Discovery and Targeted Isolation of Phenylpropanoid-Substituted Ester-Catechins (PSECs) Using Molecular Networks based on UPLC-Q/TOF-HRMS: Implication of Reaction Mechanism among Polyphenols during Green Tea Processing

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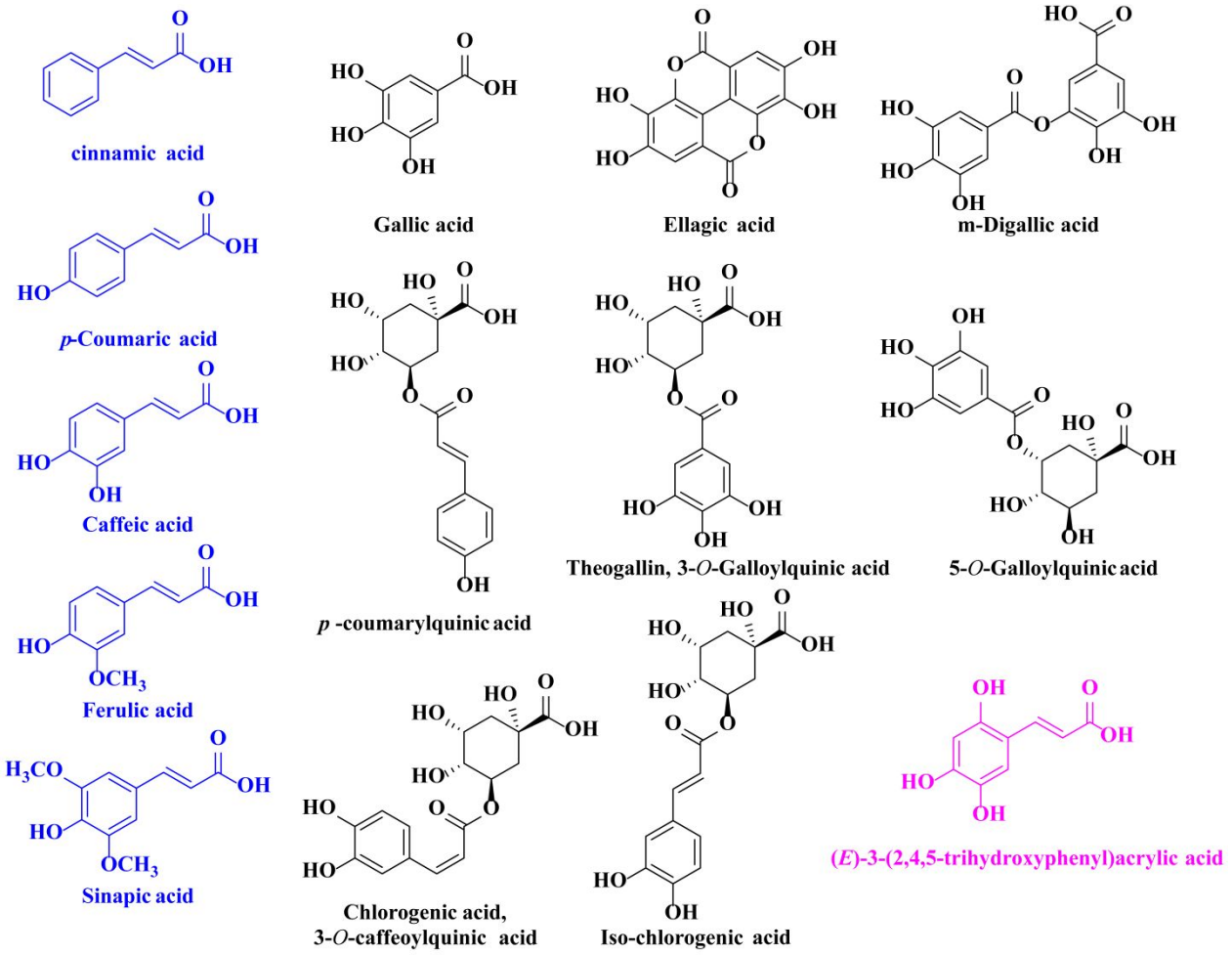
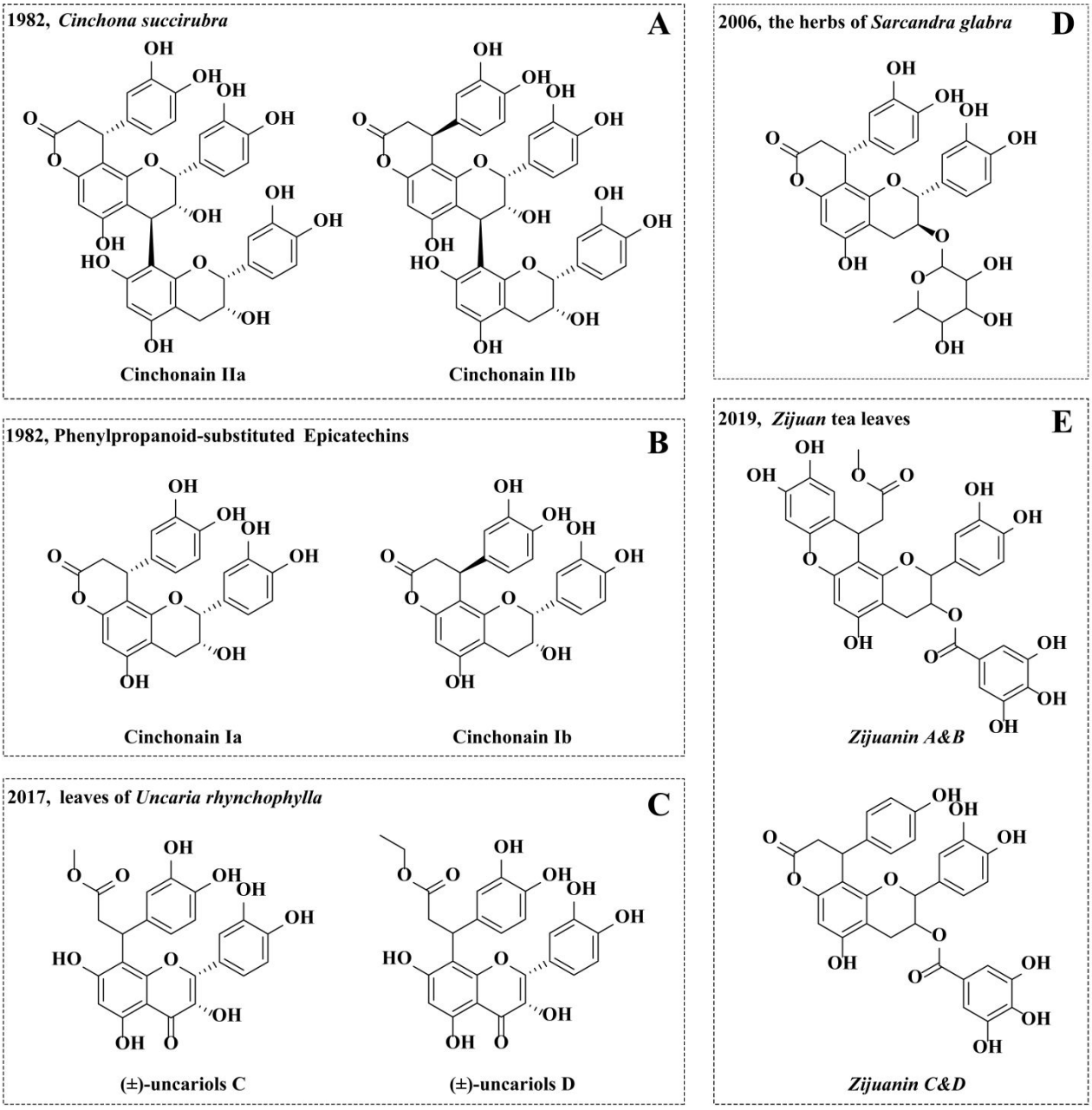
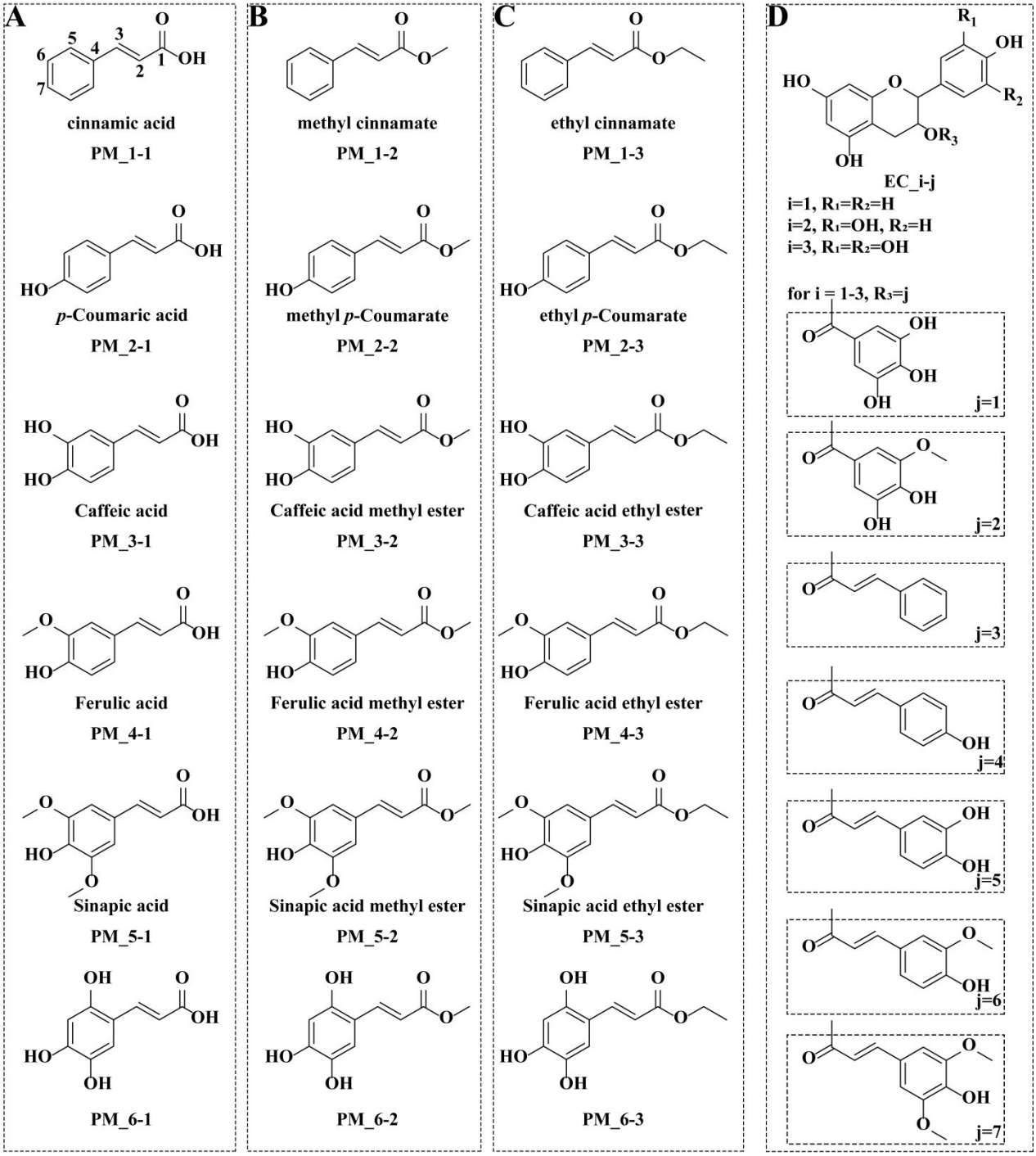
SI. Table 2. The MW of PSECs with type B combination form.
SI. Table 3. The MW of PSECs with type C combination form.
SI. Table 4. The MW of PSECs with type D combination form.
SI. Table 5. Different elution methods used in the pre-separation process.
SI. Table 6. The corresponding relationship between sample fractions and elution methods in the pre-separation process.
SI. Table 7. Tea products used for the detection of PSECs.
SI. Table 8. Tea fresh leaves used for the detection of PSECs.
SI. Table 9. The precursor ions' response intensity of the two PSECs molecules in 18 tea products.



SI. Figure 1. Phenolic acids in tea.



SI. Figure 2. The conjugates of phenolic acids with sub-class of flavonoids such as proanthocyanidins (A), flavan-3-ols (B), flavonols (C), flavanol-glycoside (D), epicatechin gallate (E).



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108 **SI. Figure 3.** The substrates source of hypothesized phenylpropanoids substituted flavan-3-ols
109 derivatives. The active phenolic acids (A) with corresponding methyl esterification structures (B)
110 and ethyl esterification structures (C), which may combine with specific flavan-3-ols derivatives (D)
111 to form varieties of PSECs.

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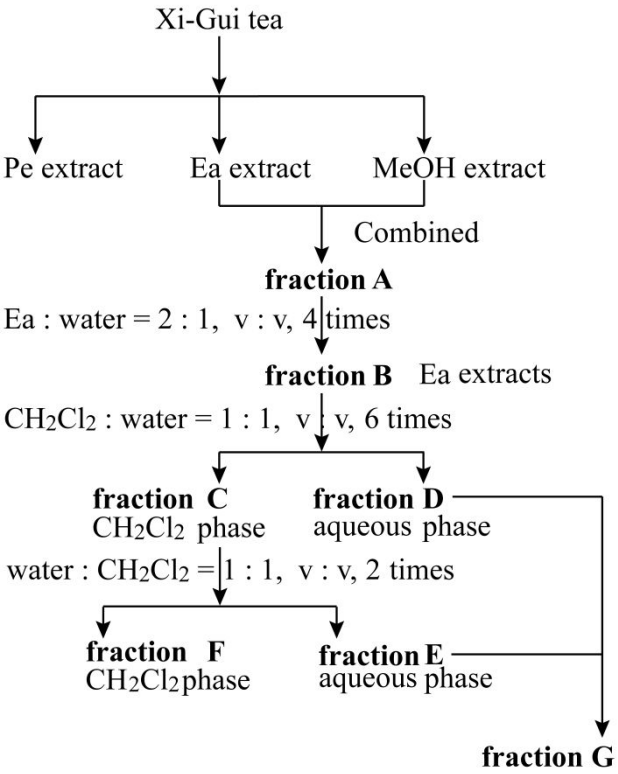
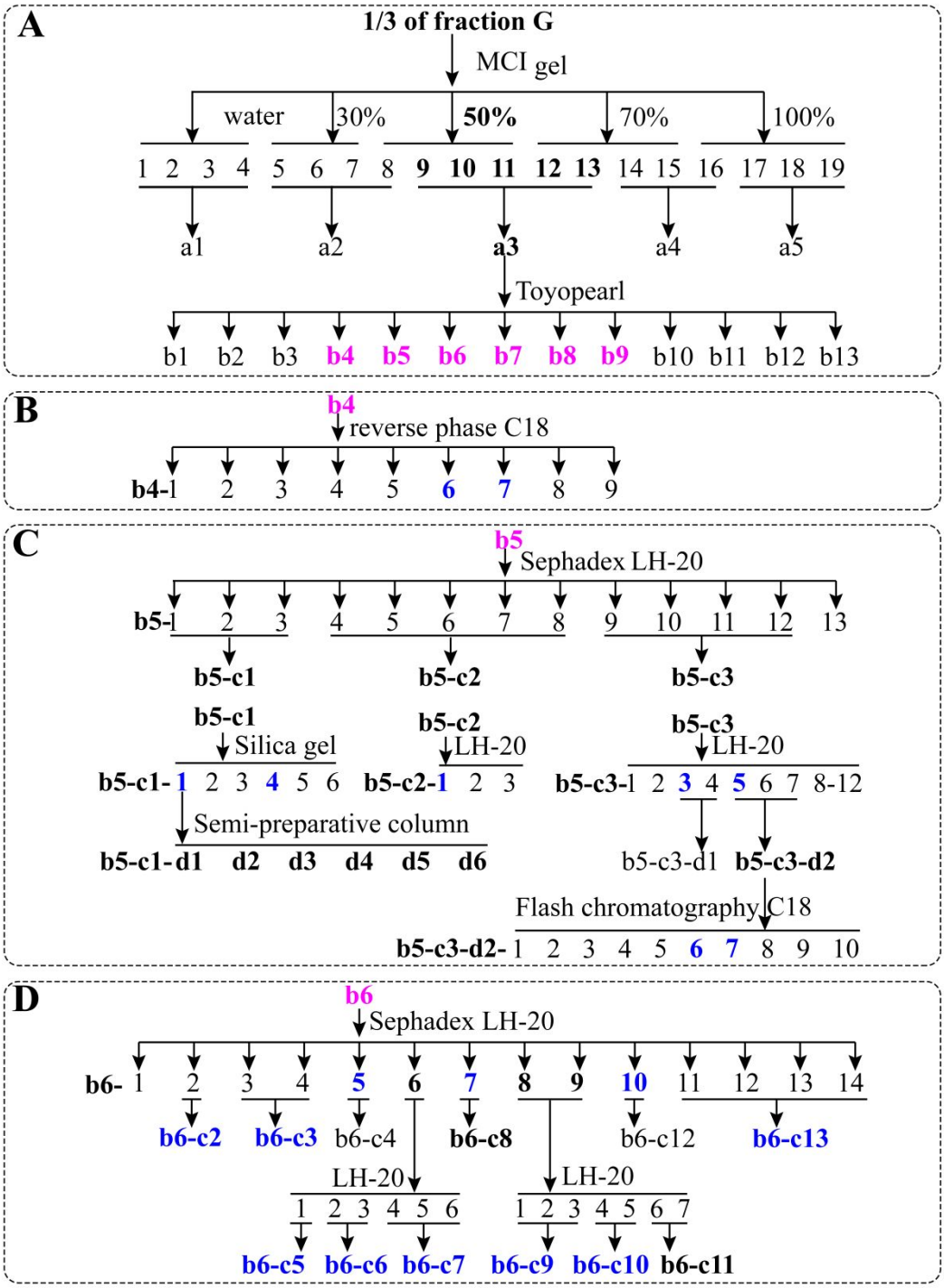
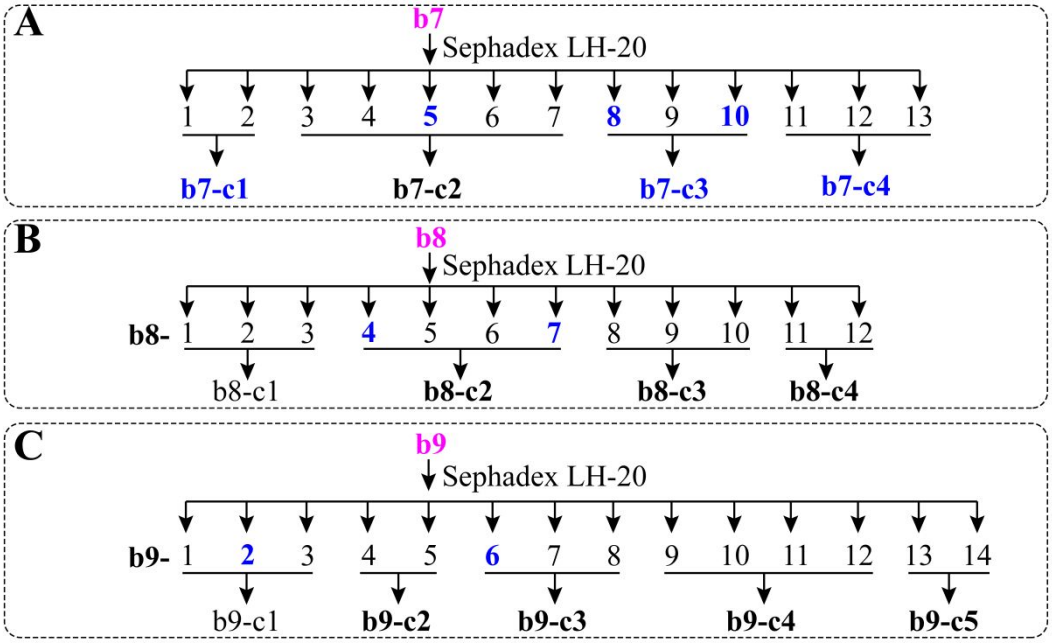


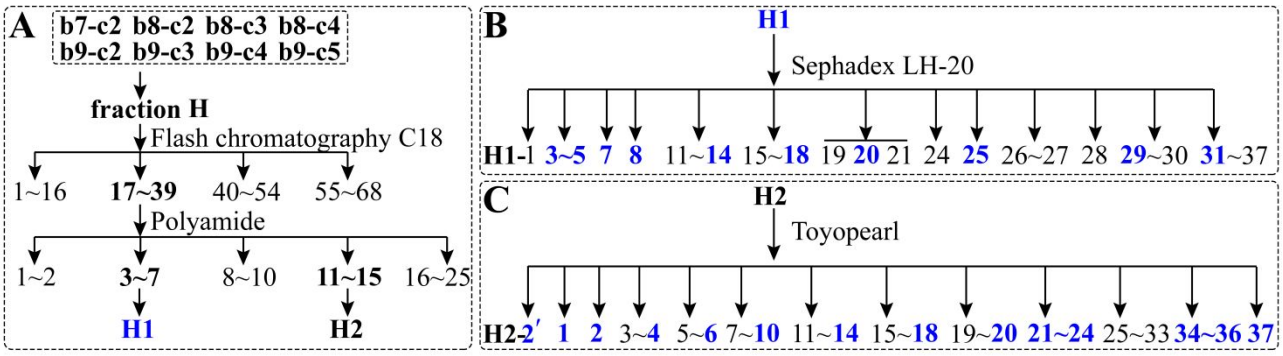
SI. Figure 4. Pre-processing of Xi-Gui tea extracts. The fraction A was first concentrated to remove MeOH as more as possible, then distributed in Ea: water = 2:1 (v:v, as a total of about 25 L) for four times to obtain Ea fractions (fraction B). The fraction B was then concentrated to viscous and then redissolved in CH_2Cl_2: water = 1:1 (v:v, as a total of about 20 L) for six times to obtained CH_2Cl_2 fraction (fraction C) and the aqueous phase (fraction D). The fraction C was then dissolved by water: CH_2Cl_2 = 1:1 (v:v) to give fraction E, which was then merged with fraction D to obtain fraction G (viscous, about 2000 g)



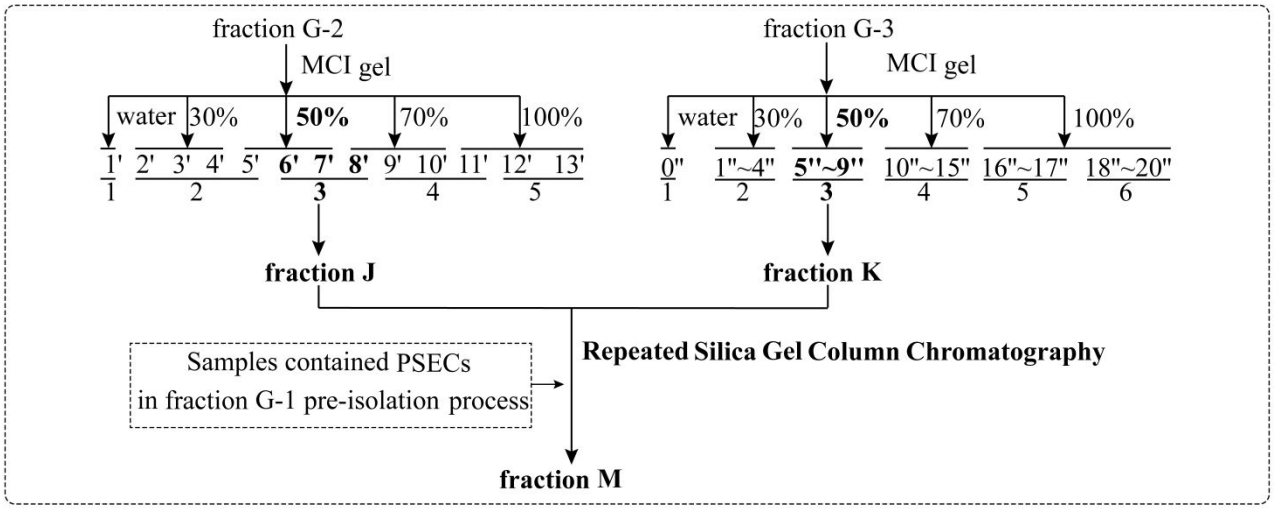
SI. Figure 5. Pre-separation of fraction G (b4–b6). The elution methods were widely used on open column chromatography that water : MeOH system from 0 to 100 with gradually increasing the ratio of MeOH in MCI, Sephadex LH-20, Toyopearl HW-40F, polyamide, and reverse-phase C18 columns, and organic solvent system from Pe: Ea to CH_2Cl_2: MeOH with gradually increasing mixed solvent polarity in silica gel column, if not otherwise specified.



SI. Figure 6. Pre-separation of fraction G (b7–b9).



SI. Figure 7. Pre-separation of fraction G (fractions from b7–b9).



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137 **SI. Figure 8.** Pre-processing of fractions G-2, 3 for enriching PSECs fractions.

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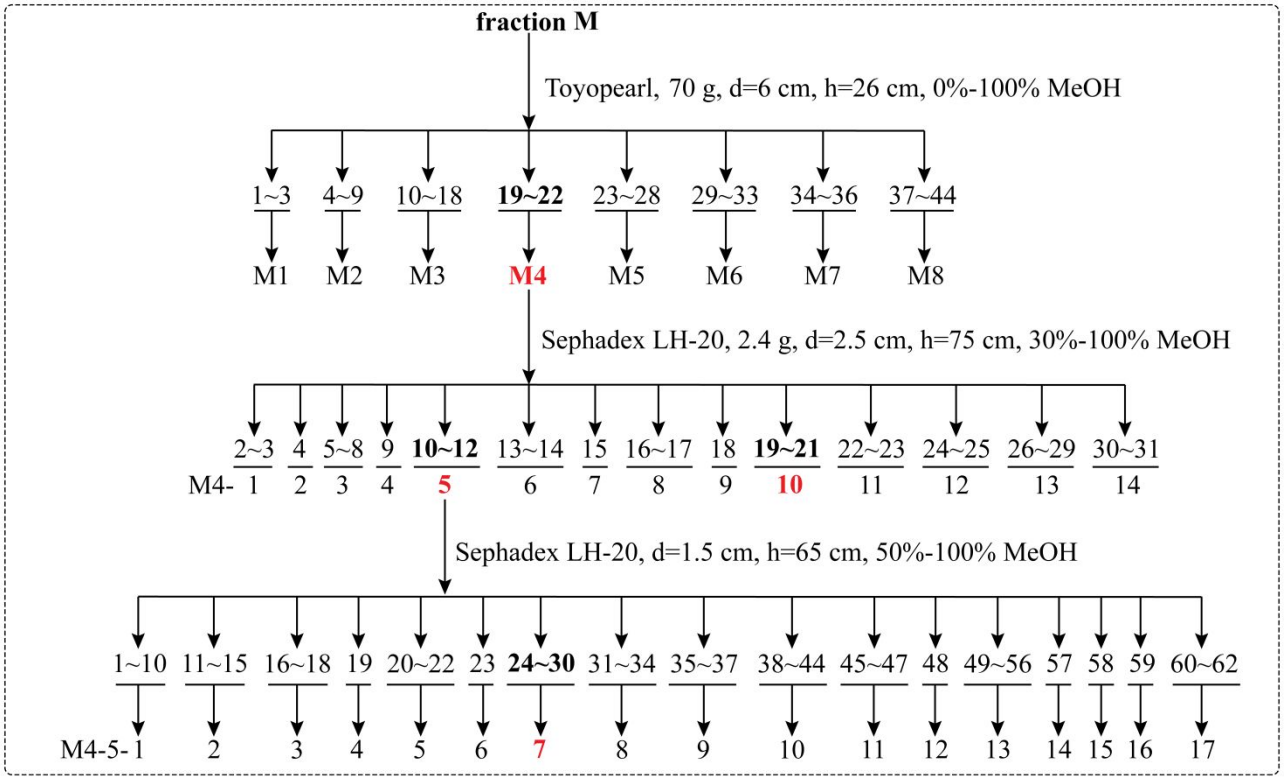

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142 **SI. Figure 9.** Isolation of compounds 1, 2 from enriched PSECs fraction M.

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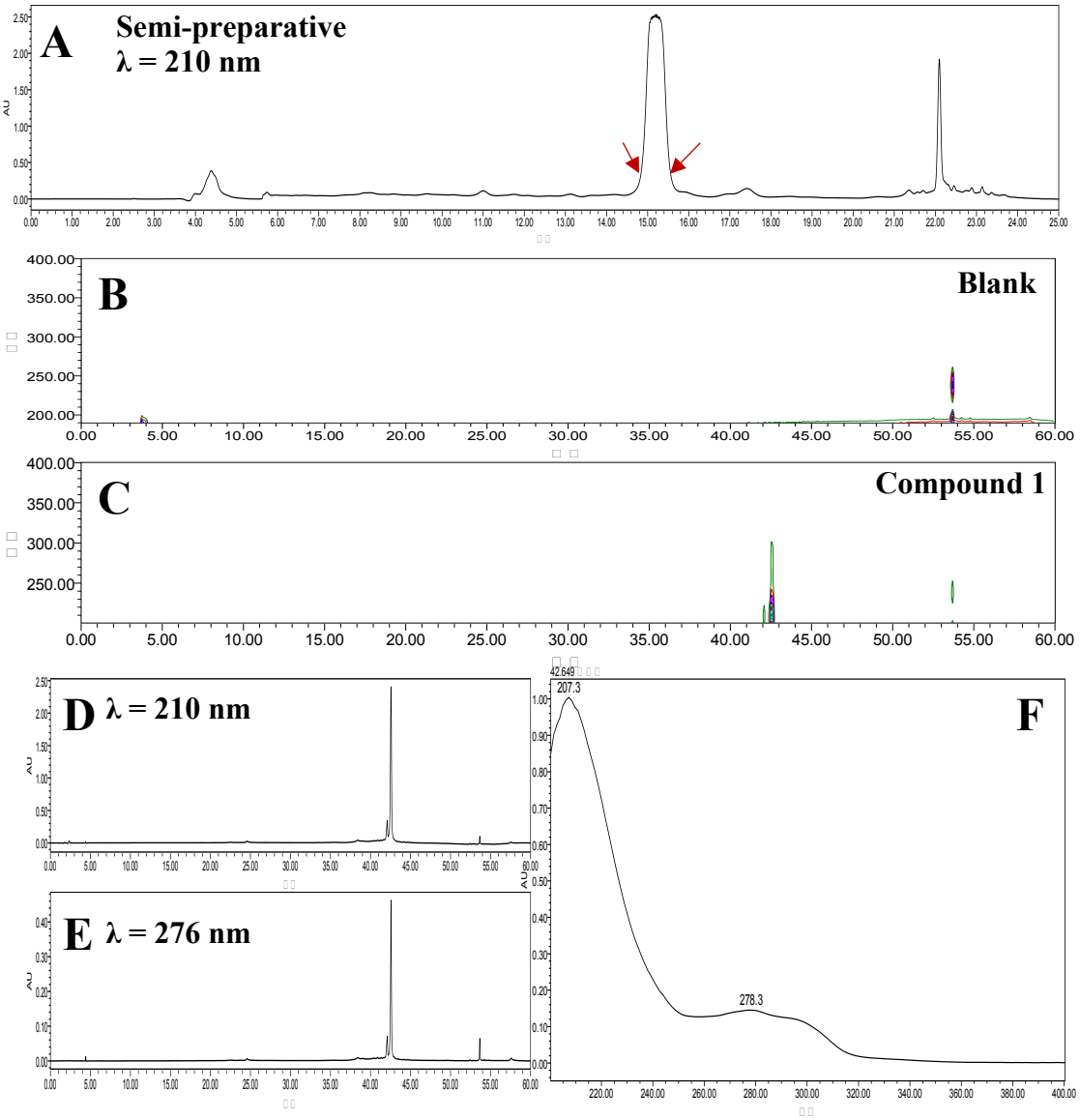


SI. Figure 10. Semi-preparative and analytical chromatography spectrum of compound **1** (purity = 87 %). (A) The semi-preparation of compound **1** at the wavelength 210 nm. (B) HPLC analysis using MeOH as blank. (C) 3D graphic of HPLC purity detection. (D) HPLC purity detection of compound **1** at the wavelength 210 nm. (E) HPLC purity detection of compound **1** at the wavelength 276 nm. (F) UV absorption curve of compound **1.**

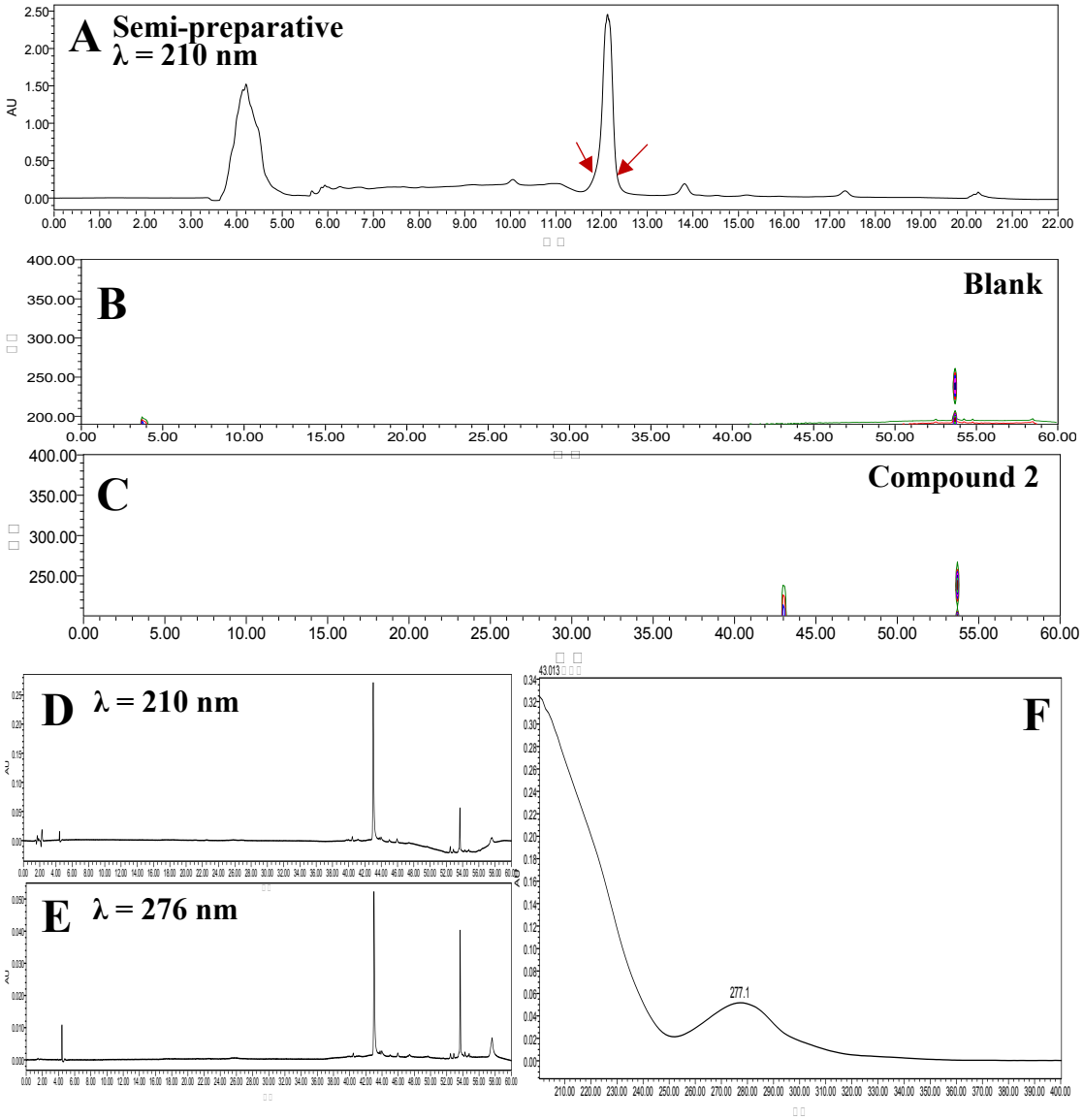
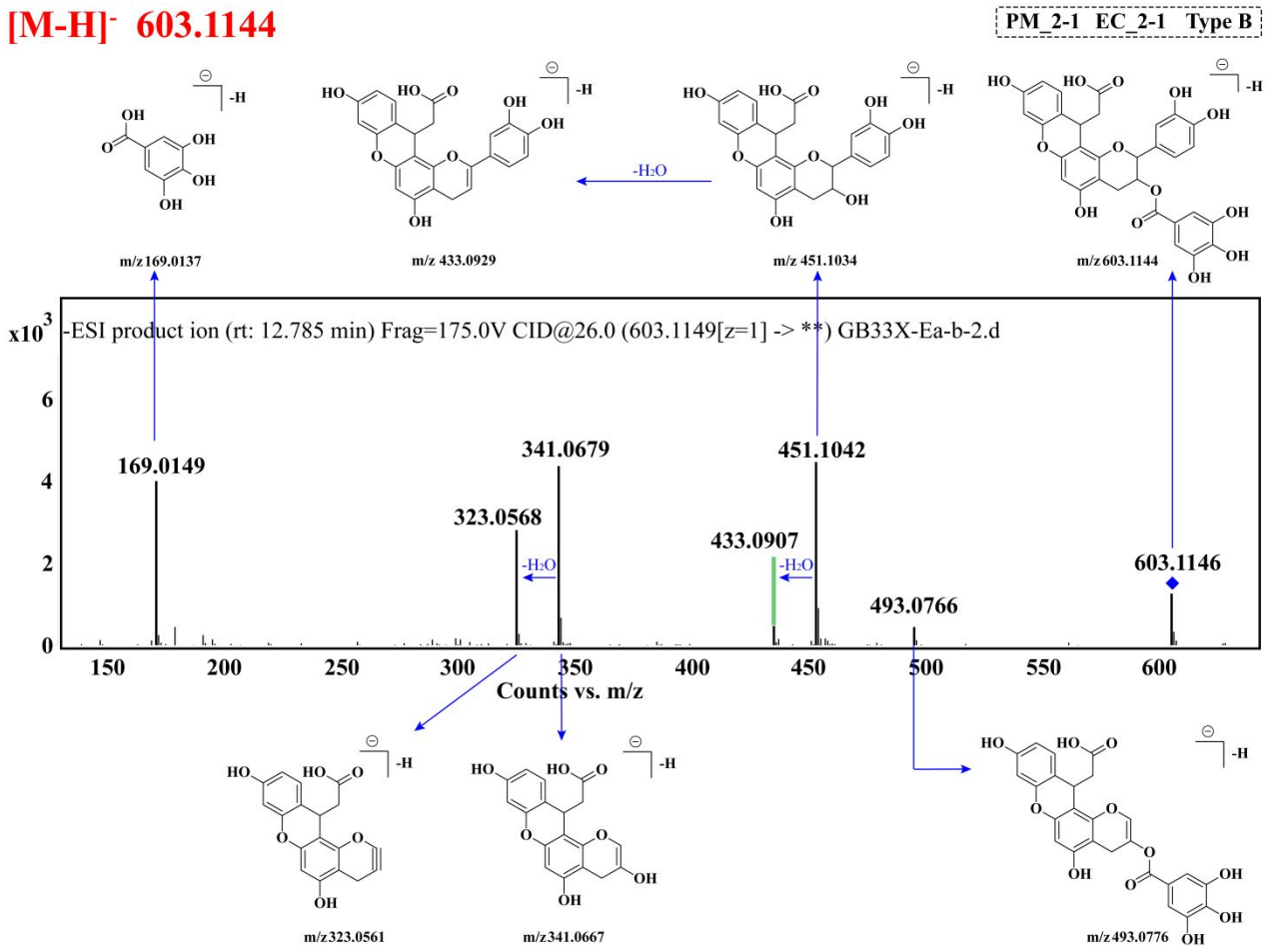
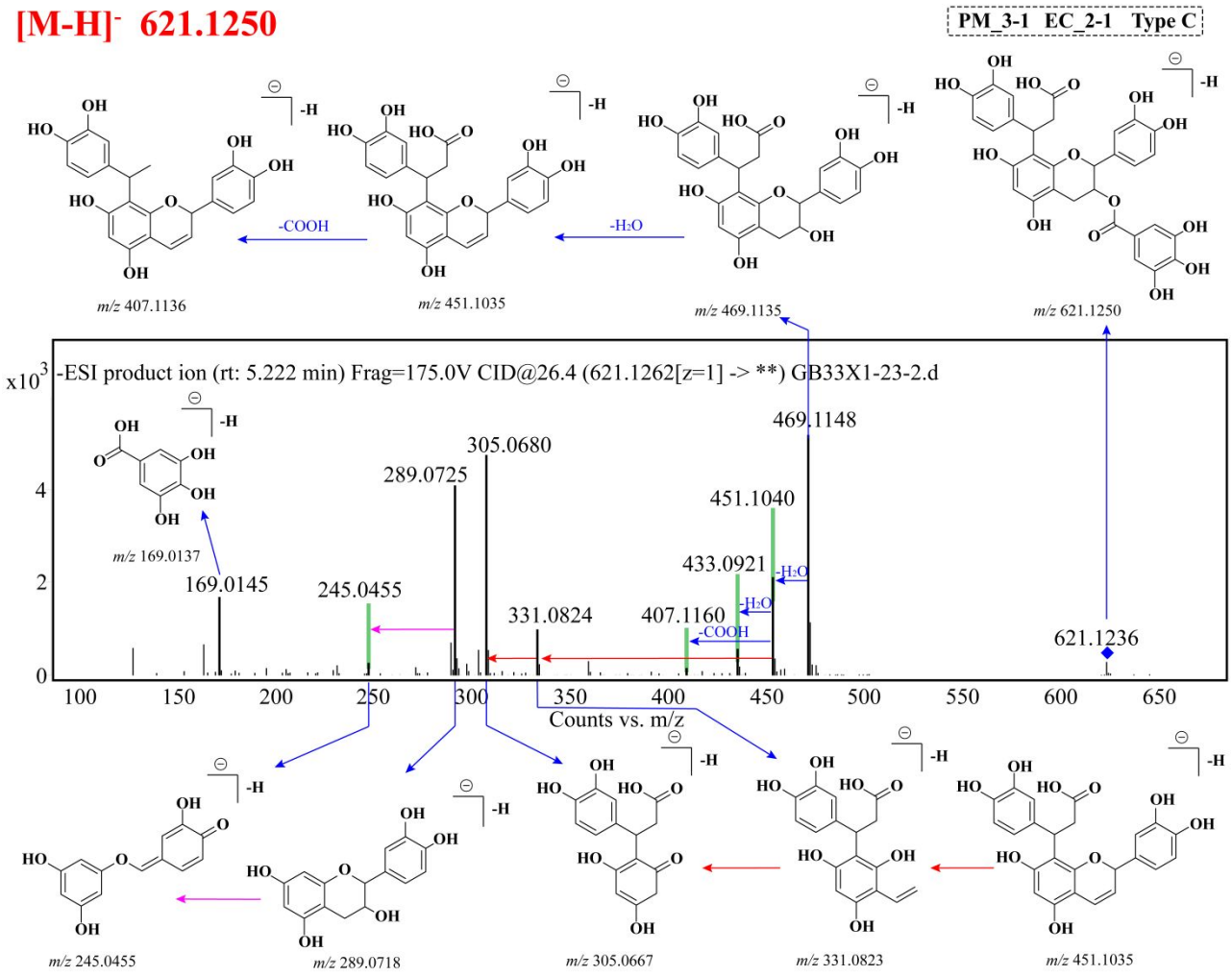


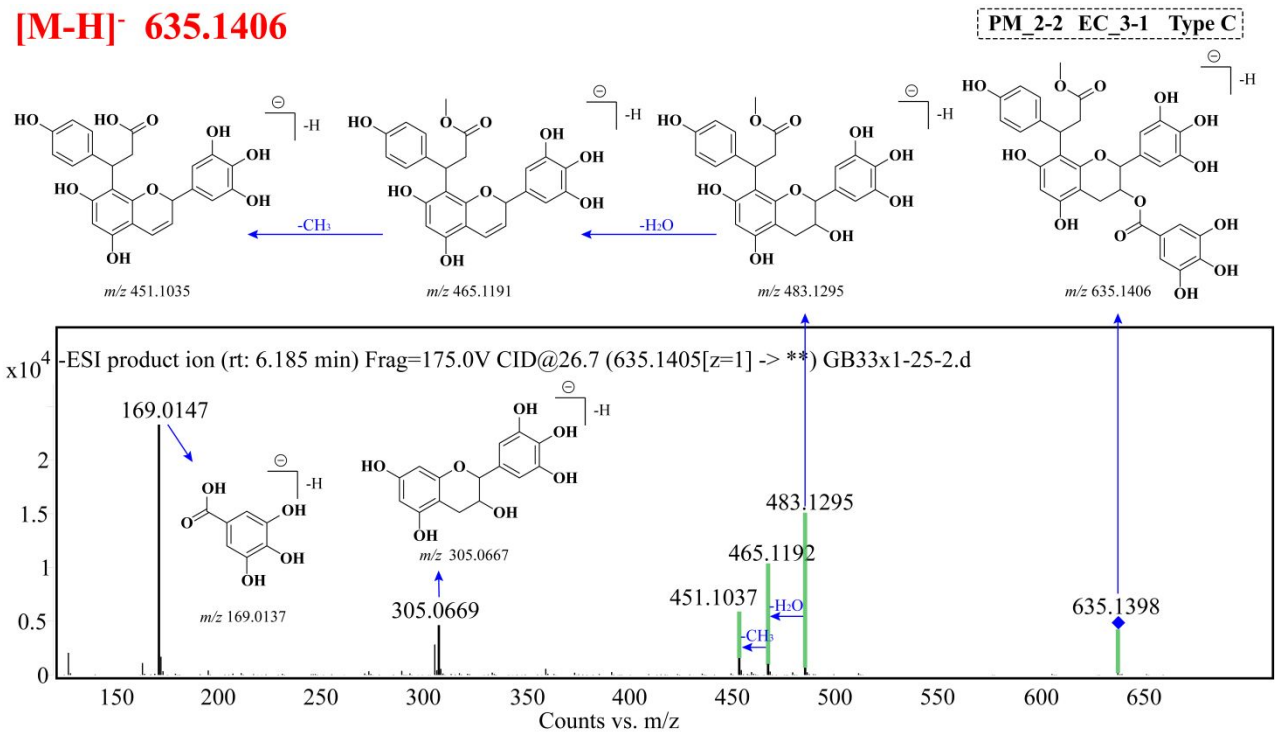
Figure 11. Semi-preparative and analytical chromatography spectrum of compound **2** (purity = 85 %). (A) The semi-preparation of compound **2** at the wavelength 210 nm. (B) HPLC analysis using MeOH as blank. (C) 3D graphic of HPLC purity detection. (D) HPLC purity detection of compound **2** at the wavelength 210 nm. (E) HPLC purity detection of compound **2** at the wavelength 276 nm. (F) UV absorption curve of compound **2.**



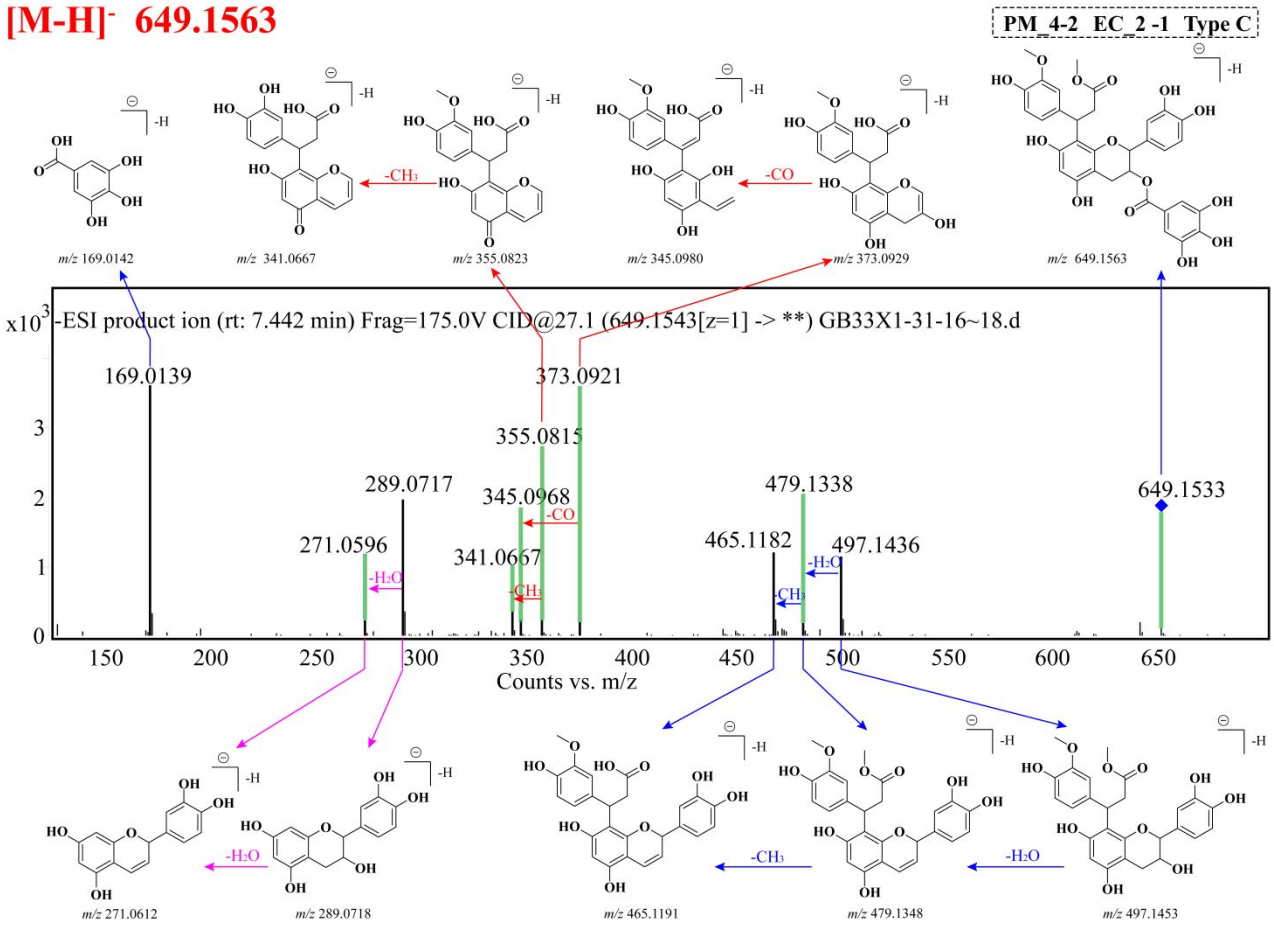
SI. Figure 12. MS/MS spectrum of precursor ion [M-H]- 603.1144**.**



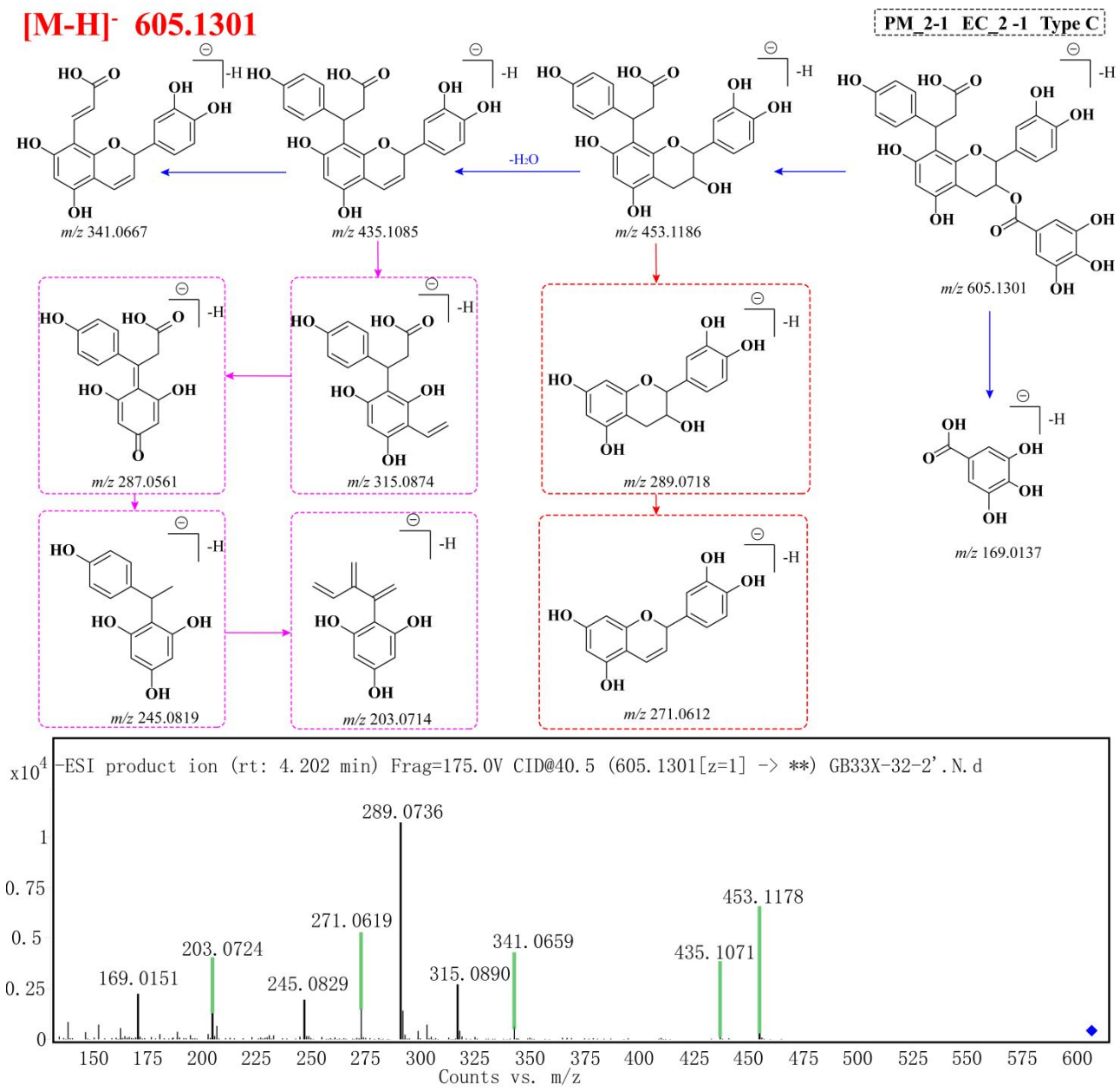
SI. Figure 13. MS/MS spectrum of precursor ion [M-H]- 621.1250**.**



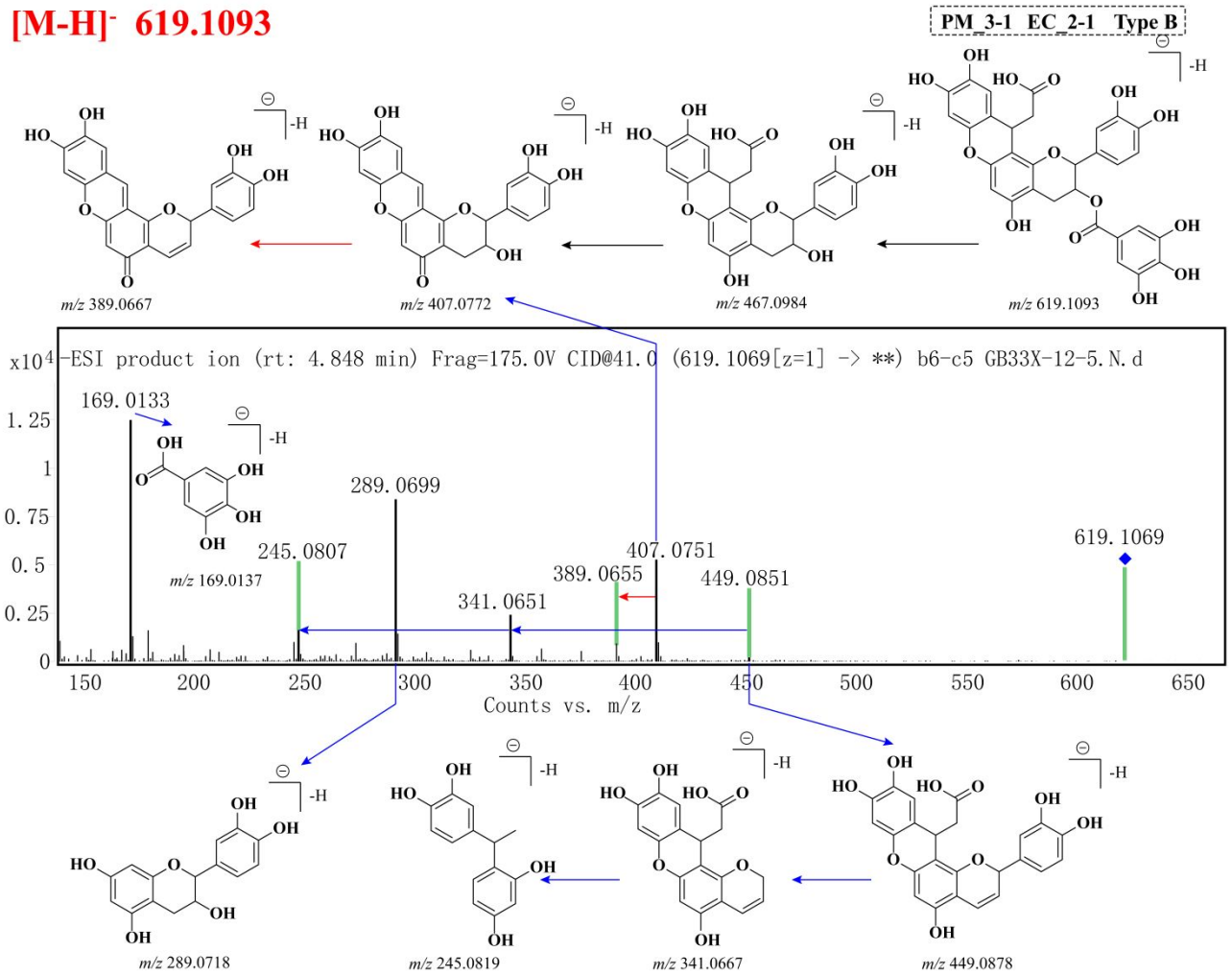
SI. Figure 14. MS/MS spectrum of precursor ion [M-H]- 635.1406**.**



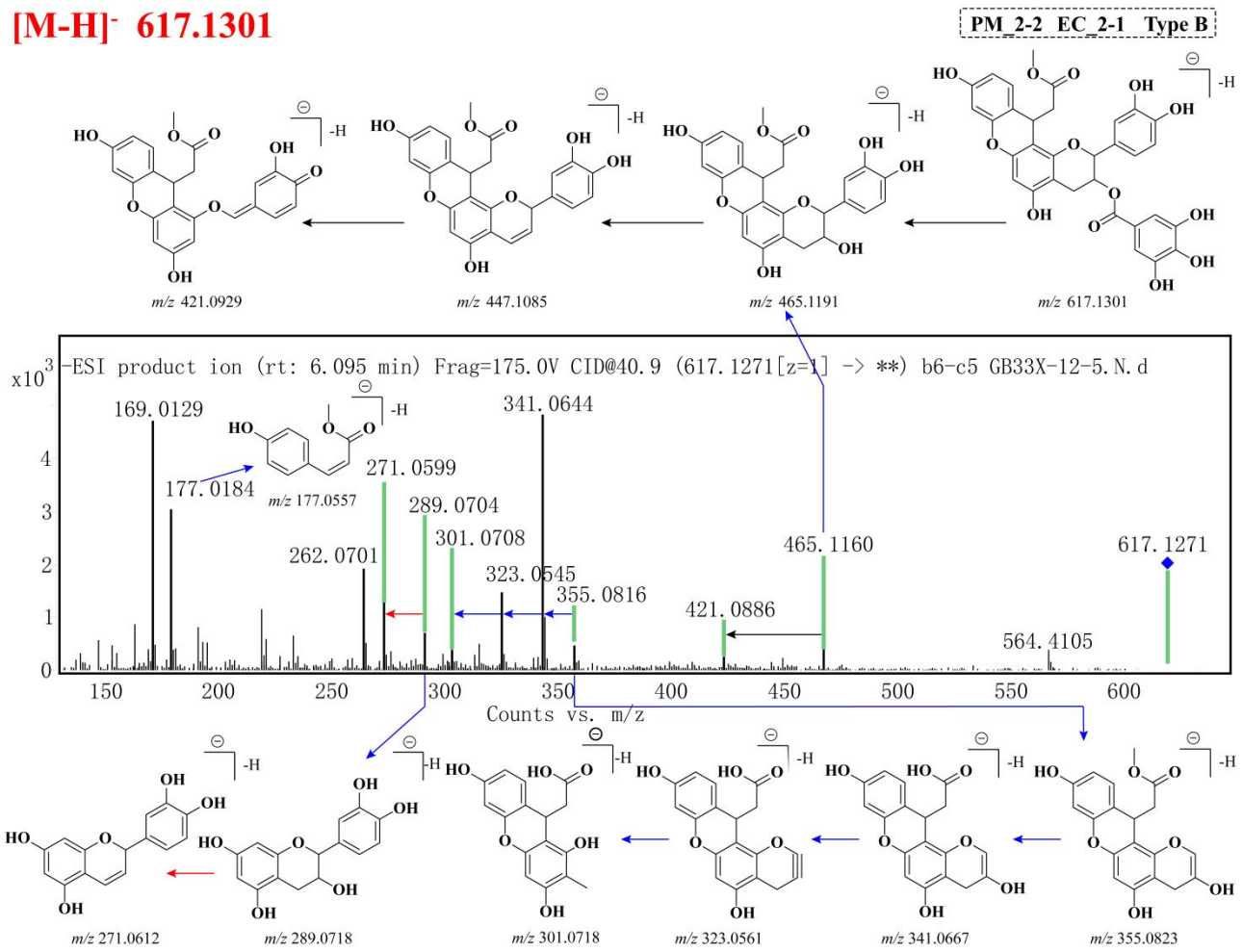
SI. Figure 15. MS/MS spectrum of precursor ion [M-H]- 649.1563**.**



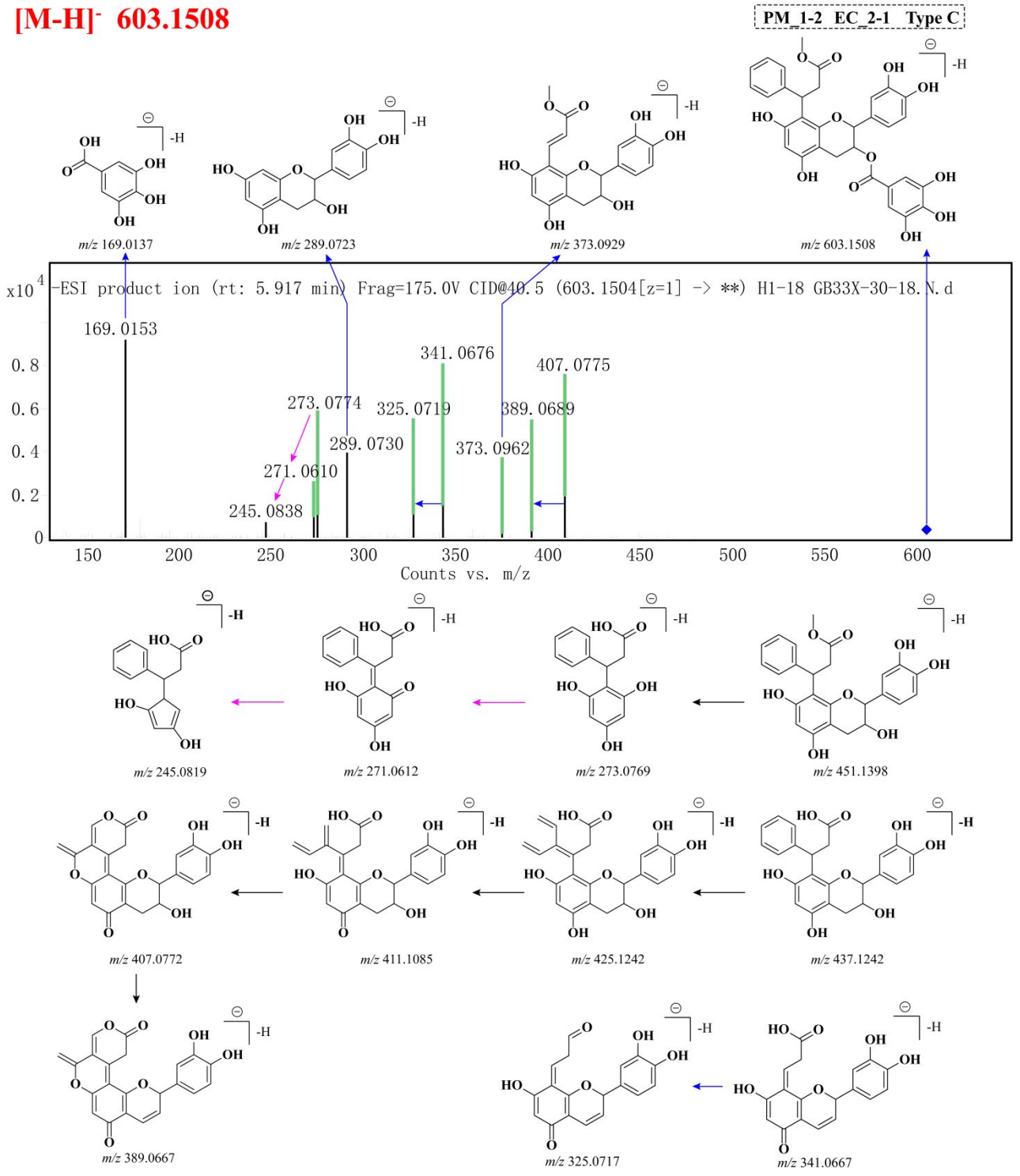
SI. Figure 16. MS/MS spectrum of precursor ion [M-H]- 605.1301.



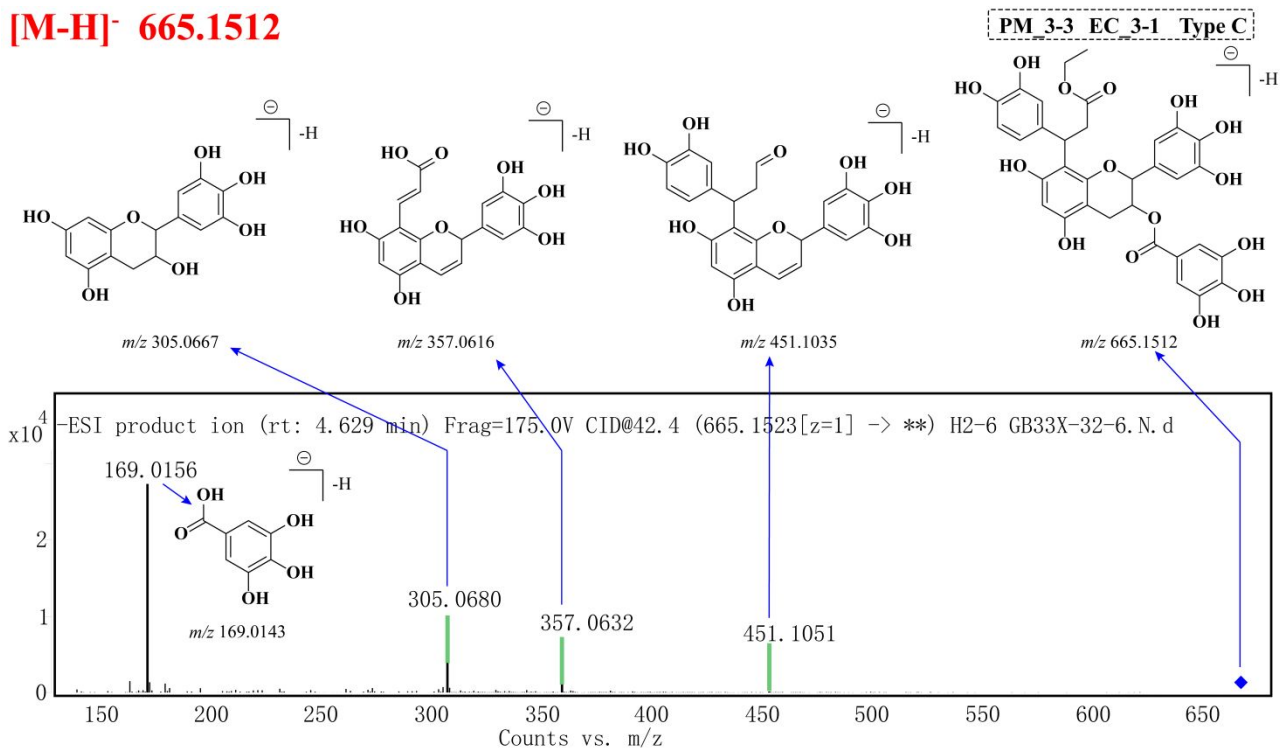
SI. Figure 17. MS/MS spectrum of precursor ion [M-H]- 619.1093.



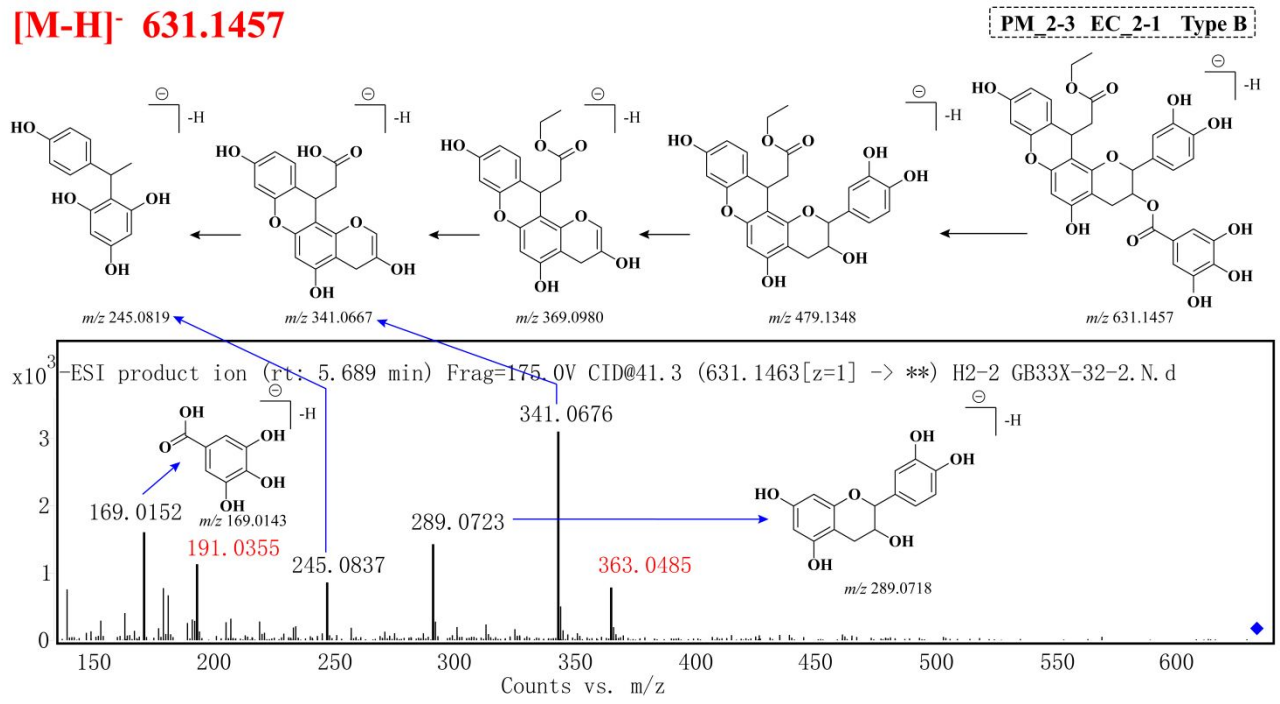
SI. Figure 18. MS/MS spectrum of precursor ion [M-H]- 617.1301.



SI. Figure 19. MS/MS spectrum of precursor ion [M-H]- 603.1508**.**



SI. Figure 20. MS/MS spectrum of precursor ion [M-H]- 665.1512**.**



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288 **SI. Figure 21.** MS/MS spectrum of precursor ion [M-H]- 631.1457.

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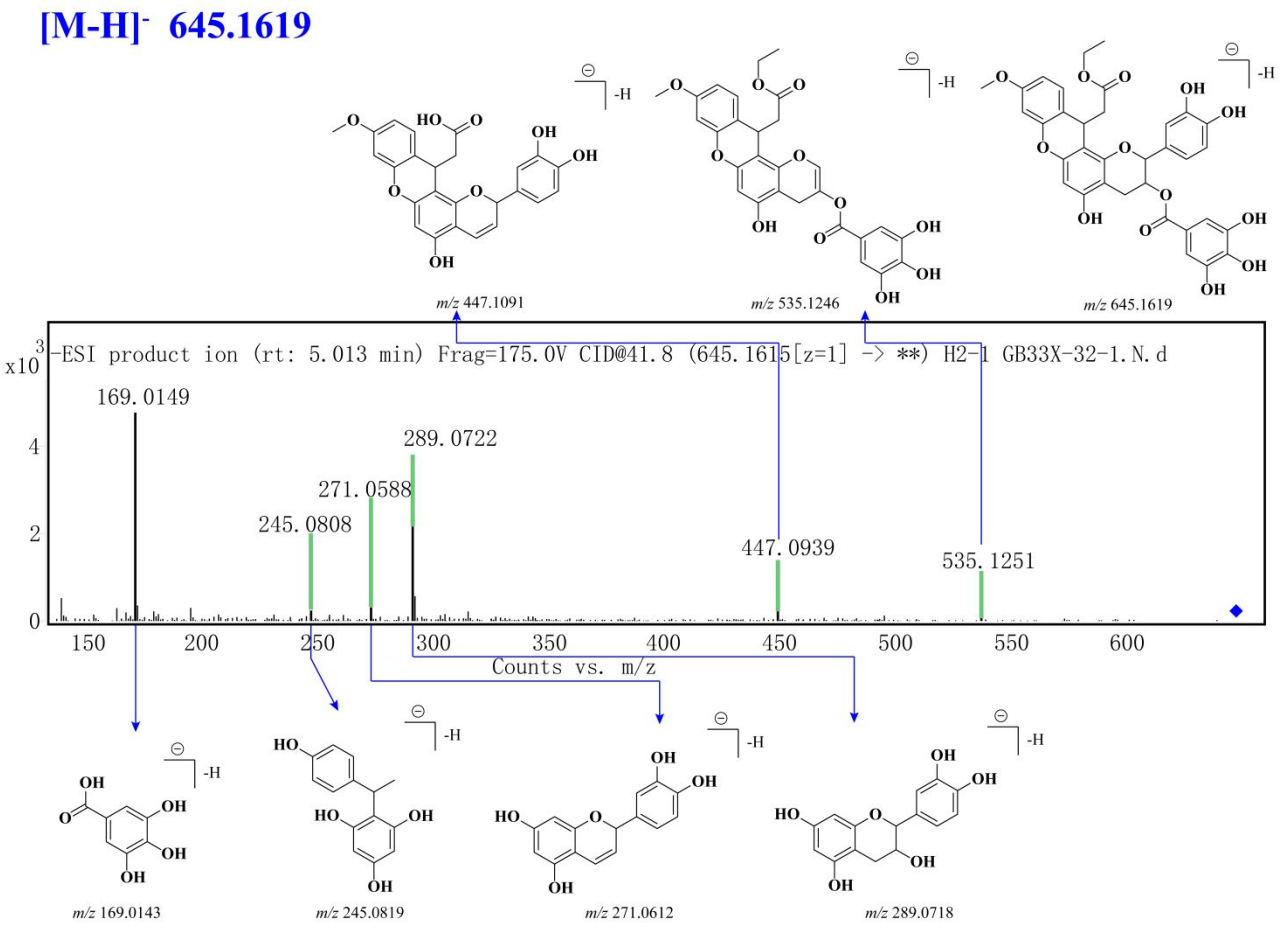

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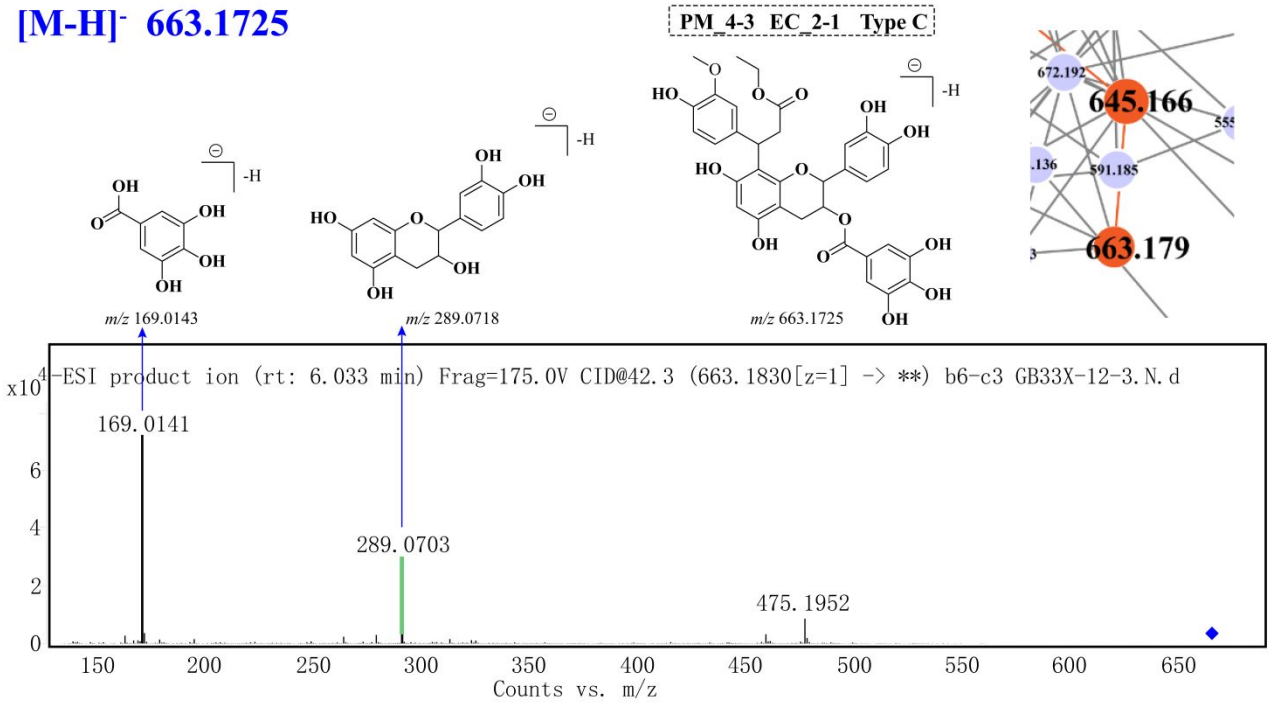
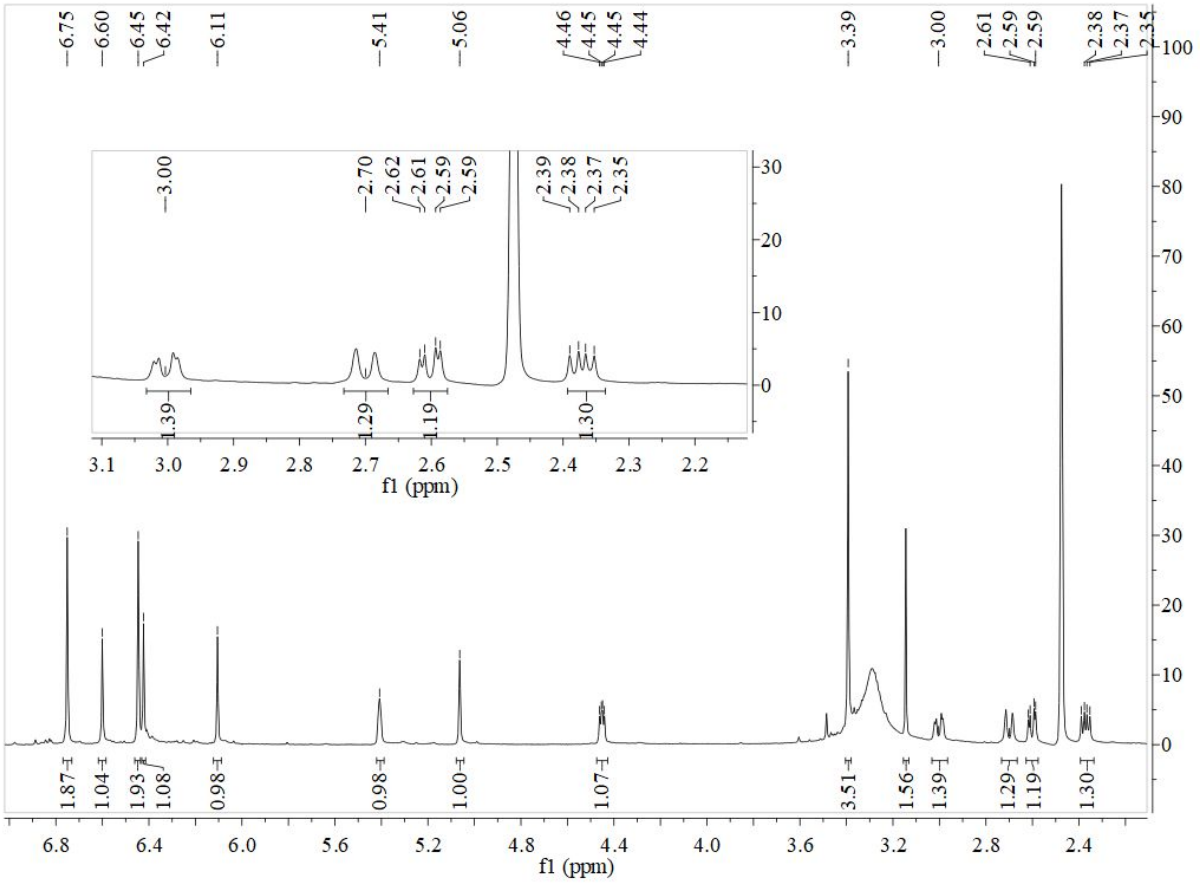
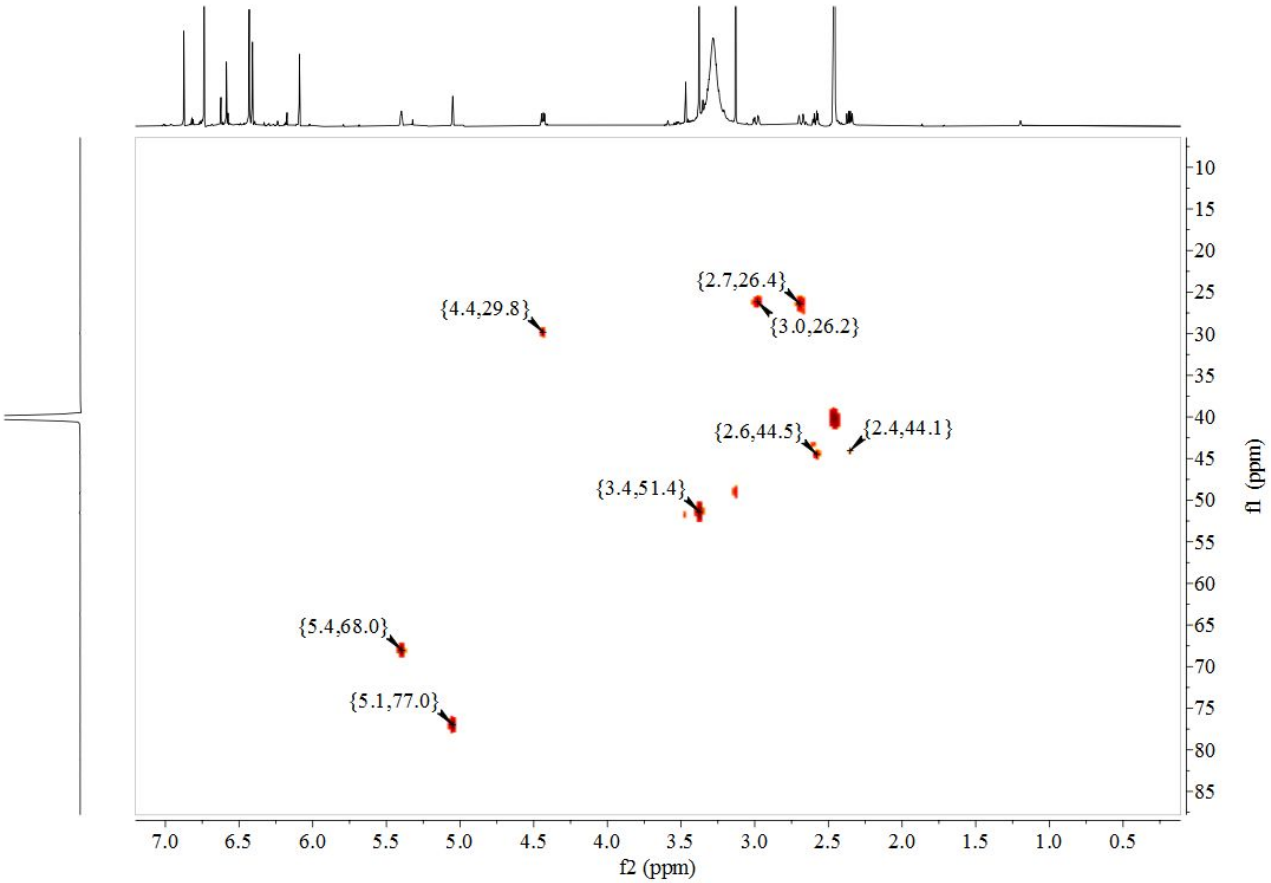
291 **SI. Figure 22.** MS/MS spectrum of precursor ion [M-H]- 645.1619.



SI. Figure 23. MS/MS spectrum of precursor ion [M-H]- 663.1725**.**



SI. Figure 24. ^{1}H NMR spectrum of compound **1** (in DMSO-d_6; δ, ppm; J, Hz).



296 **SI. Figure 25.** Local HMQC spectrum of compound **1** (δ_H 1–6).

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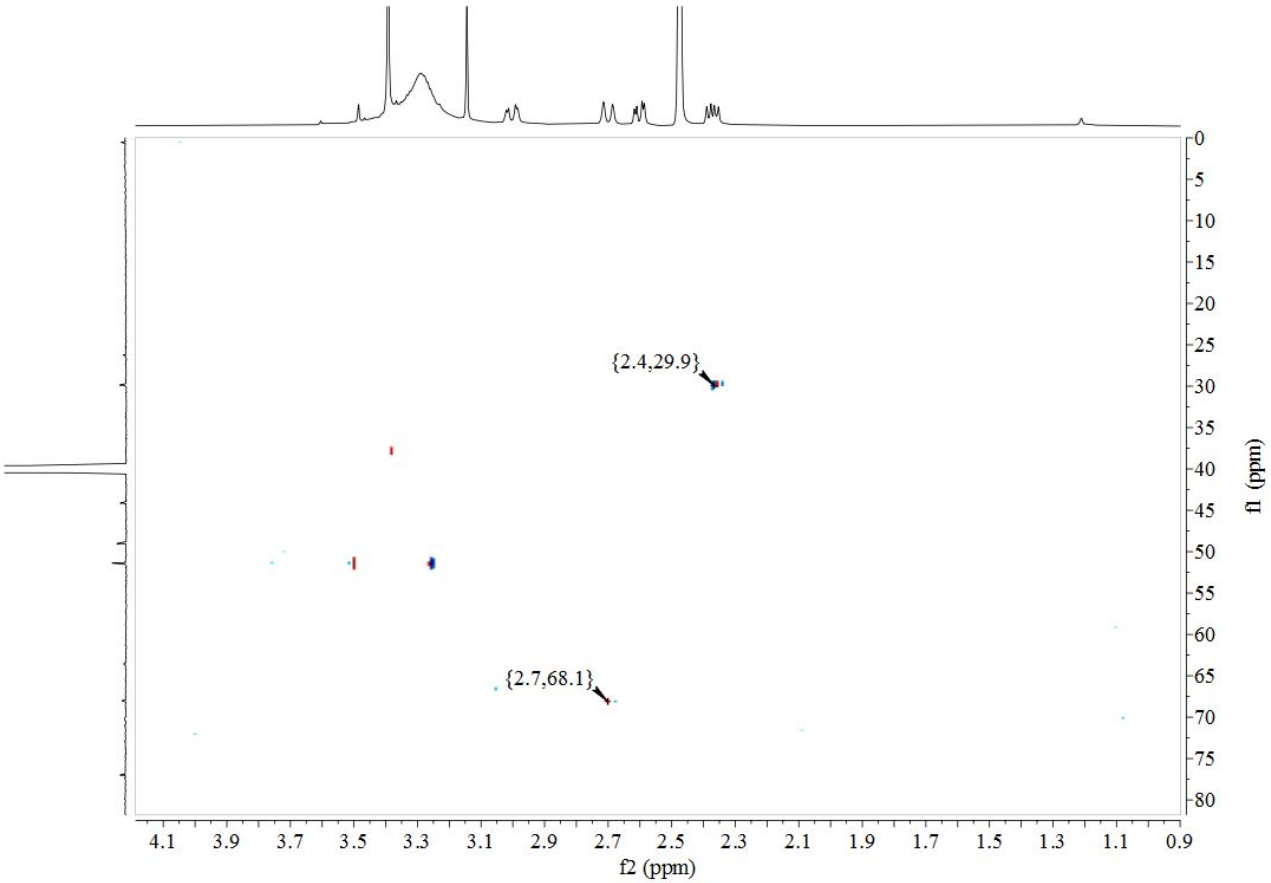
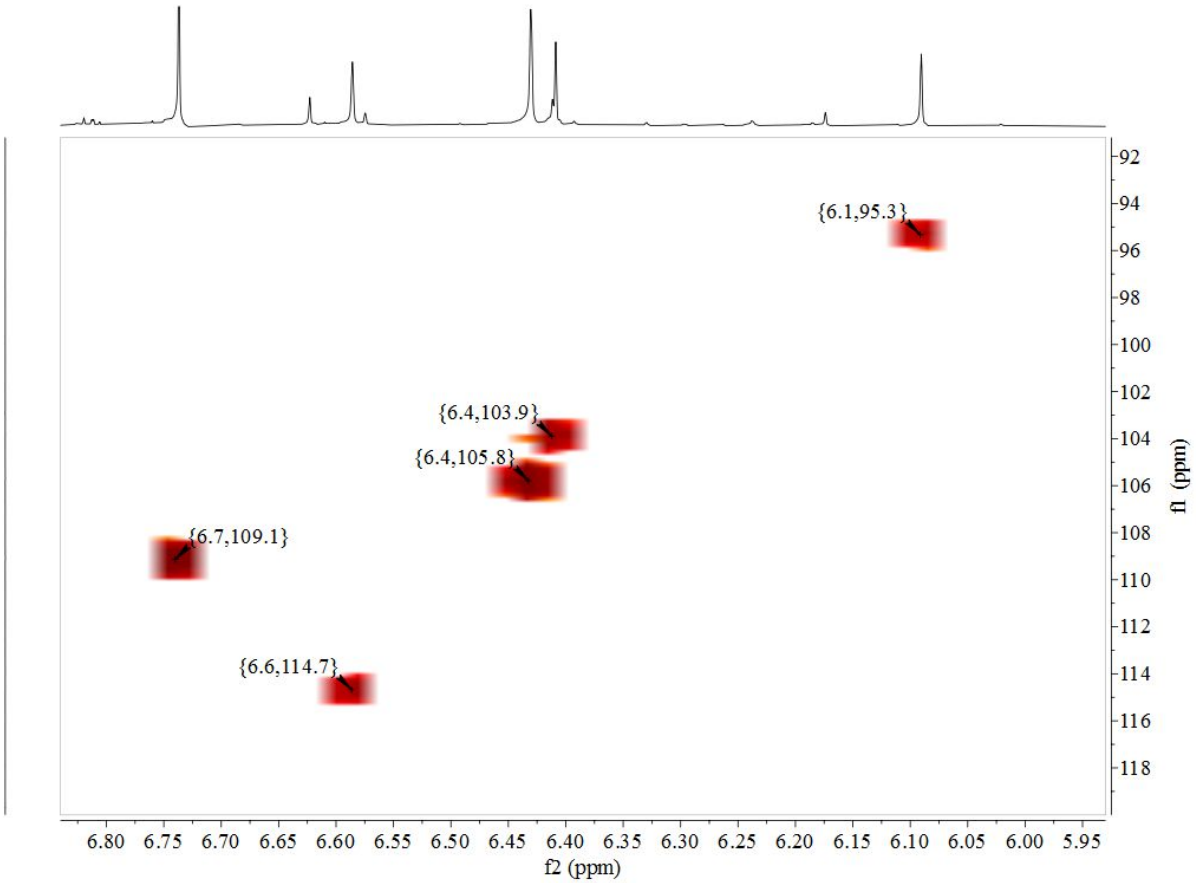
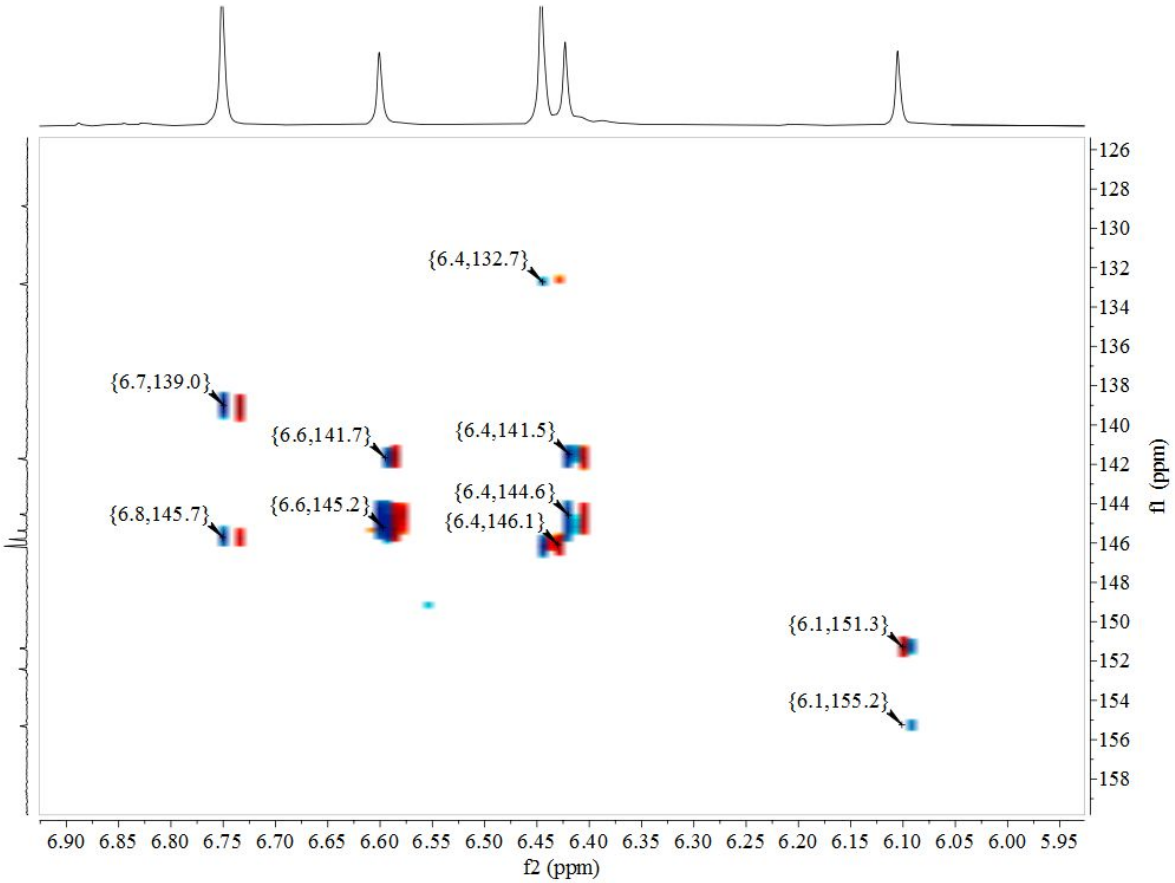


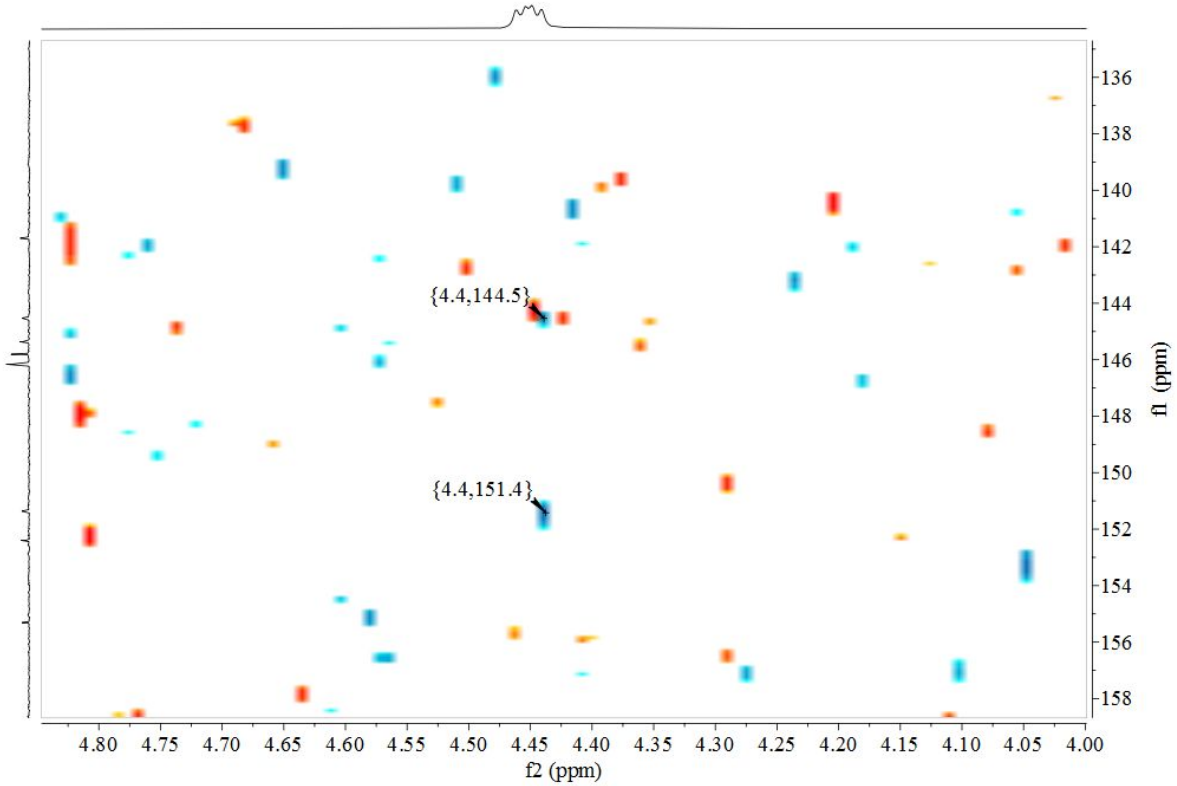
SI. Figure 26. Local HMBC spectrum of compound **1** (δ_H 1–4).



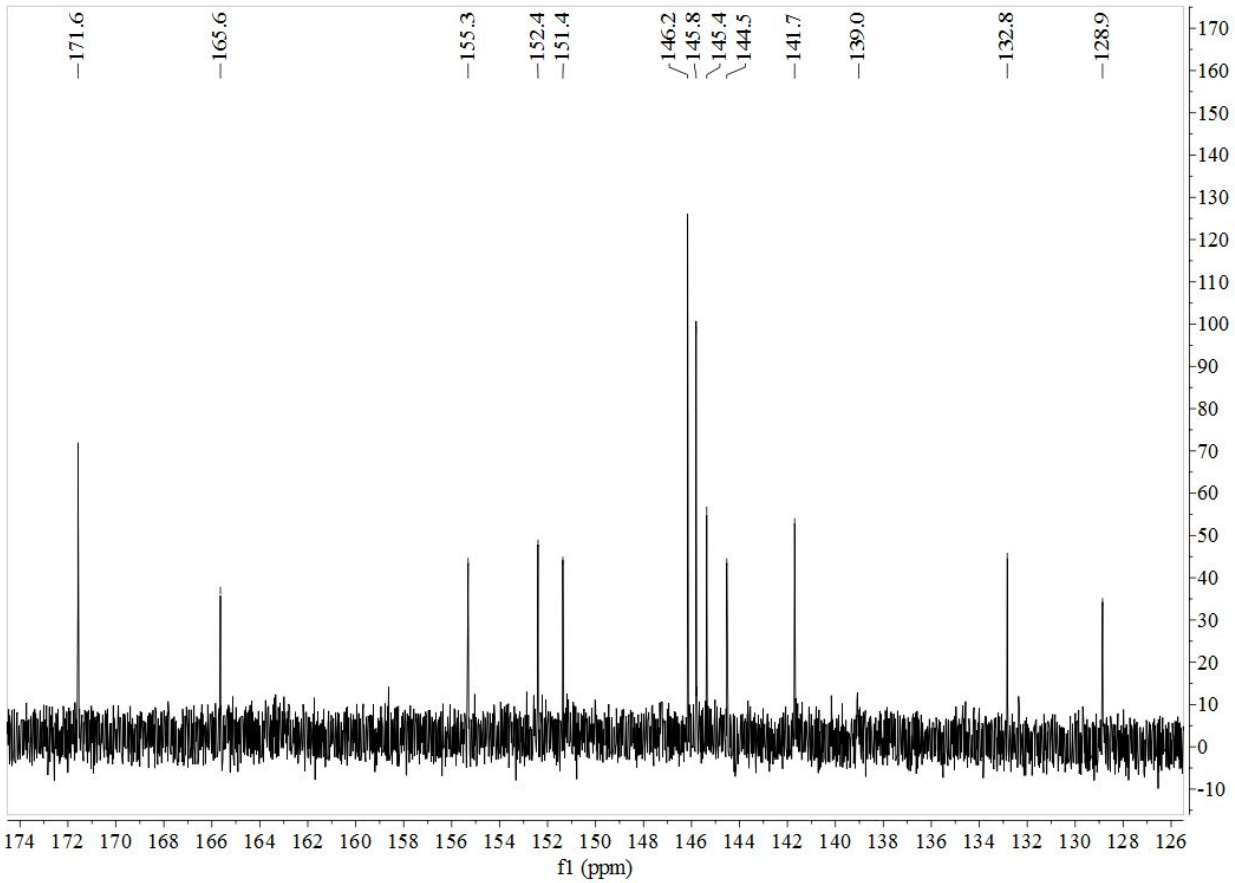
SI. Figure 27. Local HMQC spectrum of compound **1** (δ_H 6–7).



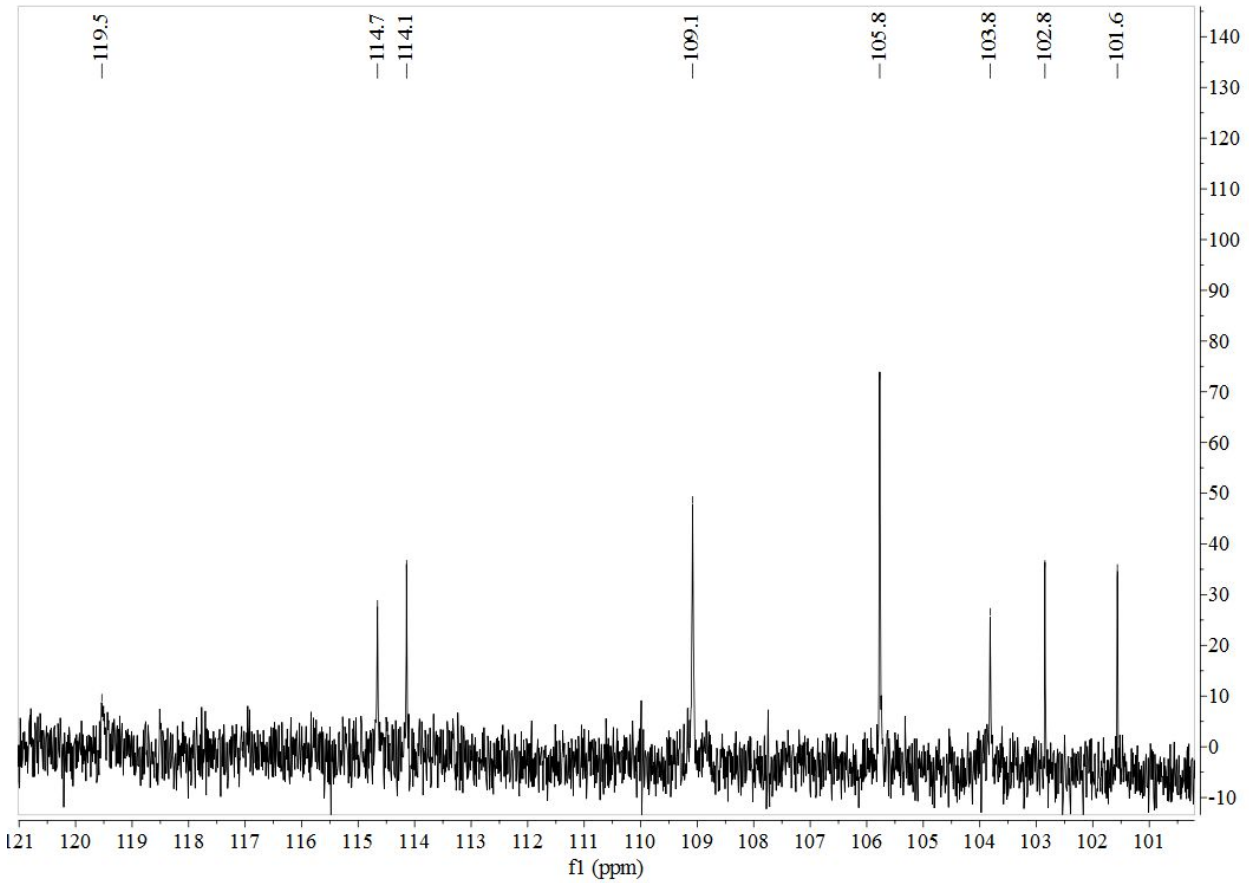
SI. Figure 28. Local HMBC spectrum of compound **1** (δ_H 6–7).



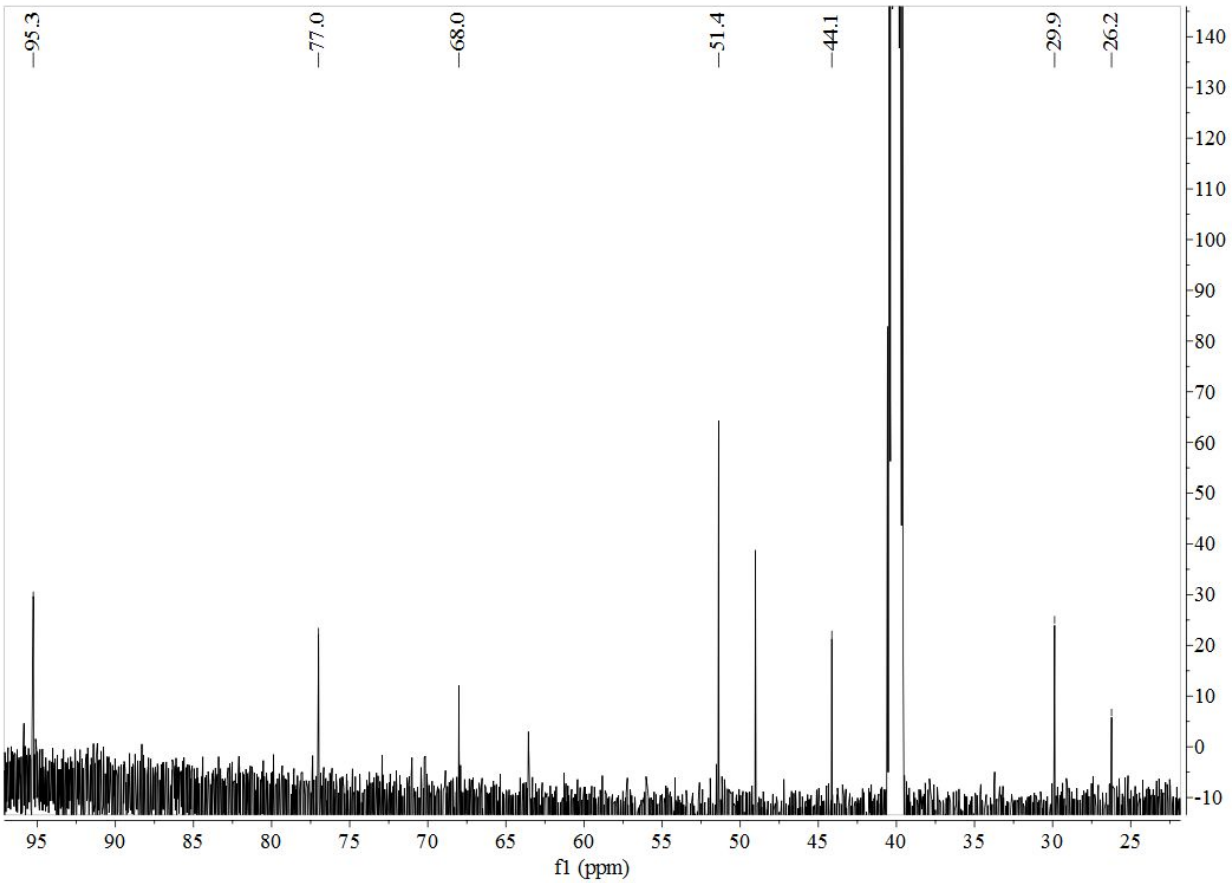
SI. Figure 29. Local HMBC spectrum of compound **1** (δ_H 4.45, H-3‴).



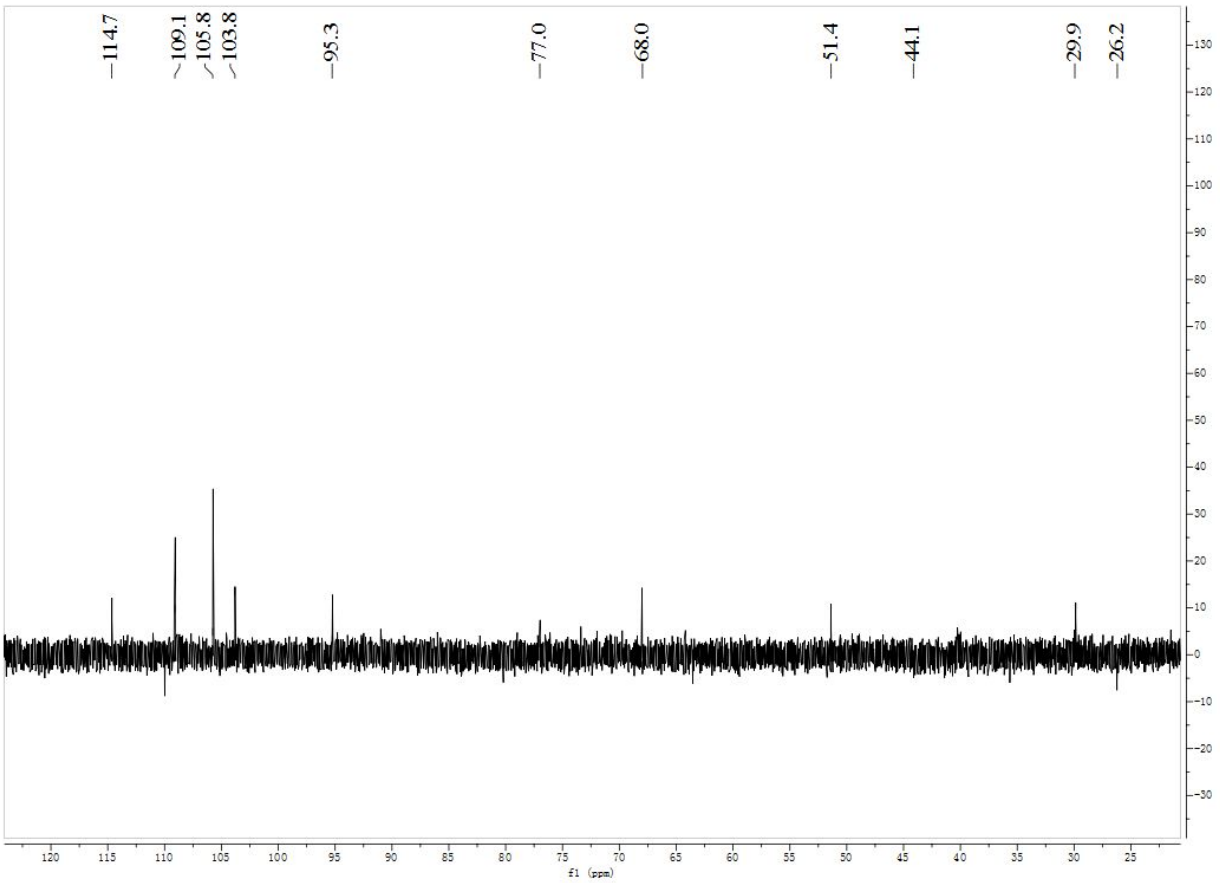
SI. Figure 30. ^{13}C NMR spectrum of compound **1** (in DMSO-d_6; δ, ppm; δ_C 125–180).



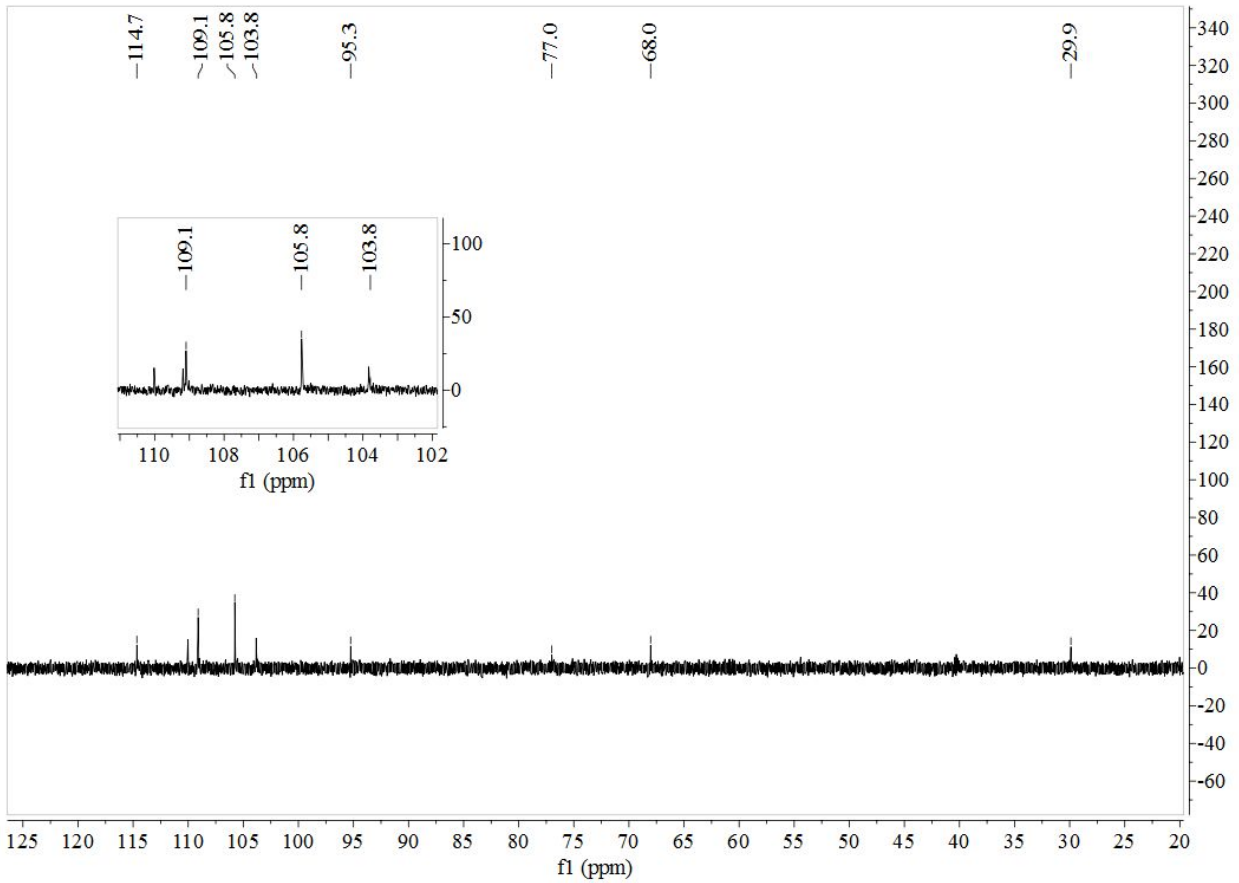
SI. Figure 31. ^{13}C NMR spectrum of compound **1** (in DMSO-d_6; δ, ppm; δ_C 100–120).



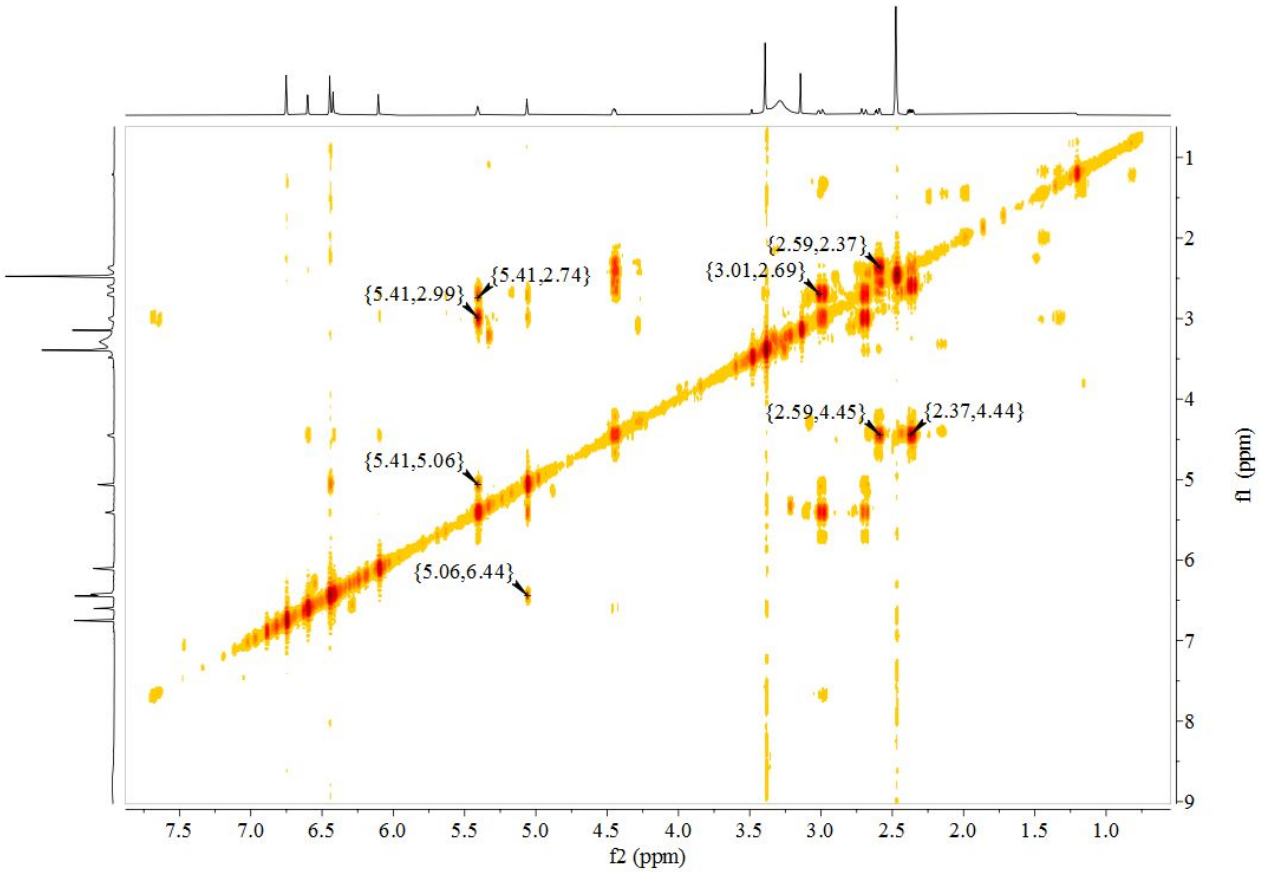
SI. Figure 32. ^{13}C NMR spectrum of compound **1** (in DMSO-d_6; δ, ppm; δ_C 20–100).



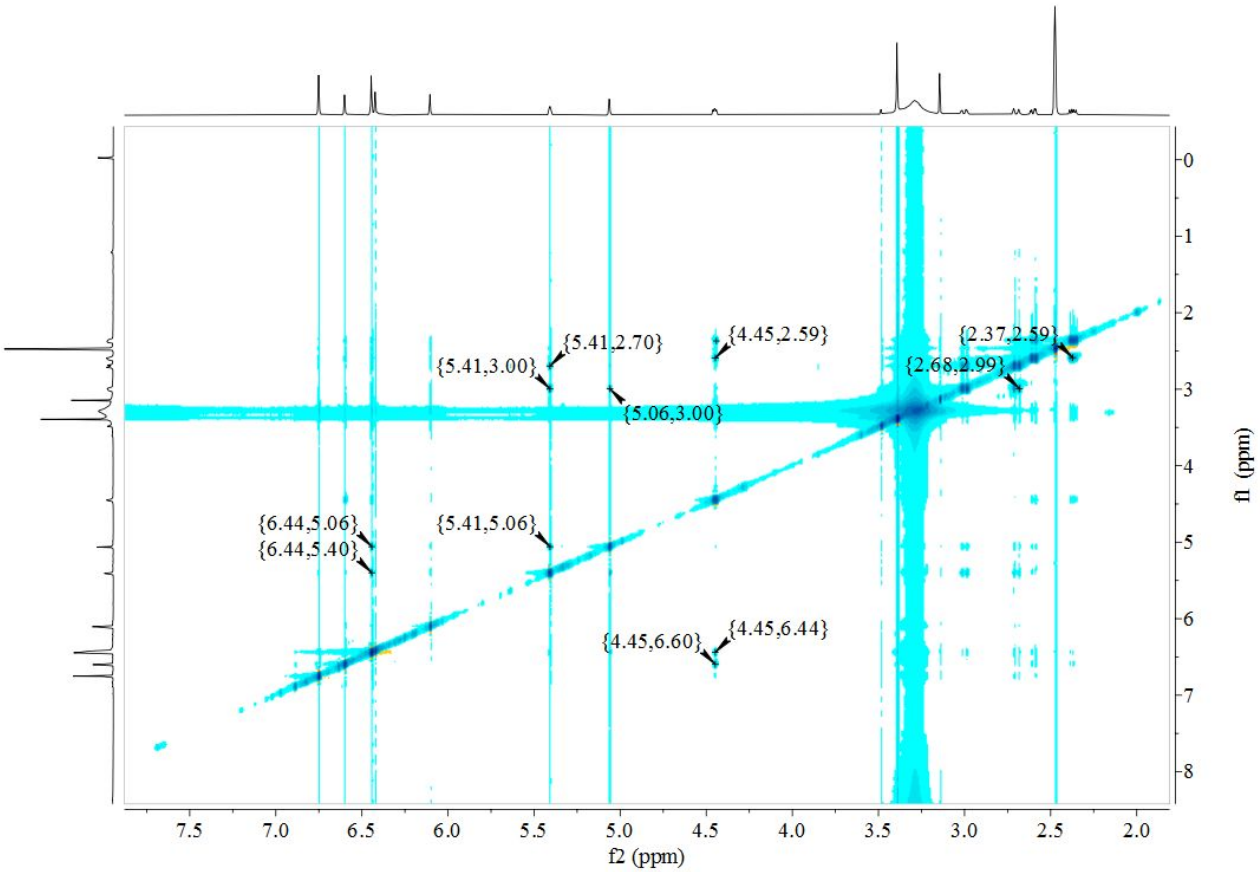
SI. Figure 33. DEPT−135 spectrum of compound **1** (in DMSO-d_6; δ, ppm).



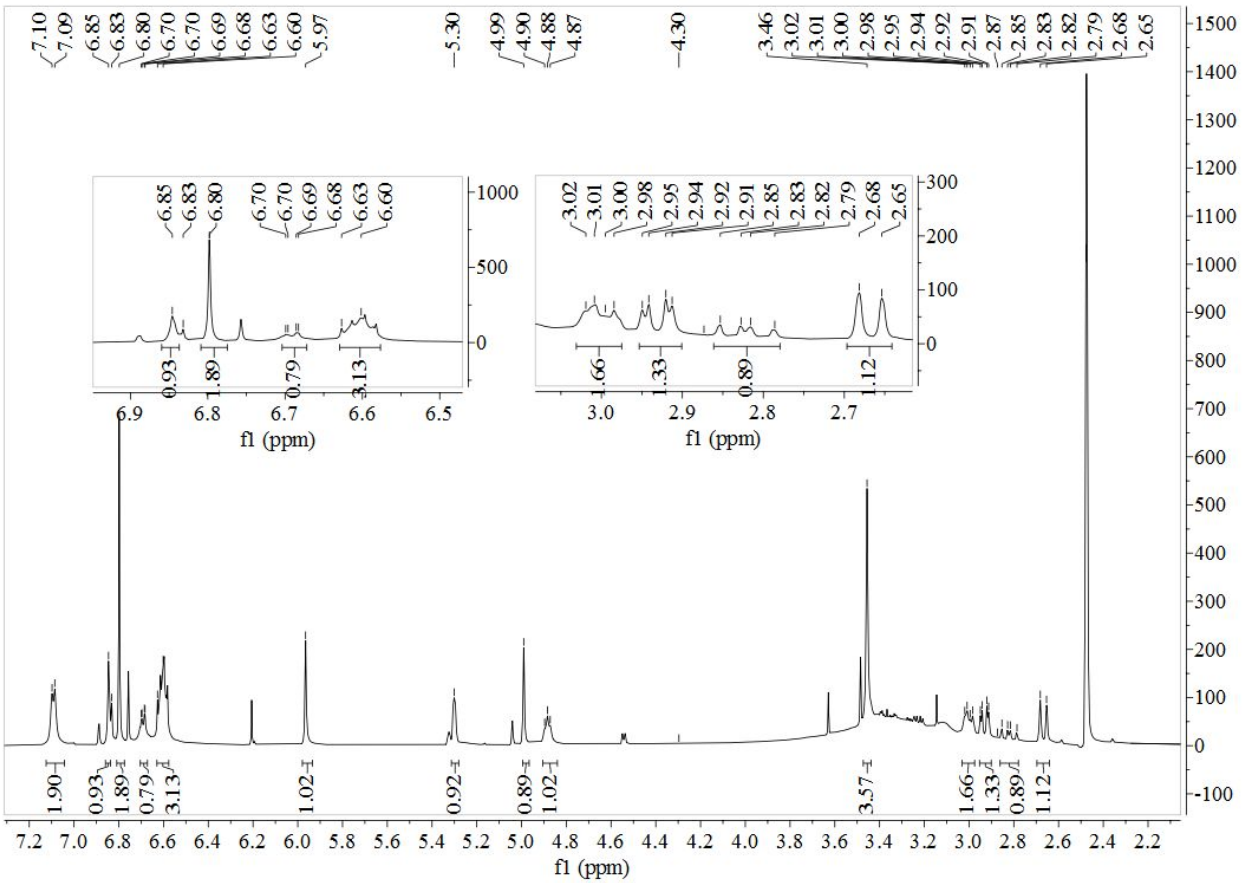
SI. Figure 34. DEPT–90 spectrum of compound **1** (in DMSO-d_6; δ, ppm).



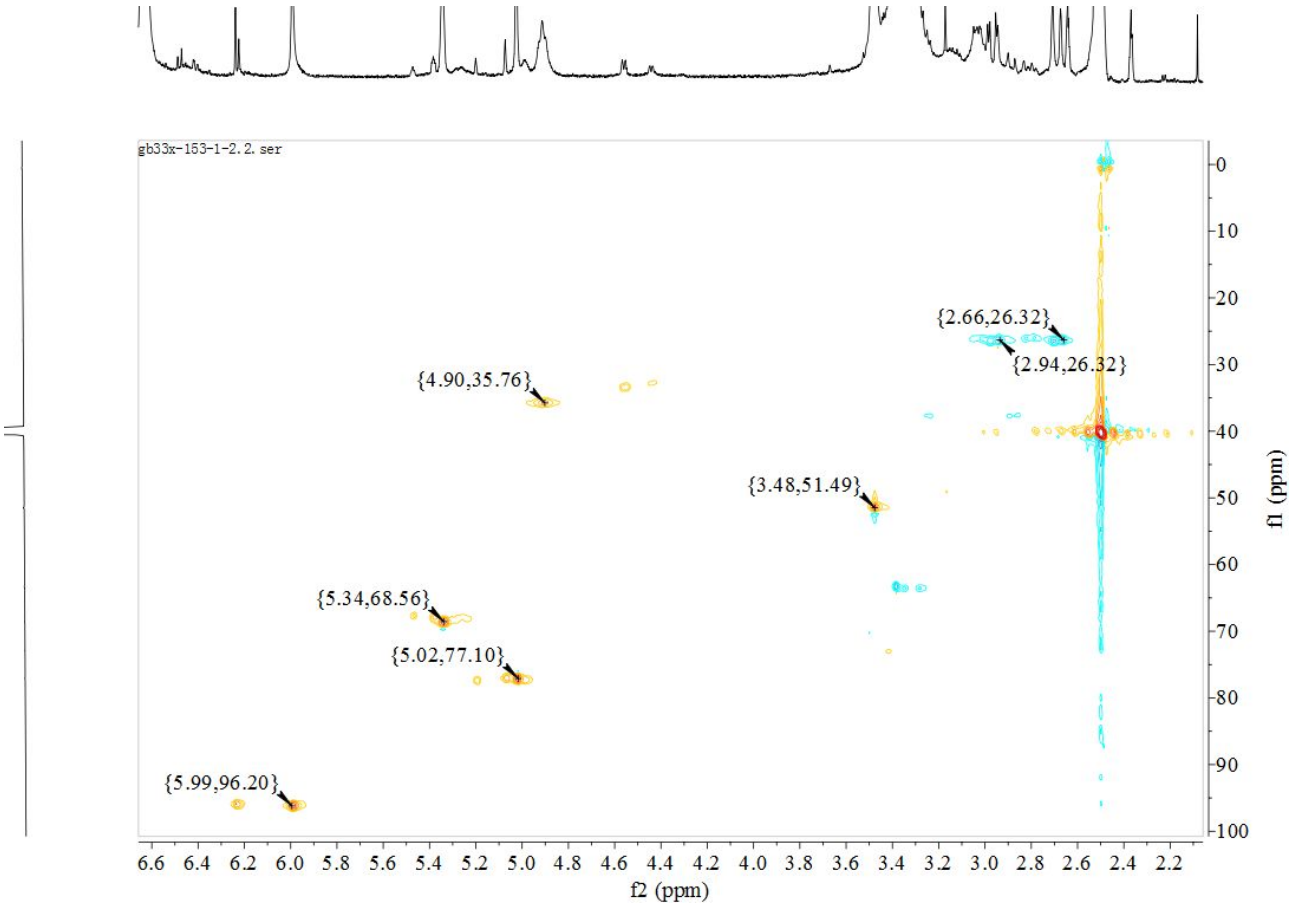
SI. Figure 35. ^{1}H–^{1}H COSY spectrum of compound **1** (in DMSO-d_6; δ, ppm).



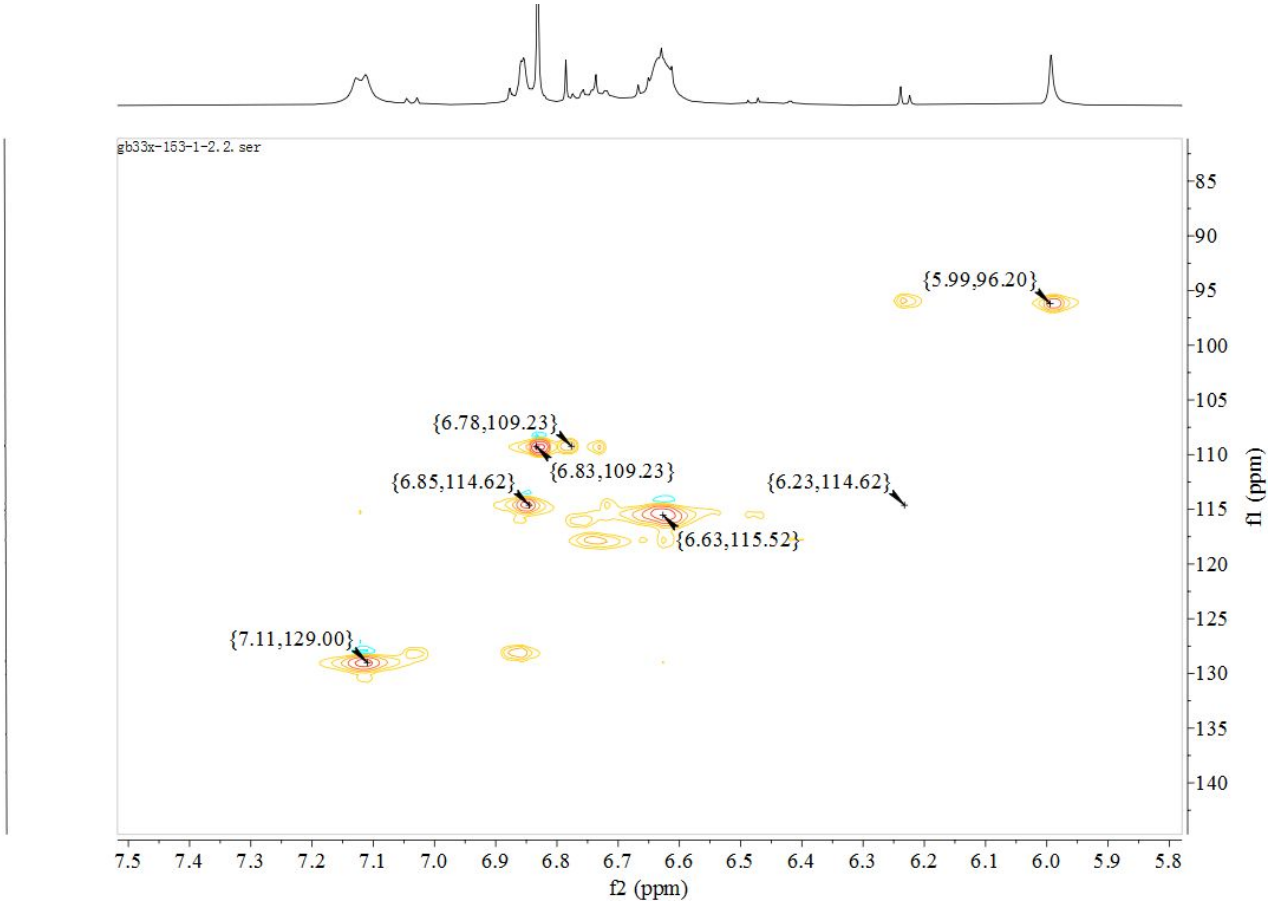
SI. Figure 36. ROESY spectrum of compound **1** (in DMSO-d_6; δ, ppm).



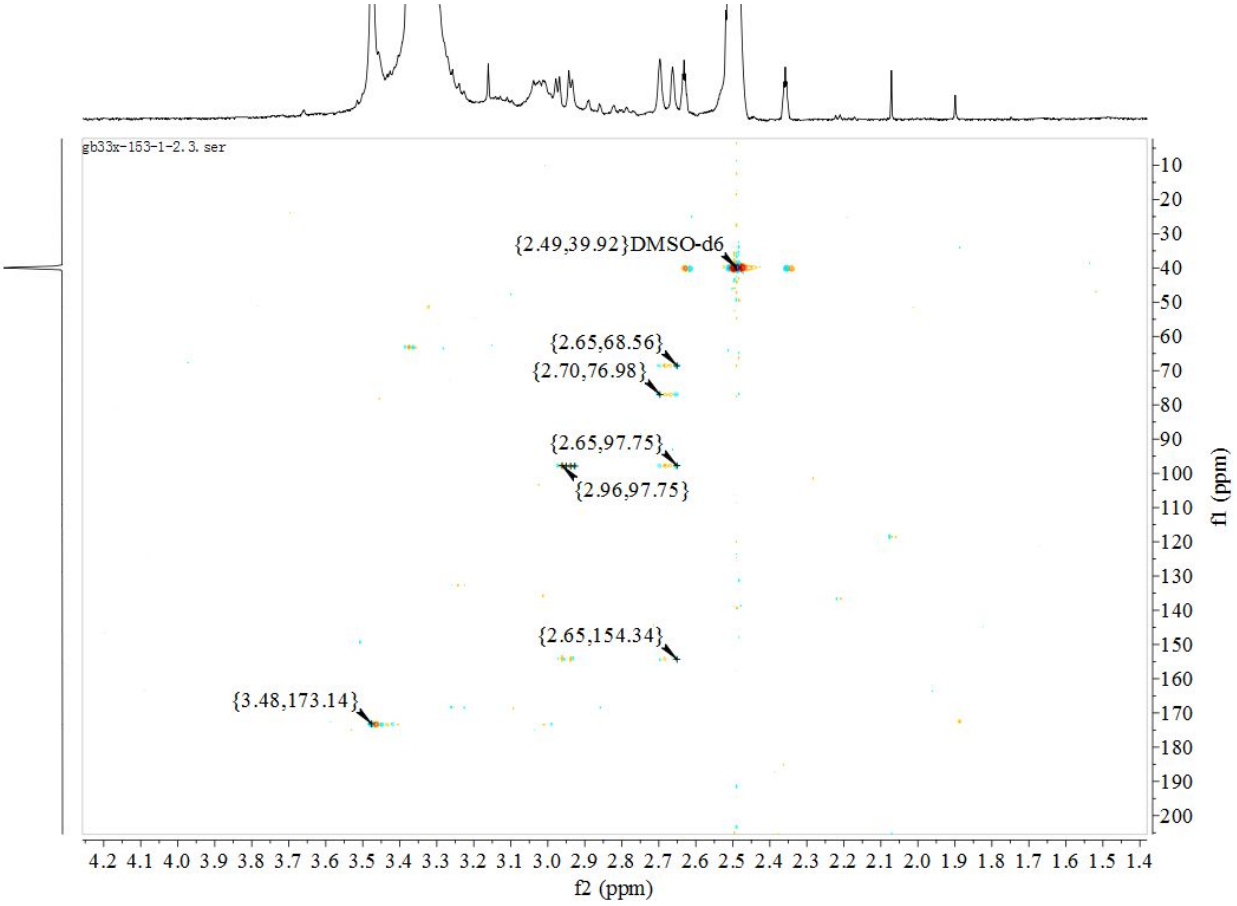
SI. Figure 37. ^{1}H NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; J, Hz).



SI. Figure 38. Local HMQC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 2.5–6.6).



SI. Figure 39. Local HMQC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 5.8–7.5).



447 **SI. Figure 40.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 1.5–4.0).

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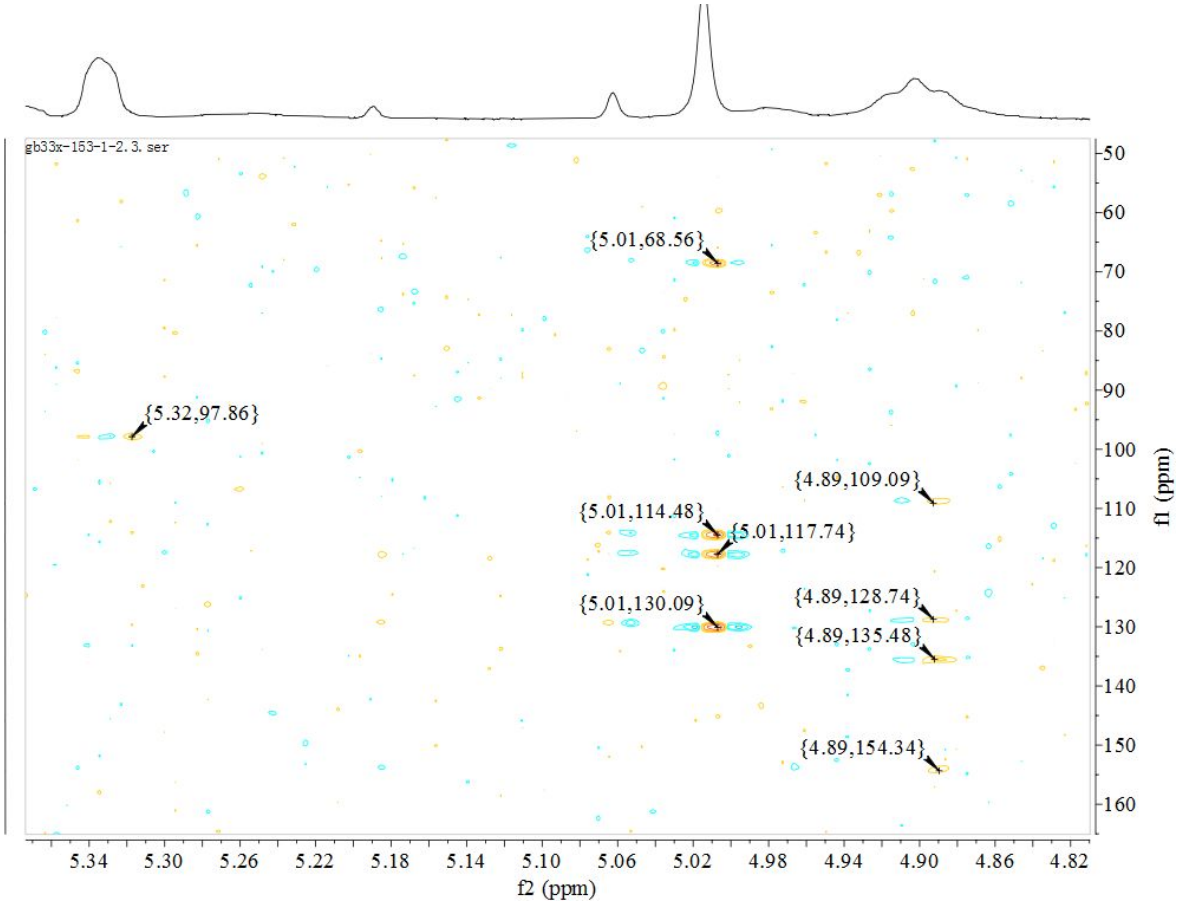

449 **SI. Figure 41.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 4.8–5.5).

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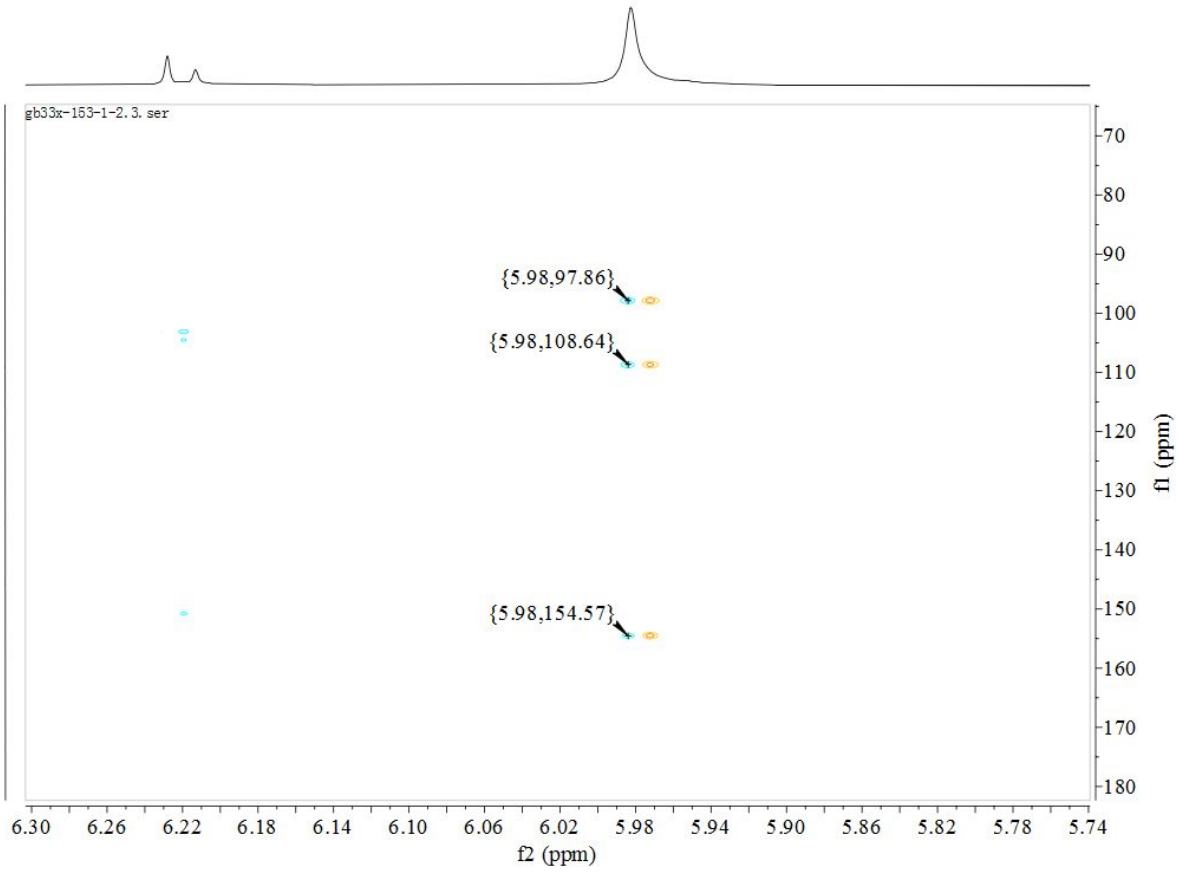

451 **SI. Figure 42.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 5.97 (calibrated

452 value), H-6).

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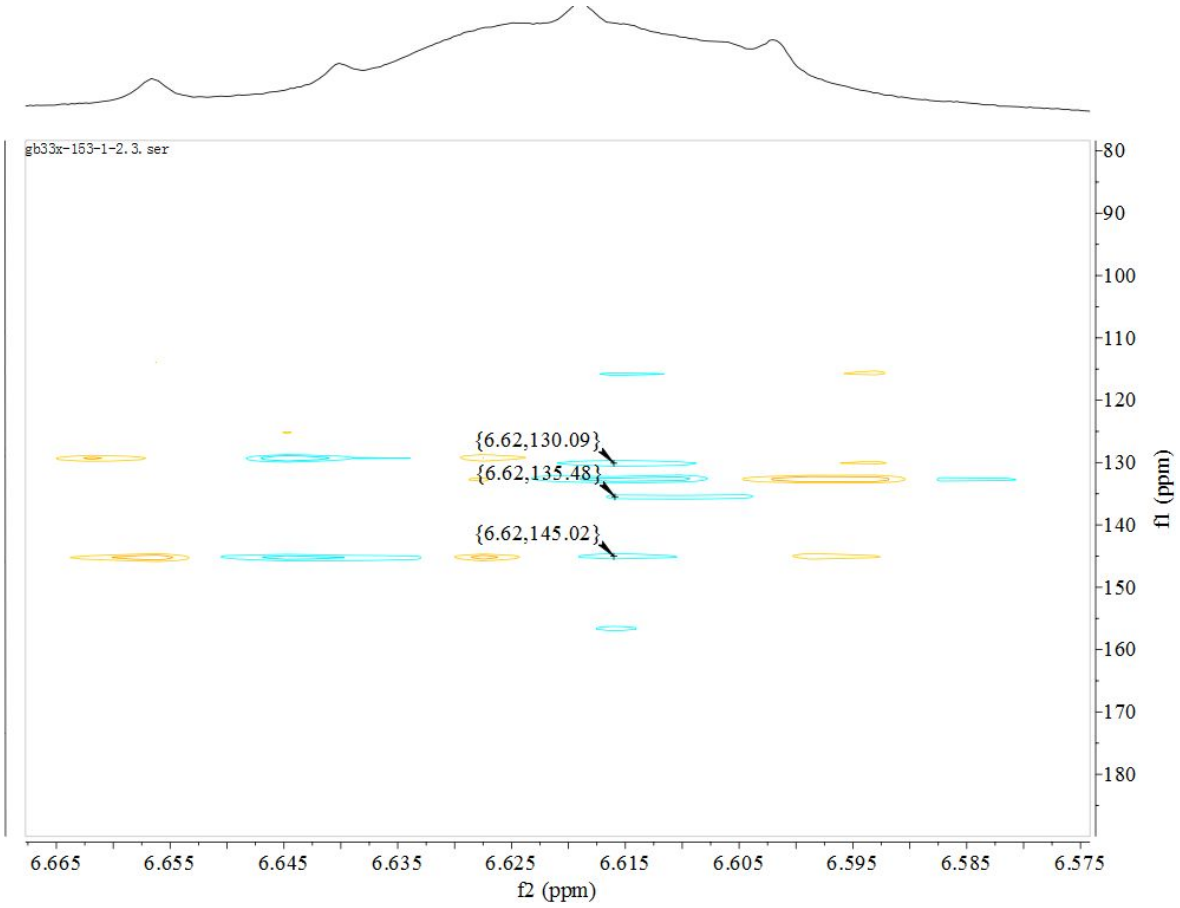
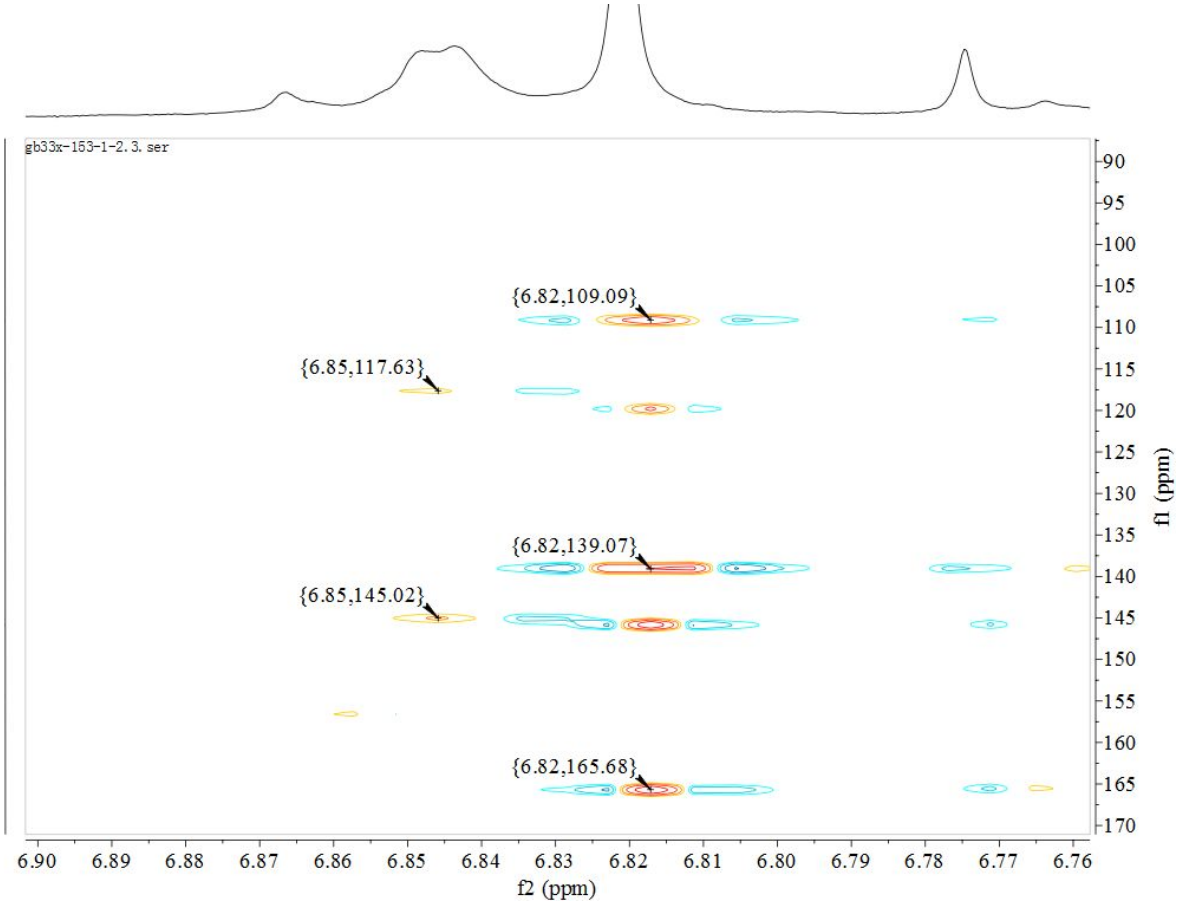


454 **SI. Figure 43.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 6.62 (calibrated

455 value), H-5′, 6‴, 8‴).



456 **SI. Figure 44.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 6.80 (calibrated

457 value), H-3″, 7″, and δ_H 6.85 (calibrated value), H-2′).

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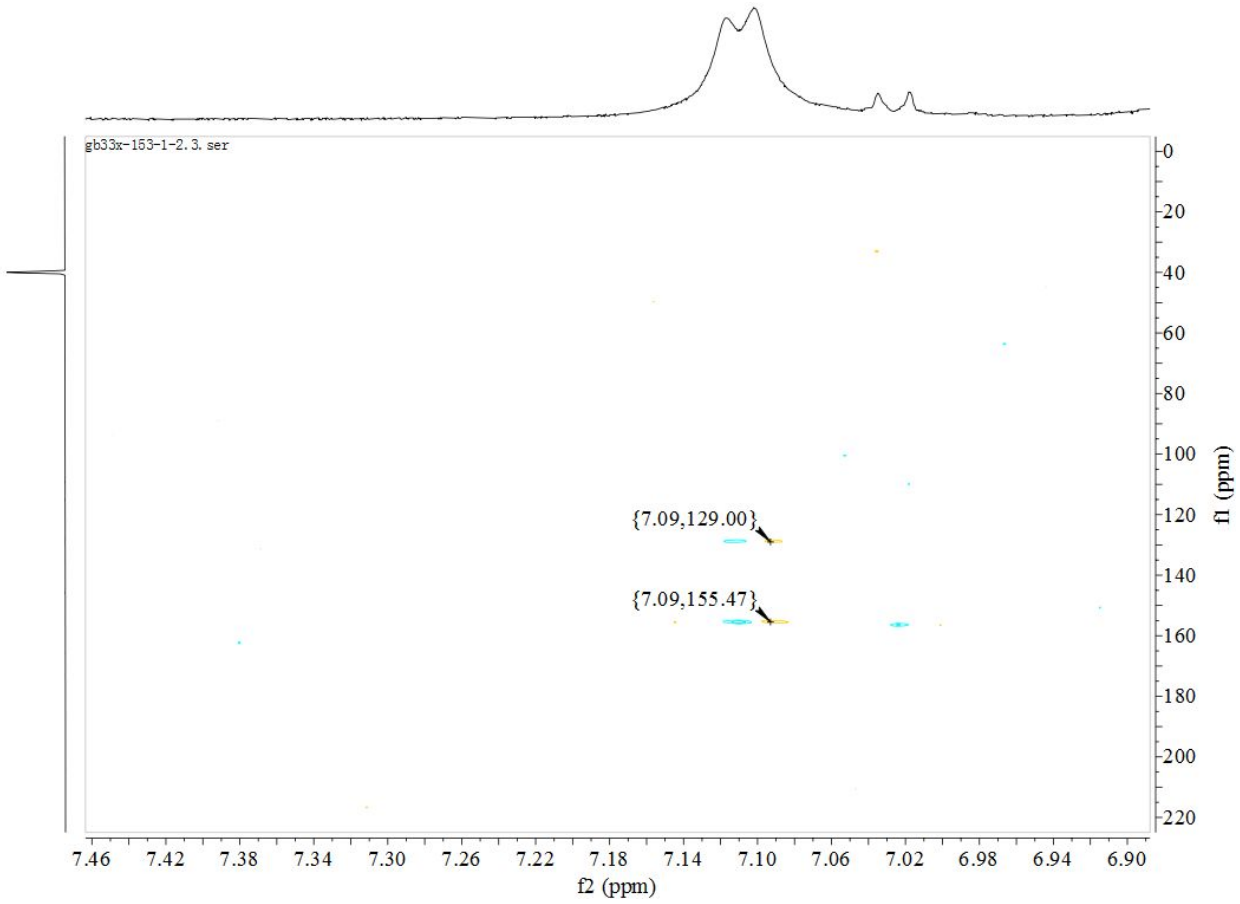
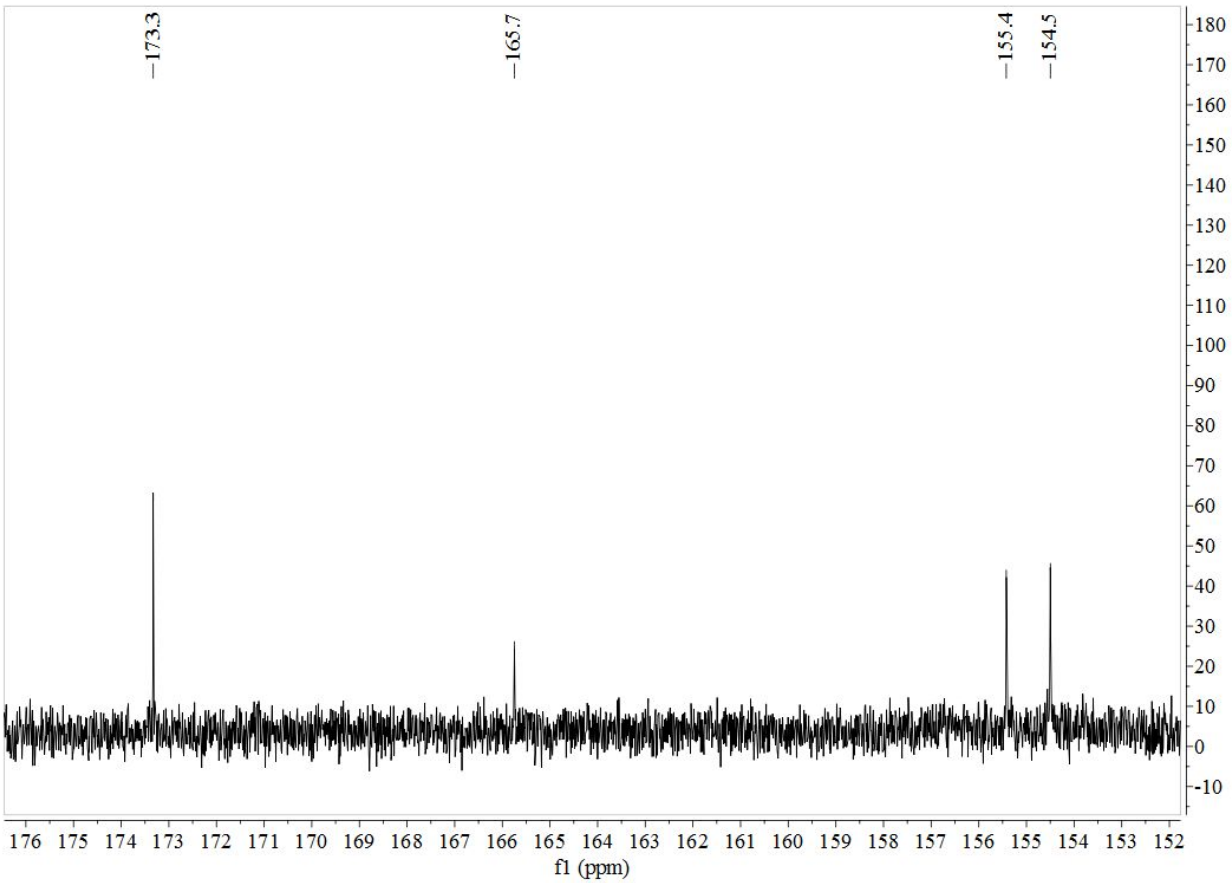
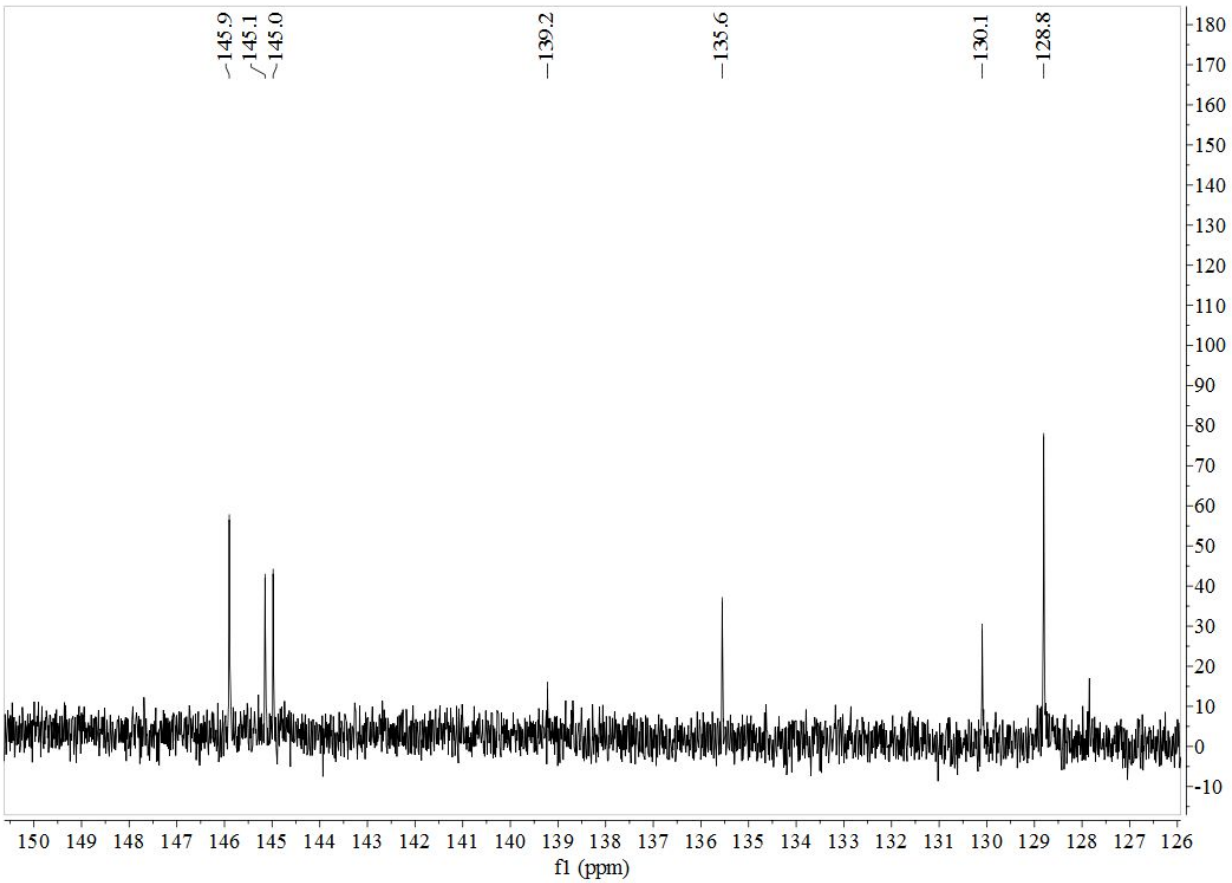


459 **SI. Figure 45.** Local HMBC spectrum of compound **2** (in DMSO-d_6; δ, ppm, δ_H 7.09 (calibrated

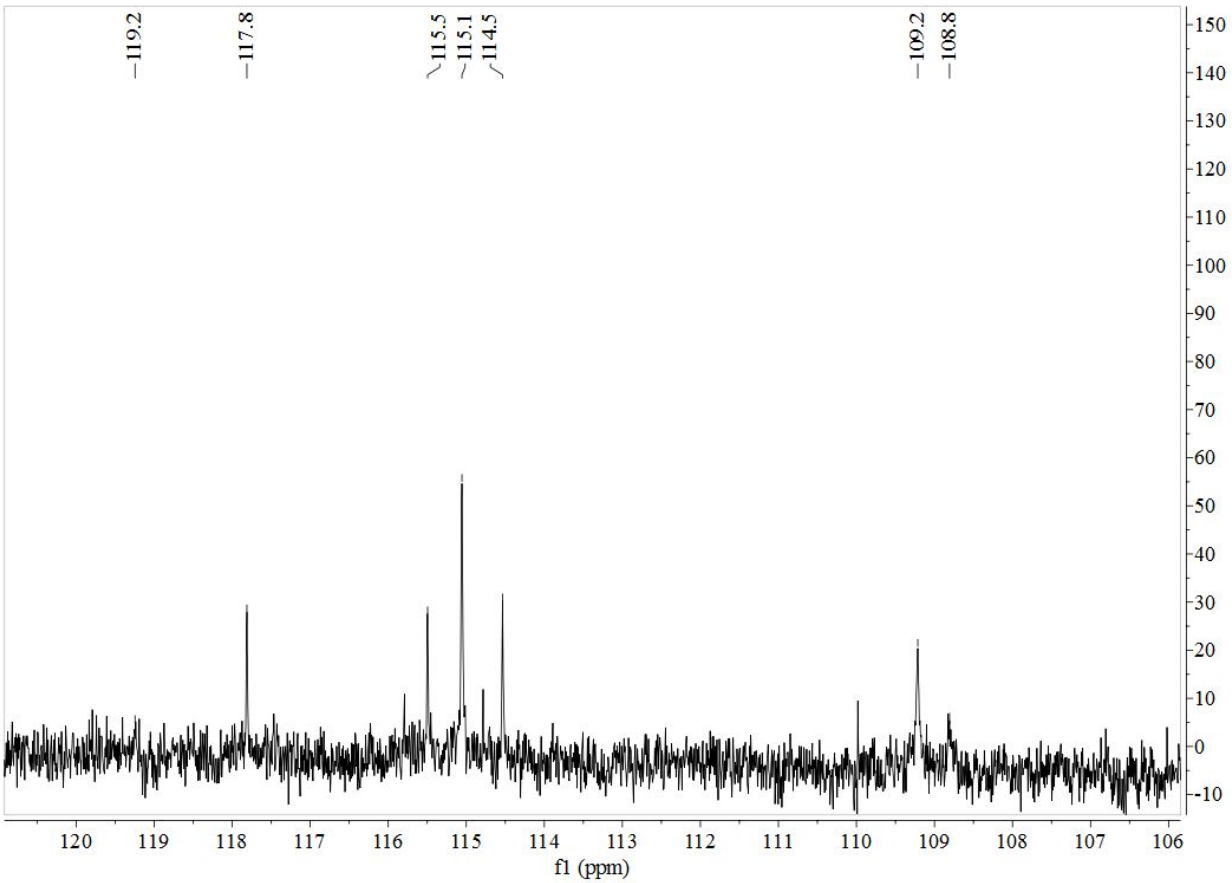
460 value), H-5‴, 9‴).



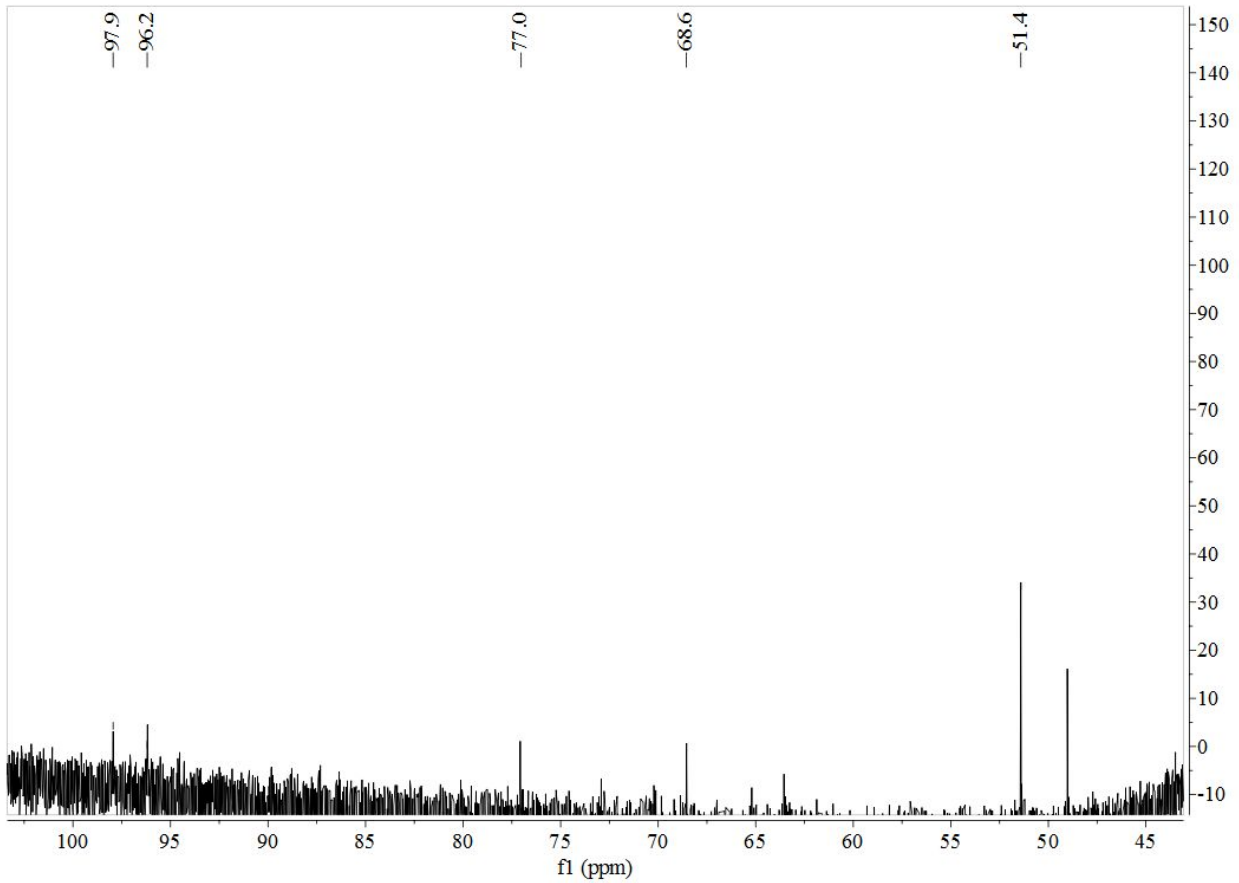
461 **SI. Figure 46.** ^{13}C NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; δ_C 150–180).



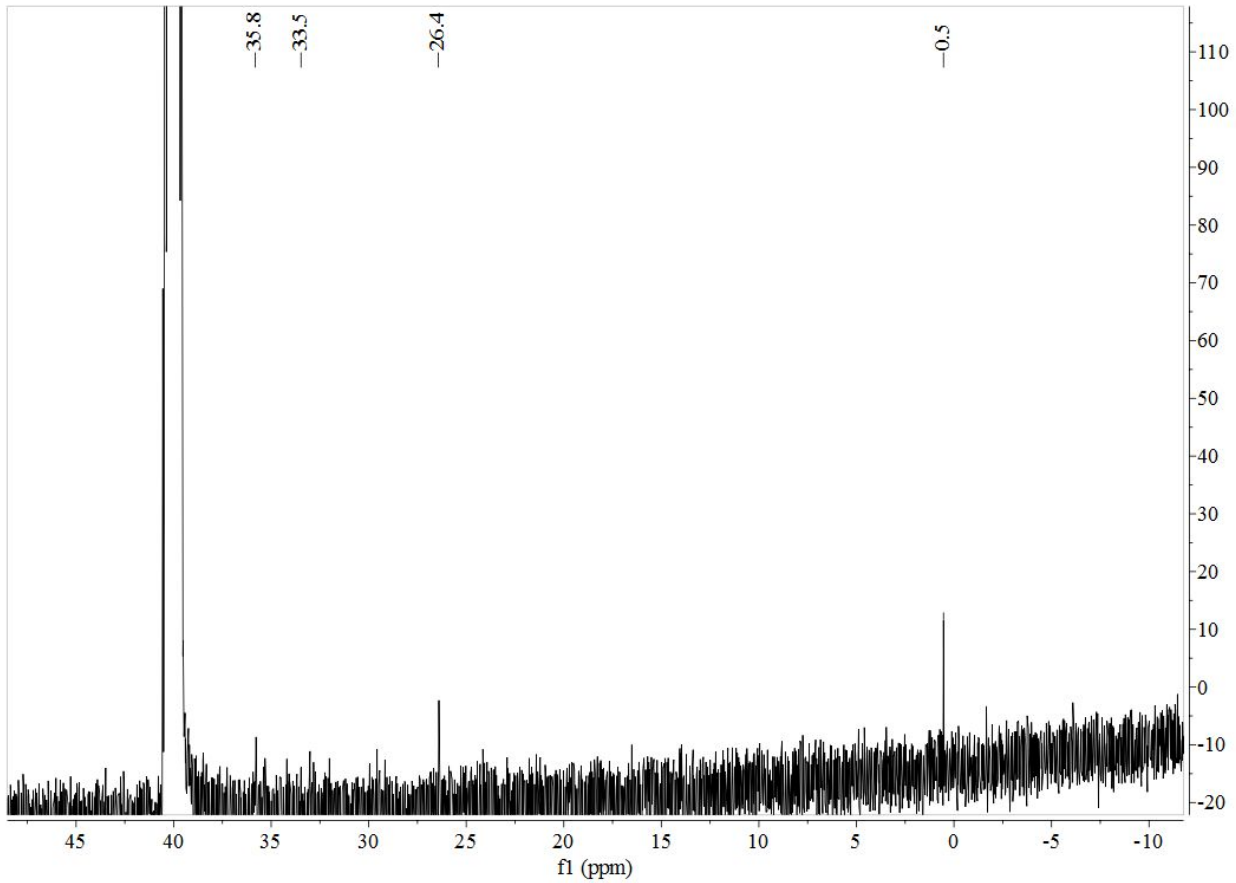
462 **SI. Figure 47.** ^{13}C NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; δ_C 120–150).



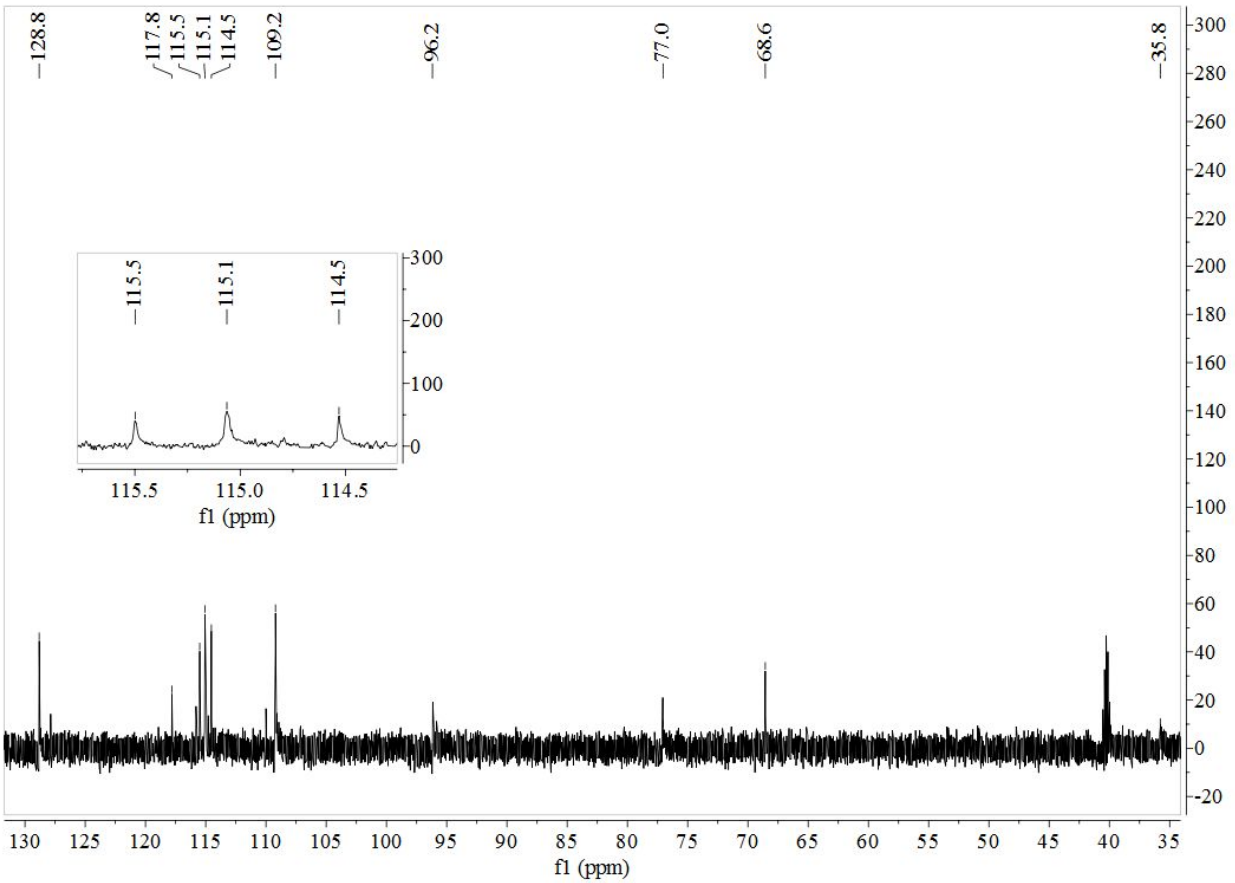
463 **SI. Figure 48.** ^{13}C NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; δ_C 100–120).



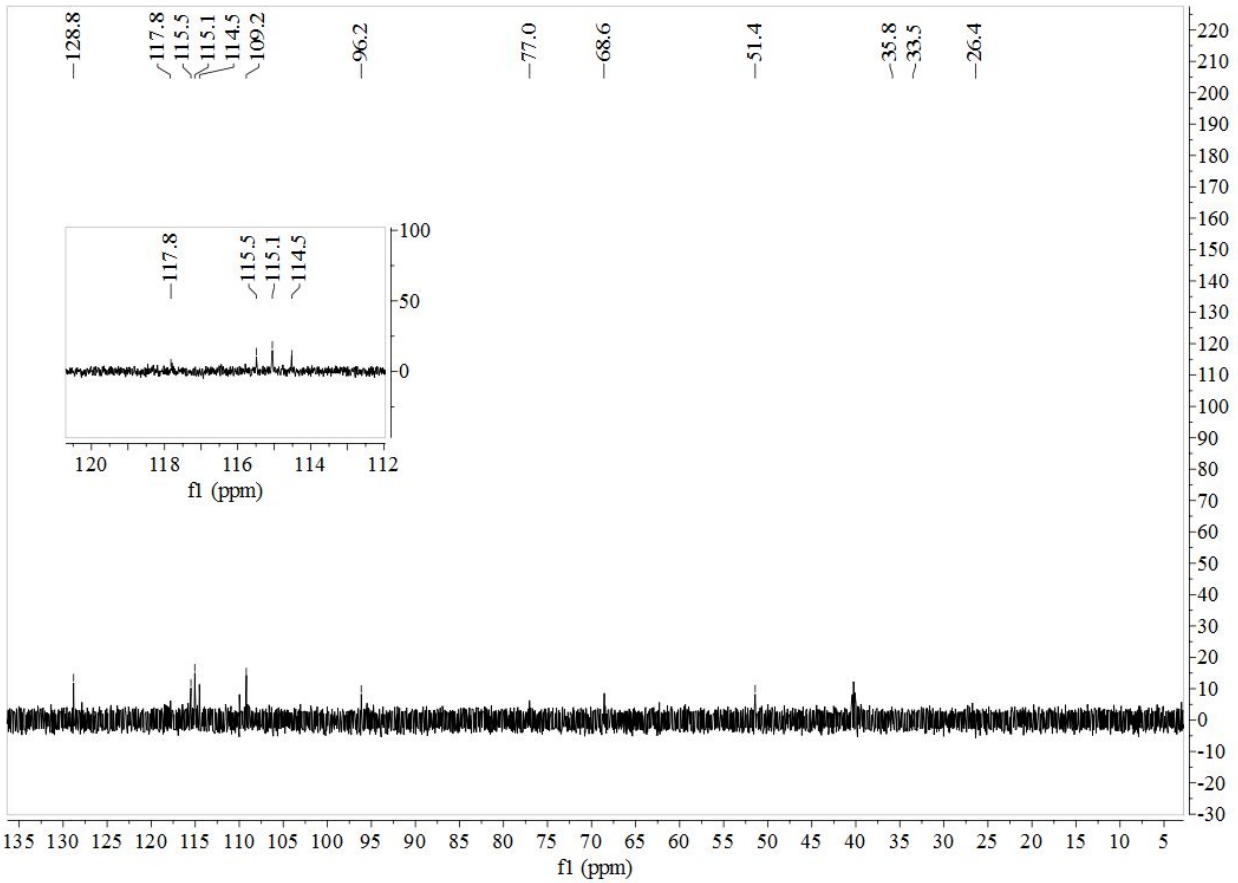
464 **SI. Figure 49.** ^{13}C NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; δ_C 50–100).



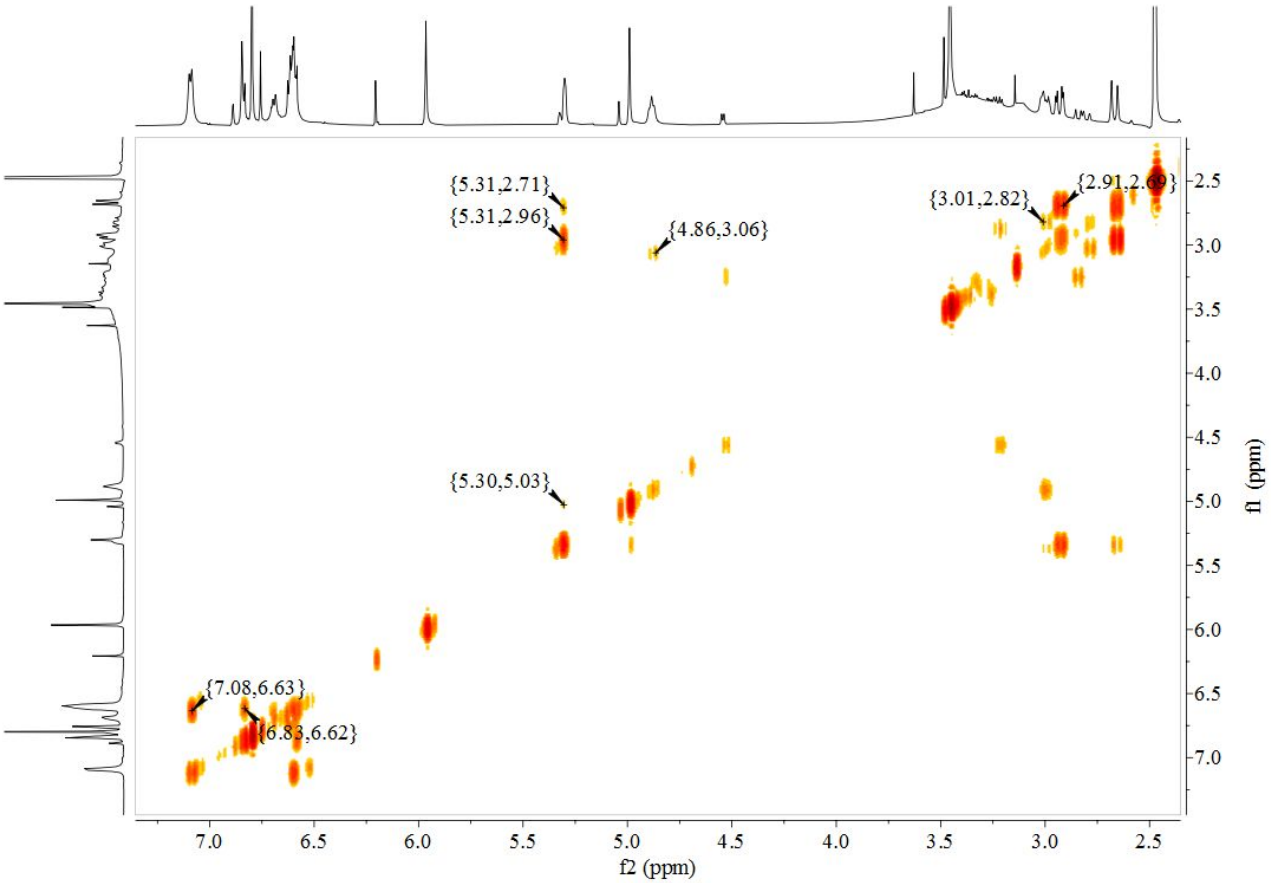
SI. Figure 50. ^{13}C NMR spectrum of compound **2** (in DMSO-d_6; δ, ppm; δ_C 0–50).



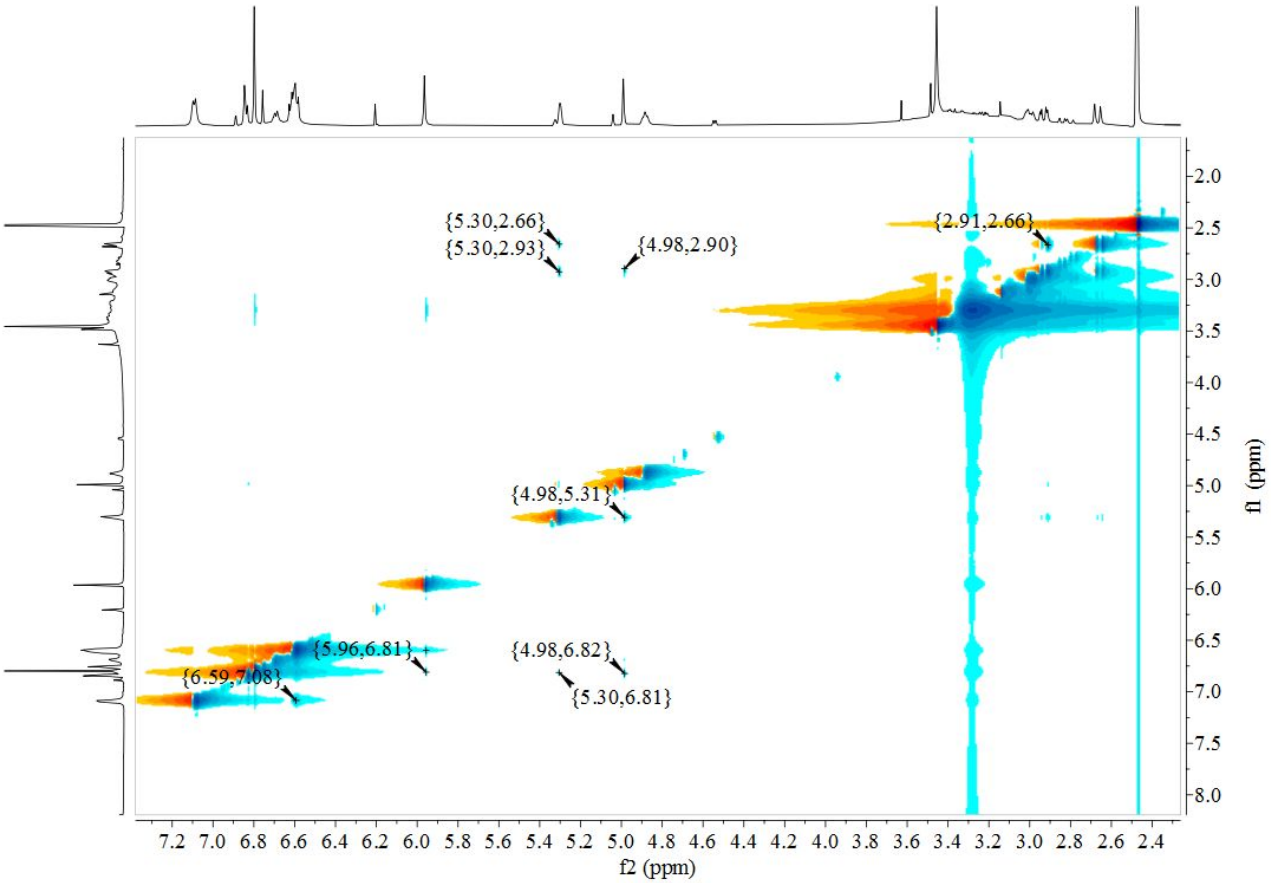
466 **SI. Figure 51.** DEPT–90 spectrum of compound **2** (in DMSO-d_6; δ, ppm).



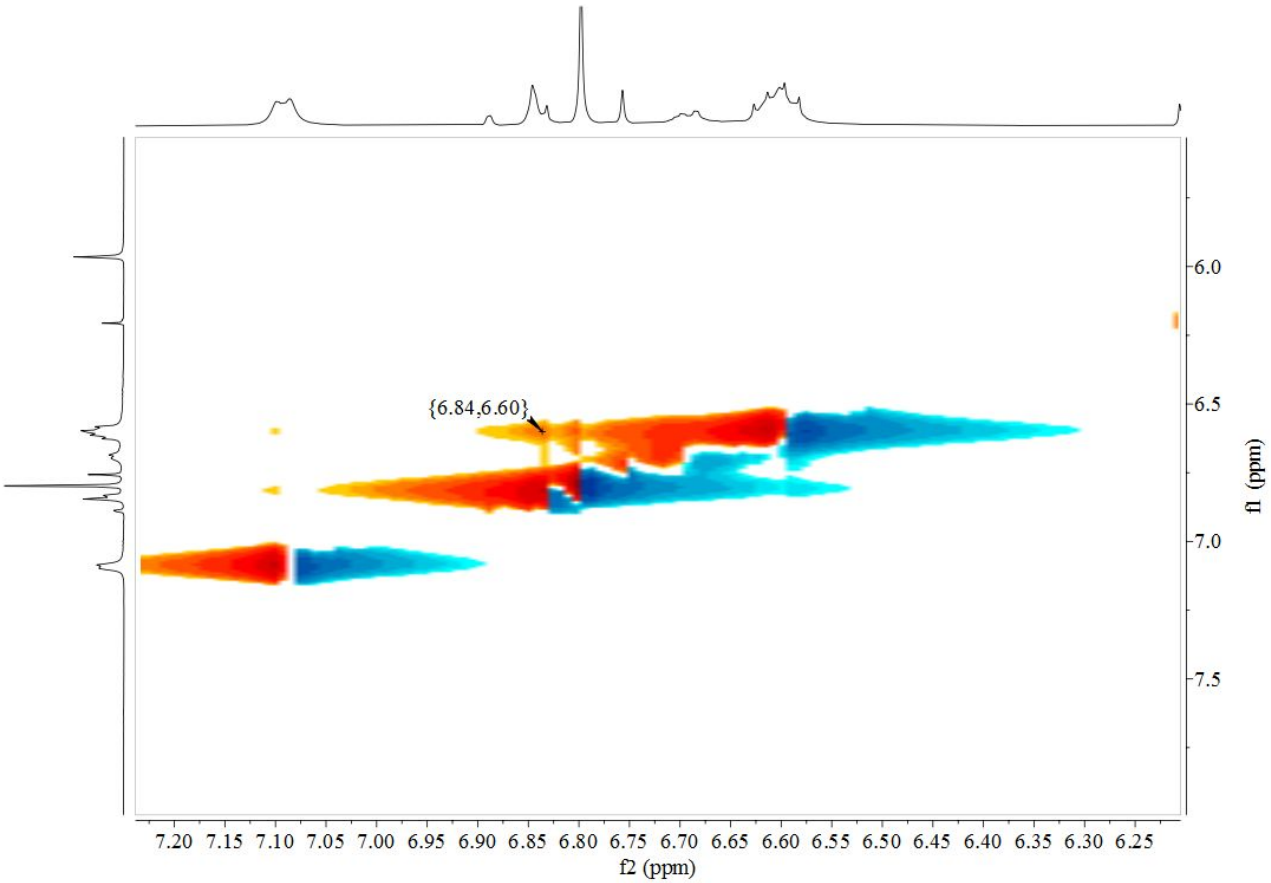
467 **SI. Figure 52.** DEPT–135 spectrum of compound **2** (in DMSO-d_6; δ, ppm).



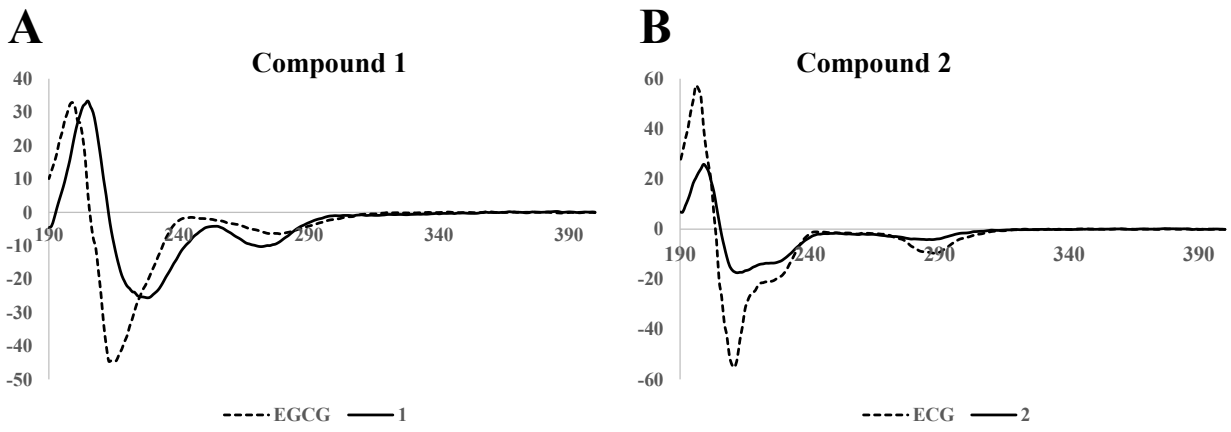
468 **SI. Figure 53.** ^{1}H–^{1}H COSY spectrum of compound **2** (in DMSO-d_6; δ, ppm).



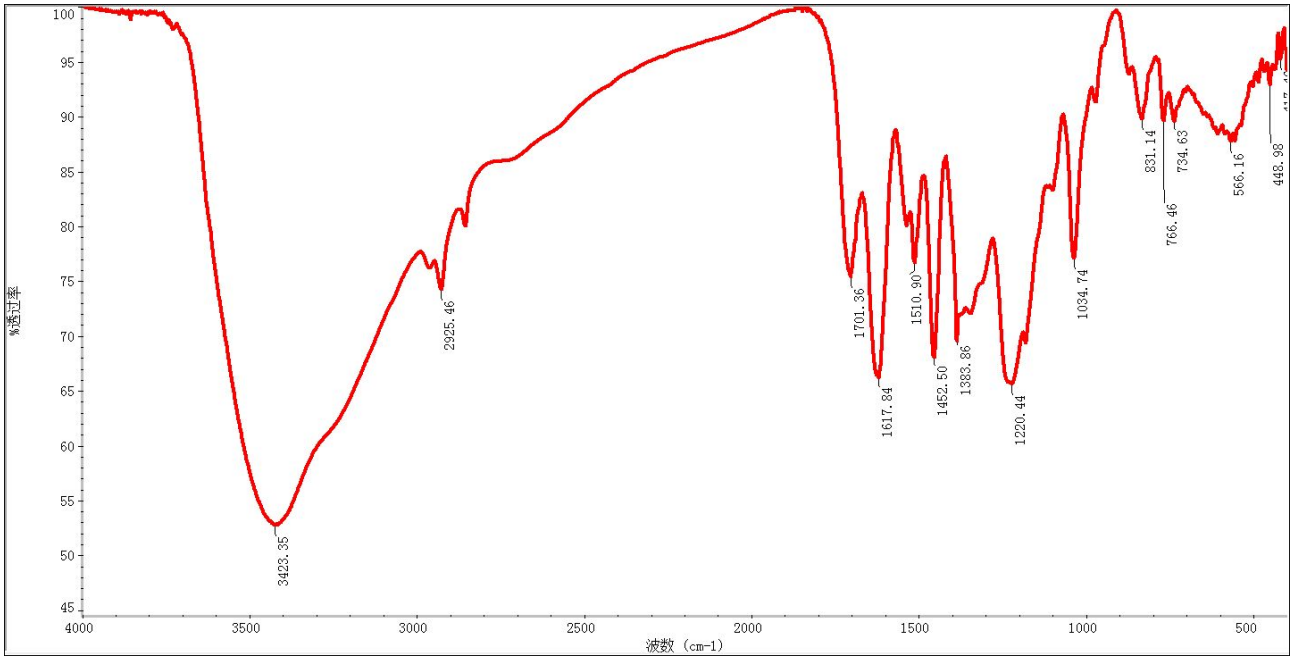
469 **SI. Figure 54.** NOESY spectrum of compound **2** (in DMSO-d_6; δ, ppm).



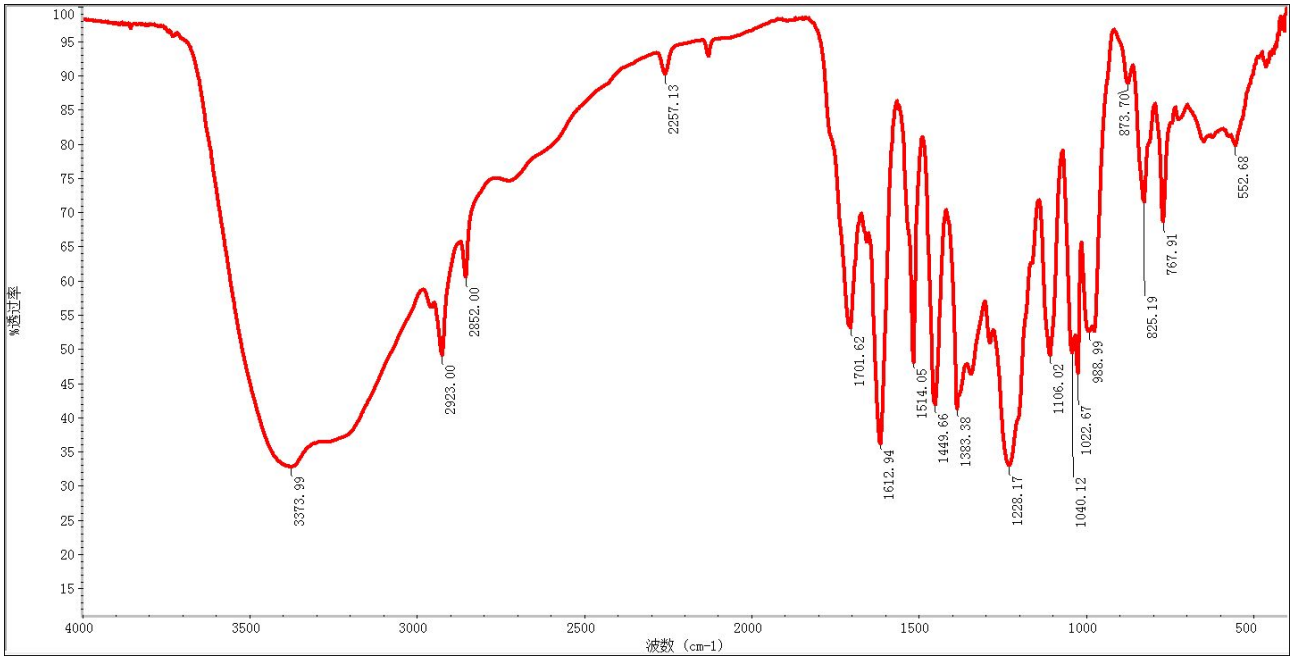
SI. Figure 55. Local NOESY spectrum of compound **2** (in DMSO-d_6; δ, ppm).



SI. Figure 56. CD spectrum of compound **1** and compound **2**.



SI. Figure 57. IR spectrum of compound **1**.



SI. Figure 58. IR spectrum of compound **2**.

485 **SI. Table 1.** The MW of PSECs with type A combination form.

Type A	MW	PM_1-1 148.05243	PM_2-1 164.04734	PM_3-1 180.04226	PM_4-1 194.05791	PM_5-1 224.06847	PM_6-1 196.03717
EC_1-1	**426.09508**	556.13694	572.13185	588.12677	602.14242	632.15298	604.12168
EC_1-2	**440.11073**	570.15259	586.14750	602.14242	616.15807	646.16863	618.13733
EC_1-3	**404.12599**	534.16785	550.16276	566.15768	580.17333	610.18389	582.15259
EC_1-4	**420.12090**	550.16276	566.15767	582.15259	596.16824	626.17880	598.14750
EC_1-5	**436.11582**	566.15768	582.15259	598.14751	612.16316	642.17372	614.14242
EC_1-6	**450.13147**	580.17333	596.16824	612.16316	626.17881	656.18937	628.15807
EC_1-7	**480.14203**	610.18389	626.17880	642.17372	656.18937	686.19993	658.16863
EC_2-1	**442.09000**	572.13186	588.12677	604.12169	618.13734	648.14790	620.11660
EC_2-2	**456.10565**	586.14751	602.14242	618.13734	632.15299	662.16355	634.13225
EC_2-3	**420.12090**	550.16276	566.15767	582.15259	596.16824	626.17880	598.14750
EC_2-4	**436.11582**	566.15768	582.15259	598.14751	612.16316	642.17372	614.14242
EC_2-5	**452.11073**	582.15259	598.14750	614.14242	628.15807	658.16863	630.13733
EC_2-6	**466.12638**	596.16824	612.16315	628.15807	642.17372	672.18428	644.15298
EC_2-7	**496.13695**	626.17881	642.17372	658.16864	672.18429	702.19485	674.16355
EC_3-1	**458.08491**	588.12677	604.12168	620.11660	634.13225	664.14281	636.11151
EC_3-2	**472.10056**	602.14242	618.13733	634.13225	648.14790	678.15846	650.12716
EC_3-3	**436.11582**	566.15768	582.15259	598.14751	612.16316	642.17372	614.14242
EC_3-4	**452.11073**	582.15259	598.14750	614.14242	628.15807	658.16863	630.13733
EC_3-5	**468.10565**	598.14751	614.14242	630.13734	644.15299	674.16355	646.13225
EC_3-6	**482.12130**	612.16316	628.15807	644.15299	658.16864	688.17920	660.14790
EC_3-7	**512.13186**	642.17372	658.16863	674.16355	688.17920	718.18976	690.15846

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SI. Table 2. The MW of PSECs with type B combination form.

Type B		PM_1-1	PM_1-2	PM_1-3	PM_2-1	PM_2-2	PM_2-3	PM_3-1	PM_3-2	PM_3-3
	MW	148.05243	162.06808	176.08373	164.04734	178.06299	192.07864	180.04226	194.05791	208.07356
EC_1-1	426.09508	572.13185	586.14750	600.16315	588.12676	602.14241	616.15806	604.12168	618.13733	632.15298
EC_1-2	440.11073	586.14750	600.16315	614.17880	602.14241	616.15806	630.17371	618.13733	632.15298	646.16863
EC_1-3	404.12599	550.16276	564.17841	578.19406	566.15767	580.17332	594.18897	582.15259	596.16824	610.18389
EC_1-4	420.12090	566.15767	580.17332	594.18897	582.15258	596.16823	610.18388	598.14750	612.16315	626.17880
EC_1-5	436.11582	582.15259	596.16824	610.18389	598.14750	612.16315	626.17880	614.14242	628.15807	642.17372
EC_1-6	450.13147	596.16824	610.18389	624.19954	612.16315	626.17880	640.19445	628.15807	642.17372	656.18937
EC_1-7	480.14203	626.17880	640.19445	654.21010	642.17371	656.18936	670.20501	658.16863	672.18428	686.19993
EC_2-1	442.09000	588.12677	602.14242	616.15807	604.12168	618.13733	632.15298	620.11660	634.13225	648.14790
EC_2-2	456.10565	602.14242	616.15807	630.17372	618.13733	632.15298	646.16863	634.13225	648.14790	662.16355
EC_2-3	420.12090	566.15767	580.17332	594.18897	582.15258	596.16823	610.18388	598.14750	612.16315	626.17880
EC_2-4	436.11582	582.15259	596.16824	610.18389	598.14750	612.16315	626.17880	614.14242	628.15807	642.17372
EC_2-5	452.11073	598.14750	612.16315	626.17880	614.14241	628.15806	642.17371	630.13733	644.15298	658.16863
EC_2-6	466.12638	612.16315	626.17880	640.19445	628.15806	642.17371	656.18936	644.15298	658.16863	672.18428
EC_2-7	496.13695	642.17372	656.18937	670.20502	658.16863	672.18428	686.19993	674.16355	688.17920	702.19485
EC_3-1	458.08491	604.12168	618.13733	632.15298	620.11659	634.13224	648.14789	636.11151	650.12716	664.14281
EC_3-2	472.10056	618.13733	632.15298	646.16863	634.13224	648.14789	662.16354	650.12716	664.14281	678.15846
EC_3-3	436.11582	582.15259	596.16824	610.18389	598.14750	612.16315	626.17880	614.14242	628.15807	642.17372
EC_3-4	452.11073	598.14750	612.16315	626.17880	614.14241	628.15806	642.17371	630.13733	644.15298	658.16863
EC_3-5	468.10565	614.14242	628.15807	642.17372	630.13733	644.15298	658.16863	646.13225	660.14790	674.16355
EC_3-6	482.12130	628.15807	642.17372	656.18937	644.15298	658.16863	672.18428	660.14790	674.16355	688.17920
EC_3-7	512.13186	658.16863	672.18428	686.19993	674.16354	688.17919	702.19484	690.15846	704.17411	718.18976

Type B		PM_4-1	PM_4-2	PM_4-3	PM_5-1	PM_5-2	PM_5-3	PM_6-1	PM_6-2	PM_6-3
	MW	194.05791	208.07356	222.08921	224.06847	238.08412	252.09977	196.03717	210.05282	224.06847
EC_1-1	426.09508	618.13733	632.15298	646.16863	648.14789	662.16354	676.17919	620.11659	634.13224	648.14789
EC_1-2	440.11073	632.15298	646.16863	660.18428	662.16354	676.17919	690.19484	634.13224	648.14789	662.16354
EC_1-3	404.12599	596.16824	610.18389	624.19954	626.17880	640.19445	654.21010	598.14750	612.16315	626.17880
EC_1-4	420.12090	612.16315	626.17880	640.19445	642.17371	656.18936	670.20501	614.14241	628.15806	642.17371
EC_1-5	436.11582	628.15807	642.17372	656.18937	658.16863	672.18428	686.19993	630.13733	644.15298	658.16863
EC_1-6	450.13147	642.17372	656.18937	670.20502	672.18428	686.19993	700.21558	644.15298	658.16863	672.18428
EC_1-7	480.14203	672.18428	686.19993	700.21558	702.19484	716.21049	730.22614	674.16354	688.17919	702.19484
EC_2-1	442.09000	634.13225	648.14790	662.16355	664.14281	678.15846	692.17411	636.11151	650.12716	664.14281
EC_2-2	456.10565	648.14790	662.16355	676.17920	678.15846	692.17411	706.18976	650.12716	664.14281	678.15846
EC_2-3	420.12090	612.16315	626.17880	640.19445	642.17371	656.18936	670.20501	614.14241	628.15806	642.17371
EC_2-4	436.11582	628.15807	642.17372	656.18937	658.16863	672.18428	686.19993	630.13733	644.15298	658.16863
EC_2-5	452.11073	644.15298	658.16863	672.18428	674.16354	688.17919	702.19484	646.13224	660.14789	674.16354
EC_2-6	466.12638	658.16863	672.18428	686.19993	688.17919	702.19484	716.21049	660.14789	674.16354	688.17919
EC_2-7	496.13695	688.17920	702.19485	716.21050	718.18976	732.20541	746.22106	690.15846	704.17411	718.18976
EC_3-1	458.08491	650.12716	664.14281	678.15846	680.13772	694.15337	708.16902	652.10642	666.12207	680.13772
EC_3-2	472.10056	664.14281	678.15846	692.17411	694.15337	708.16902	722.18467	666.12207	680.13772	694.15337
EC_3-3	436.11582	628.15807	642.17372	656.18937	658.16863	672.18428	686.19993	630.13733	644.15298	658.16863
EC_3-4	452.11073	644.15298	658.16863	672.18428	674.16354	688.17919	702.19484	646.13224	660.14789	674.16354
EC_3-5	468.10565	660.14790	674.16355	688.17920	690.15846	704.17411	718.18976	662.12716	676.14281	690.15846
EC_3-6	482.12130	674.16355	688.17920	702.19485	704.17411	718.18976	732.20541	676.14281	690.15846	704.17411
EC_3-7	512.13186	704.17411	718.18976	732.20541	734.18467	748.20032	762.21597	706.15337	720.16902	734.18467

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SI. Table 3. The MW of PSECs with type C combination form.

Type C		PM_1-1	PM_1-2	PM_1-3	PM_2-1	PM_2-2	PM_2-3	PM_3-1	PM_3-2	PM_3-3
	MW	**148.05243**	**162.06808**	**176.08373**	**164.04734**	**178.06299**	**192.07864**	**180.04226**	**194.05791**	**208.07356**
EC_1-1	**426.09508**	574.14751	588.16316	602.17881	590.14242	604.15807	618.17372	606.13734	620.15299	634.16864
EC_1-2	**440.11073**	588.16316	602.17881	616.19446	604.15807	618.17372	632.18937	620.15299	634.16864	648.18429
EC_1-3	**404.12599**	552.17842	566.19407	580.20972	568.17333	582.18898	596.20463	584.16825	598.18390	612.19955
EC_1-4	**420.12090**	568.17333	582.18898	596.20463	584.16824	598.18389	612.19954	600.16316	614.17881	628.19446
EC_1-5	**436.11582**	584.16825	598.18390	612.19955	600.16316	614.17881	628.19446	616.15808	630.17373	644.18938
EC_1-6	**450.13147**	598.18390	612.19955	626.21520	614.17881	628.19446	642.21011	630.17373	644.18938	658.20503
EC_1-7	**480.14203**	628.19446	642.21011	656.22576	644.18937	658.20502	672.22067	660.18429	674.19994	688.21559
EC_2-1	**442.09000**	590.14243	604.15808	618.17373	606.13734	620.15299	634.16864	622.13226	636.14791	650.16356
EC_2-2	**456.10565**	604.15808	618.17373	632.18938	620.15299	634.16864	648.18429	636.14791	650.16356	664.17921
EC_2-3	**420.12090**	568.17333	582.18898	596.20463	584.16824	598.18389	612.19954	600.16316	614.17881	628.19446
EC_2-4	**436.11582**	584.16825	598.18390	612.19955	600.16316	614.17881	628.19446	616.15808	630.17373	644.18938
EC_2-5	**452.11073**	600.16316	614.17881	628.19446	616.15807	630.17372	644.18937	632.15299	646.16864	660.18429
EC_2-6	**466.12638**	614.17881	628.19446	642.21011	630.17372	644.18937	658.20502	646.16864	660.18429	674.19994
EC_2-7	**496.13695**	644.18938	658.20503	672.22068	660.18429	674.19994	688.21559	676.17921	690.19486	704.21051
EC_3-1	**458.08491**	606.13734	620.15299	634.16864	622.13225	636.14790	650.16355	638.12717	652.14282	666.15847
EC_3-2	**472.10056**	620.15299	634.16864	648.18429	636.14790	650.16355	664.17920	652.14282	666.15847	680.17412
EC_3-3	**436.11582**	584.16825	598.18390	612.19955	600.16316	614.17881	628.19446	616.15808	630.17373	644.18938
EC_3-4	**452.11073**	600.16316	614.17881	628.19446	616.15807	630.17372	644.18937	632.15299	646.16864	660.18429
EC_3-5	**468.10565**	616.15808	630.17373	644.18938	632.15299	646.16864	660.18429	648.14791	662.16356	676.17921
EC_3-6	**482.12130**	630.17373	644.18938	658.20503	646.16864	660.18429	674.19994	662.16356	676.17921	690.19486
EC_3-7	**512.13186**	660.18429	672.18428	686.19993	674.16354	688.17919	702.19484	690.15846	704.17411	718.18976

Type C		PM_4-1	PM_4-2	PM_4-3	PM_5-1	PM_5-2	PM_5-3	PM_6-1	PM_6-2	PM_6-3
	MW	194.05791	208.07356	222.08921	224.06847	238.08412	252.09977	196.03717	210.05282	224.06847
EC_1-1	426.09508	620.15299	634.16864	648.18429	650.16355	664.17920	678.19485	622.13225	636.14790	650.16355
EC_1-2	440.11073	634.16864	648.18429	662.19994	664.17920	678.19485	692.21050	636.14790	650.16355	664.17920
EC_1-3	404.12599	598.18390	612.19955	626.21520	628.19446	642.21011	656.22576	600.16316	614.17881	628.19446
EC_1-4	420.12090	614.17881	628.19446	642.21011	644.18937	658.20502	672.22067	616.15807	630.17372	644.18937
EC_1-5	436.11582	630.17373	644.18938	658.20503	660.18429	674.19994	688.21559	632.15299	646.16864	660.18429
EC_1-6	450.13147	644.18938	658.20503	672.22068	674.19994	688.21559	702.23124	646.16864	660.18429	674.19994
EC_1-7	480.14203	674.19994	688.21559	702.23124	704.21050	718.22615	732.24180	676.17920	690.19485	704.21050
EC_2-1	442.09000	636.14791	650.16356	664.17921	666.15847	680.17412	694.18977	638.12717	652.14282	666.15847
EC_2-2	456.10565	650.16356	664.17921	678.19486	680.17412	694.18977	708.20542	652.14282	666.15847	680.17412
EC_2-3	420.12090	614.17881	628.19446	642.21011	644.18937	658.20502	672.22067	616.15807	630.17372	644.18937
EC_2-4	436.11582	630.17373	644.18938	658.20503	660.18429	674.19994	688.21559	632.15299	646.16864	660.18429
EC_2-5	452.11073	646.16864	660.18429	674.19994	676.17920	690.19485	704.21050	648.14790	662.16355	676.17920
EC_2-6	466.12638	660.18429	674.19994	688.21559	690.19485	704.21050	718.22615	662.16355	676.17920	690.19485
EC_2-7	496.13695	690.19486	704.21051	718.22616	720.20542	734.22107	748.23672	692.17412	706.18977	720.20542
EC_3-1	458.08491	652.14282	666.15847	680.17412	682.15338	696.16903	710.18468	654.12208	668.13773	682.15338
EC_3-2	472.10056	666.15847	680.17412	694.18977	696.16903	710.18468	724.20033	668.13773	682.15338	696.16903
EC_3-3	436.11582	630.17373	644.18938	658.20503	660.18429	674.19994	688.21559	632.15299	646.16864	660.18429
EC_3-4	452.11073	646.16864	660.18429	674.19994	676.17920	690.19485	704.21050	648.14790	662.16355	676.17920
EC_3-5	468.10565	662.16356	676.17921	690.19486	692.17412	706.18977	720.20542	664.14282	678.15847	692.17412
EC_3-6	482.12130	676.17921	690.19486	704.21051	706.18977	720.20542	734.22107	678.15847	692.17412	706.18977
EC_3-7	512.13186	704.17411	718.18976	732.20541	734.18467	748.20032	762.21597	706.15337	720.16902	734.18467

SI. Table 4. The MW of PSECs with type D combination form.

Type D		PM_1-1	PM_2-1	PM_3-1	PM_4-1	PM_5-1	PM_6-1
	MW	148.05243	164.04734	180.04226	194.05791	224.06847	196.03717
EC_1-1	426.09508	686.17880	718.16862	750.15846	778.18976	838.21088	782.14828
EC_1-2	440.11073	700.19445	732.18427	764.17411	792.20541	852.22653	796.16393
EC_1-3	404.12599	664.20971	696.19953	728.18937	756.22067	816.24179	760.17919
EC_1-4	420.12090	680.20462	712.19444	744.18428	772.21558	832.23670	776.17410
EC_1-5	436.11582	696.19954	728.18936	760.17920	788.21050	848.23162	792.16902
EC_1-6	450.13147	710.21519	742.20501	774.19485	802.22615	862.24727	806.18467
EC_1-7	480.14203	740.22575	772.21557	804.20541	832.23671	892.25783	836.19523
EC_2-1	442.09000	702.17372	734.16354	766.15338	794.18468	854.20580	798.14320
EC_2-2	456.10565	716.18937	748.17919	780.16903	808.20033	868.22145	812.15885
EC_2-3	420.12090	680.20462	712.19444	744.18428	772.21558	832.23670	776.17410
EC_2-4	436.11582	696.19954	728.18936	760.17920	788.21050	848.23162	792.16902
EC_2-5	452.11073	712.19445	744.18427	776.17411	804.20541	864.22653	808.16393
EC_2-6	466.12638	726.21010	758.19992	790.18976	818.22106	878.24218	822.17958
EC_2-7	496.13695	756.22067	788.21049	820.20033	848.23163	908.25275	852.19015
EC_3-1	458.08491	718.16863	750.15845	782.14829	810.17959	870.20071	814.13811
EC_3-2	472.10056	732.18428	764.17410	796.16394	824.19524	884.21636	828.15376
EC_3-3	436.11582	696.19954	728.18936	760.17920	788.21050	848.23162	792.16902
EC_3-4	452.11073	712.19445	744.18427	776.17411	804.20541	864.22653	808.16393
EC_3-5	468.10565	728.18937	760.17919	792.16903	820.20033	880.22145	824.15885
EC_3-6	482.12130	742.20502	774.19484	806.18468	834.21598	894.23710	838.17450
EC_3-7	512.13186	772.21558	804.20540	836.19524	864.22654	924.24766	868.18506

509 **SI. Table 5.** Different elution methods used in the pre-separation process.

Method 1	ACQUITY UPLC® BEH C18 (1.7 μm, 2.1×50 mm)			Method 3	ACQUITY UPLC® BEH C18 (1.7 μm, 2.1×50 mm)			
	Time	**Phase A**	**Phase B**	**flow(mL/min)**	**Time**	**Phase A**	**Phase B**	**flow(mL/min)**
	0	90	10	0.2	0	90	10	0.2
	0.5	90	10	0.2	0.5	90	10	0.2
	1.5	84	16	0.2	1.5	84	16	0.2
	4	71	29	0.2	4	71	29	0.2
	5.5	55	45	0.2	5.5	55	45	0.2
	7	5	95	0.2	7	5	95	0.2
	9	5	95	0.2	9	5	95	0.2
	10	90	10	0.2	10	90	10	0.2
	12	90	10	0.2	12	90	10	0.2
Method 2	ACQUITY UPLC® BEH C18 (1.7 μm, 2.1×50 mm)				Method 4	ACQUITY UPLC HSS T3 (1.8 μm, 2.1×100 mm)		
	Time	**Phase A**	**Phase B**	**flow(mL/min)**	**Time**	**Phase A**	**Phase B**	**flow(mL/min)**
	0	94	6	0.2	0	95	5	0.3
	0.5	94	6	0.2	0.5	95	5	0.3
	2.5	84	16	0.2	1.5	90	10	0.3
	3	82	18	0.2	4	75	25	0.3
	5.5	71	29	0.2	6	65	35	0.3
	8	55	45	0.2	7.5	35	65	0.3
	9	5	95	0.2	8.5	15	85	0.3
	10.5	5	95	0.2	9	5	95	0.3
	11	94	6	0.2	10	5	95	0.3
	12	94	6	0.2	11	95	5	0.3
					12	95	5	0.3

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511 **SI. Table 6.** The corresponding relationship between sample fractions and elution methods in the pre-separation process.

samples	elution method	samples	elution method	samples	elution method	samples	elution method	samples	elution method
b4-6	Method 1	b6-5	Method 2	b7-10	Method 2	H1 (2 data)	Method 1	H2-1	Method 1
b4-7	Method 1	b6-7	Method 2	b7-5	Method 2	H1-14	Method 1	H2-10	Method 1
b5-c1-1	Method 2	b6-10	Method 2	b7-8	Method 2	H1-18	Method 1	H2-14	Method 1
b5-c1-4	Method 2	b6-c10	Method 1	b7-c1	Method 1	H1-20	Method 1	H2-18	Method 1
b5-c2-1	Method 2	b6-c13	Method 1	b7-c3	Method 1	H1-25	Method 4	H2-2	Method 1
b5-c3-3	Method 2	b6-c2	Method 1	b7-c4	Method 1	H1-29	Method 4	H2-2'	Method 1
b5-c3-5	Method 2	b6-c3	Method 3	b8-4	Method 2	H1-31	Method 4	H2-20	Method 1
b5-c3-d2-6	Method 1	b6-c5	Method 3	b8-7	Method 2	H1-5	Method 1	H2-21~24	Method 4
b5-c3-d2-7	Method 1	b6-c6	Method 3	b9-2	Method 2	H1-7	Method 1	H2-34~26	Method 4
		b6-c7	Method 3	b9-6	Method 2	H1-8	Method 1	H2-37	Method 4
		b6-c9	Method 3					H2-4	Method 1
								H2-6	Method 1

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514 **SI. Table 7.** Tea products used for the detection of PSECs.

No.	Sample	Location of cultivation	Tea varieties	Tea types
1	'Zijuan'	Yunnan	*Camellia sinensis* var. *assamica* cv.	Green tea
2	'Yinghong 9'	Guangdong	*Camellia sinensis* var. *assamica* cv.	Green tea
3	'Laos gaogan tea'	Laos	*Camellia sinensis* var. *assamica*	Green tea
4	'Huangjinya'	Zhejiang	*Camellia sinensis* var. *sinensis* cv.	Green tea
5	'Huangkui'	Anhui Xuancheng	*Camellia sinensis* var. *sinensis* cv.	Green tea
6	'Yiwu'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
7	'Xigui'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
8	'Bulangshan tea'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
9	'Echa 1'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	Green tea
10	'Zhenghedabai'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	Green tea
11	'Hekai'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
12	'Mojiang'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
13	'Lancang'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
14	'Huangjingui'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	Green tea
15	'Zimudan'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	Green tea
16	'Lu'an guapian'	Anhui Lu'an	*Camellia sinensis* var. *sinensis* cv.	Green tea
17	'Bulangchunjian'	Yunnan	*Camellia sinensis* var. *assamica*	Green tea
18	'Fudingdabai'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	Green tea

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517 **SI. Table 8.** Tea fresh leaves used for the detection of PSECs.

No.	Sample	Location of cultivation	Tea varieties	Tea types
1	'Fudingdabai'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave
2	'Zhenghedabai'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave
3	'Yaoshanxiulv'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave
4	'Longjing 43'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave
5	'Shuchazao'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave
6	'Sidamingjia'	AHAU Tea base	*Camellia sinensis* var. *sinensis* cv.	fresh leave

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523 **SI. Table 9.** The precursor ions' response intensity of the two PSECs molecules in 18 tea products.

No.	Precursor ions RT (min) CE (eV)	649.1199 9.98 18	619.1457 10.20 25	No.	Precursor ions RT (min) CE (eV)	649.1199 9.98 18	619.1457 10.20 25
		-	-			-	-
1	'Zijuan'	-	325.81	10	'Zhenghedabai'	-	-
		-	1088.37			-	-
		-	372.94			-	-
2	'Yinghong 9'	-	296.16	11	'Hekai'	-	302.45
		-	356.15			-	394
		-	-			-	-
3	'Laos gaogan tea'	-	-	12	'Mojiang'	-	280.48
		-	-			-	445.75
		-	-			-	-
4	'Huangjinya'	-	-	13	'Lancang'	-	268.98
		-	-			-	416.45
		-	-			-	-
5	'Huangkui'	-	-	14	'Huangjingui'	-	-
		-	271.6			-	-
		-	-			-	-
6	'Yiwu'	-	-	15	'Zimudan'	-	313.97
		-	-			-	314.58
		-	213.29			-	-
7	'Xigui'	-	349.85	16	'Lu'an guapian'	-	-
		-	256.49			-	230.02
		-	-			-	-
8	'Bulangshan tea'	-	298.42	17	'Bulangchunjian'	-	238.28
		-	346.85			-	352.39
		-	-			-	-
9	'Echa 1'	-	-	18	'Fudingdabai'	-	-
		-	-			-	-

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