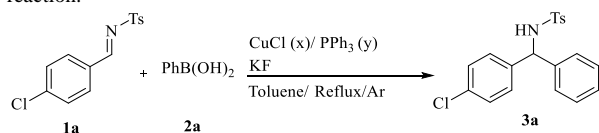


**Development of CuCl/phosphine to catalyze phenylation and methylation of
N-tosyl aldimines with phenyl boronic and methylboronic acids
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Supporting Information

Table 1.S: The effect of copper salt and ligand ratio on the model reaction.

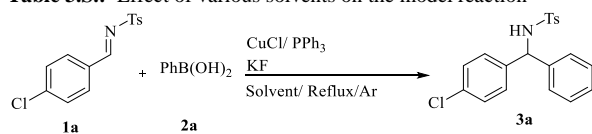


Entry	X (mol%)	Y (mol%)	Yield (%) ^b
1	5	5	10
2	10	10	23
3	5	10	65
	2.5	5	83
4	10	20	55

^a Reaction condition: *p*-chlorobenzaldimine (0.1 mmol), **2a** (0.2 mmol), CuCl, PPh₃ (0.3 mmol), toluene (0.5 mL) for 24 h under reflux in Ar atmosphere.

^b Isolated yield.

Table 3.S.: Effect of various solvents on the model reaction

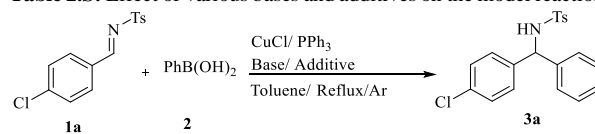


Entry	Solvent	Yield (%) ^b
1	Toluene	83
2	Dioxane	15
3	THF	trace
4	<i>o</i> -Xylene	65
5	Methanol	-
6	Ethanol	-

^a Reaction condition: *p*-chlorobenzaldimine (0.1 mmol), **2a** (0.2 mmol), CuCl (2.5 mol %), PPh₃ (5 mol %), KF (0.3 mmol) and solvent (0.5 mL) for 24 h under reflux in Ar atmosphere.

^b Isolated yield.

Table 2.S: Effect of various bases and additives on the model reaction



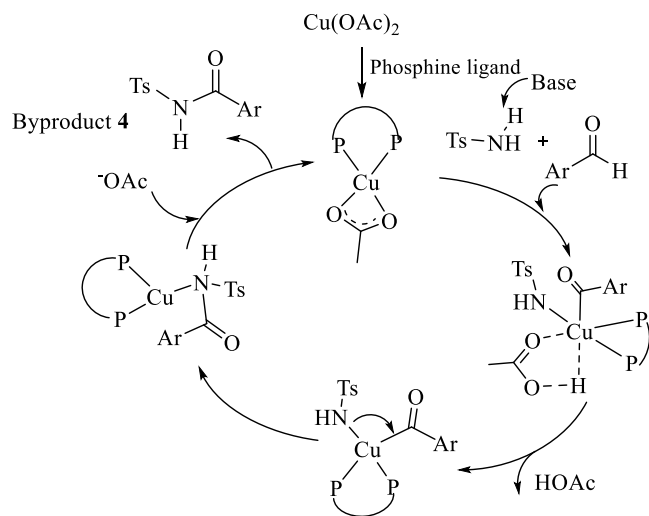
Entry	Base	Additive	Yield (%) ^b
1	KF	-	83
2	KF	Et ₃ N	45
3	Et ₃ N	-	-
4	K ₂ CO ₃	-	40
5	K ₂ CO ₃	Et ₃ N	50
6	KOH	Et ₃ N	25
7	Na ₃ PO ₄	-	15
8	K ₃ PO ₄	-	15
9	NaOAc	Et ₃ N	25
10	NaOAc	-	28

^a Reaction condition: *p*-chlorobenzaldimine (0.12 mmol), **2a** (0.2 mmol), CuCl (2.5 mol %), PPh₃ (5 mol %), base (0.3 mmol), additive (0.4 mmol) and toluene (0.5 mL) for 24 h under reflux in Ar atmosphere.

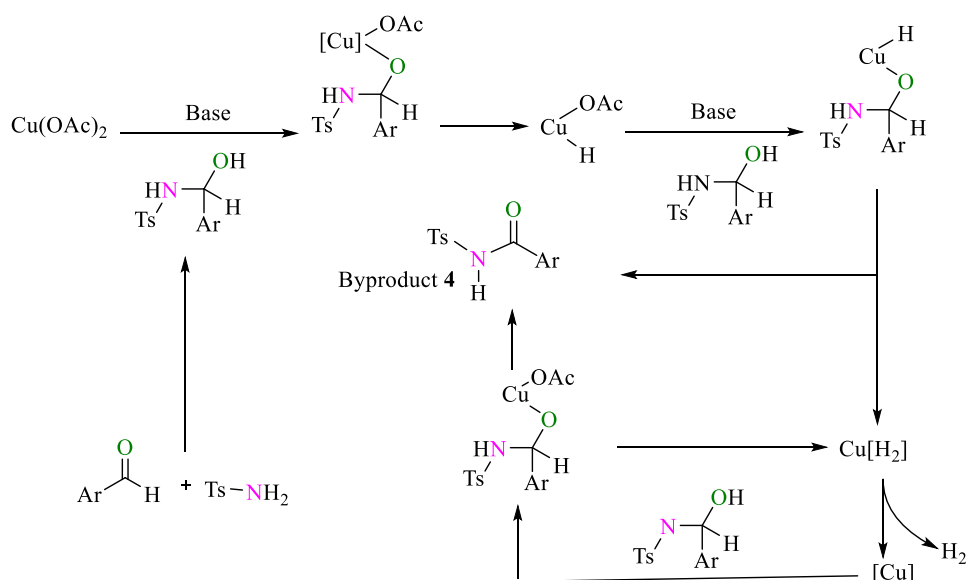
^b Isolated yield.

Extra Information:

- We presented the activity of phosphine ligands coordinated to copper salt as a first row transition metal in these additions.
- We performed the reaction using PhBF₃K instead, and only a trace amount of desired product was found. Therefore the same as other reports, KF addition to **2a** doesn't intercede PhBF₃K salt formation and PhBF₃K salt cannot be the active species in catalytic cycle. Although CuCl salt is insoluble in toluene, however the copper forms a soluble complex with the phosphine ligand in organic solvents.
- The proposed mechanisms for the formation of byproducts.

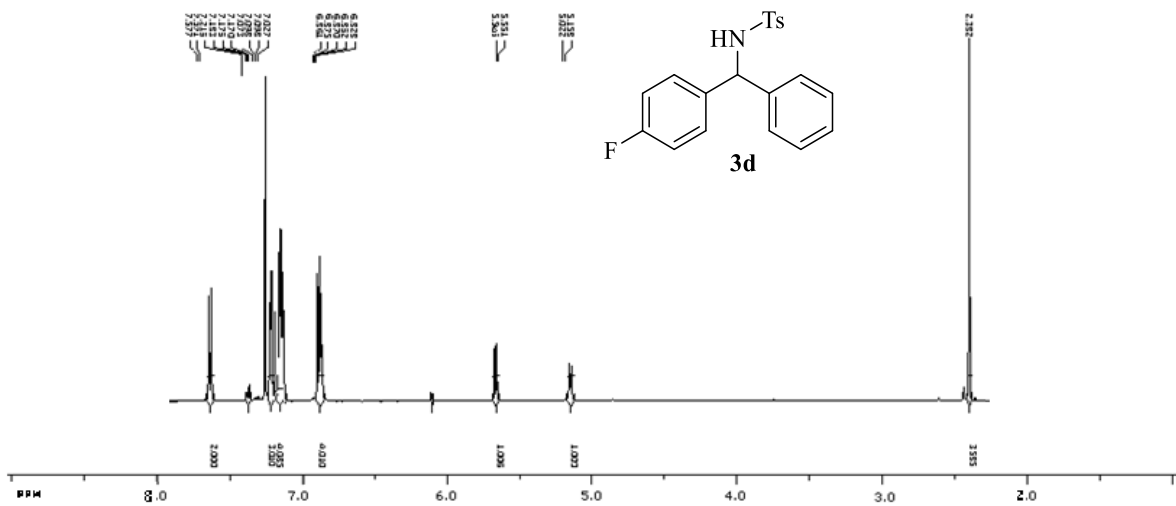
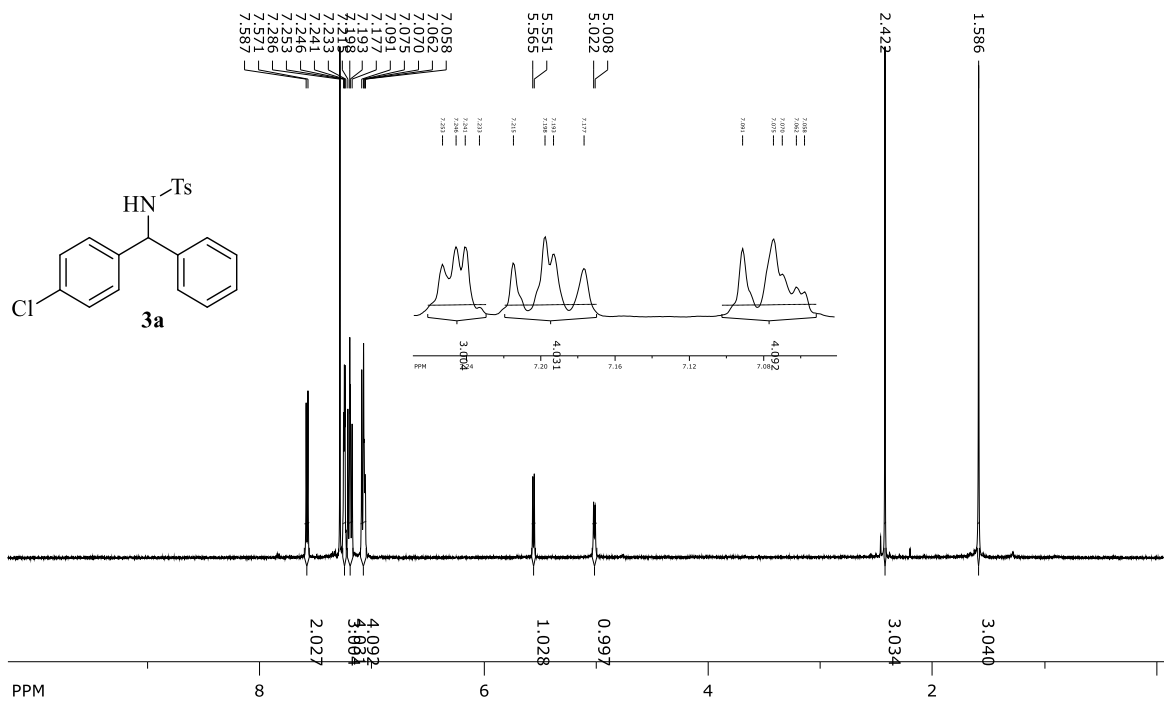


Proposed mechanism 1

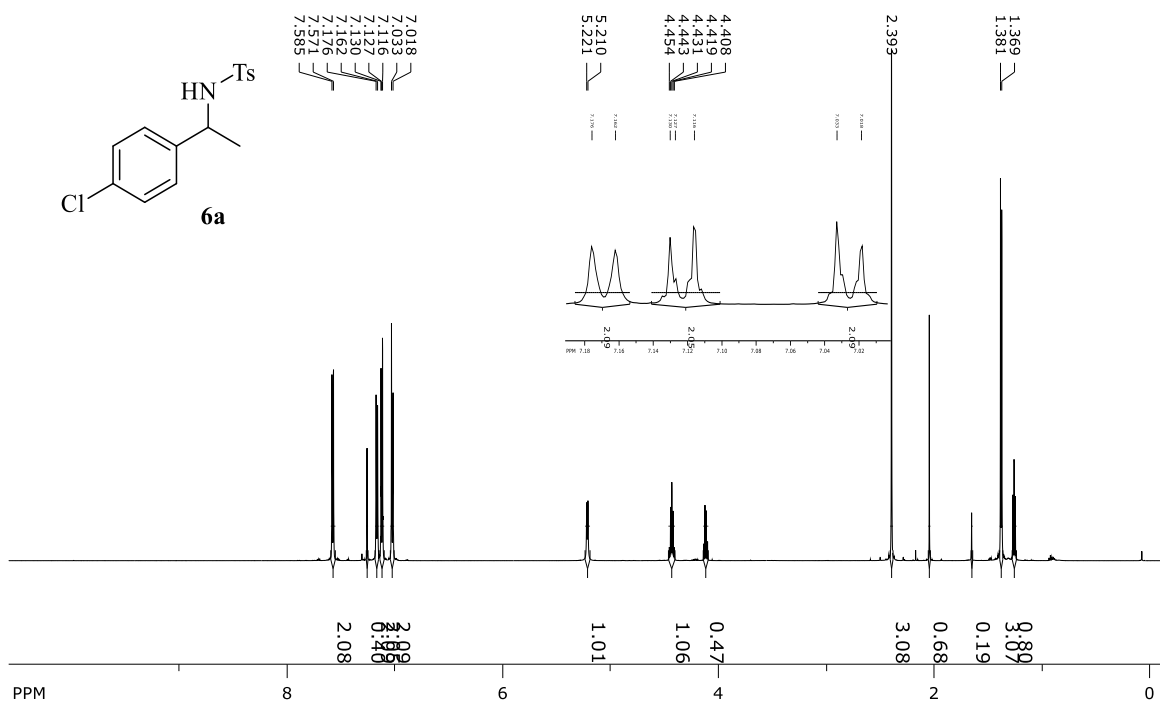


Proposed mechanism 2: via a hemiaminal for the formation of amides from aldehydes and amines by formation of Cu-OAc precatalyst (Org. Chem. Front., 2015, 2,241–247).

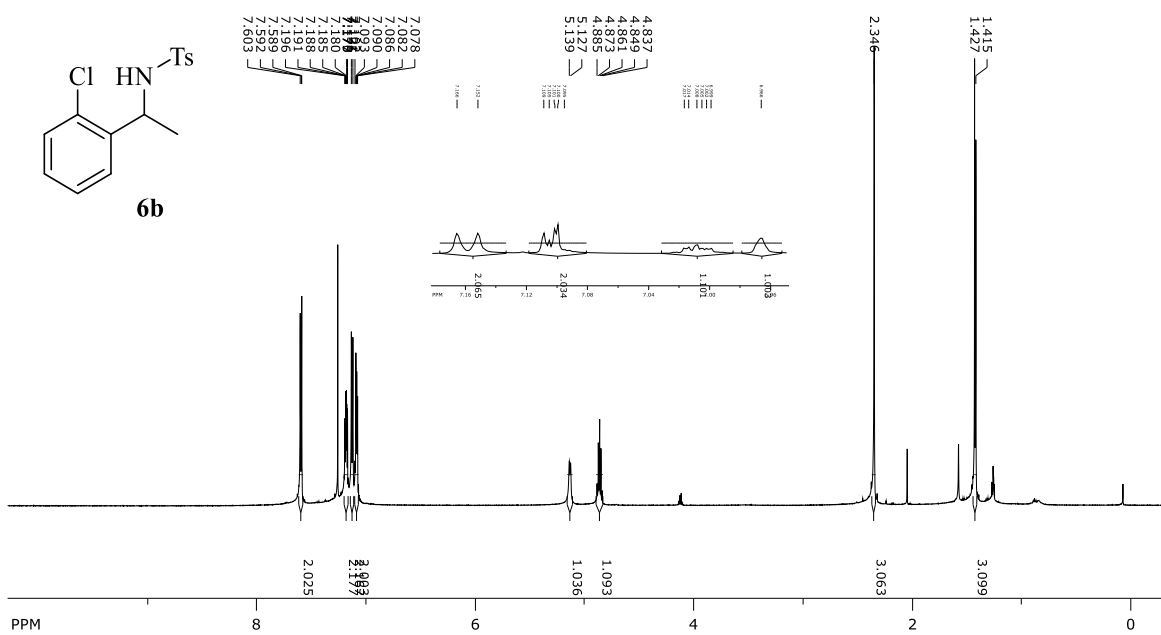
SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



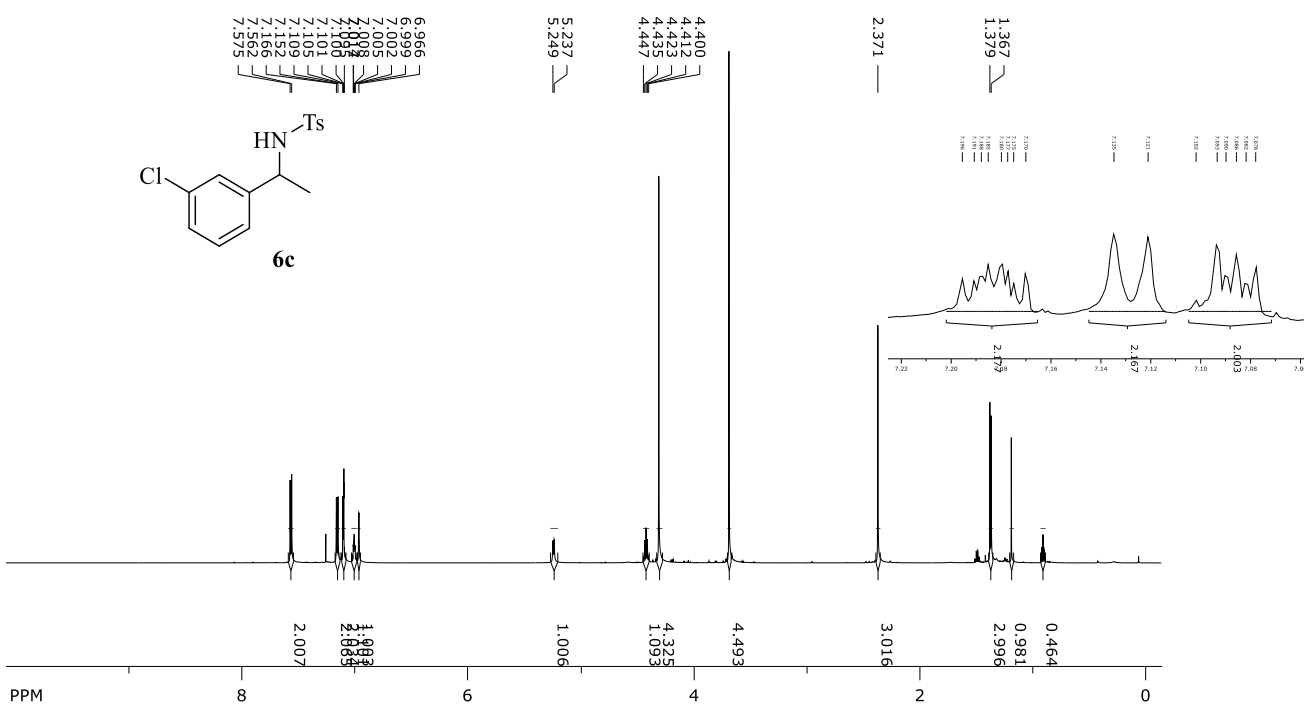
SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



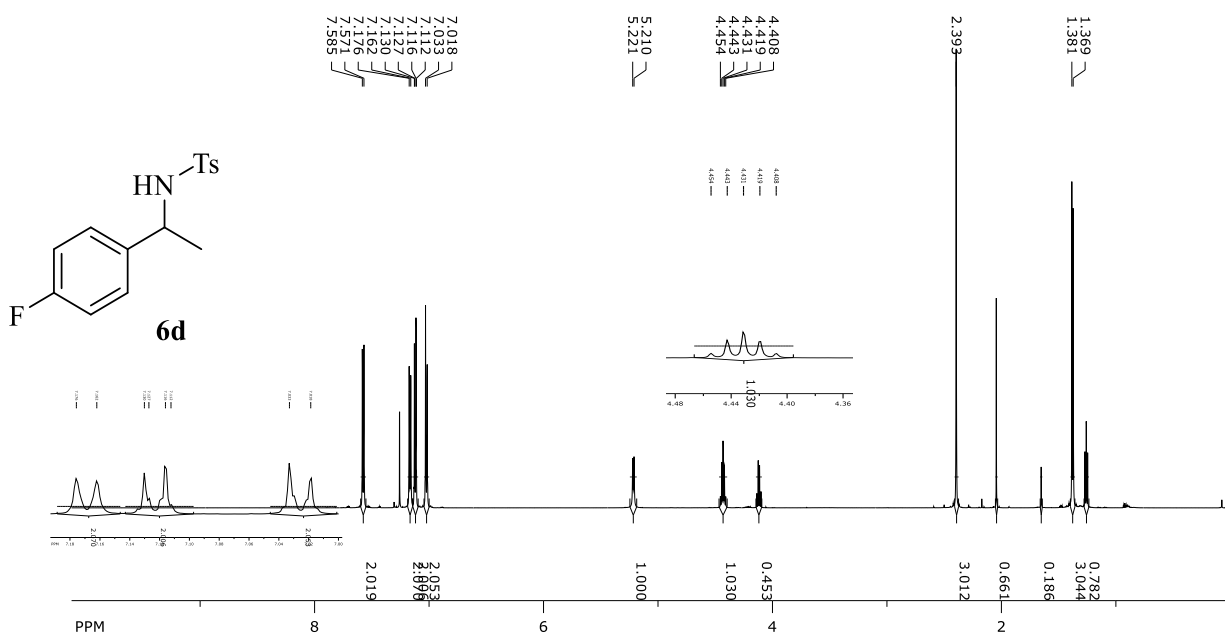
SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



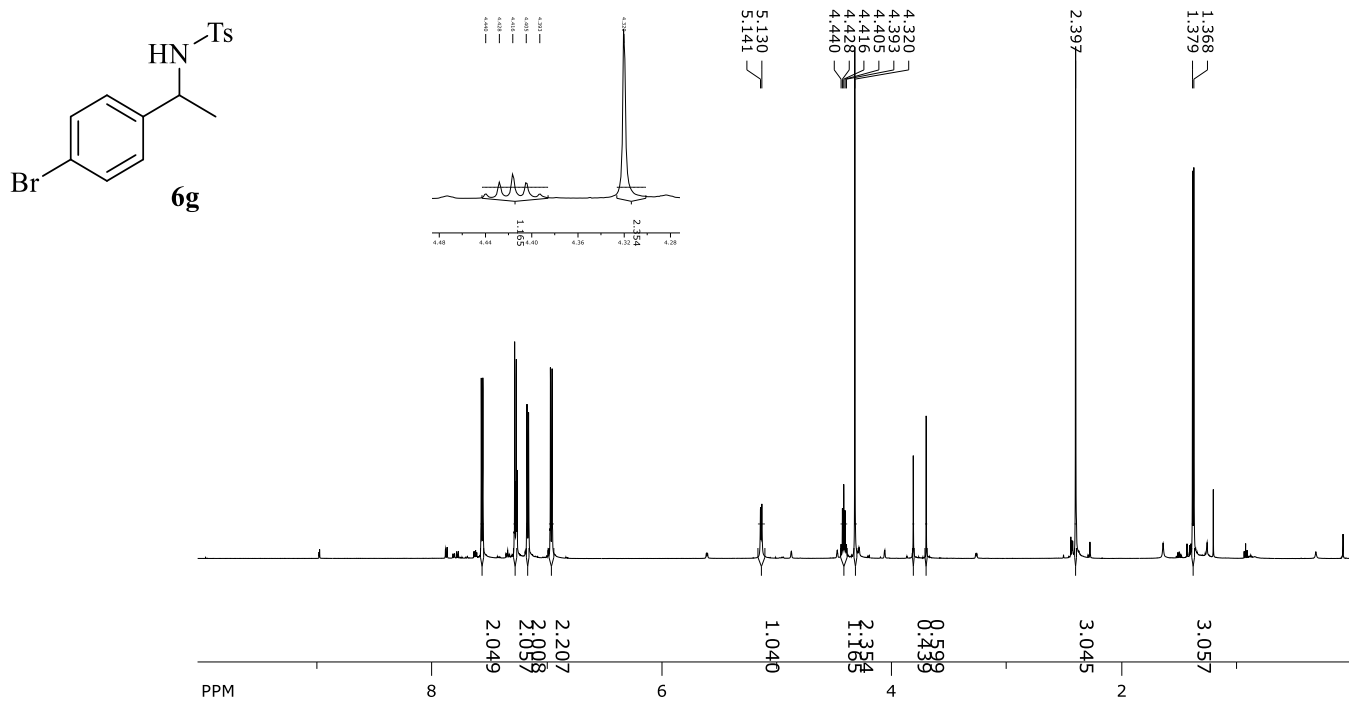
SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



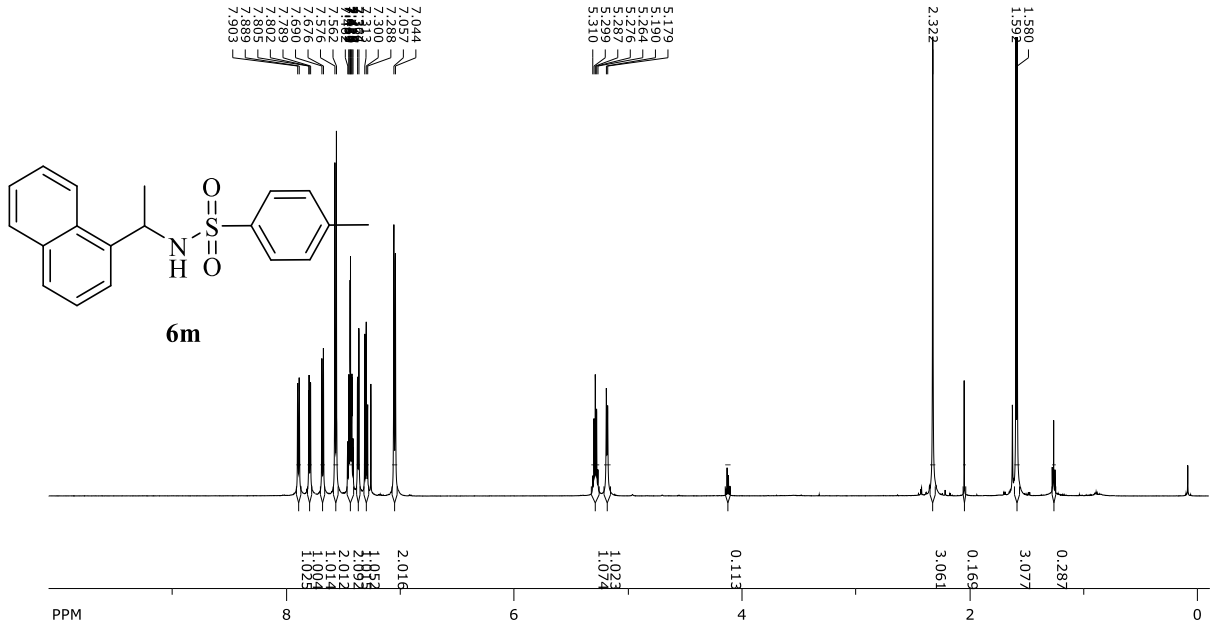
SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k



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SpinWorks 4: Nasiri 1HNMR in CDCl3 at 298k

