Supporting Information

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Studies on the Chemical Constituents from Marine Bryozoan *Cryptosula pallasiana*

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S1: Detailed extraction and isolation procedures of compounds **1**–**14**.

The fresh animals of *C. pallasiana* (20 kg), were extracted exhaustively with 95% EtOH at room temperature. The extract solution was concentrated in vacuo to yield a semi-solid (600 g), which was suspended in H_2O, and extracted with AcOEt and BuOH, and then the AcOEt extract (63 g) was partitioned between 90% MeOH and petroleum ether (1:1). The MeOH solution was adjusted to 80% MeOH and extracted with CCl_4 (1:1) to give CCl_4 extract (12.9 g). And then the MeOH solution was adjusted to 60% MeOH and extracted with CH_2Cl_2 (1:1) to afford CH_2Cl_2 extract (8.2 g). The CCl_4 extract and the CH_2Cl_2 extract were subjected to column chromatography (CC) over Sephadex LH-20 column ($CHCl_3$/MeOH, 1:1) to afford three fractions, respectively, and then the obtained six fractions were combined to yield three major fractions (Frs. A–C) based on TLC analysis. Fr. B eluted with MeOH/H_2O (10:90, 30:70, 50:50) on Reversed-phase Si gel to afford three Sub-Fractions (S-Frs. B1–B3). S-Fr. B1 was further purified by repeated CC over Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), and then with preparative HPLC (MeOH/H_2O 10:90) to yield **1** (12.1 mg), **9** (26.6 mg), **10** (30.2 mg) and **11** (14.9 mg). S-Fr. B2 was further purified by repeated CC over Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), and then with preparative HPLC (MeOH/H_2O 25:75) to afford **4** (22.1 mg), **6** (4.7 mg), **7** (16.5 mg), **8** (2.0 mg) and **12** (16.6 mg). S-Fr. B3 was subjected to repeated CC over Sephadex LH-20 ($CHCl_3$/MeOH, 1:1), and then with preparative HPLC (MeOH/H_2O 40:60) to give **2** (2.4 mg), **5** (4.8 mg), and **13** (9.0 mg). Fr. C was subjected to CC over Reversed-phase Si gel (MeOH/H_2O 55:45), and then further purified by preparative HPLC (MeOH/H_2O 40:60) to afford **3** (3.0 mg). Fr. A was subjected to CC over Reversed-phase Si gel (MeOH/H_2O 80:20), and then further purified by preparative HPLC (MeOH/H_2O 85:15) to afford **14** (13.2 mg).

S2: Spectral data of compounds **3–14**.

7-Bromo-2,4(1*H*,3*H*)-quinazolinedione (3): Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.36 (2H, *br s*, NH-1 and NH-3), 7.79 (1H, *d*, *J* = 8.4 Hz, H-5), 7.35 (1H, *d*, *J* = 1.6 Hz, H-8), 7.33 (1H, *dd*, *J* = 8.4, 1.6 Hz, H-5); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 150.1 (C-2), 162.2 (C-4), 113.6 (C-4a), 129.0 (C-5), 125.2 (C-6), 128.2 (C-7), 117.8 (C-8), 142.0 (C-8a); EI-MS *m/z*: 242/240 $[M+2]^+/[M]^+$ (100), 199/197 $[M + 2 - CO - NH]^+/[M - CO - NH]^+$ (75), 172/170 (47), 144/142 (9), 105 (15), 90 (33), 63 (56), 53 (20).

***p*-Hydroxybenzaldehyde (4)**: Colorless needle crystal (MeOH), mp 115-118 °C (dec); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 9.74 (1H, *s*, CHO), 7.76 (2H, *d*, *J* = 8.8 Hz, H-2, H-6), 6.89 (2H, *d*, *J* = 8.8 Hz, H-3, H-5); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 190.9 (CHO), 166.2 (C-4), 133.1 (C-2, C-6), 129.3 (C-1), 117.3 (C-3, C-5); EI-MS *m/z* (rel. int.): 121 $[M]^+$ (100), 93 (53), 74 (9), 65 (52).

Methylparaben (5): Colorless needle crystal (MeOH), mp 128-130 °C (dec); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 8.86 (2H, *d*, *J* = 8.8 Hz, H-2, H-6), 6.81 (2H, *d*, *J* = 8.8 Hz, H-3, H-5), 3.84 (3H, *s*, OCH_3); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 168.1 (CO), 163.5 (C-4), 132.8 (C-2, C-6), 122.2 (C-1), 116.1 (C-3, C-5), 52.2 (OCH_3); EI-MS *m/z* (rel. int.): 152 $[M]^+$ (56), 121 (100), 93 (34), 65 (34), 54 (10).

Benzamide) (6): White amorphous powder; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 7.96 (1H, *br s*, NH), 7.87 (2H, *d*, *J* = 7.3 Hz, H-2, H-6), 7.52 (1H, *t*, *J* = 7.2 Hz, H-4), 7.45 (1H, *t*, *J* = 7.2 Hz, H-3, H-5), 7.35 (1H, *br s*, NH); ^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 134.3 (C-1), 127.4 (C-2, C-6), 128.2 (C-3, C-5), 131.2 (C-4), 167.8 (CO); EI-MS *m/z*: 121 $[M]^+$ (20), 71 (29), 62 (100), 44 (100); ESI-MS (+) *m/z*: 144 $[M + Na]^+$, 265 $[2M + Na]^+$.

Phenylacetamide (7): White amorphous powder; ^{1}H-NMR (CD_3OD, 500 MHz) δ: 7.29 (4H, *dd*, *J* = 7.3, 2.6 Hz, H-2 or H-6, H-3, H-4, H-5), 7.23 (1H, *m*, H-2 or H-6), 3.30 (2H, *m*, CH_2); ^{13}C-NMR (CD_3OD, 125 MHz) δ: 136.9 (C-1), 130.1 (C-2, C-6), 129.6 (C-3, C-5), 127.9 (C-4), 43.4 (CH_2), 177.0 (CO); EI-MS *m/z*: 135 $[M]^+$ (39), 91 (100), 65 (39), 52 (13), 45 (31); ESI-MS (+) *m/z*: 158 $[M + Na]^+$, 293.13 $[2M + Na]^+$.

4(3*H*)-Quinazolinon (8): White amorphous powder; mp 215-217 °C (dec); ^{1}H-NMR (CD_3OD, 500 MHz): δ: 8.23 (1H, *d*, *J* = 8.0 Hz, H-5), 8.10 (1H, *s*, H-2), 7.84 (1H, *t*, *J* = 7.5 Hz, H-7), 7.70 (1H, *d*, *J* = 8.0 Hz, H-8), 7.56 (1H, *d*, *J* = 7.6 Hz, H-6); EI-MS *m/z* (rel. int.):

146 $[M]^+$ (100), 118 $[M - CO]^+$ (42), 103 $[M - CO - NH]^+$ (5), 90 (29), 76 (16), 62 (28), 51 (18), 44 (26).

Thymine (9): Light Yellow solid; mp 315-317 °C (dec); ^{1}H-NMR (CD_3OD, 500 MHz) δ: 7.21 (1H, *s*, H-6), 1.84 (3H, *s*, H_3-5); ^{13}C-NMR (CD_3OD, 125 MHz) δ: 153.8 (C-2), 167.5 (C-4), 110.4 (C-5), 139.2 (C-6), 12.1 (5-CH_3).

Uracil (10): Light Yellow solid; mp 333-335 °C (dec);n^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 10.91 (2H, *s*, NH), 7.49 (1H, *d*, *J* = 7.6 Hz, H-6), 5.45 (1H, *d*, *J* = 7.6 Hz, H-5); ^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 151.6 (C-2), 164.4 (C-4), 142.2 (C-5), 100.2 (C-6).

Hypoxanthine (11): Light Yellow solid; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 12.57 (1H, *br s*, NH), 8.10 (1H, *s*, H-2), 7.97 (1H, *s*, H-8), 7.28 (1H, *br. s*, OH); ^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 144.6 (C-2), 158.3 (C-4), 119.3 (C-5), 155.5 (C-6), 140.4 (C-8); EI-MS *m/z*: 136 $[M]^+$ (100), 109 (11), 81 (21), 66 (7), 54 (42).

Tryptophan (12): White amorphous powder; mp 287-290 °C (dec); ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 11.04 (1H, *s*, COOH), 7.57 (1H, *d*, *J* = 7.8 Hz, H-4), 7.35 (1H, *d*, *J* = 8.1 Hz, H-7), 7.25 (1H, *s*, H-2), 7.05 (1H, *t*, 7.4 Hz, H-6), 6.96 (1H, *t*, *J* = 7.5 Hz, H-5), 3.53 (1H, *m*, H-2'), 3.32 (1H, *d*, *J* = 13.1 Hz, H-1a'), 3.02 (1H, *dd*, *J* = 14.1, 8.7 Hz, H-1b'); ^{13}C-NMR (DMSO-d_6, 125 MHz) δ: 124.2 (C-2), 109.5 (C-3), 118.3 (C-4), 118.4 (C-5), 120.9 (C-6), 111.4 (C-7), 127.3 (C-3a), 136.4 (C-7a), 27.2 (C-1'), 54.7 (C-2'), 171.0 (C-3').

Glycerine (13): Colorless viscous liquid; ^{1}H-NMR (CD_3OD, 500 MHz) δ: 3.64 (1H, *m*), 3.58 (2H, *dd*, *J* = 11.2, 4.9 Hz), 3.51 (2H, *dd*, *J* = 11.2, 6.0 Hz); ^{13}C-NMR (CD_3OD, 125 MHz) δ: 73.8 (*d*, C-2), 64.4 (*t*, C-1, C-3).

Monoheneicosanoin (14): White amorphous powder; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.20 (1H, *dd*, *J* = 12.0, 5.0 Hz, H-1a), 4.15 (1H, *dd*, *J* = 11.5, 5.5 Hz, H-1b), 3.93 (1H, *m*, H-2), 3.69 (1H, *dd*, *J* = 11.5, 6.0 Hz, H-3a), 3.59 (1H, *dd*, *J* = 11.5, 6.0 Hz, H-3b), 2.35 (1H, *t*, *J* = 7.5 Hz, H-2'), 1.63 (2H, *m*, H-3'), 1.33 (34H, *br s*, H-4' − H-20'), 0.88 (3H, *t*, *J* = 7.0 Hz, H-21); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 174.5 (C-1'), 70.4 (C-2), 65.3 (C-1), 63.5 (C-3), 34.3 (C-2'), 32.1 (C-19'), 29.3-29.8 (C-4' − C-18'), 25.1 (C-20'), 14.3 (C-21'); EI-MS *m/z* (rel. int.): 400 $[M]^+$ (25), 382 $[M - H_2O]^+$ (35), 369 $[M - CH_2OH]^+$ (36), 359 (34), 341 (92), 327 (38), 313 (9), 298 (15), 285 (32), 267 (95), 241 (14), 213 (17), 185 (24), 161 (21), 140 (29), 134 (36), 129 (36), 112 (39), 98 (58), 83 (48), 69 (63), 57 (92), 43 (100).

S3: HR-ESI-MS (positive) spectrum of compound **1**

Elemental Composition Report **Page 1**

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Selected filters: None

Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 5-10 H: 5-20 O: 1-8 Na: 1-1 S: 1-1

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XR-3 M.W=186
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YA019
17-May-2010,13:53:18
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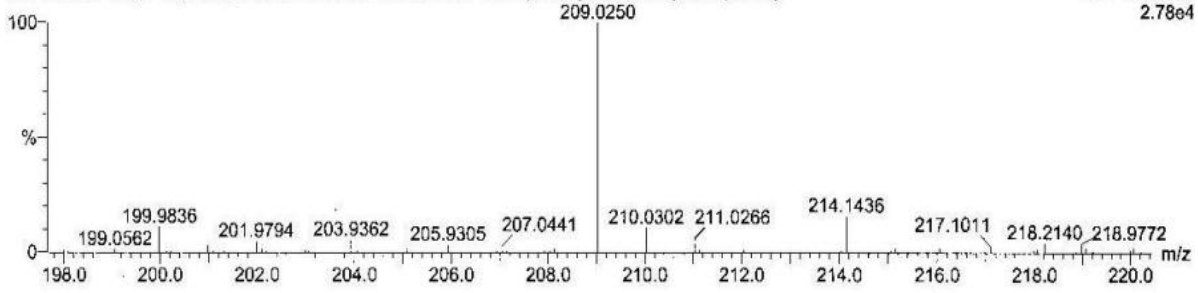
TOF MS ES+
2.78e4



Minimum:	35.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
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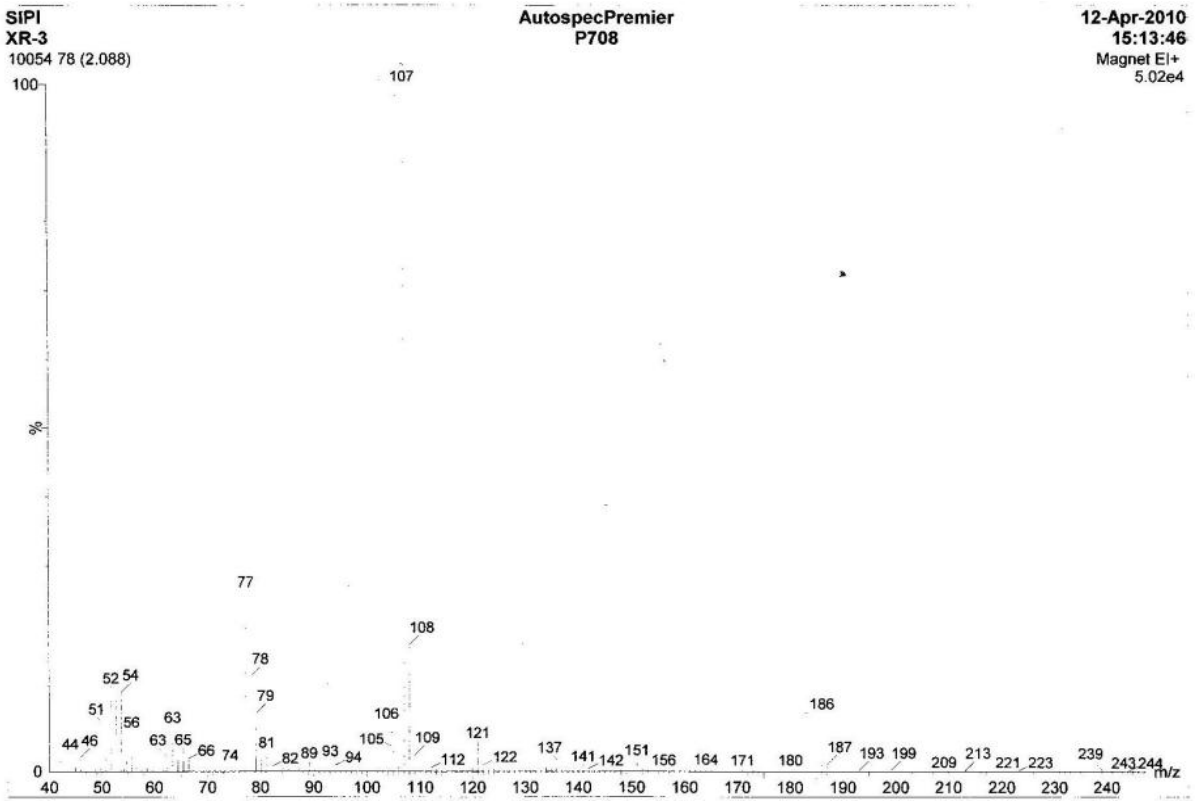
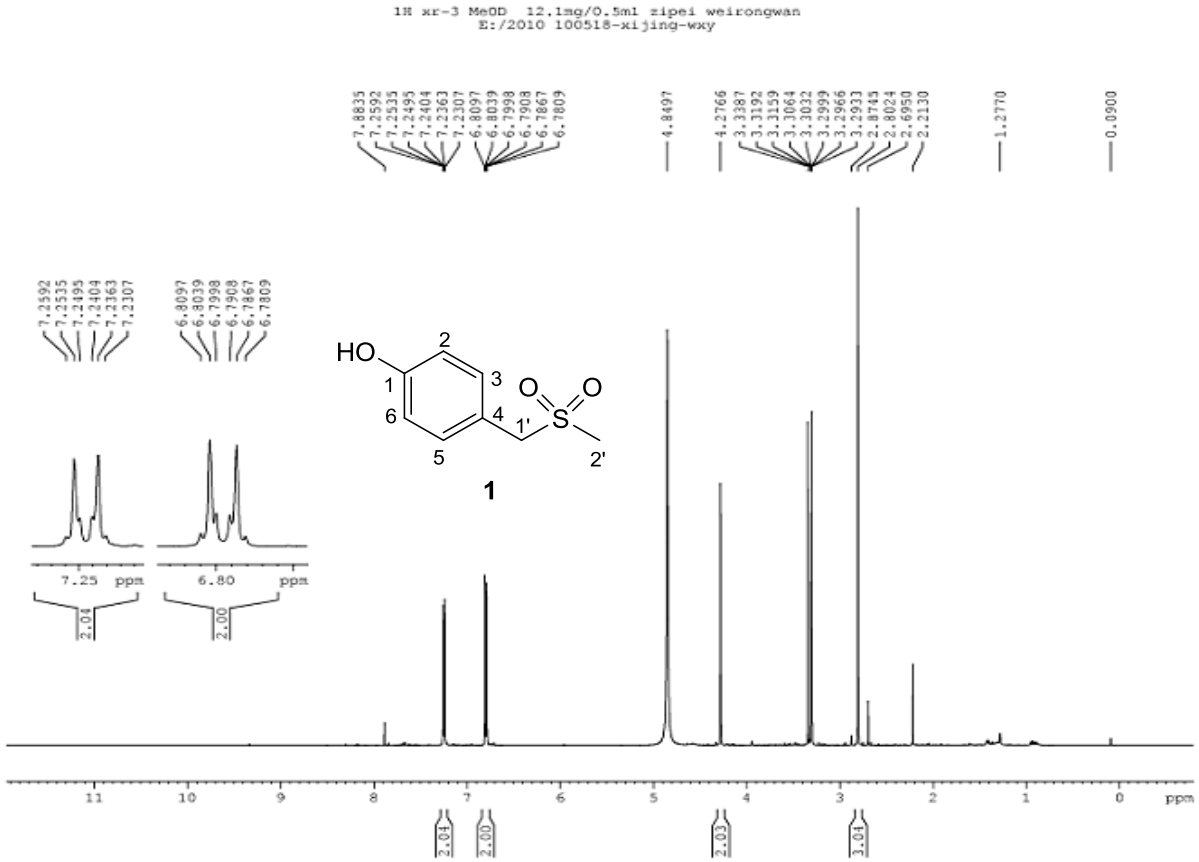
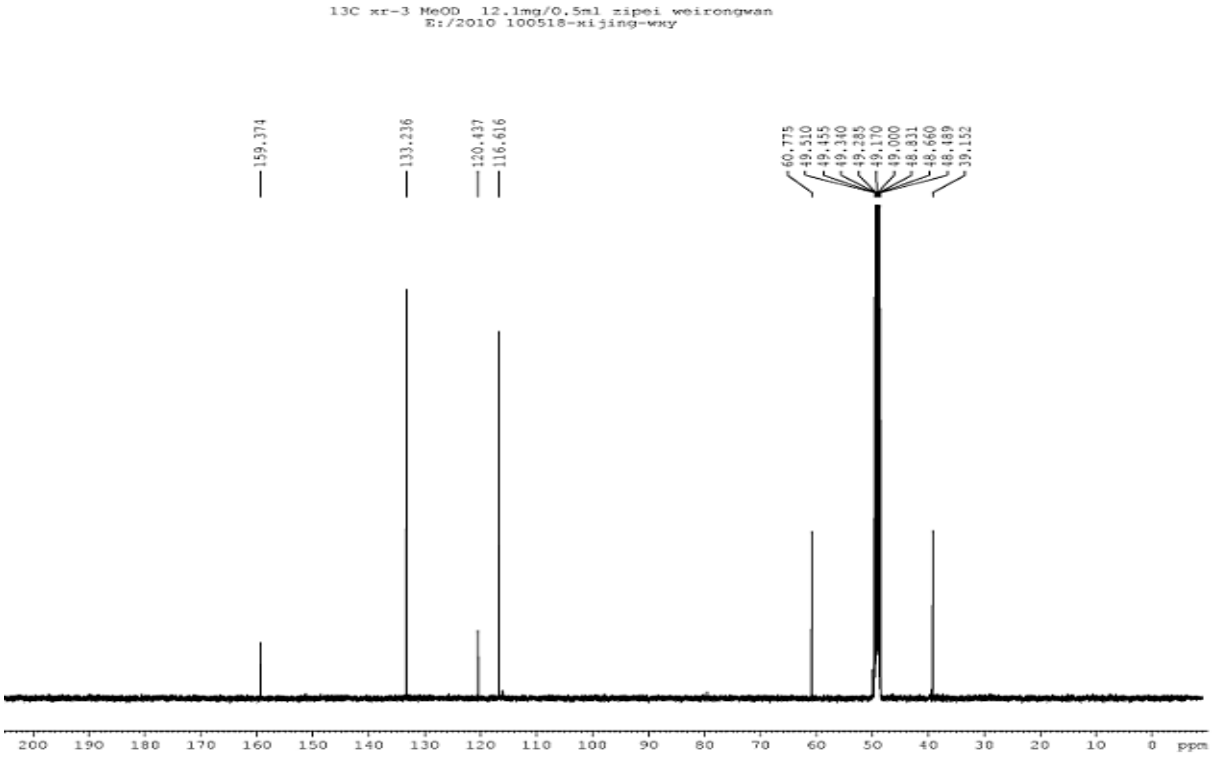
S4: EI-MS spectrum of compound **1**



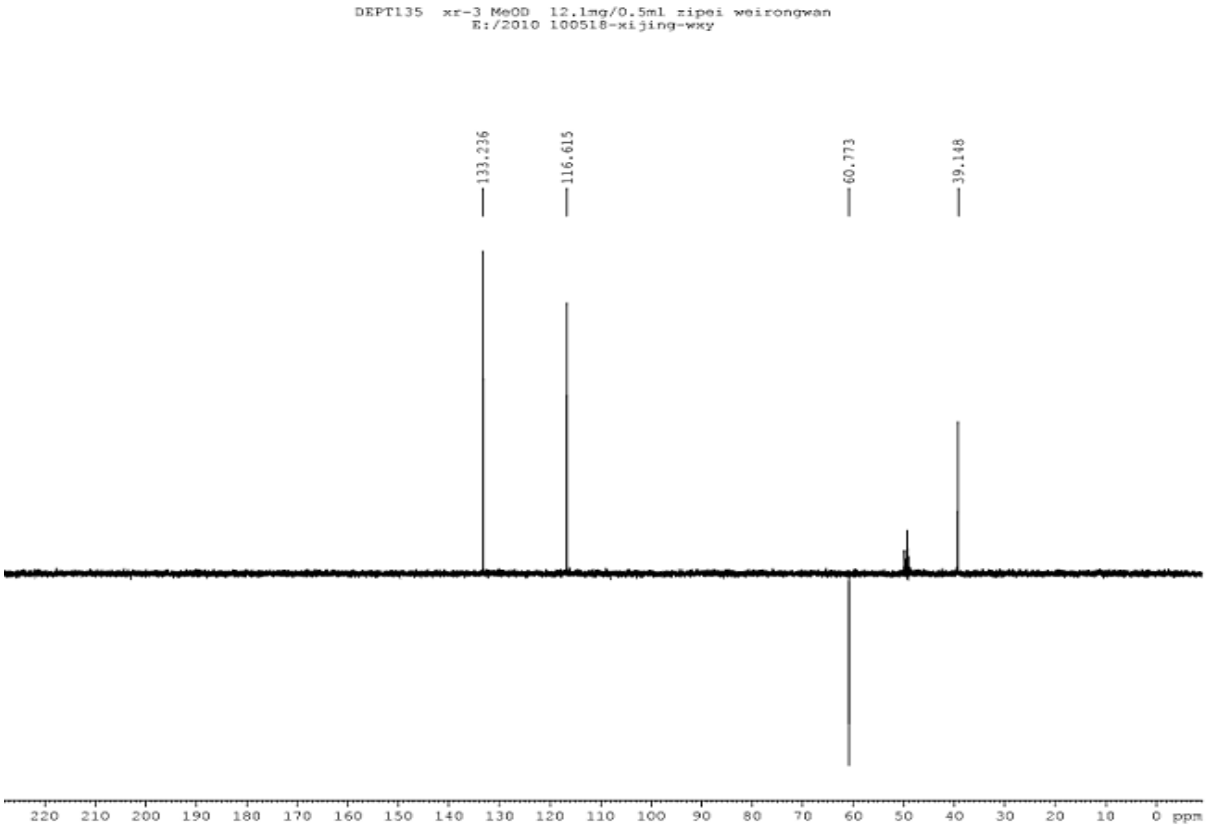
S5: ^{1}H-NMR (500 MHz, CD_3OD_3) spectrum of compound **1**



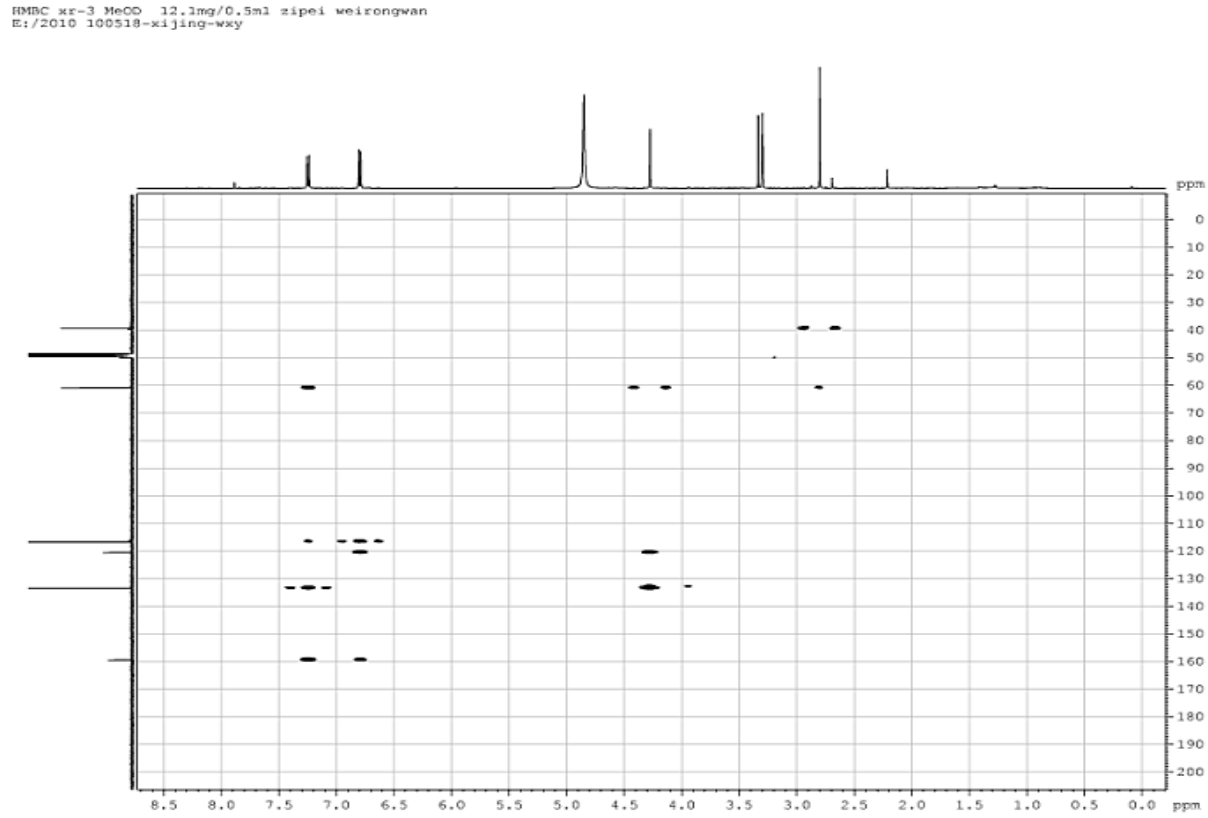
S6: ^{13}C-NMR (125 MHz, CD_3OD_3) spectrum of compound **1**



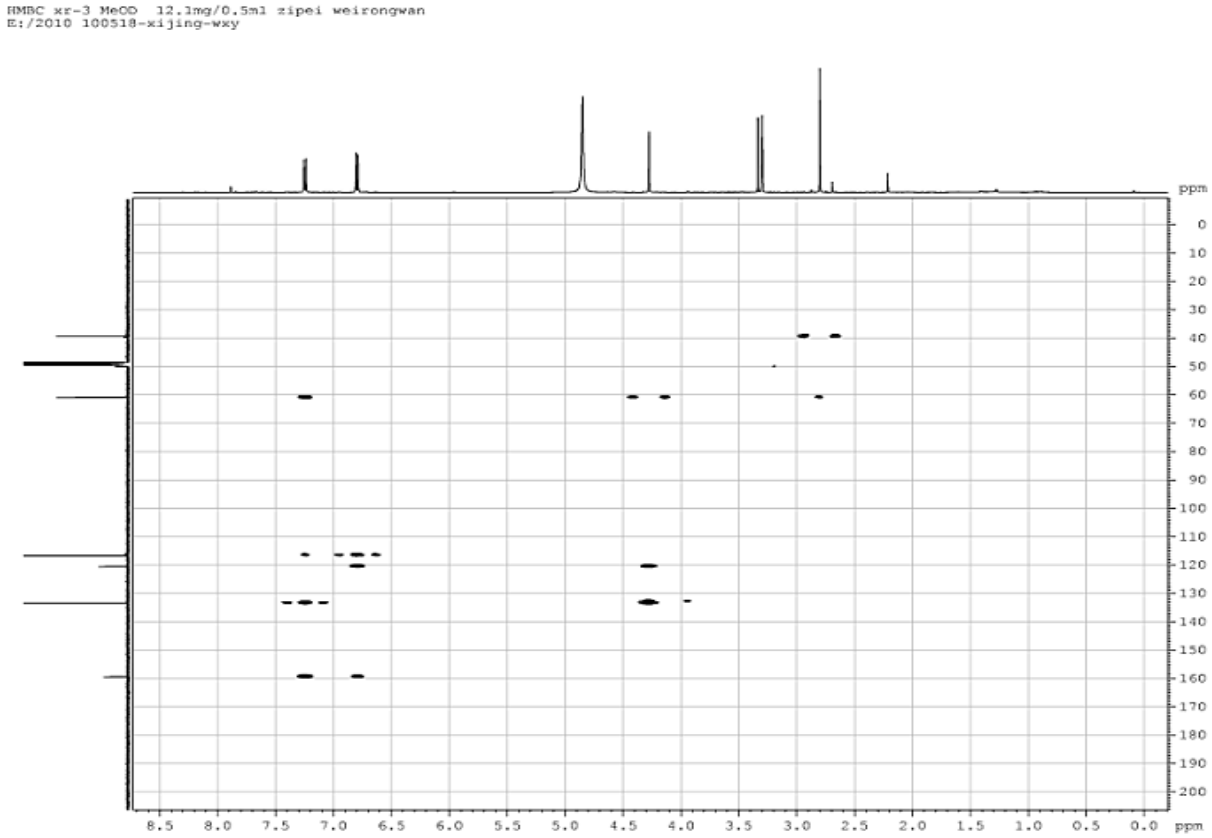
S7: DEPT135 spectrum of compound **1**



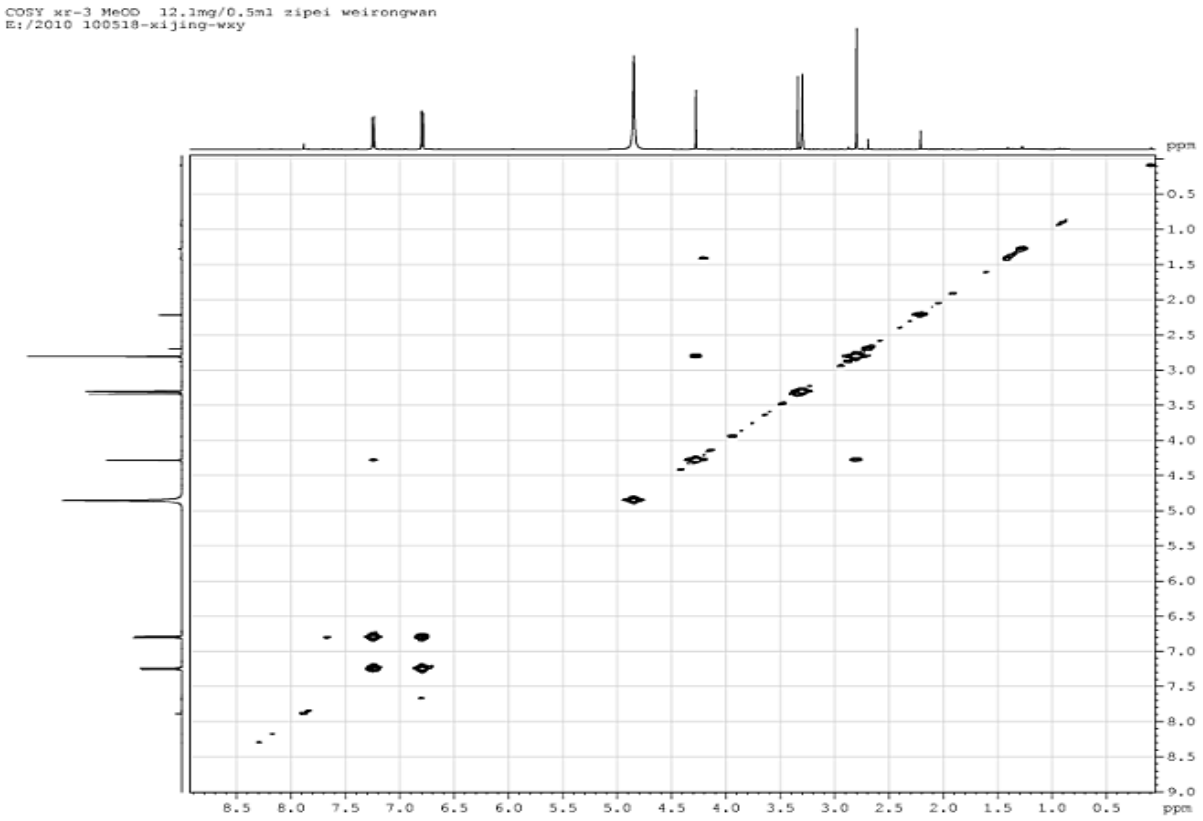
S8: HSQC spectrum of compound **1**



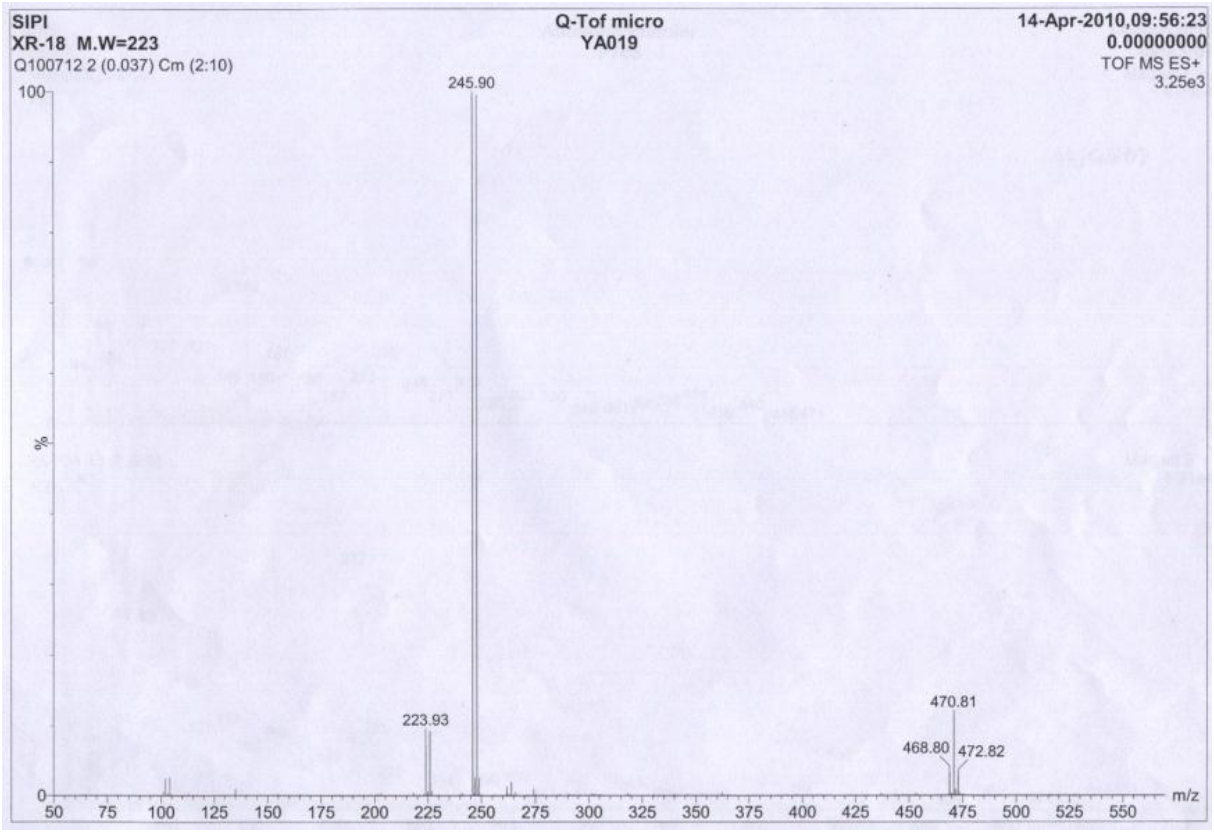
S9: HMBC spectrum of compound **1**



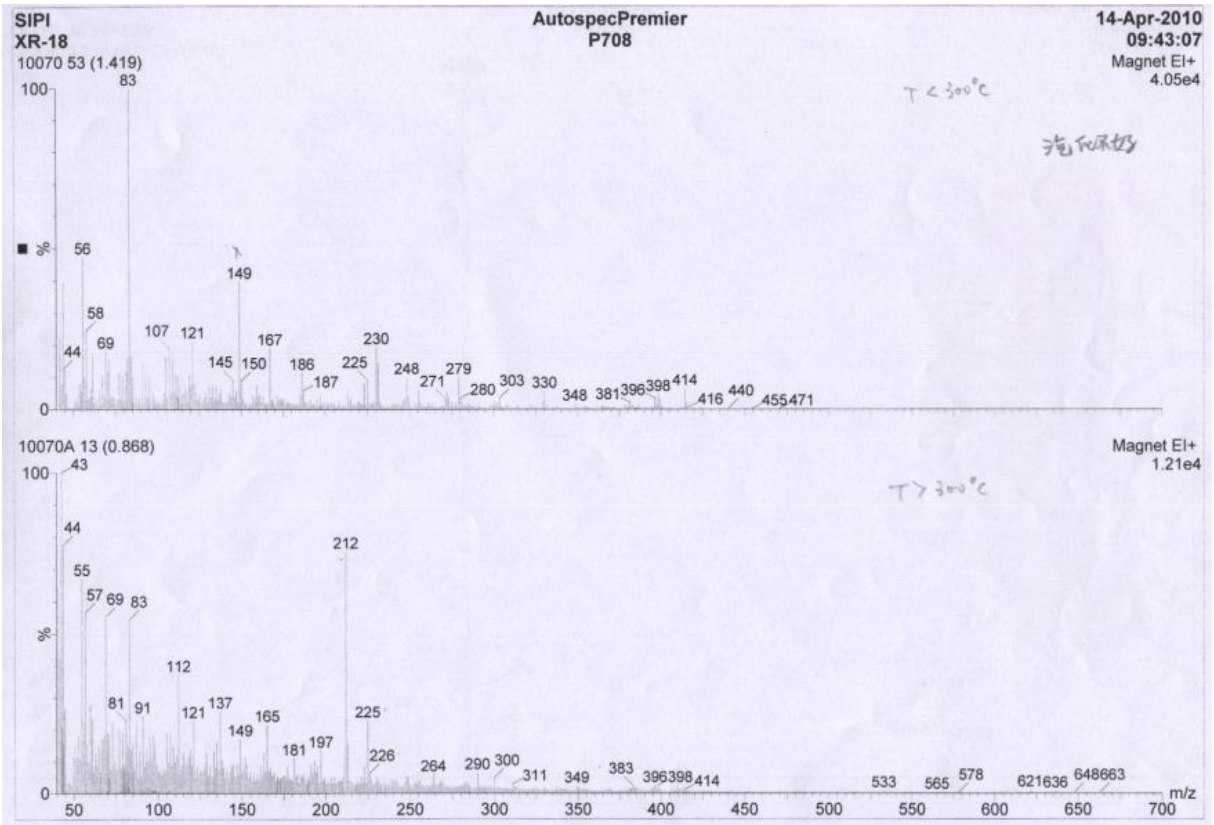
S10: ^{1}H-^{1}H COSY spectrum of compound **1**



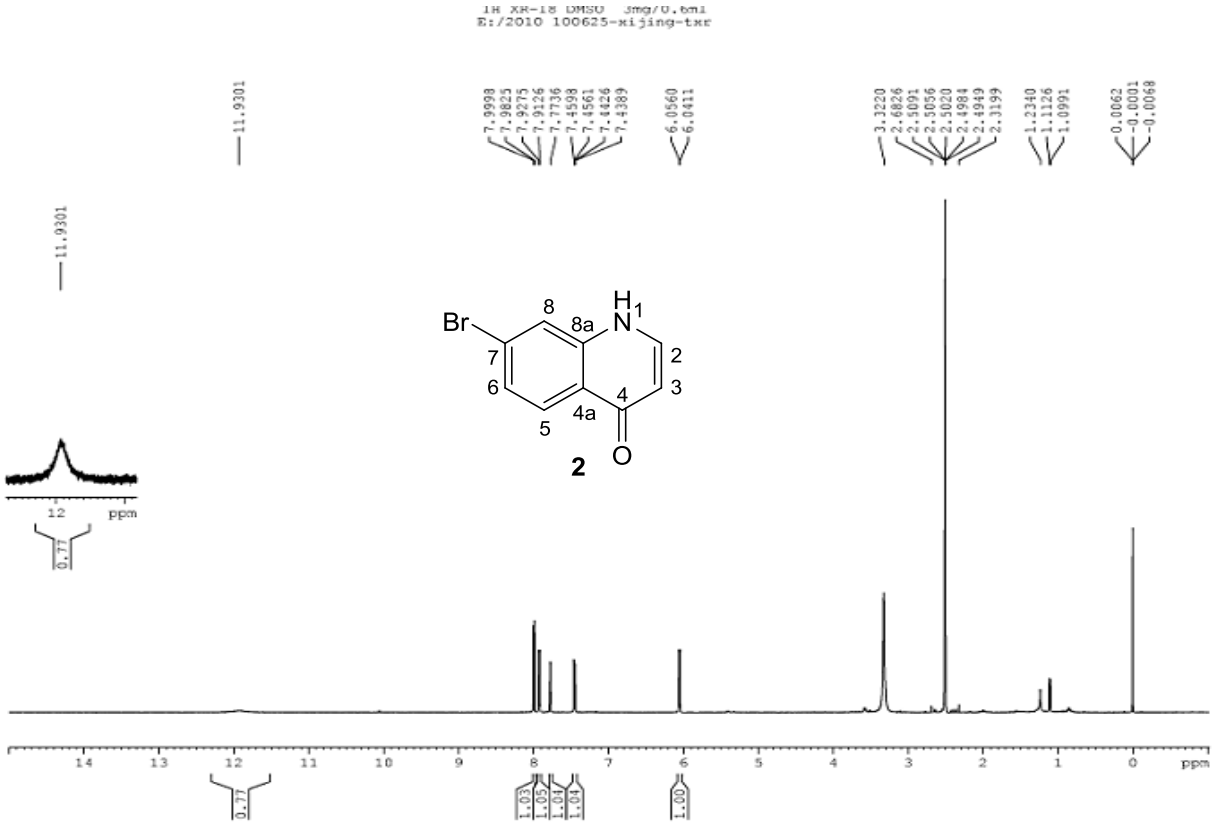
S11: ESI-MS (positive) spectrum of compound **2**



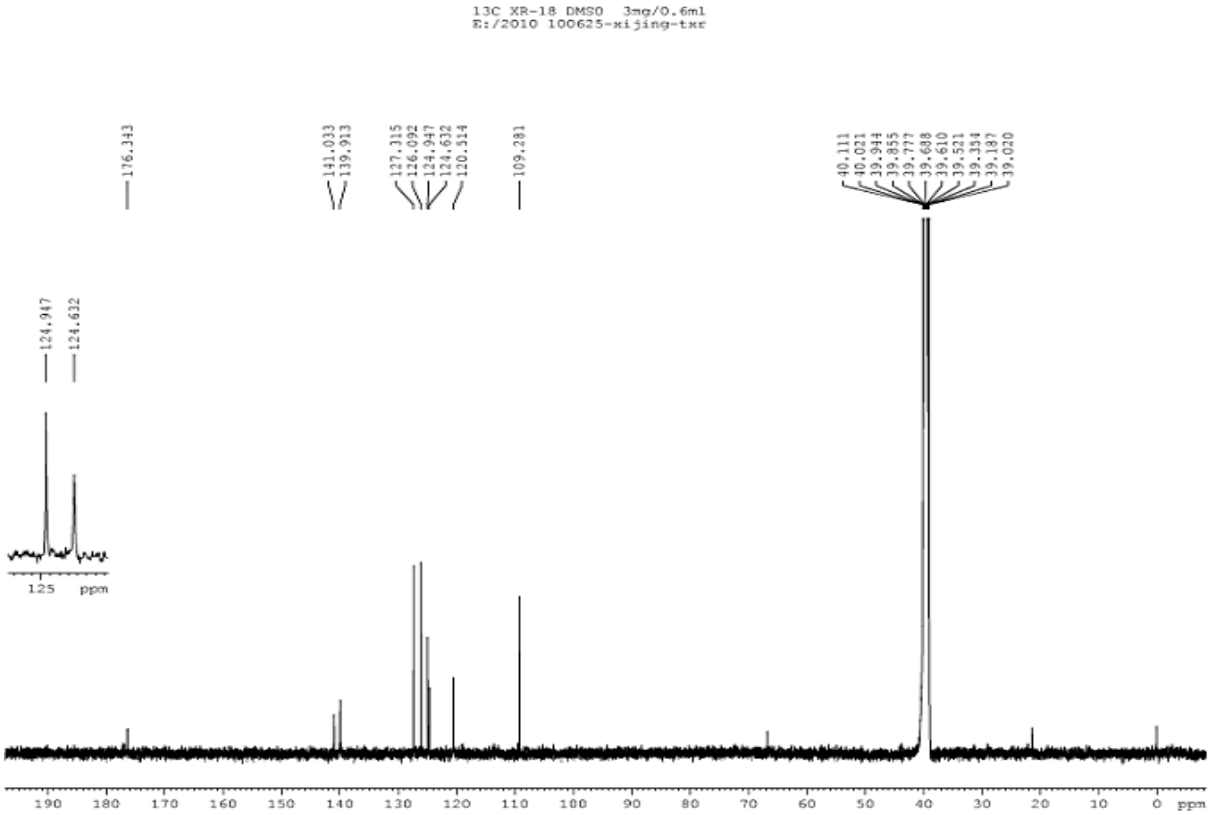
S12: EI-MS spectrum of compound **2**



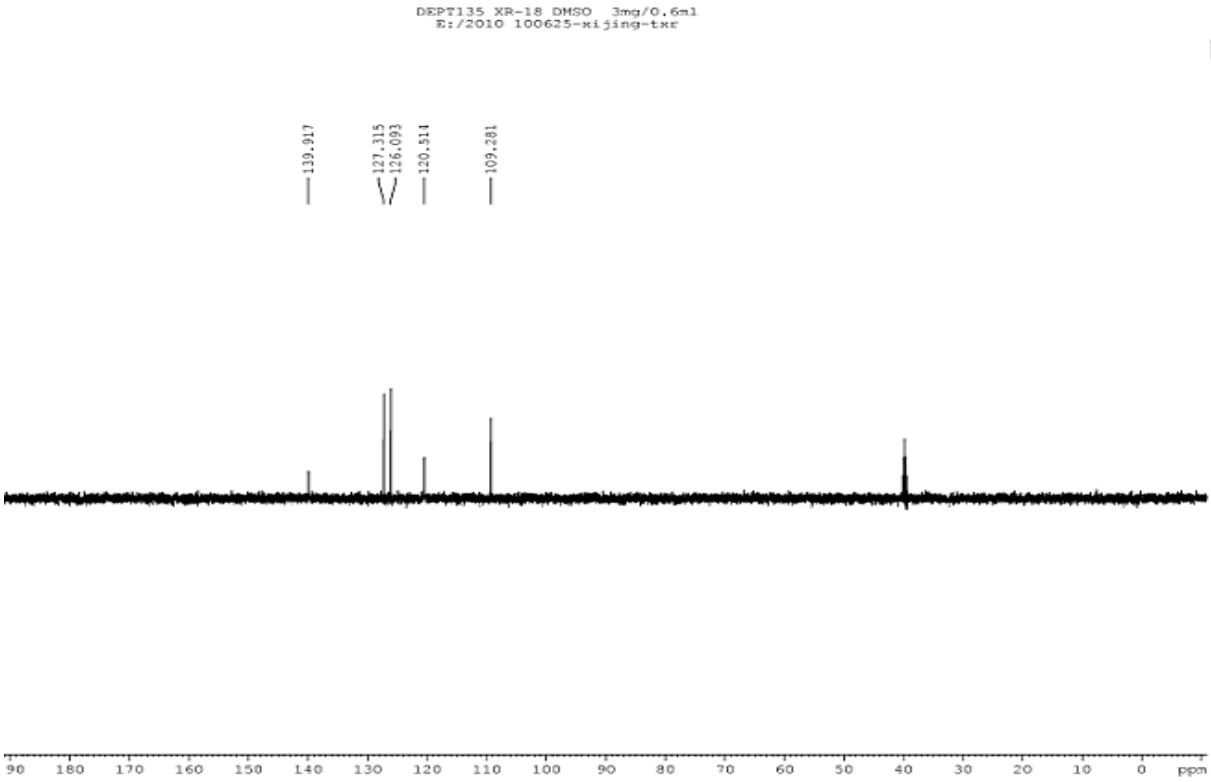
S13: ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of compound **2**



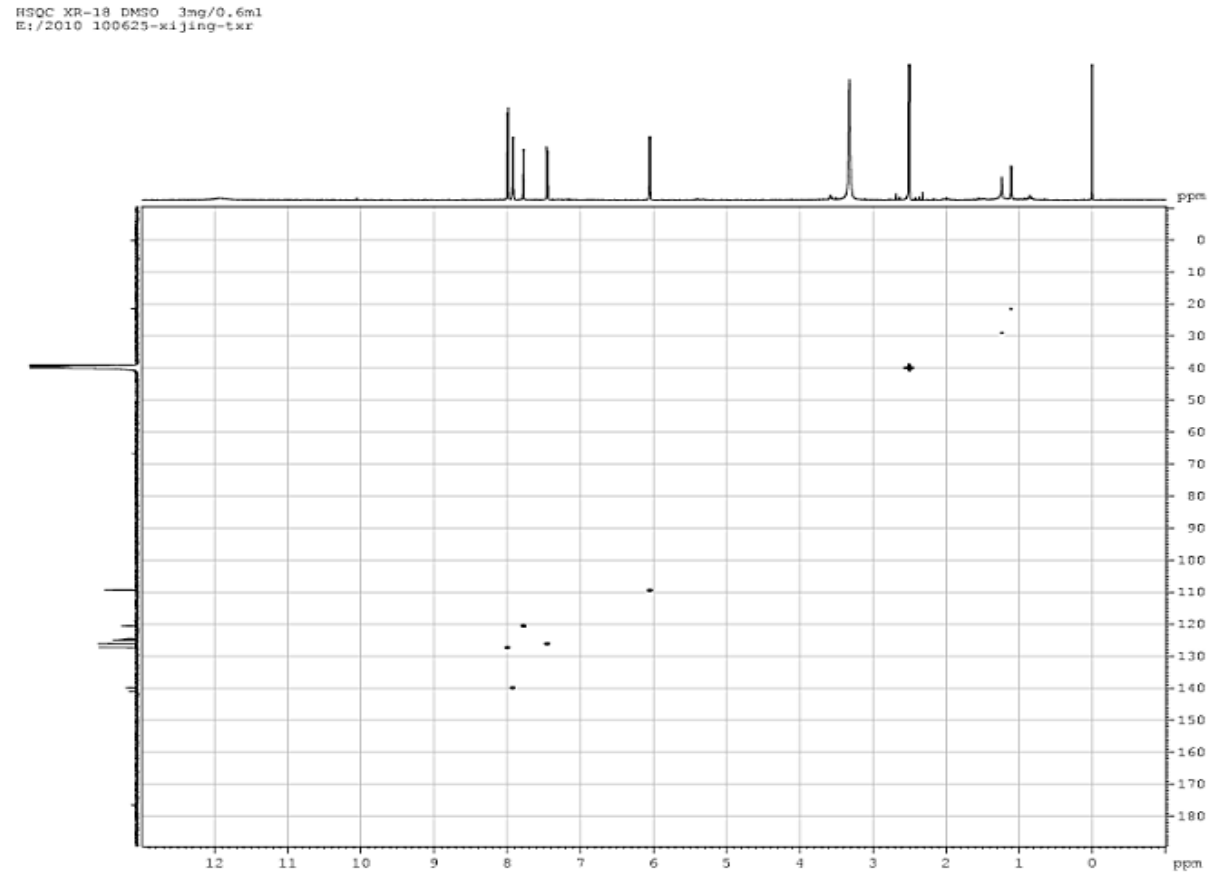
S14: ^{13}C-NMR (125 MHz, DMSO-d_6) spectrum of compound **2**



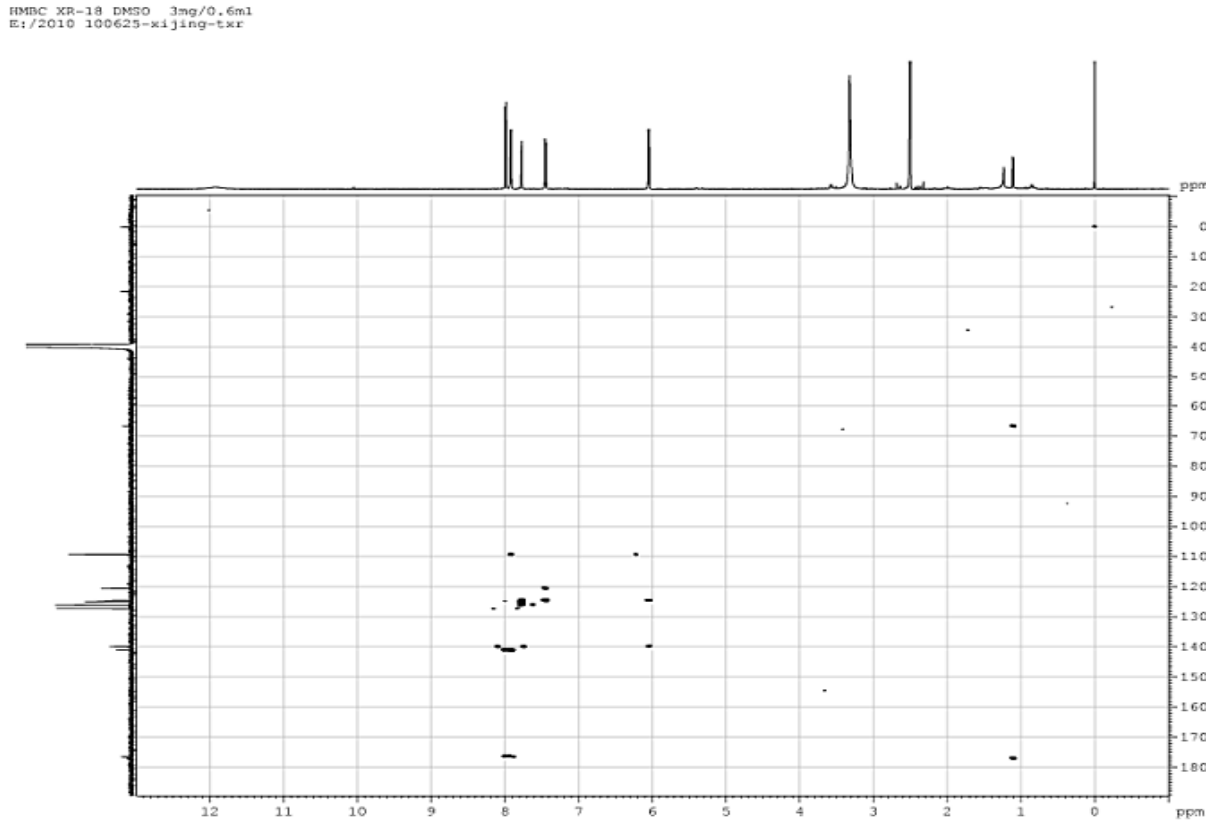
S15: DEPT135 spectrum of compound **2**



S16: HSQC spectrum of compound **2**



S17: HMBC spectrum of compound **2**



S18: ^{1}H-^{1}H COSY spectrum of compound **2**