscopic Analyses.

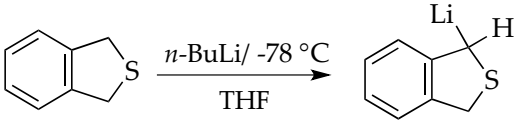
All NMR samples were prepared using stock solutions and sealed under partial vacuum. Standard ^{6}Li, ^{13}C, and ^{15}N NMR spectra were recorded on a 500 MHz spectrometer at 73.57, 125.79, and 50.66 MHz (respectively). The ^{1}H, ^{6}Li, and ^{13}C resonances are referenced to THF-d_8 (3.58 ppm), 0.30 M [^{6}Li]LiCl/MeOH at –90 ^{o}C (0.0 ppm), and the CH$_2$O resonance of THF at –90 ^{o}C (67.57 ppm), respectively.

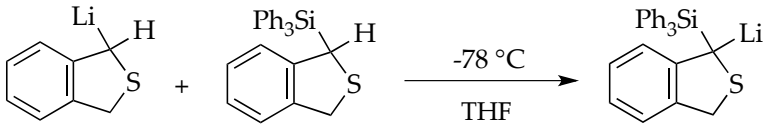


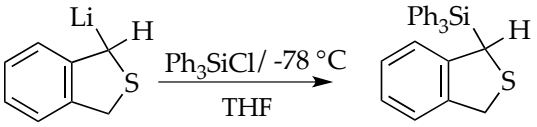


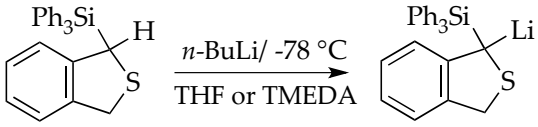


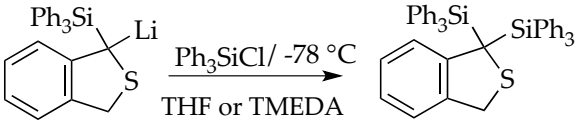
Preparation of deuterated 1,3-dihydrobenzo[*c*]thiophene (3-d_1)

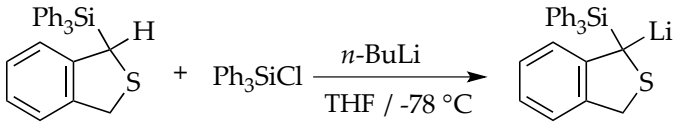












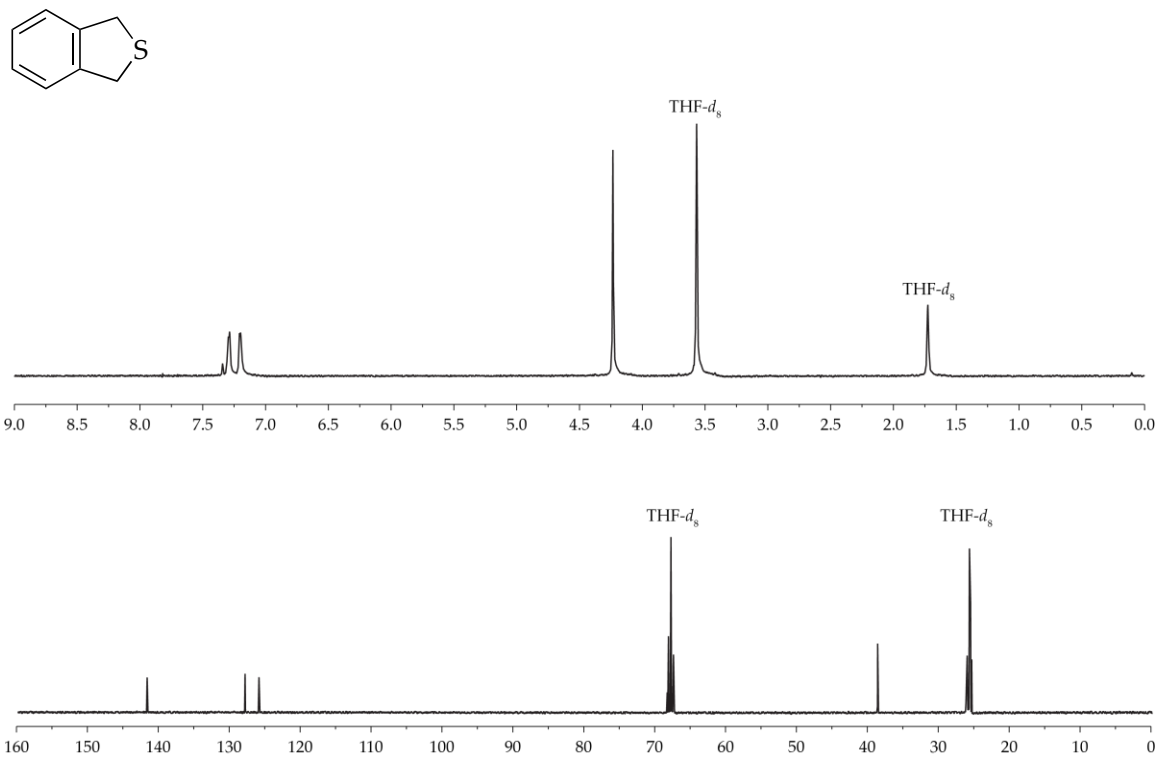


Figure 1. ^{1}H and ^{13}C NMR spectra of 1,3-dihydrobenzo[*c*]thiophene **3** in THF-d_8 recorded at -80 °C: (a) ^{1}H NMR δ 7.30 (m, 2H), 7.19 (m, 2H), 4.24 (s, 4H); (b) ^{13}C NMR δ 141.8, 127.0, 126.0, 38.8.

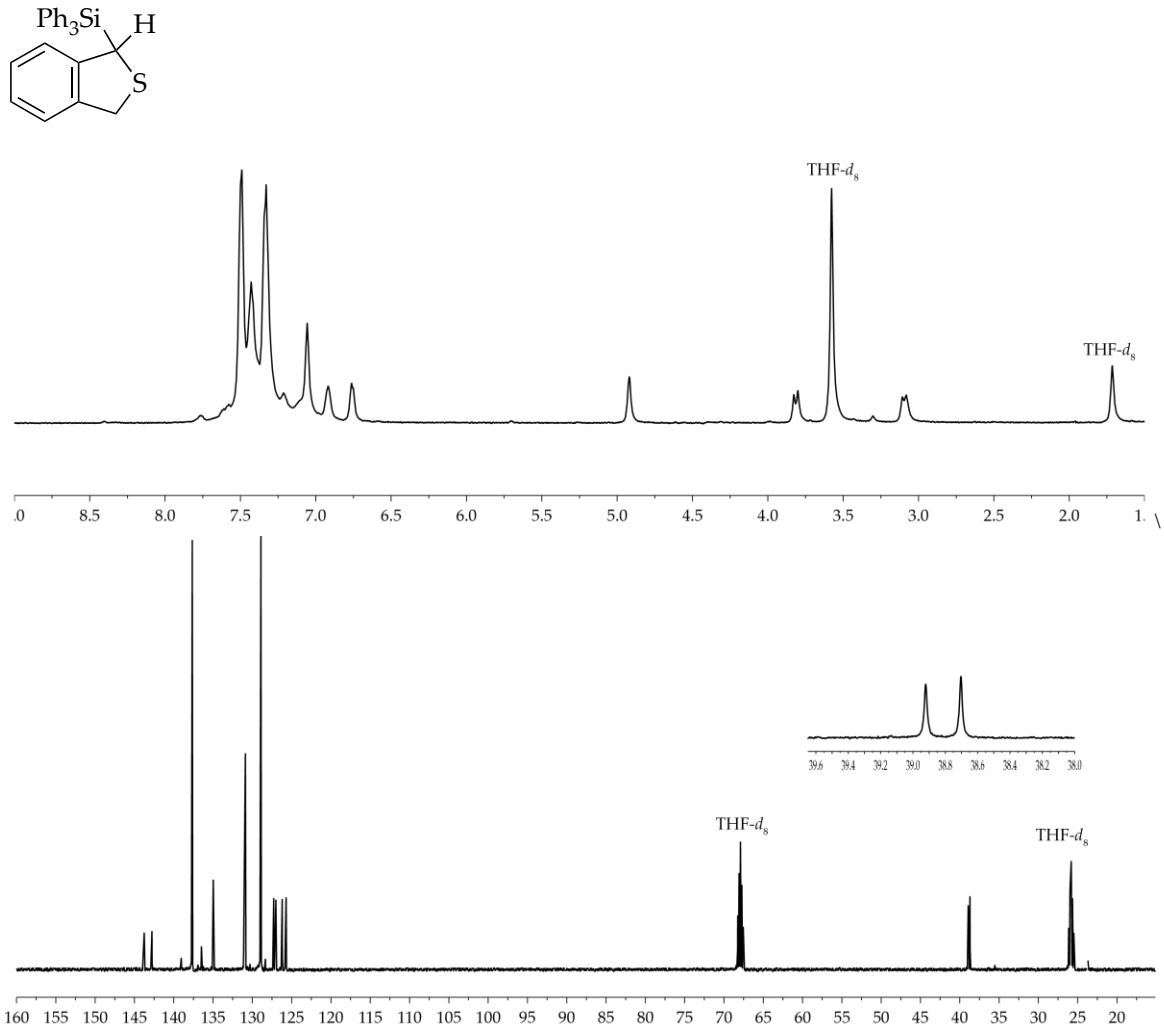


Figure 2. ^{1}H and ^{13}C NMR spectra of (1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **5** in THF-d_8 recorded at -80 °C: (a) ^{1}H NMR δ 7.49 (m, 6H); 7.43 (m, 3H), 7.33 (m, 6H), 7.06 (m, 2H), 6.91 (m, 1H), 6.79 (m, 1H), 3.92 (s, 1H), 3.09 (d, *J* = 13.0 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H); (b) ^{13}C NMR δ 137.7, 135.0, 130.9, 128.9, 127.3, 127.0, 126.2, 125.7, 38.9, 38.7.

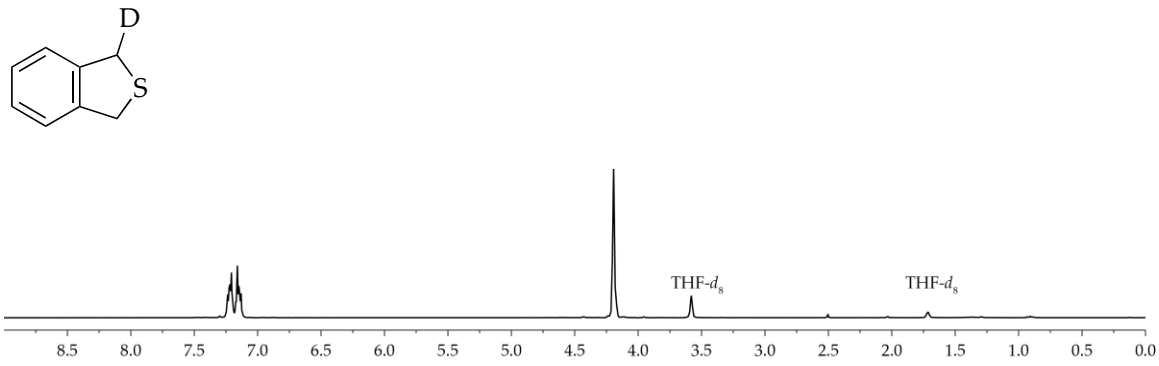


Figure 3. ^{1}H NMR spectrum of deuterated 1,3-dihydrobenzo[*c*]thiophene (**3-*d*$_1$**) in THF-d_8 δ 7.20 (m, 2H), 7.14 (m, 2H), 4.19 (s, 3H).

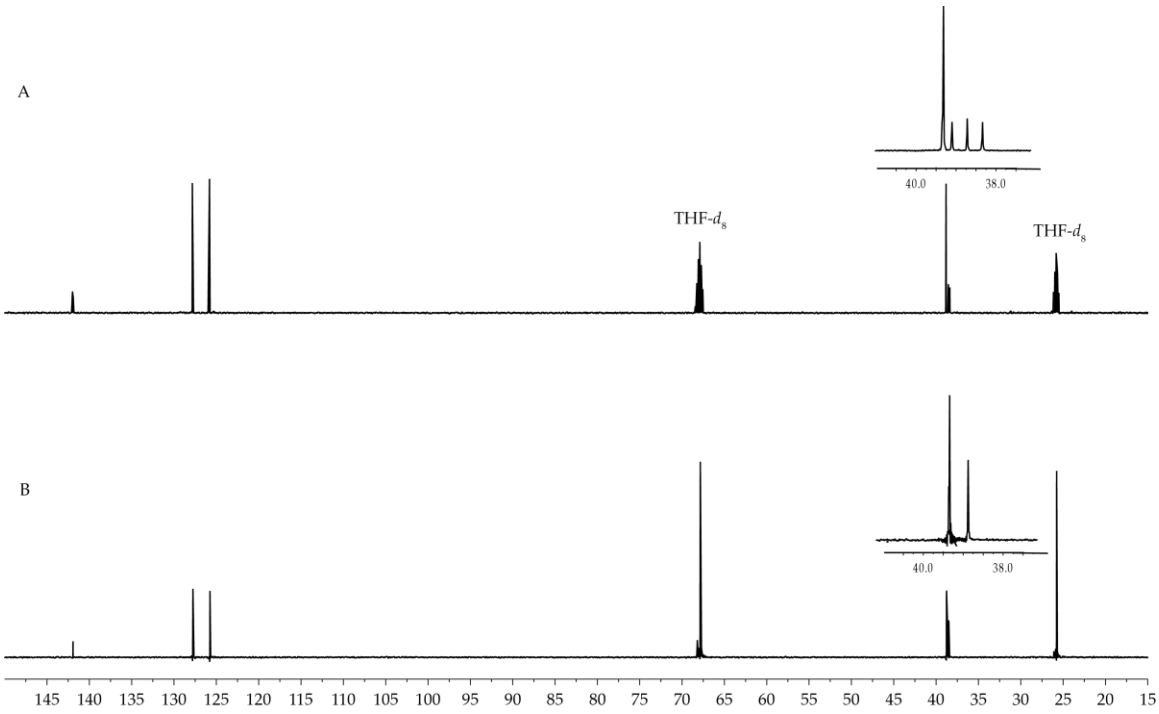


Figure 4. ^{13}C NMR spectra of 1-deutero-1,3-dihydrobenzo[*c*]thiophene (**3-*d*$_1$**) in THF-d_8: (A) ^{13}C{^{1}H} NMR δ 142.1, 127.4, 125.6, 38.8, 38.6 (t, *J* = 21.60 Hz); (B) ^{13}C{^{1}H,^{2}H} NMR δ 142.1, 127.4, 125.6, 38.8, 38.6 (s).

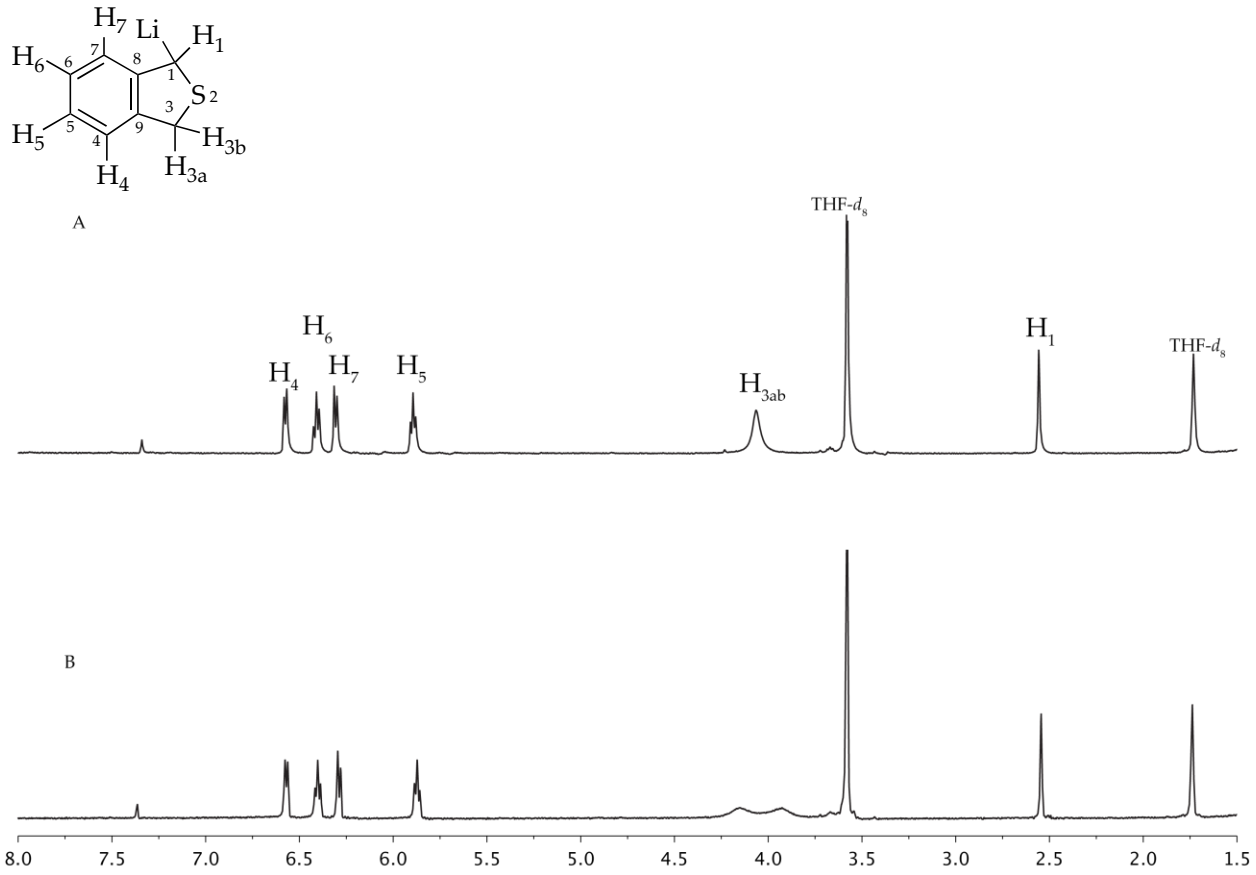


Figure 5. [1]H NMR spectra of 1-lithio-1,3-dihydrobenzo[*c*]thiophene (**6)** in THF-d_8 with aging for 12 hr at -78 °C: (A) recorded at -80 °C: δ 6.57 (t, *J* = 6.80 Hz, 1H), 6.40 (t, *J* = 6.80 Hz, 1H), 6.31 (d, *J* = 7.29 Hz, 1H), 5.89 (t, *J* = 7.29 Hz, 1H), 4.16 (s, 1H), 3.93 (s, 1H), 2.54 (s, 1H). (B) recorded at -115 °C.

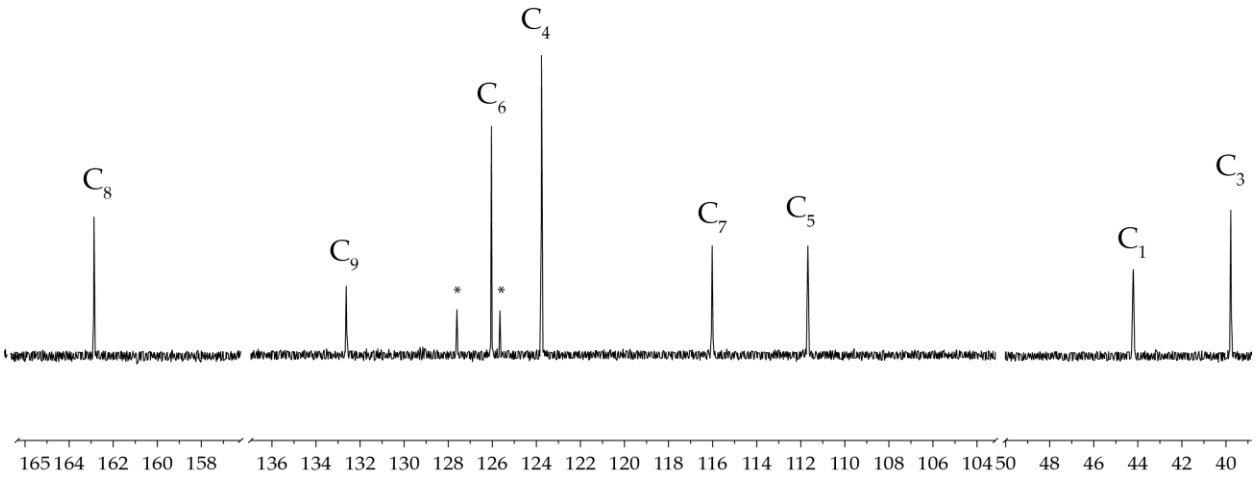


Figure 6. [13]C NMR spectrum of 1-lithio-1,3-dihydrobenzo[*c*]thiophene (**6)** in THF-d_8 with aging 12 hr at -78 °C recorded at -80 °C: δ 162.8, 132.6, 126.0, 123.7, 116.1, 111.7, 44.2, 39.8.

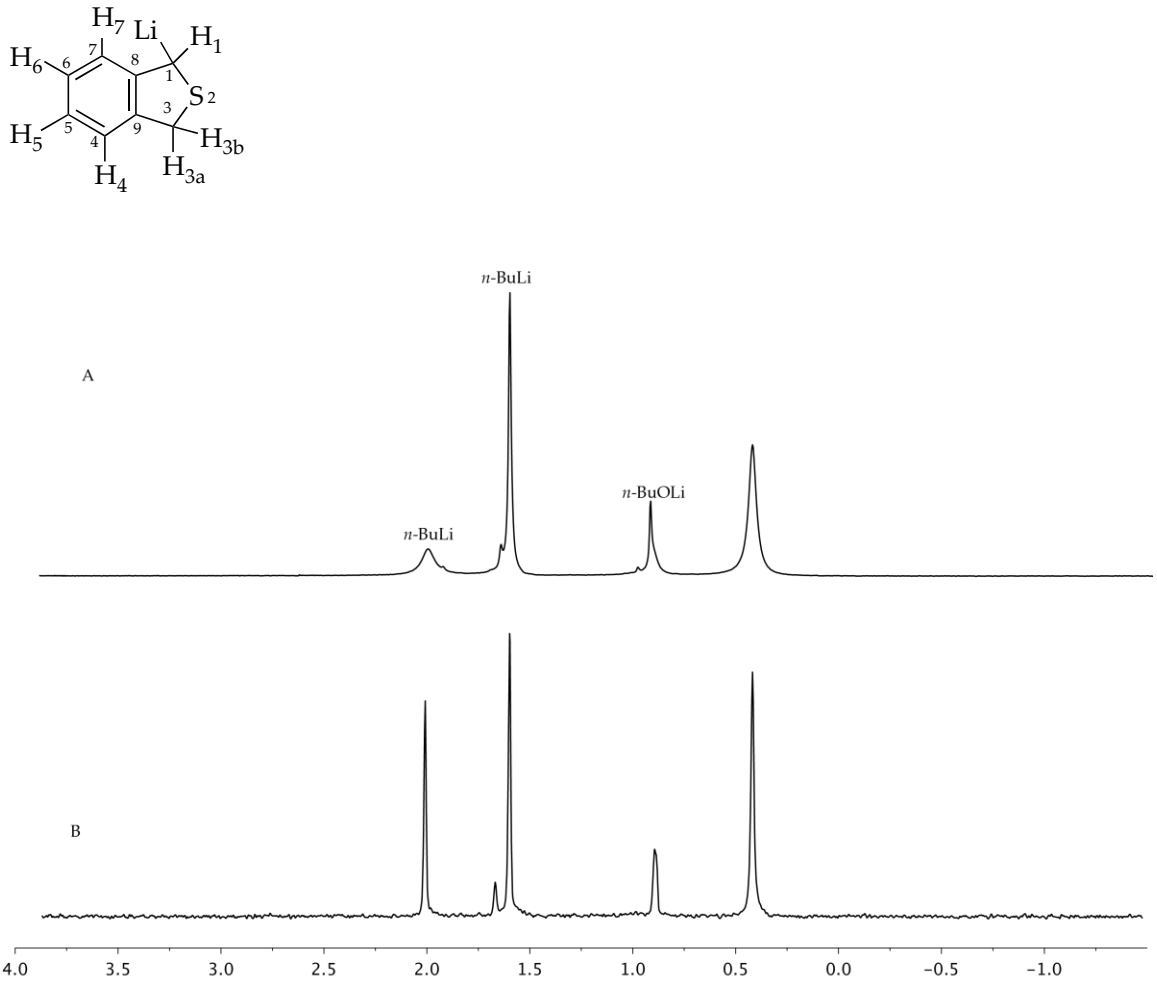
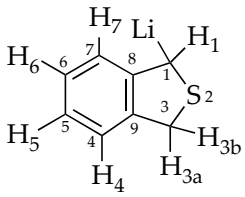


Figure 7. ^{6}Li NMR spectra of 1-lithio-1,3-dihydrobenzo[*c*]thiophene (**6)** in THF-d_8 with aging for 12 hr at -78 °C: (A) recorded at -80 °C δ 0.42; (B) recorded at -115 °C.



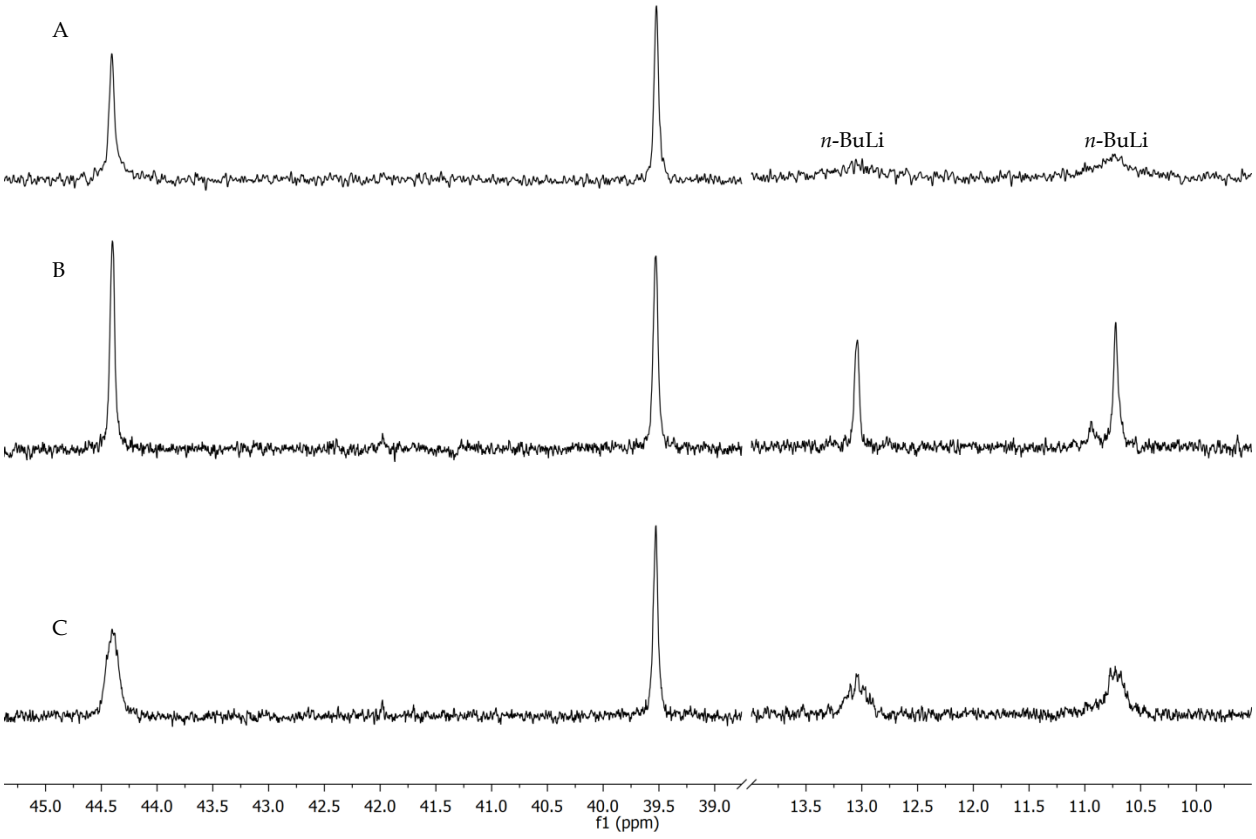


Figure 8 $^{13}C\{^{1}H\}$ spectra of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **6** with (A) selective ^{6}Li decoupling at δ 0.42 ppm; (B) broadband ^{6}Li decoupling; (C) without ^{6}Li decoupling.

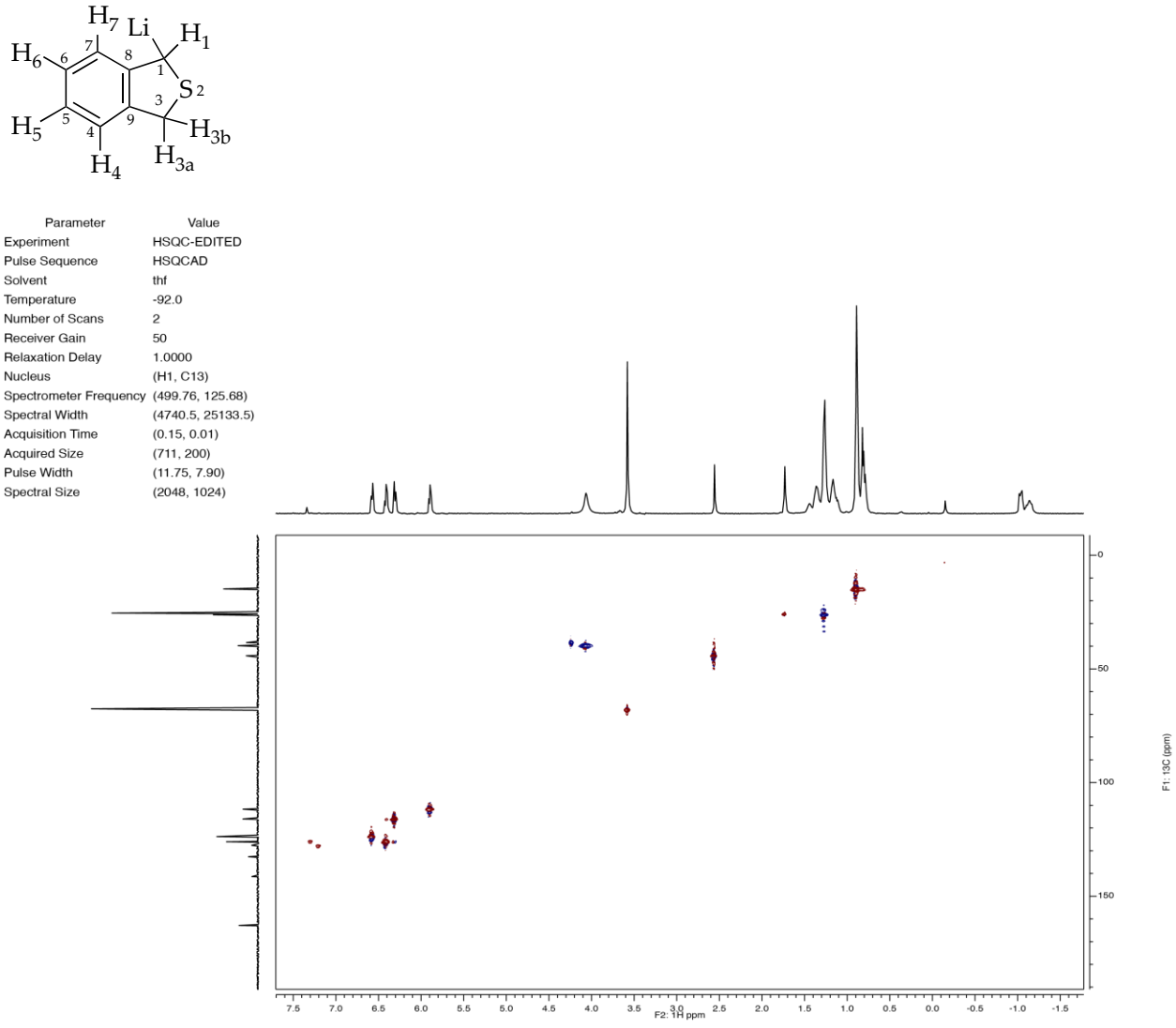
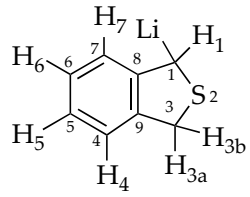


Figure 9 Multiplicity-edited HSQCAD spectrum 1-lithio-1,3-dihydrobenzo[*c*]-thiophene **6**. Red contours indicate CH/CH_3, blue contours are CH_2 (full display).



Parameter	Value
Experiment	HSQC-EDITED
Pulse Sequence	HSQCAD
Solvent	thf
Temperature	-92.0
Number of Scans	2
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	(H1, C13)
Spectrometer Frequency	(499.76, 125.68)
Spectral Width	(4740.5, 25133.5)
Acquisition Time	(0.15, 0.01)
Acquired Size	(711, 200)
Pulse Width	(11.75, 7.90)
Spectral Size	(2048, 1024)

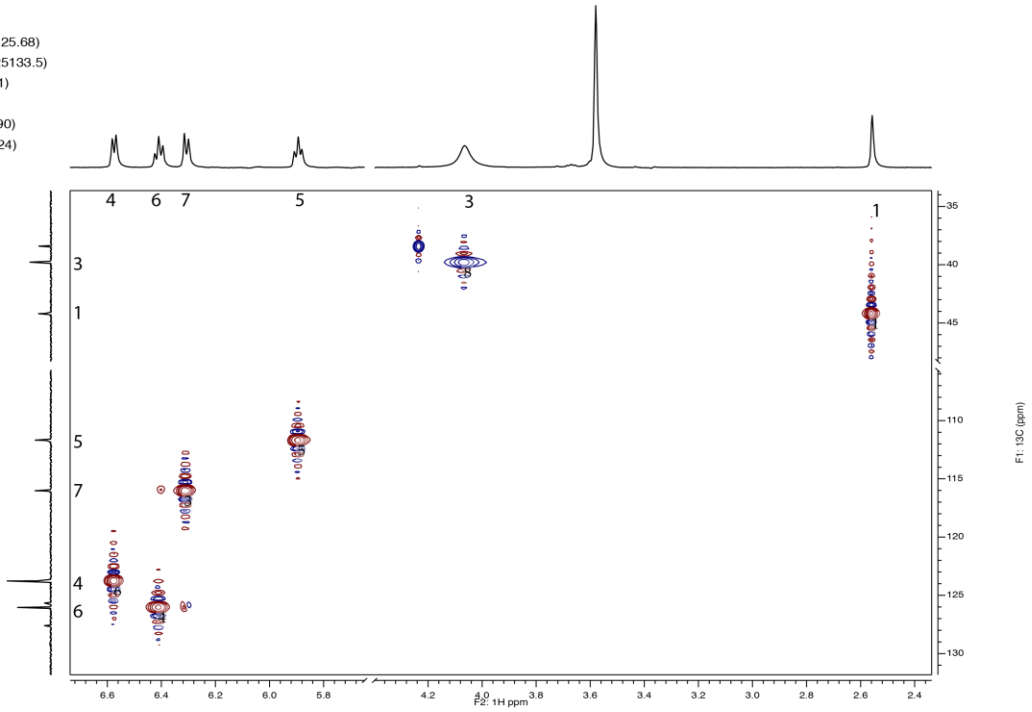


Figure 10. Multiplicity-edited HSQCAD spectrum of 1-lithio-1,3-dihydrobenzo-[*c*]thiophene **6** showing regions of interest with assignments. Red contours indicate CH/CH_3, blue contours are CH_2.

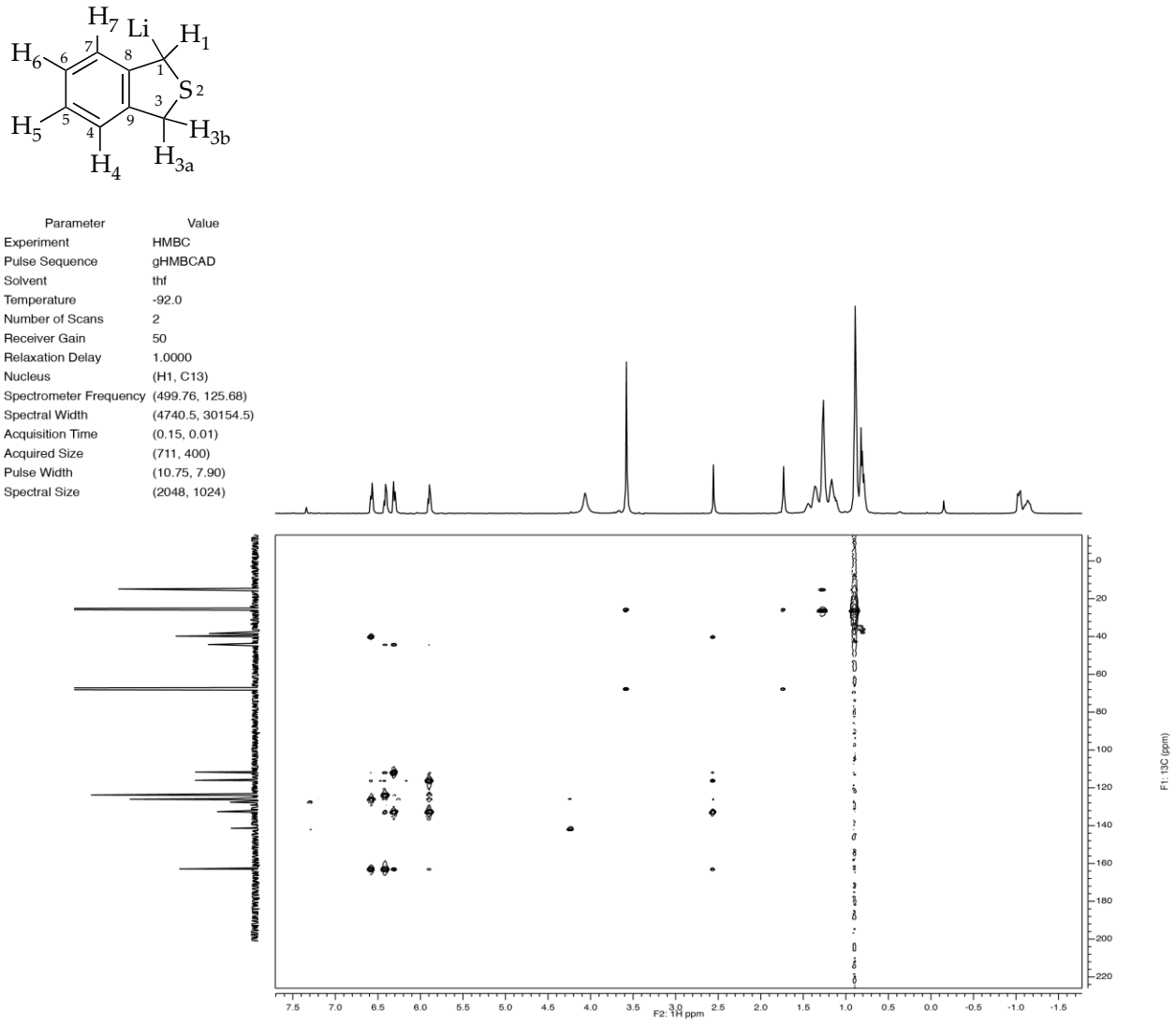


Figure 11. Full $^{1}H/^{13}C$ HMBC spectrum of 1-lithio-1,3-dihydrobenzo [*c*]thiophene **6**.

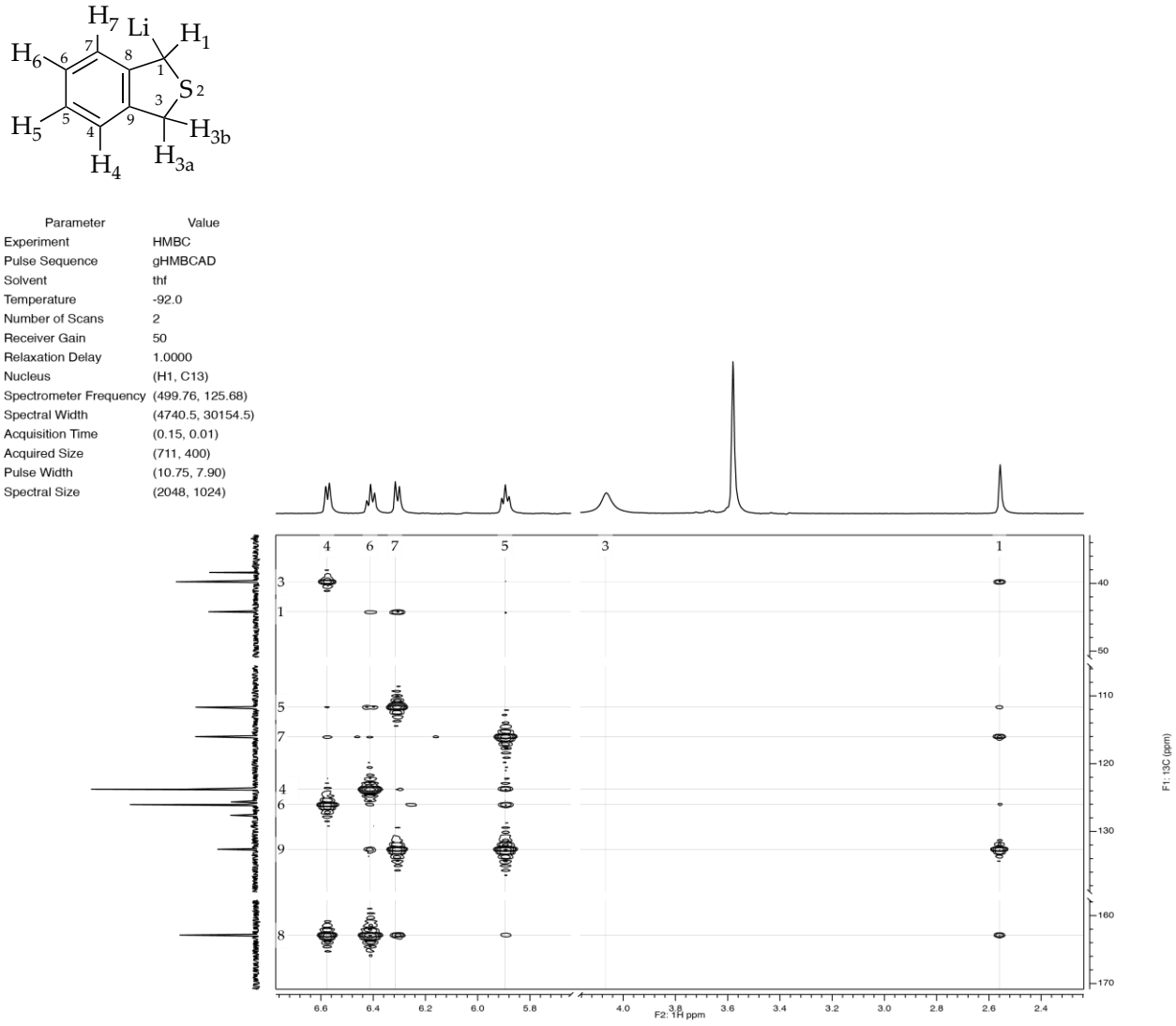


Figure 12. $^{1}H/^{13}C$ HMBC spectrum of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **6** showing regions of interest with assignments.

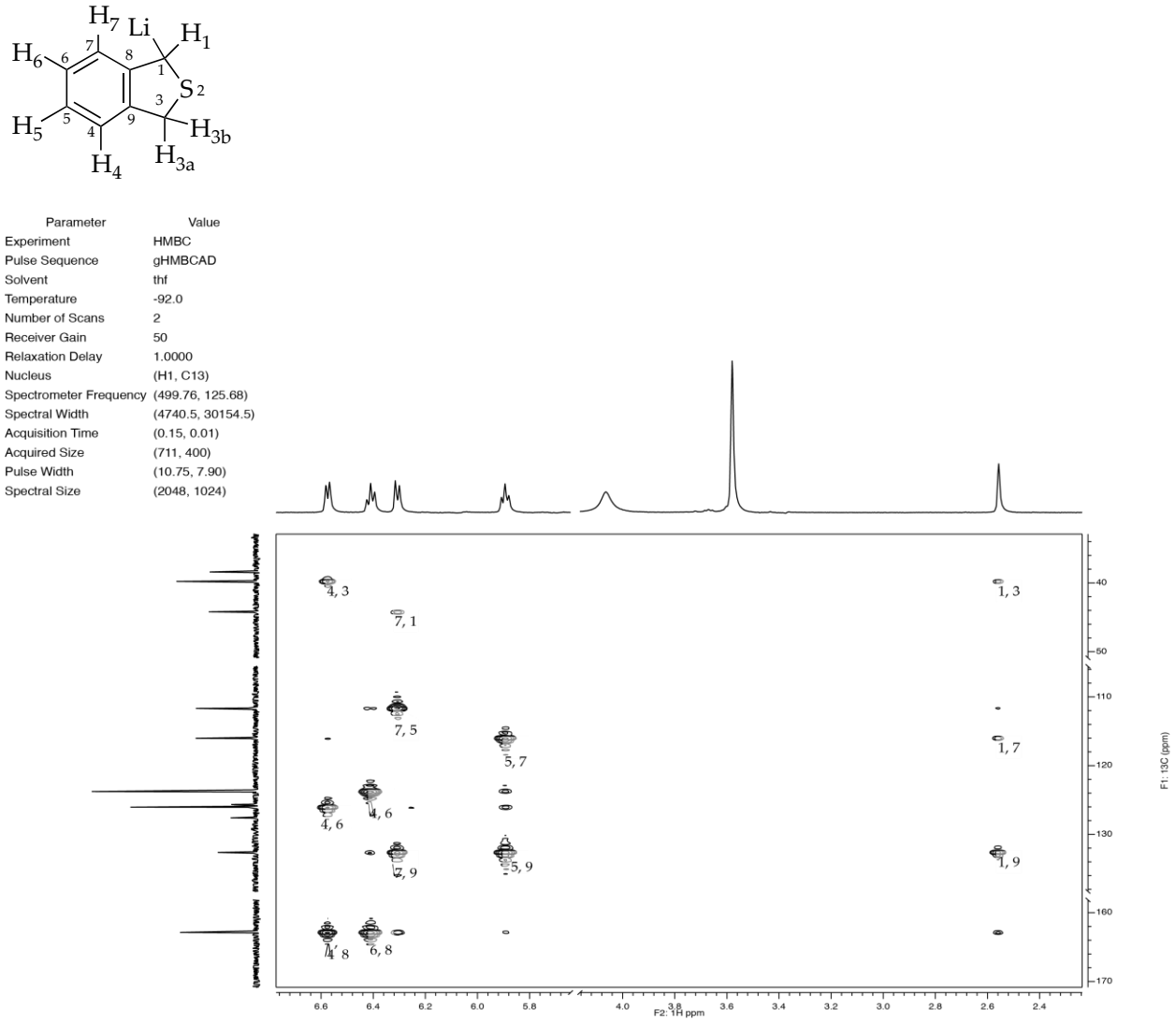


Figure 13. $^{1}H/^{13}C$ HMBC spectrum of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **6** showing regions of interest with assignments.

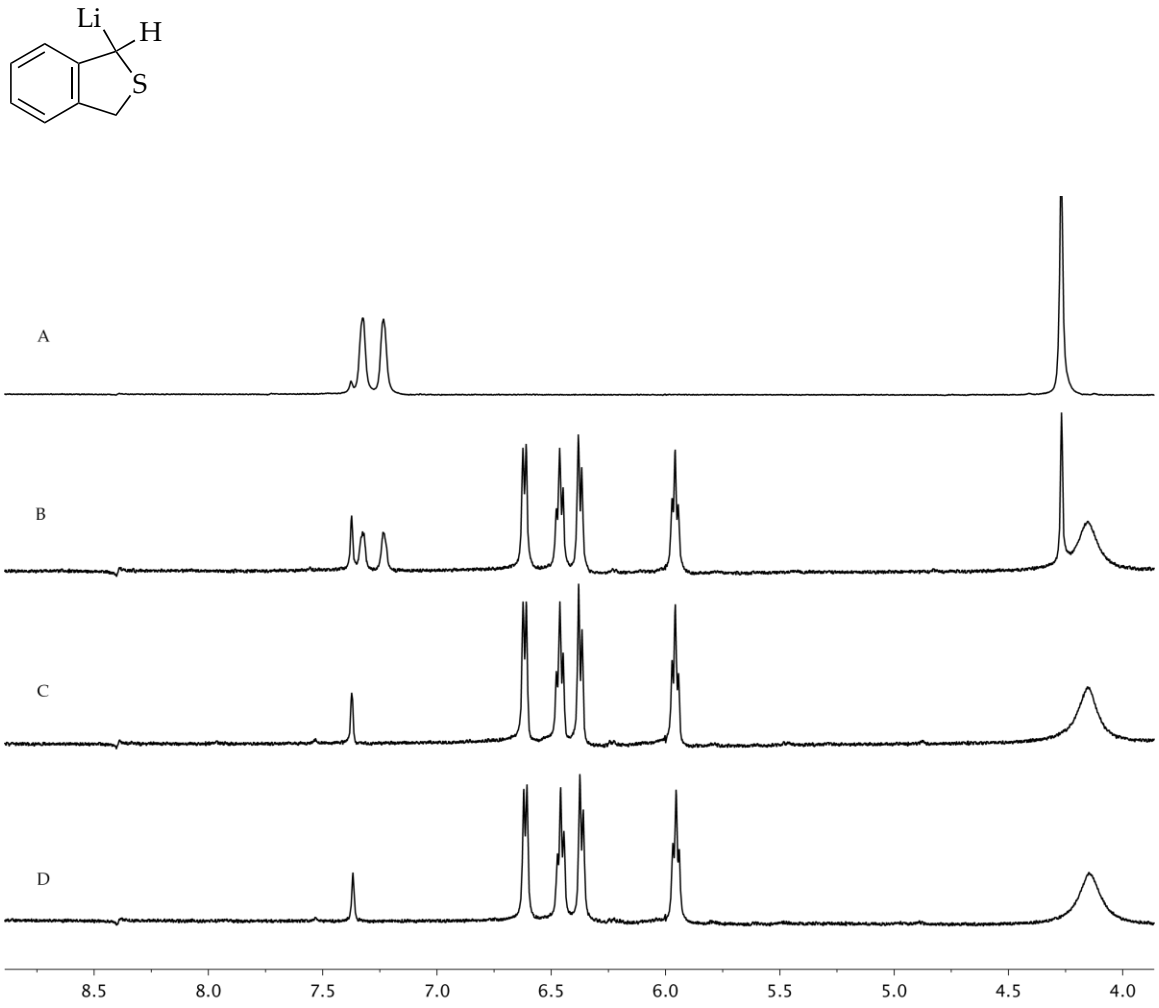


Figure 14. ^{1}H NMR spectra of 1,3-dihydrobenzo[*c*]thiophene **3** treated with varying quantities of *n*-BuLi and 4.0 equiv TMEDA in THF-d_8 with aging for 12 hr at -78 °C and recorded at -80 °C to generate **6**: (A) no *n*-BuLi; (B) 0.50 equiv *n*-BuLi; (C) 2.0 equiv *n*-BuLi; (D) 5.0 equiv *n*-BuLi.

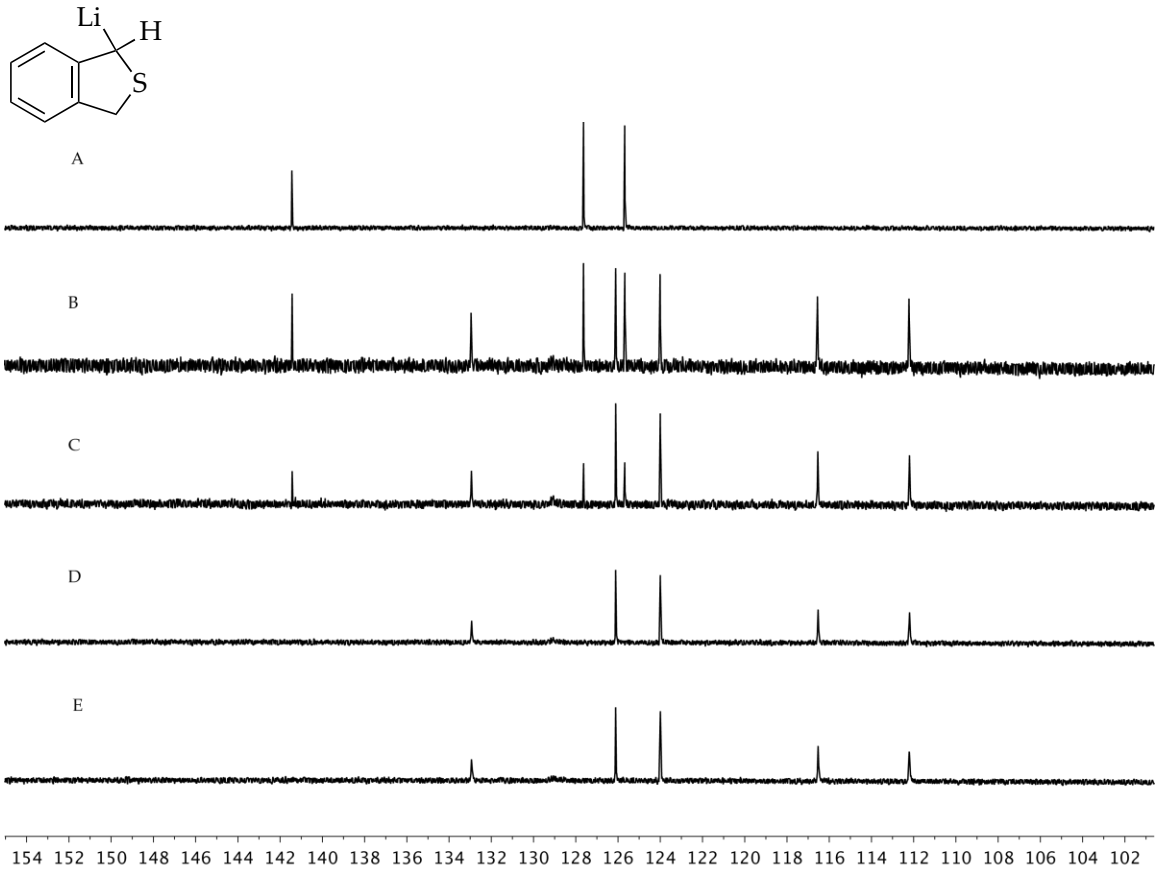


Figure 15. ^{13}C NMR spectra of 1,3-dihydrobenzo[*c*]thiophene **3** treated with varying quantities of *n*-BuLi in 4.0 equiv TMEDA in THF-d_8 with aging at -78 °C for 12 hr and recorded at -80 °C to generate **6**: (A) no *n*-BuLi; (B) 0.25 equiv *n*-BuLi; (C) 0.50 equiv *n*-BuLi; (D) 2.0 equiv *n*-BuLi; (E) 5.0 equiv *n*-BuLi.

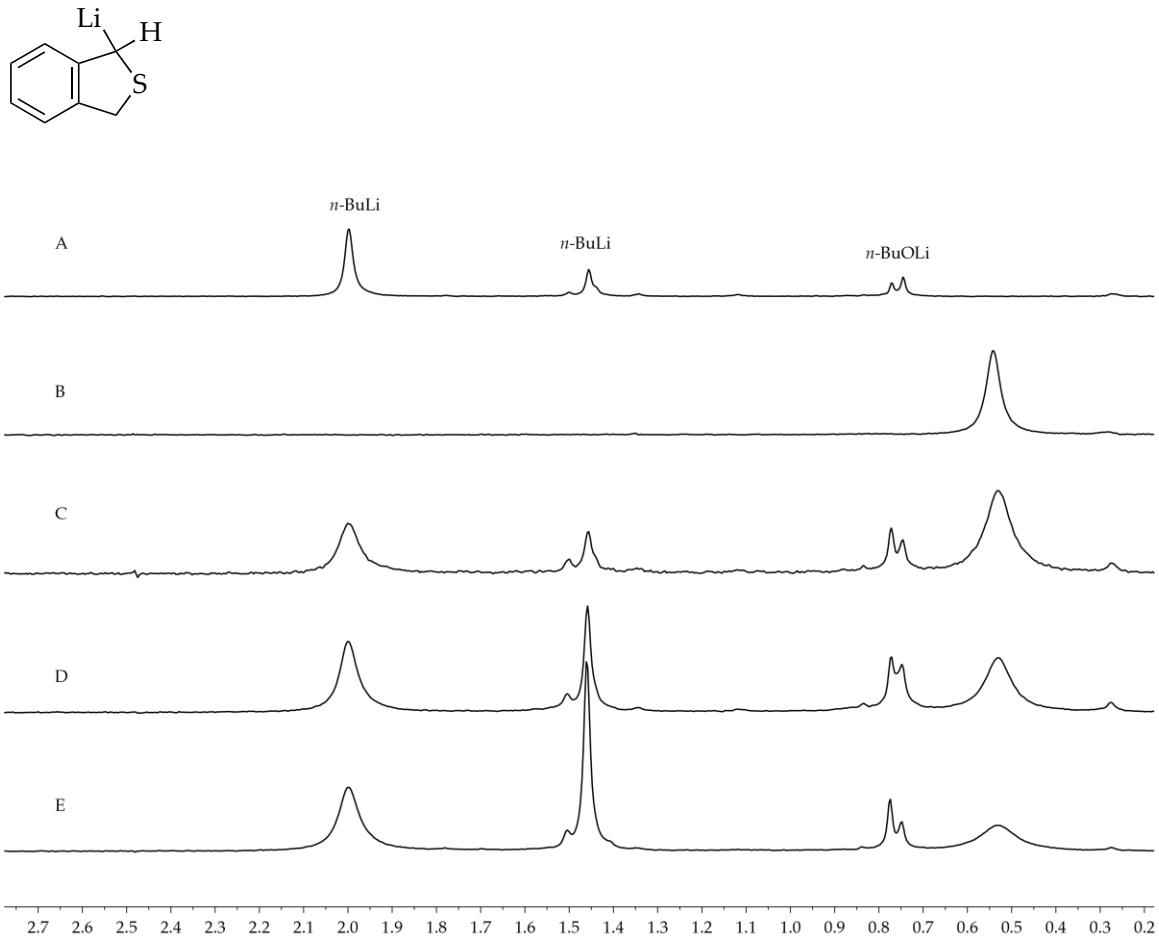


Figure 16. ^{6}Li NMR spectra of 1,3-dihydrobenzo[*c*]thiophene **3** generated with varying quantities of *n*-BuLi in 4.0 equiv TMEDA in THF-d_8 with aging at -78 °C for 12 hr and recorded at -80 °C: (A) *n*-BuLi without substrate **3**; (B) 0.50 equiv *n*-BuLi (C) 2.0 equiv *n*-BuLi; (D) 4.0 equiv *n*-BuLi; (E) 5.0 equiv *n*-BuLi.

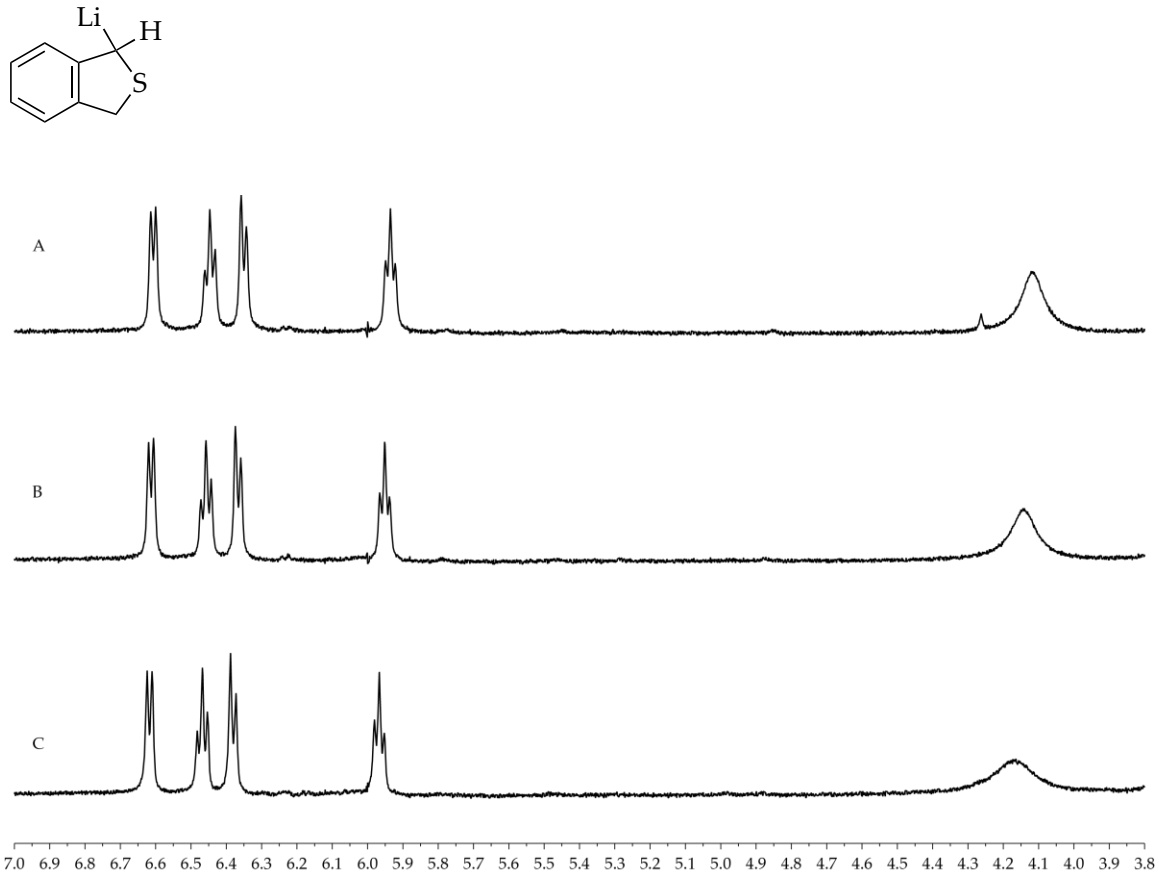


Figure 17. ^{1}H NMR spectra of 1-lithio-3-dihydrobenzo[*c*]thiophene **6** generated with 2.0 equiv *n*-BuLi and varying TMEDA in THF-d_8 with aging at -78 °C for 12 hr and recorded at -80 °C: (A) no TMEDA; (B) 2.0 equiv TMEDA; (C) 8.0 equiv TMEDA.

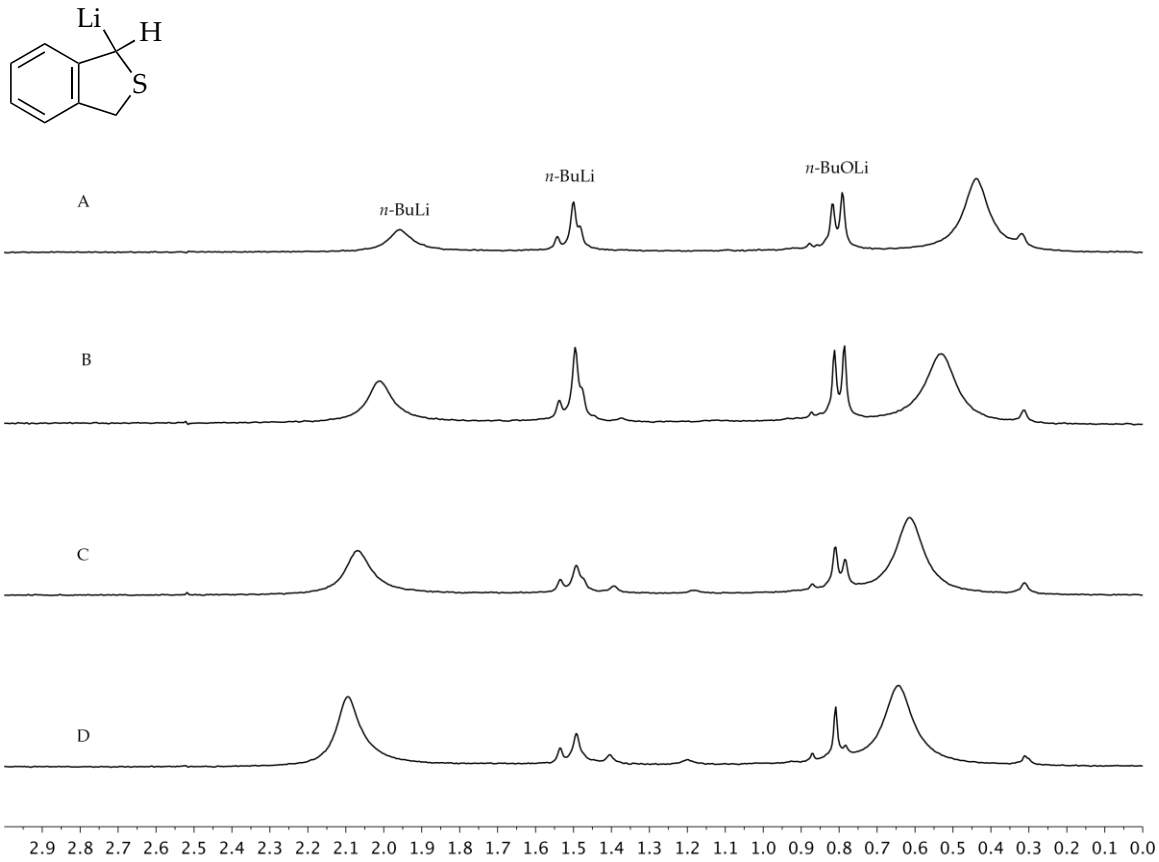


Figure 18. ^{6}Li NMR spectra of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **6** generated with 2.0 equiv *n*-BuLi in THF-d_8 with aging at -78 °C for 12 hr and recorded at -80 °C:
(A) no TMEDA; (B) 2.0 equiv TMEDA; (C) 4.0 equiv TMEDA; (D) 8.0 equiv TMEDA.

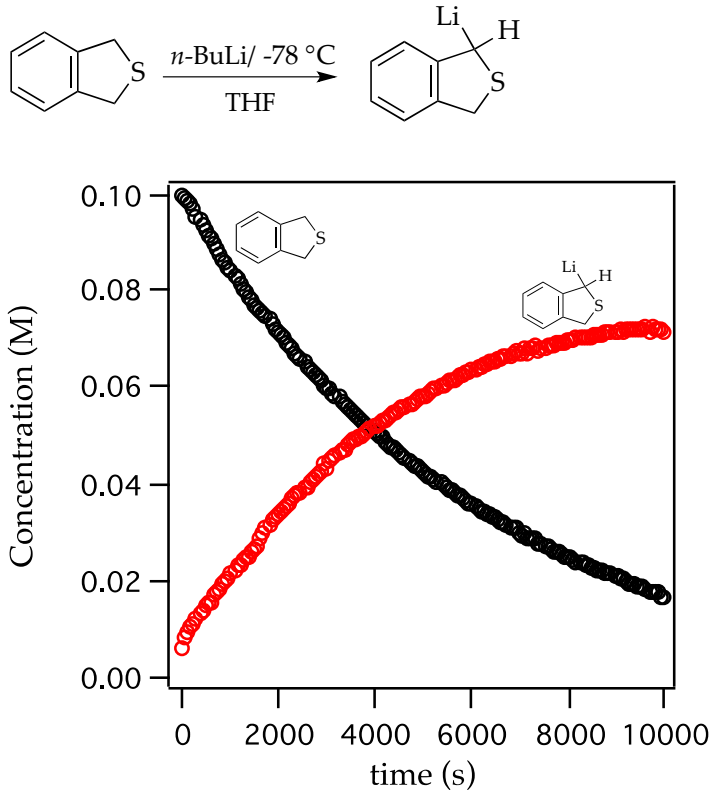


Figure 19. Plot of concentration versus time for lithiation of 1,3-dihydrobenzo-[*c*]thiophene **3** with 4.0 equiv of *n*-BuLi in THF-d_8 monitored by ^{1}H NMR spectroscopy at -78 °C.

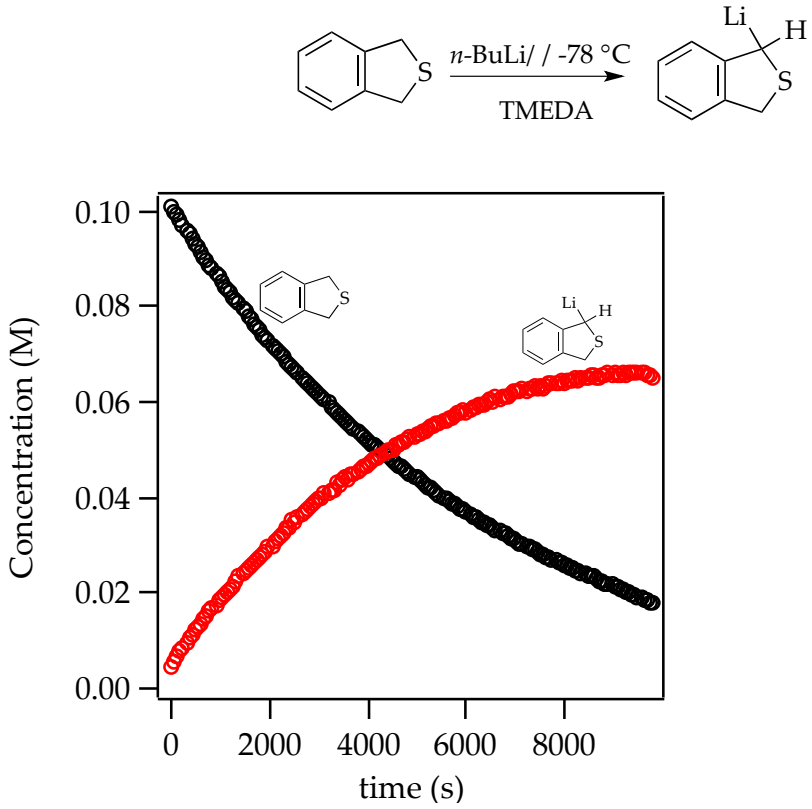


Figure 20 Plot of concentration versus time for lithiation of 1,3-dihydrobenzo-[*c*]thiophene **3** with 4.0 equiv of *n*-BuLi and 4.0 equiv TMEDA in THF-d_8 monitored by ^{1}H NMR spectroscopy at -78 °C.

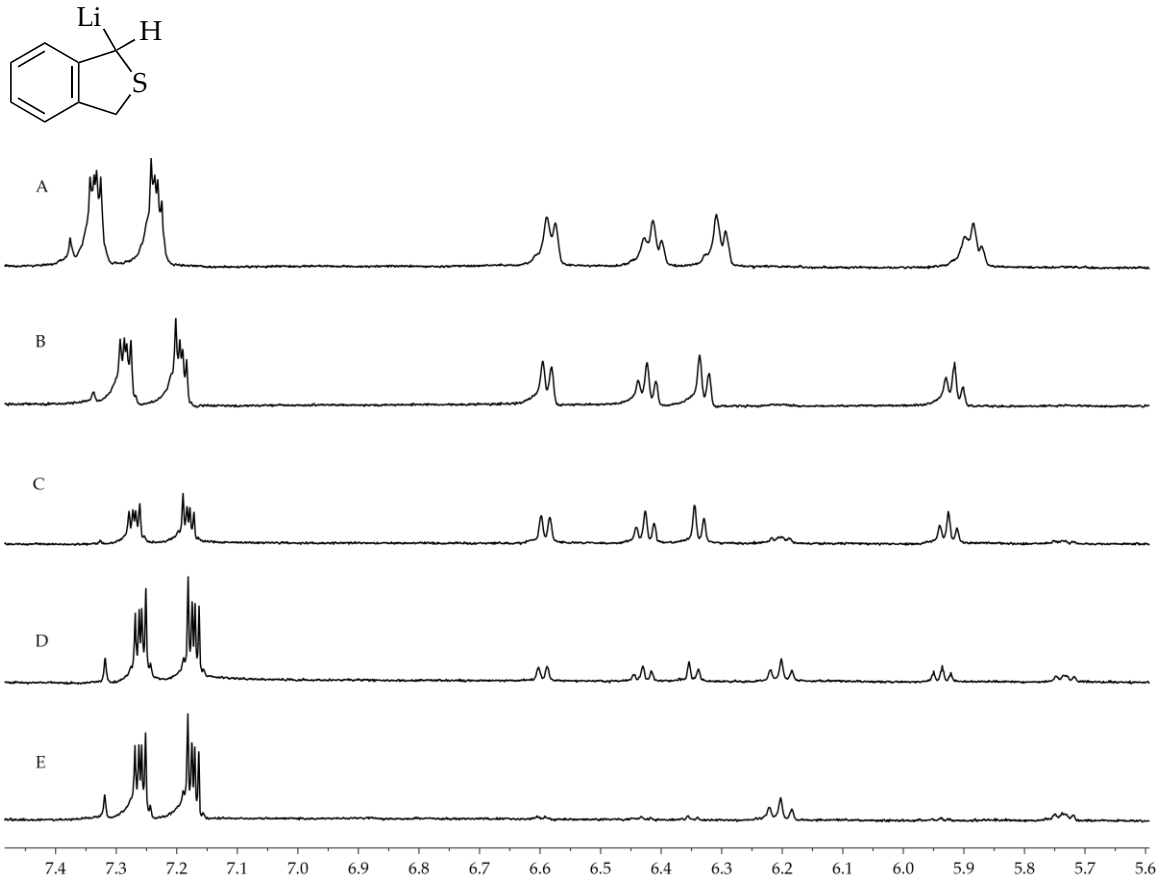


Figure 21. ^{1}H NMR spectra of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **6** with 0.50 equiv *n*-BuLi in THF-d_8 with aging at -78 °C for 12 hr with varying temperature and recorded at -115 °C: (A) -115 °C; (B) -80 °C ; (C) -60 °C for 20 mins; (D) -40 °C for 10 mins; (E) -20 °C for 5 mins.

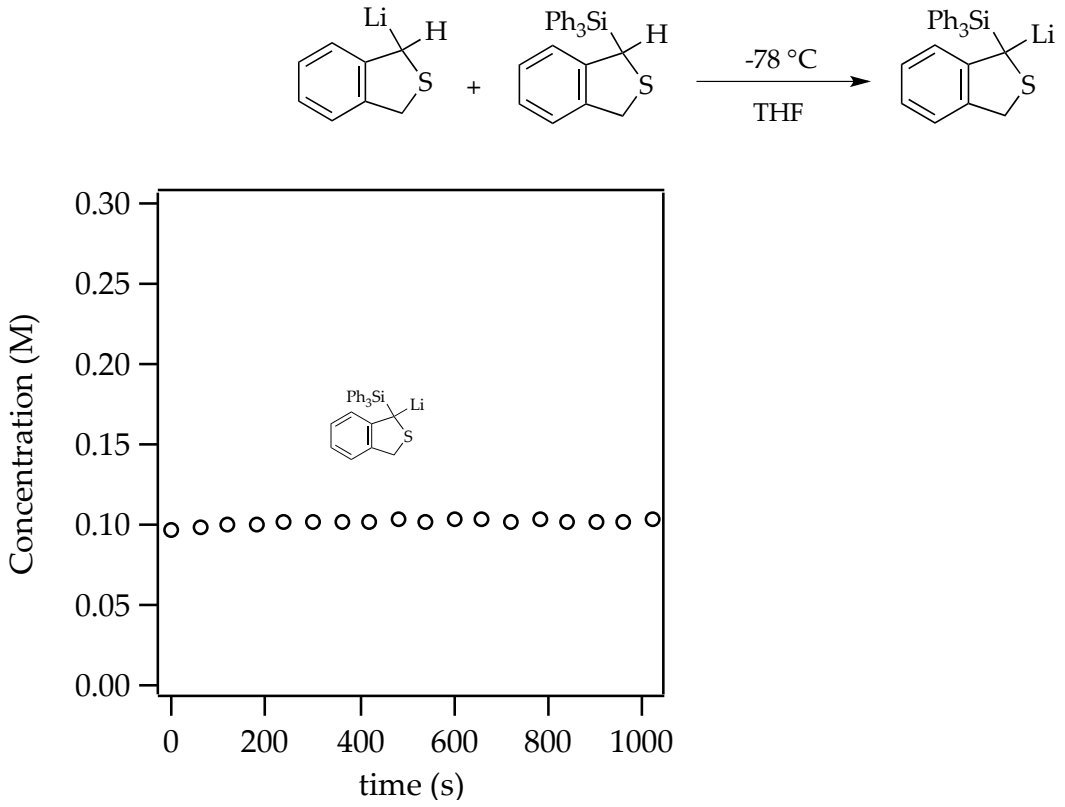


Figure 22. Plot of concentration versus time for lithiation of (1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **5** with 0.5 equiv 1-lithio-1,3-dihydrobenzo[*c*]thiophene **9** in THF-d_8 monitored by ^{1}H NMR spectroscopy at -78 °C.

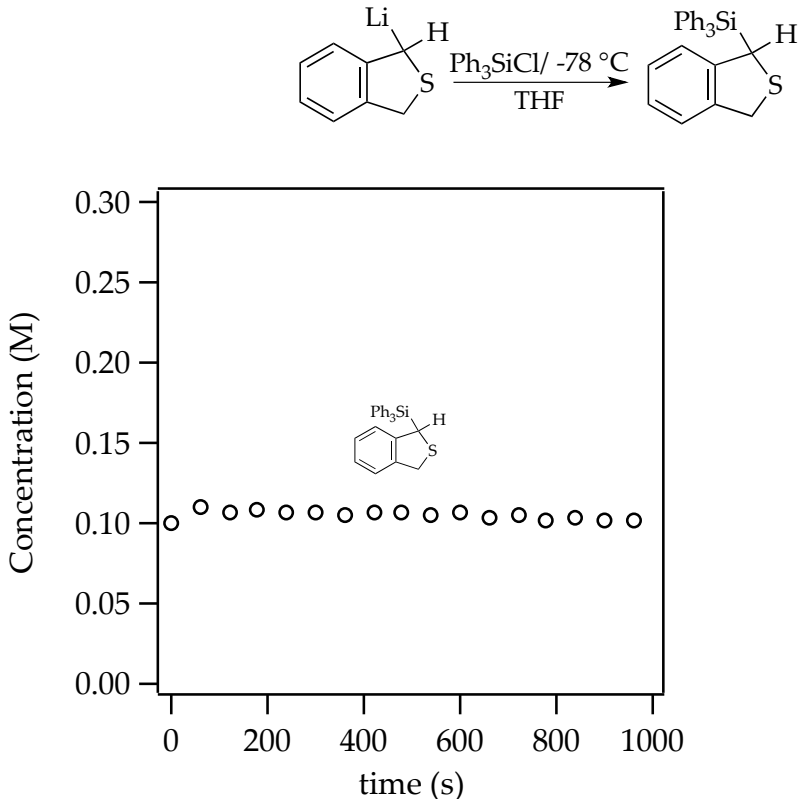


Figure 23. Plot of concentration versus time for silylation of 1-lithio-1,3-dihydrobenzo[*c*]thiophene **5** with 2.0 equiv triphenylsilylchloride in THF-d_8 monitored by ^{1}H NMR spectroscopy at -78 °C.

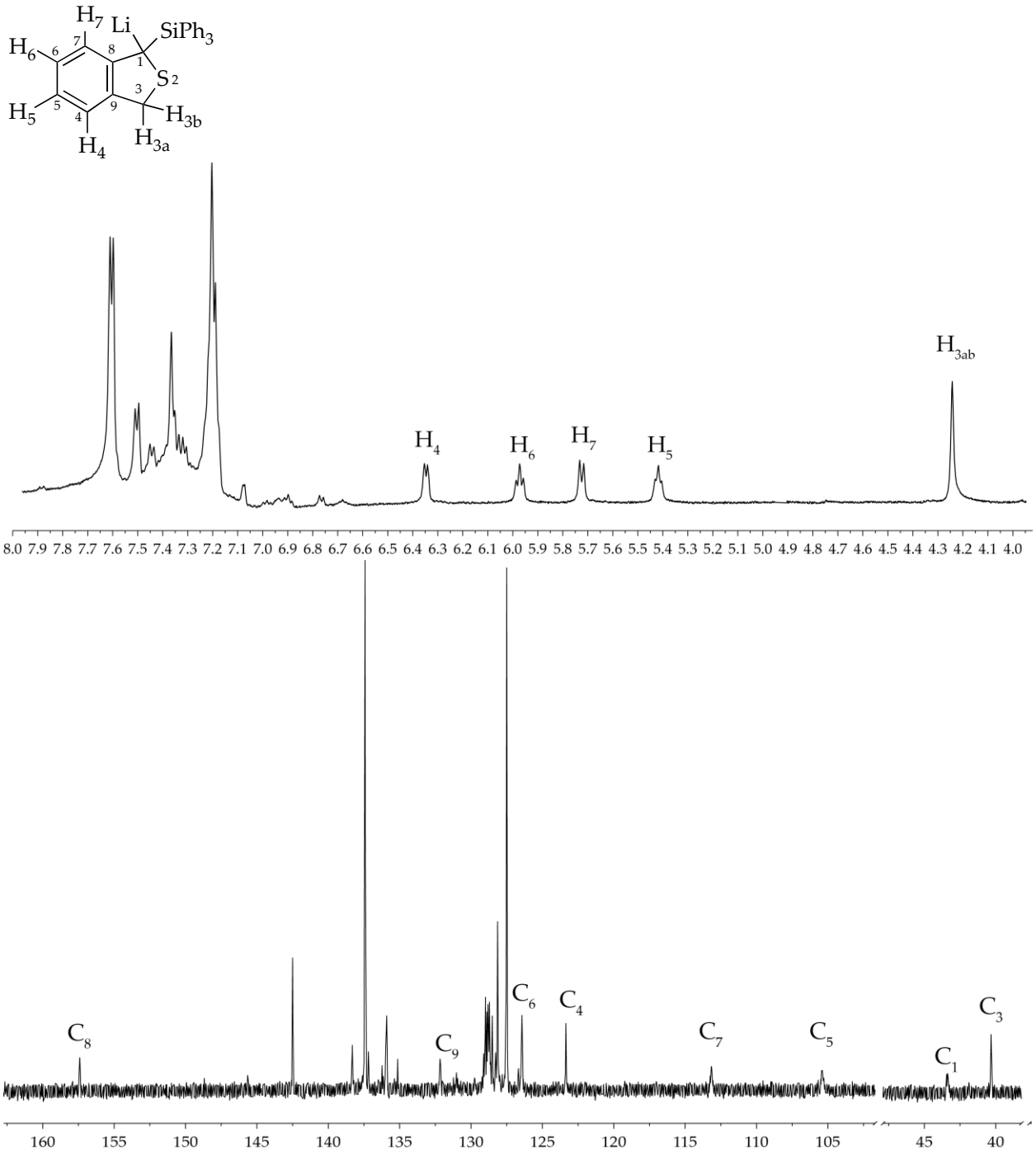


Figure 24. ^{1}H and ^{13}C NMR spectra of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** in THF-d_8 recorded at -80 °C: (a) ^{1}H NMR δ 7.60 (m, 6H); 7.32-7.50 (m, 3H), 7.20 (m, 6H), 5.72 (d, *J* = 7.20 Hz, 1H), 5.97 (t, *J*= 7.80 Hz, 1H), 5.72 (d, *J* = 7.80 Hz, 1H), 5.42 (t, *J* = 7.20 Hz, 1H), 4.24 (s, 3H); (b) ^{13}C NMR δ 157.4, 142.5, 138.3, 137.4, 135.9, 135.0, 132.2, 128.1, 127.4, 126.4, 123.4, 113.2, 105.2, 43.3, 40.3.

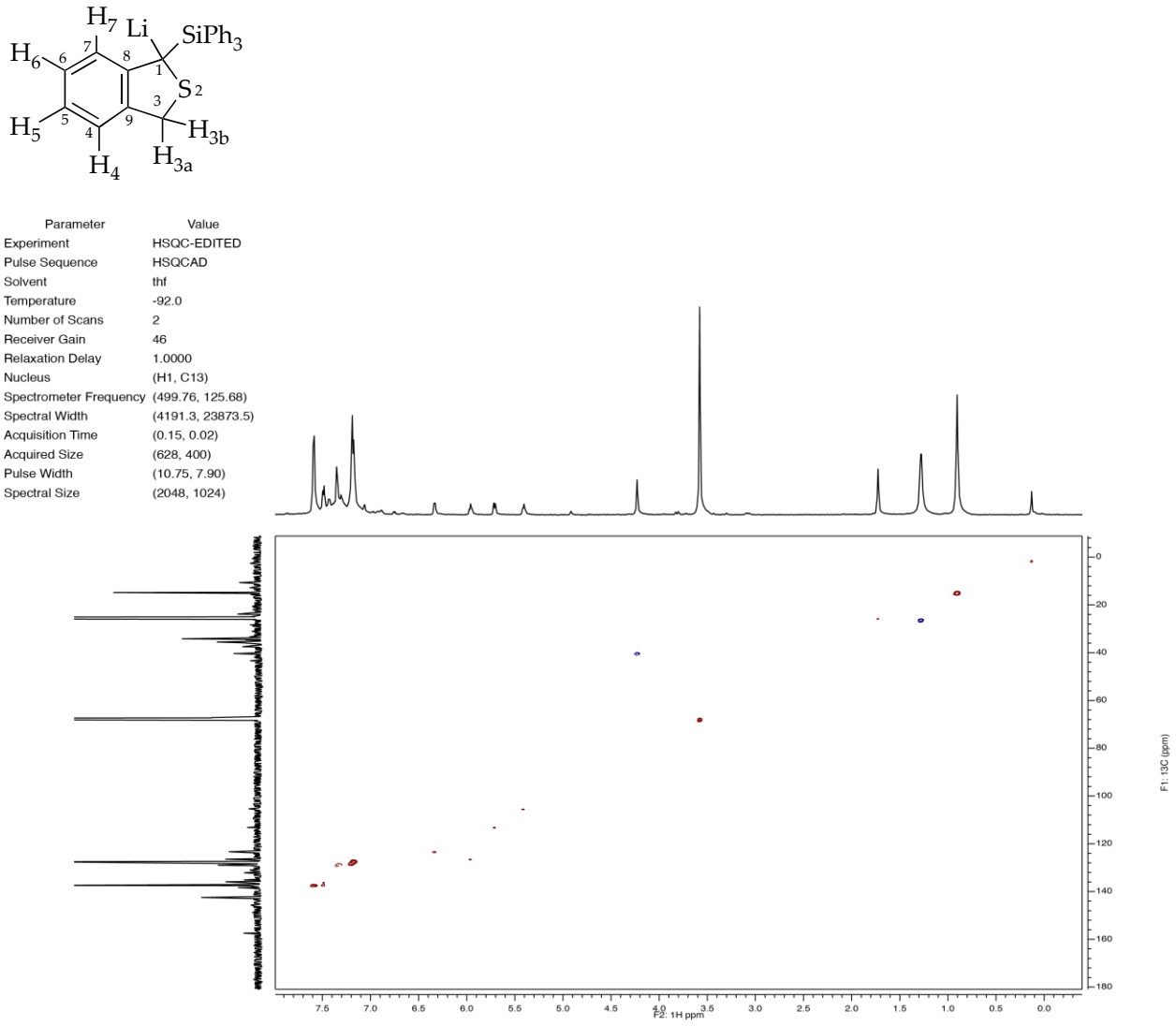


Figure 25. Multiplicity-edited $^{1}H/^{13}C$ HSQCAD spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9**. Red contours indicate CH/CH_3, blue contours are CH_2 (full display).

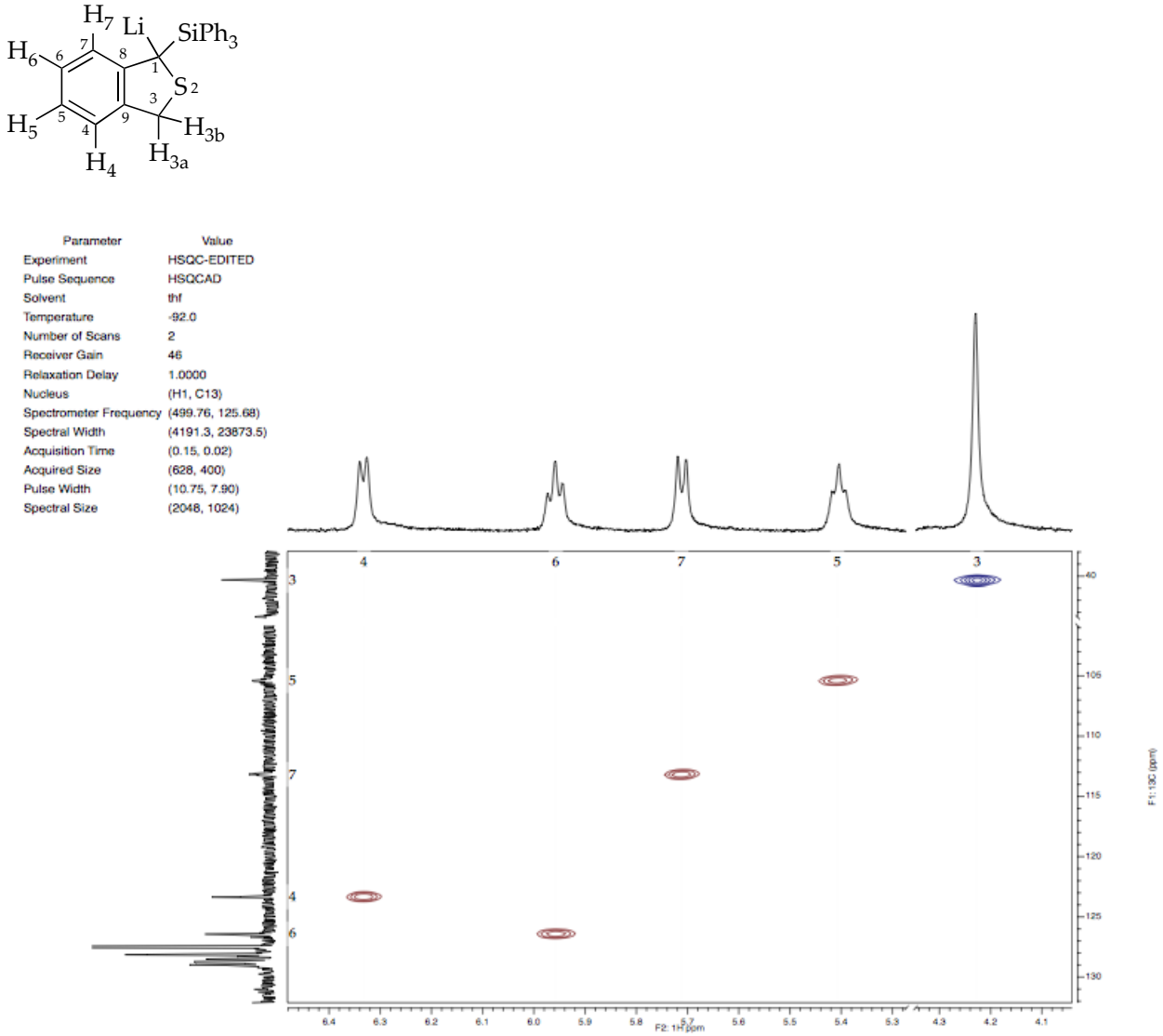
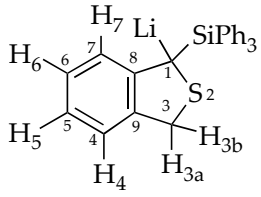


Figure 26 Multiplicity-edited $^{1}H/^{13}C$ HSQCAD spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** with assignments displaying regions of interest. Red contours indicate CH/CH_3, blue contours are CH_2.



Parameter	Value
Experiment	HSQC-EDITED
Pulse Sequence	HSQCAD
Solvent	thf
Temperature	-92.0
Number of Scans	2
Receiver Gain	46
Relaxation Delay	1.0000
Nucleus	(H1, C13)
Spectrometer Frequency	(499.76, 125.68)
Spectral Width	(4191.3, 23873.5)
Acquisition Time	(0.15, 0.02)
Acquired Size	(628, 400)
Pulse Width	(10.75, 7.90)
Spectral Size	(2048, 1024)

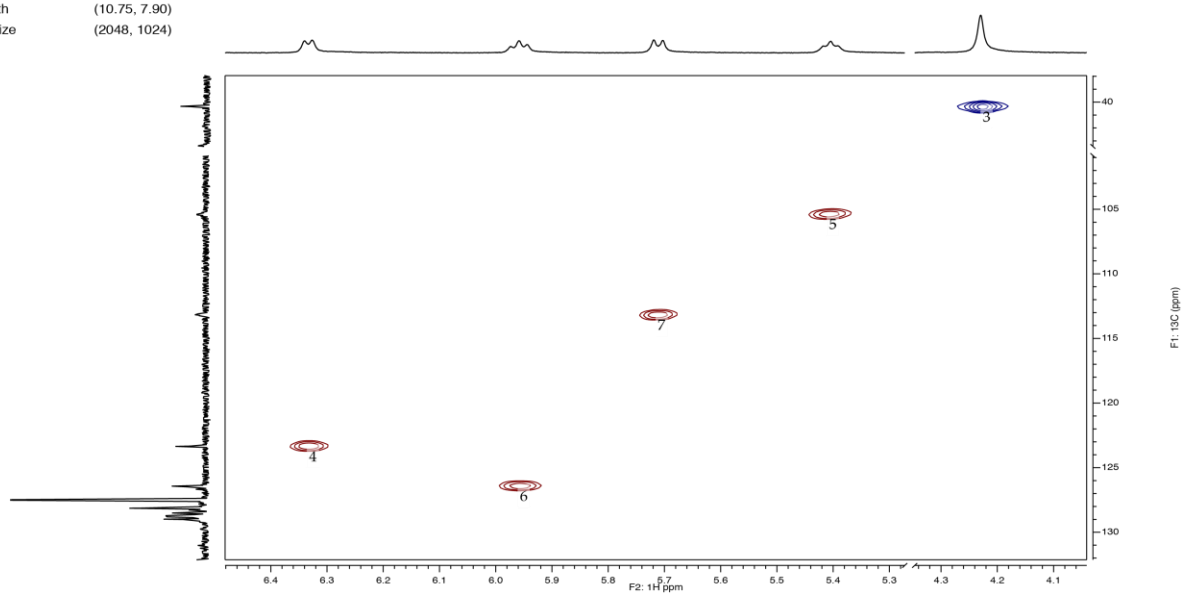


Figure 27 Multiplicity-edited $^{1}H/^{13}C$ HSQCAD spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** with assignments displaying regions of interest. Red contours indicate CH/CH_3, blue contours are CH_2.

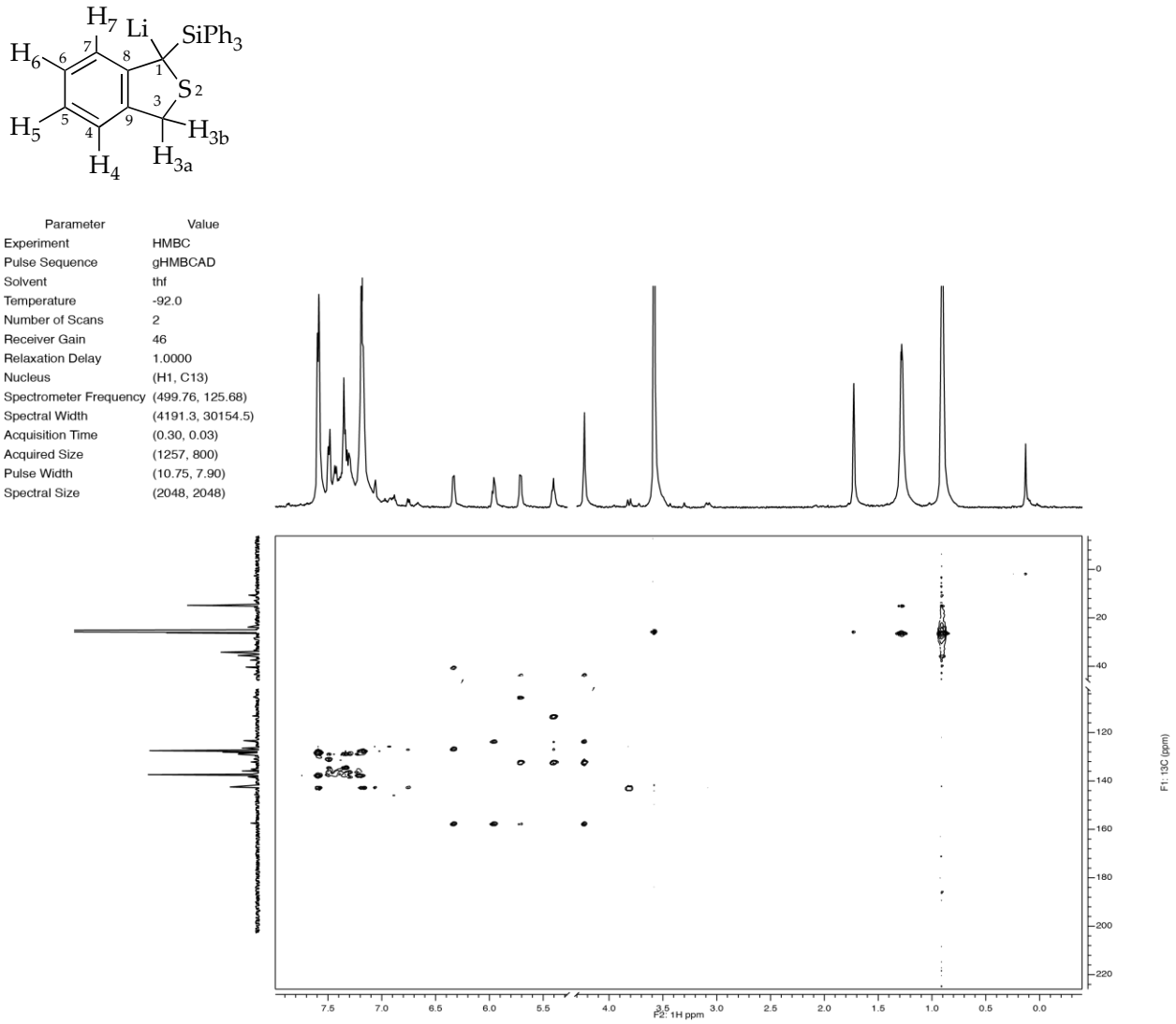
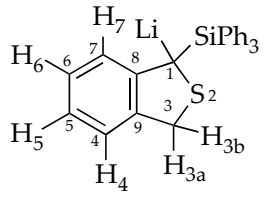


Figure 28. Full $^{1}H/^{13}C$ HMBC spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophene-1-yl)triphenylsilane **9**.



Parameter	Value
Experiment	HMBC
Pulse Sequence	gHMBCAD
Solvent	thf
Temperature	-92.0
Number of Scans	2
Receiver Gain	46
Relaxation Delay	1.0000
Nucleus	(H1, C13)
Spectrometer Frequency	(499.76, 125.68)
Spectral Width	(4191.3, 30154.5)
Acquisition Time	(0.30, 0.03)
Acquired Size	(1257, 800)
Pulse Width	(10.75, 7.90)
Spectral Size	(2048, 2048)

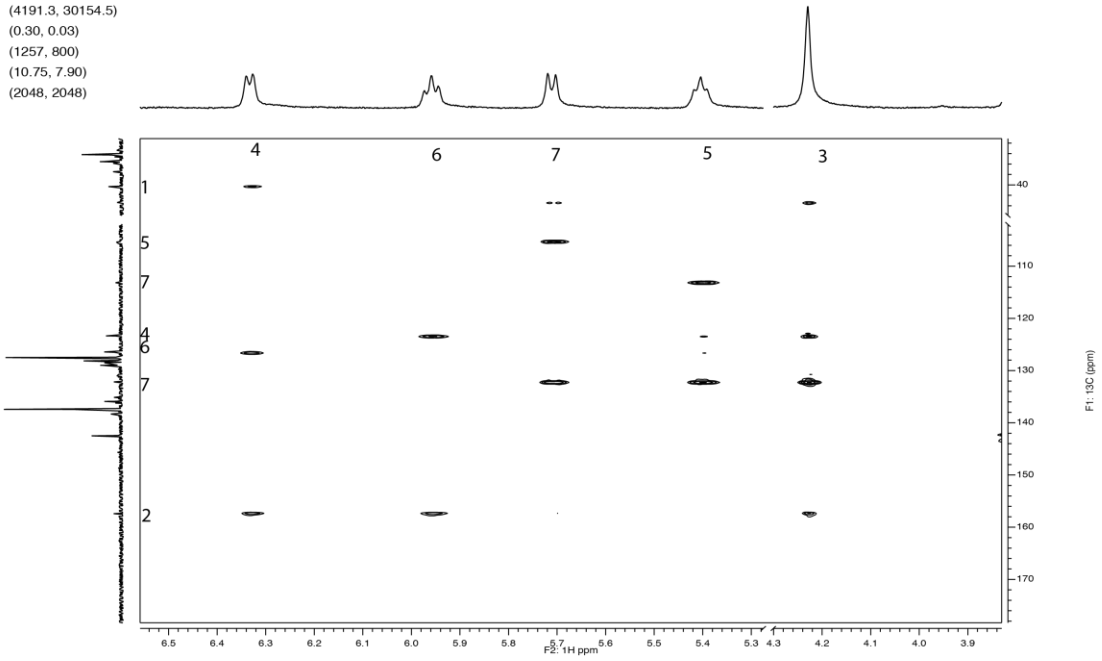


Figure 29 $^{1}H/^{13}C$ HMBC spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophene-1-yl)triphenylsilane **9** with assignment showing only regions of interest.

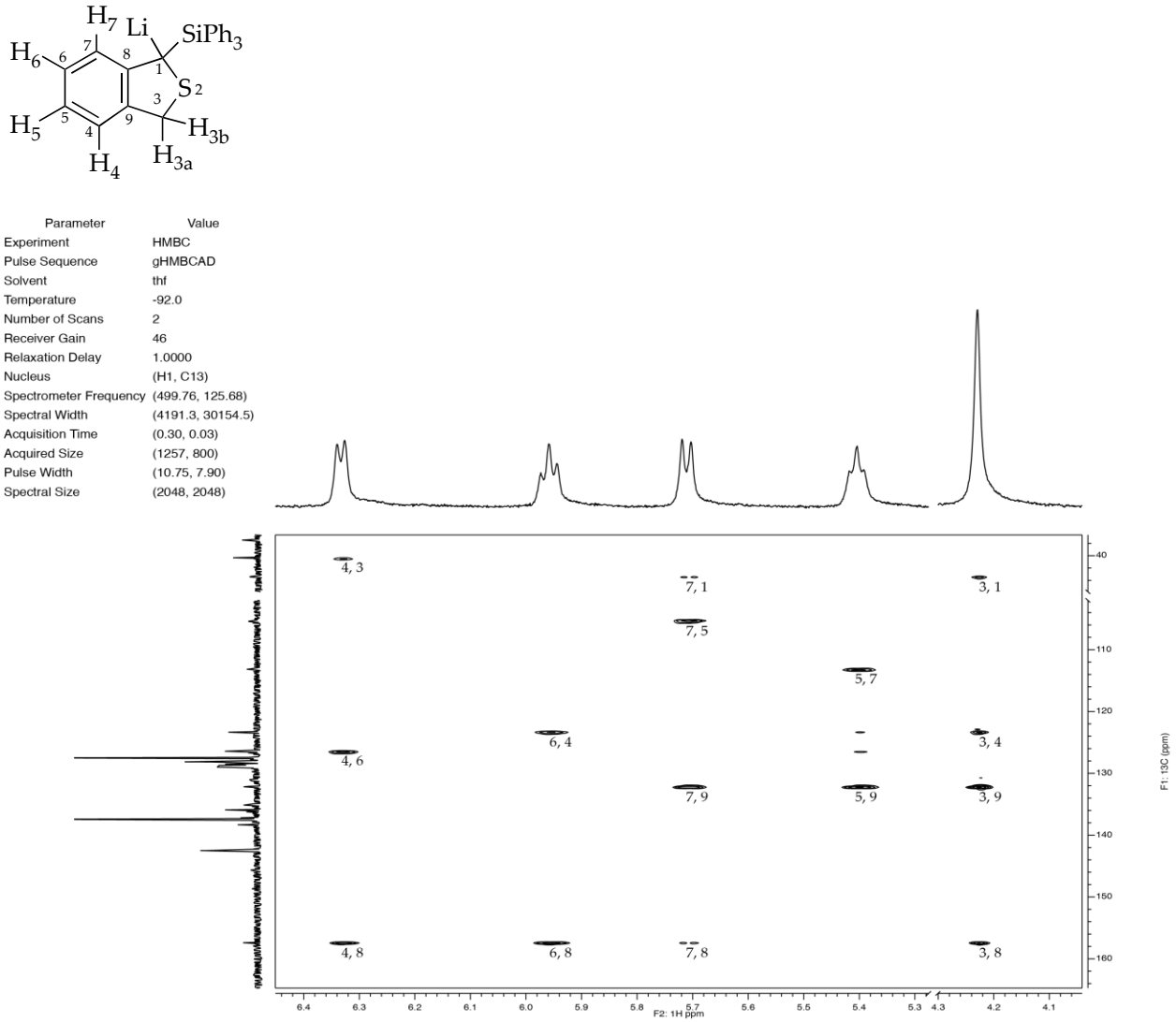


Figure 30. $^{1}H/^{13}C$ HMBC spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** with assignments ($^{1}H,^{13}C$) showing only regions of interest.

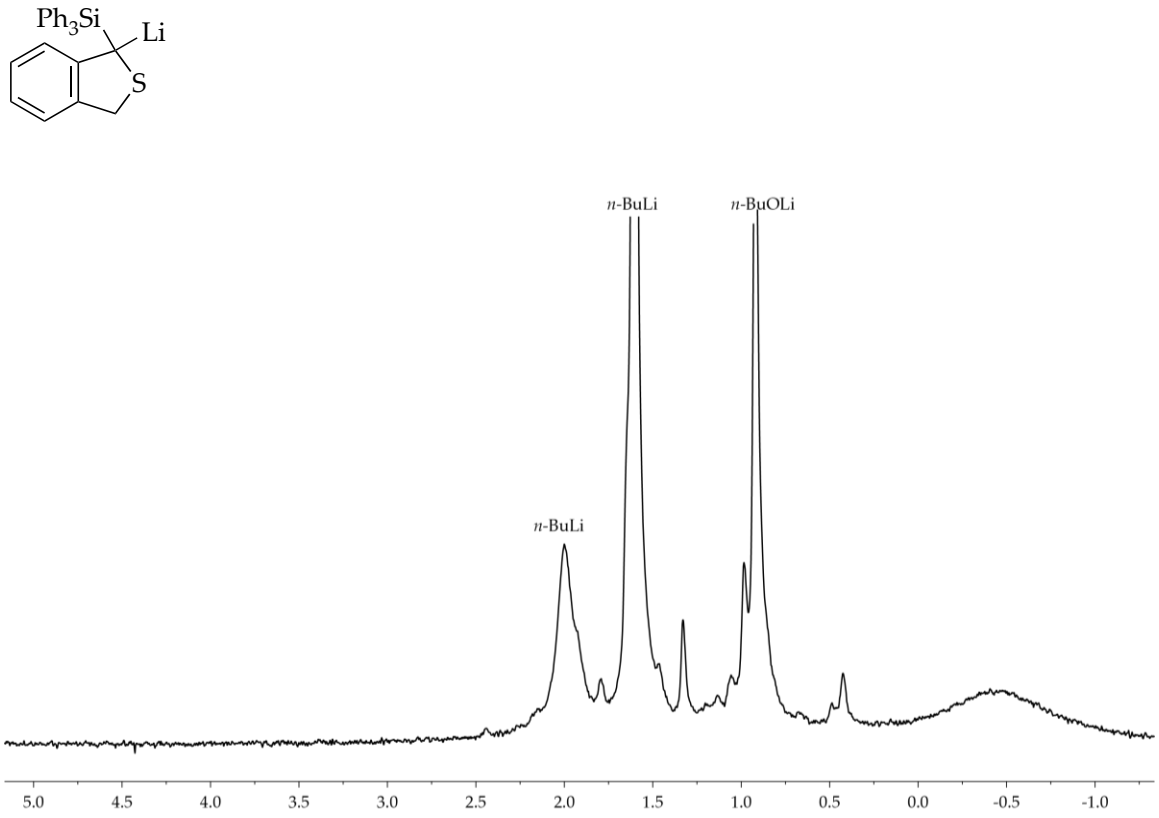


Figure 31 ^{6}Li NMR spectrum of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** in THF-d_8 with aging for 12 hr at -78 °C: δ -0.47.

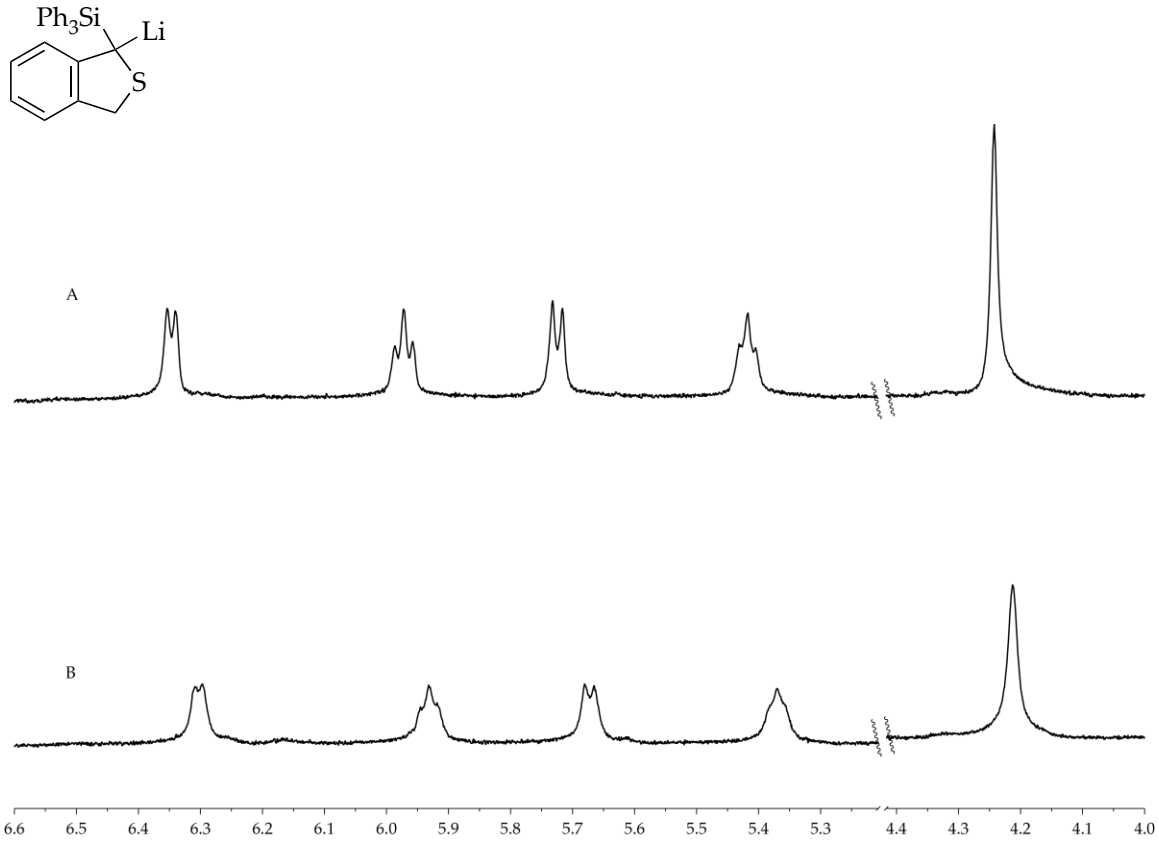


Figure 32. ^{1}H NMR spectra of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)-triphenylsilane **9** in THF-d_8 with aging for 12 hr at -78 °C and recorded at -80 °C: (A) no TMEDA; (B) 4.0 equiv TMEDA.

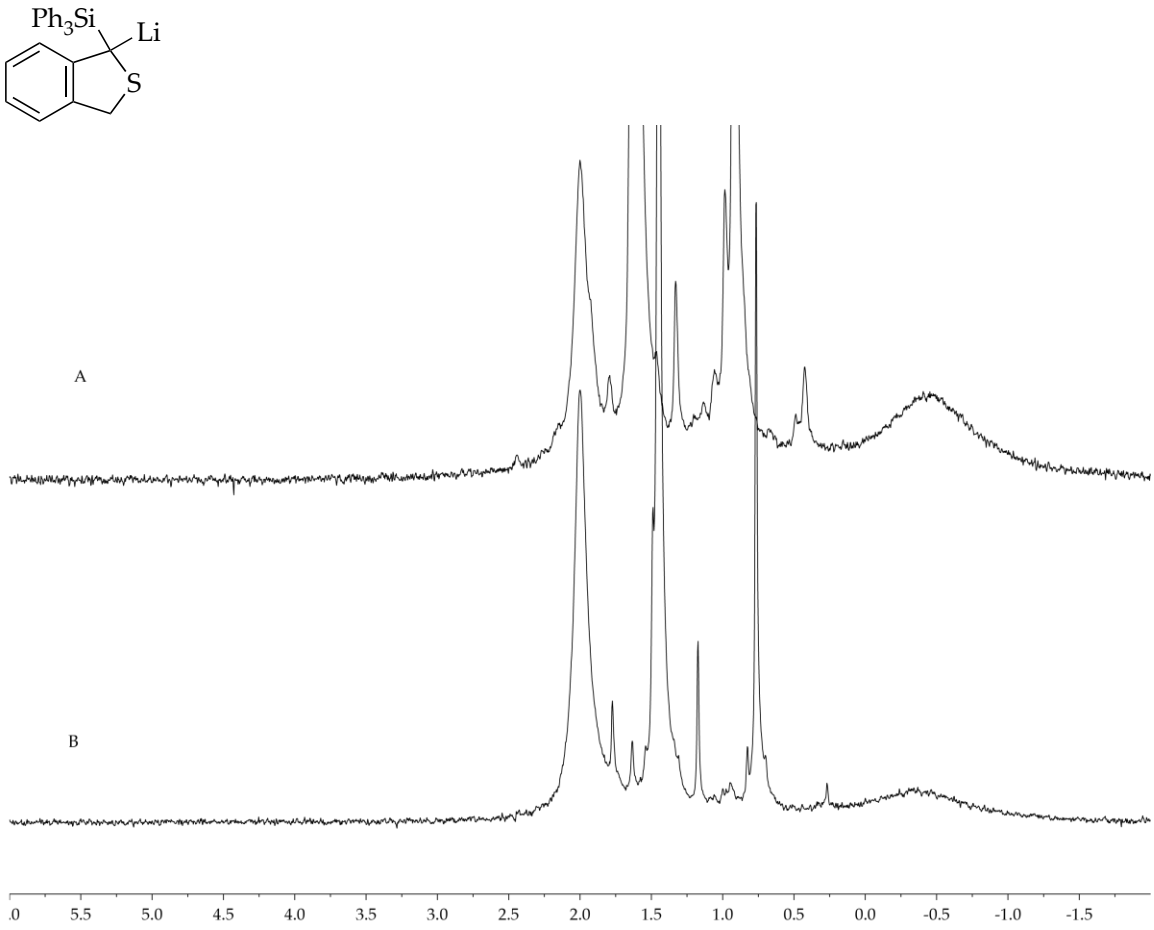


Figure 33. ^{6}Li NMR spectra of (1-lithio-1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **9** with 0.40 M *n*-BuLi in THF-d_8 with aging for 12 hr at -78 °C and recorded at -80 °C: (A) no TMEDA; (B) 4.0 equiv TMEDA.

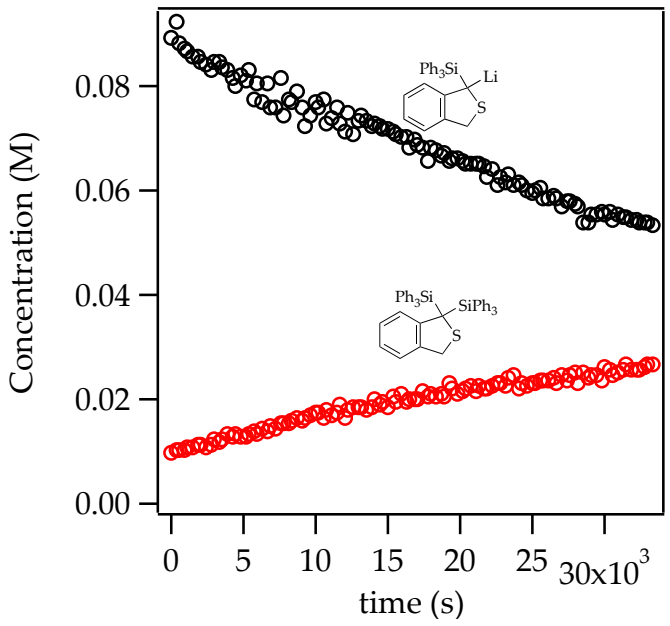


Figure 34. Plot of concentration versus time for silylation of (1-lithio-1,3- dihydrobenzo[*c*]-thiophen-1-yl)triphenylsilane **9** with 3.0 equiv triphenylsilylchloride in THF-d_8 monitored by ^{1}H NMR spectroscopy at -78 °C.

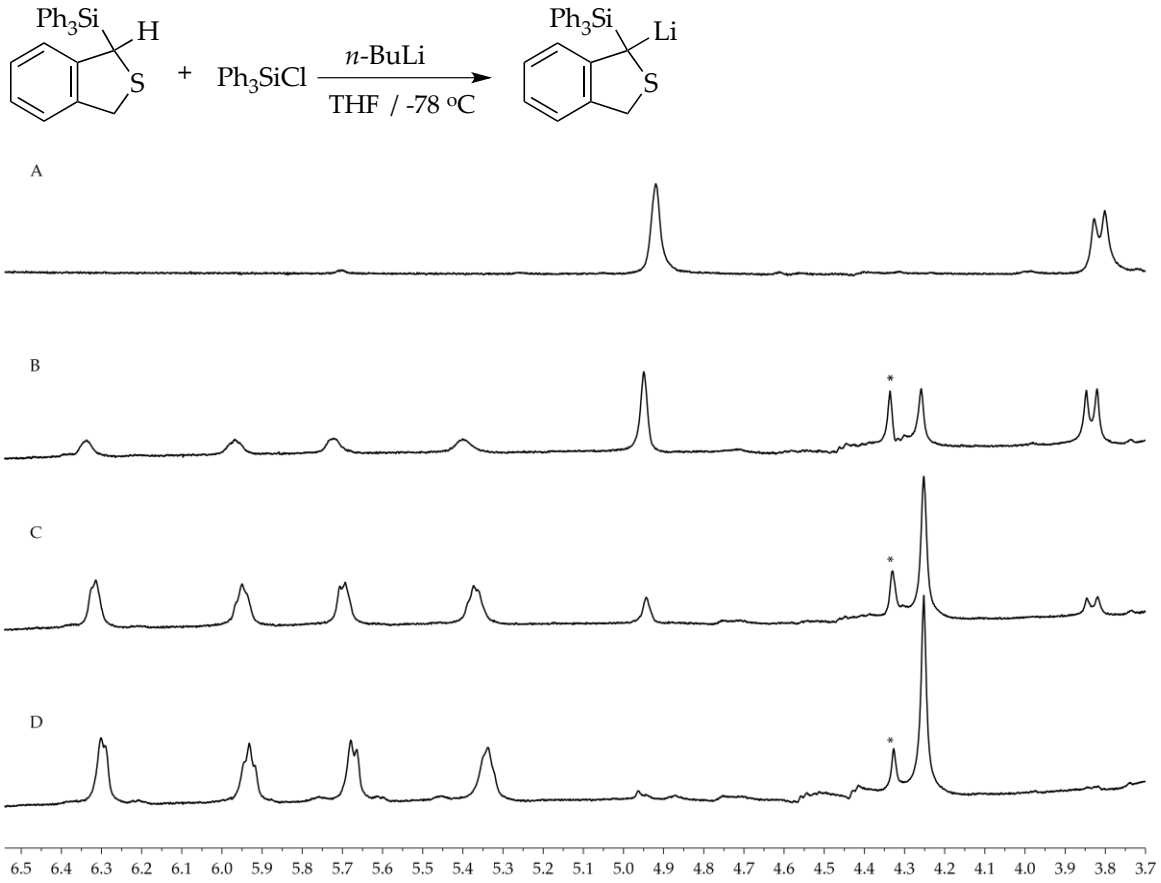


Figure 35. ^{1}H NMR spectrum of (1,3-dihydrobenzo[*c*]thiophen-1-yl)triphenylsilane **3** and 3.0 equiv triphenylsilylchloride with varying *n*-BuLi in THF-d_8 recorded at -80 °C. (A) no *n*-BuLi; (B) 0.50 equiv *n*-BuLi; (C) 1.0 equiv *n*-BuLi; (D) 2.0 equiv *n*-BuLi. *Unknown impurity.