Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Asp-containing Actinomycin and Tetracyclic Chromophoric Analogues from *Streptomyces* sp. Strain S22.

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Contents

Table S1. NMR data for compound 1 in $CDCl_3$[a]

α-ring	no.	δ_C, type	δ_H mult (J, Hz)	COSY	HMBC	NOESY
Thr	1	169.4, C				
	2	56.0, CH	5.10, dd (6.6, 2.3)	NH_{Thr}, H-3_{Thr}	C-1_{Thr}, C-13	$NH_{D\text{-}Val}$
	3	75.0, CH	5.31, qd (6.4, 2.3)	H-2_{Thr}, H-4_{Thr}	C-1_{MeVal}, C-4_{Thr}	$NH_{D\text{-}Val}$
	4	17.7, CH_3	1.35, d (6.4)	H-3_{Thr}	C-2_{Thr}, C-3_{Thr}	
	NH		7.03, d (6.6)	H-2_{Thr}	C-1_{Thr}, C-13	
MeVal	1	167.7, C				
	2	71.5, CH	2.68, d (8.6)	H-3_{MeVal}	C-1_{MeVal}, C-1_{Sar}, C-3_{MeVal}, C-4_{MeVal}, NMe_{MeVal}	NMe_{MeVal}
	3	26.8, CH	2.68, m	H-2_{MeVal}, H-4_{MeVal}, H-5_{MeVal}	C-1_{MeVal}, C-4_{MeVal}, NMe_{MeVal}	
	4	21.7, CH_3	0.96, d (6.1)	H-3_{MeVal}	C-2_{MeVal}, C-3_{MeVal}	
	5	20.5, CH_3	0.73, d (6.4)	H-3_{MeVal}	C-1_{MeVal}, C-2_{MeVal}, C-3_{MeVal}, C-4_{MeVal}	
	NMe	39.5, CH_3	2.94, s		C-1_{Sar}, C-2_{MeVal}	H-2_{MeVal}, H-2_{Sar}
Sar	1	166.4, C				
	2	51.5, CH_2	4.67, d (17.2); 3.63, d (17.2)		C-1_{Sar}, C-1_{Pro}, NMe_{Sar}	NMe_{MeVal}, H-2_{Pro}
	NMe	34.8, CH_3	2.86, s		C-1_{Pro}, C-2_{Sar}	
Pro	1	173.3, C				
	2	56.0, CH	6.25, d (8.2)	H-3_{Pro}	C-1_{Pro}, C-$1_{D\text{-}Val}$, C-3_{Pro}, C-4_{Pro}, C-5_{Pro}	H-2_{Sar}, H-$2_{D\text{-}Val}$
	3	30.7, CH_2	2.25, m; 1.74, dd (10.1, 5.2)	H-2_{Pro}, H-4_{Pro}	C-1_{Pro}, C-2_{Pro}, C-4_{Pro}	
	4	23.0, CH_2	2.25, m; 1.98, m	H-3_{Pro}, H-5_{Pro}	C-1_{Pro}, C-3_{Pro}, C-5_{Pro}	
	5	47.1, CH_2	4.15, td (10.3, 7.0) 3.66, td (10.3, 1.6)	H-4_{Pro}	C-$1_{D\text{-}Val}$, C-2_{Pro}, C-3_{Pro}, C-4_{Pro}	H-$2_{D\text{-}Val}$

D-Val	1	170.0, C				
	2	59.0, CH	3.55, dd (10.3, 6.3)	$NH_{D\text{-}Val}$, $H\text{-}3_{D\text{-}Val}$	$C\text{-}1_{D\text{-}Val}$, $C\text{-}1_{Thr}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}5_{D\text{-}Val}$	$H\text{-}2_{Pro}$, $H\text{-}5_{Pro}$
	3	31.7, CH	2.08, m	$H\text{-}2_{D\text{-}Val}$, $H\text{-}4_{D\text{-}Val}$, $H\text{-}5_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}4_{D\text{-}Val}$	
	4	19.1, CH_3	0.85, d (6.7)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}5_{D\text{-}Val}$	
	5	18.6, CH_3	1.08, d (6.7)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}4_{D\text{-}Val}$	
	NH		8.52, d (6.3)	$H\text{-}2_{D\text{-}Val}$	$C\text{-}1_{Thr}$, $C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$	$H\text{-}2_{Thr}$, $H\text{-}3_{Thr}$
β-ring	no.	δ_C, type	δ_H mult (J, Hz)	COSY	HMBC	NOESY
Thr	1	170.6, C				
	2	55.3, CH	4.95, dd (7.7, 1.5)	NH_{Thr}, $H\text{-}3_{Thr}$	$C\text{-}1_{Thr}$, 14	$NH_{D\text{-}Val}$
	3	72.5, CH	5.40, qd (6.6, 1.5)	$H\text{-}2_{Thr}$, $H\text{-}4_{Thr}$	$C\text{-}1_{Thr}$, $C\text{-}1_{Me\text{-}Val}$, $C\text{-}2_{Thr}$, $C\text{-}4_{Thr}$	$NH_{D\text{-}Val}$
	4	18.5, CH_3	1.11, d (6.6)	$H\text{-}3_{Thr}$	$C\text{-}2_{Thr}$, $C\text{-}3_{Thr}$	
	NH		8.62, d (7.7)	$H\text{-}2_{Thr}$	$C\text{-}1_{Thr}$, $C\text{-}2_{Thr}$, C-14	NMe_{MeVal}
MeVal	1	165.8, C				
	2	72.9, CH	2.58, d (11.0)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}1_{Sar}$, $C\text{-}3_{Me\text{-}Val}$, $NMe_{Me\text{-}Val}$	$NMe_{Me\text{-}Val}$
	3	22.6, CH	2.96, m	$H\text{-}2_{Me\text{-}Val}$, $H\text{-}4_{Me\text{-}Val}$, $H\text{-}5_{Me\text{-}Val}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}2_{Me\text{-}Val}$, $C\text{-}4_{Me\text{-}Val}$	
	4	18.4, CH_3	0.71, d (6.7)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$	
	5	19.5, CH_3	0.75, d (6.5)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}4_{Me\text{-}Val}$	
	NMe	39.5, CH_3	2.73, s		$C\text{-}1_{Sar}$, $C\text{-}2_{Me\text{-}Val}$	NH_{Thr}, $H\text{-}2_{Me\text{-}Val}$, $H\text{-}2_{Sar}$
Sar	1	174.4, C				
	2	53.3, CH_2	5.28, d (17.6); 3.87, d (17.6)		$C\text{-}1_{Sar}$, NMe_{Sar}	$NMe_{Me\text{-}Val}$
	NMe	35.3, CH_3	2.85, s		$C\text{-}1_{Asp}$, $C\text{-}2_{Sar}$	
Asp	1	170.7, C				
	2	50.5, CH	5.23, dt (9.2, 3.0)	NH_{Asp}, $H\text{-}3_{Asp}$	$C\text{-}1_{Asp}$, $C\text{-}1_{D\text{-}Val}$, $C\text{-}3_{Asp}$, $C\text{-}4_{Asp}$	

	3	34.6, CH_2	3.27, dd (15.7, 3.2); 2.97, m	H-2_{Asp}	C-1_{Asp}, C-$1_{D\text{-}Val}$, C-2_{Asp}, C-4_{Asp}	
	4	172.7, C				
	NH		7.48, d (3.0)	H-2_{Asp}	C-$1_{D\text{-}Val}$, C-2_{Asp}	H-$2_{D\text{-}Val}$
D-Val	1	174.4, C				
	2	63.1, CH	2.99, dd (9.2, 2.5)	$NH_{D\text{-}Val}$, H-$3_{D\text{-}Val}$	C-$3_{D\text{-}Val}$, C-$4_{D\text{-}Val}$	NH_{Asp}
	3	30.0, CH	1.96, m	H-$2_{D\text{-}Val}$, H-$4_{D\text{-}Val}$, H-$5_{D\text{-}Val}$	C-$1_{D\text{-}Val}$, C-$2_{D\text{-}Val}$, C-$4_{D\text{-}Val}$, C-$5_{D\text{-}Val}$	
	4	19.9, CH_3	1.20, d (6.6)	H-$3_{D\text{-}Val}$	C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$, C-$5_{D\text{-}Val}$	
	5	19.1, CH_3	0.98, d (6.7)	H-$3_{D\text{-}Val}$	C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$, C-$4_{D\text{-}Val}$	
	NH		7.52, d (2.5)	H-$2_{D\text{-}Val}$	C-1_{Thr}, C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$	H-2_{Thr}, H-3_{Thr}
chromophore	no.	δ_C, type	δ_H mult (*J*, Hz)	COSY	HMBC	NOESY
	1	98.3, C				
	2	150.3, C				
	3	179.1, C				
	4	113.9, C				
	4a	146.0, C				
	5a	140.3, C				
	6	127.6, C				
	7	130.4, CH	7.37, d (7.7)	H-8	C-5a, C-9, C-11	H-11
	8	125.8, CH	7.69, d (7.7)	H-7	C-5a, C-6, C-9a, C-13	
	9	132.1, C				
	9a	128.5, C				
	10a	146.5, C				
	11	15.0, CH_3	2.53, s		C-5a, C-6, C-7	H-7
	12	7.9, CH_3	2.25, s		C-3, C-4, C-4a	
	13	166.4, C				
	14	167.5, C				

NH_2	9.93, d (8.0); 6.96, d (8.0)		C-1, C-3	

[a]600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR. [b]Numbers of attached protons were determined by analysis of 2D spectra.

Table S2. NMR data for compound 2 in $CDCl_3$[a]

α-ring	no.	δ_C, type	δ_H mult (J, Hz)	COSY	HMBC	NOESY
Thr	1	168.8, C				
	2	55.1, CH	5.12, d (9.3)	NH_{Thr}	C-1_{Thr}	H-4_{Thr}
	3	70.5, CH	5.75, d (5.3)	H-4_{Thr}		
	4	17. 3, CH_3	1.13, d (6.4)	H-3_{Thr}	C-2_{Thr}, C-3_{Thr}	
	NH		8.83, d (8.4)	H-2_{Thr}	C-13	H-8
MeVal	1	169.0, C				
	2	60.4, CH	4.70, d (12.1)	H-3_{MeVal}	C-1_{MeVal}, C-3_{MeVal}, C-4_{MeVal}, C-5_{MeVal}, NMe_{MeVal}	H-4_{MeVal}
	3	27.8, CH	2.12, m	H-2_{MeVal}, H-4_{MeVal}, H-5_{MeVal}	C-2_{MeVal}	
	4	19.3, CH_3	0.80, d (6.7)	H-3_{MeVal}	C-2_{MeVal}, C-3_{MeVal}	H-2_{MeVal}
	5	18.2, CH_3	0.73, d (6.6)	H-3_{MeVal}	C-2_{MeVal}, C-3_{MeVal}	
	NMe	30.6, CH_3	3.16, s		C-1_{Sar}, C-2_{MeVal}	
Sar	1	170.6, C				
	2	49.6, CH_2	4.72, d (14.7); 3.01, d (14.7)		C-1_{Sar}, C-1_{Pro}, NMe_{Sar}	
	NMe	38.8, CH_3	3.37, s		C-1_{Pro}, C-2_{Sar}	
Pro	1	172.9, C				
	2	55.7, CH	4.82, d (6.9)	H-3_{Pro}	C-3_{Pro}, C-4_{Pro}, C-5_{Pro}	
	3	28.6, CH_2	1.99, m; 1.87, m	H-2_{Pro}, H-4_{Pro}	C-1_{Pro}, C-2_{Pro}, C-4_{Pro}, C-5_{Pro}	
	4	24.8, CH_2	2.31, m; 1.99, m	H-3_{Pro}, H-5_{Pro}	C-1_{Pro}, C-2_{Pro}, C-5_{Pro}	
	5	47.1, CH_2	4.05, m 3.47, td (7.1, 8.9)	H-4_{Pro}	C-2_{Pro}, C-3_{Pro}, C-4_{Pro}	

D-Val	1	171.4, C				
	2	56.2, CH	4.30, t (7.5)	$NH_{D\text{-}Val}$, $H\text{-}3_{D\text{-}Val}$	$C\text{-}1_{D\text{-}Val}$, $C\text{-}1_{Thr}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}5_{D\text{-}Val}$	$H\text{-}5_{D\text{-}Val}$
	3	29.8, CH	1.86, m	$H\text{-}2_{D\text{-}Val}$, $H\text{-}4_{D\text{-}Val}$, $H\text{-}5_{D\text{-}Val}$		
	4	19.4, CH_3	0.86, d (6.8)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$	
	5	18.3, CH_3	0.82, d (6.6)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$	$H\text{-}2_{D\text{-}Val}$, $NH_{D\text{-}Val}$
	NH		6.37, d (7.1)	$H\text{-}2_{D\text{-}Val}$	$C\text{-}1_{Thr}$	$H\text{-}5_{D\text{-}Val}$
β-ring	no.	δ_C, type	δ_H mult (*J*, Hz)	COSY	HMBC	NOESY
Thr	1	169.5, C				
	2	56.1, CH	4.90, d (6.7)	NH_{Thr}	$C\text{-}3_{Thr}$, $C\text{-}4_{Thr}$, 14	$H\text{-}4_{Thr}$
	3	70.2, CH	5.64, q (6.2)	$H\text{-}4_{Thr}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}4_{Thr}$	
	4	17.4, CH_3	1.22, d (6.4)	$H\text{-}3_{Thr}$	$C\text{-}2_{Thr}$, $C\text{-}3_{Thr}$	$H\text{-}2_{Thr}$
	NH		9.89, d (8.4)	$H\text{-}2_{Thr}$	$C\text{-}2_{Thr}$, $C\text{-}3_{Thr}$, C-14	$NH_{D\text{-}Val}$
MeVal	1	169.4, C				
	2	60.9, CH	4.91, d (11.0)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $NMe_{Me\text{-}Val}$	
	3	27.7, CH	2.17, m	$H\text{-}2_{Me\text{-}Val}$, $H\text{-}4_{Me\text{-}Val}$, $H\text{-}5_{Me\text{-}Val}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}2_{Me\text{-}Val}$	
	4	19.4, CH_3	0.88, d (6.5)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}5_{Me\text{-}Val}$	
	5	18.2, CH_3	0.77, d (6.7)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}4_{Me\text{-}Val}$	
	NMe	30.6, CH_3	3.04, s		$C\text{-}1_{Sar}$, $C\text{-}2_{Me\text{-}Val}$	$H\text{-}2_{Sar}$
Sar	1	169.0, C				
	2	49.2, CH_2	4.98, d (14.2); 3.05, d (14.2)		$C\text{-}1_{OPro}$, $C\text{-}1_{Sar}$, NMe_{Sar}	$NMe_{Me\text{-}Val}$
	NMe	37.5, CH_3	3.34, s		$C\text{-}1_{OPro}$, $C\text{-}2_{Sar}$	
OPro	1	171.4, C				
	2	51.5, CH	5.37, dd (7.1, 1.9)	$H\text{-}3_{OPro}$	$C\text{-}3_{OPro}$, $C\text{-}4_{OPro}$	
	3	40.6, CH_2	2.51, d (7.7); 2.50, d (2.7)	$H\text{-}2_{OPro}$	$C\text{-}1_{OPro}$, $C\text{-}2_{OPro}$, $C\text{-}4_{OPro}$	
	4	207.1, C				

	5	52.8, CH_2	4.37, d (17.2); 3.89, d (17.2)		C-2_{OPro}, C-3_{OPro}, C-4_{OPro}	
D-Val	1	171.4, C				
	2	56.7, CH	4.20, t (8.4)	$NH_{D\text{-}Val}$, H-$3_{D\text{-}Val}$	C-1_{Thr}, C-$1_{D\text{-}Val}$, C-$3_{D\text{-}Val}$, C-$5_{D\text{-}Val}$	H-$4_{D\text{-}Val}$
	3	30.2, CH	1.86, m	H-$2_{D\text{-}Val}$, H-$4_{D\text{-}Val}$, H-$5_{D\text{-}Val}$	C-$2_{D\text{-}Val}$, C-$4_{D\text{-}Val}$	
	4	18.9, CH_3	0.81, d (6.6)	H-$3_{D\text{-}Val}$	C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$	H-$2_{D\text{-}Val}$
	5	18.5, CH_3	0.79, d (6.7)	H-$3_{D\text{-}Val}$	C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$	
	NH		7.05, d (8.6)	H-$2_{D\text{-}Val}$	C-1_{Thr}, C-$2_{D\text{-}Val}$, C-$3_{D\text{-}Val}$	NH_{Thr}
chromophore	no.	δ_C, type	δ_H mult (*J*, Hz)	COSY	HMBC	NOESY
	1	100.5, C				
	2	133.9, C				
	3	144.3, C				
	4	112.0, C				
	4a	140.4, C				
	5a	141.6, C				
	6	127.9, C				
	7	122.3, CH	6.54, d (8.2)	H-8	C-5a, C-9, C-9a, C-11	H-11
	8	122.4, CH	7.57, d (7.7)	H-7	C-6, C-9a, C-13	NH_{Thr}
	9	112.9, C				
	9a	132.9, C				
	10a	132.9, C				
	11	15.3, CH_3	2.13, s		C-5a, C-6, C-7	H-7
	12	9.1, CH_3	2.26, s		C-3, C-4, C-4a	
	13	168.3, C				
	14	167.4, C				
	15	163.1, C				
	16	14.6, CH_3	2.67, s		C-2, C-3, C-15	
	10-NH		11.95, s		C-1, C-4a, C-5a, C-9, C-9a, C-10a	

[a]600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR. [b]Numbers of attached protons were determined by analysis of 2D spectra.

Table S3. NMR data for compound 3 in $CDCl_3$

α-ring	no.	δ_C, type	δ_H mult (J, Hz)	COSY	HMBC
Thr	1	168.8, C			
	2	55.1, CH	5.11, d (9.8)	NH_{Thr}	C-1$_{Thr}$, C-3$_{Thr}$, C-4$_{Thr}$
	3	70.5, CH	5.75, d (6.2)	H-4$_{Thr}$	C-1$_{MeVal}$, C-4$_{Thr}$
	4	17. 3, CH_3	1.13, d (6.5)	H-3$_{Thr}$	C-2$_{Thr}$, C-3$_{Thr}$
	NH		8.90, d (10.1)	H-2$_{Thr}$	C-13
MeVal	1	169.0, C			
	2	60.4, CH	4.69, d (10.8)	H-3$_{MeVal}$	C-1$_{MeVal}$, C-3$_{MeVal}$, C-4$_{MeVal}$, C-5$_{MeVal}$, NMe$_{MeVal}$
	3	27.9, CH	2.12, m	H-2$_{MeVal}$, H-4$_{MeVal}$, H-5$_{MeVal}$	C-2$_{MeVal}$, C-4$_{MeVal}$
	4	18.9, CH_3	0.82, d (6.5)	H-3$_{MeVal}$	C-2$_{MeVal}$, C-3$_{MeVal}$
	5	18.3, CH_3	0.73, d (6.6)	H-3$_{MeVal}$	C-2$_{MeVal}$, C-3$_{MeVal}$, C-4$_{MeVal}$
	NMe	30.5, CH_3	3.16, s		C-1$_{Sar}$, C-2$_{Sar}$, C-2$_{MeVal}$
Sar	1	170.6, C			
	2	49.6, CH_2	4.71, d (14.0); 3.01, d (14.0)		C-1$_{Sar}$, C-1$_{Pro}$, NMe$_{Sar}$
	NMe	38.8, CH_3	3.37, s		C-1$_{Pro}$, C-2$_{Sar}$
Pro	1	173.0, C			
	2	55.7, CH	4.81, d (6.7)	H-3$_{Pro}$	C-1$_{Pro}$, C-3$_{Pro}$, C-4$_{Pro}$, C-5$_{Pro}$
	3	28.5, CH_2	1.99, m; 1.86, m	H-2$_{Pro}$, H-4$_{Pro}$	C-1$_{Pro}$, C-2$_{Pro}$, C-4$_{Pro}$, C-5$_{Pro}$
	4	24.8, CH_2	2.30, m; 1.90, m	H-3$_{Pro}$, H-5$_{Pro}$	C-3$_{Pro}$, C-5$_{Pro}$
	5	47.1, CH_2	4.05, m 3.46, td (7.1, 9.6)	H-4$_{Pro}$	C-2$_{Pro}$, C-3$_{Pro}$, C-4$_{Pro}$
D-Val	1	171.3, C			
	2	56.2, CH	4.30, t (7.6)	NH$_{D\text{-}Val}$, H-3$_{D\text{-}Val}$	C-1$_{D\text{-}Val}$, C-1$_{Thr}$, C-4$_{D\text{-}Val}$, C-5$_{D\text{-}Val}$
	3	29.8, CH	1.84, m	H-2$_{D\text{-}Val}$, H-4$_{D\text{-}Val}$, H-5$_{D\text{-}Val}$	C-2$_{D\text{-}Val}$, C-4$_{D\text{-}Val}$, C-5$_{D\text{-}Val}$

	4	19.4, CH_3	0.86, d (6.7)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$
	5	18.2, CH_3	0.80, d (6.3)	$H\text{-}3_{D\text{-}Val}$	$C\text{-}2_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}4_{D\text{-}Val}$
	NH		6.37, d (8.2)	$H\text{-}2_{D\text{-}Val}$	$C\text{-}1_{Thr}$
β-ring	no.	δ_C, type	δ_H mult (*J*, Hz)	COSY	HMBC
Thr	1	169.5, C			
	2	55.8, CH	4.93, d (8.6)	NH_{Thr}	$C\text{-}1_{Thr}$, $C\text{-}3_{Thr}$, $C\text{-}4_{Thr}$, 14
	3	70.1, CH	5.66, q (6.7)	$H\text{-}4_{Thr}$	$C\text{-}1_{Me\text{-}Val}$
	4	17.3, CH_3	1.22, d (6.5)	$H\text{-}3_{Thr}$	$C\text{-}2_{Thr}$, $C\text{-}3_{Thr}$
	NH		9.84, d (8.6)	$H\text{-}2_{Thr}$	$C\text{-}2_{Thr}$, $C\text{-}3_{Thr}$, C-14
MeVal	1	169.3, C			
	2	61.0, CH	4.89, d (11.1)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}1_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}4_{Me\text{-}Val}$, $C\text{-}5_{Me\text{-}Val}$, $NMe_{Me\text{-}Val}$
	3	27.5, CH	2.15, m	$H\text{-}2_{Me\text{-}Val}$, $H\text{-}4_{Me\text{-}Val}$, $H\text{-}5_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$
	4	19.4, CH_3	0.80, d (6.3)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}5_{Me\text{-}Val}$
	5	18.4, CH_3	0.68, d (6.7)	$H\text{-}3_{Me\text{-}Val}$	$C\text{-}2_{Me\text{-}Val}$, $C\text{-}3_{Me\text{-}Val}$, $C\text{-}4_{Me\text{-}Val}$
	NMe	30.6, CH_3	3.04, s		$C\text{-}1_{Sar}$, $C\text{-}2_{Me\text{-}Val}$
Sar	1	169.0, C			
	2	49.2, CH_2	4.99, d (14.3); 3.04, d (14.3)		$C\text{-}1_{OPro}$, $C\text{-}1_{Sar}$, NMe_{Sar}
	NMe	37.4, CH_3	3.30, s		$C\text{-}1_{OPro}$, $C\text{-}2_{Sar}$
OPro	1	171.3, C			
	2	51.5, CH	5.40, d (6.3)	$H\text{-}3_{OPro}$	$C\text{-}3_{OPro}$, $C\text{-}4_{OPro}$
	3	40.6, CH_2	2.51, d (8.0); 2.50, d (2.6)	$H\text{-}2_{OPro}$	$C\text{-}1_{OPro}$, $C\text{-}2_{OPro}$, $C\text{-}4_{OPro}$
	4	207.1, C			
	5	52.7, CH_2	4.34, d (17.1); 3.88, d (17.1)		$C\text{-}2_{OPro}$, $C\text{-}3_{OPro}$, $C\text{-}4_{OPro}$
D-Val	1	171.3, C			
	2	56.7, CH	4.22, t (8.3)	$NH_{D\text{-}Val}$, $H\text{-}3_{D\text{-}Val}$	$C\text{-}1_{Thr}$, $C\text{-}1_{D\text{-}Val}$, $C\text{-}3_{D\text{-}Val}$, $C\text{-}4_{D\text{-}Val}$, $C\text{-}5_{D\text{-}Val}$

	3	30.2, CH	1.89, m	H-2$_{D\text{-}Val}$, H-4$_{D\text{-}Val}$, H-5$_{D\text{-}Val}$	C-1$_{D\text{-}Val}$, C-2$_{D\text{-}Val}$
	4	19.3, CH_3	0.84, d (6.7)	H-3$_{D\text{-}Val}$	C-2$_{D\text{-}Val}$, C-3$_{D\text{-}Val}$
	5	18.2, CH_3	0.83, d (6.4)	H-3$_{D\text{-}Val}$	C-2$_{D\text{-}Val}$, C-3$_{D\text{-}Val}$
	NH		7.15, d (8.3)	H-2$_{D\text{-}Val}$	C-1$_{Thr}$, C-2$_{D\text{-}Val}$, C-3$_{D\text{-}Val}$
chromophore	no.	δ_C, type	δ_H mult (*J*, Hz)	COSY	HMBC
	1	100.6, C			
	2	133.2, C			
	3	144.6, C			
	4	112.1, C			
	4a	140.8, C			
	5a	141.5, C			
	6	127.9, C			
	7	122.4, CH	6.54, d (8.3)	H-8	C-5a, C-6, C-8, C-9, C-9a, C-11
	8	122.5, CH	7.55, d (8.2)	H-7	C-6, C-9, C-9a, C-13
	9	113.0, C			
	9a	132.7, C			
	10a	133.6, C			
	11	15.3, CH_3	2.11, s		C-5a, C-6, C-7
	12	9.2, CH_3	2.21, s		C-3, C-4, C-4a
	13	168.3, C			
	14	167.1, C			
	15	163.9, C			
	16	34.1, CH_2	4.47, d (15.3); 4.37, d (15.1)		C-15, C-17, C-18, C-22
	17	133.7			
	18	130.5, CH	7.50, d (8.5)	H-19	C-15, C-16, C-19, C-20, C-22
	19	122.6, CH	7.08, d (8.5)	H-18	C-17, C-20, C-21
	20	141.2			

21	122.6, CH	7.08, d (8.5)	22	C-17, C-19, C-20
22	130.5, CH	7.50, d (8.5)	21	C-15, C-16, C-18, C-20, C-21
23	162.3, CH	8.37, s		C-20, C-24
24	32.1, CH_3	3.22, s		C-20, C-23
10-NH		11.94, s		C-1, C-4a, C-5a, C-9, C-10a

[a]600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR. [b]Numbers of attached protons were determined by analysis of 2D spectra.

Table S4. NMR data for compound 4 in $CDCl_3$[a]

no.	δ_H mult (*J*, Hz)	δ_C[b]	HMBC	COSY
1		119.0, C		
2		140.4, C		
3		150.6, C		
4		126.2, C		
5	7.16, dd (7.9, 0.9)	125.1, CH	1, 3, 11	6, 11
6	7.90, d (7.9)	126.9, CH	2, 4	5
7		165.6, C	6, 6a, 7a, 11a, 12a	
8		165.9, C		
9	4.02, s	52.4, CH_3	8	
10	2.73, s	14.9, CH_3	2, 3, 7	
11	2.56, s	15.5, CH_3	3, 4, 5	5

[a]600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR. [b]Numbers of attached protons were determined by analysis of 2D spectra.

Fig. S1 Neighbour-joining tree based on 16S rRNA gene sequences of strain S22 and related strains in the family Streptomycete. Numbers at nodes refer to percentage bootstrap values (based on 1000 replicates; only values. 50 % are shown). Bar, 5 substitutions per 1000 nucleotide positions.

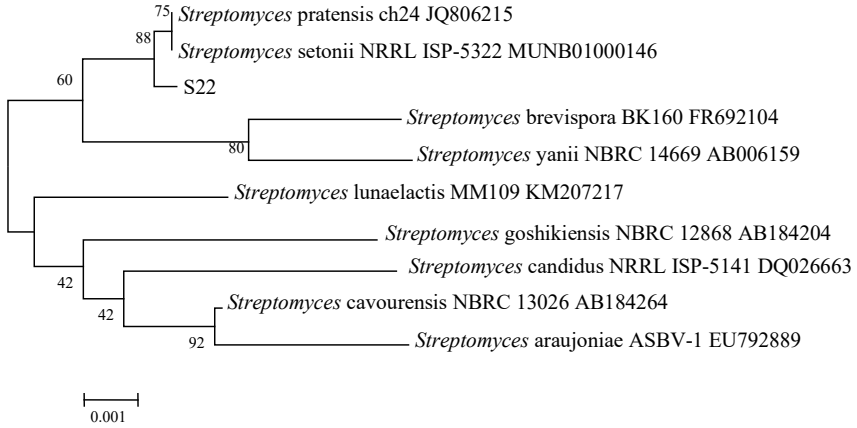
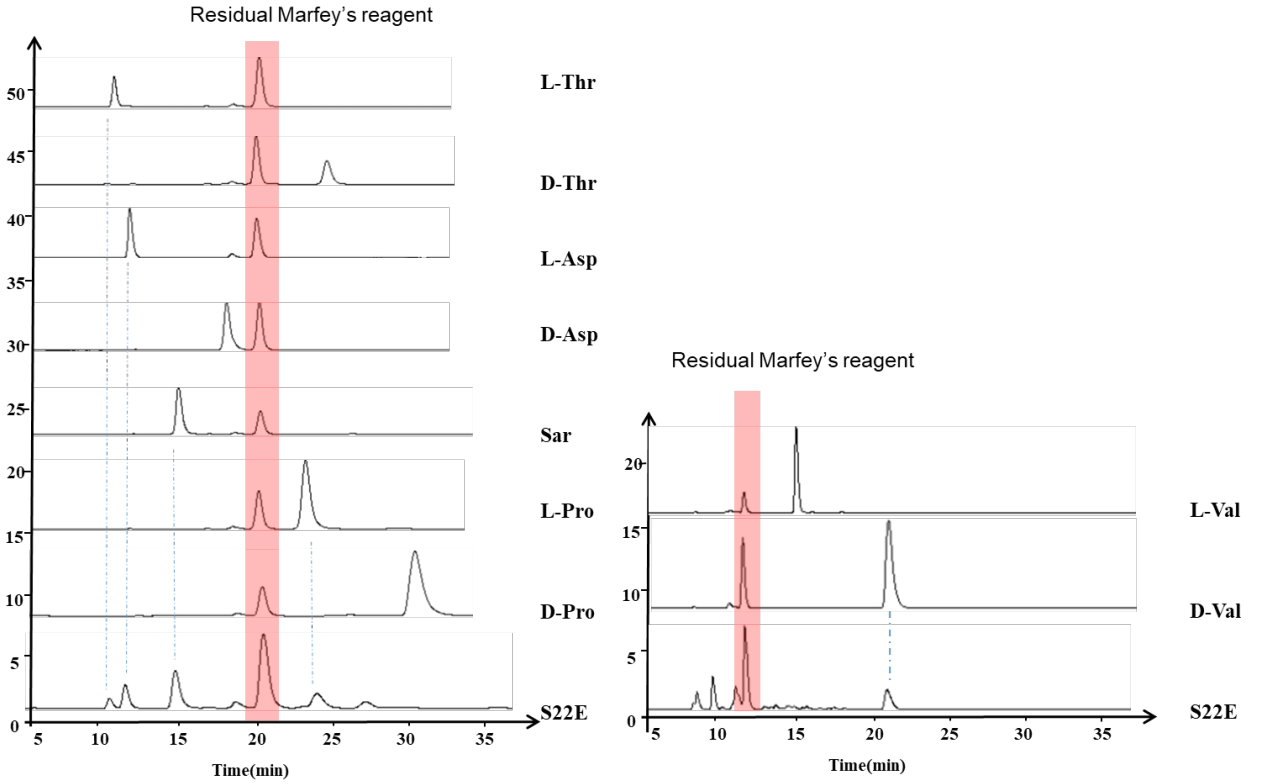


Fig. S2 Chiral amino acid analysis of **1**.



Chromatographic condition	
Waters Symmetry	C18 250mm×4.6mm 5μm
time	40min
wavelength	430nm
Mobile phase	H_2O:MeOH:50 mM TEAP buffer
isocratic elution	50:25:25
flow velocity	1mL/min

Chromatographic condition	
Waters Symmetry	C18 250mm×4.6mm 5μm
time	40min
wavelength	430nm
Mobile phase	H_2O:MeOH:50 mM TEAP buffer
gradient elution	0-10min，50:30:20
	10-30min，20:50:30
	30-40min，0:10:90
flow velocity	1mL/min

Fig. S3 UV spectrum of compound **1**.

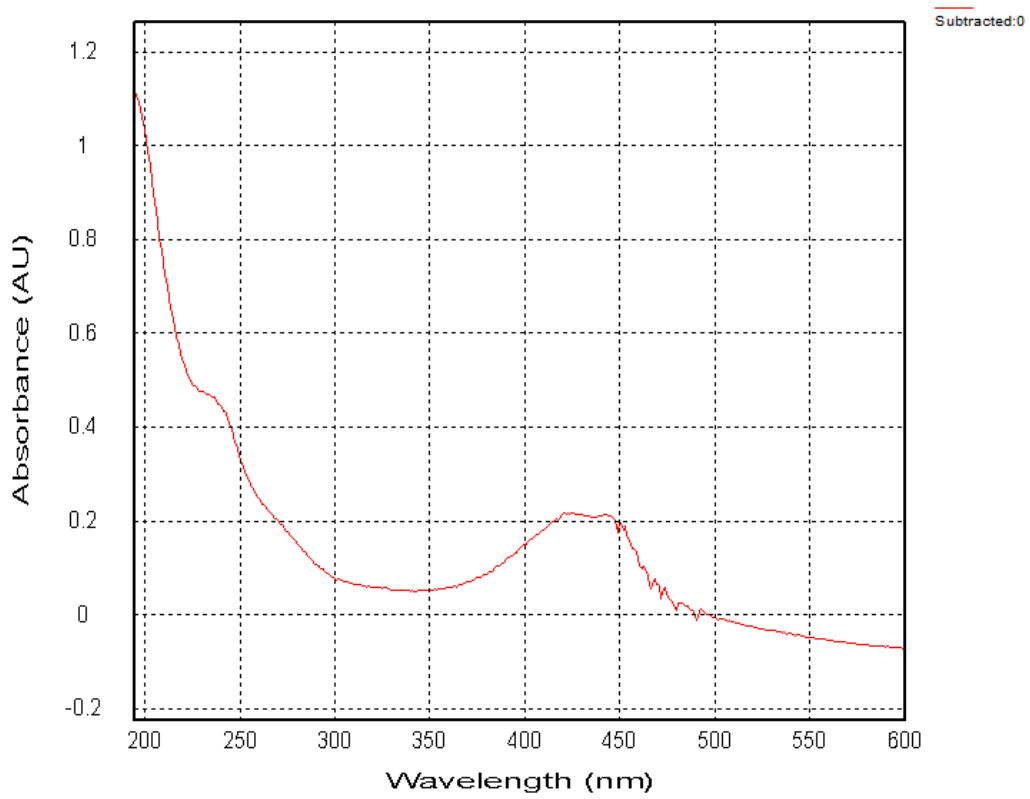


Fig. S4 UV spectrum of compound **2**.

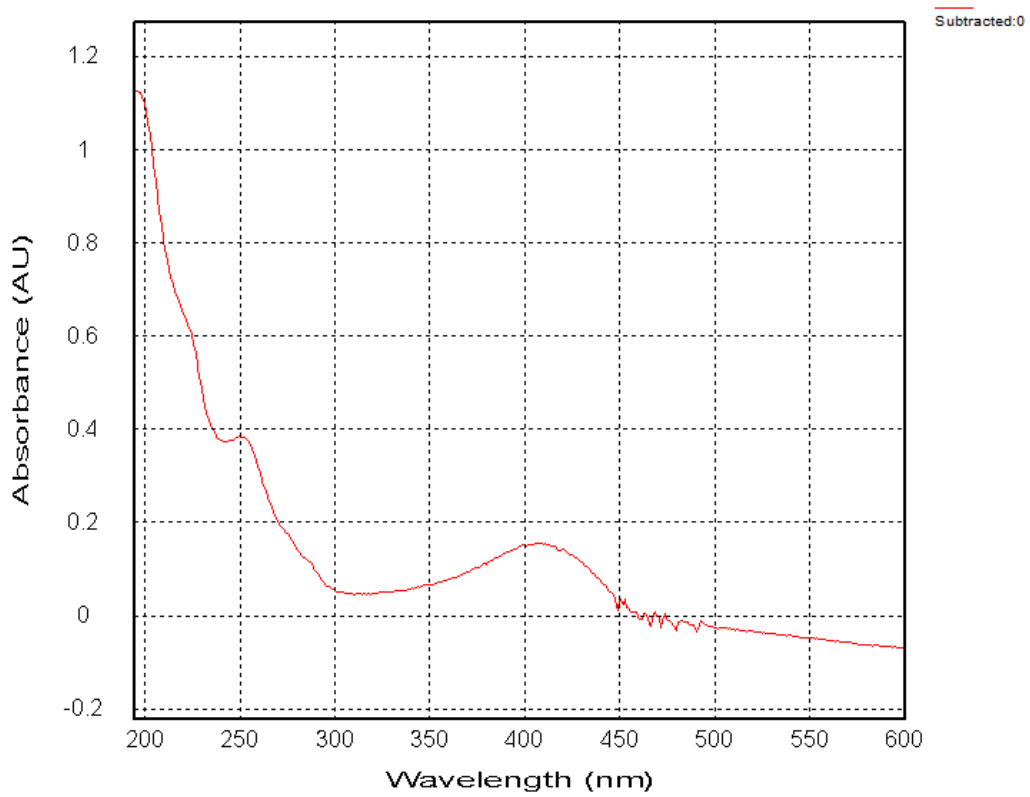


Fig. S5 UV spectrum of compound **3**.

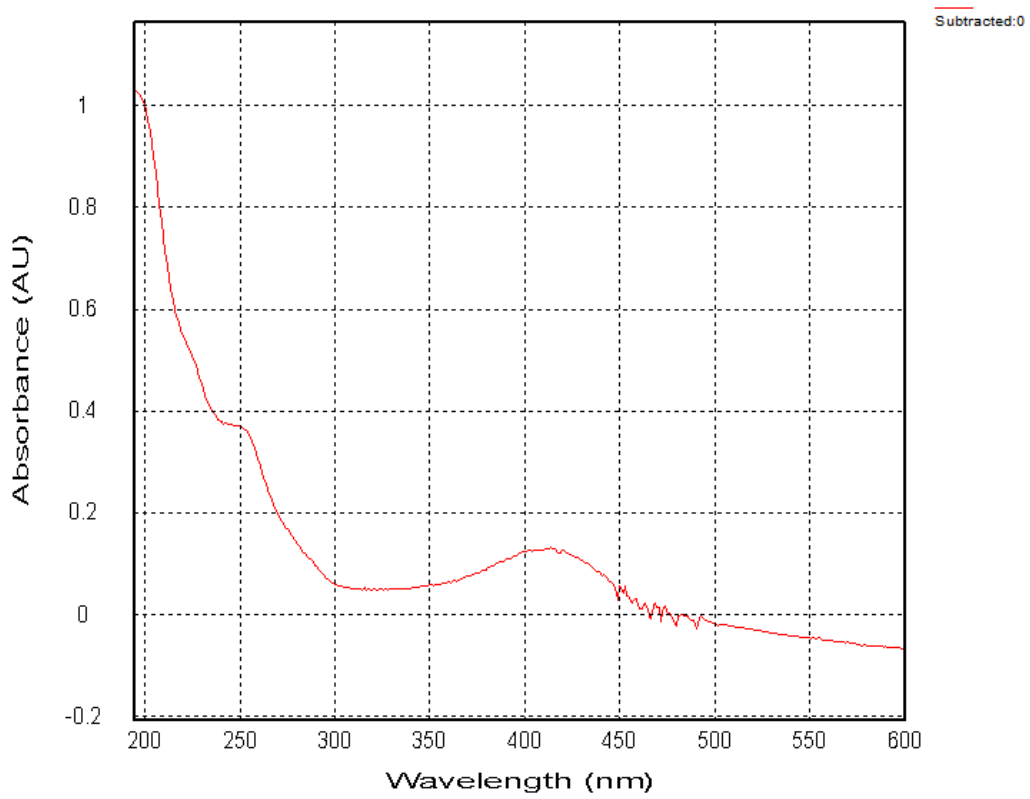


Fig. S6 CD spectrum of compound **1**.

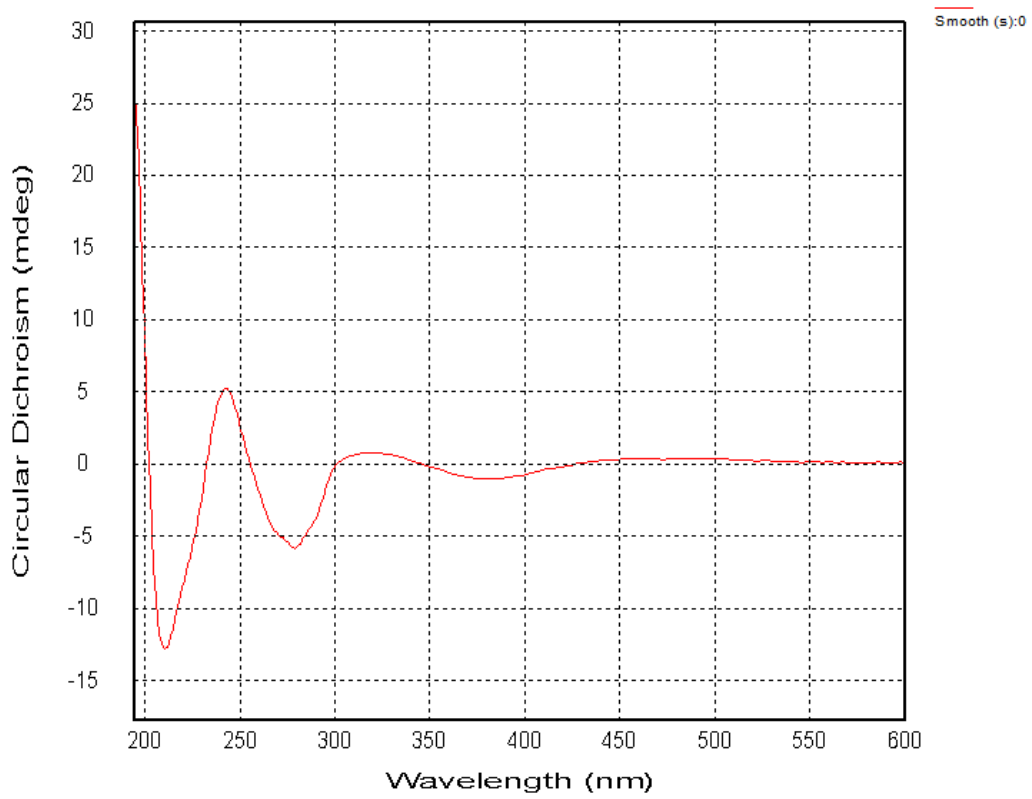


Fig. S7 CD spectrum of compound **2**.

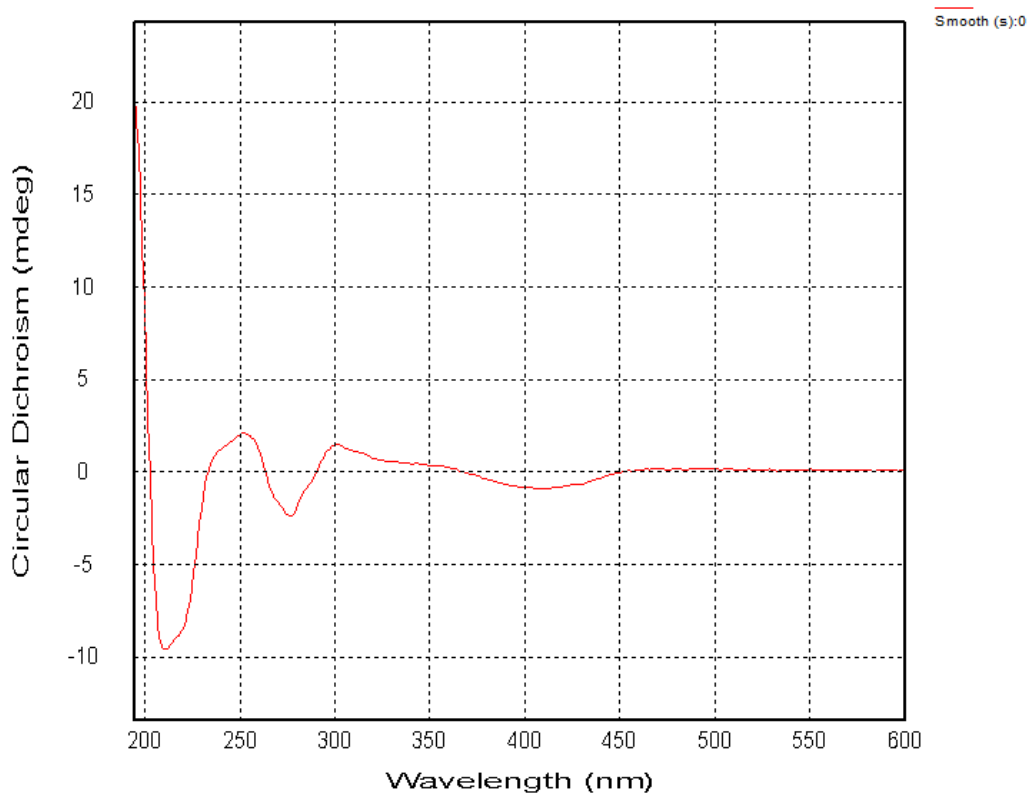


Fig. S8 CD spectrum of compound **3**.

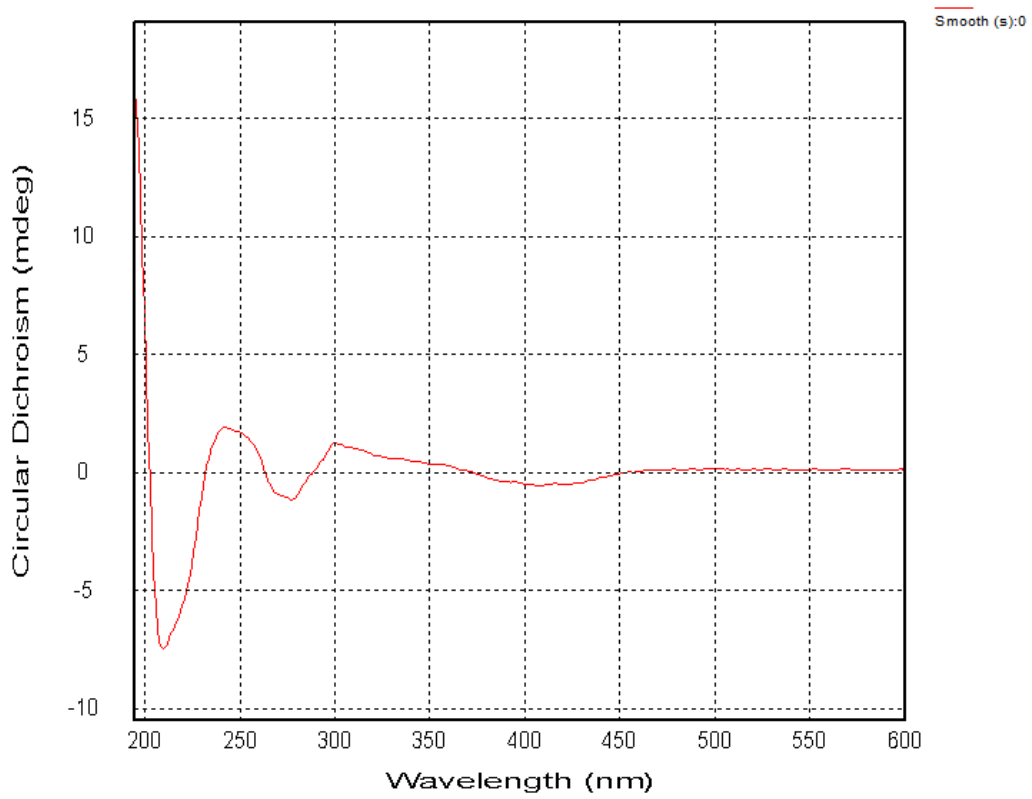
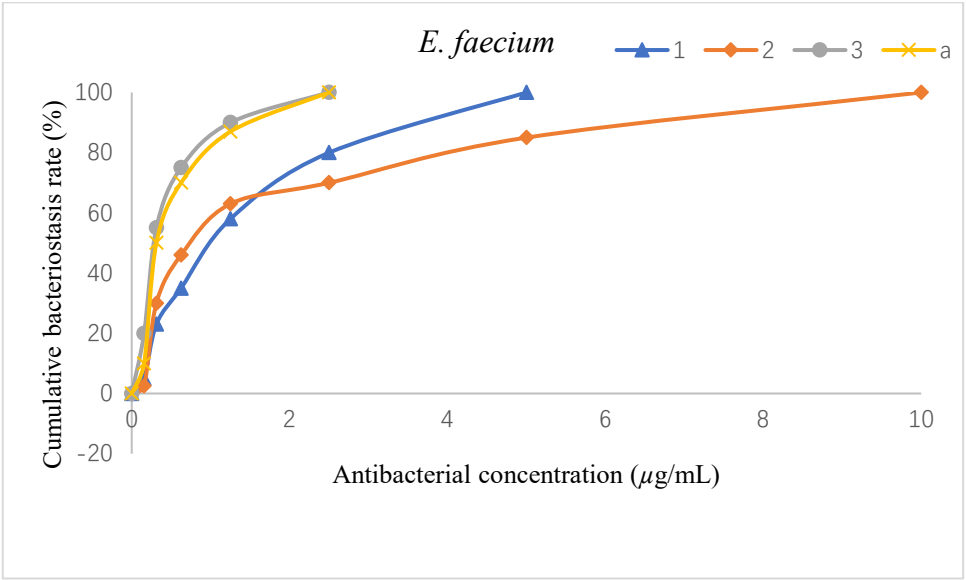
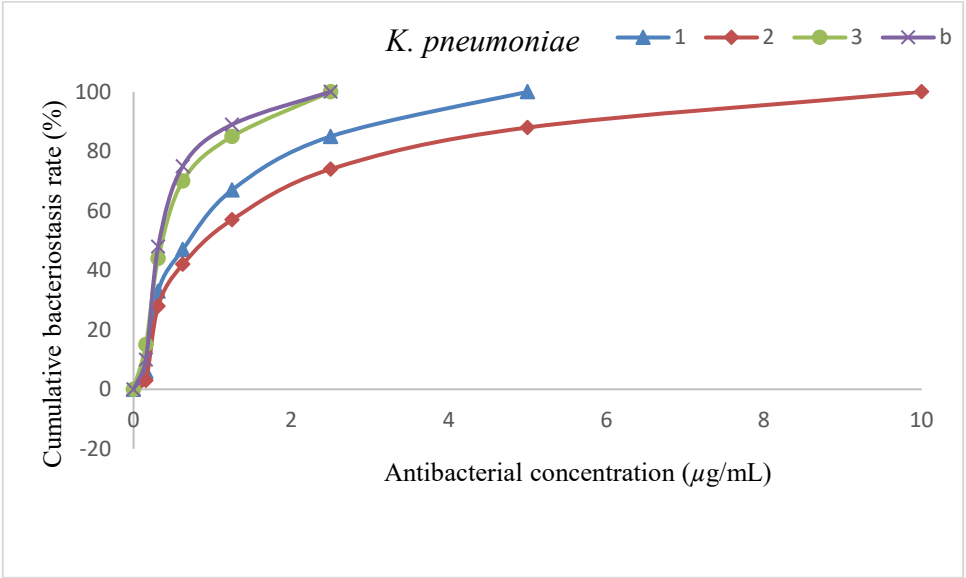
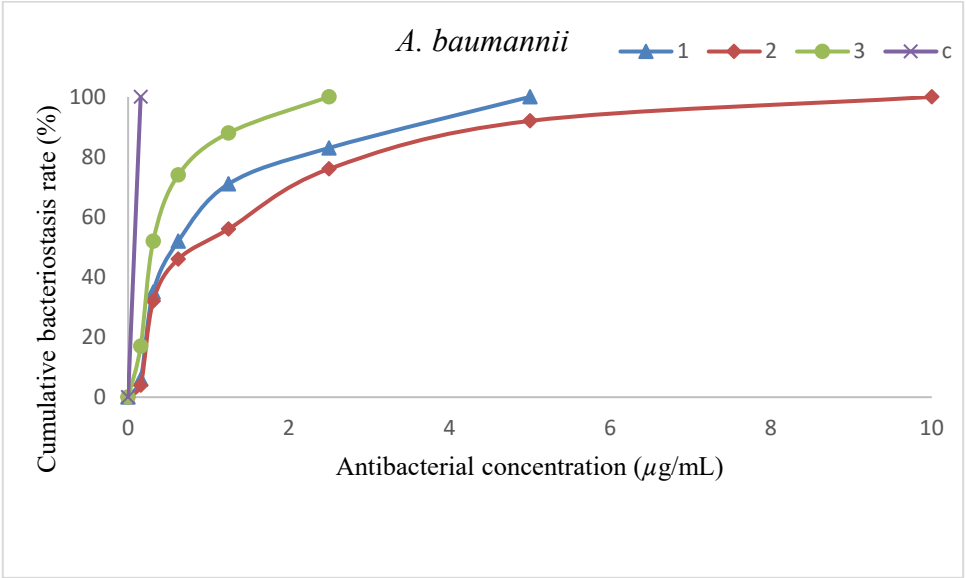
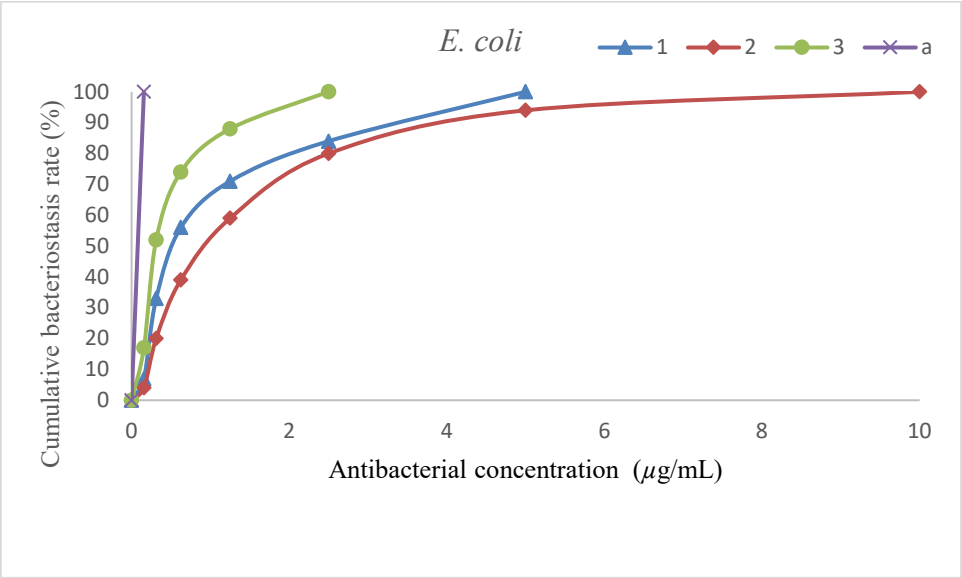


Fig. S9 The dose-response curve of antibacterial activities for actinomycins **1**–**3**.




K. pneumoniae
1
2
3
b
Cumulative bacteriostasis rate (%)
100
80
60
40
20
0
-20
0
2
4
6
8
10
Antibacterial concentration (μg/mL)


A. baumannii
1
2
3
c
Cumulative bacteriostasis rate (%)
100
80
60
40
20
0
0
2
4
6
8
10
Antibacterial concentration (μg/mL)


E. coli
1
2
3
a
Cumulative bacteriostasis rate (%)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
Antibacterial concentration (μg/mL)

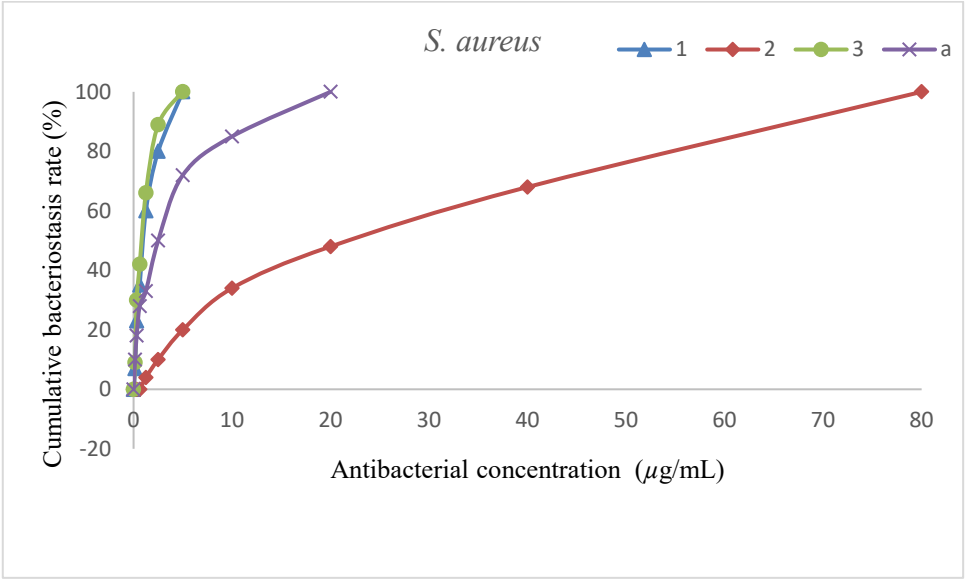

S. aureus
1
2
3
a
Cumulative bacteriostasis rate (%)
100
80
60
40
20
0
-20
0
10
20
30
40
50
60
70
80
Antibacterial concentration (μg/mL)

Fig. S10 ^{1}H NMR spectrum (600 MHz) of compound **1** in $CDCl_3$.

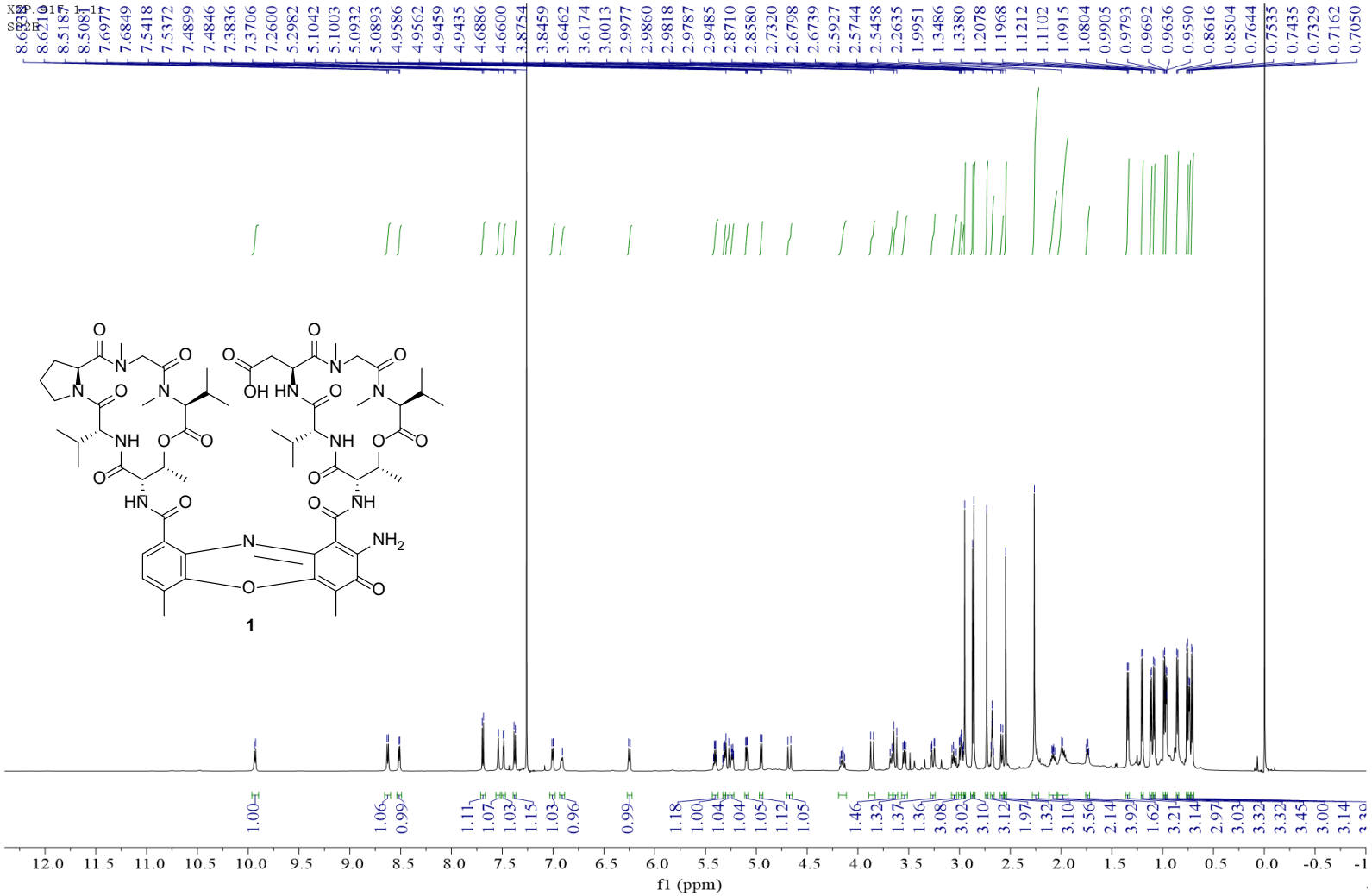


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of compound **1** in $CDCl_3$.

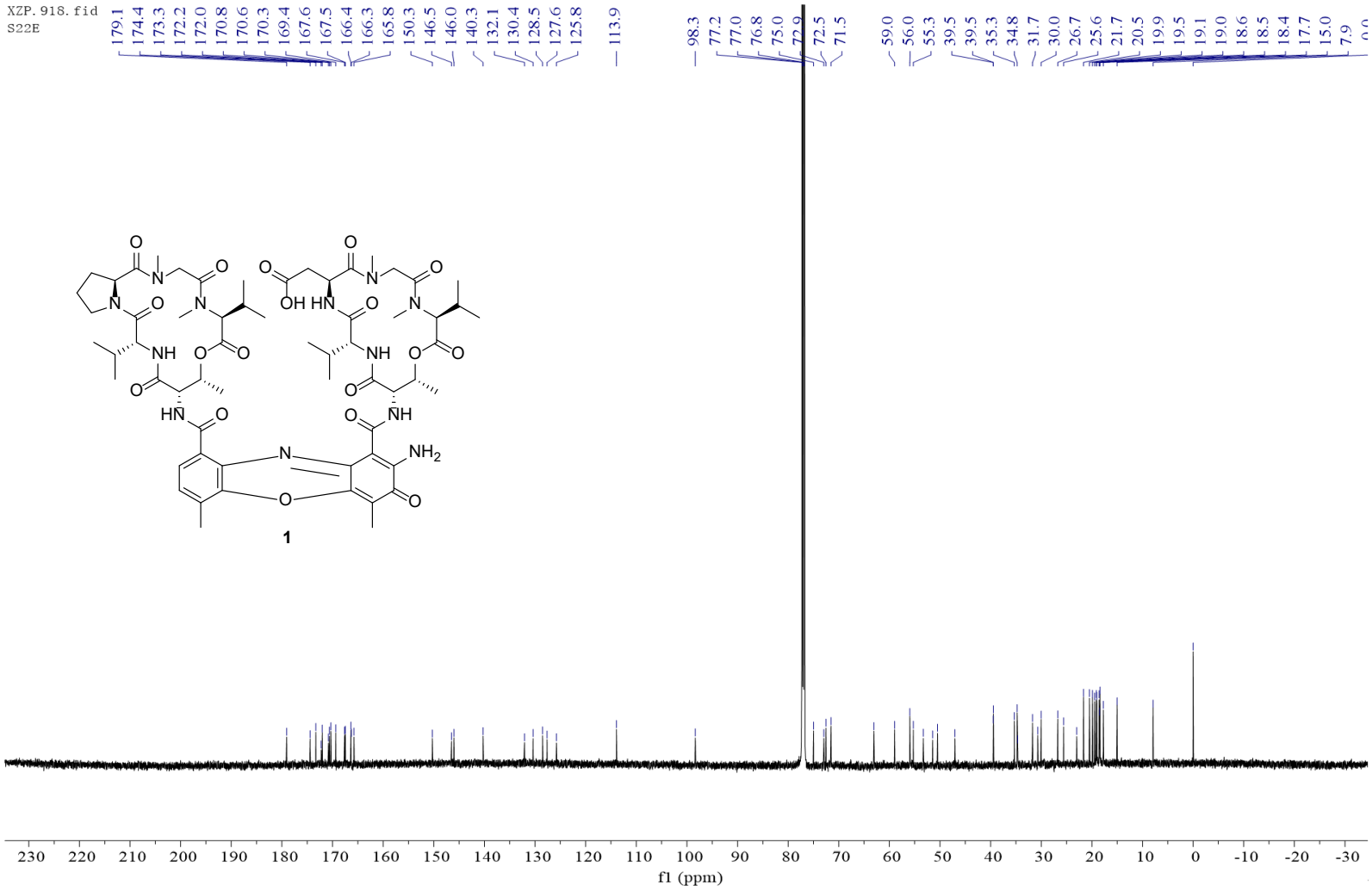


Fig. S12 DEPT-135 spectrum (150 MHz) of compound **1** in $CDCl_3$.

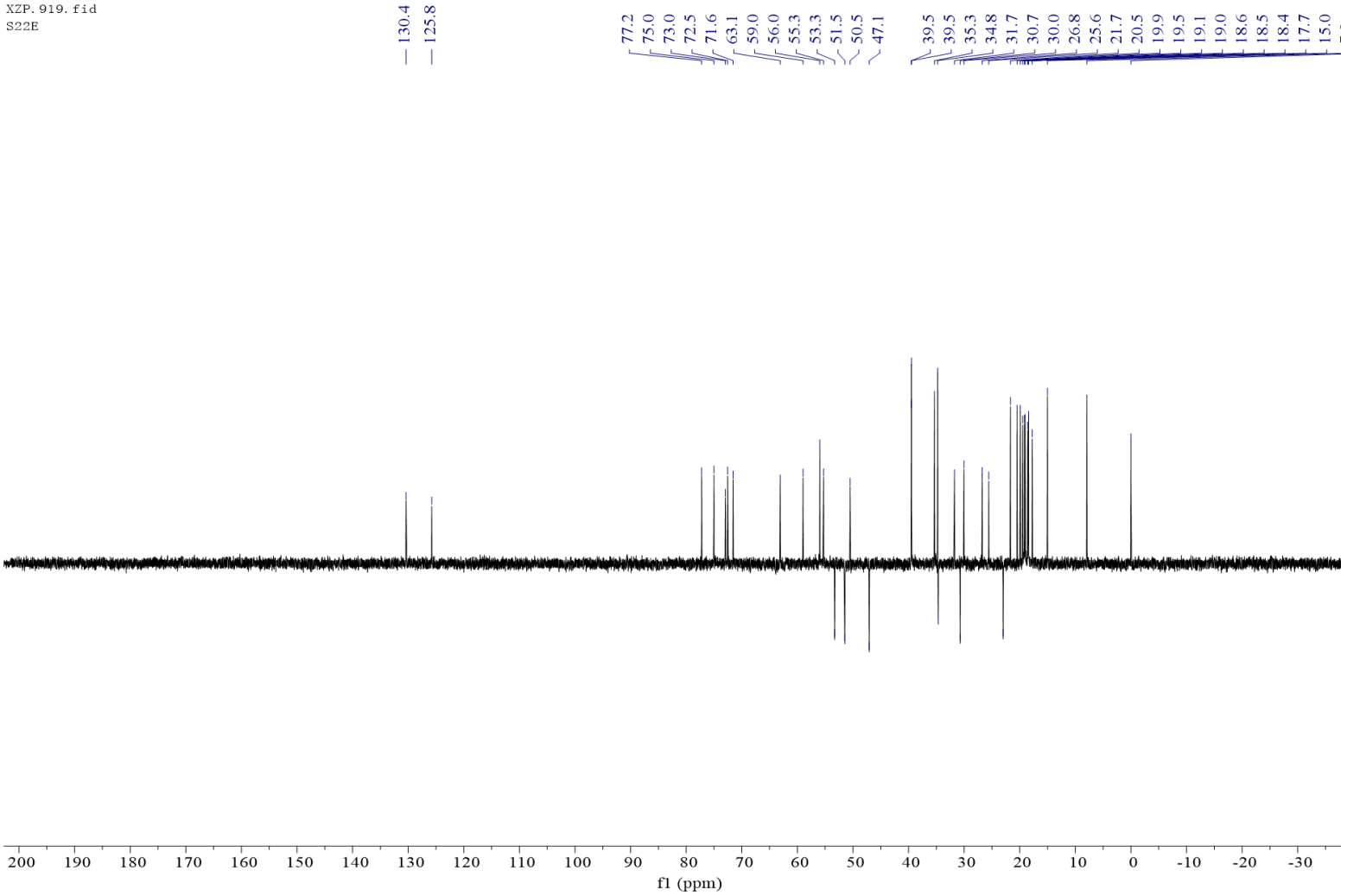


Fig. S13 COSY spectrum (600 MHz) of compound **1** in $CDCl_3$.

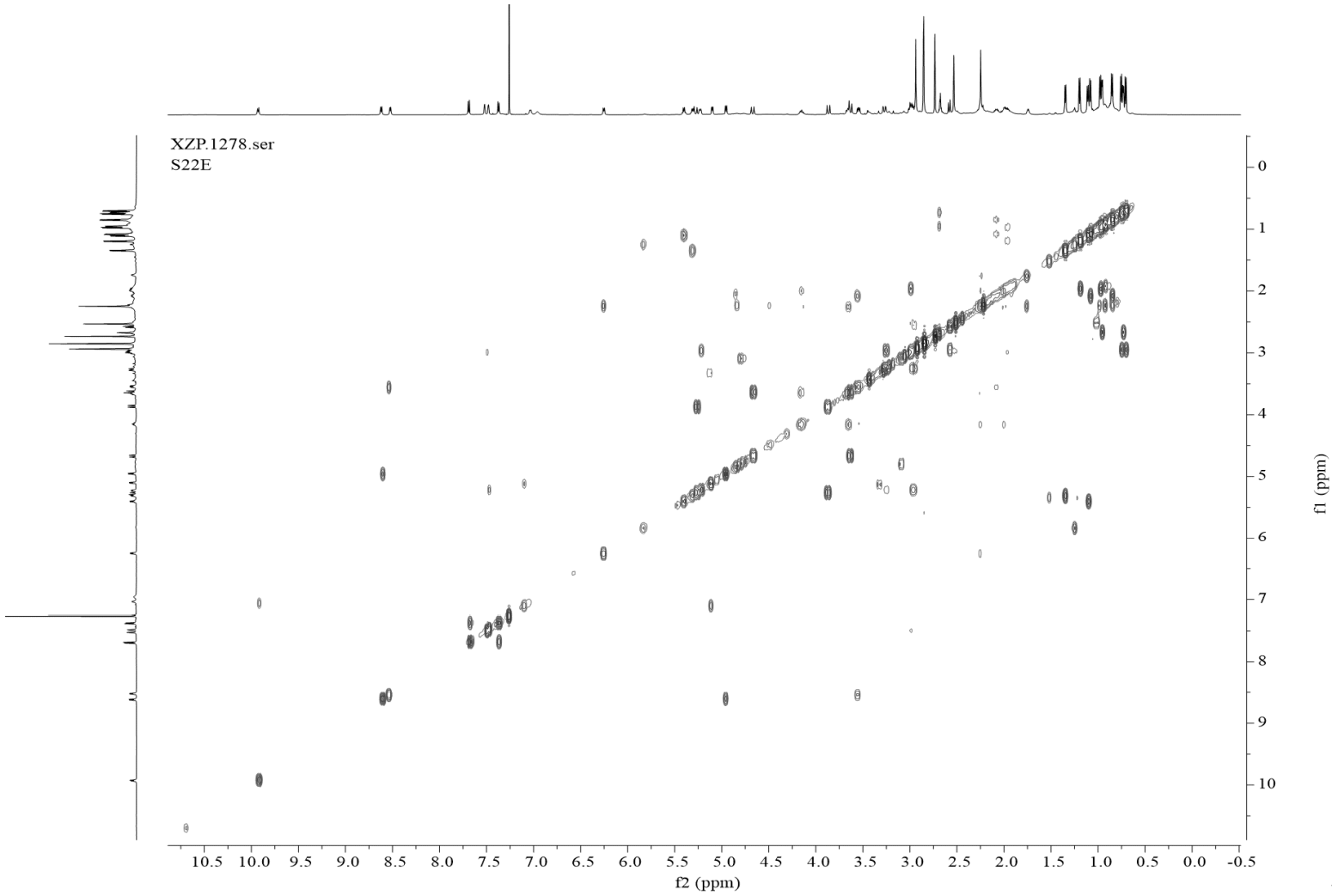


Fig. S14 HSQC spectrum (600 MHz) of compound **1** in $CDCl_3$.

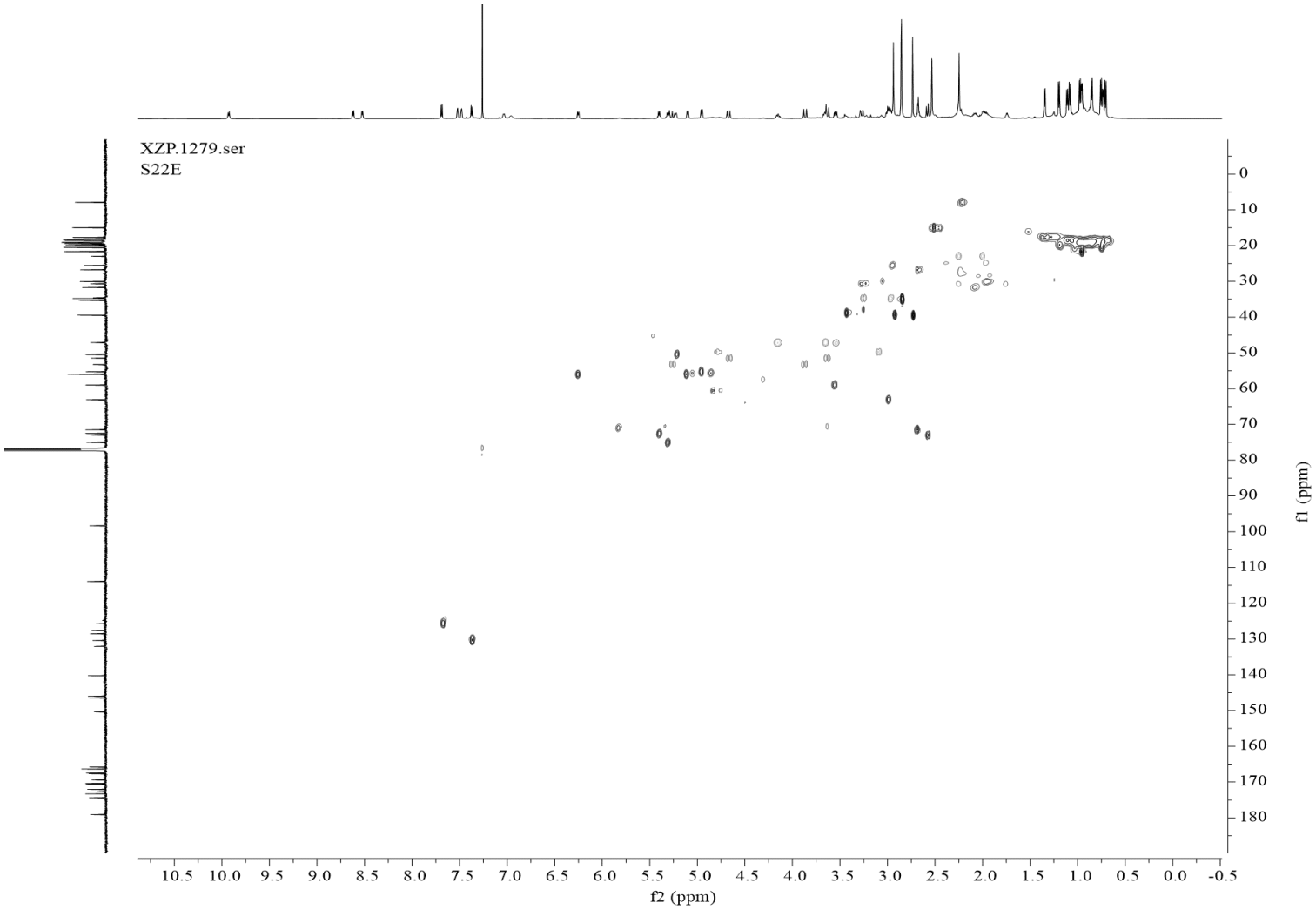


Fig. S15 HMBC spectrum (600 MHz) of compound **1** in $CDCl_3$.

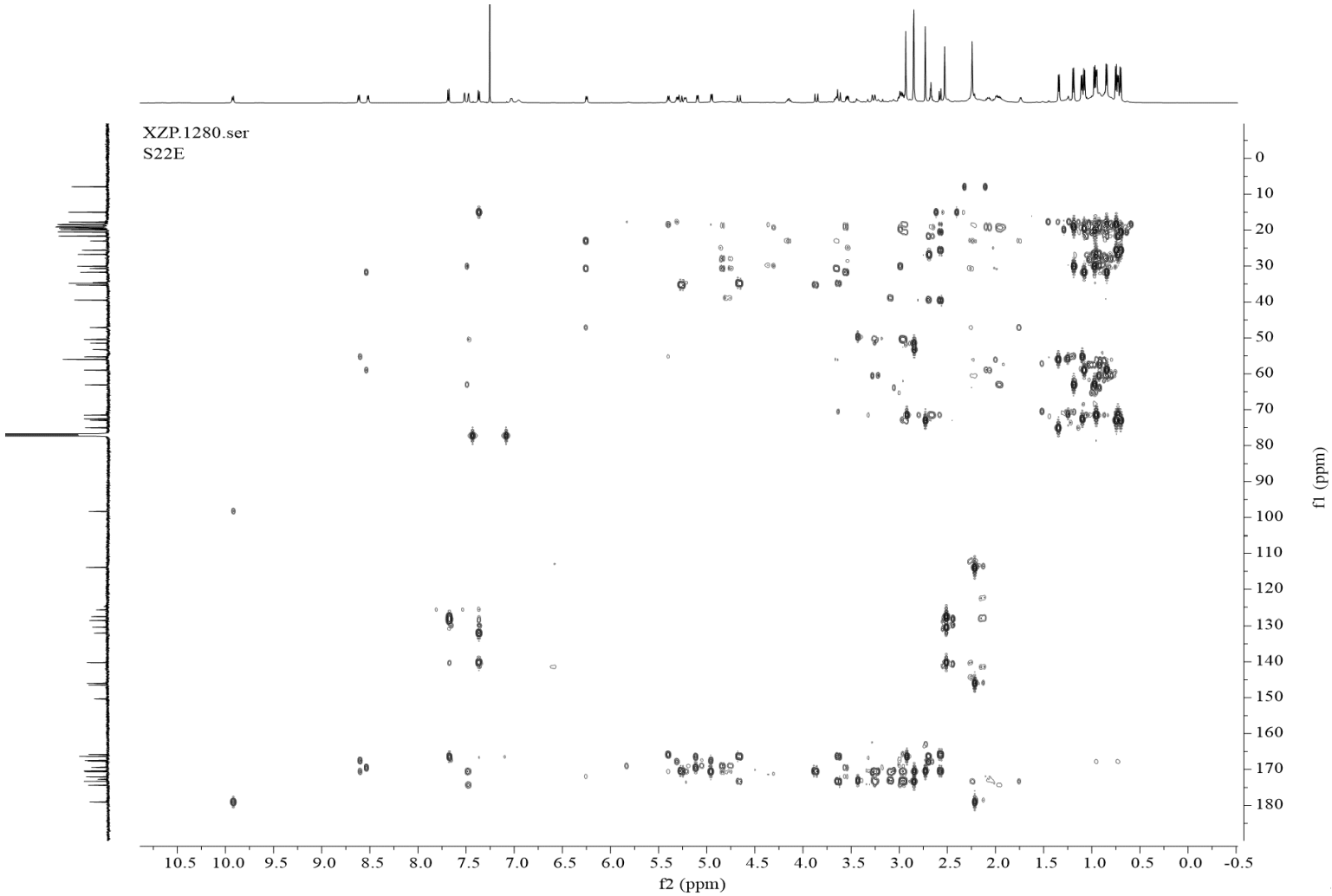


Fig. S16 NOESY spectrum (600 MHz) of compound **1** in $CDCl_3$.

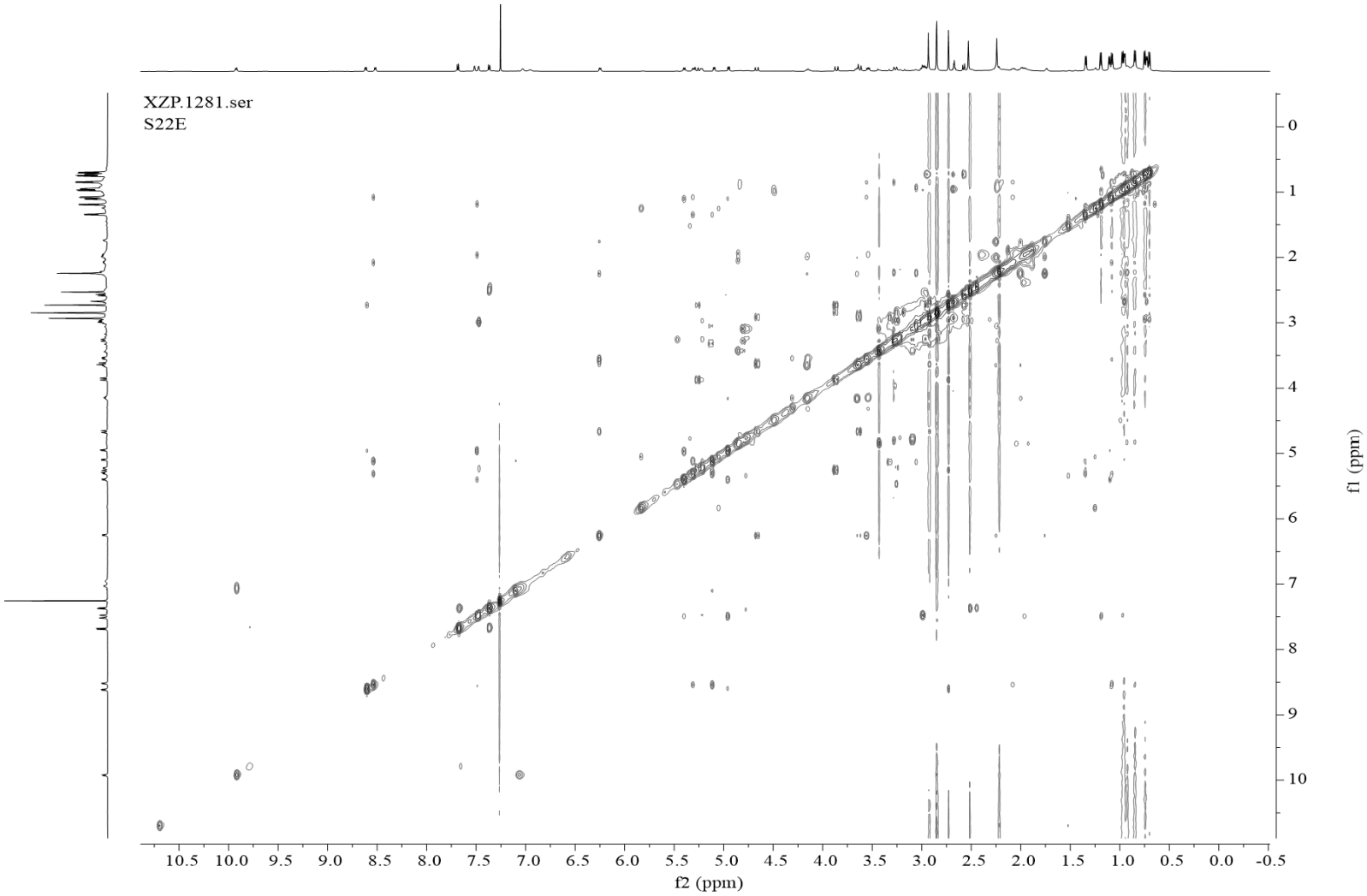


Fig. S17 HRESIMS spectrum of compound **1**.

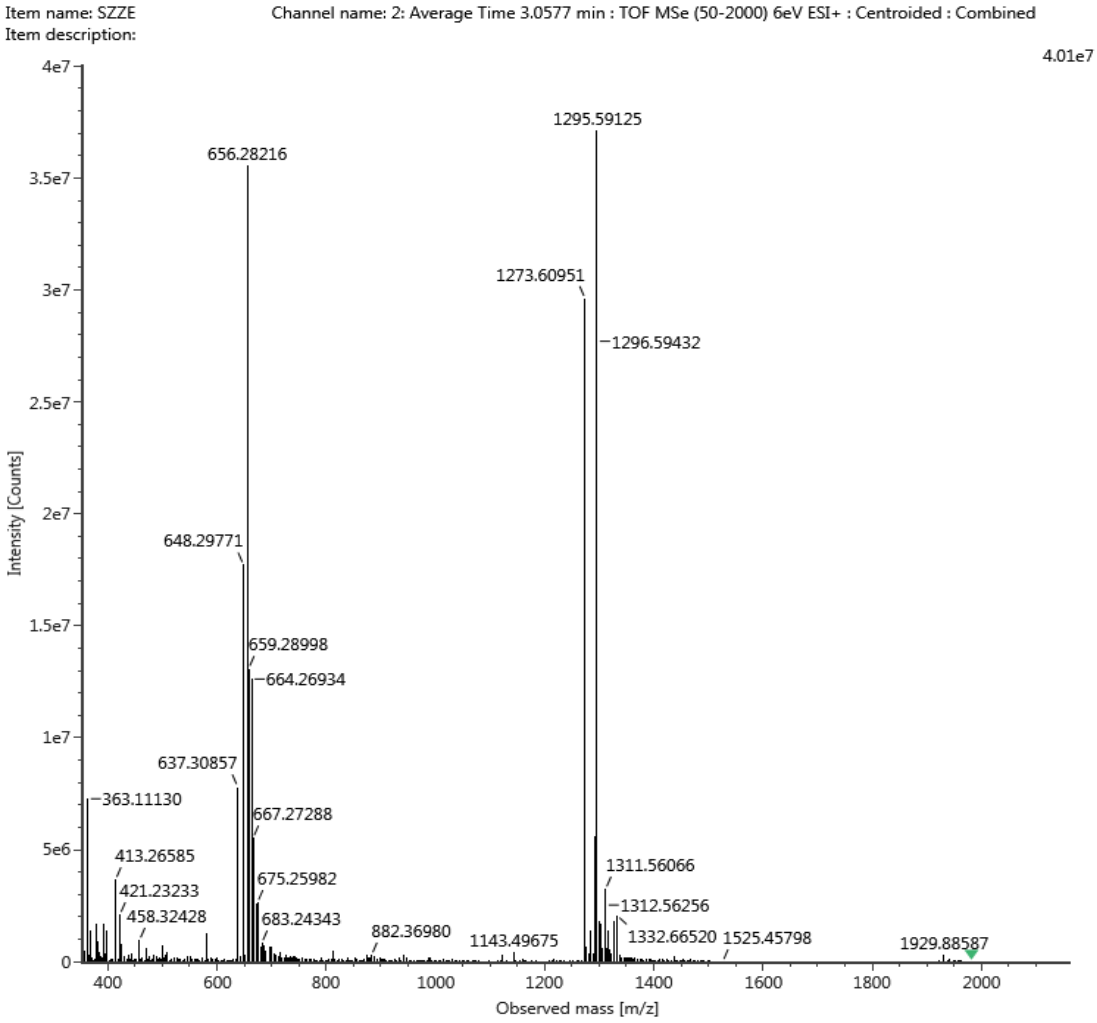


Fig. S18 ^{1}H NMR spectrum (600 MHz) of compound **2** in $CDCl_3$.

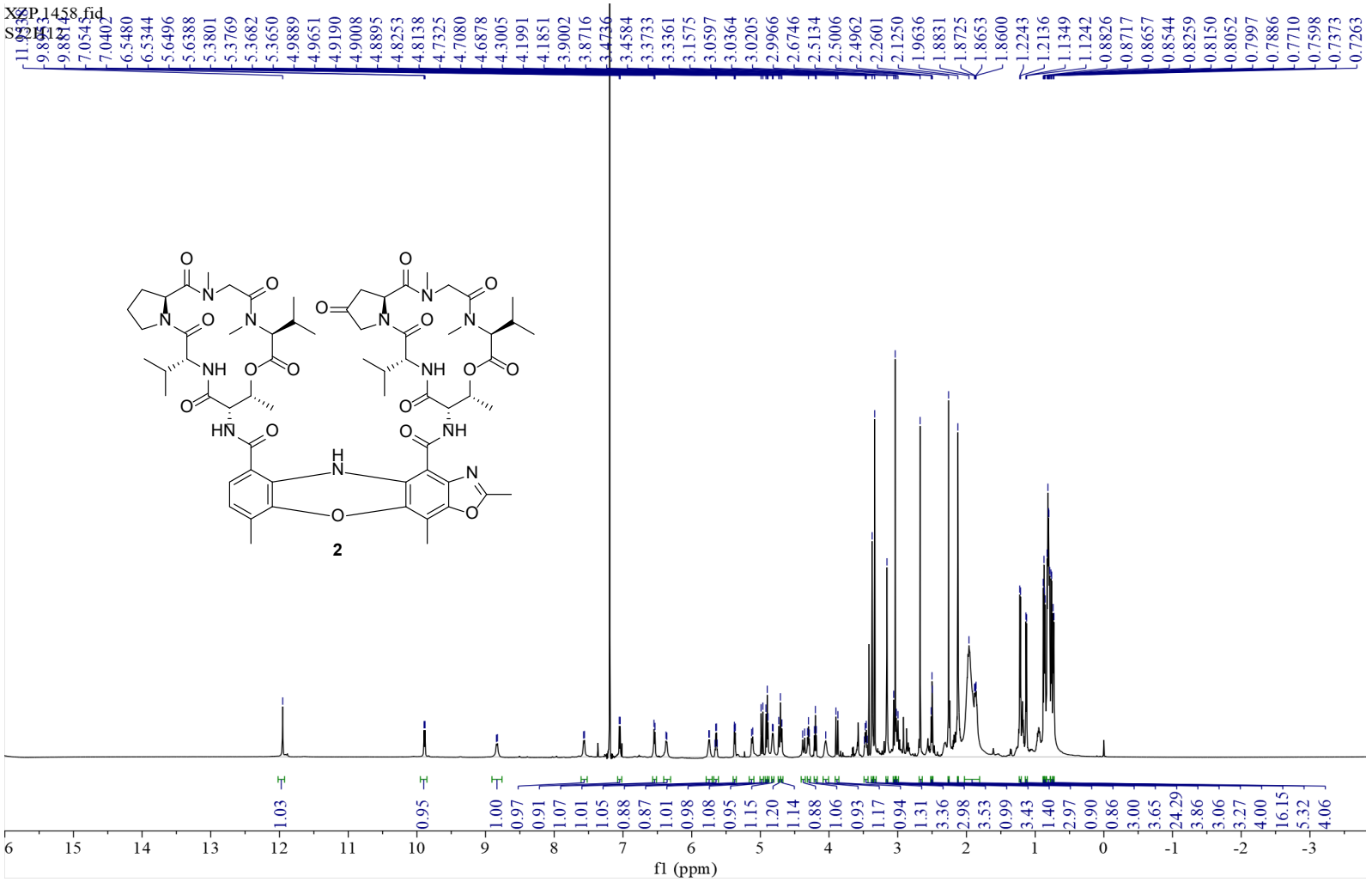


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of compound **2** in $CDCl_3$.

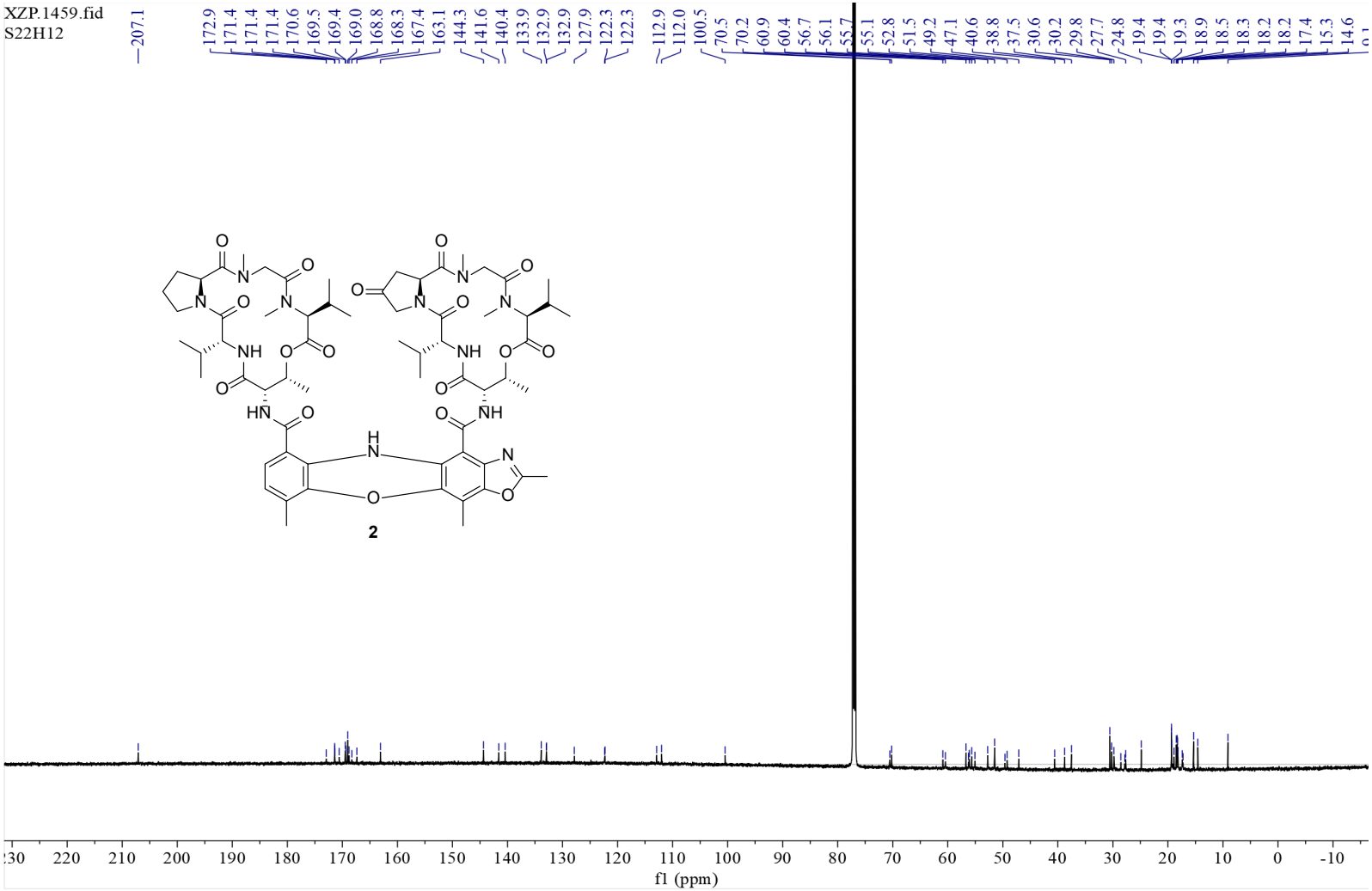


Fig. S20 DEPT-135 spectrum (150 MHz) of compound **2** in $CDCl_3$.

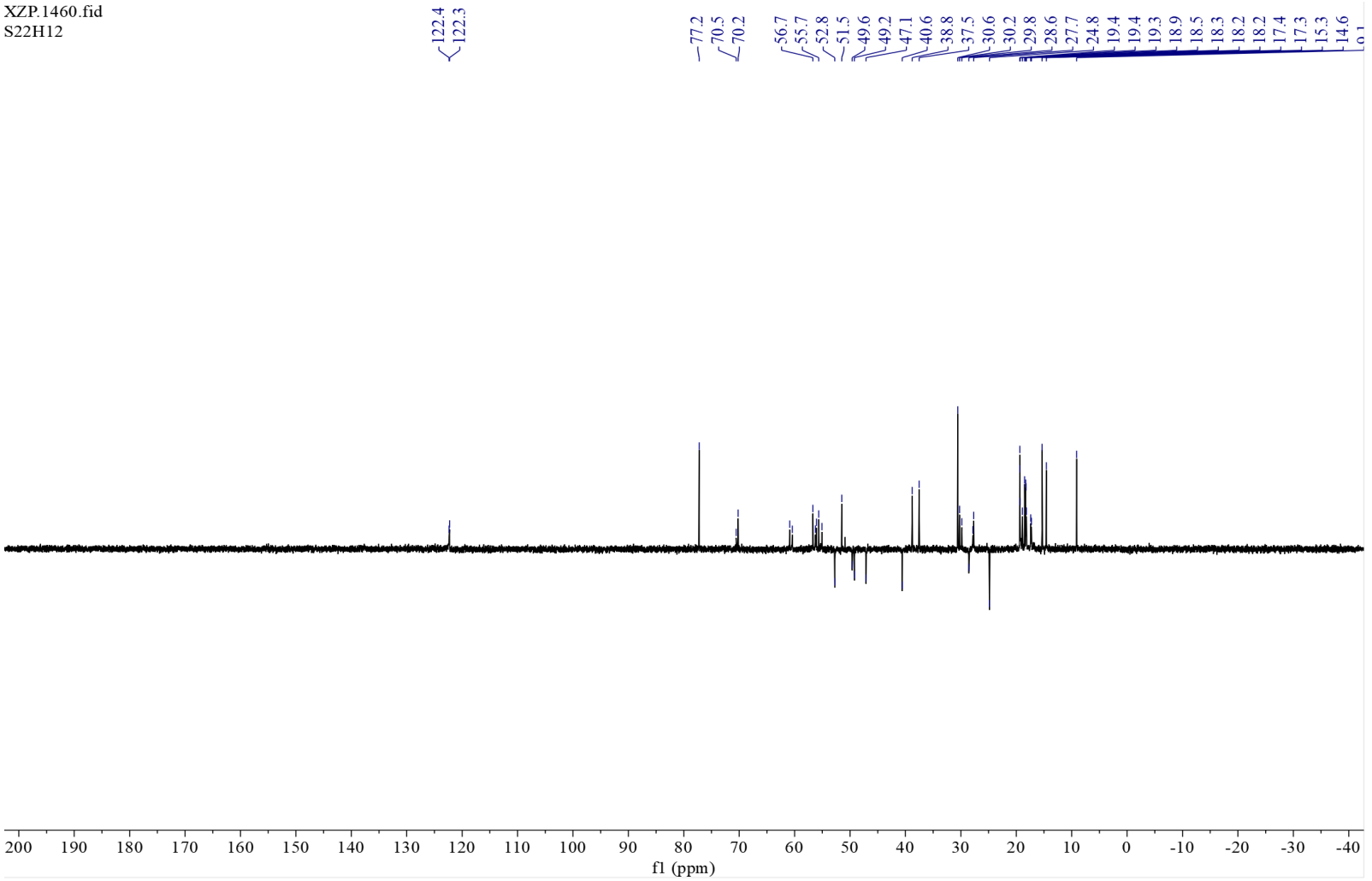


Fig. S21 COSY spectrum (600 MHz) of compound **2** in $CDCl_3$.

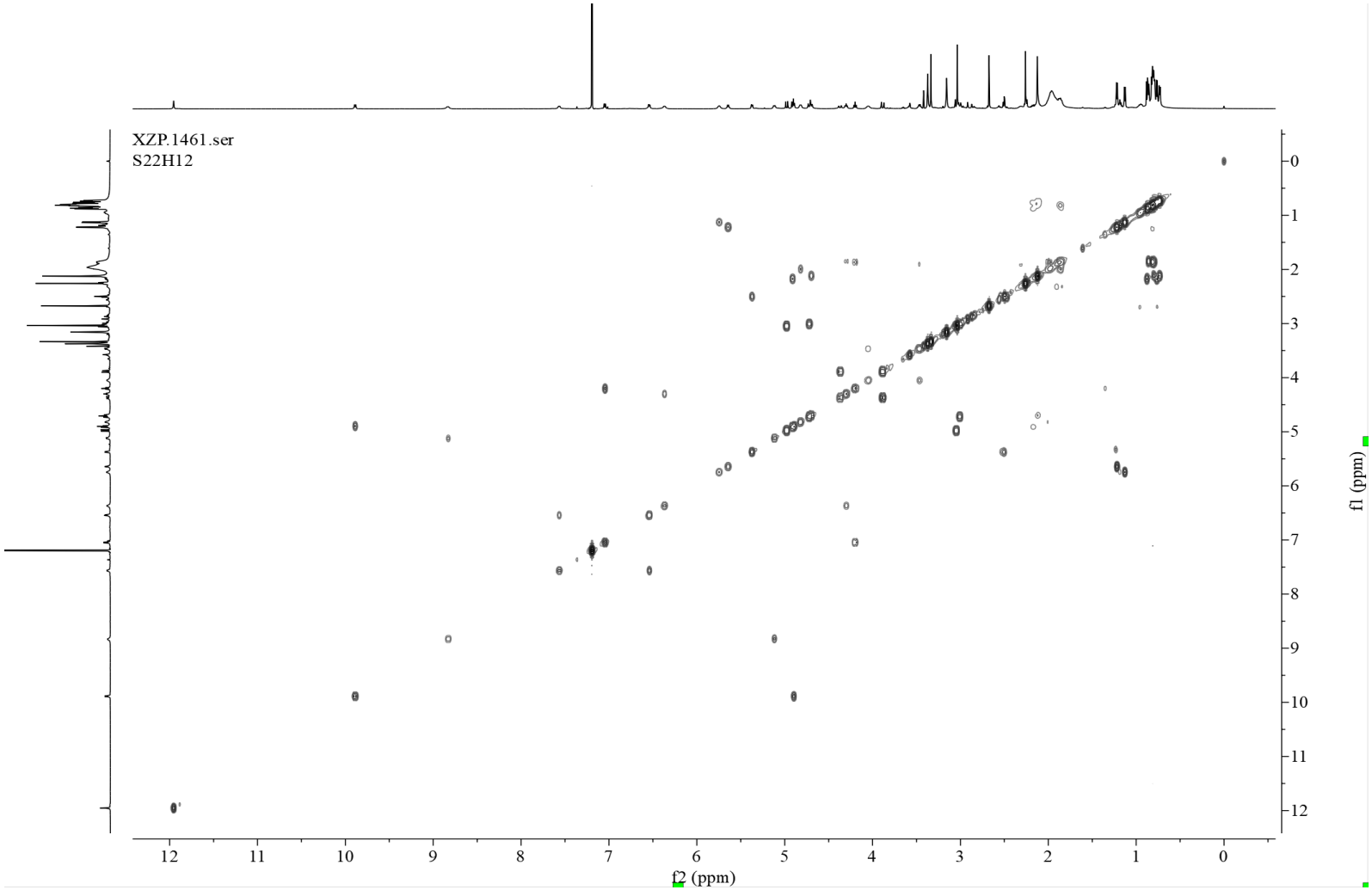


Fig. S22 HSQC spectrum (600 MHz) of compound **2** in $CDCl_3$.

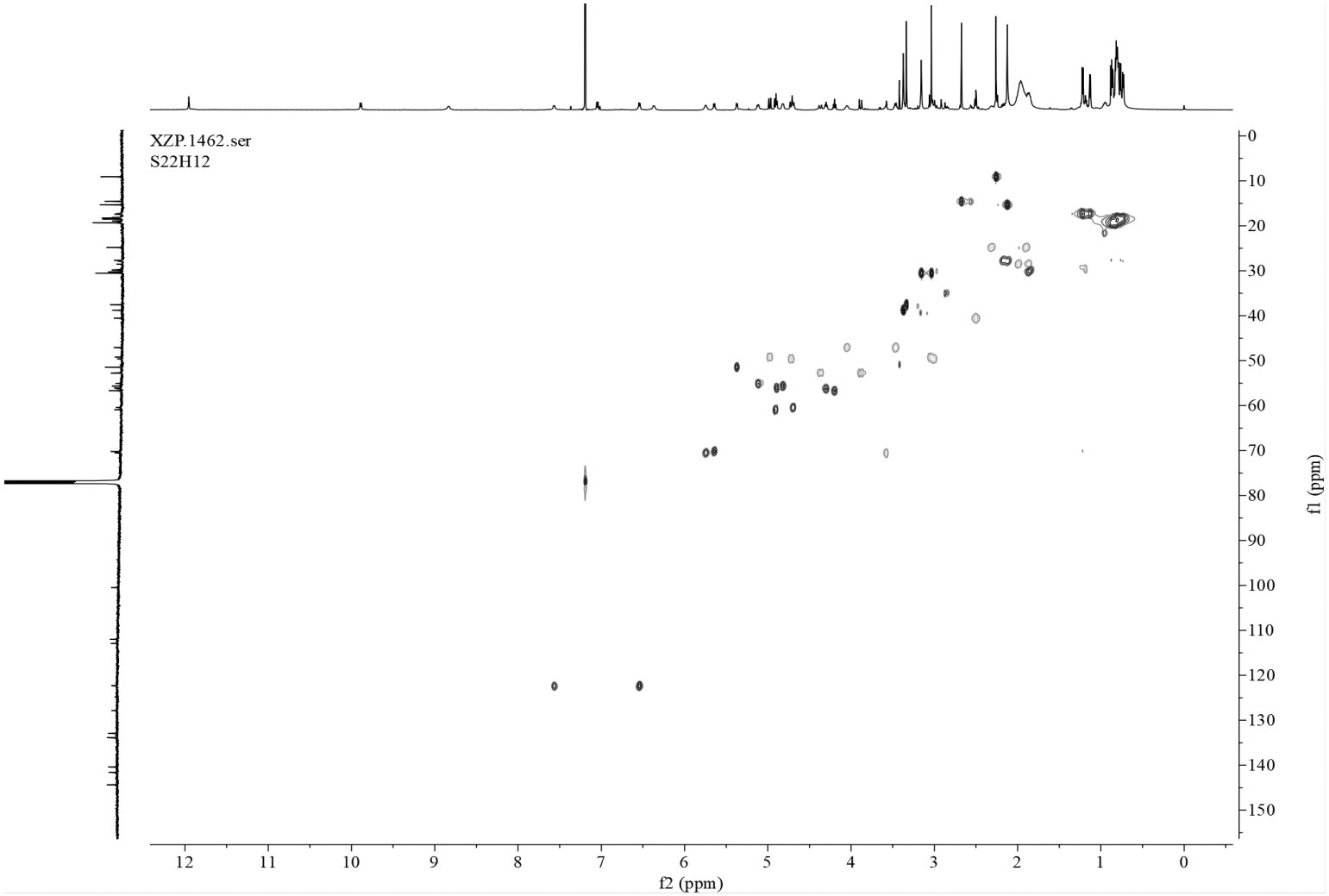


Fig. S23 HMBC spectrum (600 MHz) of compound **2** in $CDCl_3$.

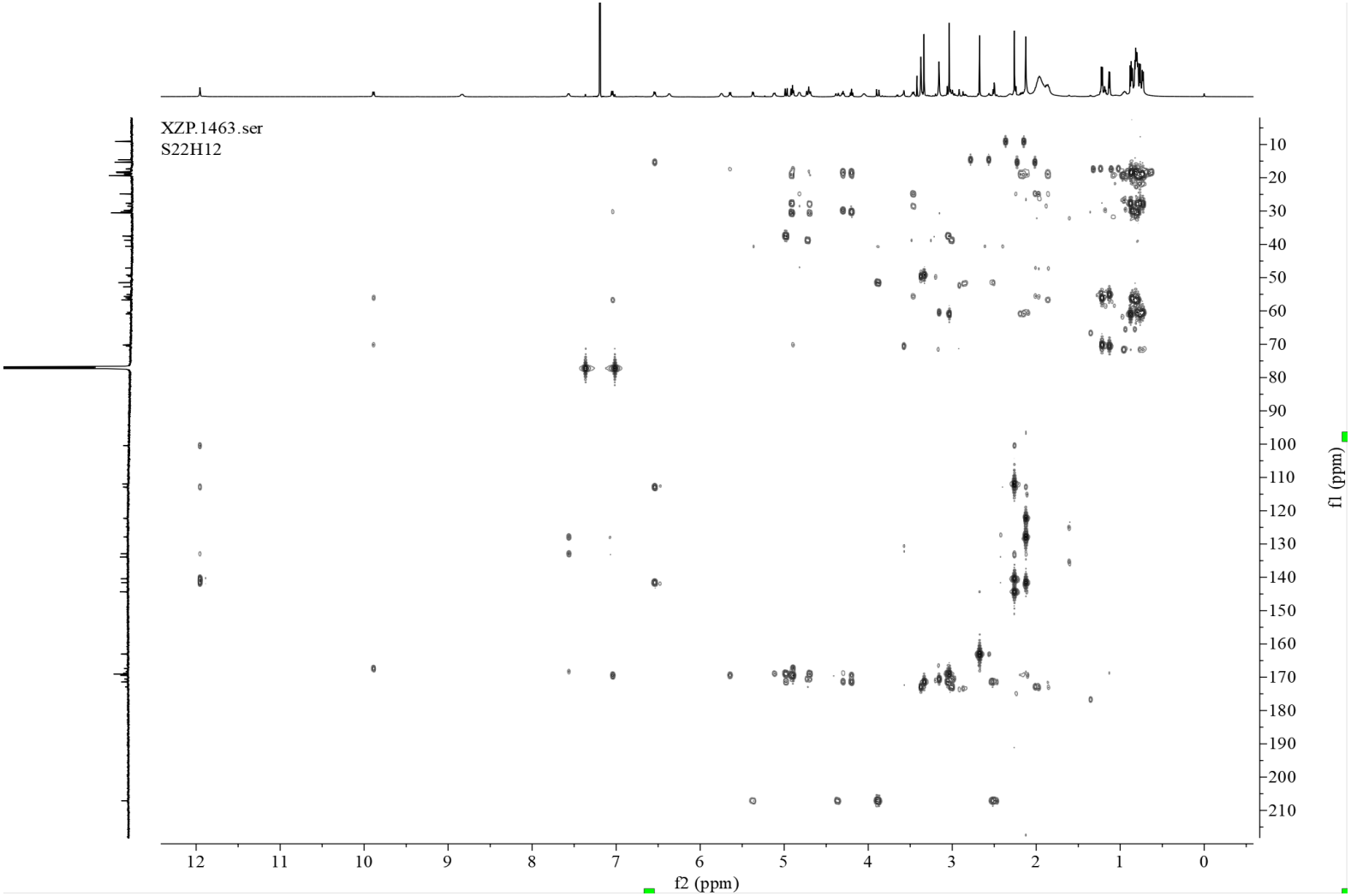


Fig. S24 NOESY spectrum (600 MHz) of compound **2** in $CDCl_3$.

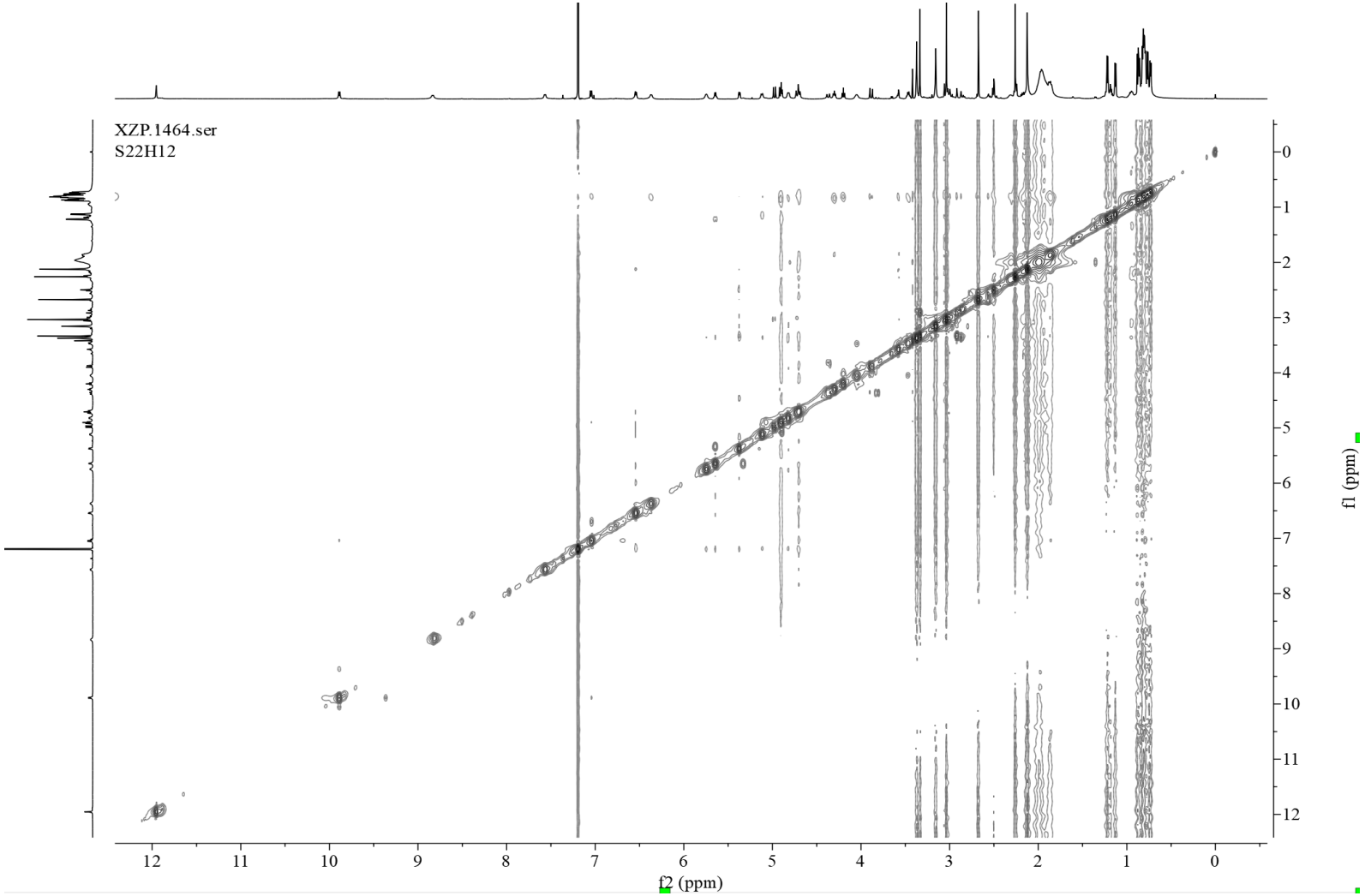


Fig. S25 HRESIMS spectrum of compound **2**.

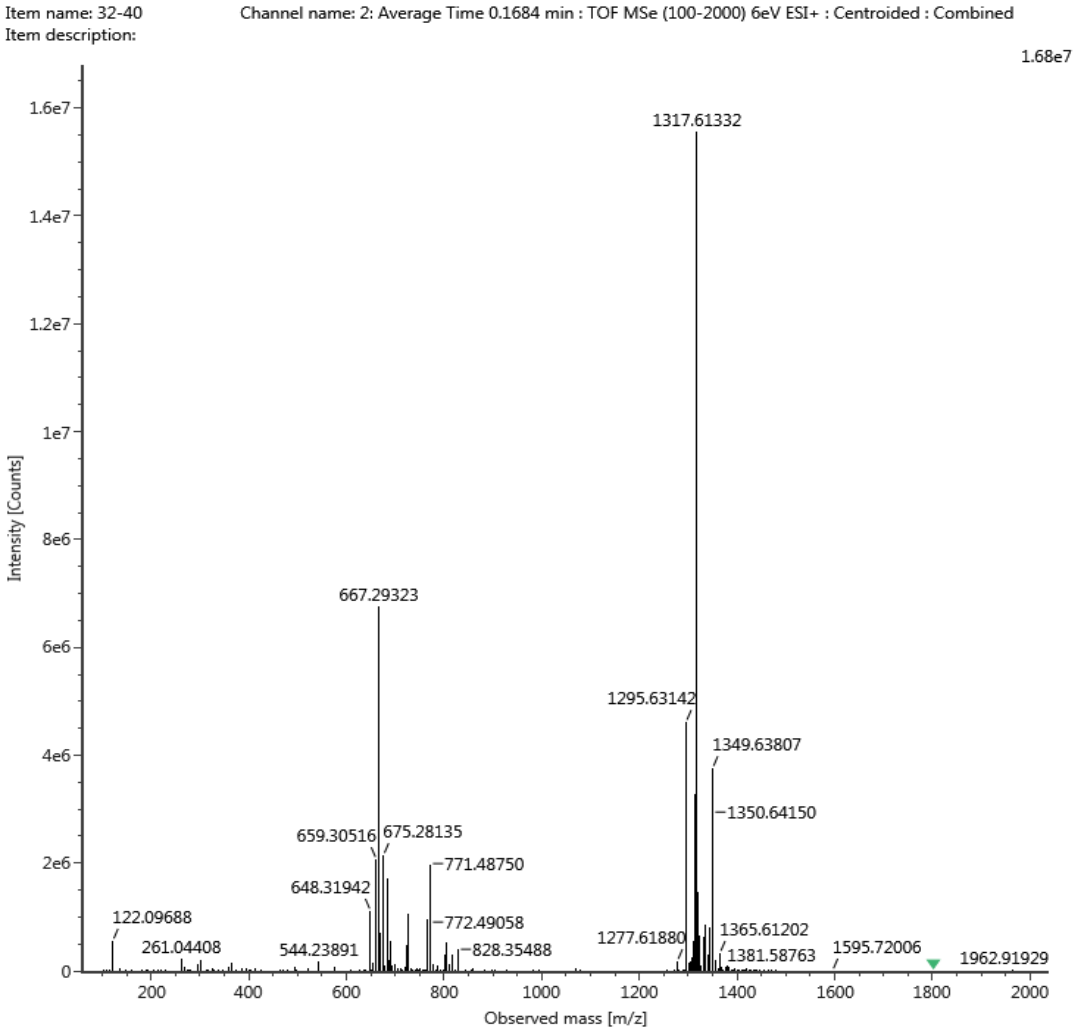


Fig. S26 ^{1}H NMR spectrum (600 MHz) of compound **3** in $CDCl_3$.

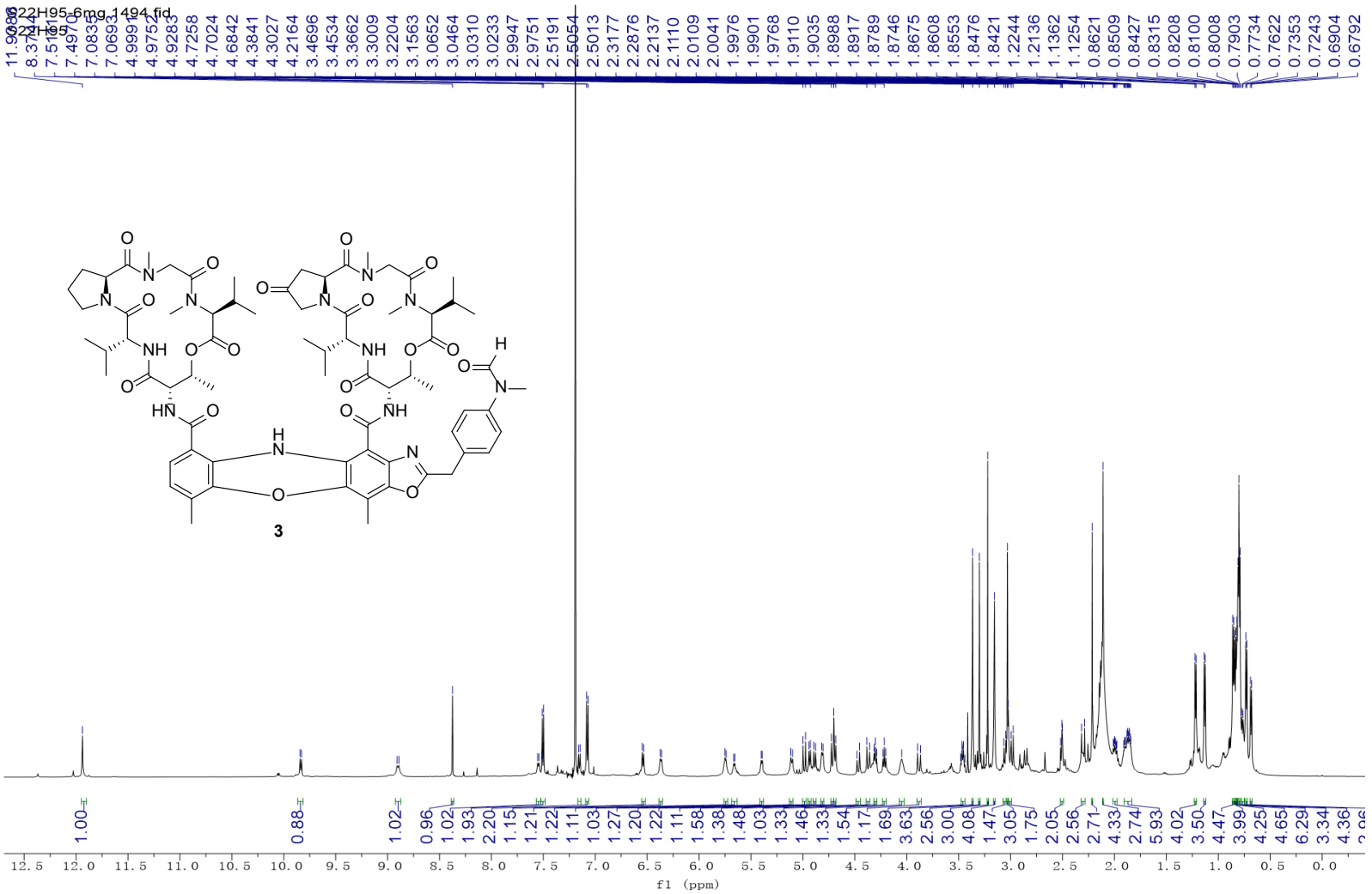


Fig. S27 $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of compound **3** in $CDCl_3$.

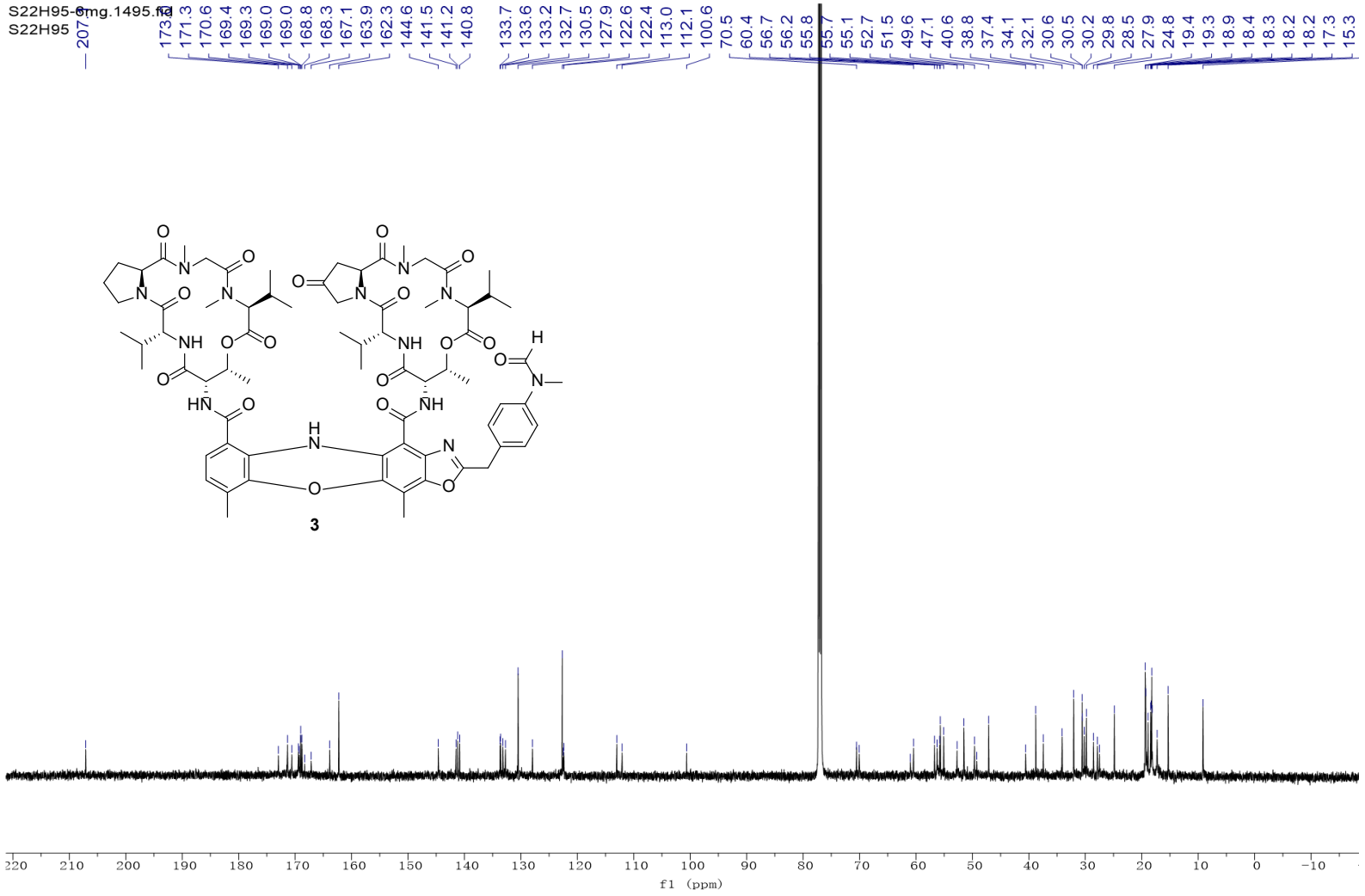


Fig. S28 DEPT-135 spectrum (150 MHz) of compound **3** in $CDCl_3$.

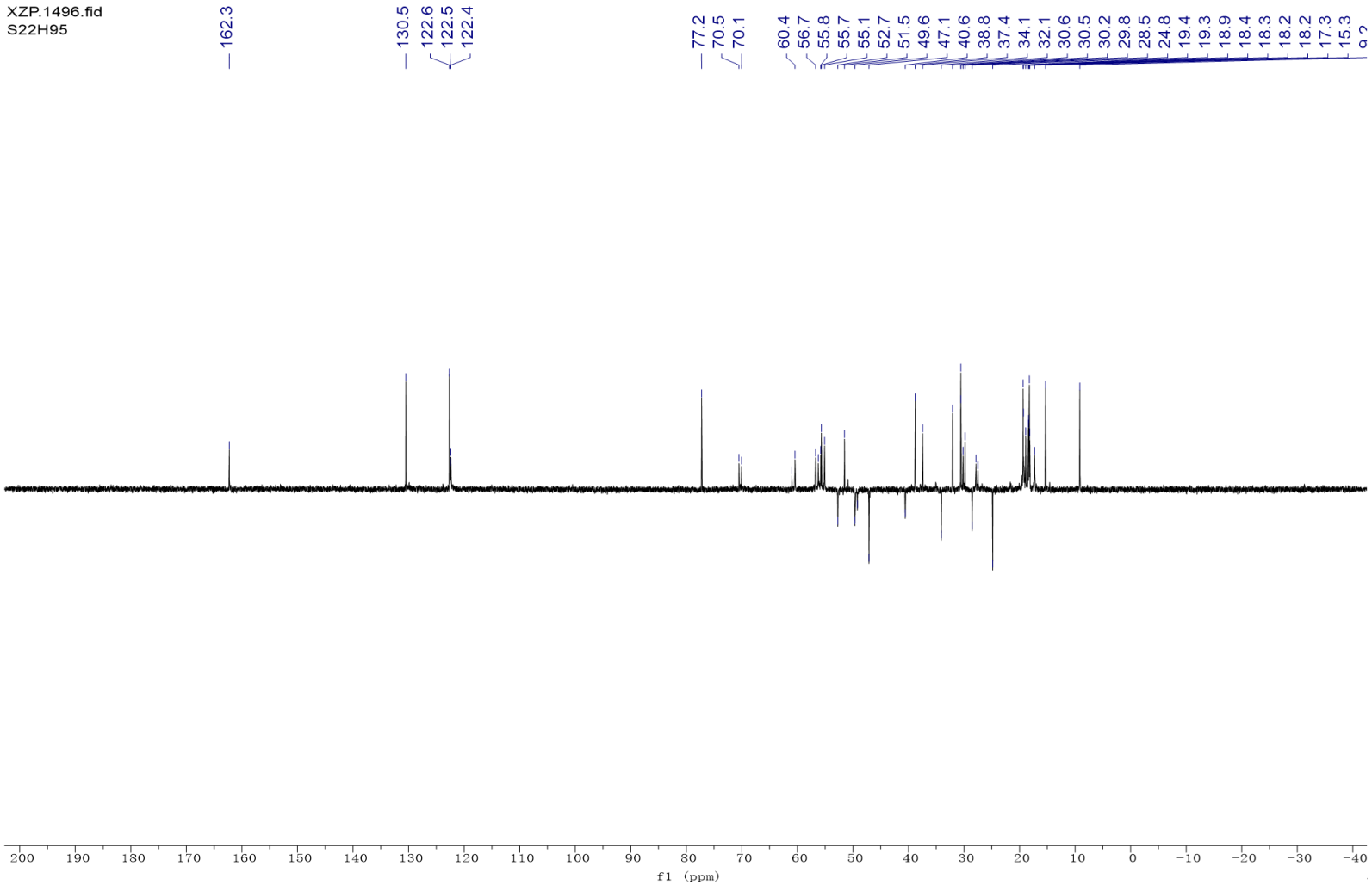


Fig. S29 COSY spectrum (600 MHz) of compound **3** in $CDCl_3$.

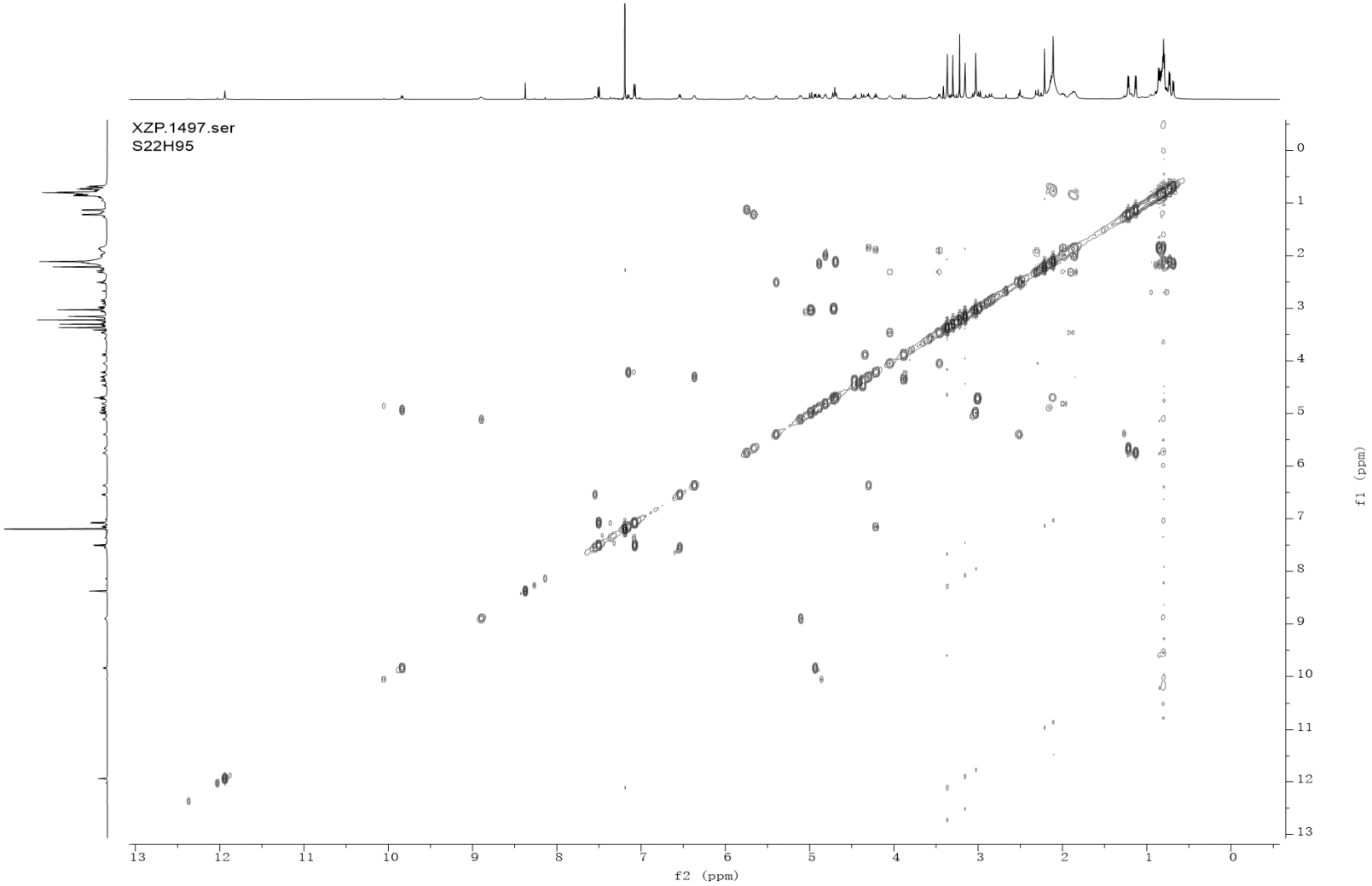


Fig. S30 HSQC spectrum (600 MHz) of compound **3** in $CDCl_3$.

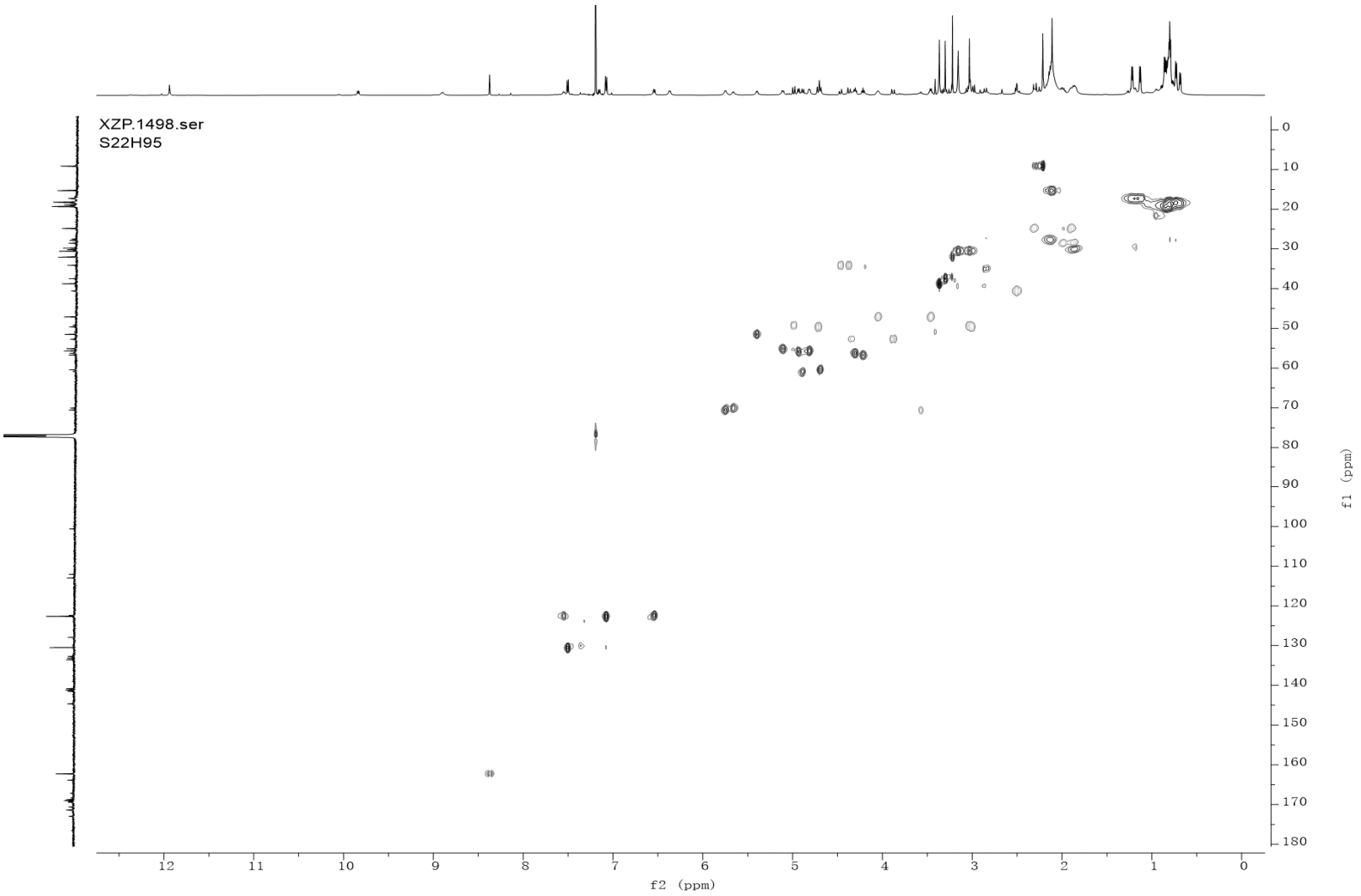


Fig. S31 HMBC spectrum (600 MHz) of compound **3** in $CDCl_3$.

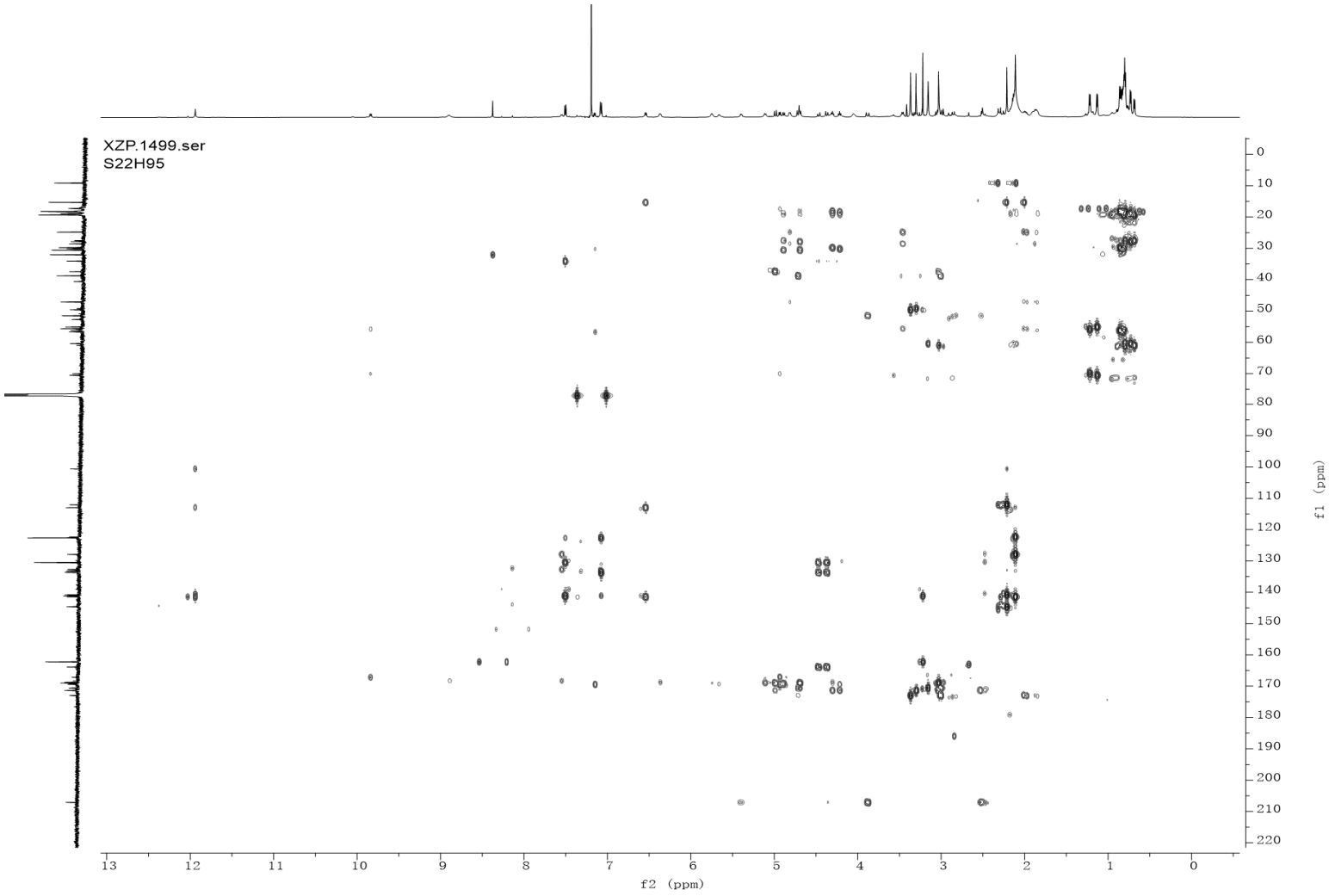


Fig. S32 NOESY spectrum (600 MHz) of compound **3** in $CDCl_3$.

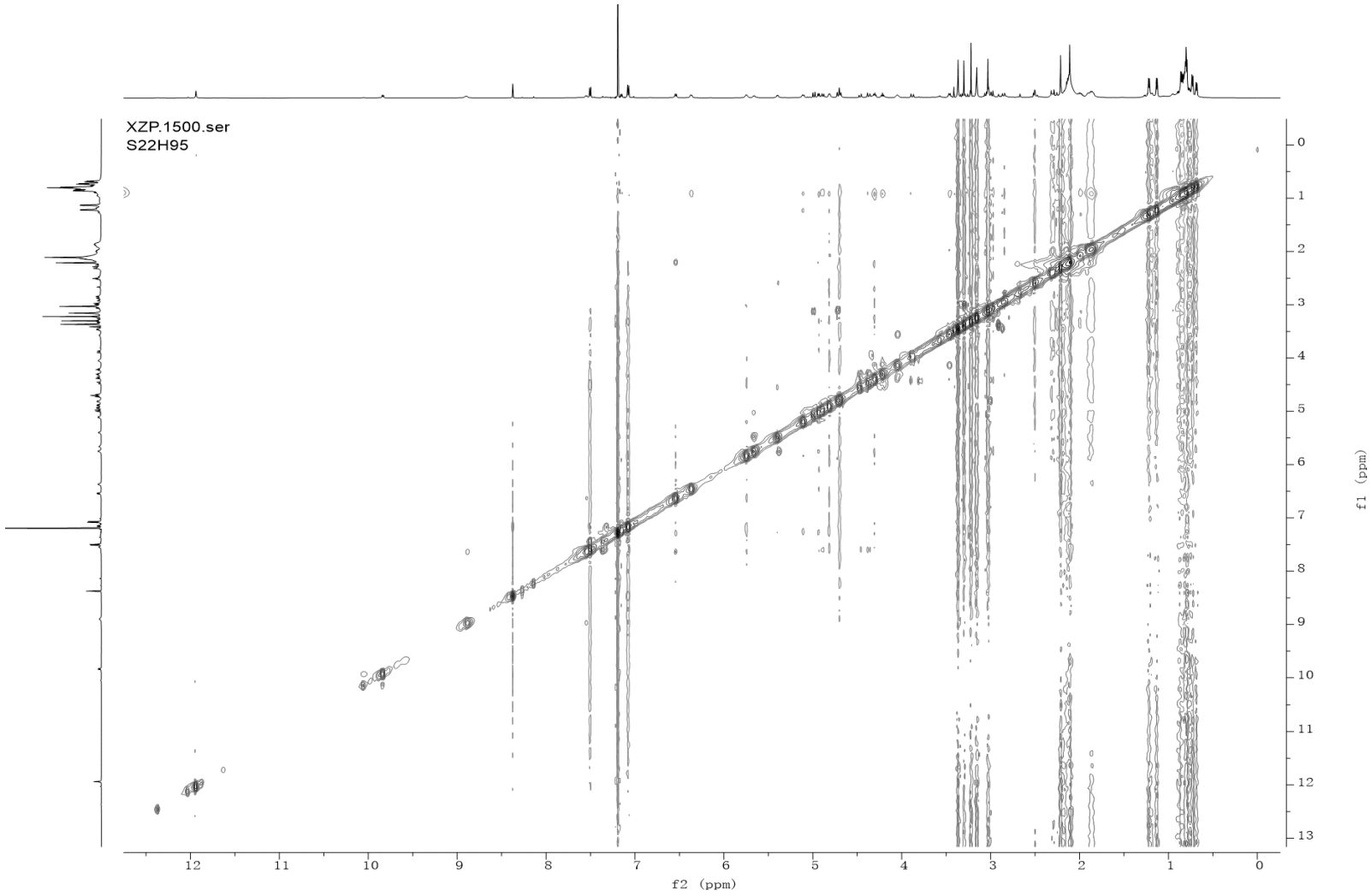


Fig. S33 HRESIMS spectrum of compound **3**.

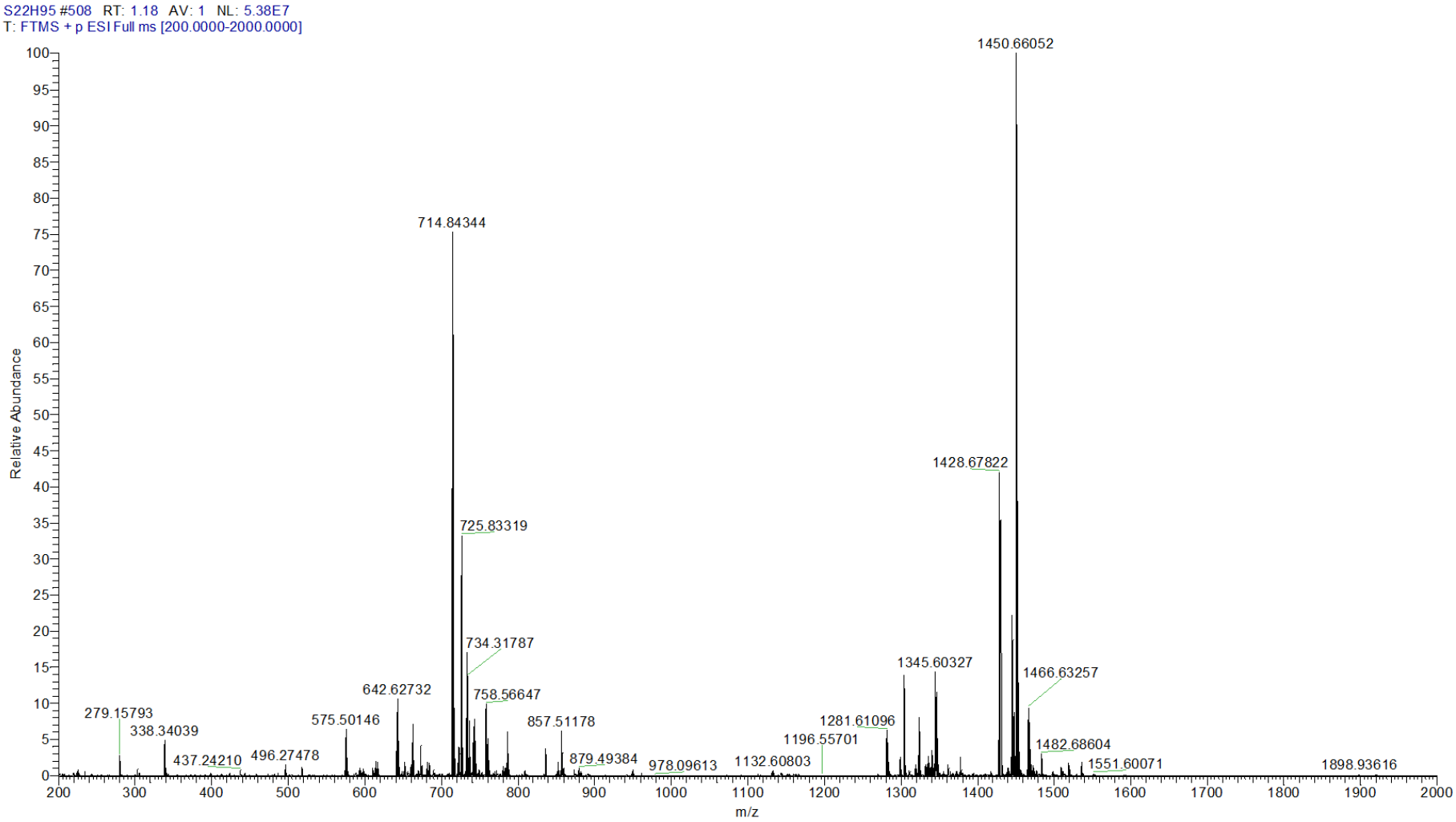


Fig. S34 ^{1}H NMR spectrum (600 MHz) of compound **4** in $CDCl_3$.

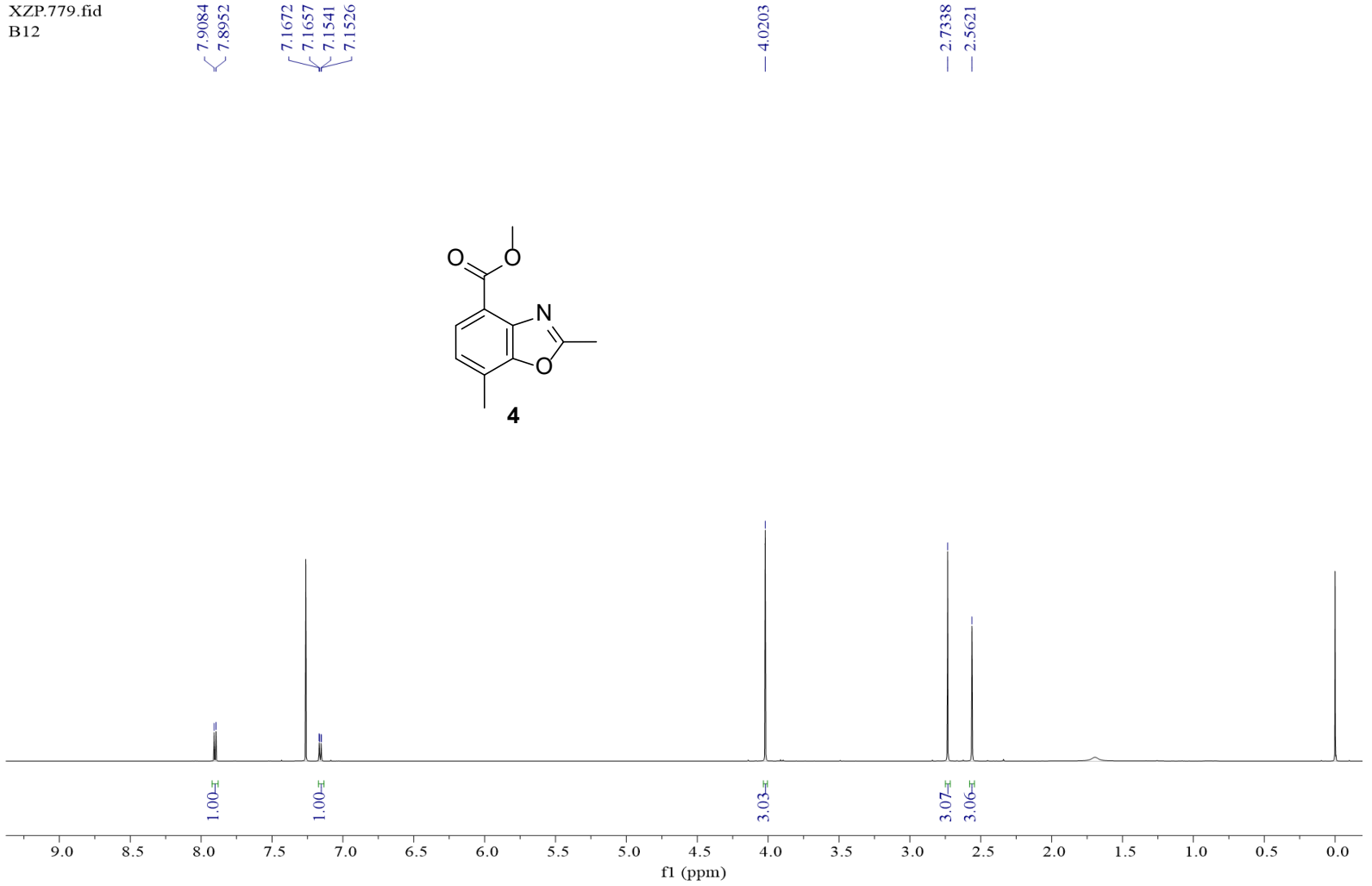


Fig. S35 $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of compound **4** in $CDCl_3$.

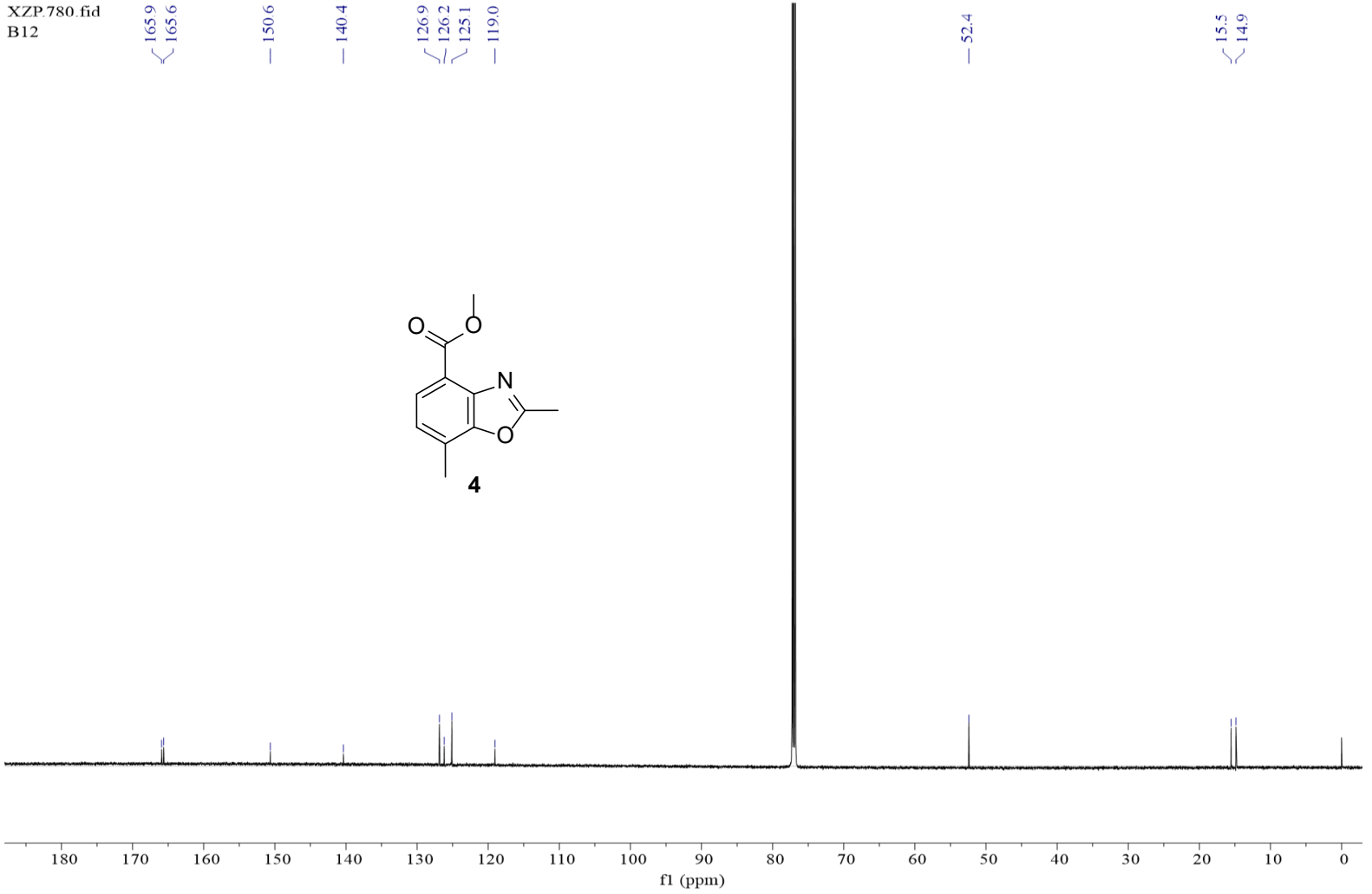


Fig. S36 DEPT-135 spectrum (150 MHz) of compound **4** in $CDCl_3$.

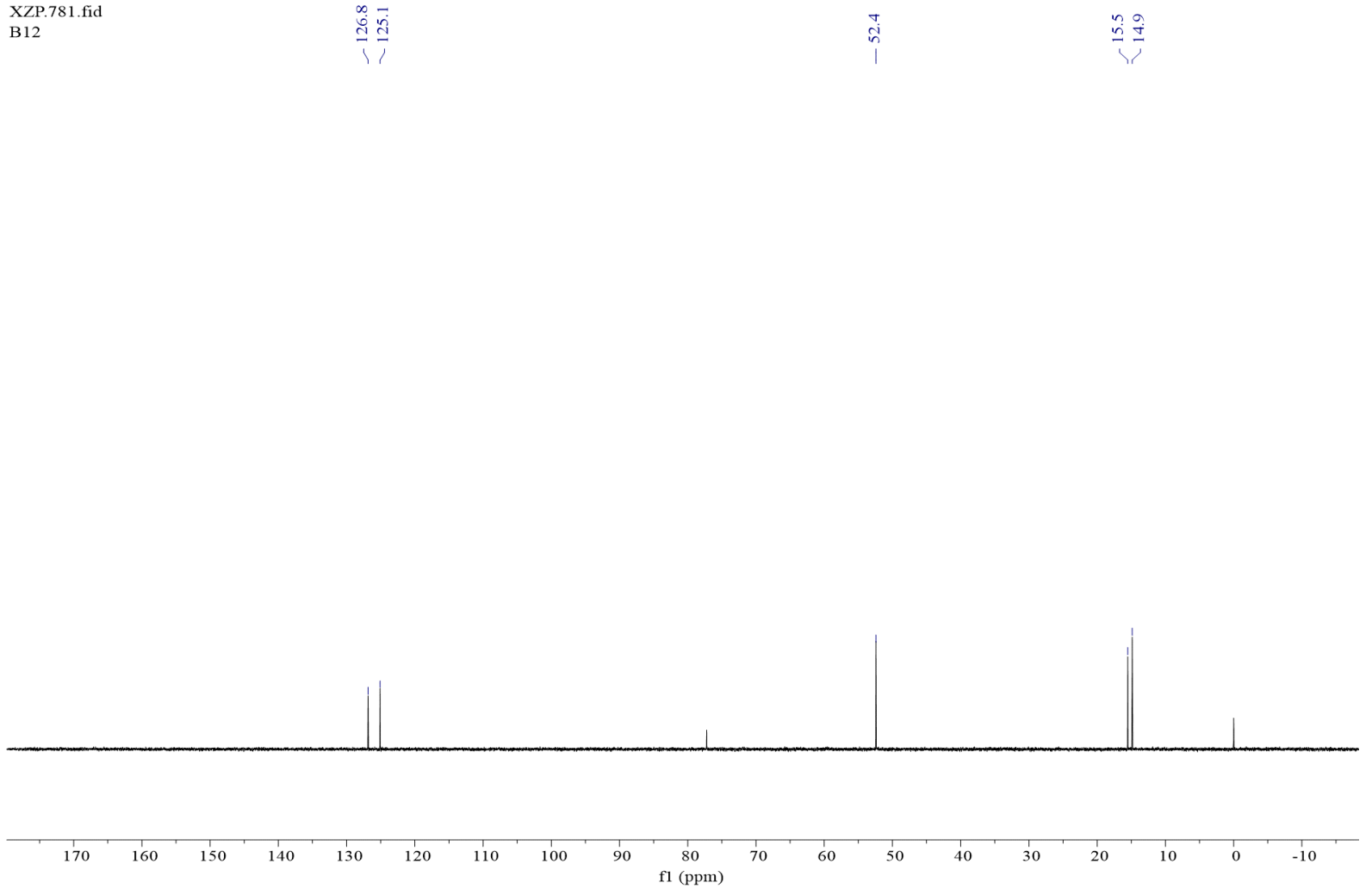


Fig. S37 COSY spectrum (600 MHz) of compound **4** in $CDCl_3$.

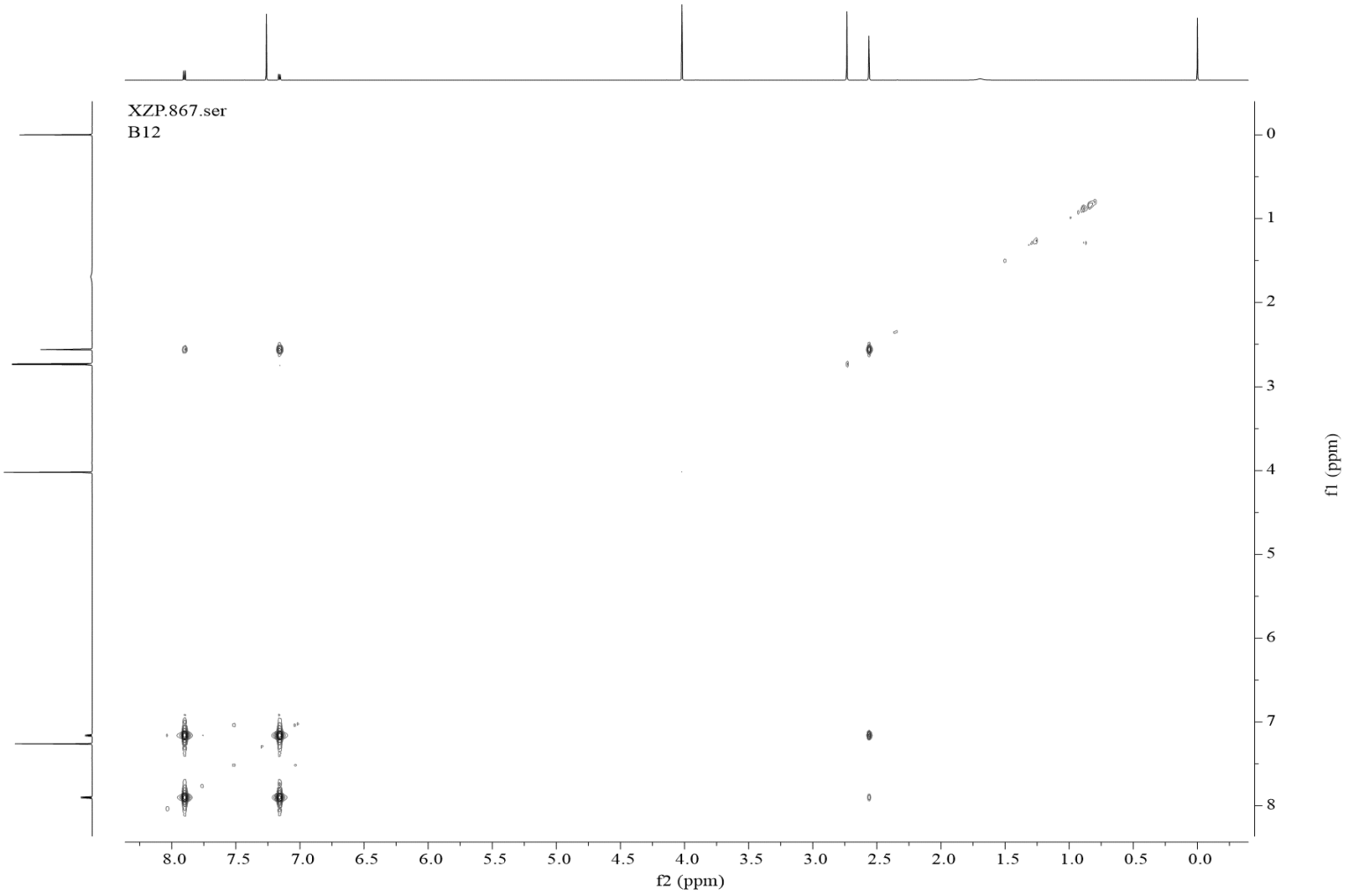


Fig. S38 HSQC spectrum (600 MHz) of compound **4** in $CDCl_3$.

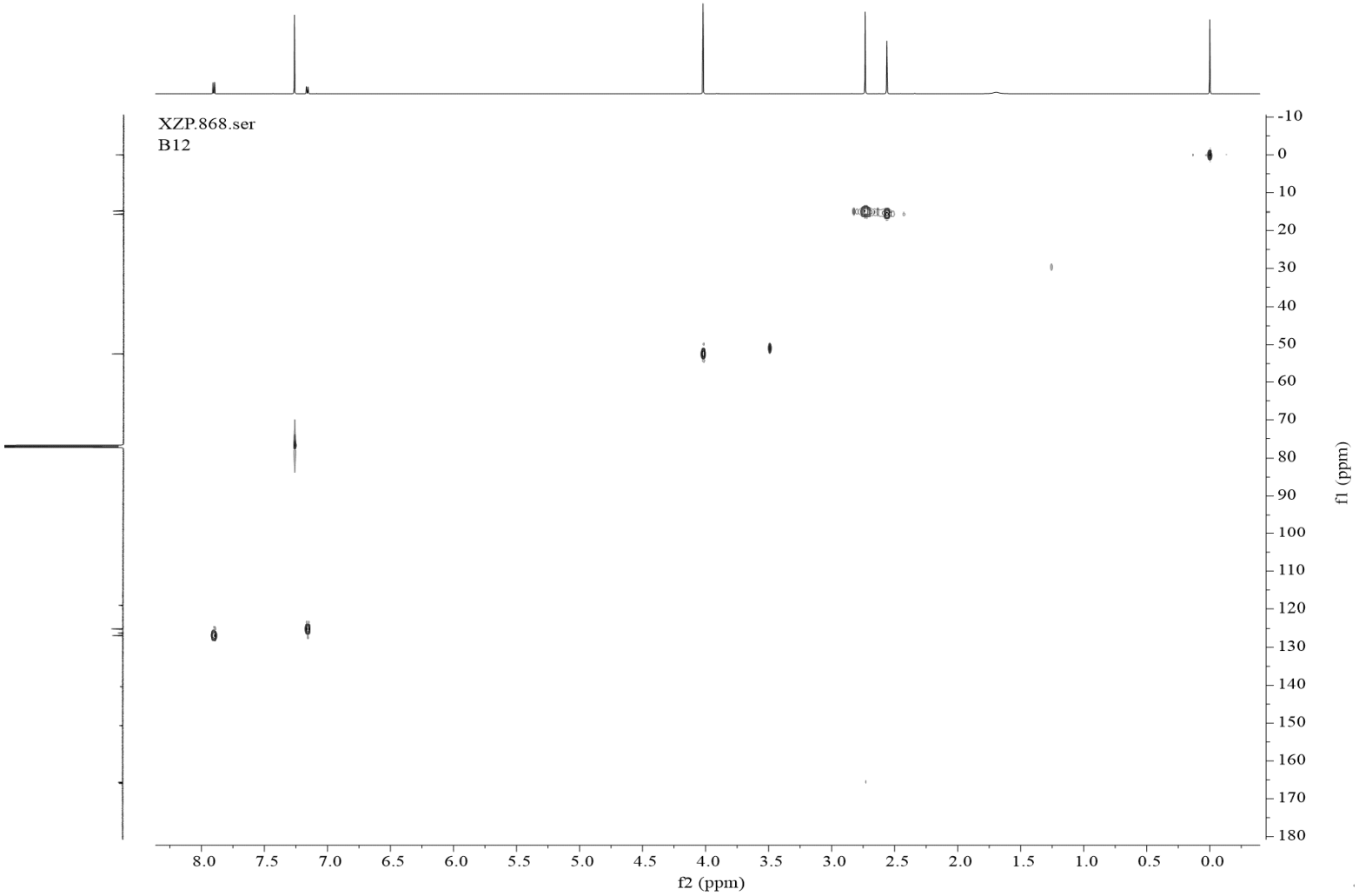


Fig. S39 HMBC spectrum (600 MHz) of compound **4** in $CDCl_3$.

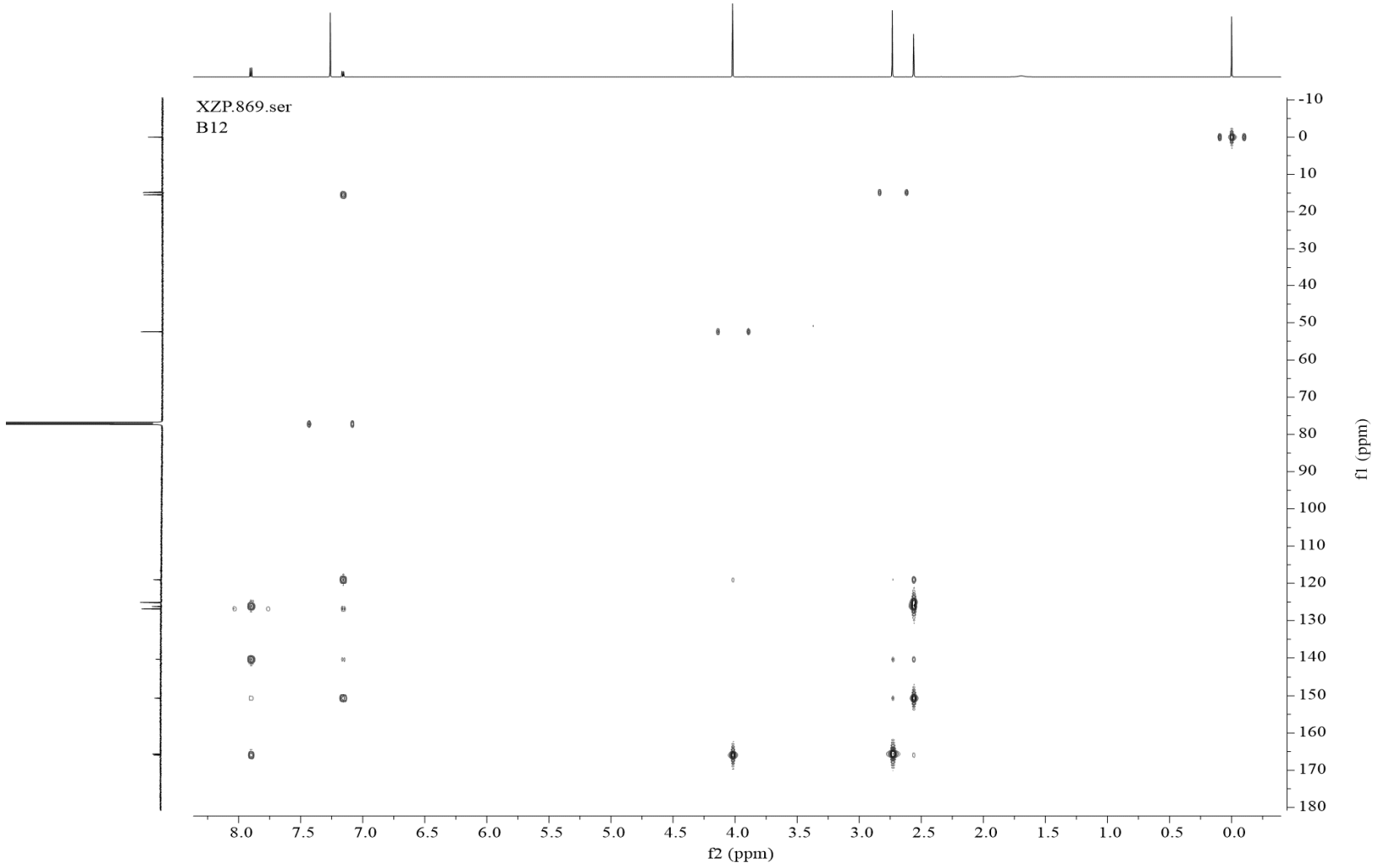


Fig. S40 ESIMS spectrum of compound **4**.