SUPPLEMENTARY INFORMATION

Table S1 Raw materials from different regions used in this experiment.

Sample No.	Producing area	Medical parts		
		Dysosma versipellis	*Sinopodophyllum hexandrum*	*Diphylleia sinensis*
1	Changsha, Hunan	Root	Rhizome	Rhizome
2	Xiangtan, Hunan	Root	Rhizome	Rhizome
3	Zhangjiajie, Hunan	Root	Rhizome	Rhizome
4	Guilin, Guangxi	Root	Rhizome	Rhizome
5	Yulin, Guangxi	Root	Rhizome	Rhizome
6	Bozhou, Anhui	Root	Rhizome	Rhizome
7	Shenzhen, Guangzhou	Root	Rhizome	Rhizome
8	Zhangshu, Jiangxi	Root	Rhizome	Rhizome
9	Xi'an, Shanxi	Root	Rhizome	Rhizome
10	Xianning, Hubei	Root	Rhizome	Rhizome

Table S2 The chemical shifts of ^{1}H NMR spectra for ionic liquids

Ionic liquids[a]	^{1}H NMR spectra (δ, ×10^{-6})[b]								
	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H
[bmim]Cl	10.31(s, 1H)	_	7.50(d, *J=2.0* *Hz*, 1H)	7.60(d, *J=2.0* *Hz*, 1H)	4.11(s, 3H)	4.34(t, *J=7.2* *Hz*, 2H)	1.89(m, 2H)	1.3(q, *J=7.6* *Hz*, 2H)	0.95(t, *J=7.2* *Hz*, 3H)
[bmim]Br	9.87(s, 1H)	_	7.40(d, *J=2.0* *Hz*, 1H)	7.52(d, *J=2.0* *Hz*, 1H)	3.91(s, 3H)	4.14(t, *J=7.2* *Hz*, 2H)	1.68(m, 2H)	1.15(q, *J=7.6* *Hz*, 2H)	0.73(t, *J=7.2* *Hz*, 3H)
[bmim]OTs	10.18(s, 1H)	_	7.48(d, *J=1.2* *Hz*, 1H)	7.60(d, *J=1.2* *Hz*, 1H)	4.11(s, 3H)	4.33(t, *J=7.2* *Hz*, 2H)	1.90(m, 2H)	1.37(q, *J=7.6* *Hz*, 2H)	0.96(t, *J=7.2* *Hz*, 3H)
[bmim]OTM	9.97(s, 1H)	_	7.35(d, *J=1.6* *Hz*, 1H)	7.42(d, *J=1.6* *Hz*, 1H)	4.09(s, 3H)	4.31(t, *J=7.4* *Hz*, 2H)	1.90(m, 2H)	1.26(t, *J=7.2* *Hz*, 2H)	0.97(t, *J=7.4* *Hz*, 3H)
[bmim][BF_4]	10.16(s, 1H)	_	7.55(d, *J=2.0*	7.66(d, *J=2.0*	4.13(s, 3H)	4.35(t, *J=7.2*	1.91(m, 2H)	1.38(q, *J=7.6*	0.96(t, *J=7.2*

			Hz, 1H)	*Hz*, 1H)		*Hz*, 2H)		*Hz*, 2H)	*Hz*, 3H)
[emim][BF_4]	10.16(s, 1H)	_	7.46(d, *J=2.0 Hz*, 1H)	7.58(d, *J=2.0 Hz*, 1H)	4.10(s, 3H)	4.34(q, *J=7.2 Hz*, 2H)	1.51(t,J=*7.2 Hz*, 3H)		
[pmim][BF_4]	10.17(s, 1H)	_	7.58(s, 1H)	7.66(s, 1H)	4.13(s, 3H)	4.32(t, *J=7.2 Hz*, 2H)	1.98(m, 2H)	0.99(t, J=*7.2 Hz*, 3H)	
[hmim][BF_4]	9.96 (s, 1H)	_	7.55(d, *J=1.6 Hz*, 1H)	7.70(d, *J=1.6 Hz*, 1H)	4.12(d, *J=4.4 Hz*,3H)	4.33(t, J=*7.2 Hz*, 2H)	2.04(m, 2H)	1.32(m, 2H)	1.29(m, 2H)
[omim][BF_4]	10.17(s, 1H)	_	7.55(s, 1H)	7.72(s, 1H)	4.15(m, 3H)	4.36(m, 2H)	1.93(m, 2H)	1.27(m, 2H)	1.27(m, 2H)
[demim][BF_4]	10.24(s, 1H)	_	7.42(d, *J=2.0 Hz*, 1H)	7.58(d, *J=2.0 Hz*, 1H)	4.13(s, 3H)	4.32(t, *J=7.2 Hz*, 2H)	1.90(m, 2H)	1.29(m, 2H)	1.27(m, 2H)
[amim][BF_4]	9.20(s, 1H)	_	7.39(d, *J=2.0 Hz*, 1H)	7.29(d, *J=2.0 Hz*, 1H)	3.92(m, 3H)	4.90(d,*J=6.8 Hz*, 2H)	6.01(m, 1H)	5.49(m, 1H) 5.46(m, 1H)	
[bpy][BF_4]	9.55(d,	8.20(d,	8.58(m, 1H)	8.20(d, *J=7.2*	9.55(d, *J=6.0*	4.50(t, *J=7.2*	2.05(m, 2H)	1.43(m, 2H)	0.96(t, *J=7.2*

	J=6.0 *HZ*, 1H)	*J=7.2* *Hz*, 1H)		*Hz*, 1H)	*Hz*,1H)	*Hz*, 2H)	*Hz*, 3H)

	11-H	12-H	13-H	14-H	15-H	16-H
[hmim][BF_4]	1.91(m, 2H)	0.87(t, *J=6.4* *Hz*, 3H)				
[omim][BF_4]	1.27(m, 2H)	1.27 (m, 2H)	1.34(m, 2H)	0.89(t, *J=3.2* *Hz*, 3H)		
[demim][BF_4]	1.27(m, 2H)	1.27(m, 2H)	1.32(m, 2H)	1.25(m, 2H)	1.33(m, 2H)	0.88(t, *J=7.2* *Hz*, 3H)

[a] All of the ILs were dissolved in $CDCl_3$. [b] ^{1}H NMR spectra were recorded at 100MHz and reported downfield from trimethylsilane (TMS). Peak shape were abbreviated as s=singlet, d=doublet, quart =quartet, t=triplet and m = multiplet.

Table S3 The chemical shifts of ^{13}C NMR spectra for ionic liquids

Ionic liquids[a]	^{13}C NMR spectra (δ, ×10^{-6})[b]													
	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C	11-C	12-C	13-C	14-C	15-C	16-C
[bmim]Cl	137.28		121.79	123.53	36.34	49.47	31.91	19.20	13.23						
[bmim]Br	137.05		121.93	123.57	36.63	49.69	32.00	19.30	13.32						
[bmim]OTs	137.16		121.90	123.54	36.58	49.68	32.01	19.31	13.34						
[bmim]OTM	137.22		121.85	123.56	36.60	49.68	32.00	19.30	13.33						
[bmim][BF_4]	137.02		121.95	123.56	36.56	49.67	31.98	19.28	13.29						
[emim][BF_4]	137.11		121.88	123.55	36.48	48.32	13.40								
[pmim][BF_4]	137.15		121.88	123.56	36.62	49.69	21.03	13.45							
[hmim][BF_4]	136.51		121.80	123.56	36.39	49.69	29.85	25.48	30.70	22.00	13.58				
[omim][BF_4]	136.76		121.80	123.57	36.41	49.77	29.98	25.89	28.68	28.60	31.32	22.23	13.73		
[demim][BF_4]	137.30		121.77	123.54	36.65	50.06	30.18	26.14	30.18	29.11	29.32	28.86	31.70	22.52	13.98

[amim][BF_4]	138.03		121.98	123.62	36.67	53.12	133.1	115.5	
[bpy][BF_4]	145.15	128.42	145.02	128.42	145.15	61.65	33.68	19.19	13.41

[a] All of the ILs were dissolved in $CDCl_3$. [b] ^{13}C NMR spectra were recorded at 400MHz and reported downfield from trimethylsilane (TMS)

Table S4 ANOVA table for the (a)*Dysosma versipellis*, (b)*Sinopodophyllum hexandrum* and (c)*Diphylleia sinensis.*

Source	Sum Sq	df	Mean Sq	F-value	Significance [a]
(a) *Dysosma versipellis*					
ILs concentration	123.3	2	61.60	57.60	*
Solid/liquid ratio	648.2	2	324.1	302.9	**
Temperature	2.100	2	1.100	1.100	
Irradiation time	3.100	2	1.600	1.500	
Error [b]	2.100	2	1.100		
(b) *Sinopodophyllum hexandrum*					
ILs concentration	576.1	2	288.1	5.600	
Solid/liquid ratio	904.4	2	452.2	9.800	-
Temperature	233.1	2	116.6	2.300	
Irradiation time	102.9	2	51.50	1.000	
Error	102.9	2	51.50		
(c) *Diphylleia sinensis*					
ILs concentration	25.40	2	12.70	9.500	-
Solid/liquid ratio	3248	2	1624	1212	**
Temperature	54.50	2	27.30	20.40	*
Irradiation time	2.700	2	1.300	1.000	
Error	2.700	2	1.300		

[a] The critical F-value is 99.01 (P<0.01,**), 19.00 (P<0.05,*) and 9.00 (P<0.1,-). [b] The factor with minimum R value was selected as error term.

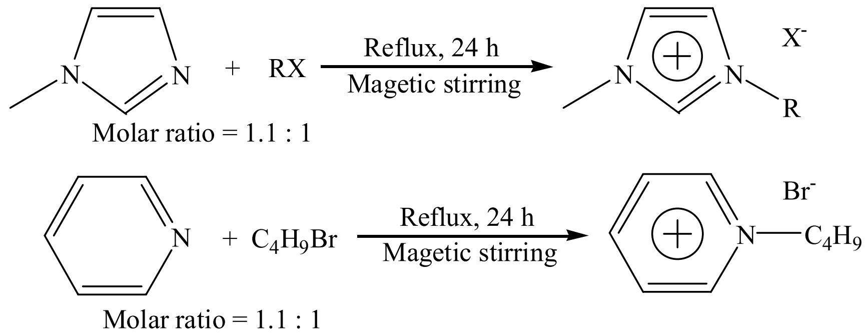
Table S5 Infrared absorption data of different components in *Dysosma versipellis, Sinopodophyllum hexandrum* and *Diphylleia sinensis*.

Chemical Compositions	Wavenumber (cm^{-1})
Podophyllotoxin [a]	3460 (O-H), 1774 (C=O), 1590, 1480 (Ar-H), 1250, 1130, 1040 (C-O-C), 930 (OCH_2O)
Deoxypodophyllotixin [a]	1760 (C=O), 1590, 1500 (Ar-H), 1240, 1125 (C-O-C), 930 (OCH_2O)
Isopicropodophyllone [a]	1773, 1685 (C=O), 1593, 1480 (Ar-H), 1270, 1130,1040 (C-O-C), 935 (OCH_2O)
Dehydropodophyllotoxin [a]	1705 (C=O), 1590, 1465 (Ar-H), 1240, 1130, 1045 (C-O-C), 940 (OCH_2O)
β-peltatin [c]	3500~3200 (O-H), 1760 (C=O), 1630, 1590, 1500 (Ar-H), 1250, 1130 (C-O-C), 930 (OCH_2O)
Diphyllin [d]	1230, 1130, 1040 (C-O-C), 930 (OCH_2O)
Picropodophyllin [a]	3445 (O-H), 1770 (C=O), 1593, 1480 (Ar-H), 1250,1130, 1040 (C-O-C), 930 (OCH_2O)
Podophyllotoxone [a]	1780, 1668 (C=O), 1590, 1480 (Ar-H), 1250, 1130, 1035 (C-O-C), 930 (OCH_2O)
4'-demethylpodophyllotoxin [b]	3505, 3480 (O-H), 1765 (C=O), 1620, 1490 (Ar-H), 1250, 1040 (C-O-C), 930 (OCH_2O)
Kaempferol [b]	3357 (O-H), 1655 (C=O), 1605, 1508 (Ar-H or Ar (C=C)), 1310, 1105 (C-O-C), 792 (Ar-H, δ)

Quercetin [b]	3362, 3226 (O-H), 1653 (C=O), 1602, 1570 (Ar-H or Ar (C=C)), 1331 (C-O-C), 794, 739 (Ar-H, δ)
Vanillic acid [b]	3585 (O-H), 1753 (C=O), 1600, 1514 (Ar(C=C), 1272, 1156 (C-O), 765 (=C-H, δ)
β-sitosterol [b]	3350 (O-H), 2944, 2872 (C-H), 1465, 1378 (C-H, δ), 1058 (C-O)
4'-demethyldeoxy podophyllotoxin [e]	3400 (O-H), 1758 (C=O), 1610, 1500 (Ar-H), 1220,1030 (C-O-C), 925 (OCH_2O)
8-isopentenyl kaempferol [e]	3360 (O-H), 2920 (=C-H), 1650 (C=O), 1610, 1505 (Ar-H or Ar(C=C))
Citrusinol [e]	3360 (O-H), 2910, 1610, 1535
4'-demethylpodophyllone [e]	3600~3400 (O-H), 1765 (C=O), 1612, 1520 (Ar(C=C)), 1505 (Ar-H), 1240, 1110 (C-O-C), 930 (OCH_2O)
Hexacosanoic acid [a]	3600~3200 (O-H), 2910 (C-H), 2800 (C-H), 1710 (C=O)

[a] Commom component of three herbs. [b] Mutual component of *Dysosma versipellis* and *Sinopodophyllum hexandrum*. [c] Specific component of *Dysosma versipellis*. [d] Mutual component of *Dysosma versipellis* and *Diphylleia sinensis*. [e] Specific component of *Sinopodophyllum hexandrum*.

Synthetic Routes 1 (Quaternization)



R=C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, CH_2-CH=CH_2
X=Br, Cl M=H, Na Y= BF_4, OTs, CH_3SO_3

Synthetic Routes 2 (Metathesis)

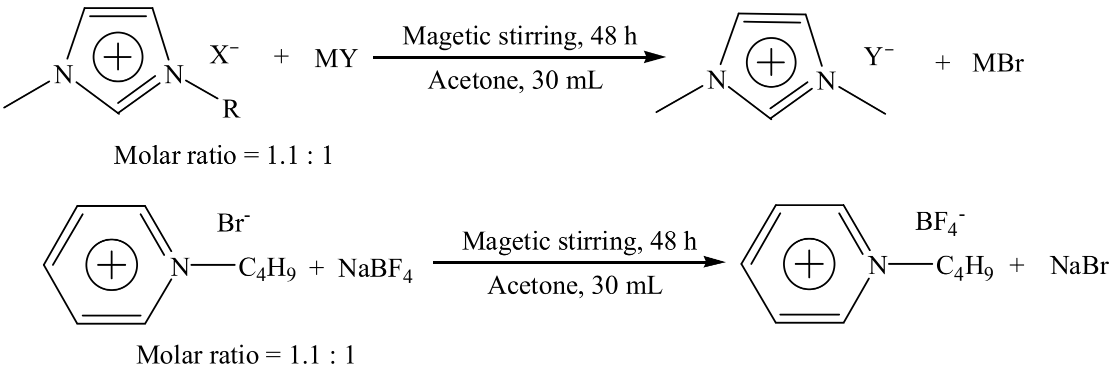


Fig. S1 Synthetic routes of ILs

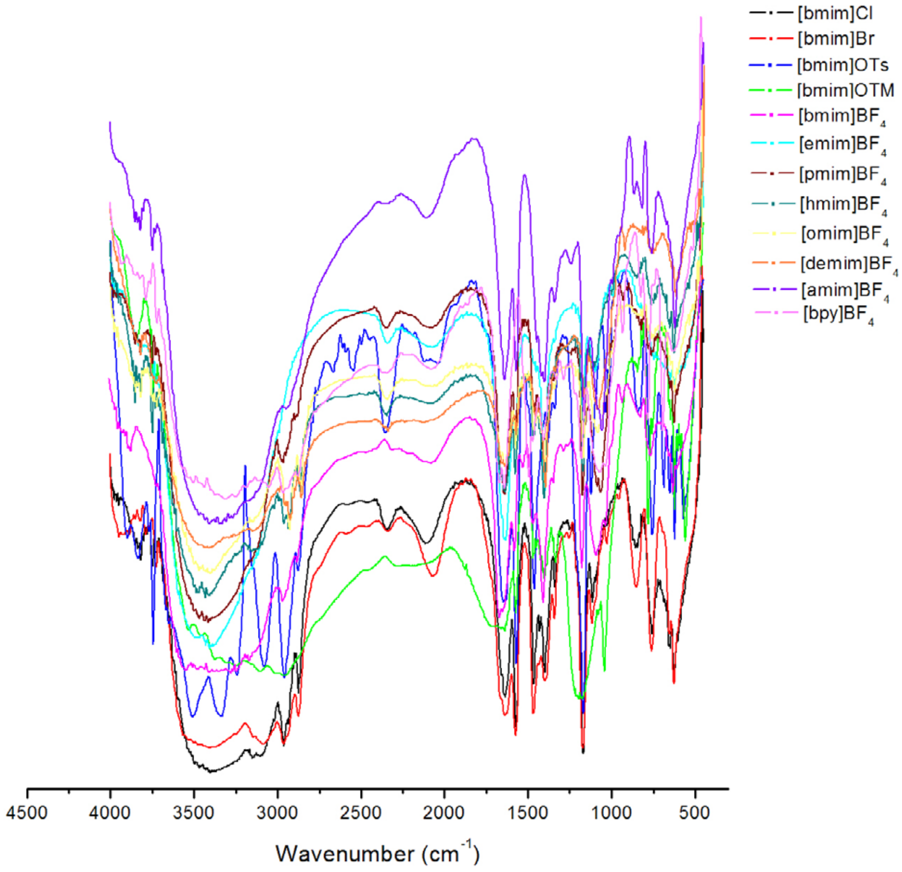


Fig. S2 FT-IR spectra of synthetic ILs