A convenient pathway to Sm(II)-mediated chemistry in acetonitrile

Todd Maisano, Kevin E. Tempest, Dhandapani V. Sadasivam, and Robert A. Flowers, II*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18064 USA

Fax: (+011) 610-758-6536, E-mail: rof2@lehigh.edu

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Materials and method: THF and acetonitrile were purified with a Pure Solv solvent purification system from Innovative Technology Inc. $Sm(OTf)_3$ was purchased from Alfa-Aesar and used without further purification. HMPA and DMPU were purified by distilling over calcium oxide and degassed with argon and stored in Innovative Technology, Inc. drybox containing argon atmosphere. UV-vis experiments were performed with a Shimadzu UV-1601 UV-vis Spectrophotometer controlled by UV Probe (version 1.11) software. Kinetic experiments in THF and acetonitrile were performed with a computer-controlled SX-18 MV stopped-flow reaction spectrophotometer (Applied Photophysics Ltd. Surrey, UK). Unless otherwise stated, reactions were performed under an inert atmosphere of argon. ^{13}C, and ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer. A Satellite FTIR from Thermo-Mattson was used to obtain IR spectra. GC-MS analysis was performed with an HP 5890 Series II Gas Chromatograph with an HP Mass Selector Detector.

UV-vis Studies:

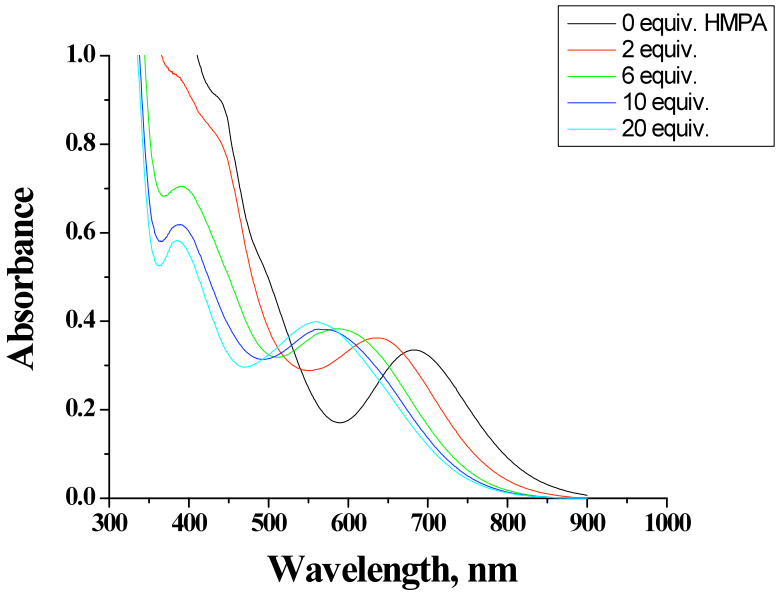


Figure S1. UV-vis spectra of SmI_2 with increasing equivalents of HMPA in CH_3CN, [SmI_2] = 1 mM

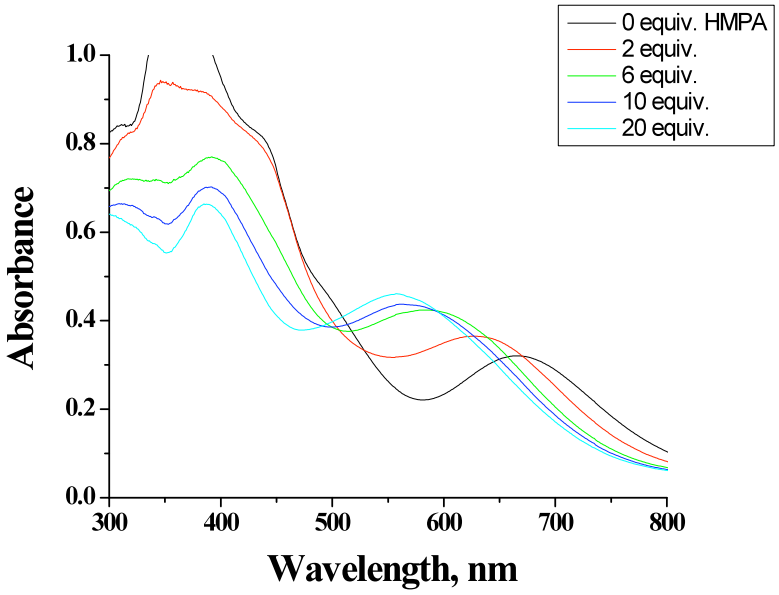


Figure S2. UV-vis spectra of $Sm(OTf)_2$ with increasing equivalents of HMPA in CH_3CN, $[Sm(OTf)_2]$ = 1 mM

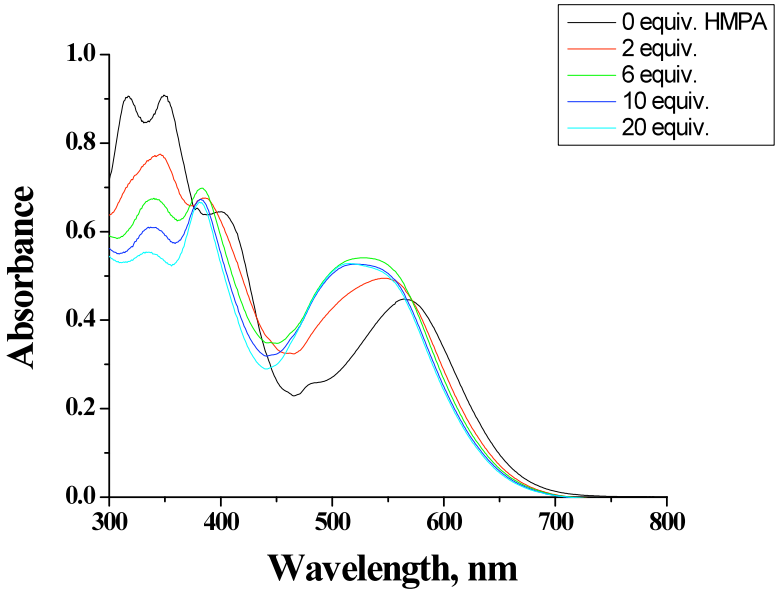


Figure S3. UV-vis spectra of $Sm(OTf)_2$ with increasing equivalents of HMPA in THF,$[Sm(OTf)_2]$ = 1 mM

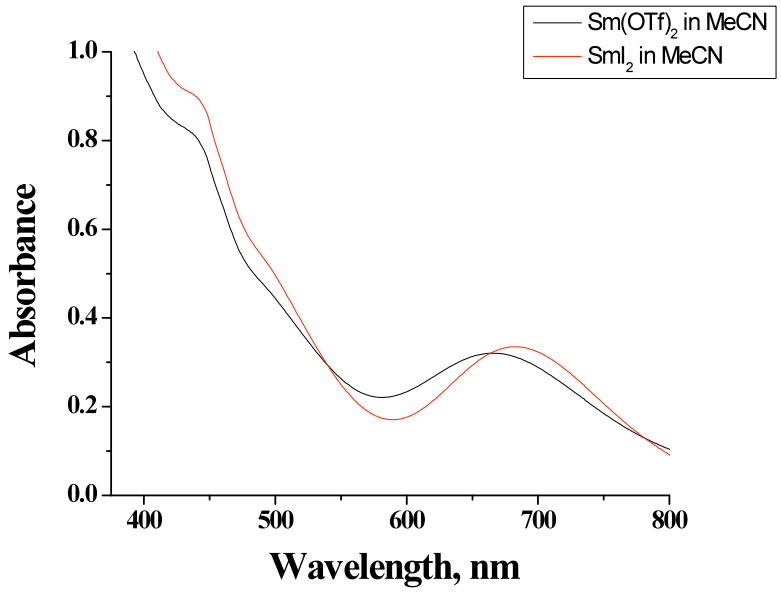


Figure S4. UV-vis spectra of $Sm(OTf)_2$ and SmI_2 with no additive, $[Sm(OTf)_2]$ = 1 mM, $[SmI_2]$ = 1 mM

Conductivity Studies:

Analytes: SmI_2, $Sm(OTf)_2$

Solvent: Acetonitrile; Additive: HMPA.

Instrument: OAKTON CON 10 Basic conductivity / TDS Meter

Procedure:

Calibration: Initially the instrument was calibrated with a standard solution of known conductivity. Then the probe was rinsed with water and finally with acetonitrile several times before taking measurements.

SmI_2: To SmI_2 / $Sm(OTf)_2$ (20 mL, 2.5 mM) under argon flow, HMPA was added sequentially and conductivity was measured.

Conductivity in THF

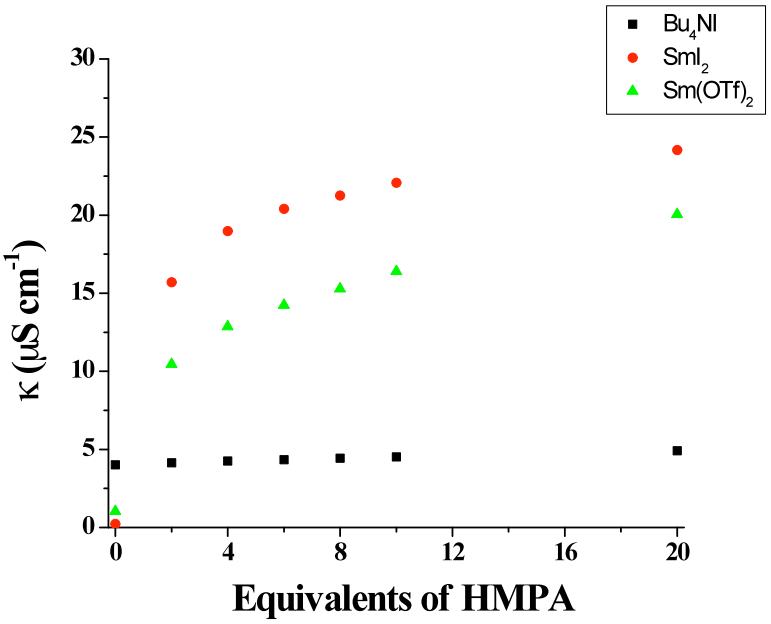


Figure S5. Conductivity of SmI_2 and $Sm(OTf)_2$ in THF with increasing equivalents of HMPA

Kinetics: SmI_2-THF-Benzyl bromide

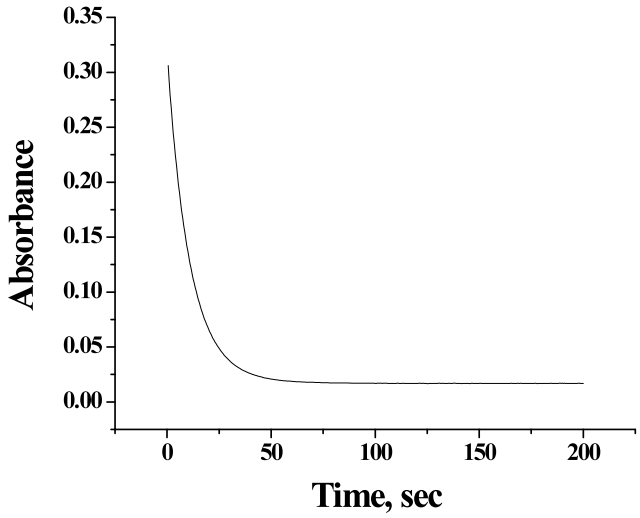


Figure S6. Representative decay of SmI_2 for the reduction of benzyl bromide under pseudo first-order conditions as monitored at 550 nm.

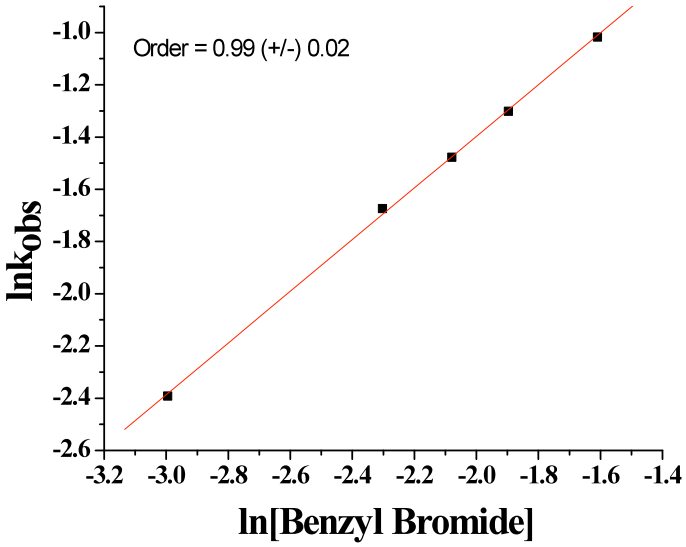


Figure S7. Plot of ln[benzyl bromide] versus ln k_{obs} for the reduction of benzyl bromide with SmI_2. Rate order of benzyl bromide=0.99. SmI_2 = 5 mM; Benzyl bromide = 10-40 equiv.

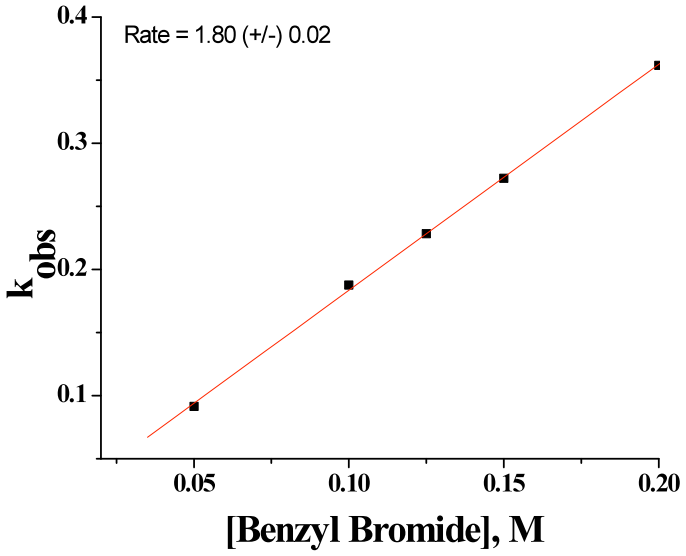


Figure S8. Plot of [benzyl bromide] versus k_{obs} for the reduction of benzyl bromide. Rate constant of for reduction of benzyl bromide = 1.80 ±0.03 $M^{-1}s^{-1}$. SmI_2 = 5 mM; Benzyl bromide = 10-40 equiv.

$Sm(OTf)_2$-THF-Benzyl bromide

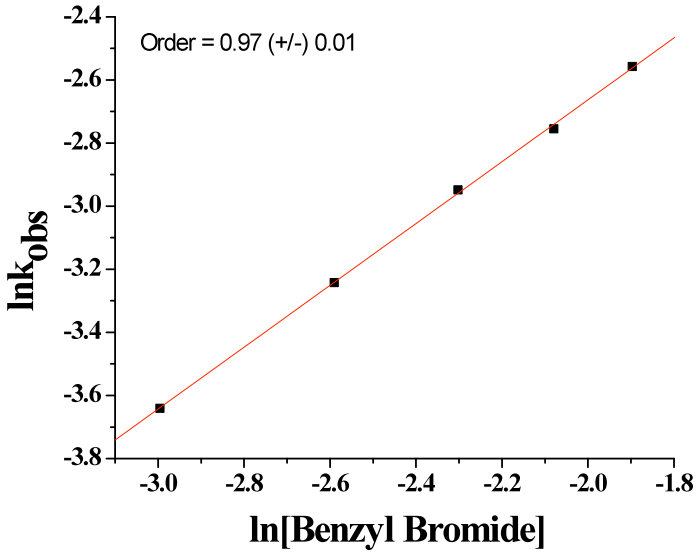


Figure S9. Plot of ln[Benzyl bromide] versus ln k_{obs} for the reduction of benzyl bromide with $Sm(OTf)_2$. Rate order of benzyl bromide= 0.97. $Sm(OTf)_2$ = 5 mM; Benzyl bromide = 10-40 equiv.

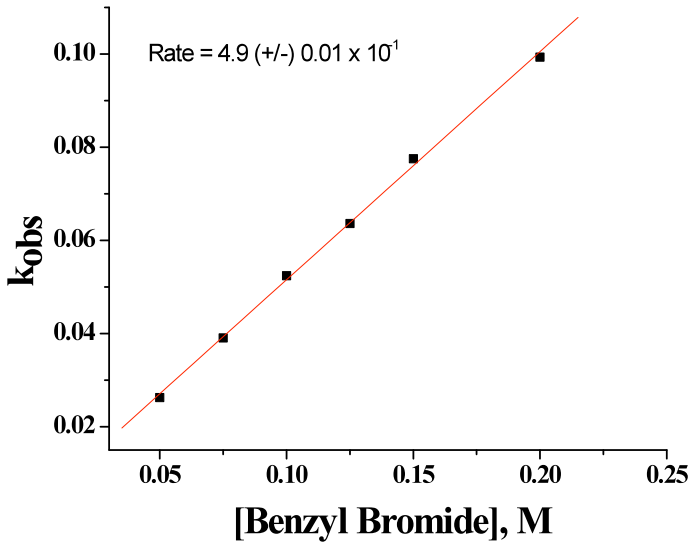


Figure S10. Plot of [benzyl bromide] versus k_{obs} for the reduction of benzyl bromide with $Sm(OTf)_2$. Rate constant of for reduction of benzyl bromide = 4.9 ± 0.01 x 10^{-1} $M^{-1}s^{-1}$. SmI_2 = 5 mM; Benzyl bromide = 10-40 equiv.

$Sm(OTf)_2$-THF-Acetophenone

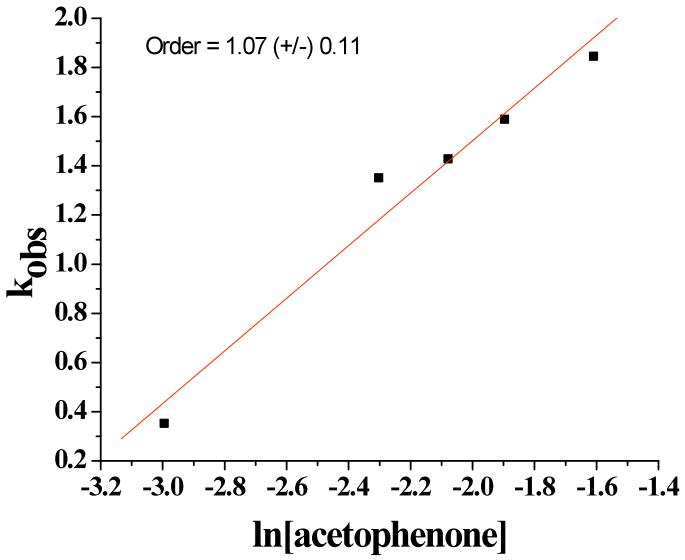


Figure S11. Plot of ln[acetophenone] versus ln k_{obs} for the reduction of acetophenone with $Sm(OTf)_2$. Rate order of acetophenone= 1.07. Sm(OTf)2 = 5 mM; acetophenone = 10-40 equiv.

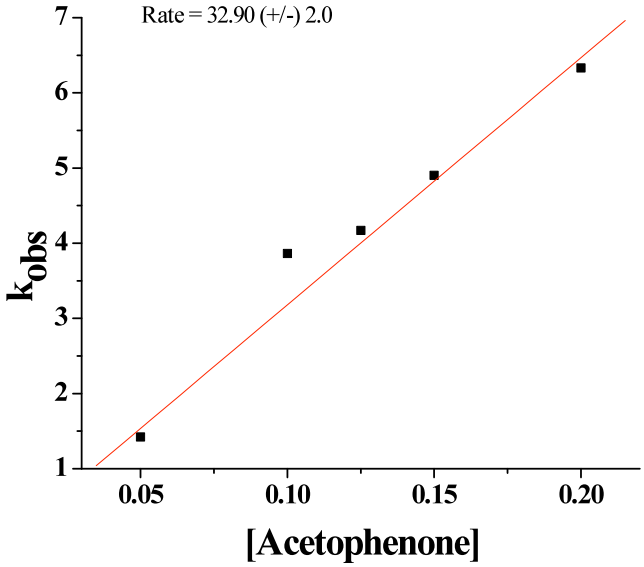


Figure S12. Plot of [acetophenone] versus k_{obs} for the reduction of acetophenone with $Sm(OTf)_2$. Rate constant of for reduction of acetophenone = 3.2 9±0.2 x 10^1 $M^{-1}s^{-1}$. $Sm(OTf)_2$ = 5 mM; acetophenone = 10-40 equiv.

SmI_2 in acetonitrile-Benzylbromide

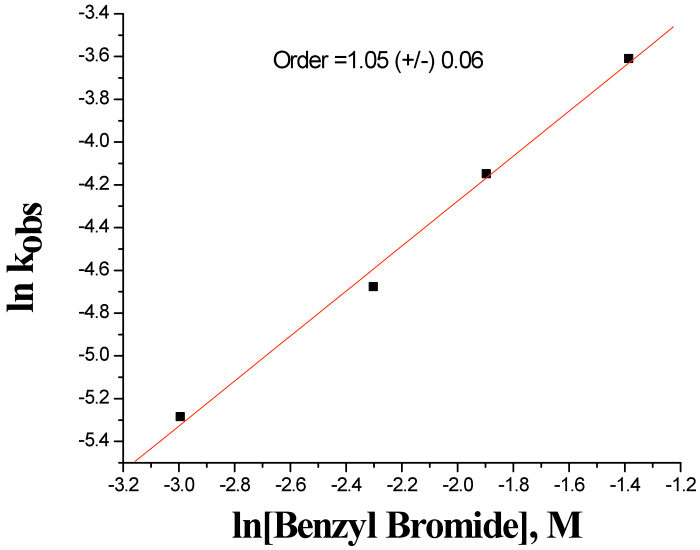


Figure S13. Plot of ln[Benzyl bromide] versus ln k_{obs} for the reduction of benzyl bromide with SmI_2. Rate order of benzyl bromide= 1.05±0.06. SmI_2 = 5 mM; Benzyl bromide = 10-50 equiv.

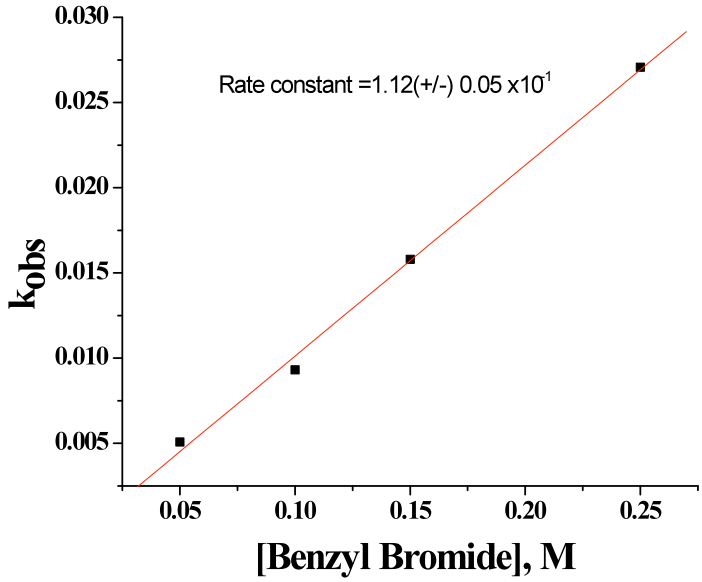


Figure S14. Plot of [benzyl bromide] versus k_{obs} for the reduction of benzyl bromide with SmI_2. Rate constant of for reduction of benzyl bromide = 1.12 ± 0.05x10^{-1} $M^{-1}s^{-1}$. SmI_2 = 5 mM; Benzyl bromide = 10-50 equiv.

SmI_2-Acetonitrile-Acetophenone

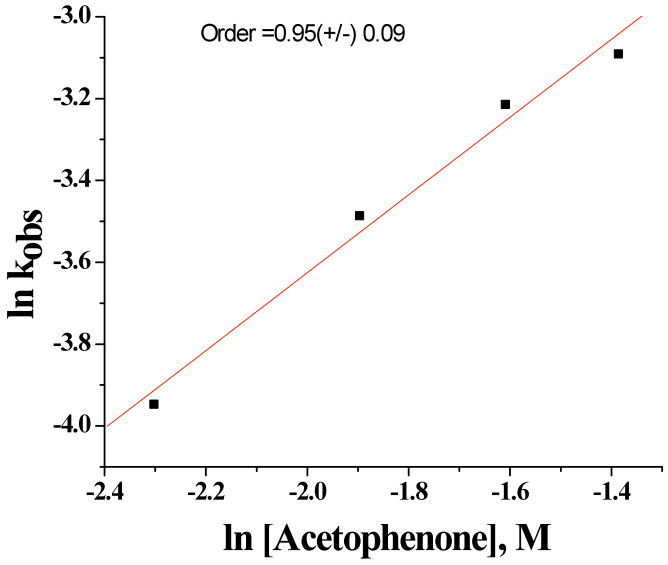


Figure S15. Plot of ln[acetophenone] versus ln k_{obs} for the reduction of acetophenone with SmI_2. Rate order of acetophenone= 1.04. SmI_2 = 5 mM; acetophenone = 10-50 equiv.

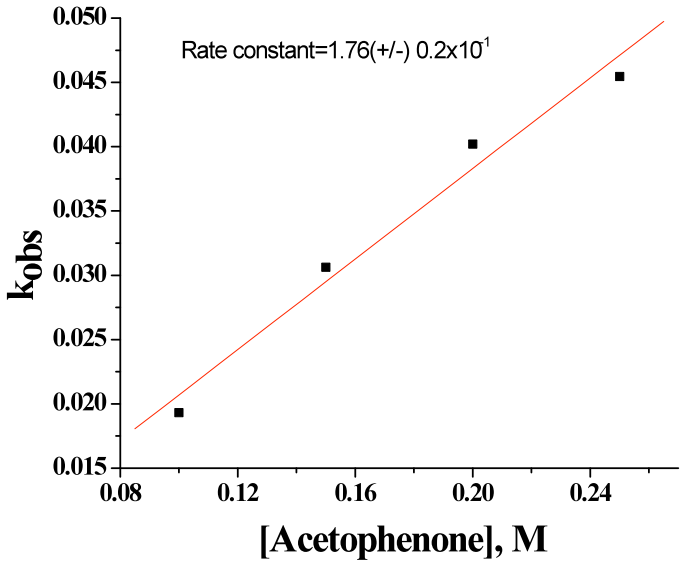


Figure S16. Plot of [acetophenone] versus k_{obs} for the reduction of acetophenone with SmI_2. Rate constant of for reduction of acetophenone =1.76±0.2 $M^{-1}s^{-1}$. SmI_2 = 5 mM; acetophenone = 10-50 equiv.

$Sm(OTf)_2$ in Acetonitrile -Benzyl bromide

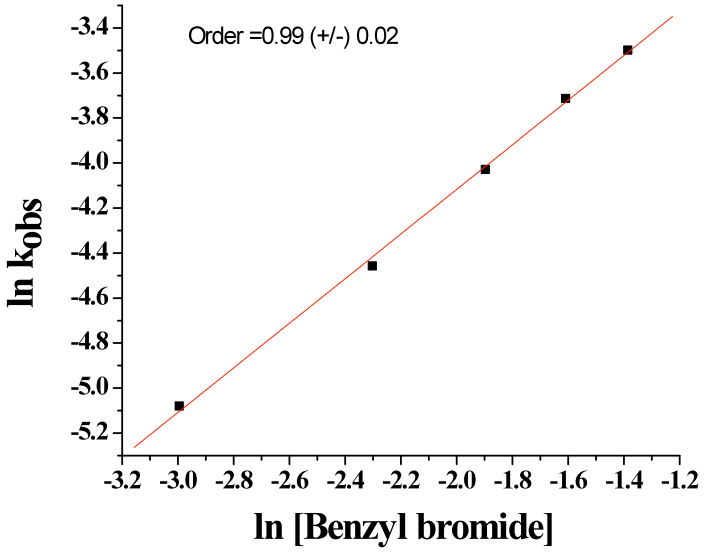


Figure S17. Plot of ln[Benzyl bromide] versus ln k_{obs} for the reduction of benzyl bromide with $Sm(OTf)_2$. $Sm(OTf)_2$ = 5 mM; Benzyl bromide = 10-50 equiv.

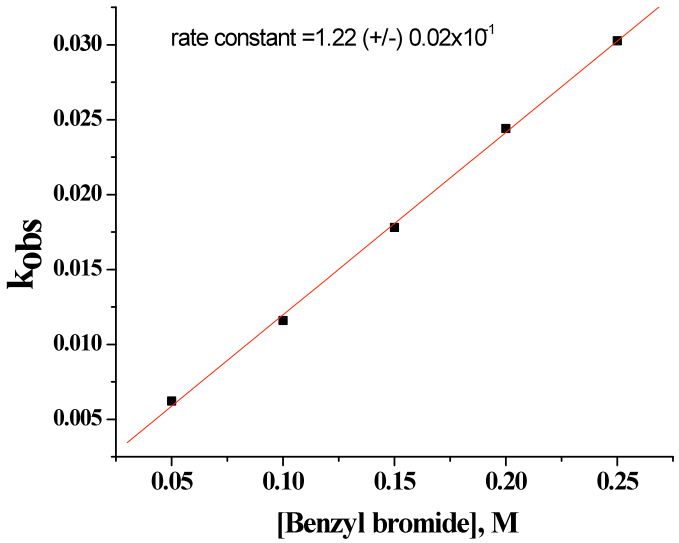


Figure S18. Plot of [benzyl bromide] versus k_{obs} for the reduction of benzyl bromide with $Sm(OTf)_2$. Rate constant of for reduction of benzyl bromide = 1.22 ± 0.02 $x10^{-1}M^{-1}s^{-1}$. $Sm(OTf)_2$ = 5 mM; Benzyl bromide = 10-50 equiv.

$Sm(OTf)_2$ in Acetonitrile -Acetophenone

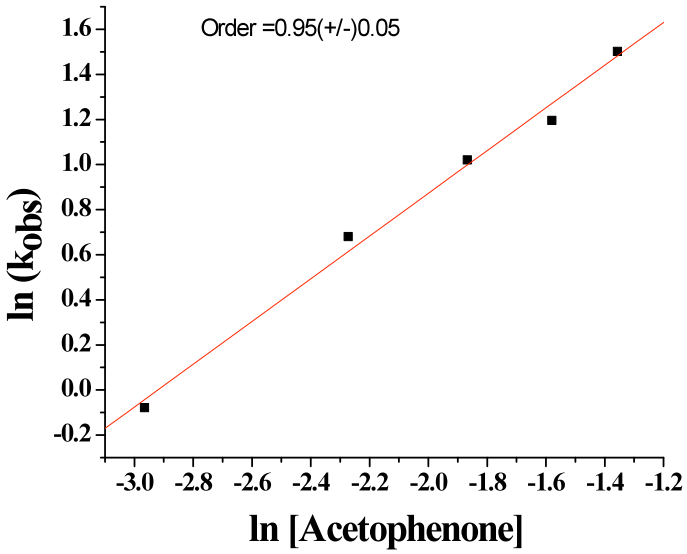
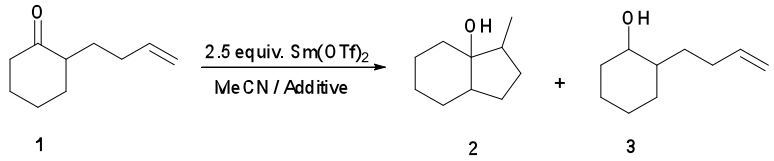


Figure S19. Plot of ln[Acetophenone] versus ln k_{obs} for the reduction of acetophenone with $Sm(OTf)_2$. $Sm(OTf)_2$ = 5 mM; Benzyl bromide = 10-50 equiv.

Generation of $Sm(OTf)_2$:

Samarium powder (40 mesh size, 0.265 g, 1.76 mmol), $Sm(OTf)_3$ (1.03 g, 1.72 mmol), and iodine (0.102 g, 0.4 mmol) were added to 20 mL of dry CH3CN in a flame-dried vial. The solution was then stirred inside glove box at room temperature for 3 hrs. A dark green solution of $Sm(OTf)_2$ was obtained with concentrations in the range of 0.09 0.10 M. The concentration of the solution was determined by iodometric titration.

Cyclization of olefinic ketone:



1 2 3

2-(3-Butenyl) cyclohexan-1-one (1): Compound **1** was synthesized using previously described procedure.[S1] ^{1}H NMR (500 MHz, CDCl3) δ 5.79- 5.71 (m, 1H), 4.99-4.90 (m, 2H), 2.34-1.20 (m, 13H).

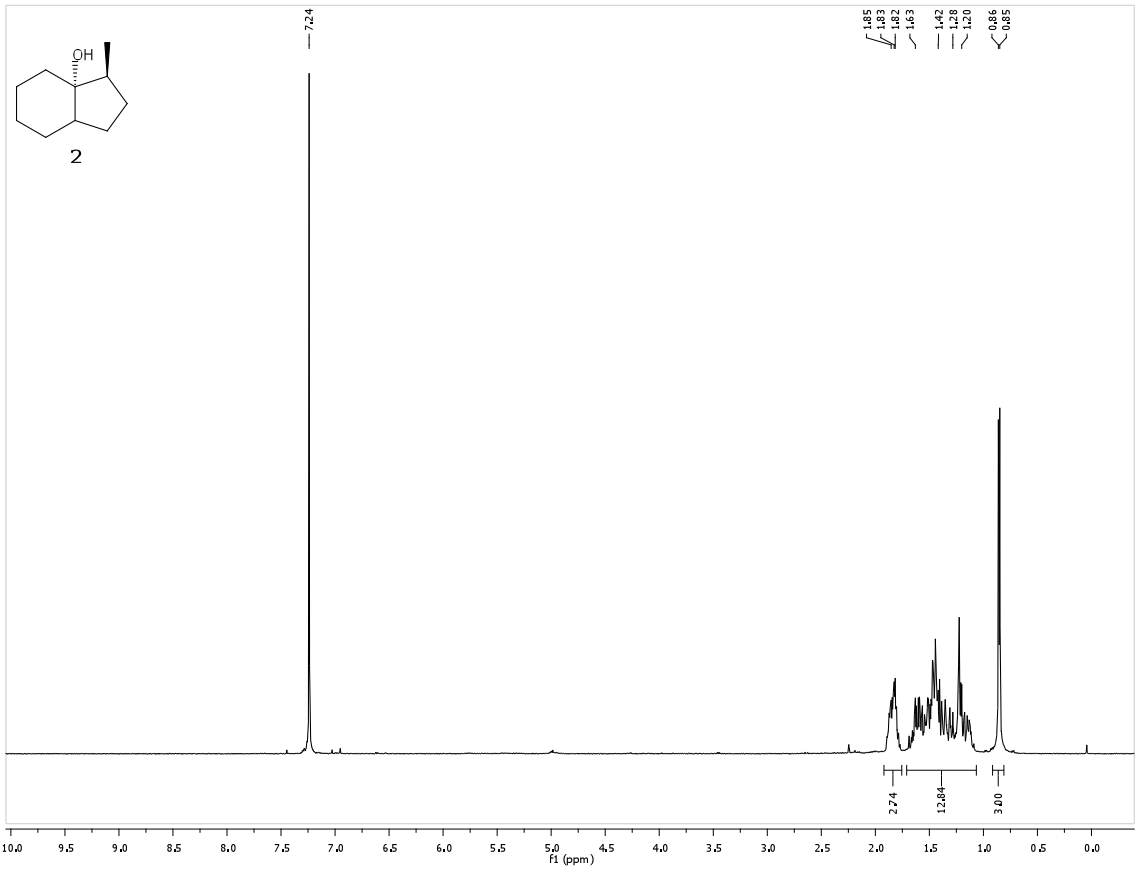
Representative procedure for cyclization reaction:

To a flame dried 50 mL round bottomed flask, 9.31 mL of $Sm(OTf)_2$ (0.09 M, 0.82 mmol, 2.5 equiv) was added. To this a 2 mL acetonitrile solution of HMPA/additive (0.143 mL, 8.2 mmol, 10 equiv w. r. to $Sm(OTf)_2$) was added under stirring. This was followed by drop-wise addition of 2 mL acetonitrile solution of cyclic alkene (**3**) (0.050 g, 0.33 mmol) and the mixture was continued to stir inside the glove box until the completion of reaction. The reaction was quenched by opening to air followed by addition of 10 mL of saturated NH_4Cl. The aqueous layer was extracted with 3 X 25 mL ether and combined organic layer was washed with water and brine and dried over magnesium sulphate. The dried organic layer was concentrated *in vacuo* and the crude product was analyzed by NMR. The products were identified by comparison with published data.[S1]

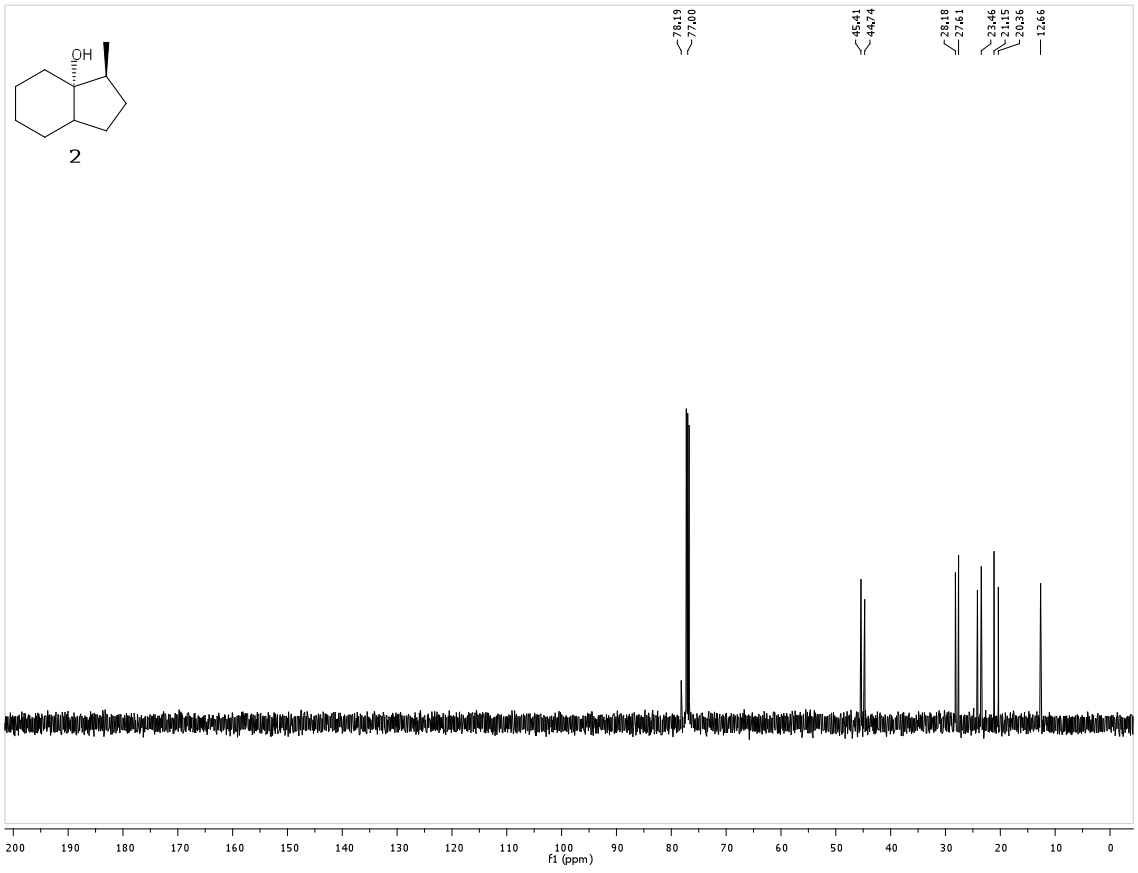
9-Methylbicyclo[4.3.0]nonan-1-ol (**2**):

^{1}H-NMR (500 MHz, CDCl3) δ 1.12-1.89 (m, 15 H), 0.84 (d, J=6.4 Hz, 3H); ^{13}C-NMR (125 MHz, CDCl3) δ 78.19, 45.41, 44.74, 28.18, 27.61, 24.16, 23.46, 21.15, 20.36, 12.66; IR ν 3398, 2932, 2871, 1459, 1006; LRMS *m/z* 154 (M^+, 18%), 111 (100%), 98 (90%), 83 (37%), 55 (73%).

^{1}H-NMR Spectrum of **2**:



^{13}C-NMR Spectrum of **2**:



References:

S1. Molander, G. A.; Mckie, J. A. *J. Org. Chem.* **1992**, *57*, 3132-3139.