Supplementary Information

An NmrA-like enzyme-catalysed redox-mediated Diels-Alder cycloaddition with *anti*-selectivity

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Supplementary Tables

Supplementary Table 1 | Strains and plasmids in this study.

Strain or plasmid	Characteristics	Source
Strains		
E.coli TOP 10	General cloning host strain	Invitrogen
E.coli BL21 (DE3)	Protein production host strain	StrataGene
Penicillin citrinum ATCC 9849	Wild-type *P. citrinum* used in this study	ATCC
Δ*ctdP*	The *ctdP* knockout mutant of *P. citrinum* ATCC 9849	This study
Δ*ctdR*	The *ctdR* knockout mutant of *P. citrinum* ATCC 9849	This study
Δ*ctdO*	The *ctdO* knockout mutant of *P. citrinum* ATCC 9849	This study
Δ*ctdN*	The *ctdN* knockout mutant of *P. citrinum* ATCC 9849	This study
Plasmids		
Modified pETDuet-1	Amp^r, vector for protein expression	This study
pUC57	Amp^r, vector for gene cloning	Addgene
ctdP-KO-P	Amp^r, gene knockout plasmid used for Δ*ctdP* mutant construction	This study
ctdR-KO-P	Amp^r, gene knockout plasmid used for Δ*ctdR* mutant construction	This study
ctdO-KO-P	Amp^r, gene knockout plasmid used for Δ*ctdO* mutant construction	This study
pET-*ctdR*	Amp^r, vector for CtdR expression	This study
pET-*ctdO*	Amp^r, vector for CtdO expression	This study
pET-*malC*	Amp^r, vector for MalC expression	This study
pET-*ctdP*	Amp^r, vector for CtdP expression	This study
pET-*ctdP (Q118A)*	Amp^r, vector for CtdP (Q118A) expression	This study
pET-*ctdP (V133A)*	Amp^r, vector for CtdP (V133A) expression	This study
pET-*ctdP (L134A)*	Amp^r, vector for CtdP (L134A) expression	This study
pET-*ctdP (W160A)*	Amp^r, vector for CtdP (W160A) expression	This study
pET-*ctdP (Y161A)*	Amp^r, vector for CtdP (Y161A) expression	This study
pET-*ctdP (N164A)*	Amp^r, vector for CtdP (N164A) expression	This study
pET-*ctdP (F170A)*	Amp^r, vector for CtdP (F170A) expression	This study
pET-*ctdP (E173A)*	Amp^r, vector for CtdP (E173A) expression	This study
pET-*ctdP (S273A)*	Amp^r, vector for CtdP (S273A) expression	This study
pET-*ctdP (F277A)*	Amp^r, vector for CtdP (F277A) expression	This study
pET-*ctdP (Y269A)*	Amp^r, vector for CtdP (Y269A) expression	This study
pET-*ctdP (Y280A)*	Amp^r, vector for CtdP (Y280A) expression	This study
pET-*ctdP (Y280F)*	Amp^r, vector for CtdP (Y280F) expression	This study
pET-*ctdP (S340A)*	Amp^r, vector for CtdP (S340A) expression	This study
pET-*ctdP (P342A)*	Amp^r, vector for CtdP (P342A) expression	This study
pET-SUMO-*ctdP (Δ330-367)*	Amp^r, vector for SUMO-CtdP (Δ330-367) expression	This study
pET-SUMO-*ctdP (Δ335-367)*	Amp^r, vector for SUMO-CtdP (Δ335-367) expression	This study
pET-SUMO-*ctdP (Δ342-367)*	Amp^r, vector for SUMO-CtdP (Δ342-367) expression	This study
pET-SUMO-*ctdP (Δ345-367)*	Amp^r, vector for SUMO-CtdP (Δ345-367) expression	This study
pET-*BmGDH*	Amp^r, vector for BmGDH expression	This study

Supplementary Table 2 | Primers used in this study.

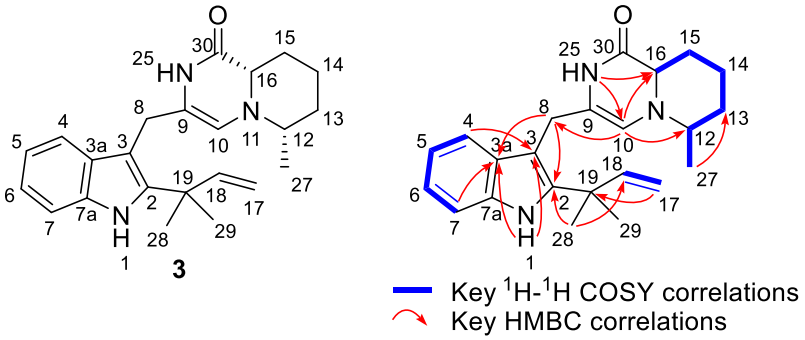
Primer	Sequence (5'-3')	Description
bar-R	TCATCGCAAGACCGGCAACAGGATTCAATC	For colony PCR verification mutant
bar-F	CATACCTTCTTAAGTTCGCCCTTCCTCCCT	
ctdP-up-F	ATGGCGGGTTCCTTTTGACTTAAGAGTCGC	For colony PCR verification of △*ctdP*
ctdP-dn-R	AGTCTGTCGCTTTGAGACTGGGAGCAGATG	
ctdO-up-F	GGGGGAAACCTGCGGAGCTTTTCAAGACTG	For colony PCR verification of △*ctdO*
ctdO-dn-R	GTGACTCCTGGAGGTAAGGACGGTCGGCAG	
ctdR-up-F	CTGATGTTGATTAGACCCAGCCTGGAGGTC	For colony PCR verification of △*ctdR*
ctdR-dn-R	CCAGGGTACCGTTCAGGGCATTCCAATCCG	
ctdN-up-F	TACATGGGGATCACCAGGAG	For colony PCR verification of △*ctdN*
ctdN-dn-R	CAACGAACTGTAATGGAGCG	
ctdN-Exp-F	CTTTAAGAAGGAGATATACCATGACCCAGGGTGTAAGAAA	Plasmid construction for CtdN expression
ctdN-Exp-R	TTAGTGATGGTGGTGGTGATGAGTCAAAAGGAACCCGCCATT	
ctdP-Exp-F	CTTTAAGAAGGAGATATACCATGACACACGAGATTAAAAC	Plasmid construction for CtdP expression
ctdP-Exp-R	TTAGTGATGGTGGTGGTGATGTTCACCAGGATCTTCTCTGAC	
ctdO-Exp-F	CTTTAAGAAGGAGATATACCATGACAATCCAACAAAAATC	Plasmid construction for CtdO expression
ctdO-Exp-R	TTAGTGATGGTGGTGGTGATGTGTTGTCAAGTTACCCTTA	
ctdR-Exp-F	CTTTAAGAAGGAGATATACCATGACTGTTGAAAGAAAGATTG	Plasmid construction for CtdR expression
ctdR-Exp-R	TAGTGATGGTGGTGGTGATGGGAAGCATTGAGACGCTTAAAA	
ctdP(Q118A)-Exp-F	TCGCATGCGCTGTCTGGCGGCAAATTTAACACCCCAGTTCTG	Plasmid construction for CtdP (Q118A) expression
ctdP(Q118A)-Exp-R	GCCGCCAGACAGCGCATGCGATGAGGGTGCCGAGCTGAACACGAC	
ctdP(V133A)-Exp-F	GTGAAAGCCTGGGGCGAGTCTTGGGGACGAGCTTGTCCCACA	Plasmid construction for CtdP (V133A) expression
ctdP(V133A)-Exp-R	AGACTCGCCCCAGGCTTTCACGTCCAGTGCTGGGGTGTTAAATTT	
ctdP(L134A)-Exp-F	GTGAAAGCCTGGGGCGAGTCTTGGGGACGAGCTTGTCCCACA	Plasmid construction for CtdP (L134A) expression
ctdP(L134A)-Exp-R	AGACTCGCCCCAGGCTTTCACGTCTGCAACTGGGGTGTTAAATTT	
ctdP(W160A)-Exp-F	TACTTCCAGAACTTTTTCATTCCATCTTTCGTGGCCGAGTTTGGTGGC	Plasmid construction for CtdP (W160A) expression
ctdP(W160A)-Exp-R	AATGAAAAAGTTCTGGAAGTATGCCGATGCCATGATCGGCGTGAAGCT	
ctdP(Y161A)-Exp-F	TTCCAGAACTTTTTCATTCCATCTTTCGTGGCCGAGTTTGGTGGCTTT	Plasmid construction for CtdP (Y161A) expression
ctdP(Y161A)-Exp-R	AATGAAAAAGTTCTGGAATGCCCACGATGCCATGATCGGCGTGAAGCT	
ctdP(N164A)-Exp-F	ATTCCATCTTTCGTGGCCGAGTTTGGTGGCTTTCCG	Plasmid construction for CtdP (N164A) expression
ctdP(N164A)-Exp-R	CTCGGCCACGAAAGATGGAATGAAAAATGCCTGGAAGTACCACGA	
ctdP(F170A)-Exp-F	GAGTTTGGTGGCTTTCCGTGGAATCAAGACGATGAA	Plasmid construction for CtdP (F170A) expression
ctdP(F170A)-Exp-R	CCACGGAAAGCCACCAAACTCGGCCACTGCAGATGGAATGAAAAA	
ctdP(E173A)-Exp-F	GGCTTTCCGTGGAATCAAGACGATGAAGGTTATCTGACTTTGCGT	Plasmid construction for CtdP (E173A) expression
ctdP(E173A)-Exp-R	ATCGTCTTGATTCCACGGAAAGCCACCAAATGCGGCCACGAAAGATGG	
ctdP(E173A)-Exp-F	GGCTTTCCGTGGAATCAAGACGATGAAGGTTATCTGACTTTGCGT	Plasmid construction for CtdP (F174A) expression
ctdP(F174A)-Exp-R	GTCTTGATTCCACGGAAAGCCACCTGCCTCGGCCACGAAAGATGGAAT	
ctdP(S273A)-Exp-F	TTCGCGTTCTATCAAATGCGTGATGGCGAACTCTTC	Plasmid construction for CtdP (S273A) expression
ctdP(S273A)-Exp-R	ACGCATTTGATAGAACGCGAATACCTGACGTGCCTCCTGGAGGTA	
ctdP(F277A)-Exp-F	GCGTTCTATCAAATGCGTGATGGCGAACTC	Plasmid construction for CtdP (F277A) expression
ctdP(F277A)-Exp-R	ATCACGCATTTGATAGAACGCTGCTACCTGACGTGACTCCTGGAGGTA	
ctdP(Y269A)-Exp-F	CTCCAGGAGTCACGTCAGGTATTCGCGTTCTATCAAATGCGTGAT	Plasmid construction for CtdP (Y269A) expression
ctdP(Y269A)-Exp-R	GAATACCTGACGTGACTCCTGGAGTGCAGGACGGTCGGCAGGCATATC	
ctdP(P280A)-Exp-F	CGTGATGGCGAACTCTTCGGTAATGGAATTACGGAAAAAAGA	Plasmid construction for CtdP (Y280A and Y280F) expression
ctdP(P280A)-Exp-R	CCGAAGAGTTCGCCATCACGCATTTGTGCGAACGCGAATACC	
ctdP(P280F)-Exp-R	ACCGAAGAGTTCGCCATCACGCATTTGGAAGAACGCGAATAC	
ctdP(S340A)-Exp-F	ATCGTCAGAGAAGATCCTGGTGAAcATCACCACCACCATCAC	Plasmid construction for CtdP (S340A) expression
ctdP(S340A)-Exp-R	ACCAGGATCTTCTCTGACGATGGGACCTGCTCTCTCGATCTT	
ctdP(P342A)-Exp-F	GAAGATCCTGGTGAAcATCACCACCACCATCACTAATGA	Plasmid construction for CtdP (P342A) expression
ctdP(P342A)-Exp-R	TTCACCAGGATCTTCTCTGACGATTGCACCCGATCTCTCGATCTT	
ctdP(Δ330-367)-Exp-F	GAGGCTCACAGAGAACAGATTGGTGGATCCACACACGAGATTAAAACAATCTCC	Plasmid construction for Sumo-CtdP(Δ330-367)-expression
ctdP(Δ330-367)-Exp-R	CTCAGCTTCCTTTCGGGCCTCGAGTGCGGCCGCTTATGCCCGGCAATGCCTTTCGAAC	
ctdP(Δ335-367)-Exp-R	AACTCAGCTTCCTTTCGGGCCTCGAGTGCGGCCGCTTAGGAAGTTTTGTTTGCCCGGC	Plasmid construction for Sumo-CtdP(Δ335-367)-expression
ctdP(Δ342-367)-Exp-R	CTCAGCTTCCTTTCGGGCCTCGAGTGCGGCCGCTTAACCCGATCTCTCGATCTTCTCG	Plasmid construction for Sumo-CtdP(Δ342-367)-expression
ctdP(Δ348-367)-Exp-R	ACTCAGCTTCCTTTCGGGCCTCGAGTGCGGCCGCTTAATCTTCTCTGACGATGGGACC	Plasmid construction for Sumo-CtdP(Δ348-367)-expression
BmGDH-Exp-F	CTTTAAGAAGGAGATATACCATGTATAAAGATTTAGAAGGAA	Plasmid construction for BmGDH expression
BmGDH-Exp-R	TTAGTGATGGTGGTGGTGATgTCCGCGTCCTGCTTGGAATGA	
pET-Exp-F	CATCACCACCACCATCACTAATGATAATTTGAACGCCAGCACA	Plasmid construction for proteins expression
pET-Exp-R	GGTATATCTCCTTCTTAAAGTTAAACAAAATTATTTCTAGAGGGG	

Supplementary Table 3 | BLASTP CtdN homologs in NCBI databases.

Description	Max Score	Total Score	Query Cover	E value	Per. Ident	Accession
Short-chain dehydrogenase/reductase **PhqE** [*Penicillium fellutanum*]	296	296	99%	$2e^{-100}$	50.57%	L0E2Z4.1
Short-chain dehydrogenase/reductase **MalC** [*Malbranchea aurantiaca*]	251	251	97%	$1e^{-82}$	45.77%	L0E4F8.1
Short-chain dehydrogenase/reductase **ATR9** [*Stachybotrys chlorohalonata* IBT 40285]	169	169	95%	$9e^{-51}$	37.89%	A0A084R1K2.1
Short-chain dehydrogenase/reductase **UcsE** [*Acremonium* sp.]	142	142	95%	$7e^{-40}$	30.08%	A0A411KUU9.1
Short-chain dehydrogenase/reductase **Fsr5** [*Fusarium fujikuroi* IMI 58289]	127	127	97%	$3e^{-34}$	31.82%	S0DRI2.1
Uncharacterized oxidoreductase **YkvO** [*Bacillus subtilis subsp. subtilis str*. 168]	87.8	87.8	95%	$2e^{-19}$	27.03%	O31680.1
3alpha-hydroxysteroid dehydrogenase [*Ruminococcus gnavus* ATCC 29149]	67.8	67.8	94%	$4e^{-12}$	25.77%	A7B3K3.1
Tropinone reductase homolog **P29X** [*Datura stramonium*]	67.4	67.4	97%	$5e^{-12}$	26.60%	P50165.1
Dihydroanticapsin 7-dehydrogenase **BacC** [*Bacillus subtilis*]	65.5	65.5	94%	$2e^{-11}$	26.54%	Q8KWT4.1
Tropinone reductase **TR-II** [*Hyoscyamus niger*]	64.7	64.7	95%	$5e^{-11}$	25.77%	P50164.1
Noroxomaritidine/norcraugsodine reductase **NorRed** [*Narcissus pseudonarcissus*]	64.3	64.3	94%	$6e^{-11}$	27.84%	A0A1A9TAK5.1
Tropinone reductase **TR-I** [*Datura stramonium*]	63.2	63.2	94%	$2e^{-10}$	25.95%	P50162.1
3alpha-hydroxy bile acid-CoA-ester 3-dehydrogenase 1/3 [*Clostridium scindens*]	62.4	62.4	95%	$2e^{-10}$	25.97%	P07914.3
Peroxisomal trans-2-enoyl-CoA reductase [*Cavia porcellus*]	40.4	40.4	25%	0.010	33.80%	Q9JIF5.1
Peroxisomal trans-2-enoyl-CoA reductase [*Pongo abelii*]	39.7	39.7	29%	0.017	29.76%	Q5RCH8

Supplementary Table 4 | BLASTP CtdP homologs in NCBI databases.

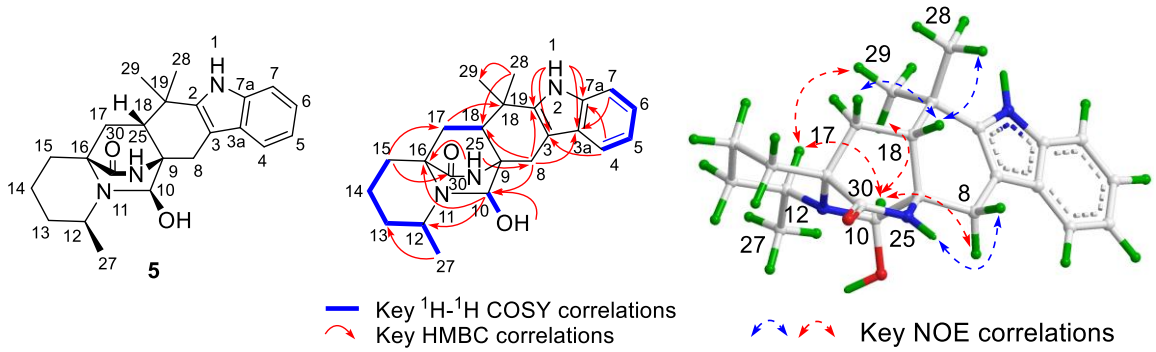
Description	Max Score	Total Score	Query Cover	E value	Per. Ident	Accession
NmrA-like family domain-containing oxidoreductase **HimF** [*Aspergillus japonicus*]	266	266	85%	$3e^{-86}$	45.62%	A0A2Z5TWF0.1
NmrA-like family domain-containing oxidoreductase **LnaB** [*Aspergillus flavus* NRRL3357]	245	245	85%	$1e^{-77}$	41.69%	B8NU00.1
NmrA-like family domain-containing oxidoreductase **PtmS** [*Penicillium simplicissimum*]	207	207	88%	$5e^{-63}$	35.87%	A0A140JWT5.1
NmrA-like family domain-containing oxidoreductase **PhqG** [*Penicillium fellutanum*]	200	200	85%	$2e^{-60}$	38.56%	L0E2U6.1
NmrA-like family domain-containing oxidoreductase **NotA'** [*Aspergillus versicolor*]	195	195	87%	$3e^{-58}$	34.97%	L7WRQ4.1
NmrA-like family domain-containing protein **DDB_G0286605** [*Dictyostelium discoideum*]	104	104	74%	$2e^{-24}$	29.02%	Q54LJ8.1
NmrA-like family domain-containing protein 1 [*Bos taurus*]	82.0	82.0	74%	$2e^{-16}$	27.30%	Q0VCN1.1
NmrA-like family domain-containing protein 1 [*Gallus gallus*]	81.3	81.3	67%	$4e^{-16}$	26.88%	Q5ZID0.1
NmrA-like family domain-containing protein 1 [*Mus musculus*]	80.5	80.5	45%	$8e^{-16}$	31.64%	Q8K2T1.1
NmrA-like family domain-containing protein 1 [*Homo sapiens*]	78.6	78.6	42%	$3e^{-15}$	33.33%	Q9HBL8.1
NmrA-like family domain-containing protein 1 [*Rattus norvegicus*]	40.0	40.0	13%	0.007	42.31%	P86172.1
CtdP aligned sequence with MalC and PhqE						
Short-chain dehydrogenase/reductase **MalC** [*Malbranchea aurantiaca*]	24.6	41.2	30%	0.004	30.00%	L0E4F8.1
Short-chain dehydrogenase/reductase **PhqE** [*Penicillium fellutanum*]	16.2	16.2	6%	2.0	20.83%	L0E2Z4.1



Supplementary Table 5 | NMR Data of compound 3 (δ in ppm, J in Hz)[a].

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC
1(NH)		10.53 s				C2, 3, 3a
2			140.7	C		
3			104.5	C		
3a			129.1	C		
4		7.32 d (7.5)	117.7	CH	H5	C3, 6, 7a
5		6.92 dd (7.5, 7.5)	118.3	CH	H4, 6	C3a, 7
6		7.00 dd (7.5, 7.5)	120.4	CH	H5, 7	C4, 7a
7		7.32 d (7.5)	110.9	CH	H6	C3a, 5
7a			134.7	C		
8		3.49 s	25.2	CH_2		C2, 3a, 10
9			115.9	C		
10		4.95 s	112.8	CH		C3, 12, 16
12		2.46 m	54.4	CH	H13, 27	
13	a	1.41 m	32.5	CH_2	H12, 14	
	b	0.98 m			H12, 14	
14	a	1.68 m	23.1	CH_2	H13, 15	C12
	b	1.30 m			H13, 15	
15	a	1.75 m	24.6	CH_2	H14	C13
	b	1.35 m			H14	
16		3.01 m	60.7	CH		
17	a	5.05 dd (17.4, 1.1)	111.1	CH_2	H18	C19
	b	5.02 dd (10.5, 1.1)			H18	
18		6.16 dd (17.4, 10.5)	146.0	CH	H17	C28, 29
19			38.9	C		
25 (NH)		9.03 s				
27		0.75 d (6.3)	20.1	CH_3	H12	C13
28		1.48 s	27.5	CH_3		C2, 18, 29
29		1.48 s	27.5	CH_3		C2, 18, 28
30			166.8	C		

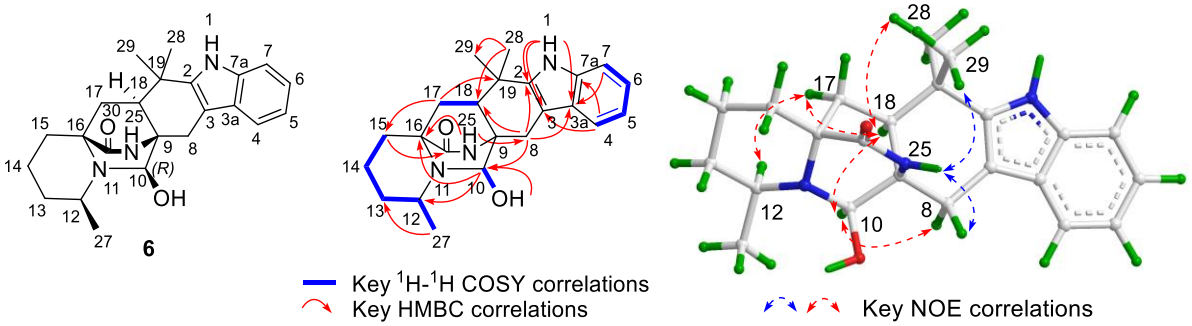
[a]Measured in DMSO-d_6, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.



Supplementary Table 6 | NMR Data of compound 5 (δ in ppm, J in Hz)[a]

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC	NOESY
1		7.83 s		NH		C2, 3, 3a, 7a	
2			140.0	C			
3			104.3	C			
3a			127.1	C			
4		7.48 d (7.8)	118.6	CH	H5	C3, 6, 7a	
5		7.18 dd (7.8, 7.8)	119.7	CH	H4, 6	C3a, 7	
6		7.11 dd (7.8, 7.8)	122.2	CH	H5, 7	C4, 7a	
7		7.32 d (7.8)	110.7	CH	H6	C3a, 5	
7a			136.5	C			
8	α	3.78 d (15.5)	26.8	CH_2		C2, 3a, 10, 18	H10
	β	2.53 d (15.5)				C2, 3a, 10, 18	H25
9			58.4	C			
10		4.44 d (7.6)	81.5	CH	OH	C12, 16	H8α, 17, 29
12		3.01 m	50.9	CH	H13, 27		H10, 29
13	a	1.64 overlapped	35.1	CH_2	H12, 14	C15	
	b	1.18 m			H12, 14		
14	a	1.73 overlapped	19.8	CH_2	H13, 15		
	b	1.50 m			H13, 15		
15	a	2.07 m	29.6	CH_2	H14	C17, 30	
	b	1.73 overlapped			H14	C13	
16			58.3	C			
17	α	2.43 m	24.5	CH_2	H18	C19, 30	H12
	β	1.60 overlapped			H18	C30	
18		2.41 m	48.1	CH	H17	C8, 10, 28, 29	H28
19			34.9	C			
25		5.91 s		NH			H8β
27		1.12 d (6.1)	23.1	CH_3	H12	C13	
28		1.38 s	31.1	CH_3		C3, 18, 29	H18
29		1.42 s	27.1	CH_3		C3, 18, 28	H10, 12
30			175.0	C			
OH		1.57 d (7.6)			H10	C10	

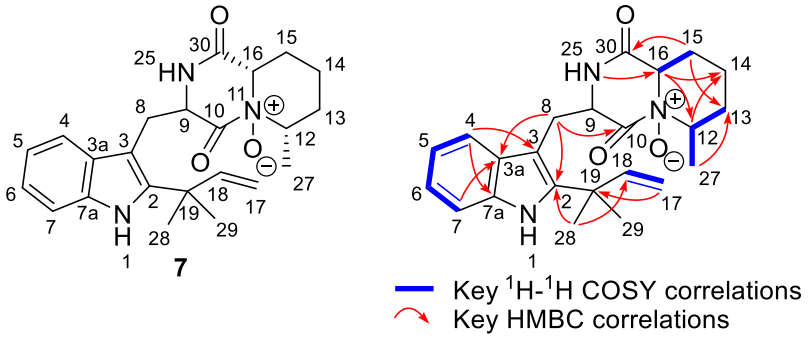
[a]Measured in $CDCl_3$, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.



Supplementary Table 7 | NMR Data of compound 6 (δ in ppm, J in Hz)[a].

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC	NOESY
1		9.10 s		NH		C2, 3, 3a	
2			142.5	C			
3			104.6	C			
3a			128.4	C			
4		7.63 d (7.7)	118.7	CH	H5	C3, 6, 7a	
5		7.08 dd (7.7, 7.7)	119.6	CH	H4, 6	C3a, 7	
6		7.01 dd (7.7, 7.7)	121.9	CH	H5, 7	C4, 7a	
7		7.31 d (7.7)	111.5	CH	H6	C3a, 5	
7a			137.5	C			
8	β	2.99 d (17.4)	27.9	CH_2		C2, 3a, 18	H25
	α	2.91 d (17.4)				C2, 10	H10
9			57.6	C			
10		3.87 d (8.1)	91.0	CH	OH	C12	H8α, 18
12		2.81 m	53.1	CH	H13, 27	C10, 16	H17α
13	a	1.64 m	35.7	CH_2	H12, 14	C15	
	b	1.13 m			H12, 14		
14	a	1.61 overlapped	20.0	CH_2	H13, 15		
	b	1.54 m			H13, 15		
15	a	1.84 m	30.2	CH_2	H14	C17	
	b	1.61 overlapped			H14	C13	
16			58.9	C			
17	α	2.62 m	24.7	CH_2	H18	C19, 30	H12, 18
	β	1.28 m			H18		
18		1.97 m	44.2	CH	H17	C8, 29	H28
19			35.0	C			
25		6.33 s		NH			H8β, 29
27		1.15 d (6.1)	23.4	CH_3	H12	C13	
28		1.28 s	28.4	CH_3		C3, 18, 29	H18
29		1.17 s	24.7	CH_3		C3, 18, 28	H25
30			174.9	C			
OH		2.61 overlapped			H10	C10	

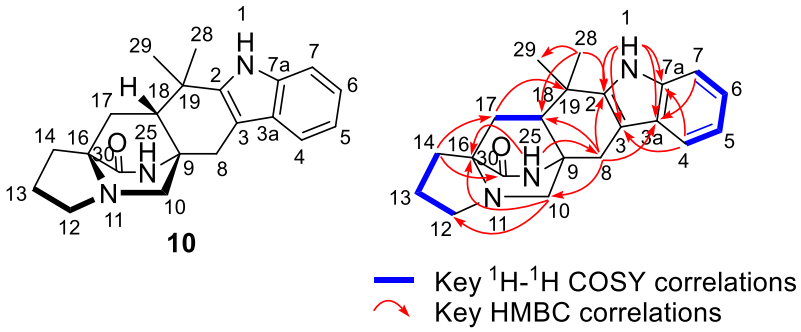
[a]Measured in CD_3CN, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.



Supplementary Table 8 | NMR Data of compound 7 (δ in ppm, J in Hz)[a].

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC
1		10.64 s		NH		C2, 3, 3a
2			141.3	C		
3			102.5	C		
3a			129.4	C		
4		7.29 d (7.8)	117.5	CH	H5	C3, 6, 7a
5		6.92 dd (7.8, 7.8)	118.4	CH	H4, 6	C3a, 7
6		7.02 dd (7.8, 7.8)	120.5	CH	H5, 7	C4, 7a
7		7.31 d (7.8)	110.9	CH	H6	C3a, 5
7a			134.6	C		
8		3.98 s	33.4	CH_2		C2, 3a, 10
9		Missing	Missing	C		
10			172.2	C		
12		4.00 overlapped	48.5	CH	H13, 27	C14
13		1.62 overlapped	27.5	CH_2	H12	
		1.52 overlapped				
14	a	1.63 overlapped	15.9	CH_2		
	b	1.51 overlapped				
15	a	2.00 m	24.7	CH_2	H16	C2, 12
	b	1.56 m				
16		4.91 m	51.2	CH		
17	a	5.06 d (17.4)	111.2	CH_2	H18	C19
	b	5.03 dd (10.6)				
18		6.08 dd (17.4, 10.6)	145.9	CH	H17	C2, 28/29
19			39.5	C		
25		8.09 s		NH		C16
27		1.21 d (7.0)	21.5	CH_3	H12	C13
28		1.44 s	27.5	CH_3		C2, 18
29		1.44 s	27.5	CH_3		C2, 18
30			171.7	C		

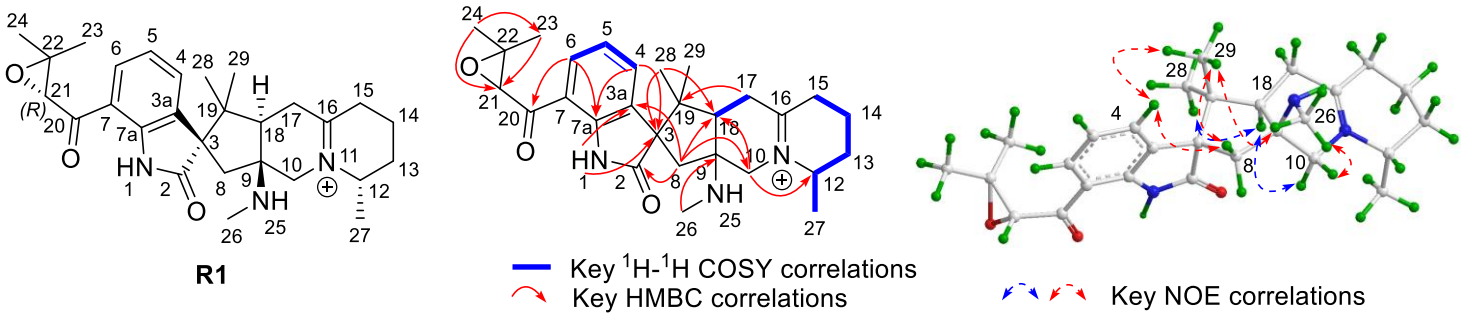
[a]Measured in DMSO-d_6, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.



Supplementary Table 9 | NMR Data of compound 10 (δ in ppm, J in Hz)[a].

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC	NOESY
1		9.12 s		NH			
2			142.9	C			
3			104.3	C			
3a			128.2	C			
4		7.40 d (7.7)	118.5	CH	H5	C3, 6, 7a	H8α
5		7.01 dd (7.7, 7.7)	119.7	CH	H4, 6	C3a, 7	
6		7.02 dd (7.7, 7.7)	121.9	CH	H5, 7	C4, 7a	
7		7.31 d (7.7)	111.5	CH	H6	C3a, 5	H1
7a			137.6	C			
8	α	2.90 d (17.0)	29.0	CH_2		C2, 3a, 18	H4, 25
	β	2.82 d (17.0)				C2, 3a, 10	H10β, 18
9			56.4	C			
10	α	3.07 d (10.1)	62.5	CH_2		C12, 16	H12
	β	2.62 d (10.1)				C8, 12, 16, 18	H8β
12	a	3.02 m	53.7	CH_2	H13		H10α
	b	2.31 dd (16.6, 8.5)			H13		
13	a	1.83 m	23.5	CH_2	H12, 14	C15	
	b	1.80 m			H12, 14	C27	
14	a	2.42 m	28.0	CH_2	H13	C12	
	b	1.36 m			H13	C16	
16			65.8	C			
17	β	2.06 m	32.2	CH_2	H18	C15, 19, 30	
	α	1.89 m			H18	C15, 19, 30	
18		2.17 overlapped	46.9	CH	H17	C8, 10, 16, 28, 29	H8β, 28
19			35.1	C			
25		6.44 s		NH		C10, 16	H8α, 29
28		1.26 s	28.0	CH_3		C2, 18, 29	H18
29		1.16 s	24.5	CH_3		C2, 18, 28	H25
30			174.2	C			

[a]Measured in CD_3CN, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.



Supplementary Table 10 | NMR Data of compound R1 (δ in ppm, J in Hz)[a].

Position		^{1}H	^{13}C		^{1}H-^{1}H COSY	HMBC	NOESY
1		9.64 s		NH		C3, 3a	
2			182.5	C			
3			64.4	C			
3a			131.8	C			
4		7.46 d (7.7)	131.1	CH	H5	C3, 6, 7a	H8β, 29
5		7.10 dd (7.7, 7.7)	121.0	CH	H4, 6	C3a, 7	
6		7.76 d (7.7)	128.0	CH	H5	C4, 7a	
7			116.8	C			
7a			144.0	C			
8	β	2.34 d (14.8)	32.9	CH_2		C2, 3a, 10, 18	H4, 29
	α	2.05 d (14.8)				C2, 3a, 10, 19	H10, 12
9			76.0	C			
10	β	4.00 m	57.9	CH_2			H18
	α	2.82 m				C12, 18	H26
12		2.81 m	63.2	CH	H13, 27	C14	
13	a	1.85 overlapped	30.7	CH_2	H12, 14		
	b	1.69 overlapped			H12, 14		
14		1.86 overlapped	20.4	CH_2	H13, 15	C12, 16	
		1.69 overlapped					
15	a	2.26 overlapped	27.7	CH_2	H14, 16		
	b	2.24 overlapped			H14, 16	C13	
16		missing	missing	C			
17	a	2.42 overlapped	38.9	CH_2	H18		
	b	1.66 overlapped			H18	C19	
18		3.05 m	52.5	CH	H17	C10	H-28
19			47.3	C			
20			194.9	C			
21		4.02 s	64.4	CH		C23, 24	
22			61.6	C			
23		1.60 s	24.4	CH_3		C21, 24	
24		1.25 s	18.8	CH_3		C21, 23	
26		2.47 s	30.7	CH_3		C9	H29
27		1.35 d (3.5)	20.4	CH_3	H12	C13	
28		0.72 s	23.5	CH_3		C3, 18, 29	H18
29		1.06 s	22.1	CH_3		C3, 18, 28	H4, 8β, 26

[a]Measured in $CDCl_3$, 600 MHz for ^{1}H and 150 MHz for ^{13}C NMR. Overlapped signals are reported without designating multiplicity.

Supplementary Table 11 | Crystal data and structure refinement for compound 5.

Empirical formula	$C_{23}H_{29}N_3O_2$
Formula weight	379.49
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.17410(10)
b/Å	22.2451(2)
c/Å	11.6697(2)
α/°	90
β/°	106.2410(10)
γ/°	90
Volume/Å^3	2286.50(5)
Z	4
ρ_{calc}g/cm^3	1.102
μ/mm^{-1}	0.562
F(000)	816.0
Crystal size/mm^3	0.38 × 0.28 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.89 to 149
Index ranges	$-11 \le h \le 11$, $-22 \le k \le 27$, $-14 \le l \le 14$
Reflections collected	25927
Independent reflections	7483 [R_{int} = 0.0289, R_{sigma} = 0.0242]
Data/restraints/parameters	7483/1/582
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0980
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0984
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22
Flack parameter	0.04(9)
CCDC number	2127333

Supplementary Table 12 | Crystal data and structure refinement for compound 10.

Empirical formula	$C_{23}H_{29}N_3O_2$
Formula weight	379.49
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.17410(10)
b/Å	22.2451(2)
c/Å	11.6697(2)
α/°	90
β/°	106.2410(10)
γ/°	90
Volume/Å3	2286.50(5)
Z	4
ρcalcg/cm3	1.102
μ/mm-1	0.562
F(000)	816.0
Crystal size/mm3	0.38 × 0.28 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.89 to 149
Index ranges	$-11 \leq h \leq 11$, $-22 \leq k \leq 27$, $-14 \leq l \leq 14$
Reflections collected	25927
Independent reflections	7483 [R_{int} = 0.0289, R_{sigma} = 0.0242]
Data/restraints/parameters	7483/1/741
Goodness-of-fit on F2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0344, wR2 = 0.0942
Final R indexes [all data]	R1 = 0.0348, wR2 = 0.0946
Largest diff. peak/hole / e Å-3	0.26/-0.21
Flack parameter	0.05(9)
CCDC number	2127332

Supplementary Table 13 | Crystallographic data collection and structure refinement statistics.

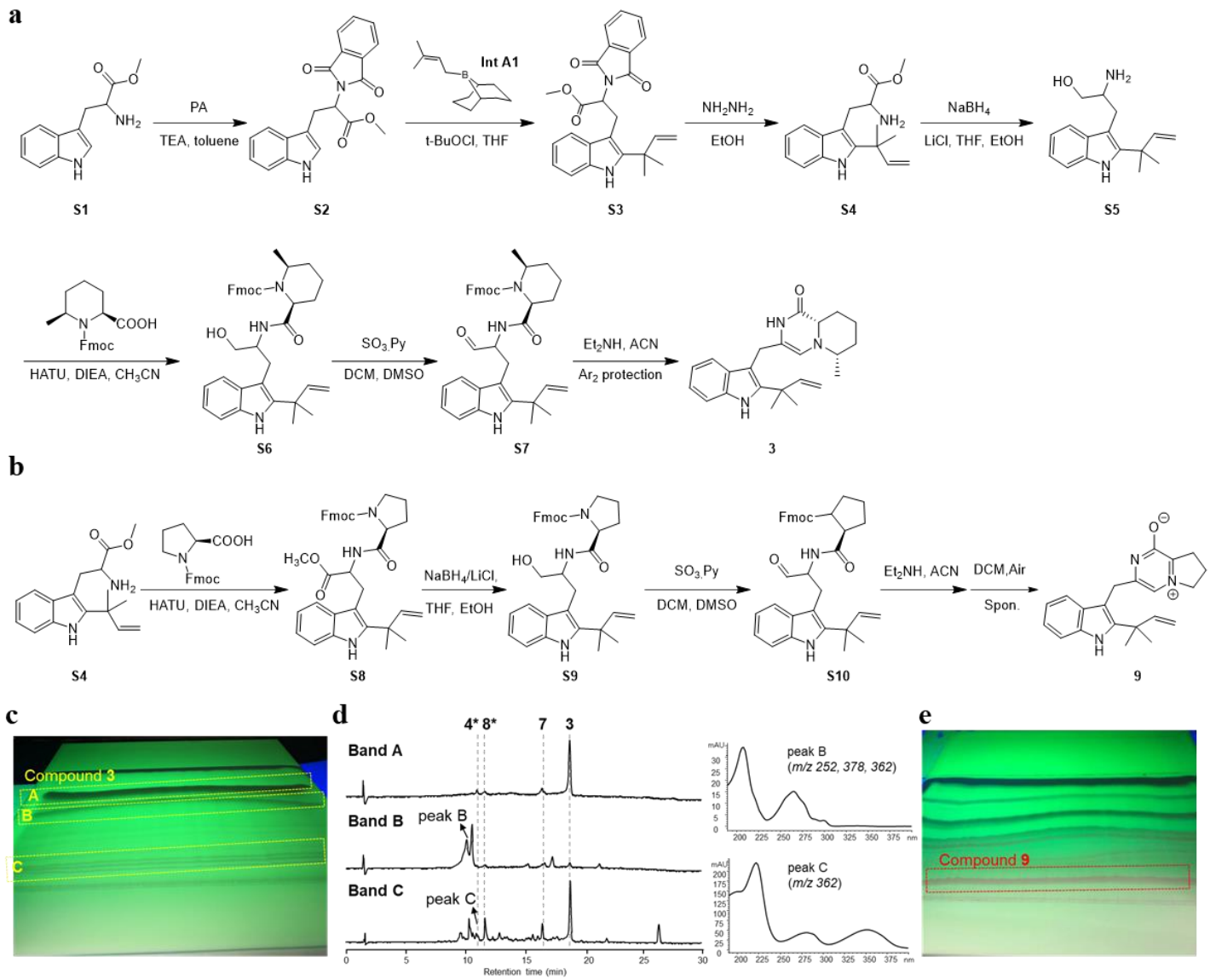
	SeMet CtdP
PDB code	7UF8
Data Collection*	
Space group	P 6_1 2 2
Cell Dimensions	
a, *b*, *c* (Å)	166.8, 166.8, 195.4
α, β, γ (º)	90, 90, 120
Wavelength (Å)	0.979
Resolution range (Å)	48.14 - 2.5 (2.589 - 2.5)
R_{meas}(%)	18.45 (3.161)
$I / \sigma I$	24.52 (2.07)
Completeness (%)	99.77 (99.18)
Redundancy	39.8 (39.3)
Refinement	
Resolution range (Å)	48.14 - 2.5
No. Reflections	55726
R_{work} / R_{free}	0.214 / 0.245
No. Atoms	
Protein	10397
Ligand	462
Water	1325
B-factors (Å^2)	
Protein	71.97
Ligand	74.51
Water	58.56
R.M.S. deviations	
Bond lengths (Å)	0.011
Bond angles (º)	1.26

***Values in parentheses are for highest-resolution shell**

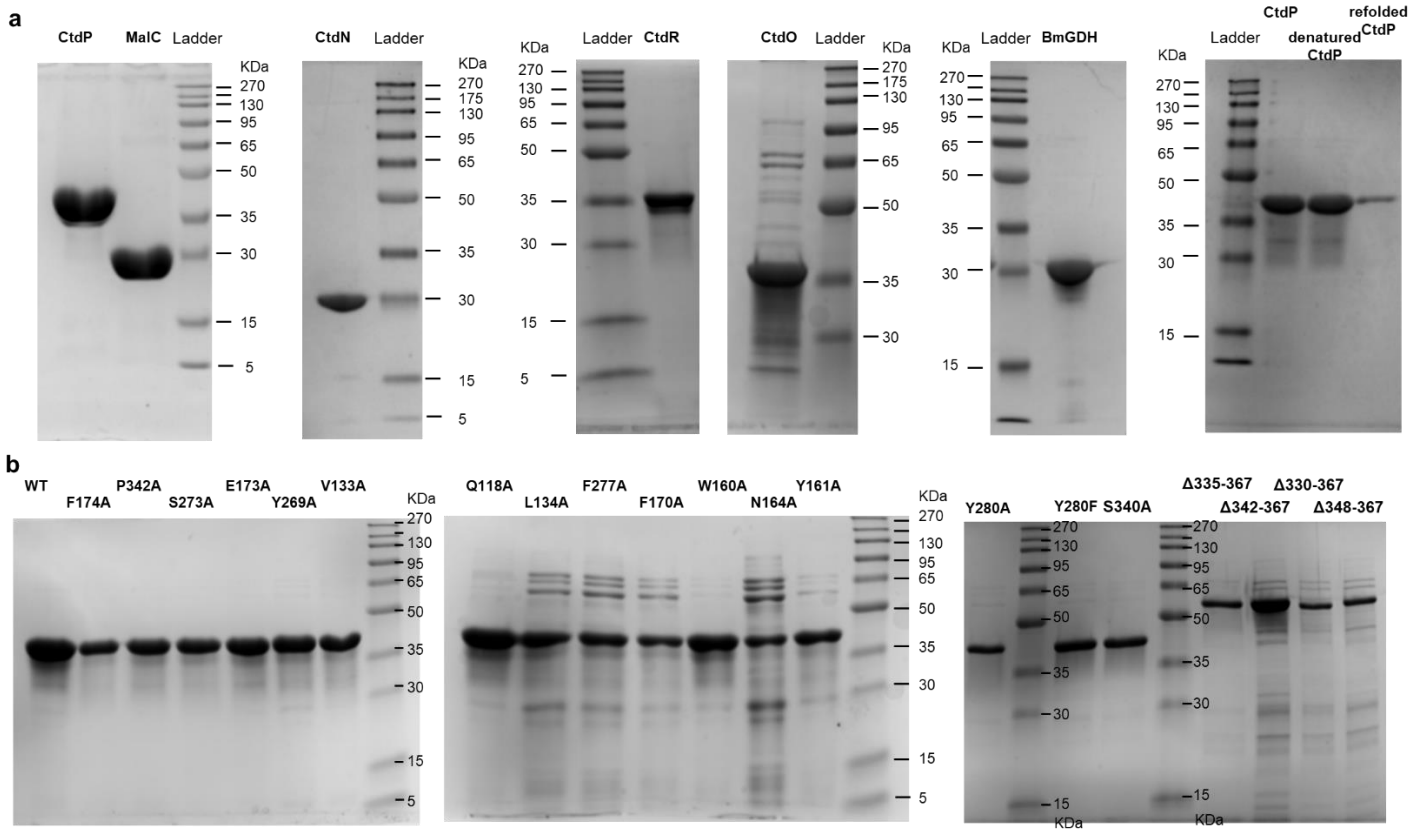
Supplementary Table 14 | Structural homologs of CtdP identified by DALI server[1].

No	Protein	PDB-Chain	Z score	rmsd	Number of structurally equivalent residues	Total number of amino acids	%identity
1	NADP(H) sensor HSCARG protein (*Homo sapiens*)	2exx-A	31.8	2	290	305	24
2	NmrA-like family domain containing protein 1 (*Homo sapiens*)	2wmd-A	31.9	2.1	289	295	24
3		2wm3-A	31.8	2.1	289	296	24
4	NmrA-like family domain containing protein 1	3dxf-A	31.5	2.1	288	292	24
5		3e5m-A	31.4	2	287	294	24
6		3e5m-B	31.1	2	287	295	24
7	NmrA (*Aspergillus nidulans*)	1k6i-A	30.2	2.6	294	318	20
8	NmrA	1xgk-A	30.2	2.6	295	325	21
9	NmrA-like family domain containing protein 1	3dxf-B	30.1	2.1	280	282	24
10	NmrA	1k6j-B	30.1	2.7	296	321	20
11		1ti7-A	30	2.6	294	324	20
12		2vuu-A	29.8	2.7	294	318	20
13		2vus-E	29.8	2.9	297	318	20
14		2vus-D	29.8	2.9	297	318	20
15		2vus-B	29.7	2.7	294	318	20
16		2vuu-F	29.7	2.7	294	318	20
17		2vus-F	29.7	2.7	294	318	20
18		2vuu-G	29.7	2.7	294	319	20
19		2vuu-E	29.7	2.7	294	318	20
20		2vus-G	29.7	2.7	294	318	20
21		1k6x-A	29.6	2.6	293	324	21
22		2vuu-D	29.6	2.7	295	319	20
23		1k6j-A	29.5	2.6	294	322	21
24		2vut-G	29.5	2.8	295	319	20
25		2vut-D	29.4	2.8	294	320	20
26		2vuu-B	29.4	2.8	293	319	20
27		2vus-A	29.3	2.6	291	318	21
28		2vus-C	29.2	2.6	292	318	21
29		2vuu-C	29.2	2.6	292	318	21
30		2vus-H	29.1	2.6	292	318	21
31		2vuu-H	29.1	2.7	292	319	21
32		2vut-F	29.1	2.6	291	318	21
33		2vut-A	29.1	2.7	293	318	21
34		2vut-C	29.1	2.6	291	318	21
35		2vut-E	29.0	2.6	291	318	21
36		2vut-H	29.0	2.7	292	319	21
37	NmrA-like protein KstA11 (*Micromonospora sp.* TP-A0468)	5f5n-A	28.9	2.5	281	289	26

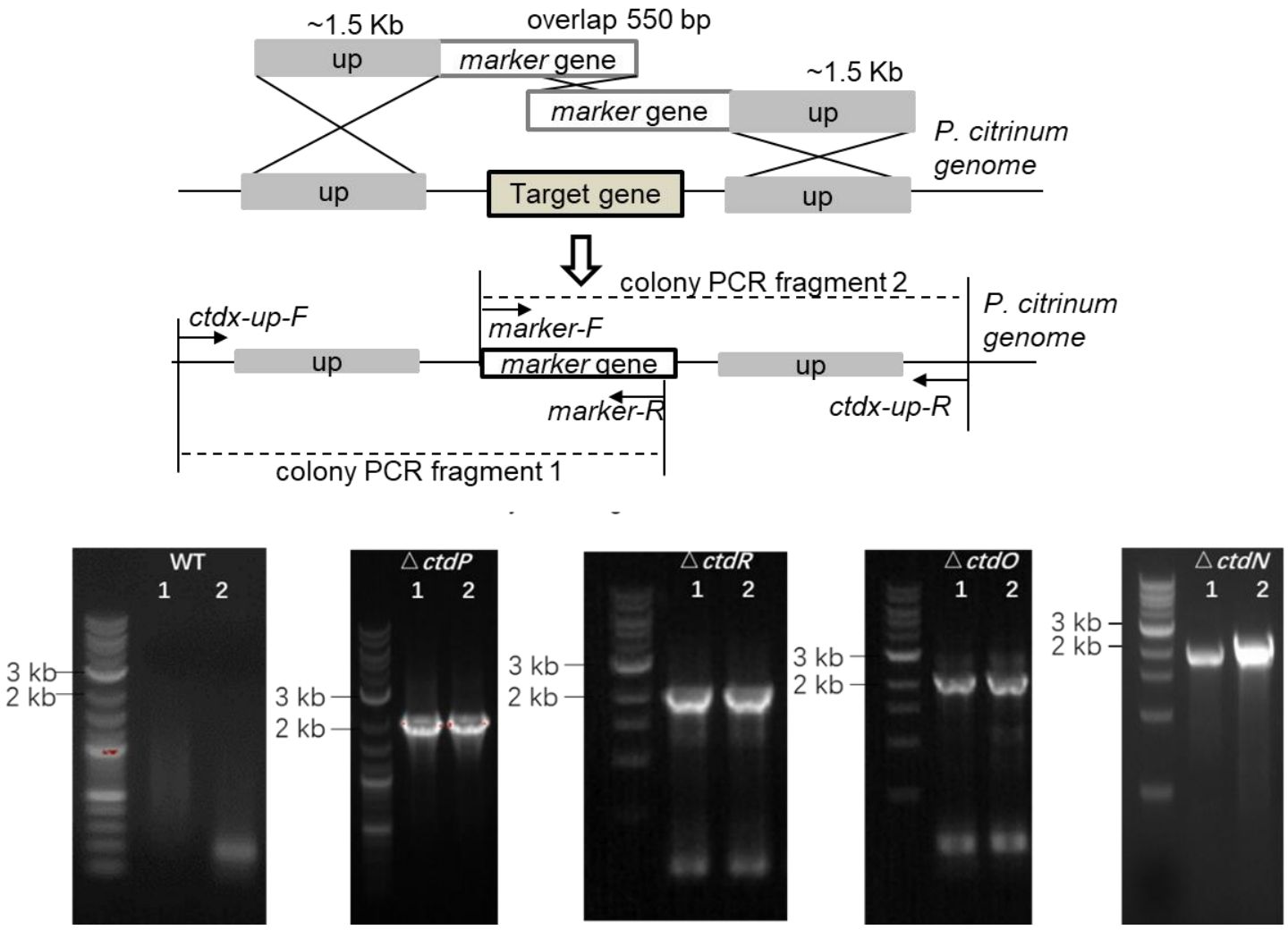
Supplementary Figures



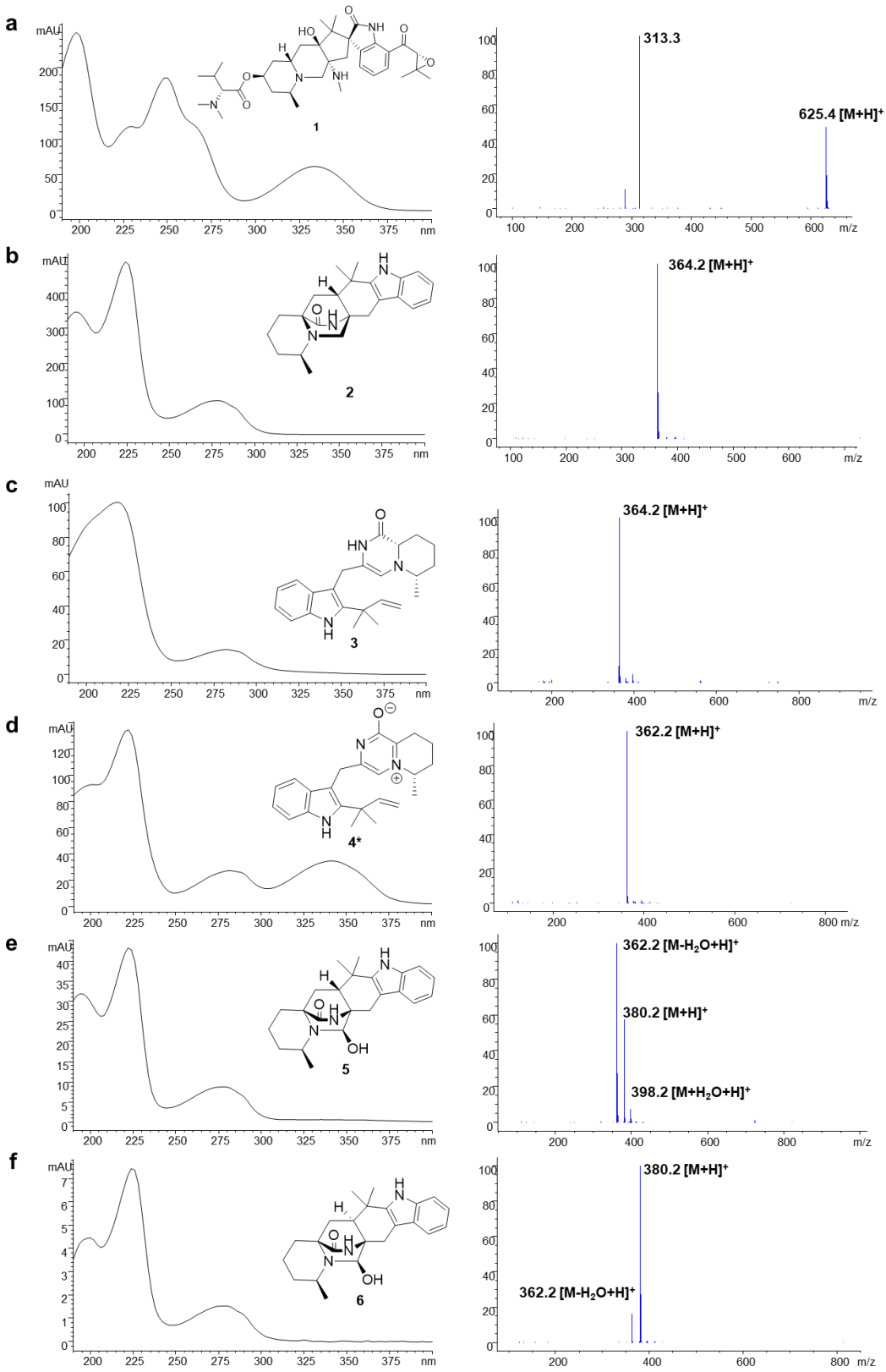
Supplementary Fig. 1 | **Biomimetic synthesis of the CtdP and MalC substrates. a**, Compound **3** synthetic pathway. **b**, Compound **9** synthetic pathway. **c**, Thin-layer chromatography (TLC) purification of compound **3** after the reaction from **S7**. **d**, LCMS analysis of bands A-C in **c**. Band A is pure **3**, while band C is presumed to be tautomerized to major **3** and proposed to contain compound **4** based on its UV and MS data. **e**, TLC purification of compound **9** after the reaction from **S10**. The symbol * represents the compound identified by MS and UV spectra.



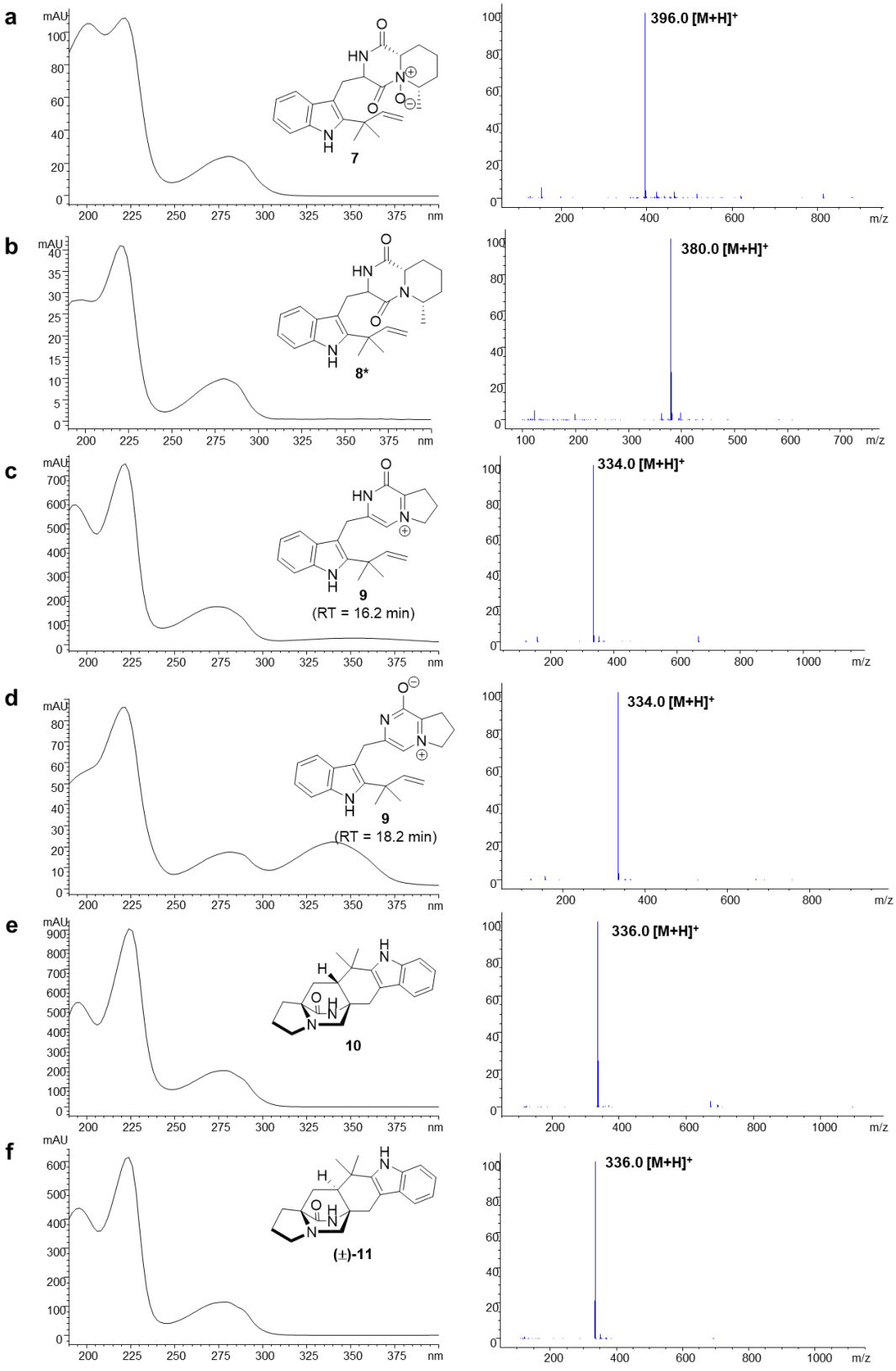
Supplementary Fig. 2 | SDS-PAGE (12%) analysis of purified proteins. a. *C*-His-tagged proteins of CtdP, MalC, CtdN, CtdR, CtdO, BmGDH, and refolded CtdP enzymes. **b**. *C*-His-tagged proteins of CtdP mutants. Experiments in **a** and **b** were repeated independently with similar results for three times.



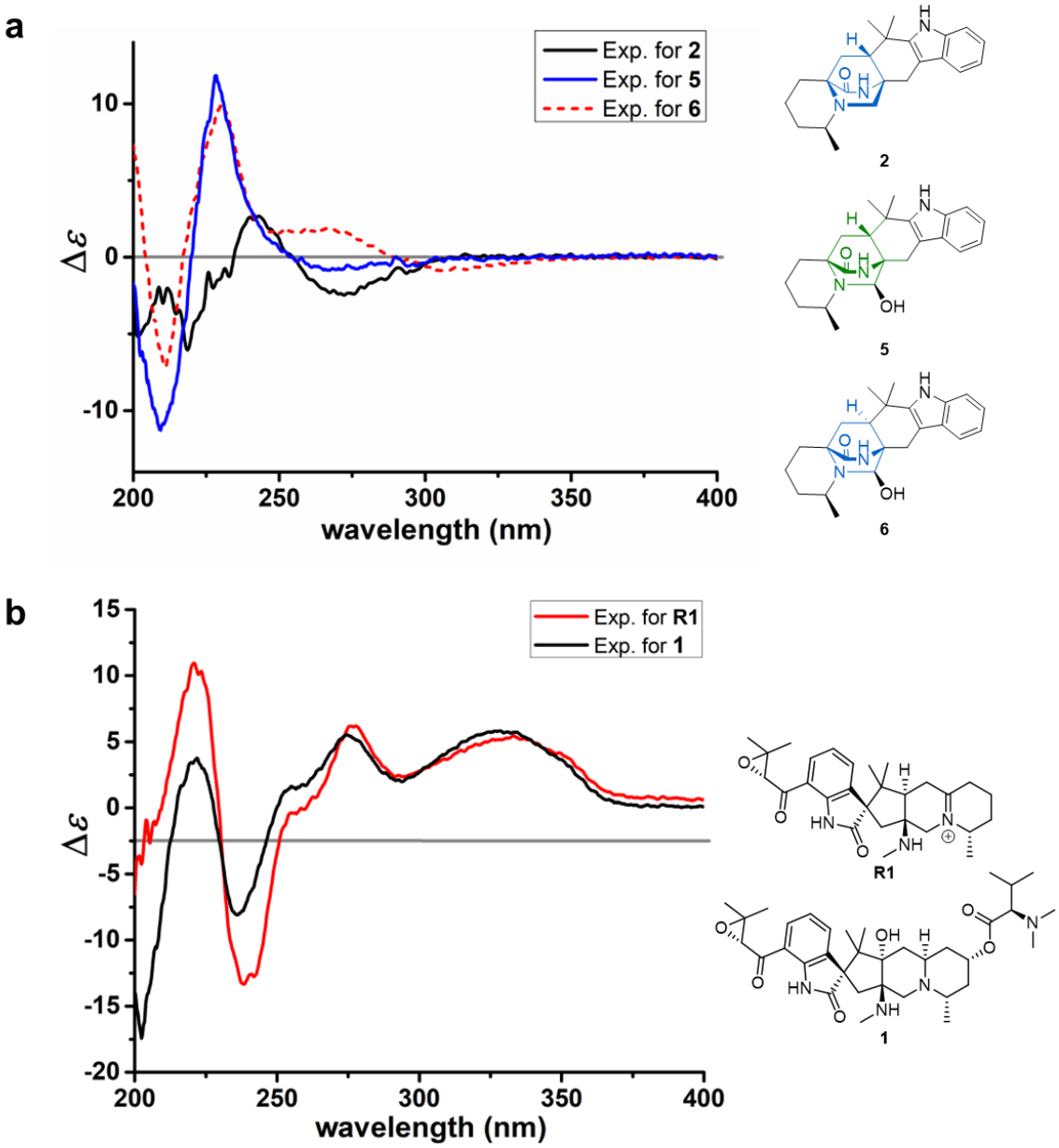
Supplementary Fig. 3 | **PCR confirmation of *ctd* mutants.** *ctd* transformants were screened by PCR using primers *ctdx-up-F* and *bar-R* for up-stream screening, primers *bar-F* and *ctdx-dn-R* for down-stream screening.



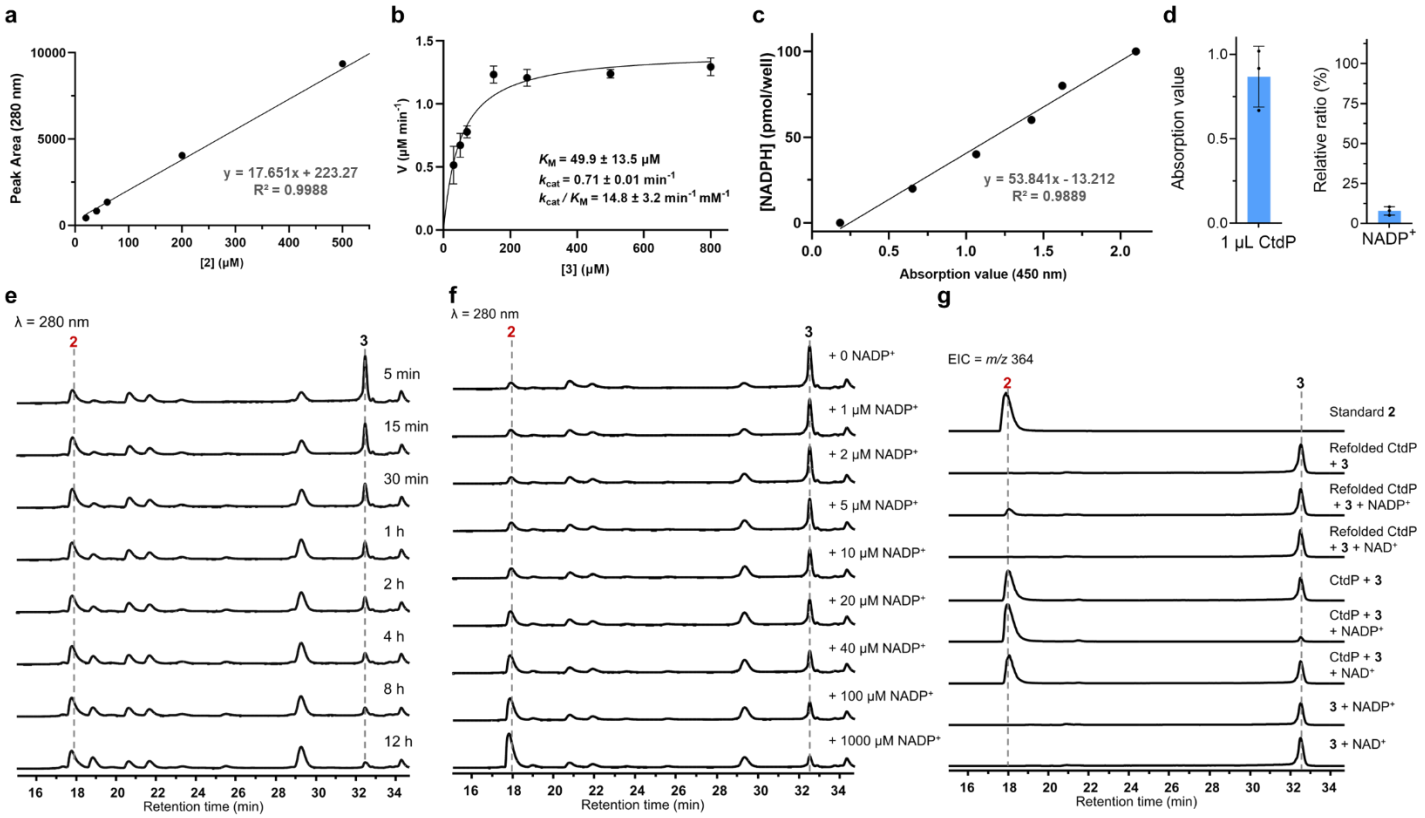
Supplementary Fig. 4 | UV and mass spectra of compounds 1-6.



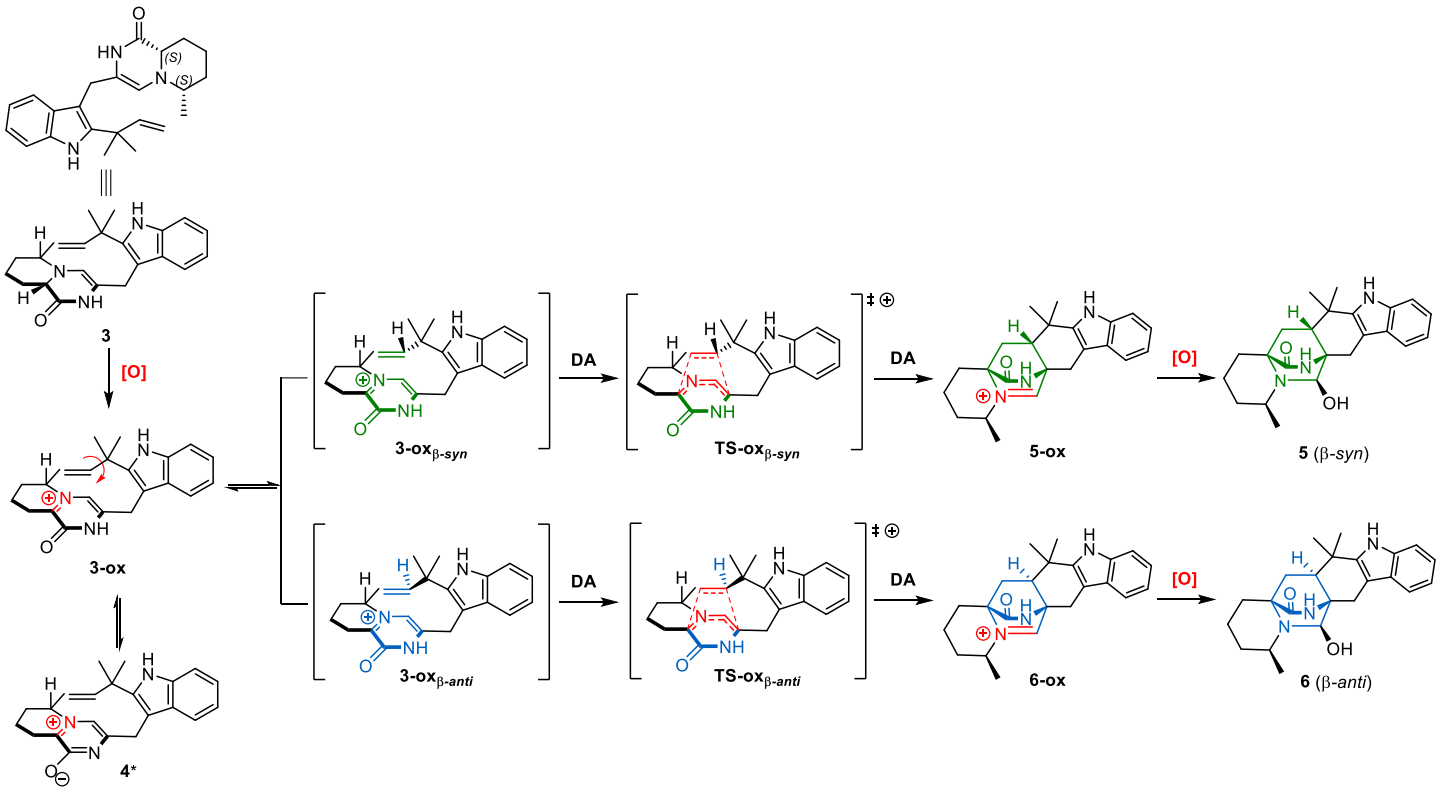
Supplementary Fig. 5 | UV and mass spectra of compounds 7-11.



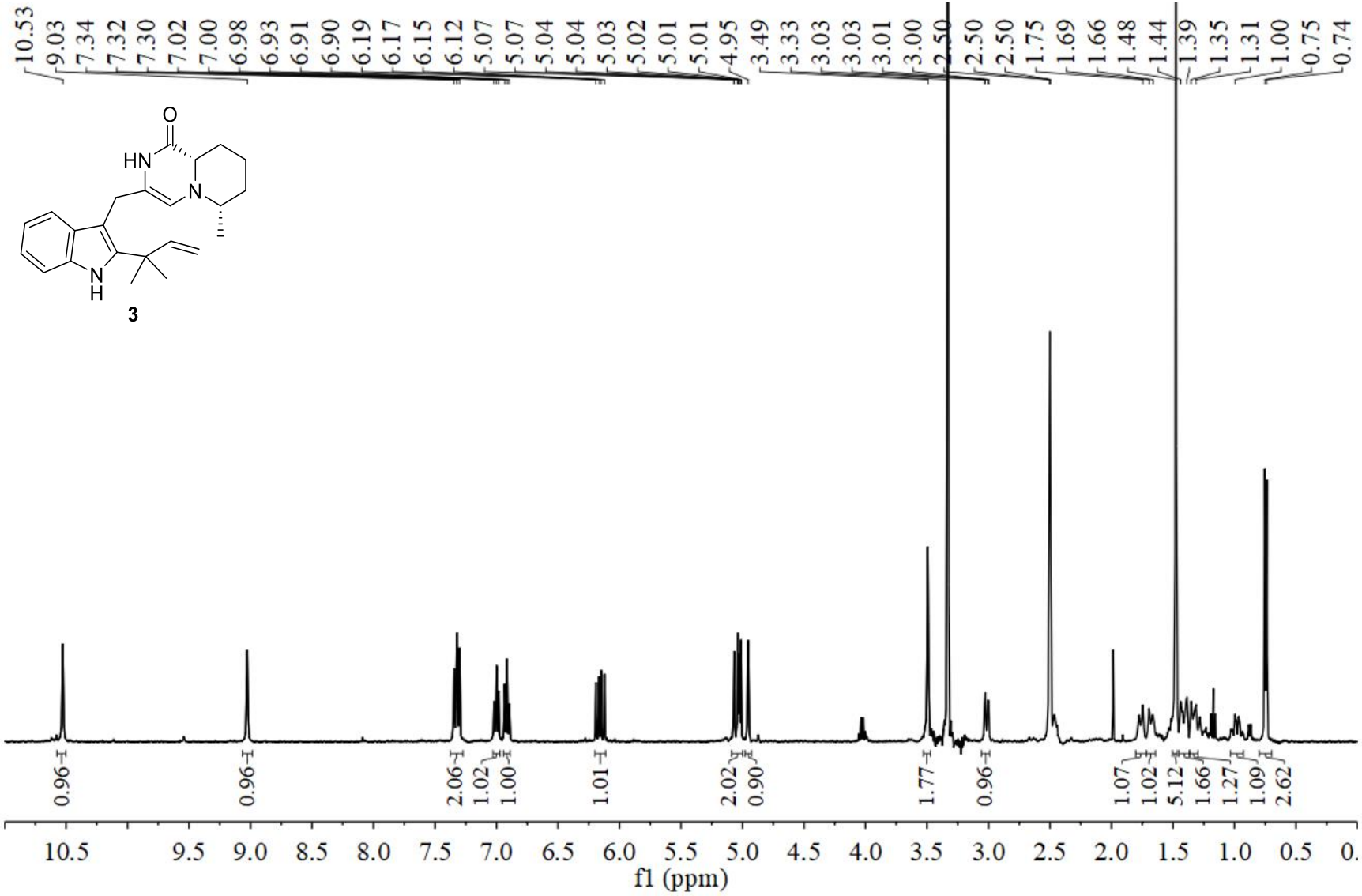
Supplementary Fig. 6 | **Electronic circular dichroism spectra. a,** Compounds **2**, **5**, and **6**. **b,** Compounds **R1** and **1.**



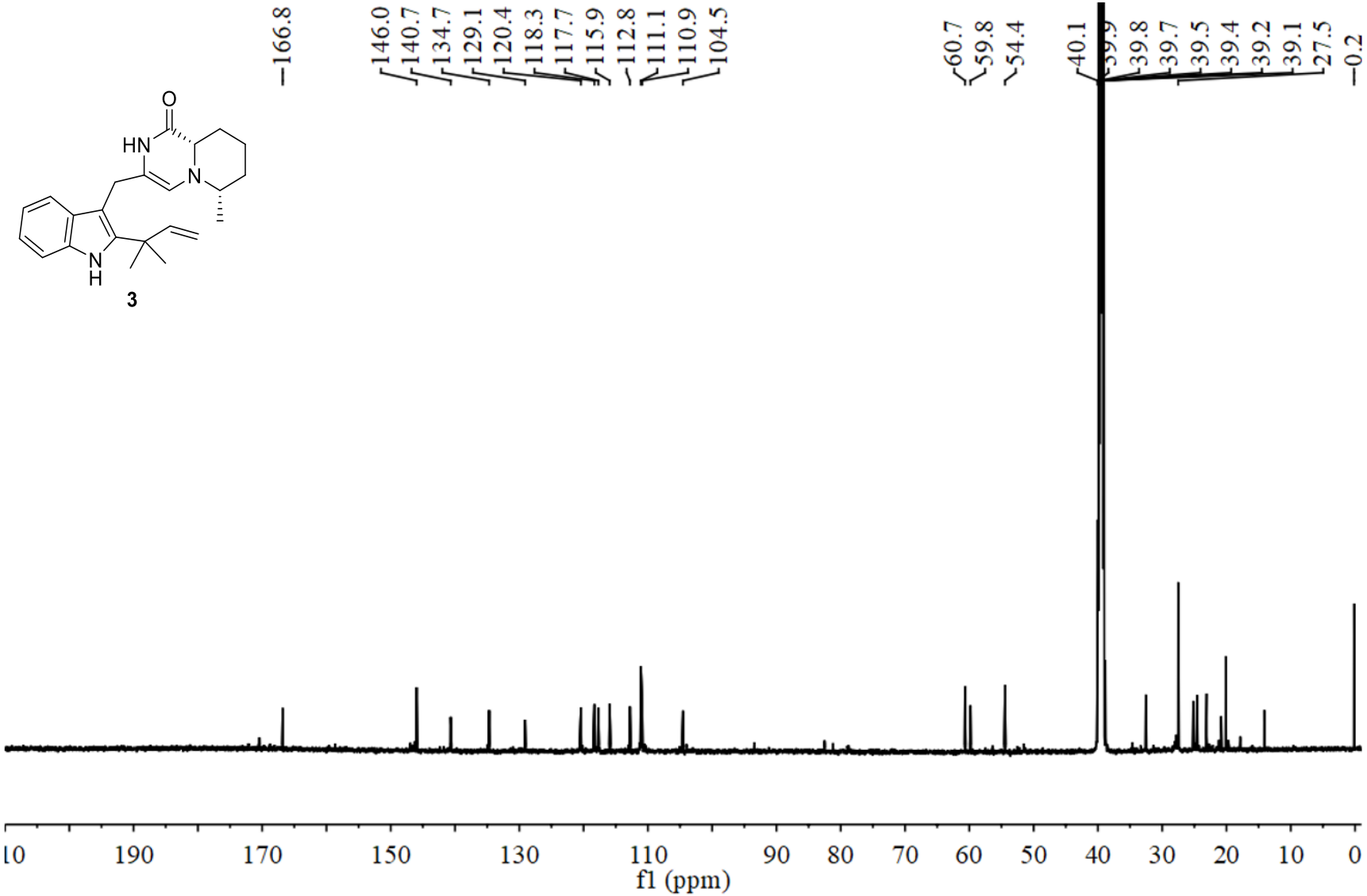
Supplementary Fig. 7 | Kinetic analysis of CtdP, NADP$^+$ content in the purified CtdP protein, and refold CtdP assays. a, Standard curve of compound **2**. **b**, Michaelis-Menton kinetic analysis of CtdP with and **3**. Data was presented as mean ± s.d. from triplicate independent experiments (n = 3). **c**, Standard curve of NADPH. **d**, Left: absorption value of NADP$^+$ in 1 μL CtdP (0.88 ± 0.18). NADP$^+$ amount = total NADP – NADPH. Right: the relative ratio of NADP$^+$ in CtdP protein (7.8 ± 2.6%). Data was presented as mean ± s.d. from triplicate independent experiments (n = 3). **e**, 20 μM CtdP (no addition of extra NADP$^+$) reacts with 200 μM **3** in time course. The conversion rate reaches a maximum of 33.8% at 30 min. **f**, 10 μM CtdP and 200 μM **3** react with the addition of different concentrations of NADP$^+$ for 15 min. The conversion rate of **2** increased from 10.4% to 63.9% with the increased amount of additional NADP$^+$ from 0 to 1000 μM. **g**, CtdP (40 μM) and refolded CtdP (40 μM) react with **3** (200 μM) for 1 hour, respectively. The reaction buffer is 50 mM Tris-HCl (pH 7.0) and the reaction temperature is 28 ℃. The 100% conversion of **2** as the control.



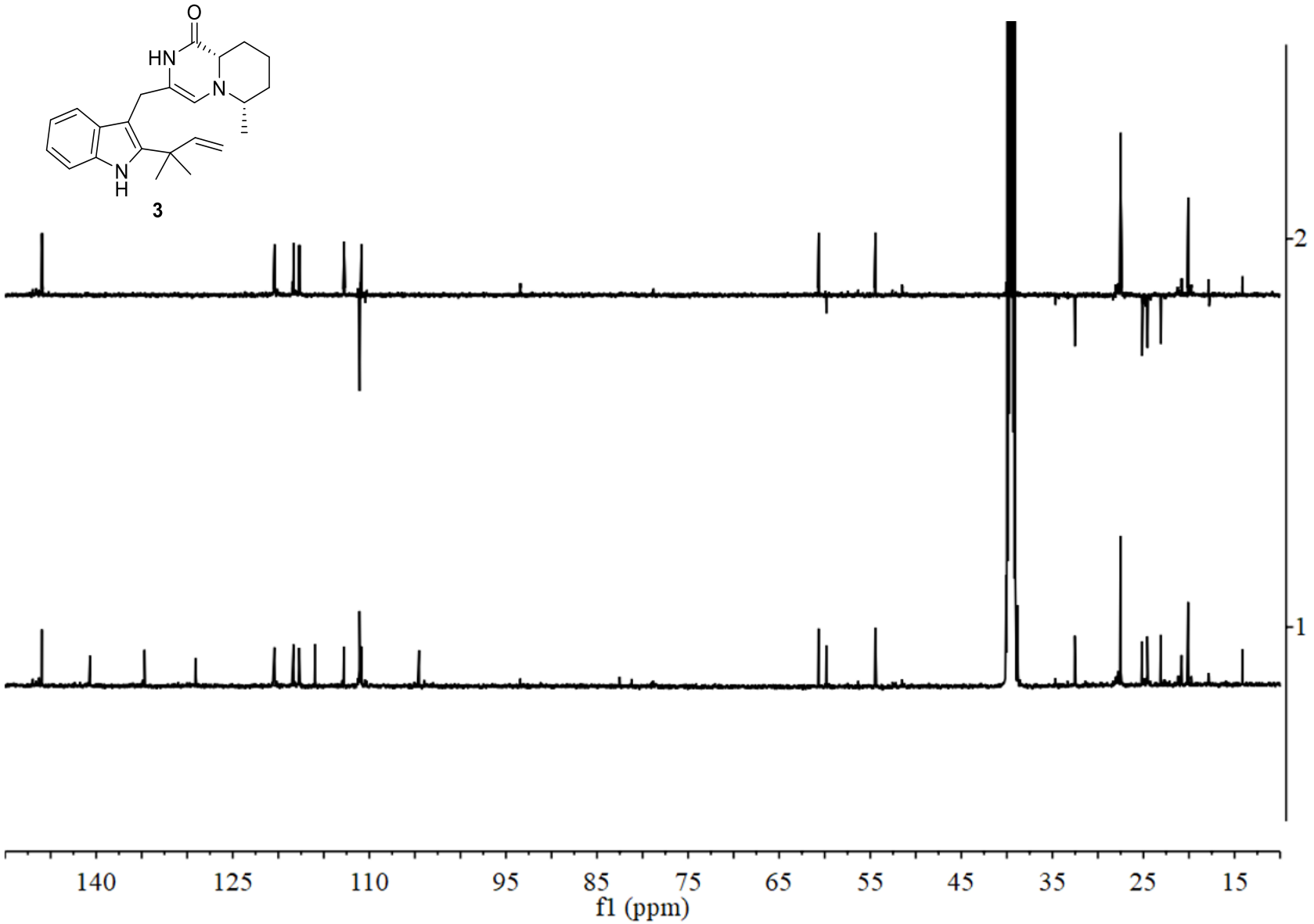
Supplementary Fig. 8 | The proposed pathways of spontaneous Diels-Alder reactions of compound 3.



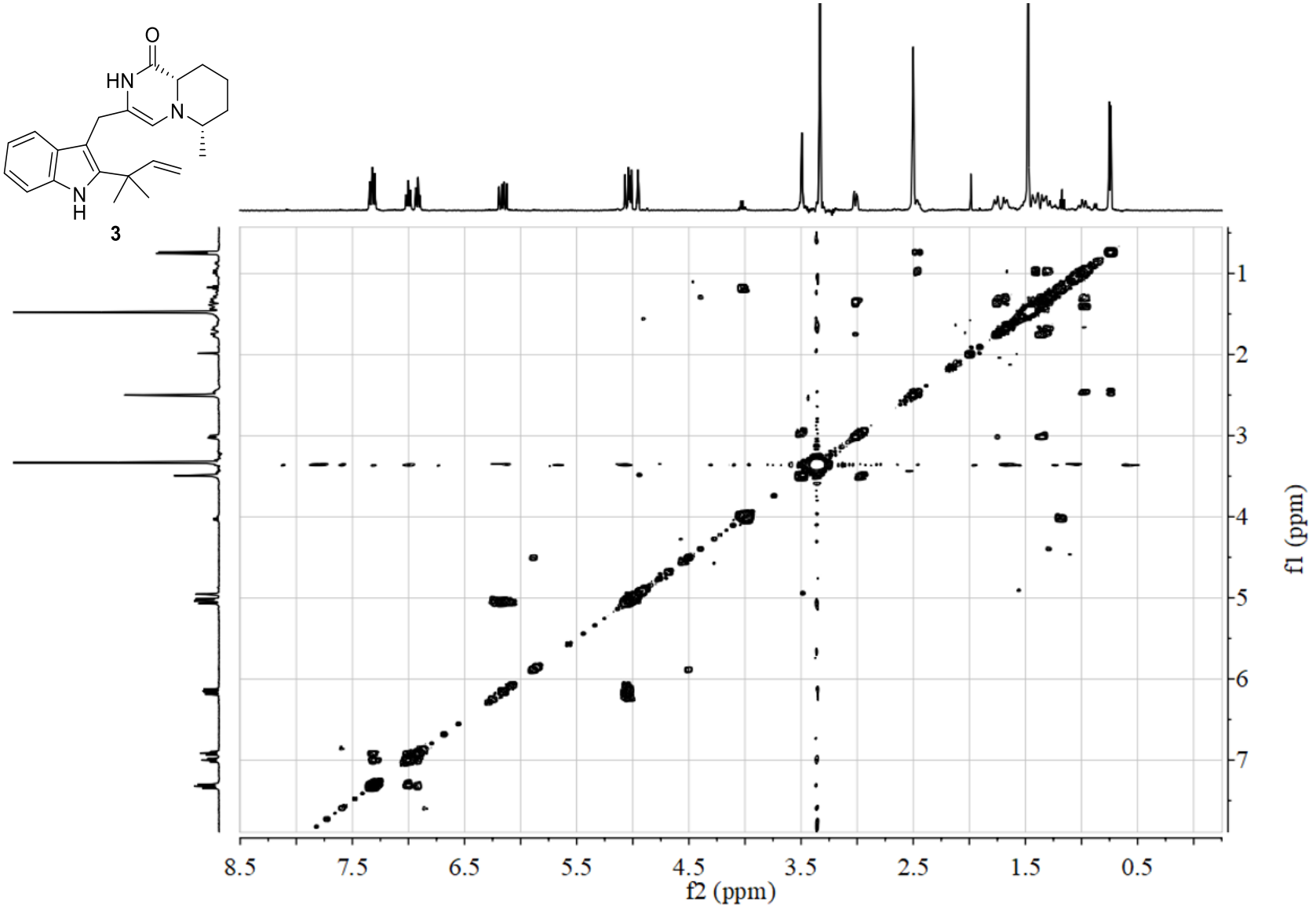
Supplementary Fig. 9-1| ^{1}H NMR spectrum of 3 in DMSO-d_6.



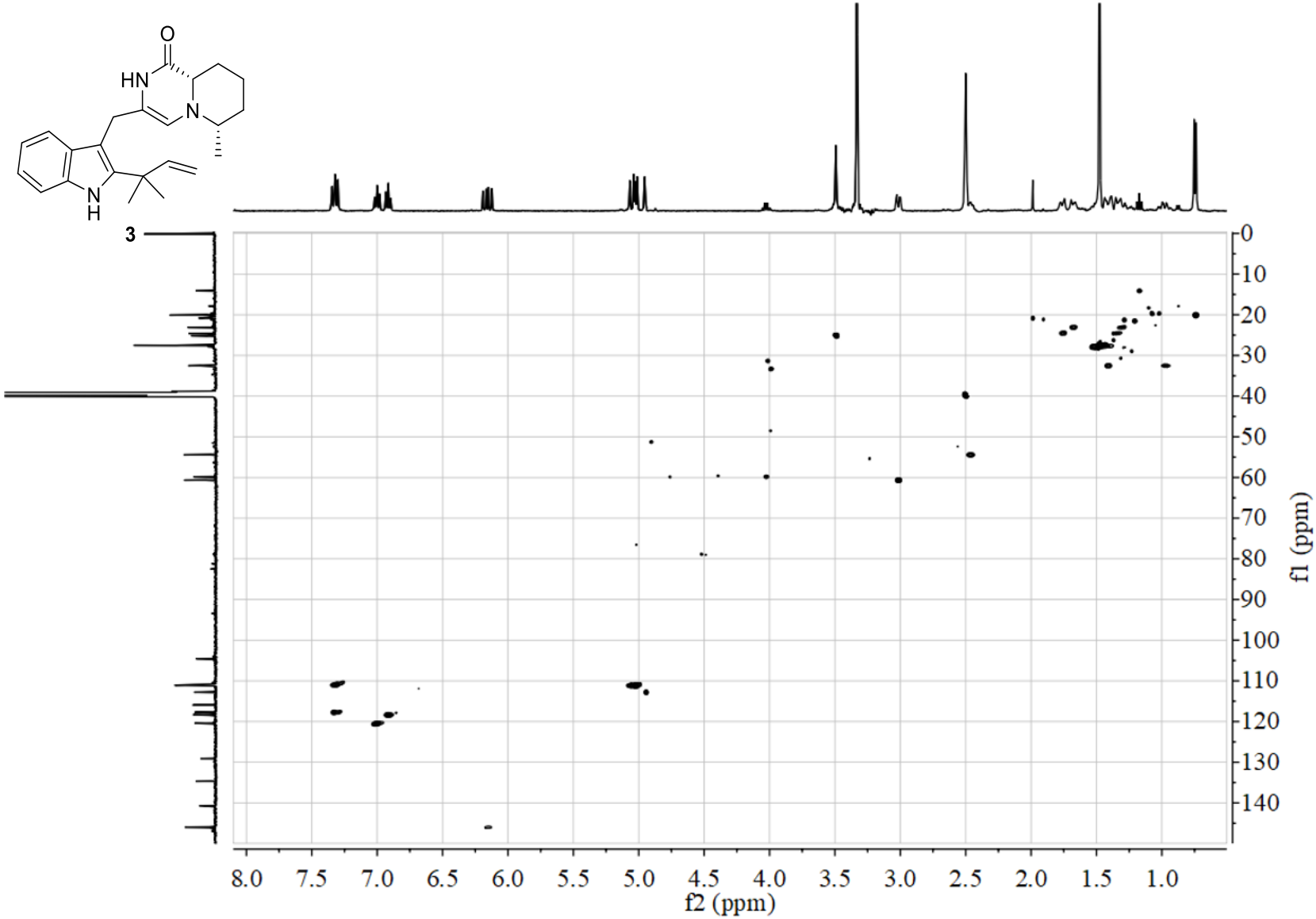
Supplementary Fig. 9-2| ^{13}C NMR spectrum of 3 in DMSO-*d*$_6$.



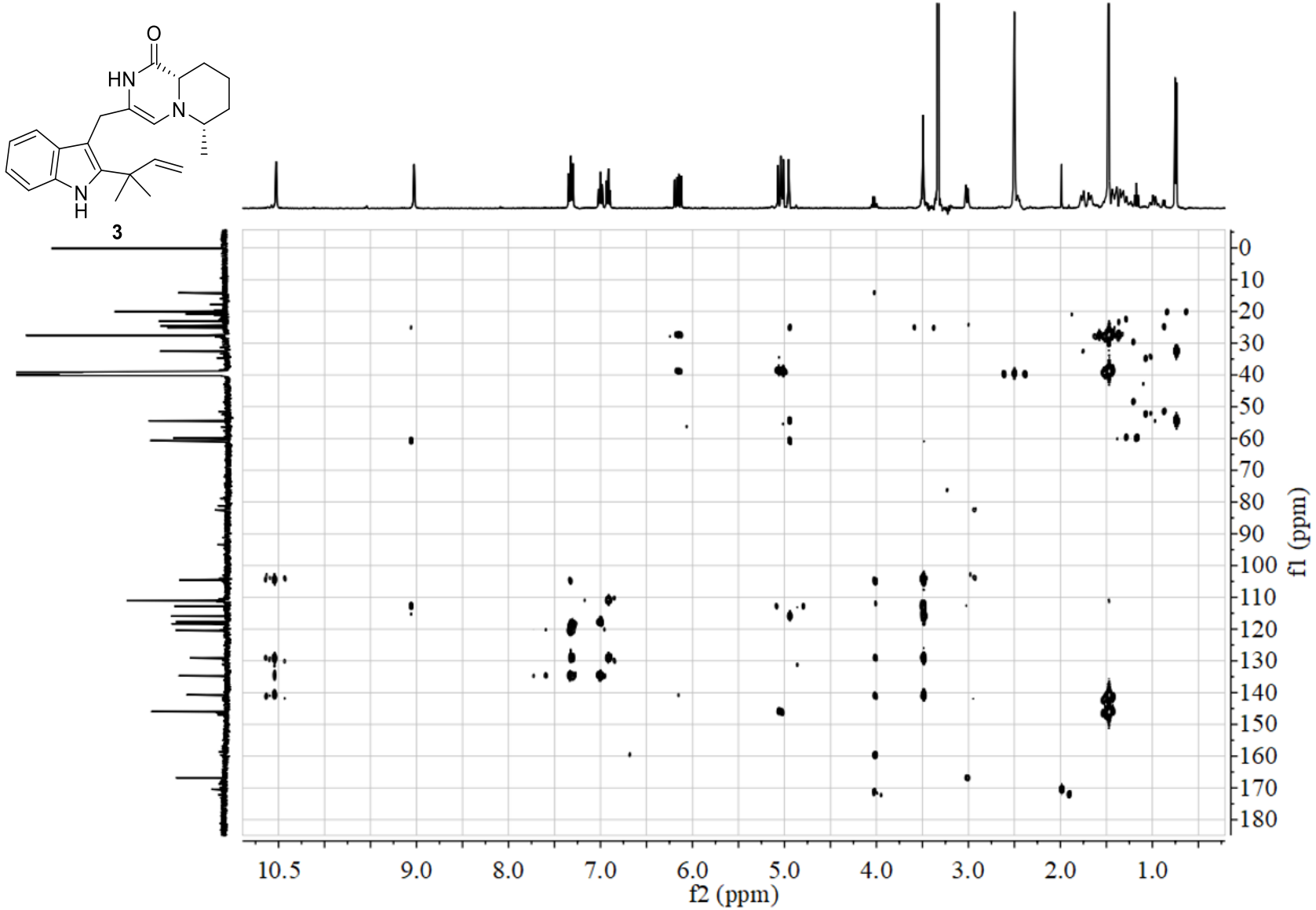
Supplementary Fig. 9-3 | DEPT135 and ^{13}C NMR spectra of 3 in DMSO-d_6.



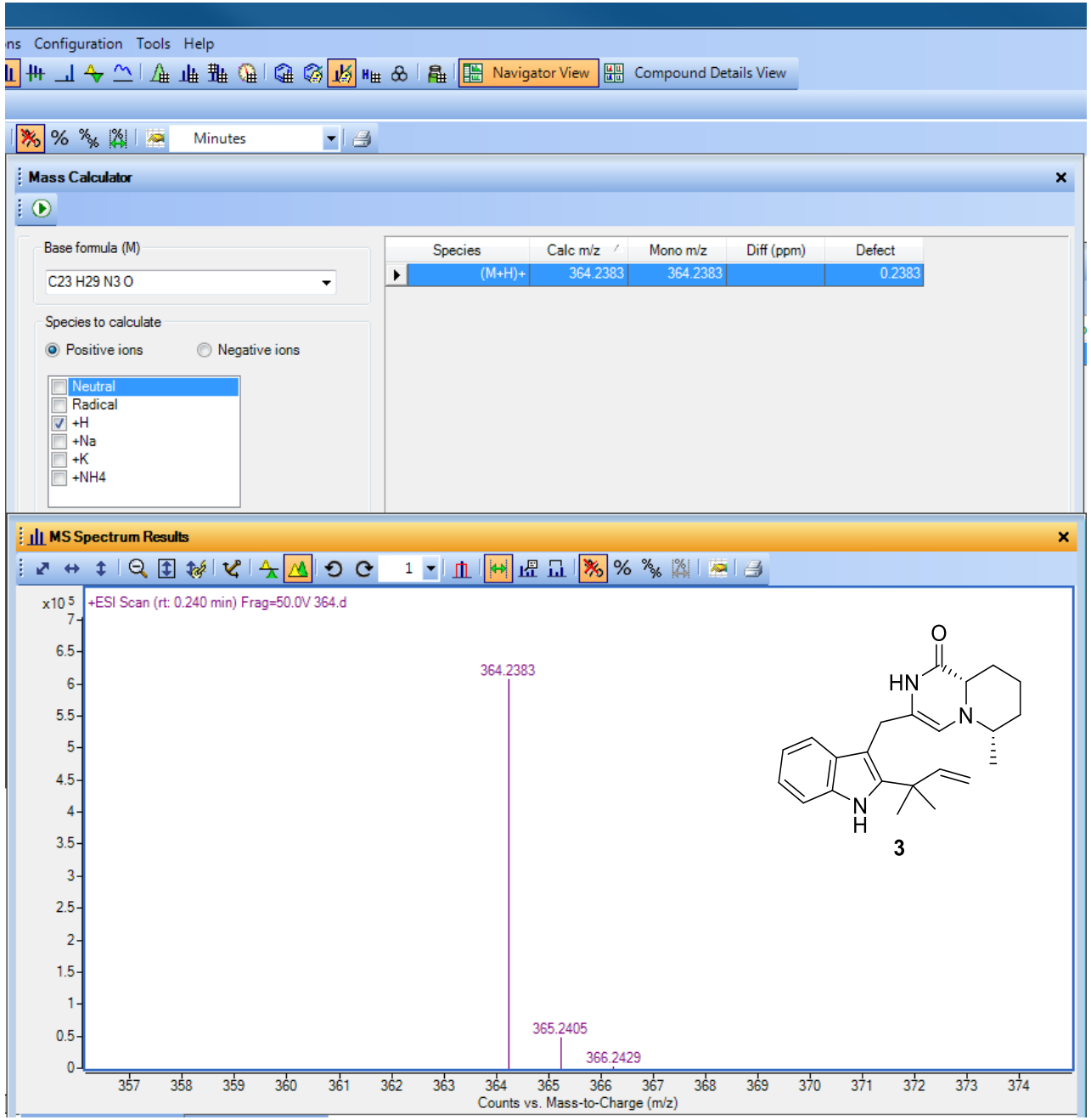
Supplementary Fig. 9-4 | ^{1}H-^{1}H COSY NMR spectrum of 3 in DMSO-*d*$_6$.



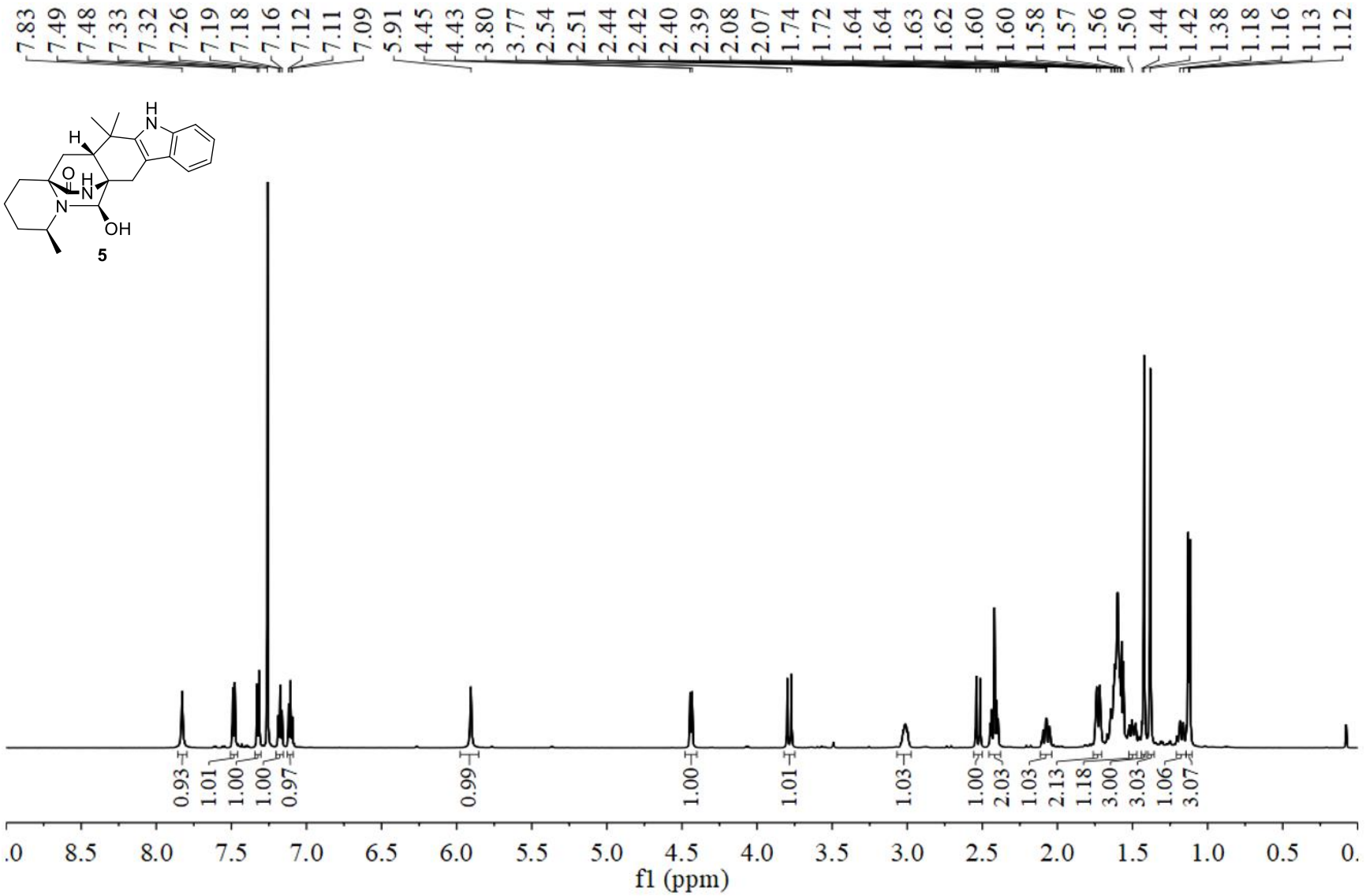
Supplementary Fig. 9-5 | HSQC NMR spectrum of 3 in DMSO-d_6.



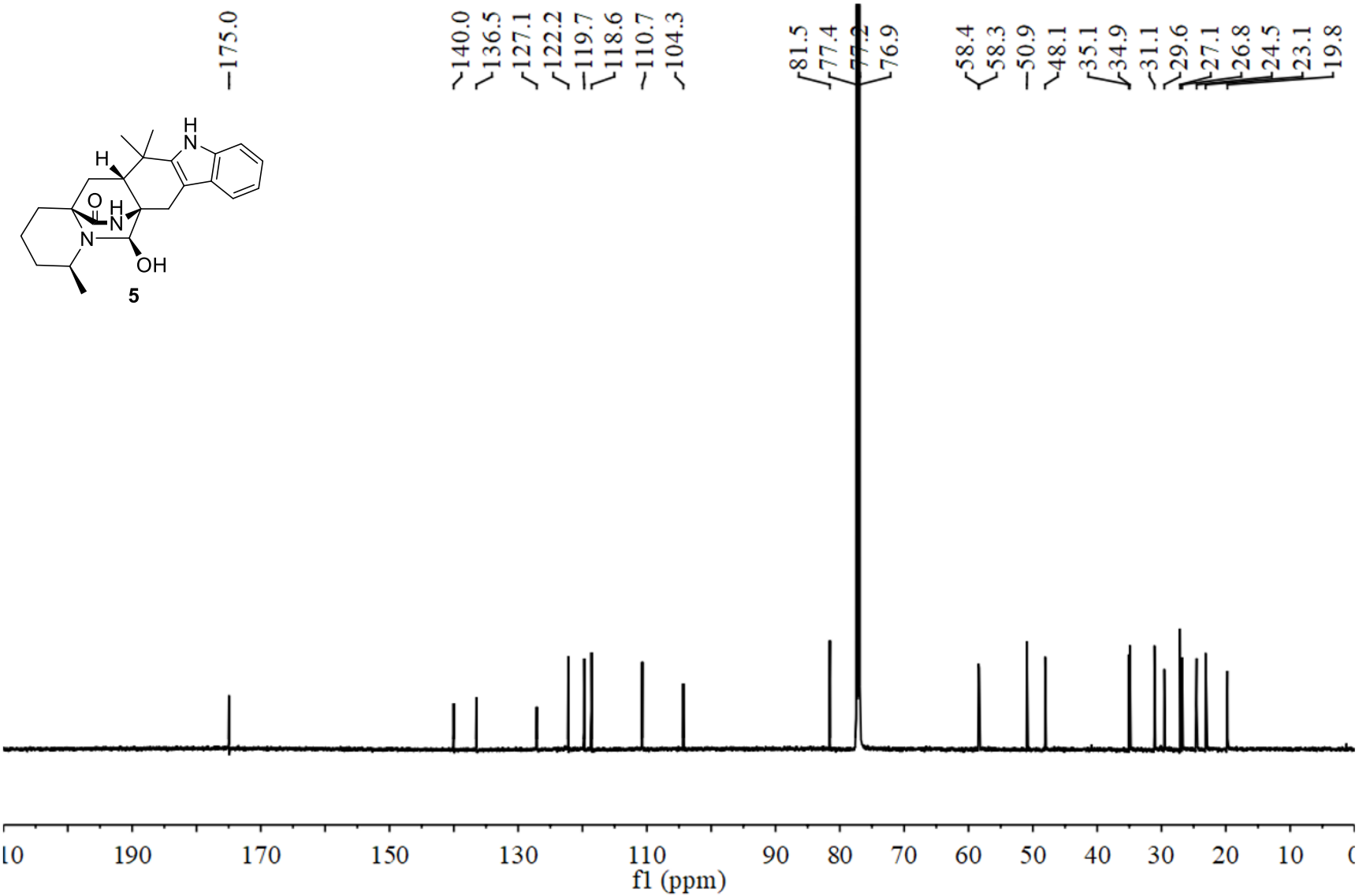
Supplementary Fig. 9-6 | HMBC NMR spectrum of 3 in DMSO-*d*$_6$.



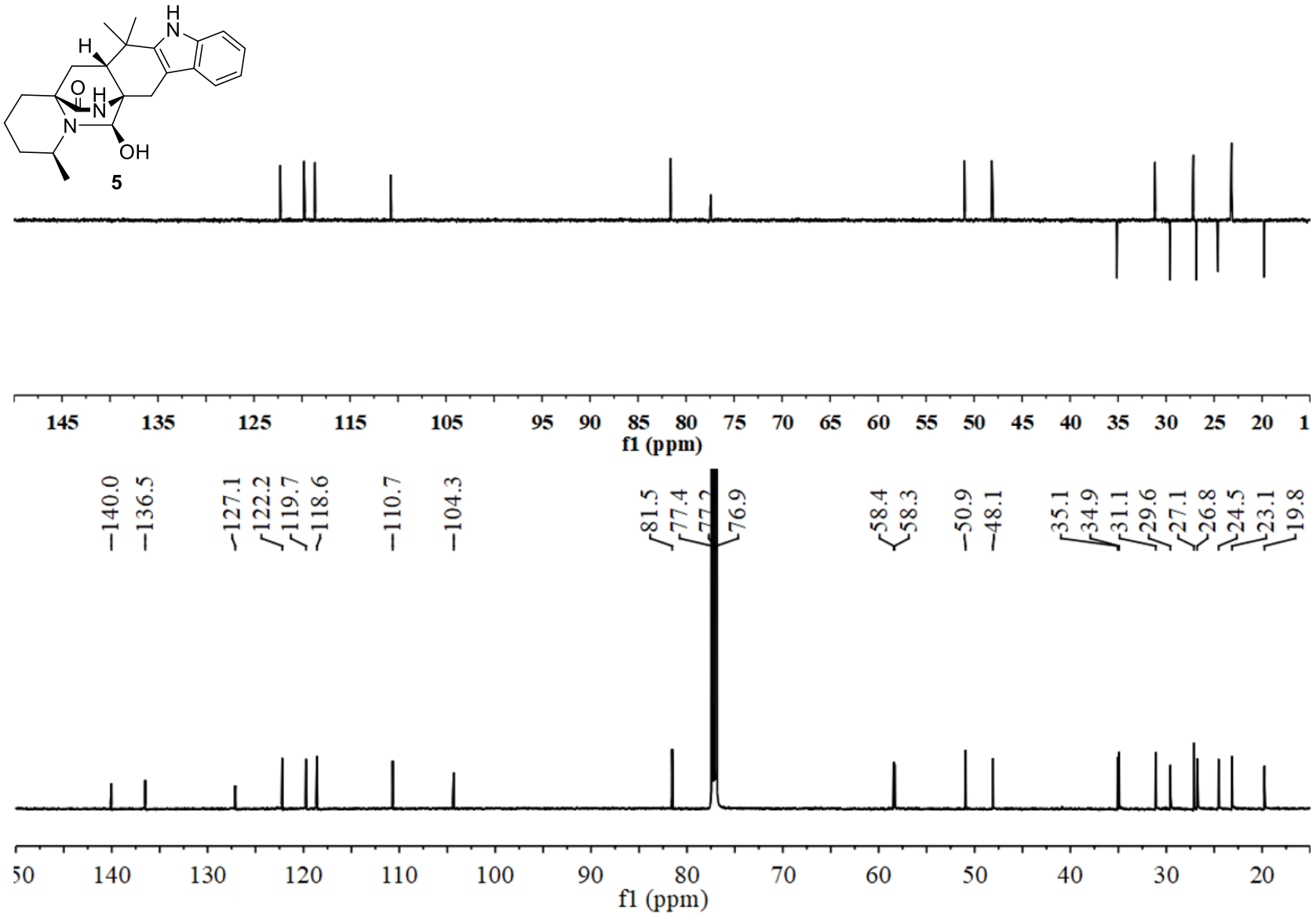
Supplementary Fig. 9-7 | HRMS spectrum of 3.



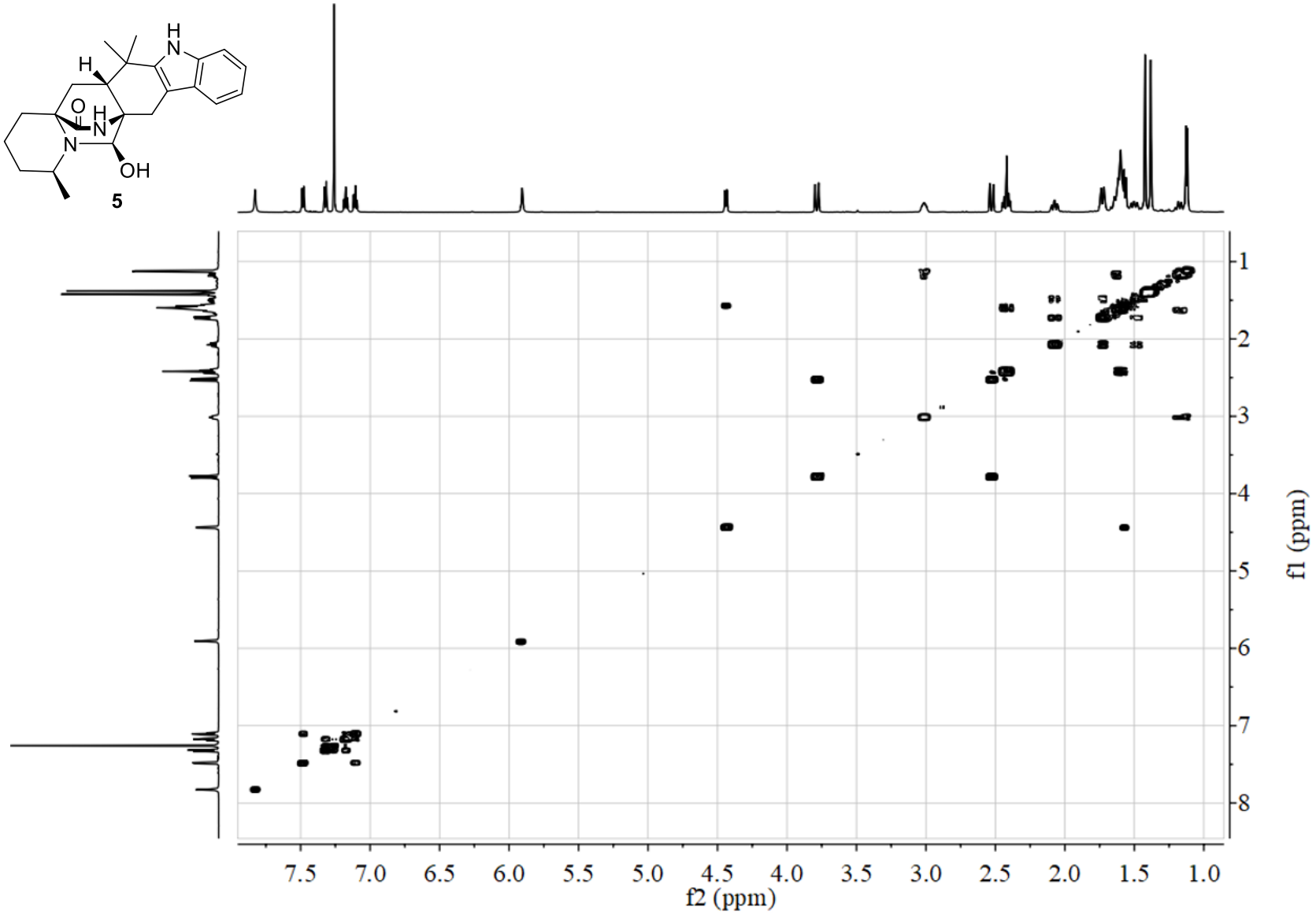
Supplementary Fig. 10-1 | ^{1}H NMR spectrum of 5 in $CDCl_3$.



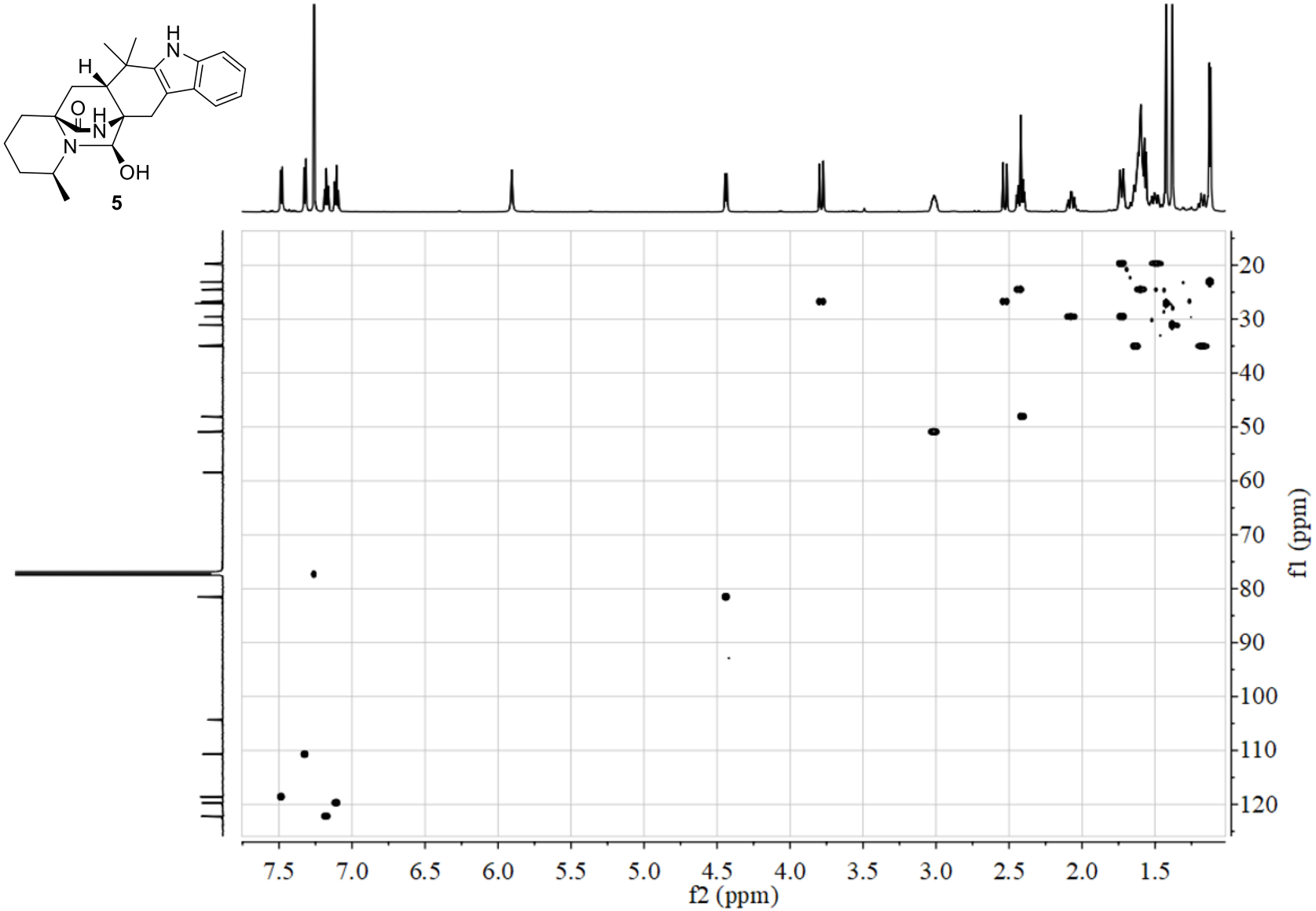
Supplementary Fig. 10-2 | ^{13}C NMR spectrum of 5 in $CDCl_3$.



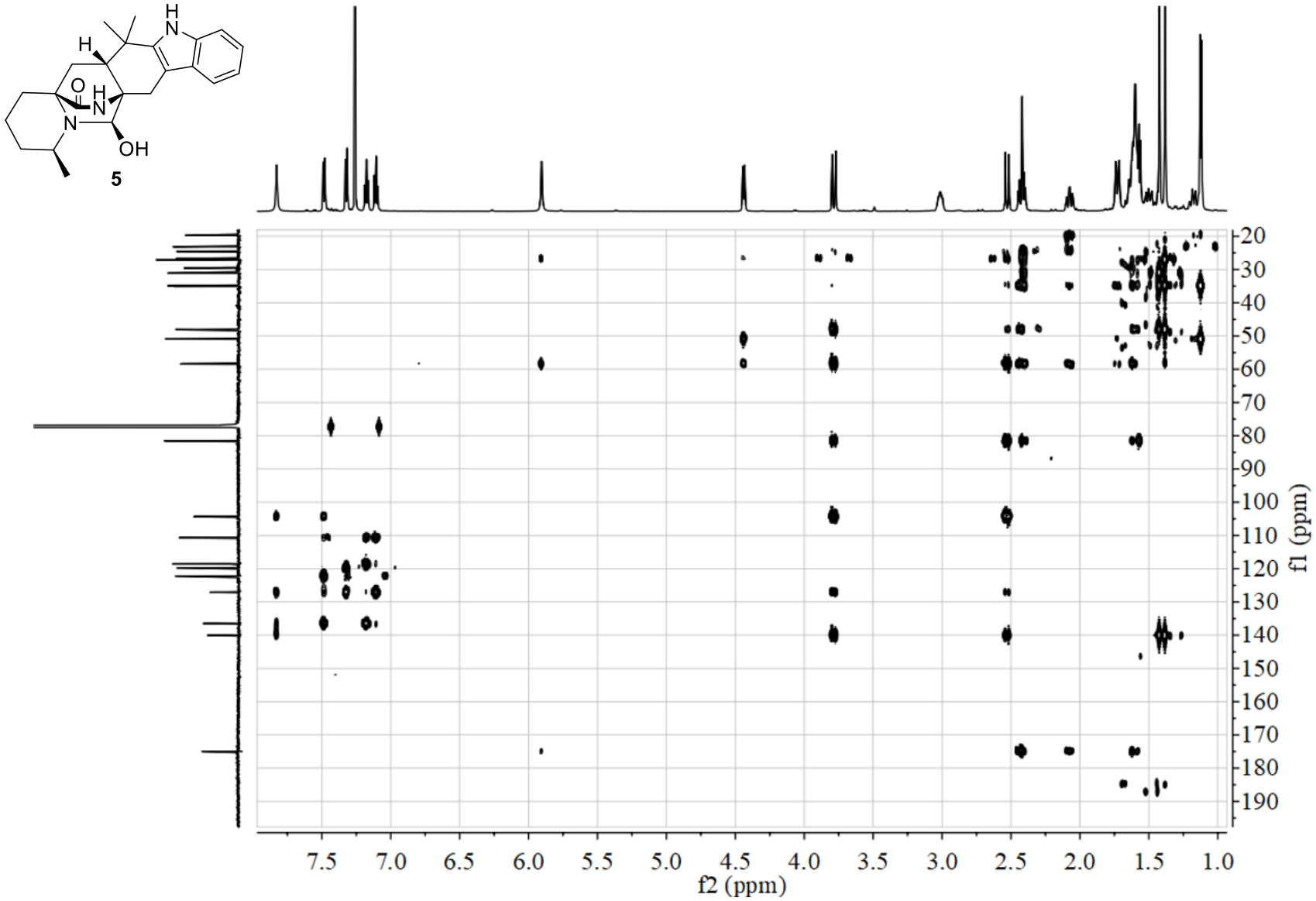
Supplementary Fig. 10-3 | DEPT135 and ^{13}C NMR spectra of 5 in $CDCl_3$.



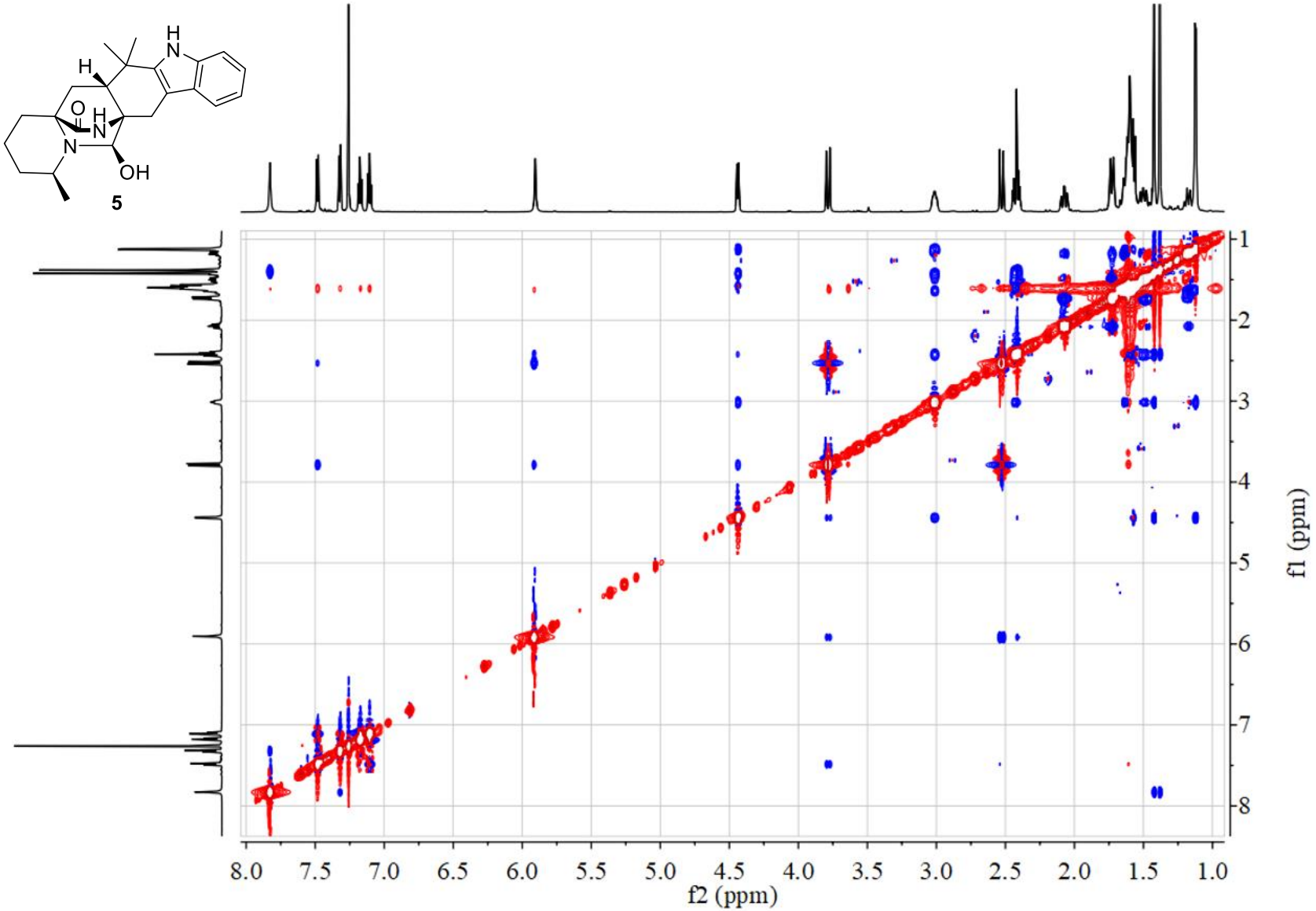
Supplementary Fig. 10-4 | ^{1}H-^{1}H COSY NMR spectrum of 5 in $CDCl_3$.



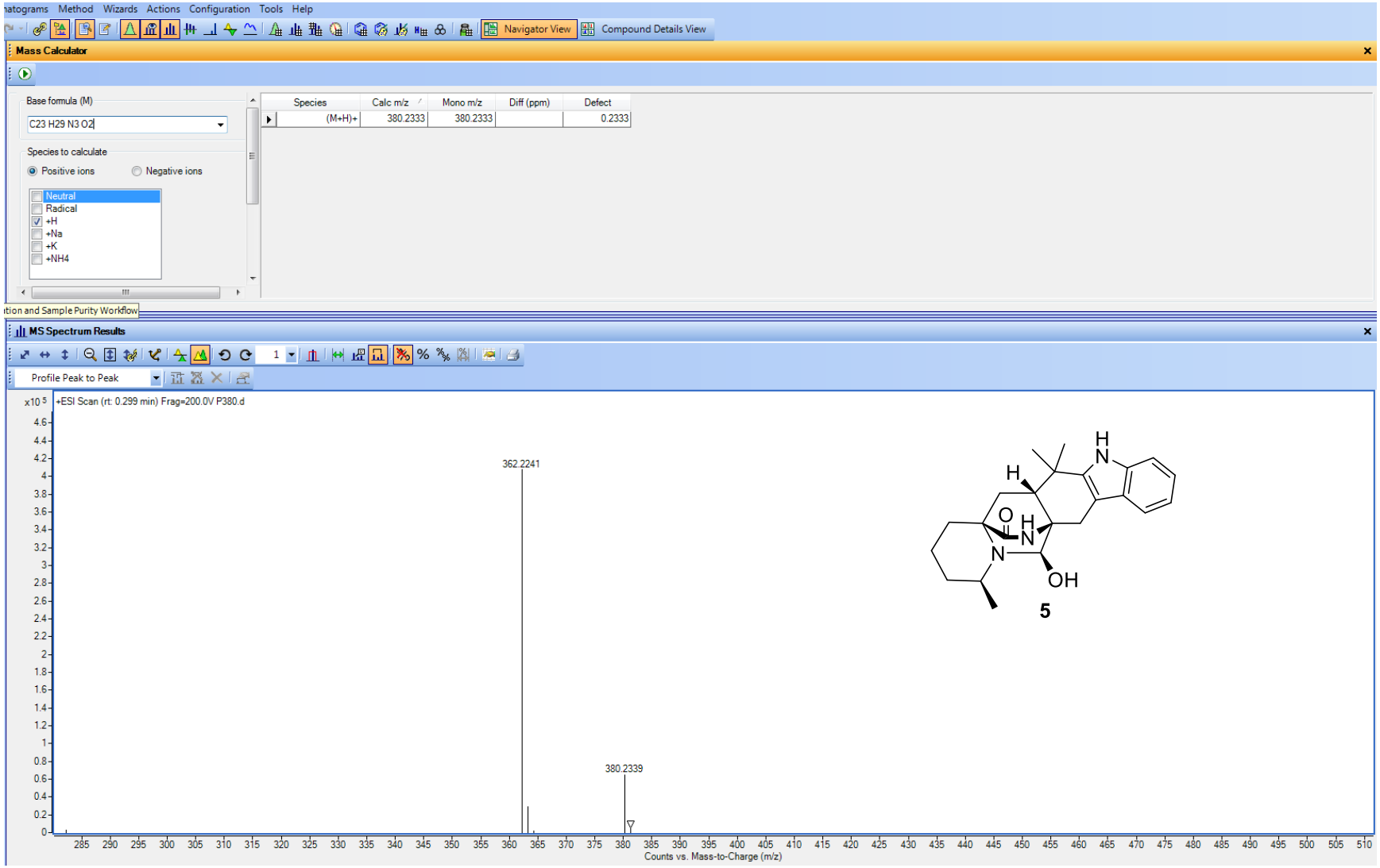
Supplementary Fig. 10-5 | HSQC NMR spectrum of 5 in $CDCl_3$.



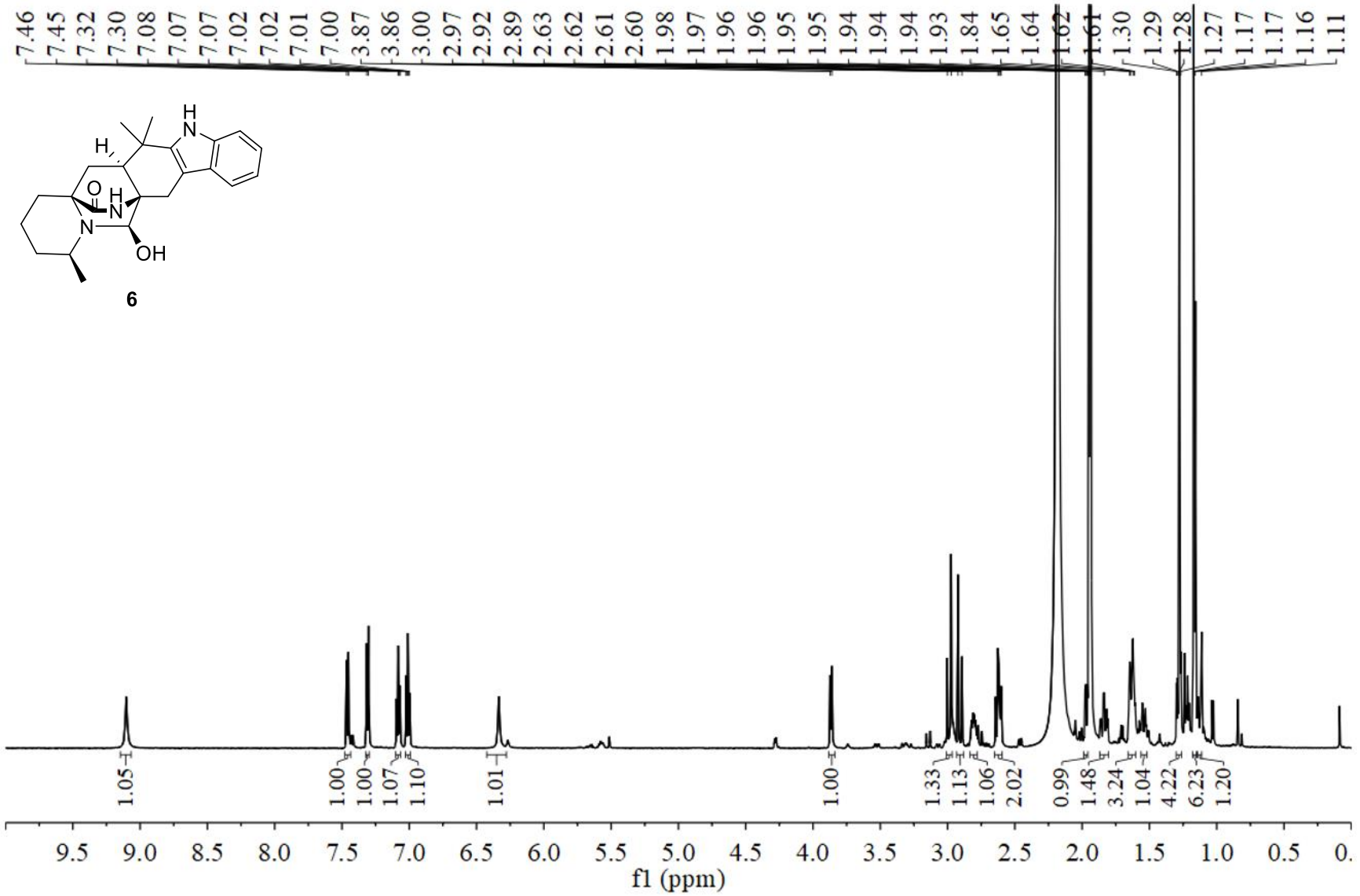
Supplementary Fig. 10-6 | HMBC NMR spectrum of 5 in $CDCl_3$.



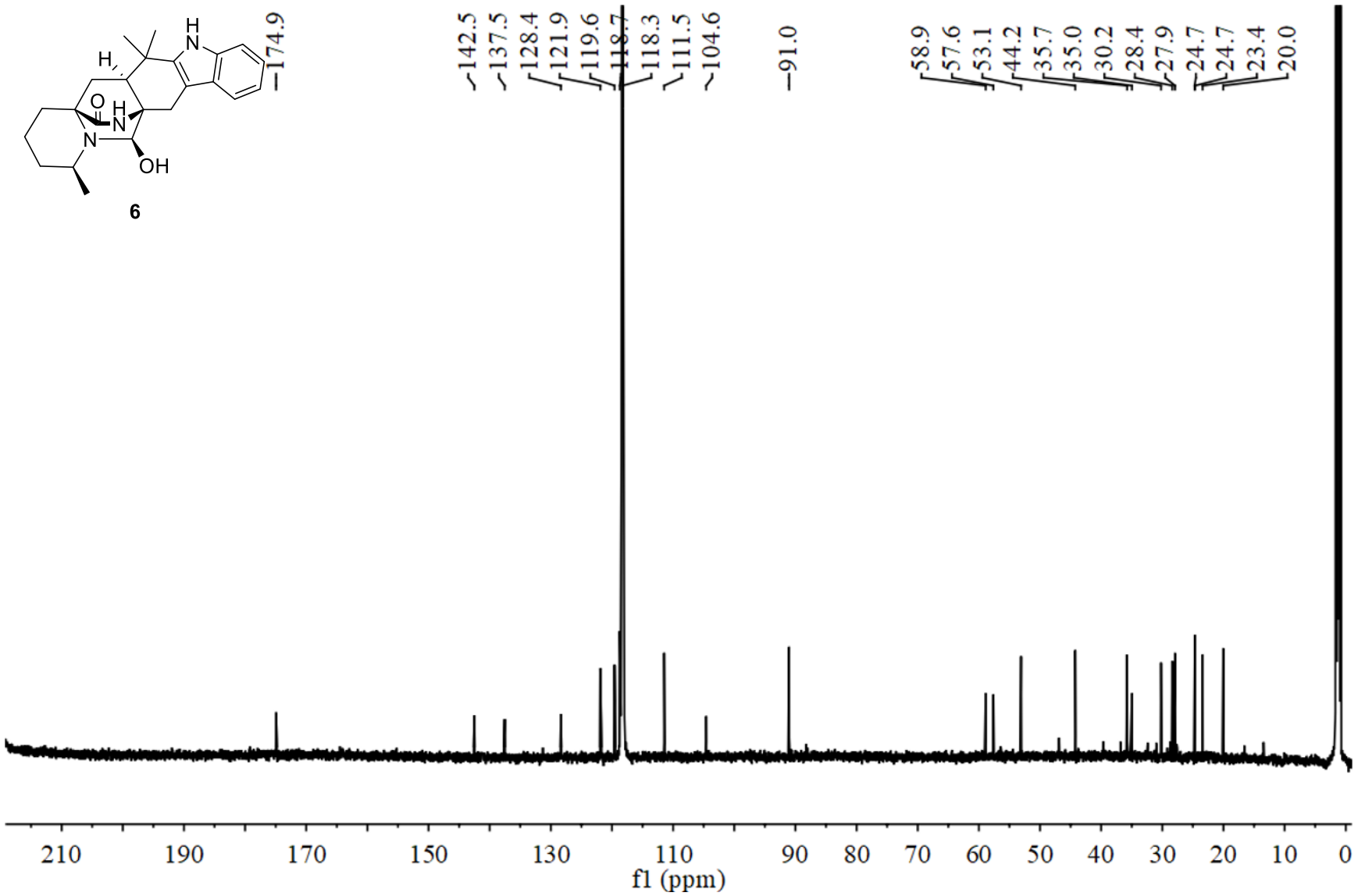
Supplementary Fig. 10-7 | NOESY NMR spectrum of 5 in $CDCl_3$.



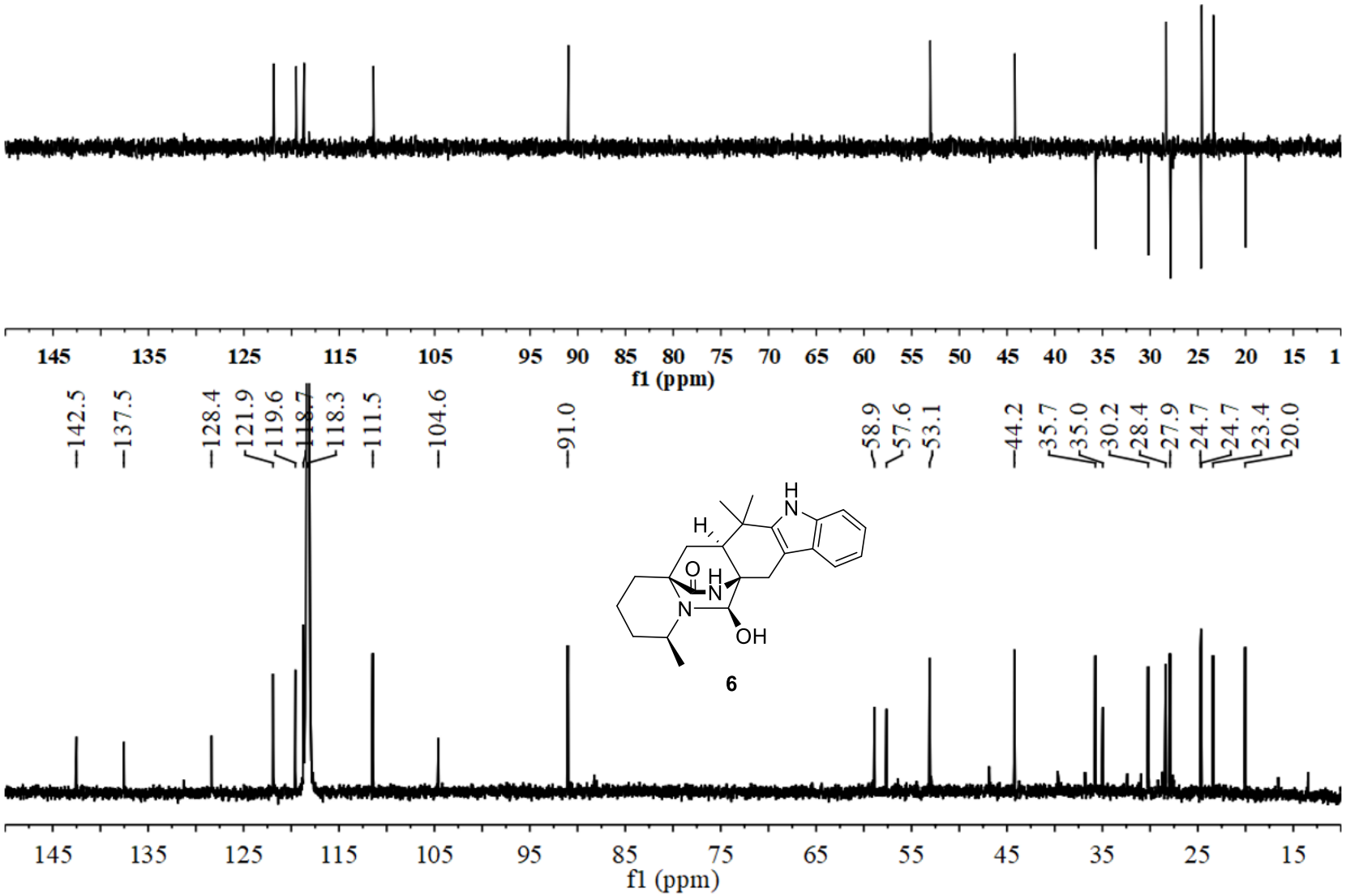
Supplementary Fig. 10-8 | HRMS spectrum of 5.



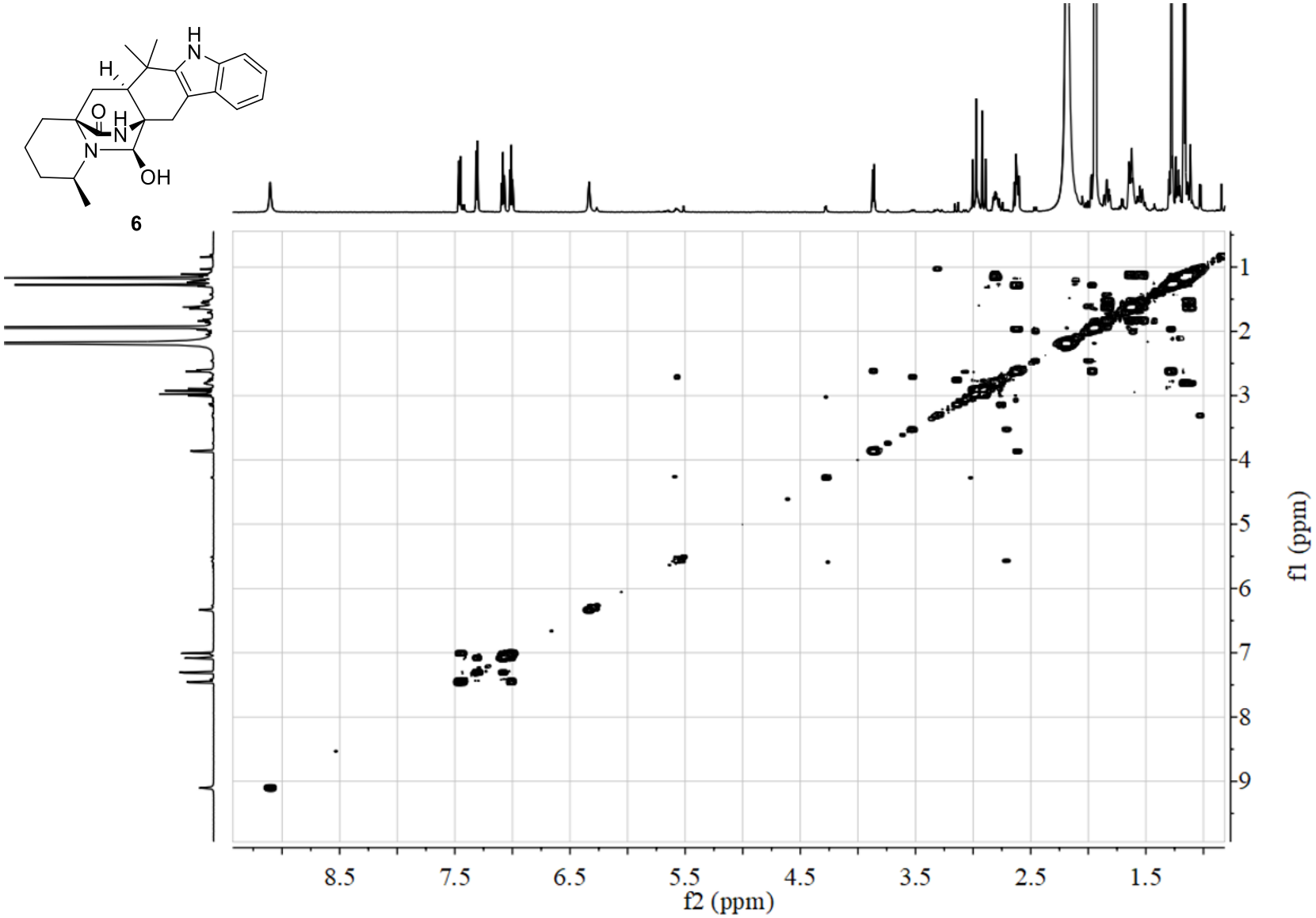
Supplementary Fig. 11-1 | ^{1}H NMR spectrum of 6 in CD_3CN.



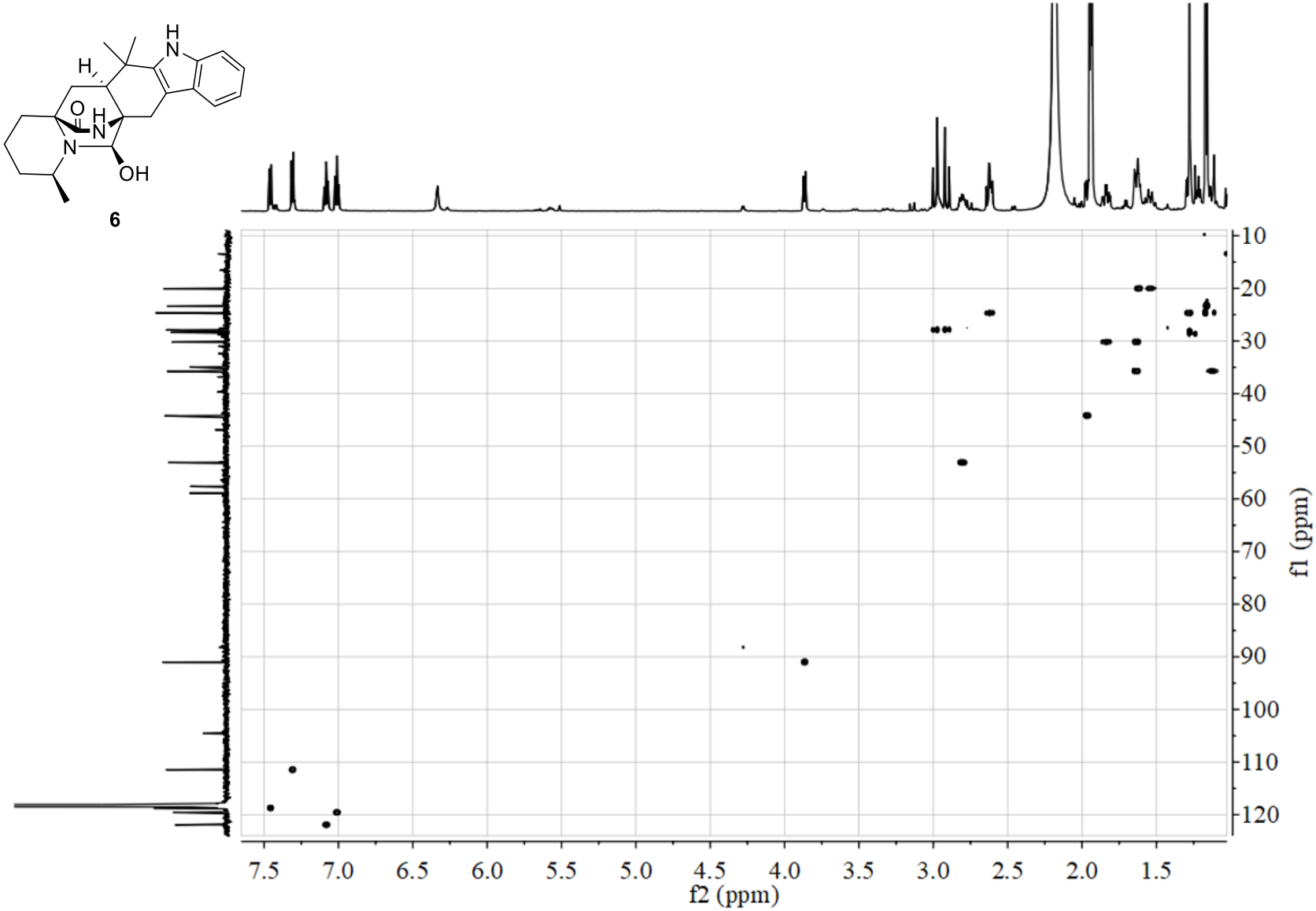
Supplementary Fig. 11-2 | ^{13}C NMR spectrum of 6 in CD_3CN.



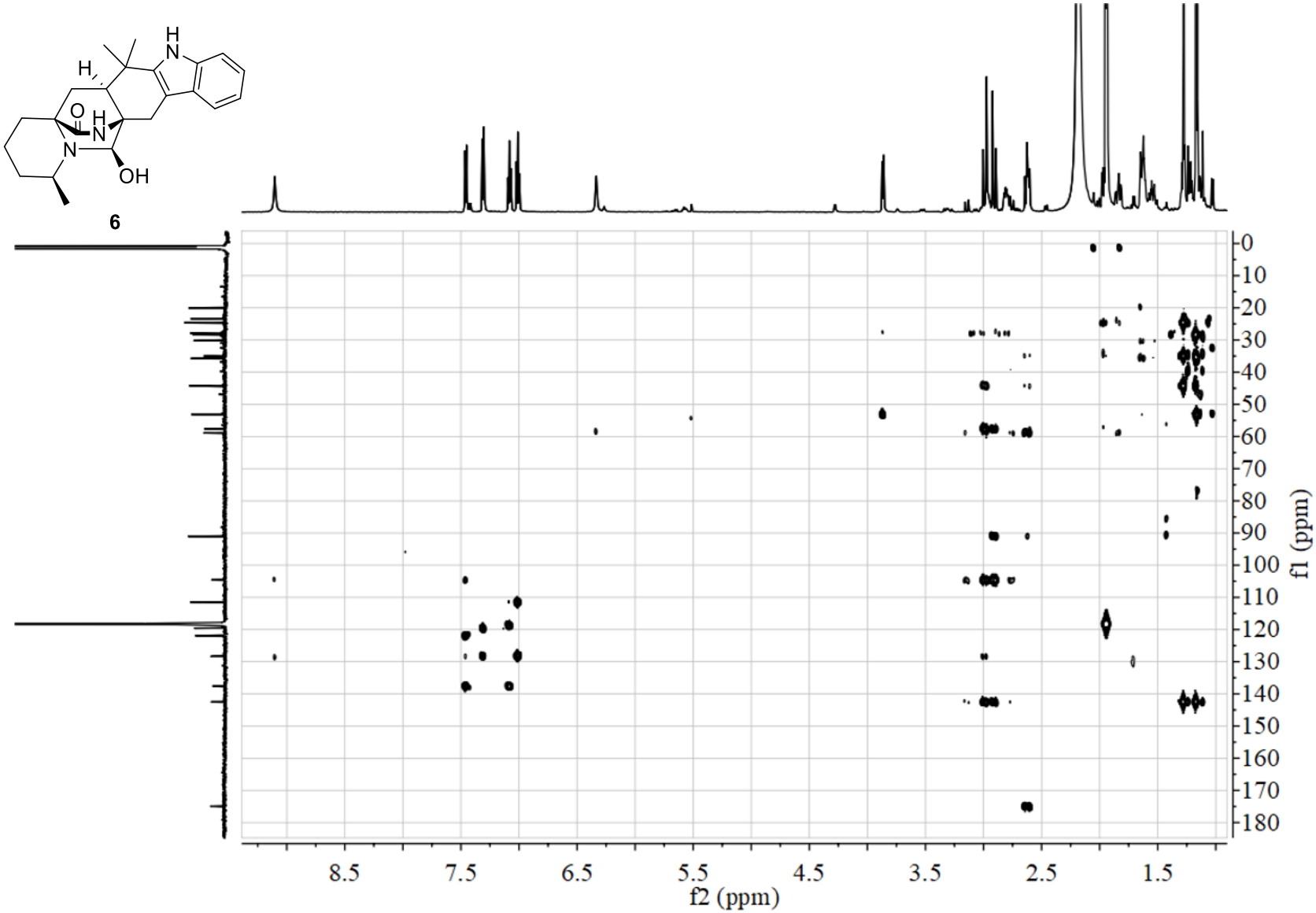
Supplementary Fig. 11-3 | DEPT135 and ^{13}C NMR spectra of 6 in CD_3CN.



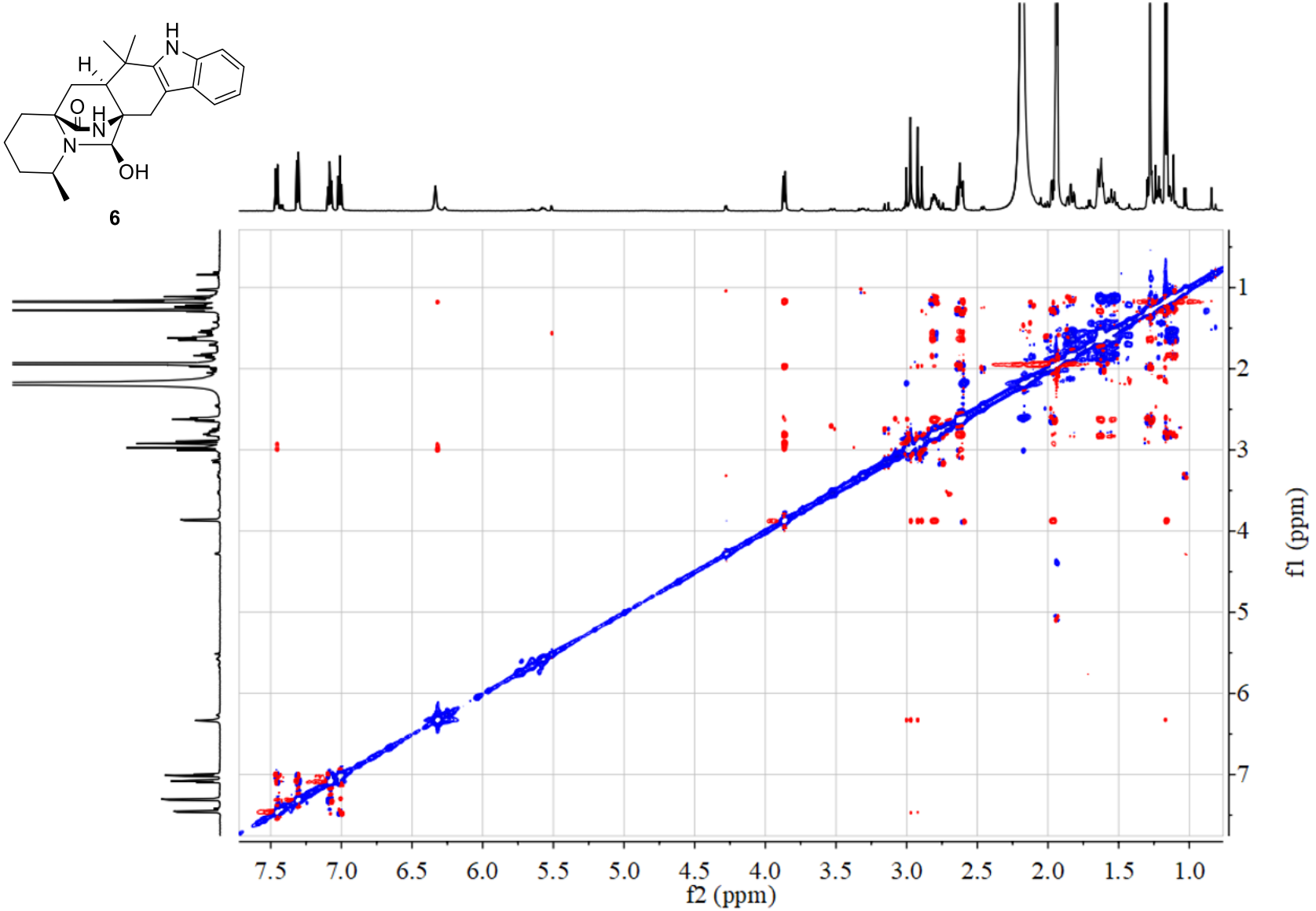
Supplementary Fig. 11-4 | ^{1}H-^{1}H COSY NMR spectrum of 6 in CD_3CN.



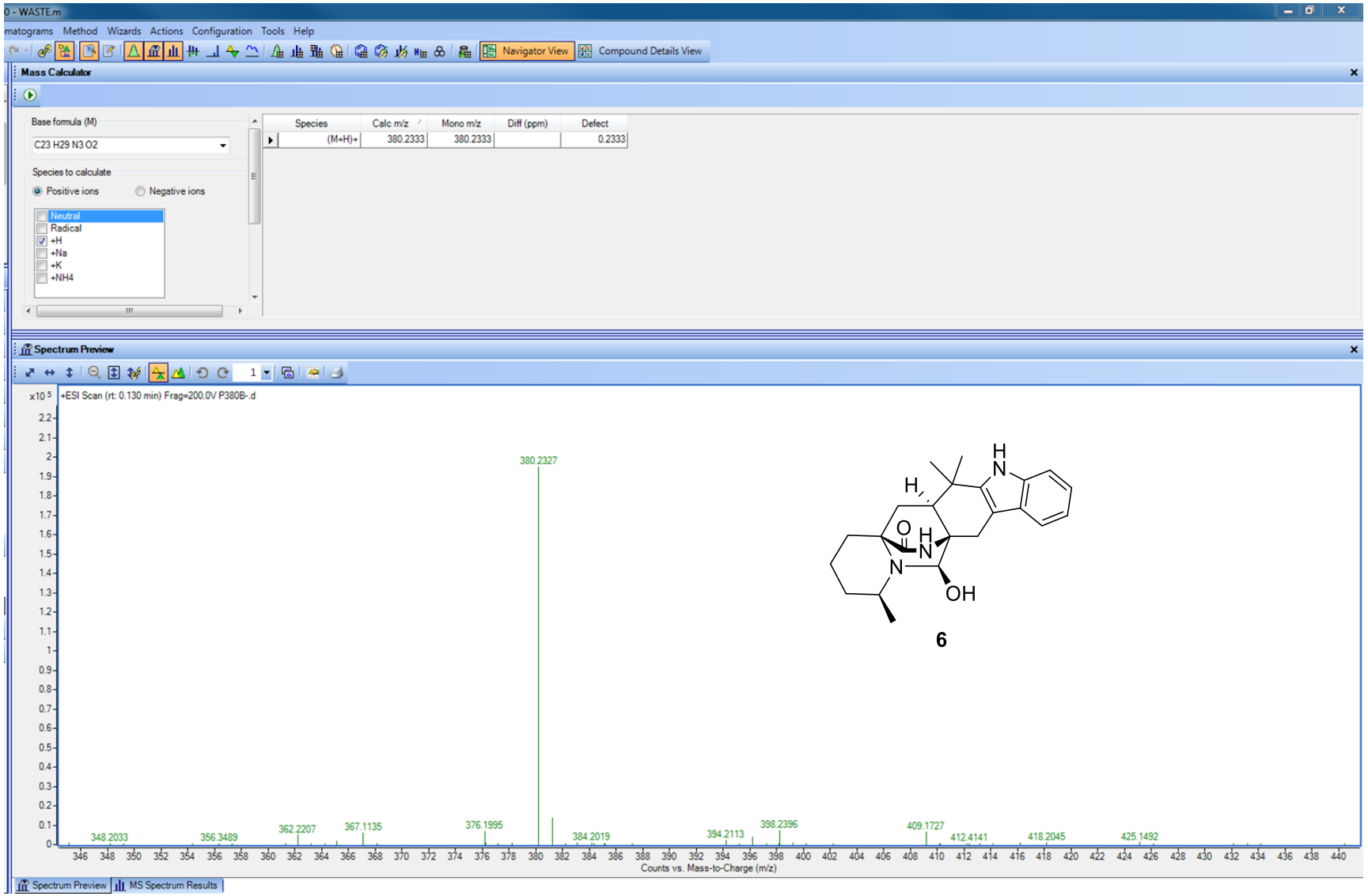
Supplementary Fig. 11-5 | HSQC NMR spectrum of 6 in CD_3CN.



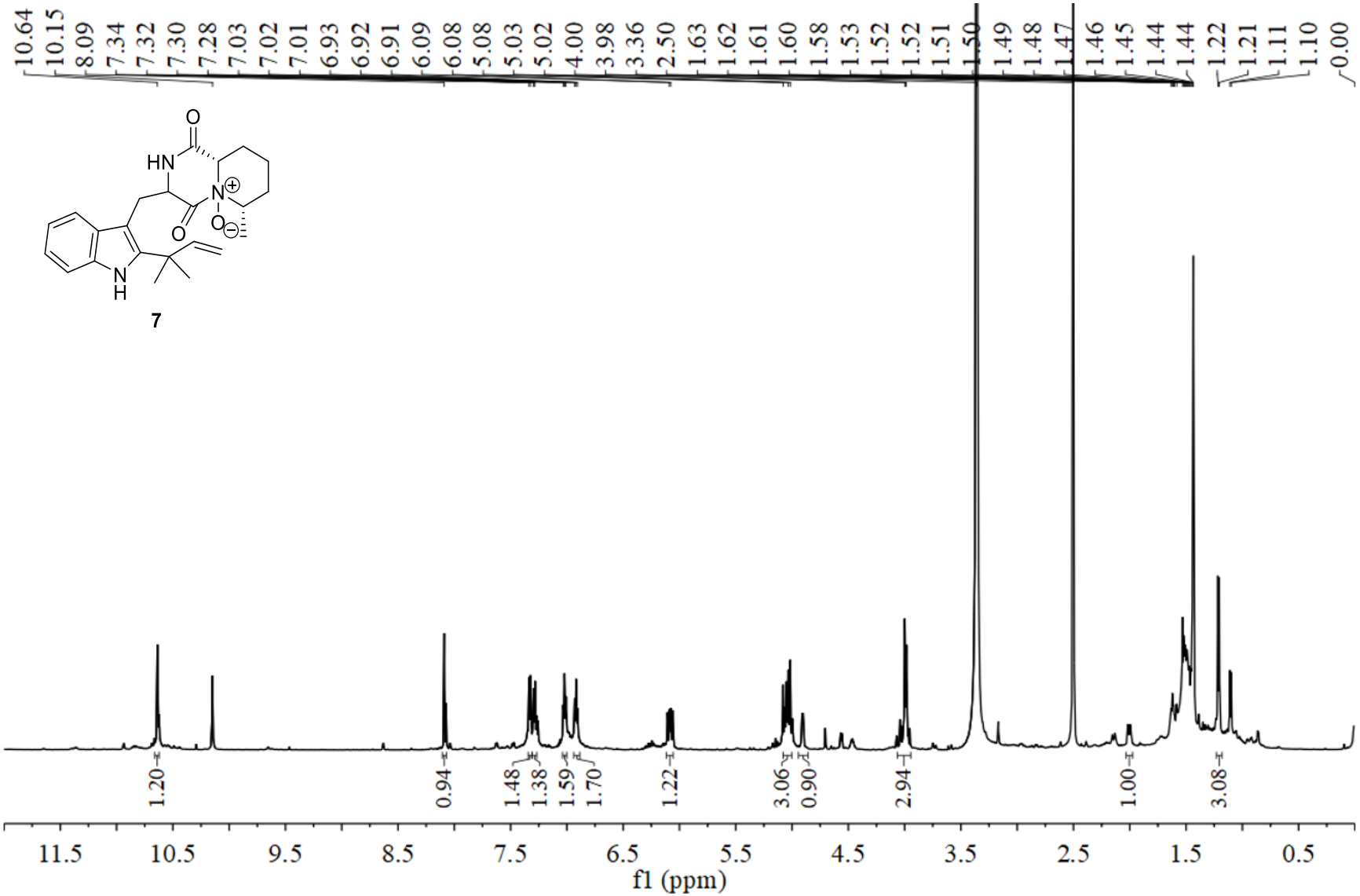
Supplementary Fig. 11-6 | HMBC NMR spectrum of 6 in CD_3CN.



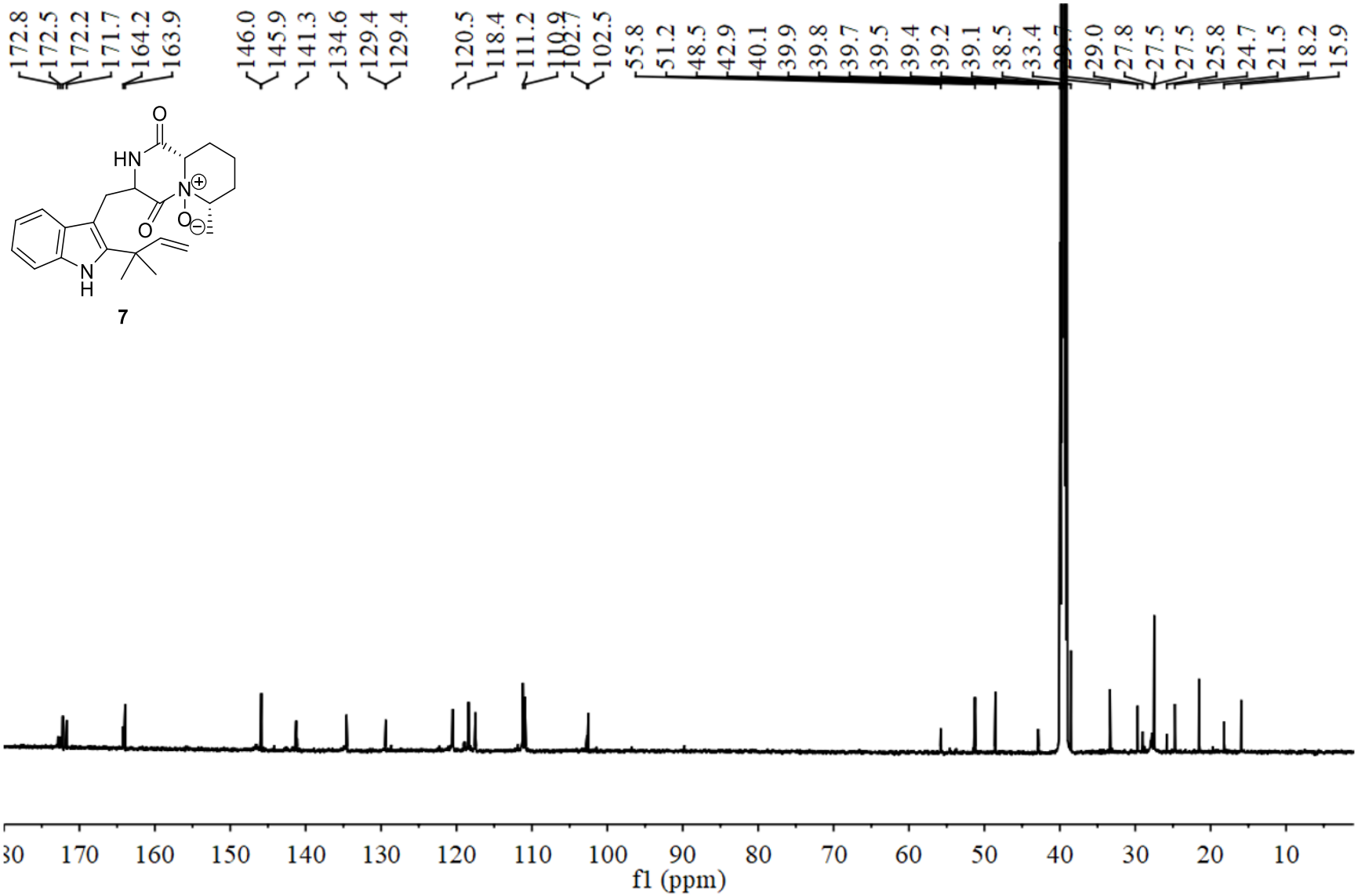
Supplementary Fig. 11-7 | NOESY NMR spectrum of 6 in CD_3CN.



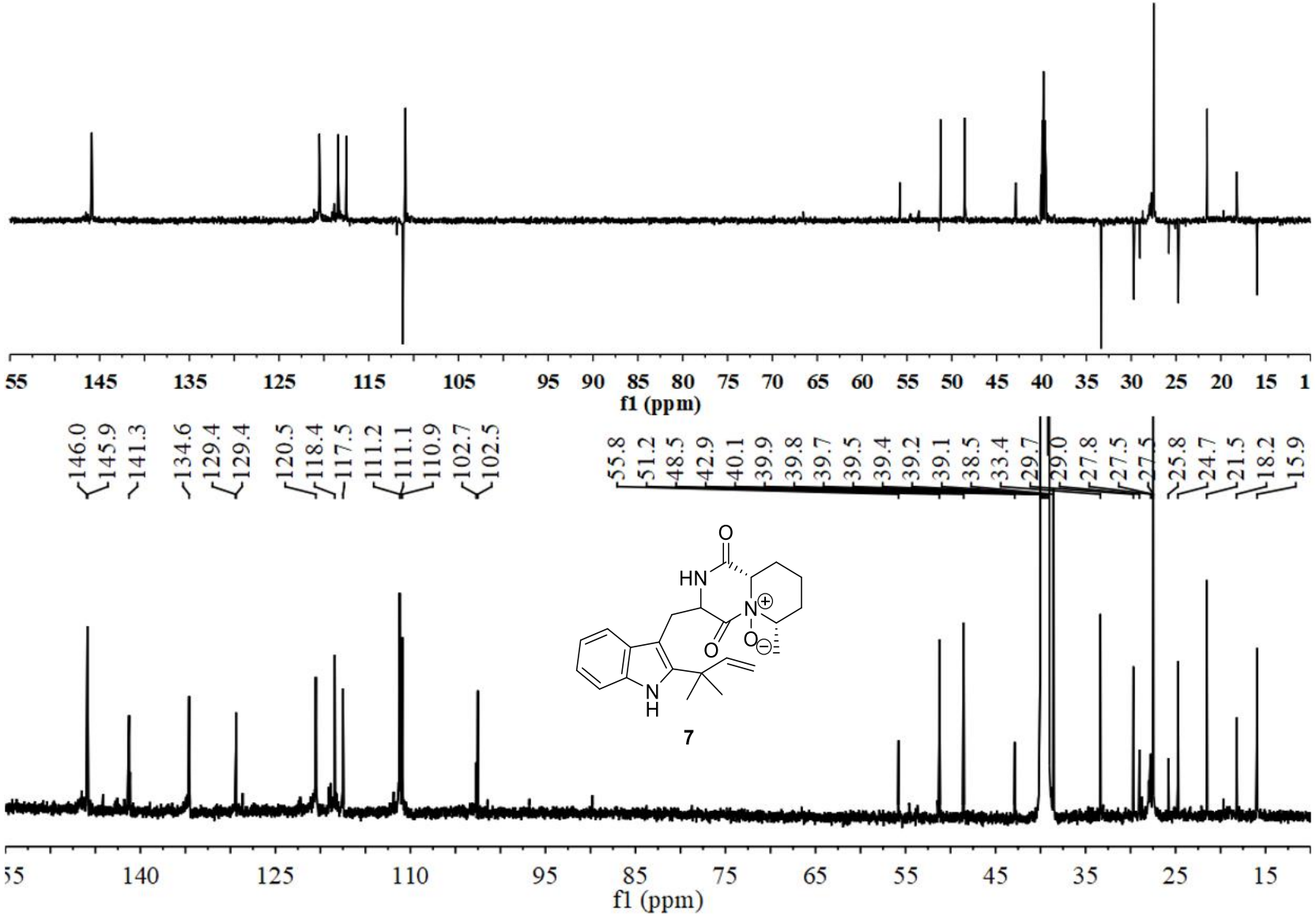
Supplementary Fig. 11-8 | HRMS spectrum of 6.



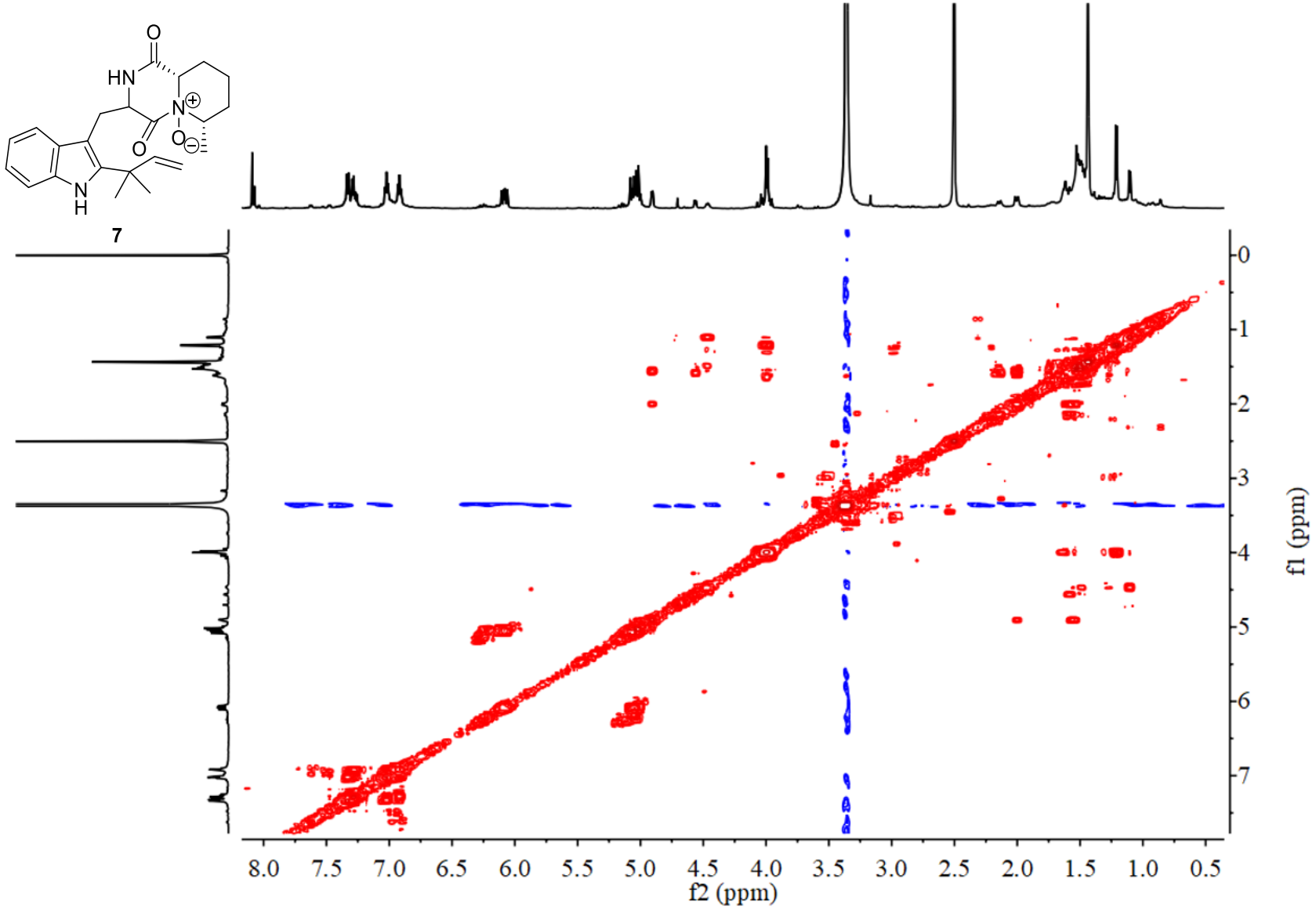
Supplementary Fig. 12-1 | ^{1}H NMR spectrum of 7 in DMSO-*d*$_6$.



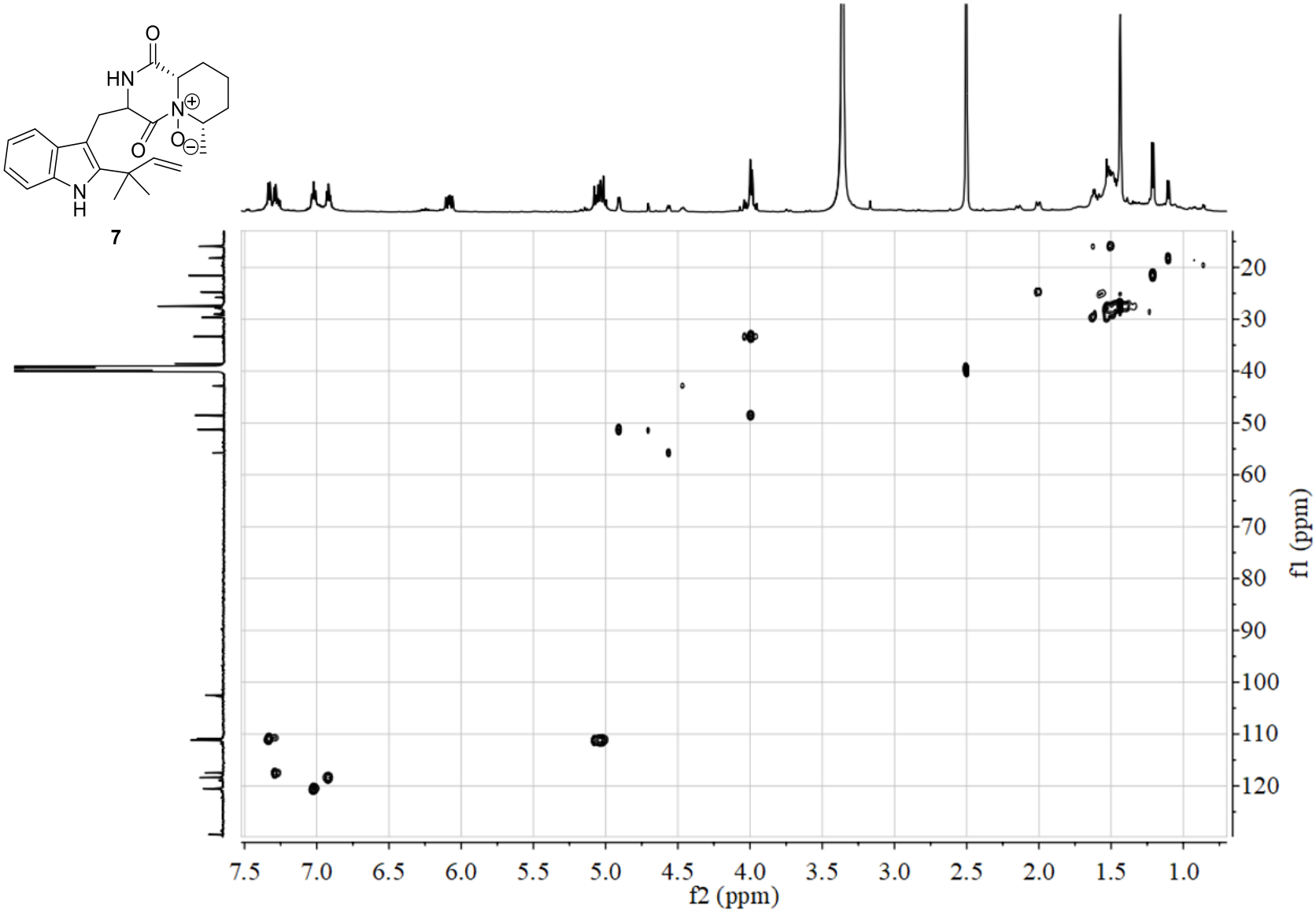
Supplementary Fig. 12-2 | ^{13}C NMR spectrum of 7 in DMSO-*d*$_6$.



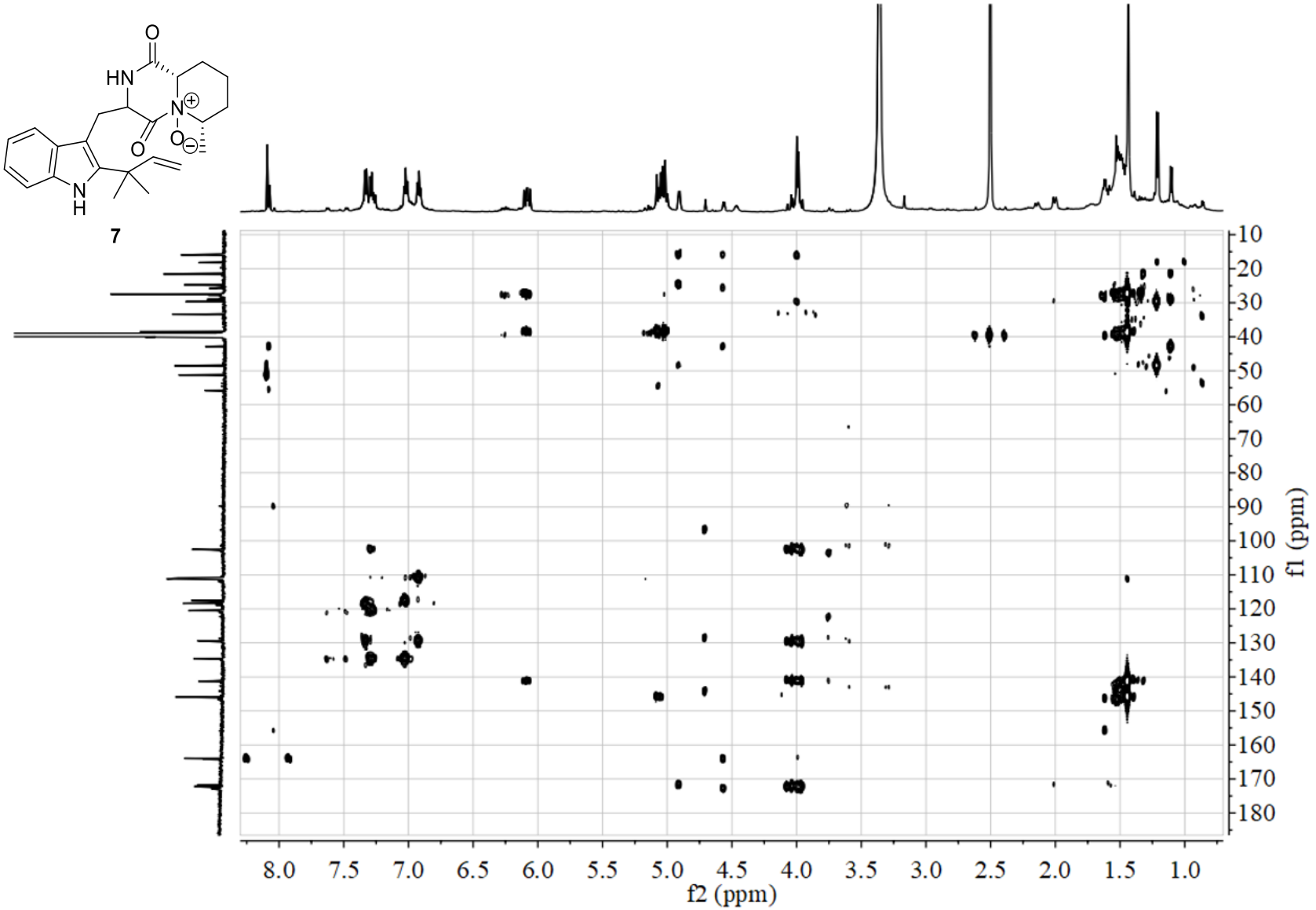
Supplementary Fig. 12-3 | DEPT135 and ^{13}C NMR spectra of 7 in DMSO-*d*$_6$.



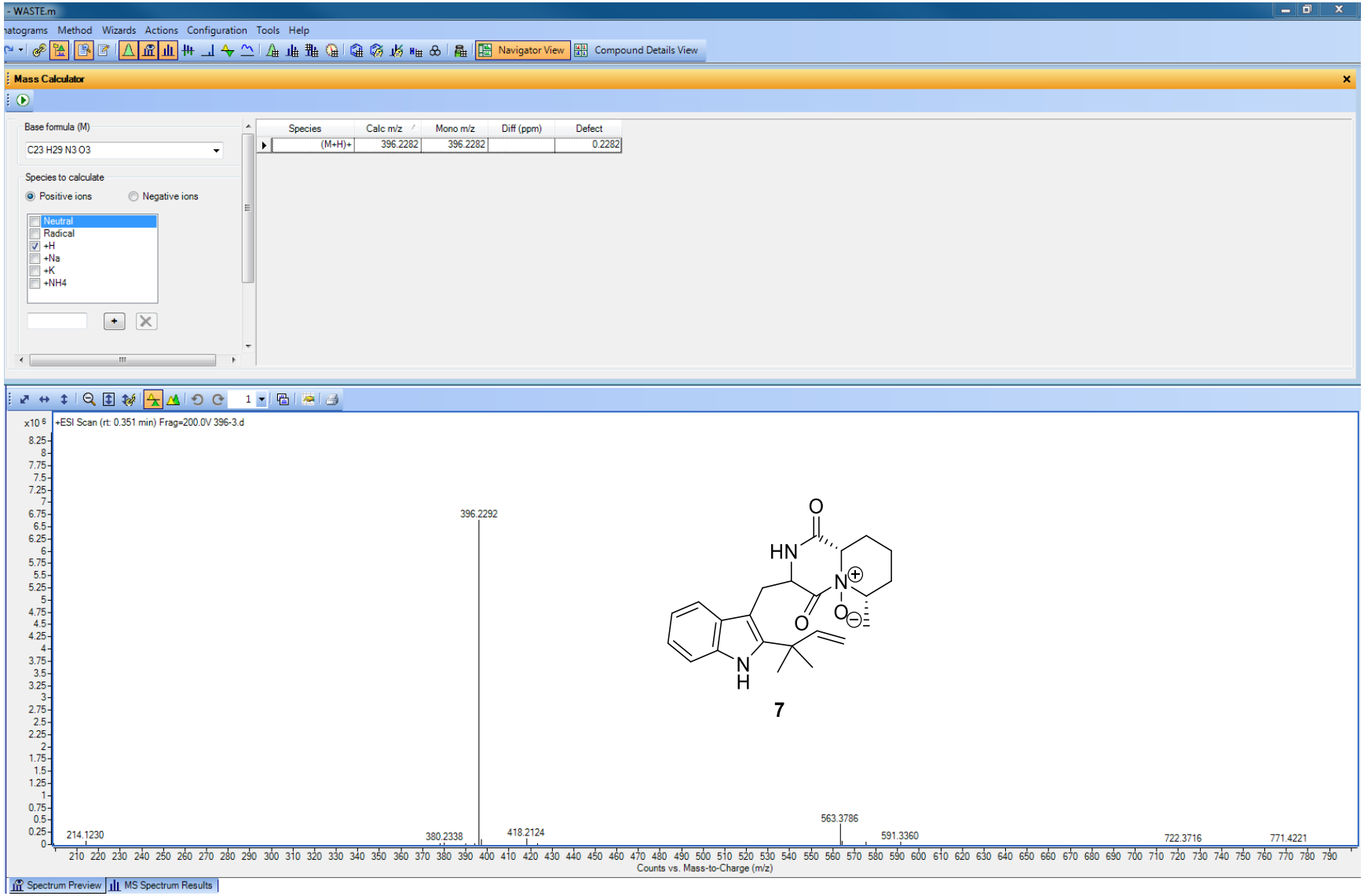
Supplementary Fig. 12-4 | ^{1}H-^{1}H COSY NMR spectrum of 7 in DMSO-*d*$_6$.



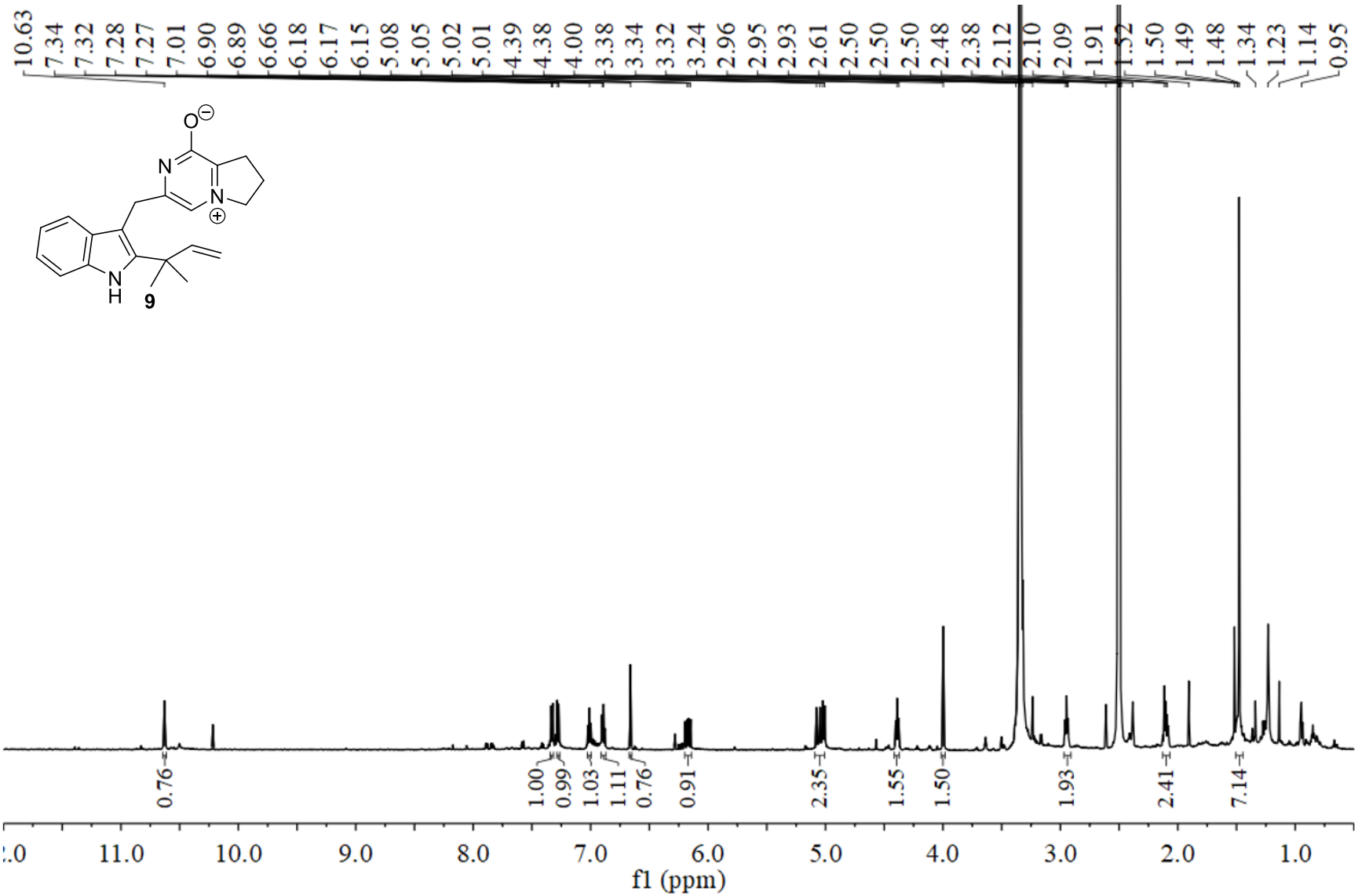
Supplementary Fig. 12-5 | HSQC NMR spectrum of 7 in DMSO-*d*$_6$.



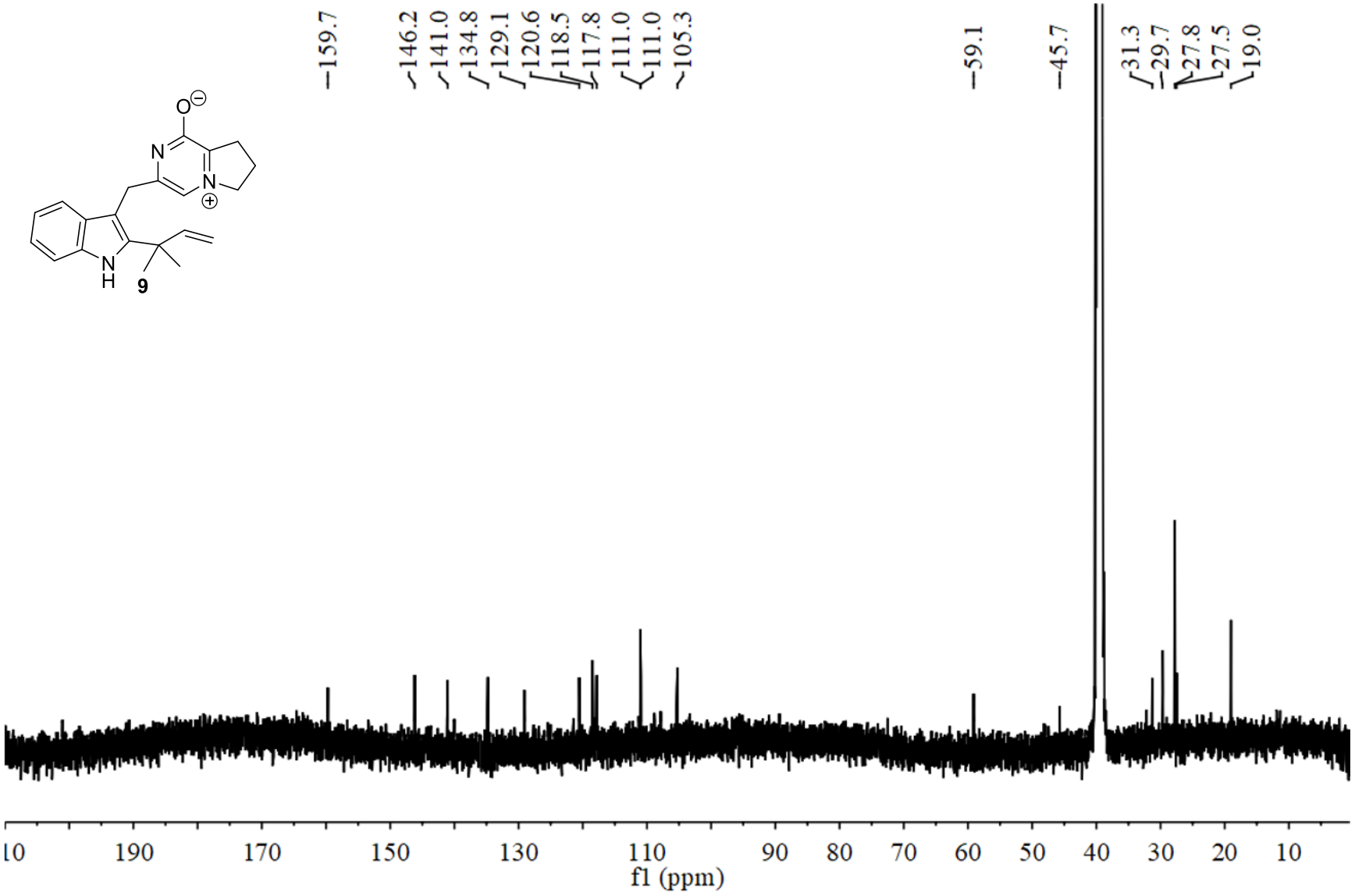
Supplementary Fig. 12-6 | HMBC NMR spectrum of 7 in DMSO-d_6.



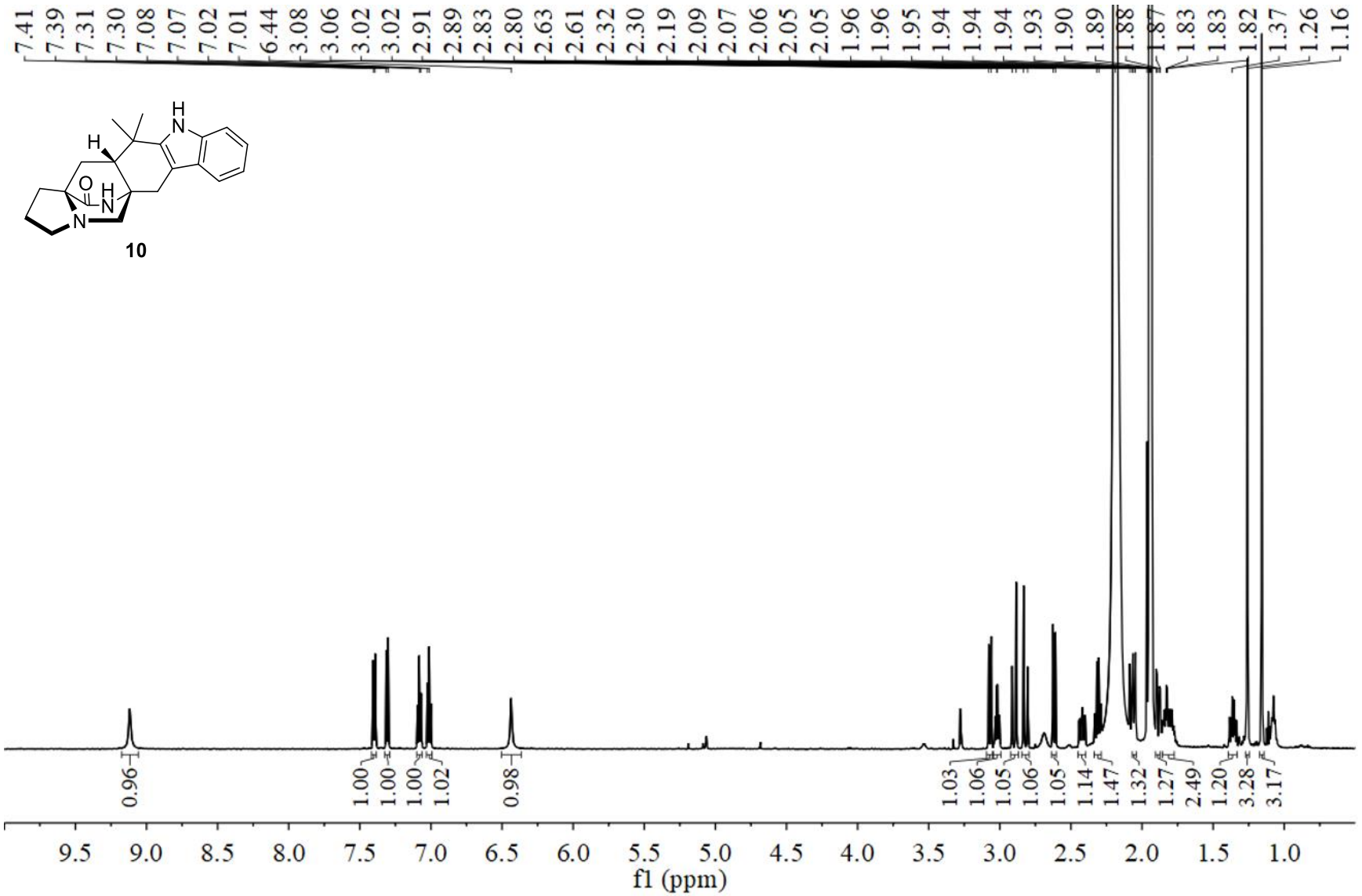
Supplementary Fig. 12-7 | HRMS spectrum of 7.



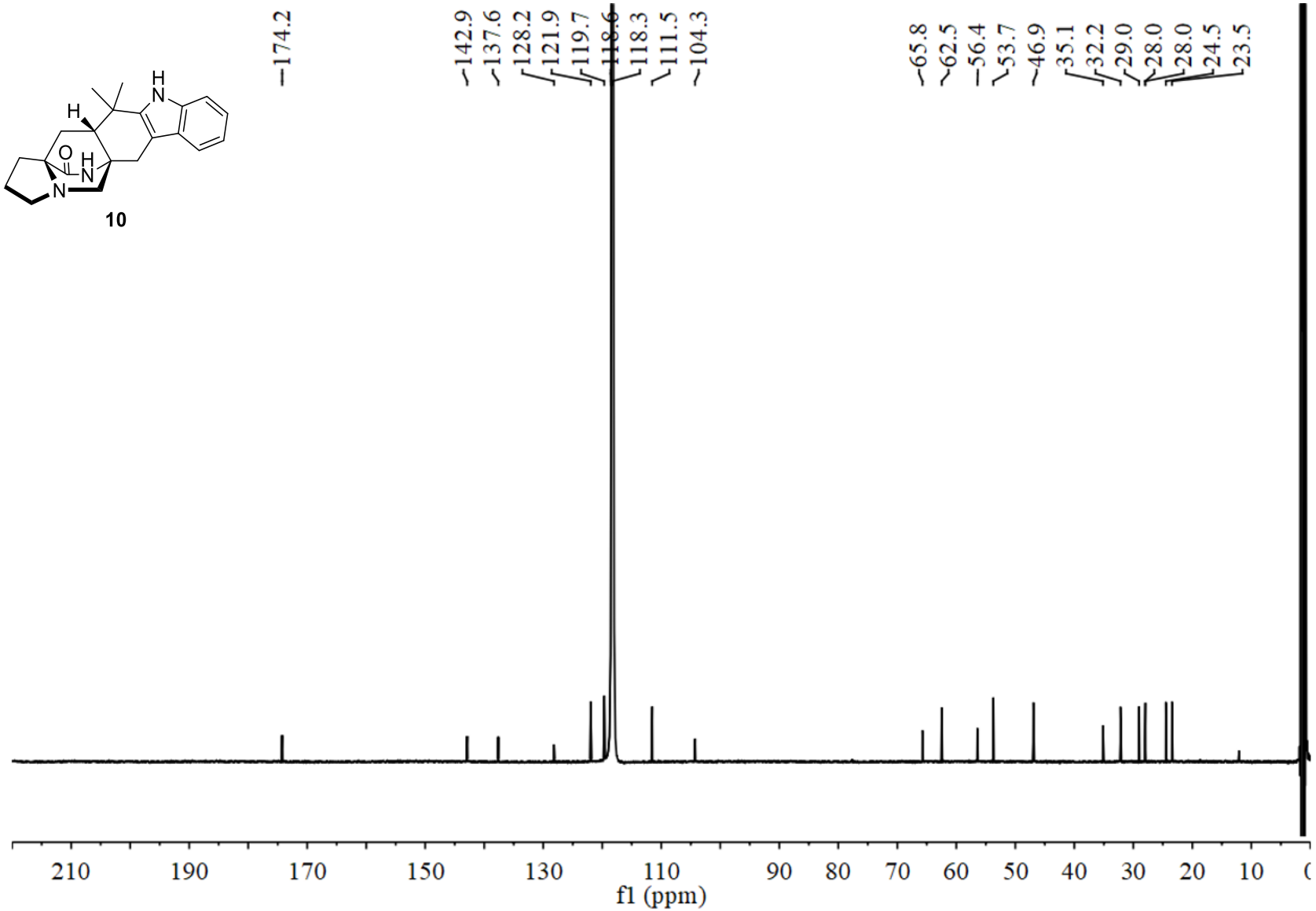
Supplementary Fig. 13-1 | ^{1}H NMR spectrum of 9 in DMSO-*d*$_6$.



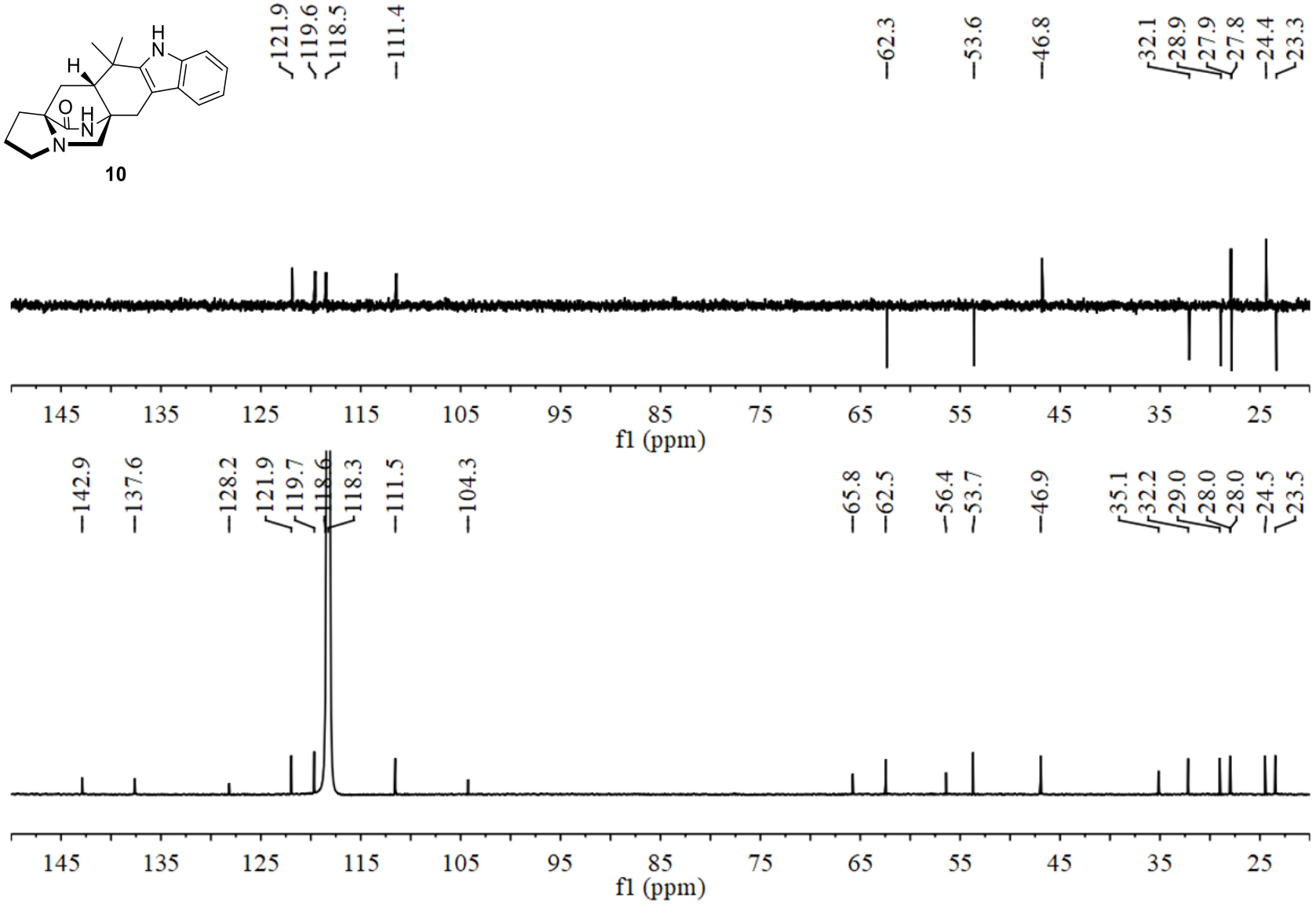
Supplementary Fig. 13-2 | ^{13}C NMR spectrum of 9 in DMSO-*d*$_6$.



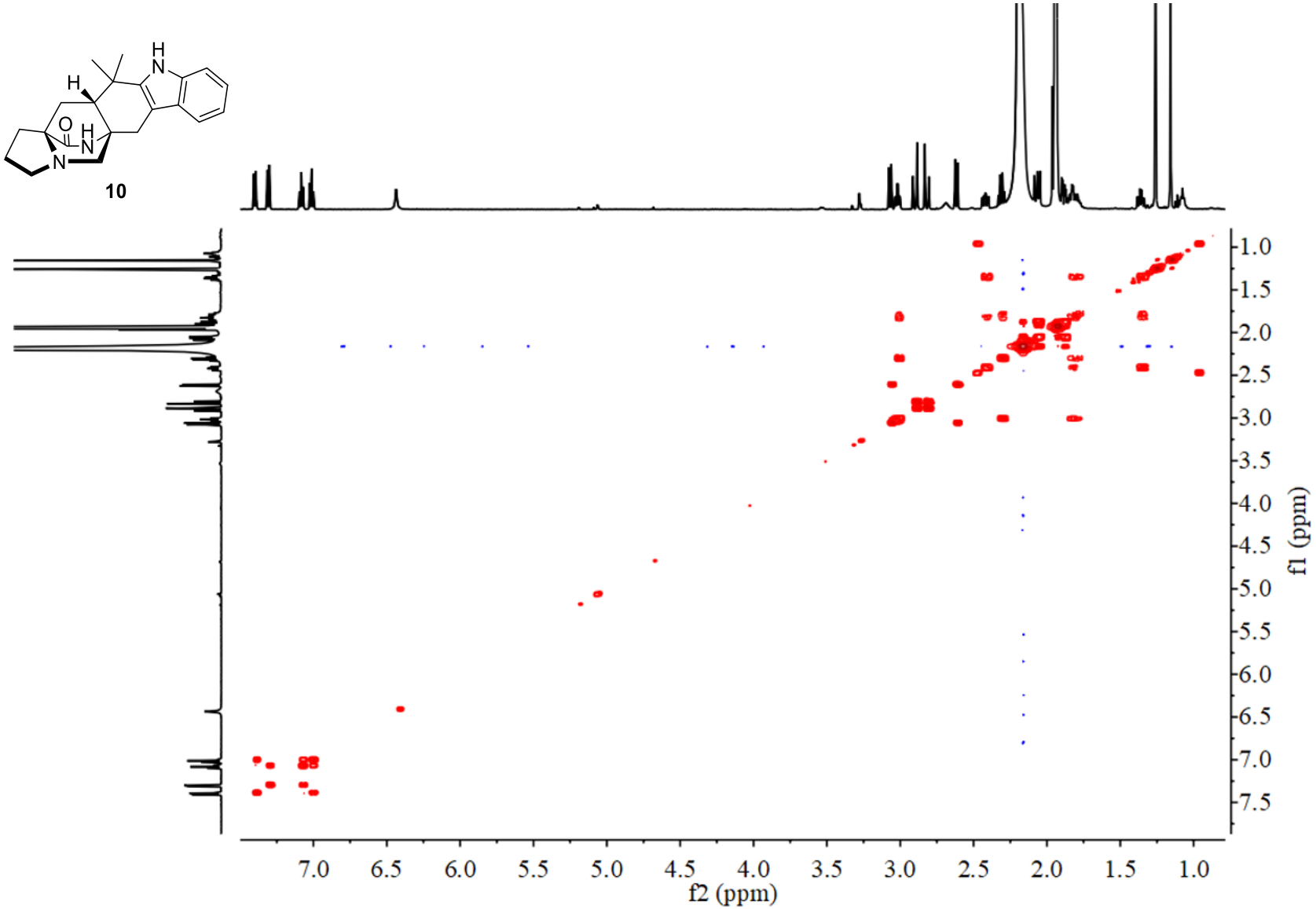
Supplementary Fig. 14-1 | ^{1}H NMR spectrum of 10 in CD_3CN.



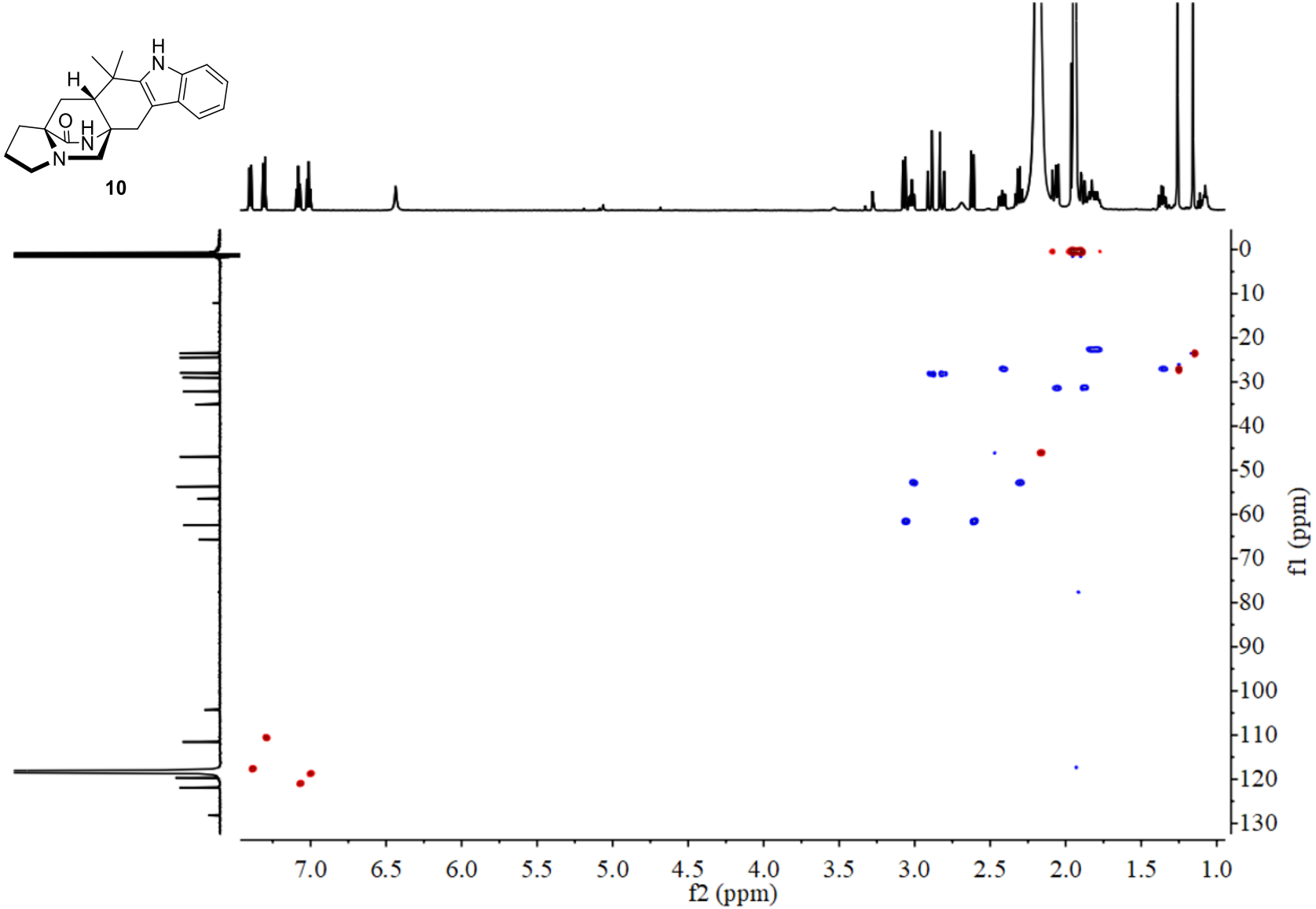
Supplementary Fig. 14-2 | ^{13}C NMR spectrum of 10 in CD_3CN.



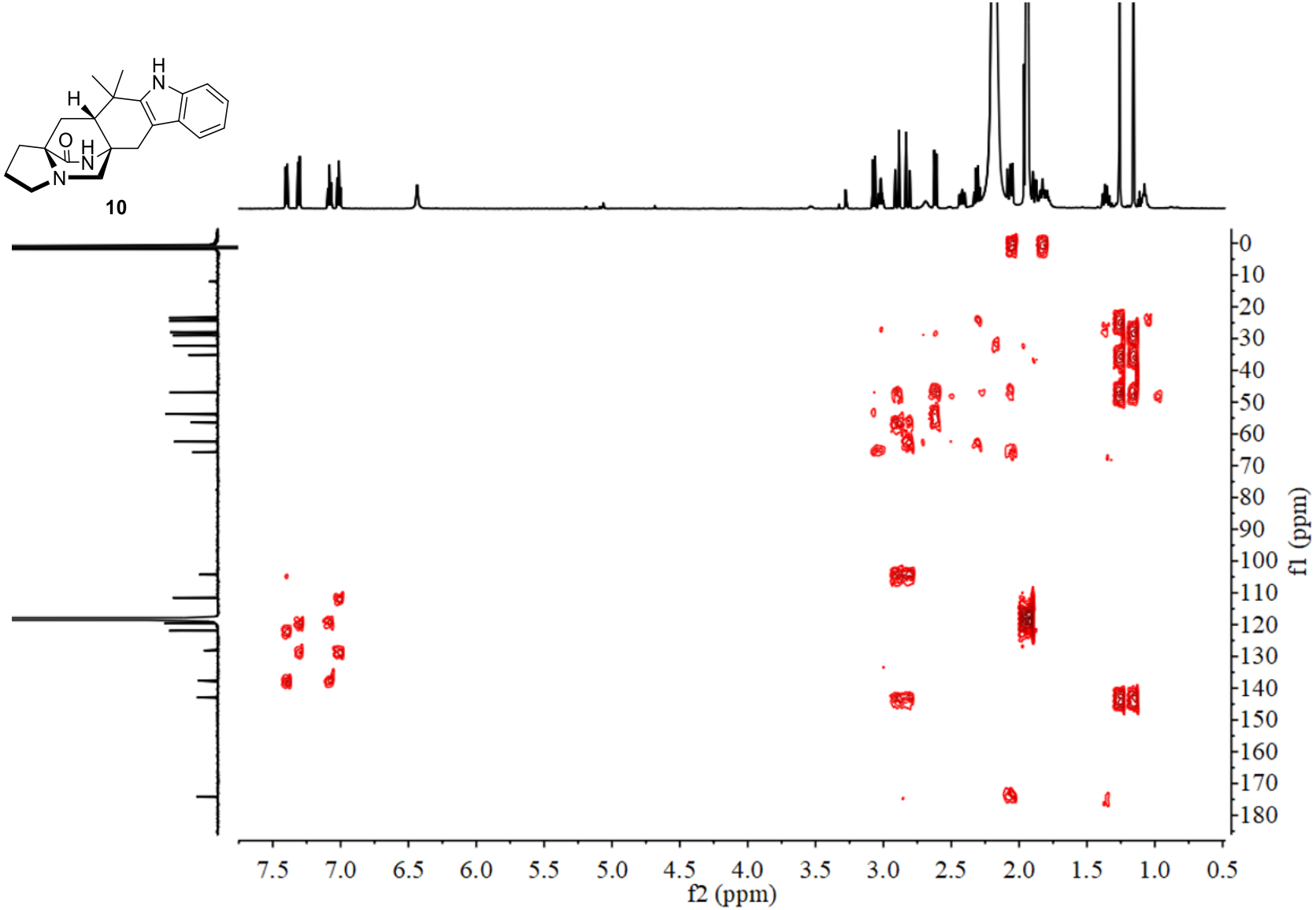
Supplementary Fig. 14-3 | DEPT135 and ^{13}C NMR spectra of 10 in CD_3CN.



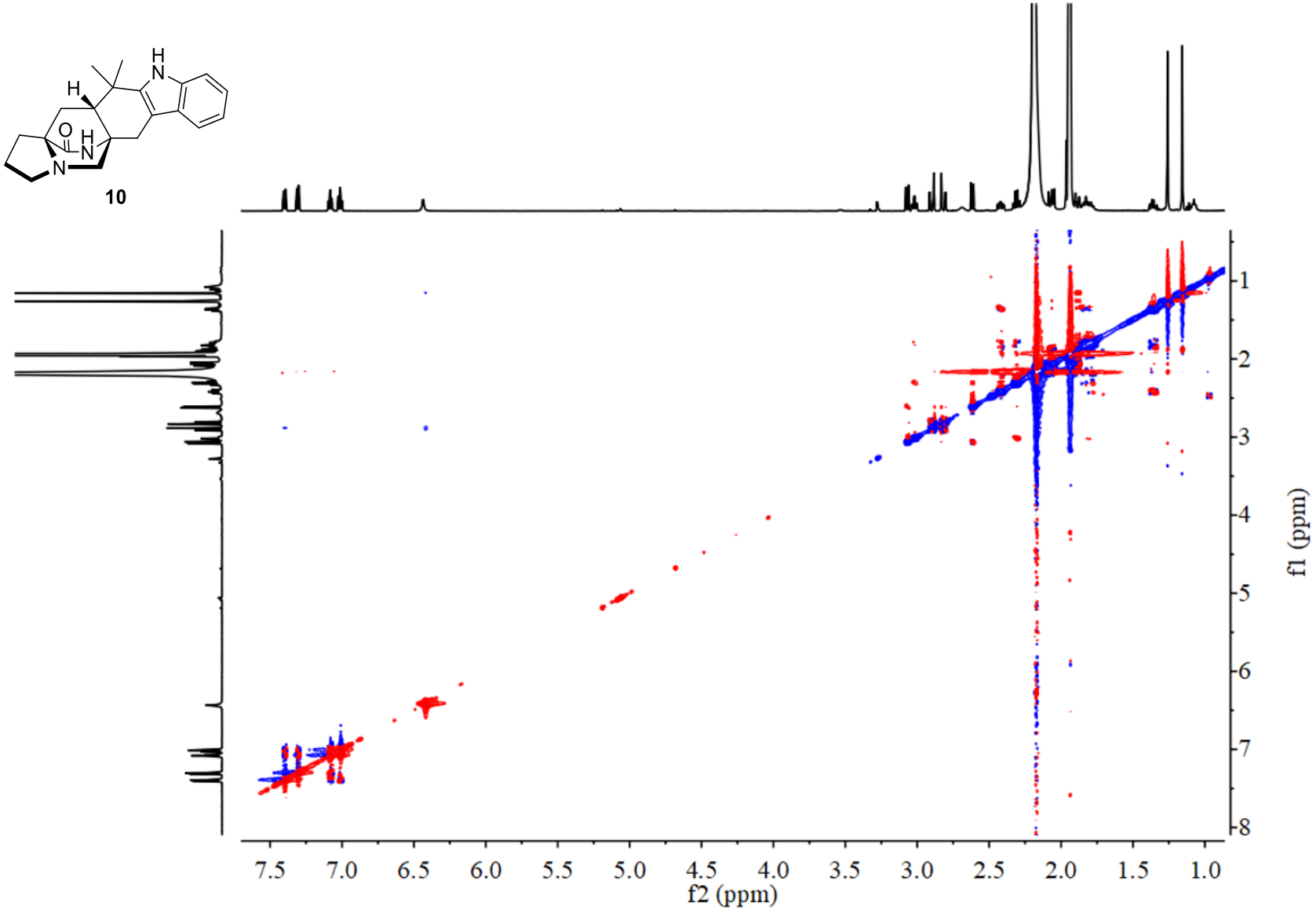
Supplementary Fig. 14-4 | ^{1}H-^{1}H COSY NMR spectrum of 10 in CD_3CN.



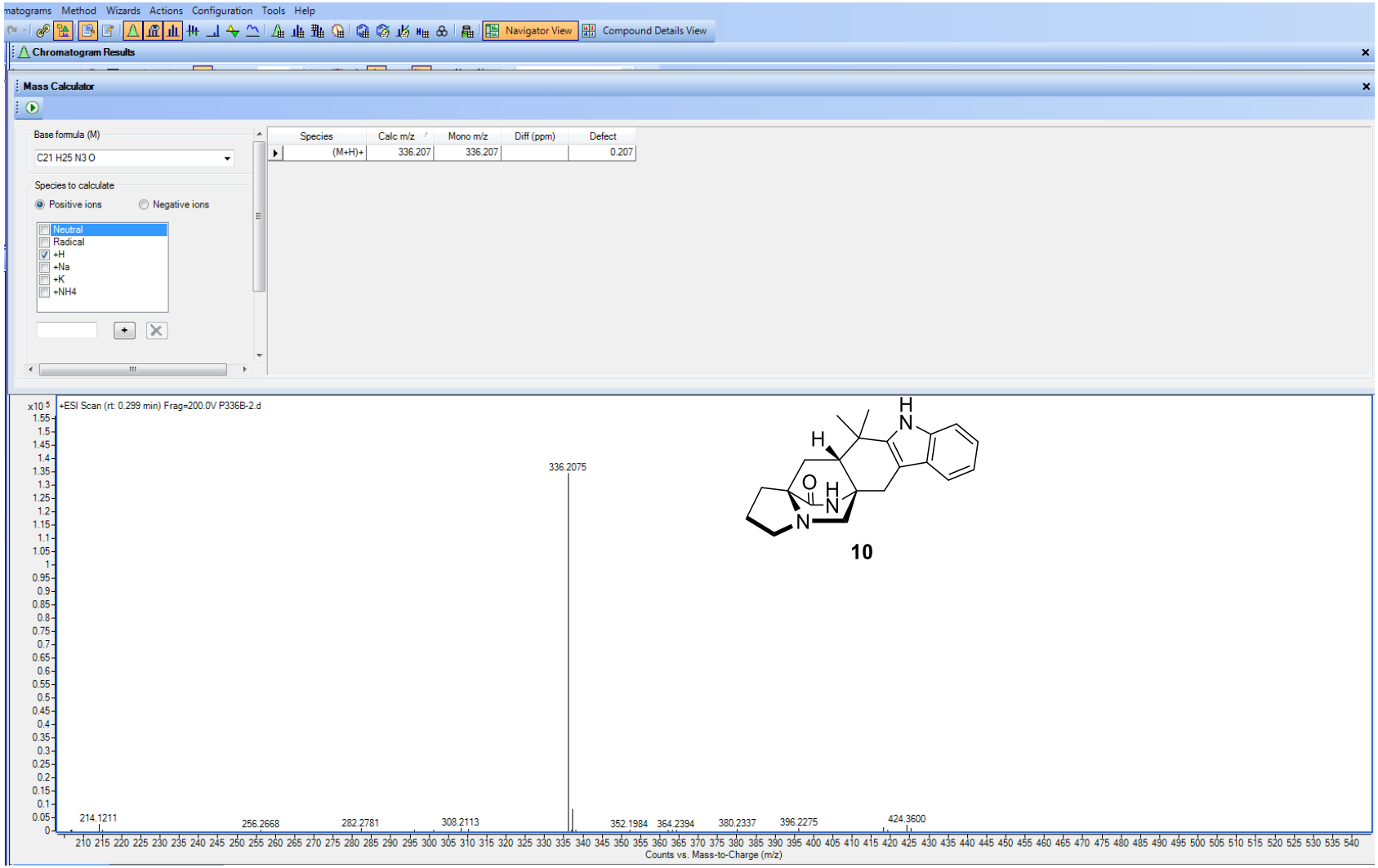
Supplementary Fig. 14-5 | HSQC NMR spectrum of 10 in CD_3CN.



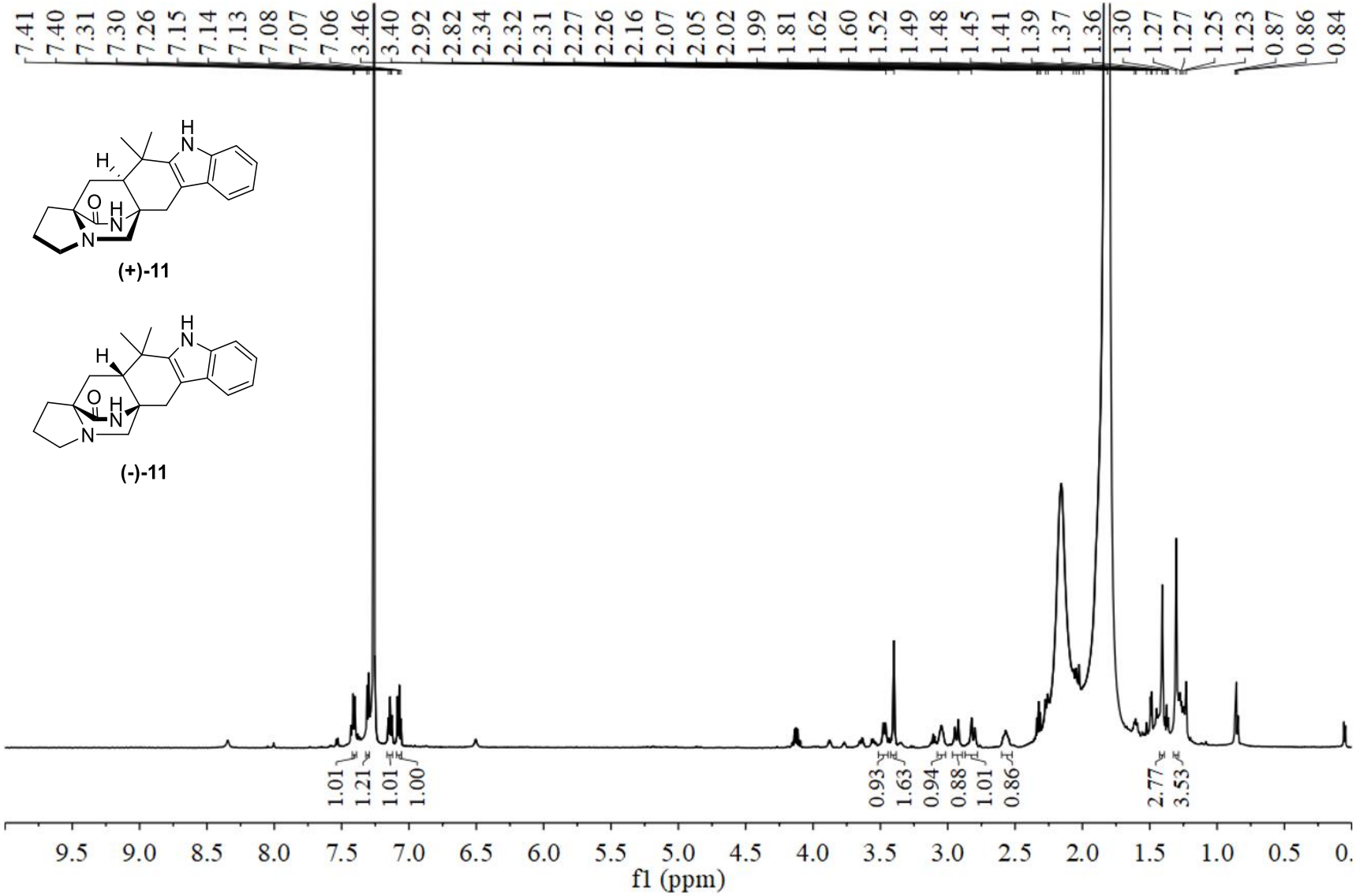
Supplementary Fig. 14-6 | HMBC NMR spectrum of 10 in CD_3CN.



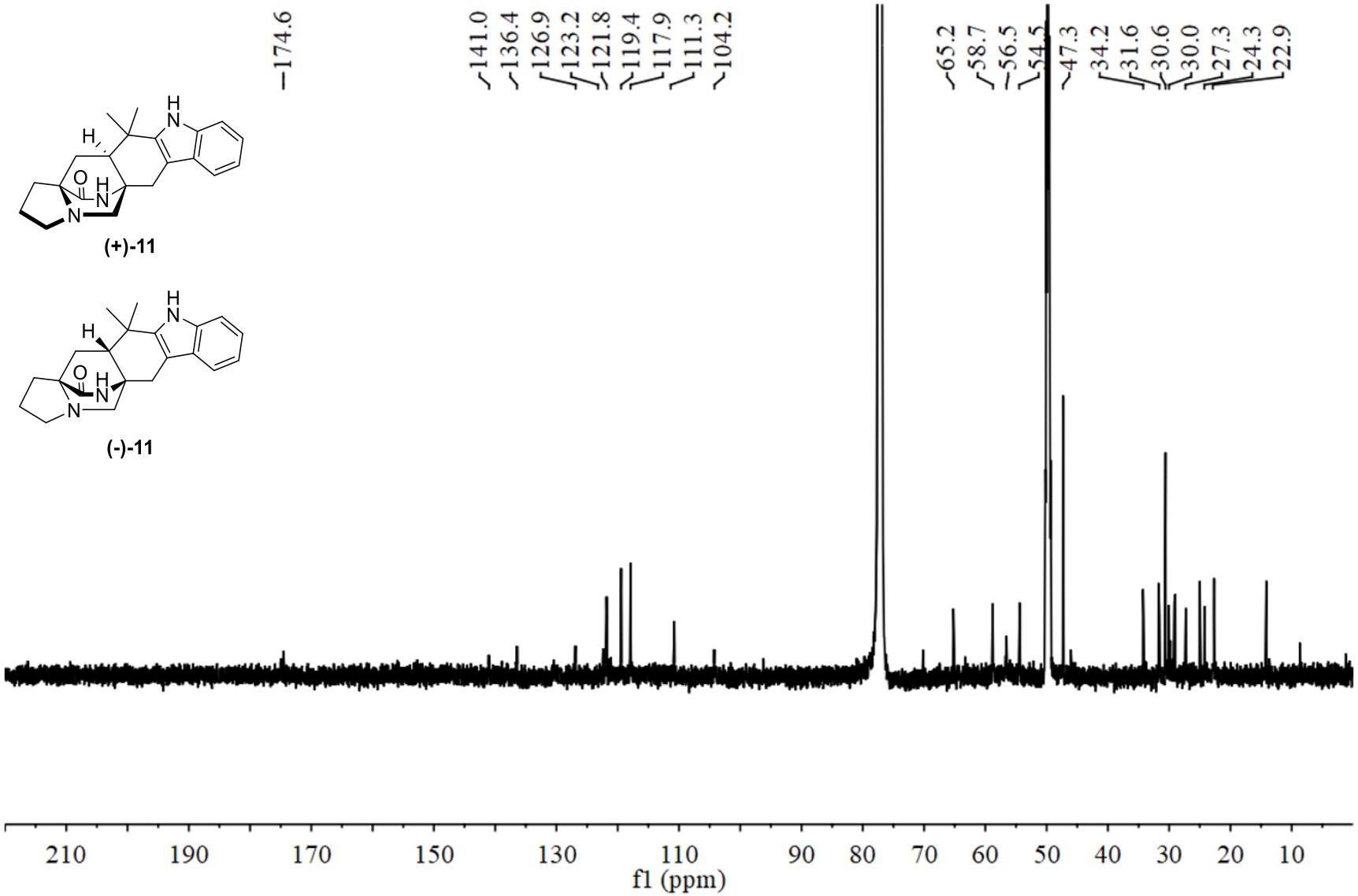
Supplementary Fig. 14-7 | NOESY NMR spectrum of 10 in CD_3CN.



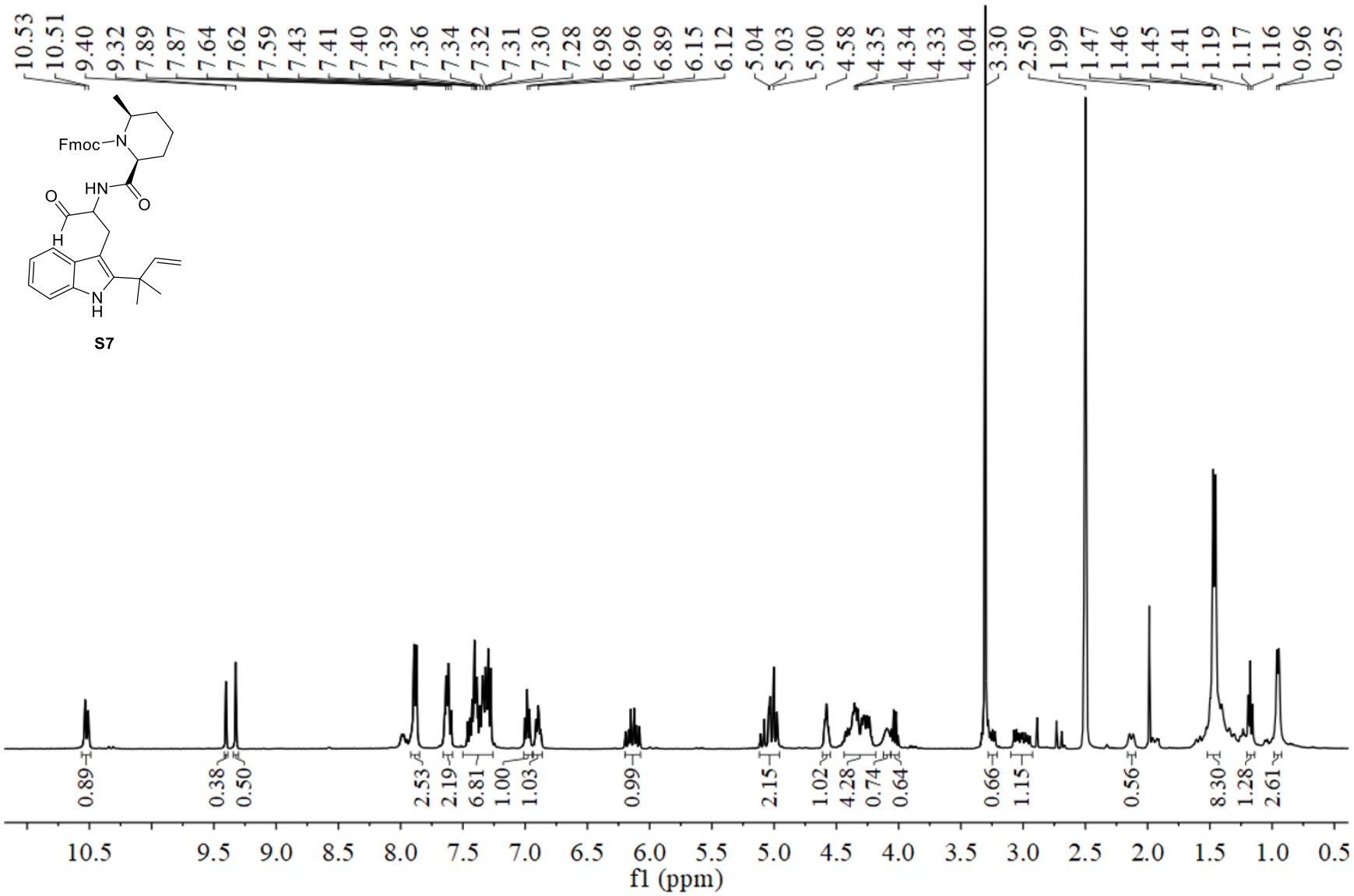
Supplementary Fig. 14-8 | HRMS spectrum of 10.



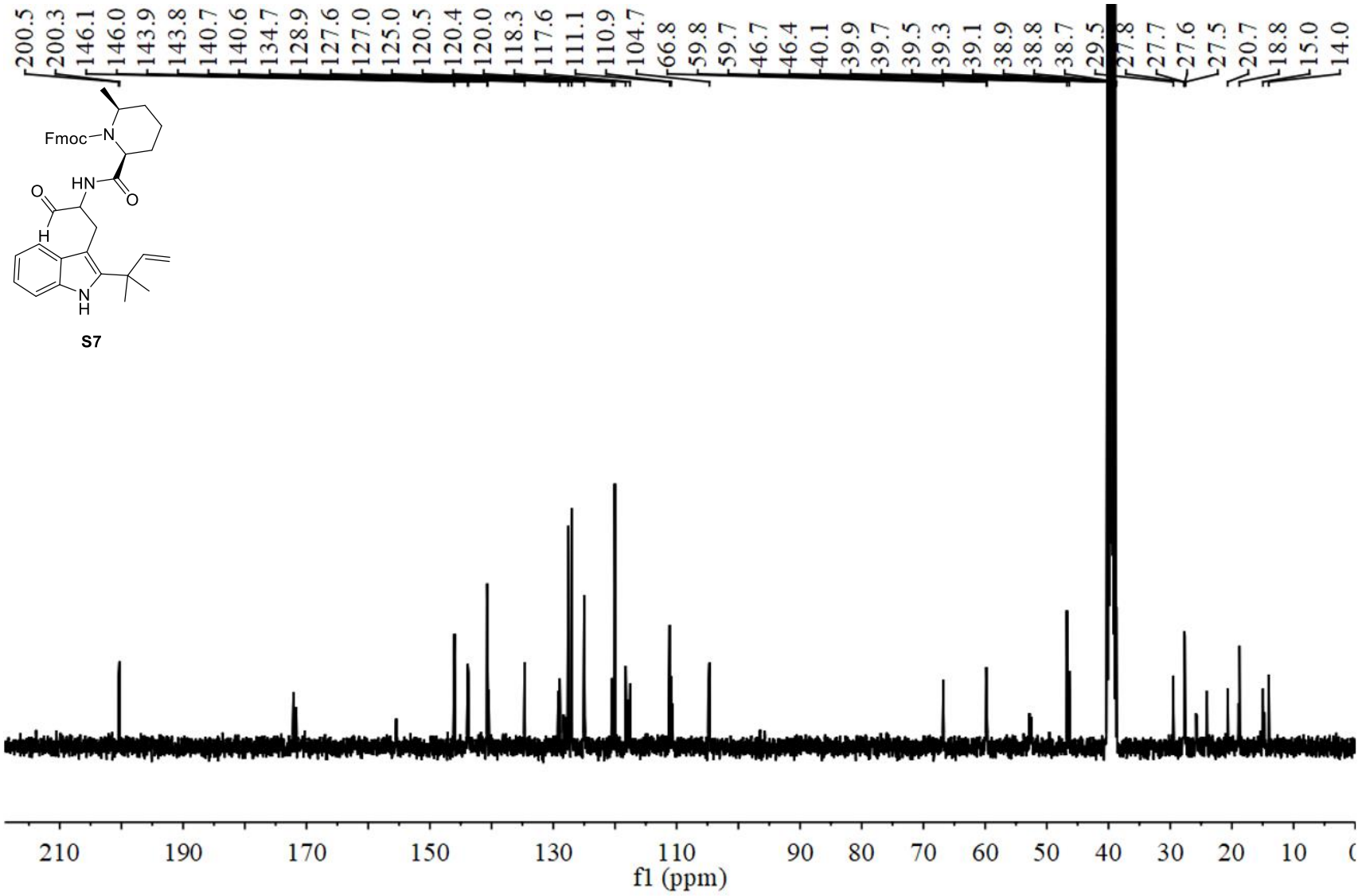
Supplementary Fig. 15-1 | ^{1}H NMR spectrum of 11 in $CD_3CD/CDCl_3$ (1/10).



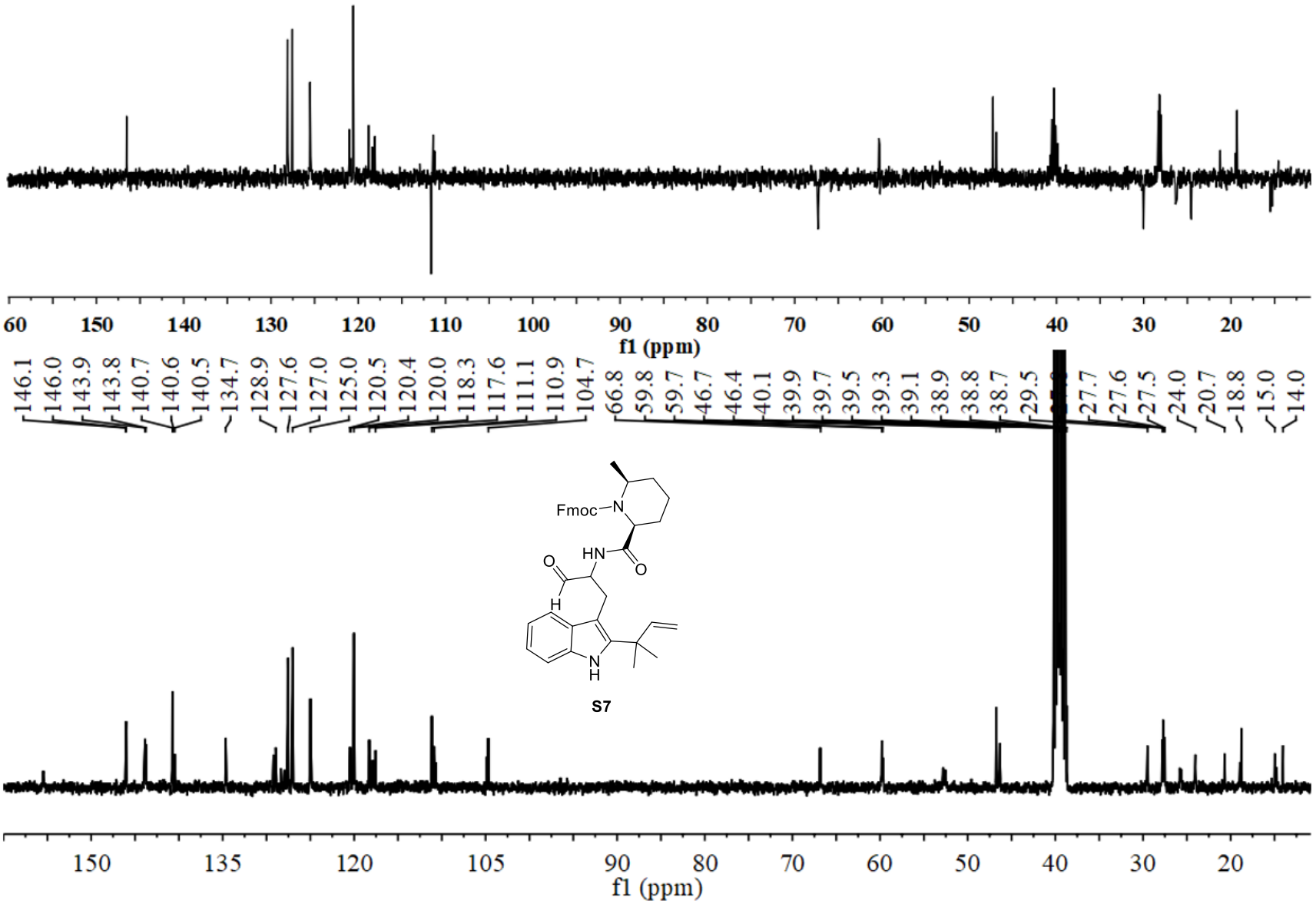
Supplementary Fig. 15-2 | ^{13}C NMR spectrum of 11 in $CD_3CD/CDCl_3$ (1/10)[2].



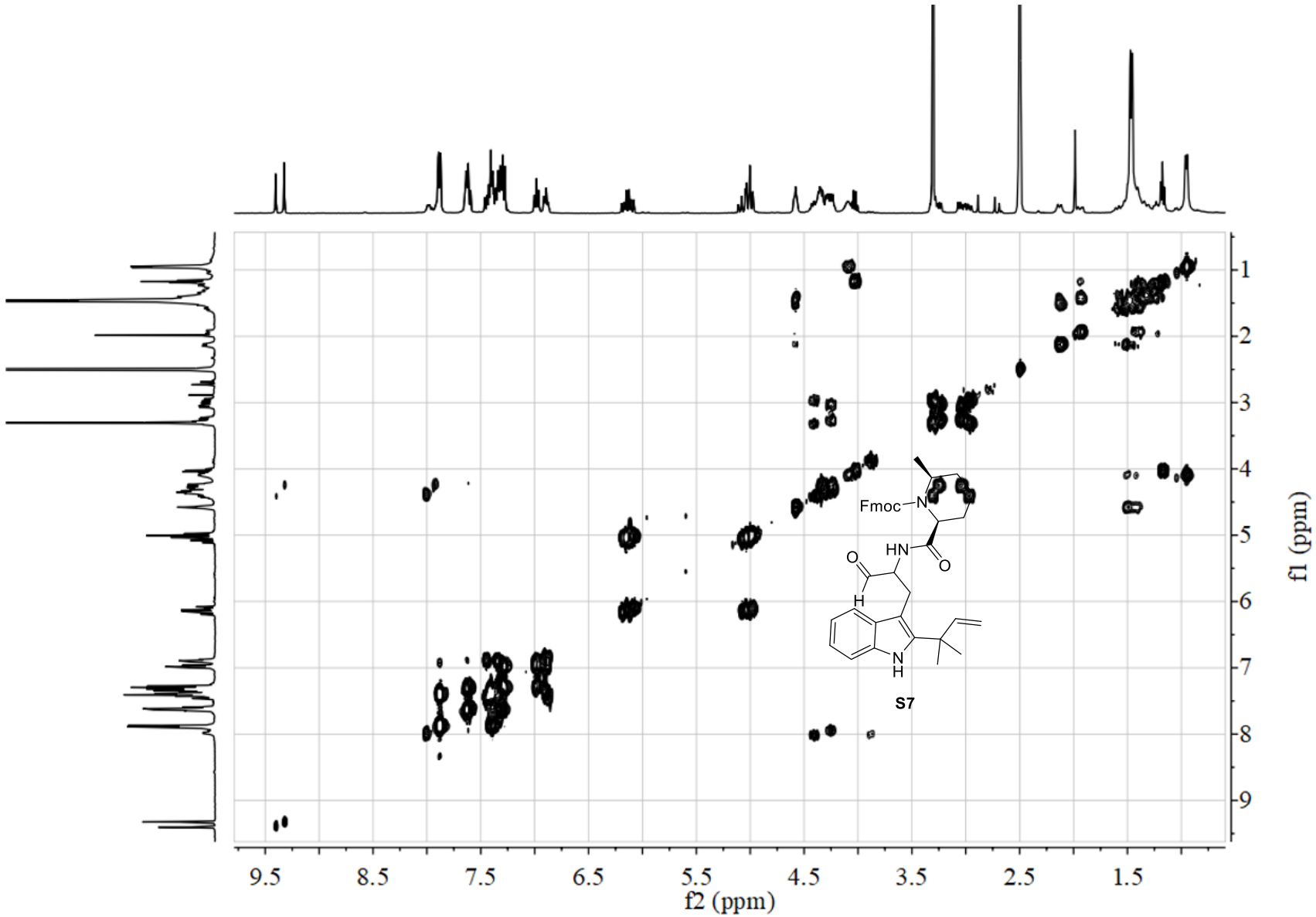
Supplementary Fig. 16-1 | ^{1}H NMR spectrum of S7 in DMSO-*d*$_6$.



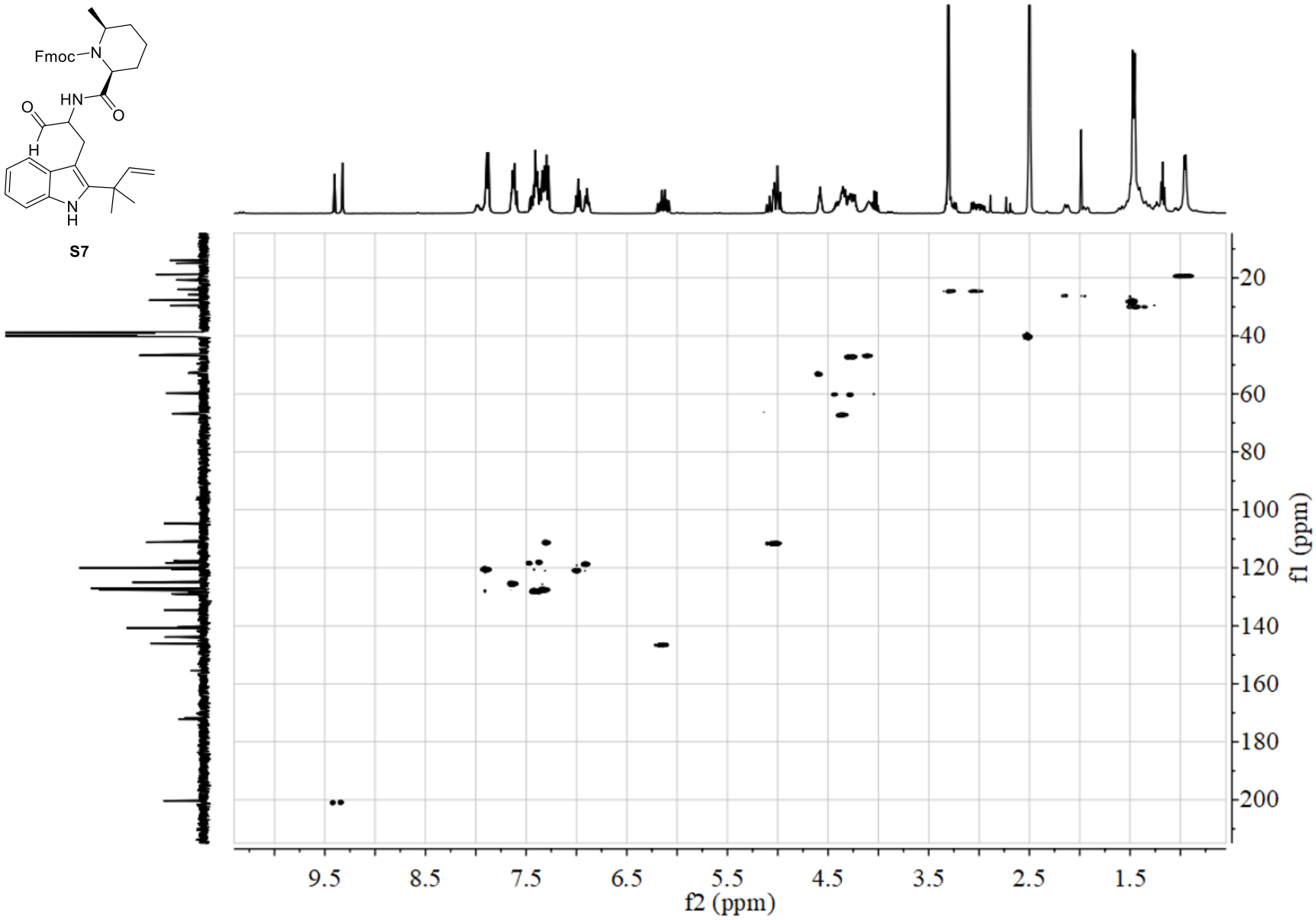
Supplementary Fig. 16-2 | ^{13}C NMR spectrum of S7 in DMSO-*d*$_6$.



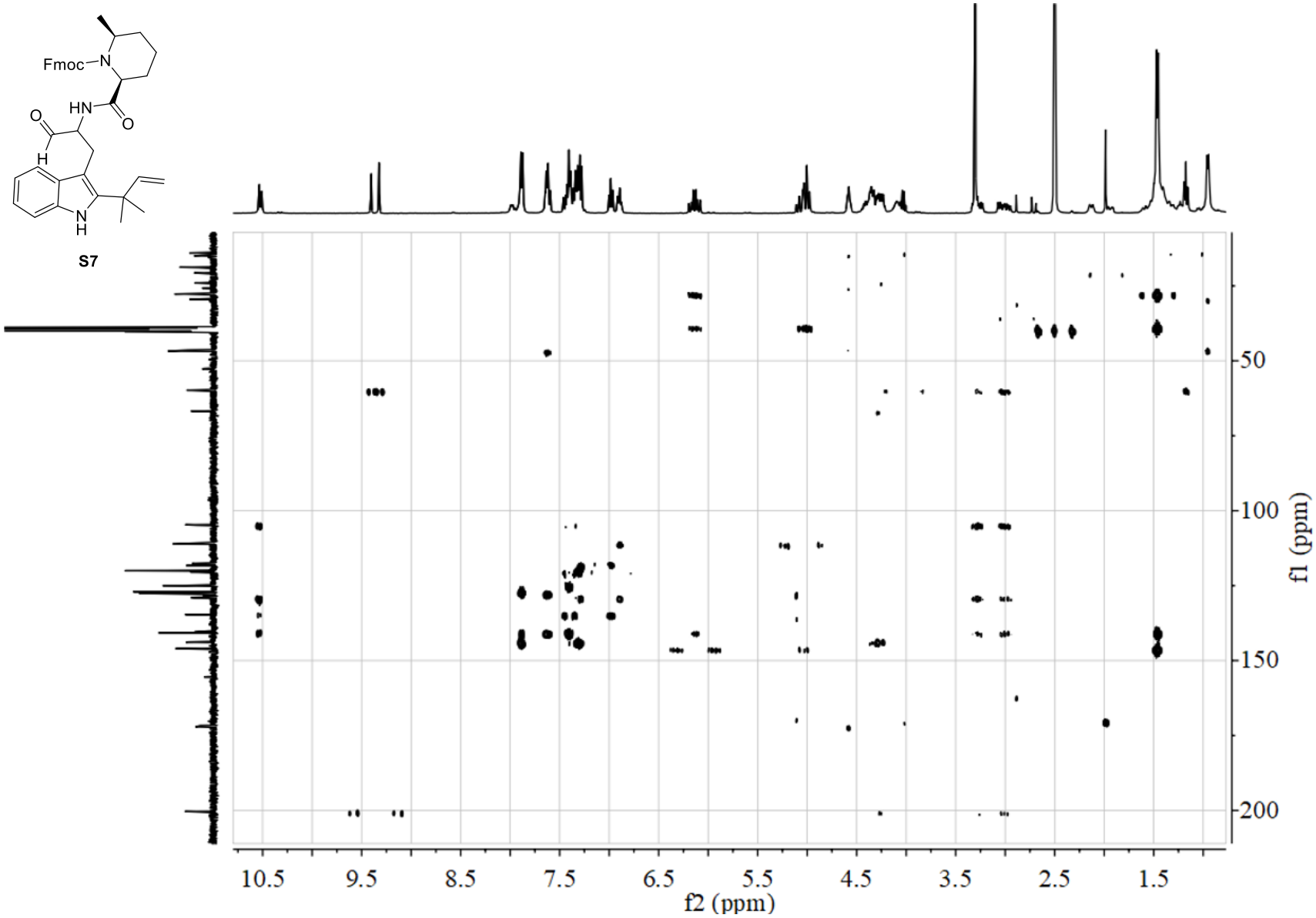
Supplementary Fig. 16-3 | DEPT135 and ^{13}C NMR spectra of S7 in DMSO-d_6.



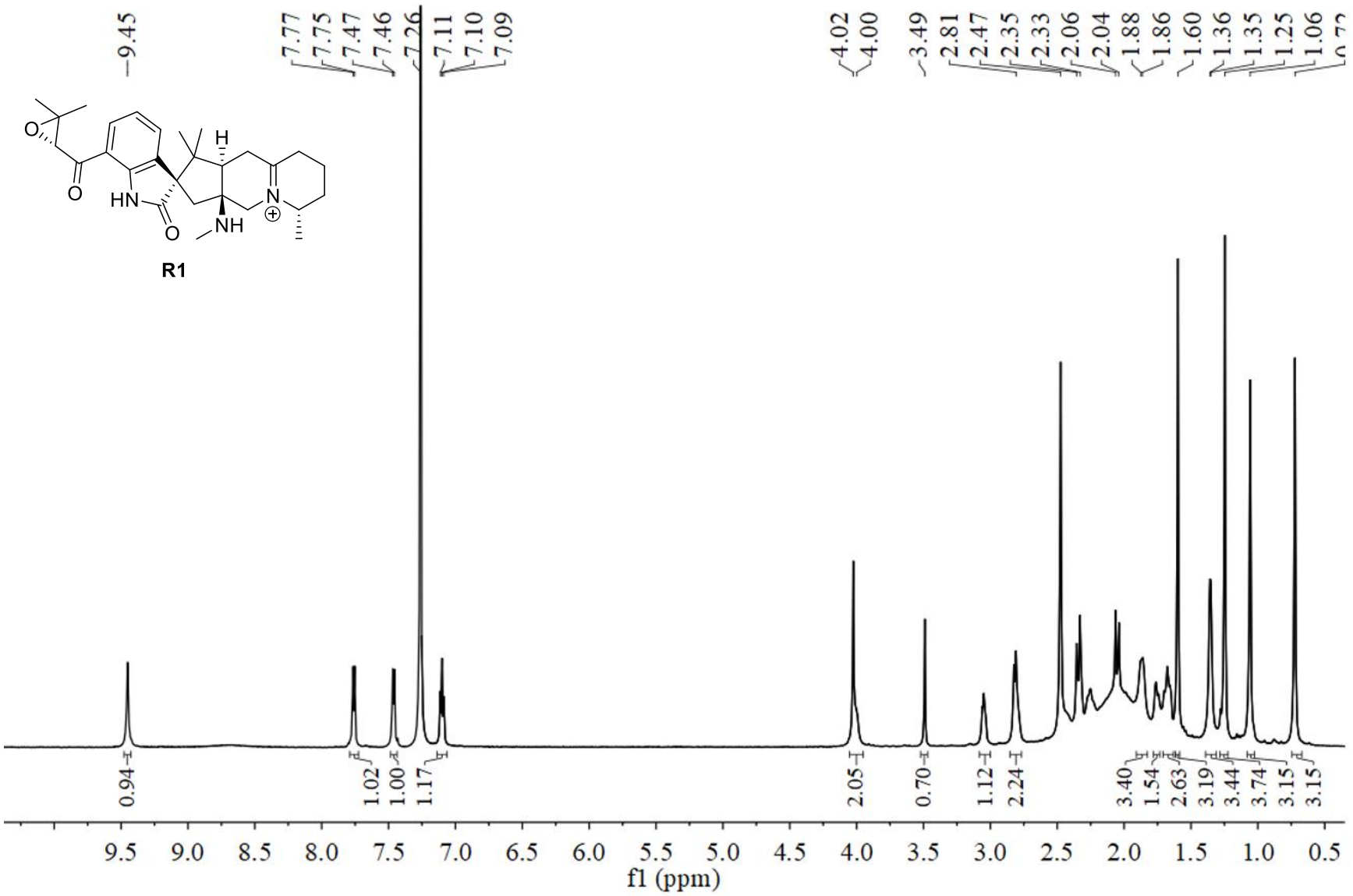
Supplementary Fig. 16-4 | ^{1}H-^{1}H COSY NMR spectrum of S7 in DMSO-*d*$_6$.



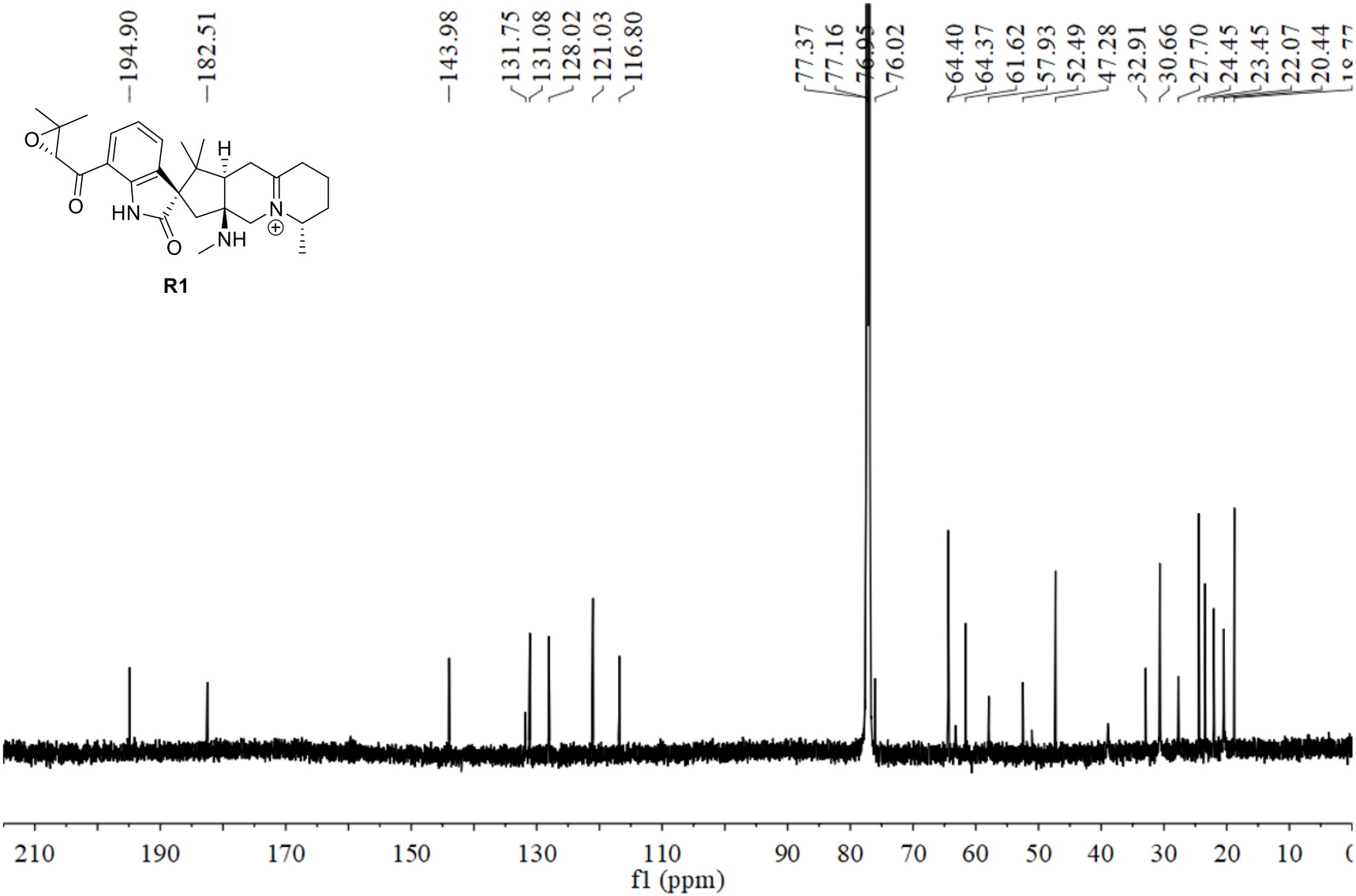
Supplementary Fig. 16-5 | HSQC NMR spectrum of S7 in DMSO-d_6.



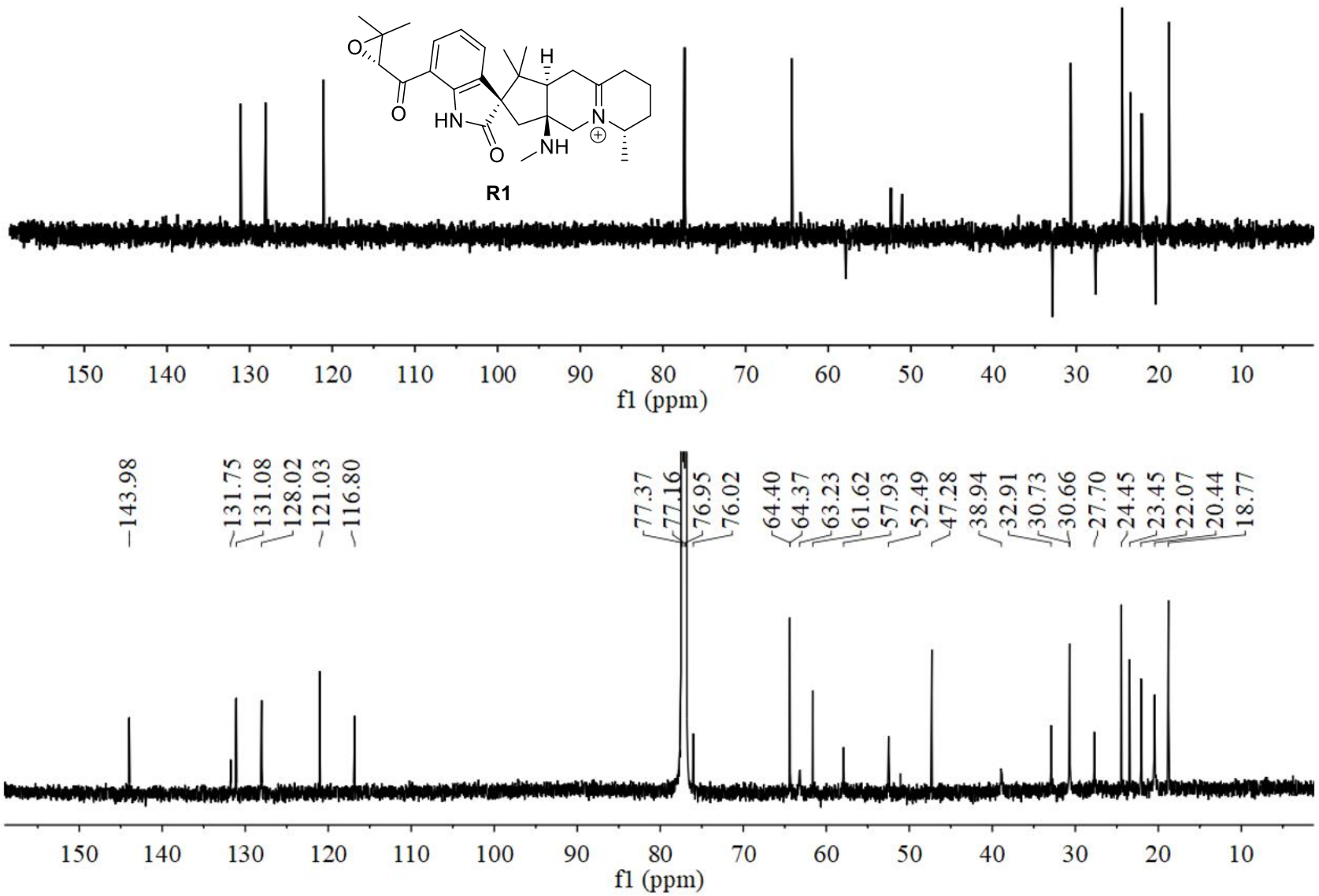
Supplementary Fig. 16-6 | HMBC NMR spectrum of S7 in DMSO-*d*$_6$.



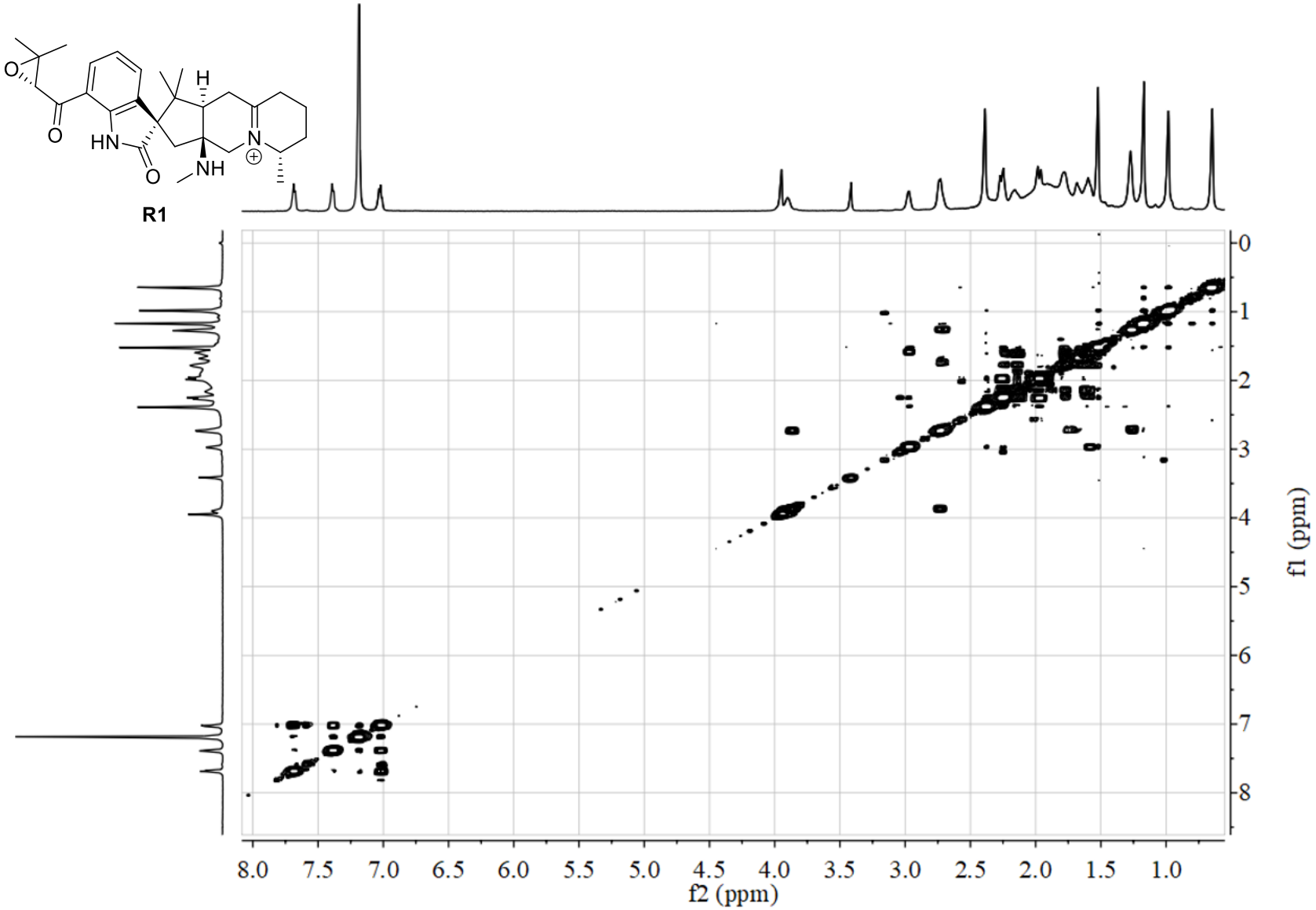
Supplementary Fig. 17-1 | ^{1}H NMR spectrum of R1 in $CDCl_3$.



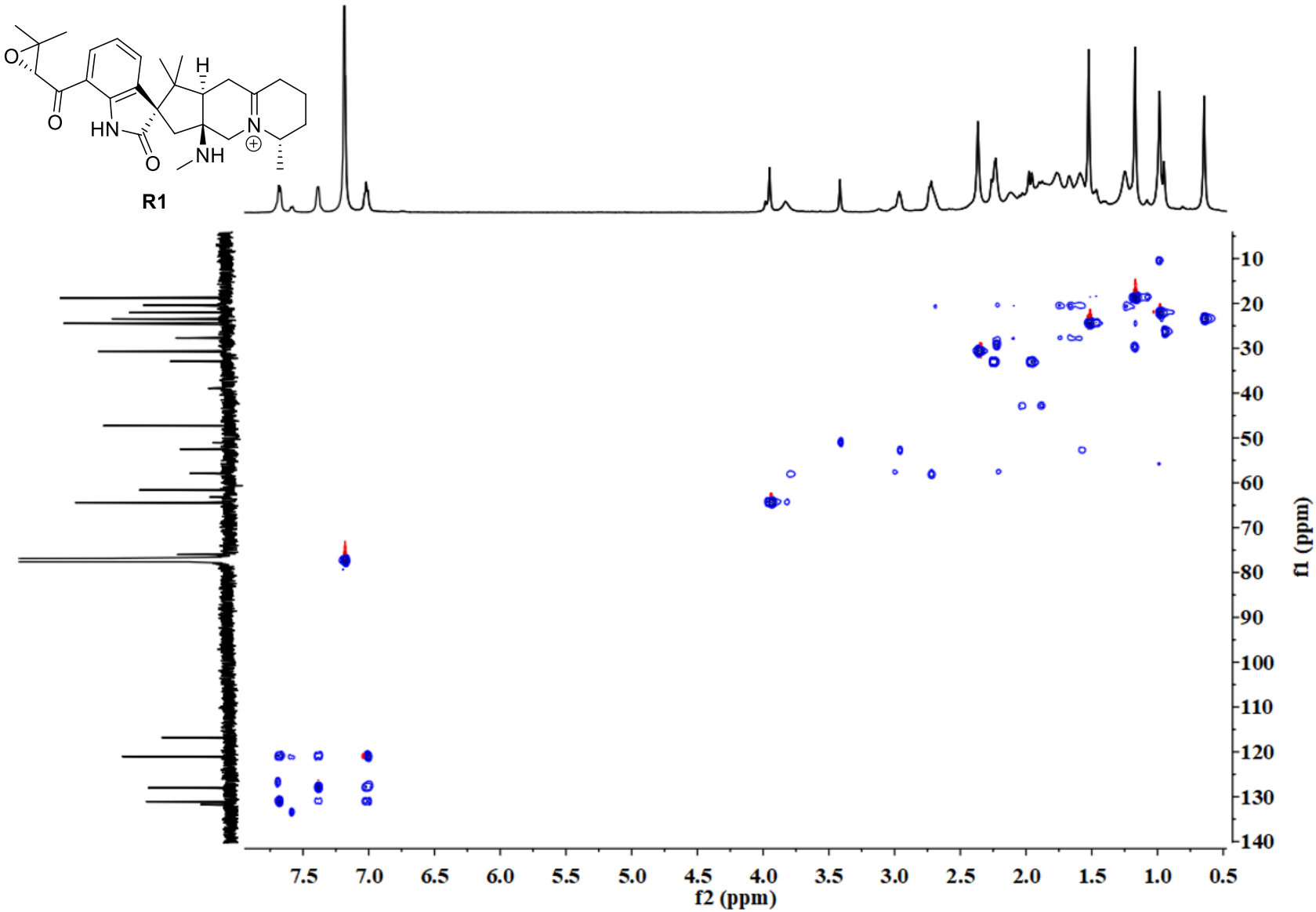
Supplementary Fig. 17-2 | ^{13}C NMR spectrum of R1 in $CDCl_3$.



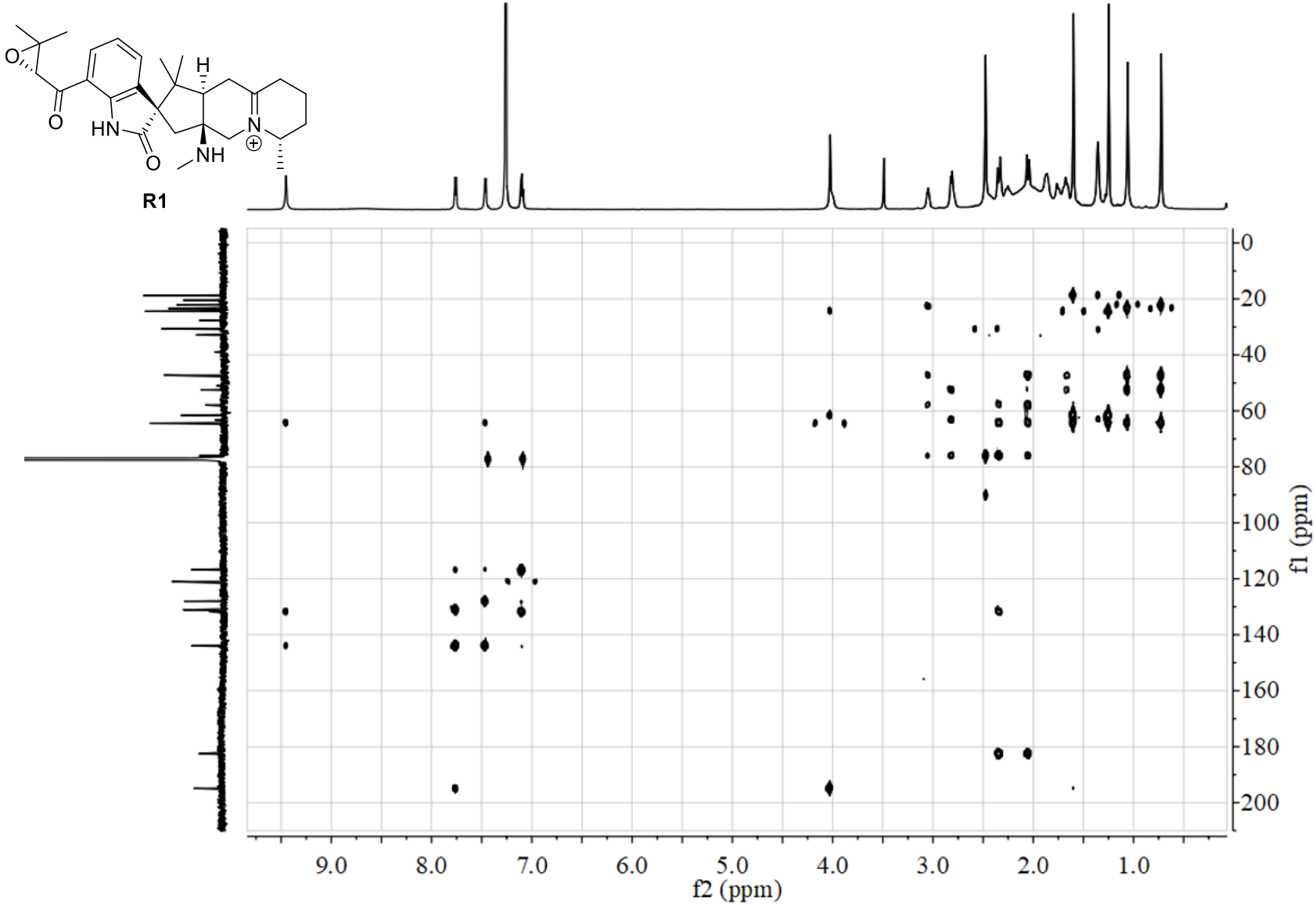
Supplementary Fig. 17-3 | DEPT135 and ^{13}C NMR spectra of R1 in $CDCl_3$.



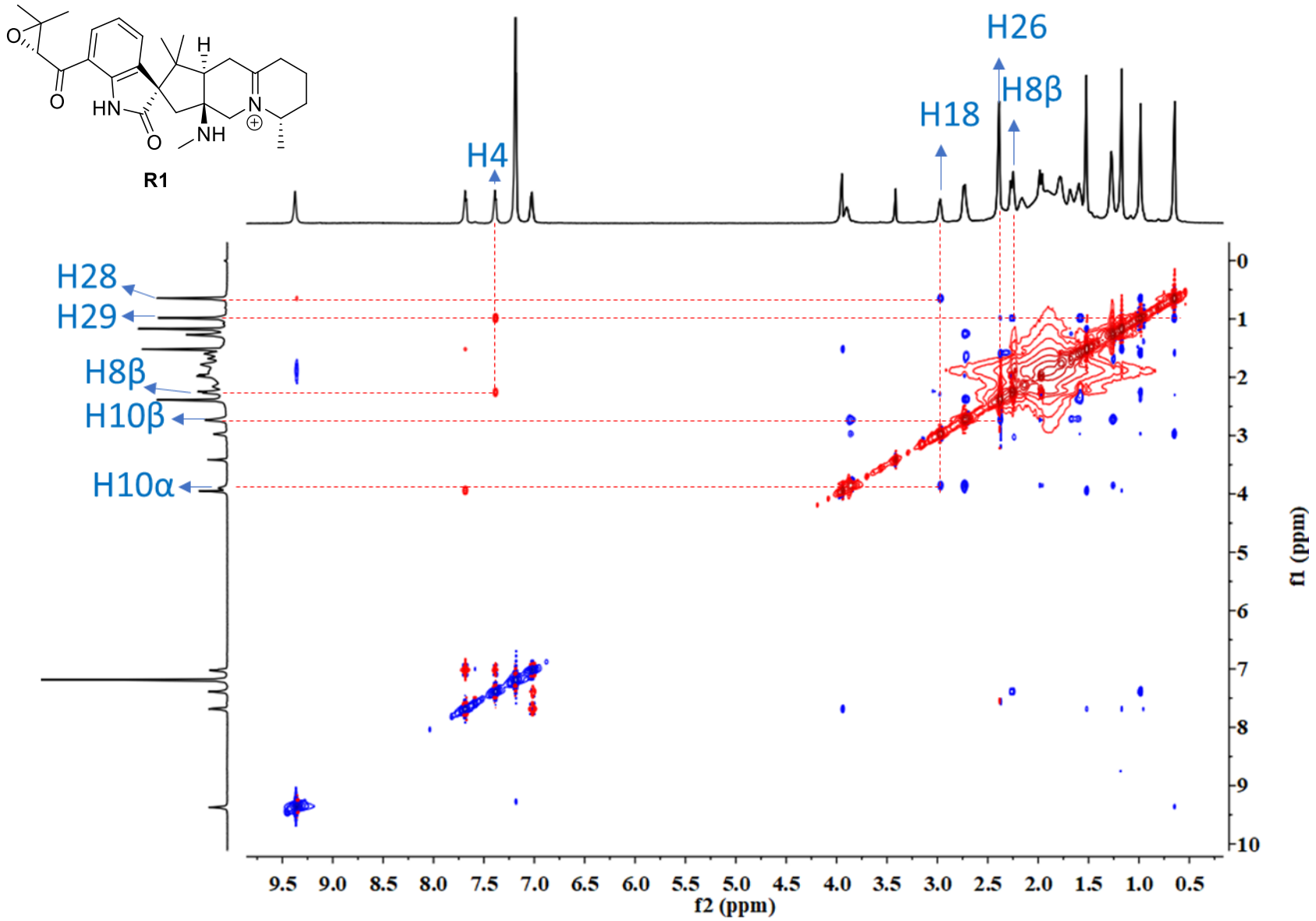
Supplementary Fig. 17-4 | ^{1}H-^{1}H COSY NMR spectrum of R1 in $CDCl_3$.



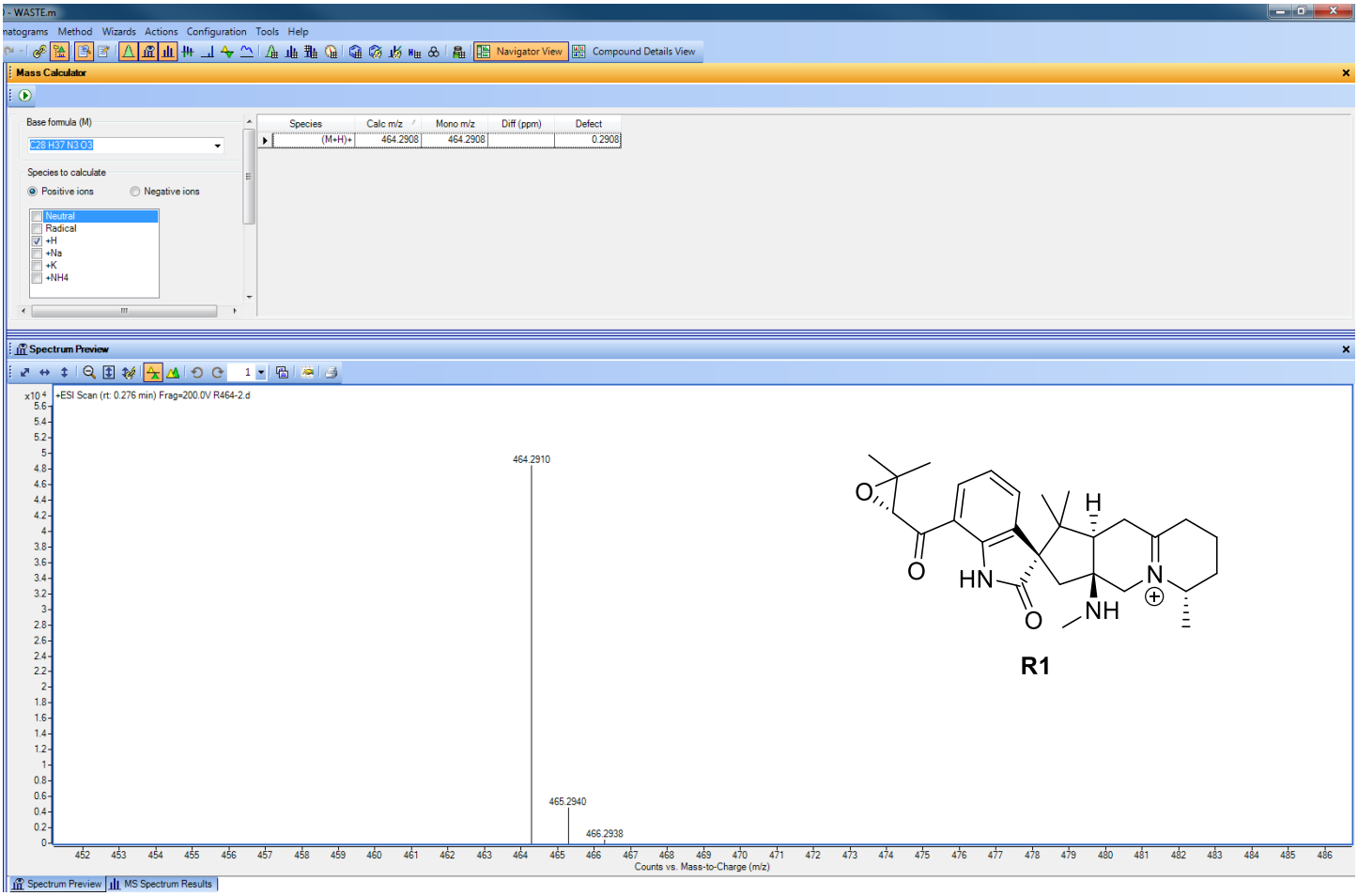
Supplementary Fig. 17-5 | HSQC-TOCSY NMR spectrum of R1 in $CDCl_3$.



Supplementary Fig. 17-6 | HMBC NMR spectrum of R1 in $CDCl_3$.



Supplementary Fig. 17-7 | NOESY NMR spectrum of R1 in $CDCl_3$.



Supplementary Fig. 17-8 | HRMS spectrum of R1 in $CDCl_3$.

Energies and Molecular Coordinates of Calculated Structures.

Structure	**Single-Point Energy** (Hartree) M06-2X/ 6-311++G(2d,2p) CPCM water solvent	**Enthalpy Correction** (Hartree) M06-2X/6-31+G(d) CPCM water solvent	**Gibbs Free Energy Correction** (Hartree) M06-2X/6-31+G(d) CPCM water solvent
Substrate **3**	-1133.27763795	0.512919	0.432077
Substrate **3-taut**	-1133.24220759	0.512060	0.431172
Substrate **3-ox**	-1132.51988010	0.503054	0.423583
TS-taut$_{\alpha\text{-}anti}$	-1133.20758299	0.510622	0.436393
TS-ox$_{\alpha\text{-}anti}$	-1132.48695913	0.502384	0.429517
Product **2-taut**	-1133.30637638	0.515543	0.443782
Product **2-ox**	-1132.54357524	0.505760	0.433204
Product **2**	-1133.32726952	0.515808	0.443338
Substrate **3-ox**$_{\alpha\text{-}syn}$	-1132.51871022	0.503050	0.423882
Substrate **3-ox**$_{\beta\text{-}syn}$	-1132.51660234	0.503183	0.424415
Substrate **3-ox**$_{\beta\text{-}anti}$	-1132.51549387	0.503060	0.425197
TS-ox$_{\alpha\text{-}syn}$	-1132.48734470	0.502322	0.430120
TS-ox$_{\beta\text{-}syn}$	-1132.49035735	0.502212	0.429479
TS-ox$_{\beta\text{-}anti}$	-1132.48763403	0.502498	0.429897
$NADP^+$ Model	-456.702066786	0.169217	0.124487
NADPH Model	-457.446769424	0.178720	0.131205
Substrate **4**	-1132.06562844	0.488953	0.408388
Substrate **9**	-1053.44990317	0.428902	0.353768
Substrate **9-red**	-1054.65441754	0.453013	0.376677

Substrate **3**

0 1

N	-1.707056	-1.291350	-1.810658
C	-2.999269	-1.405467	-1.416401
O	-3.839078	-2.009447	-2.077905
C	-3.318343	-0.771696	-0.058276
N	3.297103	0.430707	0.880042
C	3.580603	-2.855172	-1.129870
N	-2.525273	0.454711	0.113926
C	3.099662	-3.046384	0.098080
C	-0.727432	-0.631251	-1.038922
C	0.704299	-0.943344	-1.387339
C	1.705779	-0.171221	-0.582238
C	2.002182	1.223259	-0.769252
C	1.505957	2.213515	-1.636554
C	2.020547	3.498543	-1.549285
C	3.023993	3.819523	-0.607850
C	3.529536	2.863045	0.261120
C	3.005978	1.567551	0.166459
C	2.513840	-0.620209	0.441014
C	2.610946	-1.991868	1.077538
C	3.596712	-1.990267	2.262194
C	1.226192	-2.406332	1.619648
C	-1.152630	0.218713	-0.095708
H	3.975810	0.377227	1.626435
H	3.630500	-1.866177	-1.580001
H	3.933645	-3.692115	-1.725305
H	3.067252	-4.060260	0.502322
H	0.855675	-0.720489	-2.455976
H	0.877879	-2.021615	-1.285739
H	0.726951	1.974344	-2.357103
H	1.647177	4.274800	-2.210944
H	3.405786	4.835261	-0.562293
H	4.299621	3.108185	0.986868
H	3.271723	-1.296572	3.046063
H	3.637334	-2.991208	2.702533
H	4.611855	-1.729524	1.944470
H	0.886956	-1.685716	2.371538
H	0.472546	-2.450595	0.828958
H	1.290735	-3.393732	2.090387
C	-4.815556	-0.514956	0.057646
H	-5.132730	0.111887	-0.785724
C	-2.823058	1.212077	1.348728
H	-2.505806	0.607499	2.220363
C	-5.136771	0.183290	1.372528
H	-6.208357	0.398426	1.437630
H	-4.887283	-0.477330	2.214478
C	-4.324833	1.468589	1.469711
H	-4.627446	2.158454	0.669065
H	-4.508513	1.975005	2.423610
H	-5.339672	-1.470179	-0.030184
C	-2.079865	2.547254	1.362549
H	-0.995863	2.445112	1.451799
H	-2.300889	3.104066	0.444981
H	-2.422105	3.139485	2.216701
H	-3.019373	-1.516981	0.710864
H	-1.440270	-1.774992	-2.662344
H	-0.434737	0.751667	0.513516

Substrate **3-taut**

0 1

C	0.459260	-0.629075	-0.864877
C	-0.750694	-0.079799	-1.582561
C	-1.945099	0.172469	-0.709773
C	-2.137760	1.183512	0.210396
C	-1.225570	2.311206	0.663786
C	-0.434324	2.826272	-0.522193
C	0.893086	2.879288	-0.628438
C	2.722359	-1.206661	0.578036
C	1.509850	-1.760620	0.809606
N	0.339251	-1.327199	0.203816
C	-3.983600	-0.117287	0.313656
C	-5.227325	-0.685564	0.615272
C	-5.584497	-1.838983	-0.068701
C	-4.725861	-2.414484	-1.031120
C	-3.497431	-1.842564	-1.328103
C	-3.110094	-0.670033	-0.653713
N	-3.365938	0.998406	0.820605
C	1.823217	-0.440748	-1.480362
N	2.810111	-0.219933	-0.429447
C	4.135323	0.097518	-0.995887
C	5.242627	0.009480	0.051612
C	5.219672	-1.326852	0.778389
C	3.883318	-1.455126	1.501070
O	1.330104	-2.661936	1.835327
C	4.140817	1.487913	-1.629471
C	-2.057022	3.501149	1.188558
C	-0.318756	1.805389	1.797661
H	-1.048909	3.209075	-1.339943
H	-5.883678	-0.241411	1.358131
H	-6.540865	-2.308908	0.141348
H	-5.035663	-3.320291	-1.544242
H	-2.844911	-2.297529	-2.069596
H	-3.772420	1.617012	1.508095
H	4.355069	-0.654033	-1.780097
H	-0.450150	0.824807	-2.117451
H	-1.022066	-0.806345	-2.363694
H	1.556035	2.493732	0.141541
H	1.363324	3.298614	-1.514310
H	2.085045	-1.350544	-2.068030
H	1.809670	0.409443	-2.162750
H	6.198802	0.169010	-0.458159
H	5.119119	0.827149	0.776502
H	6.044994	-1.398215	1.493863
H	5.337785	-2.145052	0.055429
H	3.852343	-0.716640	2.317075
H	3.761379	-2.438595	1.961002
H	3.428909	1.592698	-2.451691
H	5.137291	1.695994	-2.031941
H	3.909597	2.243704	-0.871407
H	-2.780965	3.845431	0.442463
H	-1.386314	4.332054	1.426644
H	-2.593341	3.245177	2.109136
H	-0.932856	1.425470	2.620885
H	0.301497	2.622942	2.182051
H	0.334169	0.996615	1.456567
H	0.383324	-2.873196	1.858087

Substrate **3-ox**

1 1

C	0.529772	-0.354241	-0.932042
C	-0.720620	0.066585	-1.658313
C	-1.915192	0.183780	-0.753813
C	-2.224274	1.182511	0.151307
C	-1.472454	2.441897	0.543732
C	-0.825718	3.046922	-0.686888
C	0.456524	3.386501	-0.816306
C	2.784237	-1.242056	0.427477
C	1.457417	-1.798626	0.781275
N	0.409535	-1.277339	0.063629
C	-3.848359	-0.376646	0.348926
C	-4.982191	-1.111550	0.715315
C	-5.186105	-2.325456	0.076570
C	-4.286886	-2.797822	-0.904638
C	-3.168860	-2.062401	-1.267030
C	-2.937656	-0.825033	-0.636048
N	-3.387626	0.835152	0.801806
C	1.767577	0.113531	-1.229887
N	2.871842	-0.352578	-0.533567
C	4.190420	0.262471	-0.937380
C	5.342061	-0.647958	-0.533057
C	5.254444	-1.021566	0.941851
C	3.950411	-1.768849	1.195083
O	1.316125	-2.645738	1.649149
C	4.260238	1.669808	-0.349015
C	-2.446701	3.501183	1.101717
C	-0.447188	2.089103	1.634000
H	-1.515506	3.245392	-1.509579
H	-5.669844	-0.745208	1.471820
H	-6.052993	-2.925426	0.336612
H	-4.477382	-3.754492	-1.381737
H	-2.485733	-2.440150	-2.024155
H	-3.854097	1.402385	1.496177
H	4.134737	0.318743	-2.027010
H	-0.504465	0.993761	-2.192264
H	-0.924535	-0.695730	-2.421229
H	1.183831	3.215880	-0.026774
H	0.820920	3.853830	-1.726860
H	5.321426	-1.553470	-1.150408
H	6.273507	-0.121068	-0.756823
H	5.304708	-0.126415	1.569191
H	6.095546	-1.657746	1.225629
H	3.666522	-1.771000	2.252674
H	4.040011	-2.828825	0.916043
H	3.450152	2.299414	-0.725681
H	5.208714	2.123986	-0.646634
H	4.206089	1.650799	0.742524
H	-3.246104	3.726484	0.388452
H	-1.894862	4.423513	1.303493
H	-2.895853	3.178717	2.047569
H	-0.951279	1.614211	2.481382
H	0.053100	2.993286	1.996621
H	0.317571	1.399904	1.260170
H	1.950012	0.842792	-2.006360
H	-0.524825	-1.606832	0.313884

TS-taut$_{\alpha\text{-}anti}$

0 1

C	0.428085	-0.781343	-0.034476
C	-0.880332	-1.446132	-0.390417
C	-2.070004	-0.548121	-0.258990
C	-2.102003	0.814559	-0.426143
C	-1.008545	1.807348	-0.753842
C	0.272615	1.109271	-1.214764
C	1.517475	1.666667	-1.010278
C	2.769787	0.373842	0.462571
C	1.753959	0.324433	1.402995
N	0.568505	-0.259457	1.172656
C	-4.219360	0.192045	0.063938
C	-5.591154	0.145308	0.337831
C	-6.147980	-1.098871	0.602827
C	-5.360883	-2.270438	0.595930
C	-4.001044	-2.217050	0.322547
C	-3.409946	-0.970465	0.051987
N	-3.401684	1.255193	-0.230432
C	1.630910	-1.390039	-0.733500
N	2.886760	-0.670550	-0.505038
C	4.025899	-1.583303	-0.271610
C	5.318414	-0.797683	-0.045785
C	5.177230	0.267310	1.037111
C	4.010063	1.189976	0.670976
O	1.837040	1.111276	2.520426
C	4.196534	-2.523068	-1.462410
C	-1.475695	2.685360	-1.940423
C	-0.775986	2.718069	0.465265
H	0.142388	0.473730	-2.092818
H	-6.195784	1.047711	0.343003
H	-7.209803	-1.171503	0.819457
H	-5.830493	-3.226710	0.807377
H	-3.404175	-3.125969	0.316964
H	-3.708616	2.216371	-0.285990
H	3.816077	-2.185223	0.636014
H	-0.806932	-1.847133	-1.410063
H	-1.000816	-2.319579	0.267002
H	1.646096	2.567414	-0.416459
H	2.338067	1.409087	-1.669779
H	1.702564	-2.412777	-0.315173
H	1.431925	-1.501128	-1.806564
H	6.112004	-1.509838	0.207002
H	5.601799	-0.317098	-0.993076
H	6.104394	0.842016	1.135925
H	4.978596	-0.206674	2.007600
H	4.251464	1.708455	-0.267699
H	3.834636	1.946511	1.439215
H	3.333053	-3.176205	-1.613750
H	5.071833	-3.160837	-1.304091
H	4.352510	-1.938739	-2.376415
H	-1.705287	2.069554	-2.816273
H	-0.681806	3.389316	-2.208086
H	-2.368353	3.268486	-1.687528
H	-1.724975	3.138156	0.813320
H	-0.121554	3.557149	0.210682
H	-0.328601	2.157423	1.290034
H	0.950162	1.135476	2.918431

TS-ox*α-anti*

1 1

C	0.357901	-1.105925	0.271298
C	-0.993548	-1.642493	-0.075817
C	-2.048015	-0.580765	-0.156731
C	-1.911260	0.768164	-0.391316
C	-0.710998	1.673711	-0.601367
C	0.565103	0.940412	-1.007963
C	1.824753	1.386019	-0.598861
C	2.719403	0.091810	0.716184
C	1.671619	0.204073	1.778020
N	0.520733	-0.465752	1.482620
C	-4.127821	0.382472	-0.149443
C	-5.520740	0.488864	-0.057072
C	-6.231590	-0.677229	0.187575
C	-5.577755	-1.919655	0.336211
C	-4.197345	-2.017264	0.242436
C	-3.453607	-0.849914	-0.002201
N	-3.172034	1.339930	-0.383962
C	1.495842	-1.557268	-0.368928
N	2.695295	-1.051620	-0.044956
C	3.885339	-1.556938	-0.816058
C	5.176797	-1.118722	-0.134128
C	5.171627	0.382369	0.137451
C	4.041519	0.703969	1.105662
O	1.820013	0.885395	2.781651
C	3.812323	-1.130013	-2.282918
C	-0.994185	2.588797	-1.826879
C	-0.535078	2.578760	0.635492
H	0.488266	0.395744	-1.946857
H	-6.022469	1.445041	-0.172521
H	-7.313867	-0.633508	0.265498
H	-6.168707	-2.810780	0.525358
H	-3.703832	-2.979450	0.354172
H	-3.370821	2.322443	-0.511439
H	3.792845	-2.644374	-0.756842
H	-0.912435	-2.196949	-1.017250
H	-1.275358	-2.374986	0.693459
H	1.885748	2.254003	0.052030
H	2.647575	1.290620	-1.300500
H	5.295510	-1.661806	0.810722
H	6.008767	-1.405253	-0.783500
H	5.062961	0.950409	-0.793151
H	6.120167	0.691087	0.583752
H	3.896595	1.780297	1.230842
H	4.282535	0.313834	2.103335
H	2.854740	-1.389687	-2.741612
H	4.597868	-1.660127	-2.827873
H	3.980178	-0.058447	-2.413096
H	-1.240189	1.997491	-2.713472
H	-0.114130	3.201202	-2.041904
H	-1.825076	3.270361	-1.620435
H	-1.498589	3.018948	0.906207
H	0.149201	3.404887	0.421442
H	-0.163746	2.037933	1.510031
H	1.442993	-2.279792	-1.174622
H	-0.286493	-0.319616	2.085234

Product **2-taut**

0 1

C	-0.374464	0.577250	-0.155862
C	0.920966	1.395286	-0.191594
C	2.133656	0.520714	-0.137266
C	2.107702	-0.836254	-0.322207
C	0.892276	-1.697449	-0.527430
C	-0.266551	-0.747003	-0.960642
C	-1.663192	-1.403192	-0.935223
C	-2.626848	-0.599823	-0.031644
C	-1.871020	-0.343117	1.260418
N	-0.752409	0.265300	1.229896
C	4.270316	-0.305226	0.006537
C	5.660171	-0.312460	0.168743
C	6.284612	0.906289	0.401847
C	5.546391	2.106825	0.471200
C	4.167596	2.108737	0.307604
C	3.508030	0.890320	0.071922
N	3.393311	-1.338295	-0.232566
C	-1.513482	1.416943	-0.769405
N	-2.808817	0.715065	-0.701517
C	-3.870590	1.568741	-0.138571
C	-5.187696	0.800860	-0.039591
C	-5.039687	-0.486143	0.761669
C	-3.946504	-1.344937	0.133220
O	-2.411123	-0.779470	2.415452
C	-4.069053	2.799402	-1.022430
C	1.122628	-2.702775	-1.669828
C	0.649020	-2.489200	0.776390
H	-0.030577	-0.447969	-1.991338
H	6.228282	-1.236872	0.115043
H	7.362399	0.935076	0.533393
H	6.068603	3.041329	0.654996
H	3.605482	3.037982	0.361897
H	3.655255	-2.309668	-0.329951
H	-3.582489	1.904500	0.879277
H	0.937974	2.001178	-1.109020
H	0.903962	2.102427	0.647329
H	-1.626866	-2.436909	-0.578435
H	-2.109775	-1.420747	-1.934153
H	-1.554156	2.351836	-0.192051
H	-1.267776	1.674498	-1.807228
H	-5.939297	1.457954	0.412747
H	-5.529167	0.566144	-1.058076
H	-5.984594	-1.039922	0.778708
H	-4.781755	-0.250349	1.800717
H	-4.268934	-1.662219	-0.867421
H	-3.764507	-2.252191	0.719435
H	-3.179381	3.431597	-1.080036
H	-4.886867	3.409526	-0.625861
H	-4.332742	2.484054	-2.038465
H	1.410088	-2.191038	-2.594284
H	0.206693	-3.273051	-1.862066
H	1.906420	-3.425236	-1.417385
H	1.509050	-3.141431	0.965662
H	-0.232714	-3.134398	0.706141
H	0.529815	-1.823770	1.633242
H	-1.793686	-0.553793	3.135725

Product **2-ox**

1 1

C	0.349574	-0.690078	0.206323
C	-0.959165	-1.471386	0.121065
C	-2.117943	-0.543788	-0.045596
C	-2.001445	0.767573	-0.422966
C	-0.736393	1.550457	-0.649951
C	0.435867	0.525136	-0.795011
C	1.838929	1.156615	-0.633036
C	2.659290	0.413548	0.461708
C	1.791658	0.446939	1.747732
N	0.618287	-0.185526	1.547948
C	-4.207147	0.373311	-0.220199
C	-5.603538	0.460977	-0.192026
C	-6.308103	-0.683980	0.153931
C	-5.643930	-1.889950	0.464397
C	-4.259209	-1.972199	0.434089
C	-3.520677	-0.827533	0.088949
N	-3.259510	1.324602	-0.525177
C	1.533426	-1.549557	-0.143785
N	2.688781	-1.014373	-0.013171
C	3.916942	-1.723372	-0.529475
C	5.185722	-1.057167	-0.008854
C	5.131083	0.457733	-0.179627
C	4.038594	1.008711	0.728655
O	2.129390	1.023053	2.768264
C	3.847950	-1.754467	-2.057067
C	-0.813370	2.332031	-1.974978
C	-0.587411	2.571005	0.501029
H	0.344622	0.093376	-1.798851
H	-6.114590	1.388843	-0.431764
H	-7.393130	-0.650764	0.185743
H	-6.229552	-2.765146	0.729678
H	-3.754566	-2.904961	0.672870
H	-3.463839	2.279400	-0.787766
H	3.836533	-2.739181	-0.135404
H	-0.894341	-2.156908	-0.733643
H	-1.061236	-2.100439	1.014110
H	1.784618	2.203458	-0.331297
H	2.405329	1.121024	-1.568032
H	5.324930	-1.299098	1.050872
H	6.026446	-1.494398	-0.554725
H	4.961389	0.734469	-1.226566
H	6.087071	0.900598	0.111366
H	3.946965	2.094911	0.636423
H	4.304120	0.802353	1.769779
H	2.942237	-2.256167	-2.406938
H	4.711140	-2.310562	-2.431272
H	3.874153	-0.748764	-2.484688
H	-1.053438	1.669789	-2.812360
H	0.144883	2.821505	-2.181180
H	-1.574593	3.117305	-1.924068
H	-1.500458	3.171707	0.558421
H	0.235882	3.269321	0.326232
H	-0.447437	2.093498	1.472714
H	1.444656	-2.556672	-0.547721
H	-0.080039	-0.239207	2.282925

Product **2**

0 1

C	-0.381757	0.587523	-0.269892
C	0.910257	1.402316	-0.332063
C	2.114402	0.524834	-0.192899
C	2.082911	-0.839536	-0.318982
C	0.872707	-1.705778	-0.540796
C	-0.282576	-0.768160	-1.013723
C	-1.687420	-1.411144	-0.948900
C	-2.630549	-0.608651	-0.022575
C	-1.890201	-0.406406	1.314777
N	-0.768953	0.324822	1.118583
C	4.236272	-0.305166	0.062241
C	5.619507	-0.314536	0.273998
C	6.244631	0.909282	0.474342
C	5.514231	2.116669	0.463631
C	4.142337	2.120652	0.252047
C	3.482532	0.896623	0.048450
N	3.360322	-1.342775	-0.162523
C	-1.542421	1.392832	-0.874258
N	-2.833959	0.705137	-0.680533
C	-3.851748	1.571450	-0.059239
C	-5.169891	0.814156	0.103517
C	-4.996974	-0.492171	0.867848
C	-3.946351	-1.350447	0.170217
O	-2.242638	-0.846482	2.409038
C	-4.092834	2.805957	-0.927878
C	1.133654	-2.721771	-1.667879
C	0.600818	-2.495366	0.759687
H	-0.051847	-0.515636	-2.057420
H	-0.116745	0.458441	1.885235
H	6.181462	-1.244091	0.281864
H	7.317309	0.937251	0.642274
H	6.037437	3.054990	0.623122
H	3.586431	3.055028	0.244148
H	3.619403	-2.318856	-0.208133
H	-3.507646	1.901476	0.942872
H	0.934495	1.936877	-1.291663
H	0.883494	2.176181	0.446674
H	-1.648791	-2.447837	-0.602570
H	-2.157665	-1.420540	-1.937256
H	-1.545491	2.363562	-0.362749
H	-1.352468	1.572708	-1.940125
H	-5.886314	1.470845	0.610378
H	-5.570874	0.605167	-0.898827
H	-5.948193	-1.032824	0.922302
H	-4.678910	-0.284849	1.896232
H	-4.311860	-1.643894	-0.822771
H	-3.747137	-2.267349	0.734753
H	-3.212368	3.446172	-1.022205
H	-4.895793	3.408855	-0.491937
H	-4.400442	2.494227	-1.932604
H	1.454075	-2.218635	-2.585901
H	0.219954	-3.286787	-1.884692
H	1.904066	-3.446654	-1.383908
H	1.473029	-3.116935	0.989698
H	-0.252949	-3.171816	0.655556
H	0.424357	-1.842479	1.616631

Substrate **3-ox**$_{\alpha\text{-}syn}$

1 1

C	-0.614527	0.237283	-1.304445
C	-3.217008	-0.253574	-0.458409
C	-2.978838	0.726914	-1.541163
N	-1.658551	0.891558	-1.885780
C	-0.886961	-0.659306	-0.322073
N	-2.195363	-0.890097	0.065747
C	-2.365886	-1.912736	1.164263
C	-3.784975	-2.464666	1.153509
C	-4.811423	-1.338659	1.181907
C	-4.638575	-0.471343	-0.059568
O	-3.887908	1.336699	-2.082350
C	-1.946652	-1.271985	2.485191
H	-1.663743	-2.706312	0.897808
H	-3.928007	-3.078388	0.256519
H	-3.889639	-3.122845	2.020187
H	-4.693596	-0.733361	2.085951
H	-5.824906	-1.745209	1.199533
H	-5.097748	0.516616	0.051144
H	-5.131705	-0.925050	-0.931481
H	-0.896494	-0.968933	2.467695
H	-2.073013	-2.008070	3.283109
H	-2.557267	-0.395094	2.715979
H	-0.114559	-1.220924	0.184957
H	-1.474402	1.569002	-2.624861
N	3.190737	0.394549	0.996384
C	-0.324337	3.525240	-0.284787
C	0.944816	3.127335	-0.196417
C	0.774139	0.521685	-1.813852
C	1.846740	0.279698	-0.791438
C	2.708105	-0.874237	-0.787397
C	2.848538	-1.990928	-1.631914
C	3.807878	-2.944122	-1.325844
C	4.636075	-2.808186	-0.190005
C	4.516985	-1.719957	0.661481
C	3.542452	-0.764526	0.348958
C	2.168483	1.031204	0.323811
C	1.552212	2.289958	0.910573
C	0.516726	1.893547	1.975101
C	2.642873	3.159973	1.572983
H	3.634270	0.737199	1.837530
H	-1.079791	3.236798	0.441791
H	-0.651531	4.159110	-1.104443
H	1.656447	3.451364	-0.958829
H	0.795104	1.545446	-2.196234
H	0.942887	-0.131022	-2.680030
H	2.216281	-2.110437	-2.508389
H	3.926633	-3.811872	-1.967843
H	5.378756	-3.571624	0.021646
H	5.149919	-1.613232	1.537406
H	0.981737	1.259743	2.736813
H	0.117038	2.785945	2.468625
H	-0.318405	1.340682	1.533291
H	3.075102	2.671355	2.452745
H	3.448454	3.392213	0.869170
H	2.196646	4.099566	1.911761

Substrate **3-ox$_{\beta\text{-}syn}$**

1 1

C	-3.020343	0.515190	1.665661
C	1.818988	0.333673	0.781782
C	2.145266	1.121119	-0.306943
C	2.698727	-0.807066	0.757123
C	-0.645704	0.219419	1.293792
C	3.548691	-0.651990	-0.361875
C	-0.898623	-0.510131	0.178540
C	-0.597328	3.328300	0.155476
C	-2.345669	-1.635659	-1.449330
C	1.526904	2.384134	-0.882527
C	0.715244	3.097322	0.179181
C	0.737114	0.524532	1.804476
C	-4.710200	-0.749044	-1.534289
C	-1.551277	-2.924670	-1.249958
C	-3.805439	-1.950690	-1.751510
C	-4.643802	-0.365016	-0.063899
C	0.678041	2.010241	-2.108760
O	-3.946928	0.956714	2.327197
N	-1.703649	0.685861	2.014589
N	-2.203585	-0.756096	-0.219087
N	3.189932	0.520932	-0.979738
C	4.540901	-1.584478	-0.687345
C	-3.236308	-0.250693	0.416143
C	3.819284	-2.876891	1.251563
C	2.842126	-1.945990	1.570545
C	2.638781	3.362910	-1.320114
C	4.662272	-2.696079	0.133258
H	-3.844812	-2.302598	-2.786019
H	-5.127195	0.593780	0.147084
H	1.293653	1.501927	-2.857141
H	0.257964	2.912182	-2.566436
H	-0.146702	1.343240	-1.839316
H	3.631331	0.887881	-1.812070
H	5.185692	-1.443374	-1.549633
H	3.940348	-3.761602	1.869543
H	2.198502	-2.100253	2.433169
H	5.418669	-3.442731	-0.089480
H	-1.238904	2.976785	-0.648980
H	-1.078365	3.879986	0.958550
H	0.729724	1.539364	2.212000
H	0.923082	-0.142429	2.656457
H	-1.912991	-1.031148	-2.253344
H	1.303814	3.478190	1.016401
H	2.183810	4.293712	-1.672344
H	3.236719	2.959462	-2.143760
H	3.308646	3.596690	-0.486593
H	-5.740693	-0.985795	-1.807645
H	-4.386285	0.092754	-2.157224
H	-0.471020	-2.776828	-1.227008
H	-1.776478	-3.583388	-2.092842
H	-1.866535	-3.425445	-0.329770
H	-4.134084	-2.780766	-1.113019
H	-5.158031	-1.106257	0.564017
H	-1.533882	1.225579	2.862432
H	-0.105338	-0.898166	-0.440890

Substrate **3-ox$_{\beta\text{-}anti}$**

1 1

C	-0.529385	-0.917047	-0.383022
C	0.759043	-1.163204	-1.122443
C	1.942433	-0.392719	-0.599941
C	2.126387	0.968052	-0.409759
C	1.249657	2.198865	-0.601046
C	-0.026841	1.867173	-1.345980
C	-1.262977	2.214915	-0.982314
C	-2.844028	-0.186157	0.943839
C	-1.544711	-0.075421	1.640641
N	-0.464218	-0.492313	0.904577
C	4.055623	-0.032882	0.228250
C	5.348542	-0.310305	0.688942
C	5.738781	-1.640382	0.719598
C	4.866429	-2.669118	0.301683
C	3.588524	-2.384819	-0.154674
C	3.165075	-1.043689	-0.194993
N	3.399716	1.163758	0.085140
C	-1.752159	-1.079527	-0.950953
N	-2.892852	-0.731444	-0.252953
C	-4.033750	0.378602	1.644477
O	-1.444202	0.361788	2.777614
C	2.007705	3.217335	-1.488435
C	0.964351	2.838720	0.768208
H	0.116915	1.365376	-2.304794
H	6.015406	0.485085	1.008244
H	6.734079	-1.896061	1.070547
H	5.205801	-3.699908	0.338652
H	2.932575	-3.190121	-0.475096
H	3.793623	2.062080	0.330101
H	0.572821	-0.978002	-2.185030
H	0.984242	-2.233159	-1.040163
H	-1.477977	2.740941	-0.055278
H	-2.111517	1.989370	-1.623546
H	-3.694017	1.281442	2.161210
H	2.264536	2.776253	-2.456511
H	1.372167	4.091164	-1.659801
H	2.930416	3.562985	-1.012058
H	1.896732	3.069757	1.291159
H	0.414918	3.776696	0.641383
H	0.372232	2.177372	1.410802
C	-4.196735	-0.974058	-0.992022
H	-4.131159	-0.310375	-1.860611
C	-5.176905	0.647958	0.677767
H	-6.076707	0.918547	1.234384
H	-4.923454	1.491218	0.024122
C	-5.408302	-0.610629	-0.142285
H	-6.251762	-0.495362	-0.828612
H	-5.645461	-1.447634	0.526861
H	-4.336527	-0.325248	2.432478
C	-4.263478	-2.435708	-1.428427
H	-4.149263	-3.094430	-0.562537
H	-5.252326	-2.606928	-1.862040
H	-3.520822	-2.701501	-2.181501
H	0.457706	-0.376100	1.329132
H	-1.877733	-1.403491	-1.972439

TS-ox*α-syn*

1 1

N	1.360779	2.373123	-0.379573
C	2.676280	2.008306	-0.481812
O	3.535686	2.707717	-0.996900
C	2.937210	0.645962	0.044154
N	-2.787496	-1.334119	-0.710377
C	2.012997	-0.275617	-1.677385
N	2.114208	0.199733	1.038982
C	0.644108	-0.041813	-1.664538
C	0.404605	1.503277	0.091013
C	-1.039200	1.876291	-0.079849
C	-1.927965	0.673581	-0.213294
C	-3.289236	0.627946	0.252265
C	-4.123157	1.547637	0.912630
C	-5.419219	1.166843	1.226276
C	-5.903093	-0.116640	0.891514
C	-5.102443	-1.041937	0.238141
C	-3.795585	-0.650166	-0.076029
C	-1.655690	-0.546225	-0.796849
C	-0.419301	-1.109504	-1.471508
C	0.089889	-2.331695	-0.694249
C	-0.800573	-1.556569	-2.907753
C	0.812659	0.523681	0.984825
H	-2.864917	-2.285629	-1.043537
H	2.391100	-1.266171	-1.440819
H	2.638355	0.308230	-2.347866
H	0.291938	0.825426	-2.224102
H	-1.129211	2.537367	-0.950483
H	-1.350089	2.469554	0.789424
H	-3.763439	2.540061	1.172274
H	-6.076117	1.865000	1.736351
H	-6.923287	-0.384389	1.149947
H	-5.472703	-2.029337	-0.021060
H	-0.707993	-3.069378	-0.574335
H	0.909339	-2.824453	-1.226228
H	0.432611	-2.055569	0.306649
H	-1.548952	-2.354704	-2.881997
H	-1.209063	-0.720037	-3.482366
H	0.085056	-1.940178	-3.422647
C	4.360847	0.184788	0.069331
H	4.838347	0.497107	-0.861742
C	2.687597	-0.785664	2.013778
H	3.428651	-0.205540	2.575545
C	4.503934	-1.328021	0.305991
H	4.487515	-1.852566	-0.653399
H	5.488012	-1.509944	0.743851
C	3.399361	-1.886241	1.224328
H	2.648014	-2.437662	0.648698
H	3.817214	-2.592083	1.946866
H	4.862947	0.747164	0.869664
C	1.650594	-1.320391	2.984165
H	1.151433	-0.520000	3.536475
H	0.900348	-1.945260	2.489902
H	2.174074	-1.947463	3.709672
H	1.074752	3.221698	-0.862344
H	0.100423	-0.011111	1.598729

TS-ox$_{\beta\text{-}syn}$

1 1

C	2.645427	1.101914	1.666884
C	-1.963821	0.382474	0.549866
C	-1.733512	-0.945709	0.254115
C	-3.313166	0.679168	0.145300
C	0.393606	1.148706	0.867381
C	-3.854528	-0.509845	-0.393786
C	0.822253	0.885937	-0.421424
C	1.910032	-1.398121	1.184940
C	2.531605	0.315054	-2.076909
C	-0.524499	-1.843611	0.435553
C	0.542311	-1.162736	1.273384
C	-1.051663	1.385247	1.197716
C	4.586218	-0.762844	-1.102739
C	2.028630	1.418501	-3.001492
C	4.041568	0.153846	-2.187576
C	4.338062	-0.104217	0.245202
C	-0.022450	-2.325479	-0.933825
O	3.498085	1.298234	2.518370
N	1.345522	1.511949	1.789669
N	2.119953	0.613235	-0.656877
N	-2.878123	-1.472097	-0.312742
C	-5.161037	-0.580648	-0.891658
C	2.907644	0.322066	0.424602
C	-5.405905	1.774035	-0.299626
C	-4.110551	1.836587	0.191388
C	-0.942500	-3.084062	1.270921
C	-5.925254	0.575570	-0.835936
H	4.246686	-0.242134	-3.186095
H	4.602474	-0.753669	1.084590
H	-0.808412	-2.886105	-1.447574
H	0.835659	-2.995697	-0.829851
H	0.255618	-1.489960	-1.581774
H	-2.982988	-2.420359	-0.647028
H	-5.558312	-1.504022	-1.302508
H	-6.034684	2.658877	-0.271621
H	-3.724104	2.764472	0.605333
H	-6.944026	0.558486	-1.211501
H	2.296411	-2.053680	0.408612
H	2.495301	-1.376022	2.100480
H	-1.167150	1.381898	2.288374
H	-1.320878	2.395615	0.864474
H	2.054936	-0.640001	-2.328118
H	0.173050	-0.815274	2.239144
H	-0.075850	-3.733605	1.424946
H	-1.710912	-3.663550	0.750386
H	-1.337883	-2.785177	2.246106
H	5.658347	-0.926884	-1.235329
H	4.098430	-1.744257	-1.155967
H	0.940356	1.465943	-3.069218
H	2.410170	1.218057	-4.006166
H	2.409387	2.390208	-2.673221
H	4.519944	1.139796	-2.120844
H	4.962174	0.793414	0.348182
H	1.061809	1.900217	2.686145
H	0.117488	0.834927	-1.240957

TS-ox$_{\beta\text{-}anti}$

1 1

C	-0.391625	-1.029075	0.217560
C	0.946037	-1.605762	-0.119853
C	2.034481	-0.577342	-0.179927
C	1.942621	0.773127	-0.427723
C	0.774026	1.708542	-0.680006
C	-0.510452	1.001257	-1.102571
C	-1.768704	1.482873	-0.737014
C	-2.706932	0.262638	0.623029
C	-1.666691	0.348428	1.693633
N	-0.540926	-0.372500	1.420601
C	4.139797	0.327149	-0.123179
C	5.532197	0.395381	0.006597
C	6.203010	-0.788138	0.278973
C	5.510596	-2.010558	0.418824
C	4.131056	-2.070344	0.288078
C	3.427187	-0.884710	0.014684
N	3.218058	1.309306	-0.389922
C	-1.537185	-1.436071	-0.435662
N	-2.726959	-0.897058	-0.115532
C	-3.996563	0.958184	0.972127
O	-1.797883	1.048889	2.686244
C	1.110168	2.592924	-1.914780
C	0.594407	2.639434	0.536547
H	-0.425462	0.427279	-2.022827
H	6.063766	1.336155	-0.101992
H	7.283589	-0.774104	0.386155
H	6.070804	-2.916324	0.630611
H	3.608149	-3.017632	0.393262
H	3.448297	2.284137	-0.523171
H	0.857266	-2.151095	-1.065941
H	1.195477	-2.352208	0.646991
H	-1.829751	2.379173	-0.125800
H	-2.576995	1.363374	-1.453926
H	-3.773960	2.013601	1.147517
H	1.356109	1.978988	-2.785862
H	0.253747	3.227685	-2.158532
H	1.957345	3.252305	-1.702296
H	1.561322	3.065960	0.816903
H	-0.069333	3.474793	0.295505
H	0.197214	2.121857	1.413646
C	-3.923059	-1.316622	-0.930911
H	-3.748928	-0.902035	-1.932688
C	-5.079107	0.756822	-0.077031
H	-6.023404	1.161113	0.296019
H	-4.838850	1.300105	-0.998890
C	-5.208164	-0.732499	-0.358676
H	-6.000781	-0.931312	-1.085483
H	-5.469057	-1.267129	0.564052
H	-4.328471	0.553159	1.937553
C	-4.002372	-2.838643	-0.994481
H	-4.036772	-3.258087	0.015391
H	-4.926624	-3.107400	-1.512596
H	-3.177733	-3.296625	-1.542964
H	0.265666	-0.248365	2.028991
H	-1.489160	-2.128691	-1.265037

$NADP^+$ Model

1 1

C	2.790063	-1.392824	0.158797
N	1.705279	-0.391857	0.053557
C	0.421878	-0.781114	0.056584
C	-0.603546	0.149820	-0.025245
C	-0.278816	1.499882	-0.133451
C	1.061863	1.881738	-0.145606
C	2.039401	0.913533	-0.045207
C	-2.007053	-0.404586	-0.034389
N	-2.985189	0.434961	0.347536
O	-2.199639	-1.560682	-0.393977
H	0.219375	-1.843532	0.123012
H	-1.050201	2.257244	-0.230332
H	1.351904	2.921105	-0.235254
H	3.099418	1.138415	-0.043286
H	-3.933108	0.079769	0.380652
H	-2.807902	1.316283	0.809492
H	2.346753	-2.383747	0.217120
H	3.420956	-1.315322	-0.725881
H	3.366557	-1.185181	1.059742

NADPH Model

0 1

C	2.804645	-1.420812	0.046659
N	1.737492	-0.438670	-0.066344
C	0.424910	-0.795876	-0.034847
C	-0.601348	0.090465	-0.008902
C	-0.368709	1.590423	-0.004480
C	1.113469	1.880448	0.020453
C	2.048215	0.923566	-0.010146
C	-1.961838	-0.473088	0.003684
N	-2.977515	0.430043	0.022826
O	-2.204118	-1.690726	0.003519
H	0.218394	-1.861939	-0.037528
H	-0.823865	2.065153	-0.888780
H	1.436491	2.915861	0.056101
H	3.110202	1.146716	0.002971
H	-3.929717	0.090575	0.010576
H	-2.832420	1.428218	-0.012397
H	2.405103	-2.408712	-0.185188
H	3.599379	-1.188959	-0.666868
H	3.225411	-1.434775	1.058130
H	-0.851952	2.063304	0.864925

Substrate **4**

0 1

N	-1.653566	-1.443146	-1.806768
C	-2.974416	-1.335511	-1.516315
O	-3.863219	-1.895274	-2.195457
C	-3.379938	-0.528575	-0.354653
N	3.224166	0.526881	0.844709
C	3.680073	-2.739551	-1.185734
N	-2.452993	0.129521	0.328734
C	3.219104	-2.958944	0.045106
C	-0.763580	-0.798956	-1.042950
C	0.696335	-0.980887	-1.412691
C	1.664462	-0.163215	-0.613394
C	1.867801	1.249866	-0.786884
C	1.295475	2.214793	-1.635757
C	1.721676	3.531002	-1.535107
C	2.711499	3.906894	-0.599910
C	3.290239	2.976094	0.251309
C	2.854098	1.649673	0.145274
C	2.506527	-0.567940	0.401165
C	2.686444	-1.933632	1.032258
C	3.682696	-1.880065	2.206715
C	1.331788	-2.423128	1.588084
C	-1.126610	-0.003219	0.021925
H	3.913169	0.509447	1.583500
H	3.677444	-1.747703	-1.632196
H	4.068947	-3.555903	-1.787388
H	3.239554	-3.974623	0.445496
H	0.787614	-0.726848	-2.477719
H	0.932398	-2.048263	-1.344642
H	0.528515	1.933406	-2.354220
H	1.289436	4.288487	-2.182471
H	3.024376	4.945443	-0.544784
H	4.049535	3.263785	0.972719
H	3.324518	-1.212678	2.998926
H	3.788677	-2.879586	2.639224
H	4.676555	-1.556026	1.880236
H	0.951811	-1.714061	2.331314
H	0.580146	-2.528729	0.801248
H	1.458307	-3.397962	2.072151
C	-4.826315	-0.519207	0.025387
H	-5.371037	0.117244	-0.686448
C	-2.774861	1.053792	1.480893
H	-2.375200	0.539455	2.361469
C	-5.046279	-0.040126	1.452257
H	-6.112736	0.110556	1.638453
H	-4.690775	-0.796087	2.163336
C	-4.276837	1.257081	1.639300
H	-4.620604	1.997977	0.904986
H	-4.439055	1.686134	2.632424
H	-5.200256	-1.534173	-0.139497
C	-2.076443	2.398421	1.284264
H	-0.990263	2.345173	1.375399
H	-2.331534	2.816475	0.305239
H	-2.440568	3.083123	2.055296
H	-0.414112	0.517378	0.641646

Substrate **9**

0 1

N	-2.174768	-0.794634	-1.699387
C	-3.479053	-0.638782	-1.330516
O	-4.439116	-0.993530	-2.048699
C	-3.723065	-0.027350	-0.036473
N	3.039611	0.251152	0.841516
C	3.014969	-2.664727	-1.679730
N	-2.701278	0.365695	0.703932
C	2.600086	-3.036108	-0.469125
C	-1.185127	-0.376414	-0.902387
C	0.224019	-0.609766	-1.413295
C	1.320114	-0.031563	-0.571604
C	1.683556	1.359762	-0.557268
C	1.188548	2.498558	-1.218360
C	1.782175	3.727244	-0.969221
C	2.864795	3.844393	-0.069461
C	3.371662	2.737939	0.597211
C	2.767316	1.501031	0.341175
C	2.169263	-0.677375	0.302921
C	2.233445	-2.138059	0.701038
C	3.291920	-2.373192	1.796103
C	0.866458	-2.578783	1.266501
C	-1.406805	0.225986	0.327607
H	3.763545	0.046527	1.515891
H	3.093912	-1.617797	-1.964210
H	3.282285	-3.405786	-2.427402
H	2.534213	-4.100567	-0.234661
H	0.269647	-0.182732	-2.424270
H	0.358563	-1.689014	-1.544756
H	0.352354	2.416871	-1.909326
H	1.411550	4.616405	-1.470899
H	3.308397	4.820259	0.104957
H	4.203333	2.826786	1.290196
H	3.053937	-1.807845	2.704398
H	3.310007	-3.434443	2.061982
H	4.296405	-2.103923	1.452821
H	0.603268	-1.966991	2.135930
H	0.067084	-2.483650	0.526833
H	0.914881	-3.626859	1.582310
H	-0.636492	0.575763	1.000905
C	-3.142864	1.028586	1.957634
C	-4.608184	0.593662	2.071577
C	-5.028695	0.279279	0.621431
H	-3.023786	2.105445	1.811898
H	-2.505167	0.700021	2.778495
H	-5.220880	1.369098	2.531872
H	-4.676883	-0.310205	2.681887
H	-5.723034	-0.560388	0.541614
H	-5.496351	1.139855	0.126150

Substrate **9-red**

0 1

N	-2.214608	-0.574435	-1.688337
C	-3.508914	-0.646115	-1.272715
O	-4.436927	-0.943849	-2.019499
C	-3.670206	-0.378290	0.211961
N	3.113313	0.158812	0.850912
C	2.938336	-2.739603	-1.666171
N	-2.751139	0.681541	0.606993
C	2.516116	-3.096380	-0.453663
C	-1.128125	-0.209988	-0.853350
C	0.238801	-0.559956	-1.379389
C	1.365474	-0.034940	-0.541591
C	1.802898	1.334712	-0.536295
C	1.367493	2.495596	-1.200769
C	2.033020	3.689896	-0.966833
C	3.128776	3.751615	-0.077151
C	3.578017	2.622377	0.592482
C	2.902903	1.419841	0.349195
C	2.189019	-0.723723	0.323971
C	2.188261	-2.186676	0.719048
C	3.235994	-2.470679	1.813151
C	0.804209	-2.570184	1.284287
C	-1.413681	0.426002	0.294738
H	3.831243	-0.082059	1.519441
H	3.054870	-1.696015	-1.950155
H	3.174255	-3.489381	-2.415730
H	2.412208	-4.157999	-0.219905
H	0.334270	-0.150414	-2.397767
H	0.318042	-1.648403	-1.492803
H	0.519640	2.456076	-1.881125
H	1.708927	4.595390	-1.471621
H	3.628523	4.701893	0.086411
H	4.420245	2.667159	1.277000
H	3.025763	-1.893321	2.720707
H	3.203368	-3.531248	2.080517
H	4.252311	-2.250299	1.469529
H	0.576106	-1.960329	2.165044
H	0.006313	-2.420104	0.552401
H	0.804020	-3.624383	1.583279
H	-3.406578	-1.321845	0.736951
H	-2.030489	-0.835975	-2.651949
H	-0.639317	0.780754	0.967025
C	-3.149632	1.065048	1.955465
C	-4.686918	1.079456	1.864110
C	-5.032922	0.129805	0.683705
H	-2.718238	2.031600	2.227335
H	-2.810573	0.311144	2.686440
H	-5.044978	2.090485	1.655468
H	-5.139660	0.753189	2.802801
H	-5.683349	-0.694738	0.981367
H	-5.527975	0.671309	-0.126761

Supplementary References

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