

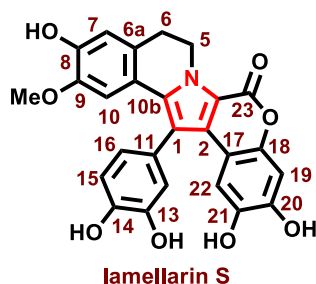
Concise and Scalable Total Syntheses of Lamellarin Z and other Natural Lamellarins: Regiocontrolled Assembly of the Central Pyrrole Core and Cross Dehydrogenative Coupling Enroute to the Pentacyclic Coumarin-Pyrrole-Isoquinoline Scaffold

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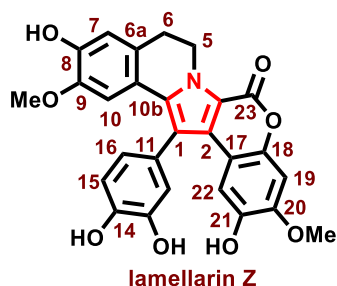
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Table S1: ^1H & ^{13}C NMR comparison of presently synthesized lamellarin S with the reported data.

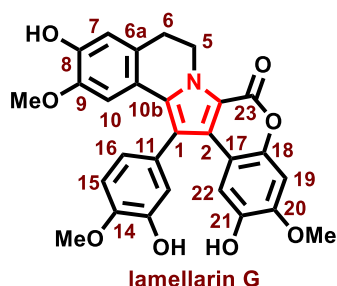
Carbon No.	^1H NMR (reported) ¹	^1H NMR (Synthesized)	^{13}C NMR (reported) ¹	^{13}C NMR (Synthesized)
1			116.4	116.4
2			129.9	129.9
3			113.8	113.8
5	4.67-4.53 (m, 2H)	4.70-4.54 (m, 2H)	43.5	43.5
6	2.97 (m, 2H)	3.00 (t, $J = 6.8$ Hz, 2H)	29.3	29.3
6a			128.7	128.7
7	6.67 (s, 1 H)	6.70 (s, 1 H)	115.8	115.8
8			148.0	148.1
9			147.2	147.3
10	6.59 (s, 1 H)	6.62 (s, 1 H)	110.4	110.4
10a			120.2	120.2
10b			138.5	138.6
11			128.1	128.1
12	6.86 (s, 1 H)	6.87 (d, 1 H, $J = 2$)	119.0	119.0
13			147.4	147.46
14			146.6 ^a	146.7 ^a
15	6.96 (d, 1 H, $J = 8.0$ Hz)	6.98 (d, 1 H, $J = 8$)	117.5	117.5
16	6.75 (d, 1 H, $J = 8.0$ Hz)	6.77 (dd, 1 H, $J = 8.0, 2.0$ Hz))	123.7	123.7
17			111.3	111.3
18			147.4	147.41
19	6.72 (s, 1 H)	6.75 (s, 1 H)	104.2	104.2
20			146.7 ^b	146.73 ^b
21			143.4	143.4
22	6.81 (s, 1 H)	6.83 (s, 1 H)	109.8	109.8
23			157.6	157.6
OMe	3.36 (s, 3 H)	3.38 (s, 3 H)	55.6	55.6

^{a-b} interchangeable assignments.

Table S2: ^1H and ^{13}C NMR comparison of presently synthesized lamellarin Z with the reported data.

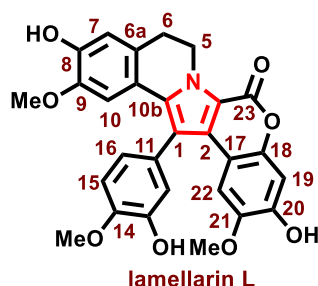
Carbon No.	^1H NMR (reported) ²	^1H NMR (Synthesized)	^{13}C NMR (reported) ²	^{13}C NMR (Synthesized)
1			114.7	114.7
2			126.9	126.9
3			112.4	112.5
5	4.66 (dm, 1 H, $J = 13.2$ Hz), 4.52 (dm, 1 H, $J = 13.2$ Hz)	4.71-4.65 (m, 1 H), 4.55-4.49 (m, 1 H)	41.9	41.9
6	2.98 (m, 2H)	2.97 (m, 2H)	27.5	27.5
6a			127.1	127.1
7	6.71 (s, 1 H)	6.72 (s, 1 H)	115.2	115.2
8			147.0	146.9
9			145.9	145.9
10	6.54 (s, 1 H)	6.55 (s, 1 H)	109.3	109.3
10a			118.0	118.1
10b			136.0	136.0
11			125.3	125.4
12	6.74 (d, 1 H, $J = 2.4$ Hz)	6.76 (d, 1 H, $J = 2.0$ Hz)	117.8	117.7
13			146.2	146.1
14			145.4	145.3
15	6.92 (d, 1 H, $J = 7.8$ Hz)	6.93 (d, 1 H, $J = 8.0$ Hz)	116.7	116.6
16	6.67 (dd, 1 H, $J = 7.8, 2.4$ Hz)	6.69 (dd, 1 H, $J = 8.0, 2.0$ Hz)	121.4	121.5
17			110.2	110.2
18			144.6 ^e	144.6 ^e
19	6.99 (s, 1 H)	7.00 (s, 1 H)	100.7	100.7
20			147.8	147.8
21			142.8 ^f	142.8 ^f
22	6.70 (s, 1 H)	6.70 (s, 1 H)	108.4	108.4
23			154.3	154.3
OMe-9	3.29 (s, 3 H)	3.29 (s, 3 H)	54.7	54.6
OMe-20	3.79 (s, 3 H)	3.80 (s, 3 H)	55.8	55.8
OH-8		9.34 (br s, 1 H) ^a		
OH-13		9.12 (br s, 1 H) ^b		
OH-14		9.08 (br s, 1 H) ^c		
OH-21		8.92 (br s, 1 H) ^d		

^{a-d} Interchangeable proton assignment & protons with variable position^{e-f} Interchangeable carbon assignment

Table S3: ^1H and ^{13}C NMR comparison of presently synthesized lamellarin G with the reported data.

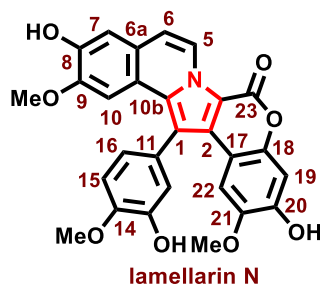
Carbon No.	^1H NMR (reported) ³	^1H NMR (Synthesized)	^{13}C NMR (reported) ³	^{13}C NMR (Synthesized)
1			114.2	114.4
2			126.7	126.9
3			112.4	112.6
5	4.70-4.53 (m, 2 H)	4.69-4.63 (m, 1 H); 4.57-4.51 (m, 1H)	41.9	42.0
6	3.00 (m, 2H)	2.98 (t, 2H, $J = 6.8$ Hz)	27.4	27.6
6a			127.0	127.2
7	6.73 (s, 1 H)	6.72 (s, 1 H)	115.2	115.3
8			146.9	147.0
9			145.8	146.0
10	6.49 (s, 1 H)	6.48 (s, 1 H)	109.0	109.2
10a			117.8	118.0
10b			135.9	136.1
11			127.1	127.2
12	6.83 (s, 1 H)	6.81 (d, 1 H, $J = 2.0$ Hz)	117.6	117.6
13			147.3	147.5
14			147.3	147.7
15	7.13 (d, 1 H, $J = 8.0$ Hz)	7.13 (d, 1 H, $J = 8.0$ Hz)	113.3	113.3
16	6.84 (d, 1 H, $J = 8.0$ Hz)	6.83 (dd, 1 H, $J = 8.0, 2.0$ Hz)	121.3	121.5
17			110.0	110.1
18			144.5 ^d	144.7 ^d
19	7.01 (s, 1 H)	7.00 (s, 1 H)	100.6	100.8
20			147.7 ^e	147.9 ^e
21			142.6	142.8
22	6.68 (s, 1 H)	6.66 (s, 1 H)	108.2	108.3
23			154.2	154.4
OMe-20	3.81 (s, 3 H)	3.80 (s, 3 H)	55.7	55.9
OMe-14	3.86 (s, 3 H)	3.85 (s, 3 H)	55.6	55.8
OMe-9	3.27 (s, 3 H)	3.25 (s, 3 H)	54.5	54.6
OH-8		9.43 (br s, 1 H) ^a		
OH-13		9.30 (br s, 1 H) ^b		
OH-21		8.99 (br s, 1 H) ^c		

^{a-c} Interchangeable proton assignment & protons with variable position^{e-f} Interchangeable carbon assignment

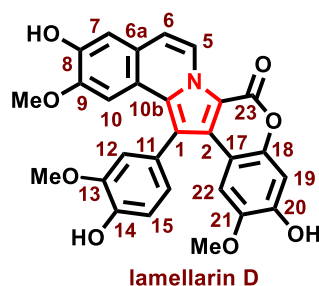
Table S4: ^1H and ^{13}C NMR comparison of presently synthesized lamellarin L with the reported data.

Carbon No.	^1H NMR (reported) ⁴	^1H NMR (Synthesized)	^{13}C NMR (reported) ⁴	^{13}C NMR (Synthesized)
1			115.2	115.5
2			127.3	127.7
3			113.4	113.6
5	4.69-4.60 (m, 1H); 4.60-4.51 (m, 1H)	4.65-4.58 (m, 1H) 4.56-4.50 (m, 1H)	41.9	42.2
6	3.01 (t, 2H, J = 6.8 Hz)	2.99 (t, 2H, J = 6.8 Hz,)	27.4	27.7
6a			127.1	127.4
7	6.75 (s, 1H)	6.74 (s, 1 H)	112.2	112.5
8			147.0	147.3
9			145.9	146.2
10	6.68 (s, 1H)	6.67 (s, 1 H)	108.6	108.9
10a			117.9	118.2
10b			135.7	136.0
11			127.3	127.5
12	6.92-6.88 (m, 1H)	6.90-6.87 (m, 1H)	113.8	114.2
13			147.5	147.8
14			147.4	147.7
15	7.16 (d, J = 7.9 Hz)	7.15 (d, J = 8.0 Hz)	117.8	118.0
16	6.92-6.88 (m, 1H)	6.90-6.87 (m, 1H)	121.6	121.9
17			109.2	109.4
18			146.7	147.0
19	6.80 (s, 1H)	6.79 (s, 1H)	103.5	103.8
20			145.6	145.8
21			144.4	144.7
22	6.68 (s, 1H)	6.65 (s, 1 H)	104.9	105.2
23			154.2	154.5
OMe-21	3.38 (s, 3 H)	3.36 (s, 3 H)	55.0	55.2
OMe-14	3.83 (s, 3 H)	3.81 (s, 3 H)	56.0	56.2
OMe-9	3.29 (s, 3 H)	3.27 (s, 3 H)	54.6	54.9
OH-8	9.67 (br s, 1 H) ^a	9.78 (br s, 1 H) ^a		
OH-13	9.44 (br s, 1 H) ^b	9.53 (br s, 1 H) ^b		
OH-20	9.30 (br s, 1 H) ^c	9.40 (br s, 1 H) ^c		

^{a-c} Protons with variable position

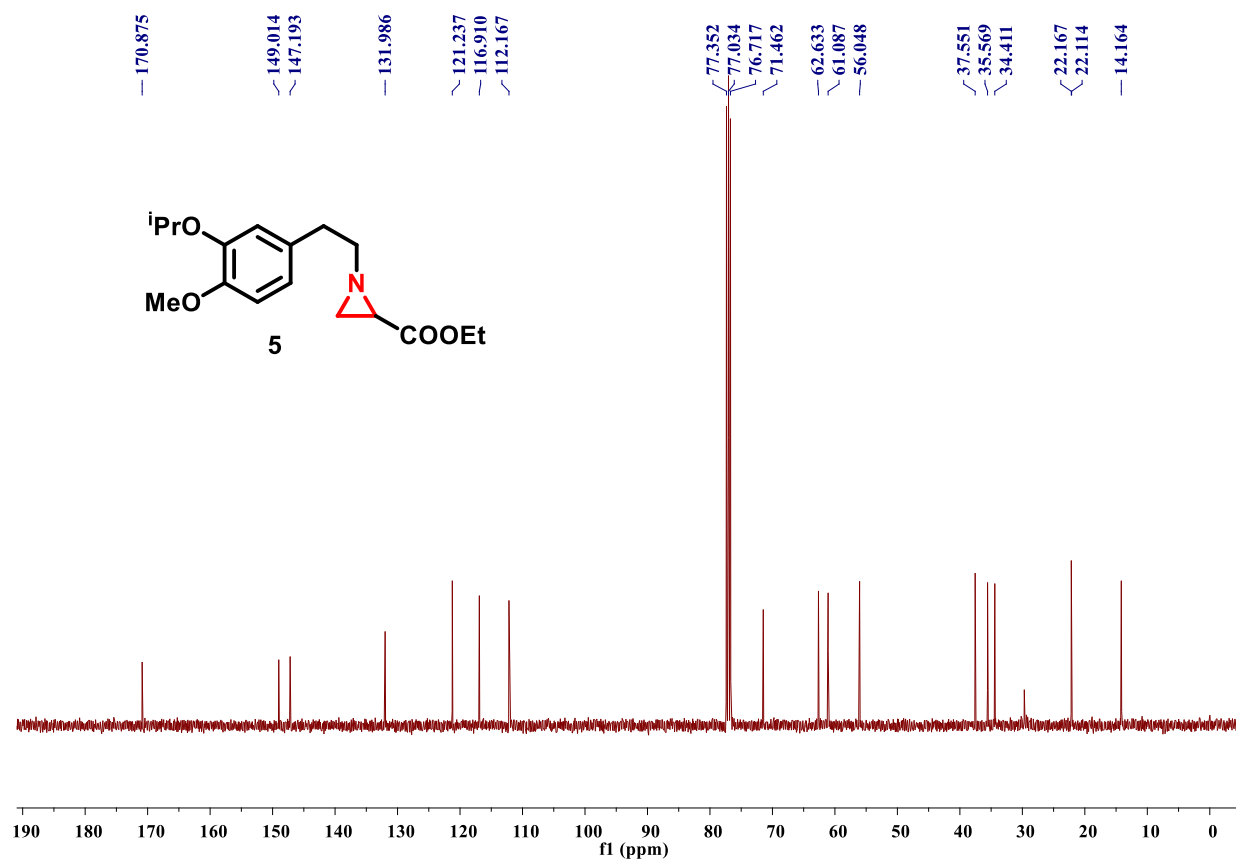
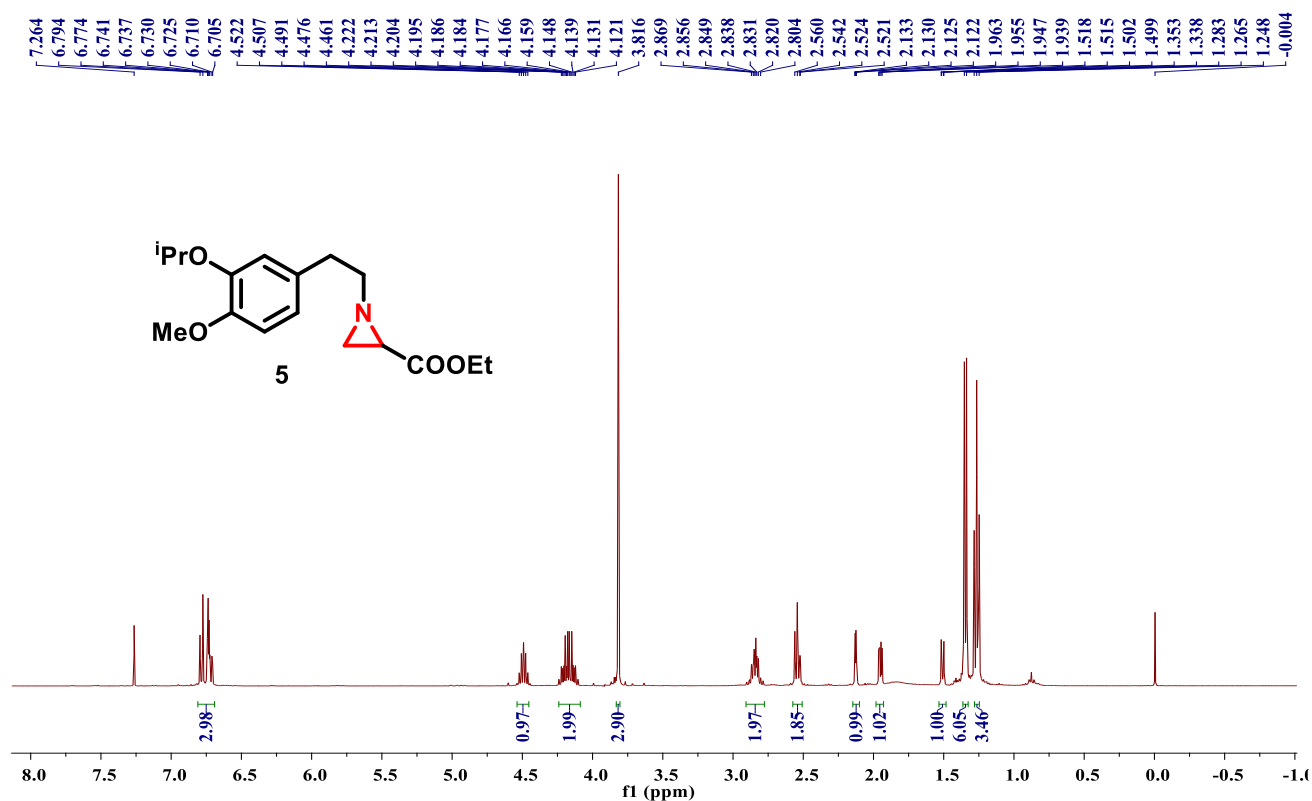
Table S5: ^1H and ^{13}C NMR comparison of presently synthesized lamellarin N with the reported data.

^1H NMR (reported) ⁴	^1H NMR (Synthesized)	^{13}C NMR (reported) ⁴	^{13}C NMR (Synthesized)
9.90 (br, s, 2H)	9.98 (br, s, 1H); 9.88 (br s, 1H)	154.2	154.4
9.40 (br, s, 1H)	9.42 (br, s, 1H) ⁱ	148.4	148.6
9.01 (d, 1H, $J=7.4$ Hz)	9.01 (d, 1H, $J=7.2$ Hz)	148.2	148.4
7.25 (d, 1H, $J=8.7$ Hz)	7.25 (d, 1H, $J=8.0$ Hz)	147.9	148.0
7.22 (d, 1H, $J=7.4$ Hz)	7.22 (d, 1H, $J=7.6$ Hz)	147.7	147.9
7.20 (s, 1 H)	7.19 (s, 1 H)	147.6	147.7
7.17 (s, 1 H)	7.17 (s, 1 H)	146.2	146.4
7.05–7.01 (m, 2H)	7.04–7.01 (m, 2H)	144.5	144.6
6.87 (s, 1H)	6.87 (s, 1H)	133.8	133.9
6.76 (s, 1 H)	6.76 (s, 1 H)	128.7	128.8
3.87 (s, 3H)	3.87 (s, 3H)	127.3	127.4
3.40 (s, 3H)	3.40 (s, 3H)	124.6	124.7
3.40 (s, 3H)	3.39 (s, 3H)	122.0	122.2
		121.9	122.1
		118.1	118.3
		117.3	117.5
		113.6	113.7
		112.3	112.5
		111.4	111.6
		110.4	110.6
		108.1	108.3
		106.4	106.5
		105.6	105.7
		105.2	105.3
		103.7	103.8
		56.0	56.2
		55.0	55.1
		54.4	54.6

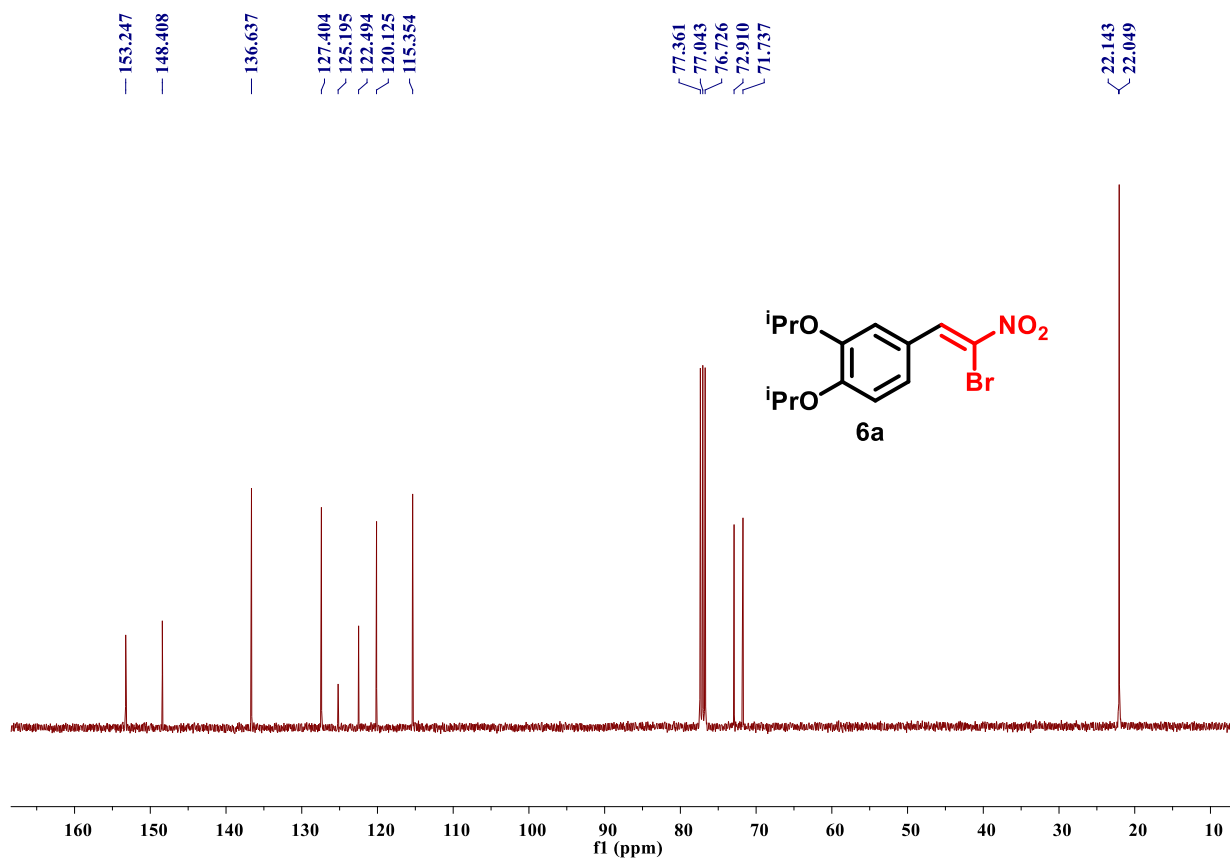
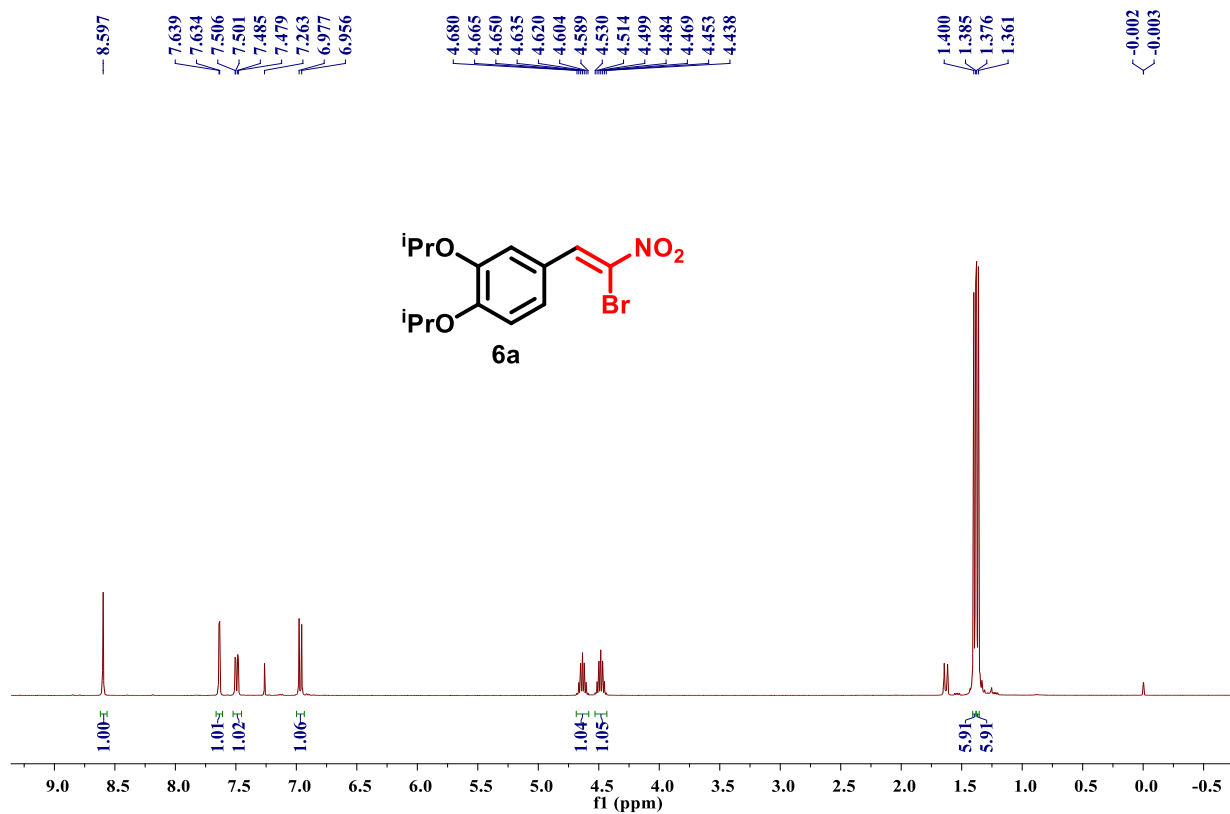
Table S6: ^1H and ^{13}C NMR comparison of presently synthesized lamellarin D with the reported data.

^1H NMR (reported) ⁵	^1H NMR (Synthesized)	^{13}C NMR (reported) ⁵	^{13}C NMR (Synthesized)
9.91 (s, 1H)	9.90 (br s, 2H)	154.3	154.4
9.80 (s, 1H)		148.7	148.7
9.32 (s, 1H)	9.39 (br s, 1H)	148.4	148.5
8.96 (d, 1H, $J=7.6$ Hz)	9.02 (d, 1H, $J=7.6$ Hz)	148.2	148.4
7.17-7.13 (m, 3H)	7.22 (d, 1H, $J=7.6$ Hz); 7.21 (s, 1 H); 7.17 (d, 1H, $J=1.6$ Hz)	147.8	147.9
7.07 (d, 1H, $J=8.0$ Hz),	7.11 (d, 1H, $J=8.0$ Hz),	146.8	146.8
7.11 (s, 1 H)	7.15 (s, 1 H)	146.3	146.4
6.98 (dd, 1H, $J=1.6, 8.0$ Hz)	7.03 (dd, 1H, $J=1.6, 8.0$ Hz)	144.5	144.6
6.69 (s, 1 H)	6.73 (s, 1 H)	134.0	134.1
6.85 (s, 1H)	6.88 (s, 1H)	128.9	129.0
3.37 (s, 3H)	3.39 (s, 3H)	125.5	125.5
3.37 (s, 3H)	3.39 (s, 3H)	124.6	124.7
3.76 (s, 3H)	3.79 (s, 3H)	123.8	123.8
		121.9	122.1
		117.5	117.6
		116.4	116.4
		115.1	115.0
		112.3	112.4
		111.5	111.5
		110.7	110.9
		108.3	108.4
		106.4	106.4
		105.8	105.7
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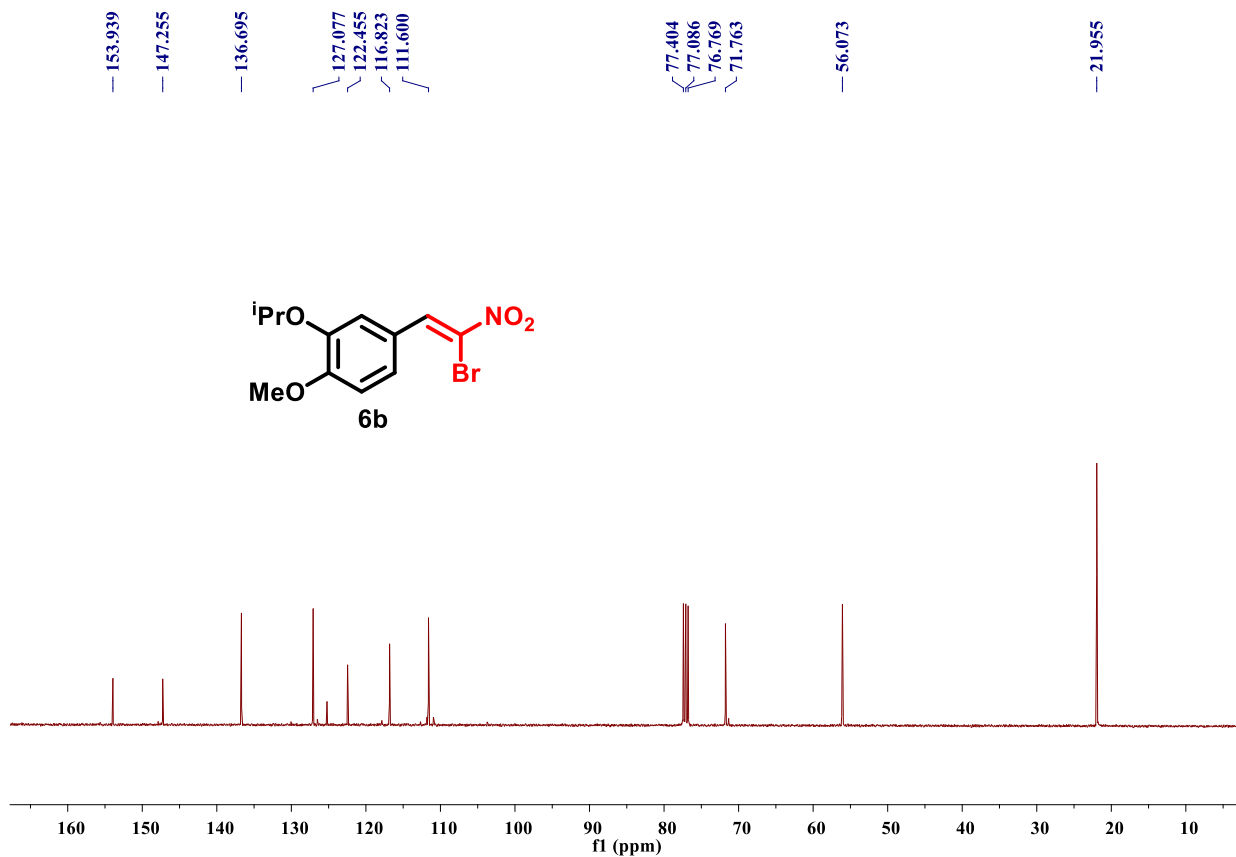
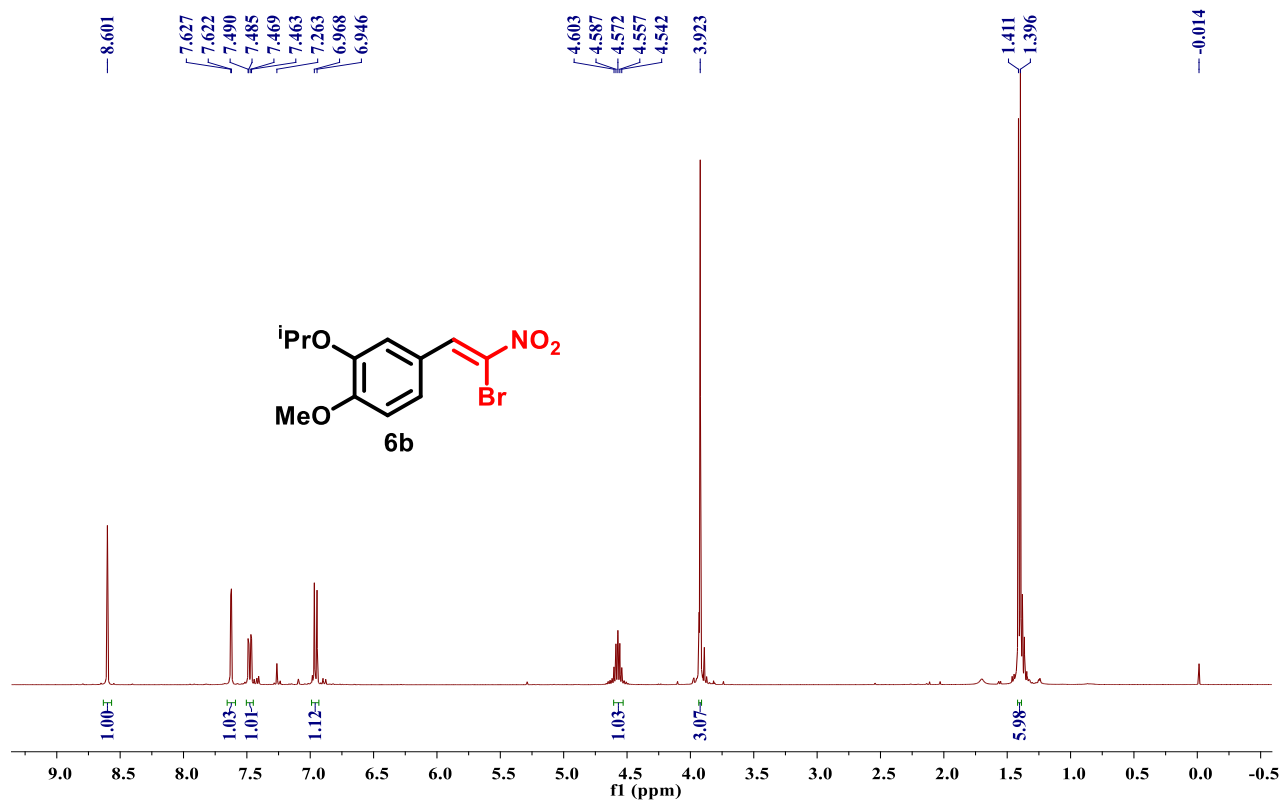
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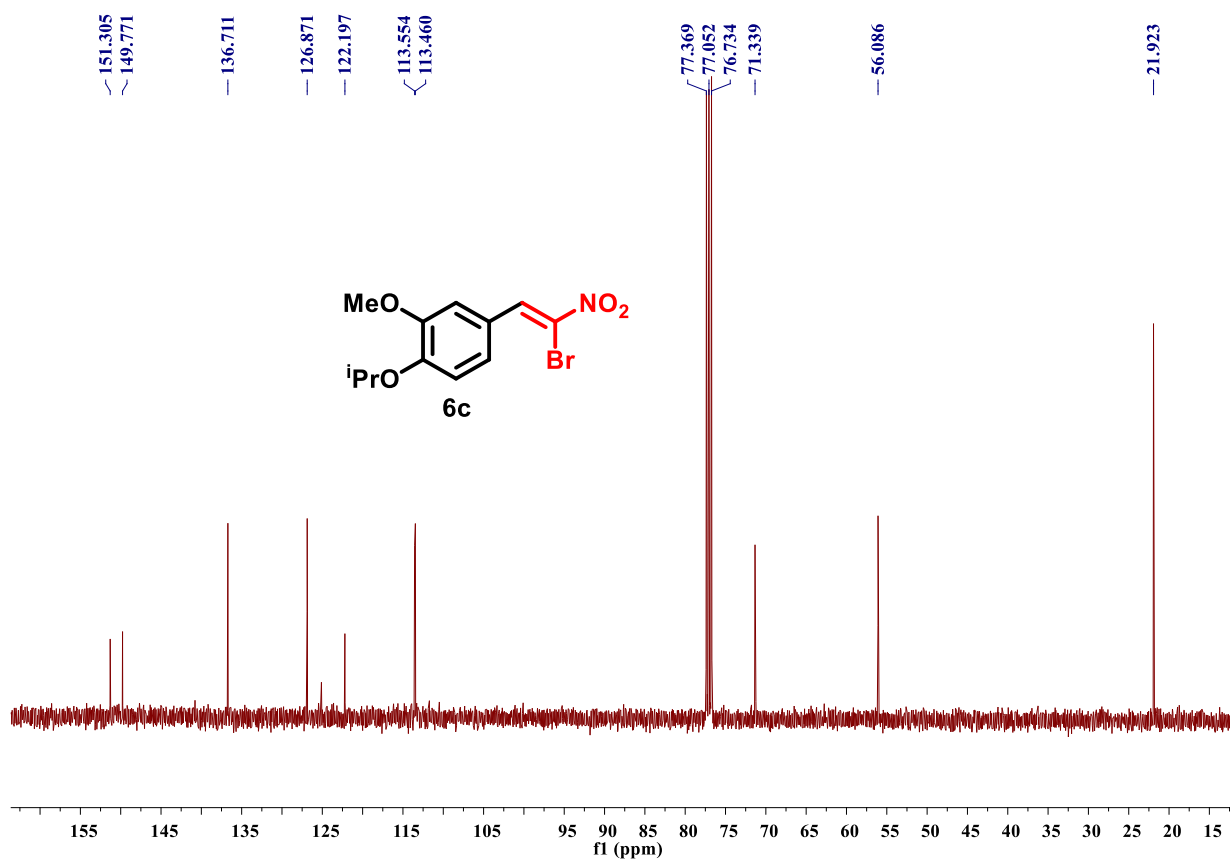
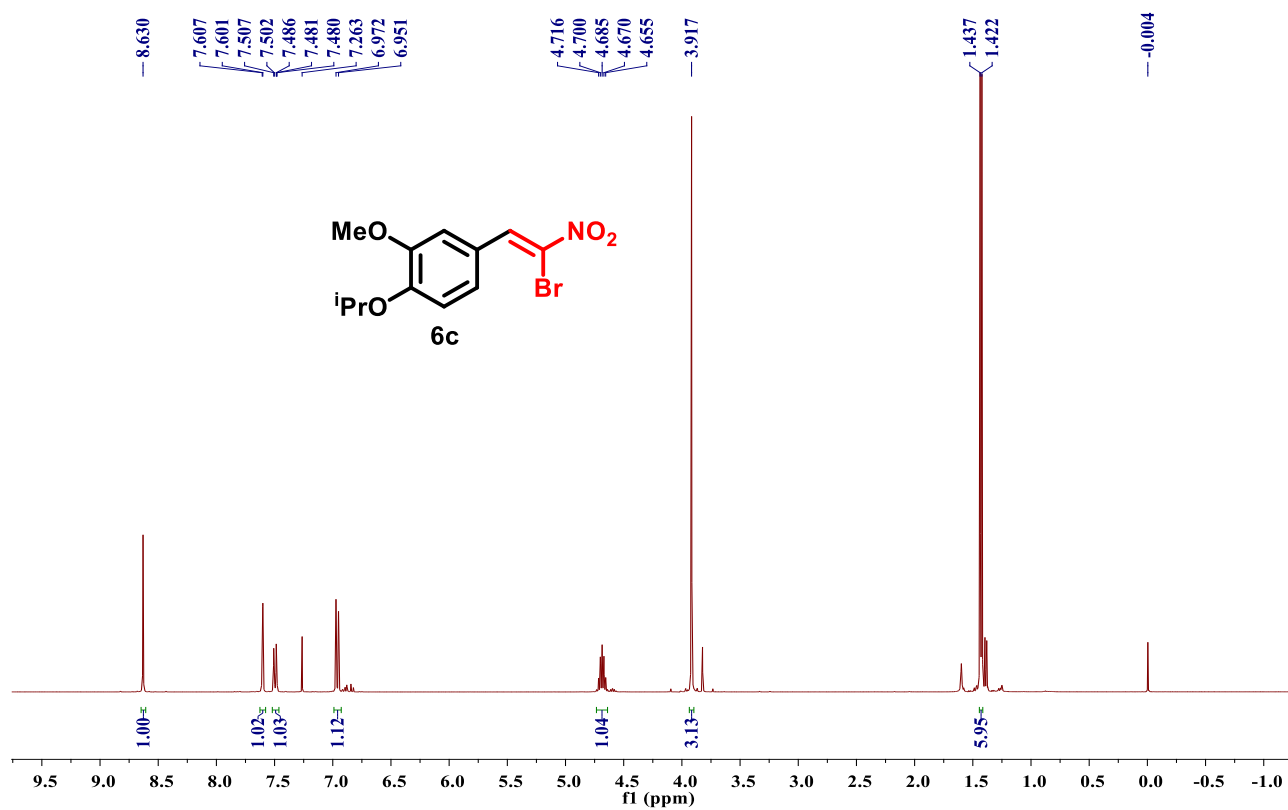


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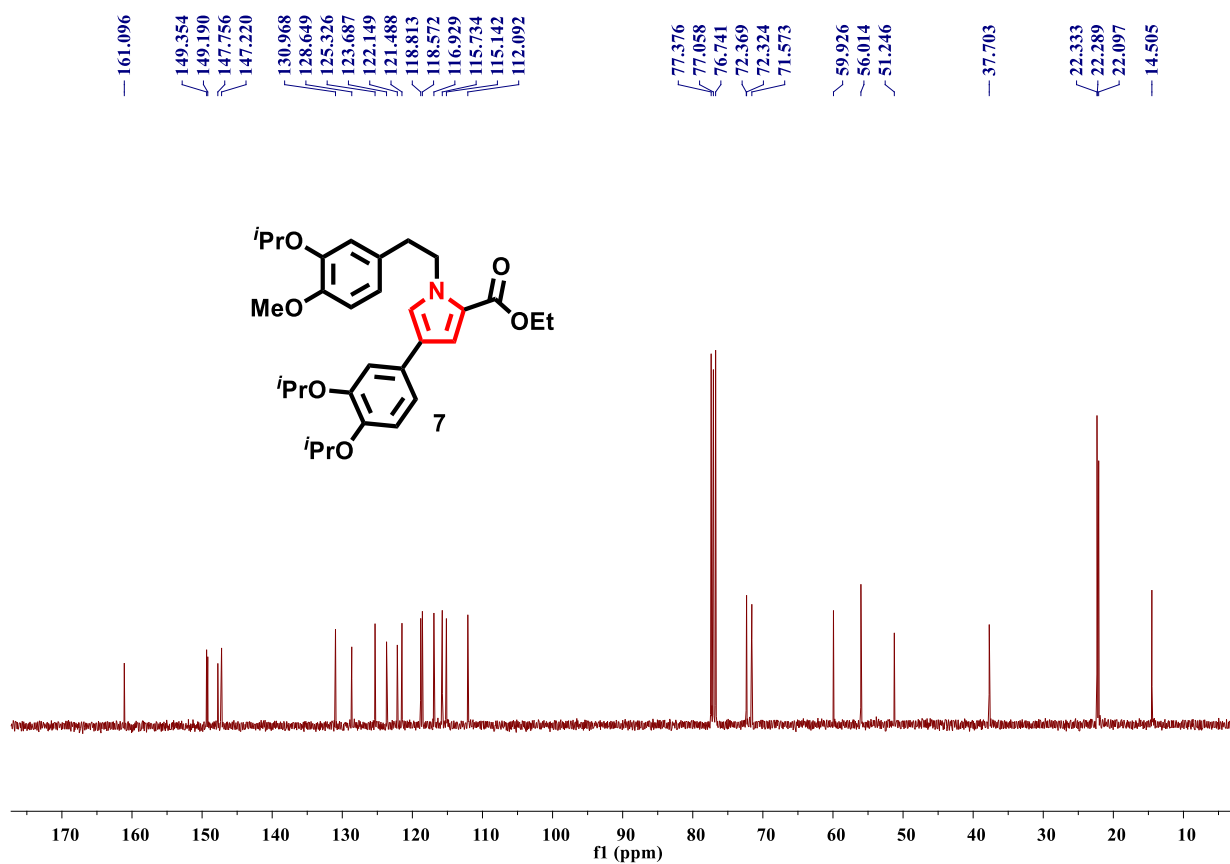
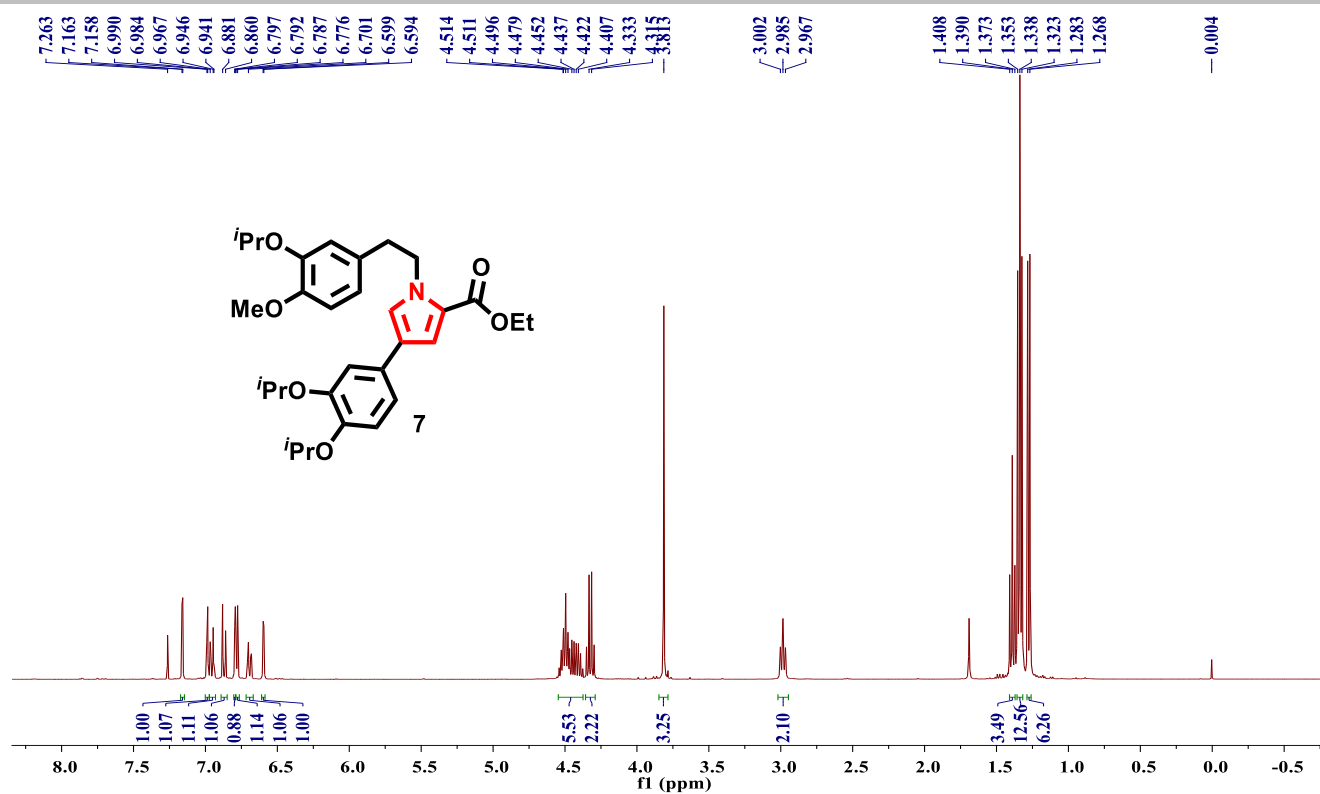


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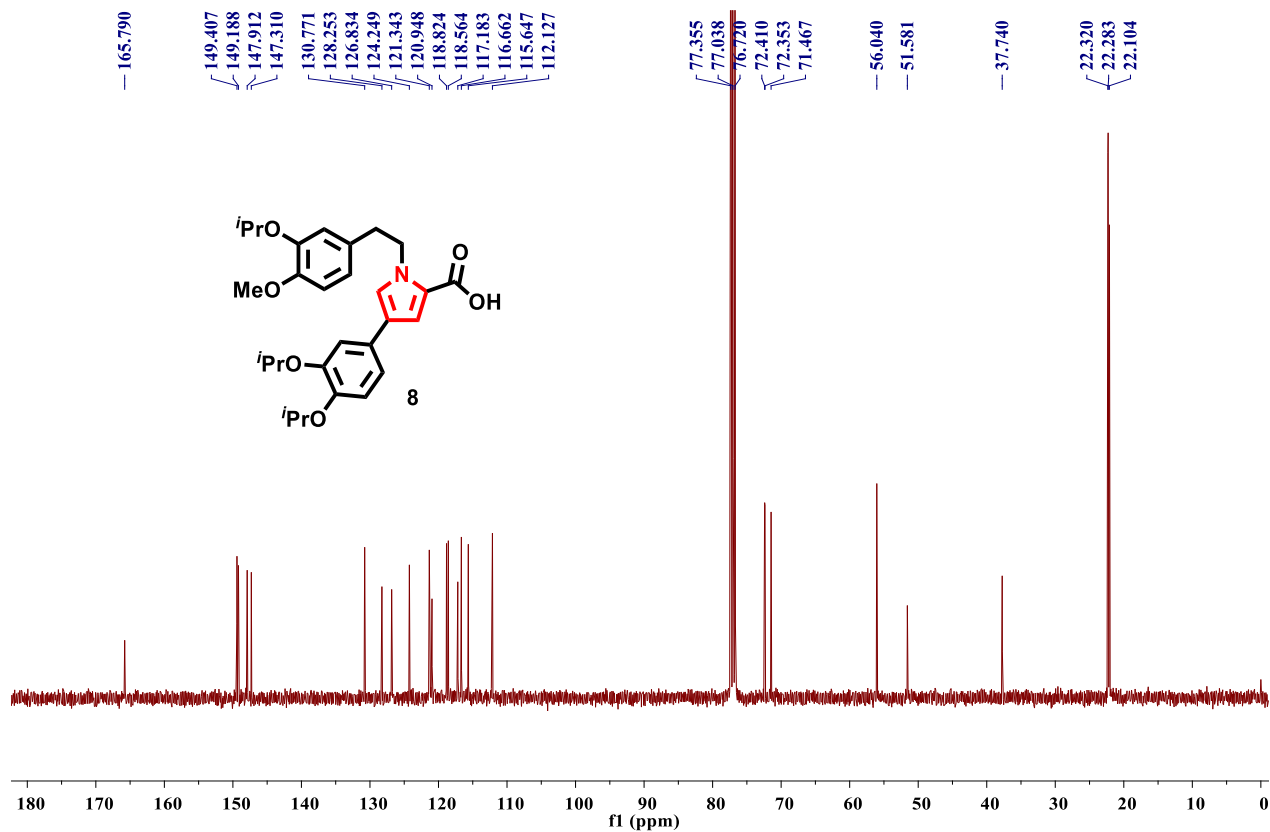
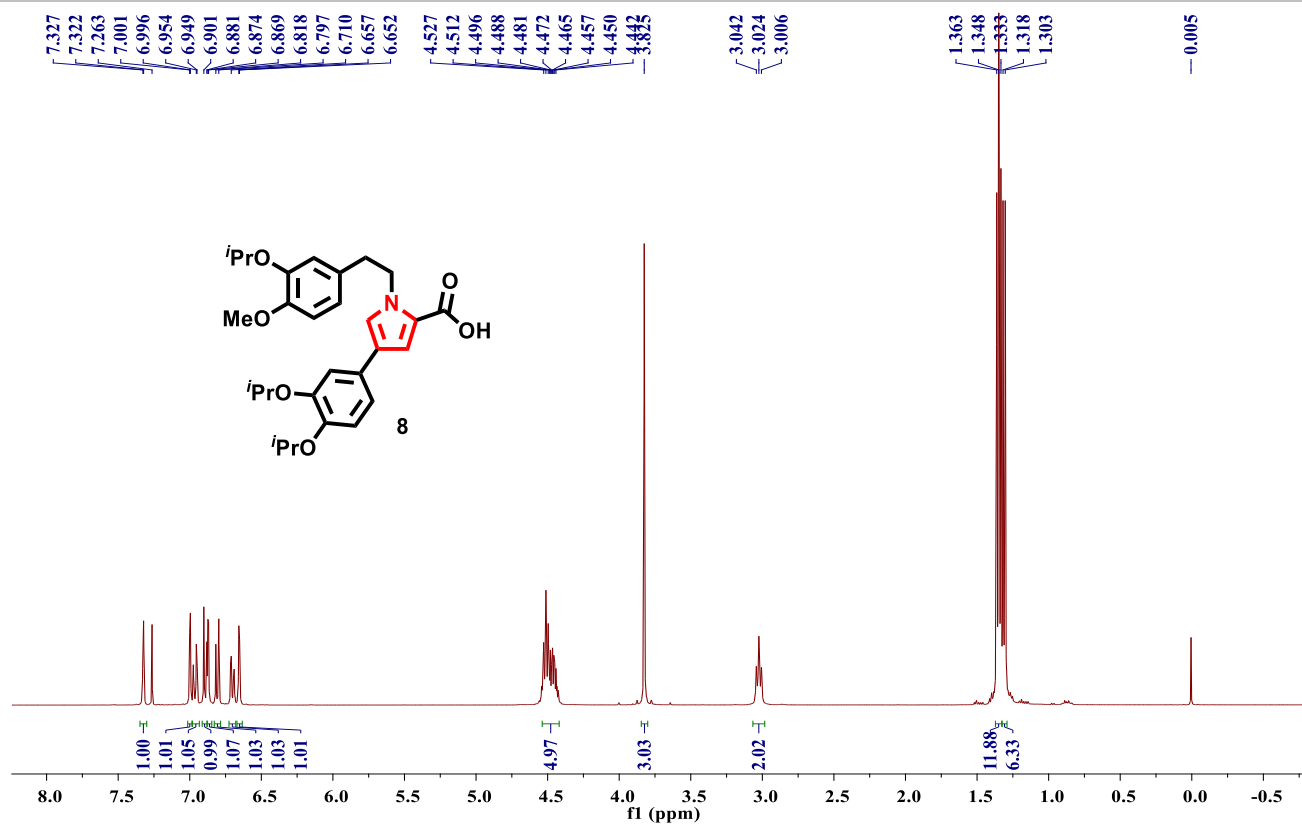




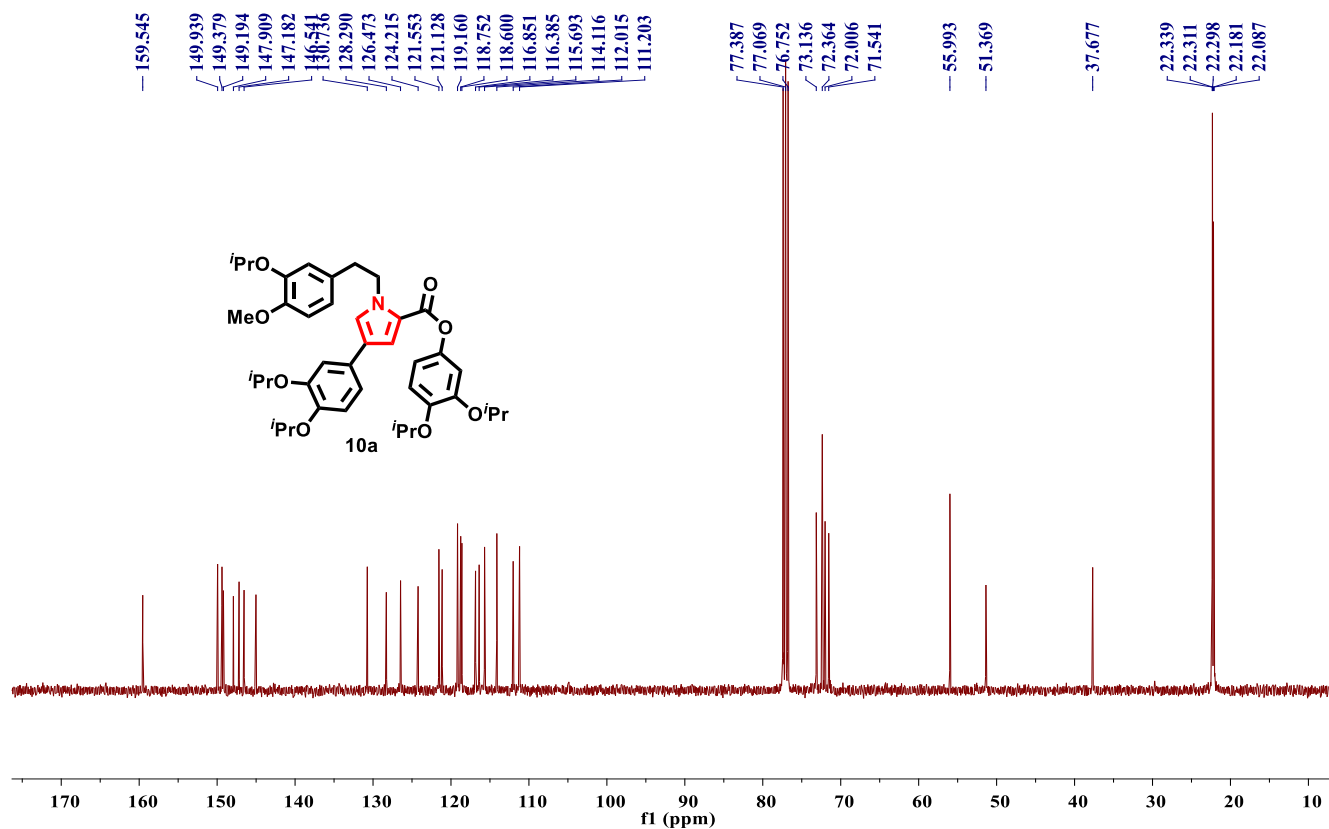
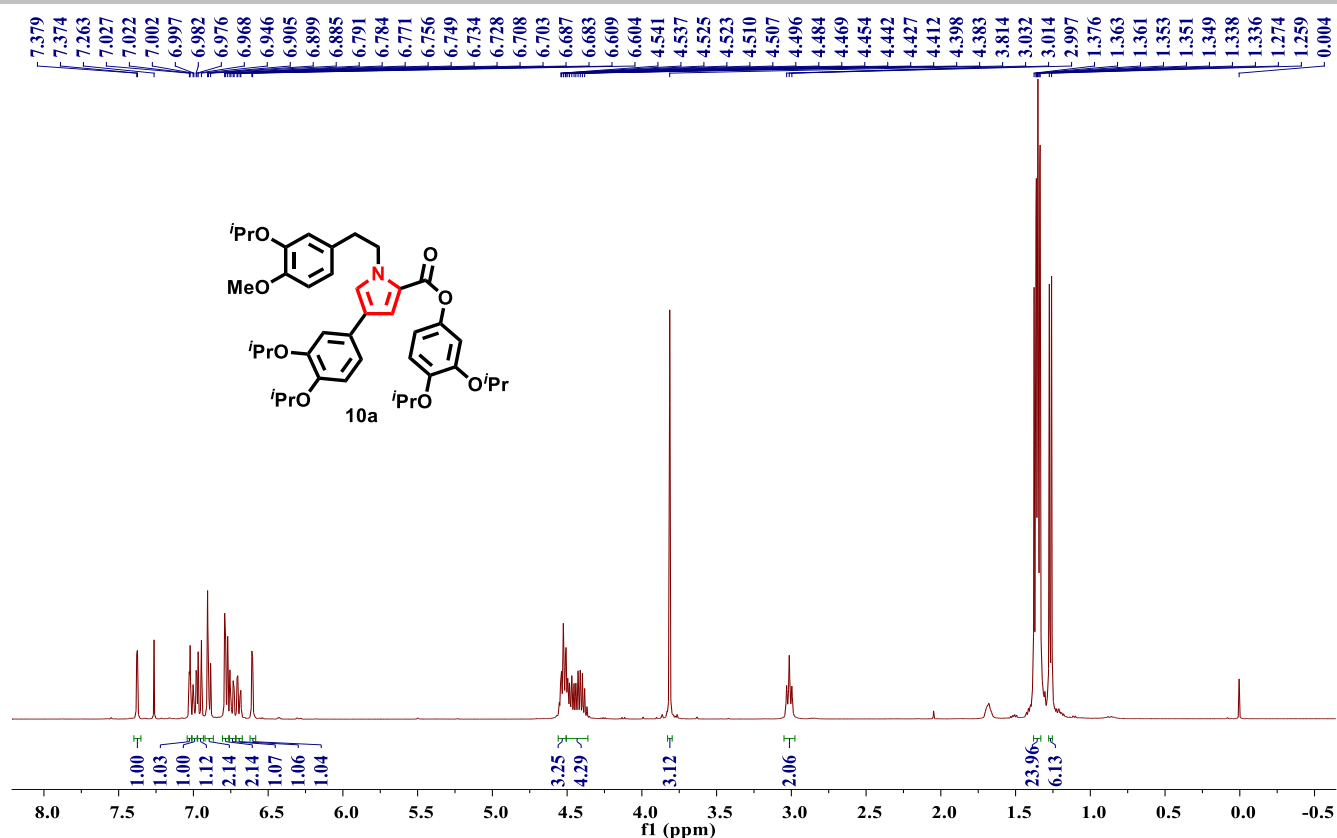
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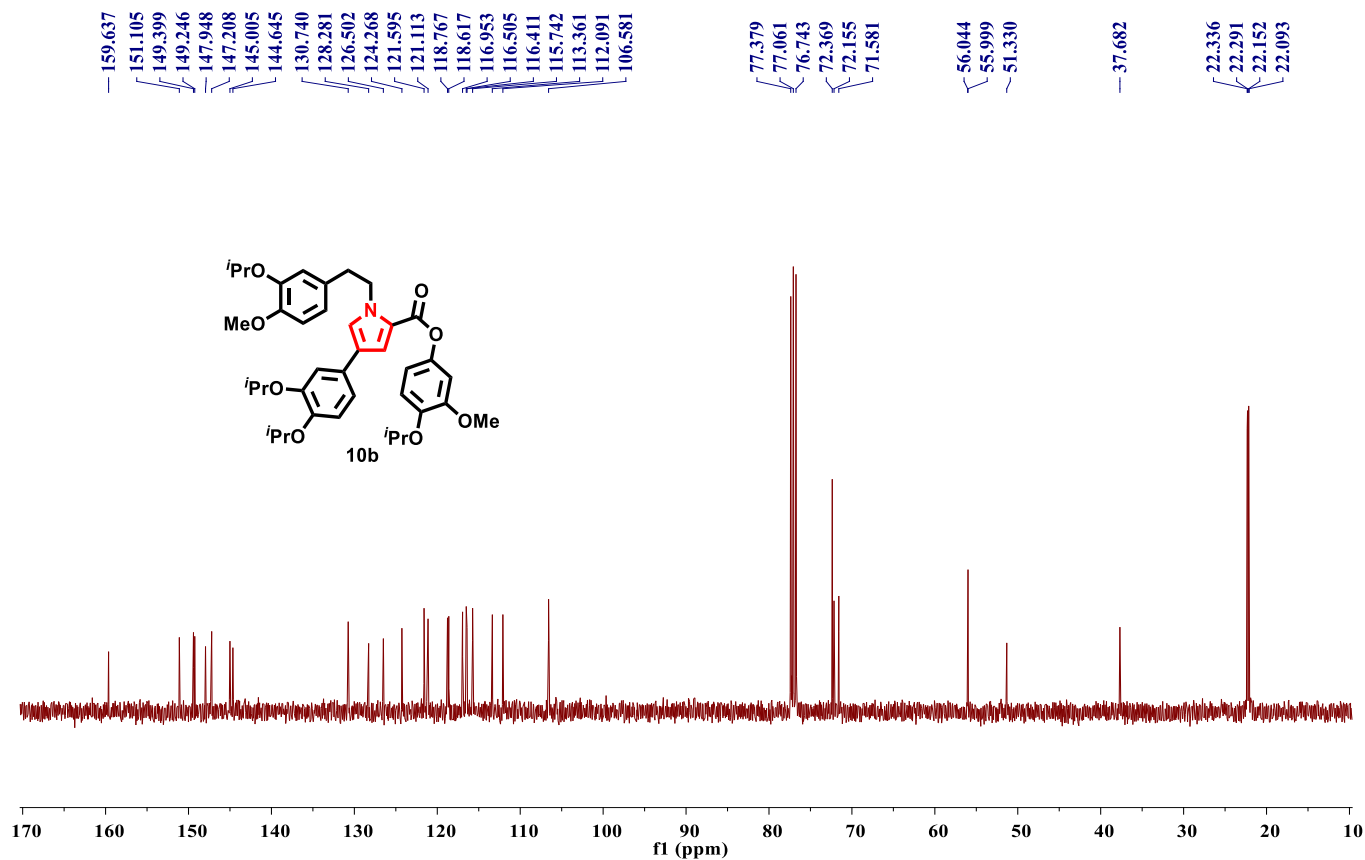
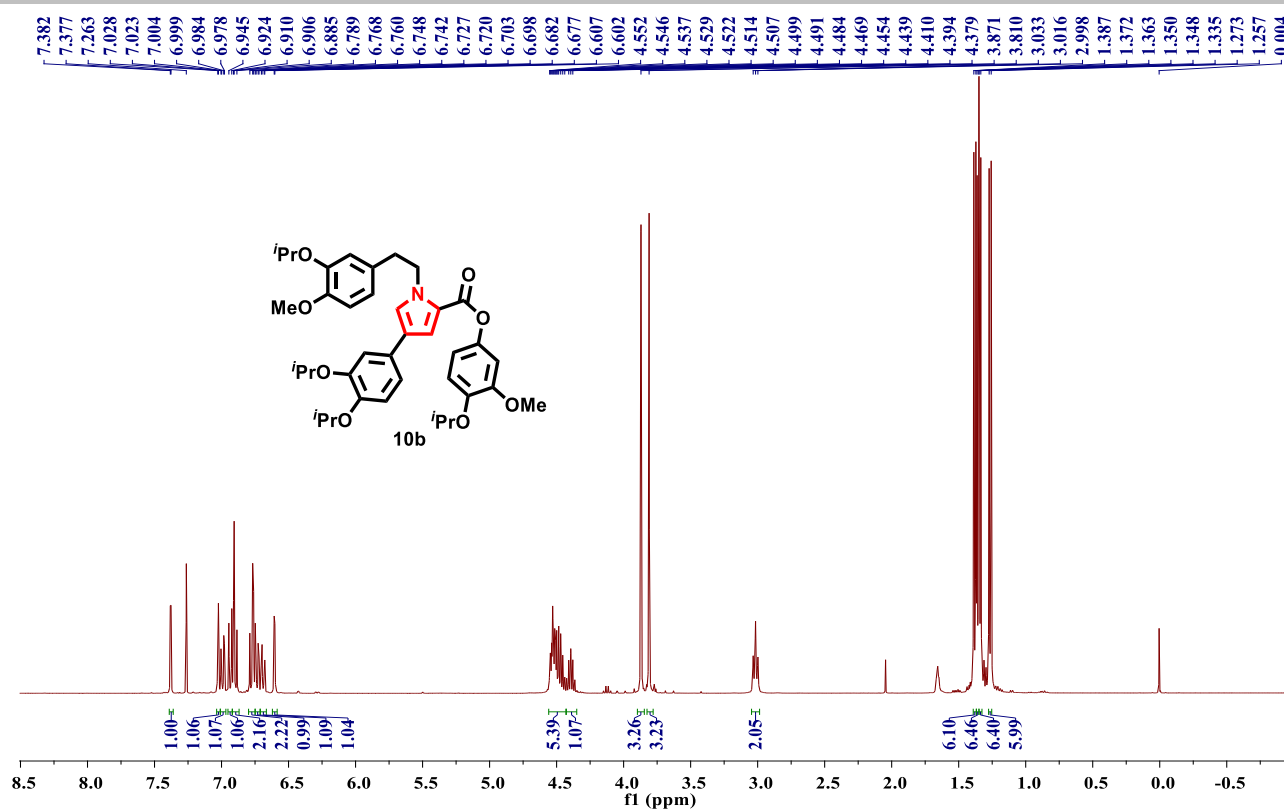
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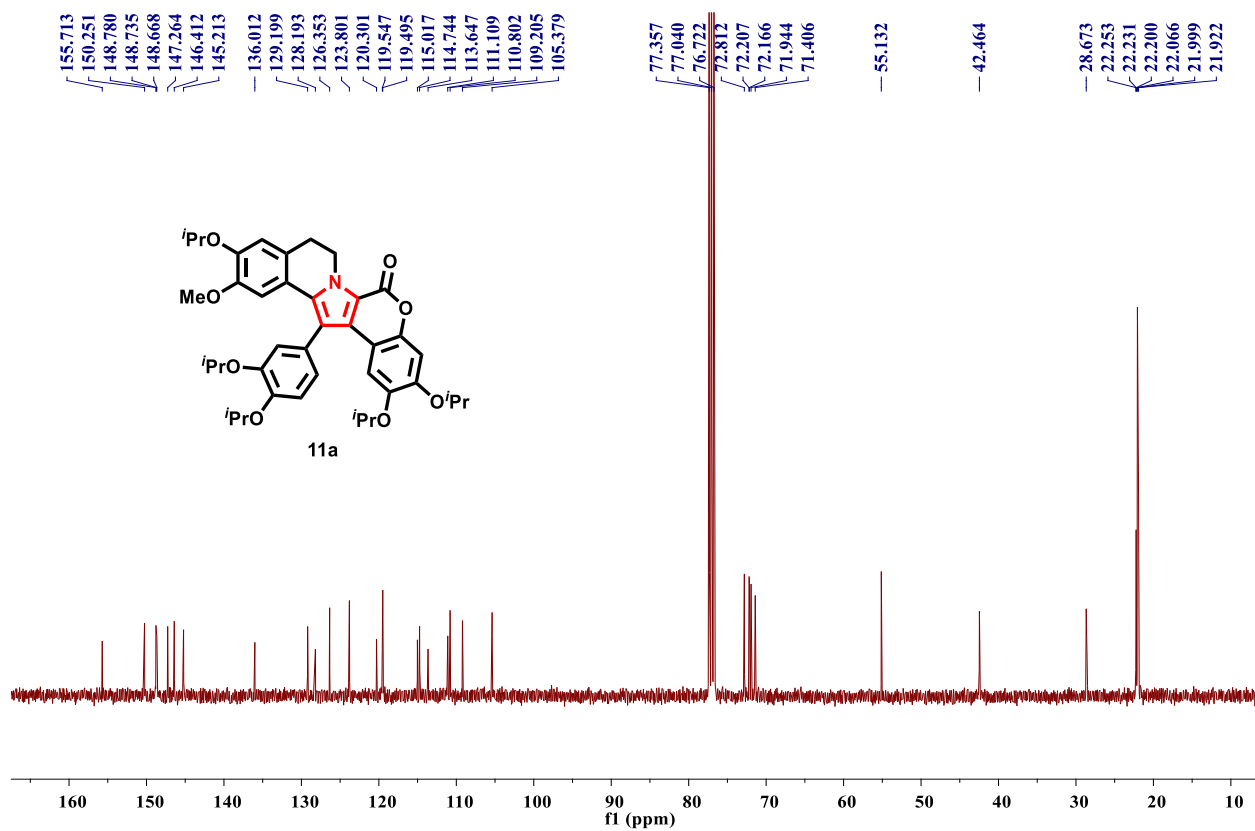
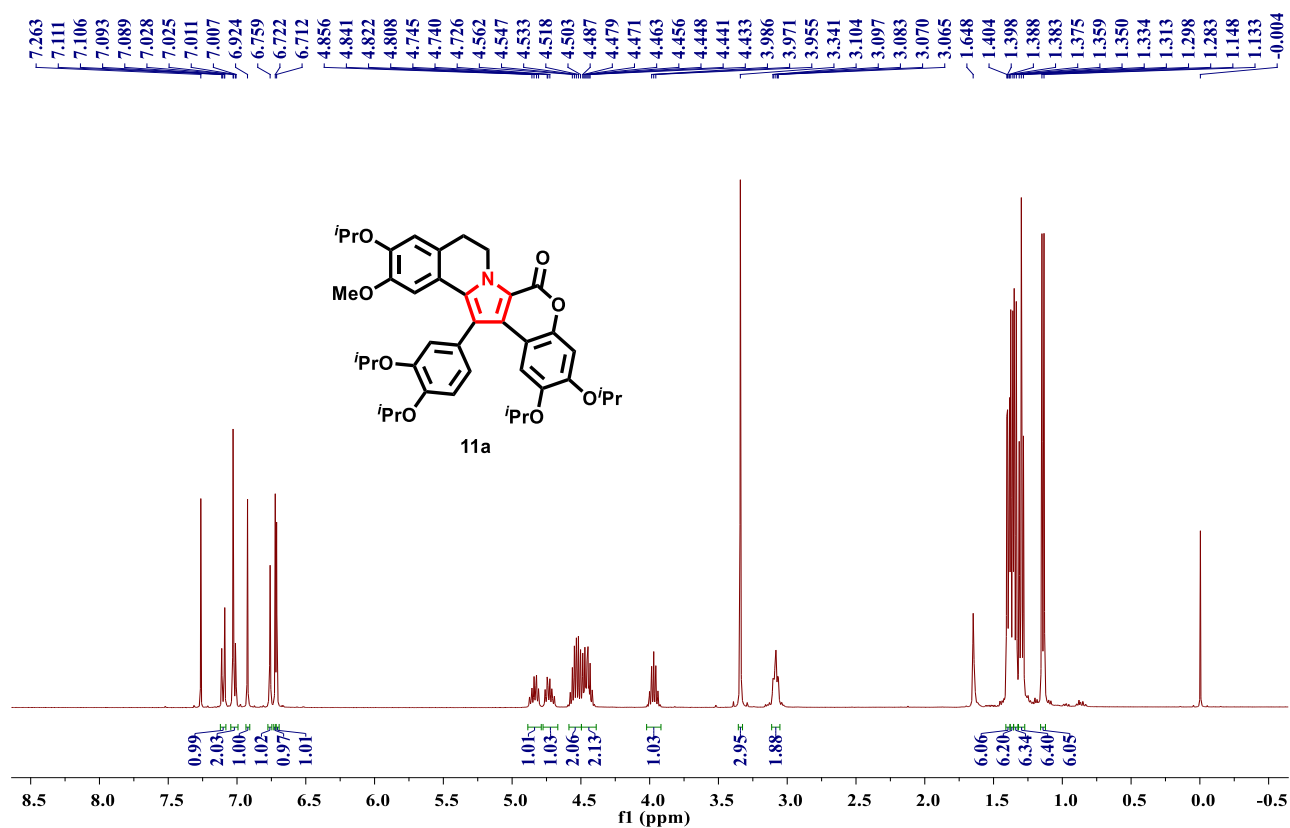


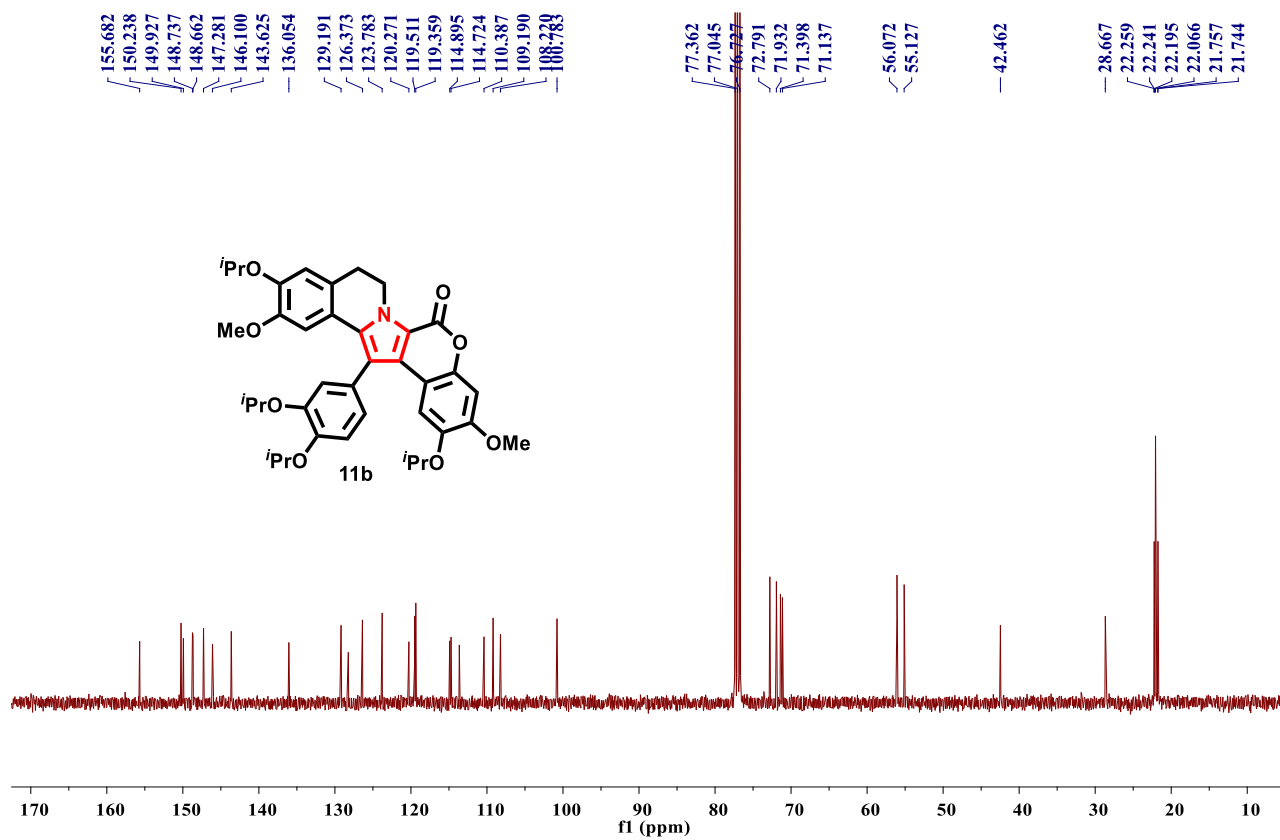
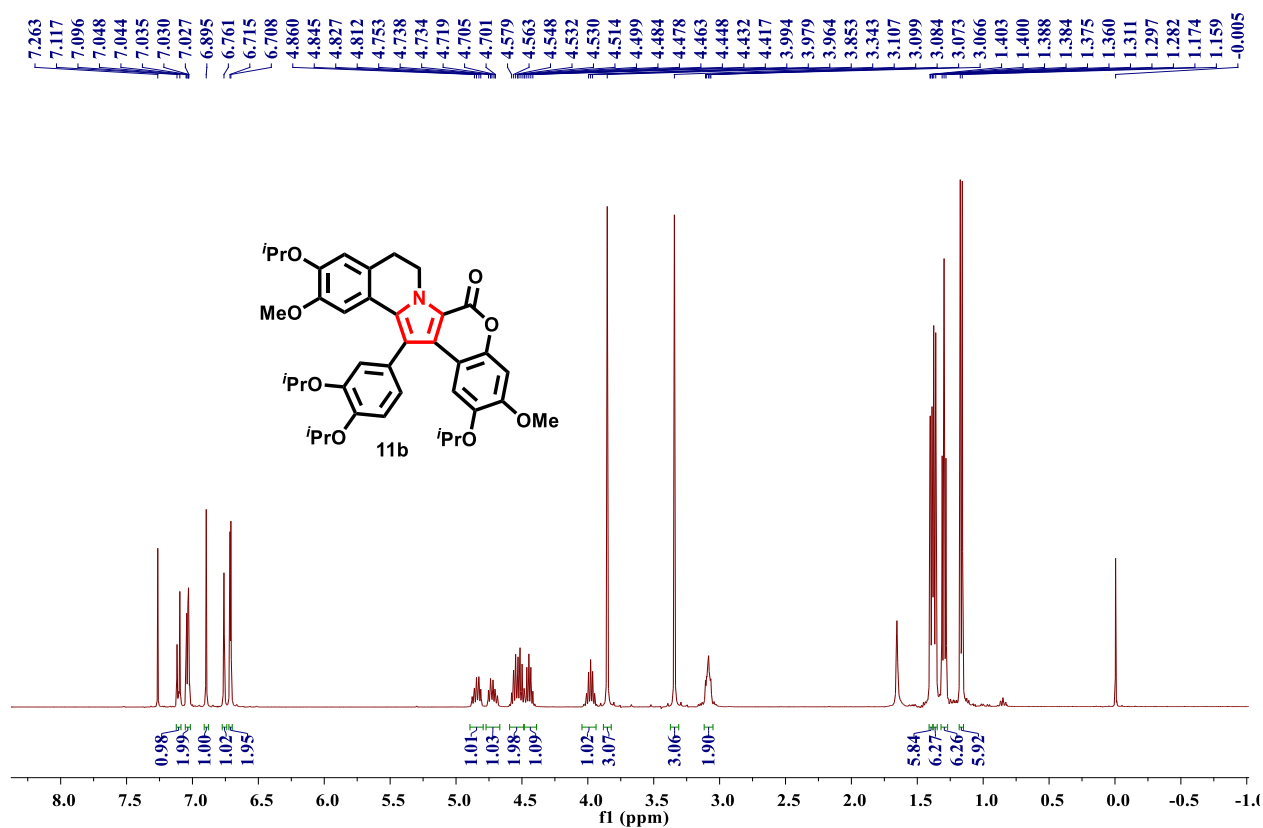
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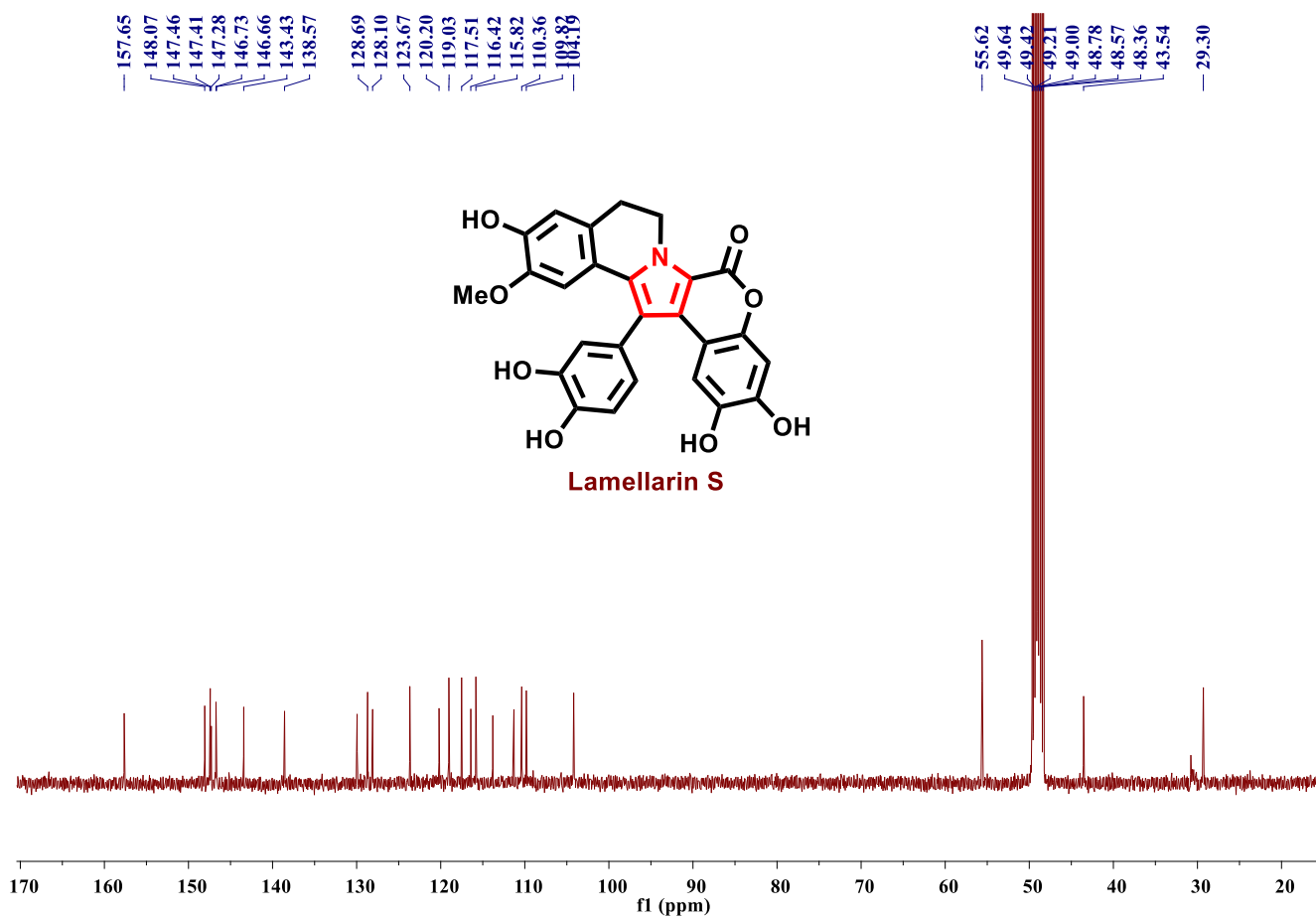
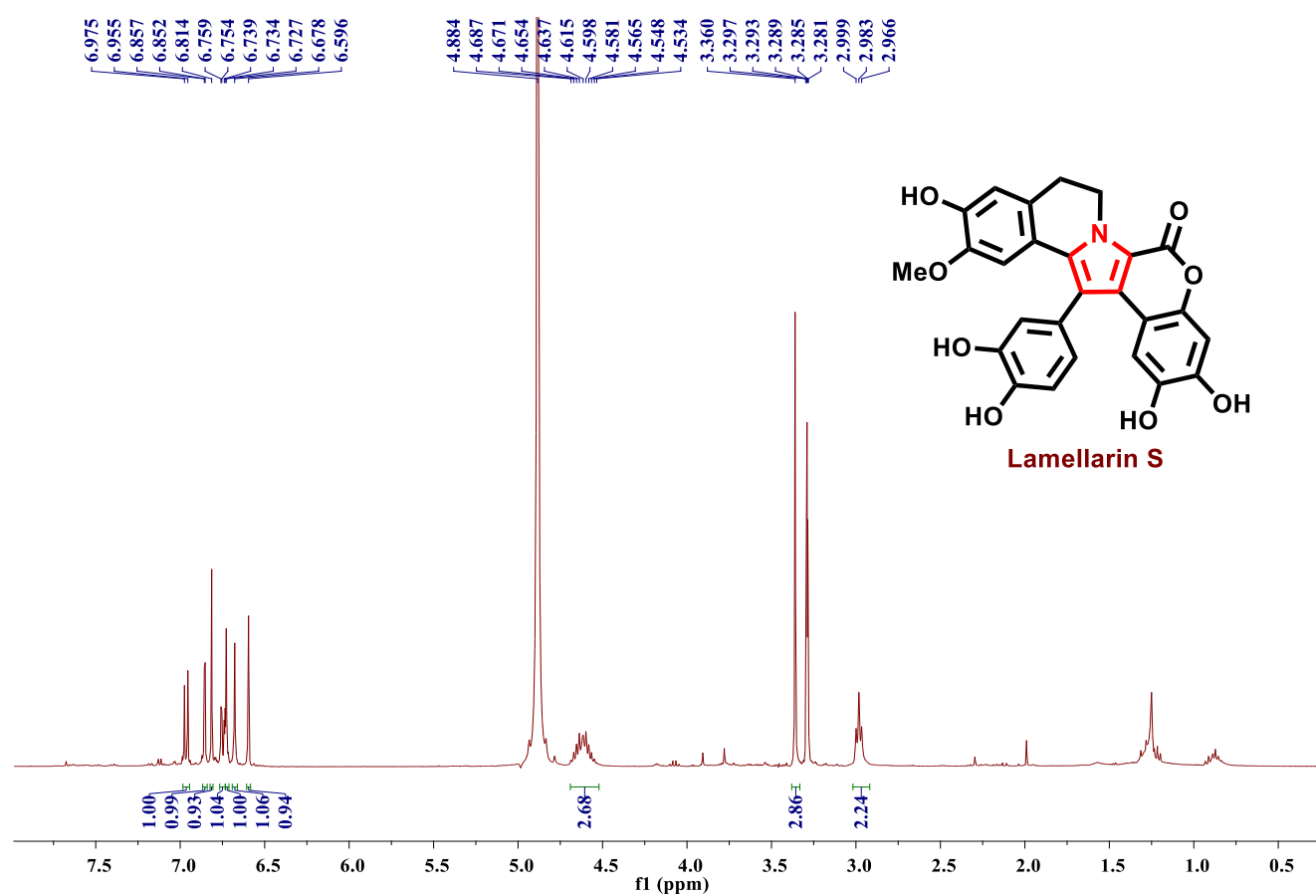


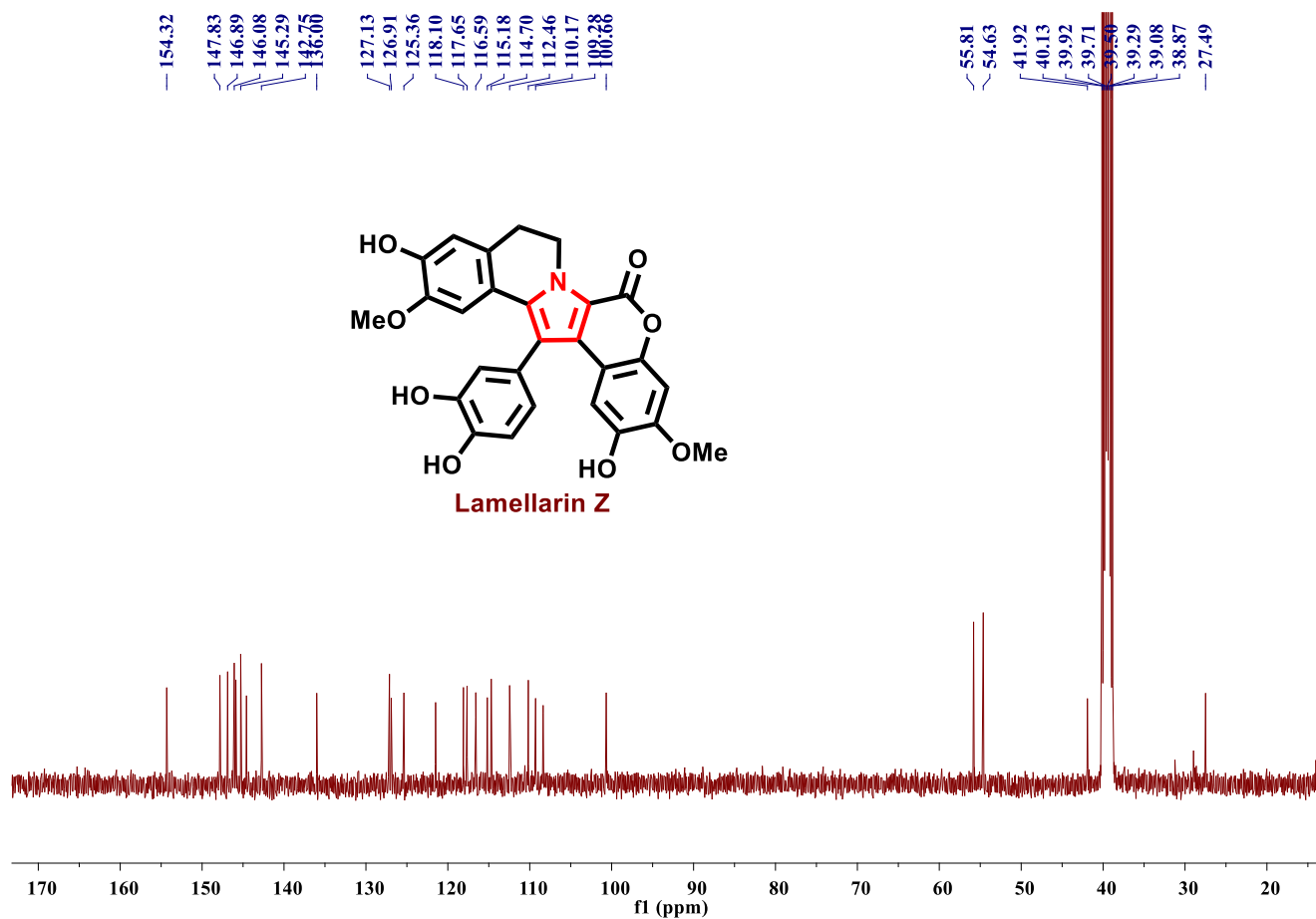
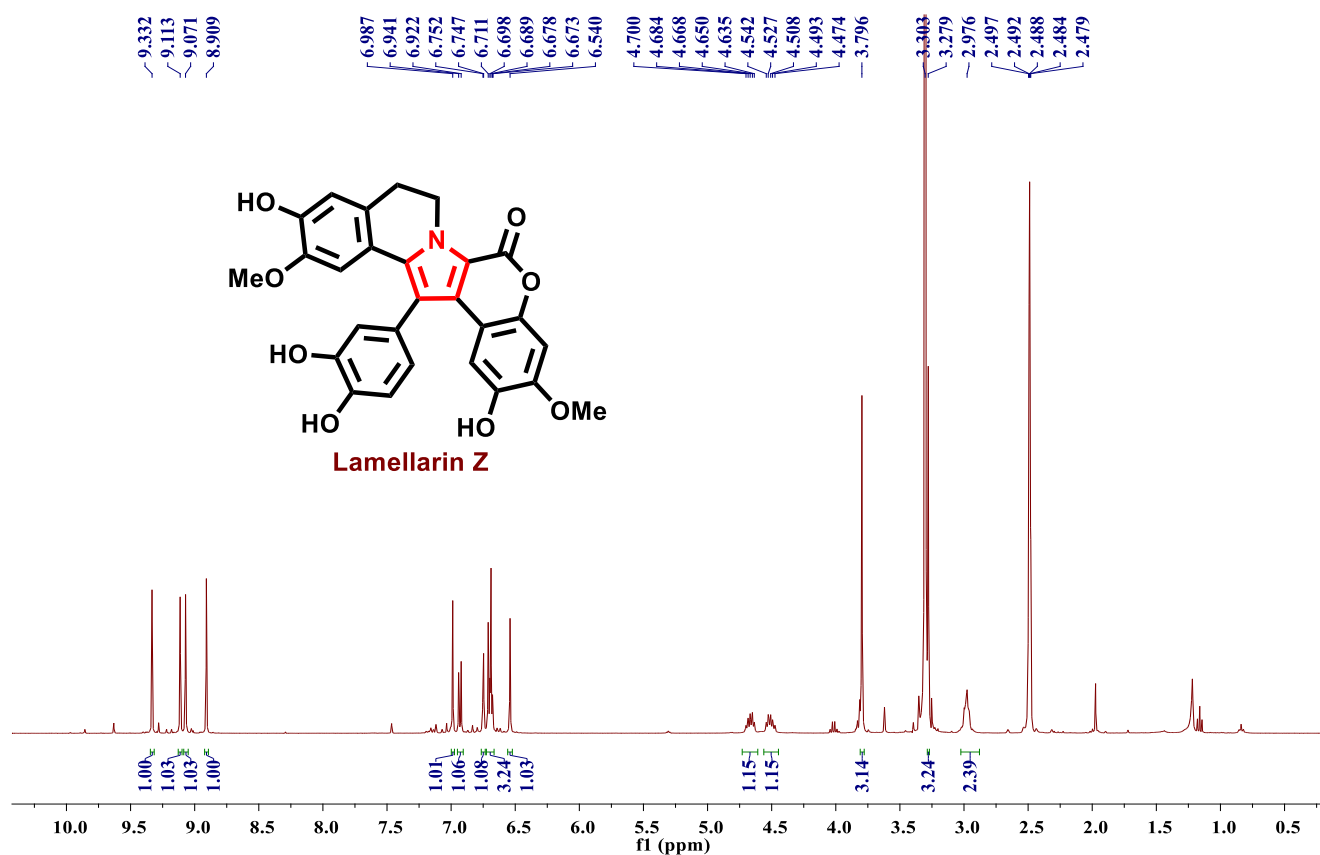
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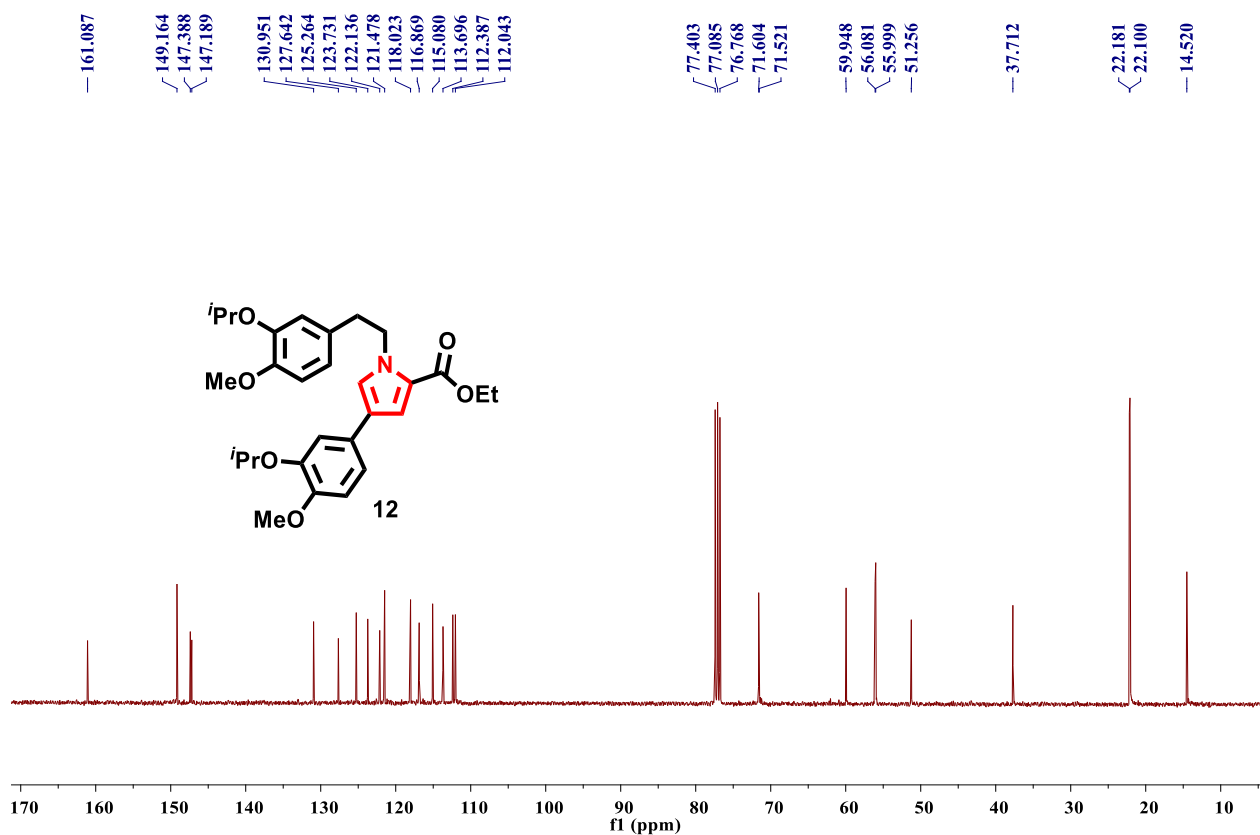
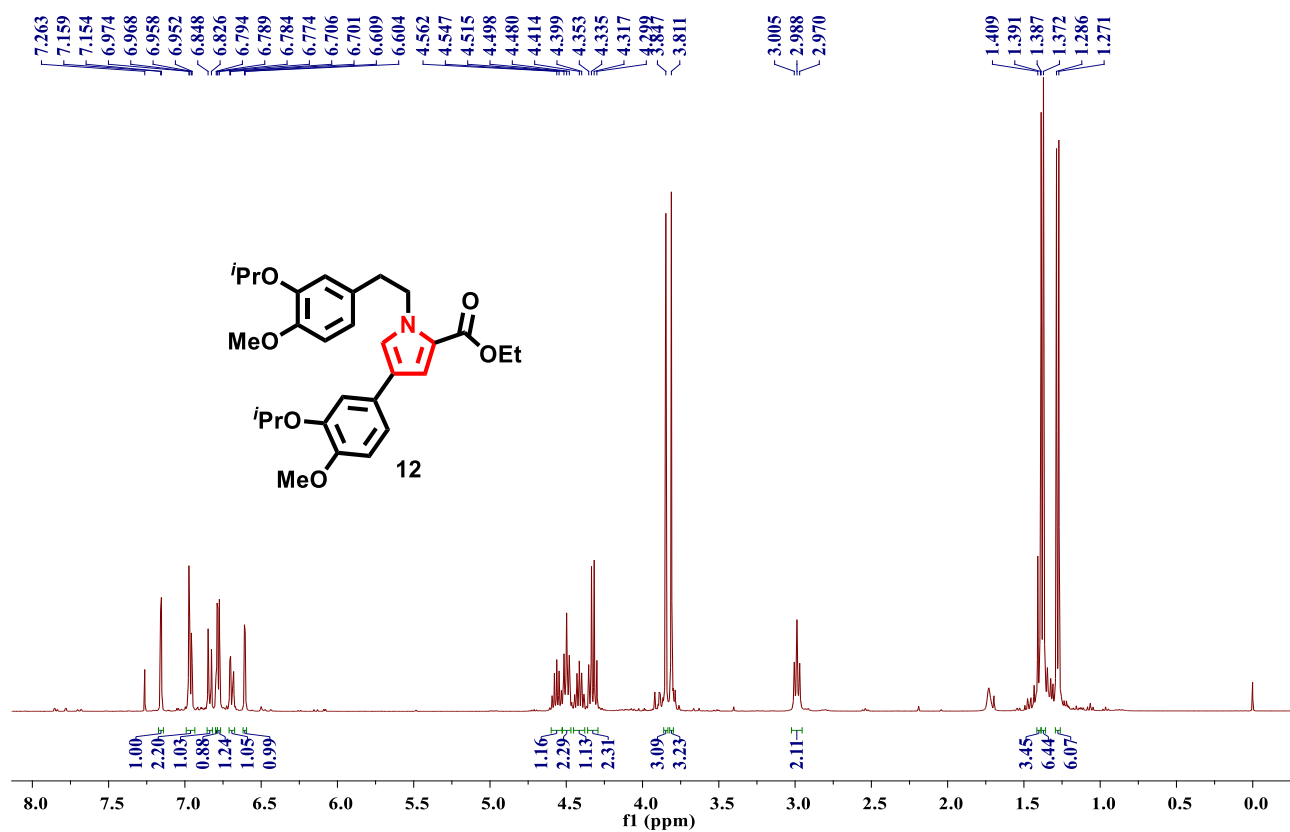




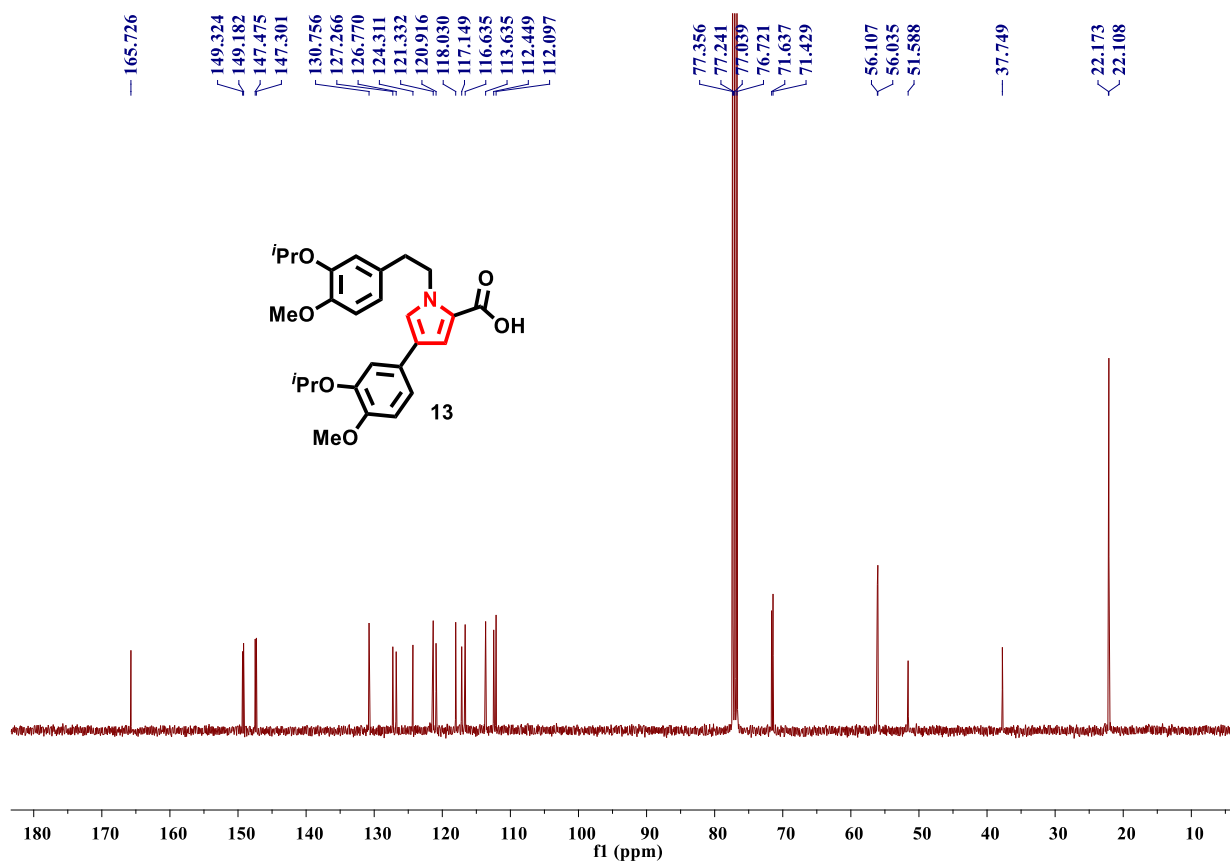
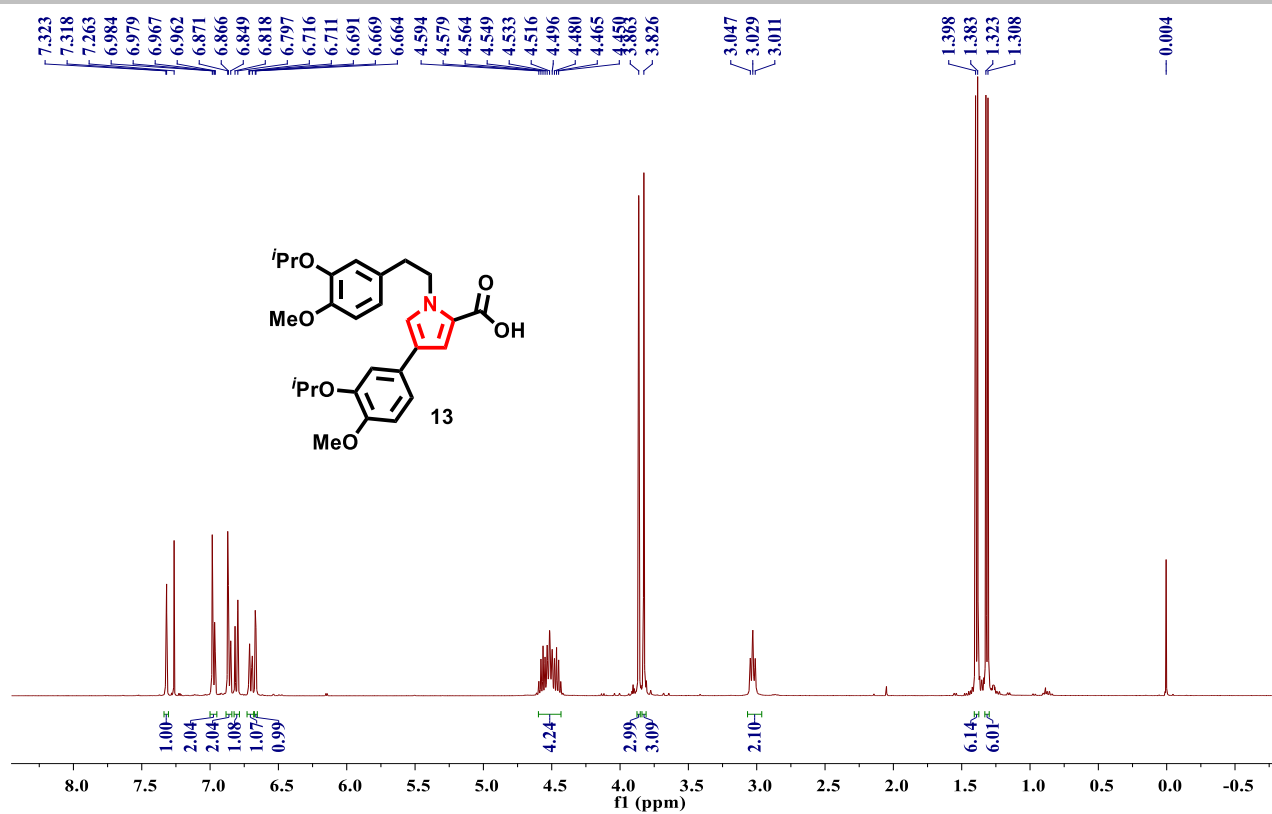




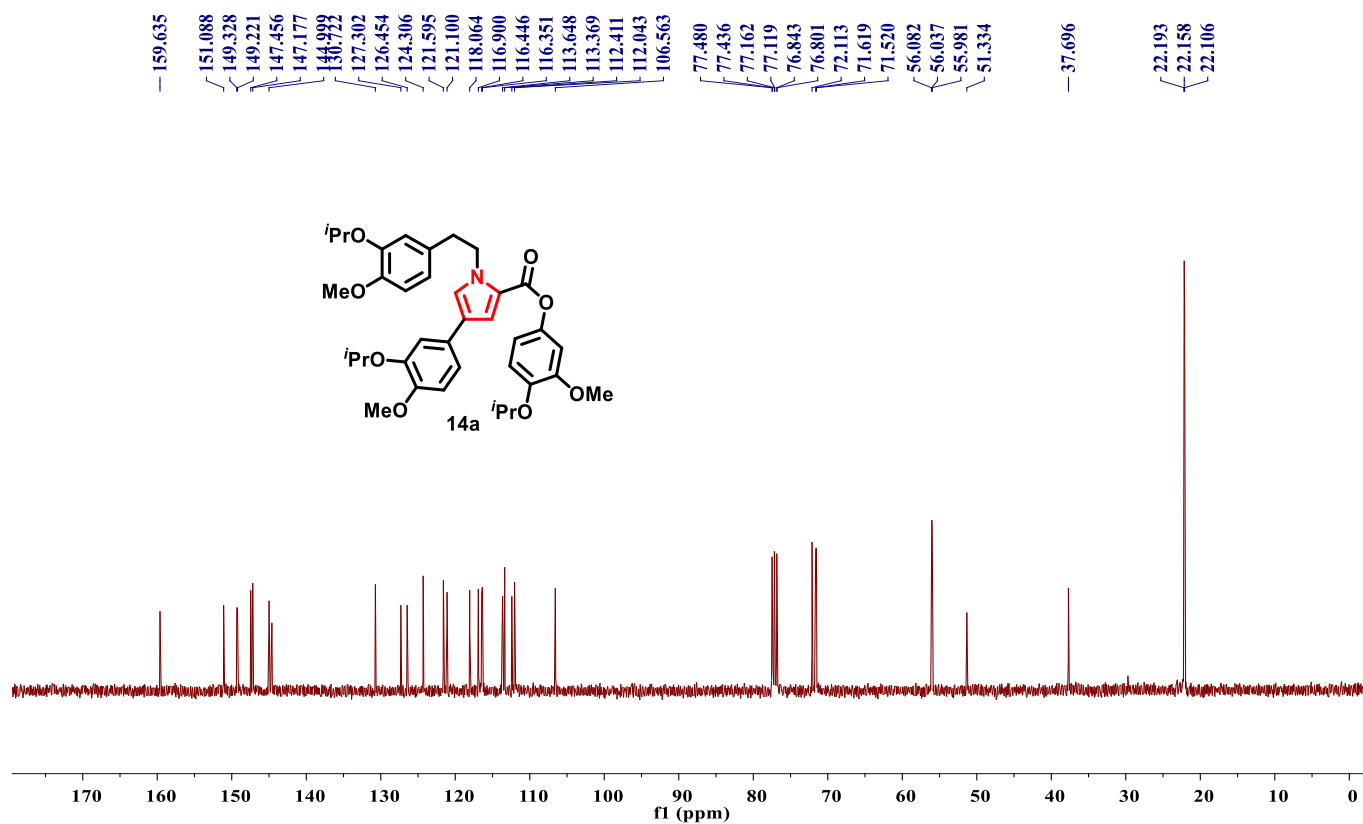
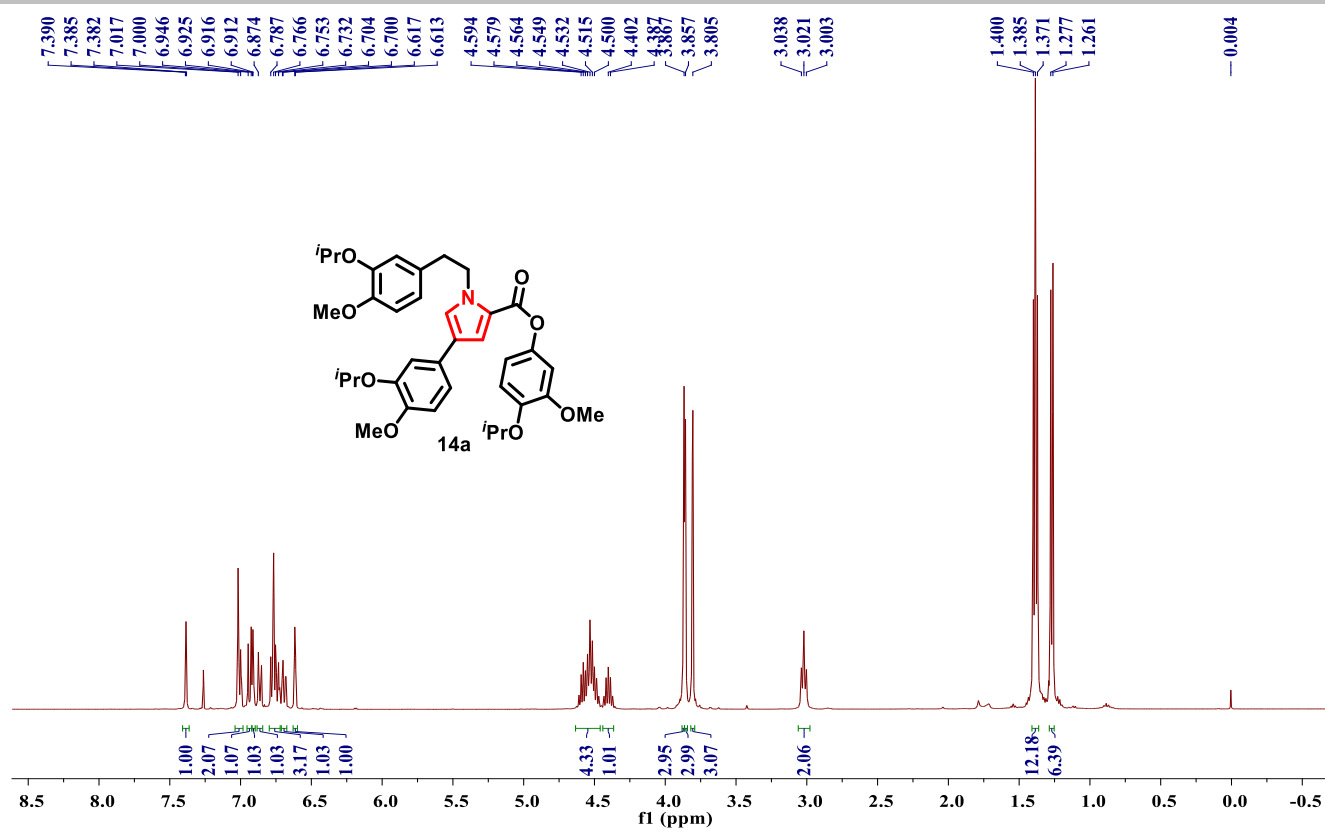




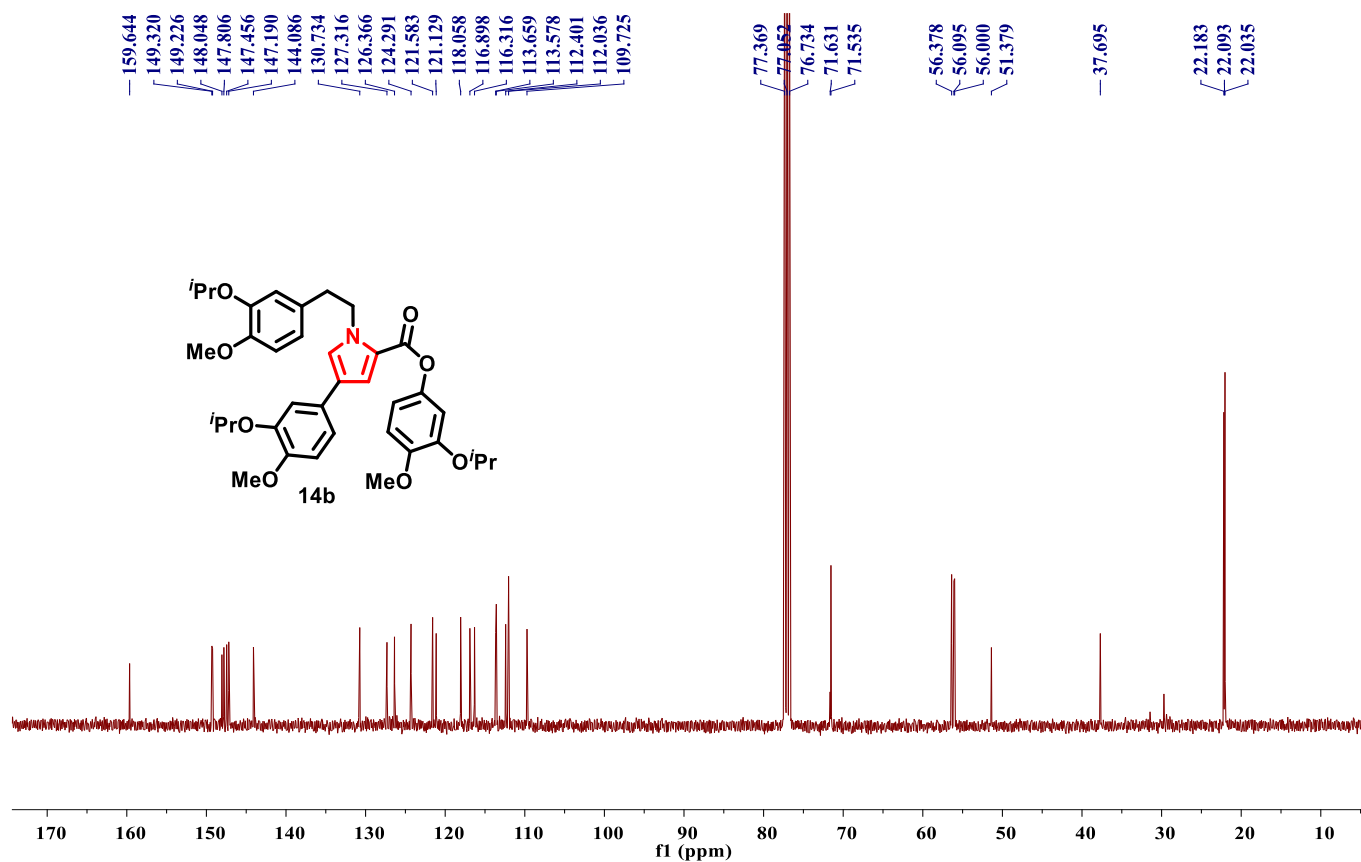
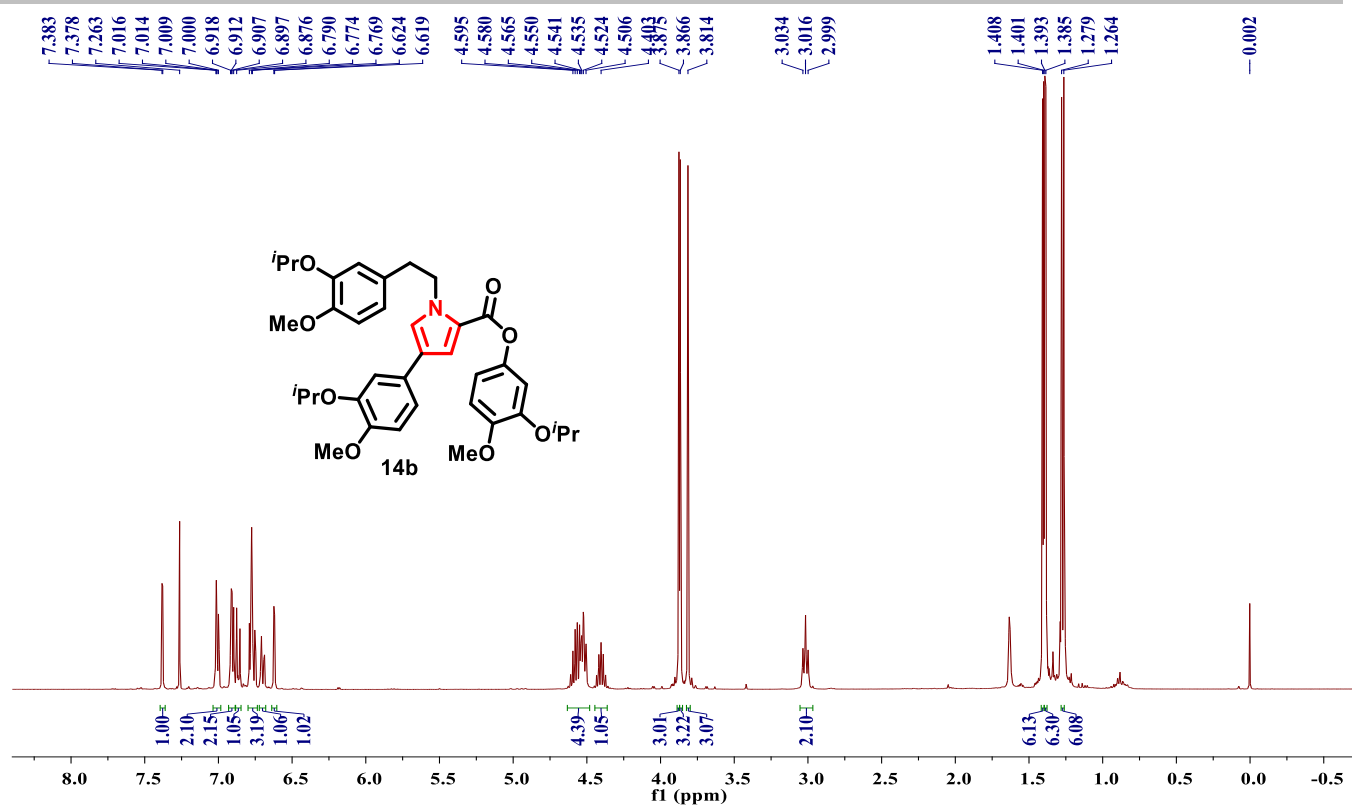
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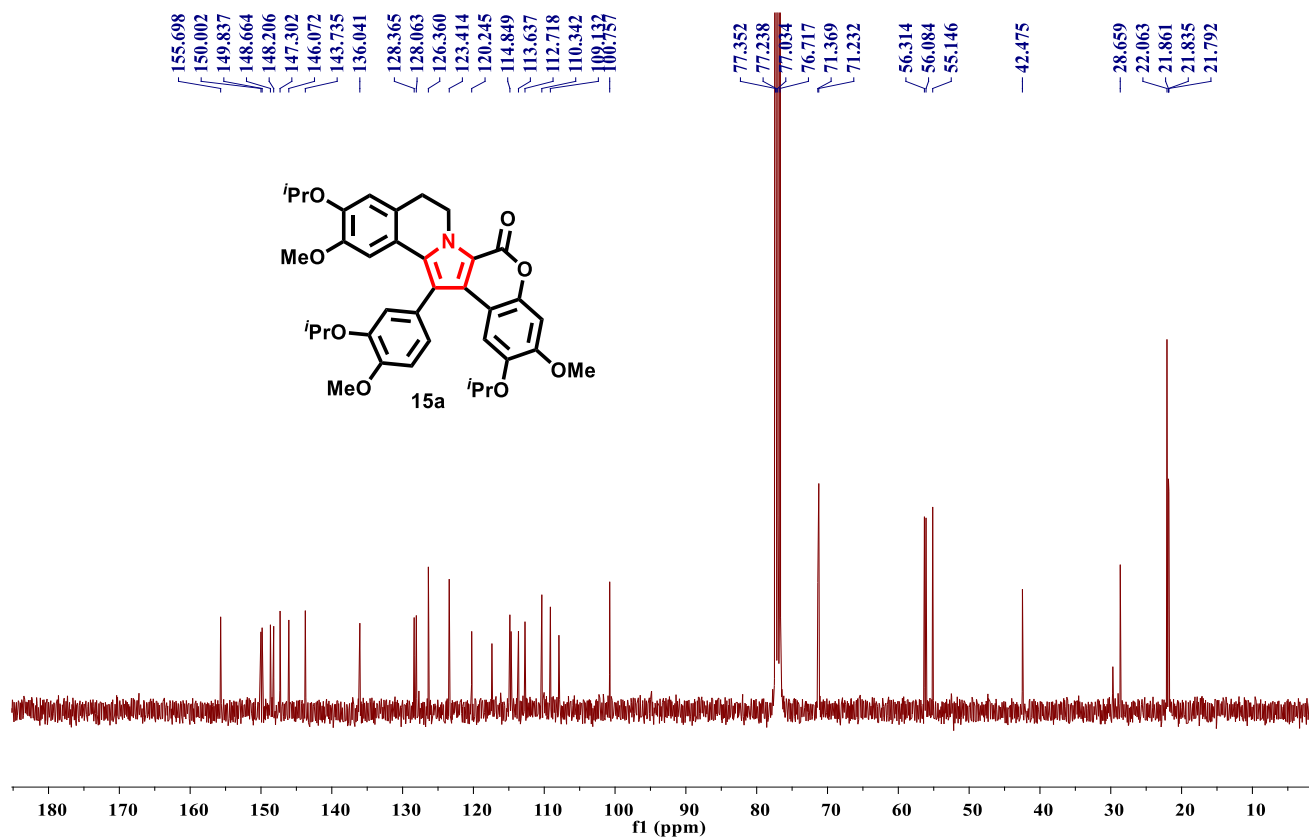
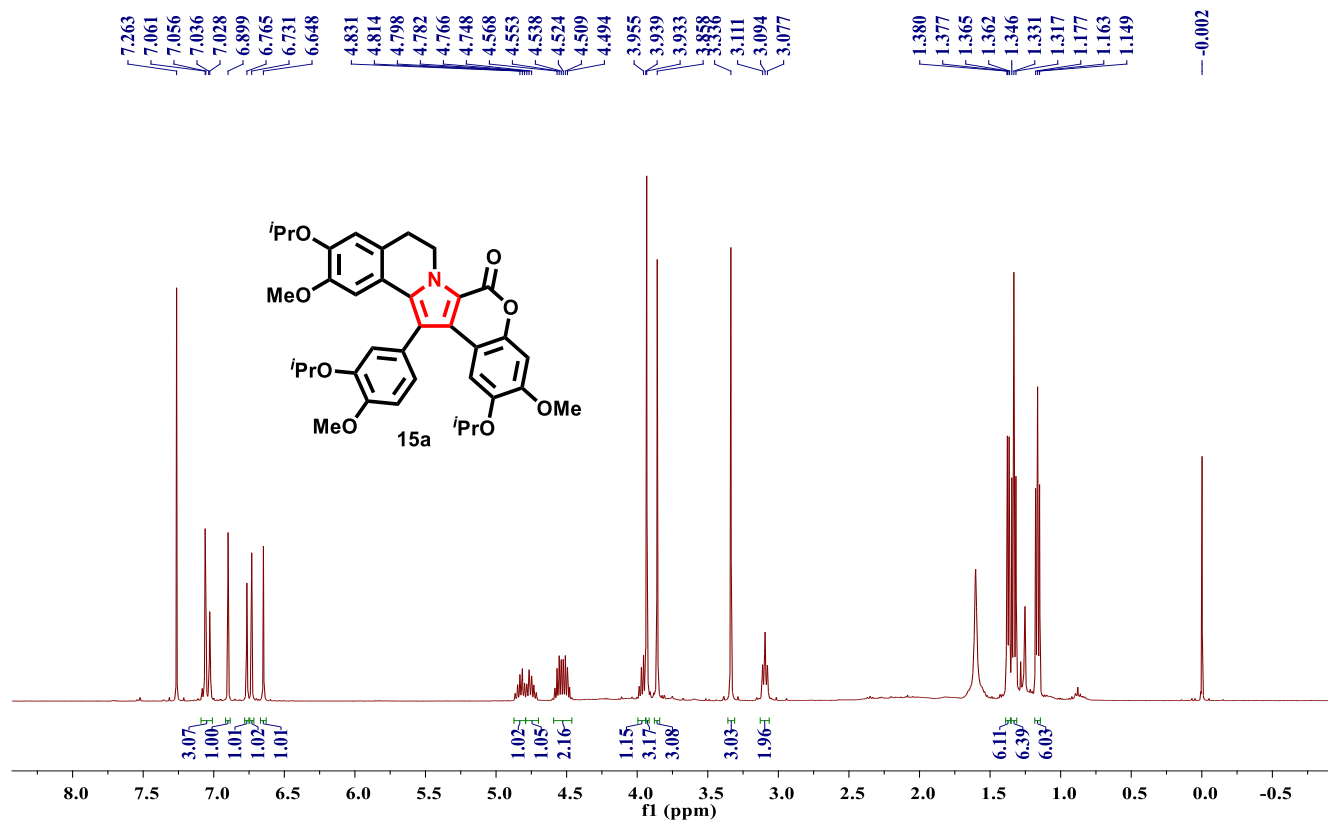
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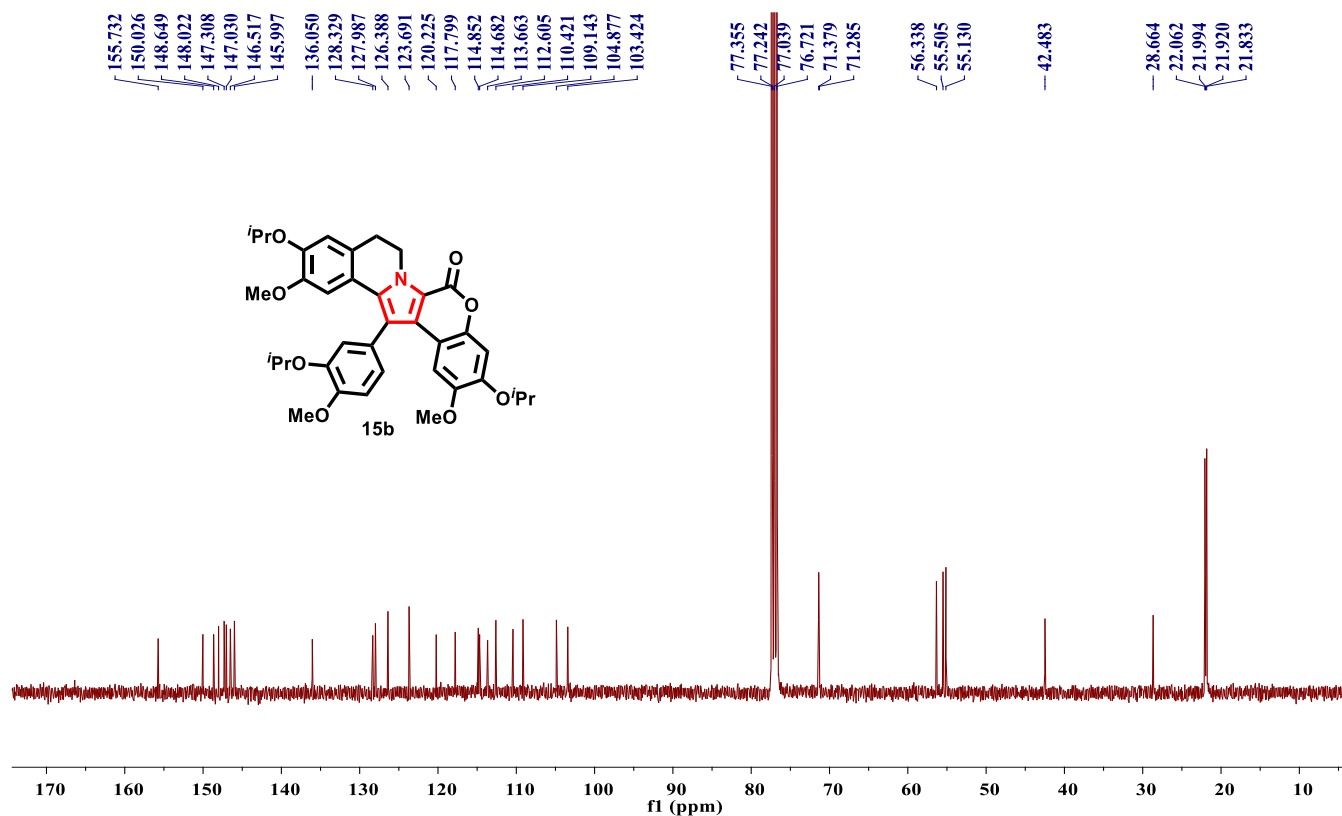
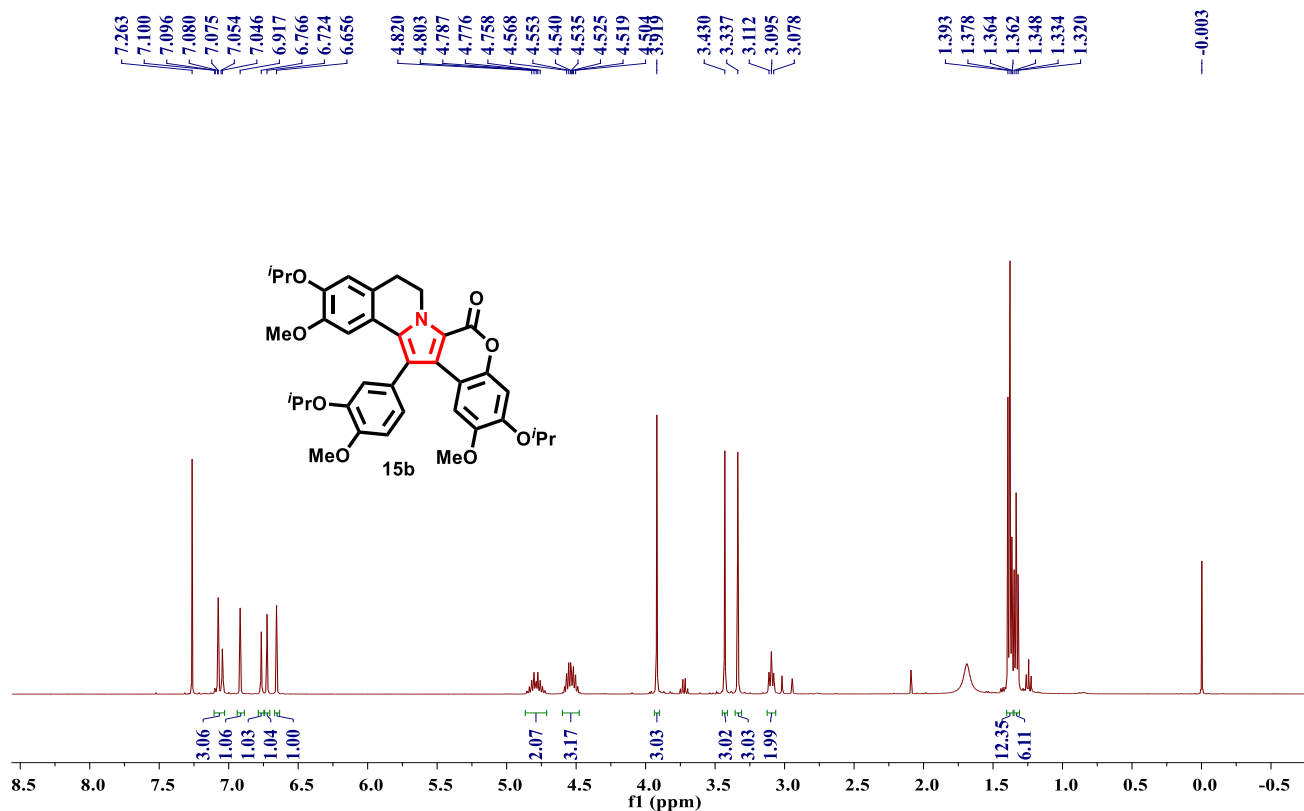
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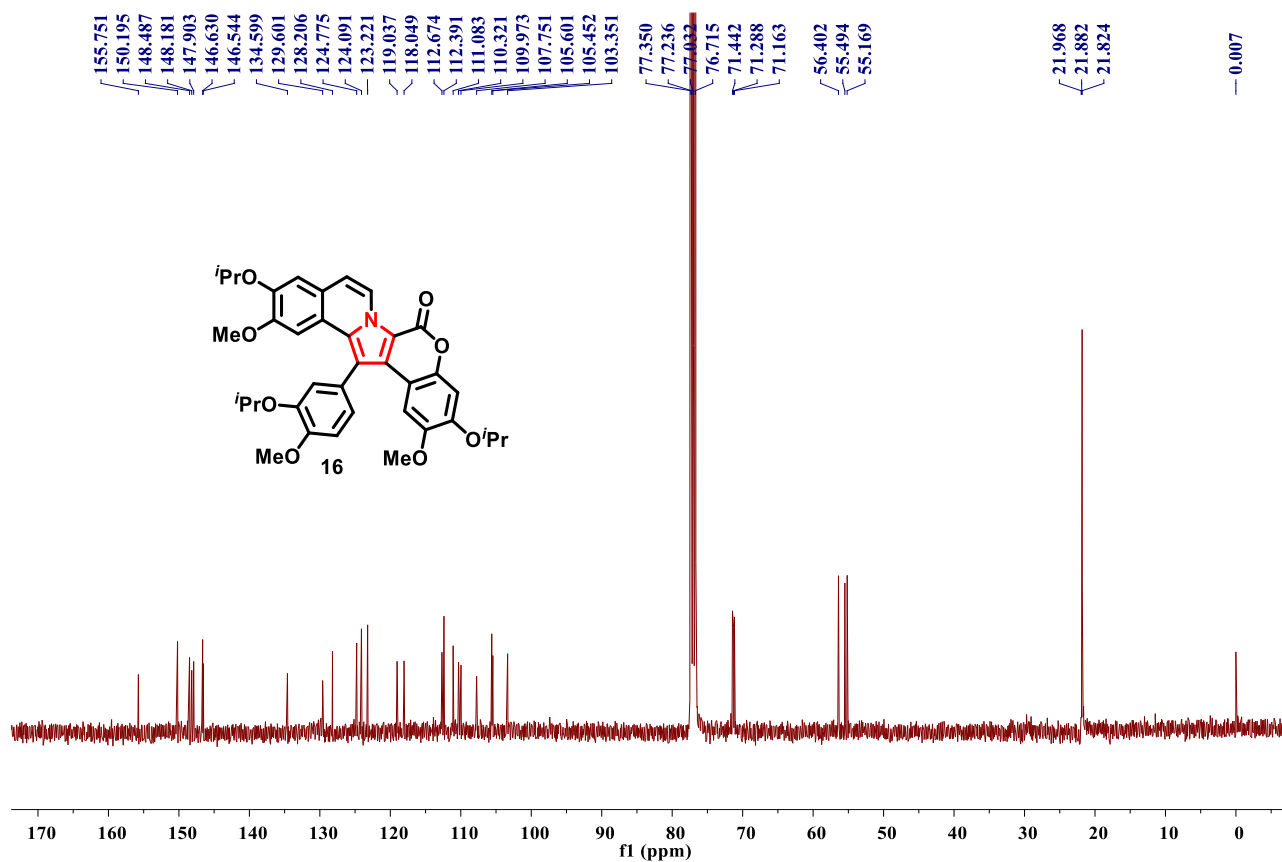
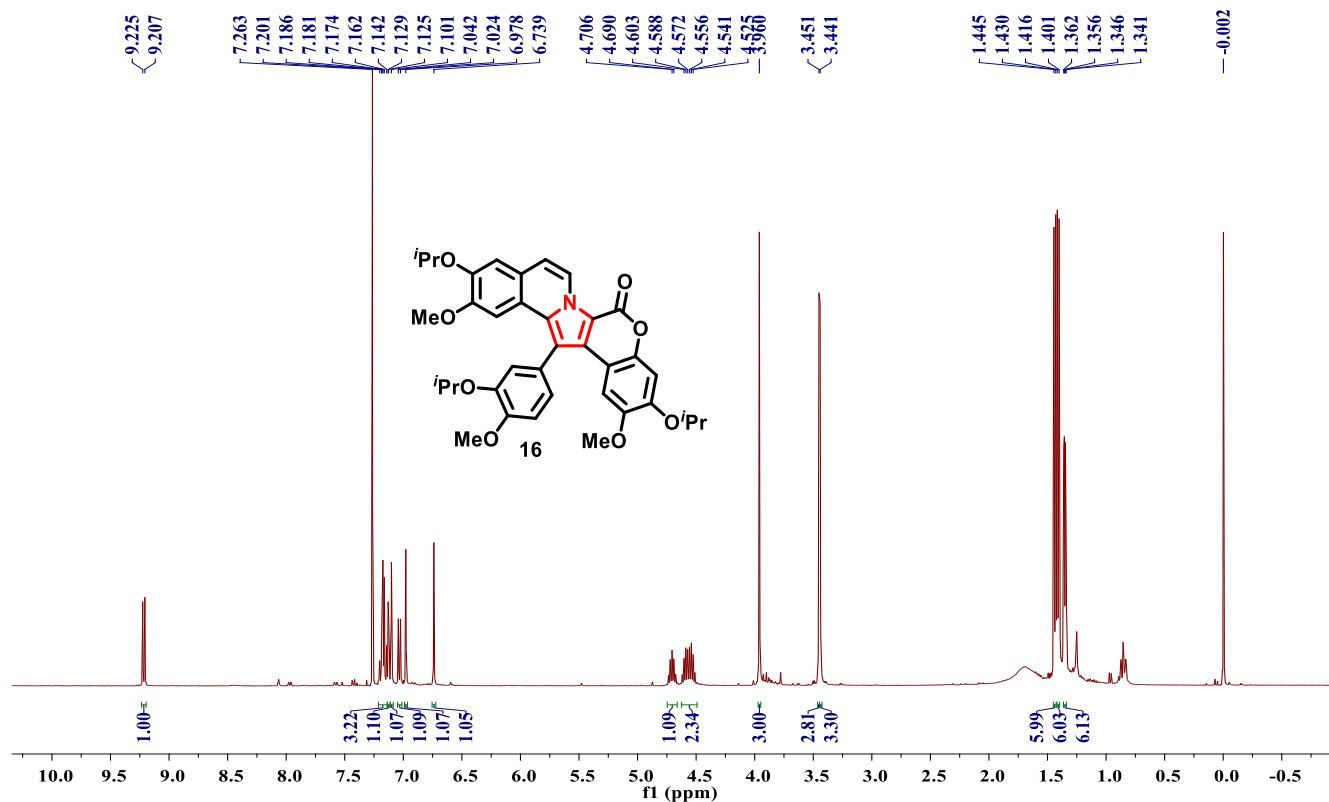
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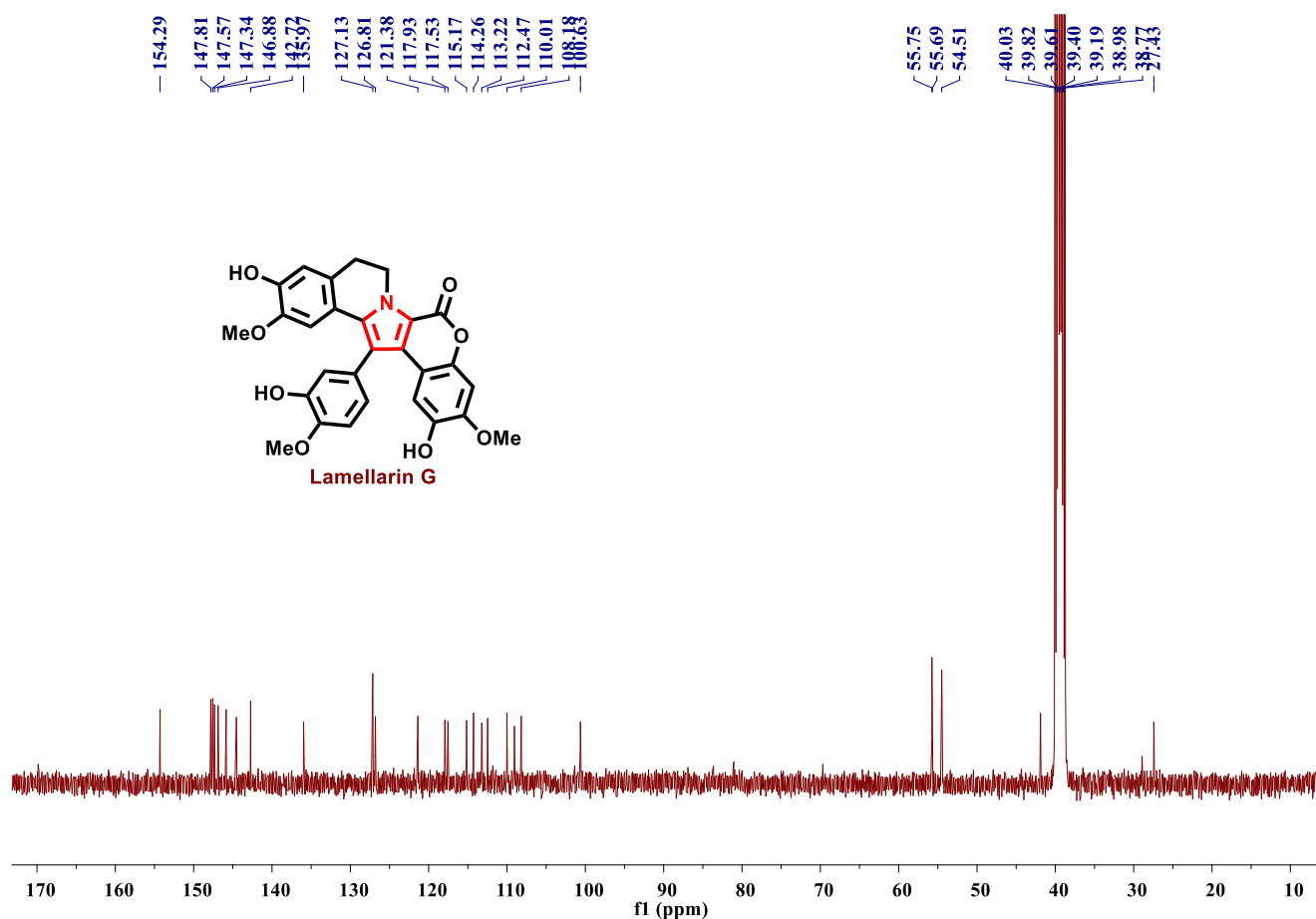
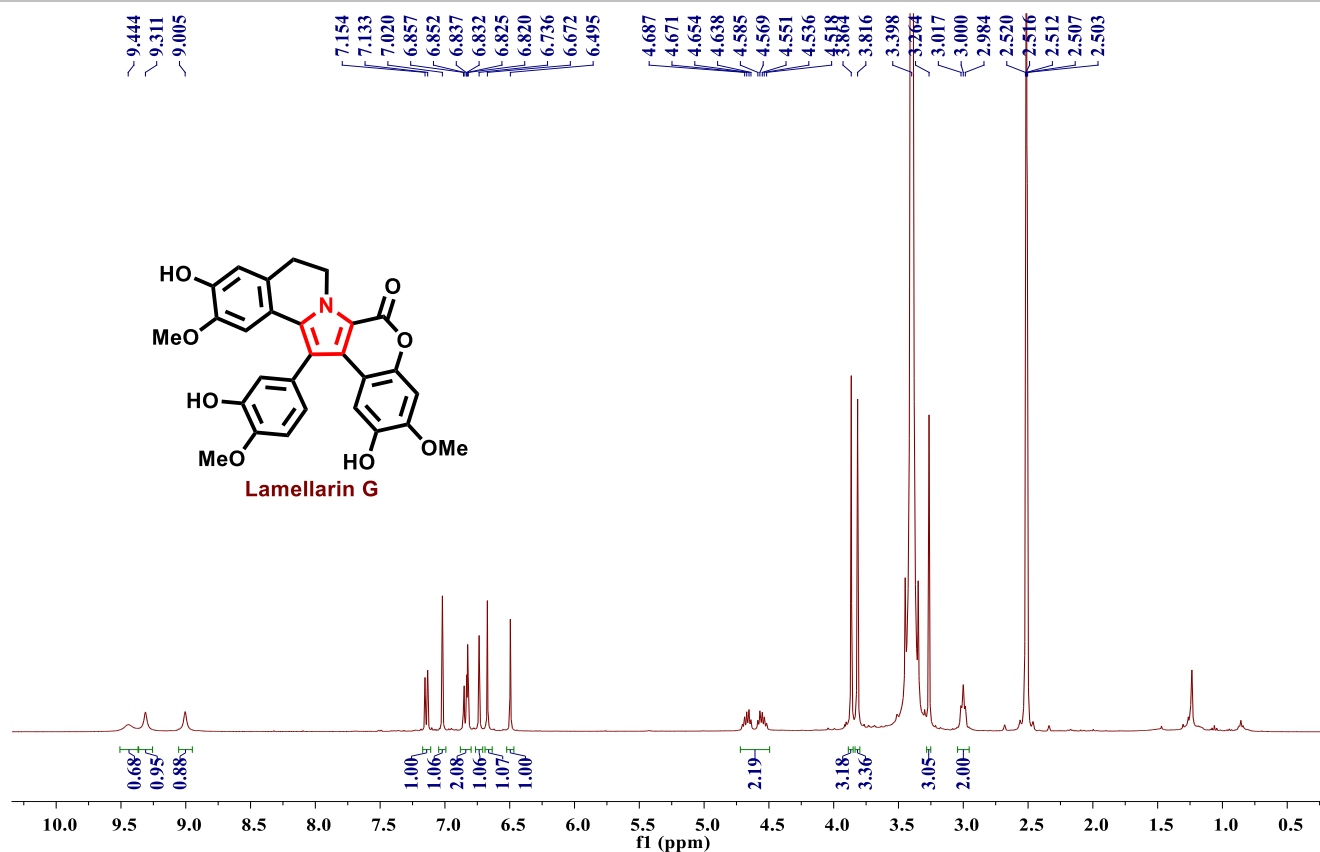
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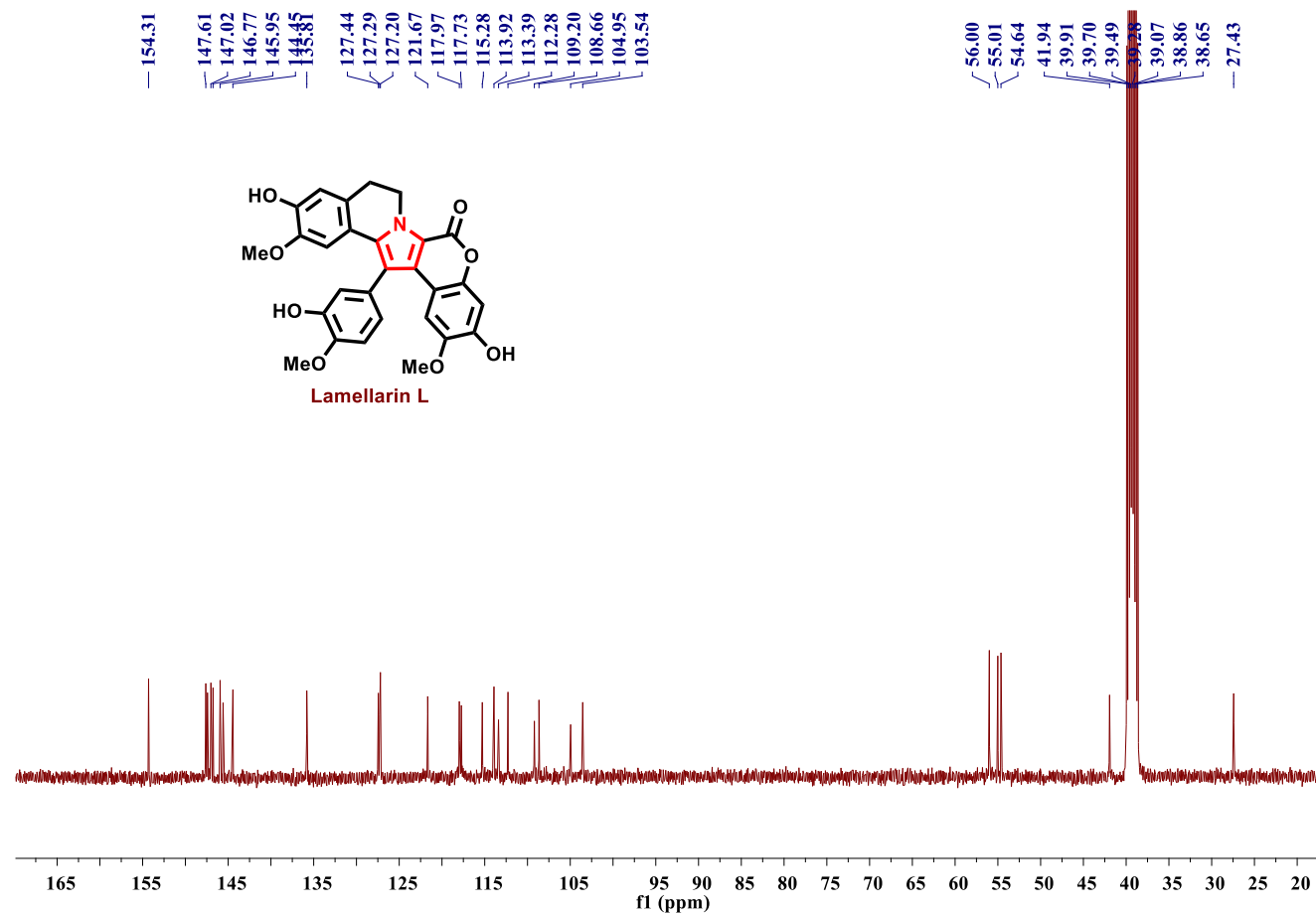
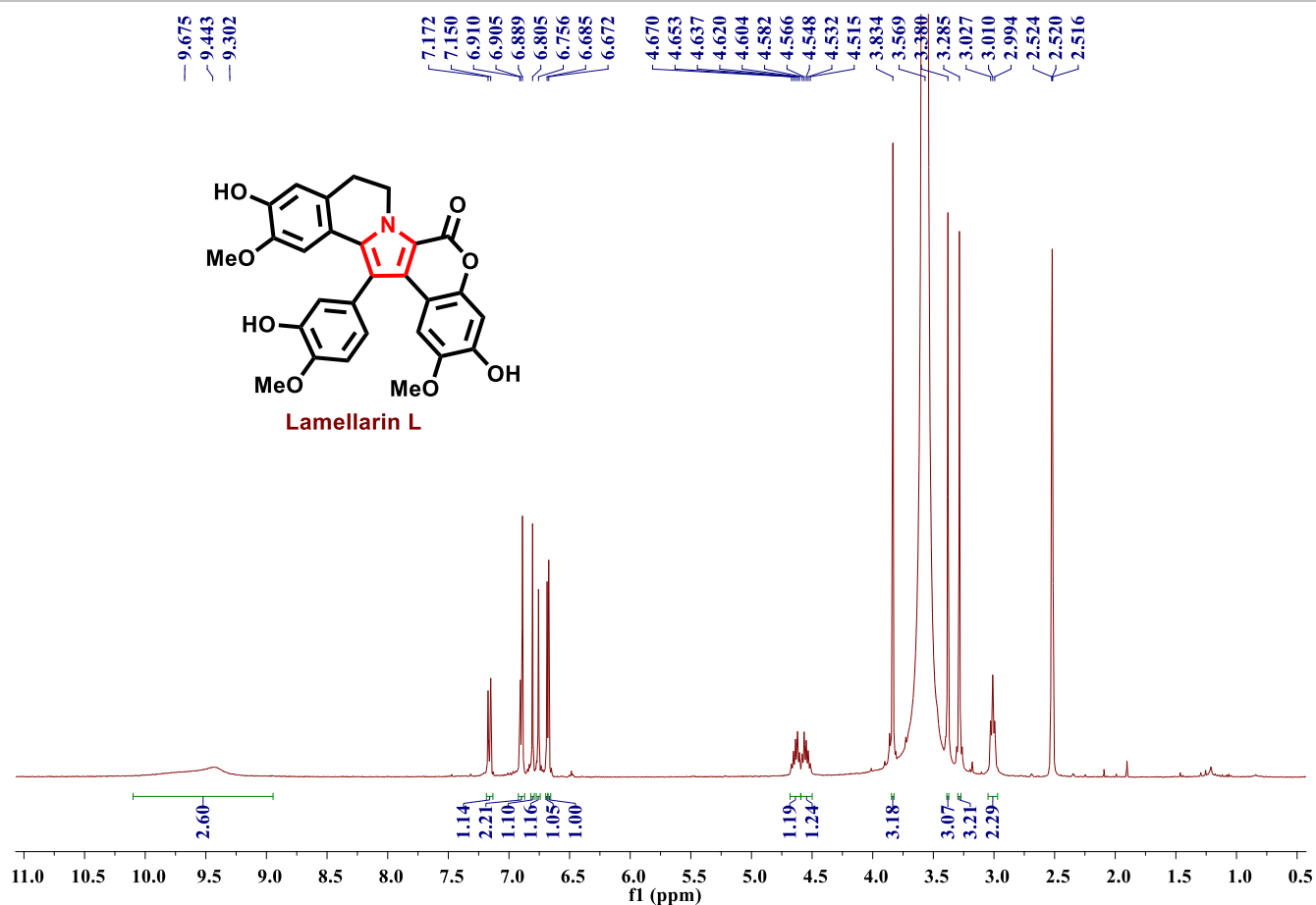
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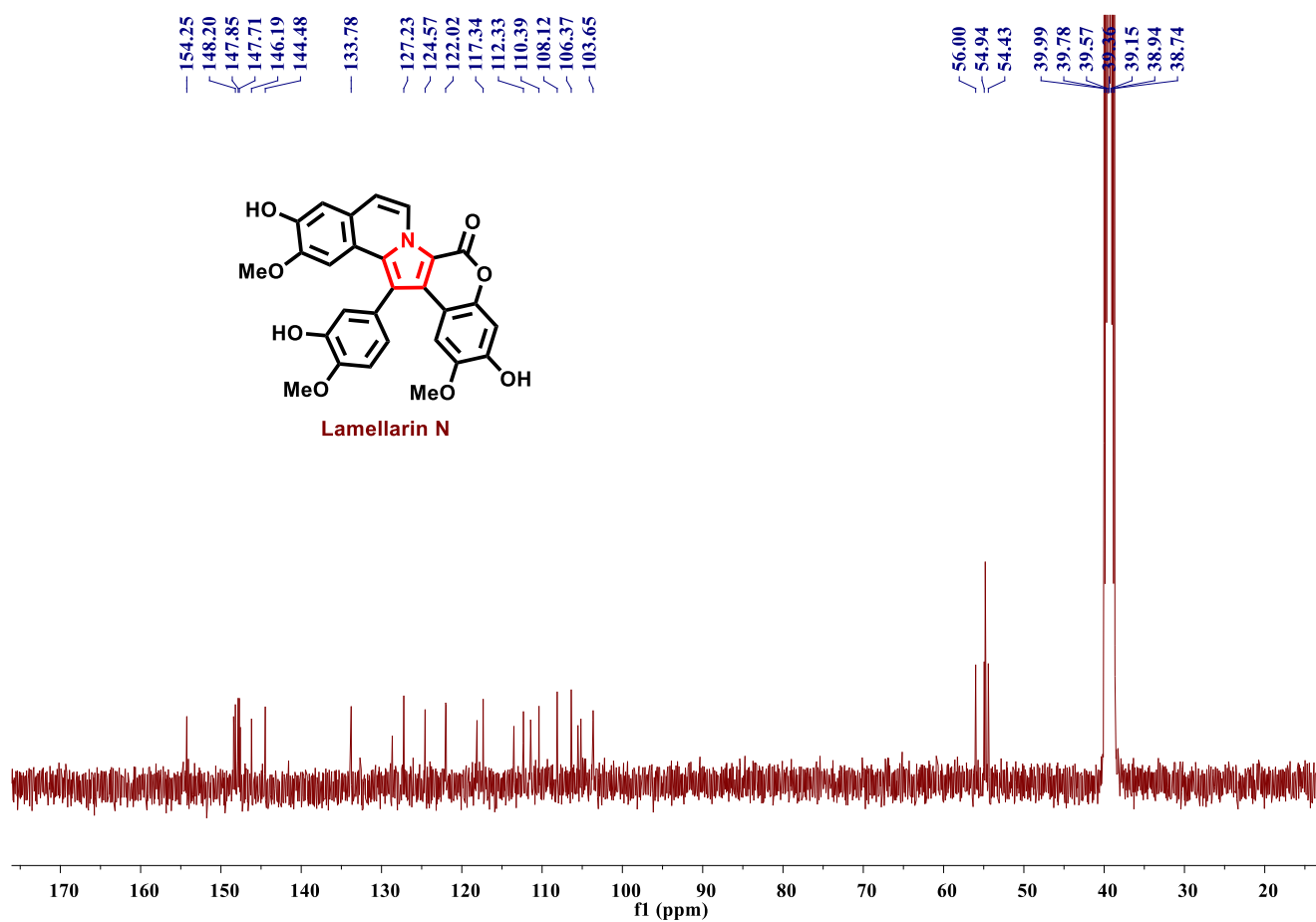
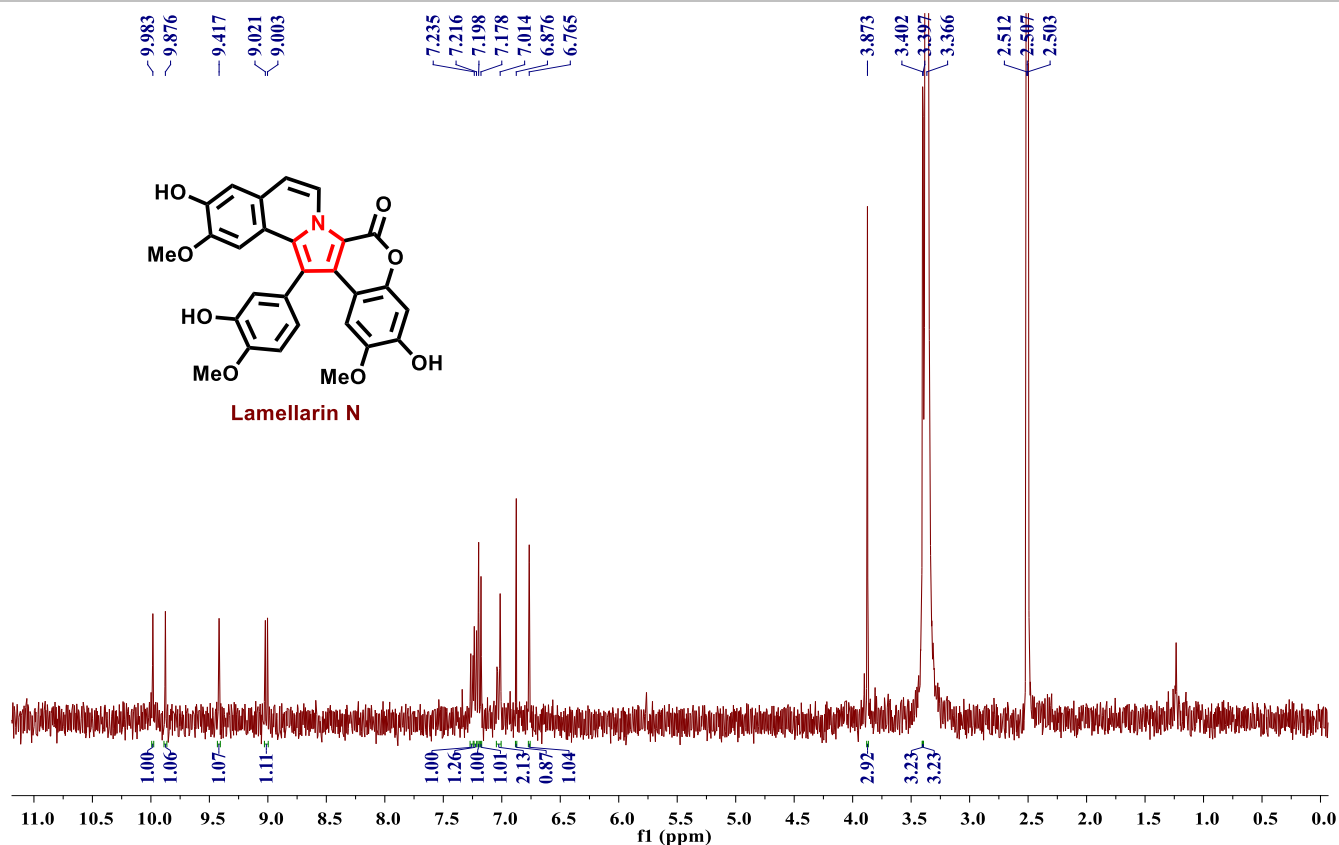
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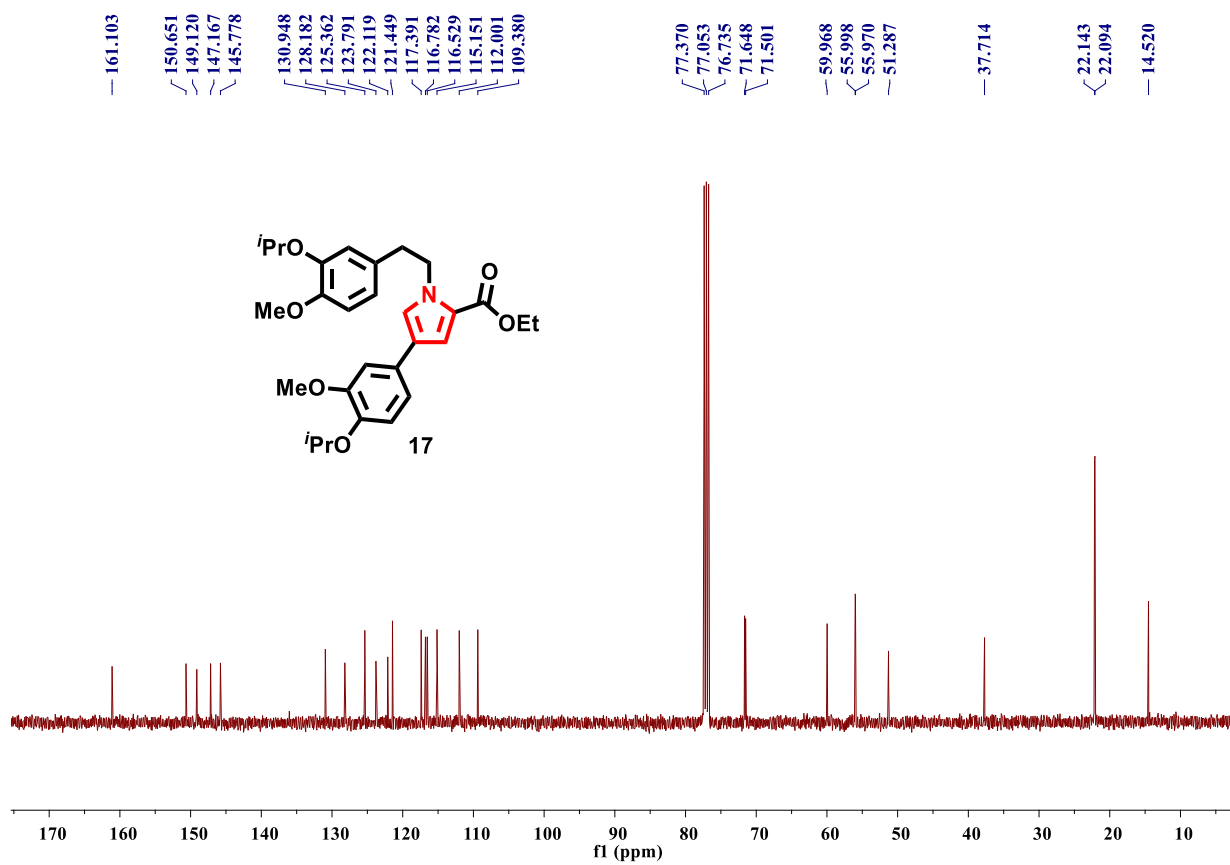
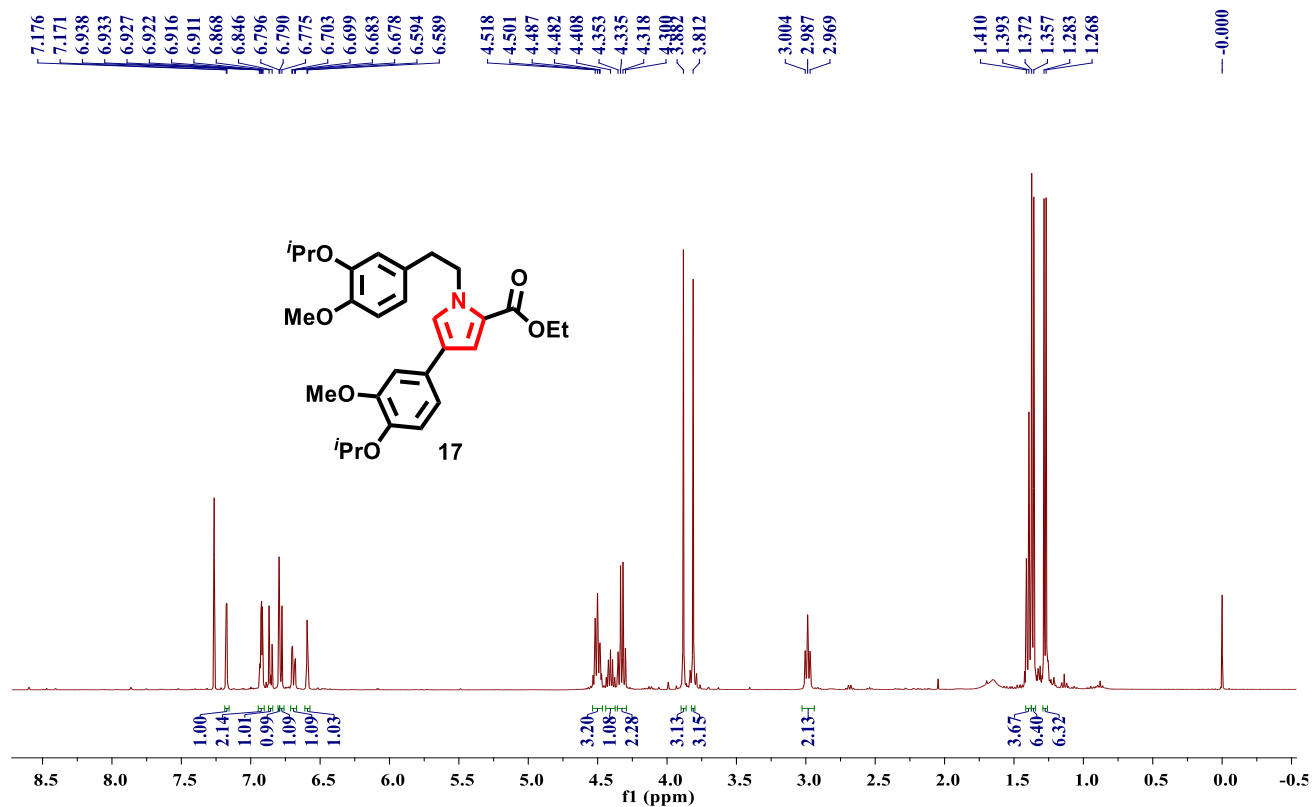
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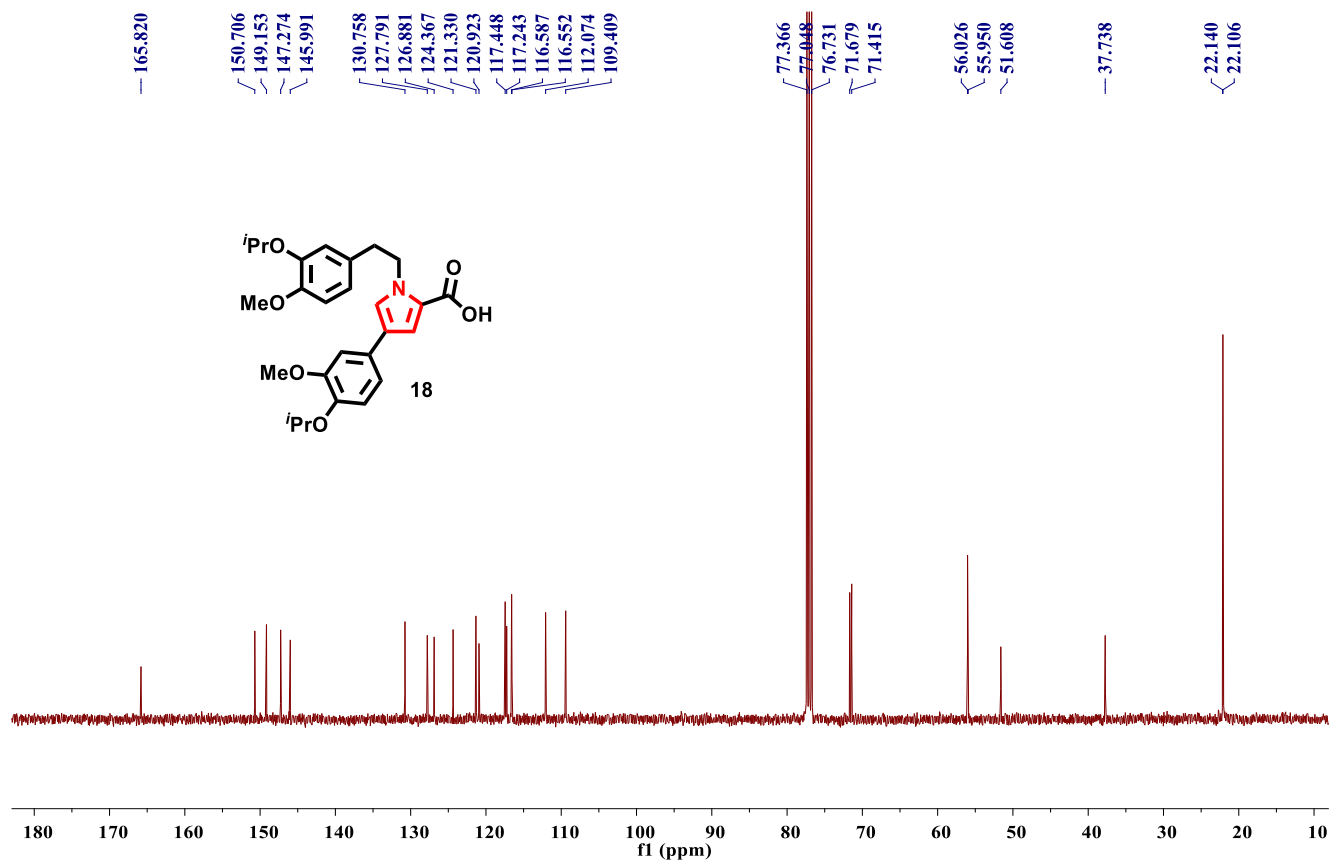
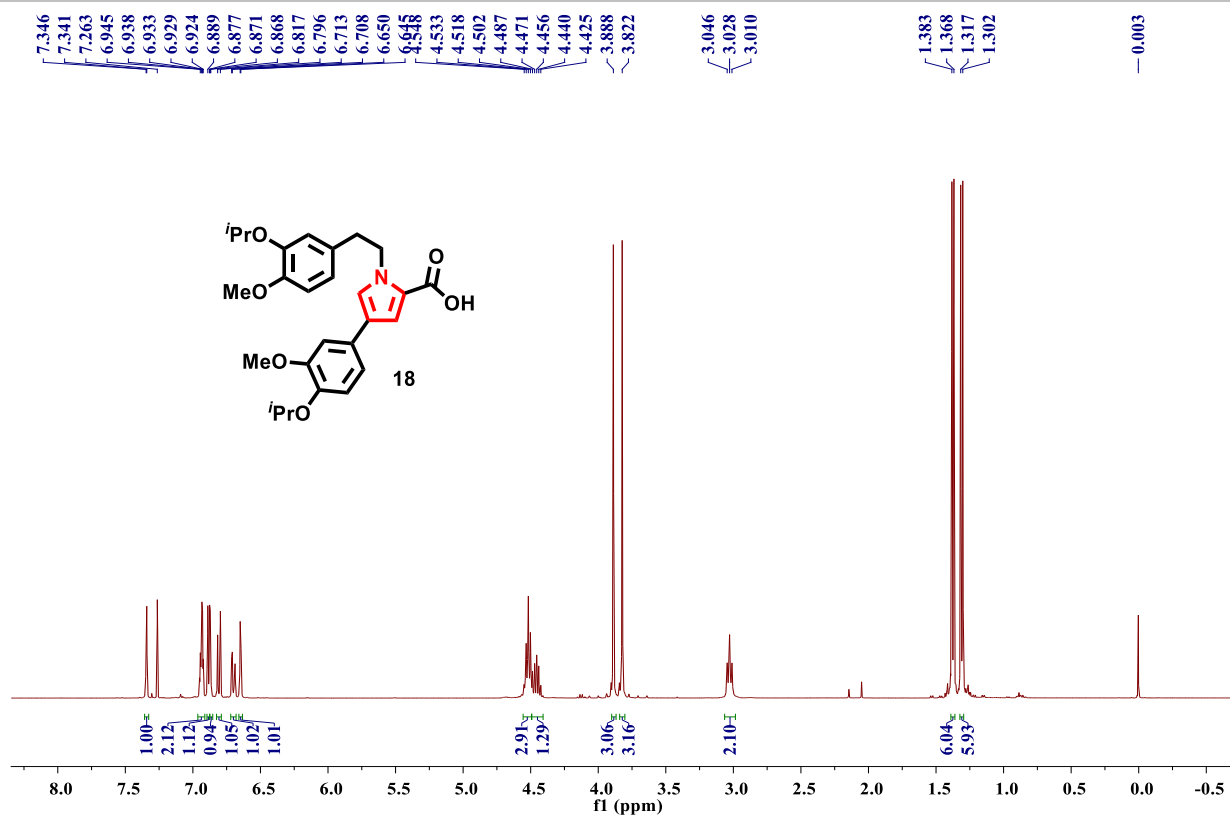
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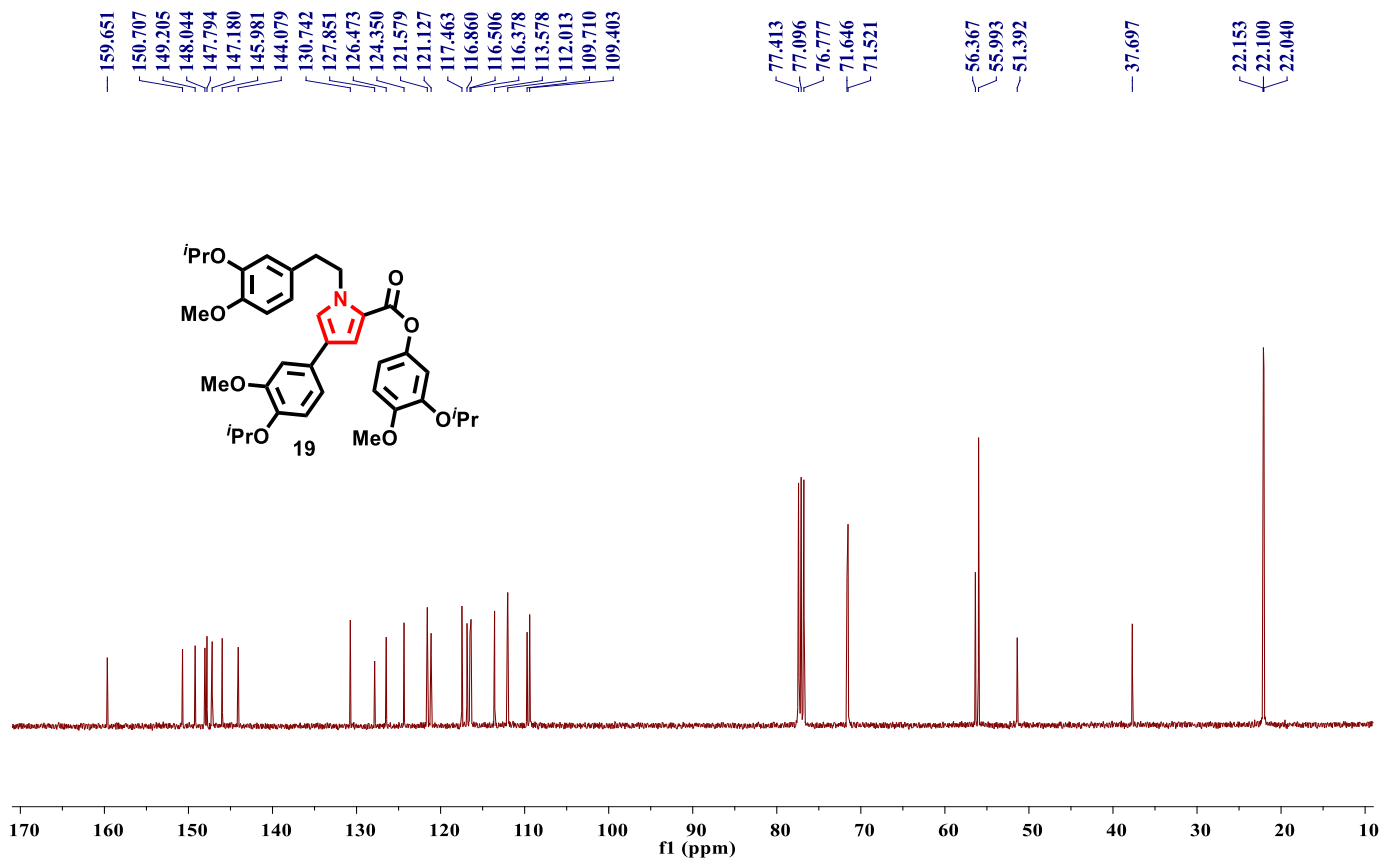
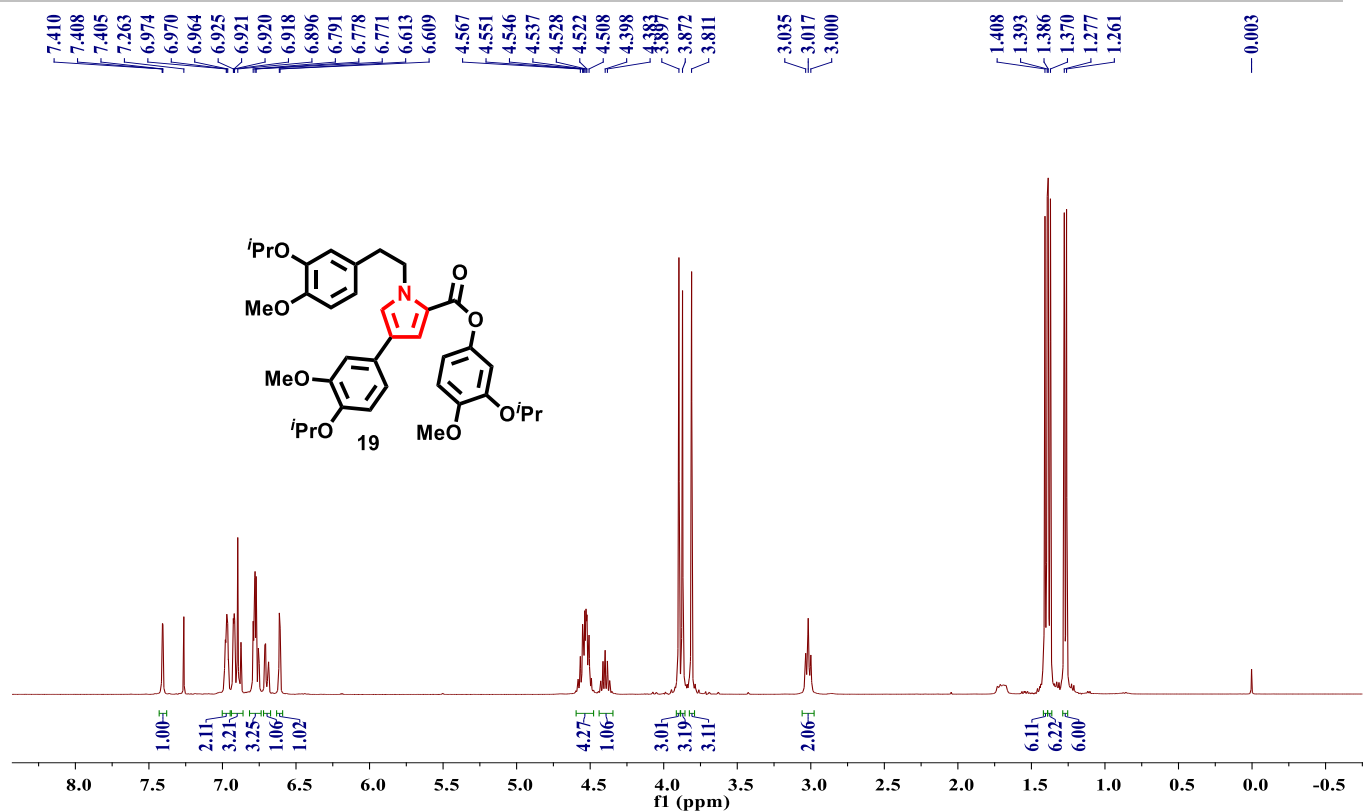
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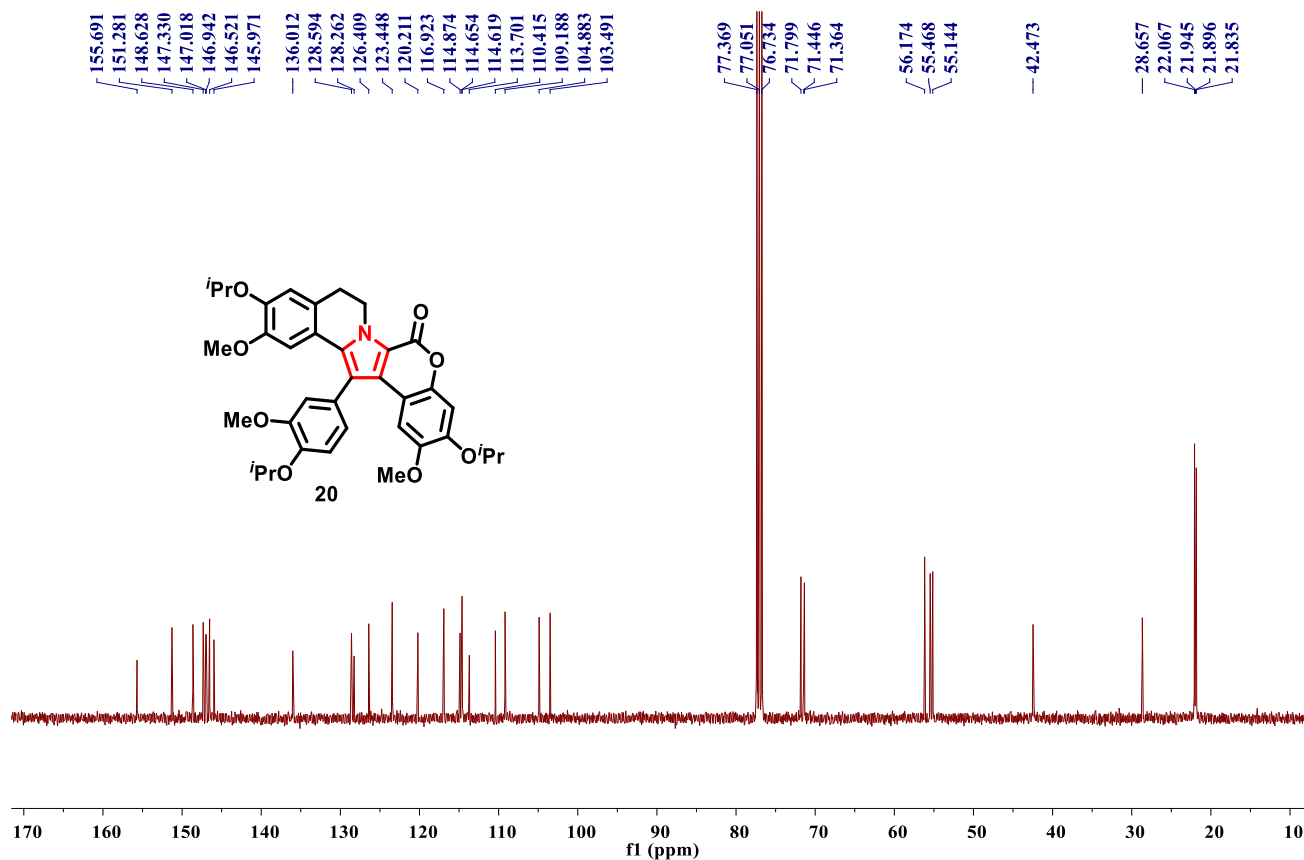
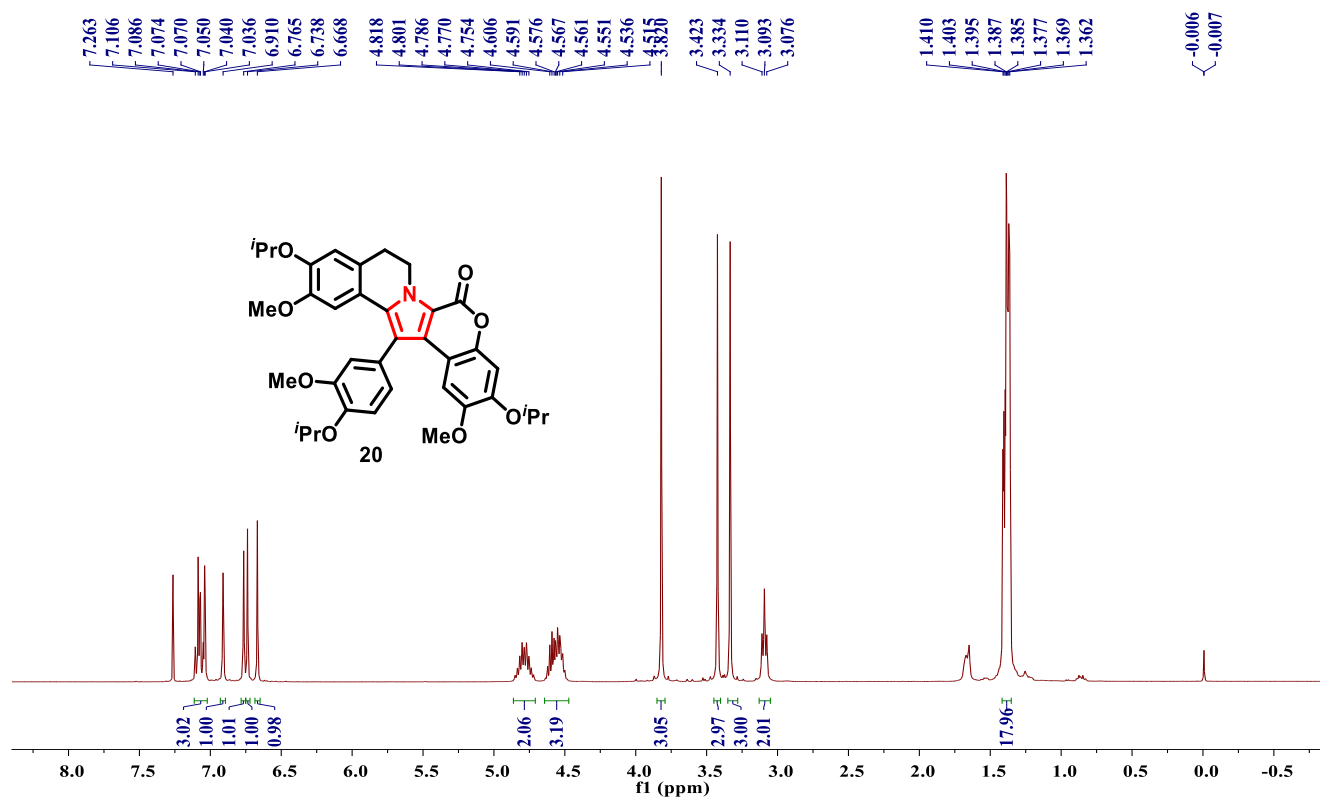
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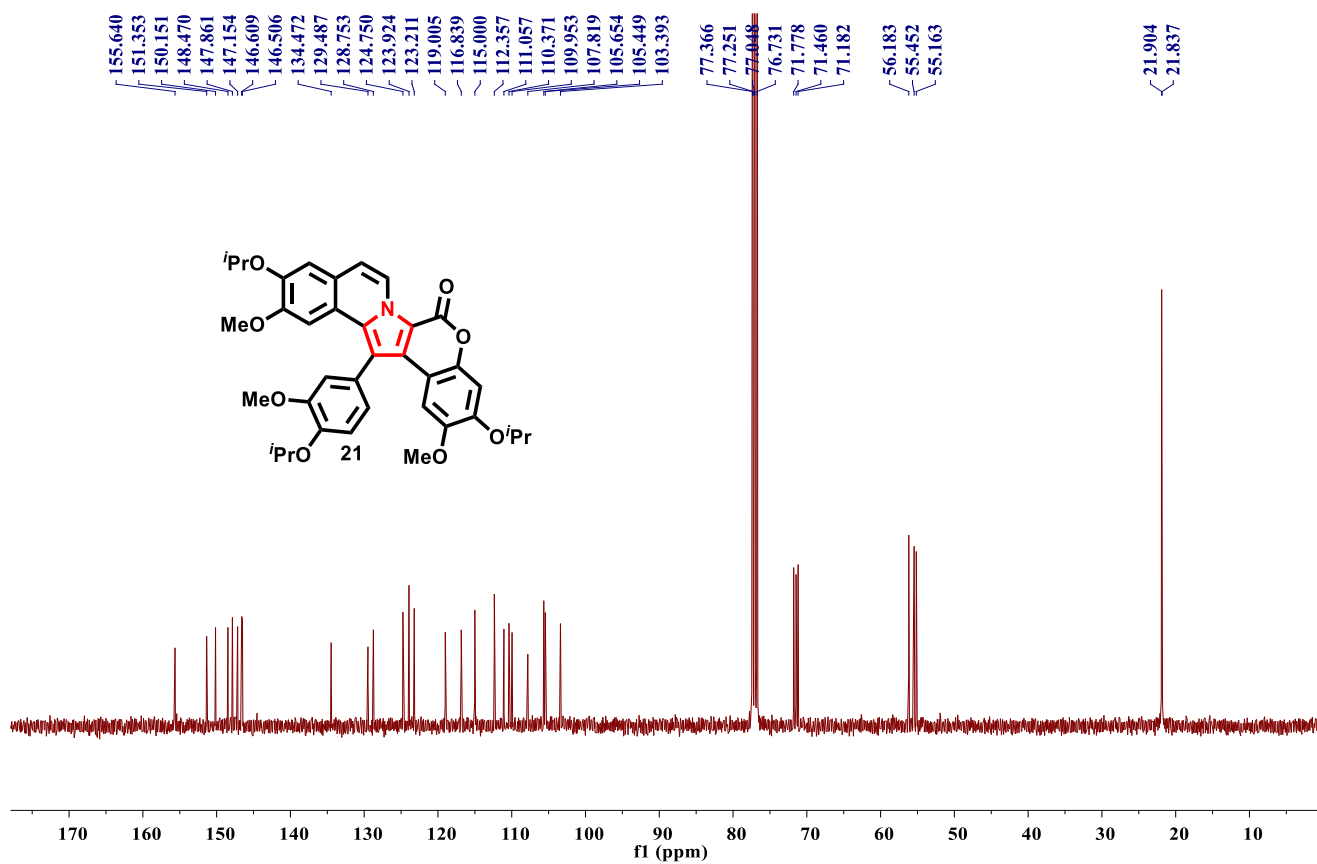
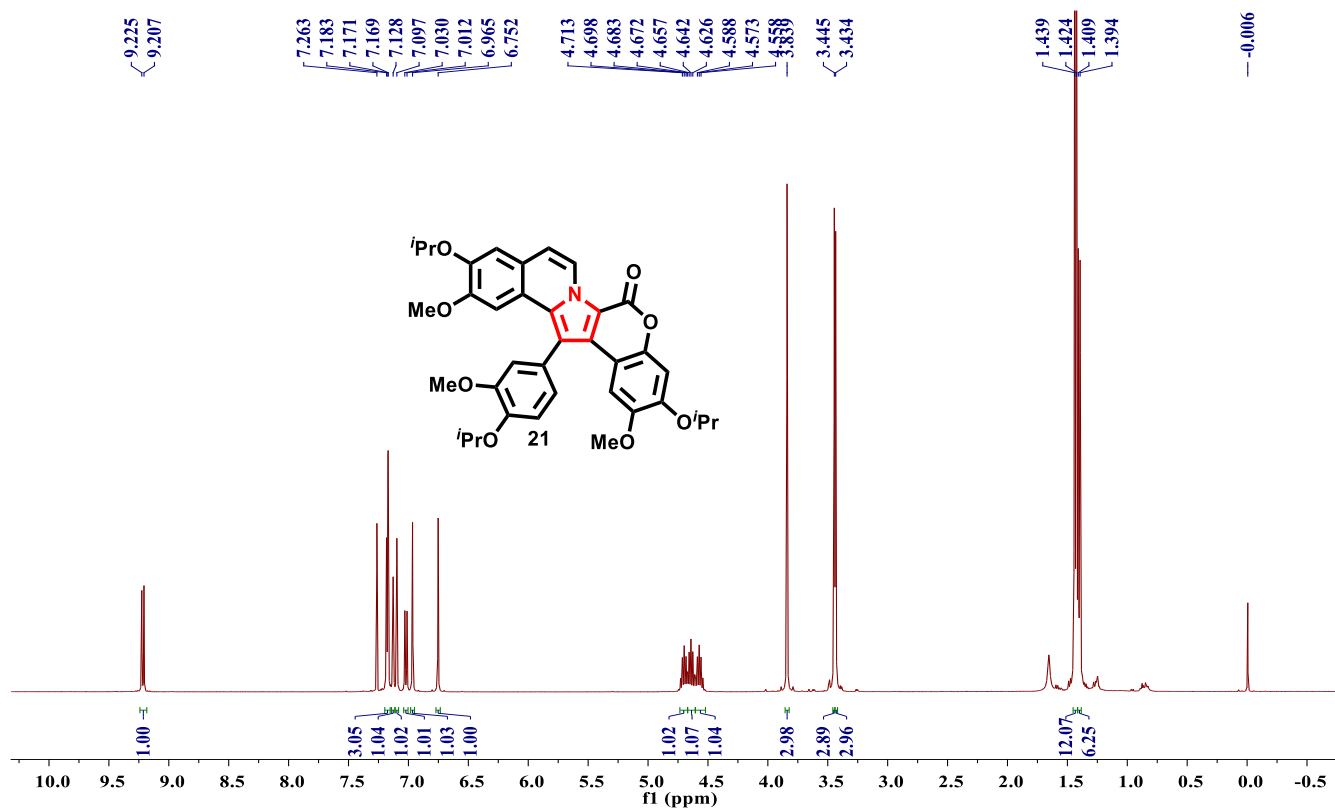
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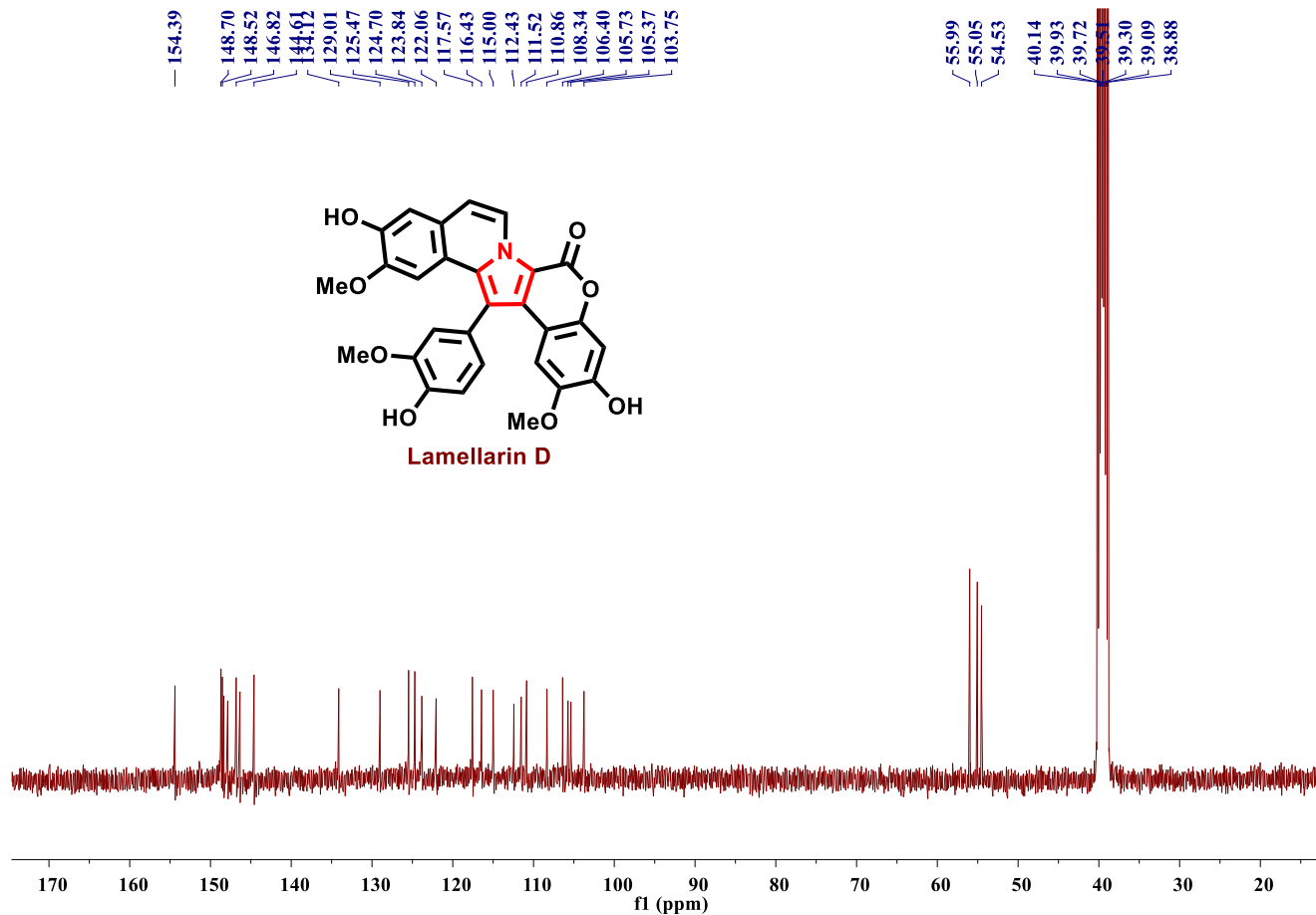
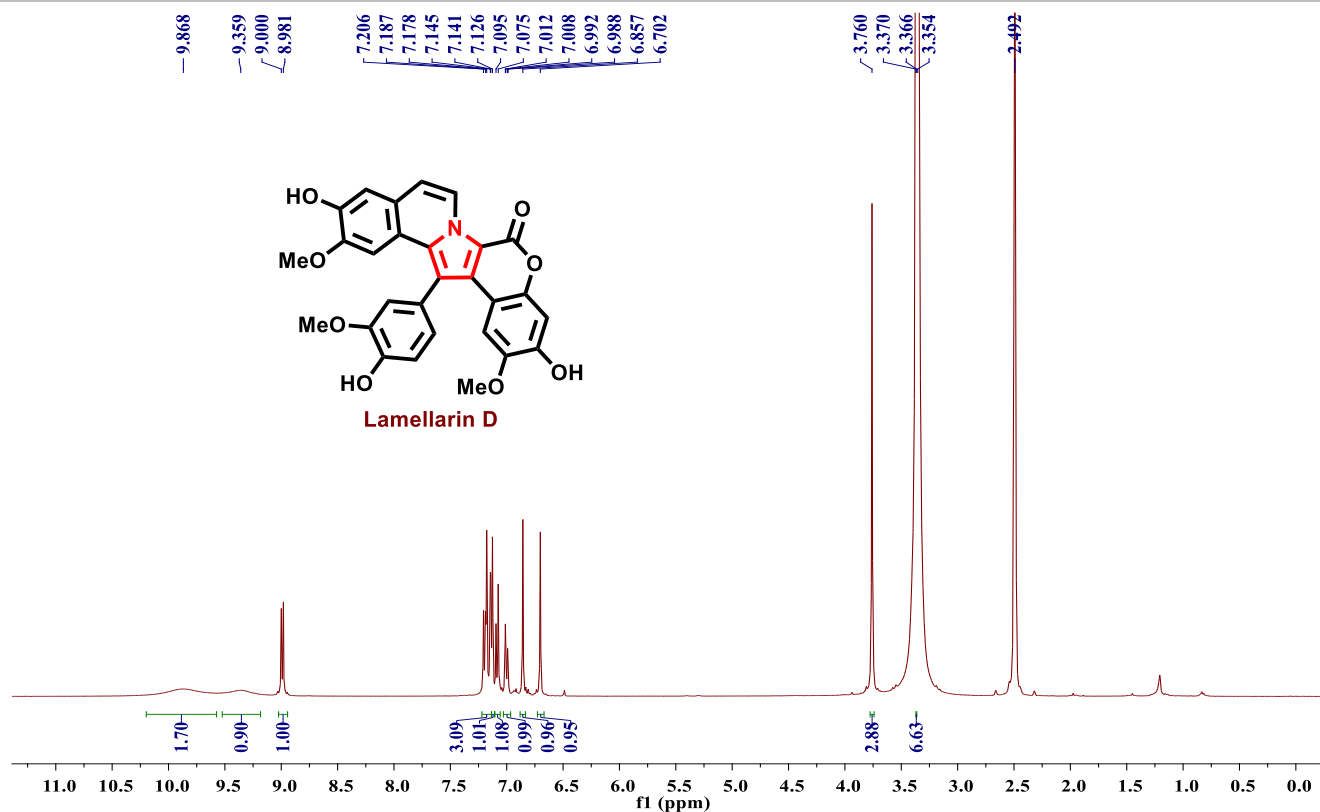


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