Supporting Information

Phytochemical profiling and isolation of bioactive compounds from *Leucosidea sericea* (Rosaceae)

Tshifhiwa Ramabulana,[†] Musawenkosi Ndlovu,[‡] Rebamang A. Mosa,[‡] Molahlehi S. Sonopo,[§,*] Mamoalosi A. Selepe[†,*]

[†]Department of Chemistry, University of Pretoria, Lynnwood Rd, Hatfield, Pretoria 0002, South Africa

[‡]Department of Biochemistry, Genetics and Microbiology, University of Pretoria, Lynnwood Rd, Hatfield, Pretoria 0002, South Africa

[§]Radiochemistry, South African Nuclear Energy Corporation Ltd, Pelindaba, Brits 0240, South Africa

***Corresponding authors**

M.S. Sonopo E-mail address: molahlehi.sonopo@necsa.co.za, Tel: +27 12 305 5674

M.A. Selepe E-mail address: mamoalosi.selepe@up.ac.za, Tel: +27 12 420 2345

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UPLC-QTOf-MS Chromatogram

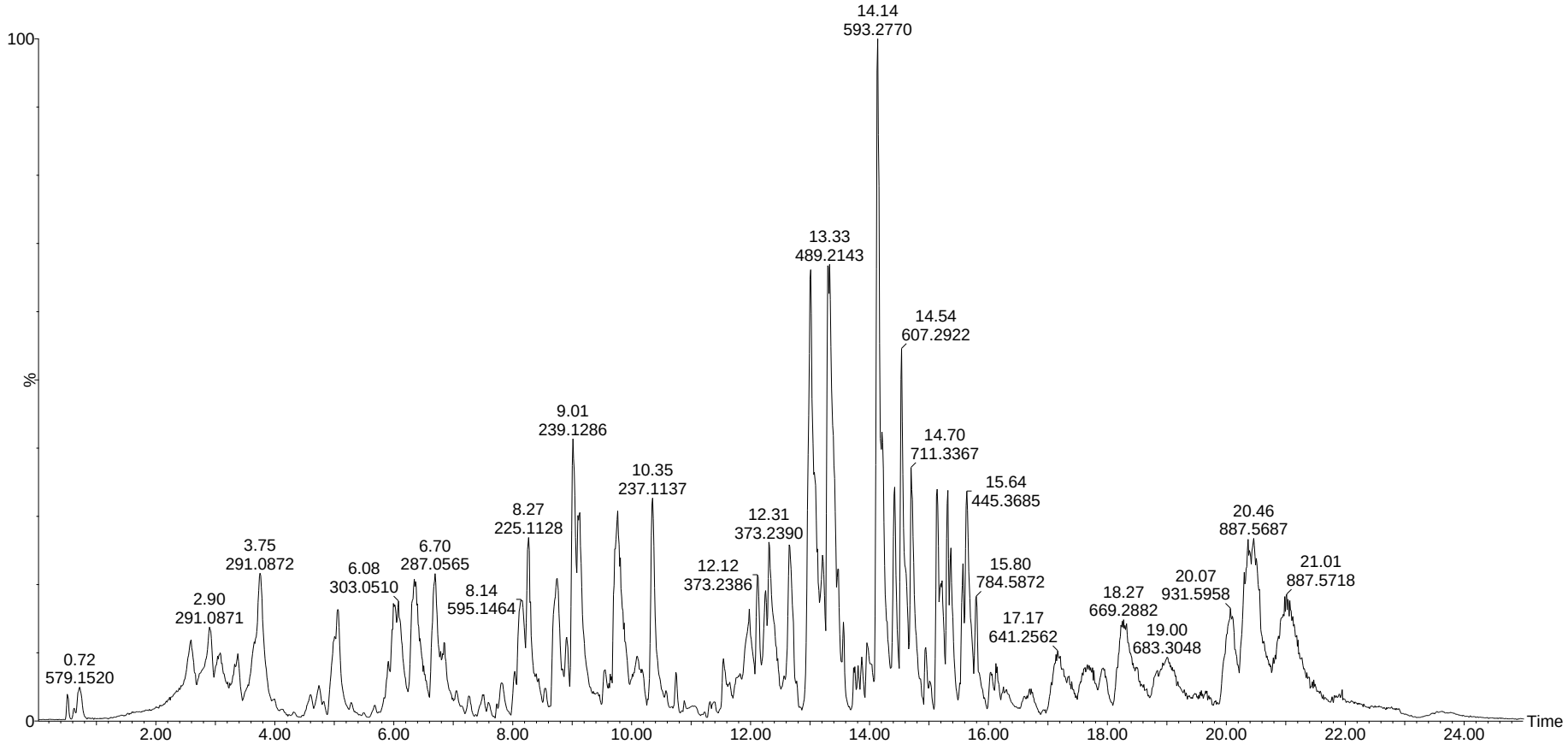


Figure S1. UPLC-MS base peak ion (BPI) chromatogram of EtOAc extract of *L. sericea*

Table S1: Tentatively identified compounds from negative and positive ionisation mode of *L. sericea* EtOAc extract.

Entry	Rt	*m/z* [Adduct]	Cal mass	Mass Error ppm	Fragments	Name	Chemical formula	Ref
1	2.59	577.1347 $[M-H]^-$	577.1346	0.2	425.0865, 407.0816, 289.0708	B-type procyanidin[a,c]	$C_{30}H_{26}O_{12}$	[1-3]
		579.1520 $[M+H]^+$	579.1503	2.9	427.2037, 291.0865, 247.0596, 165.0531, 139.0425			
2	2.90	289.0705 $[M-H]^-$	289.0712	-2.4	245.0794, 203.0686, 151.0383, 137.0233, 125.0240	(+)-Catechin[c]	$C_{15}H_{14}O_6$	[4,5]
		291.0871 $[M+H]^+$	291.0869	0.7	247.0607, 179.0347, 139.0346, 123.0453			
3	3.02	577.1348 $[M-H]^-$	577.1346	0.3	425.0879, 289.0712, 177.0188	B-type procyanidin [a,c]	$C_{30}H_{26}O_{12}$	[1-3]
		579.1503* $[M+H]^+$	579.1503	0.0	427.1022, 341.0863, 291.0869, 179.0346, 139.0433		$C_{30}H_{26}O_{12}$	
4	3.36	577.1354 $[M-H]^-$	577.1346	1.4	425.0857, 357.1109, 289.0721	B-type procyanidin[a,c]	$C_{30}H_{26}O_{12}$	[1-3]
		579.1499 $[M+H]^+$	579.1503	-0.7	441.0847, 291.0863, 179.0464, 139.0406			
5	3.75	289.0712 $[M-H]^-$	289.0712	0.0	245.0793, 221.0788, 203.0705, 137.0227, 125.0233, 109.0276	(−)-Epicatechin[c]	$C_{15}H_{14}O_6$	[4,5]
		291.0868 $[M+H]^+$	291.0869	-0.3	247.0607, 139.0401, 123.0453			
6	5.01	179.0353 $[M+H]^+$	179.0344	5.0	163.0386, 139.0386, 123.0446	5,7-Dihydroxychromone[a,b]	$C_9H_6O_4$	[2,6]
		177.0186 $[M-H]^-$	177.0188	-1.1	161.0246, 137.0214, 125.0238			
7	5.90	447.0927 $[M-H]^-$	447.0927	0.0	284.0388, 255.0302, 145.0292, 133.0287	Kaempferol-3-*O*-glucoside[b]	$C_{21}H_{20}O_{11}$	[1,7]
		895.1981 $[2M-H]^-$						
		449.1100 $[M+H]^+$	449.1084	3.6	287.0559, 153.0208, 135.0481			
8	5.99	463.0885 $[M-H]^-$	463.0877	1.7	300.0261, 271.0248, 255.0293, 243.0304	Quercetin-3-*O*-glucoside[b]	$C_{21}H_{20}O_{12}$	[8]
		465.1043 $[M+H]^+$	465.1044	-0.2	487.0857 $[M + Na]^+$, 303.0509, 287.0602, 153.0191, 137.0243			

9	6.04	609.1484 $[M-H]^-$	609.1456	4.6	463.0877, 301.0248, 271.0241, 255.0307, 243.0299, 151.0103	Quercetin-3-*O*-rutinoside[c]	$C_{27}H_{30}O_{16}$	[2,4]
10	6.08	609.1464 $[M-H]^-$ 611.1646 $[M+H]^+$	609.1456 611.1612	1.3 0.3	463.0882, 301.0267, 271.0246, 255.0278, 243.0308, 151.0069 465.0992, 449.1035, 303.0513, 271.0617	Quercetin-3-*O*-rutinoside isomer[c]	$C_{27}H_{30}O_{16}$	[2,4]
11	6.34	433.0782 $[M-H]^-$ 435.0939$[M+H]^+$	433.0771 435.0927	2.5 2.8	300.0286, 271.0225, 255.0294, 243.0310, 151.0128 303.0513, 221.0811, 177.0890	Quercetin-*O*-pentoside[b,c]	$C_{20}H_{18}O_{11}$	[4,9]
12	6.43	433.0784$[M-H]^-$ 435.0935 $[M+H]^+$	433.0771 435.0927	3.0 1.8	300.0274, 271.0225, 255.0301, 243.0297, 151.0119 303.0512, 221.0827, 177.0917	Quercetin-*O*-pentoside[b,c]	$C_{20}H_{18}O_{11}$	[9]
13	6.50	433.0786$[M-H]^-$	433.0771	3.5	300.0273, 271.0259, 255.0316, 243.0269, 151.0141	Quercetin-*O*-pentoside[b,c]	$C_{20}H_{18}O_{11}$	[9]
14	6.65	593.1504 $[M-H]^-$ 595.1670 $[M+H]^+$	593.1506 595.1663	-0.3 1.2	447.0923, 284.0323, 255.0398 449.1097, 287.0560	Kaempferol-3-*O*-rutinoside[b,c]	$C_{27}H_{30}O_{15}$	[2,3,10]
15	6.69	593.1494 $[M-H]^-$ 595.1688 $[M+H]^+$	593.1506 595.1663	-2.0 4.2	447.0906, 284.0317, 255.0293, 227.0347 449.1091, 325.0031, 287.0555, 153.0184	Kaempferol-3-*O*-rutinoside isomer[b,c]	$C_{27}H_{30}O_{15}$	[2,3,10]
16	7.51	491.1203 $[M+H]^+$ 489.1033 $[M-H]^-$	491.1190 489.1033	2.6 0	287.0555, 147.0459 475.1243, 285.0406, 255.0298, 227.0337, 161.0253, 125.0245	Kaempferol-3-*O*-acetylglucoside[c]	$C_{23}H_{22}O_{12}$	[11,12]
17	8.12	595.1437 $[M+H]^+$ 593.1288 $[M-H]^-$	595.1452 593.1295	-2.5 -1.2	285.0400, 255.0305, 227.0352, 145.0302 309.0989, 207.0706, 147.0454	Tiliroside [a,b,c]	$C_{30}H_{26}O_{13}$	[2,6]

18	8.25	593.1292 $[M-H]^-$	593.1295	-0.5	285.0400, 255.0298, 227.0351, 145.0281	Tiliroside isomer[a,b,c]	$C_{30}H_{26}O_{13}$	[2,6]
19	8.66	635.1372 $[M-H]^-$ 637.1570 $[M+H]^+$	635.1377 637.1557	-4.6 2.0	523.1555, 285.0400, 255.0308, 227.0336, 145.0292 525.1923, 499.1609, 347.1131, 303.0954, 209.0818, 147.0479	Kaempferol-3-*O*-[6"-*O*-acetyl-2"-*O*-*p*-coumaroyl]-glucoside[c]	$C_{32}H_{28}O_{14}$	[13]
20	9.54	527.1907 $[M+H]^+$	527.1937	2.5	291.1835, 271.1189, 238.1205, 211.0966, 181.0547	Pilosanol B[c]	$C_{28}H_{30}O_{10}$	[14]
21	9.56	527.1927 $[M+H]^+$ 525.1771 $[M-H]^-$	527.1937 525.1761	-1.9 1.9	291.1835, 271.1190, 238.1203, 211.0966, 181.0537 289.0730, 223.0961, 137.0264	Epipilosanol B[c]	$C_{28}H_{30}O_{10}$	[14]
22	9.75	527.1937 $[M+H]^+$ 549.1774 $[M+Na]^+$	527.1937	0.0	375.1453, 303.0939, 237.1131	Pilosanol C[c]	$C_{28}H_{30}O_{10}$	[14]
23	9.77	527.1924 $[M+H]^+$ 549.1727 $[M+Na]^+$	527.1937	1.3	375.1443*, 303.0940, 237.1130	Epipilosanol C[c]	$C_{28}H_{30}O_{10}$	[14]
24	10.35	259.0944 $[M+Na]^+$ 237.1135$[M+H]^+$ 235.0973 $[M+H]^-$	259.0946 235.0970	-0.4 1.3	219.1031 191.0361, 167.0364, 137. 0244, 123.0458, 121.0301	3-Dimethylallyl-4-hydroxymandelic[c]	$C_{13}H_{16}O_4$	[15]
25	10.75	383.1628 $[M+Na]^+$ 361.1659 $[M+H]^+$	383.1623	1.3	361.1659, 337.1660, 237.1134, 209.0827, 203.1796	Unknown phloroglucinol derivative[d]	$C_{20}H_{24}O_6$	
26	11.54	475.1988 $[M+H]^+$ 473.1818 $[M+H]^-$	475.1968 473.1812	2.0 1.3	405.1716, 345.2040, 237.1131, 209.0824 235.0969, 223.0968, 195.0650, 193.0871, 177.0190,	Robustaol A[c]	$C_{25}H_{30}O_9$	[16]
27	11.97	511.1989 $[M+Na]^+$ 489.2146 $[M+H]^+$	511.2003 489.2125	-2.7 4.3	470.1120, 417.0820, 259.0835, 237.1043, 209.0777	isomallotolerin[c]	$C_{26}H_{32}O_9$	[17,18]

28	12.66	461.2186 $[M+H]^+$	461.2175	2.4	237.1149, 209.0809	α-Kosin[a,c]	$C_{25}H_{32}O_8$	[2,19]
29	13.00	475.2099 $[M+H]^+$	475.2121	-4.6	259.0933, 237.1126, 219.1017, 204.0782, 175.0760, 161.0607, 147.0811, 105.0702	Unknown phloroglucinol derivative[d]	$C_{29}H_{30}O_6$	
30	13.31	489.2170 $[M+H]^+$	489.2125	4.5	470.1941, 417.2745, 259.0950, 237.1106, 209.0843	Isomallotolerin isomer[c]	$C_{26}H_{32}O_9$	[17,18]
31	13.96	469.1852 $[M+Na]^+$ 447.2016$[M+H]^+$	469.1838	3.0	282.2785, 237.1124, 225.1122, 223.0864, 209.0855	Unknown phloroglucinol derivative[d]	$C_{24}H_{30}O_8$	
32	10.77	503.3367$[M-H]^-$ 505.3460$[M+H]^+$	503.3373 505. 3446	-1.2 2.8	485.3195, 439.2953, 421.2897, 289.083 487.3235, 423.2504, 277.1920, 237.1139	1-Hydroxyeuscaphic acid[c]	$C_{30}H_{48}O_6$	[20]
33	10.96	501.3231$[M-H]^-$	501.3216	3.0	483.3059, 465.2980, 421.2912, 137.0359	1-hydroxy-2-oxopomolic acid[a,b]	$C_{30}H_{46}O_6$	[2,6]
34	11.06	501.3230$[M-H]^-$	501.3216	2.8	483.3104, 465.2899, 421.3042,	1-hydroxy-2-oxopomolic acid[a,b]	$C_{30}H_{46}O_6$	[2,6]
35	11.14	503.3342$[M-H]^-$ 505.3454$[M+H]^+$	503.3349 505.3446	-1.4 1.6	485.3271, 465.2861, 441.3400, 421.3062, 289.0834 487.3320, 277.1982, 237.1128, 209.0826	1-Hydroxyeuscaphic acid[c]	$C_{30}H_{48}O_6$	[20]
37	15.64	445.3685*$[M+H]^+$	445.3682	0.7	427.3587, 307.3001. 289.2890	unknown phytosterol[d]	$C_{29}H_{48}O_3$	

[a] Previously isolated from the plant; [b]Presence of compound/isomer from extract confirmed by preparative isolation; [c]Tentatively identified by comparison with reported MS data, [d]Class of compounds tentatively assigned.

Diagram of Isolation Procedure

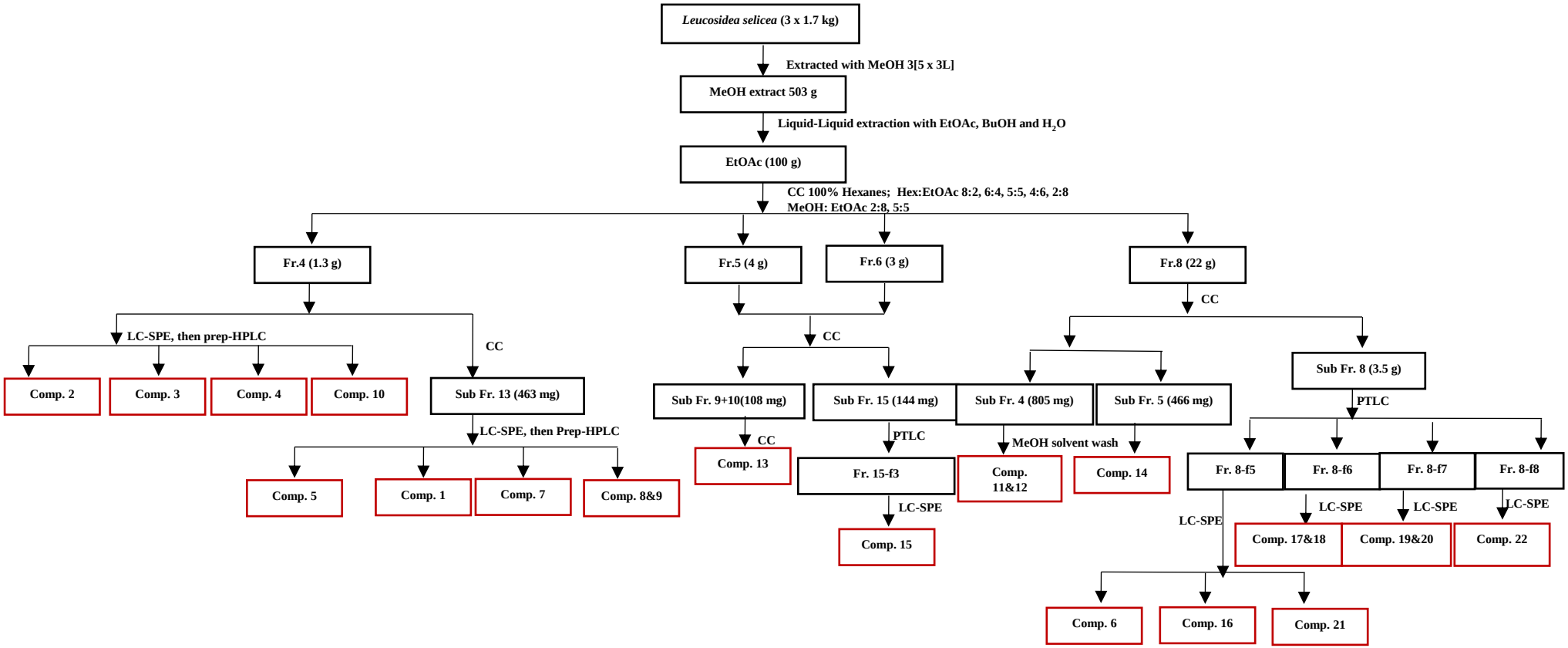


Figure S2. Procedure for extraction and isolation of compounds from *L. sericea*.

Structures of the compounds 1-22 isolated from *L. sericea* extract.

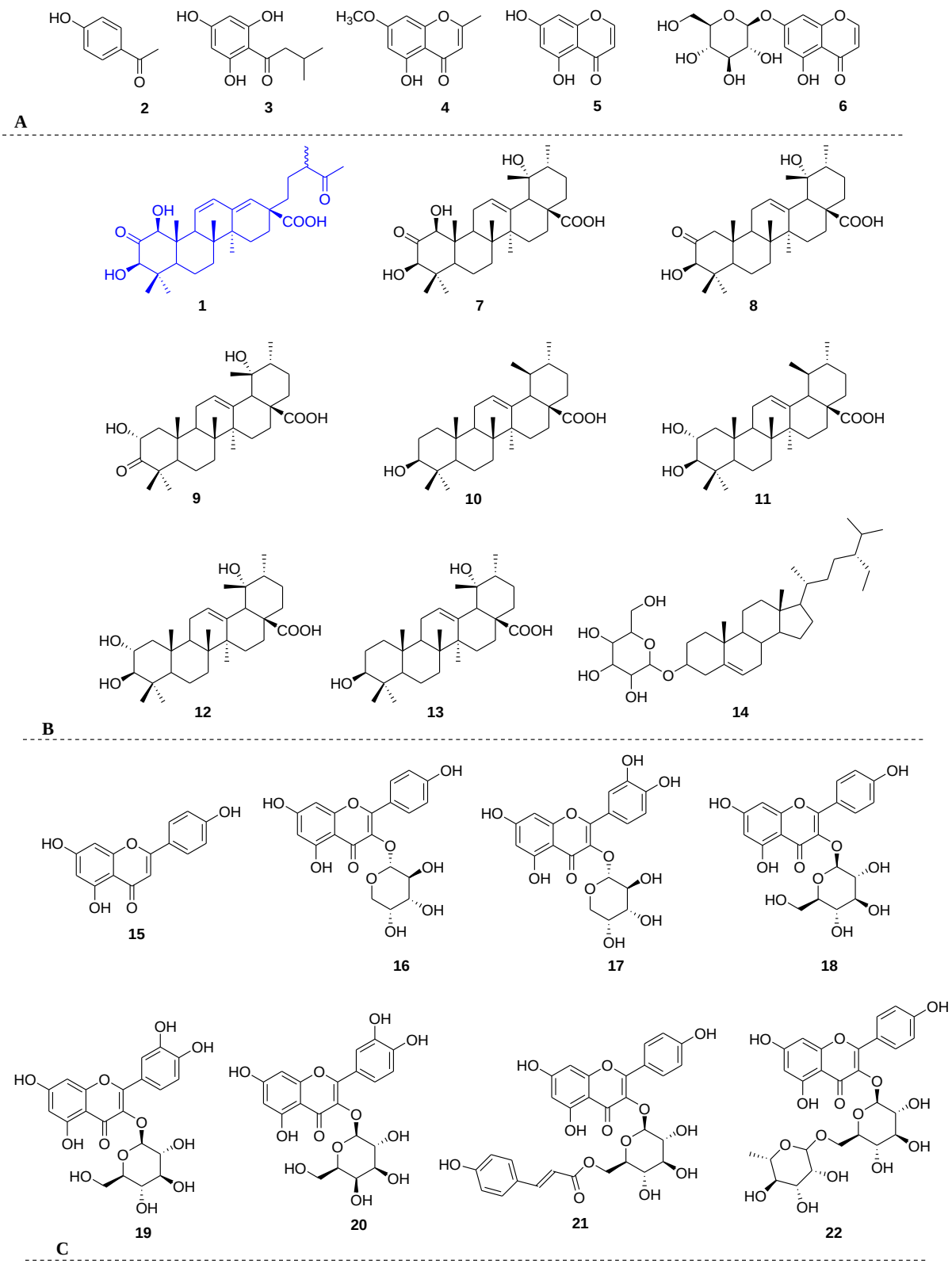


Figure S3. Structures of new triterpenoid **1** and known compounds **2-22** isolated from L. sericea extract A) acetophenone derivative, phloroglucinol derivative, and chromones. B) triterpenoids C) flavonoid and flavonoid glycosides

Analytical data of isolated compounds

Leucosidic A (1): White powder; $[\alpha]^{20}_{D}$ +16.7 (c 0.003, CH_3OH); HRESIMS *m/z* 501.3211 $[M+H]^+$ (calcd for $C_{30}H_{45}O_6$, 501.3216); MS^E *m/z* 523.3188 $[M+Na]^+$, 503.3236 $[M+H]^+$, 477.2648, 461.3272, 455.3162, 437.3072, 383.2585, 315.1970; ^1H and ^{13}C NMR data are provided in Table 2.

Piceol (**2**)**:** White powder, HRESIMS *m/z* 137.0608 $[M+H]^+$ (calcd for $C_8H_9O_2$, 137.0597); ^1H NMR(400 MHz, $CDCl_3$) δ 2.55 (3H, s, $COC\underline{H}_3$), 5.29 (1H, brs , OH), 6.87 (2H, d, *J* = 8.2 Hz, Ar-H-3' and H-5'), 7.91 (2H, d, *J* = 8.2 Hz, Ar-H-2' and H-6').

Phlorisovalerophenone (**3**)**:** White powder, HRESIMS *m/z* 211.0970 $[M+H]^+$ (calcd for $C_{11}H_{15}O_4$, 211.0970); MS^E *m/z* 211.0976 $[M+H]^+$, 193.0866, 175.0765; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (6H, d, *J* = 6.6 Hz, $CH(C\underline{H}_3)_2$), 1.87 (1H, sept, *J* = 6.6 Hz, $C\underline{H}(CH_3)_2$), 2.77 (2H, d, *J* = 6.9 Hz, CH_2), 6.20 (1H, d, *J* = 2.7 Hz, Ar-H-5), 6.30 (1H, d, *J* = 2.7 Hz, Ar-H-3). The analytical data were data were consistent with those previously reported.[21]

Eugenin (4): White powder; HRESIMS *m/z* 207.0671 $[M+H]^+$ (calcd for $C_{11}H_{11}O_4$, 207.0657). ^1H NMR data were consistent with those previously reported.[22]

5,7-Dihydroxychromone (5): White powder; HRESIMS *m/z m/z* 179.0340 $[M+H]^+$ (calcd for $C_9H_7O_4$, 179.0344). ^1H NMR data were consistent with those previously reported.[6,22]

5-Hydroxychromone-7-*O*-glucoside (6): Yellow amorphous solid; HRESIMS *m/z* 341.0867 $[M+H]^+$ (calcd for $C_{15}H_{17}O_9$, 341.0867). MS^E *m/z* 363.0686 $[M+Na]^+$, 341.0867 $[M+H]^+$, 179.0340; ^1H and ^{13}C NMR data were consistent with those previously reported.[23]

1-Hydroxy-2-oxopomolic acid (7): White powder; HRESIMS *m/z* 503.3378 $[M+H]^+$ (calcd for $C_{30}H_{47}O_6$, 503.3373); MS^E *m/z* 1027.6497 $[2M+Na]^+$, 525.3188 $[M+Na]^+$, 503.3378 $[M+H]^+$, 485.3264, 439.3204; ^1H and ^{13}C NMR data were consistent with those previously reported.[6,24]

2-Oxopomolic acid (8) and 2*α*-hydroxy-3-oxopomolic acid (9): White powder;

HRESIMS *m/z* 487.3412 $[M+H]^+$ (calcd for $C_{30}H_{47}O_5$, 487.3423); MS^E *m/z* 995.6696 $[2M+Na]^+$; 504.3688 $[M+NH_4]^+$, 487.3412 $[M+H]^+$, 469.3305, and 423.3277; ^1H and ^{13}C NMR data were consistent with those previously reported.[25-27]

Ursolic acid (10): White powder; HRESIMS *m/z* 457.3632 $[M+H]^+$ (calcd for $C_{30}H_{49}O_3$, 457.3682). MS^E *m/z* 479.3503 $[M+Na]^+$, 457.3632 $[M+H]^+$, 443.3805, 439.3578, 425.3736, 411.3653; ^1H NMR data were consistent with those previously reported.[25,28]

Corosolic acid (11): White powder; HRASAPMS *m/z* 471.3444 $[M-H]^-$ (calcd for $C_{30}H_{47}O_4$, 471.3474); ^1H and ^{13}C NMR data were consistent with those previously reported.[25,28]

Tormentic acid (12): White powder; White powder; HRASAPMS *m/z* 487.3337 $[M-H]^-$ (calcd for $C_{30}H_{47}O_5$, 487.3429); ^1H and ^{13}C NMR data were consistent with those previously reported.[25]

Pomolic acid (13): White powder; HRAPIMS *m/z* 473.3624 $[M+H]^+$ (calcd for $C_{30}H_{49}O_4$, 473.3631); MSAPI *m/z* 495.3383 $[M+Na]^+$, 473.3624 $[M+H]^+$, 455.3554, 427.3590, 339.2442, and 301.1389. ^1H and ^{13}C NMR data were consistent with those previously reported.[25]

***β*-sitosterol glucoside (14):** White powder; ESIMS *m/z* 577.4516 $[M+H]^+$ (calcd for $C_{35}H_{61}O_6$, 577.4468). ^1H and ^{13}C NMR data were consistent with those previously reported.[28,29]

Apigenin (15): Yellow amorphous solid; HRESIMS *m/z* 293.0424 $[M+Na]^+$ (calcd for $C_{15}H_{10}O_5Na$ 293.0426); MS^E *m/z* 293.0424 $[M+Na]^+$, 271.0515 $[M+H]^+$, 153.0184, and 119.0426. ^1H and ^{13}C NMR data were consistent with those previously reported.[30,31]

Kaempferol-3-*O*-*α*-arabinopyranoside (16): Light-yellow gum; HRESIMS (*m/z* 417.0816 $[M-H]^-$ (calcd for $C_{20}H_{17}O_{10}$, 417.0822); MS^E *m/z* 417.0816 $[M-H]^-$, 284.0335, 255.0316, 227.0344, and 183.0481; ^1H and ^{13}C NMR data were consistent with those previously reported.[31,32]

Q**uercetin-3-*O*-*α*-arabinopyranoside (17):** Yellow gum; HRESIMS *m/z* 433.0777 $[M-H]^-$ (calcd for $C_{20}H_{17}O_{11,}$ 433.0771); MS^E *m/z* 433.0777 $[M-H]^-$, 300.0271, 271.0233, 243.0233, and 215.0360; ^1H and ^{13}C NMR data were consistent with those previously reported.[9,33]

Astragalin (18): Yellow gum; HRESIMS *m/z* 447.0927 $[M-H]^-$ (calcd for $C_{21}H_{19}O_{11,}$ 447.0927); MS^E *m/z* 447.0927 $[M-H]^-$, 284.0324, 255.0290, 277.0353, and 183.0494; ^1H and ^{13}C NMR data were consistent with those previously reported.[30]

Quercetin-3-*O*-glucoside (19): Yellow gum; HRESIMS *m/z* 463.0876 $[M-H]^-$ (calcd for $C_{21}H_{19}O_{12,}$ 463.0877); MS^E *m/z* 463.0876 $[M-H]^-$, 300.0275, 271.0219, 255.0290, and 243.0283; ^1H and ^{13}C NMR data were consistent with those previously reported.[9]

Quercetin-3-*O*-*β*-galactopyranoside (20): Yellow gum; HRESIMS data showed (*m/z* 463.0876 $[M-H]^-$ (calcd for $C_{21}H_{19}O_{12,}$ 463.0877); ^1H and ^{13}C NMR data were consistent with those previously reported.[9,31]

Tiliroside (21): Yellow gum; HRESIMS *m/z* 593.1298 $[M-H]^-$ (calcd for $C_{30}H_{25}O_{13,}$ 593.1295). MS^E *m/z* 593.1299 $[M-H]^-$, 285.0371, 255.0256, 227.0317, and 145.0288; ^1H and ^{13}C NMR data were consistent with those previously reported.[6]

Kaempferol-3-*O*-rutinoside (22): Yellow gum; HRESIMS *m/z* 593.1510 $[M-H]^-$ (calcd for $C_{27}H_{29}O_{15,}$ 593.1506). The MS^E *m/z* 593.1510 $[M-H]^-$, 285.0392, 255.0284, 227.0343, and 183.0323; ^1H NMR data were consistent with those previously reported.[30,34]

NMR and MS spectra of the new compound 1

Figure S4. 1H NMR (400 MHz, CD_3OD) spectrum of compound 1.

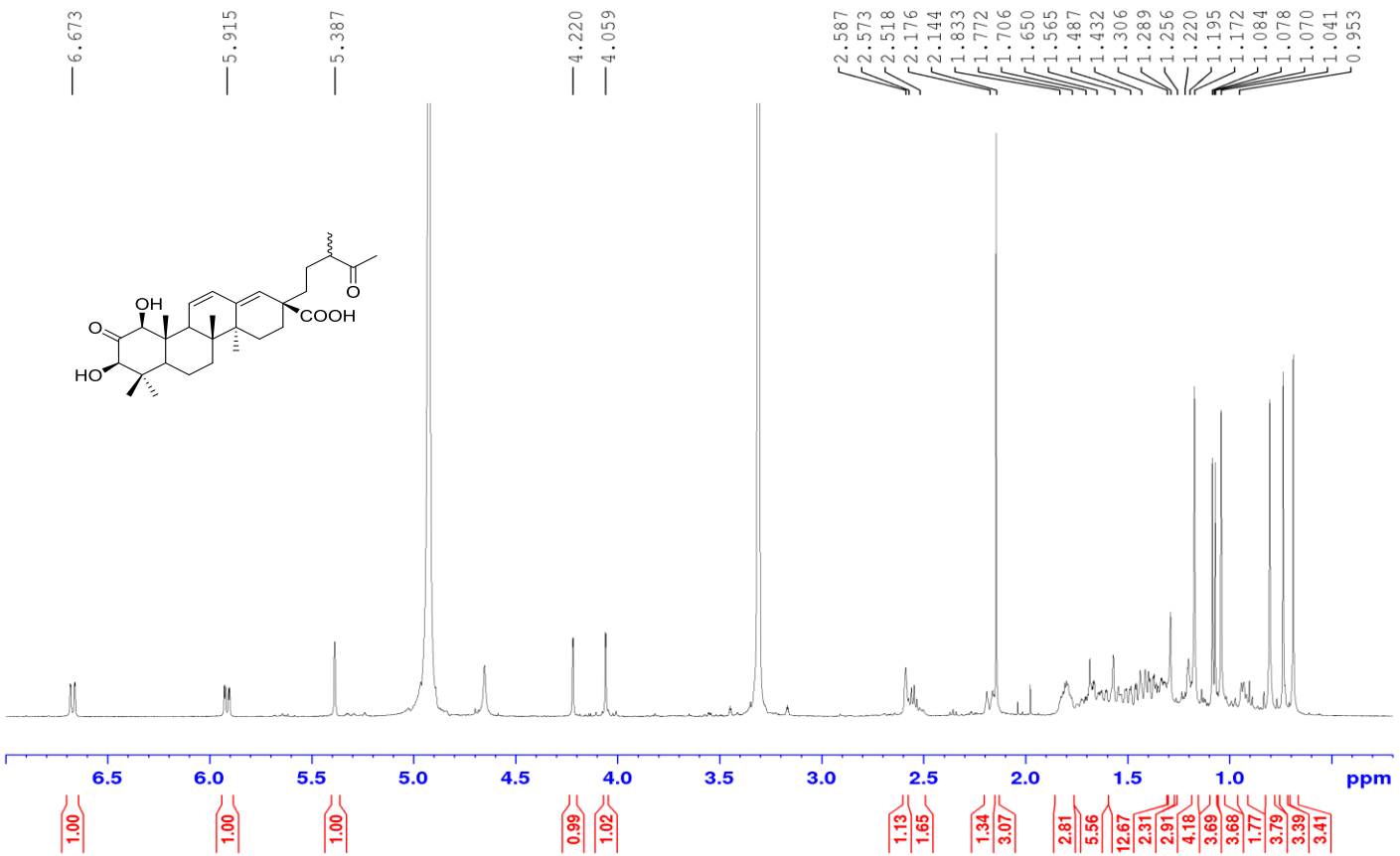


Figure S5. ^{13}C NMR (125 MHz, CD_3OD) spectrum of compound 1.

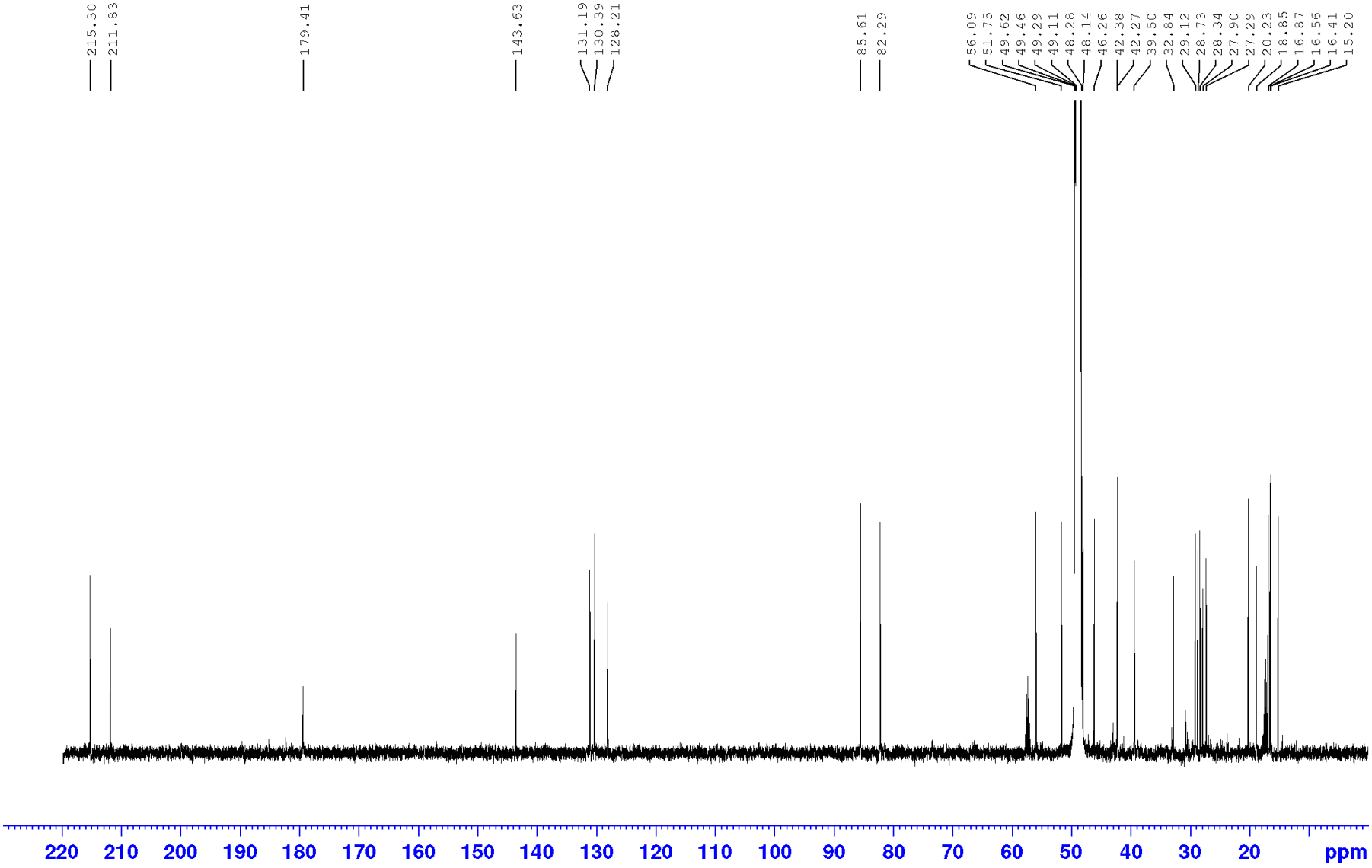


Figure S6. Dept-135 NMR (125 MHz, CD_3OD) spectrum of compound 1.

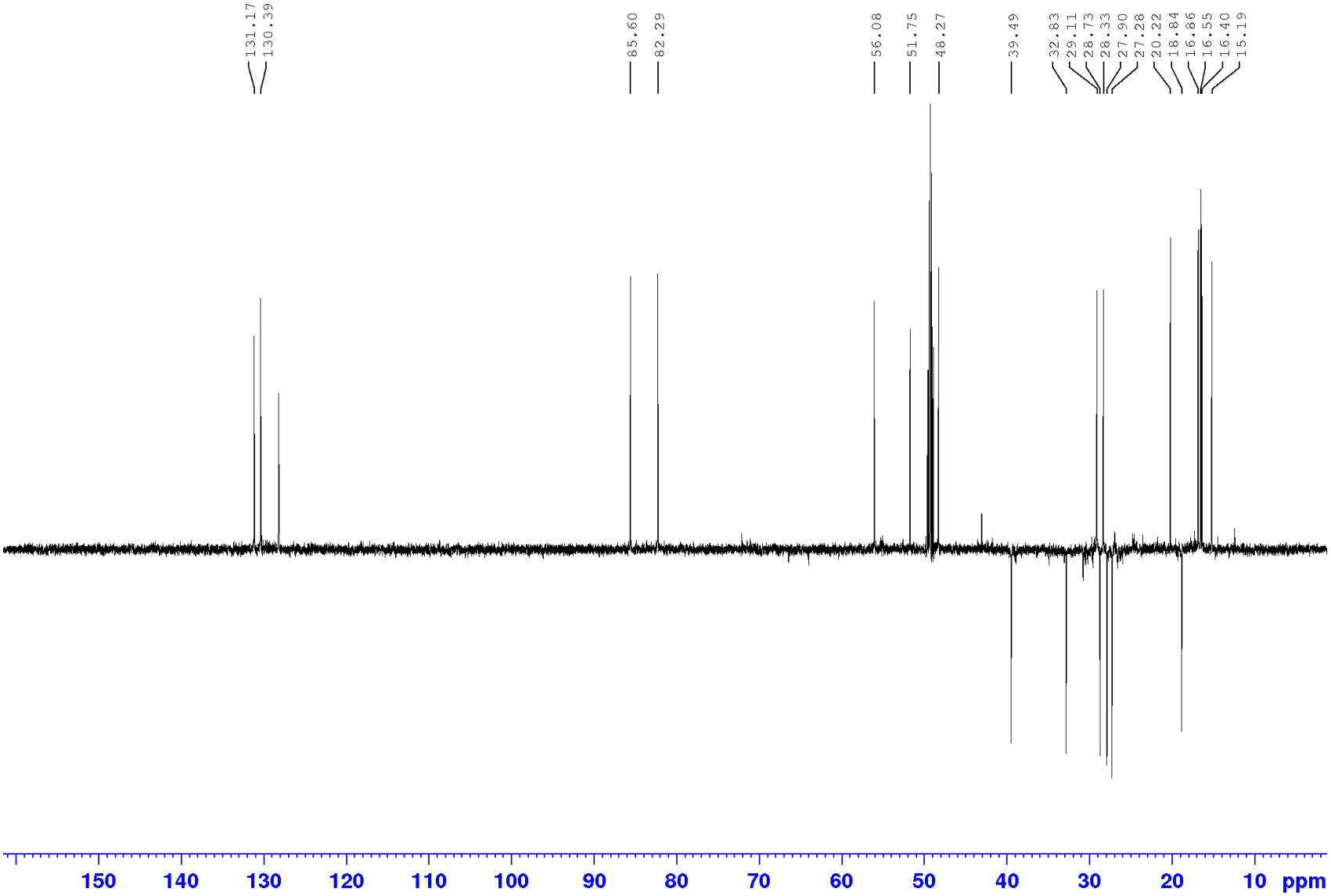


Figure S7. Dept-90 NMR (125 MHz, CD_3OD) spectrum of compound 1.

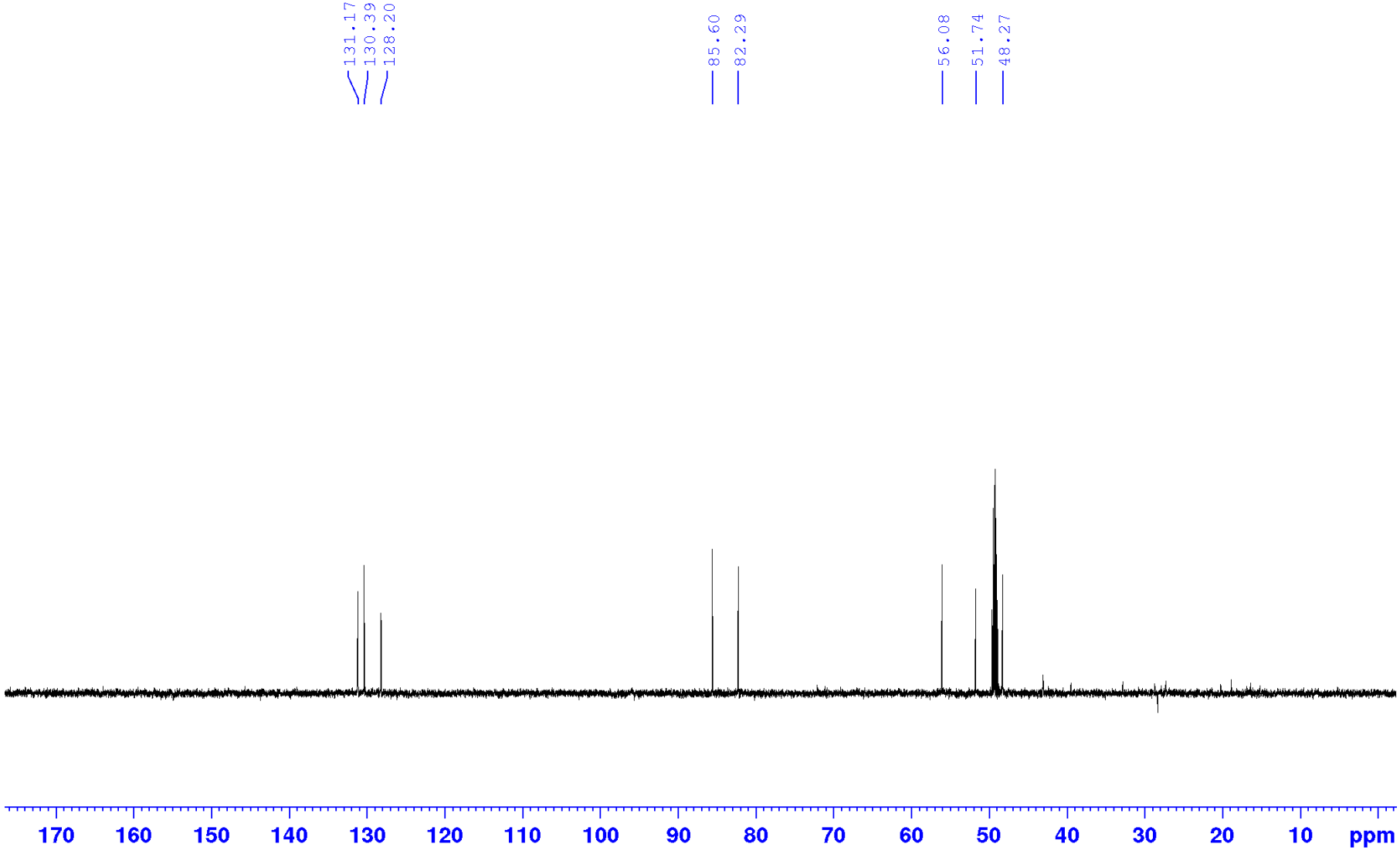


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of compound 1.

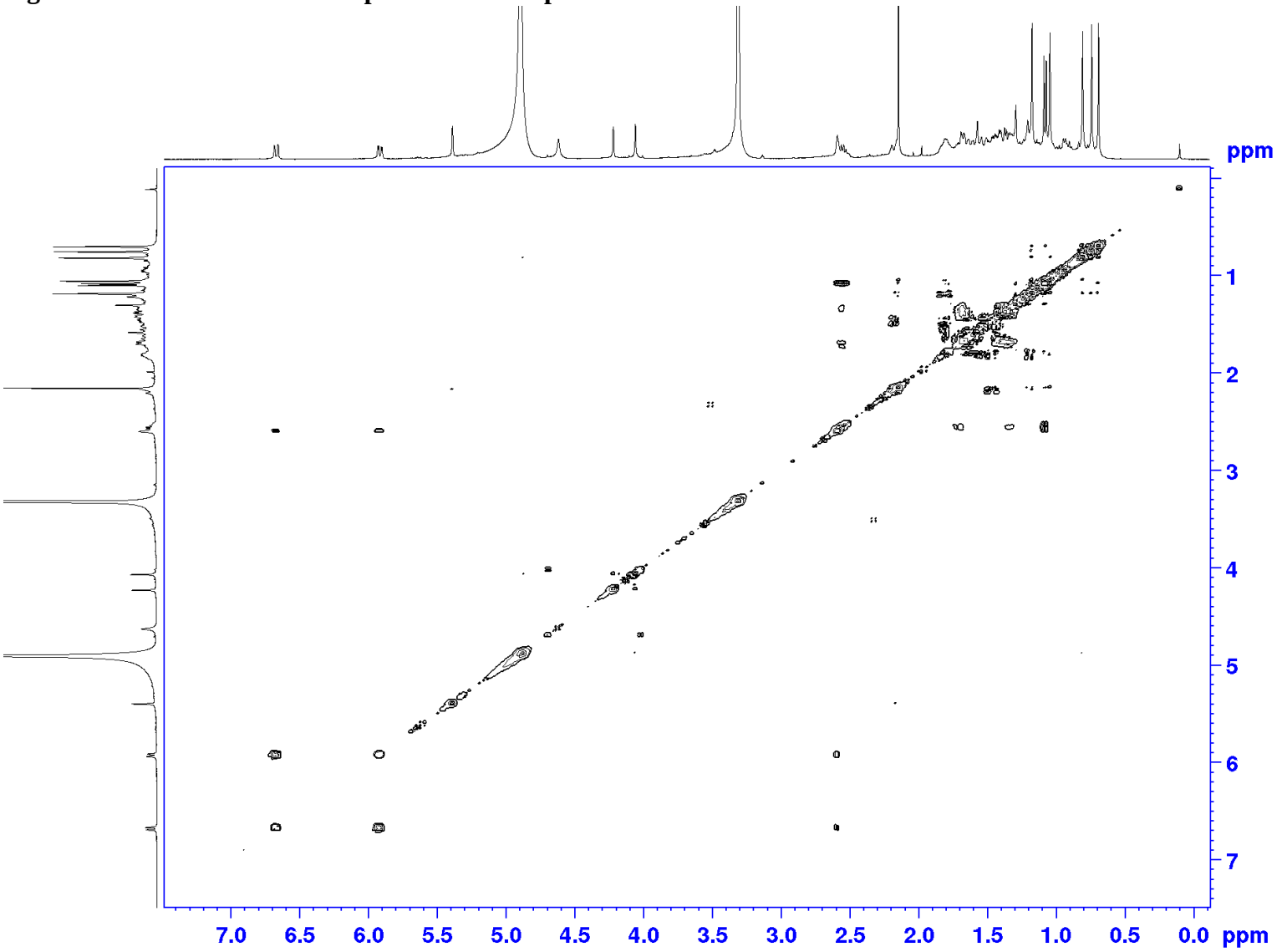


Figure S9. HSQC NMR spectrum of compound 1.

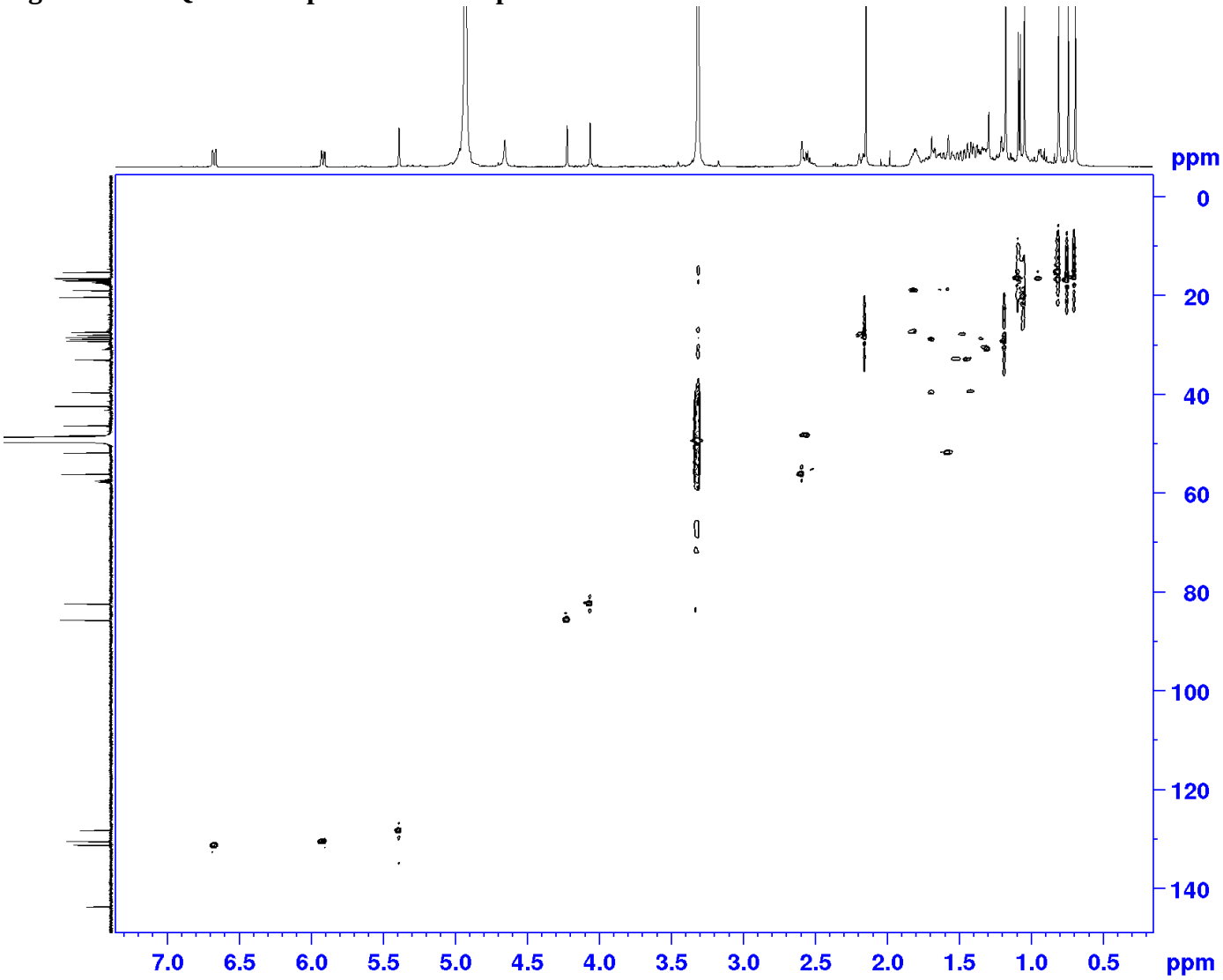


Figure S10. HMBC NMR spectrum of compound 1.

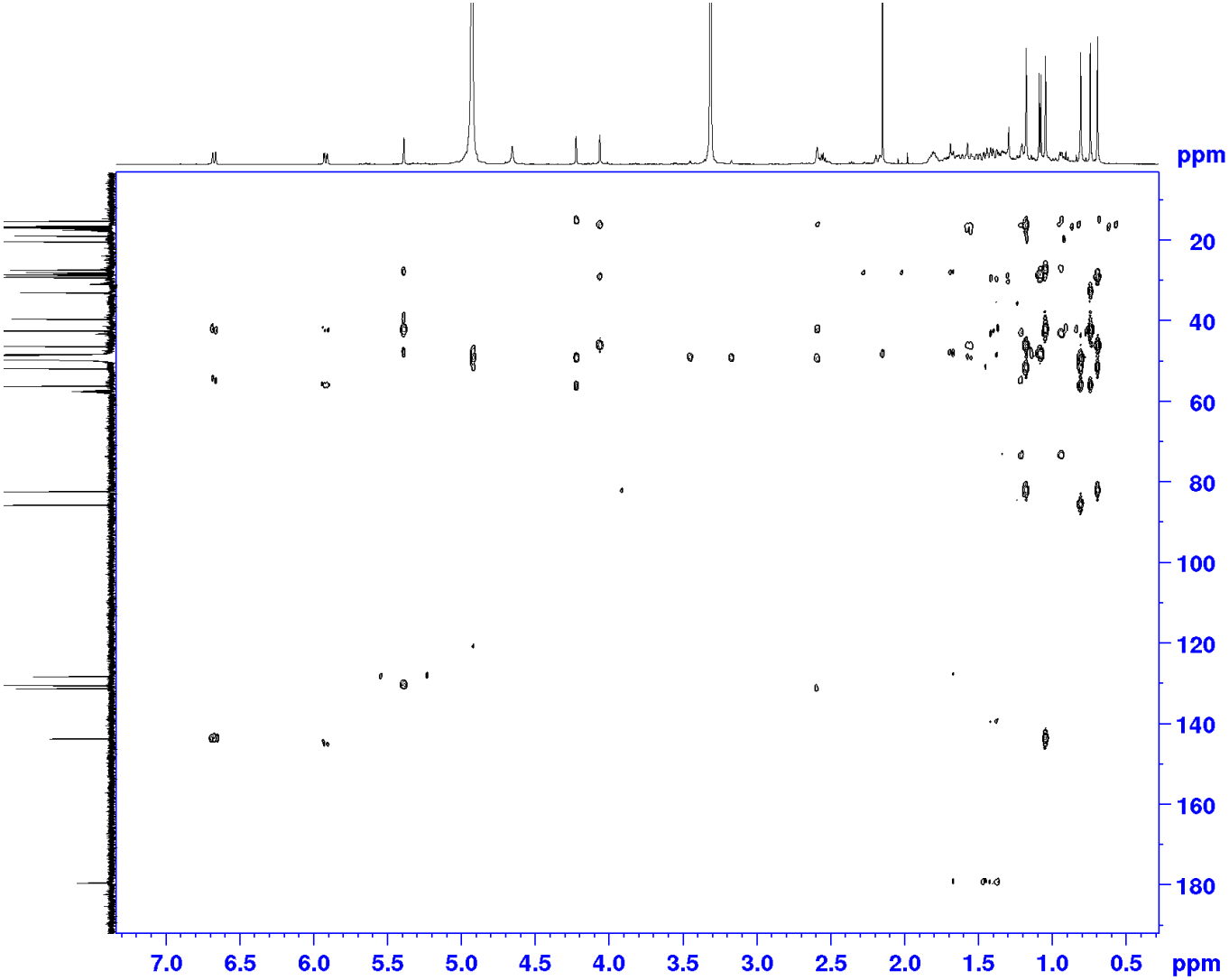


Figure S11. HMBC NMR spectrum of compound 1 (^{13}C spectral width extended to 240 ppm)

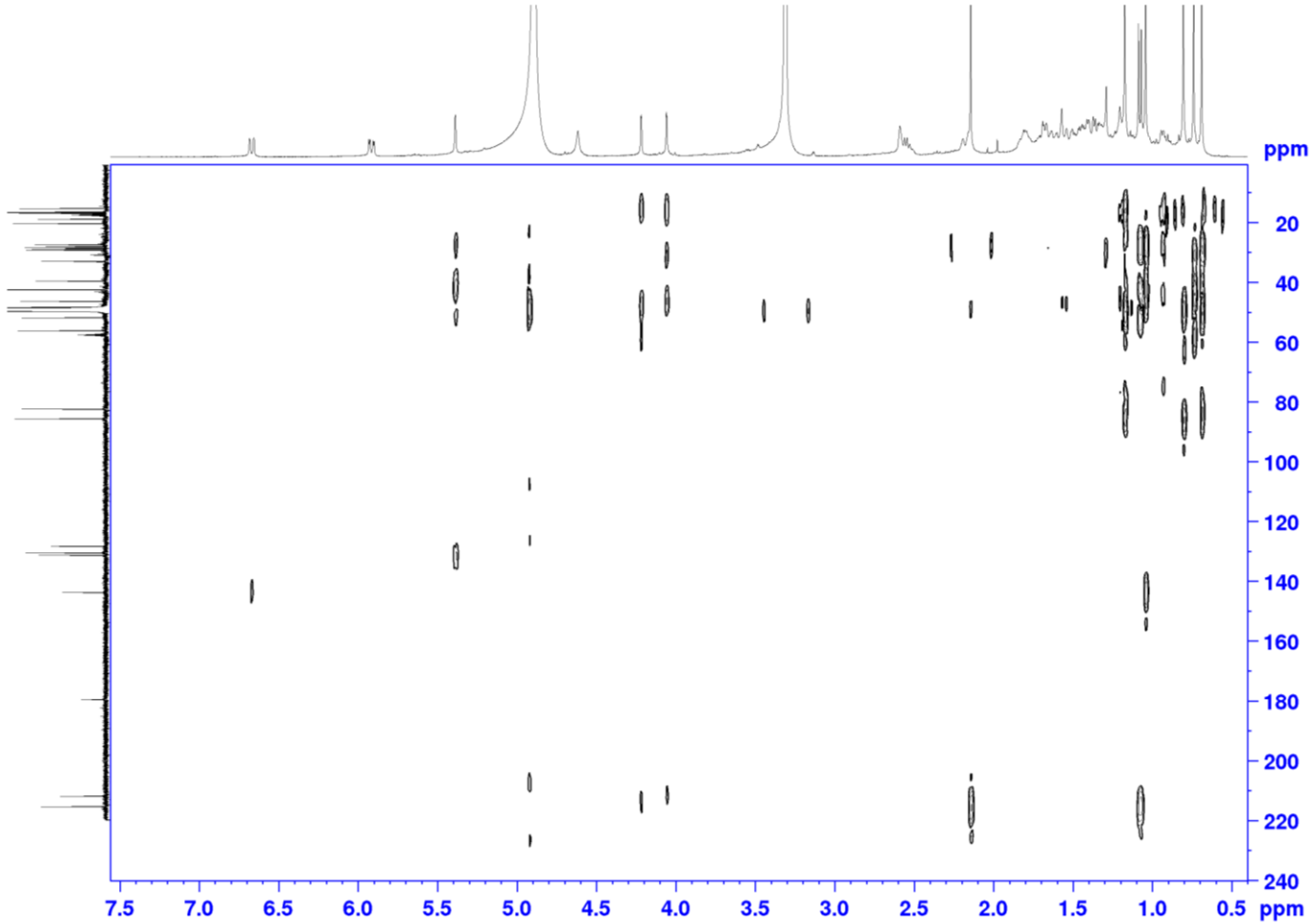


Figure S12. NOESY NMR spectrum of compound 1

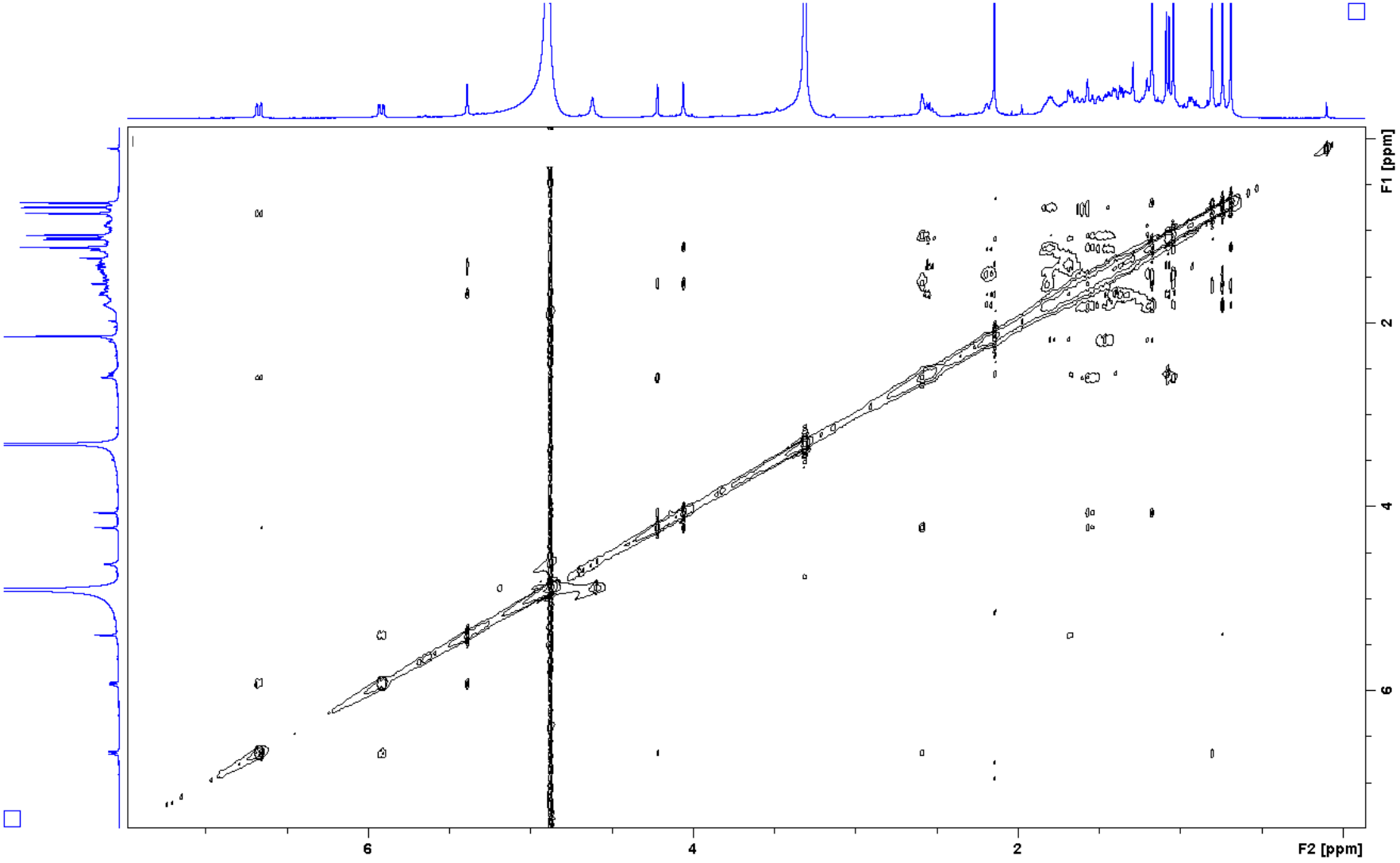
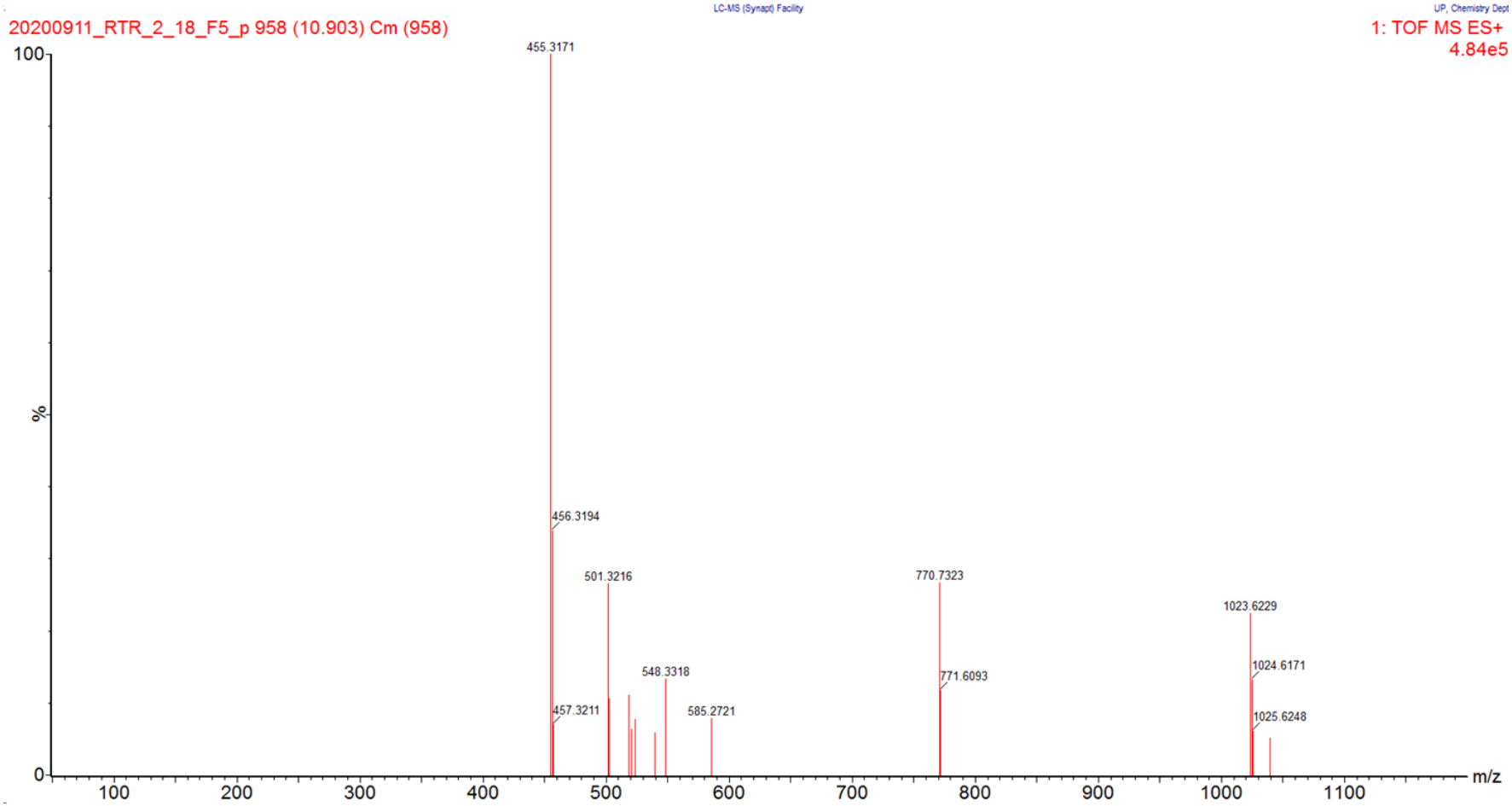


Figure S13. HRESIMS spectrum of spectrum of compound 1.



REFERENCES

(1) Fromm, M.; Loos, H. M.; Bayha, S.; Carle, R.; Kammerer, D. R. Recovery and Characterisation of Coloured Phenolic Preparations from Apple Seeds. *Food Chem.* **2013**, *136*, 1277-1287.

(2) Sehlakgwe, P. F.; Lall, N.; Prinsloo, G. ^{1}H-NMR Metabolomics and LC-MS Analysis to Determine Seasonal Variation in a Cosmeceutical Plant *Leucosidea sericea*. *Front. Pharmacol.* **2020**, *11*, 219.

(3) Badeggi, U. M.; Ismail, E.; Adeloye, A. O.; Botha, S.; Badmus, J. A.; Marnewick, J. L.; Cupido, C. N.; Hussein, A. A. Green Synthesis of Gold Nanoparticles Capped with Procyanidins from *Leucosidea sericea* as Potential Antidiabetic and Antioxidant agents. *Biomolecules* **2020**, *10*, 452.

(4) Masike, K.; de Villiers, A.; Hoffman, E. W.; Brand, D. J.; Causon, T.; Stander, M. A. Detailed Phenolic Characterization of Protea Pure and Hybrid Cultivars by Liquid Chromatography-Ion Mobility-High Resolution Mass Spectrometry (LC-IM-HR-MS). *J. Agric. Food Chem.* **2020**, *68*, 485-502.

(5) Qi, D.; Li, J.; Qiao, X.; Lu, M.; Chen, W.; Miao, A.; Guo, W.; Ma, C. Non-targeted Metabolomic Analysis Based on Ultra-High-Performance Liquid Chromatography Quadrupole Time-of-Flight Tandem Mass Spectrometry Reveals the Effects of Grafting on Non-volatile Metabolites in Fresh Tea Leaves (*Camellia sinensis* L.). *J. Agric. Food Chem.* **2019**, *67*, 6672-6682.

(6) Pendota, S. C.; Aremu, A. O.; Slavetinska, L. P.; Rarova, L.; Gruz, J.; Dolezal, K.; Van Staden, J. Identification and Characterization of Potential Bioactive Compounds from the Leaves of *Leucosidea sericea*. *J. Ethnopharmacol.* **2018**, *220*, 169-176.

(7) Zhang, J.; Yu, Q.; Cheng, H.; Ge, Y.; Liu, H.; Ye, X.; Chen, Y. Metabolomic Approach for the Authentication of Berry Fruit Juice by Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry Coupled to Chemometrics. *J. Agric. Food Chem.* **2018**, *66*, 8199-8208.

(8) Monzón Daza, G.; Meneses Macías, C.; Forero, A. M.; Rodríguez, J.; Aragón, M.; Jiménez, C.; Ramos, F. A.; Castellanos, L. Identification of α-Amylase and α-Glucosidase Inhibitors and Ligularoside A, a New Triterpenoid Saponin from *Passiflora ligularis* Juss (Sweet Granadilla) Leaves, by a Nuclear Magnetic Resonance-Based Metabolomic Study. *J. Agric. Food Chem.* **2021**, *69*, 2919-2931.

(9) Vvedenskaya, I. O.; Rosen, R. T.; Guido, J. E.; Russell, D. J.; Mills, K. A.; Vorsa, N. Characterization of Flavonols in Cranberry (*Vaccinium macrocarpon*) Powder. *J. Agric. Food Chem.* **2004**, *52*, 188-195.

(10) Morcol, T. B.; Matthews, P. D.; Kennelly, E. J. Differences in Leaf Chemistry and Glandular Trichome Density between Wild Southwestern American Hop (*Humulus neomexicanus*) and Commercial Hop Cultivars. *J. Agric. Food Chem.* 2021, *69*, 7798-7814.

(11) Kajdzanoska, M.; Gjamovski, V.; Stefova, M. HPLC-DAD-ESI-MS^n Identification of Phenolic Compounds in Cultivated Strawberries from Macedonia. *Maced. J. Chem. Chem. Eng.* **2010**, *29*, 181-194.

(12) Garzón, G. A.; Manns, D. C.; Riedl, K.; Schwartz, S. J.; Padilla-Zakour, O. Identification of Phenolic Compounds in Petals of Nasturtium Flowers (*Tropaeolum majus*) by High-Performance Liquid Chromatography Coupled to Mass Spectrometry and Determination of Oxygen Radical Absorbance Capacity (ORAC). *J. Agric. Food Chem.* **2015**, *63*, 1803-1811.

(13) Ouyang, H.; Li, T.; He, M.; Li, Z.; Tan, T.; Zhang, W.; Li, Y.; Feng, Y.; Yang, S. Identification and Quantification Analysis on the Chemical Constituents from Traditional Mongolian Medicine Flos Scabiosae using UHPLC-DAD-Q-TOF-MS Combined with UHPLC-QqQ-MS. *J. Chromatogr. Sci.* **2016**, *54*, 1028-1036.

(14) Kim, H. W.; Choi, S. Y.; Jang, H. S.; Ryu, B.; Sung, S. H.; Yang, H. Exploring Novel Secondary Metabolites from Natural Products using Pre-processed Mass Spectral Data. *Sci. Rep.* **2019**, *9*, 1-11.

(15) Pojer, F.; Kahlich, R.; Kammerer, B.; Li, S.-M.; Heide, L. CloR, a Bifunctional Non-heme Iron Oxygenase Involved in Clorobiocin Biosynthesis*. *J. Biol. Chem.* **2003**, *278*, 30661-30668.

(16) Qin, G.-W.; Chen, Z.-X.; Wang, H.-C.; Qian, M.-K. Structure and Synthesis of Robustaol A. *Acta Chimica Sinica* **1981**, *39*, 83-89.

(17) Arisawa, M.; Fujita, A.; Hayashi, T.; Morita, N.; Kikuchi, T.; Tezuka, Y. Studies on Cytotoxic Constituents in Pericarps of *Mallotus japonicus*. IV. *Chem. Pharm. Bull.* **1990**, *38*, 698-700.

(18) Saito, Y.; Iga, S.; Nakashima, K.; Okamoto, Y.; Gong, X.; Kuroda, C.; Tori, M. Terpenoids from *Ligularia virgaurea* Collected in China: the First Example of Two Bakkane Derivatives with an Anhydride-type Ring C and Nineteen New Chemical Constituents. *Tetrahedron* **2015**, *71*, 8428-8435.

(19) Sharma, R.; Kishore, N.; Hussein, A.; Lall, N. The Potential of *Leucosidea sericea* against *Propionibacterium acnes*. *Phytochem. Lett.* **2014**, *7*, 124-129.

(20) Wu, C.; Cui, B.; Dong, H.; Ren, Y.; Yang, C.; Yao, M.; Li, W.; Gan, C. Simultaneous Determination and Pharmacokinetics Study of Six Triterpenes in Rat Plasma by UHPLC-MS/MS after Oral Administration of *Sanguisorba officinalis* L. Extract. *Molecules* **2018**, *23*.

(21) Zhou, W.; Zhuang, Y.; Bai, Y.; Bi, H.; Liu, T.; Ma, Y. Biosynthesis of Phlorisovalerophenone and 4-Hydroxy-6-isobutyl-2-pyrone in *Escherichia coli* from Glucose. *Microbial Cell Factories* **2016**, *15*, 149.

(22) Pendse, R.; Rao, A. V. R.; Venkataraman, K. 5,7-Dihydroxychromone from *Arachis hypogoea* Shells. *Phytochemistry* **1973**, *12*, 2033-2034.

(23) Simon, A.; Chulia, A. J.; Kaouadji, M.; Delage, C. Quercetin 3-[triacetylarabinosyl(1→6)galactoside] and Chromones from *Calluna vulgaris*. *Phytochemistry* **1994**, *36*, 1043-1045.

(24) Kashiwada, Y.; Wang, H.-K.; Nagao, T.; Kitanaka, S.; Yasuda, I.; Fujioka, T.; Yamagishi, T.; Cosentino, L. M.; Kozuka, M.; Okabe, H.; Ikeshiro, Y.; Hu, C.-Q.; Yeh, E.; Lee, K.-H. Anti-AIDS Agents. 30. Anti-HIV Activity of Oleanolic Acid, Pomolic Acid, and Structurally Related Triterpenoids. *J. Nat. Prod.* **1998**, *61*, 1090-1095.

(25) Liu, W.-j.; Hou, X.-q.; Chen, H.; Liang, J.-y.; Sun, J.-b. Chemical constituents from *Agrimonia pilosa* Ledeb. and their Chemotaxonomic Significance. *Nat. Prod. Res.* **2016**, *30*, 2495-2499.

(26) Xu, H.-X.; Zeng, F.-Q.; Wan, M.; Sim, K.-Y. Anti-HIV Triterpene Acids from *Geum japonicum*. *J. Nat. Prod.* **1996**, *59*, 643-645.

(27) Jia, Z.-J.; Liu, X.-Q.; Liu, Z.-M. Triterpenoids from *Sanguisorba alpina*. *Phytochemistry* **1992**, *32*, 155-159.

(28) Sun, S.; Huang, S.; Shi, Y.; Shao, Y.; Qiu, J.; Sedjoah, R.-C. A.-A.; Yan, Z.; Ding, L.; Zou, D.; Xin, Z. Extraction, Isolation, Characterization and Antimicrobial Activities of Non-extractable Polyphenols from Pomegranate Peel. *Food Chem.* **2021**, *351*, 129232.

(29) Faizi, S.; Ali, M.; Saleem, R.; Irfanullah; Bibi, S. Complete ^{1}H and ^{13}C NMR Assignments of Stigma-5-en-3-*O*-*β*-glucoside and its Acetyl Derivative. *Magn Reson Chem.* **2001**, *39*, 399-405.

(30) Markham, K. R.; Ternai, B.; Stanley, R.; Geiger, H.; Mabry, T. J. Carbon-13 NMR Studies of Flavonoids. III. Naturally Occurring Flavonoid Glycosides and their Acylated Derivatives. *Tetrahedron* **1978**, *34*, 1389-1397.

(31) Loizzo, M. R.; Said, A.; Tundis, R.; Rashed, K.; Statti, G. A.; Hufner, A.; Menichini, F. Inhibition of Angiotensin Converting Enzyme (ACE) by Flavonoids Isolated from *Ailanthus excelsa* (Roxb) (Simaroubaceae). *Phytotherapy research : PTR* **2007**, *21*, 32-36.

(32) De Cássia Lemos Lima, R.; T. Kongstad, K.; Kato, L.; José das Silva, M.; Franzyk, H.; Staerk, D. High-Resolution PTP1B Inhibition Profiling Combined with HPLC-HRMS-SPE-NMR for Identification of PTP1B Inhibitors from *Miconia albicans*. *Molecules* **2018**, *23*, 1755.

(33) Wubshet, S. G.; Moresco, H. H.; Tahtah, Y.; Brighente, I. M. C.; Staerk, D. High-resolution Bioactivity Profiling Combined with HPLC-HRMS-SPE-NMR: α-Glucosidase Inhibitors and Acetylated Ellagic Acid Rhamnosides from *Myrcia palustris* DC. (Myrtaceae). *Phytochemistry* **2015**, *116*, 246-252.

(34) Hou, W.-C.; Lin, R.-D.; Lee, T.-H.; Huang, Y.-H.; Hsu, F.-L.; Lee, M.-H. The Phenolic Constituents and Free Radical Scavenging Activities of *Gynura formosana* Kiamnra. *J. Sci. Food Agric.* **2005**, *85*, 615-621.