

Supplementary data

Stereoselective synthesis and antiproliferative activity of *allo*-gibberic acid-based 1,3-aminoalcohols regioisomers

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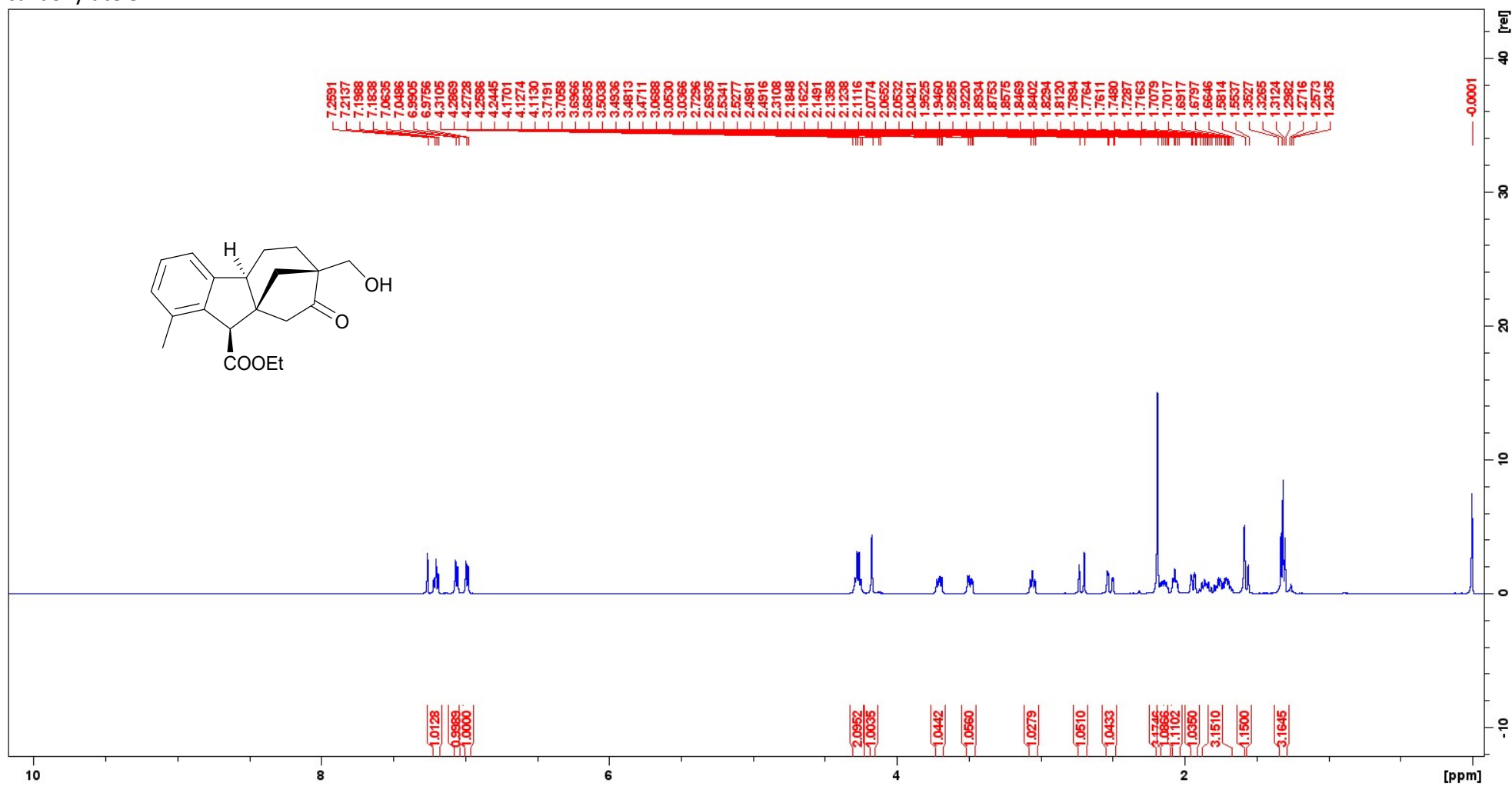
Table S1: Antiproliferative effects of the investigated compounds

Compound	Cc μM	Growth inhibition (%) ± SEM Calculated IC ₅₀ (μM) [95%CI]					
		HeLa	SiHa	MCF-7	MDA-MB-231	A2780	NIH/3T3
8	10	< 20	< 20	51.01 ± 1.01	< 20	30.44 ± 1.51	< 20
	30	20.64 ± 1.03	5.68 ± 8.09	63.75 ± 3.47	15.87 ± 2.46	68.53 ± 1.34	26.41 ± 1.55
9	10	< 20	< 20	49.36 ± 1.97	< 20	28.61 ± 2.28	< 20
	30	90.21 ± 1.35	87.21 ± 1.11	88.74 ± 0.75	91.79 ± 1.12	96.61 ± 0.32	97.04 ± 0.23
10	10	22.03 ± 2.06	< 20	54.31 ± 2.13	< 20	38.34 ± 1.09	< 20
	30	91.68 ± 1.02	82.31 ± 0.99	89.41 ± 1.09	92.30 ± 0.71	96.54 ± 0.47	81.75 ± 1.81
11	10	< 20	< 20	34.99 ± 1.75	< 20	35.70 ± 1.81	< 20
	30	98.56 ± 1.32	98.01 ± 2.95	99.09 ± 0.64	80.28 ± 0.58	97.74 ± 0.98	97.75 ± 1.42
12	10	73.71 ± 4.03	< 20	89.89 ± 1.25	82.45 ± 1.35	92.72 ± 0.72	83.77 ± 3.26
	30	90.23 ± 1.46	90.15 ± 0.87	96.41 ± 0.85	91.98 ± 1.09	96.59 ± 0.55	95.93 ± 1.22
		20.70 [14.72-29.10]	22.34 [14.02-35.59]	3.43 [2.87-4.09]	10.38 [9.55-11.28]	6.17 [4.45-8.55]	6.02 [5.09-7.11]
13	10	< 20	< 20	75.63 ± 3.89	< 20	54.23 ± 1.10	< 20
	30	91.76 ± 1.51	91.03 ± 1.21	96.58 ± 0.62	93.06 ± 1.31	96.99 ± 0.32	97.34 ± 0.30
		18.55 [14.69-23.43]	22.73 [15.75-32.81]	7.07 [5.91-8.46]	19.29 [15.86-23-46]	4.57 [3.73-5.59]	14.47 [12.00-17.45]
14	10	22.08 ± 2.93	21.86 ± 2.03	53.30 ± 1.31	< 20	35.55 ± 1.57	< 20
	30	81.08 ± 3.99	46.02 ± 1.48	90.39 ± 1.08	88.02 ± 0.65	96.13 ± 0.59	83.41 ± 2.09
15	10	< 20	< 20	54.92 ± 1.31	< 20	26.83 ± 2.19	< 20
	30	< 20	< 20	79.74 ± 0.85	64.50 ± 2.35	74.51 ± 3.25	75.76 ± 7.06
16	10	92.44 ± 1.30	84.17 ± 0.86	92.37 ± 1.54	86.55 ± 0.70	96.39 ± 0.71	89.85 ± 1.28
	30	92.83 ± 1.27	83.97 ± 1.31	93.78 ± 1.14	87.21 ± 0.53	96.06 ± 0.76	93.92 ± 0.54
		4.01 [3.44-4.68]	4.12 [3.32-5.11]	3.14 [2.75-3.59]	4.71 [3.64-6.09]	4.57 [3.73-5.59]	12.95 [11.85-14.14]
17	10	< 20	< 20	37.91 ± 2.19	< 20	< 20	< 20
	30	< 20	< 20	45.58 ± 1.18	27.22 ± 0.93	33.08 ± 2.09	22.29 ± 1.16
18	10	96.46 ± 0.29	< 20	95.49 ± 0.71	92.38 ± 0.98	96.51 ± 0.26	< 20
	30	96.09 ± 0.51	96.34 ± 0.59	97.91 ± 0.61	93.39 ± 0.98	95.81 ± 0.49	99.31 ± 0.14
		5.06 [4.68-5.46]	21.87 [14.74-32.45]	3.85 [3.55-4.17]	6.48 [5.09-8.25]	5.08 [4.63-5.59]	19.71 [14.25-27.26]
19	10	< 20	< 20	45.00 ± 4.12	< 20	< 20	< 20
	30	< 20	< 20	48.73 ± 3.87	< 20	38.36 ± 1.37	< 20
20	10	< 20	< 20	26.64 ± 0.96	21.27 ± 0.72	32.98 ± 3.85	< 20
	30	< 20	< 20	54.07 ± 1.41	40.28 ± 2.31	83.69 ± 1.11	< 20
21	10	< 20	21.18 ± 2.61	26.24 ± 1.38	< 20	< 20	< 20
	30	29.33 ± 2.22	30.01 ± 1.78	43.16 ± 2.59	22.37 ± 1.67	39.58 ± 1.98	< 20
26	10	98.56 ± 0.39	97.15 ± 0.65	98.76 ± 0.48	95.14 ± 0.51	96.67 ± 0.39	99.82 ± 0.11
	30	97.58 ± 0.58	97.07 ± 0.88	98.35 ± 0.65	94.58 ± 0.84	96.59 ± 0.43	99.39 ± 0.20
		5.10 [4.66-5.59]	4.36 [3.62-5.25]	3.66 [3.16-4.23]	4.47 [4.06-4.93]	4.57 [4.22-4.95]	4.62 [4.03-5.29]
27	10	96.42 ± 0.44	96.22 ± 0.78	97.53 ± 0.23	95.86 ± 0.83	95.04 ± 0.98	99.84 ± 0.05
	30	96.48 ± 0.36	95.25 ± 1.77	96.97 ± 0.31	95.51 ± 0.85	96.72 ± 0.58	99.46 ± 0.14
		5.83 [4.72-7.20]	4.09 [2.95-5.67]	3.86 [3.30-4.51]	5.10 [4.28-6.08]	4.53 [3.91-5.24]	6.25 [5.31-7.35]
28	10	99.55 ± 0.16	99.07 ± 0.43	99.20 ± 0.29	97.46 ± 0.38	97.65 ± 0.25	82.62 ± 1.19
	30	98.98 ± 0.26	98.45 ± 0.66	99.28 ± 0.31	95.93 ± 0.97	96.90 ± 0.42	99.47 ± 0.19
		3.89 [3.28-4.62]	3.83 [2.96-4.96]	3.40 [2.91-3.99]	5.17 [4.39-6.09]	4.52 [3.80-5.37]	8.83 [8.34-9.34]
29	10	93.88 ± 0.59	< 20	91.20 ± 0.93	83.84 ± 1.46	70.55 ± 3.61	24.48 ± 0.62
	30	97.06 ± 0.53	95.23 ± 0.98	97.29 ± 0.91	95.71 ± 1.15	95.22 ± 1.10	99.19 ± 0.23
		5.51 [4.34-7.01]	13.52 [10.44-17.52]	4.47 [4.16-4.79]	7.09 [6.09-8.25]	7.51 [6.75-8.35]	13.48 [12.05-15.08]
30	10	< 20	24.64 ± 0.68	39.43 ± 2.02	< 20	< 20	< 20
	30	84.87 ± 2.54	69.06 ± 3.42	94.82 ± 0.91	90.68 ± 0.79	71.96 ± 1.54	57.62 ± 3.74
31	10	24.69 ± 1.53	71.65 ± 1.82	90.42 ± 1.63	75.35 ± 0.29	52.60 ± 1.08	< 20
	30	99.40 ± 0.85	99.29 ± 2.05	99.89 ± 0.15	82.22 ± 0.18	98.42 ± 0.97	99.98 ± 0.23

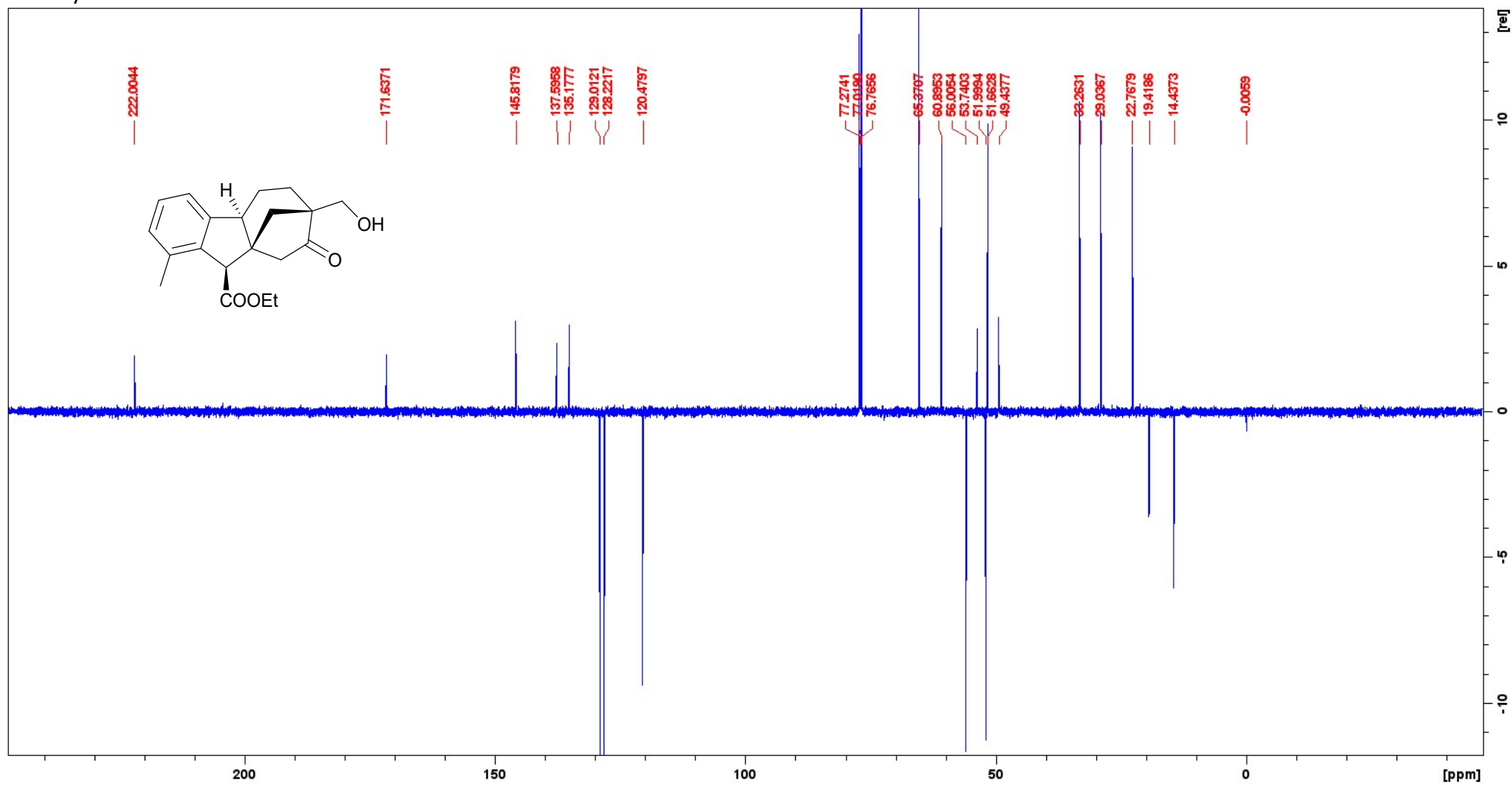
32	10	< 20	< 20	97.19 ± 0.26	83.56 ± 1.46	26.03 ± 0.92	25.64 ± 2.16
	30	97.58 ± 0.56	97.26 ± 0.86	97.53 ± 0.88	94.13 ± 0.81	96.60 ± 0.40	99.06 ± 0.16
		18.78 [14.95-23.59]	8.40 [5.08-13.88]	4.40 [4.03-4.81]	7.71 [6.89-8.62]	15.03 [12.50-18.07]	15.17 [13.48-17.07]
33	10	< 20	< 20	96.15 ± 0.29	84.12 ± 0.94	24.01 ± 0.78	23.56 ± 1.64
	30	98.18 ± 0.55	98.73 ± 0.66	99.17 ± 0.38	95.72 ± 1.12	97.05 ± 0.54	99.56 ± 0.25
		12.91 [9.66-17.27]	17.67 [14.74-21.19]	4.08 [3.43-4.86]	6.50 [6.05-6.98]	13.83 [9.38-20.40]	14.74 [13.77-15.79]
34	10	98.81 ± 0.36	87.91 ± 3.30	98.52 ± 0.24	95.34 ± 0.55	88.27 ± 2.73	33.83 ± 1.05
	30	98.43 ± 0.37	98.49 ± 0.58	99.13 ± 0.44	95.20 ± 0.30	96.74 ± 0.24	99.38 ± 0.20
		4.71 [3.77-5.88]	20.55 [13.43-31.45]	2.42 [1.90-3.08]	4.99 [3.58-6.98]	5.39 [4.40-6.62]	13.02 [11.88-14.26]
35	10	71.86 ± 1.79	< 20	97.65 ± 0.30	92.18 ± 0.69	33.51 ± 1.18	49.95 ± 2.66
	30	95.91 ± 0.32	94.97 ± 0.58	97.60 ± 0.53	94.79 ± 0.81	95.93 ± 0.71	99.58 ± 0.16
36	10	< 20	25.03 ± 1.05	39.94 ± 1.63	< 20	< 20	< 20
	30	26.47 ± 2.06	26.96 ± 2.13	82.56 ± 2.11	69.95 ± 1.37	86.12 ± 0.68	22.19 ± 2.21
37	10	< 20	24.59 ± 0.58	21.14 ± 1.38	< 20	< 20	< 20
	30	21.38 ± 0.69	27.53 ± 1.89	39.89 ± 2.47	< 20	21.04 ± 0.76	< 20
38	10	< 20	< 20	< 20	< 20	< 20	< 20
	30	42.90 ± 3.52	38.70 ± 2.32	92.85 ± 1.02	25.63 ± 1.13	69.87 ± 0.87	41.81 ± 3.24
39	10	< 20	< 20	30.74 ± 0.78	< 20	< 20	< 20
	30	36.10 ± 3.67	26.45 ± 3.51	87.20 ± 1.09	32.73 ± 1.32	70.26 ± 1.46	40.93 ± 2.43

*: data from reference 10.3390/ijms24021121 (Bai D, Int J Mol Sci 2023)

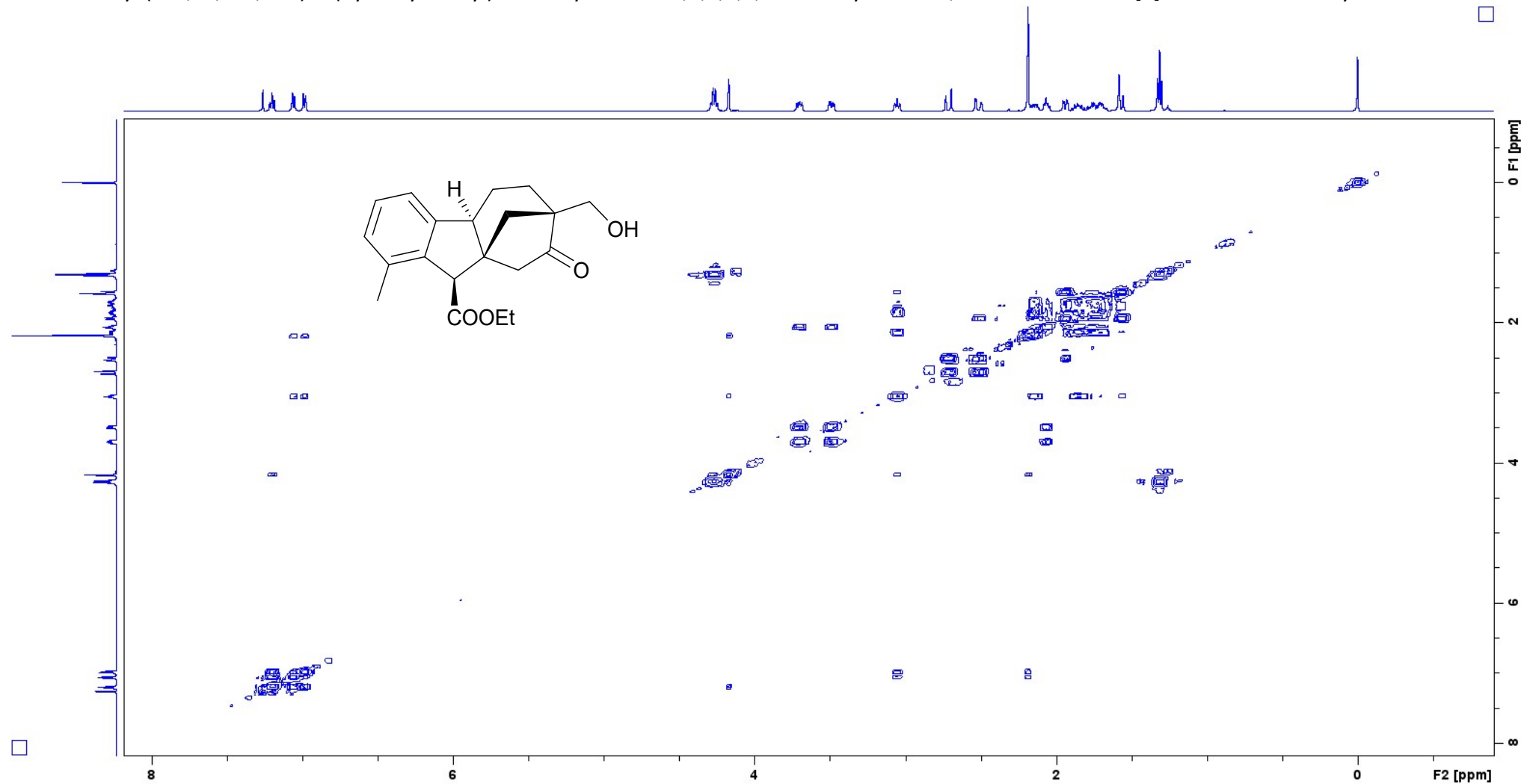
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¹³C-NMR of ethyl (4*bS*,7*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-oxo-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **5**

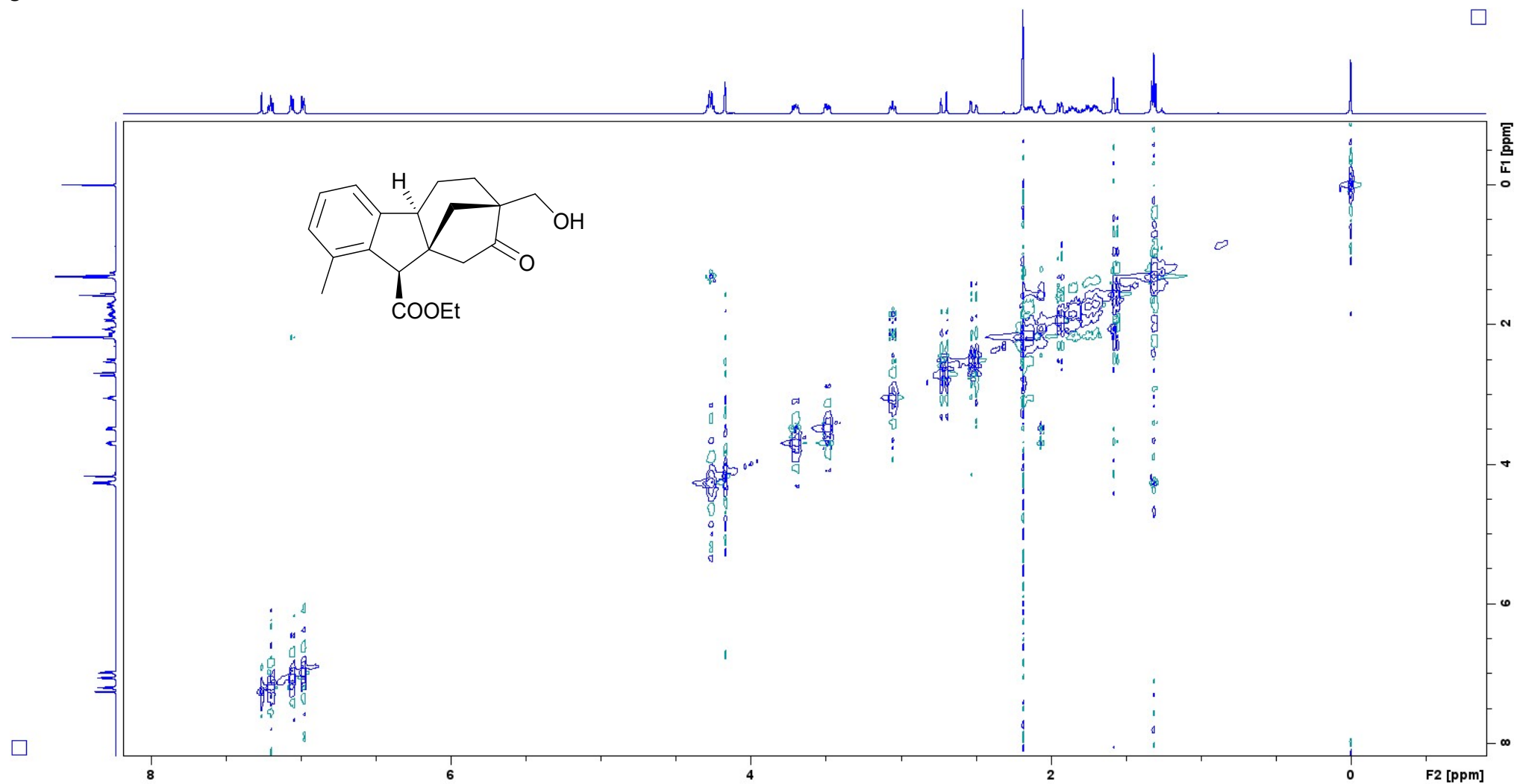


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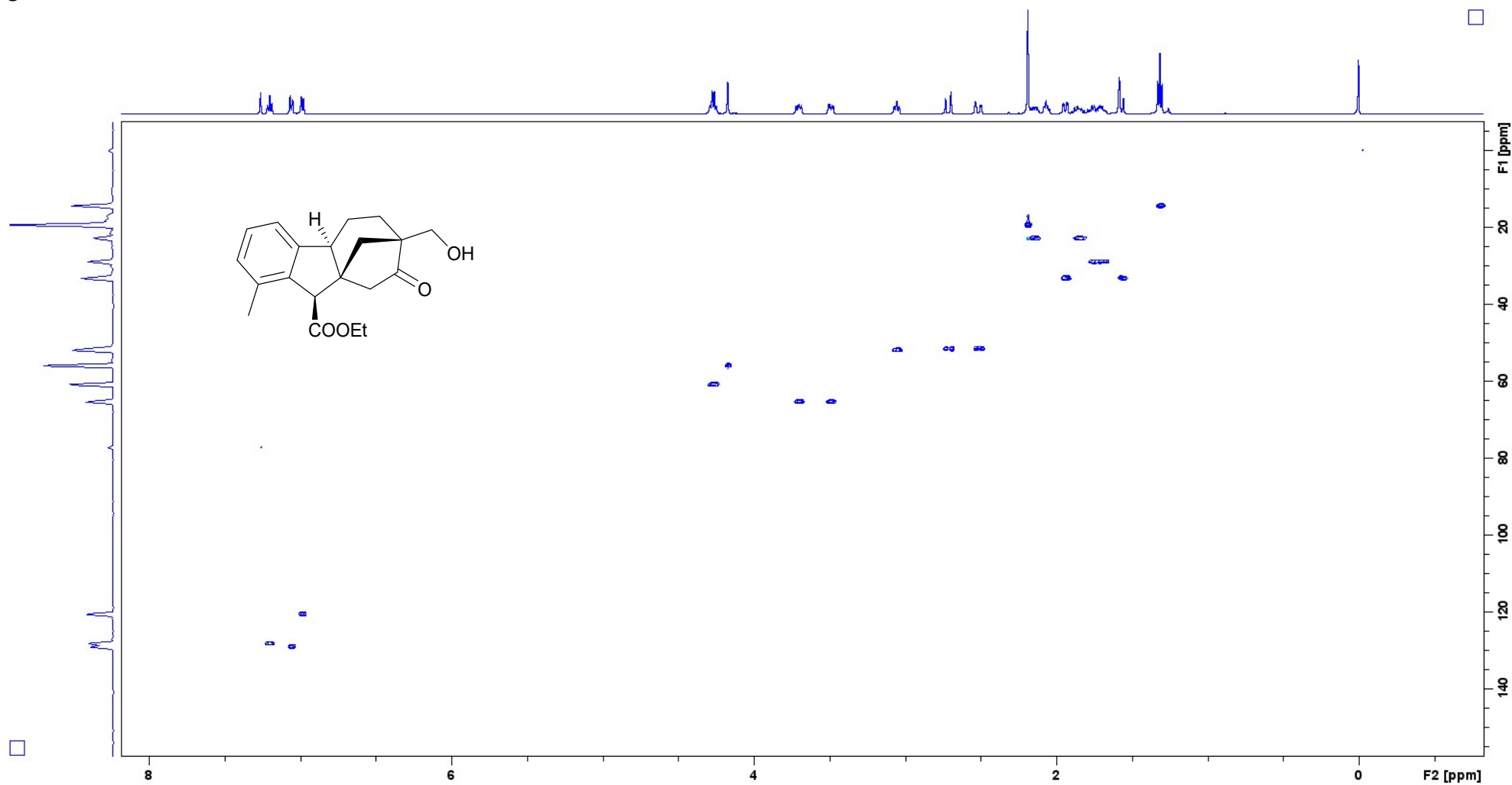


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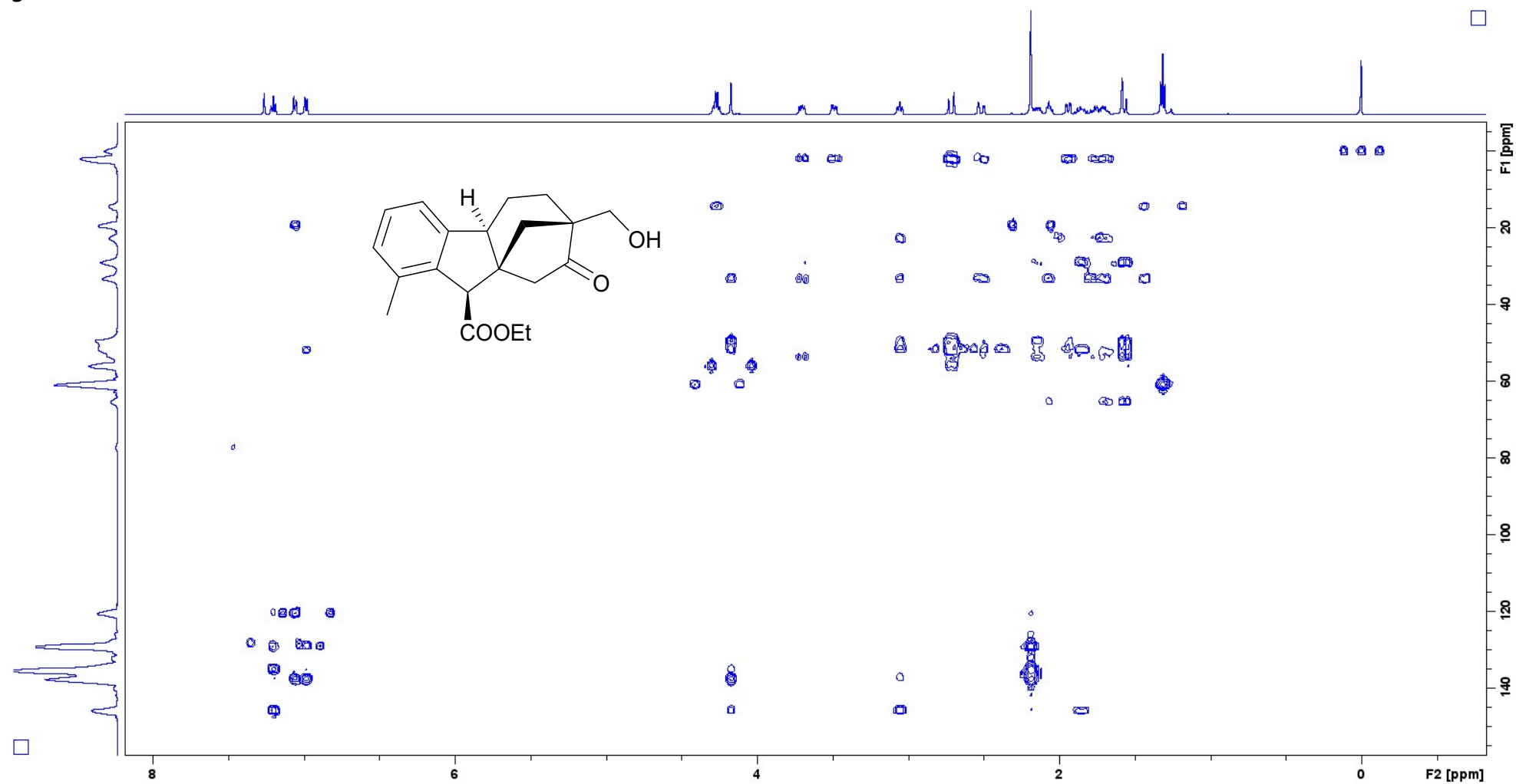
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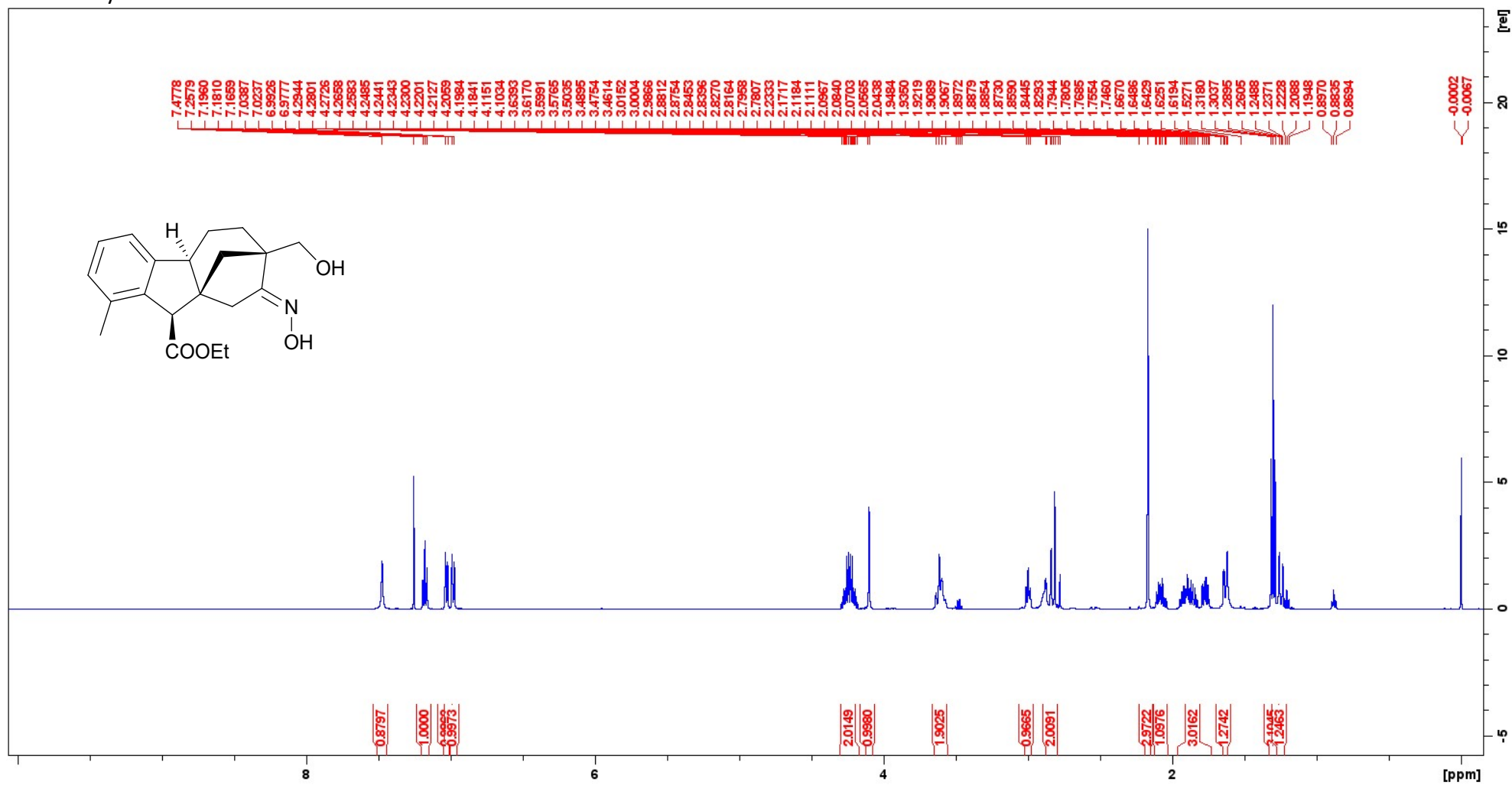
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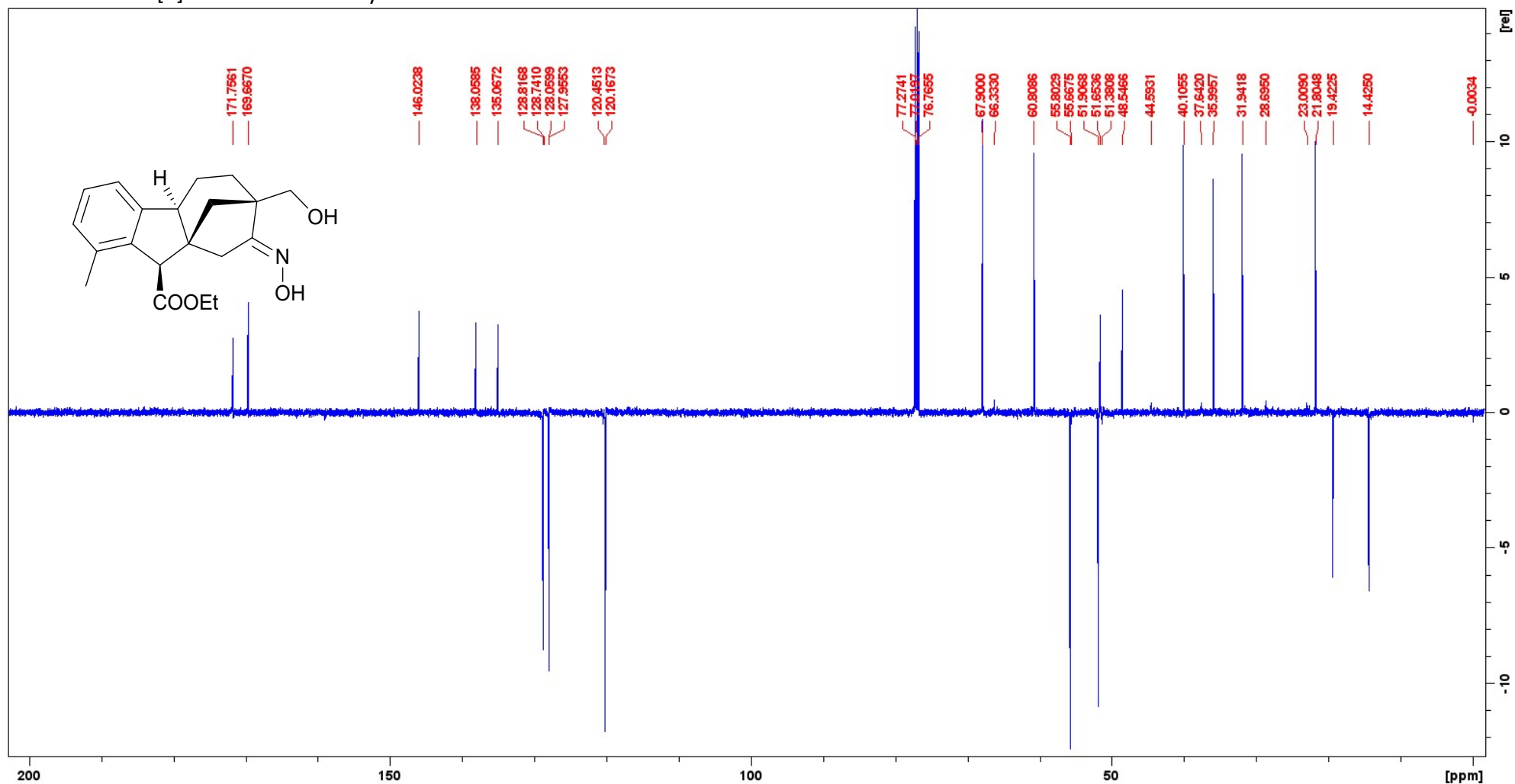
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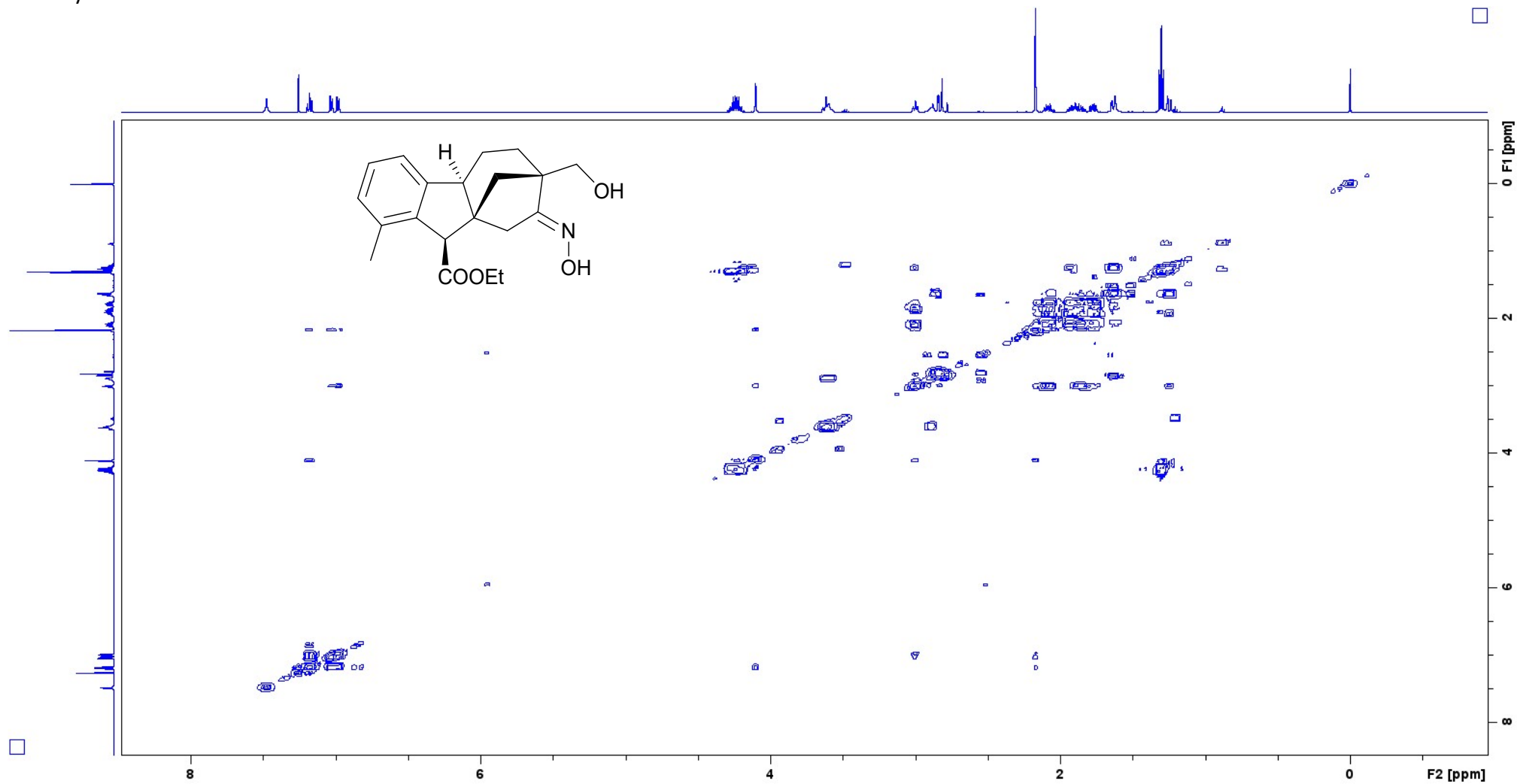
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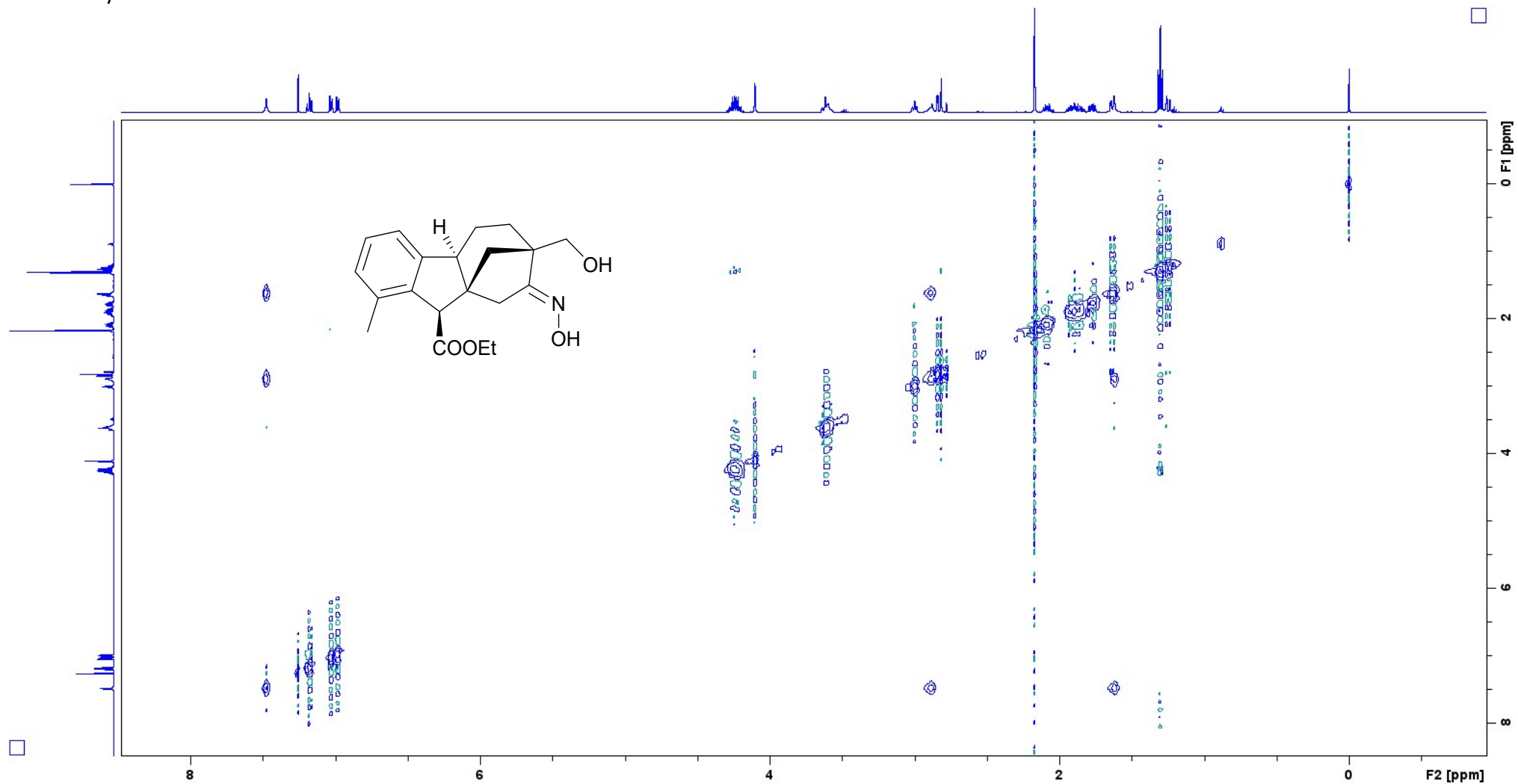
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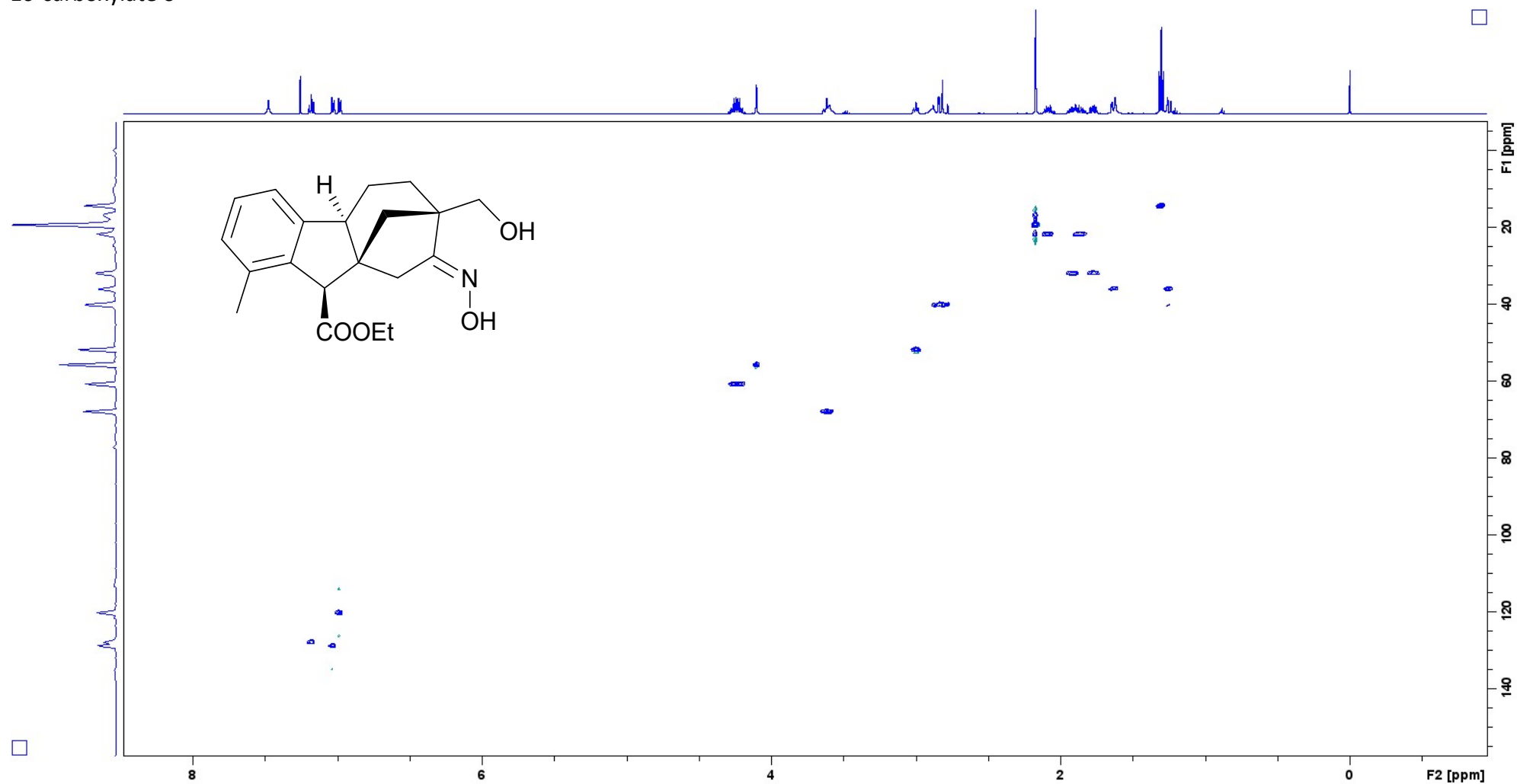
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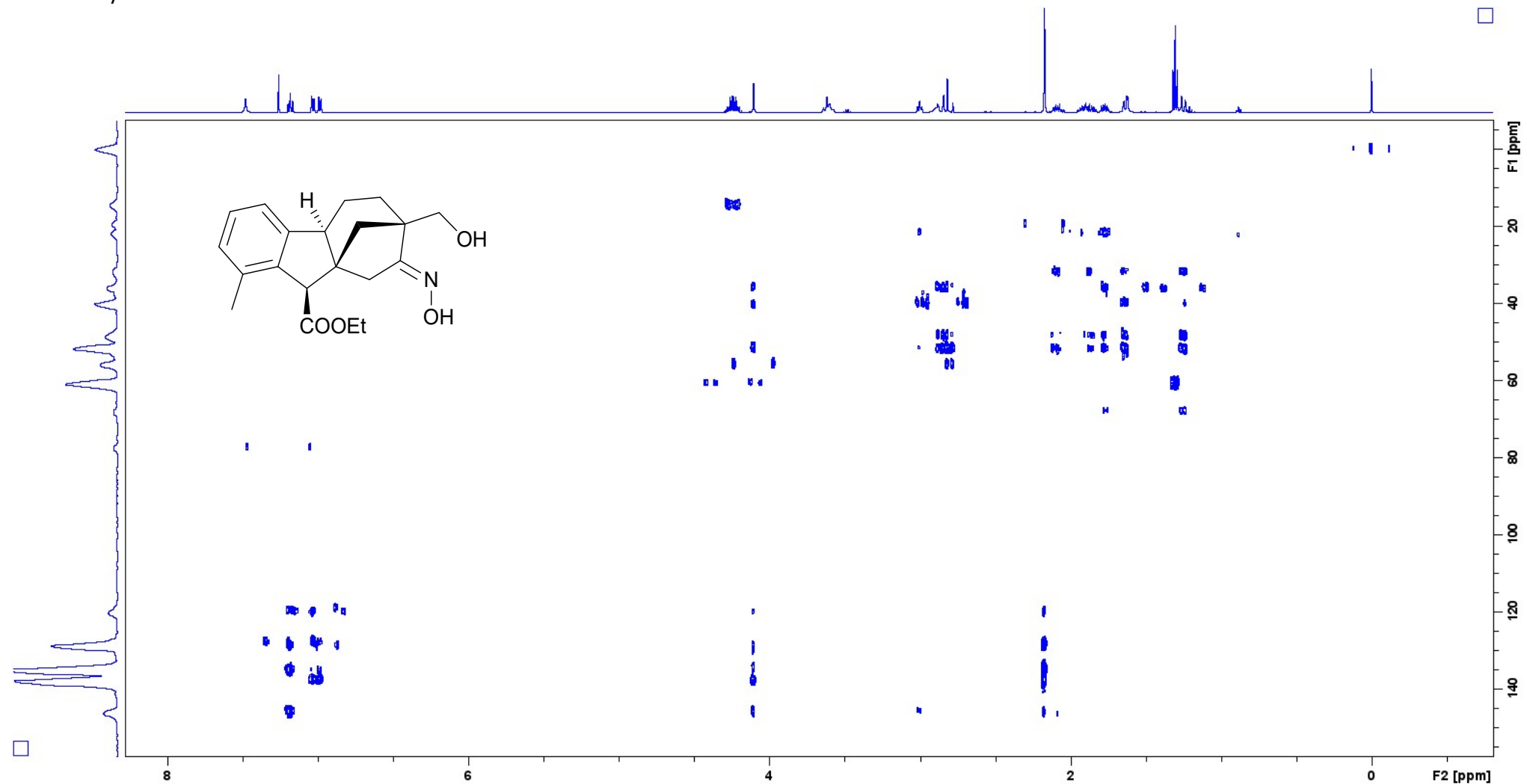
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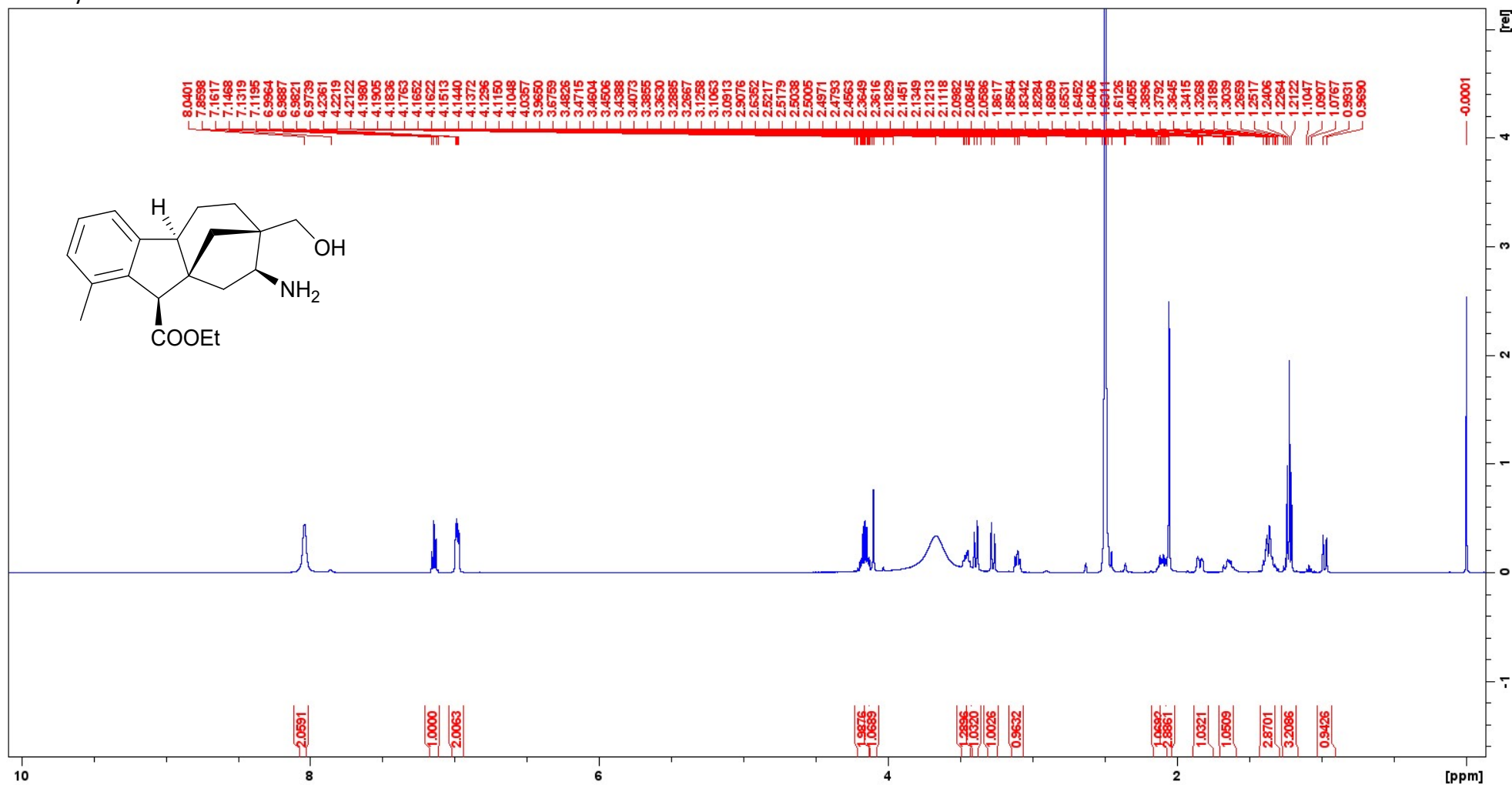
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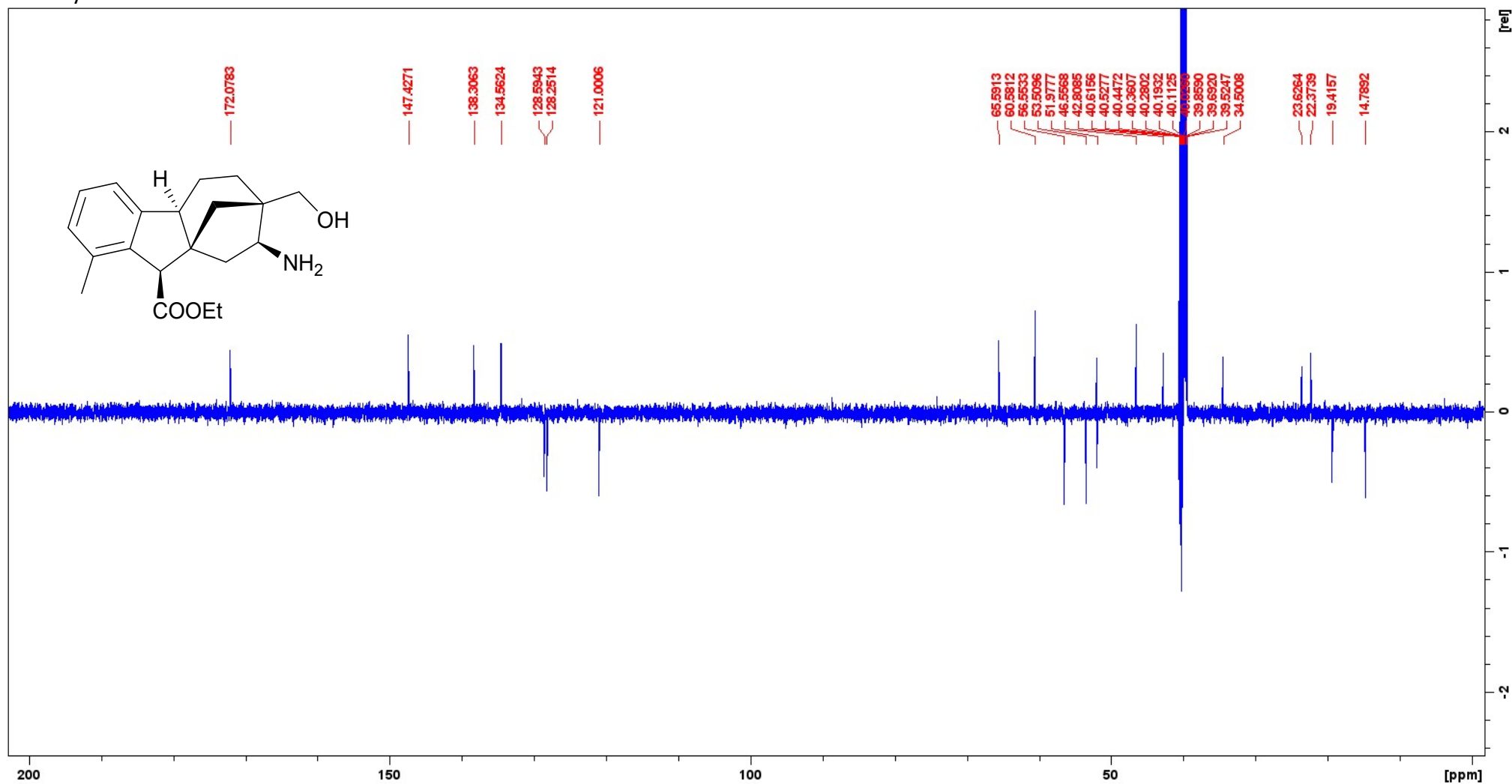
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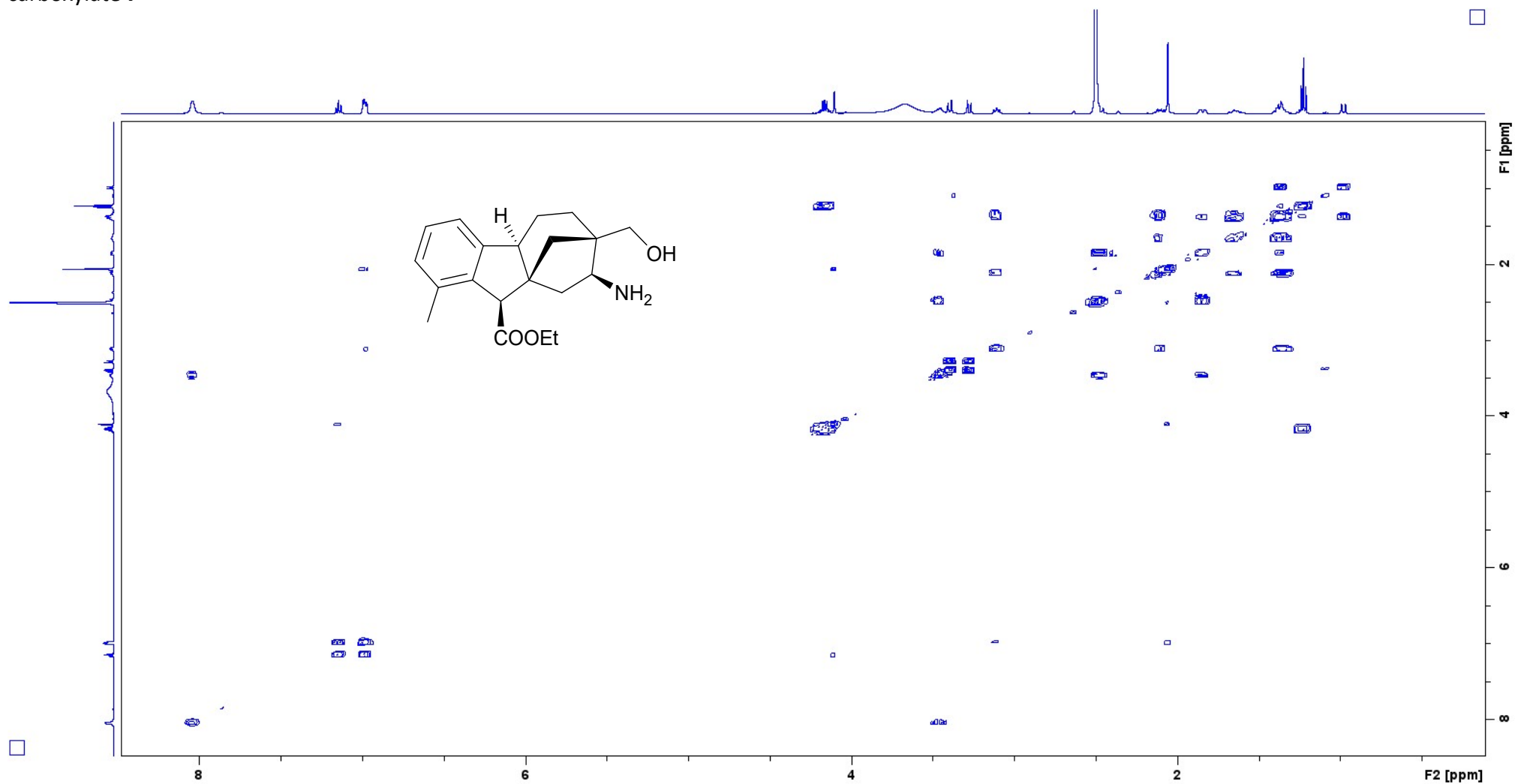
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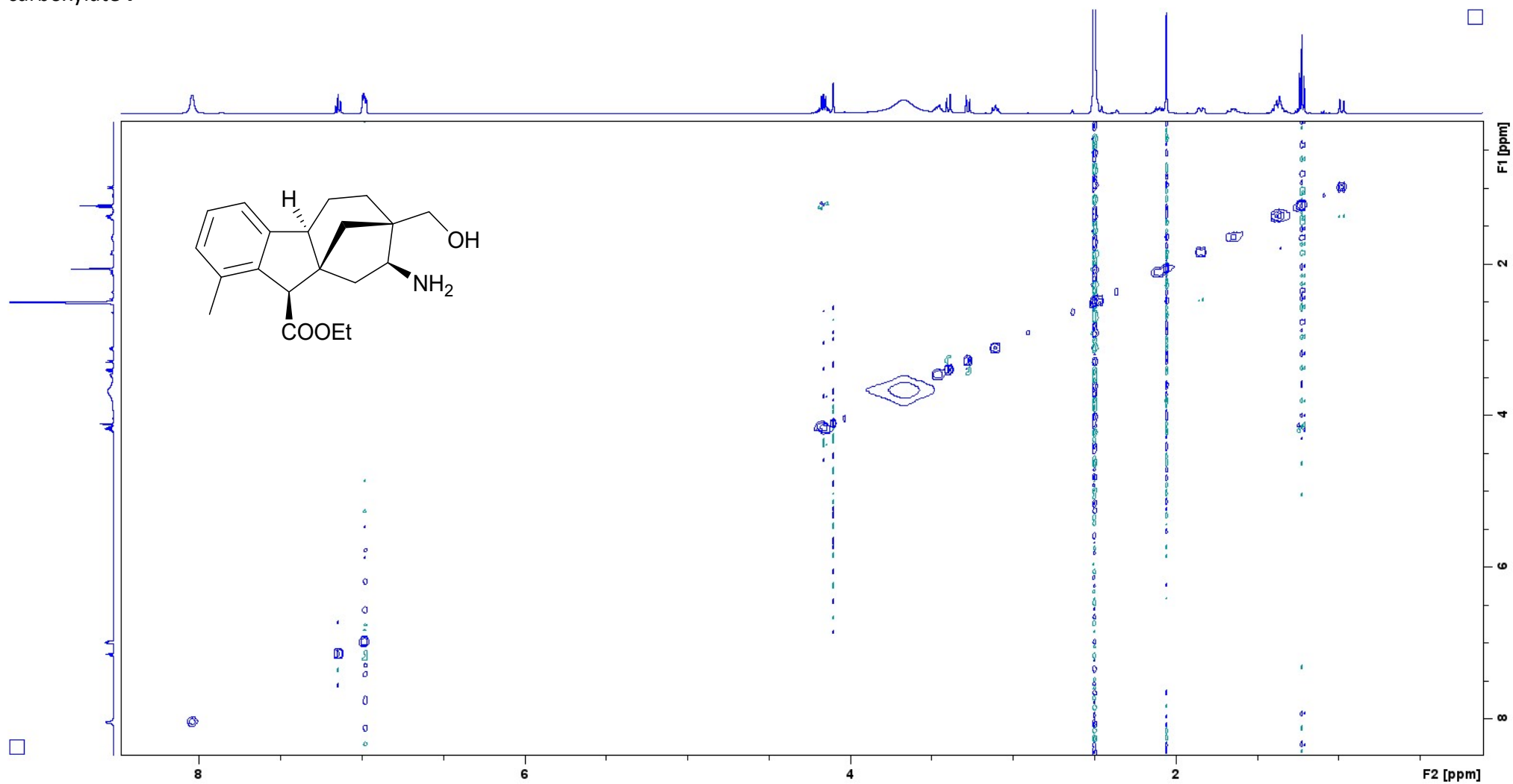
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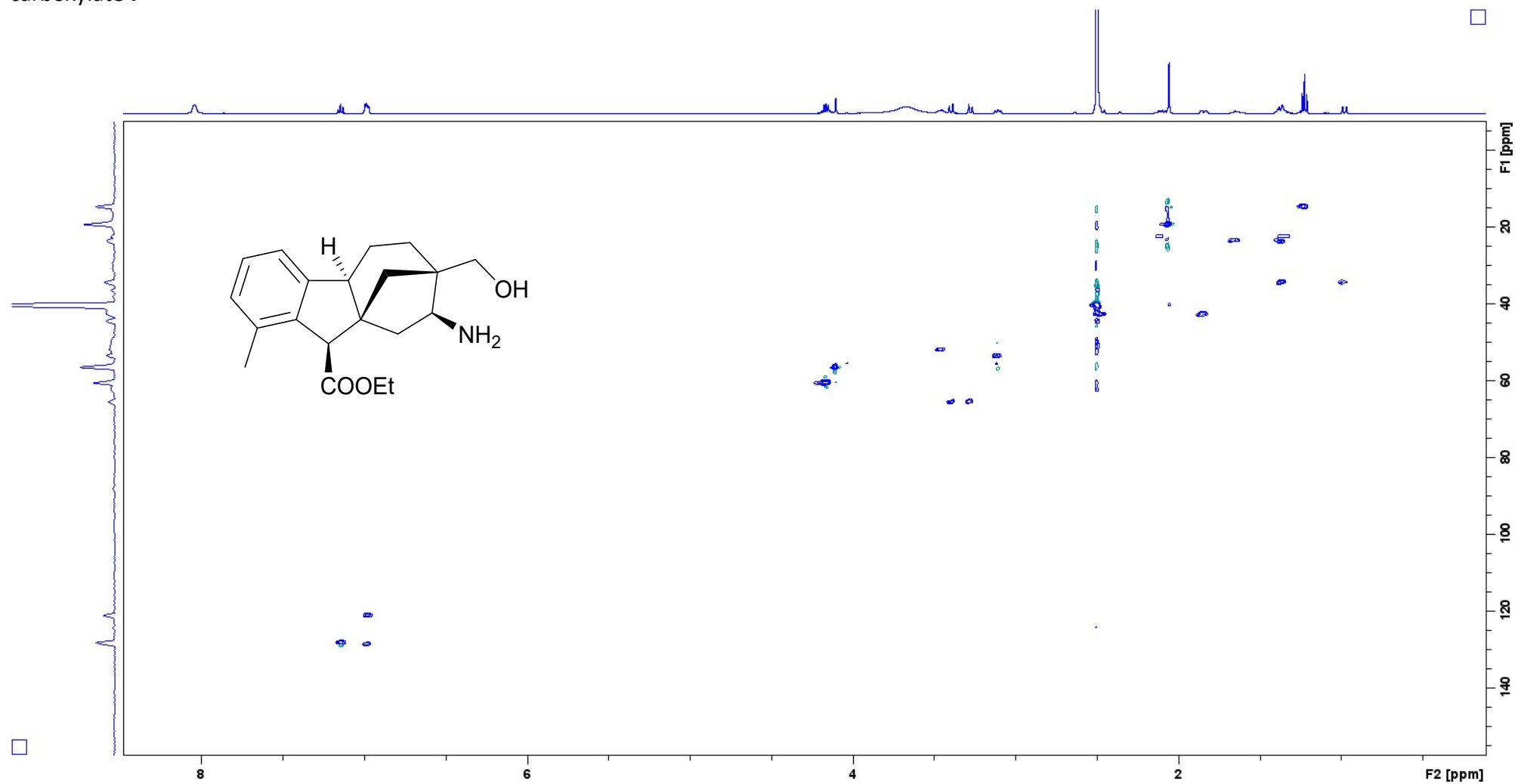
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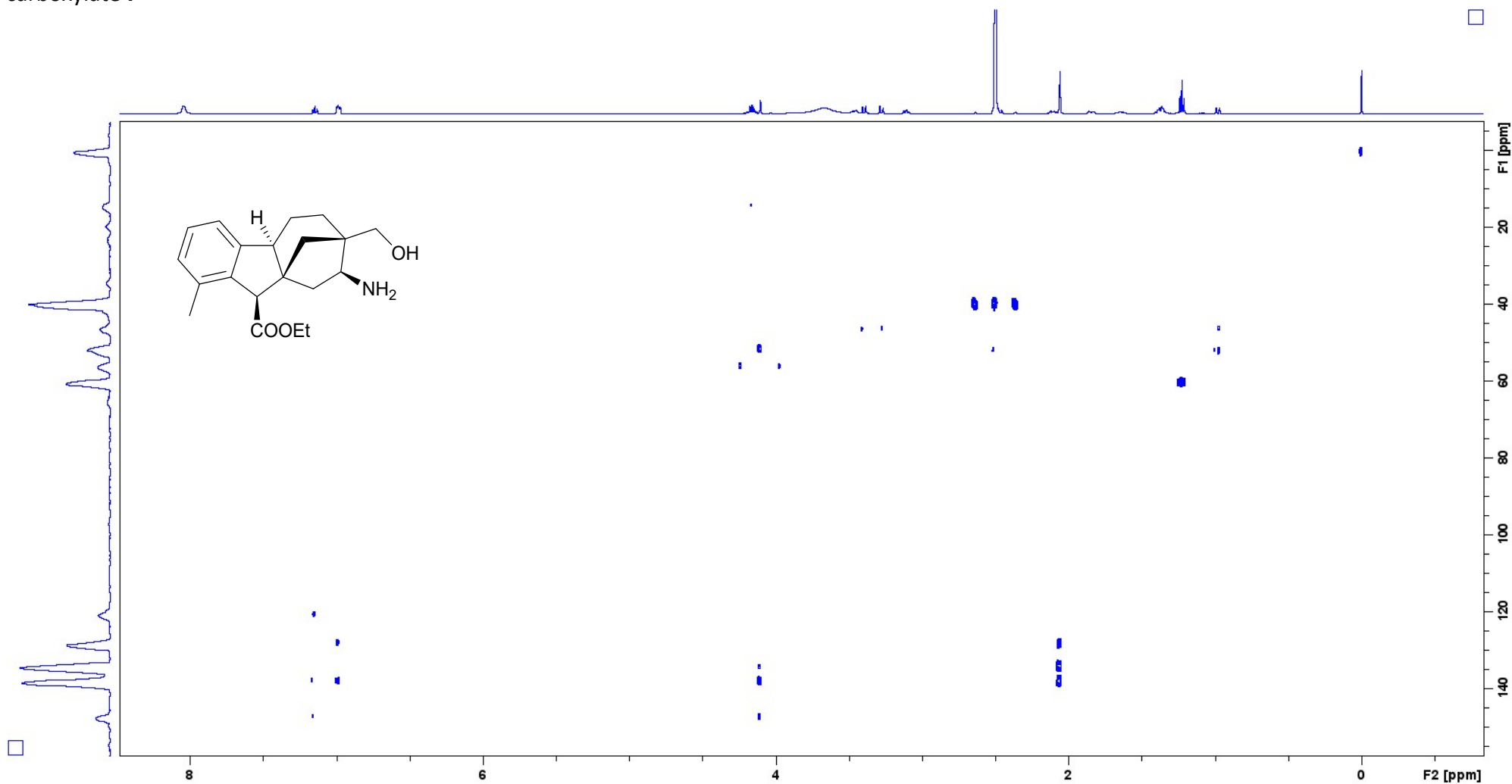
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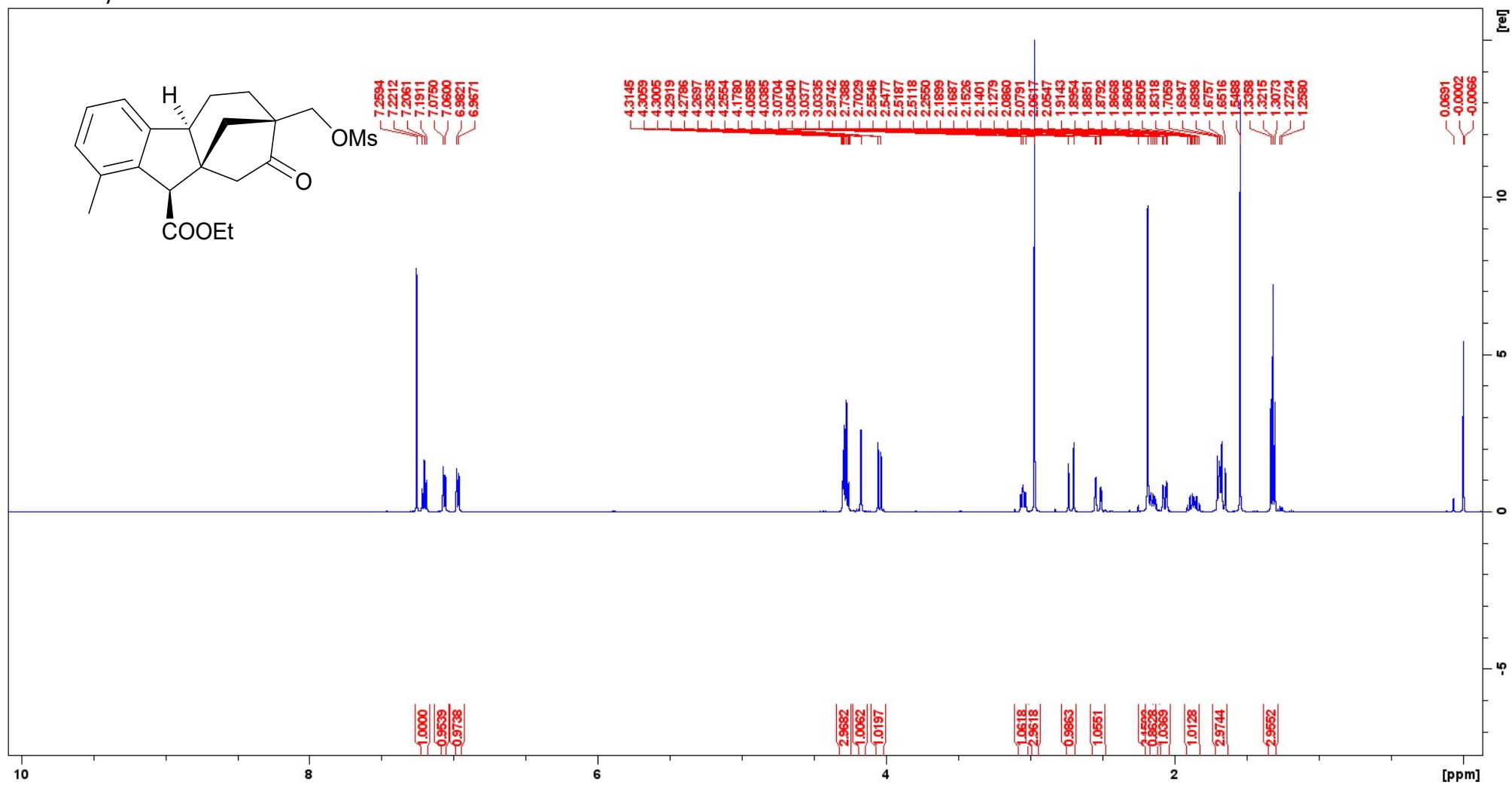
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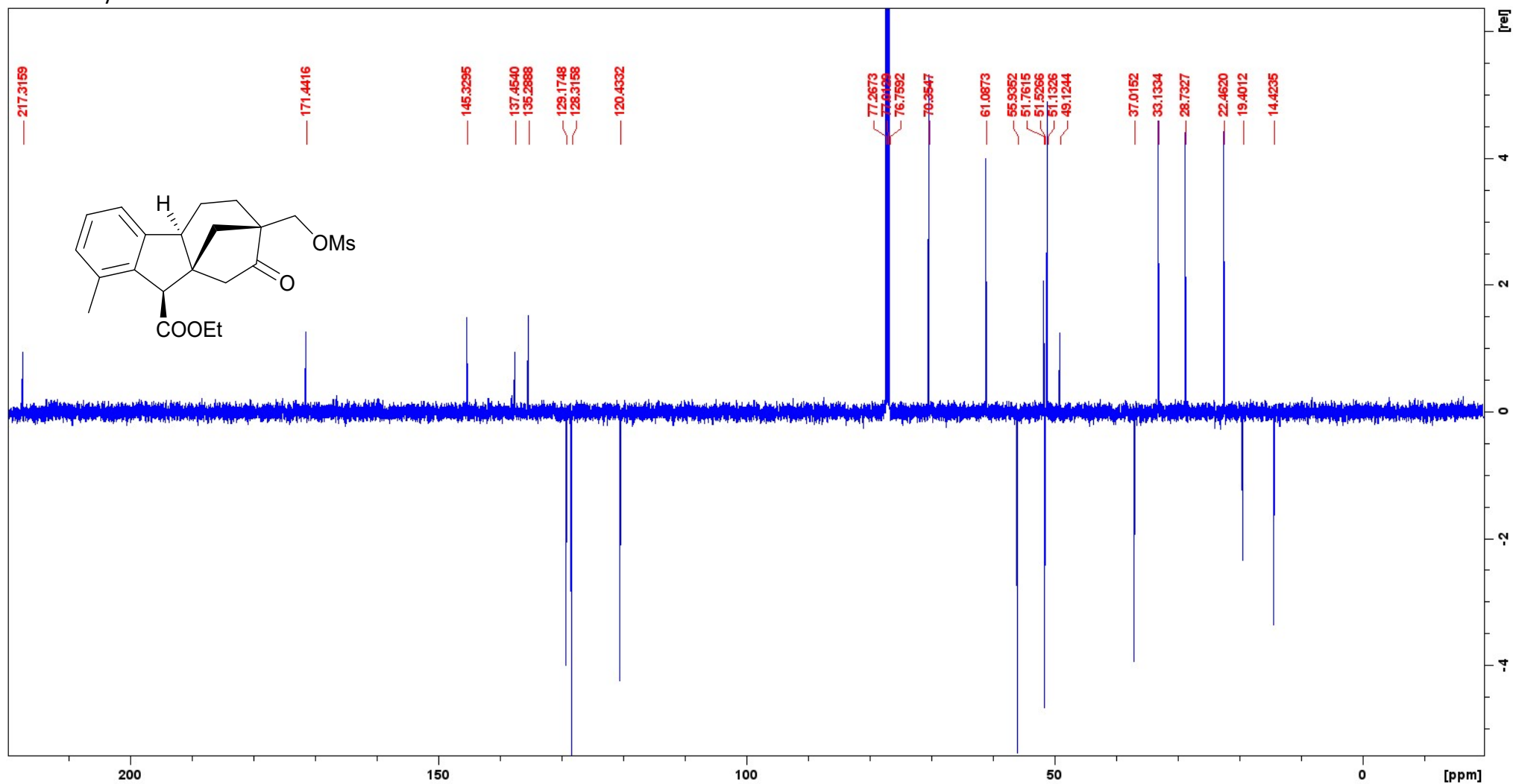
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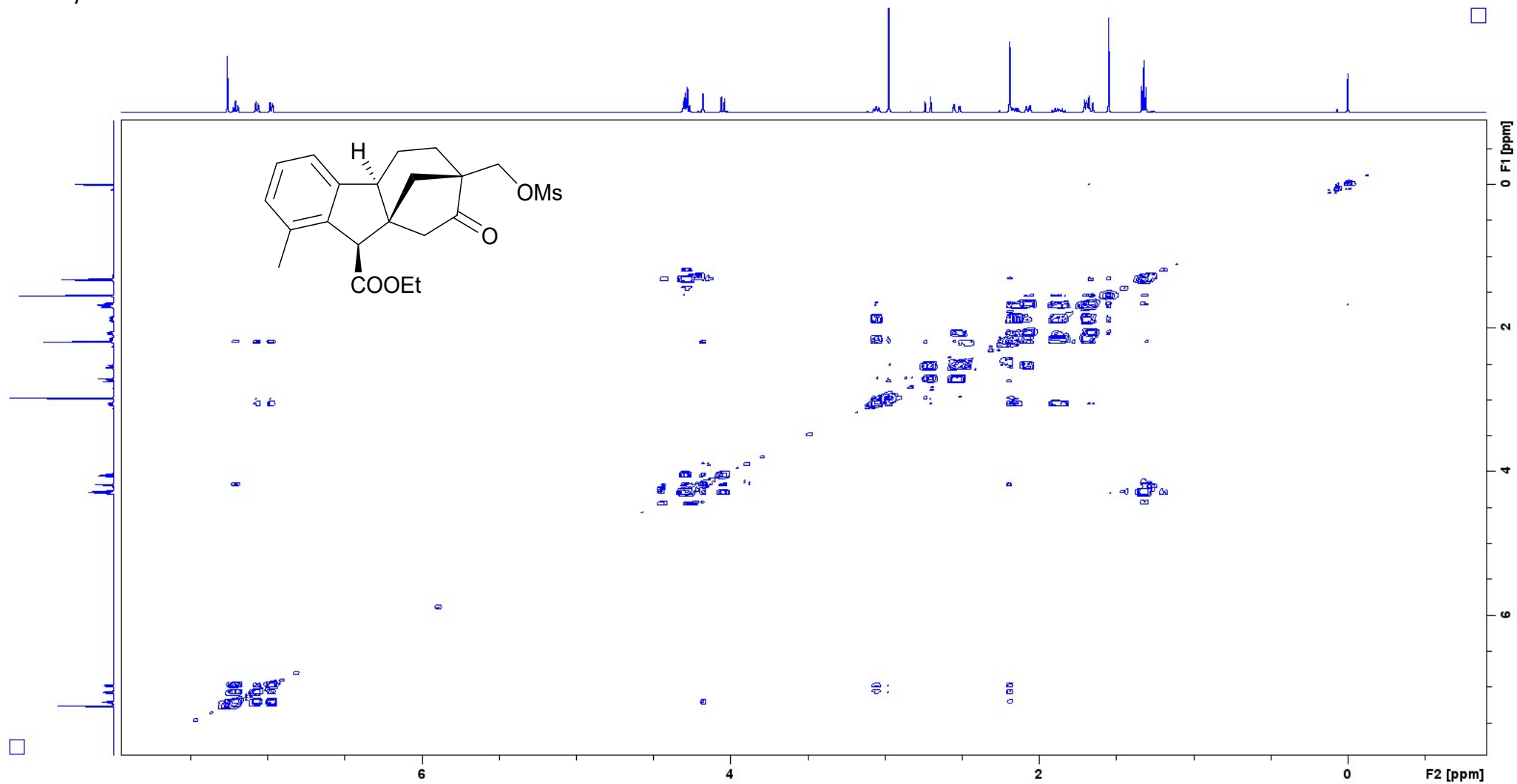
$^1\text{H-NMR}$ of ethyl (4*b**S*,7*S*,9*a**S*,10*R*)-1-methyl-7-(((methylsulfonyl)oxy)methyl)-8-oxo-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **22**



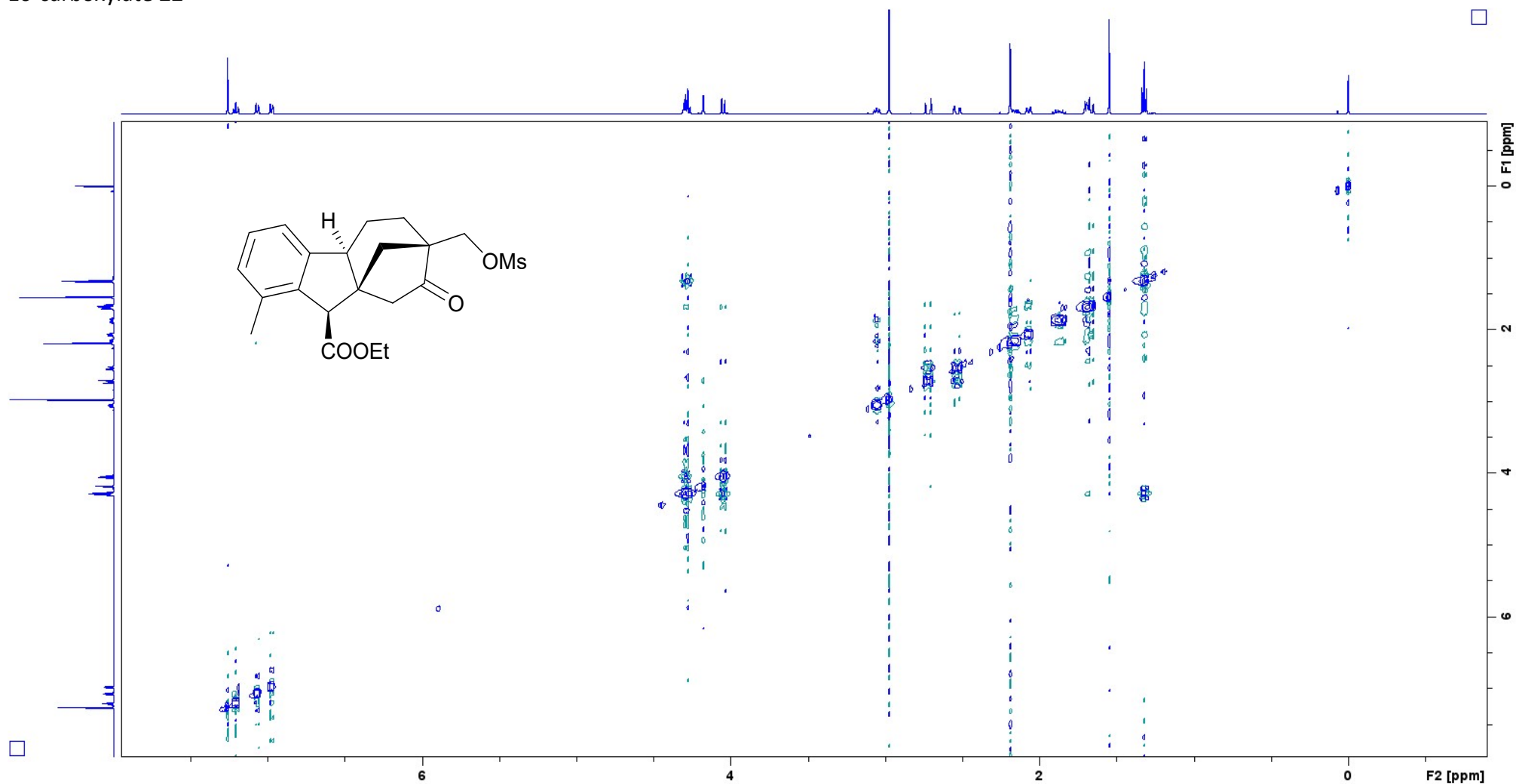
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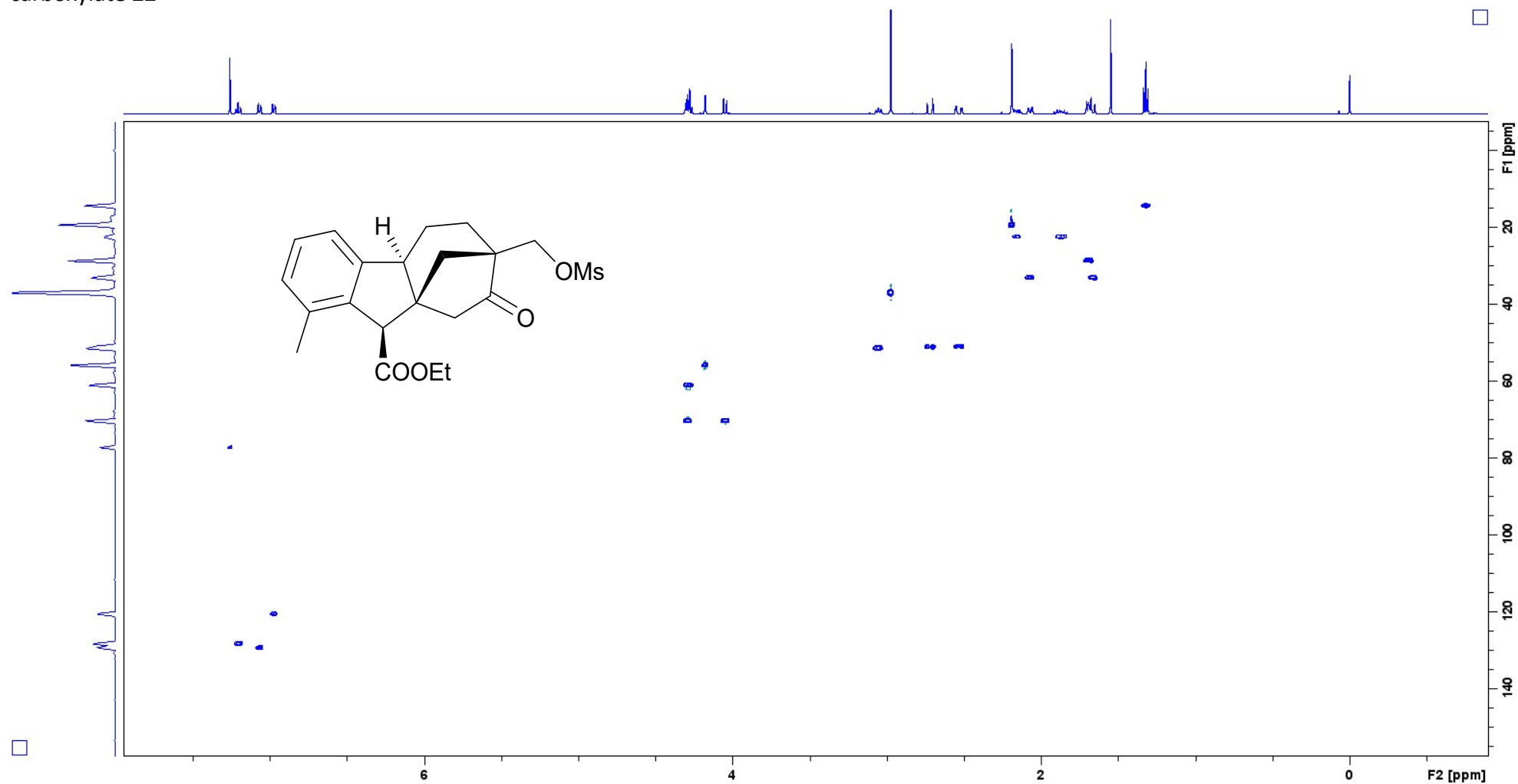
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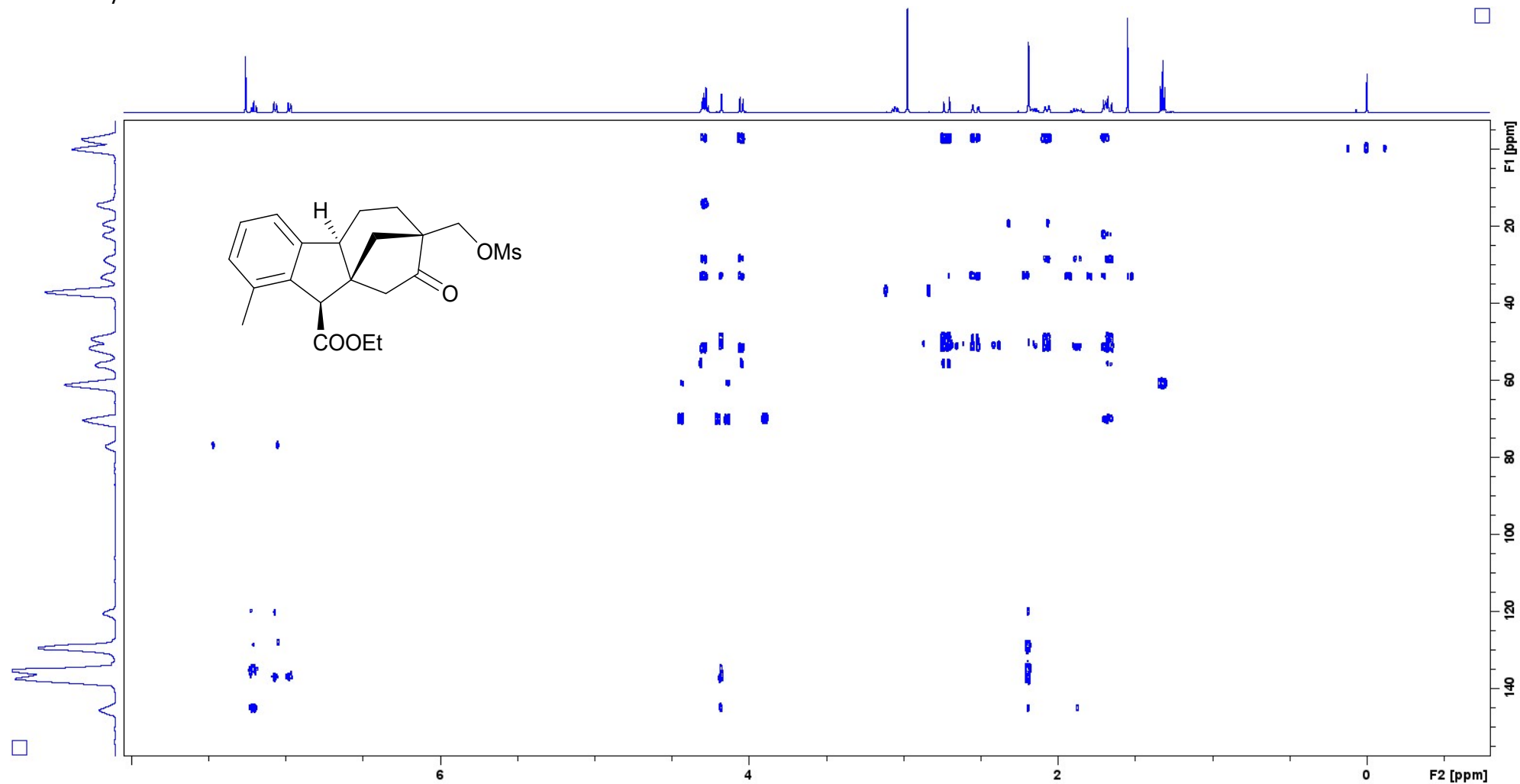
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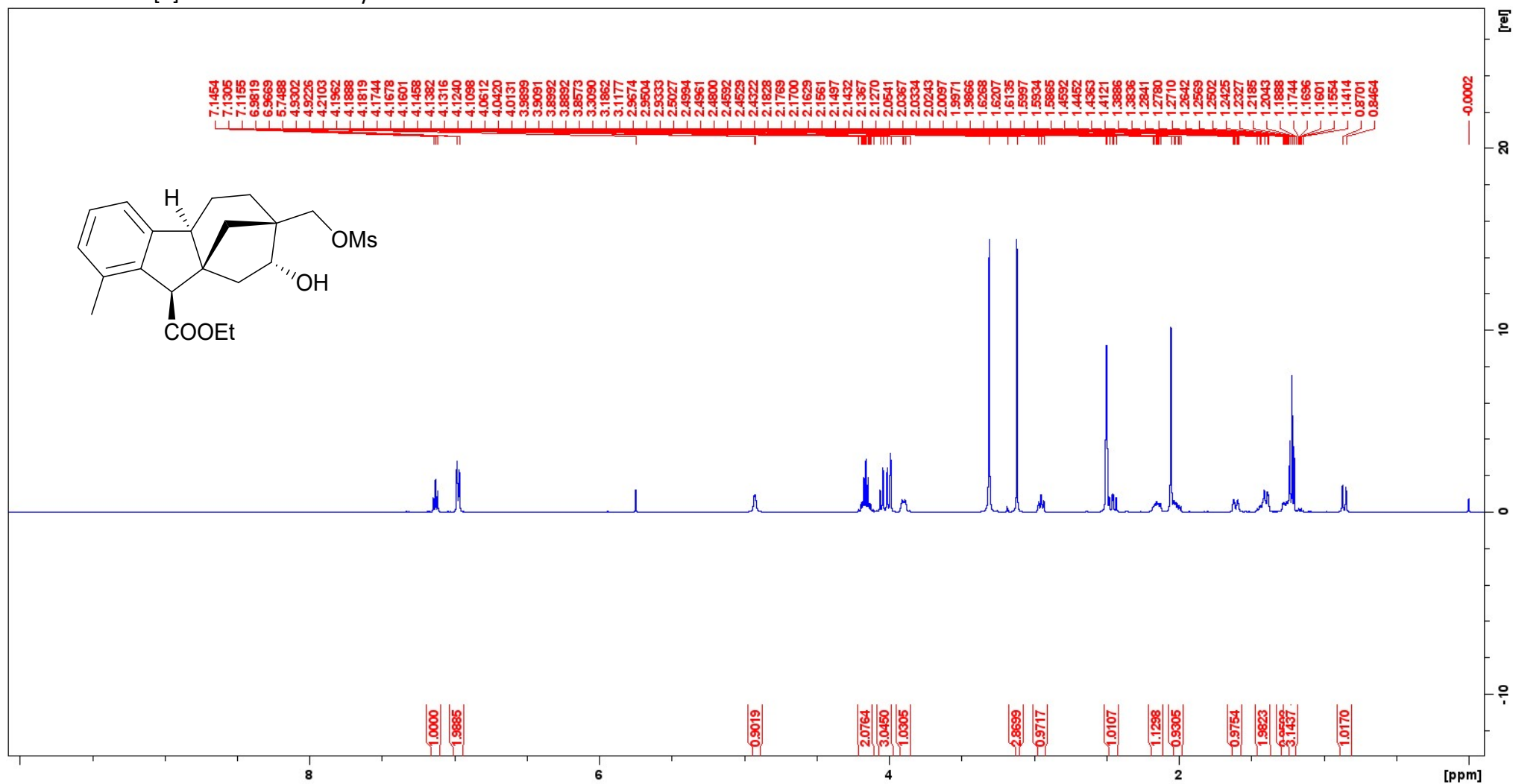
HSQC of ethyl (4*b**S*,7*S*,9*a**S*,10*R*)-1-methyl-7-(((methylsulfonyl)oxy)methyl)-8-oxo-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **22**



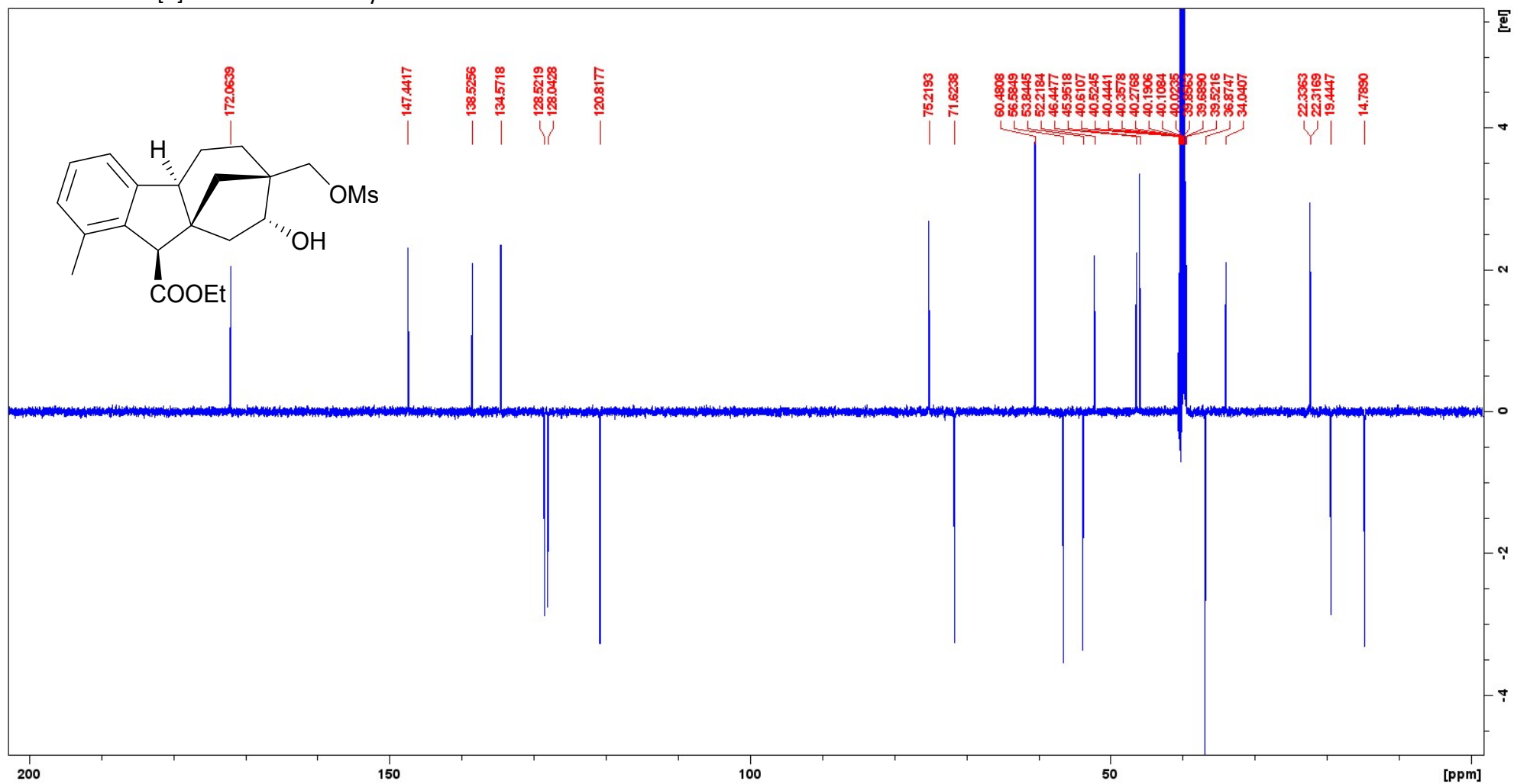
HMBC of ethyl (4*b**S*,7*S*,9*a**S*,10*R*)-1-methyl-7-(((methylsulfonyl)oxy)methyl)-8-oxo-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **22**



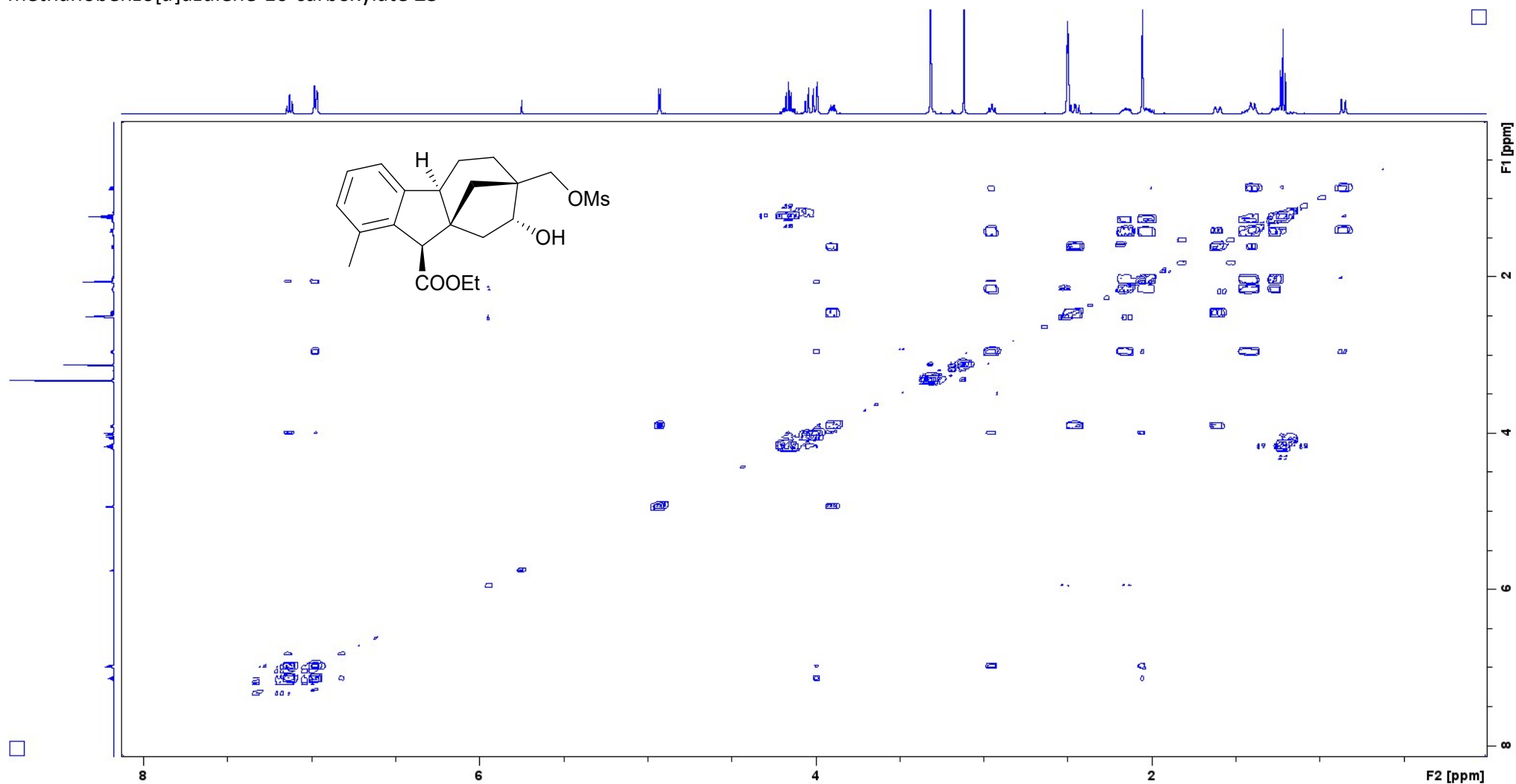
¹H-NMR of ethyl (4bS,7S,8R,9aS,10R)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4b,6,7,8,9,10-hexahydro-5H-7,9a-methanobenzo[a]azulene-10-carboxylate **23**



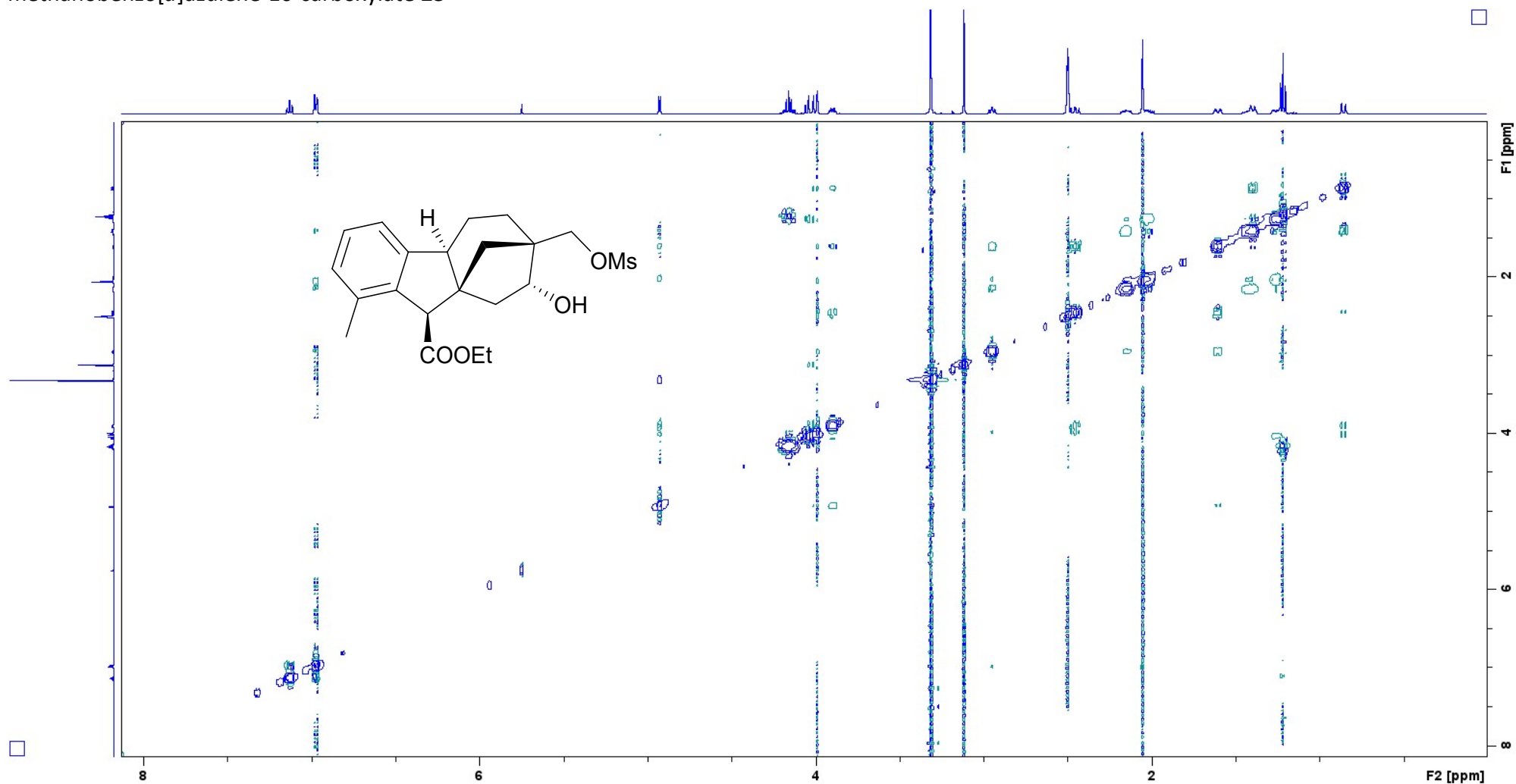
¹³C-NMR of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **23**



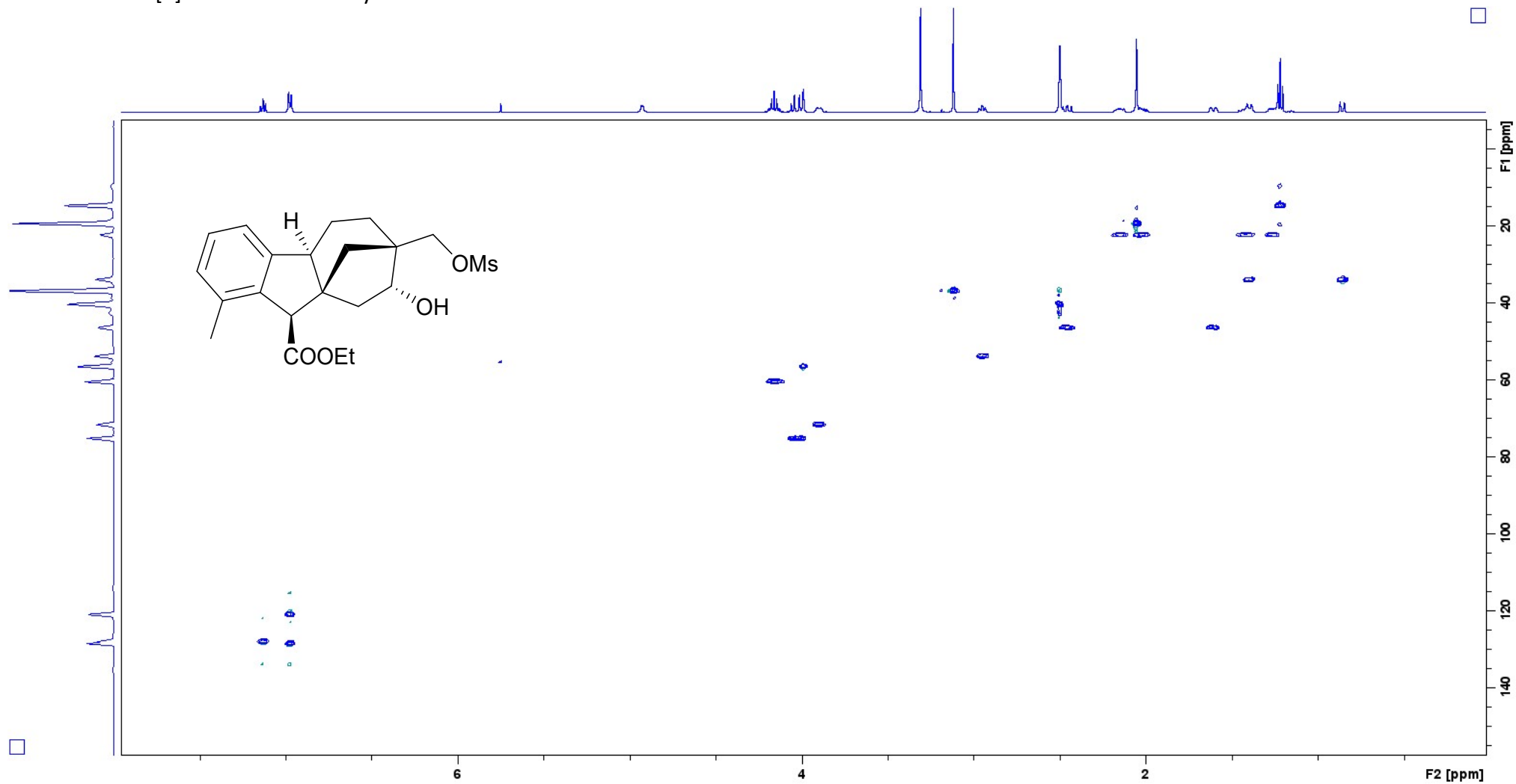
COSY of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **23**



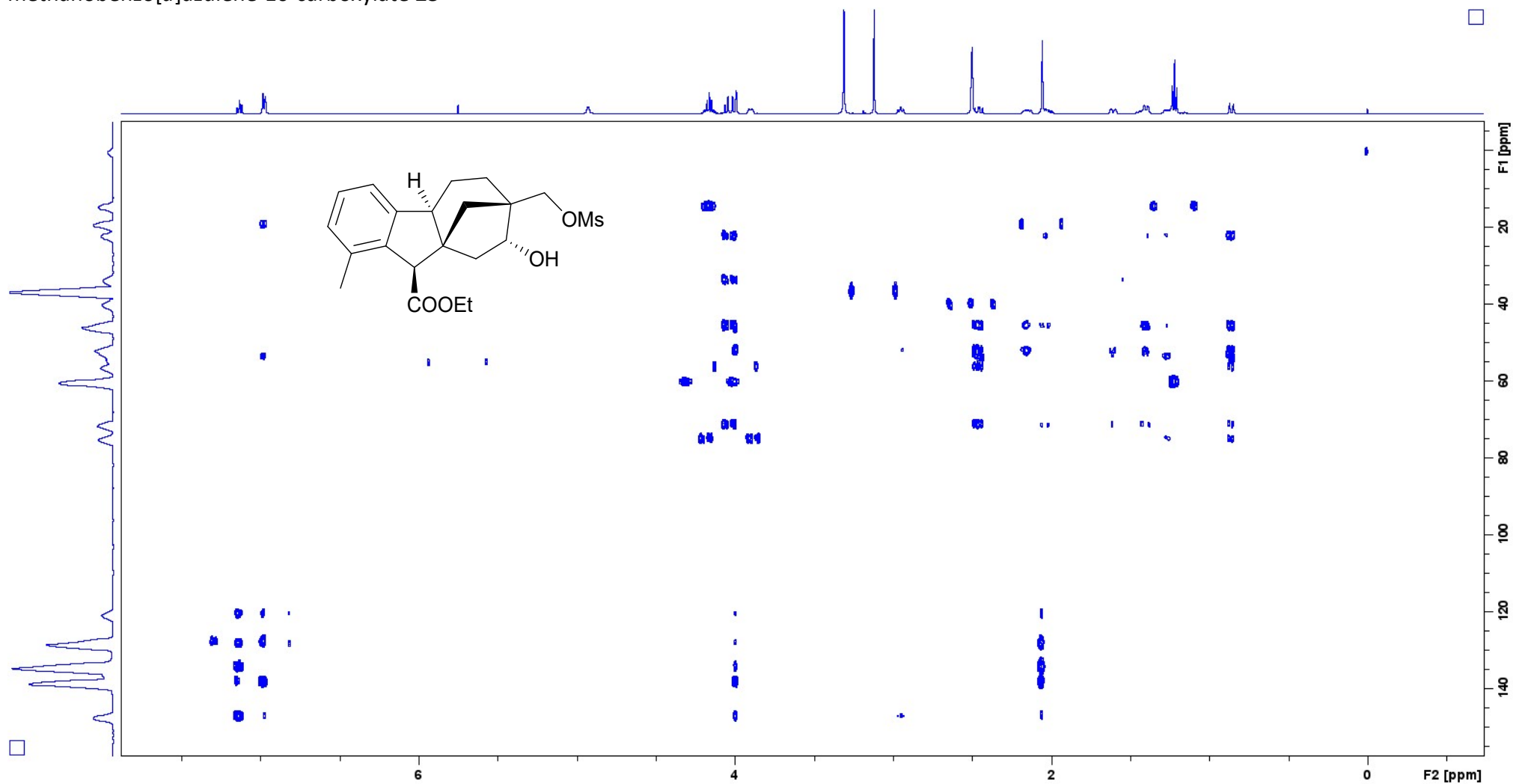
NOESY of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **23**



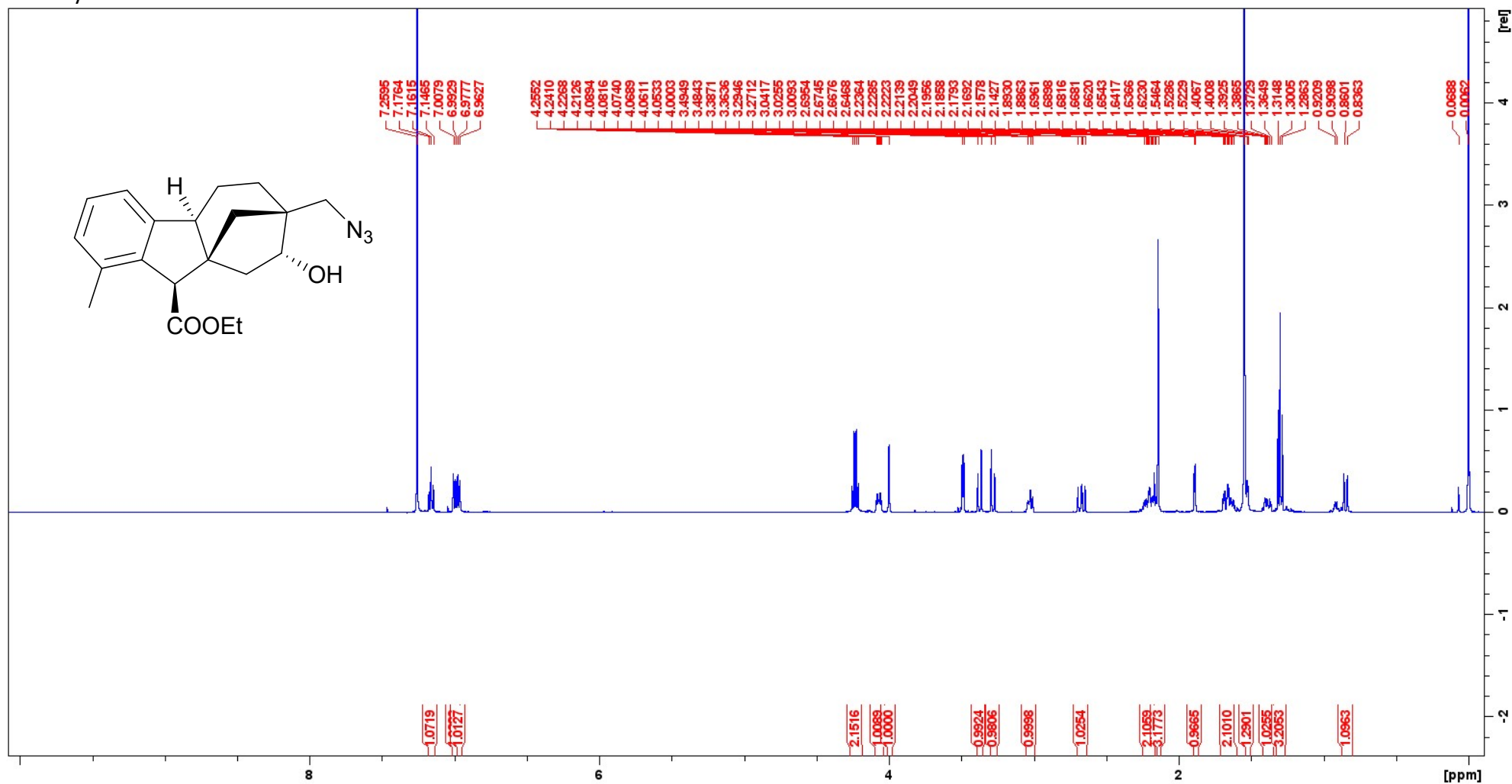
HSQC of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **23**



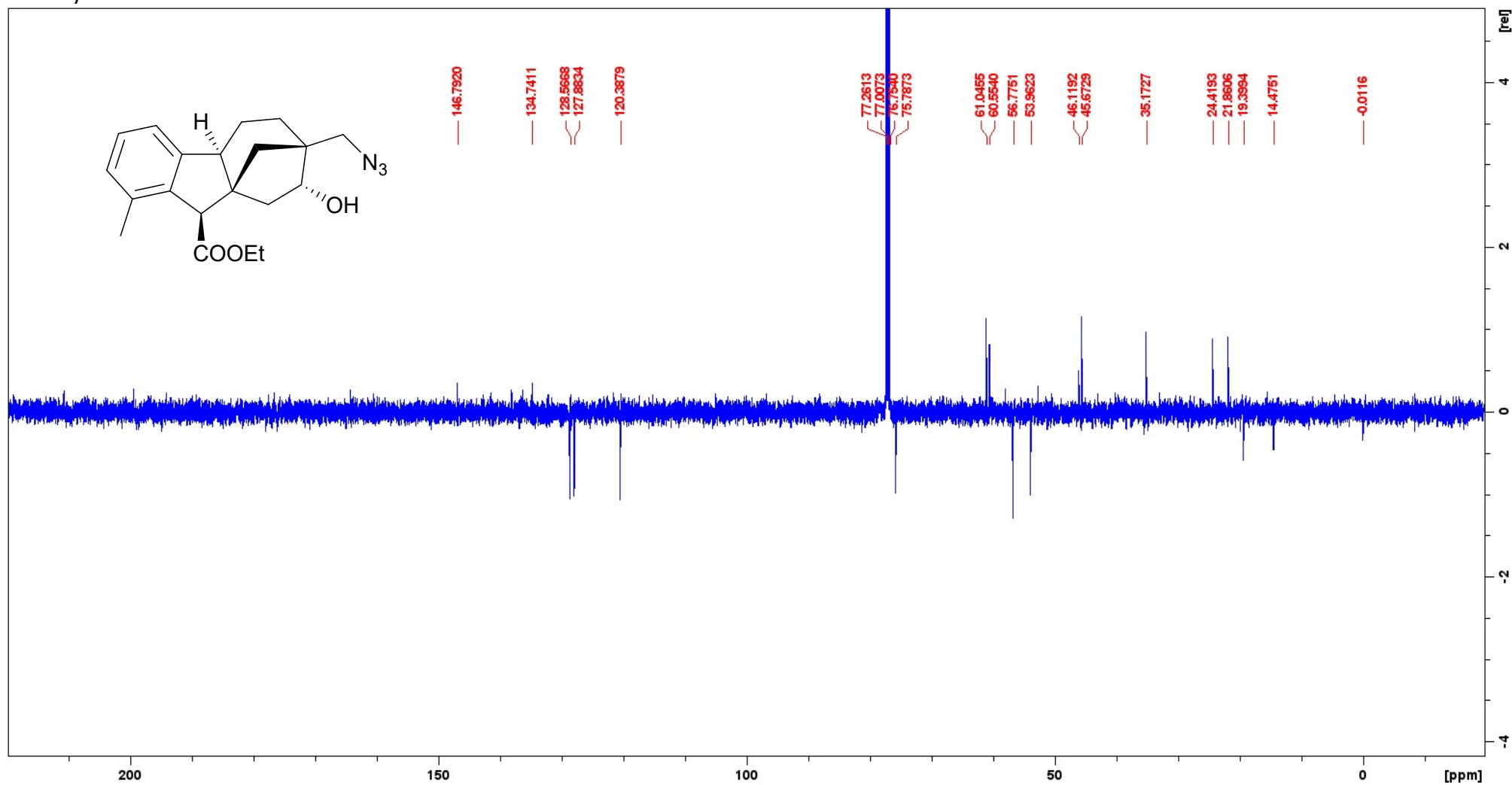
HMBC of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((methylsulfonyl)oxy)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **23**



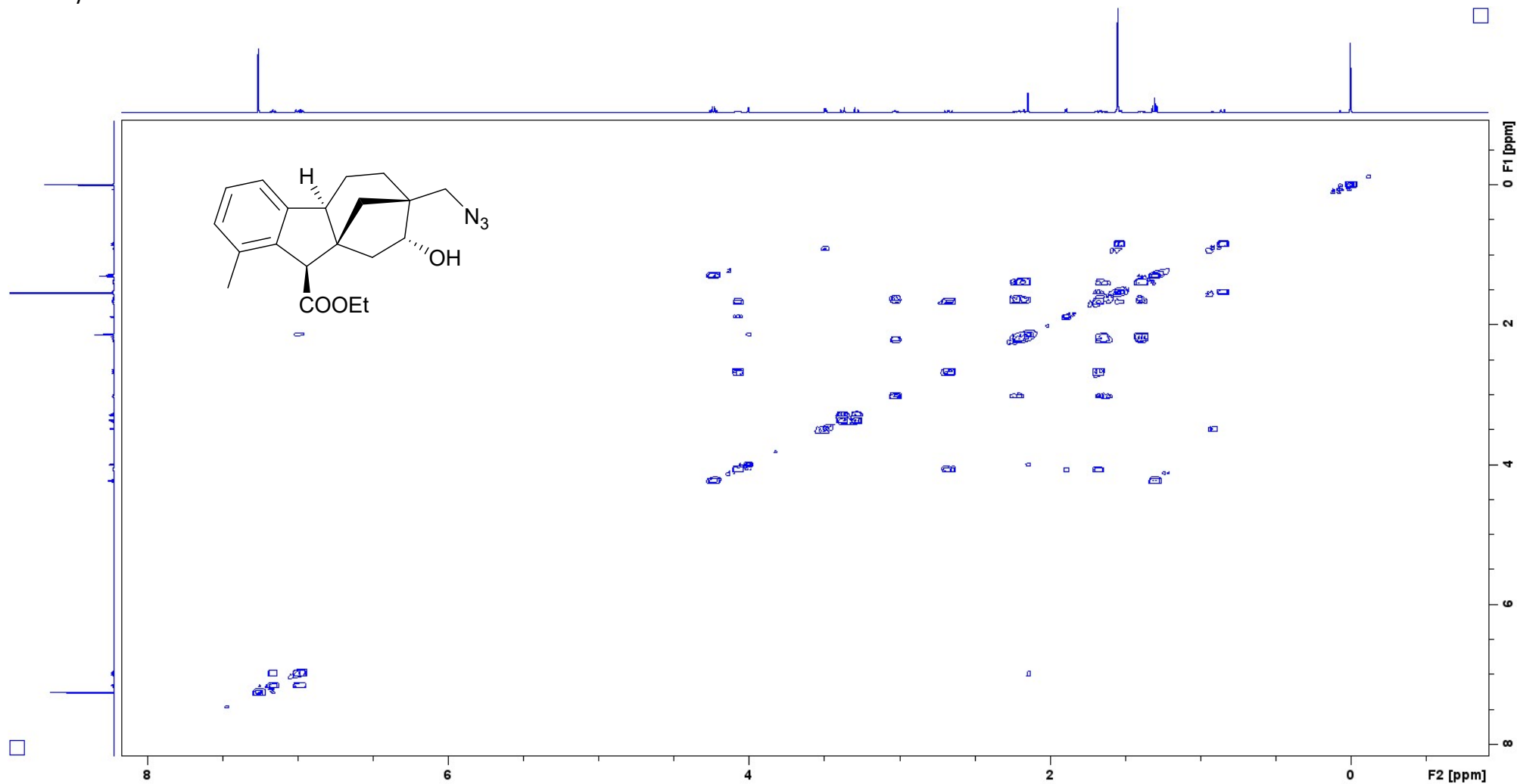
¹H-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



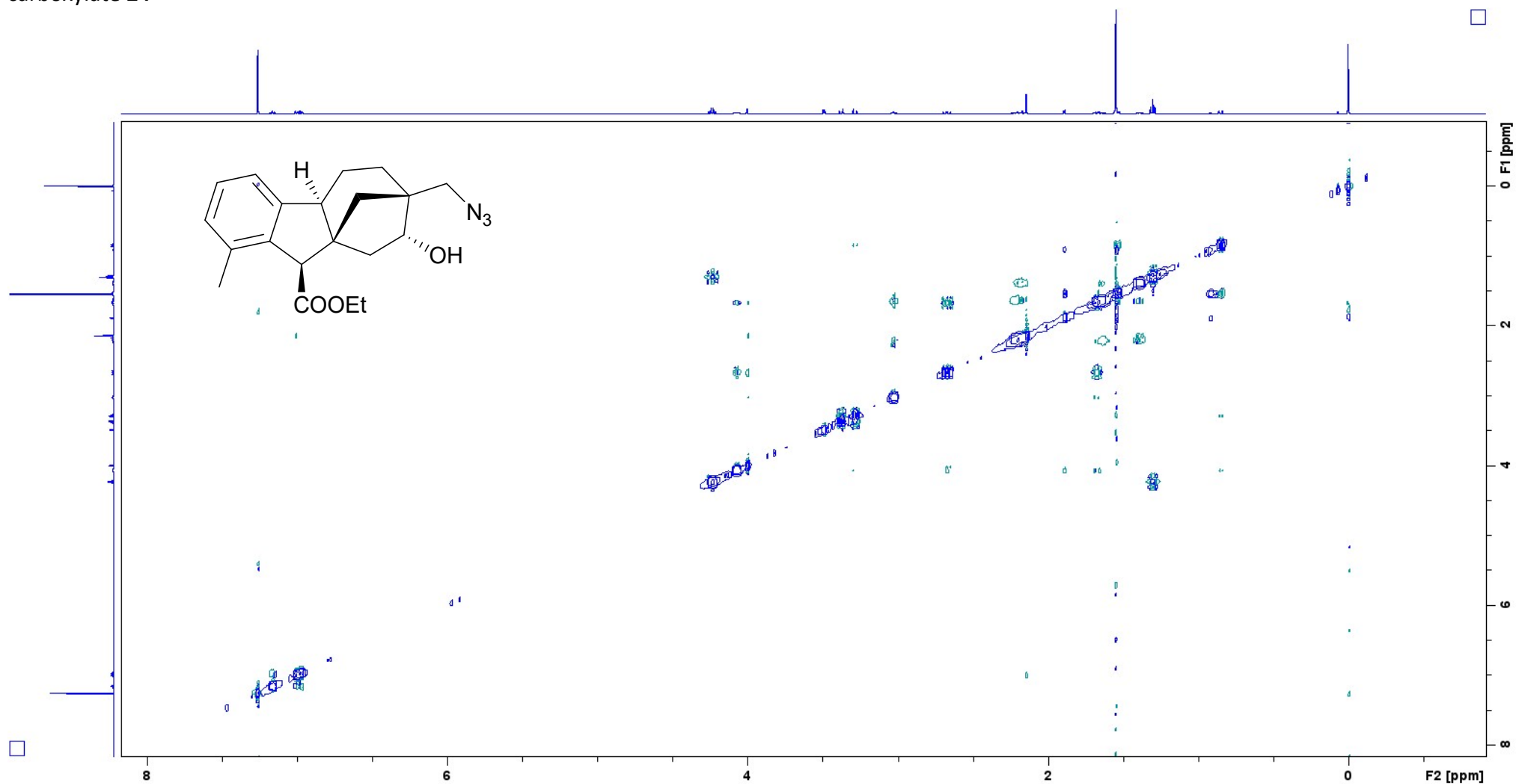
¹³C-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



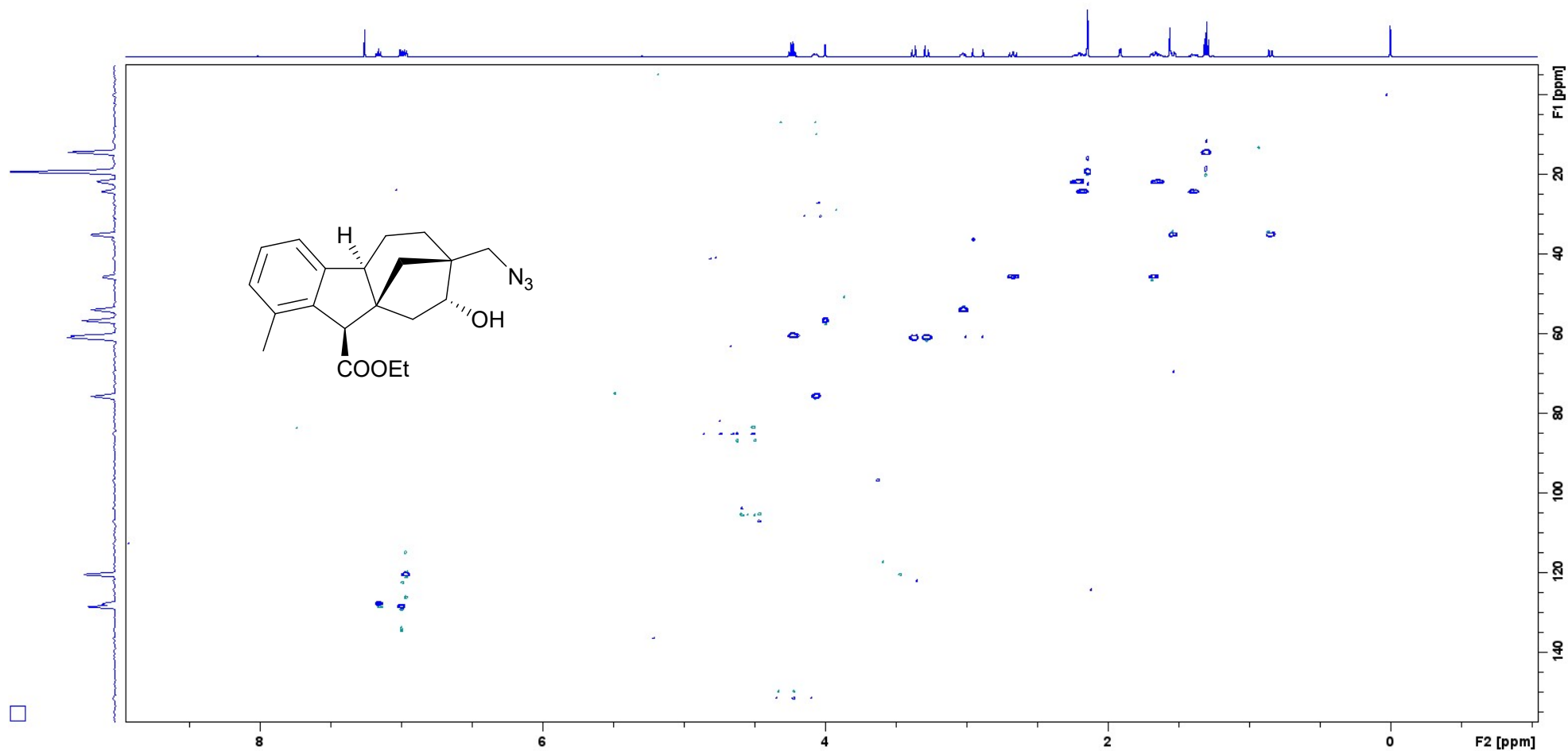
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



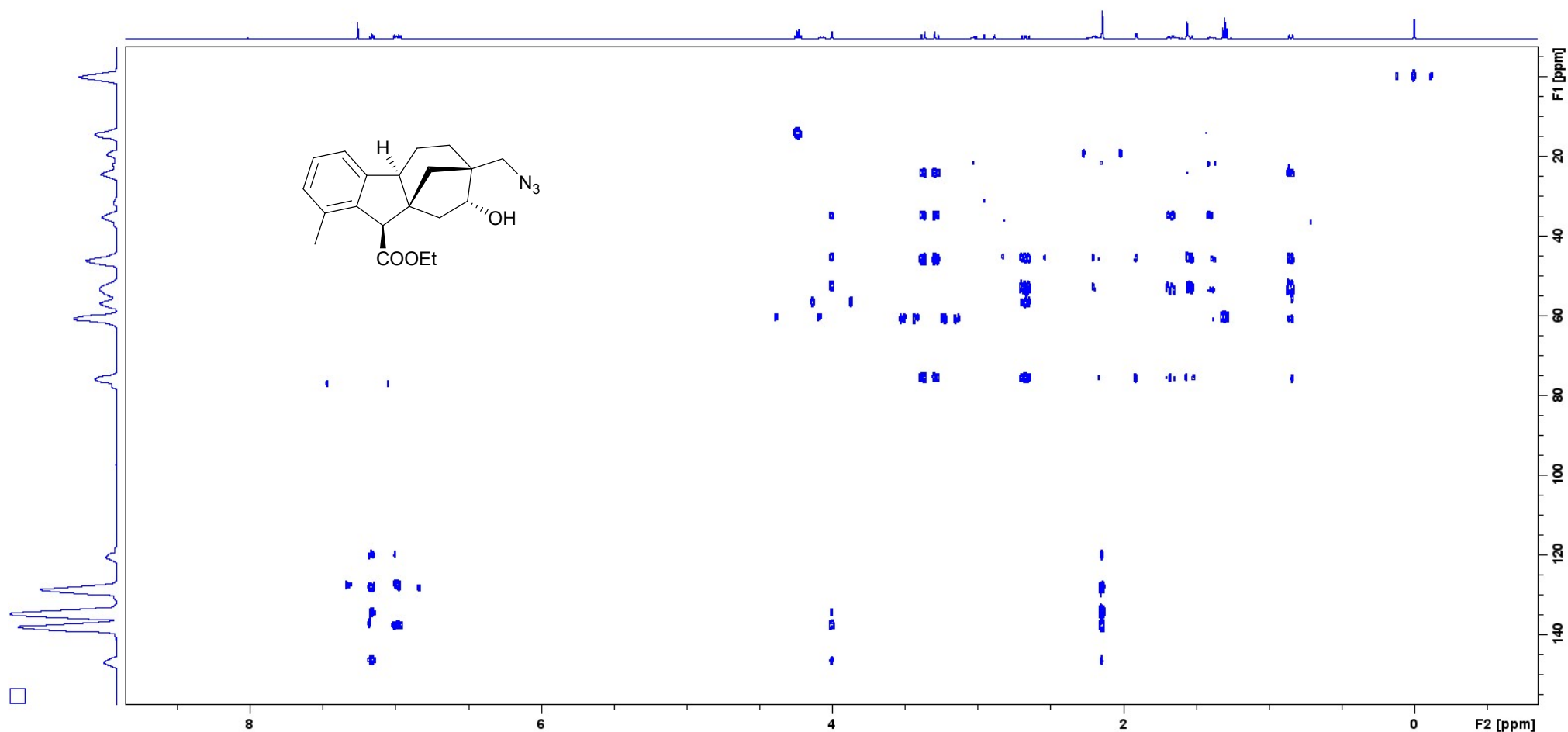
NOESY of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



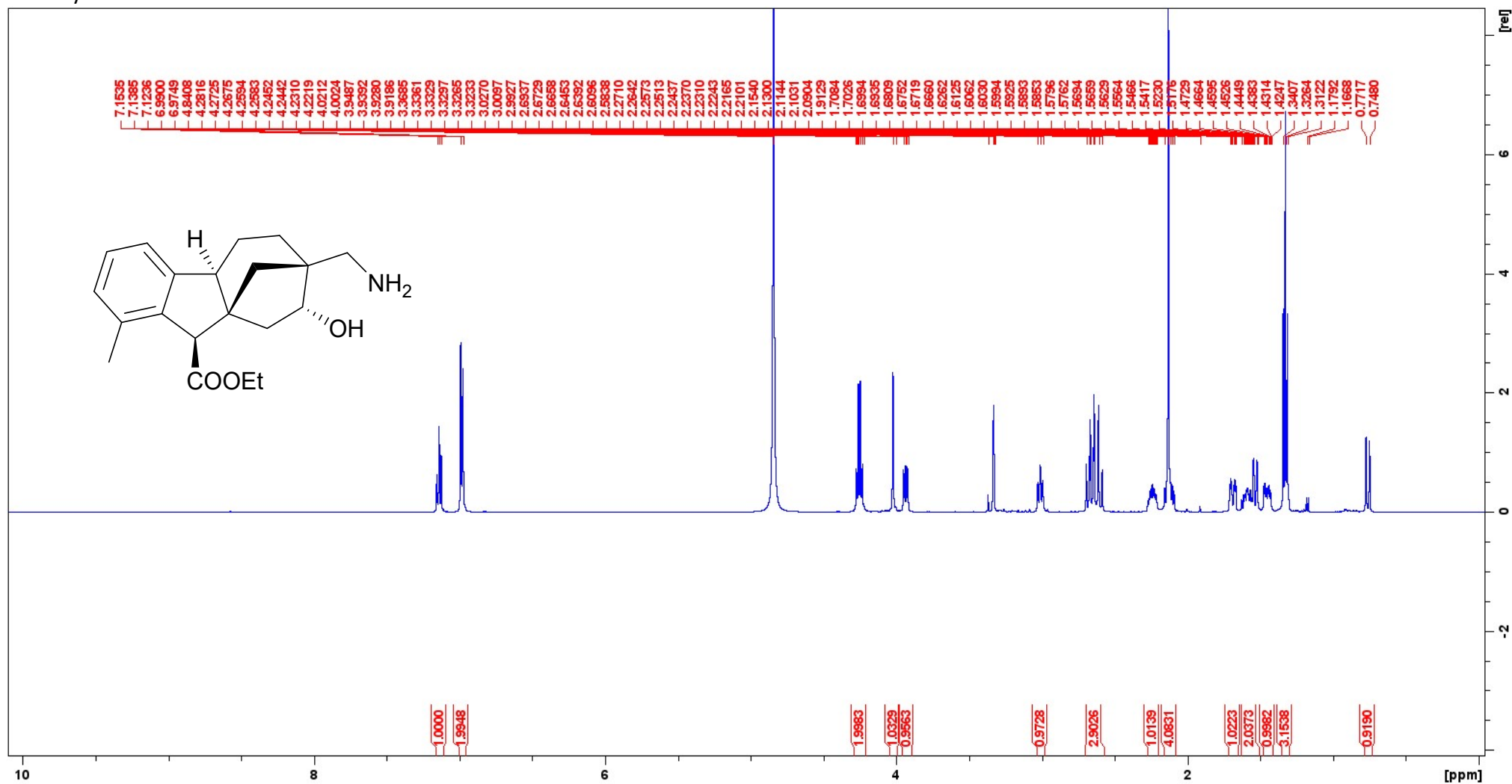
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



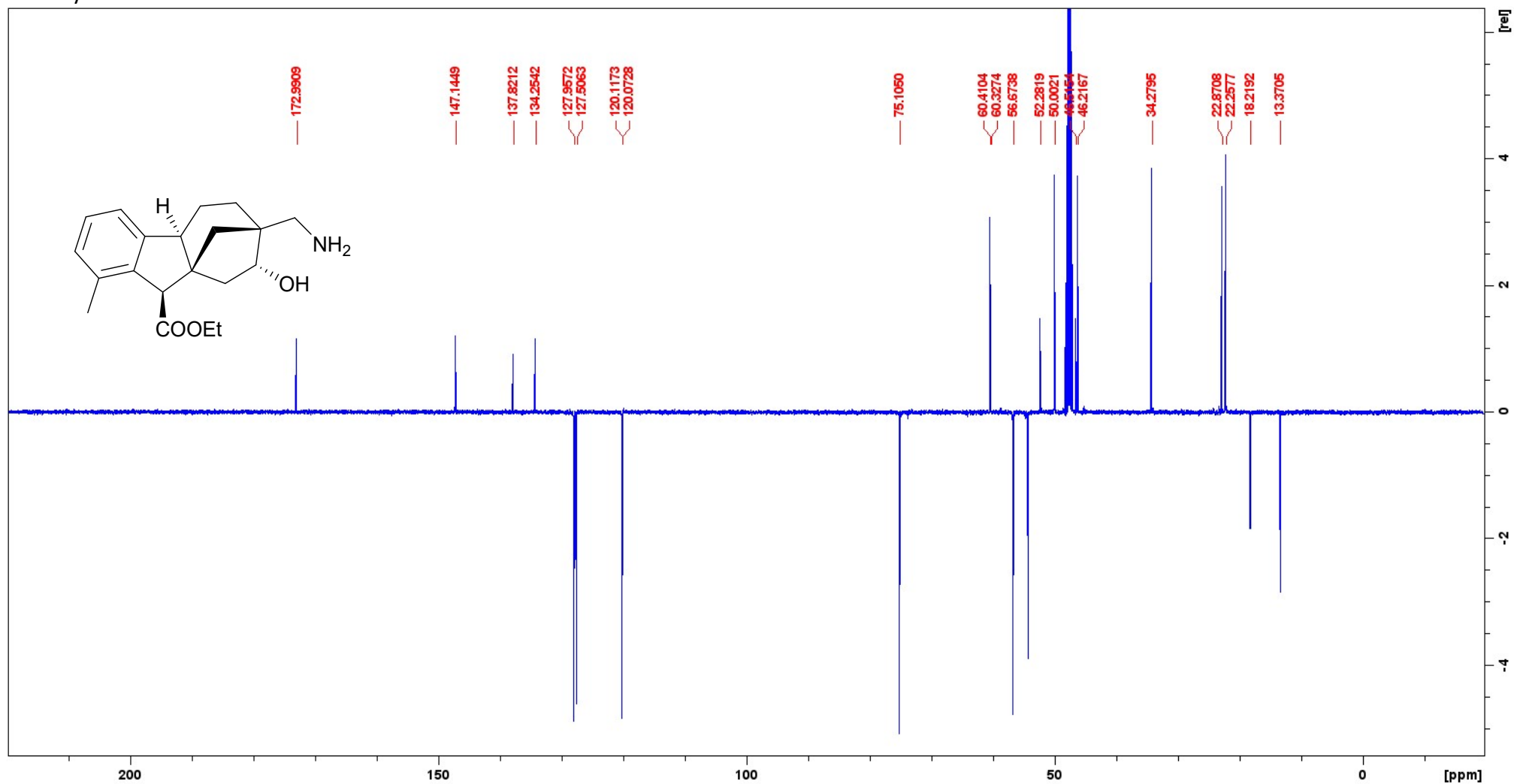
HMBC of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(azidomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **24**



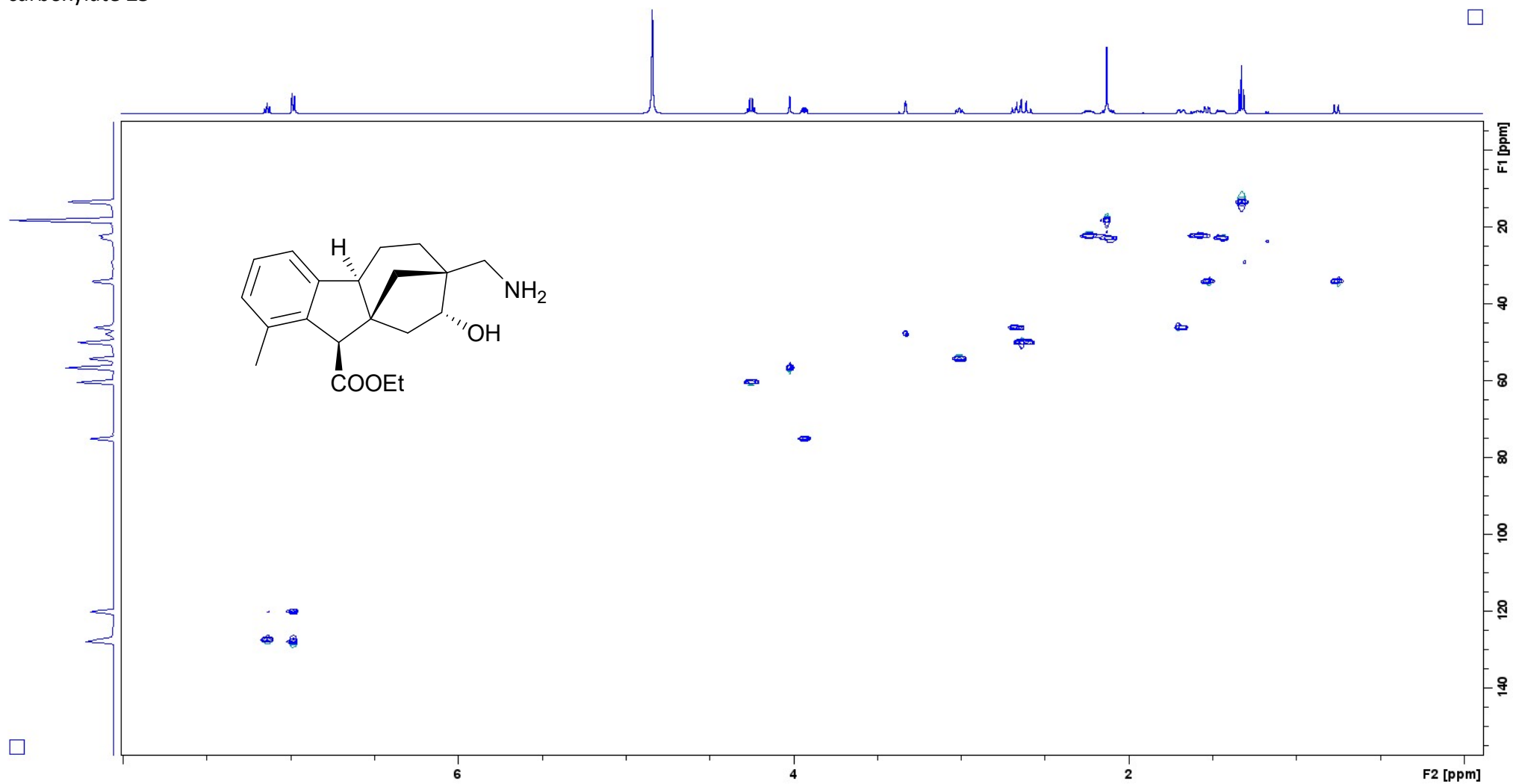
¹H-NMR of ethyl (4b*S*,7*S*,8*R*,9*aS*,10*R*)-7-(aminomethyl)-8-hydroxy-1-methyl-4b,6,7,8,9,10-hexahydro-5H-7,9a-methanobenzo[*a*]azulene-10-carboxylate **25**



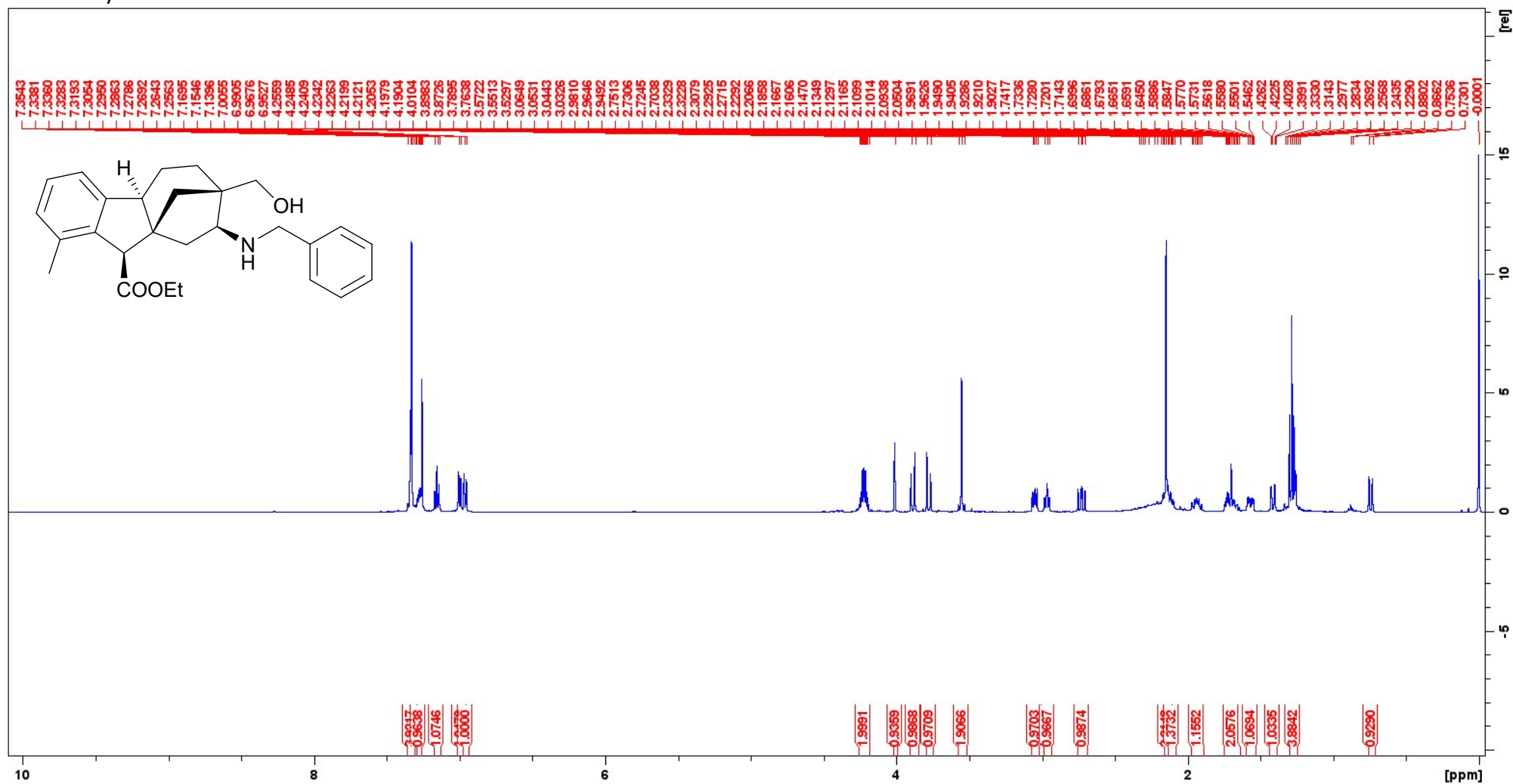
¹³C-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(aminomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **25**



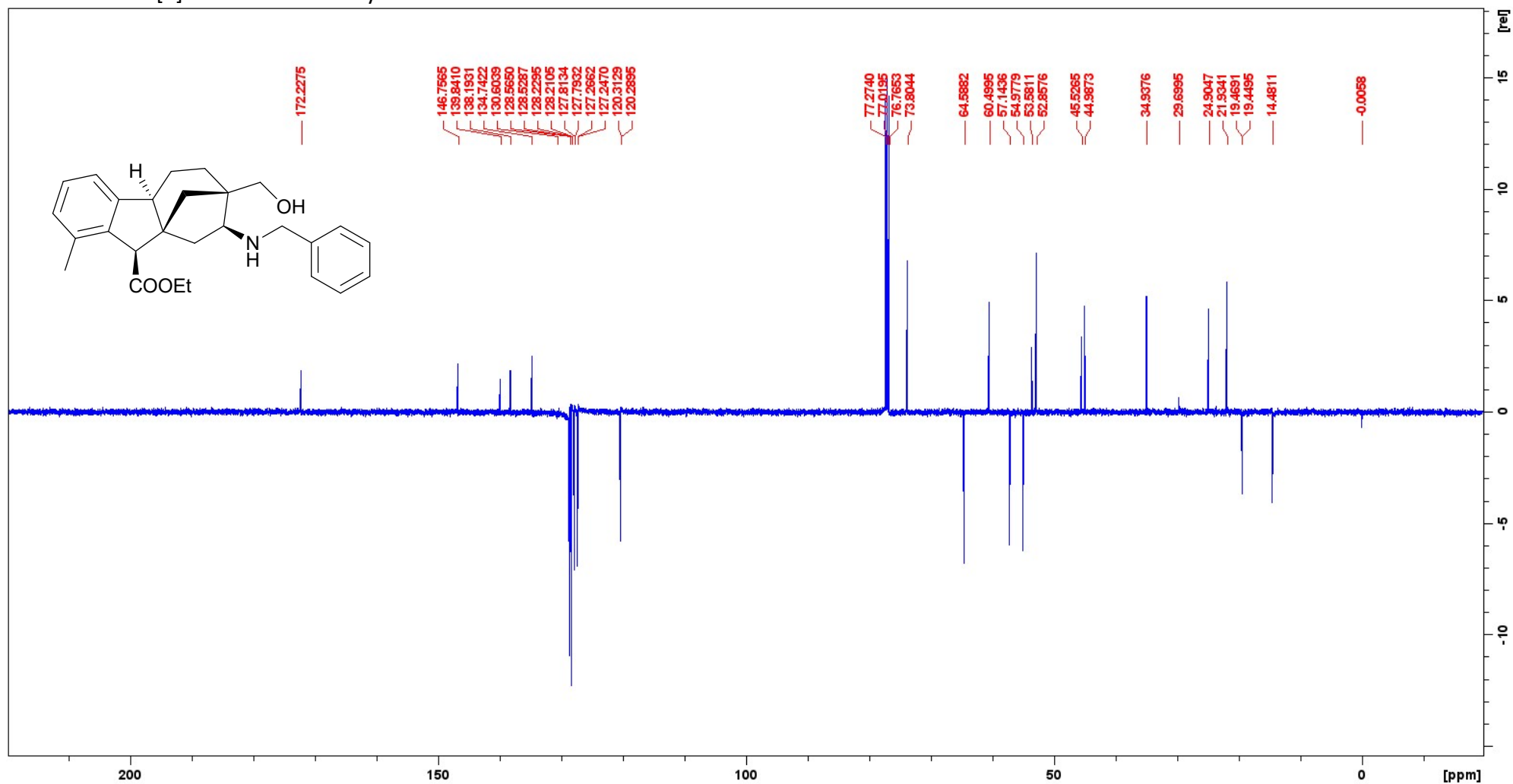
HSQC of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(aminomethyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **25**



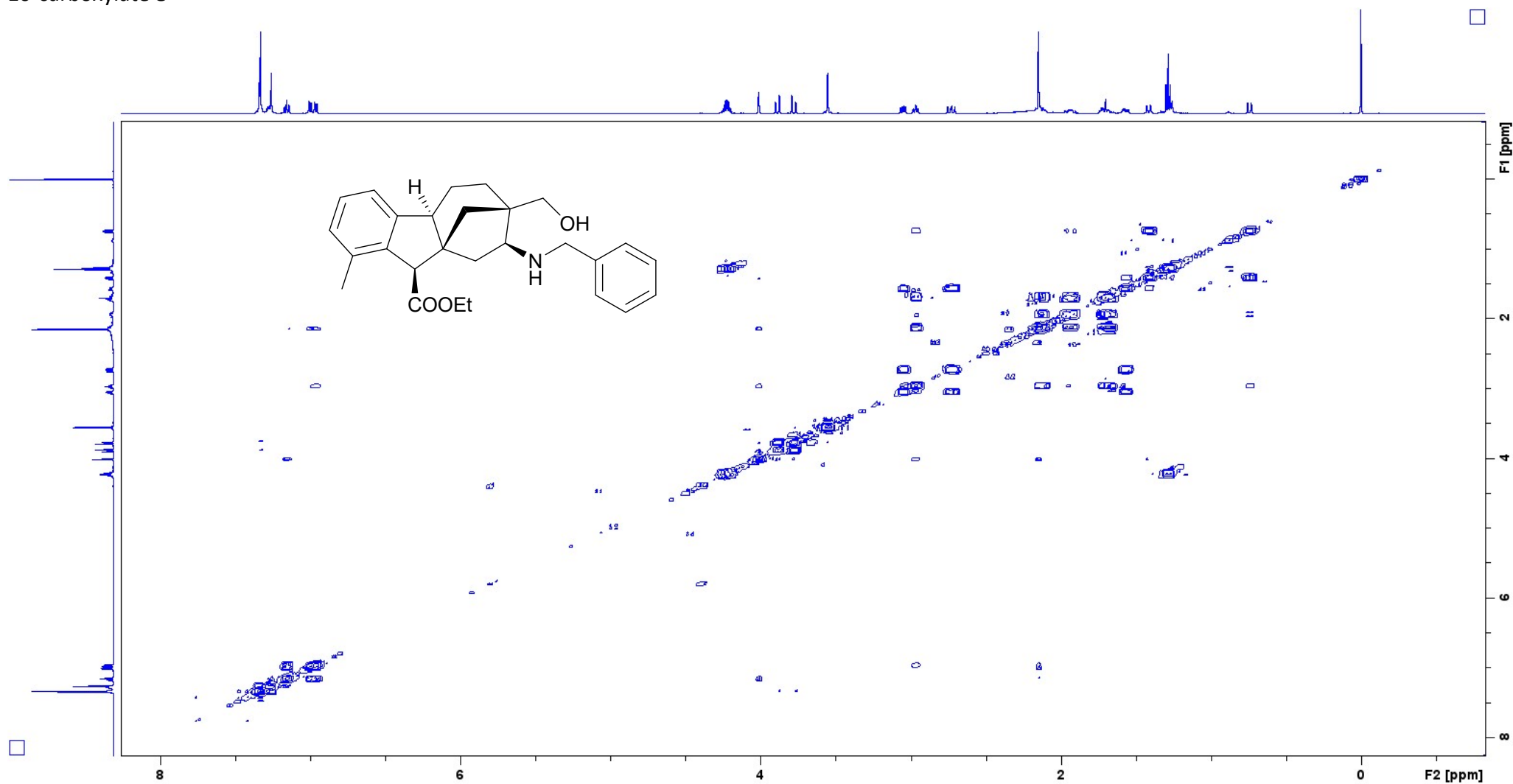
¹H-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



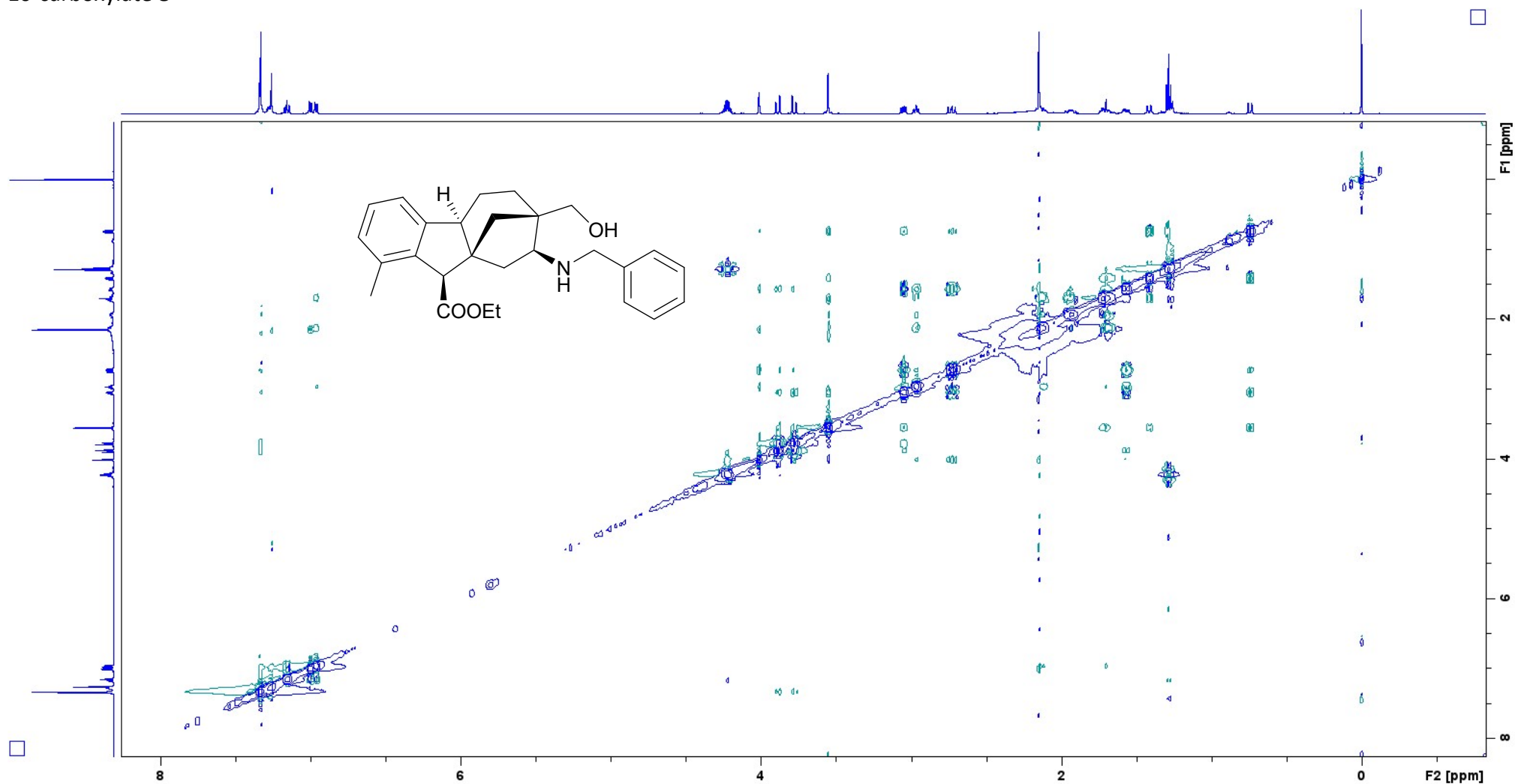
¹³C-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



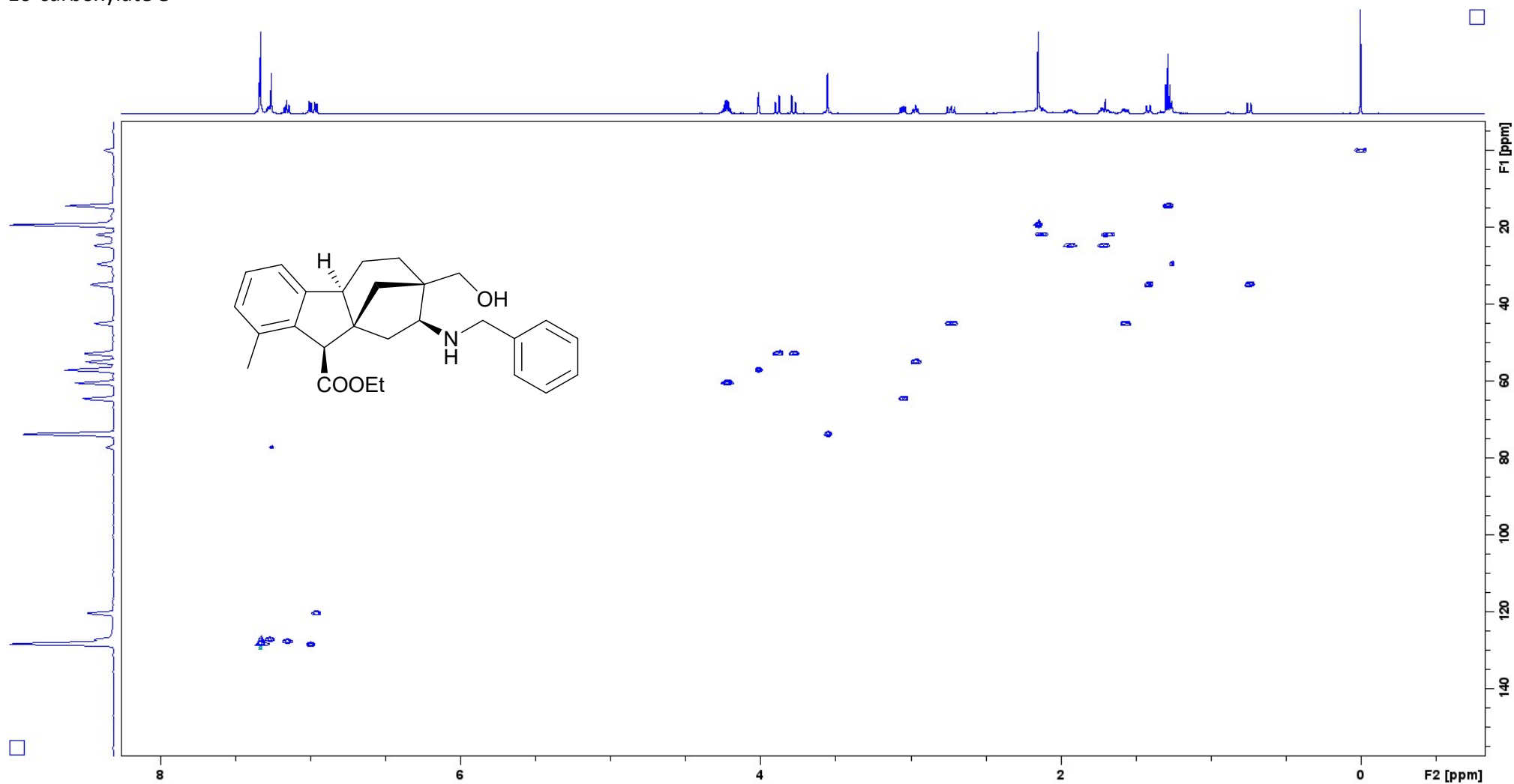
COSY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



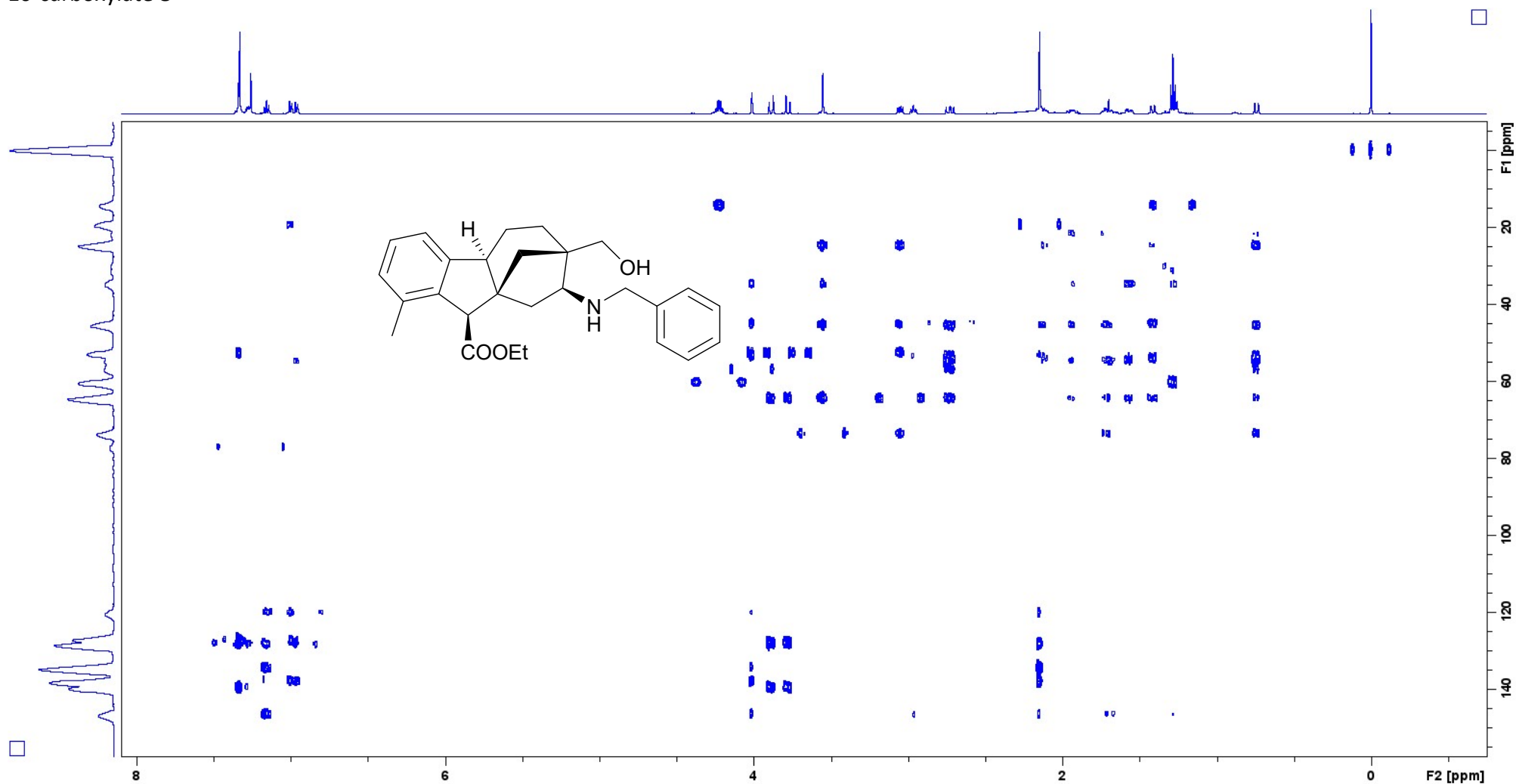
NOESY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



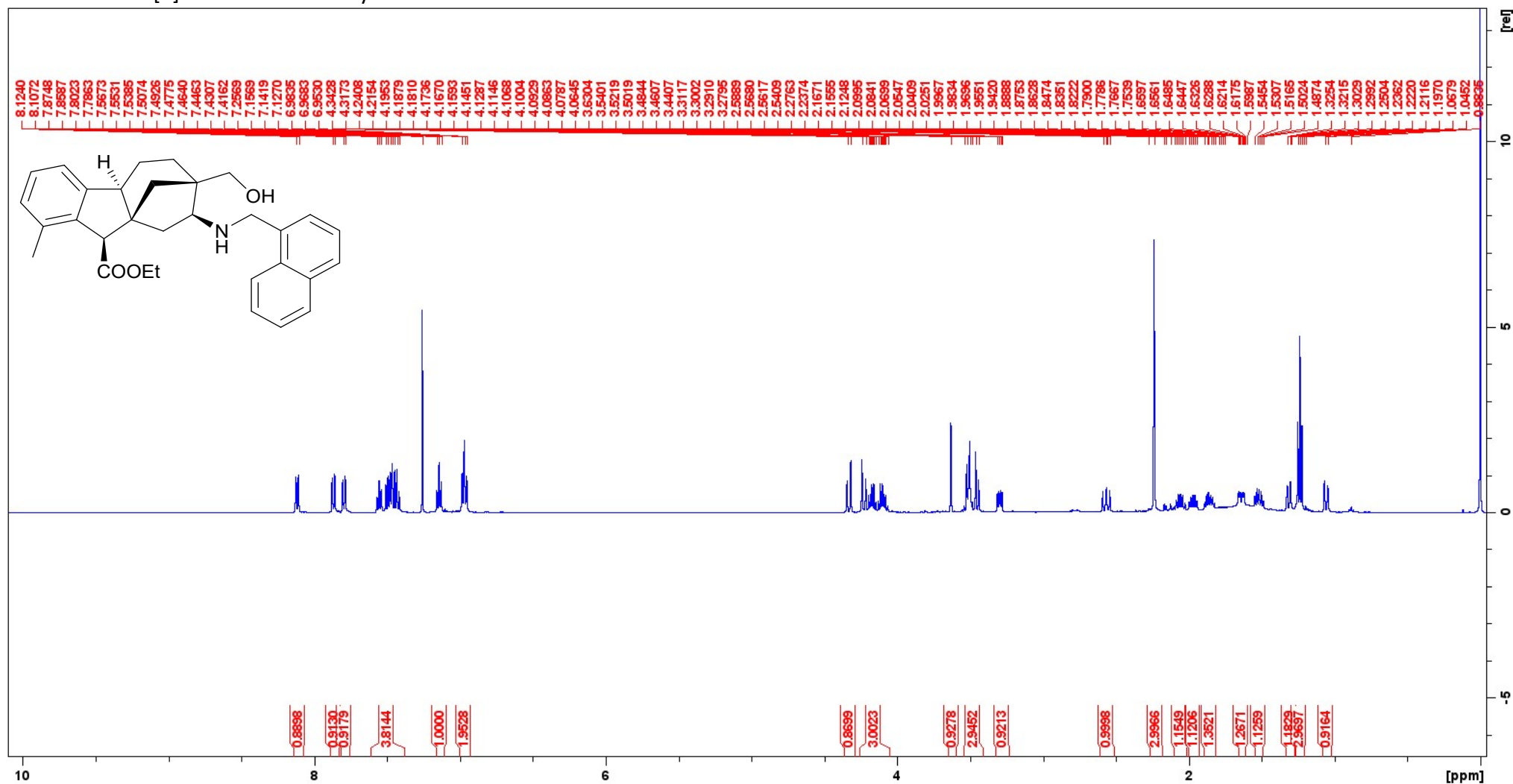
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



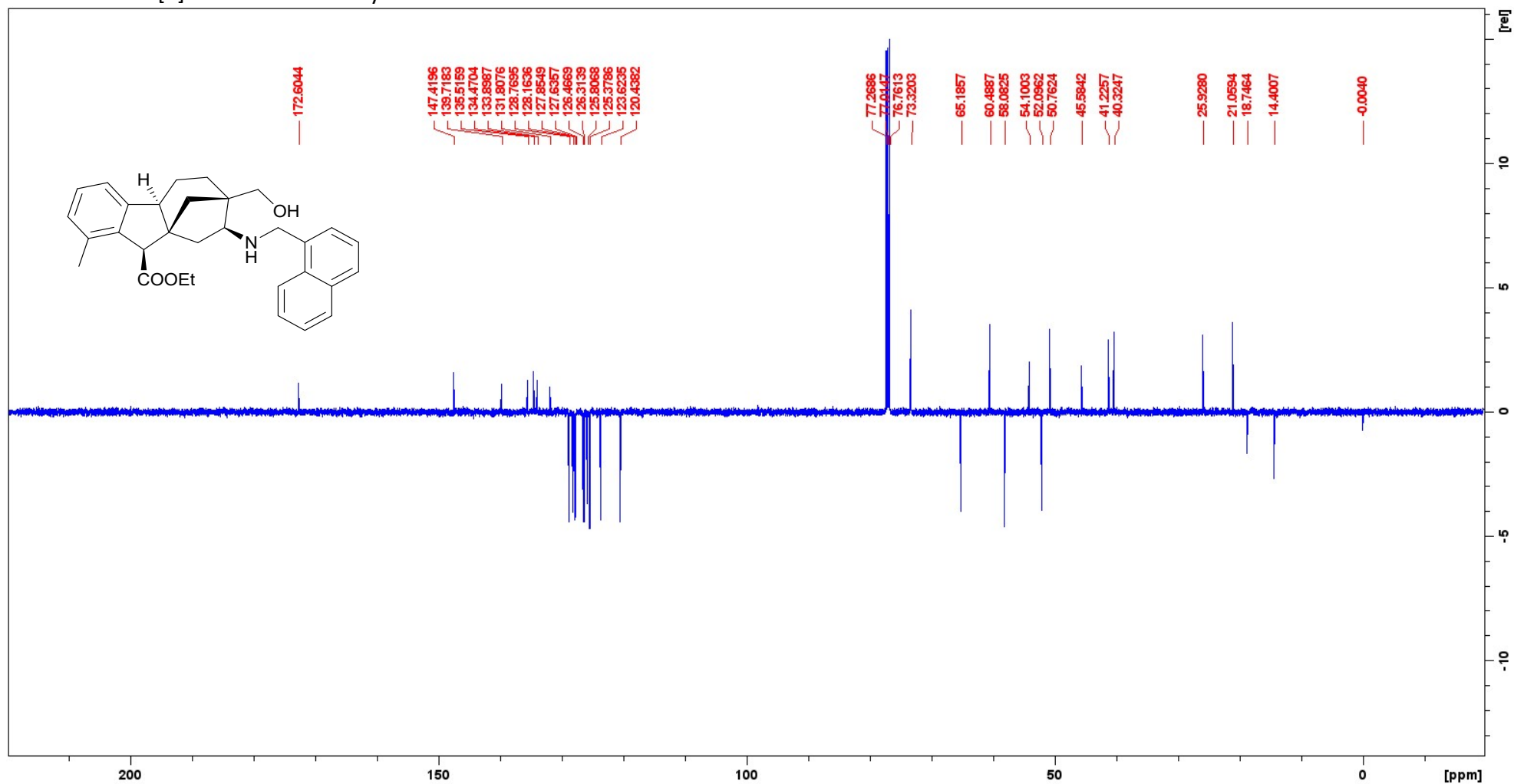
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-8-(benzylamino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **8**



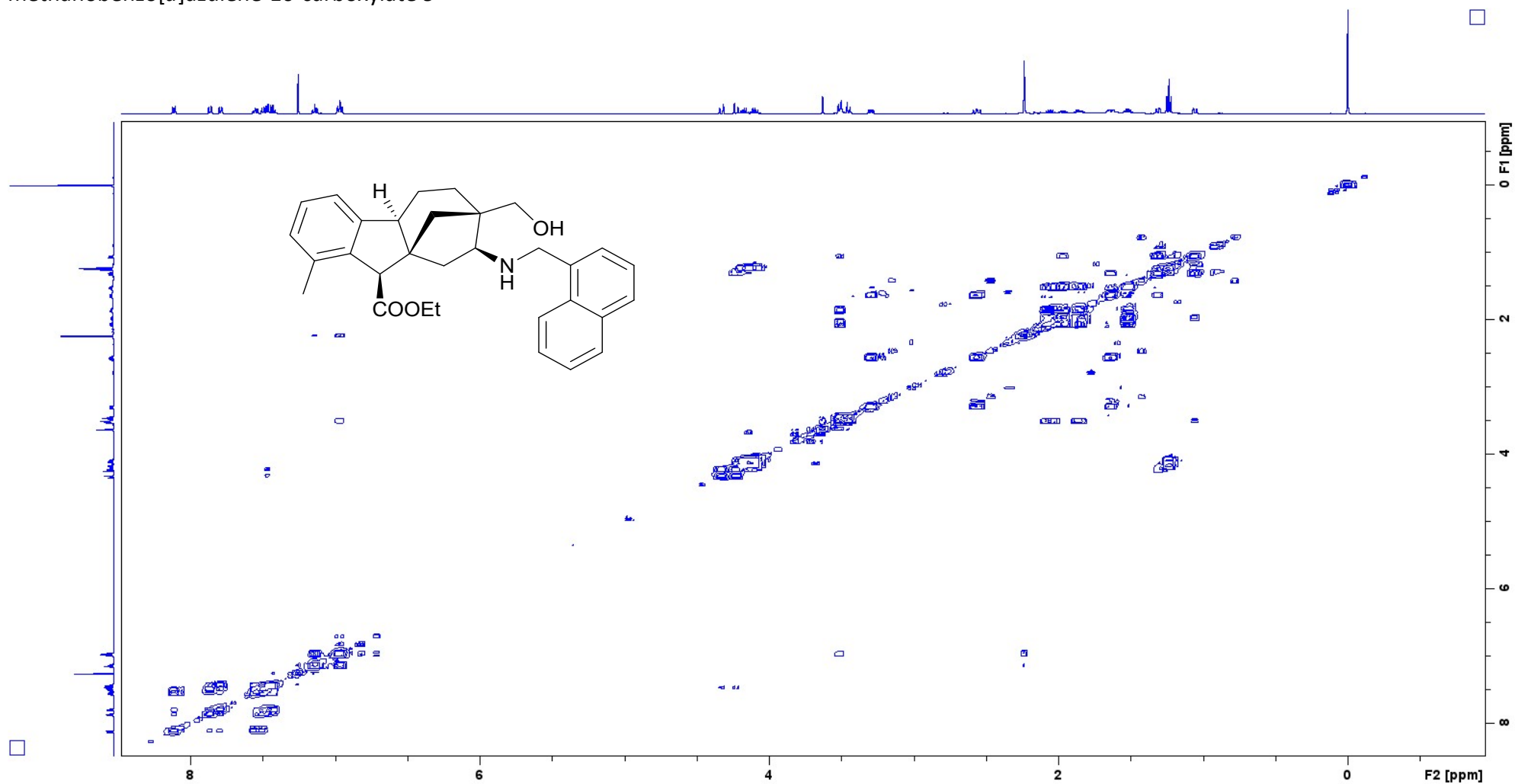
¹H-NMR of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



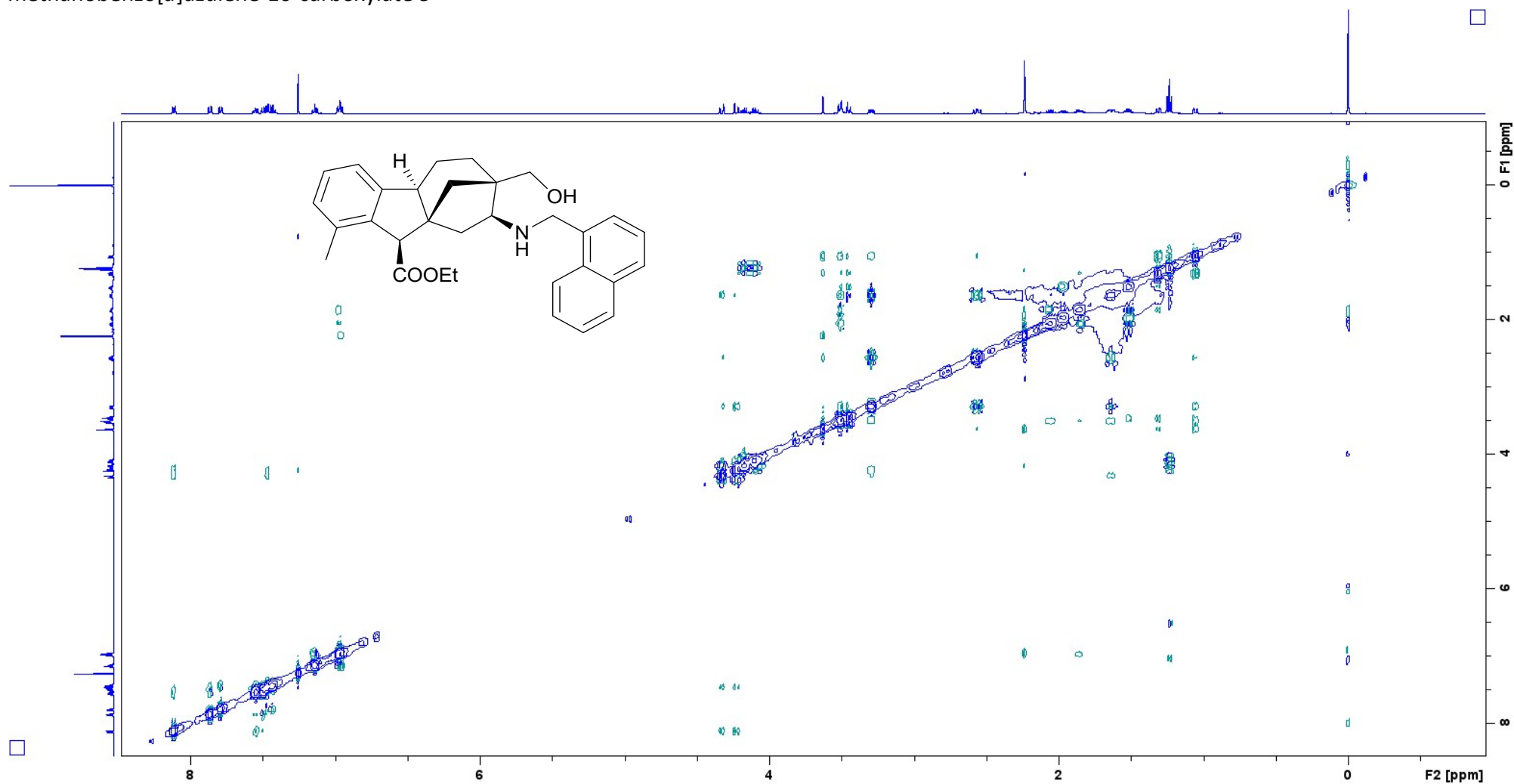
¹³C-NMR of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



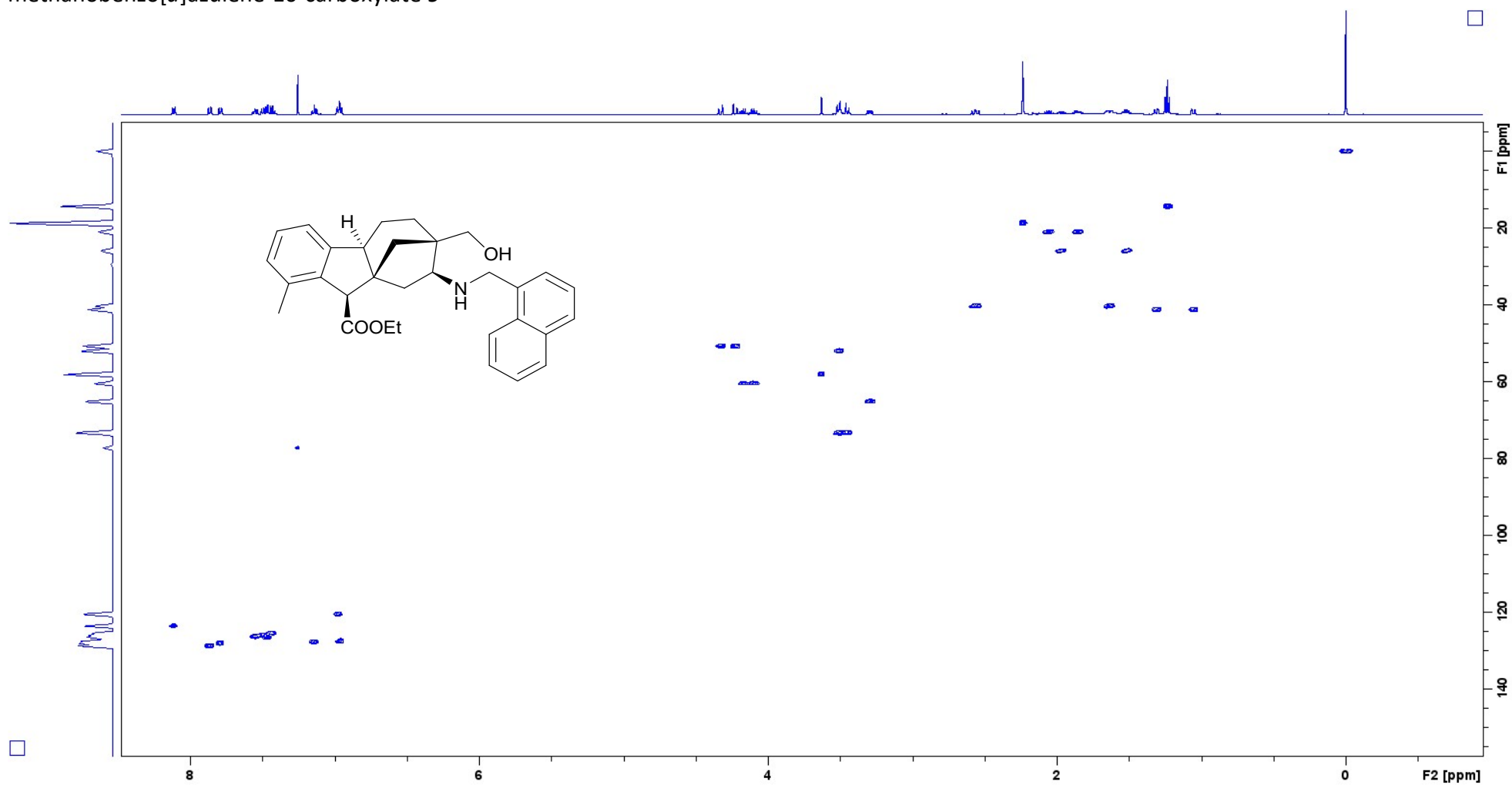
COSY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



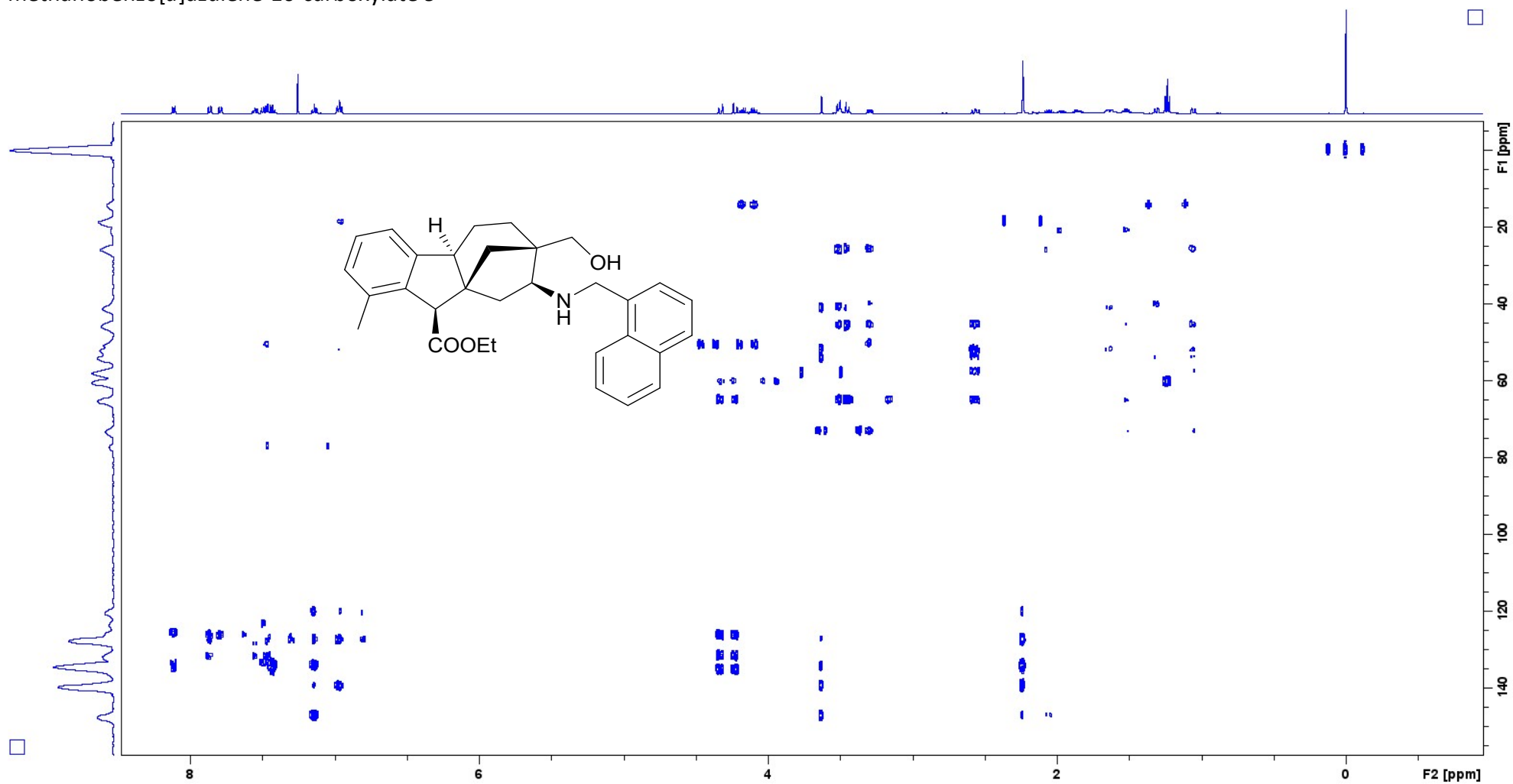
NOESY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



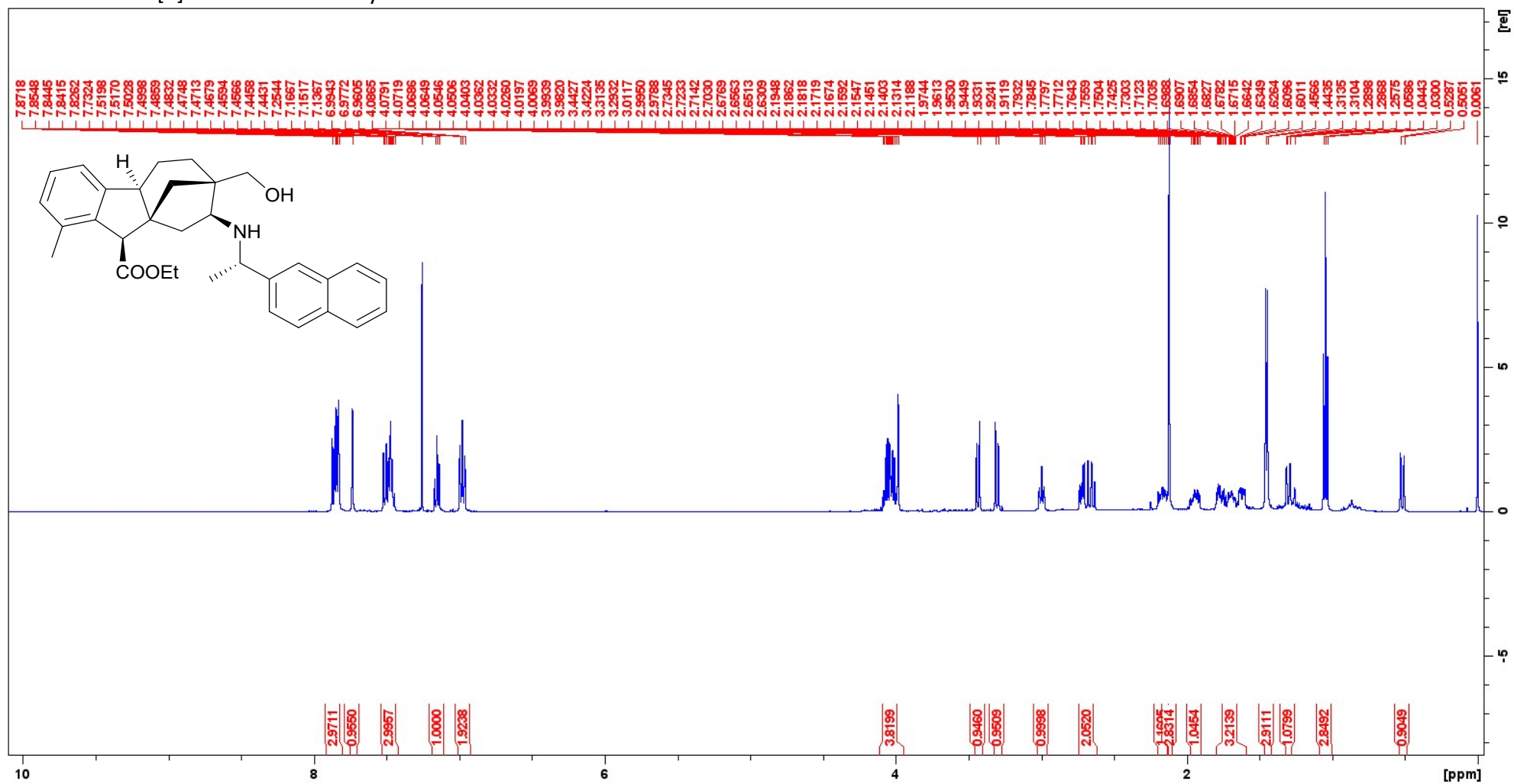
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



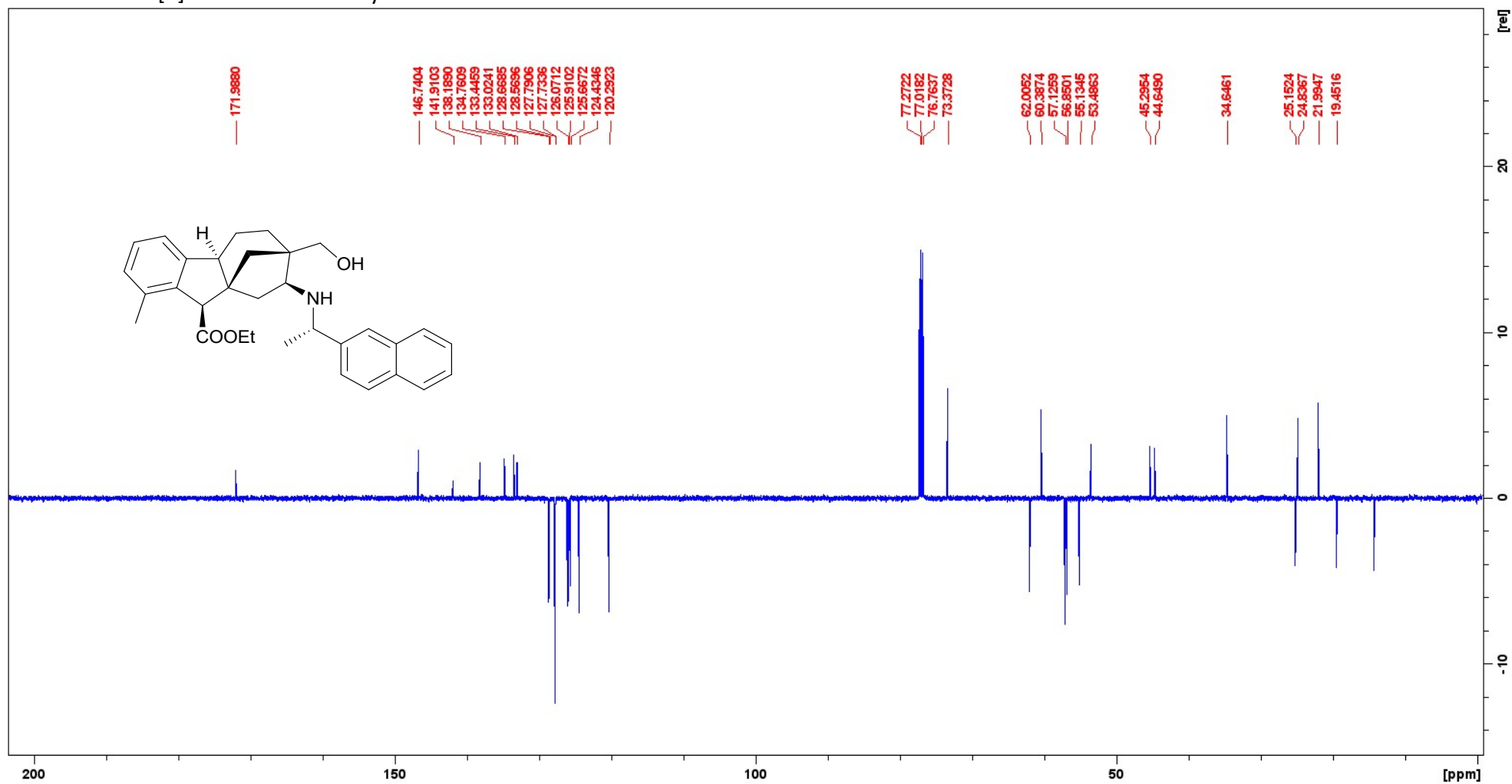
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((naphthalen-1-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **9**



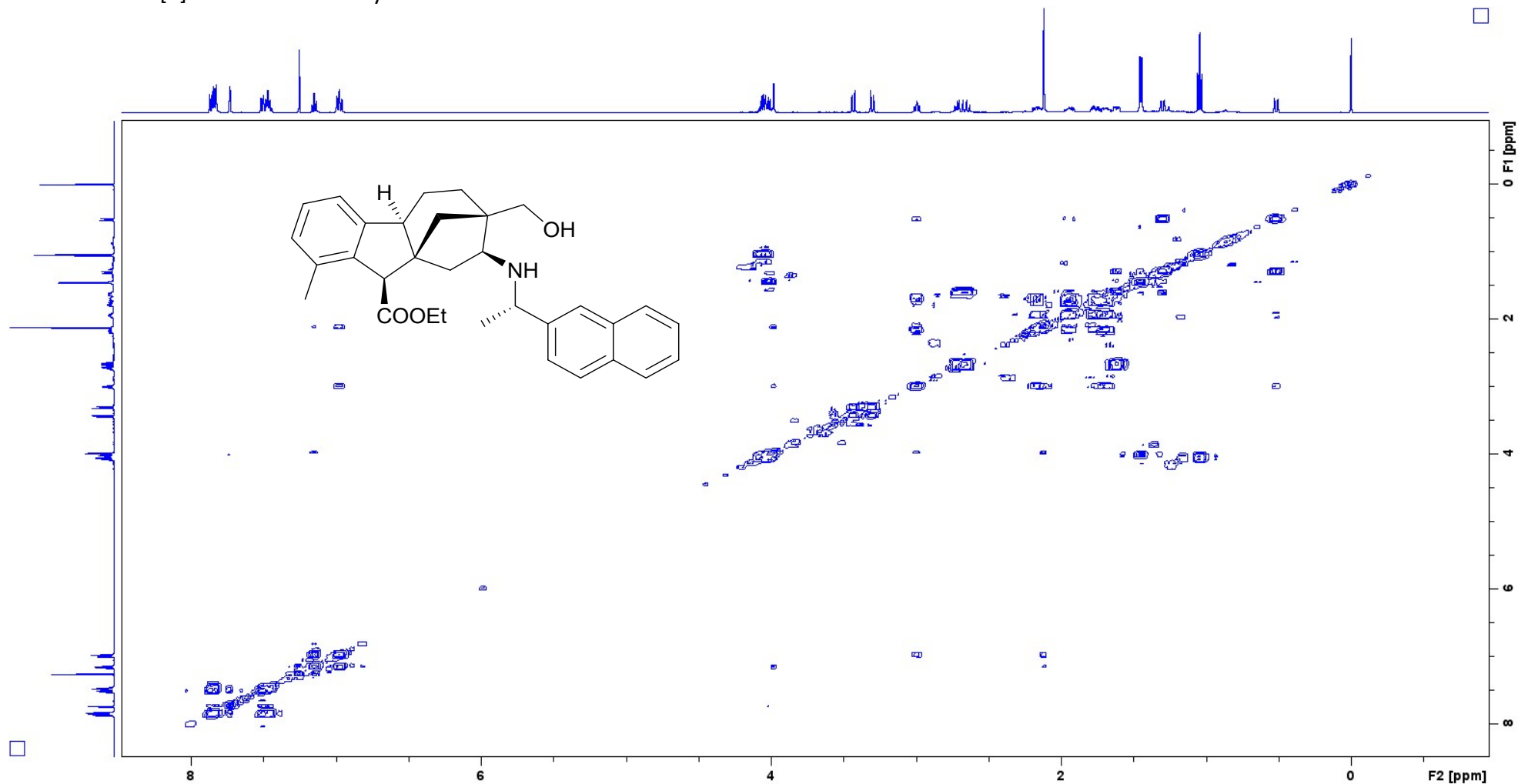
$^1\text{H-NMR}$ of ethyl (4*S*,7*R*,8*S*,9*a*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **10**



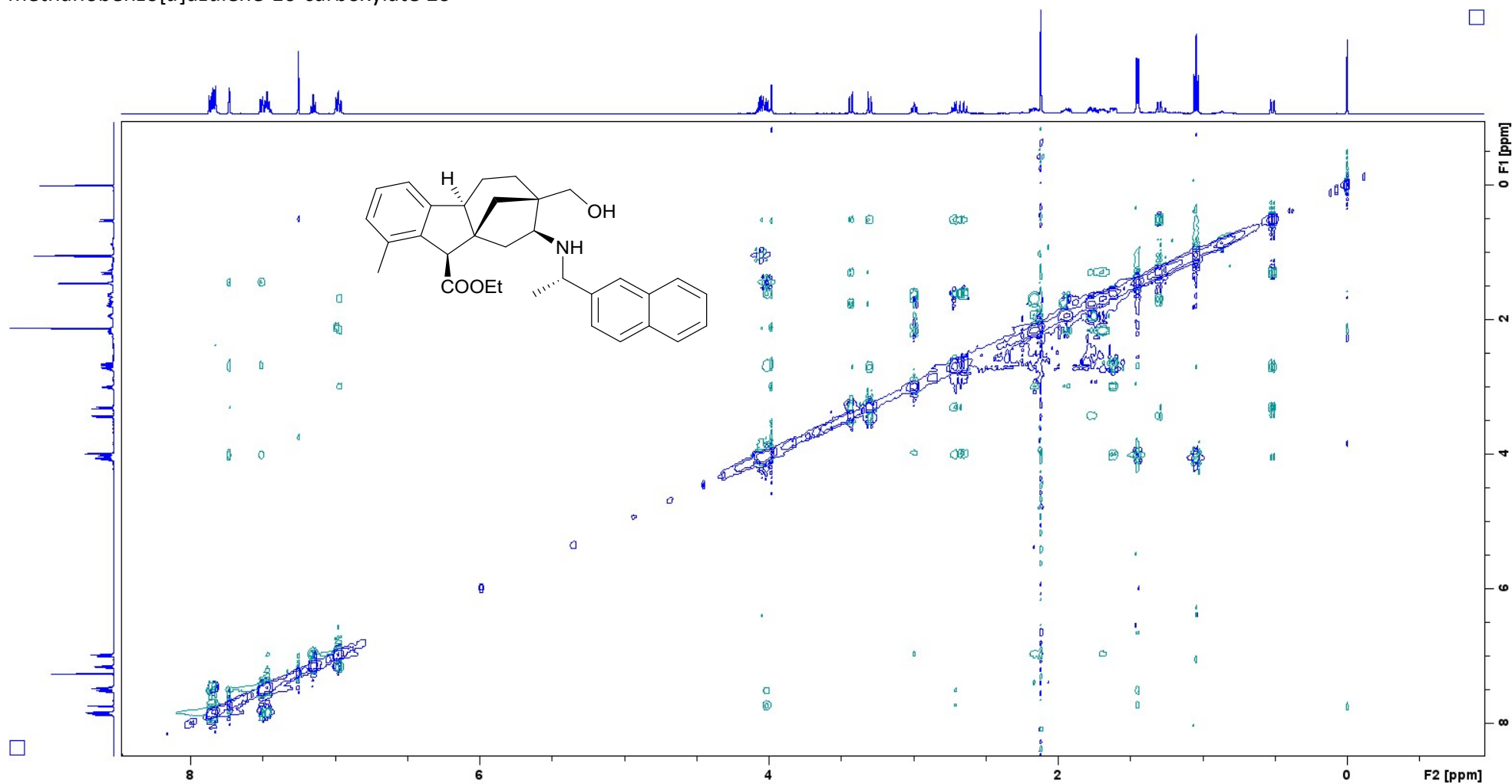
¹³C-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **10**



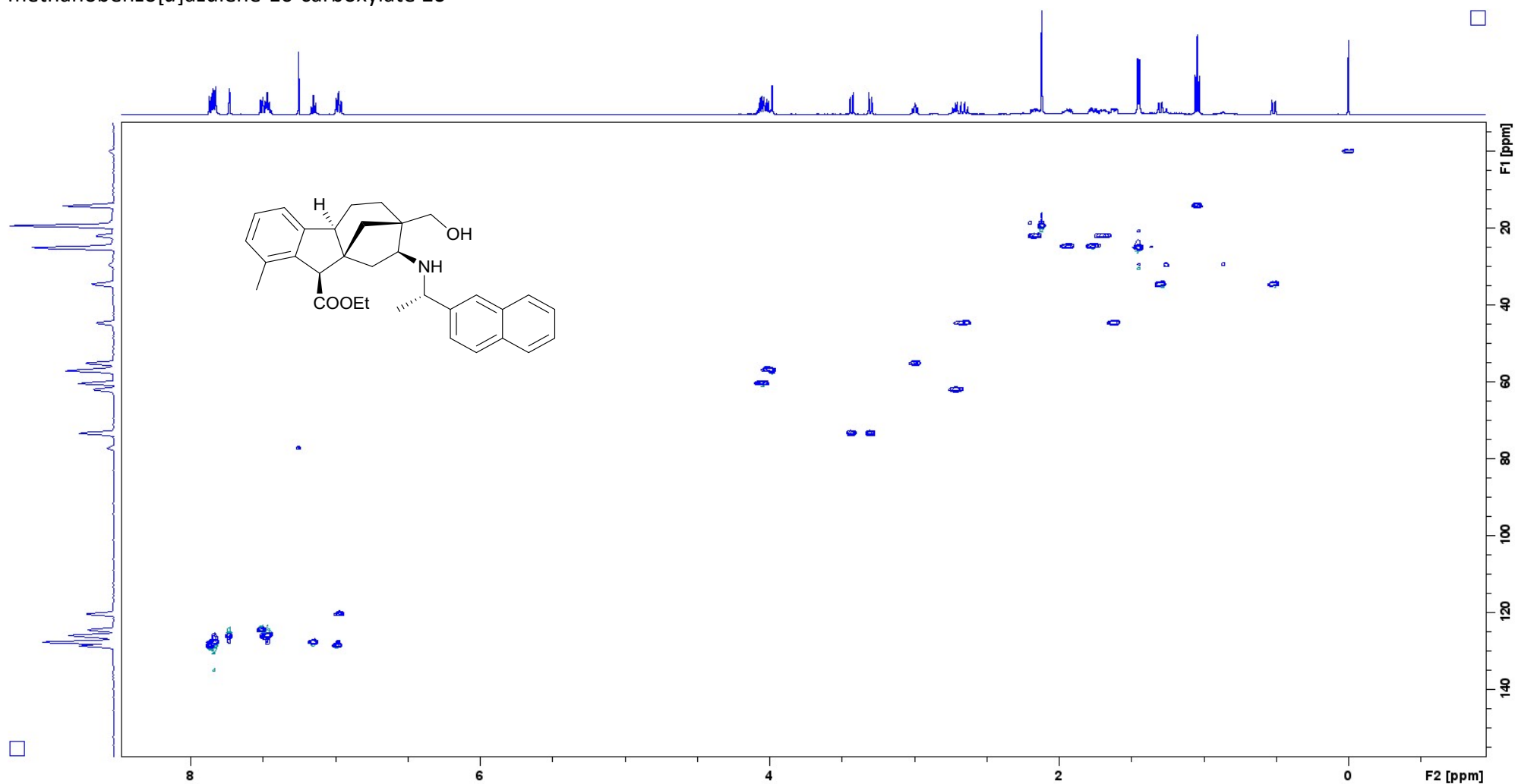
COSY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **10**



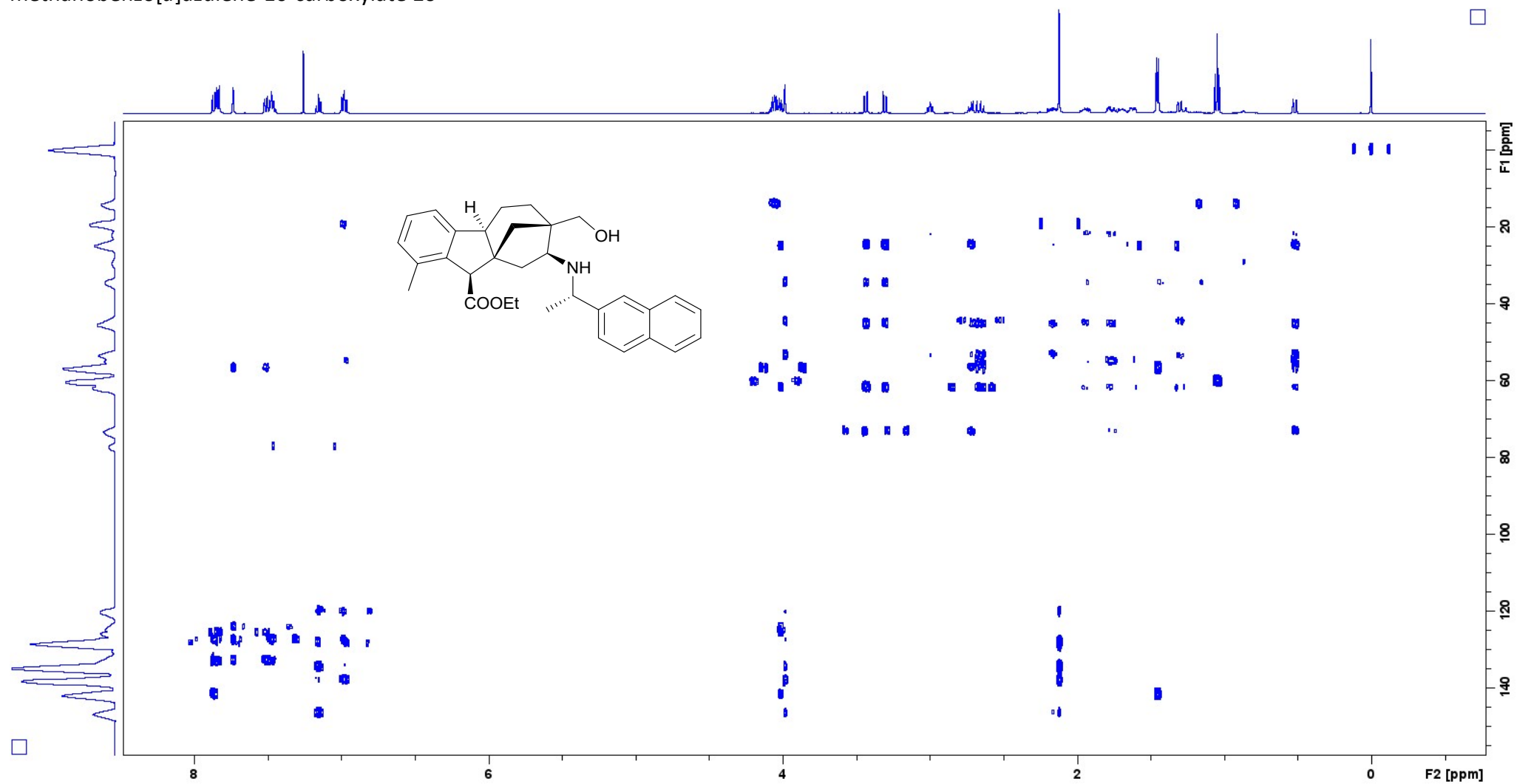
NOESY of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **10**



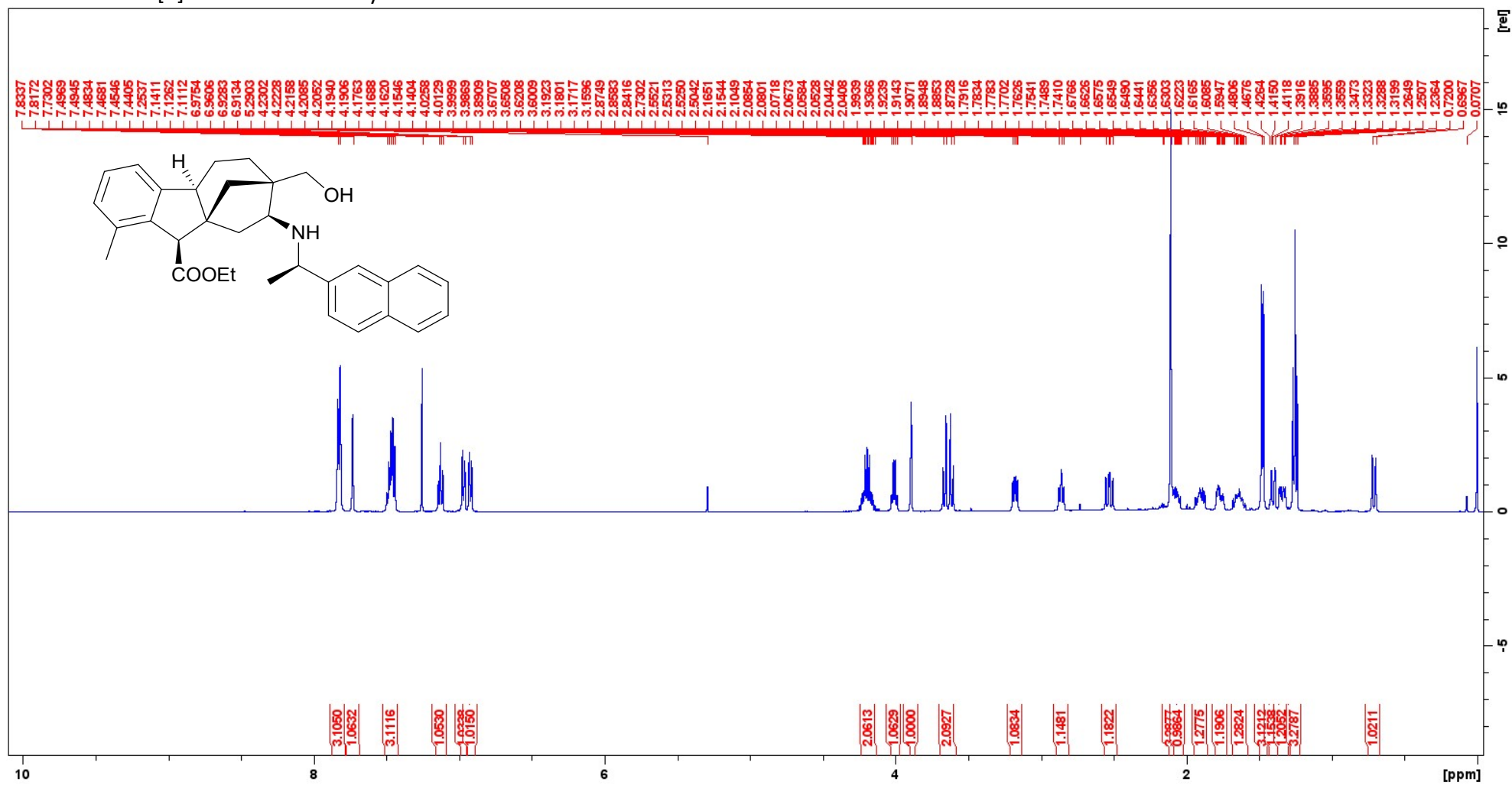
HSQC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **10**



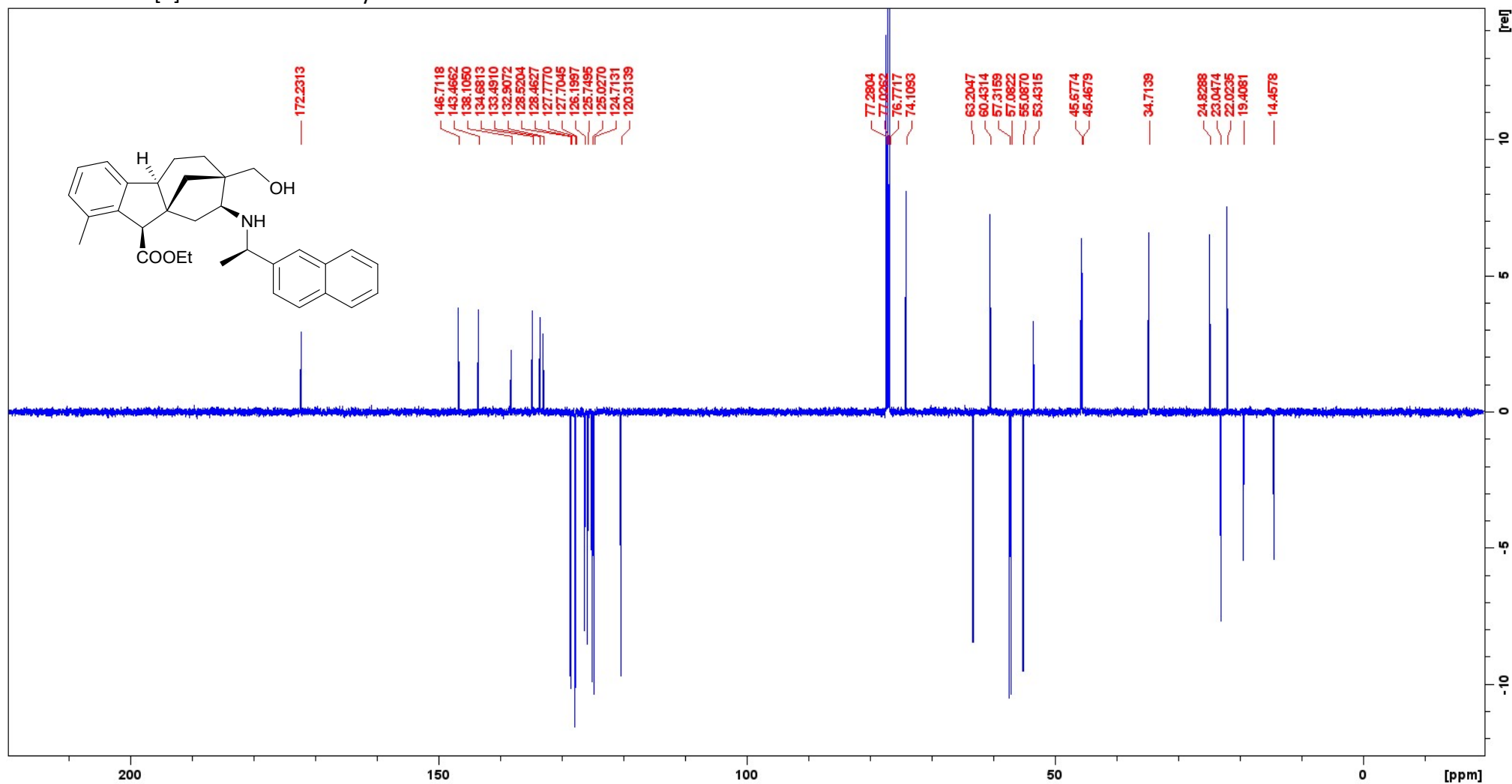
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **10**



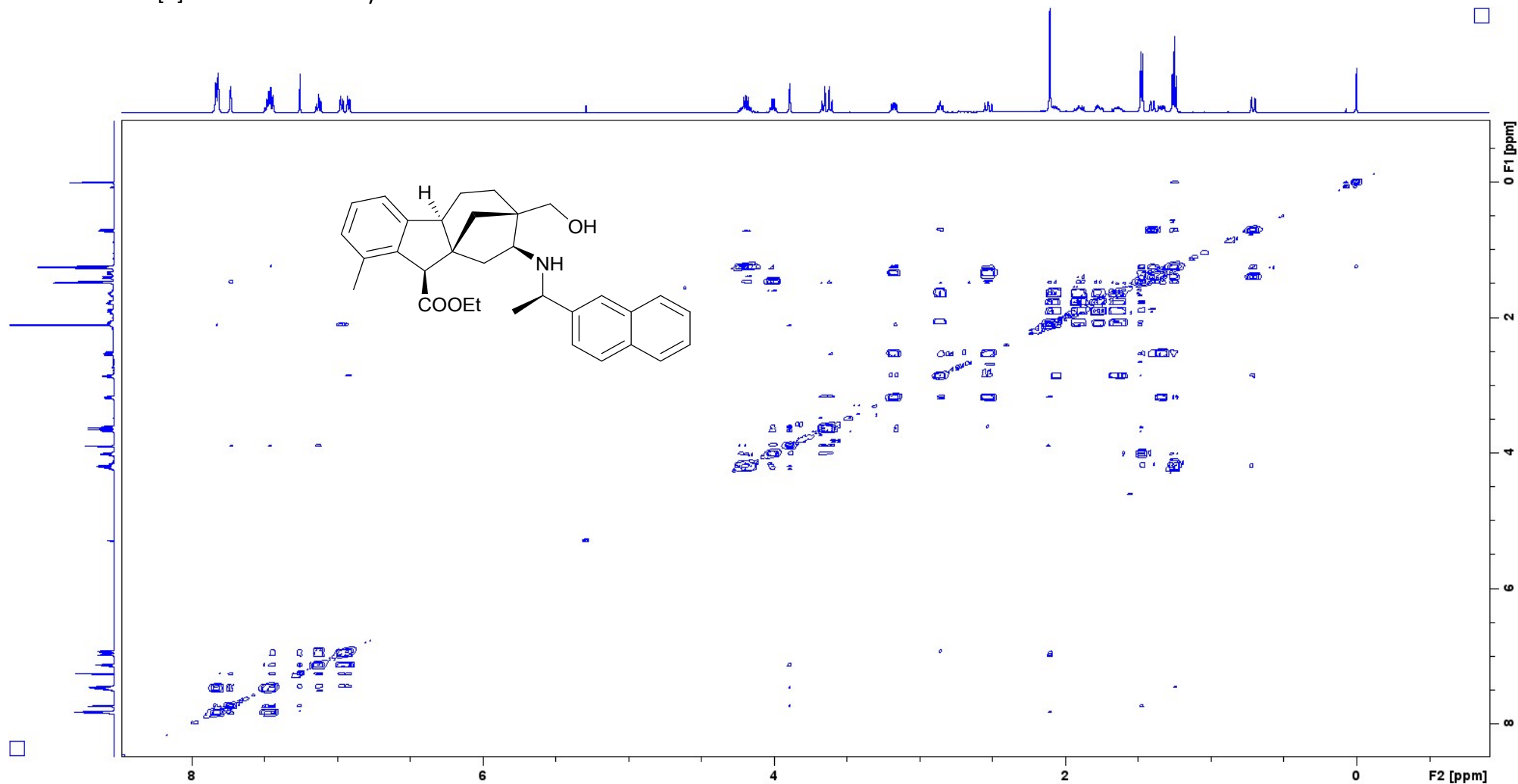
$^1\text{H-NMR}$ of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



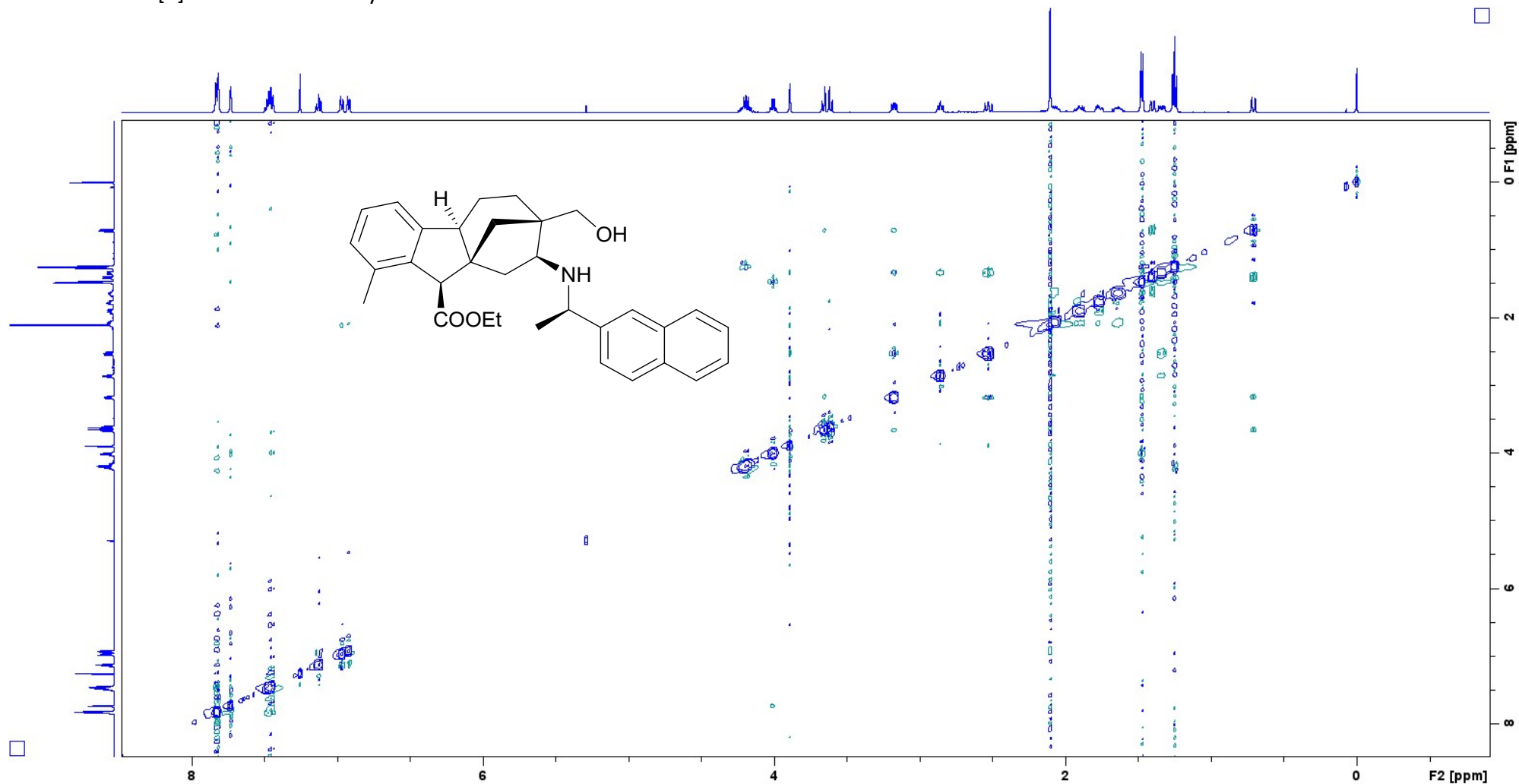
¹³C-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



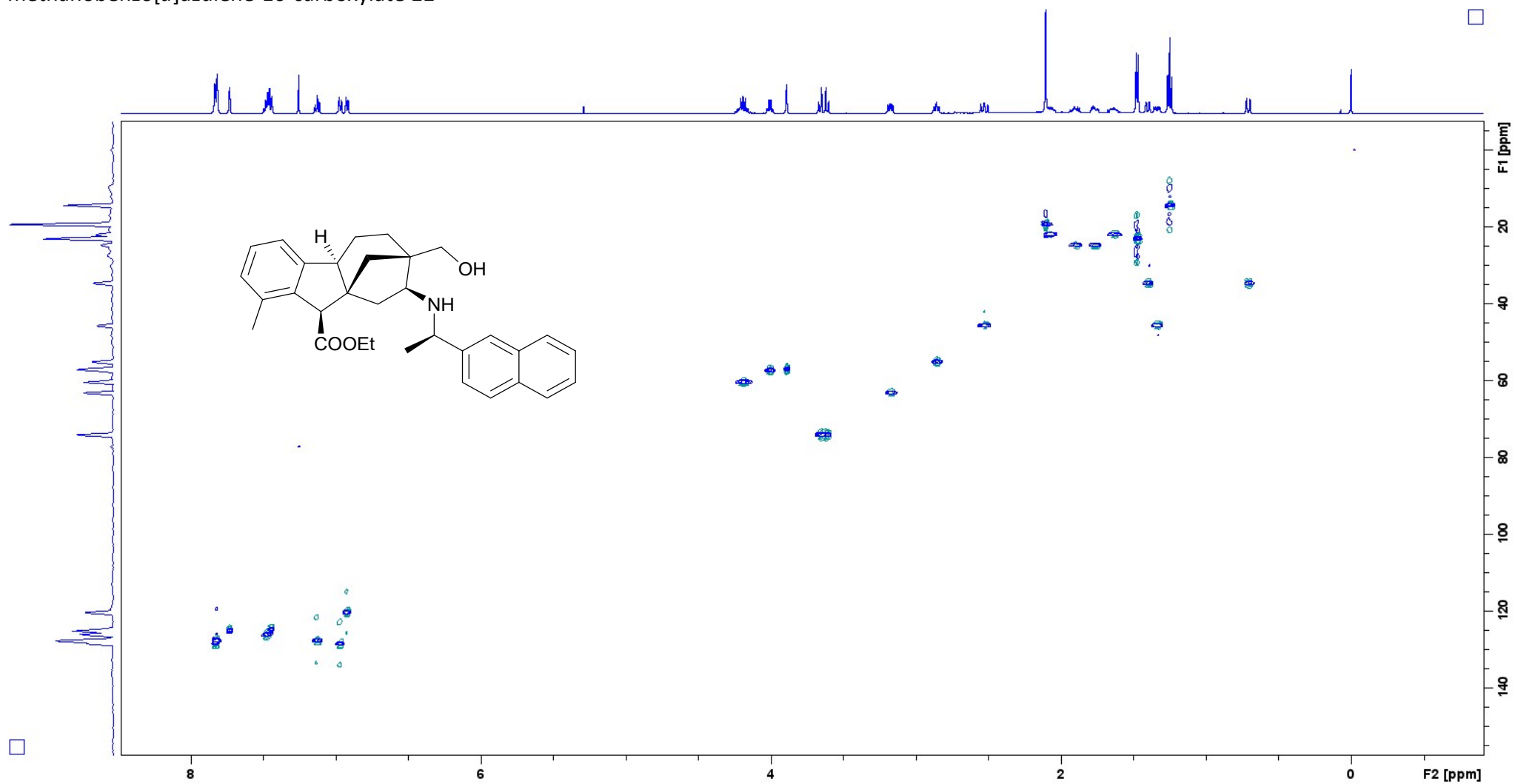
COSY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



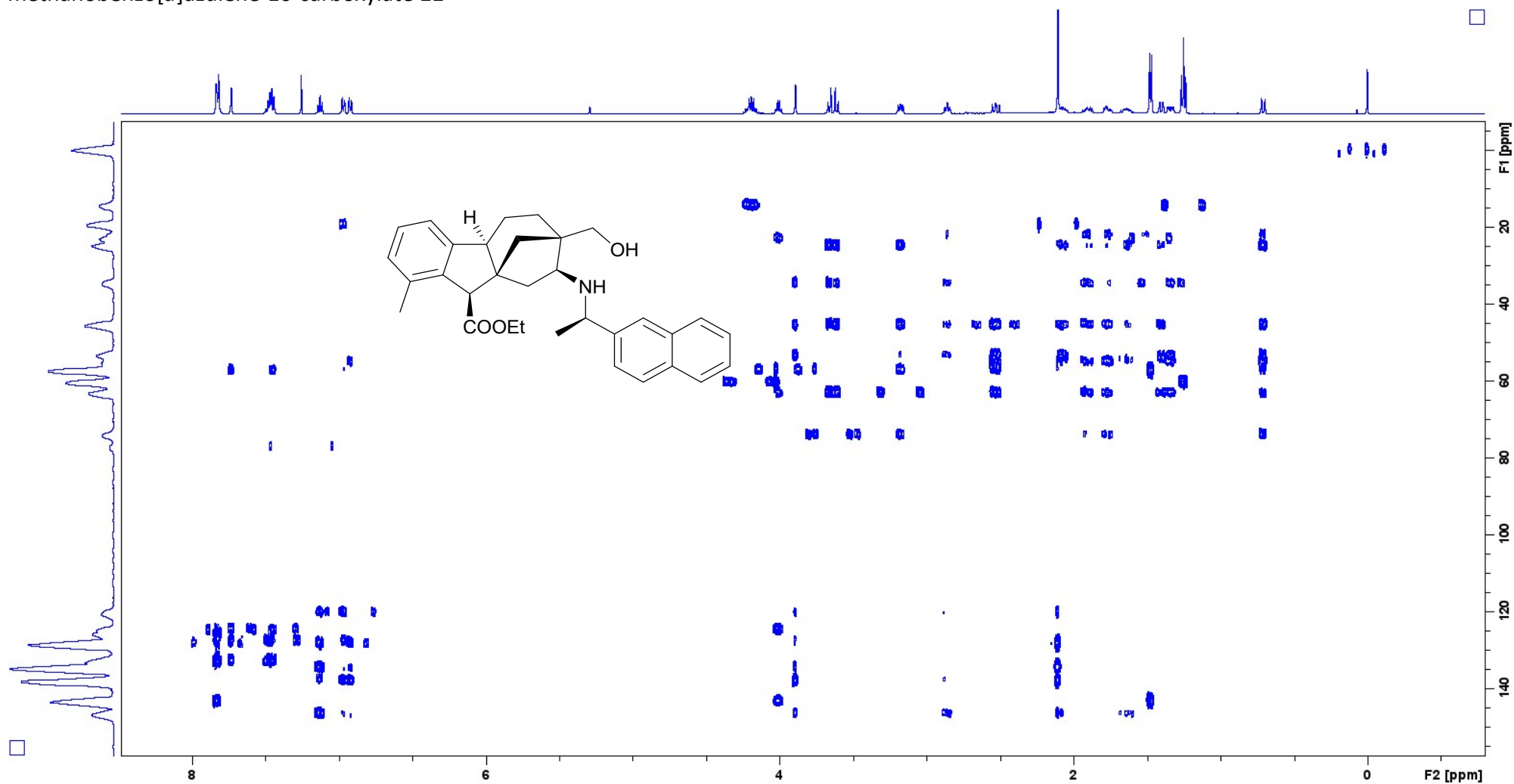
NOESY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



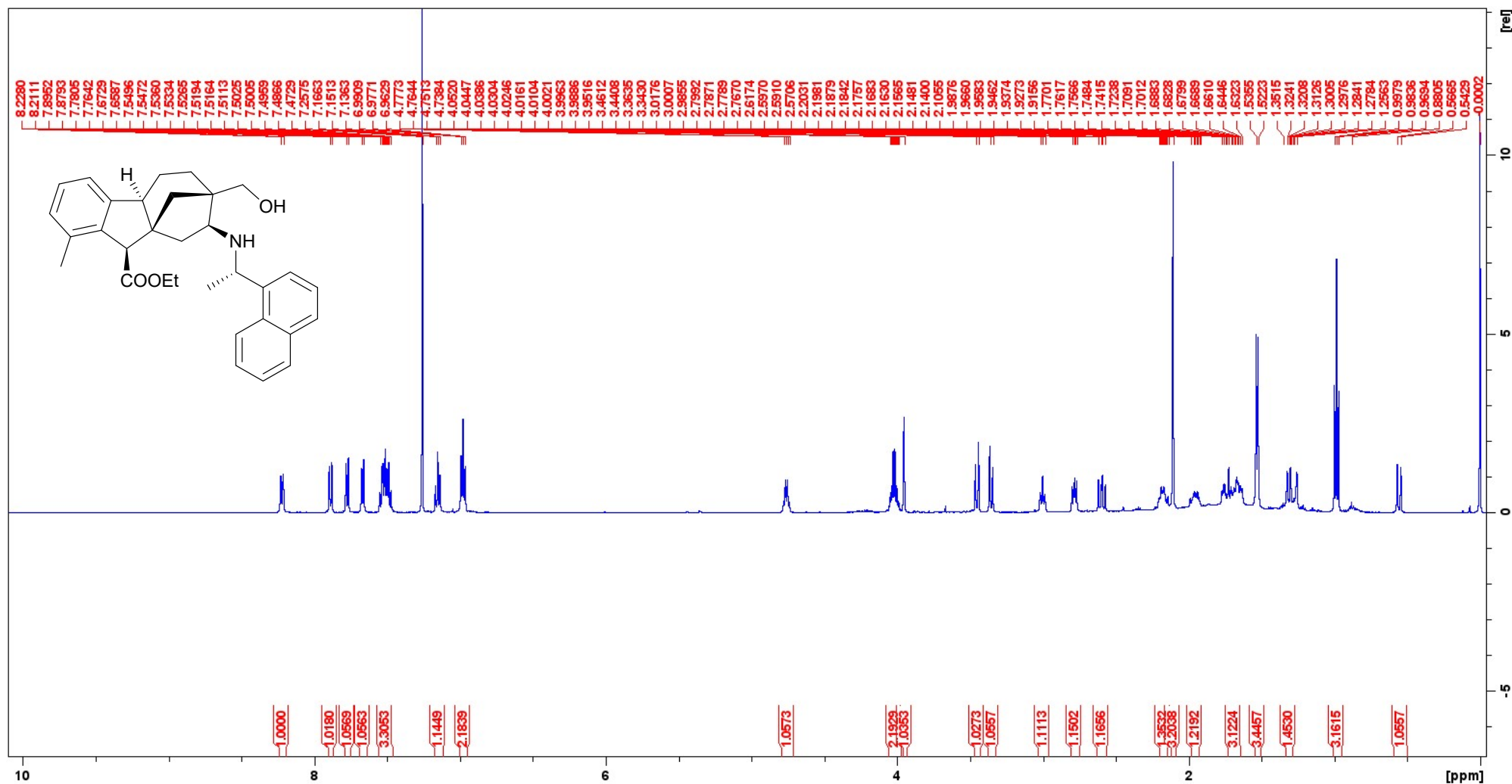
HSQC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



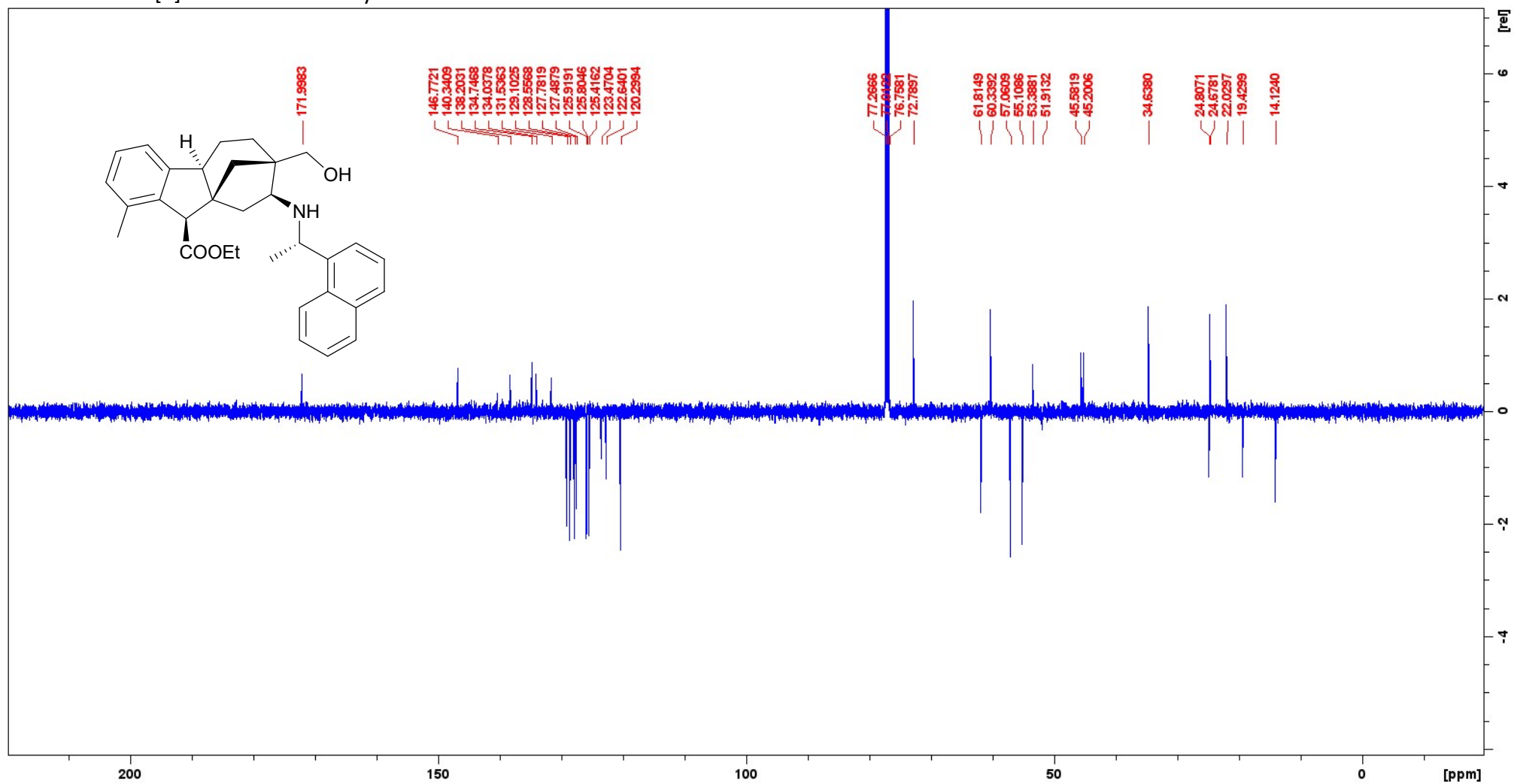
HMBC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **11**



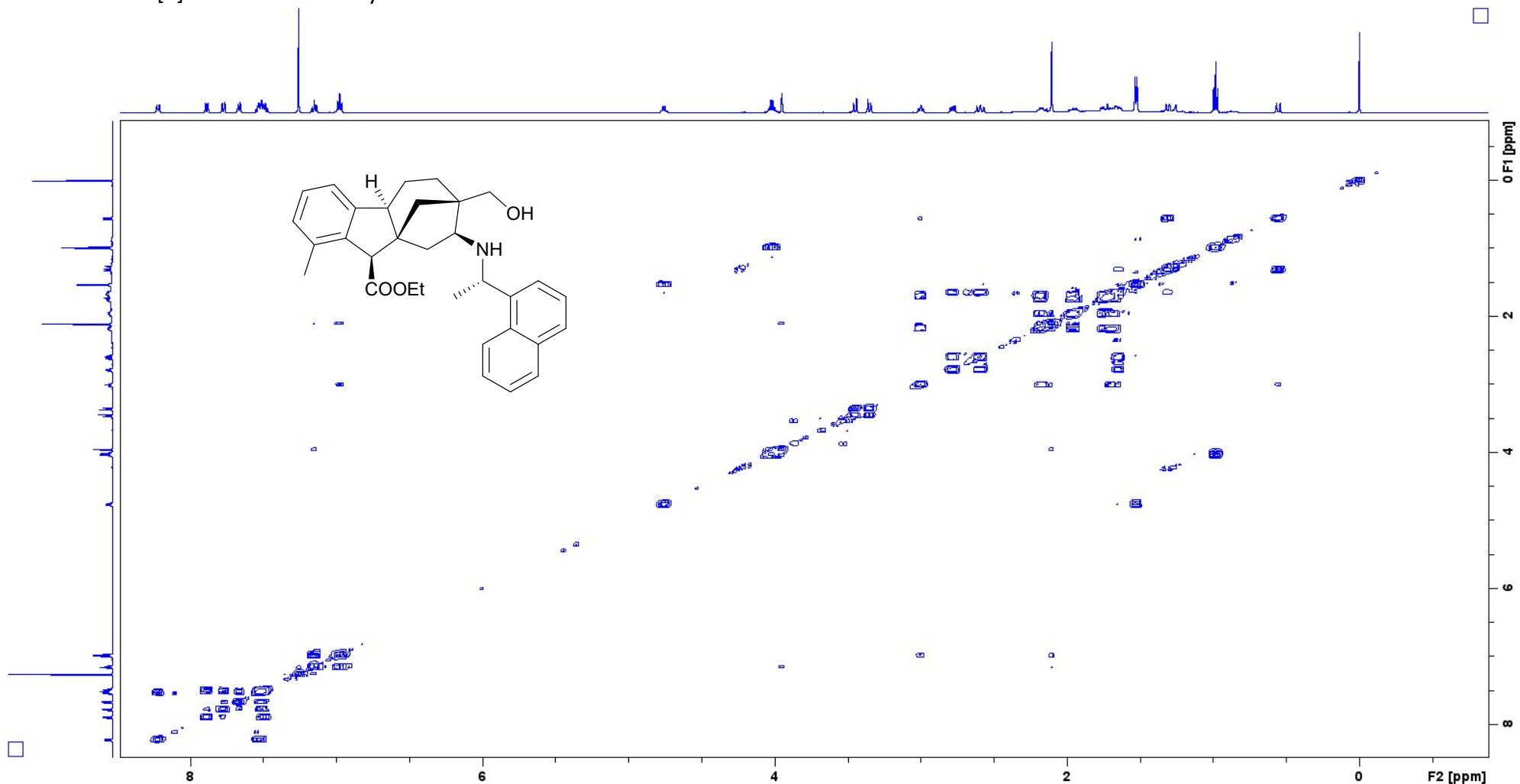
¹H-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **12**



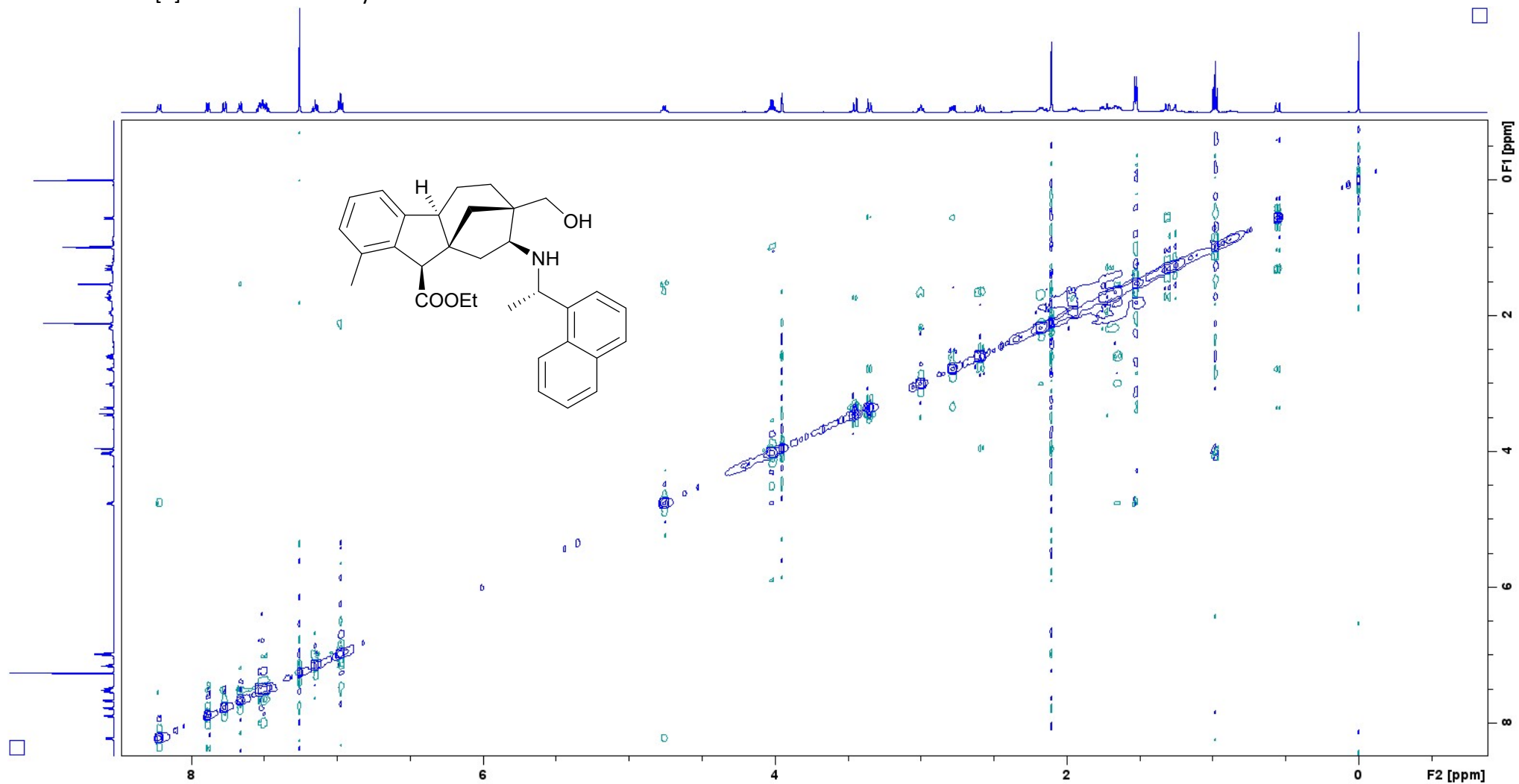
¹³C-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **12**



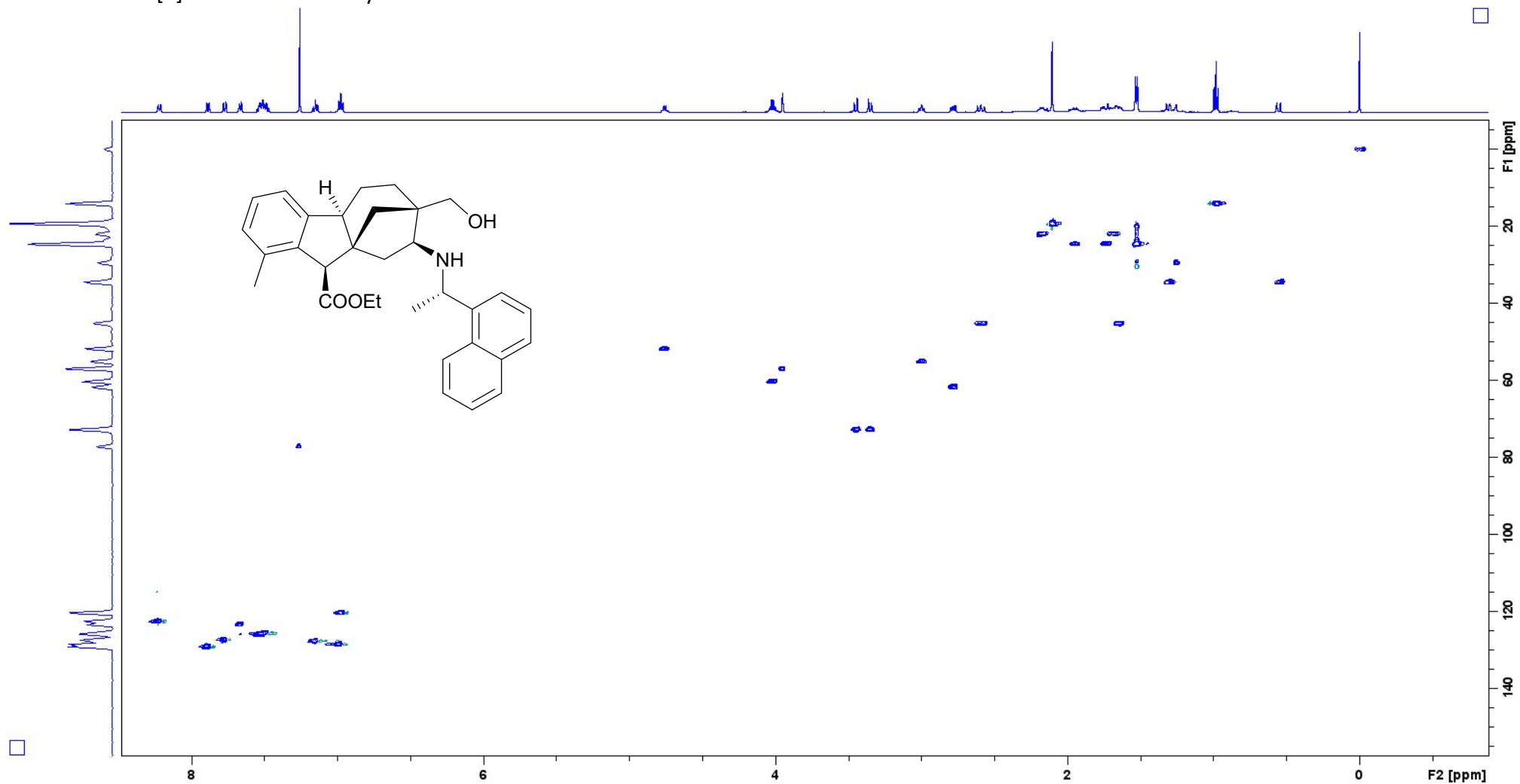
COSY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **12**



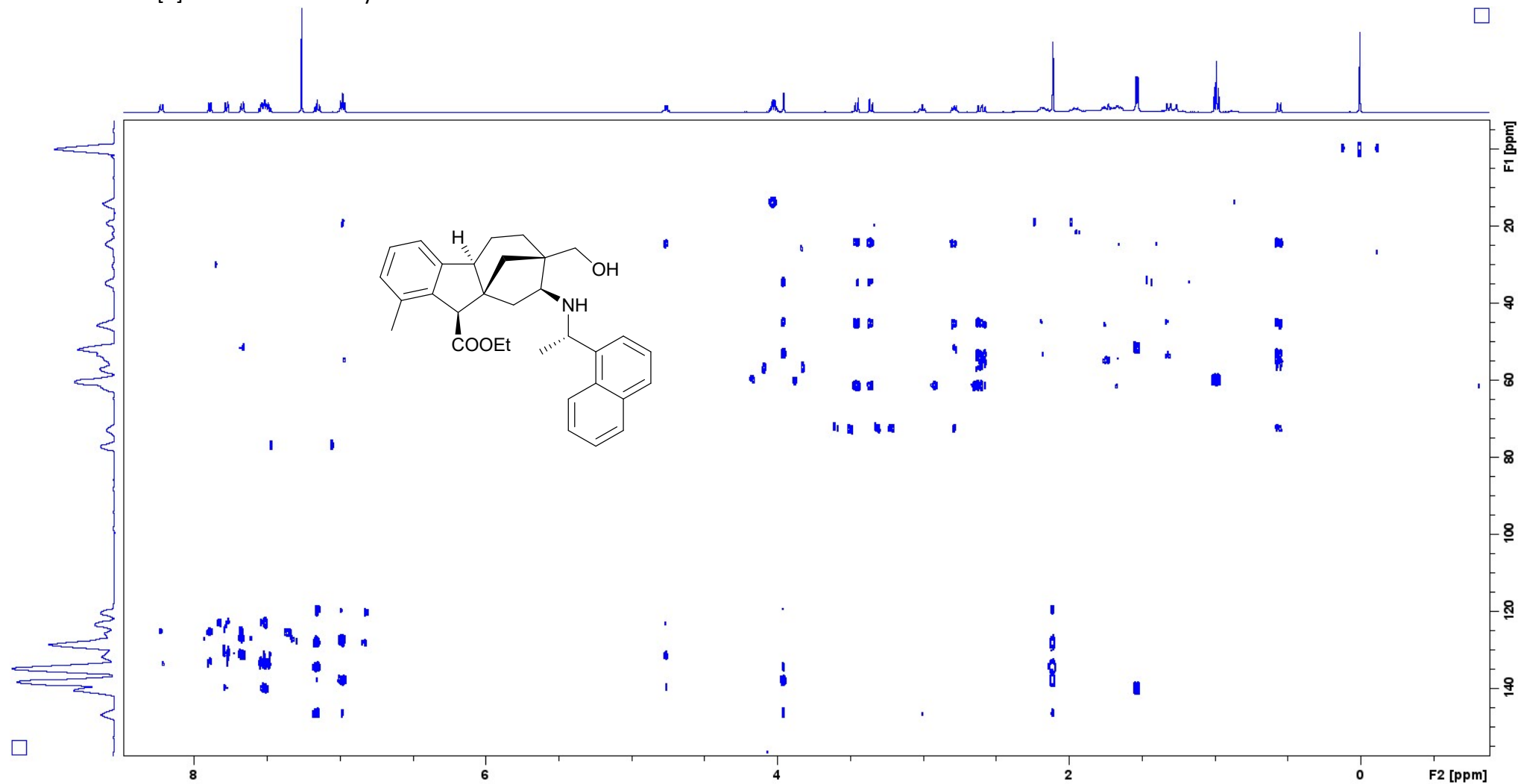
NOESY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **12**



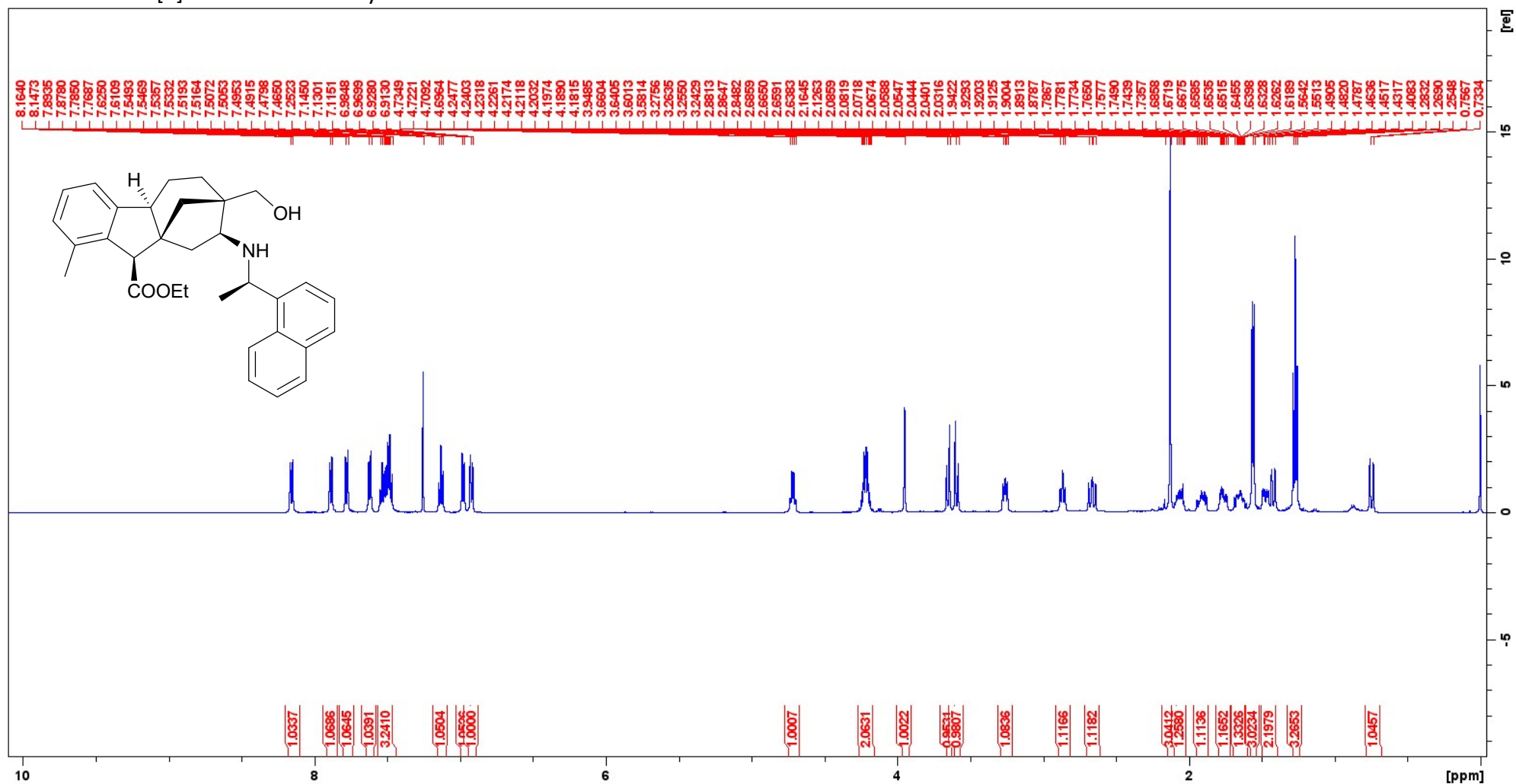
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **12**



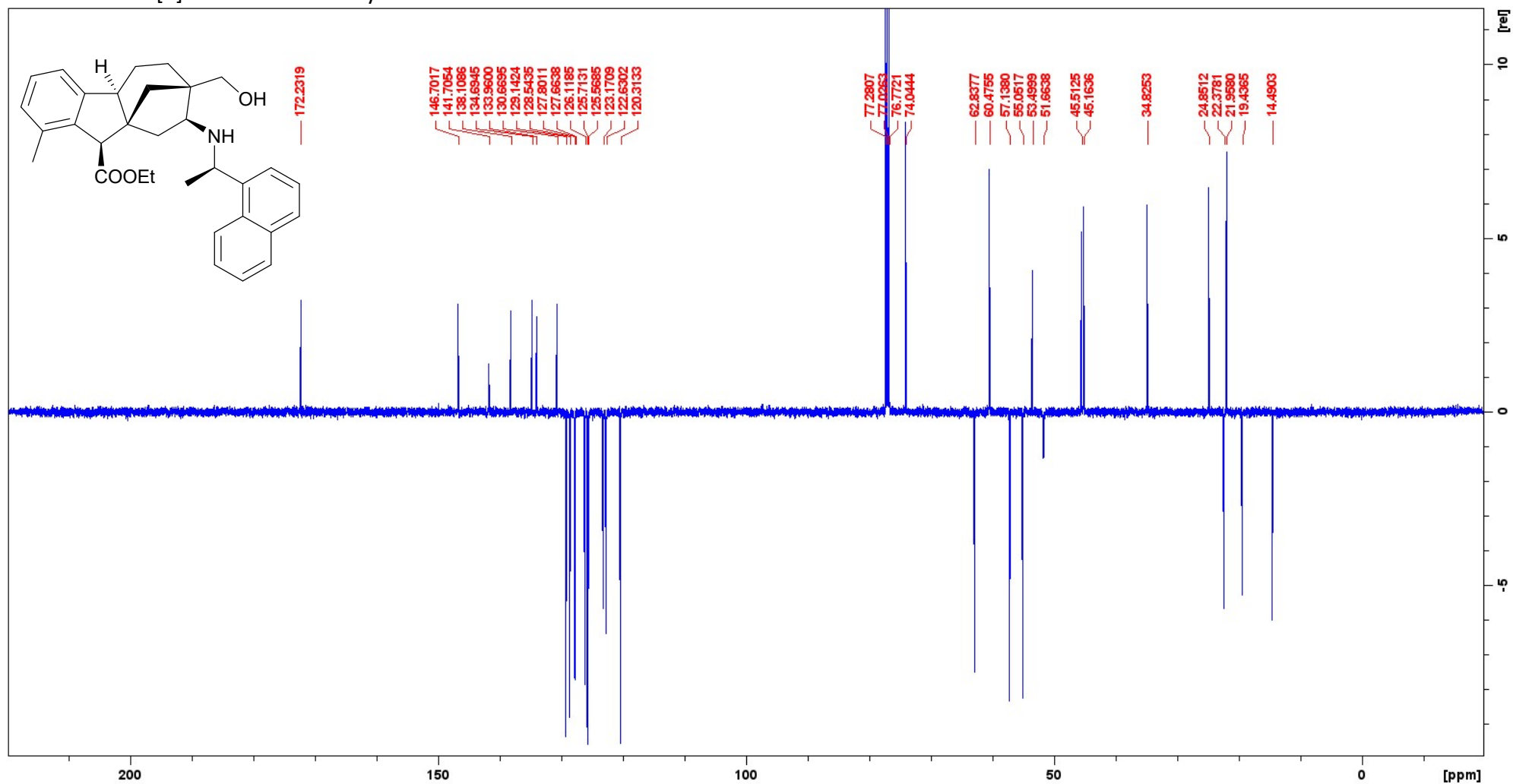
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **12**



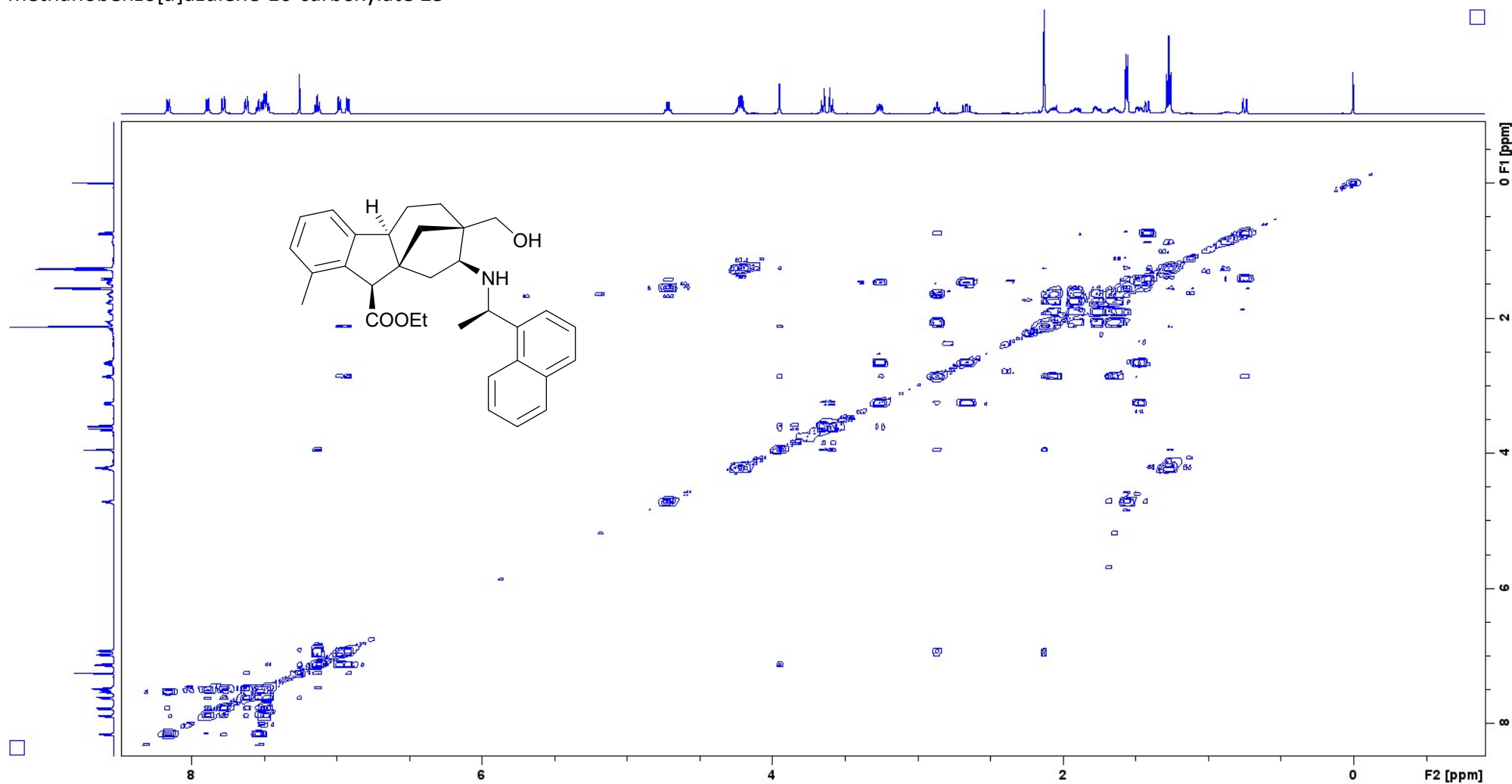
¹H-NMR of ethyl (4*S*,7*R*,8*S*,9*a*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



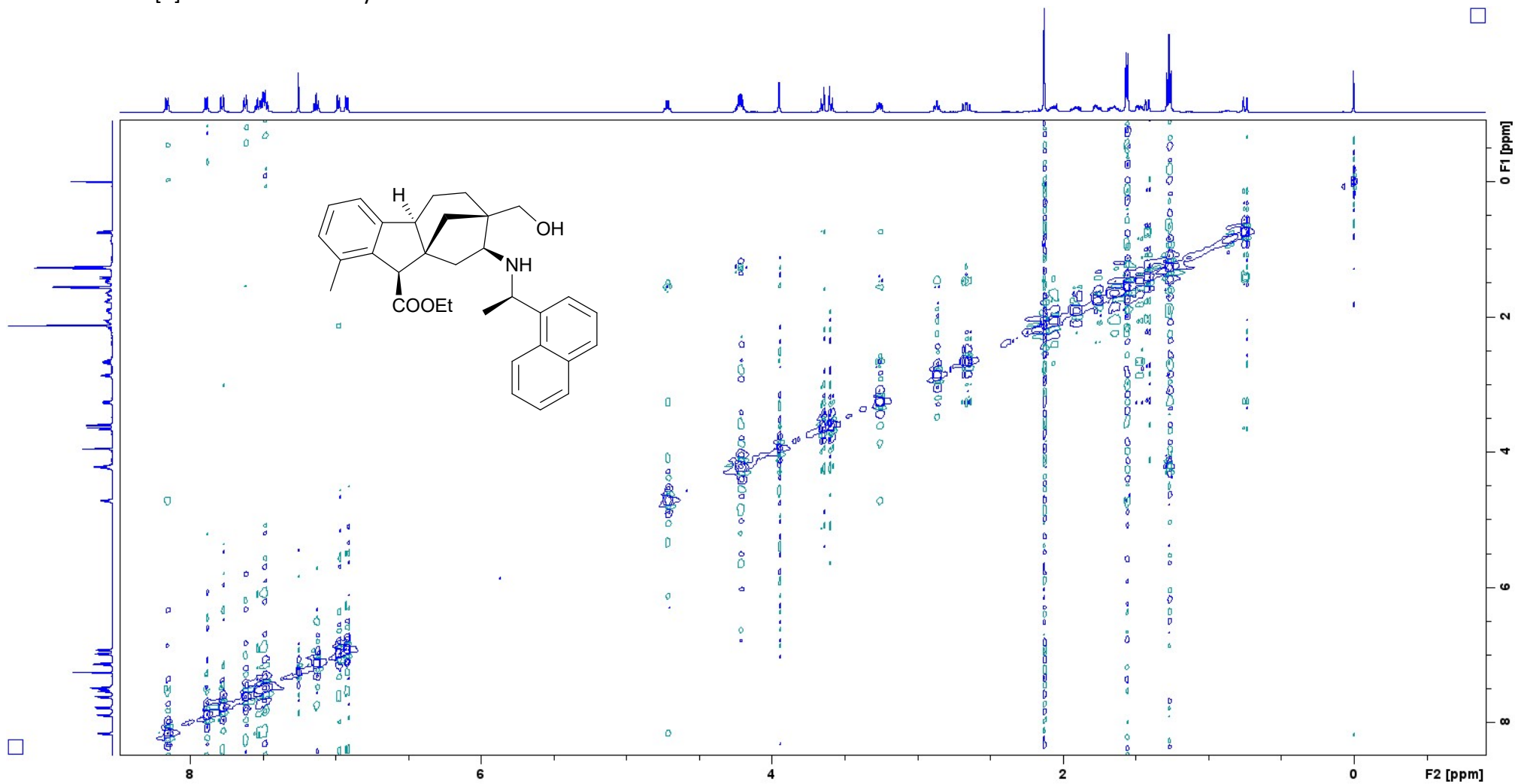
¹³C-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



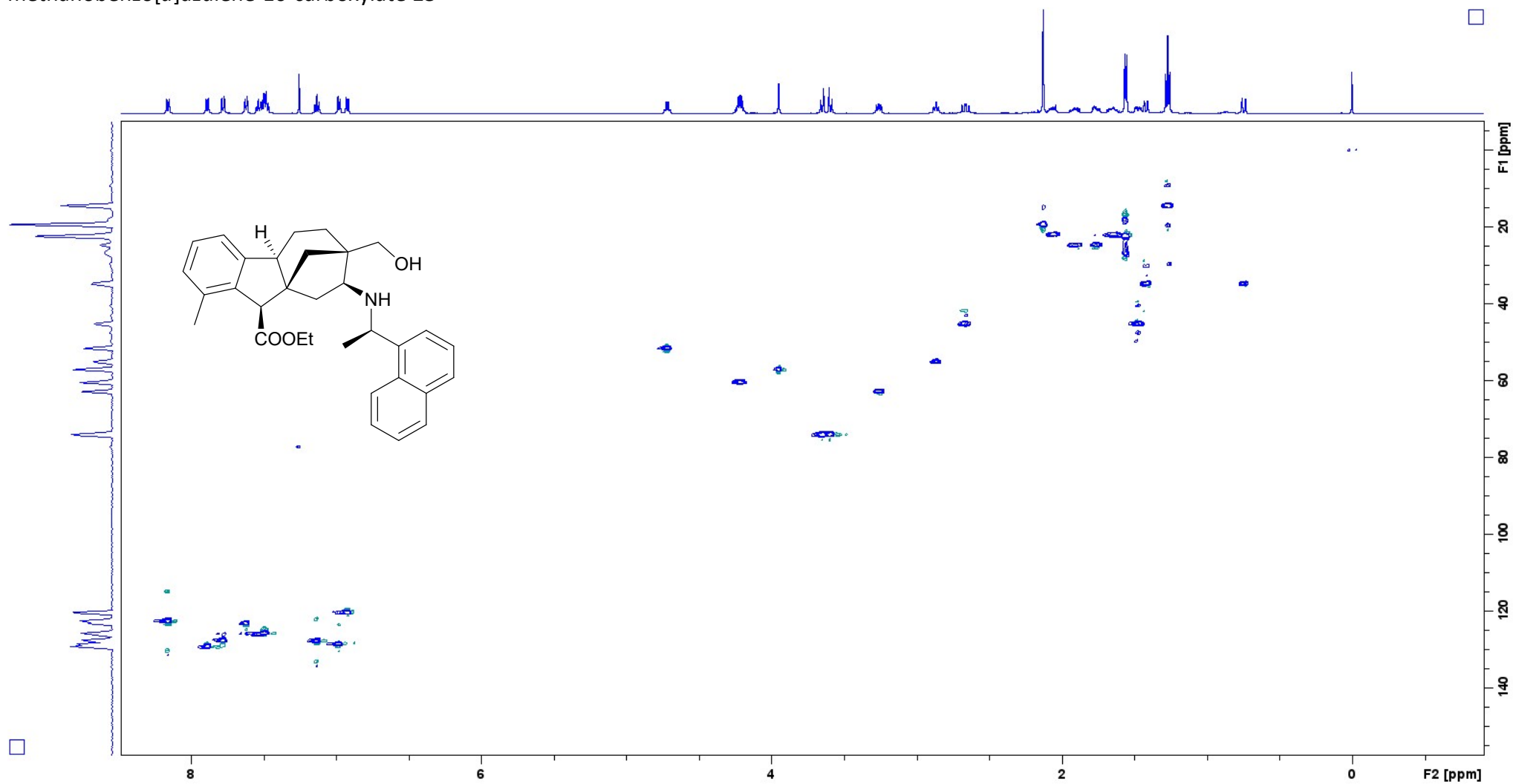
COSY of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



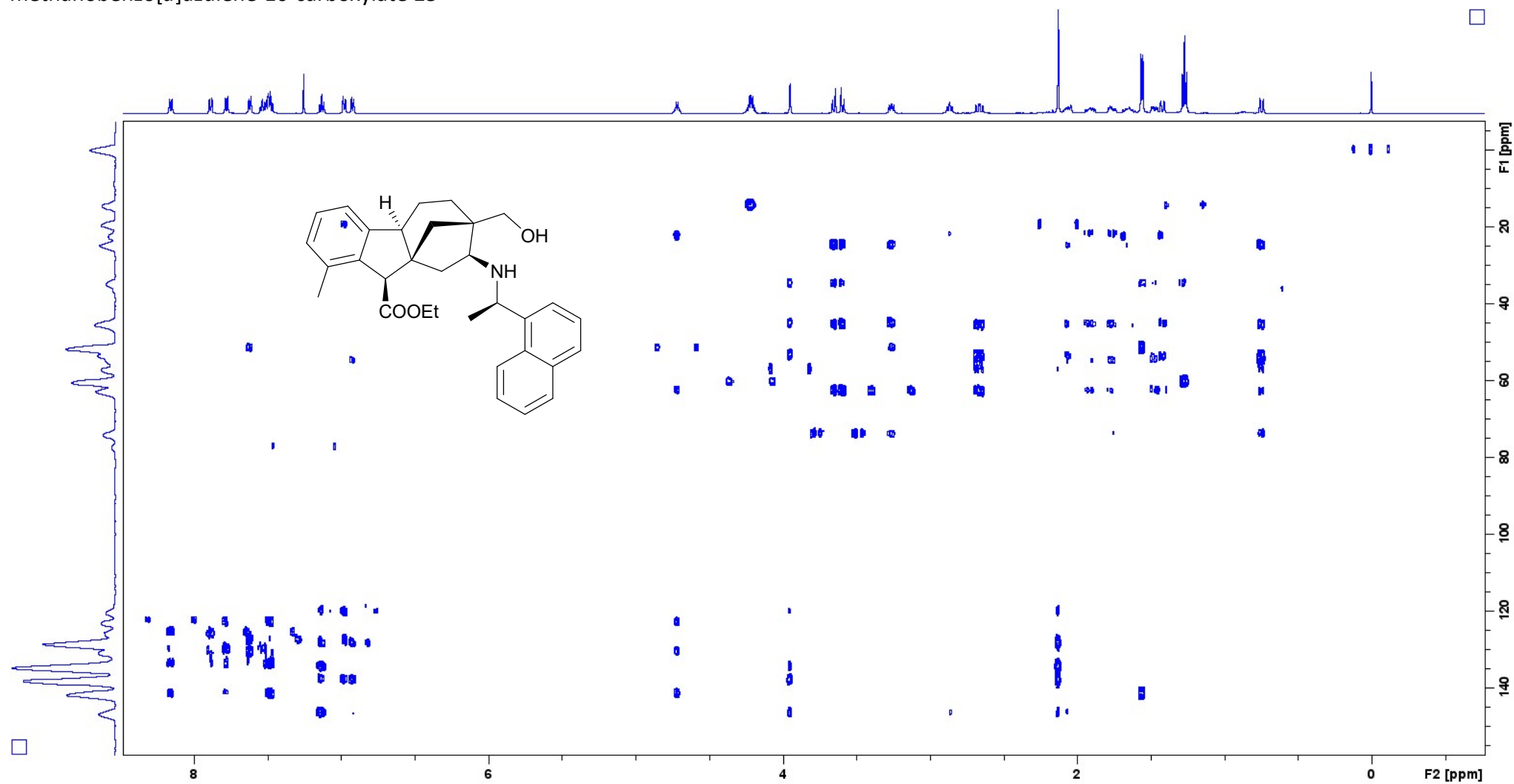
NOESY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



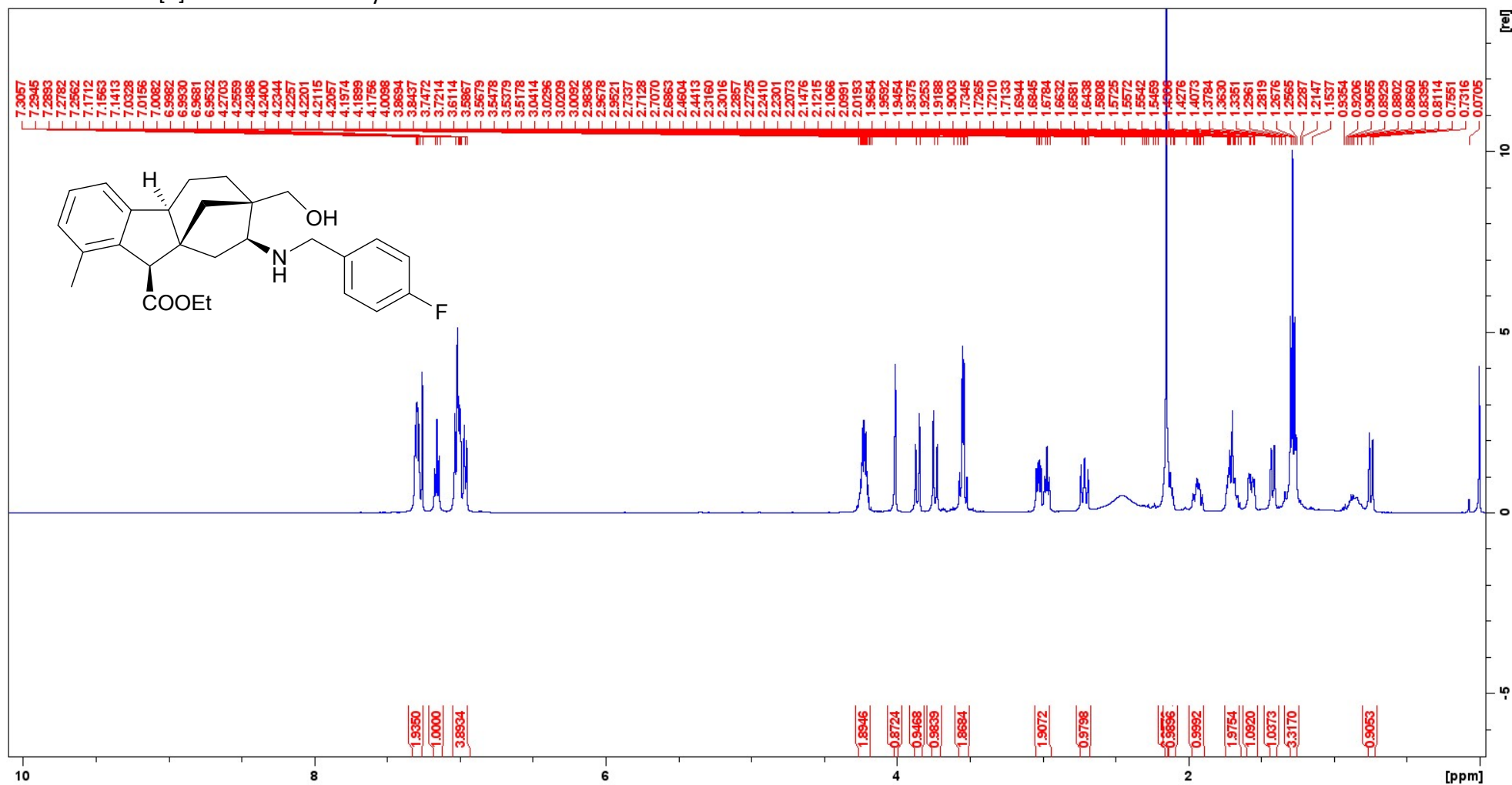
HSQC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



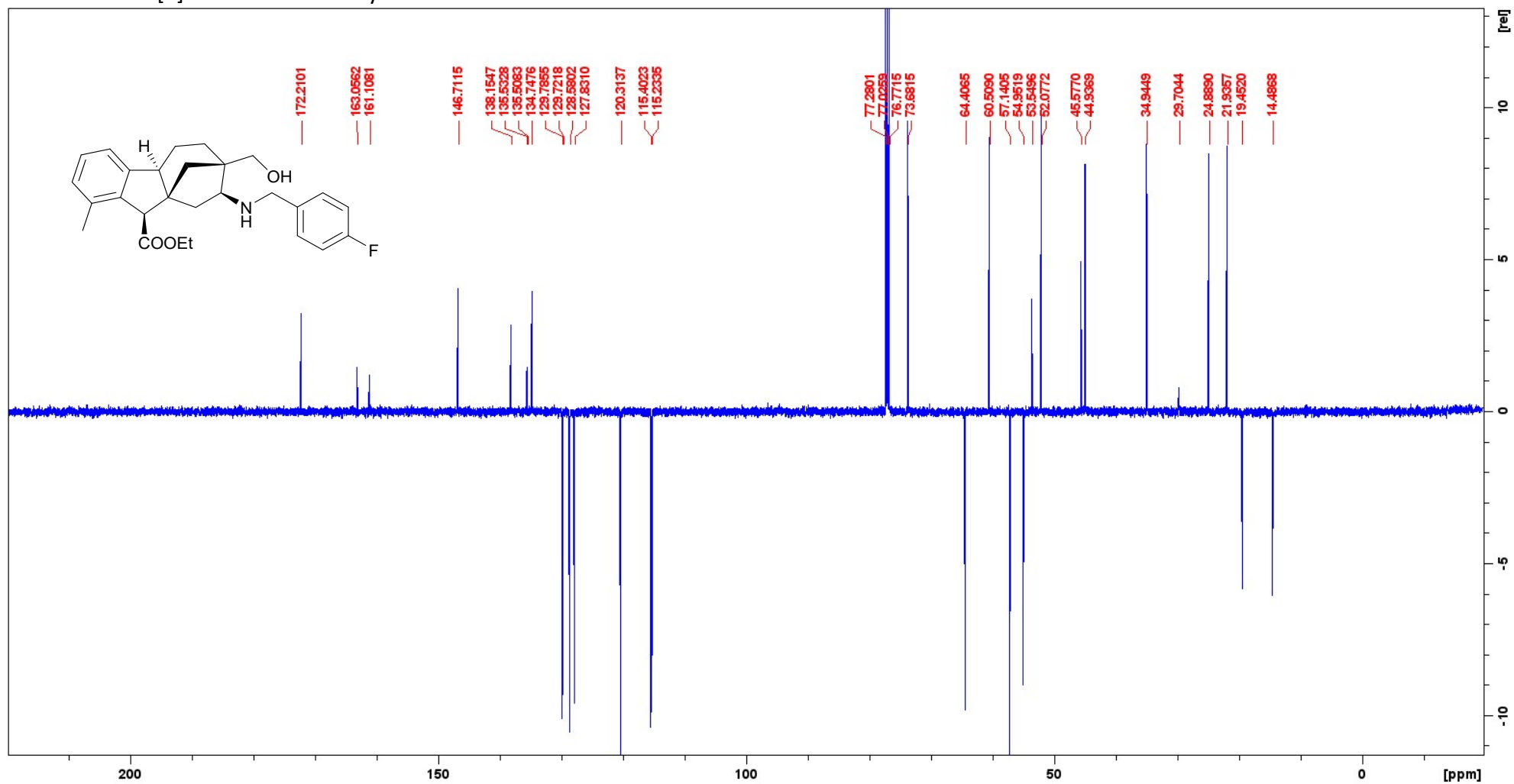
HMBC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **13**



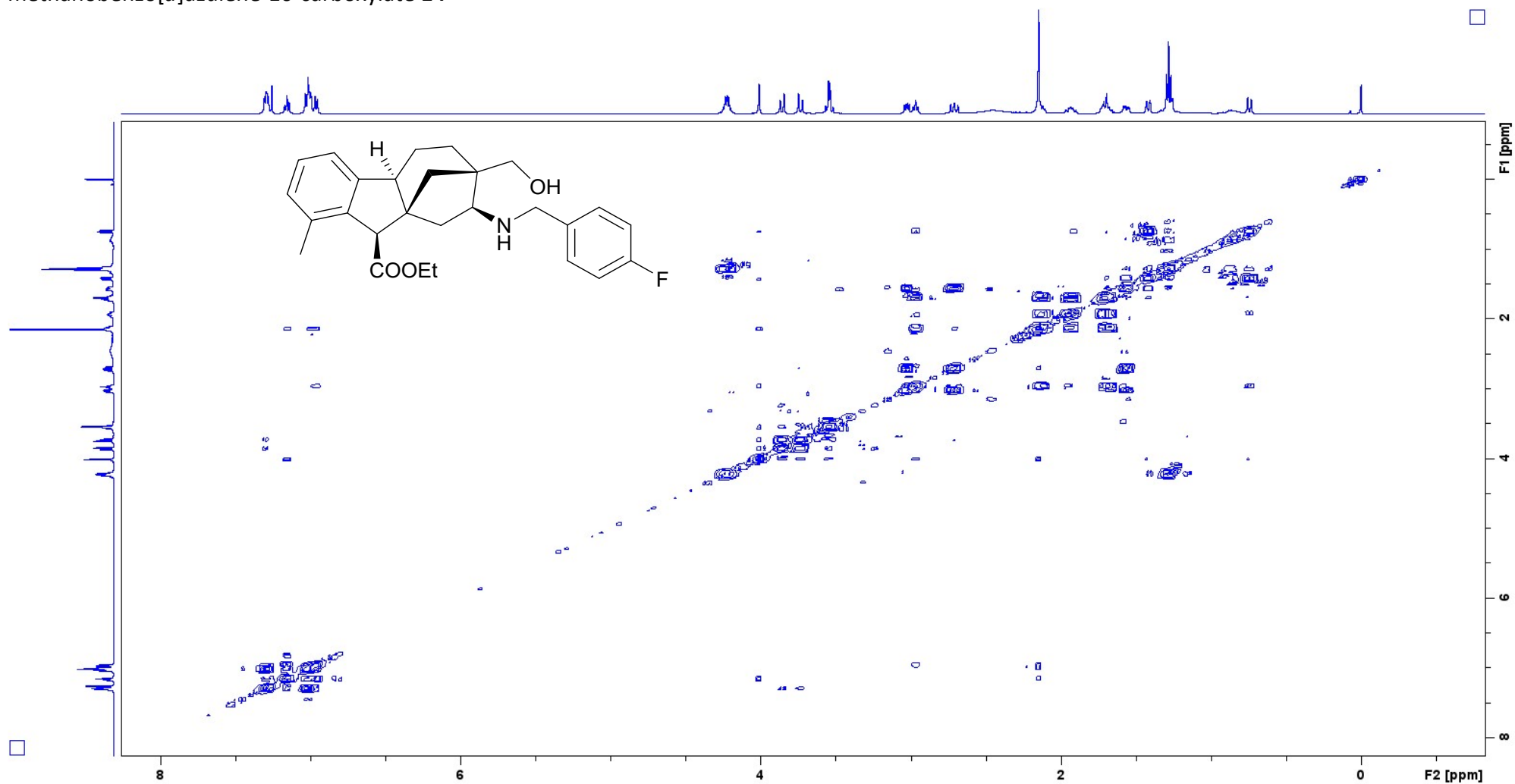
¹H-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **14**



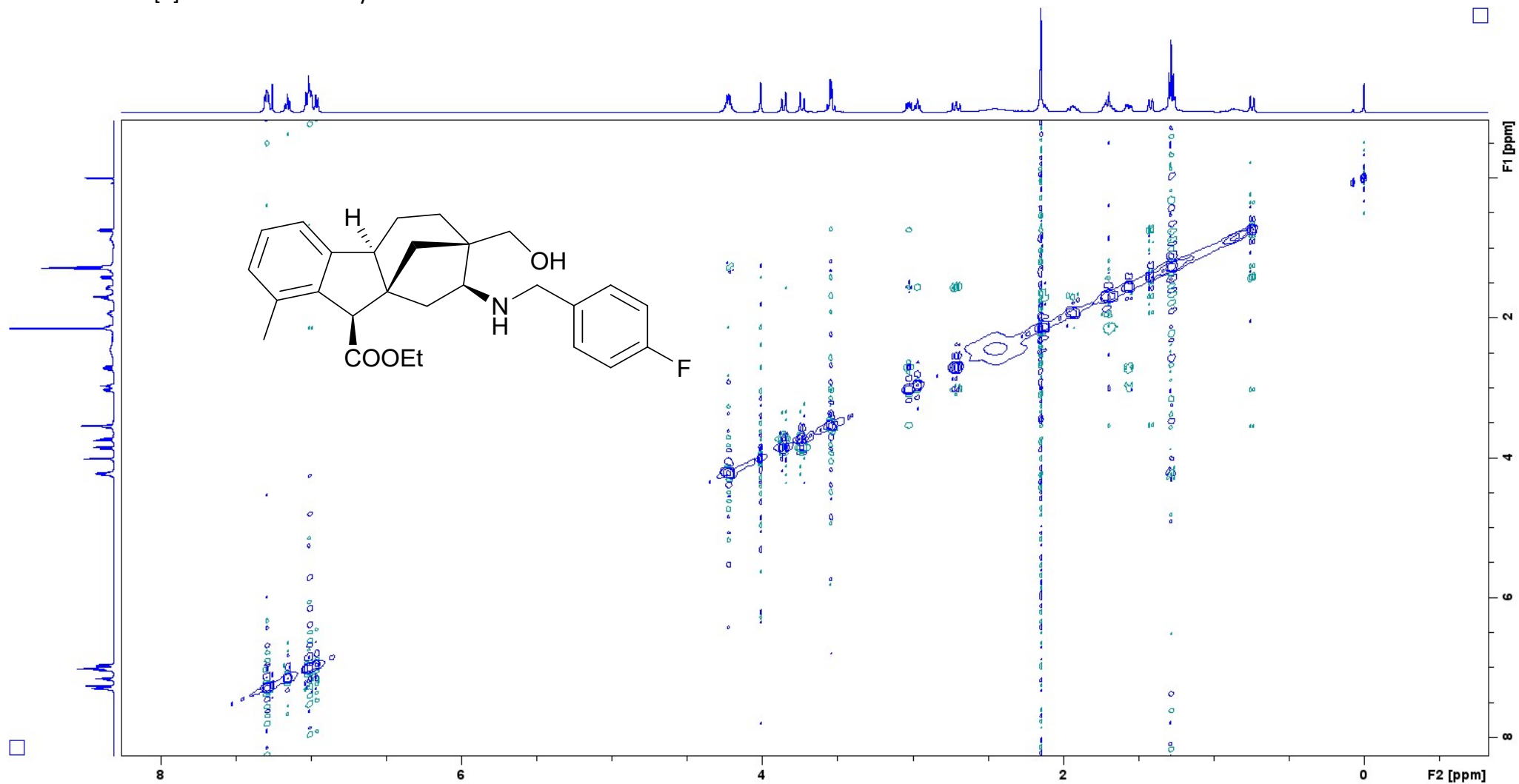
¹³C-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **14**



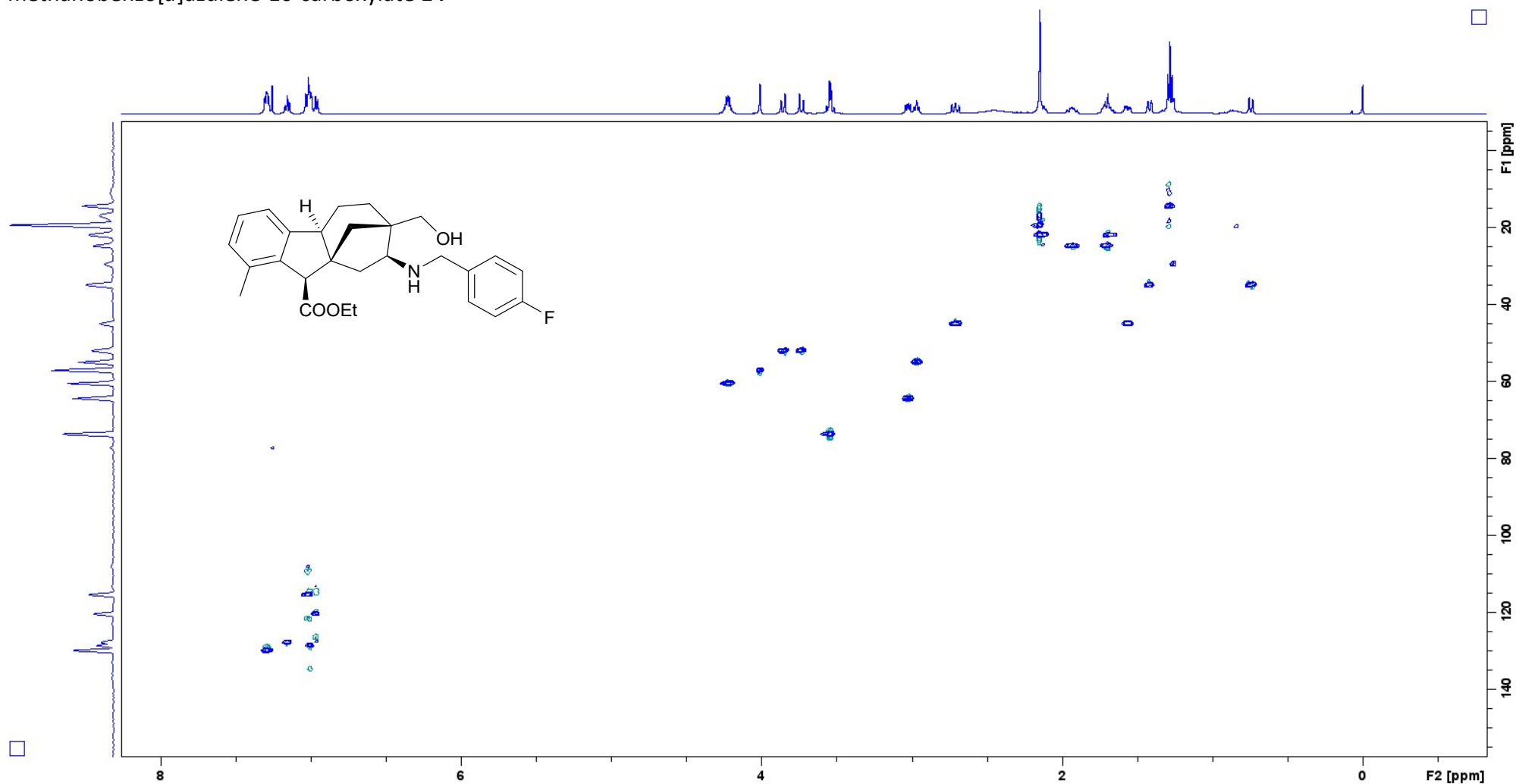
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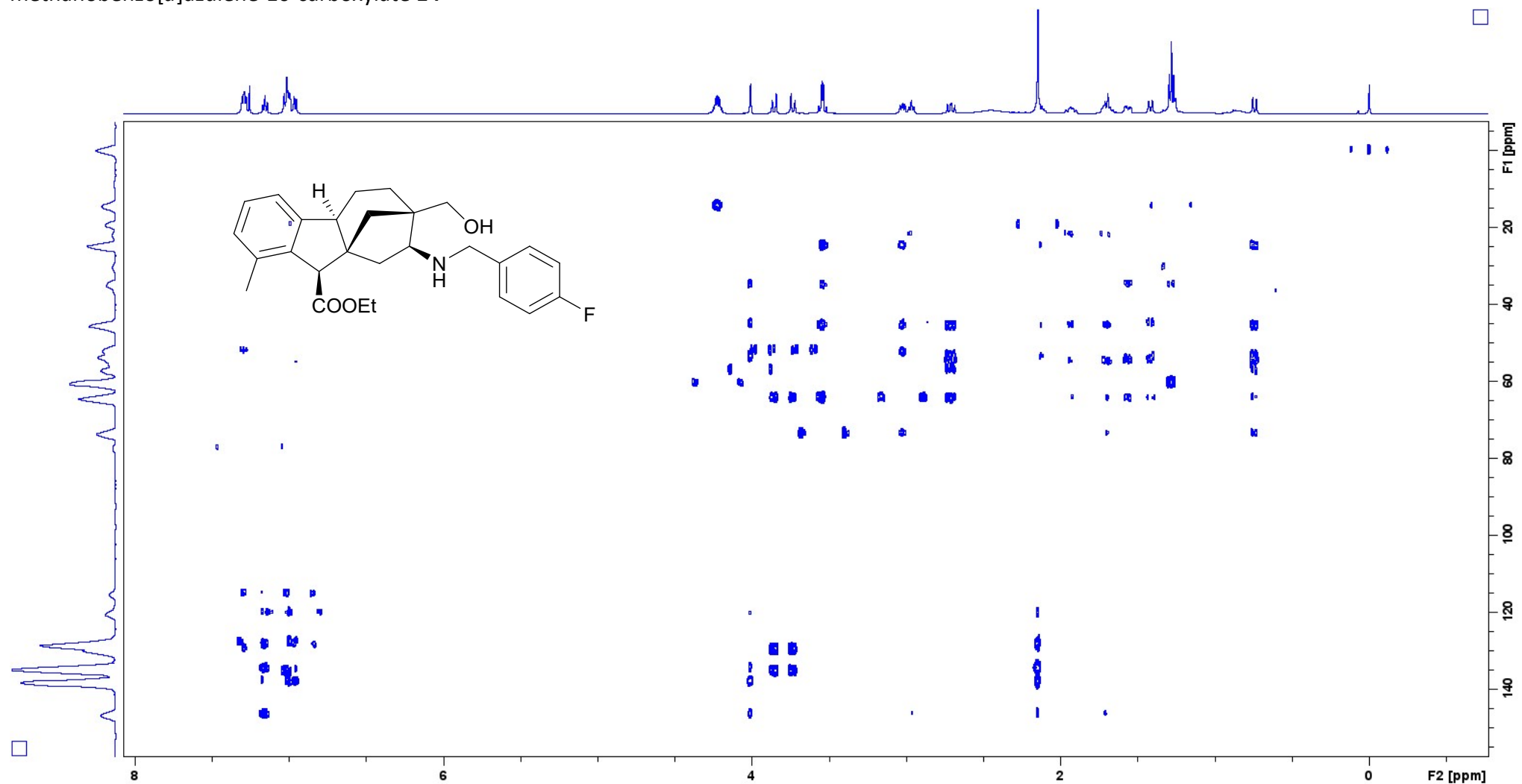
NOESY of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **14**



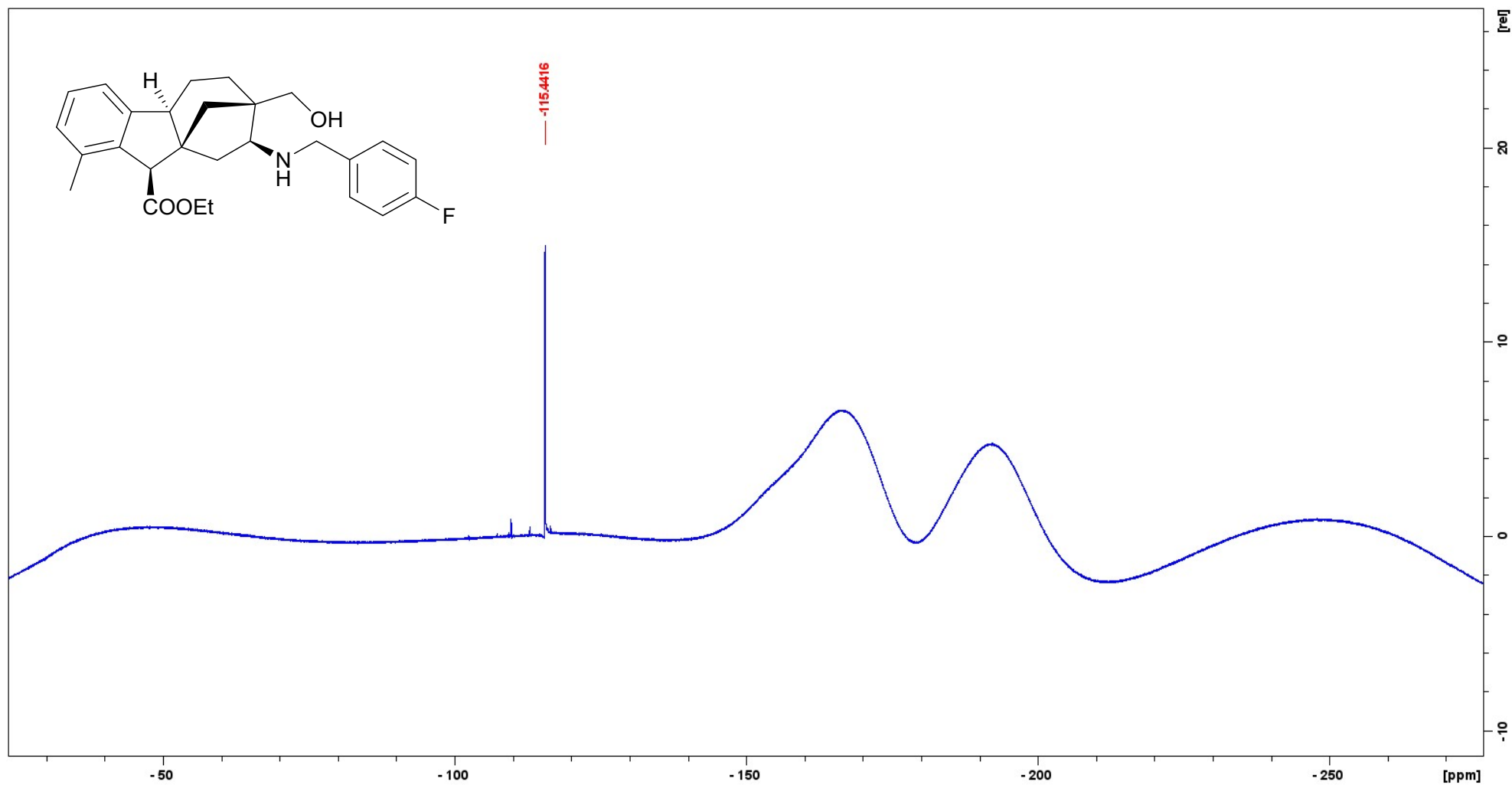
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **14**



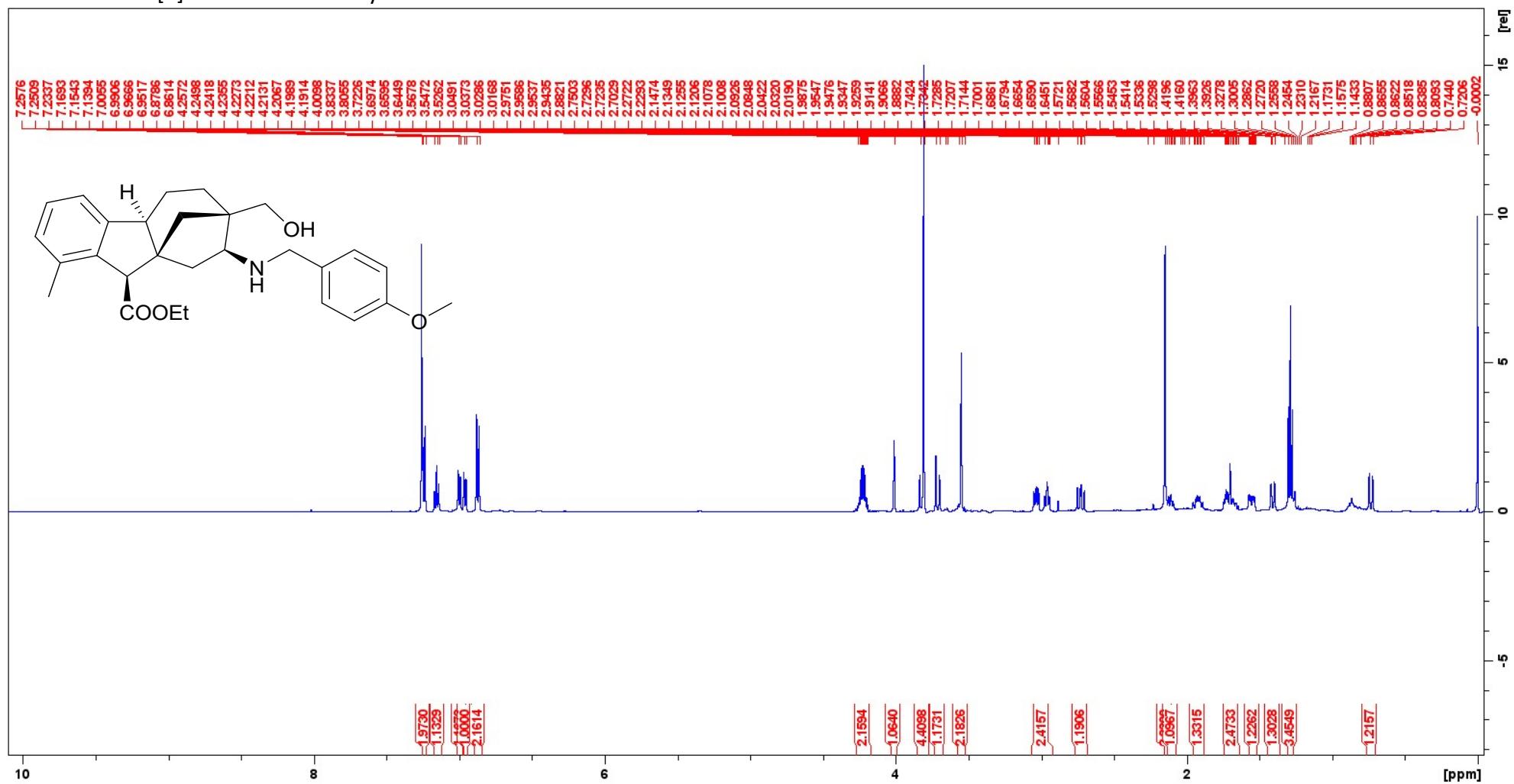
HMBC of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **14**



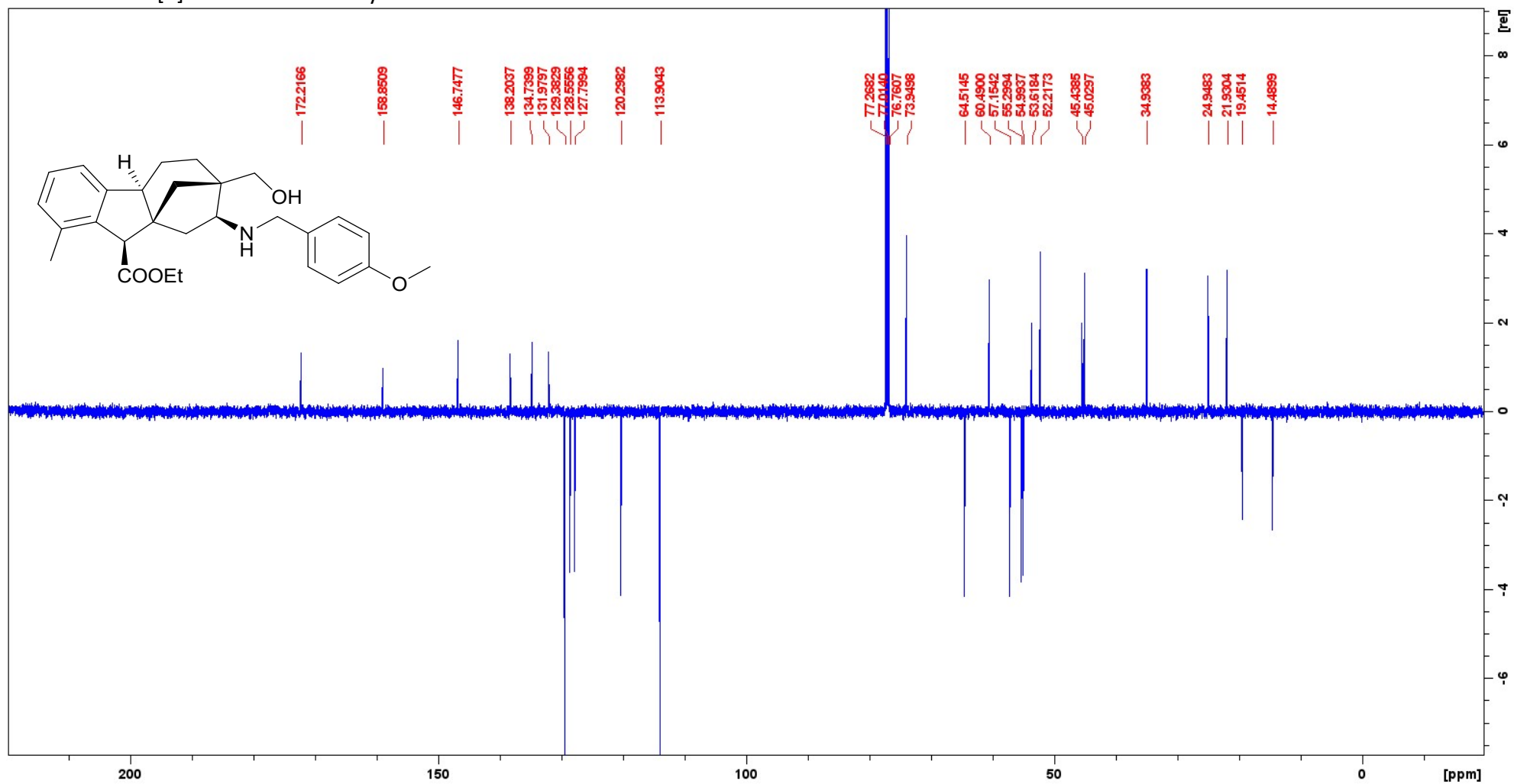
¹⁹F-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-8-((4-fluorobenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **14**



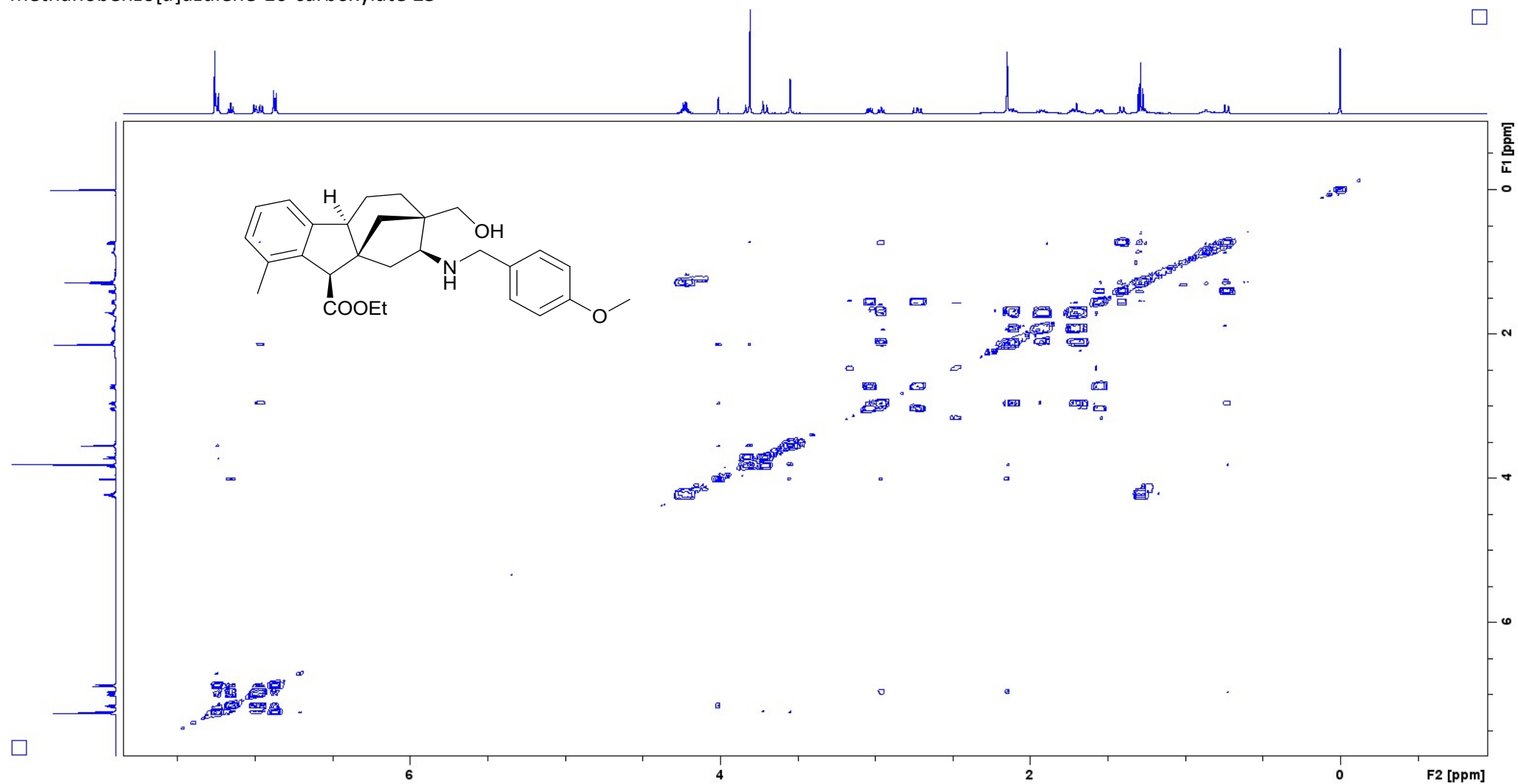
¹H-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-8-((4-methoxybenzyl)amino)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **15**



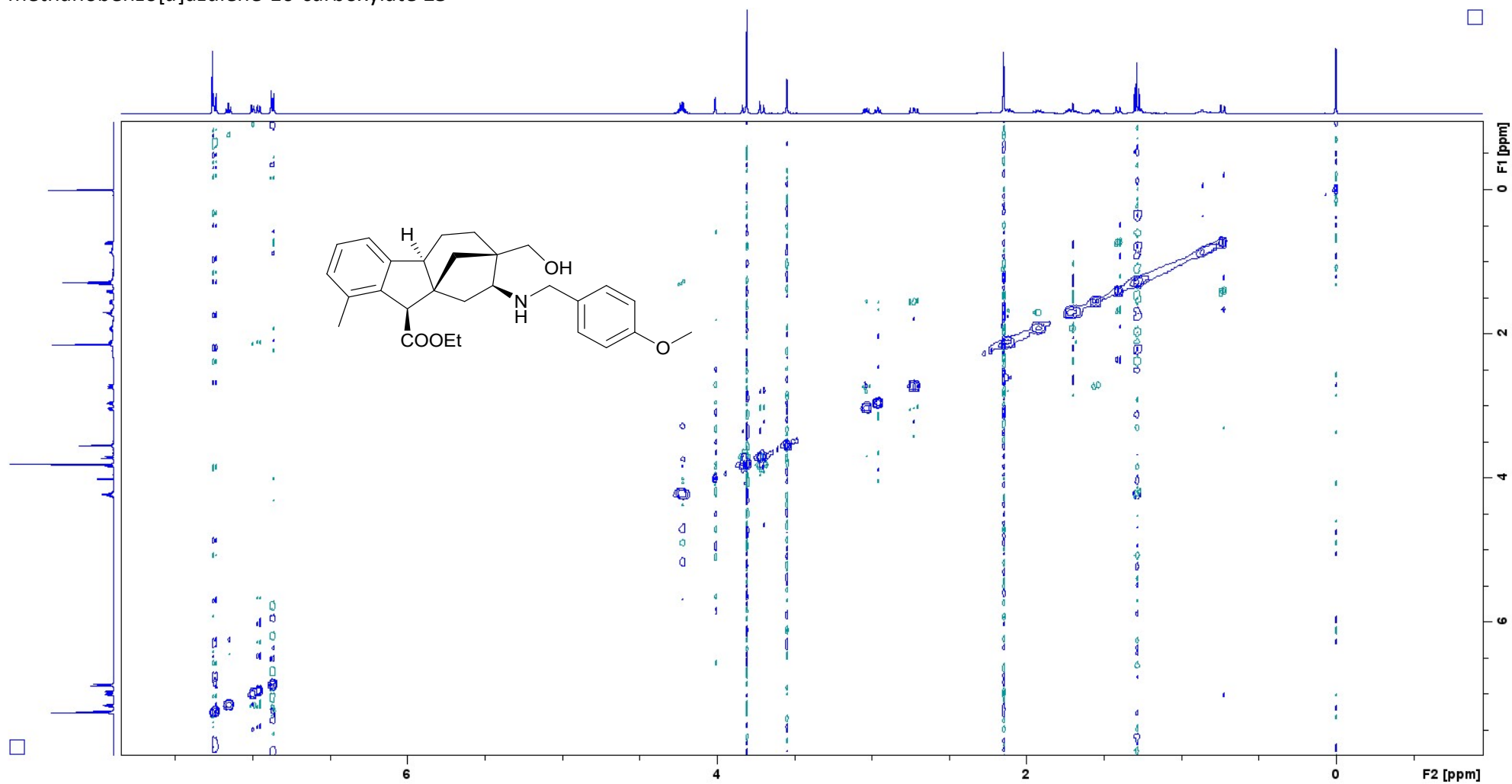
¹³C-NMR of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-8-((4-methoxybenzyl)amino)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **15**



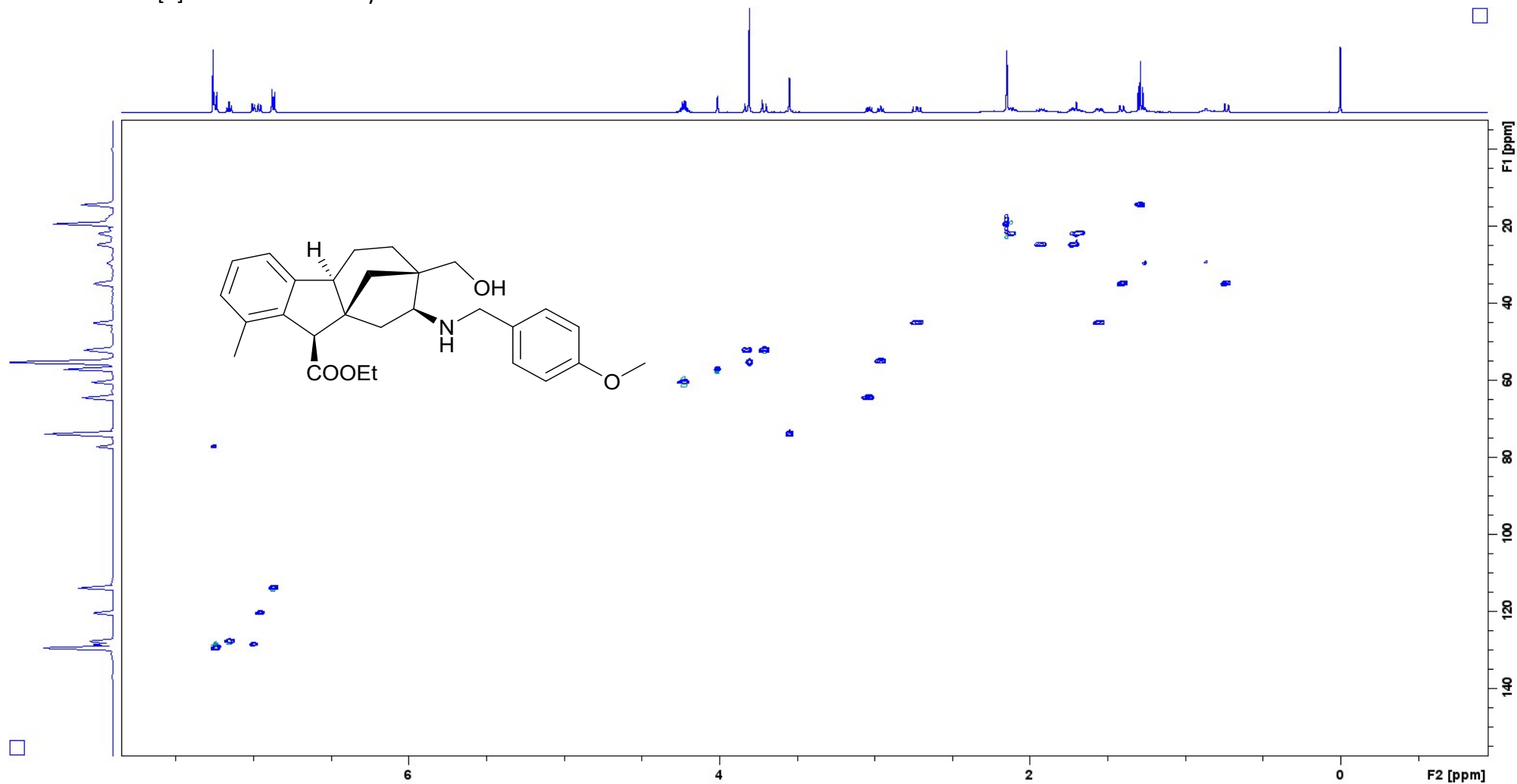
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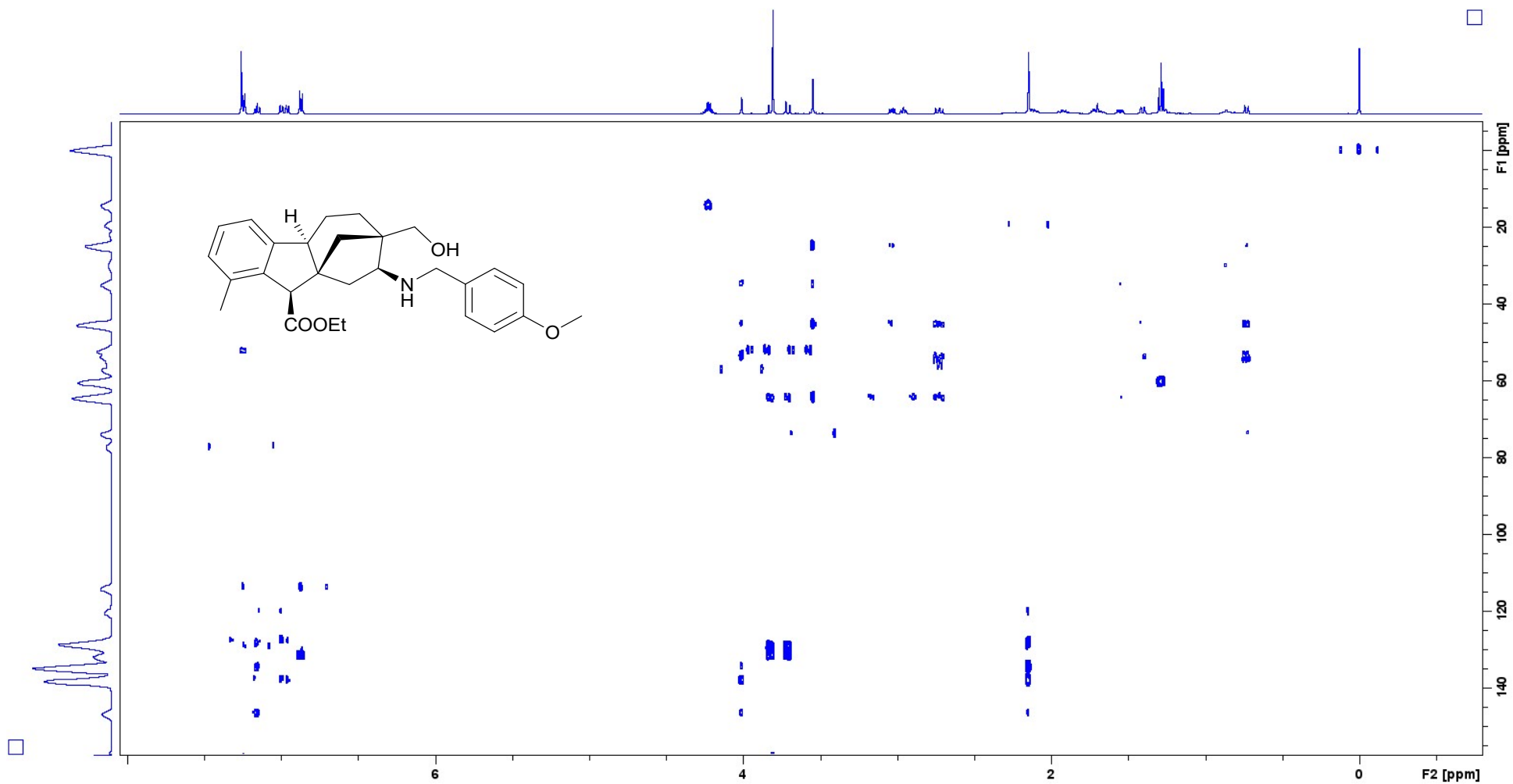
NOESY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-8-((4-methoxybenzyl)amino)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **15**



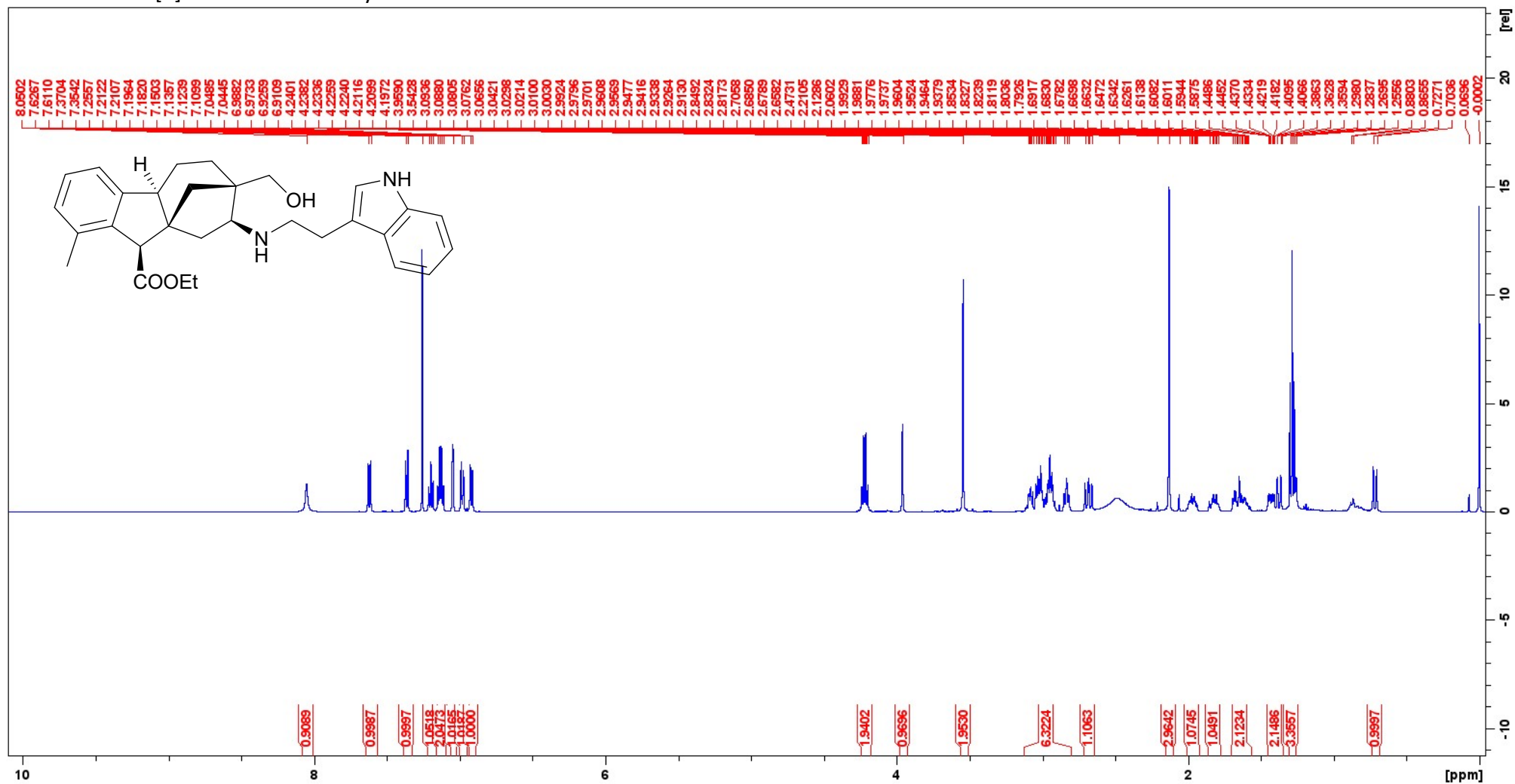
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-8-((4-methoxybenzyl)amino)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **15**



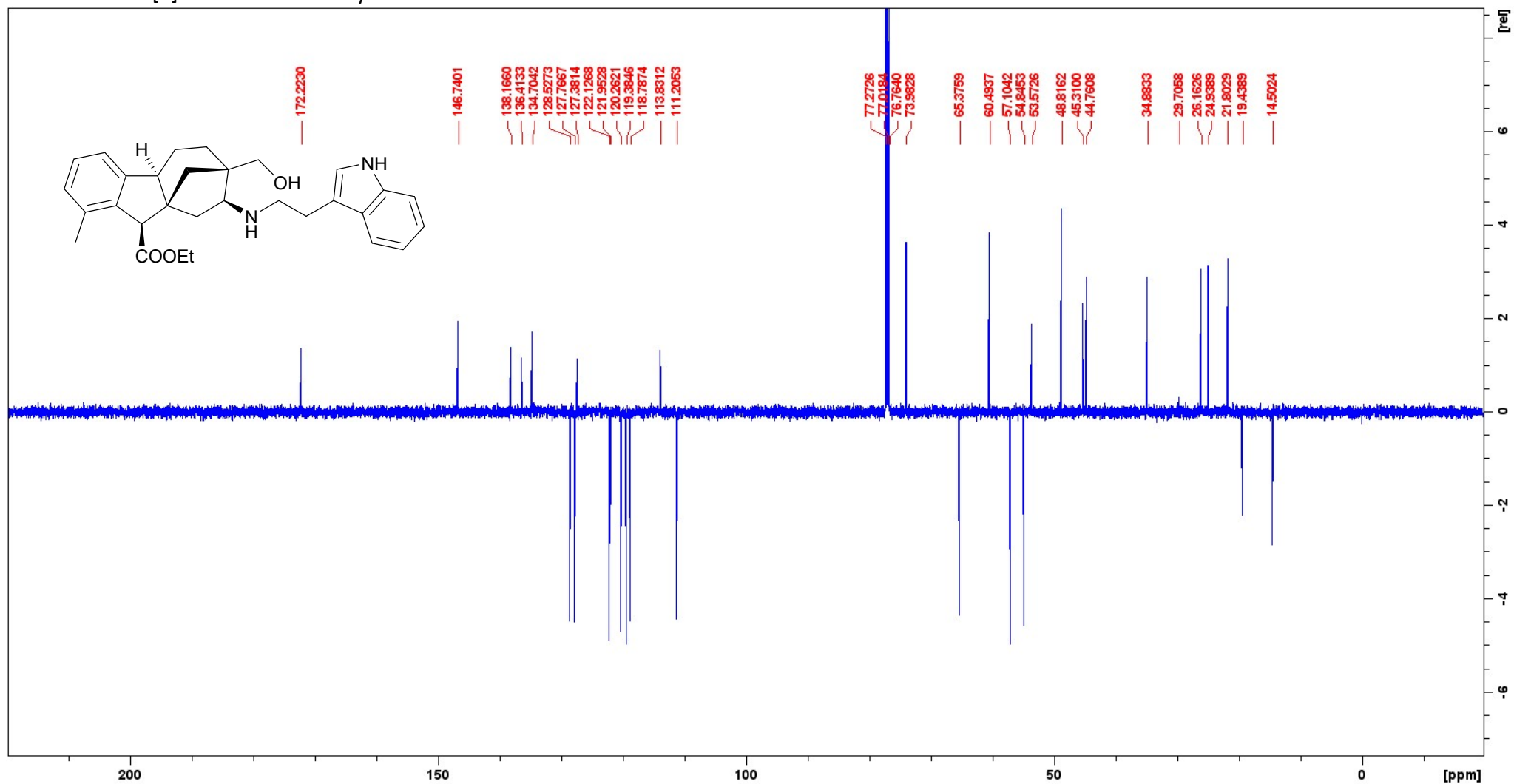
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-8-((4-methoxybenzyl)amino)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **15**



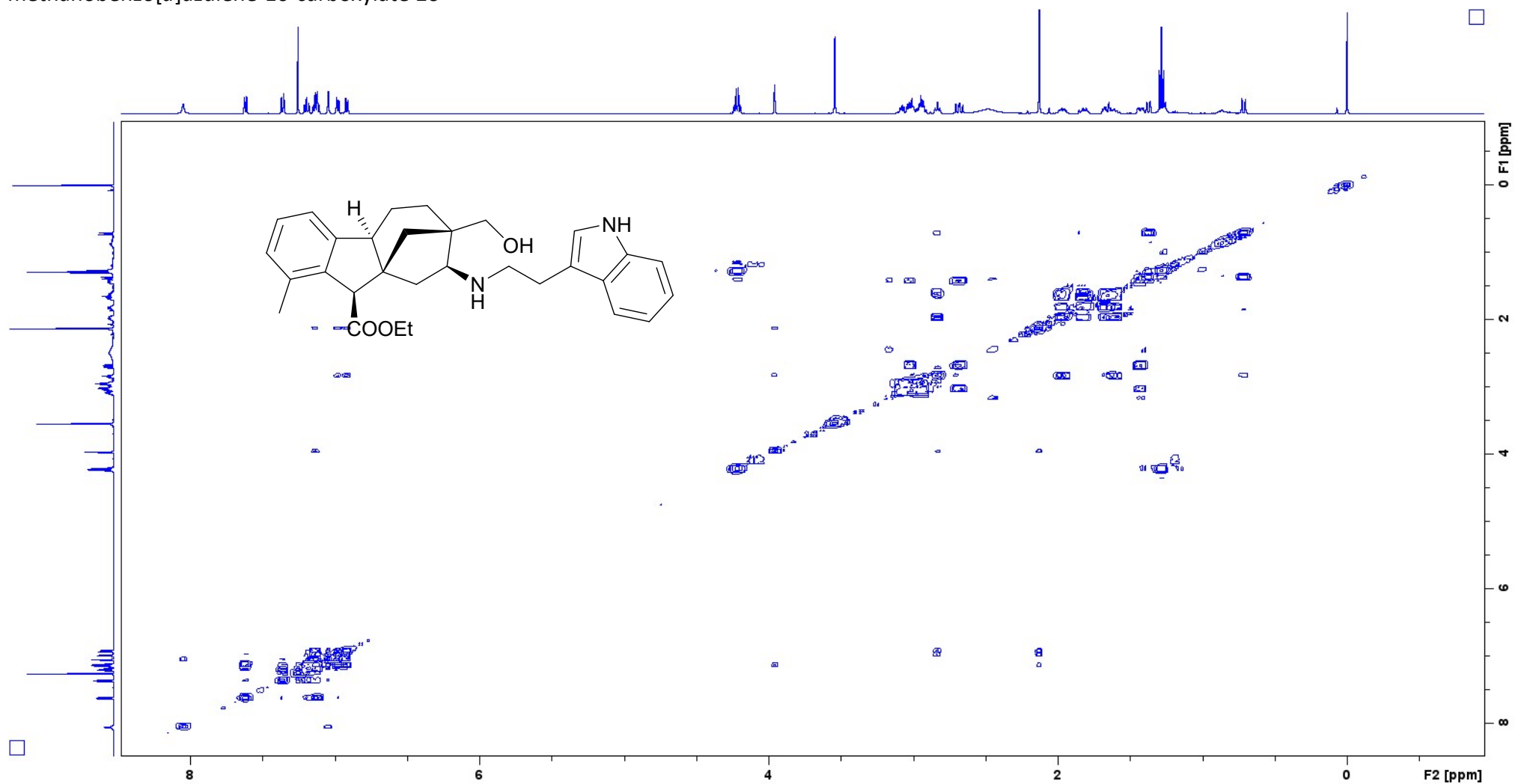
¹H-NMR of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-8-((2-(1*H*-indol-3-yl)ethyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **16**



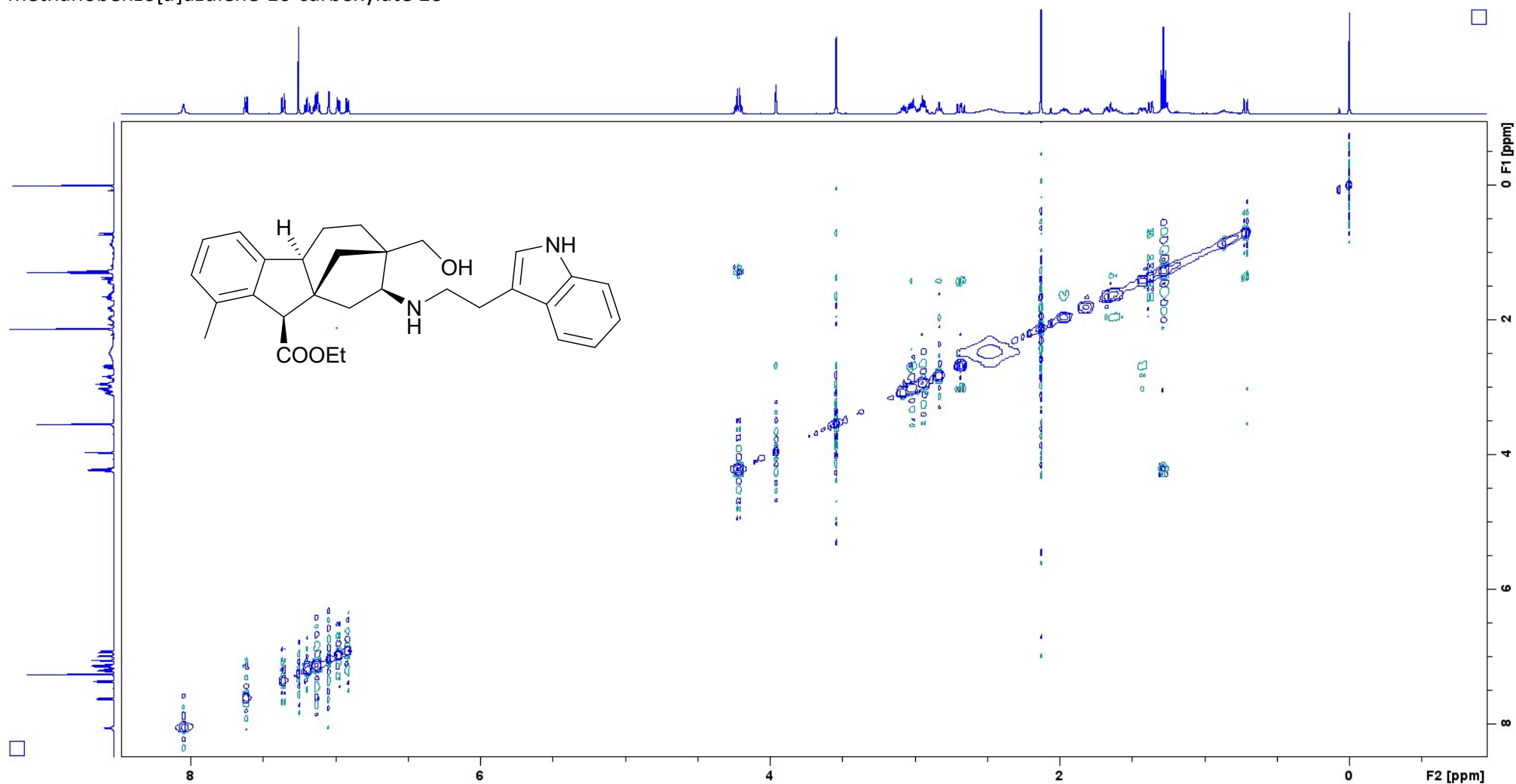
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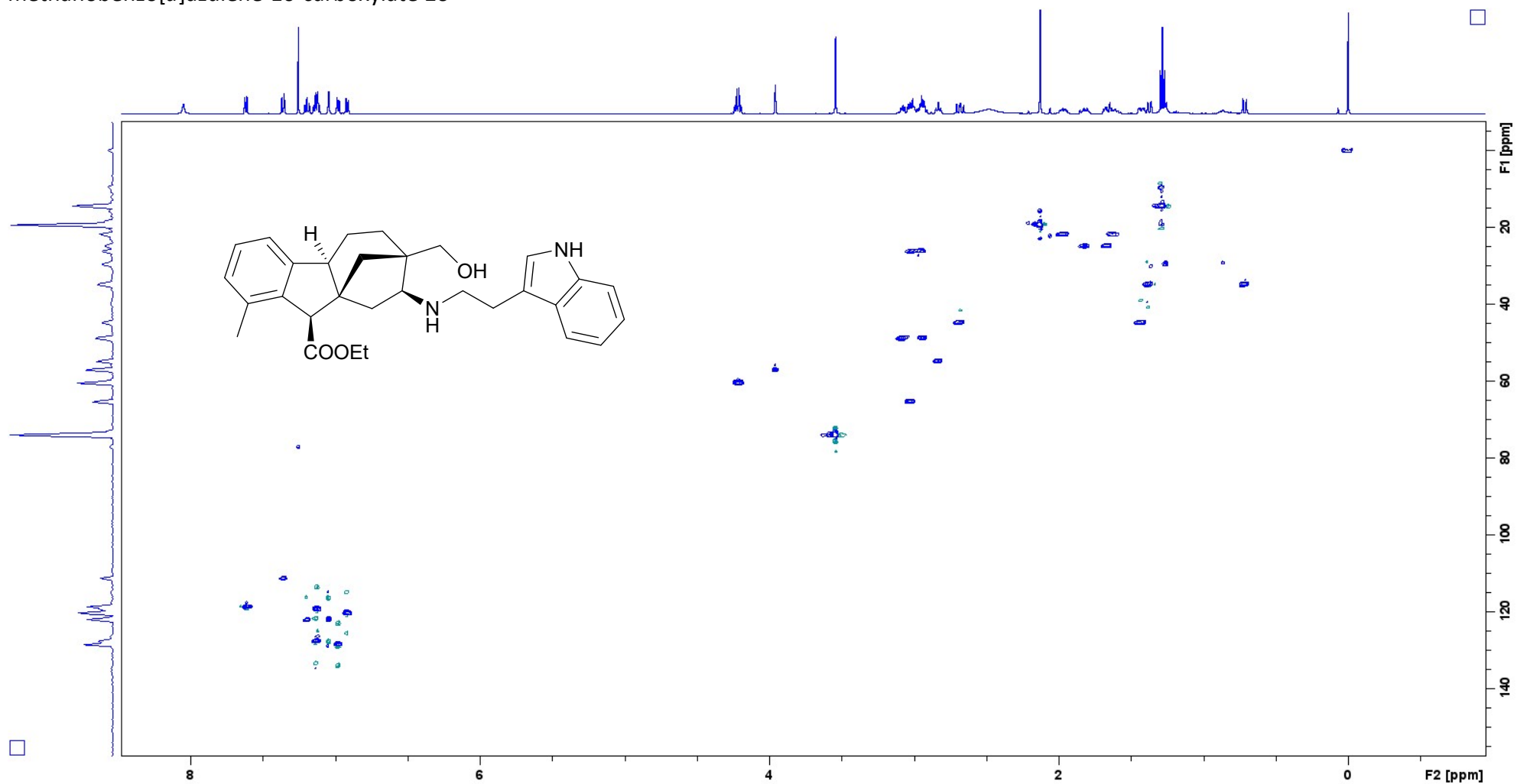
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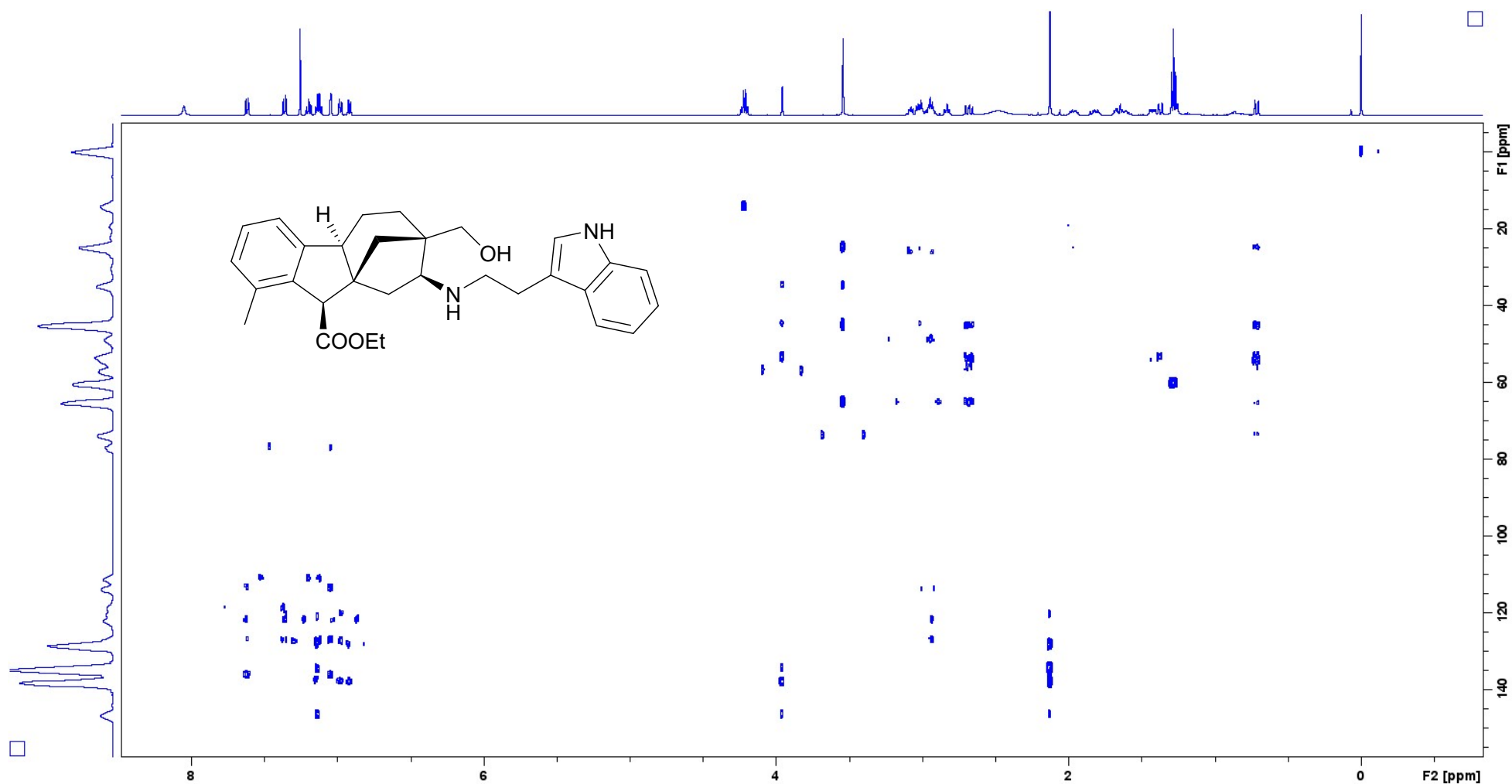
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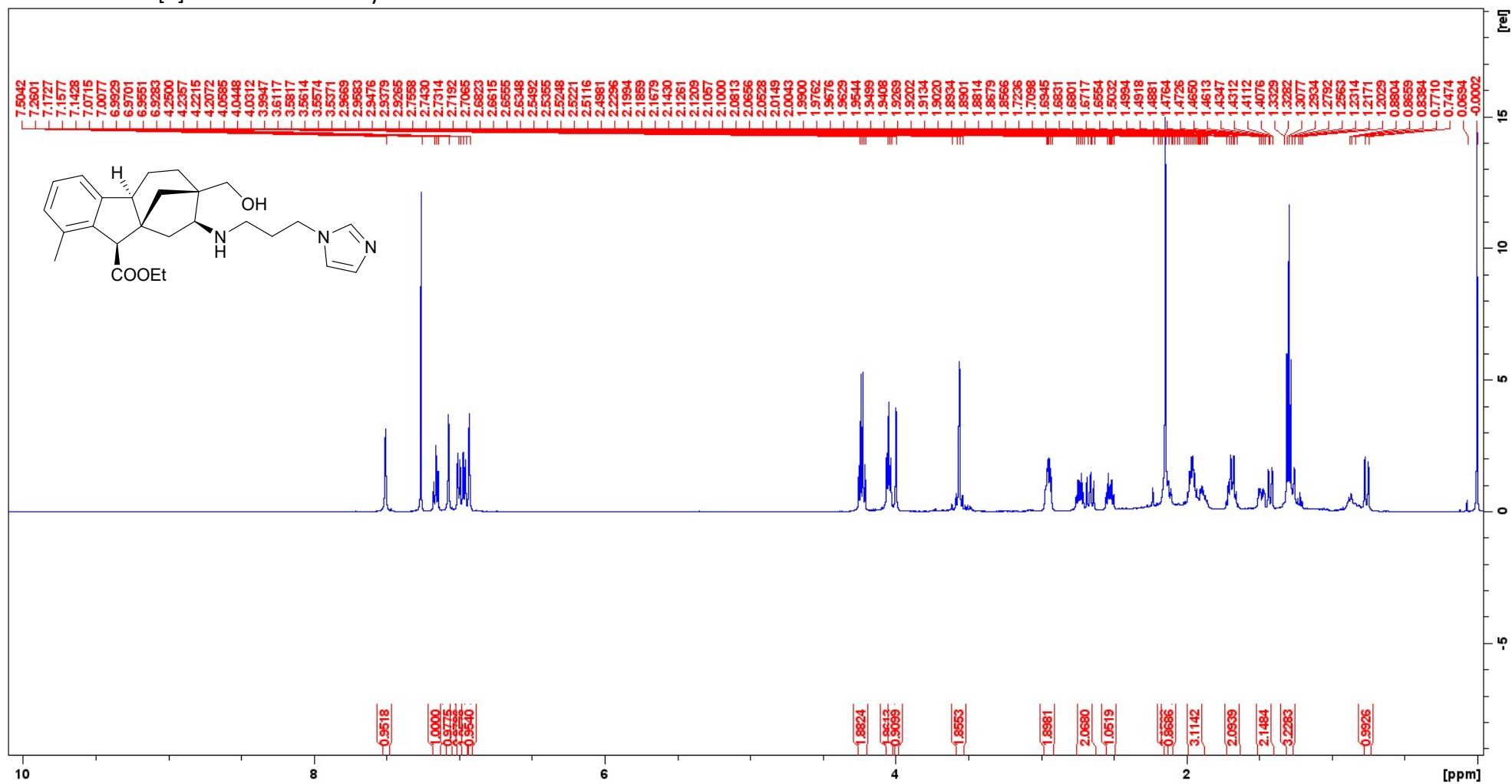
HSQC of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-8-((2-(1*H*-indol-3-yl)ethyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **16**



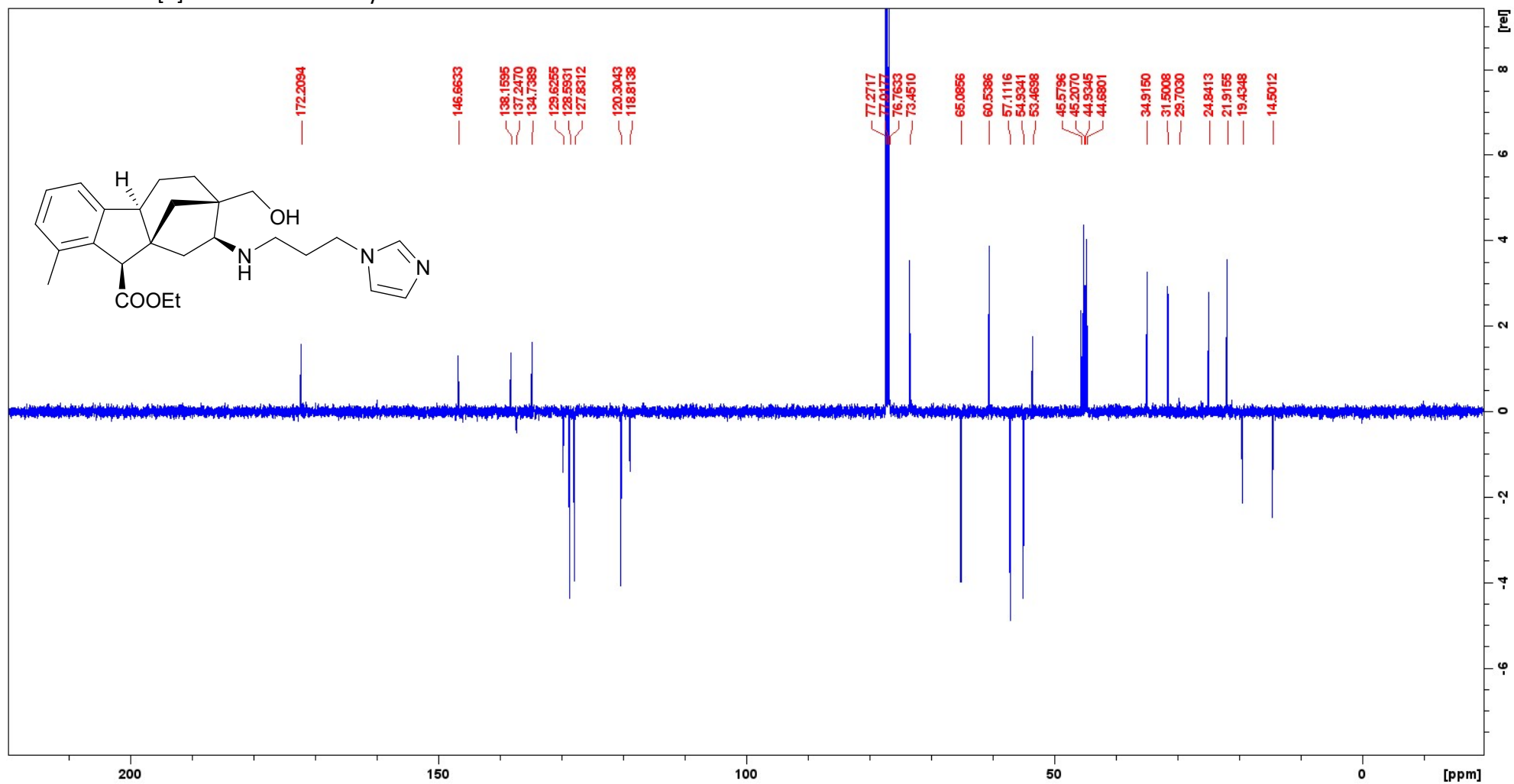
HMBC of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-8-((2-(1*H*-indol-3-yl)ethyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **16**



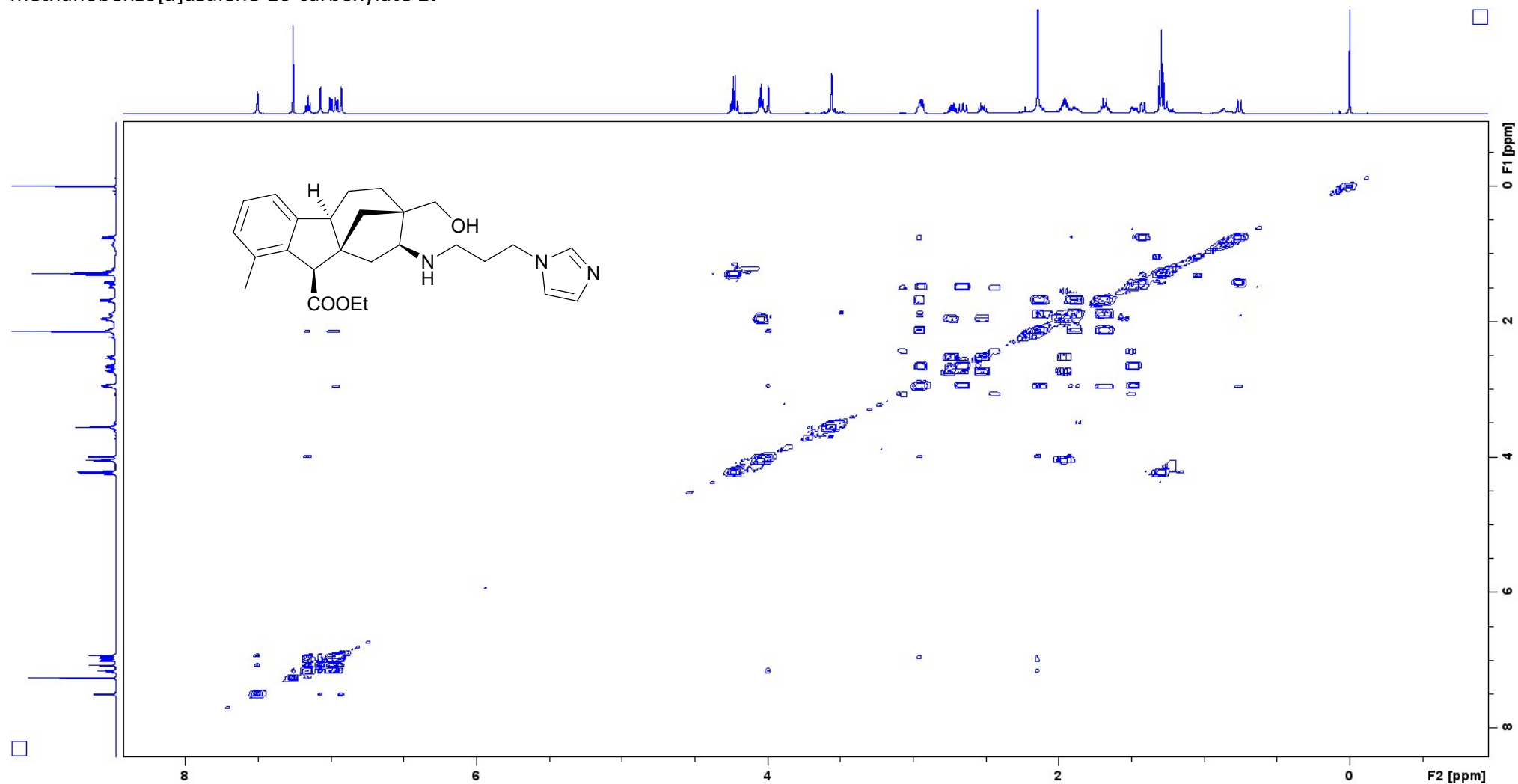
¹H-NMR of ethyl (4b*S*,7*R*,8*S*,9*aS*,10*R*)-8-((3-(1*H*-imidazol-1-yl)propyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **17**



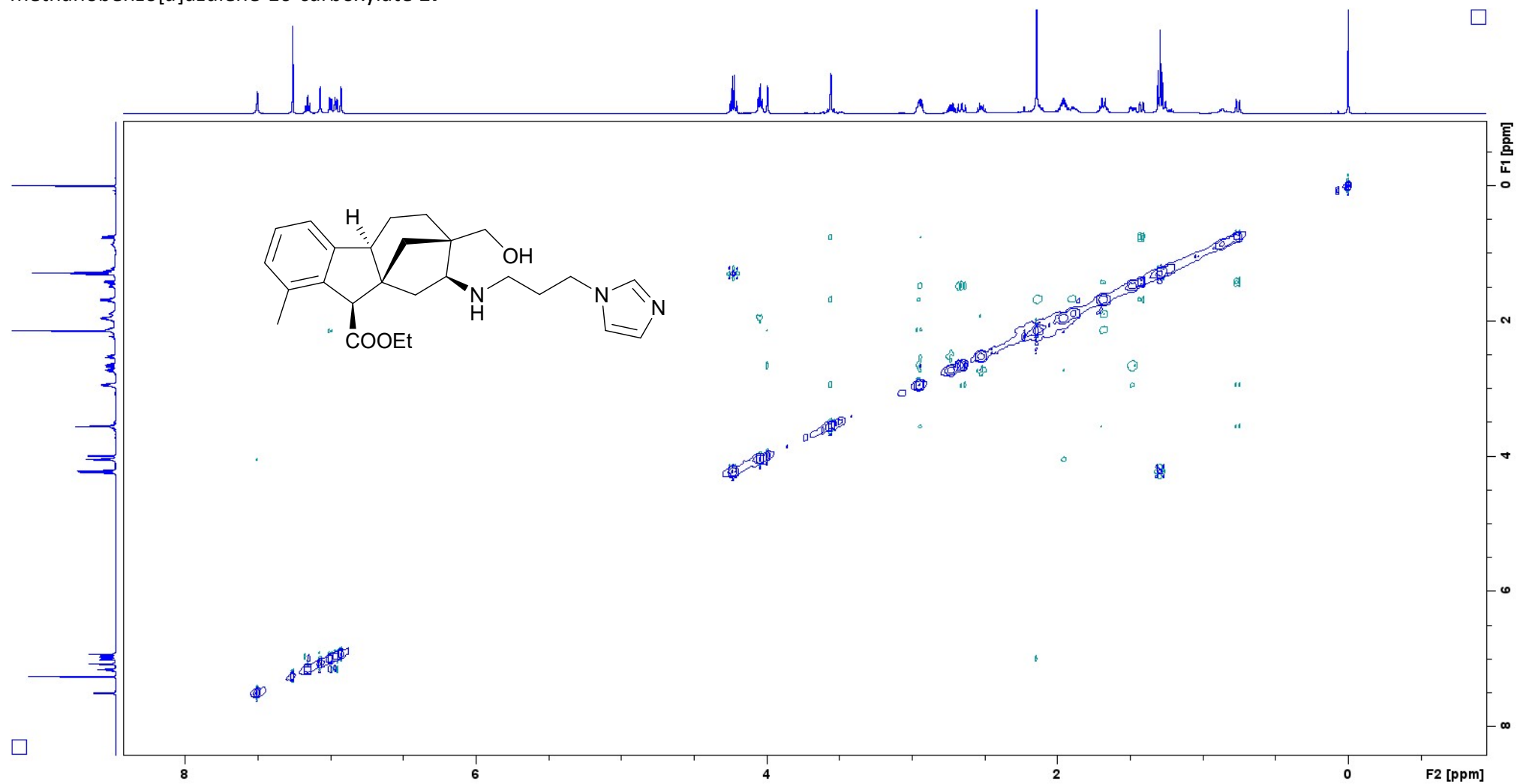
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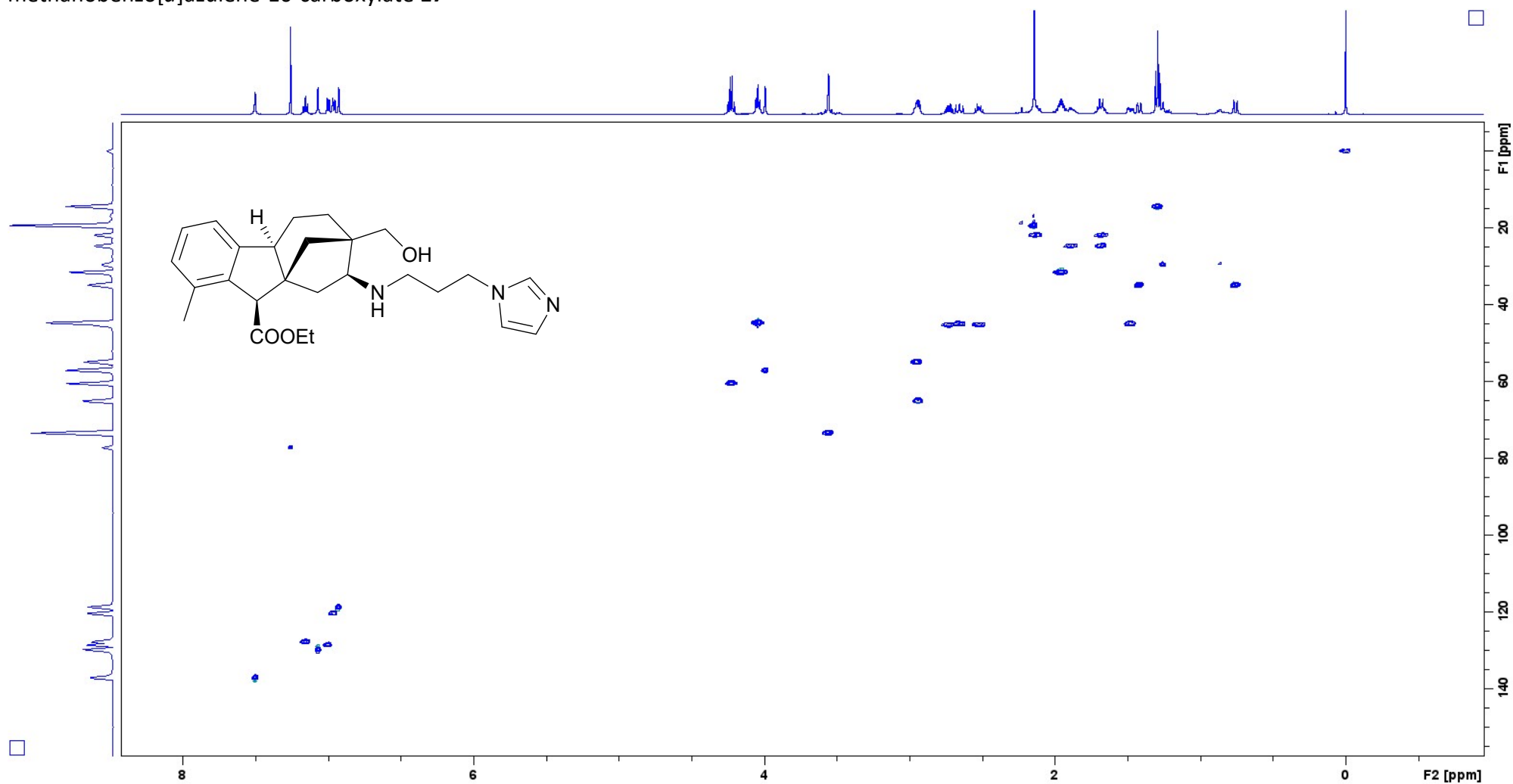
COSY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-8-((3-(1*H*-imidazol-1-yl)propyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **17**



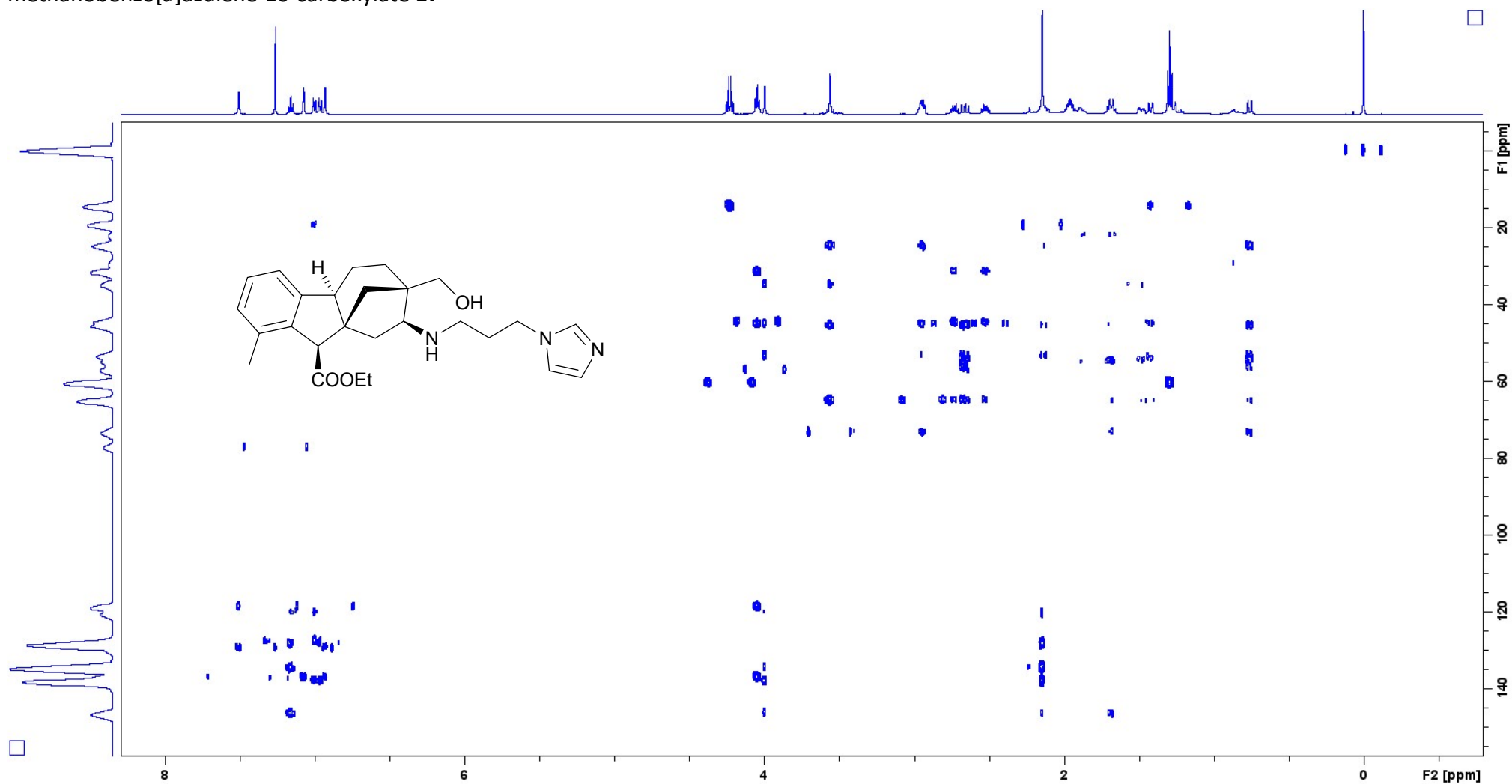
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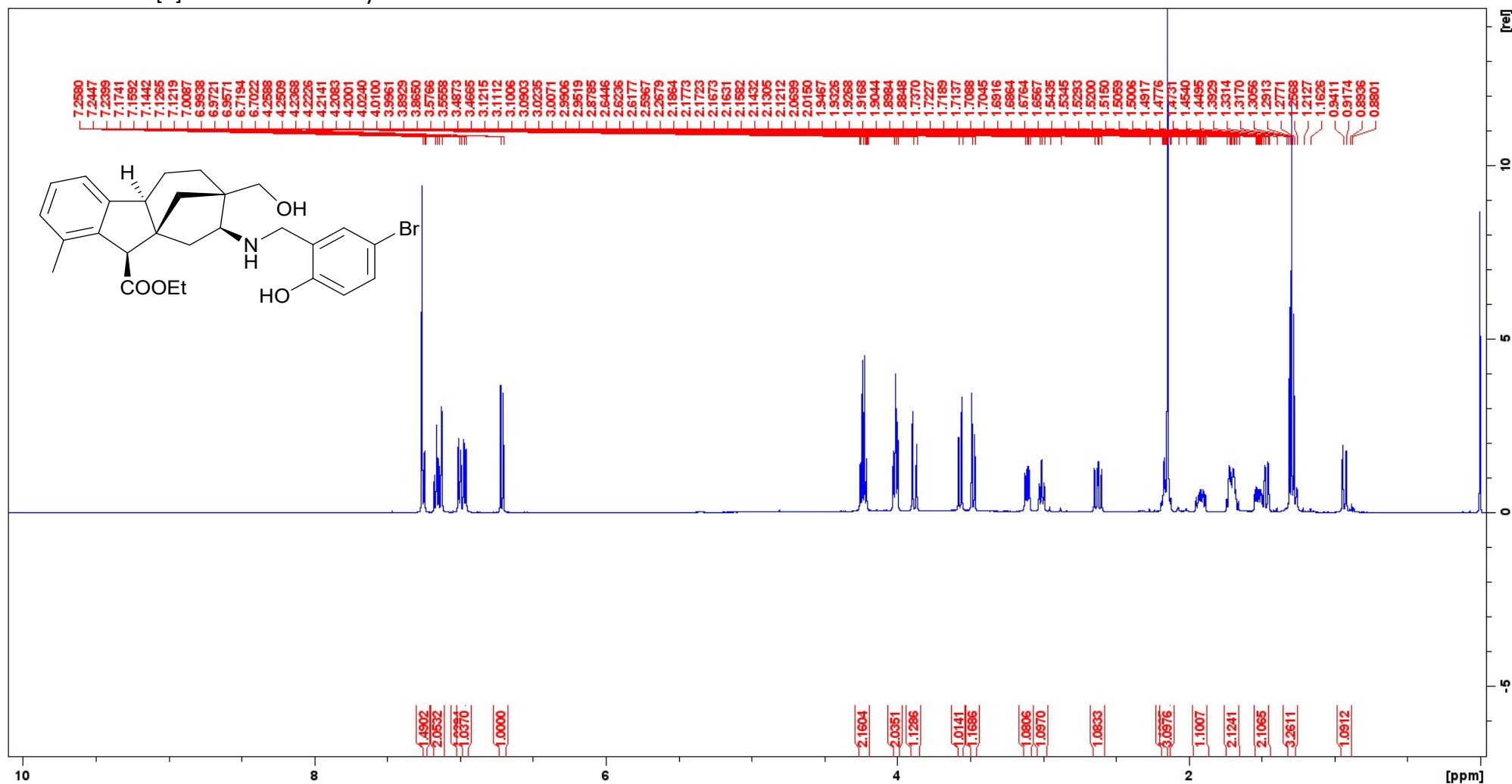
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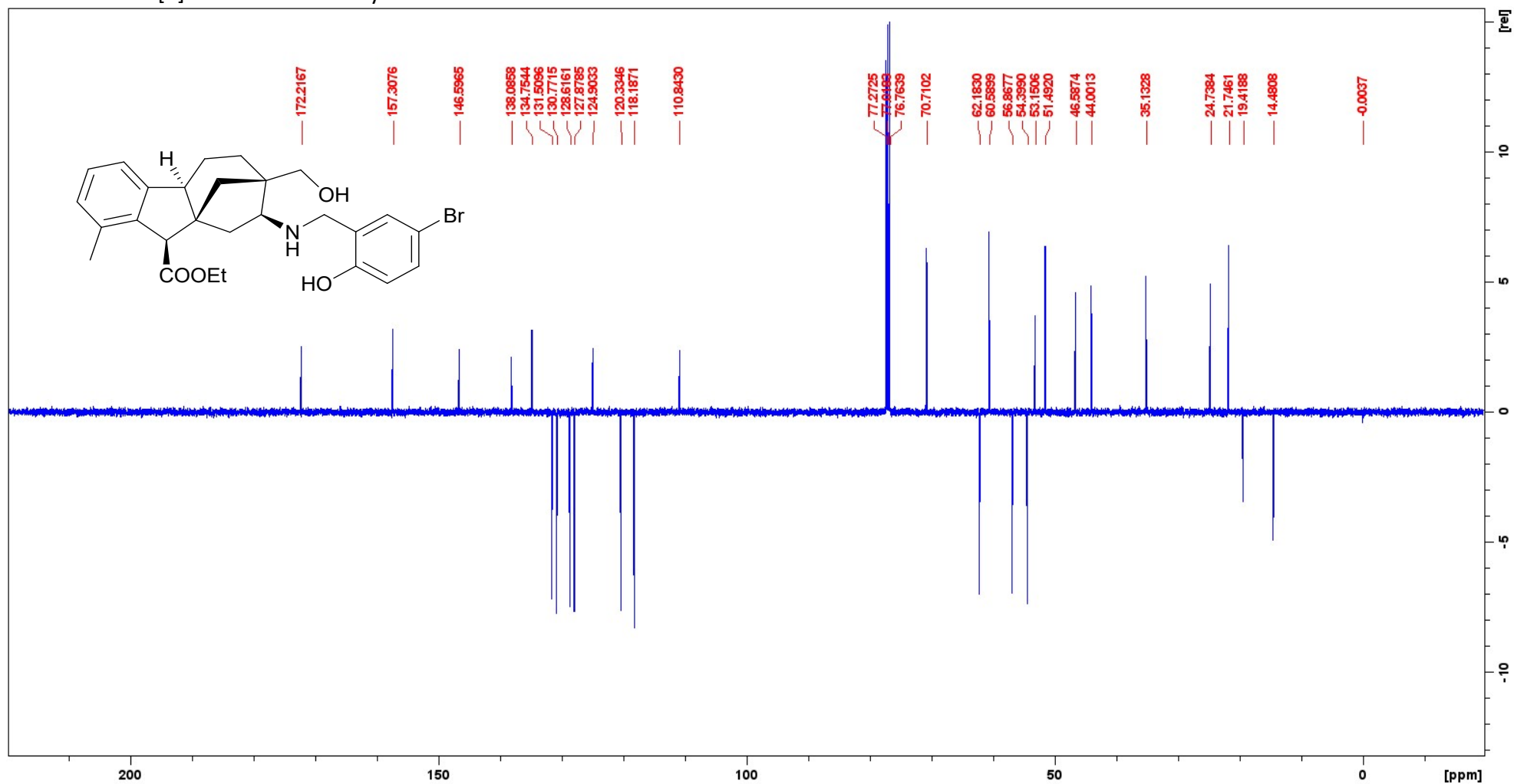
HMBC of ethyl (4*b*S,7*R*,8*S*,9*a*S,10*R*)-8-((3-(1*H*-imidazol-1-yl)propyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **17**



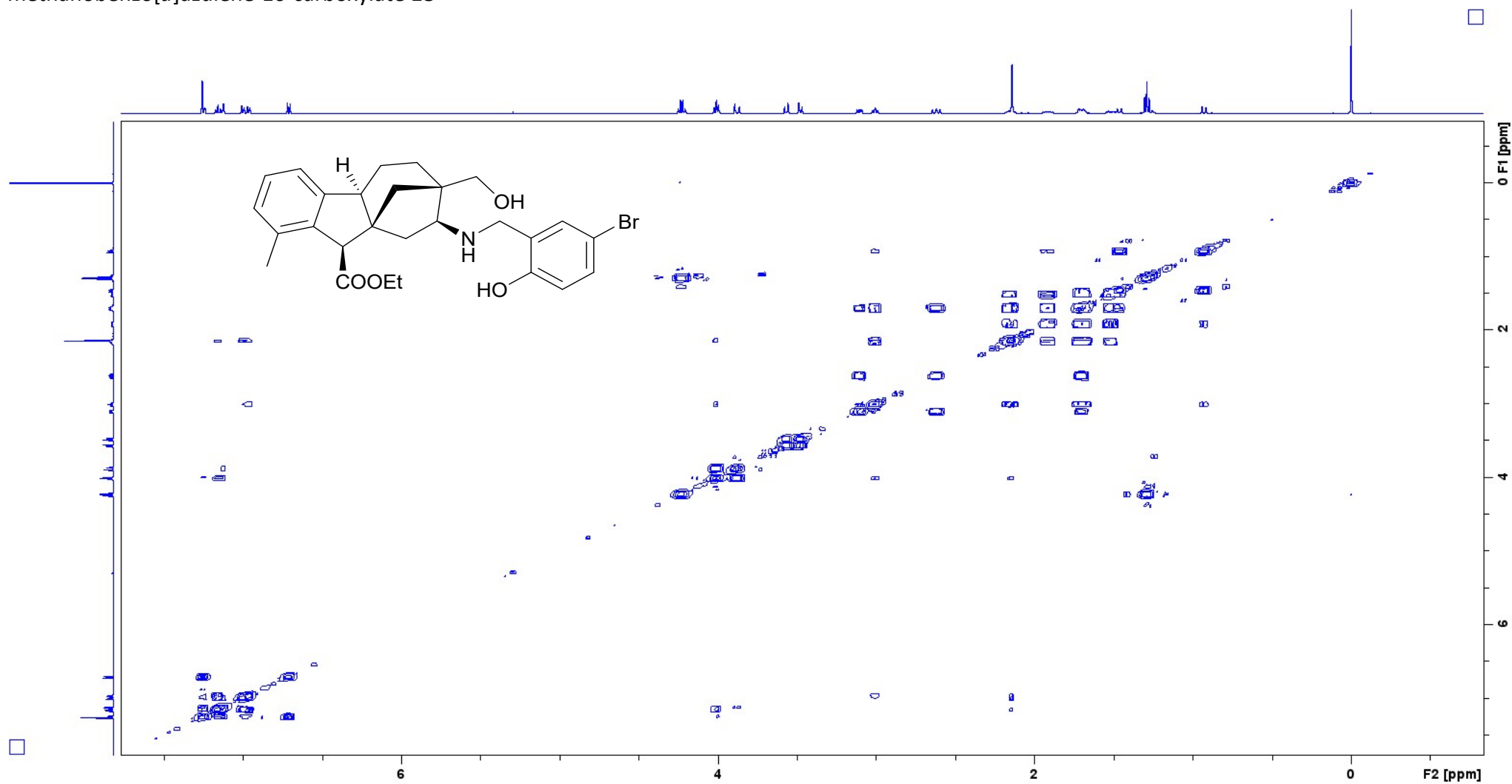
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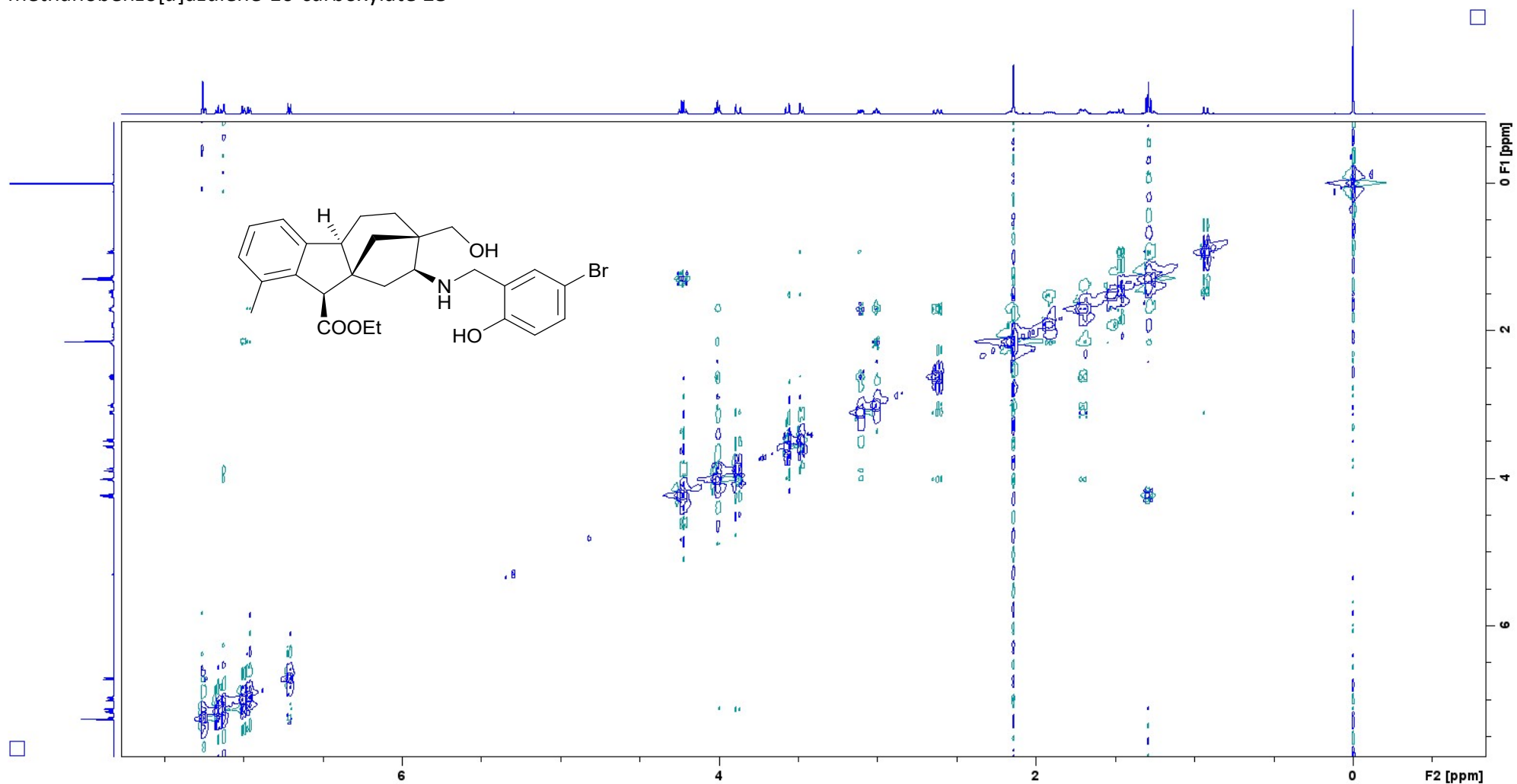
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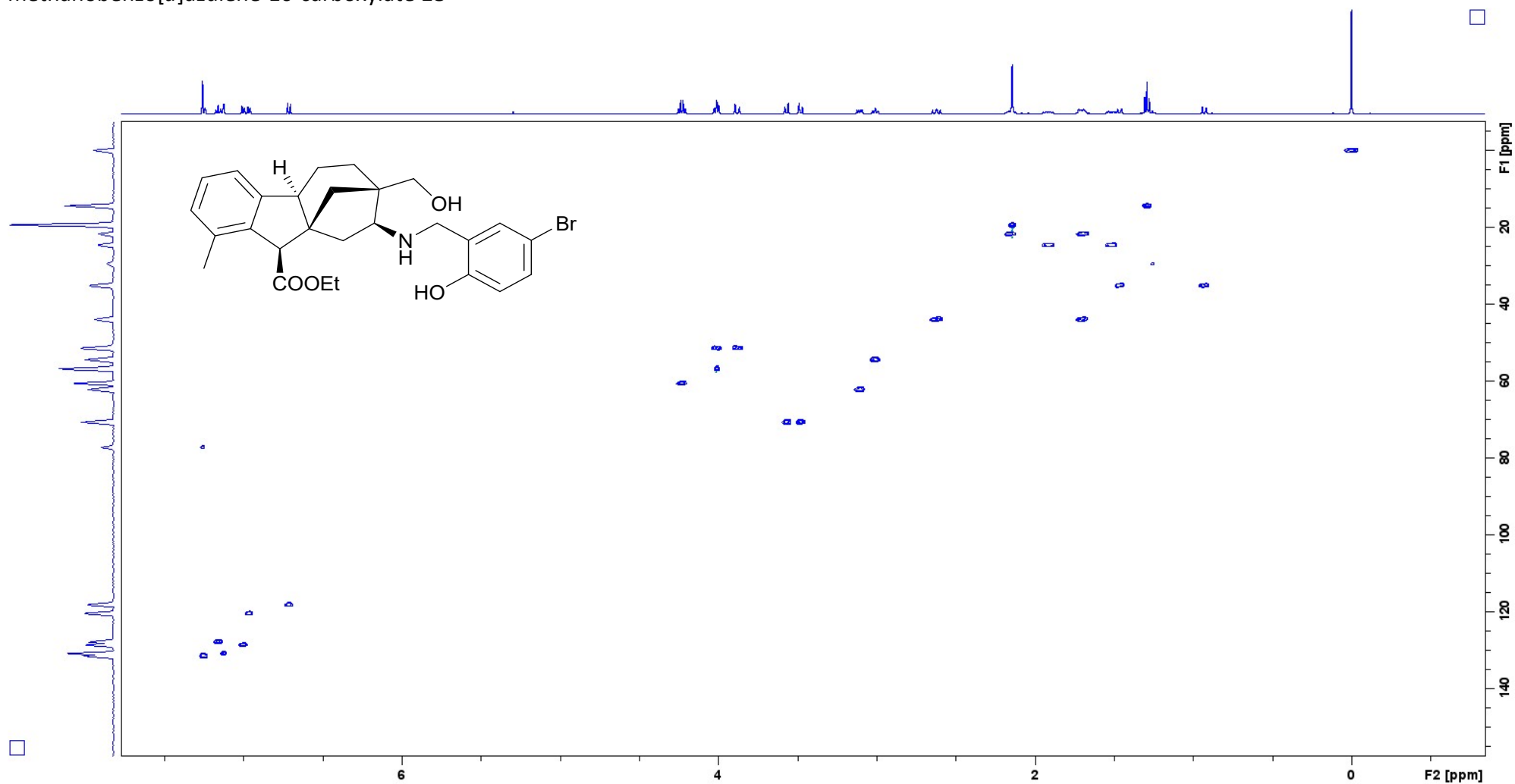
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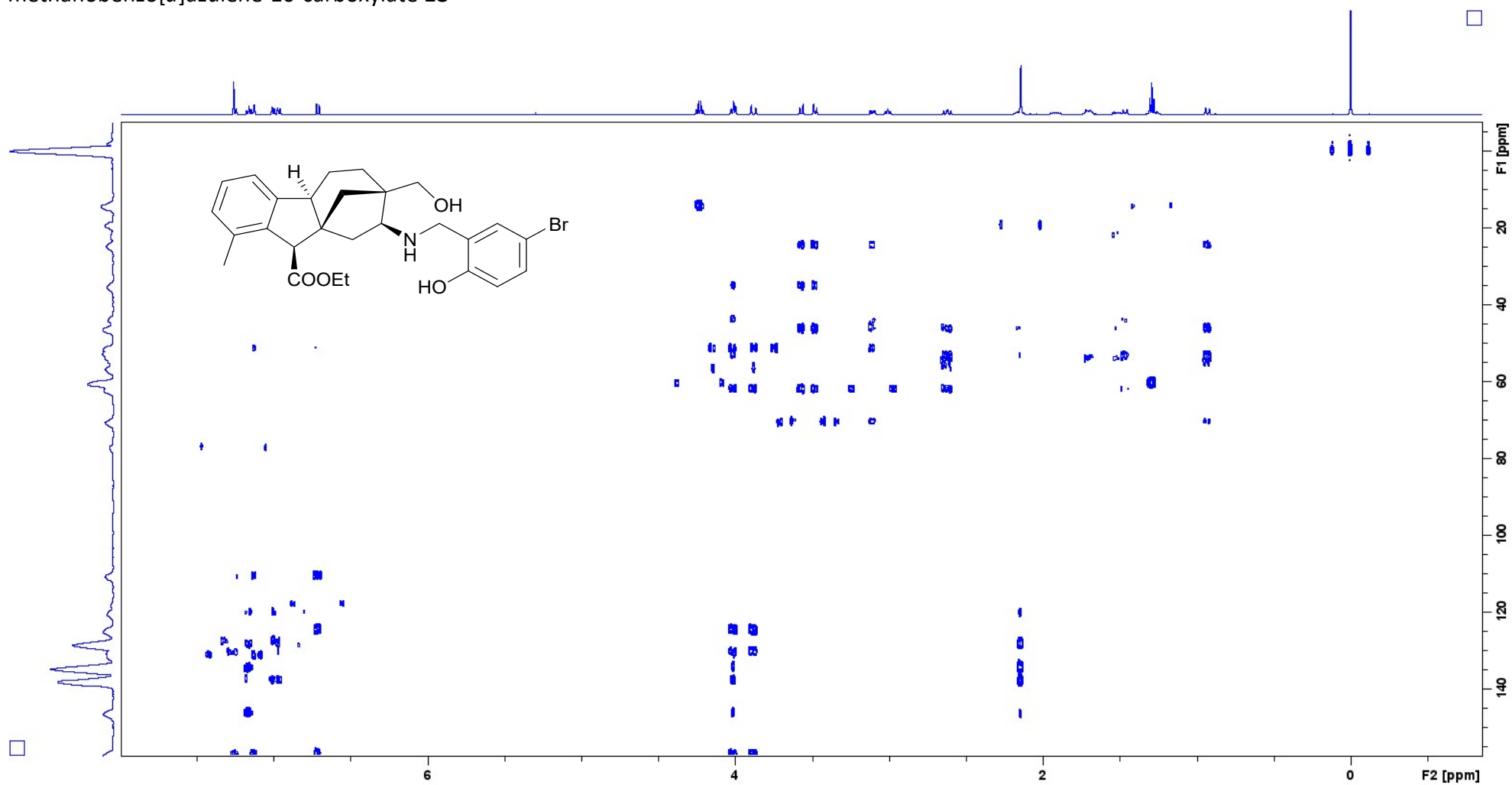
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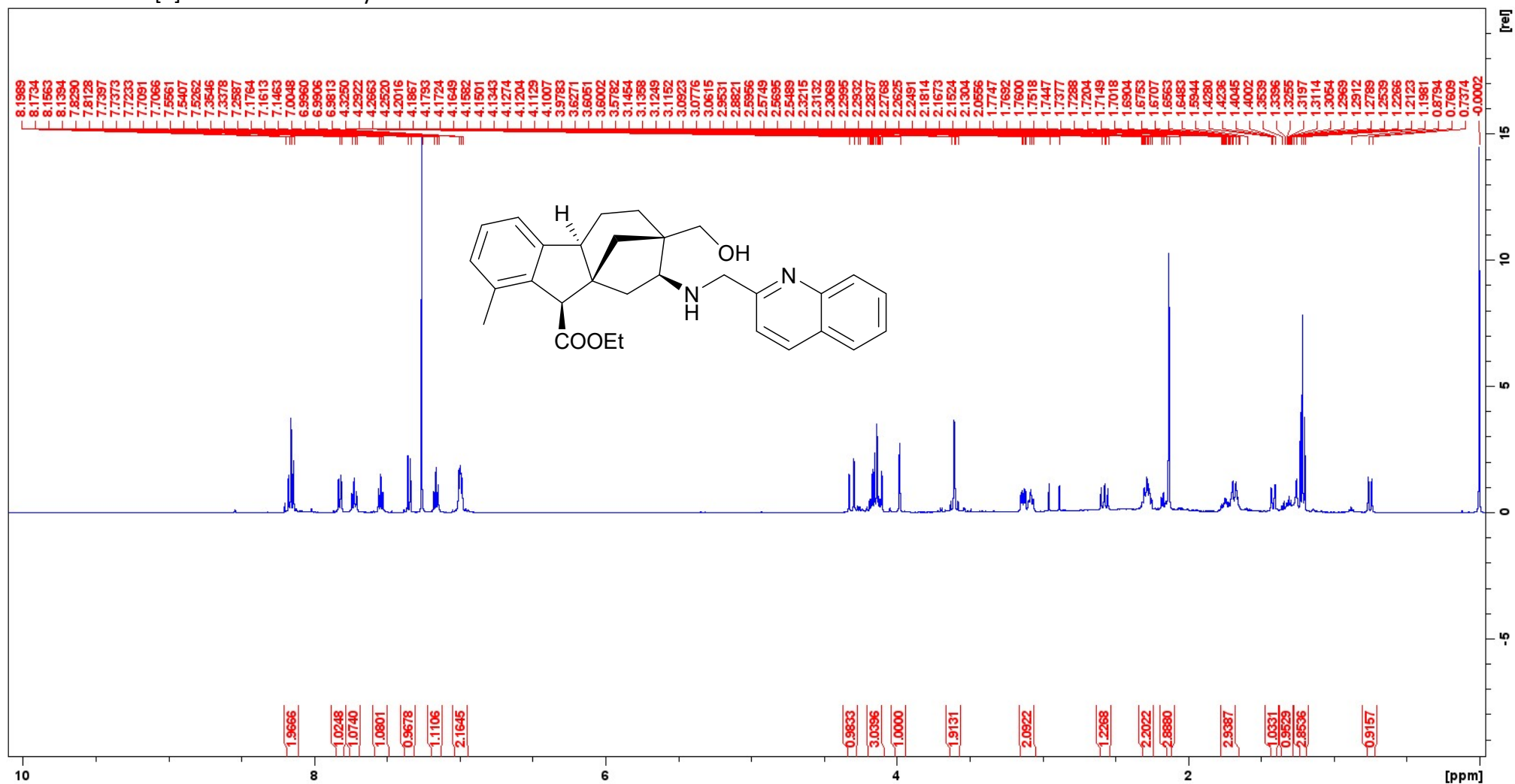
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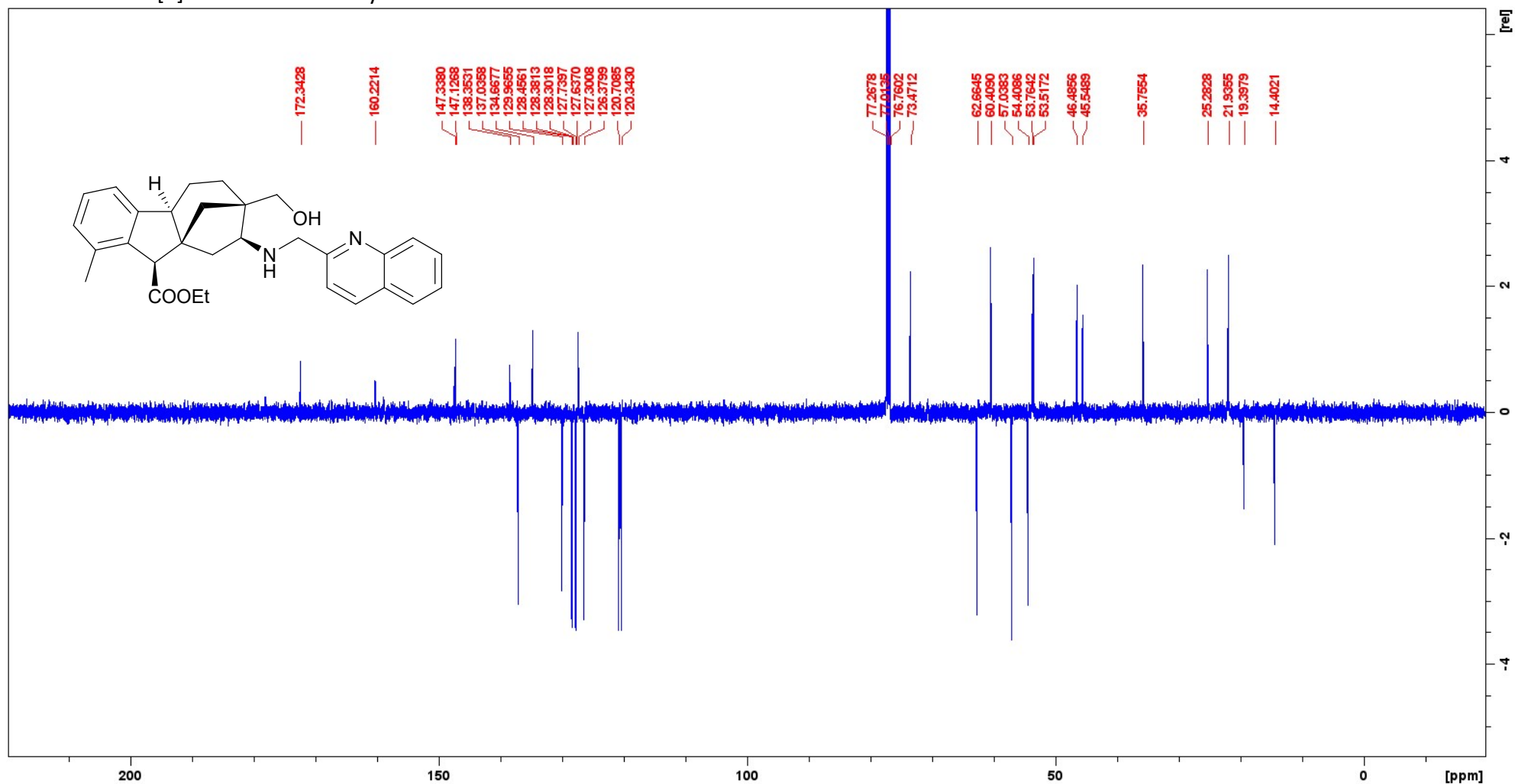
HMBC of ethyl (4*b*,7*R*,8*S*,9*a*,10*R*)-8-((5-bromo-2-hydroxybenzyl)amino)-7-(hydroxymethyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **18**



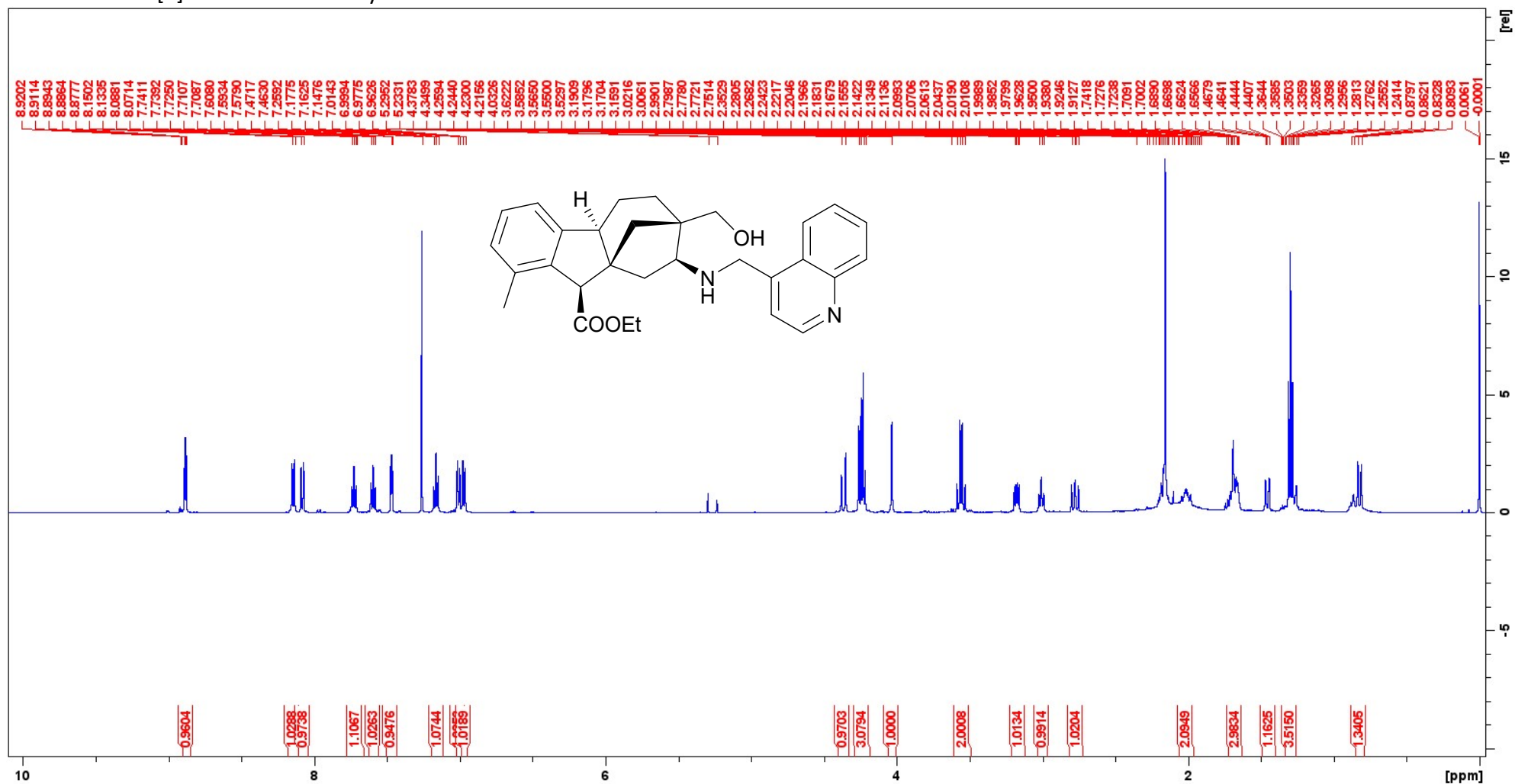
¹H-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-2-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **19**



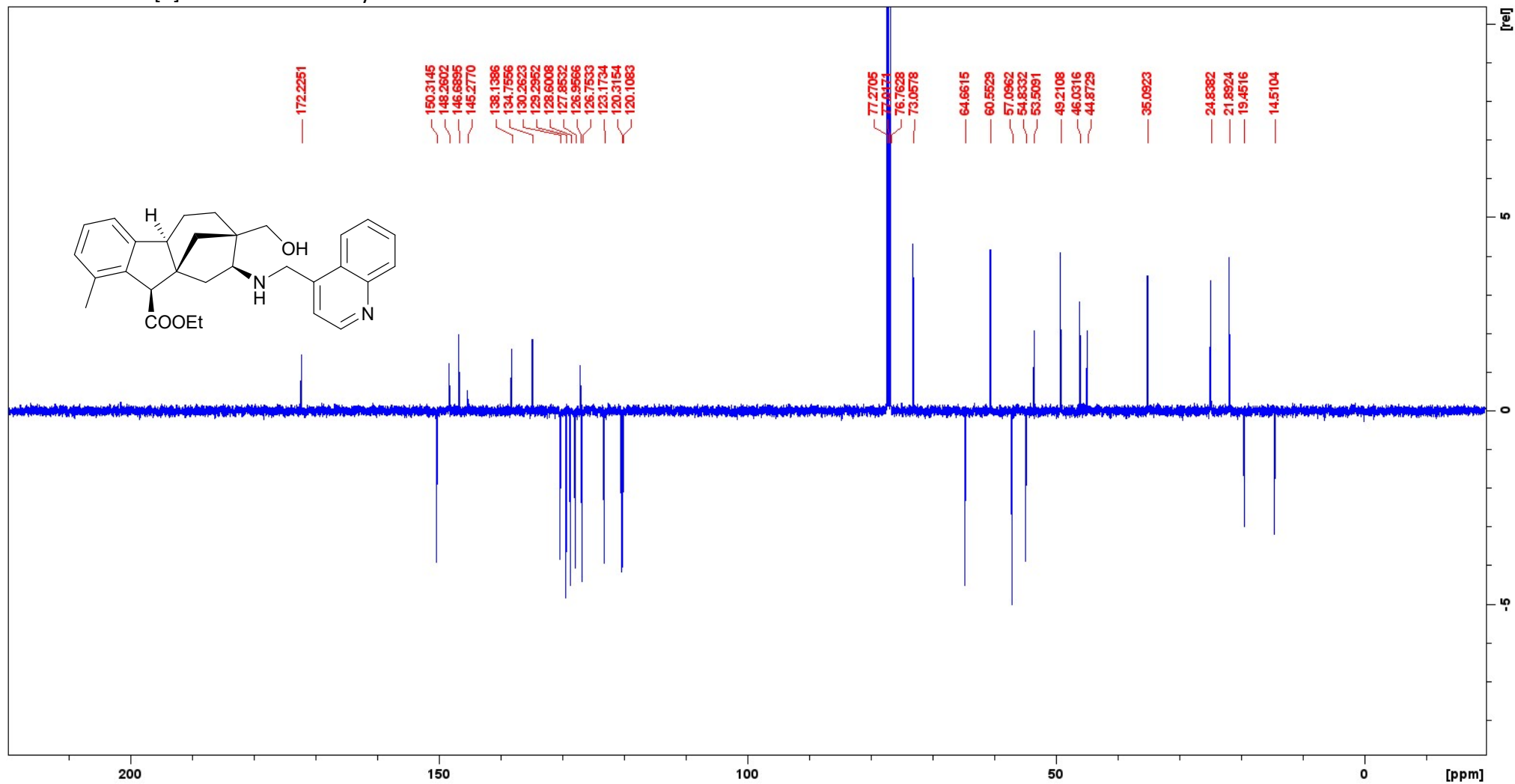
¹³C-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-2-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **19**



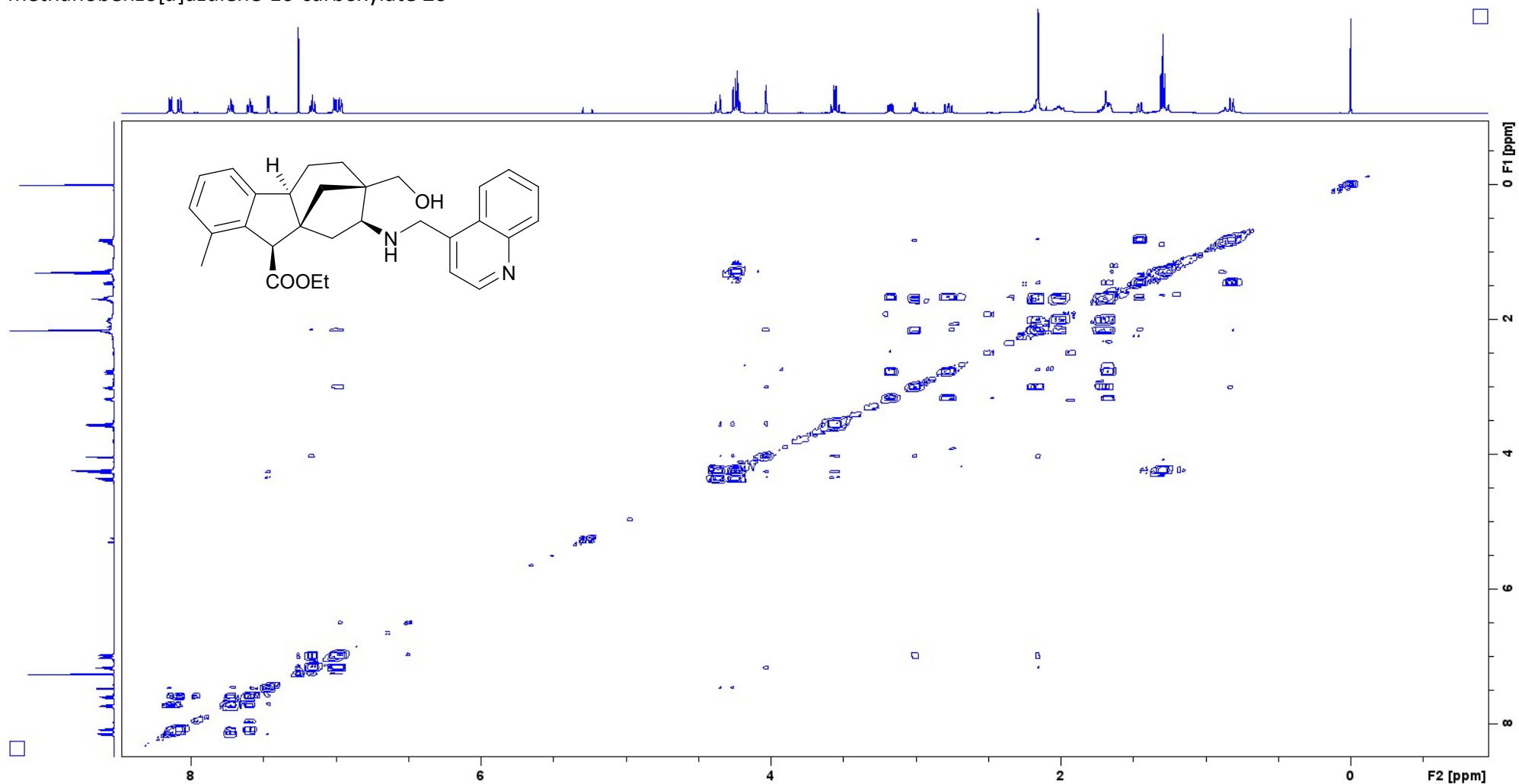
¹H-NMR of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **20**



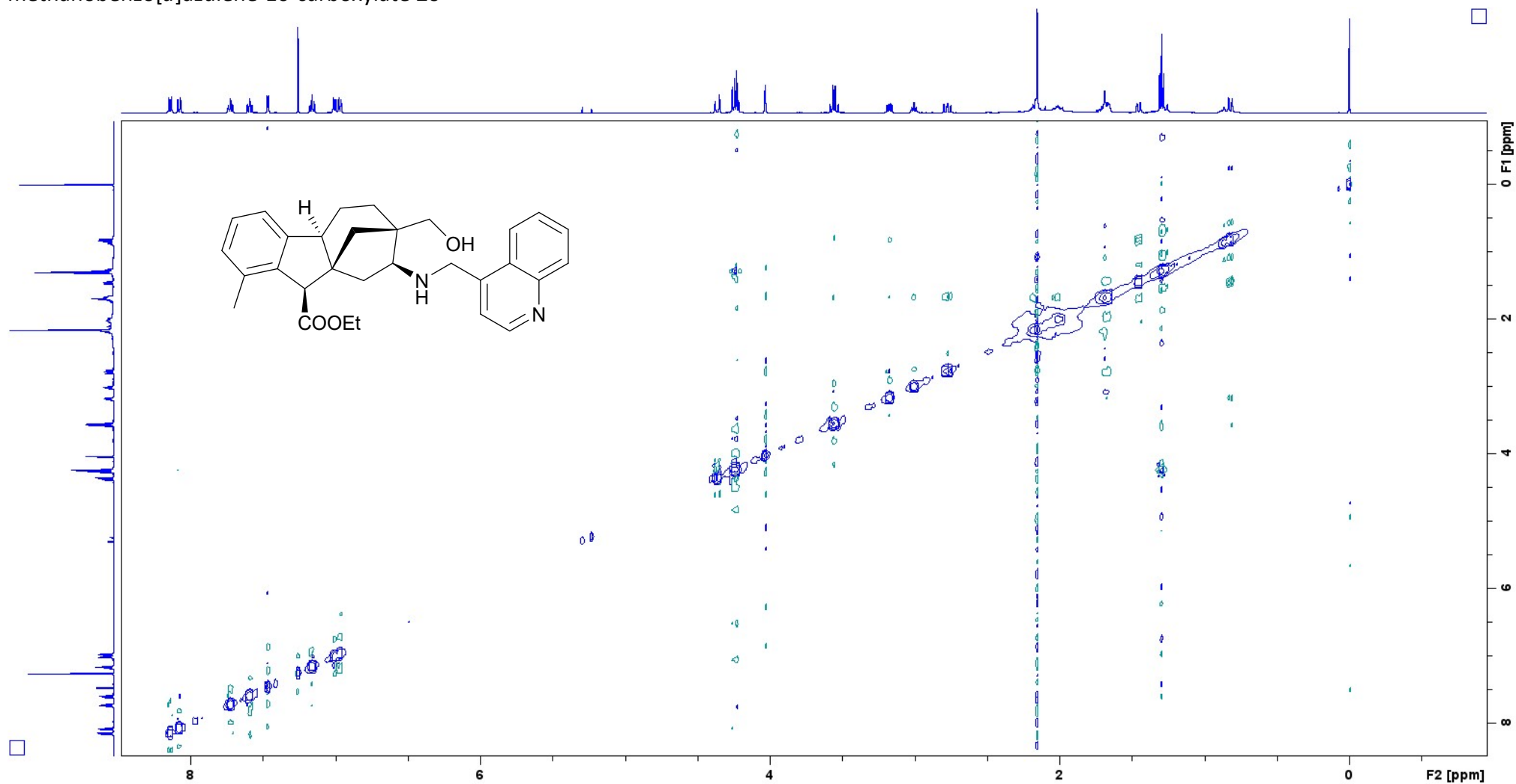
¹³C-NMR of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **20**



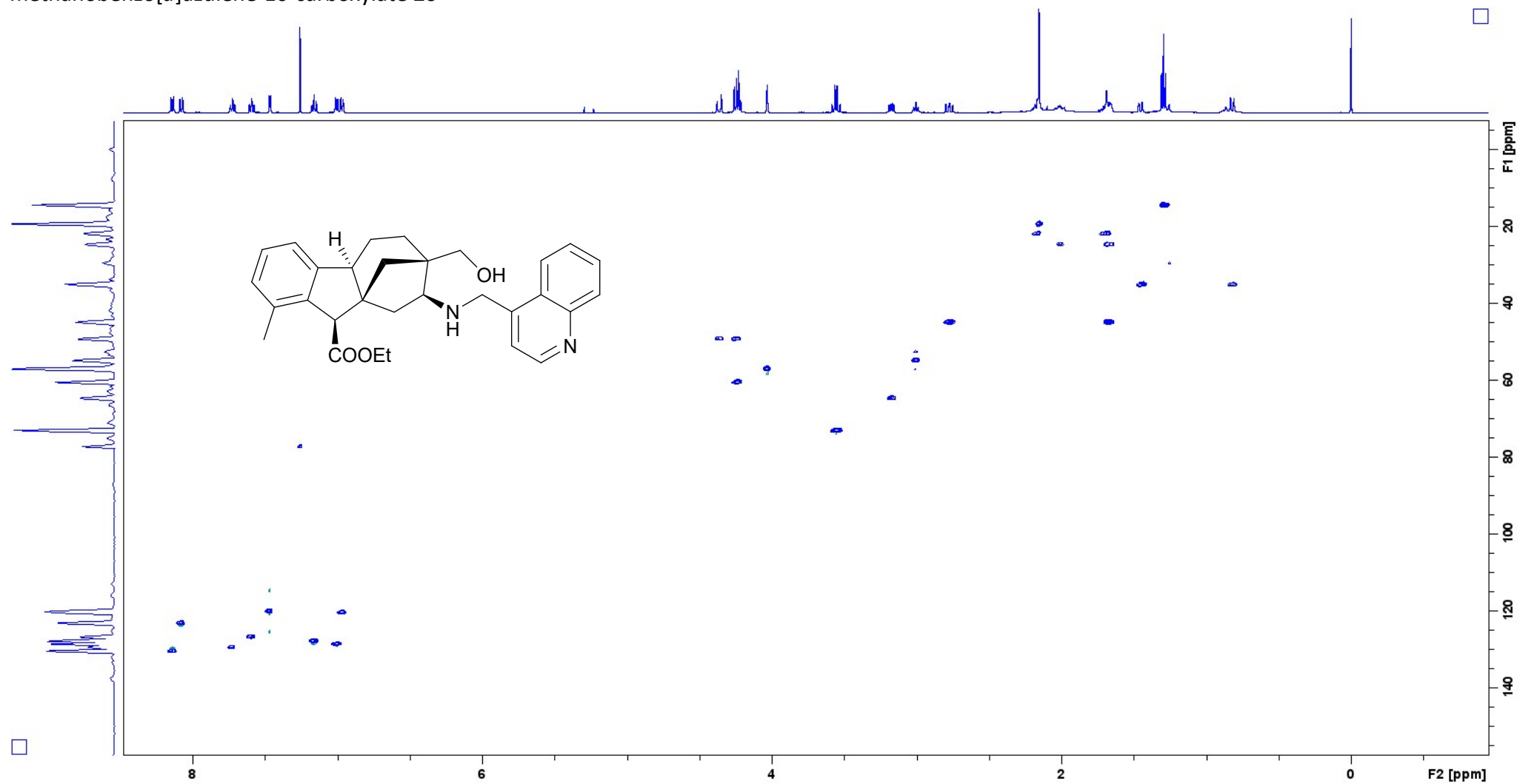
COSY of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **20**



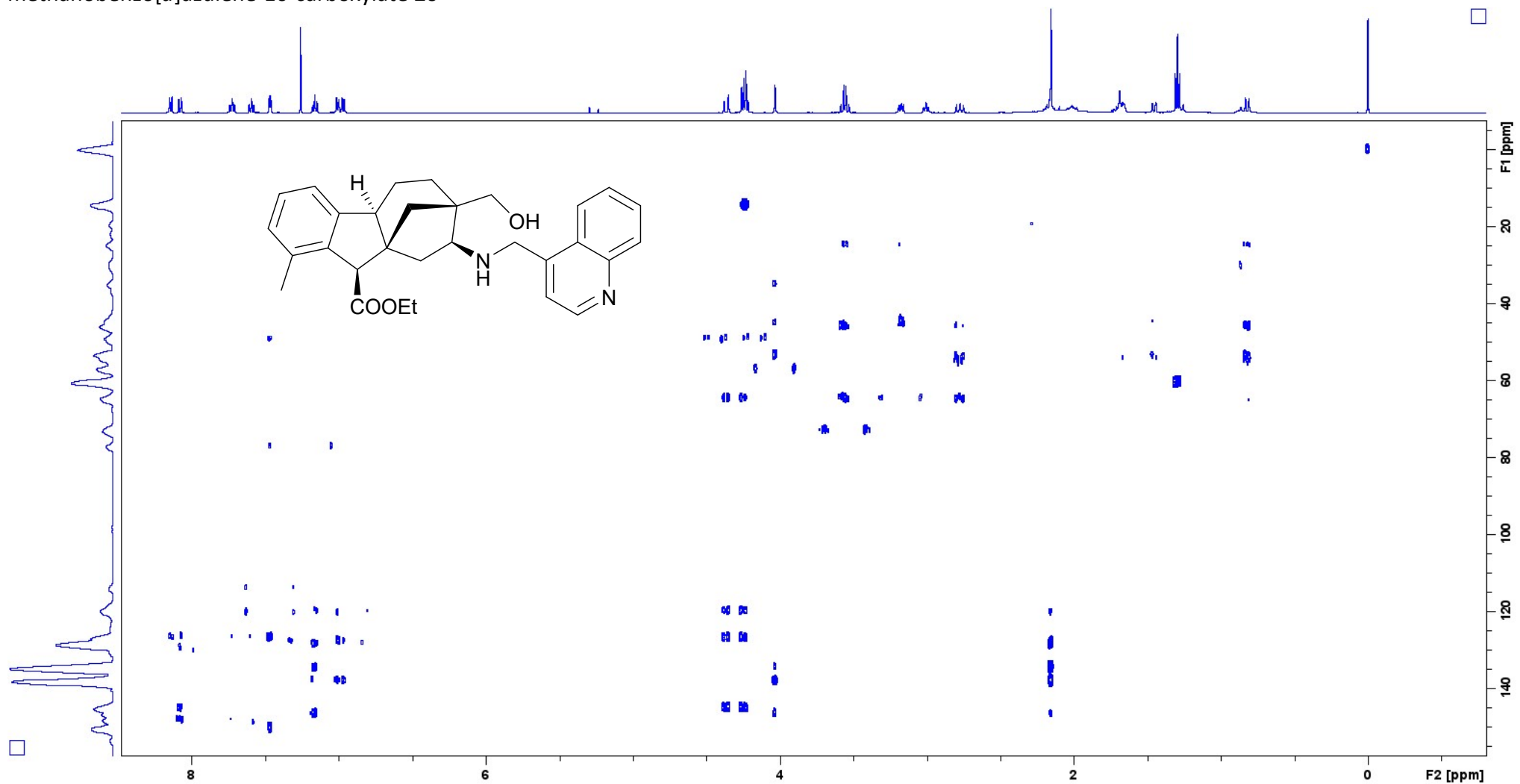
NOESY of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **20**



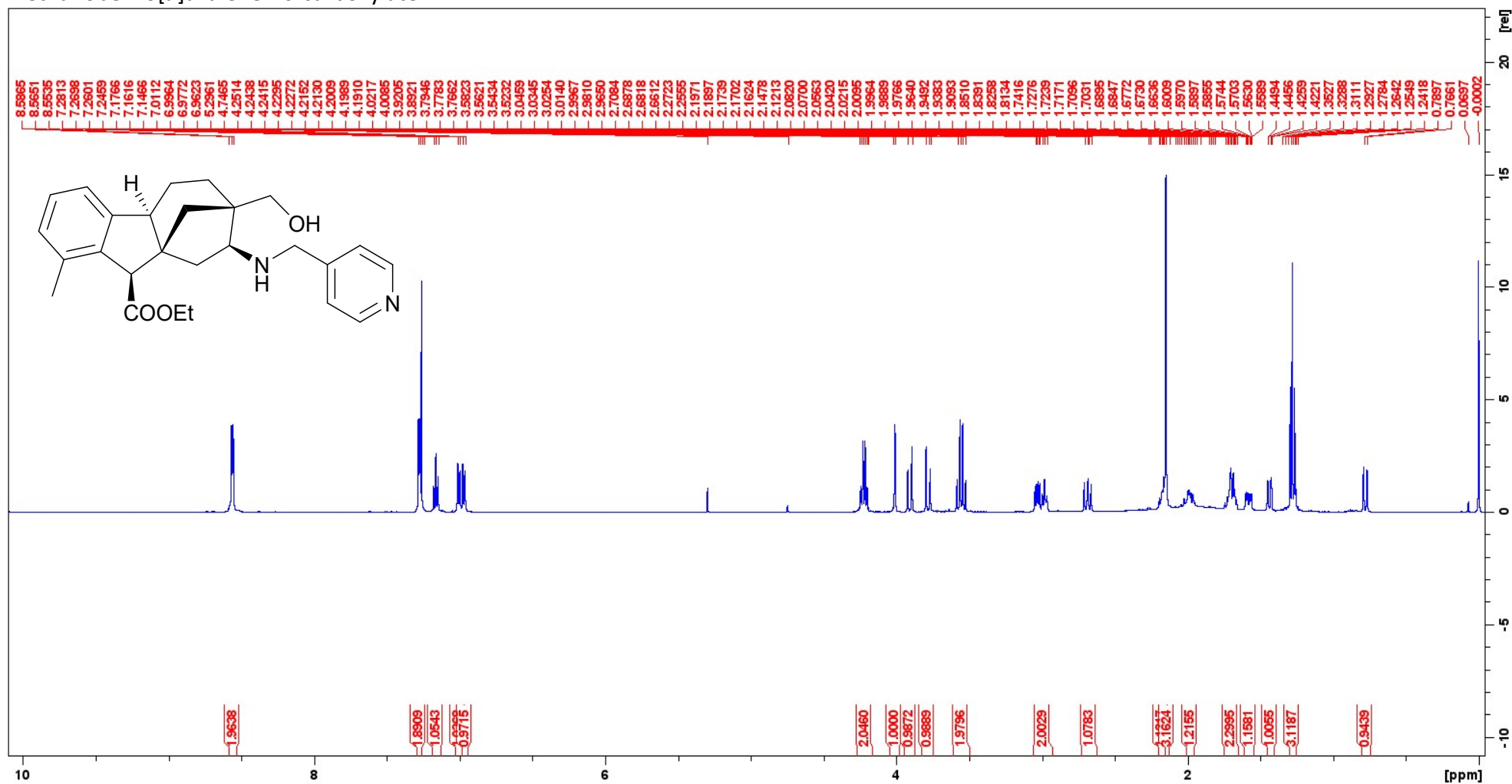
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **20**



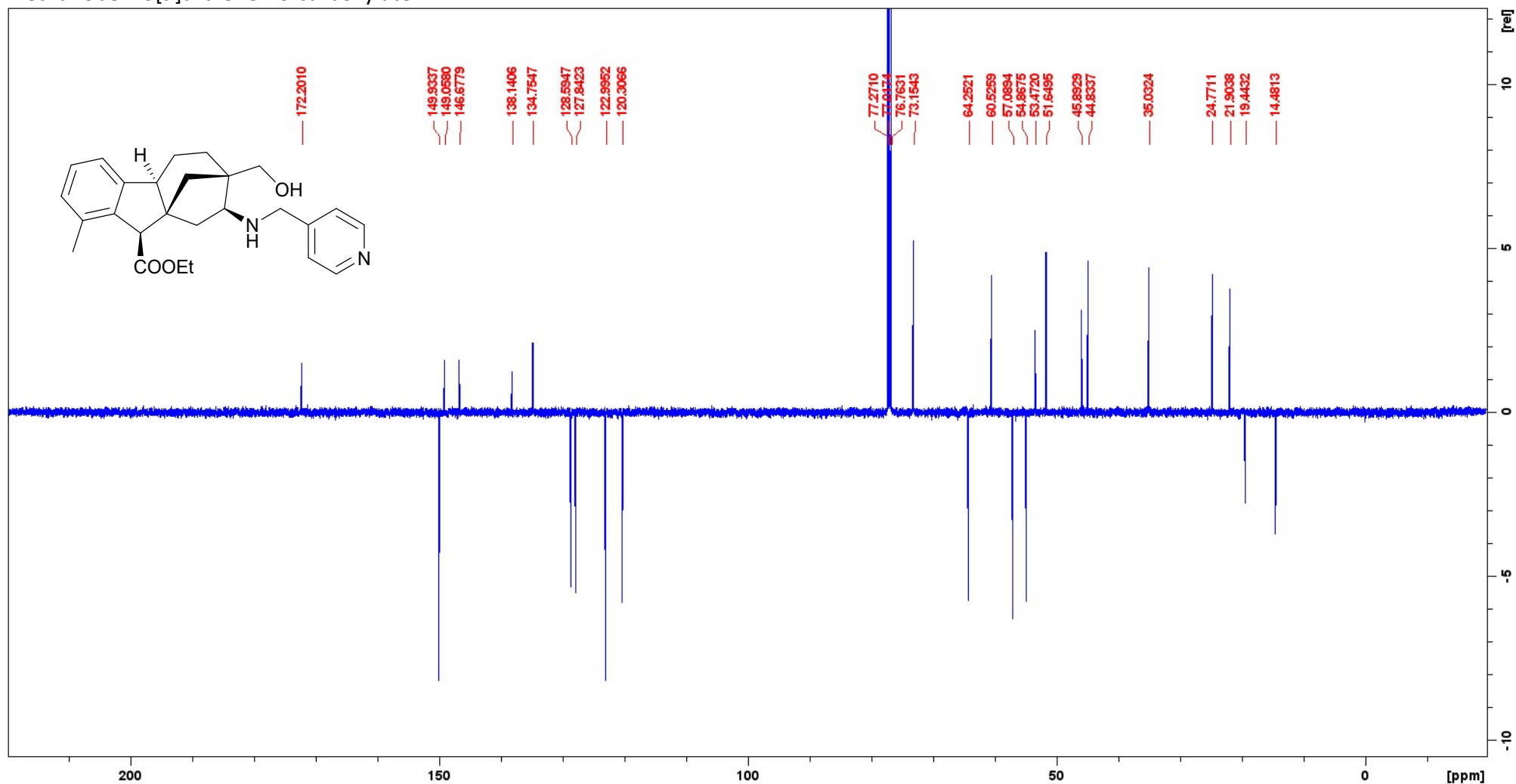
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((quinolin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **20**



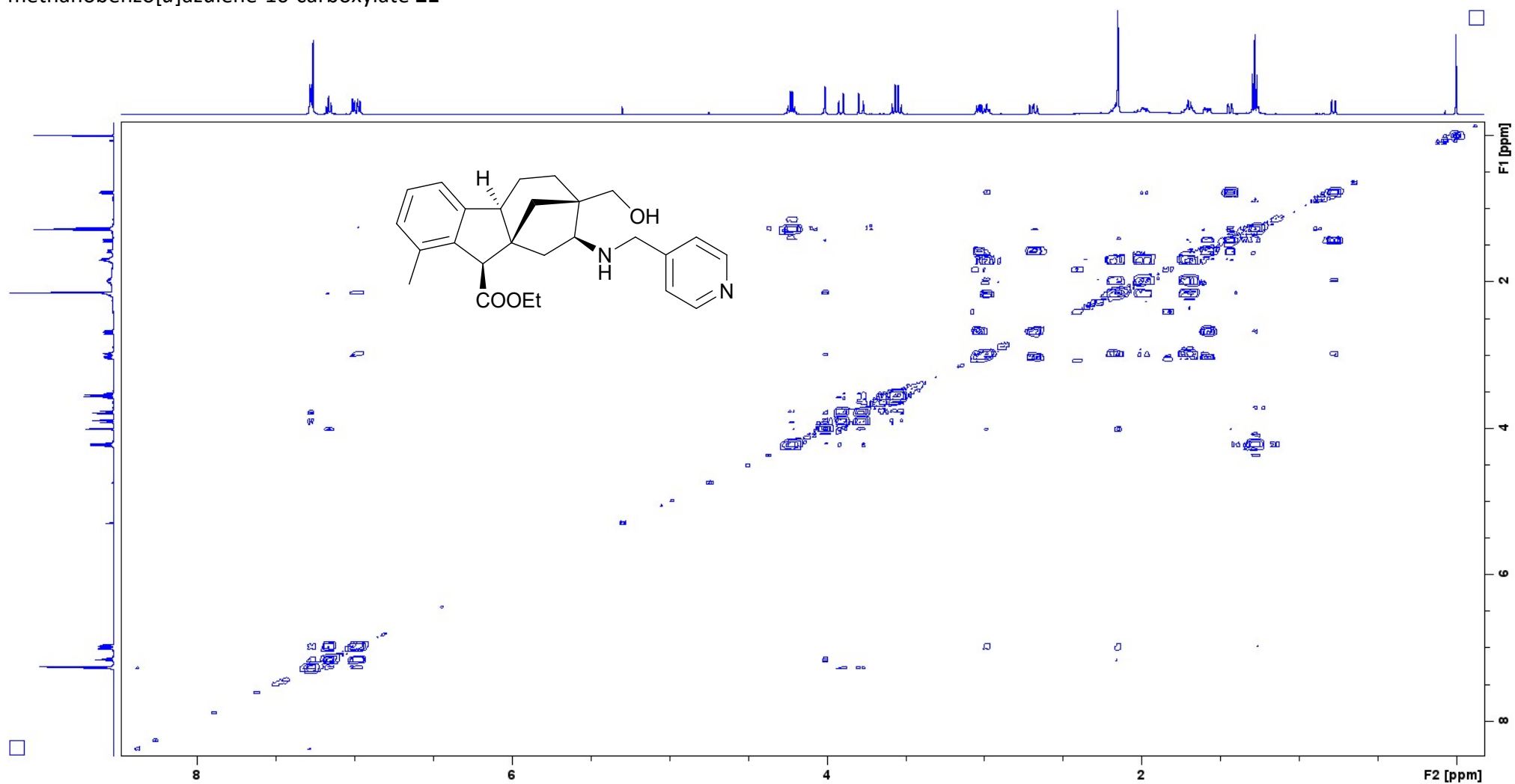
¹H-NMR of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



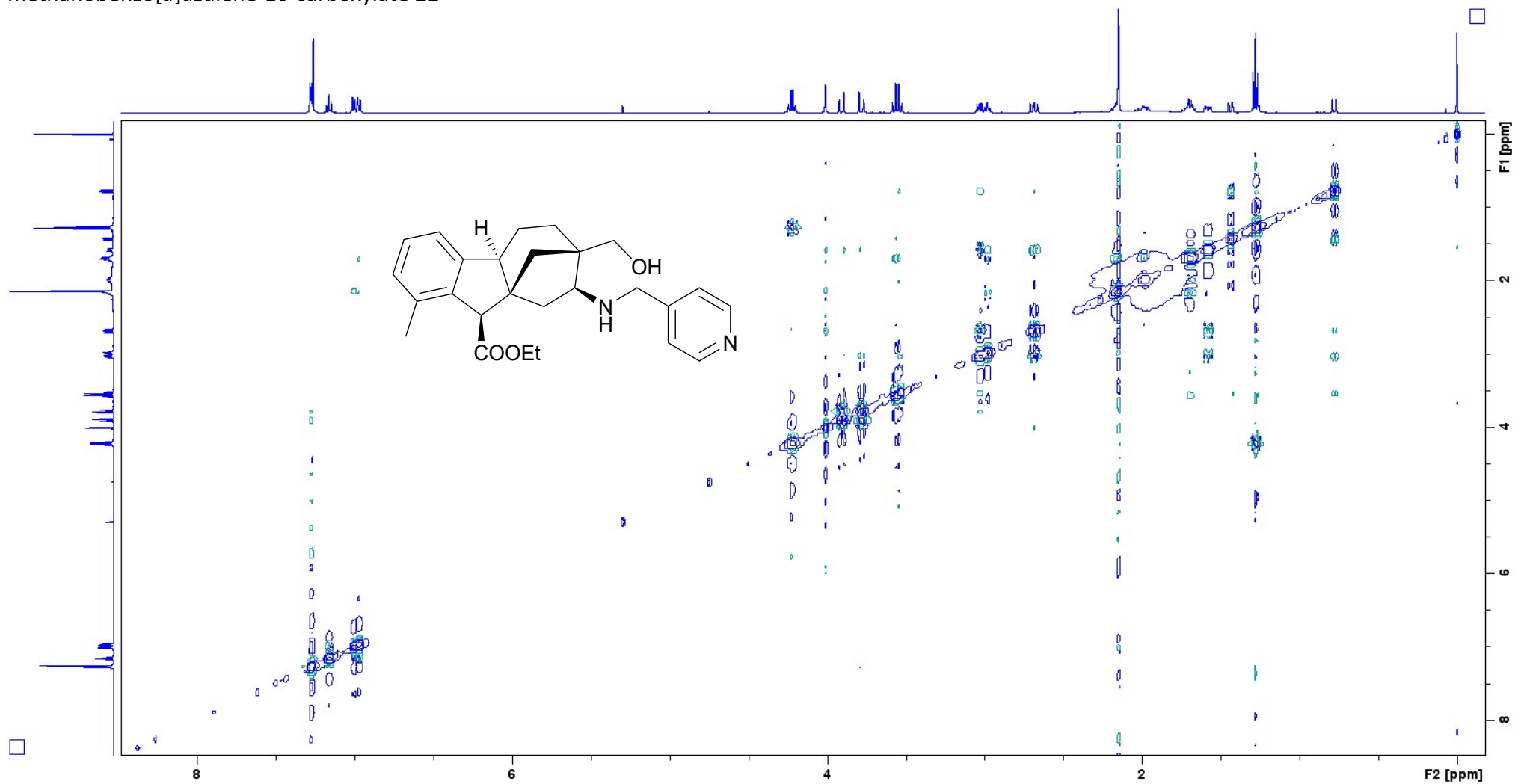
¹³C-NMR of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



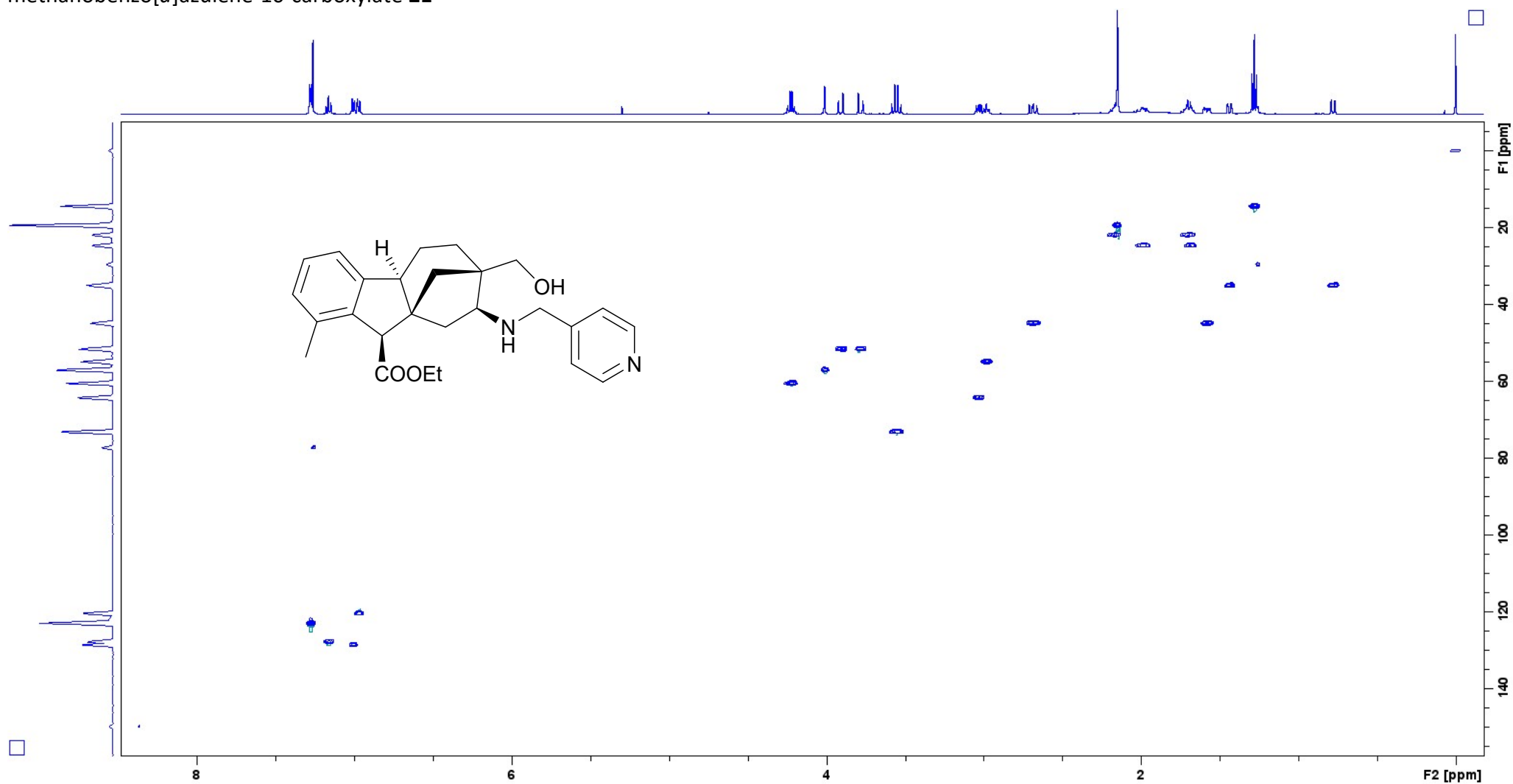
COSY of ethyl (4*b**S*,7*R*,8*S*,9*a**S*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



NOESY of ethyl (4*bS*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



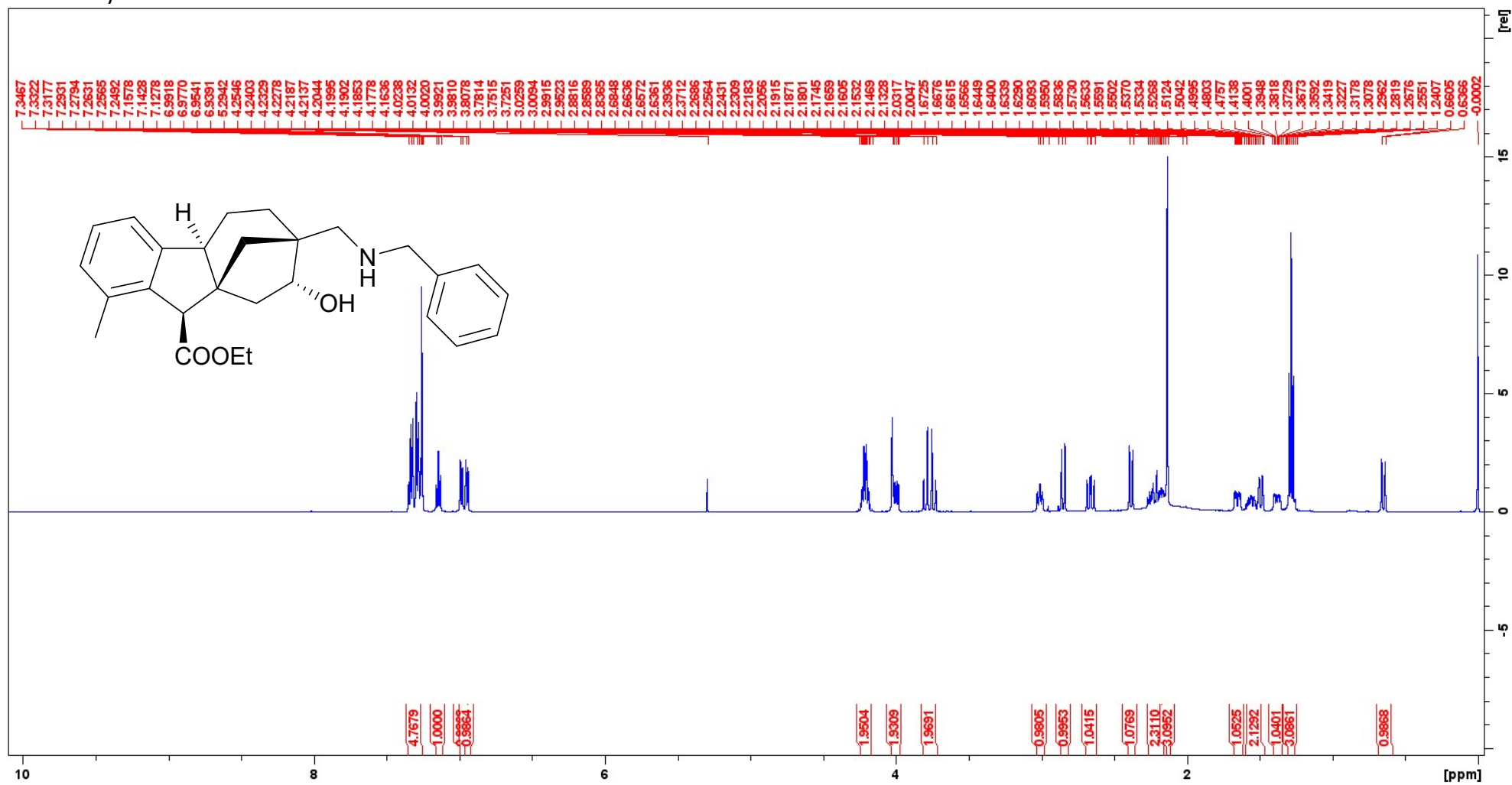
HSQC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



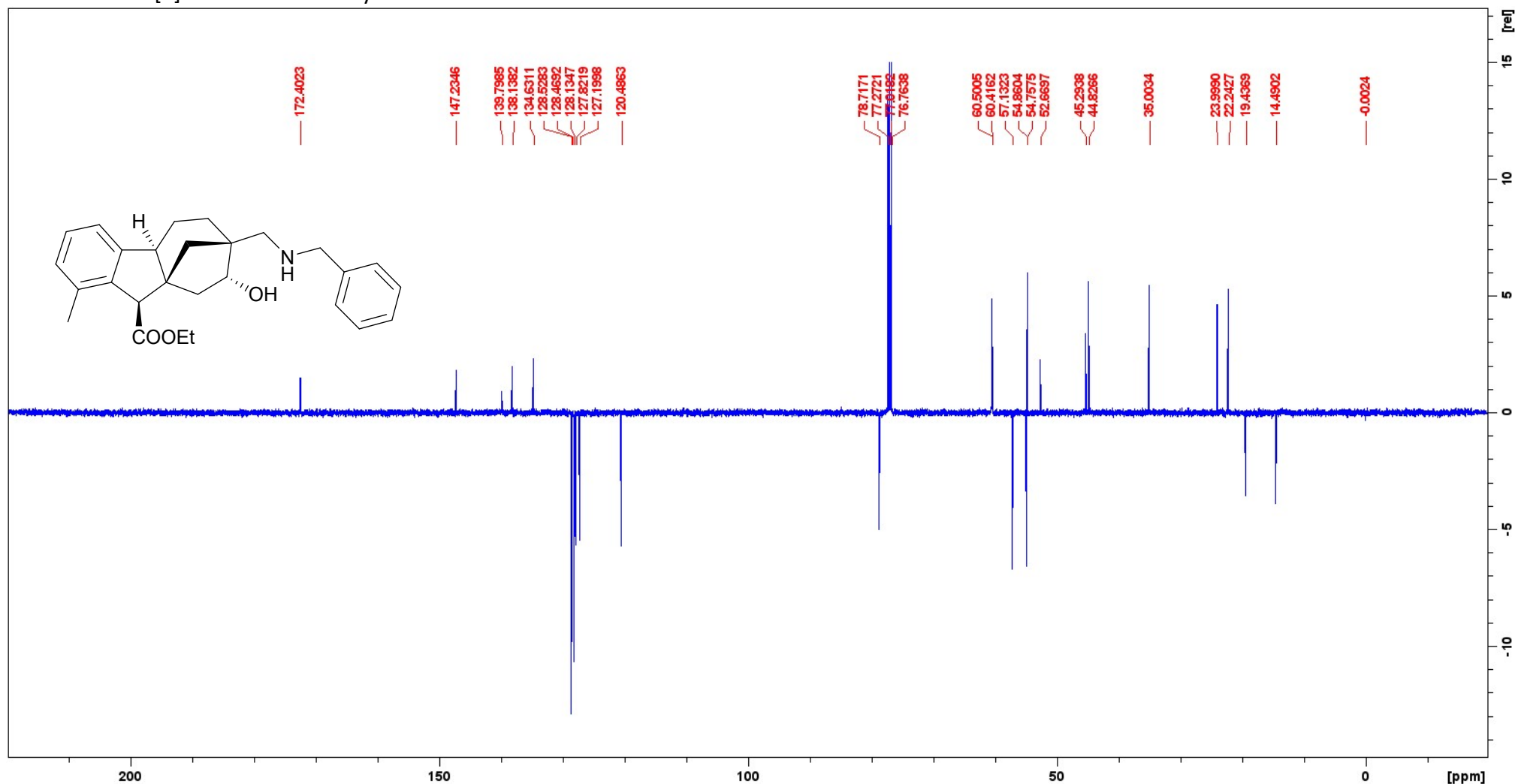
HMBC of ethyl (4*S*,7*R*,8*S*,9*aS*,10*R*)-7-(hydroxymethyl)-1-methyl-8-((pyridin-4-ylmethyl)amino)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **21**



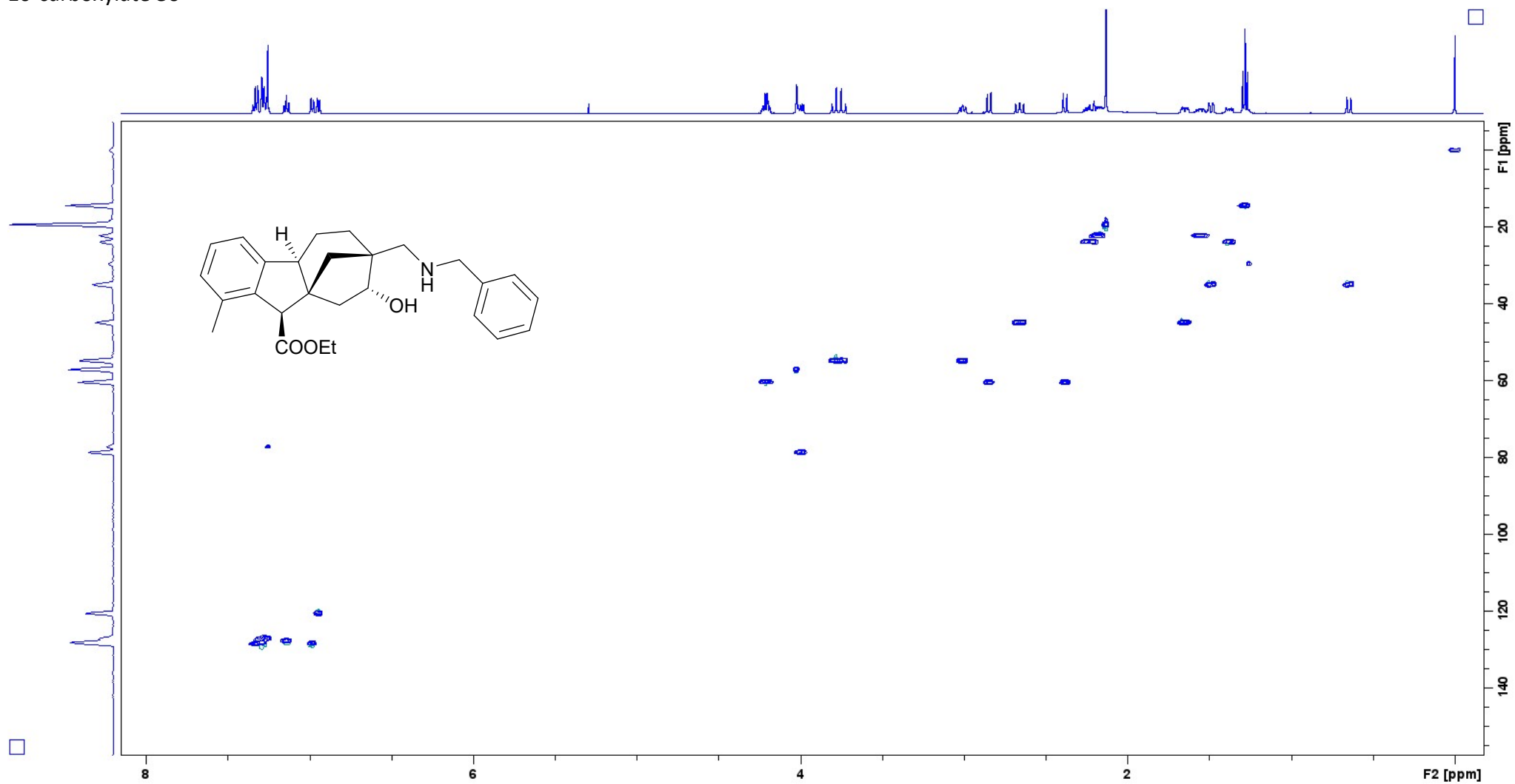
¹H-NMR of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-7-((benzylamino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **30**



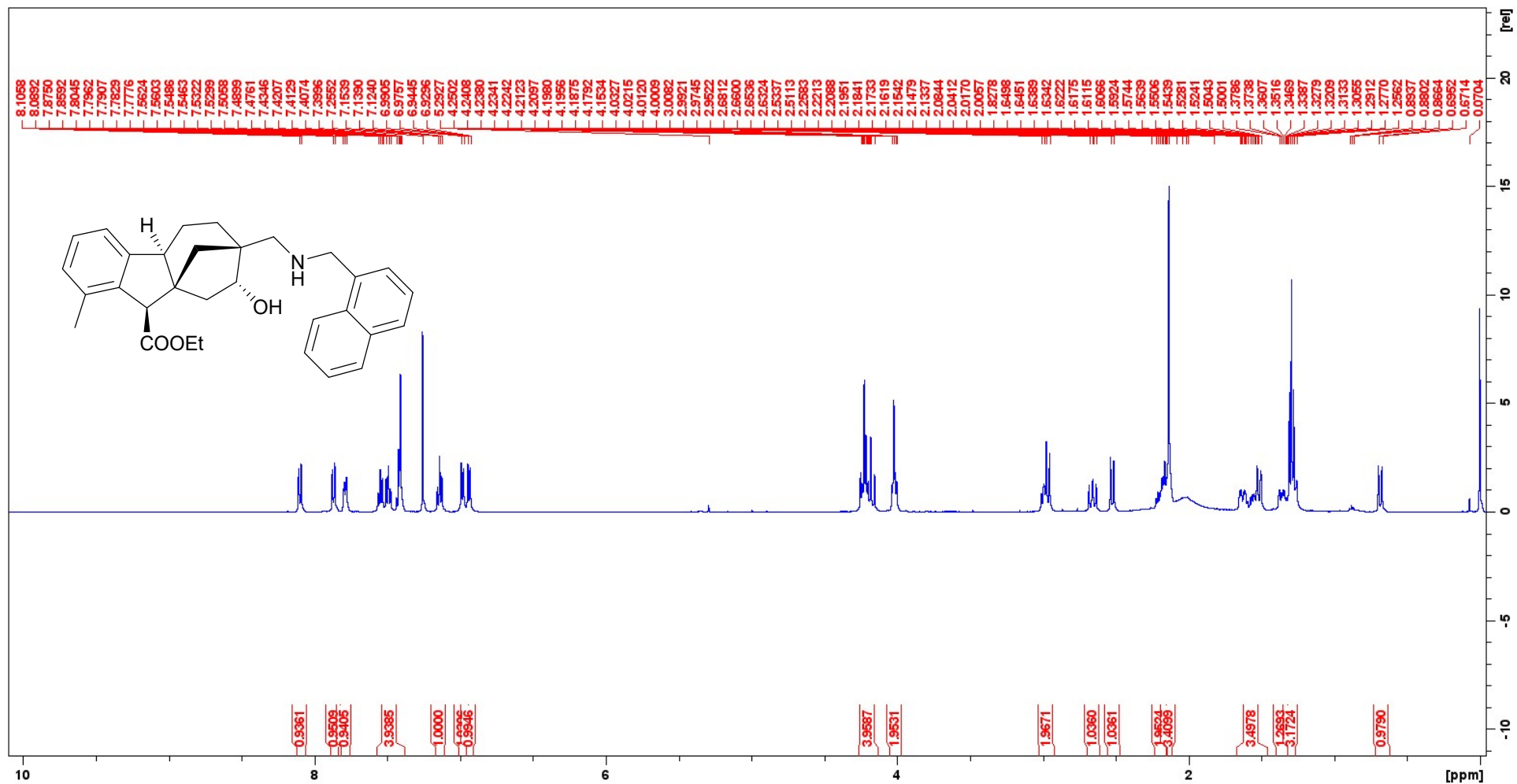
¹³C-NMR of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-7-((benzylamino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **30**



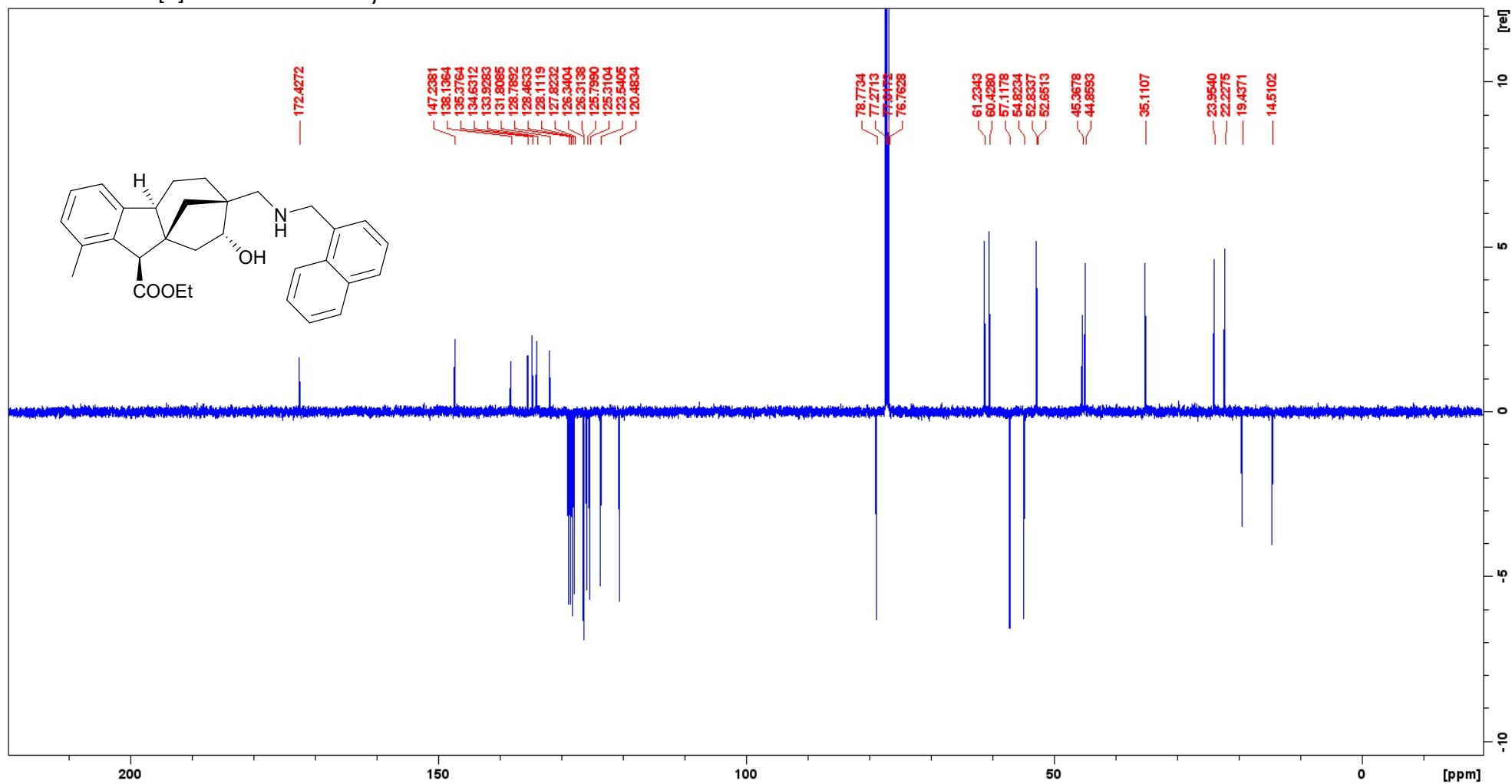
HSQC of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-((benzylamino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **30**



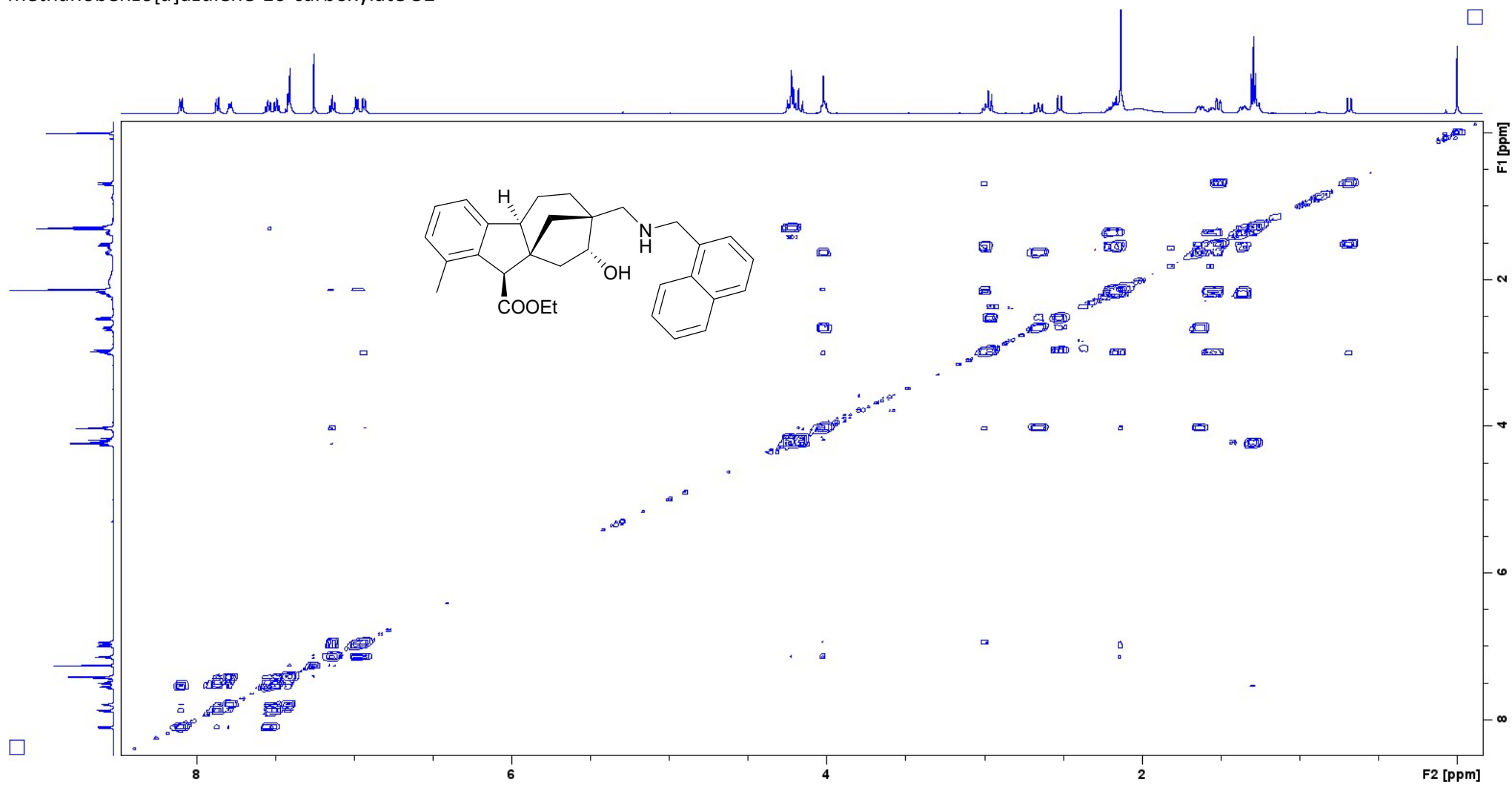
$^1\text{H-NMR}$ of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **31**



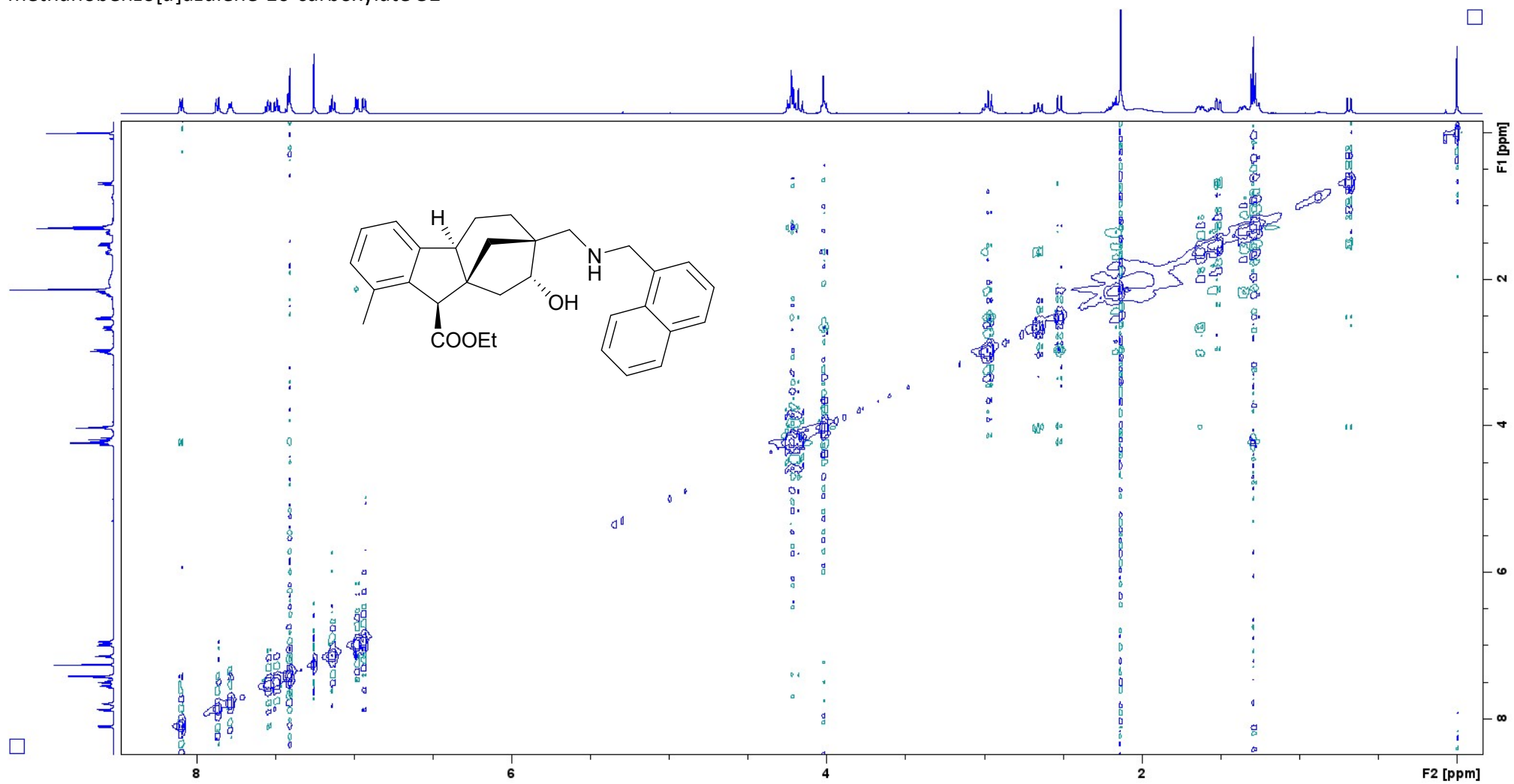
^{13}C -NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **31**



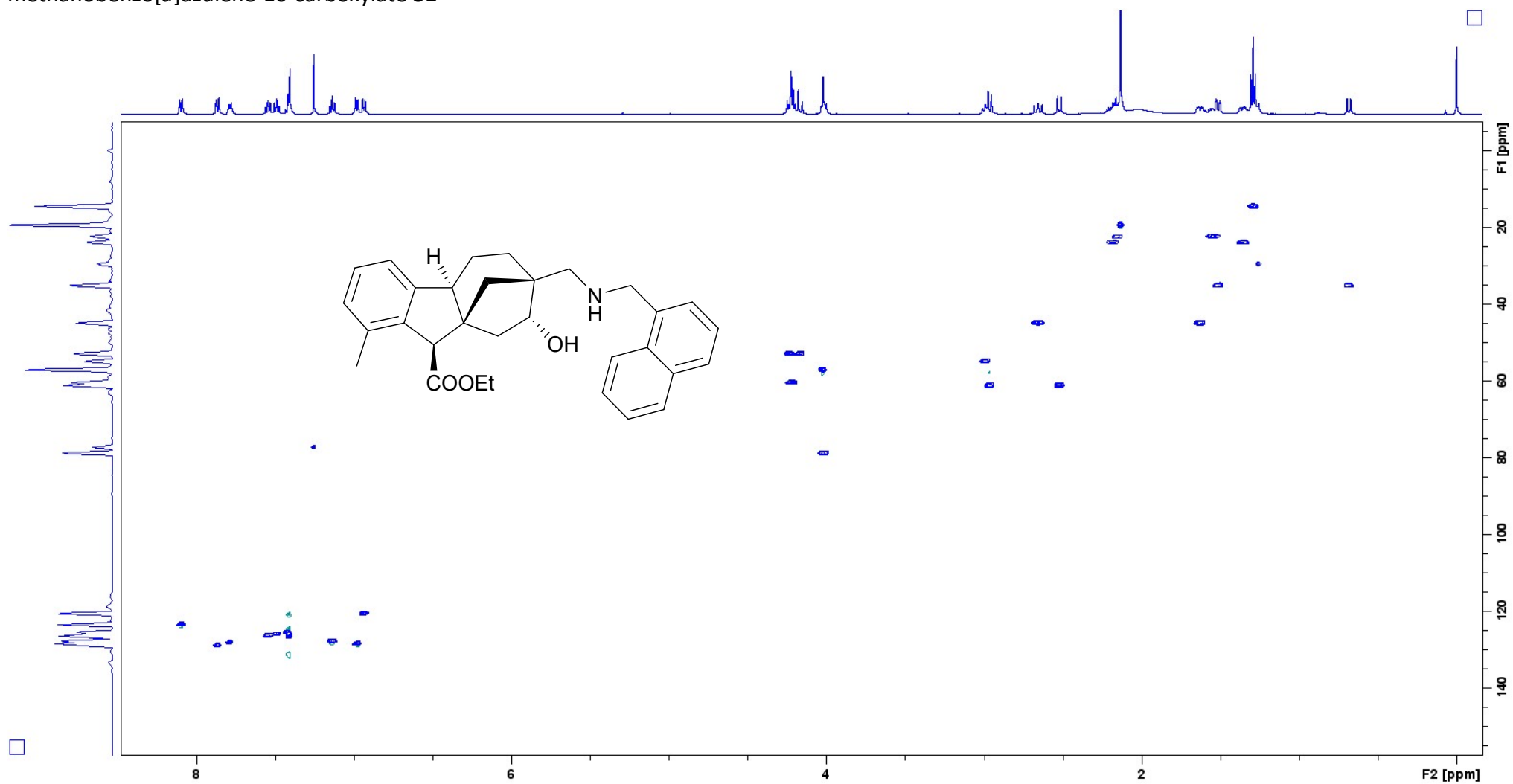
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **31**



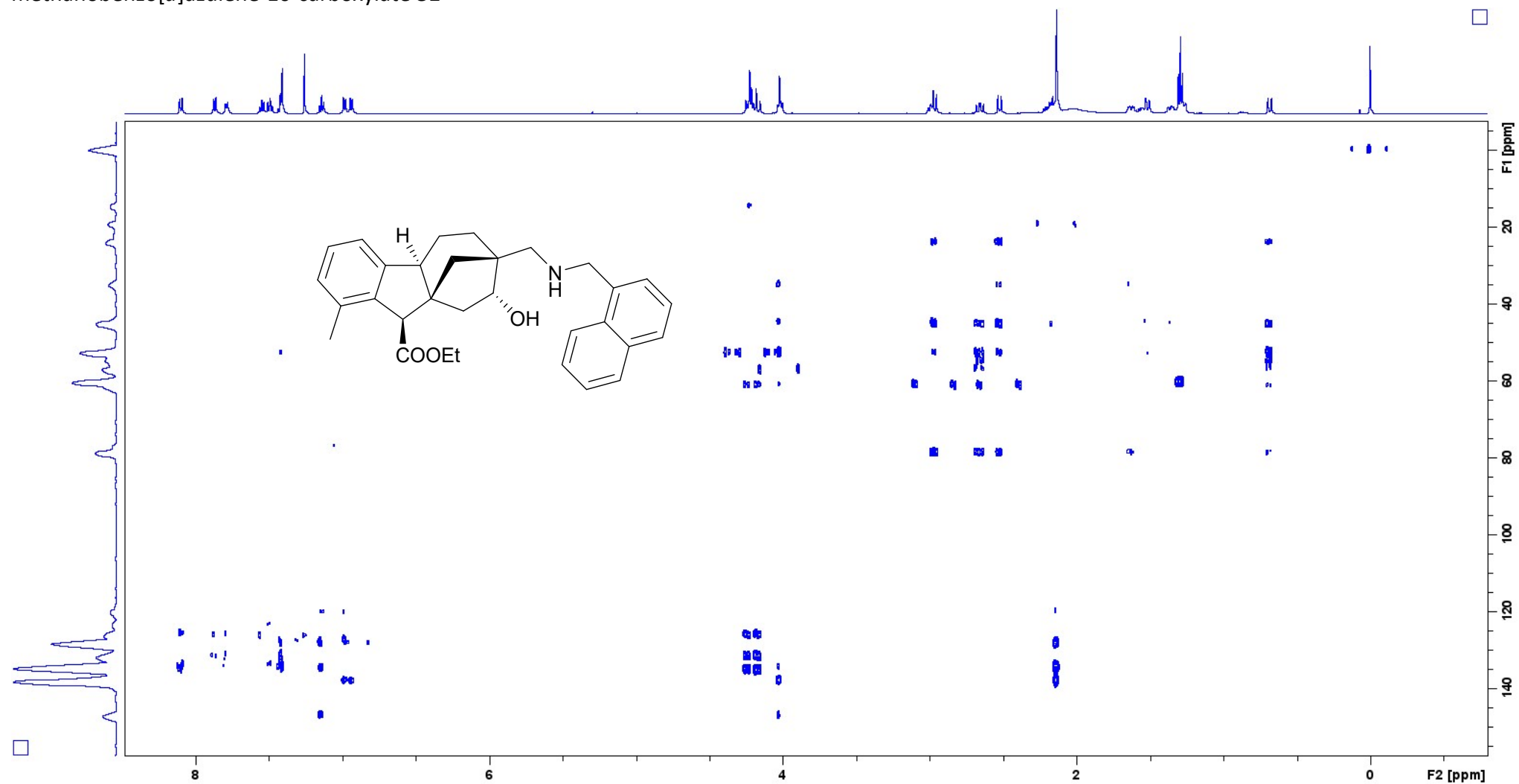
NOESY of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **31**



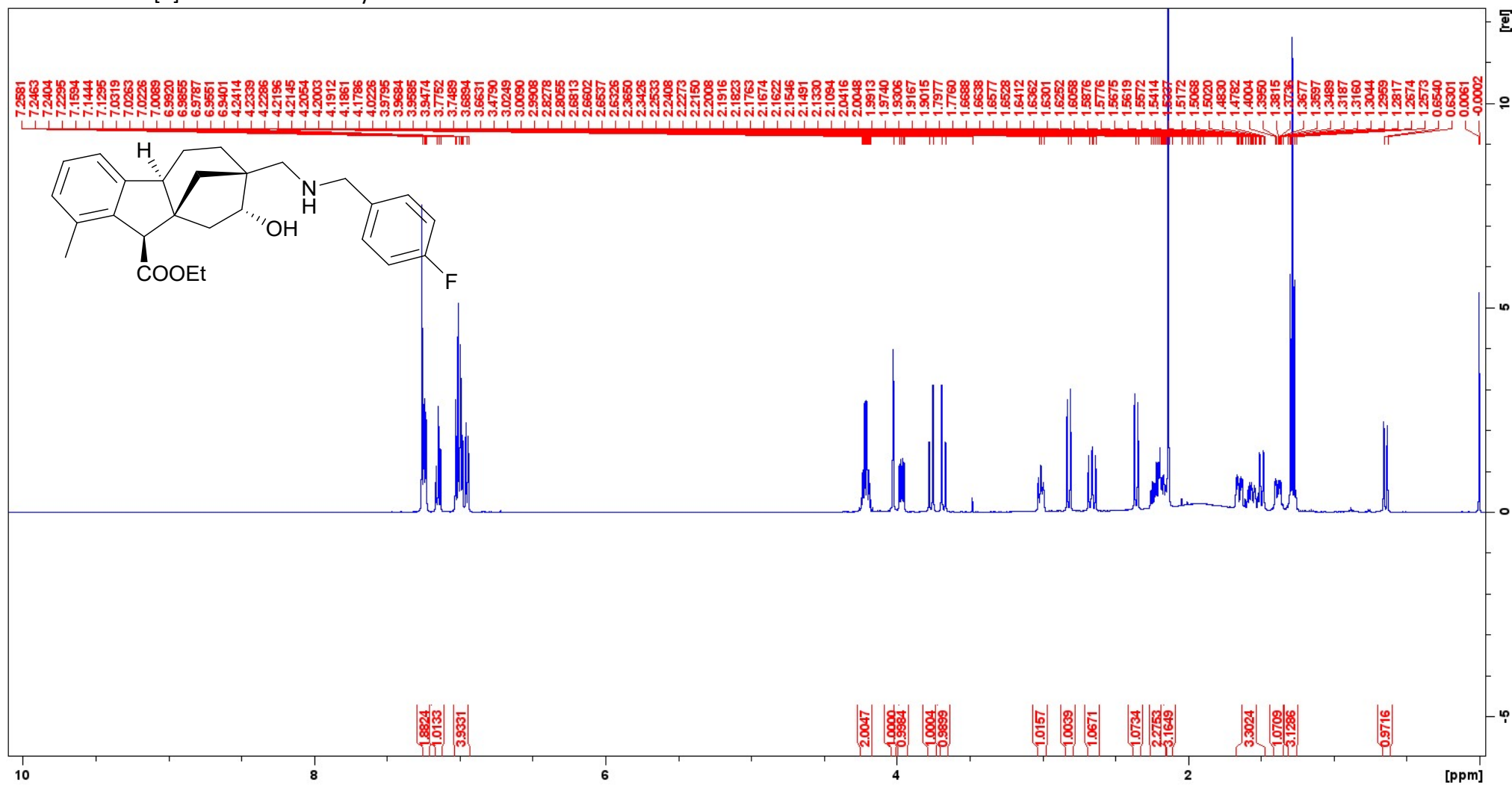
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **31**



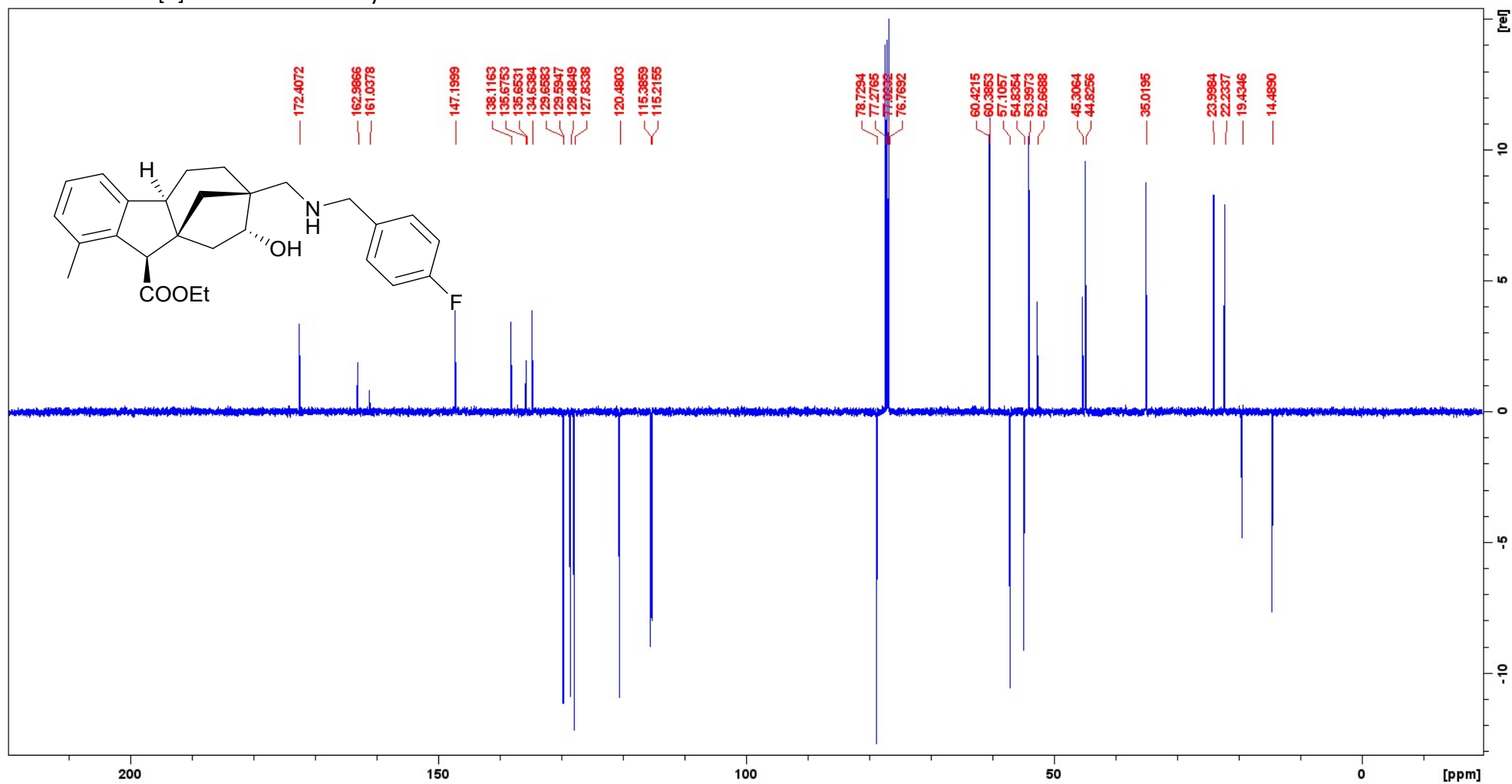
HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((naphthalen-1-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **31**



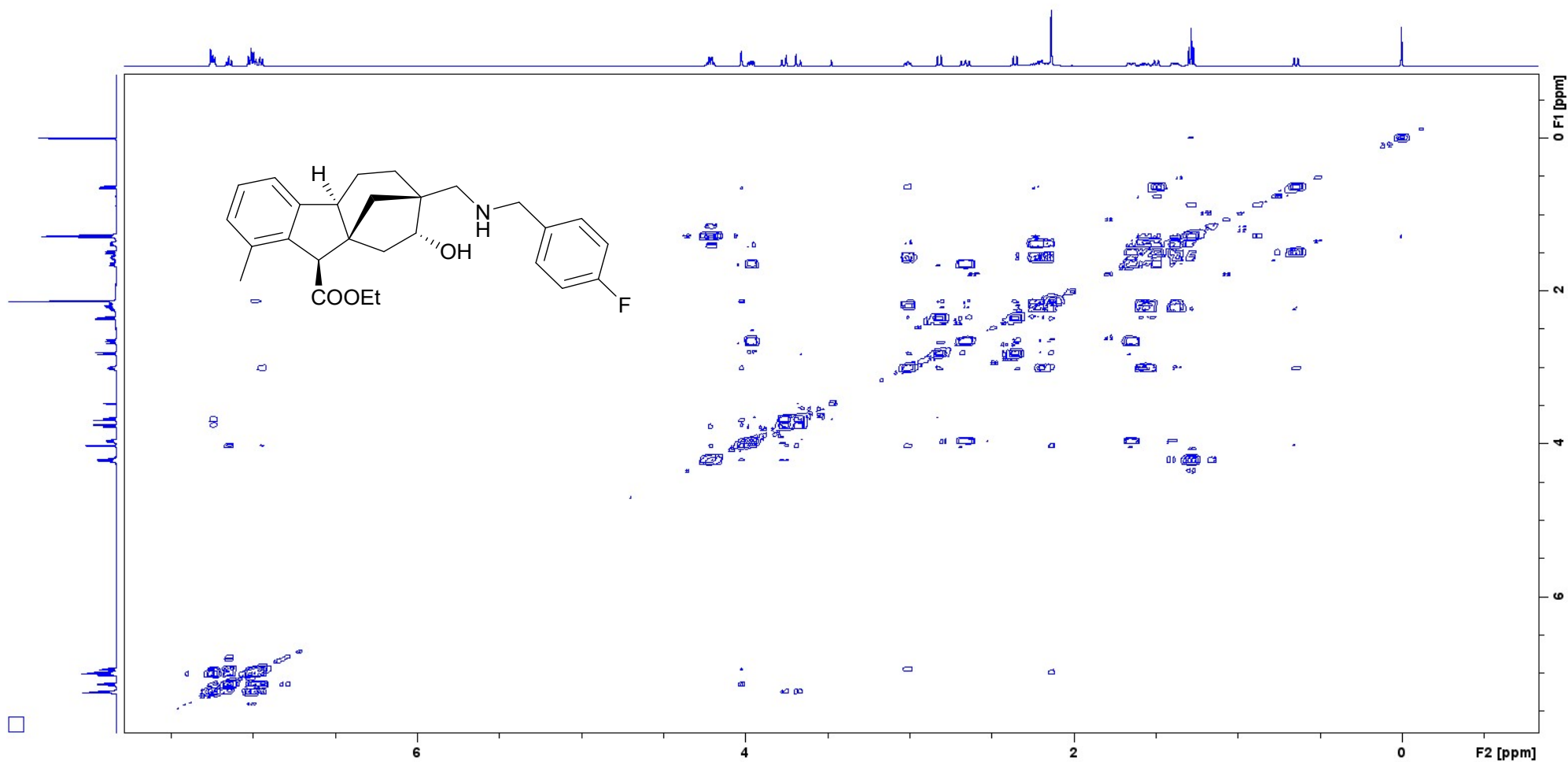
¹H-NMR of ethyl (4bS,7S,8R,9aS,10R)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4b,6,7,8,9,10-hexahydro-5H-7,9a-methanobenzo[*a*]azulene-10-carboxylate **32**



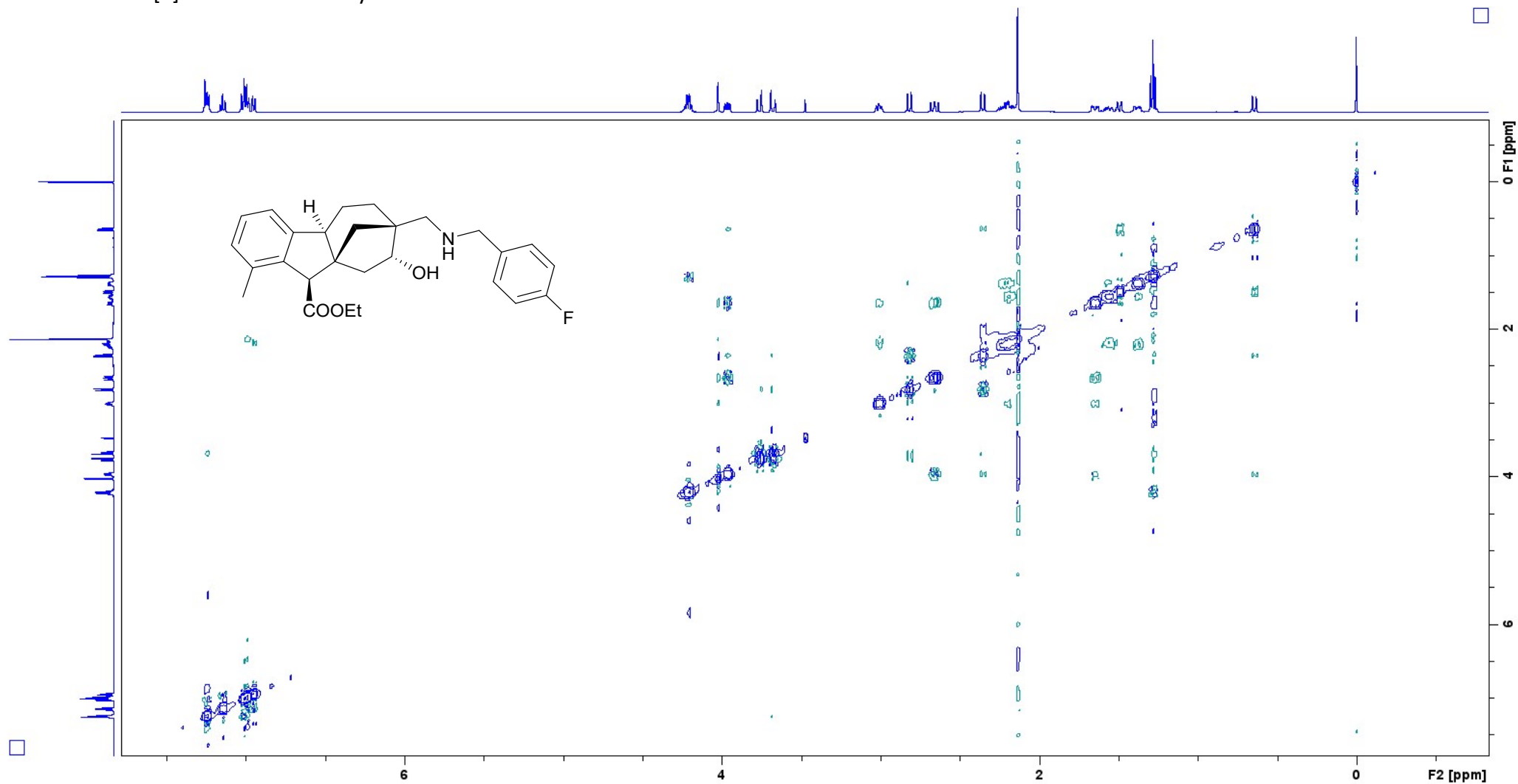
¹³C-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **32**



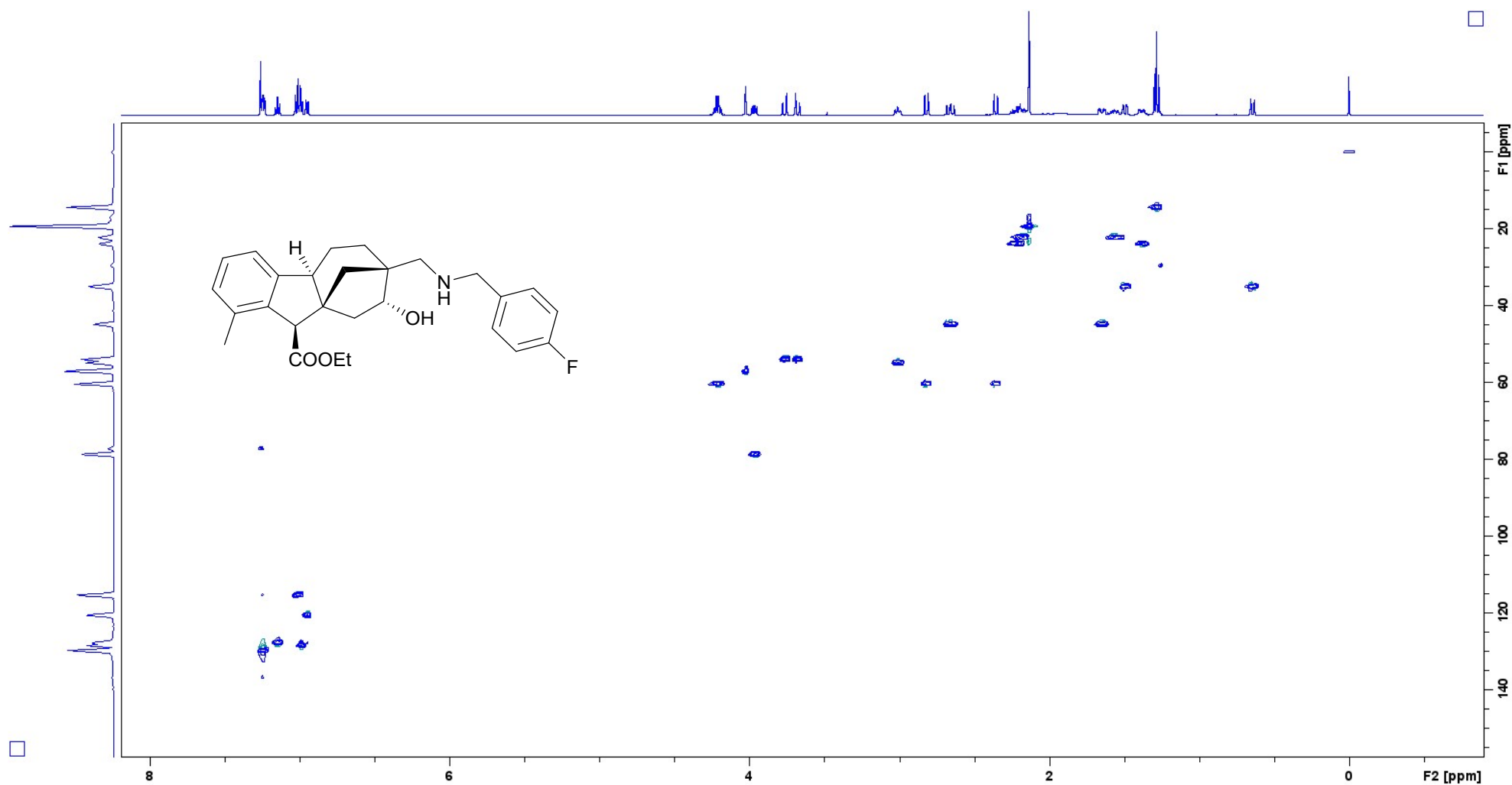
COSY of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **32**



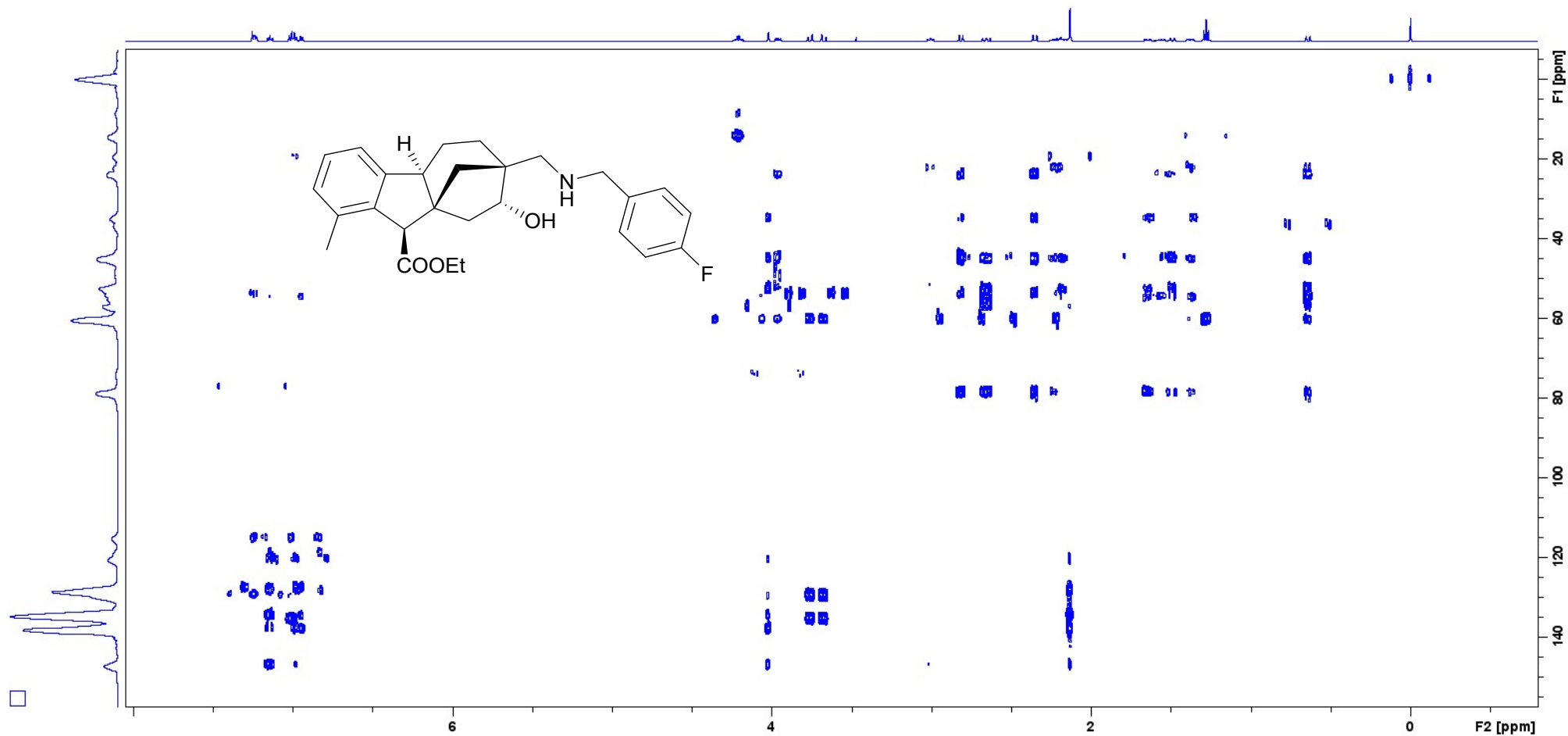
NOESY of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **32**



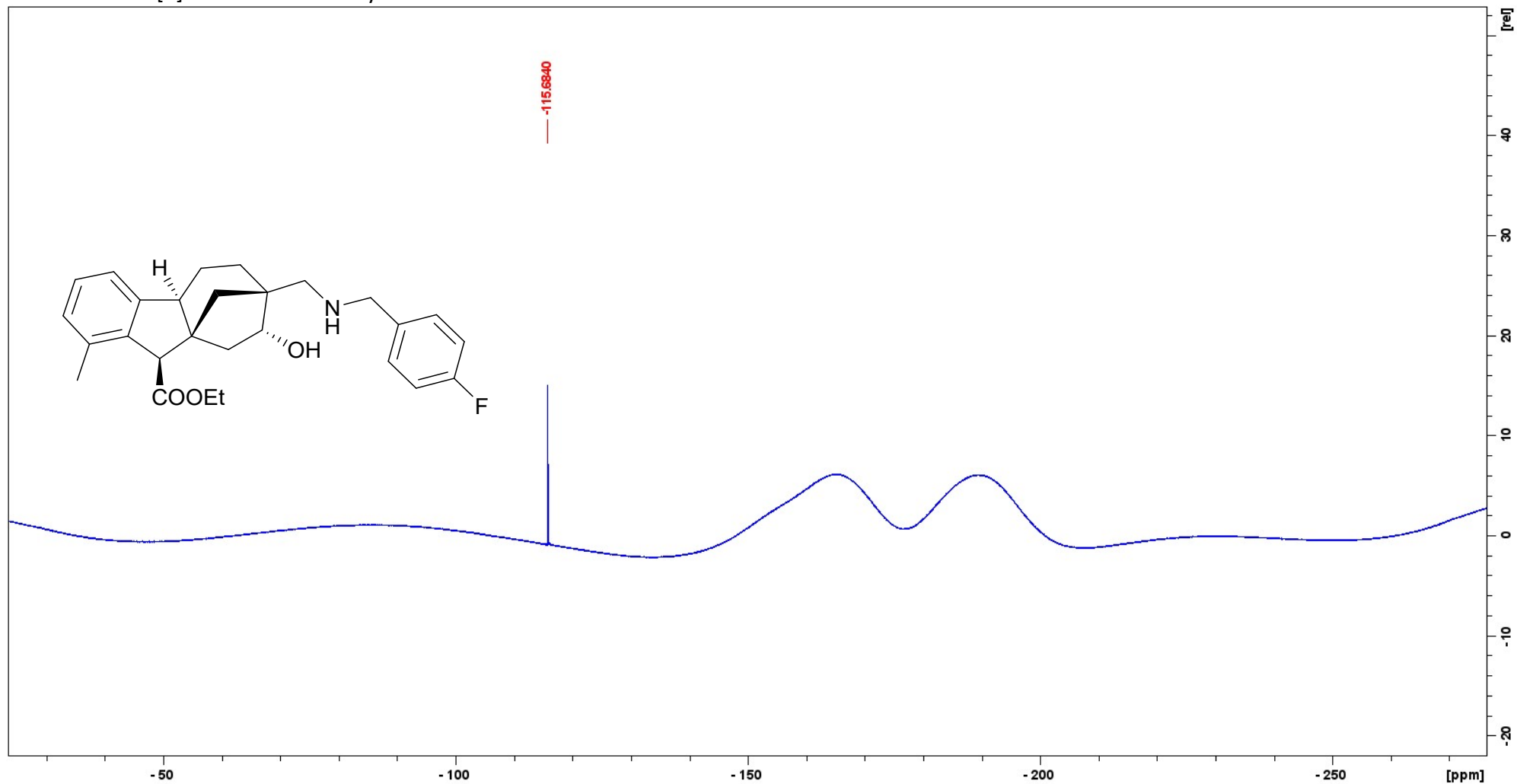
HSQC of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **32**



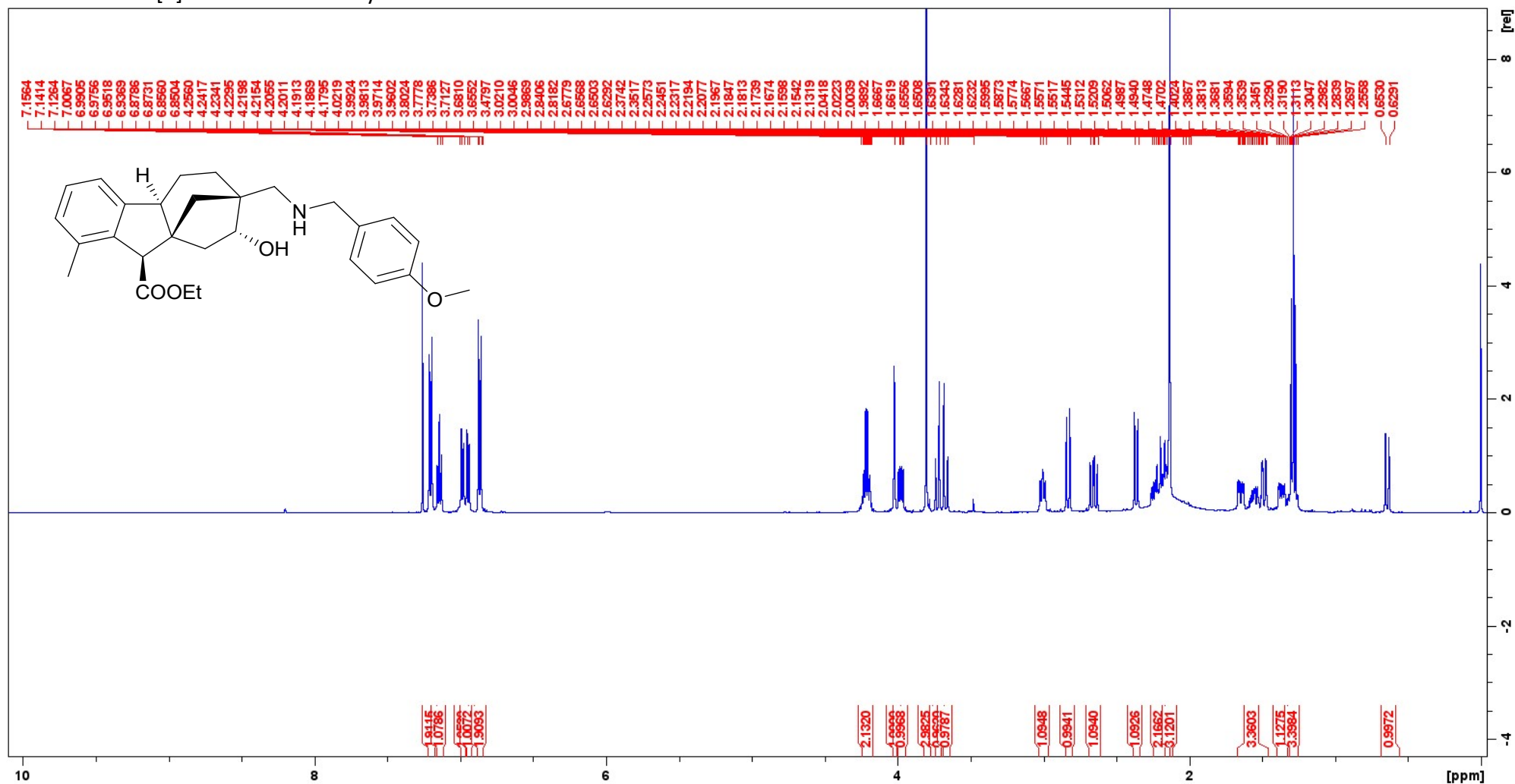
HMBC of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **32**



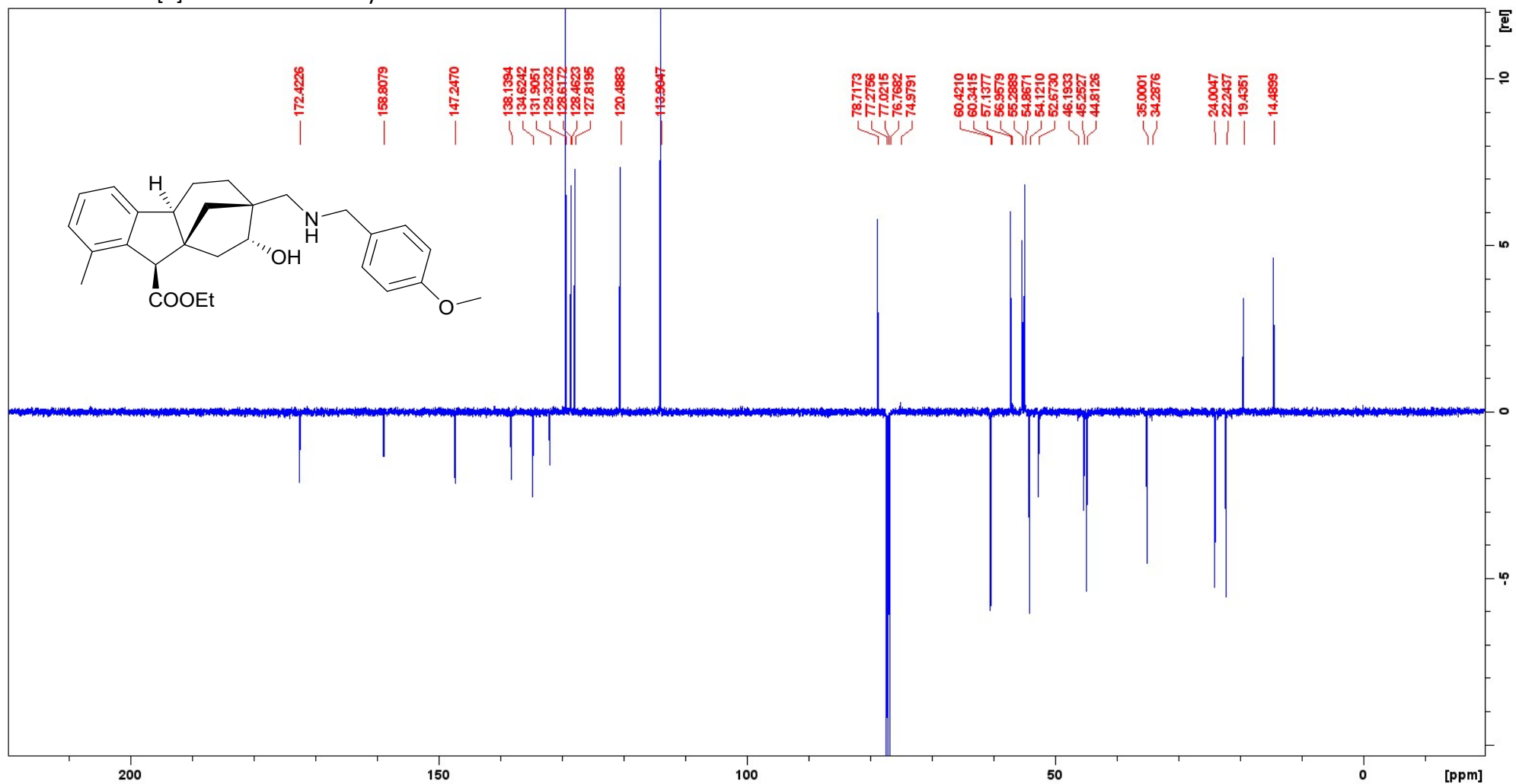
¹⁹F-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-7-(((4-fluorobenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **32**



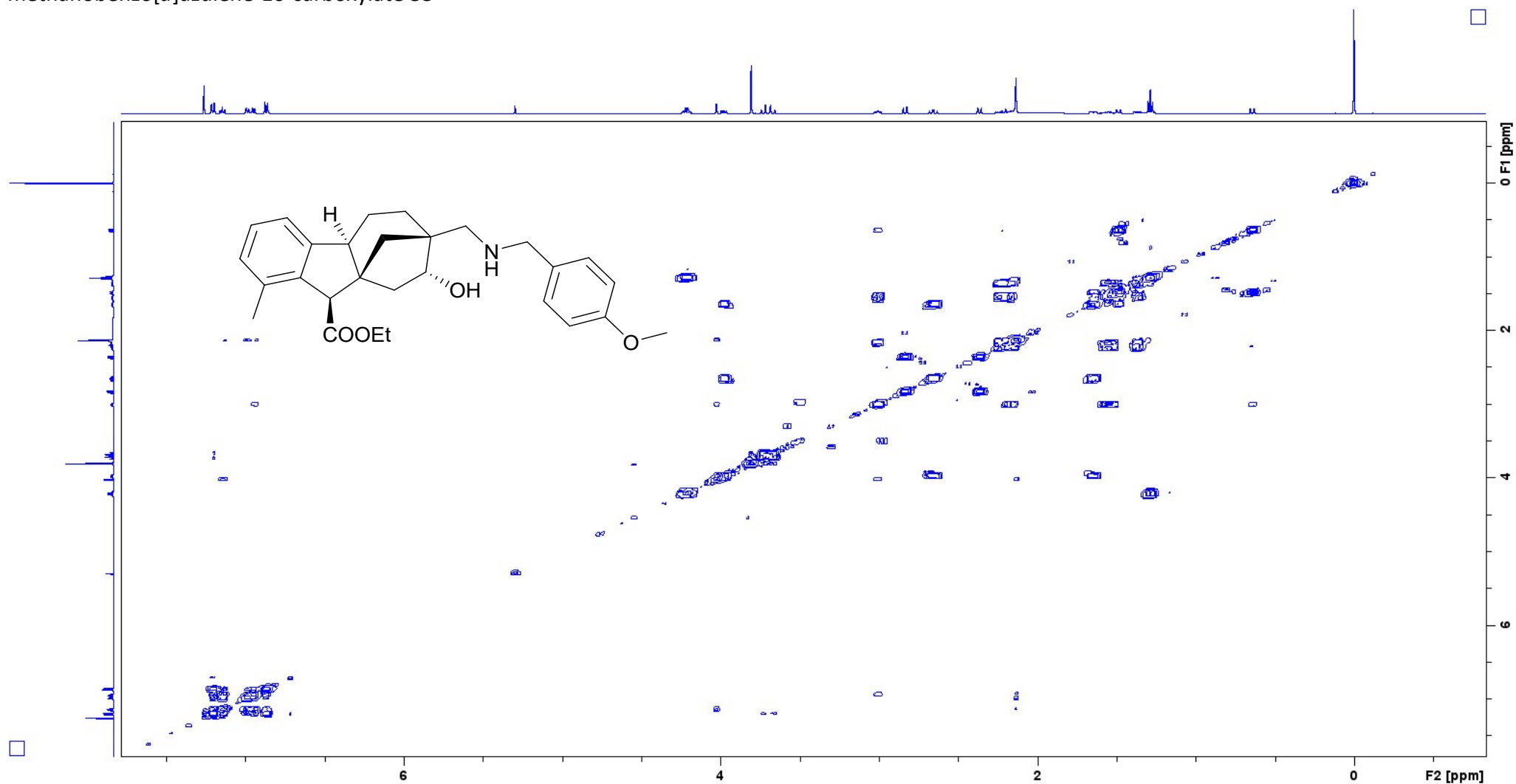
¹H-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



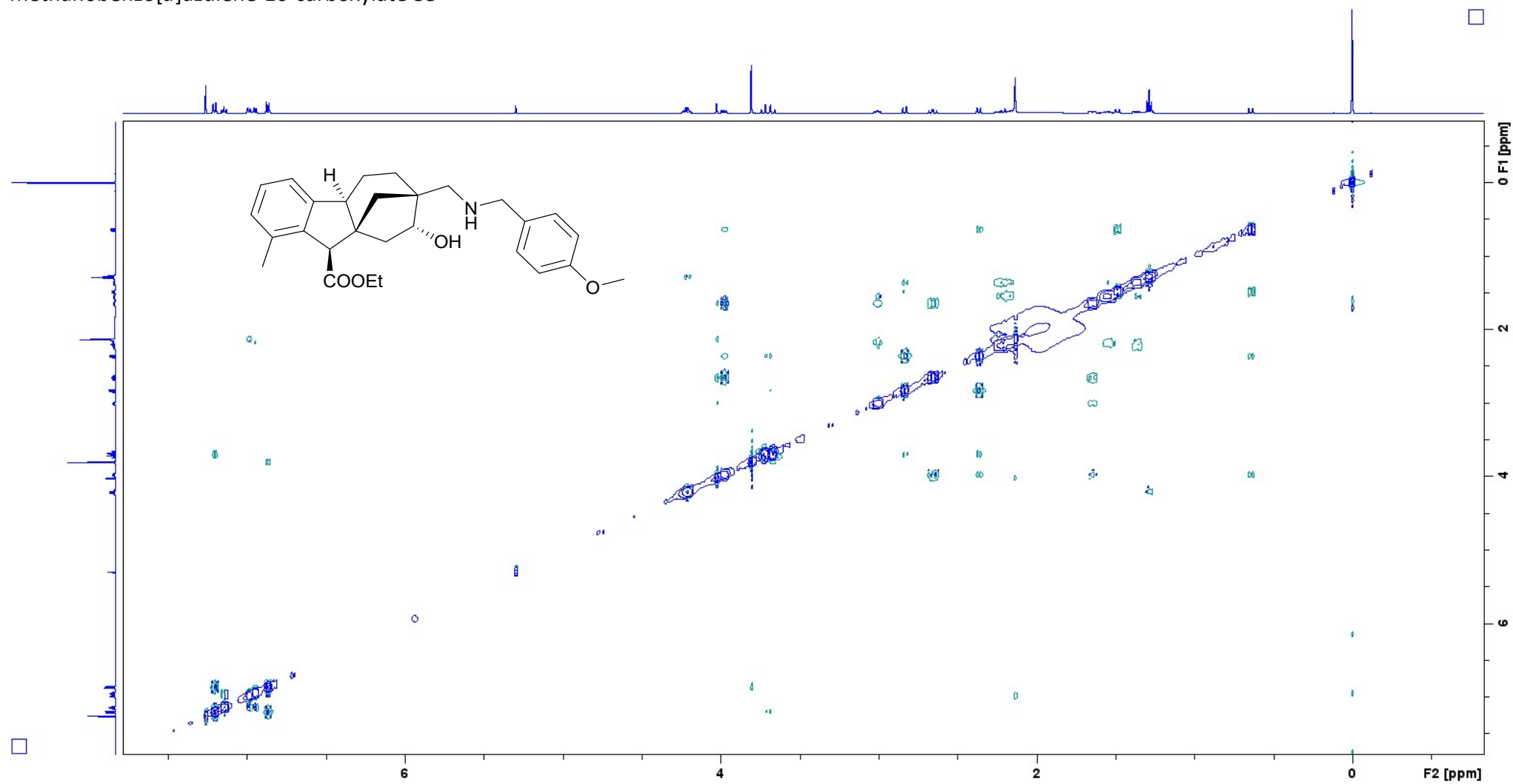
¹³C-NMR ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



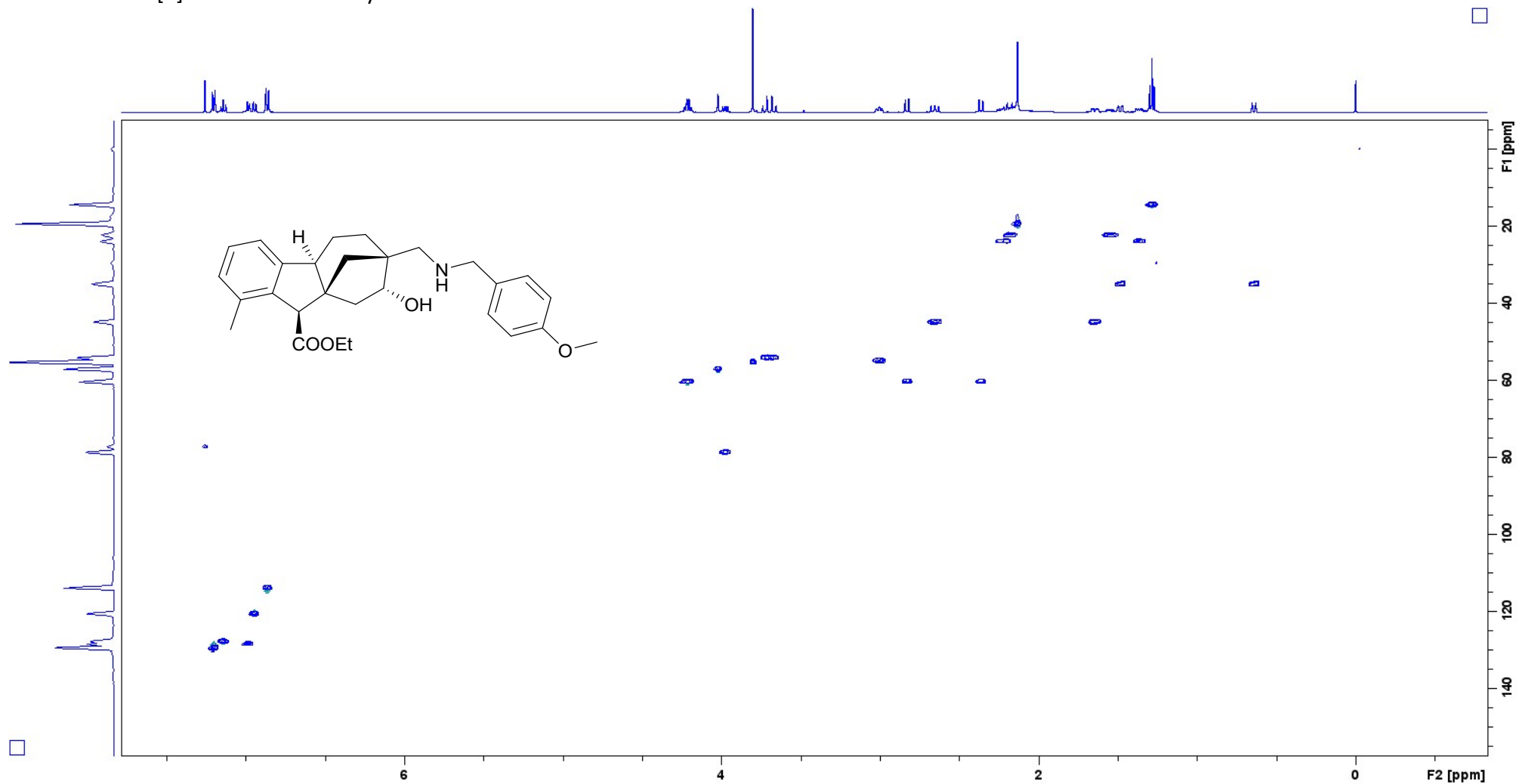
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



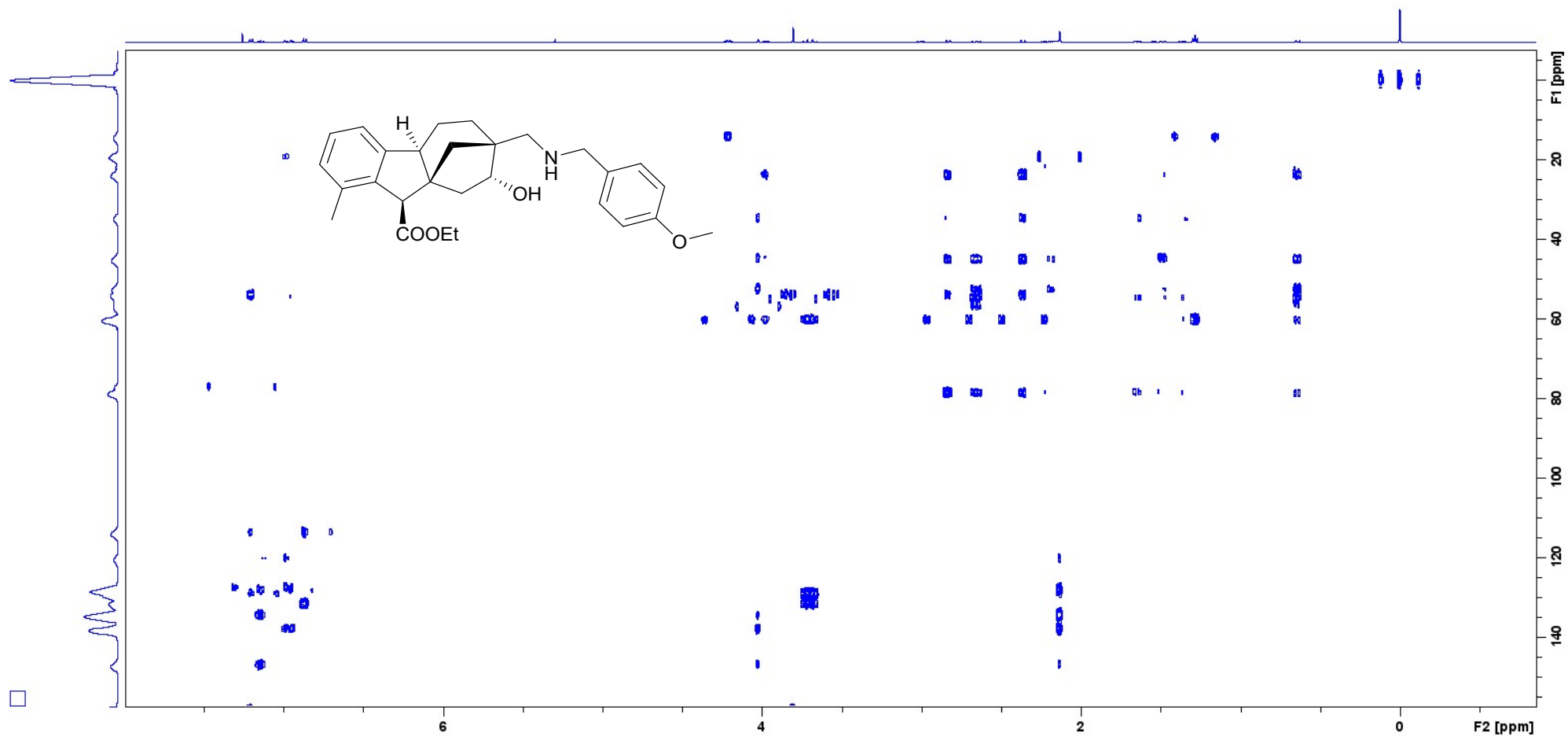
NOESY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



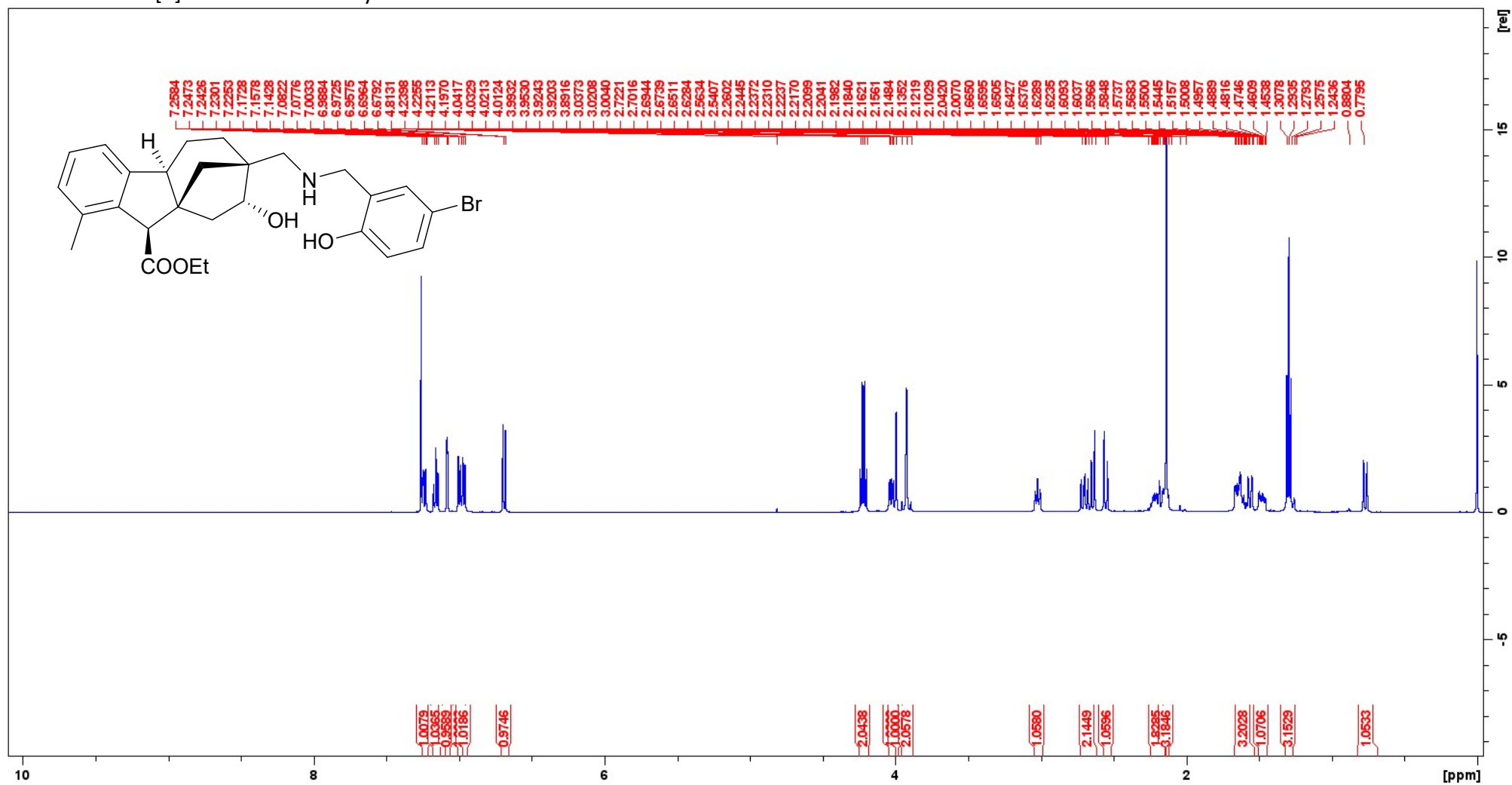
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



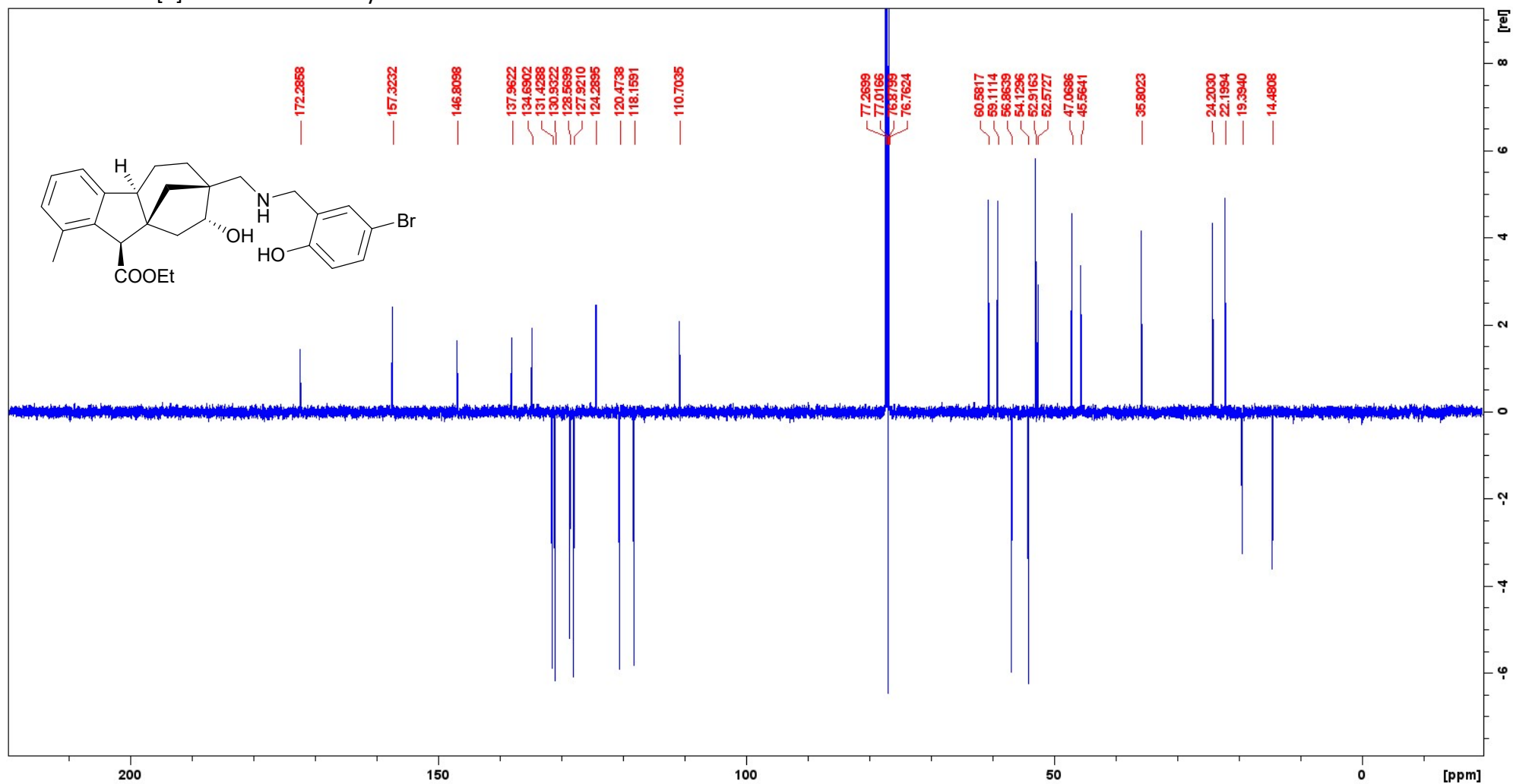
HMBC of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-8-hydroxy-7-(((4-methoxybenzyl)amino)methyl)-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **33**



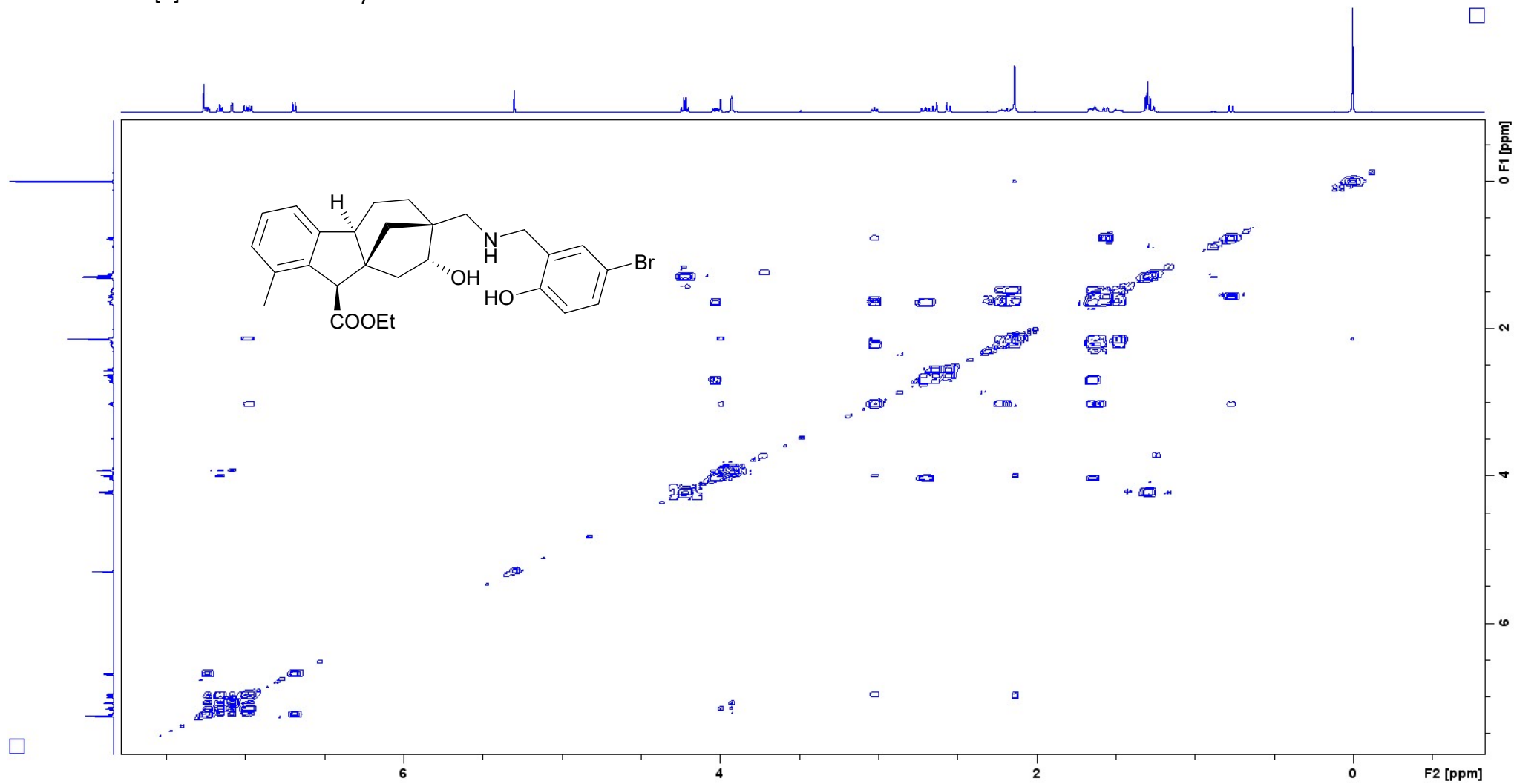
¹H-NMR of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-(((5-bromo-2-hydroxybenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **34**



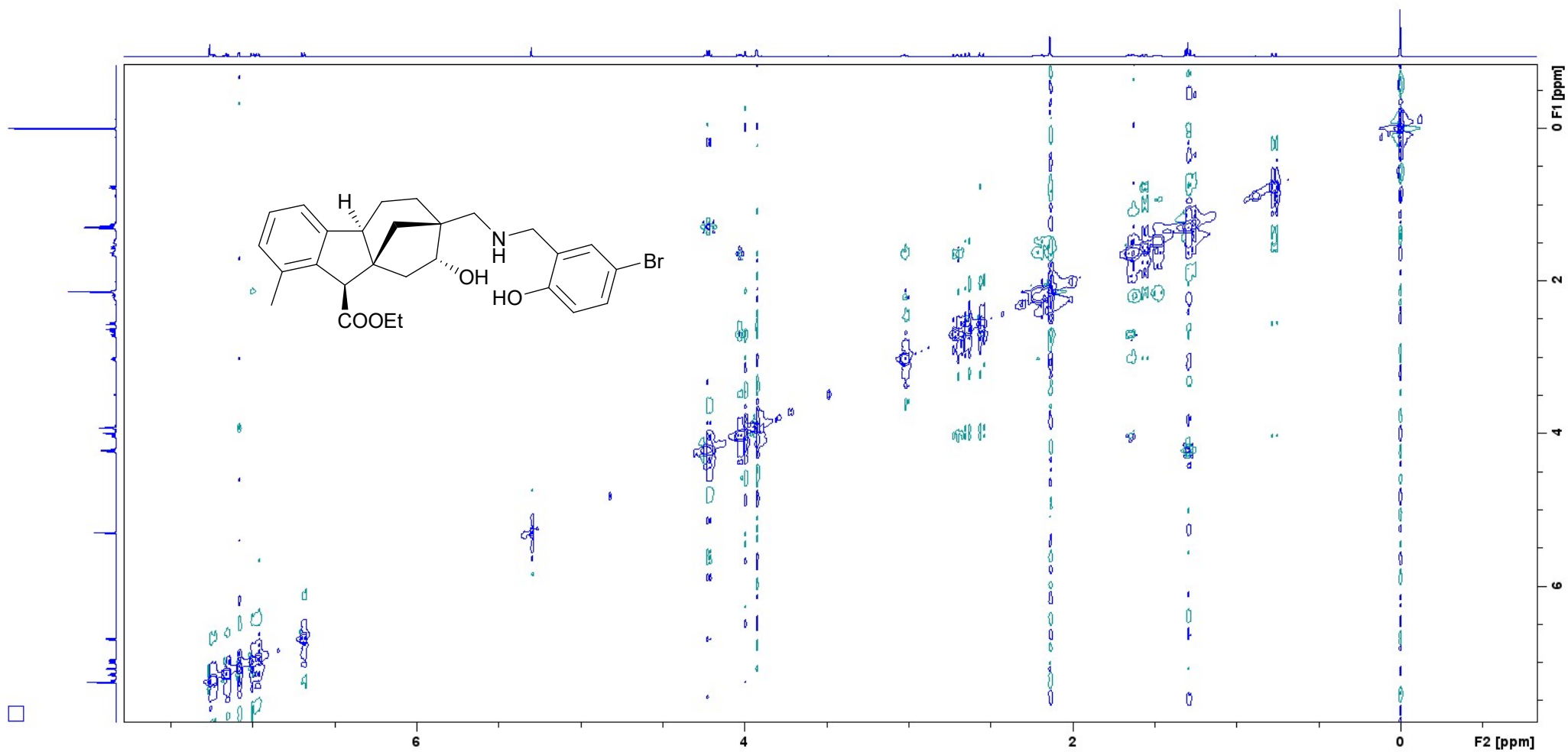
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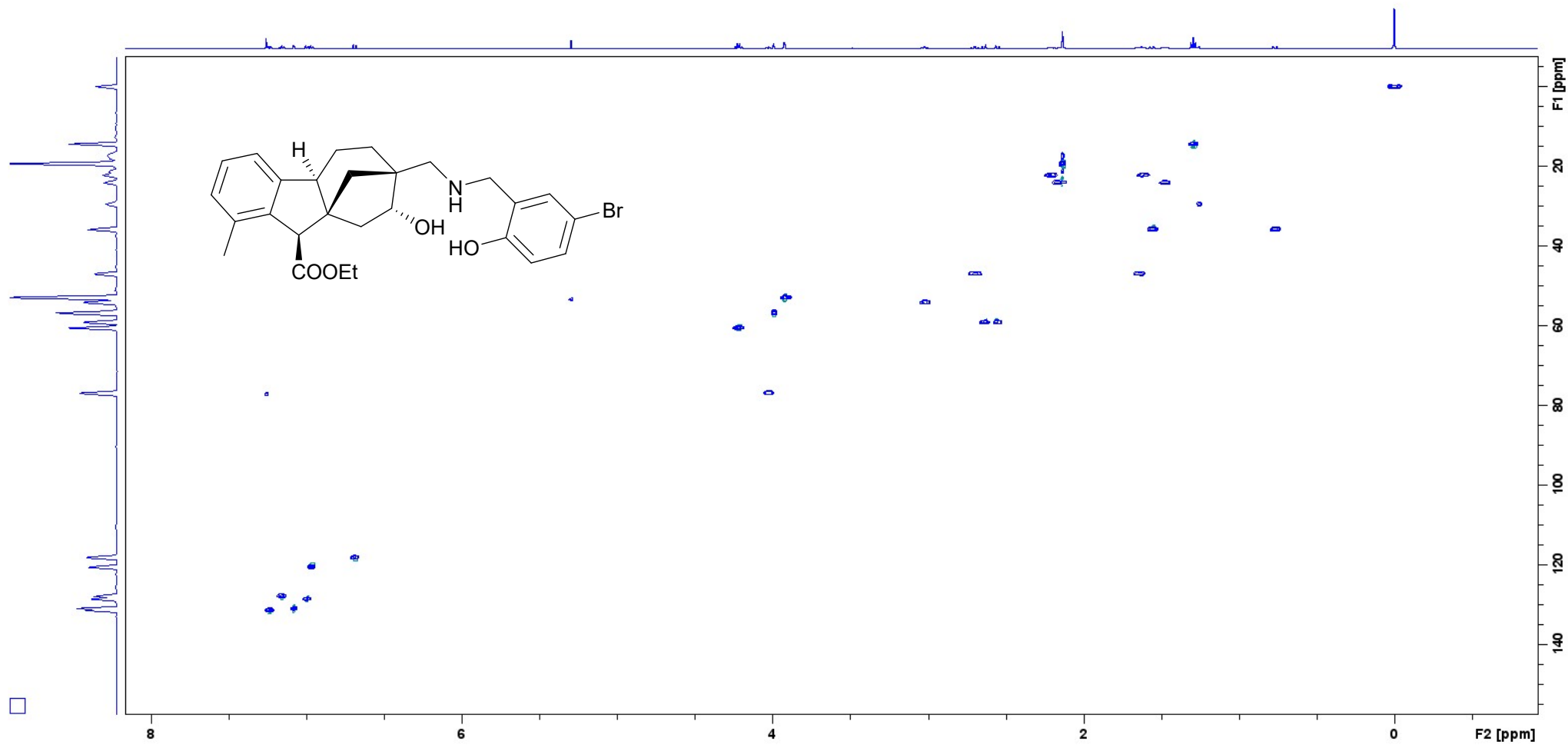
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(((5-bromo-2-hydroxybenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **34**



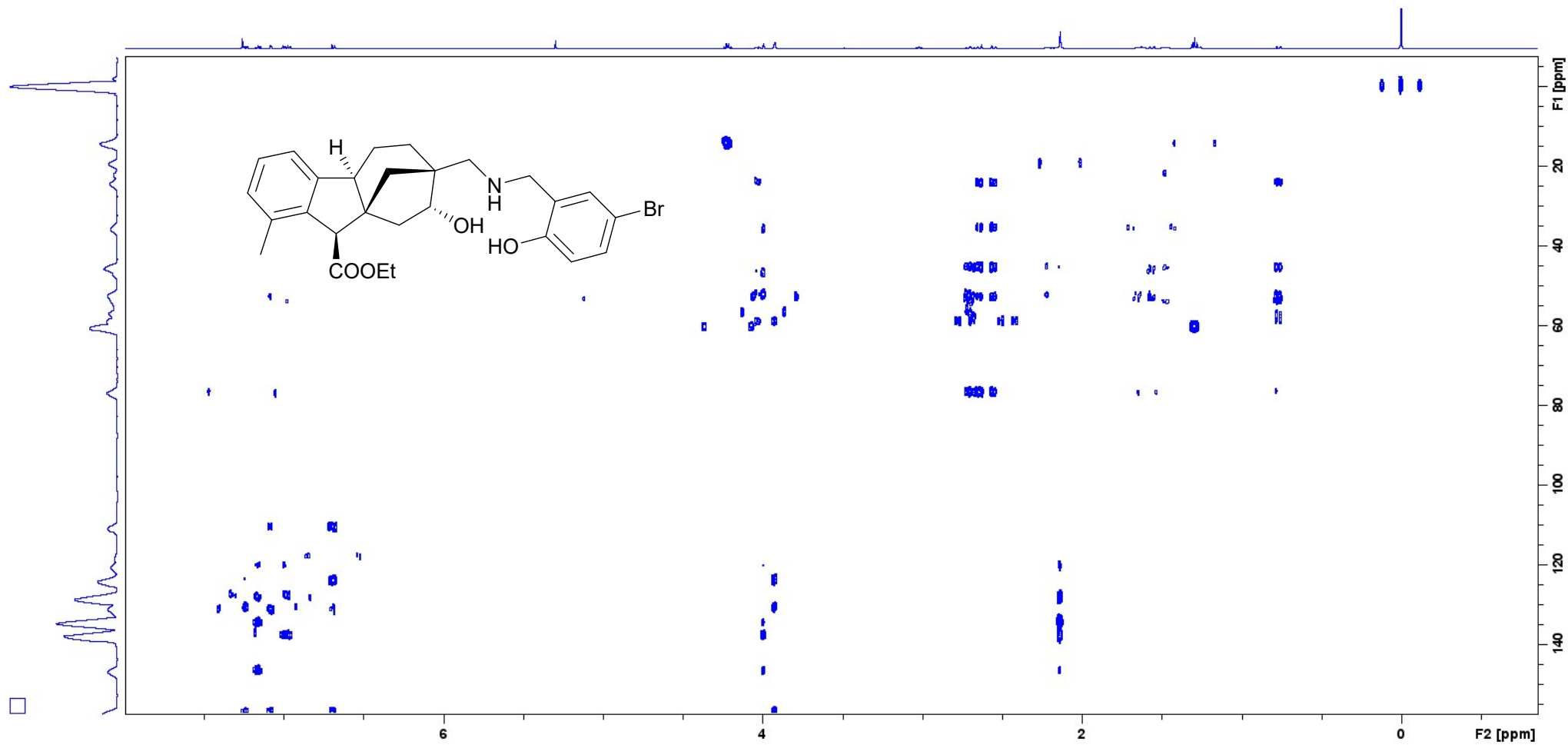
NOESY of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-(((5-bromo-2-hydroxybenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **34**



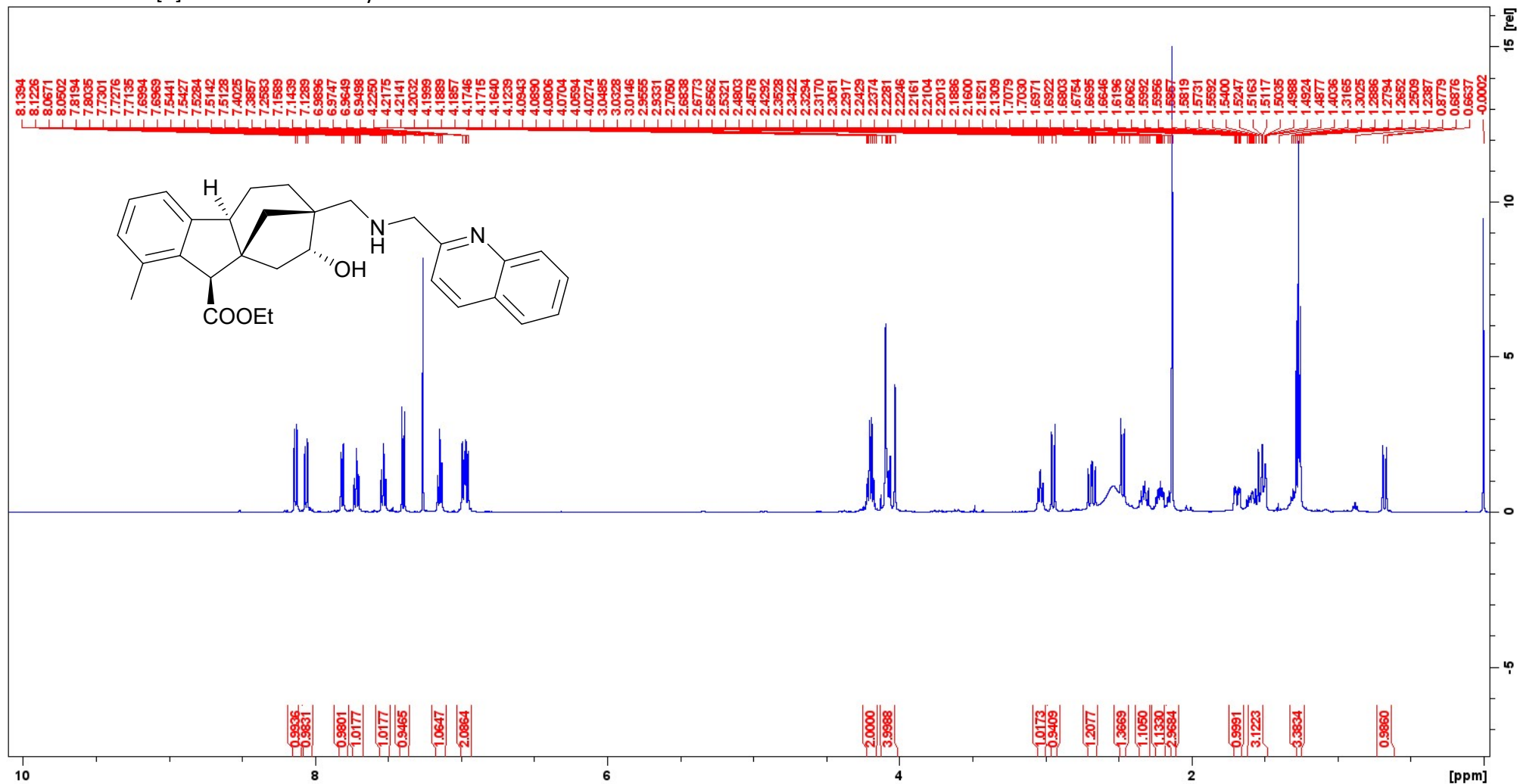
HSQC of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-(((5-bromo-2-hydroxybenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **34**



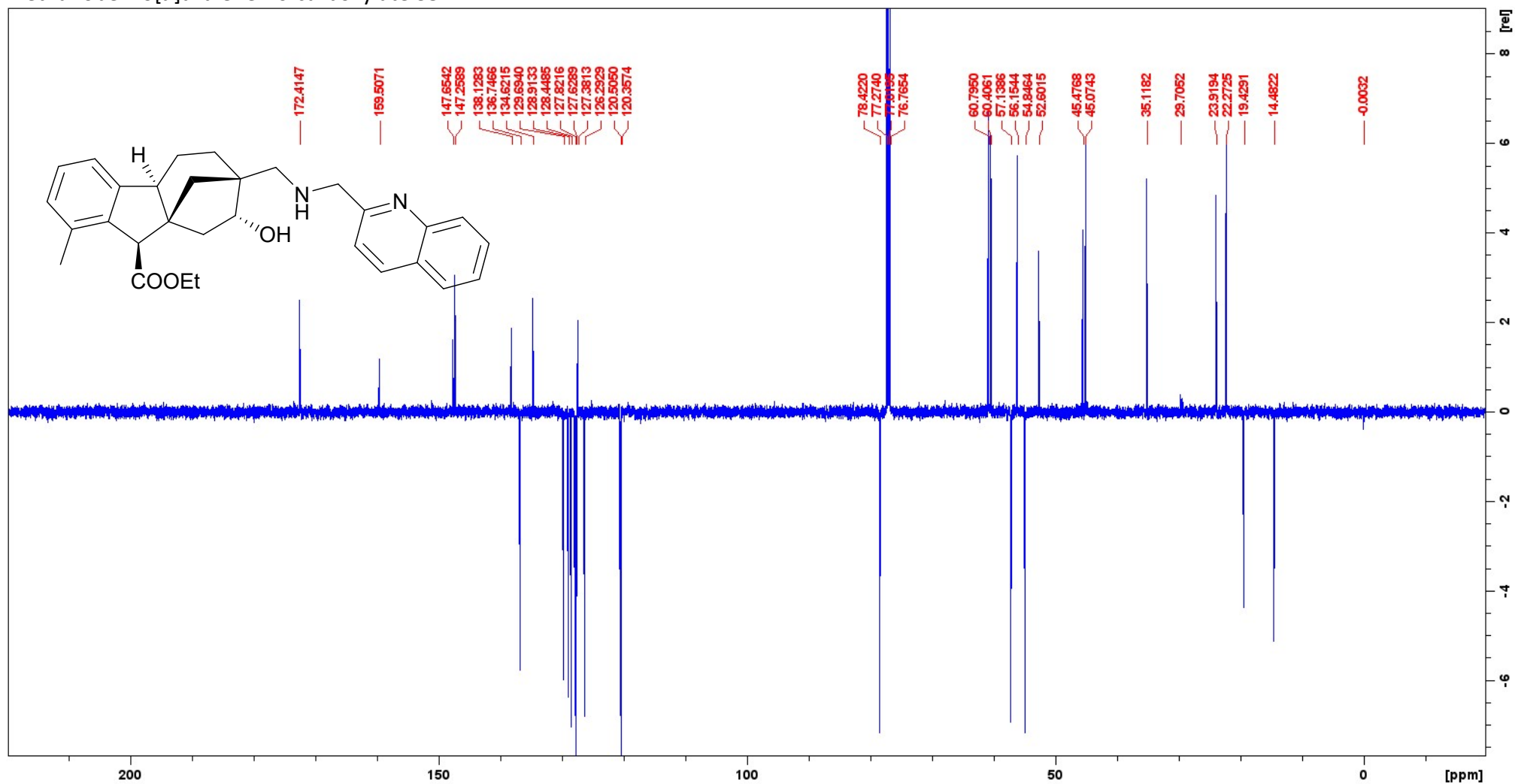
HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-(((5-bromo-2-hydroxybenzyl)amino)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **34**



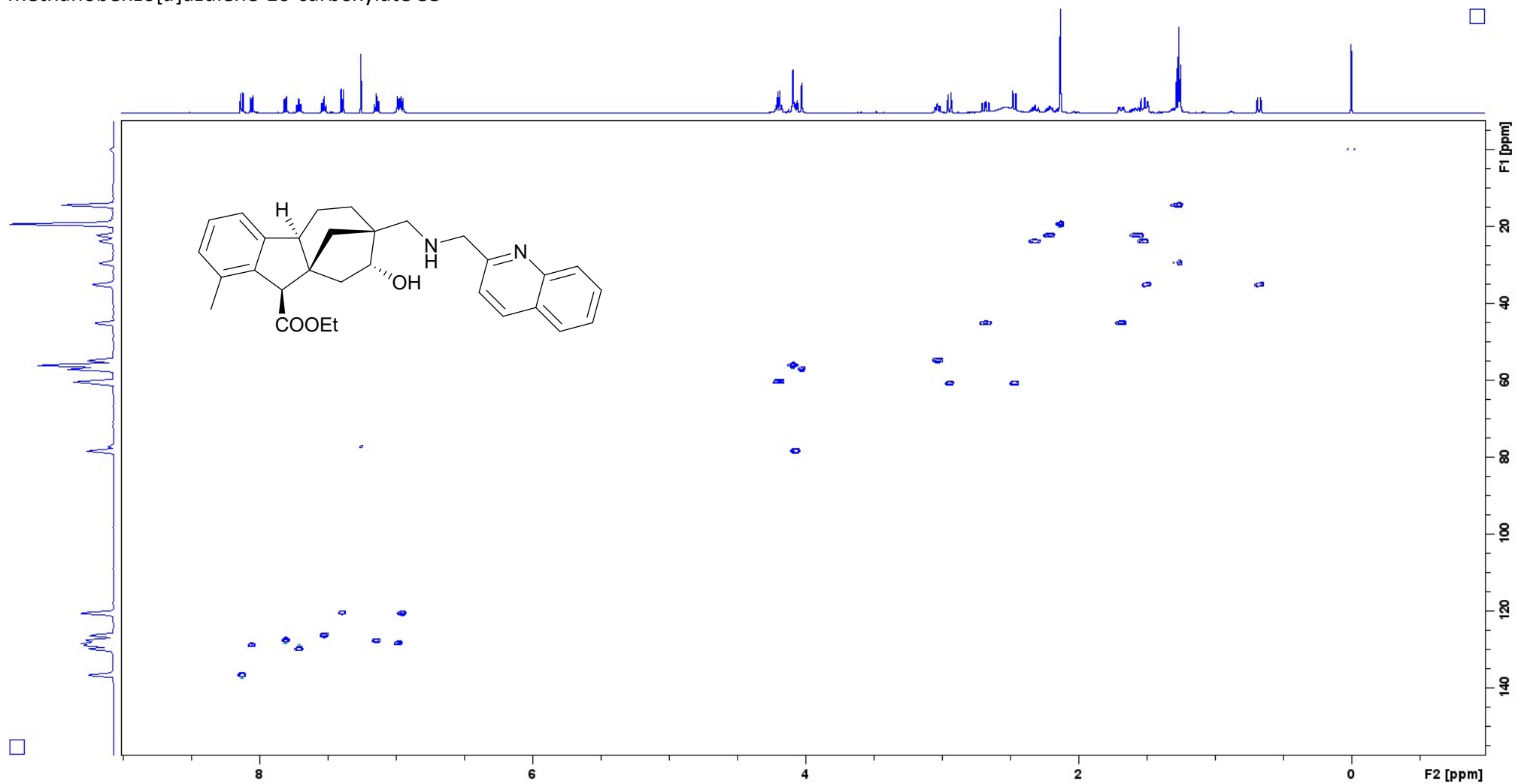
¹H-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((quinolin-2-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **35**



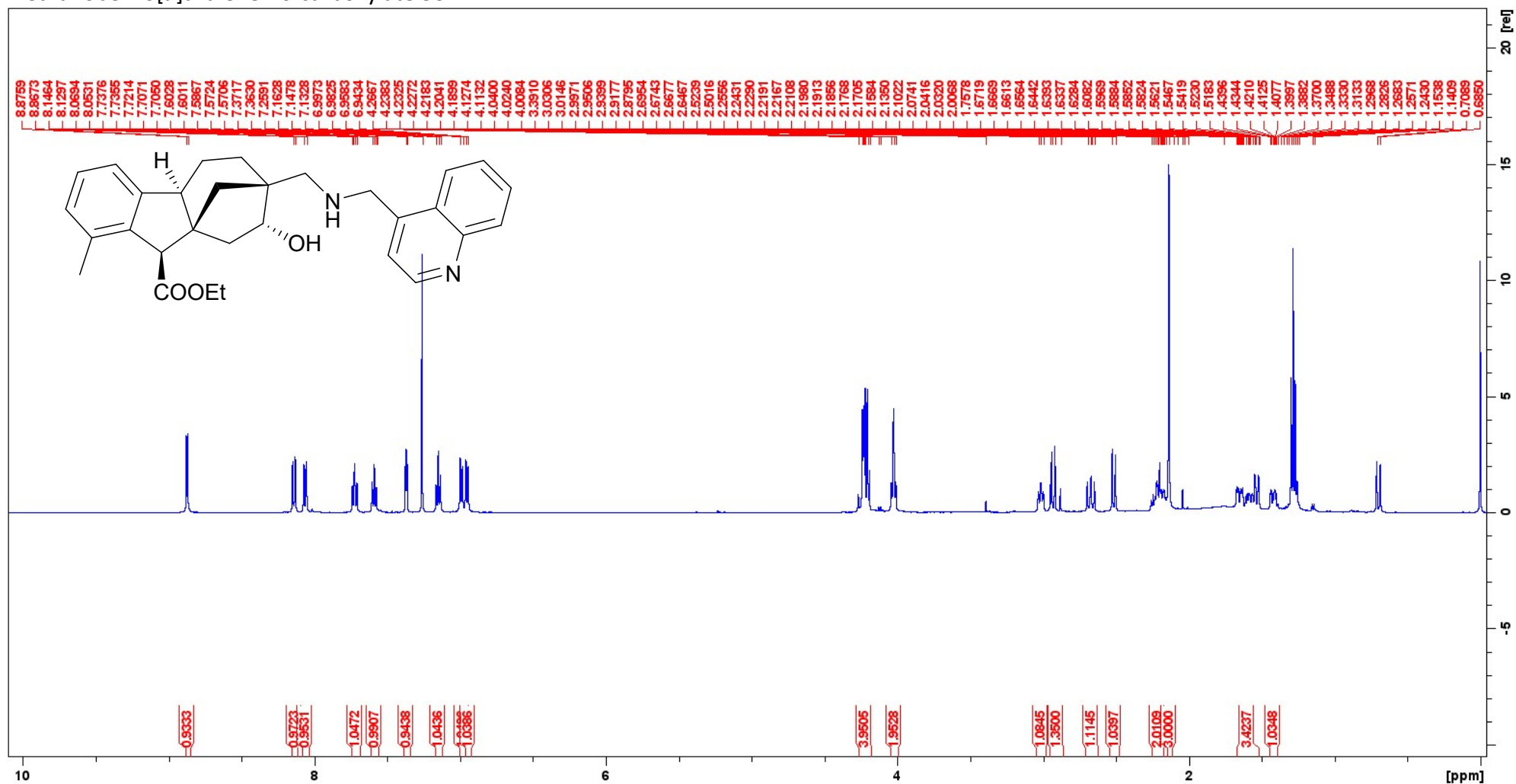
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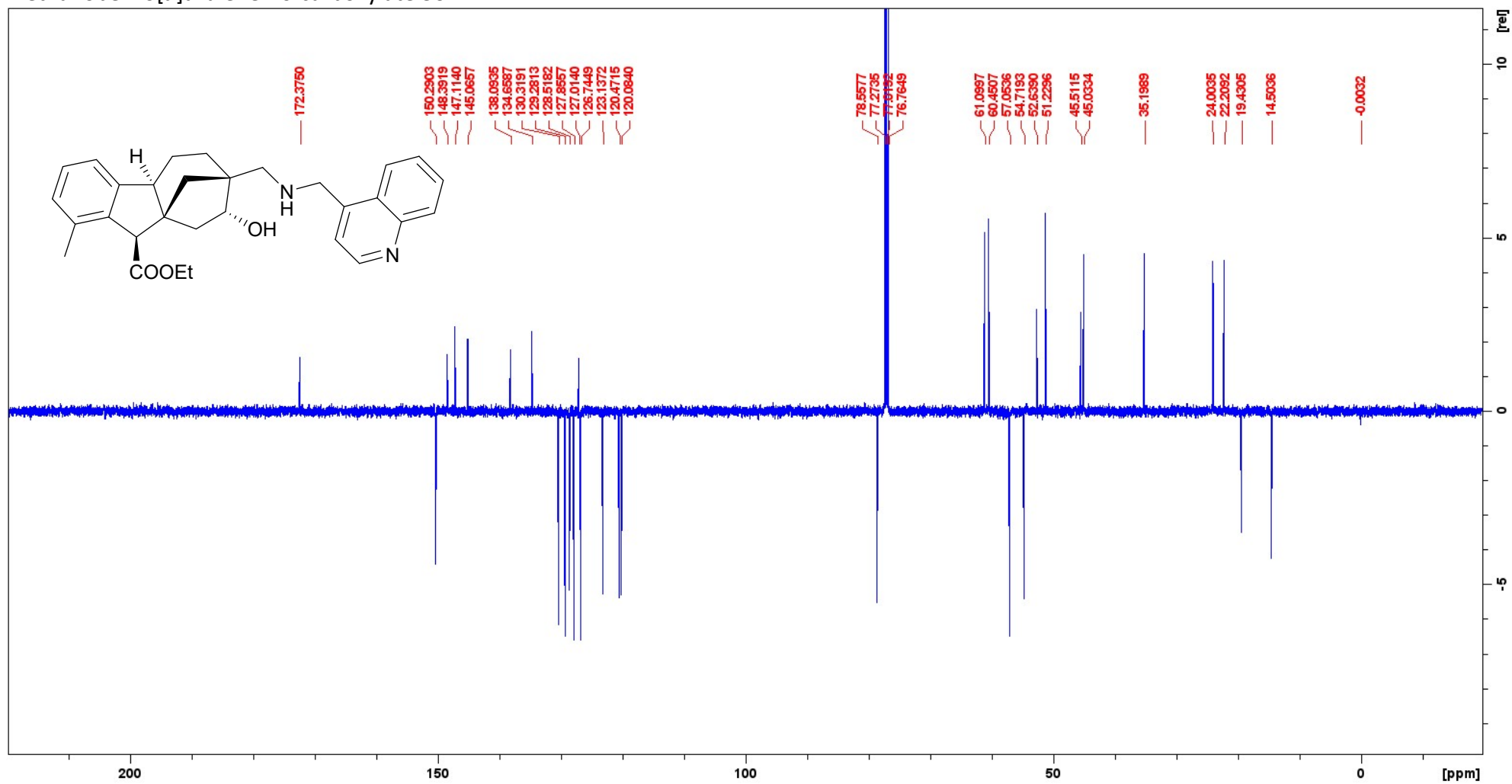
HSQC of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((quinolin-2-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **35**



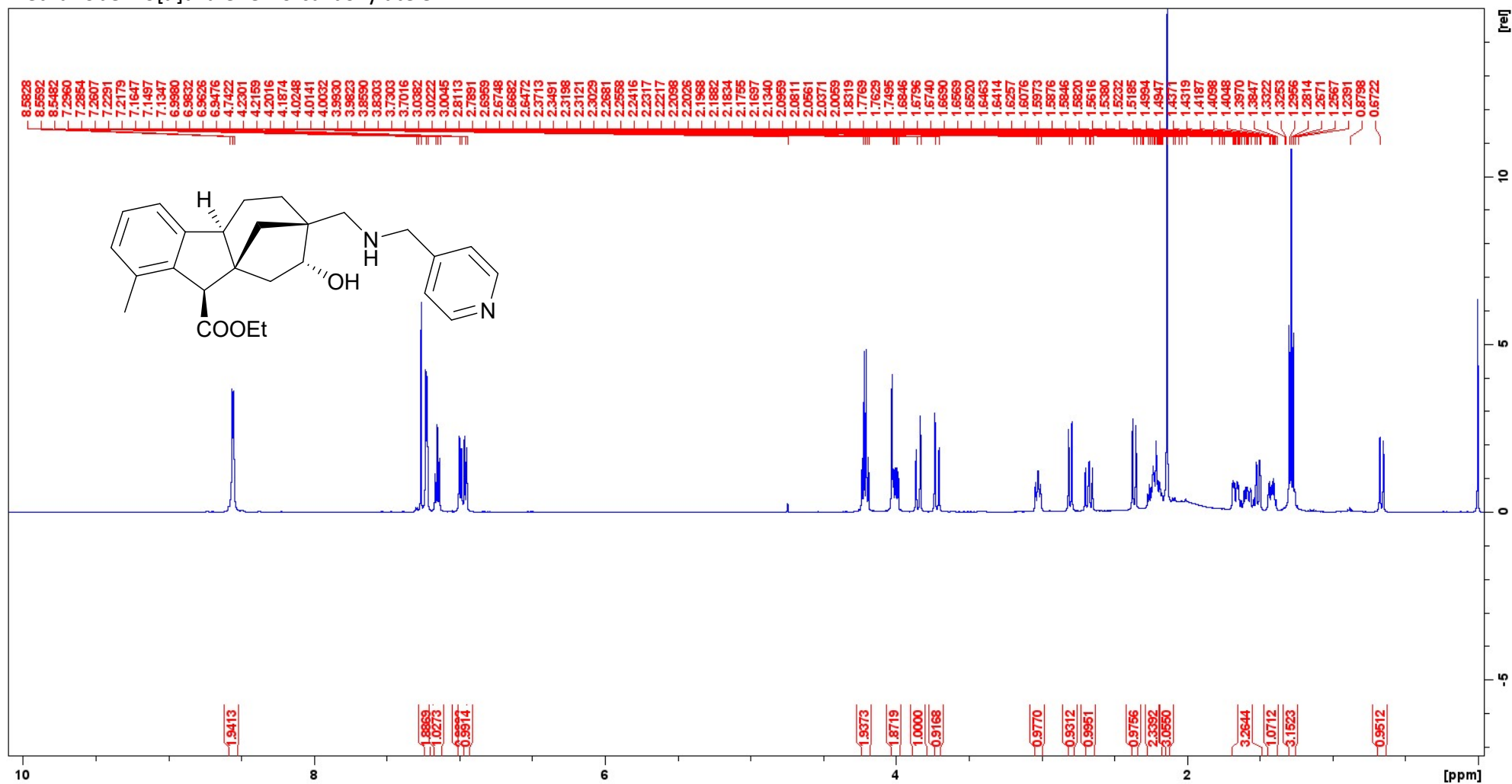
¹H-NMR of ethyl (4*b*S,7*S*,8*R*,9*a*S,10*R*)-8-hydroxy-1-methyl-7-(((quinolin-4-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **36**



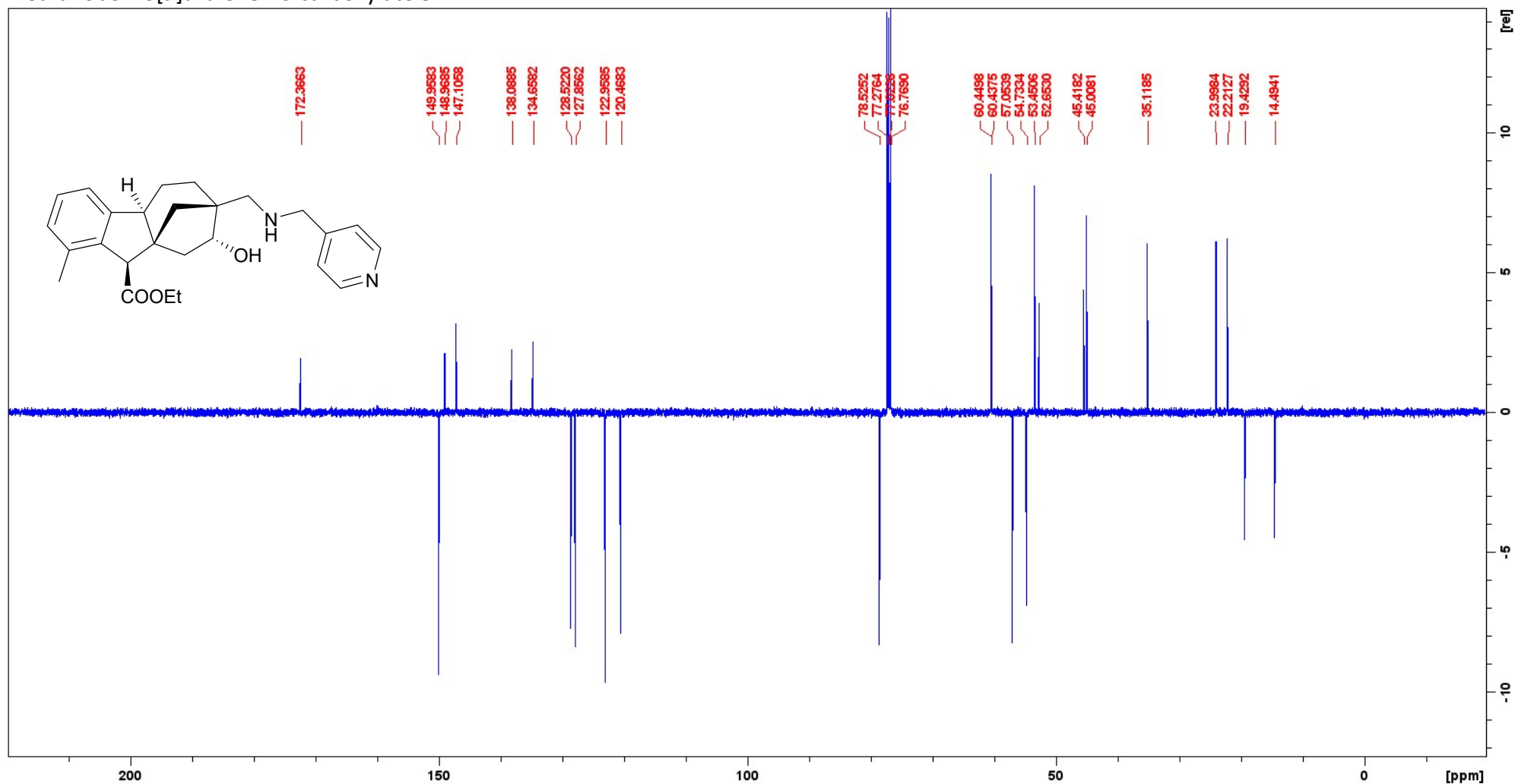
^{13}C -NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((quinolin-4-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **36**



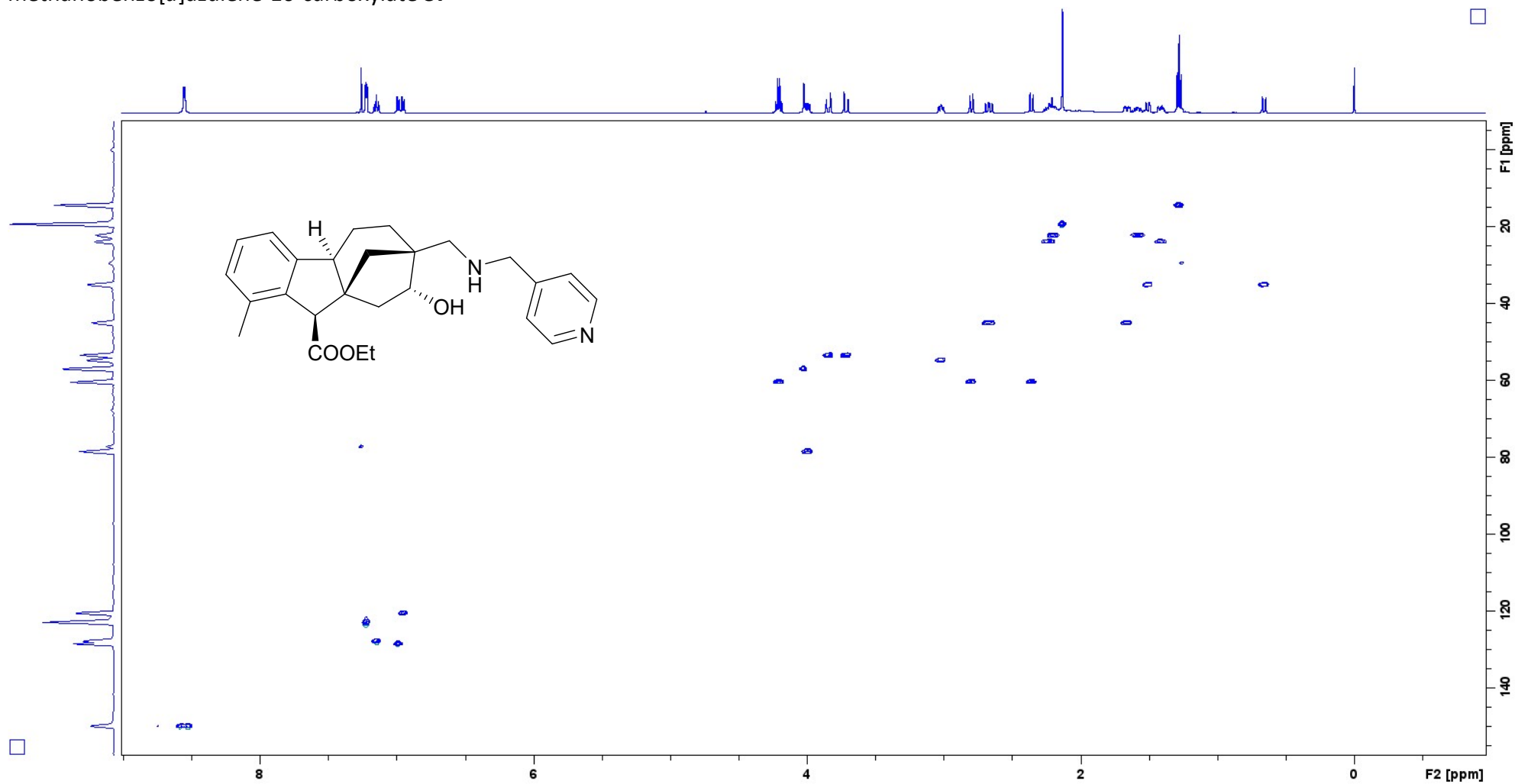
¹H-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((pyridin-4-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **37**



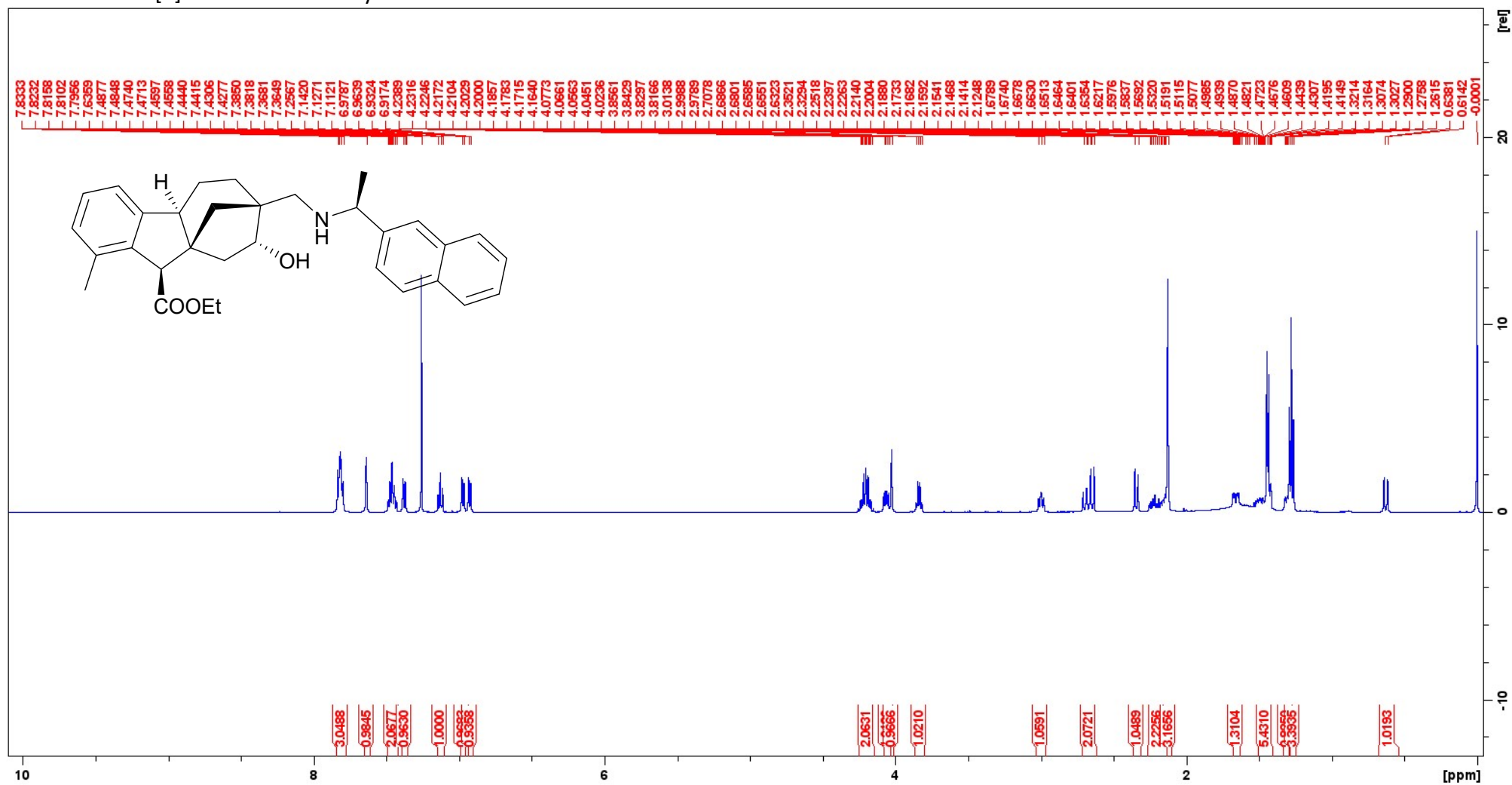
¹³C-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((pyridin-4-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **37**



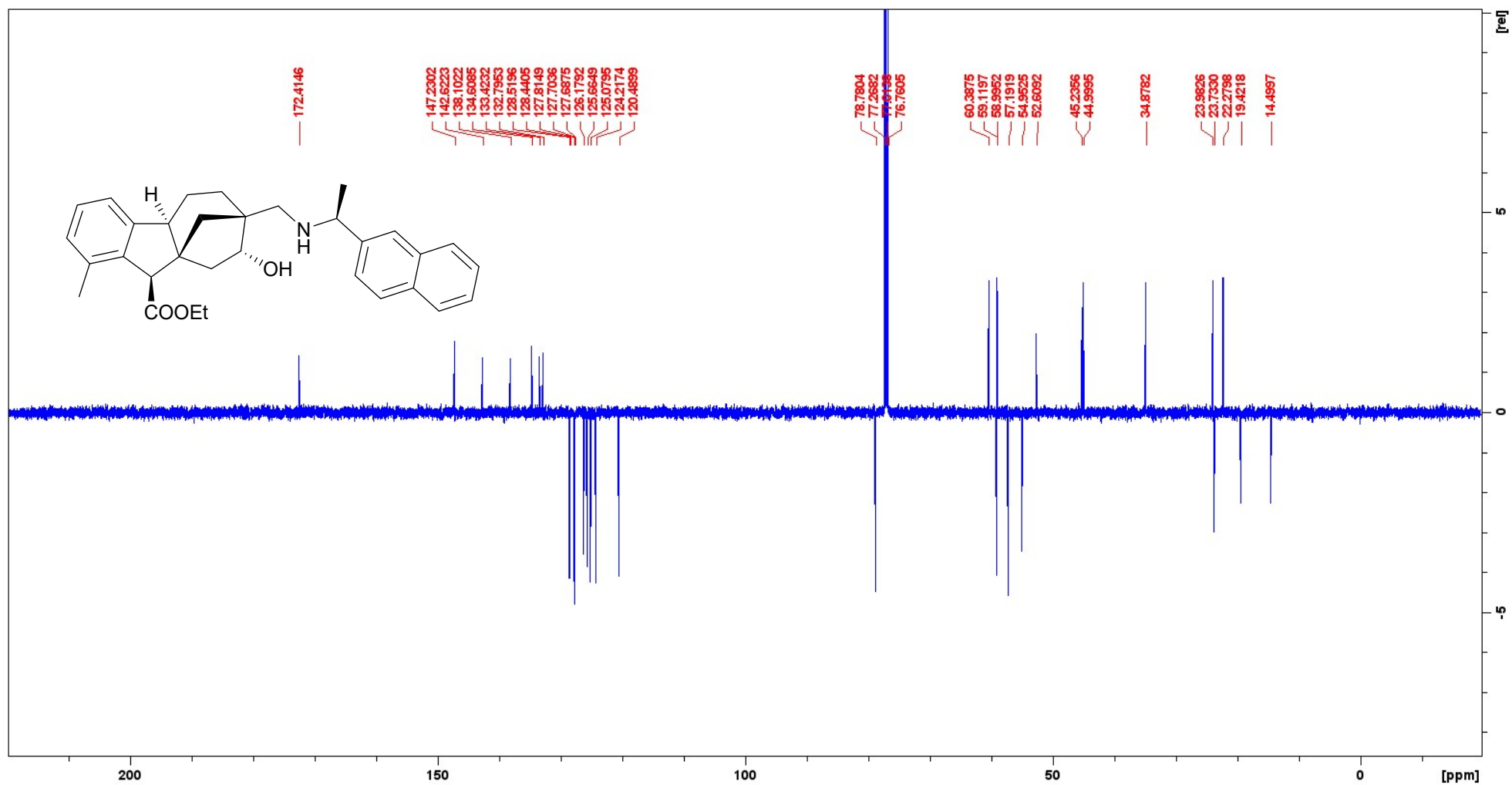
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((pyridin-4-ylmethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **37**



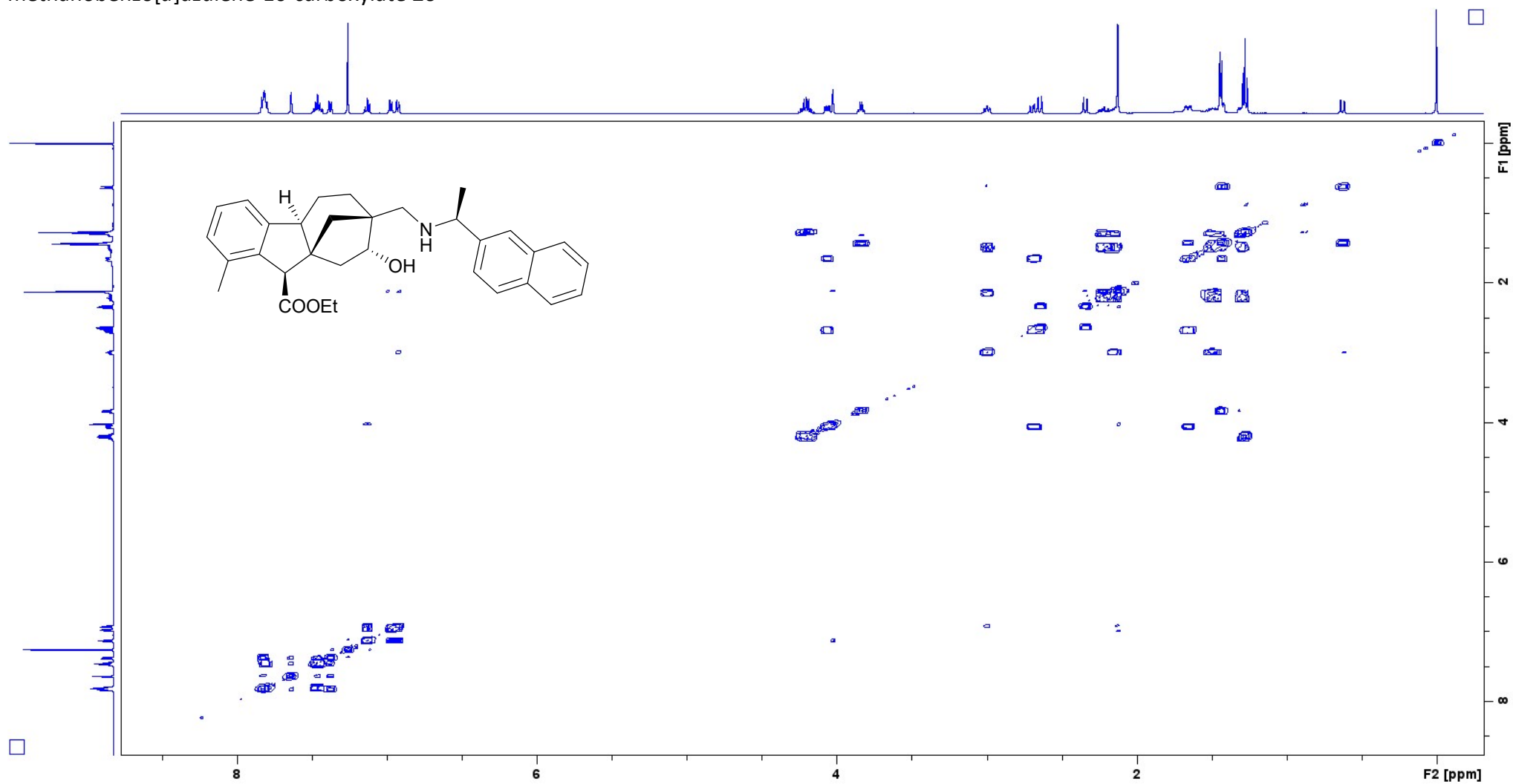
$^1\text{H-NMR}$ of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **26**



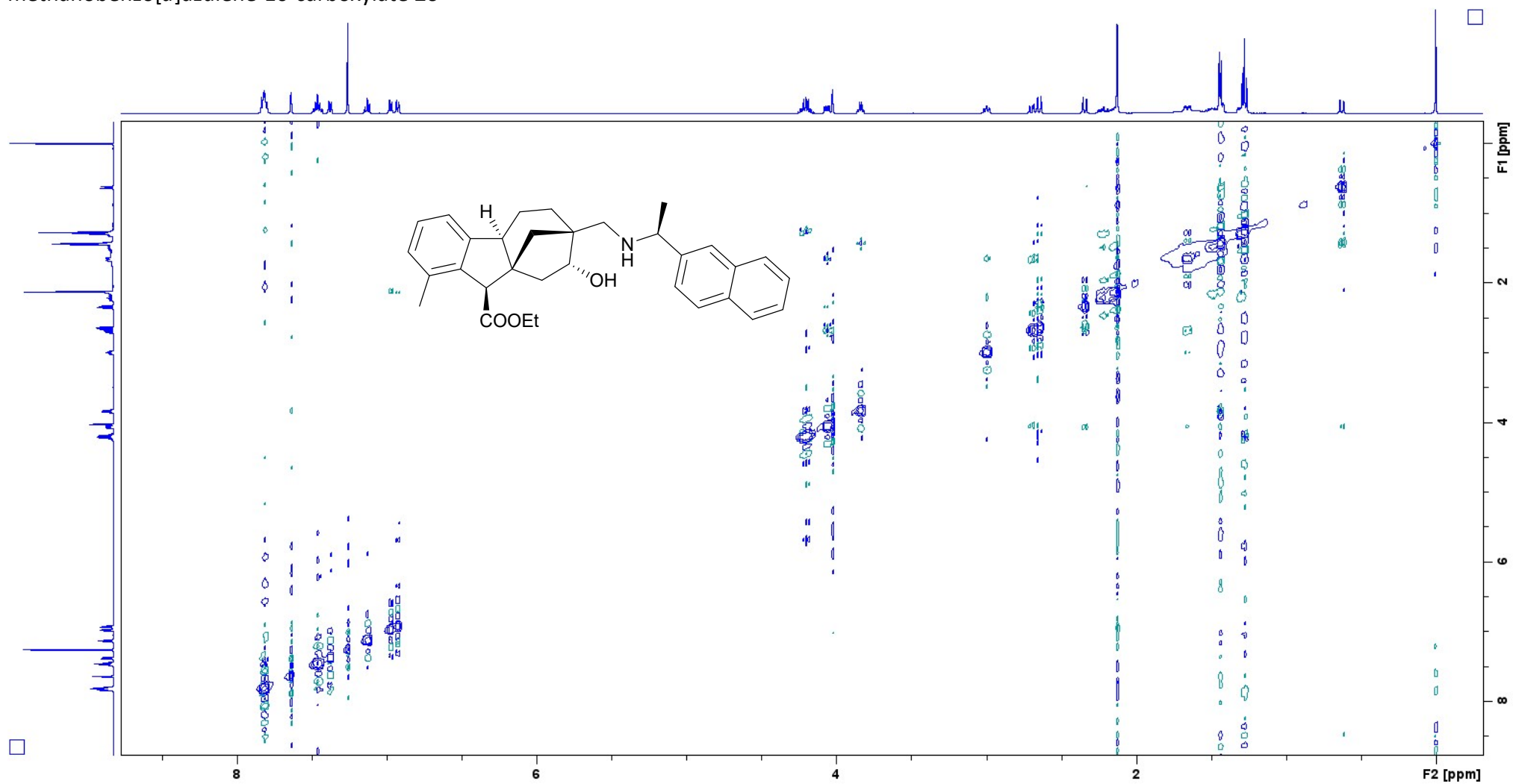
¹³C-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **26**



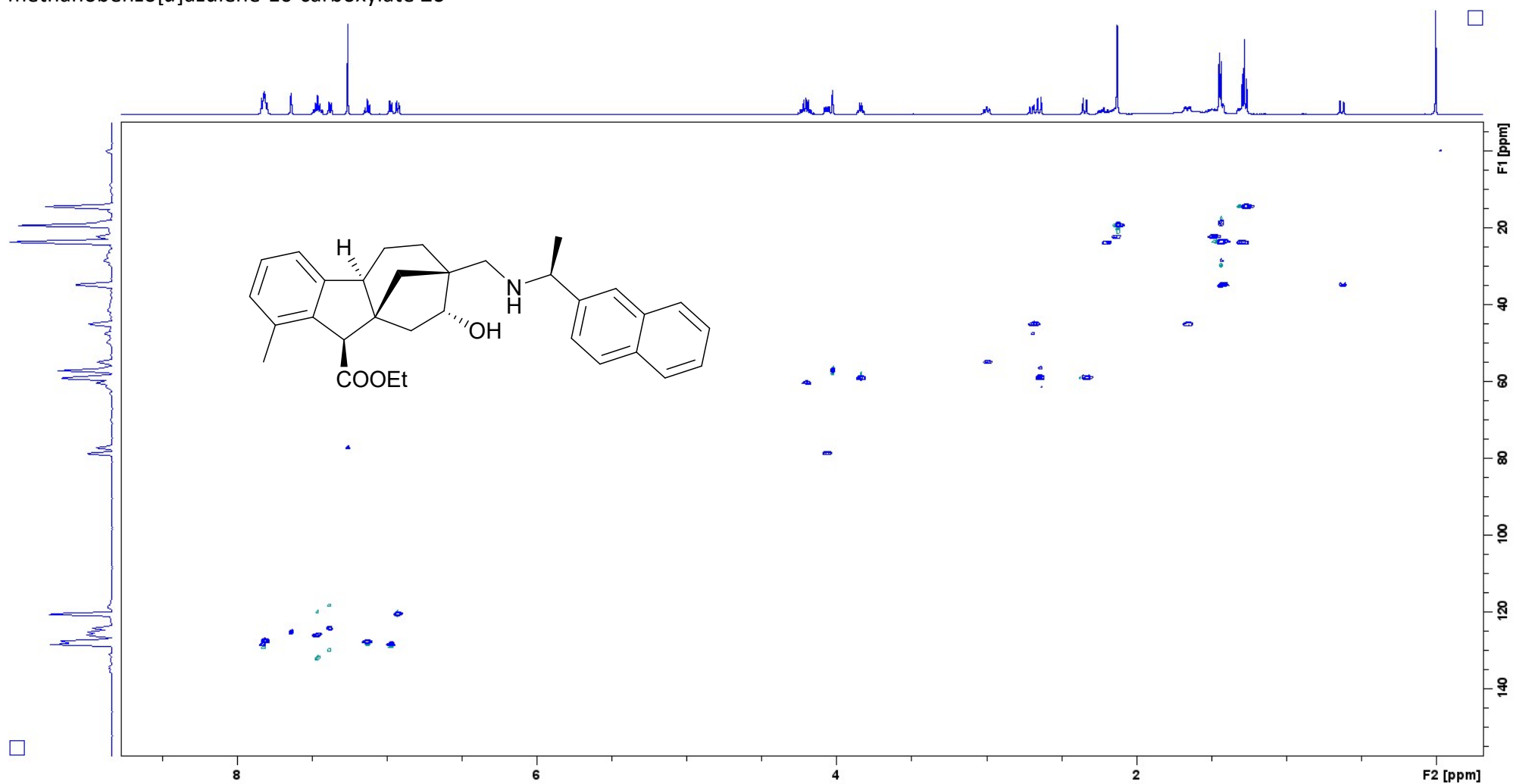
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **26**



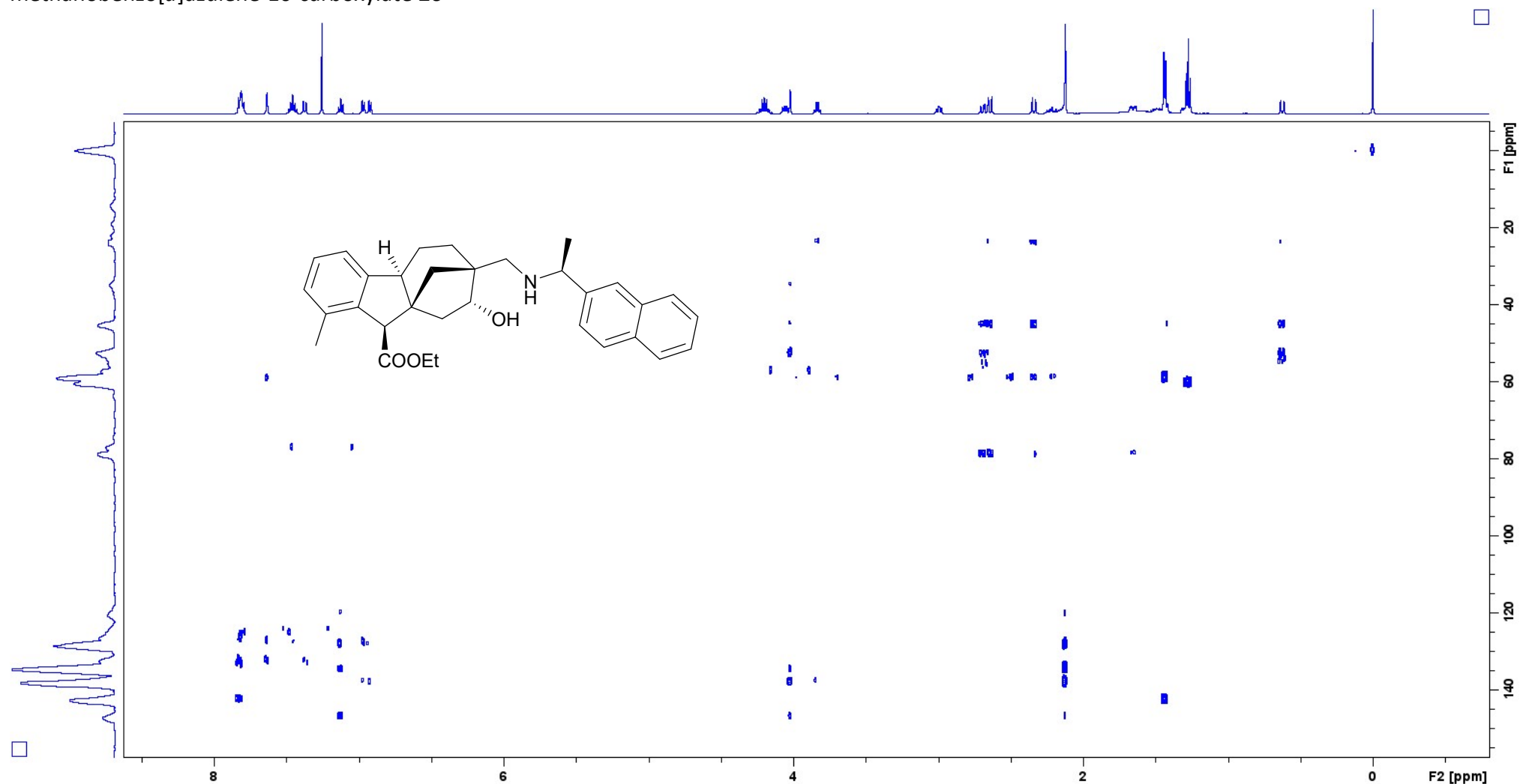
NOESY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **26**



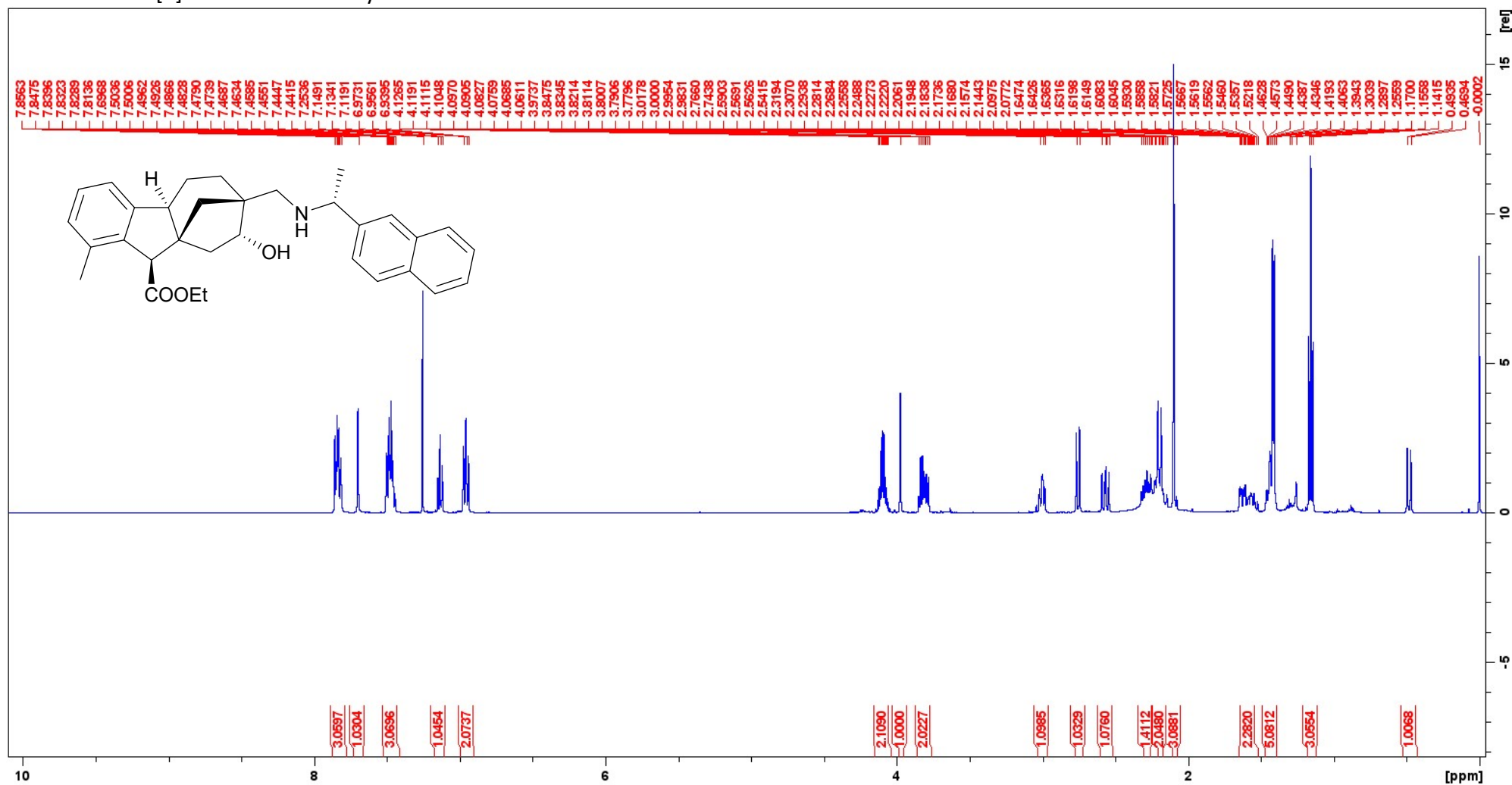
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **26**



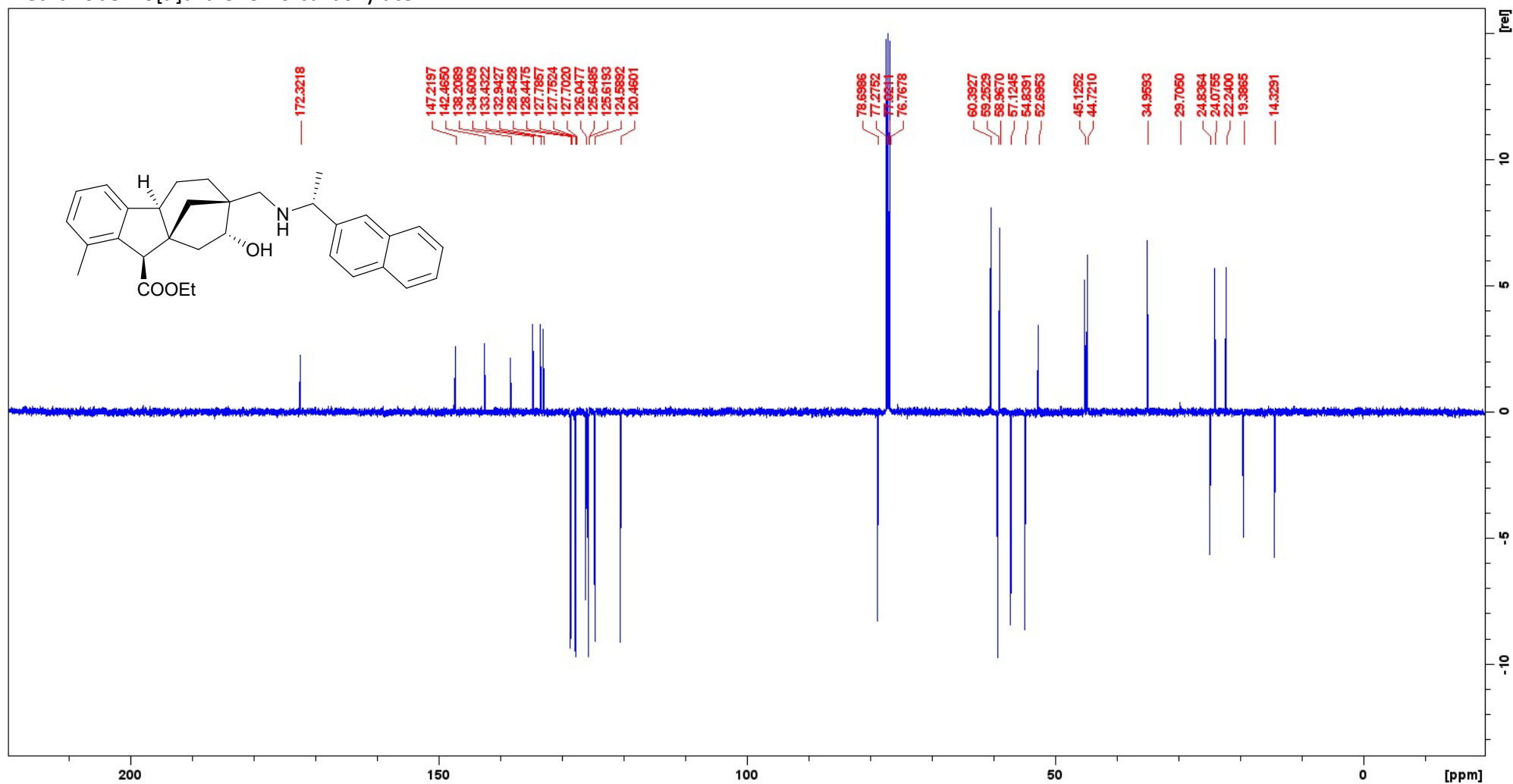
HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **26**



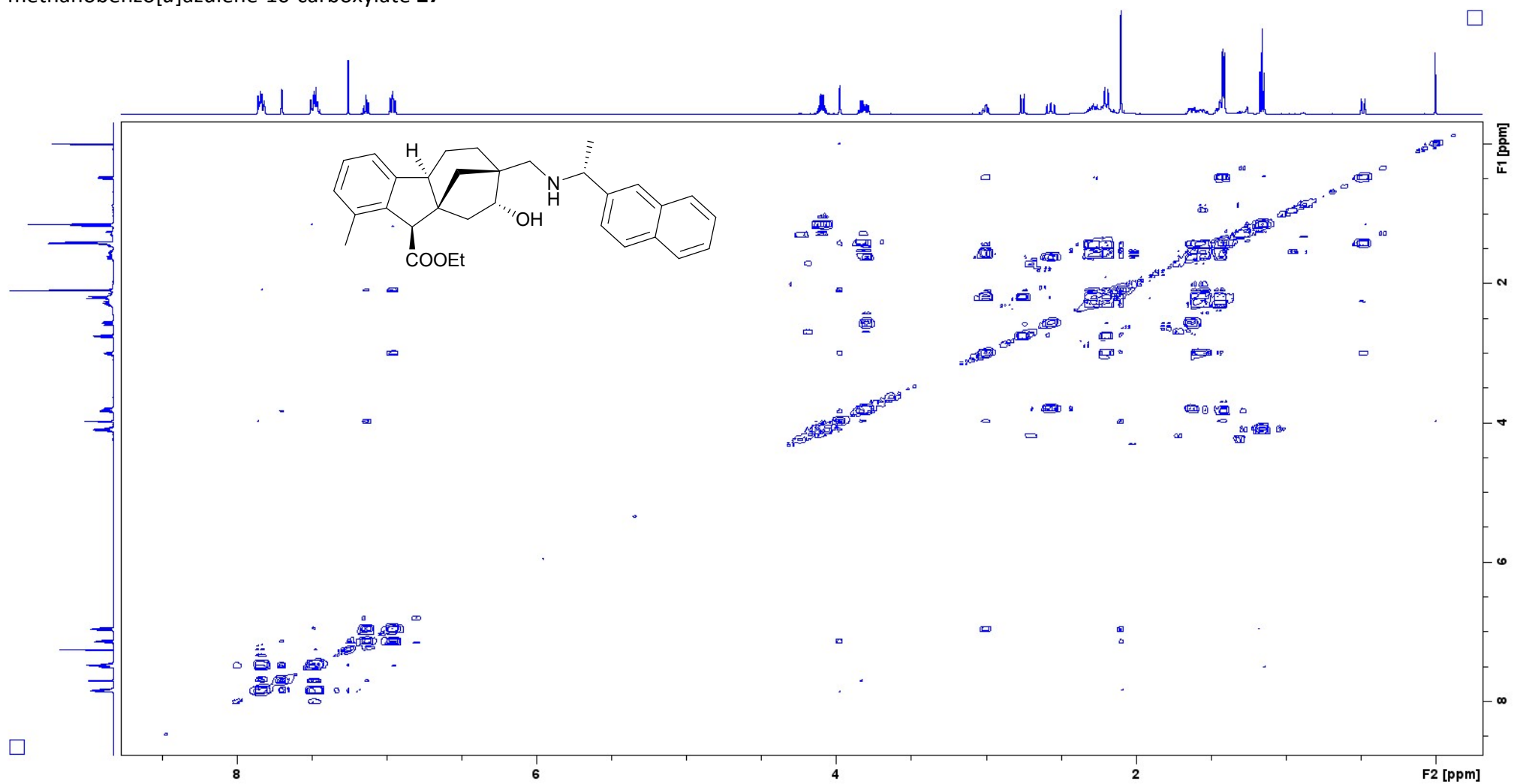
¹H-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **27**



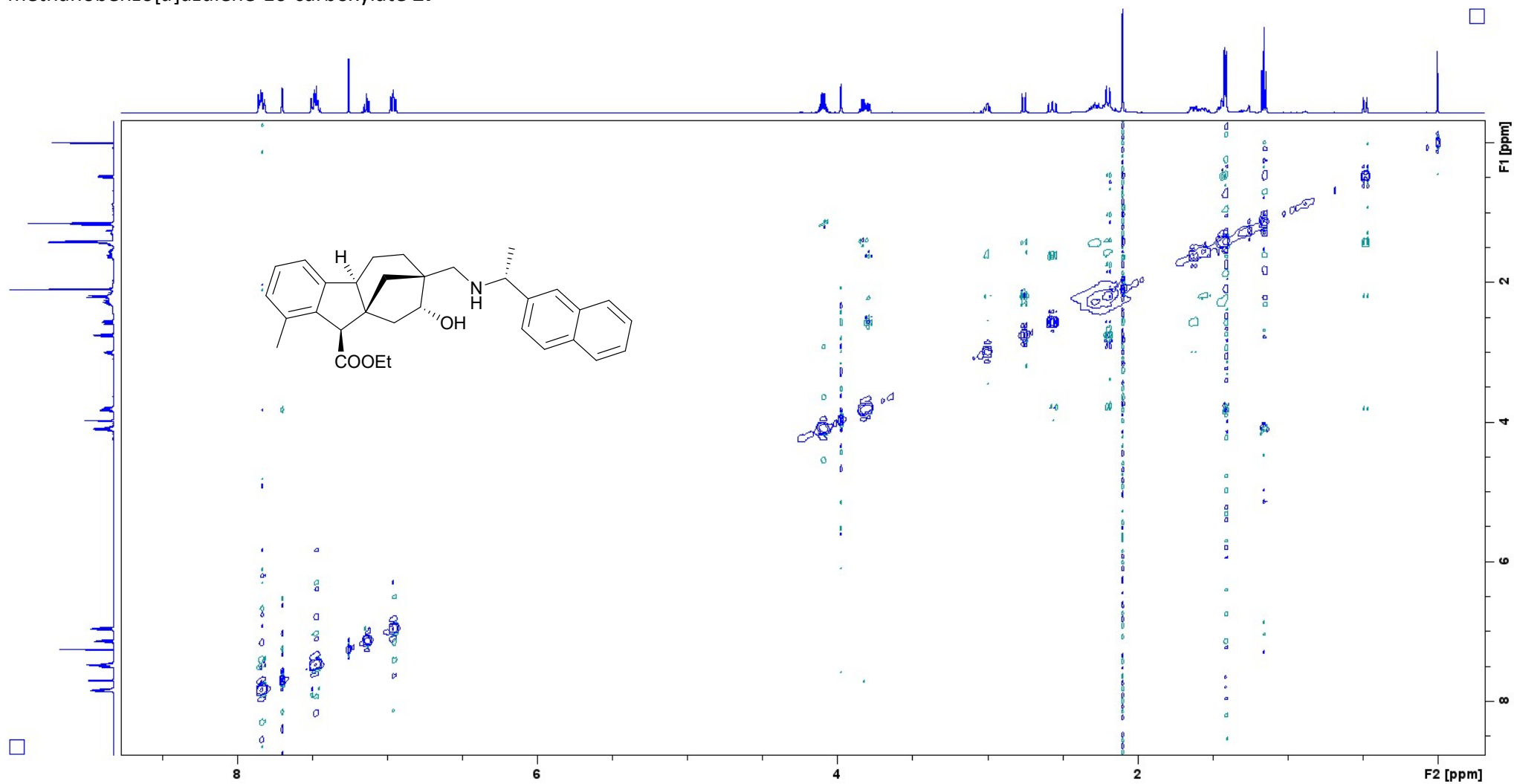
¹³C-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **27**



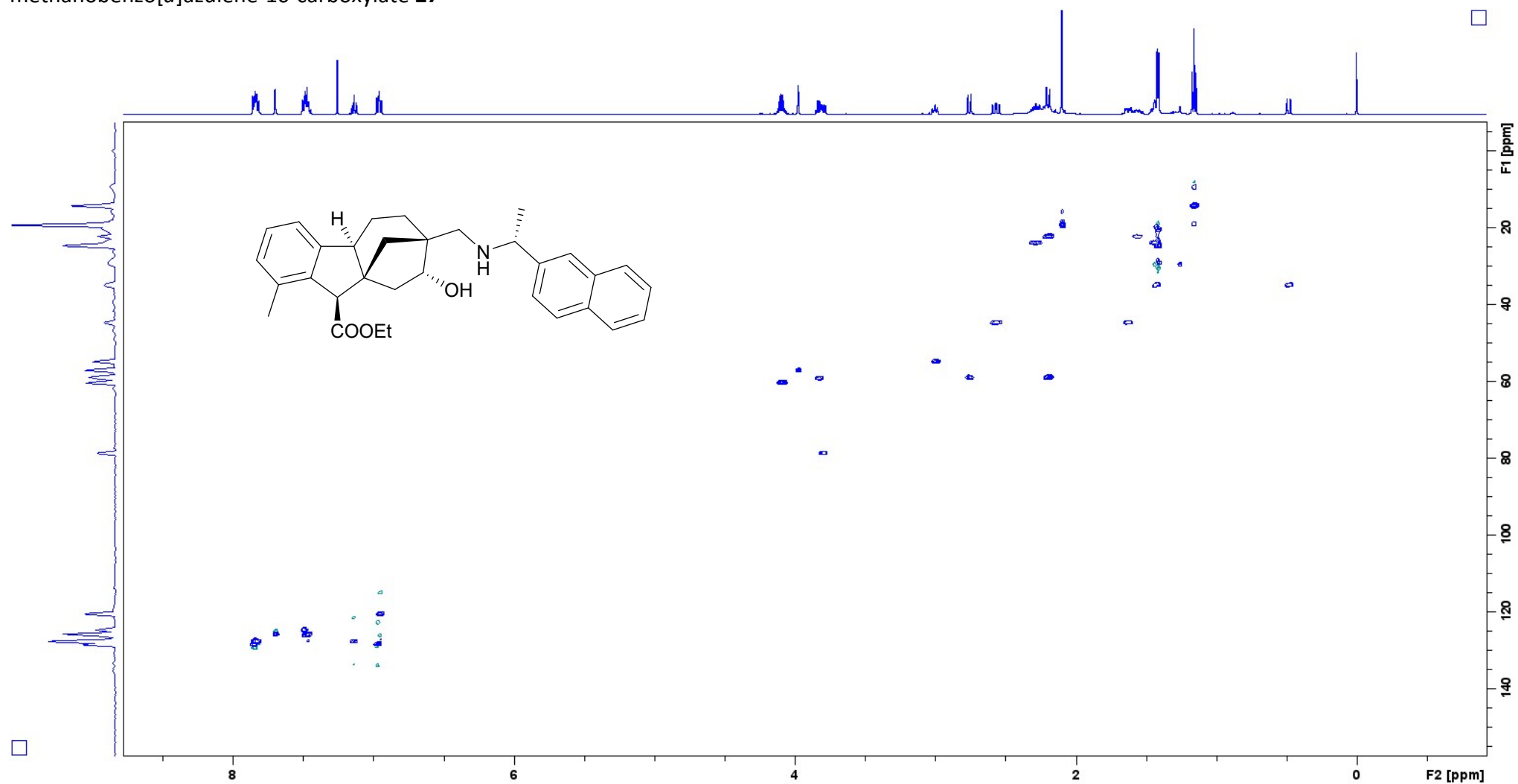
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **27**



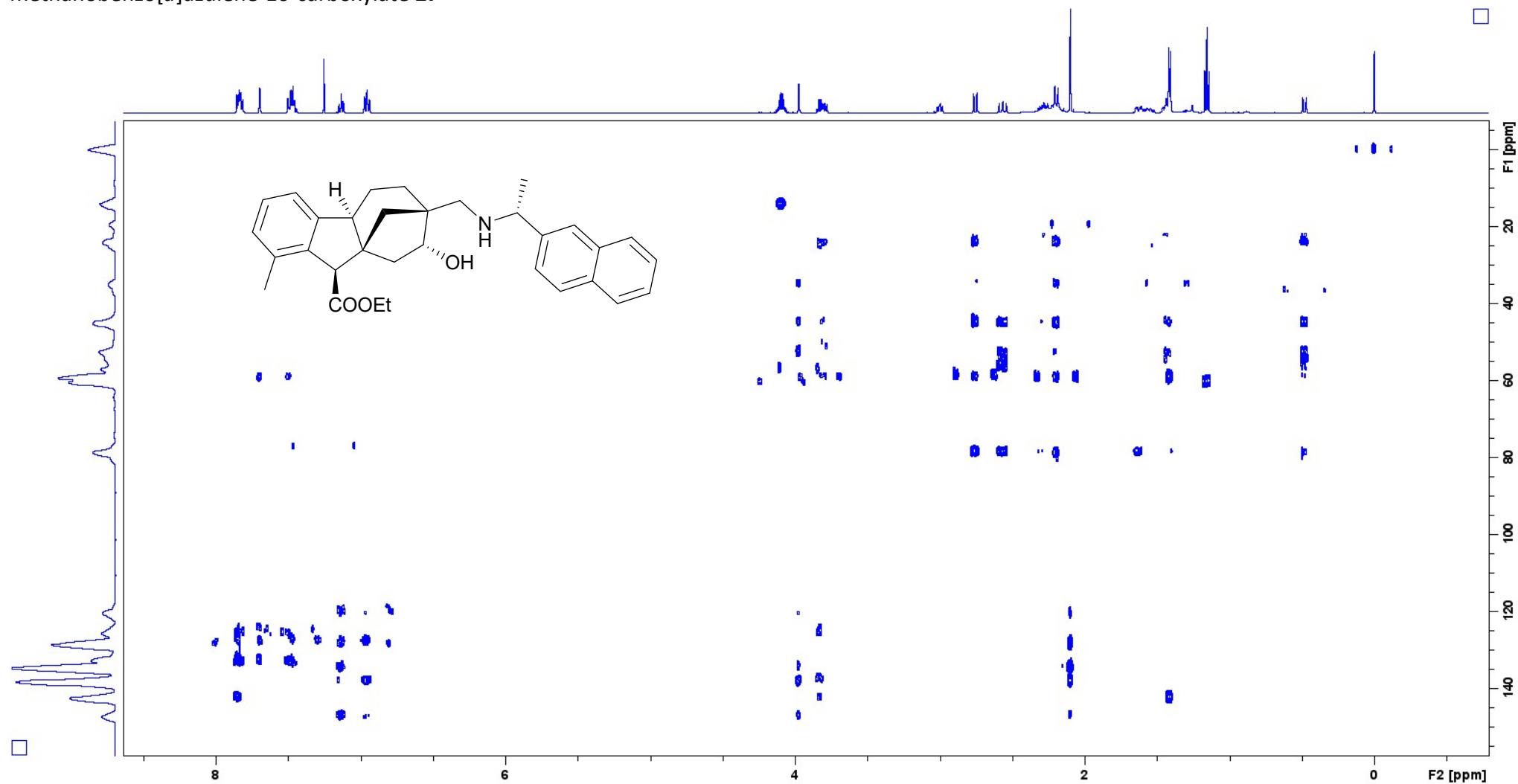
NOESY of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **27**



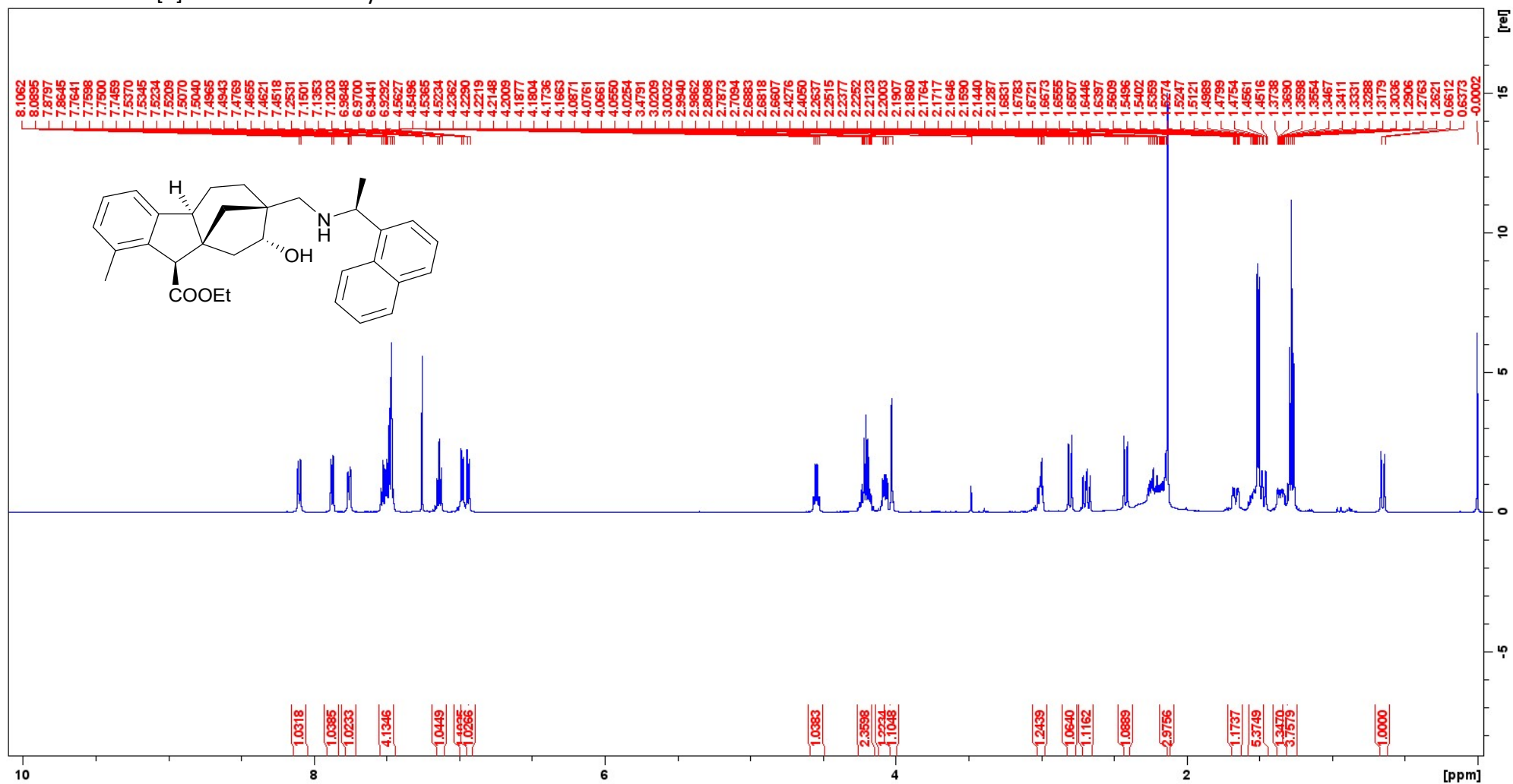
HSQC of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **27**



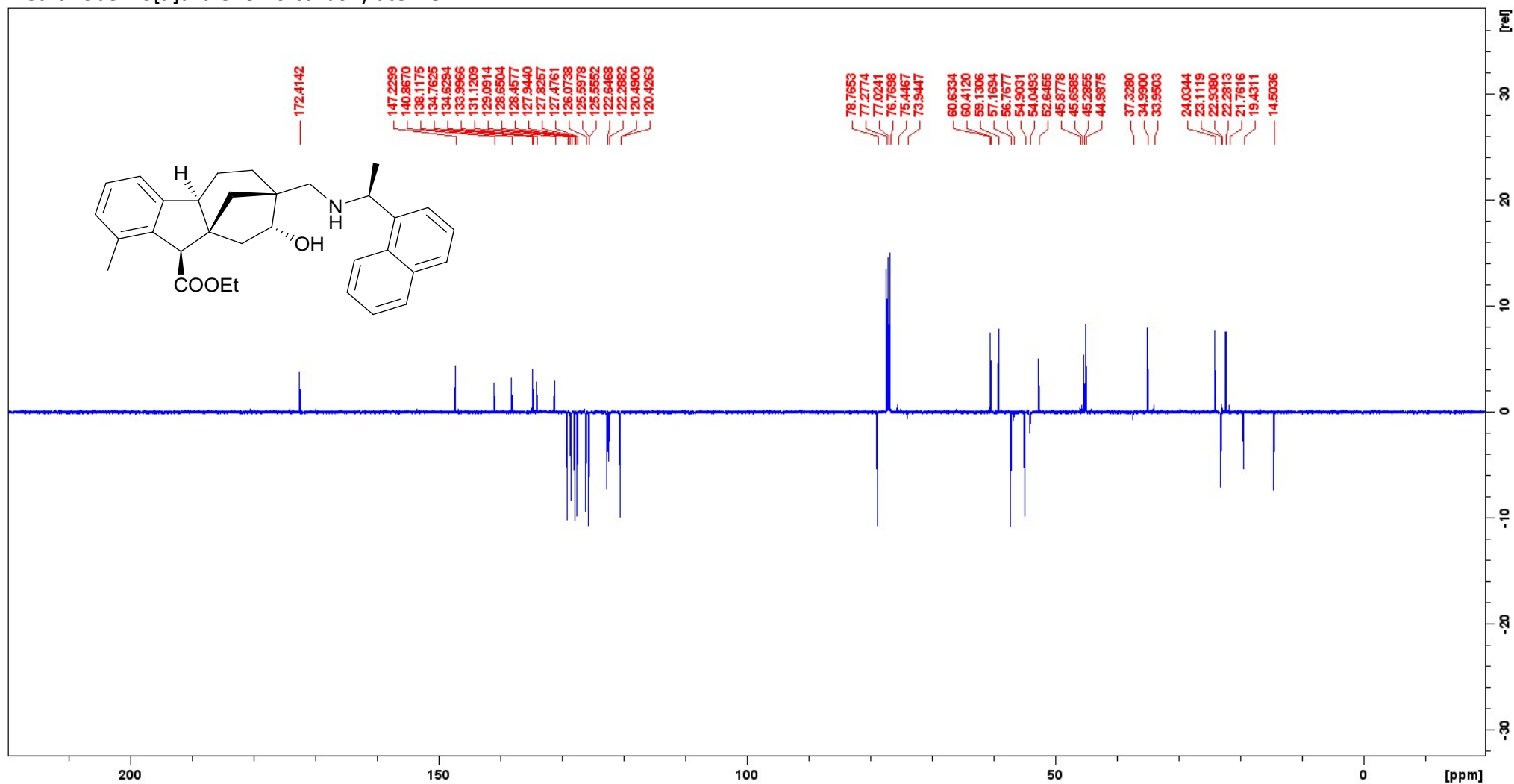
HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-2-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **27**



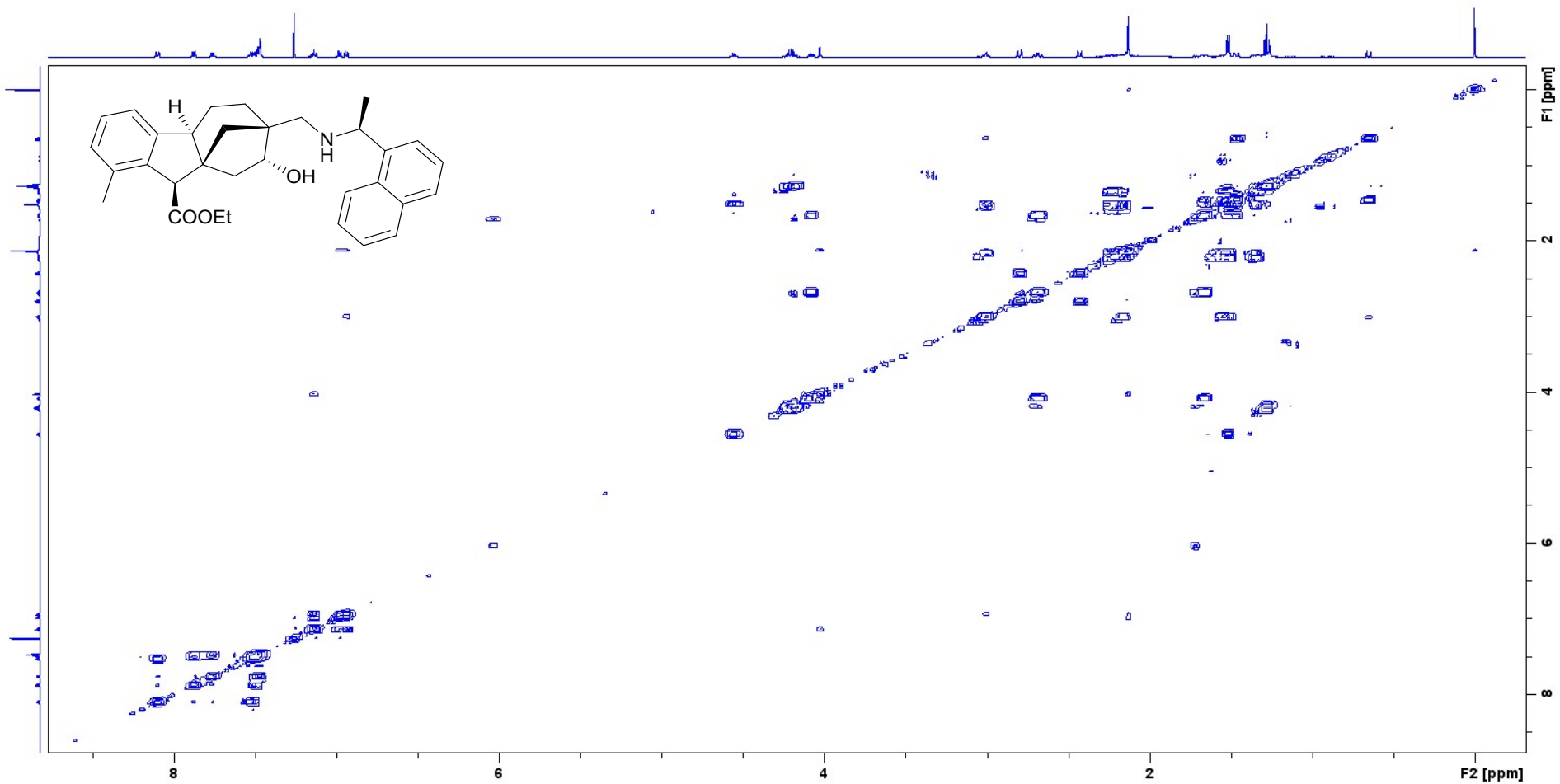
¹H-NMR of ethyl (4*S*,7*S*,8*R*,9*a**S*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **28**



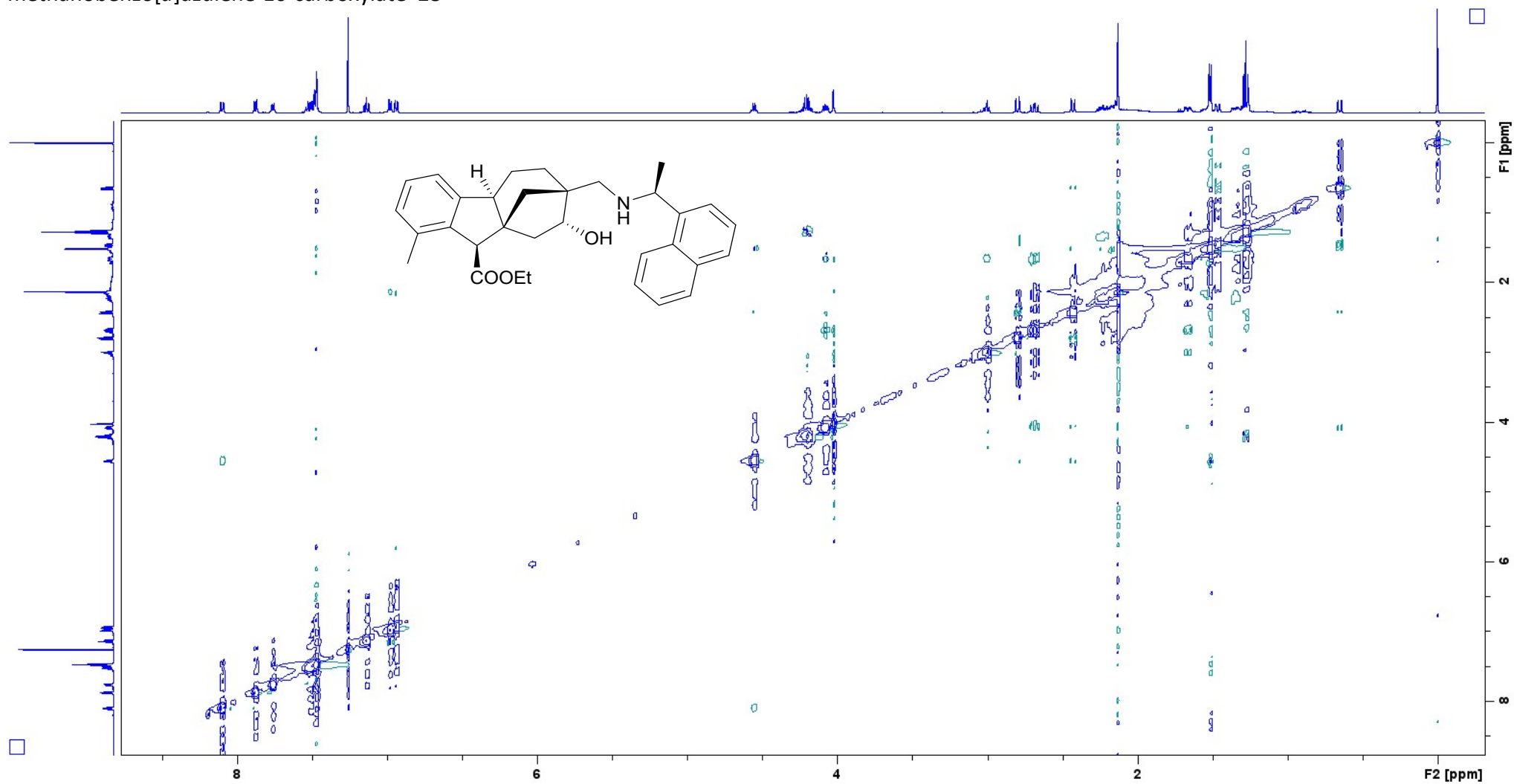
^{13}C -NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **28**



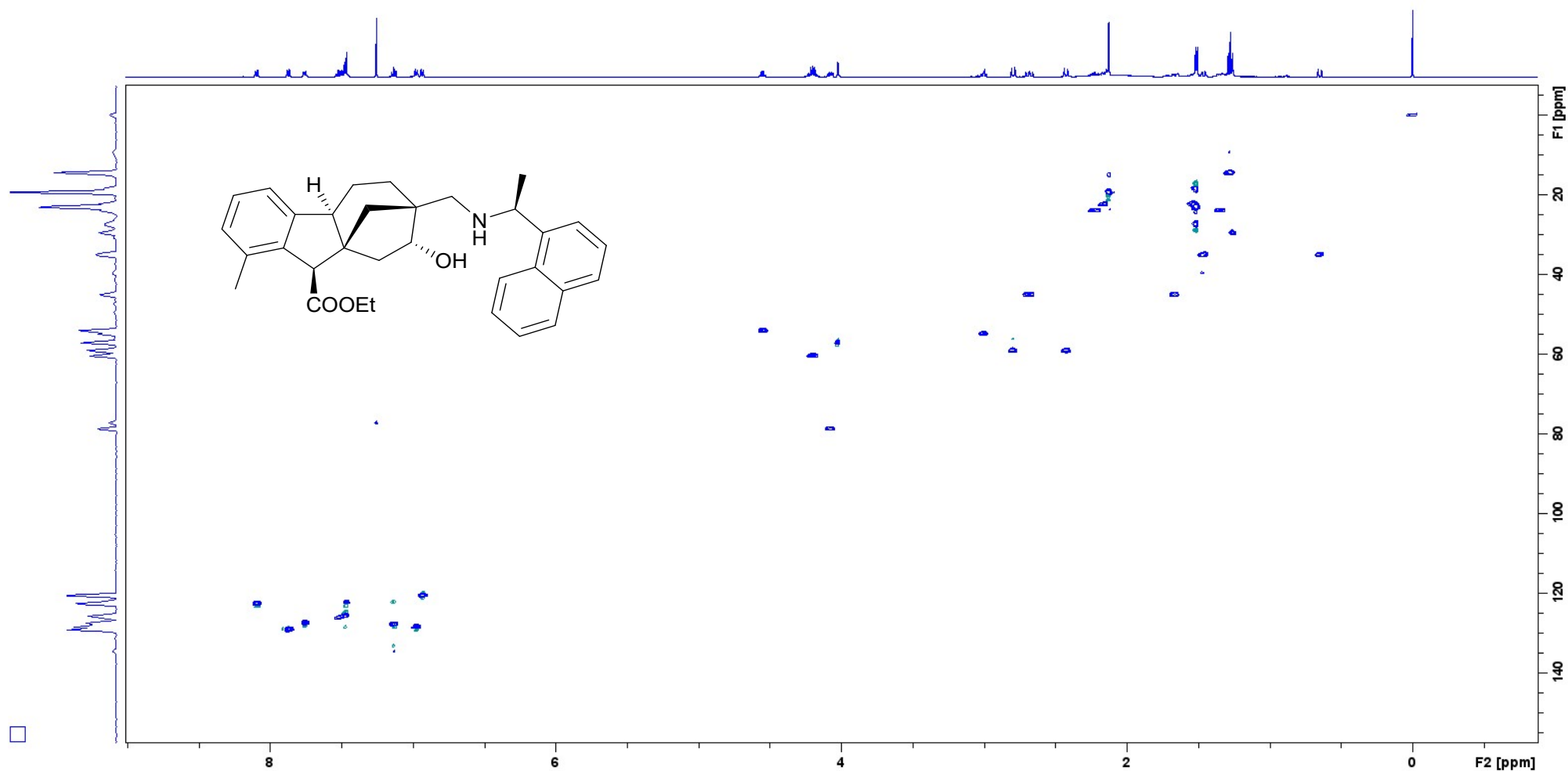
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **28**



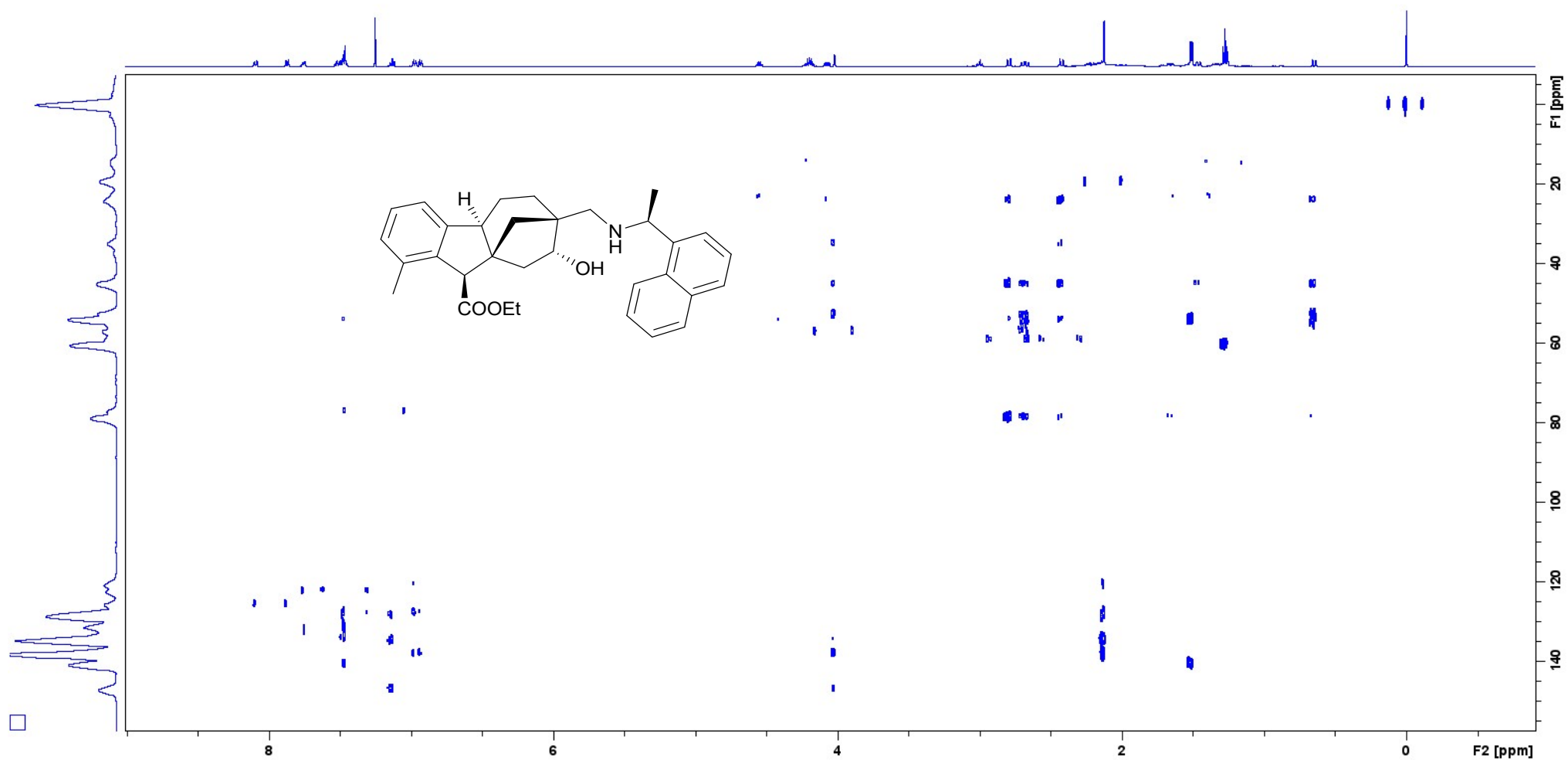
NOESY of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate 28



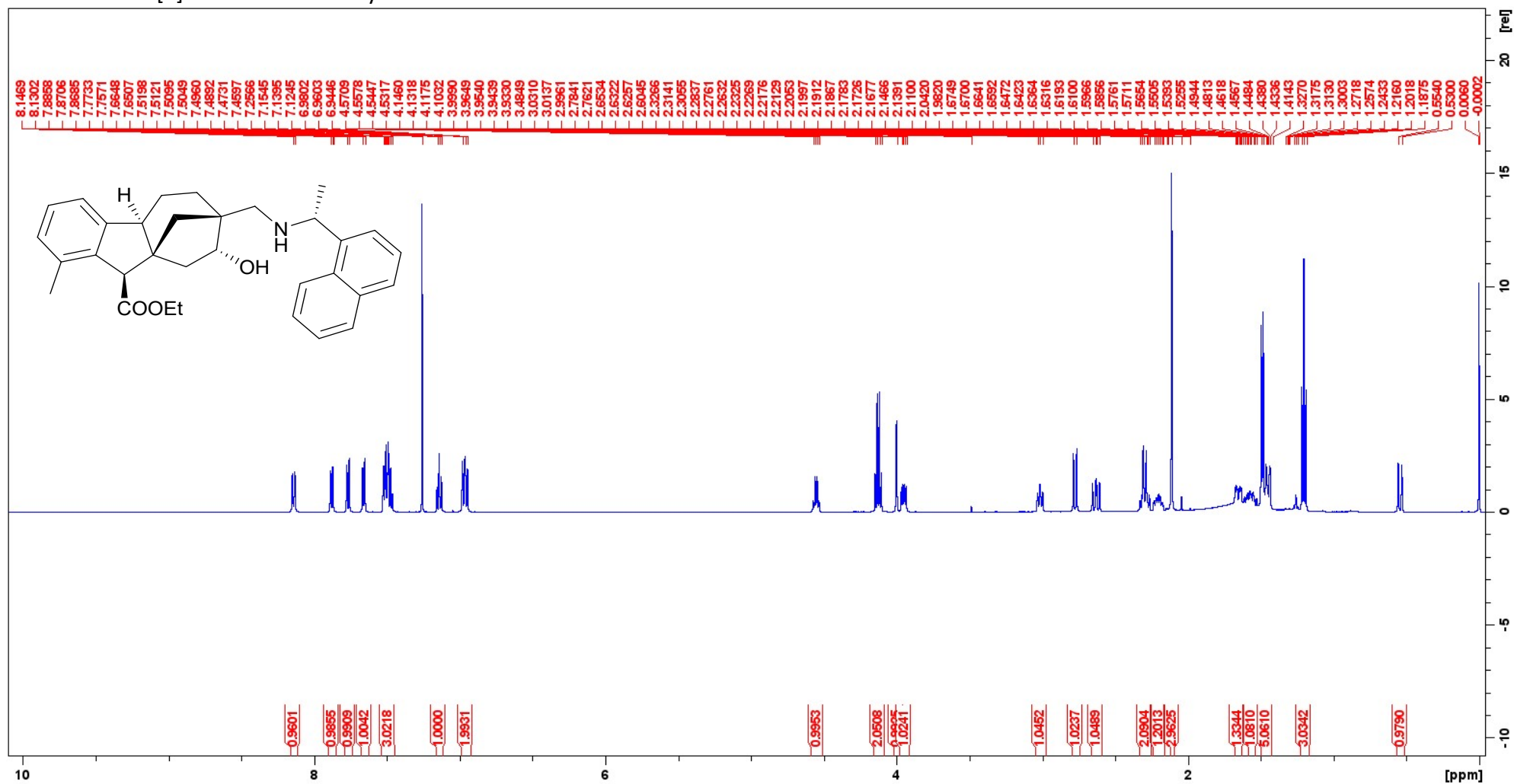
HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate 28



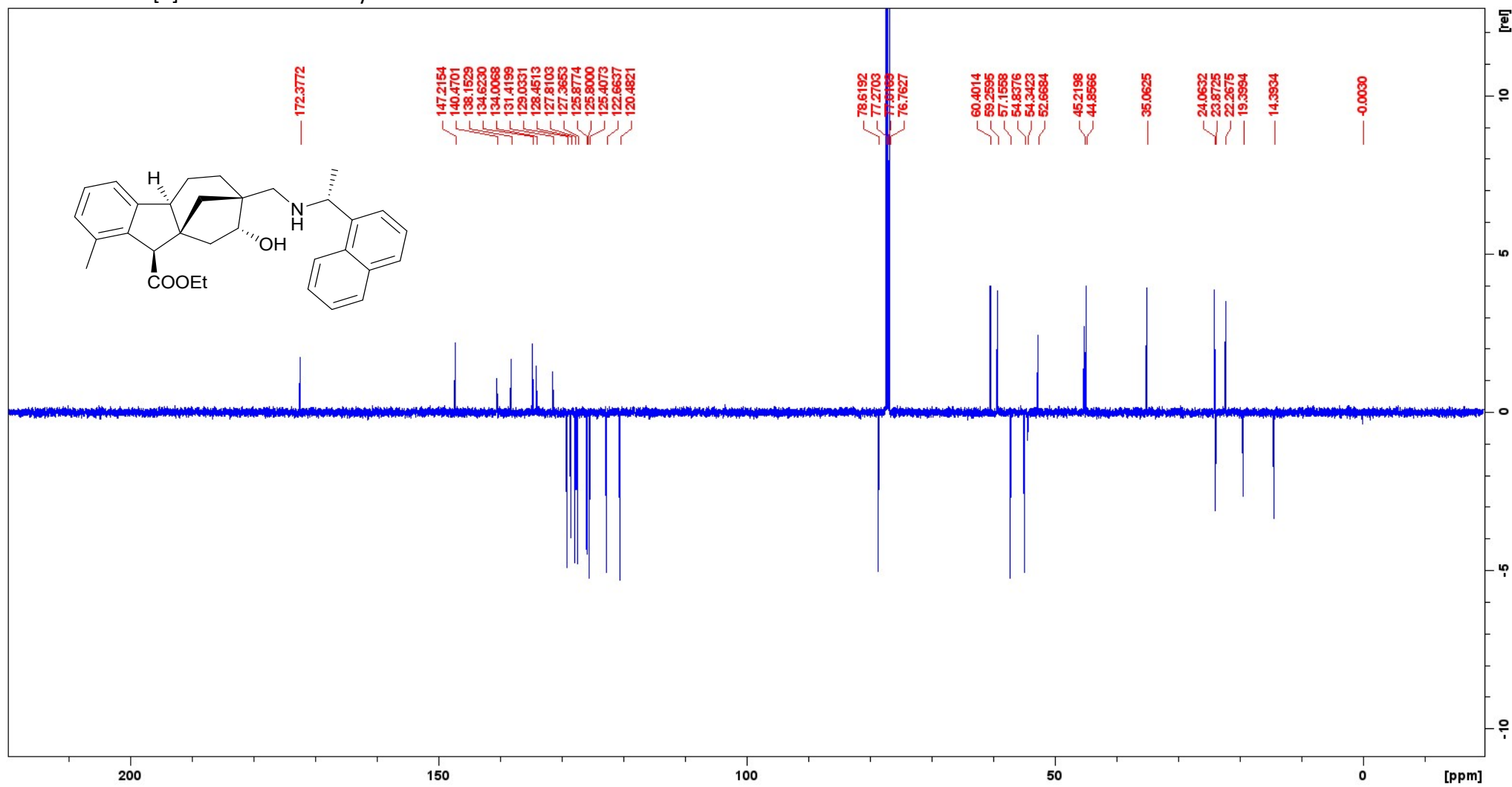
HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **28**



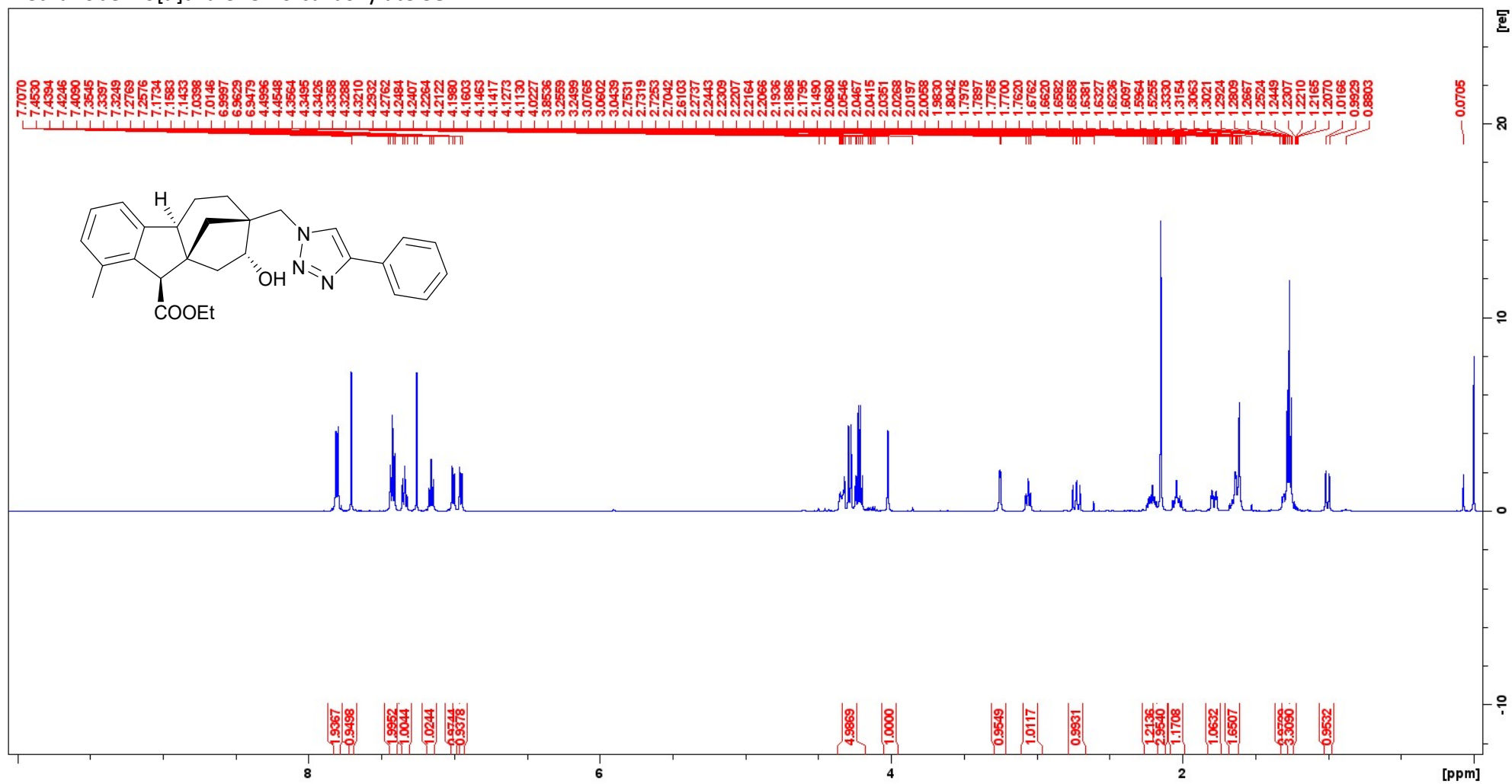
¹H-NMR of ethyl (4*bS*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9a-methanobenzo[*a*]azulene-10-carboxylate **29**



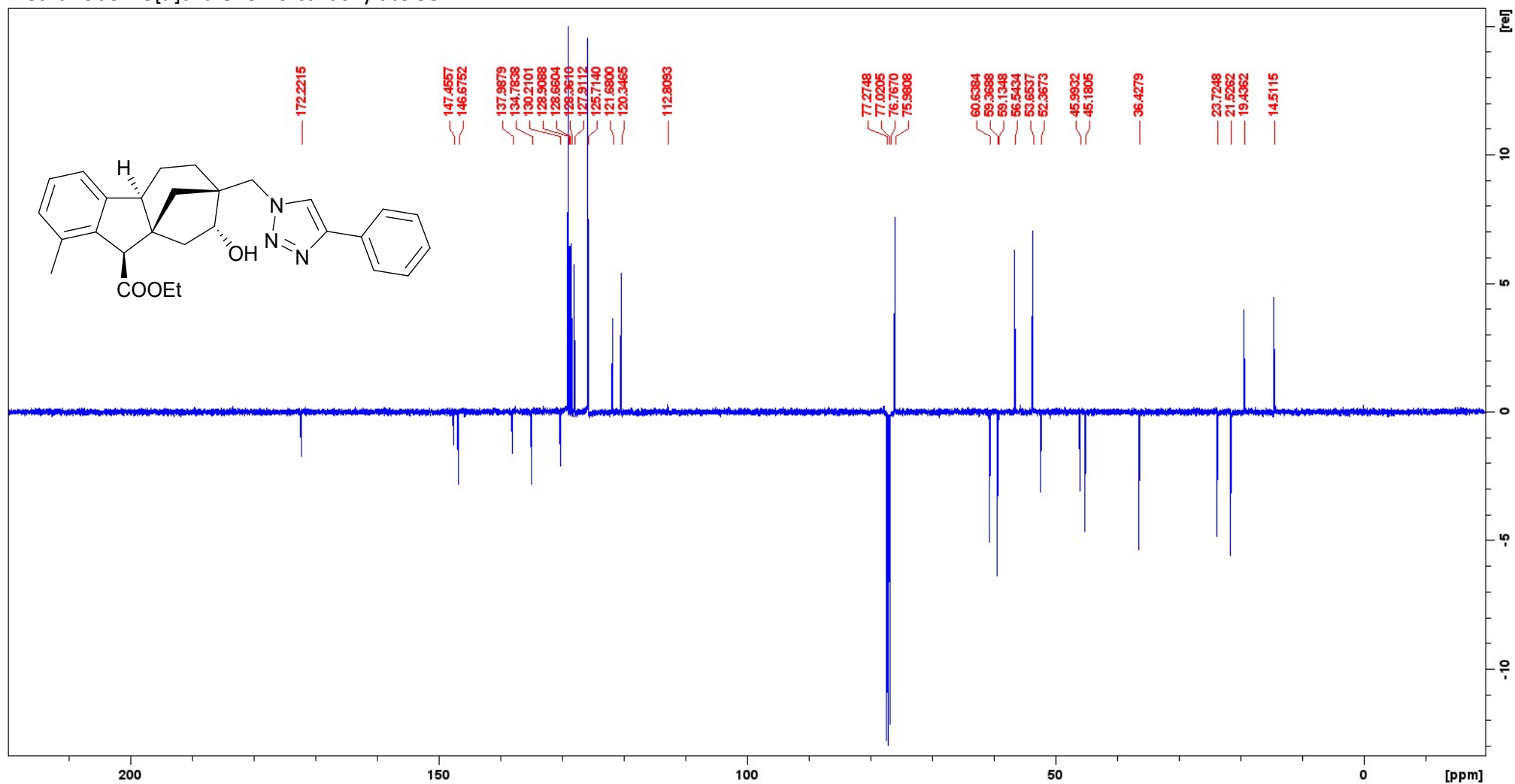
¹³C-NMR of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **29**



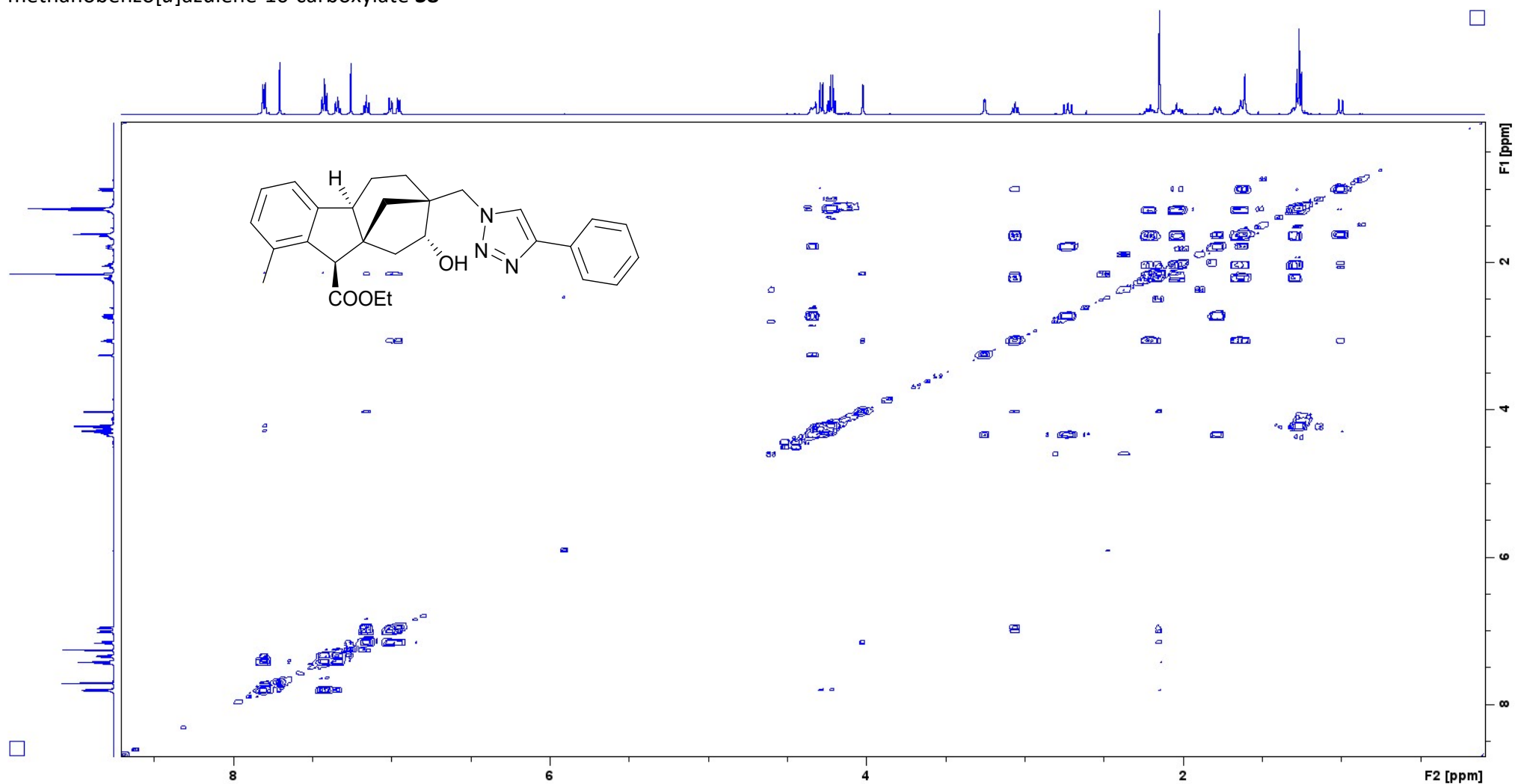
¹H-NMR of Ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **38**



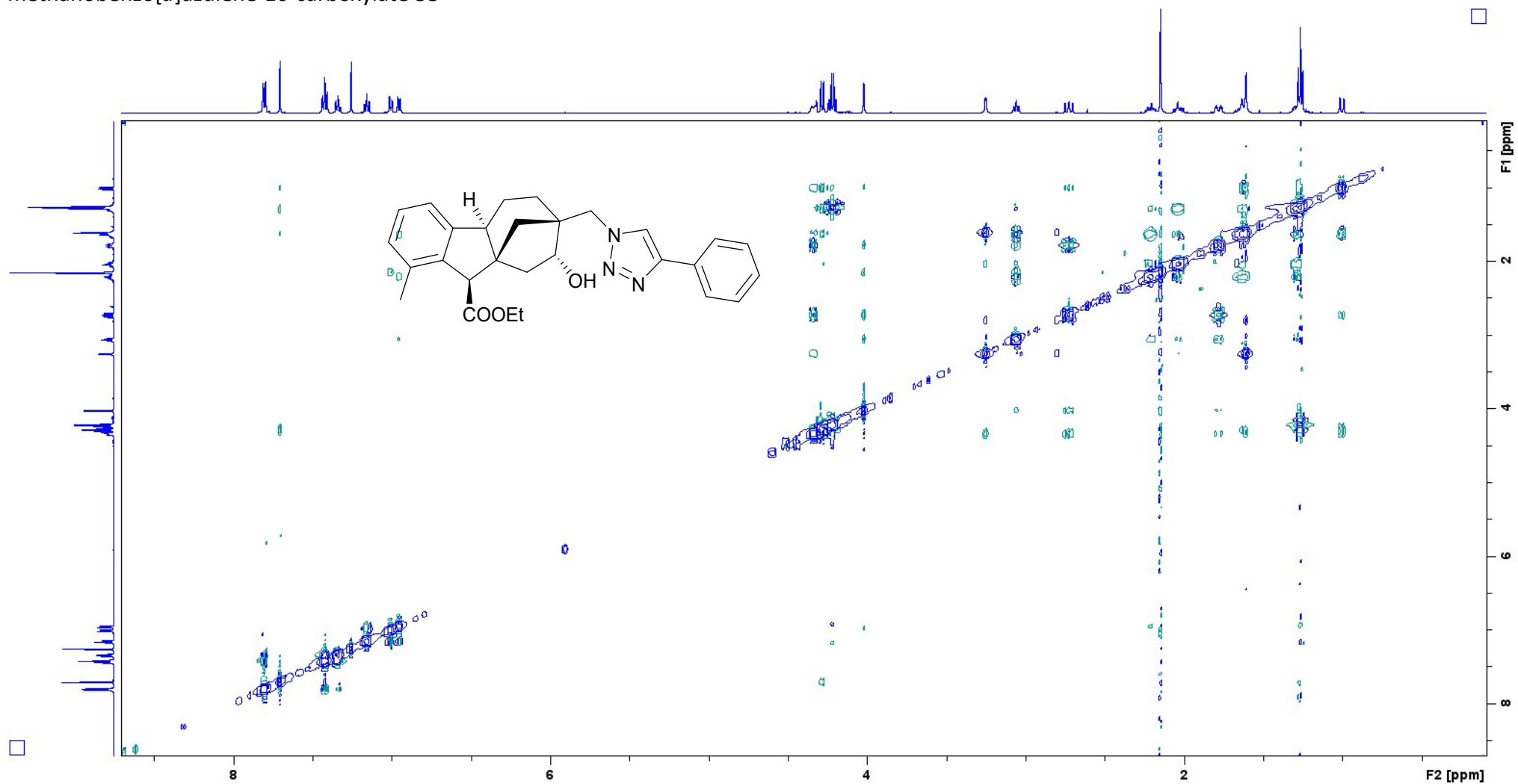
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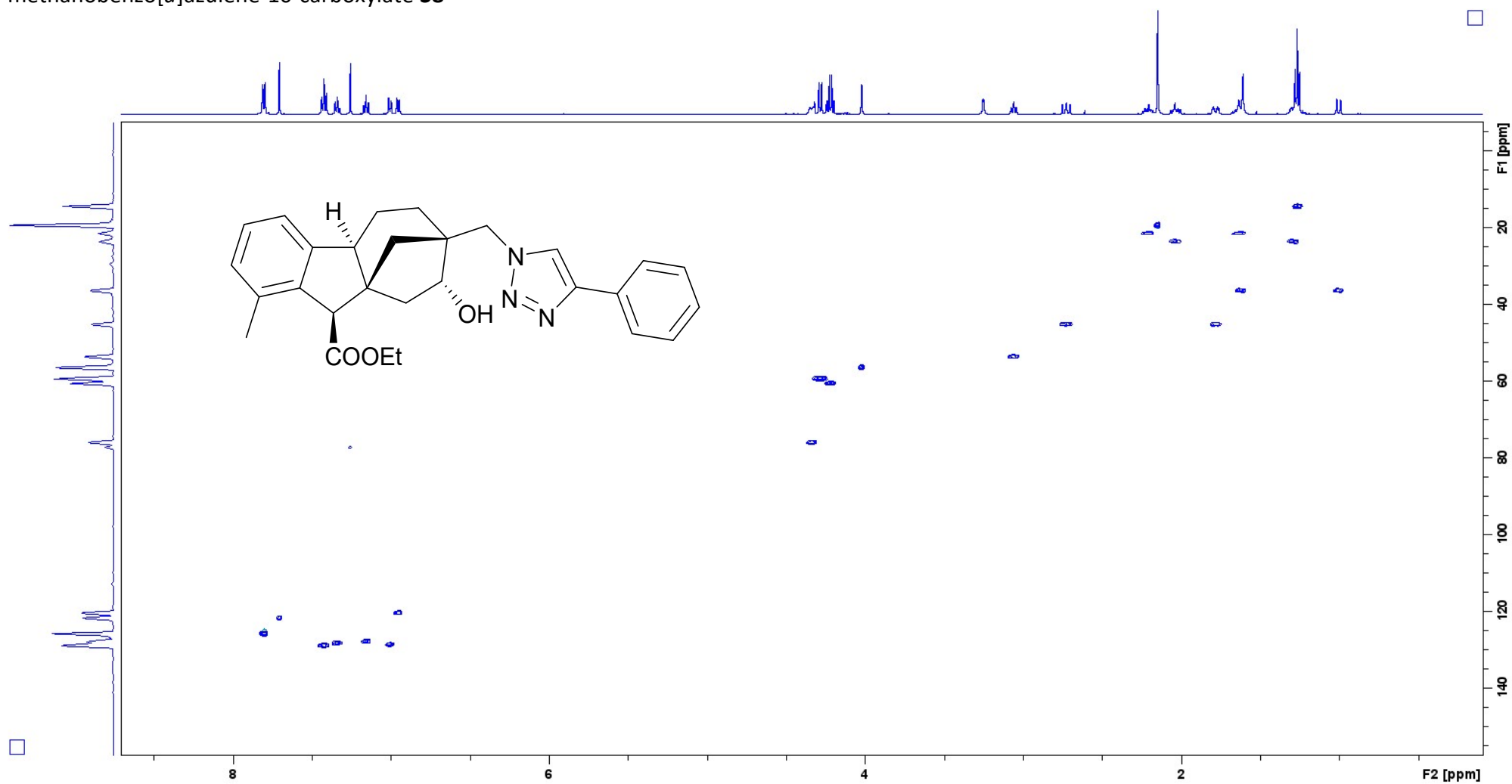
COSY of Ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **38**



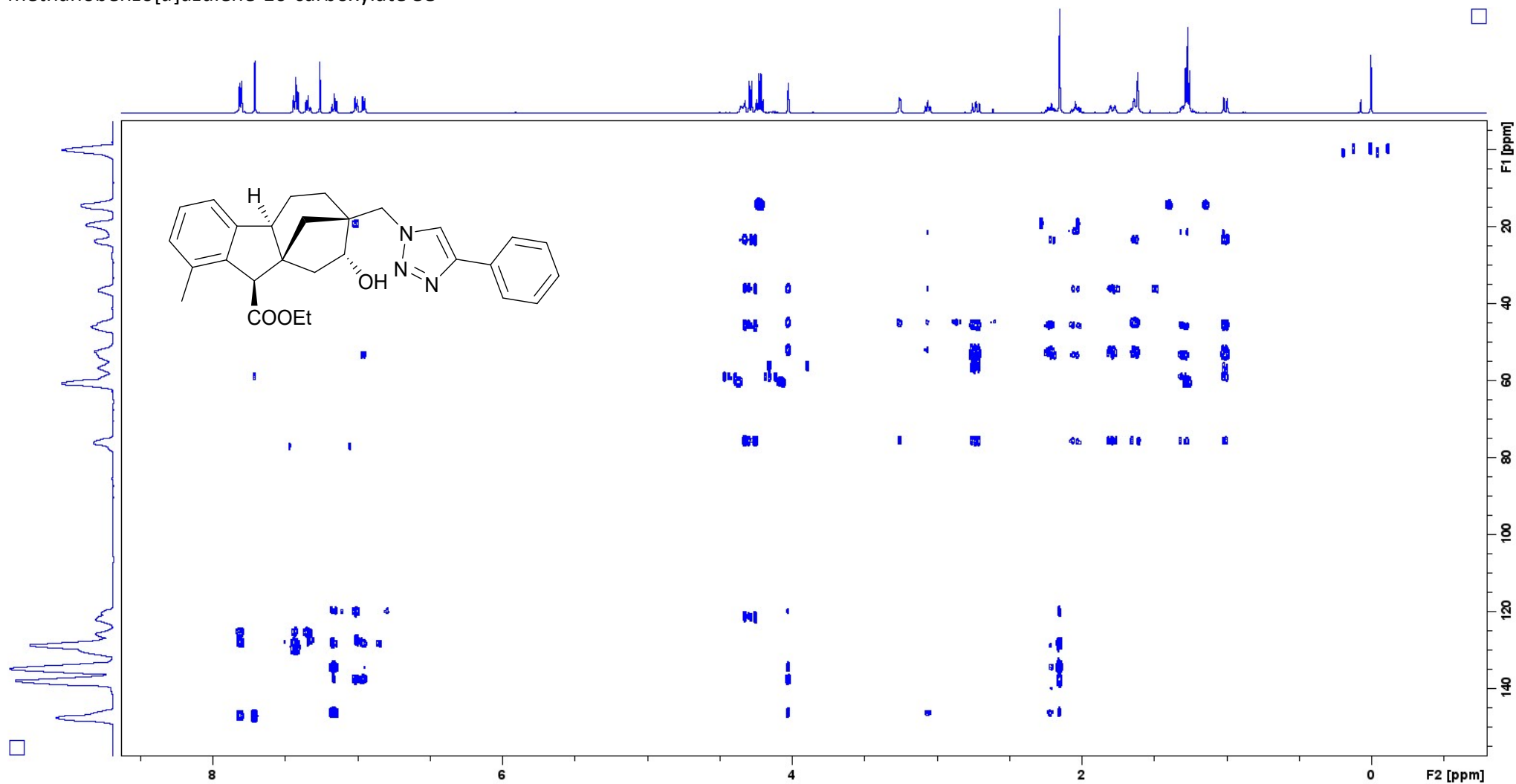
NOESY of Ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **38**



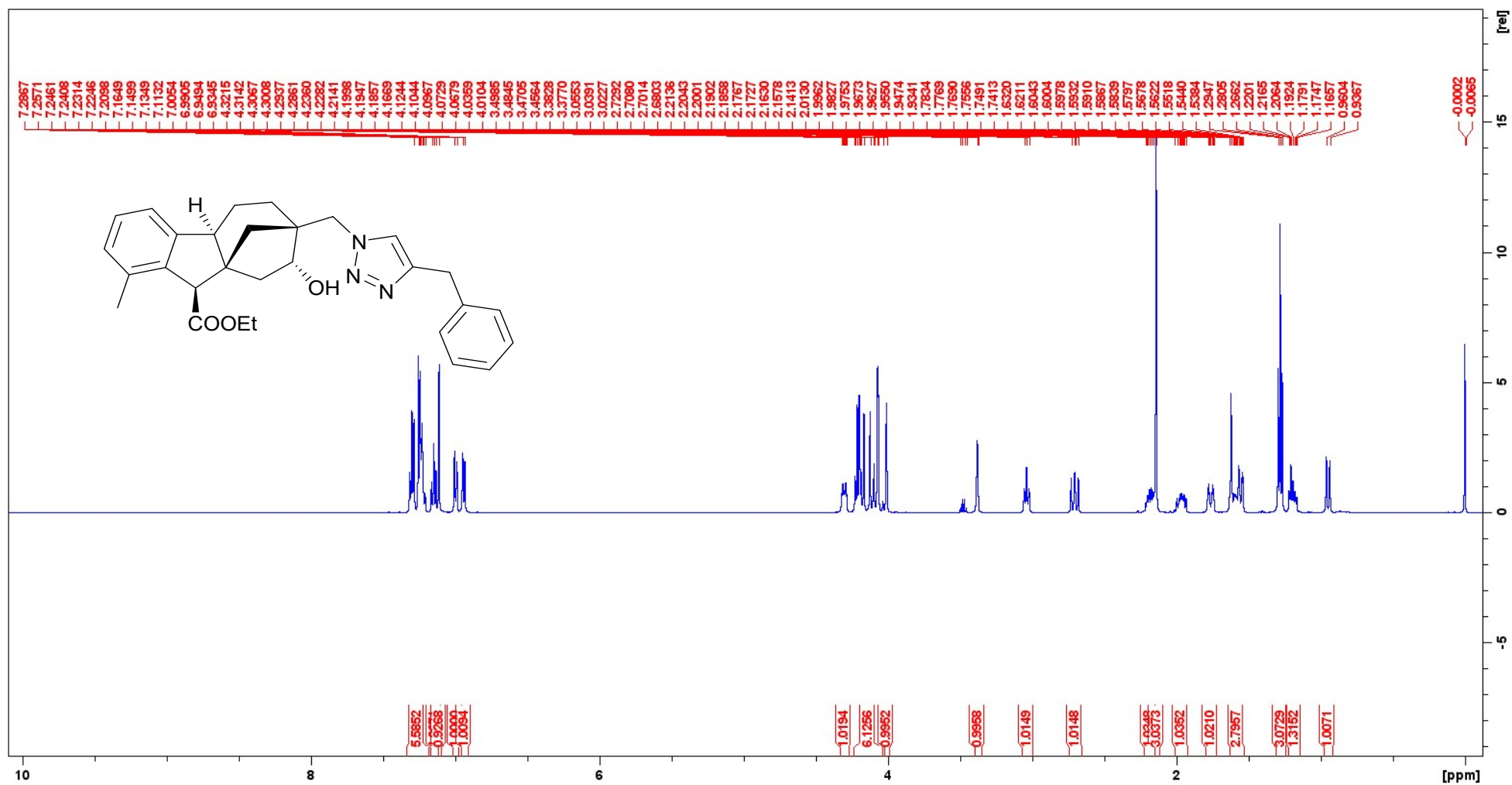
HSQC of Ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **38**



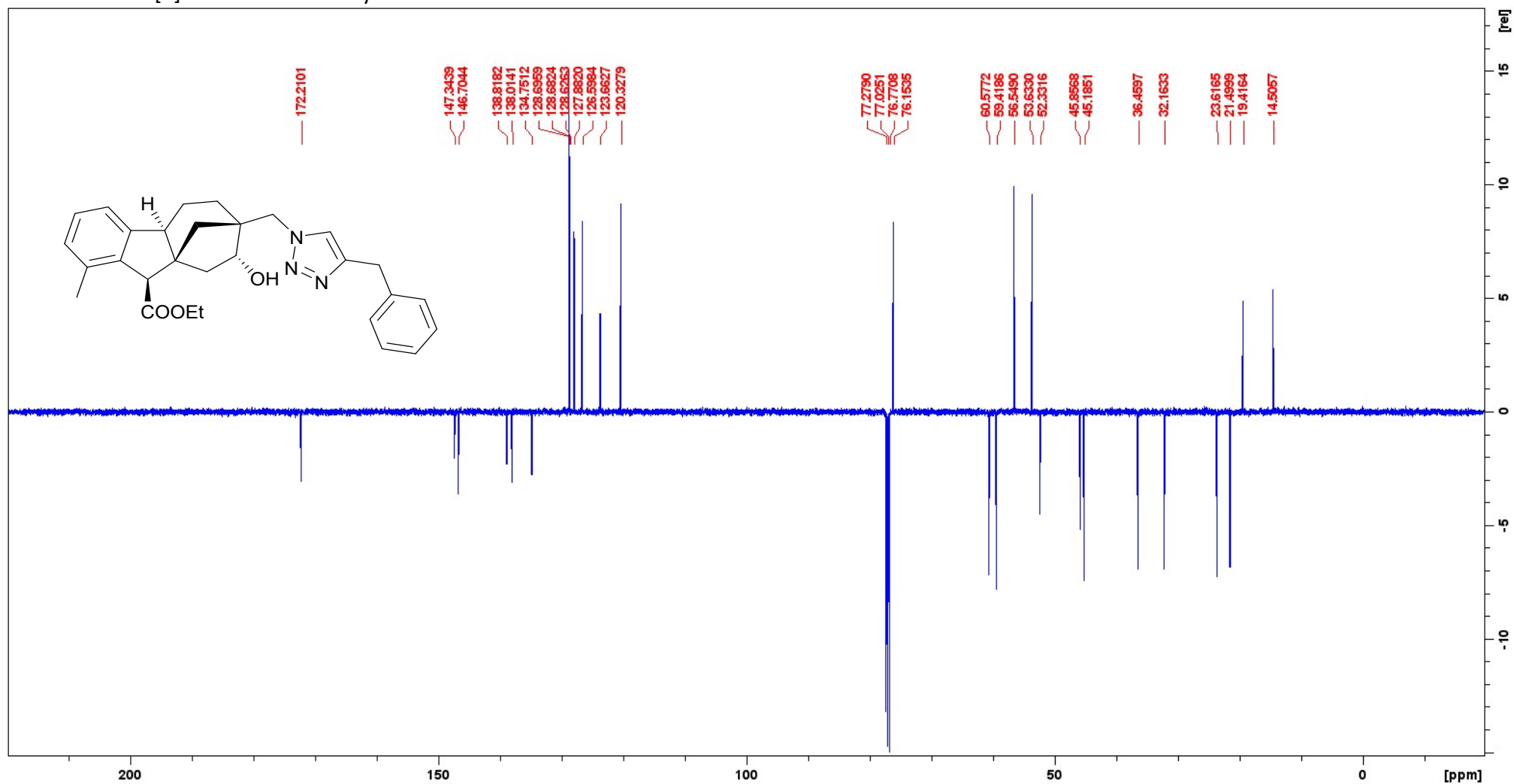
HMBC of Ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-8-hydroxy-1-methyl-7-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **38**



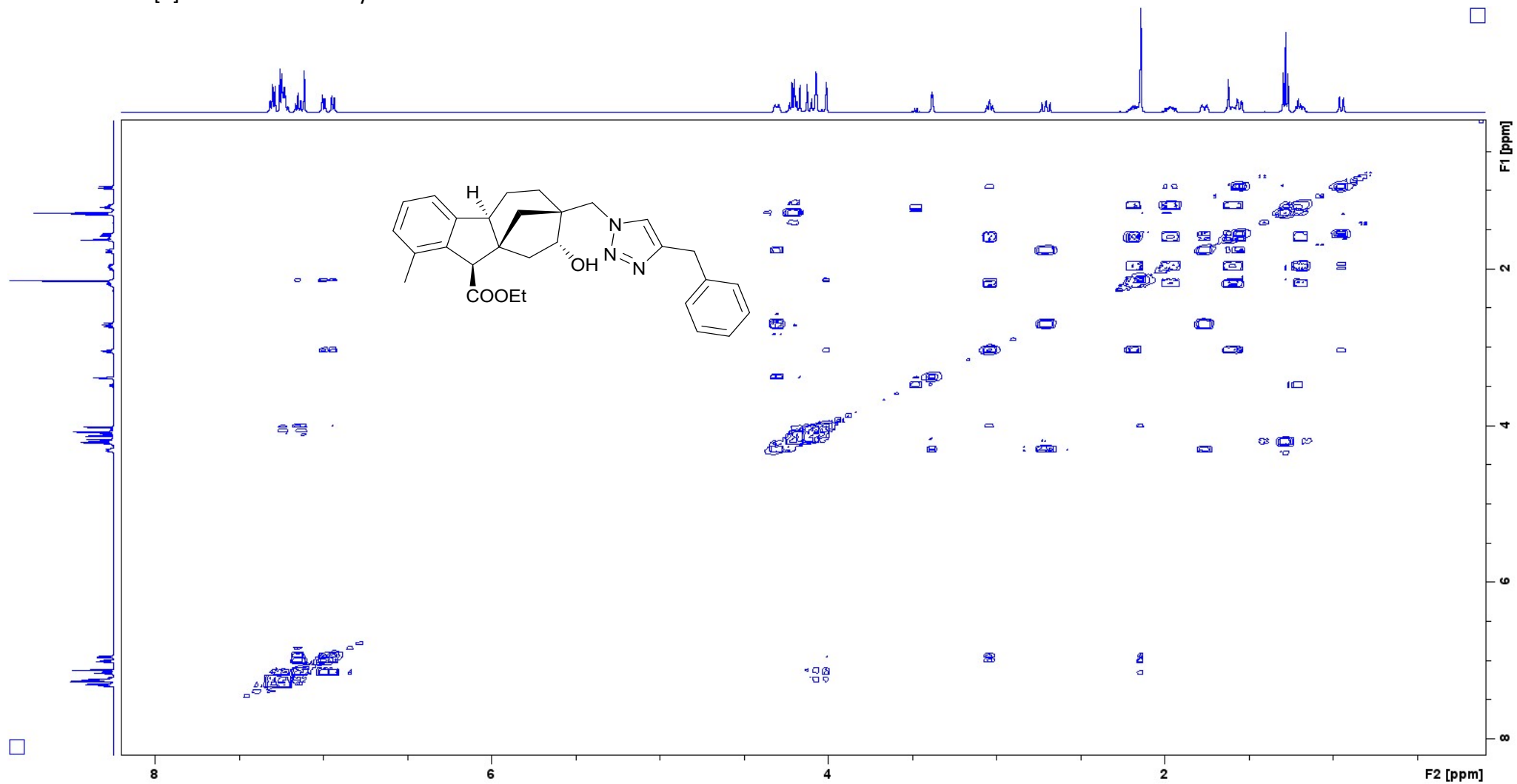
¹H-NMR of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**



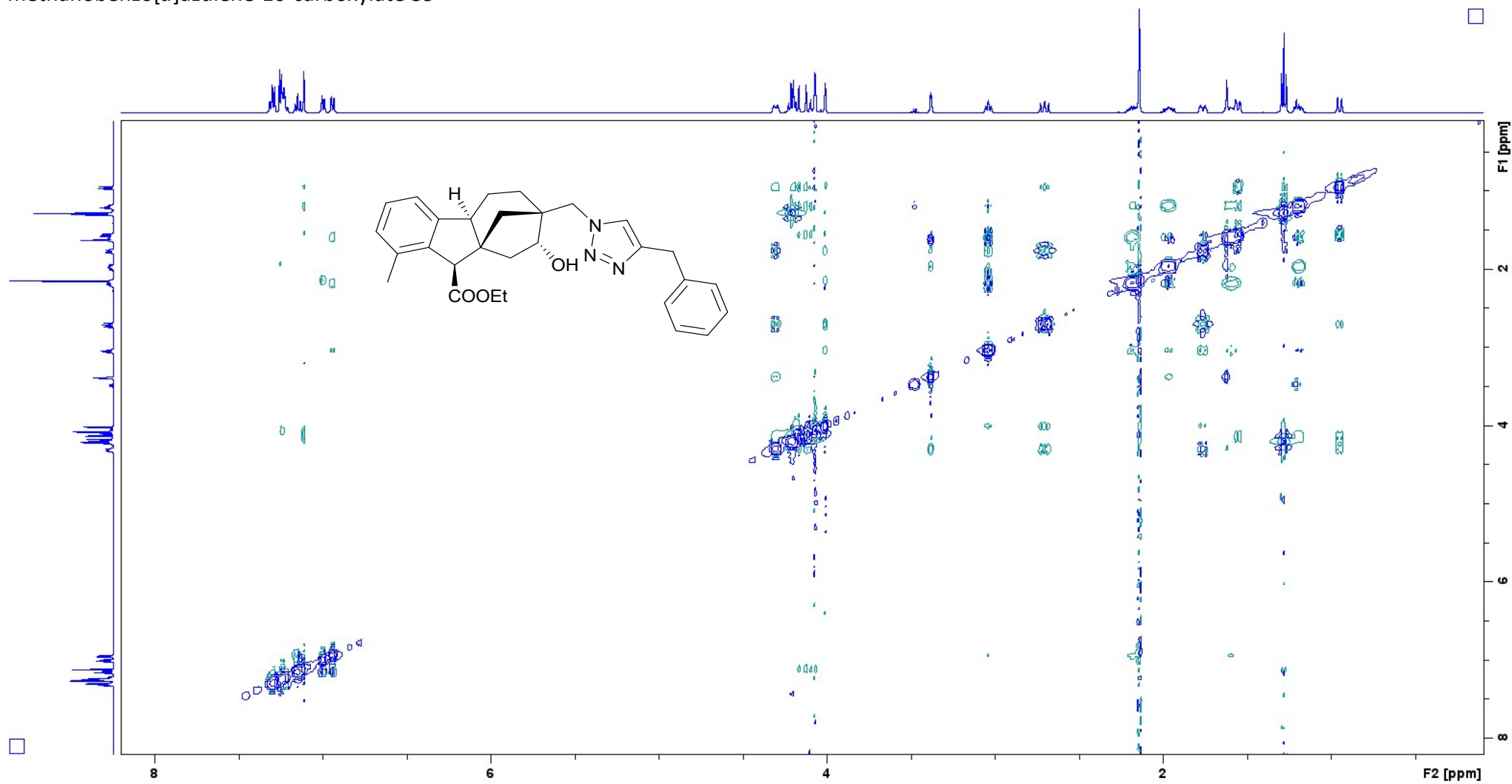
¹³C-NMR of ethyl (4*b**S*,7*S*,8*R*,9*a**S*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**



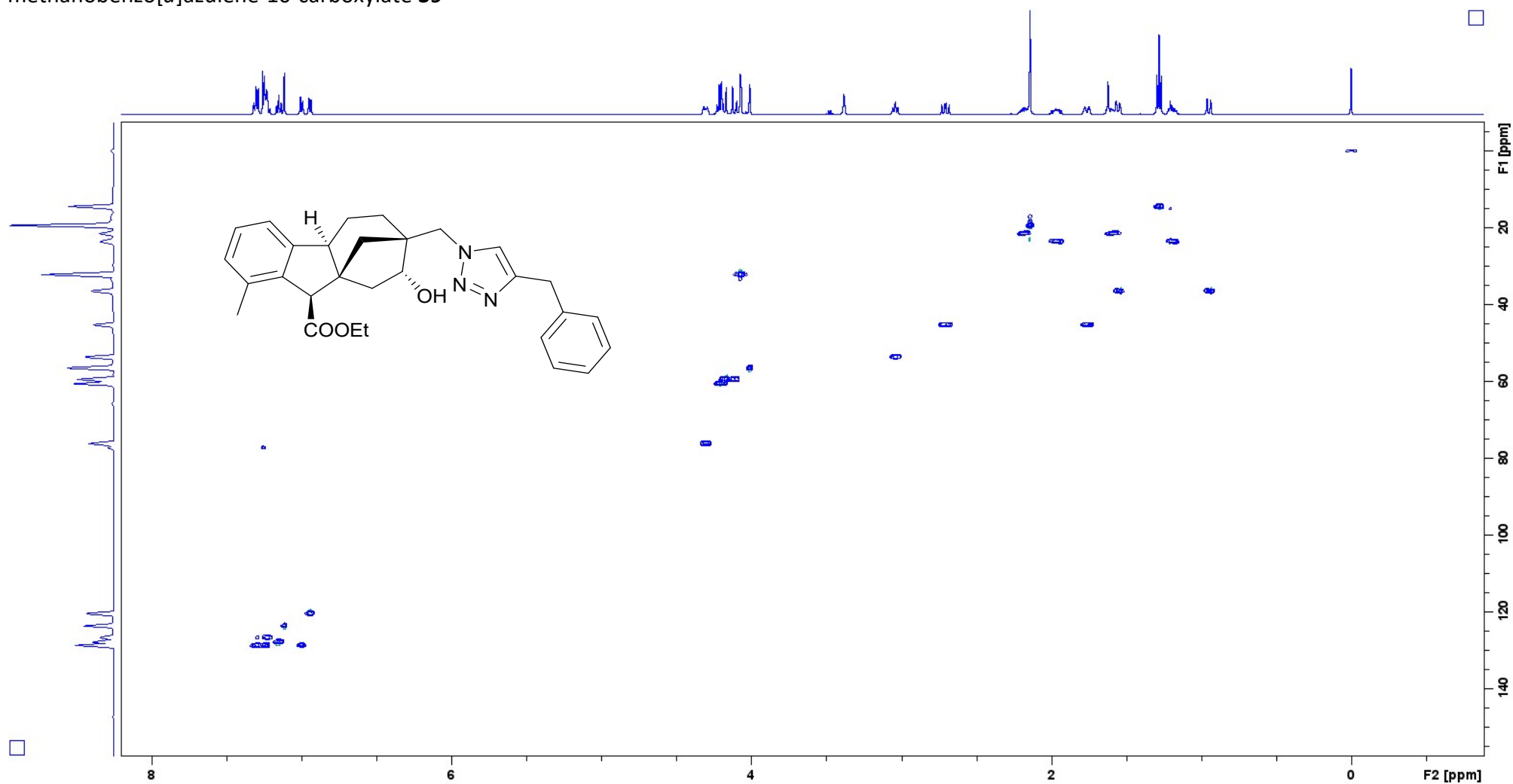
COSY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**



NOESY of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**



HSQC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**



HMBC of ethyl (4*S*,7*S*,8*R*,9*aS*,10*R*)-7-((4-benzyl-1*H*-1,2,3-triazol-1-yl)methyl)-8-hydroxy-1-methyl-4*b*,6,7,8,9,10-hexahydro-5*H*-7,9*a*-methanobenzo[*a*]azulene-10-carboxylate **39**

