Supporting Information

A new thiophene and two new monoterpenoids from *Xanthium sibiricum*

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Figure S1. UV spectra of compound **1** in MeOH

Figure S2. IR spectrum of compound **1**

Figure S3. ¹H-NMR spectrum of compound **1** in MeOH-*d*₄ (600 MHz)

DD2-500 13C-NMR EF-M40-5-4 IN cd3od Jun 13 2013 coldprobe-Probe

Figure S4. ¹³C-NMR spectrum of compound **1** in MeOH-*d*₄ (150 MHz)

DD2-506 DEPT EF-M40-5-4 IN cd3od Jun 13 2013 coldprobe-Probe

Figure S5. DEPT spectrum of compound **1** in MeOH-*d*₄ (150 MHz)

Figure S6. HSQC spectrum of compound **1** in MeOH-*d*₄ (600 MHz)

Figure S7. HMBC spectrum of compound **1** in $\text{MeOH-}d_4$ (600 MHz)

Temp. 25.0 C / 298.1 K
 Sample #4, Operator: vjwalk
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 6377.6 Hz
 2D Width 6377.6 Hz
 2 repetitions
 256 increments
 OBSERVE H1, 599.6900465 MHz
 DATA PROCESSING
 Sq. sine bell 0.075 sec
 F1 DATA PROCESSING
 Sq. sine bell 0.027 sec
 FT size 2048 x 2048
 Total time 10 min

2.52
b/s

3.18

Figure S8. ^1H - ^1H COSY spectrum of compound 1 in $\text{MeOH-}d_4$ (600 MHz)

MS Formula Results: + Scan (4.385 min) Sub (2014031904.d)

m/z	Ion	Formula	Abundance
198.0581	(M+H) ⁺	C ₉ H ₁₂ N O ₂ S	3757159.3

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☒	C ₉ H ₁₁ N O ₂ S	C ₉ H ₁₂ N O ₂ S	198.0583	99.83		197.0508	197.051	1.25	1.25	99.61	99.83	99.96	198.0581	5
☐	C ₇ H ₉ N ₄ O S	C ₇ H ₁₀ N ₄ O S	198.057	99.03		197.0508	197.0497	-5.57	5.57	98.87	98.99	99.15	198.0581	5.5

m/z	Ion	Formula	Abundance
220.0401	(M+Na) ⁺	C ₉ H ₁₁ N Na O ₂ S	440556.6

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☒	C ₉ H ₁₁ N O ₂ S	C ₉ H ₁₁ N Na O ₂ S	220.0403	99.95		197.0509	197.051	0.62	0.62	99.89	99.94	99.99	220.0401	5

Figure S9. HR-ESIMS spectrum of compound **1**

Figure S10. UV spectra of compound **2** in MeOH

Figure S11. IR spectrum of compound 2

Figure S12. ^1H -NMR spectrum of compound **2** in $\text{MeOH-}d_4$ (600 MHz)

Figure S13. ^{13}C -NMR spectrum of compound **2** in $\text{MeOH-}d_4$ (150 MHz)

Figure S14. HSQC spectrum of compound **2** in MeOH- d_4 (600 MHz)

Figure S15. HMBC spectrum of compound **2** in MeOH- d_4 (600 MHz)

Figure S16. ^1H - ^1H COSY spectrum of compound **2** in $\text{MeOH-}d_4$ (600 MHz)

Figure S17. NOESY spectrum of compound **2** in $\text{MeOH-}d_4$ (600 MHz)

Figure S18. NOE spectrum of compound **2** in $\text{MeOH-}d_4$ (600 MHz)

MS Formula Results: + Scan (4.455 min) Sub (2013091603.d)

m/z	Ion	Formula	Abundance
209.1153	(M+Na)+	C10 H18 Na O3	3267219.5

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☒	C10 H18 O3	C10 H18 Na O3	209.1148	99.88		186.1261	186.1256	-2.53	2.53	99.84	99.97	99.86	209.1153	2

Figure S19. HR-ESIMS spectrum of compound **2**

Figure S20. The HPLC separation chromatogram of **2** on chiral AD-H column ($5\ \mu\text{m}$, $250 \times 5\ \text{mm}$). Flow rate: 1.0 mL/min; solvent: iPrOH-n-hexane (15:85); detector wavelength: 210 nm; temperature 25 °C.

Figure S21. ¹H-NMR spectrum of compound (+)-2 in MeOH-*d*₄ (600 MHz)

Figure S22. ^1H -NMR spectrum of compound (-)-**2** in $\text{MeOH-}d_4$ (600 MHz)

Figure S23. IR spectrum of compound 3

Figure S24. CD spectrum of compound **3**

Figure S25. ^1H -NMR spectrum of compound **3** in $\text{MeOH-}d_4$ (600 MHz)

Figure S26. ¹³C-NMR spectrum of compound **3** in MeOH-*d*₄ (150 MHz)

Figure S27. DEPT spectrum of compound **3** in MeOH-*d*₄ (150 MHz)

Figure S28. HSQC spectrum of compound **3** in $\text{MeOH-}d_4$ (600 MHz)

Figure S29. HMBC spectrum of compound **3** in $\text{MeOH-}d_4$ (600 MHz)

Figure S30. ^1H - ^1H COSY spectrum of compound **3** in $\text{MeOH-}d_4$ (600 MHz)

Figure S31. NOESY spectrum of compound **3** in MeOH- d_4 (600 MHz)

MS Formula Results: - Scan (4.155 min) Sub (2014121601.d)

m/z	Ion	Formula	Abundance
281.1398	(M-H) ⁻	C ₁₅ H ₂₁ O ₅	764383.6

Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
☒	C ₁₅ H ₂₂ O ₆	C ₁₅ H ₂₁ O ₅	99.96		282.147	282.1467	281.1394	-1.11	1.11	99.96	99.99	99.9	5
☐	C ₁₂ H ₂₃ F O ₆	C ₁₂ H ₂₂ F O ₆	99.52		282.147	282.1479	281.1406	2.94	2.94	99.73	98.83	99.9	1
☐	C ₁₆ H ₂₃ F O ₅ S	C ₁₆ H ₂₂ F O ₅ S	98.65		282.147	282.1454	281.1381	-5.94	5.94	98.92	97.3	99.73	5
☐	C ₁₂ H ₂₇ F O ₂ S Si	C ₁₂ H ₂₆ F O ₂ S Si	97.15		282.147	282.1485	281.1412	5.18	5.18	99.17	91.76	99.58	0
☐	C ₁₆ H ₂₆ S ₂	C ₁₆ H ₂₅ S ₂	97.07		282.147	282.1476	281.1403	1.96	1.96	99.88	90.23	99.65	4

Figure S32. HR-ESIMS spectrum of compound **3**

Figure S33 Optimized geometries of **3** at the B3LYP/6–31G (d) level in methanol

Computational details. All quantum-chemical calculations have been performed at 298K on (1'*S*, 2'*R*, 4'*S*, 6'*R*) configuration of **3** by the Gaussian09 program package.¹ A system conformational analysis was employed using the MMFF94 force field via the MOE software package.²⁻³ The main resultant conformers were further optimized and checked as the true minima of potential energy surface by the density functional theory method at the 6-31G (d) basis set level. Conductor-like polarizable continuum model (CPCM) was adopted to consider solvent effects using the dielectric constant of methanol ($\epsilon = 32.6$). The 40 lowest electronic transitions were calculated and rotational strengths of each electronic excitation were given using both dipole length (R_{len}) and dipole velocity (R_{vel}) representations. The rotational strengths in R_{vel} form were converted to a Gaussian-type curve with a half-bandwidth of 0.4 eV. ECD spectrum was compared with the experimental ECD data of **3** (Figure S33).

Figure S34 Comparison of the experimental and calculated ECD spectra of **3**

Figure S35. The HPLC separation chromatogram of **4** on chiral AD-H column (5 μ m, 250 $\times$ 20 mm). Flow rate: 2.0 mL/min; solvent: iPrOH-n-hexane (25:75); detector wavelength: 254 nm; temperature 25 $^{\circ}$ C.

Figure S36. UV spectrum of compound (+)-4 in MeOH

Figure S37. UV spectrum of compound (-)-4 in MeOH

Figure S38. Structural basis for exciton-coupled circular dichroism (ECCD) spectra of (+)-4

Figure S39. Structural basis for exciton-coupled circular dichroism (ECCD) spectra of (-)-4