

**Table ESI 1.** Reactions attempted in siloxane solvents that gave poorer outcome than in conventional solvents

Reaction Type	Reagents	VMS	Comments	Student
Pd catalysed Suzuki cross coupling	PhBr + phenyl boronic acid	M2	Low catalyst solubility led to low yields compared to THF or dimethoxyethane	RH and MM
Pd catalysed Heck reaction	iodobenzene + ethyl acrylate  iodobenzene + styrene	M2	Consistently lower yields in VMS than in THF	RH
Pd catalysed Hydrogenation – 5% Pd on C	Limonene Cycloheptene Nitrobenzene	M2 or D4	Consistently lower rates in VMS than in methanol	RH
Aq PTC Reduction of carbonyl with	sodium borohydride + l-hexanal  sodium borohydride + cyclohexanone	M2 or PDMS	yields were moderate cf toluene due to poor work-up	RH
Robinson Annulation	MVK + 2-methylcyclohexanone	MM or MDM	MVK polymer formed instead	MM
Williamson ether synthesis	ethoxybenzene was using tetrabutylamm onium bromide (TBAB) as the catalyst	M2, PDMS-2000	Consistently lower yields in VMS than in cyclohexane, n-octane, toluene	JS
addition of singlet oxygen to $\alpha$ -terpinene	$\alpha$ -terpinene + O <sub>2</sub>  rose Bengal and TPP	D5	Due to the poor solubility of the used photosensitizers rose Bengal and TPP, no product formation was observed in pure siloxane solvent (D5).	VC