Supporting Information

An Additive-Free, Base-Catalyzed Protodesilylation of Organosilanes

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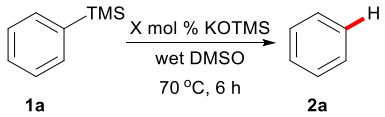
Contents

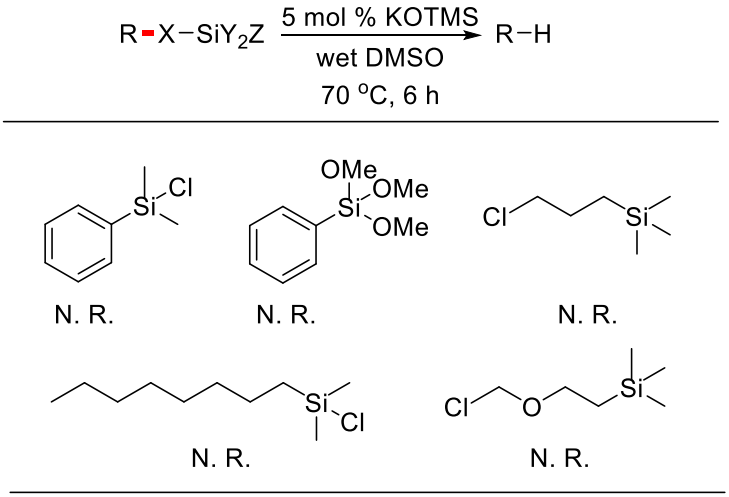
1. Optimization of the reaction conditions (Table S1) [a]



Entry	[Cat.]	Additive	Base (mol %)	Solvent	t/h	Yield (%)[b]
1[c]	KOTMS	18-Crown-6	5	EtOH	6	0
2[c]	KOTMS	18-Crown-6	5	THF	6	0
3[c]	KOTMS	18-Crown-6	5	MTBE	6	0
4[c]	KOTMS	18-Crown-6	5	PhMe	6	0
5[c]	KOTMS	18-Crown-6	5	DCM	6	0
6[c]	KOTMS	18-Crown-6	5	*n*-hexane	6	0
7[c]	KO*t*Bu	18-Crown-6	5	DMSO	6	80
8[d]	KOTMS	0.5 equiv. H_2O	5	DMSO	6	99
9[d]	KOTMS	1.0 equiv. H_2O	5	DMSO	6	99
10[d]	KOTMS	3.0 equiv. H_2O	5	DMSO	6	99
11[d]	KOTMS	5.0 equiv. H_2O	5	DMSO	6	99
12[d]	KOTMS	10 equiv. H_2O	5	DMSO	6	99
13[d]	KOTMS	20 equiv. H_2O	5	DMSO	6	99
14	KOTMS	--	5	H_2O	6	0
15[e]	KOTMS	*n*Bu_4NCl	5	DMSO	6	6
16[f]	KOTMS	*n*Bu_4NCl	5	DMSO	6	8
17[e]	KOTMS	*n*Bu_4NCl	5	THF	6	<1
18[f]	KOTMS	*n*Bu_4NCl	5	THF	6	<1
19	KOTMS	--	5	DMSO	0.5	49
20	KOTMS	--	5	DMSO	1	90

[a]Reaction conditions: PhTMS **1a** (1.0 mmol), KOTMS (50 μmol, 5 mol %), solvent (2.0 mL), at 70 °C, 6 h. [b]Determined by GC and GC-MS analysis. [c]18-Crown-6 (50 μmol, 5 mol %). [d] Anhydrous DMSO (2.0 mL). [e]At 25 °C, *n*Bu_4NCl (50 μmol, 5 mol %). [f]At 70 °C, *n*Bu_4NCl (50 μmol, 5 mol %).

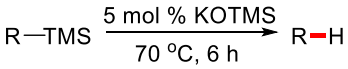
2. The unreactive substrates



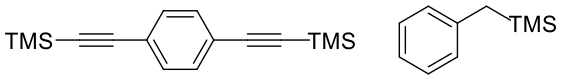
Reaction conditions: Silane (1.0 mmol), KOTMS (50 μmol, 5 mol %), wet DMSO (2.0 mL), at 70 °C, 6 h; Determined by GC and GC-MS analysis.

3. Mechanistic Studies

3.1 The changes of PH on the protodesilylation process[a]



Substrate	PKa[b]	PKa[c]	Yield (%)[d]
3p	11.0	10.9	88
5a	11.0	11.1	99



3p **5a**

[a]Reaction conditions: RTMS (1.0 mmol), KOTMS (50 μmol, 5 mol %), wet DMSO, at 70 °C, 6 h. [b]Before reaction, at 17 °C. [c]After reaction, at 17 °C. [d]Determined by GC analysis.

3.2 Deuterium experiment

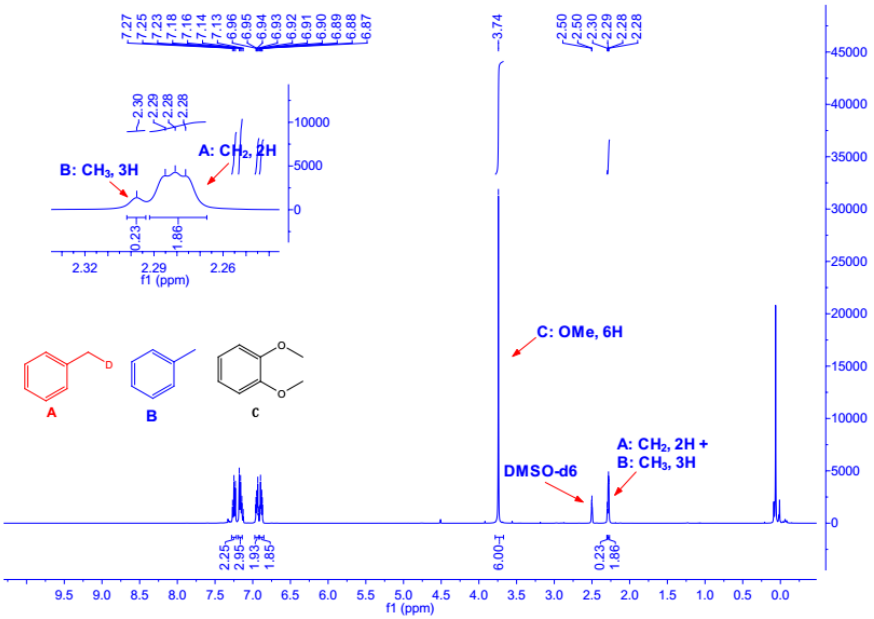
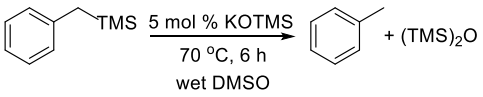


Figure S1. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **6a'**

3.3 The ^{1}H NMR experiment



Entry	Time	PhMe (%)	$(TMS)_2O$ (%)
1	10 min	98	42
2	30 min	99	42
3	1 h	99	41
4	4 h	99	38

Reaction conditions: **5a** (0.5 mmol), KOTMS (5 mol %), wet DMSO (2 mL), at 70 °C, 6 h. Yield is determined by GC analysis.

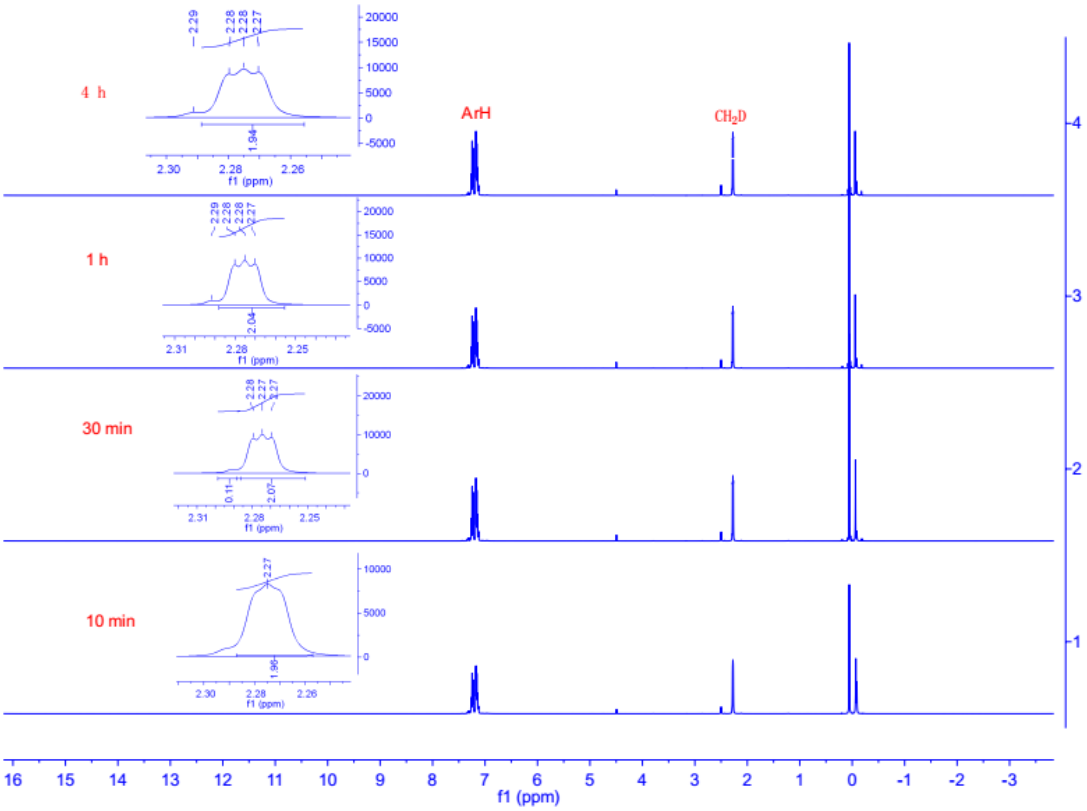


Figure S2. The ^{1}H NMR reaction profile for **5a** in DMSO-d_6 and D_2O

Reaction conditions: **5a** (0.5 mmol), KOTMS (5 mol %), anh.DMSO-d_6 (0.5 mL), D_2O (0.5 mmol, 1.0 equiv.), at 70 °C.

3.4 The ^{29}Si NMR experiment

Silane	^{29}Si NMR lit. (δ)	^{29}Si NMR (δ)
PhTMS	-4.7	-4.3
KOTMS	-17.5	-17.5
TMS_2O	7.4	7.5
TMSOH	10.5	--

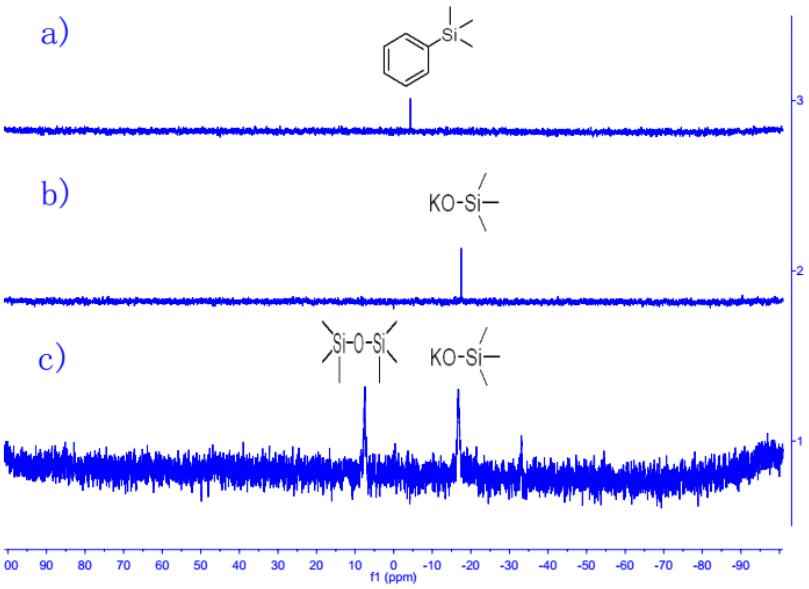


Figure S3. The ^{29}Si NMR reaction profile for **1a** in wet DMSO-d_6

Reaction conditions: trimethylphenylsilane **1a** (0.2 mmol), KOTMS (0.2 mmol, 1.0 equiv.), wet DMSO-d_6 (0.5 mL), at 70 °C, 1 h.

4. NMR spectra

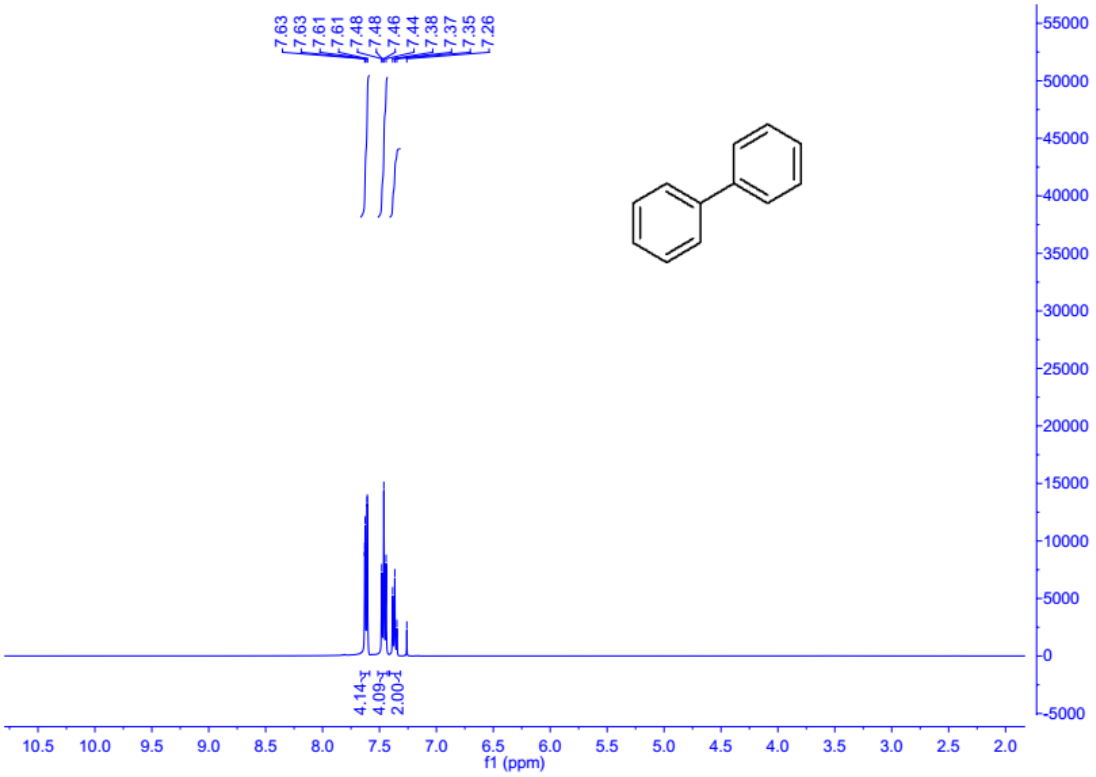


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **2q**

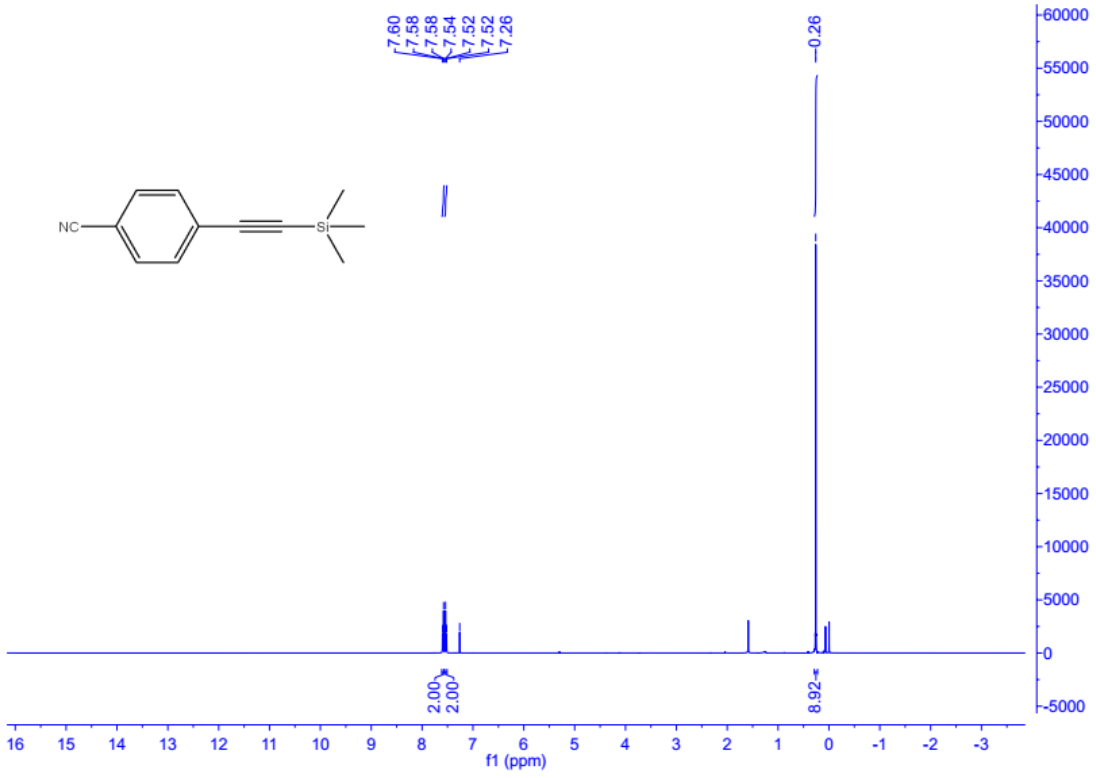


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3i**

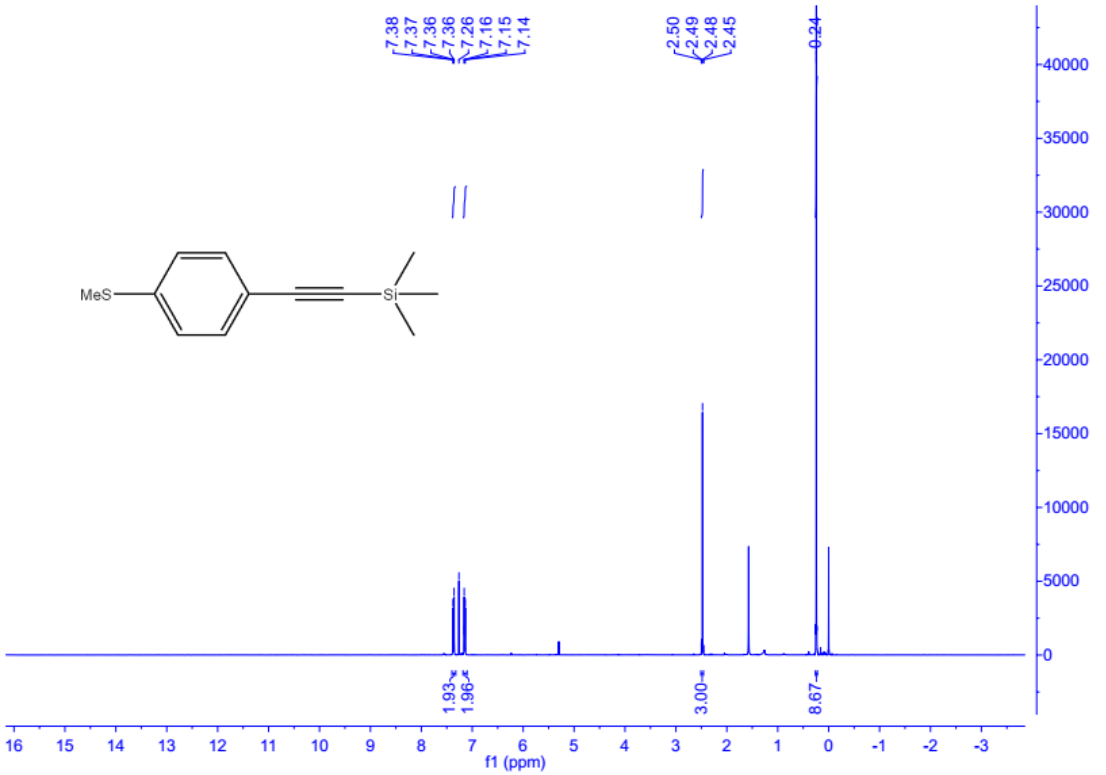


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3j**

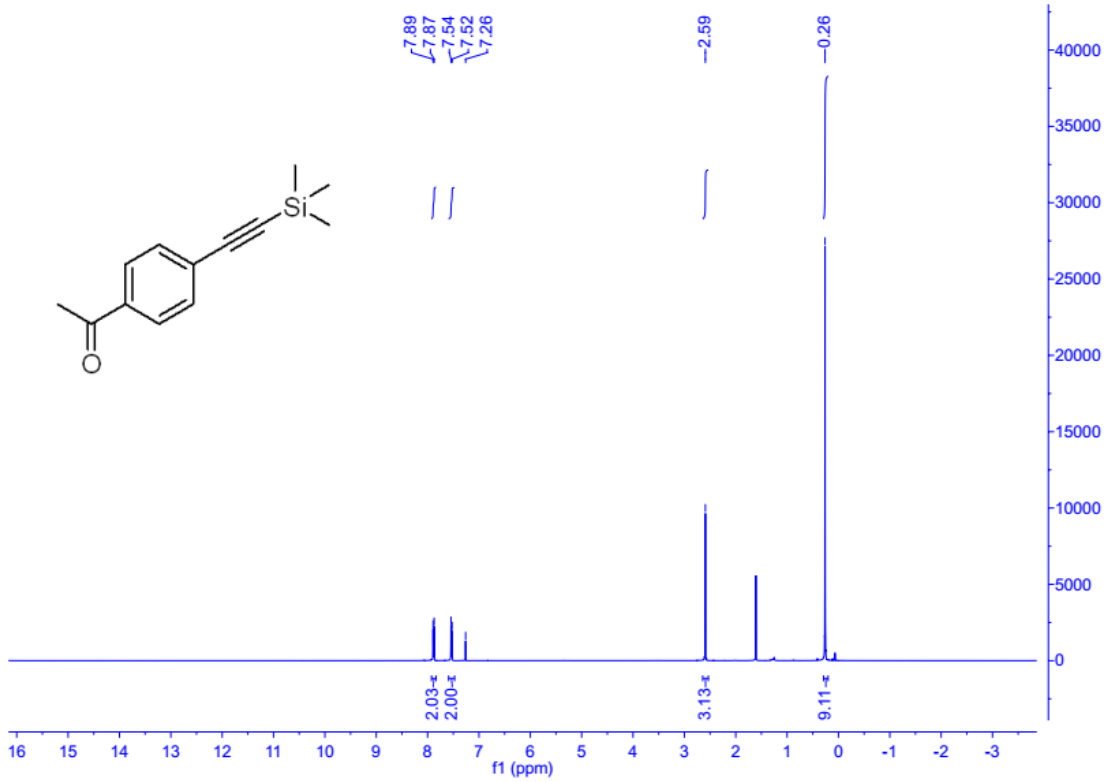


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3k**

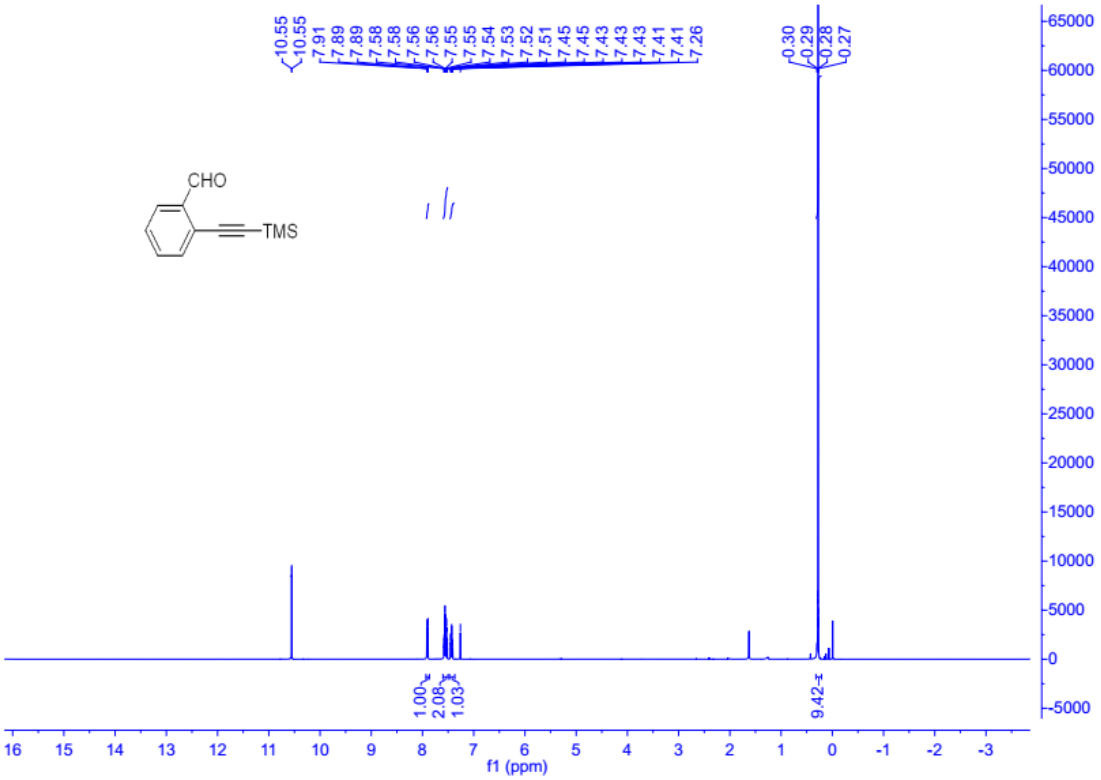


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3l**

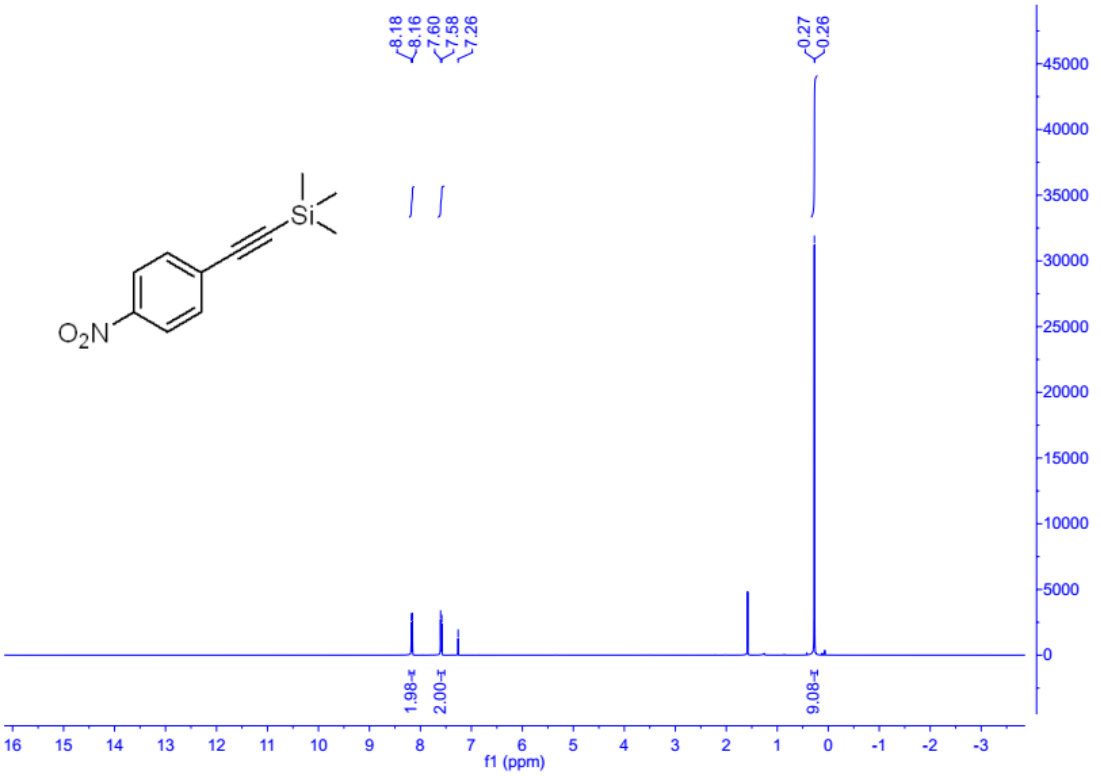


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3m**

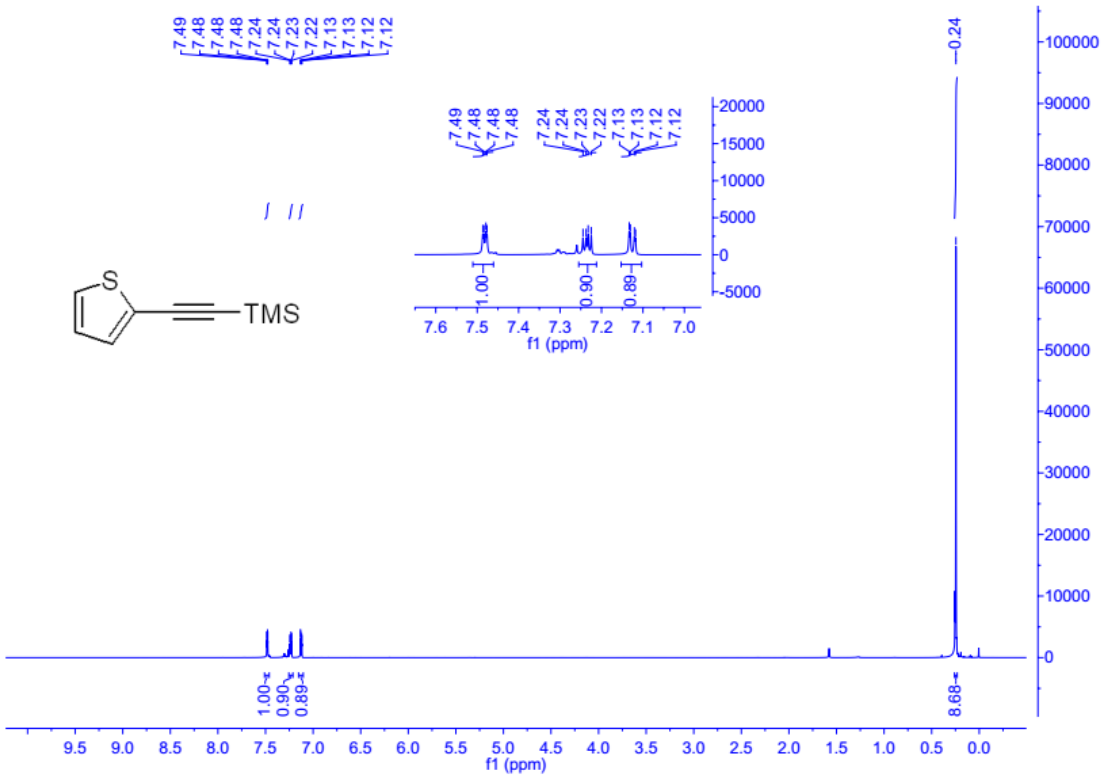


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3n**

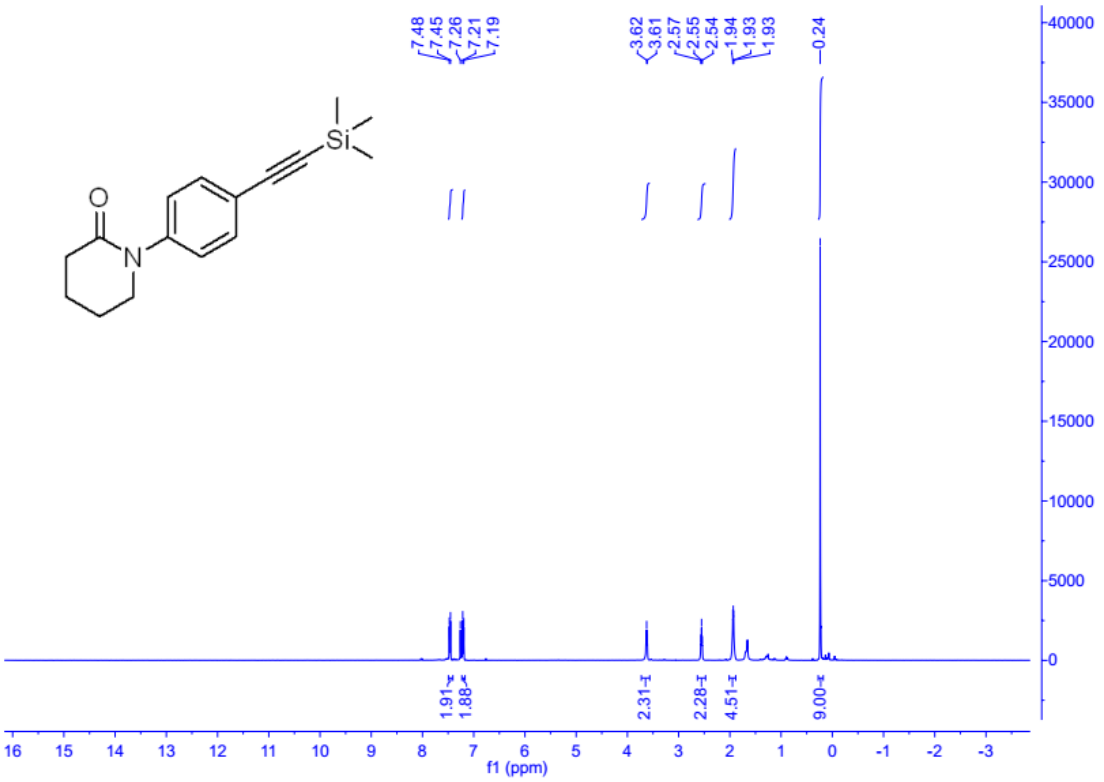


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3o**

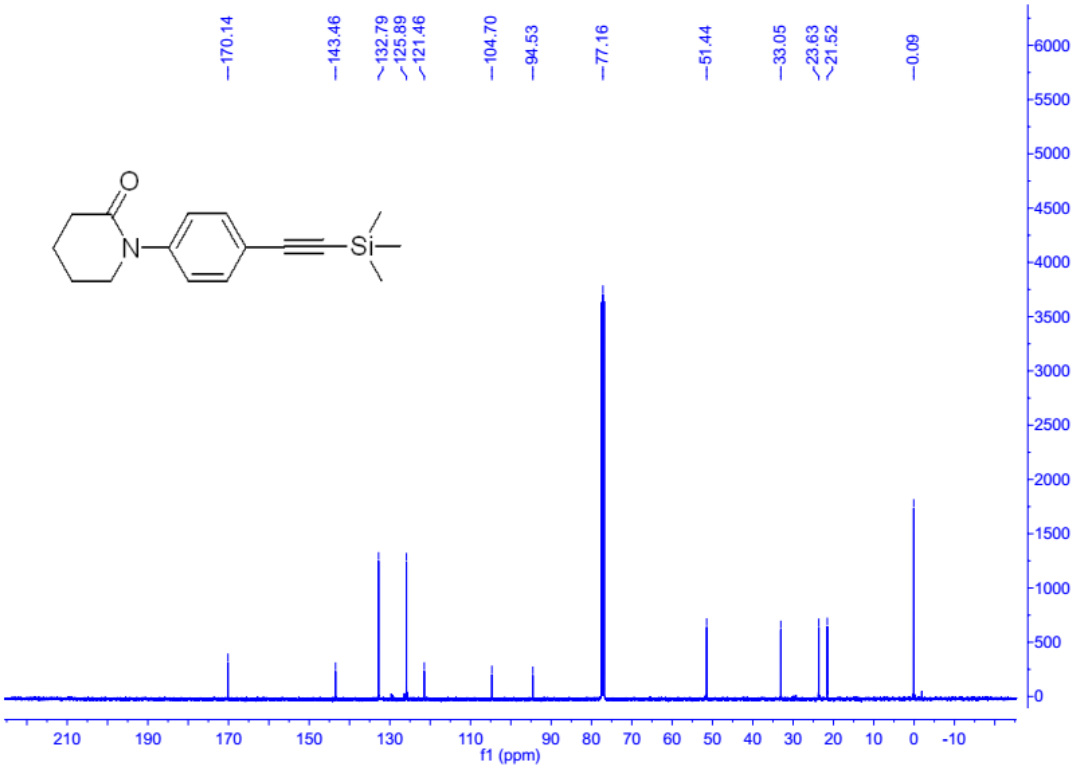


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C) of **3o**

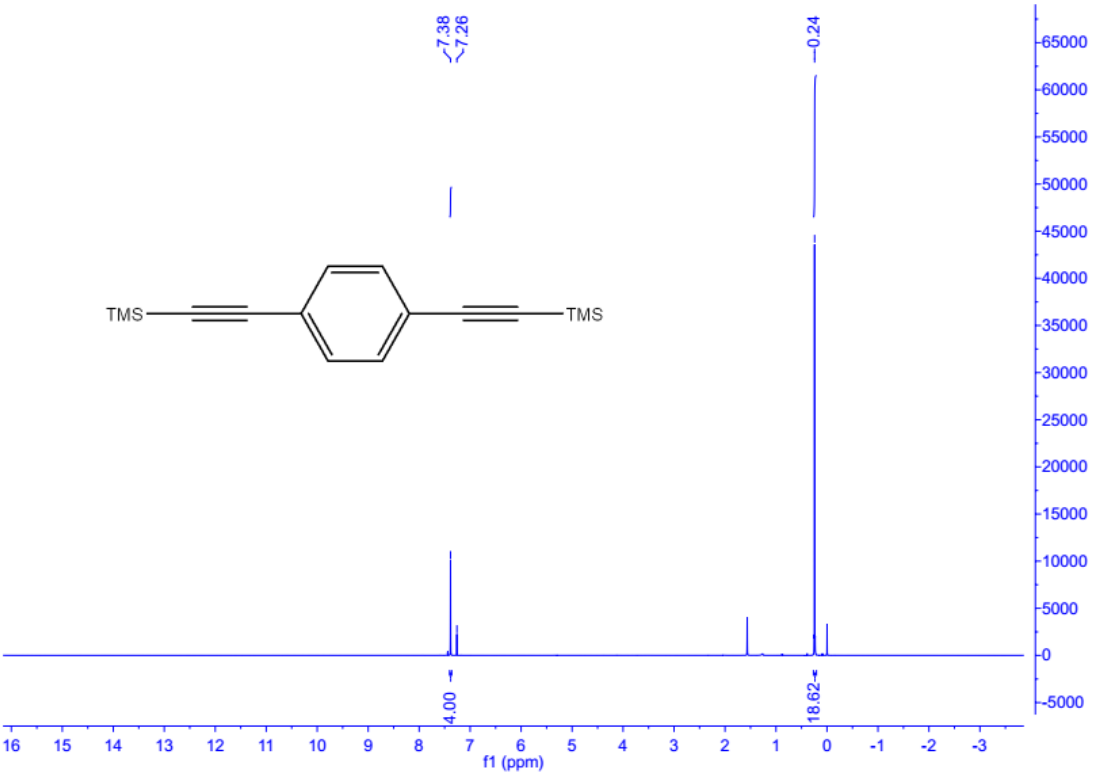


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3p**

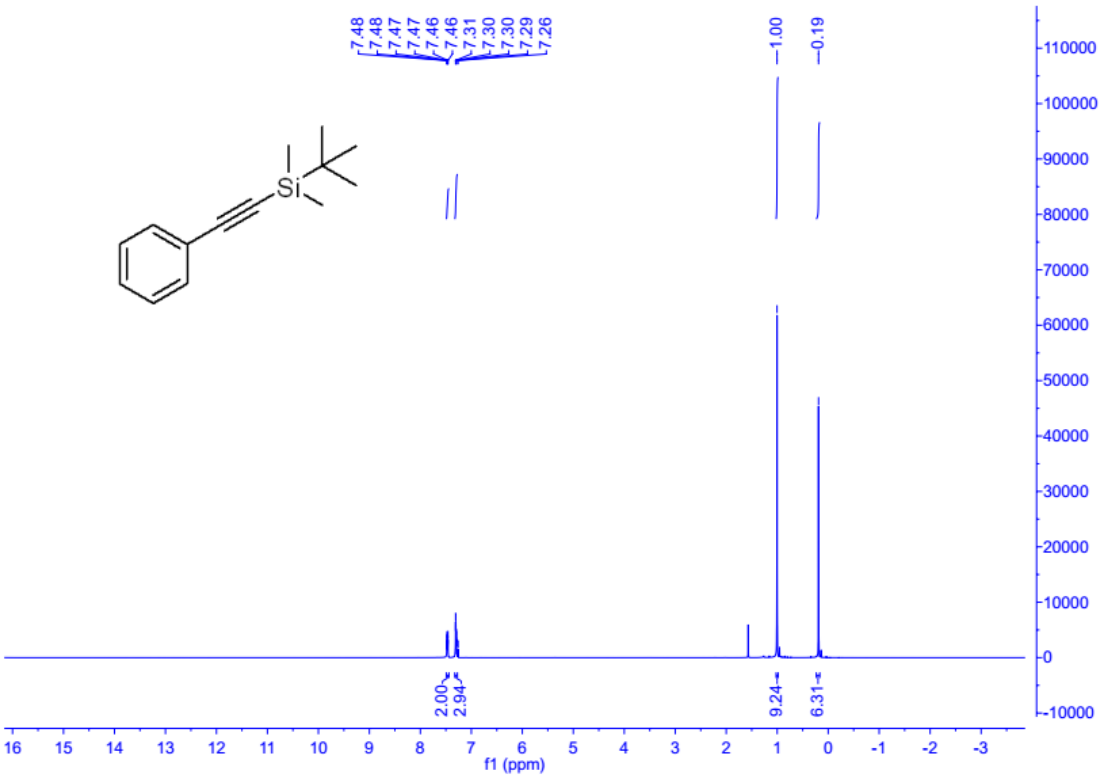


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3q**

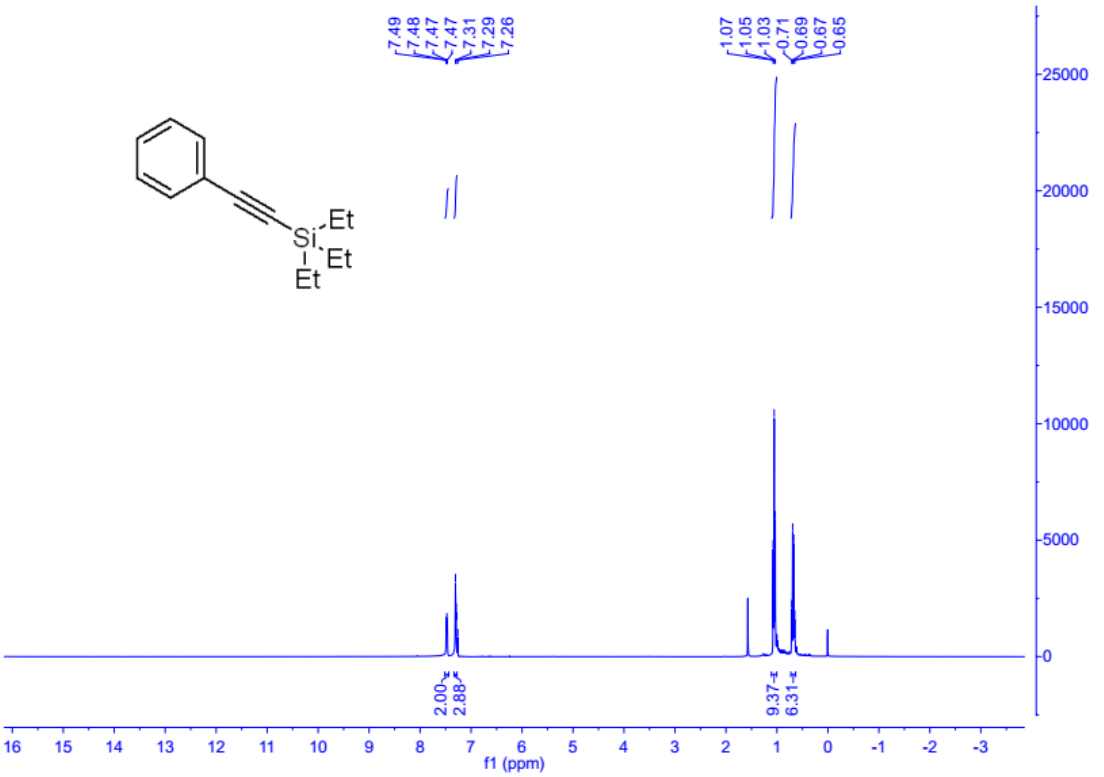


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **3r**

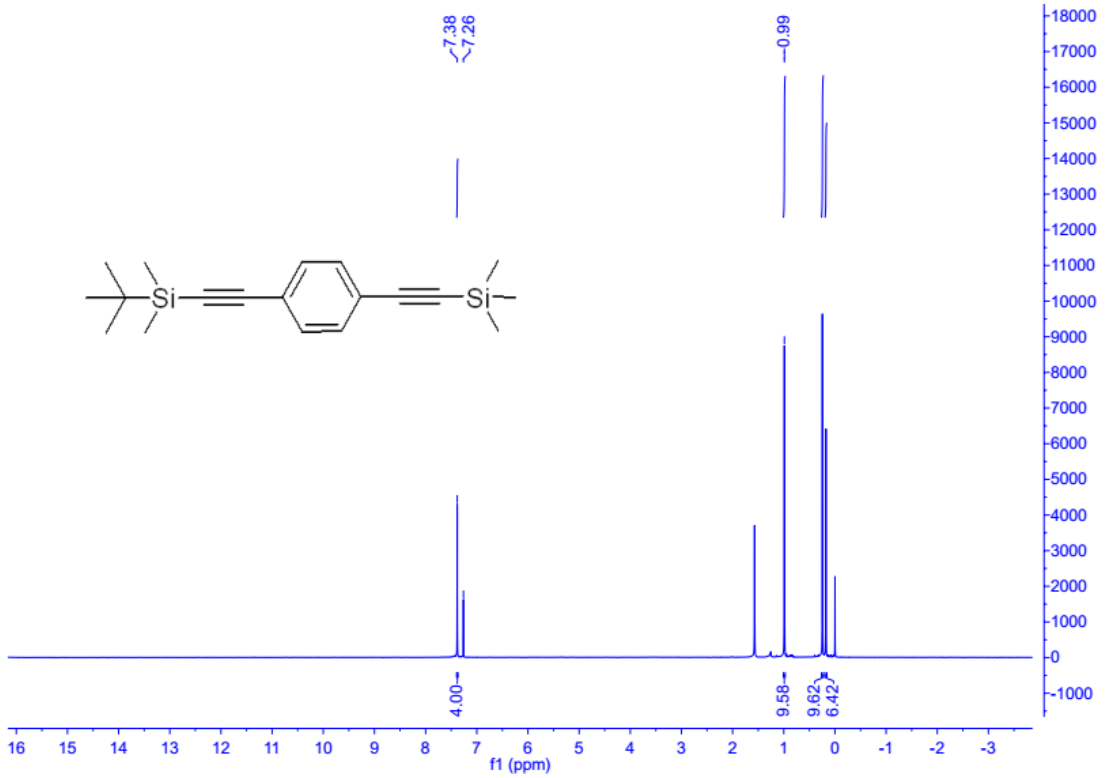


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **3s**

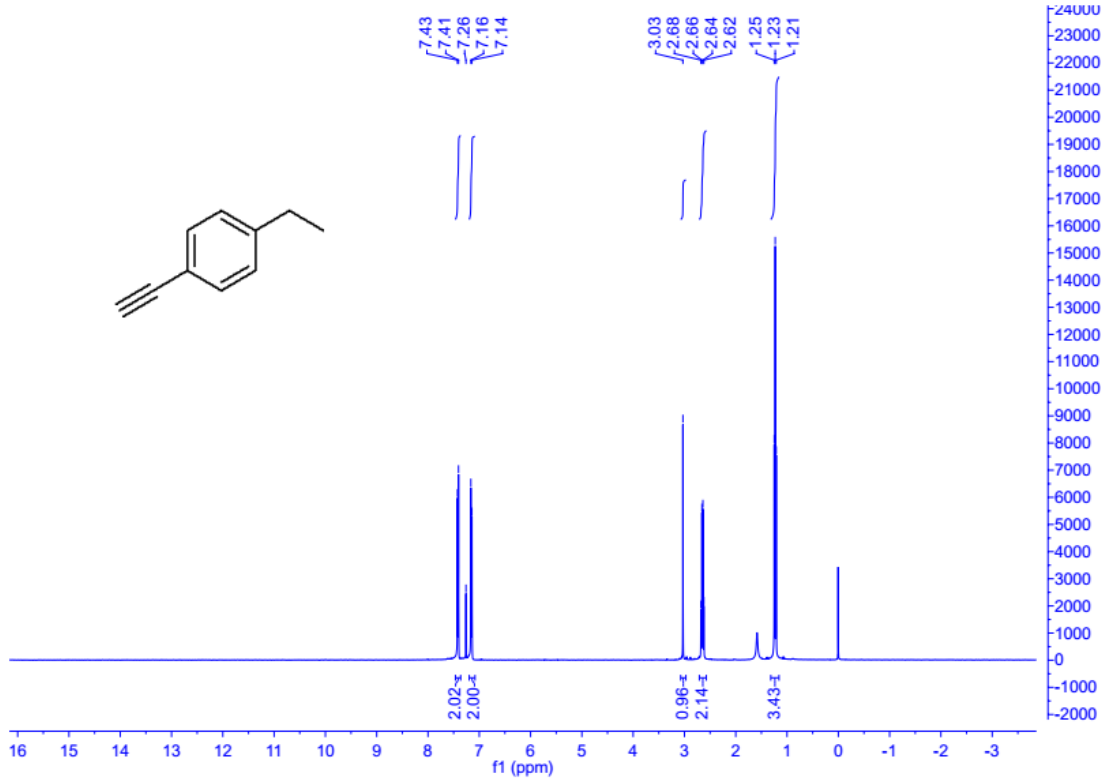


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **4c**

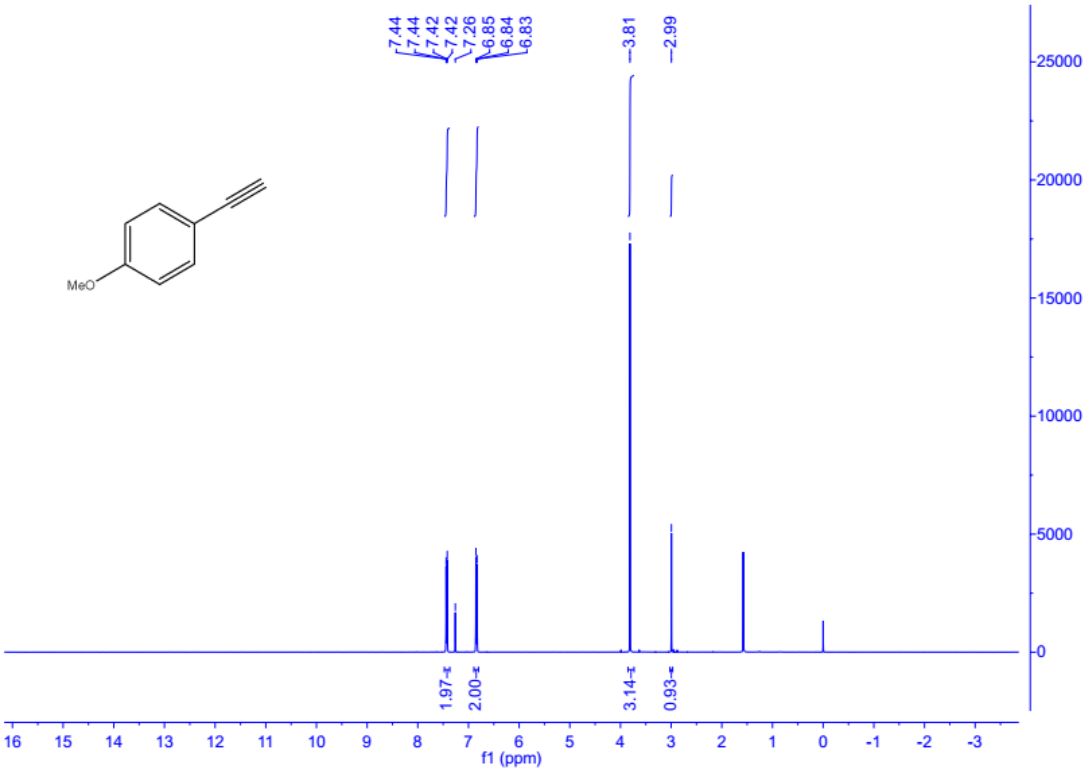


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4d**

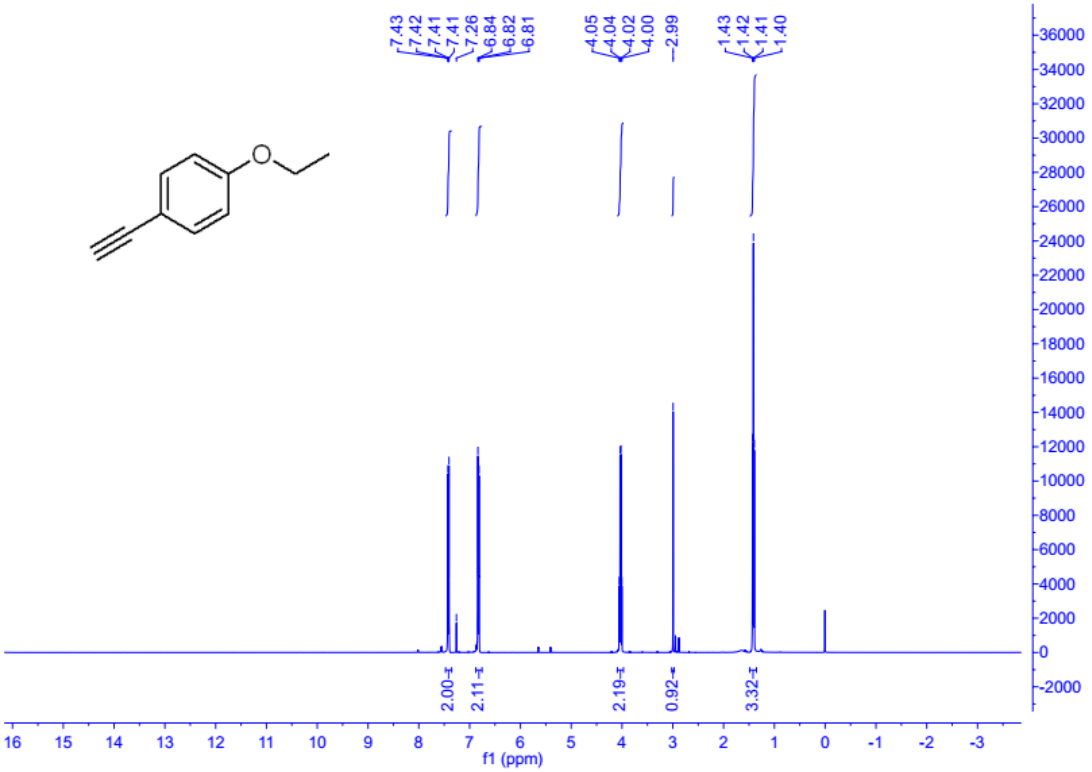


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4e**

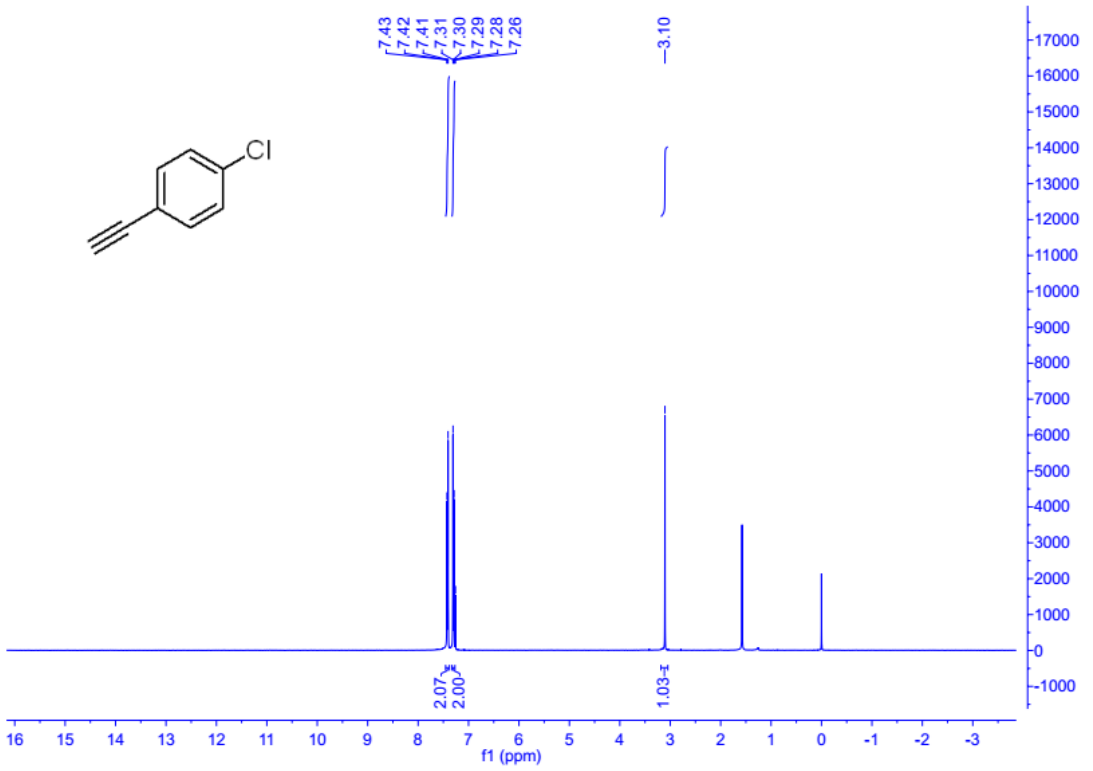


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4g**

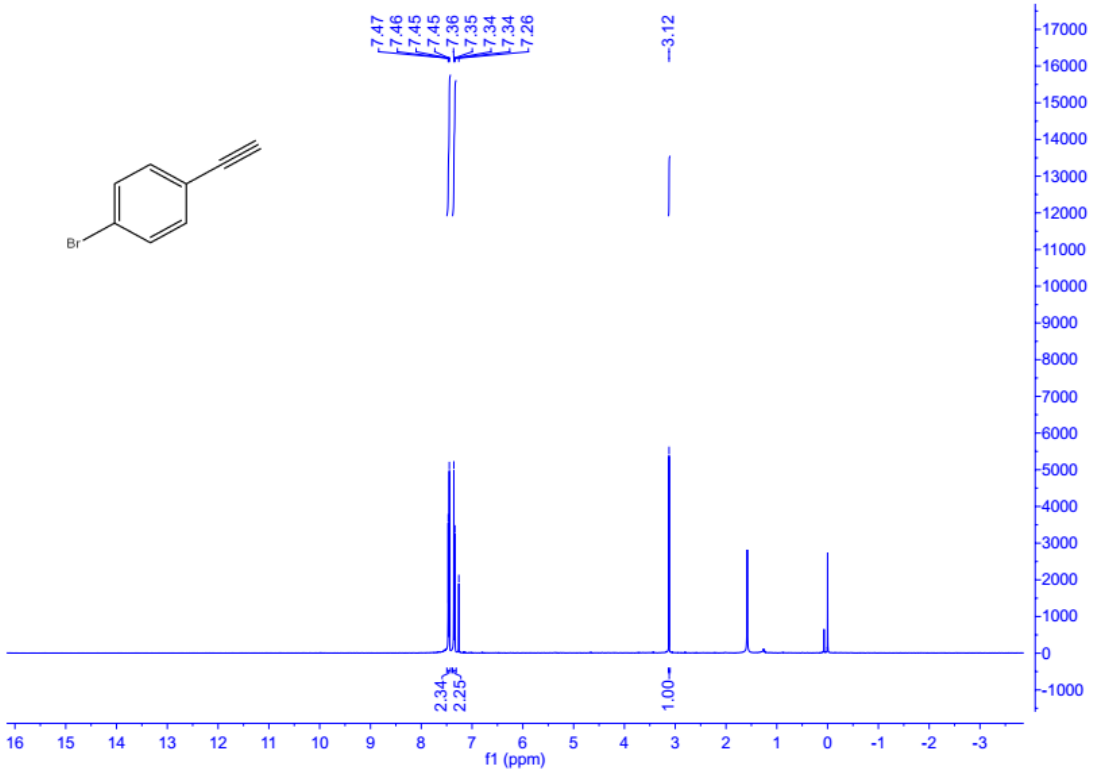


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4h**

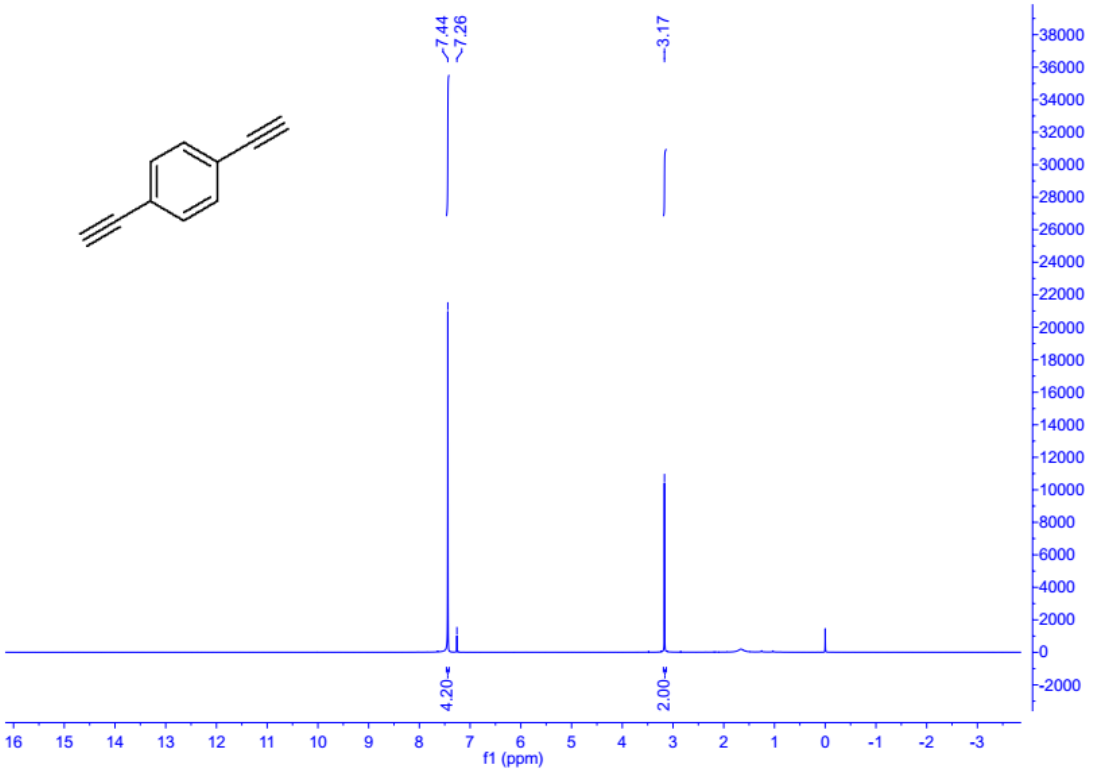


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **4p**

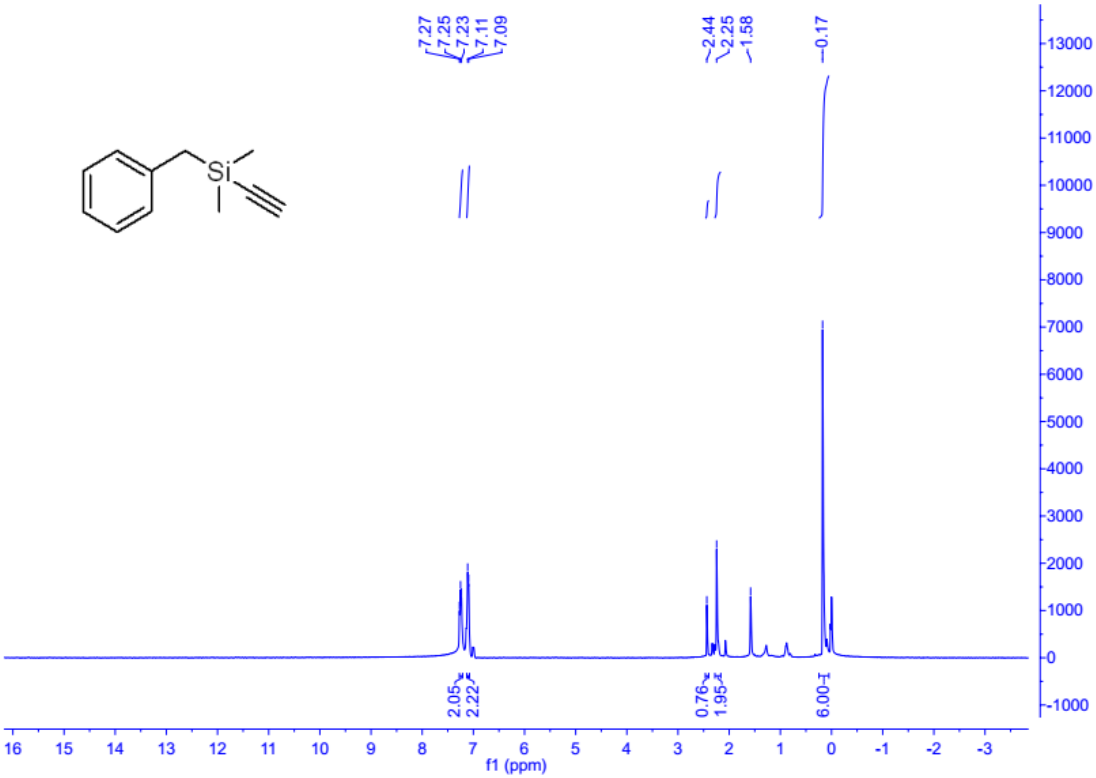


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) of **5p**

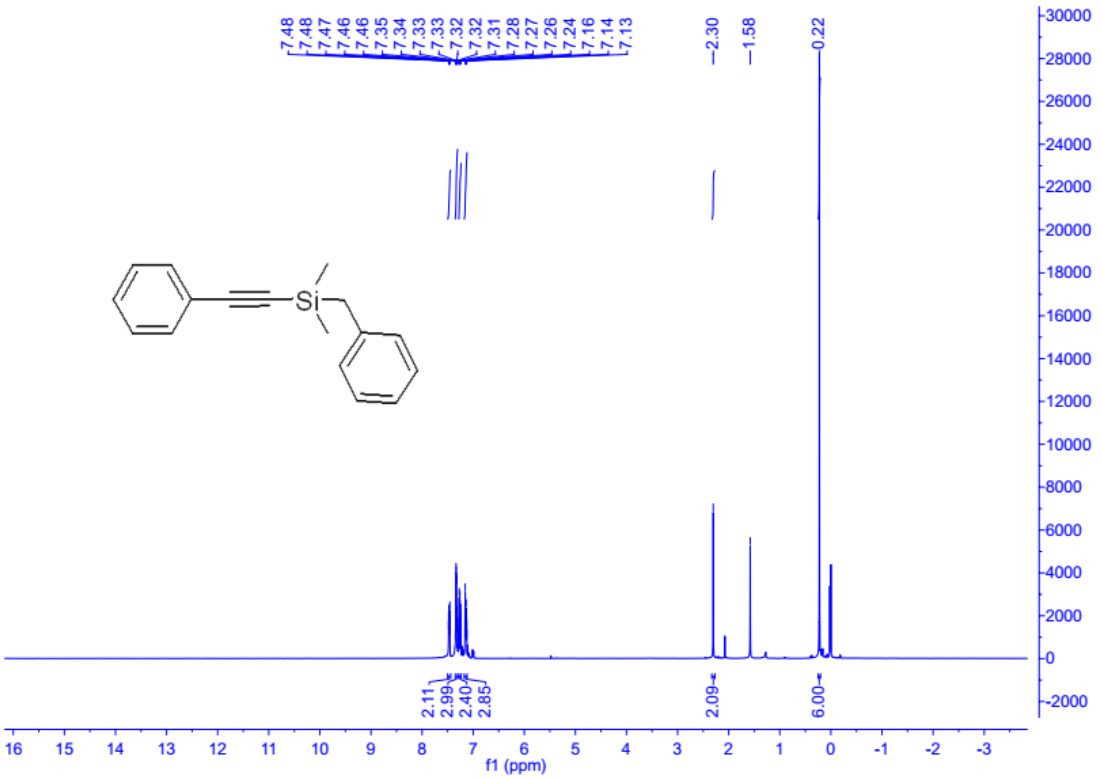


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **5q**

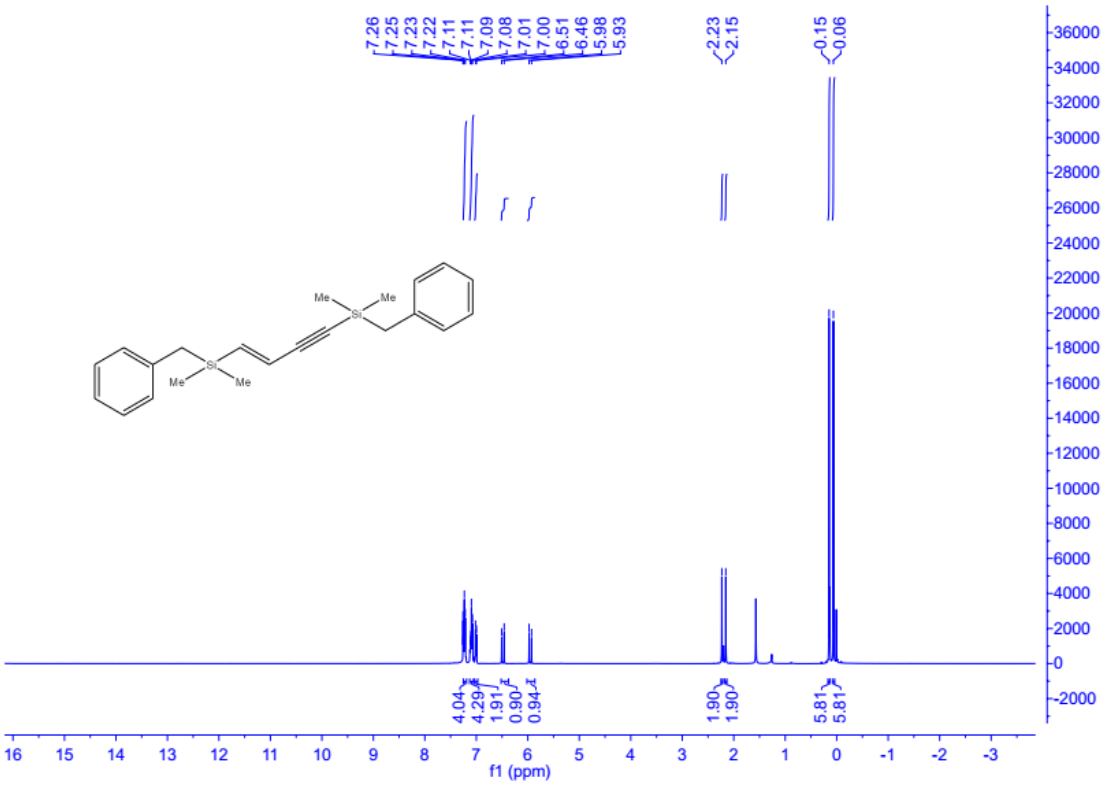


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **5t**