Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Interaction of Acetonitrile with Trifluoromethanesulfonic Acid: Unexpected Formation of a Wide Variety of Structures

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Electronic Supplementary Information

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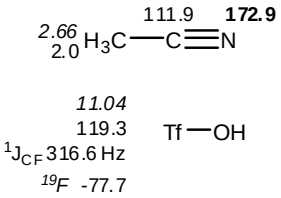
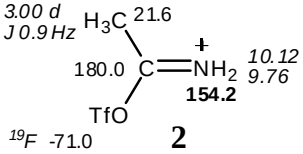
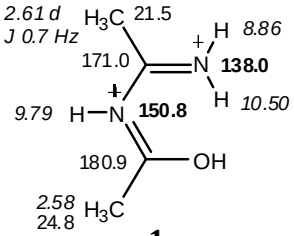
Chemical shifts of MeCN, TfOH (molar ratio 1:14) and of the products of their interaction.

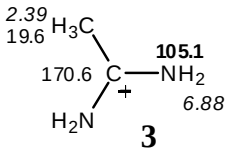
^{1}H chemical shifts are given in italics, ^{13}C in ordinary font, ^{15}N in bold face.

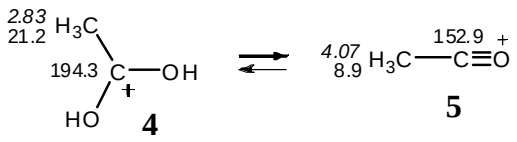
Here and further the chemical shifts of acetonitrile are in fact those of its mixture with the protonated form, the NMR signals are averaged due to a rapid exchange.

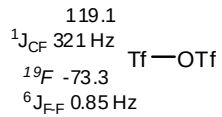


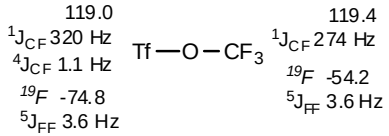


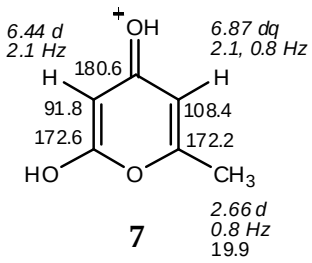


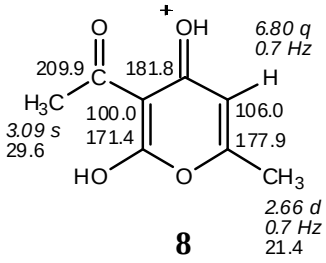












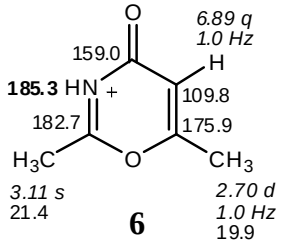
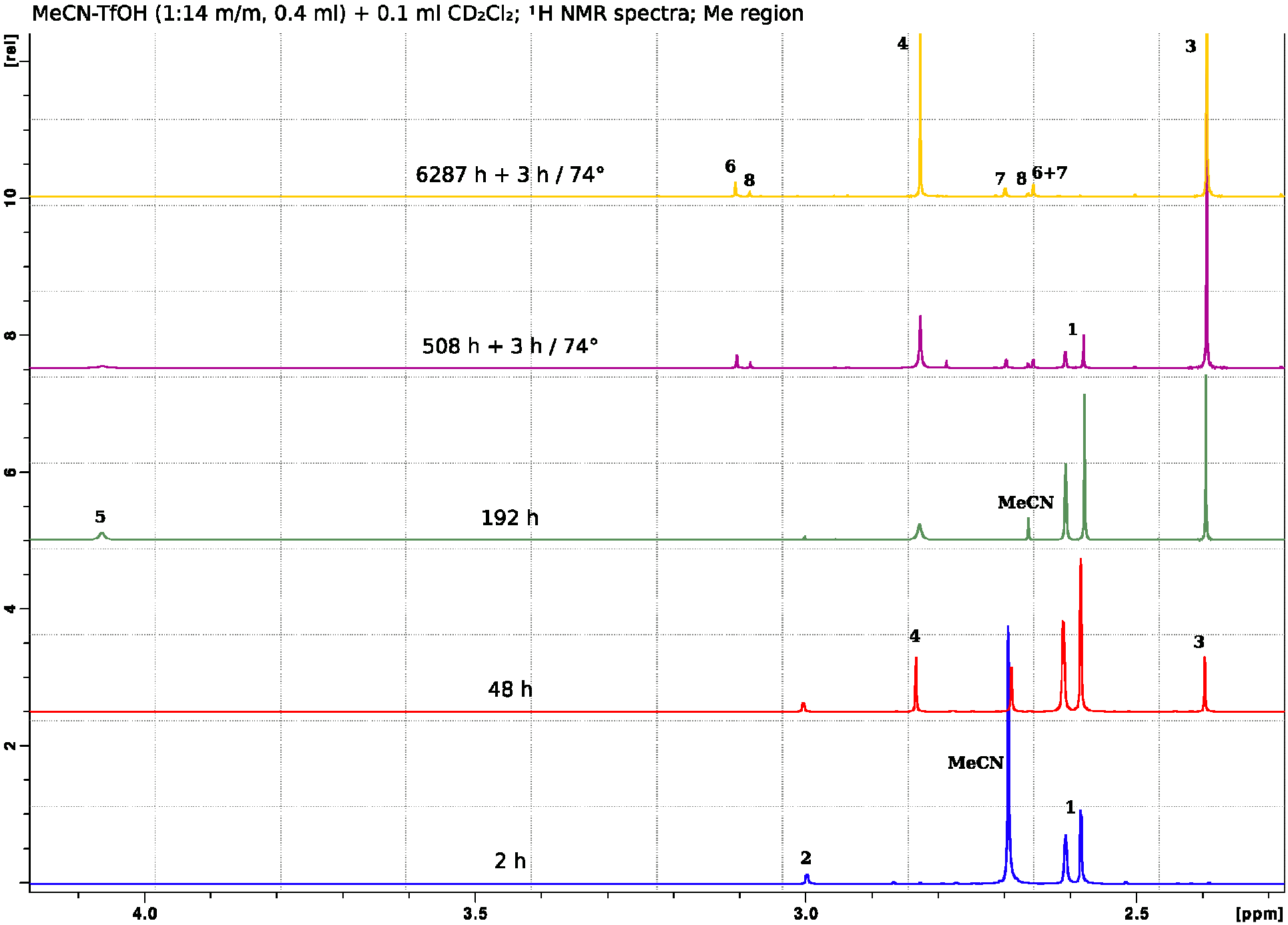
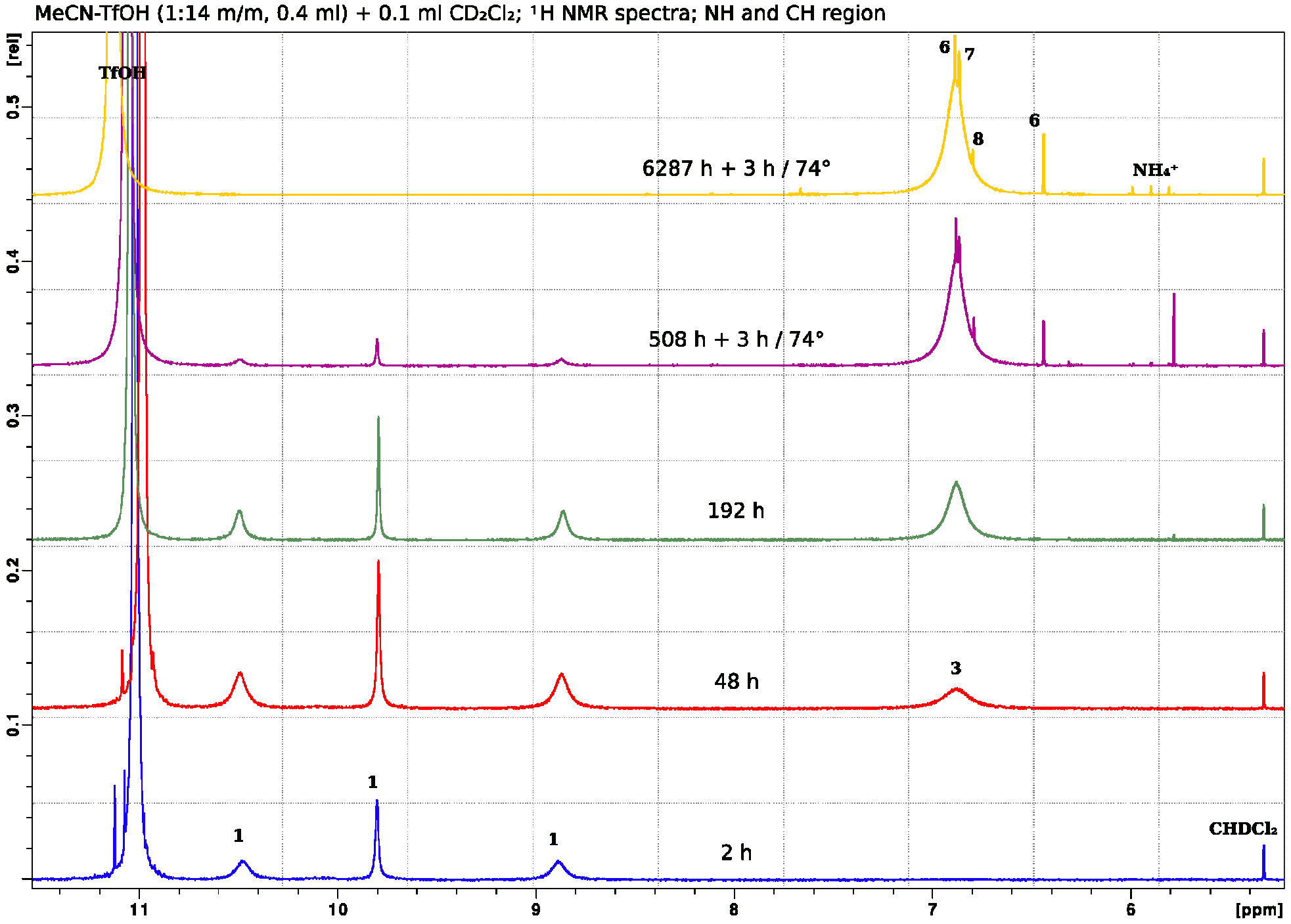


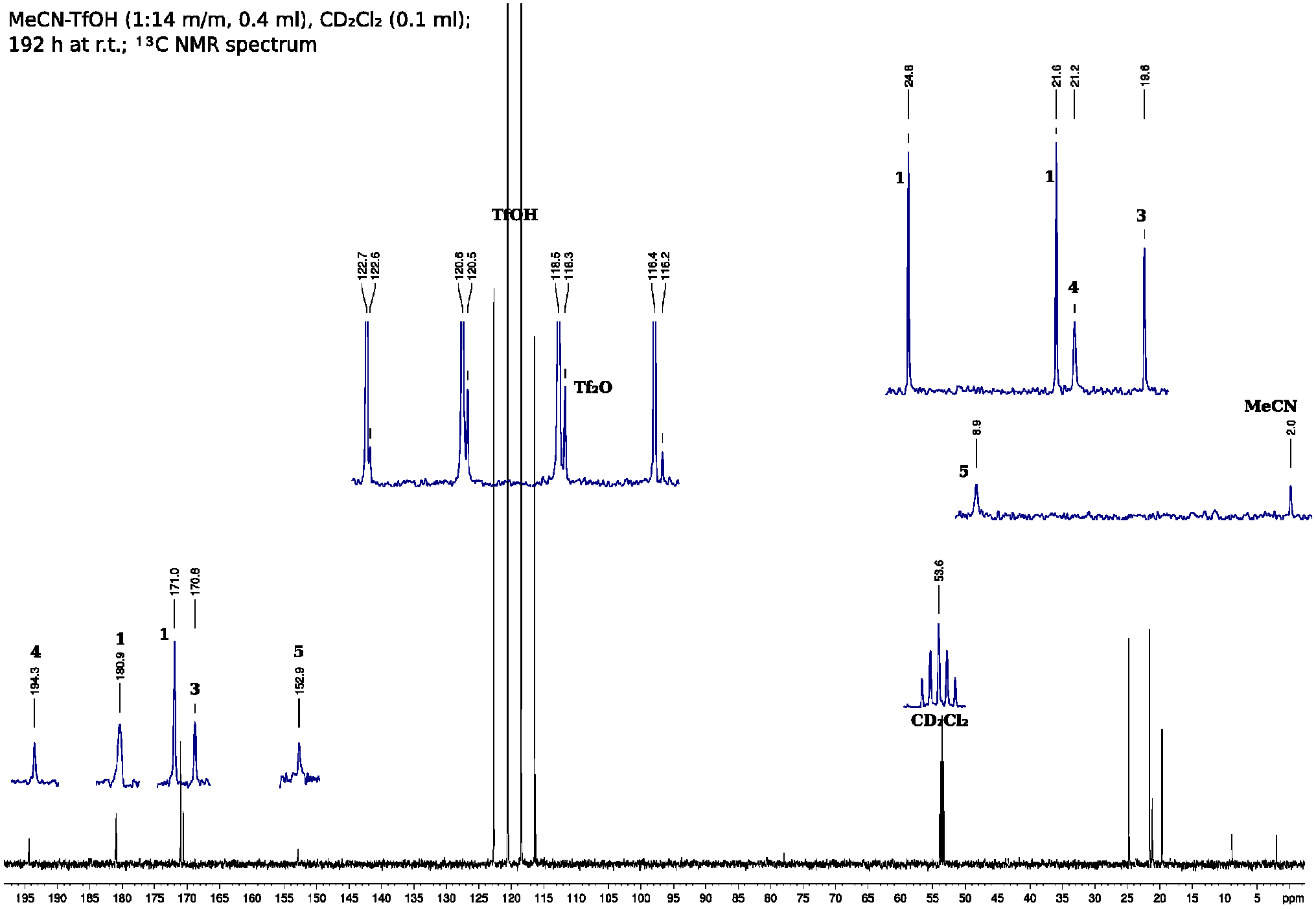
Table 1. Products of the interaction of MeCN with TfOH (mol. ratio 1:14).
Given in italics are logarithms of diffusion coefficients (m^2/s) derived from the DOSY spectra.

Time (h) [e]	MeCN	**1** [a]	**2** [a]	**3** [a]	**4** [a]	**5** [a]	**6**	**7**	**8**	sum	Tf_2O [b]	CF_3OTf [b]
0.25	84.7	11.5	0.9							97.1		
2.0	62.5	31.8	2.9	0.2	0.2					97.2	15	
48	10	66.5	3.0	9.0	9.3	0.03				97.8	35	
171	4.5	49.3	1.2	20.9	14.0	7.4				97.2	36	
192	3.8	47.5	1.0	22.8	13.8	9.0	0.4			98.3	40.7	
^{1}H DOSY	*-9.36*	*-9.56*	*-9.52*	*-9.42*	*-9.45*	*-9.45*	*-9.56*					
215											40.8	1.5
^{19}F DOSY [c]											*-9.24*	*-9.16*
247	2.9	42.5	0.7	26.3	13.6	11.5	1.0			98.5		
317+1/74º	1.3	23.2	0	37.7	20.0	5.3	4.4	1.5	2.3	95.6	36.6	4.5
335+3/74º	0	12.4		42.9	20	4.3	6.9	4.0	6.2	95.8	31.2	8.8
508+3/74º		10.5		42.8	20.6	3.7	7.3	4.2	7.3	96.4		
1568+3/74º		5.7		46.1	24.3	1.6	7.3	4.0	8.6	97.6	25.0	13.8
^{1}H DOSY [d]		*-9.64*		*-9.53*	*-9.55*	*-9.55*	*-9.62*	*-9.60*	*-9.57*			
5572+3/74º		0.5		47.7	29.0	0	7.3	3.3	9.0	96.8	12	21.6
6287+3/74º		0		47.2	29.0		7.0	2.8	9.1	95.1	9.5	23.1
^{1}H DOSY				*-9.39*	*-9.43*		*-9.53*	*-9.47*	*-9.46*			

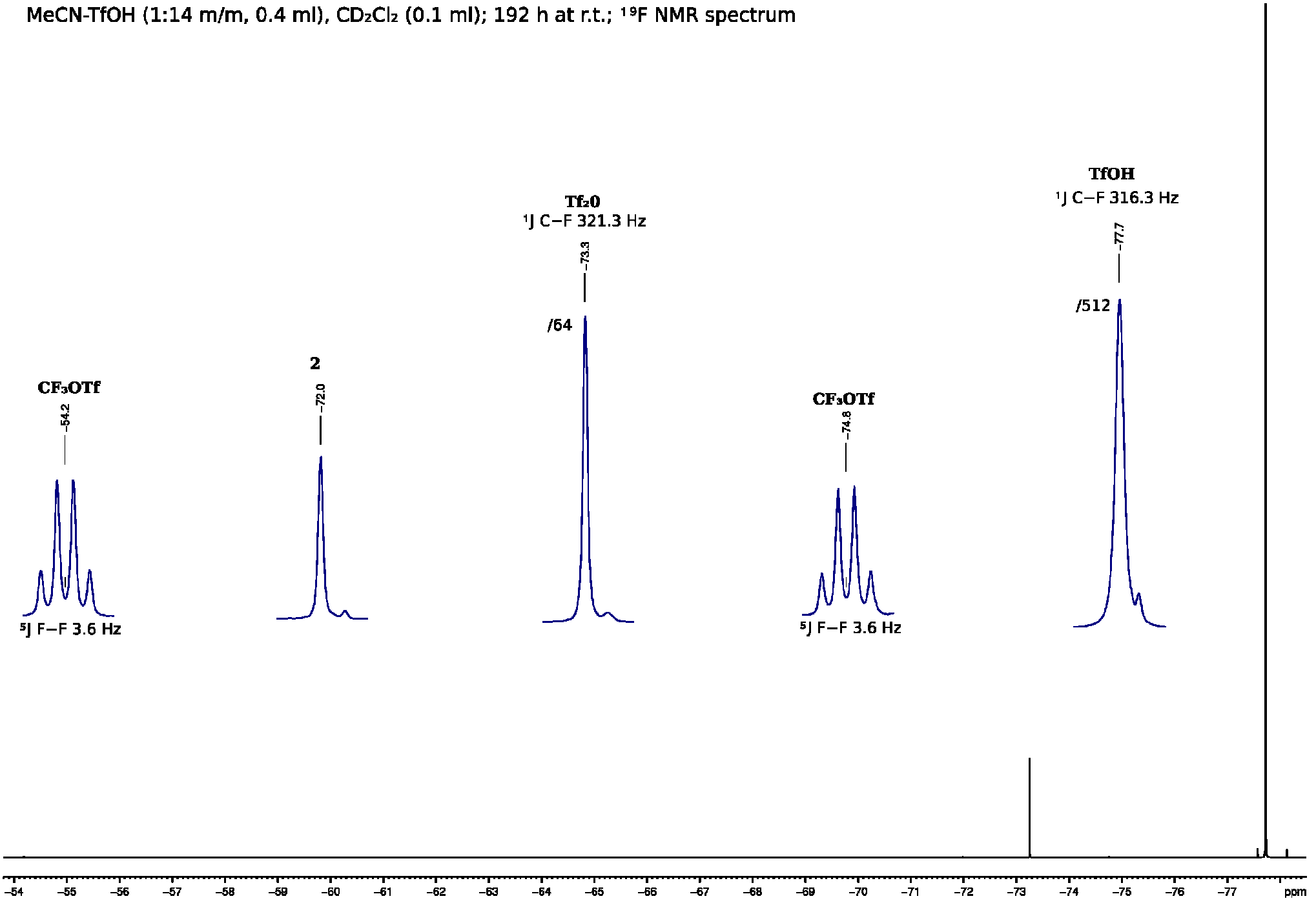
[a] Percentage of the acetonitrile turned into the corresponding product as determined from the ^{1}H NMR spectra.
[b] Molar part (%) relative to the initial quantity of acetonitrile.
[c] For TfOH lg D = -9.37 (from ^{19}F DOSY).
[d] At –7 ºC.
[e] In Fig. 1 of the paper an hour at 74 ºC was set equal to 300 hours at room temperature



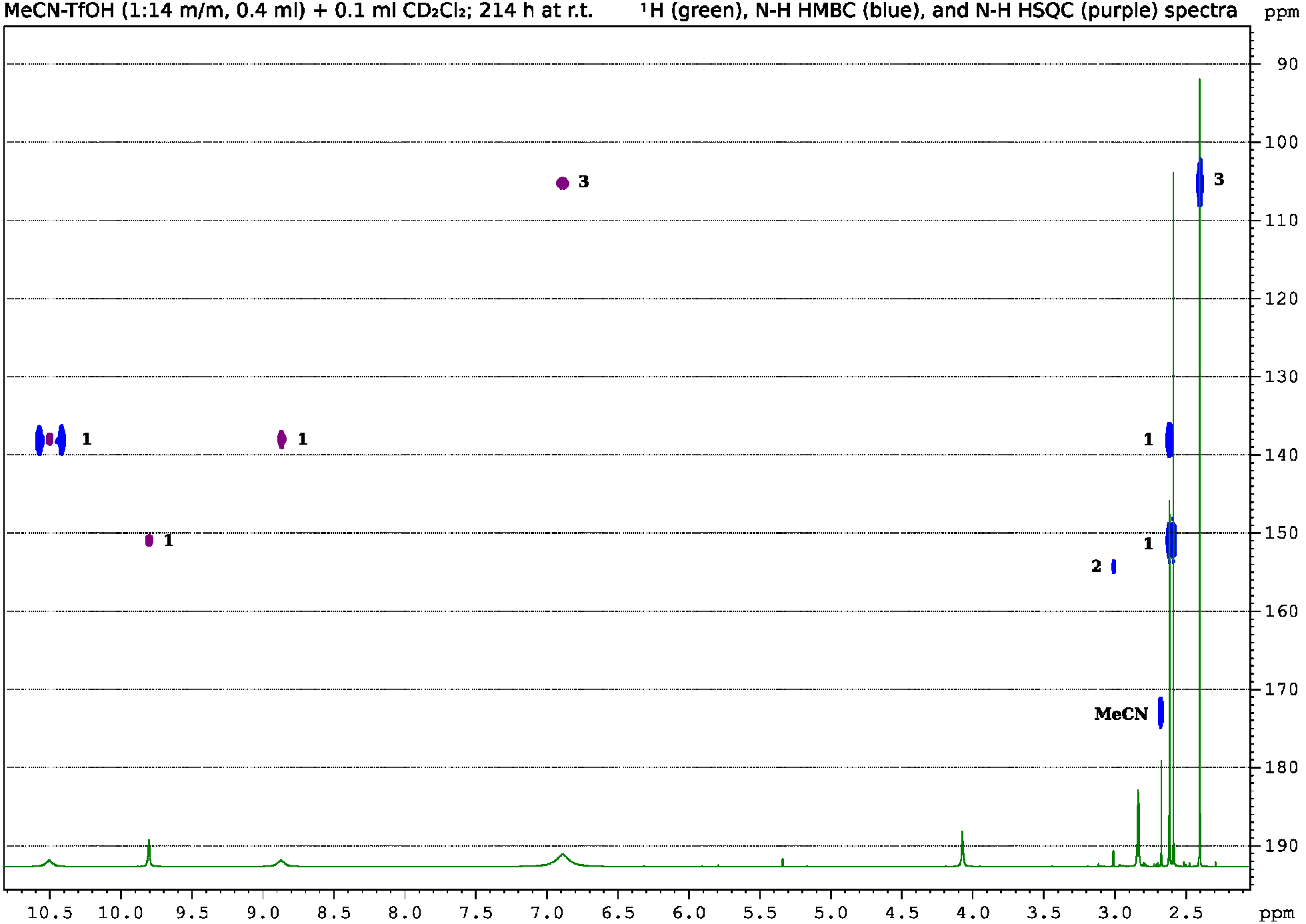




MeCN-TfOH (1:14 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml); 192 h at r.t.; ^{19}F NMR spectrum

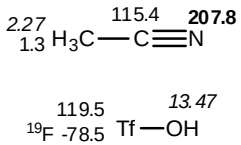


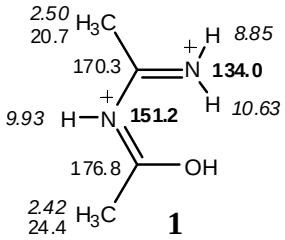
MeCN-TfOH (1:14 m/m, 0.4 ml) + 0.1 ml CD_2Cl_2; 214 h at r.t. ^1H (green), N-H HMBC (blue), and N-H HSQC (purple) spectra



Chemical shifts of MeCN, TfOH (molar ratio 1:2) and of the products of their interaction.

^{1}H chemical shifts are given in italics, ^{13}C in ordinary font, ^{15}N in bold face.





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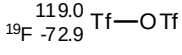

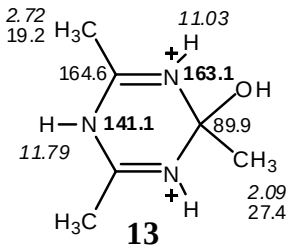

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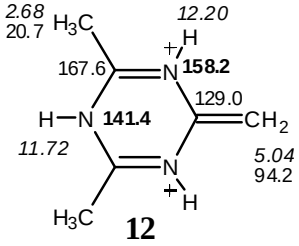

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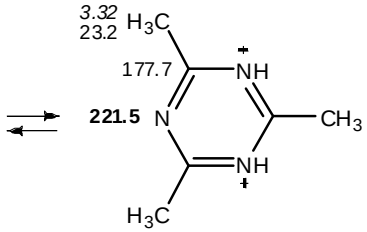

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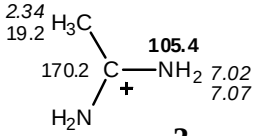

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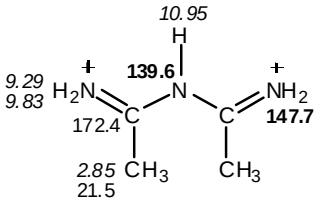

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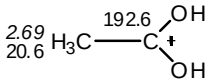

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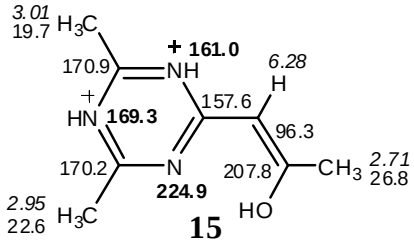

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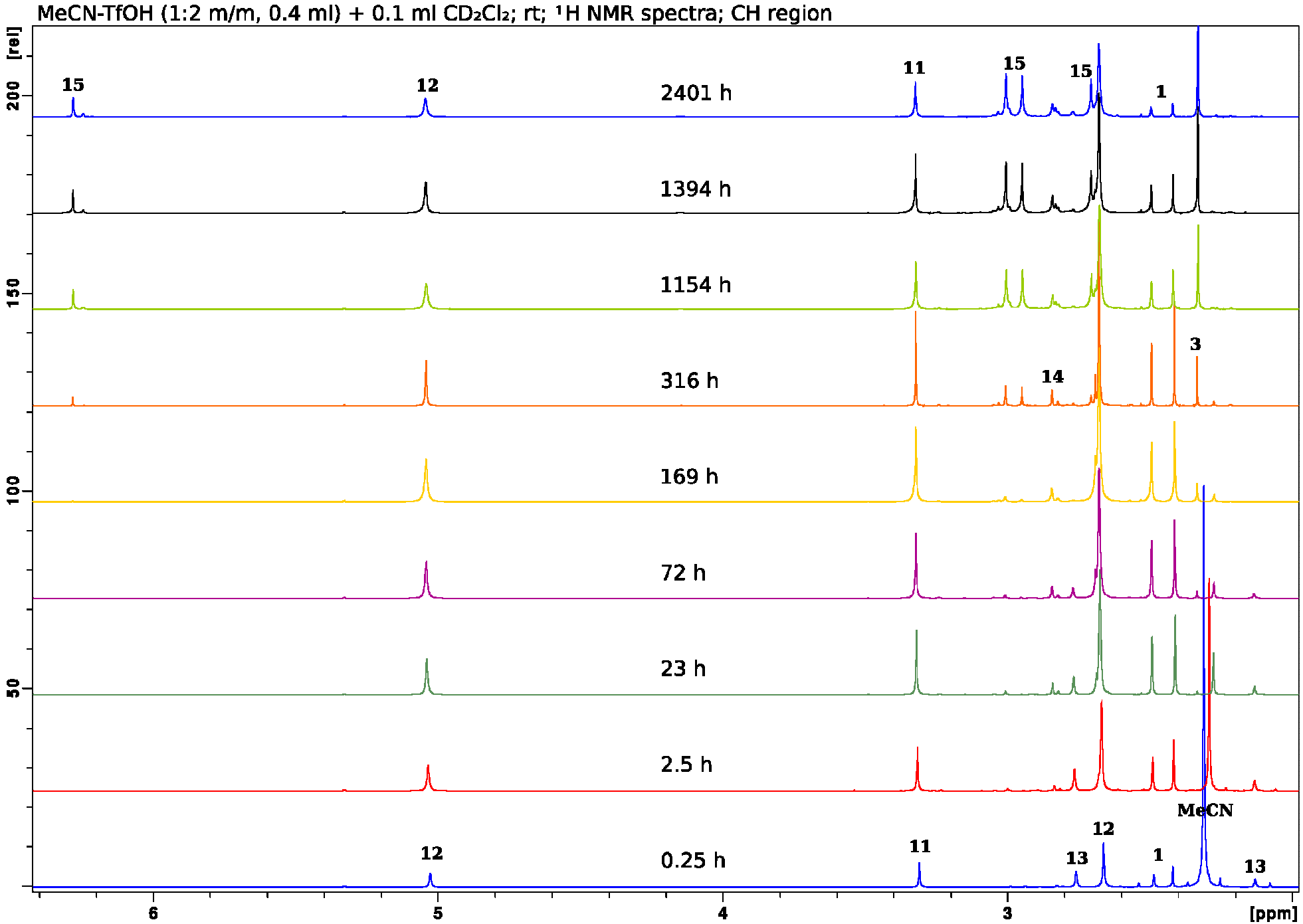
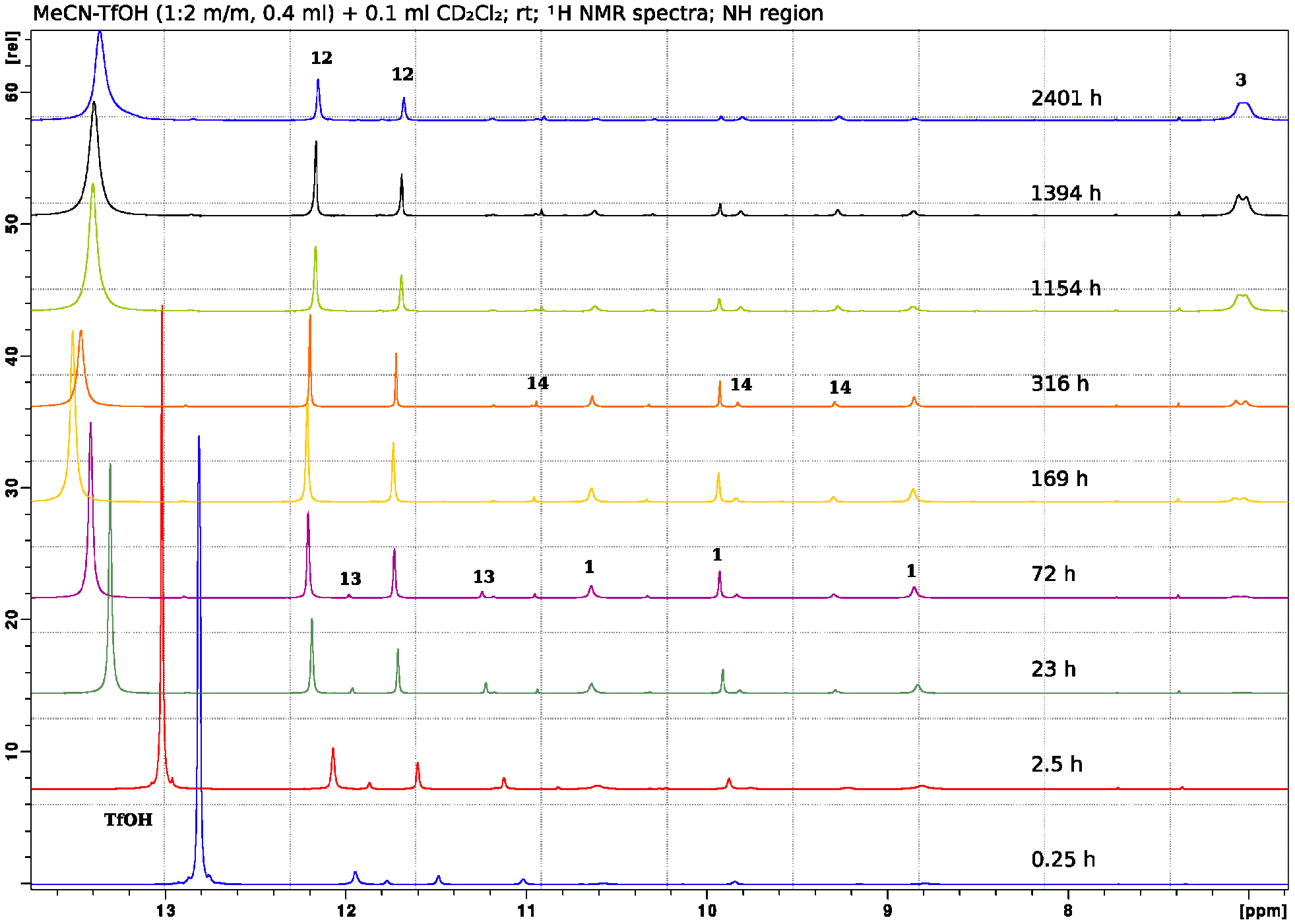
Table 2. Products of the interaction of MeCN with TfOH (mol. ratio 1:2).

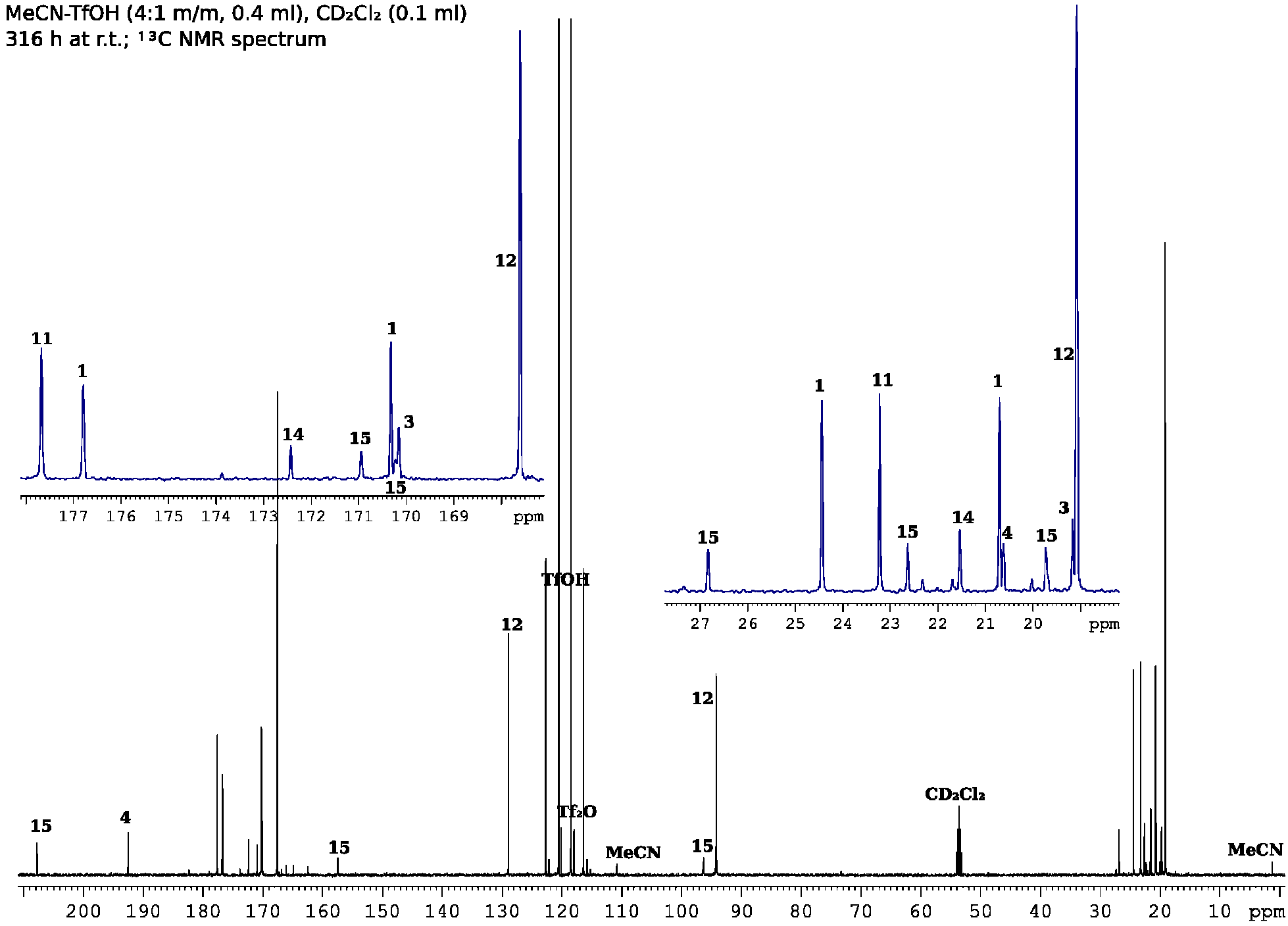
Given in italics are logarithms of diffusion coefficients (m^2/s) derived from the DOSY spectra.

Time (h)	MeCN	**12**[a]	**1**[a]	**13**[a]	**11**[a]	**4**[a]	**14**[a]	**3**[a]	**15**[a]	sum	Tf_2O[b]
0.25	70.3	12.9	4.6	4.6	3.4	0.3	0.3			96.4	2.6
^{1}H DOSY[c]	*-9.60*	*-9.70*	*-9.66*	-9.70	*-9.70*						
2.5	30.5	33.4	12.4	8.0	7.3	1.2	1.0			93.7	
23	7.6	46.5	19.2	6.4	11.0	2.4	1.9			94.9	9.7
26	6.7	47.3	19.5	6.2	11.3	2.5	2.1	0.0		95.5	
72	2.8	50.9	19.8	4.0	12.0	3.3	2.4	0.8	0.0	96.0	
169	1.3	53.6	18.3		12.5	3.8	2.5	1.9	1.5	95.4	
316	0.7	48.1	15.5		11.1	3.0	2.4	3.2	10.4	94.4	7.9
^{1}H DOSY	*-10.02*	*-10.56*	*-10.19*		*-10.51*		*-10.52*	*-10.10*	*-10.50*		
1154	0.0	36.0	8.3		7.9	2.0	2.6	7.1	26.5	90.3	
1394		33.8	7.2		7.7	1.9	2.9	8.0	28.5	90.0	6.2
2401		28.6	3.4		6.3	0.9	2.8	9.6	35.7	87.3	

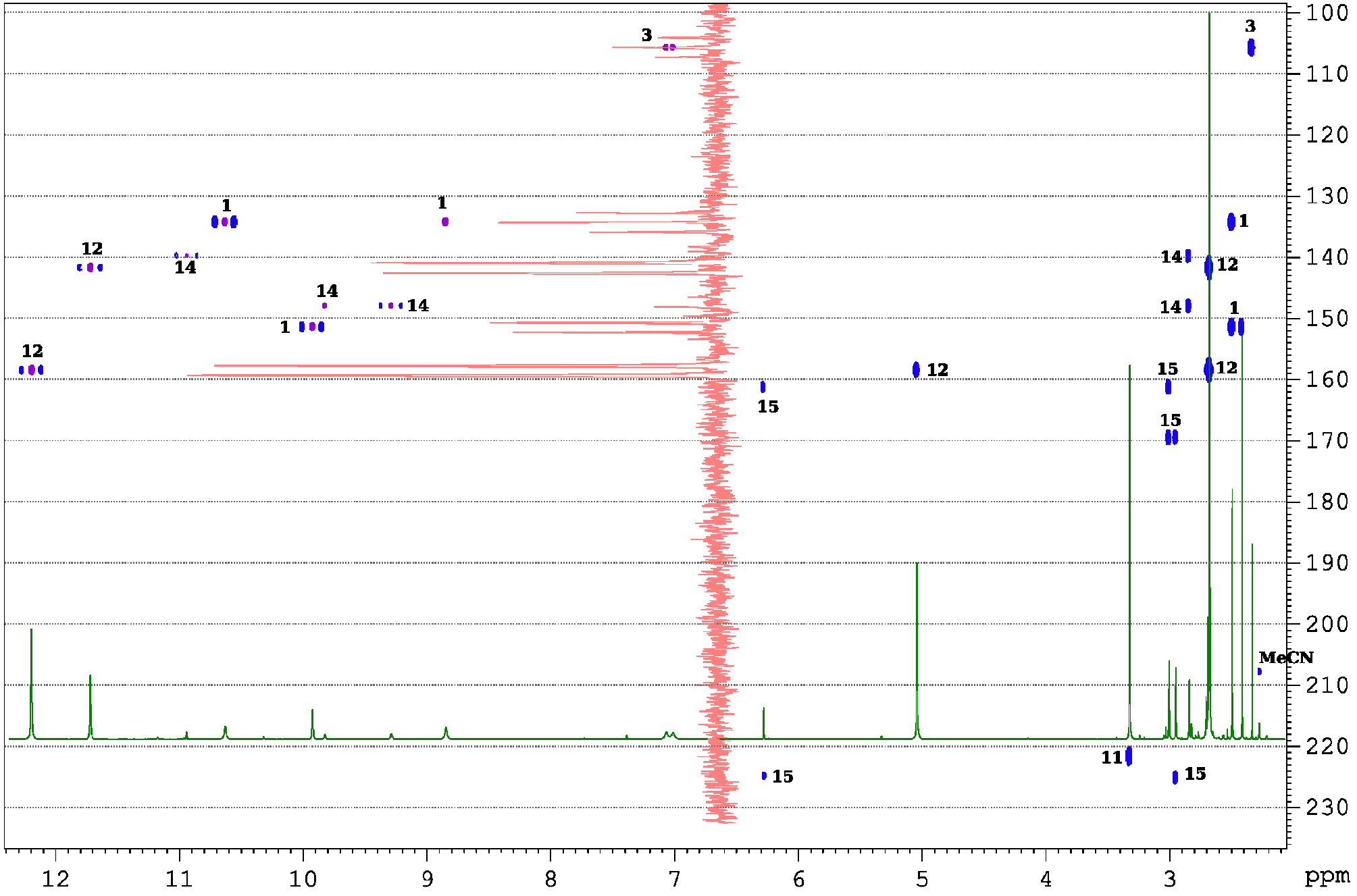
[a] Percentage of the acetonitrile turned into the corresponding product as determined from the ^{1}H NMR spectra.
[b] Molar part (%) relative to the initial quantity of acetonitrile.
[c] At –7°C.

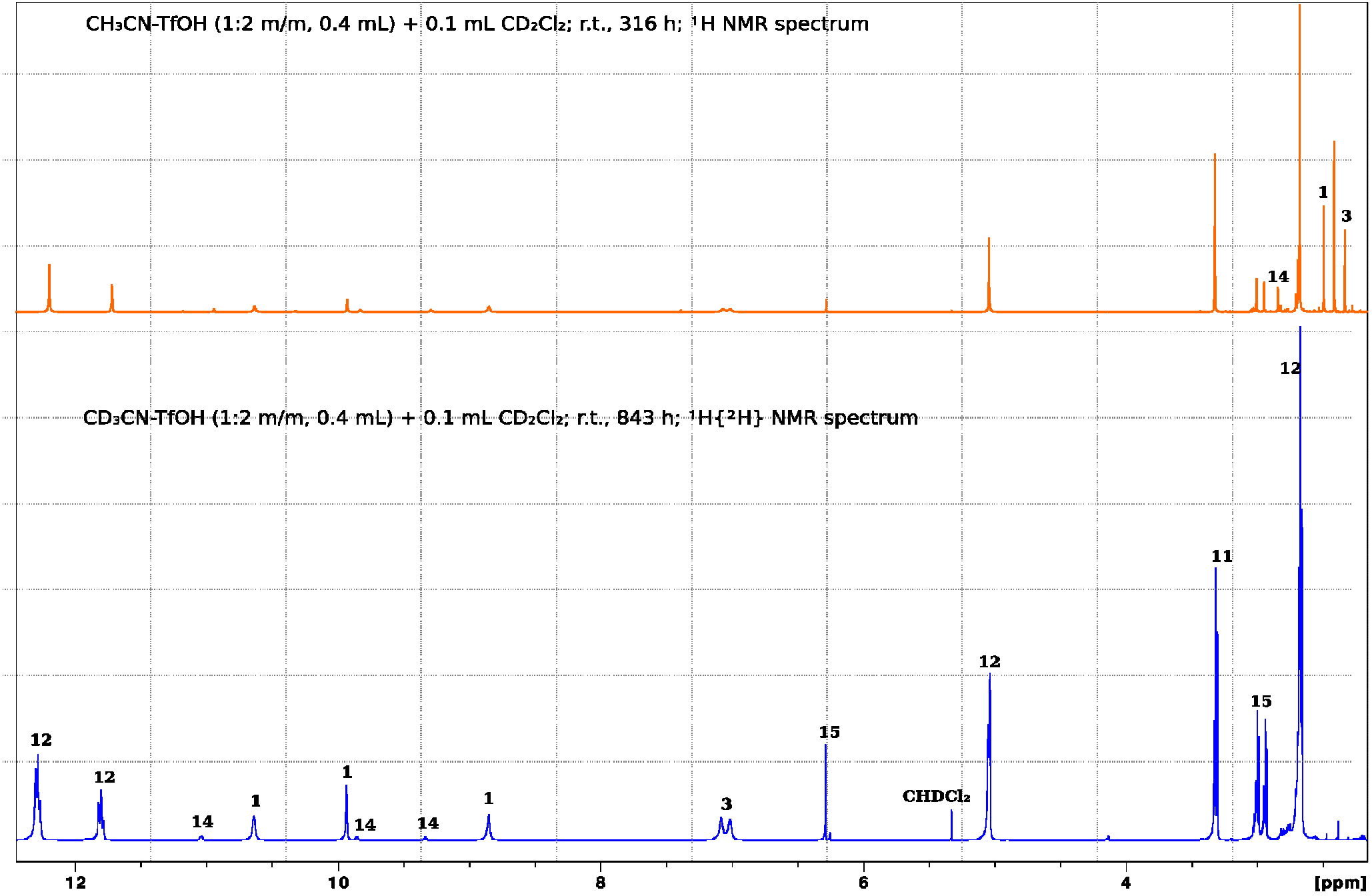






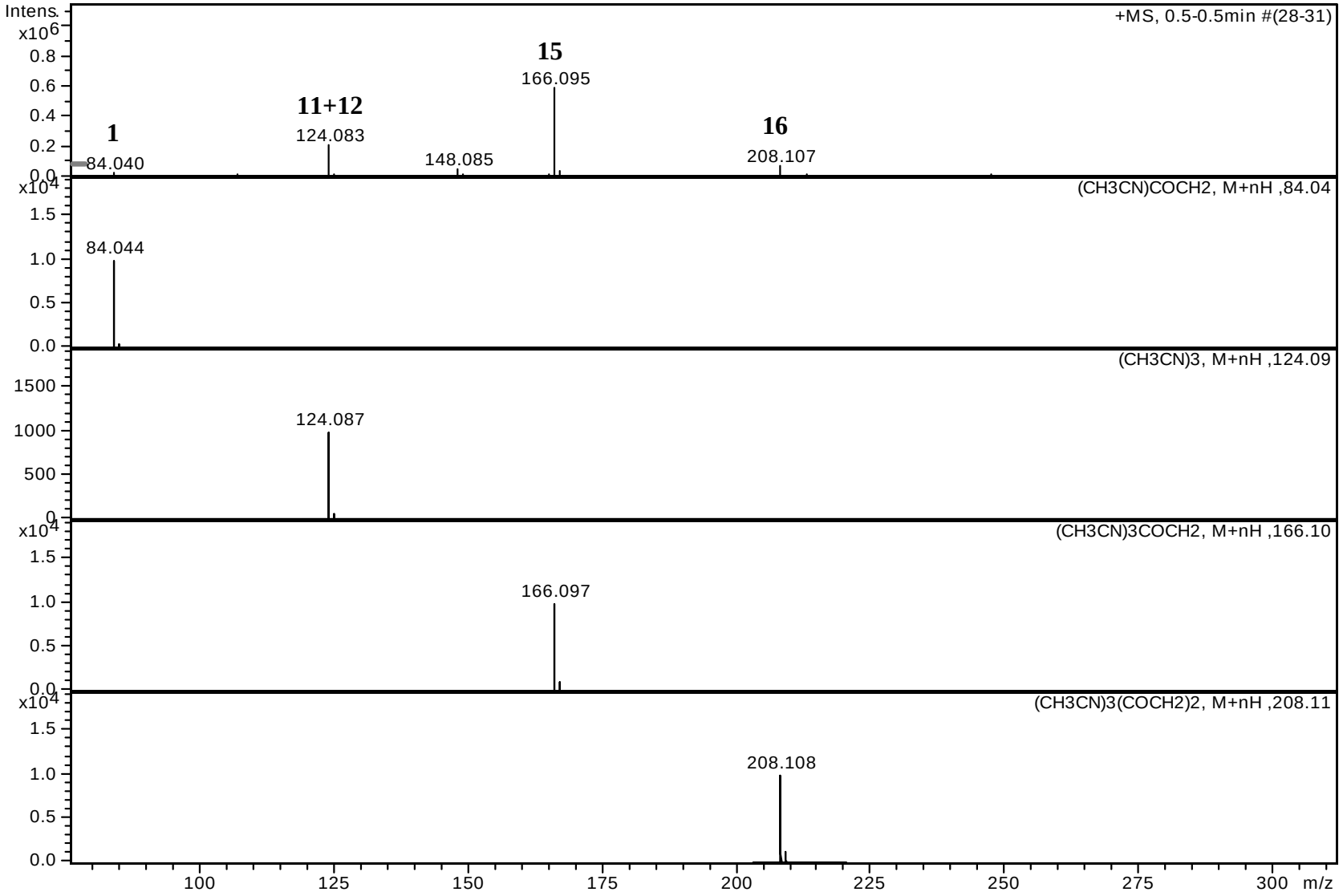
MeCN-TfOH (1:2 m/m) + 0.1 ml CD_2Cl_2; 316 h at r.t.
^1H (green), ^{15}N INEPT (red), N-H HMBC (blue), and N-H HSQC (purple) spectra





ESI-MS spectra

MeCN-TfOH (1:2 m/m, 4000 h, 5 mg) in MeCN (1 ml)
FIA , MeCN, 0.1ml/min, 4 μL , tune_low.m , ES 80-3000



Chemical shifts of MeCN, TfOH (molar ratio 1:1) and of the products of their interaction.
^{1}H chemical shifts are given in italics, ^{13}C in ordinary font, ^{15}N in bold face.

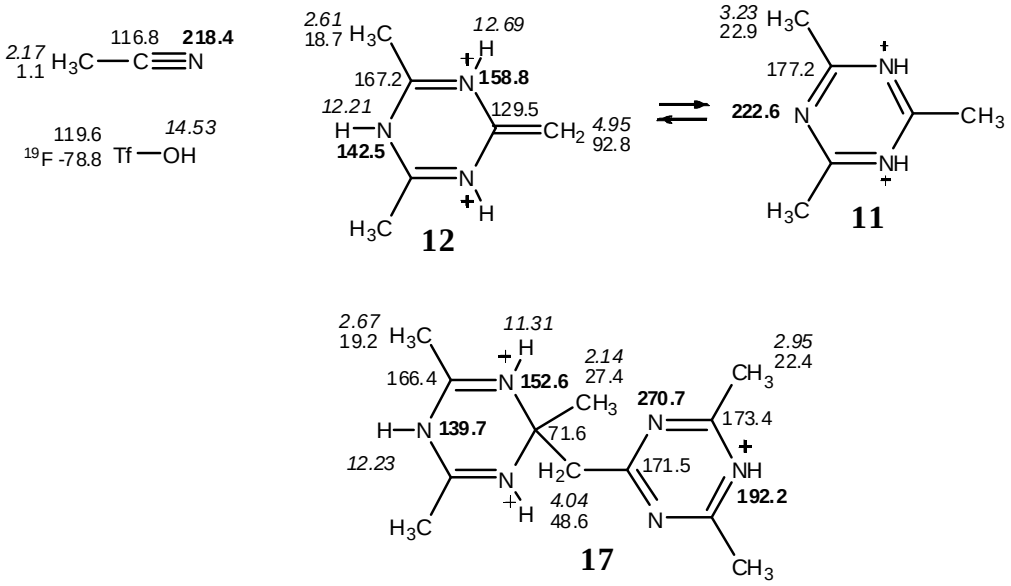
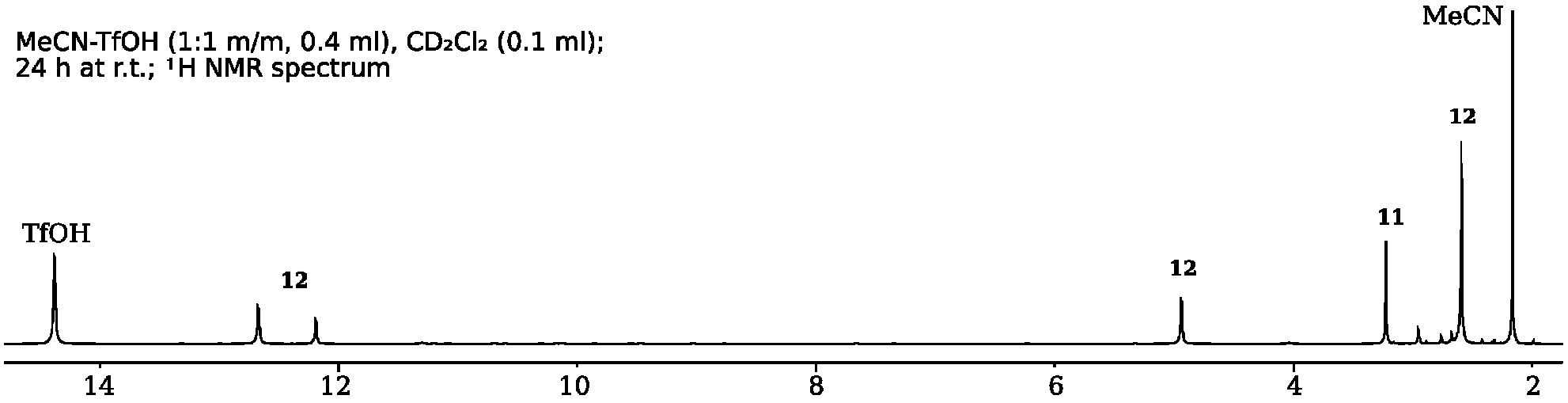


Table 4. Products of the interaction of MeCN with TfOH (mol. ratio 1:1).[a]
Given in italics are logarithms of diffusion coefficients (m^2/s) derived from the DOSY spectra.

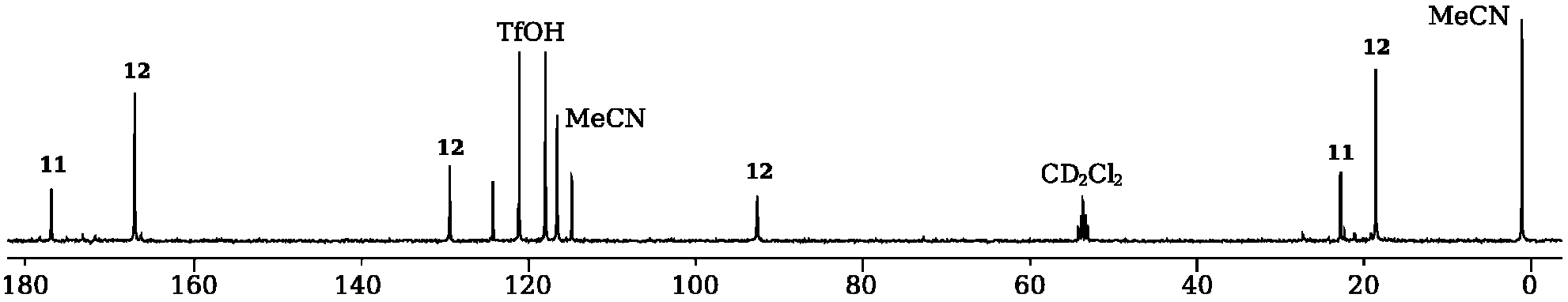
Time (h)	MeCN	**12**	**11**	**17**	Sum
0.25	92.5	4.5	1.2	0.0	98.2
0.4	88.1	7.6	2.0	0.0	97.7
5.4	52.5	33.9	8.4	0.2	95.0
24	30.1	46.6	11.8	4.8	93.3
96	18.5	42.5	11.2	18.7	90.9
^{1}H DOSY	*-10.38*	*-11.30*	*-11.19*	*-11.48*	

[a] Percentage of the acetonitrile turned into the corresponding product as determined from the ^{1}H NMR spectra.

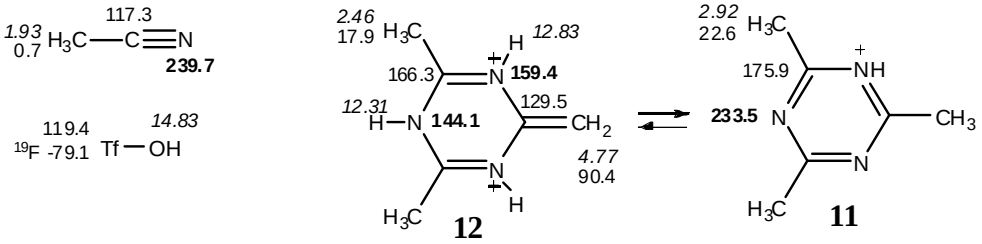
MeCN-TfOH (1:1 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml);
24 h at r.t.; ^1H NMR spectrum



MeCN-TfOH (1:1 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml);
24 h at r.t.; ^{13}C NMR spectrum



Chemical shifts of MeCN, TfOH (molar ratio 4:1) and of the products of their interaction.
^{1}H chemical shifts are given in italics, ^{13}C in ordinary font, ^{15}N in bold face.



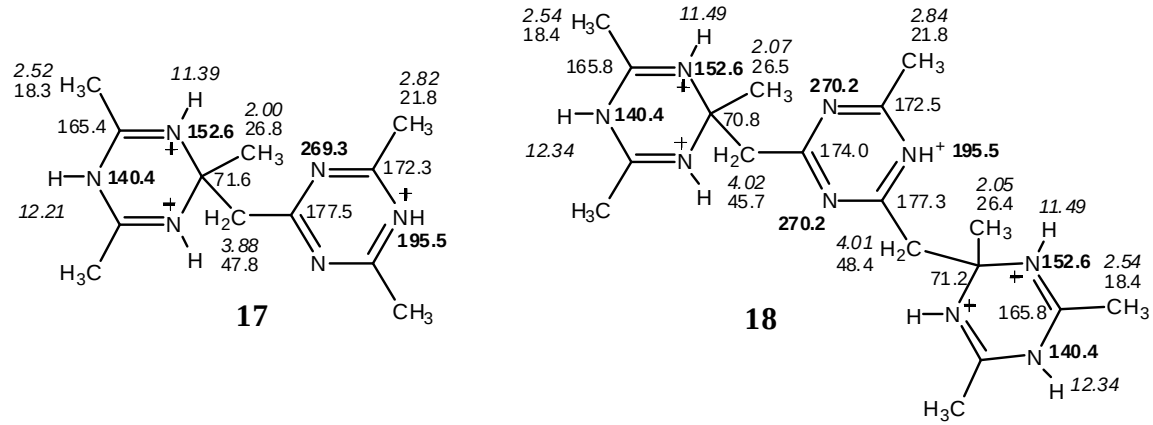
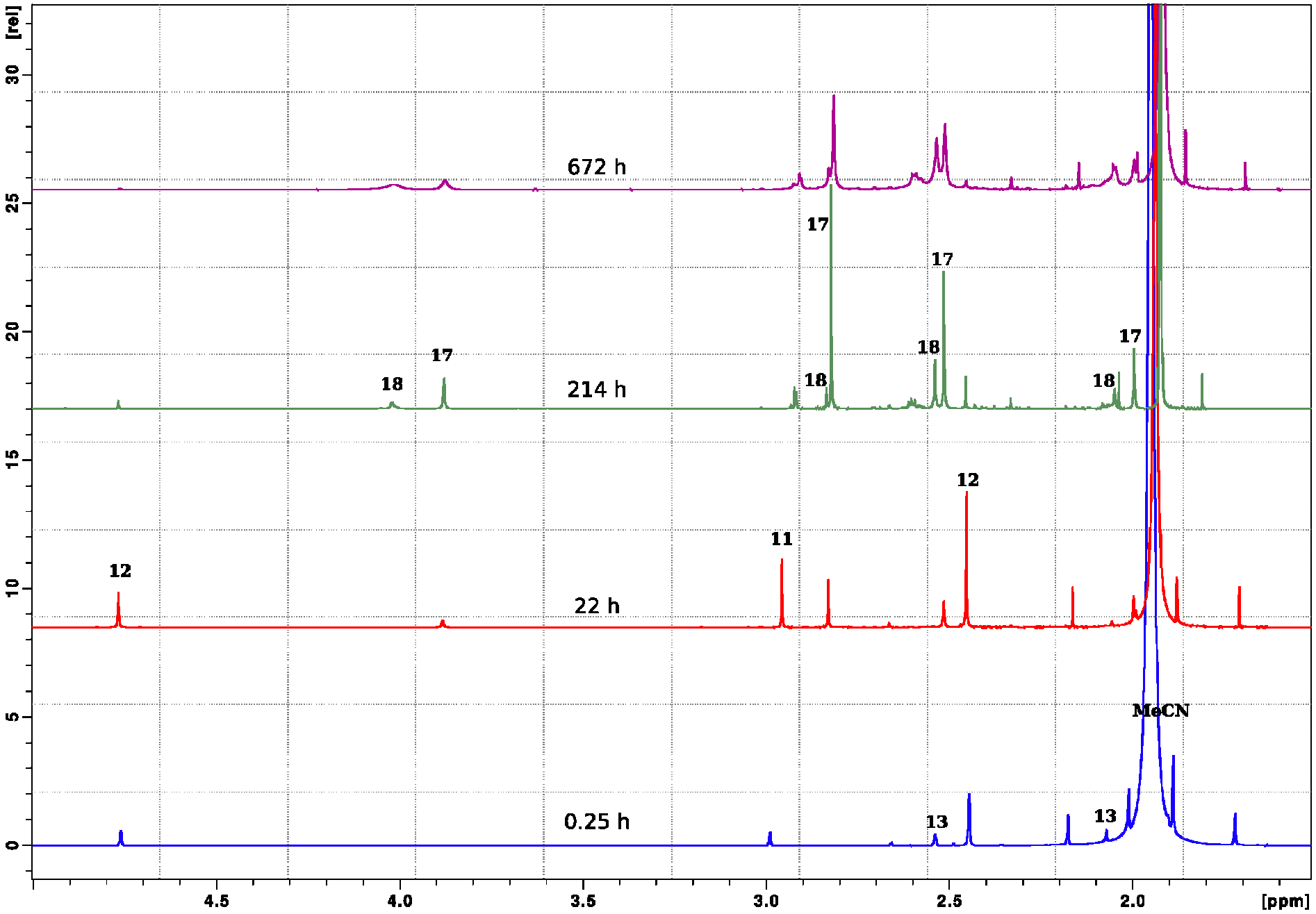


Table 3. Products of the interaction of MeCN with TfOH (mol. ratio 4:1).[a]
Given in italics are logarithms of diffusion coefficients (m^2/s) derived from the DOSY spectra.

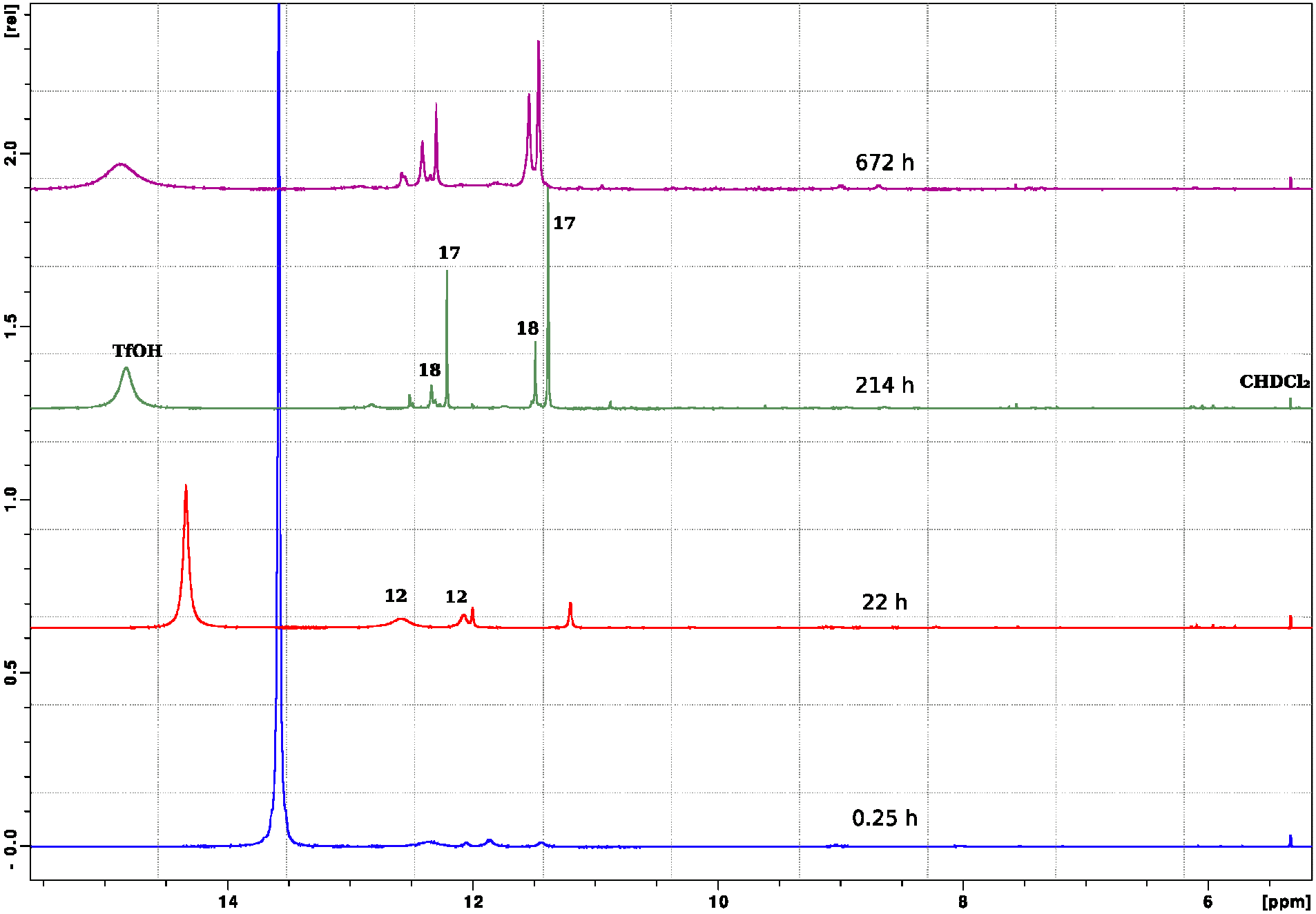
Time (h)	MeCN	**13**	**12**	**11**	**17**	**18**	Sum MeCN
0.25	96.4	0.6	1.4	0.3	0		98.7
22	87.2	0	5.4	1.6	4.2	0	98.3
167	74.8		1.1	0.5	15.4	6.9	98.7
214	72.7		0.9	0.4	15.3	8.5	97.7
^{1}H DOSY	*-8.92*		*-9.73*		*-9.85*	*-9.98*	
672	64.5		0.3		12.1	18.4	95.3

[a] Percentage of the acetonitrile turned into the corresponding product as determined from the ^{1}H NMR spectra.

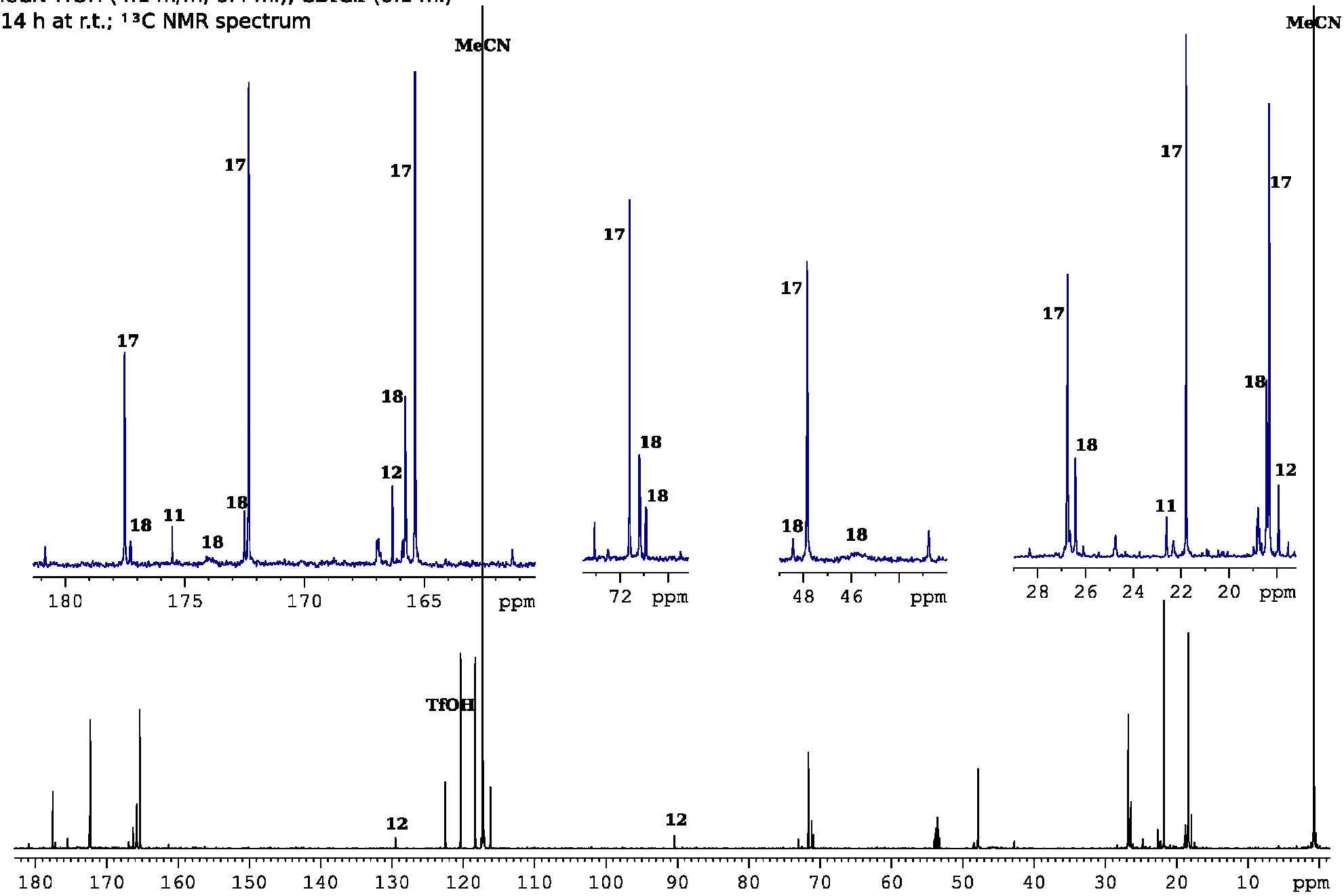
MeCN-TfOH (4:1 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml); ^1H NMR spectra; CH region



MeCN-TfOH (4:1 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml); ^1H NMR spectra; CH region

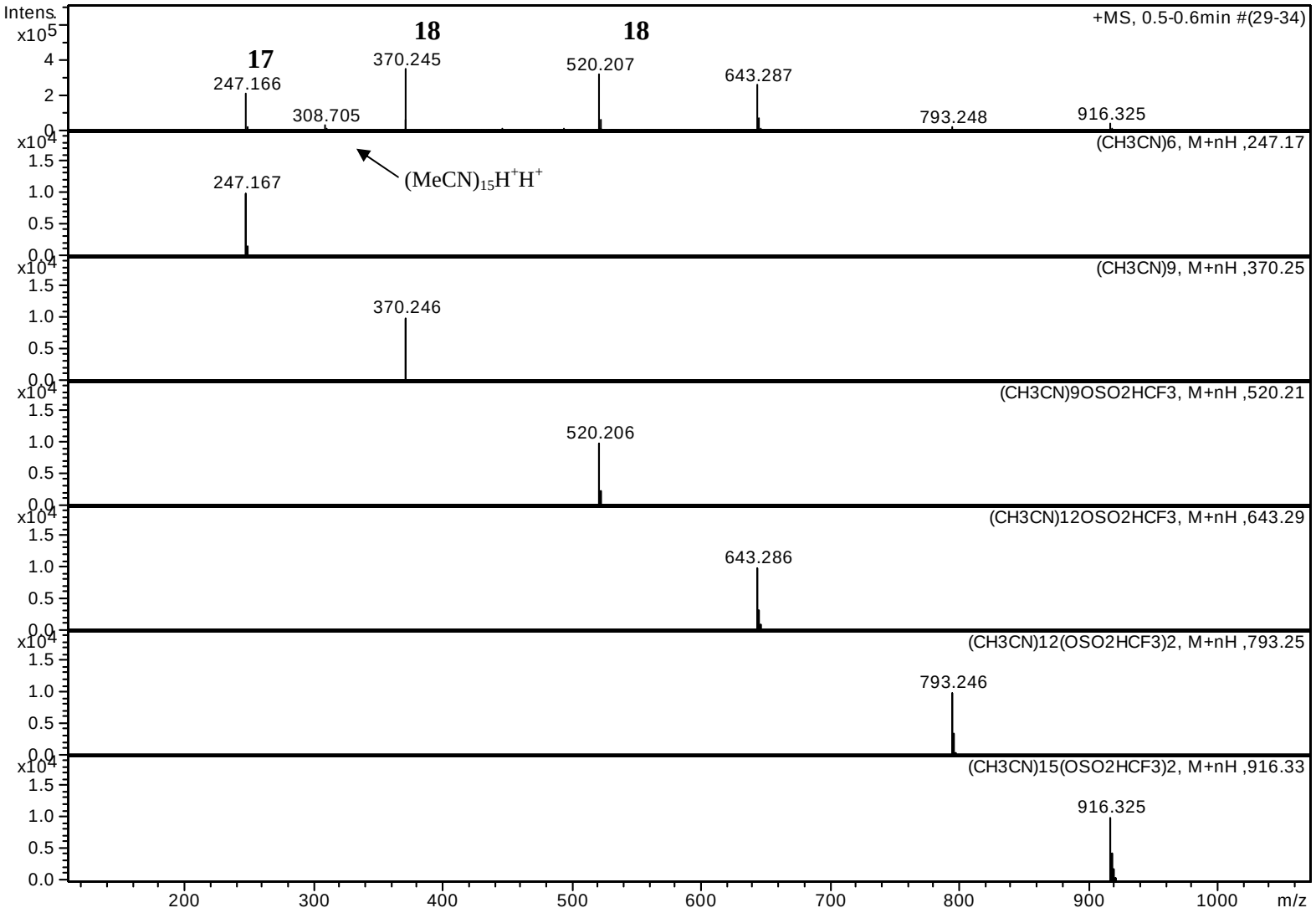


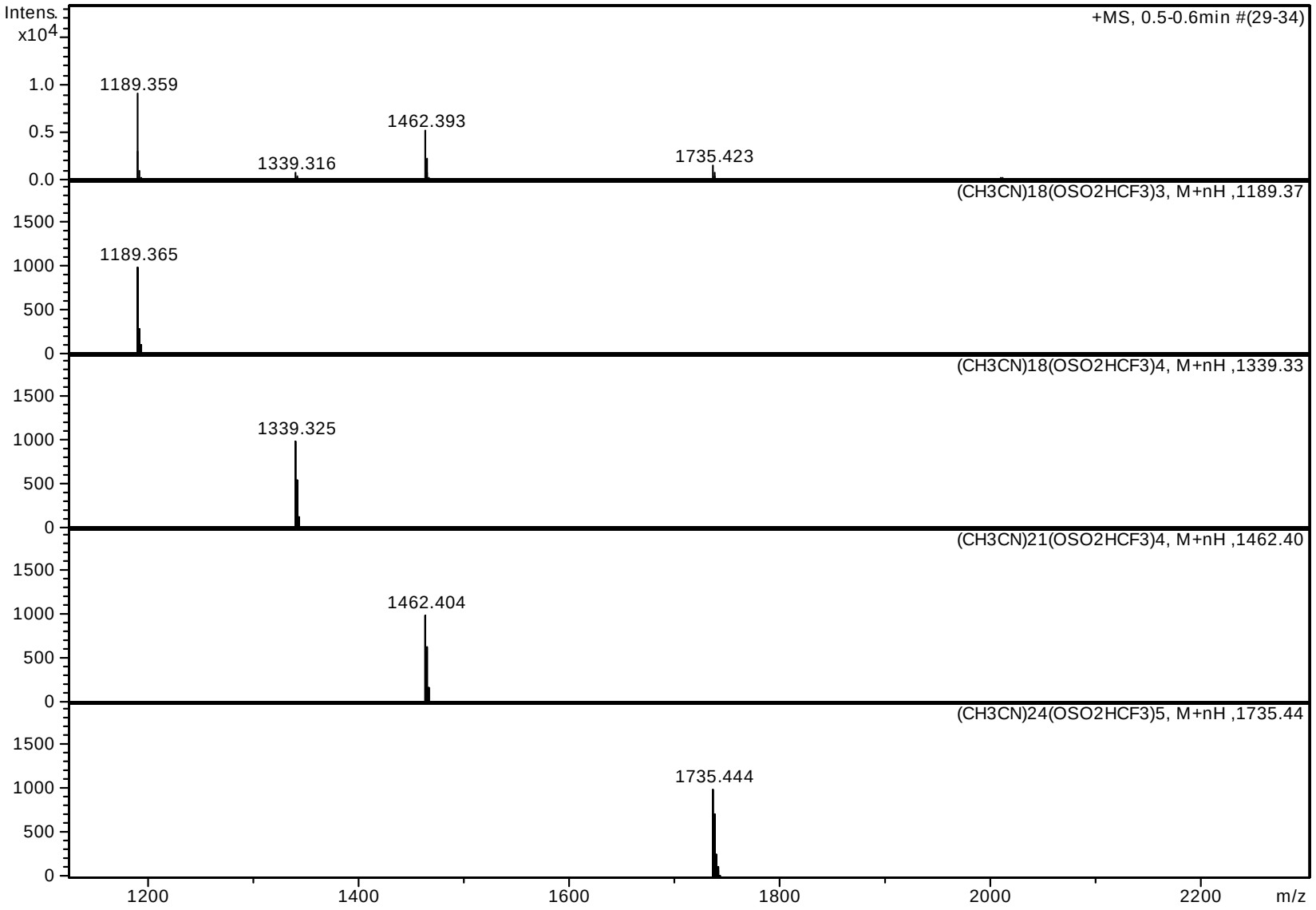
MeCN-TfOH (4:1 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml)
214 h at r.t.; ^{13}C NMR spectrum



ESI-MS spectra

MeCN-TfOH (4:1 m/m, 5000 h, 5mg) in MeCN (1 mL)
FIA, MeCN 0.1 ml/min, 2 µL , ES 100-3000

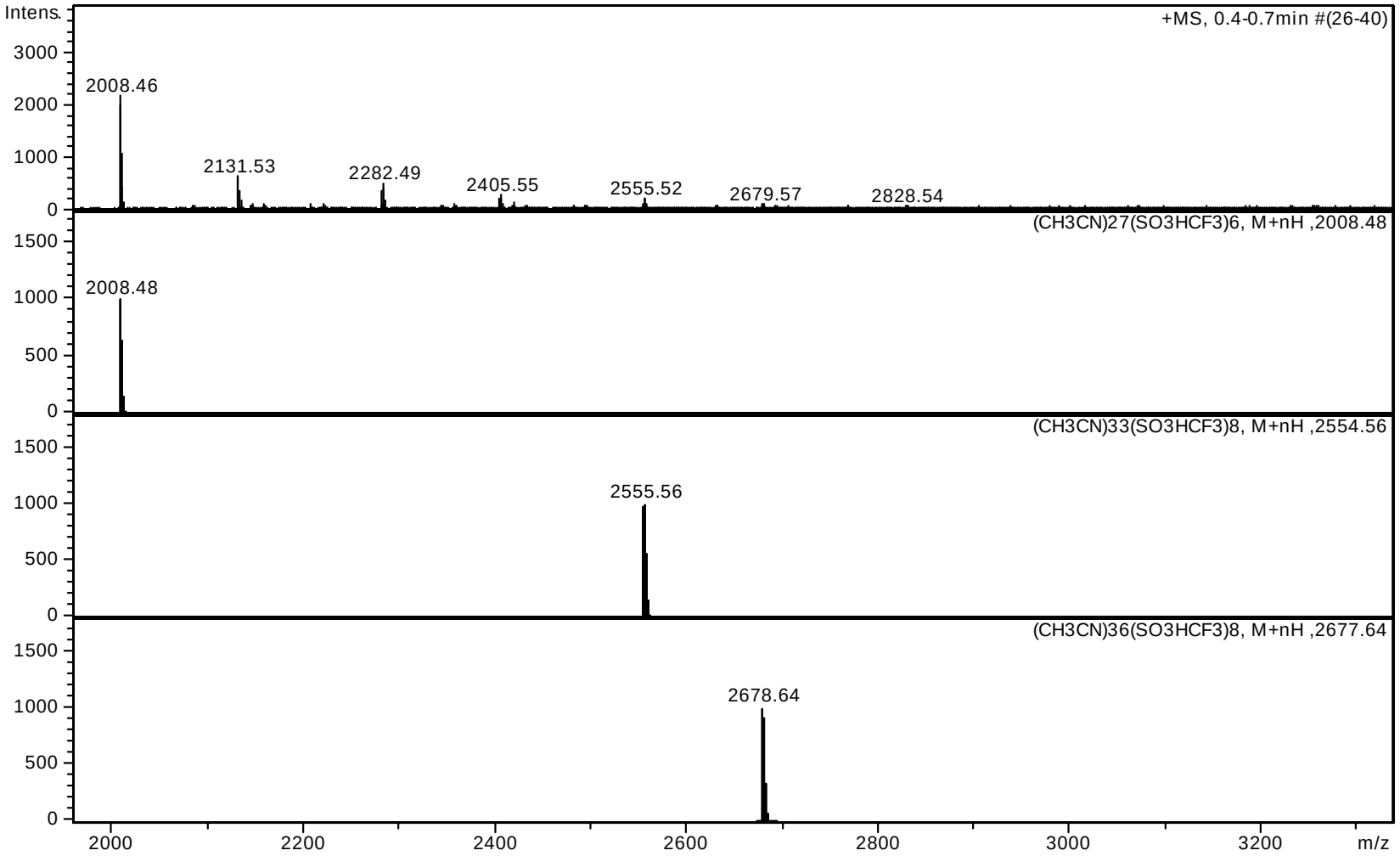




MeCN-TfOH (4:1 m/m, 5000 h, 5mg) in MeCN (1 mL)

FIA, MeCN, 0.1 ml/min, 4 µL,, tune_high.m , ES 200-10000

Heavy ions detection



^{1}H chemical shifts of MeCN, TfOH (molar ratio 17:1, 34 h at r.t.) and of the products of their interaction.

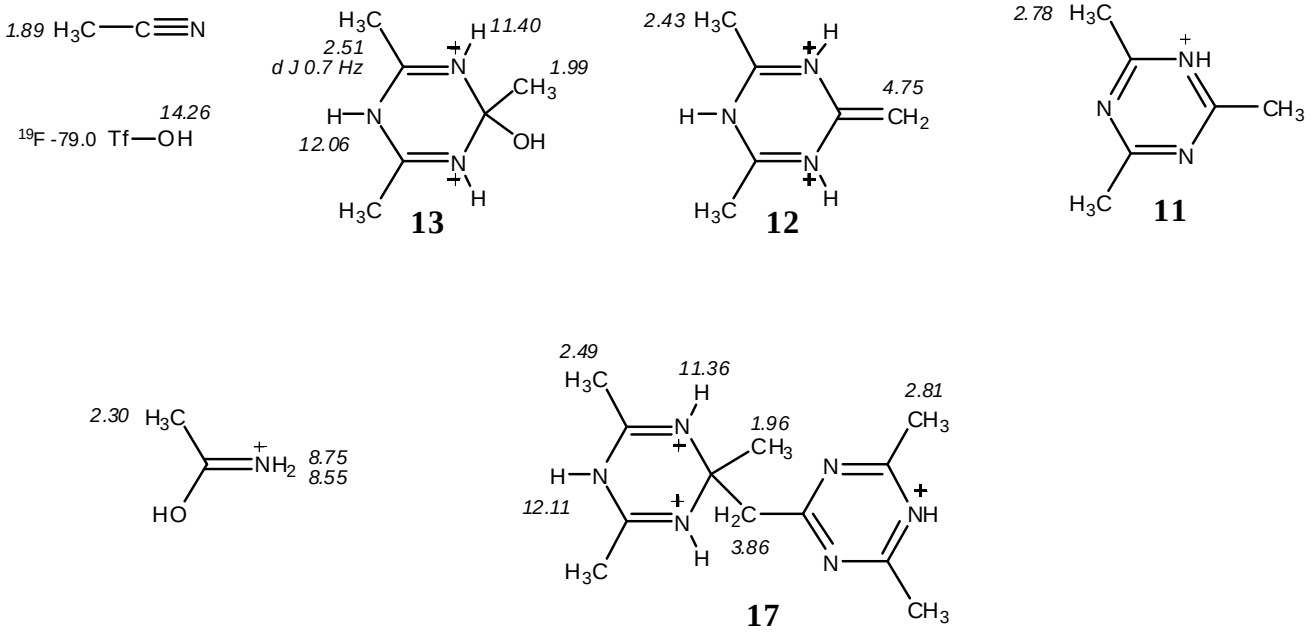
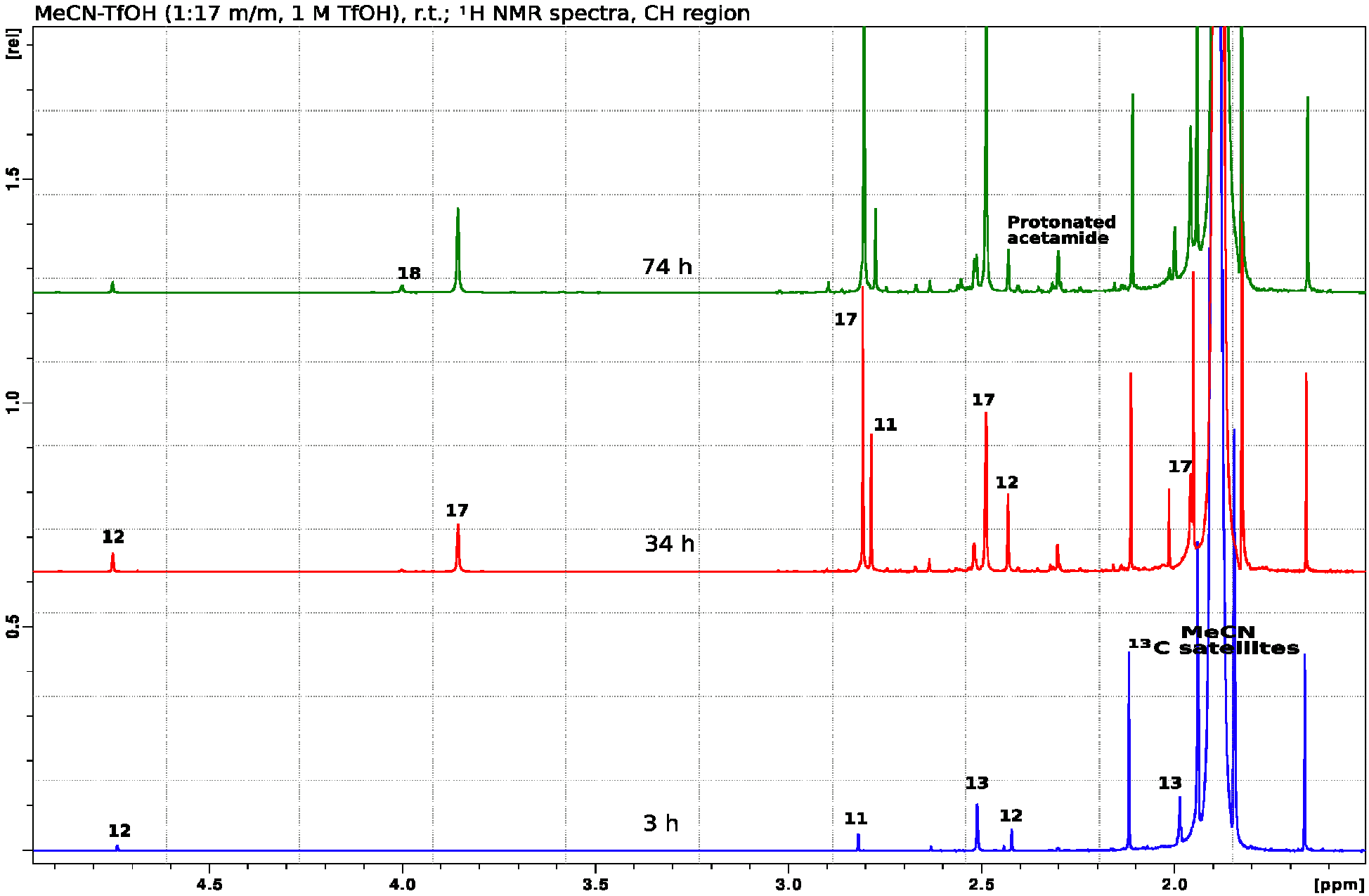
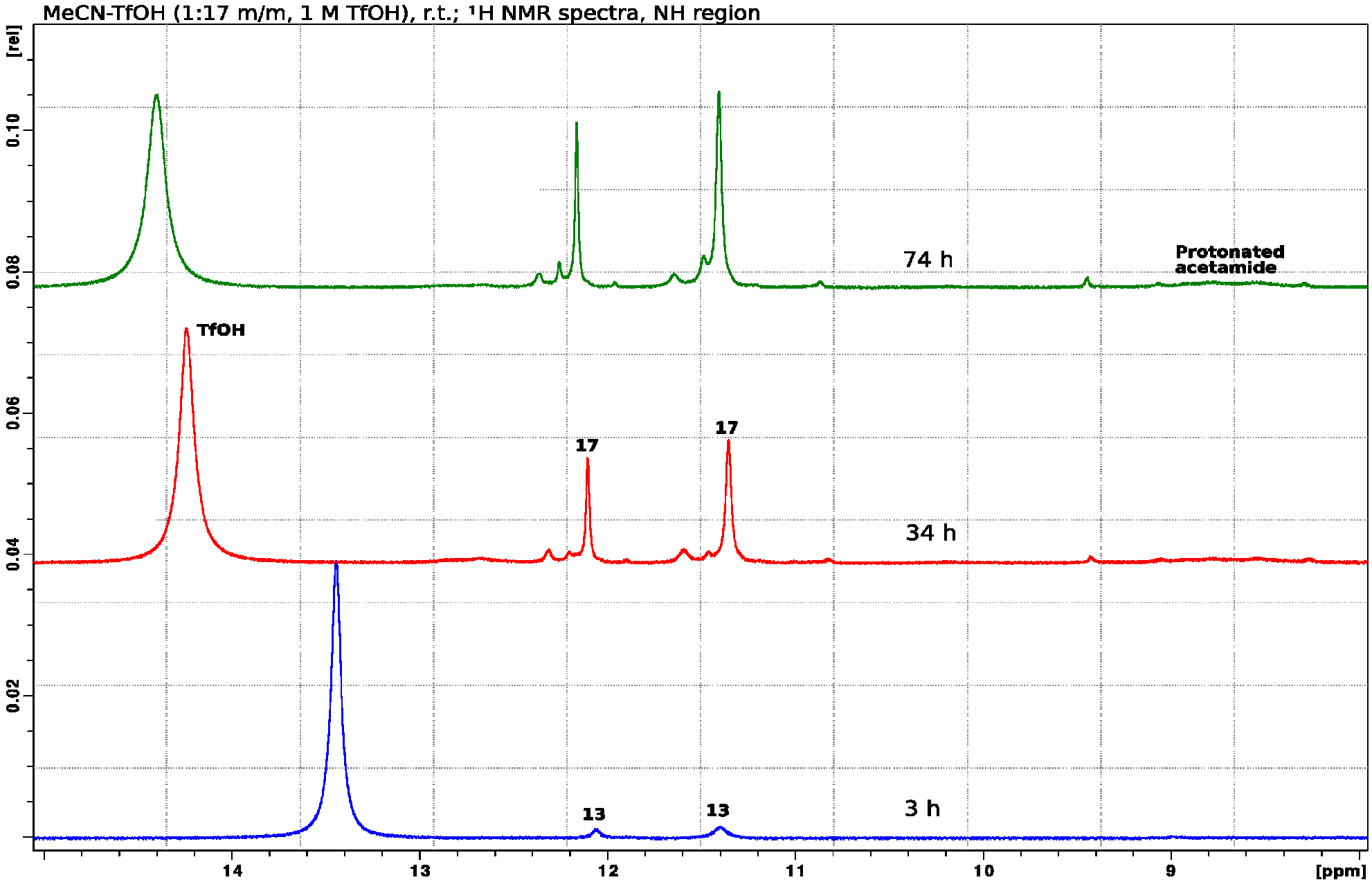


Table 5. Products of the interaction of MeCN with TfOH (mol. ratio 17:1, 1 M TfOH).[a]

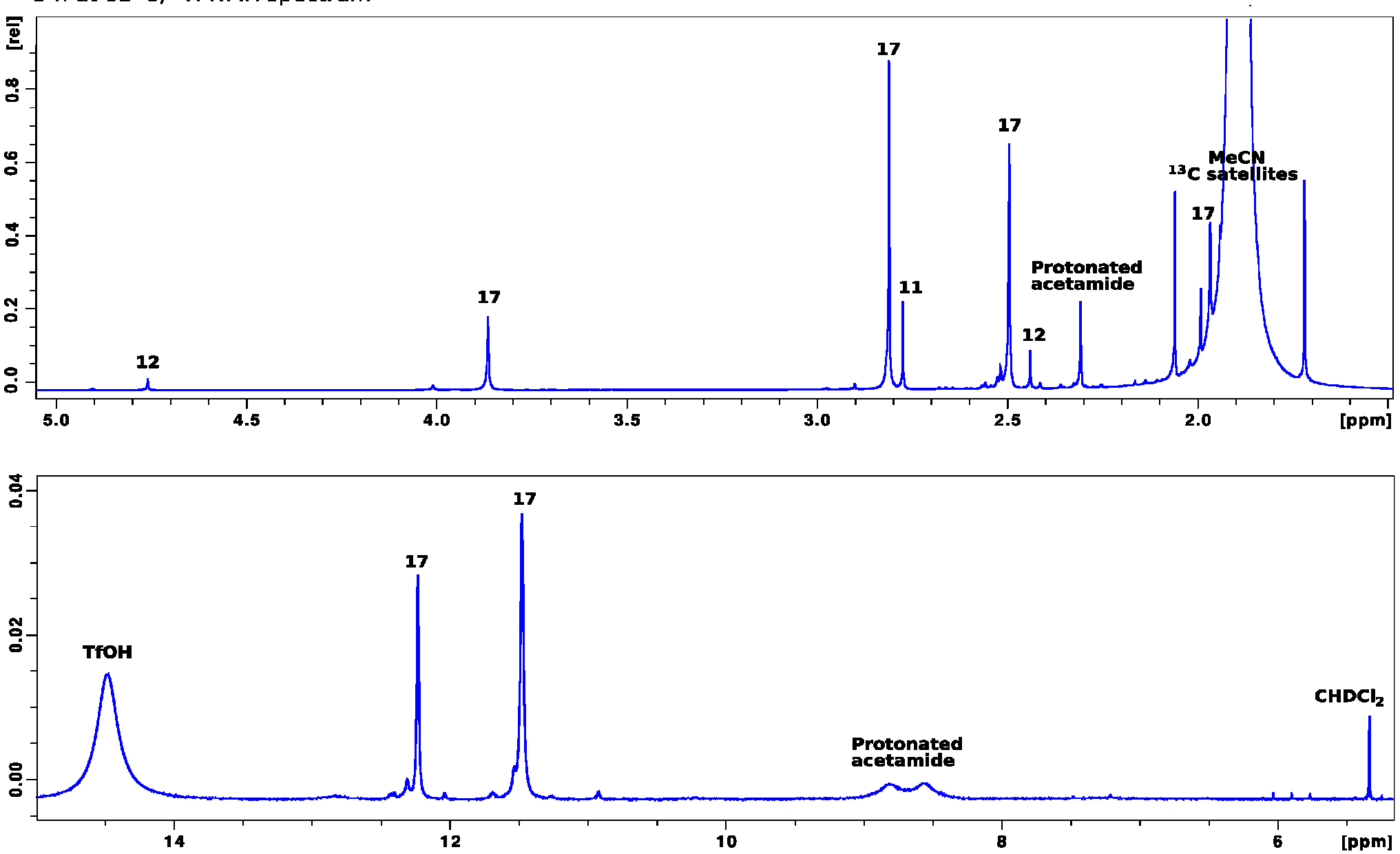
Time (h)	MeCN	**13**	**12**	**11**	**17**	**18**	acetamide H^+	Sum MeCN
3	99.2	0.42	0.22	0.02	0		0.02	99.8
34	95.9	0.32	0.33	0.35	2.43	0.10	0.13	99.5
74	94.8	0.19	0.15	0.19	3.43	0.32	0.16	99.2

[a] Percentage of the acetonitrile turned into the corresponding product as determined from the ^{1}H NMR spectra.





MeCN-TfOH (1:20 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml);
5 h at 82°C; ^1H NMR spectrum



MeCN-TfOH (1:20 m/m, 0.4 ml), CD_2Cl_2 (0.1 ml);
5 h at 82°C; ^{13}C NMR spectrum