SUPPORTING INFORMATION FOR :

Characterization, diversity, and structure-activity relationship study of lipoamino acids from *Pantoea* sp. and synthetic analogues

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Table des matières

Table S1. Full NMR spectroscopic data for compound 1 in CD_3OD

Position	δ_C type	δ_H m (*J* in Hz)	COSY	HMBC
1	176.02. C			
2	55.9. CH	4.6. m	H3a. H3b	C3. C4
3	38.7. CH_2	2.98. dd (13.9. 8.2)	H2. H3b	C2. C4. C5
		3.21. dd (13.9. 4.5)	H2. H3a	C1. C2. C4. C5
4	139.0. C			
5	130.5. CH	7.24. m		C3. C7
6	129.3. CH	7.25. m		C4. C7
7	127.6. CH	7.18. m		C5
1’	173.8. C			
2’	44.6. CH_2	2.29. dd (14.4. 5.2)		C1’. C3’. C4’
		2.34. dd (14.4. 7.4)		
3’	69.6. CH	3.85. m	H2’a. H4’	
4’	38.0. CH_2	1.40. m	H5’	
5’	30.9. CH_2	1.29. br s	H4’	
6’	30.9. CH_2	1.29. br s		
7’	30.9. CH_2	1.29. br s		
8’	30.9. CH_2	1.29. br s		
9’	30.9. CH_2	1.29. br s		
10’	30.9. CH_2	1.29. br s		
11’	30.9. CH_2	1.29. br s		
12’	30.9. CH_2	1.29. br s		
13’	23.6. CH_2	1.31. m	14’	
14’	14.4. CH_3	0.90. t (6.8)	13’	13’

Figure S1. ^{1}H NMR spectrum of 1 recorded at 500 MHz in CD_3OD.

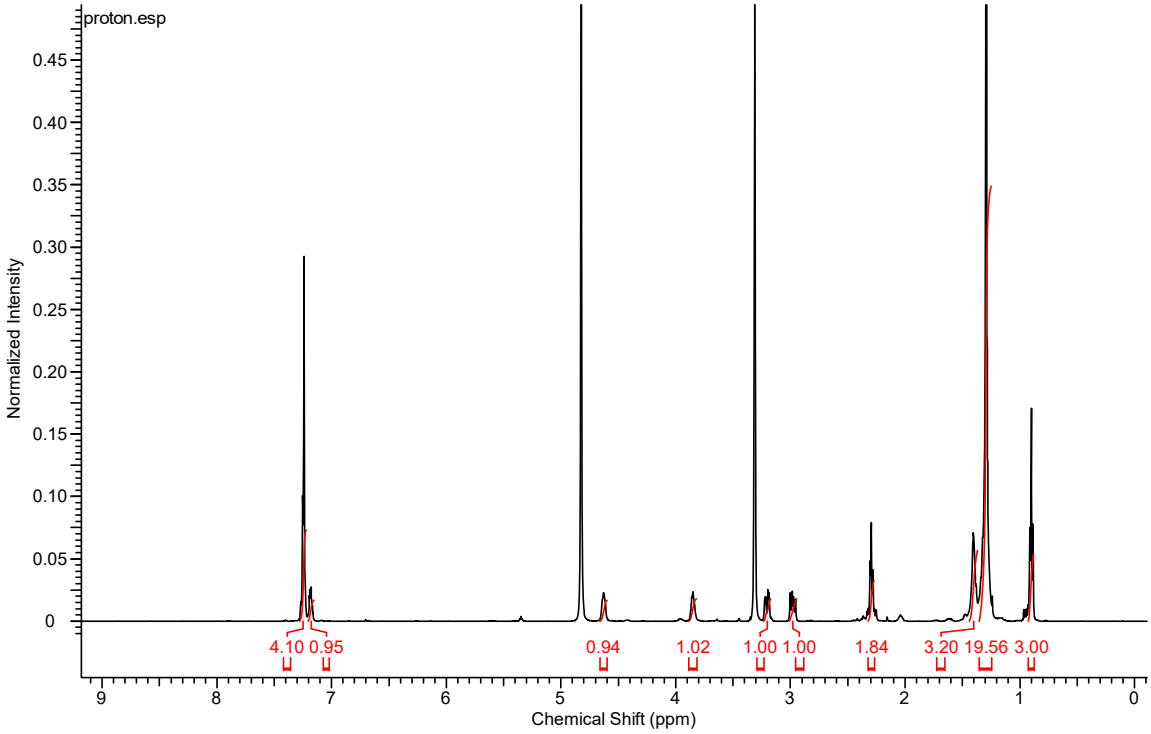

Figure S2. ^{13}C NMR spectrum of 1 recorded at 125 MHz in CD_3OD.

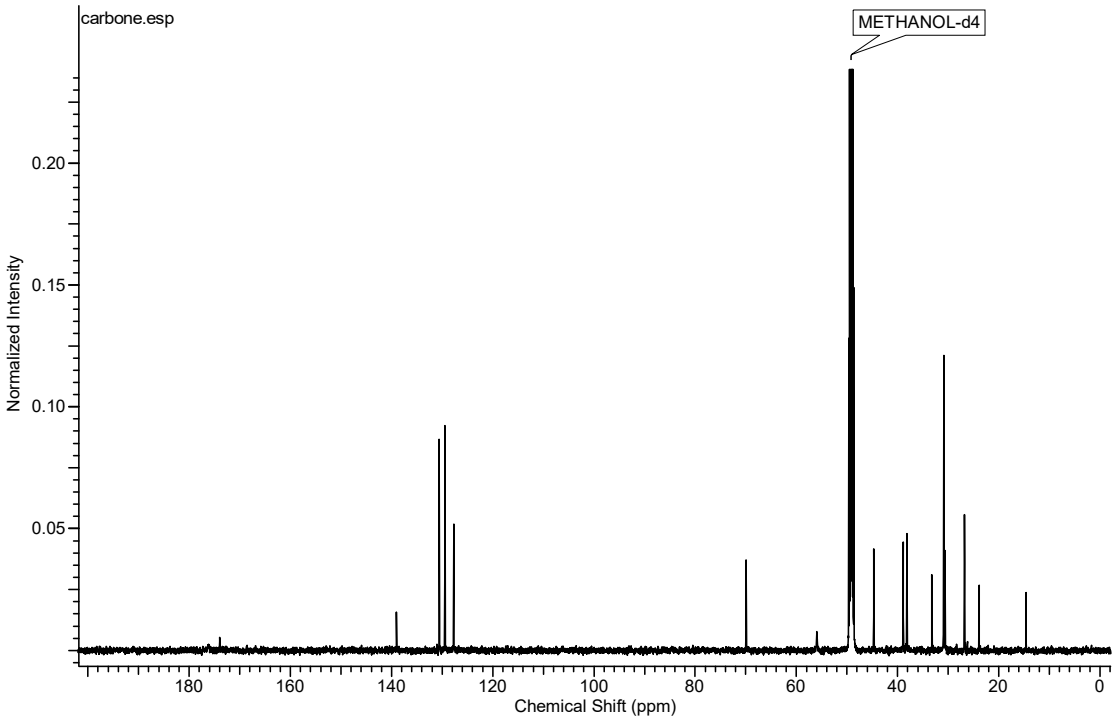

Figure S3. COSY NMR spectrum of 1 recorded at 500 MHz in CD_3OD.

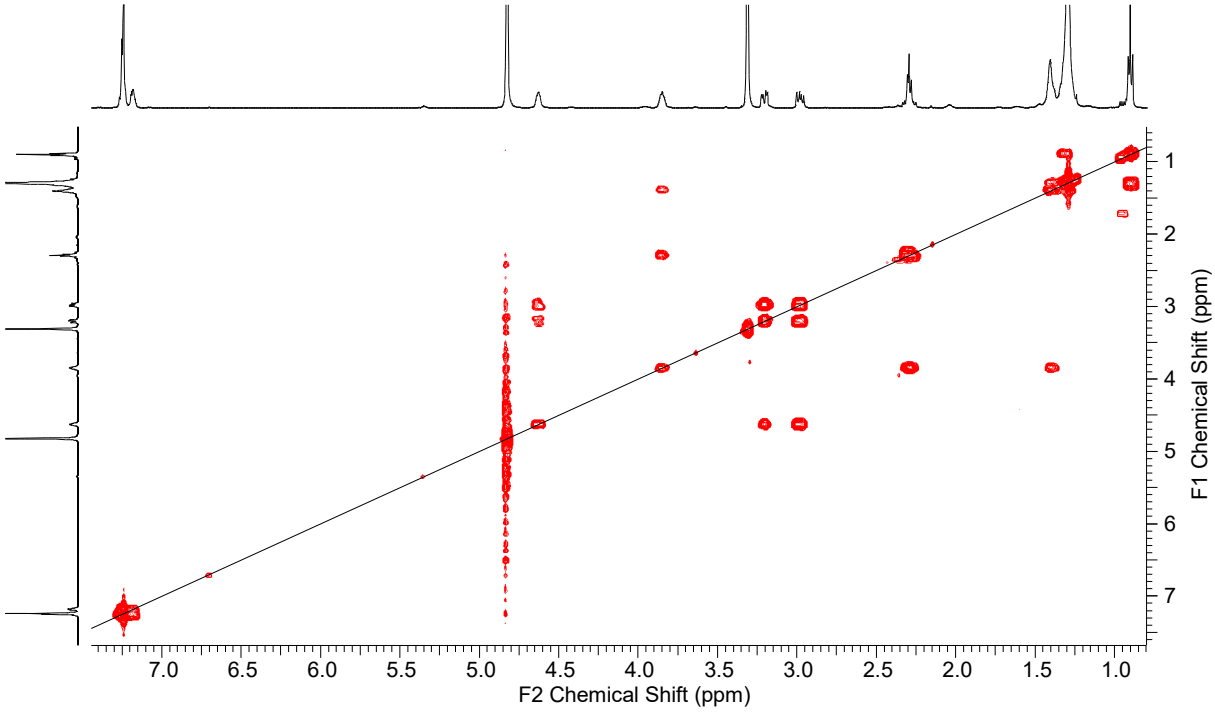

Figure S4. HSQC NMR spectrum of 1 recorded at 500 MHz in CD_3OD.

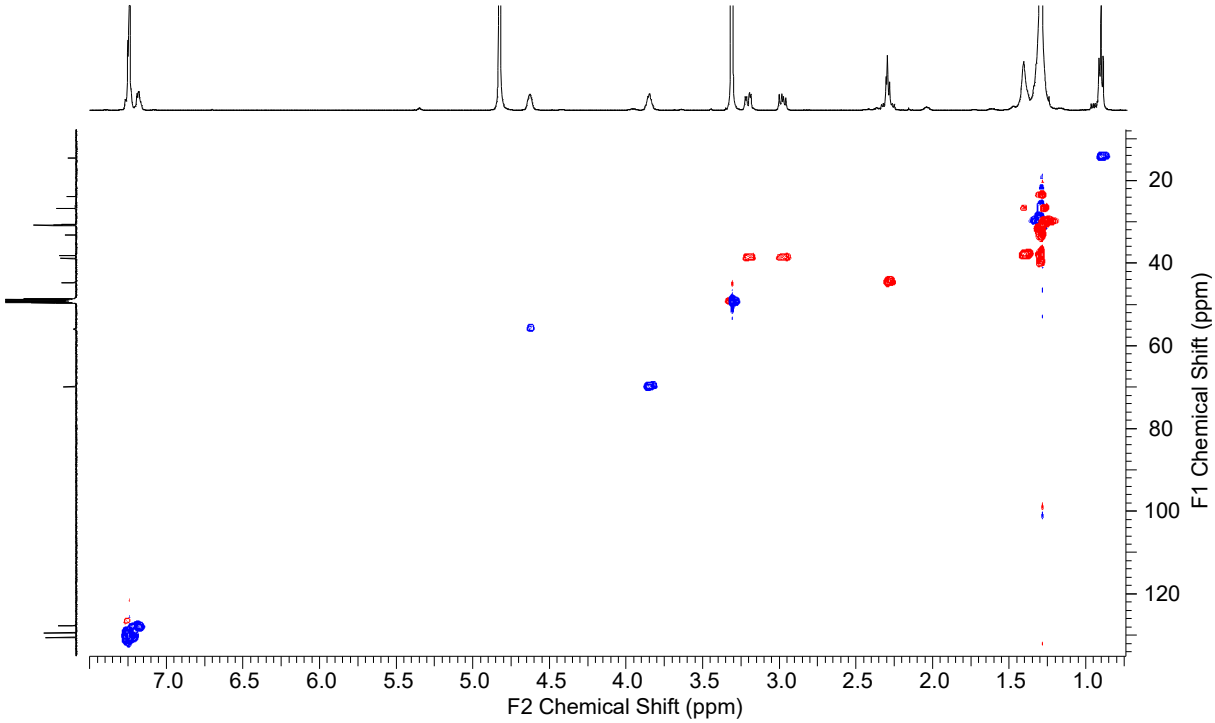

Figure S5. HMBC NMR spectrum of 1 recorded at 500 MHz in CD_3OD.

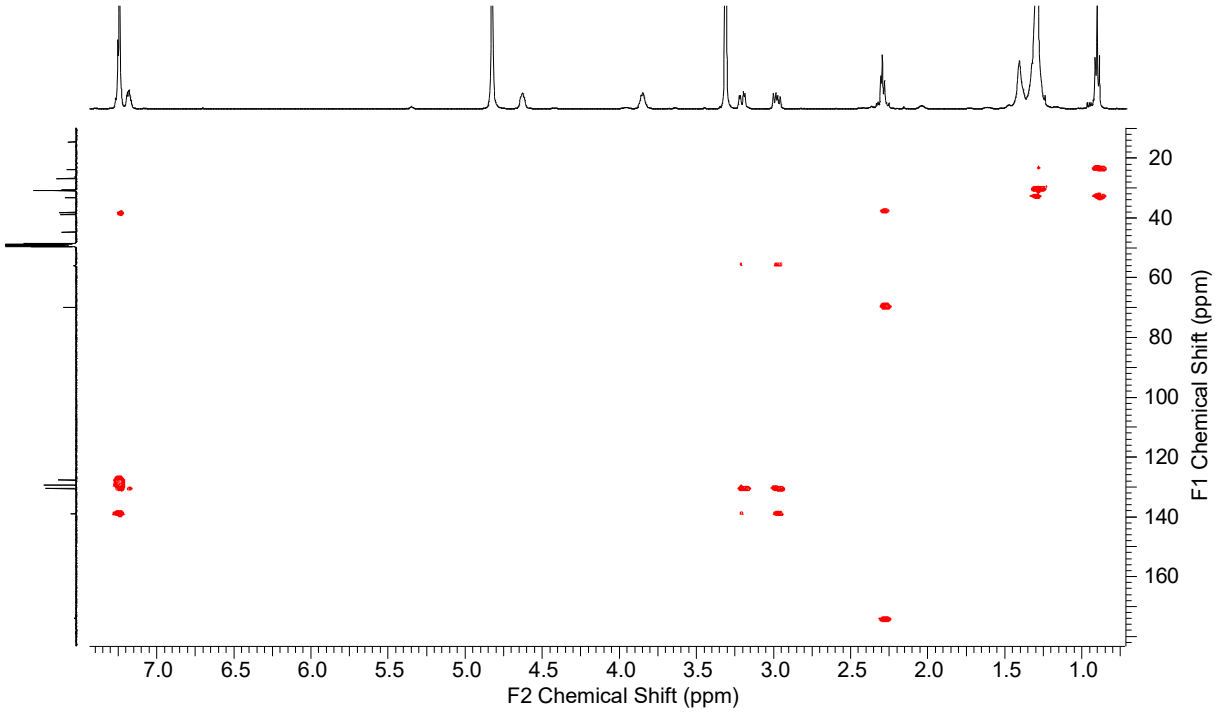

Figure S6. HRMS of compound 1 in MeOH.

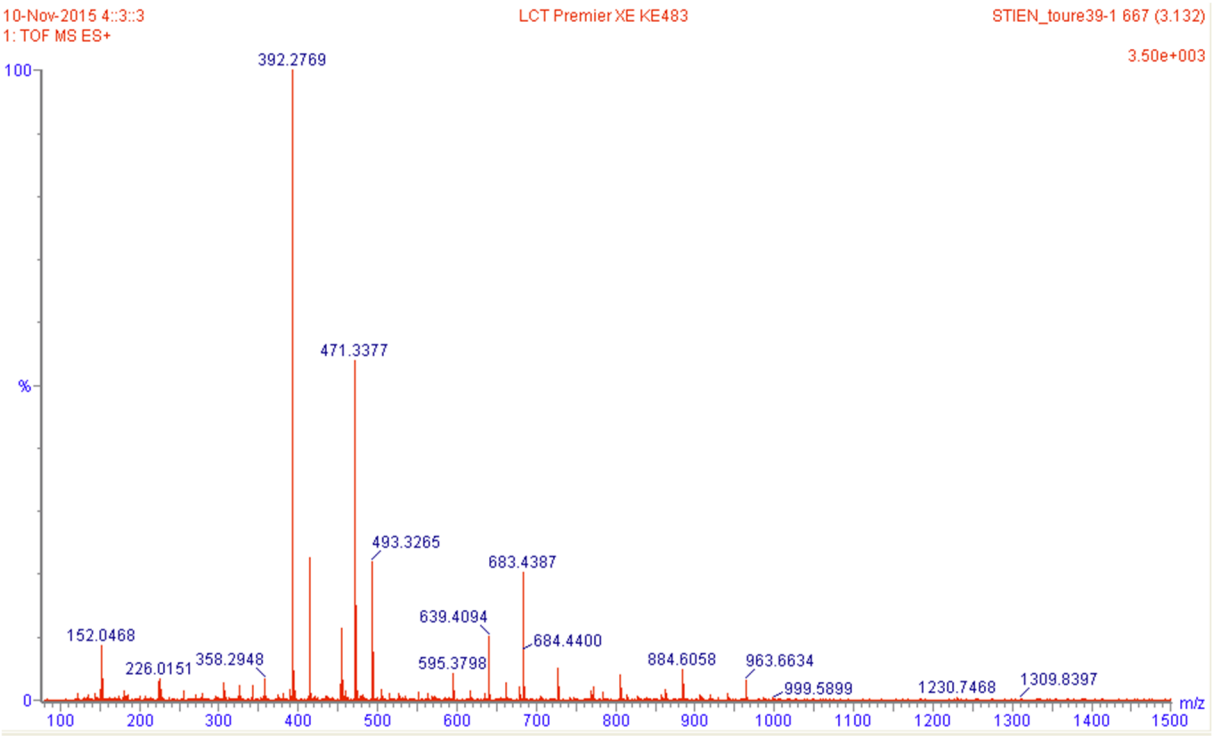

Table S2. Full NMR spectroscopic data for compound 2 (VECD14BF5-17) in CD_3OD

Position	δ_C type	δ_H m (*J* in Hz)	COSY	HMBC
1	176.3. C			
2	57.6. CH	4.53. m	H3	
3	39.4. CH_2	2.97. dd (14.0. 7.7)	H2	C2. C4. C5
		3.21. dd (14.0. 4.5)		
4	139.8. C			
5	130.7. CH	7.24. m	H6. H7	C3. C7
6	129.3. CH	7.22. m	H5. H7	C4. C7
7	127.3. CH	7.15. m	H5. H6	C5
1′	173.5. C			
2′	44.9. CH_2	2.25. dd (14.4. 7.8)	H3′	C1′. C3′. C4′
		2.30. dd (14.5. 4.9)		C1′. C3′. C4′
3′	67.9. CH	3.85. m	H2′. H4′	C1′
4′	38.2. CH_2	1.39. m	H3′	
5′	31.0. CH_2	1.30. m		C3′
6′	31.0. CH_2	1.30. m		
7′	31.0. CH_2	1.30. m		
8′	28.3. CH_2	2.04. m	H9′	C7′. C9′
9′	130.9. CH	5.4. m	H8′	C8′
10′	130.9. CH	5.4. m	H11′	C11′
11′	28.3. CH_2	2.04. m	H10′	C10′. C12′
12′	31.0. CH_2	1.30. m		
13′	31.0. CH_2	1.30. m		
14′	31.0. CH_2	1.30. m		
15′	23.9. CH_2	1.30. m	H16′	
16′	14.6. CH_3	0.90. t (6.8)	H15′	C14′. C15′

Figure S7. ^{1}H NMR spectrum of 2 recorded at 500 MHz in CD_3OD.

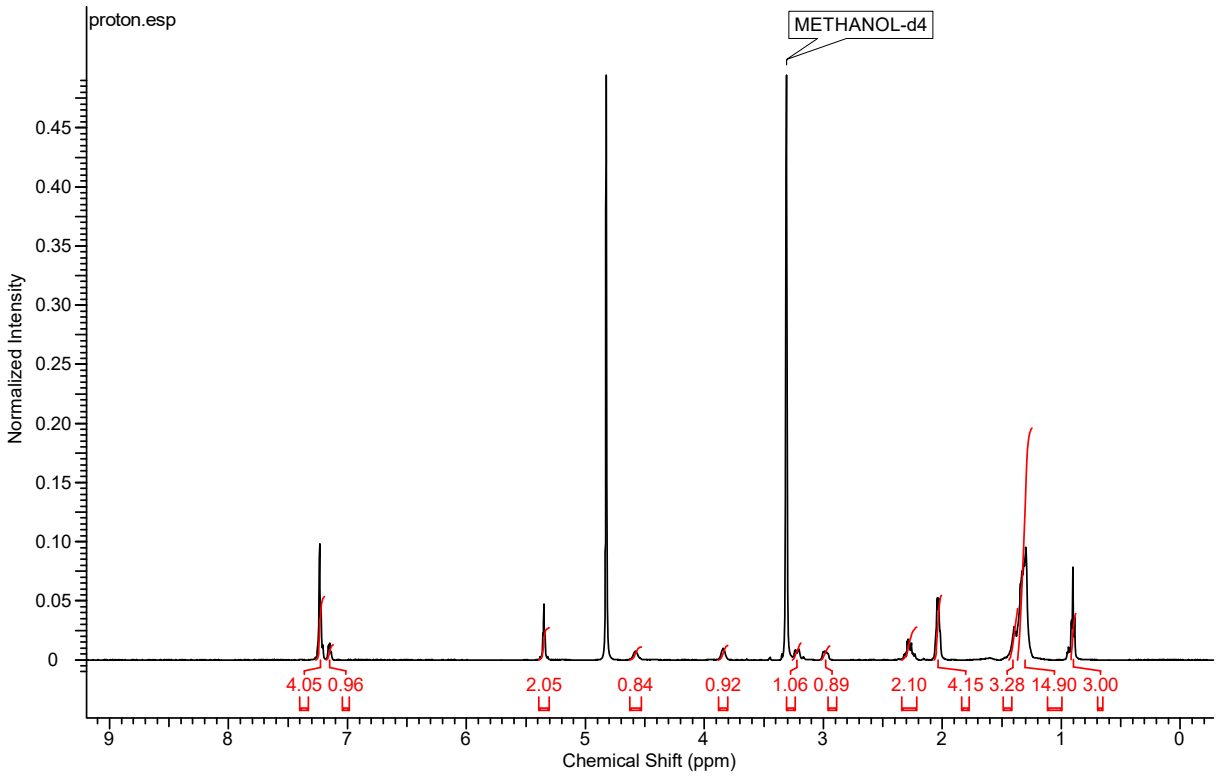

Figure S8. 13C NMR spectrum of 2 recorded at 125 MHz in CD_3OD.

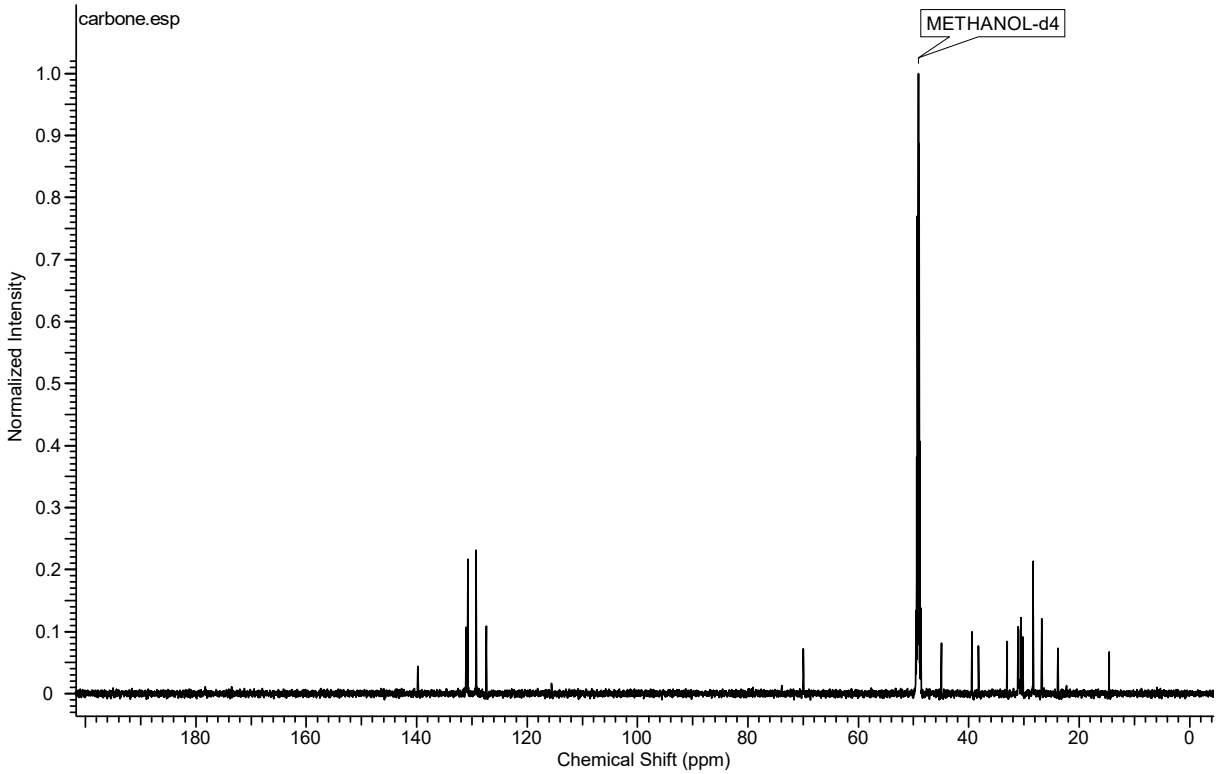

Figure S9. COSY NMR spectrum of 2 recorded at 500 MHz in CD_3OD.

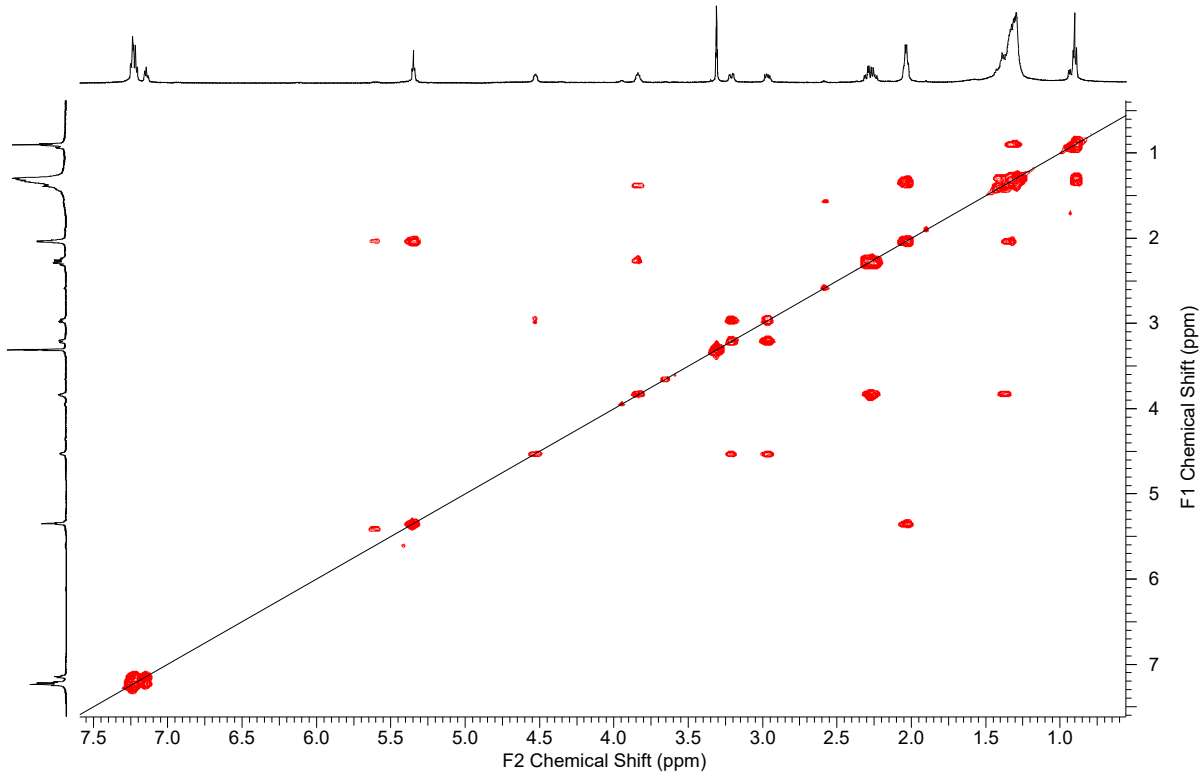

Figure S10. HSQC NMR spectrum of 2 recorded at 500 MHz in CD_3OD.

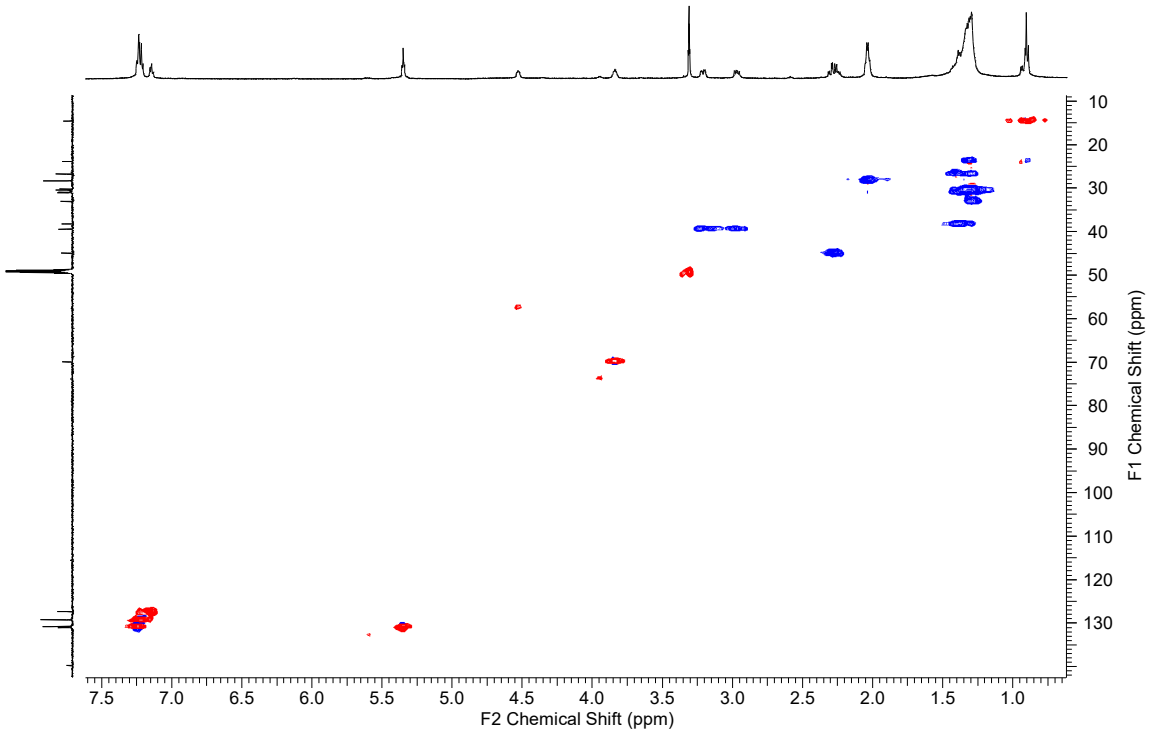

Figure S11. HMBC NMR spectrum of 2 recorded at 500 MHz in CD_3OD.

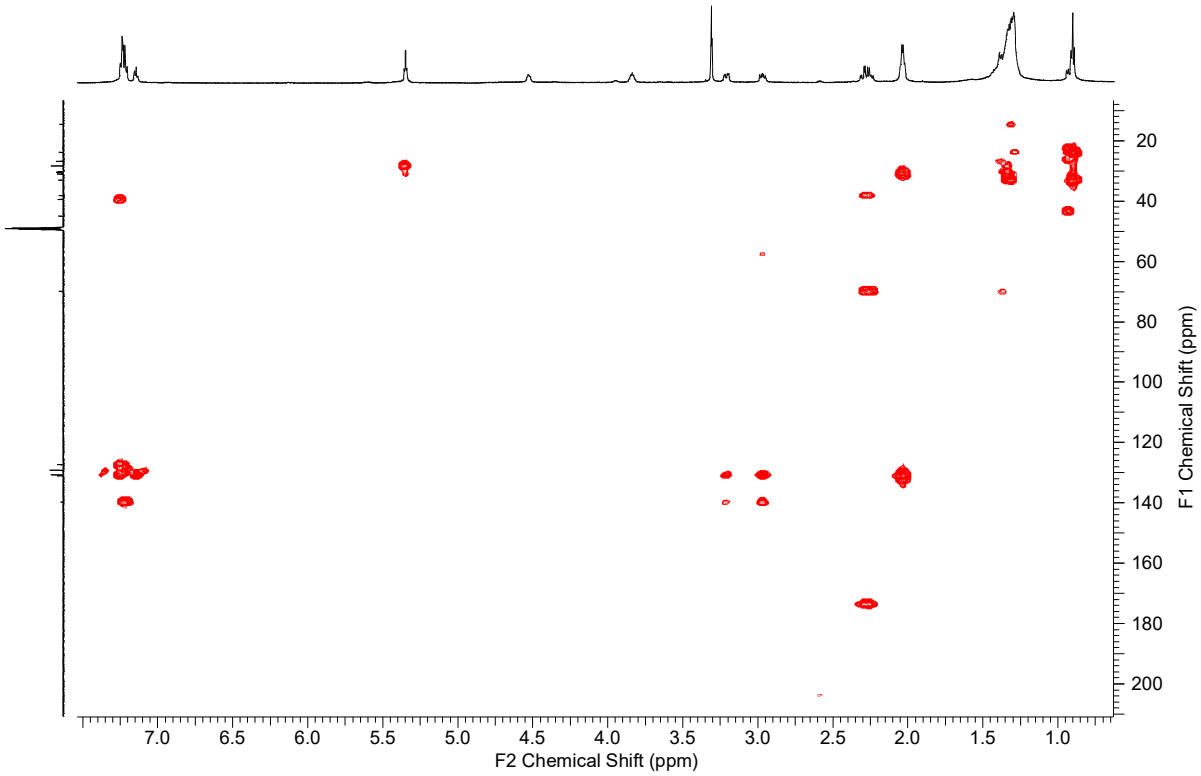

Figure S12. HRMS of compound 2 in MeOH.

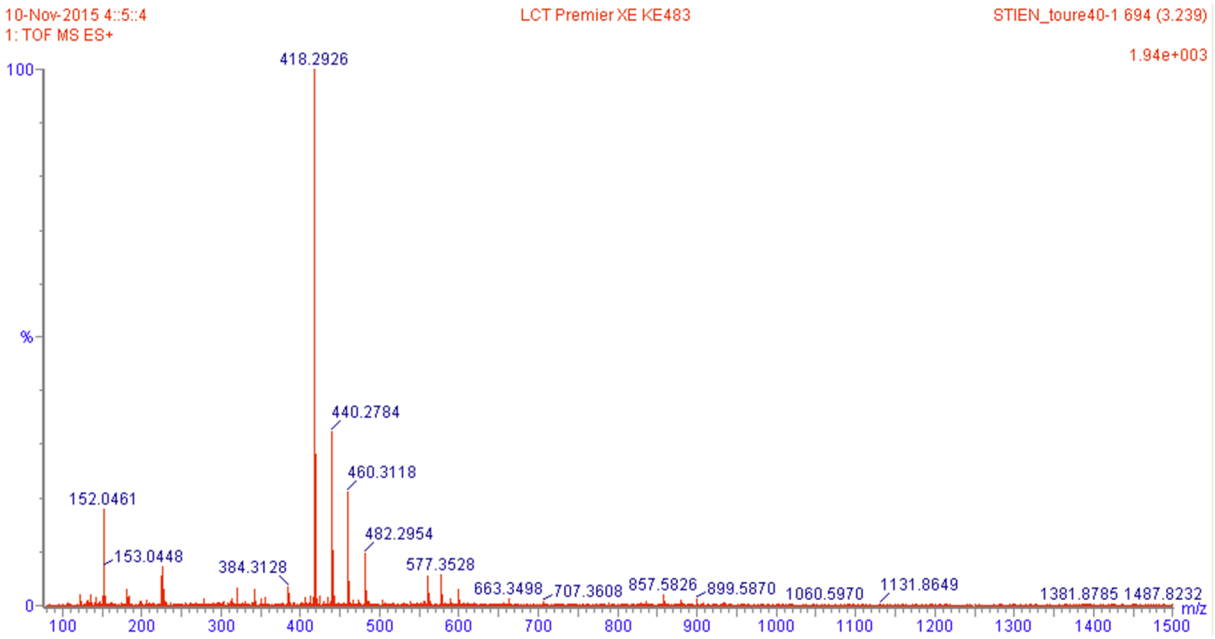

Table S3. Full NMR spectroscopic data for compound 3 in CD_3OD

Position	δ_C type	δ_H m (*J* in Hz)	COSY	HMBC
1	176.5. C			
2	56.02. CH	4.62. dd (8.0. 4.7)	H3a. H3b	C1. C3. C4. C1’
3	39.0. CH_2	2.94. dd (13.8. 8.7)	H2	C1. C2. C4. C5
		3.22. dd (13.8. 4.7)	H2	C1. C2. C4. C5
4	139.2. C			
5	130.5. CH	7.23. m		C3. C4. C7
6	129.4. CH	7.24. m		C4. C7
7	127.6. CH	7.17. m		C5
1’	175.8. C			
2’	37.2. CH_2	2.13. t (7.5)	H3’	C1’. C3’. C4’
		2.23. t (7.5)		C1’. C3’. C4’
3’	27.1. CH_2	1.48. m	H2’a. H4’	C1’. C2’. C4’
4’	30.3. CH_2	1.29. br s	H3’	
5’	30.3. CH_2	1.29. br s		
6’	30.3. CH_2	1.29. br s		
7’	30.3. CH_2	1.29. br s		
8’	30.3. CH_2	2.03. m	H9’	C7’. C9’
9’	131.0. CH	5.35. m	H8’	C7’. C8’
10’	131.0. CH	5.35. m	H11’	C11’. C12’
11’	30.3. CH_2	2.03. m	H10’. H12’	C10’
12’	30.5. CH_2	1.33. br s	H11’	
13’	30.5. CH_2	1.33. br s		
14’	30.5. CH_2	1.33. br s		
15’	23.8. CH_2	1.31. br s	H16’	
16’	14.6. CH_3	0.90. t (6.8)	H15’	C15’. C14’

Figure S13. ^{1}H NMR spectrum of 3 recorded at 500 MHz in CD_3OD.

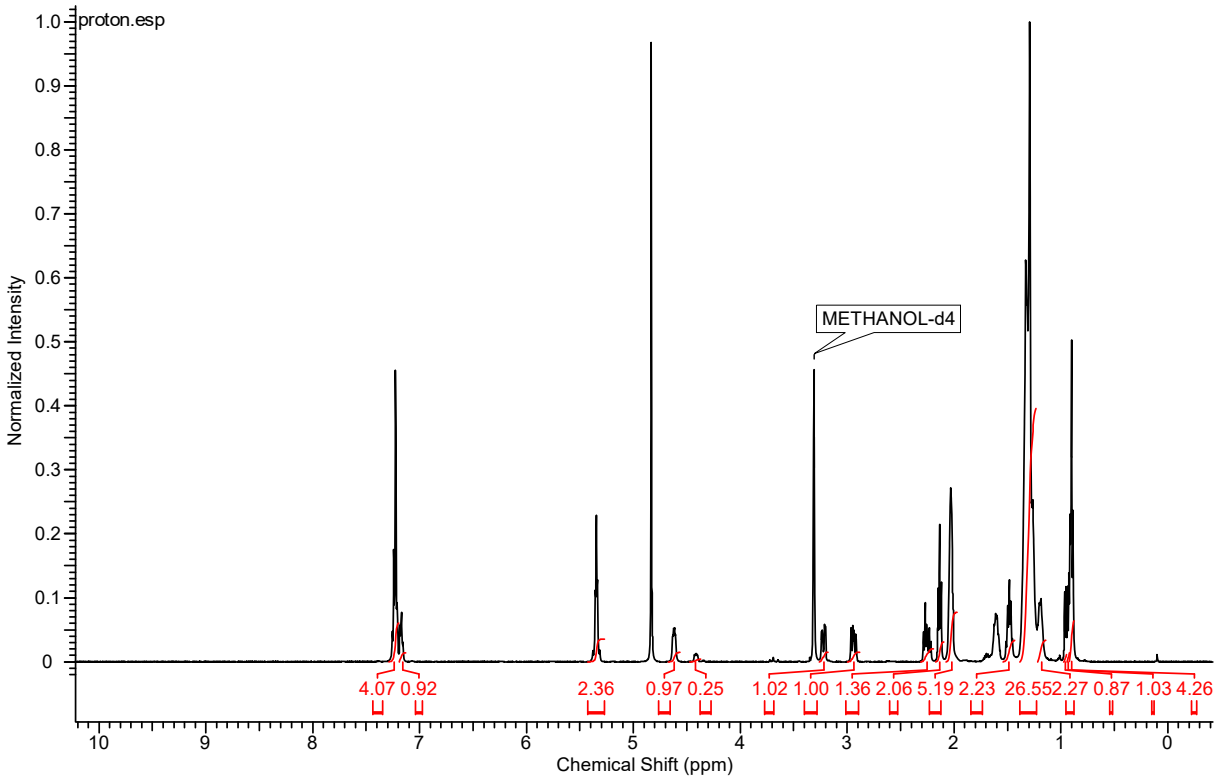

Figure S14. ^{13}C NMR spectrum of 3 recorded at 125 MHz in CD_3OD.

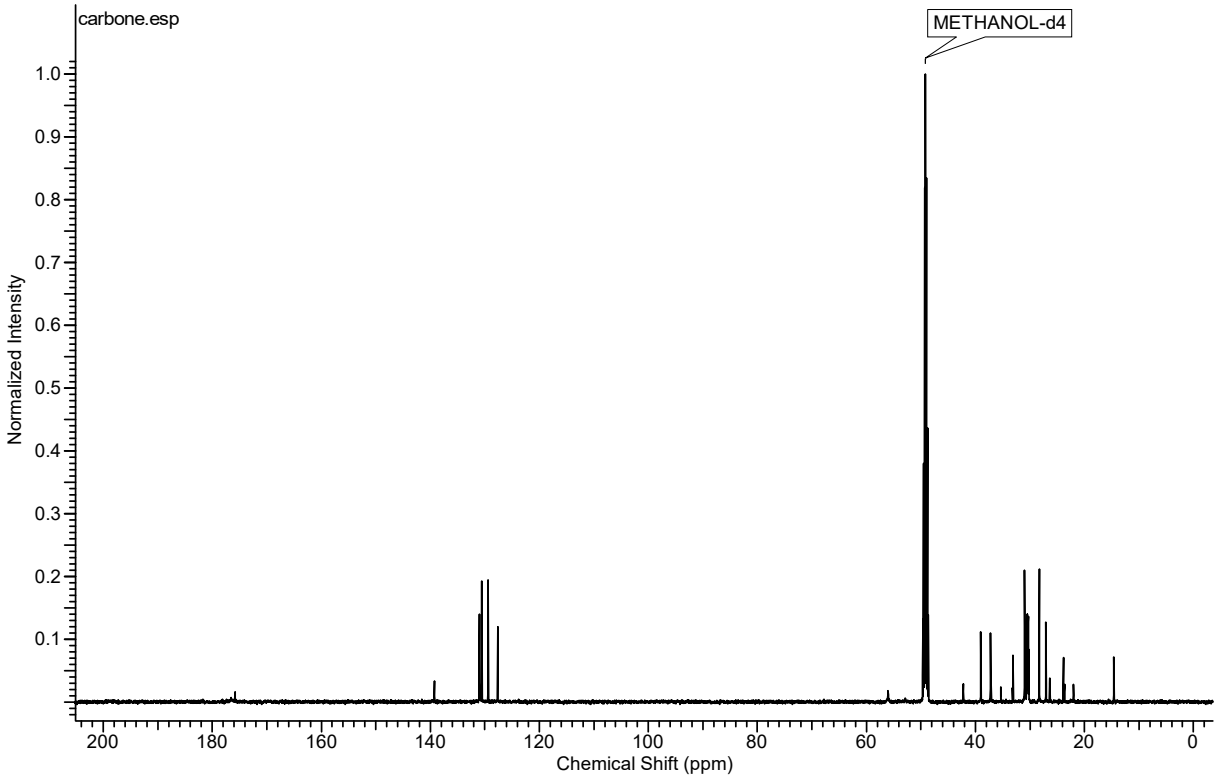

Figure S15. COSY NMR spectrum of 3 recorded at 500MHz in CD_3OD.

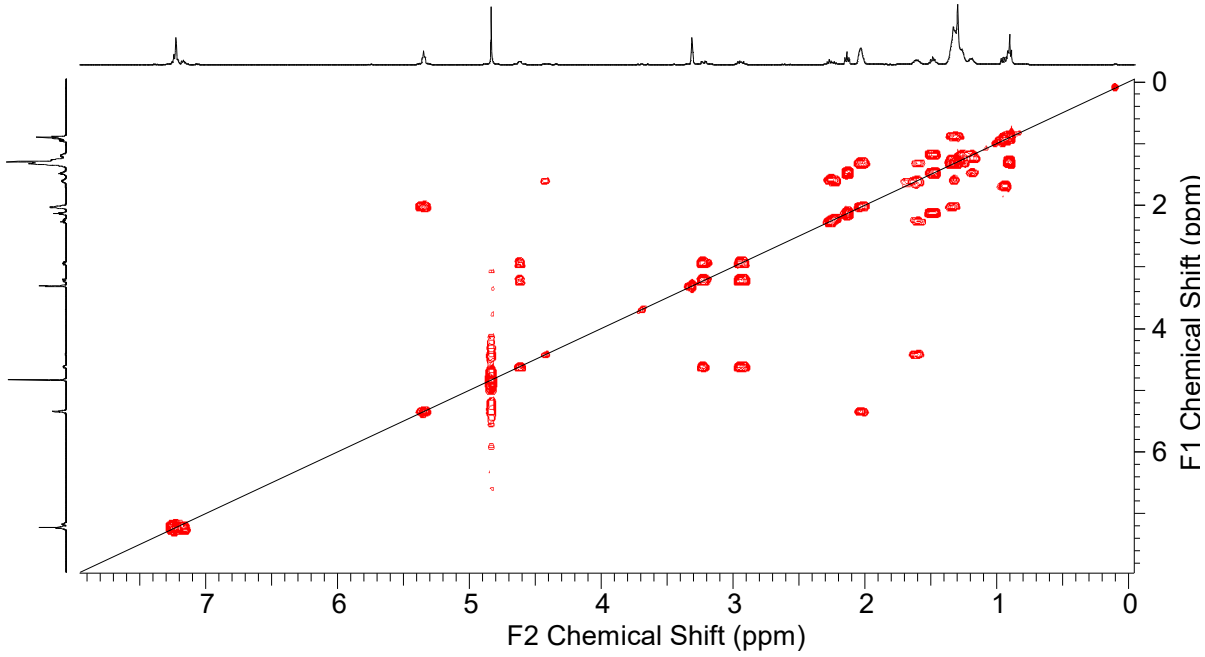

Figure S16. HSQC spectrum of 3 recorded at 500MHz in CD_3OD.

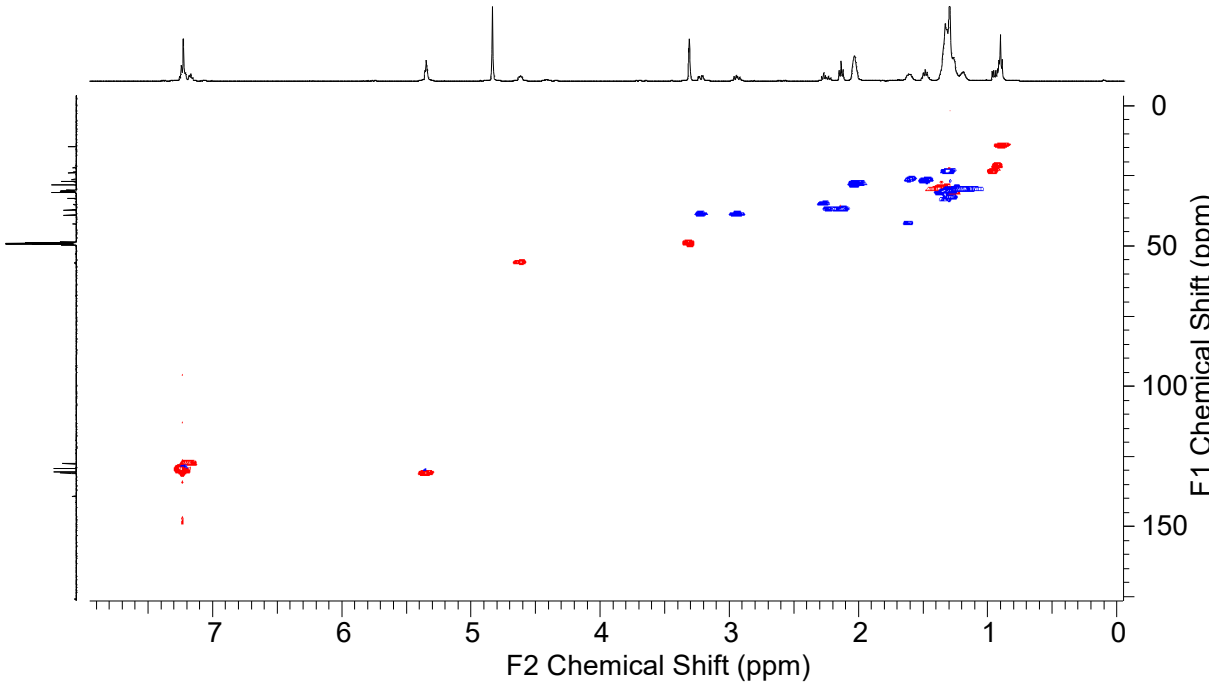

Figure S17. HMBC spectrum of 3 recorded at 500MHz in CD_3OD.

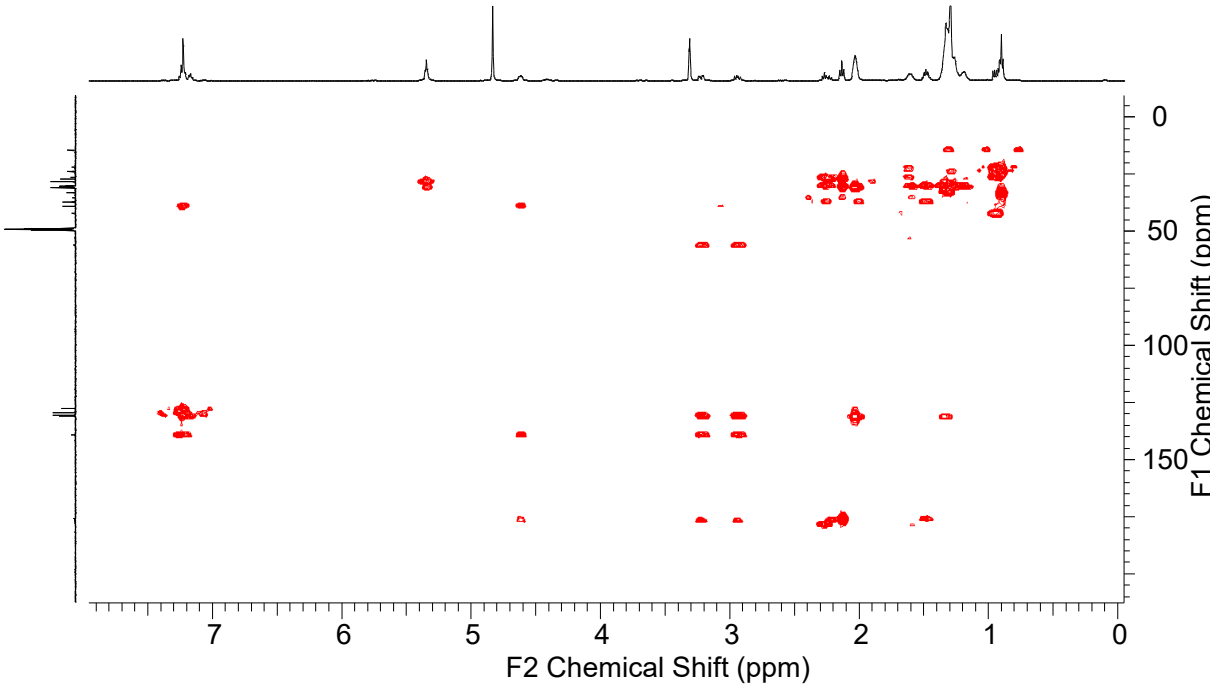

Figure S18. HRMS of compound 3 recorded in MeOH.

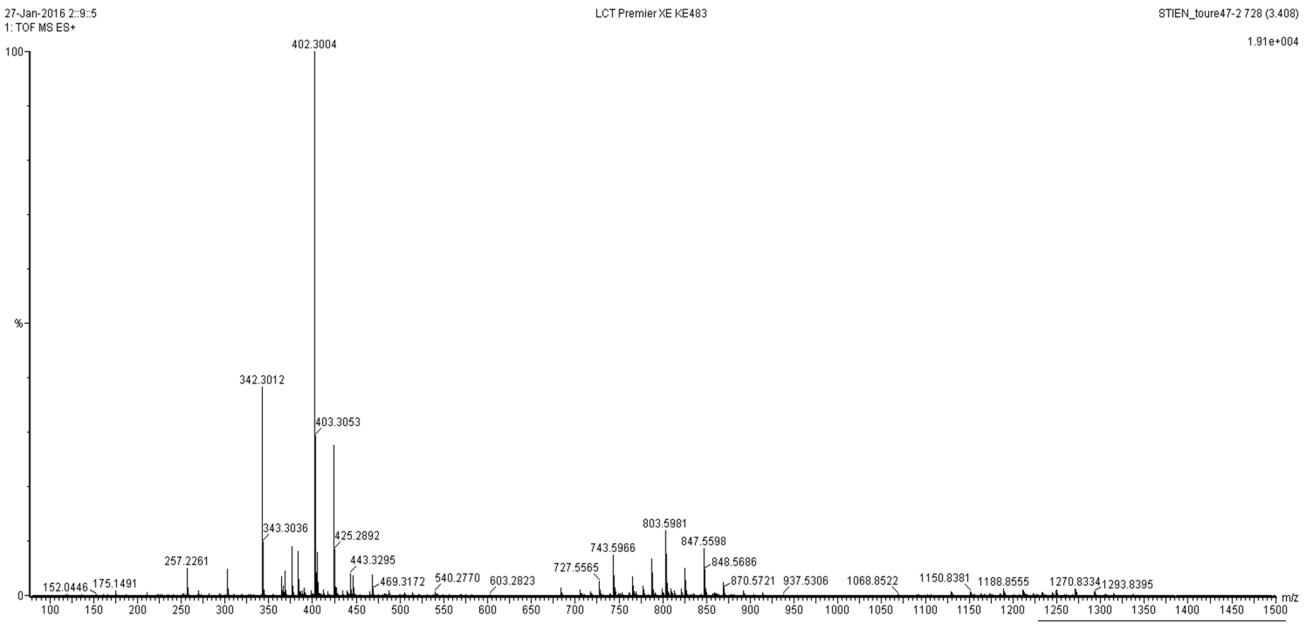

Figure S19. ^{1}H spectrum of 4 recorded at 500 MHz in CD_3OD.

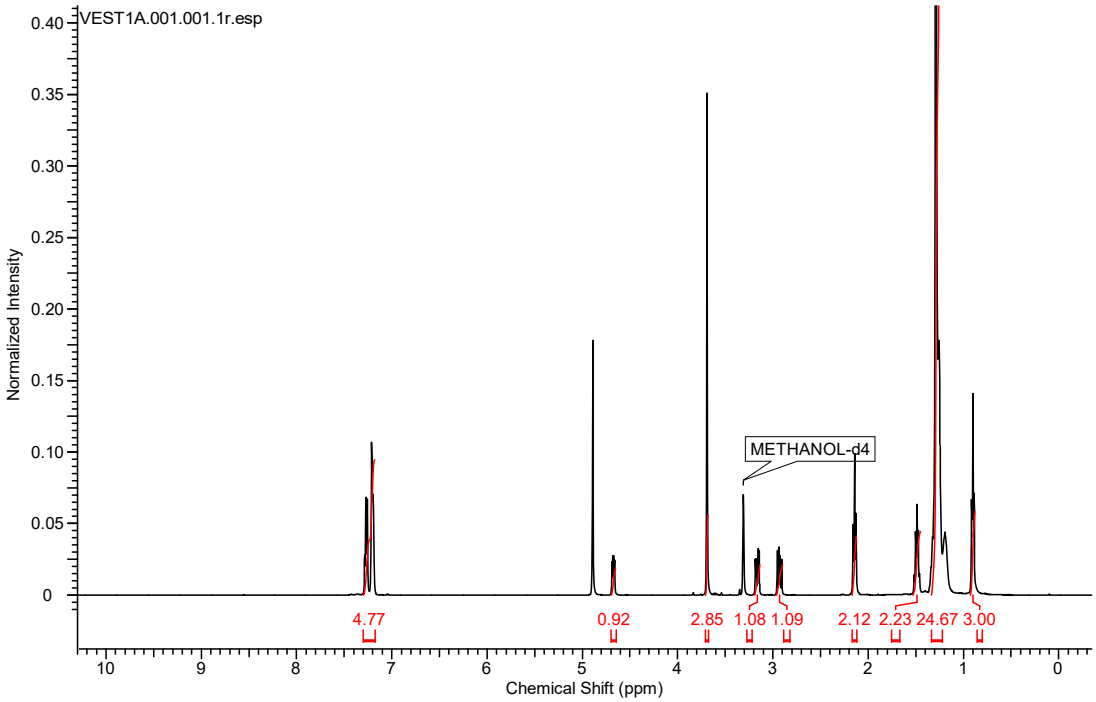

Figure S20. ^{13}C spectrum of 4 recorded at 125 MHz in CD_3OD.

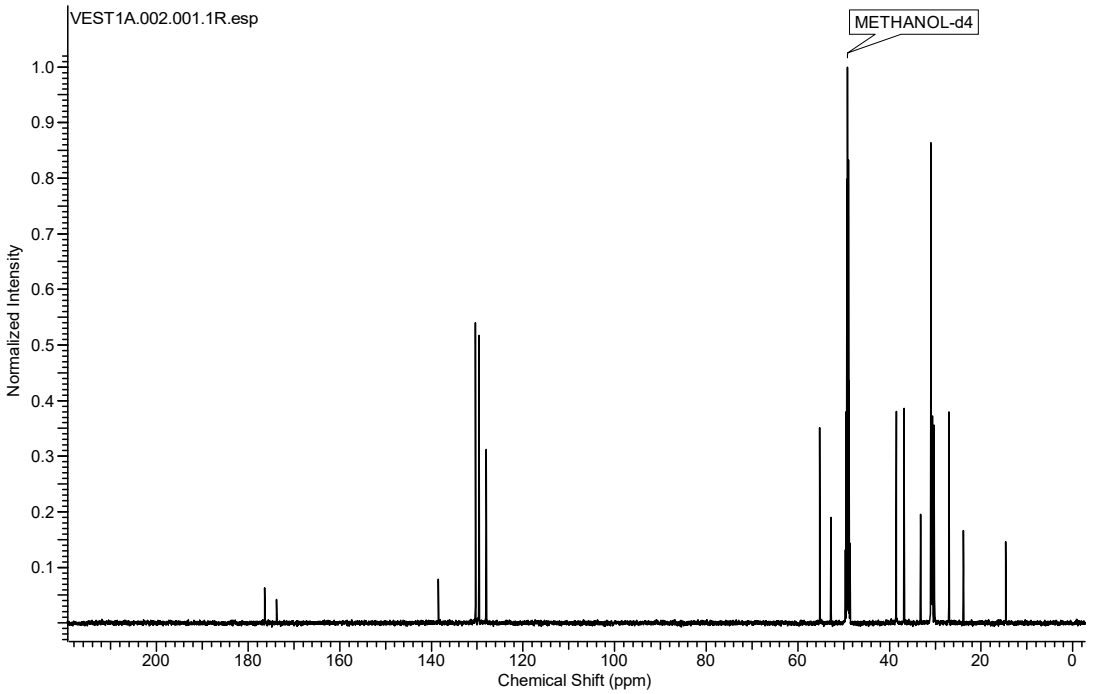

Figure S21. HRMS of compound 4 recorded in MeOH.

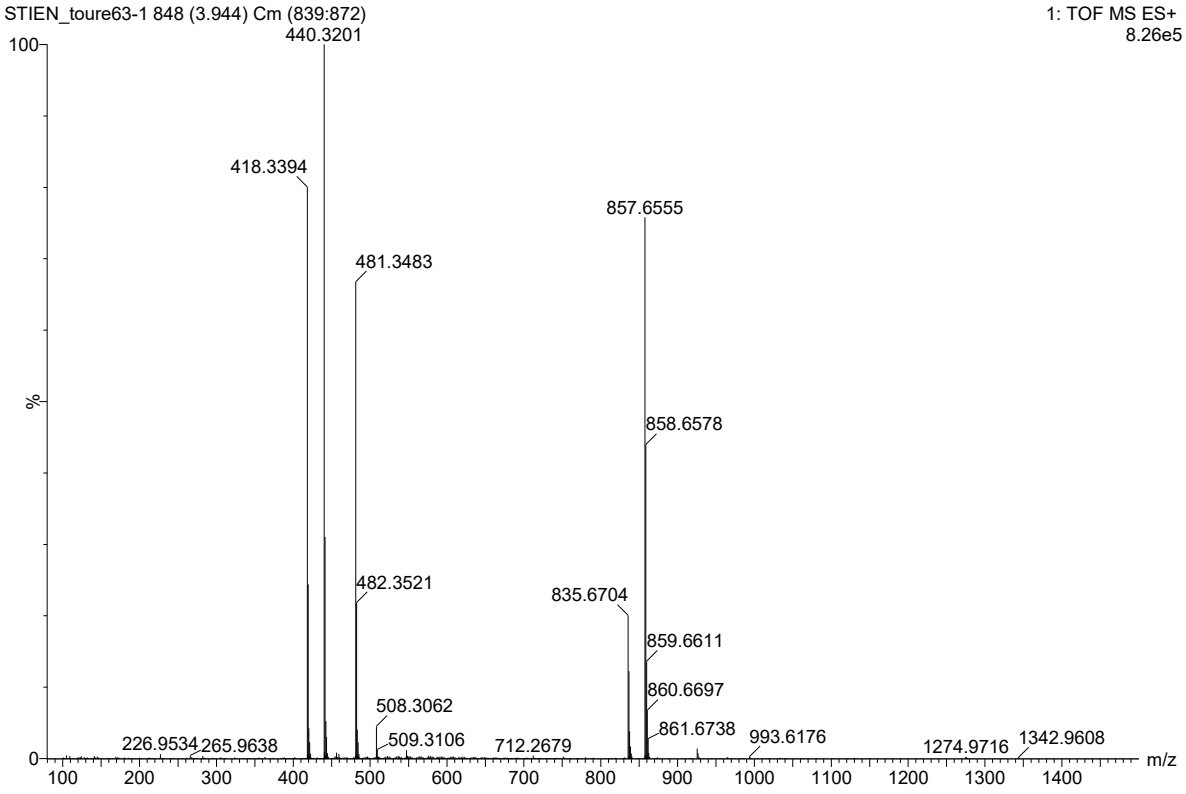

Figure S24. HRMS of compound 3-OMe recorded in MeOH.

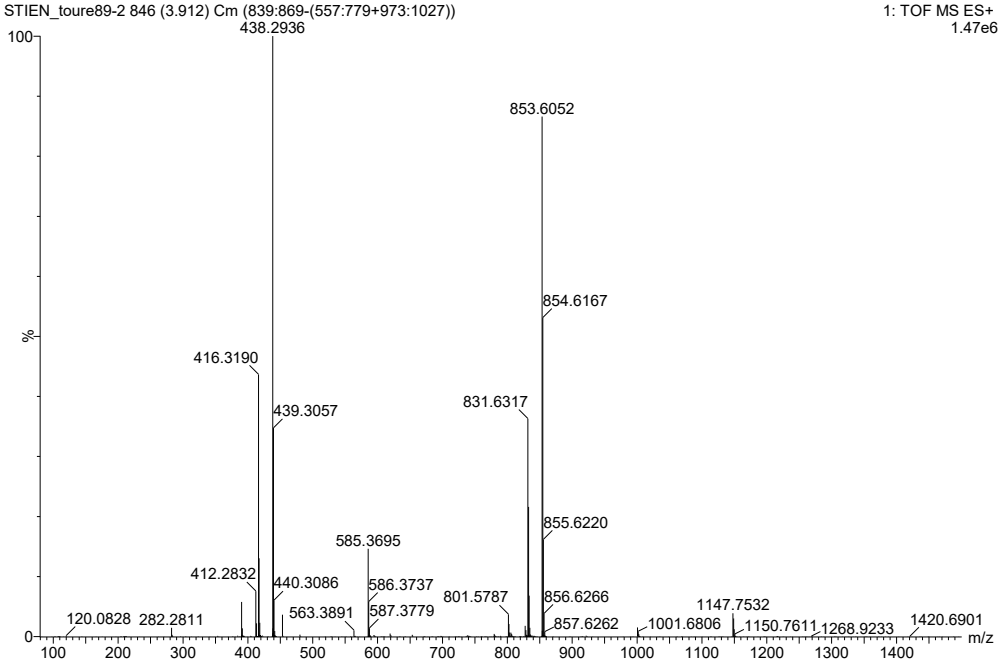

Figure S25. ^{1}H spectrum of 5 recorded at 500 MHz in CD_3OD.

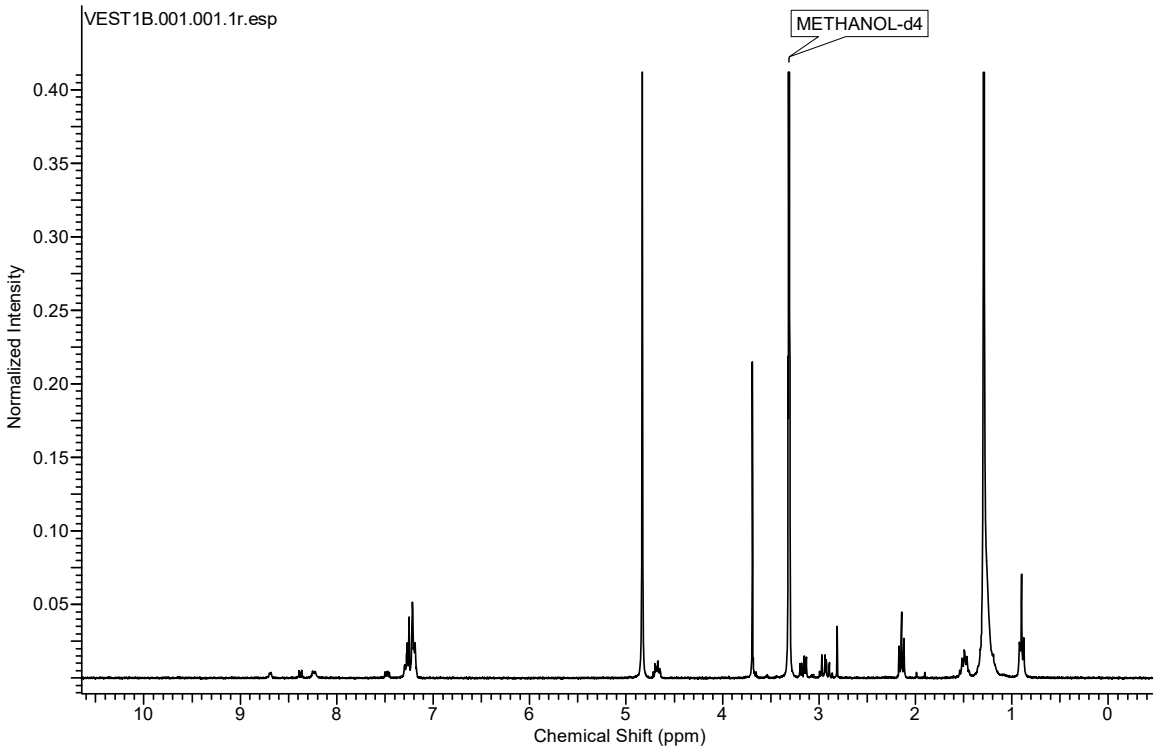

Figure S26. ^{13}C NMR spectrum for compound 5 in CD_3OD

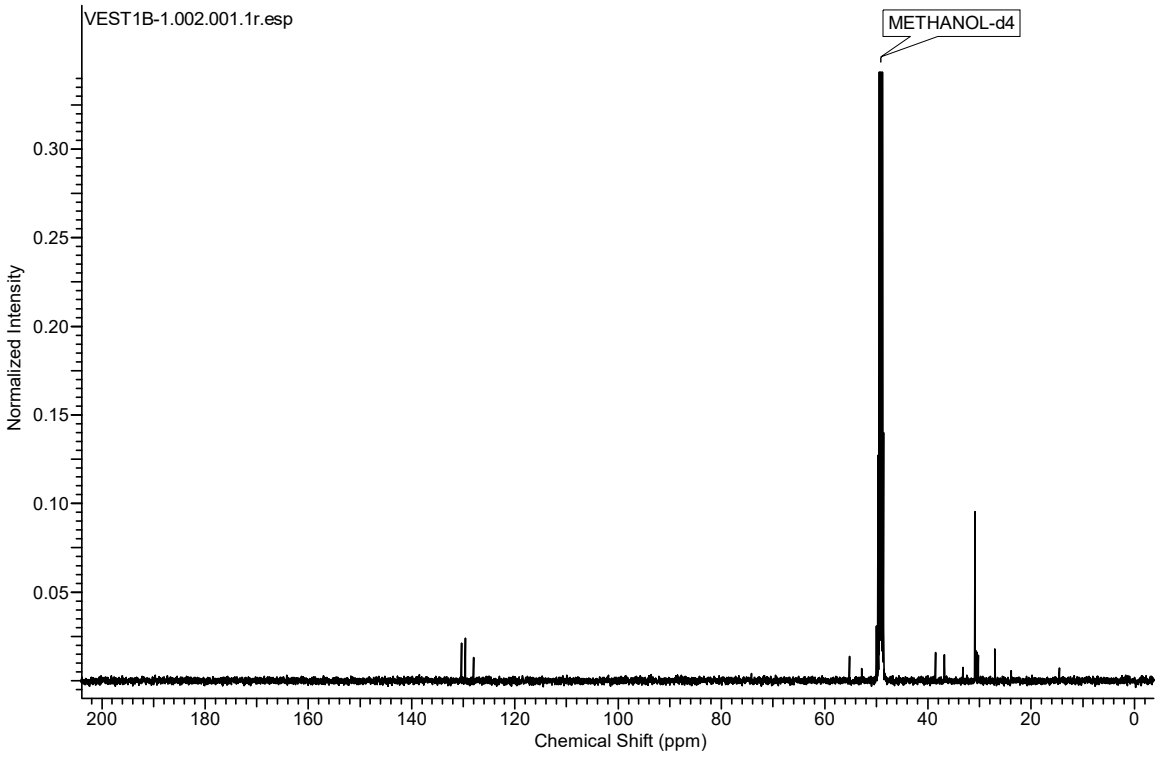

Figure S27. HRMS of compound 5 recorded in MeOH.

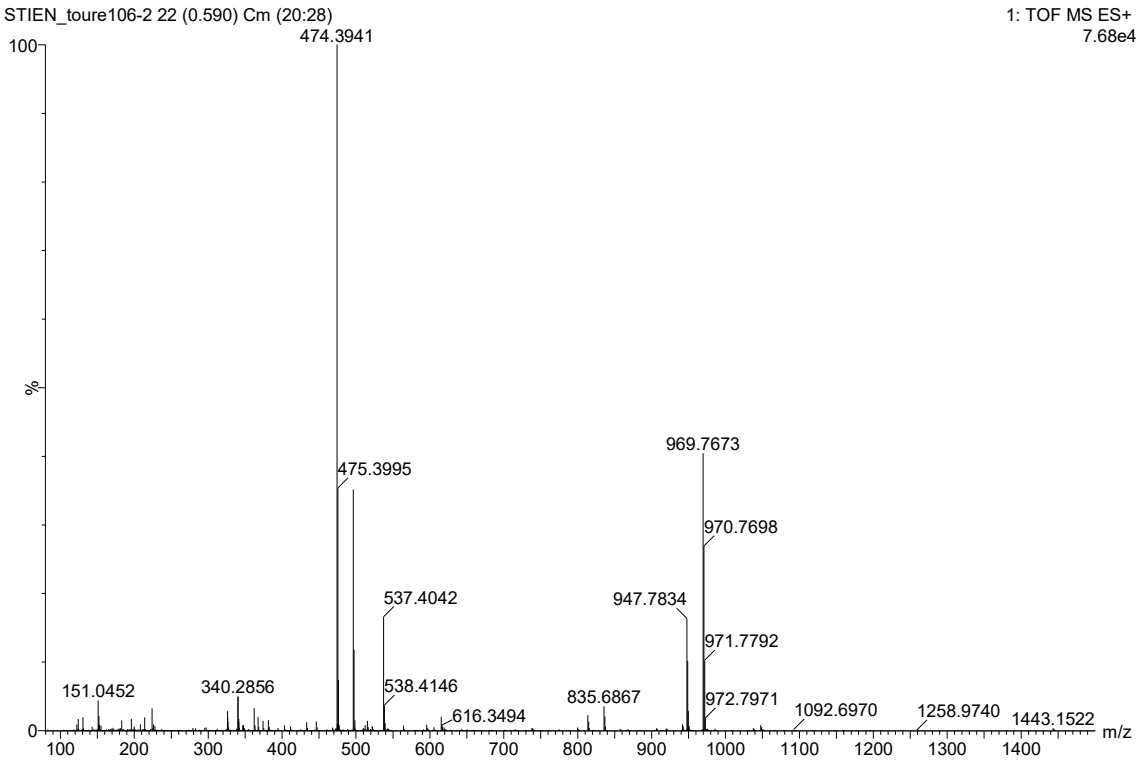

Figure S28. 1H NMR spectrum for compound 6 in CD_3OD

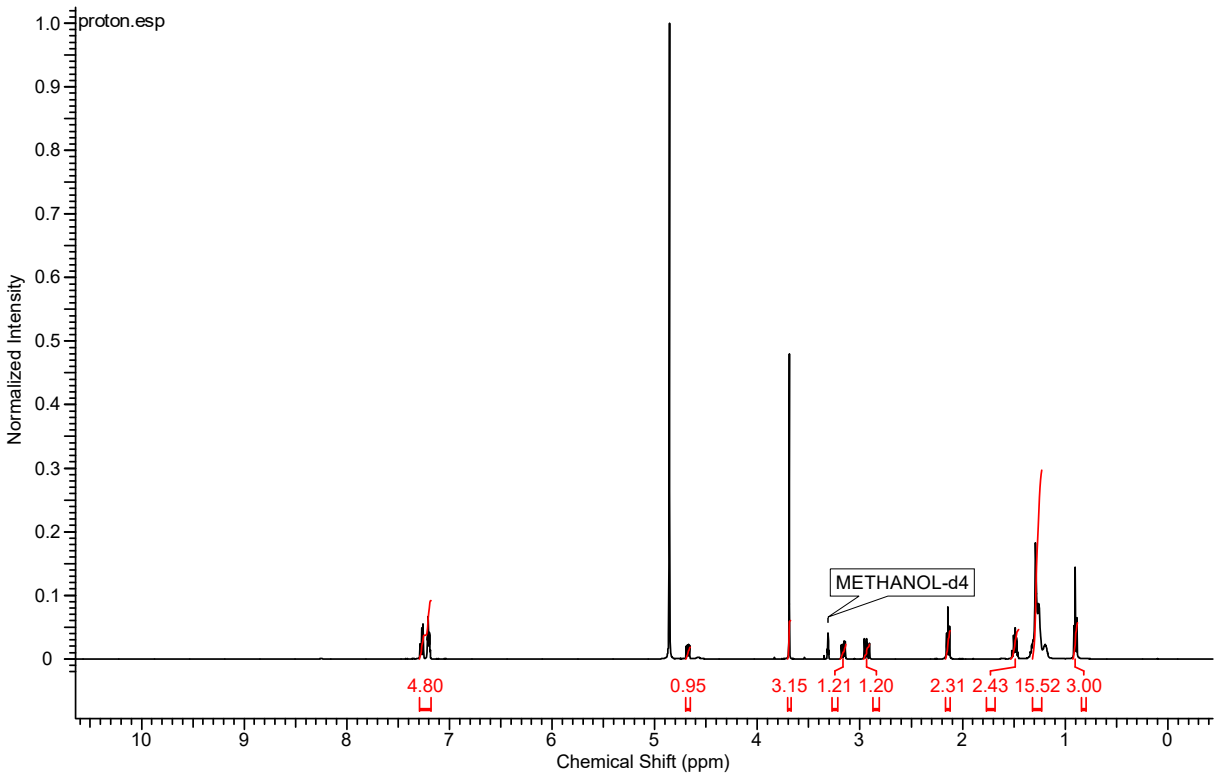

Figure S29. 13C NMR spectrum for compound 6 in CD_3OD

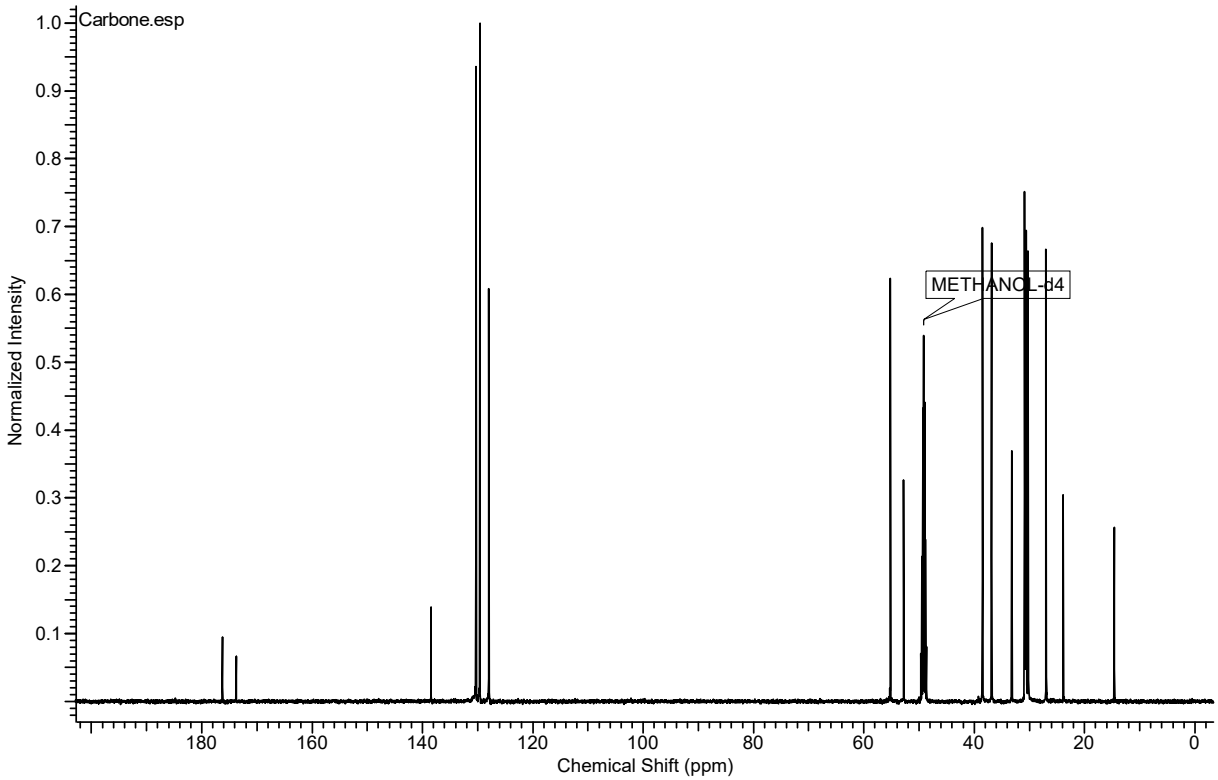

Figure S30. HRMS of compound 6 in MeOH

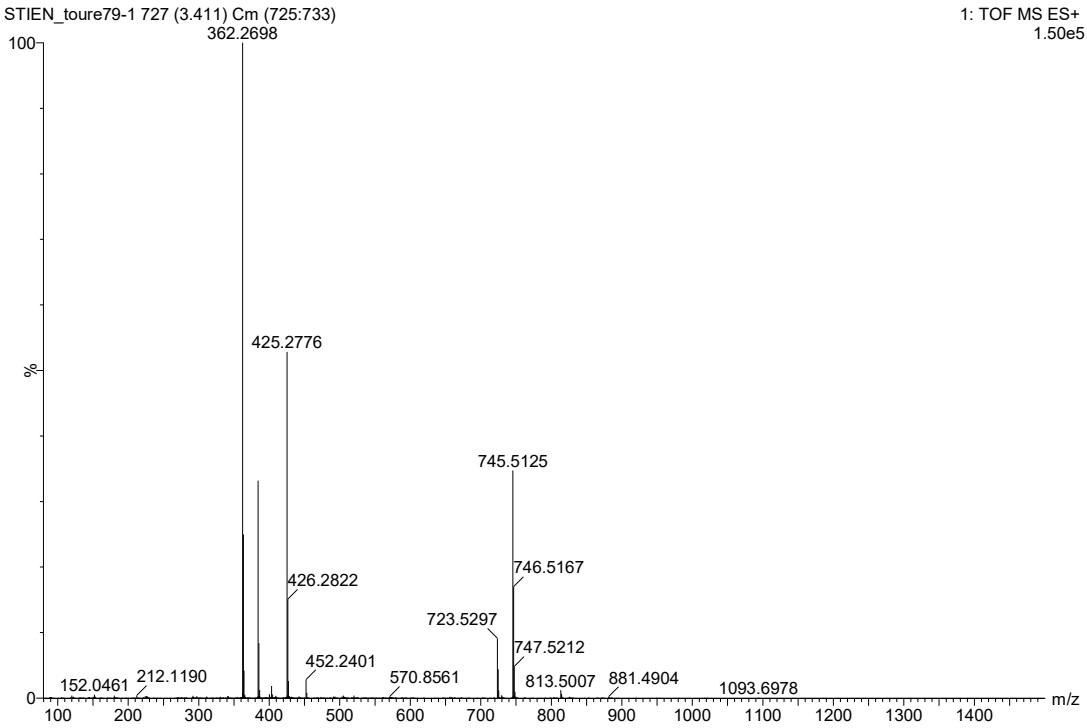

Figure S31. 1H NMR spectrum for compound 7 in CD_3OD

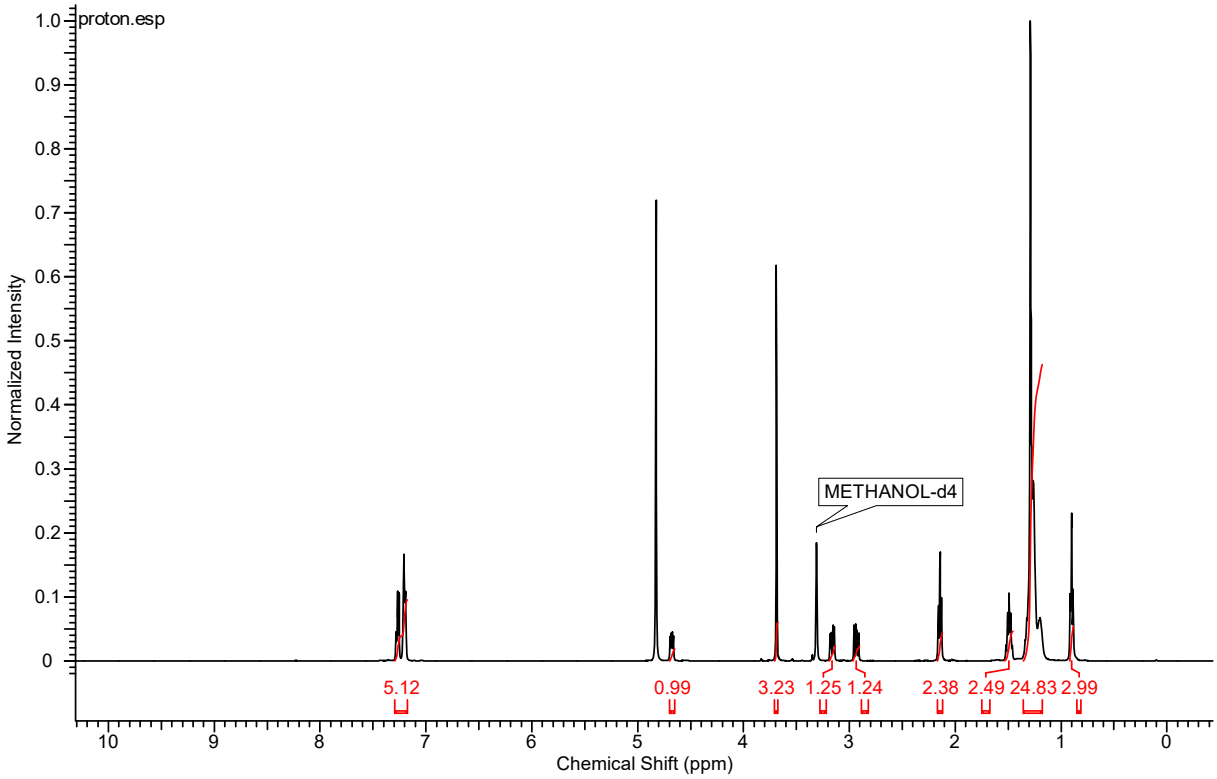

Figure S32. ^{13}C NMR spectrum for compound 7 in CD_3OD

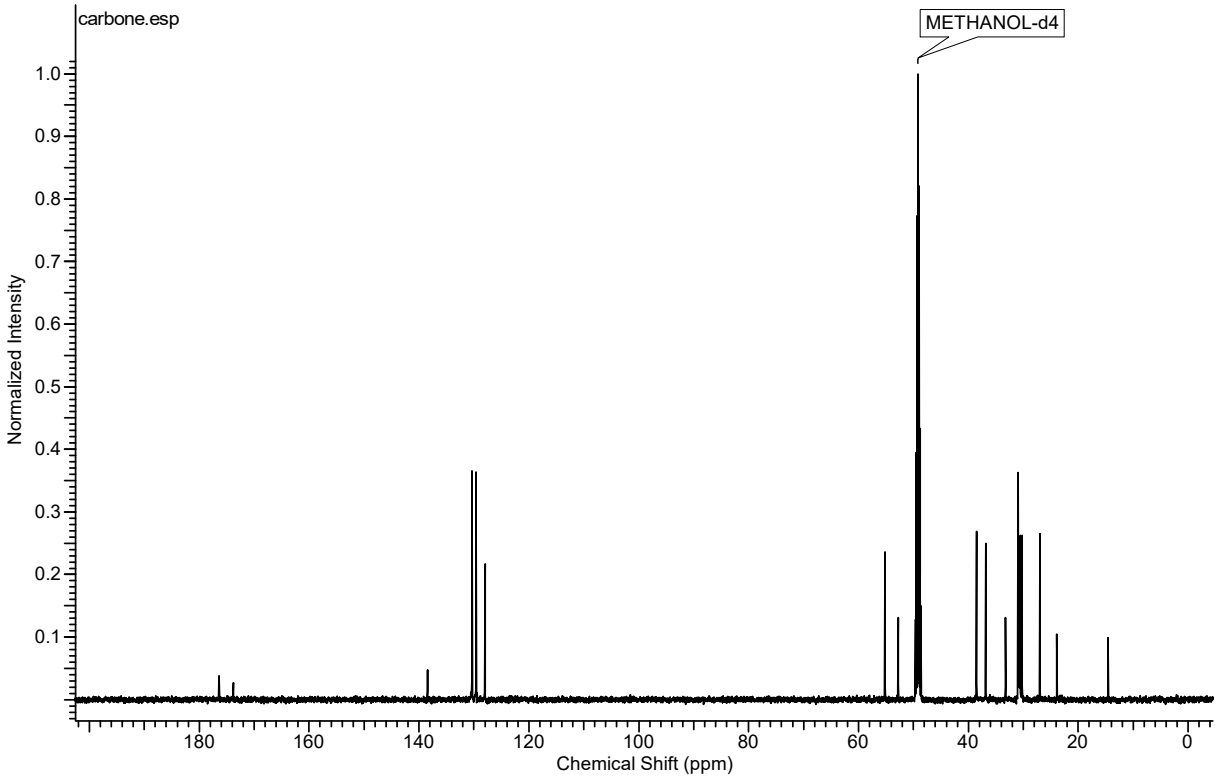

Figure S33. HRMS of compound 7 in MeOH

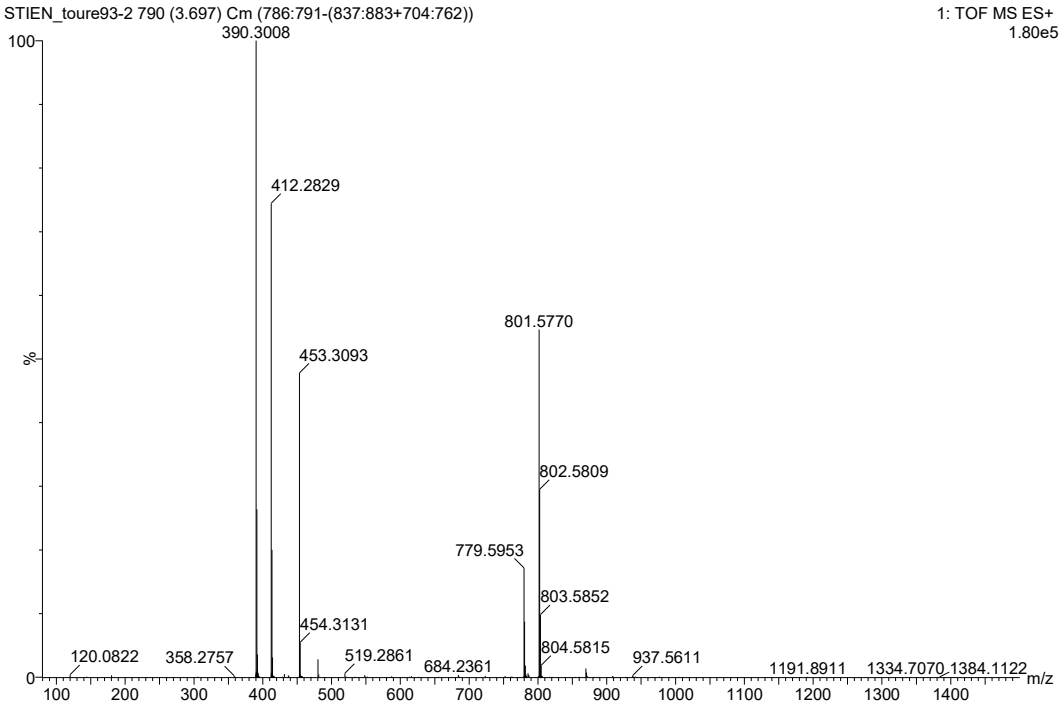

Figure S34. 1H NMR spectrum for compound 8 in CD_3OD

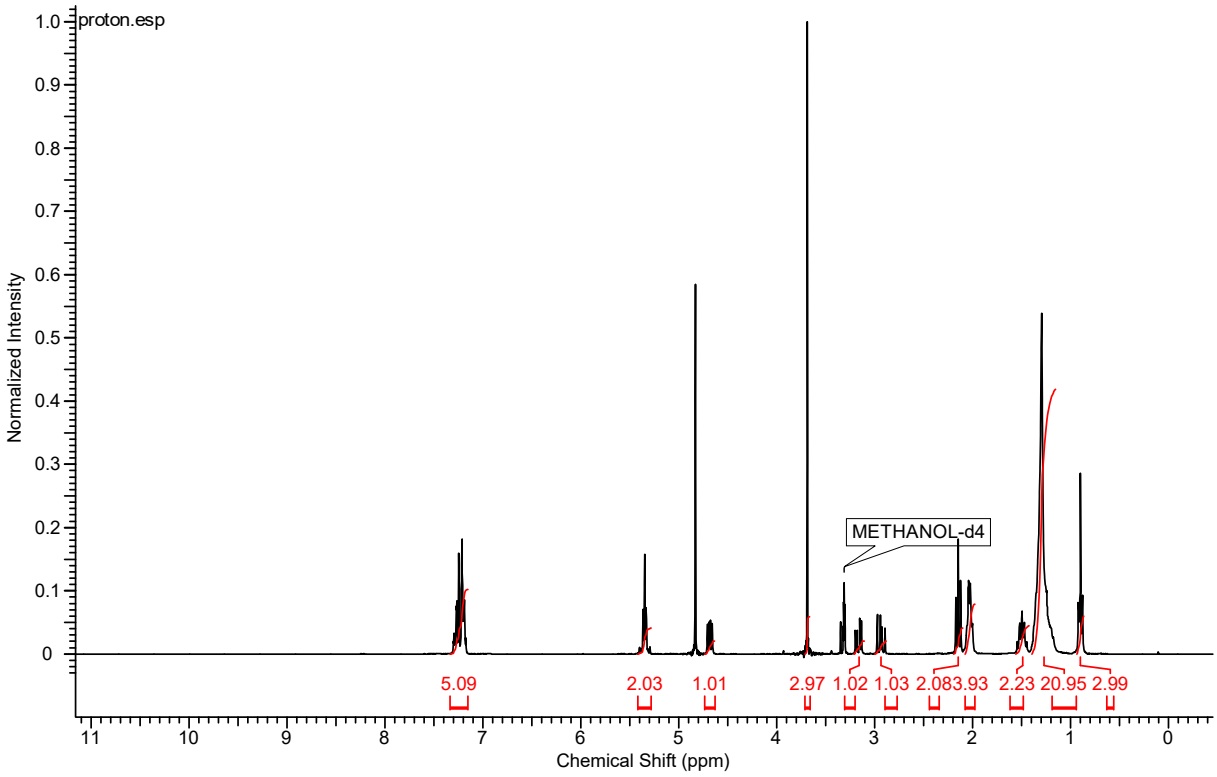

Figure S35. ^{13}C NMR spectrum for compound 8 in CD_3OD

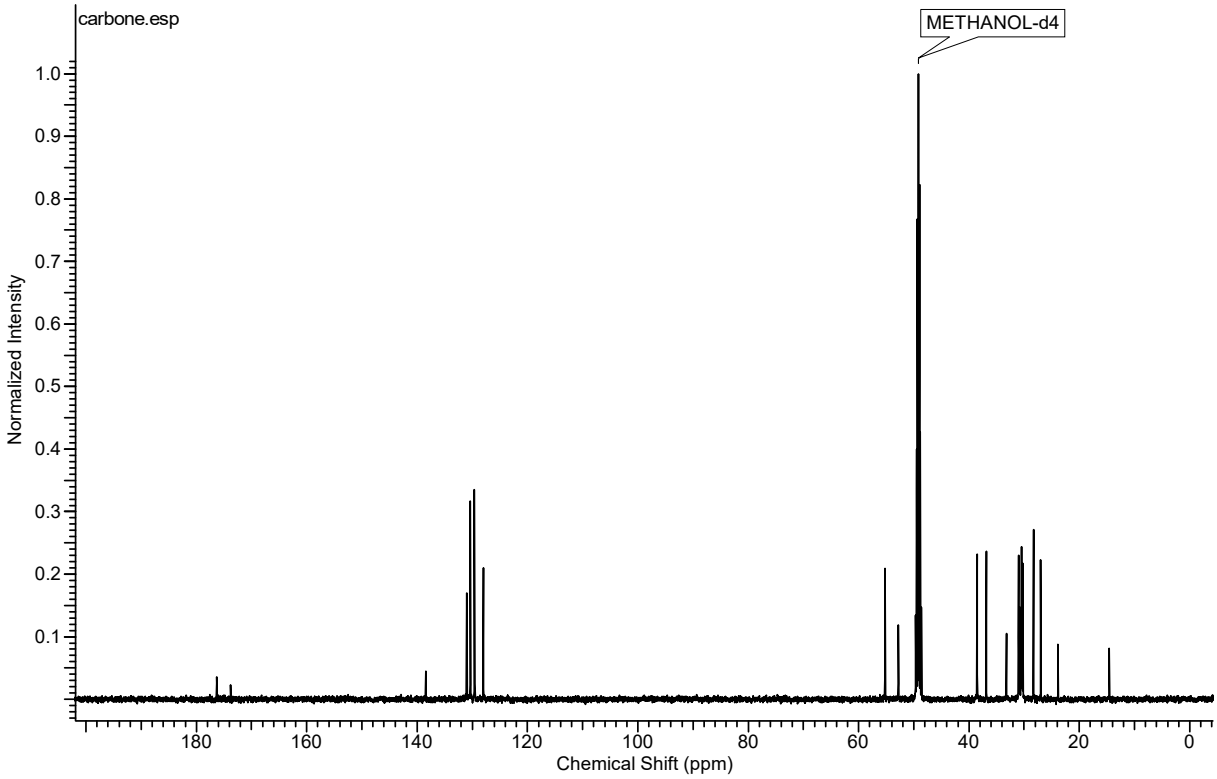

Figure S36. HRMS of compound 8 in MeOH

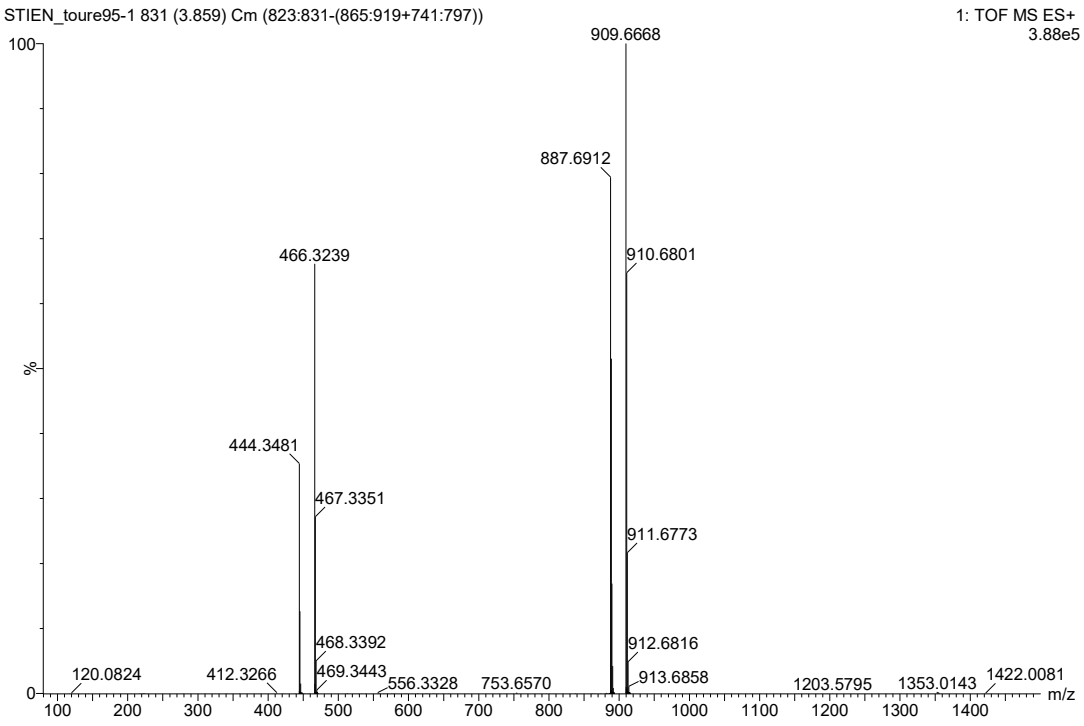

Figure S37. 1H NMR spectrum for compound 9 in CD_3OD

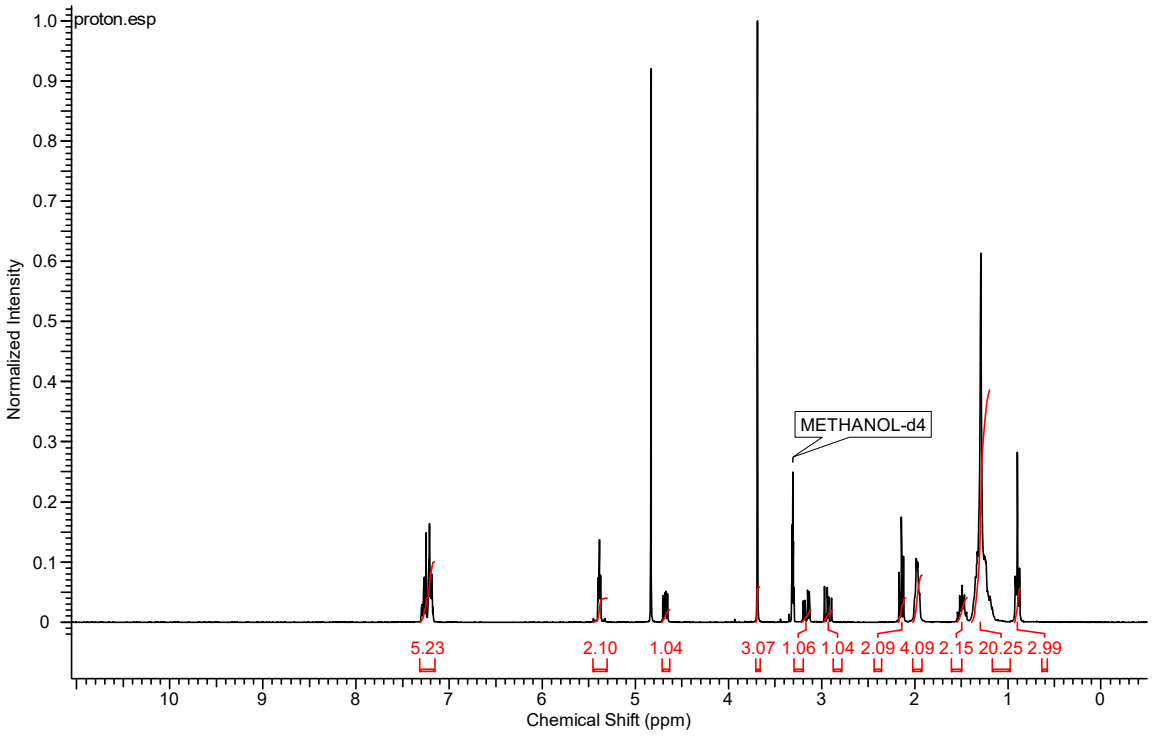

Figure S38. ^{13}C NMR spectrum for compound 9 in CD_3OD

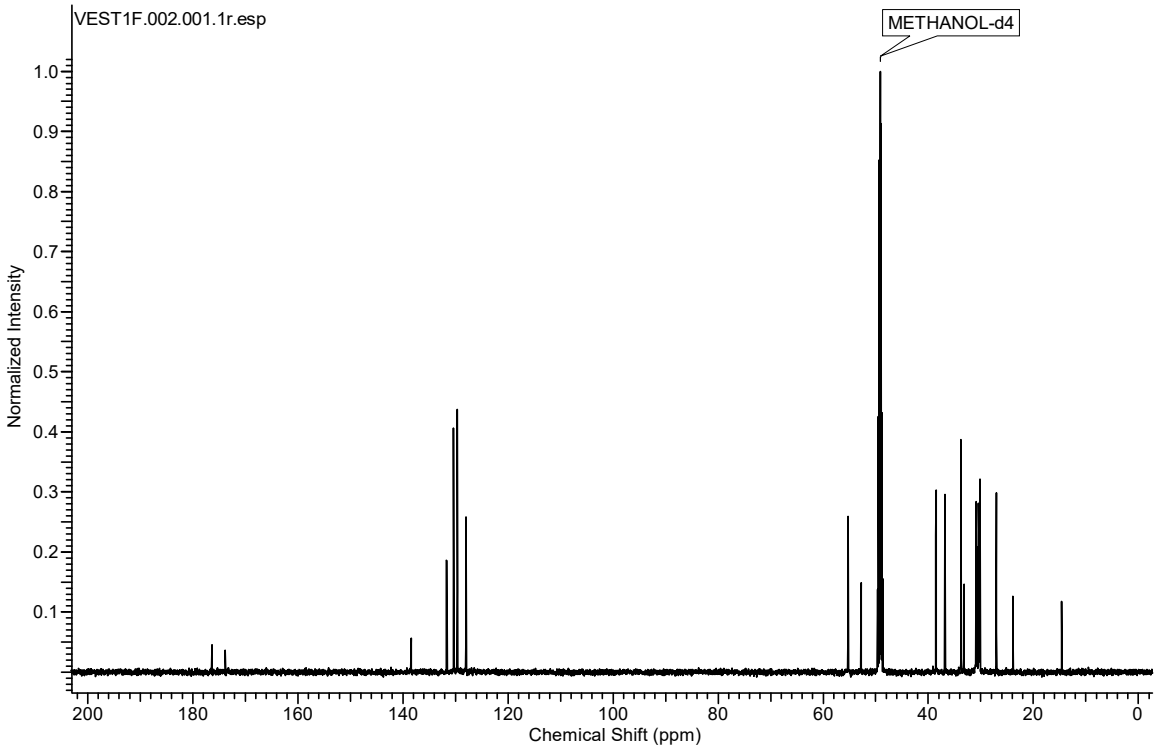

Figure S39. HRMS of compound 9 in MeOH

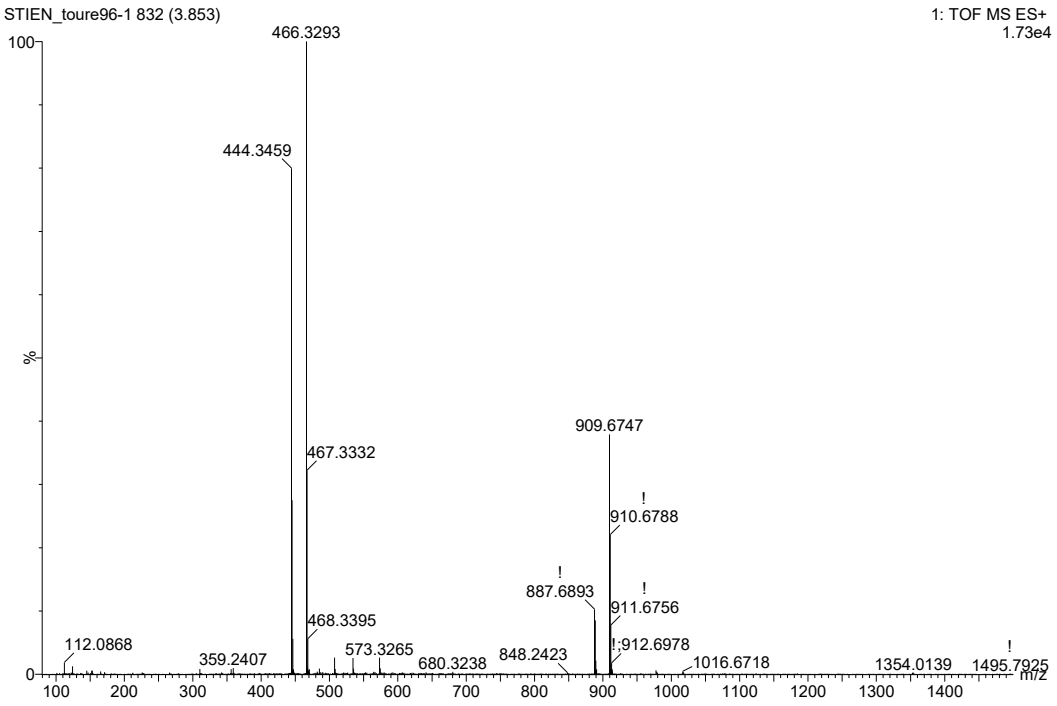

Figure S40. 1H NMR spectrum for compound 10 in CD_3OD

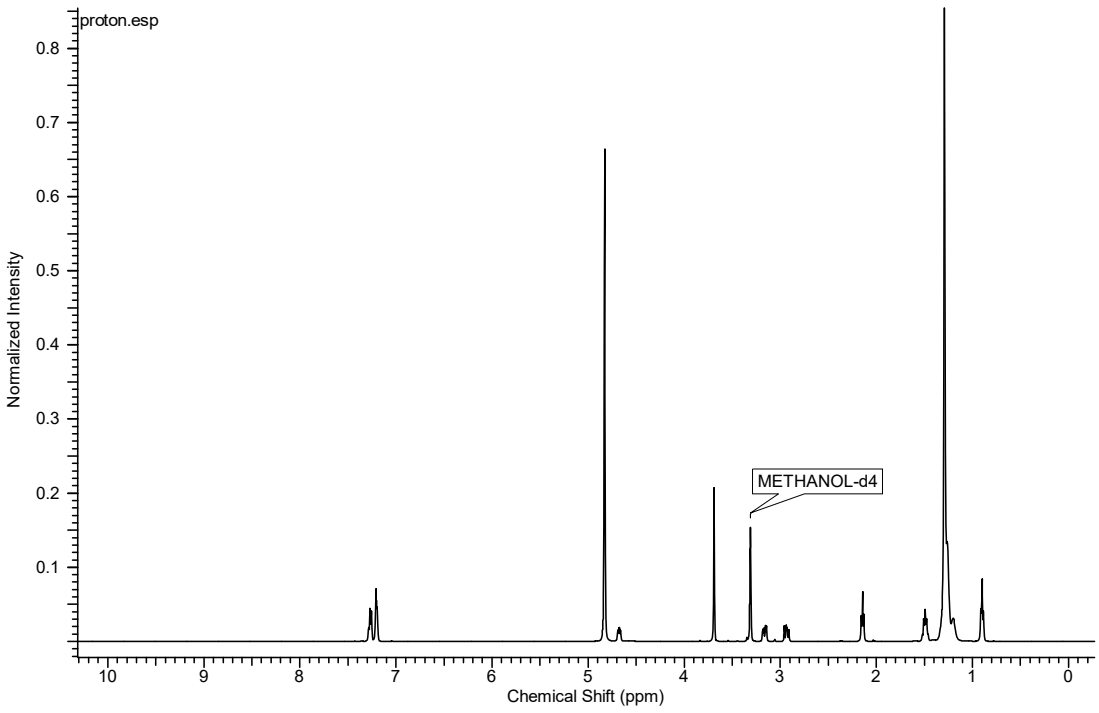

Figure S41. ^{13}C NMR spectrum for compound 10 in CD_3OD

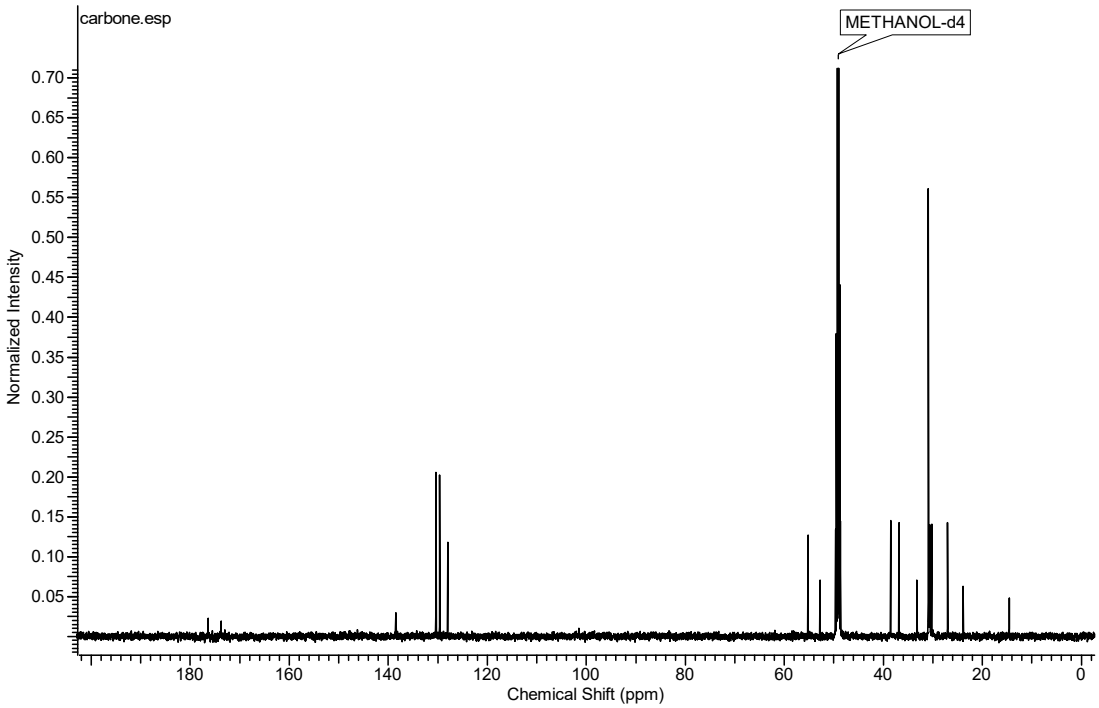

Figure S42. HRMS of compound 10 in MeOH

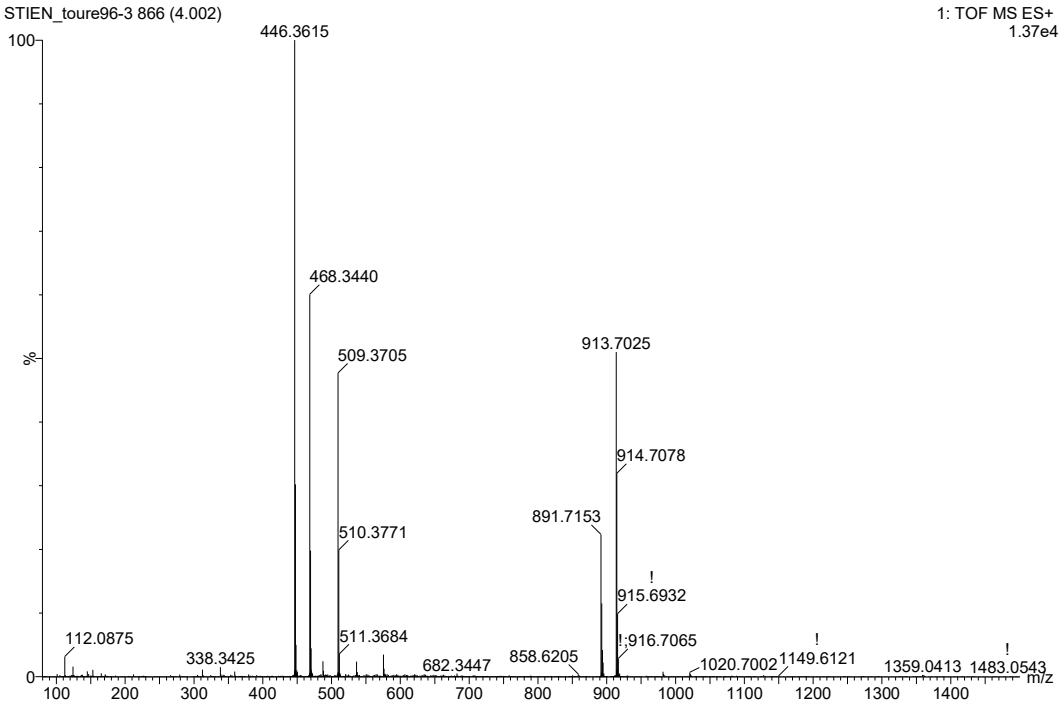

Figure S43. 1H NMR spectrum for compound 11 in CD_3OD

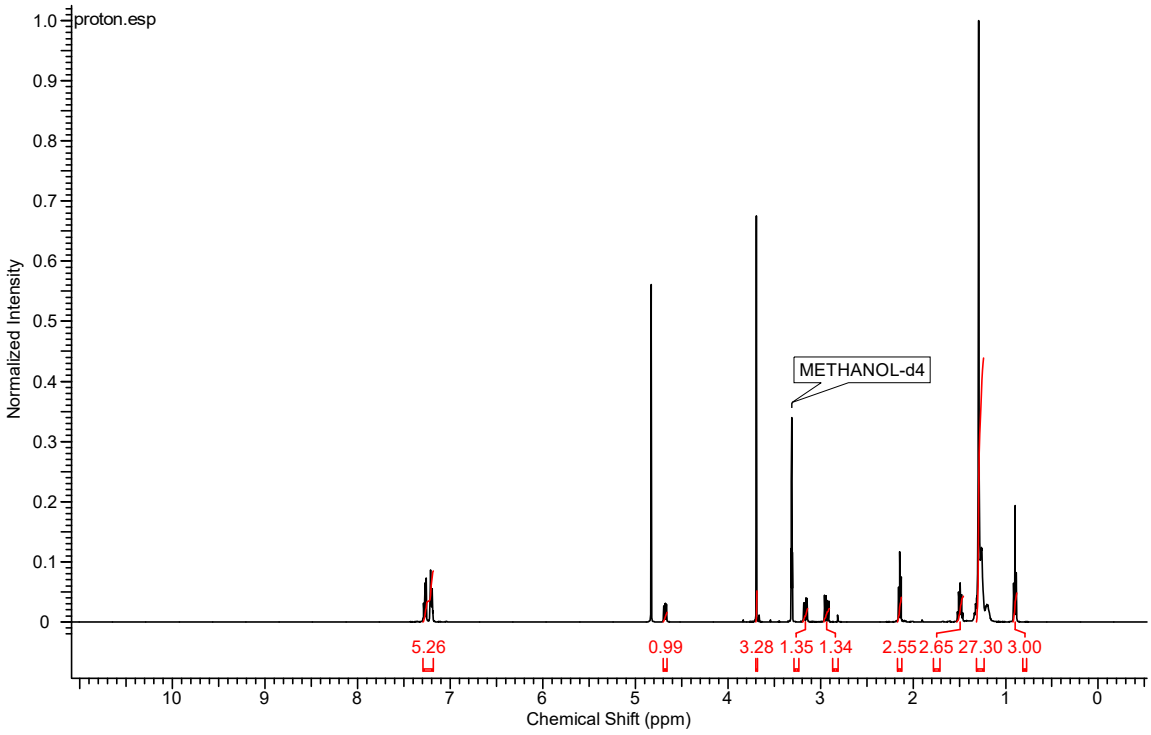

Figure S44. ^{13}C NMR spectrum for compound 11 in CD_3OD

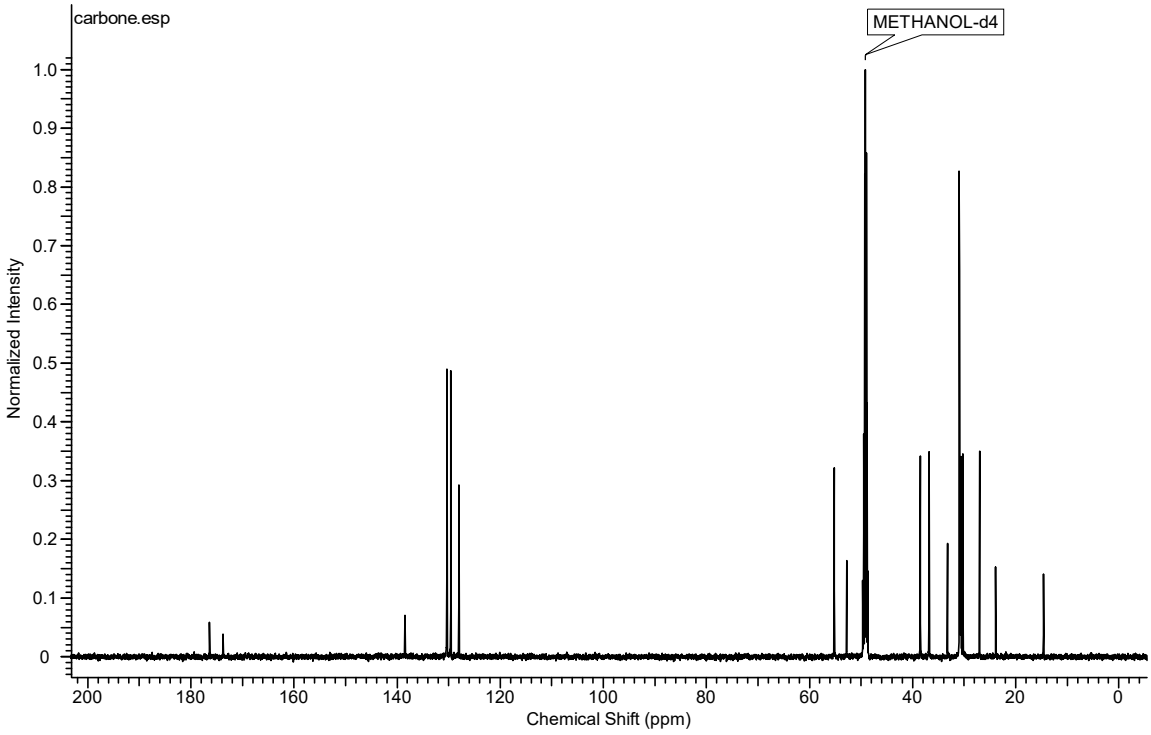

Figure S45. HRMS of compound 11 in MeOH

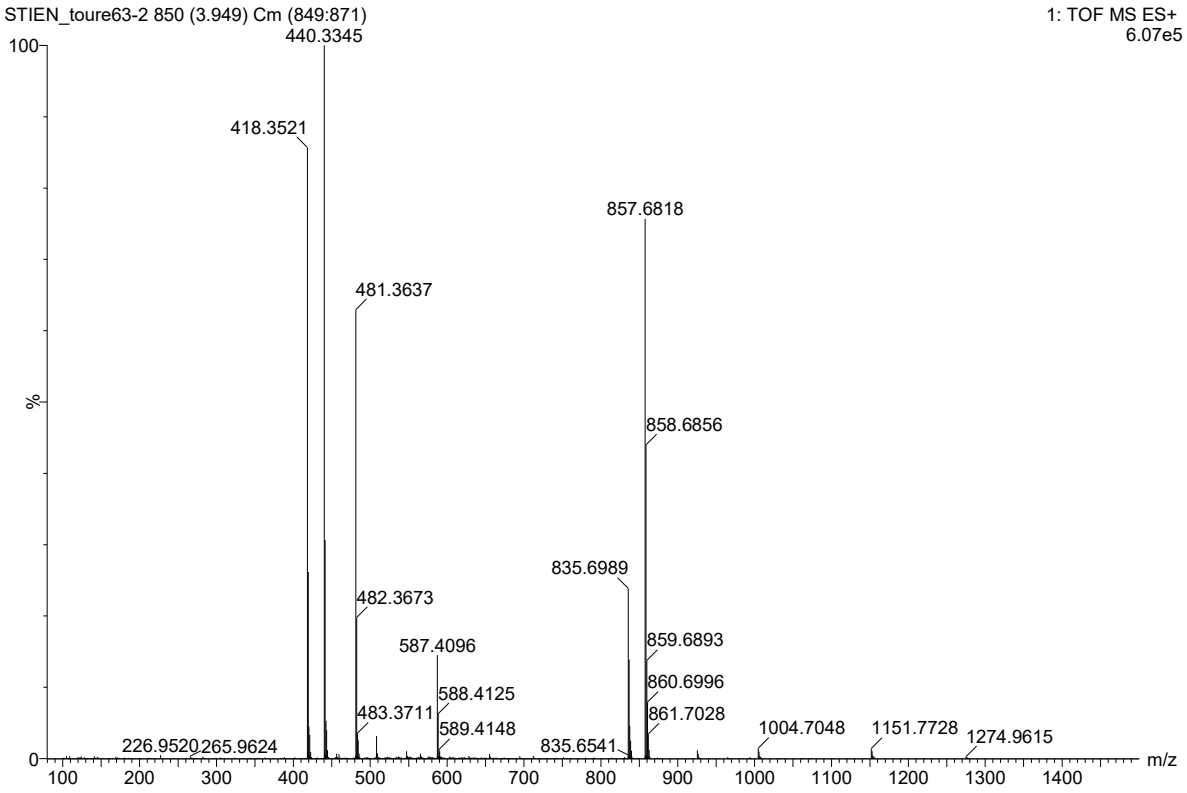

Figure S46. 1H NMR spectrum for compound *ent*-3OMe in CD_3OD

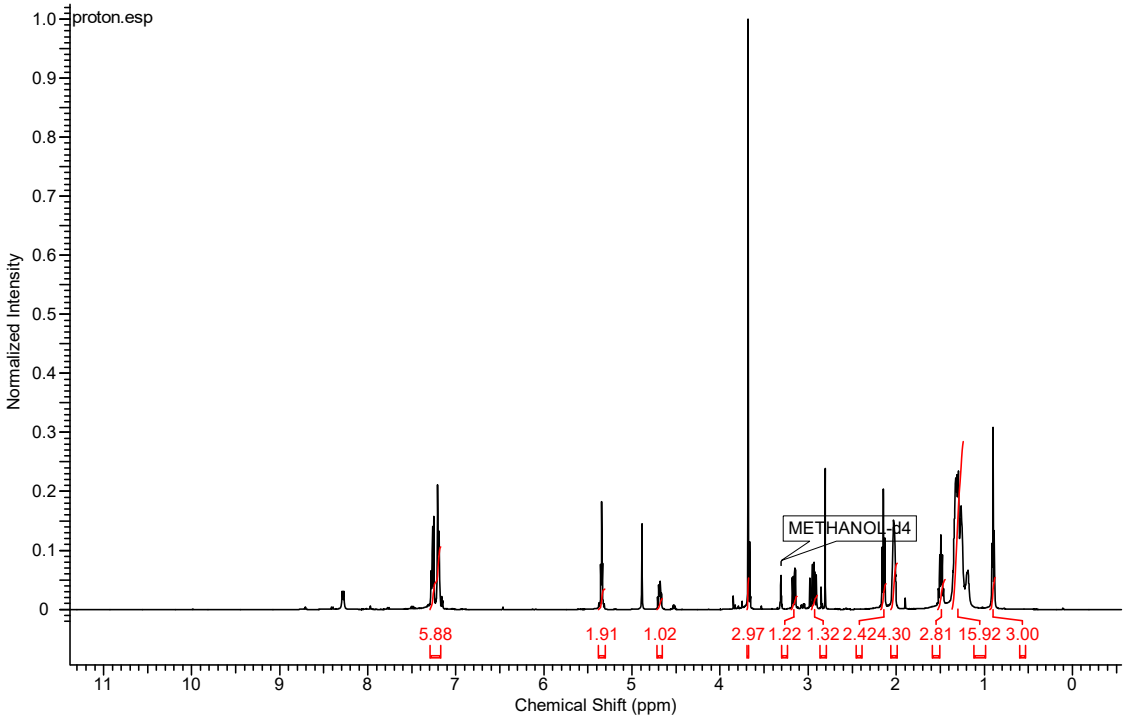

Figure S47. ^{13}C NMR spectrum for compound *ent*-3OMe in CD_3OD

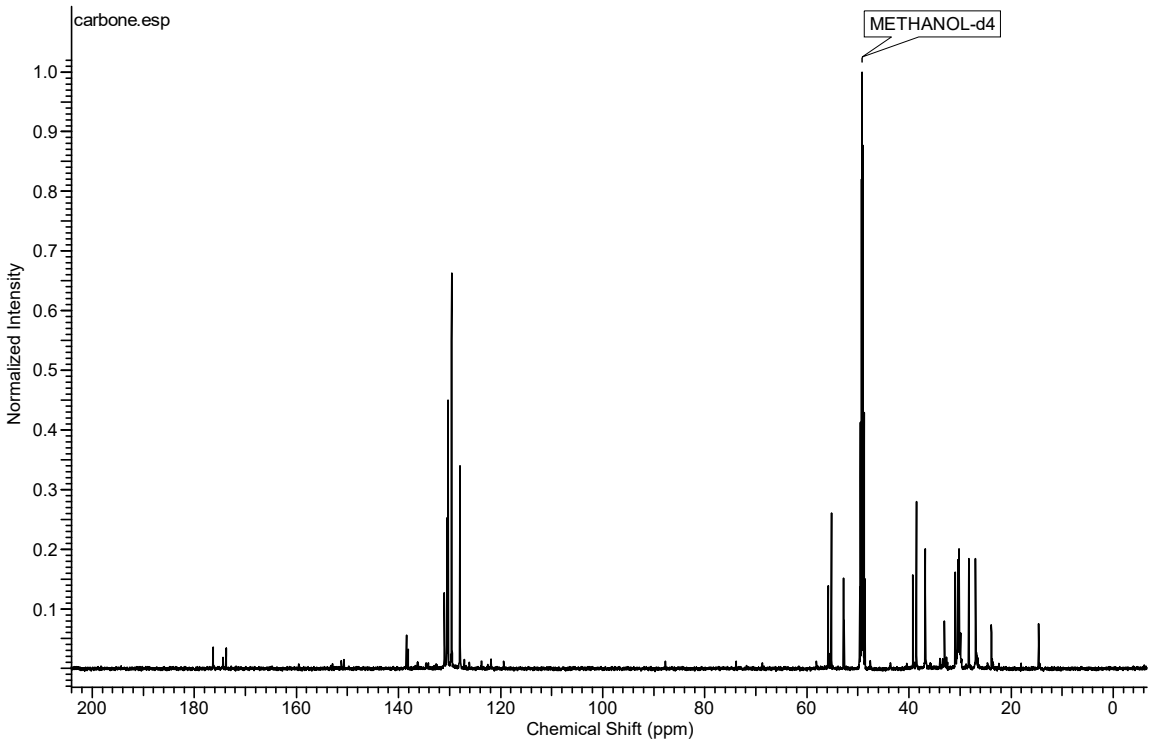

Figure S48. HRMS of compound *ent*-3OMe in MeOH

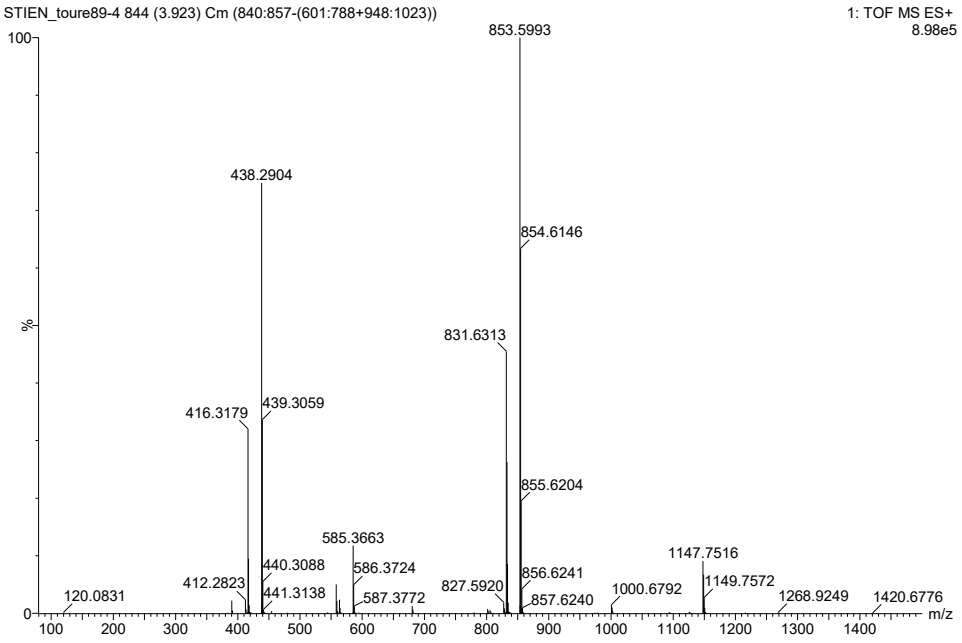

Figure S49. ^{1}H NMR spectrum for compound 12 in CD_3OD

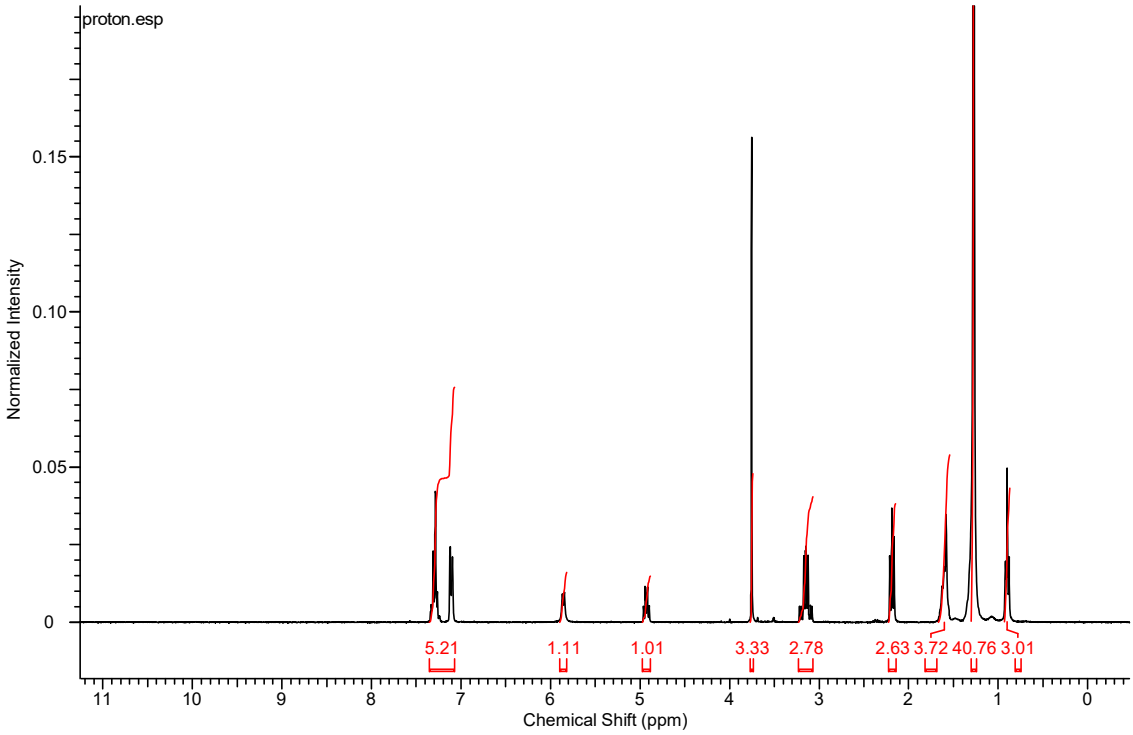

Figure S50. ^{13}C NMR spectrum for compound 12 in CD_3OD

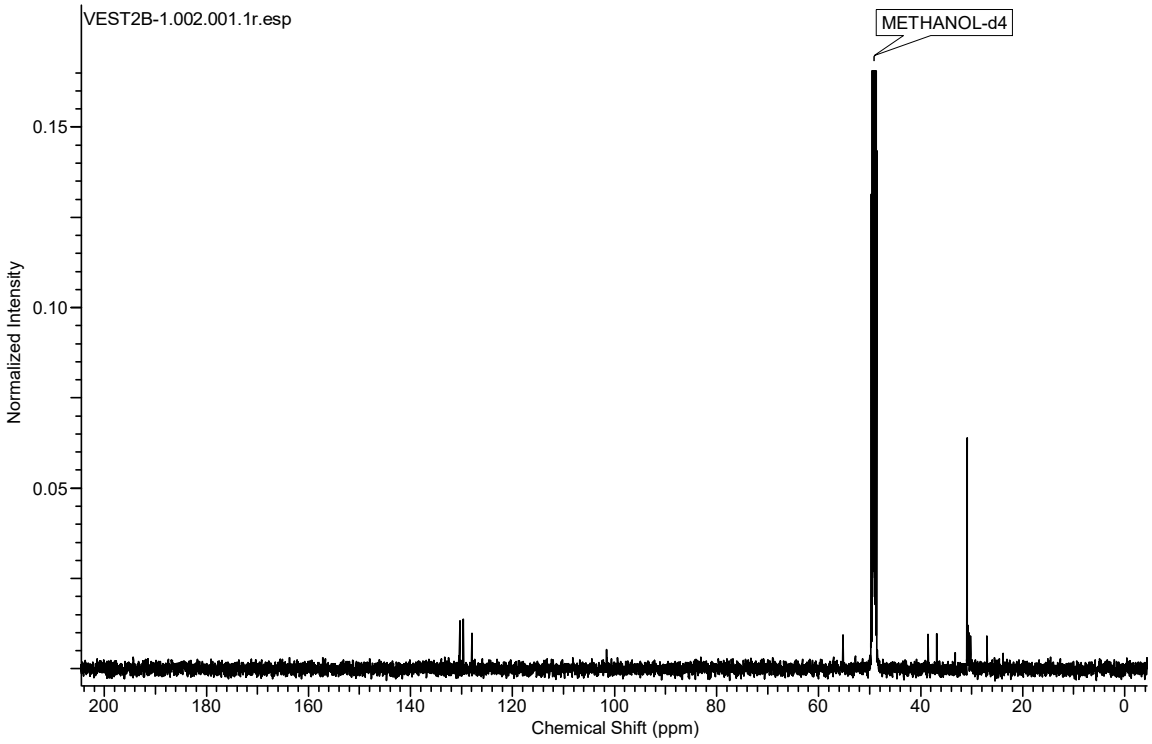

Figure S51. HRMS of compound 12 in MeOH

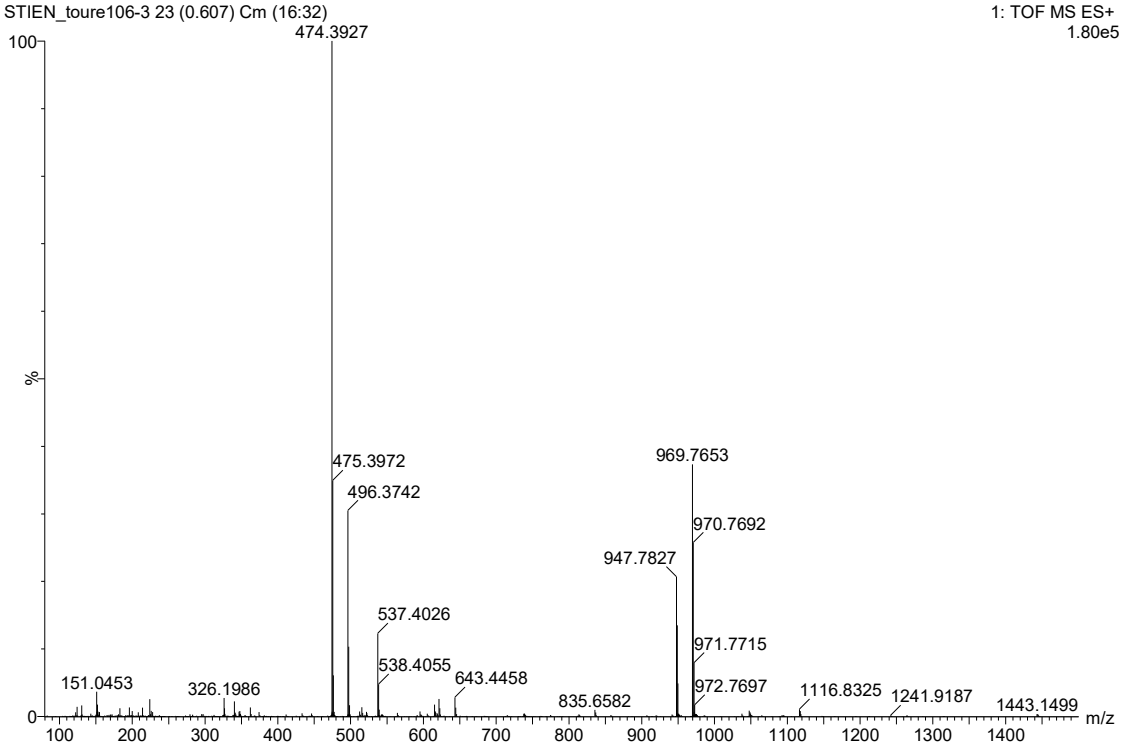

Figure S52. 1H NMR spectrum for compound 13 in CD_3OD

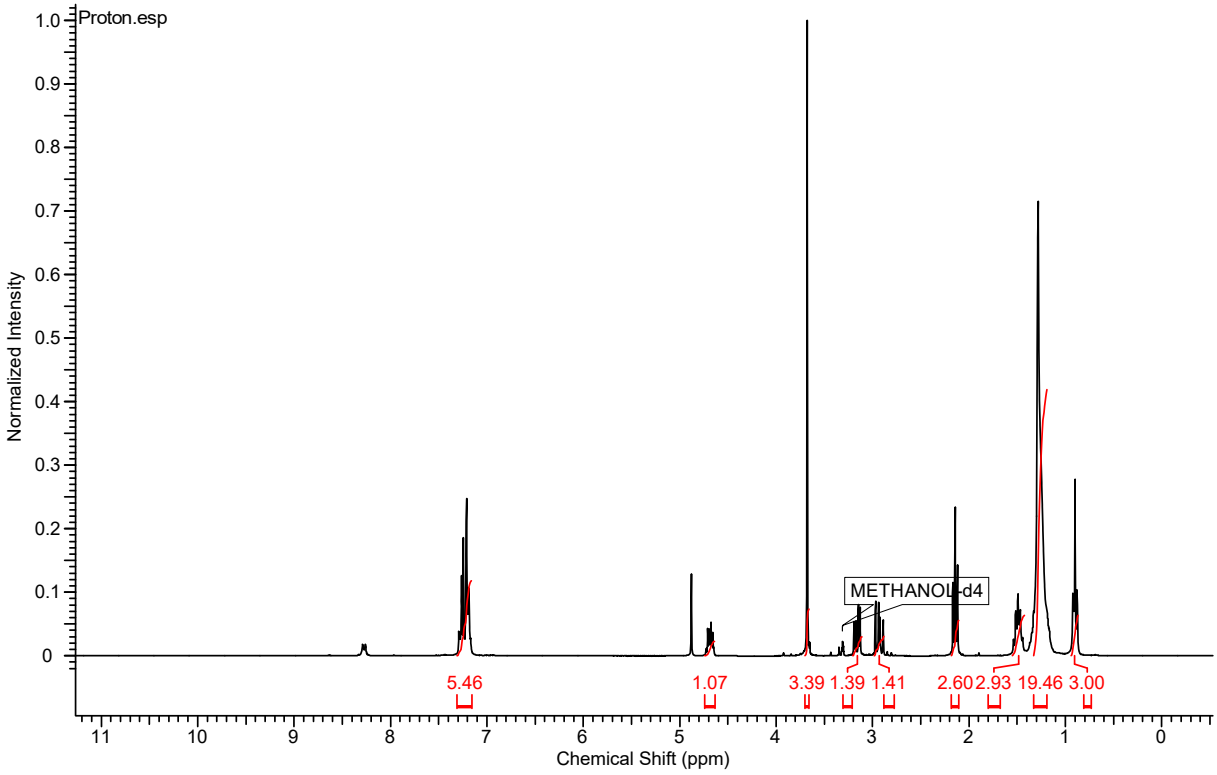

Figure S53. ^{13}C NMR spectrum for compound 13 in CD_3OD

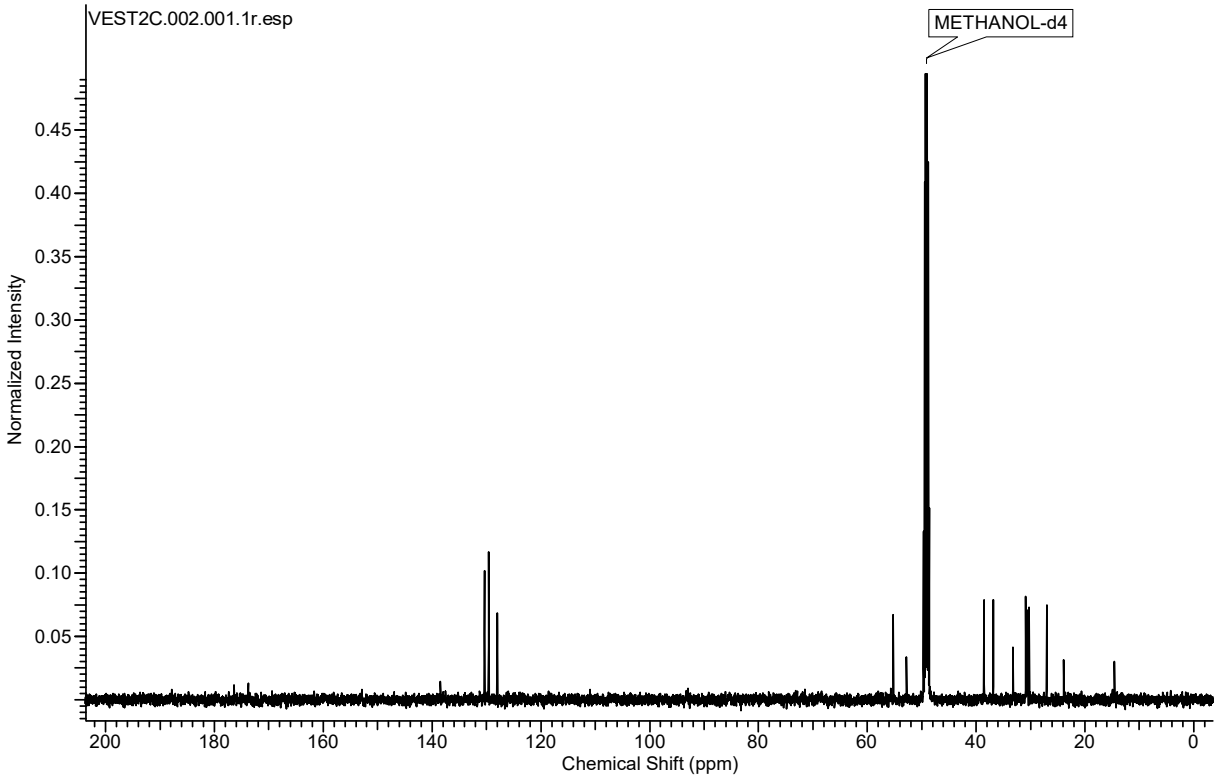

Figure S54. HRMS of compound 13 in MeOH

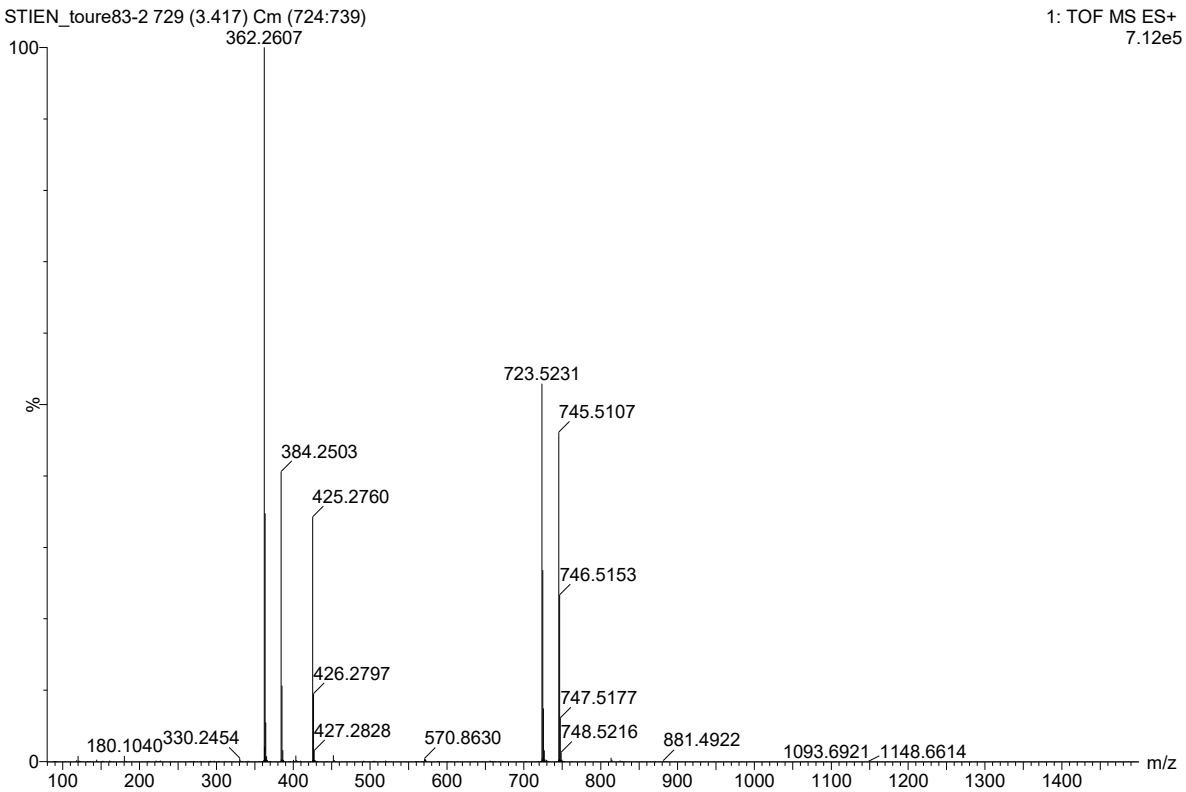

Figure S55. 1H NMR spectrum for compound 14 in CD_3OD

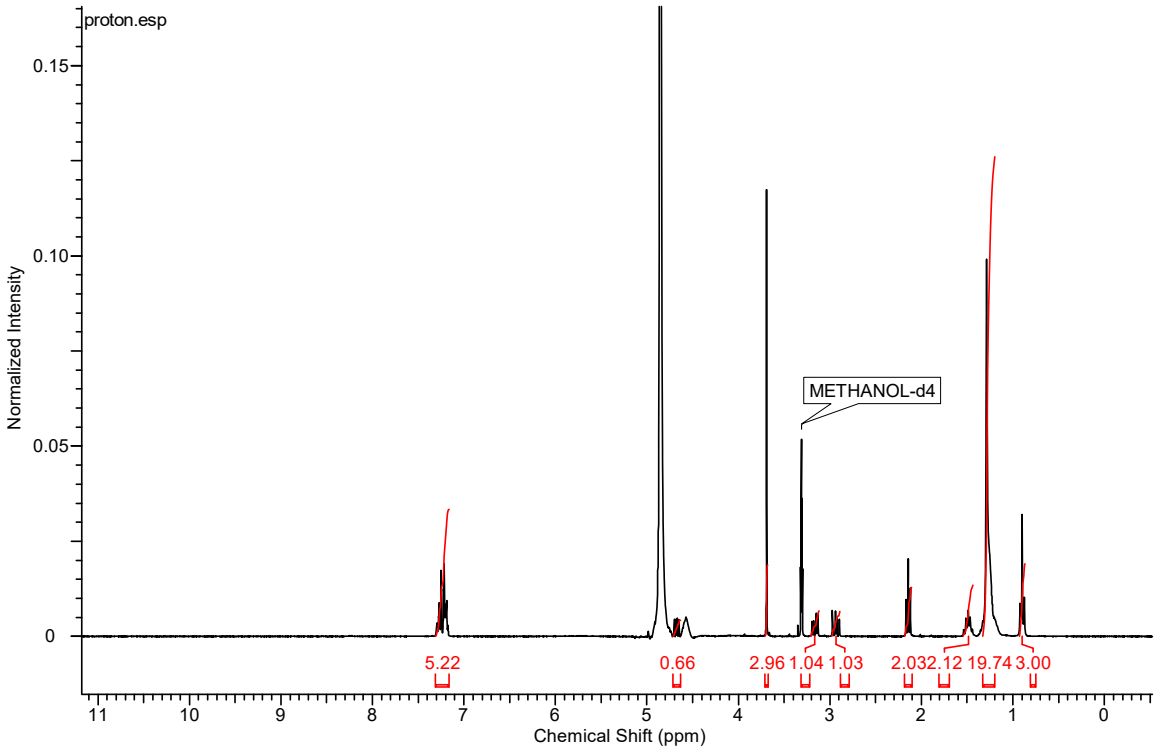

Figure S56. 13C NMR spectrum for compound 14 in CD3OD

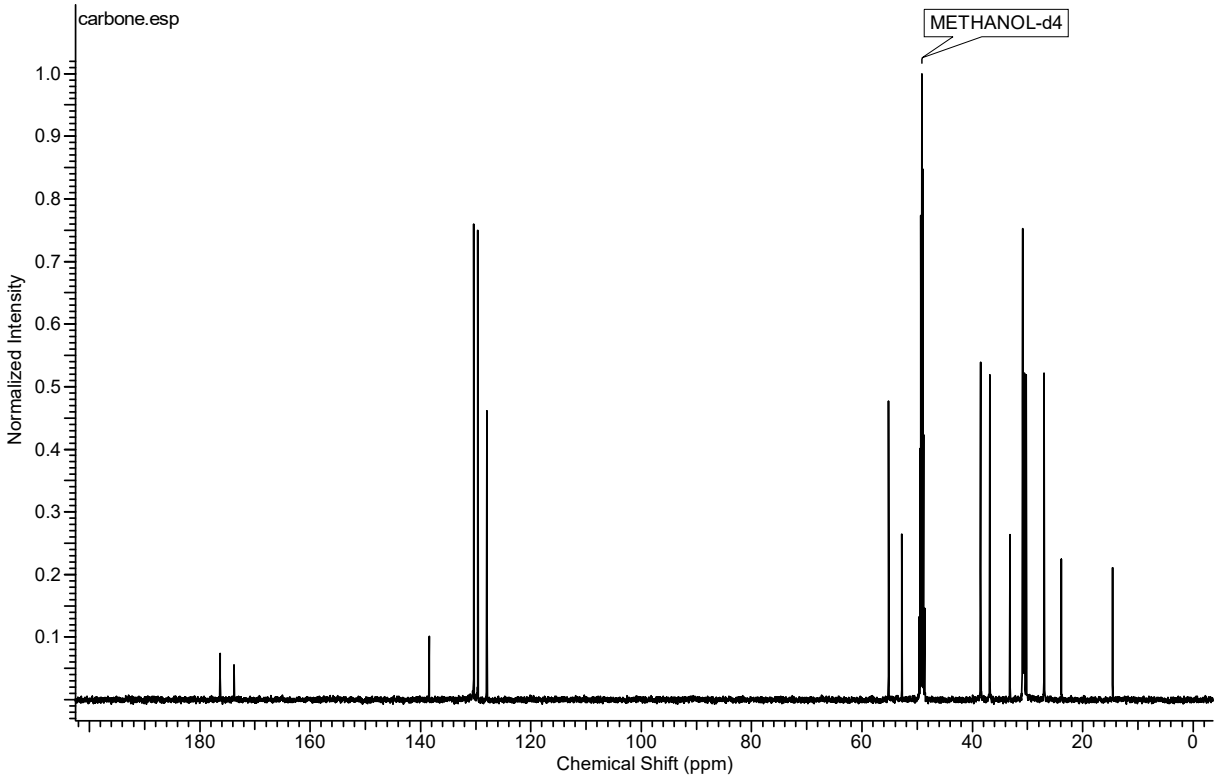

Figure S57. HRMS of compound 14 in MeOH

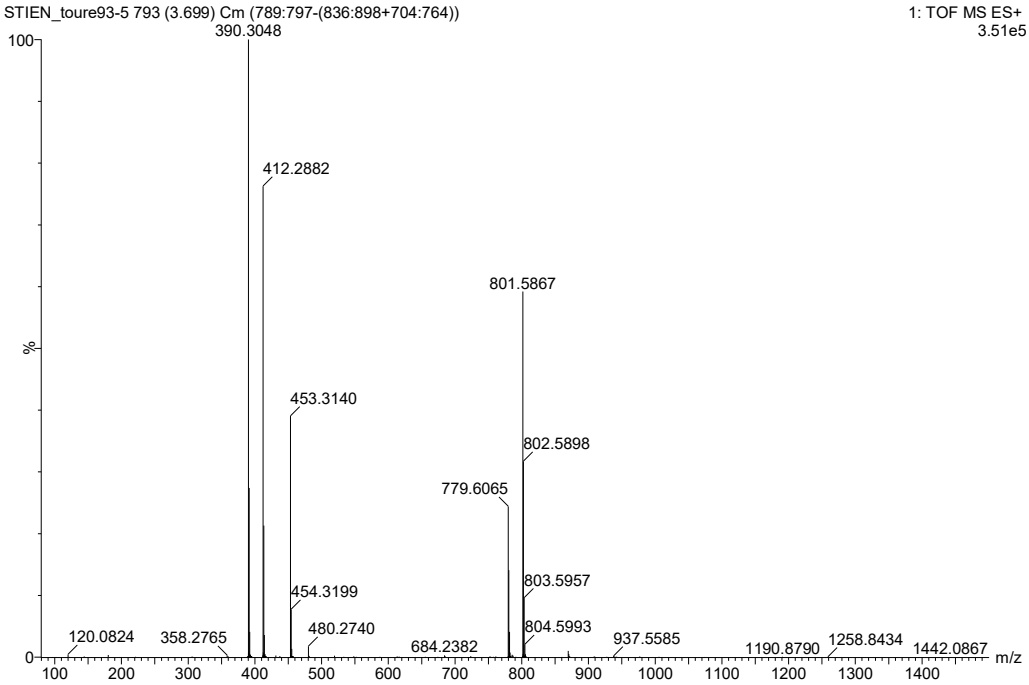

Figure S58. 1H NMR spectrum for compound 15 in CD_3OD

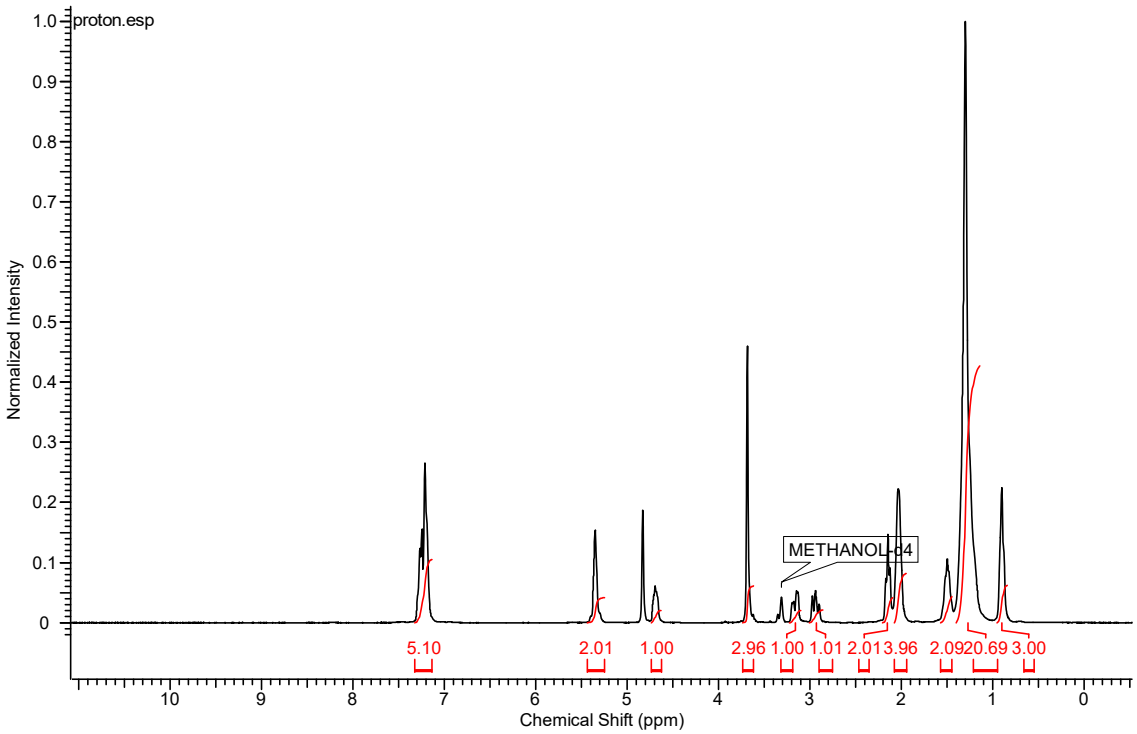

Figure S59. ^{13}C NMR spectrum for compound 15 in CD_3OD

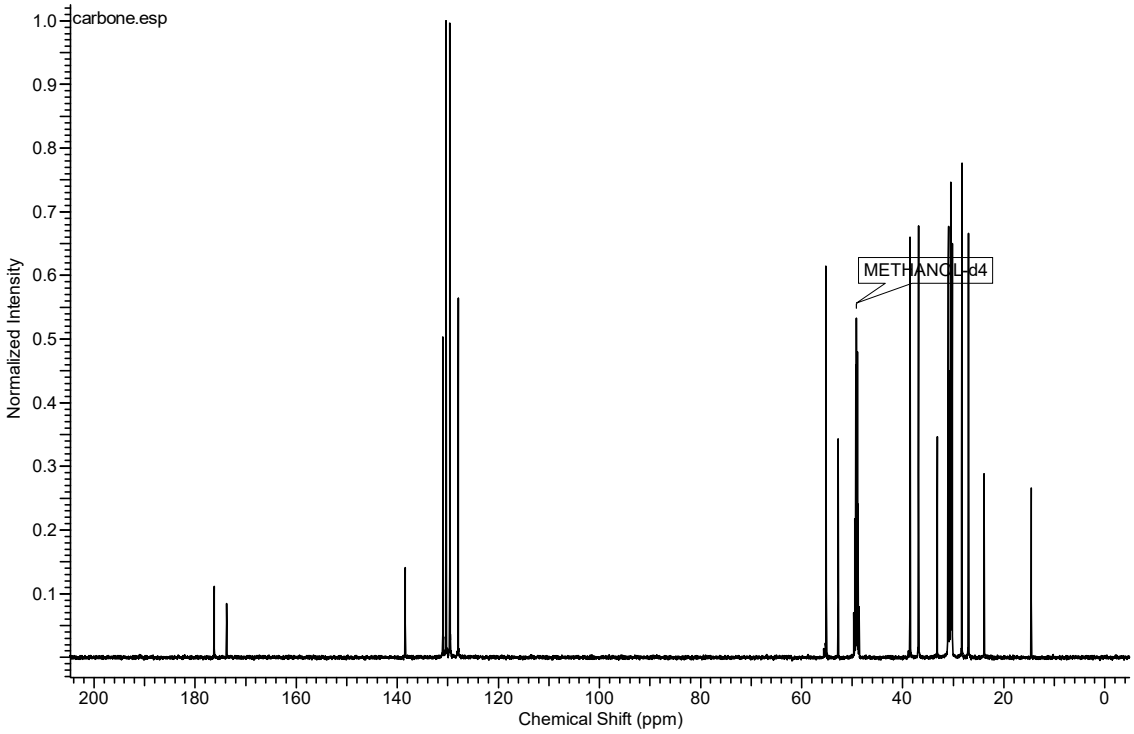

Figure S60. HRMS of compound 15 in MeOH

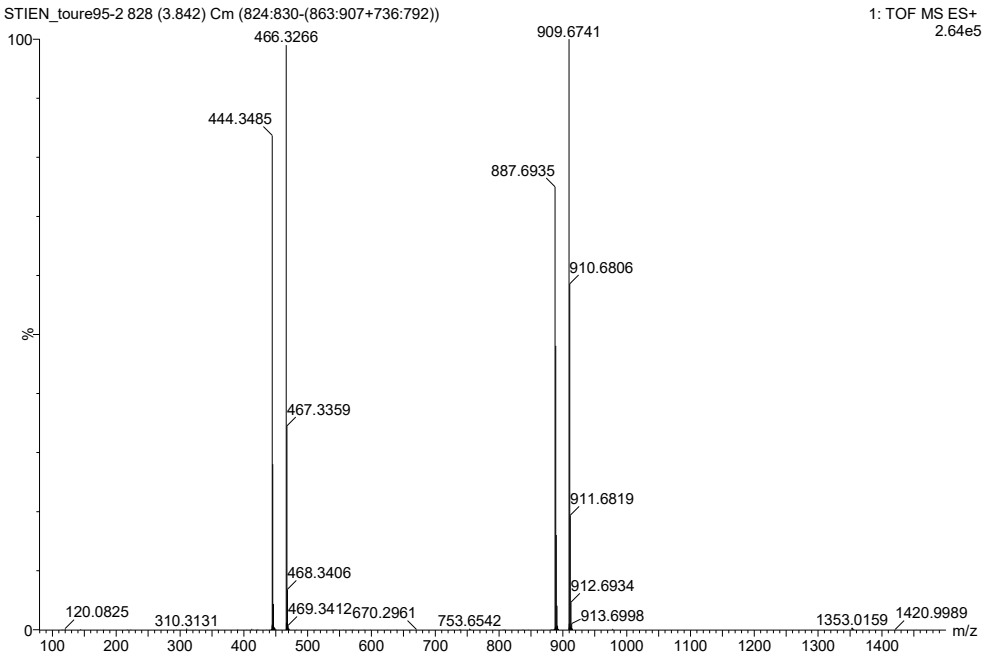

Figure S61. 1H NMR spectrum for compound 16 in CD_3OD

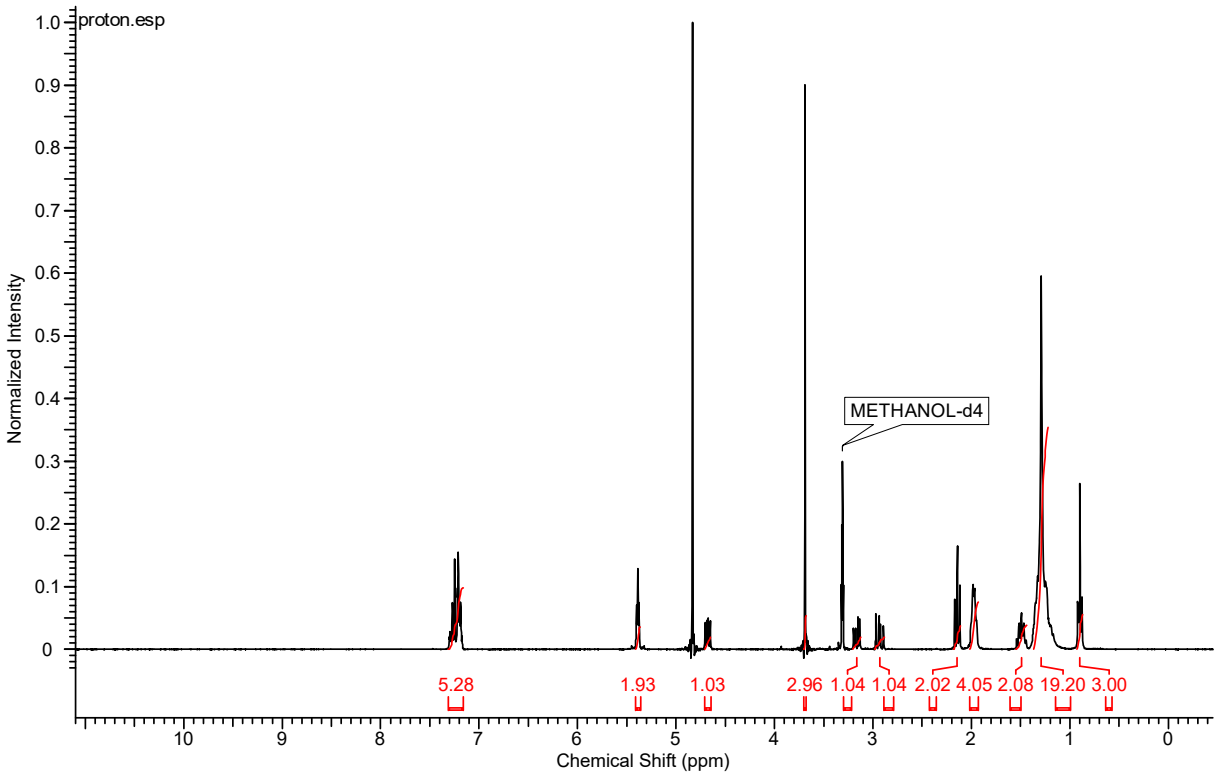

Figure S62. ^{13}C NMR spectrum for compound 16 in CD_3OD

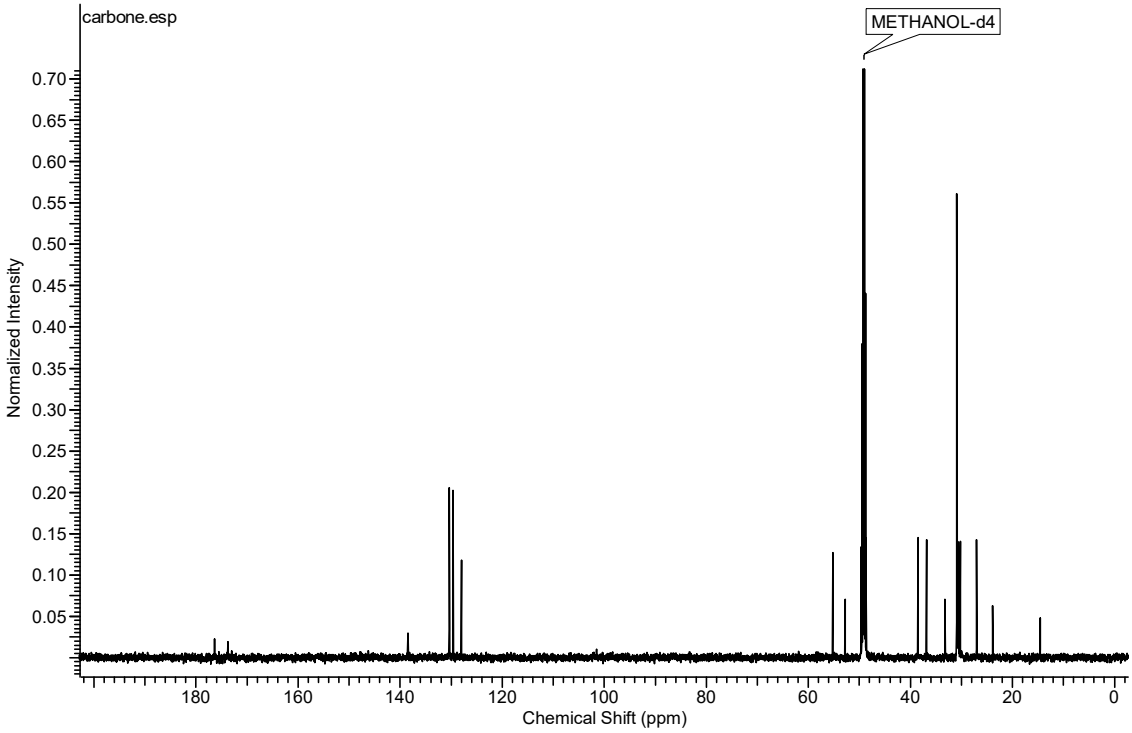

Figure S63. HRMS of compound 16 in MeOH

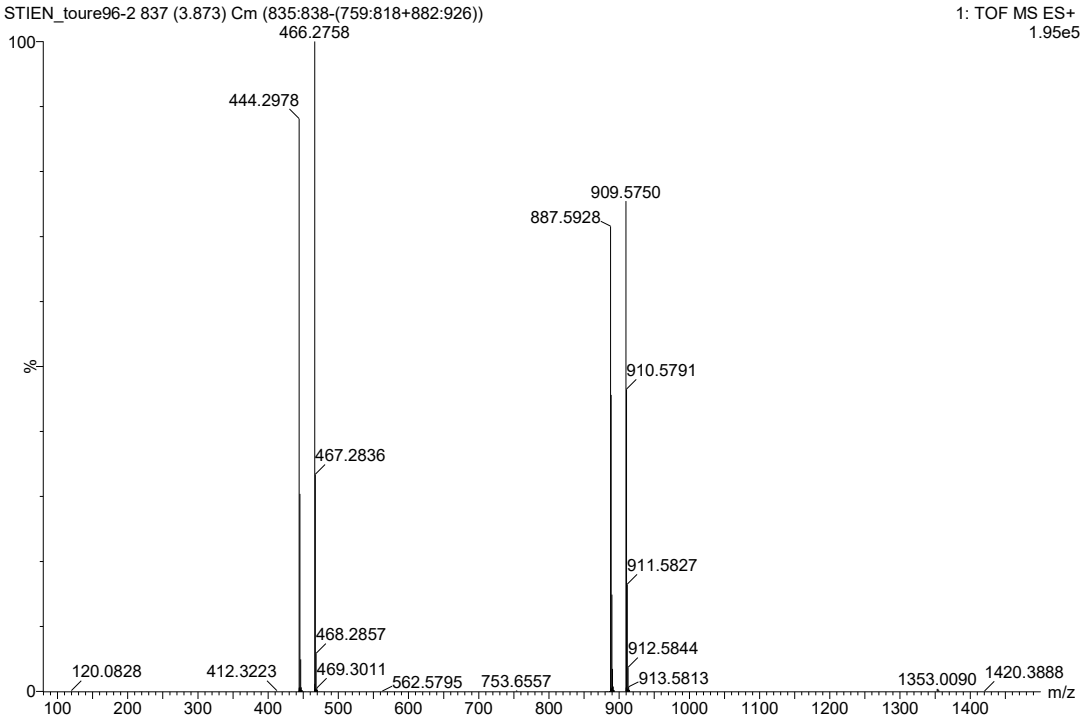

Figure S64. 1H NMR spectrum for compound 17 in CD_3OD

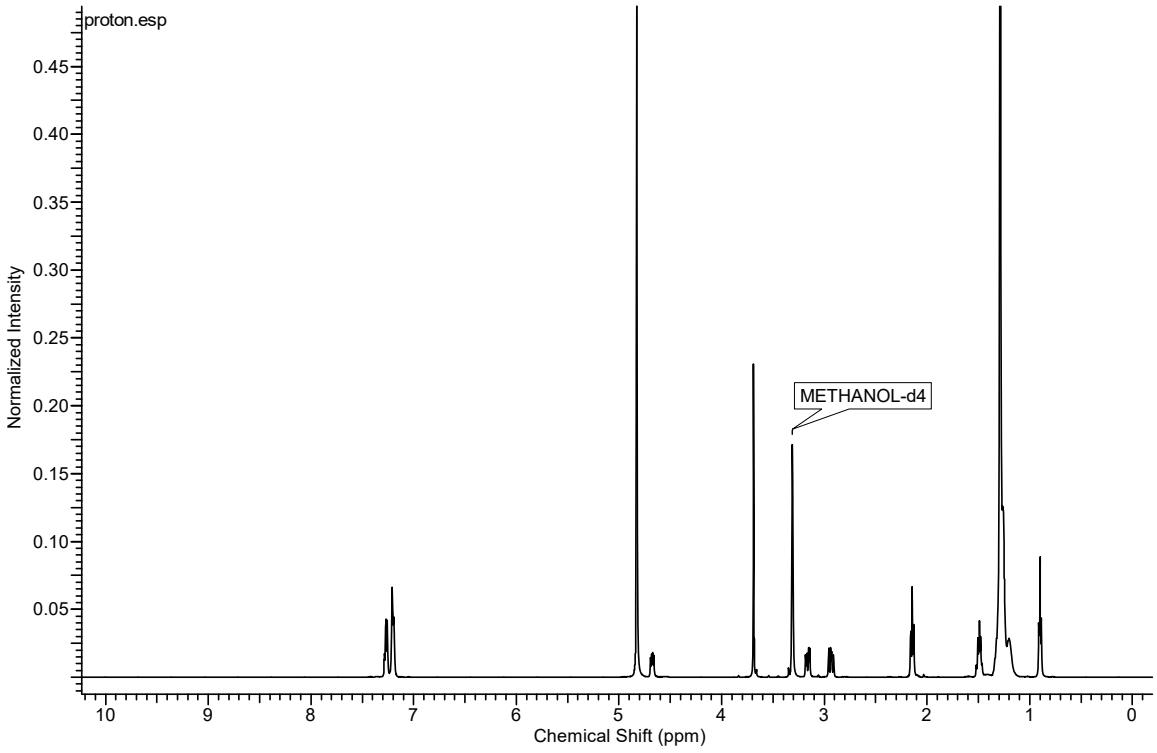

Figure S65. ^{13}C NMR spectrum for compound 17 in CD_3OD

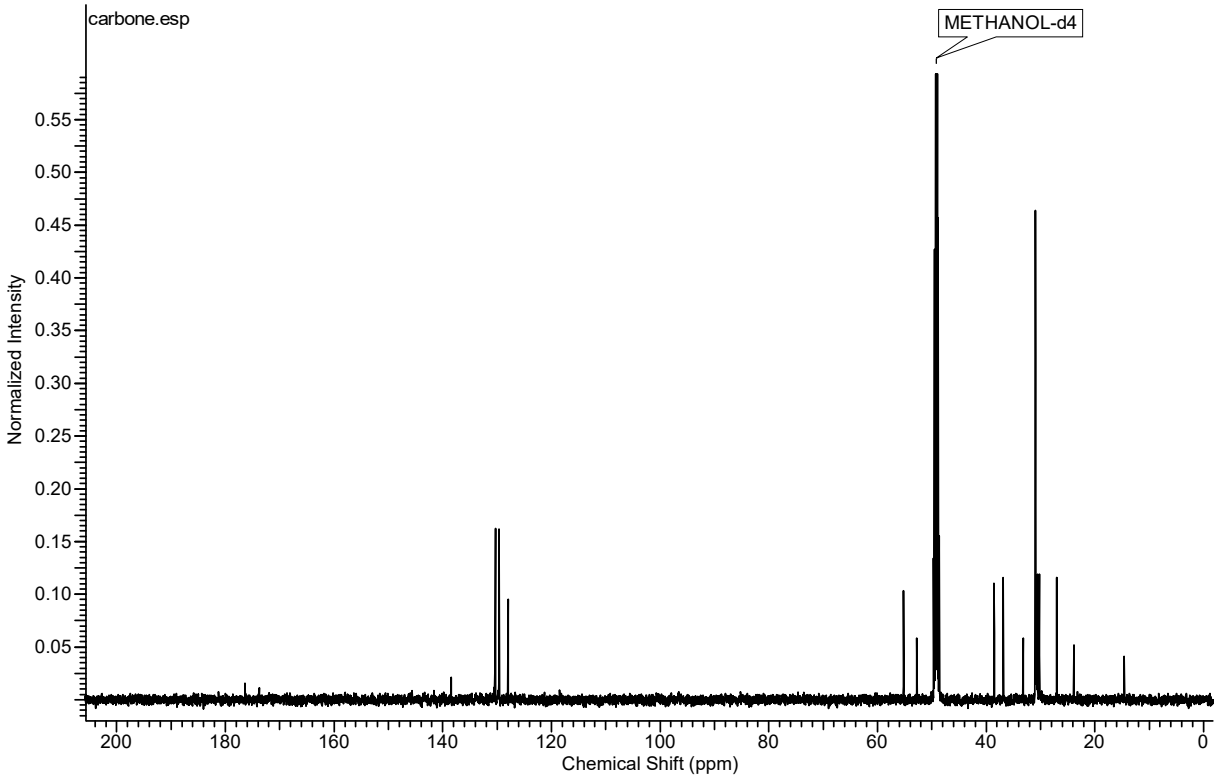

Figure S66. HRMS of compound 17 in MeOH

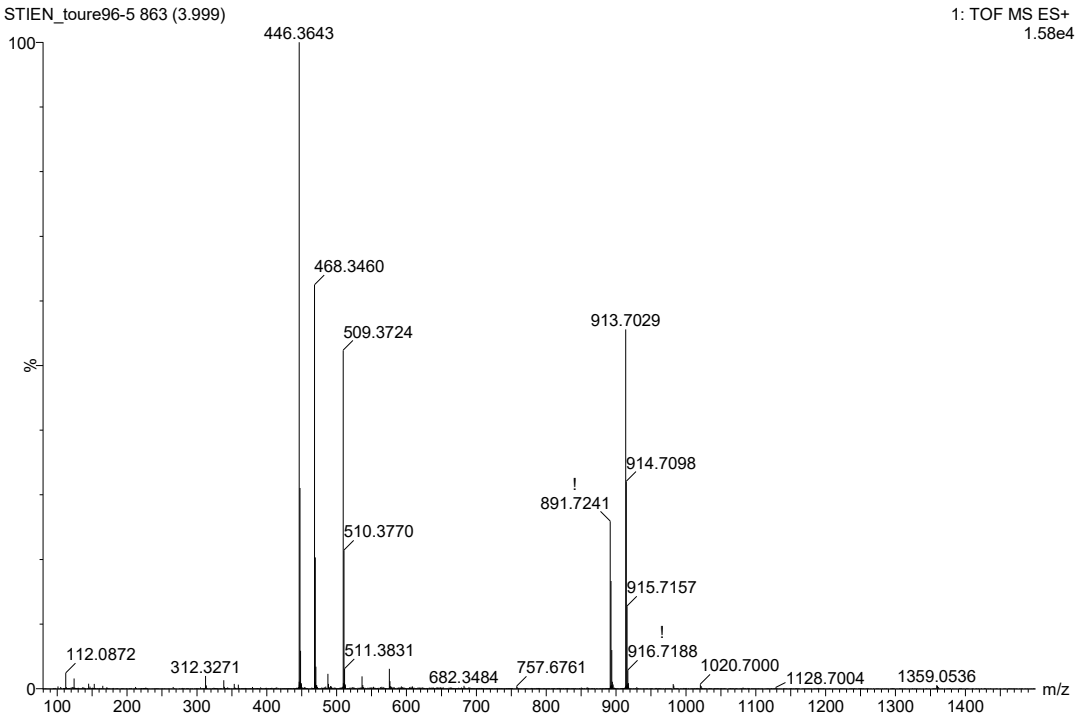

Figure S67. 1H NMR spectrum for compound 18 in CD_3OD

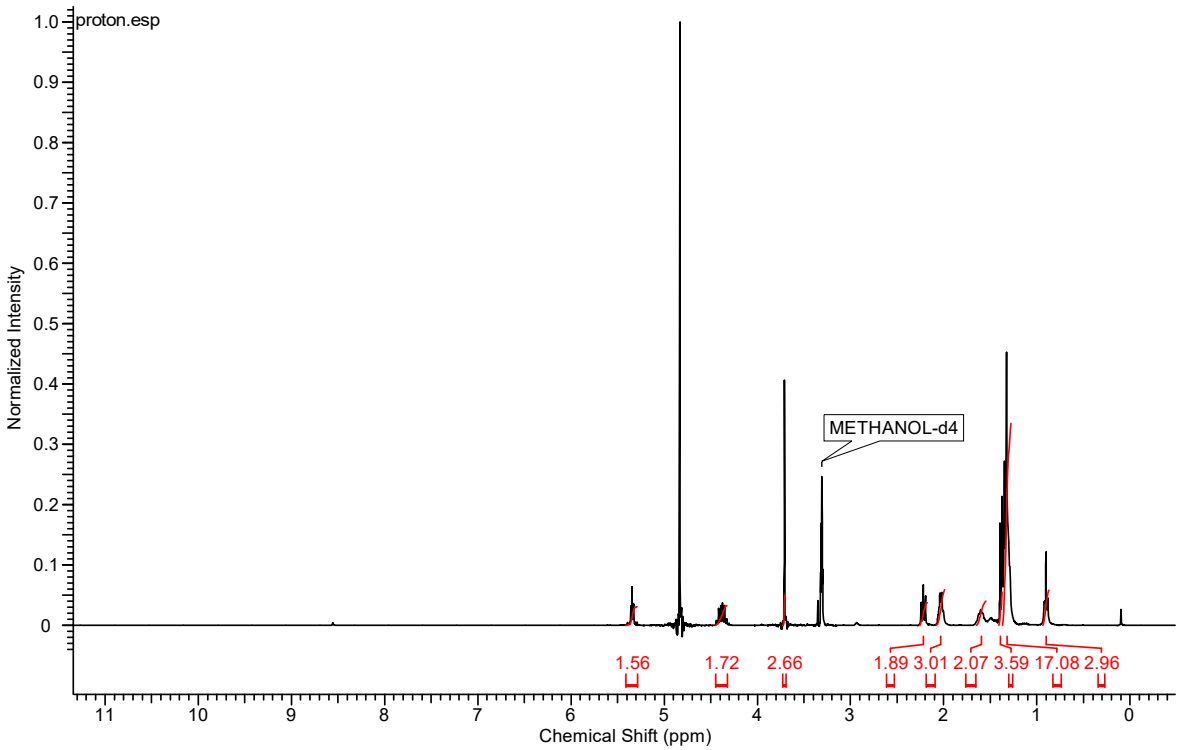

Figure S68. 13C NMR spectrum for compound 18 in CD3OD

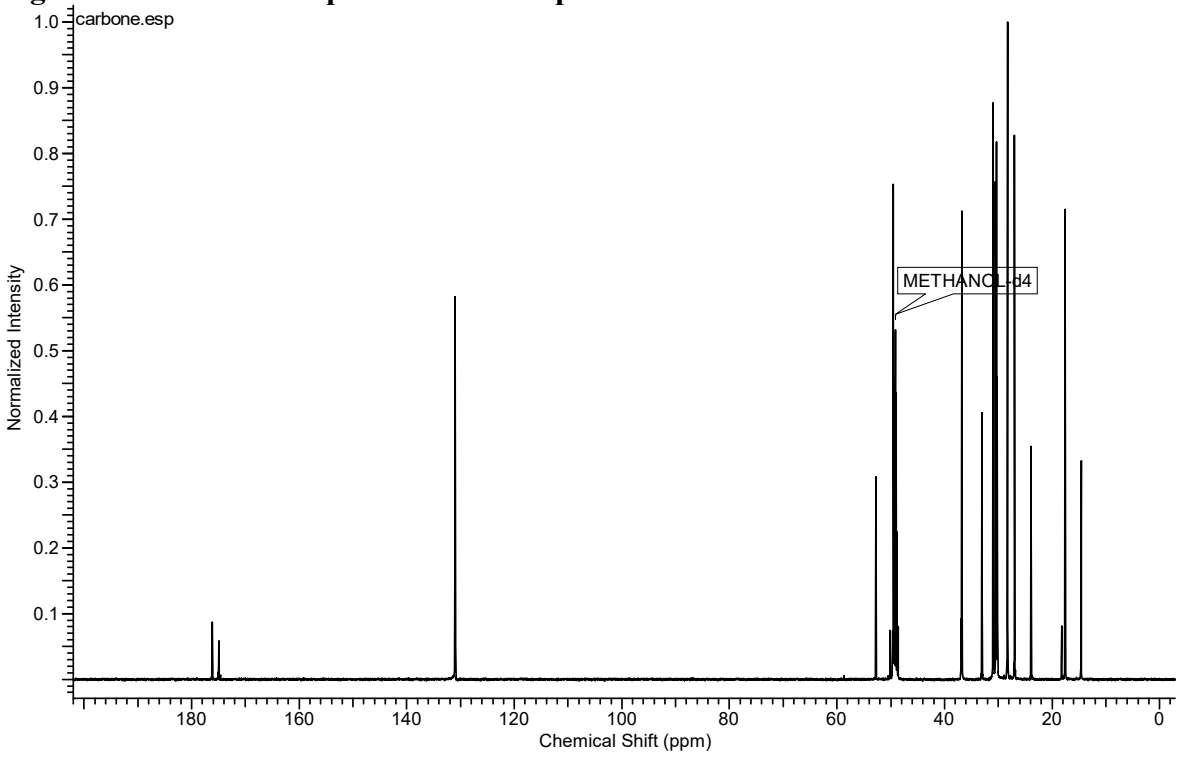

Figure S69. HRMS of compound 18 in MeOH

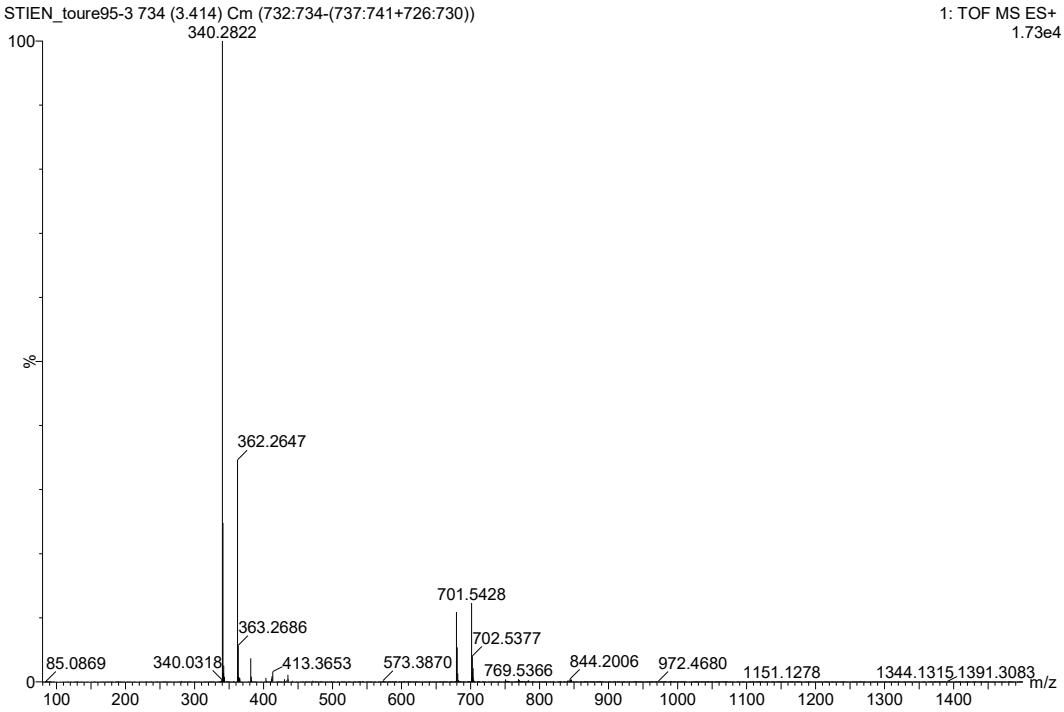

Figure S70. 1H NMR spectrum for compound 19 in CD_3OD

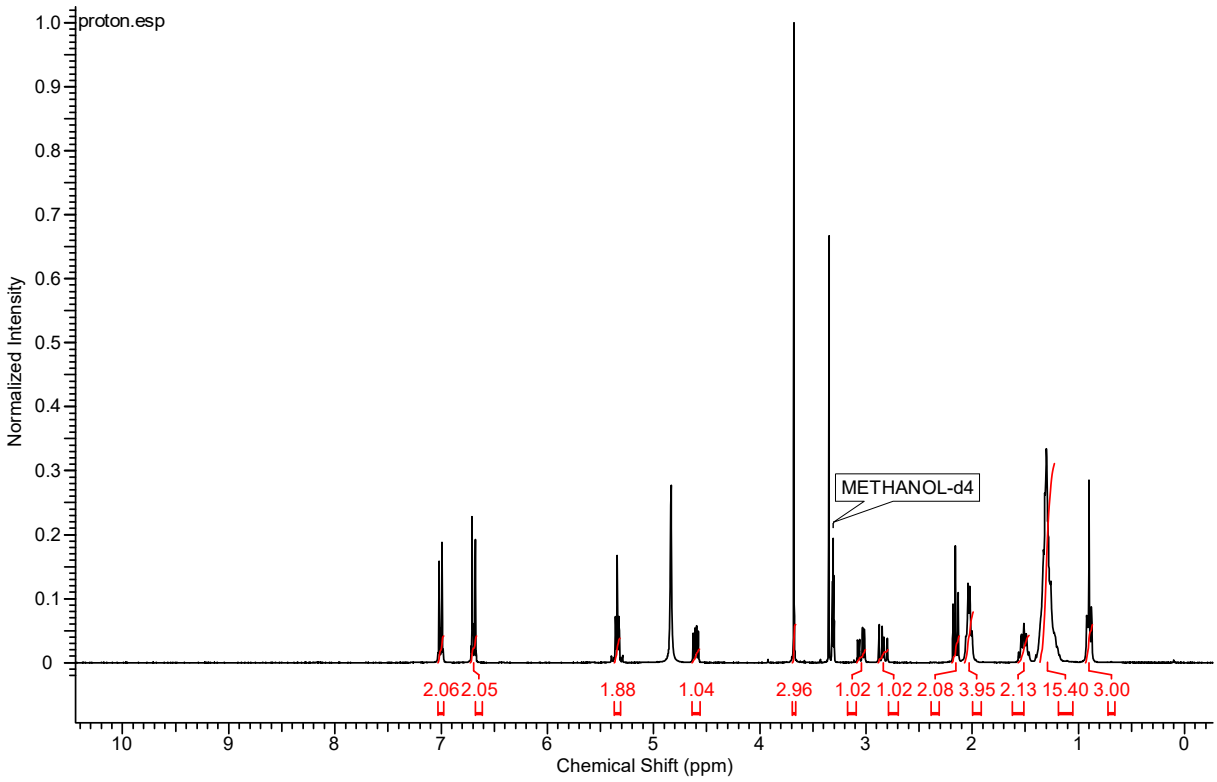

Figure S71. 13C NMR spectrum for compound 19 in CD3OD

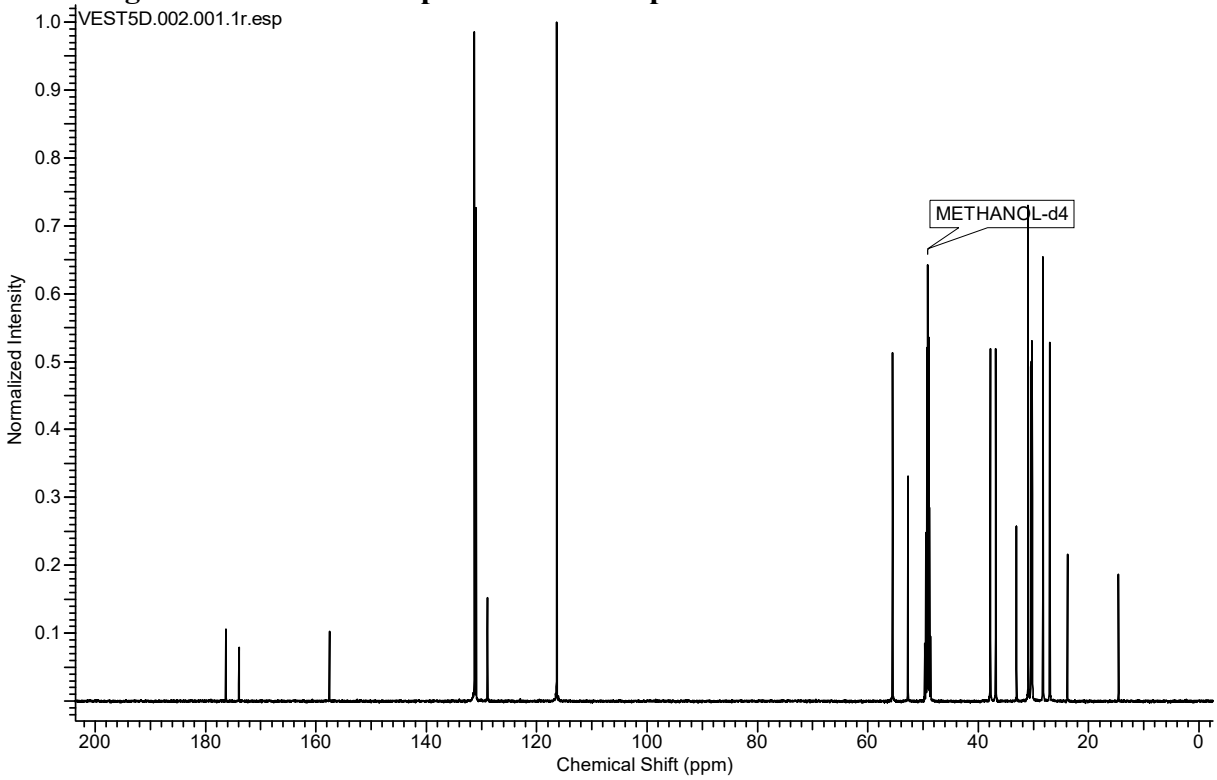

Figure S72. HRMS of compound 19 in MeOH

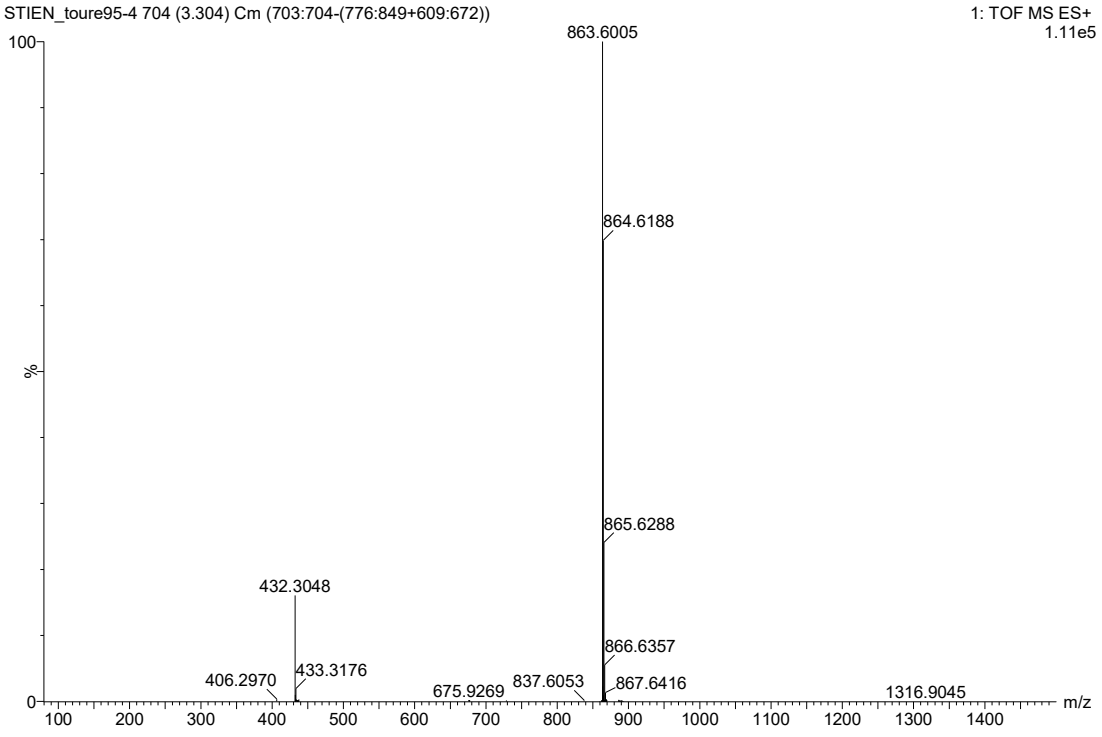

Figure S73. 1H NMR spectrum for compound 20 in CD_3OD

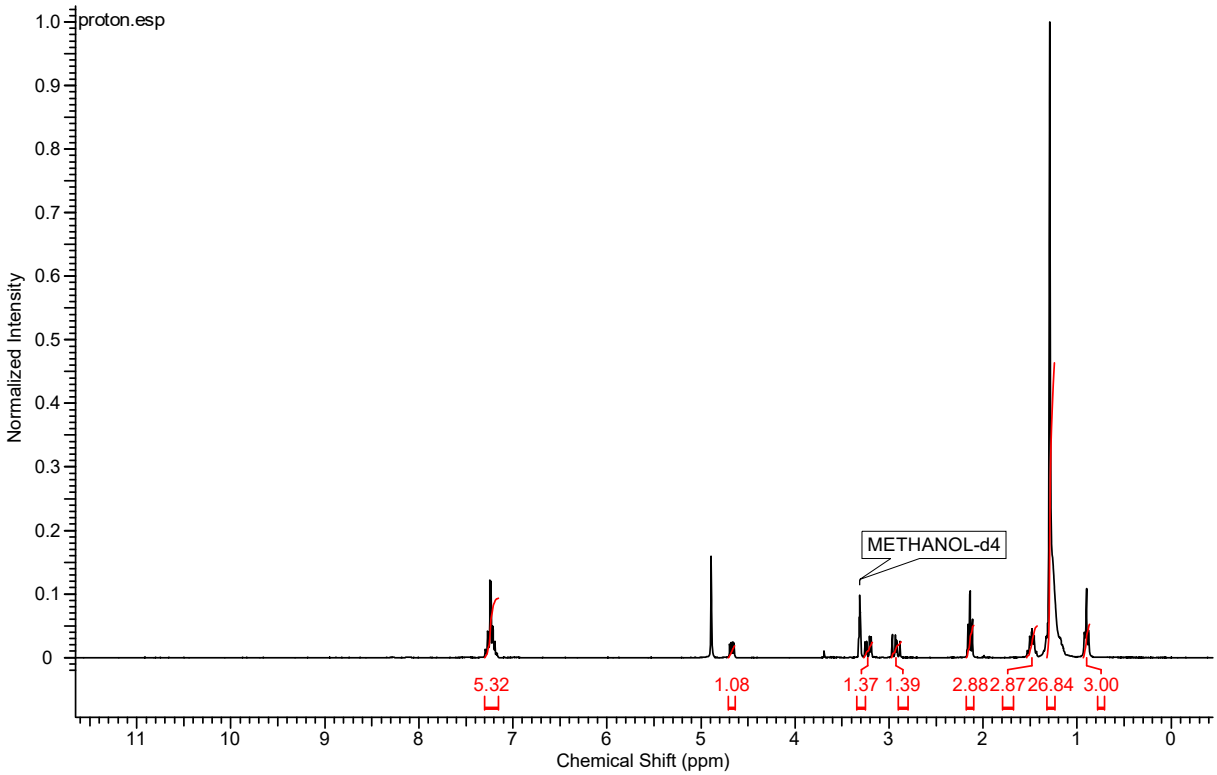

Figure S74. 13C NMR spectrum for compound 20 in CD3OD

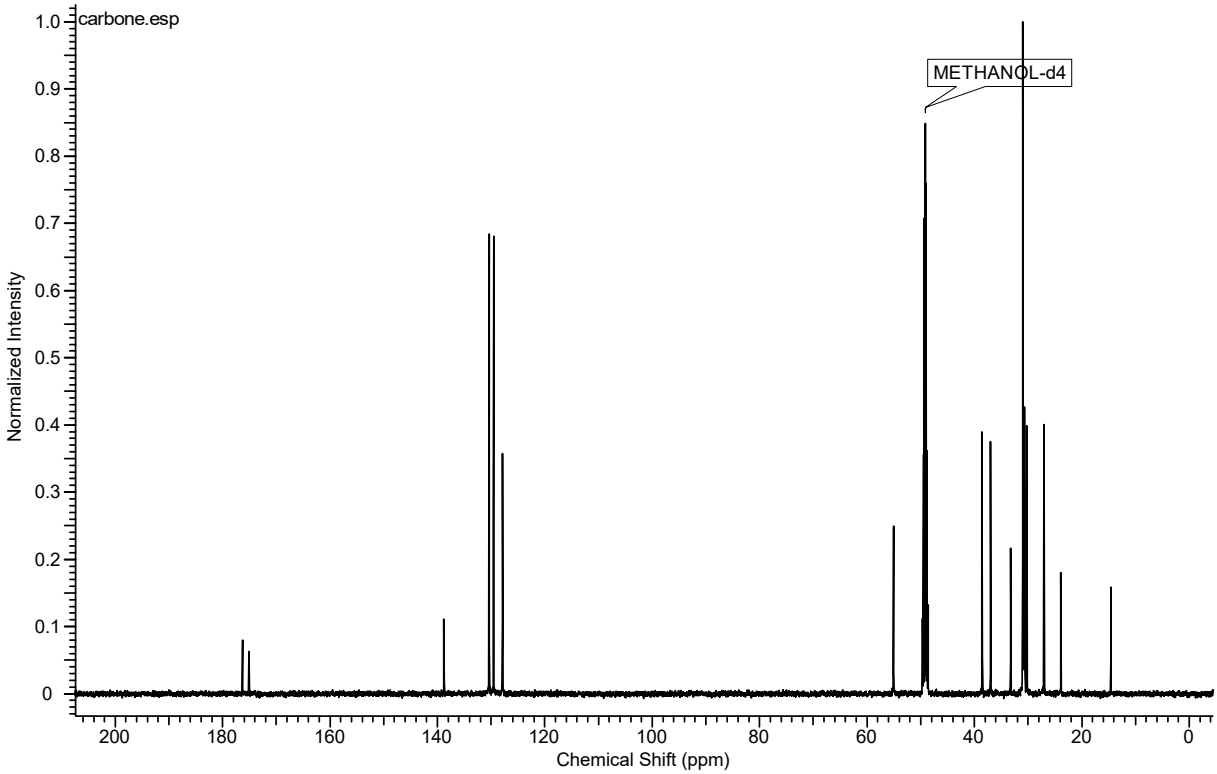

Figure S75. HRMS of compound 20 in MeOH

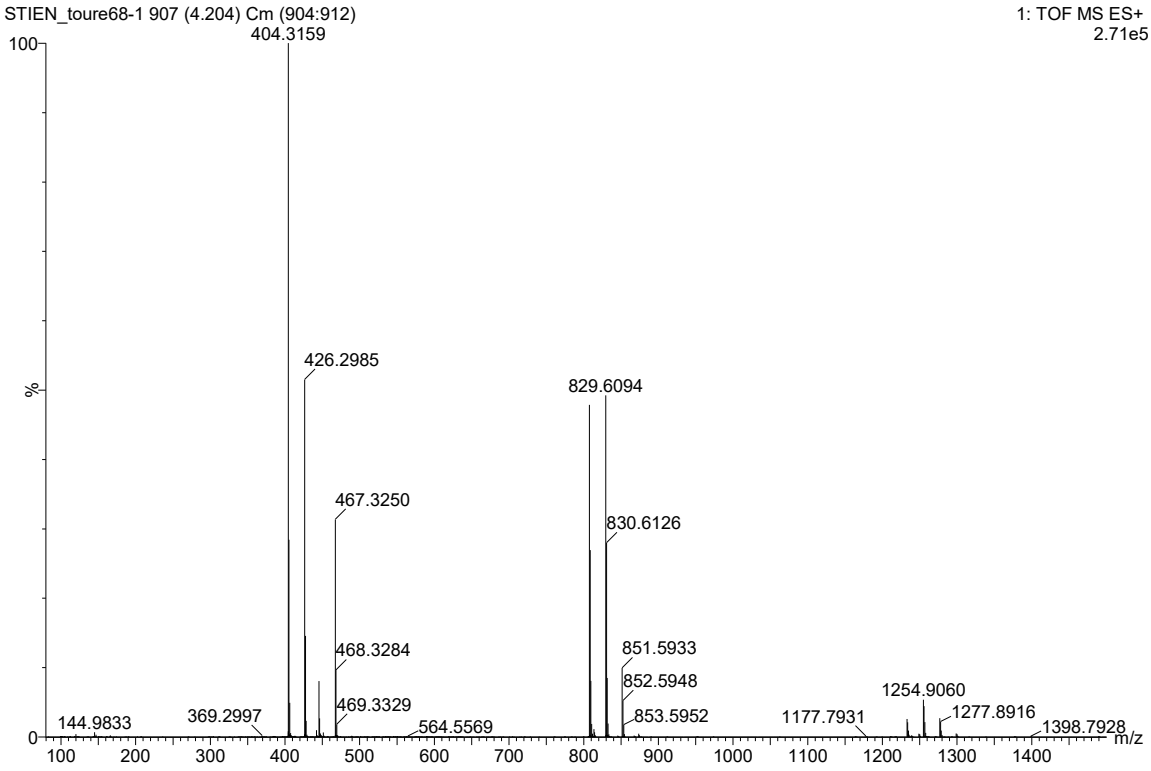

Figure S76. 1H NMR spectrum for compound 3 in CD_3OD

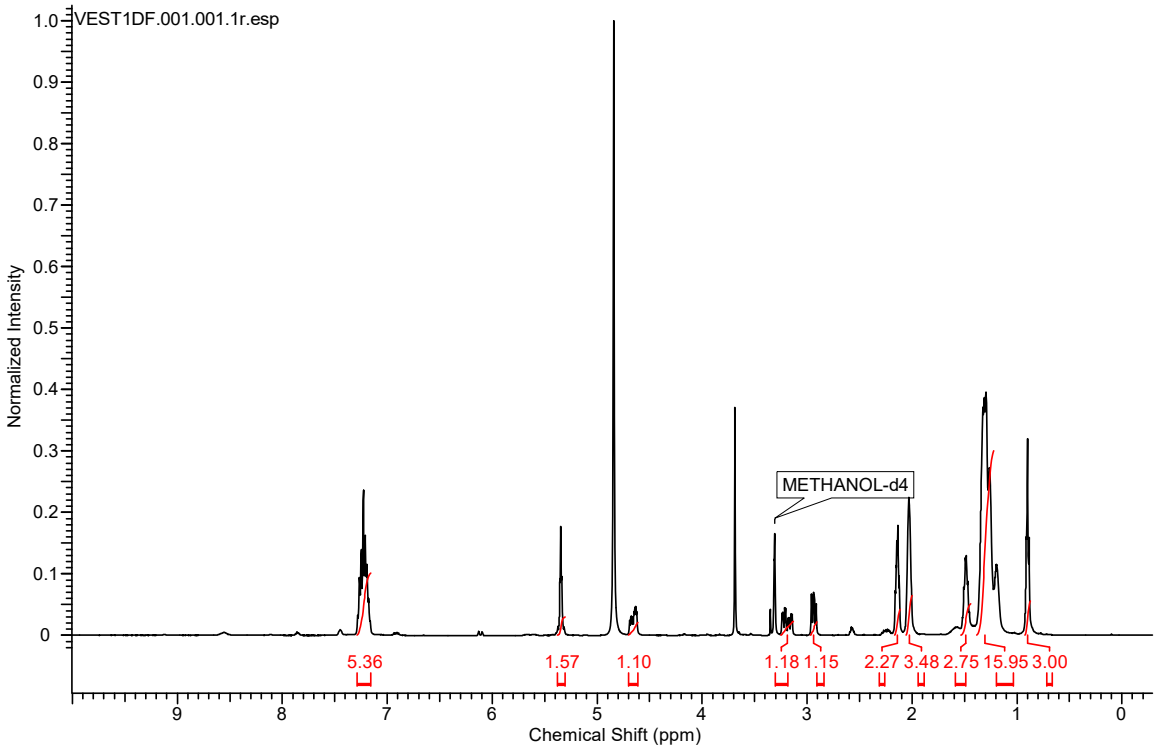

Figure S77. 13C NMR spectrum for compound 3 in CD3OD

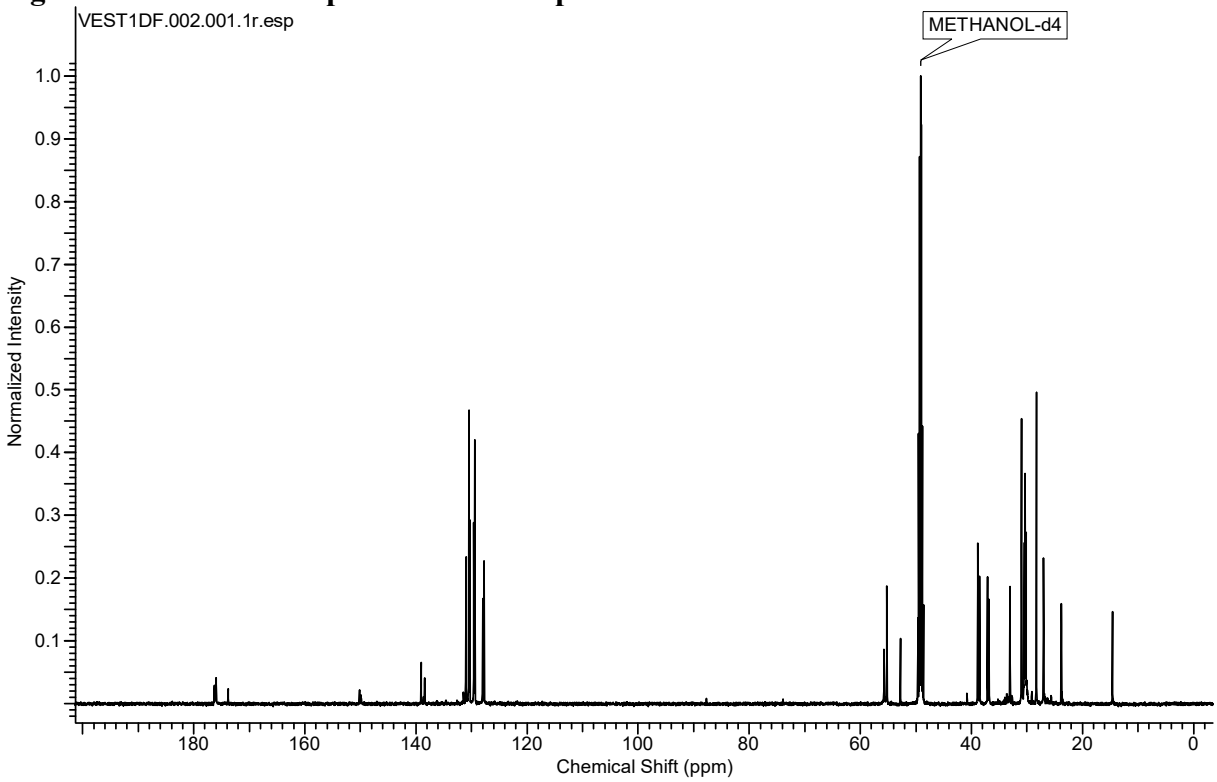

Figure S78. HRMS of compound 3 in MeOH

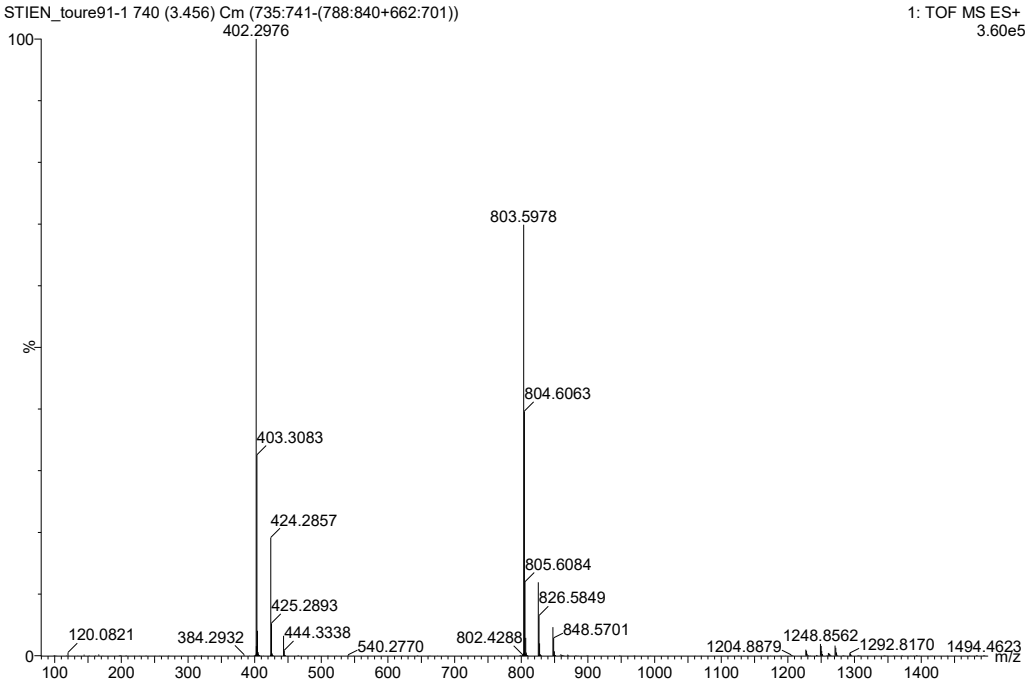

Figure S79. 1H NMR spectrum for compound 21 in CD_3OD

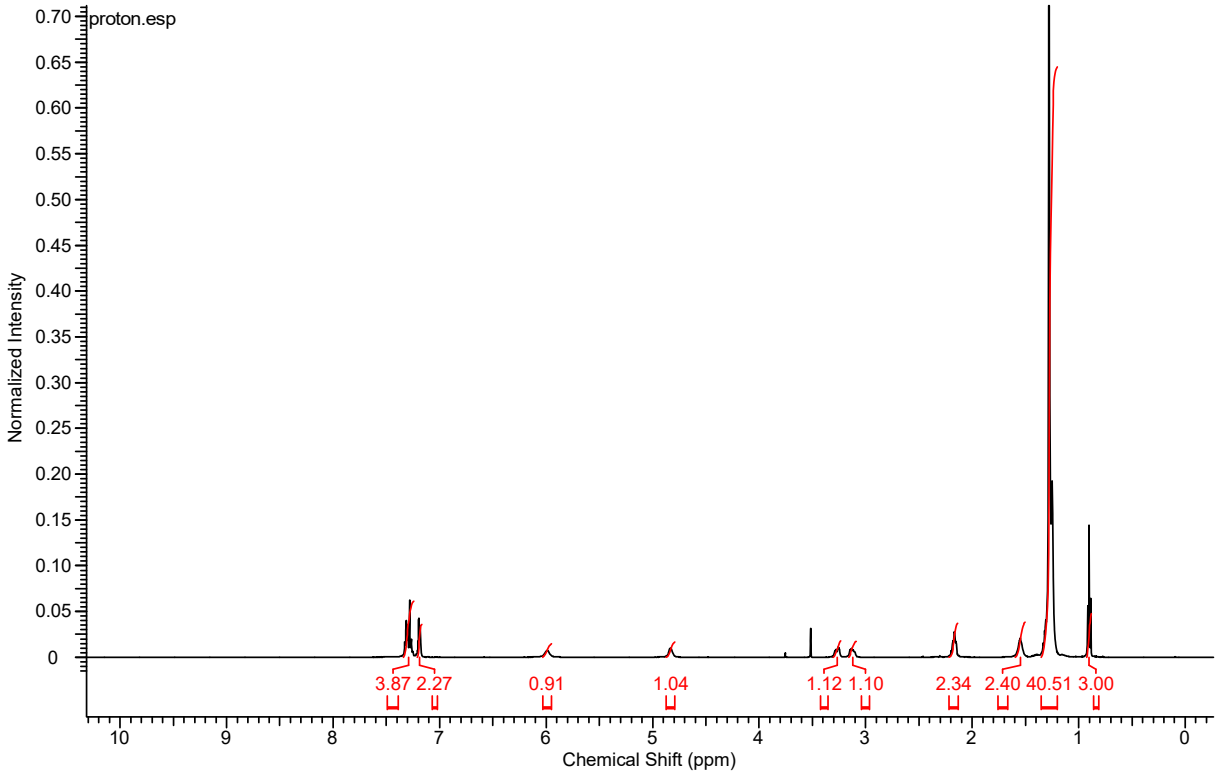

Figure S80. ^{13}C NMR spectrum for compound 21 in CD_3OD

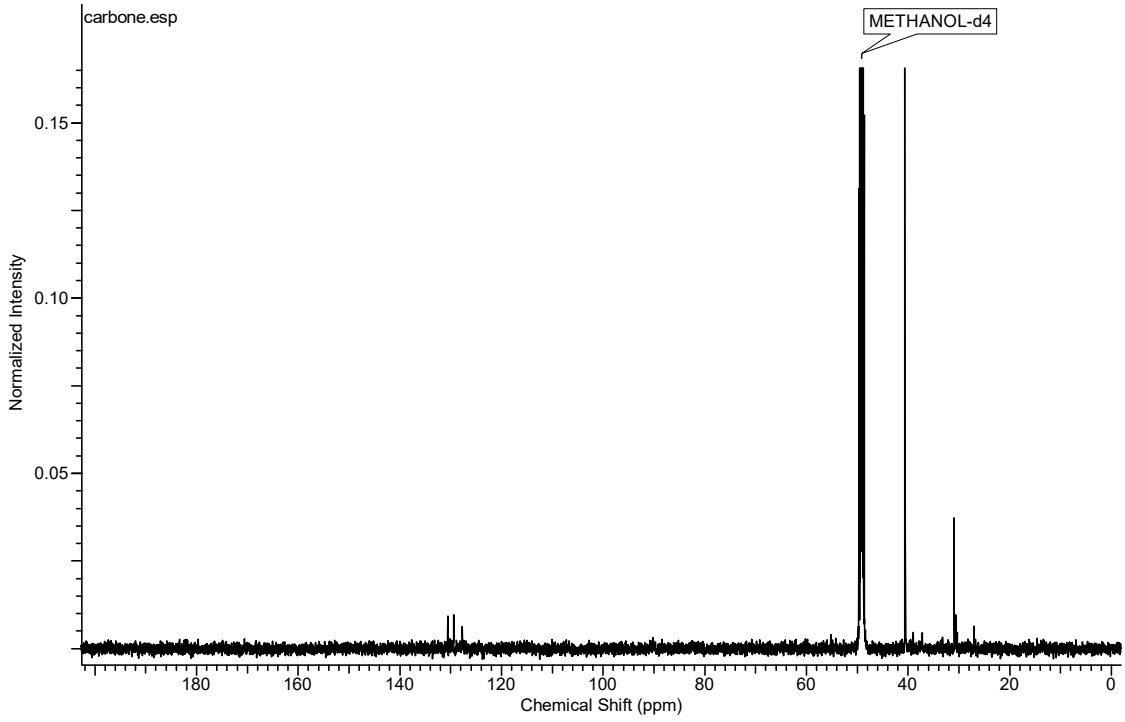

Figure S81. HRMS of compound 21 in MeOH

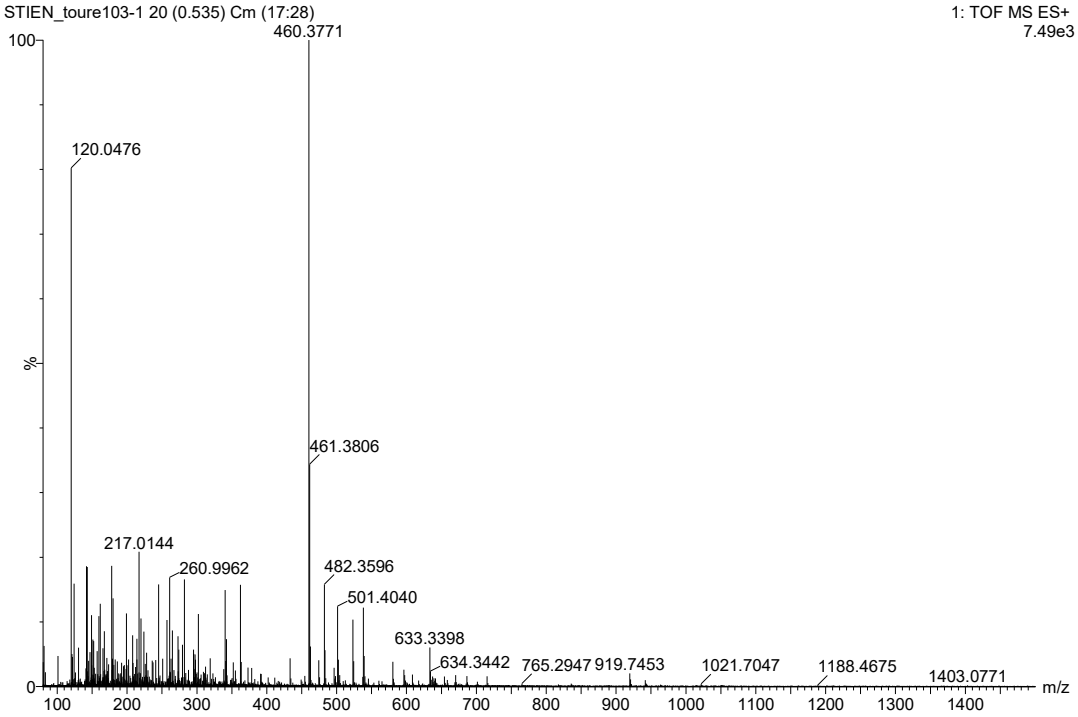

Figure S82. 1H NMR spectrum for compound 22 in CD_3OD

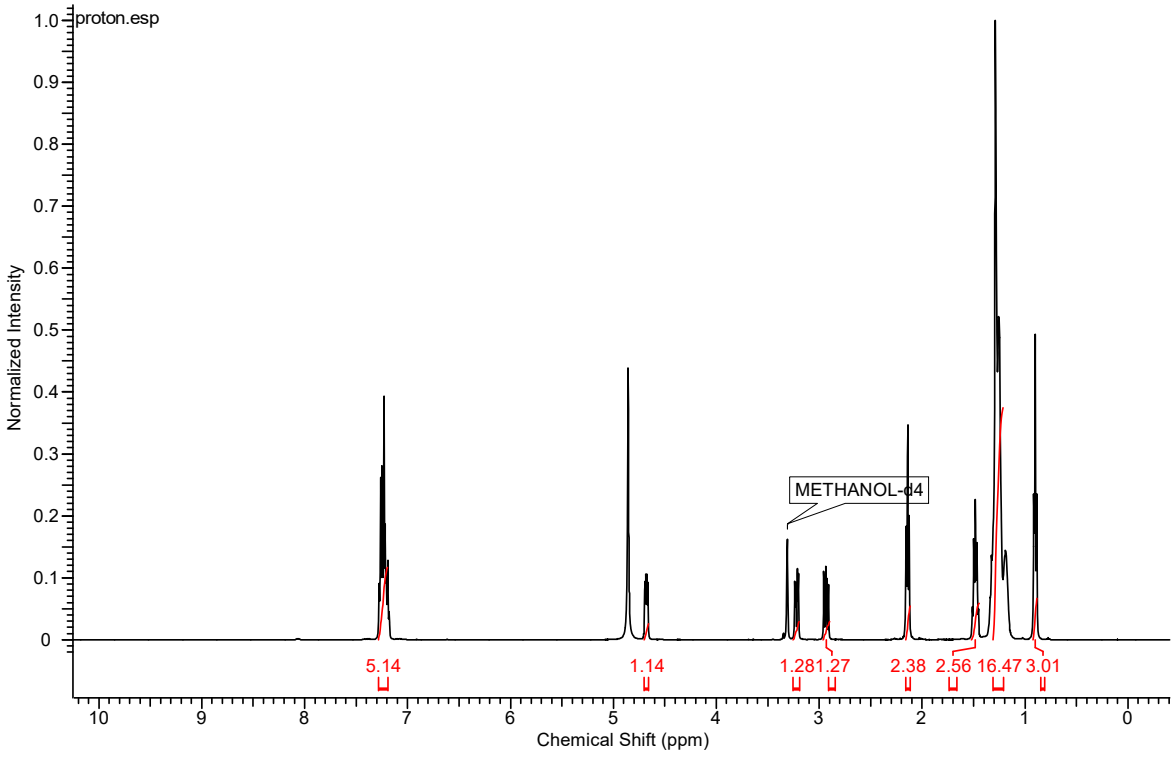

Figure S83. ^{13}C NMR spectrum for compound 22 in CD_3OD

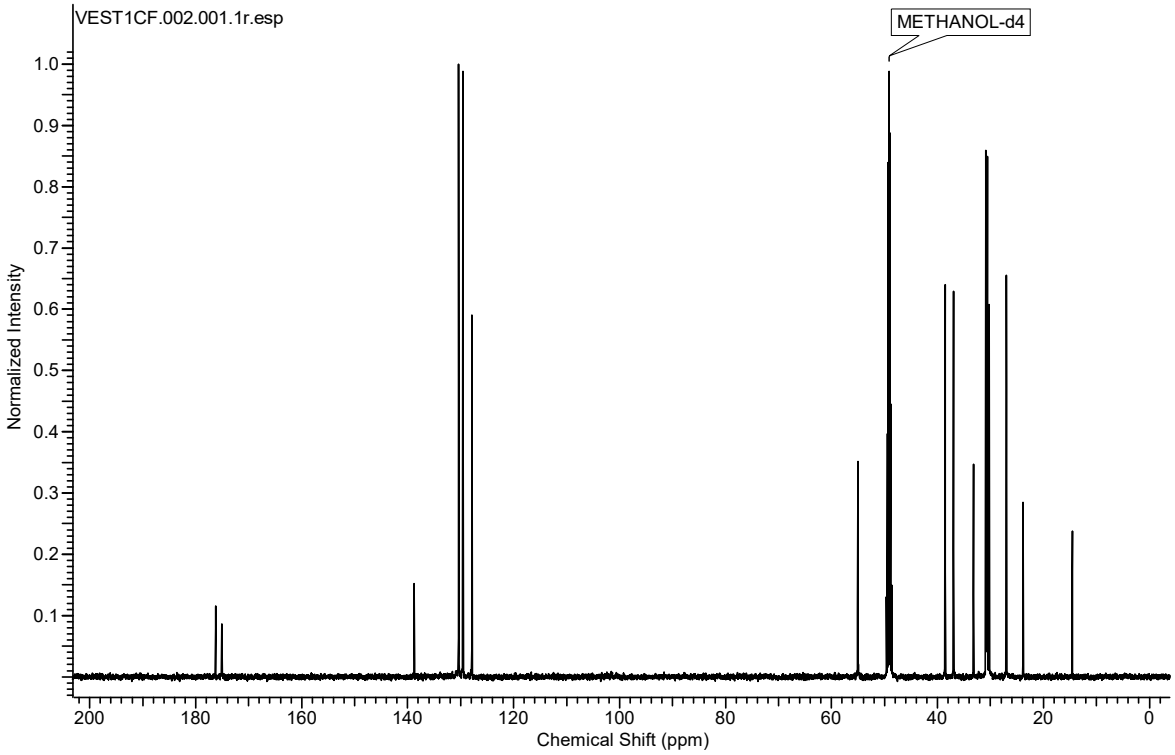

Figure S84. HRMS of compound 22 in MeOH

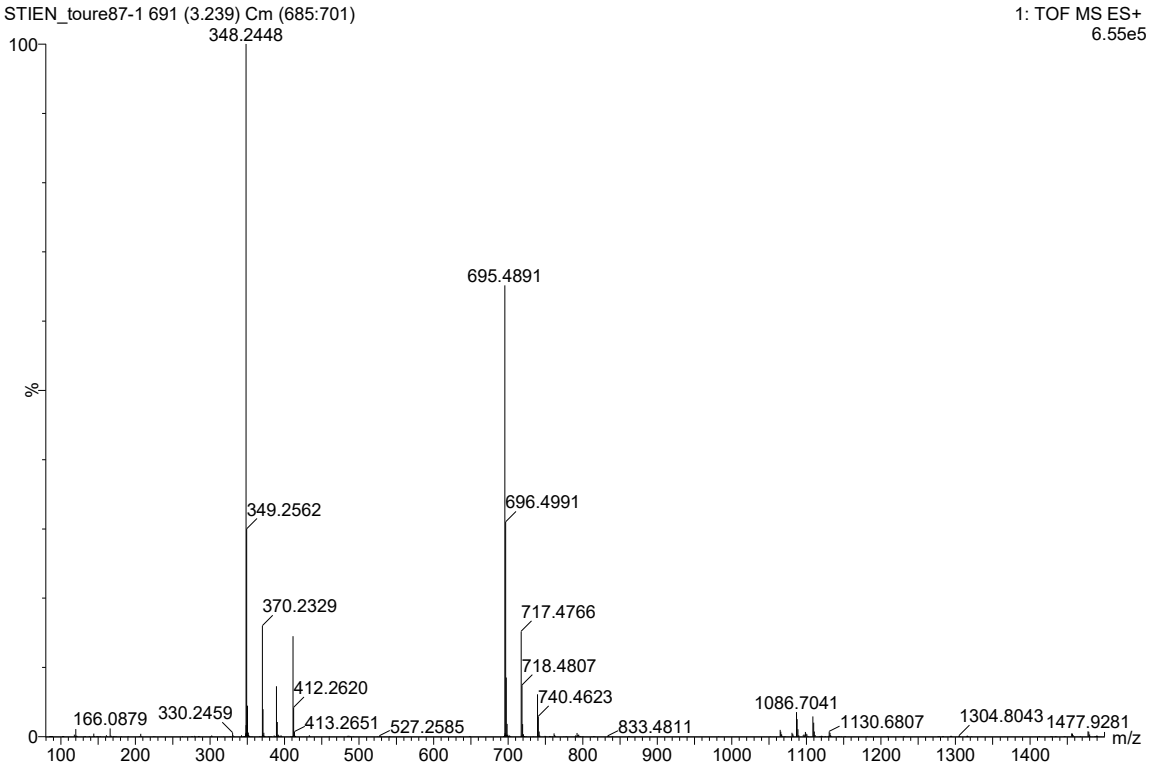

Figure S85. 1H NMR spectrum for compound 23 in CD_3OD

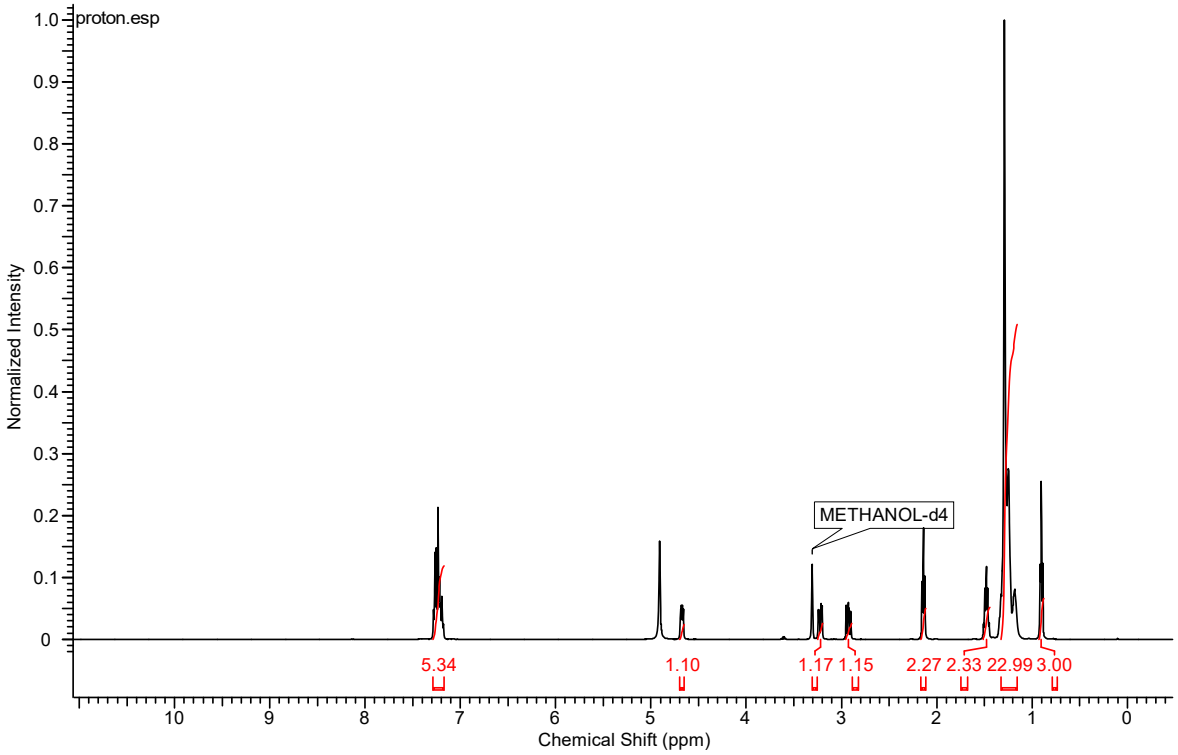

Figure S86. ^{13}C NMR spectrum for compound 23 in CD_3OD

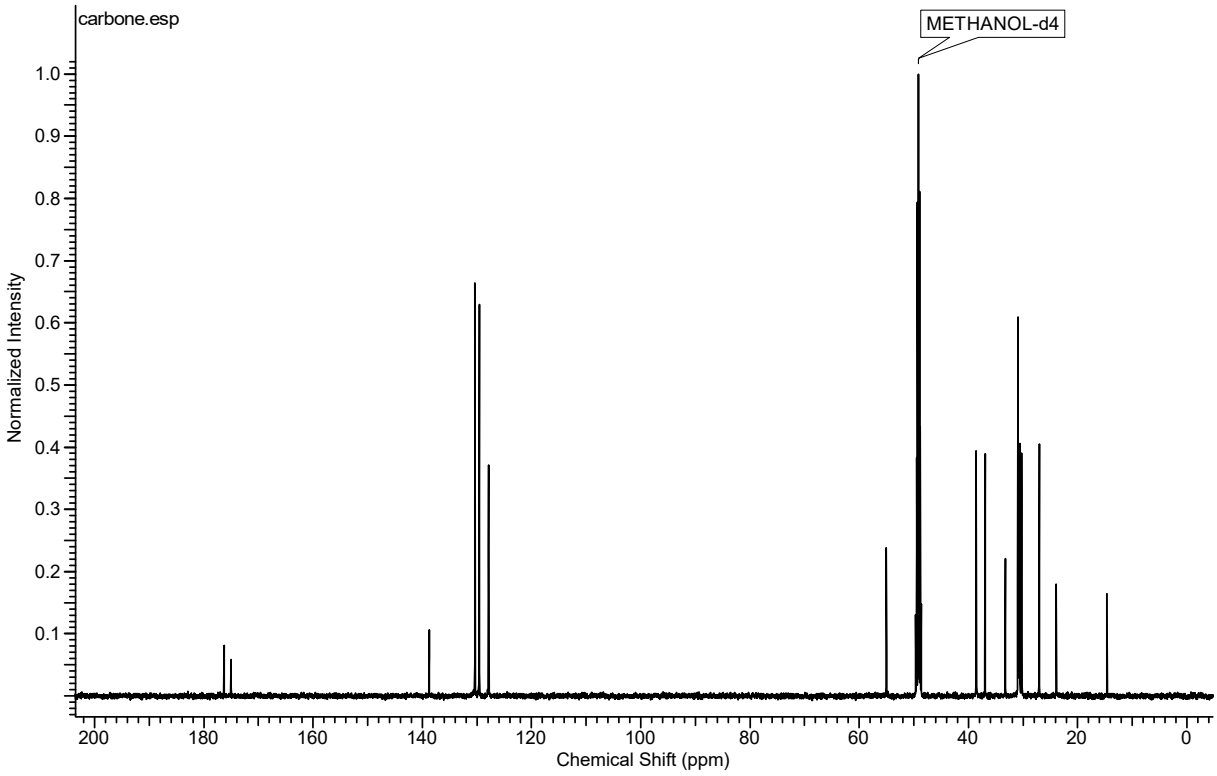

Figure S87. HRMS of compound 23 in MeOH

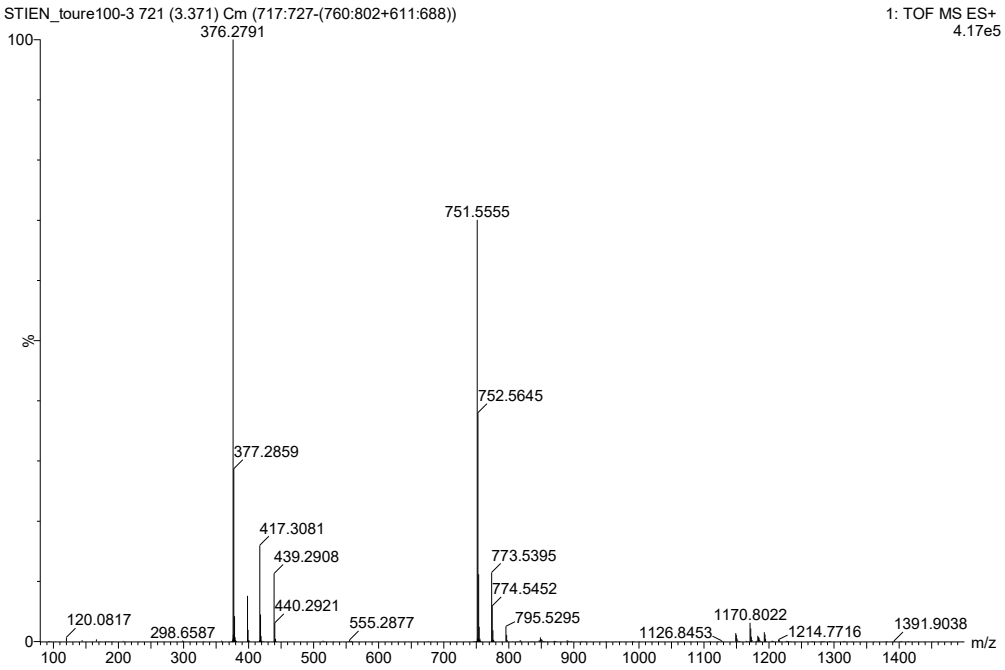

Figure S88. 1H NMR spectrum for compound 24 in CD_3OD

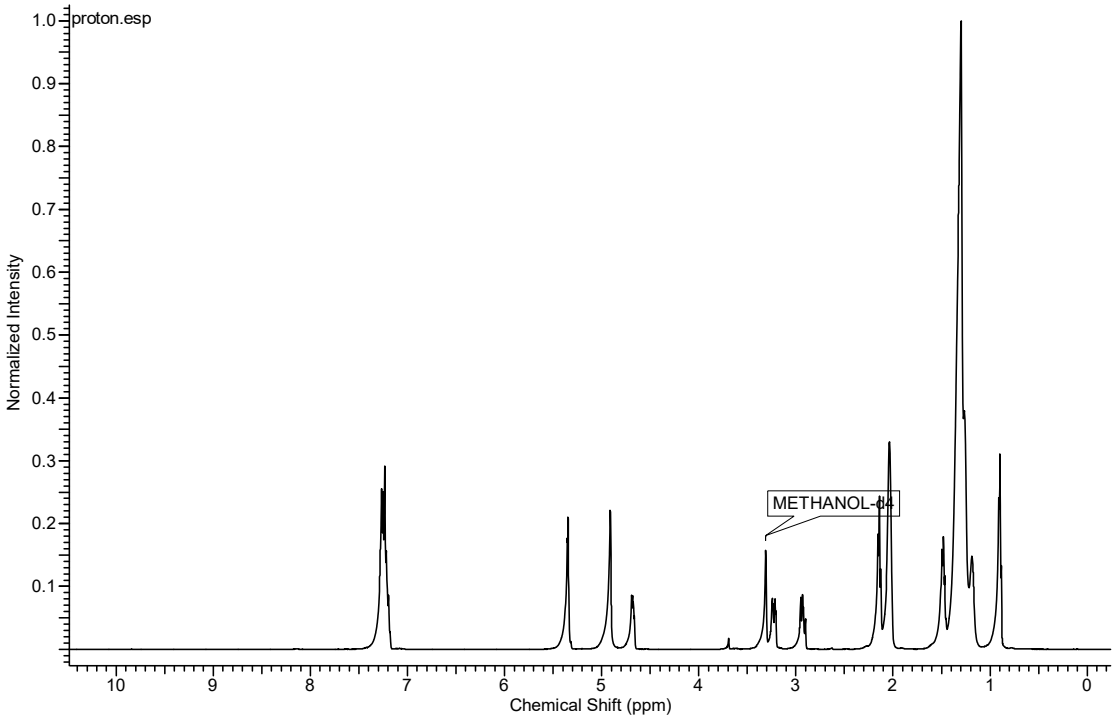

Figure S89. ^{13}C NMR spectrum for compound 24 in CD_3OD

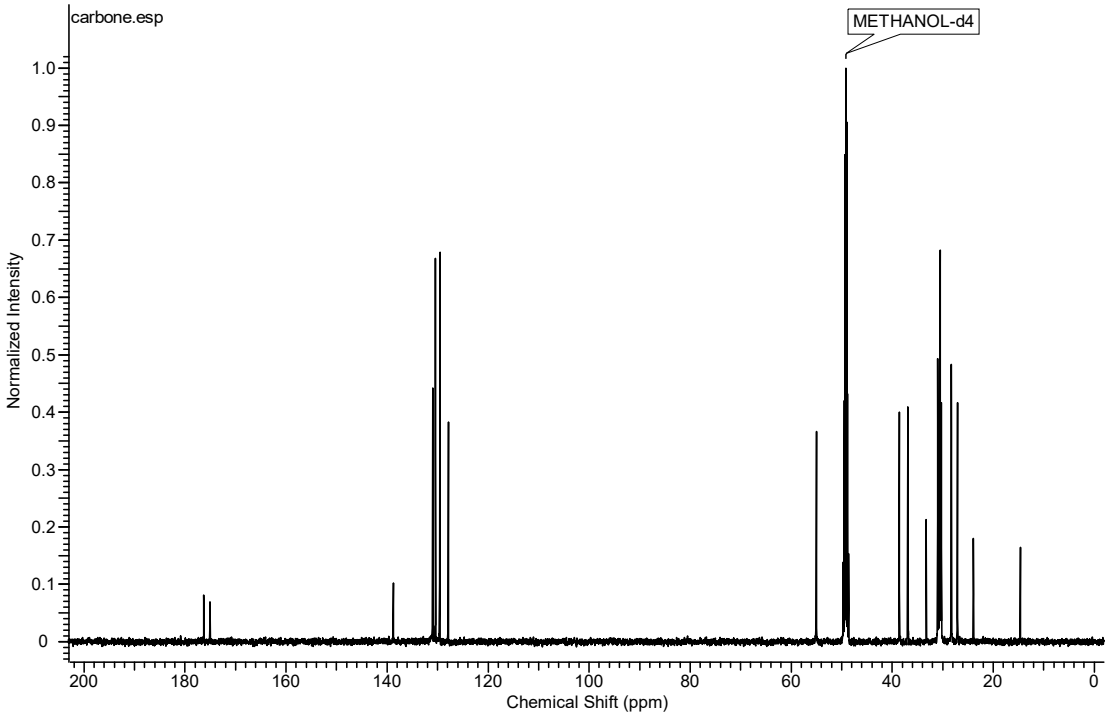

Figure S90. HRMS of compound 24 in MeOH

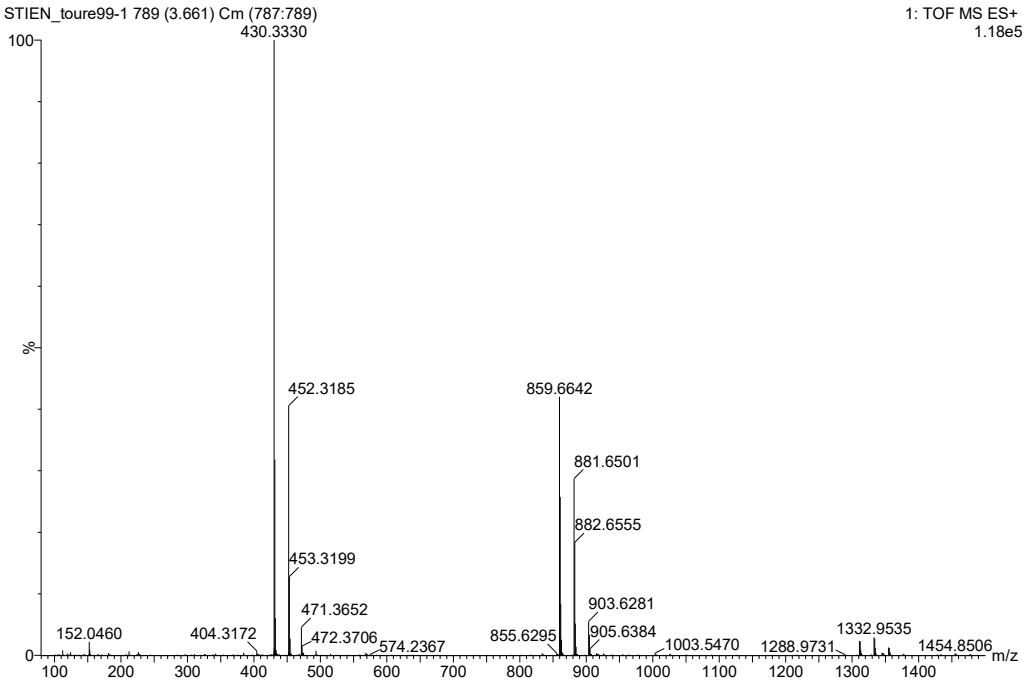

Figure S91. 1H NMR spectrum for compound 25 in CD_3OD

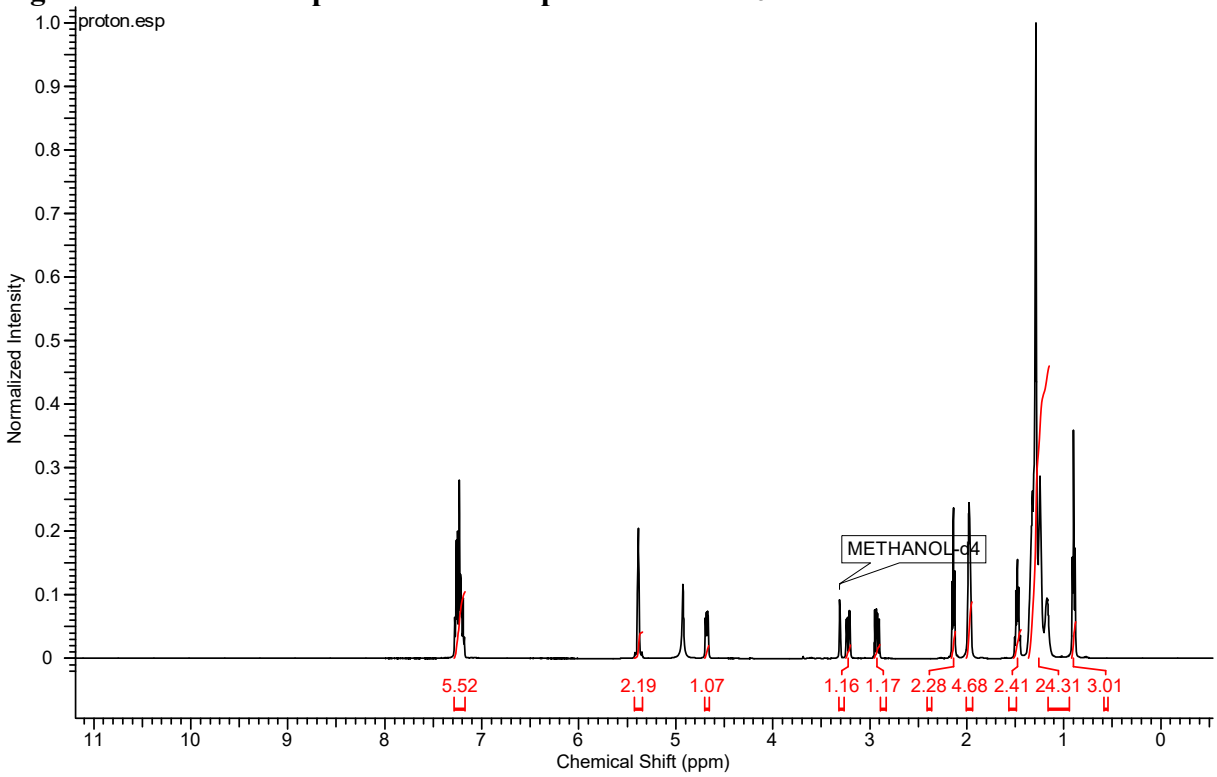

Figure S92. 13C NMR spectrum for compound 25 in CD_3OD

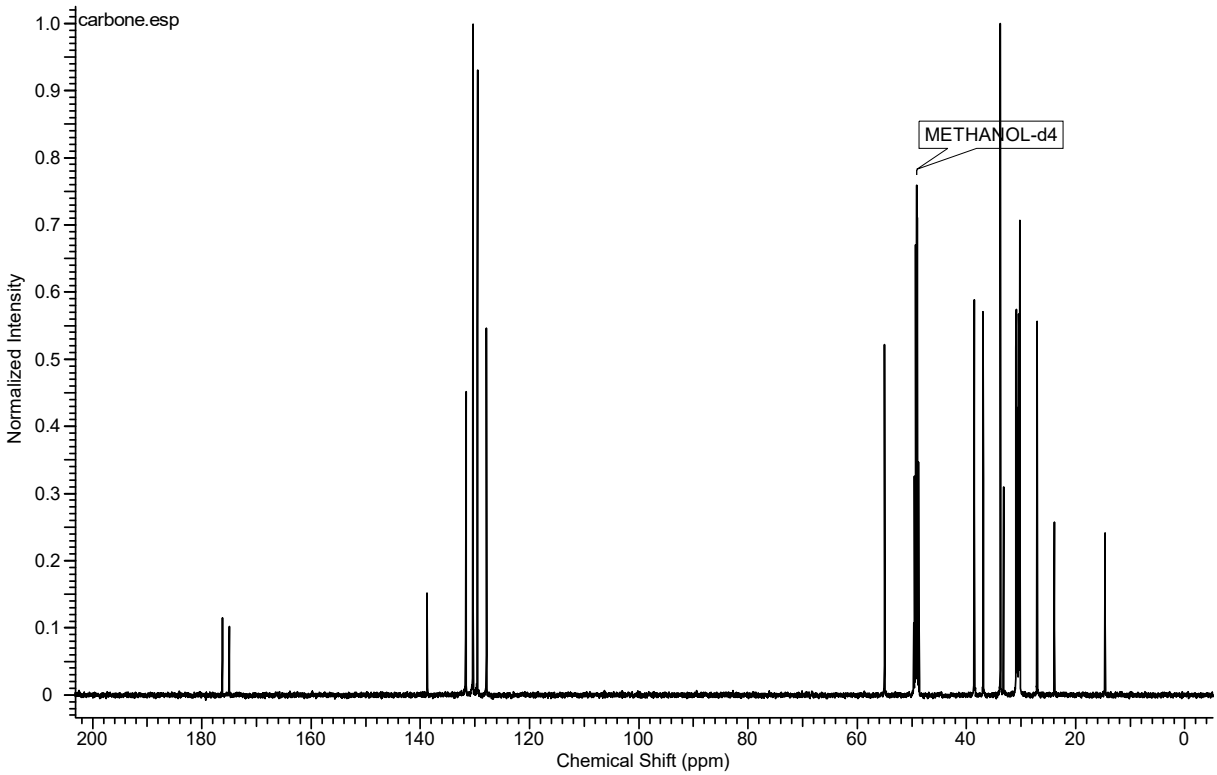

Figure S93. HRMS of compound 25 in MeOH

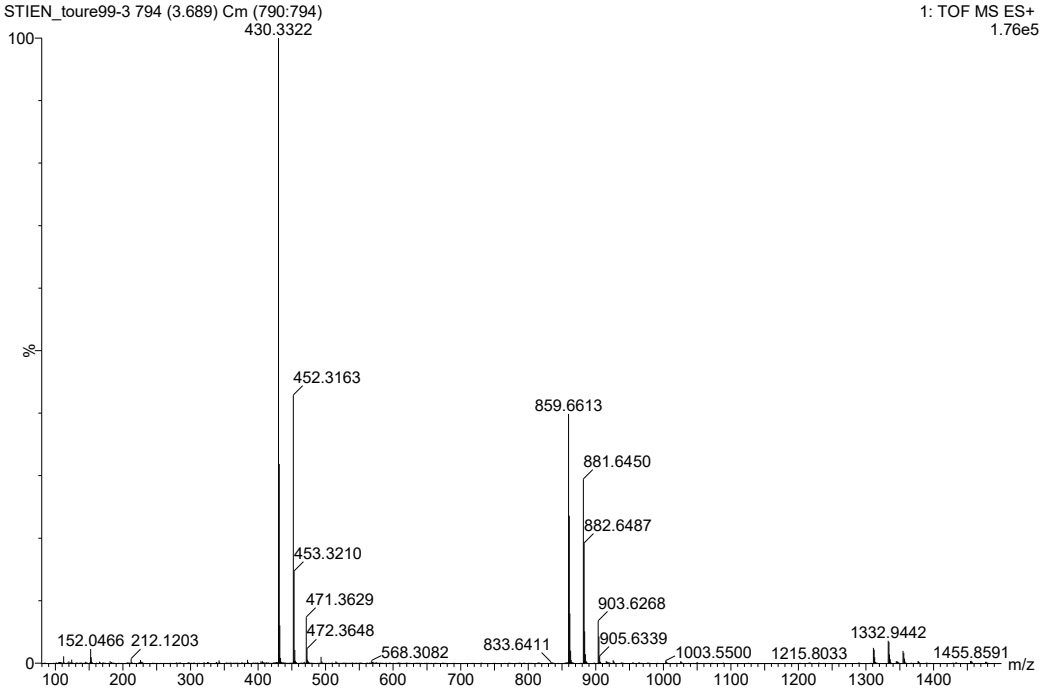

Figure S94. 1H NMR spectrum for compound 26 in CD_3OD

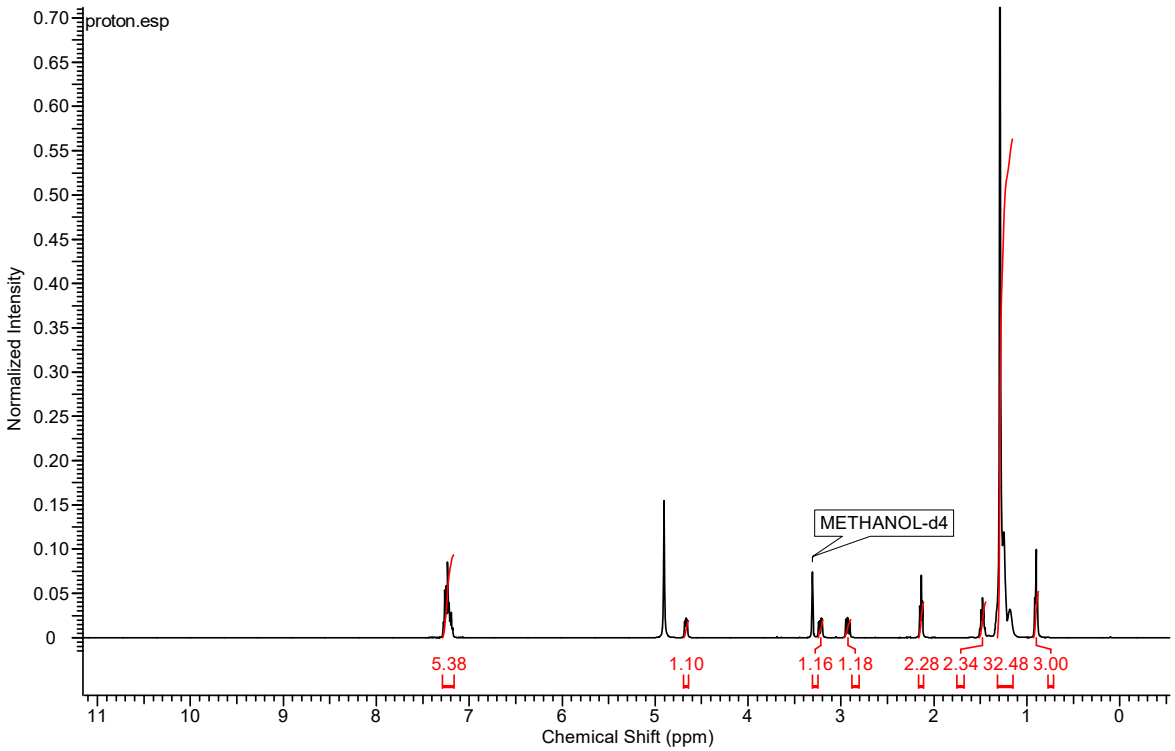

Figure S95. ^{13}C NMR spectrum for compound 26 in CD_3OD

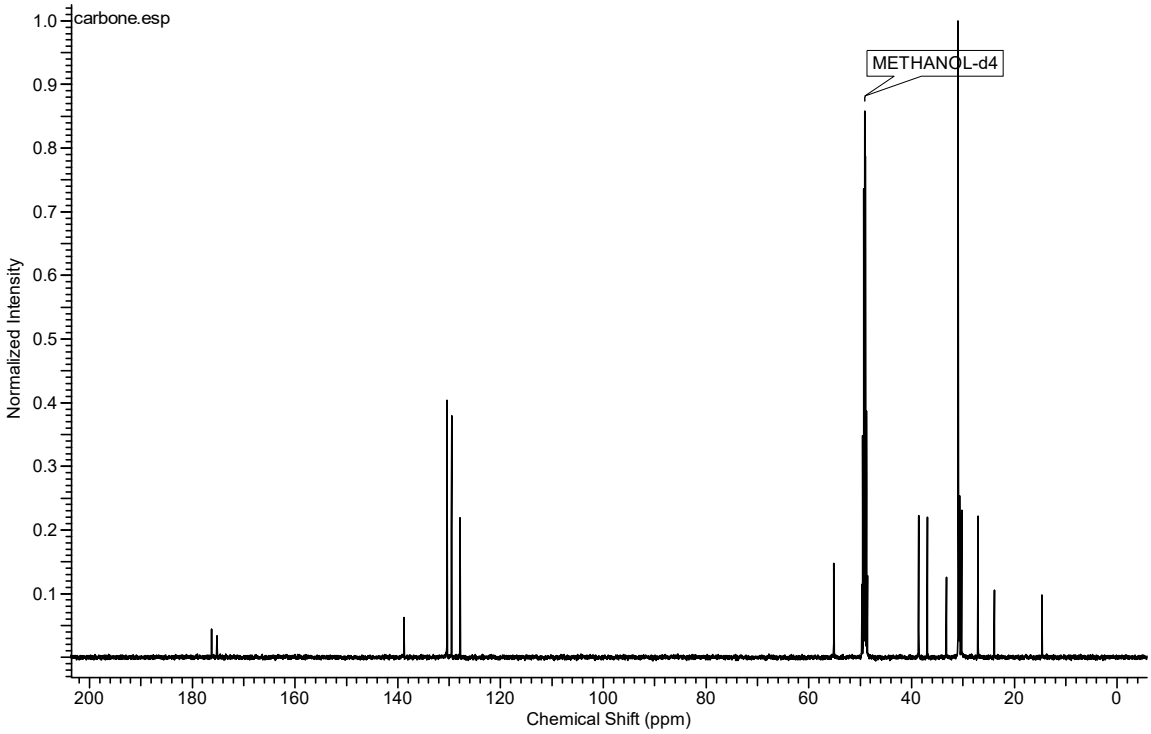

Figure S96. HRMS of compound 26 in MeOH

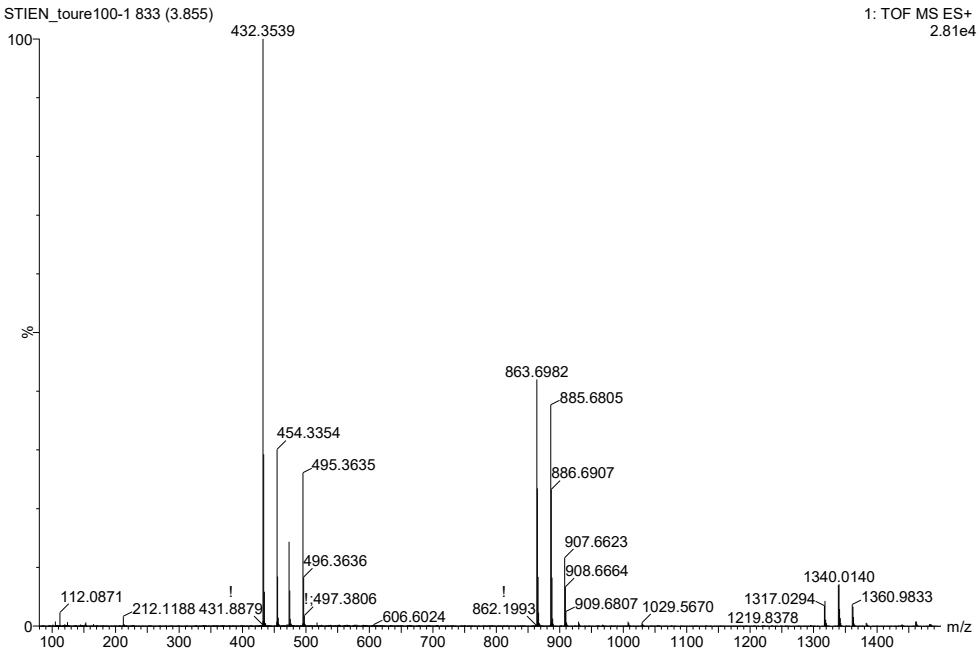

Figure S97. 1H NMR spectrum for compound 27 in CD_3OD

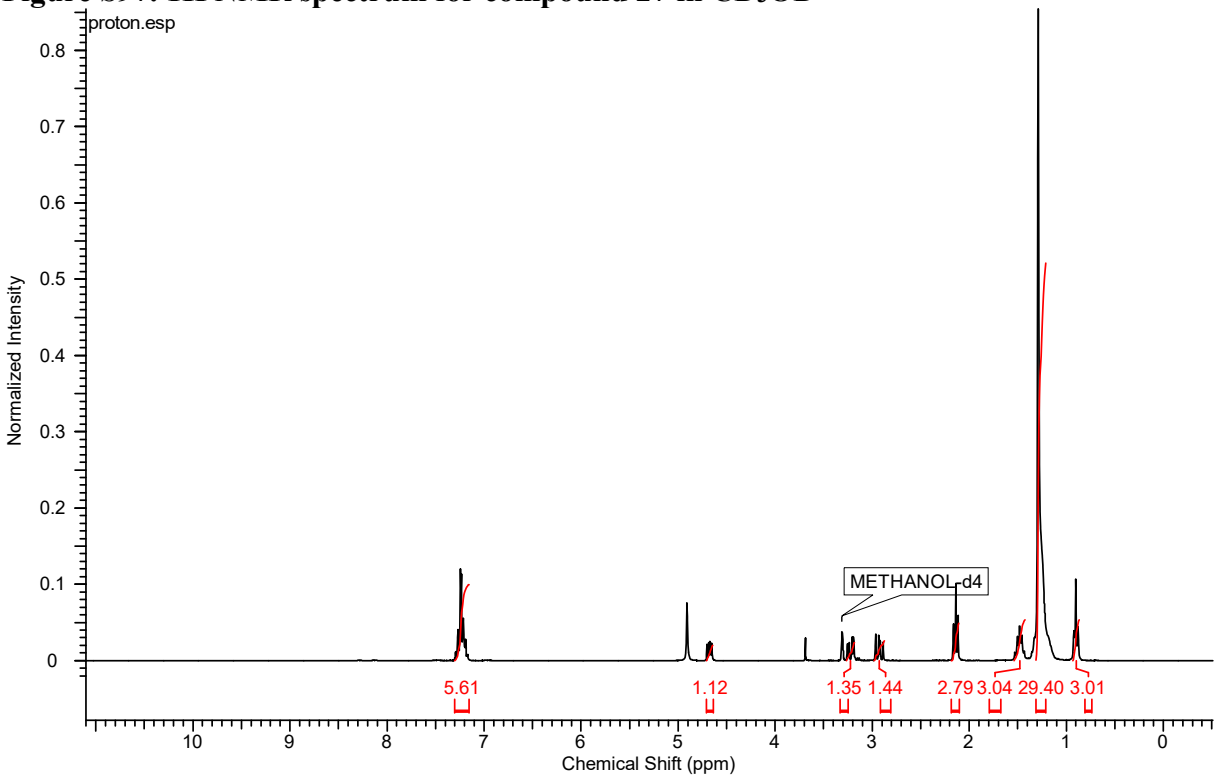

Figure S98. 13C NMR spectrum for compound 27 in CD_3OD

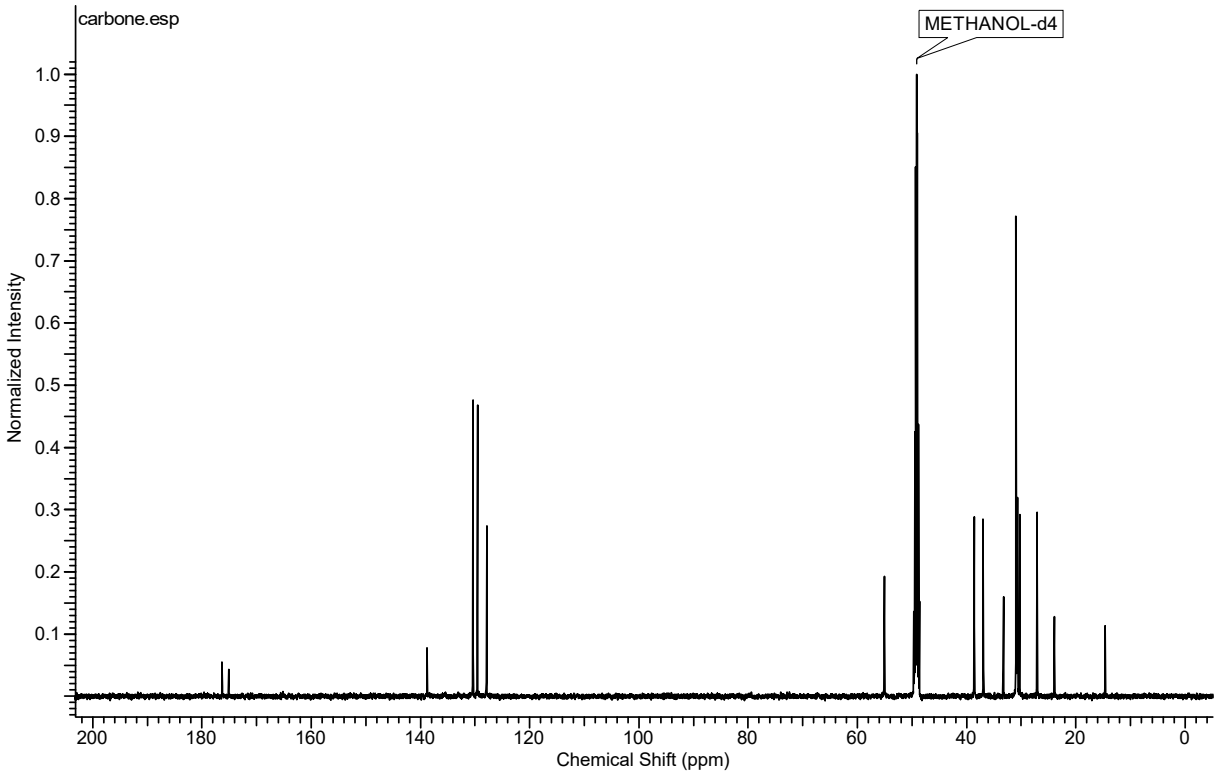

Figure S99. HRMS of compound 27 in MeOH

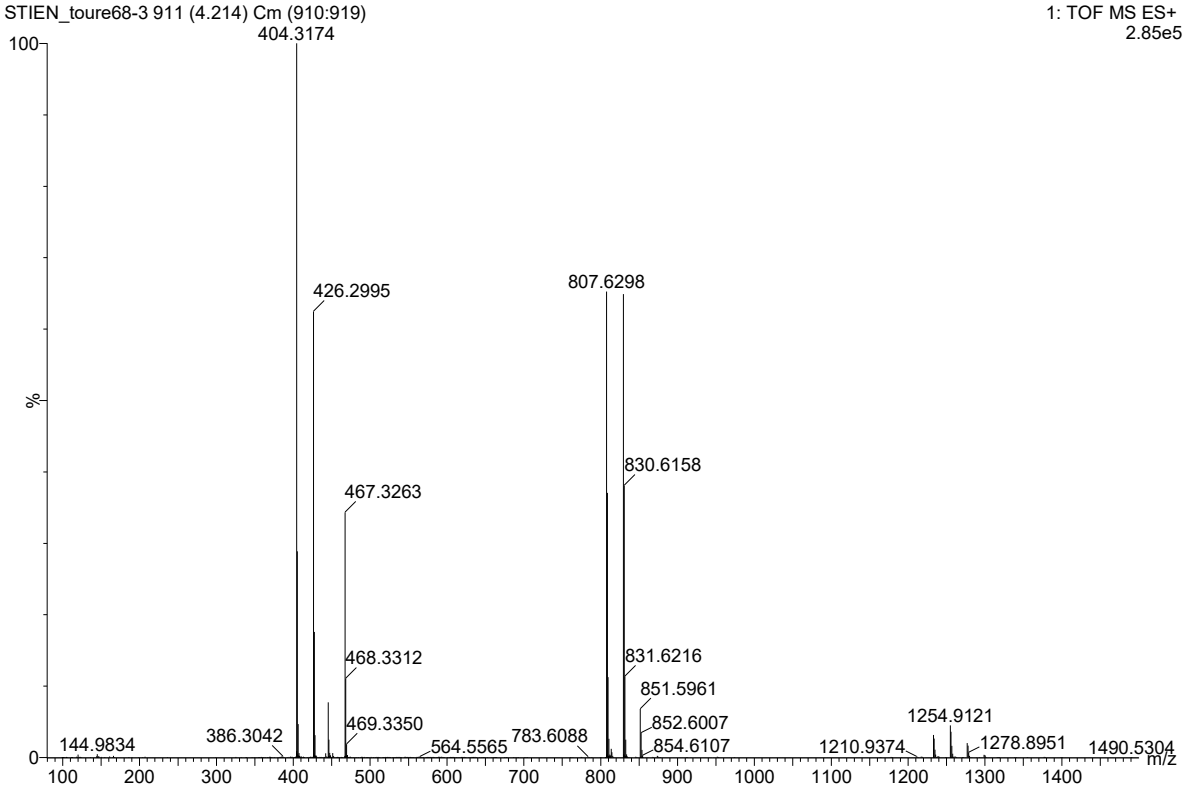

Figure S100. 1H NMR spectrum for compound *ent*-3 in CD_3OD

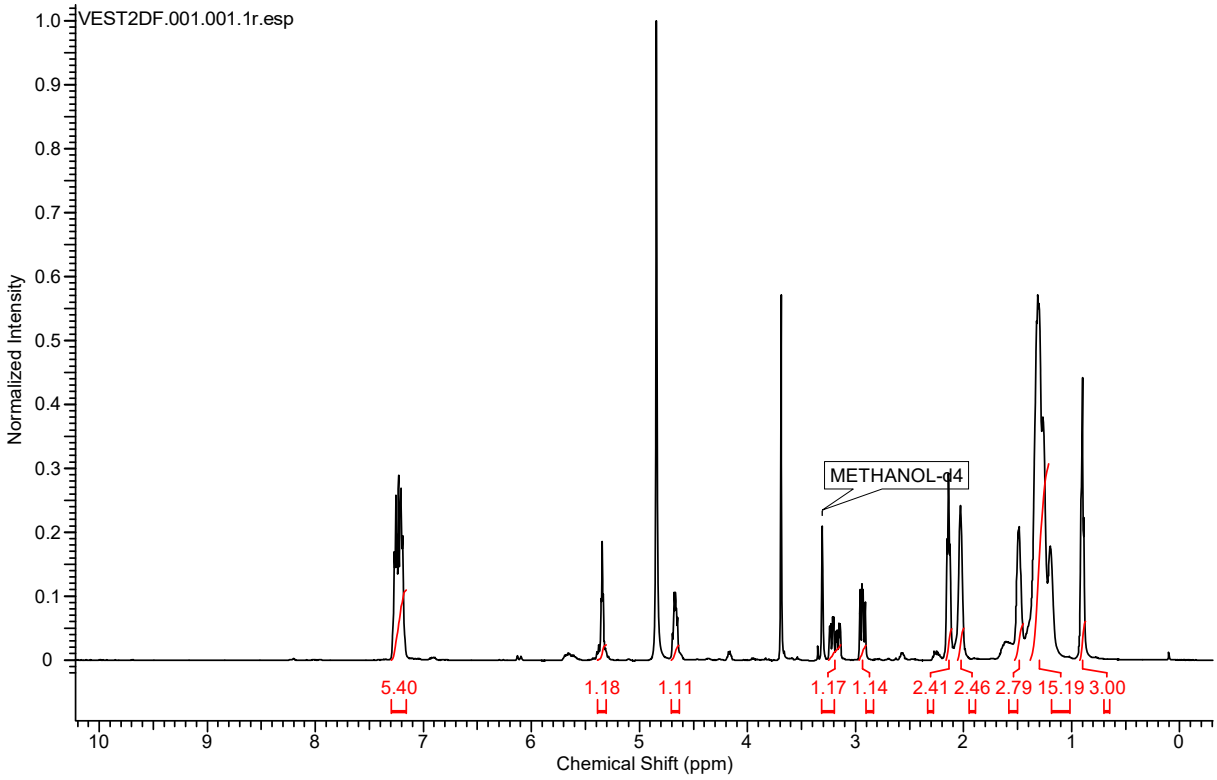

Figure S101. 13C NMR spectrum for compound *ent*-3 in CD_3OD

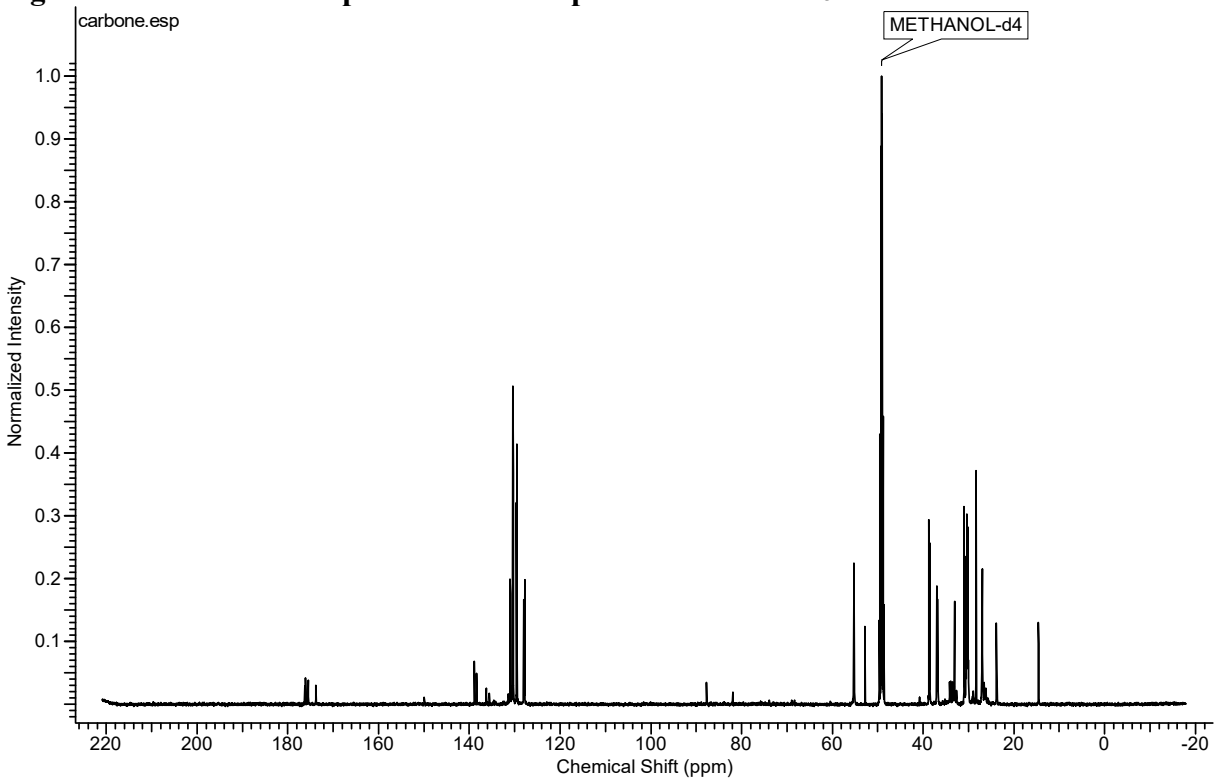

Figure S102. HRMS of compound *ent*-3 in MeOH

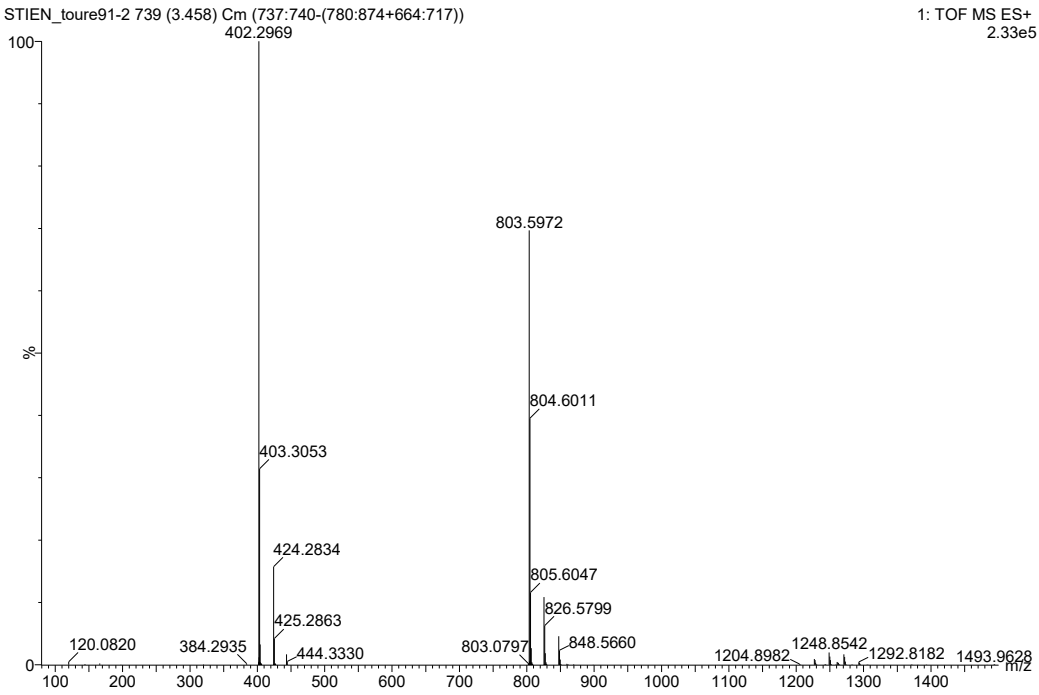

Figure S103. 1H NMR spectrum for compound 28 in CD_3OD

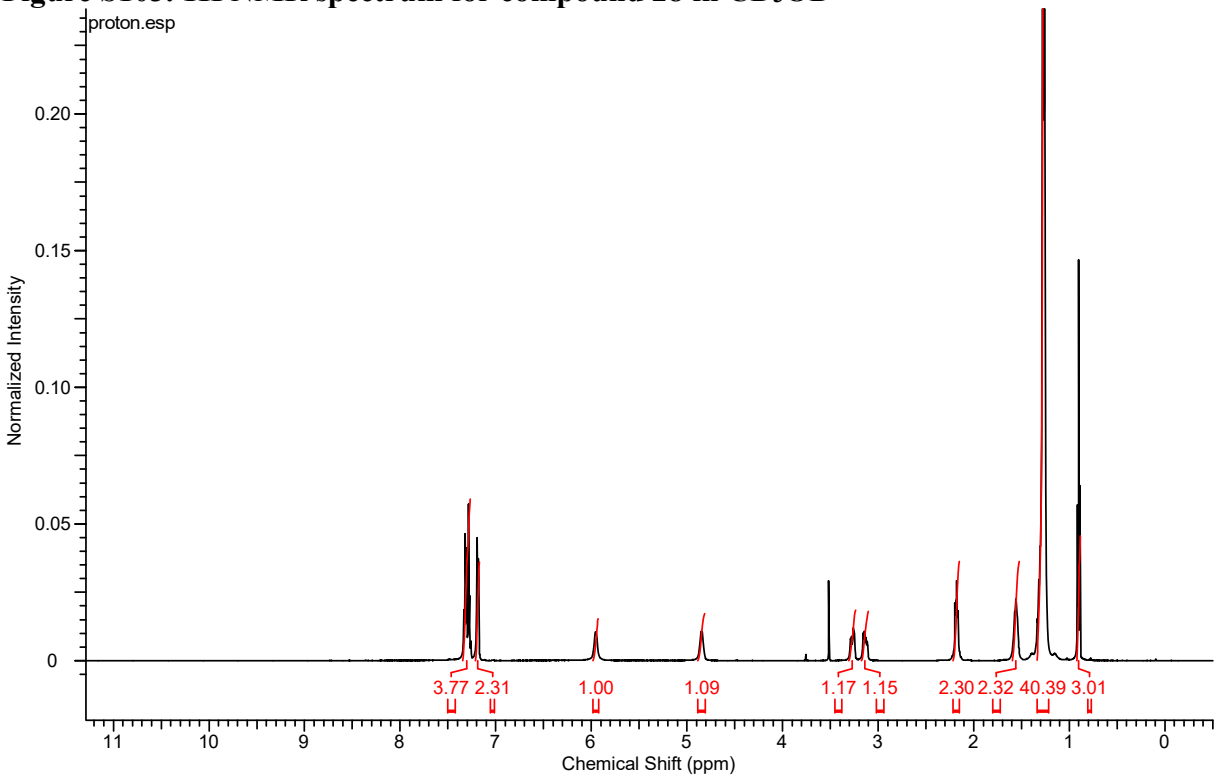

Figure S104. ^{13}C NMR spectrum for compound 28 in CD_3OD

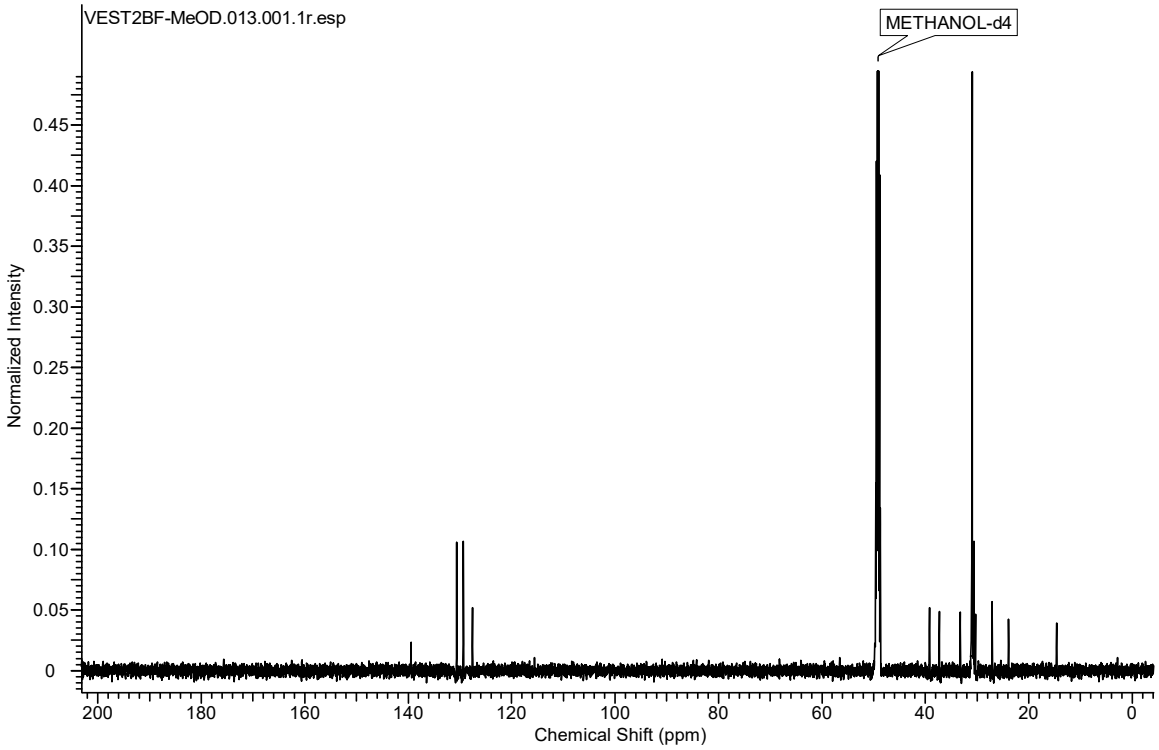

Figure S105. HRMS of compound 28 in MeOH

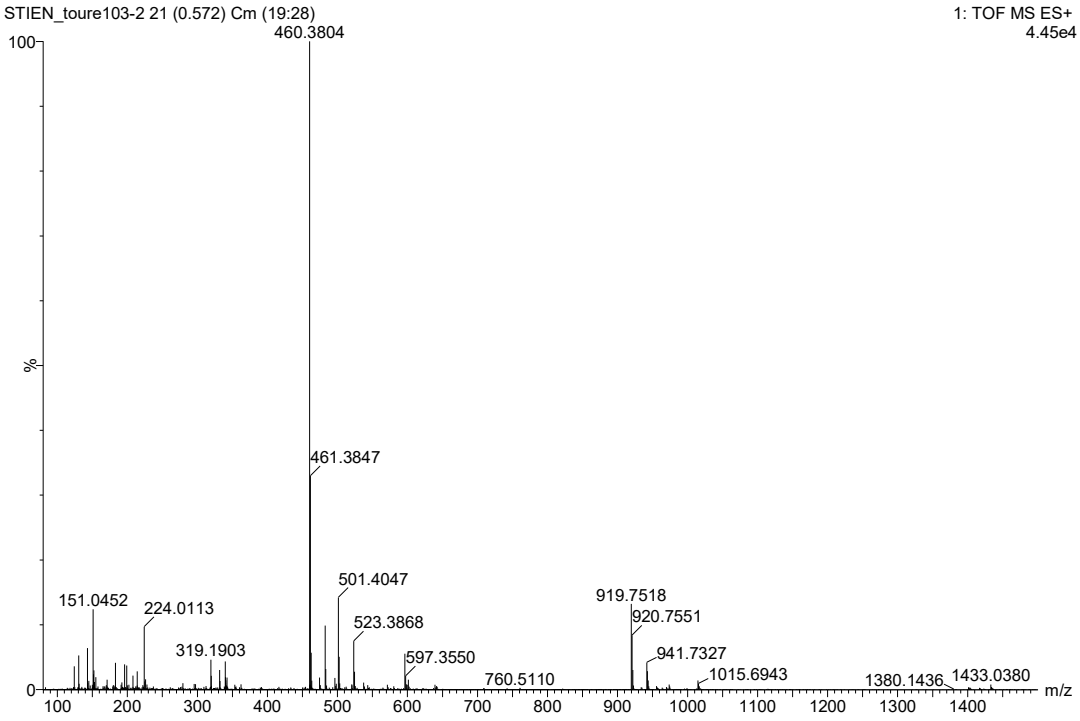

Figure S106. 1H NMR spectrum for compound 29 in CD_3OD

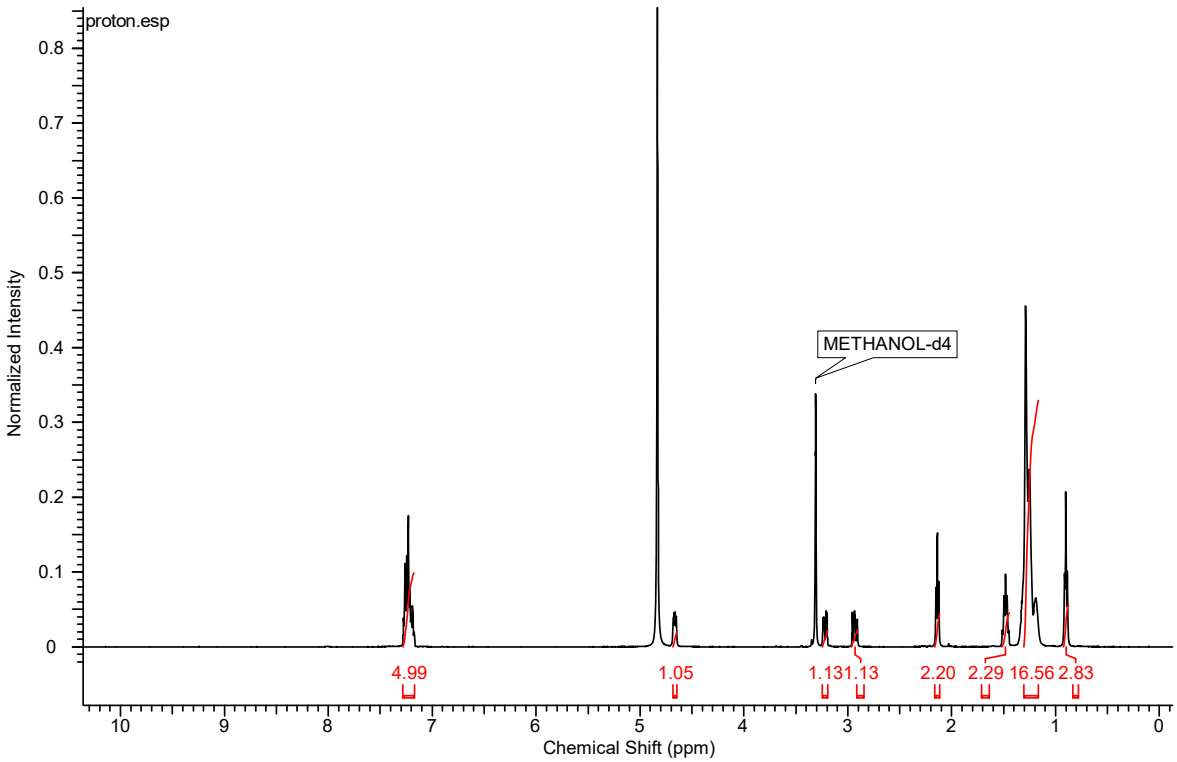

Figure S107. ^{13}C NMR spectrum for compound 29 in CD_3OD

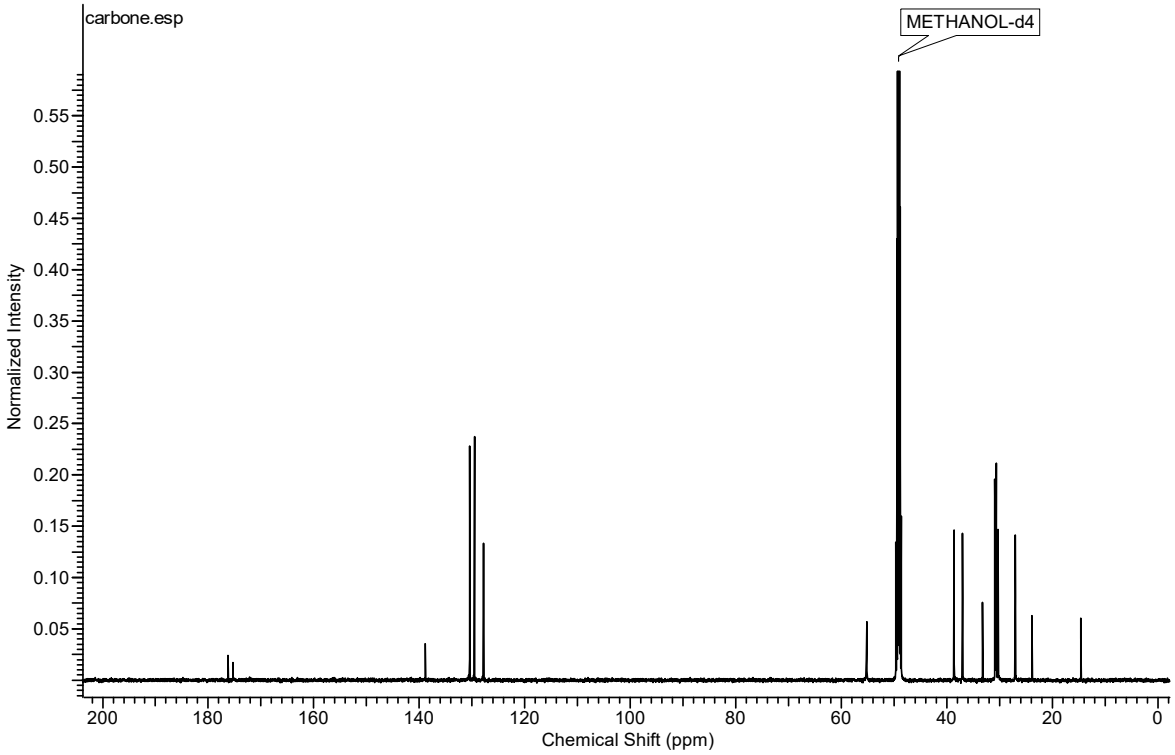

Figure S108. HRMS of compound 29 in MeOH

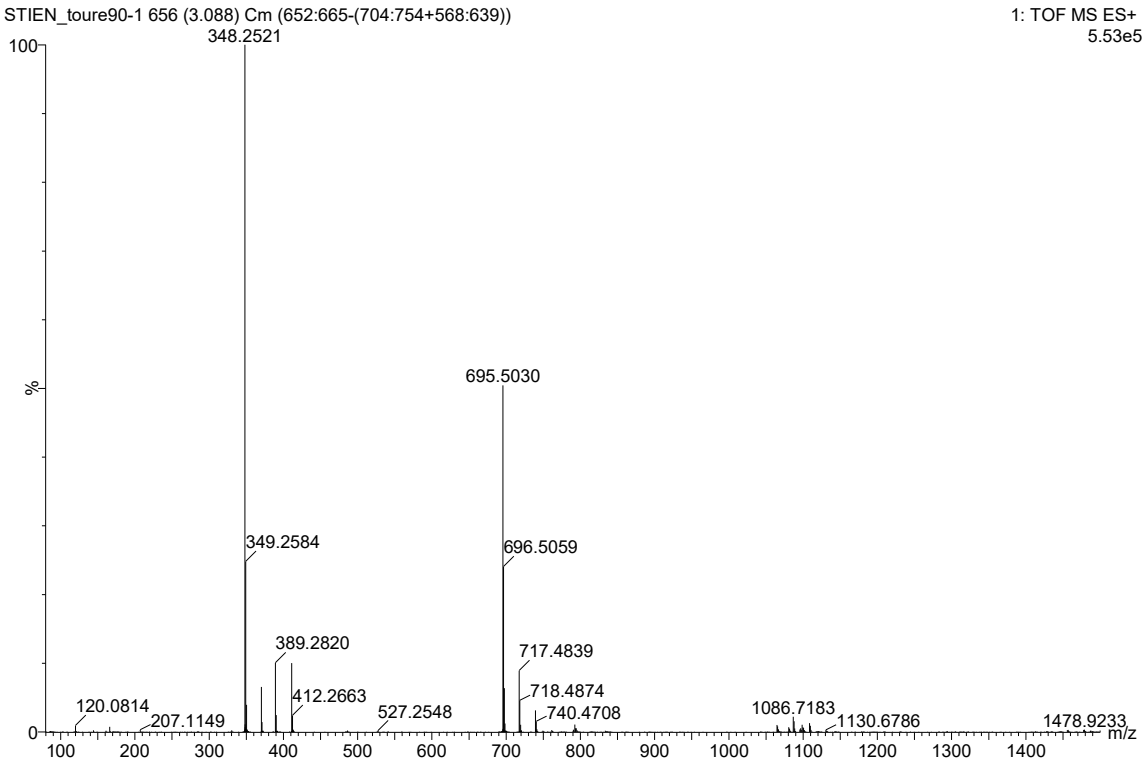

Figure S109. 1H NMR spectrum for compound 30 in CD_3OD

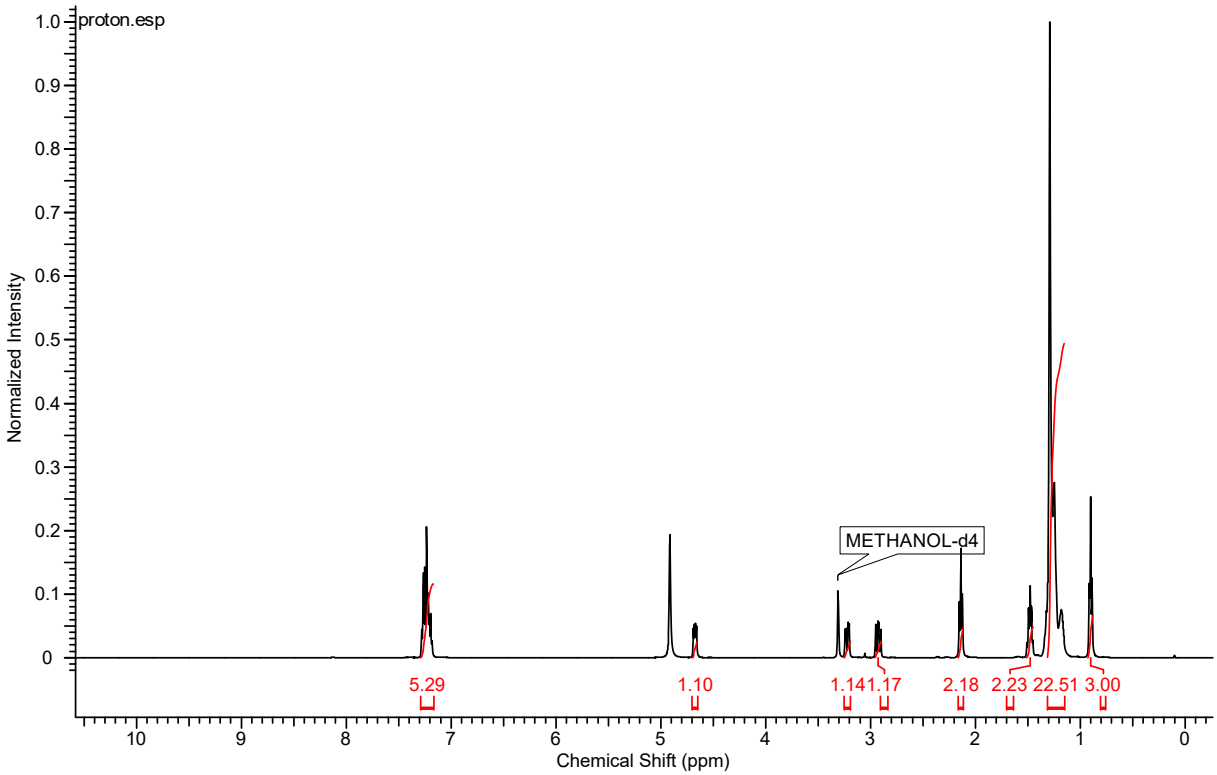

Figure S110. 13C NMR spectrum for compound 30 in CD_3OD

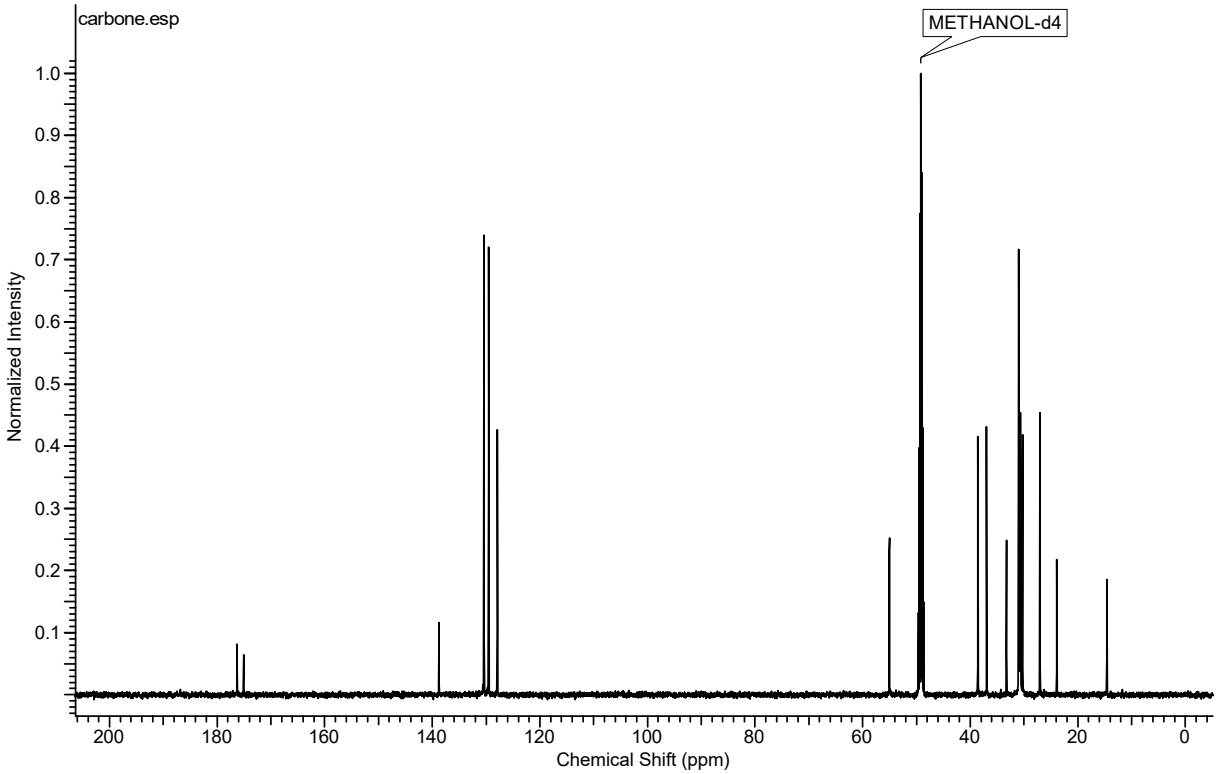

Figure S111. HRMS of compound 30 in MeOH

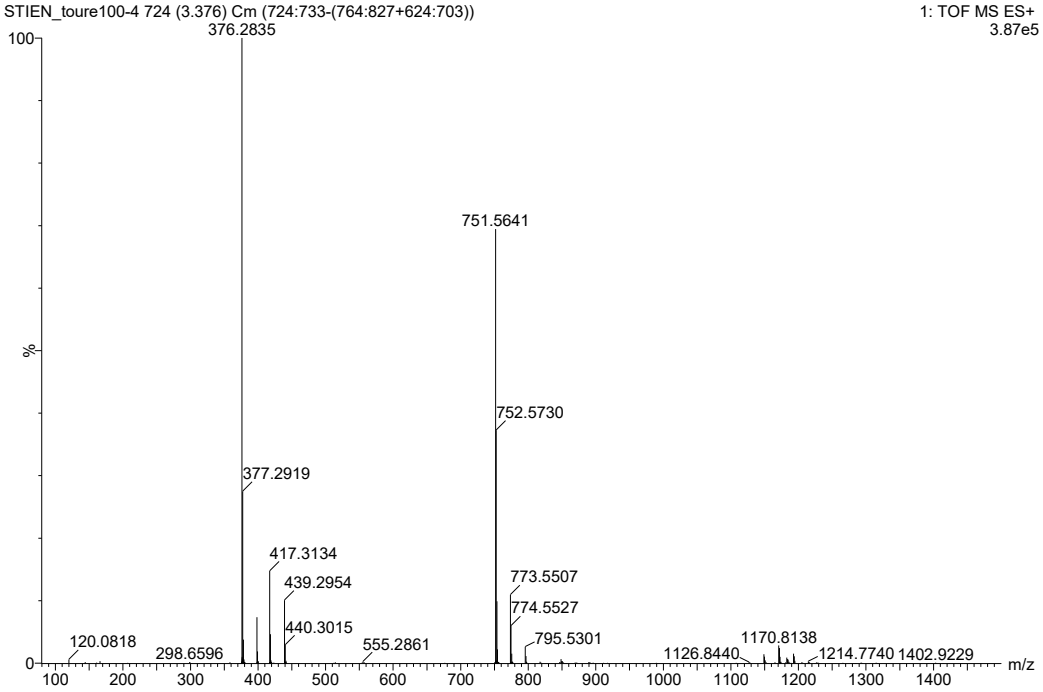

Figure S112. 1H NMR spectrum for compound 31 in CD_3OD

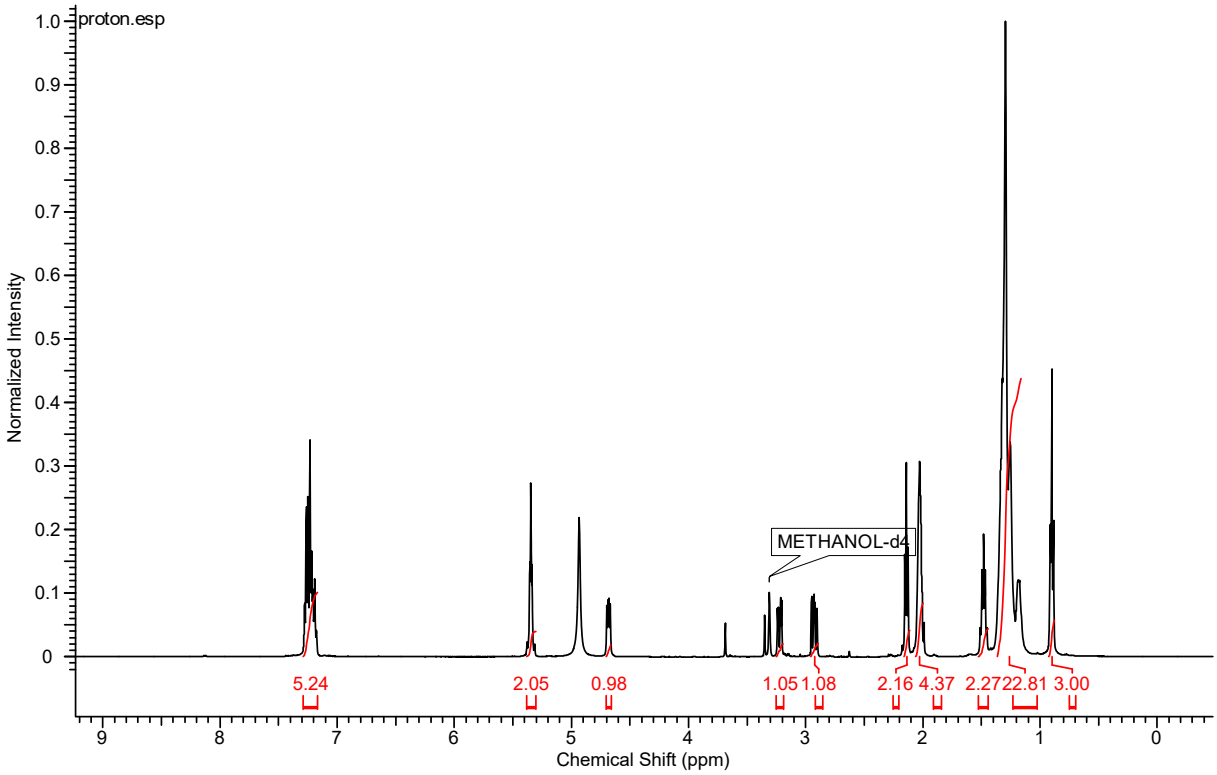

Figure S113. 13C NMR spectrum for compound 31 in CD_3OD

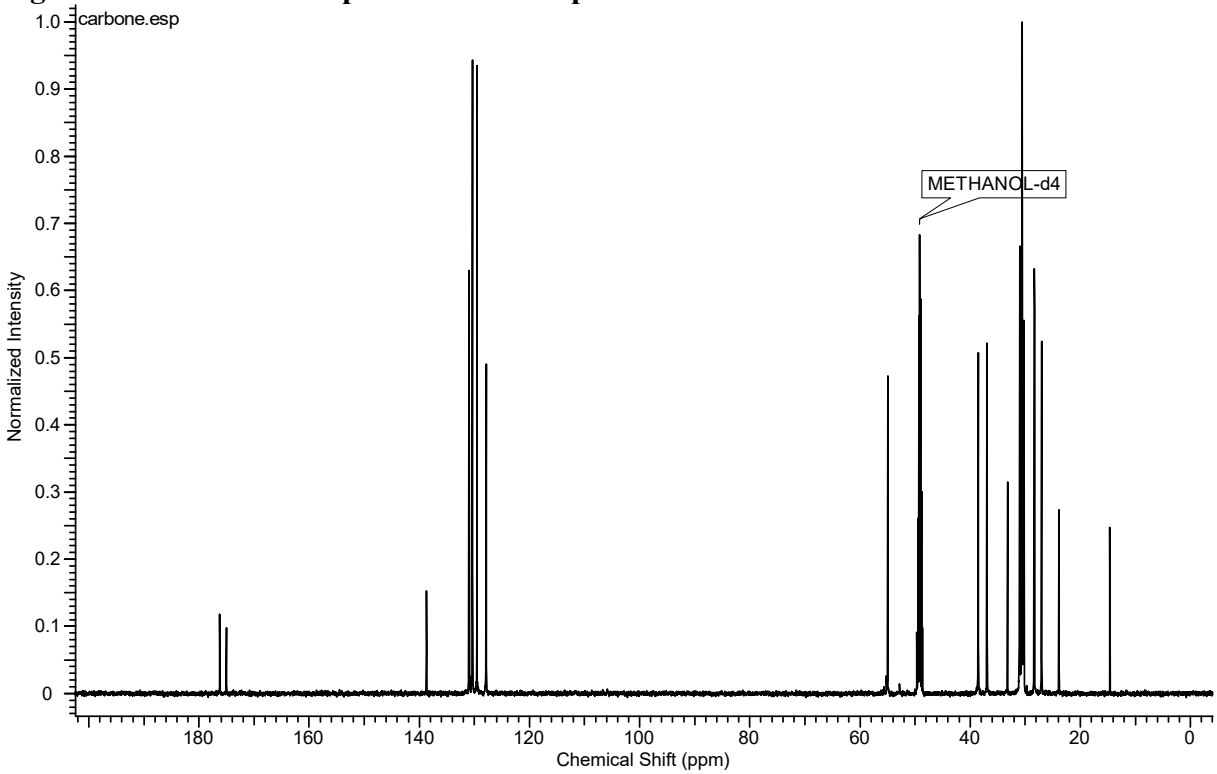

Figure S114. HRMS of compound 31 in MeOH

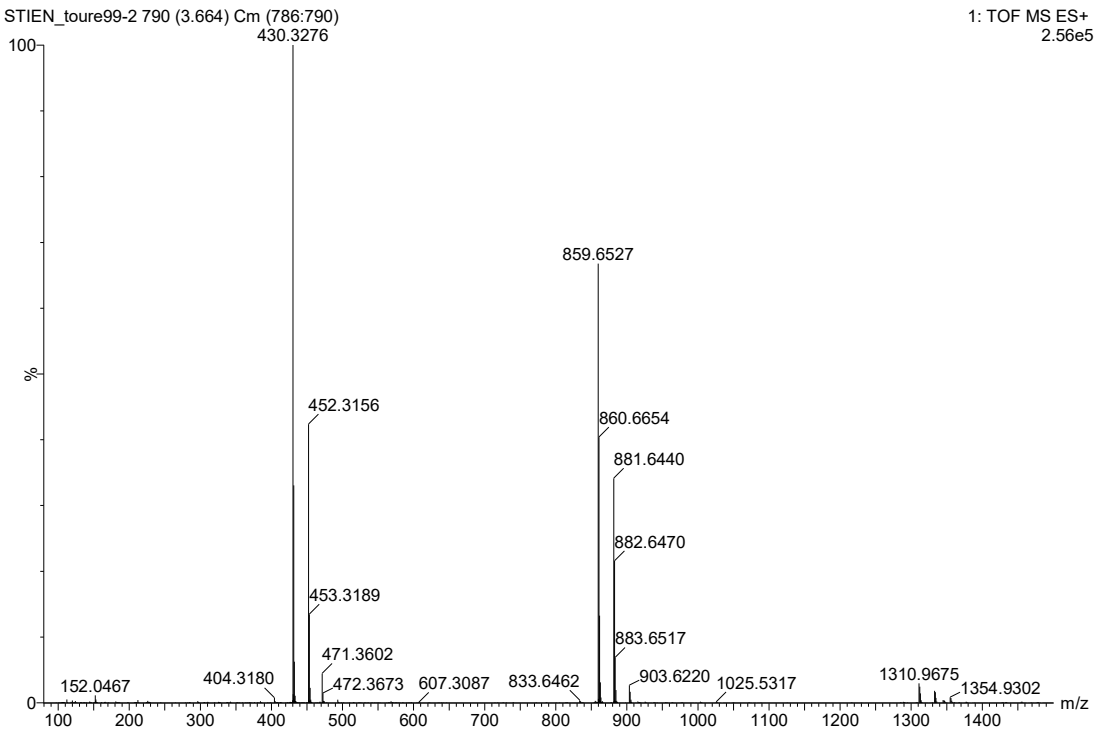

Figure S115. 1H NMR spectrum for compound 32 in CD_3OD

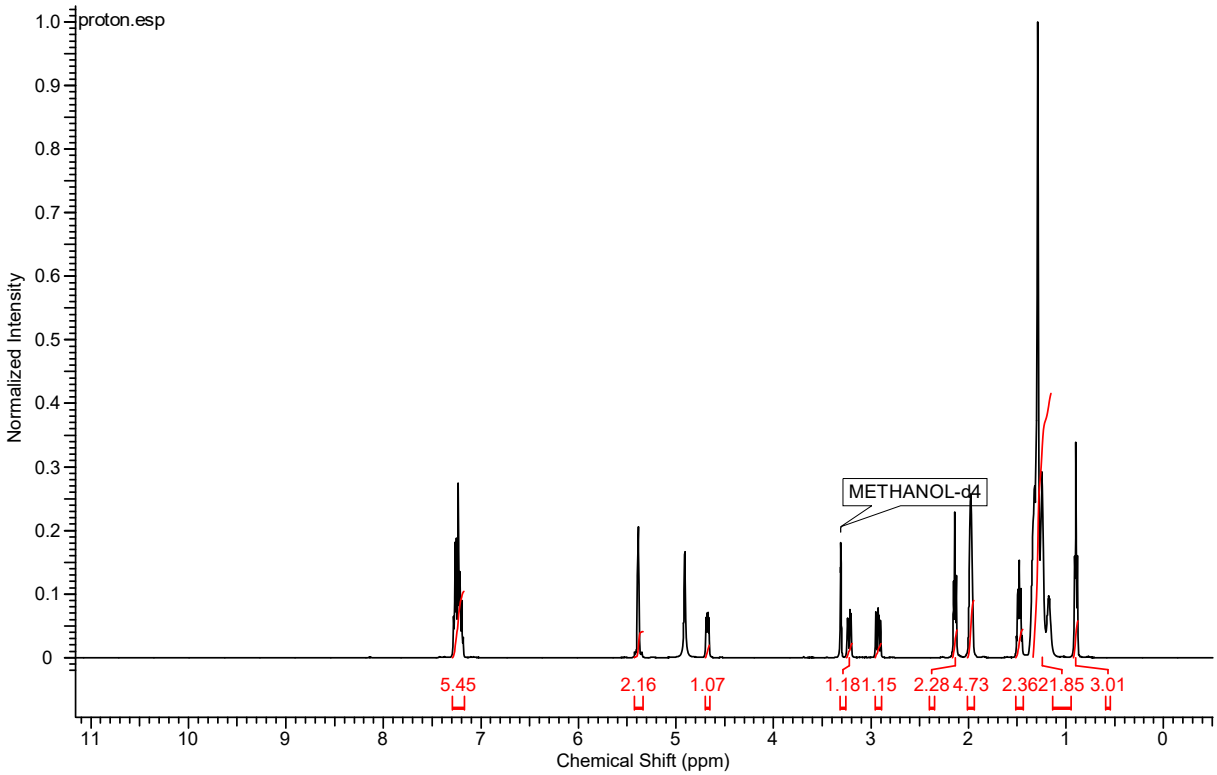

Figure S116. 13C NMR spectrum for compound 32 in CD_3OD

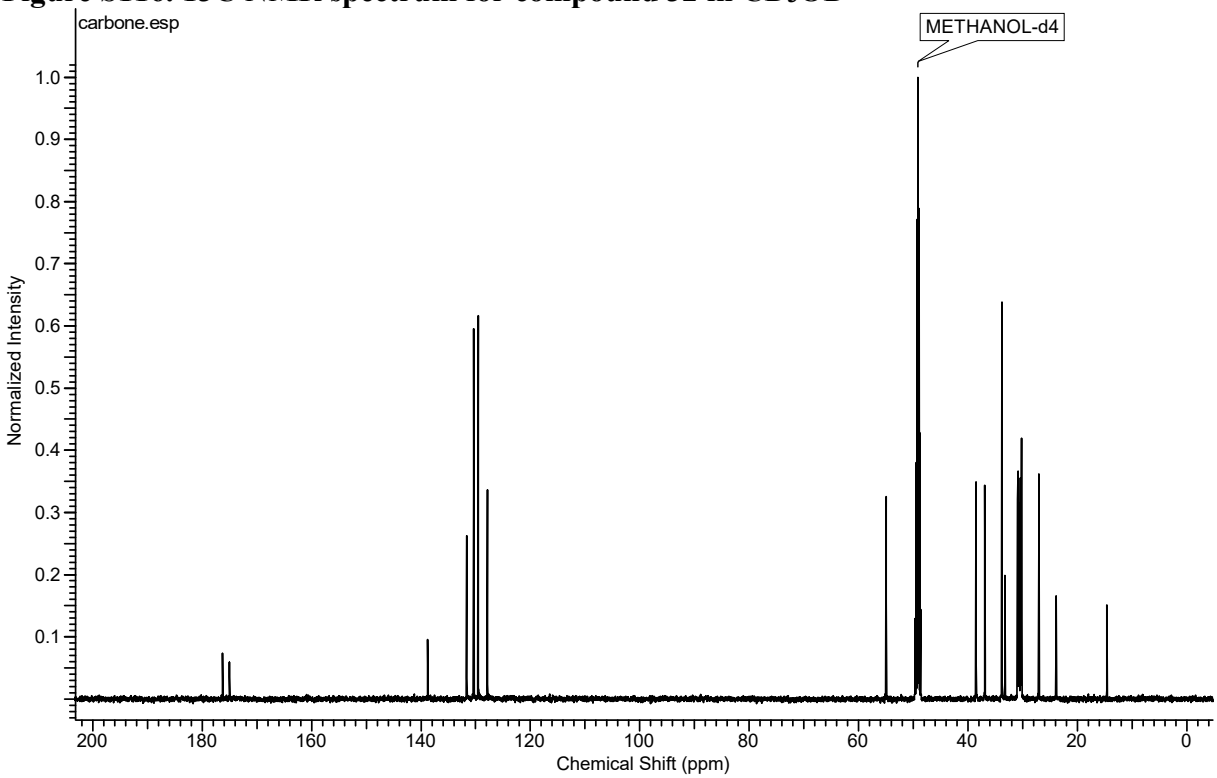

Figure S117. HRMS of compound 32 in MeOH

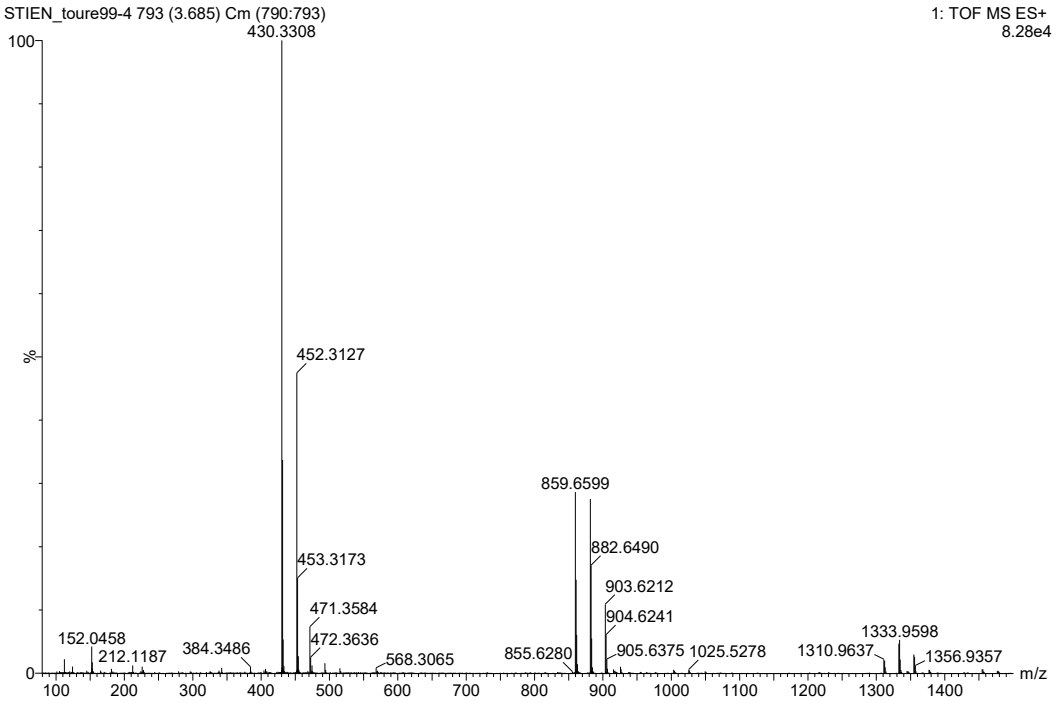

Figure S118. 1H NMR spectrum for compound 33 in CD_3OD

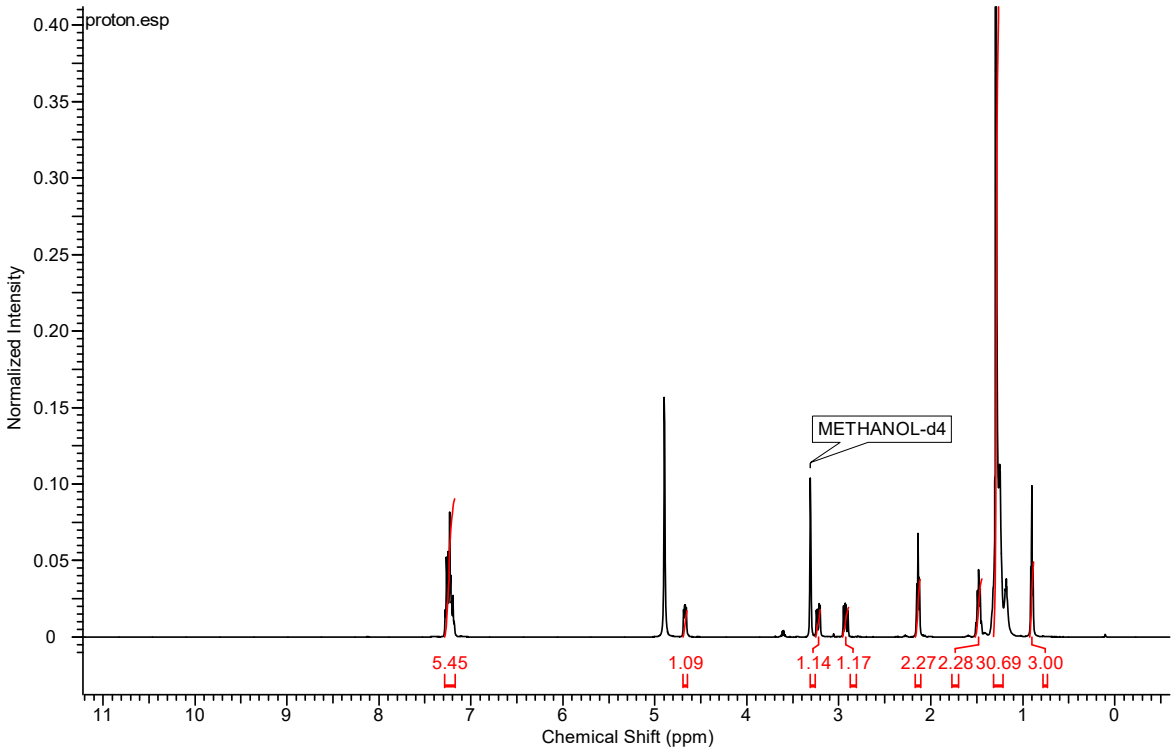

Figure S119. 13C NMR spectrum for compound 33 in CD_3OD

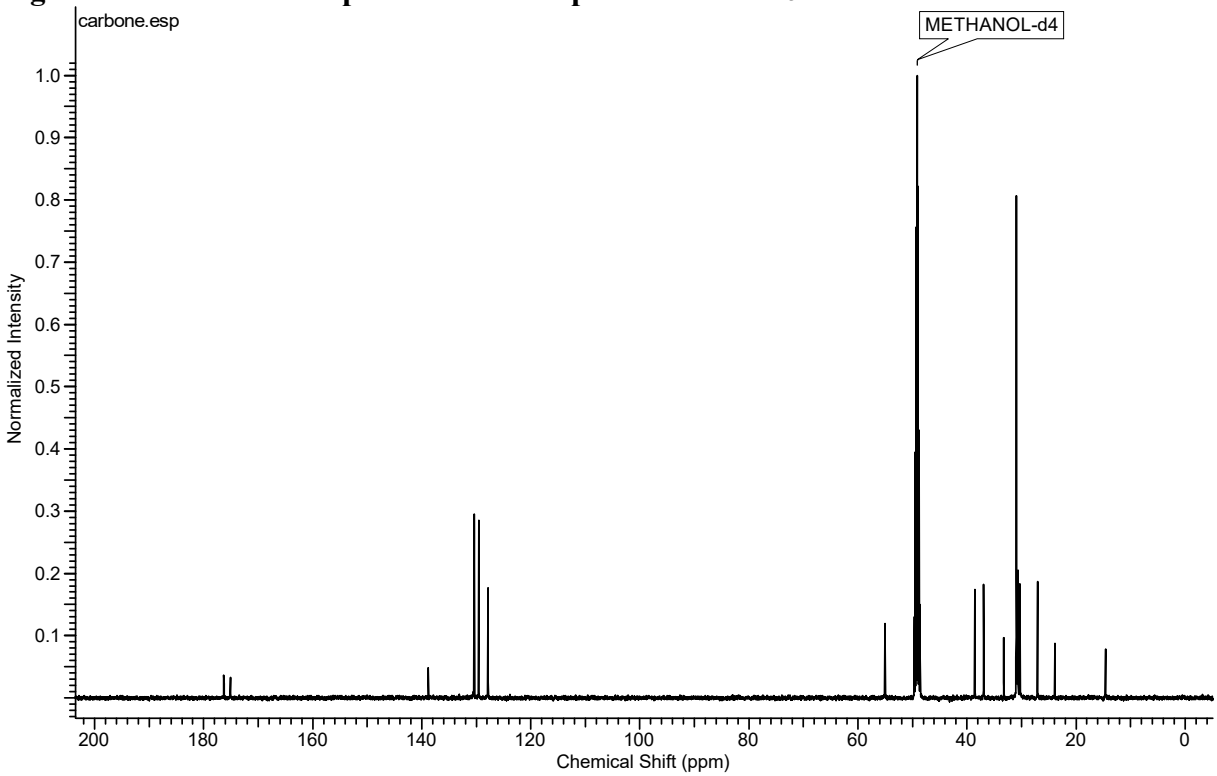

Figure S120. HRMS of compound 33 in MeOH

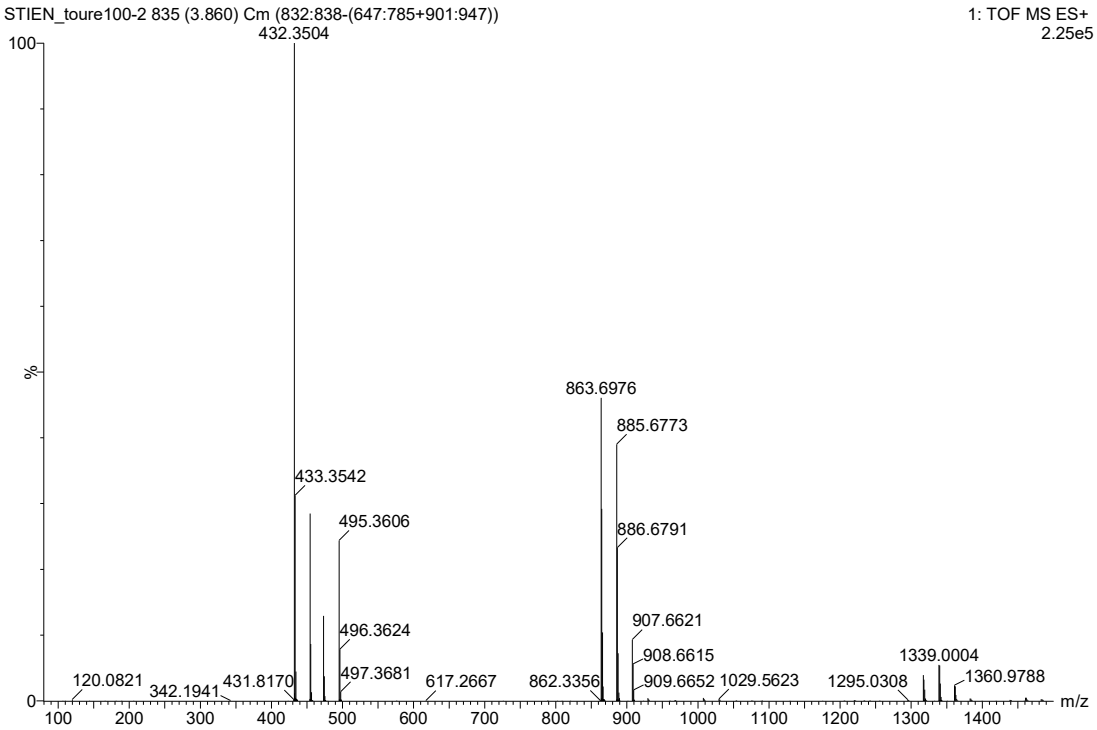

Figure S121. ^{1}H NMR spectrum for compound 34 in CD_3OD

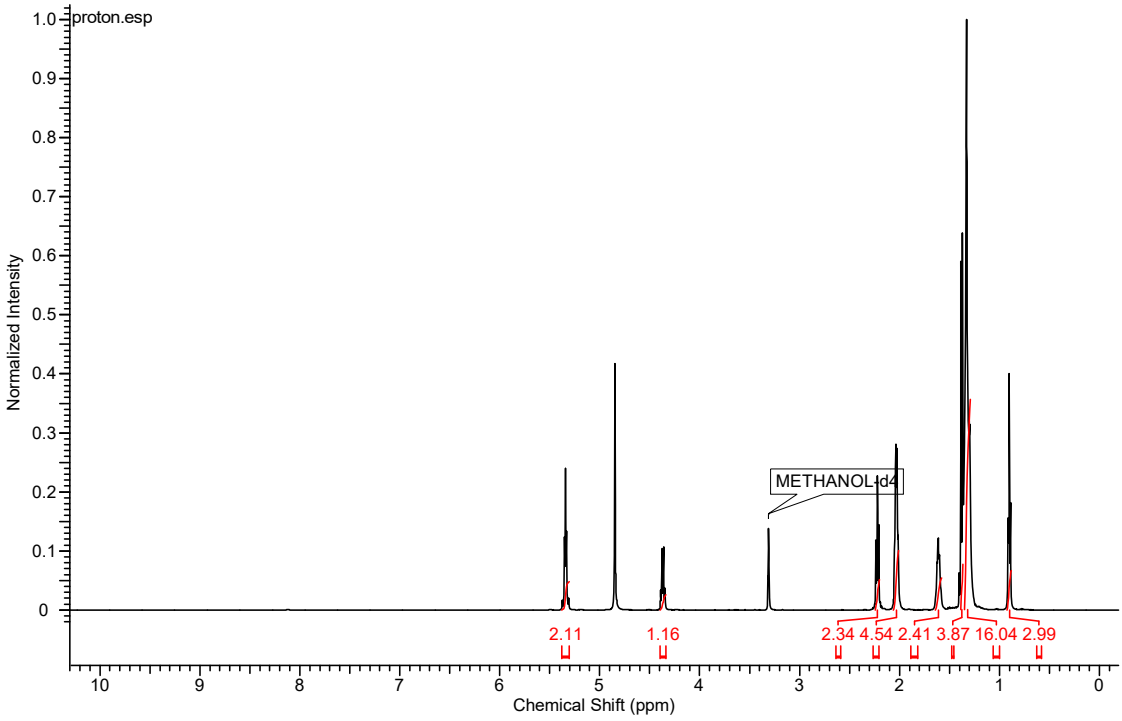

Figure S122. ^{13}C NMR spectrum for compound 34 in CD_3OD

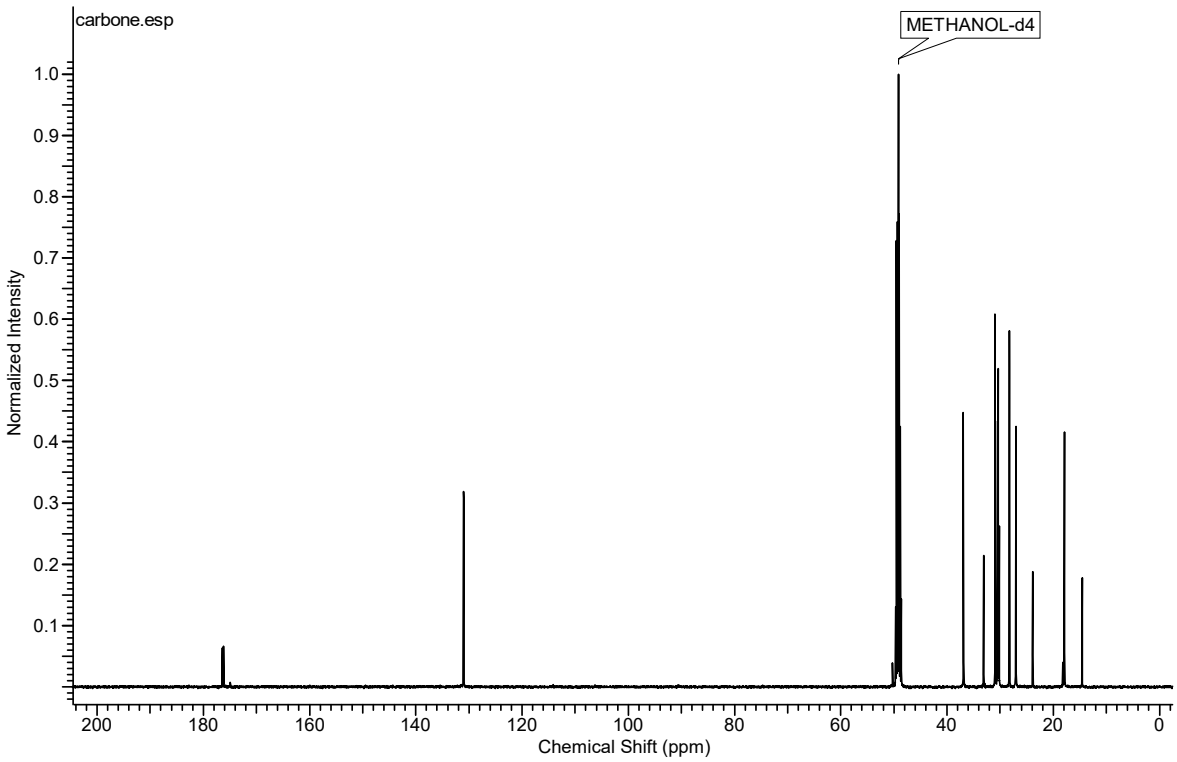

Figure S123. HRMS of compound 34 in MeOH

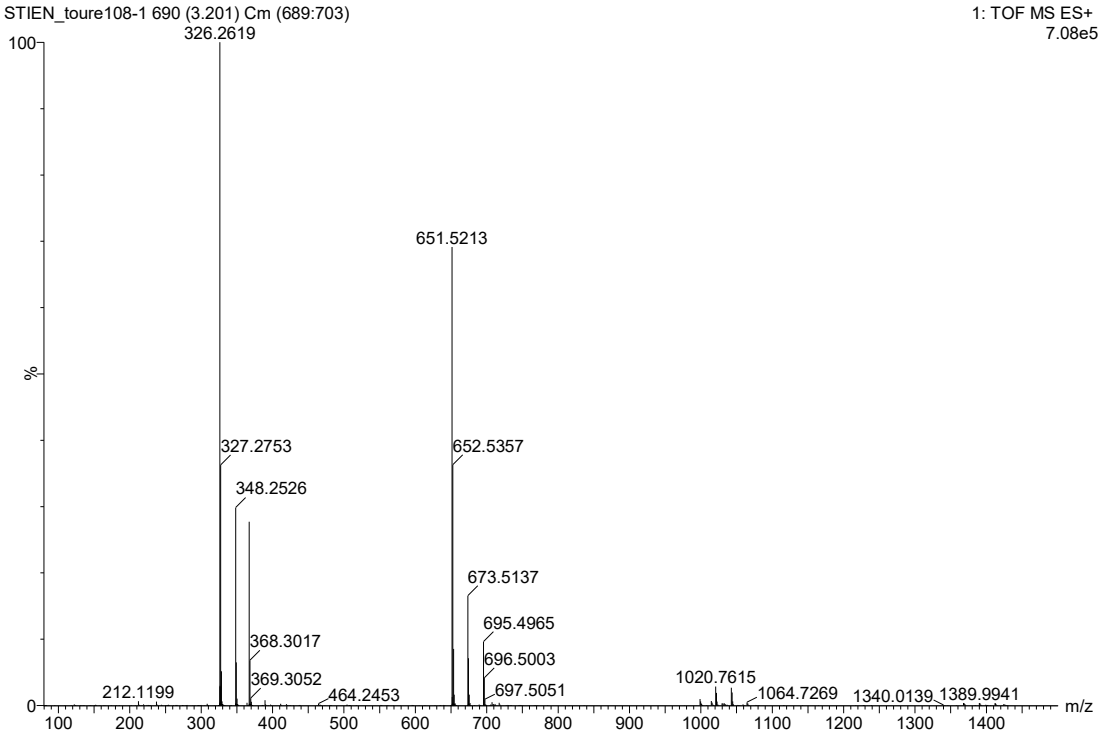

Figure S124. 1H NMR spectrum for compound 35 in CD_3OD

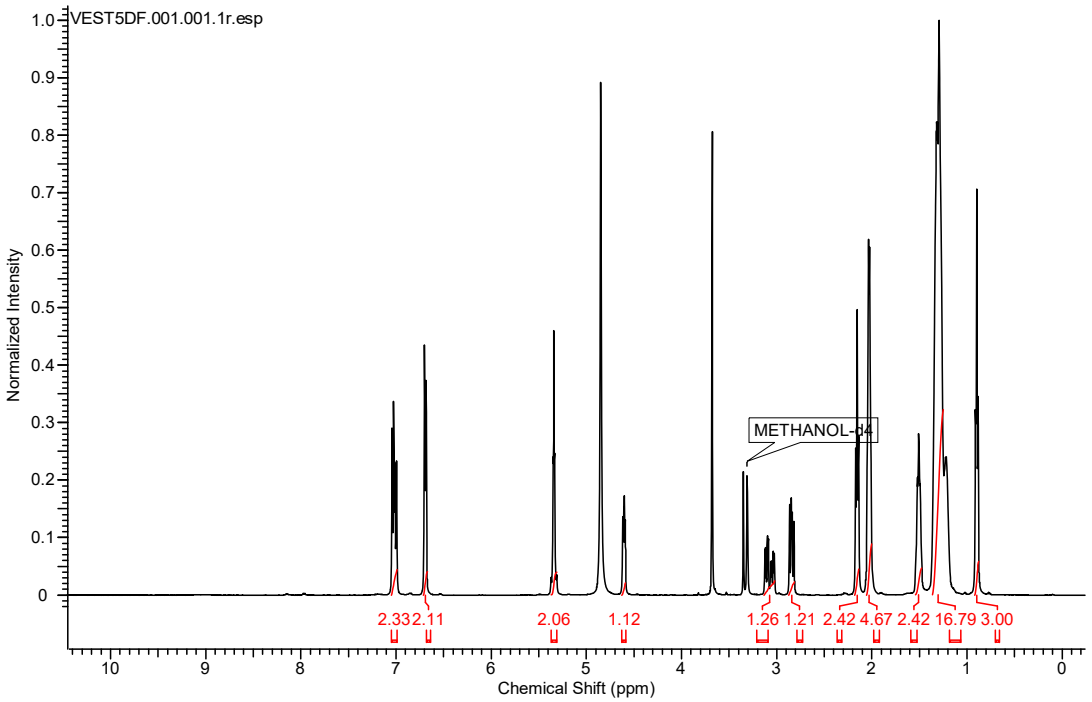

Figure S125. ^{13}C NMR spectrum for compound 35 in CD_3OD

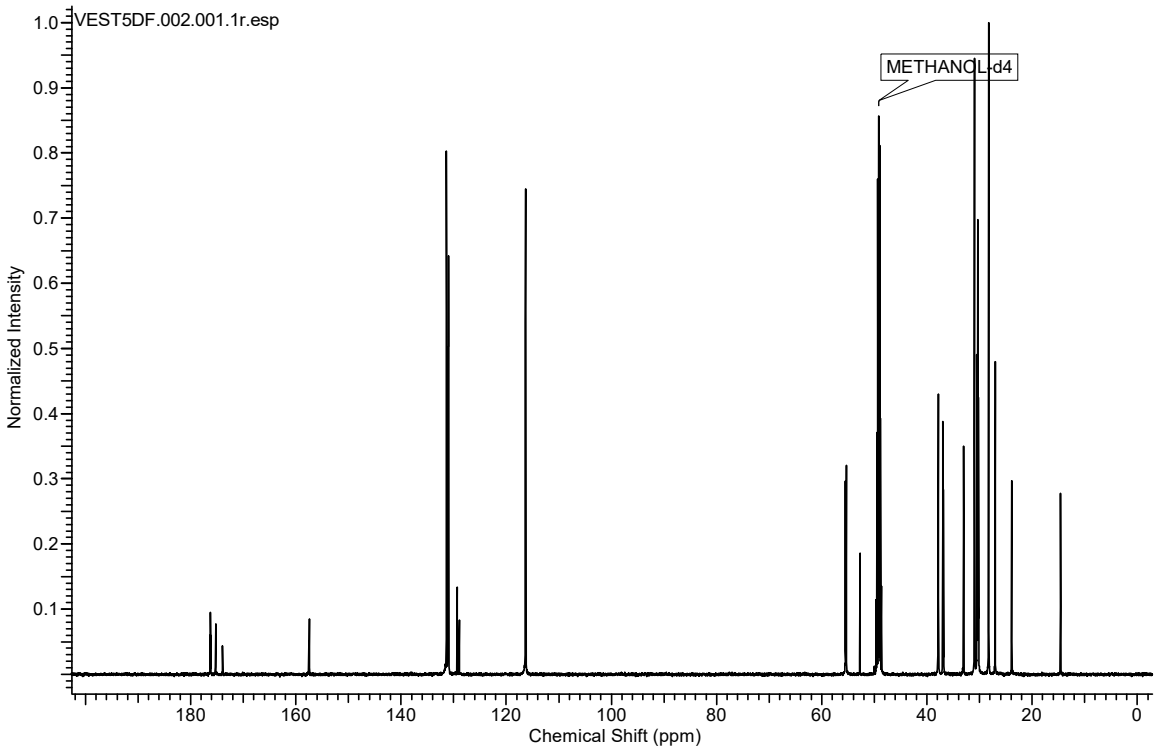

Figure S126. HRMS of compound 35 in MeOH

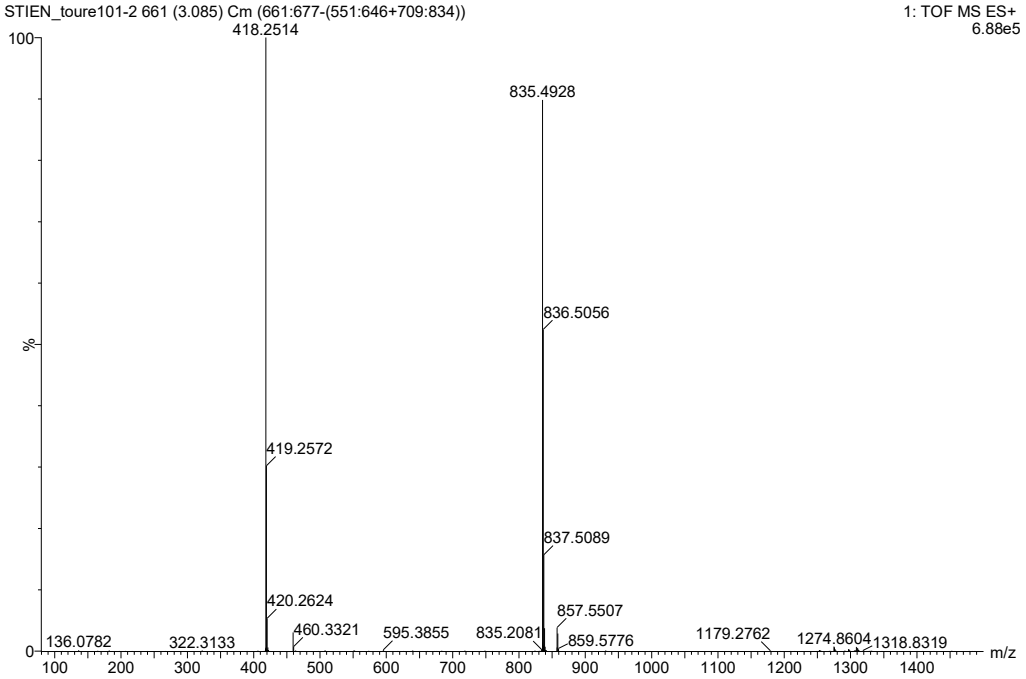

Table S4. Annotation of possible adduct or complexes

Cluster_Pantoea_attributes

SUID	Precursor Intensity in *Pantoea* extract	Precursor mass	Row identity (all IDs)	Row m/z	Row retention time	Molecular formula	Exact mass	RDBE	Mass difference (ppm)	Isotope pattern score	Sirius molecular formula	Phenylalanine typical fragment Exact Mass: 166.09	Phenylalanine methyl ester typical fragment Exact Mass: 180.10	Leucine/Isoleucine typical fragments Exact Mass: 132.10	Leucine/Isoleucine methyl ester typical fragments Exact Mass: 146.12	Valine typical fragments Exact Mass: 118.09
459	3.6793E+09	396.348		396.34750	5.7970	C24H45NO3	395.33994	3.00	0.60	98.40	C24H45NO3	-	-	X	-	-
452	3.3043E+09	370.332		370.33185	5.7350	C22H43NO3	369.32429	2.00	0.60	99.00	C22H43NO3	-	-	X	-	-
460	2.8036E+09	368.321		368.32065	5.3541	C22H41NO3	367.3133	3.00	12.70	-	-	-	-	X	-	-
522	1.6071E+09	342.301		342.30096	5.2237	C20H39NO3	341.29299	2.00	2.10	99.10	C20H39NO3	-	-	X	-	-
464	8.0000E+08	412.343		412.34286	5.2237	C24H45NO4	411.33486	3.00	1.80	97.10	C24H45NO4	-	-	X	-	-
446	6.7868E+08	430.332		430.33170	5.7626	C27H43NO3	429.32429	7.00	0.20	99.30	C27H43NO3	X	-	-	-	-
521	6.1632E+08	382.333		382.33270	5.6377	C23H43NO3	381.32429	3.00	2.90	99.40	C23H43NO3	-	-	-	X	-
543	5.1876E+08	739.656	Complex of 370.33 and 370.33	739.65619	5.7350	-										

506	5.1686E+08	404.316	Compound 22	404.31639	5.6967	C25H41NO3	403.30864	6.00	0.10	96.30	C25H41NO3	X	-	-	-	-
513	4.9354E+08	402.305		402.30524	5.3197	C25H39NO3	401.2939	7.00	12.00	-	-	X	-	-	-	-
541	4.7154E+08	791.687	Complex of 396.347 and 396.347	791.68744	5.7902	-										
490	4.2551E+08	735.634	Complex of 368.321 and 368.321	735.63391	5.3403	-										
454	4.2179E+08	340.286		340.28568	4.8731	C20H37NO3	339.27734	3.00	3.10	96.80	C20H37NO3	-	-	X	-	-
466	3.4560E+08	368.317		368.31683	5.4021	C22H41NO3	367.30864	3.00	2.30	96.80	C22H41NO3	-	-	X	-	-
496	3.2235E+08	446.327		446.32730	5.2579	C27H43NO4	445.31921	7.00	1.80	92.50	C27H43NO4	X	-	-	-	-
480	3.0801E+08	384.348		384.34814	6.0759	C23H45NO3	383.33994	2.00	0.90	96.80	C22H41NO4	-	-	-	X	-
477	2.9037E+08	358.296		358.29568	4.5795	C20H39NO4	357.28791	2.00	1.70	95.80	C20H39NO4	-	-	X	-	-
502	2.7532E+08	376.285		376.28522	5.2237	C23H37NO3	375.27734	6.00	1.50	97.60	C23H37NO3	X	-	-	-	-
514	2.4637E+08	410.364		410.36404	6.1193	C25H47NO3	409.35559	3.00	2.70	98.10	C25H47NO3	-	-	-	X	-
500	2.4420E+08	354.3		354.30032	5.1758	C21H39NO3	353.29299	3.00	0.00	97.50	C21H39NO3	-	-	-	X	-
481	2.3223E+08	356.317		356.31699	5.6377	C21H41NO3	355.30864	2.00	3.00	96.50	C21H41NO3	-	-	X	-	-
453	1.9196E+08	314.27		314.26950	4.6819	C18H35NO3	313.26169	2.00	4.60	96.90	C18H35NO3	-	-	X	-	-

501	1.5699E+08	382.333		382.33270	5.7350	C23H43NO3	381.3254	3.00	2.90	96.00	C23H43NO3	-	-	-	X	-
474	1.5298E+08	384.311		384.31125	4.7437	C22H41NO4	383.30356	3.00	0.90	96.00	C22H41NO4	-	-	-	X	-
483	1.4718E+08	825.672	Complex of 396.3475 and 430.3317 m/z	825.67169	5.7694	-										
511	1.3885E+08	765.672	Complex of 394.3319 and 394.3319 m/z	765.67163	5.7558	-										
461	1.1970E+08	356.317		356.31699	5.4824	C21H41NO3	355.3097	2.00	3.00	97.20	C21H41NO3	-	-	X	-	-
488	1.1755E+08	683.594	Complex of 342.3010 and 342.3010 m/z	683.59442	5.2374	-										
523	1.1663E+08	386.326		386.32635	5.1207	C22H43NO4	385.3191	2.00	0.30	96.90	C22H43NO4	-	-	X	-	-
478	**1.1572E+08**	**392.28**	**Compound 1**	**392.28015**	**4.6271**	**C23H37NO4**	**391.2729**	**6.00**	**1.60**	**97.80**	**C23H37NO4**	**X**	**-**	**-**	**-**	**-**
484	1.0407E+08	799.656	Complex of 370.3318 and 430.3317 m/z	799.65607	5.7558	-										
527	1.0315E+08	773.641	Complex of 370.3318 and 404.3164 m/z	773.64050	5.7281	-										
489	8.5408E+07	342.305		342.30472	5.2992	C20H39NO3	341.29740	2.00	12.90	-	-	-	-	X	-	-
450	8.4230E+07	328.284		328.28455	5.0452	C19H37NO3	327.2772	2.00	0.40	94.50	C19H37NO3	-	-	-	-	X
467	8.1141E+07	398.364		398.36435	6.1410	C24H47NO3	397.357	2.00	3.50	97.50	C24H47NO3	-	-	X	-	-
473	7.7545E+07	416.318		416.31802	5.6760	C26H41NO3	415.3094	7.00	1.20	97.70	C26H41NO3	-	X	-	-	-

475	**6.7081E+07**	**418.295**	**Compound 2**	**418.29517**	**4.7877**	**C25H39NO4**	**417.2875**	**7.00**	**0.00**	**97.60**	**C25H39NO4**	**X**	**-**	**-**	**-**	**-**
456	6.5245E+07	374.27		374.26999	4.8731	C23H35NO3	373.26270	7.00	2.70	97.80	C23H35NO3	X	-	-	-	-
445	6.2314E+07	444.348	Compound 8 / Compound 9	444.34761	6.0674	C28H45NO3	443.3411	7.00	2.60	92.70	C28H45NO3	-	X	-	-	-
504	5.6593E+07	426.358		426.35834	5.6241	C25H47NO4	425.35	3.00	1.20	95.10	C25H47NO4	-	-	-	X	-
536	5.2965E+07	426.297	MZ+2Na-2H+ 43.9639 m/z adduct of 382.3327 m/z	426.29663	5.6377											
493	5.2741E+07	859.656	Complex of 430.3317 and 430.3317	859.65613	5.7558											
505	5.0209E+07	418.332	Compound 4	418.33189	6.0100	C26H43NO3	417.3246	6.00	0.70	98.40	C26H43NO3	-	X	-	-	
498	4.9744E+07	420.313		420.31256	5.1549	C25H41NO4	419.30530	6.00	4.10	96.20	C25H41NO4	X	-	-	-	-
479	4.6746E+07	446.332	MZ+Na-H+ 21.9819 m/z adduct of 368.3206 m/z	446.33212	5.2992											
449	**4.1934E+07**	**402.301**	**Compound 3 / compound *ent*-3**	**402.30092**	**5.3658**	**C25H39NO3**	**401.2938**	**7.00**	**2.00**	**93.40**	**C25H39NO3**	**X**	**-**	**-**	**-**	**-**
447	4.1469E+07	368.317		368.31683	5.6377	C22H41NO3	367.3095	3.00	2.30	93.80	C22H41NO3	-	-	X	-	-
528	3.9023E+07	717.579	Complex of 342.3009 and 376..2875	717.57904	5.2374											
495	3.4215E+07	384.348		384.34814	5.9403	C23H45NO3	383.3408	2.00	2.20	95.10	C23H45NO3	-	-	-	X	-
526	3.3885E+07	354.3		354.30032	5.2923	C21H39NO3	353.2930	3.00	0.00	95.60	C21H39NO3	-	-	-	X	-

519	3.2348E+07	348.253	Compound 22	348.25327	4.7068	C21H33NO3	347.2459	6.00	0.40	95.30	C21H33NO3	X	-	-	-	-
469	3.0608E+07	763.658	Complex of 382.33 and 382.33	763.65814	5.6377											
491	3.0448E+07	390.302	Compound 14	390.30176	5.6024	C24H39NO3	389.2951	6.00	5.40	?	C24H39NO3	-	X	-	-	-
503	2.8560E+07	426.297	MZ+Na-H+ 21.9819 m/z adduct of 404.3167 m/z	426.29755	5.6933											
533	2.7014E+07	412.347		412.34729	5.2992	C24H45NO4	411.3	3.00	12.50	-	-	-	-	X	-	-
512	2.6148E+07	354.305		354.30478	5.2992	C21H39NO3	353.2975	3.00	12.50	-	-	-	-	-	X	-
531	2.3163E+07	807.625	2M+H of 404.3167 m/z	807.62521	5.6886											
494	2.1671E+07	803.602	Complex of 402.3052 and 402.3052 m/z	803.60248	5.3266											
509	2.0780E+07	390.302		390.30237	5.4824	C24H39NO3	389.2951	6.00	5.40	93.6	C24H39NO3	X	-	-	-	-
462	1.9570E+07	424.379		424.37918	6.1706	C26H49NO3	423.37190	3.00	1.50	95.80	C26H49NO3	-	-	X	-	-
532	1.8960E+07	455.422		455.42206	6.1262	-										
472	1.8484E+07	460.343		460.34280	5.6172	C28H45NO4	459.33550	7.00	1.40	90.40	C28H45NO4	-	X	-	-	-
463	1.6858E+07	344.279		344.27927	4.3946	C19H37NO4	343.272	2.00	0.80	95.50	C19H37NO4	-	-	-	-	X
540	1.6769E+07	751.656	Complex of 396.3475 and 356.317 m/z	751.65564	5.7350											

524	1.5413E+07	414.358	MZ+CH3OH 32.0262 m/z adduct of 382.3327 m/z	414.35843	5.6241	C24H47NO4	413.3511	2.00	1.40	92.00	C24H47NO4	-	-	X	-	-
451	1.4940E+07	376.289	MZ+Na-H+ 21.9819 m/z adduct of 354.3048 m/z	376.28894	5.2992	-										
457	1.4074E+07	286.238		286.23843	4.1356	C16H31NO3	285.2311	2.00	2.50	95.70	C16H31NO3	-	-	X	-	-
517	1.3691E+07	767.689	Complex of 384.3481 and 384.3481 m/z	767.68866	6.0691											
486	1.2397E+07	412.285	MZ+2Na-2H+ 43.9639 m/z adduct of 368.3206 m/z	412.28497	5.3884											
535	1.1930E+07	429.406		429.40601	6.0691	-										
485	1.0689E+07	412.28	MZ+2Na-2H+ 43.9639 m/z adduct of 368.3206 m/z	412.28055	5.4021											
516	8.4877E+06	370.296		370.29611	4.5659	C21H39NO4	369.28880	3.00	2.40	94.20	C21H39NO4	-	-	X	-	-
476	8.0609E+06	356.28		356.27963	4.2648	C20H37NO4	355.2723	3.00	0.10	95.60	C20H37NO4	-	-	-	-	X
510	7.9807E+06	369.298	MZ+Na-H+ 21.9819 m/z adduct of 347.3153 m/z	369.29771	5.5360											
499	7.1568E+06	418.332		418.33240	5.9256	C26H43NO3	417.3246	6.00	0.70	98.40	C26H43NO3	-	X	-	-	-
455	6.9899E+06	312.253		312.25333	4.4015	C18H33NO3	311.246	3.00	0.10	95.00	C18H33NO3	-	-	X	-	-
470	6.5649E+06	300.253		300.25281	4.4909	C17H33NO3	299.246	2.00	0.10	95.10	C17H33NO3	-	-	-	-	-
537	6.2433E+06	382.294		382.29422	4.3014	C22H39NO4	381.28690	4.00	2.60	94.10	C22H39NO4	-	-	X	-	-

448	6.0605E+06	366.301		366.30118	4.1892	C22H39NO3	365.2939	4.00	2.50	94.00	C22H39NO3	-	-	-	-	-
518	5.2887E+06	819.721	Complex of 410.3640 and 410.3640 m/z	819.72046	6.1193											
465	5.0036E+06	330.264		330.26404	4.0308	C18H35NO4	329.2567	2.00	0.30	96.10	C18H35NO4	-	-	X	-	-
458	4.2644E+06	320.222		320.22226	4.1650	C19H29NO3	319.21540	6.00	2.10	95.60	C19H29NO3	X	-	-	-	-
482	4.1600E+06	398.364		398.36435	6.2616	C24H47NO3	397.357	2.00	3.50		C24H47NO3	-	-	X	-	-
468	4.1596E+06	412.379		412.37878	6.4385	C25H49NO3	411.3719	2.00	1.60		C25H49NO3	-	-	-	X	
539	3.8162E+06	428.312	MZ+2Na-2H+ 43.9639 m/z adduct of 384.3481 m/z	428.31189	5.9403											
515	3.5006E+06	463.39	2M+Na of 418.3314 m/z	463.38972	6.0216											
530	3.1346E+06	489.405	M+2Na adduct of 444.3472 m/z	489.40532	6.0579											
542	3.0963E+06	458.364		458.36368	6.1410	C29H47NO3	457.3564	7.00	1.80	90.50	C29H47NO3	x	-	-	-	-
492	1.7258E+06	435.359	M+2Na of 390.3011 m/z	435.35910	5.5954											
497	0.0000E+00	831.631	2M+H of 416.31 m/z	831.63123	5.6655											
507	0.0000E+00	947.779	2M+H of 474.3936 m/z	947.77942	6.5812											
508	0.0000E+00	779.595	2M+H of 390.3011 m/z	779.59497	5.5877											

520	0.0000E+00	695.499	2M+H of 348.2533 m/z	695.49933	4.7258											
525	0.0000E+00	803.593	2M+H of 402.3006 m/z	803.59332	5.3191											
529	0.0000E+00	887.687	2M+H adduct of 444.3473 m/z	887.68680	6.0596											
534	0.0000E+00	835.655	2M+H of 418.3314 m/z	835.65515	5.9878											
538	0.0000E+00	891.719	2M+H adduct of 446.3633 m/z	891.71893	6.3044											
471	0.0000E+00	474.394	Compound 5	474.39355	6.5731	C30H51NO3	473.3863	6.00	1.30	98.50	C30H51NO3	-	X	-	-	-
487	0.0000E+00	446.363	Compound 10	446.36331	6.3044	C28H47NO3	445.35600	6.00	0.90	99.00	C28H47NO3	-	X	-S	-	-

Table S5. Optical rotation of all synthetic compounds

Compound	Optical rotation $[\alpha]_D^{20}$ (c 0.1, MeOH)
(L)-methyl (*Z*)-hexadec-9-enoylphenylalaninate (3-OMe)	+54
(L)-methyl palmitoylphenylalaninate (4)	+48
(L)-methyl icosanoylphenylalaninate (5)	+56
(L)-methyl dodecanoylphenylalaninate (6)	+78
(L)-methyl tetradecanoylphenylalaninate (7)	+97
(L)-methyl oleoylphenylalaninate (8)	+60
(L)-methyl (E)-octadec-9-enoylphenylalaninate (9)	+58
(L)-methyl stearoylphenylalaninate (10)	+63
(D)-methyl palmitoylphenylalaninate (11)	–67
(D)-methyl (*Z*)-hexadec-9-enoylphenylalaninate (*ent*-3-OMe)	–49
(D)-methyl icosanoylphenylalaninate (12)	–50
(D)-methyl dodecanoylphenylalaninate (13)	–49
(D)-methyl tetradecanoylphenylalaninate (14)	–87
(D)-methyl oleoylphenylalaninate (15)	–55
(D)-methyl-(*E*)-octadec-9-enoylphenylalaninate (16)	–83
(D)-methyl stearoylphenylalaninate (17)	–46
(L)-methyl (Z)-hexadec-9-enoylalaninate (18)	–1
(L)-methyl (*Z*)-hexadec-9-enoyltyrosinate (19)	+69
(L)-palmitoylphenylalanine (20)	+66
(L)-(*Z*)-hexadec-9-enoylphenylalanine (3)	+49
(L)-icosanoylphenylalanine (21)	+40
(L)-dodecanoylphenylalanine (22)	+67
(L)-tetradecanoylphenylalanine (23)	+80
(L)-oleoylphenylalanine (24)	+56
(L)-(*E*)-octadec-9-enoylphenylalanine (25)	+54
(L)-stearoylphenylalanine (26)	+49
(D)-palmitoylphenylalanine (27)	–54
(D)-(Z)-hexadec-9-enoylphenylalanine (*ent*-3)	–49
(D)-icosanoylphenylalanine (28)	–22
(D)-dodecanoylphenylalanine (29)	–68
(D)-tetradecanoylphenylalanine (30)	–64
(D)-oleoylphenylalanine (31)	–41
(D)-(*E*)-octadec-9-enoylphenylalanine (32)	–70
(D)-stearoylphenylalanine (33)	–50
(L)-(*Z*)-hexadec-9-enoylalanine (34)	+1
(L)-(Z)-hexadec-9-enoyltyrosine (35)	+53