

Table 3. ^1H and ^{15}N chemical shifts for the MMP12-NNGH adduct (pH 7.2, 298K)

Residue	Chemical shifts (ppm)						
	N	HN	H $^{\alpha}$	H $^{\beta}$	H $^{\gamma}$	H $^{\delta}$	Others
105 M							
106 G							
107 P							
108 V							QG2 (0.39),
109 W				(1.88)			HD1 7.28, HE1 9.32
110 R	115.94	7.50	4.47	(1.80)	(1.30)	(3.34)	
111 K				1.58, 2.03	1.14, 1.33		
112 H		6.88	4.08	2.77, 3.25			
113 Y	120.29	6.93	4.73	2.67, 2.80			
114 I	128.57	8.26	4.09	1.31	0.20, 0.69	(0.07)	QG2 (0.32)
115 T	117.36	9.18	5.30	4.05			QG2 (1.03)
116 Y	117.42	8.59	5.78	2.29, 2.89			CG (6.37), CZ (6.04), HH (6.61)
117 R	119.17	8.35	4.61	(1.53)	(1.47)	(2.90)	
118 I	127.25	9.12	4.24	1.70	0.83, 1.68	(0.93)	QG2 (0.03)
119 N	128.68	9.64	4.26	2.48, 3.03			HD21 7.41, HD22 6.80
120 N	113.17	7.76	4.63	2.89, 2.98			HD21 7.93, HD22 7.00
121 Y	115.09	8.56	4.00	2.50, 2.83			QE (7.22), CG (7.33), CZ (6.84)
122 T	115.79	8.07	4.86	3.10	(2.62)		
123 P			4.02	2.00, 2.16	(1.86)	3.53, 3.81	
124 D	121.93	8.79	4.65	2.48, 2.67			
125 M	113.37	6.90	4.54	1.32, 2.18	(2.24)		QE (0.34)
126 N	118.79	8.85	4.64	2.77, 2.80			HD21 7.60, HD22 6.93
127 R	126.15	8.92	3.67	1.31, 1.42	(0.90)	2.55, 2.63	
128 E	116.21	9.08	4.06	(1.92)	(2.26)		
129 D	119.89	7.43	4.61	2.59, 2.79			
130 V	124.05	7.73	3.39	2.59	(0.95)		QG2 (0.86)
131 D	118.41	8.33	4.25	2.63, 2.70			
132 Y	119.74	8.12	4.16	3.04, 3.20			CG (7.12), CZ (6.67)
133 A	121.42	8.01	3.88	(1.47)			
134 I	113.97	8.02	3.47	2.10	1.02, 1.57	(0.23)	QG2 (0.72)
135 R	119.79	8.24	4.08	1.96, 2.03	1.57, 1.72	(3.25)	
136 K	119.04	8.50	3.98	(1.51)	0.86, 0.98		
137 A	123.61	8.01	3.85	(1.05)			
138 F	114.37	7.74	3.69	(2.52)			CG (5.54), CZ (5.79)
139 Q	119.10	8.04	4.13	(2.23)	2.40, 2.56		HE21 7.56, HE22 6.94
140 V	117.31	7.60	3.55	2.09	(1.09)		QG2 (0.41)
141 W	116.89	6.70	4.70	3.02, 3.04			HD1 6.84, HE19.99
142 S	118.58	9.03	4.22	4.13, 4.27			
143 N	115.33	7.91	4.66	(2.92)			HD21 7.56, HD22 6.94
144 V	106.51	7.12	4.76	2.60	(0.85)		QG2 (1.06)
145 T	110.38	7.42	5.15	3.92			QG2 (1.39)
146 P			4.23			(3.47)	
147 L	110.67	7.21	4.39	1.63, 2.02	1.43	(0.69)	QD2 (0.57)
148 K	122.43	8.12	4.23	1.32, 1.57	(1.50)		QE (2.06)
149 F	119.48	8.18	5.64	2.12, 2.45			CG (6.84)
150 S	116.71	8.03	4.58	3.37, 3.47			
151 K	127.74	8.09	3.39	1.03, 1.35	(0.68)	(2.97)	
152 I	123.89	8.72	4.65	1.82	0.84, 1.09	(0.59)	QG2 (0.70)
153 N	119.47	8.77	4.72	(2.78)			HD21 7.85, HD22 6.64
154 T	111.76	7.43	4.38	4.04			QG2 (1.07)
155 G	109.98	8.28	3.46, 4.26				
156 M	119.05	8.18	4.20	(1.90)	(2.46)		
157 A	127.16	7.92	4.40	(0.90)			
158 D	121.49	7.99	4.48	2.21, 2.94			
159 I	124.35	8.85	4.16	1.80	(1.44)	(1.05)	QG2 (0.89)
160 L	130.06	7.59	5.02	1.41, 1.62		(0.92)	QD2 (0.83)
161 V	125.43	8.74	5.10	2.09	(0.91)		QG2 (0.83)
162 V	127.05	8.79	4.51	1.74	(0.71)		QG2 (0.85)
163 F	125.72	8.38	5.32	2.69, 2.97			CG (6.88)
164 A	125.99	9.10	4.77	(0.94)			

165	R	118.17	8.77	5.21	1.60, 1.84	(1.52)	(3.19)	
166	G	108.11	9.43	3.77, 3.88				
167	A	134.13	9.15	4.28	(1.44)			
168	H	121.94	8.00		(3.00)			
169	G							
170	D							
171	D	115.46	8.36	4.38	(2.89)			
172	H	120.60	7.54	4.57	2.06, 2.48			HD2 8.28, HE1 6.55
173	A	123.32	7.95	4.12	(1.25)			
174	F	119.98	7.94	4.86	(1.68)			CG (6.73), CZ (7.15)
175	D	116.40	8.24	4.64	2.52, 3.04			
176	G	110.11	8.81	4.23, 4.40				
177	K	124.09	8.70	3.40	(1.52)	0.92, 1.23	(1.50)	QE (2.84)
178	G	121.24	10.75	3.50, 4.17				
179	G	110.72	8.44	3.36, 4.08				
180	I	129.77	10.61	3.88	2.07	1.36, 1.67	(0.98)	QG2 (1.20)
181	L	128.22	8.45	4.39	(1.34)	1.55	(0.21)	QD2 (-0.04)
182	A	114.54	7.40	4.66	(1.02)			
183	H	116.74	9.25	4.78	3.07, 3.27			HD2 6.43, HE1 8.04
184	A	119.92	7.95	4.11	(1.23)			
185	F	131.21	11.91	4.47	(1.90)			CG (6.97)
186	G	105.40	8.18	3.46, 4.29				
187	P			4.48	-0.12, 0.59	1.35, 1.63	2.79, 3.01	
188	G	106.91	5.65	3.59, 4.06				
189	S	108.19	7.34	4.55				
190	G	111.89	8.91	3.70, 3.92				
191	I	133.99	8.93	4.15	1.43	0.49, 0.92	(0.36)	QG2 (0.42)
192	G	106.10	7.60	3.00, 3.72				
193	G	119.65	7.81	4.12, 4.56				
194	D	122.60	8.28	4.64	(2.90)			
195	A	119.80	8.61	4.70	(0.94)			
196	H	121.82	9.34	5.73	2.41, 3.20			HD2 6.88, HE1 9.24
197	F	122.80	9.14	4.16	1.65, 2.01			CG 6.23
198	D	121.00	8.06	4.14				
199	E	120.40	8.03	4.84	(2.95)			
200	D	122.63	8.13	4.33	(2.66)			
201	E	130.71	9.40	4.27	1.64, 1.95			
202	F	119.41	9.02	4.72	(2.50)			
203	W	116.82	7.37	4.37	0.55, 1.00			HE1 10.15, HE3 7.12, HZ3 6.82
204	T	126.02	8.37	4.67	4.46			QG2 (2.68)
205	T	122.80	7.94	4.57	4.41			QG2 (1.22)
206	H	119.97	7.94	4.11	2.79, 3.03			HD2 9.36, HE1 6.92
207	S	116.51	6.90	3.58	2.65, 3.30			
208	G	109.56	8.14	3.77, 4.08				
209	G	108.17	7.84	(3.89)				
210	T	125.17	9.15	3.59	2.44			QG2 (0.20)
211	N	125.46	8.49	4.71	(3.09)			HD21 7.94, HD22 6.31
212	L	131.80	8.54	4.36	1.47, 1.80	1.01	(0.75)	QD2 (-0.20)
213	F	120.30	9.20	3.85	3.09, 3.36			CG (7.16), CZ (6.49)
214	L	118.35	8.84	3.07	1.51, 1.72	0.95	(0.48)	
215	T	112.55	7.35	4.09	4.31			QG2 (1.34)
216	A	124.16	9.37	3.92	(1.02)			
217	V	118.57	8.35	3.13	1.68	(0.67)		QG2 (0.08)
218	H	118.15	6.99	4.35	3.07, 3.90			HD2 9.86
219	E	115.73	8.84	3.85	(1.75)	(1.43)		
220	I	117.99	8.95	3.43	1.30	0.20, 0.90	(-0.46)	QG2 (0.13)
221	G	108.20	7.53	2.29, 3.79				
222	H	119.71	7.12	4.86	2.39, 3.73			HD2 6.70, HE1 8.29
223	S	122.48	8.78	4.06	(3.48)			
224	L	114.25	7.68	4.48	(1.90)	1.55	(0.74)	QD2 (0.23)

225	G	106.68	8.13	3.33, 4.60				
226	L	120.95	8.37	4.73	(1.41)	1.23	(0.70)	QD2 (0.23)
227	G	109.83	8.27	4.34, 4.60				
228	H	115.65	8.37	3.78	2.72, 2.91			HD2 7.68, HE1 8.49
229	S	114.26	6.85	4.68	3.10, 4.16			
230	S	119.91	8.79	4.69	3.90, 4.01			
231	D	126.75	8.89	4.70	2.37, 2.96			
232	P			2.43	(1.44)		3.66, 4.00	
233	K	116.71	8.18	4.05	(1.70)	1.27, 1.35	(2.42)	QE (2.95)
234	A	123.87	8.13	4.52	(1.72)			
235	V	131.43	11.47	4.35	2.36	(0.02)		QG2 (0.98)
236	M	115.47	7.62	4.53	2.13, 2.58	(0.98)		QE (0.47)
237	F	128.35	8.06	4.95	3.18, 3.66			CG (7.22), CZ (6.10)
238	P			3.83				
239	T	116.50	7.68	4.62	3.96			QG2 (1.20)
240	Y	127.99	9.04	4.54	2.22, 2.67			CG (6.72), CZ (7.41)
241	K	129.94	7.90	3.90	1.53, 1.56	(1.16)	(1.55)	QE (3.01)
242	Y	124.10	8.51	3.90	2.65, 2.98			CG (6.82), CZ (9.04)
243	V	124.38	5.75	3.77	1.80	(0.79)		QG2 (0.77)
244	D	119.10	7.81	4.17	(2.66)			
245	I	124.41	7.73	3.76	1.83	(1.14)	(0.67)	QG2 (1.04)
246	N	118.47	8.49	4.57	2.75, 2.88			HD21 7.53, HD22 7.01
247	T	109.39	7.56	4.34	4.27			QG2 (1.05)
248	F	123.31	7.18	4.10	2.81, 3.02			CZ (6.48)
249	R	126.23	7.12	3.92	1.39, 1.60	1.35, 1.42	2.99, 3.08	
250	L	121.13	8.09	3.82	1.31, 1.40	1.32	(0.70)	QD2 (0.15)
251	S	118.27	8.89	4.46	3.82, 4.15			
252	A	123.58	8.78	4.00	(1.40)			
253	D	117.66	8.21	4.25	2.43, 2.77			
254	D	118.79	7.40	4.67	2.71, 3.01			
255	I	118.91	7.91	3.66	1.67	0.74, 1.71	(0.68)	QG2 (0.89)
256	R	119.17	8.50	3.98	1.82, 1.87	1.55, 1.73	(3.16)	
257	G	106.84	8.26	3.74, 3.96				
258	I	123.60	8.62	4.43	2.11	1.50, 1.72	(0.85)	QG2 (1.52)
259	Q	123.52	8.63	4.42	1.98, 2.20	2.74, 2.89		HE21 8.29, HE22 7.69
260	S	115.51	7.89	4.21	(3.96)			
261	L	119.13	6.93	4.06	0.77, 1.82	1.69	(0.59)	QD2 (0.58)
262	Y	109.54	8.16					CG (7.24)
263	G	110.20	8.29					

The numbers in parentheses indicate resonances for which degeneracy is assumed among diastereotopic protons or methyl groups. CG and CZ are used for Phe and Tyr residues to indicate the pseudoatoms representing the pair of HD and HE ring protons, respectively, when no stereospecific assignment is available for them.