Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information for

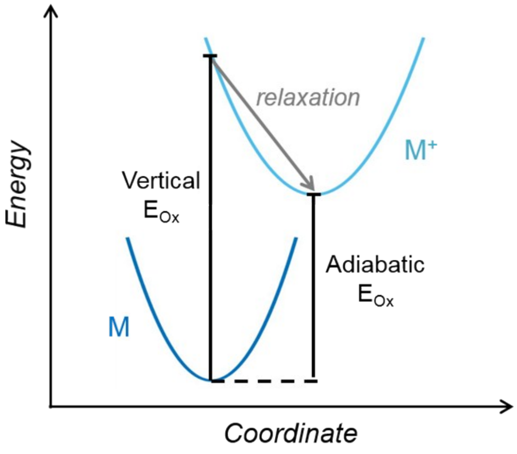
Mapping a Stable Solvent Structure Landscape for Aprotic Li-Air Battery Organic Electrolytes

Shuting Feng,†[a] Mao Chen,†[b] Livia Giordano,[c] Mingjun Huang,[b] Wenxu Zhang,[b] Chibueze V. Amanchukwu,[a] Robinson Anandakathir,[d] Yang Shao-Horn*[c] and Jeremiah A. Johnson*[b]

[a] *Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States*
[b] *Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States*
[c] *Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*
[d] *Samsung Advanced Institute of Technology (SAIT), 3 Van de Graaff Drive, Burlington, MA 01803, United States*
† These authors contributed equally.

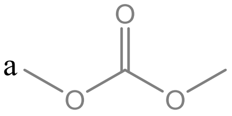
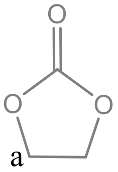
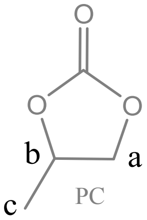
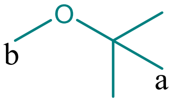
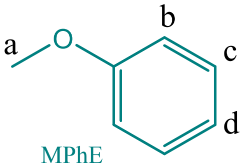
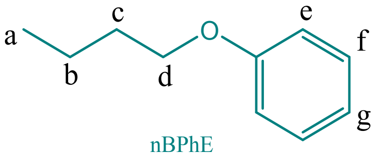
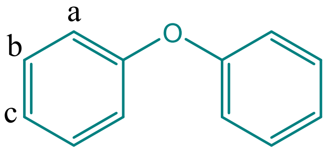
$$\begin{tikzcd}
\mathrm{RC-H}_{(g)} \arrow[r, "\Delta G_{g,deprot}"] & \mathrm{RC}^{-}_{(g)} \arrow[d, "\Delta \mathrm{G}_{s}(\mathrm{RC}^{-})"] & +\,\mathrm{H}^{+}_{(g)} \arrow[d, "\Delta \mathrm{G}_{s}(\mathrm{H}^{+})"] \\
\mathrm{RC-H}_{(s)} \arrow[u, "-\Delta \mathrm{G}_{s}(\mathrm{RC-H})"] \arrow[r, "\Delta G_{deprot}"] & \mathrm{RC}^{-}_{(s)} & +\,\mathrm{H}^{+}_{(s)}
\end{tikzcd}$$

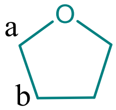
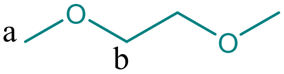
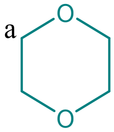
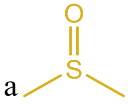
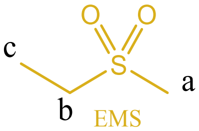
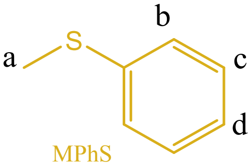
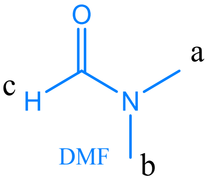
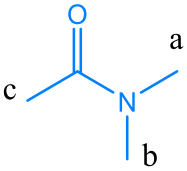
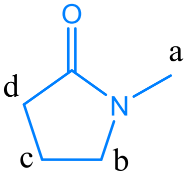
Figure S1. Thermodynamic cycle employed in the calculations of deprotonation energies (b) in dimethyl sulfoxide (DMSO).

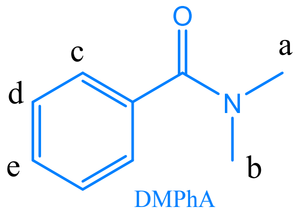
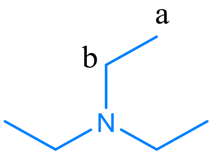
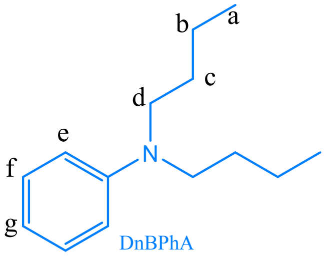
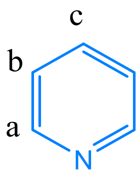
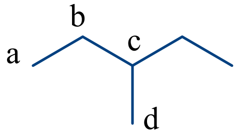
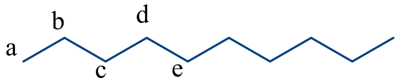
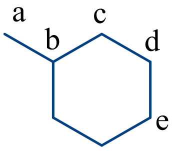
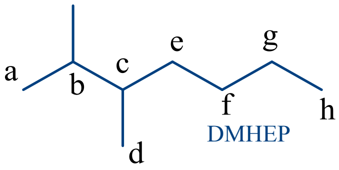


Scheme S1. A graphical comparison between the adiabatic and vertical oxidation energy. Adiabatic oxidation energy calculations allow for geometry optimization of the charged species.

Table S1. Calculated BDEs, deprotonation free energies, vertical and adiabatic redox energies of the compounds in Fig. 1. BDEs and deprotonation energies were obtained at the B3LYP/6-31G(d,p) level of theory. Redox energies were calculated at B3LYP/6-311++G(d,p) with geometries fully optimized at B3LYP/6-31G(d,p). O stands for oxidation; R stands for reduction.

#	Family	Structure with site labeling	BDE (kJ/mol)	Deprotonation energy (kJ/mol)	Vertical energy (eV)	Adiabatic energy (eV)
1	Carbonate	 DMC	a: 382.25	a: 336.31	O: -8.82 R: -0.74	O: -8.51 R: -1.42
2		 EC	a: 370.48	a: 287.94	O: -8.96 R: -0.79	O: -8.36 R: -1.57
3		 PC	a: 371.12 b: 358.71 c: 392.06	a: 304.95 b: 308.68 c: 116.90	O: -8.88 R: -0.80	O: -8.38 R: -1.54
4	Ether	 MtBE	a: 387.54 b: 361.07	a: 243.68 b: 382.91	O: -7.31 R: -0.73	O: -6.94 R: -0.83
5		 MPhE	a: 371.53 b: 432.38 c: 431.88 d: 437.93	a: 346.03 b: 315.79 c: 342.66 d: 348.66	O: -6.34 R: -0.82	O: -6.12 R: -1.25
6	Ether	 nBPhE	a: 386.20 b: 367.38 c: 372.89 d: 360.05 e: 440.64 f: 432.29 g: 437.85	a: 401.11 b: 395.97 c: 149.78 d: 349.33 e: 328.49 f: 341.82 g: 346.84	O: -6.30 R: -0.80	O: -6.08 R: -1.29
7		 DPhE	a: 441.57 b: 433.61 c: 437.43	a: 306.32 b: 329.96 c: 336.67	O: -6.29 R: -1.12	O: -6.16 R: -0.65

8		 THF	a: 353.47 b: 371.12	a: 378.01 b: 362.98	O: -7.41 R: -0.71	O: -6.94 R: -0.17
9		 DME	a: 366.20 b: 351.70	a: 373.79 b: 353.77	O: -7.35 R: -0.43	O: -7.17 R: -0.59
10		 Dioxane	a: 346.16	a: 339.62	O: -7.11 R: -0.68	O: -6.86 R: -1.56
11	S-containing	 DMSO	a: 390.38	a: 264.61	O: -6.75 R: -0.43	O: -6.46 R: -1.92
12		 EMS	a: 404.85 b: 375.81 c: 385.47	a: 215.44 b: 239.03 c: 125.56	O: -8.33 R: -0.87	O: -7.80 R: -2.88
13		 MPhS	a: 366.79 b: 434.64 c: 433.71 d: 434.62	a: 281.40 b: 315.18 c: 333.84 d: 331.92	O: -5.98 R: -0.90	O: -5.87 R: -1.54
14	N-containing	 DMF	a: 355.26 b: 350.39 c: 359.19	a: 342.18 b: 339.80 c: 311.22	O: -7.05 R: -0.75	O: -6.79 R: -1.13
15	N-containing	 DMA	a: 354.74 b: 350.57 c: 373.33	a: 354.65 b: 344.42 c: 254.10	O: -6.86 R: -0.77	O: -6.54 R: -1.04
16		 NMP	a: 352.41 b: 346.79 c: 366.63 d: 348.02	a: 345.63 b: 353.24 c: 373.86 d: 252.49	O: -6.86 R: -0.74	O: -6.54 R: -0.83

17		 DMPhA	a: 355.52 b: 351.86 c: 426.46 d: 434.09 e: 435.03	a: 340.79 b: 334.41 c: 315.83 d: 331.11 e: 331.47	O: -6.92 R: -1.38	O: -6.51 R: -2.01
18		 TEA	a: 383.57 b: 339.05	a: 380.80 b: 403.36	O: -6.03 R: -0.54	O: -5.29 R: -0.64
19		 DnBPhA	a: 386.24 b: 367.24 c: 368.83 d: 327.91 e: 434.35 f: 433.04 g: 434.98	a: 406.00 b: 407.12 c: 392.66 d: 346.86 e: 344.27 f: 345.10 g: 346.03	O: -6.20 R: -0.79	O: -5.04 R: -1.21
20		 Pyr	a: 411.30 b: 436.99 c: 431.27	a: 341.15 b: 318.95 c: 313.09	O: -7.51 R: -1.37	O: -6.94 R: -1.74
21	Alkane	 MP	a: 383.52 b: 366.10 c: 356.10 d: 383.43	a: 405.96 b: 412.92 c: 399.00 d: 403.16	O: -8.46 R: -0.62	O: -7.38 R: -0.83
22		 Decane	a: 386.04 b: 366.97 c: 366.89 d: 366.75 e: 367.23	a: 405.50 b: 408.23 c: 406.10 d: 405.21 e: 405.52	O: -8.07 R: -0.60	O: -7.33 R: -2.25
23	Alkane	 McHex	a: 387.32 b: 356.68 c: 372.02 d: 370.88 e: 371.36	a: 406.25 b: 397.42 c: 410.01 d: 410.28 e: 408.96	O: -8.00 R: -0.60	O: -7.24 R: -0.90
24		 DMHEP	a: 388.06 b: 350.90 c: 352.21 d: 384.86 e: 364.99 f: 368.77 g: 370.58	a: 409.14 b: 406.19 c: 396.42 d: 406.31 e: 410.83 f: 405.44 g: 412.76	O: -8.11 R: -0.57	O: -7.10 R: -2.32

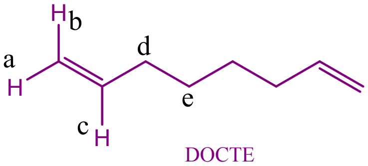
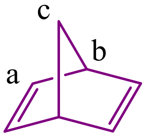
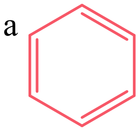
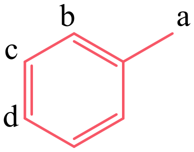
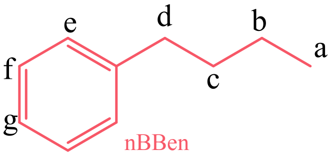
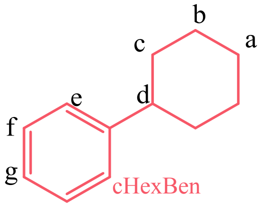
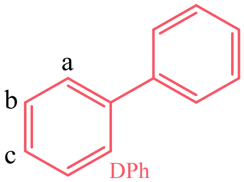
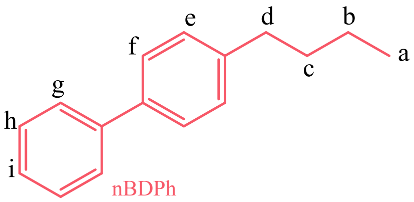
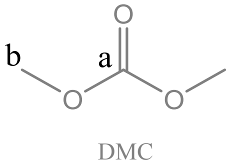
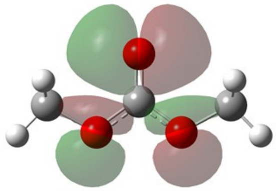
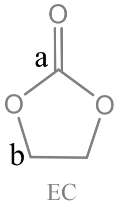
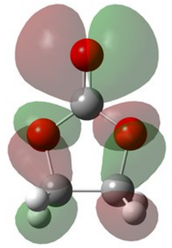
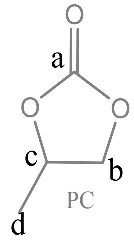
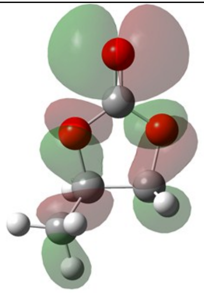
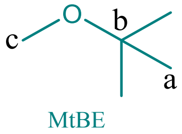
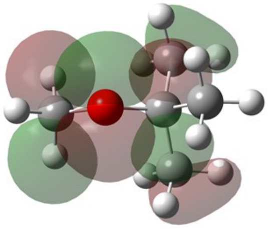
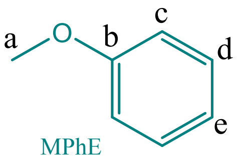
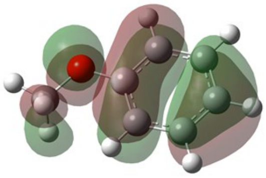
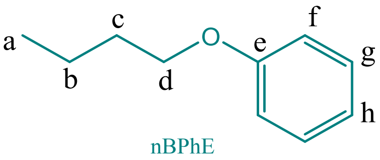
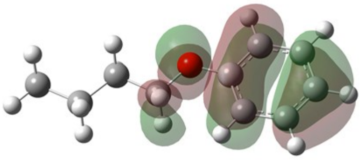
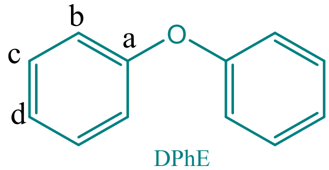
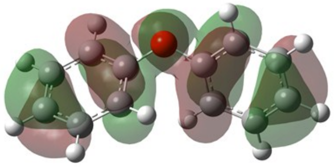
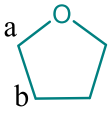
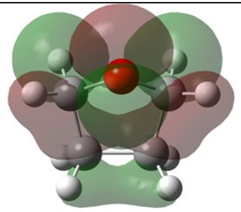
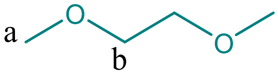
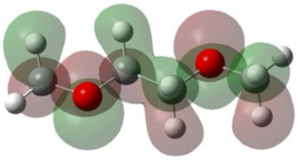
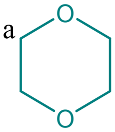
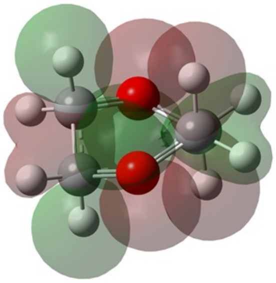
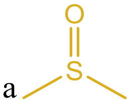
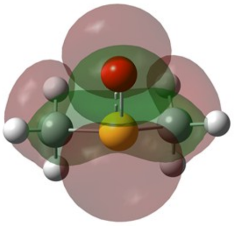
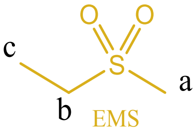
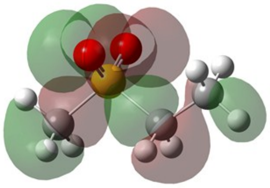
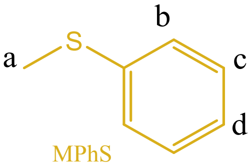
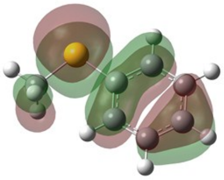
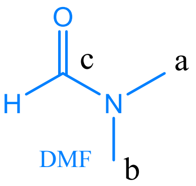
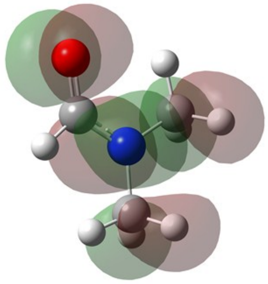
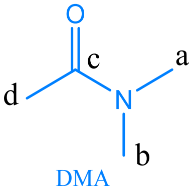
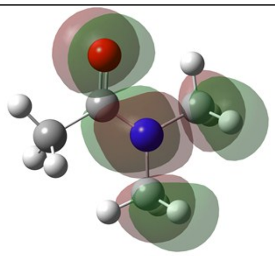
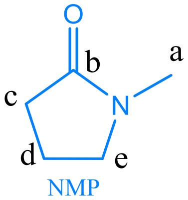
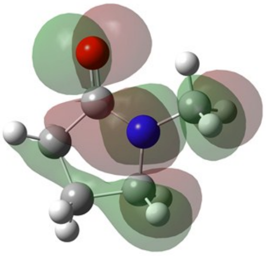
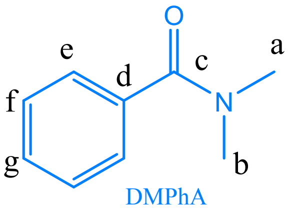
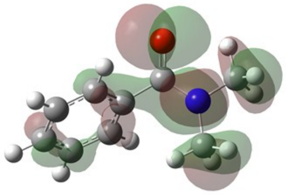
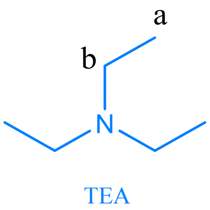
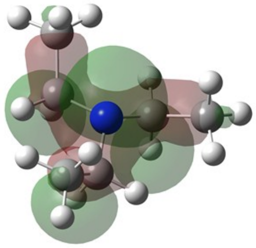
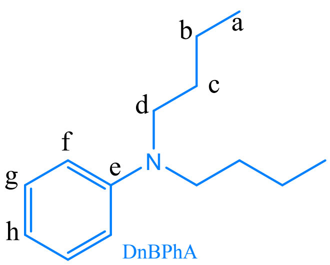
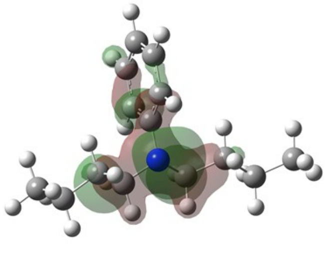
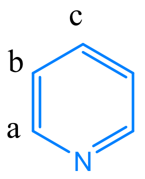
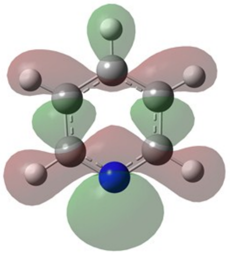
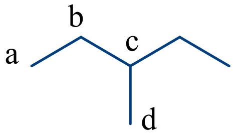
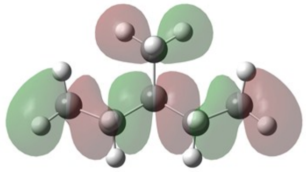
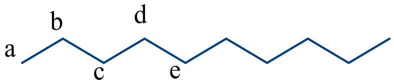
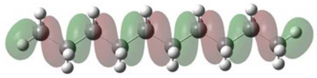
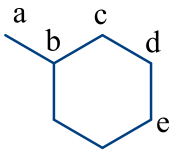
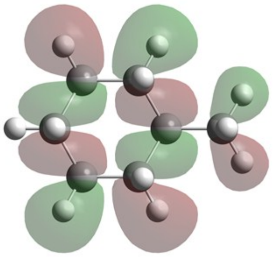
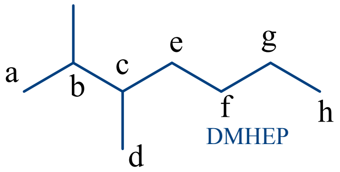
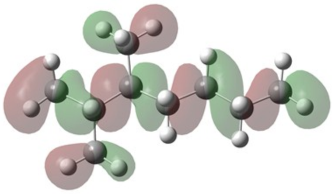
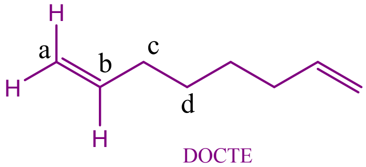
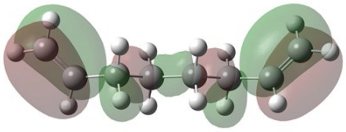
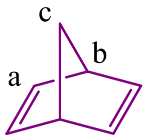
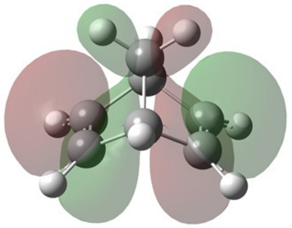
			h: 388.40	h: 412.03		
25	Alkene	 DOCTE	a: 427.96 b: 427.27 c: 407.03 d: 306.93 e: 368.71	a: 360.01 b: 352.91 c: 354.92 d: 285.31 e: 394.68	O: -7.06 R: -0.68	O: -6.79 R: -0.96
26		 NBNDE	a: 442.03 b: 415.87 c: 395.24	a: 336.63 b: 379.02 c: 404.32	O: -6.38 R: -0.98	O: -5.97 R: -1.39
27	Aromatic	 Benzene	a: 433.05	a: 345.22	O: -7.14 R: -0.79	O: -6.90 R: -1.25
28		 Toluene	a: 340.46 b: 431.01 c: 431.25 d: 433.64	a: 281.46 b: 350.64 c: 348.21 d: 347.61	O: -6.80 R: -0.77	O: -6.54 R: -1.20
29		 nBBen	a: 385.92 b: 367.89 c: 368.46 d: 324.68 e: 430.91 f: 432.71 g: 434.17	a: 403.96 b: 403.59 c: 393.63 d: 280.82 e: 349.67 f: 348.10 g: 345.04	O: -6.77 R: -0.76	O: -6.54 R: -1.16
30		 cHexBen	a: 371.22 b: 370.61 c: 369.24 d: 320.19 e: 426.40 f: 431.54 g: 434.30	a: 405.34 b: 397.30 c: 396.40 d: 285.56 e: 344.90 f: 349.10 g: 347.70	O: -6.74 R: -0.72	O: -6.50 R: -1.20
31		 DPh	a: 429.16 b: 432.93 c: 435.01	a: 329.83 b: 338.60 c: 338.14	O: -6.39 R: -1.46	O: -6.20 R: -1.94
32		 nBDPh	a: 386.32 b: 368.10 c: 368.88 d: 321.54 e: 431.53 f: 429.00 g: 429.68 h: 432.82 i: 434.96	a: 402.43 b: 404.14 c: 391.79 d: 255.16 e: 342.31 f: 332.81 g: 332.89 h: 339.80 i: 339.57	O: -6.21 R: -1.40	O: -6.01 R: -1.86

Table S2. The NPA atomic partial charges of all inequivalent carbon, nitrogen, and sulfur of the compounds shown in Figure 1 performed at B3LYP/6-311++G(d,p) with geometries fully optimized at B3LYP/6-31G(d,p). The highest occupied molecular orbitals (HOMOs) are shown in the last column.

#	Family	Structure with site labeling	NPA charge	HOMO
1	Carbonate		a: +1.03 b: -0.21	
2			a: +1.03 b: -0.05	
3			a: +1.03 b: -0.05 c: +0.10 d: -0.60	
4	Ether		a: -0.58 b: +0.27 c: -0.21	
5			a: -0.21 b: +0.32 c: -0.30 d: -0.19 e: -0.25	
6			a: -0.57 b: -0.38 c: -0.39 d: -0.02 e: +0.32 f: -0.25 g: -0.20 h: -0.25	

7		 DPhE	a: +0.30 b: -0.25 c: -0.20 d: -0.23	
8		 THF	a: -0.03 b: -0.42	
9		 DME	a: -0.20 b: -0.03	
10		 Dioxane	a: -0.06	
11	S-containing	 DMSO	a: -0.75 S: 1.15	
12		 EMS	a: -0.78 b: -0.57 c: -0.60 S: 2.02	
13		 MPhS	a: -0.71 b: -0.18 c: -0.23 d: -0.20 e: -0.23 S: 0.24	

14	N-containing	 DMF	a: -0.37 b: -0.35 c: +0.54 N: -0.47	
15		 DMA	a: -0.37 b: -0.36 c: +0.69 d: -0.67 N: -0.49	
16		 NMP	a: -0.36 b: +0.70 c: -0.46 d: -0.39 e: -0.16 N: -0.49	
17		 DMPhA	a: -0.36 b: -0.36 c: +0.68 d: -0.14 e: -0.18 f: -0.21 g: -0.20 N: -0.48	
18		 TEA	a: -0.17 b: -0.58 N: -0.59	
19		 DnBPhA	a: -0.57 b: -0.38 c: -0.39 d: -0.15 e: +0.16 f: -0.23 g: -0.21 h: -0.22 N: -0.59	

20		 Pyr	a: +0.05 b: -0.25 c: -0.16 N: -0.50	
21	Alkane	 MP	a: -0.58 b: -0.38 c: -0.22 d: -0.58	
22		 Decane	a: -0.57 b: -0.38 c: -0.38 d: -0.37 e: -0.37	
23		 McHex	a: -0.57 b: -0.22 c: -0.38 d: -0.38 e: -0.38	
24		 DMHEP	a: -0.57 b: -0.22 c: -0.21 d: -0.57 e: -0.37 f: -0.38 g: -0.38 h: -0.57	
25	Alkene	 DOCTE	a: -0.40 b: -0.16 c: -0.42 d: -0.37	
26		 NBNDE	a: -0.19 b: -0.29 c: -0.33	

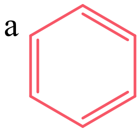
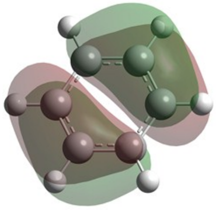
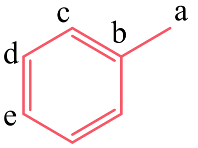
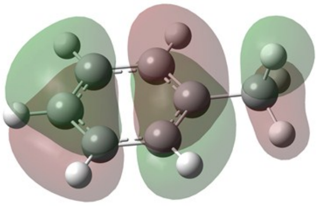
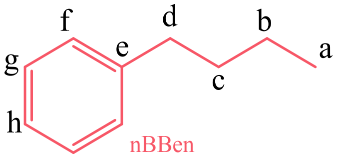
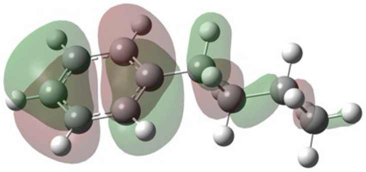
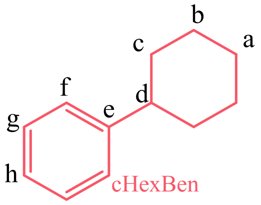
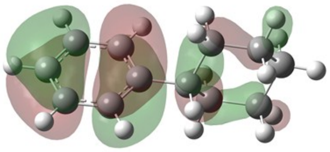
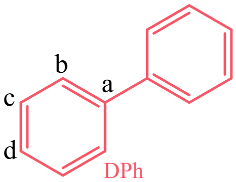
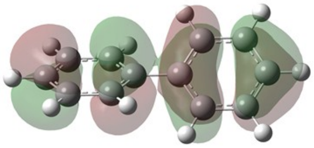
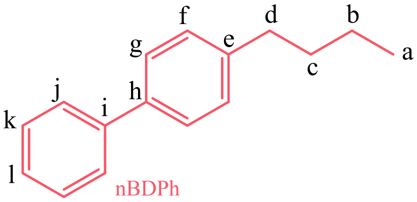
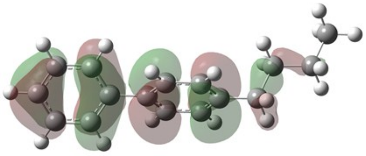
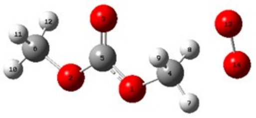
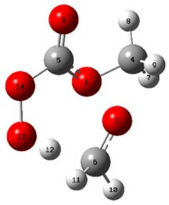
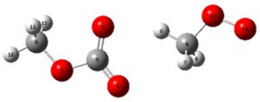
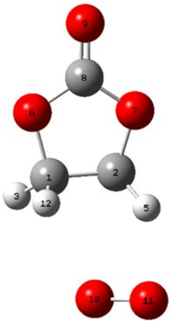
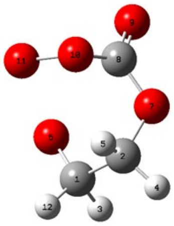
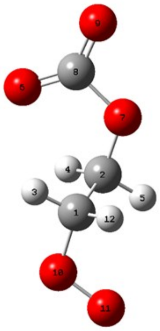
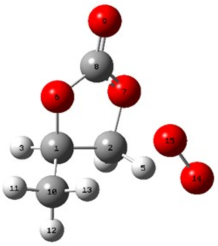
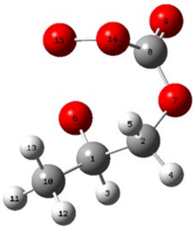
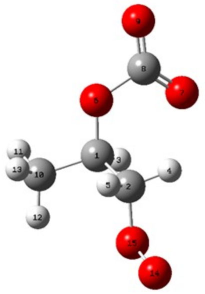
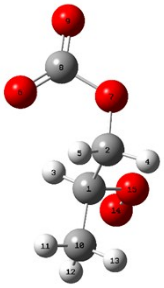
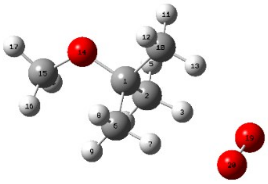
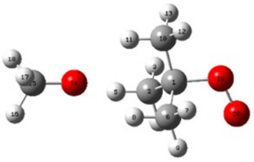
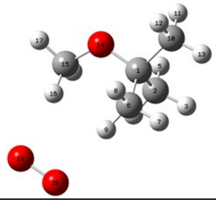
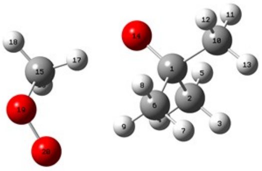
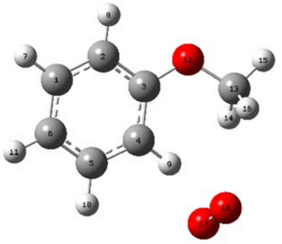
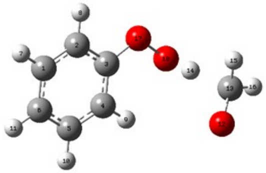
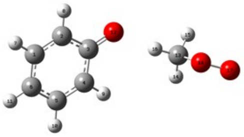
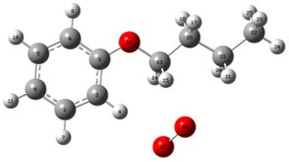
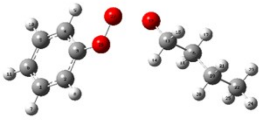
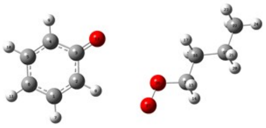
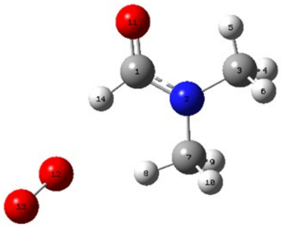
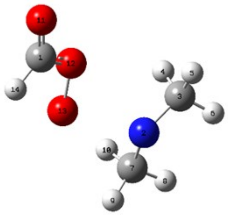
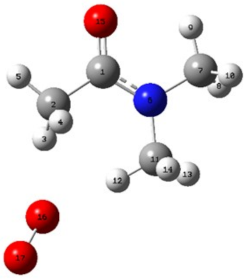
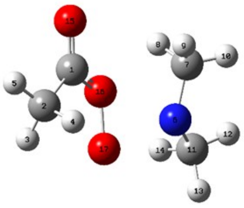
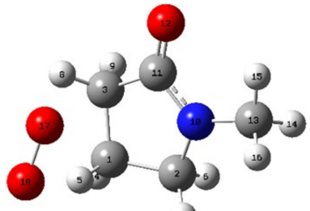
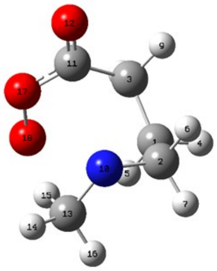
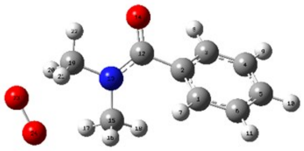
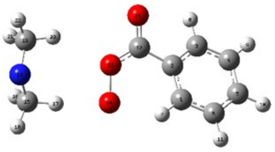
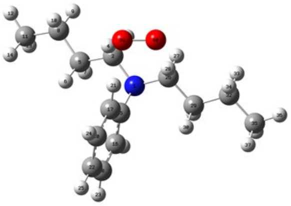
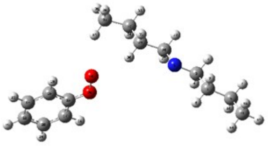
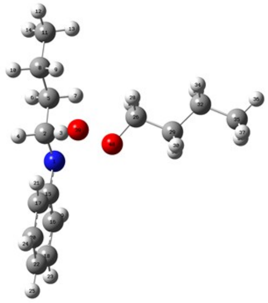
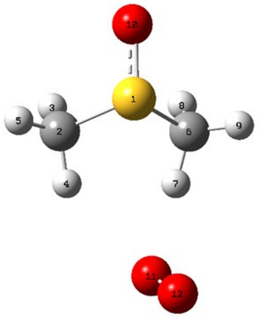
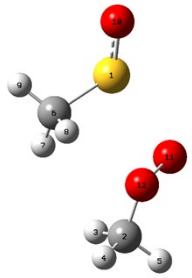
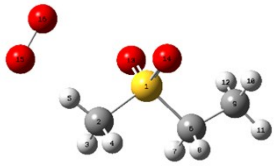
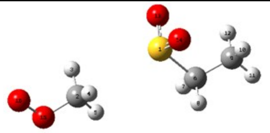
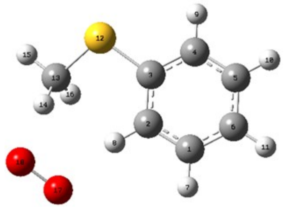
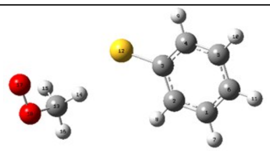
27	Aromatic	 Benzene	a: -0.21	
28	Aromatic	 Toluene	a: -0.59 b: -0.03 c: -0.21 d: -0.21 e: -0.23	
29		 nBBen	a: -0.57 b: -0.38 c: -0.37 d: -0.40 e: -0.03 f: -0.21 g: -0.21 h: -0.22	
30		 cHexBen	a: -0.38 b: -0.38 c: -0.37 d: -0.24 e: -0.02 f: -0.21 g: -0.21 h: -0.22	
31		 DPh	a: -0.06 b: -0.20 c: -0.20 d: -0.21	
32		 nBDPh	a: -0.57 b: -0.38 c: -0.37 d: -0.40 e: -0.02 f: -0.20 g: -0.19 h: -0.07 i: -0.04 j: -0.20 k: -0.20 l: -0.22	

Table S3. The NPA partial charges of the select carbon attack sites in the absence of nucleophile, Z_{c0}, the optimized geometries of the reactants and products of the nucleophilic substitution of various solvents by superoxide radical, the NPA partial charges of the attacked carbon before and after the attack, Z_{ci} and Z_{cf}, and the NPA partial charges of the attacking oxygen before and after the attack, Z_{oi} and Z_{of}.

Carbon site (Z_{c0})	Optimized geometry of the reactants	Optimized geometry of the Product(s)	Z_{ci}	Z_{cf}	Z_{oi}	Z_{of}
DMC-C= (1.035)			1.035	1.039	-0.482	-0.326
DMC-CH_3 (-0.210)			-0.237	-0.245	-0.482	-0.171
EC-C= (1.028)			1.026	1.051	-0.461	-0.405
EC-CH_2 (-0.054)			-0.054	-0.067	-0.461	-0.173
PC-C= (1.030)			1.041	1.053	-0.469	-0.408

PC-CH_2 (-0.047)			-0.075	-0.061	-0.469	-0.173
PC-CH (0.102)			0.106	0.087	-0.469	-0.178
MtBE-Quaternary-O (0.271)			0.273	0.270	-0.481	-0.192
MtBE-CH_3-O (-0.208)			-0.230	-0.269	-0.484	-0.202
MPhE-α-Ph-O (0.318)			0.316	0.303	-0.482	-0.314
MPhE-CH_3-O (-0.211)			-0.219	-0.258	-0.482	-0.168
nBPhE-α-Ph-O (0.321)			0.321	0.304	-0.473	-0.310
nBPhE-α-nB-O (-0.022)			-0.05	-0.038	-0.473	-0.173

DMF-C= (0.544)			0.521	0.650	-0.485	-0.351
DMA-C= (0.694)			0.697	0.793	-0.479	-0.359
NMP-C= (0.702)			0.708	0.799	-0.481	-0.358
DMPhA-C= (0.681)			0.674	0.782	-0.477	-0.344
DnBPhA-α-Ph-O (0.164)			0.161	0.318	-0.481	-0.365
DnBPhA-α-nB-O (-0.154)			-0.173	-0.015	-0.479	-0.402

DMSO-CH_3 (-0.754)			-0.755	-0.207	-0.466	-0.395
EMS-CH_3 (-0.782)			-0.826	-0.243	-0.474	-0.169
MPhS-CH_3 (-0.708)			-0.723	-0.242	-0.474	-0.173

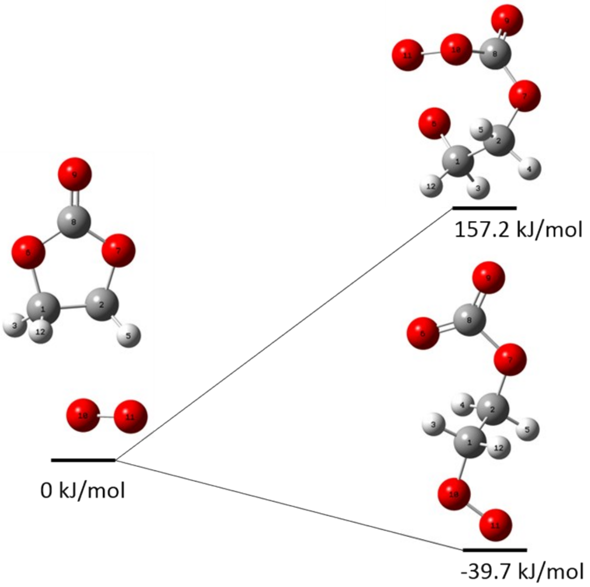


Figure S2. The optimized structures of the reactants and products of superoxide substitution reaction with EC at the carbonyl carbon (top) and the ethereal carbon (bottom), and the corresponding ΔG_{nuc}.

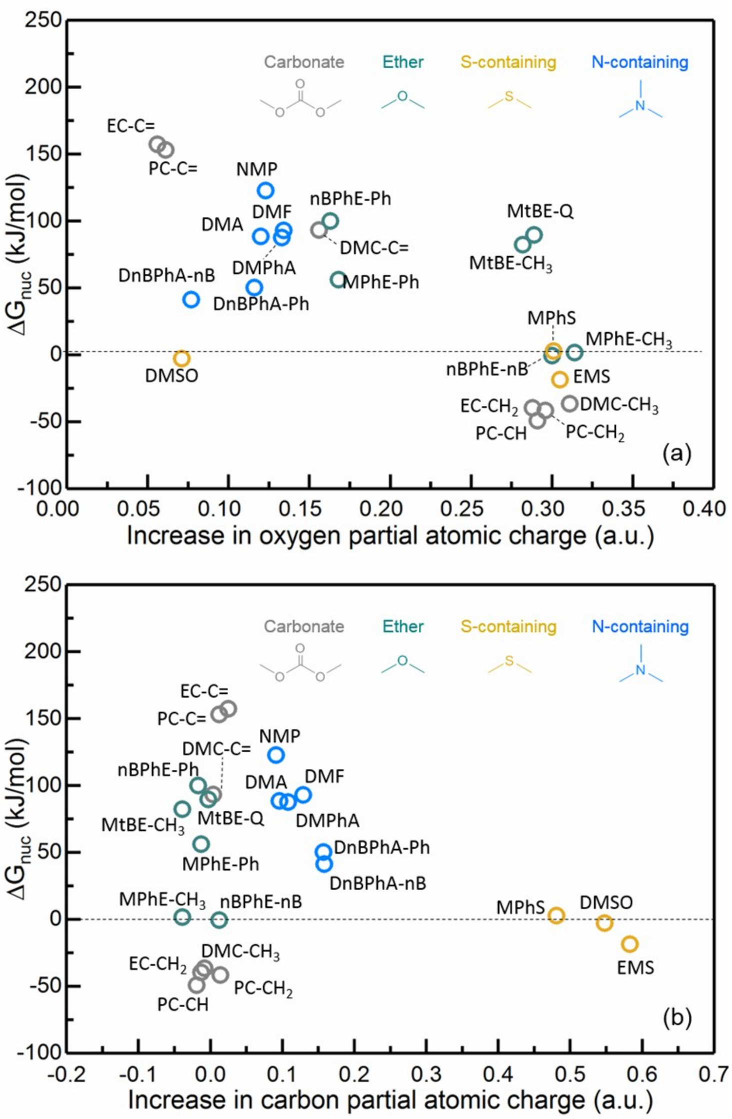


Figure S3. Nucleophilic substitution free energies ΔG_{nuc} at select carbon sites plotted against the (a) increase in the partial charge of the attacking oxygen in superoxide (the partial charge of the oxygen after the attack minus the partial charge before the attack) and the (b) increase in the partial charge of the attacked carbon (the partial charge of the carbon after the attack minus the partial charge before the attack) obtained at B3LYP/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory (Table S3).

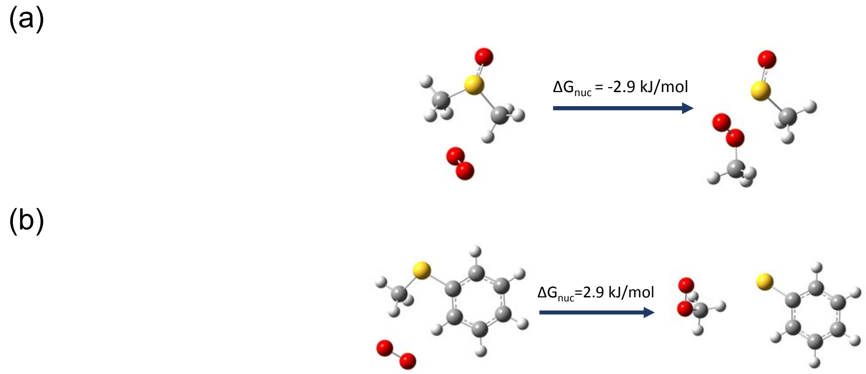


Figure S4. Optimized structures of the reactants and products of the nucleophilic substitution of (a) DMSO and (b) MPhS by superoxide radical. The computed ΔG_{nuc} is shown above the arrow. Atom color code: red – oxygen, grey – carbon, white – hydrogen, and yellow – sulfur. The optimized geometries of all reactions in Table 1 are summarized in Table S3.

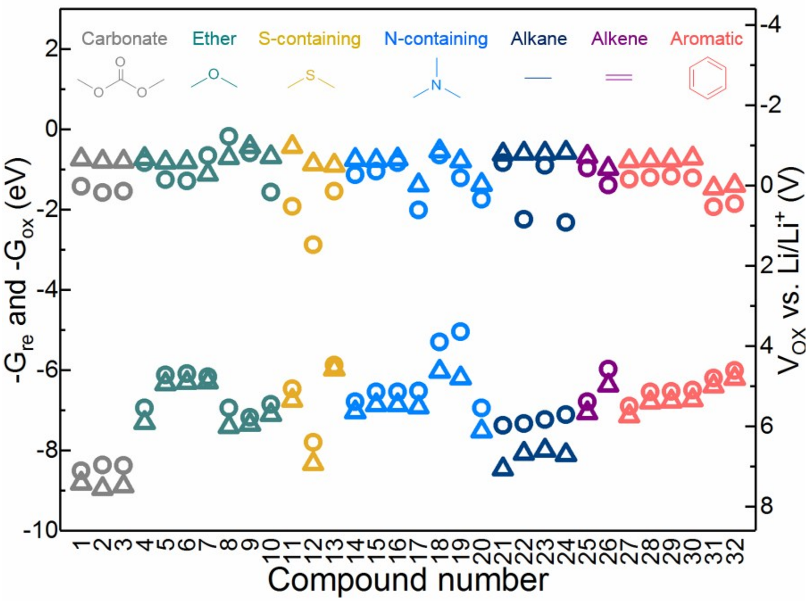


Figure S5. Redox energies of the compounds shown in Figure 1 computed using B3LYP/6-311++G(d,p) with geometries fully optimized at B3LYP/6-31G(d,p). Triangles indicate the vertical redox energies while spheres adiabatic energies. The redox energy in eV is converted to the experimentally measured scale versus Li/Li$^+$ by the subtraction of 1.4 V.[1,2] The converted potential vs Li/Li$^+$ is plotted against the right axis. Carbonates show the widest electrochemical stability windows among the compounds considered in this study.

Table S4. Adiabatic oxidative potentials computed at B3LYP/6-311++G(d,p)//B3LYP/6-31G(d,p) of selected compounds compared to literature theoretical and experimental values. Values in V vs. Li$^+$/Li.

#	Compound	This work (ε = 46.8)	Published theoretical value	Experimental literature value
1	DMC	7.1	6.9[a], 7.0[c]	6.7[e], 5.3[f]
2	EC	7.0	7.1[a], 7.0[c]	6.7[g], 6.2[e], 5.5[f]
3	PC	7.0	7.0[a], 7.1[b], 7.0[c]	6.8[h], 6.6[e], 6.0[g],
7	DPhE	4.8	7.5[d]	4.5[i]
8	THF	5.5	5.8[c]	4.2[j], 4.0[k]
9	DME	5.8	5.7[a], 5.5[c]	5.1[d], 4.6[j]
12	EMS	6.4	6.9[a]	5.9[l]
31	DPh	4.8	7.7[d]	4.5[i]

[a] ε = 20, G4MP2, from ref 3. [b] ε = 20.5, B3LYP/6-311++G(d), from ref 4. [c] ε = 78, B3LYP/6-31+G(d), from ref 5, values are converted to the Li$^+$/Li scale. [d] PM3, from ref 6. [e] Glassy carbon (GC) and 0.65 M Bu_4NBF_4 from ref 7. [f] Pt and 1 M $LiPF_6$, from ref 6. [g] GC and 1 M $EtMe_3NPF_6$, from ref 8. [h] GC and 0.65 M Et_4NPF_6, from ref 7. [i] Pt and 1 M LiPF6, 2% in PC, from ref 6. [j] GC and LiClO4, from ref 9. [k] Pt microelectrode and neat THF, from ref 10. [l] Pt and 1 M LiTFSI, from ref 3.

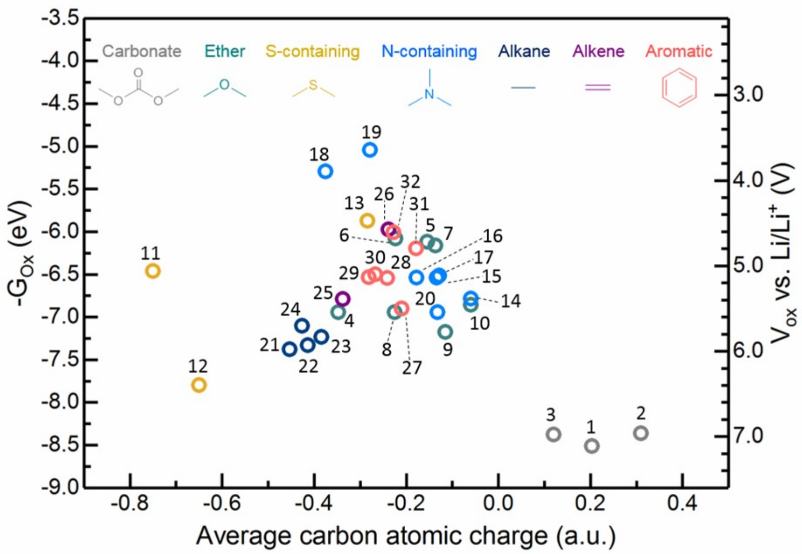


Figure S6. Adiabatic –G$_{ox}$ and V$_{ox}$ of the compounds shown in Figure 1 are plotted against the average carbon atomic partial charges obtained by NPA. The oxidation energy in eV is converted to the experimentally measured scale versus Li/Li$^+$ by the subtraction of 1.4 V.[1,2] The converted potential vs Li/Li$^+$ is plotted against the right axis.

General Procedure for Chemical Stability Test

For liquid samples: A 10 mL microwave vial was charged with 5 mmol liquid sample and a stir bar. The liquid was deoxygenated with three freeze, pump, thaw cycles under N_2 atmosphere and transferred into a glove box. 2.0 mmol Li_2O_2 and 2.0 mmol KO_2 were added into the vial after opening the vial cap. After the vial was sealed, it was moved into a 60 ^oC oil bath outside of the glove box, and stirred for three days. Then, the reaction mixture was cooled down and treated with d_6-DMSO or d_7-DMF. The mixture was centrifuged. The liquid layer was analyzed with NMR spectroscopy.

For solid samples: A 10 mL microwave vial was charged with 0.2 mmol solid sample and a stir bar, and transferred into the glove box. 0.5 mL DMF, 2.0 mmol Li_2O_2 and 2.0 mmol KO_2 were added into the vial. After the vial was sealed, it was moved out of the glove box and heated in an oil bath at 60 ^oC for 3 days. Then, the reaction mixture was cooled down and treated with d_6-DMSO. The mixture was further centrifuged and analyzed with NMR spectroscopy.

NMR results of chemical stability test

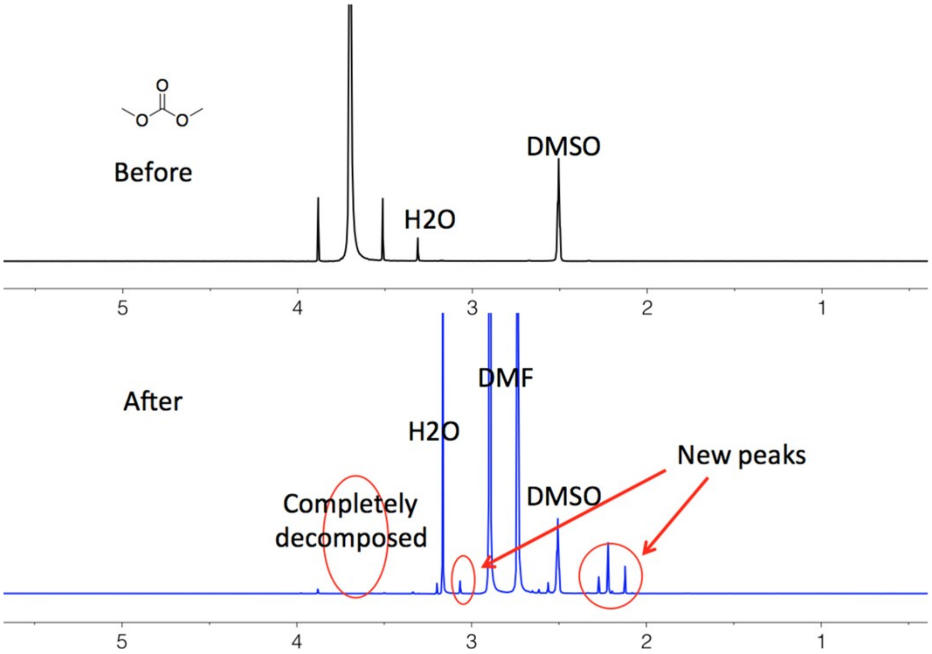


Figure S7. Chemical stability test results of DMC determined by ^{1}H NMR analysis. Black and blue spectra were collected before and after the chemical stability test, respectively.

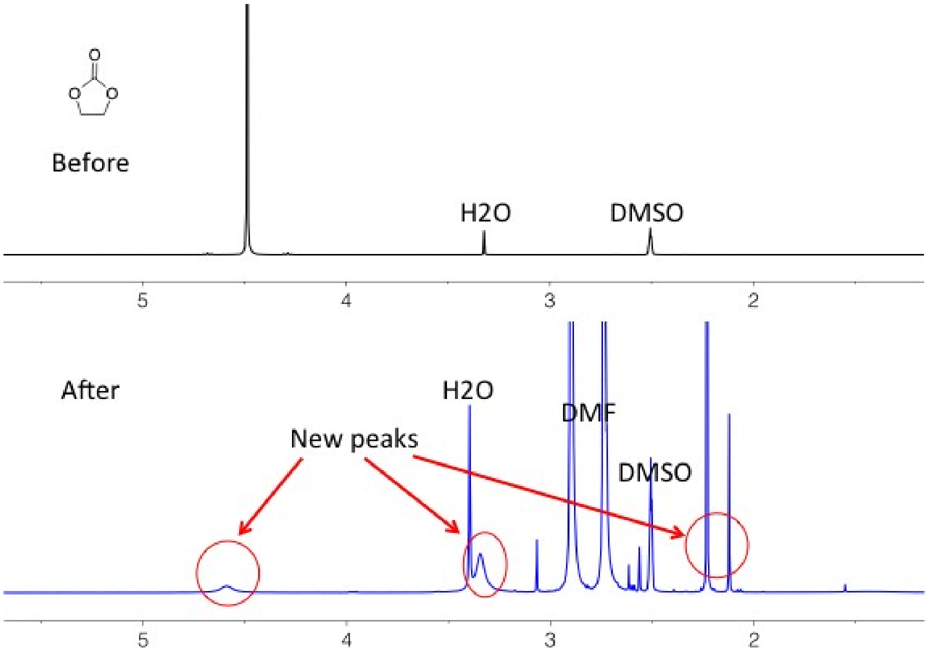


Figure S8. Chemical stability test results of EC determined by ^{1}H NMR analysis.

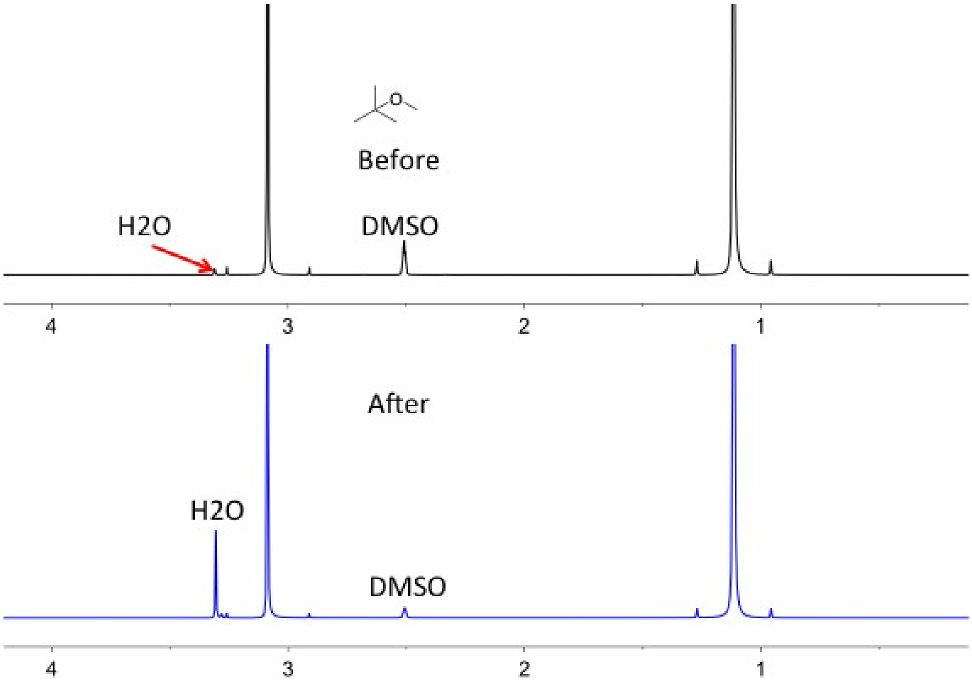


Figure S9. Chemical stability test results of MtBE determined by ^1H NMR analysis.

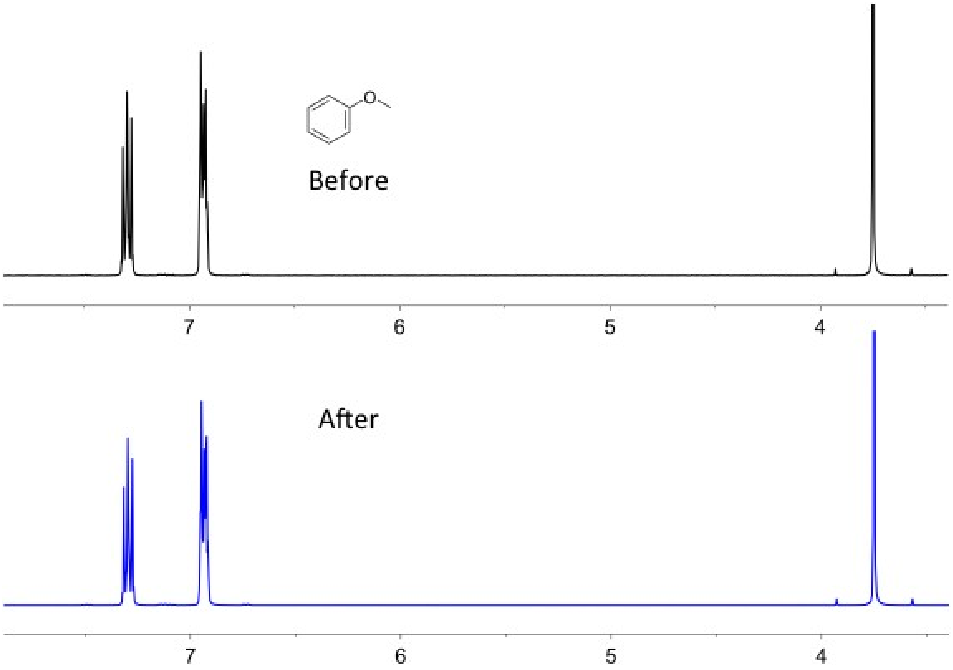


Figure S10. Chemical stability test results of MPhE determined by ^1H NMR analysis.

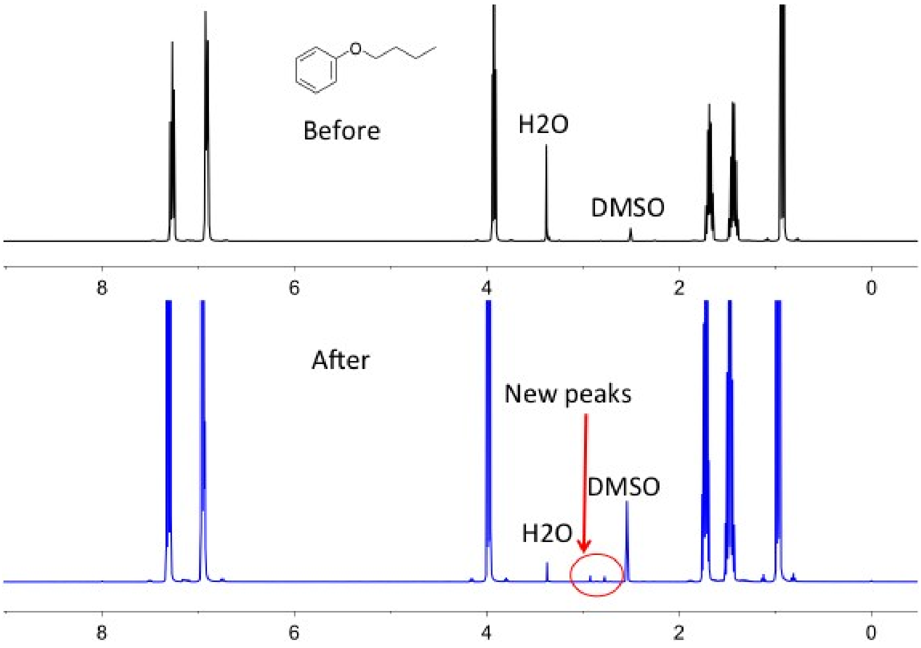


Figure S11. Chemical stability test results of nBPhE determined by ^{1}H NMR analysis.

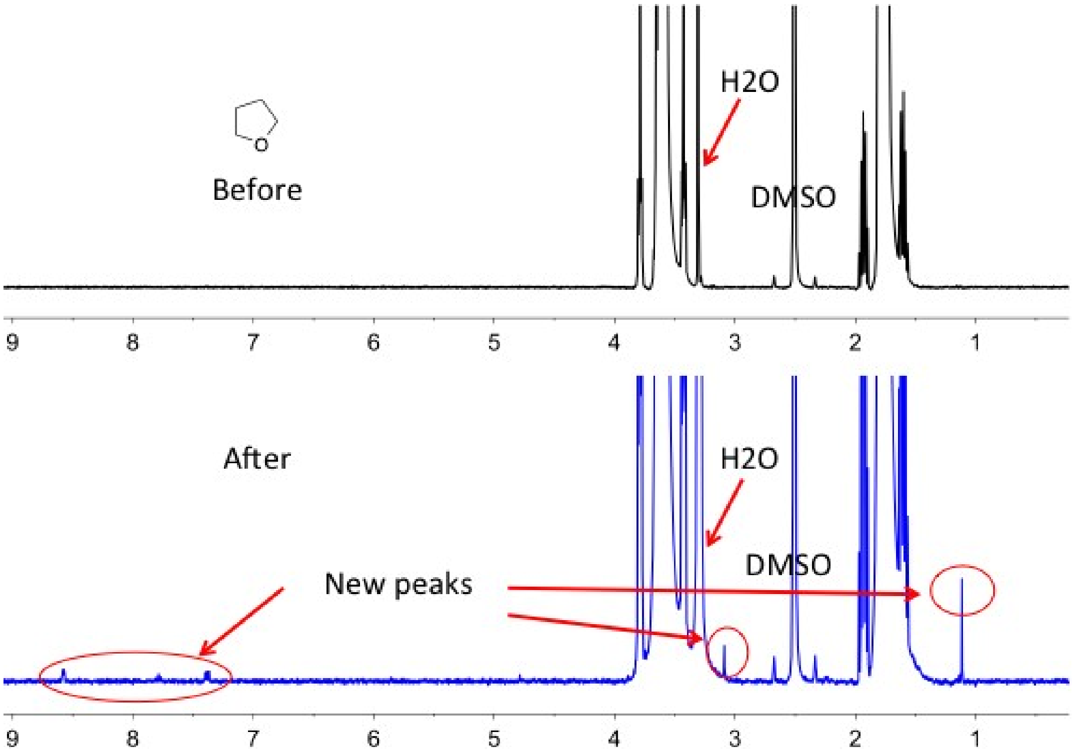


Figure S12. Chemical stability test results of THF determined by ^{1}H NMR analysis.

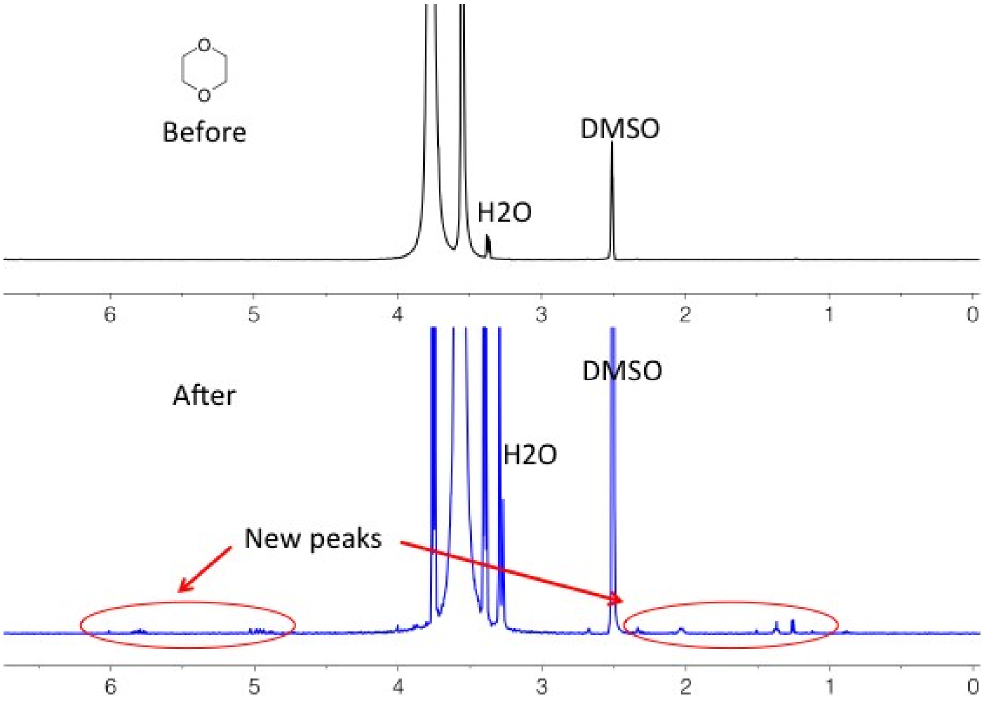


Figure S13. Chemical stability test results of dioxane determined by ^{1}H NMR analysis.

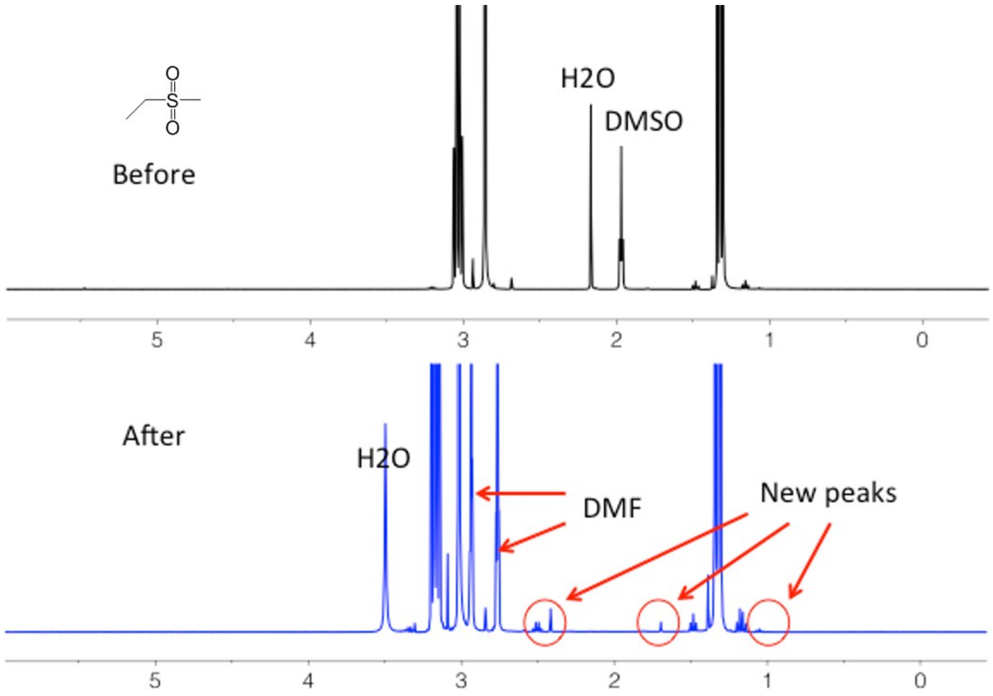


Figure S14. Chemical stability test results of EMS determined by ^{1}H NMR analysis.

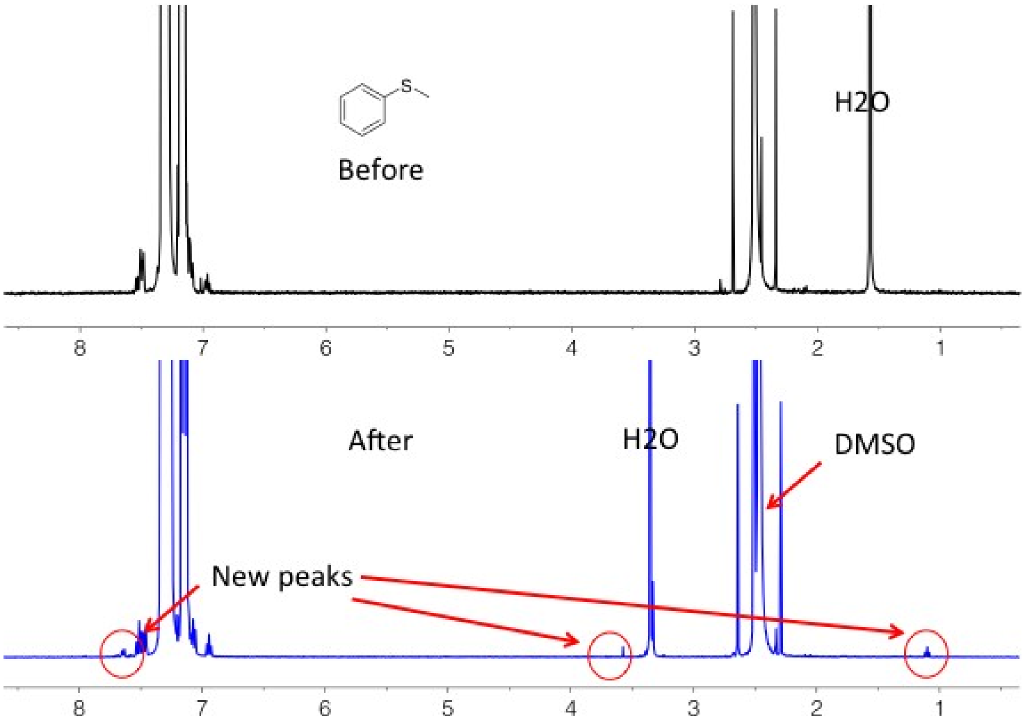


Figure S15. Chemical stability test results of MPhS determined by ^{1}H NMR analysis.

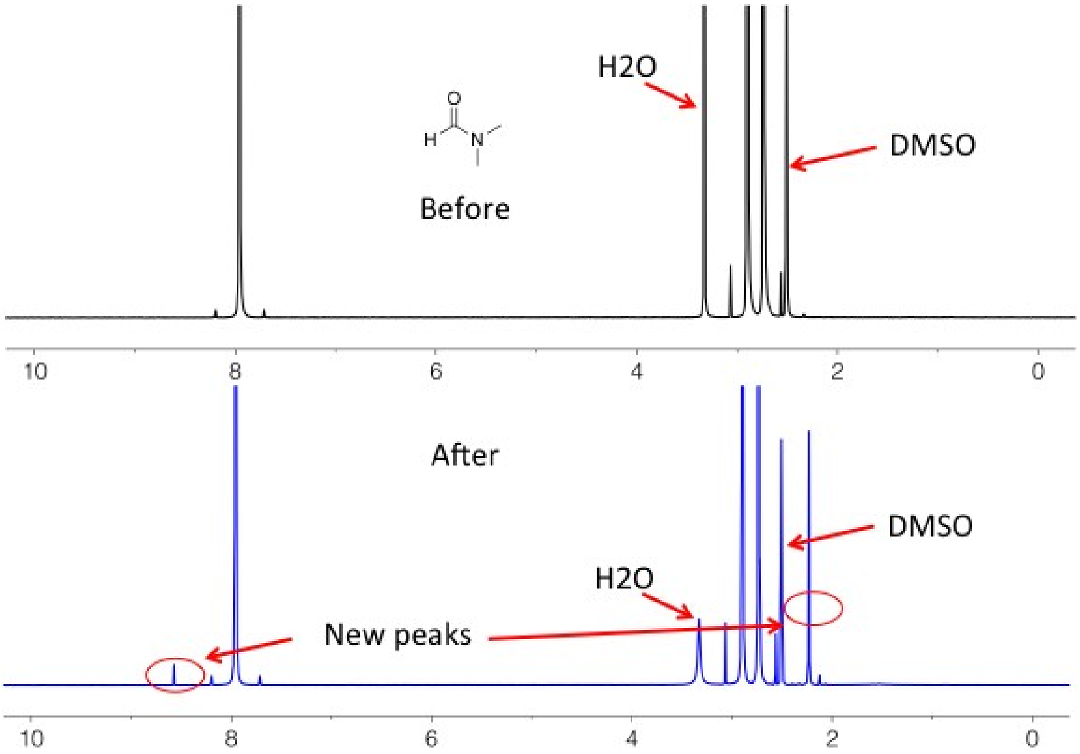


Figure S16. Chemical stability test results of DMF determined by ^{1}H NMR analysis.

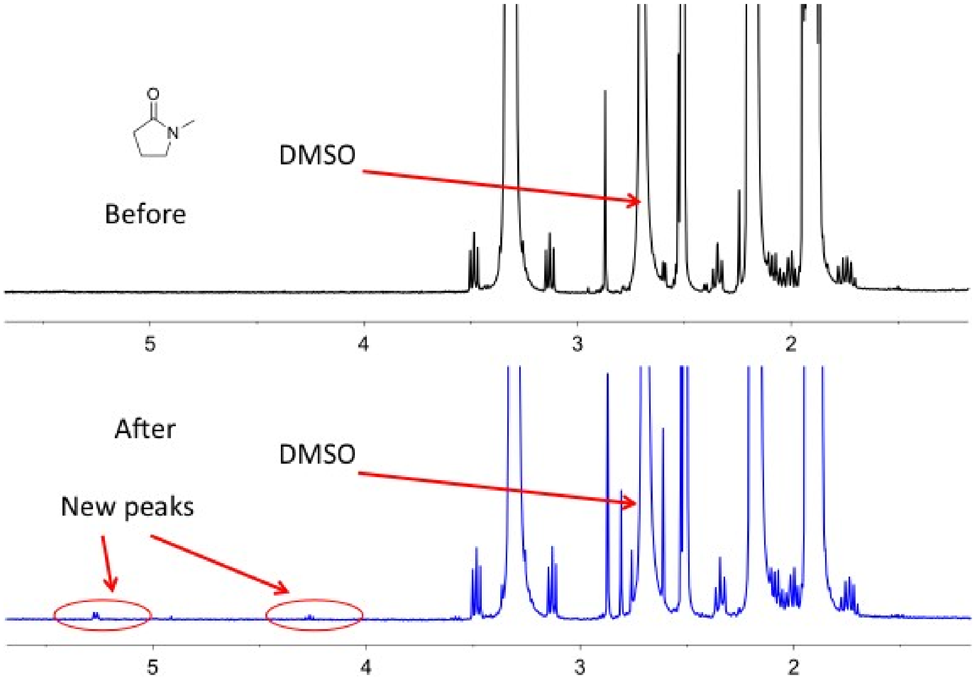


Figure S17. Chemical stability test results of NMP determined by ^{1}H NMR analysis.

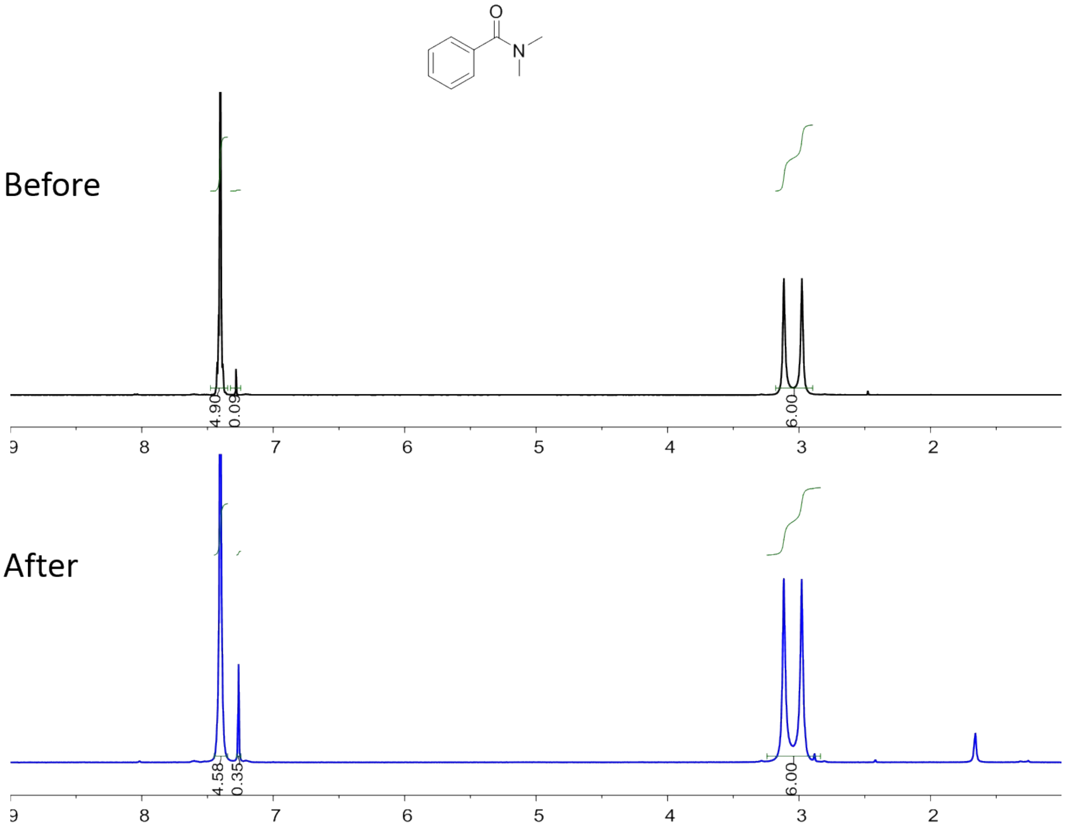


Figure S18. Chemical stability test results of DMPhA determined by ^{1}H NMR analysis.

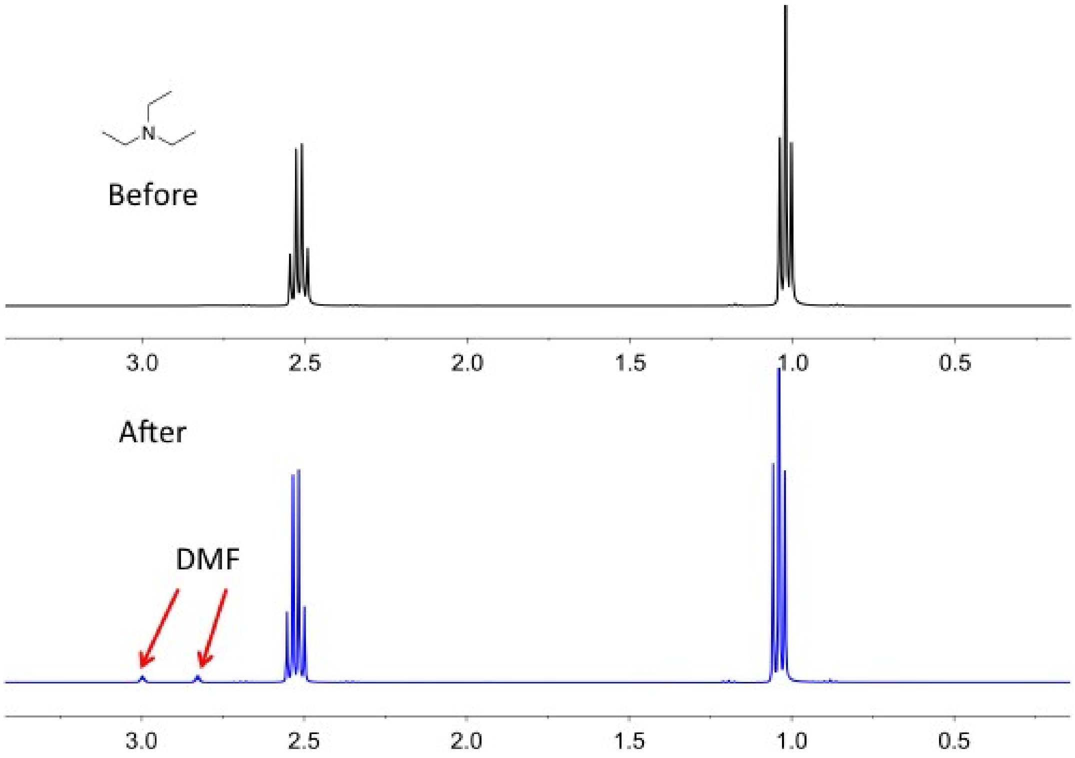


Figure S19. Chemical stability test results of TEA determined by ^{1}H NMR analysis.

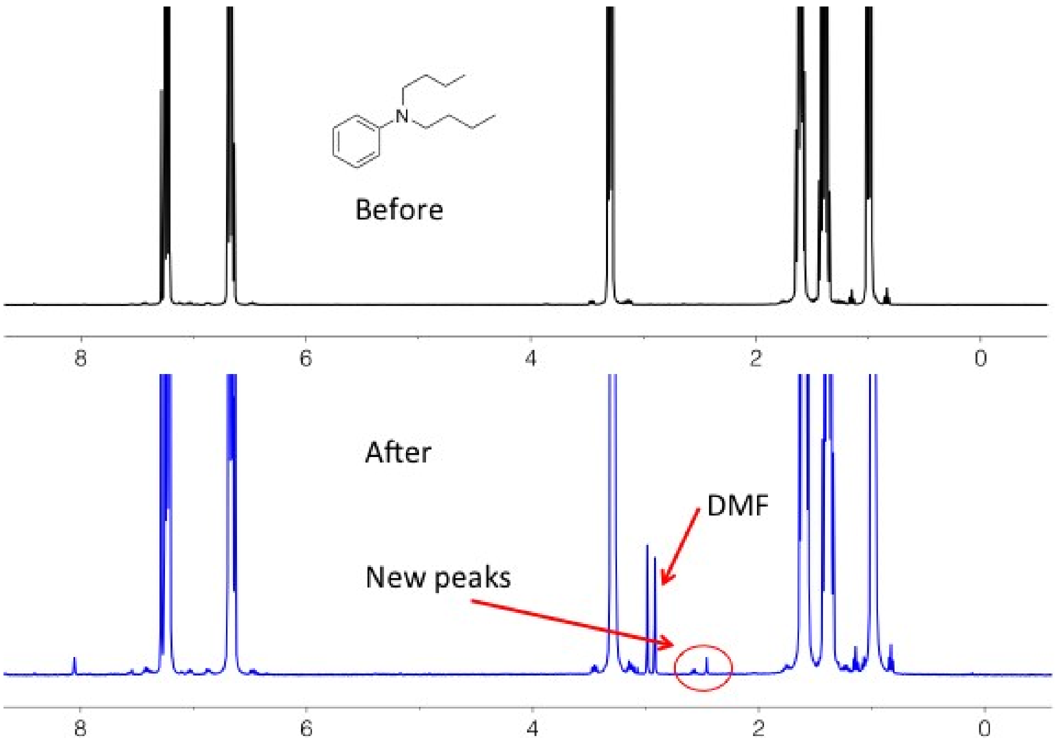


Figure S20. Chemical stability test results of DnBPhA determined by ^{1}H NMR analysis.

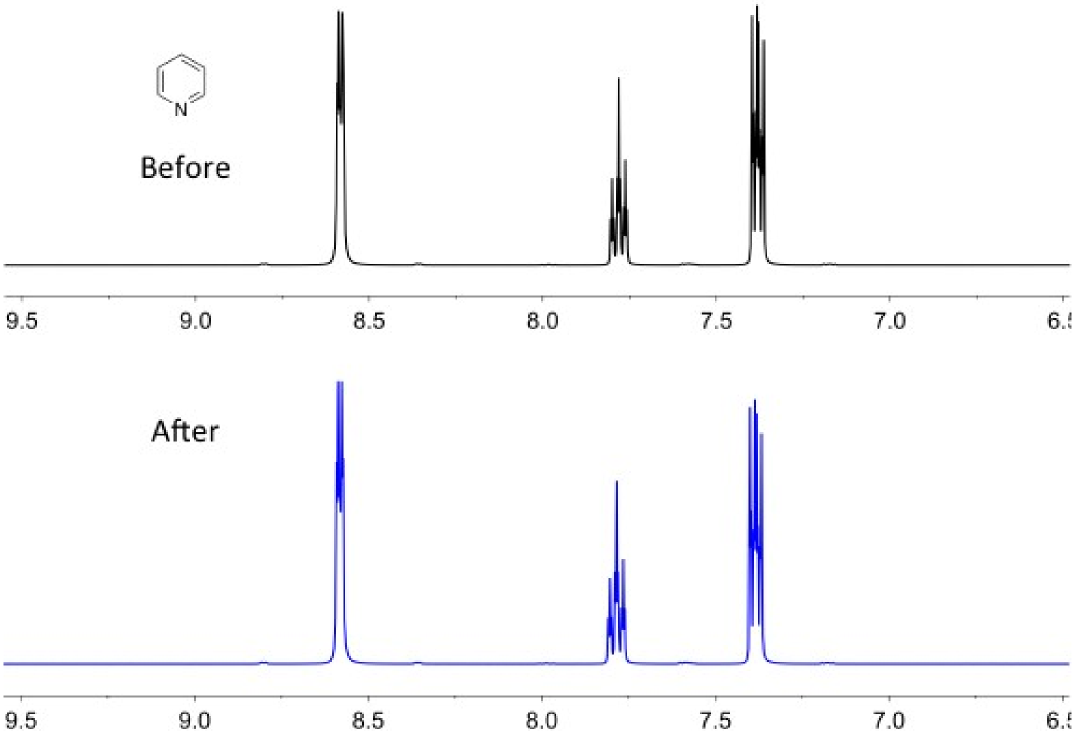


Figure S21. Chemical stability test results of Pyr determined by ^{1}H NMR analysis.

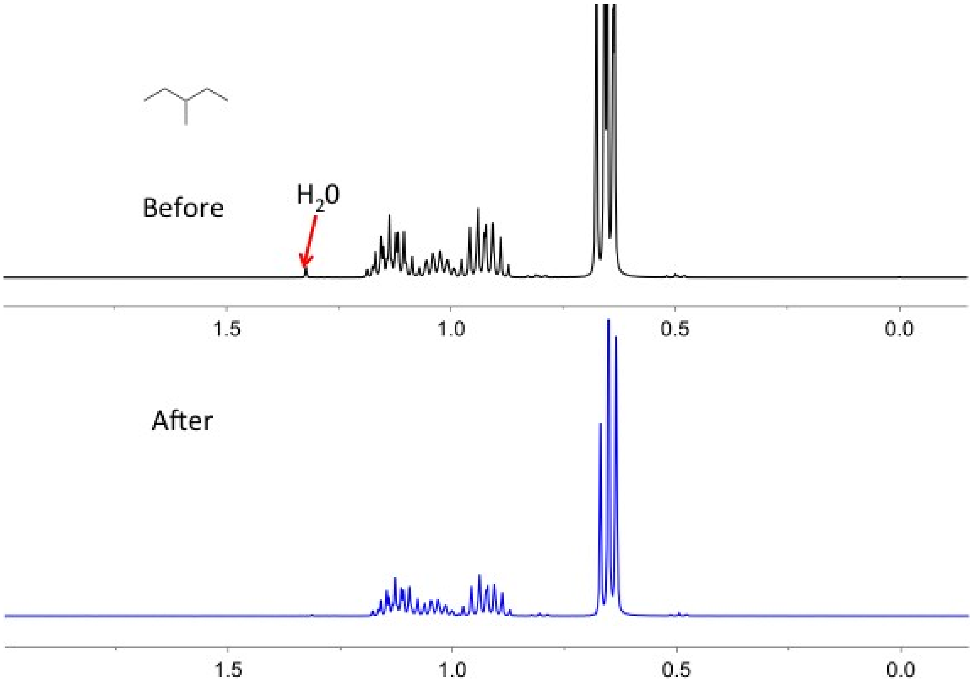


Figure S22. Chemical stability test results of MP determined by ^{1}H NMR analysis.

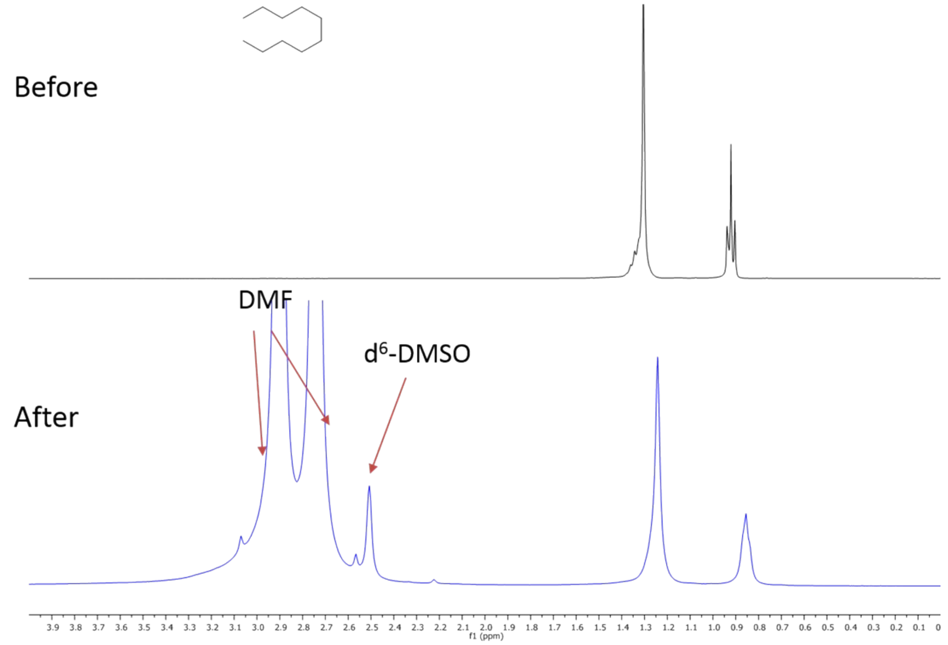


Figure S23. Chemical stability test results of decane determined by ^{1}H NMR analysis.

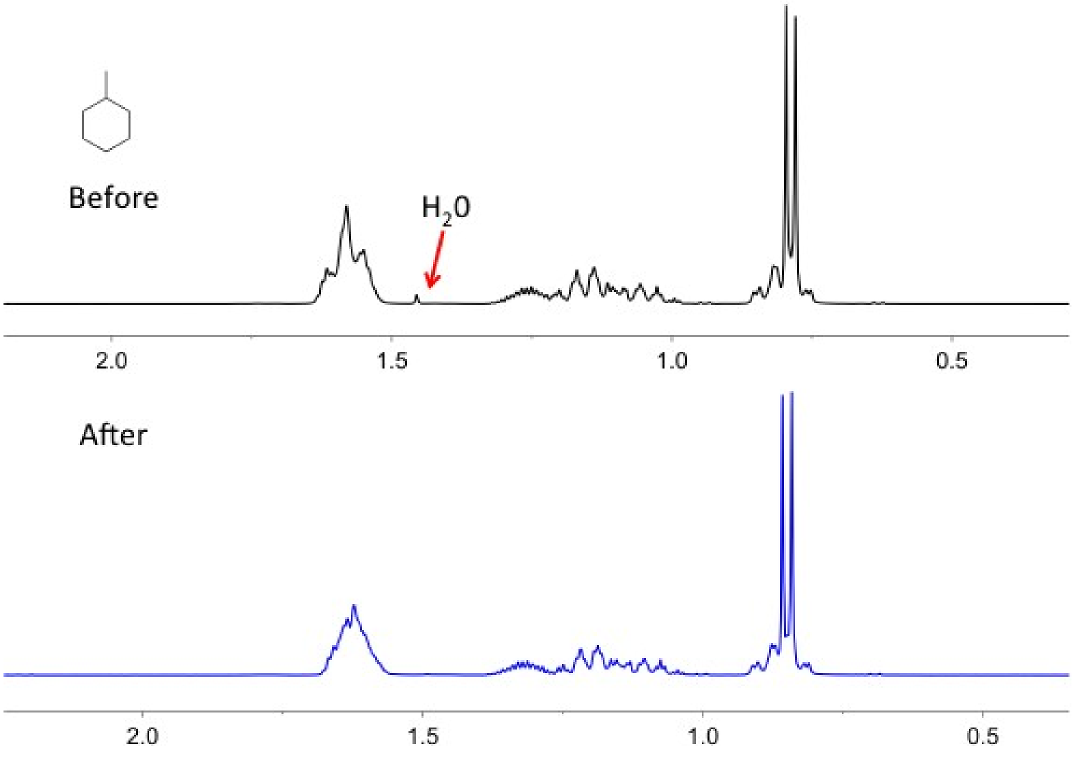


Figure S24. Chemical stability test results of McHex determined by ^{1}H NMR analysis.

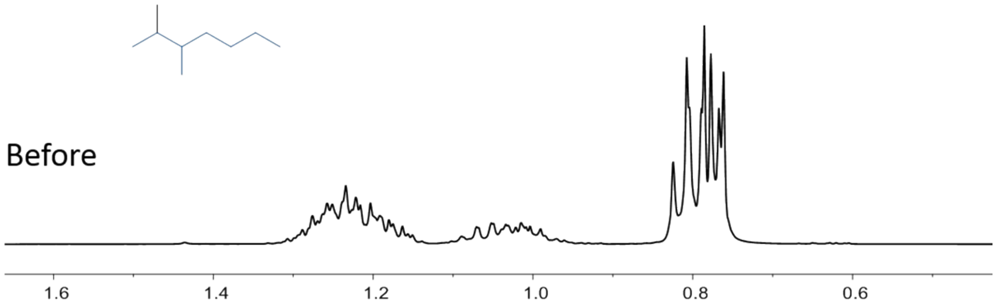


Figure S25. Chemical stability test results of DMHEP determined by ^{1}H NMR analysis.

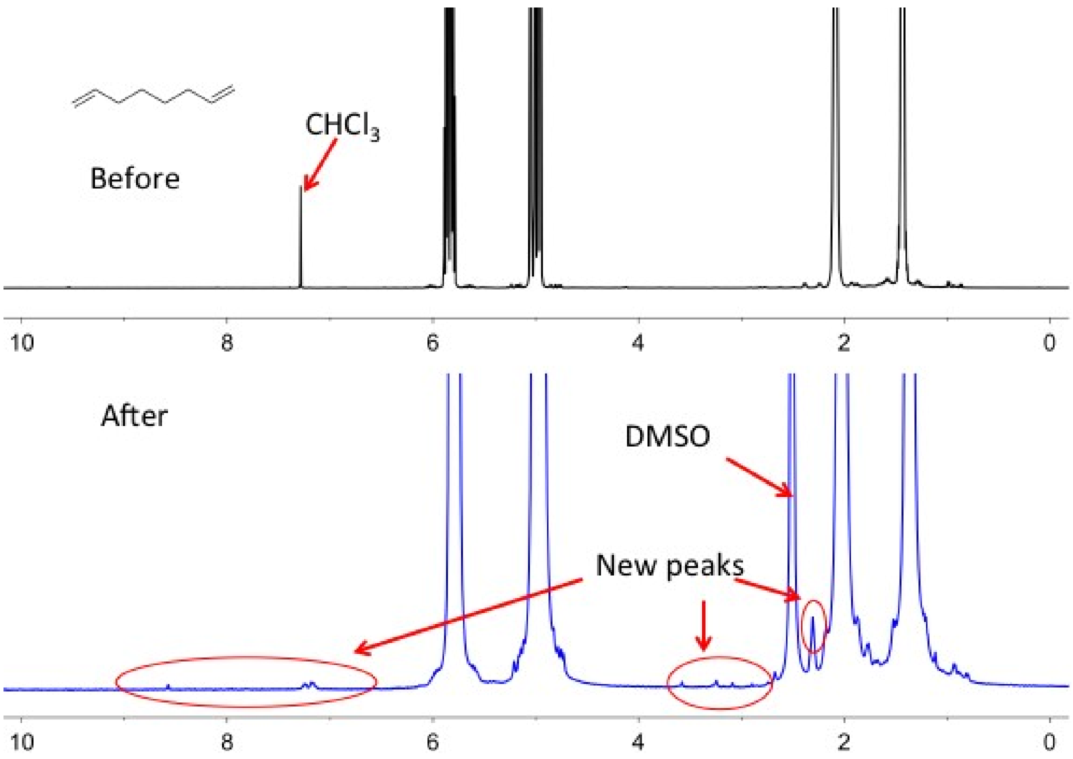


Figure S26. Chemical stability test results of DOCTE determined by ^{1}H NMR analysis.

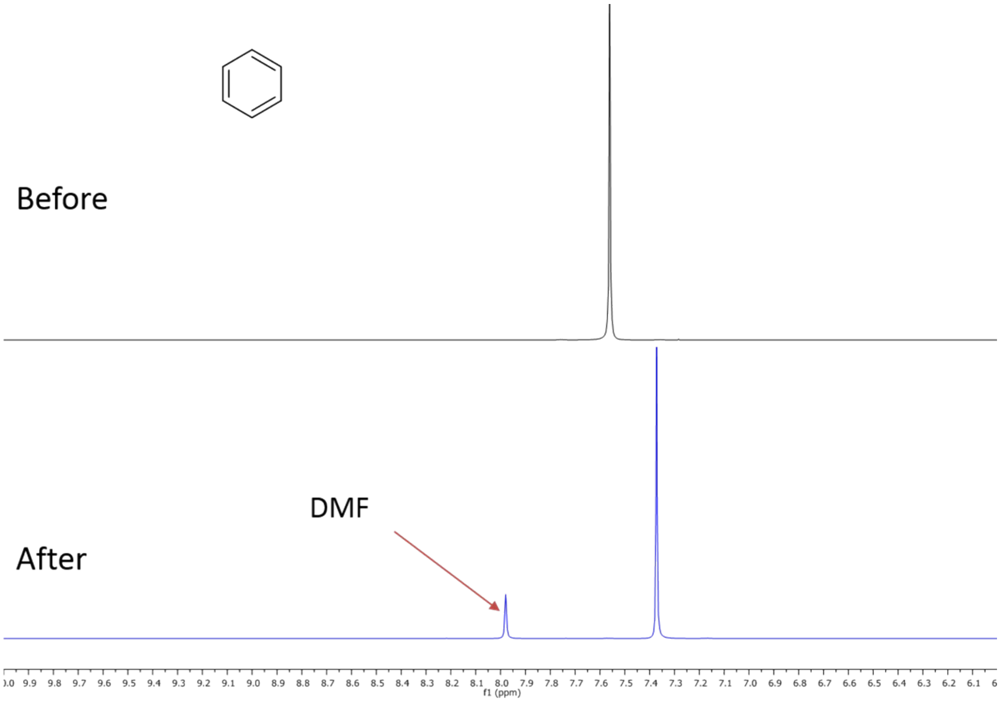


Figure S27. Chemical stability test results of Benzene determined by ^{1}H NMR analysis.

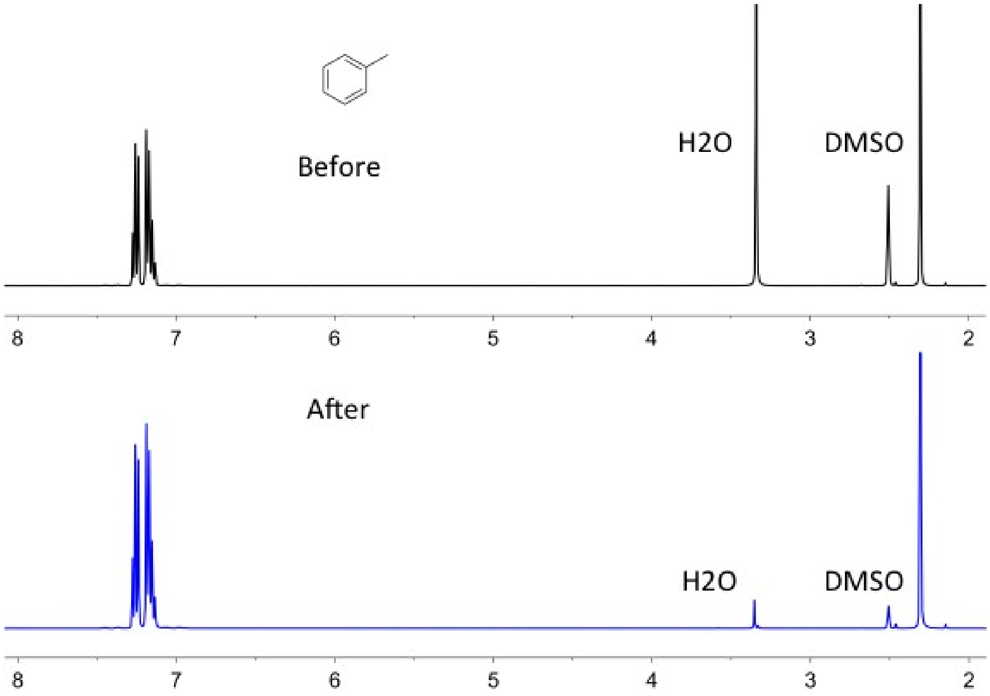


Figure S28. Chemical stability test results of Toluene determined by ^{1}H NMR analysis.

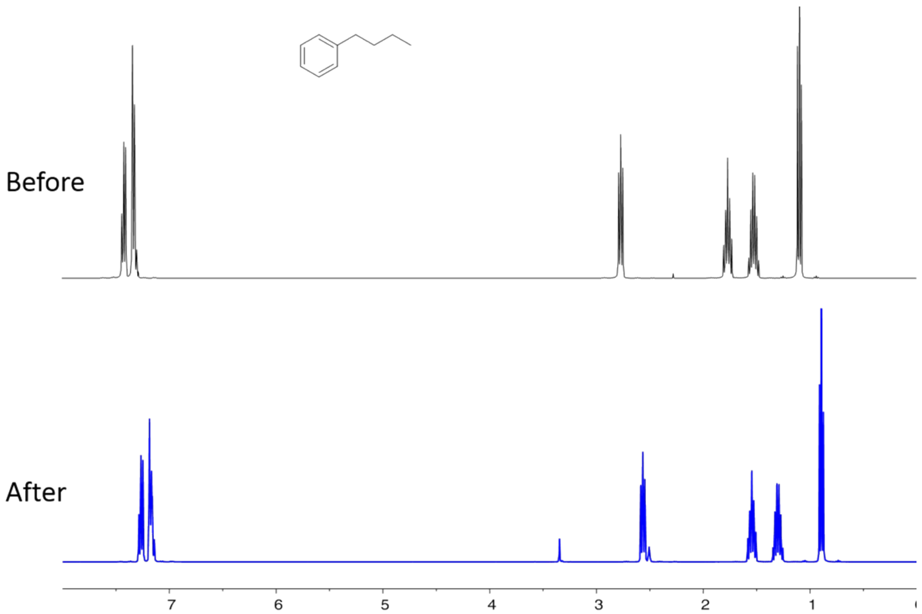


Figure S29. Chemical stability test results of nBBen determined by ^{1}H NMR analysis.

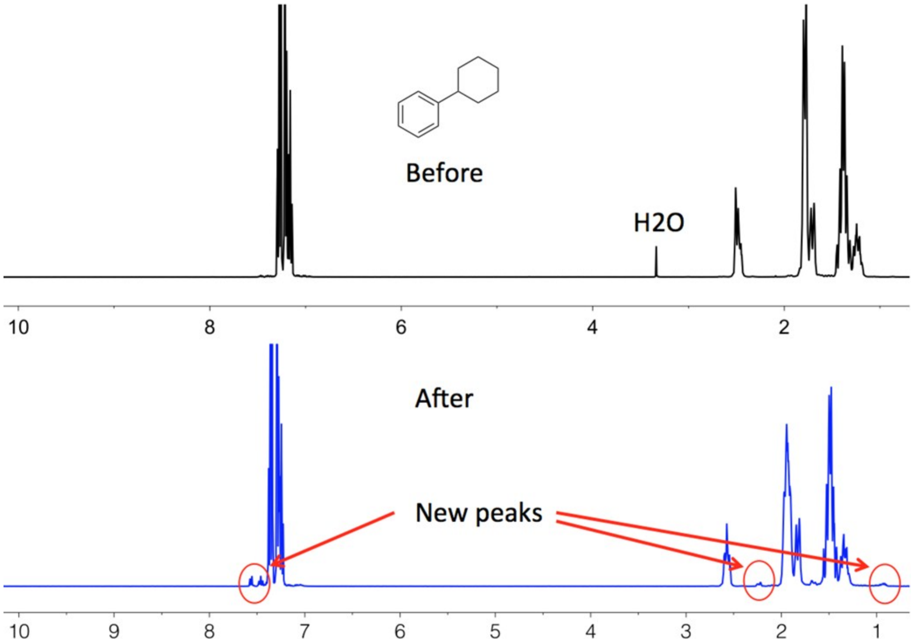


Figure S30. Chemical stability test results of cHexBen determined by ^{1}H NMR analysis.

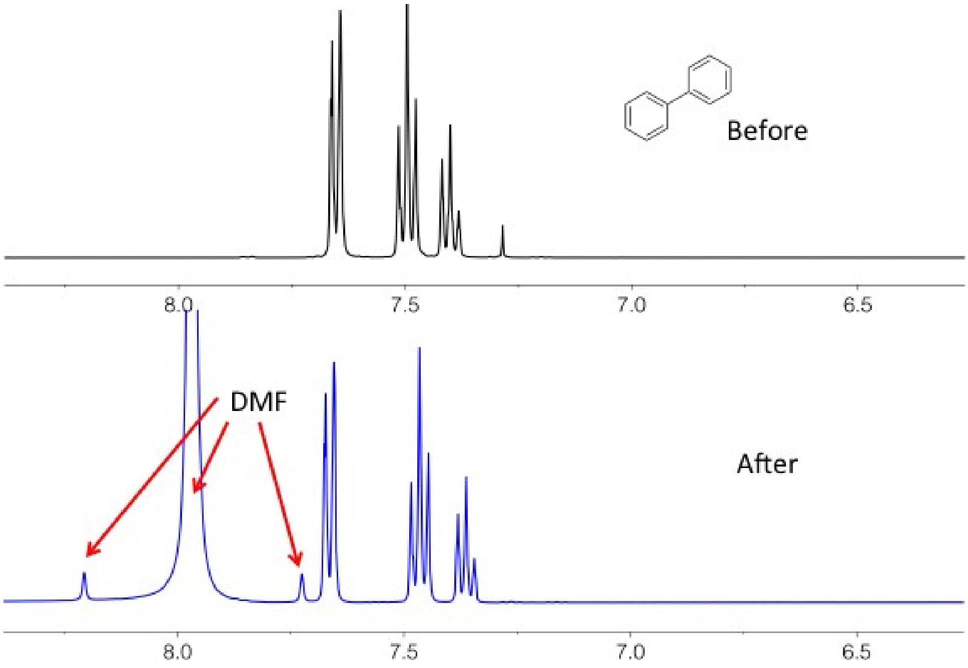


Figure S31. Chemical stability test results of DPh determined by ^{1}H NMR analysis.

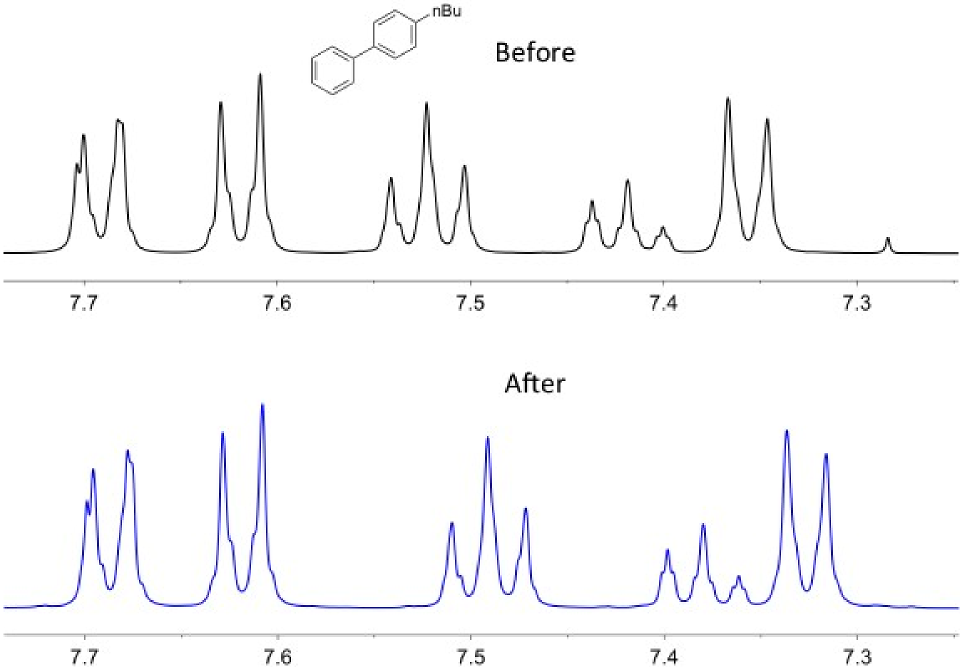


Figure S32. Chemical stability test results of nBDPh determined by ^{1}H NMR analysis.

Procedure for Chemical Stability Test of Carbonates against KO_2

A 10 mL microwave vial was charged with 0.300 g tested carbonate (DMC, EC or PC), 0.0432 g (0.235 mmol) 4-Methoxybiphenyl and a stir bar in the glove box. 4-Methoxybiphenyl has been proved to be stable under test condition and is chosen as the inner standard for quantitative calculation of remaining carbonate compounds via ^{1}H-NMR integration. Then 0.5 equivalent KO_2 and 0.5 mL DMF were added into the vial. After the vial was sealed, it was moved out of the glove box and stirred under nitrogen for 16 hours. The reaction mixture was treated with 0.5 mL d^6-DMSO and further centrifuged. The liquid layer was analyzed with ^{1}H-NMR.

The remaining fractions of DMC, EC, and PC are 0.51, 0.33, and 0.35, respectively.

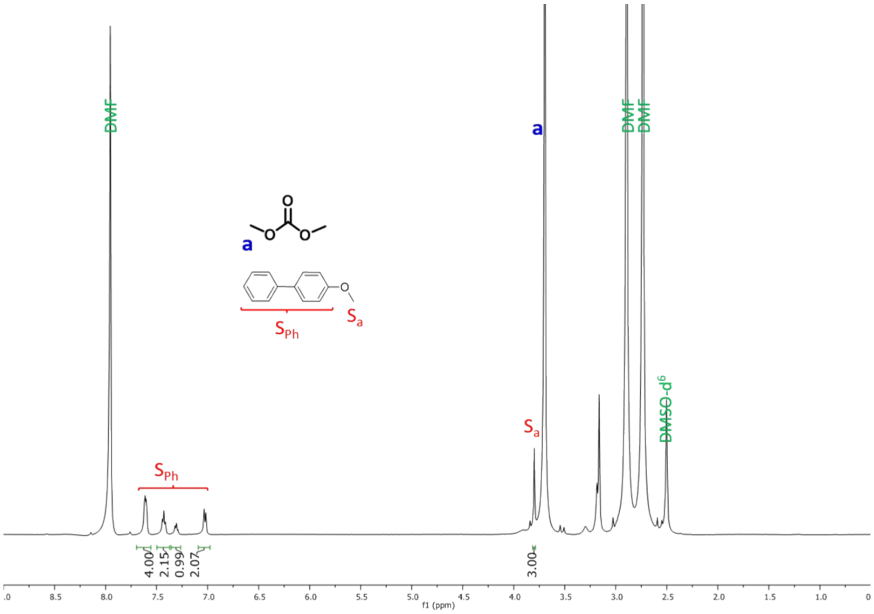


Figure S33. Chemical stability test results of DMC determined by ^{1}H NMR analysis.

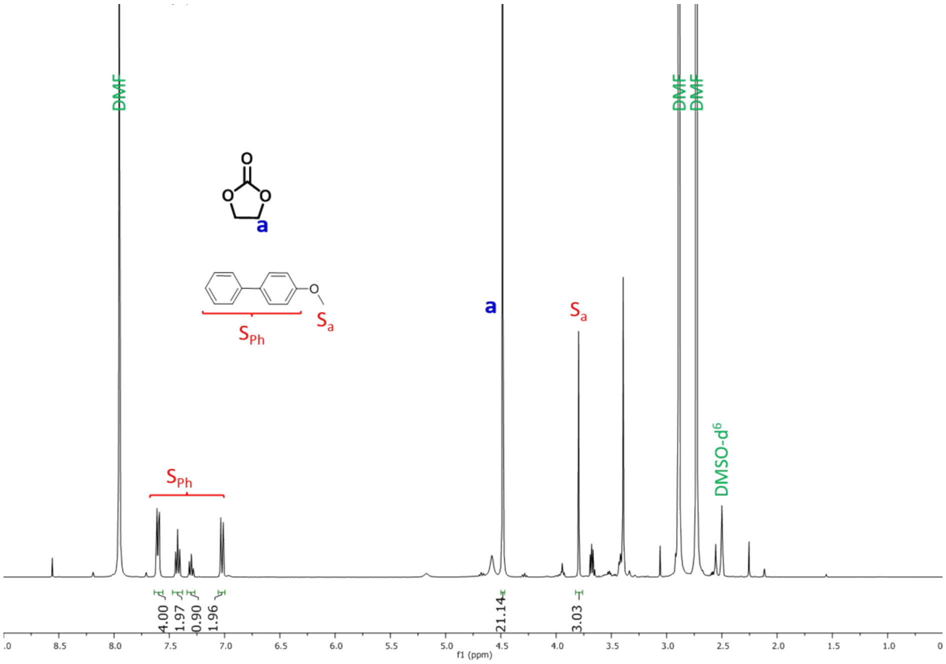


Figure S34. Chemical stability test results of EC determined by ^{1}H NMR analysis.

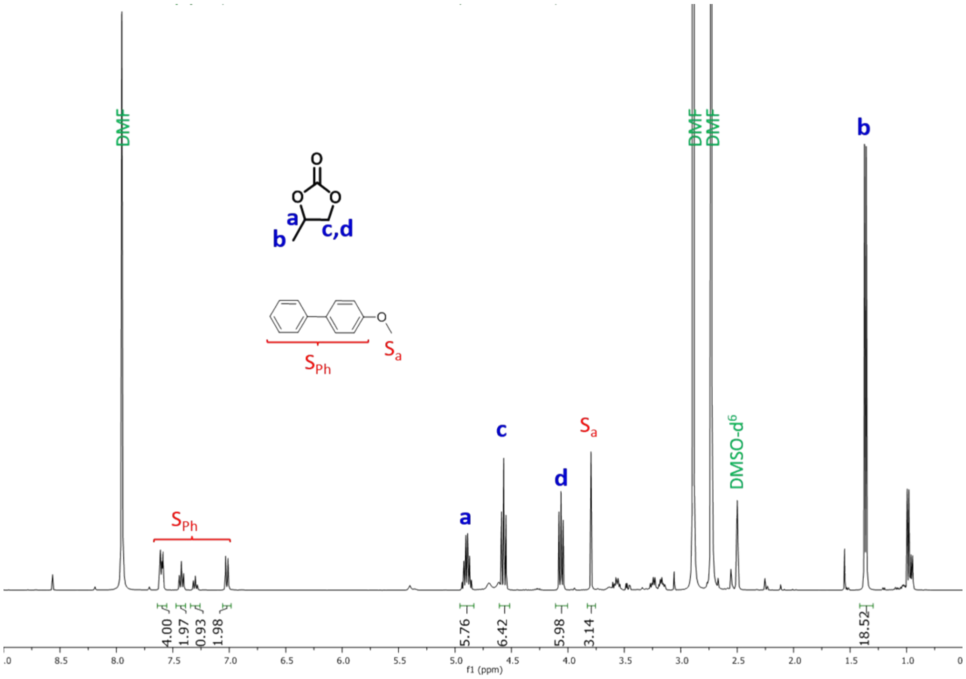


Figure S35. Chemical stability test results of PC determined by ^{1}H NMR analysis.

References

1 L. Xing, O. Borodin, D. Smith and W. Li, *J. Phys. Chem. C*, 2011, 13896–13905.

2 S. T. Tti, *Pure Appl. Chem.*, 1986, **58**, 955–966.

3 O. Borodin, W. Behl and T. R. Jow, *J. Phys. Chem. C*, 2013, **117**, 8661–8682.

4 L. Xing, O. Borodin, G. D. Smith and W. Li, *J. Phys. Chem. A*, 2011, **115**, 13896–13905.

5 X. Zhang, J. K. Pugh, P. N. Ross, E. Orlando and L. Berkeley, *J. Electrochem. Soc.*, 2001, **148**, E183–E188.

6 K. Abe, Y. Ushigoe, H. Yoshitake and M. Yoshio, *J. Power Sources*, 2006, **153**, 328–335.

7 M. Ue, M. Takehara, S. Mori and M. C. Corporation, *J. Electrochem. Soc.*, 1997, **144**, 2684–2688.

8 K. Xu, S. P. Ding and T. R. Jow, *J. Electrochem. Sci. Technol.*, 1999, **146**, 4172–4178.

9 F. Ossola, G. Pistoia, R. Seeber and P. Ugo, *Electrochim. Acta*, 1988, **33**, 47–50.

10 S. A. Campbell, C. Bowes and R. S. McMillan, *J. Electroanal. Chem.*, 1990, **284**, 195–204.