Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Aerobic α-Hydroxylation of 2-Me-1-Tetralone in 1-Alkyl-3-Methylimidazolium Ionic Liquids

Yongtao Wang,[†a] Zeyu Wen,[†a] Yue Zhang,[a] Xinyu Wang,[a] Jia Yao,[*a] Haoran Li[*ab]

[†]These authors contributed equally

[a]Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, 38 Zheda Road, Hangzhou, 310027, China. E-mail: lihr@zju.edu.cn

[b]State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

*To whom correspondence should be addressed.

Contents

α-Hydroxylation of 1

GC-MS characterization during the oxidation:

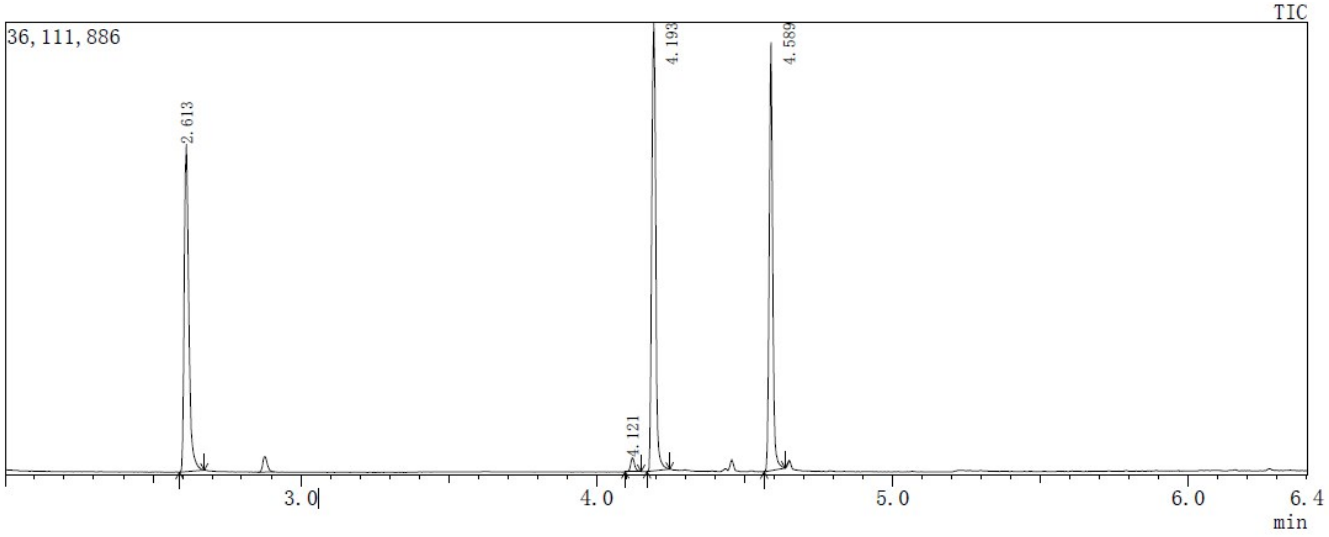
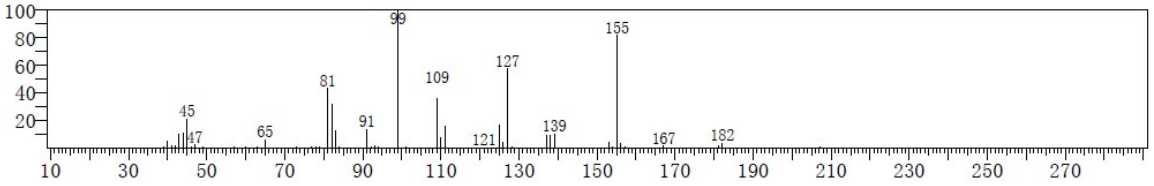
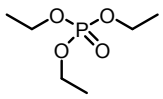


Figure S1 The GC-MS spectrogram for the aerobic oxidation of **1**.

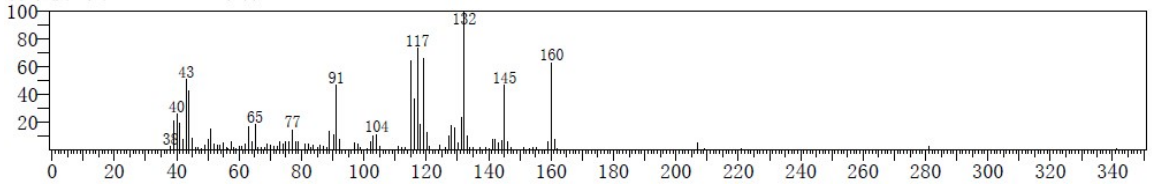
The corresponding mass spectrogram of the above GC-MS peak at 2.61 min:

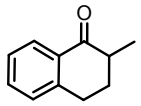




Exact Mass: 182.07

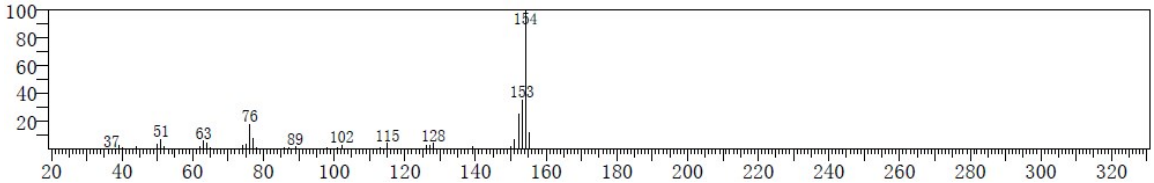
The corresponding mass spectrogram of the above GC-MS peak at 4.12 min:

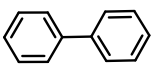




Exact Mass: 160.09

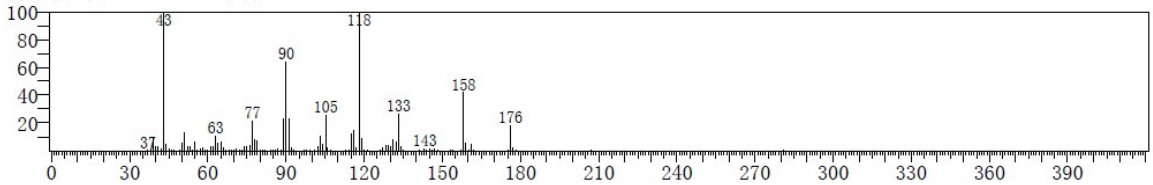
The corresponding mass spectrogram of the above GC-MS peak at 4.20 min:

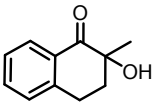




Exact Mass: 154.08

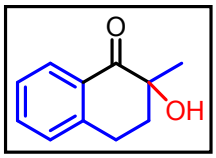
The corresponding mass spectrogram of the above GC-MS peak at 4.60 min:





Exact Mass: 176.08

*Characterization of **2**:*



2-Hydroxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (**2**).[1] The oxidation of 2-methyl-3,4-dihydronaphthalen-1(2H)-one **1** (88 mg, 0.5 mmol) in DMSO (2.0 mL) was performed under 1atm O_2, catalyzed by TBD (14 mg, 0.1 mmol), at 25 °C for 24 h, afforded 79 mg (90%) of **2a** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 3.96 (s, 1H), 3.15 – 2.97 (m, 2H), 2.31 – 2.16 (m, 2H), 1.39 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.7, 143.4, 134.1, 130.0, 129.0, 128.0, 126.9, 73.6, 35.9, 26.8, 23.9. **HRMS** *m/z* (EI): 176.0838 (M^+).

NMR Spectroscopic Data

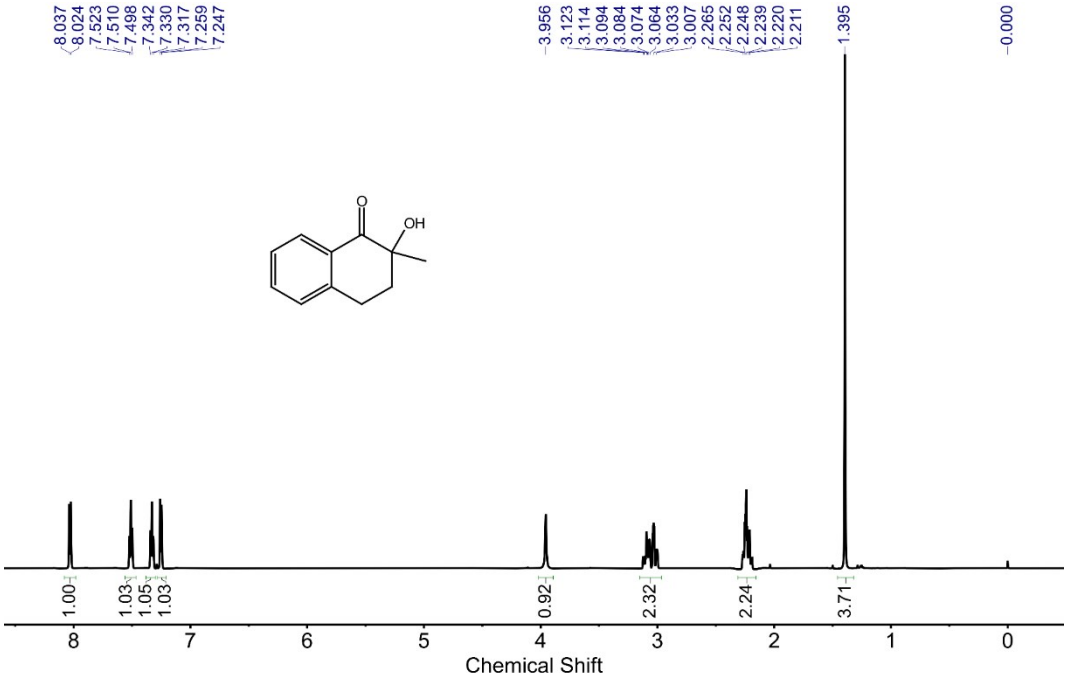


Figure S2 ^{1}H NMR (600 MHz, $CDCl_3$) of 2-hydroxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (**2**).

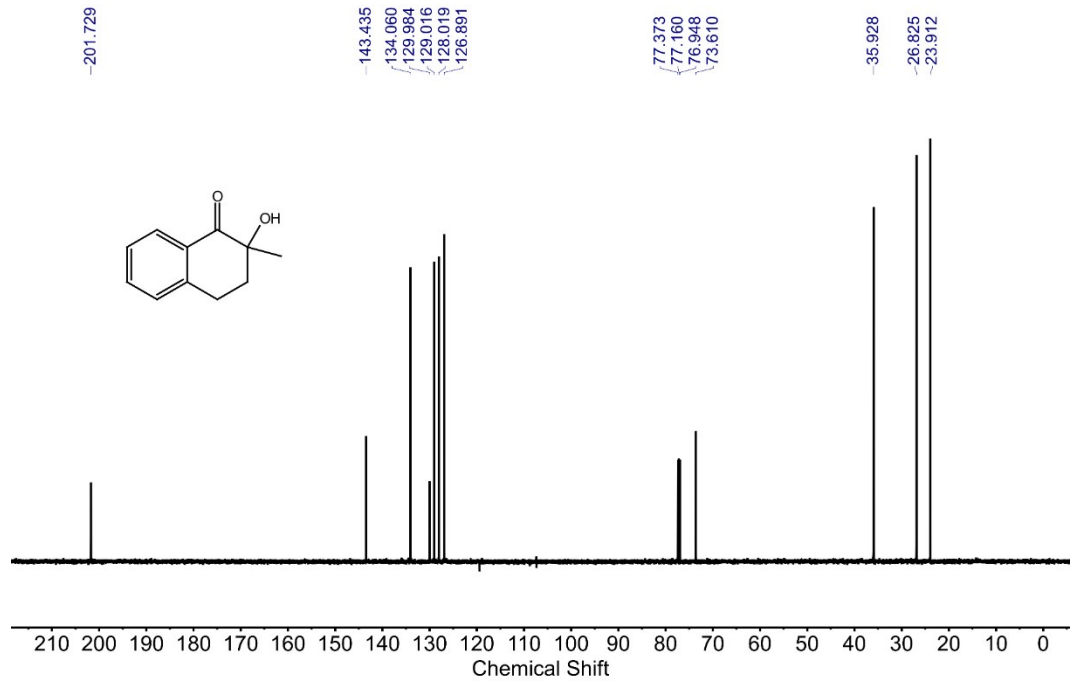


Figure S3 ^{13}C NMR (150 MHz, $CDCl_3$) of 2-hydroxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (**2**).

Property Data

Table S1 The property data for ionic liquids used in this work[2-6]

ILs	η[a] [mPa·s]	ε[b]	$E_T(30)$ [c] [kcal/mol]	$\delta_{\alpha\text{-H}}$ [ppm]	$\delta_{N\text{-Me}}$ [ppm]	Linewidth [gauss]
[Emim]BF_4	61.7	12.8	53.7	2.347	3.714	1.189
[Pmim]BF_4	73	--	53.1	2.387	3.753	1.301
[Bmim]BF_4	101.1	13.9	52.5	2.428	3.788	1.385
[Hmim]BF_4	257.2	--	53.6	2.474	3.827	1.182
[Emim]TFA	162	--	49.8	2.592	4.111	1.434
[Emim]AcO	35	--	--	2.486	3.963	1.236
[Emim]Et_2PO_4	--	16.9	50.4	2.601	4.078	1.430
[Pmim]Tf_2N	42.8	13.3	51.9	2.533	3.859	--
[Bmim]Tf_2N	49.4	14.0	50	2.54	3.868	1.388
[Bmim]TfO	89.9	12.9	52.3	2.521	3.89	--
[Bmim]PF_6	225	14.0	52.3	2.423	3.732	1.145
[Bmim]NO_3	166.4	--	51.8	2.617	4.085	1.547

[a] The viscosity of ILs are from the ref. S2-3. [b] The relative permittivities are from the ref. S4-5. [c] The $E_T(30)$ values are from the ref. 6.

Cartesian Coordinates and Energies

G: B3LYP-D3(BJ)/6-31+G(d,p) free energy at 303 K, given in Hartree.

2-methyl-1-tetralone
H = -501.507838
none imaginary frequency

H	2.1457361	0.6233638	-0.6620365
C	1.2228211	1.2301028	-0.6758065
C	0.8414711	1.5135718	0.7873735
C	0.1778421	0.3317148	-1.3427505
C	0.6722441	0.2126908	1.5776355
H	-0.0950919	2.0880068	0.8134935
H	1.6103011	2.1409088	1.2532175
O	-0.0650959	0.4173048	-2.5402935
C	1.4918181	2.5000238	-1.4872265
H	0.6055801	3.1440748	-1.5079605
H	2.3158571	3.0670478	-1.0415515
H	1.7479351	2.2589248	-2.5209795
C	-0.5168759	-0.6790492	-0.4839765
C	-1.4111339	-1.5763362	-1.0942635
C	-0.2929949	-0.7411442	0.9075685
C	-2.0773419	-2.5355482	-0.3399235
H	-1.5622239	-1.4970232	-2.1659295
C	-0.9773979	-1.7099072	1.6551055
C	-1.8582149	-2.6006192	1.0422715
H	-2.7648249	-3.2269722	-0.8179435
H	-0.8199949	-1.7601012	2.7298425
H	-2.3793319	-3.3418922	1.6417955
H	1.6529361	-0.2788382	1.6723075
H	0.3359811	0.4196958	2.6000295

2-methyl-1-tetralone anion
H = -500.937671
none imaginary frequency

C	0.9420989	1.4117316	-0.7155427
C	0.8317249	1.5767316	0.7806783
C	0.3291939	0.3531456	-1.3853947
C	0.7861189	0.2302666	1.5122373
H	-0.0651891	2.1702786	1.0716473
H	1.6898449	2.1549266	1.1614503
O	0.2695789	0.1854256	-2.6578627
C	1.5222029	2.5561886	-1.4950227
H	0.9283059	3.4870856	-1.3904167
H	2.5464639	2.8157856	-1.1714347
H	1.5463959	2.2975076	-2.5581257
C	-0.3821491	-0.6625954	-0.5191477
C	-1.2531161	-1.5840234	-1.1241657
C	-0.2174381	-0.7079904	0.8839693
C	-1.9619521	-2.5181124	-0.3641757
H	-1.3418911	-1.5313804	-2.2054167
C	-0.9301001	-1.6462624	1.6386453
C	-1.8070341	-2.5522384	1.0261313
H	-2.6362531	-3.2193674	-0.8536297
H	-0.7939451	-1.6716434	2.7198283
H	-2.3572181	-3.2731924	1.6277533

H	1.7843859	-0.2320534	1.4350903
H	0.5699709	0.3597856	2.5829053

References

S1 G. J. Chuang, W. Wang, E. Lee and T. Ritter, J. Am. Chem. Soc., 2011, 133, 1760-1762.

S2 H. Shirota, T. Mandai, H. Fukazawa and T. Kato, J. Chem. Eng. Data, 2011, 56, 2453-2459.

S3 K. Tochigi and H. Yamamoto, J. Phys. Chem. C, 2007, 111, 15989-15994.

S4 M.-M. Huang, Y. Jiang, P. Sasisanker, G. W. Driver and H. Weingärtner, J. Chem. Eng. Data, 2011, 56, 1494-1499.

S5 J. P. Hallett and T. Welton, Chem. Rev., 2011, 111, 3508-3576.

S6 V. G. Machado, R. I. Stock and C. Reichardt, Chem. Rev., 2014, 114, 10429-10475.