

Electronic Supplementary Information (ESI)

**Metal-free C–H amination of unactivated hydrocarbons with sulfonylimino- λ^3 -
bromanes generated in situ from diacetoxybromobenzene**

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2. ¹H NMR spectrum of (2,2,2-trichloroethoxysulfonyl)imino-λ³-bromane (Scheme S1)

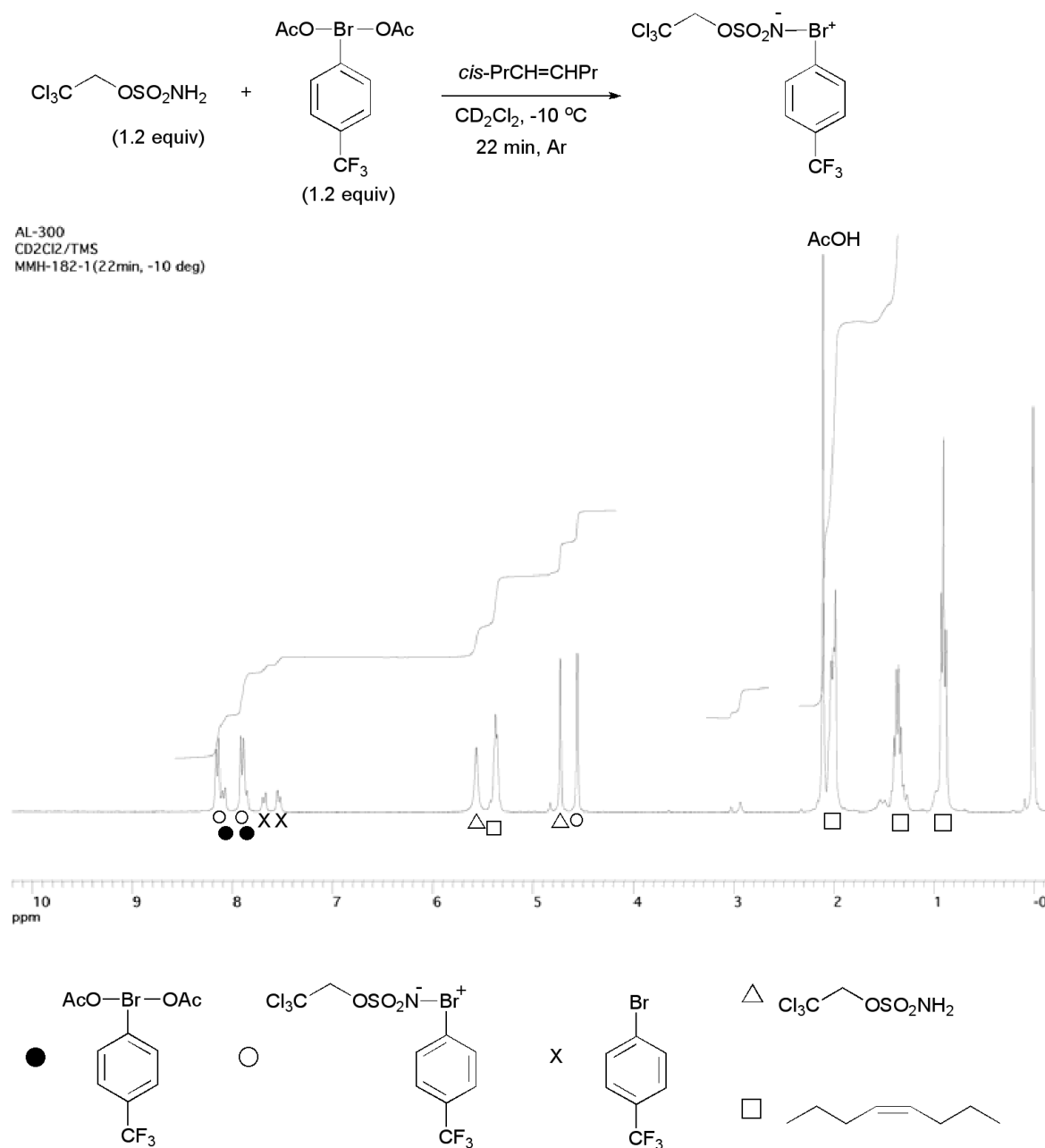
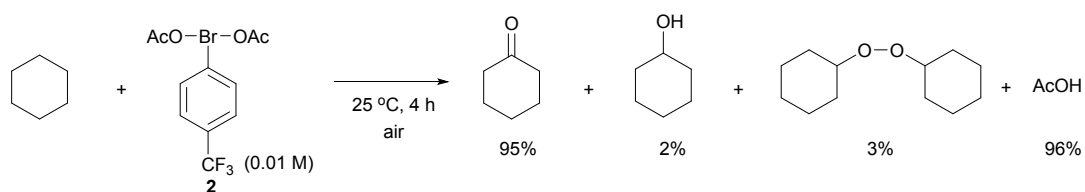


Figure S1. ¹H NMR spectrum of *N*-(2,2,2-trichloroethoxysulfonyl)imino-λ³-bromane measured at -10 °C in the presence of *cis*-4-octene: *p*-CF₃C₆H₄Br(OAc)₂ (1.2 equiv)/CCl₃CH₂OSO₂NH₂ (1.2 equiv)/*cis*-4-octene (1 equiv, 0.03 M)/CD₂Cl₂/-10 °C/22 min.

We could not detect desired *N*-(2,2,2-trichloroethoxysulfonyl)imino-λ³-bromane (open circle in the figure) in the absence of *cis*-4-octene. Coordination of olefin to the electron-deficient hypervalent bromine(III) center may occur under the conditions, which stabilizes transient imino-λ³-bromane (Cl₃CH₂OSO₂N=BrAr).

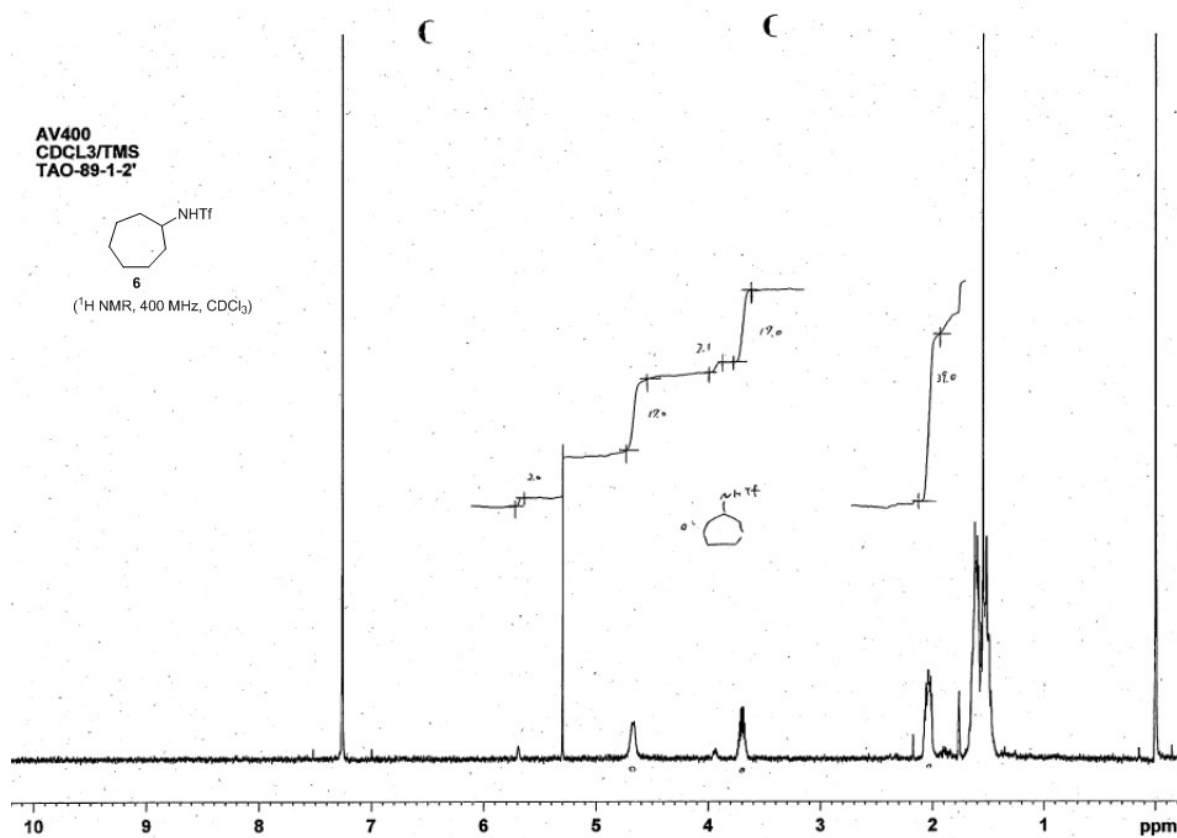
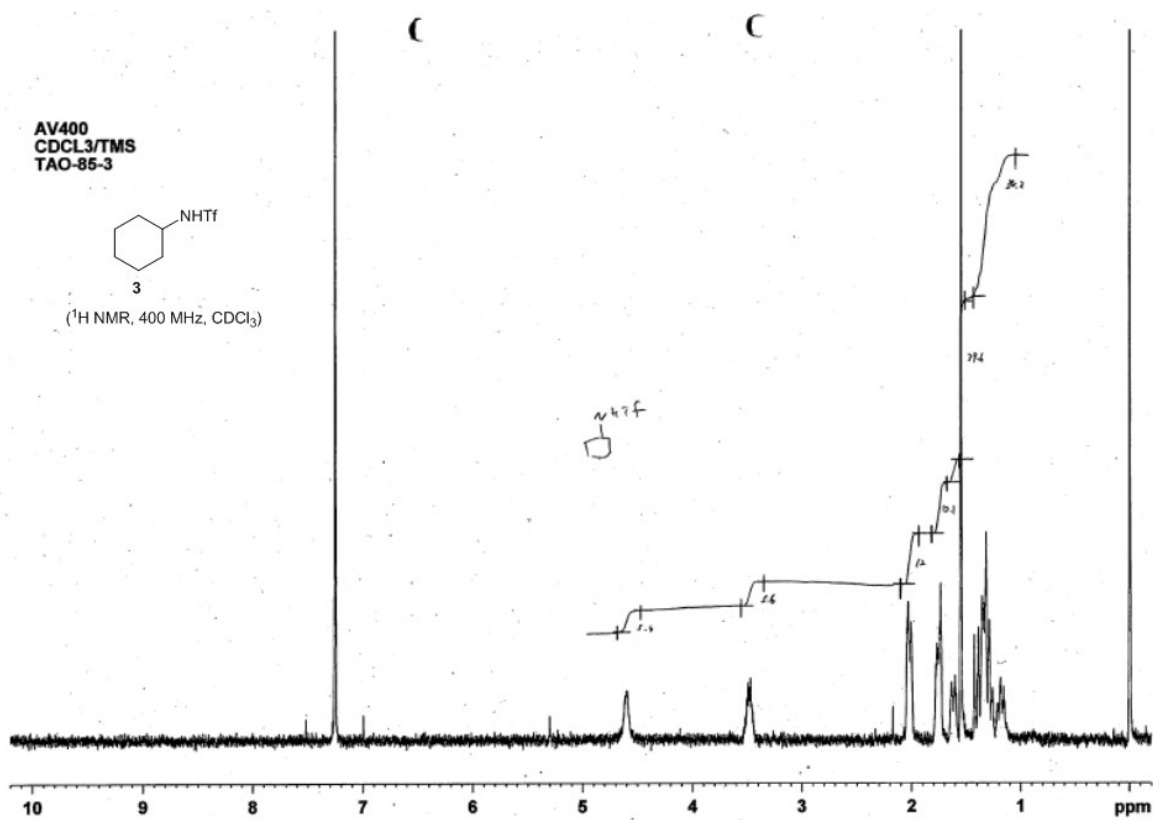
3. Oxidation of cyclohexane with diacetoxy- λ^3 -bromane **2** in the presence of oxygen.



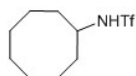
Scheme S1. Oxidation of cyclohexane with diacetoxy- λ^3 -bromane **2** under air. Yields of products were determined by GC (for cyclohexanone) and ^1H NMR (CyOH, C_2O_2 , and AcOH).

Formation of small amount of cyclohexanol/dicyclohexyl peroxide suggests the reaction mechanism involves the generation of cyclohexyl radical. Scopes and limitations of the reaction and mechanistic studies are now underway in our laboratory and will be reported in due course.

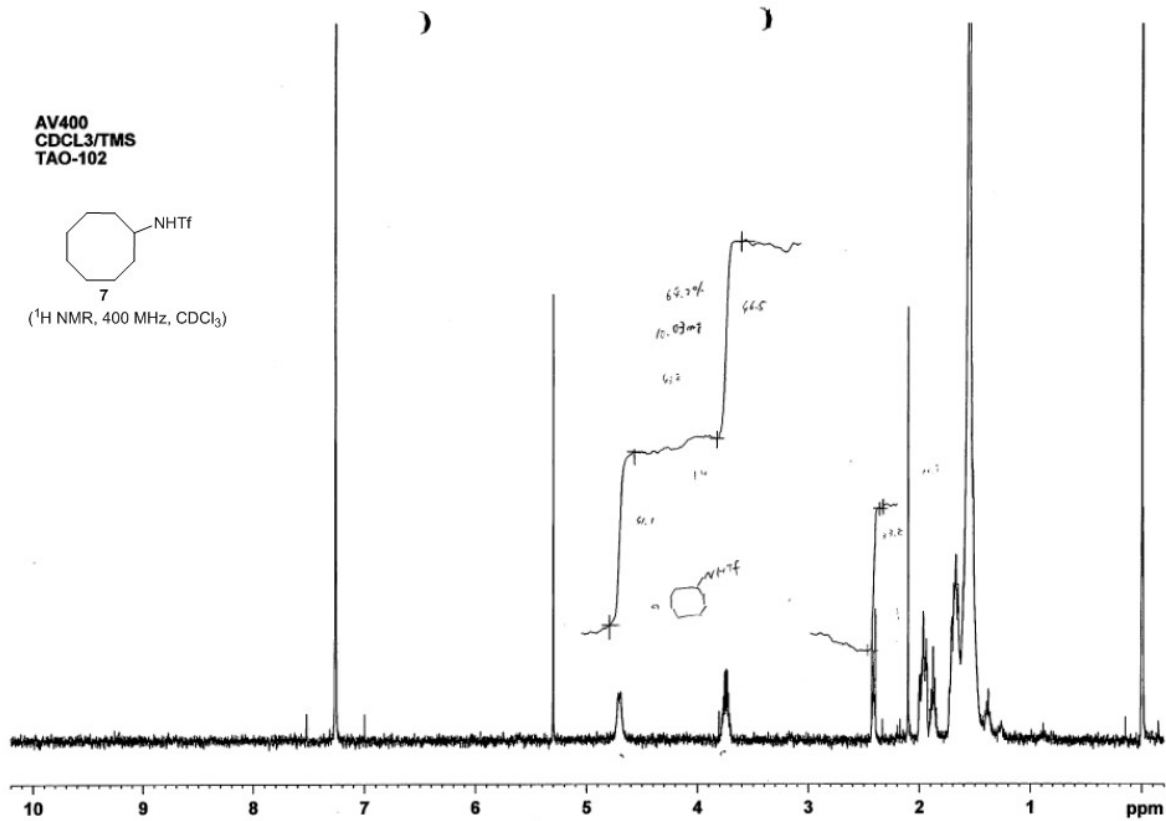
3. NMR spectra



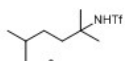
AV400
CDCL3/TMS
TAO-102



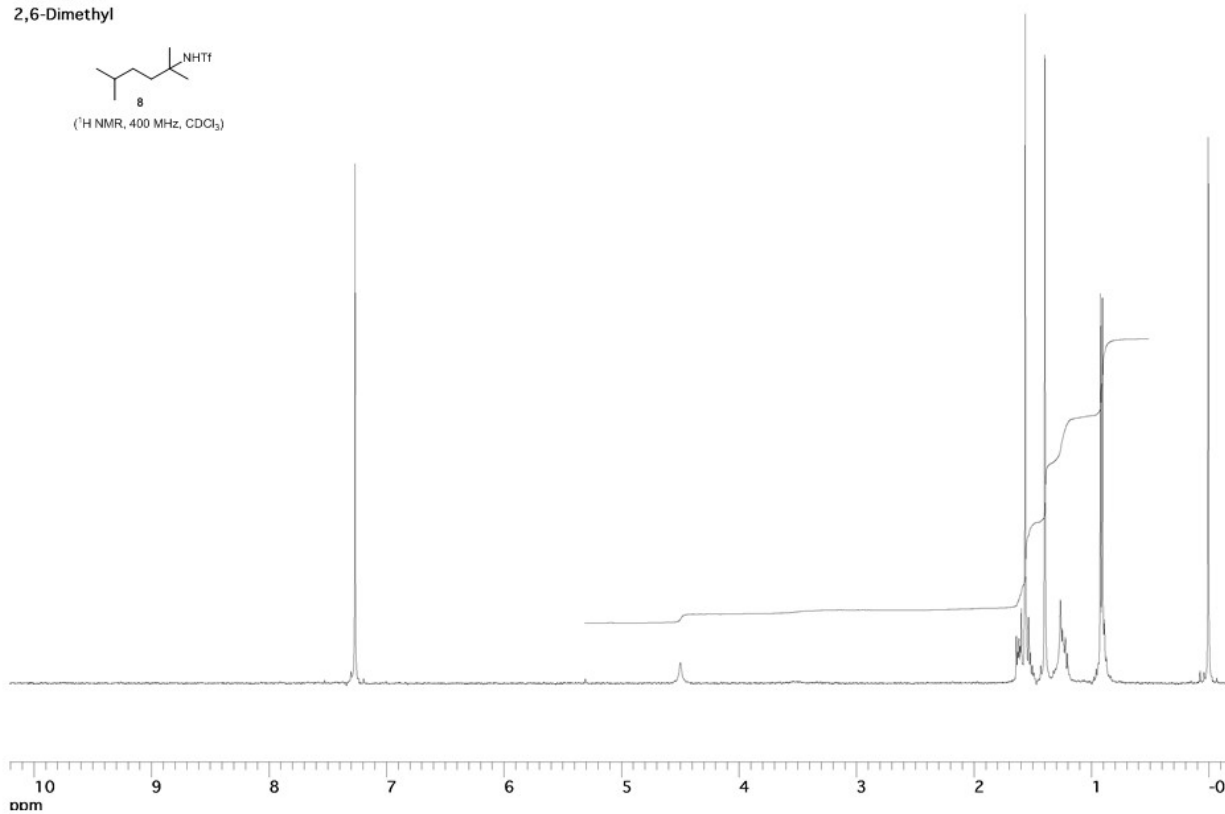
7
(¹H NMR, 400 MHz, CDCl₃)



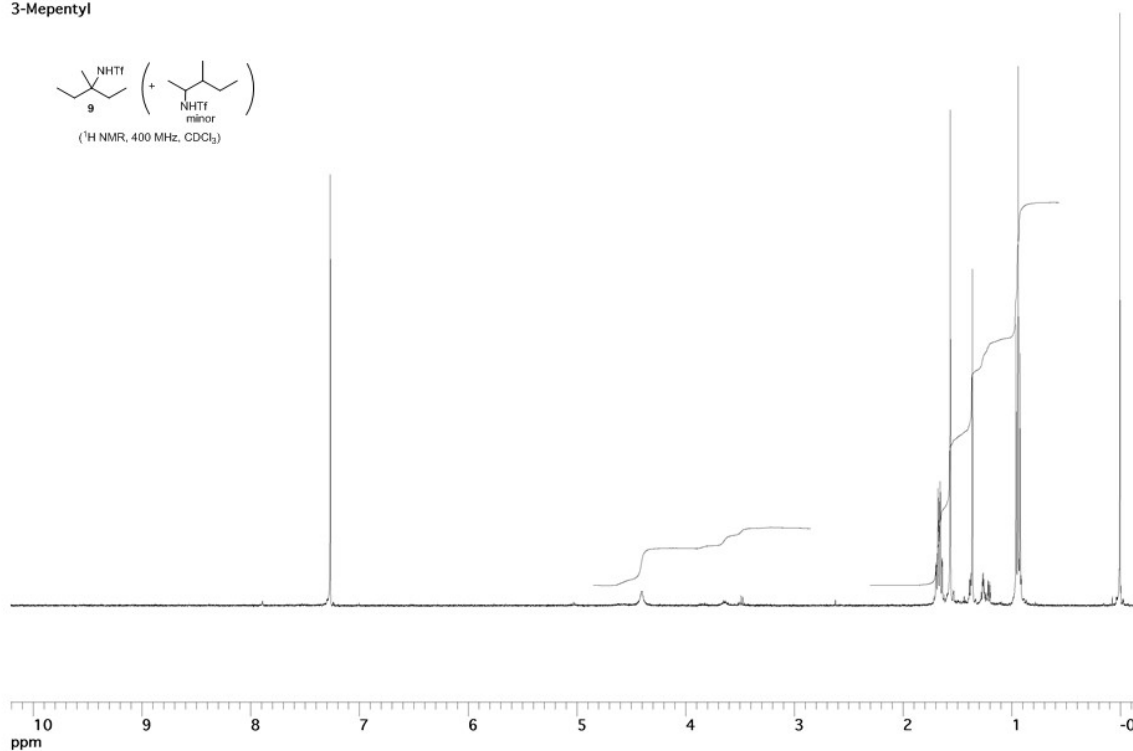
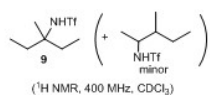
AL400
CDCL3/TMS
2,6-Dimethyl



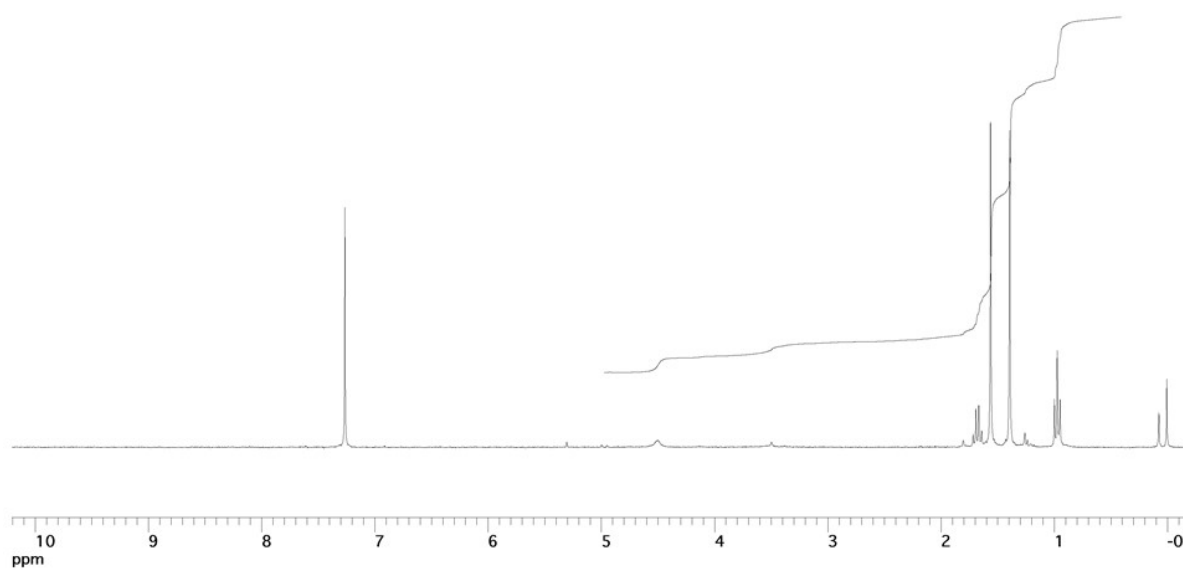
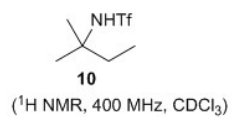
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(¹H NMR, 400 MHz, CDCl₃)

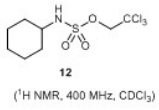
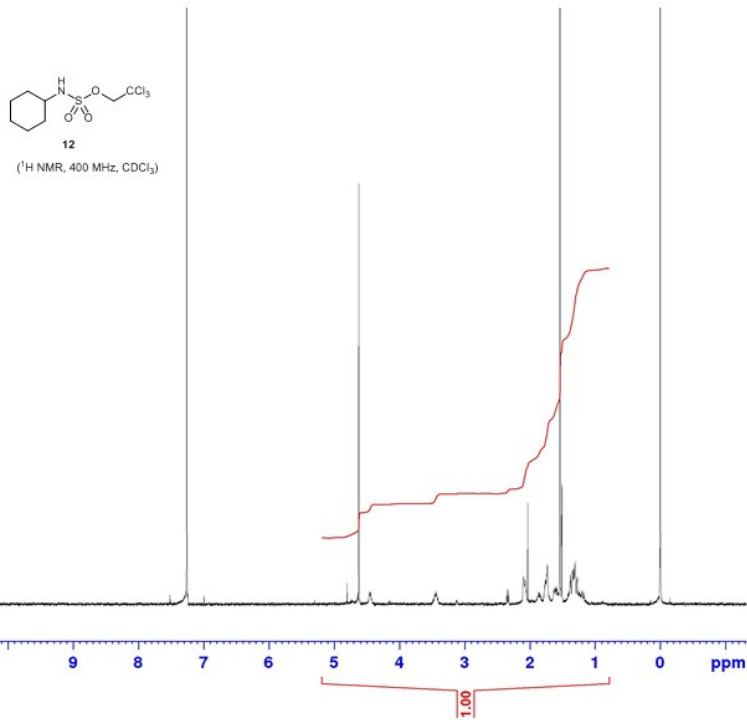


AL400
CDCL₃/TMS
3-Mepentyl

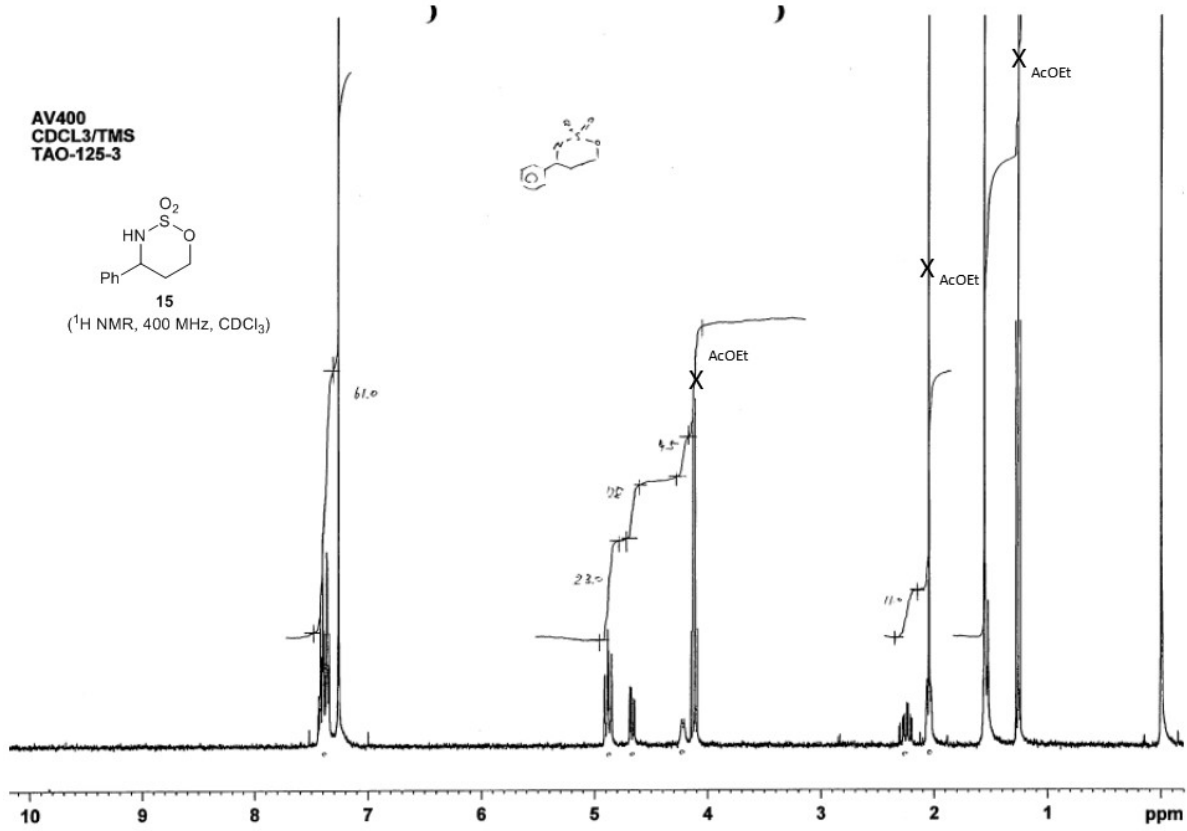


AL300
CDCL₃/TMS
2-MeBu





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AV400
 CDCL3/TMS
 TAO-125-3

