Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Total Synthesis of Putative Montamine and a Proposed Structural Reassignment

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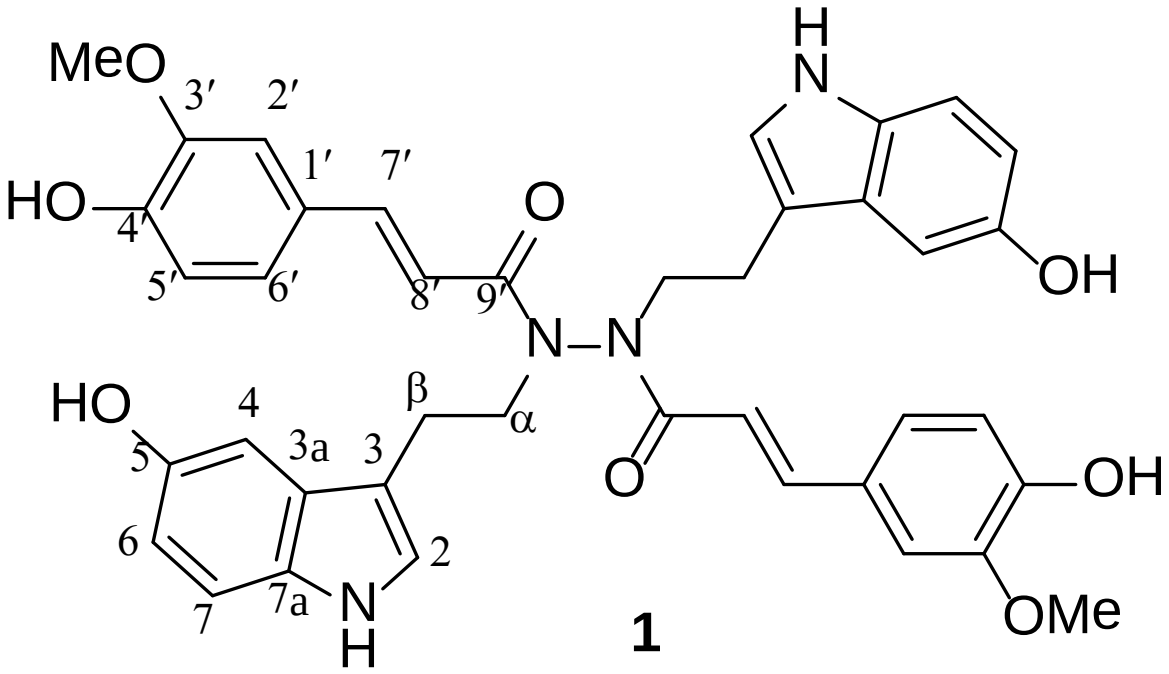


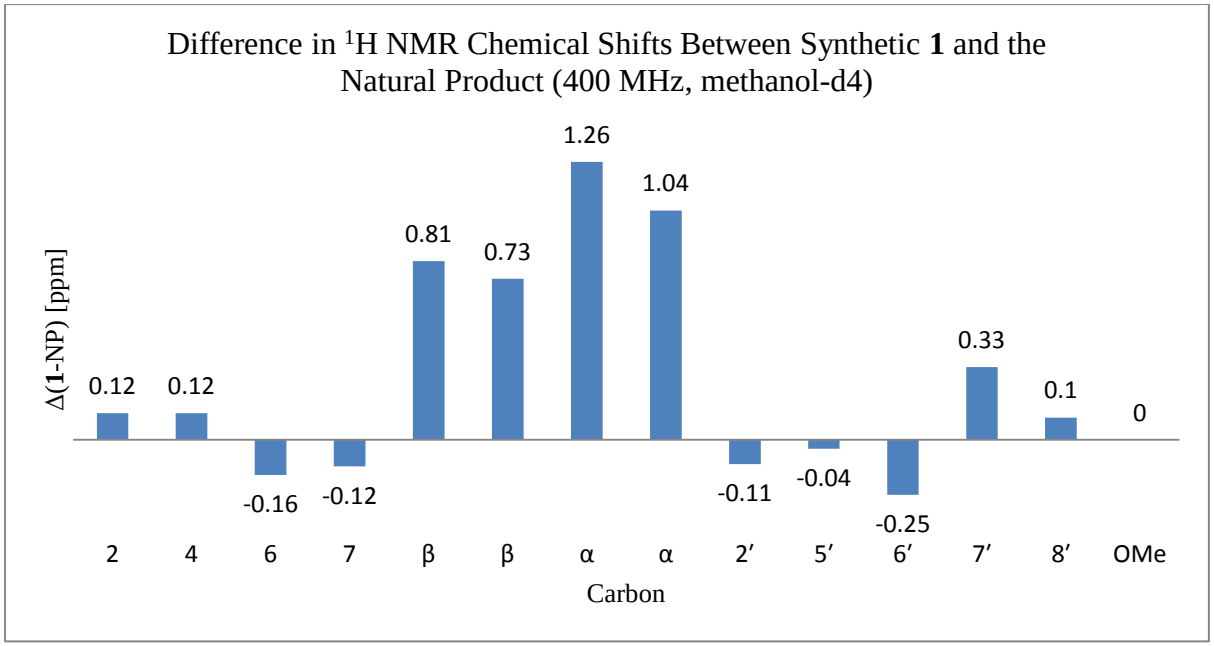
1

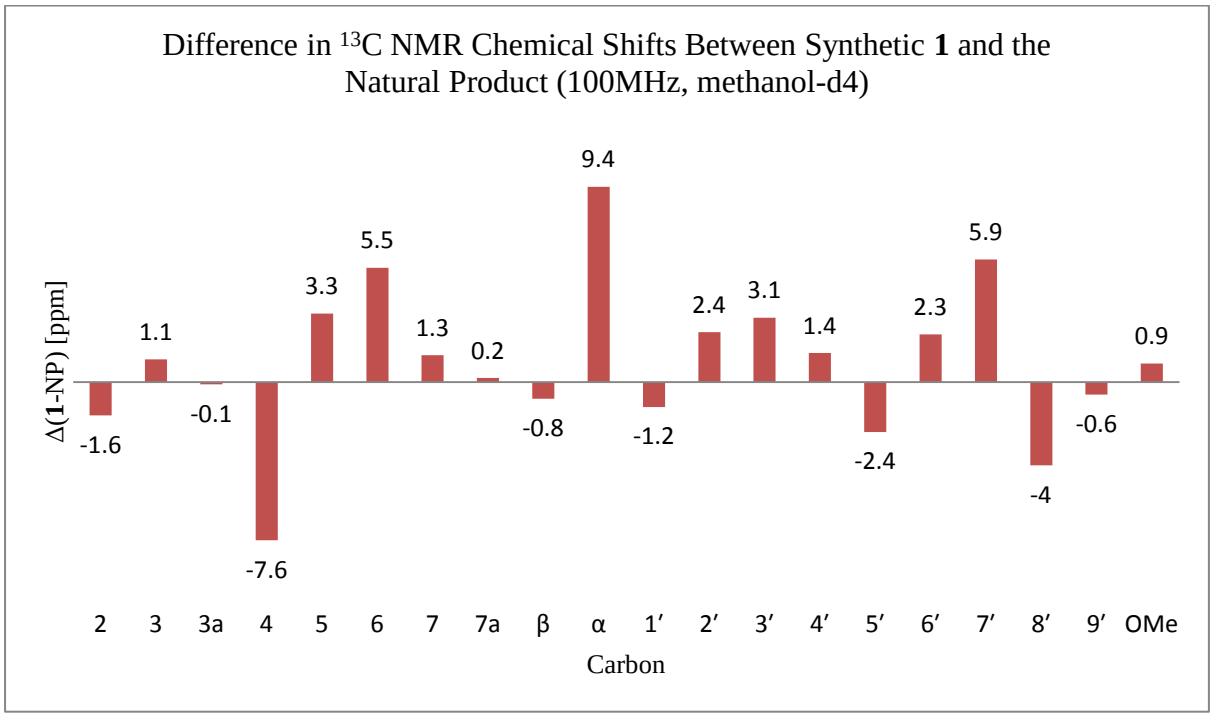
Table S1 – NMR data for synthetic **1**

Assignment	Synthetic **1** in d_4-methanol				Synthetic **1** in d_6-acetone			
	Chemical Shift		**HMBC (^{1}H->^{13}C)**		**Chemical Shift**		**HMBC (^{1}H->^{13}C)**	
	^{1}H, mult., *J* (Hz)	**^{13}C**	**^2J**	**^3J**	**^{1}H, mult., *J* (Hz)**	**^{13}C**	**^2J**	**^3J**
NH	-	-	-	-	9.81, br s	-	C-2	C-3, C-3a
2	7.05, s	124.4	C-3	C-3a, C-7a	7.18, s	124.2	C-3	C-3a, C-7a
3	-	112.1	-	-	-	112.1	-	-
3a	-	129.4	-	-	-	129.2	-	-
4	6.95, s	103.6	C-5	C-7a	7.11, s	103.6	-	C-6, C-7a
5	-	151.3	-	-	-	151.6	-	-
6	6.66, m	116.6	-	C-7a	6.71, d, 8.6	112.6	C-5	C-4, C-7a
7	7.14, d, 8.6	112.8	-	C-3a, C-5	7.21, d, 8.6	112.5	-	C-3a, C-5
7a	-	133.2	-	-	-	132.5	-	-
β-CH_2	3.08, m 2.92, m	24.2	-	-	3.19, m 3.11, m	24.5	α-CH_2, C-3	C-2, C-3a
α-CH_2	4.12, m 3.81, m	50.4	-	-	4.07, m 3.97, m	50.6	-	-
1′	-	127.8	-	-	-	127.9	-	-
2′	6.88, s	112.4		C-4′, C-6′, C-7′	7.11, s	112.4	-	C-4′, C-6′, C-7′
3′	-	149.1	-	-	-	148.5	-	-
4′	-	150.4	-	-	-	149.7	-	-
5′	6.66, m	112.6	-	C-1′	6.76, d, 8.0	116.2	-	C-1′, C-3′
6′	6.66, m	123.3	-	C-2′, C-4′	6.92, d, 8.0	122.8	-	C-2′, C-4′, C-7′
7′	7.60, d, 15.4	146.9		C-2′, C-6′, C-9′	7.66, d, 15.4	145.3	-	C-2′, C-6′, C-9′
8′	6.41, d, 15.4	113.5	C-9′	C-1′	6.68, d, 15.4	114.3	C-9'	C-1′
9′	-	171.4	-	-	-	169.1	-	-
OMe	3.78, s	56.4	-	C-3′	3.80, s	56.3	-	C-3′
OH	-	-	-	-	8.06, br s	-	-	-
OH	-	-	-	-	7.73, br s	-	-	-

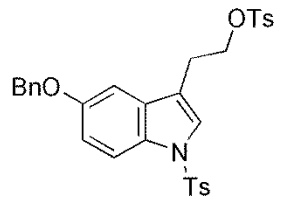
Table S2. NMR data for synthetic **1** vs montamine, including HMBC (d_4-methanol)

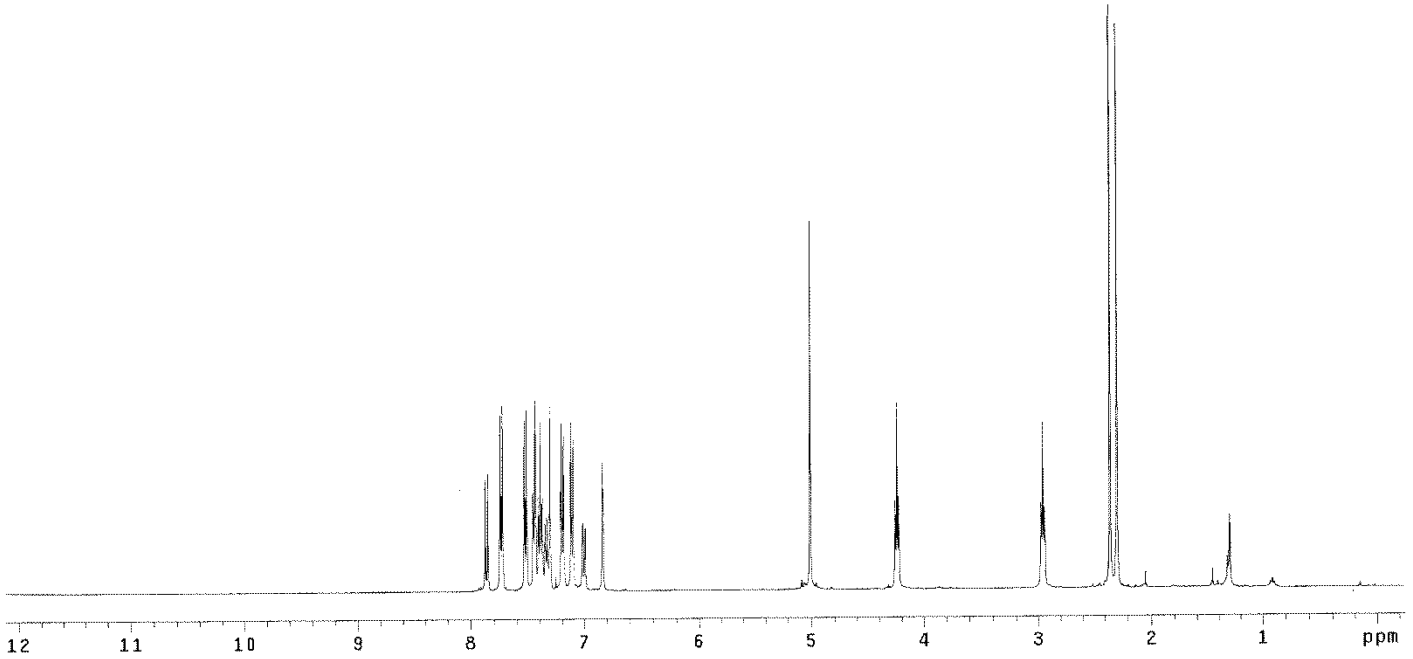
	^{1}H, mult., *J* (Hz) (CD_3OD, 400 MHz)			**^{13}C (CD_3OD, 100 MHz)**			**HMBC (^{1}H→^{13}C)**			
Carbon	Synthetic **1**	Montamine	diff.	Synthetic **1**	Montamine	diff.	Synthetic **1**		Montamine	
							^2J	^3J	^2J	^3J
2	7.05, s	6.93, s	**+0.12**	124.4	126.0	**-1.6**	C-3	C-3a, C-7a	C-3	C-3a, C-7a
3	-	-	-	112.1	111.0	**+1.1**	-	-	-	-
3a	-	-	-	129.4	129.5	**-0.1**	-	-	-	-
4	6.95, s	6.83, d, 2.0	**+0.12**	103.6	111.2	**-7.6**	C-5	C-7a	C-5	C-7a
5	-	-	-	151.3	148.0	**+3.1**	-	-	-	-
6	6.66, m	6.82, dd, 2.0, 8.0	**-0.16**	116.6	111.1	**+5.5**	-	C-7a	C-5	C-7a
7	7.14, d, 8.6	7.26, d, 8.0	**-0.12**	112.8	111.5	**+1.3**	-	C-3a, C-5	C-7a	C-3a, C-5
7a	-	-	-	133.2	133.0	**+0.2**	-	-	-	-
β-CH_2	3.08, m 2.92, m	2.27, m 2.19, m	**+0.81, +0.73**	24.2	25.0	**-0.8**	-	-	C-3	C-2, C-α-CH_2
α-CH_2	4.12, m 3.81, m	2.86, m 2.77, m	**+1.26, +1.04**	50.4	41.0	**+9.4**	-	-	C-β-CH_2	C-3, C-9′
1′	-	-	-	127.8	129.0	**-1.2**	-	-	-	-
2′	6.88, s	6.99, d, 2.0	**-0.11**	112.4	110.0	**+2.4**		C-4′, C-6′, C-7′	-	C-6′, C-4′, C-7'
3′	-	-	-	149.1	146.0	**+3.1**	-	-	-	-
4′	-	-	-	150.4	149.0	**+1.4**	-	-	-	-
5′	6.66, m	6.70, d, 8.4	**-0.04**	112.6	115.0	**-2.4**	-	C-1′	-	C-1′, C-3′
6′	6.66, m	6.91, dd, 2.0, 8.4	**-0.25**	123.3	121.0	**+2.3**	-	C-2′, C-4′	-	C-2', C-4', C-7'
7′	7.60, d, 15.4	7.27, d, 15.6	**+0.33**	146.9	141.0	**+5.9**		C-2′, C-6′, C-9′	-	C-2′, C-6′, C-9′
8′	6.41, d, 15.4	6.31, d, 15.6	**+0.10**	113.5	117.5	**-4.0**	C-9′	C-1′	C-9′	C-1′
9′	-	-	-	171.4	172.0	**-0.6**	-	-	-	-
OMe	3.78, s	3.78, s	**0**	56.4	55.5	**+0.9**	-	C-3′	-	C-3′


Difference in ^{1}H NMR Chemical Shifts Between Synthetic **1** and the Natural Product (400 MHz, methanol-d4)
Δ(**1**-NP) [ppm]
0.12
0.12
-0.16
-0.12
0.81
0.73
1.26
1.04
-0.11
-0.04
-0.25
0.33
0.1
0
2
4
6
7
β
β
α
α
2′
5′
6′
7′
8′
OMe
Carbon

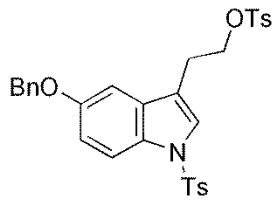

Difference in ^{13}C NMR Chemical Shifts Between Synthetic **1** and the Natural Product (100MHz, methanol-d4)
Δ(**1**-NP) [ppm]
-1.6
1.1
-0.1
-7.6
3.3
5.5
1.3
0.2
-0.8
9.4
-1.2
2.4
3.1
1.4
-2.4
2.3
5.9
-4
-0.6
0.9
2
3
3a
4
5
6
7
7a
β
α
1′
2′
3′
4′
5′
6′
7′
8′
9′
OMe
Carbon

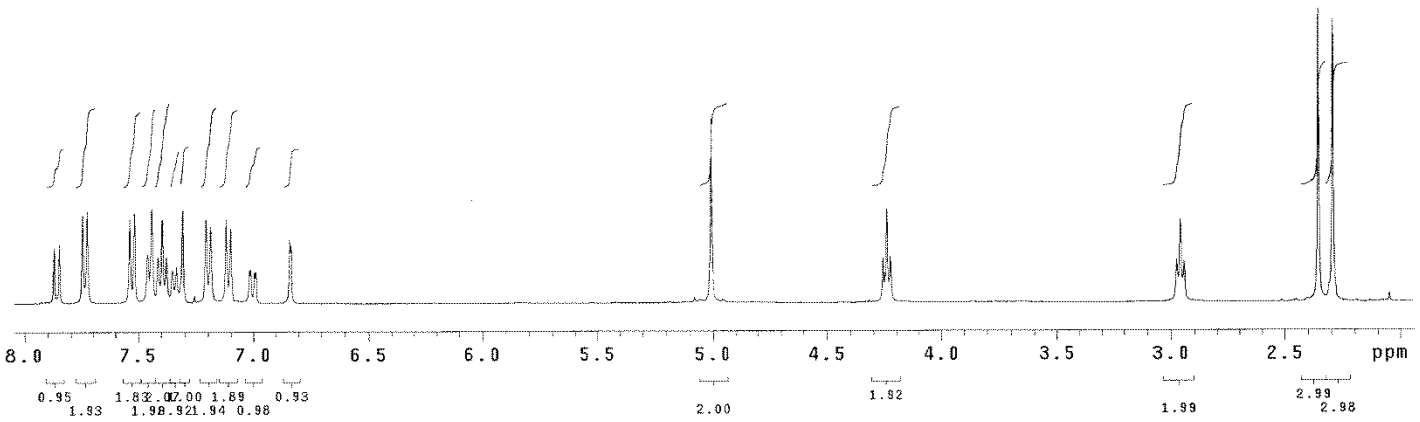
400MHz, $CDCl_3$



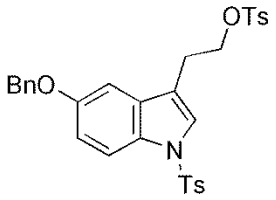


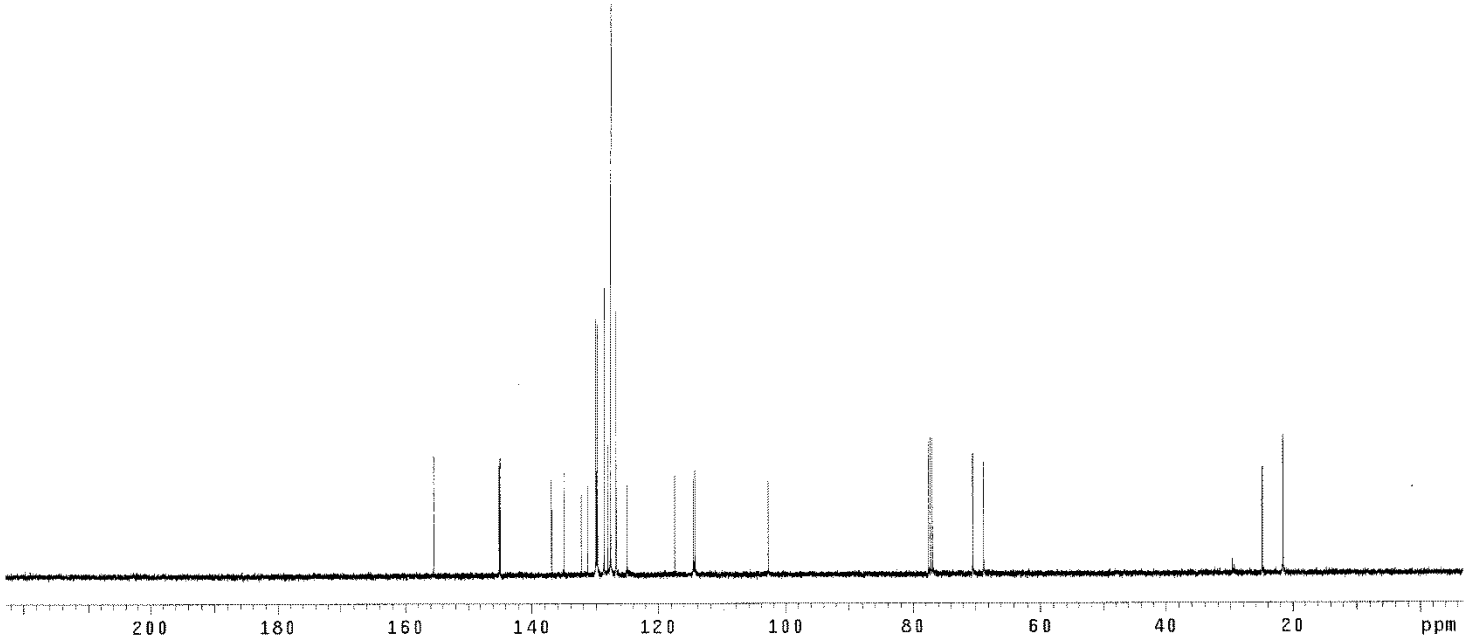
400MHz, $CDCl_3$





100MHz, $CDCl_3$





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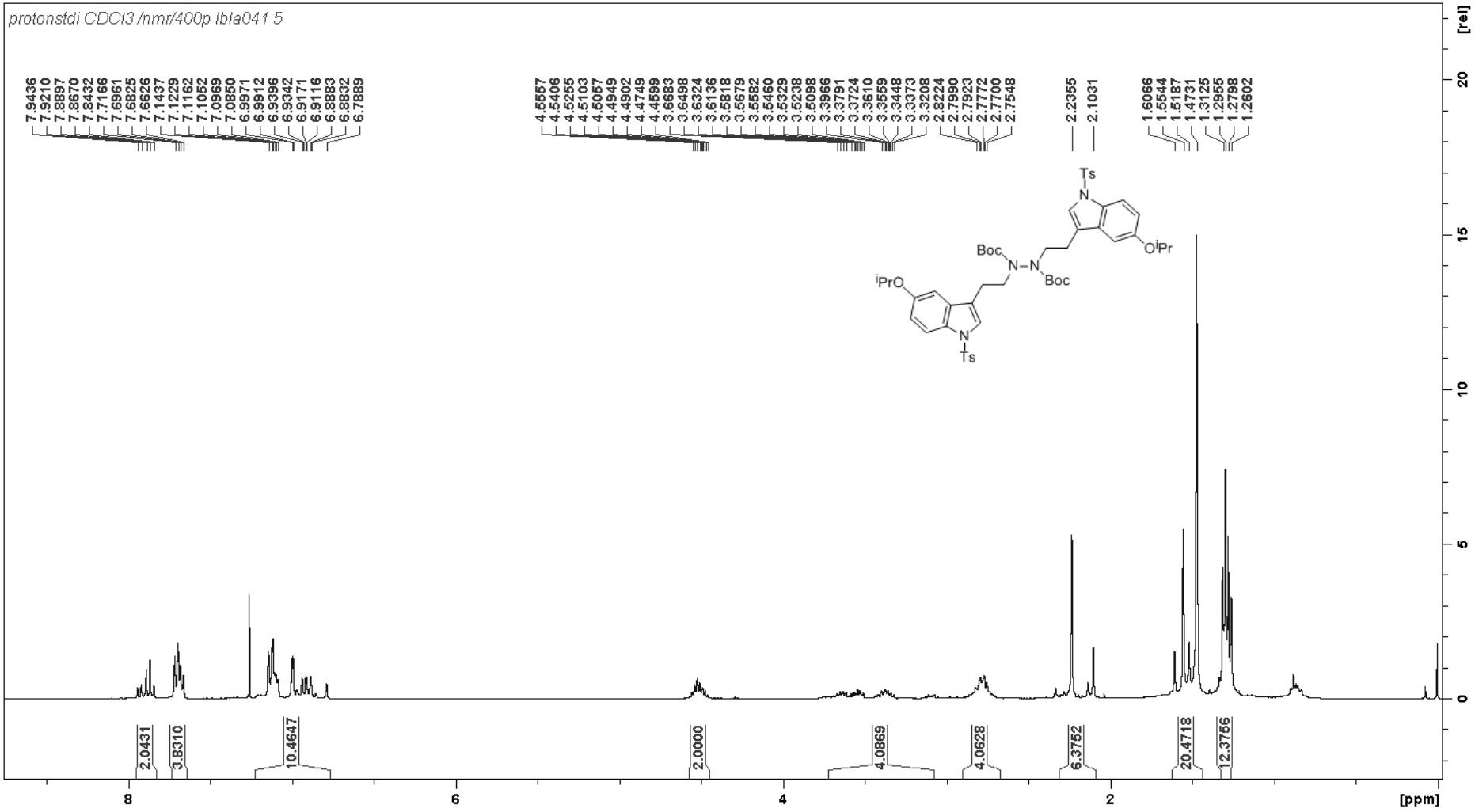

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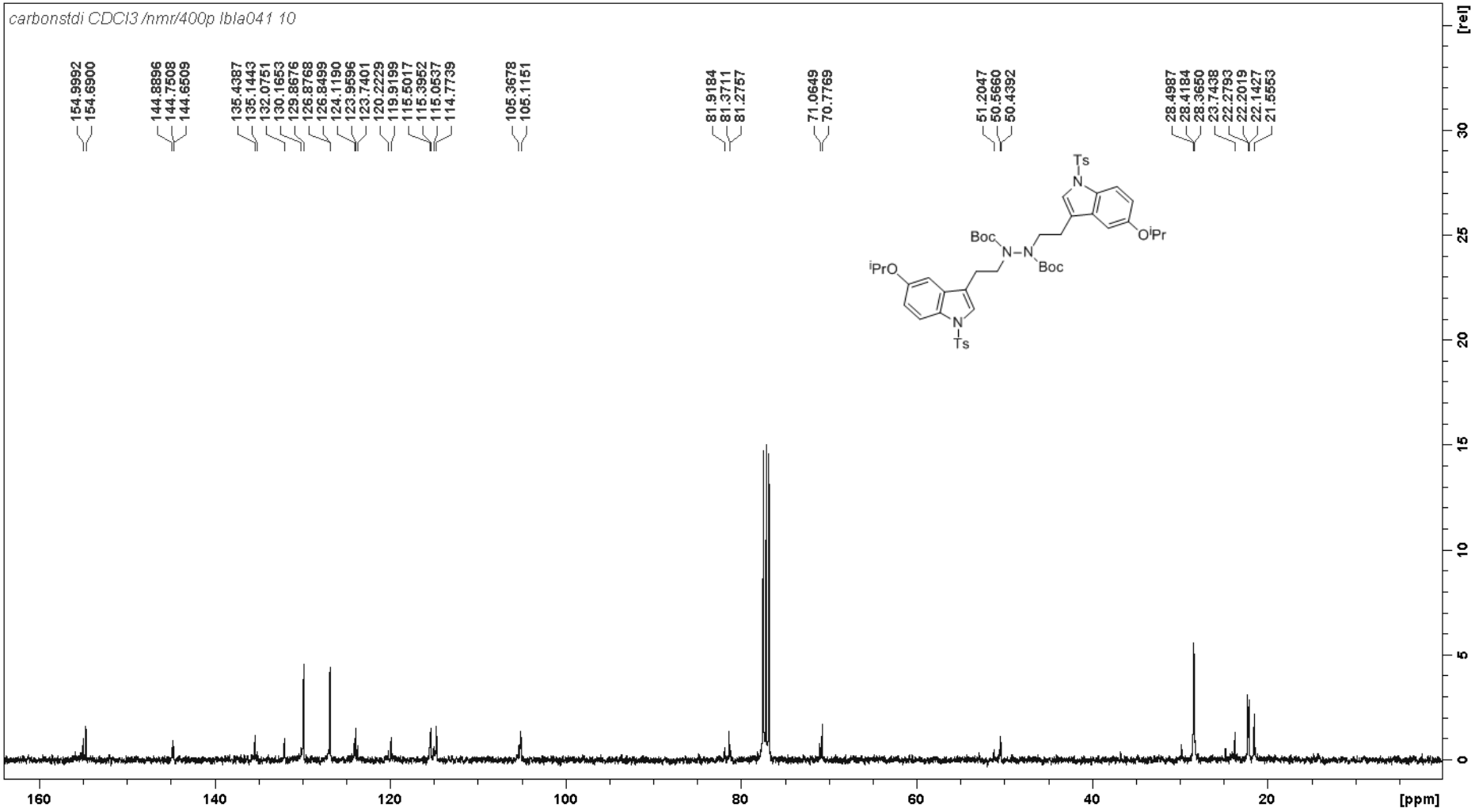

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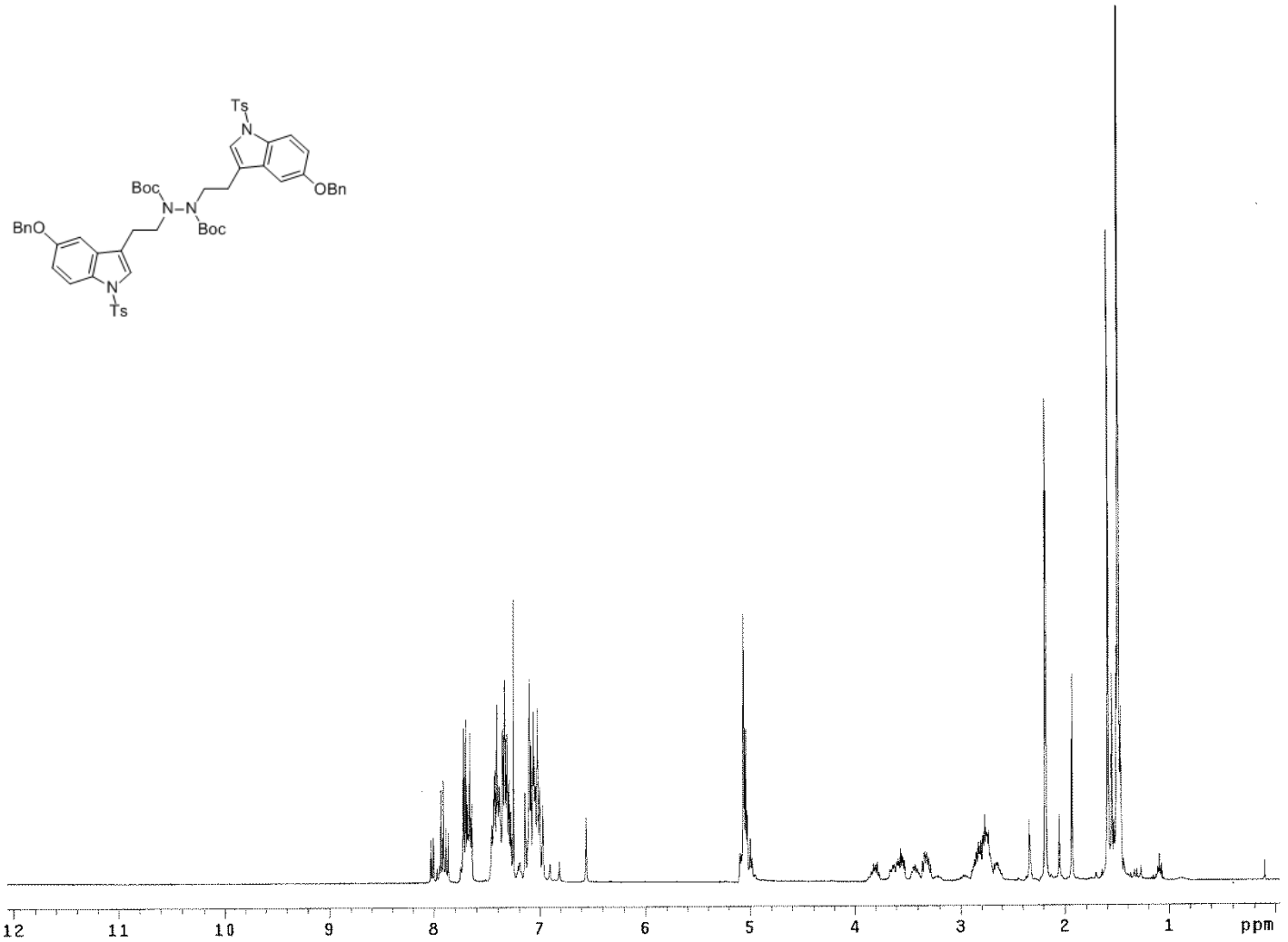

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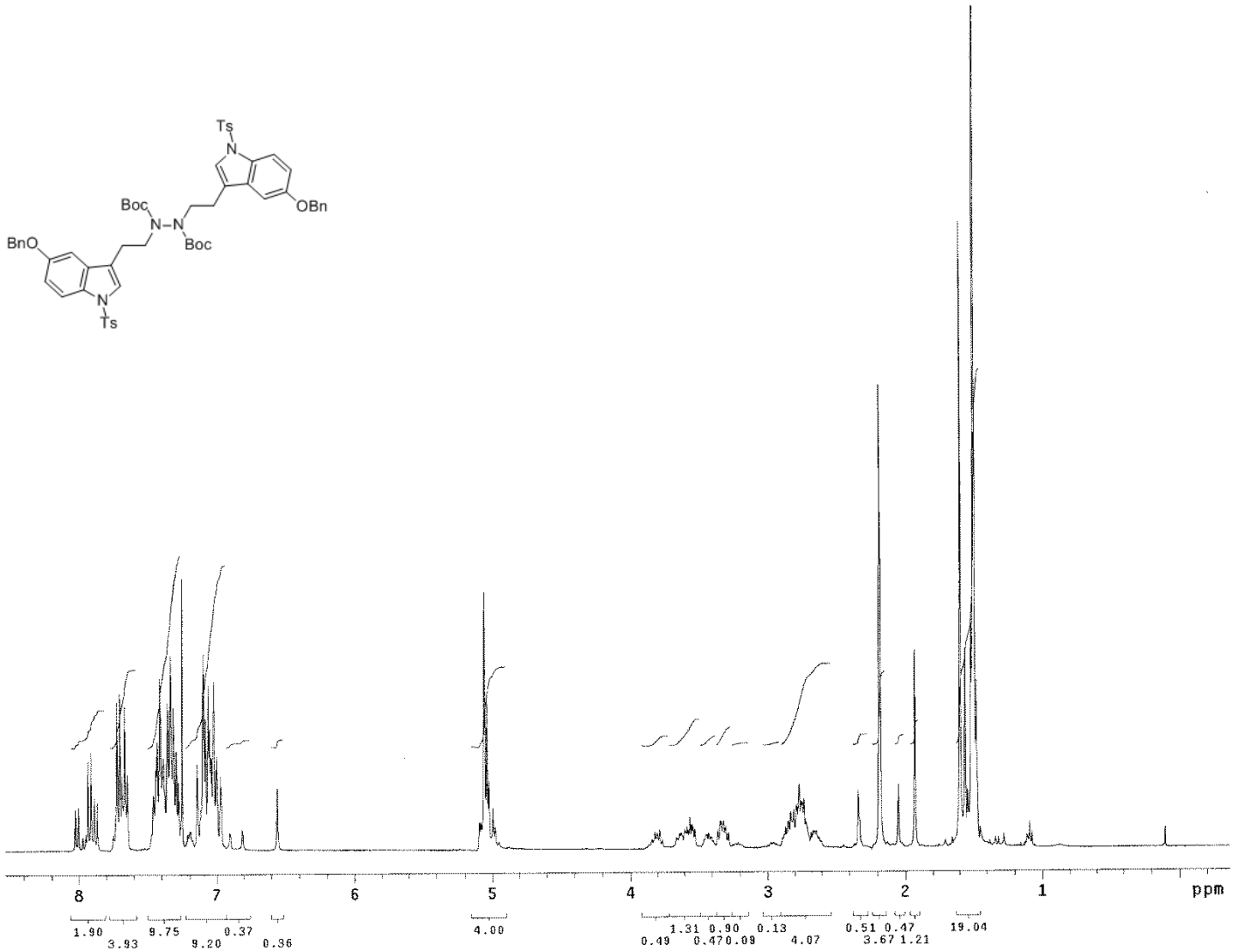

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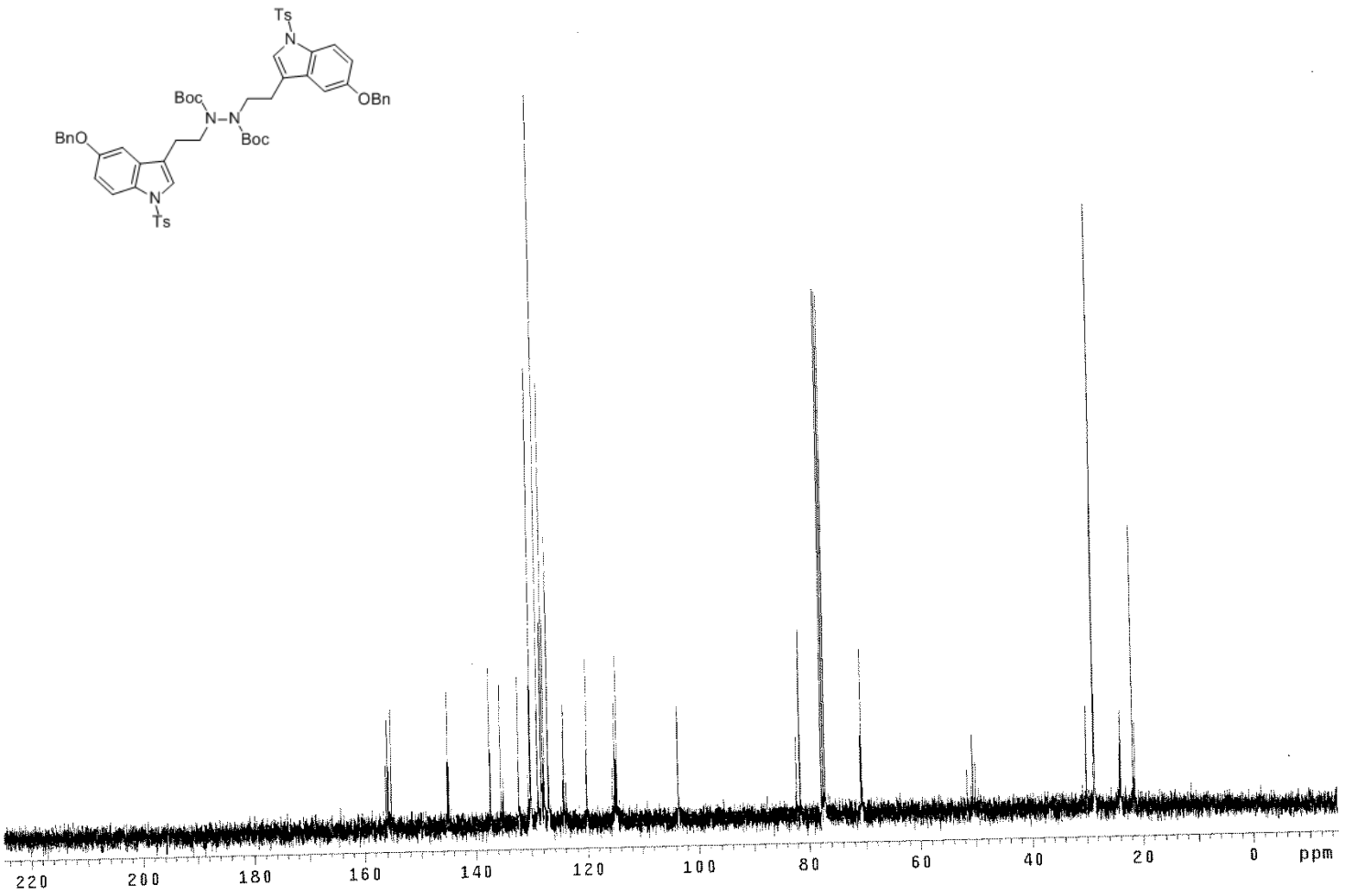

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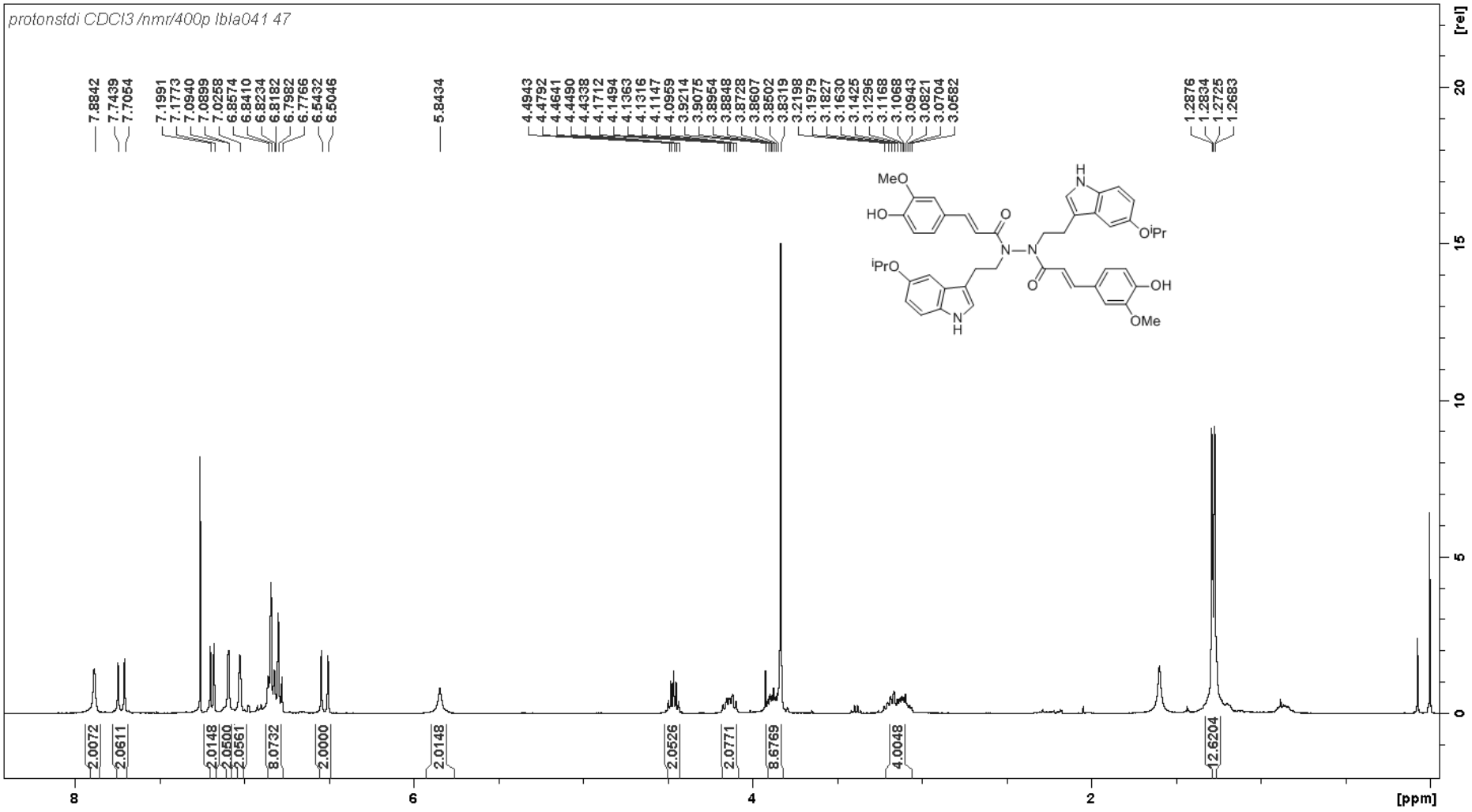
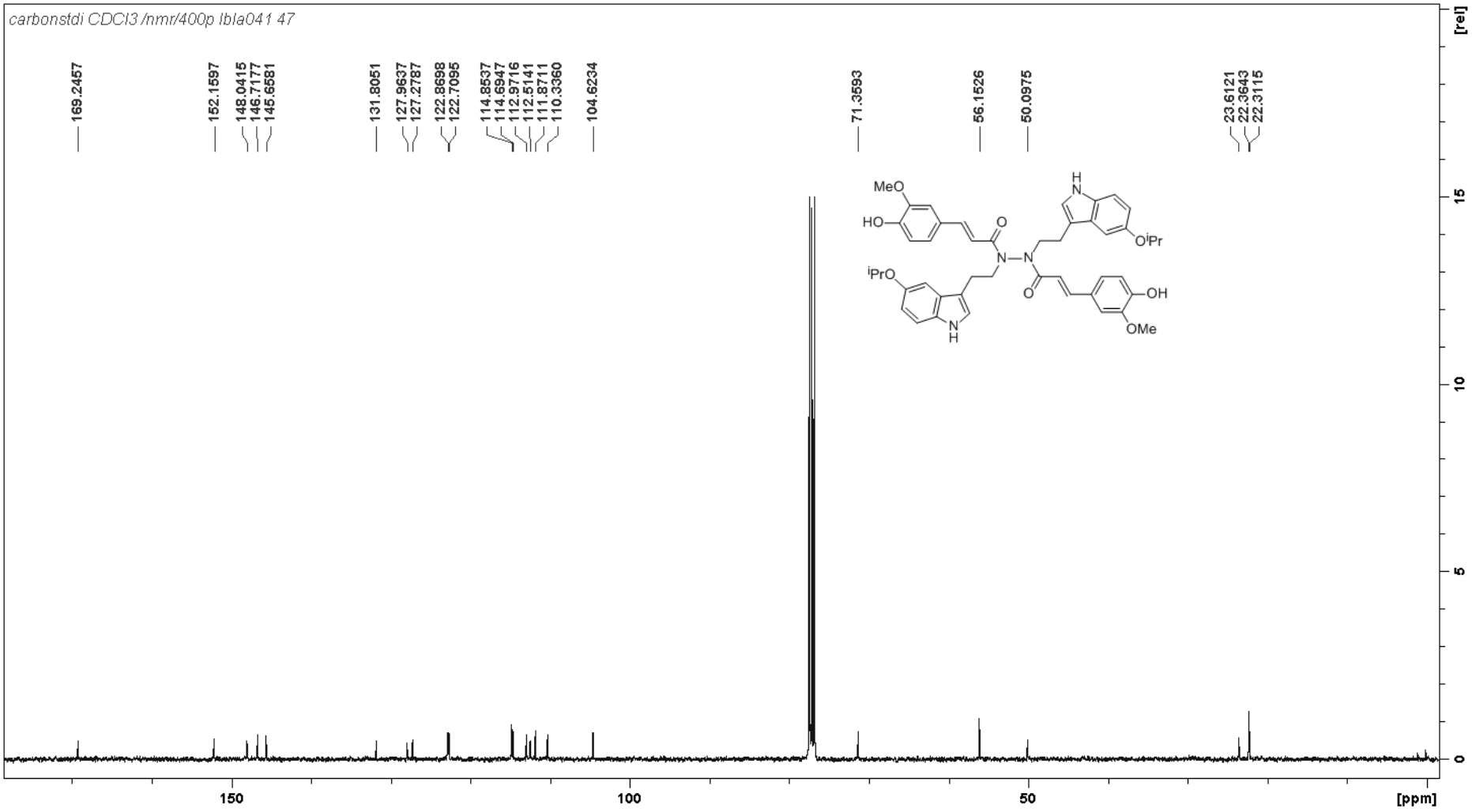
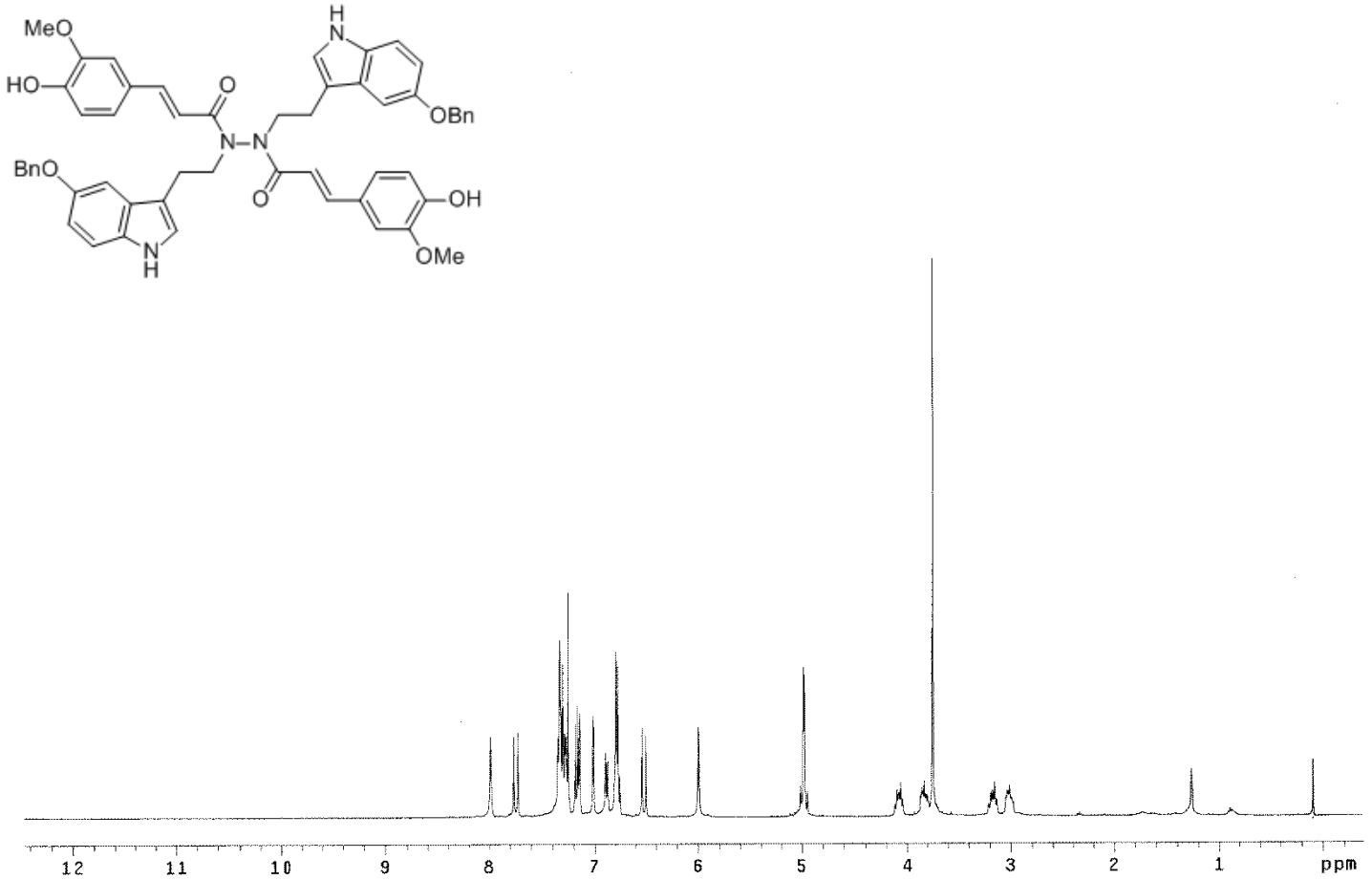


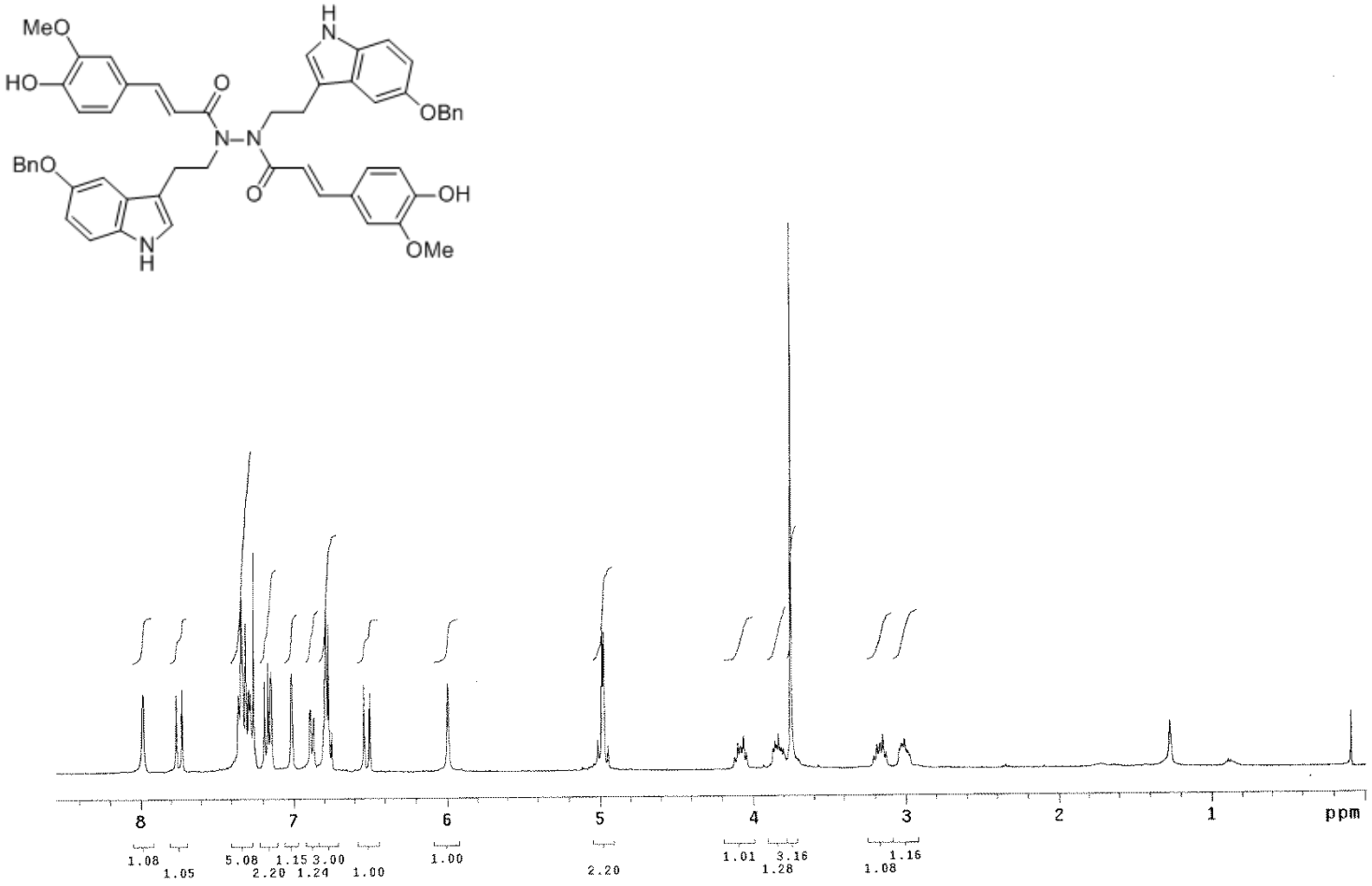
100MHz, $CDCl_3$



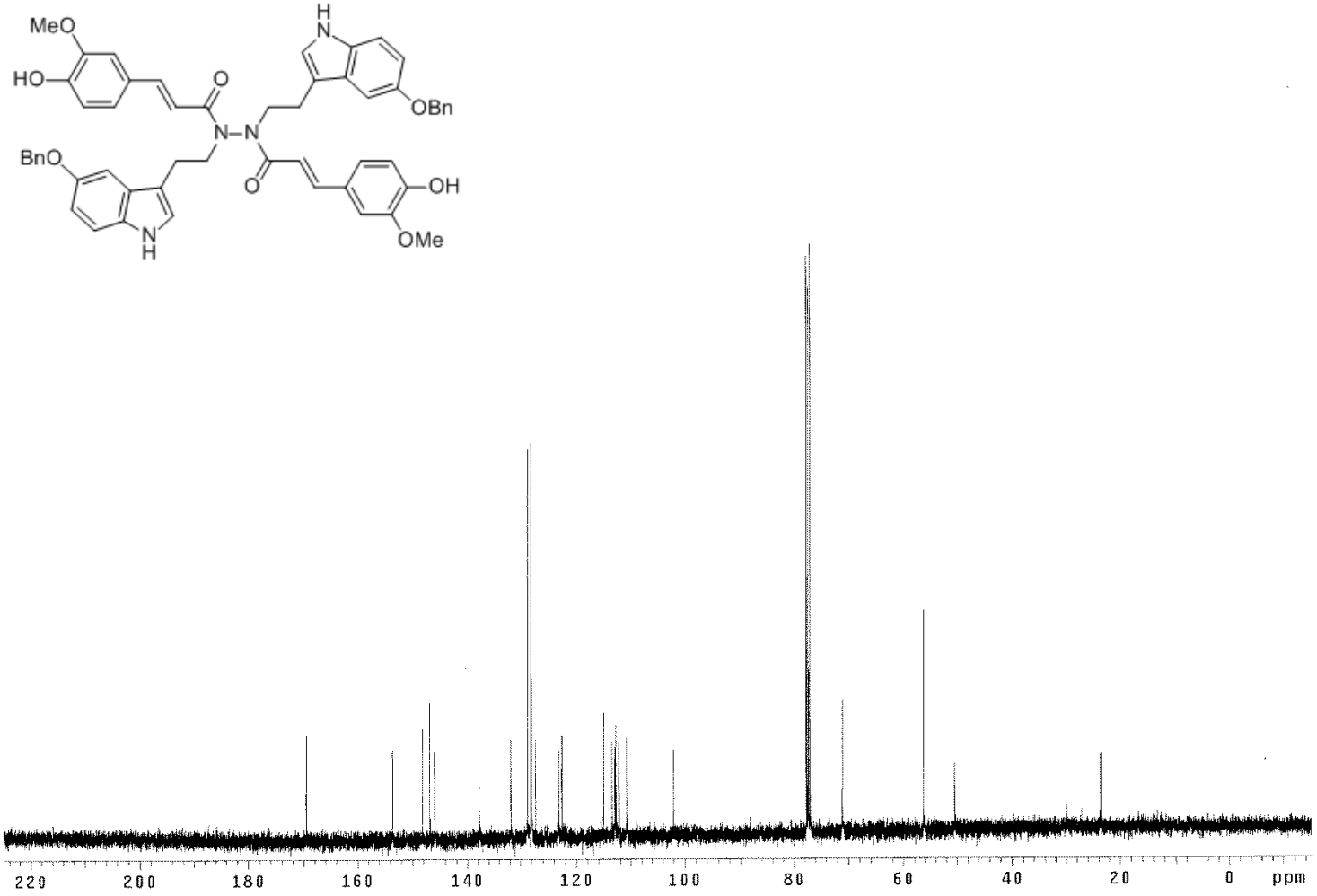
400MHz, $CDCl_3$



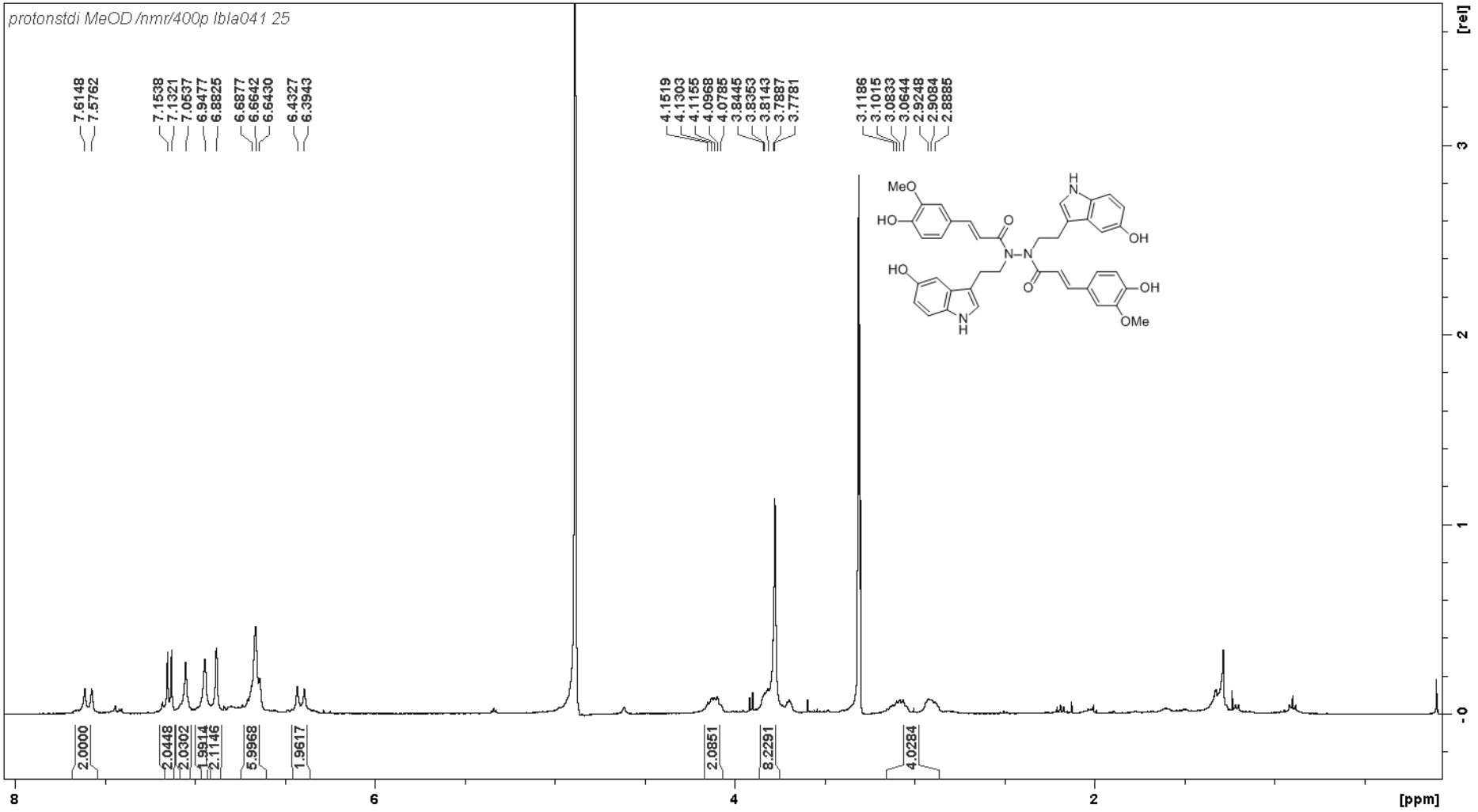
400MHz, $CDCl_3$



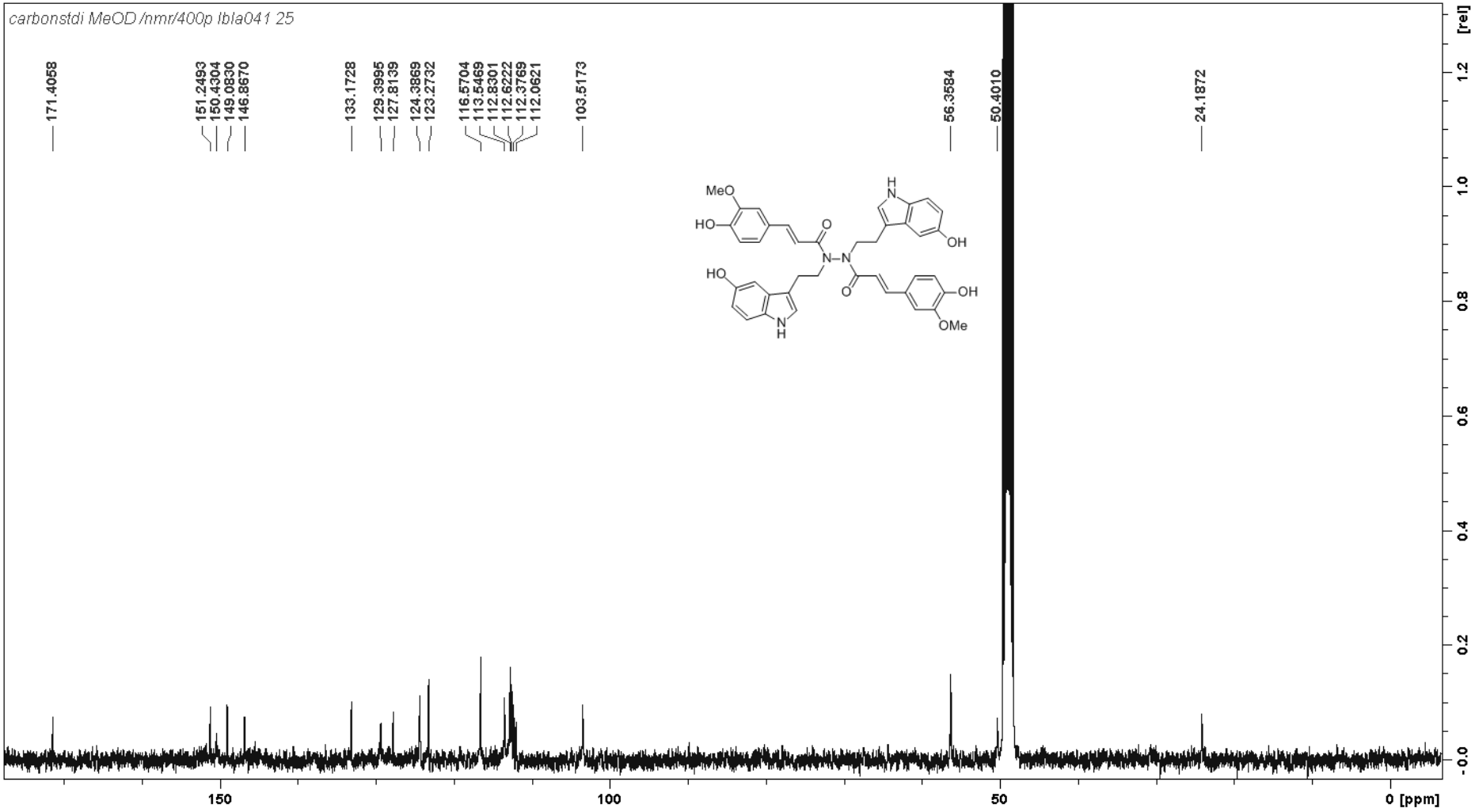
100MHz, $CDCl_3$



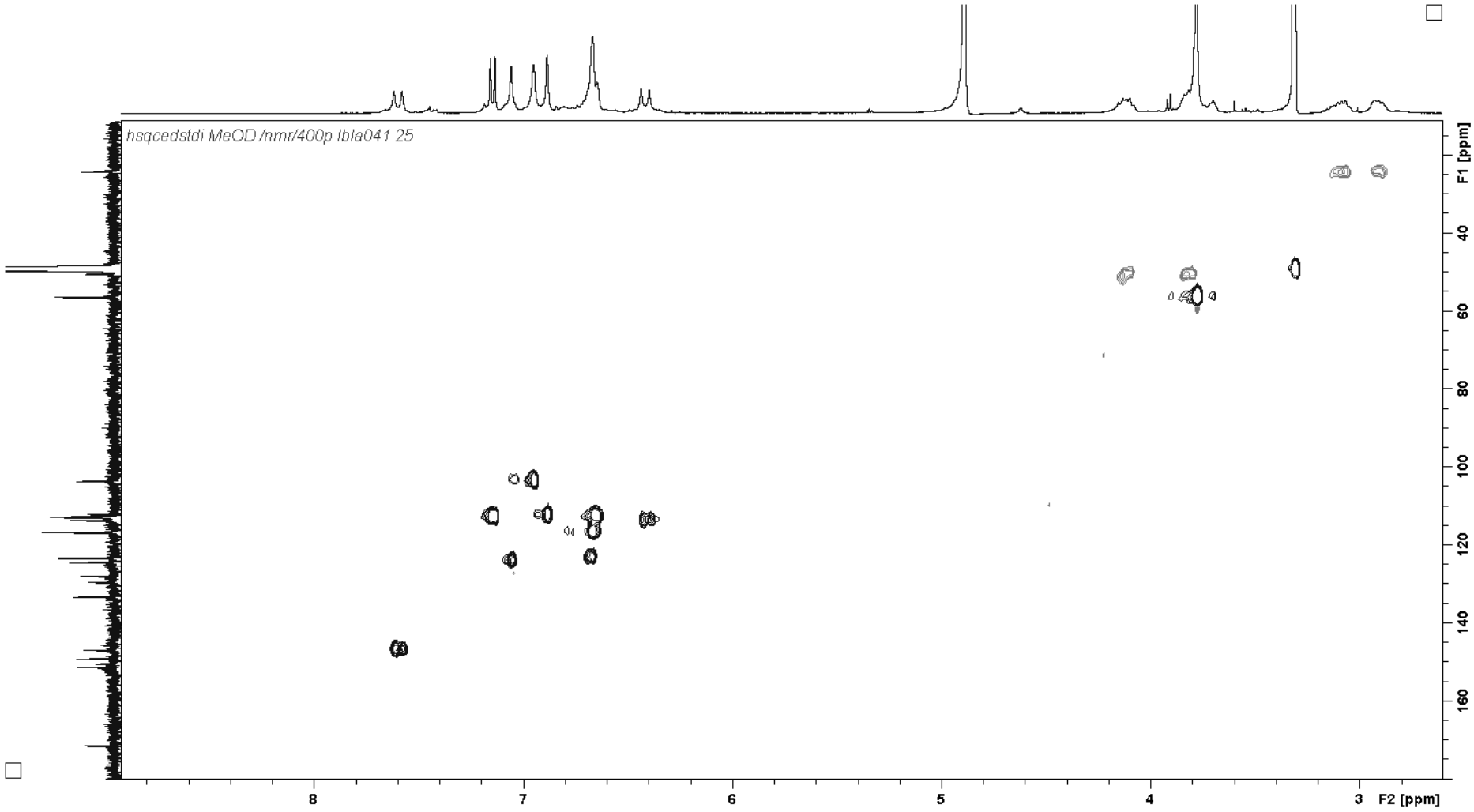
400MHz, methanol-d4



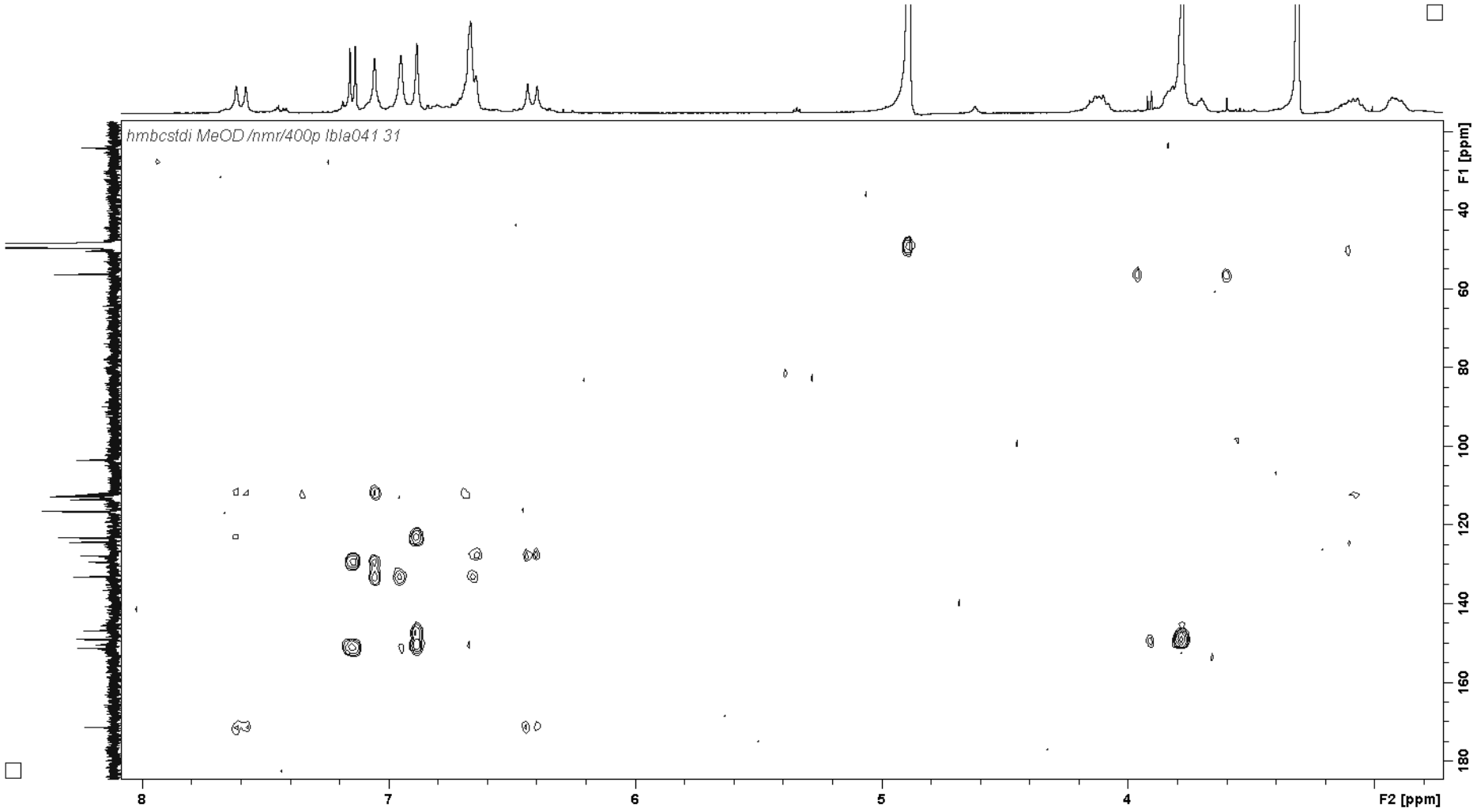
100MHz, methanol-d4



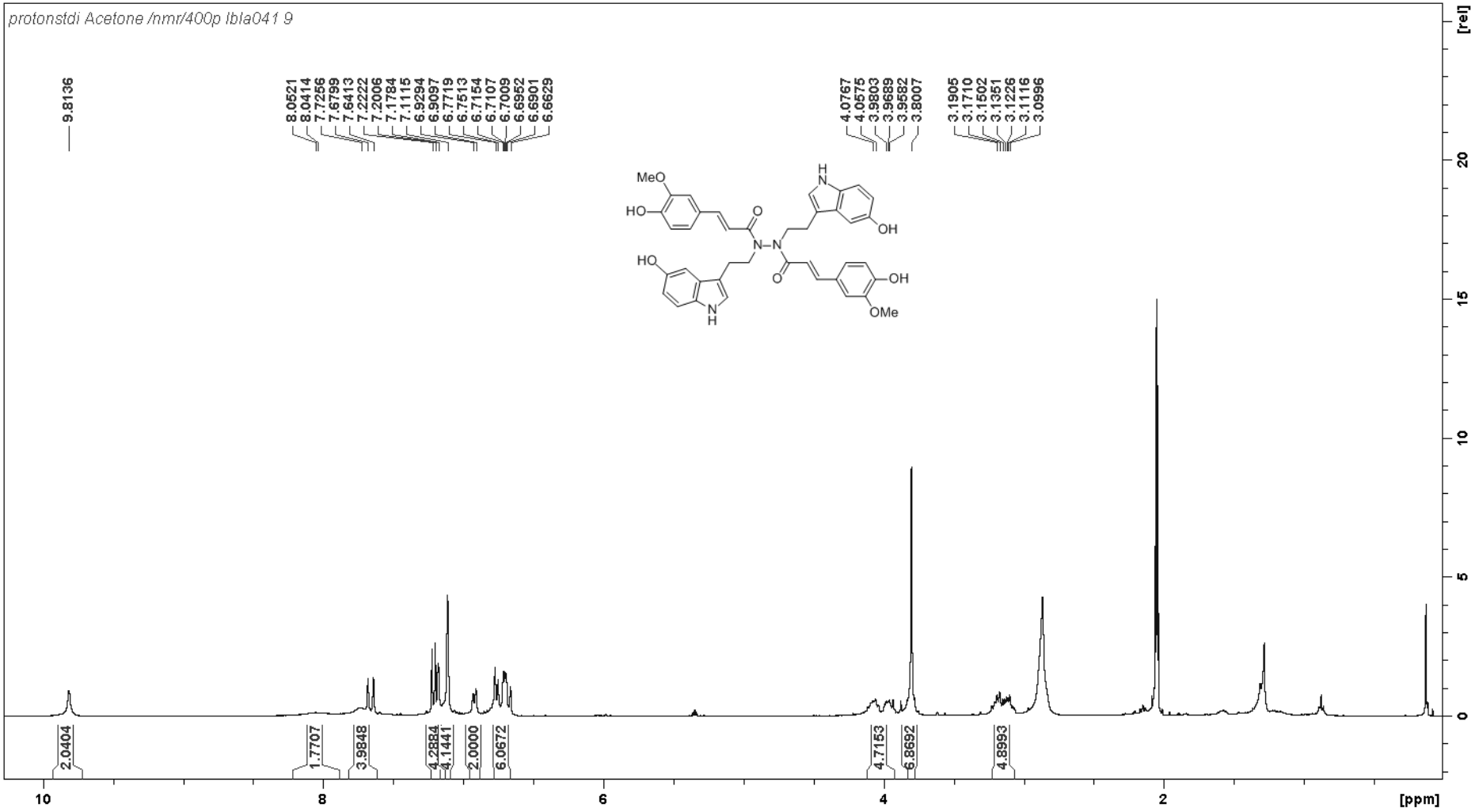
HSQC of synthetic **1** in methanol-d4



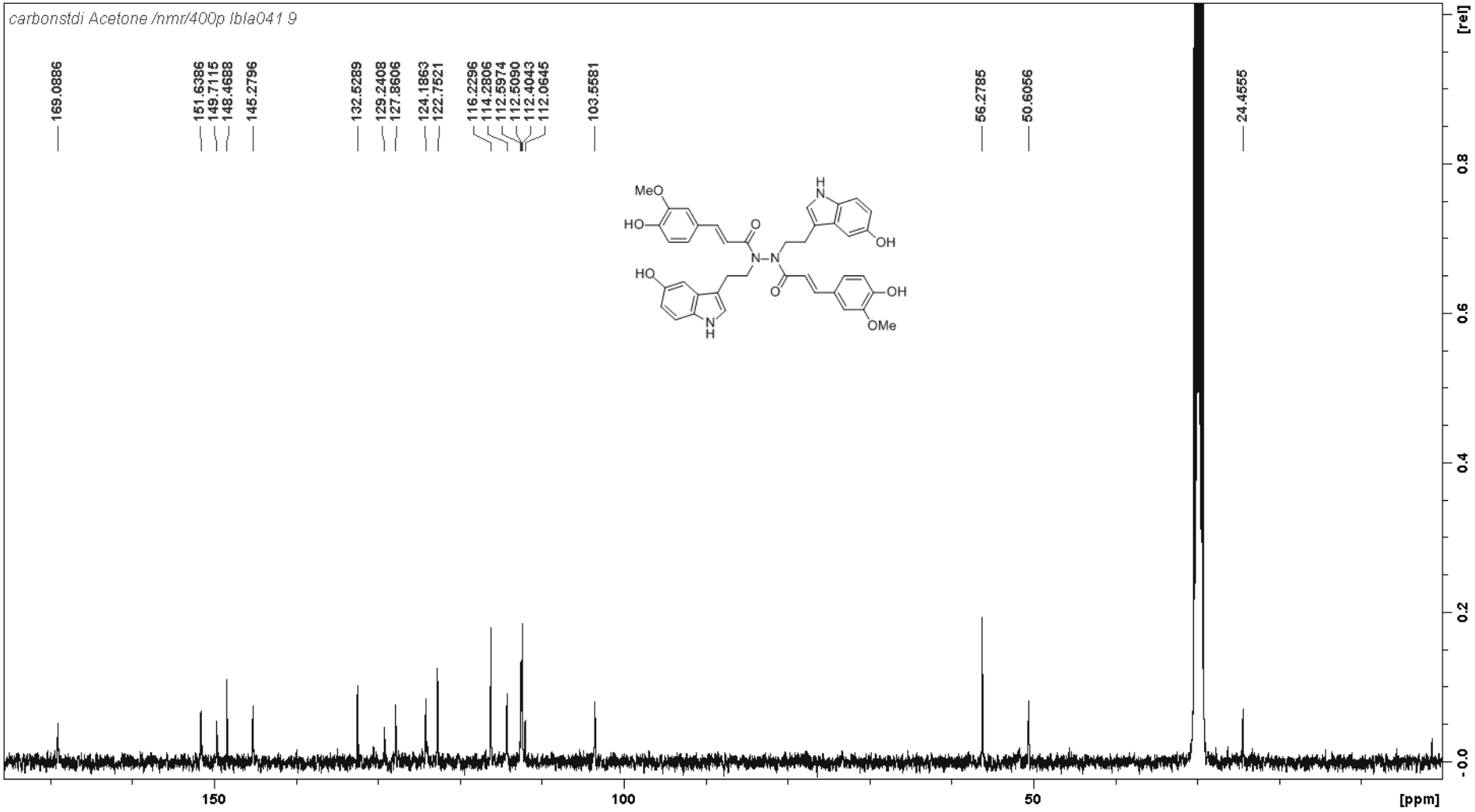
HMBC of synthetic **1** in methanol-d4. For tabulated data, **see Table S2.**



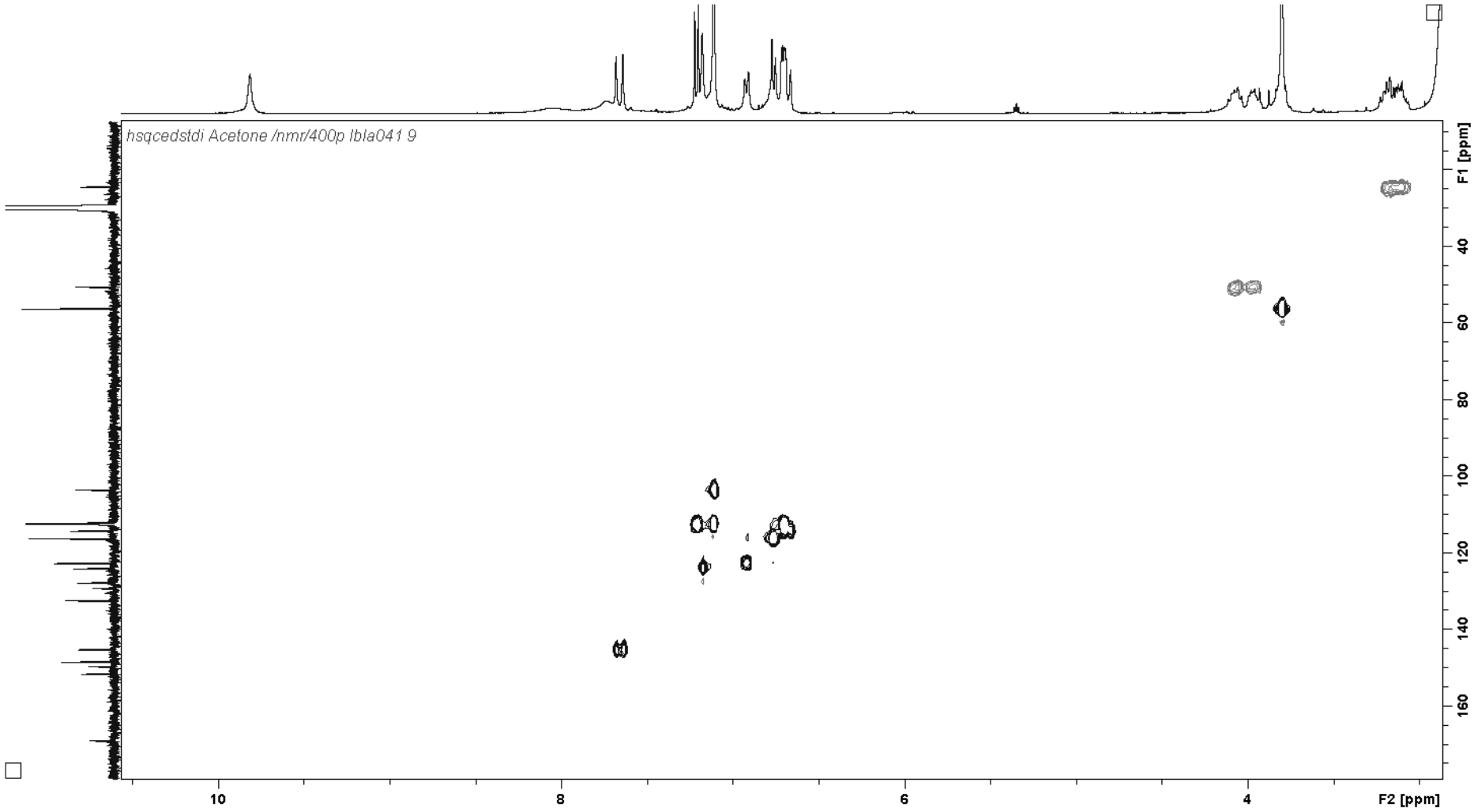
400MHz, acetone-d6



100MHz, acetone-d6



HSQC of synthetic **1** in acetone-d6



HMBC of synthetic **1** in acetone-d6