SUPPORTING INFORMATION

Improved odorless access to benzo[1,2-d;4,5-d']bis[1,3]dithioles and *tert*-butyl arylsulfides via C-S cross coupling

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1. Analytical data of products

1.1 NMR spectroscopy

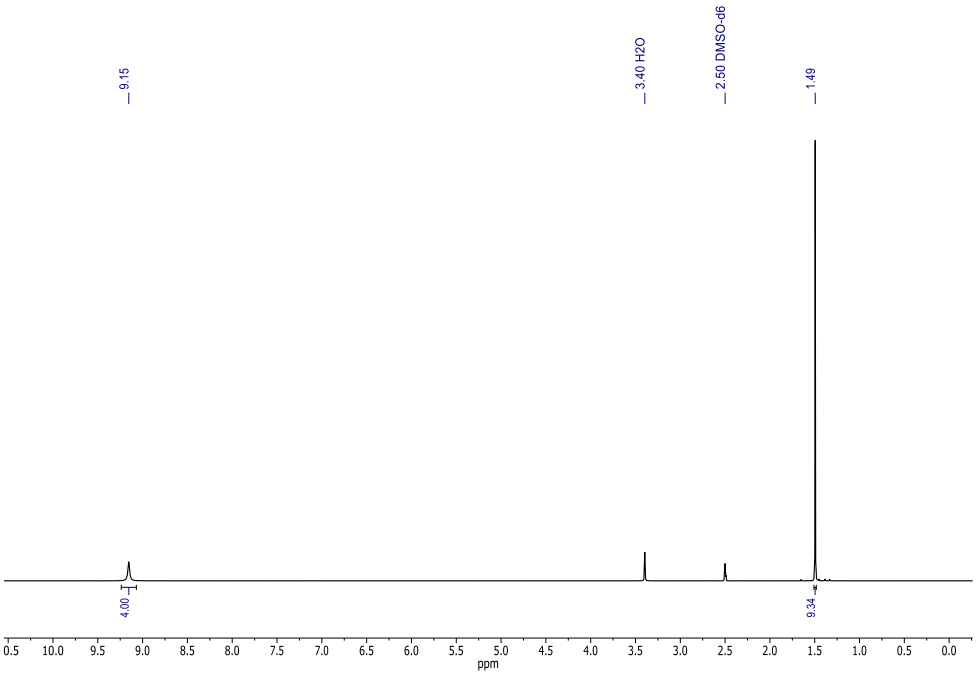


Figure S1. ^{1}H-NMR (400 MHz, 298 K, DMSO-d6) spectrum of S-*tert*-butyl isothiouronium bromide **6**.

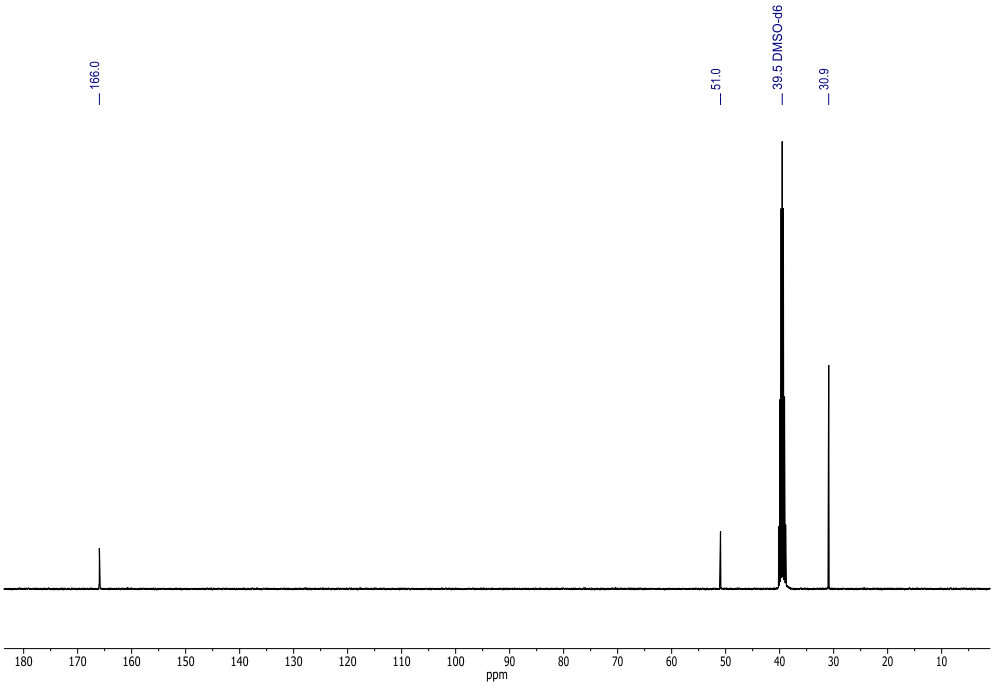
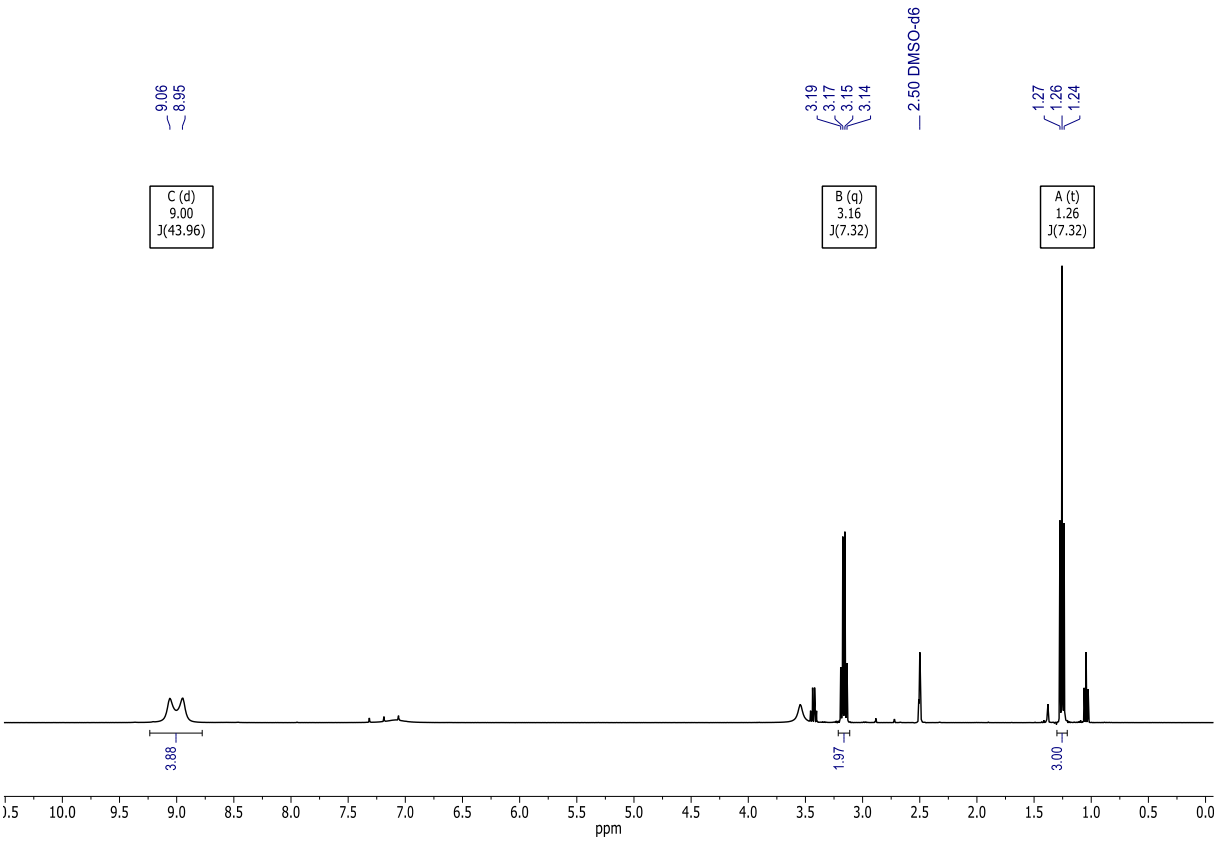


Figure S2. ^{13}C-NMR (100 MHz, 298 K, DMSO-d6) of S-tert-butyl isothiouronium bromide **6**.



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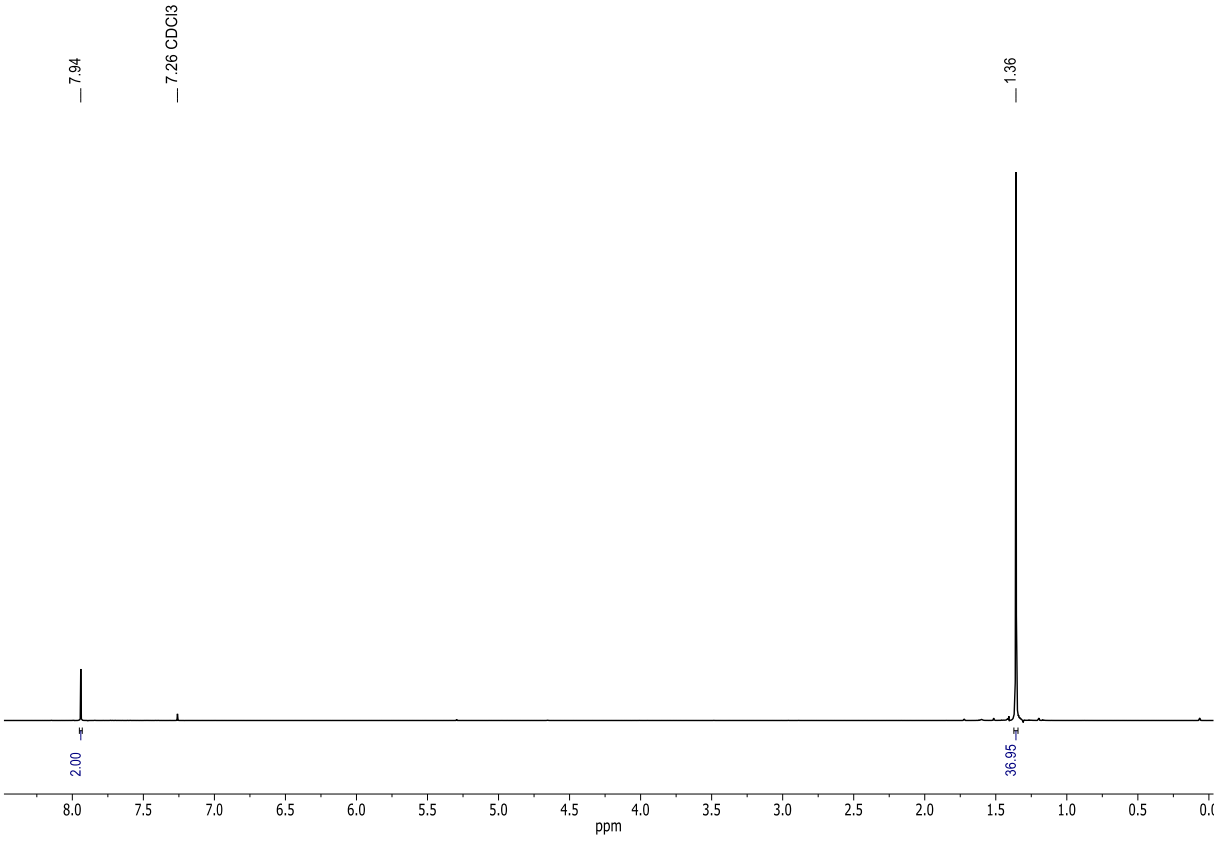
2 ***Figure S3.*** ^{1}H-NMR (400 MHz, 298 K, DMSO-d6) of reaction 2.1 when using EtOH as solvent.



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4 ***Figure S4.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of 1,2,4,5-Tetrakis(*tert*-butylthio)benzene **5**.

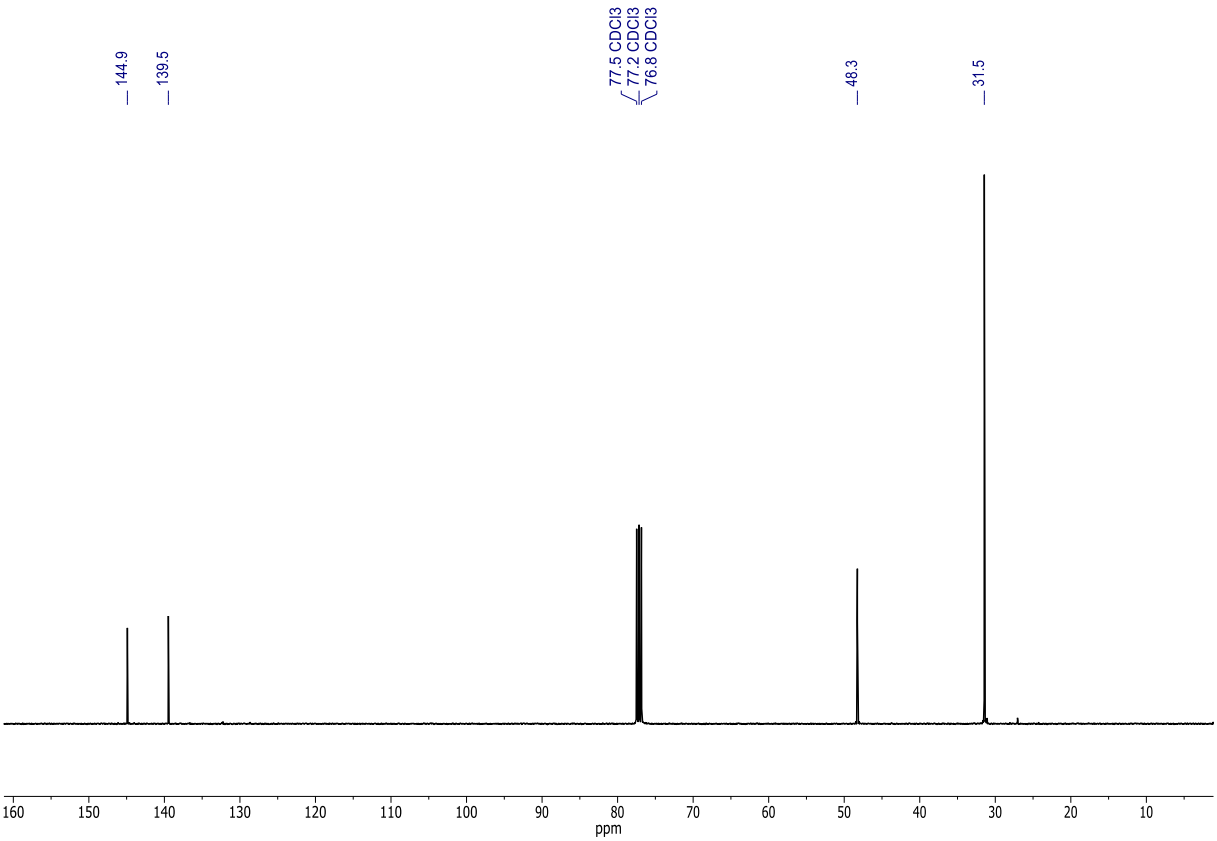


Figure S5. ^{13}C-NMR (100 MHz, 298 K, $CDCl_3$) of 1,2,4,5-Tetrakis(*tert*-butylthio)benzene **5**.

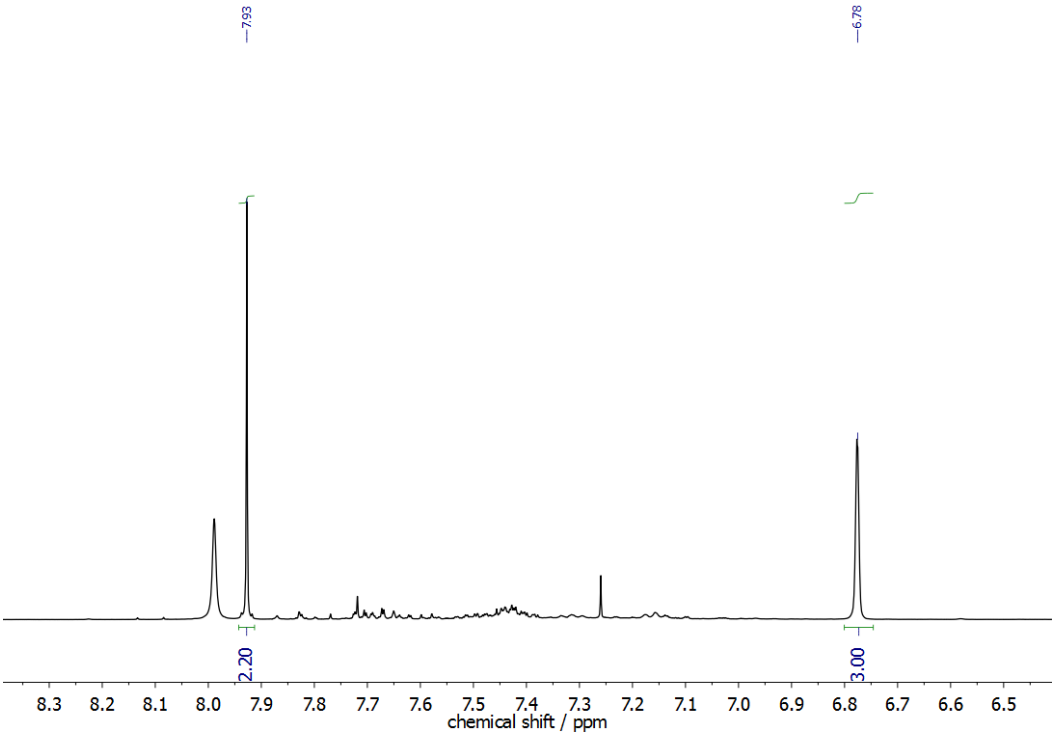


Figure S6. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reaction mixture converting 1,2,4,5-tetrabromobenzene to **5** containing mesitylene as an internal standard.

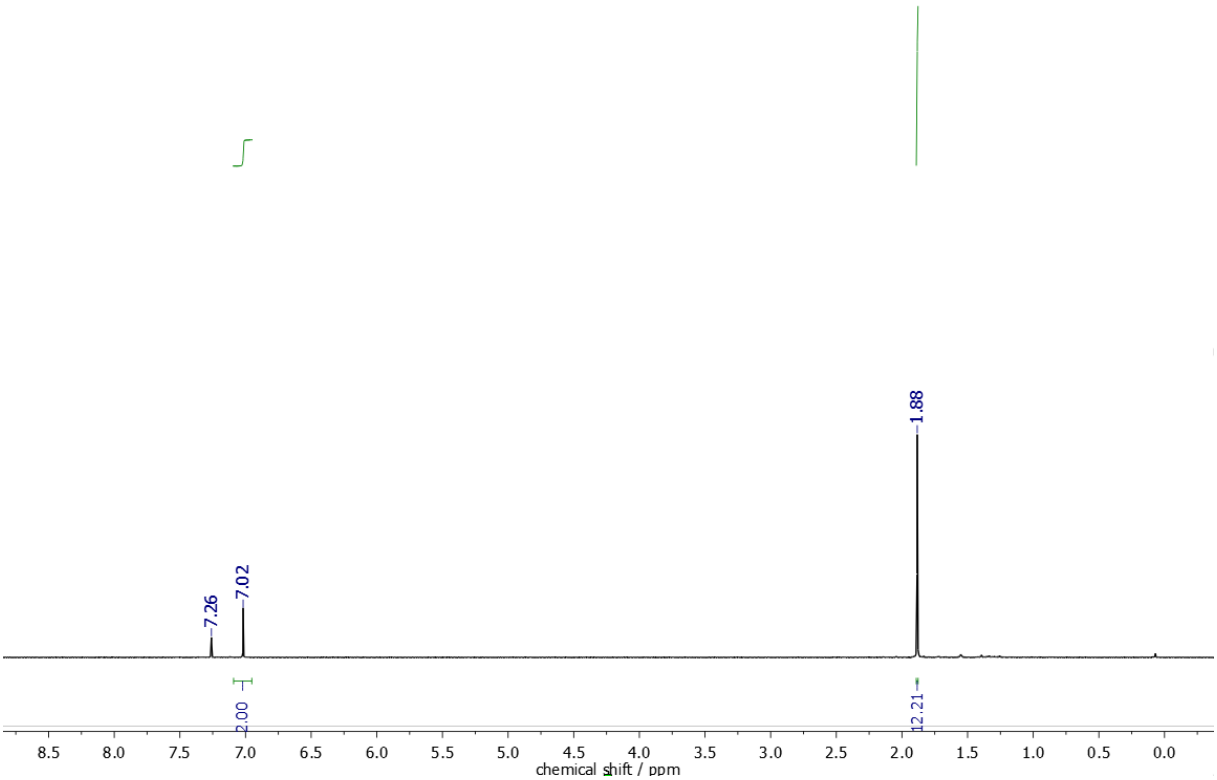


Figure S7. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of **1a**.

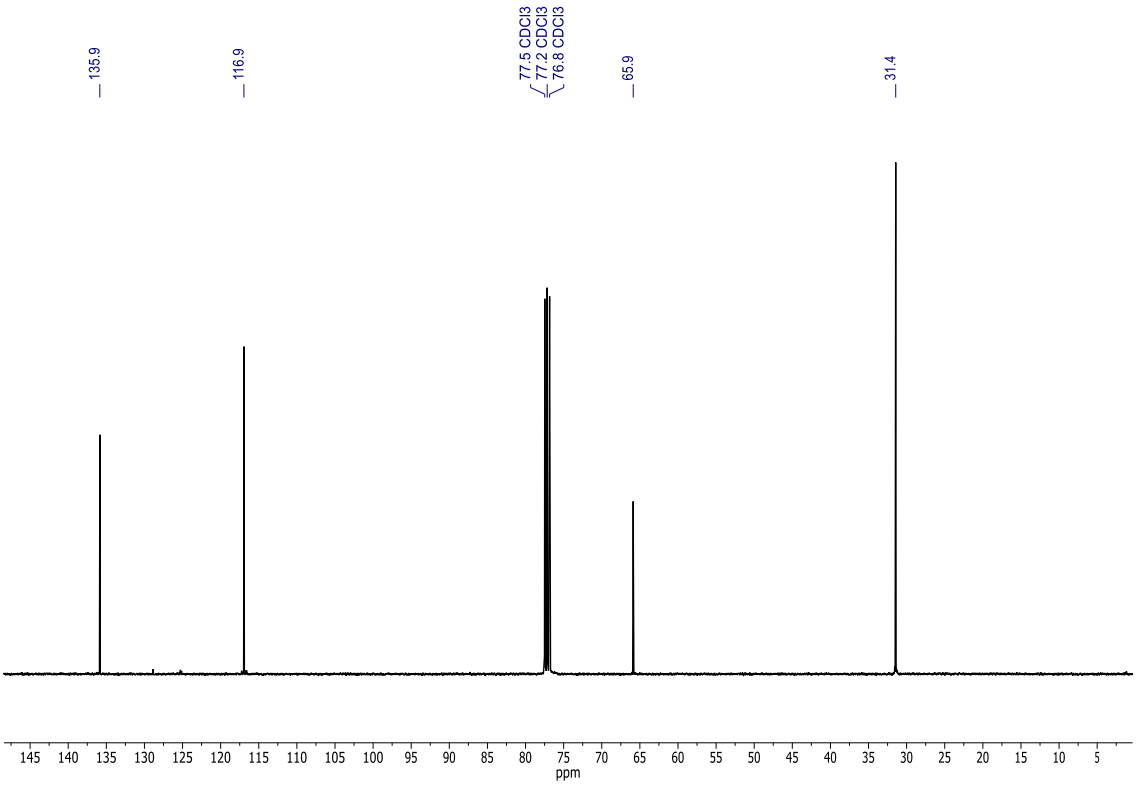
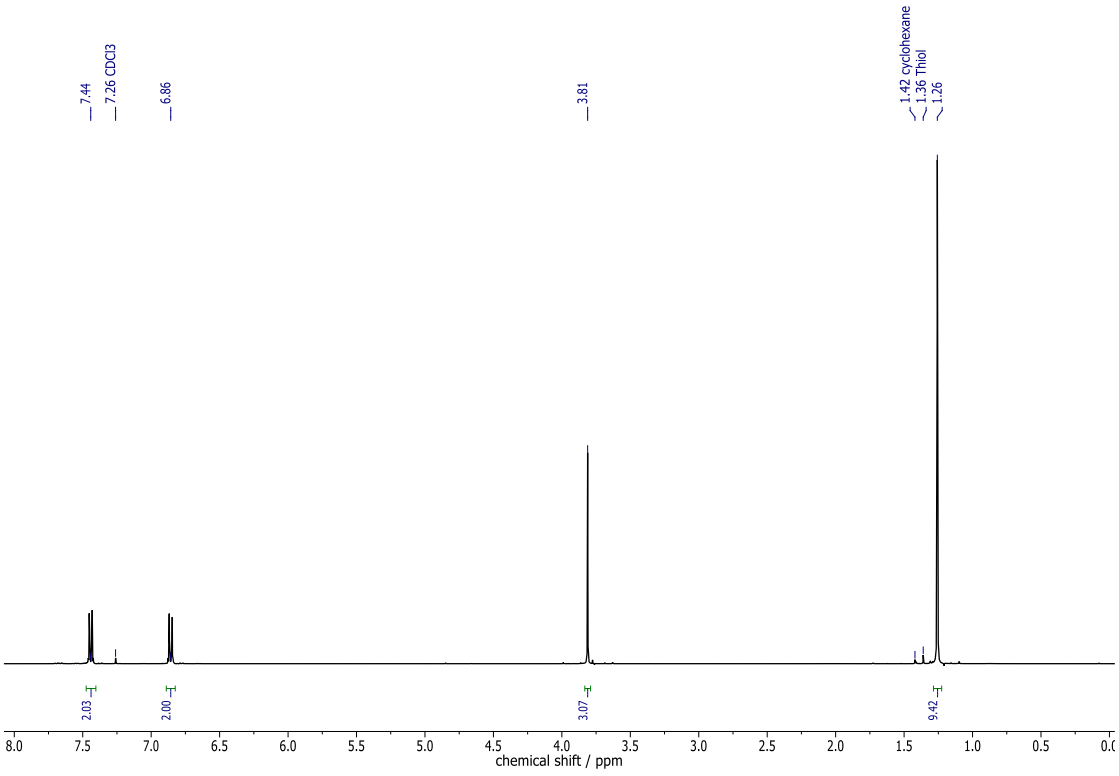


Figure S8. ^{13}C-NMR (100 MHz, 298 K, $CDCl_3$) of **1a**.



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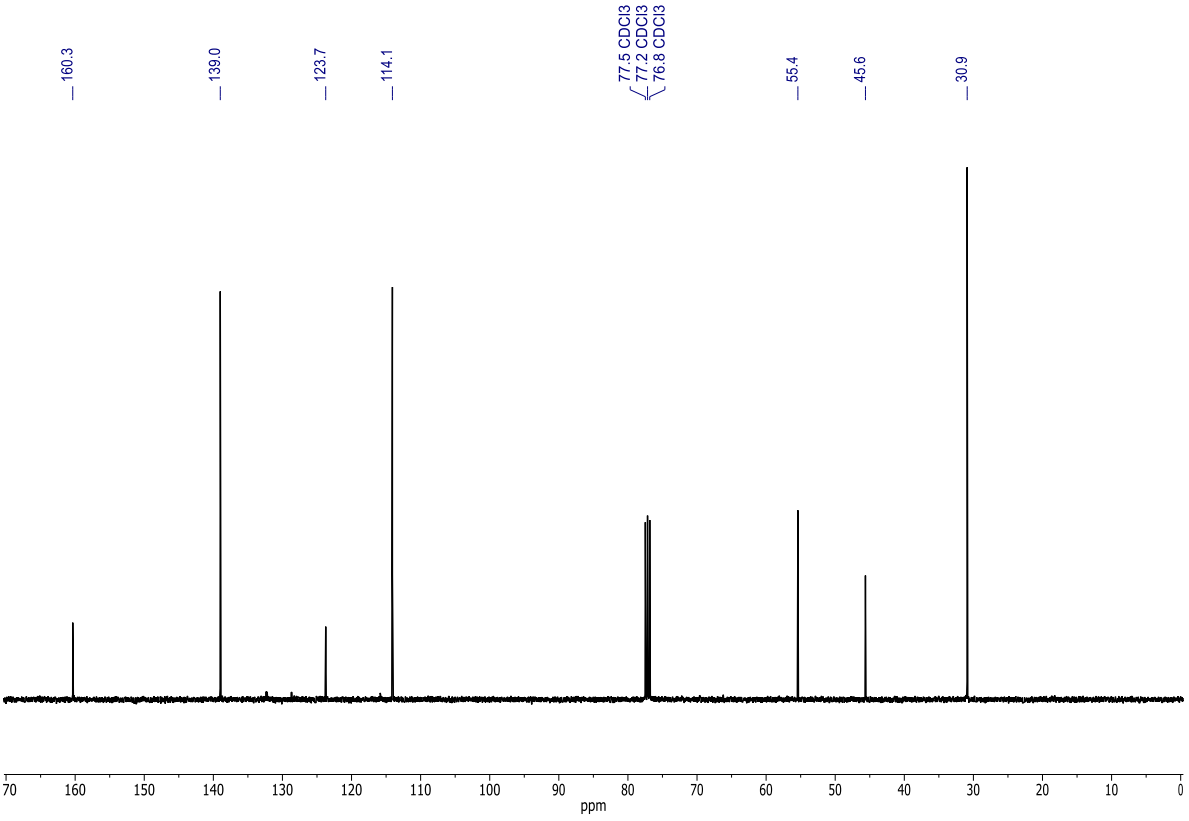
2 ***Figure S9.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of 4-methoxy-*tert*-butylthiobenzene **7**.



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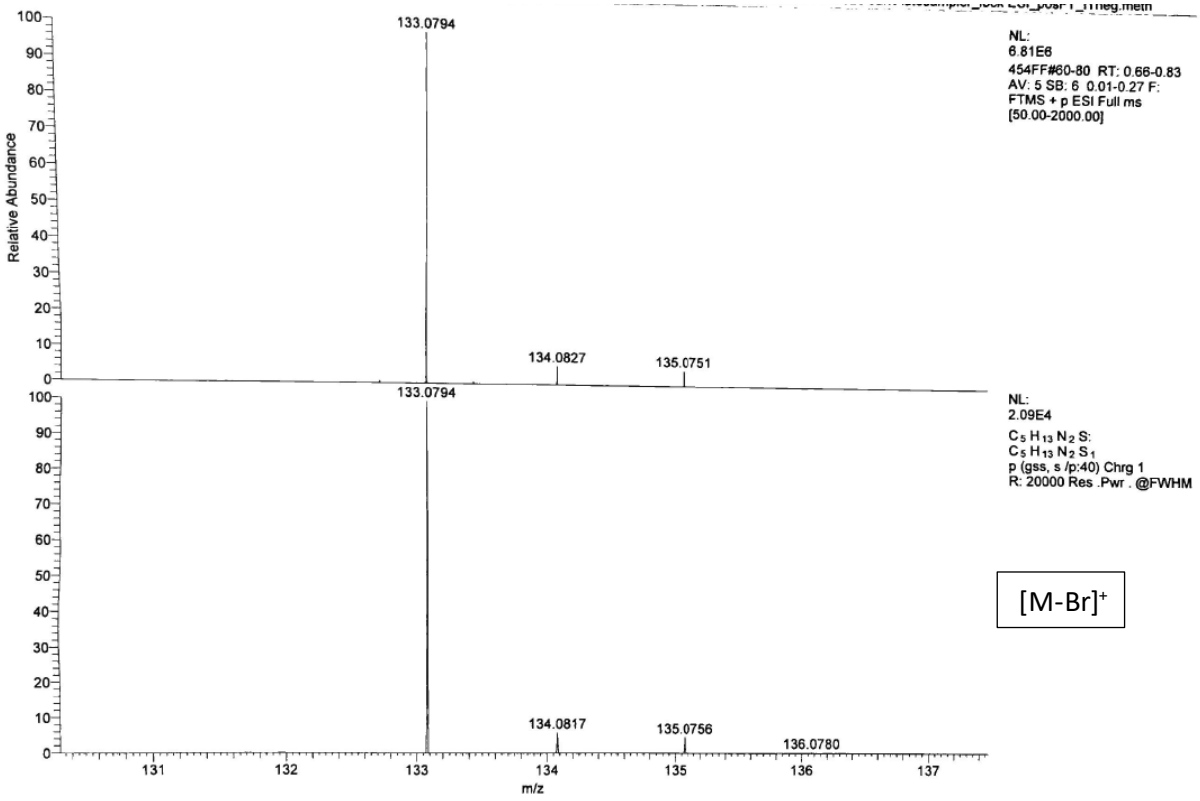
4 ***Figure S10.*** ^{13}C-NMR of 4-methoxy-*tert*-butylthiobenzene **7**.

1 1.2 Mass spectrometry

2



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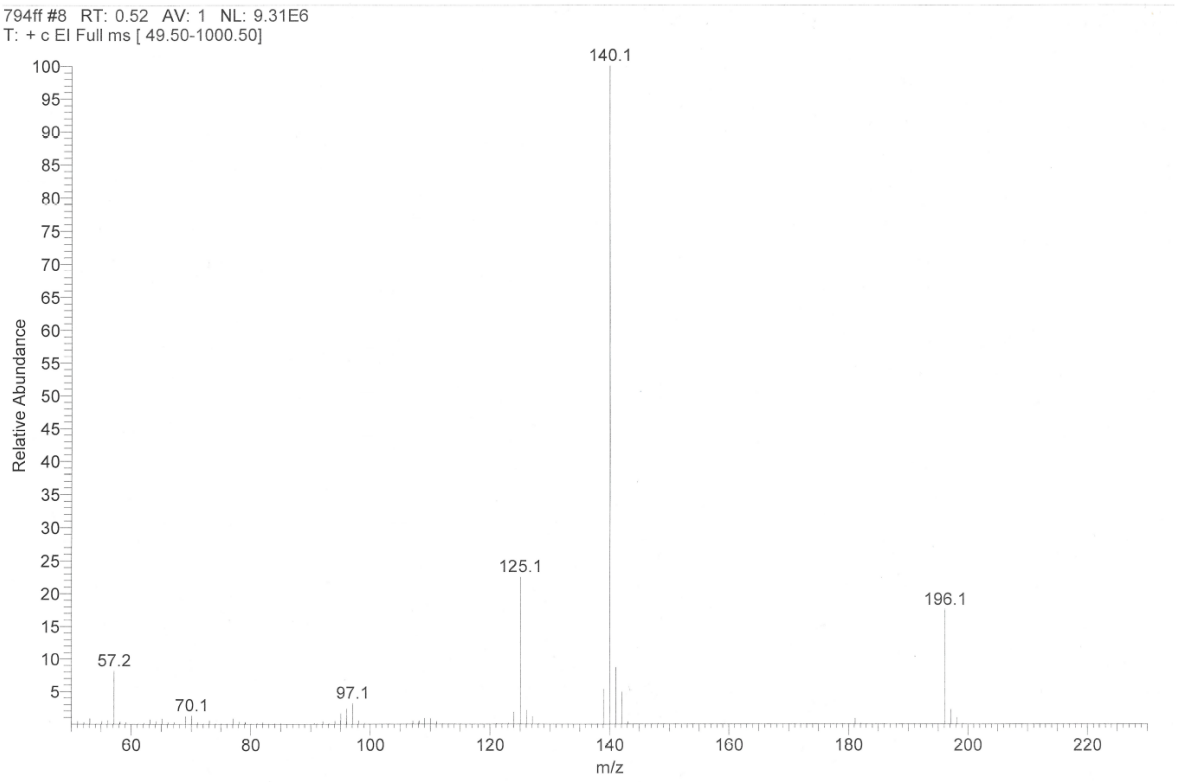
4 ***Figure S11.*** ESI(+)-MS (top) of S-*tert*-butyl isothiouronium bromide **6** and calculated isotope pattern

5 (bottom).



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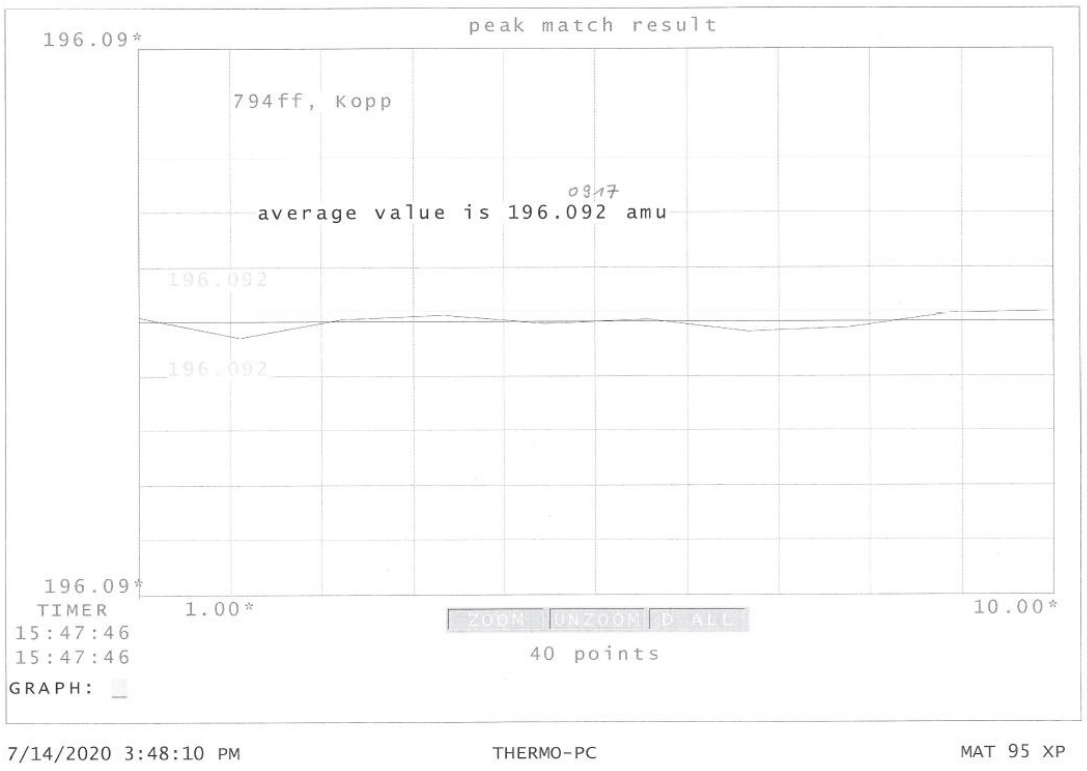

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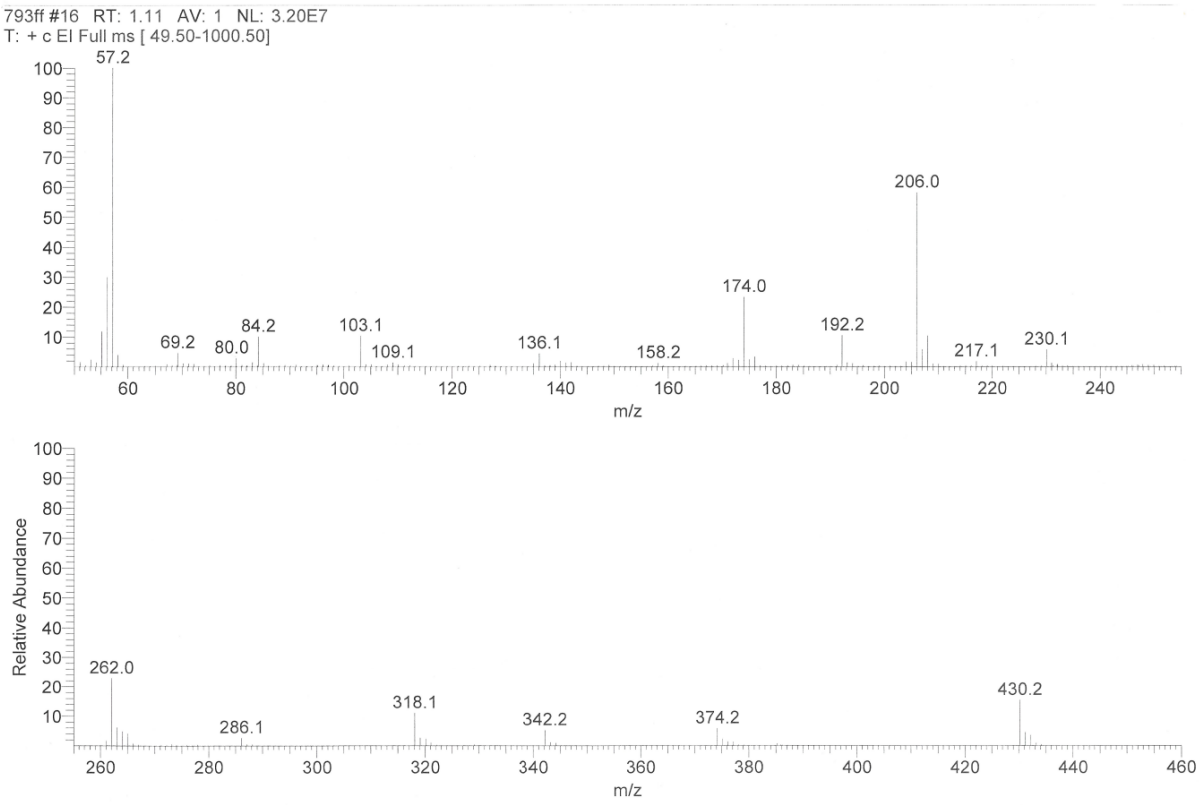
3 ***Figure S12.*** EI(+)-MS (top) of 4-methoxy-*tert*-butylthiobenzene **7** and average value of exact mass
4 (bottom).



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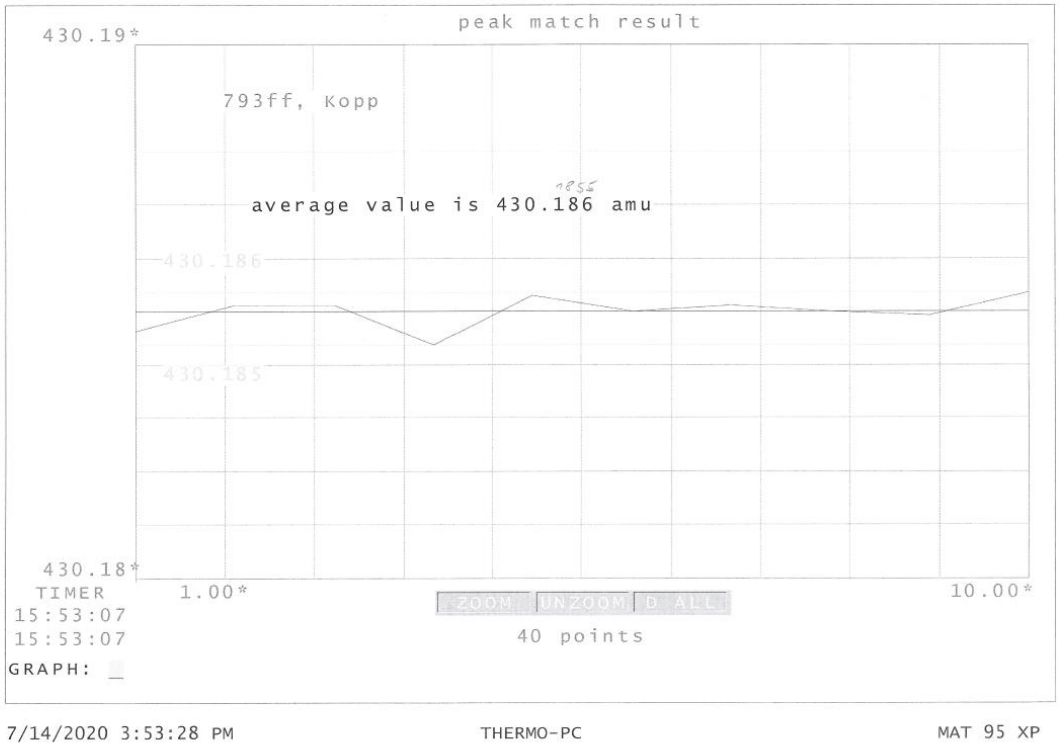

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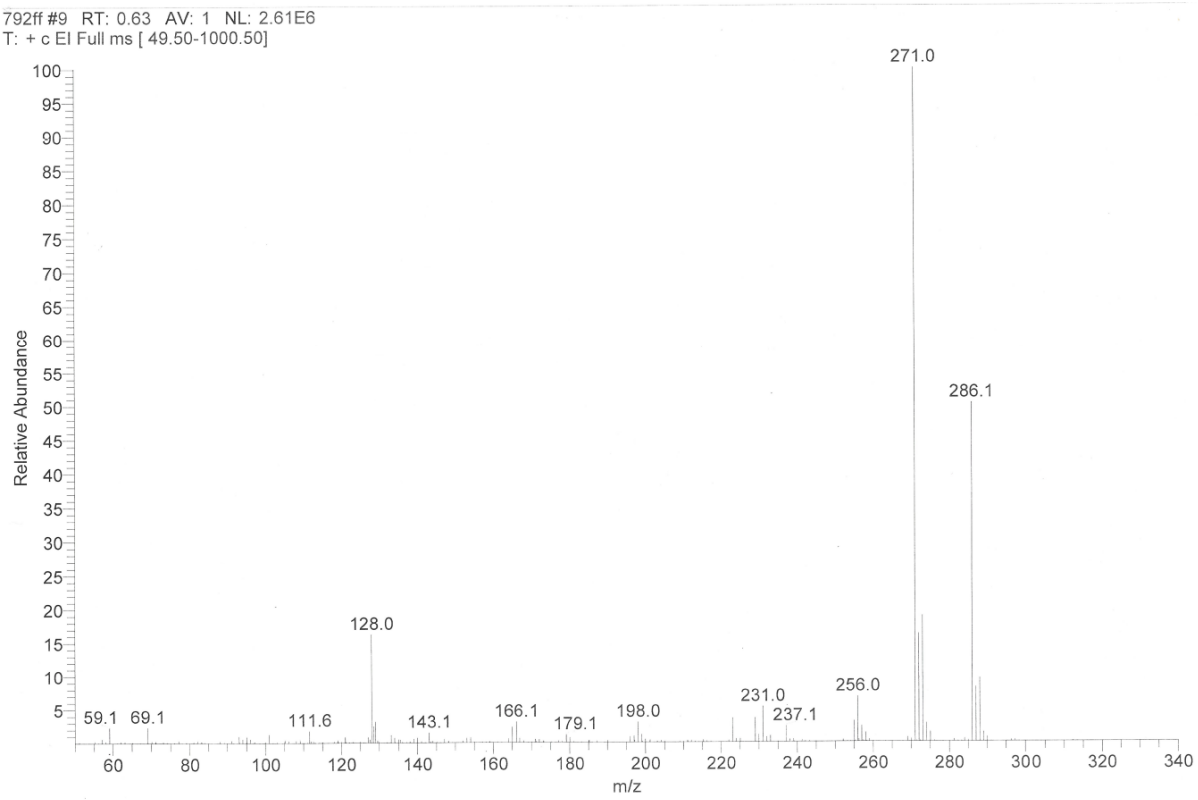
3 ***Figure S13.*** EI(+)-MS (top) of 1,2,4,5-tetrakis(*tert*-butylthio)benzene **5** and average value of exact
4 mass (bottom).



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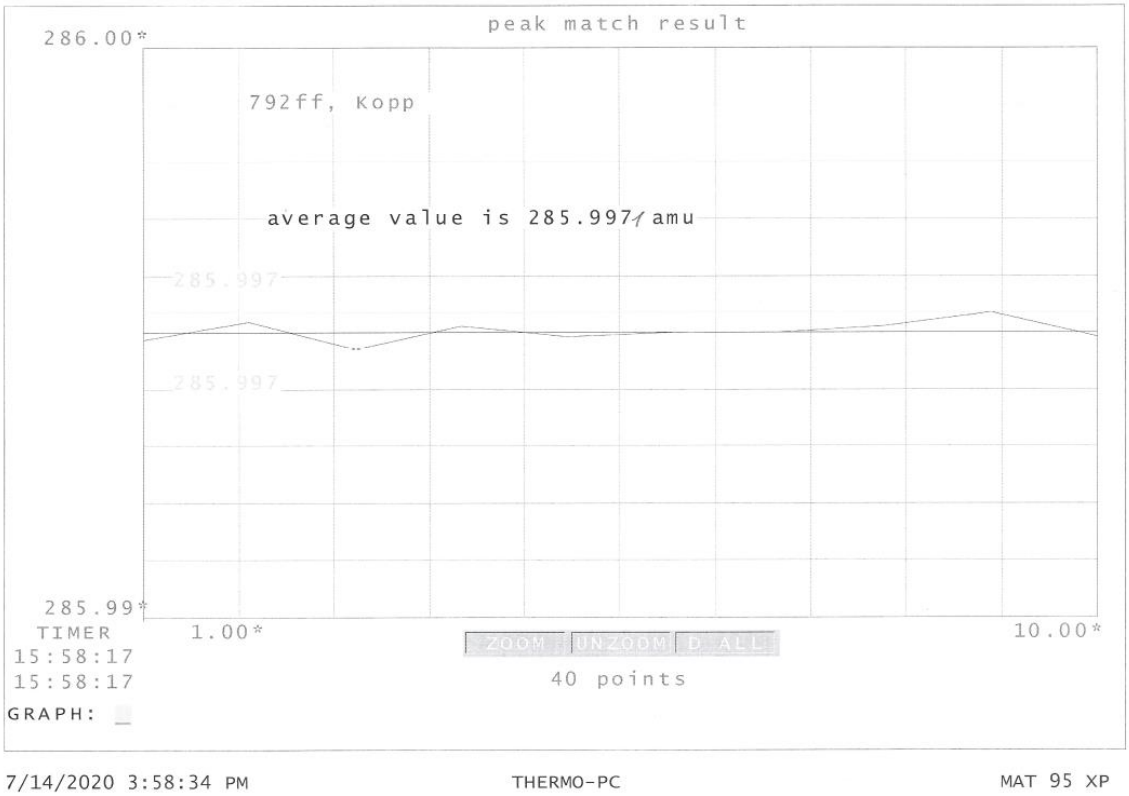

2

3 ***Figure S14.*** EI(+)-MS (top) of **1a** and average value of exact mass (bottom).

4

2. Condition screening

Screening of conditions with other substrates

The analysis of the reaction mixtures was carried out via ^{1}H-NMR, products were identified via comparison of literature values for 1,4-bis(*tert*-butylthio)benzene[4], 4-chlorophenol[5], 4-fluorophenol[6], and 4-(*tert*-butylthio)nitrobenzene[7].

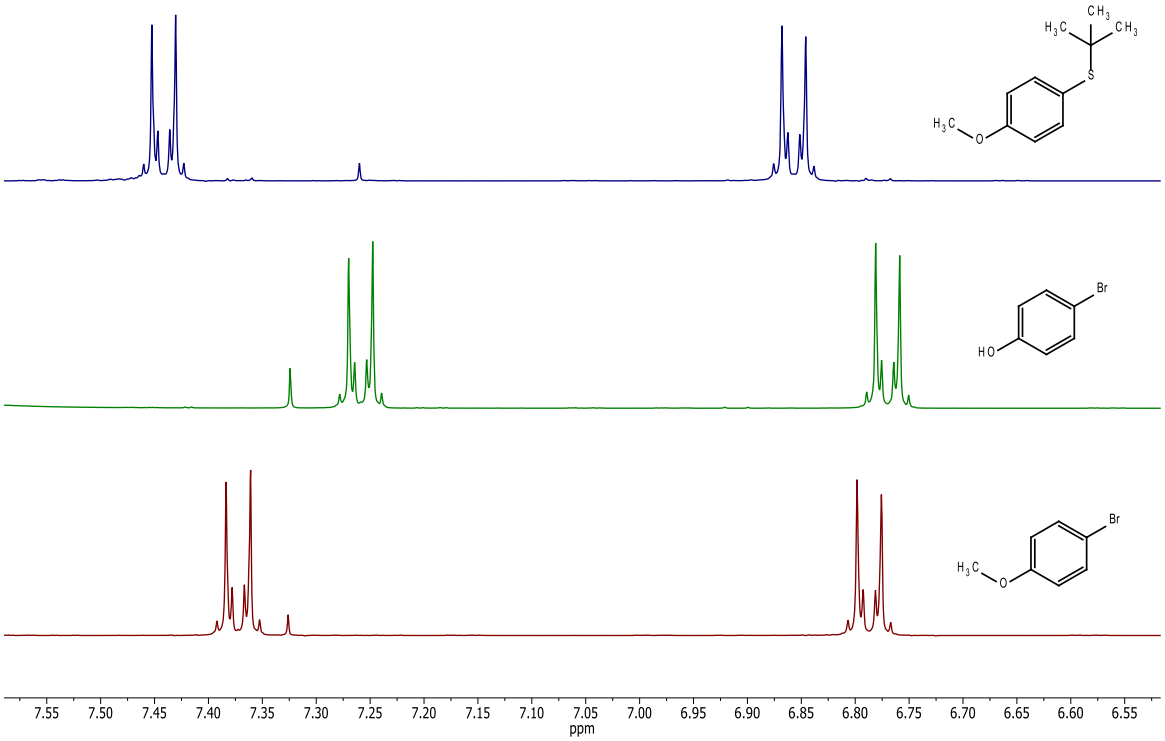

Figure S15. Reference spectra of 4-bromoanisole (bottom), 4-bromophenol (middle) and 4-methoxy-*tert*-butylthiobenzene (top).

Table S1. Reaction conditions.

Reaction No.	Temperature [°C]	ligand	base	Solvent
1	50	Ph_3P	KO^tBu	DMF
2	50	XPhos	KO^tBu	DMF
3	50	Xantphos	KO^tBu	DMF

4	80	Ph_3P	KO^tBu	DMF
5	80	XPhos	KO^tBu	DMF
6	80	Xantphos	KO^tBu	DMF
7	80	dppf	KO^tBu	DMF
8	80	SPhos	KO^tBu	DMF
9	80	BrettPhos	KO^tBu	DMF
10	80	$^nBu_3P$	KO^tBu	DMF
11	80	none	KO^tBu	DMF
12*	80	none	KO^tBu	DMF
13*	80	SPhos	KO^tBu	DMF
14	80	Ph_3P	KO^tBu	^{n}BuOH
15	80	Ph_3P	K_2CO_3	DMF
16	80	Ph_3P	Cs_2CO_3	DMF
17	80	Ph_3P	K_3PO_4	DMF
18**	80	Ph_3P	KO^tBu	DMF
19***	80	Ph_3P	K_2CO_3	DMF
20***	80	Ph_3P	K_3PO_4	DMF

1 *without Pd_2dba_3. **reduced amounts of base to 2.4 eq. ***addition of 10mol% of 18-C-6.

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2.2 ^{1}H-NMR data

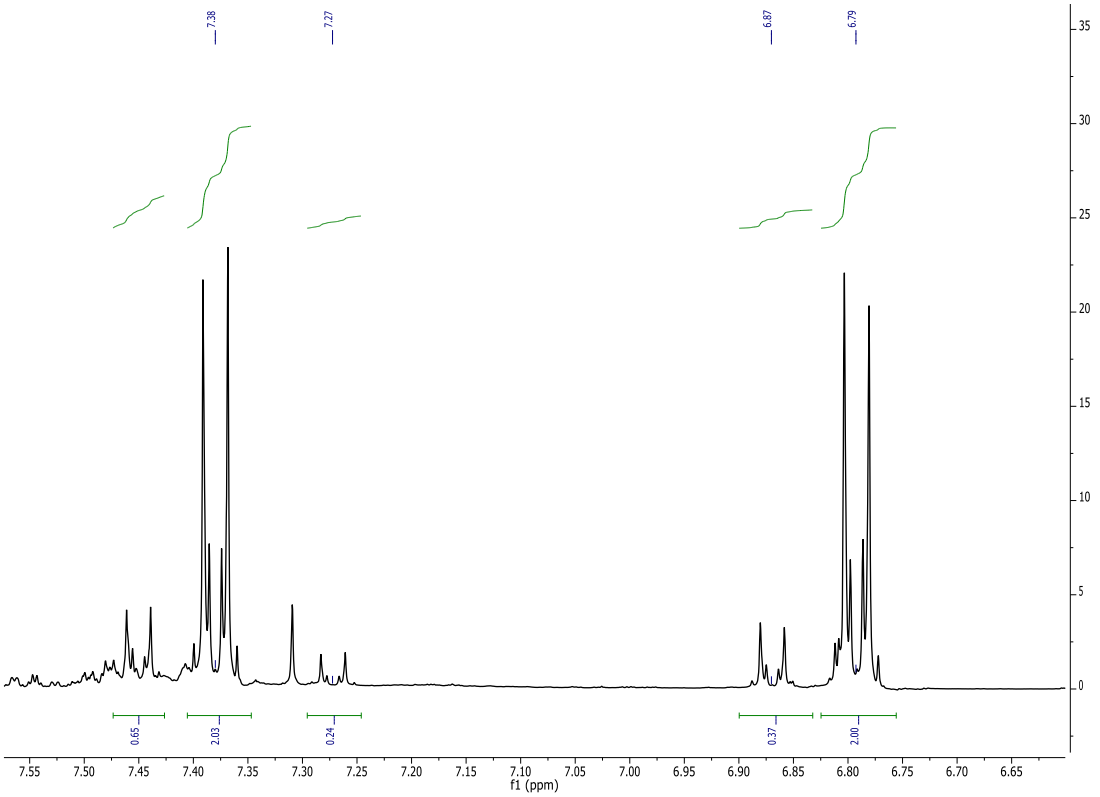


Figure S16. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 1.

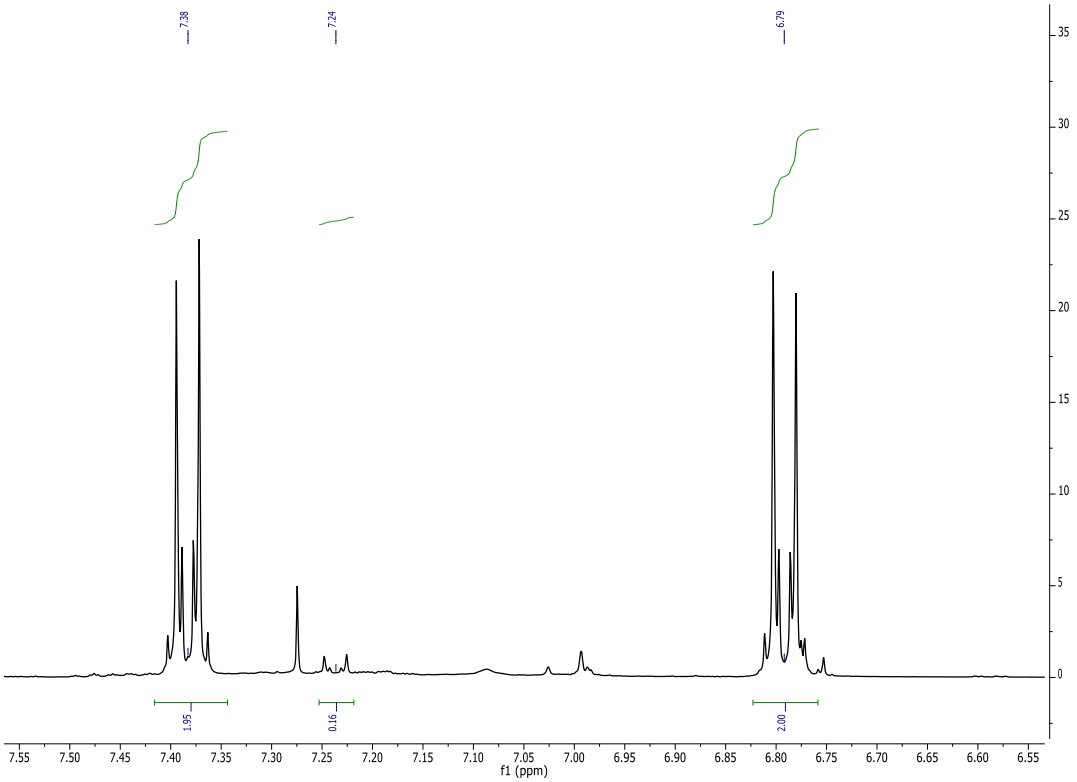


Figure S17. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of Reaction 2.

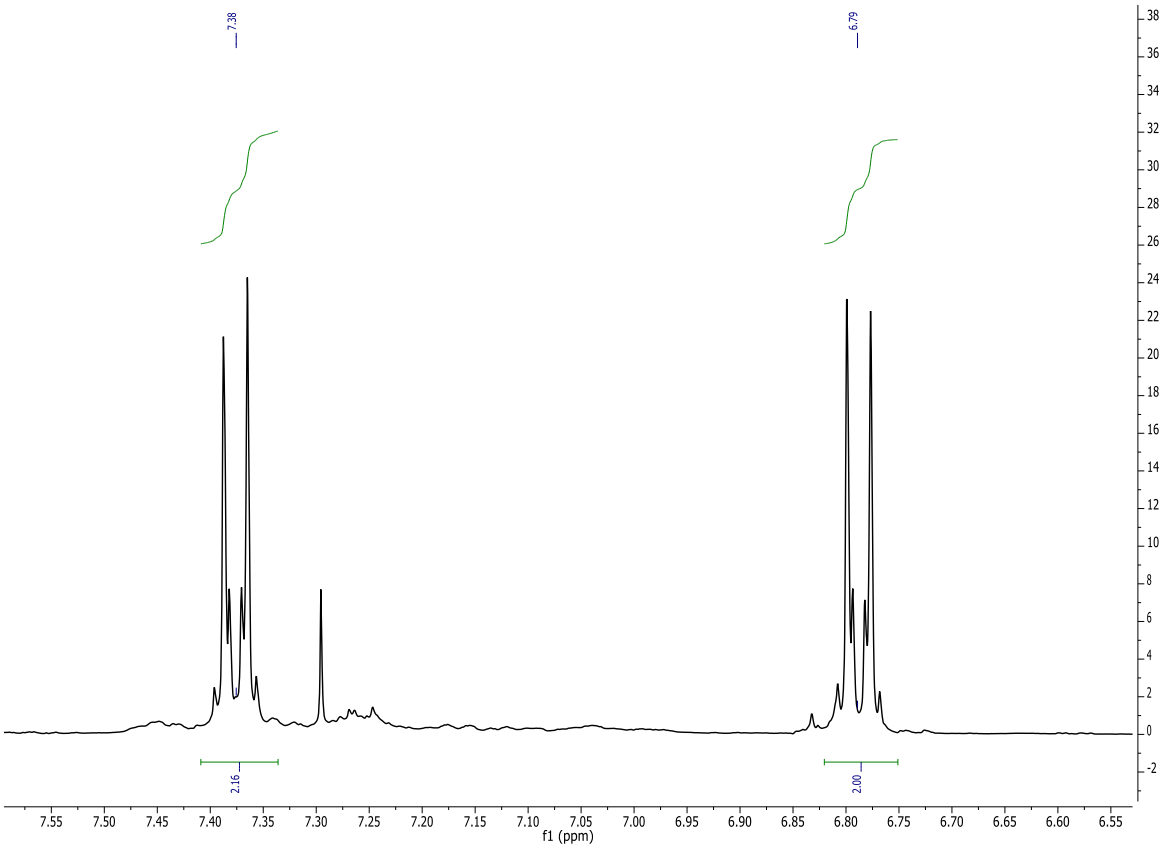


Figure S18. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 3.

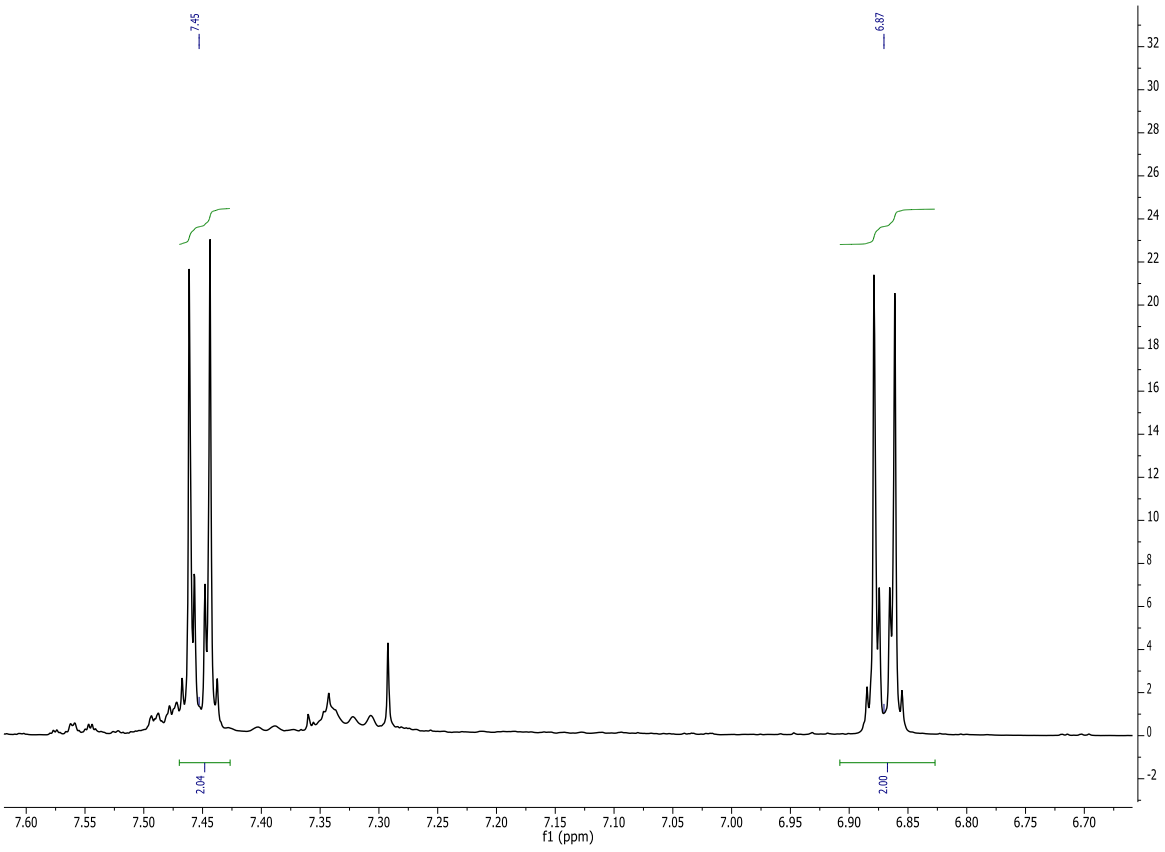


Figure S19. ^{1}H-NMR (500 MHz, 298 K, $CDCl_3$) of reaction 4.

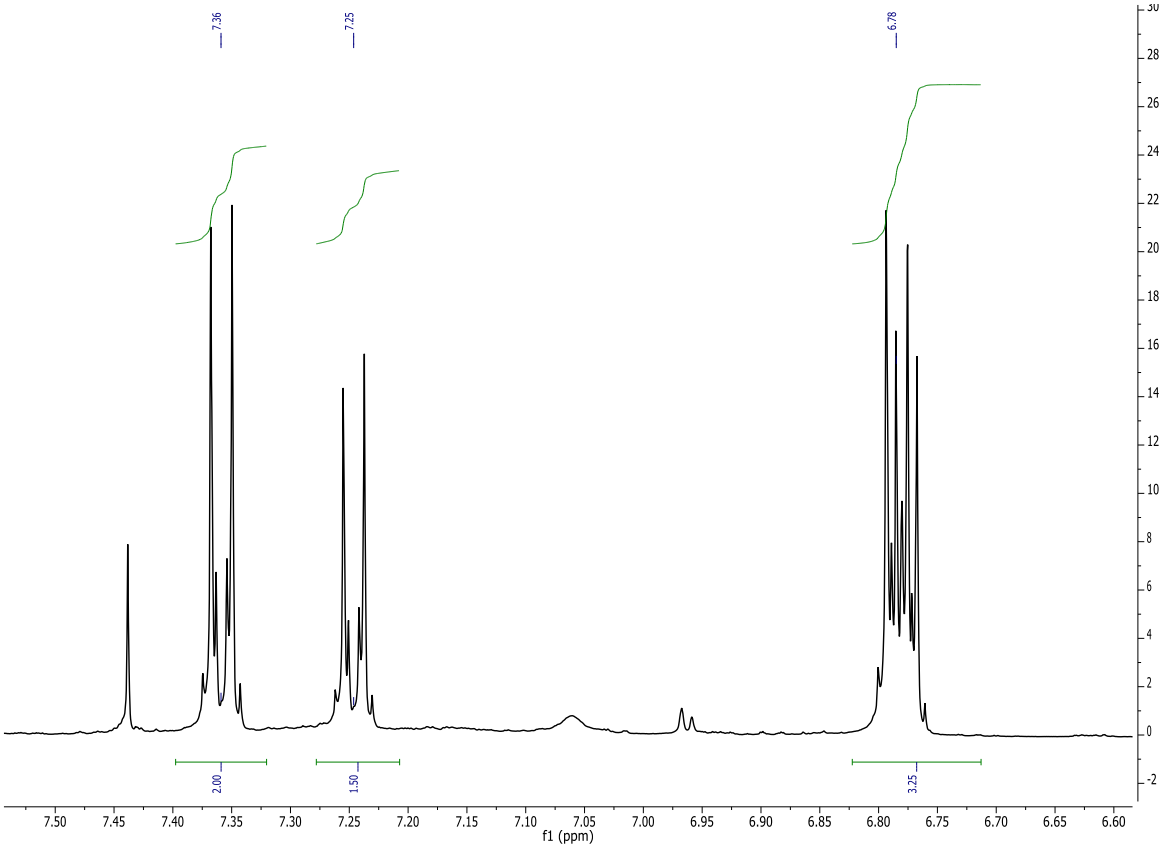


Figure S20. ^{1}H-NMR (500 MHz, 298 K, $CDCl_3$) of reaction 5.

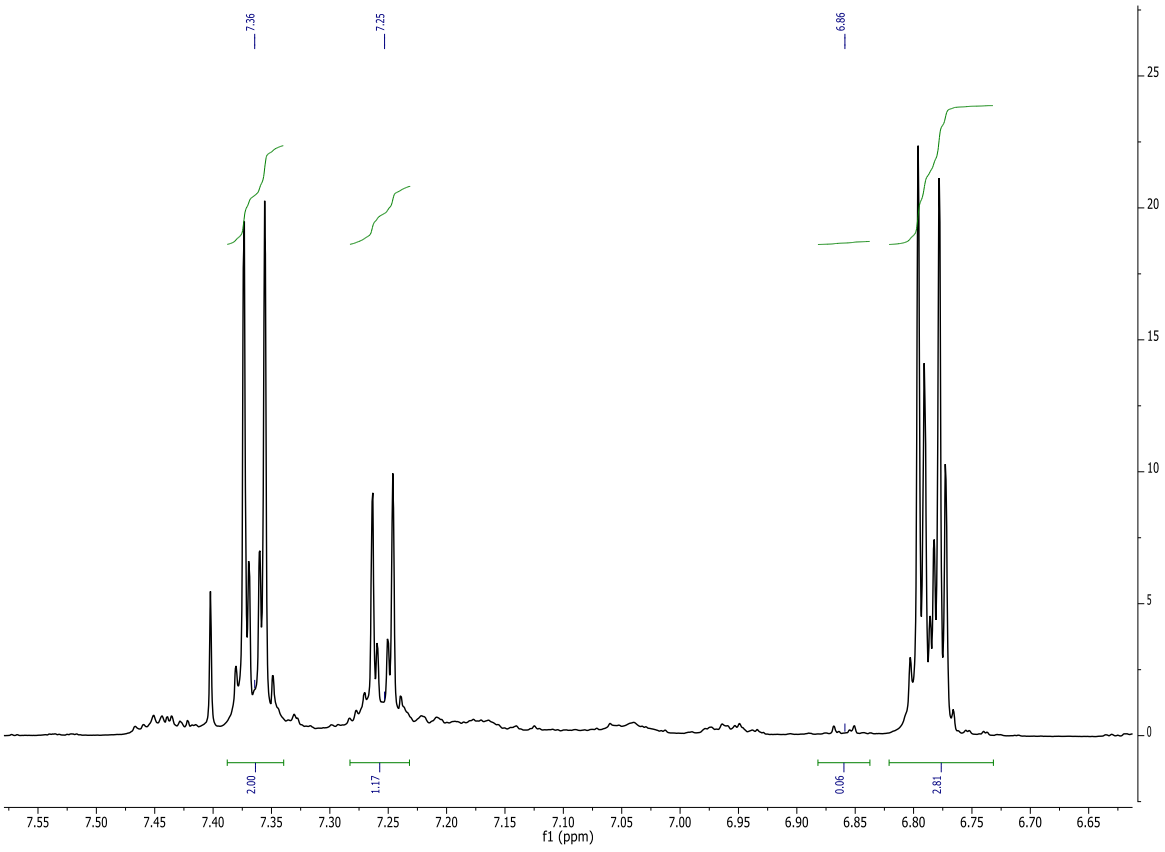
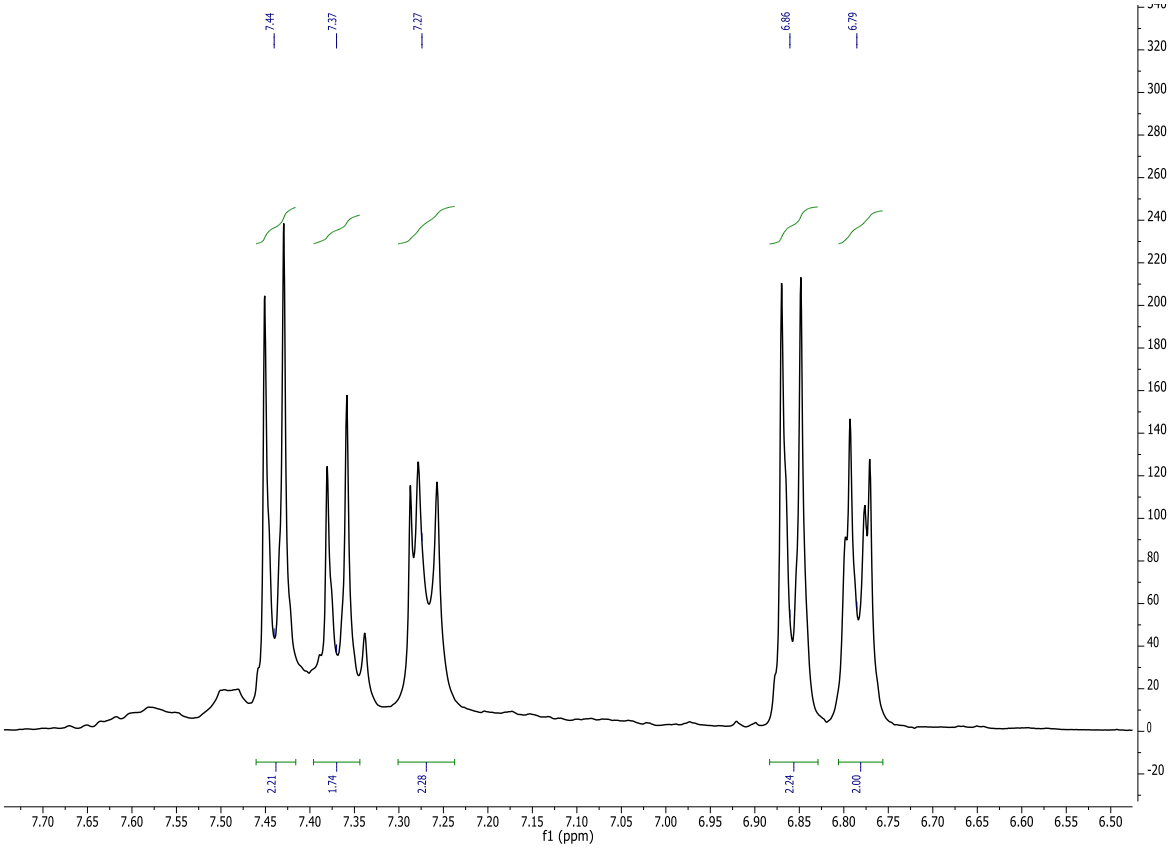


Figure S21. ^{1}H-NMR (500 MHz, 298 K, $CDCl_3$) of reaction 6.



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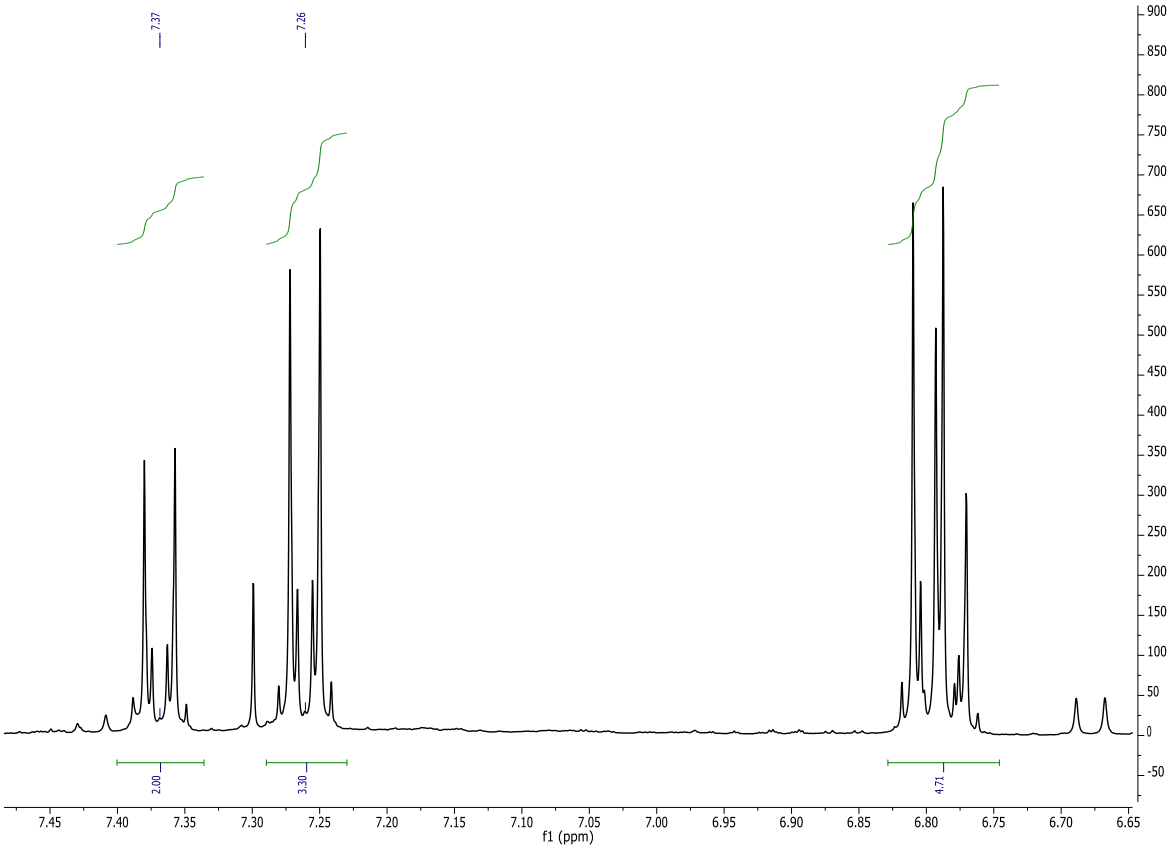
2 ***Figure S22.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 7.



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4 ***Figure S23.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 8.

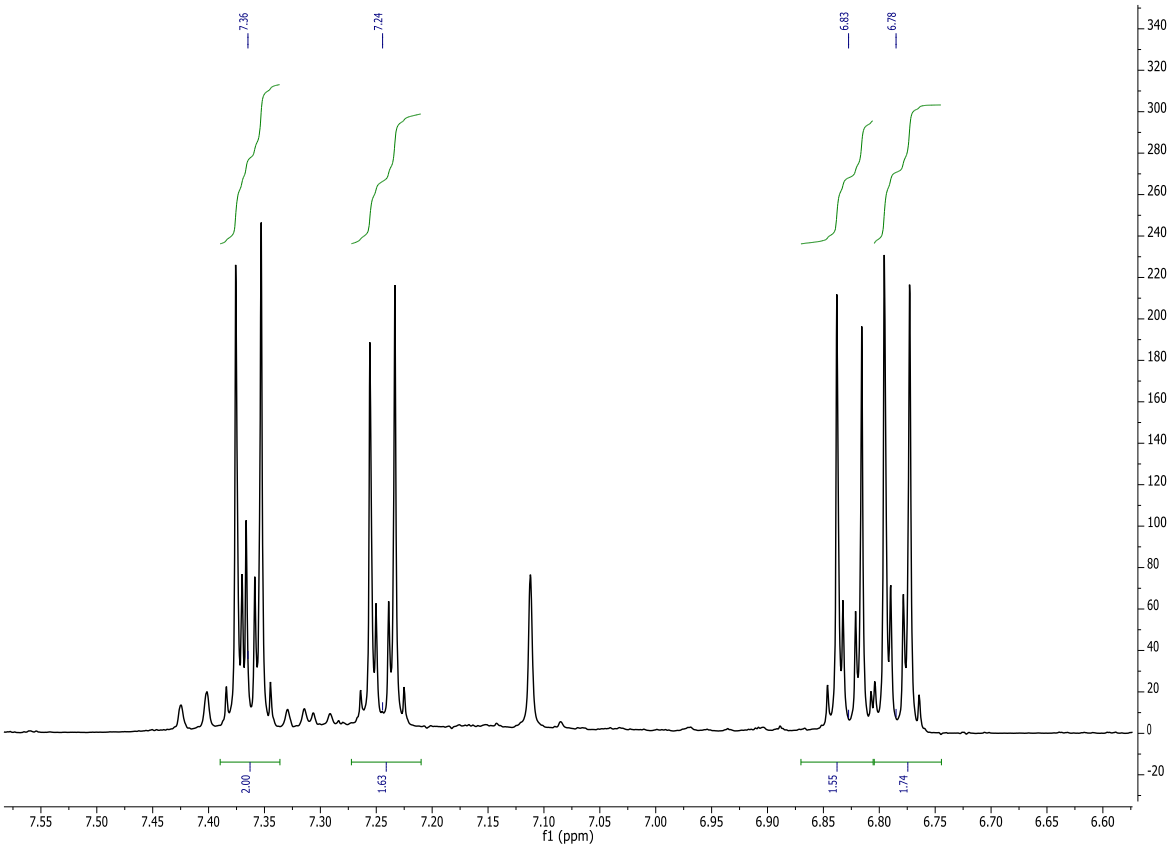


Figure S24. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 9.

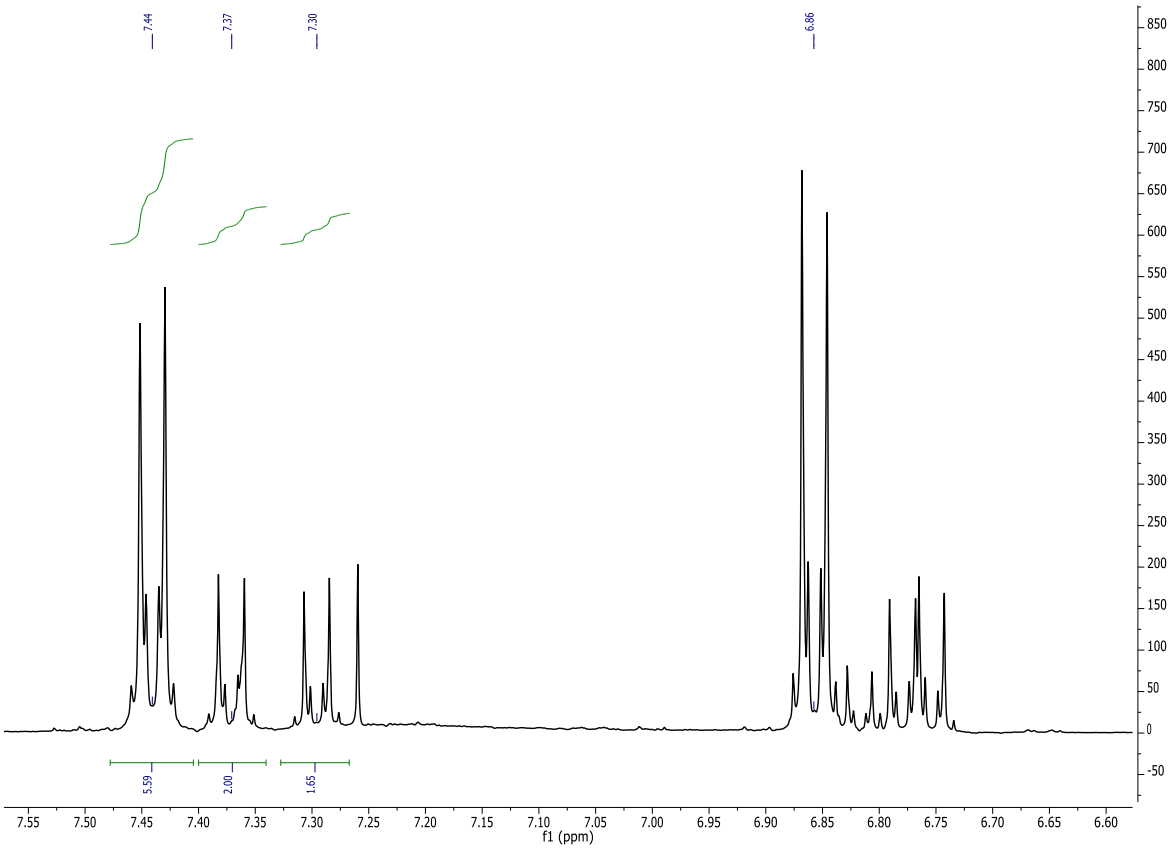
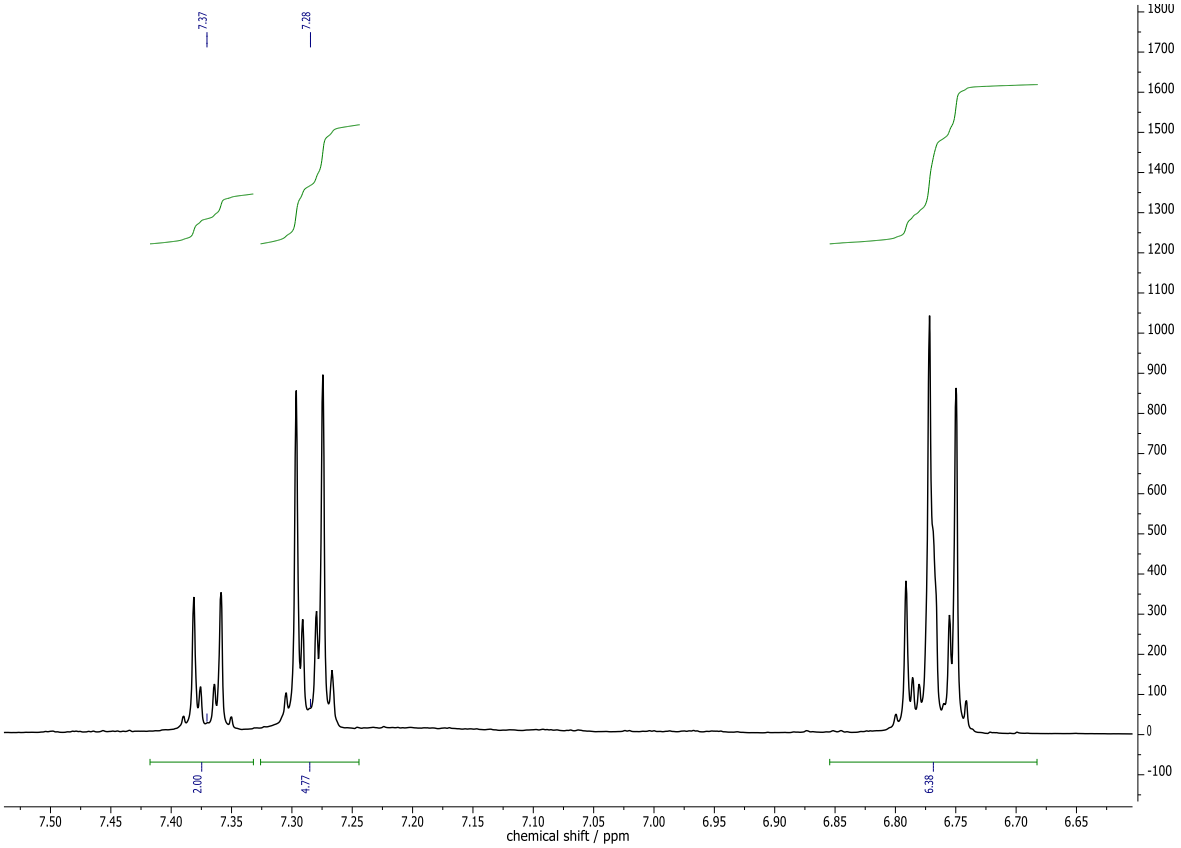


Figure S25. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 10.



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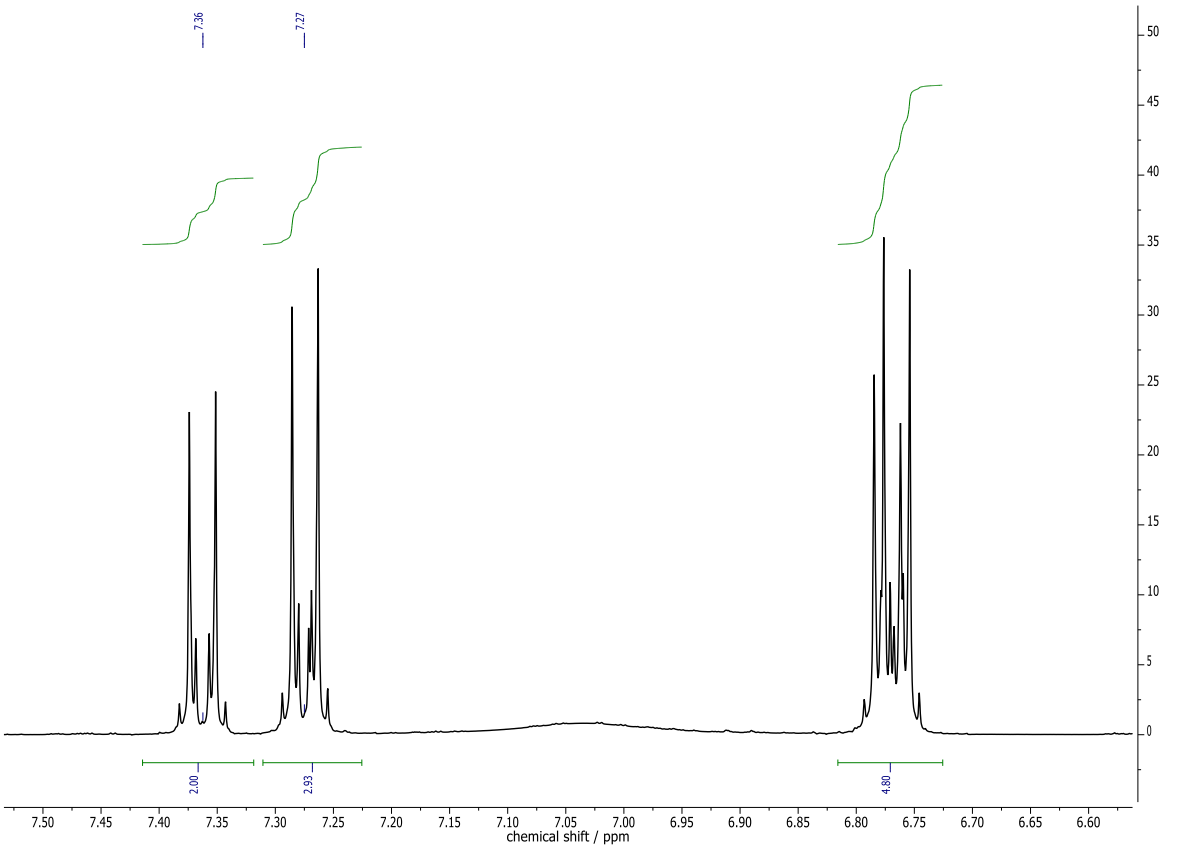
2 ***Figure S26.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 11.



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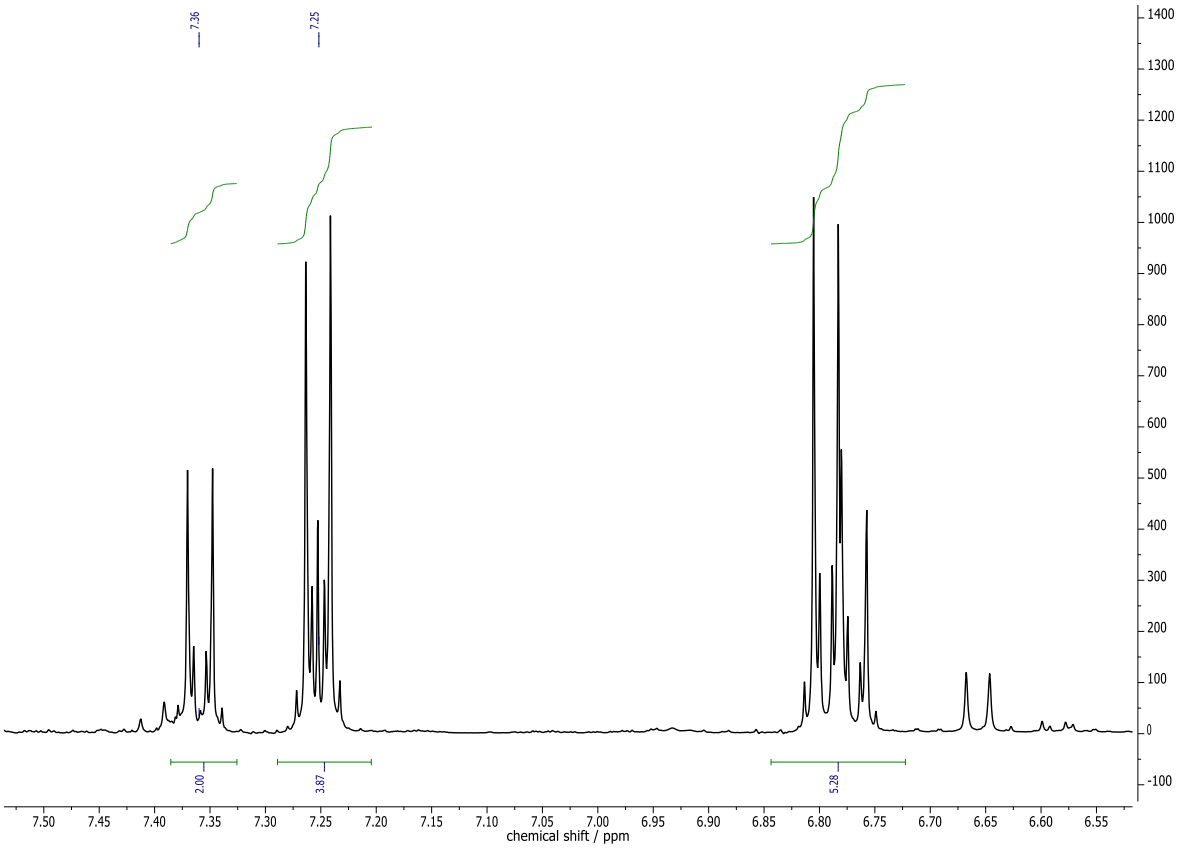
4 ***Figure S27.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 12.



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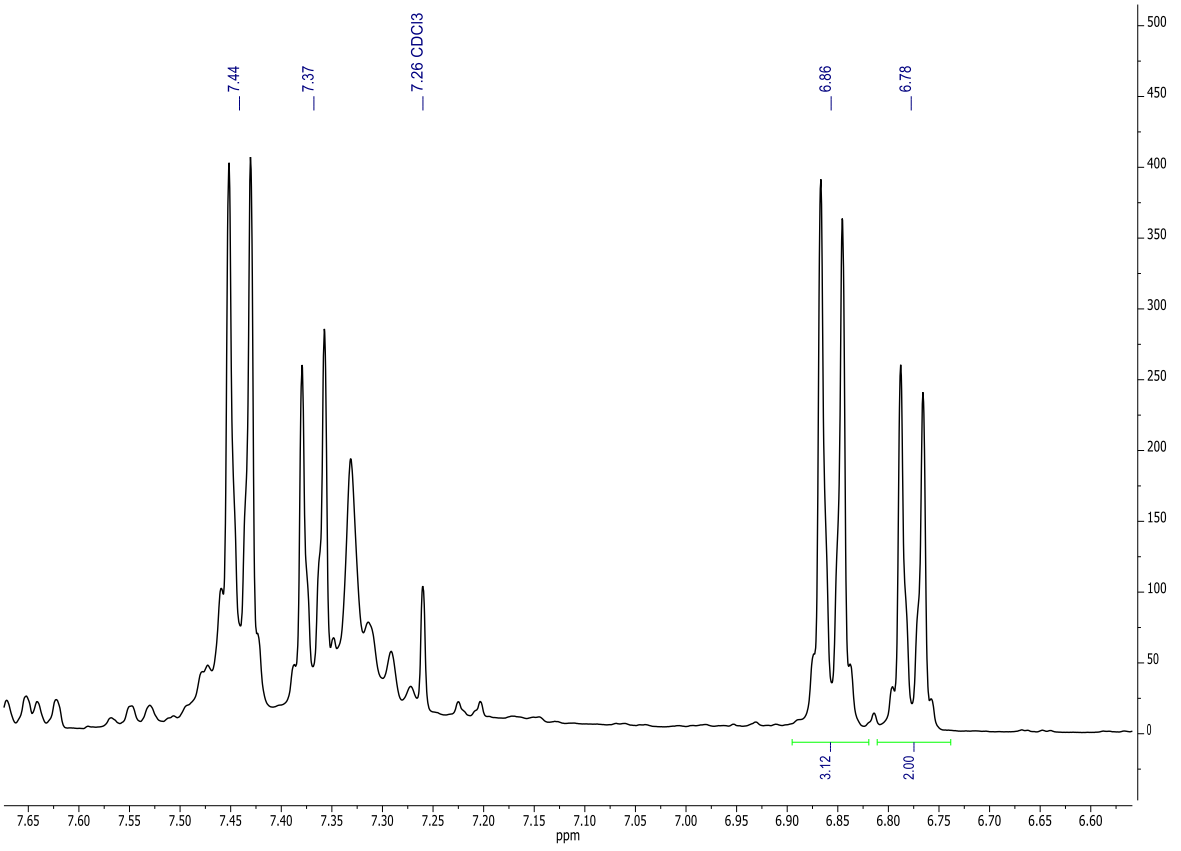
2 ***Figure S28.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 13.



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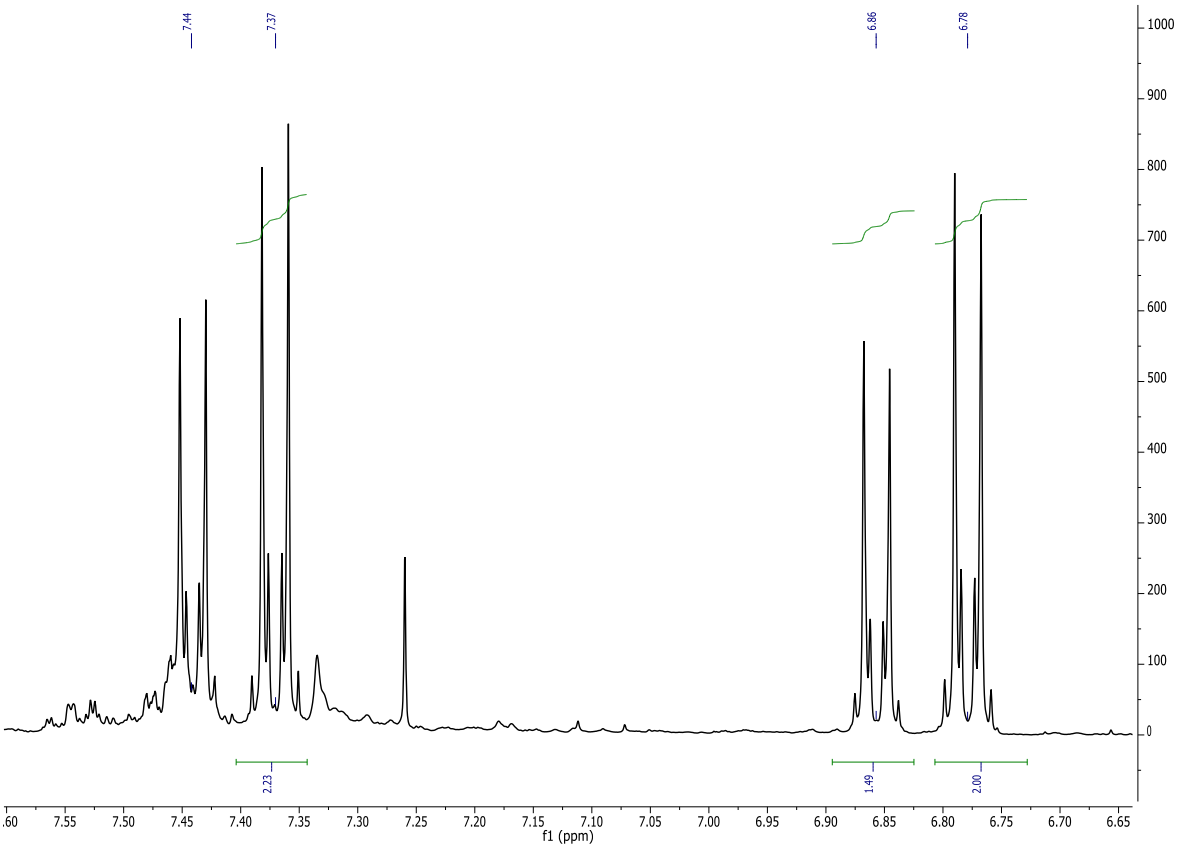
4 ***Figure S29.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 14.



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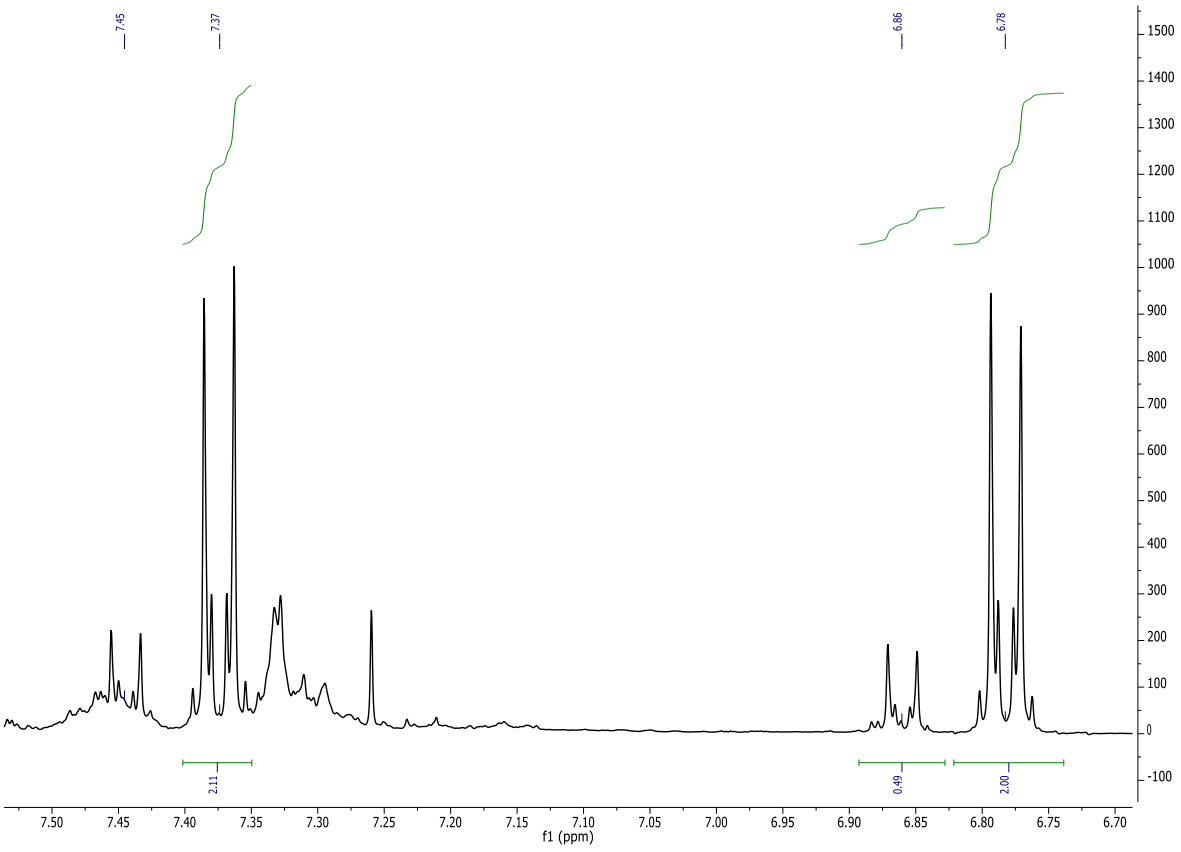
2 ***Figure S30*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 15.



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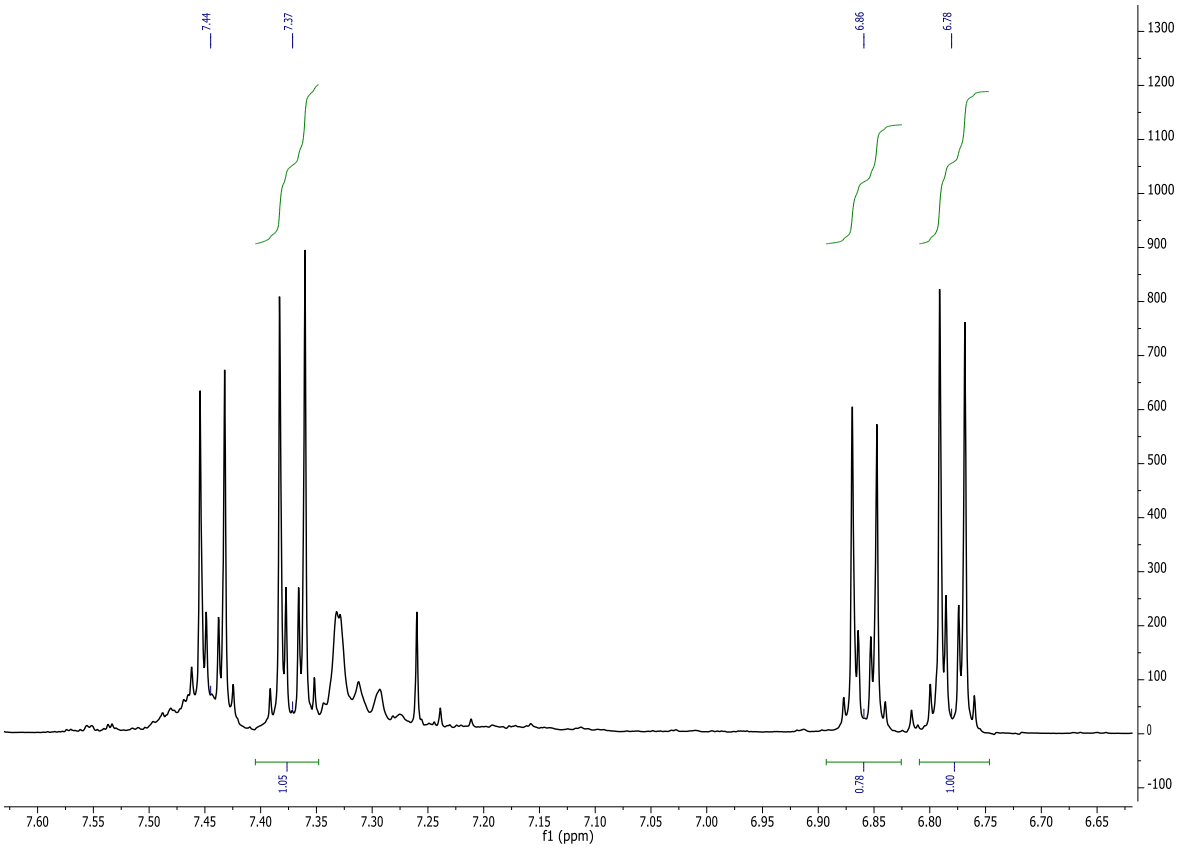
4 ***Figure S31.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 16.



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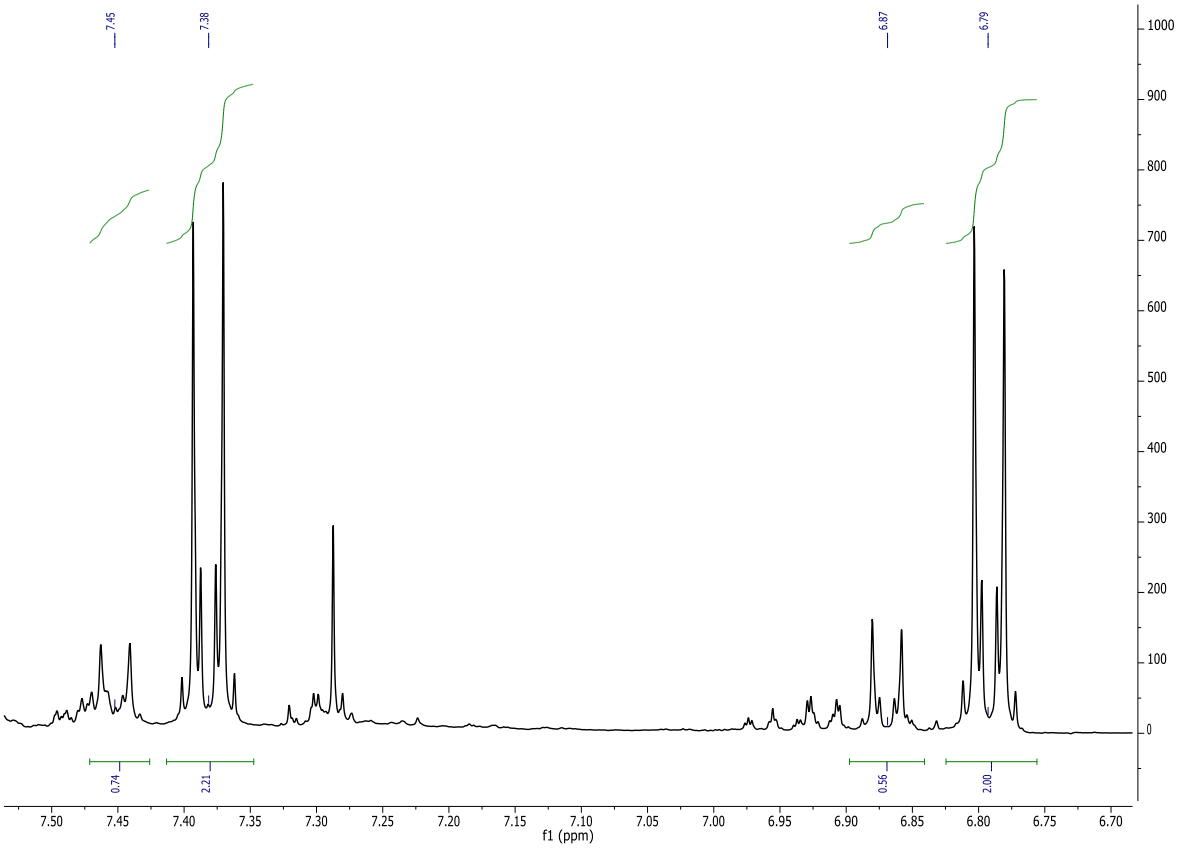
2 ***Figure S32.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 17.



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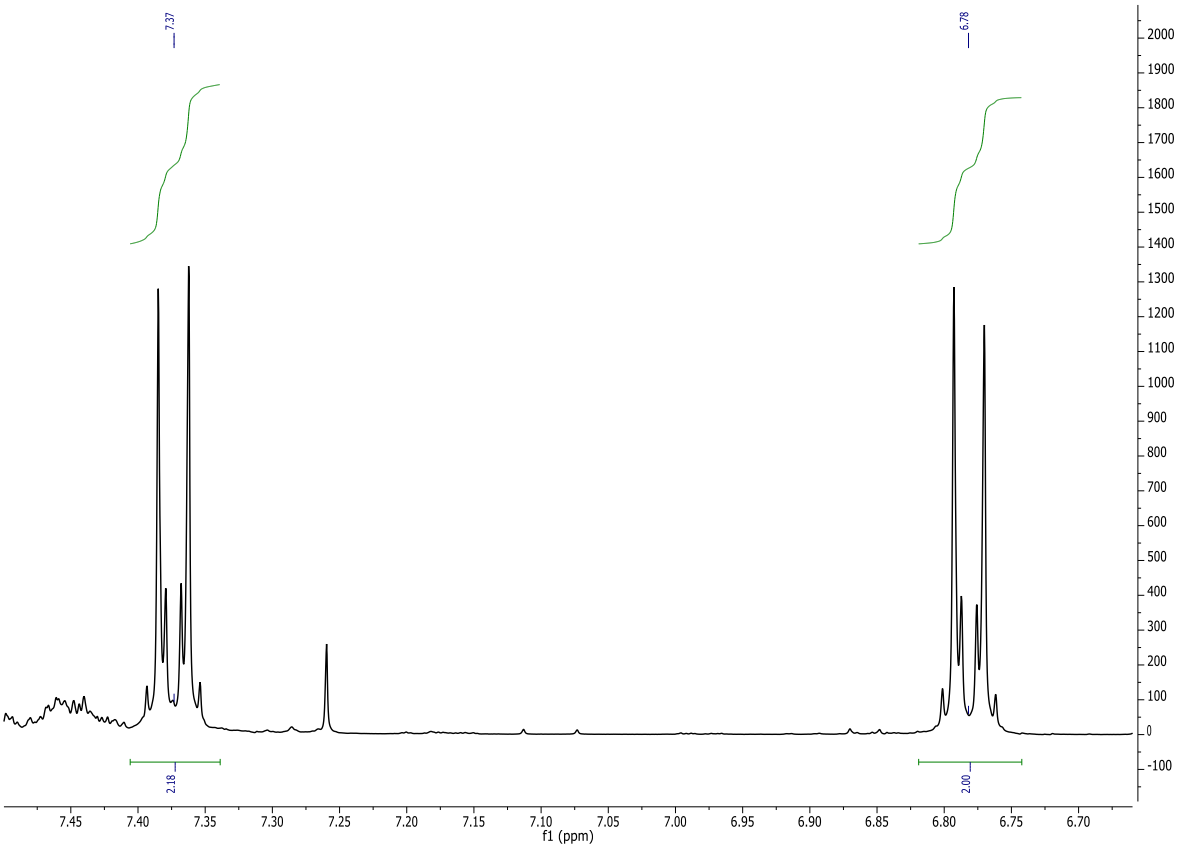
4 ***Figure S33.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 18.



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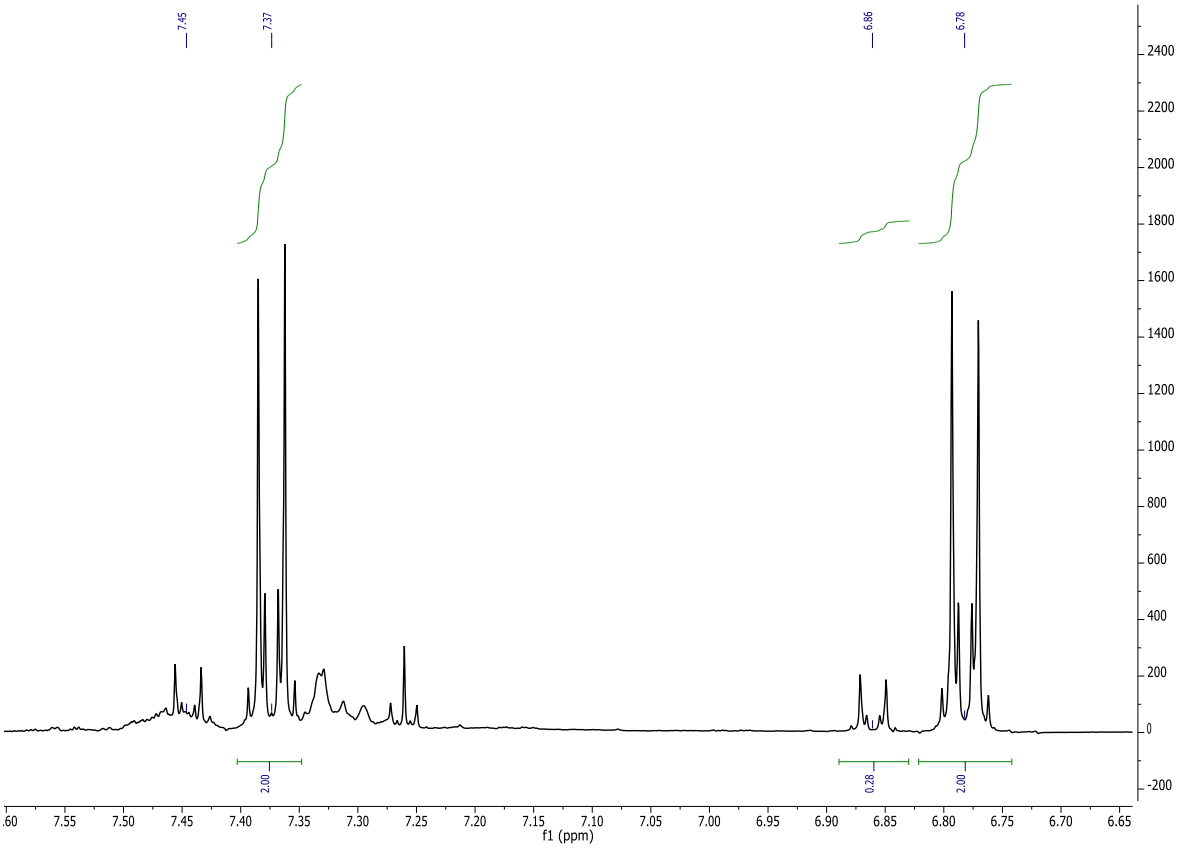
2 ***Figure S34.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 19.



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4 ***Figure S35.*** ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of reaction 20.

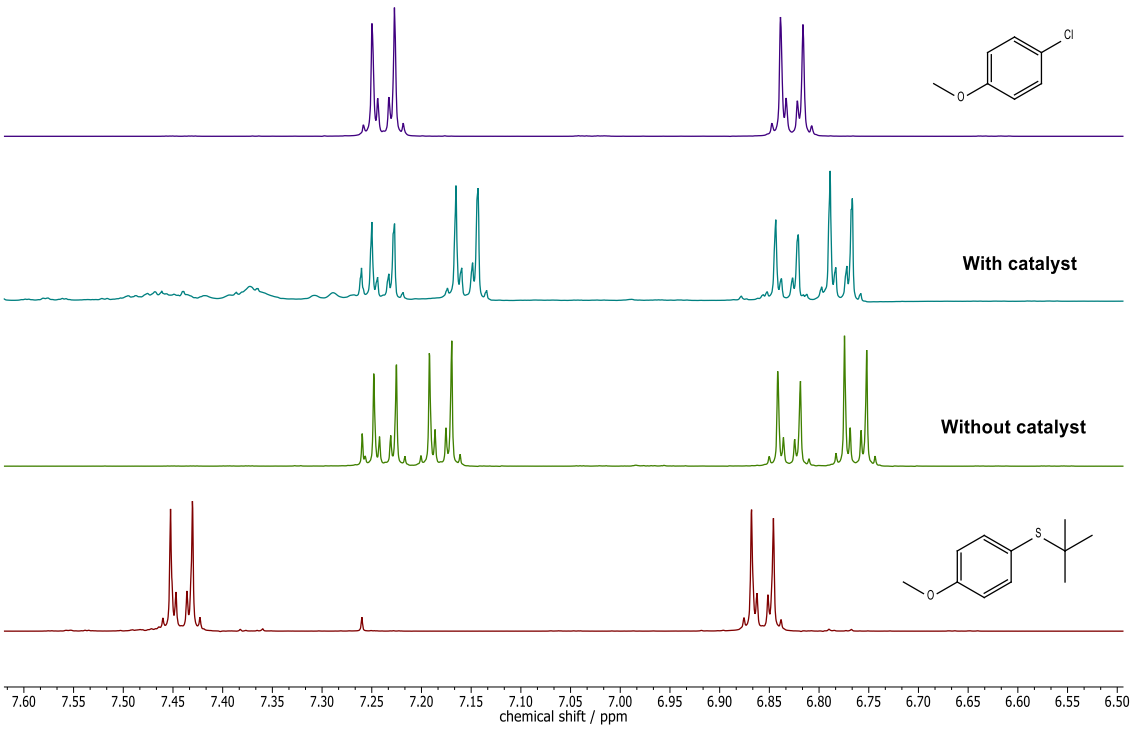

Figure S36. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reactions with 4-chloroanisole.

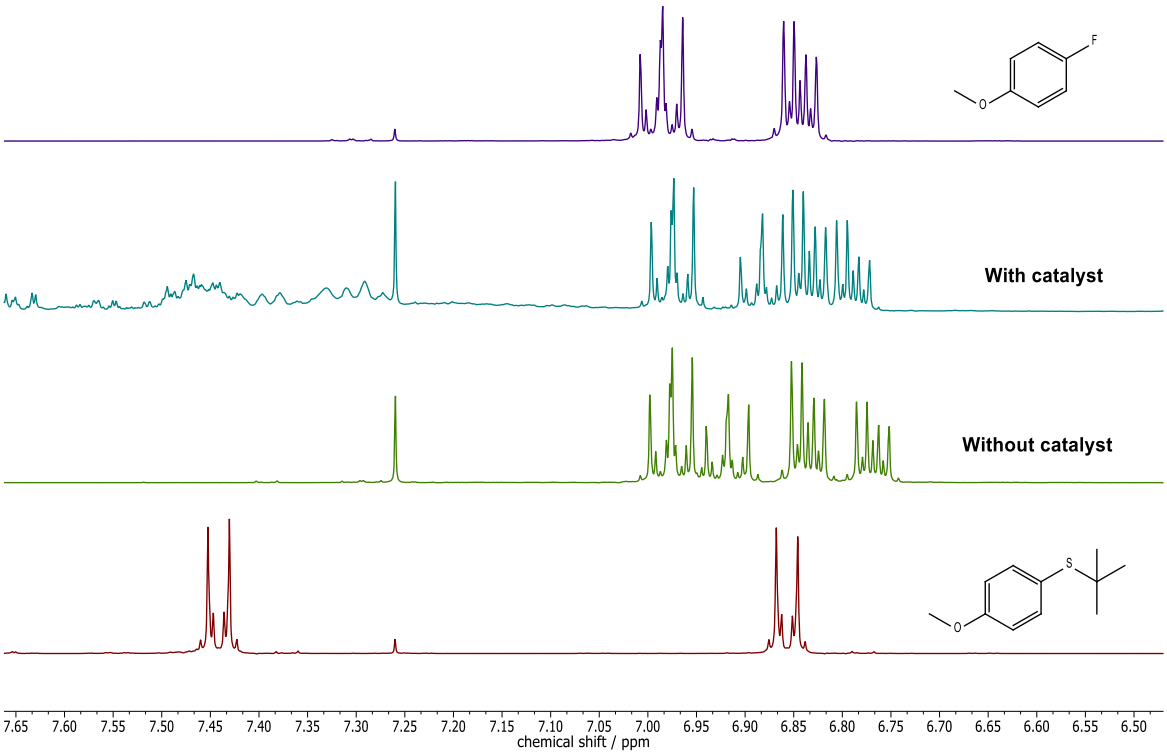

Figure S37. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reactions with 4-fluoroanisole.

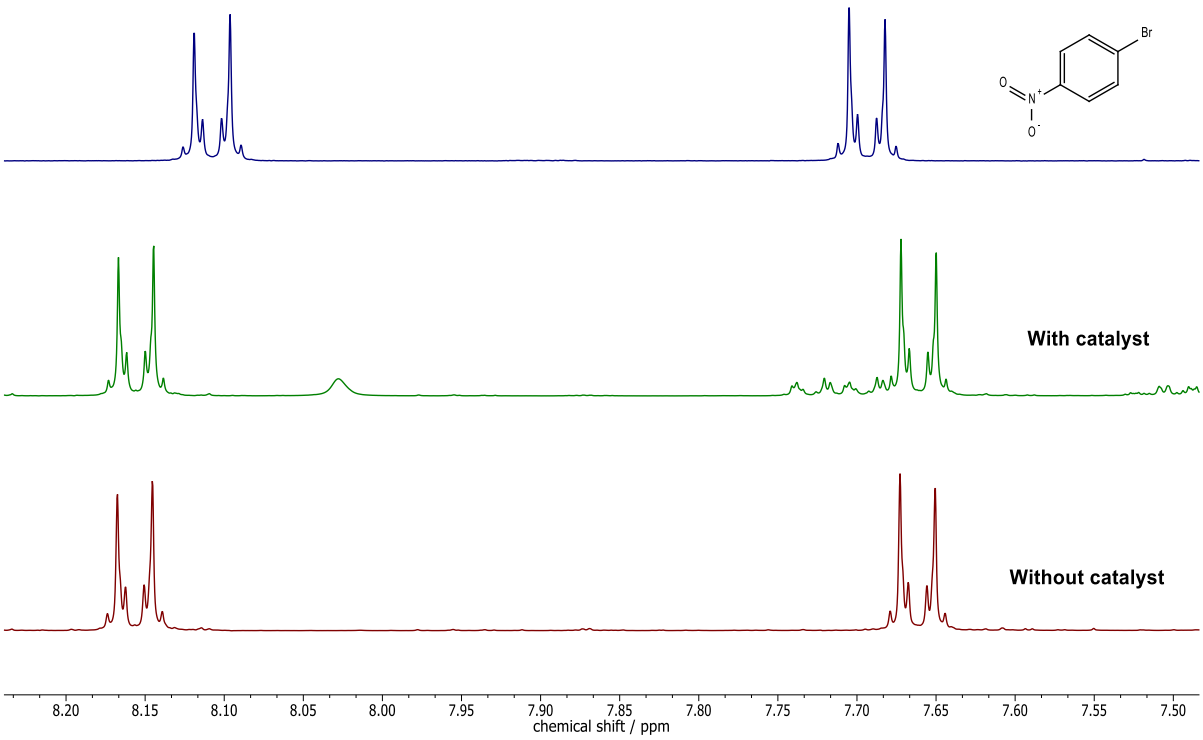

Figure S38. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reactions with 4-nitrobromobenzene

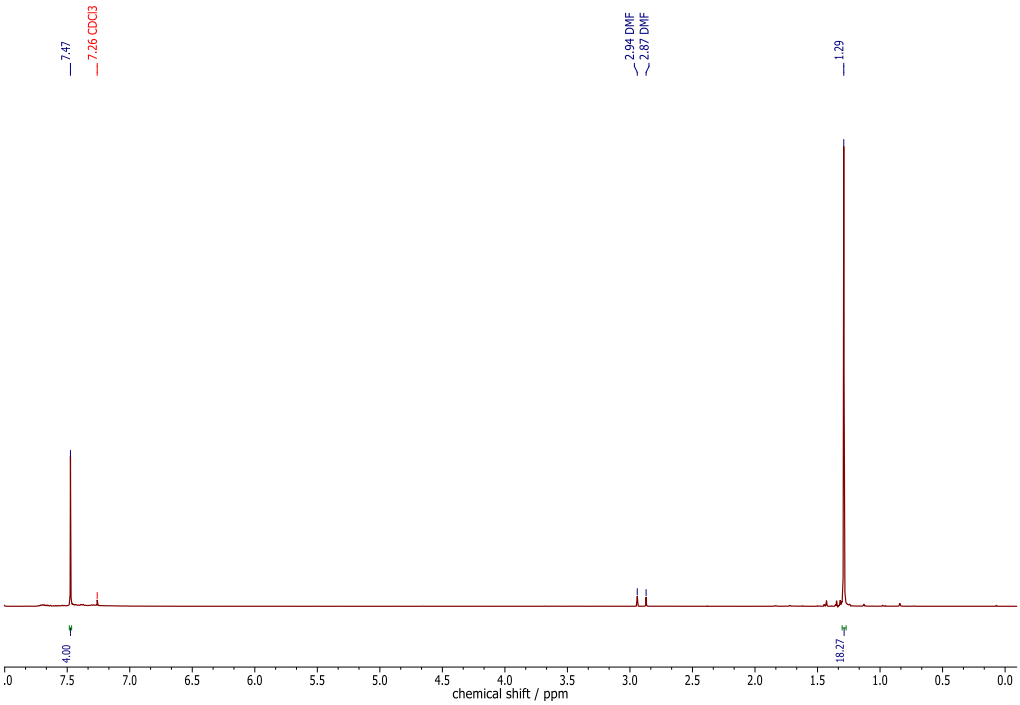

Figure S39. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reaction with 1,4-diiodobenzene at 50 °C.

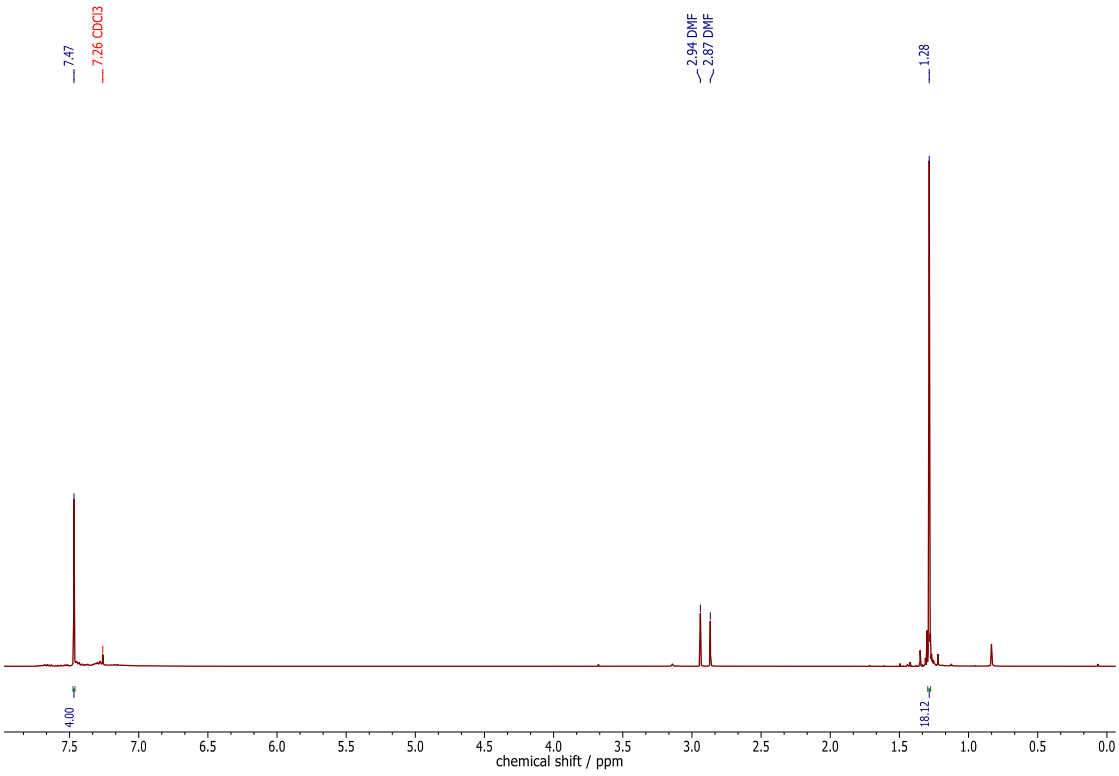

Figure S40. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) of the reaction with 1,4-diiodobenzene at 80 °C.

3 Literature

(1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I.; Gan, R.; Apiezon, H. NMR Chemical Shifts of Trace Impurities : Common Laboratory Solvents , Organics , and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.

(2) Wang, L.; Zhou, W.-Y.; Chen, S.-C.; He, M.-Y.; Chen, Q. A Highly Efficient Palladium-Catalyzed One-Pot Synthesis of Unsymmetrical Aryl Alkyl Thioethers under Mild Conditions in Water. *Adv. Synth. Catal.* **2012**, *354*, 839–845.

(3) Reddy, T. J.; Iwama, T.; Halpern, H. J.; Rawal, V. H. General Synthesis of Persistent Trityl Radicals for EPR Imaging of Biological Systems. *J. Org. Chem.* **2002**, 4635–4639.

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