

Supplementary information

Table S1 Chemical shifts of ^1H NMR spectra for twenty kinds of ILs

| Ionic liquids ^a | ^1H NMR spectra (δ , $\times 10^{-6}$) ^b | | | | | | | | |
|----------------------------|---|-----|---------|---------|----------|----------|----------|----------|------|
| | 2-H | 3-H | 4-H | 5-H | 6-H | 7-H | 8-H | 9-H | 10-H |
| [Emim][Br] | 10.05 | — | 7.58 | 7.69 | 2.98 | 4.34 | 1.51 | | |
| | (1H, s) | | (1H, s) | (1H, s) | (3H, s) | (2H, q) | (3H, t) | | |
| [Emim][BF ₄] | 10.12 | — | 7.41 | 7.54 | 4.07 | 4.30 | 1.47 | | |
| | (1H, s) | | (1H, d) | (1H, d) | (3H, s) | (2H, q) | (3H, t) | | |
| [Amim][Cl] | 9.89 | — | 7.51 | 7.68 | 4.08 | 4.33 | 1.91 | 0.96 | |
| | (1H, s) | — | (1H, s) | (1H, s) | (3H, s) | (2H, q) | (2H, t) | (3H, t) | |
| [Amim][BF ₄] | 9.25 | — | 7.41 | 7.34 | 3.86 | 4.96 | 6.07 | 5.45 | |
| | (1H, s) | — | (1H, d) | (1H, d) | (3H, m) | (2H, d) | (1H ,m) | (1H, m) | |
| [Pmim][Br] | 10.03 | — | 7.65 | 7.69 | 3.68 | 4.32 | 1.91 | 0.96 | |
| | (1H, s) | — | (1H, s) | (1H, s) | (3H, s) | (2H, q) | (2H, t) | (3H, t) | |
| [Pmim][BF ₄] | 10.15 | — | 7.42 | 7.58 | 4.07 | 4.29 | 1.95 | 0.98 | |
| | (1H, s) | — | (1H, s) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (3H, t) | |

| | | | | | | | | | |
|---------------------------|---------|---|---------|---------|---------|---------|---------|---------|---------|
| [Bmim][Br] | 10.06 | — | 7.61 | 7.72 | 3.02 | 4.35 | 1.91 | 1.38 | 0.96 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, q) | (3H, t) |
| [Bmim][Cl] | 10.17 | — | 7.51 | 7.66 | 4.11 | 4.35 | 1.87 | 1.38 | 0.95 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, q) | (3H, t) |
| [Bmim][BF ₄] | 10.09 | — | 7.43 | 7.59 | 4.07 | 4.32 | 1.89 | 1.36 | 0.96 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, q) | (3H, t) |
| [Bmim][HSO ₄] | 10.12 | — | 7.38 | 7.54 | 4.13 | 4.34 | 1.93 | 1.31 | 0.92 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, q) | (3H, t) |
| [Bmim][OTM] | 10.02 | — | 7.44 | 7.48 | 4.14 | 4.27 | 1.87 | 1.22 | 0.91 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, t) | (3H, t) |
| [Bmim][PTSA] | 10.16 | — | 7.44 | 7.56 | 4.08 | 4.29 | 1.86 | 1.33 | 0.93 |
| | (1H, s) | | (1H, d) | (1H, s) | (3H, s) | (2H, t) | (2H, m) | (2H, q) | (3H, t) |
| [Hmim][Br] | 9.92 | — | 7.73 | 7.67 | 3.04 | 4.31 | 1.88 | 1.34 | 0.92 |
| | (1H, s) | | (1H, d) | (1H, d) | (3H, d) | (2H, t) | (2H, m) | (2H, m) | (2H, m) |
| [Hmim][BF ₄] | 9.94 | — | 7.54 | 7.71 | 4.11 | 4.34 | 2.02 | 1.34 | 1.31 |
| | (1H, s) | | (1H, d) | (1H, d) | (3H, d) | (2H, t) | (2H, m) | (2H, m) | (2H, m) |

| | 10.14 | — | 7.77 | 7.69 | 3.08 | 4.37 | 1.78 | 1.28 | 0.93 |
|---------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| [Omim][Br] | (1H, s) | | (1H, s) | (1H, s) | (3H, m) | (2H, m) | (2H, m) | (2H, m) | (2H, m) |
| | | | | | | | | | |
| [Omim][BF ₄] | 10.17 | — | 7.55 | 7.72 | 4.15 | 4.36 | 1.93 | 1.27 | 1.25 |
| | (1H, s) | | (1H, s) | (1H, s) | (3H, m) | (2H, m) | (2H, m) | (2H, m) | (2H, m) |
| [Demim][Br] | 10.24 | — | 7.65 | 7.52 | 3.04 | 4.32 | 1.72 | 1.26 | 0.94 |
| | (1H, s) | | (1H, d) | (1H, d) | (3H, s) | (2H, t) | (2H, m) | (2H, m) | (2H, m) |
| [Demim][BF ₄] | 10.27 | — | 7.43 | 7.59 | 4.11 | 4.33 | 1.87 | 1.27 | 1.25 |
| | (1H, s) | | (1H, d) | (1H, d) | (3H, s) | (2H, t) | (2H, m) | (2H, m) | (2H, m) |
| [Bpy][Br] | 9.51 | 8.14 | 8.72 | 8.14 | 9.47 | 4.52 | 2.01 | 1.45 | 0.84 |
| | (1H, d) | (1H, d) | (1H, m) | (1H, d) | (1H, d) | (2H, t) | (2H, m) | (2H, m) | (3H, t) |
| [Bpy][BF ₄] | 9.54 | 8.21 | 8.56 | 8.21 | 9.52 | 4.51 | 2.04 | 1.44 | 0.94 |
| | (1H, d) | (1H, d) | (1H, m) | (1H, d) | (1H, d) | (2H, t) | (2H, m) | (2H, m) | (3H, t) |

11-H 12-H 13-H 14-H 15-H 16-H

| | | |
|--------------------------|---------|---------|
| | 1.84 | 0.82 |
| [Hmim][Br] | (2H, m) | (3H, t) |
| [Hmim][BF ₄] | 1.92 | 0.89 |

| | (2H, m) | (3H, t) | | | |
|---------------------------|---------|---------|---------|---------|---------|
| a | | | | | |
| [Omim][Br] | 1.18 | 1.18 | 1.29 | 0.86 | |
| | (2H, m) | (2H, m) | (2H, m) | (3H, t) | |
| | 1.28 | 1.28 | 1.35 | 0.87 | |
| [Omim][BF ₄] | | | | | |
| | (2H, m) | (2H, m) | (2H, m) | (3H, t) | |
| [Demim][Br] | 1.18 | 1.15 | 1.27 | 1.26 | 1.38 |
| | (2H, m) |
| | 1.26 | 1.26 | 1.34 | 1.24 | 1.35 |
| [Demim][BF ₄] | | | | | |
| | (2H, m) |
| | | | | | (3H, t) |

Twenty kinds of ILs were all dissolved in CDCl₃ and recorded on Varian-INOVA 400 NMR spectrometry.

^b ¹H NMR chemical shifts were recorded at 100MHz and reported downfield from trimethylsilane (TMS). Multiplicities are abbreviated as s=singlet, d=doublet, q=quartet, t=triplet and m=multiplet.

Table S2 Chemical shifts of ^{13}C NMR spectra for twenty kinds of ILs

| Ionic liquids ^a | ^{13}C NMR spectra (δ , $\times 10^{-6}$) ^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 |
| [Emim][Br] | 137.13 | - | 121.86 | 123.57 | 36.54 | 48.35 | 13.43 | | | | | | | | |
| [Emim][BF ₄] | 137.12 | - | 121.88 | 123.54 | 36.47 | 48.33 | 13.42 | | | | | | | | |
| [Amim][Cl] | 138.07 | - | 121.96 | 123.64 | 36.74 | 53.11 | 133.11 | 115.54 | | | | | | | |
| [Amim][BF ₄] | 138.06 | - | 121.97 | 123.62 | 36.66 | 53.13 | 133.09 | 115.51 | | | | | | | |
| [Pmim][Br] | 137.19 | - | 121.85 | 123.57 | 36.68 | 49.72 | 21.01 | 13.49 | | | | | | | |
| [Pmim][BF ₄] | 137.14 | - | 121.87 | 123.56 | 36.64 | 49.68 | 21.01 | 13.46 | | | | | | | |
| [Bmim][Br] | 137.05 | - | 121.93 | 123.57 | 36.63 | 49.69 | 32.00 | 19.30 | 13.32 | | | | | | |
| [Bmim][Cl] | 137.28 | - | 121.79 | 123.53 | 36.34 | 49.47 | 31.91 | 19.20 | 13.23 | | | | | | |
| [Bmim][BF ₄] | 137.02 | - | 121.95 | 123.56 | 36.56 | 49.67 | 31.98 | 19.28 | 13.29 | | | | | | |
| [Bmim][HSO ₄] | 137.12 | - | 121.77 | 123.44 | 36.52 | 49.56 | 31.93 | 19.23 | 13.24 | | | | | | |
| [Bmim][OTM] | 137.22 | - | 121.85 | 123.56 | 36.60 | 49.68 | 32.00 | 19.30 | 13.33 | | | | | | |
| [Bmim][PTSA] | 137.16 | - | 121.90 | 123.54 | 36.58 | 49.68 | 32.01 | 19.31 | 13.34 | | | | | | |
| [Hmim][Br] | 136.55 | - | 121.75 | 123.58 | 36.47 | 49.72 | 29.88 | 25.51 | 30.73 | 22.01 | 13.59 | | | | |

| | | | | | | | | | | | |
|---------------------------|--------|--------|--------|--------|--------|-------|-------|-------|-------|-------|-------|
| [Hmim][BF ₄] | 136.52 | - | 121.79 | 123.57 | 36.38 | 49.68 | 29.86 | 25.47 | 30.71 | 22.00 | 13.58 |
| [Omim][Br] | 136.79 | - | 121.78 | 123.59 | 36.49 | 49.80 | 29.99 | 25.91 | 28.69 | 28.61 | 31.33 |
| [Omim][BF ₄] | 136.77 | - | 121.80 | 123.56 | 36.40 | 49.78 | 29.97 | 25.88 | 28.67 | 28.60 | 31.32 |
| [Demim][Br] | 137.33 | - | 121.74 | 123.58 | 36.72 | 50.09 | 30.22 | 26.17 | 30.23 | 29.12 | 29.34 |
| [Demim][BF ₄] | 137.30 | - | 121.78 | 123.55 | 36.64 | 50.06 | 30.17 | 26.13 | 30.17 | 29.10 | 29.32 |
| [Bpy][Br] | 145.17 | 128.41 | 145.01 | 128.44 | 145.22 | 61.68 | 33.71 | 19.22 | 13.44 | | |
| [Bpy][BF ₄] | 145.14 | 128.43 | 145.03 | 128.41 | 145.14 | 61.65 | 33.67 | 19.18 | 13.40 | | |

^a Twenty kinds of ILs were all dissolved in CDCl₃ and recorded on Varian-INOVA 400 NMR spectrometry.

^b ¹³C NMR chemical shifts were recorded at 400MHz and reported downfield from trimethylsilane (TMS)

Fig.S1

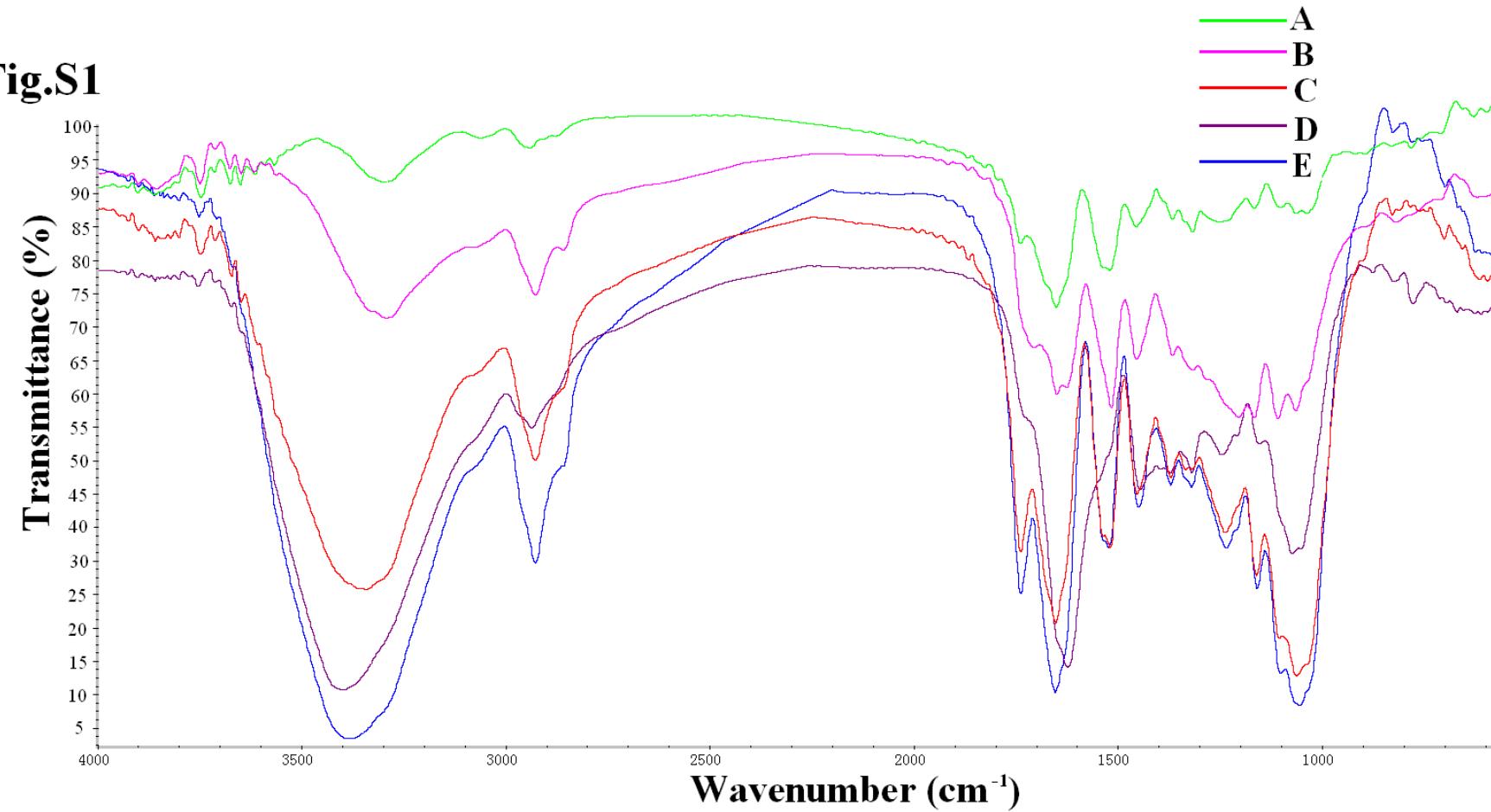


Fig. S1. FT-IR spectra of *Toona sinensis* samples before and after different extraction techniques. The FT-IR spectrograms of: (A) untreated, (B) after ME for 24 h, (C) after HE for 4 h, (D) after UAE for 2 h, (E) after MAE for 20 min.

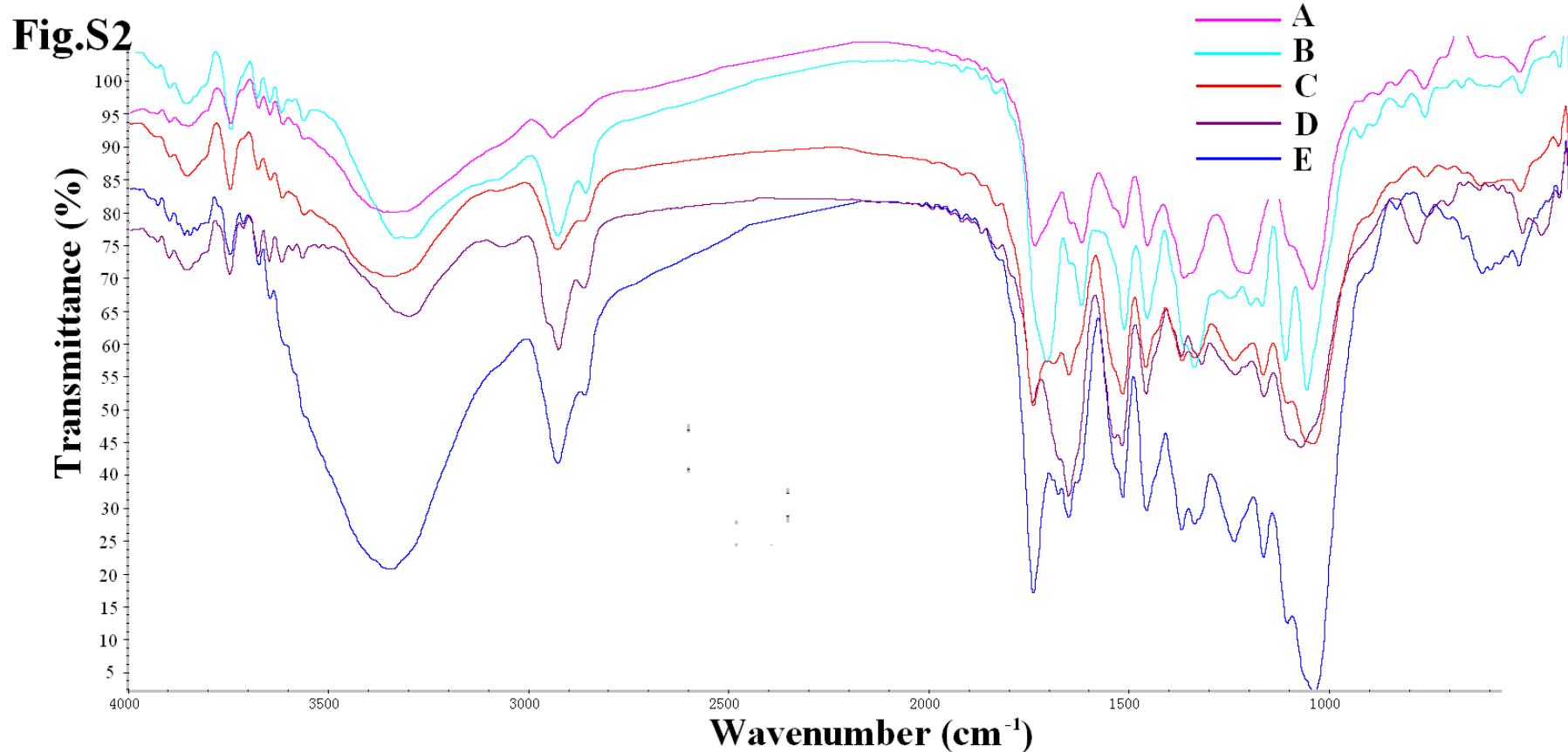


Fig. S2. FT-IR spectra of *Rosa chinensis* samples before and after different extraction techniques. The FT-IR spectrograms of: (A) untreated, (B) after ME for 24 h, (C) after HE for 4 h, (D) after UAE for 2 h, (E) after MAE for 20 min.

Fig. S3

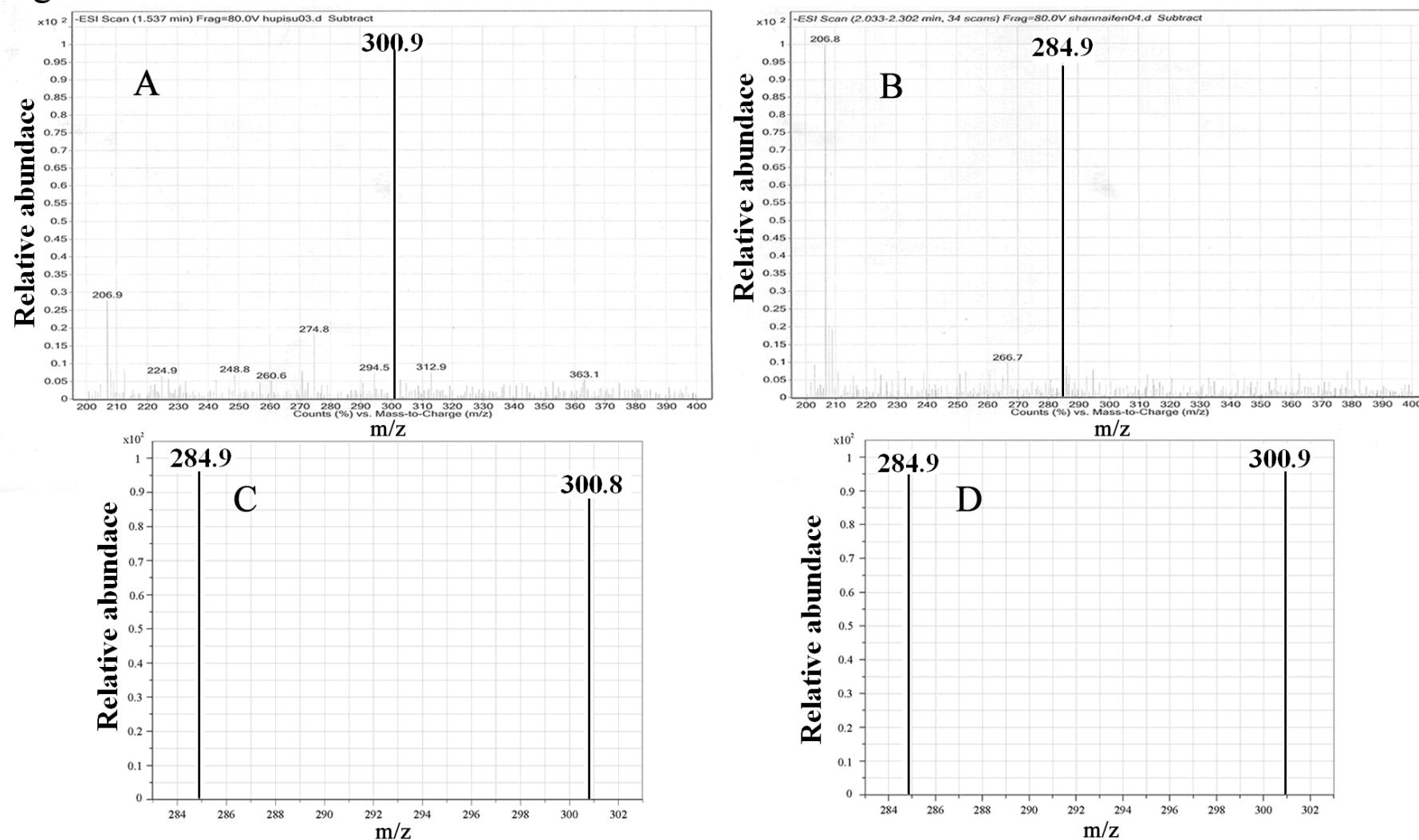


Fig. S3. Negative ion mass spectrums of quercetin standard solution (A), kaempferol standard solution (B), extracted *Toona sinensis* sample (C) and extracted *Rosa chinensis* sample (D), respectively.