Accessing Unusual Reactivity through Chelation-Promoted Bond Weakening

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Supporting Information

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1. Instrumentation:

Proton NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Carbon NMR were performed at 125 MHz in $CDCl_3$. GC-MS analyses were performed with a Shimadzu GCMS-QP2010 Ultra. GC analyses were performed using a Shimadzu Gas Chromatograph GC-2010 Plus with biphenyl as an internal standard. Kinetic experiments were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). The kinetic 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), DI H_2O (3x), and THF (3x) before additional anhydrous deoxygenated THF washes (3x). The reaction rates were determined from the decay of $SmBr_2$ at 540 nm.

2. Materials for Synthetic and Kinetic 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.[1] Iodometric titrations were performed to verify concentration of SmI_2. 1-methoxynaphthalene was purchased from Alfa Aesar. All chemicals were used without further purification. Substrates were stored over sieves and deoxygenated prior to use. Tetrahydrofuran was purified by a Solvent Purification system (Innovative Technology Inc.; MA).

3. Experimental Methods:

Procedure for Preparation of $SmBr_2$

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. The solution of SmI_2 was then allowed to settle and the supernatant was withdrawn and added to a flame dried vial equipped with a magnetic stir bar. This solution was further charged with four equivalents of either tetrabutylammonium bromide (TBABr) or LiBr and allowed to stir for 15 minutes until the solution was observed to change color from the characteristic blue of SmI_2 to the deep purple of samarium dibromide ($SmBr_2$).

Synthetic Procedure for the GC Yield:

Substrate (0.33 mmol arenes, 0.2 mmol esters, 0.33 mmol alkynes, 0.33 mmol N-containing substrates) was added to a 10 mL solution of 0.1 M $SmBr_2$ in a flame dried vial equipped with a magnetic stir bar under an argon atmosphere. Under stirring, NMEA (15 mmol, 1.2 mL) was added to the solution, which was allowed to react until discoloration of the characteristic purple of $SmBr_2$ was observed. Quenching of the solution in air and with 0.1 M HCl was followed by the addition of biphenyl (0.33 mmol, 0.051 g for arenes, alkynes, and N-containing substrates; 0.031 g for esters). The solution was then extracted into diethyl ether and dried over magnesium sulfate. The dry solution was then analyzed by GCMS.

Synthetic Procedure for Product Isolation:

Substrate (0.33 mmol arenes, 0.2 mmol esters, 0.33 mmol alkynes) was added to a 10 mL solution of 0.1 M $SmBr_2$ in a flame dried vial equipped with a magnetic stir bar under an argon atmosphere. Under stirring, NMEA (15 mmol, 1.2 mL) was added to the solution, which was allowed to react until discoloration of the characteristic purple of $SmBr_2$ was observed. Quenching of the solution in air and with 0.1 M HCl was followed by extraction into diethyl ether and drying of the combined organic layers over magnesium sulfate. The dry solution was then concentrated under reduced pressure.

Synthetic Procedure for Ester Olefin Cyclization with $SmBr_2$-NMEA:

Substrate (0.25 mmol) was reacted with 1.5 mmol of $SmBr_2$ and 6 mmol of NMEA at room temperature in dry and degassed THF for 24 hrs. Quenching of the solution in air and with 0.1 M HCl was followed by extraction into dichloromethane and drying of the combined organic layers over magnesium sulfate. Organic layers were concentrated over reduced pressure for NMR of crude samples. The products were purified with column chromatography using silica as stationary phase and hexanes/ethyl acetate as eluting solvent.

13 C NMR Data of the Products:

2-benzyl-5-methylcyclopentan-1-ol:
^{1}H NMR: 1H NMR: 7.36-7.16 (m, 5H); 3.81-3.67 (m, 1H); 2.94-2.52 (m, 2H); 2.26-1.06 (m, 5H); 1.03-0.96 (d, 3H)

^{13}C NMR: 141.98, 128.96, 128.88, 128.44, 125.83, 80.99, 45.2, 42.42, 35.48, 31.05, 29.1, 19.94 (1st isomer); 141.29, 128.96, 128.88, 128.44, 125.83, 80.04, 48.71, 40.74, 37.55, 30.7, 29.02, 14.05 (2nd isomer).

2-methyl-5-(3-methoxybenzyl)cyclopentan-1-ol:
^{1}H NMR: 7.25-7.16 (m, 1H); 6.88-6.70 (m, 3H); 3.8-3.78 (s, 3H); 3.78-3.67 (m, 1H); 2.94-2.46 (m, 2H); 2.27-1.03 (m, 6H); 1.02-0.96 (d, 3H).

^{13}C NMR: 159.6; 143.63; 129.31; 121.31; 114.65; 111.15; 80.92; 55.14; 55.14; 45.02; 42.25; 37.47; 30.96; 29.03; 19.86 (1st isomer); 159.6; 142.9; 129.3; 121.26; 114.63; 110.9; 79.96; 48.46; 40.71; 35.47; 30.63; 28.93; 14.02 (2nd isomer).

2-methyl-5-(3-methylbenzyl)cyclopentan-1-ol:
^{1}H NMR: 7.24-7.17 (m, 1H); 7.11-7.00 (m, 3H); 3.82-3.68 (m, 1H); 2.92-2.49 (m, 2H); 2.38-2.35 (s, 3H); 2.27-1.05 (m, 6H); 1.04-0.99 (d, 3H).

^{13}C NMR:141.21; 137.93; 129.75; 128.30; 126.70; 125.92; 80.99; 45.17; 42.3; 37.49; 31.03; 29.11; 19.91 (1st isomer); 141.21; 137.92; 129.66; 128.30; 126.54; 125.84; 80.00; 48.67; 40.67; 35.38; 30.68; 29.01; 21.52; 14.06 (2nd isomer).

2-allyl-5-methylcyclopentan-1-ol:
^{1}H NMR: 5.92-5.75 (m, 1H); 5.11-4.96 (m, 2H); 3.75-3.65 (m, 1H); 2.33-1.01 (m, 8H); 1.01-0.96 (d, 3H).

^{13}C NMR: 137.76; 115.69; 81.14; 46.68; 39.06; 37.81; 30.81; 28.98; 13.9 (one isomer)

Mass Spectrometric Data

HRMS data of 2-methyl-5-(3-methoxybenzyl)cyclopentan-1-ol.

Measured m/z: 243.136718; ion formula: $C_{14}H_{20}NaO_2$ expected m/z 243.135551

HRMS data of 2-methyl-5-(3-methylbenzyl)cyclopentan-1-ol.

Measured m/z: 227.142162; Ion formula: $C_{14}H_{20}NaO$ expected: m/z: 227.140636.

GC-MS data of 2-allyl-5-methylcyclopentan-1-ol

Measured m/z: 140.1201; Ion formula: $C_9H_{16}O$, expected: m/z: 140.1197

Measured m/z: 122.1096 (M-H_2O peak); Ion formula C_9H_{14}, expected m/z: 122.1068.

Synthetic Procedure for Reduction of 1d **with $SmBr_2$-water-Et_3N:**

Substrate (0.09 g, 0.36 mmol) was added to a 15 mL solution of 0.1 M $SmBr_2$ in a flame dried vial equipped with a magnetic stir bar under an argon atmosphere. Under stirring, Et_3N (3.7 mmol) followed by water (7.5 mmol) were added to the solution, which was allowed to react

until discoloration of the characteristic purple of $SmBr_2$ was observed. Quenching of the solution in air and with 0.1 M HCl was followed by extraction into diethyl ether and drying of the combined organic layers over magnesium sulfate. The dry solution was then concentrated under reduced pressure. This reaction yielded 37% of the cyclized product **2d**, 35% of the acyclic reduced alcohol, and 27% of the unreacted starting material.

Generation Procedure for synthesis of substrates for Ester-Olefin cyclization

1 g (0.0078 mol) of methyl hex-5-enoate was dissolved in 20 mL of dry THF and taken in 100 ml of three neck round bottom flask. With the help of a syringe, 5 mL of 2.0 M LDA (in THF/heptane/ethyl benzene) was added slowly maintaining the temperature at -78˚C. After 30 min, 0.0085 mol of corresponding electrophile (benzyl bromide, m-methyl benzyl bromide and m-methoxy benzyl bromide) dissolved in 5 mL of dry THF was added slowly to the reaction mixture keeping the temperature -78˚C. After 2 hrs, the reaction was allowed to reach the room temperature. The reaction was quenched with slow addition of Na_2SO_4 solution. The reaction mixture was worked up using diethyl ether and dilute HCl solution. The organic layers were combined and concentrated under the reduced pressure. The products were purified with column chromatography using silica as stationary phase and hexanes/ethyl acetate as eluting solvent.

4. Kinetic Conditions for $SmBr_2$-NMEA Reductions:

Kinetic experiments were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). Solutions were injected separately into the stopped-flow system using airtight, capped BD syringes prepared in a glove box under argon atmosphere. Between each experiment, the cell block was washed with dilute HNO_3 (1x), Deionized H_2O (1x), and THF (3x) before additional anhydrous deoxygenated THF washes (3x). The reaction rates were determined from the decay of $SmBr_2$ at 540 nm. Kinetic measurements were carried out at 25°C unless otherwise specified.

5. Rate of Decay of $SmBr_2$-NMEA

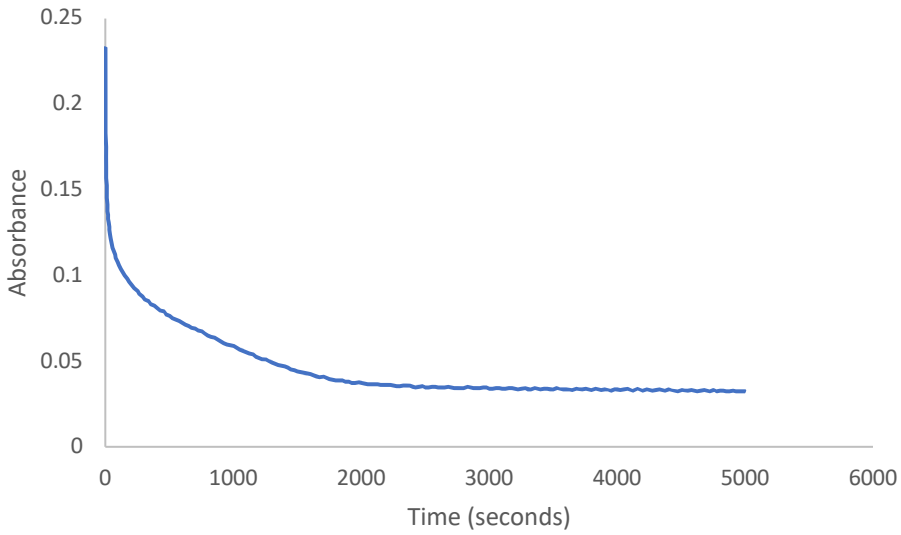

Figure S1. Sample decay curve for $SmBr_2$-NMEA in the absence of substrate

Table S1: Table of the rate of decay of $SmBr_2$-NMEA complexes in the absence of substrate

Proton Donor	Concentration of Proton Donor	Rate of Natural Decay (s^{-1})
N-Methylethanolamine	0.15 M	0.0014

6. Sample Determination of k_{obs} under Pseudo-first Order Conditions:

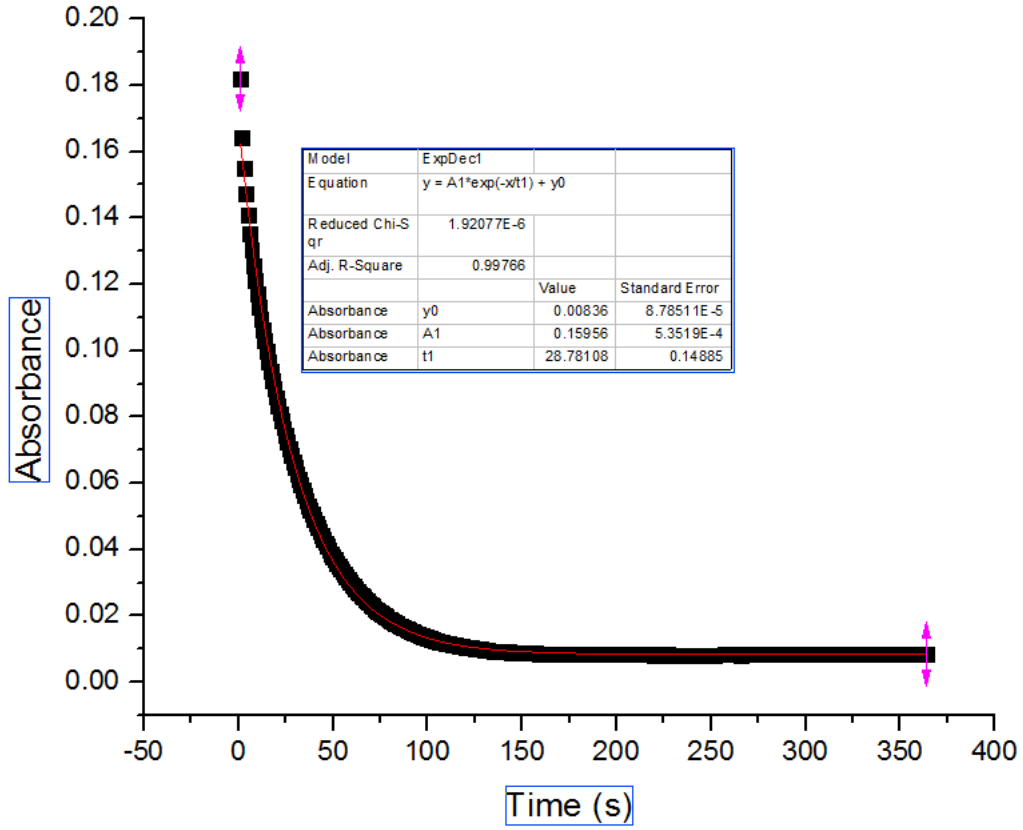

Figure S2. Plot of the decay of 10 mM Sm(II) at 540 nm in the presence of excess 1-methoxynaphthalene and N-Methylethanolamine fit to a single exponential equation where y = y0 + A $^{(R0*x)}$ and k_{obs} is represented by |R0|.

7. Kinetic Conditions and Data for Reduction of 1-methoxynaphthalene:

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

Sample Decay $SmBr_2$-2-methylamino ethanol-1-methoxynaphthalene:

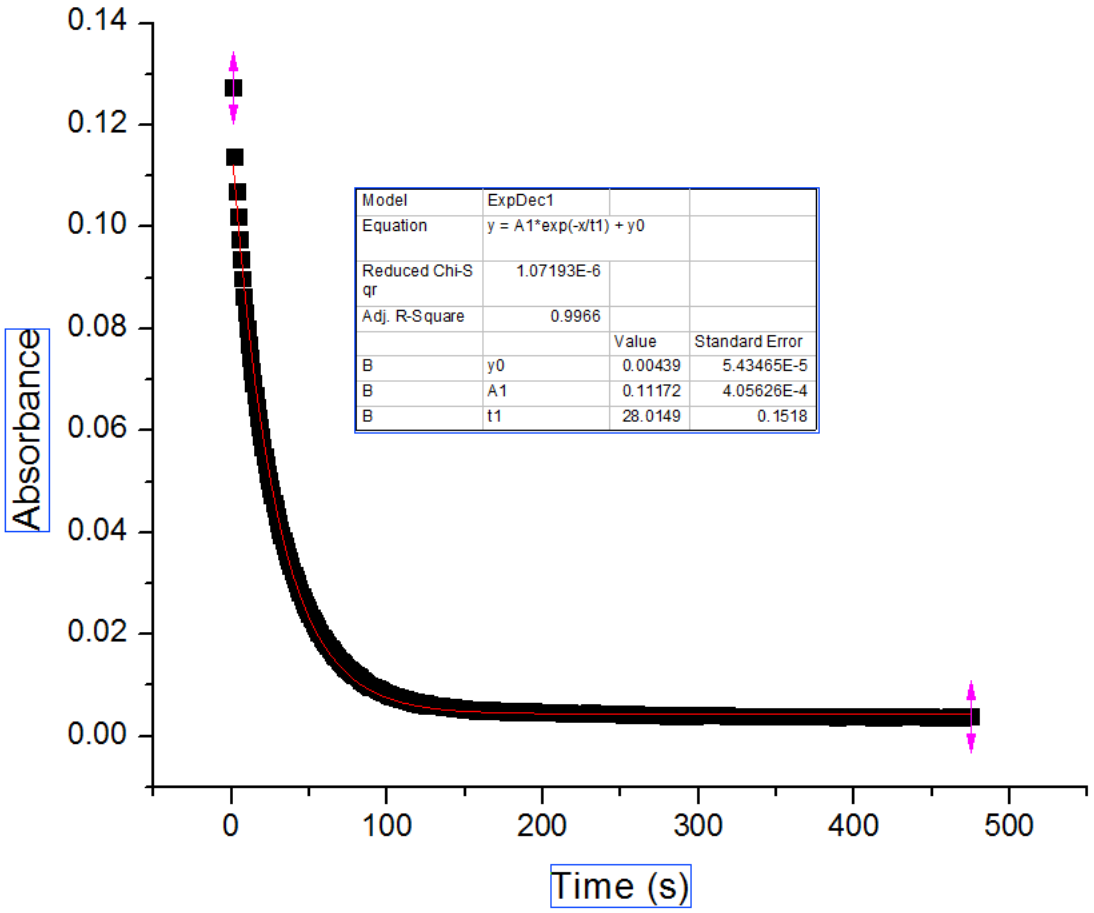

Figure S3. Sample decay for 0.15 M 2-methylaminoethanol, 100 mM 1-methoxynaphthalene, 10 mM SmBr2, measured at 25 °C, 540 nm fit to a single exponential equation to provide k_{obs}.

Order of 2-methylamino ethanol:

For the order of water, the concentration of 1-methoxynaphthalene was kept constant at 100 mM and was combined with 10 mM $SmBr_2$. Concentration of 2-methoxynaphthalene was varied from 50-250 mM at 25 °C.

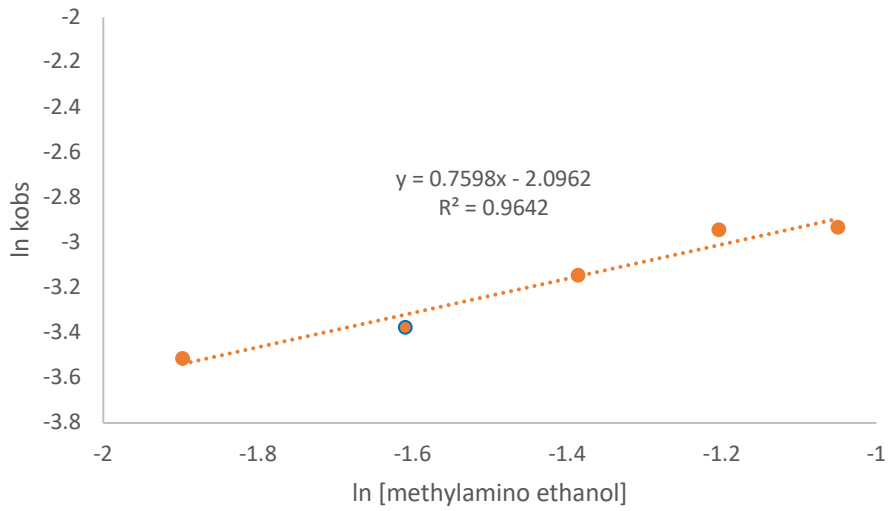

Figure S4. Plot of the reduction of 100 mM 1-methoxynaphthalene with 10mM $SmBr_2$ with [2-methylamino ethanol] varied from 50-250 mM.

Order and Rate Constant of 1-methoxynaphthalene:

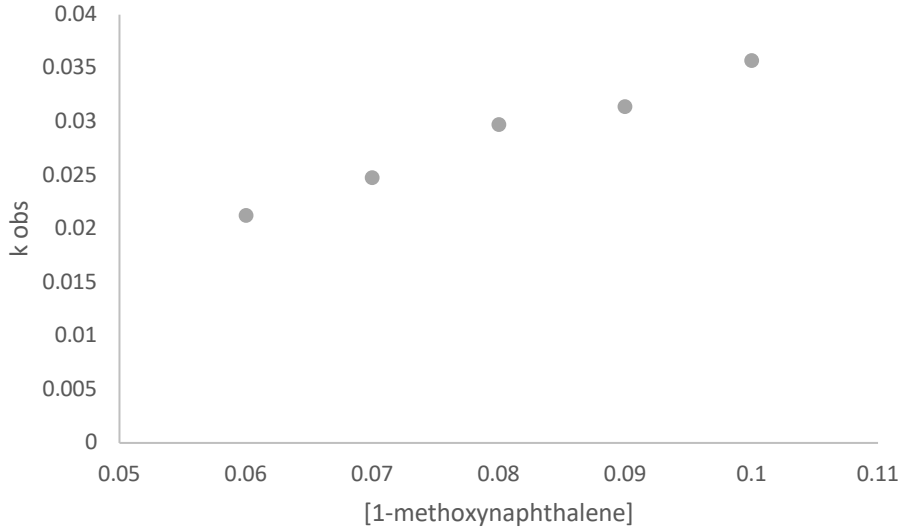

Figure S5. Plot of *k*obs vs. concentration of anthracene with 10 mM $SmBr_2$ and 15 equiv 2-methylamino ethanol where [1-methoxynaphthalene] is varied from 0.06 M to 0.1 M and a linear regression provides y = 0.49x – 0.0011 with $R^2 = 0.99$.

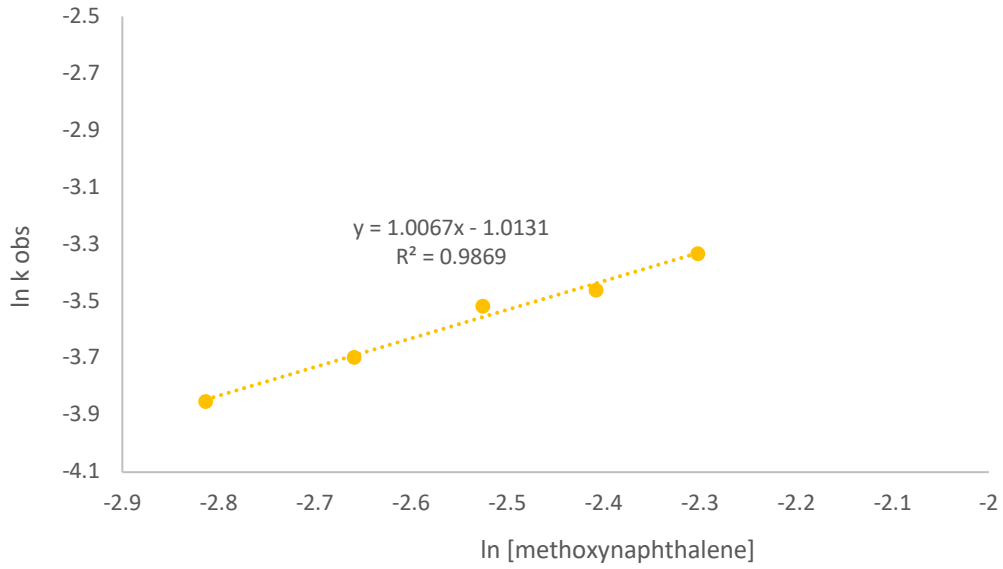

Figure S6. Natural log plot for *k*obs vs. [Anthracene] where the rate order is provided by a linear regression where y = 1.0x + 1.0131 with $R^2 = 0.99$.

Order of $SmBr_2$ using Fractional Times Method:

Fractional times method was applied to determine the order of $SmBr_2$ over a range of concentrations of anthracene with a constant concentration of 0.33 M H_2O. The value for $(t_{3/4}-t_{1/2})/t_{1/2}$ was computed for each decay to provide an order as described below.[2]

[Anthracene] (mM)	Trial	A_0	$A_{1/2}$	$A_{3/4}$	$t_{1/2}$	$t_{3/4}$	$(t_{3/4}-t_{1/2})/t_{1/2}$
60	A	0.134525	0.0672625	0.03363125	16	35	1.2
60	B	0.122343	0.0611715	0.03058575	17	39	1.3
70	A	0.128034	0.064017	0.0320085	12	30	1.5
70	B	0.140525	0.0702625	0.03513125	14	33	1.4
80	A	0.141632	0.070816	0.035408	12	30	1.5

90	A	0.138176	0.069088	0.034544	12	24	1.0
100	A	0.131247	0.0656235	0.03281175	11	25	1.3
						Average:	1.3
						Order:	1

Table S2. Fractional times table to calculate the rate order of $SmBr_2$ in the reduction of 1-methoxynaphthalene by $SmBr_2$-NMEA

Rate Constant:

$-d[Sm^{II}]/dt = k'[Sm^{II}][1\text{-methoxynaphthalene}][MAE] = k_{obs}[Sm^{II}]$

$k' = 3.7\ M^{-3}s^{-1}$

Kinetic Isotope Effect:

Activation Parameters for $SmBr_2$-2-methylamino ethanol-1-methoxynaphthalene:

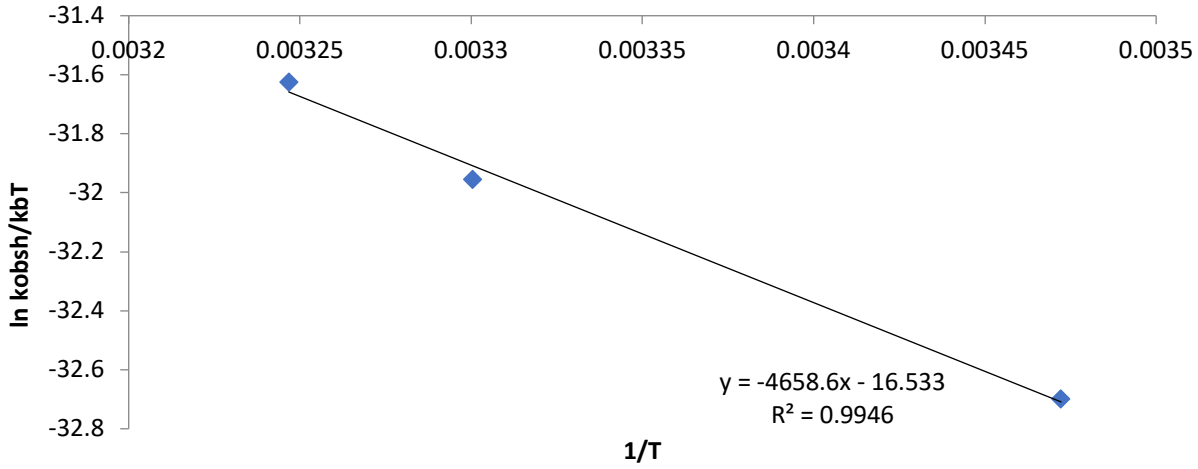

Figure S7. Plot of $\ln(k_{obs}*h/T*kb)$ vs 1/T for the reduction of acenaphthalene by 1-methoxynaphthalene by $SmBr_2$-NMEA

Temp °C	Temp °K	1/T (K^{-1})	k_{obs}	$k_{obs}h/k_bT$	ln $k_{obs}h/k_bT$
15	288	0.003472	0.037816	6.29995E-15	-32.6982
20	293	0.003413	0.103377	1.69284E-14	-31.7098
25	298	0.003356	0.125	2.01257E-14	-31.53698
30	303	0.0033	0.083838	1.32757E-14	-31.9528
35	308	0.003247	0.11836	1.84379E-14	-31.6244

Figure S8. Plot and data points for the reduction of 1-methoxynaphthalene where *k* was measured under constant concentrations of $SmBr_2$ (10 mM), 1-methoxynaphthalene (100 mM), and 2-methylaminoethanol (15 equiv vs Sm) with the temperature varied from 15-35 °C.

Kinetic conditions used were those described in Section 5. Each kinetic trace was measured at the specified temperature after the solutions were allowed to equilibrate to the desired temperature after ten minutes, which was monitored by a thermocouple in the reaction cell. Activation parameters were derived from the activated complex theory plot provided above and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated as described by Espenson.[3] Reported values are an average of three individual trials.

8. Conductivity Experiments:

Analytes: $SmBr_2$

Solvent: THF; Co-solvent: N-methylethanolamine (NMEA), N,N-dimethylethanolamine (DMEA), and ethanolamine (EA)

Instrument: VWR Scientific Conductivity Meter

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

Procedure: To $SmBr_2$ (25 mL, 2.5 mM) under argon flow, additive was added sequentially and conductivity was measured.

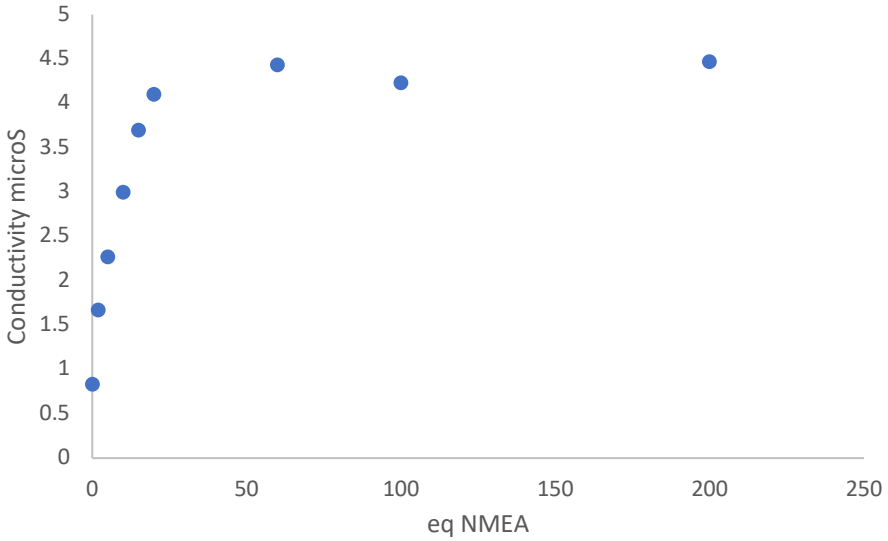

Figure S9. Plot of conductivity vs. equivalents of NMEA with respect to $SmBr_2$ in THF

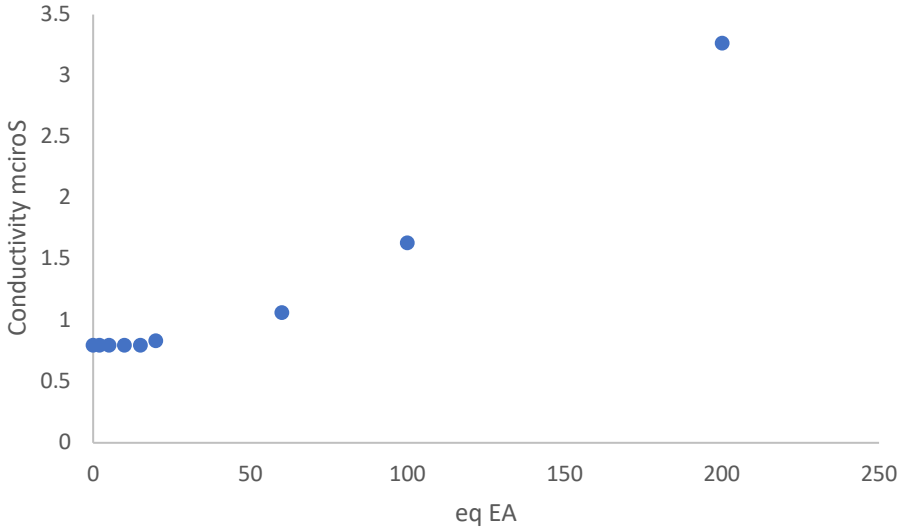

Figure S10. Plot of conductivity vs. equivalents of EA with respect to $SmBr_2$ in THF

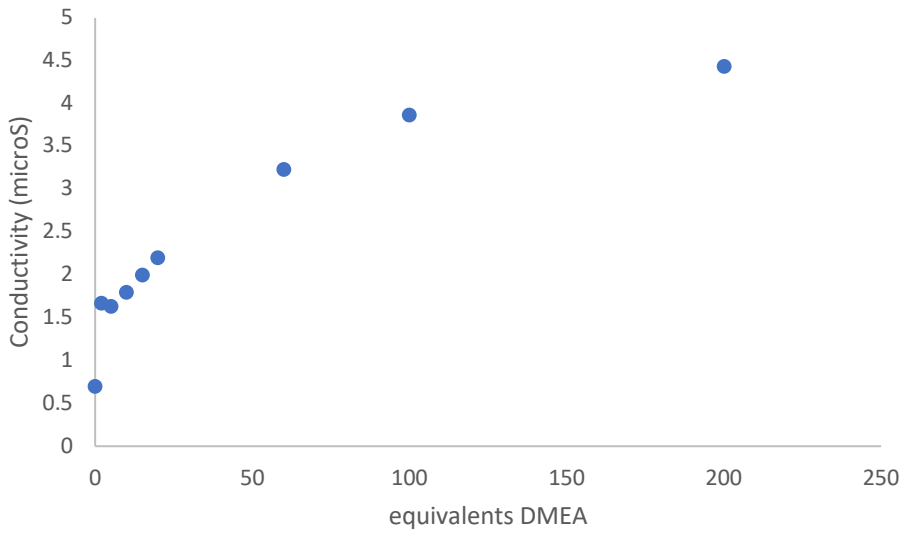

Figure S11. Plot of conductivity vs. equivalents of DMEA with respect to $SmBr_2$ in THF

9. Hydrogen Gas Evolution Experiments:

Analytes: $SmBr_2$

Solvent: THF; Co-solvents: DMEA, NMEA, EA

Instrument: Vernier Gas Pressure Sensor

Procedure: To $SmBr_2$ (5 mL, 0.1 M) in a sealed test tube, stopper was removed and 200 eq additive was added, stopper was then placed back on test tube. Pressure data was then collected over a certain period of time.

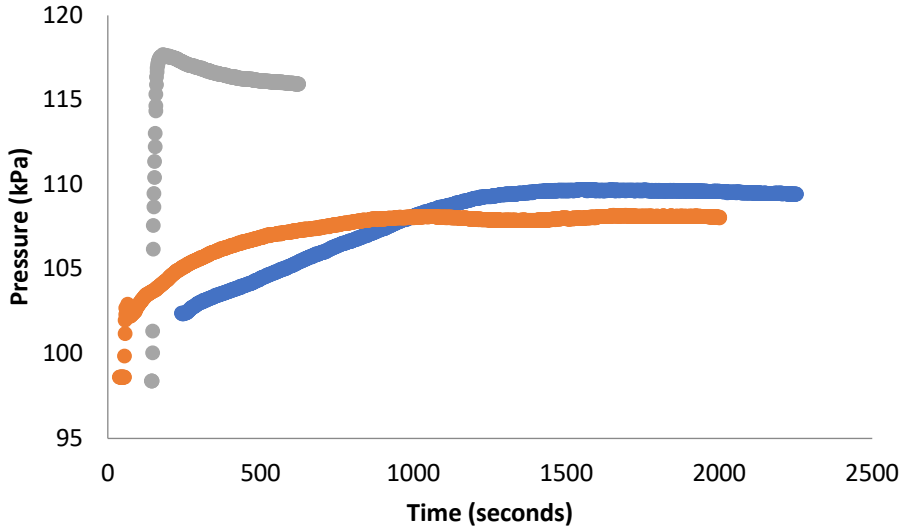

Figure S12: Plot of the liberation of H_2 gas upon addition of 200 equiv. EA (grey), NMEA (orange), and DMEA (blue) to a solution of 0.1M 0.1 M $SmBr_2$ in THF.

10. UV-vis Spectra of $SmBr_2$:

Spectra were obtained using the Spectra setting for the stopped-flow spectrophotometer (described in Section 2) so that one solution of $SmBr_2$ could be generated for one syringe and would remain at a constant concentration while concentration of additive/s or substrate was changed in the other syringe. All spectra were measured at 25 °C.

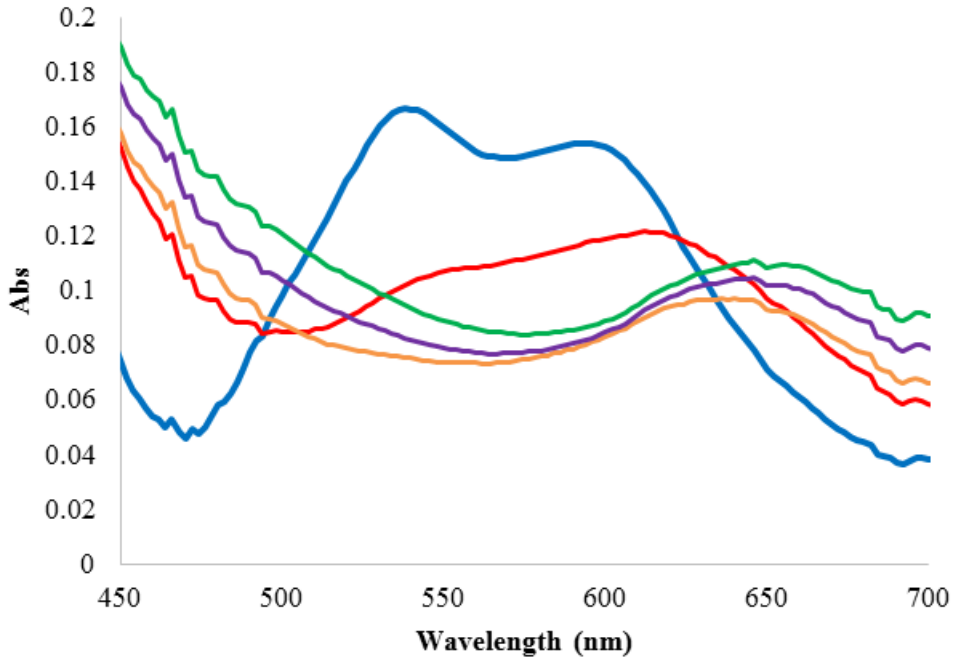

Figure S13. UV-Vis spectrum of $SmBr_2$ in the presence of increasing [EA] (0 eq blue, 5 eq red, 10 eq orange, 15 eq purple, 20 eq green)

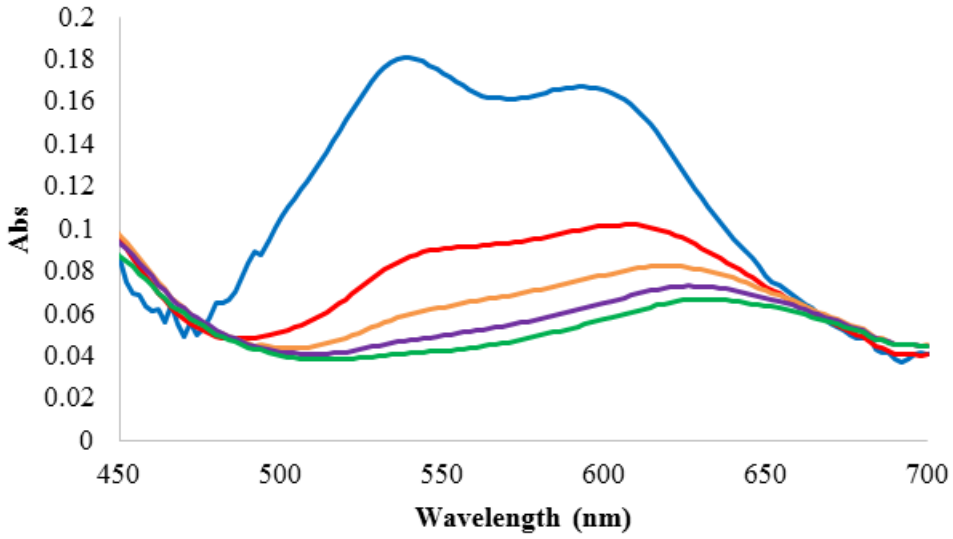

Figure S14. UV-Vis spectrum of $SmBr_2$ in the presence of increasing [NMEA] (0 eq blue, 5 eq red, 10 eq orange, 15 eq purple, 20 eq green)

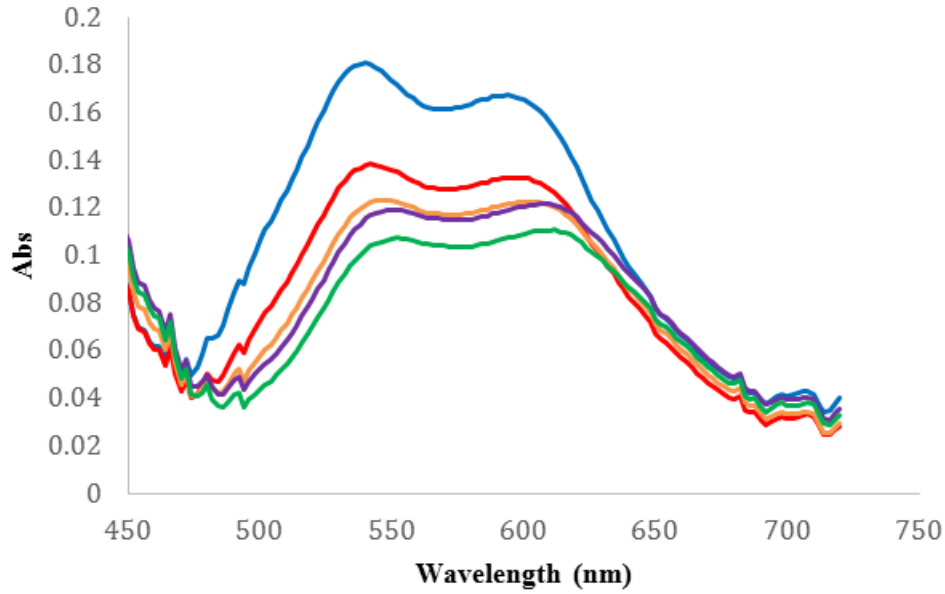

Figure S15. UV-Vis spectrum of $SmBr_2$ in the presence of increasing [DMEA] (0 eq blue, 5 eq red, 10 eq orange, 15 eq purple, 20 eq green)

11. ^{1}H NMR Spectra of Products:

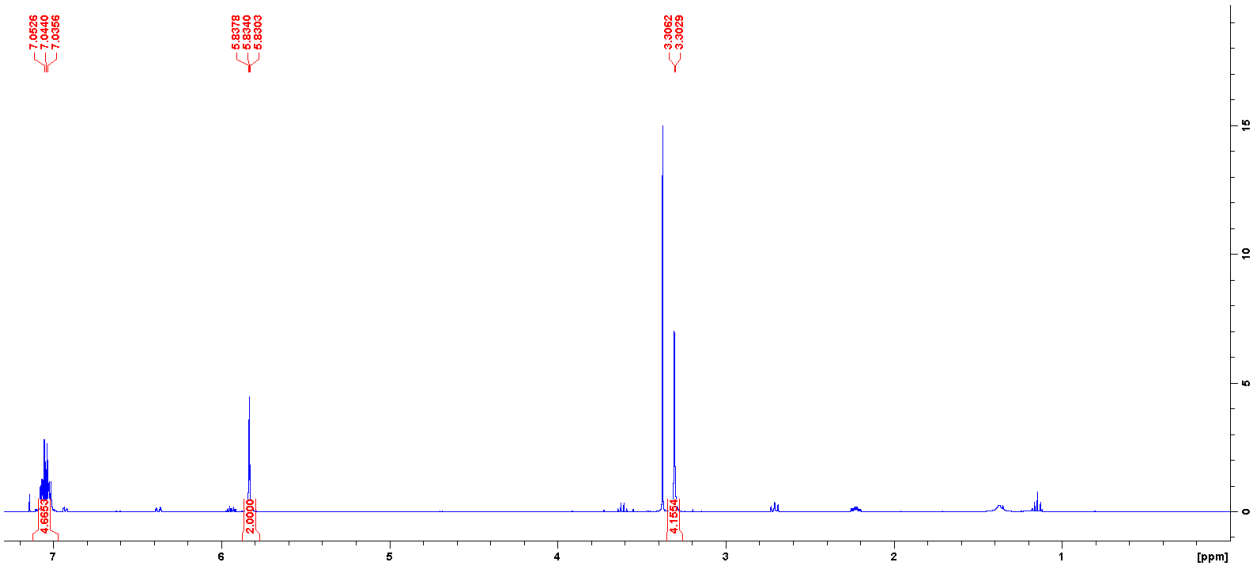

Figure S16. ^{1}H NMR spectrum of 1,4-dihydronaphthalene

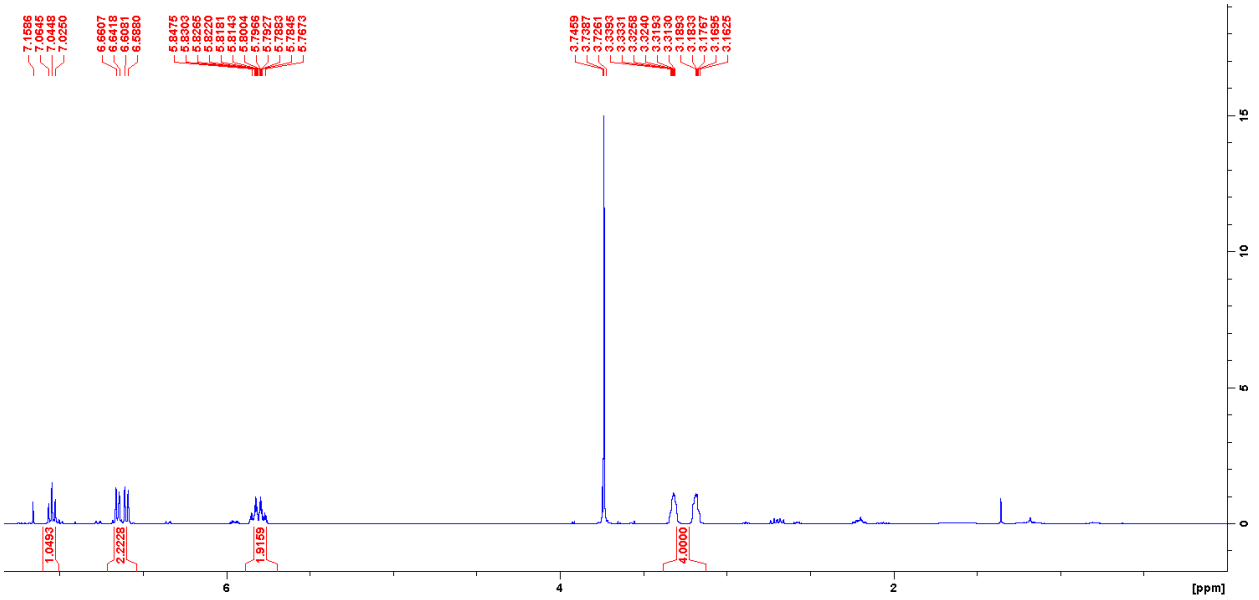

Figure S17. ^{1}H NMR spectrum of 1,4-dihydro-5-methoxynaphthalene

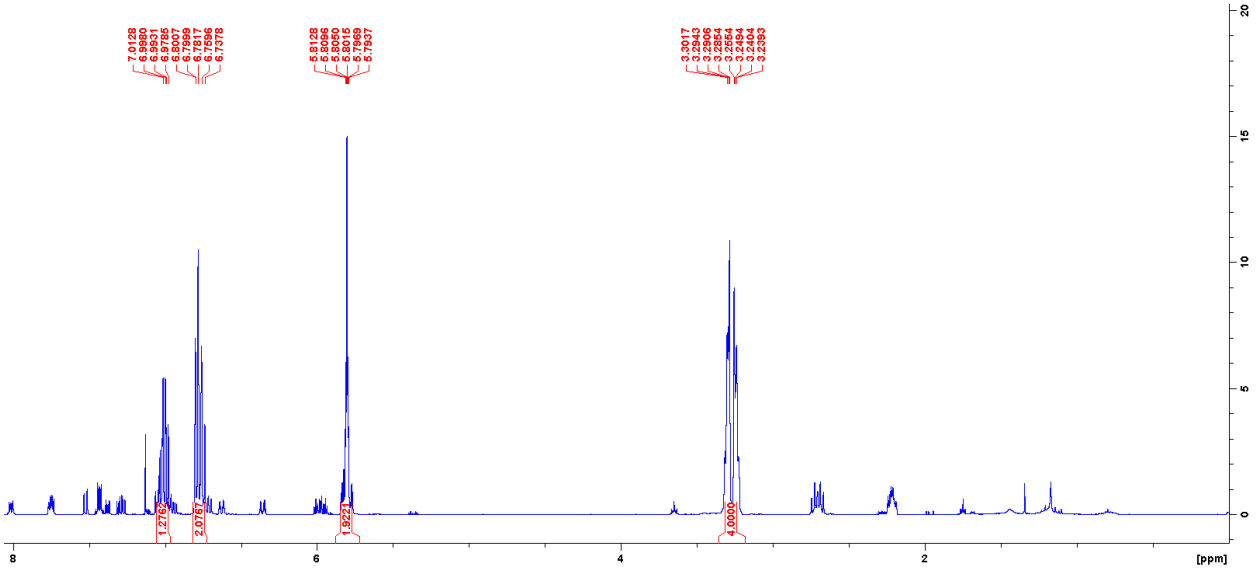

Figure S18. ^{1}H NMR spectrum of 1,4-dihydro-5-fluoronaphthalene

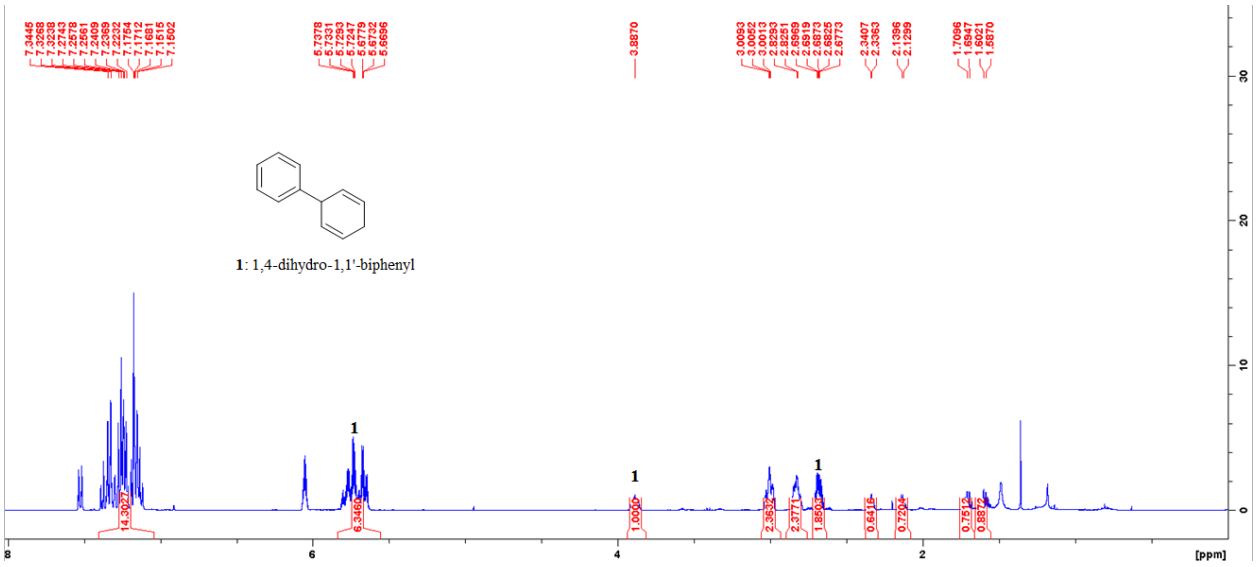

Figure S19. ^{1}H NMR spectrum of the products of the reduction of biphenyl by $SmBr_2$-NMEA

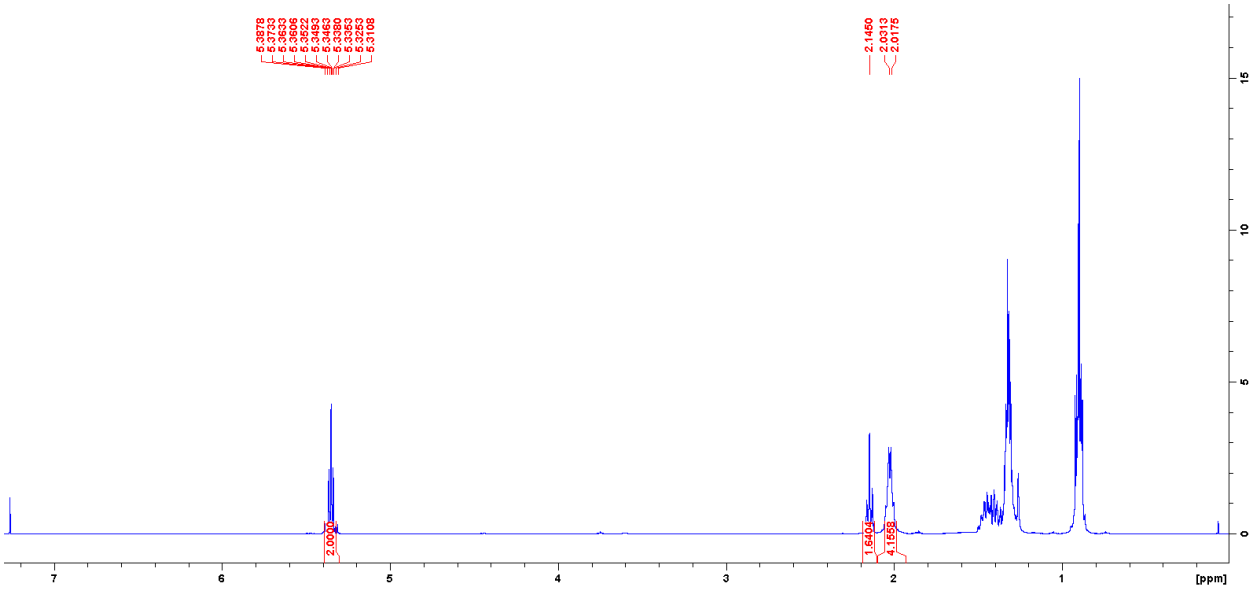

Figure S20. ^{1}H NMR spectrum of *cis*-5-decene

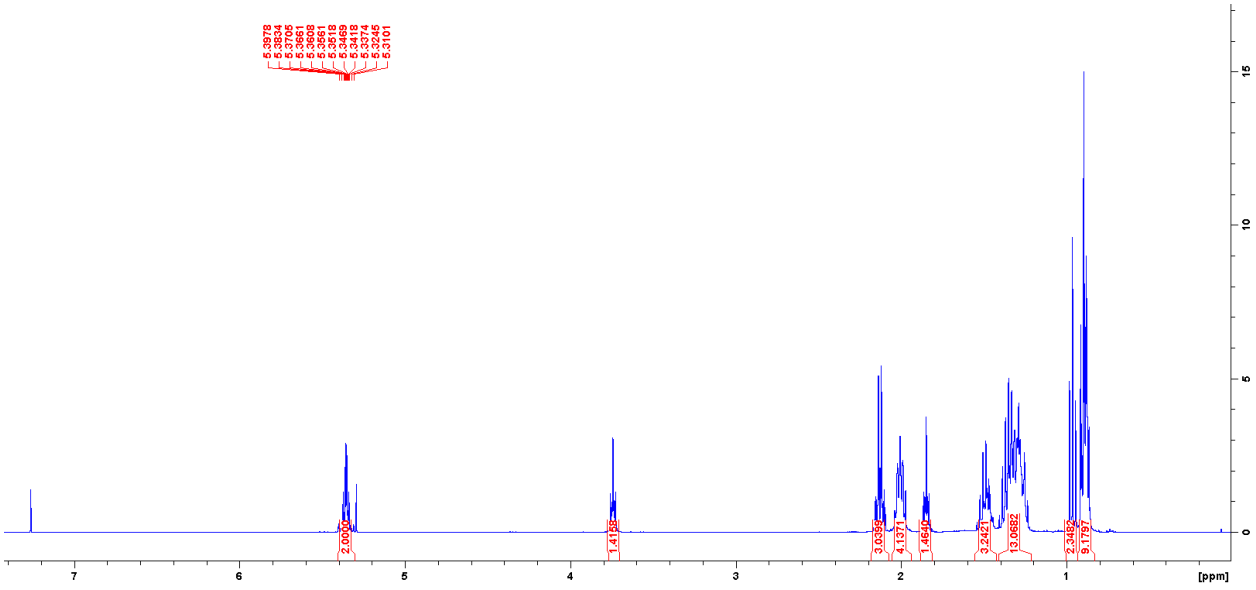

Figure S21. ^{1}H NMR spectrum of *cis*-4-decene

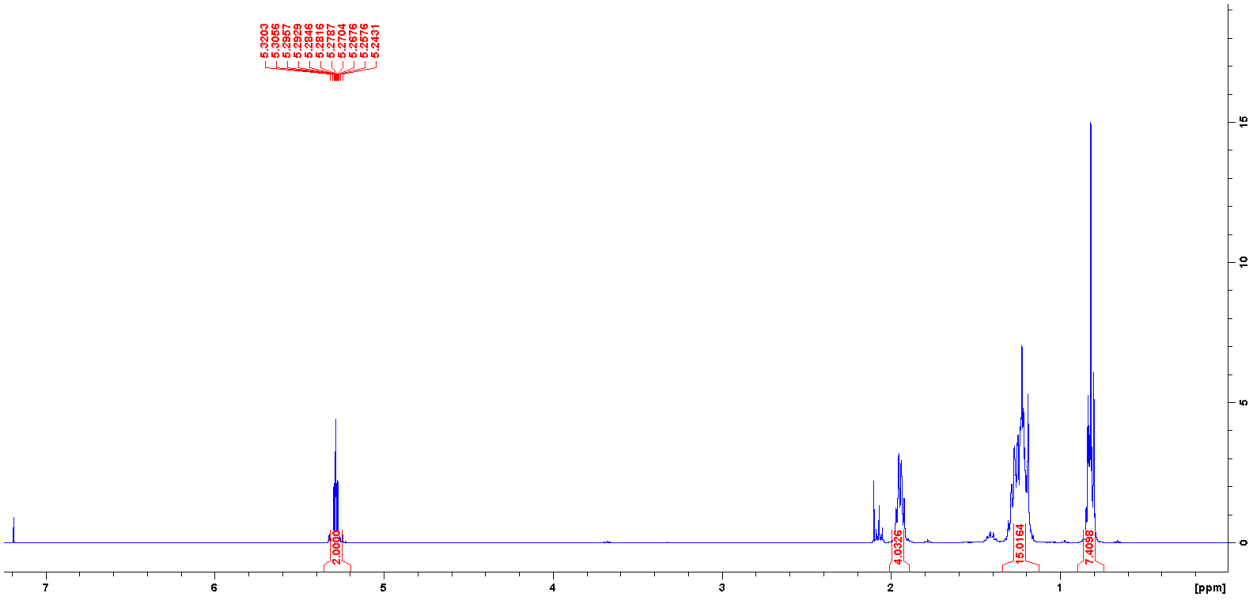

Figure S22. ^{1}H NMR spectrum of *cis*-6-dodecene

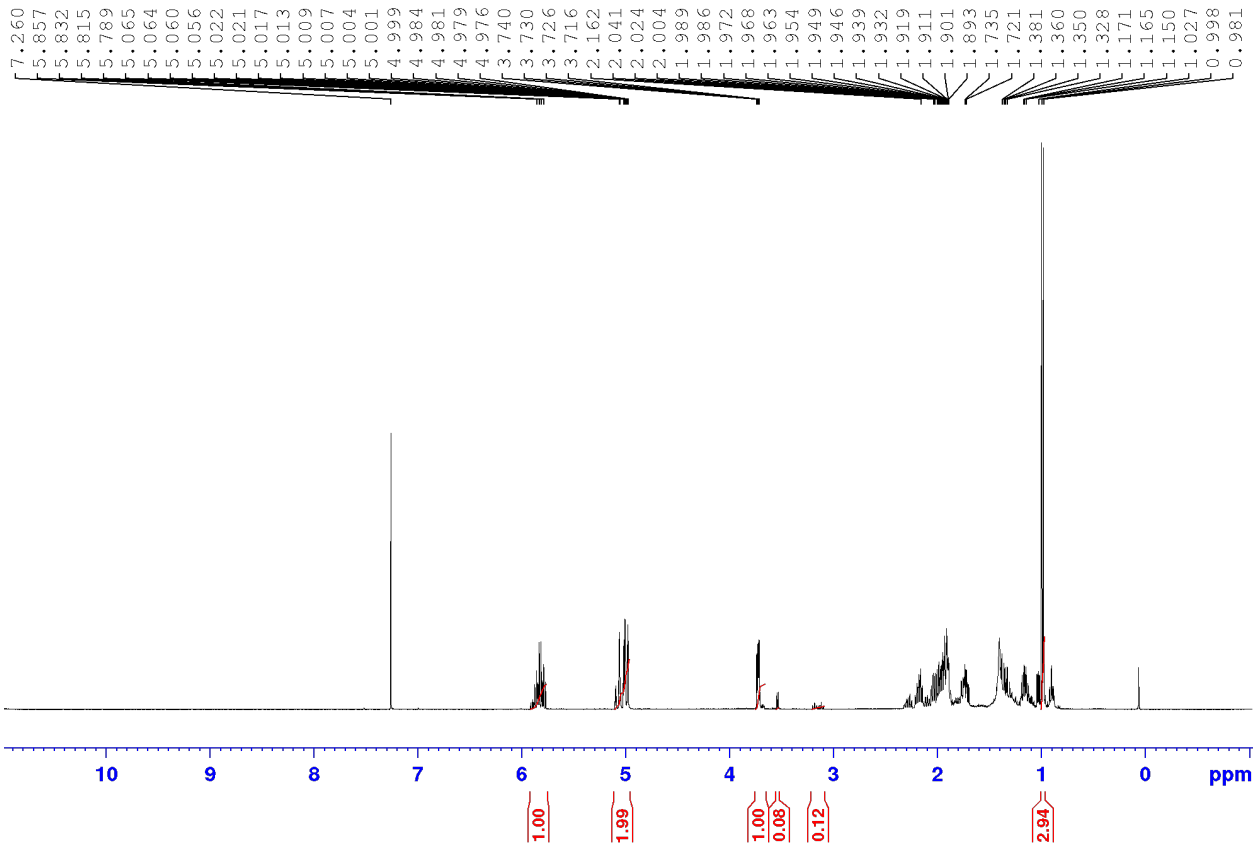

Figure S23. ^{1}H NMR spectrum of 2-allyl-5-methylcyclopentan-1-ol. (peak at 7.26 corresponds to $CDCl_3$)

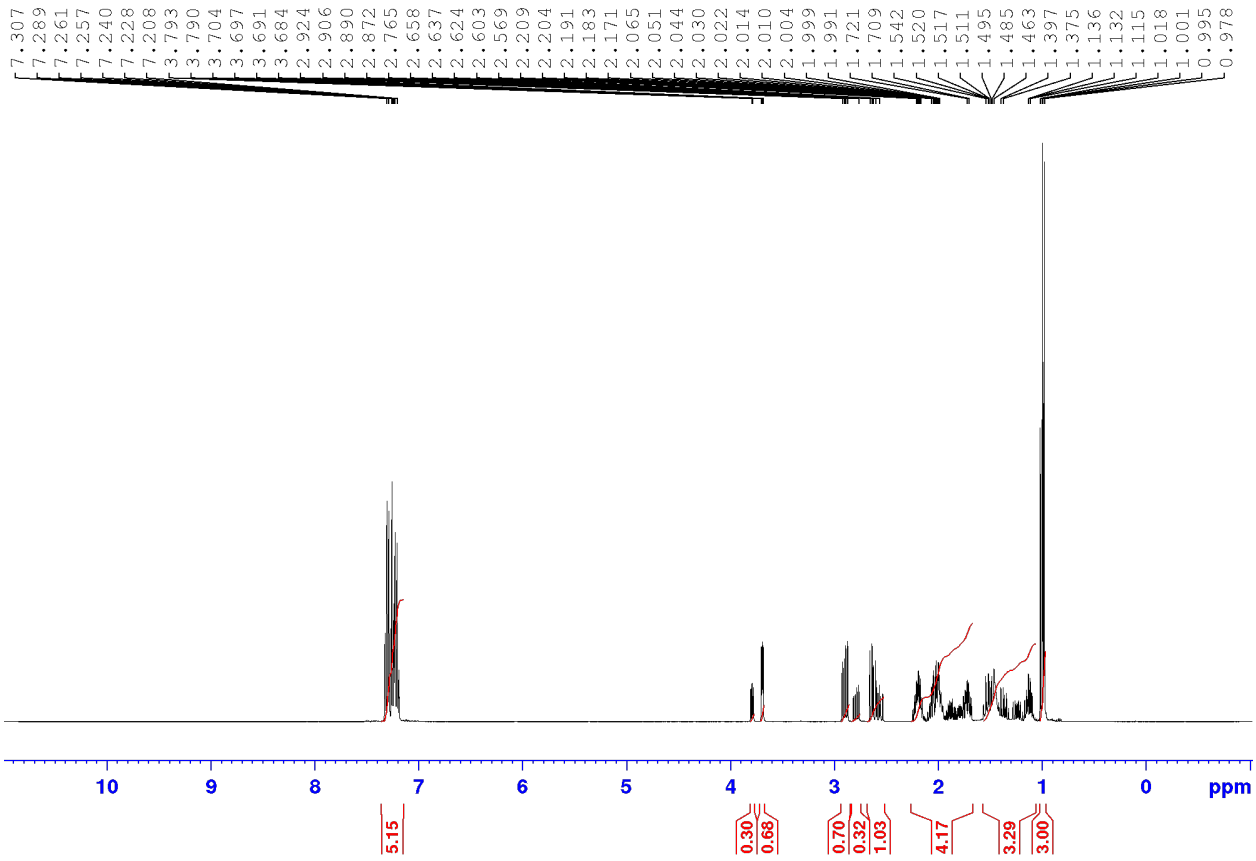

Figure S24. ^{1}H NMR spectrum of 2-benzyl-5-methylcyclopentan-1-ol

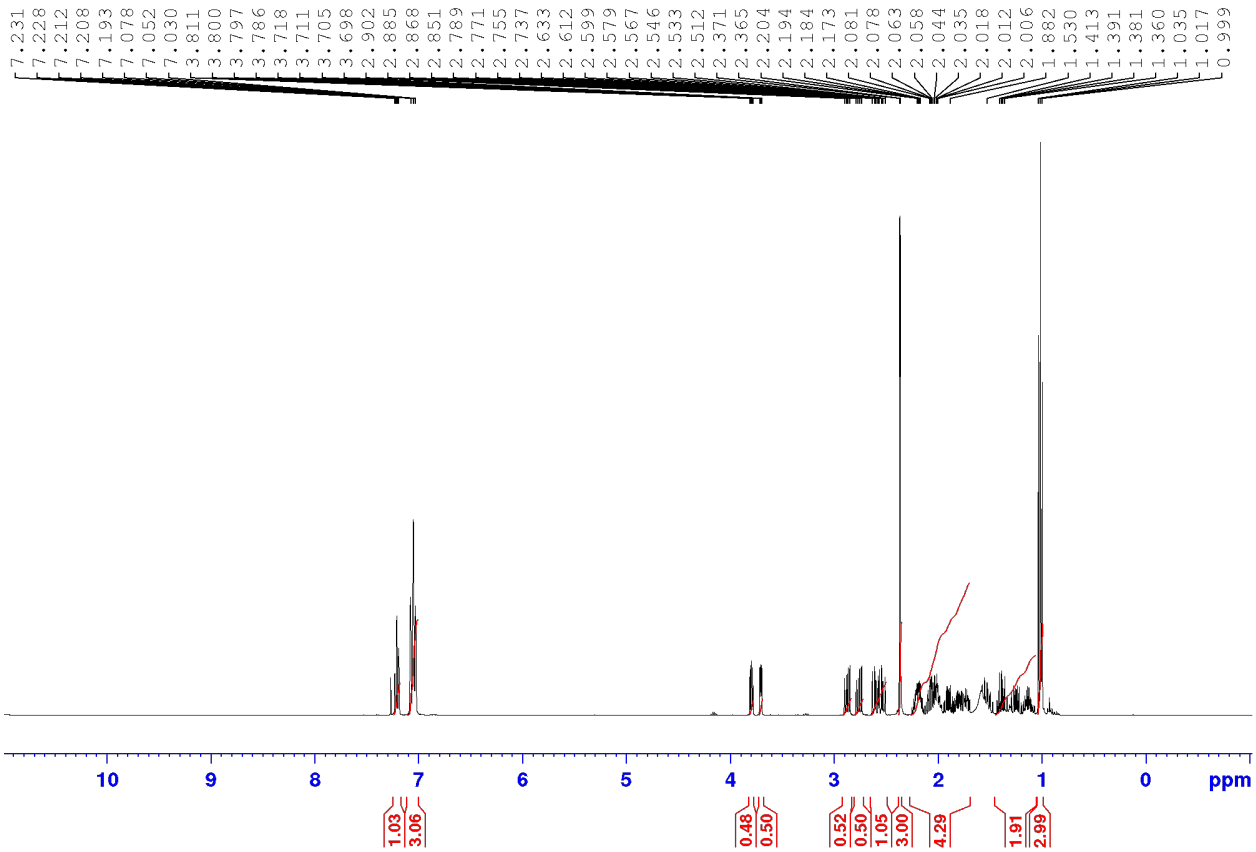

Figure S25. ^{1}H NMR spectrum of 2-methyl-5-(3-methylbenzyl)cyclopentan-1-ol

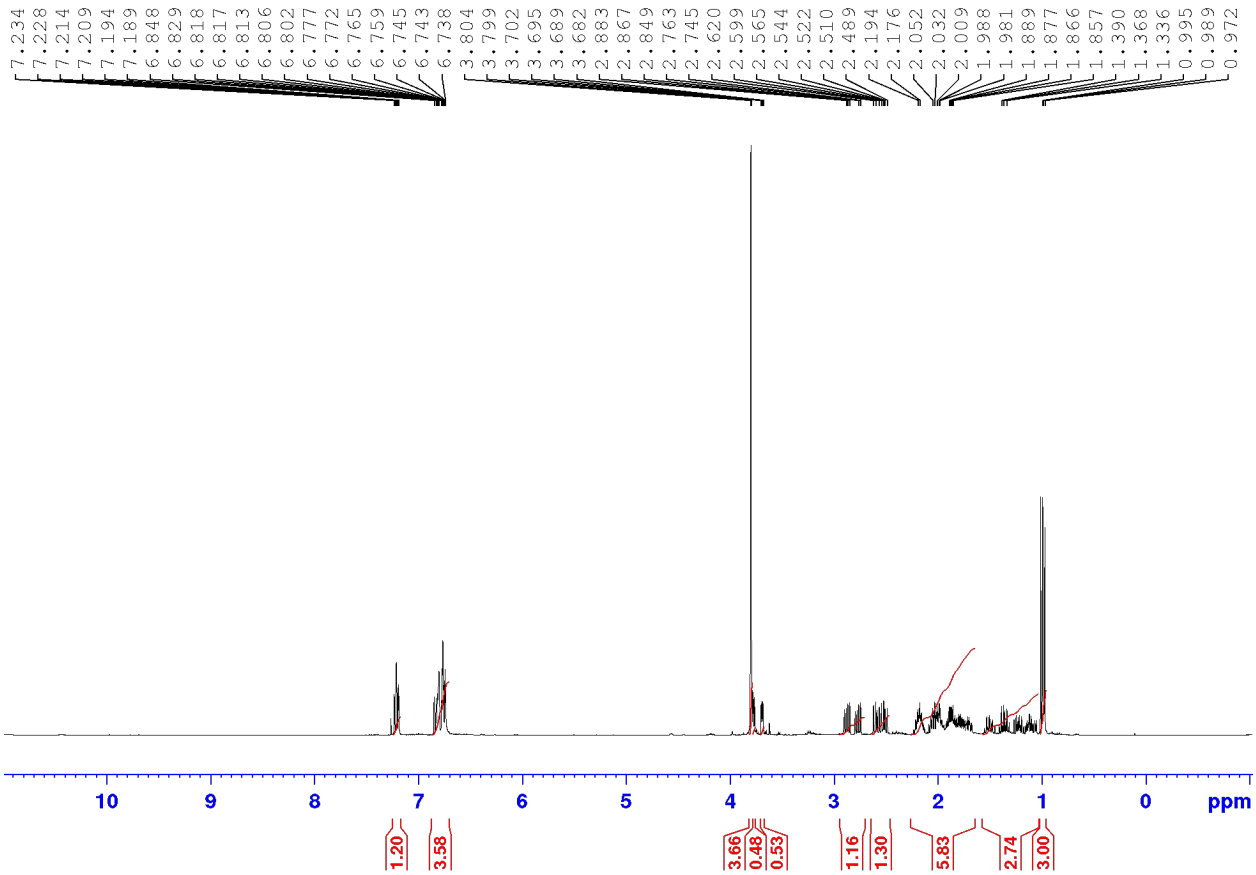

Figure S26. [1]H NMR spectrum of 2-methyl-5-(3-methoxybenzyl)cyclopentan-1-ol

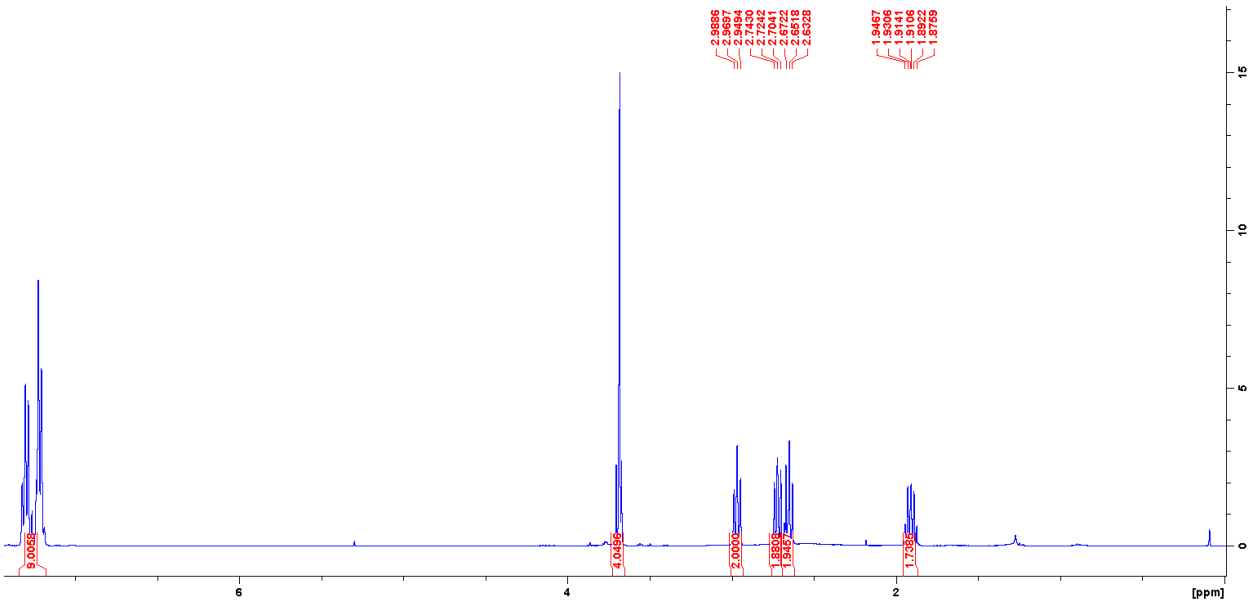

Figure S27. [1]H NMR spectrum of 3-phenylpropan-1-ol

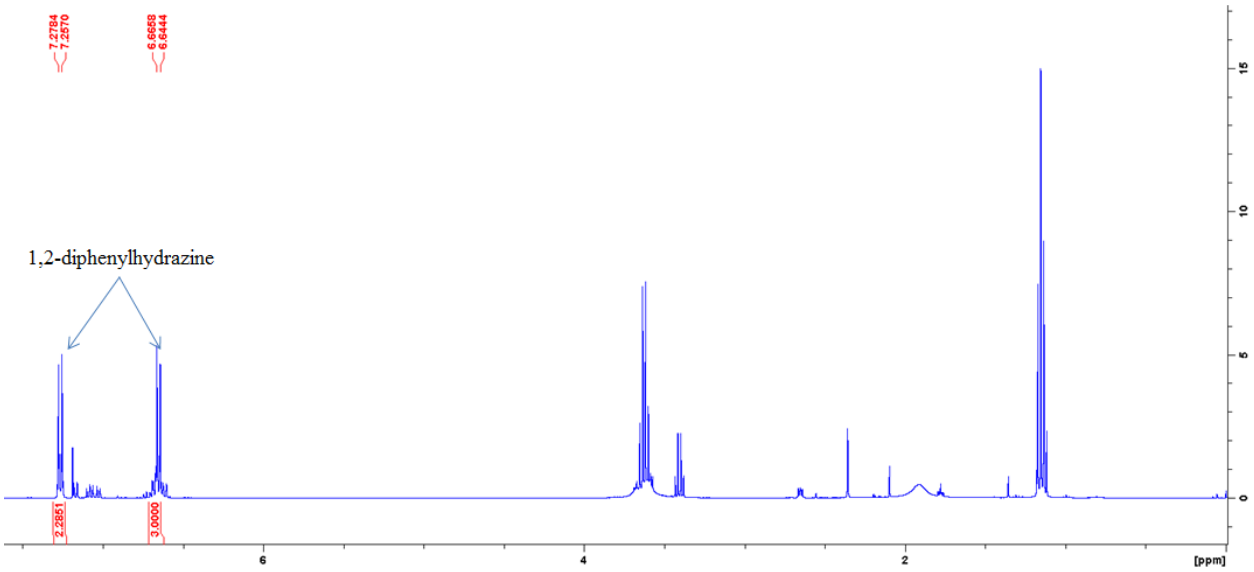

Figure S28. Crude ^{1}H NMR spectrum of 1,2-diphenylhydrazine

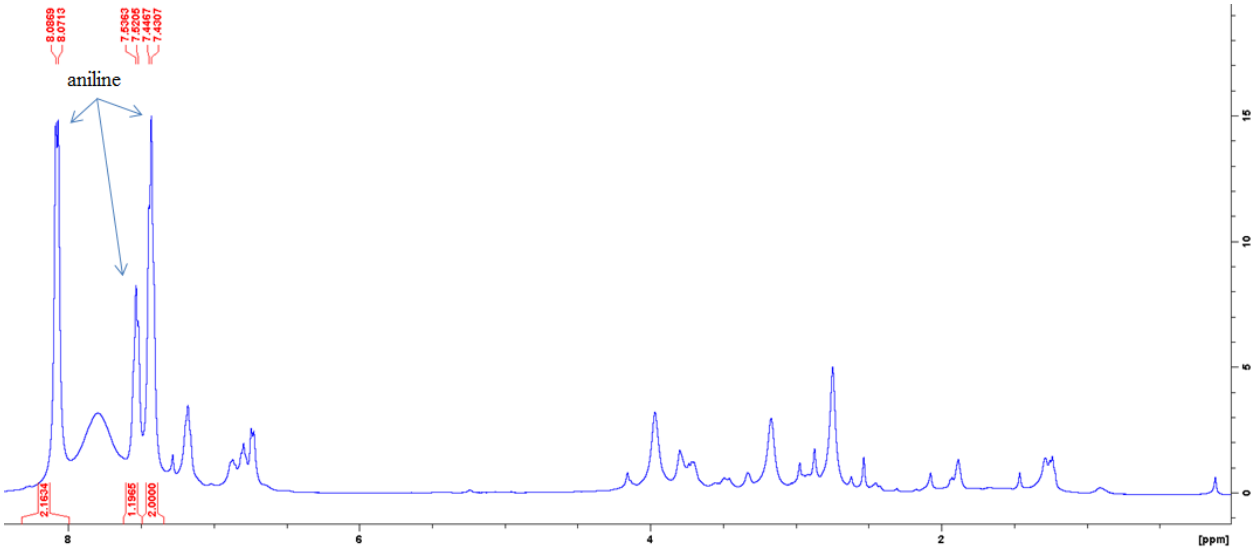

Figure S29. Crude ^{1}H NMR spectrum of aniline

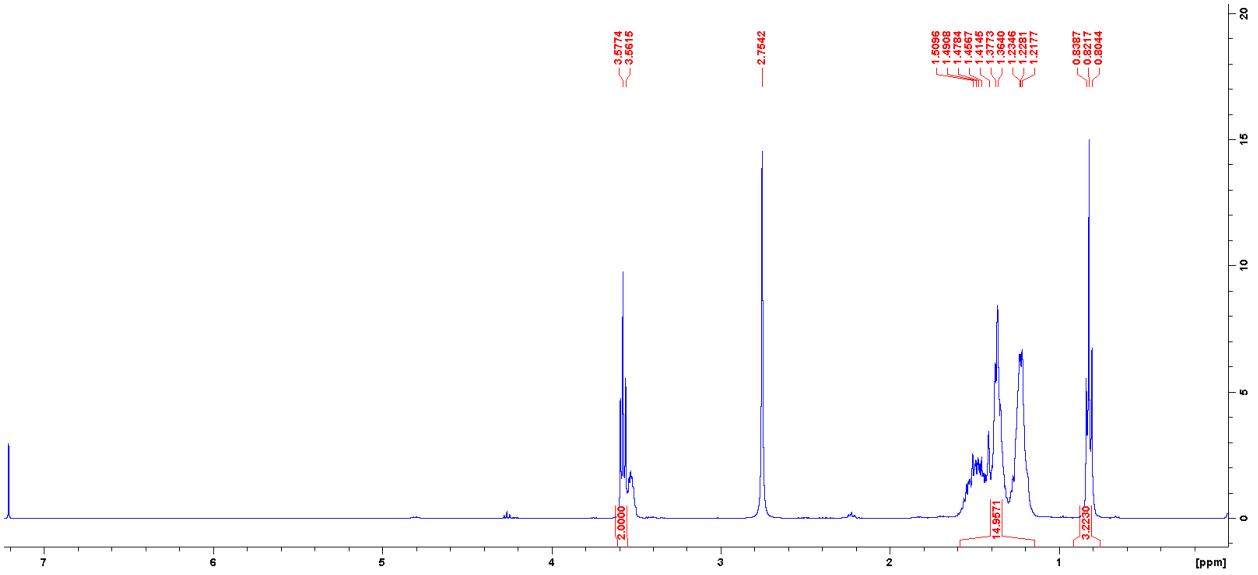

Figure S30. ^{1}H NMR spectrum of decane-1,5-diol

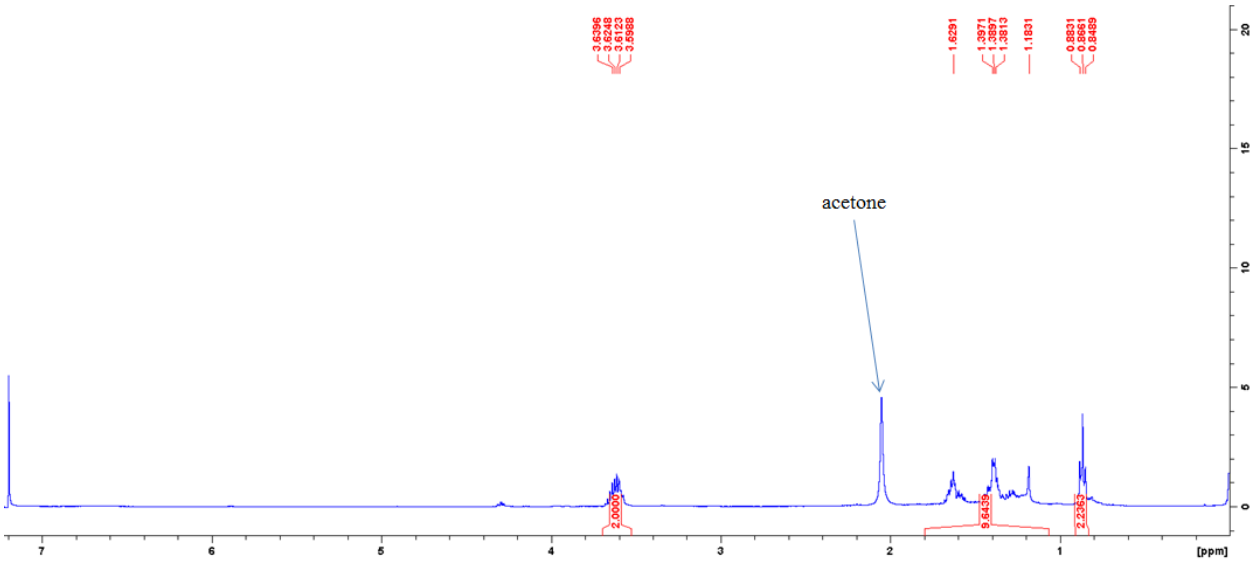

Figure S31. Crude ^{1}H NMR spectrum of hexane-1,6-diol

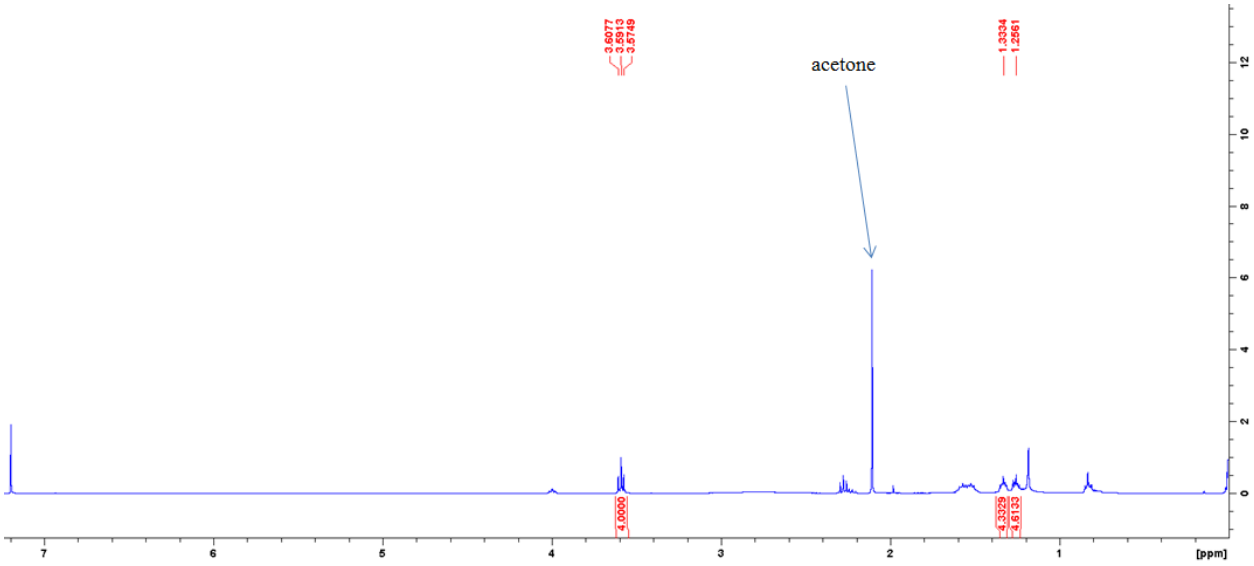

Figure S32. Crude ^{1}H NMR spectrum of heptane-1,4-diol

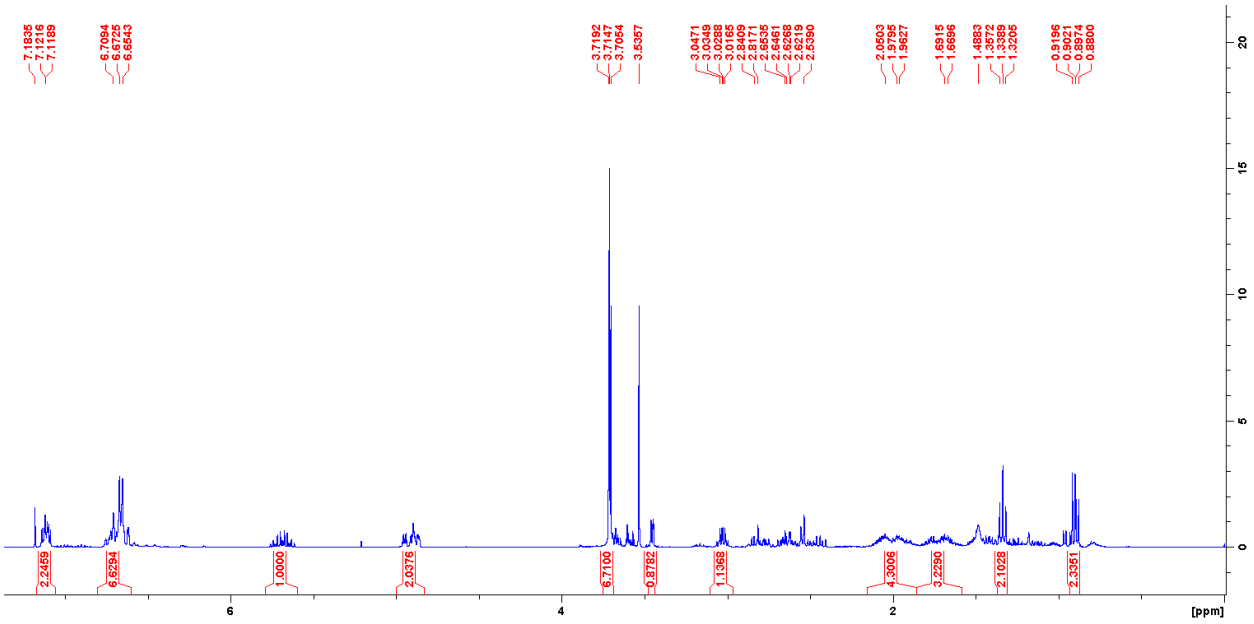

Figure S33. ^{1}H NMR spectrum of the reduction of **1d** by $SmBr_2$-water-Et_3N

12. ^{13}C NMR Spectra of Products:

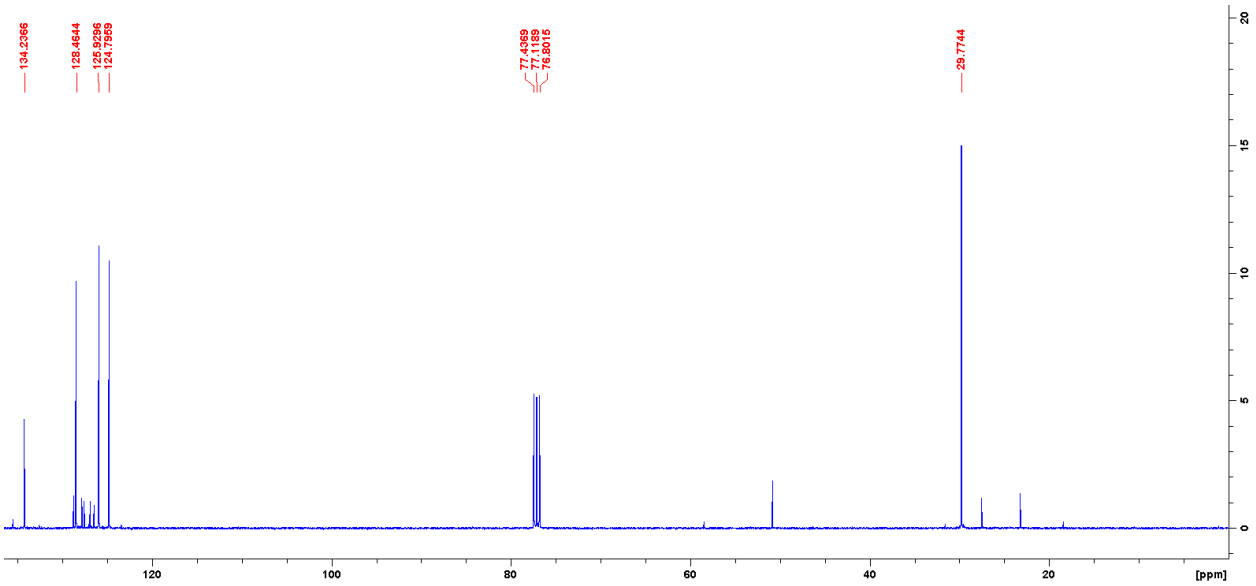

Figure S34. ^{13}C NMR spectrum of 1,4-dihydronaphthalene

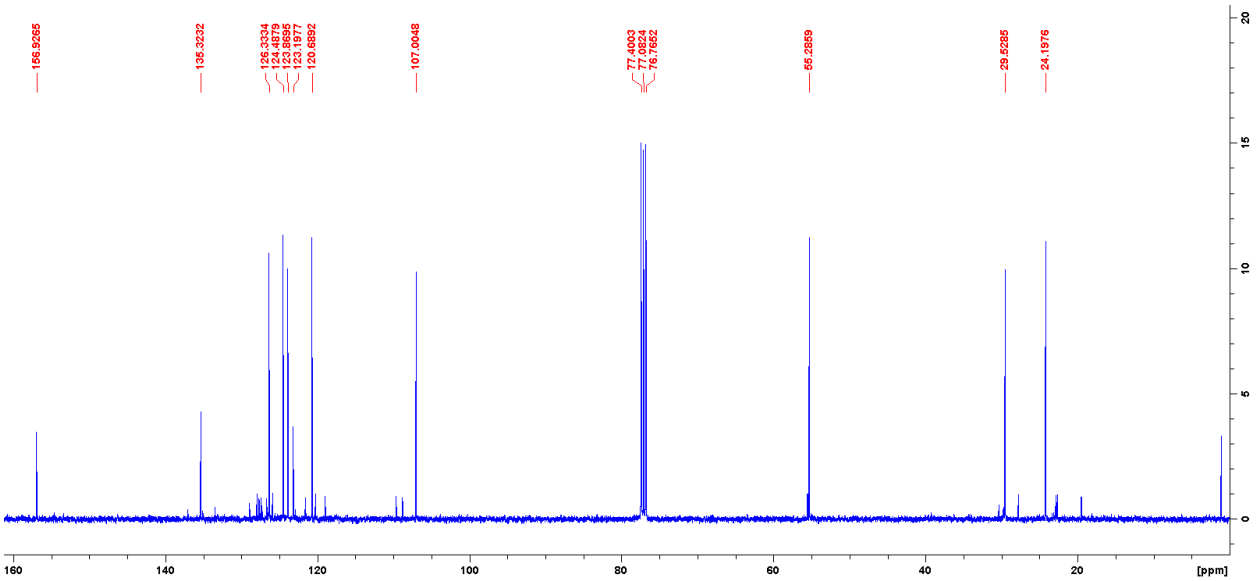

Figure S35. ^{13}C NMR spectrum of 1,4-dihydro-5-methoxynaphthalene

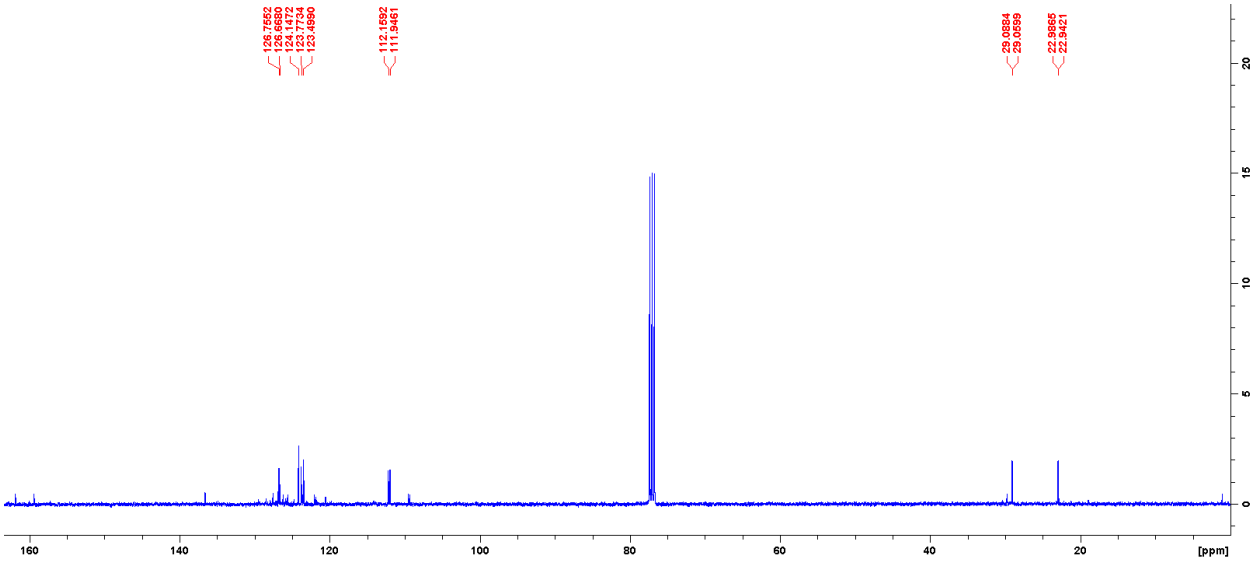

Figure S36. ^{13}C NMR spectrum of 1,4-dihydro-5-fluoronaphthalene

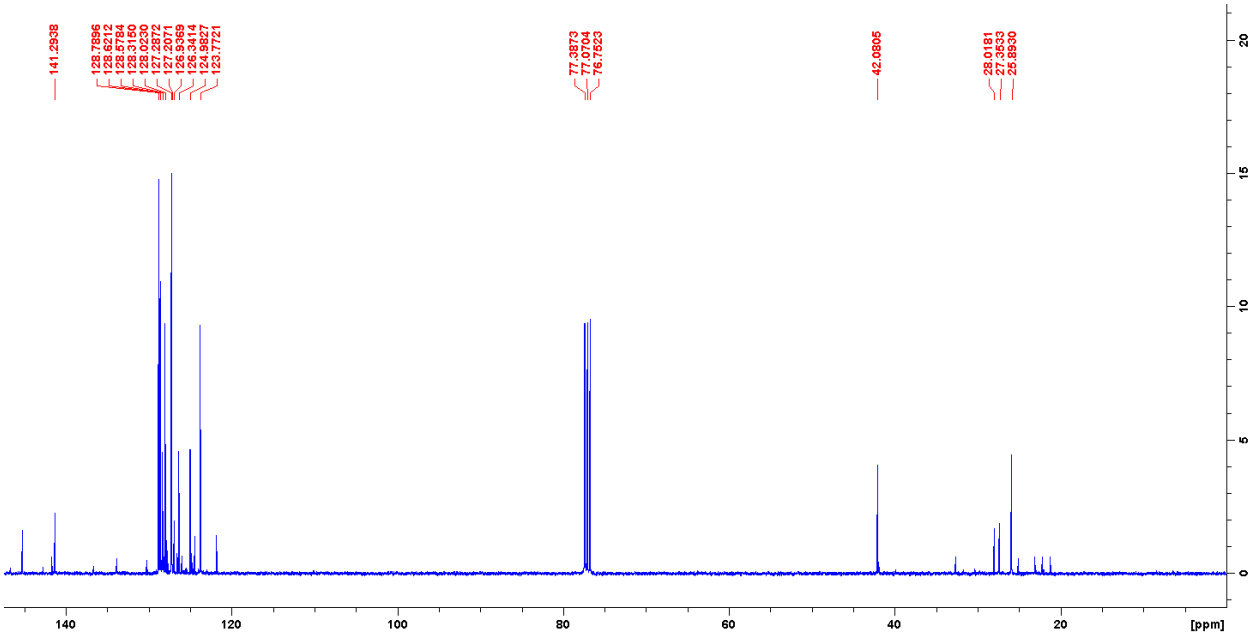

Figure S37. ^{13}C NMR spectrum of the products of the reduction of biphenyl by $SmBr_2$-NMEA

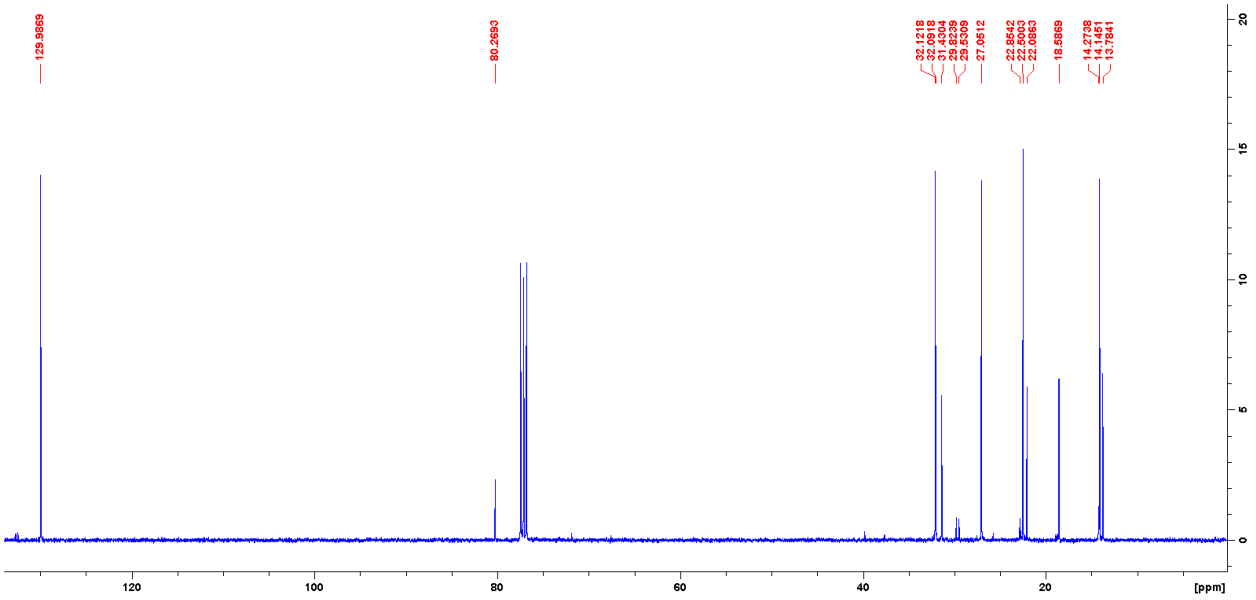

Figure S38. ^{13}C NMR spectrum of *cis*-5-decene

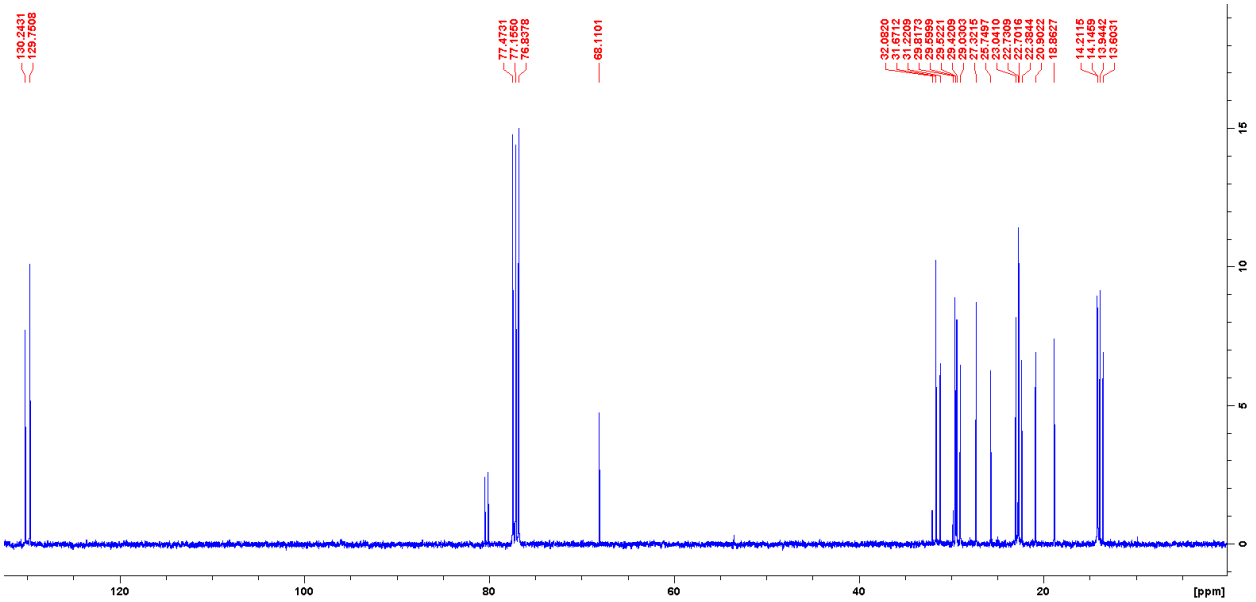

Figure S39. ^{13}C NMR spectrum of c*is*-4-decene

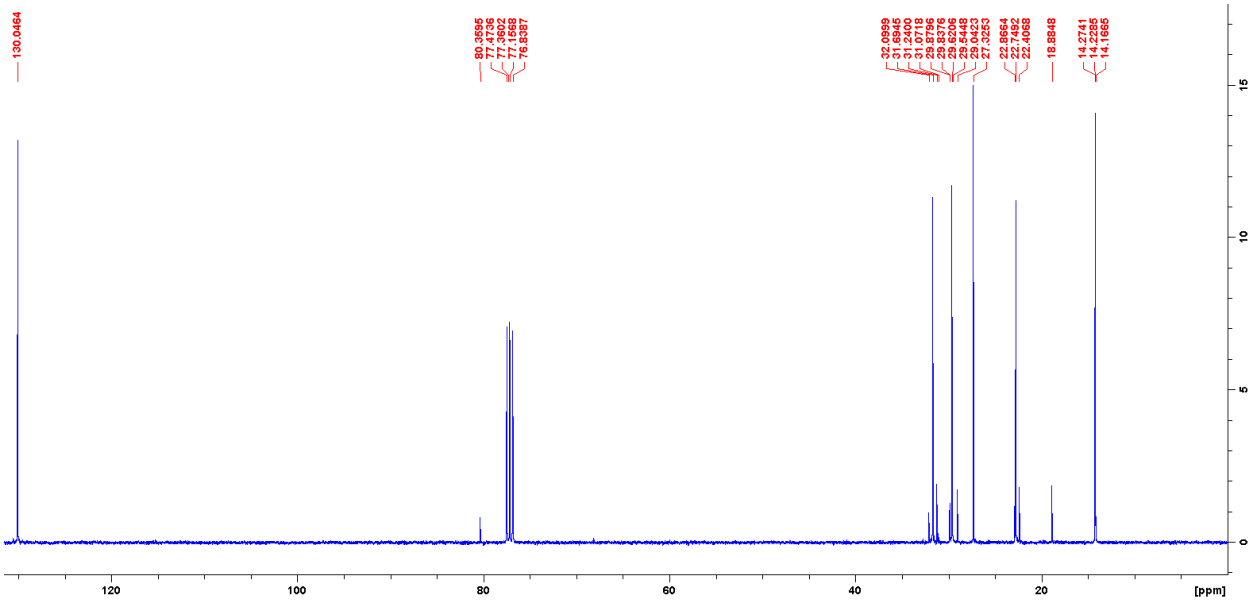

Figure S40. ^{13}C NMR spectrum of *cis*-6-dodecene

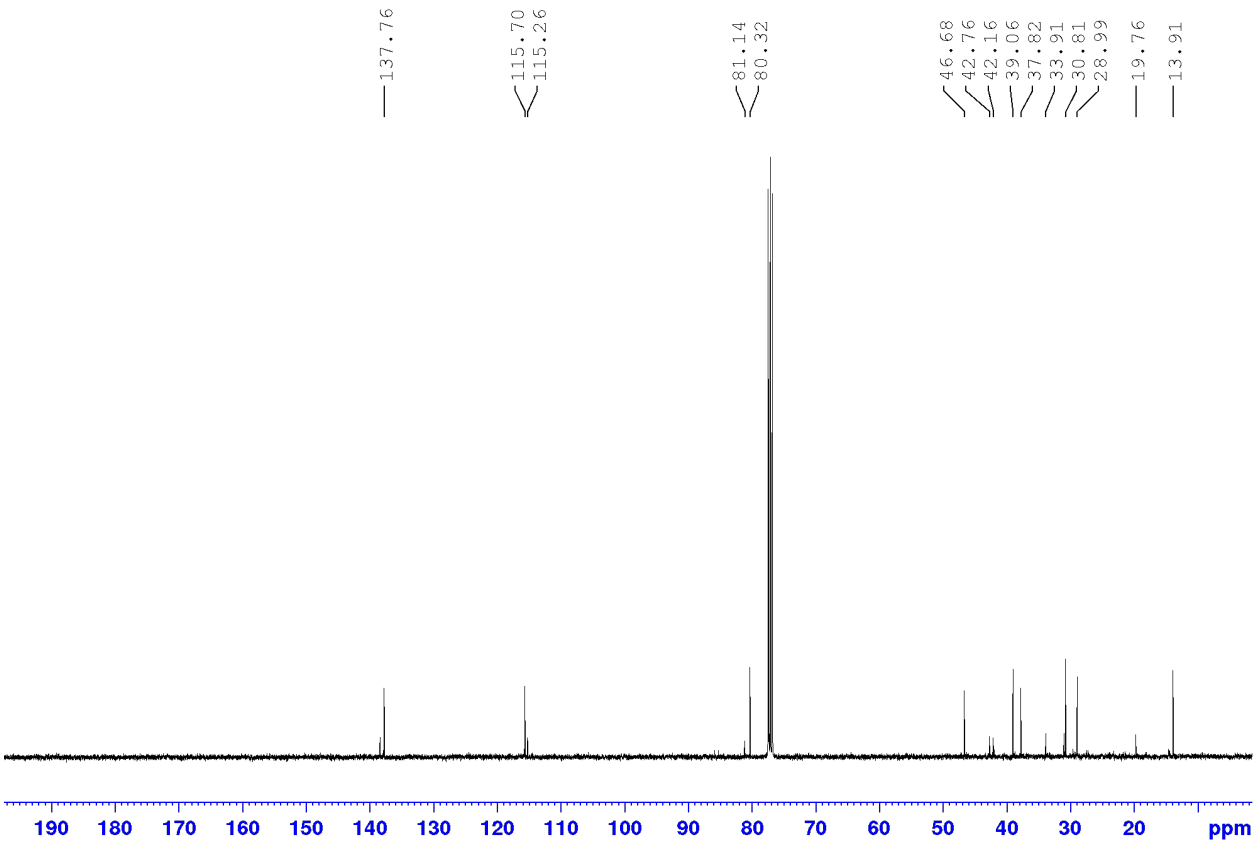

Figure S41. ^{13}C NMR spectrum of 2-allyl-5-methylcyclopentan-1-ol

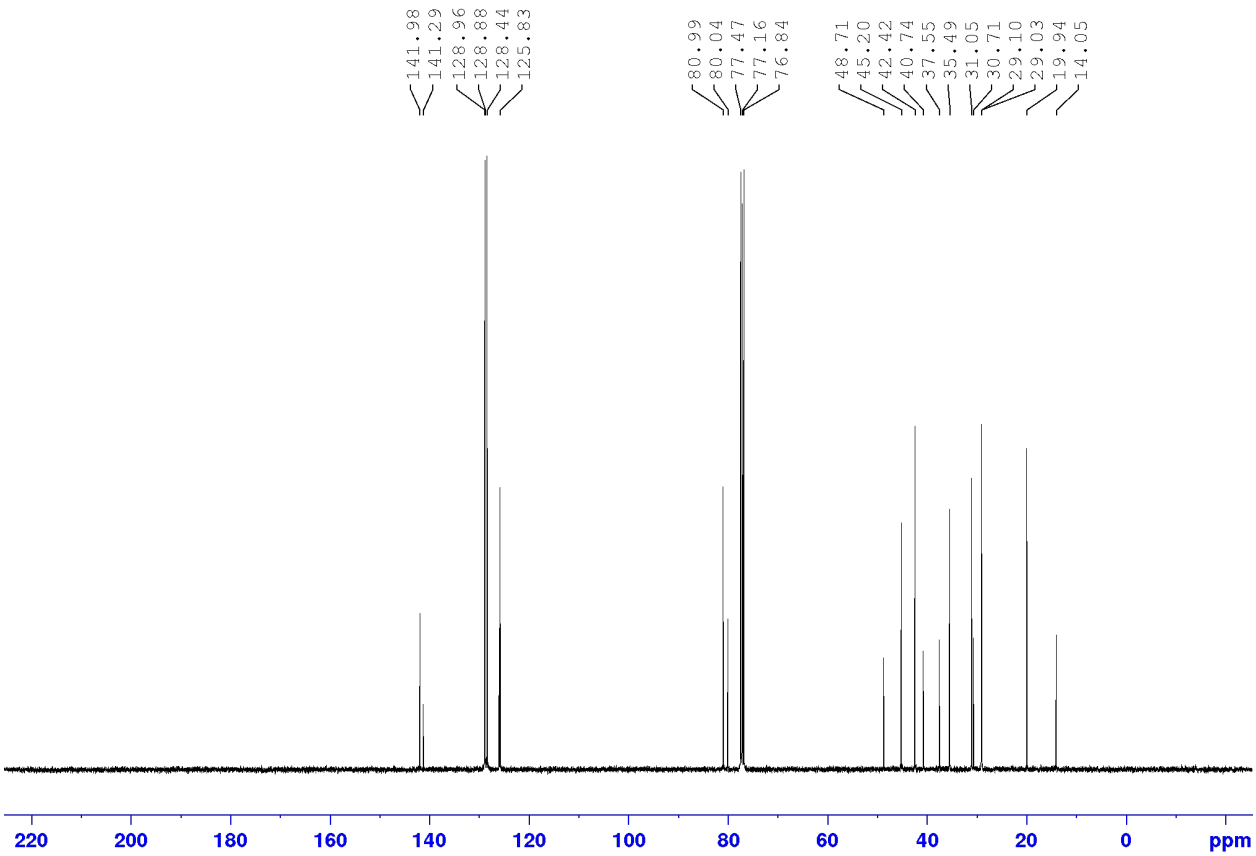

Figure S42. ^{13}C NMR spectrum of 2-benzyl-5-methylcyclopentan-1-ol.

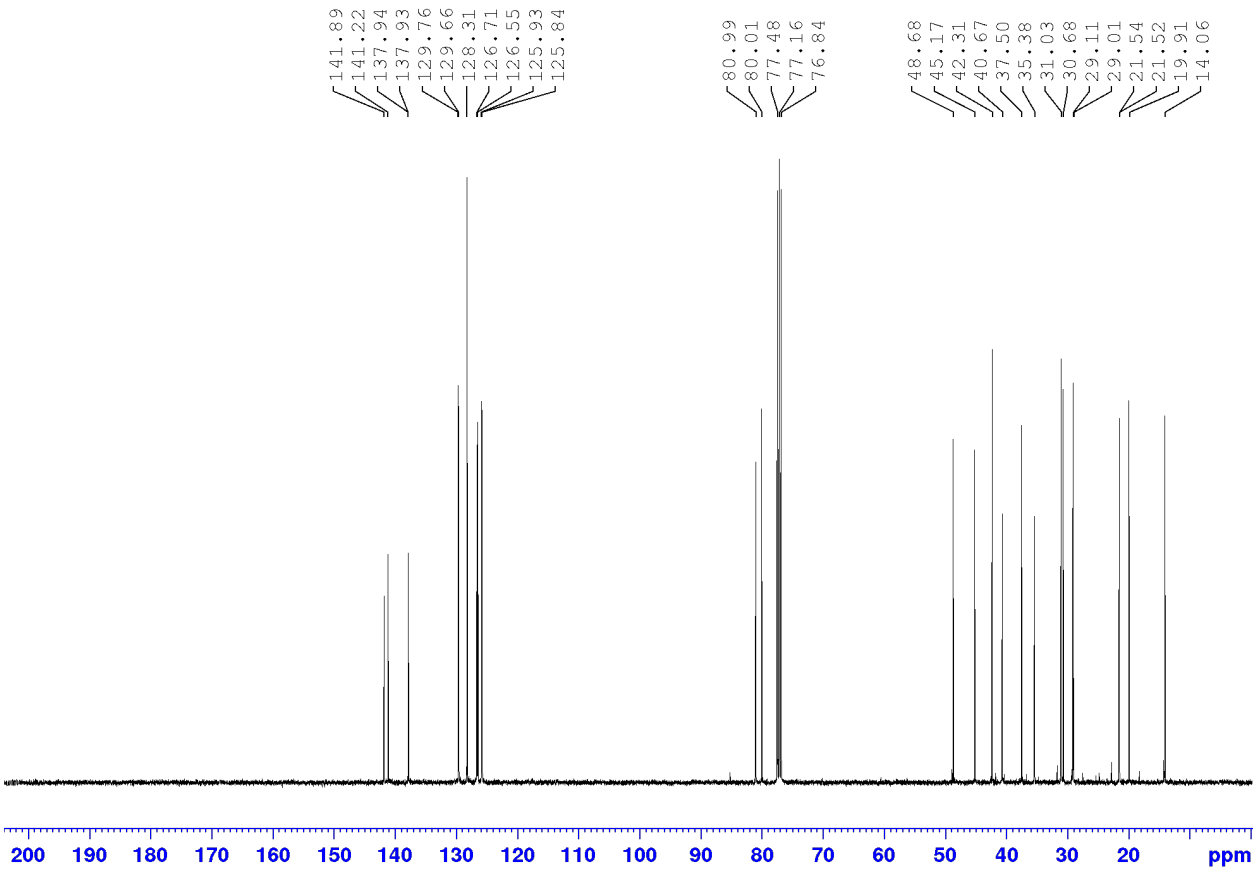

Figure S43. ^{13}C NMR spectrum of 2-methyl-5-(3-methylbenzyl)cyclopentan-1-ol

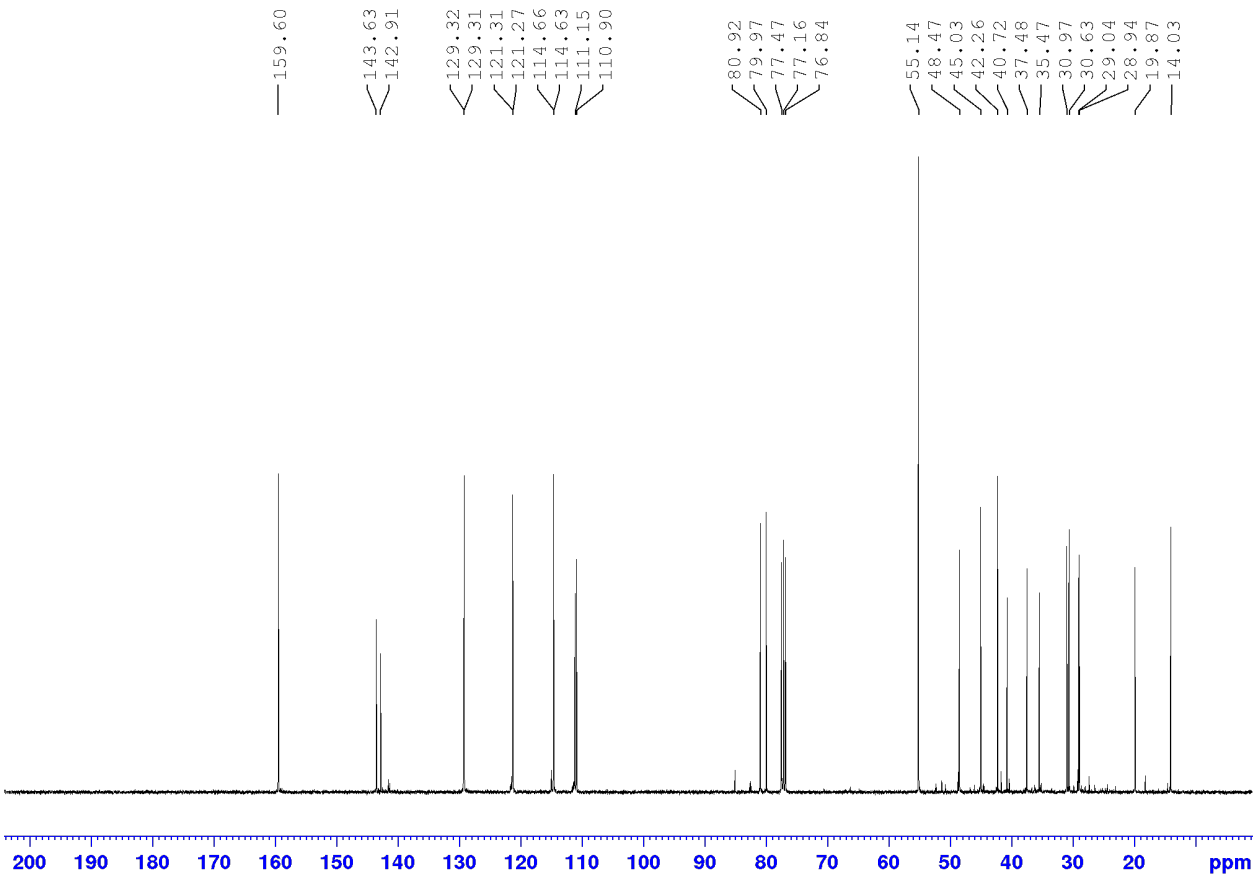

Figure S44. ^{13}C NMR spectrum of 2-methyl-5-(3-methoxybenzyl)cyclopentan-1-ol.

14. Computational Details

Gaussian09 programs were used for the calculations with the APF-D hybrid DFT method and the 6-311+G(2d,p) basis set.[4–7] Natural-population analysis was obtained by including pop=npa.[8] Solvation values were calculated using the polarizable continuum model with integral equation formalism IEFPCM with tetrahydrofuran as the solvent.[9,10] The geometries and frequencies were calculated with the keywords uapfd/6-311+g(2d,p) opt=(calcfc,tight) int=(ultrafine,acc2e=12) pop=npa scrf=(iefpcm,solvent=thf)

Table S3. DFT Results for Hydrogen Atom

	E+ZPE	G	H	S
Gas Phase				
Hydrogen atom	-0.502246	-0.512900	-0.499886	27.392
IEFPCM(THF)				
Hydrogen atom	-0.502264	-0.512918	-0.499903	27.392

Hydrogen atom (gas)

```
SCF Done:  E(UAPFD) =                          -0.502246024723
Zero-point correction=                      0.000000 (Hartree/Particle)
Thermal correction to Energy=               0.001416
Thermal correction to Enthalpy=             0.002360
Thermal correction to Gibbs Free Energy=   -0.010654
Sum of electronic and zero-point Energies=          -0.502246
Sum of electronic and thermal Energies=             -0.500830
Sum of electronic and thermal Enthalpies=           -0.499886
Sum of electronic and thermal Free Energies=        -0.512900

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   0.889             2.981            27.392
 Electronic              0.000             0.000             1.377
 Translational           0.889             2.981            26.014
 Rotational              0.000             0.000             0.000
 Vibrational             0.000             0.000             0.000

Charge =  0 Multiplicity = 2    Standard orientation

 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          1           0        0.000000    0.000000    0.000000
```

Hydrogen atom (iefpcm,thf)

```
SCF Done:  E(UAPFD) =                          -0.502263907129
Zero-point correction=                      0.000000 (Hartree/Particle)
Thermal correction to Energy=               0.001416
Thermal correction to Enthalpy=             0.002360
Thermal correction to Gibbs Free Energy=   -0.010654
Sum of electronic and zero-point Energies=          -0.502264
Sum of electronic and thermal Energies=             -0.500848
Sum of electronic and thermal Enthalpies=           -0.499903
Sum of electronic and thermal Free Energies=        -0.512918

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   0.889             2.981            27.392
```

Electronic	0.000	0.000	1.377
Translational	0.889	2.981	26.014
Rotational	0.000	0.000	0.000
Vibrational	0.000	0.000	0.000

Charge = 0 Multiplicity = 2 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Table S4. DFT Results for N-Methylethanolamine and Associated Radical

NMEA (gas)

SCF Done: E(UAPFD) = -249.557496353
Zero-point correction= 0.125431 (Hartree/Particle)
Thermal correction to Energy= 0.132273
Thermal correction to Enthalpy= 0.133217
Thermal correction to Gibbs Free Energy= 0.095148
Sum of electronic and zero-point Energies= -249.439551
Sum of electronic and thermal Energies= -249.432709
Sum of electronic and thermal Enthalpies= -249.431765
Sum of electronic and thermal Free Energies= -249.469834

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	83.003	22.601	80.124
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	38.863
Rotational	0.889	2.981	25.833
Vibrational	81.225	16.639	15.427

Charge = 0 Multiplicity = 1 Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.883651	-0.390455	0.290124
2	1	0	-0.833169	-0.414963	1.288549
3	6	0	-0.065034	0.721241	-0.214752
4	1	0	-0.119051	0.747463	-1.283066
5	1	0	-0.431973	1.644012	0.183681
6	6	0	1.398423	0.520032	0.220458
7	1	0	2.008633	1.282426	-0.216918
8	1	0	1.464626	0.578231	1.286821
9	6	0	-2.280587	-0.198392	-0.125303
10	1	0	-2.334346	-0.170231	-1.193581
11	1	0	-2.876100	-1.008588	0.240549
12	1	0	-2.648132	0.723443	0.274736
13	8	0	1.853355	-0.763486	-0.216027
14	1	0	2.811421	-0.797999	-0.165846

NMEA (iefpcm, thf)

SCF Done: E(UAPFD) = -249.565908209
Zero-point correction= 0.125645 (Hartree/Particle)
Thermal correction to Energy= 0.132399
Thermal correction to Enthalpy= 0.133343
Thermal correction to Gibbs Free Energy= 0.095576
Sum of electronic and zero-point Energies= -249.447108
Sum of electronic and thermal Energies= -249.440354
Sum of electronic and thermal Enthalpies= -249.439410
Sum of electronic and thermal Free Energies= -249.477178

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	83.082	22.484	79.488
Electronic	0.000	0.000	0.000

Translational	0.889	2.981	38.863
Rotational	0.889	2.981	25.842
Vibrational	81.304	16.522	14.783

Charge = 0 Multiplicity = 1 Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.883651	-0.390455	0.290124
2	1	0	-0.833169	-0.414963	1.288549
3	6	0	-0.065034	0.721241	-0.214752
4	1	0	-0.119051	0.747463	-1.283066
5	1	0	-0.431973	1.644012	0.183681
6	6	0	1.398423	0.520032	0.220458
7	1	0	2.008633	1.282426	-0.216918
8	1	0	1.464626	0.578231	1.286821
9	6	0	-2.280587	-0.198392	-0.125303
10	1	0	-2.334346	-0.170231	-1.193581
11	1	0	-2.876100	-1.008588	0.240549
12	1	0	-2.648132	0.723443	0.274736
13	8	0	1.853355	-0.763486	-0.216027
14	1	0	2.811421	-0.797999	-0.165846

NMEA O-Oxidized Radical (gas)

SCF Done: E(UAPFD) = -248.884458230

Zero-point correction=	0.111618 (Hartree/Par$
Thermal correction to Energy=	0.117922
Thermal correction to Enthalpy=	0.118866
Thermal correction to Gibbs Free Energy=	0.081361
Sum of electronic and zero-point Energies=	-248.783203
Sum of electronic and thermal Energies=	-248.776899
Sum of electronic and thermal Enthalpies=	-248.775955
Sum of electronic and thermal Free Energies=	-248.813460

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	73.997	21.160	78.935
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	38.823
Rotational	0.889	2.981	25.725
Vibrational	72.220	15.199	13.010

Charge = 0 Multiplicity = 2 Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.824315	-0.392514	0.284019
2	1	0	-0.769546	-0.434113	1.281651
3	6	0	0.021209	0.704799	-0.207807
4	1	0	-0.037394	0.749310	-1.275273
5	1	0	-0.318946	1.630619	0.206985
6	6	0	1.480909	0.457815	0.216310
7	1	0	2.109102	1.210483	-0.212367
8	1	0	1.553941	0.497391	1.283081
9	6	0	-2.217665	-0.156756	-0.120820
10	1	0	-2.275959	-0.110314	-1.188221
11	1	0	-2.832798	-0.956466	0.235515
12	1	0	-2.558443	0.768118	0.295566
13	8	0	1.899191	-0.830323	-0.242646

NMEA O-Oxidized Radical (iefpcm, thf)

SCF Done: E(UAPFD) = -248.891641012

Zero-point correction=	0.111461 (Hartree/Par$
Thermal correction to Energy=	0.117789
Thermal correction to Enthalpy=	0.118733
Thermal correction to Gibbs Free Energy=	0.081269
Sum of electronic and zero-point Energies=	-248.790005

```
 Sum of electronic and thermal Energies=             -248.783677
 Sum of electronic and thermal Enthalpies=           -248.782733
 Sum of electronic and thermal Free Energies=        -248.820197

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  73.914             21.328             78.850
 Electronic              0.000              0.000              1.377
 Translational           0.889              2.981             38.823
 Rotational              0.889              2.981             25.725
 Vibrational            72.136             15.367             12.925

Charge =  0 Multiplicity = 2    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          7           0       -0.824315   -0.392514    0.284019
      2          1           0       -0.769546   -0.434113    1.281651
      3          6           0        0.021209    0.704799   -0.207807
      4          1           0       -0.037394    0.749310   -1.275273
      5          1           0       -0.318946    1.630619    0.206985
      6          6           0        1.480909    0.457815    0.216310
      7          1           0        2.109102    1.210483   -0.212367
      8          1           0        1.553941    0.497391    1.283081
      9          6           0       -2.217665   -0.156756   -0.120820
     10          1           0       -2.275959   -0.110314   -1.188221
     11          1           0       -2.832798   -0.956466    0.235515
     12          1           0       -2.558443    0.768118    0.295566
     13          8           0        1.899191   -0.830323   -0.242646
```

Table S5. DFT Results for *trans*-Stilbene and Associated Radical

Trans stilbene (gas)

```
 SCF Done:  E(UAPFD) =                               -540.392686521
 Zero-point correction=                           0.214889 (Hartree/Particle)
 Thermal correction to Energy=                    0.226211
 Thermal correction to Enthalpy=                  0.227155
 Thermal correction to Gibbs Free Energy=         0.175248
 Sum of electronic and zero-point Energies=          -540.177797
 Sum of electronic and thermal Energies=             -540.166476
 Sum of electronic and thermal Enthalpies=           -540.165532
 Sum of electronic and thermal Free Energies=        -540.217439

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 141.949             44.550            109.247
 Electronic              0.000              0.000              0.000
 Translational           0.889              2.981             41.472
 Rotational              0.889              2.981             31.883
 Vibrational           140.172             38.588             35.892

Charge =  0 Multiplicity = 1    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.490315    0.456729   -0.011896
      2          1           0        0.222897    1.511117    0.010382
      3          6           0       -0.490322   -0.456766   -0.012165
      4          1           0       -0.222928   -1.511172    0.009562
      5          6           0        1.924332    0.192462   -0.012496
      6          6           0        2.806347    1.262664    0.174415
      7          6           0        2.471352   -1.084611   -0.194201
      8          6           0        4.179888    1.068340    0.194215
      9          1           0        2.401735    2.261595    0.310947
     10          6           0        3.841491   -1.280125   -0.174318
     11          1           0        1.817218   -1.933106   -0.364018
     12          6           0        4.704610   -0.205460    0.021901
```

13	1	0	4.842475	1.914897	0.343673
14	1	0	4.243650	-2.277904	-0.319178
15	1	0	5.778193	-0.362239	0.034319
16	6	0	-1.924338	-0.192480	-0.012654
17	6	0	-2.806352	-1.262665	0.174360
18	6	0	-2.471350	1.084593	-0.194372
19	6	0	-4.179886	-1.068312	0.194309
20	1	0	-2.401742	-2.261600	0.310876
21	6	0	-3.841484	1.280135	-0.174344
22	1	0	-1.817215	1.933054	-0.364360
23	6	0	-4.704601	0.205496	0.022018
24	1	0	-4.842475	-1.914851	0.343858
25	1	0	-4.243642	2.277912	-0.319227
26	1	0	-5.778180	0.362294	0.034542

Trans stilbene (iefpcm,thf)

SCF Done: E(UAPFD) = -540.397938661
Zero-point correction= 0.214930 (Hartree/Particle)
Thermal correction to Energy= 0.226262
Thermal correction to Enthalpy= 0.227206
Thermal correction to Gibbs Free Energy= 0.174764
Sum of electronic and zero-point Energies= -540.183009
Sum of electronic and thermal Energies= -540.171677
Sum of electronic and thermal Enthalpies= -540.170732
Sum of electronic and thermal Free Energies= -540.223175

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	141.982	44.503	110.375
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	41.472
Rotational	0.889	2.981	31.886
Vibrational	140.204	38.541	37.017

Charge = 0 Multiplicity = 1 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.491806	0.455933	0.000030
2	1	0	0.230205	1.511896	0.000022
3	6	0	-0.491797	-0.455877	0.000018
4	1	0	-0.230181	-1.511837	-0.000013
5	6	0	1.926149	0.188122	0.000020
6	6	0	2.810423	1.274009	-0.000152
7	6	0	2.471385	-1.103767	0.000177
8	6	0	4.185514	1.082586	-0.000180
9	1	0	2.407493	2.282842	-0.000269
10	6	0	3.842983	-1.295685	0.000150
11	1	0	1.817460	-1.969172	0.000335
12	6	0	4.709033	-0.204214	-0.000031
13	1	0	4.849438	1.941219	-0.000318
14	1	0	4.243467	-2.304583	0.000277
15	1	0	5.782992	-0.359134	-0.000050
16	6	0	-1.926144	-0.188093	0.000014
17	6	0	-2.810391	-1.274002	-0.000154
18	6	0	-2.471416	1.103781	0.000171
19	6	0	-4.185487	-1.082617	-0.000177
20	1	0	-2.407435	-2.282825	-0.000272
21	6	0	-3.843018	1.295662	0.000149
22	1	0	-1.817517	1.969206	0.000319
23	6	0	-4.709040	0.204169	-0.000027
24	1	0	-4.849387	-1.941268	-0.000311
25	1	0	-4.243529	2.304550	0.000274
26	1	0	-5.783003	0.359061	-0.000042

Trans stilbene radical (gas)

SCF Done: E(UAPFD) = -540.969963709
Zero-point correction= 0.225003 (Hartree/Particle)

```
 Thermal correction to Energy=                    0.236512
 Thermal correction to Enthalpy=                  0.237456
 Thermal correction to Gibbs Free Energy=         0.184607
 Sum of electronic and zero-point Energies=           -540.744960
 Sum of electronic and thermal Energies=              -540.733452
 Sum of electronic and thermal Enthalpies=            -540.732508
 Sum of electronic and thermal Free Energies=         -540.785356

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 148.414             45.966           111.230
 Electronic              0.000              0.000             1.377
 Translational           0.889              2.981            41.488
 Rotational              0.889              2.981            31.810
 Vibrational           146.636             40.005            36.554

Charge =  0 Multiplicity = 2    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.635468   -1.411954   -0.666081
      2          1           0       -0.304523   -1.150337   -1.676801
      3          6           0        0.501566   -1.348807    0.295094
      4          1           0        0.370530   -1.871308    1.239098
      5          6           0       -1.789030   -0.510590   -0.272547
      6          6           0       -3.094266   -0.993015   -0.248793
      7          6           0       -1.562338    0.824373    0.061196
      8          6           0       -4.154619   -0.160858    0.091056
      9          1           0       -3.284075   -2.033031   -0.500019
     10          6           0       -2.618790    1.658858    0.397617
     11          1           0       -0.546491    1.207756    0.063718
     12          6           0       -3.919976    1.168905    0.413823
     13          1           0       -5.166189   -0.554526    0.105912
     14          1           0       -2.425576    2.696094    0.653048
     15          1           0       -4.745822    1.820264    0.681037
     16          6           0        1.684883   -0.606522    0.125570
     17          6           0        2.673804   -0.616909    1.143882
     18          6           0        1.950609    0.179946   -1.024578
     19          6           0        3.842760    0.102695    1.016852
     20          1           0        2.493825   -1.208322    2.036878
     21          6           0        3.124604    0.897657   -1.140989
     22          1           0        1.218672    0.226182   -1.823453
     23          6           0        4.081299    0.867344   -0.126776
     24          1           0        4.580982    0.075172    1.812330
     25          1           0        3.301720    1.493145   -2.031349
     26          1           0        5.000940    1.434119   -0.224797
     27          1           0       -1.004214   -2.441953   -0.727552
```

Trans stilbene radical (iefpcm.thf)

```
 SCF Done:  E(UAPFD) =                               -540.974539180
 Zero-point correction=                           0.224935 (Hartree/Particle)
 Thermal correction to Energy=                    0.236464
 Thermal correction to Enthalpy=                  0.237408
 Thermal correction to Gibbs Free Energy=         0.184077
 Sum of electronic and zero-point Energies=           -540.749605
 Sum of electronic and thermal Energies=              -540.738075
 Sum of electronic and thermal Enthalpies=            -540.737131
 Sum of electronic and thermal Free Energies=         -540.790462

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 148.383             45.958           112.245
 Electronic              0.000              0.000             1.377
 Translational           0.889              2.981            41.488
 Rotational              0.889              2.981            31.823
 Vibrational           146.606             39.996            37.556

Charge =  0 Multiplicity = 2    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
```

Number	Number	Type	X	Y	Z
1	6	0	-0.631721	-1.338191	-0.799262
2	1	0	-0.287405	-0.991402	-1.778327
3	6	0	0.482669	-1.336819	0.191247
4	1	0	0.320735	-1.905046	1.103709
5	6	0	-1.793690	-0.478923	-0.344049
6	6	0	-3.068501	-1.017197	-0.191853
7	6	0	-1.599931	0.874701	-0.064388
8	6	0	-4.132118	-0.221579	0.222886
9	1	0	-3.232301	-2.070625	-0.401321
10	6	0	-2.659040	1.672704	0.345727
11	1	0	-0.606879	1.302850	-0.165106
12	6	0	-3.930930	1.126306	0.491515
13	1	0	-5.119650	-0.657941	0.336660
14	1	0	-2.492197	2.724662	0.555739
15	1	0	-4.758931	1.748712	0.815293
16	6	0	1.679530	-0.602495	0.091053
17	6	0	2.633980	-0.670669	1.141038
18	6	0	1.995585	0.226346	-1.016753
19	6	0	3.817260	0.036149	1.083182
20	1	0	2.416031	-1.295513	2.002330
21	6	0	3.183666	0.930269	-1.063865
22	1	0	1.295057	0.314677	-1.839762
23	6	0	4.105377	0.844294	-0.019587
24	1	0	4.527513	-0.035586	1.901148
25	1	0	3.399512	1.558182	-1.922906
26	1	0	5.035615	1.400591	-0.063185
27	1	0	-0.989919	-2.362945	-0.945630

Table S6. DFT Results for Naphthalene and Associated Radical

Napthalene (gas)

SCF Done: E(UAPFD) = -385.666386714
Zero-point correction= 0.147444 (Hartree/Particle)
Thermal correction to Energy= 0.154288
Thermal correction to Enthalpy= 0.155232
Thermal correction to Gibbs Free Energy= 0.117518
Sum of electronic and zero-point Energies= -385.518943
Sum of electronic and thermal Energies= -385.512099
Sum of electronic and thermal Enthalpies= -385.511155
Sum of electronic and thermal Free Energies= -385.548869

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	96.817	28.905	79.375
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	40.455
Rotational	0.889	2.981	26.158
Vibrational	95.039	22.943	12.762

Charge = 0 Multiplicity = 1 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	-2.419990	0.705452
2	6	0	0.000000	-1.237328	1.396292
3	6	0	0.000000	0.000000	0.712084
4	6	0	0.000000	0.000000	-0.712084
5	6	0	0.000000	-1.237328	-1.396292
6	6	0	0.000000	-2.419990	-0.705452
7	1	0	0.000000	1.234133	2.482481
8	1	0	0.000000	-3.363547	1.241649
9	1	0	0.000000	-1.234133	2.482481
10	6	0	0.000000	1.237328	1.396292
11	6	0	0.000000	1.237328	-1.396292
12	1	0	0.000000	-1.234133	-2.482481
13	1	0	0.000000	-3.363547	-1.241649

14	6	0	0.000000	2.419990	-0.705452
15	6	0	0.000000	2.419990	0.705452
16	1	0	0.000000	1.234133	-2.482481
17	1	0	0.000000	3.363547	-1.241649
18	1	0	0.000000	3.363547	1.241649

Napthalene (iefpcm,thf)

SCF Done: E(UAPFD) = -385.669898554
Zero-point correction= 0.147479 (Hartree/Particle)
Thermal correction to Energy= 0.154320
Thermal correction to Enthalpy= 0.155265
Thermal correction to Gibbs Free Energy= 0.117543
Sum of electronic and zero-point Energies= -385.522420
Sum of electronic and thermal Energies= -385.515578
Sum of electronic and thermal Enthalpies= -385.514634
Sum of electronic and thermal Free Energies= -385.552356

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	96.837	28.865	79.393
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	40.455
Rotational	0.889	2.981	26.161
Vibrational	95.060	22.904	12.776

Charge = 0 Multiplicity = 1 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	2.420972	0.705947
2	6	0	0.000000	1.237842	1.397714
3	6	0	0.000000	0.000000	0.712458
4	6	0	0.000000	0.000000	-0.712458
5	6	0	0.000000	1.237842	-1.397714
6	6	0	0.000000	2.420972	-0.705947
7	1	0	0.000000	-1.234739	2.483879
8	1	0	0.000000	3.364748	1.241770
9	1	0	0.000000	1.234739	2.483879
10	6	0	0.000000	-1.237842	1.397714
11	6	0	0.000000	-1.237842	-1.397714
12	1	0	0.000000	1.234739	-2.483879
13	1	0	0.000000	3.364748	-1.241770
14	6	0	0.000000	-2.420972	-0.705947
15	6	0	0.000000	-2.420972	0.705947
16	1	0	0.000000	-1.234739	-2.483879
17	1	0	0.000000	-3.364748	-1.241770
18	1	0	0.000000	-3.364748	1.241770

Napthalene radical (gas)

SCF Done: E(UAPFD) = -386.227060580
Zero-point correction= 0.156314 (Hartree/Particle)
Thermal correction to Energy= 0.163833
Thermal correction to Enthalpy= 0.164777
Thermal correction to Gibbs Free Energy= 0.123508
Sum of electronic and zero-point Energies= -386.070747
Sum of electronic and thermal Energies= -386.063227
Sum of electronic and thermal Enthalpies= -386.062283
Sum of electronic and thermal Free Energies= -386.103553

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	102.807	31.012	86.859
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.479
Rotational	0.889	2.981	29.012
Vibrational	101.029	25.050	15.990

Charge = 0 Multiplicity = 2 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.477360	0.682460	0.000000
2	6	0	1.290721	1.388792	-0.000001
3	6	0	0.050973	0.725473	0.000000
4	6	0	0.034216	-0.686559	0.000001
5	6	0	1.237066	-1.379748	0.000002
6	6	0	2.454520	-0.711273	0.000002
7	1	0	-1.144404	2.538244	0.000000
8	1	0	3.425022	1.211426	0.000000
9	1	0	1.301814	2.475014	-0.000002
10	6	0	-1.179093	1.454012	-0.000001
11	6	0	-1.270521	-1.439598	-0.000004
12	1	0	1.220634	-2.466825	0.000002
13	1	0	3.382861	-1.272986	0.000002
14	6	0	-2.486919	-0.577993	0.000001
15	6	0	-2.409694	0.786258	0.000001
16	1	0	-1.298995	-2.117952	-0.867831
17	1	0	-3.454216	-1.070457	0.000009
18	1	0	-3.325480	1.370565	0.000005
19	1	0	-1.299000	-2.117963	0.867816

Napthalene radical (iefpcm,thf)

SCF Done: E(UAPFD) = -386.230381619
Zero-point correction= 0.156241 (Hartree/Particle)
Thermal correction to Energy= 0.163768
Thermal correction to Enthalpy= 0.164712
Thermal correction to Gibbs Free Energy= 0.123410
Sum of electronic and zero-point Energies= -386.074141
Sum of electronic and thermal Energies= -386.066614
Sum of electronic and thermal Enthalpies= -386.065670
Sum of electronic and thermal Free Energies= -386.106972

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	102.766	31.024	86.927
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.479
Rotational	0.889	2.981	29.015
Vibrational	100.988	25.062	16.055

Charge = 0 Multiplicity = 2 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.478719	0.682670	0.000001
2	6	0	1.291548	1.389983	-0.000001
3	6	0	0.050980	0.725880	-0.000002
4	6	0	0.033608	-0.687087	0.000000
5	6	0	1.237095	-1.380976	0.000002
6	6	0	2.455408	-0.712133	0.000003
7	1	0	-1.144719	2.539955	-0.000004
8	1	0	3.426586	1.211453	0.000002
9	1	0	1.303088	2.476249	-0.000003
10	6	0	-1.179418	1.455594	-0.000004
11	6	0	-1.271114	-1.439995	-0.000007
12	1	0	1.220057	-2.467884	0.000004
13	1	0	3.383700	-1.274075	0.000005
14	6	0	-2.487275	-0.578342	0.000005
15	6	0	-2.410760	0.786774	0.000003
16	1	0	-1.300421	-2.119712	-0.866249
17	1	0	-3.454049	-1.071769	0.000016
18	1	0	-3.326557	1.371310	0.000010
19	1	0	-1.300423	-2.119736	0.866216

Table S7. DFT Results for Biphenyl and Associated Radical

Biphenyl (gas)

```
 SCF Done:  E(UAPFD) =                                -463.035608980
 Zero-point correction=                           0.181723 (Hartree/Particle)
 Thermal correction to Energy=                    0.190606
 Thermal correction to Enthalpy=                  0.191550
 Thermal correction to Gibbs Free Energy=         0.147780
 Sum of electronic and zero-point Energies=           -462.853886
 Sum of electronic and thermal Energies=              -462.845003
 Sum of electronic and thermal Enthalpies=            -462.844059
 Sum of electronic and thermal Free Energies=         -462.887829

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 119.607             36.250             92.121
 Electronic              0.000              0.000              0.000
 Translational           0.889              2.981             41.007
 Rotational              0.889              2.981             29.041
 Vibrational           117.829             30.289             22.073

Charge =  0 Multiplicity = 1    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.000000    0.737791    0.000000
      2          6           0        0.424383    1.452865   -1.122255
      3          6           0        0.425040    2.840375   -1.122774
      4          6           0        0.000000    3.540017    0.000000
      5          6           0       -0.425040    2.840375    1.122774
      6          6           0       -0.424383    1.452865    1.122255
      7          6           0        0.000000   -0.737791    0.000000
      8          6           0       -0.424383   -1.452865   -1.122255
      9          6           0       -0.425040   -2.840375   -1.122774
     10          6           0        0.000000   -3.540017    0.000000
     11          6           0        0.425040   -2.840375    1.122774
     12          6           0        0.424383   -1.452865    1.122255
     13          1           0        0.780753    0.912172   -1.993378
     14          1           0        0.767352    3.378292   -2.001219
     15          1           0        0.000000    4.625163    0.000000
     16          1           0       -0.767352    3.378292    2.001219
     17          1           0       -0.780753    0.912172    1.993379
     18          1           0       -0.780753   -0.912172   -1.993378
     19          1           0       -0.767352   -3.378292   -2.001219
     20          1           0        0.000000   -4.625163    0.000000
     21          1           0        0.767352   -3.378292    2.001219
     22          1           0        0.780753   -0.912172    1.993379
```

Biphenyl (iefpcm,thf)

```
 SCF Done:  E(UAPFD) =                                -463.039582016
 Zero-point correction=                           0.181716 (Hartree/Particle)
 Thermal correction to Energy=                    0.190591
 Thermal correction to Enthalpy=                  0.191535
 Thermal correction to Gibbs Free Energy=         0.147140
 Sum of electronic and zero-point Energies=           -462.857866
 Sum of electronic and thermal Energies=              -462.848991
 Sum of electronic and thermal Enthalpies=            -462.848047
 Sum of electronic and thermal Free Energies=         -462.892442

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 119.597             36.238             93.438
 Electronic              0.000              0.000              0.000
 Translational           0.889              2.981             41.007
 Rotational              0.889              2.981             30.422
 Vibrational           117.820             30.276             22.009

Charge =  0 Multiplicity = 1    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
```

1	6	0	-0.738250	0.000000	0.000000
2	6	0	-1.453873	-1.128559	-0.409527
3	6	0	-2.842194	-1.129004	-0.410225
4	6	0	-3.542415	0.000000	0.000000
5	6	0	-2.842194	1.129004	0.410225
6	6	0	-1.453873	1.128559	0.409527
7	6	0	0.738250	0.000000	0.000000
8	6	0	1.453873	-1.128559	0.409527
9	6	0	2.842194	-1.129004	0.410225
10	6	0	3.542415	0.000000	0.000000
11	6	0	2.842194	1.129004	-0.410225
12	6	0	1.453873	1.128559	-0.409527
13	1	0	-0.915706	-2.006719	-0.752090
14	1	0	-3.379737	-2.012383	-0.740170
15	1	0	-4.627581	0.000000	0.000000
16	1	0	-3.379737	2.012383	0.740170
17	1	0	-0.915706	2.006719	0.752090
18	1	0	0.915706	-2.006719	0.752090
19	1	0	3.379737	-2.012383	0.740170
20	1	0	4.627581	0.000000	0.000000
21	1	0	3.379737	2.012383	-0.740170
22	1	0	0.915706	2.006719	-0.752090

Biphenyl radical (gas)

SCF Done: E(UAPFD) = -463.587605856
Zero-point correction= 0.190381 (Hartree/Particle)
Thermal correction to Energy= 0.199908
Thermal correction to Enthalpy= 0.200853
Thermal correction to Gibbs Free Energy= 0.154440
Sum of electronic and zero-point Energies= -463.397224
Sum of electronic and thermal Energies= -463.387697
Sum of electronic and thermal Enthalpies= -463.386753
Sum of electronic and thermal Free Energies= -463.433166

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	125.444	38.576	97.684
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	41.026
Rotational	0.889	2.981	30.504
Vibrational	123.667	32.614	24.777

Charge = 0 Multiplicity = 2 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.672314	-0.000004	-0.000012
2	6	0	1.416938	-1.188224	-0.263994
3	6	0	2.769659	-1.211662	-0.276634
4	6	0	3.593794	0.000003	0.000010
5	6	0	2.769655	1.211668	0.276640
6	6	0	1.416934	1.188217	0.263983
7	6	0	-0.781203	-0.000004	-0.000004
8	6	0	-1.512404	-1.170281	0.268513
9	6	0	-2.897023	-1.168925	0.269436
10	6	0	-3.601090	0.000004	0.000006
11	6	0	-2.897019	1.168929	-0.269430
12	6	0	-1.512400	1.170277	-0.268517
13	1	0	0.876603	-2.099380	-0.500205
14	1	0	3.291034	-2.135718	-0.508412
15	1	0	4.279165	0.190953	-0.844375
16	1	0	3.291021	2.135729	0.508417
17	1	0	0.876590	2.099370	0.500187
18	1	0	-0.984965	-2.086224	0.511392
19	1	0	-3.433286	-2.086279	0.491740
20	1	0	-4.686015	0.000006	0.000010
21	1	0	-3.433279	2.086286	-0.491732
22	1	0	-0.984957	2.086216	-0.511403

23	1	0	4.279153	-0.190945	0.844404

Biphenyl radical (iefpcm,thf)

```
 SCF Done:  E(UAPFD) =                              -463.591695813
 Zero-point correction=                          0.190341 (Hartree/Particle)
 Thermal correction to Energy=                   0.199866
 Thermal correction to Enthalpy=                 0.200810
 Thermal correction to Gibbs Free Energy=        0.154381
 Sum of electronic and zero-point Energies=          -463.401355
 Sum of electronic and thermal Energies=             -463.391830
 Sum of electronic and thermal Enthalpies=           -463.390886
 Sum of electronic and thermal Free Energies=        -463.437315

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 125.418             38.582             97.719
 Electronic              0.000              0.000              1.377
 Translational           0.889              2.981             41.026
 Rotational              0.889              2.981             30.507
 Vibrational           123.640             32.620             24.808

Charge =  0 Multiplicity = 2    Standard orientation
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.672827    0.000000   -0.000001
      2          6           0        1.418573   -1.193723   -0.243460
      3          6           0        2.772008   -1.216142   -0.255218
      4          6           0        3.595438    0.000000    0.000003
      5          6           0        2.772005    1.216142    0.255217
      6          6           0        1.418571    1.193724    0.243458
      7          6           0       -0.780964    0.000000    0.000000
      8          6           0       -1.513933   -1.175671    0.247687
      9          6           0       -2.899350   -1.174127    0.248416
     10          6           0       -3.604545    0.000000    0.000001
     11          6           0       -2.899350    1.174127   -0.248415
     12          6           0       -1.513933    1.175670   -0.247687
     13          1           0        0.881146   -2.111242   -0.460834
     14          1           0        3.294044   -2.144124   -0.468914
     15          1           0        4.282172    0.175870   -0.845944
     16          1           0        3.294040    2.144126    0.468908
     17          1           0        0.881143    2.111243    0.460831
     18          1           0       -0.989620   -2.098225    0.471023
     19          1           0       -3.435031   -2.095924    0.453283
     20          1           0       -4.689504    0.000000    0.000001
     21          1           0       -3.435031    2.095924   -0.453282
     22          1           0       -0.989620    2.098224   -0.471025
     23          1           0        4.282165   -0.175870    0.845955
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