Supplementary data for

Investigation on Metabolites in Structural Diversity from The Deep-Sea Sediment-Derived Bacterium *Agrococcus* sp. SCSIO 52902 and Their Biosynthesis

Wenping Ding [1,3], Yanqun Li [1,3], Xinpeng Tian [1], Min Chen [1,3], Zhihui Xiao [1], Rouwen Chen [1], Hao Yin [1,2,*], Si Zhang [1,2,*]

[1] *CAS Key Laboratory of Tropical Marine Bio-resources and Ecology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*

[2] *Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou 511458, China*

[3] *University of Chinese Academy of Sciences, Beijing 100049, China*

Content

Table S1 Compositions of eleven liquid media

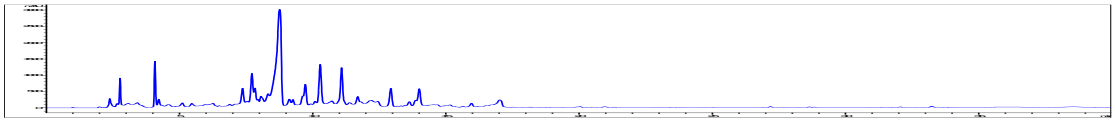
Media	Compositions
1 mA	Glucose (10 g/L), Yeast extract (5 g/L), Soluble starch (12 g/L), Bacterial peptone (5 g/L), NaCl (4 g/L), KH_2PO_4 (0.5 g/L), $MgSO_4•7H_2O$ (0.5 g/L), $CaCO_3$ (2 g/L), Sea salt (30 g/L).
2 mK	Yeast extract (2 g/L), Bacterial peptone (2 g/L), Glucose (2 g/L), Mannitol (3 g/L), Malt extract (5 g/L), Peptone from soybean (5 g/L), Soluble starch (5 g/L), Sea salt (30 g/L).
3 m2216E	2216E (37.4 g/L), Glucose (15 g/L), Sea salt (30 g/L).
4 mAm2ab	Soluble starch (5 g/L), Peptone from soybean (5 g/L), Glucose (20 g/L), Yeast extract (2 g/L), Bacterial peptone (2 g/L), KH_2PO_4 (1 g/L), $MgSO_4•7H_2O$ (0.5 g/L), $CaCO_3$ (2 g/L), Sea salt (30 g/L).
5 mBHI	BHI broth (38.5 g/L), Sea salt (30 g/L).
6 mISP2	Yeast extract (4 g/L), Malt extract (10 g/L), Glucose (4 g/L), Sea salt (30 g/L).
7 mISP4	Soluble starch (10 g/L), KH_2PO_4 (2 g/L), $MgSO_4•7H_2O$ (1 g/L), NaCl (1 g/L), $(NH_4)_2SO_4$ (2 g/L), $CaCO_3$ (3 g/L), TS (1 mL/L), Yeast extract (0.5 g/L), Bacterial peptone (1 g/L), Sea salt (30 g/L).
8 mRA	Soluble starch (20 g/L), Glucose (10 g/L), Malt extract (10 g/L), Maltose (10 g/L), Corn steep liquor (5 g/L), $CaCO_3$ (2 g/L), Sea salt (30 g/L).
9 mJNP1A	Soluble starch (20 g/L), Peptone of fish powder (2 g/L), Trehalose Dihydrate (2 g/L), Beef extract (3 g/L), Sea salt (30 g/L).
10 mM20	Soybean flour (15 g/L), Soluble starch (20 g/L), Yeast extract (5 g/L), Bacterial peptone (2 g/L), NaCl (4 g/L), $CaCO_3$ (2 g/L), Sea salt (30 g/L).
11 mMCQ1	Soluble starch (10 g/L), Glucose (10 g/L), Bacterial peptone (5 g/L), Yeast extract (3 g/L), Beef extract (2 g/L), KH_2PO_4 (0.5 g/L), $MgSO_4•7H_2O$ (0.5 g/L), KBr (1 g/L), $CaCO_3$ (2 g/L), Sea salt (30 g/L).

TS: Trace salts solution, $FeSO_4•7H_2O$ 0.1 g, $MnCl_2•4H_2O$ 0.1 g, $ZnSO_4•7H_2O$ 0.1 g, in H_2O 100 mL.

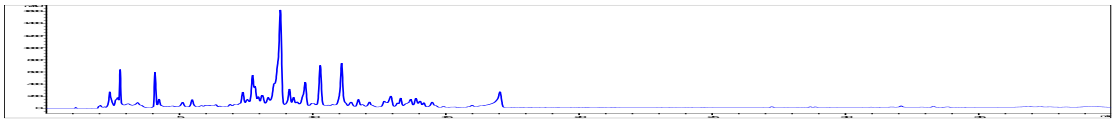
Fig. S1 HPLC analysis profiles of eleven fermentation conditions at 202 nm

Experimental group

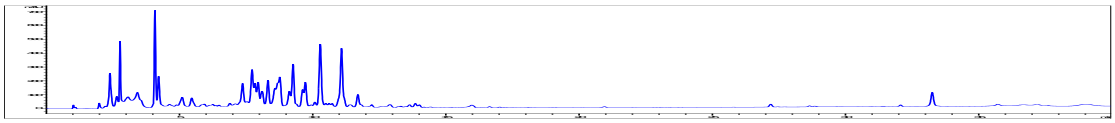
1 mA



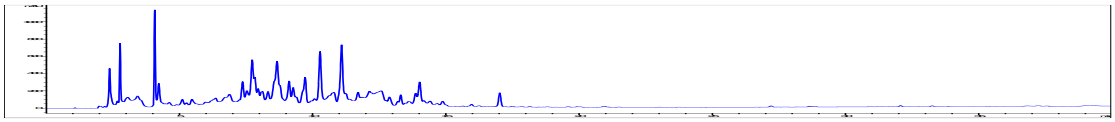
2 mK



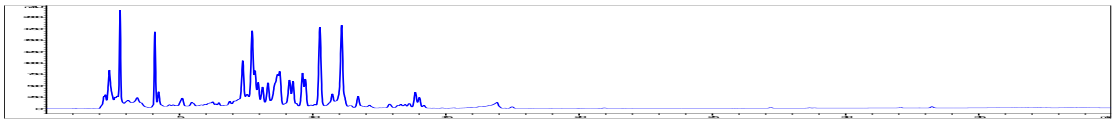
3 m2216E



4 mAm2ab

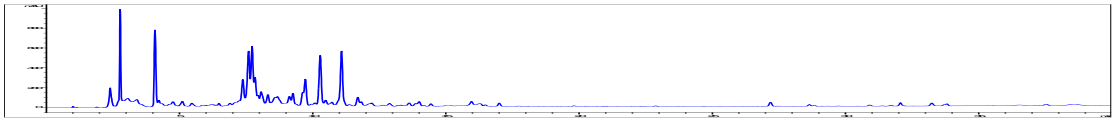


5 mBHI



6 mISP2

7 mISP4



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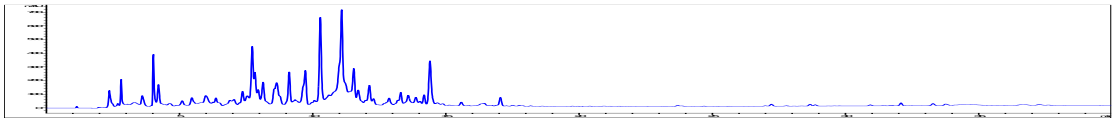
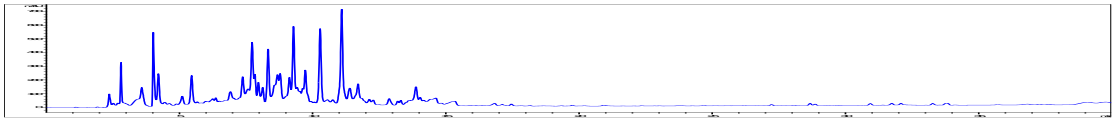
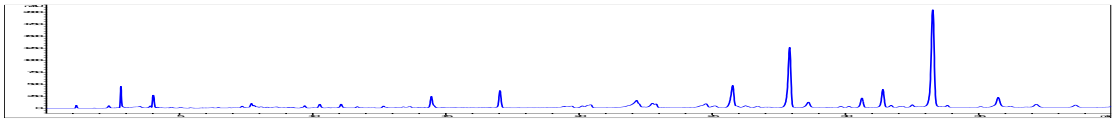


9 mJNP1A



10 mM20



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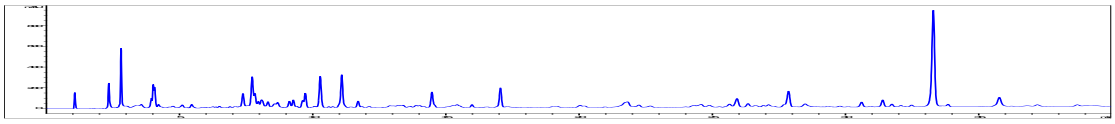
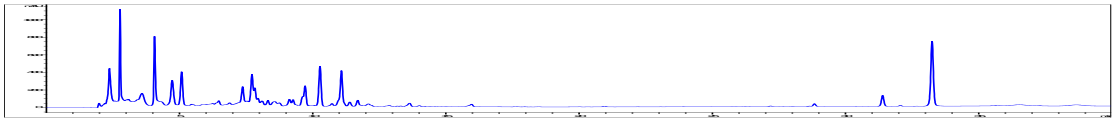
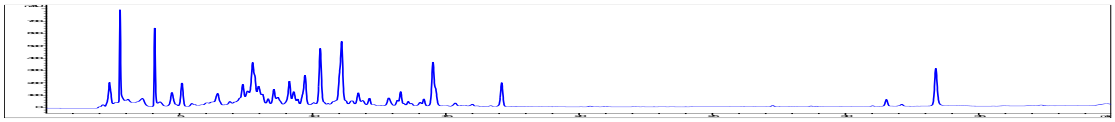


Blank group

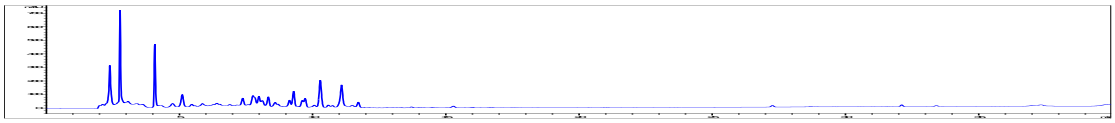
1 mA



2 mK



3 m2216E



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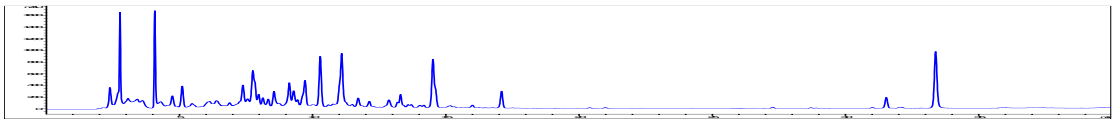
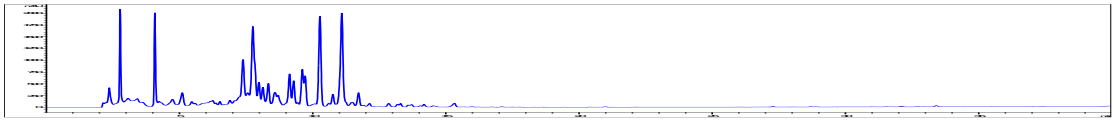
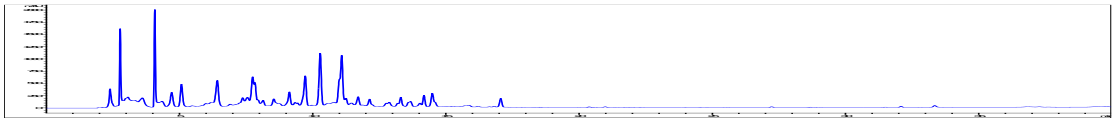


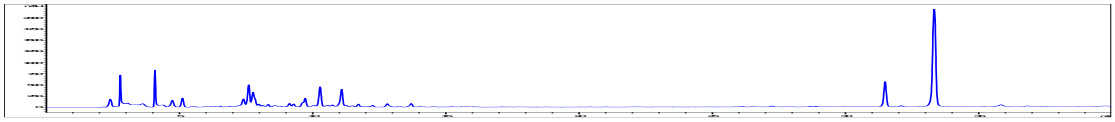
5 mBHI



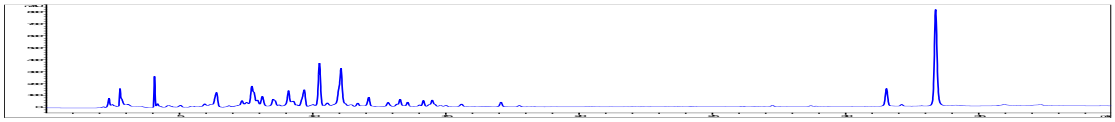
6 mISP2



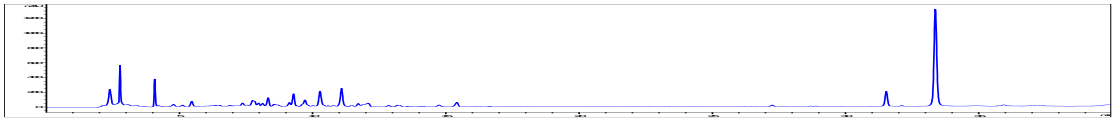
7 mISP4



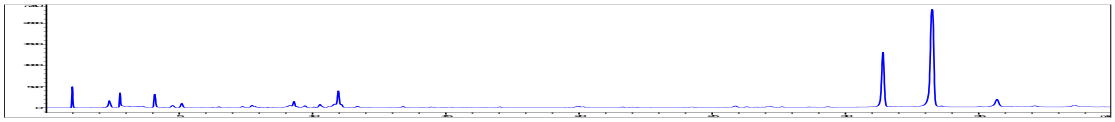
8 mRA



9 mJNP1A



10 mM20



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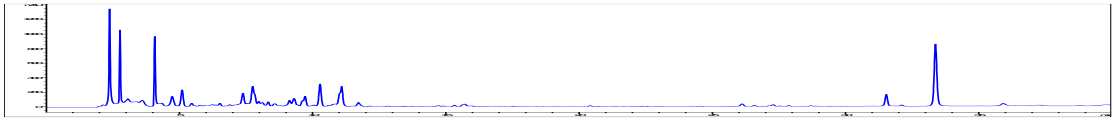
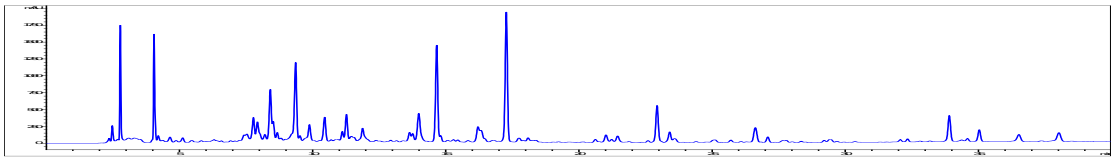
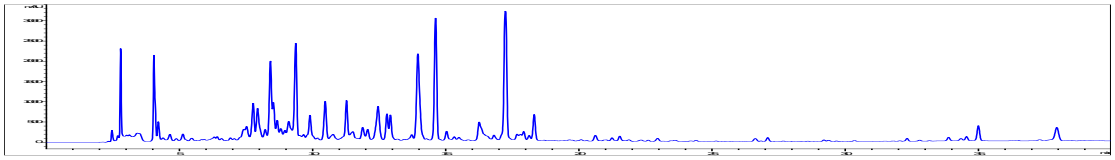


Fig. S2 HPLC analysis profiles of monitoring different time sample in fermenter at 202 nm

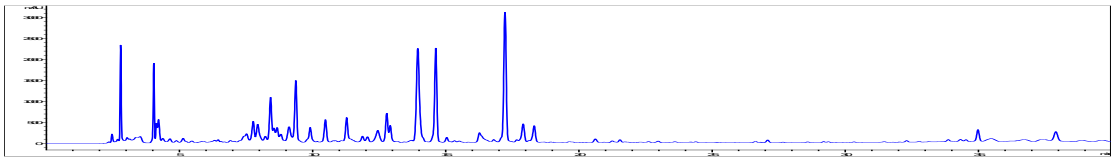
23 h



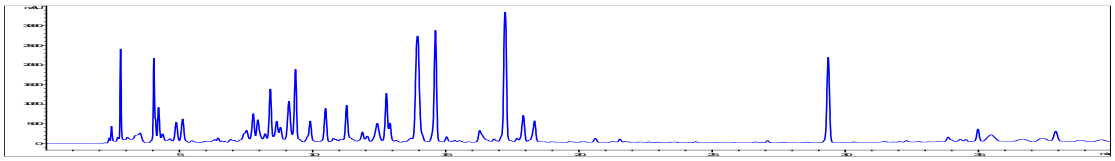
48 h



72 h



96 h



115 h

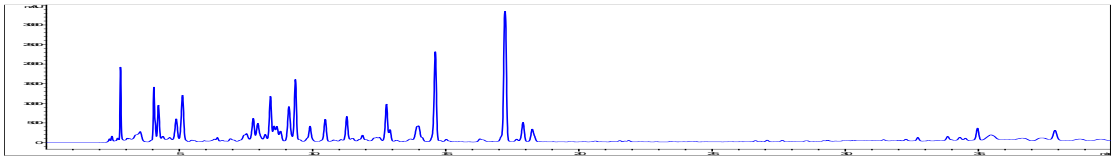


Fig. S3 Variation in pH and DO of the large-scale fermentation

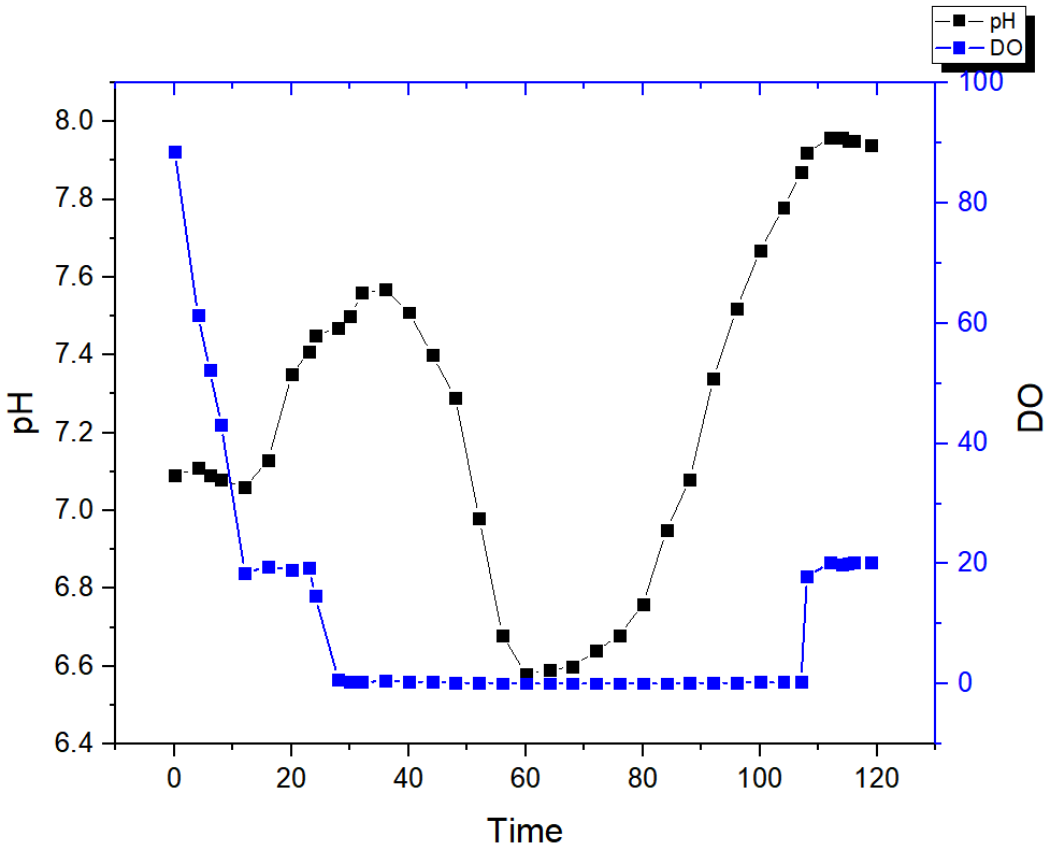
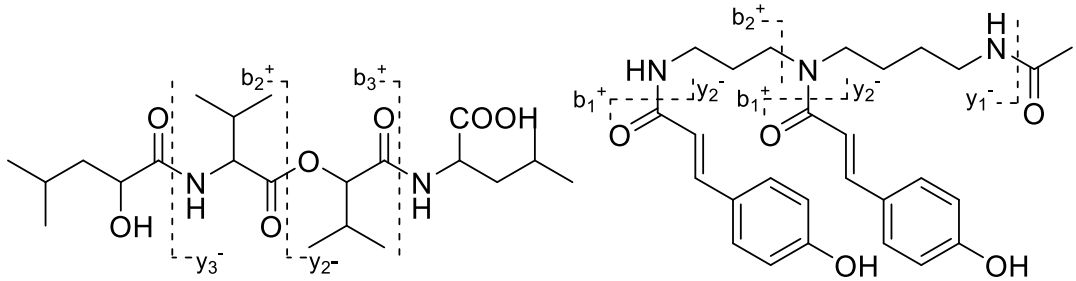


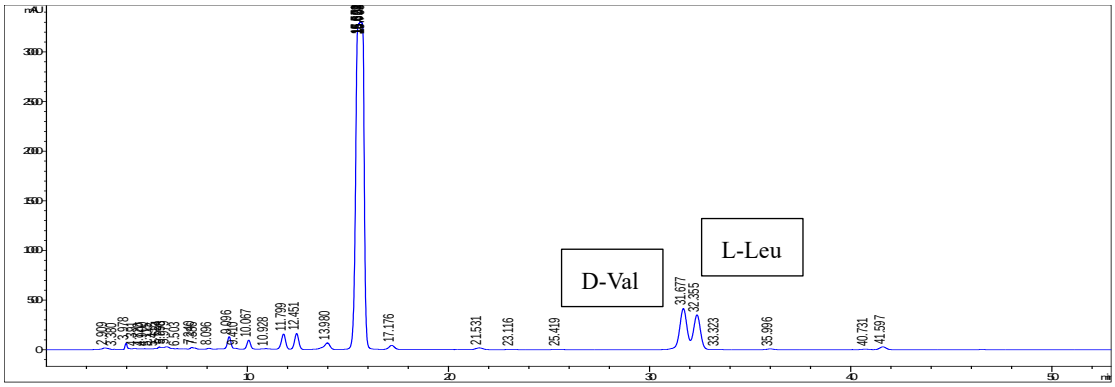
Fig. S4 Sets of fragmentation ions obtained in ESI-MS/MS of compounds **2** and **3**



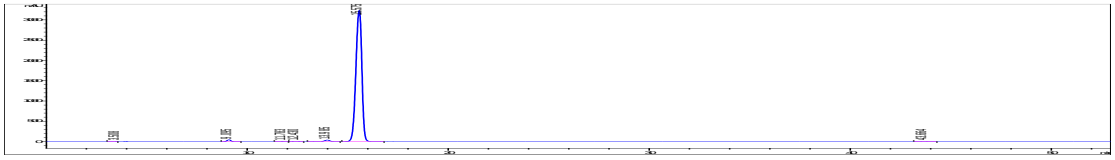
2		**3**	
fragmentation ions	*m*/*z*	fragmentation ions	*m*/*z*
precursor	445.2818	precursor	480.2358
b_2^+	214.14	b_1^+	147.04
$[b_2\text{-CO}]^+$	186.15	b_2^+	204.1
b_3^+	314.2	$[y_2+2H]^+$	334.21
$[y_2+2H]^+$	232.16	$[y_2+2H-H_2O]^+$	316.2
$[y_3+2H]^+$	331.22	$[y_2+3H-b_1]^+$	188.18
		$[y_1+3H-b_1-NH_3]^+$	275.18

Fig. S5 HPLC analysis profiles of Marfey's derivatives of **2** at 340 nm

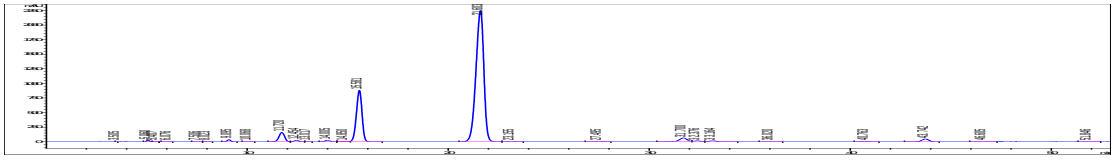
Marfey's derivatives of **2**



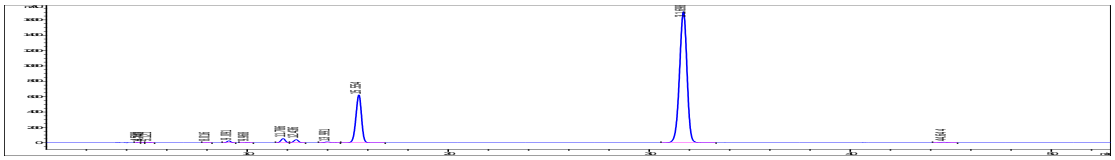
L-FDAA



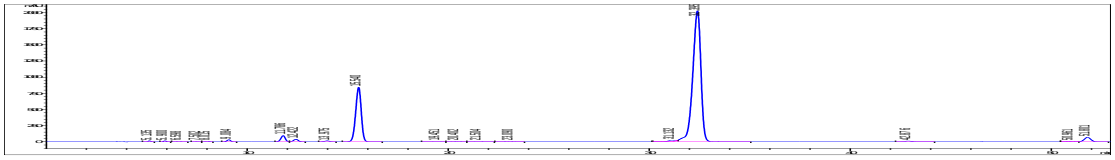
L-Val-FDAA



D-Val-FDAA



L- Leu -FDAA



D-Leu-FDAA

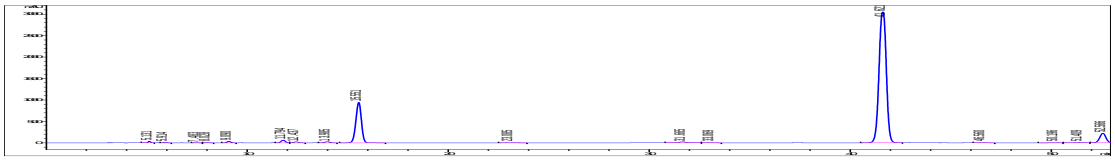
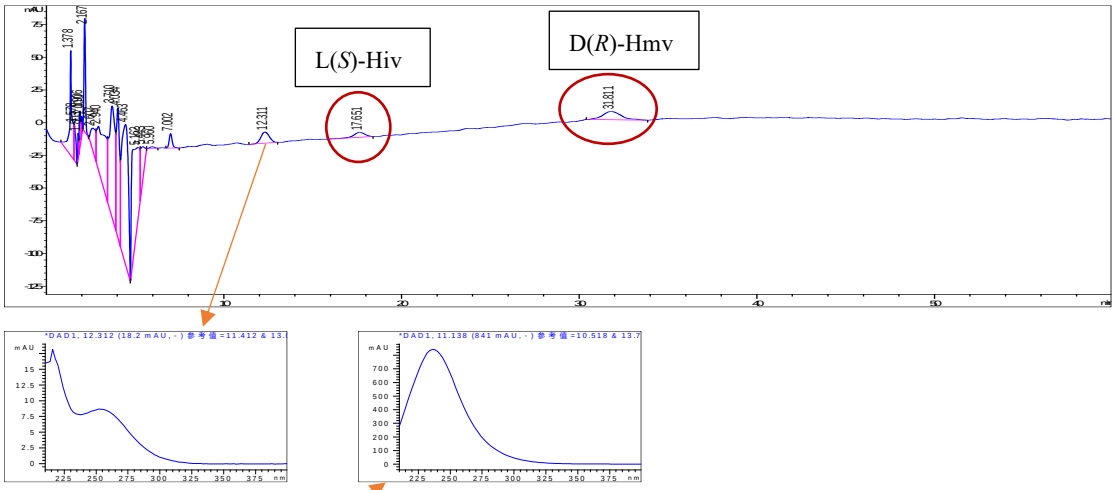


Fig. S6 HPLC analysis profiles of hydrolysate of **2** at 254 nm

Hydrolysate of **2**



Four standard α-hydroxy acids

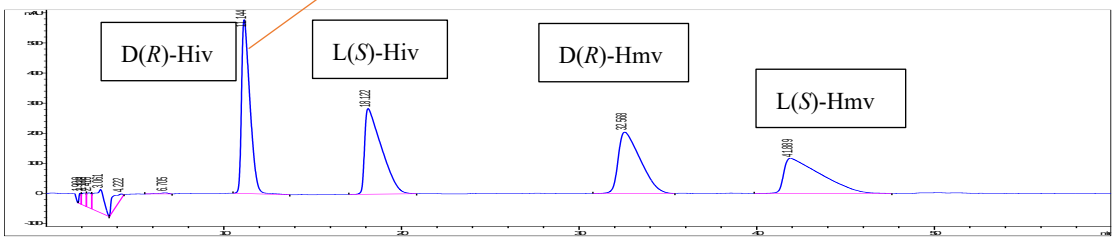
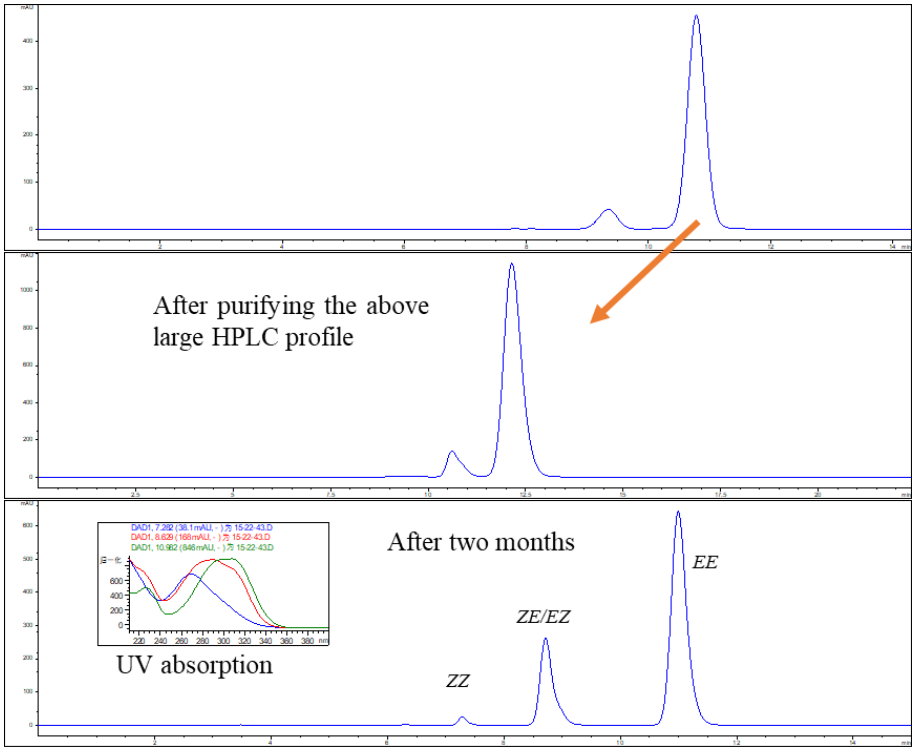


Fig. S7 HPLC analysis profiles of **3** at 280 nm



Using different analysis conditions

Table S2 The retention times of Marfey's derivatives of **8** and **10-13**

Sample	t_{RL}[a]					
	Pro	Ala	Val	Phe	Ile	Leu
standard	25.277	21.721	33.574	44.178	40.167	41.202
8	12.309[d]					41.156
10					40.049	
11	12.137[d]				40.052	
12		21.243			40.077	
13			33.036	43.545		

Sample	t_{RD}[b]						t_R[c]
	Pro	Ala	Val	Phe	Ile	Leu	L-FDAA
standard	27.718	37.388	40.945	49.916	47.595	47.926	25.648
8							25.532
10	27.18						25.286
11							25.311
12							25.332
13							25.386

[a] The retention times of L-amino acid derivatives. [b] The retention times of D- L-amino acid derivatives. [c] The retention time of L-FDAA. [d] The retention time of 3(*R*)-OH-Pro derivative.

Fig. S8 Circular genome map of SCSIO 52902

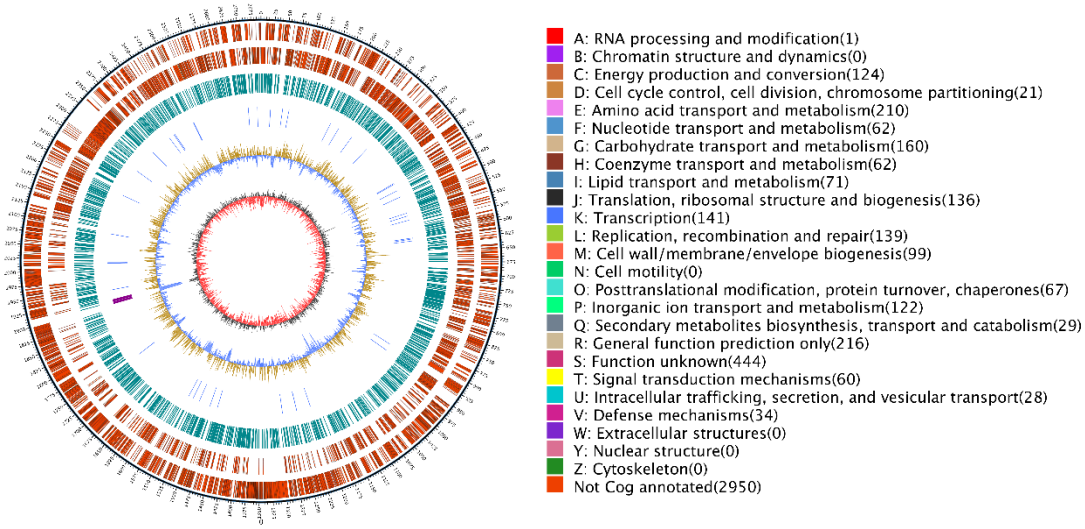


Table S3 The putative biosynthetic gene clusters from SCSIO 52902 using antiSMASH platform

Settings	Regions	Types	Location	Total
with the "relaxed strictness" setting	1.1	terpene	839,348 - 860,262 nt	20,915 nt
	1.2	T3PKS	1,327,415 - 1,368,557 nt	41,143 nt
	1.3	oligosaccharide	1,548,516 - 1,600,123 nt	51,608 nt
	1.4	betalactone	1,949,843 - 1,976,478 nt	26,636 nt
	1.5	redox-cofactor	2,027,514 - 2,055,420 nt	27,907 nt
with the "loose strictness" setting	2.1	saccharide	3 - 21,446 nt	21,444 nt
	2.2	saccharide, fatty_acid	247,226 - 289,189 nt	41,964 nt
	2.3	saccharide	314,706 - 377,916 nt	63,211 nt
	2.4	saccharide	398,747 - 420,622 nt	21,876 nt
	2.5	saccharide	485,313 - 527,212 nt	41,900 nt
	2.6	saccharide	528,766 - 565,722 nt	36,957 nt
	2.7	saccharide	669,928 - 691,728 nt	21,801 nt
	2.8	terpene	839,348 - 860,262 nt	20,915 nt
	2.9	saccharide	977,063 - 1,009,209 nt	32,147 nt
	2.10	saccharide	1,217,315 - 1,244,224 nt	26,910 nt
	2.11	T3PKS	1,327,415 - 1,368,557 nt	41,143 nt
	2.12	saccharide	1,437,602 - 1,498,602 nt	61,001 nt
	2.13	saccharide, oligosaccharide	1,544,536 - 1,600,123 nt	55,588 nt
	2.14	betalactone, saccharide	1,949,843 - 1,992,667 nt	42,825 nt
	2.15	redox-cofactor	2,027,514 - 2,055,420 nt	27,907 nt
	2.16	saccharide	2,168,764 - 2,231,223 nt	62,460 nt
	2.17	fatty_acid	2,413,831 - 2,436,419 nt	22,589 nt
	2.18	saccharide	2,537,533 - 2,567,647 nt	30,115 nt
	2.19	saccharide	2,599,638 - 2,652,795 nt	53,158 nt

Fig. S9 Partial biosynthetic gene clusters from SCSIO 52902

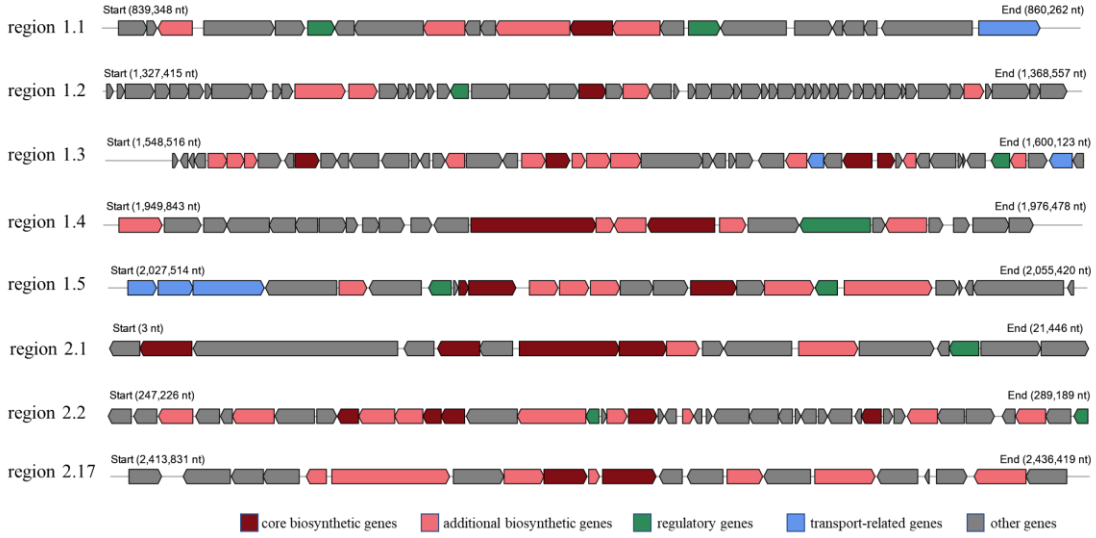


Table S4 The key genes information related to the shikimate and OBS pathway.

Gene	Orientation	Location	Swissprot_target_ID	E-value	Identity	Cover
aroH	(+)	1967385-1968767 (1383 nt)	P80574(AROF_STRCO)	3.00E-157	61.24%	94.57%
aroB	(-)	2329535-2328474 (1062 nt)	Q6AF95(AROB_LEIXX)	1.00E-128	65.72%	99.43%
aroK	(-)	2330095-2329556 (540 nt)	Q9KXQ5(AROK_STRCO)	8.30E-23	45.45%	83.24%
aroC	(-)	2331279-2330092 (1188 nt)	A5CRZ1(AROC_CLAM3)	2.20E-169	77.92%	99.49%
aroE	(-)	2332133-2331282 (852 nt)	Q39VU8(AROE_GEOMG)	8.30E-17	40.11%	61.84%
trpG	(-)	928266-927607 (660 nt)	P9WN34(TRPG_MYCTO)	2.20E-57	58.08%	88.58%
pchA	(+)	564511-565722 (1212 nt)	Q51508(PCHA_PSEAE)	5.60E-35	31.84%	89.58%
menD	(-)	570394-568727 (1668 nt)	Q6AHC2(MEND_LEIXX)	1.90E-118	48.48%	98.38%
menC	(+)	579653-580621 (969 nt)	A0QRG0(MENC_MYCS2)	7.60E-83	57.78%	97.52%
menE	(-)	574492-573491 (1002 nt)	P9WQ38(MENE_MYCTO)	7.20E-36	35.03%	90.09%
menB	(-)	575427-574528 (900 nt)	A0QRD3(MENB_MYCS2)	6.30E-124	74.33%	97.99%

Table S5 Inhibition rate against three human tumor cell lines

	Inhibition rate (30 μM)		
Compounds	A-549	HL-60	HCT-116
1	3.93%	-2.36%	2.00%
2	3.24%	-10.65%	1.42%
3	2.79%	-1.82%	5.74%
4	1.84%	2.63%	1.14%
5	24.01%	77.12%	5.34%
6	3.65%	4.42%	1.72%
7	3.25%	1.38%	0.97%
8	4.24%	3.54%	1.07%
9	7.17%	-1.55%	0.82%
10	8.02%	-1.38%	1.05%
11	-0.88%	-1.61%	2.41%
12	-2.04%	-2.89%	0.48%
13	-1.37%	-1.67%	1.60%
14	-1.22%	-3.48%	-0.09%
15	-1.98%	-6.37%	1.62%
16	-2.63%	5.86%	-0.40%
17	-1.59%	-7.34%	-3.47%

Fig. S10 HRESIMS spectrum of compound **1**

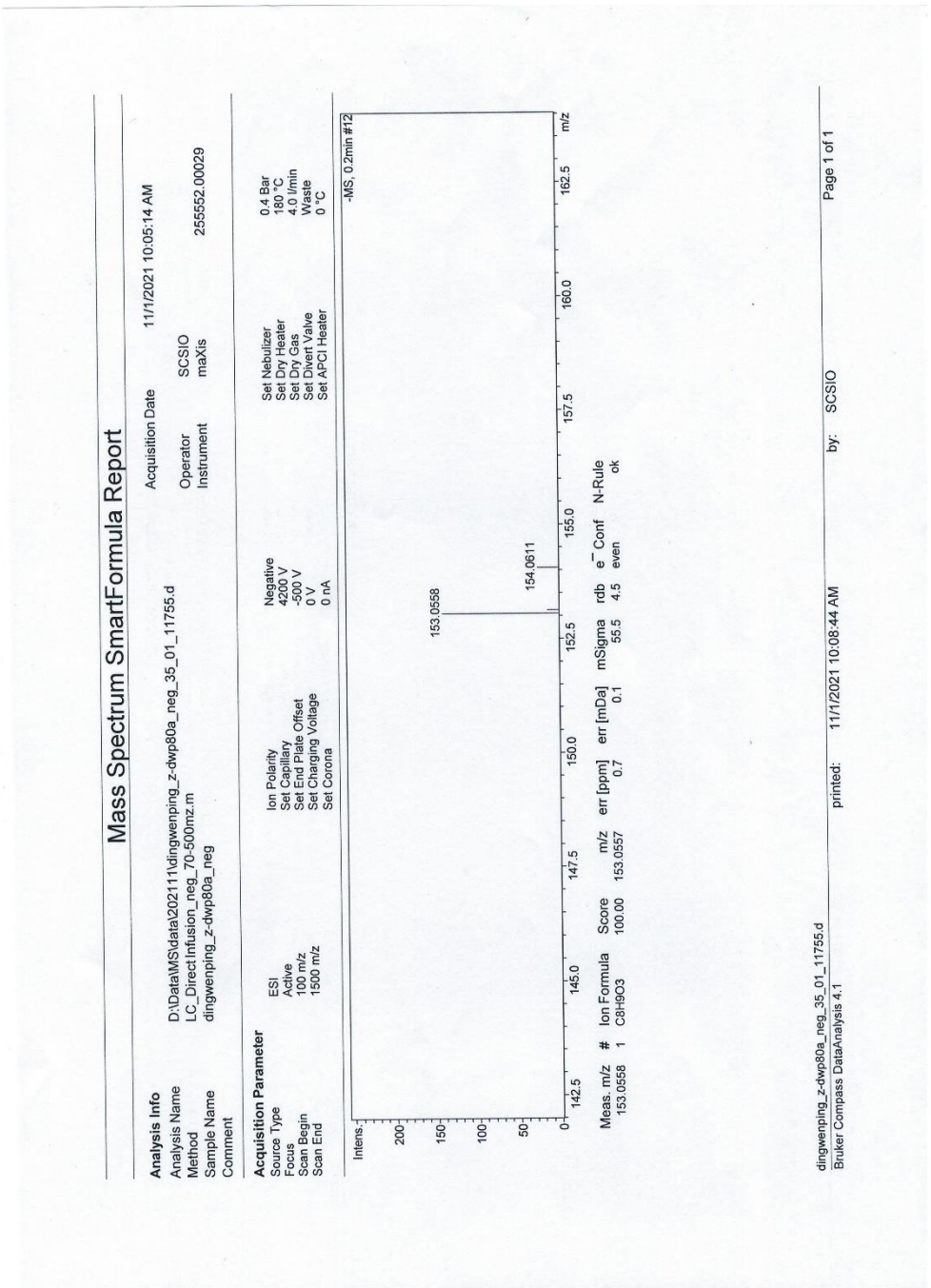


Fig. S11 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **1**

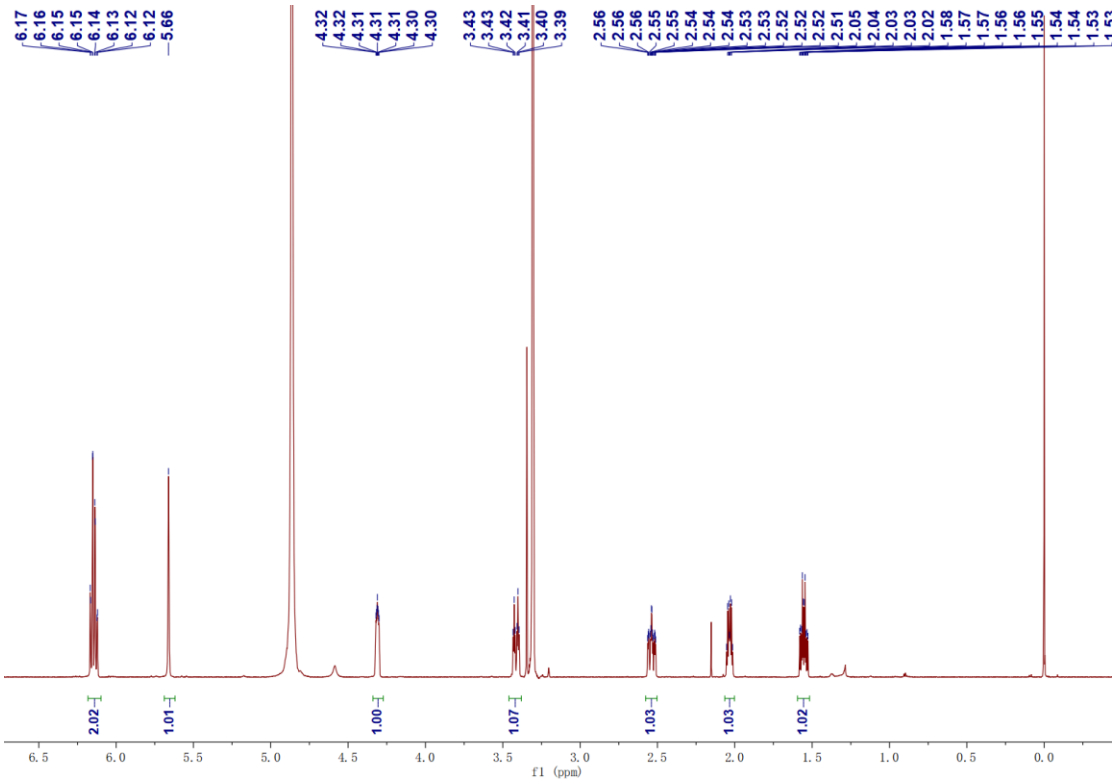


Fig. S12 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **1**

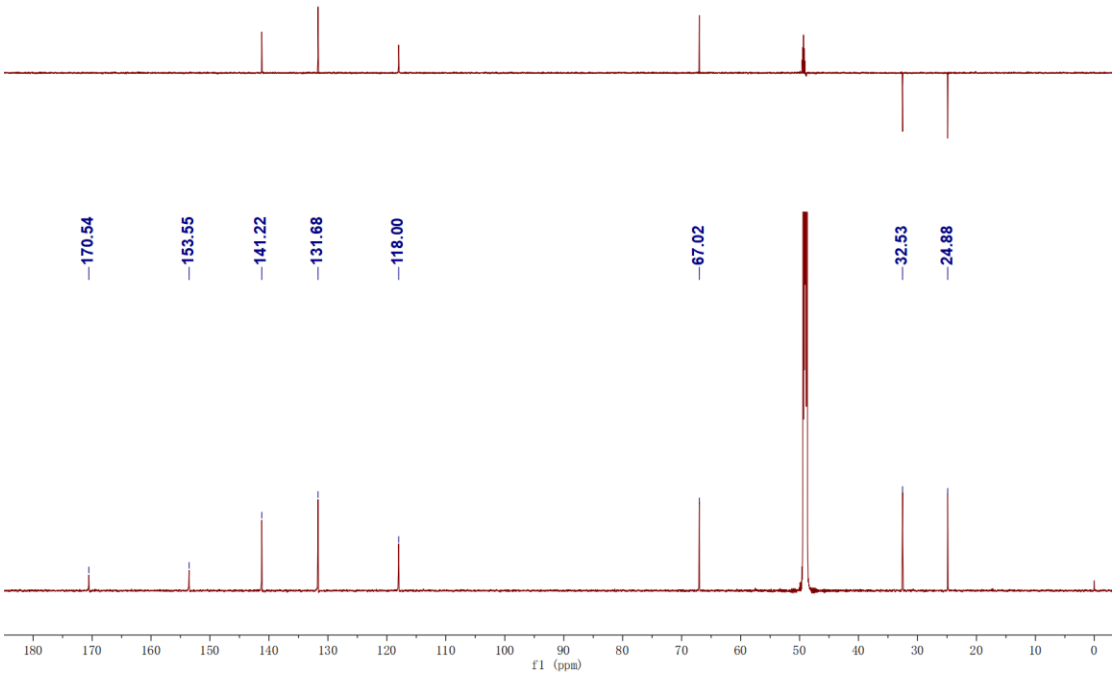


Fig. S13 HSQC spectrum of compound **1**

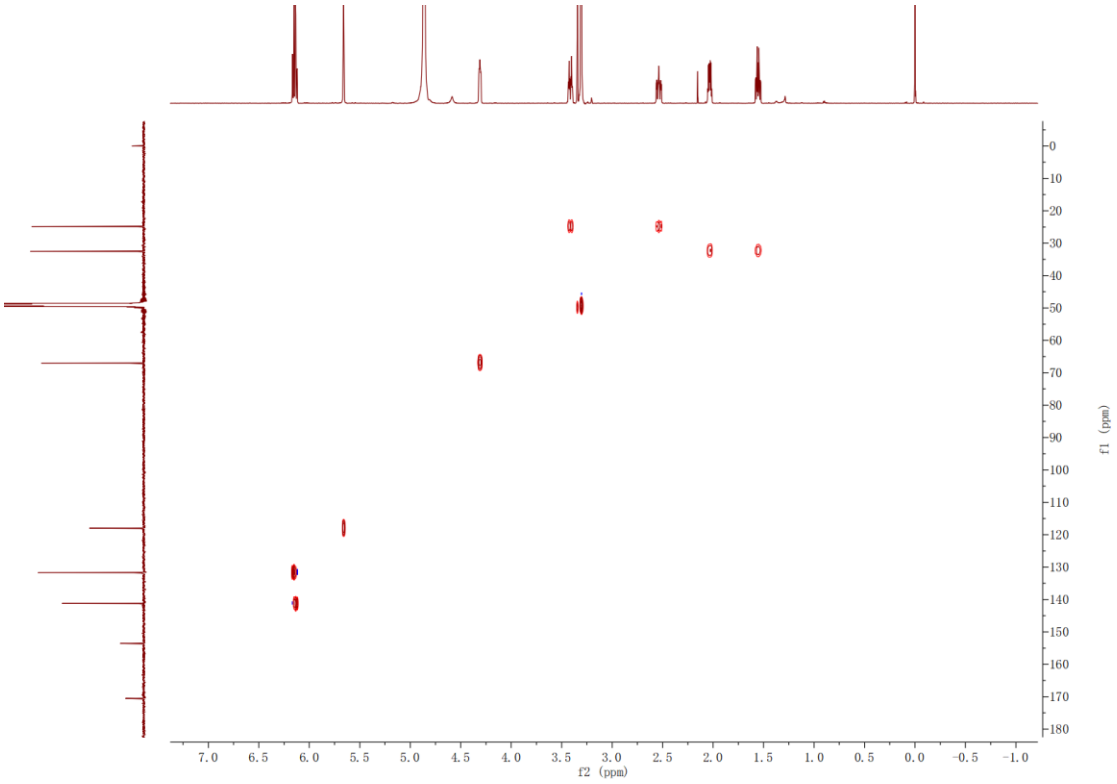


Fig. S14 HMBC spectrum of compound **1**

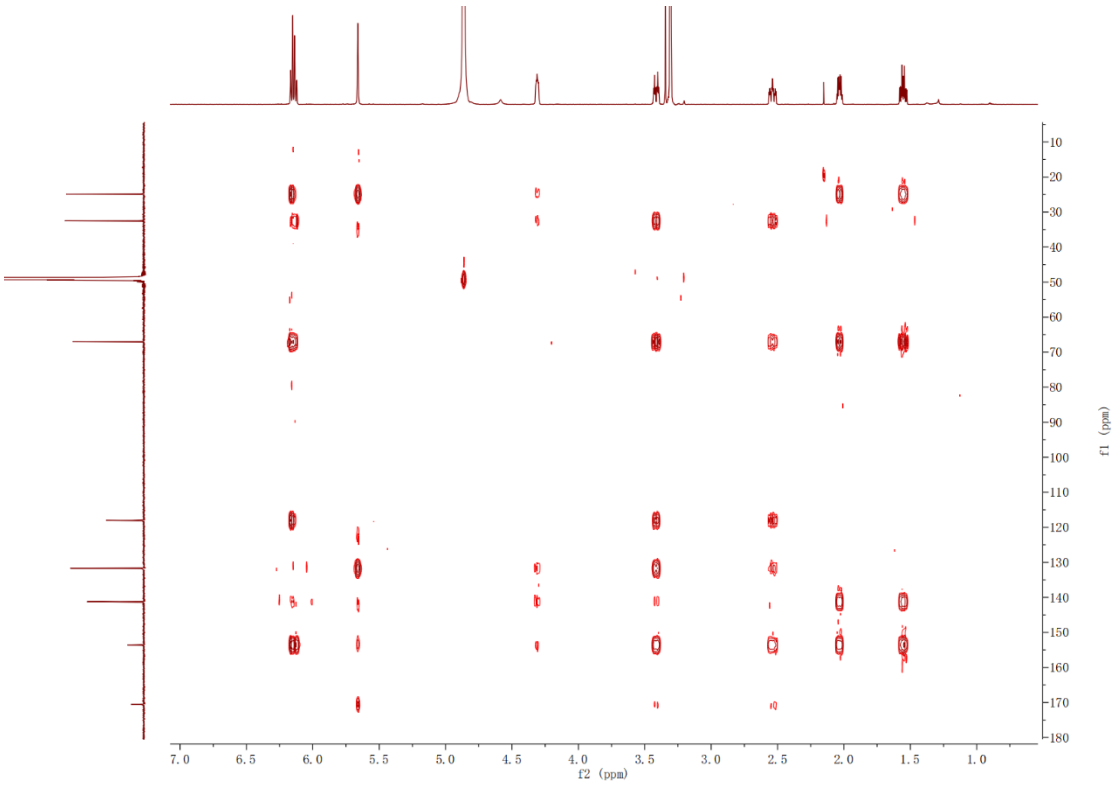


Fig. S15 ^{1}H–^{1}H COSY spectrum of compound **1**

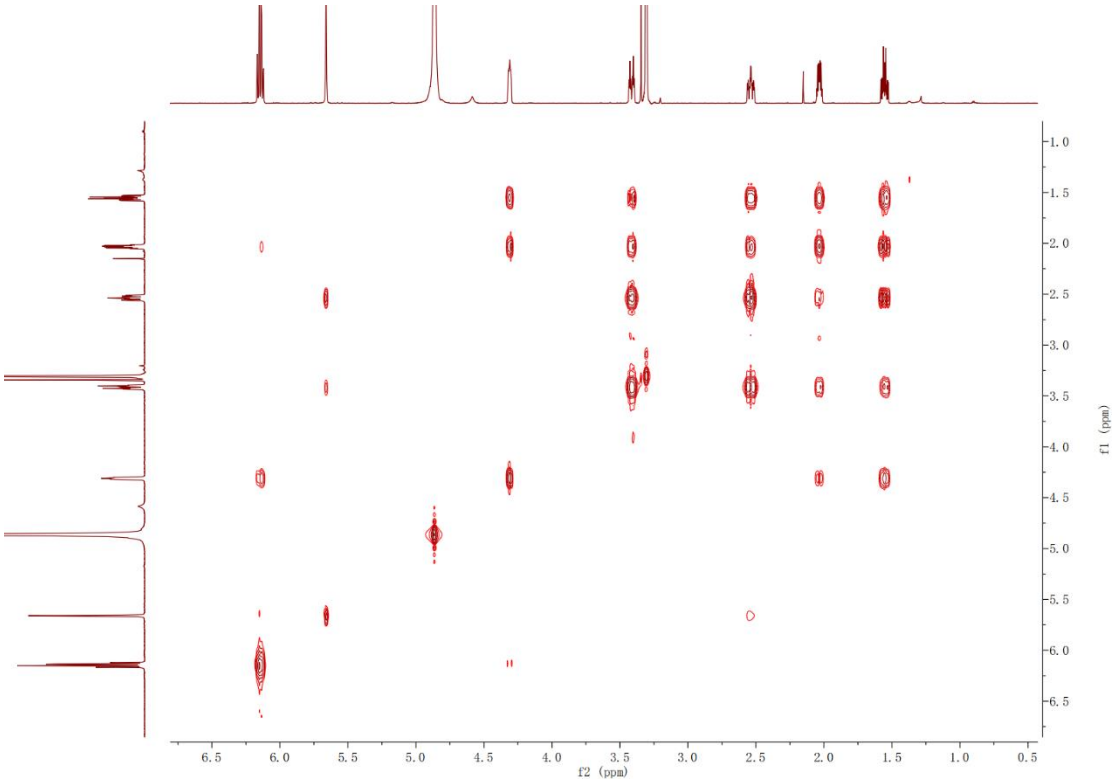
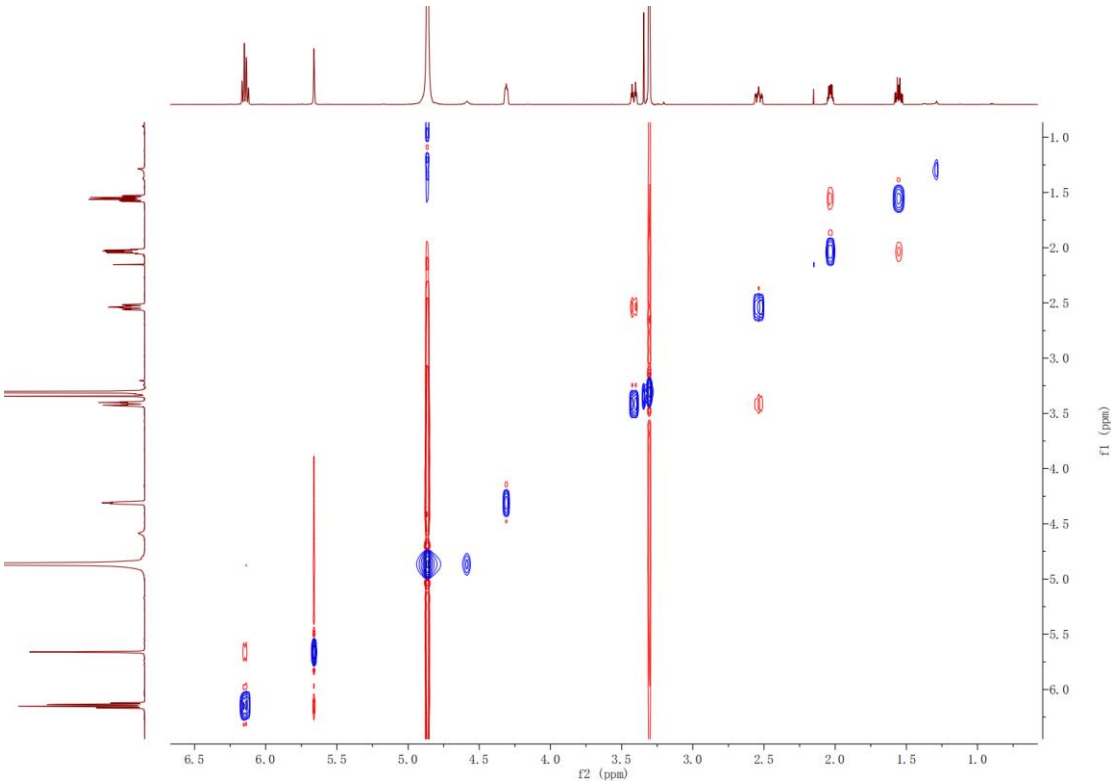
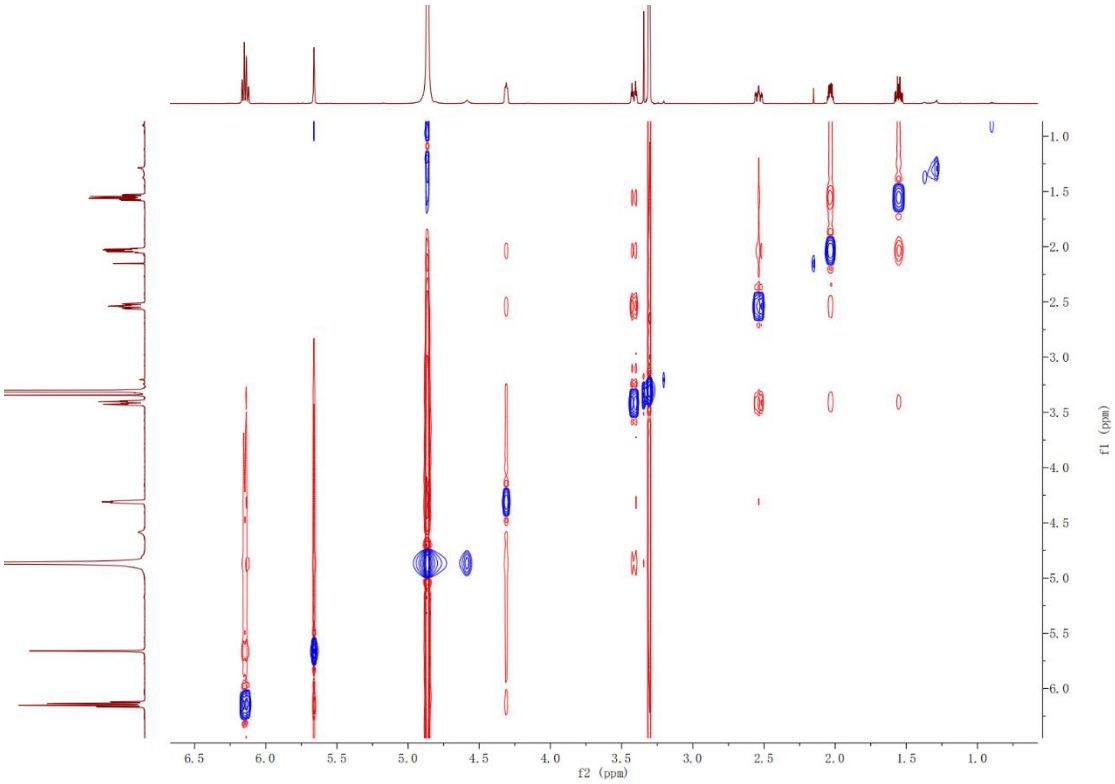


Fig. S16 NOESY spectrum of compound **1**

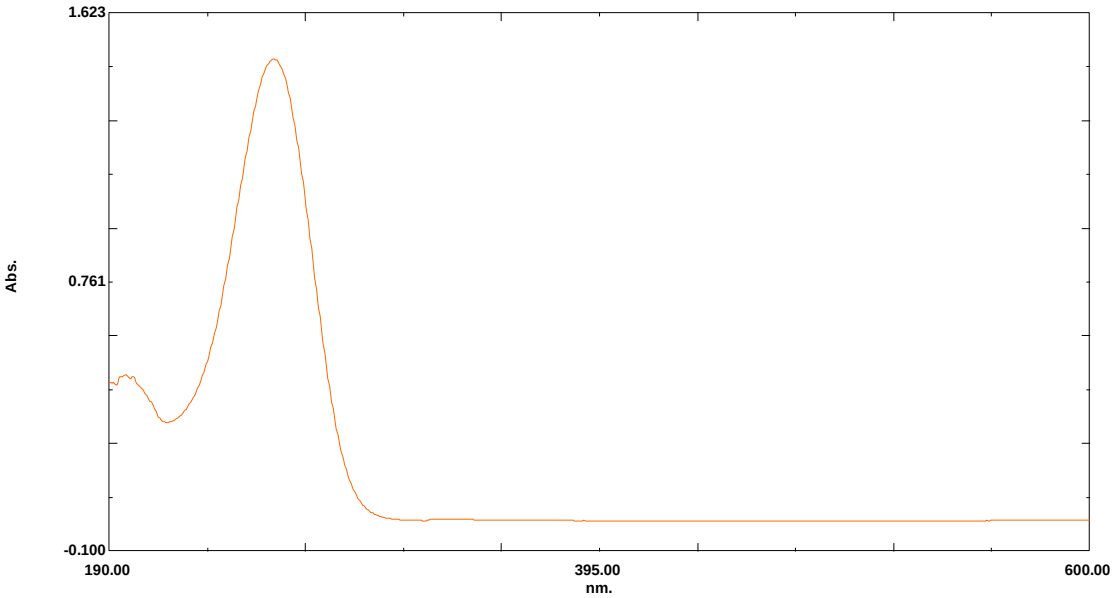




Crystallographic data of compound **1**

Crystal Data for $C_{16}H_{20}O_6$ (*M* =308.32 g/mol): triclinic, space group P1 (no. 1), *a* = 6.0982(3) Å, *b* = 7.5360(3) Å, *c* = 9.0518(3) Å, *α* = 71.293(3)°, *β* = 70.575(4)°, *γ* = 80.927(4)°, *V* = 370.97(3) Å^3, *Z* = 1, *T* = 100.00(10) K, μ(Cu Kα) = 0.883 mm^{-1}, *Dcalc* = 1.380 g/cm^3, 6840 reflections measured (10.822° ≤ 2Θ ≤ 149.022°), 2732 unique (R_{int} = 0.0350, R_{sigma} = 0.0384) which were used in all calculations. The final R_1 was 0.0724 (I > 2σ(I)) and wR_2 was 0.1809 (all data).

Fig. S17 UV spectrum of compound **1**



No.	wavelength (nm)	Abs
1	259.00	1.475
2	197.00	0.465

Fig. S18 ECD spectrum of compound **1**

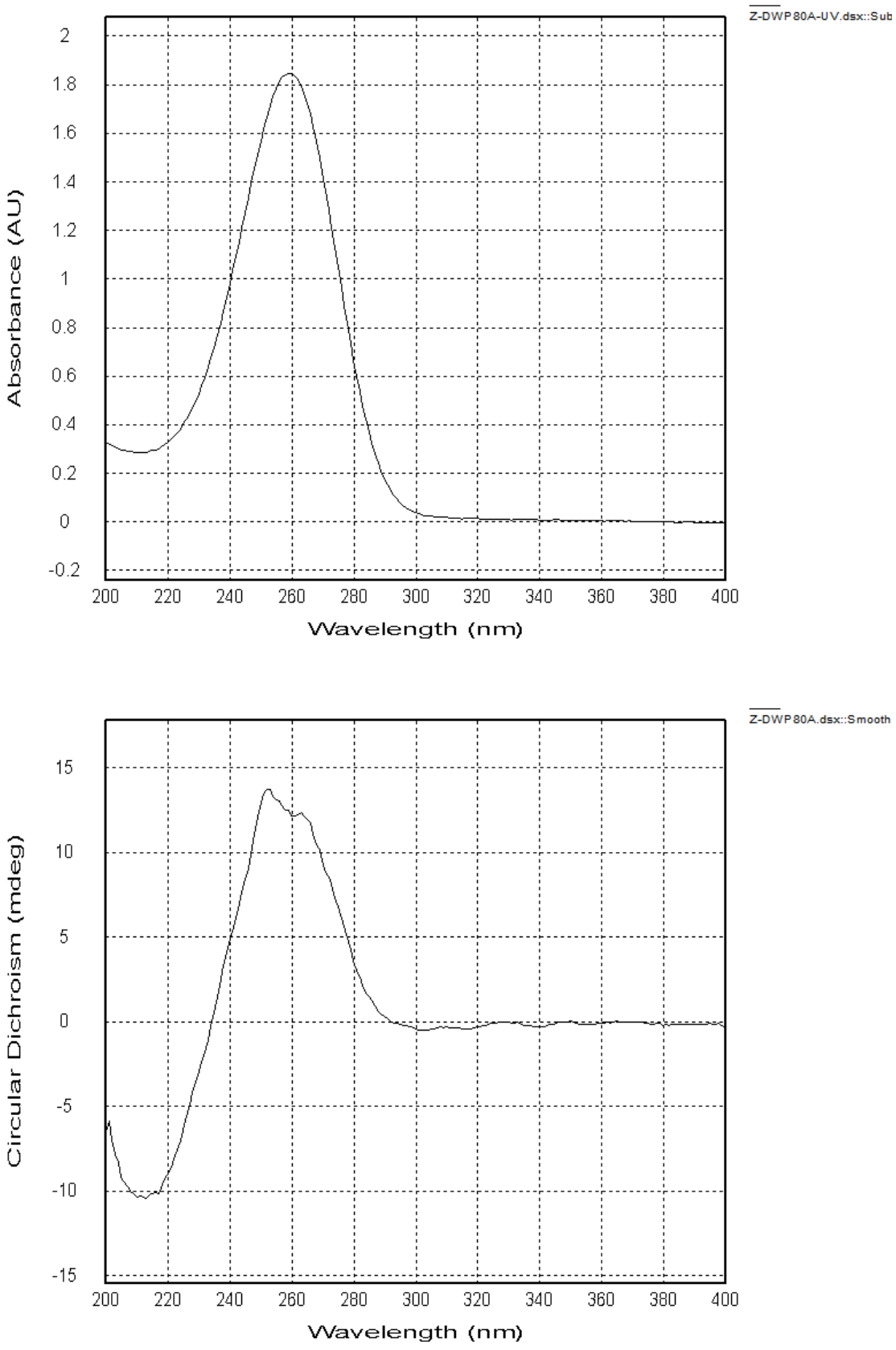


Fig. S19 IR spectrum of compound **1**

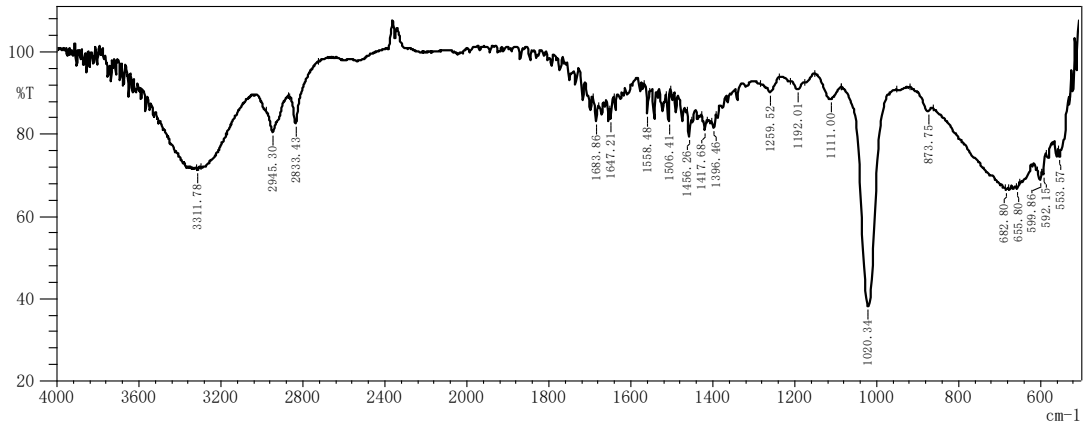


Fig. S20 HRESIMS spectrum of compound **2**

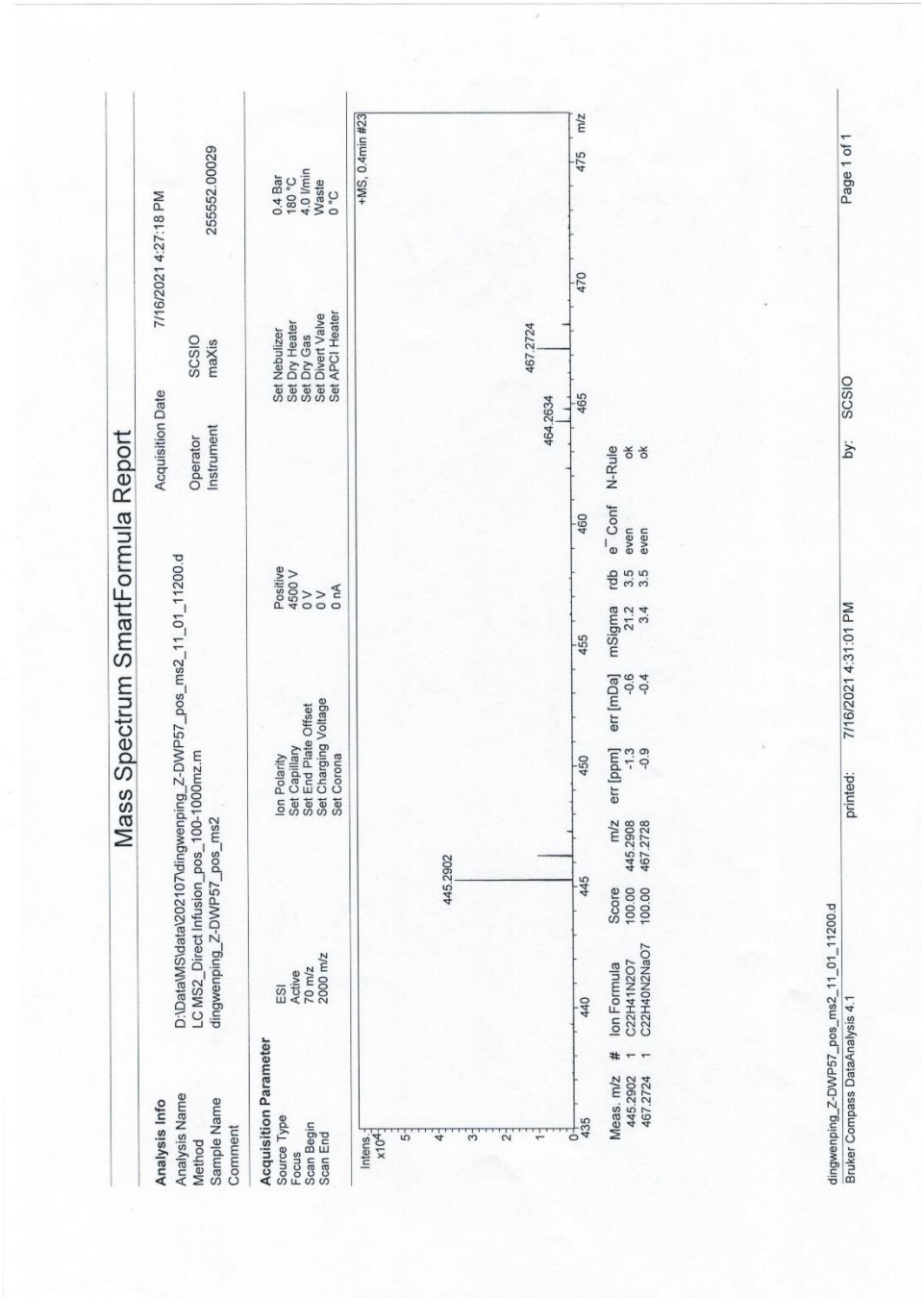


Fig. S21 HRESI-MS/MS-positive spectrum of compound **2**

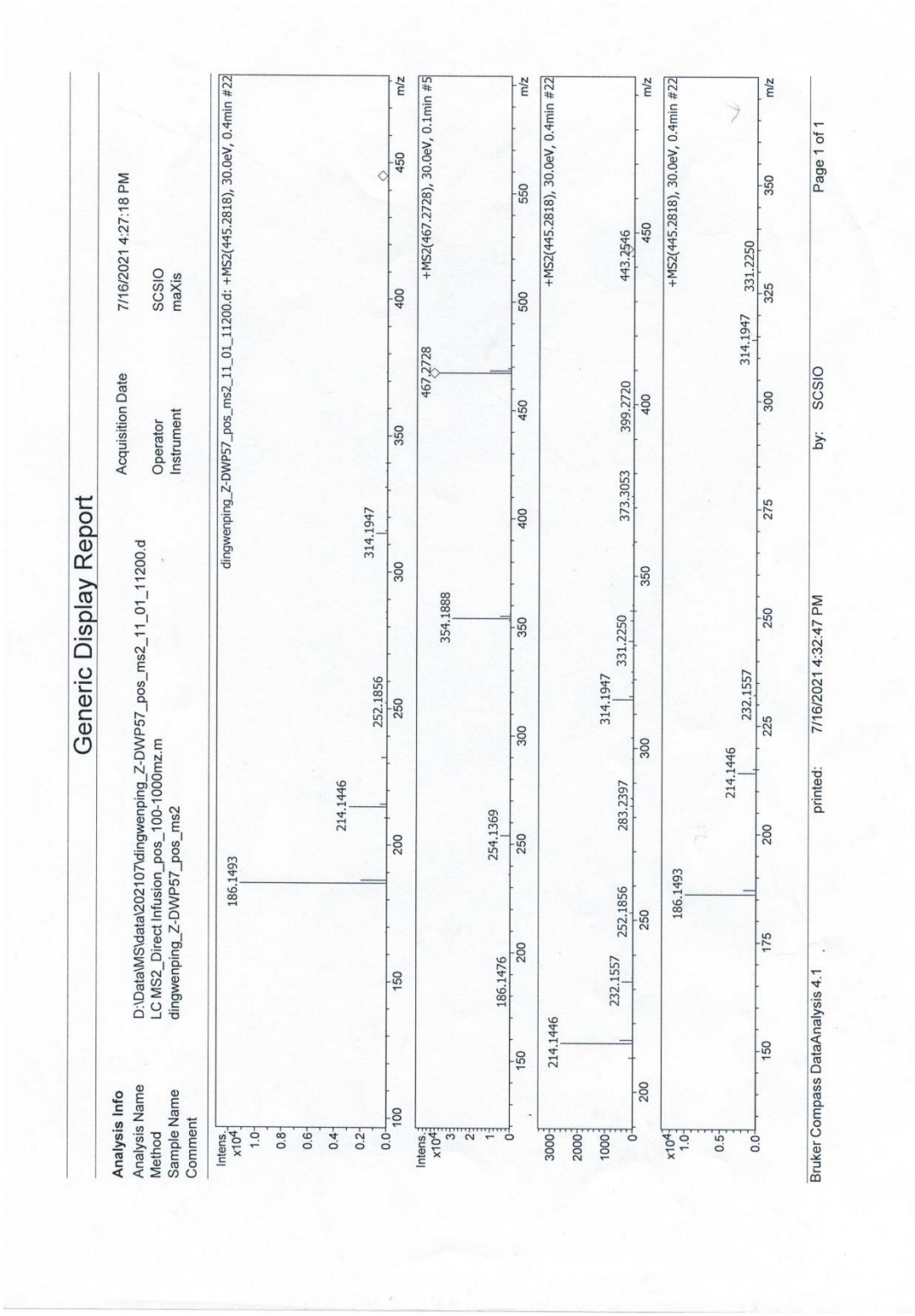


Fig. S22 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **2**

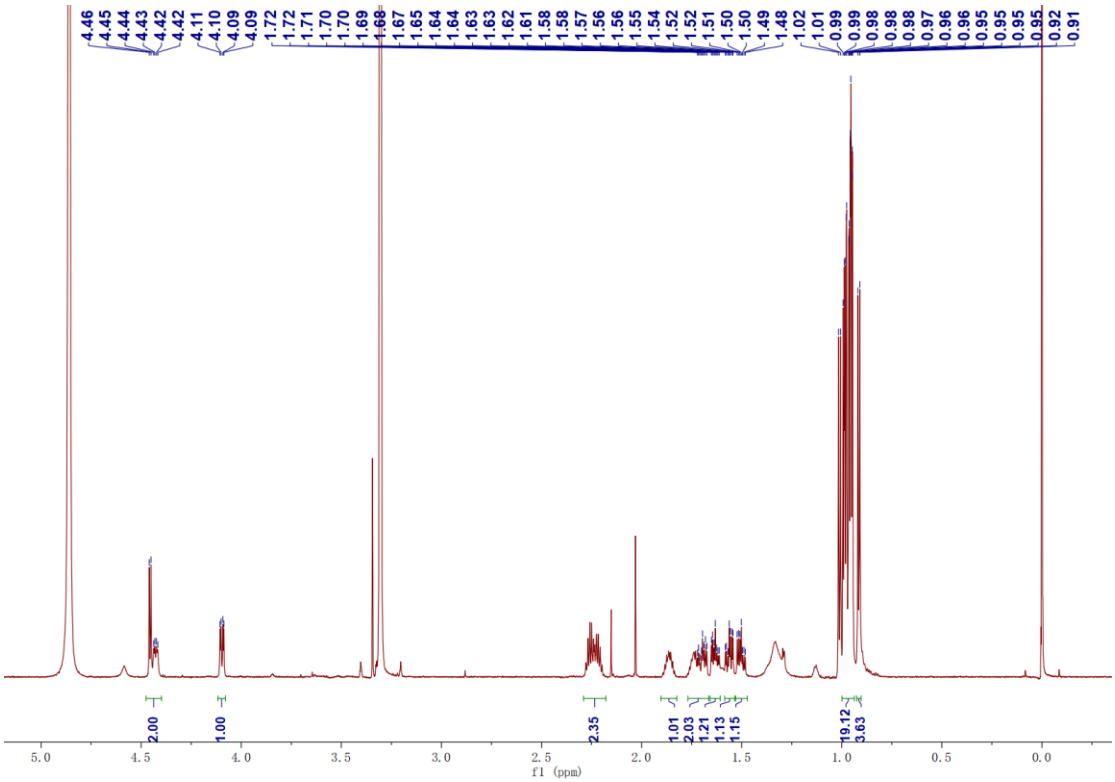


Fig. S23 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **2**

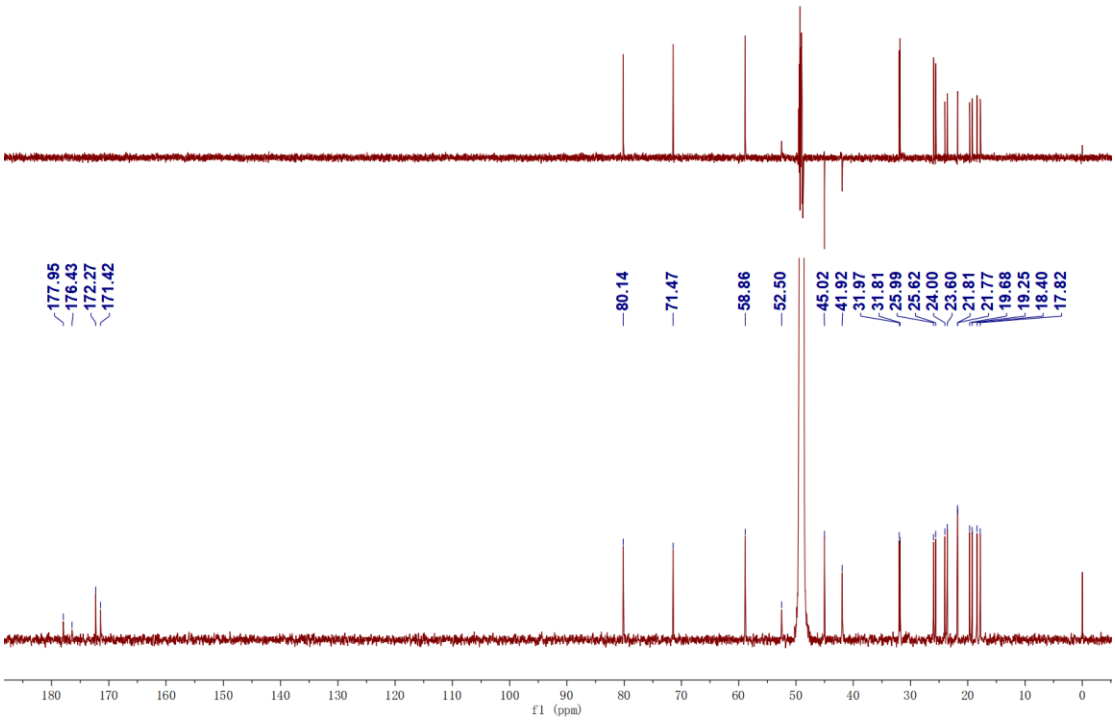


Fig. S24 HSQC spectrum of compound **2**

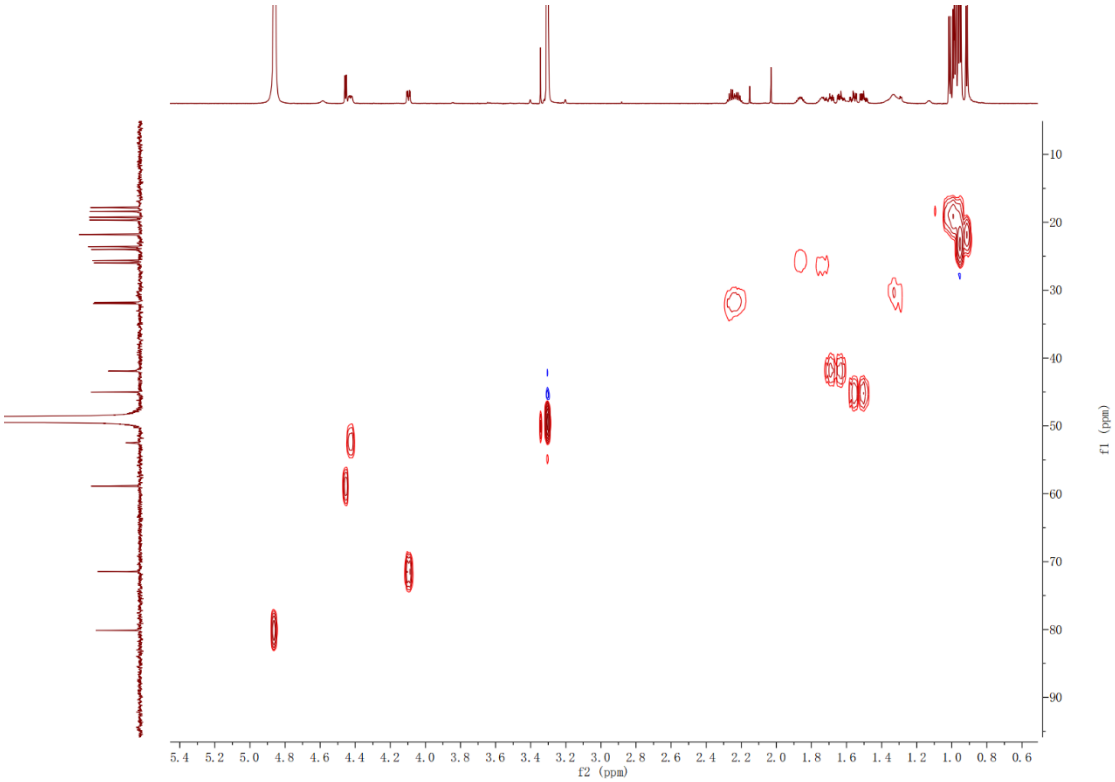


Fig. S25 HMBC spectrum of compound **2**

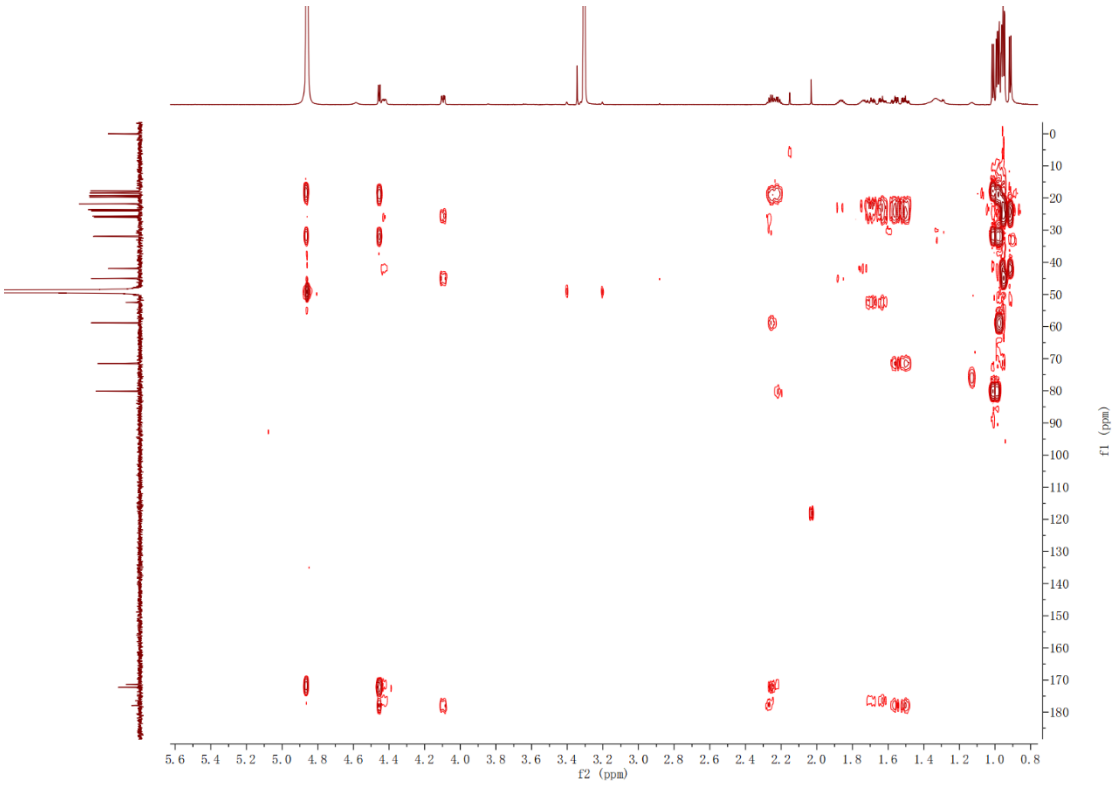


Fig. S26 $^{1}H–^{1}H$ COSY spectrum of compound **2**

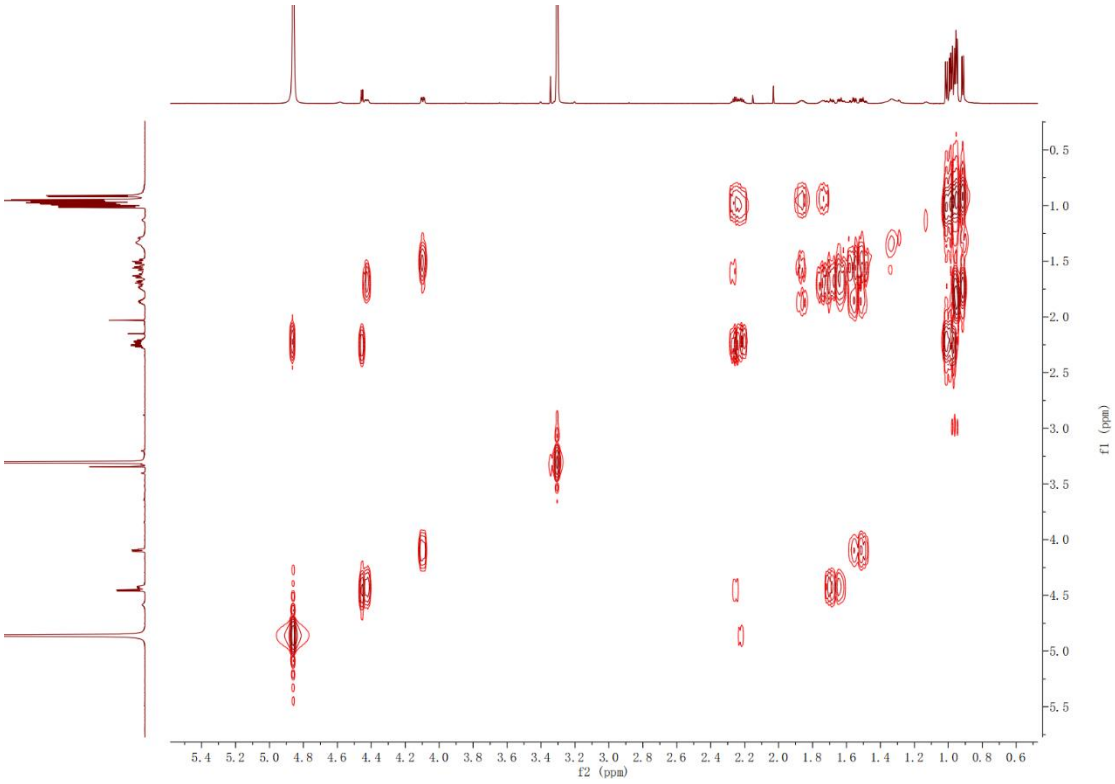


Fig. S27 NOESY spectrum of compound **2**

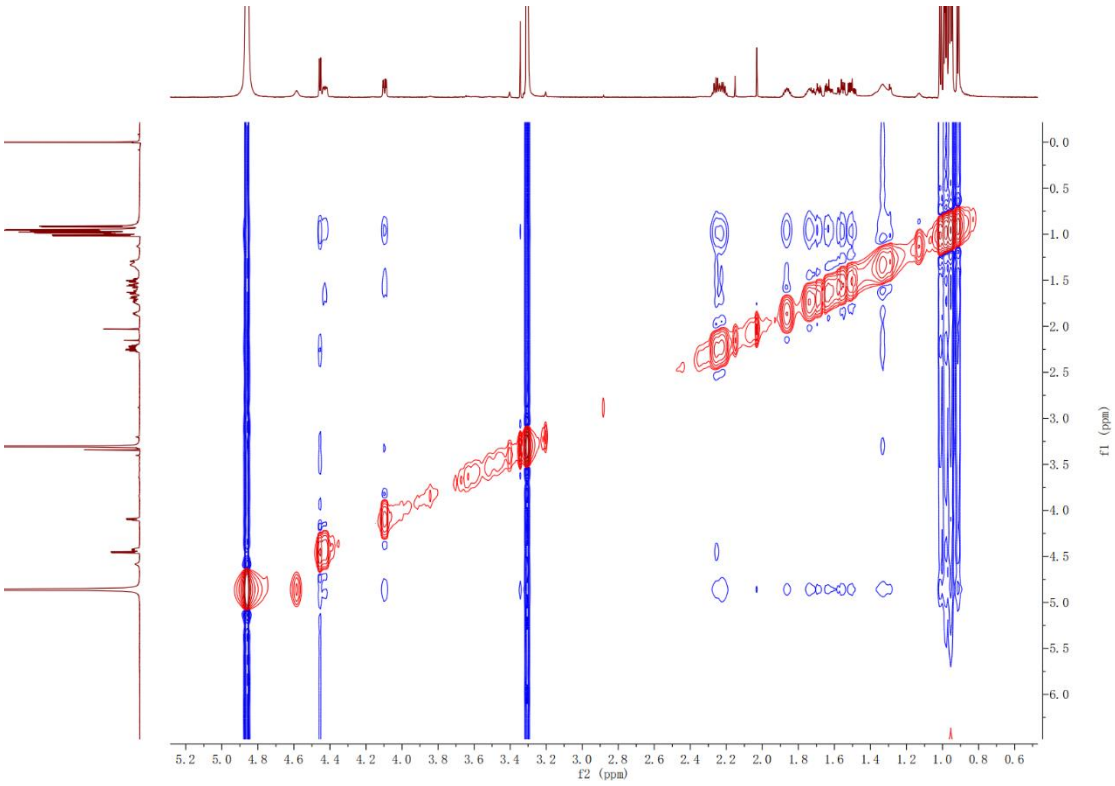
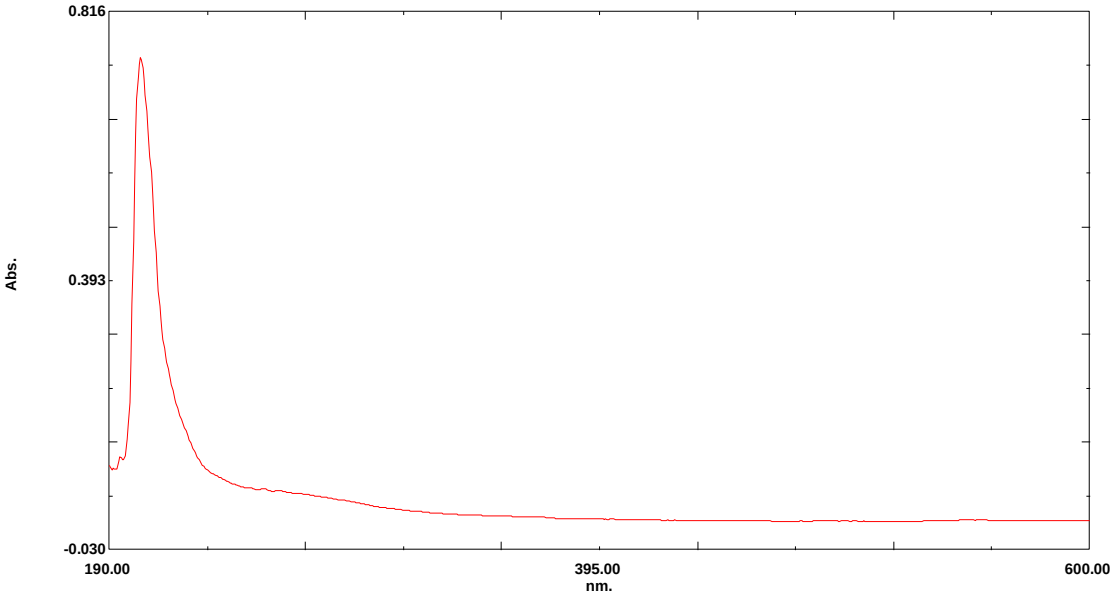


Fig. S28 UV spectrum of compound **2**



No.	wavelength (nm)	Abs
1	203.00	0.743

Fig. S29 ECD spectrum of compound **2**

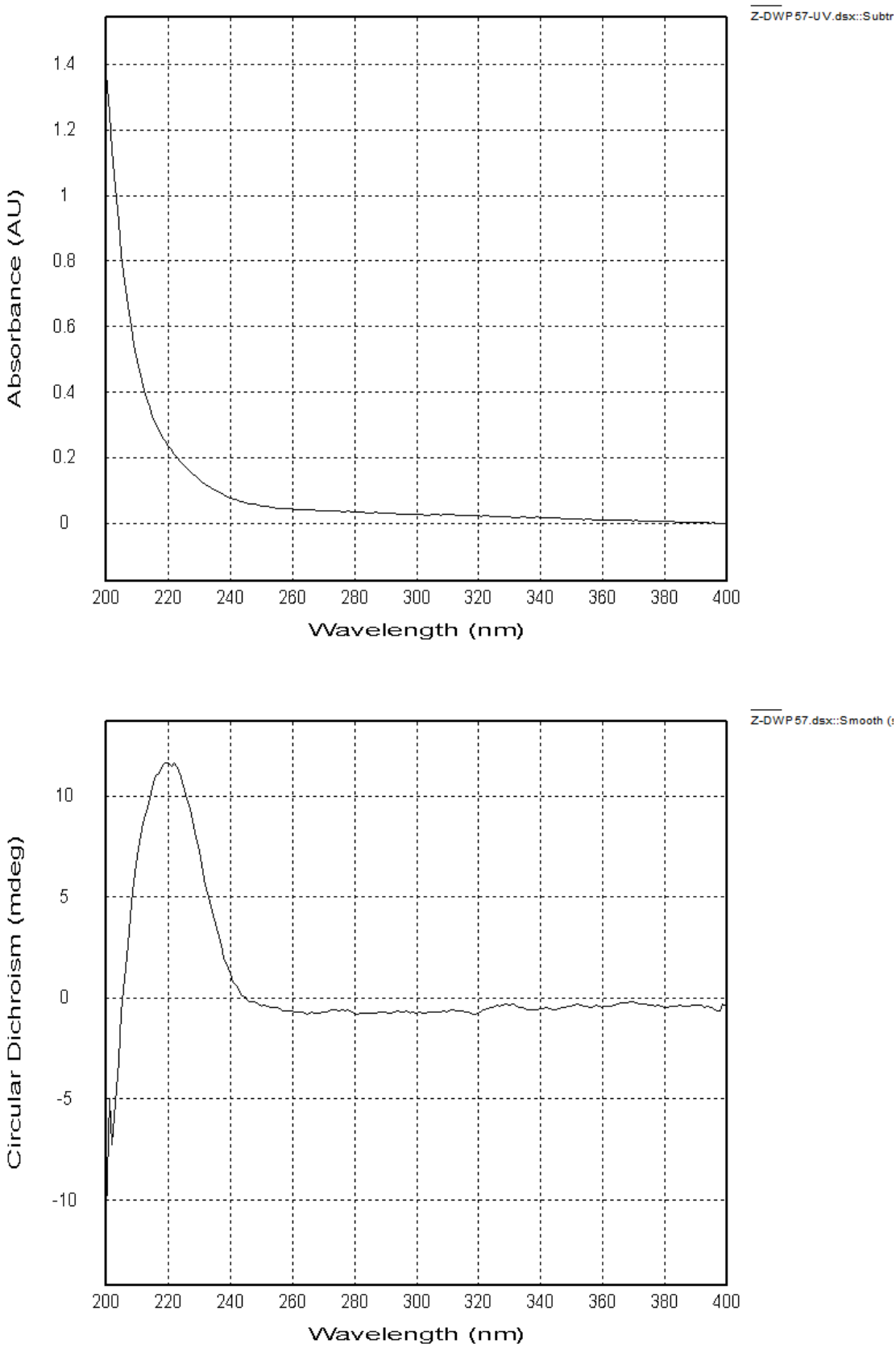


Fig. S30 IR spectrum of compound **2**

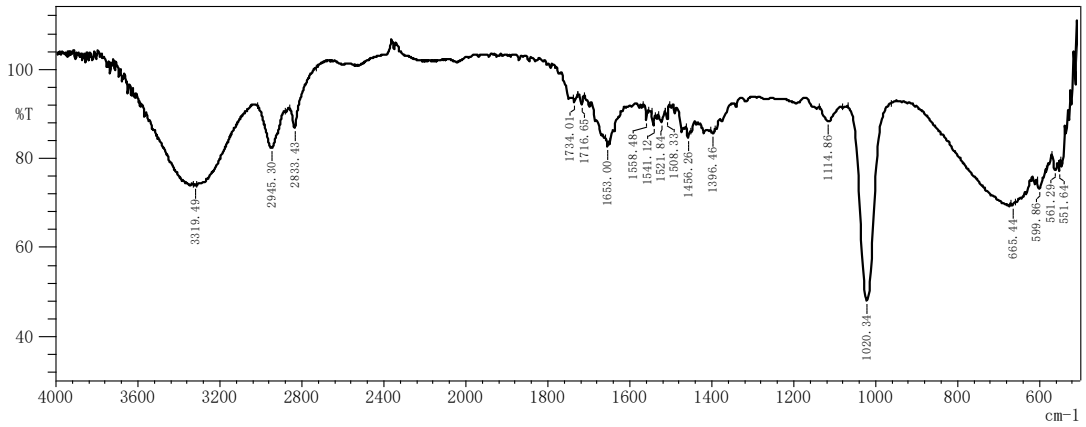


Fig. S31 HRESIMS spectrum of compound **3**

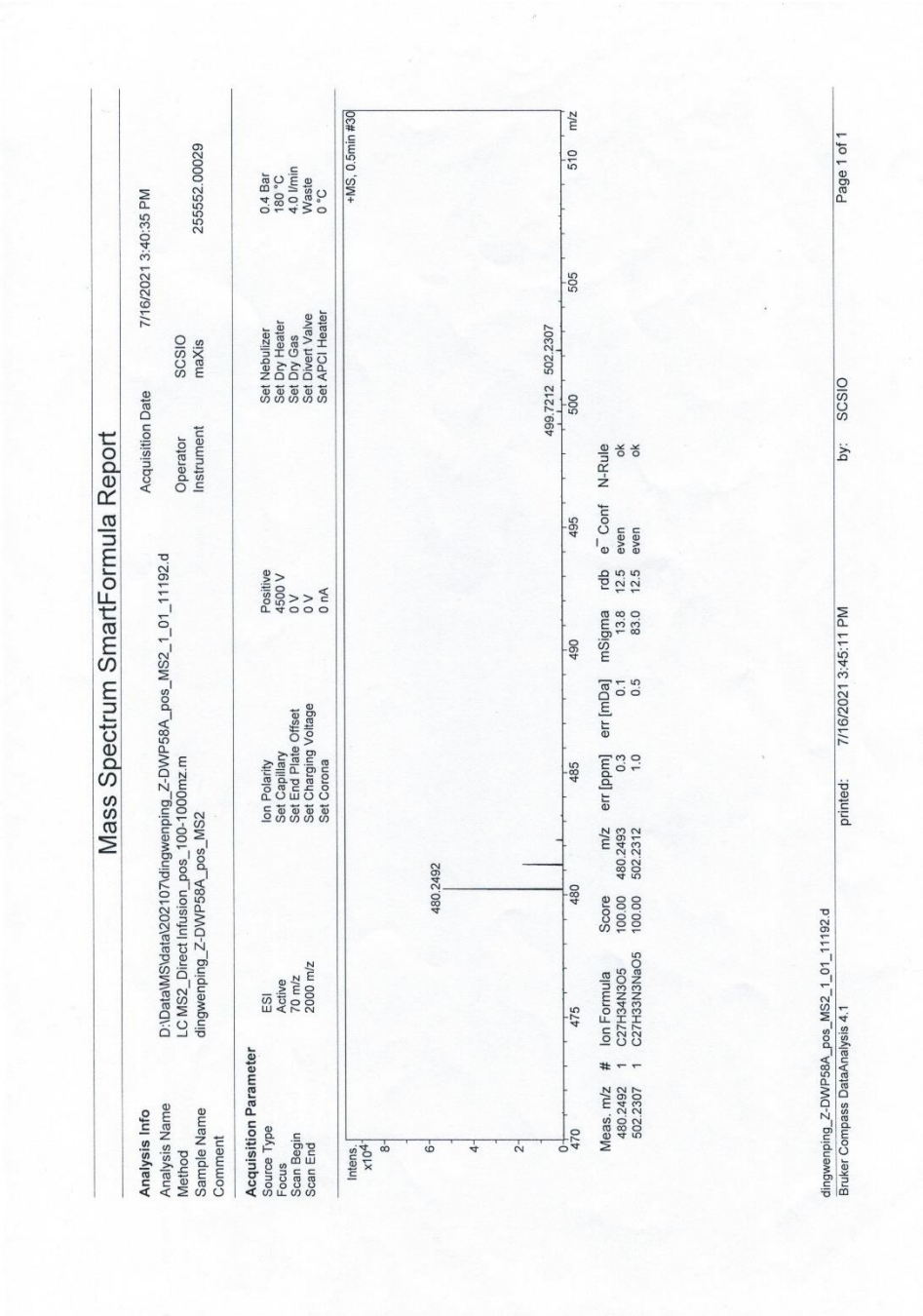


Fig. S32 HRESI-MS/MS-positive spectrum of compound **3**

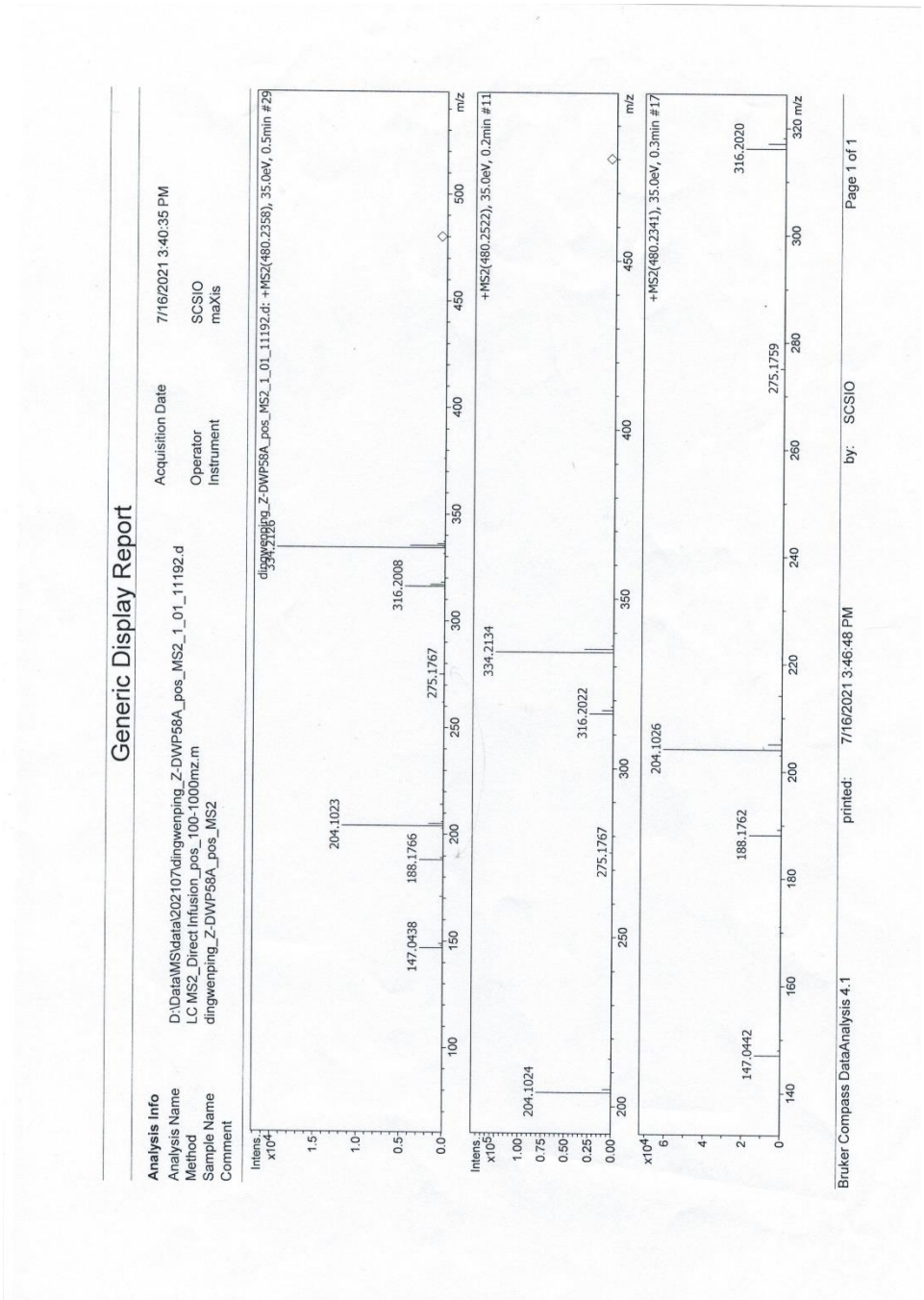


Fig. S33 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **3** (1)

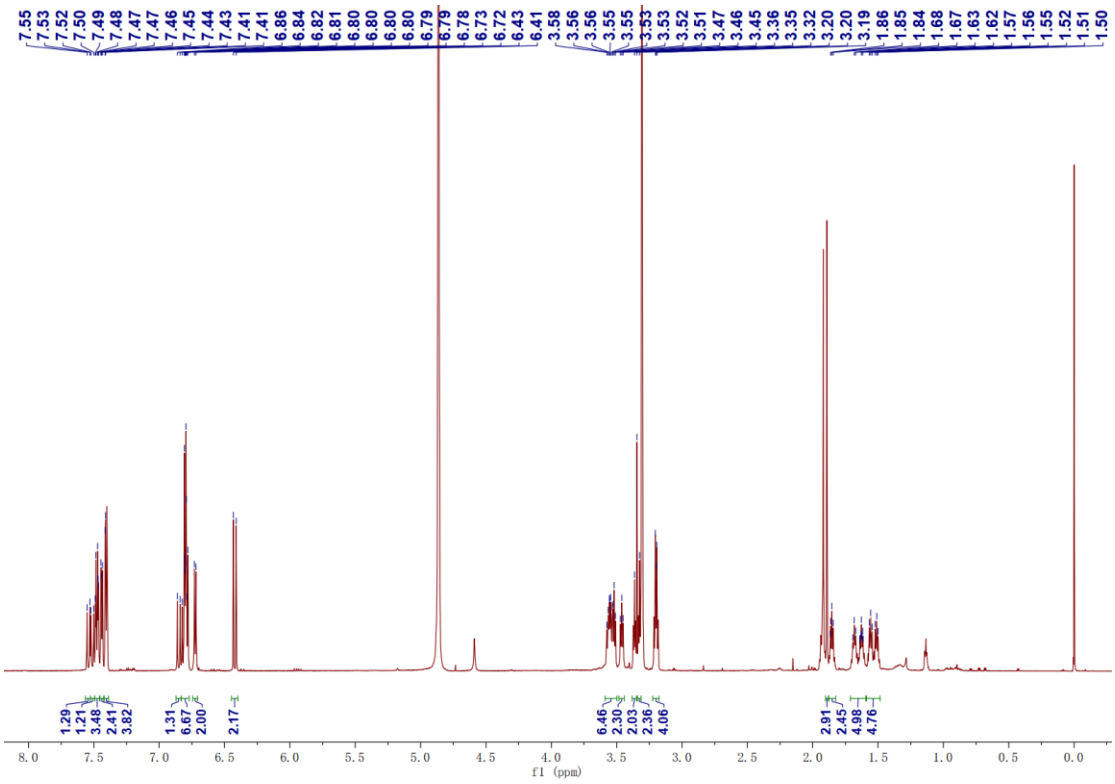


Fig. S34 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **3** (1)

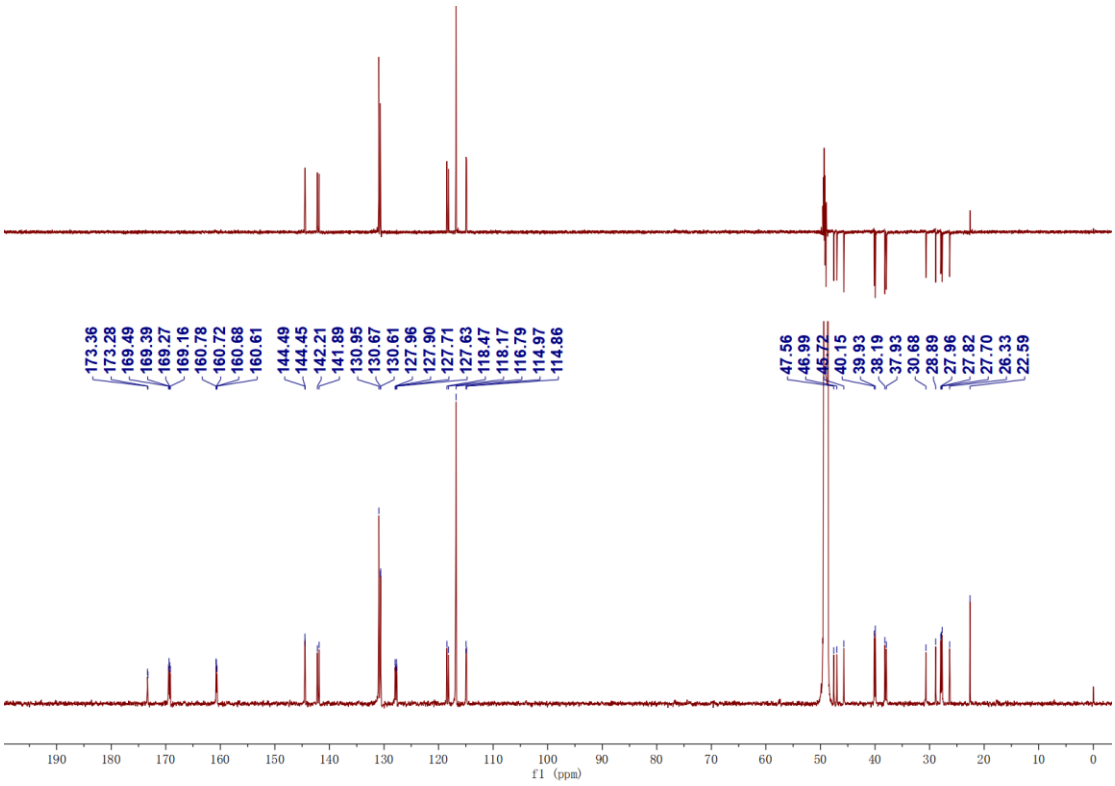


Fig. S35 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **3**

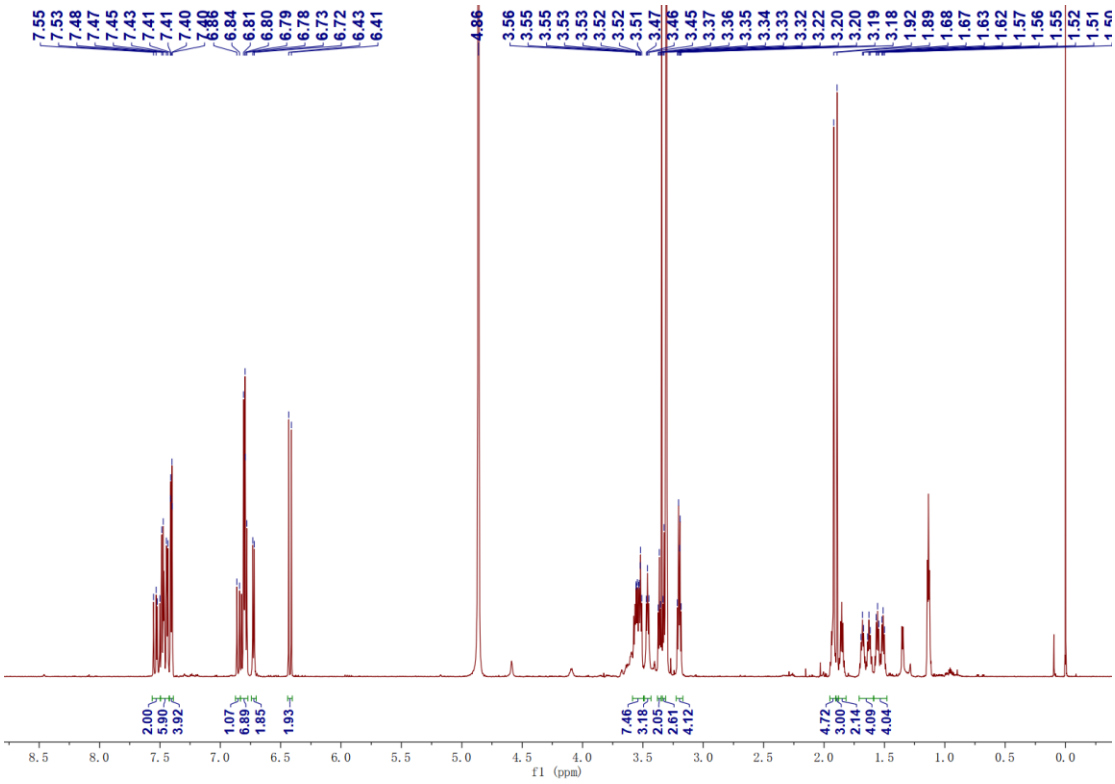


Fig. S36 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **3**

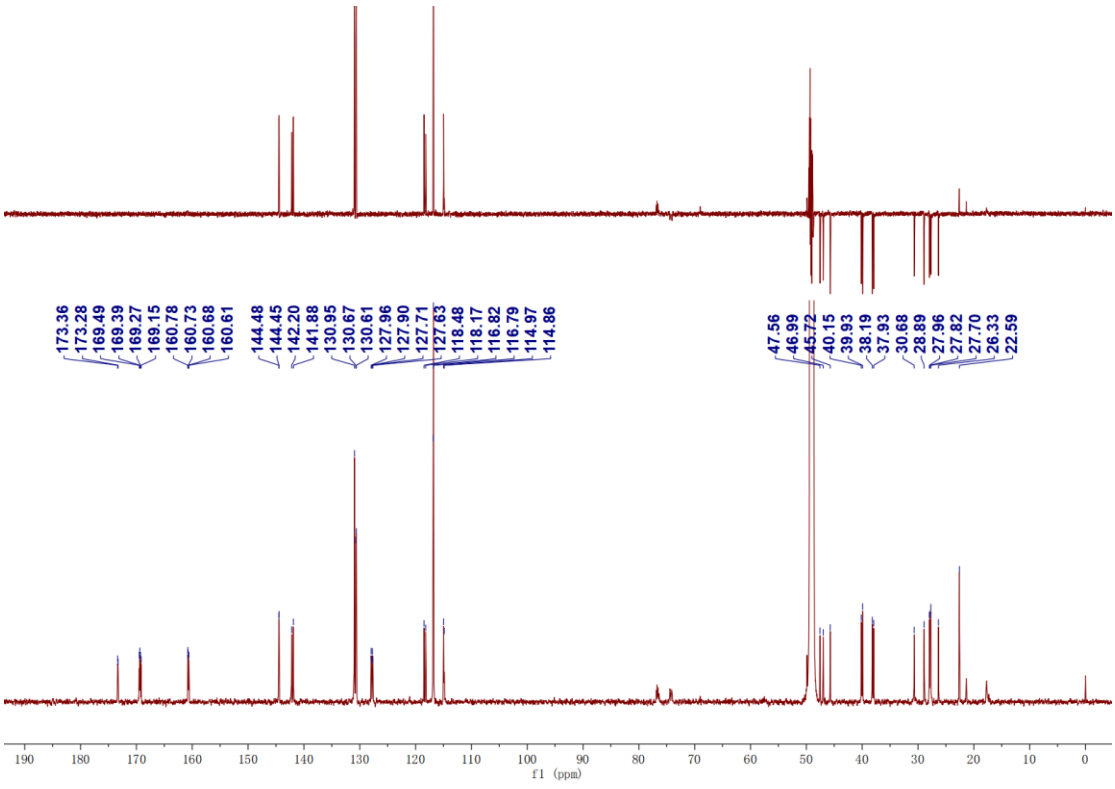


Fig. S37 HSQC spectrum of compound **3**

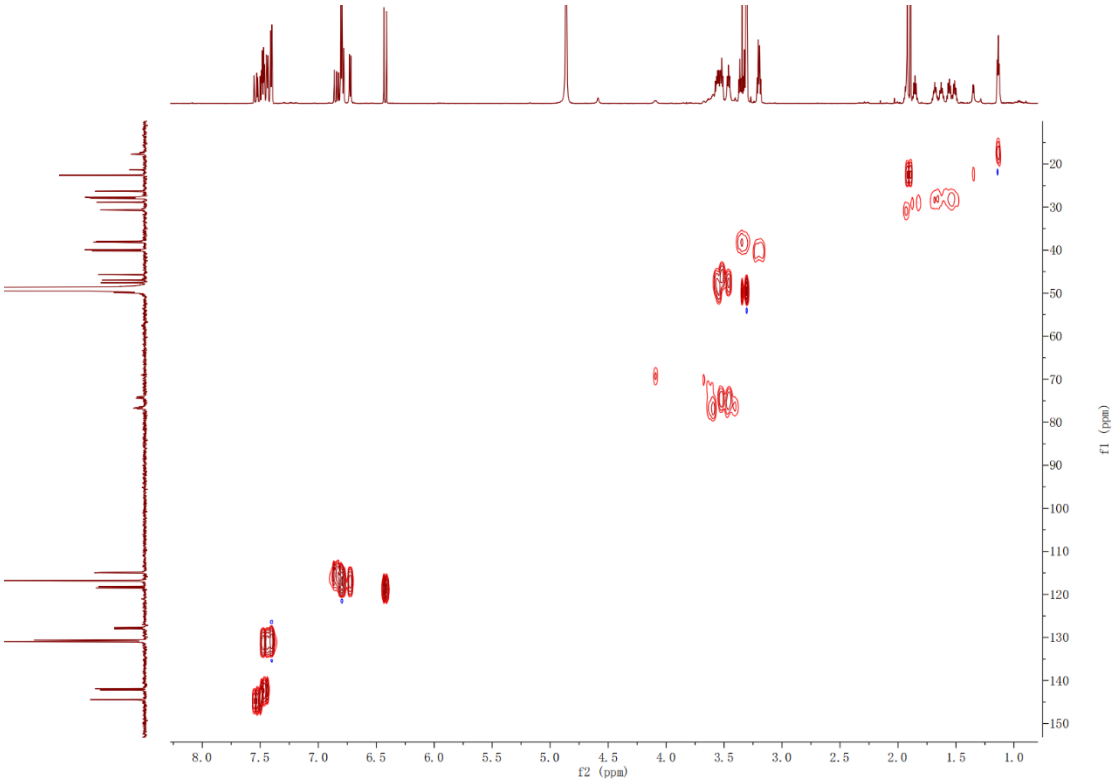


Fig. S38 HMBC spectrum of compound **3**

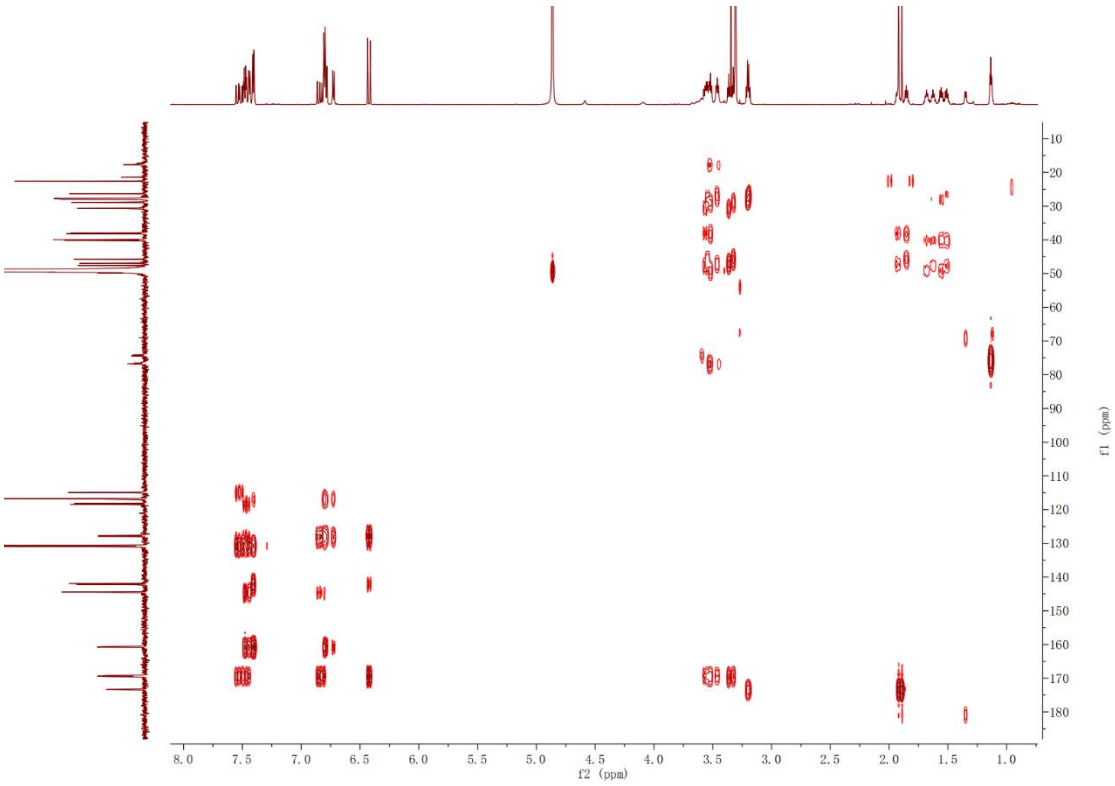


Fig. S39 ^{1}H–^{1}H COSY spectrum of compound **3**

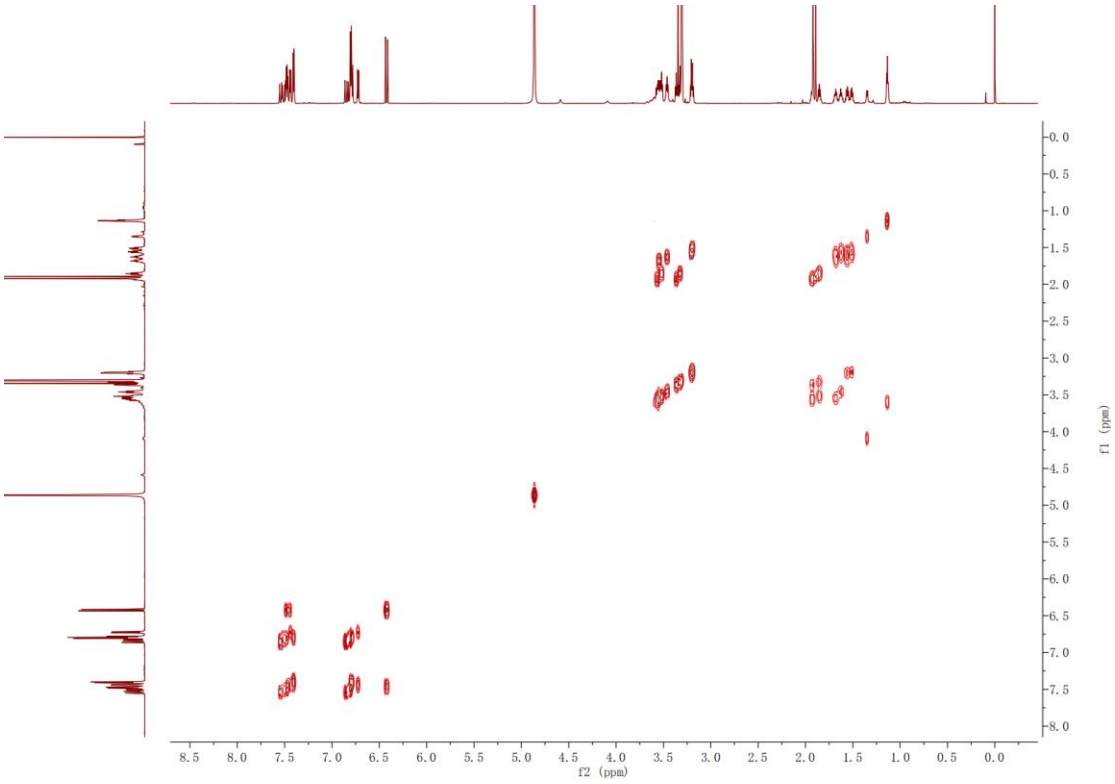


Fig. S40 NOESY spectrum of compound **3**

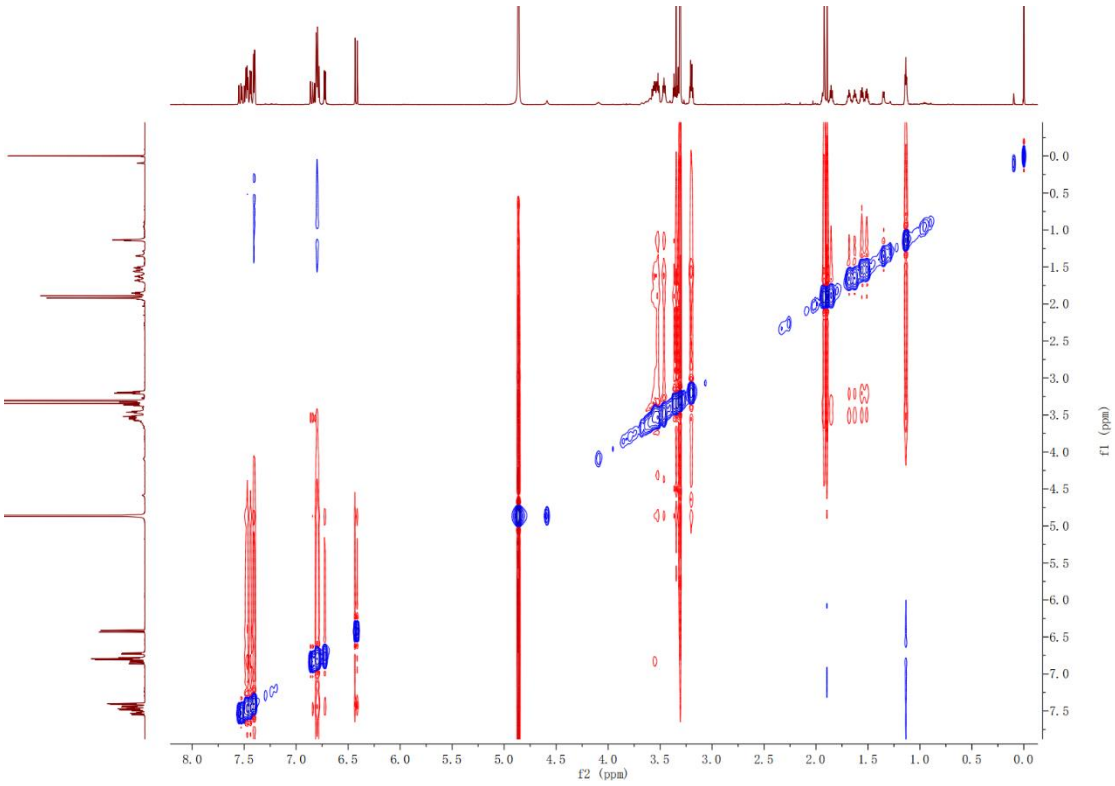
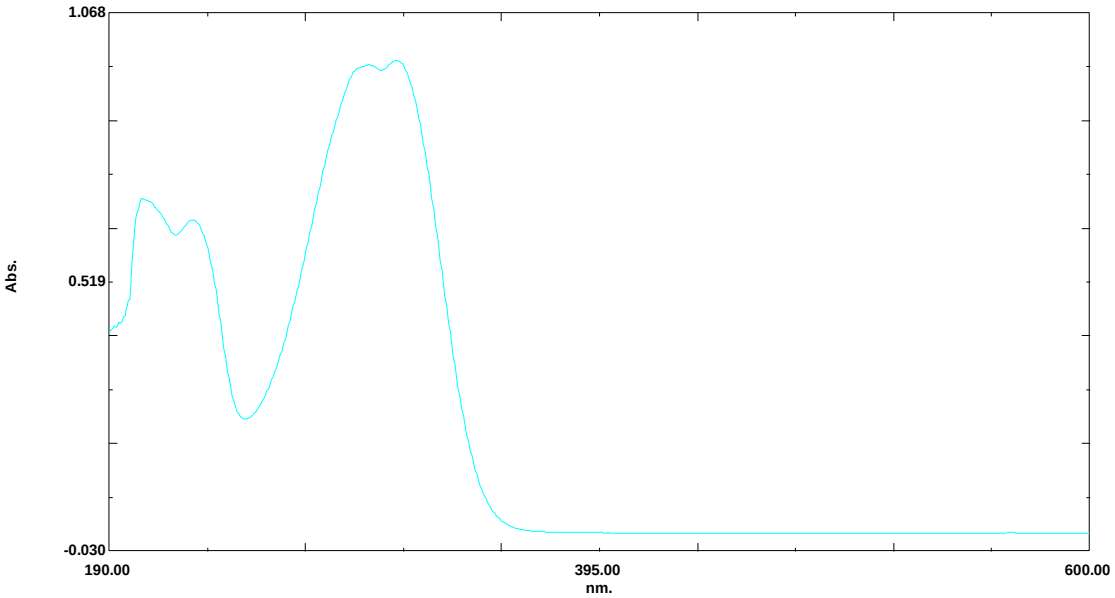


Fig. S41 UV spectrum of compound **3**



No.	wavelength (nm)	Abs
1	310.00	0.972
2	298.50	0.962
3	224.50	0.646
4	204.00	0.690

Fig. S42 IR spectrum of compound **3**

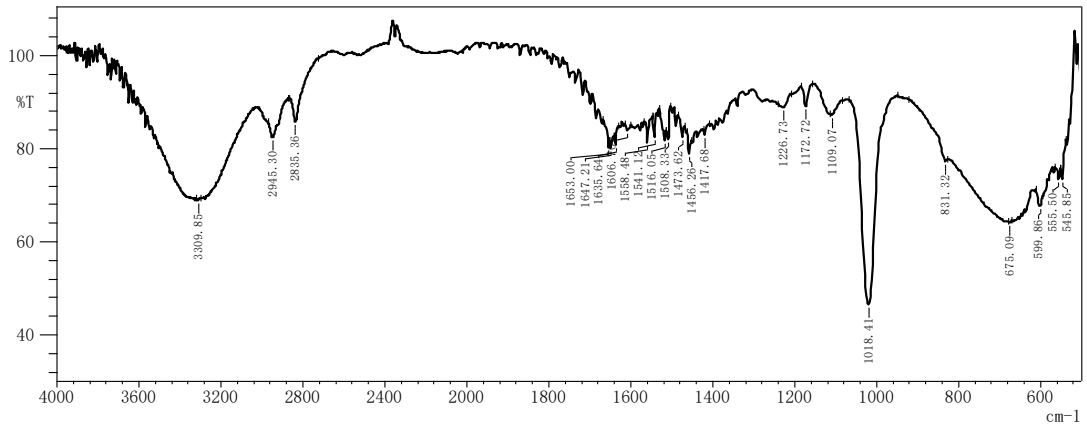


Fig. S43 HRESIMS spectrum of compound **4**

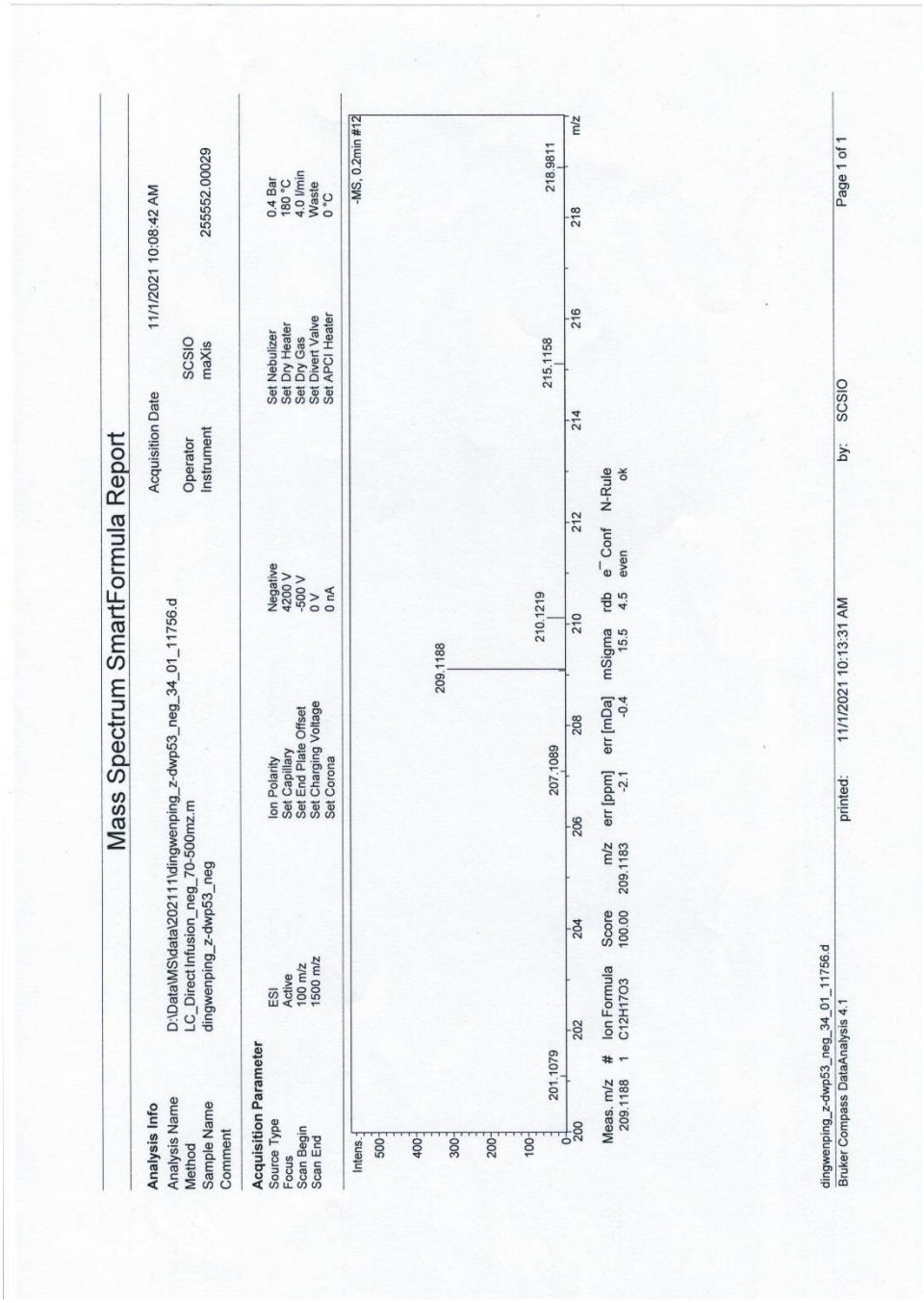


Fig. S44 ^{1}H NMR spectrum (CD_3Cl, 700 MHz) of compound **4**

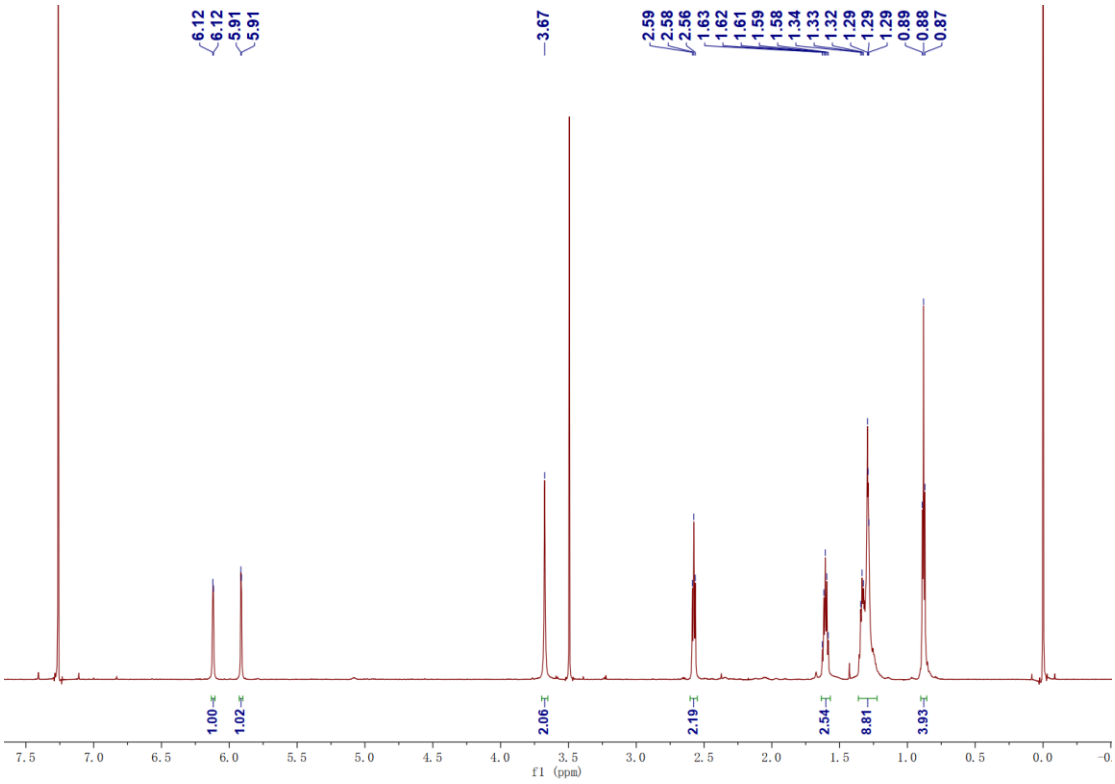


Fig. S45 ^{13}C NMR spectrum (CD_3Cl, 176 MHz) of compound **4**

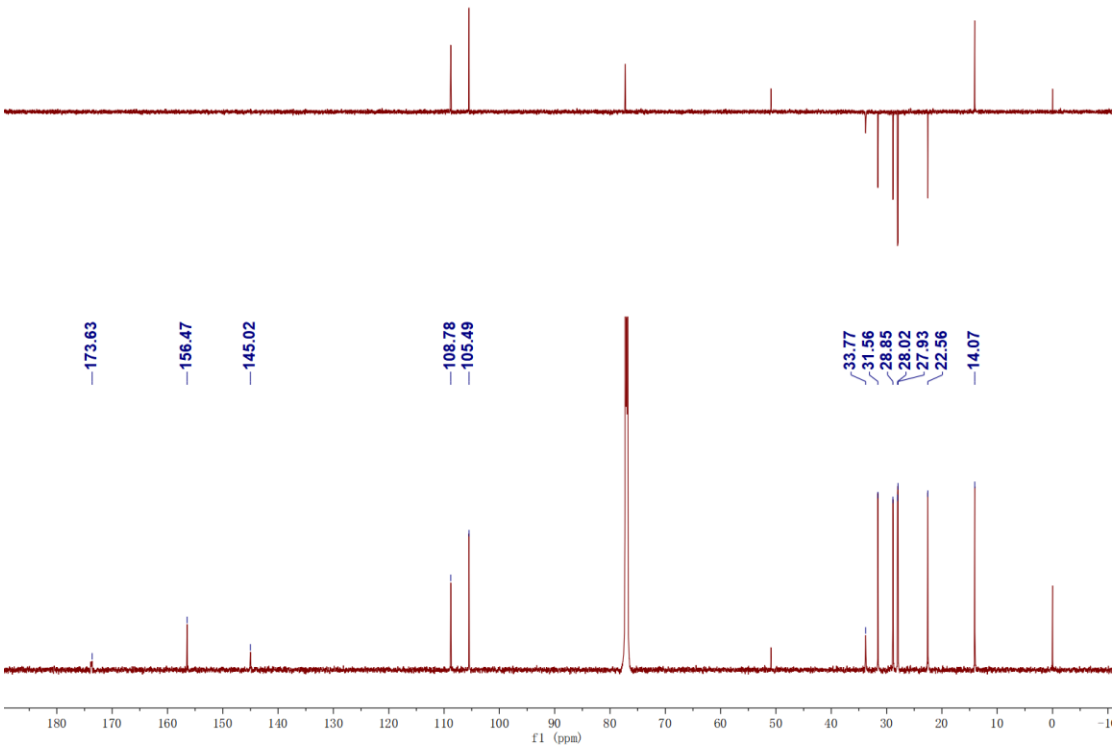


Fig. S46 HSQC spectrum of compound **4**

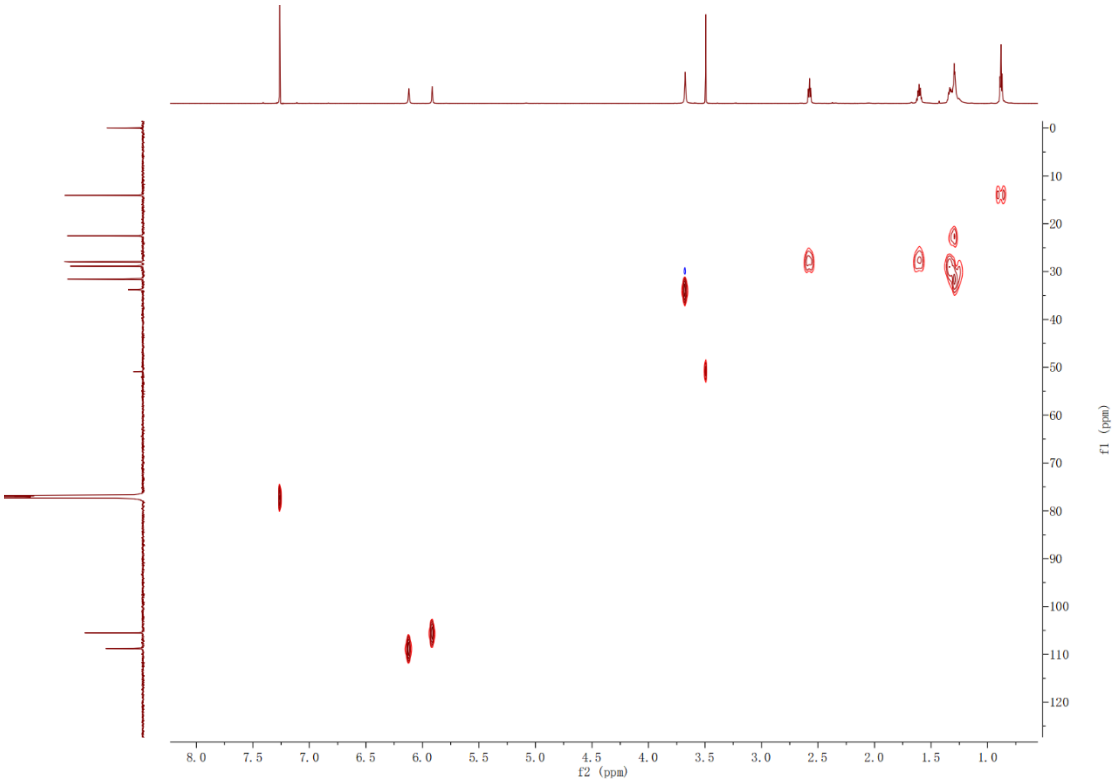


Fig. S47 HMBC spectrum of compound **4**

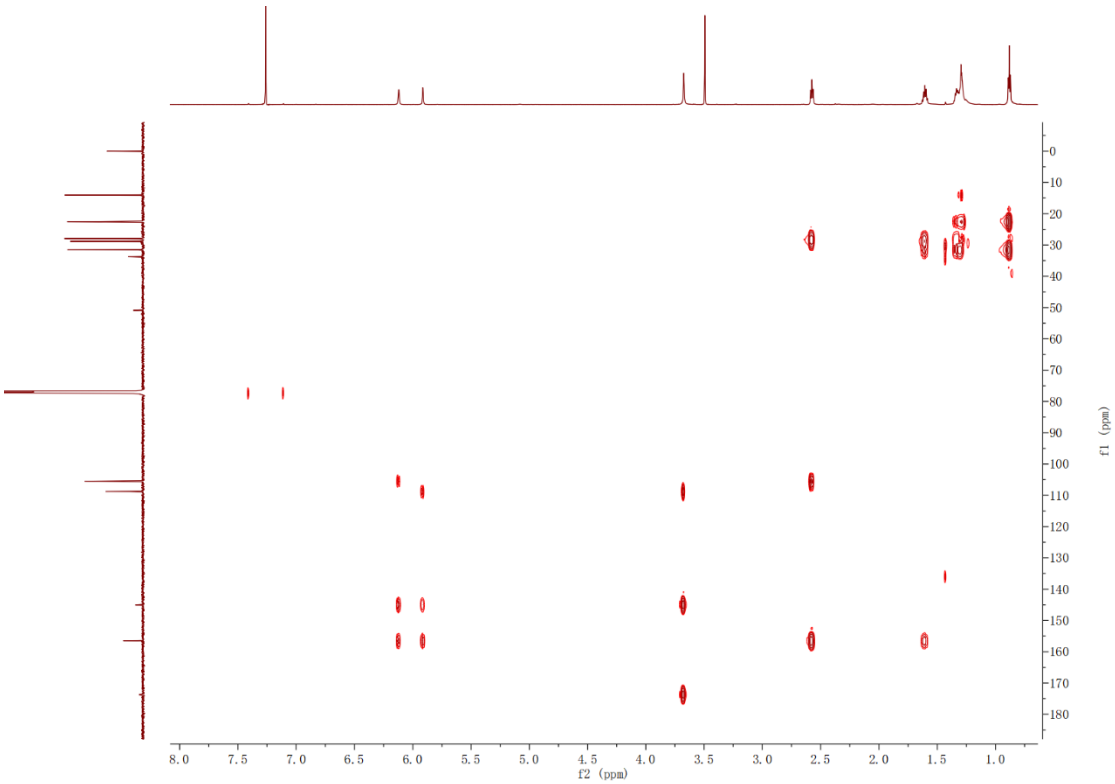


Fig. S48 $^{1}H–^{1}H$ COSY spectrum of compound **4**

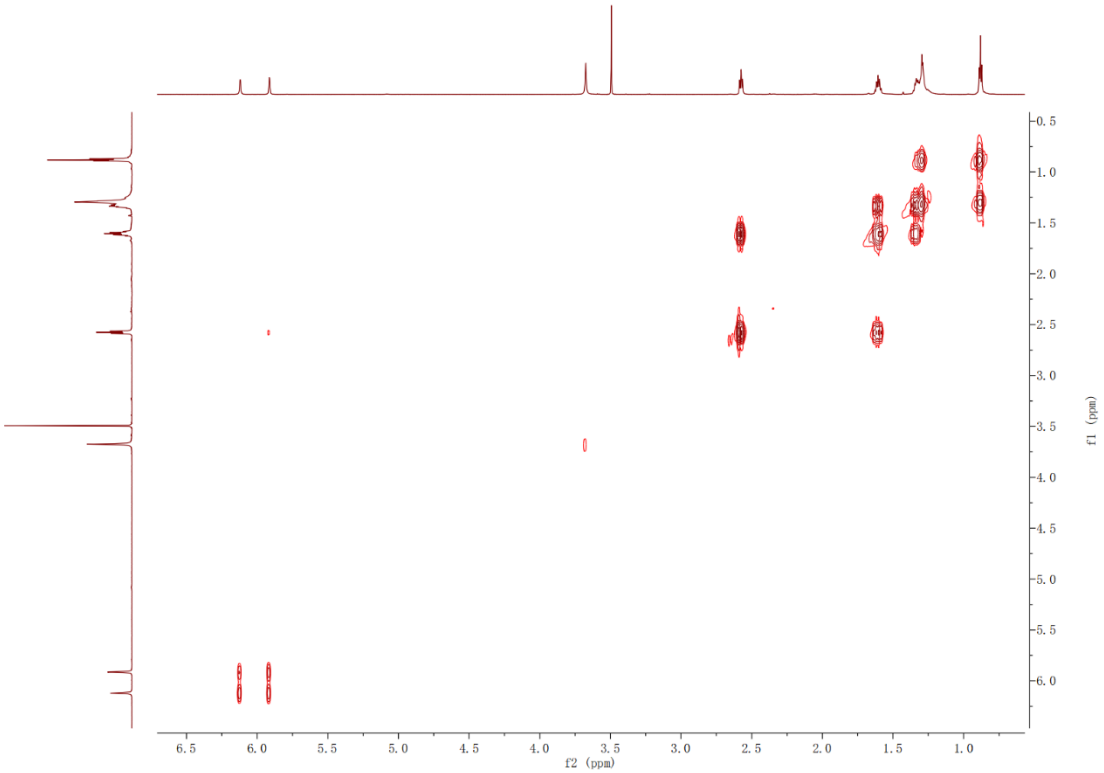
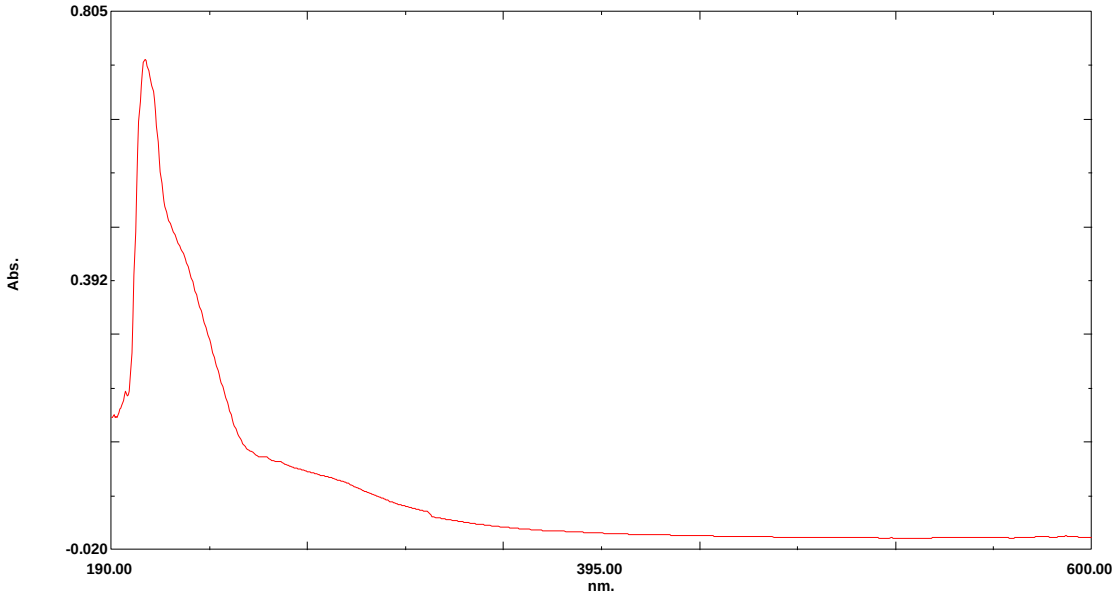


Fig. S49 UV spectrum of compound **4**



No.	wavelength (nm)	Abs
1	204.00	0.731

Fig. S50 IR spectrum of compound **4**

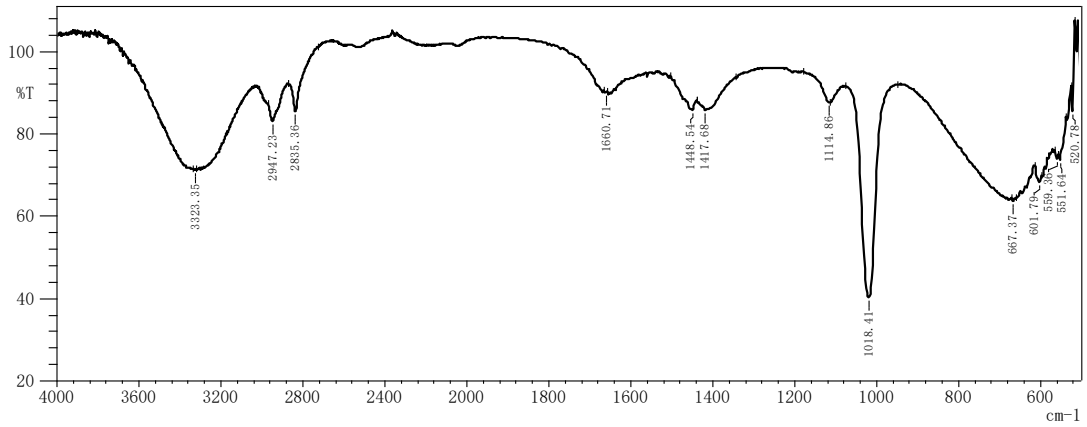


Fig. S51 HRESIMS spectrum of compound **5**

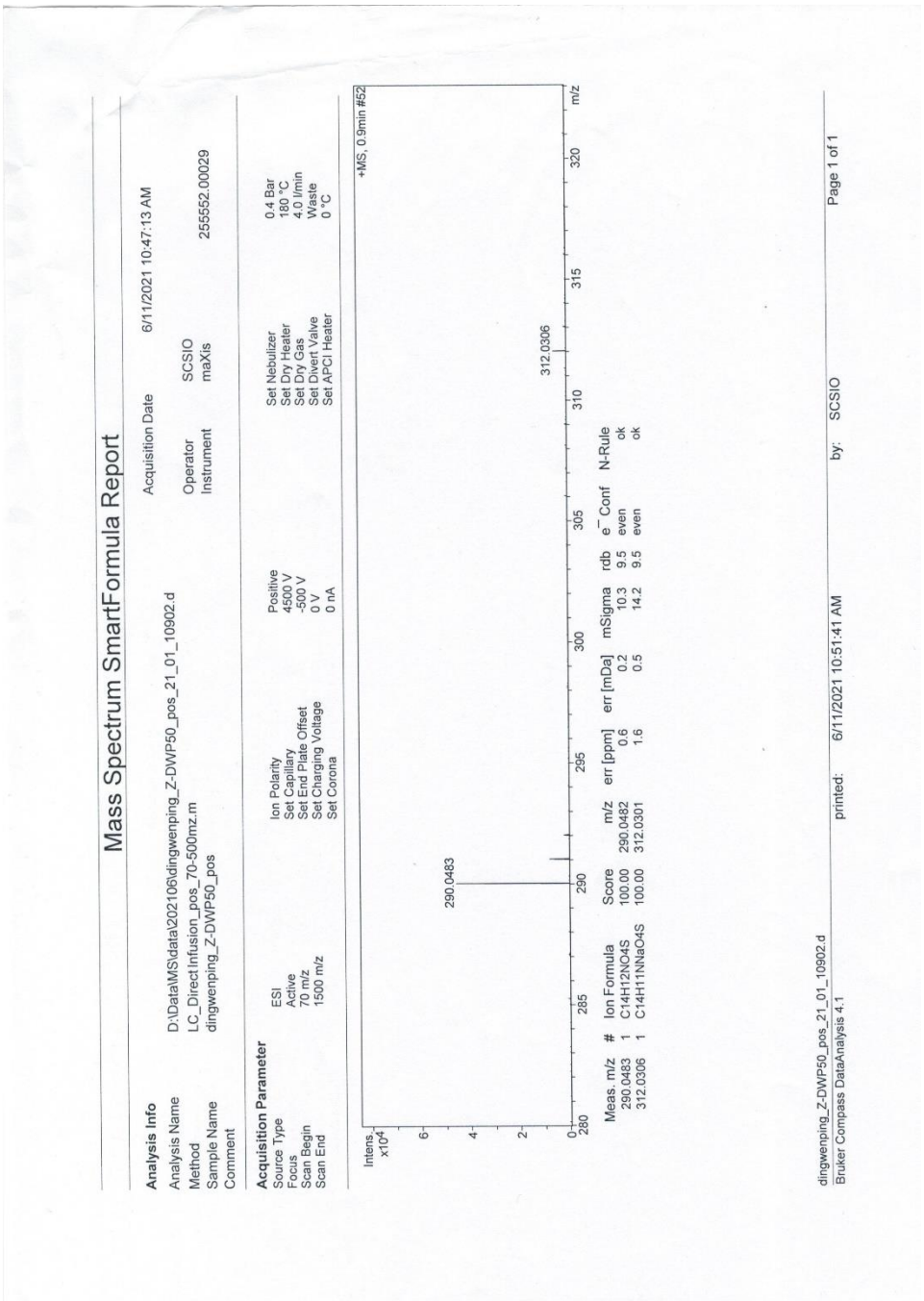


Fig. S52 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **5**

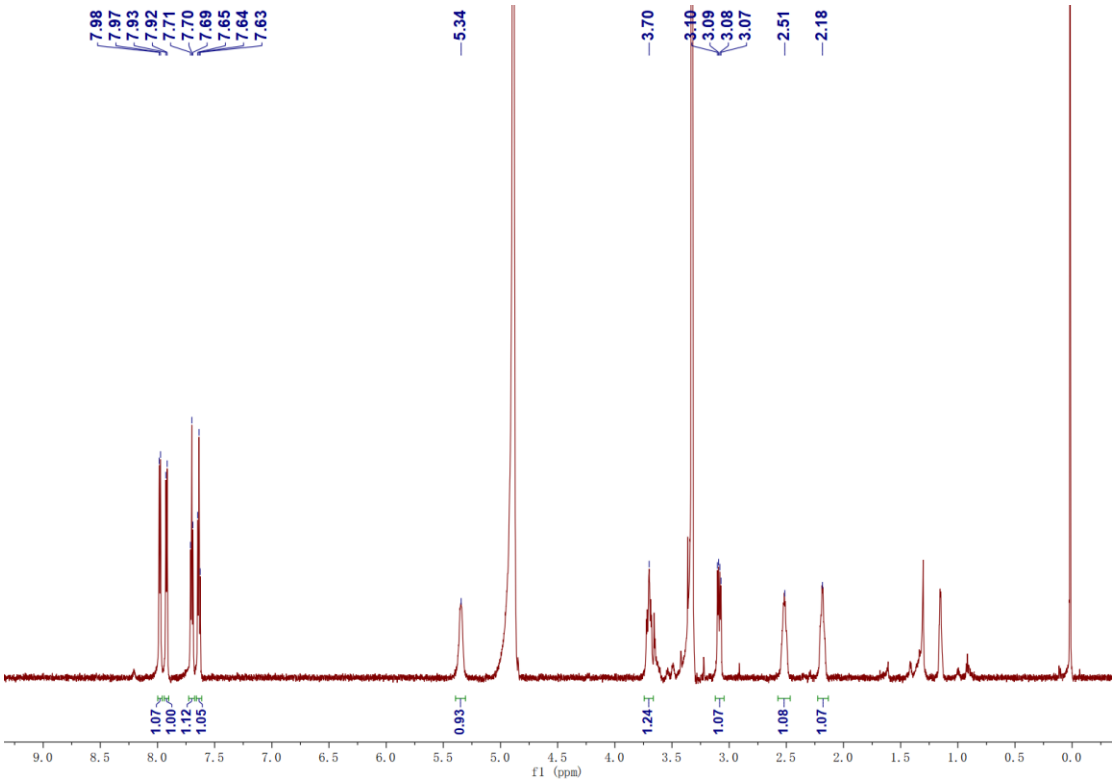


Fig. S53 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **5**

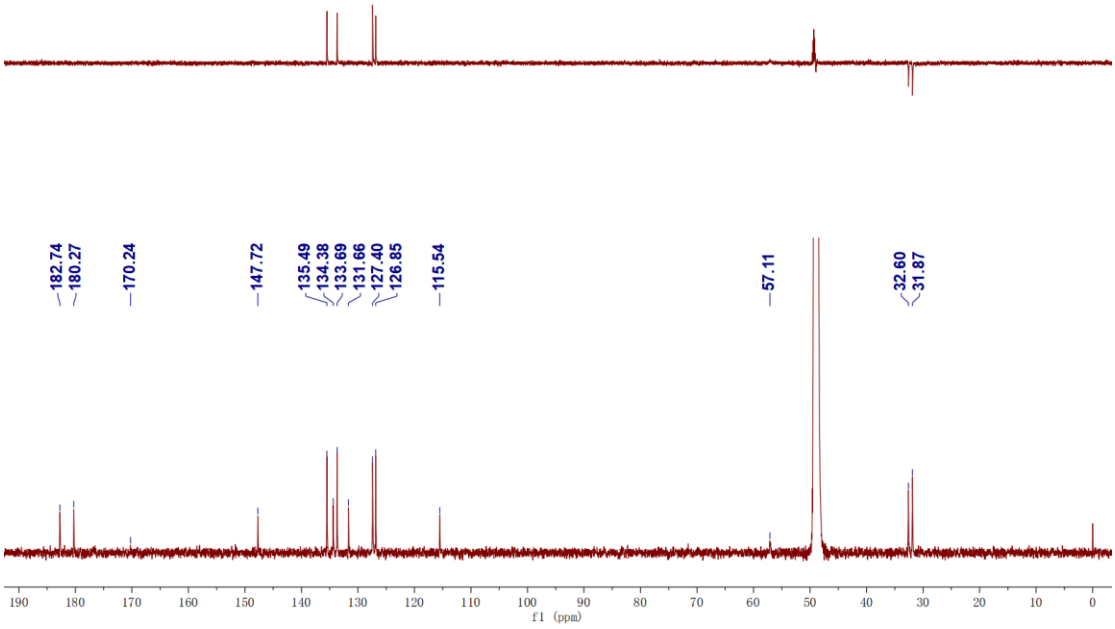


Fig. S54 HSQC spectrum of compound **5**

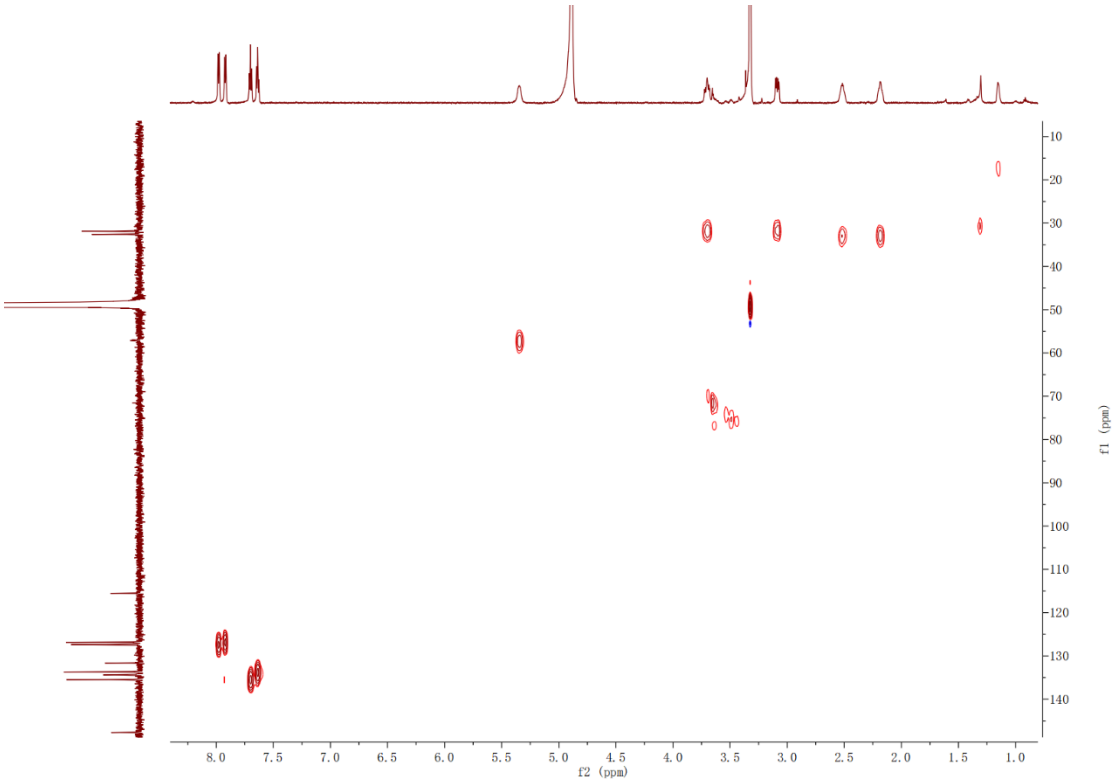


Fig. S55 HMBC spectrum of compound **5**

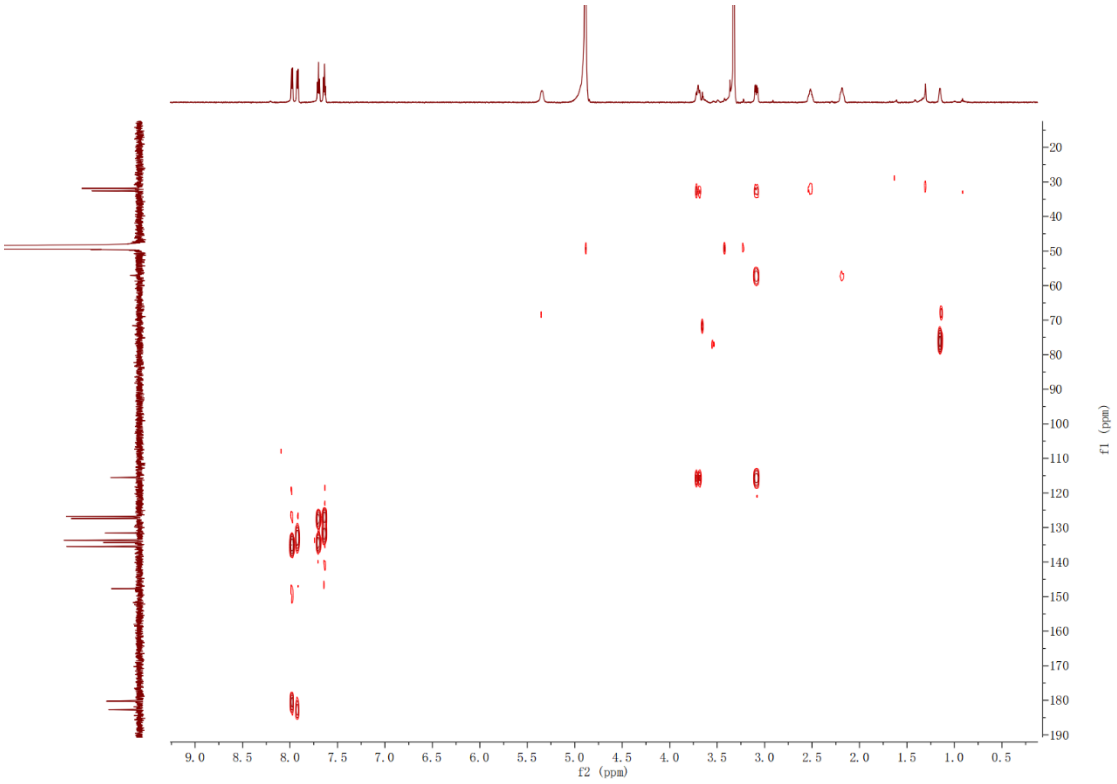


Fig. S56 $^{1}H–^{1}H$ COSY spectrum of compound **5**

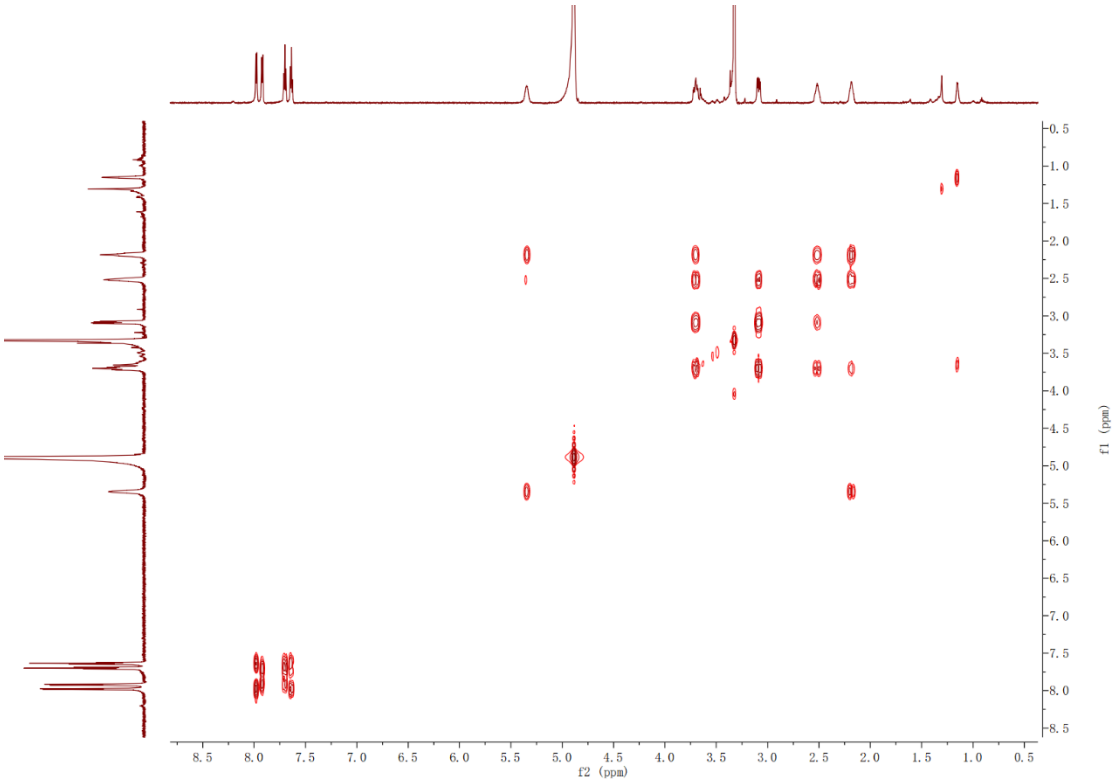


Fig. S57 ESI-MS spectrum of compound **6**

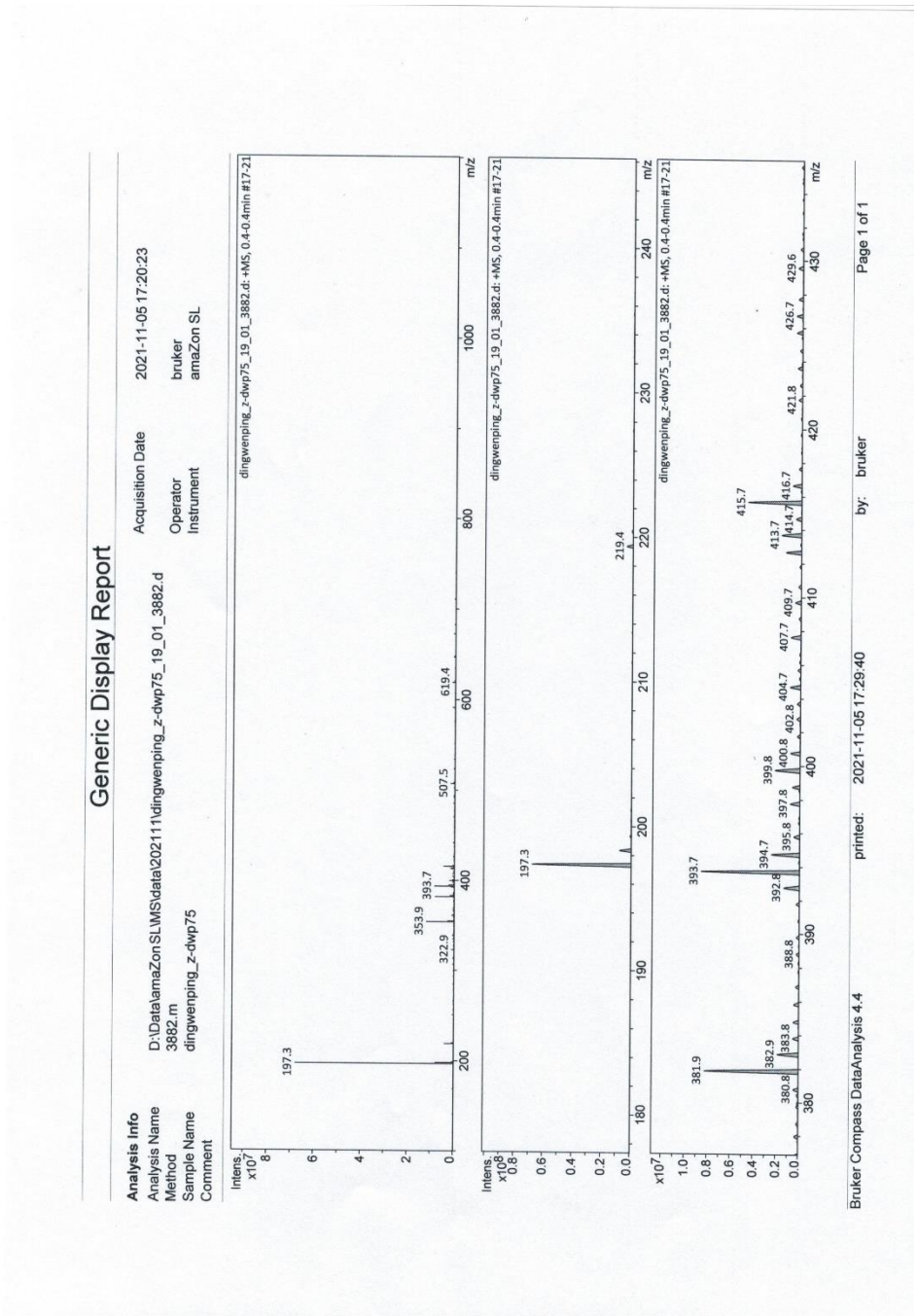


Fig. S58 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **6**

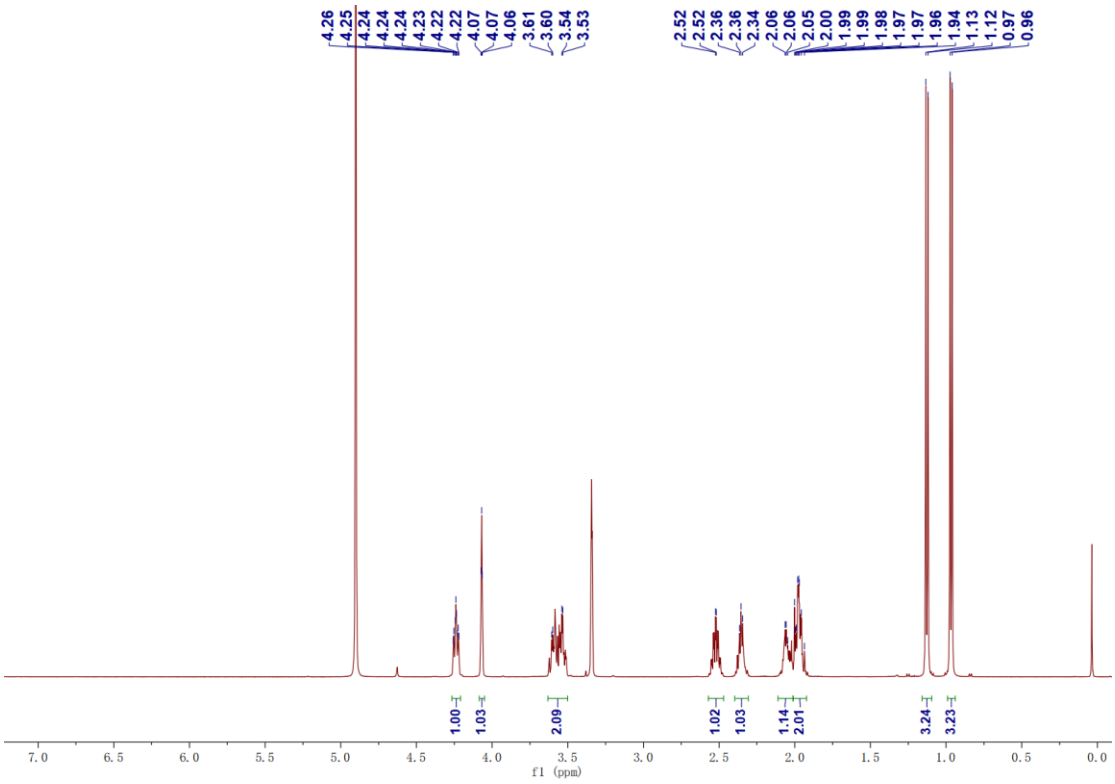
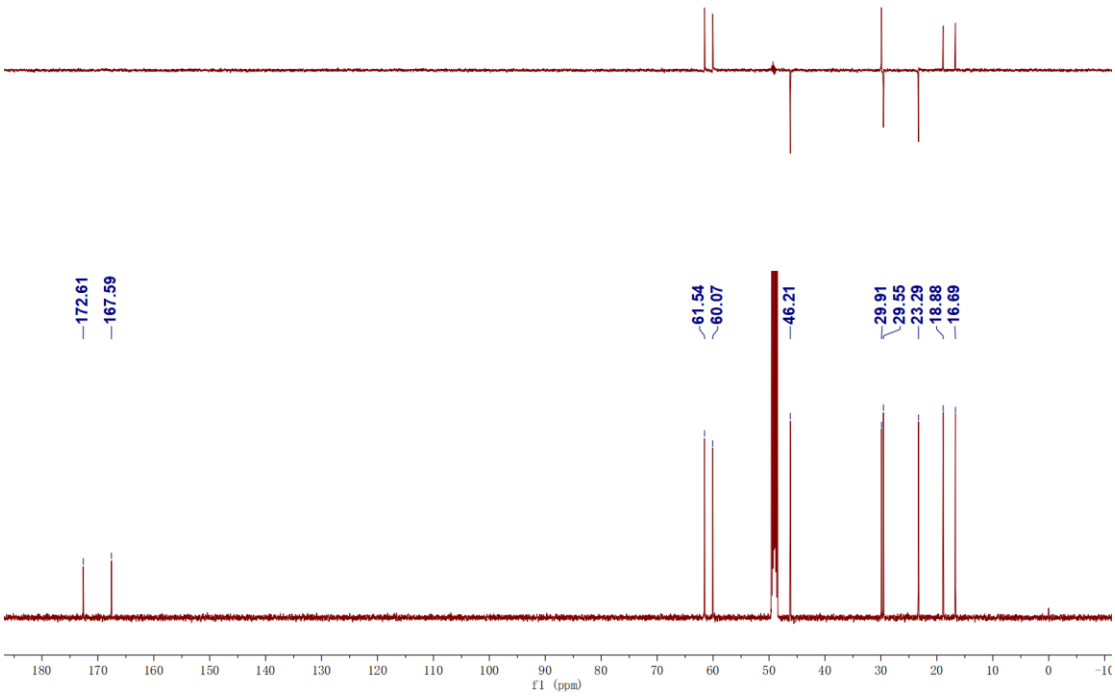


Fig. S59 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **6**



Crystallographic data of compound **6**

Crystal Data for $C_{10}H_{16}N_2O_2$ (M =1569.98 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.61820(10) Å, b = 10.25990(10) Å, c = 34.2074(4) Å, V = 1971.79(5) Å^3, Z = 8, T = 99.99(10) K, μ(Cu Kα) = 0.756 mm^{-1}, *Dcalc* = 1.322 g/cm^3, 19431 reflections measured (5.166° ≤ 2Θ ≤ 148.834°), 3939 unique (R_{int} = 0.0292, R_{sigma} = 0.0222) which were used in all calculations. The final R_1 was 0.0283 (I > 2σ(I)) and wR_2 was 0.0720 (all data).

Fig. S60 ESI-MS spectrum of compound **7**

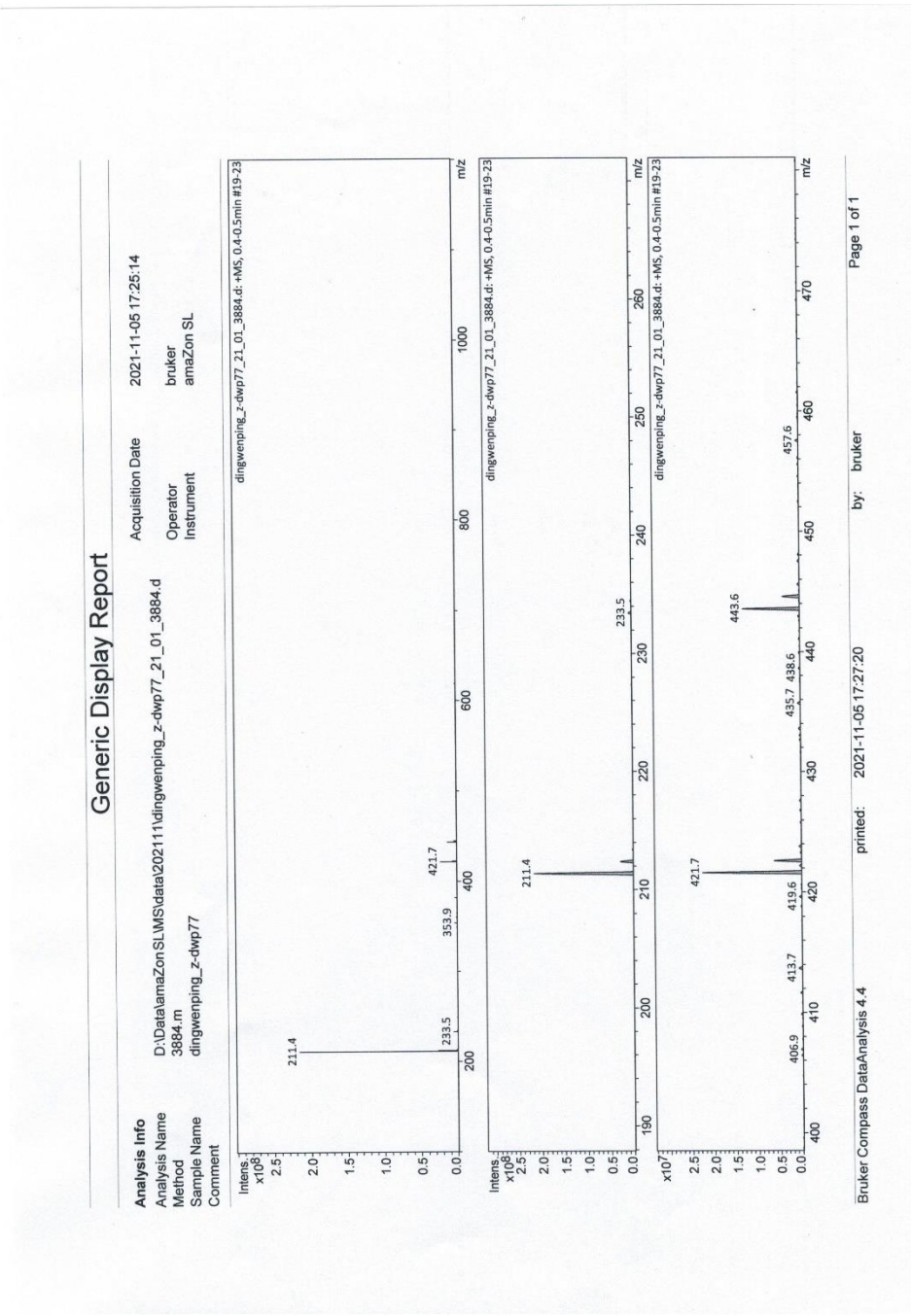


Fig. S61 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **7**

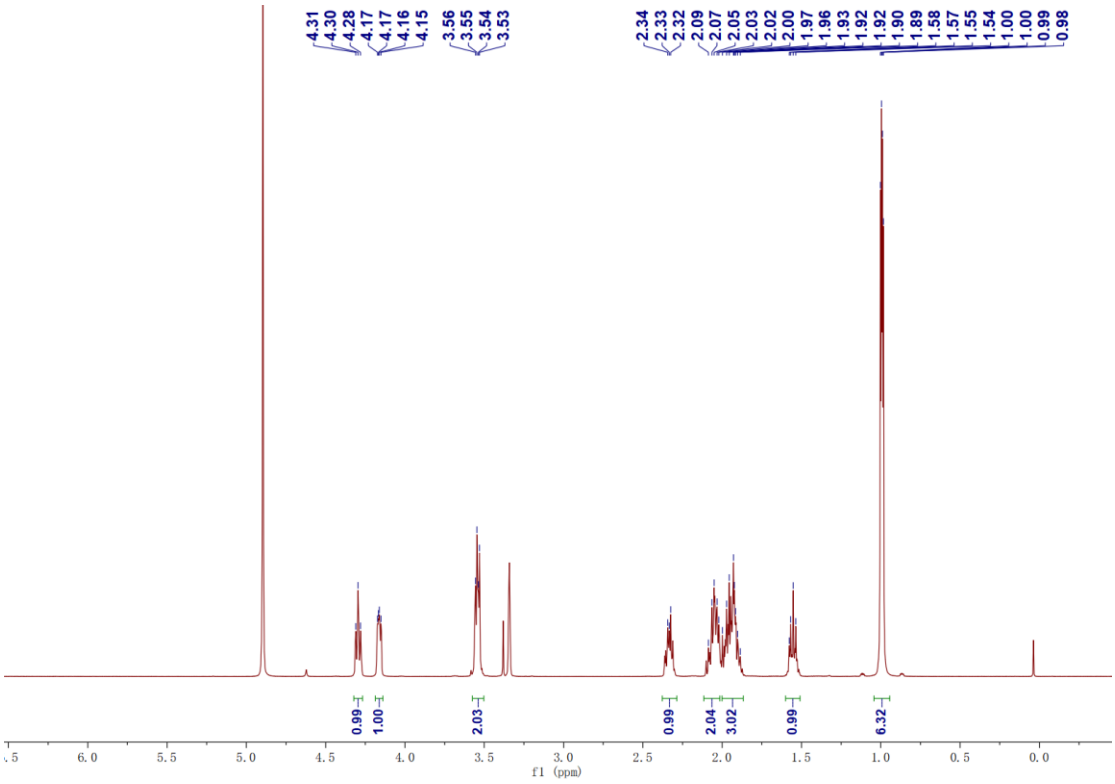
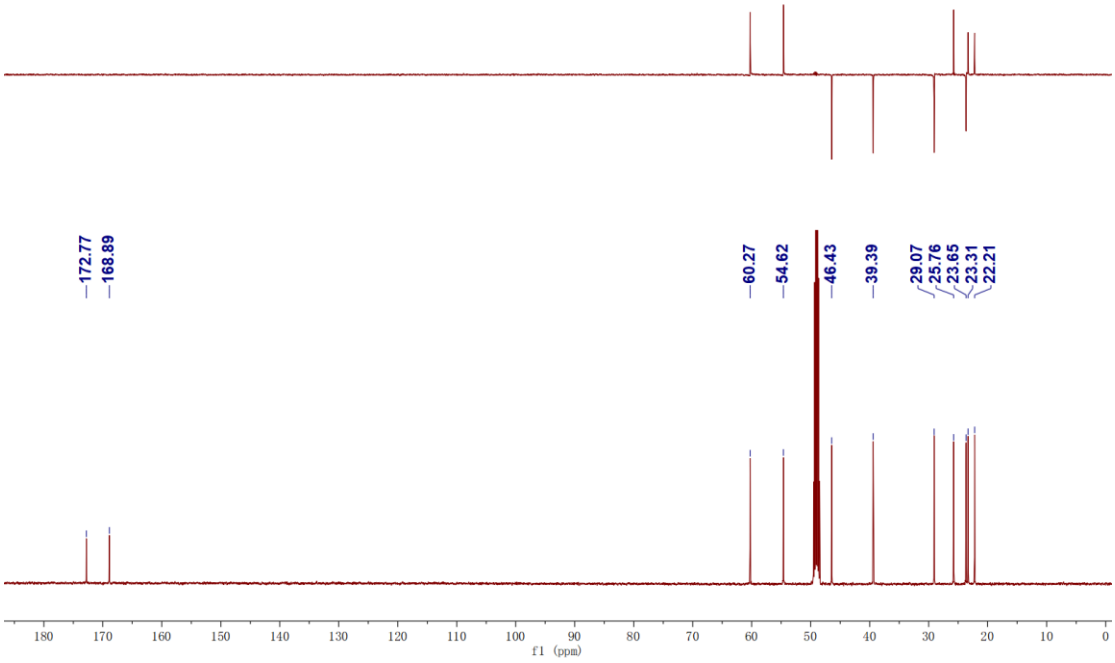


Fig. S62 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **7**



Crystallographic data of compound **7**

Crystal Data for $C_{11}H_{18}N_2O_2$ (M =210.27 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.3034(2) Å, b = 9.2289(3) Å, c = 19.5991(7) Å, V = 1140.15(7) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.686 mm^{-1}, *Dcalc* = 1.225 g/cm^3, 10779 reflections measured (9.024° ≤ 2Θ ≤ 147.842°), 2274 unique (R_{int} = 0.0609, R_{sigma} = 0.0335) which were used in all calculations. The final R_1 was 0.0547 (I > 2σ(I)) and wR_2 was 0.1469 (all data).

Fig. S63 ESI-MS spectrum of compound **8**

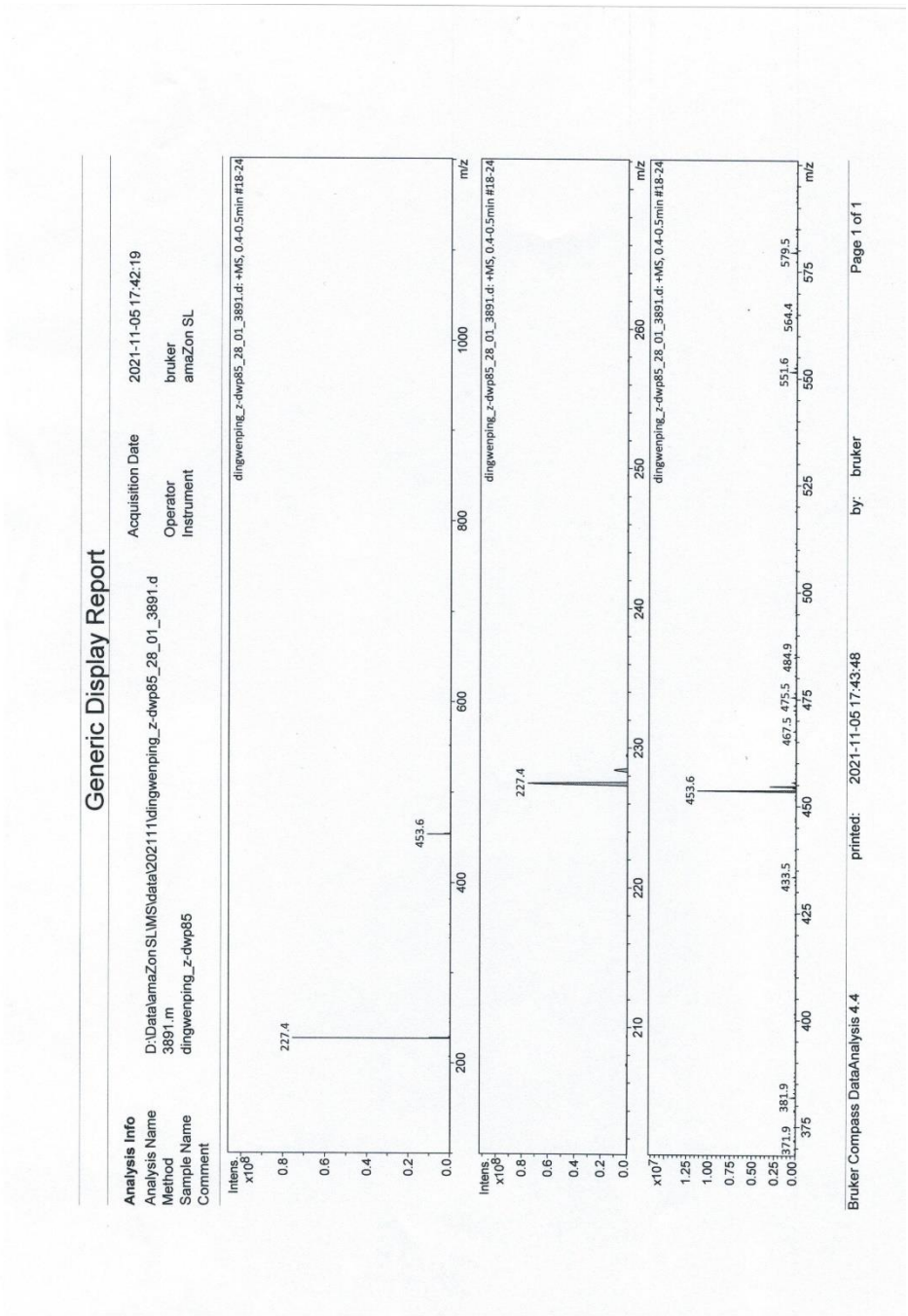


Fig. S64 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **8**

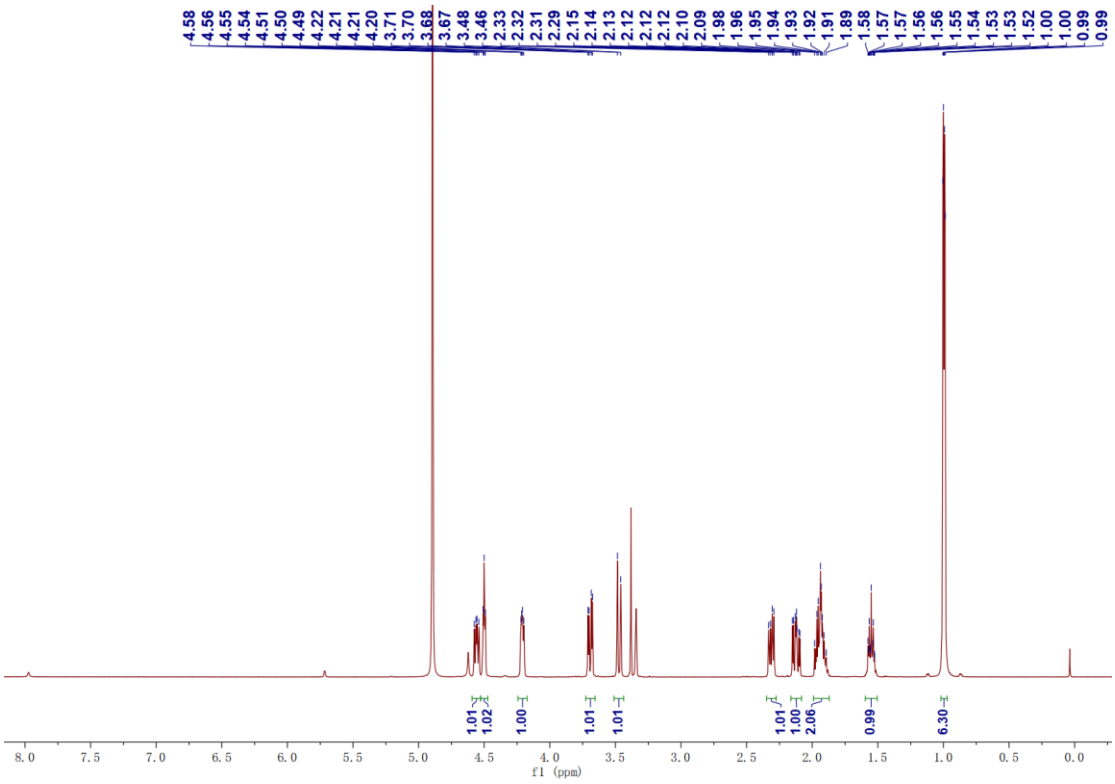
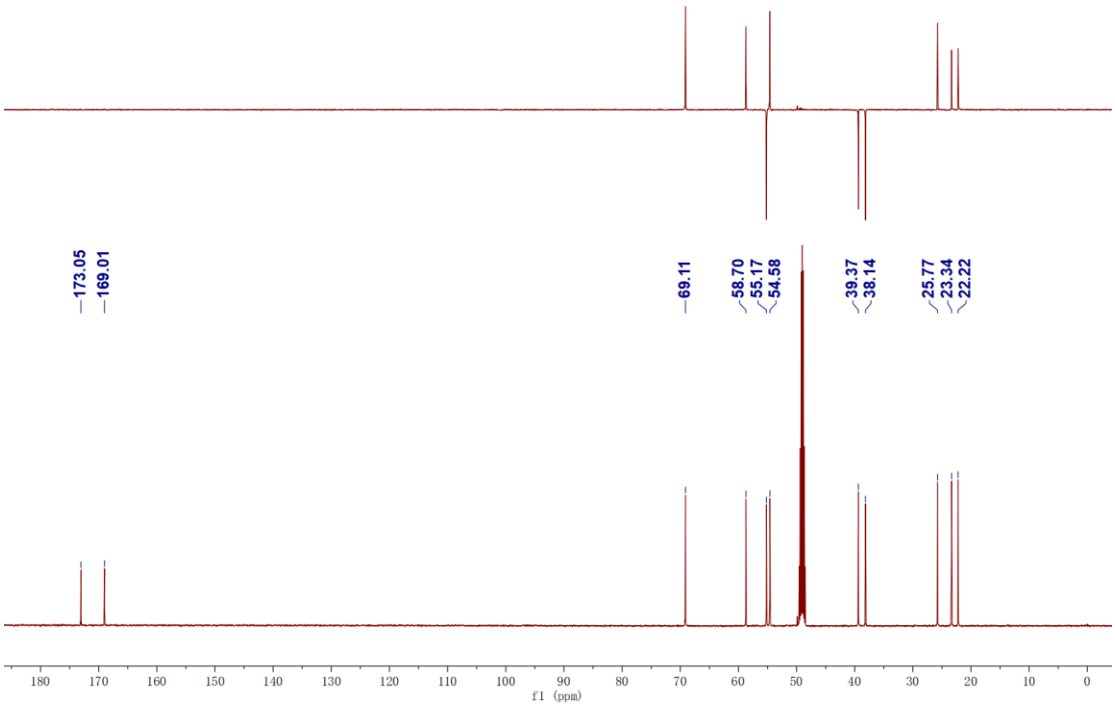


Fig. S65 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **8**



Crystallographic data of compound **8**

Crystal Data for $C_{11}H_{18}N_2O_3$ (M =226.27 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.28190(10) Å, b = 9.4412(2) Å, c = 19.6668(3) Å, V = 1166.41(4) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 0.775 mm^{-1}, $Dcalc$ = 1.289 g/cm^3, 5357 reflections measured (8.992° ≤ 2Θ ≤ 148.308°), 2286 unique (R_{int} = 0.0248, R_{sigma} = 0.0276) which were used in all calculations. The final R_1 was 0.0296 (I > 2σ(I)) and wR_2 was 0.0781 (all data).

Fig. S66 ESI-MS spectrum of compound **9**

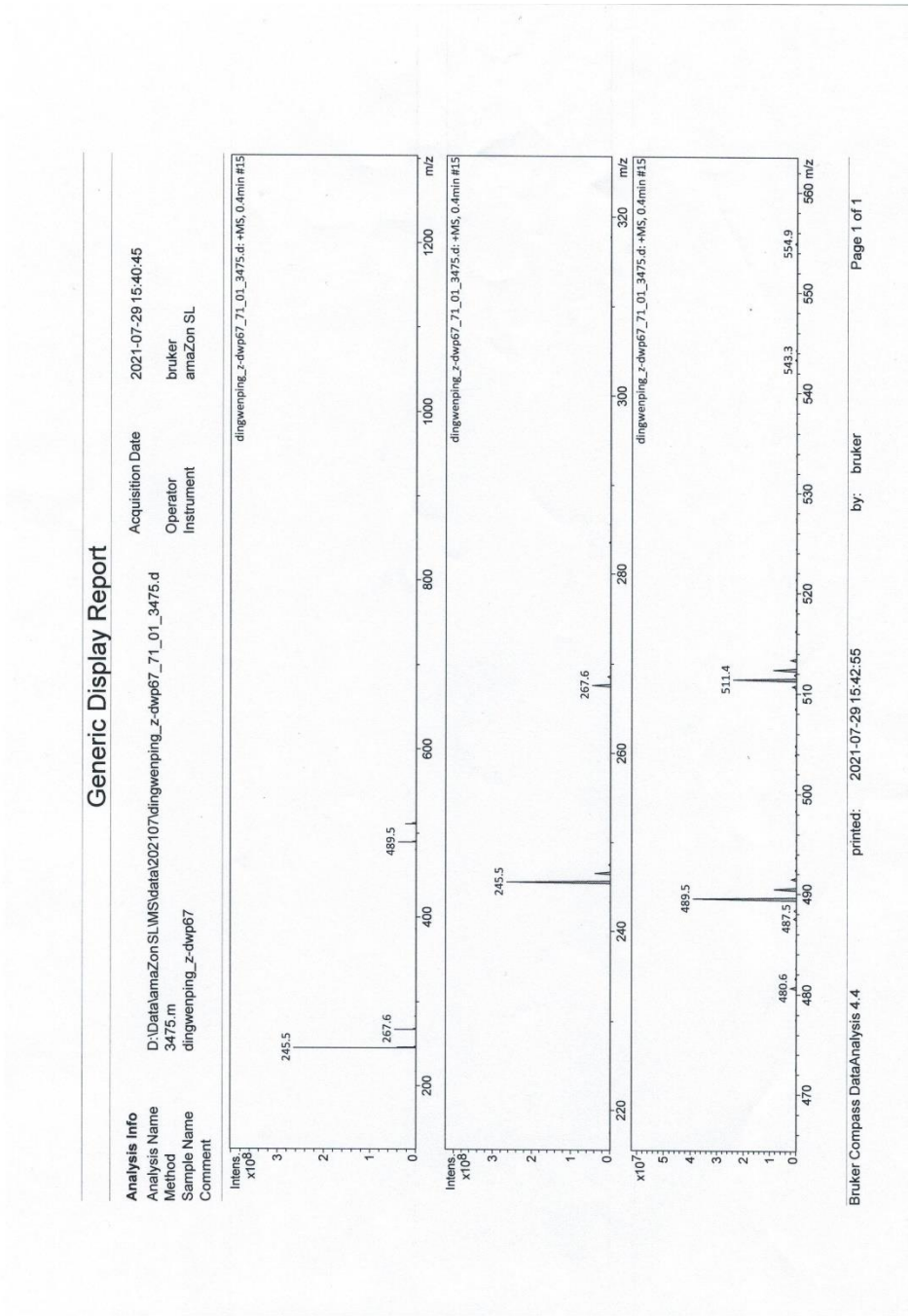


Fig. S67 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **9**

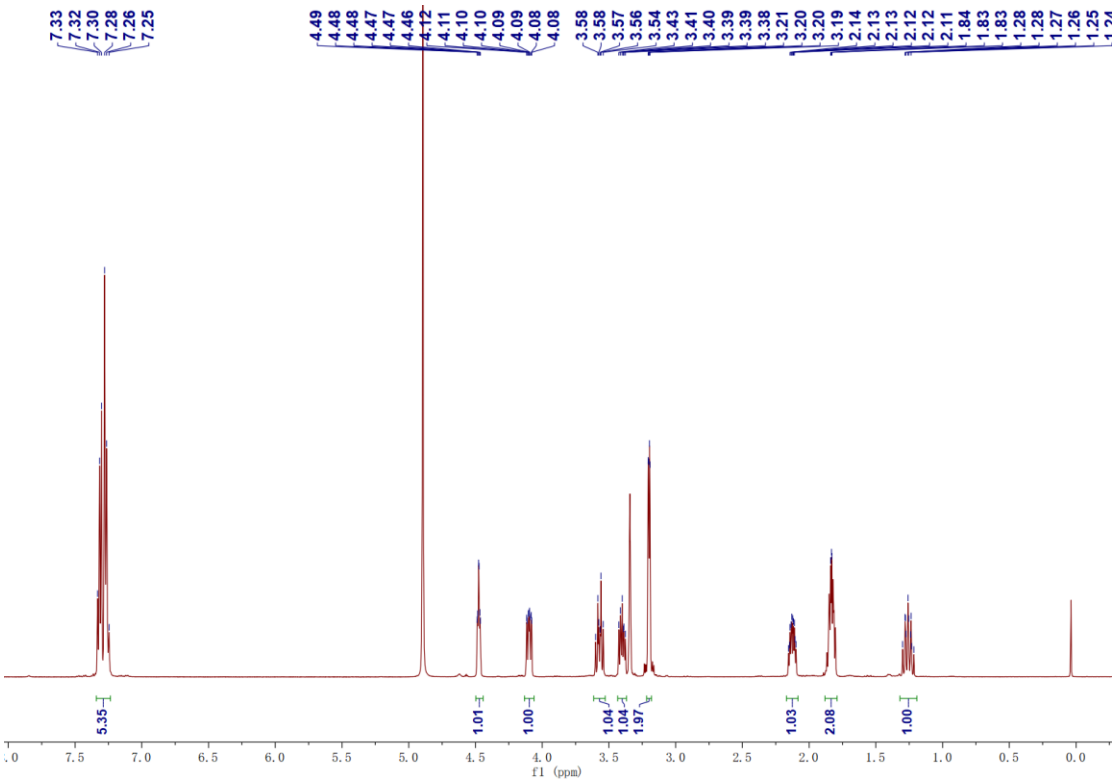
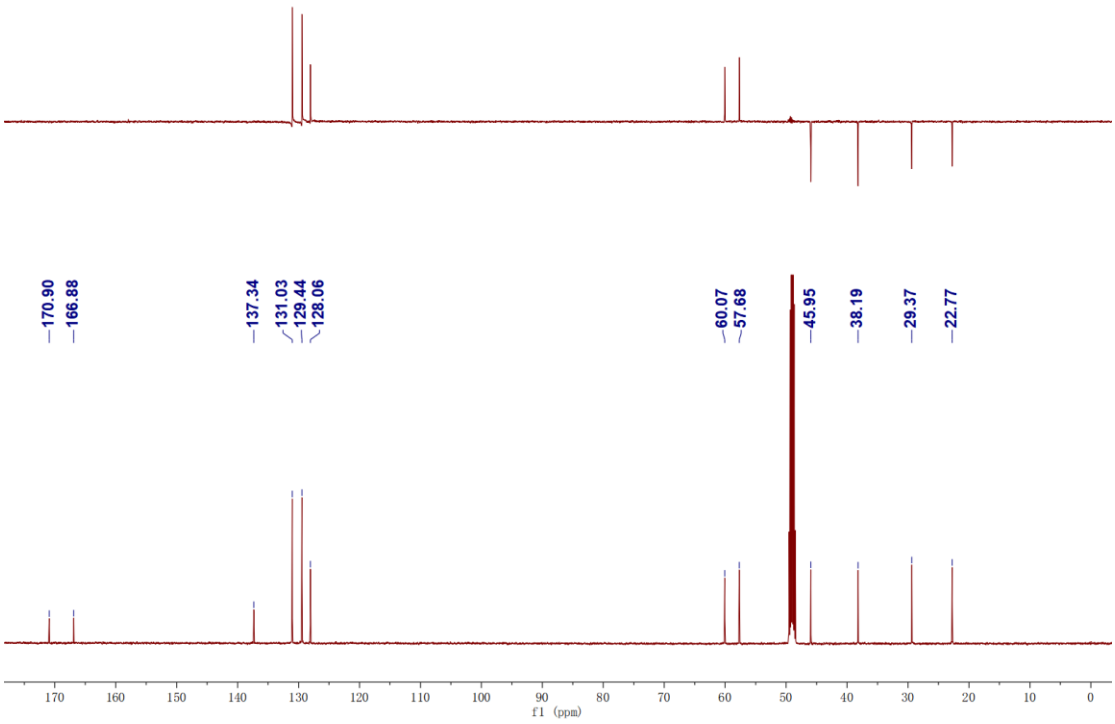


Fig. S68 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **9**



Crystallographic data of compound **9**

Crystal Data for $C_{14}H_{16}N_2O_2$ (M =244.29 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 11.9476(2) Å, b = 8.86980(10) Å, c = 12.3429(2) Å, β = 109.501(2)°, V = 1232.98(3) Å^3, Z = 4, T = 99.99(10) K, μ(Cu Kα) = 0.721 mm^{-1}, $Dcalc$ = 1.316 g/cm^3, 22922 reflections measured (7.598° ≤ 2Θ ≤ 148.674°), 4840 unique (R_{int} = 0.0468, R_{sigma} = 0.0353) which were used in all calculations. The final R_1 was 0.0453 (I > 2σ(I)) and wR_2 was 0.1227 (all data).

Fig. S69 ESI-MS spectrum of compound **10**

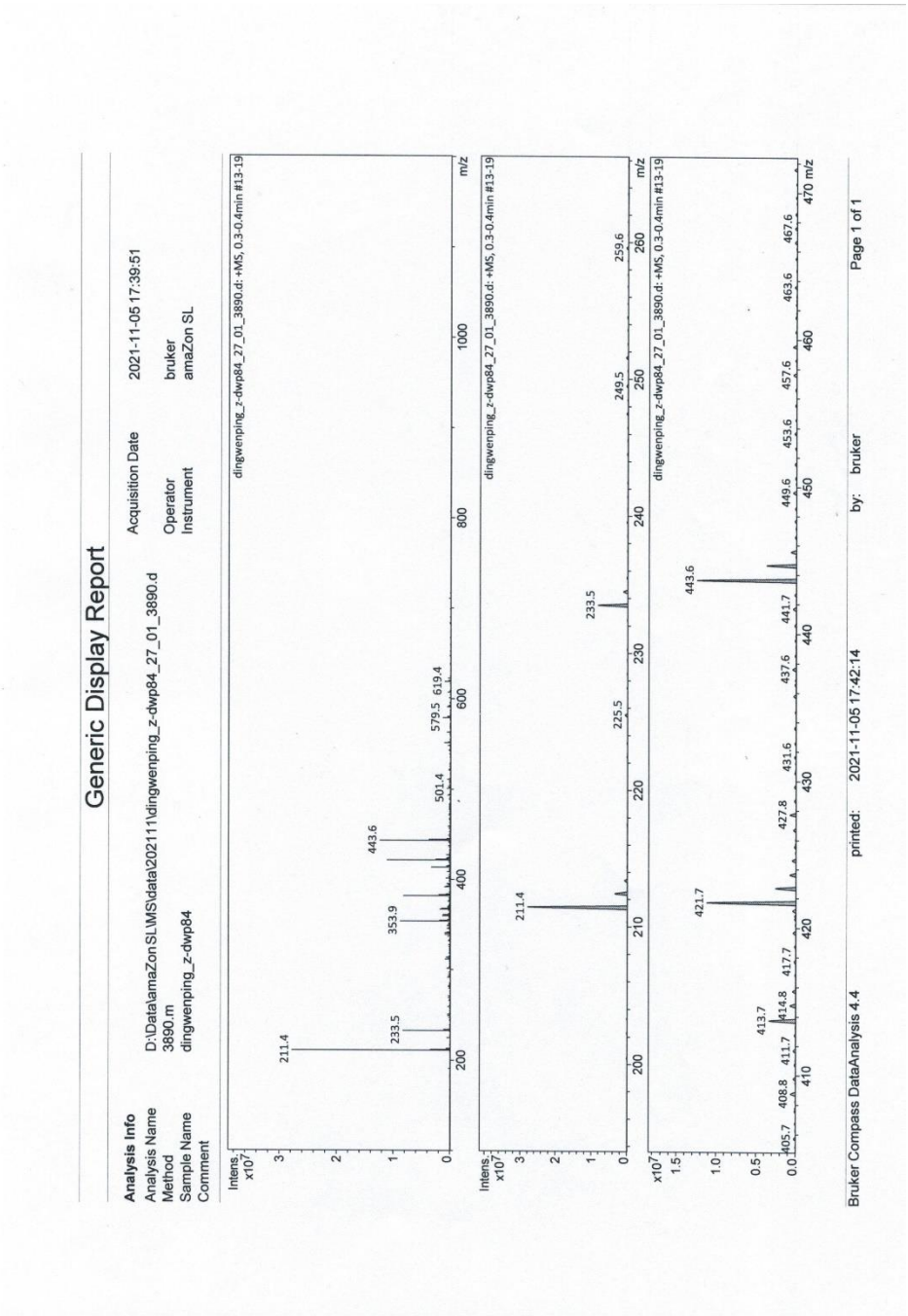


Fig. S70 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **10**

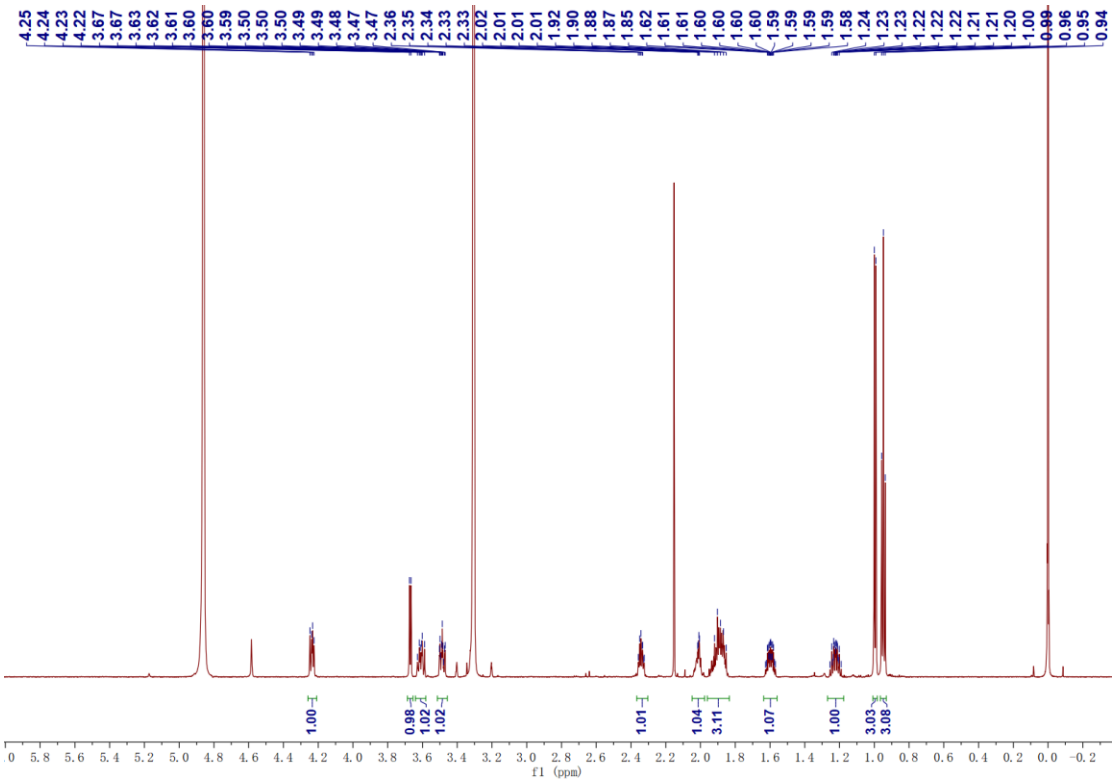


Fig. S71 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **10**

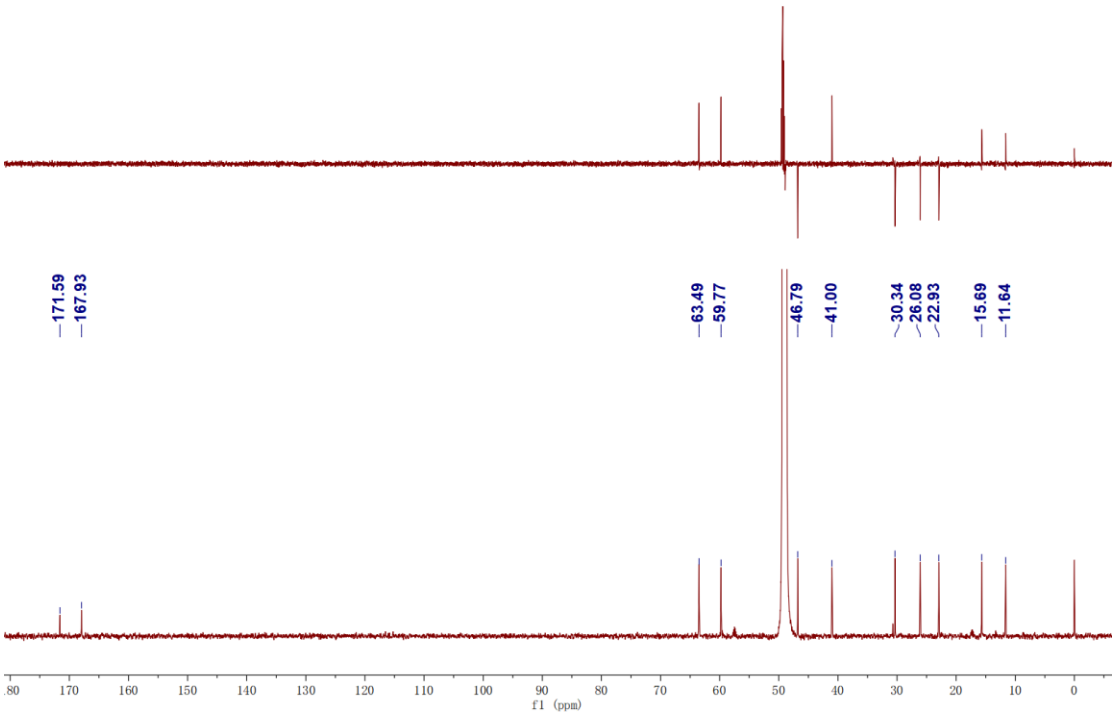


Fig. S72 ESI-MS spectrum of compound **11**

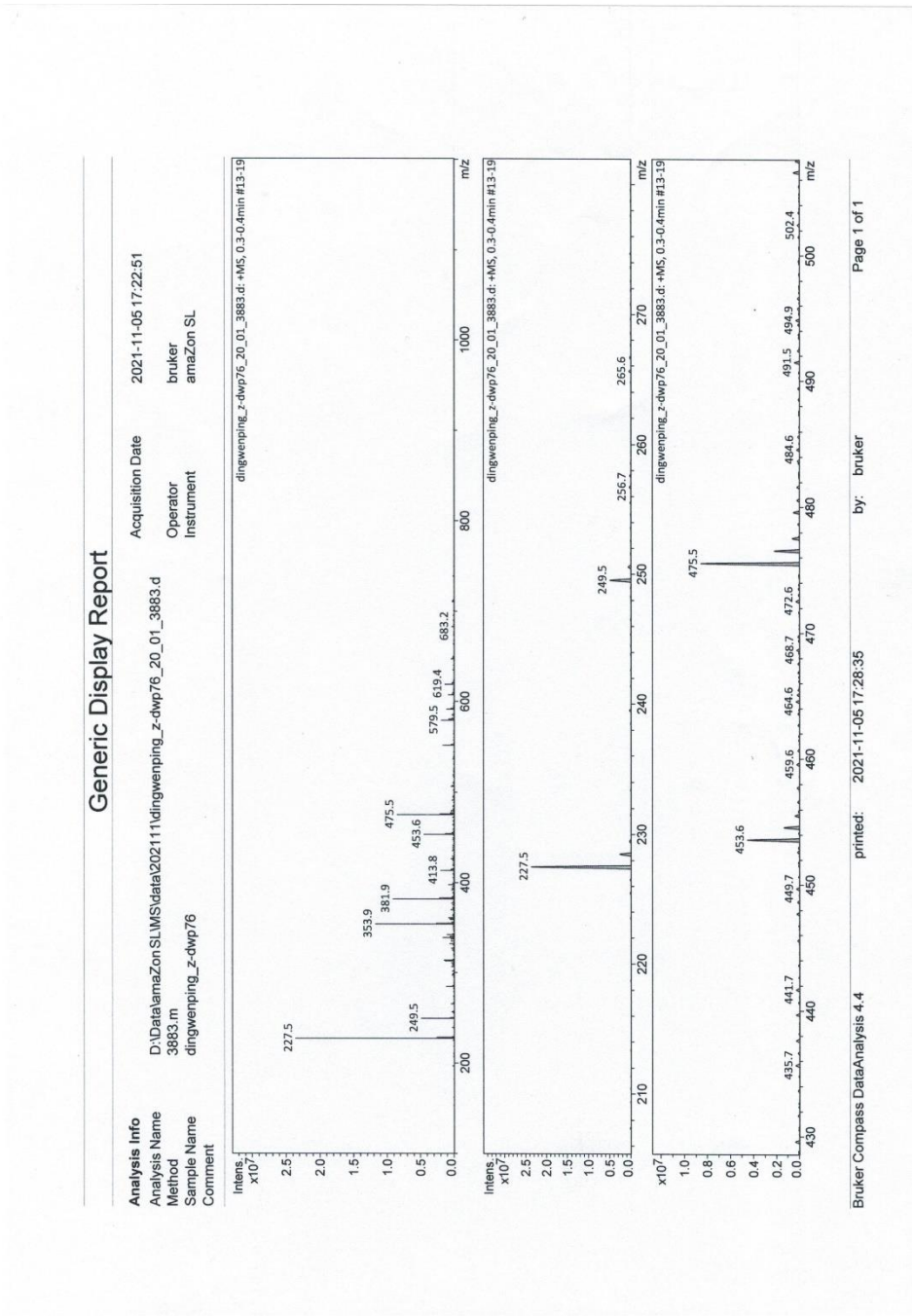


Fig. S73 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **11**

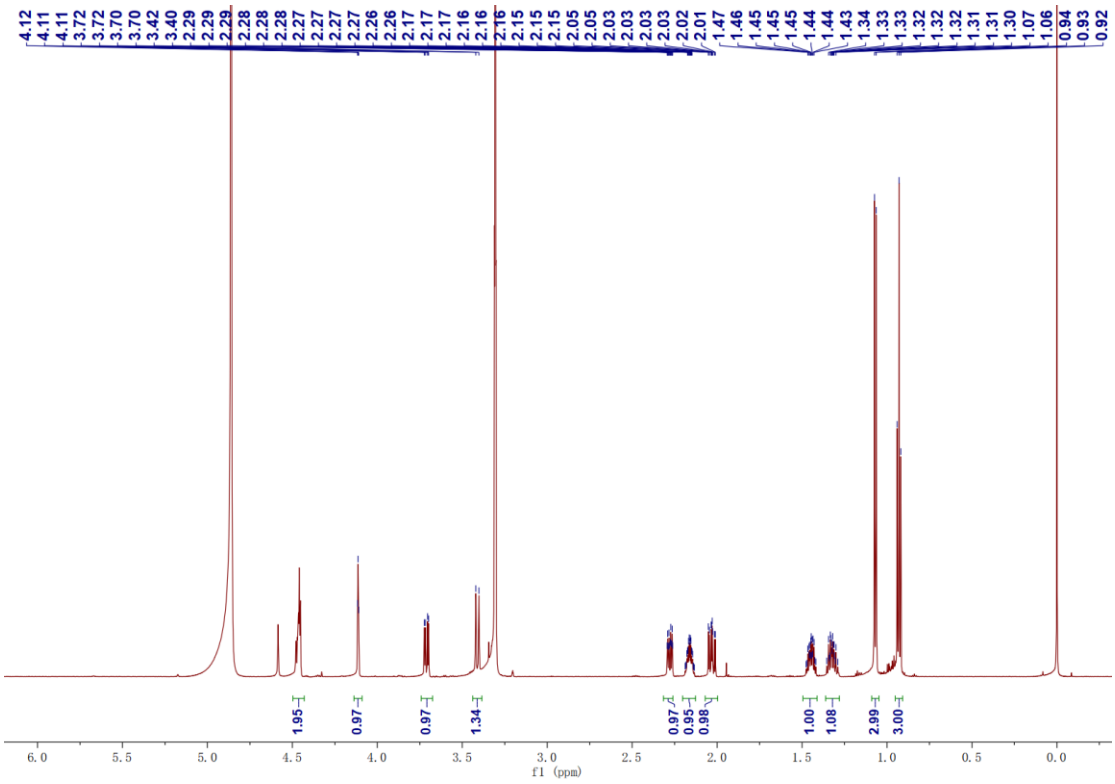


Fig. S74 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **11**

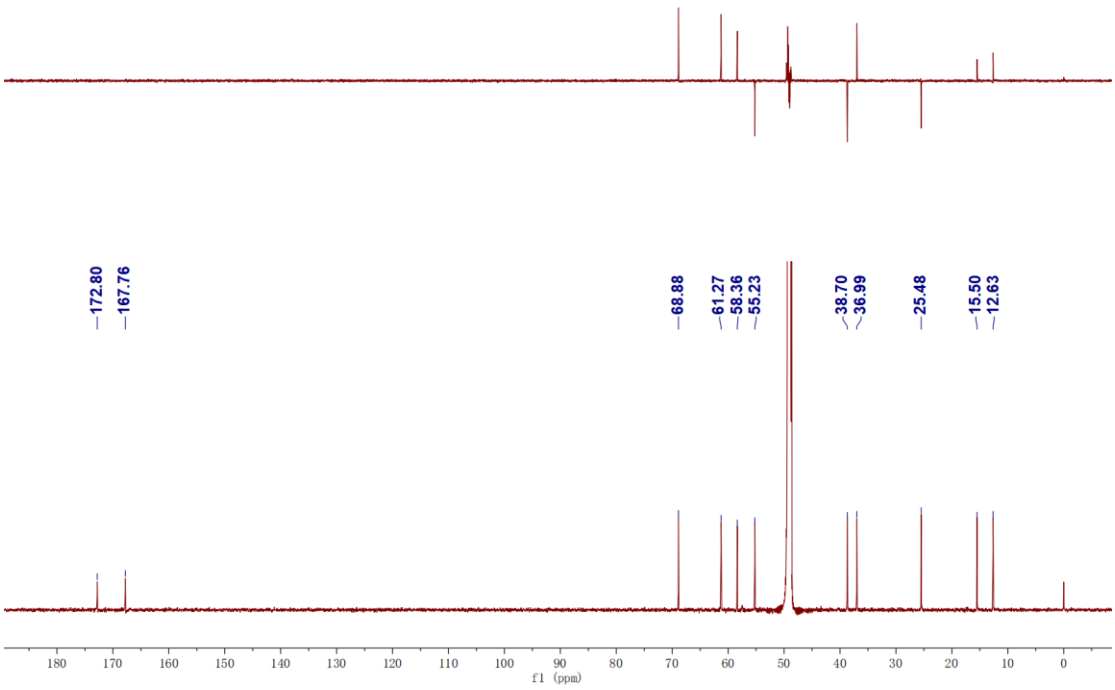


Fig. S75 ESI-MS spectrum of compound **12**

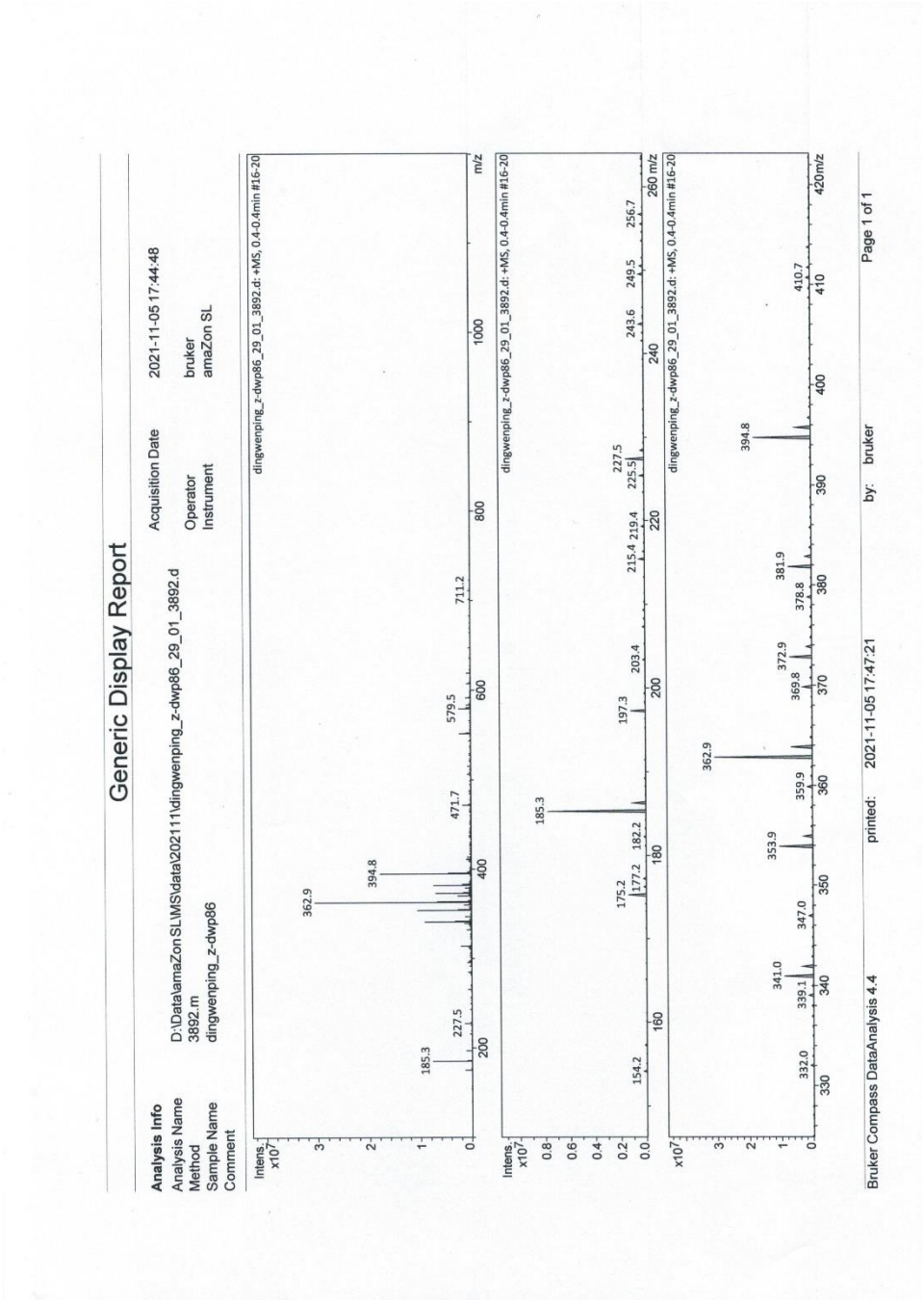


Fig. S76 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **12**

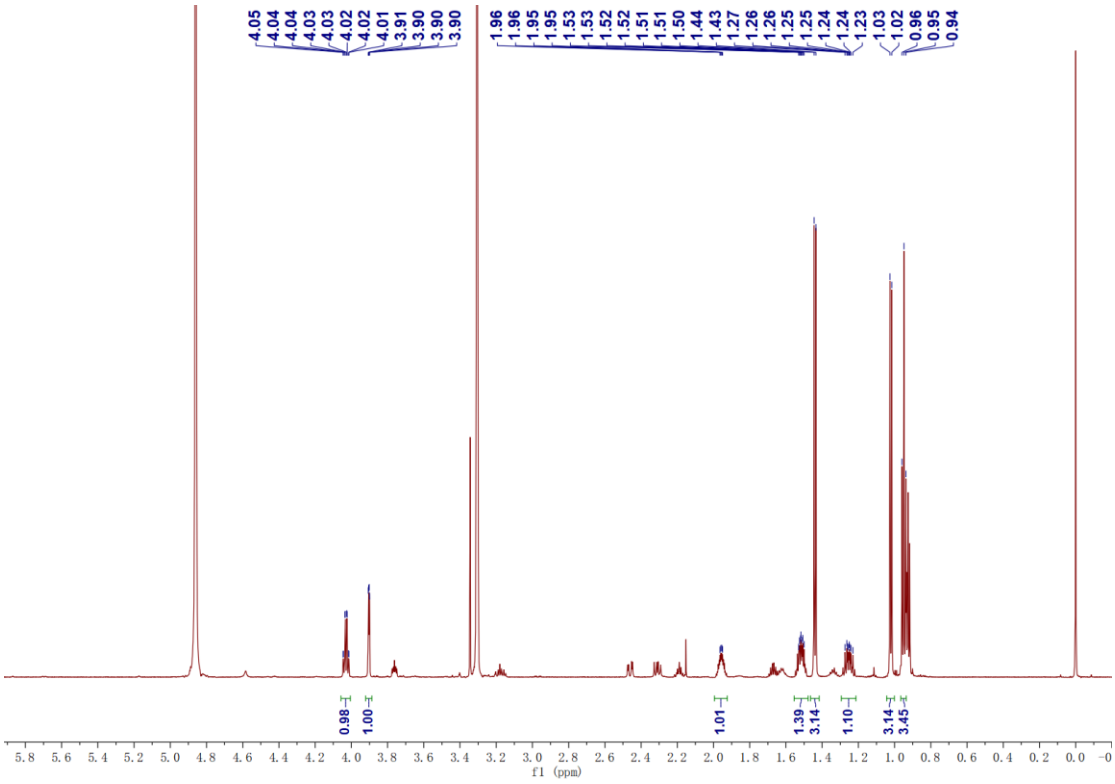


Fig. S77 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **12**

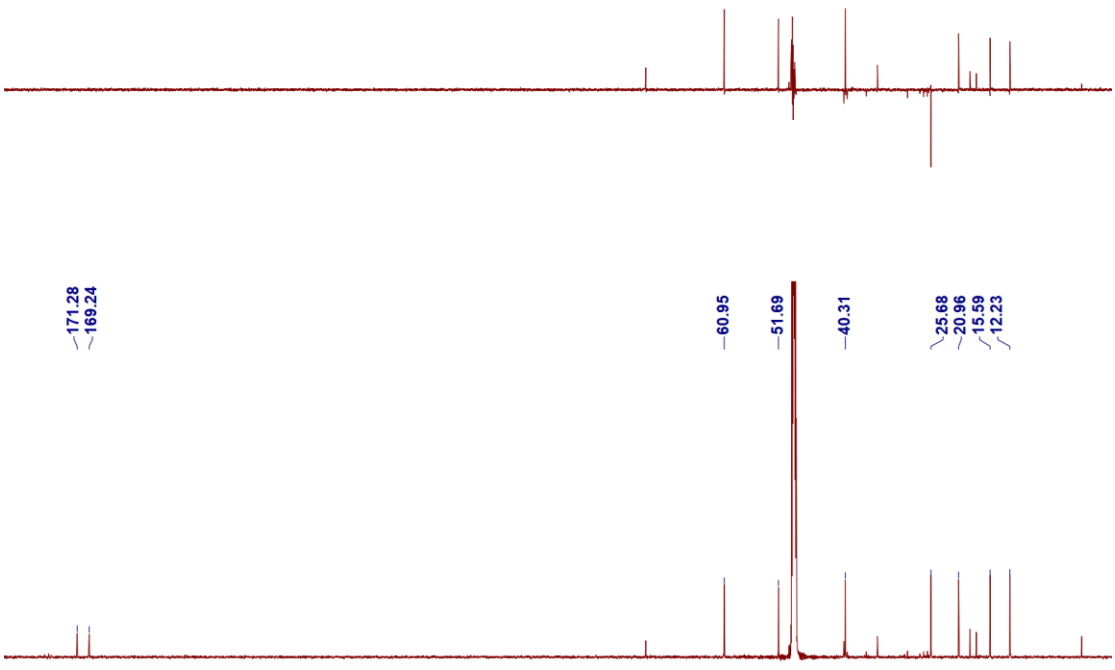
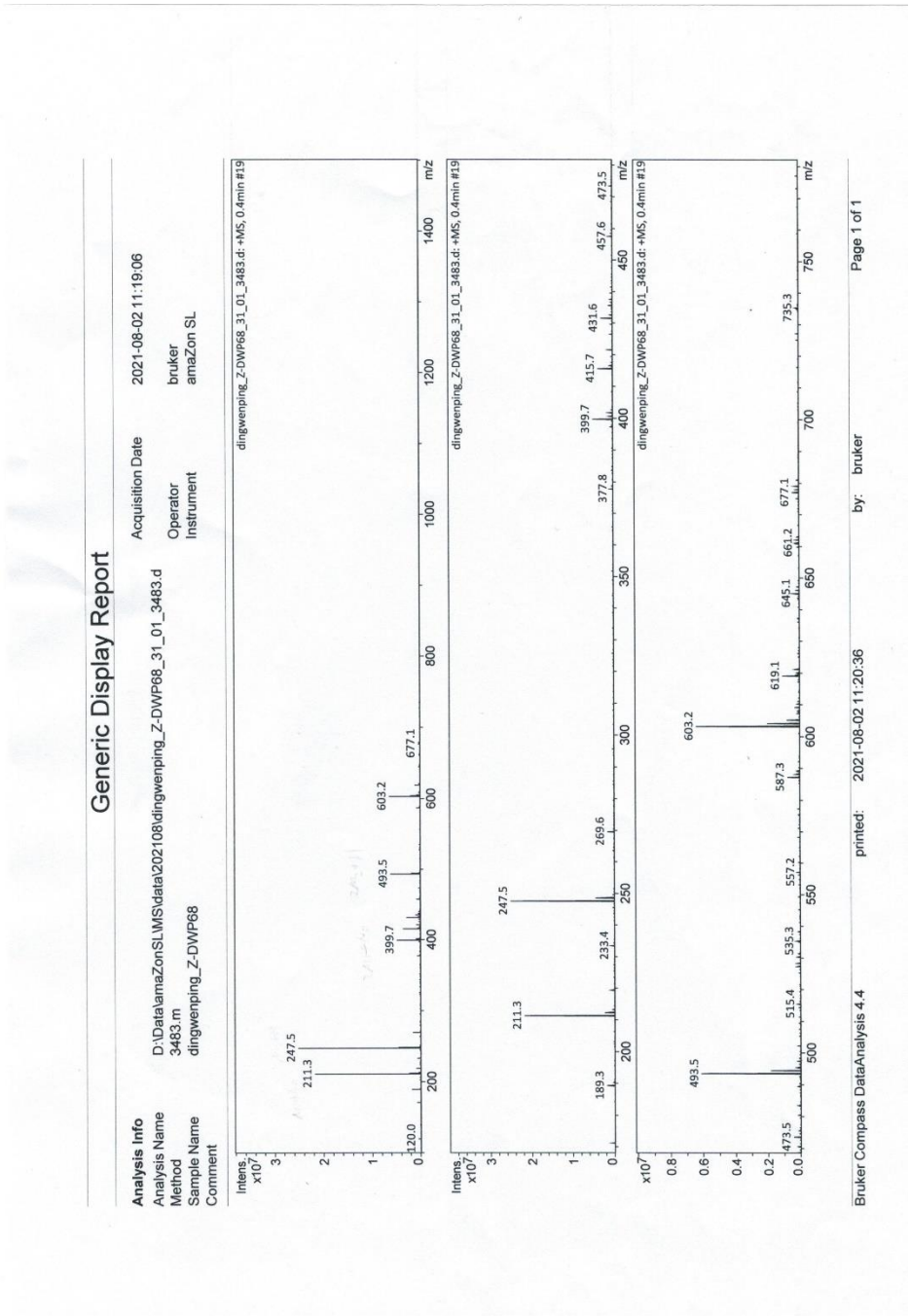
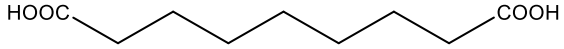


Fig. S78 ESI-MS spectrum of compound **13**



Structure of impurity:



Nonanedioic acid

Fig. S79 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **13**

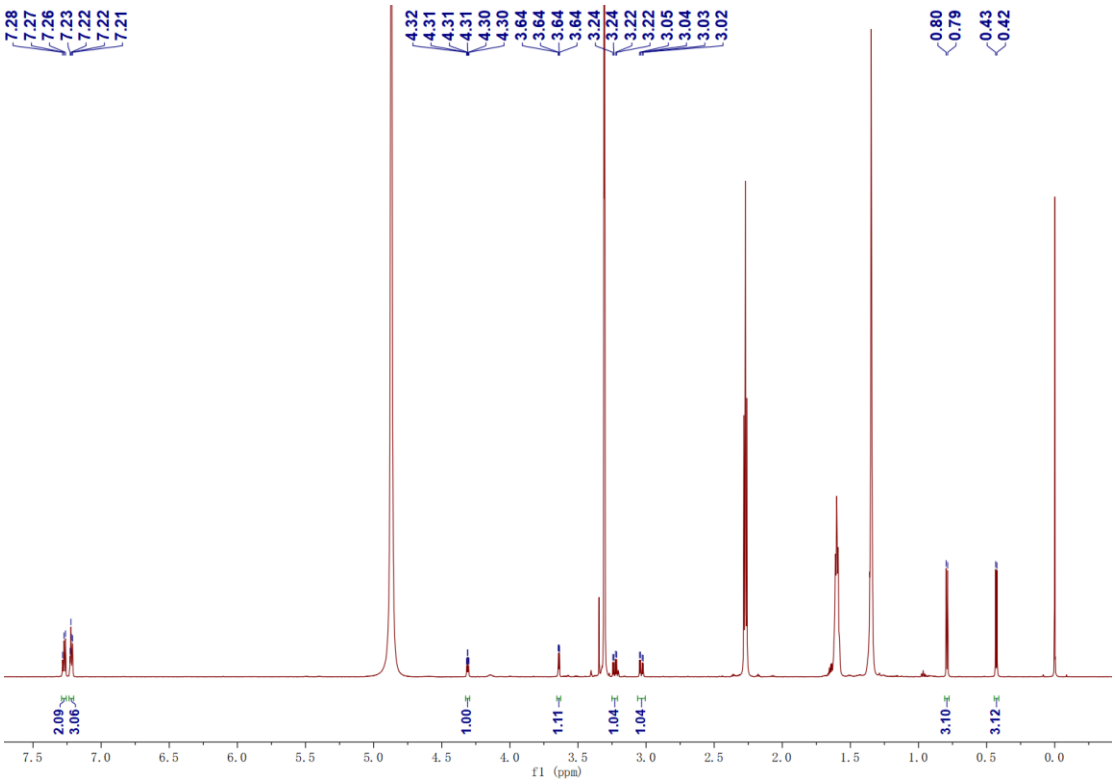


Fig. S80 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **13**

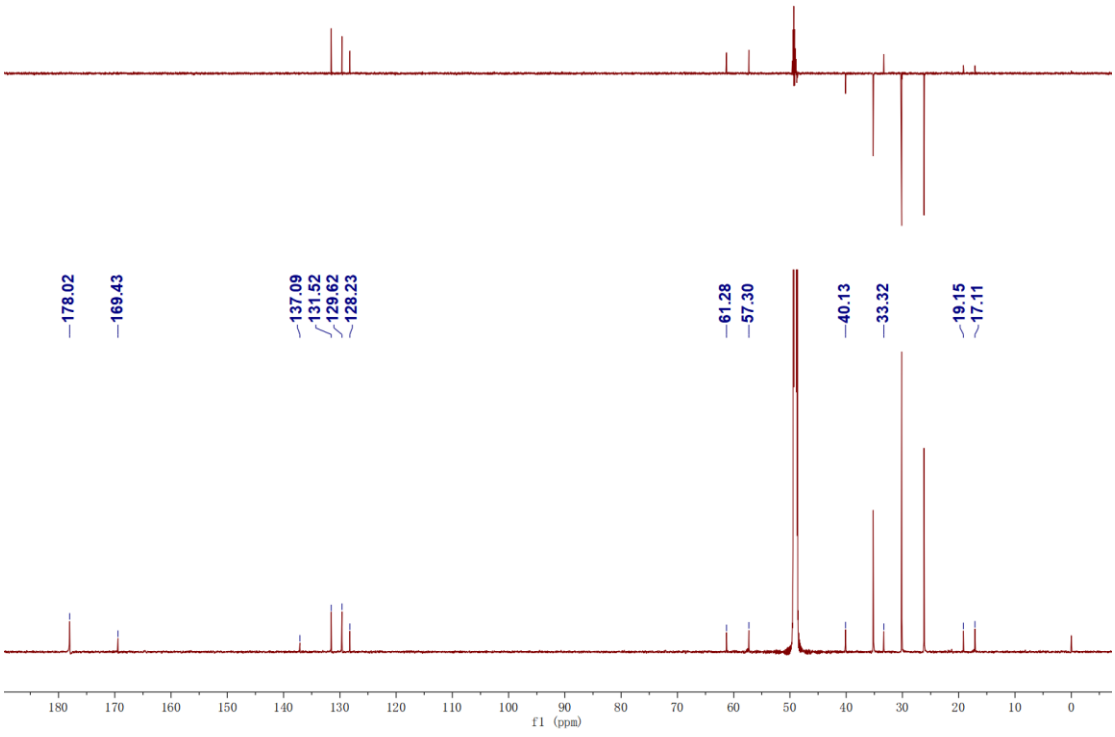


Fig. S81 ESI-MS spectrum of compound **14**

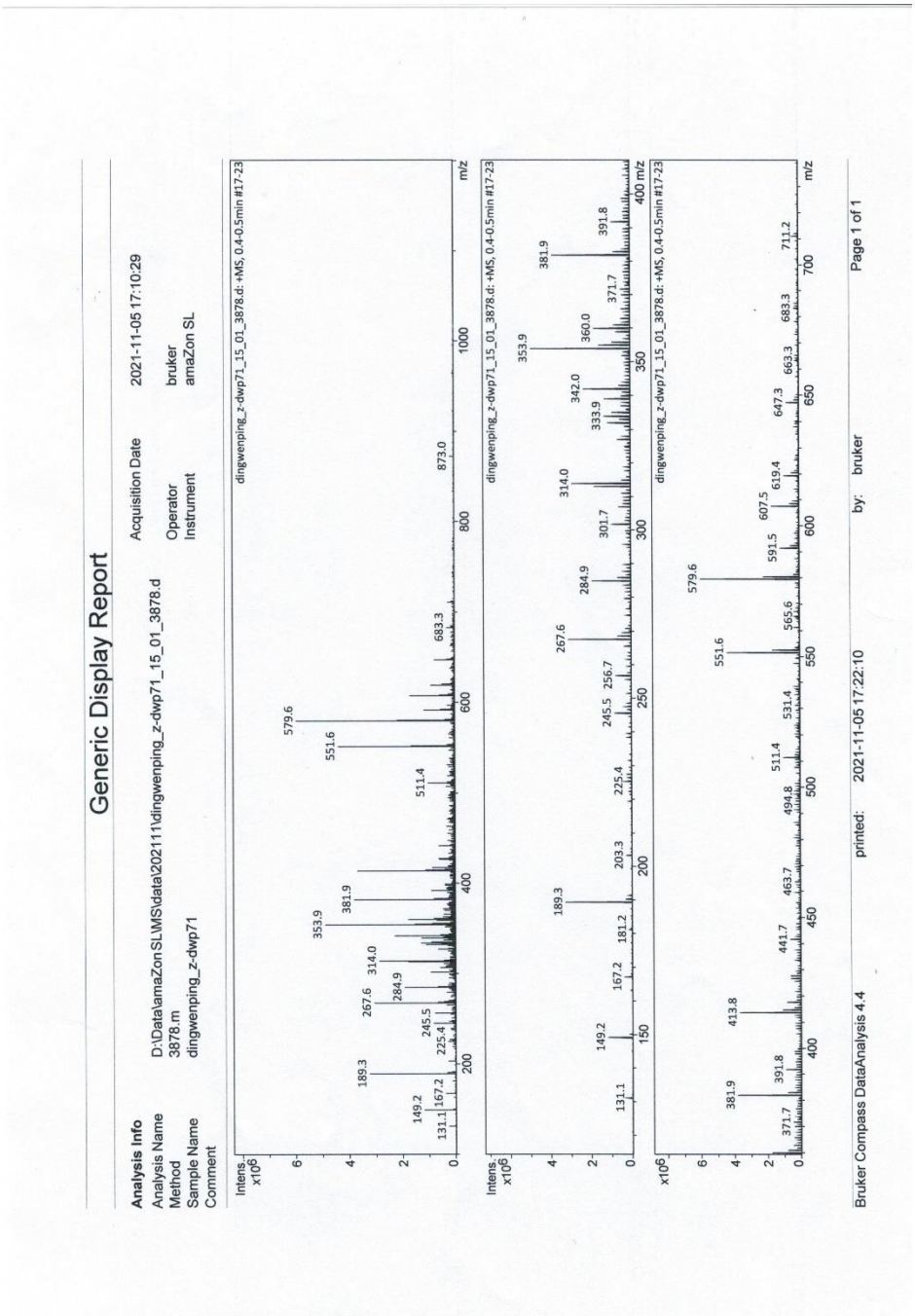


Fig. S82 ^{1}H NMR spectrum (CD_3Cl, 700 MHz) of compound **14**

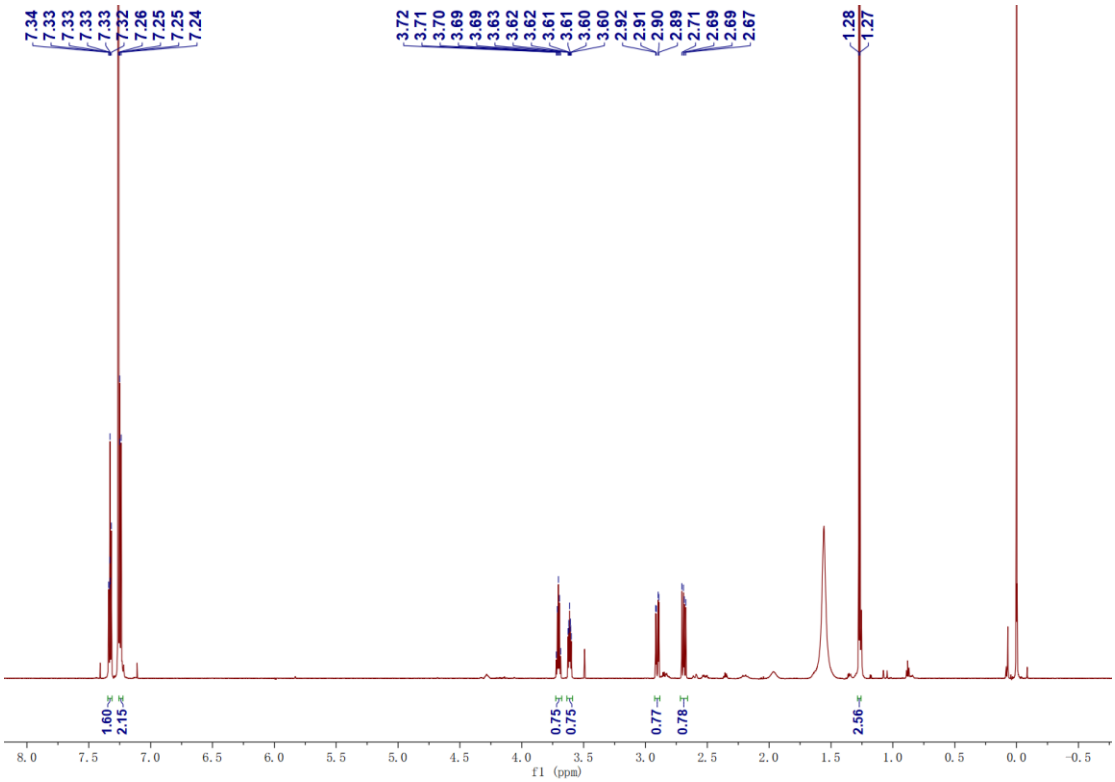


Fig. S83 ^{13}C NMR spectrum (CD_3Cl, 176 MHz) of compound **14**

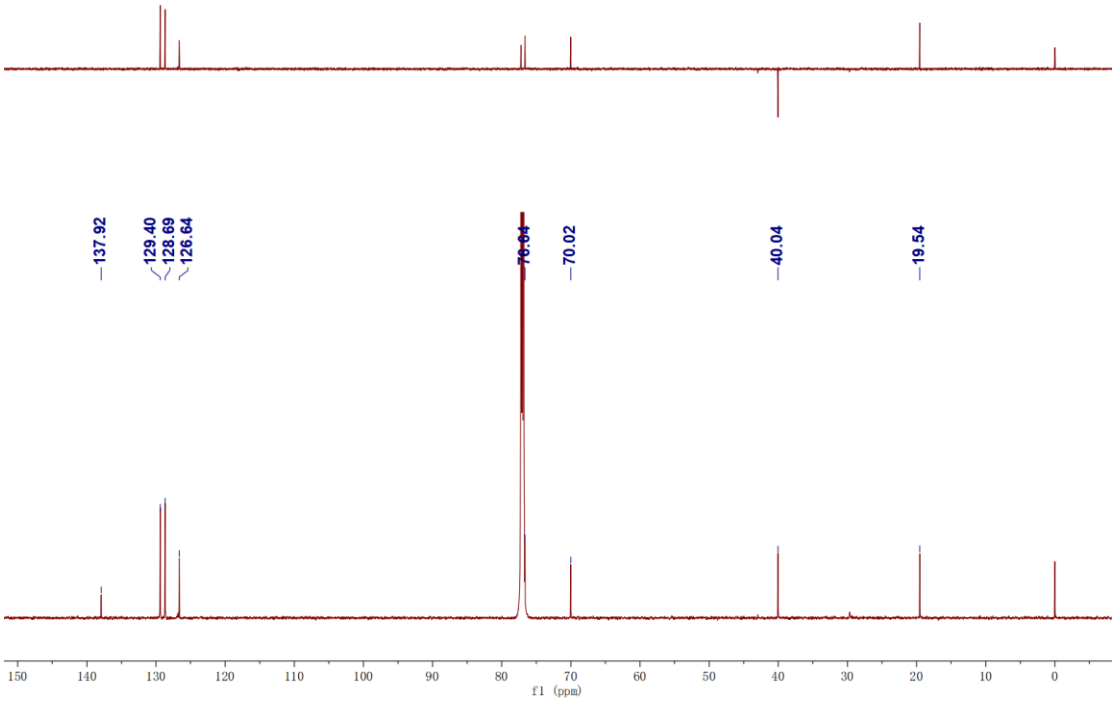


Fig. S84 ESI-MS spectrum of compound **15**

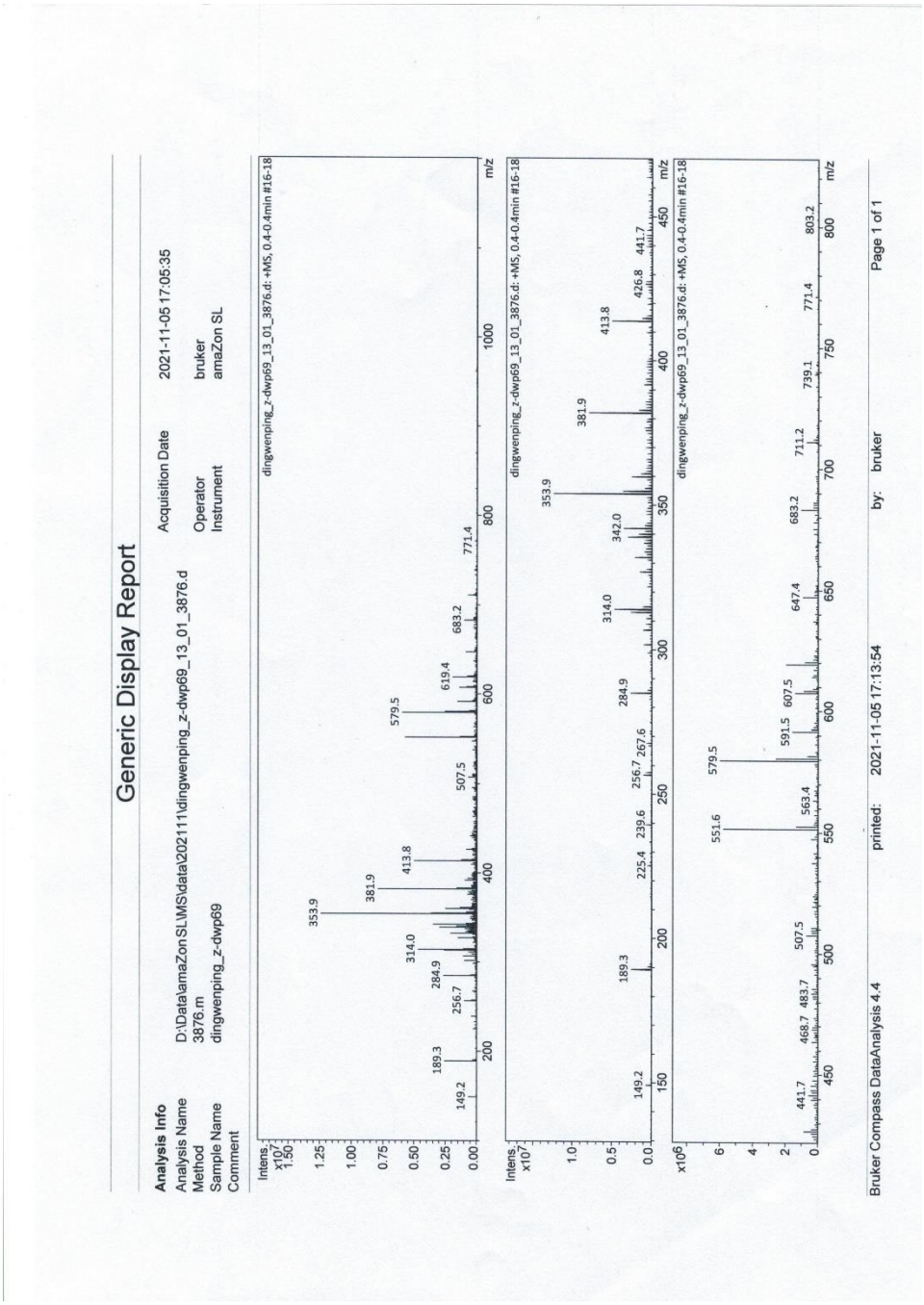


Fig. S85 ^{1}H NMR spectrum (CD_3Cl, 700 MHz) of compound **15**

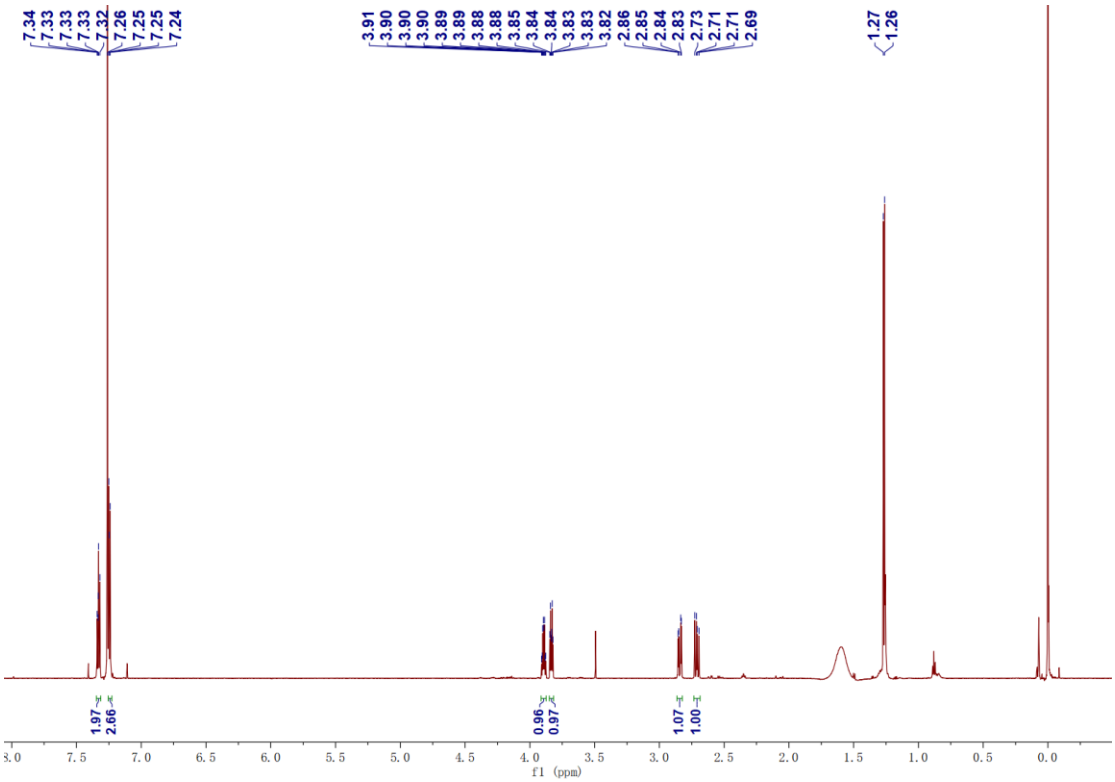


Fig. S86 ^{13}C NMR spectrum (CD_3Cl, 176 MHz) of compound **15**

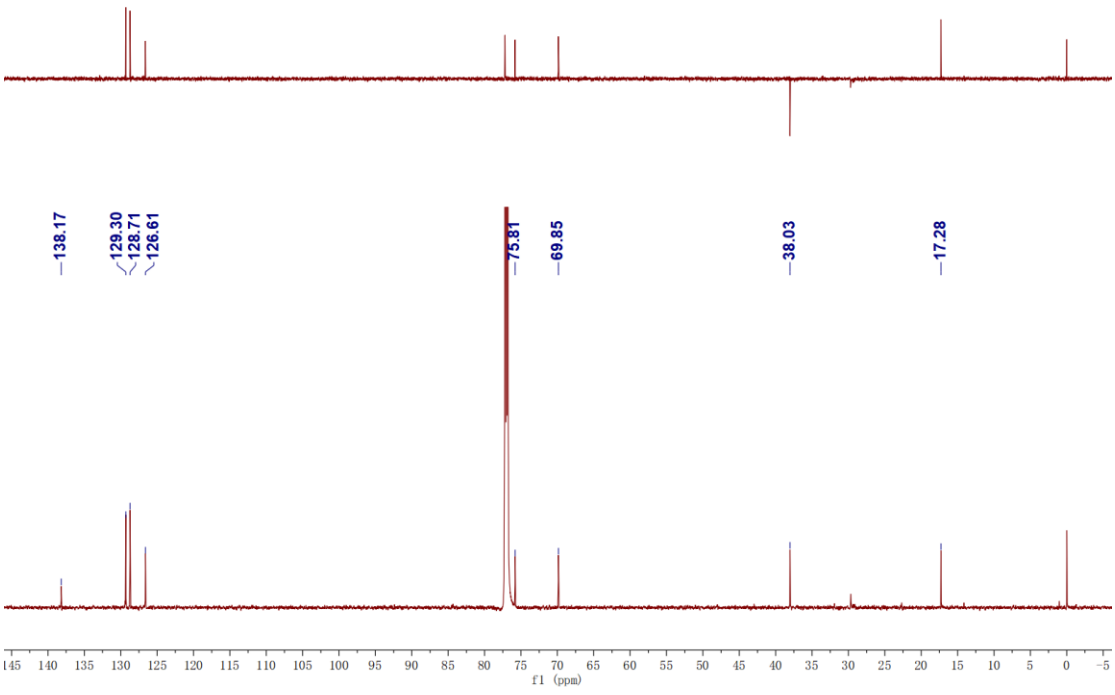


Fig. S87 ESI-MS spectrum of compound **16**

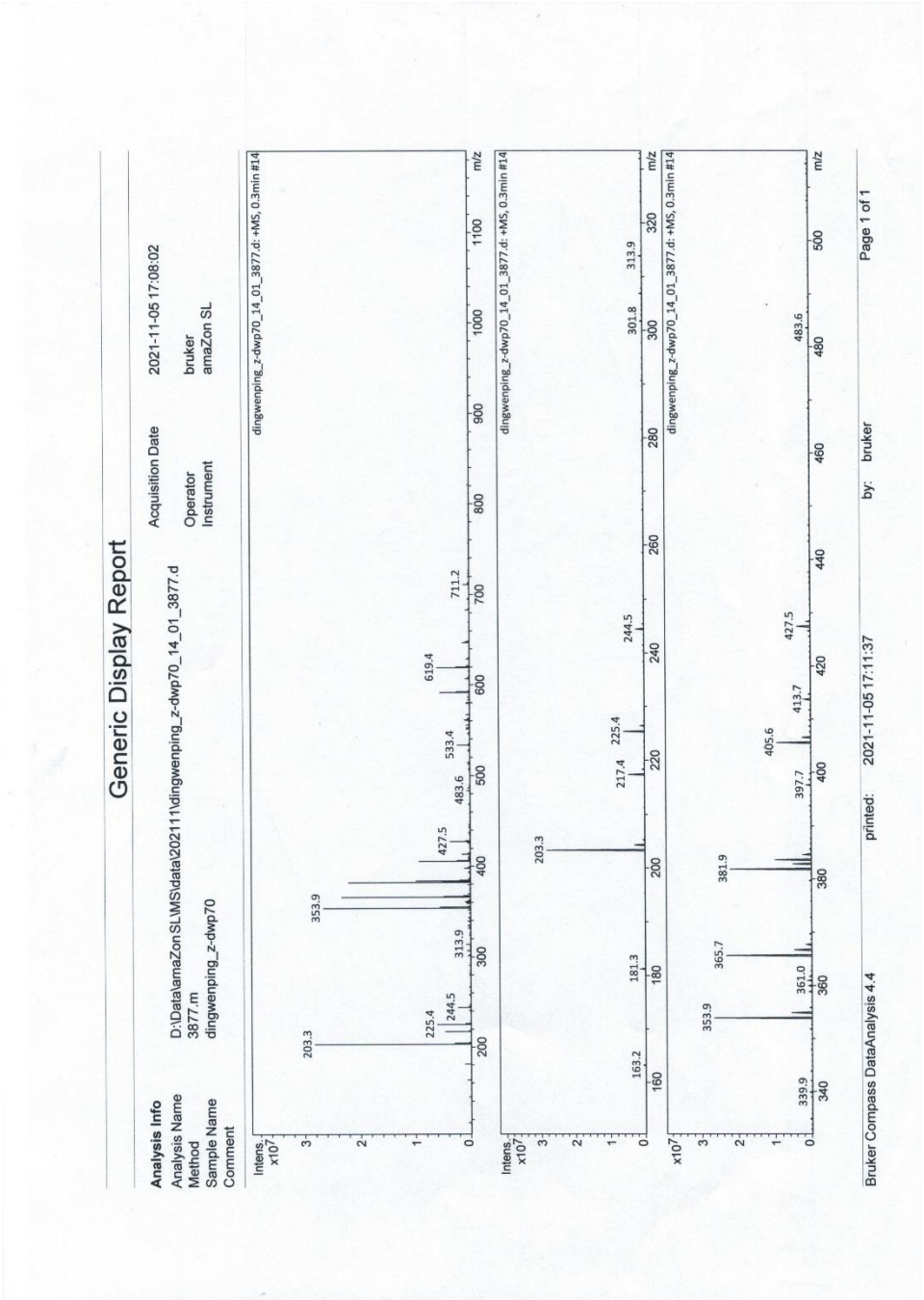


Fig. S88 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **16**

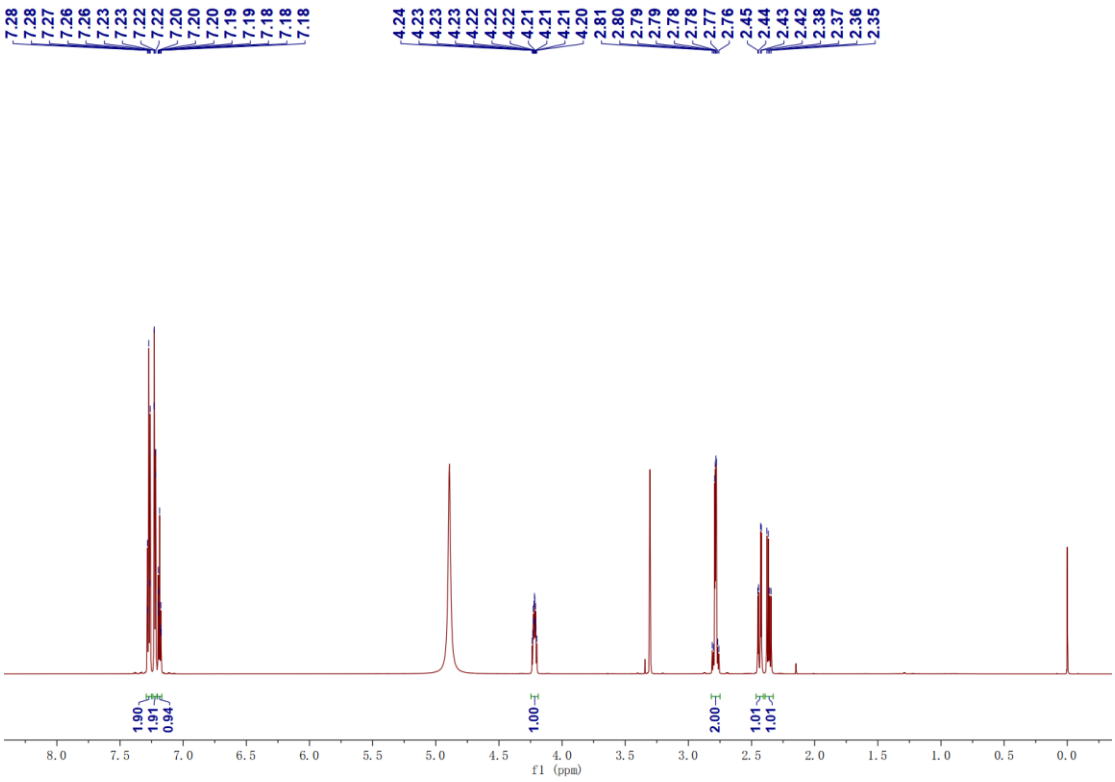


Fig. S89 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **16**

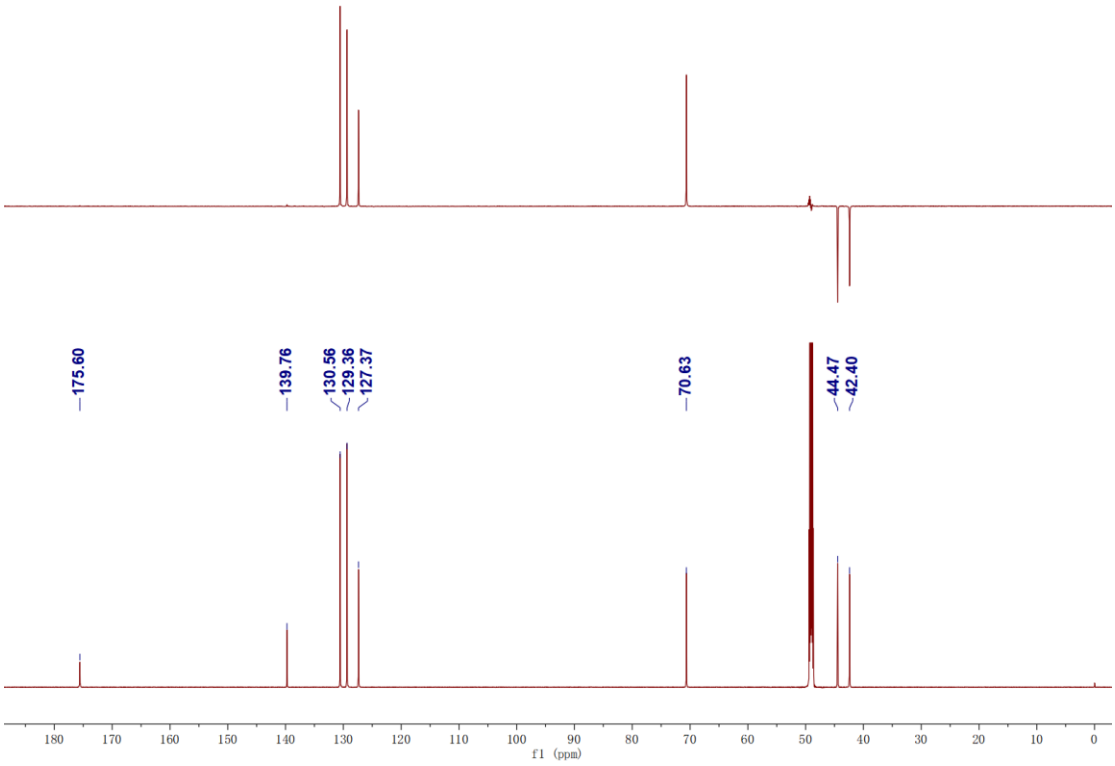


Fig. S90 ESI-MS spectrum of compound **17**

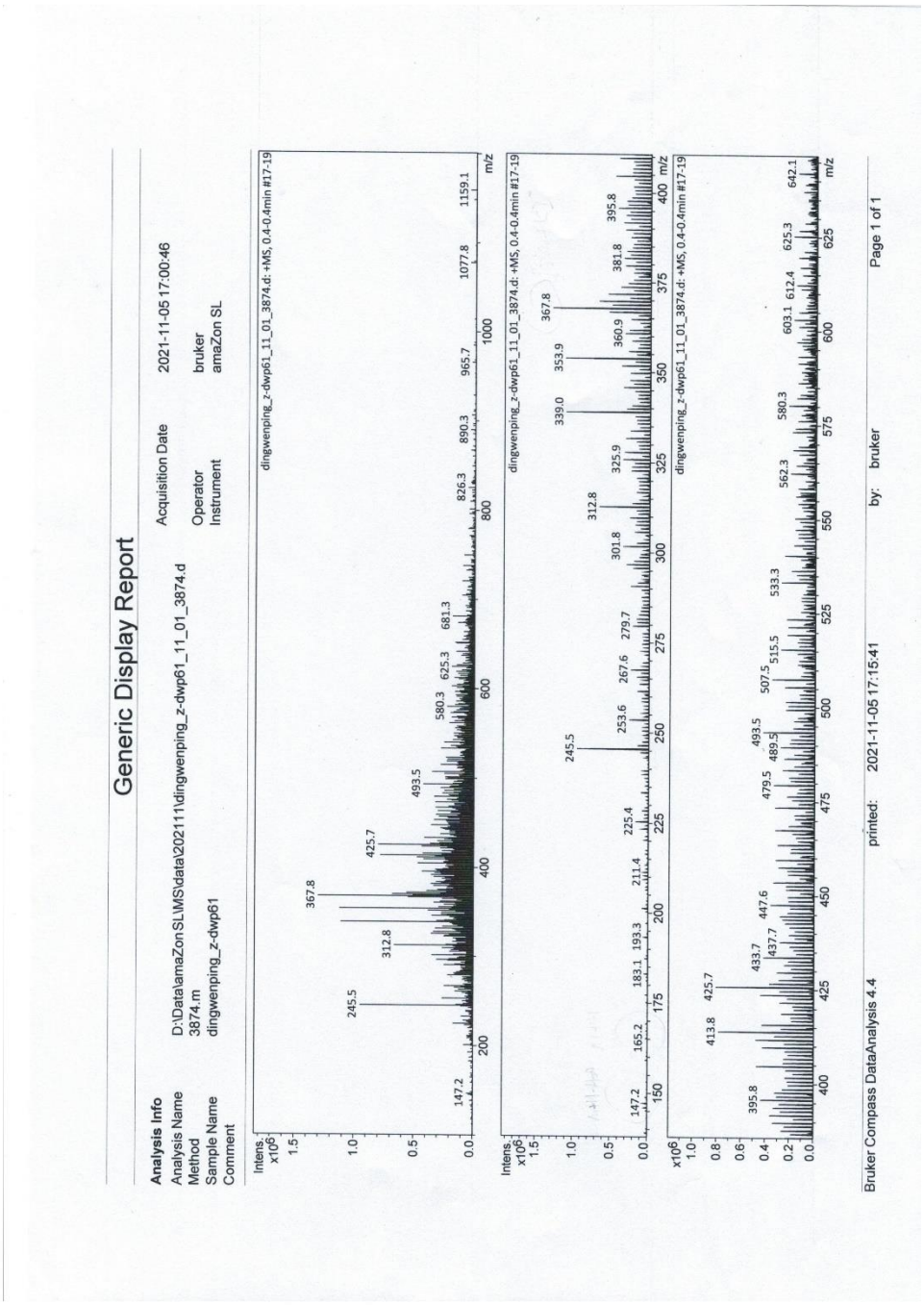


Fig. S91 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **17**

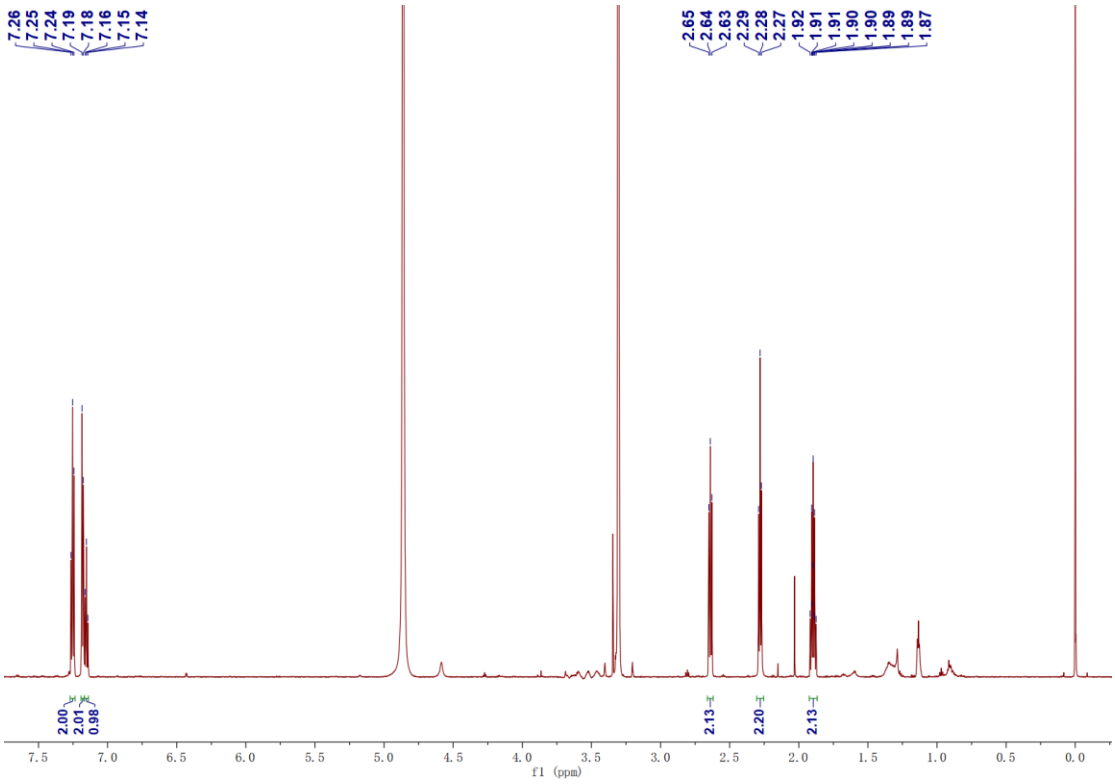


Fig. S92 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **17**

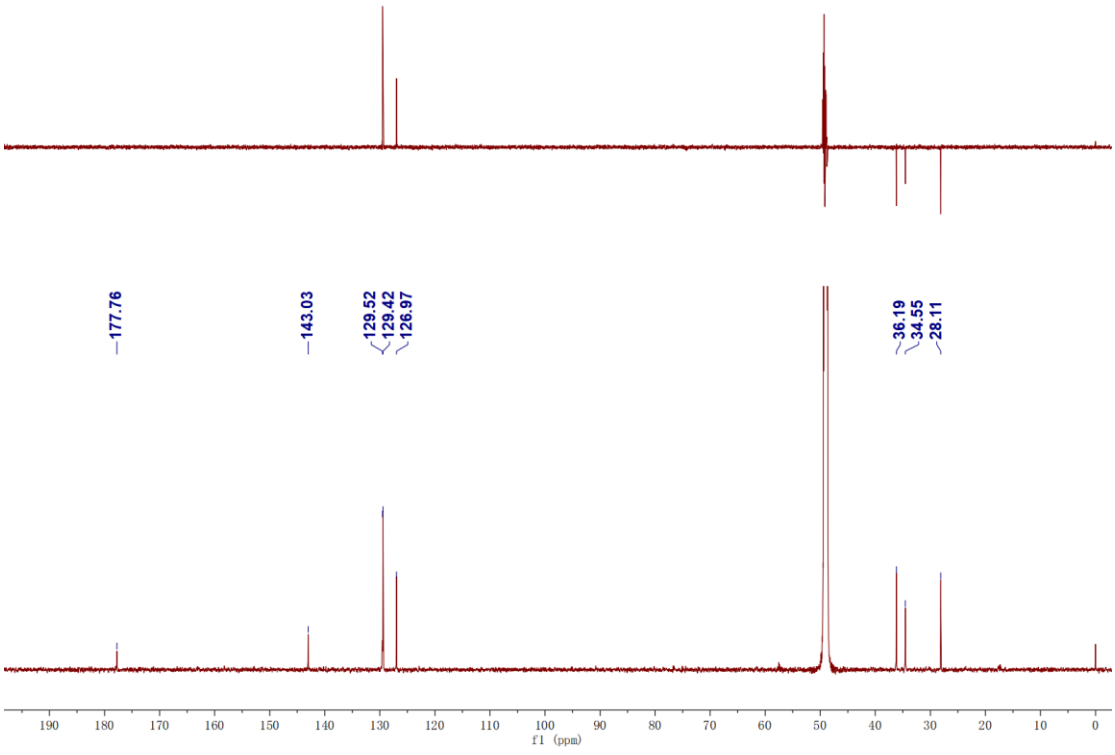


Fig. S93 ESI-MS spectrum of compound **18**

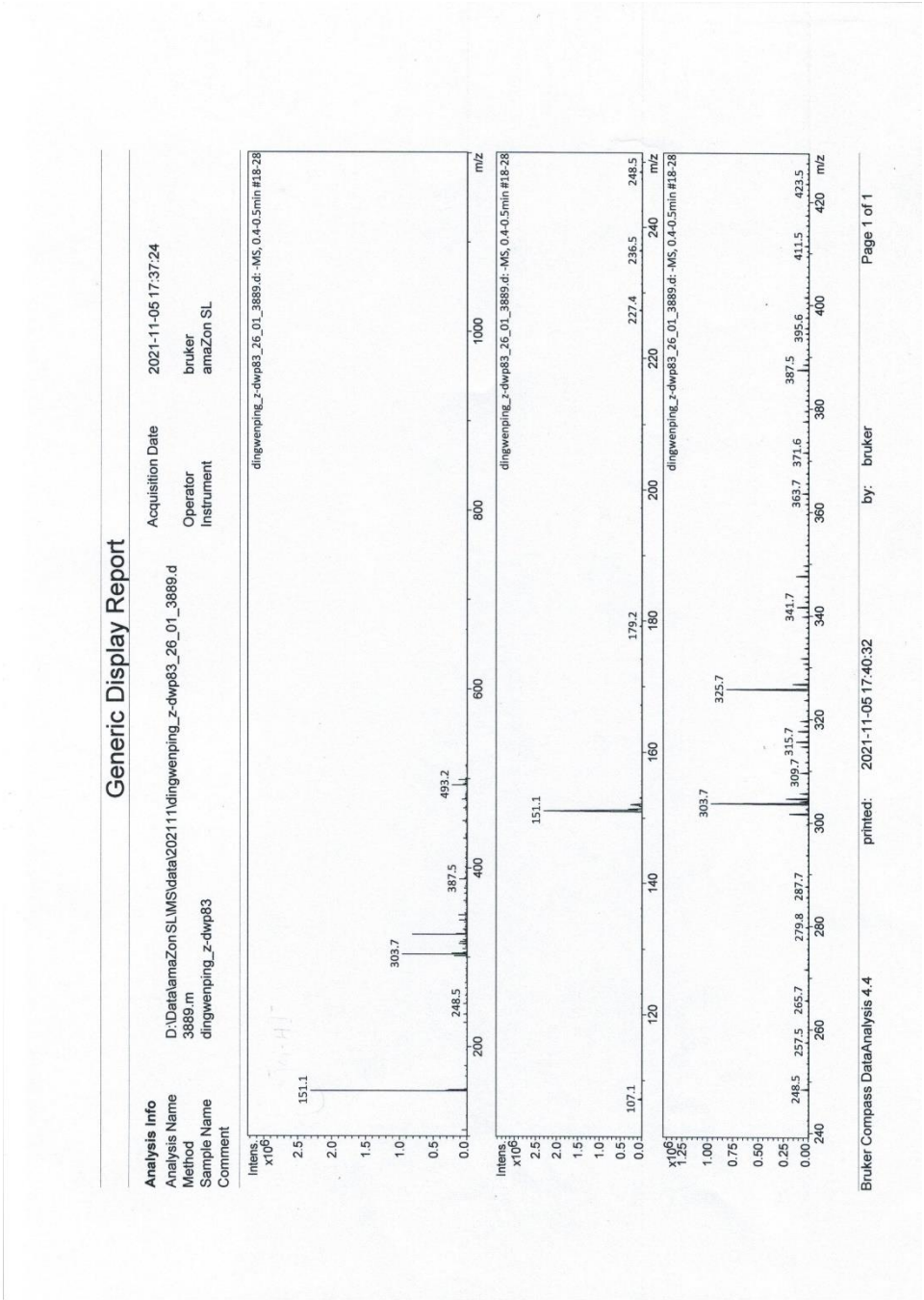


Fig. S94 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **18**

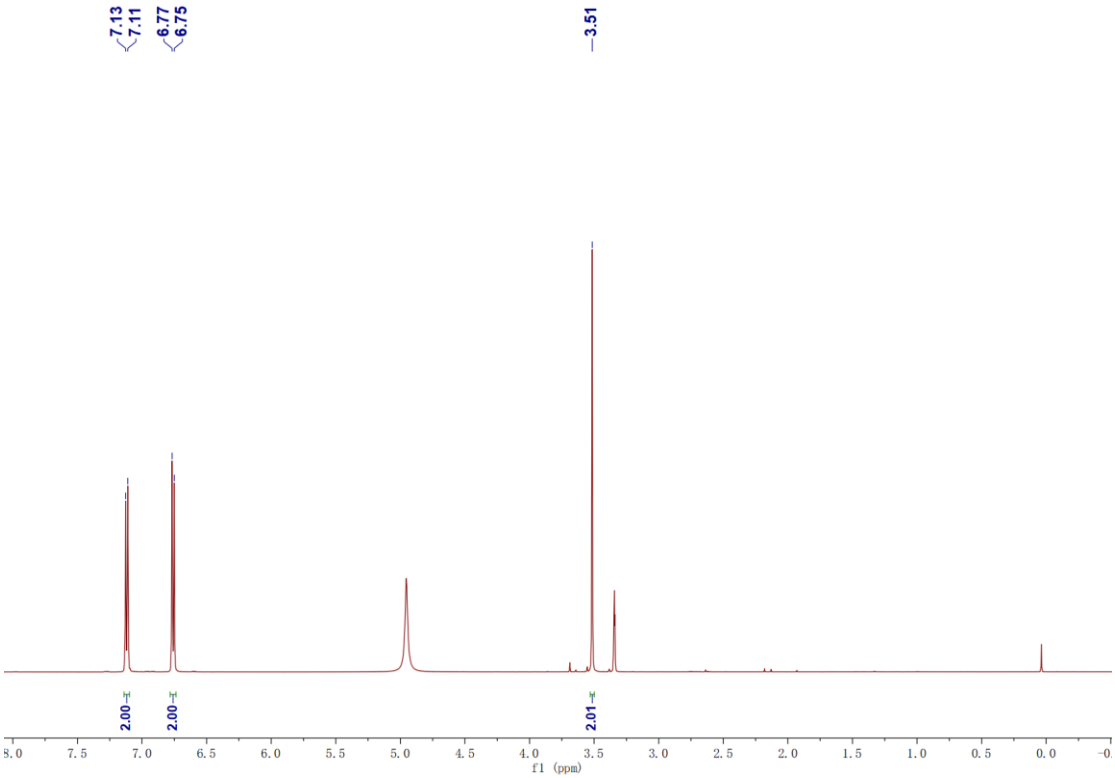


Fig. S95 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **18**

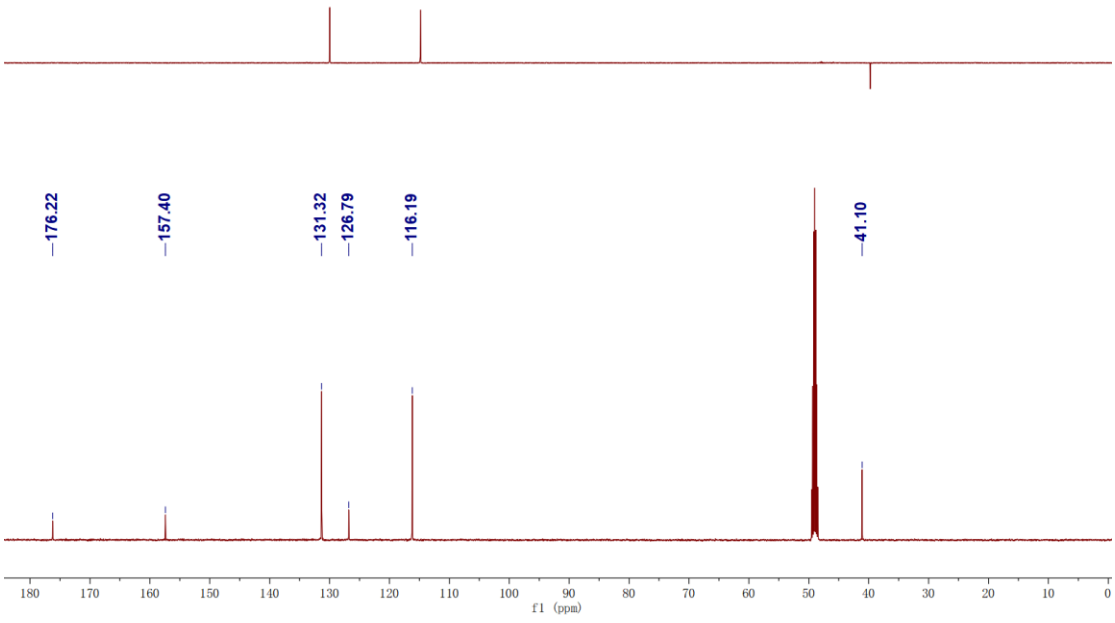


Fig. S96 ESI-MS spectrum of compound **19**

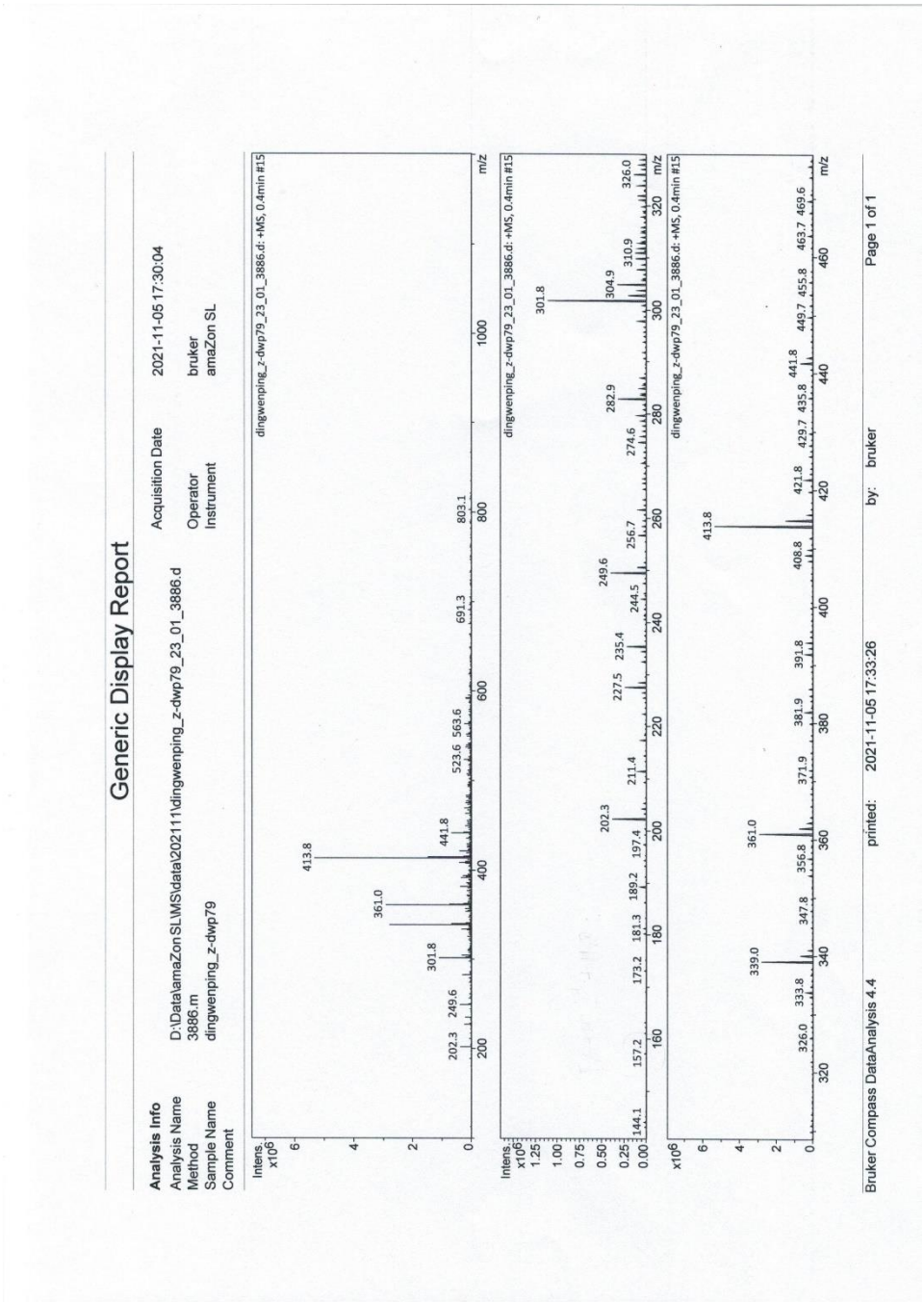


Fig. S97 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **19**

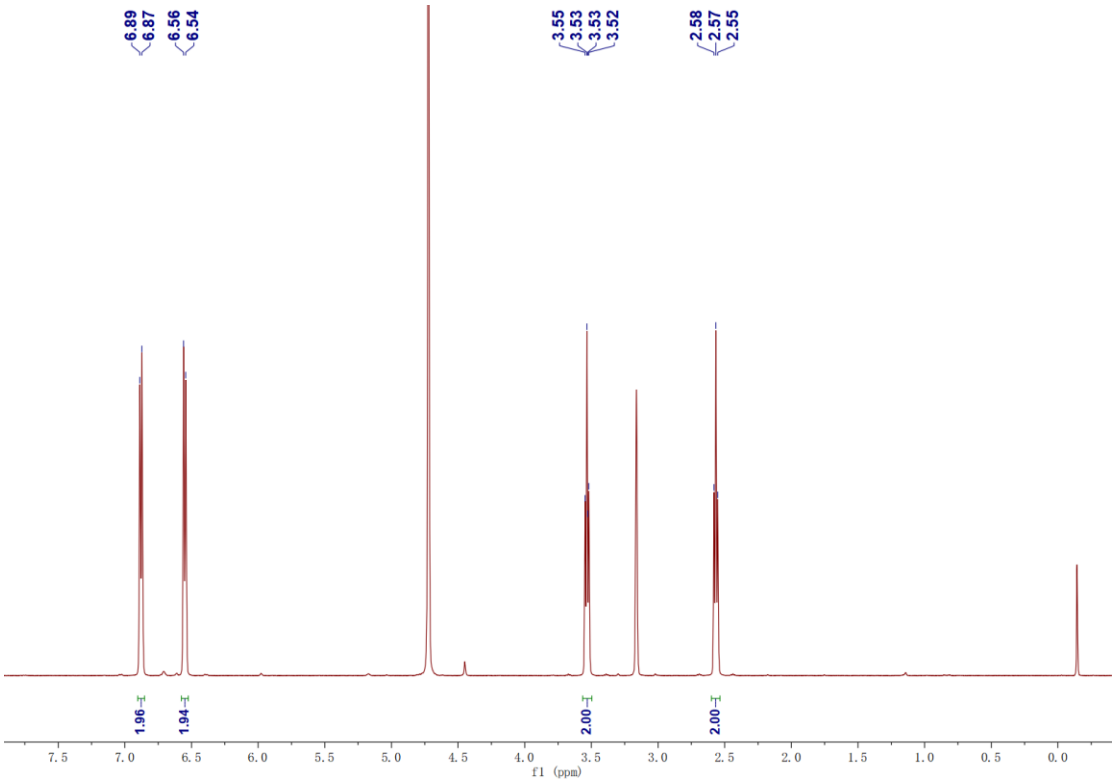


Fig. S98 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **19**

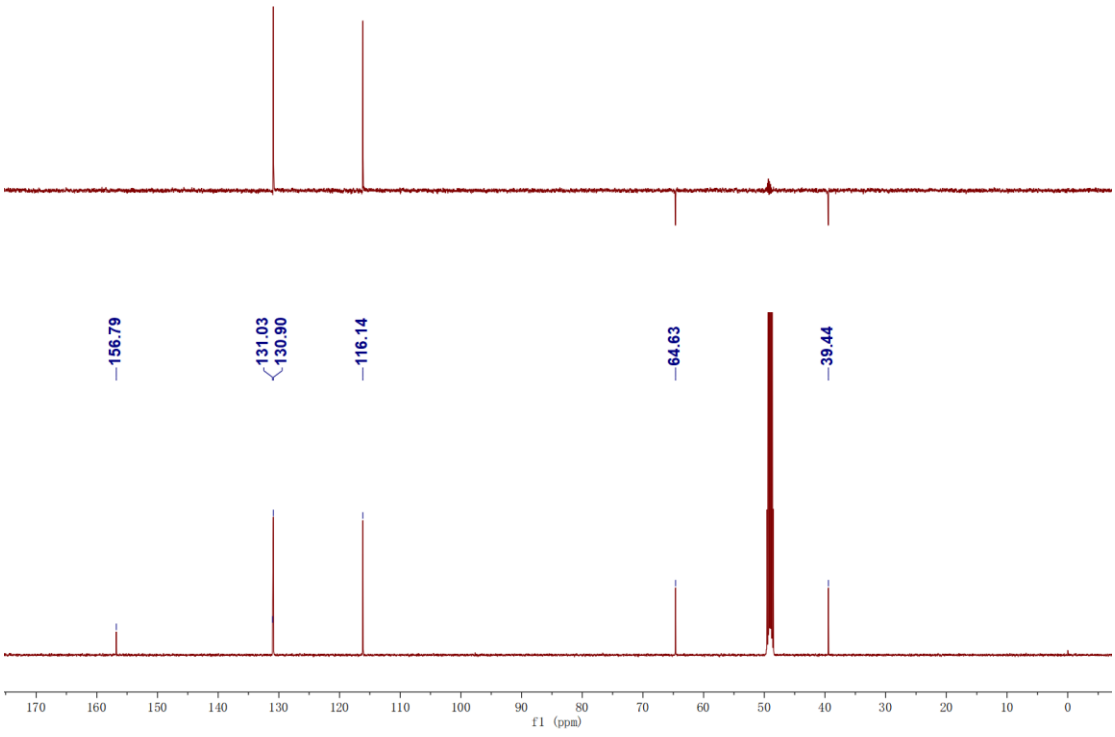


Fig. S99 ESI-MS spectrum of compound **20**

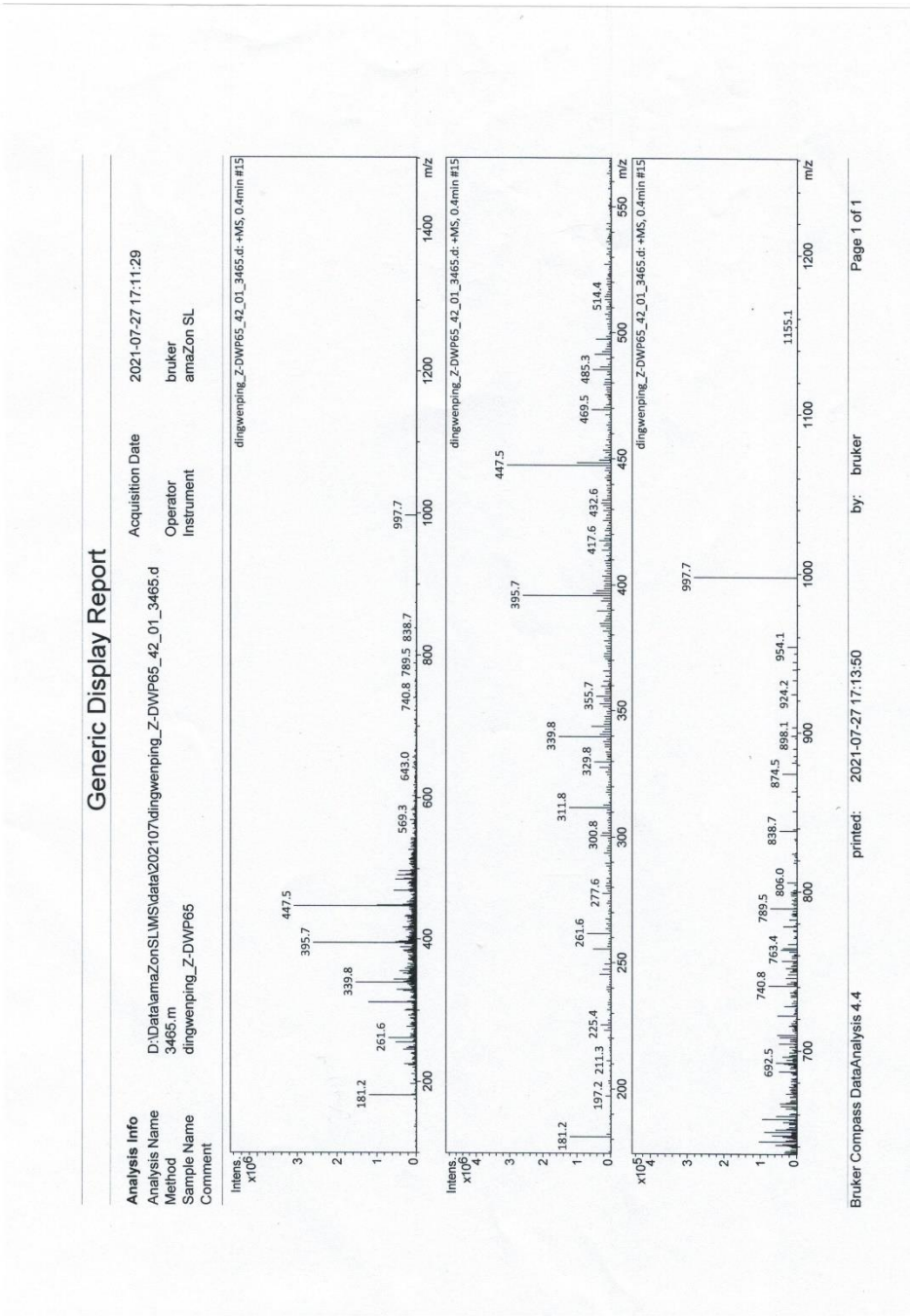


Fig. S100 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **20**

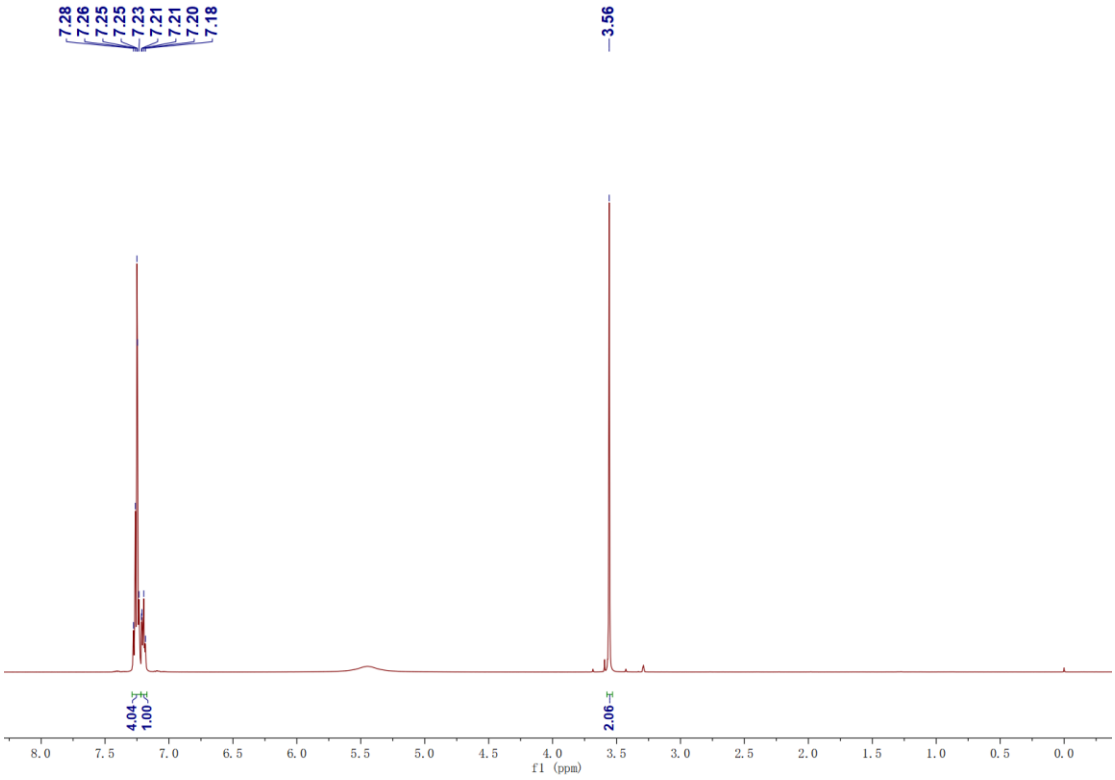


Fig. S101 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **20**

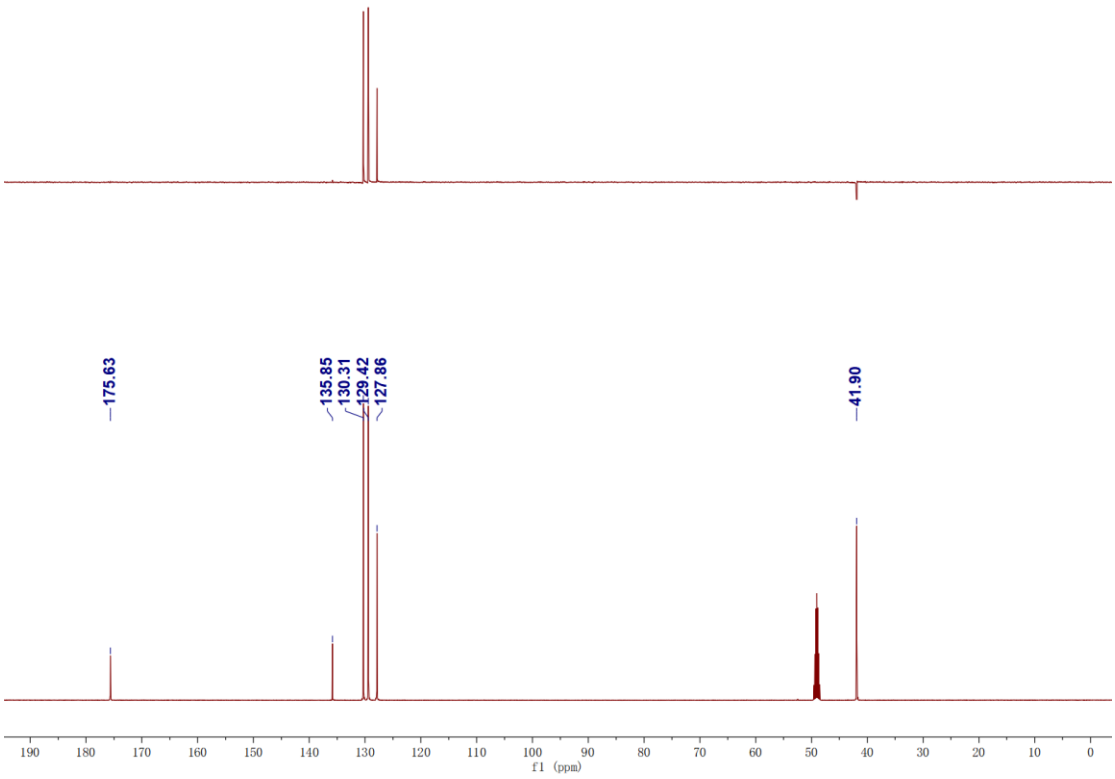


Fig. S102 ESI-MS spectrum of compound **21**

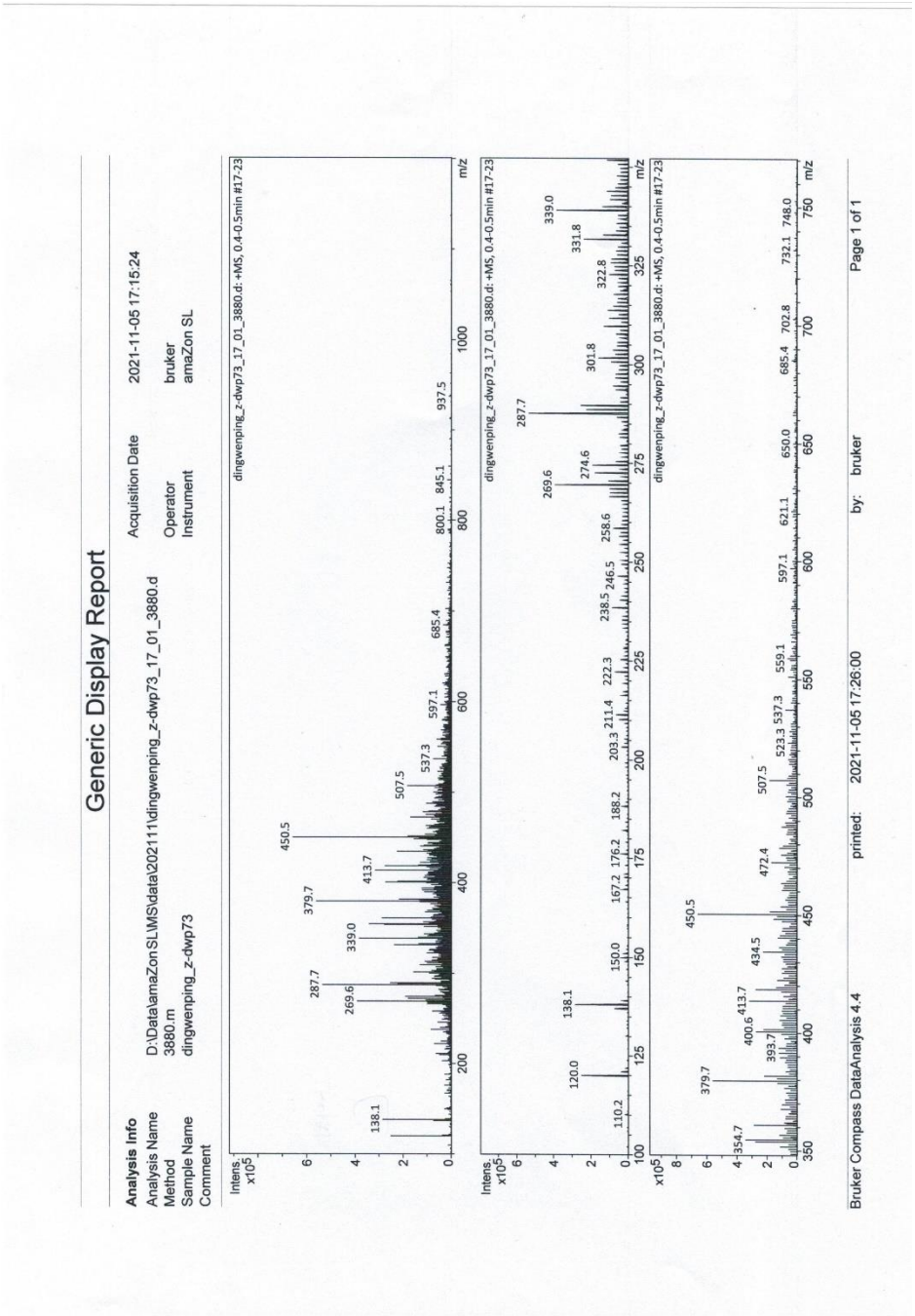


Fig. S103 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **21**

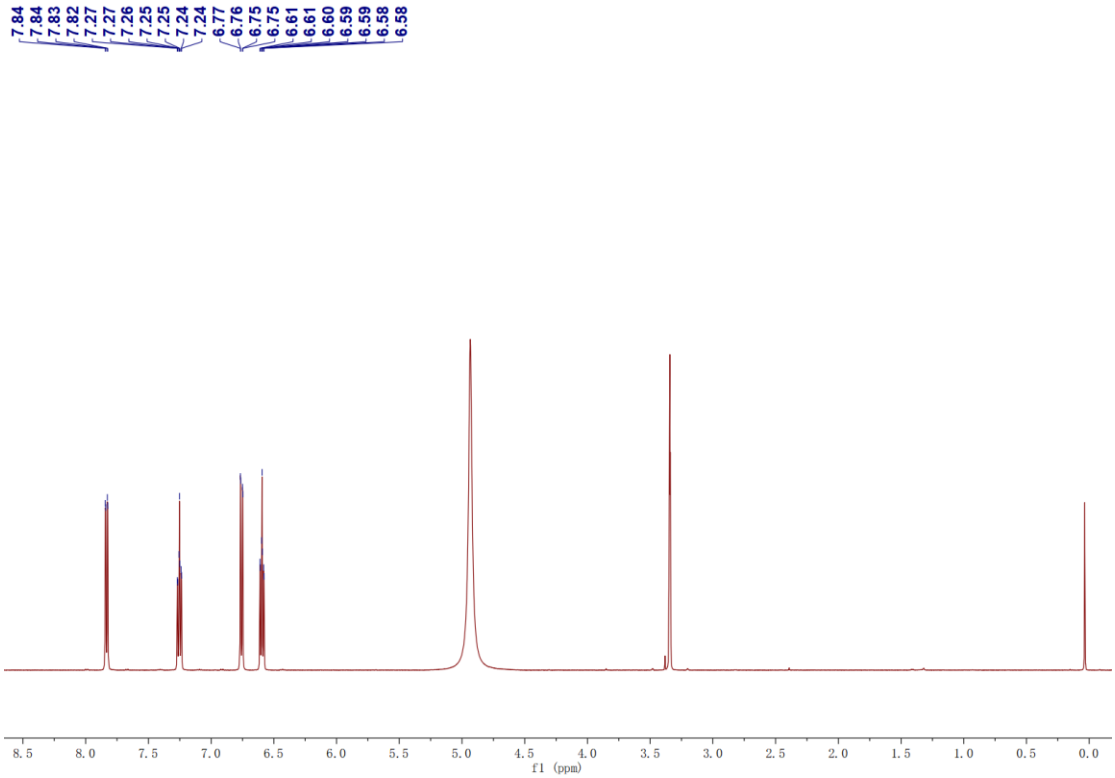


Fig. S104 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **21**

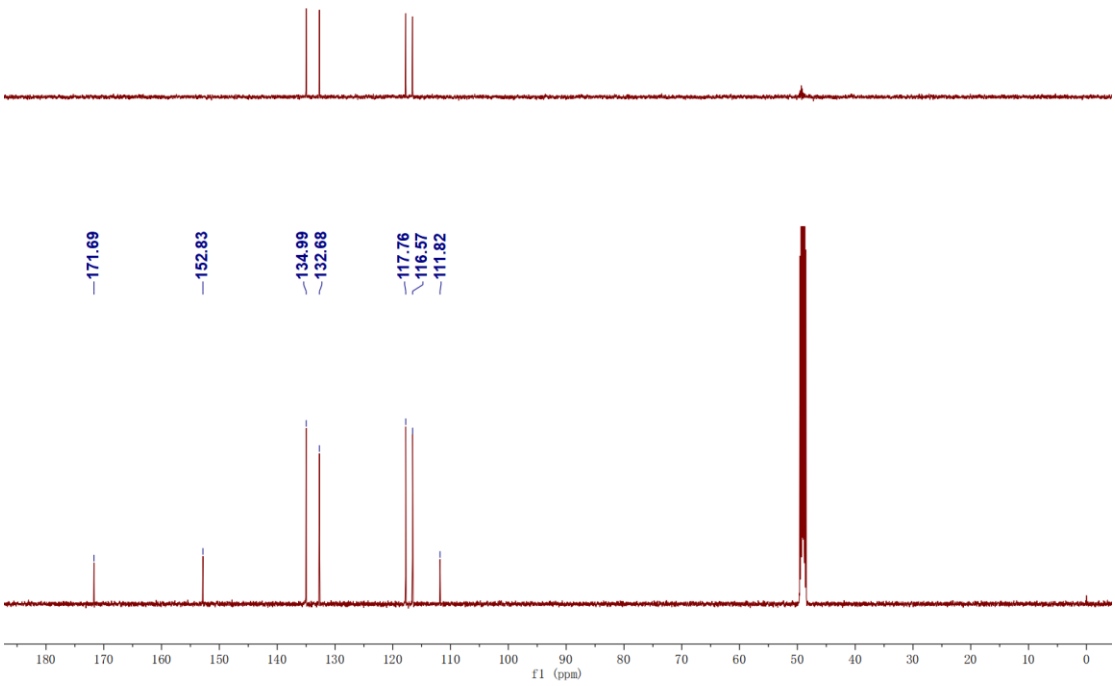


Fig. S105 ESI-MS spectrum of compound **22**

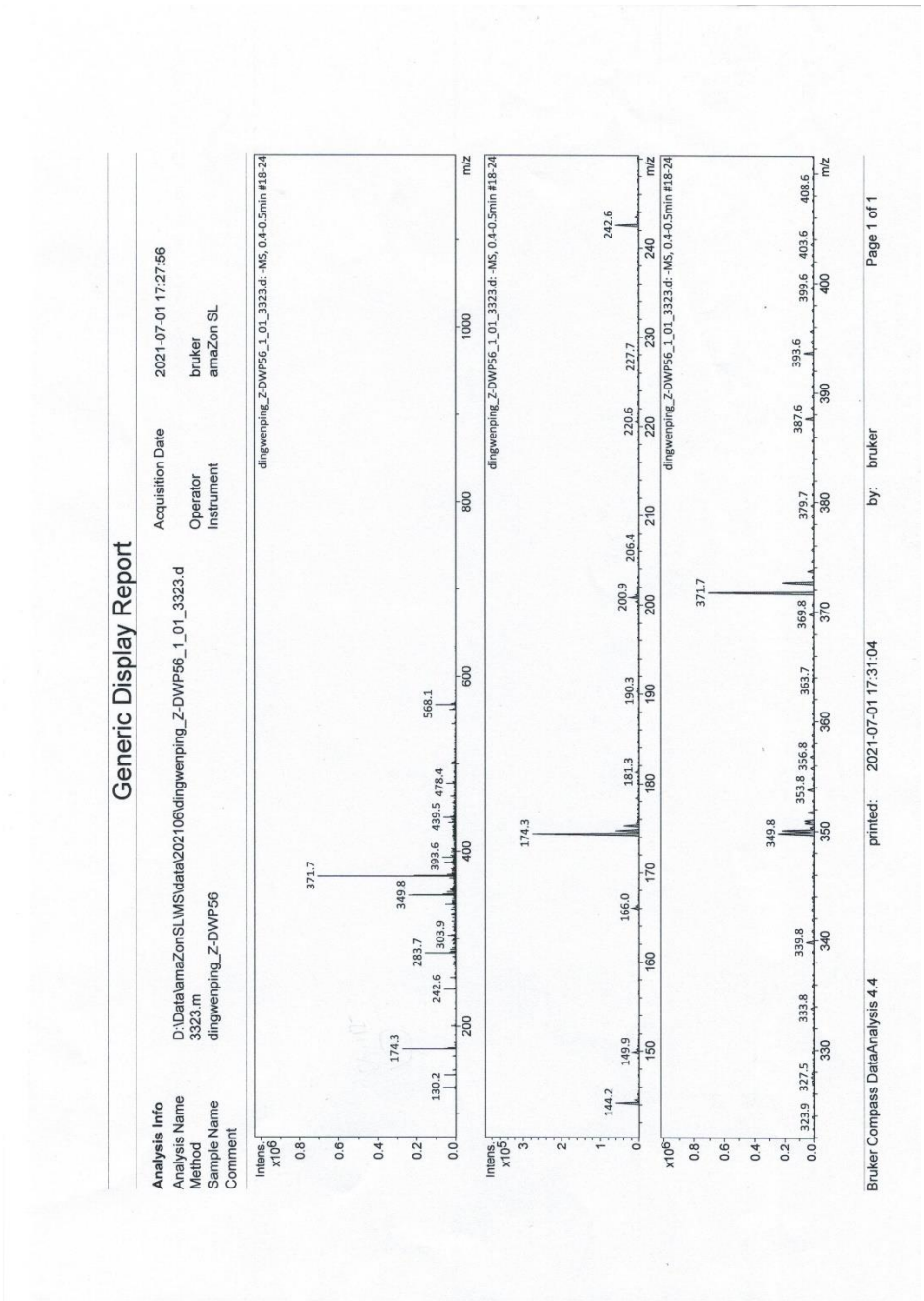


Fig. S106 ^{1}H NMR spectrum (CD_3OD, 700 MHz) of compound **22**

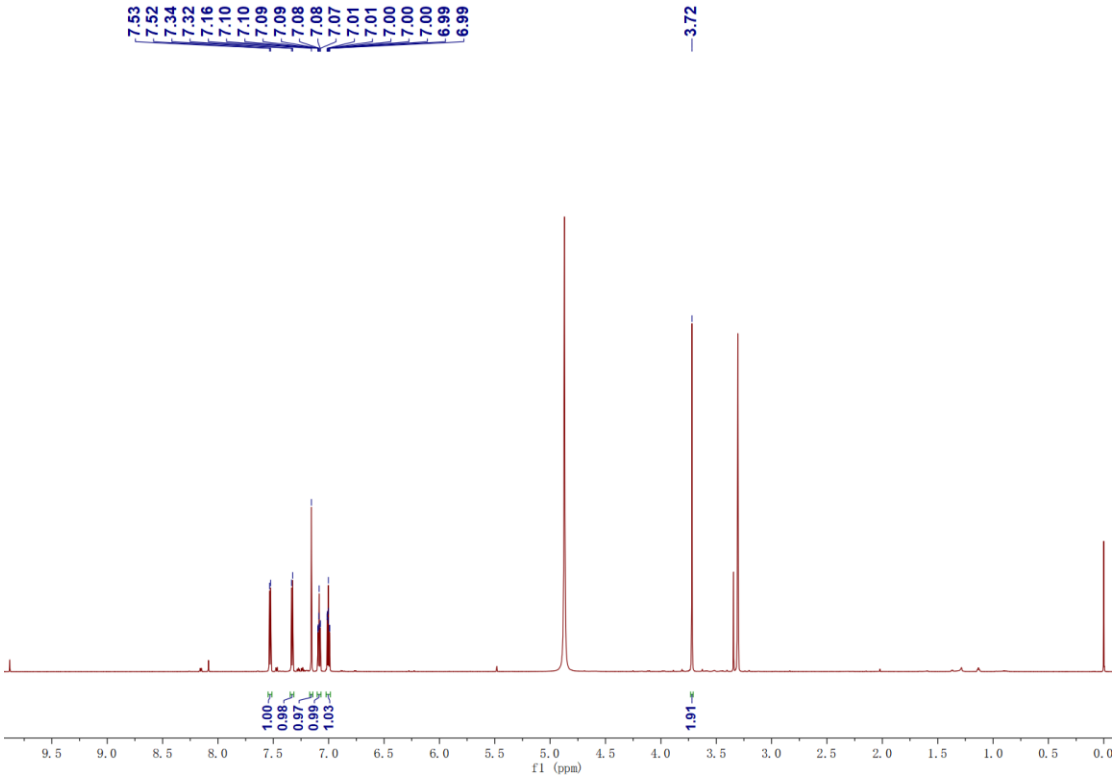


Fig. S107 ^{13}C NMR spectrum (CD_3OD, 176 MHz) of compound **22**

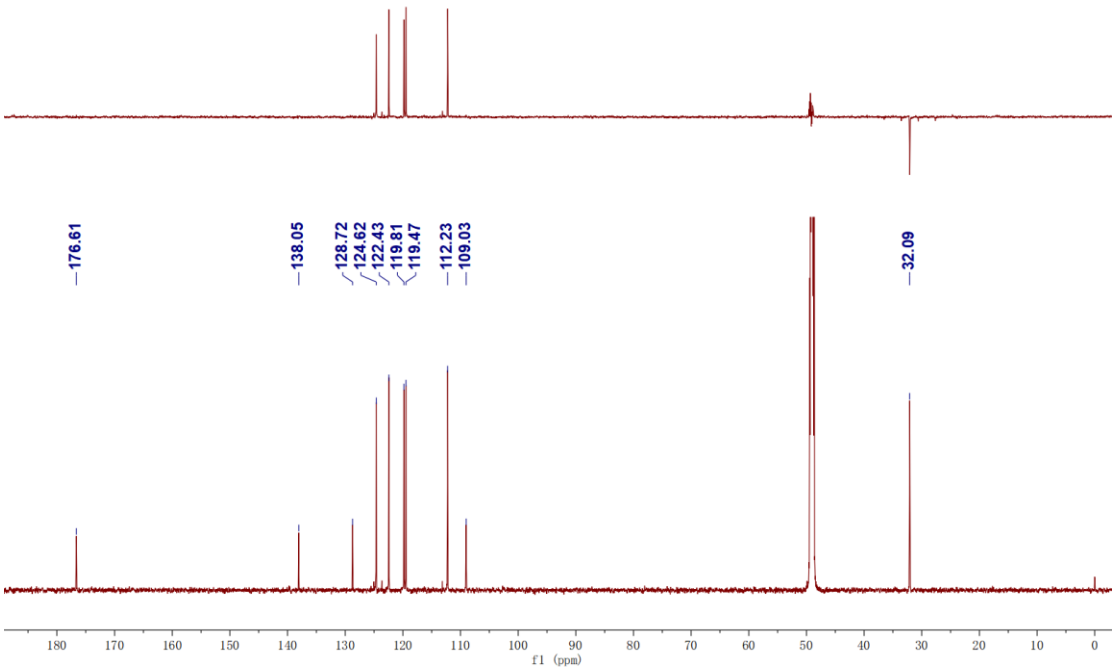


Fig. S108 ESI-MS spectrum of compound **23**

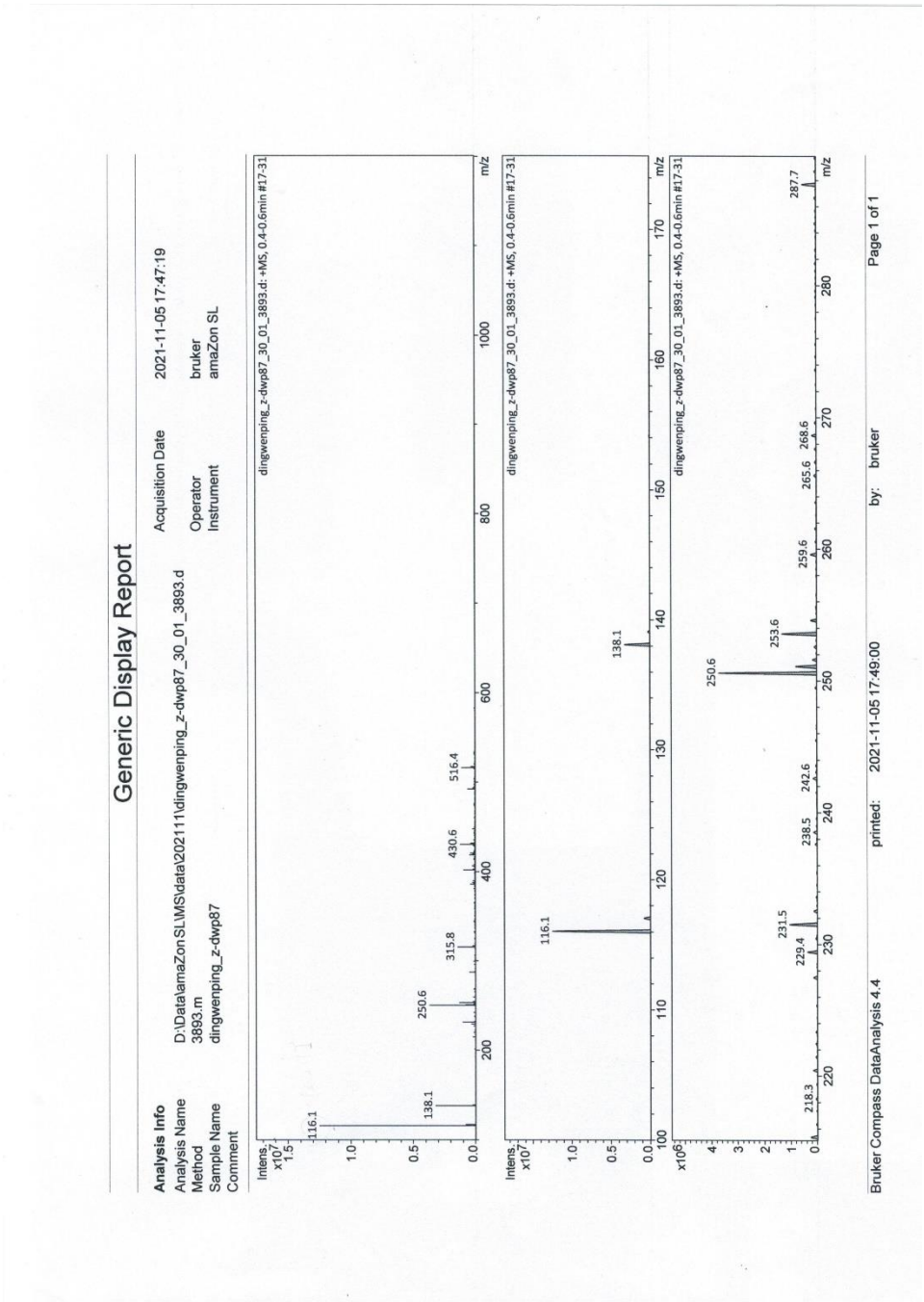


Fig. S109 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **23**

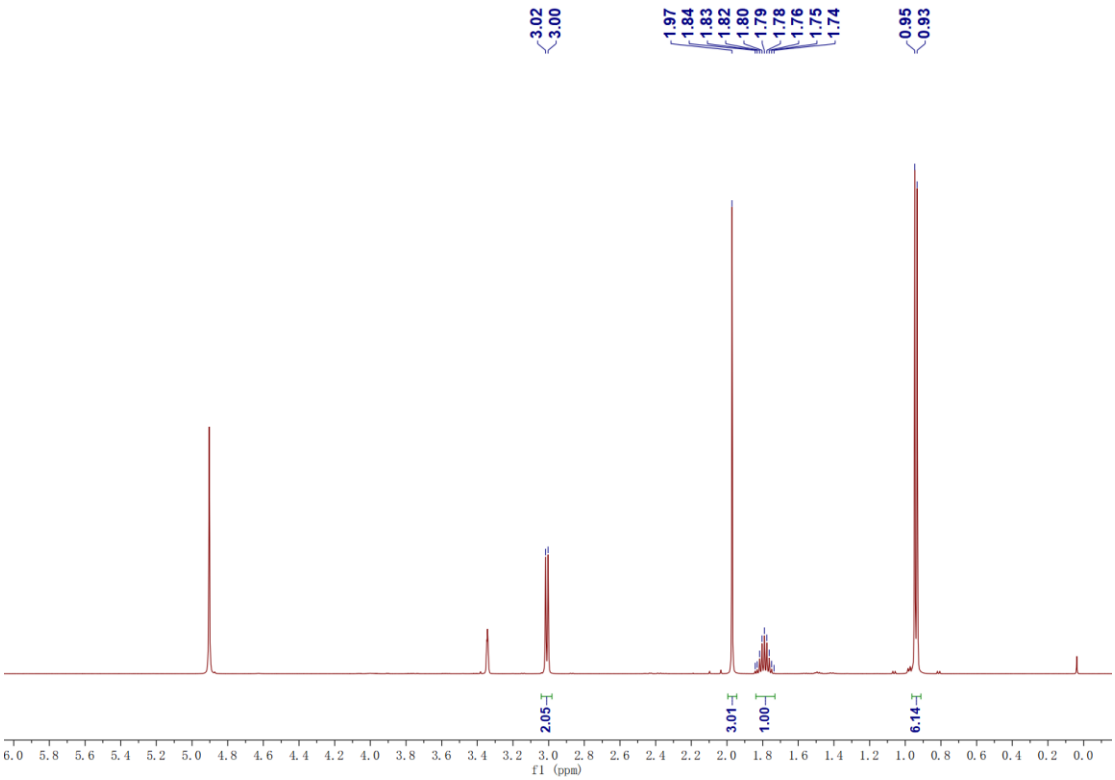


Fig. S110 ^{13}C NMR spectrum (CD_3OD, 126 MHz) of compound **23**

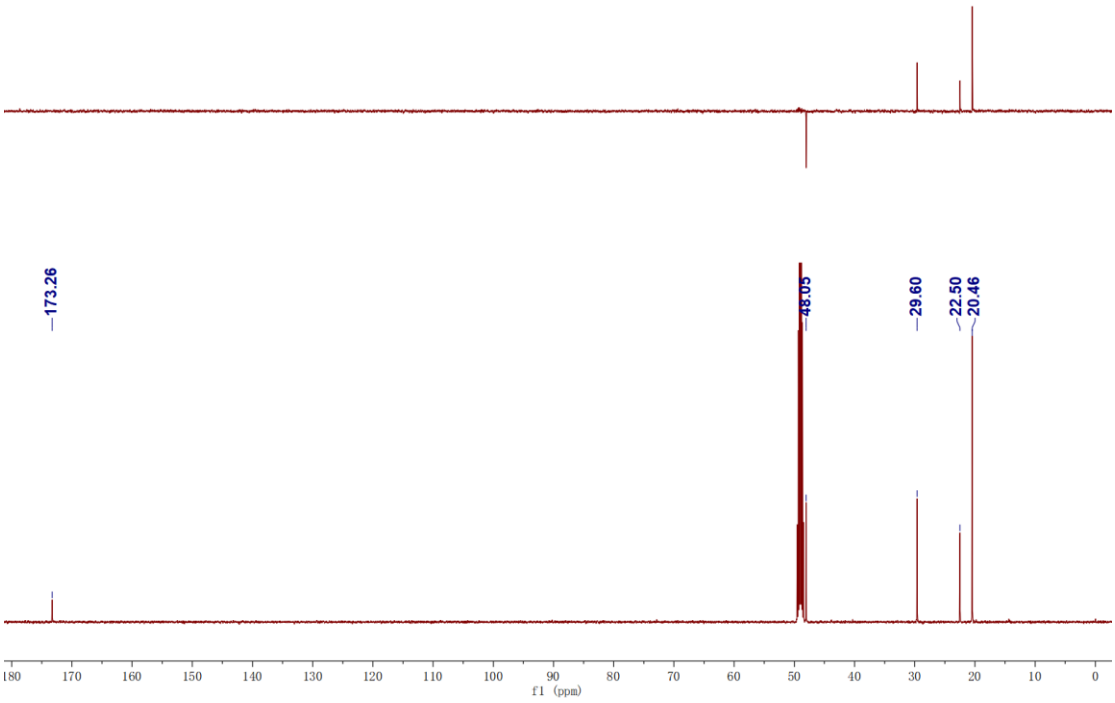


Fig. S111 Integrated cluster-node diagram of Molecular Networking