Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Supporting Information

Proton Donor Effects on the Reactivity of SmI_2. Experimental and Theoretical Studies on Methanol Solvation *vs.* Aqueous Solvation

Alejandro Ramírez-Solís[a]*, Caroline O. Bartulovich,[b] César Iván León-Pimentel[c], Humberto Saint-Martin[c], Nicholas G. Boekell,[b] and Robert A. Flowers II[b*]

[a]Depto. de Física, Centro de Investigación en Ciencias-IICBA Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos 62209 México. [b]Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015, United States

[c]Instituto de Ciencias Físicas, UNAM. Cuernavaca, Morelos. 62210 México.

2. Instrumentation

Proton NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Carbon NMR were performed at 125 MHz in CDCl3. GC-MS analyses were done with an HP 5890 Series II Gas Chromatograph with an HP Mass Selector Detector. GC analyses were done using a Shimadzu Gas Chromatograph GC-14B with biphenyl standard. UV-Visible spectra experiments were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). The solutions were injected separately into the stopped-flow system from airtight Hamilton syringes prepared in a glove box. The cell block and the drive syringes of the stopped flow reaction analyzer were flushed a minimum of three times with dry, deoxygenated THF to make the system anaerobic. Between each experiment, the cell block was washed with dilute HNO_3 (2x), Deionized H_2O (3x), and THF (3x) before additional anhydrous deoxygenated THF washes (3x).

3. Materials for Synthetic Studies

Samarium powder was purchased from Acros Organics. SmI_2 was generated by the standard method of samarium metal combined with iodine in THF and allowed to stir for at least 4 hours.[S1] Iodometric titrations were performed to verify concentration of SmI_2. Acenaphthylene was purchased from Alfa Aesar and used without further purification. Tetrahydrofuran was purified by a Solvent Purification system (Innovative Technology Inc.; MA).

4. Synthetic Yields

Table S1: Reduction of substrates by SmI_2-MeOH

Entry [a]	**Substrate**	**Yield (%)**
1	acenaphthylene	92[b]

[a]Conditions: 3 eq SmI_2, 10 eq MeOH vs Sm, rt, overnight. [b] GC yield.

Synthetic Procedure for the GC Yield

Inside an Ar glove box, the quantity of substrate (15 mg acenaphthylene, 0.1 mmol) given above was combined with the listed quantity of SmI_2 in a vial with a magnetic stirrer. The vial was removed from the box and THF was removed via rotary evaporation. Biphenyl-containing ether extraction solvent added along with 0.1 M HCl solution.

Workup Procedure for Isolated Product

1,2-dihydroacenaphthylene was extracted using ether and washed with water. The organic layer was then treated with saturated aqueous sodium thiosulfate, and then brine. The remaining solution was then dried with magnesium sulfate, filtered and then solvent was removed by rotary evaporation. The resulting product was then placed under a high vacuum system to ensure complete removal of solvent. 9,10-dihydrophenanthrene was analyzed by 1 H NMR (400 MHz, CDCl3) δ (ppm): 3.4, 7.30, 7.46, 7.61 ; 13C NMR (125 MHz, CDCl3) δ (ppm): 30.43, 119.20, 122.40, 127.84, 131.51, 139.30, 146.22

5. Kinetic Conditions for SmI_2-MeOH Reductions:

Kinetic experiments were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). The SmI_2, substrate, and MeOH solutions were injected separately into the stopped-flow system from airtight Hamilton syringes prepared in a glove box. The cell block and the drive syringes of the stopped flow reaction analyzer were flushed a minimum of three times with dry, degassed THF to make the system anaerobic. The reaction rates were determined from the decay of SmI_2 at 560 nm. Unless specified otherwise, all kinetic measurements for the reduction of acenaphthylene were carried out at 25 °C.

6. Kinetic Conditions and Data for SmI_2-MeOH-Acenaphthylene:

All kinetic data in this section was measured under the conditions described in Section 5, unless specified.

Order and Rate Constant of Acenaphthylene:

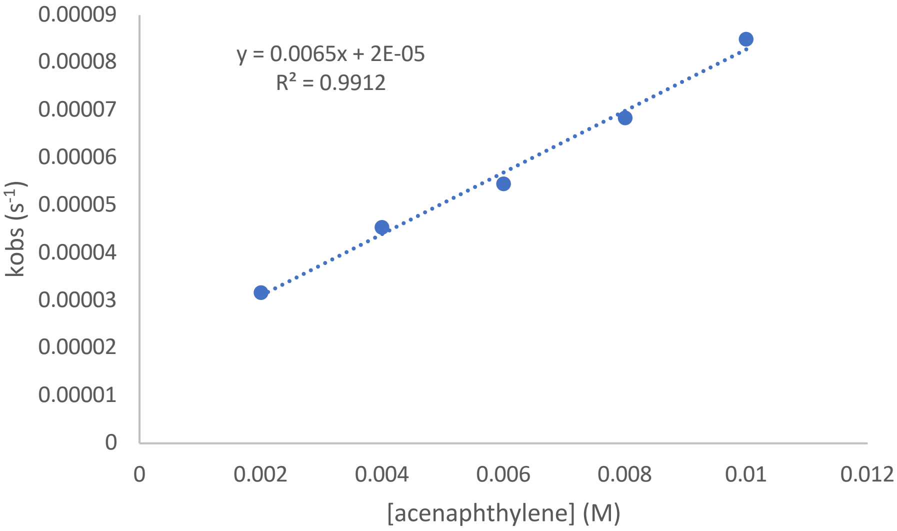


Figure S1. Plot of k_{obs} vs. concentration of acenaphthylene with 6 mM SmI_2 and 60 mM MeOH where [acenaphthylene] is varied from 0.002 M to 0.008M and a linear regression provides y =

0.006x+0.00002 with $R^2 = 0.9941$

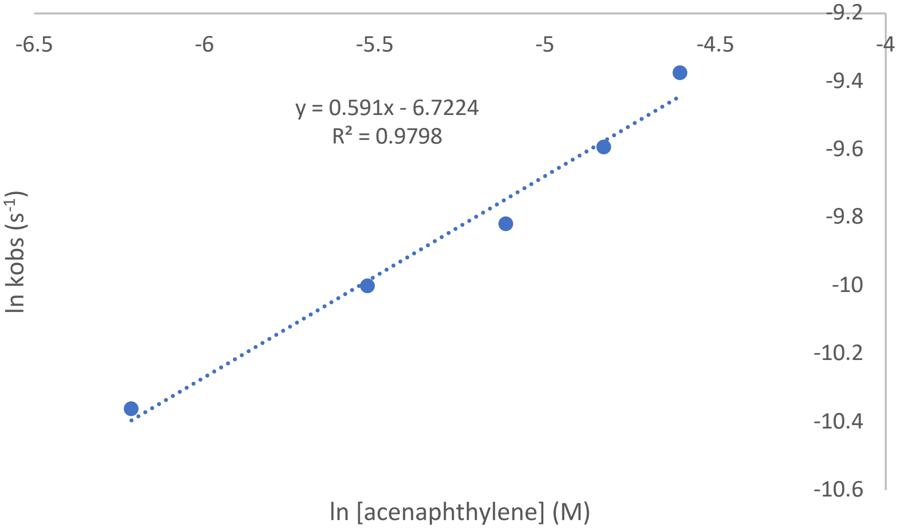


Figure S2. Natural log plot for k_{obs} vs. [acenaphthylene] where the rate order is provided by a linear regression where y = 0.59x + 6.7224 with $R^2 = 0.9798$.

Order of SmI_2

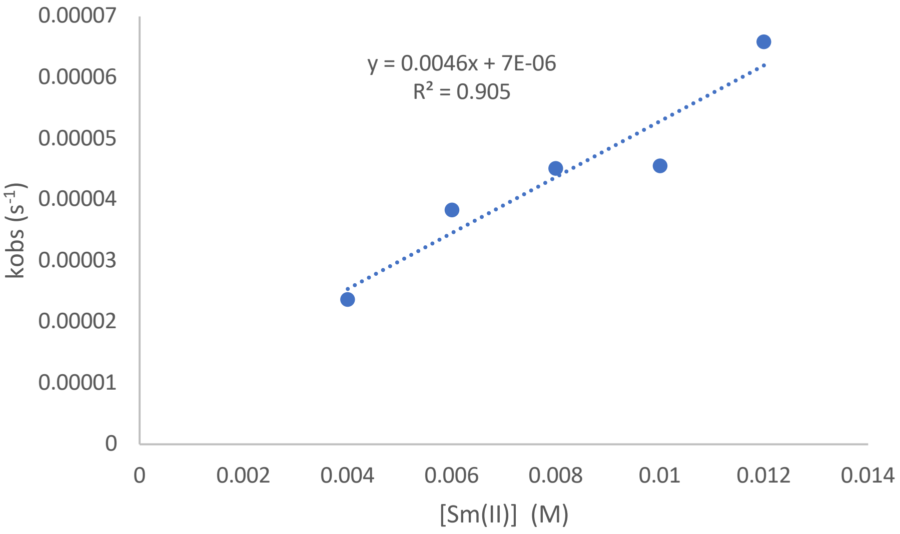


Figure S3. Plot of k_{obs} vs. concentration of SmI_2 with 60 mM MeOH and 2 mM acenaphthylene where [Sm(II)] is varied from 0.004 M to 0.012M and a linear regression provides y = 0.0046x+ 7E-06 with $R^2 = 0.905$

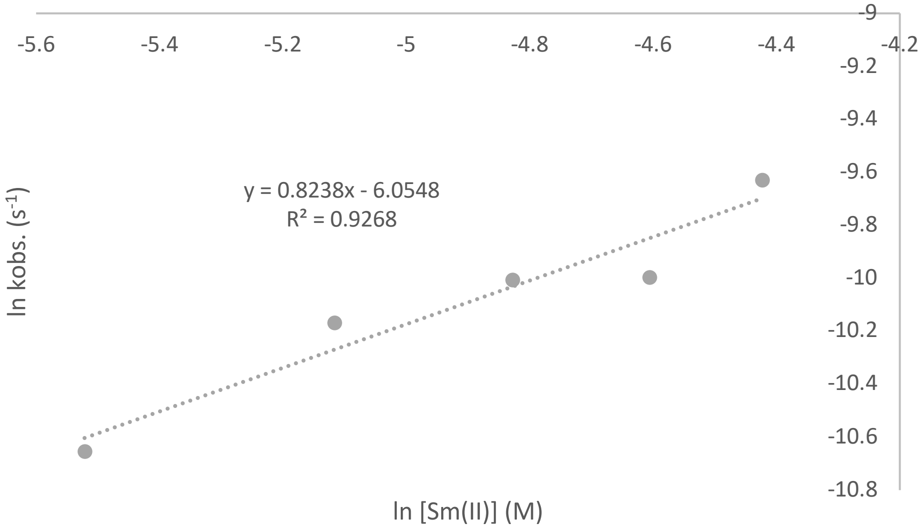


Figure S4. Natural log plot for k_{obs} vs. [Sm(II)] where the rate order is provided by a linear regression where y = 0.8238x + 6.0548 with $R^2 = 0.9268$.

7. Kinetic Conditions for SmI_2-H_2O Reductions:

Kinetic experiments were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). The $SmBr_2$, substrate, and water solutions were injected separately into the stopped-flow system from airtight Hamilton syringes prepared in a glove box. The cell block and the drive syringes of the stopped flow reaction analyzer were flushed a minimum of three times with dry, degassed THF to make the system anaerobic. The reaction rates were determined from the decay of SmI_2 at 560 nm. Unless specified otherwise, all kinetic measurements for the reduction of acenaphthylene were carried out at 25 °C.

Sample Decay SmI_2-H_2O-Acenaphthylene:

Order of Water:

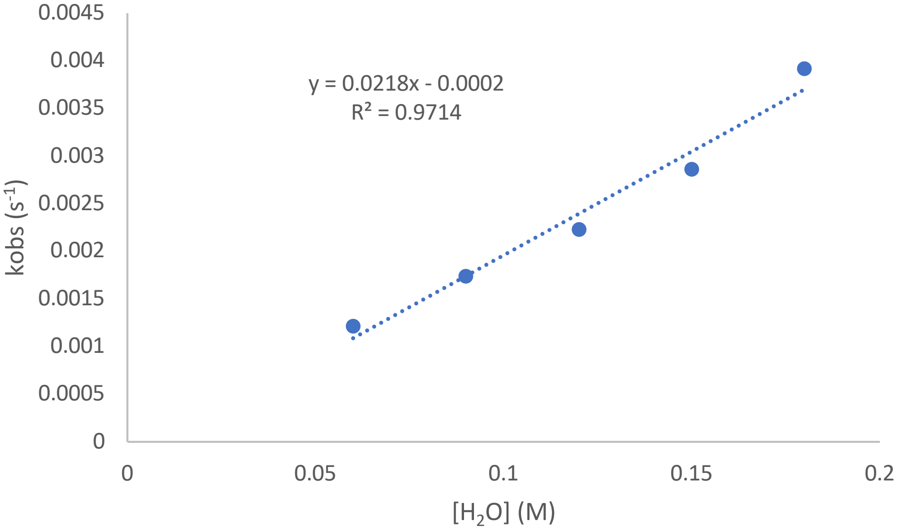


Figure S5. Plot of k_{obs} vs. concentration of H_2O with 2mM acenaphthylene and 6 mM SmI_2 where [H_2O] is varied from 0.06 M to 0.18M and a linear regression provides y = 0.00218x+ 0.0002 with $R^2 = 0.9714$

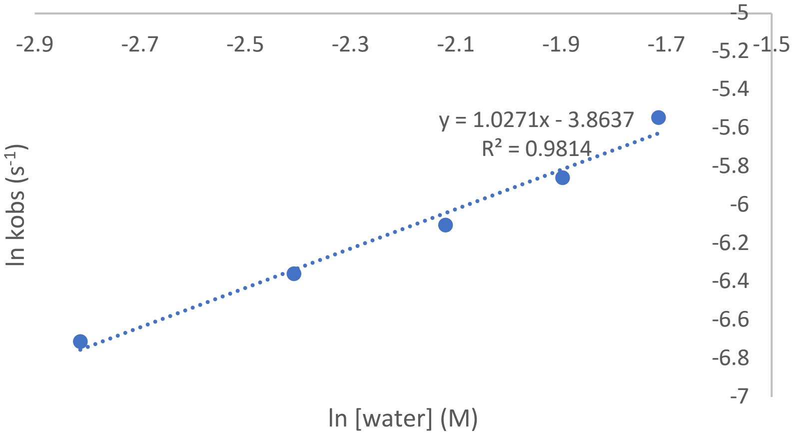


Figure S6. Natural log plot for k_{obs} vs. [water] where the rate order is provided by a linear regression where y = 1.0271x + 3.837 with $R^2 = 0.9814$.

Order and Rate Constant of Acenaphthylene

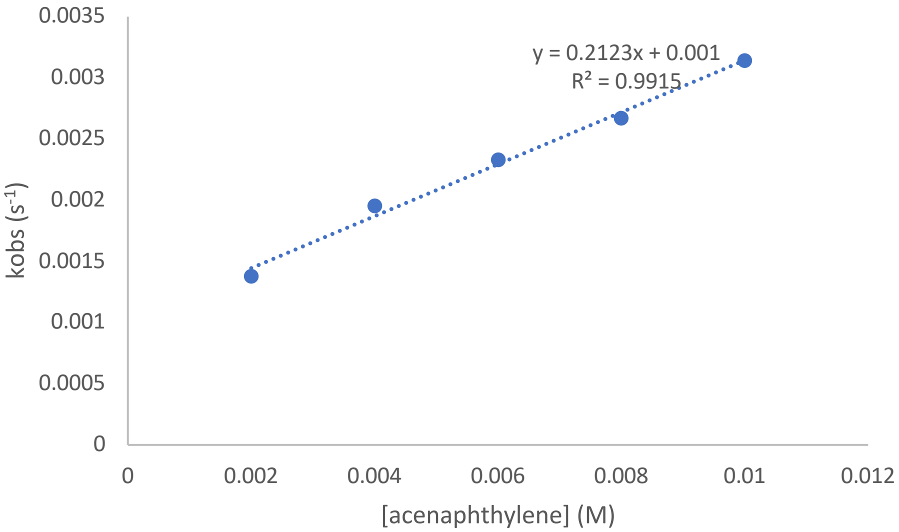


Figure S7. Plot of k_{obs} vs. concentration of acenaphthylene with 60 mM water and 6 mM SmI_2 where [acenaphthylene] is varied from 0.002 M to 0.01M and a linear regression provides y = 0.2123x+ 0.001 with $R^2 = 0.9915$

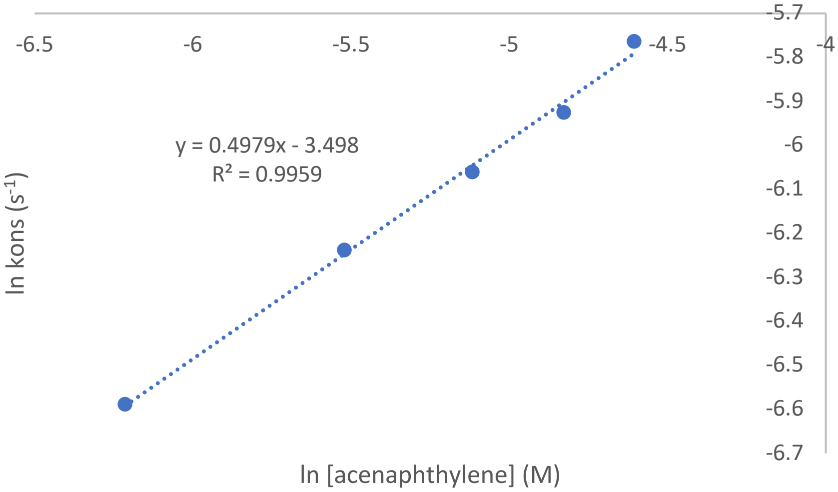


Figure S8. Natural log plot for k_{obs} vs. [acenaphthylene] where the rate order is provided by a linear regression where y = 0.4979x + 3.498 with $R^2 = 0.9959$.

Order of SmI_2

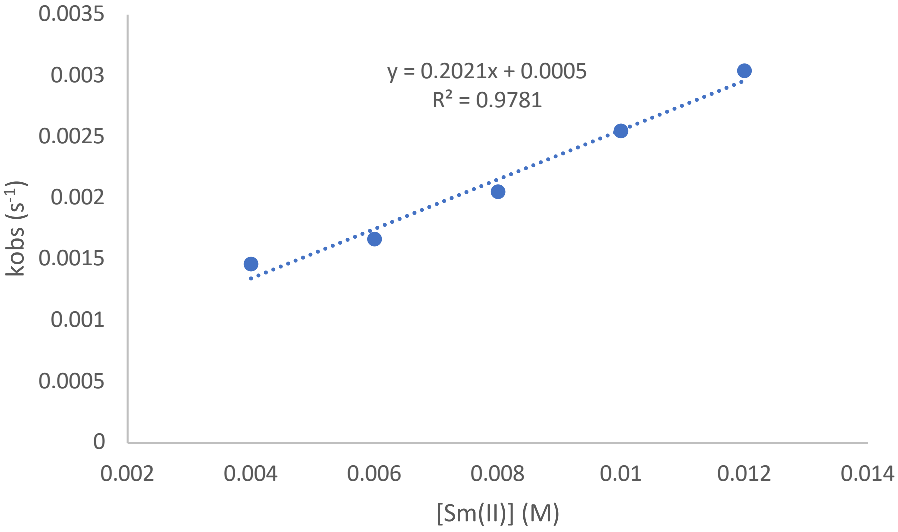


Figure S9. Plot of k_{obs} vs. concentration of SmI_2 with 60 mM water and 2 mM acenaphthylene where [Sm(II)] is varied from 0.004 M to 0.012M and a linear regression provides y = 0.2021x+ 0.0005 with $R^2 = 0.9781$

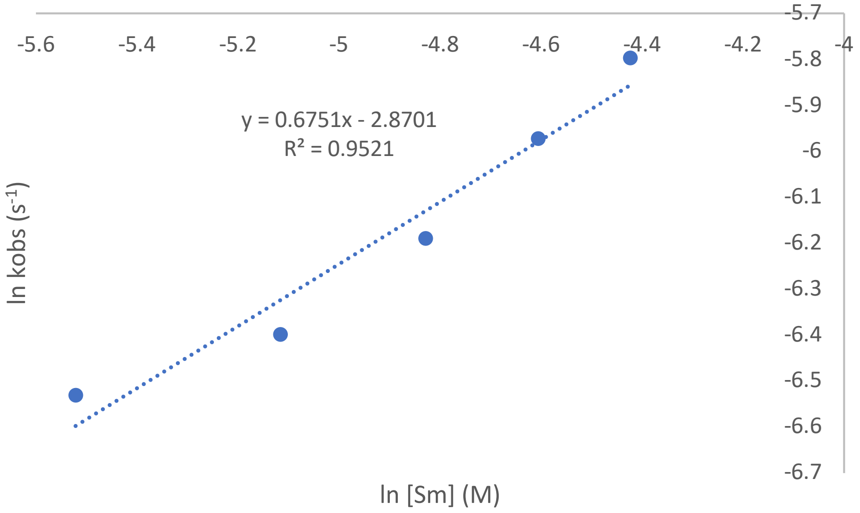


Figure S10. Natural log plot for k_{obs} vs. [SmI_2] where the rate order is provided by a linear regression where y = 0.6751x + 2.8701 with $R^2 = 0.9521$.

8. UV-Vis Spectra of SmI_2

Spectra were obtained using the Spectra setting for the stopped-flow spectrophotometer (described in Section 2) so that one solution of SmI_2 could be generated for one syringe and would remain at a constant concentration while concentration of additive or substrate was changed in the other syringe. All spectra were measured at 25 °C.

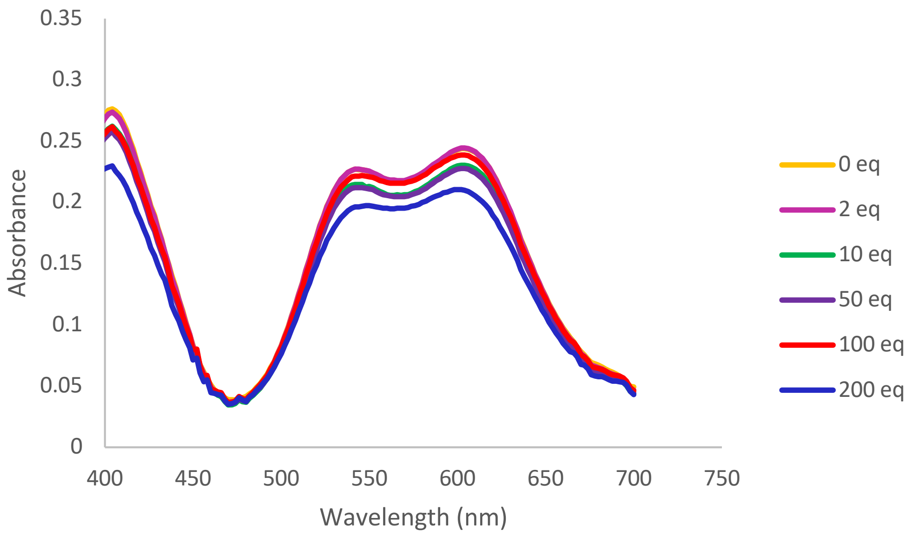
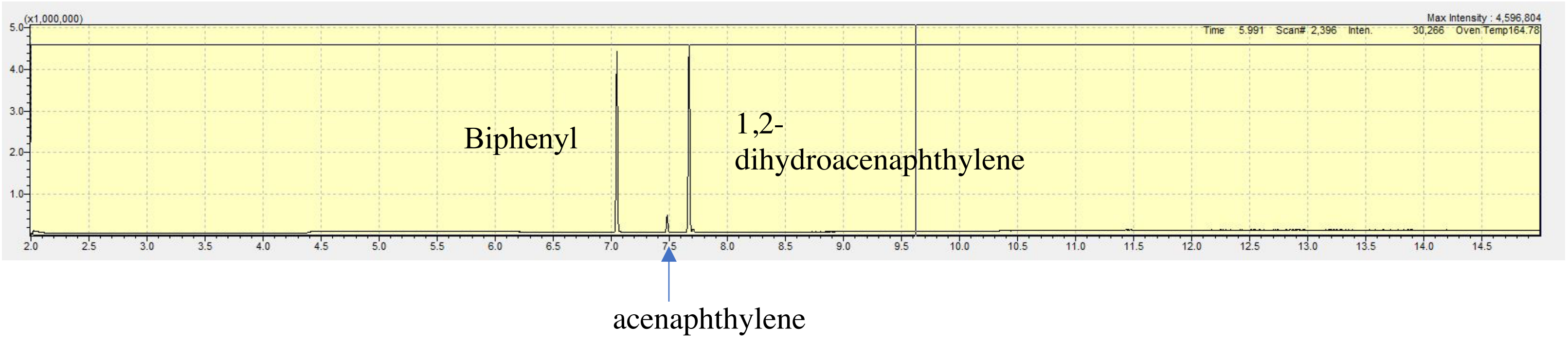


Figure S11. UV-vis spectra of 2.5 mM SmI_2 in the presence of increasing amounts of MeOH (0, 2, 10, 50, 100, and 200 equivalents vs SmI_2).

9. GC-Chromatograms of Yield



10. NMR Spectra

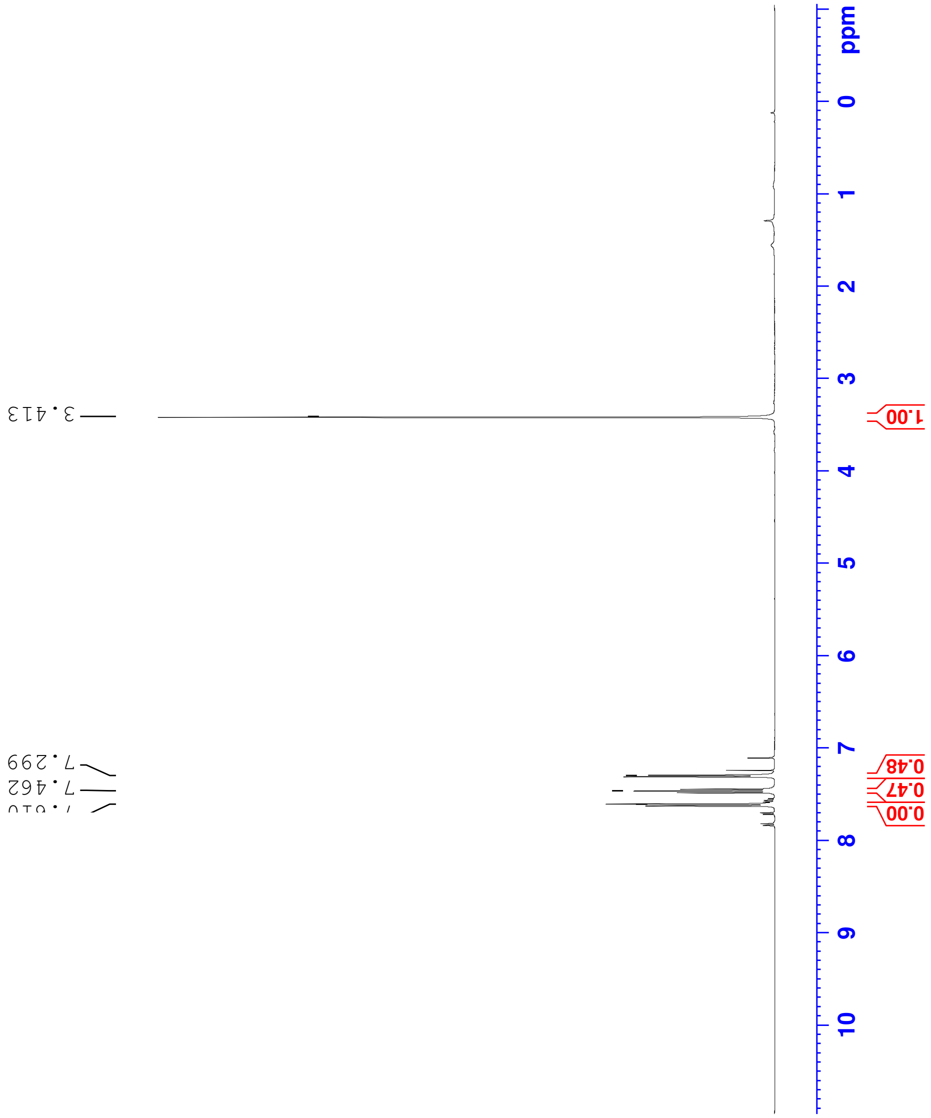


Figure S12. ^{1}H NMR spectra of 1,2-dihydroacenaphthylene

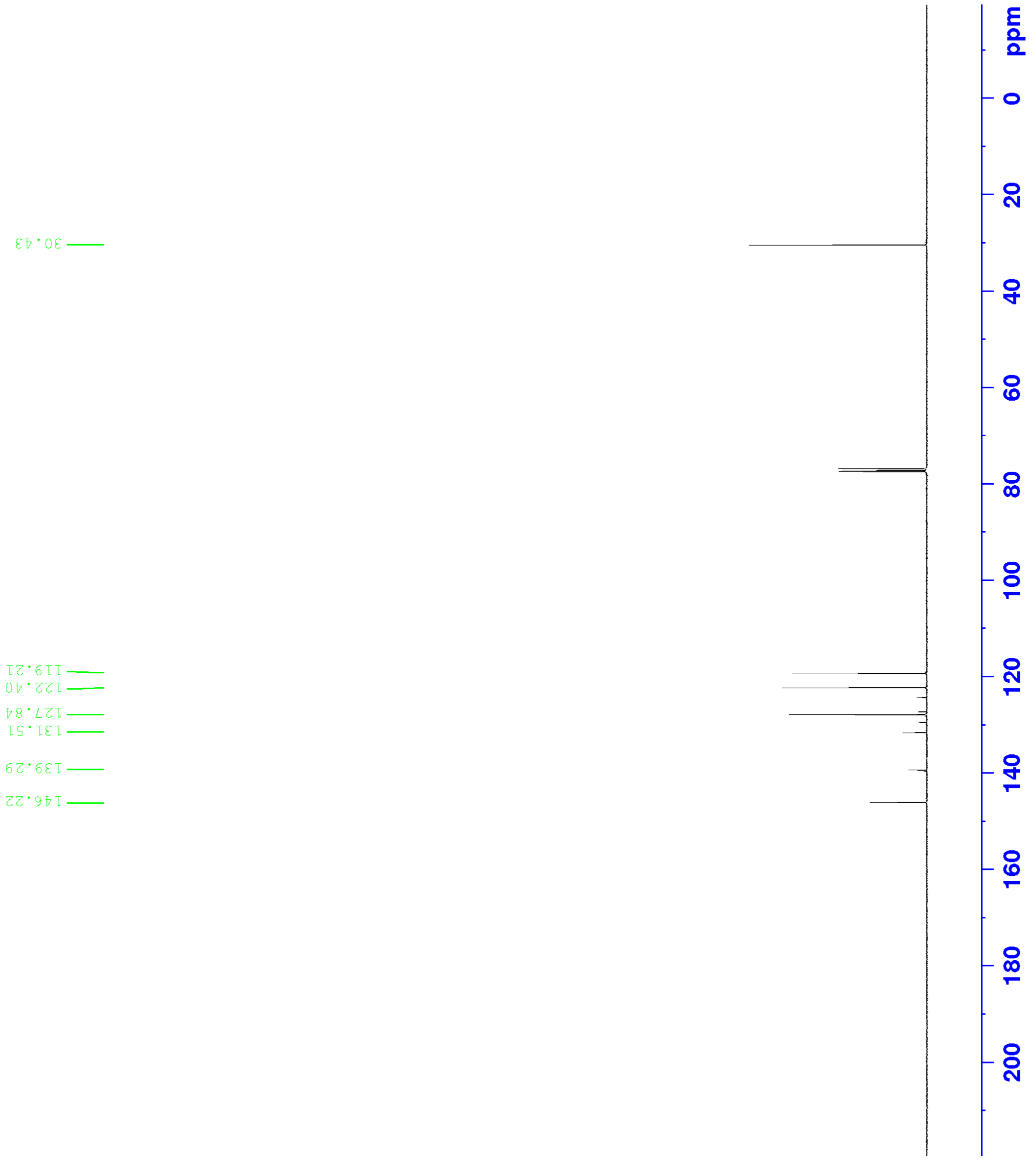


Figure S13. ^{13}C NMR spectra of 1,2-dihydroacenaphthylene

11. References

S1) Imamoto, T.; Ono, M. Chem. Lett. 1987, 501–502.