Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Total synthesis of diazaquinomycins H and J using double Knorr cyclization in the presence of triisopropylsilane

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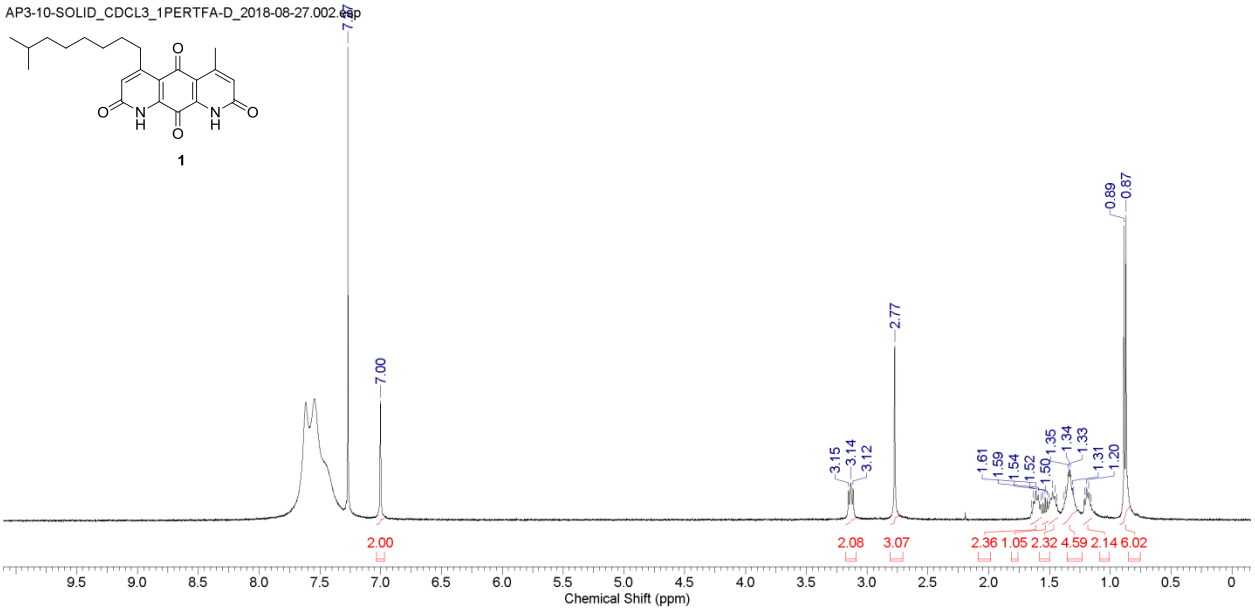
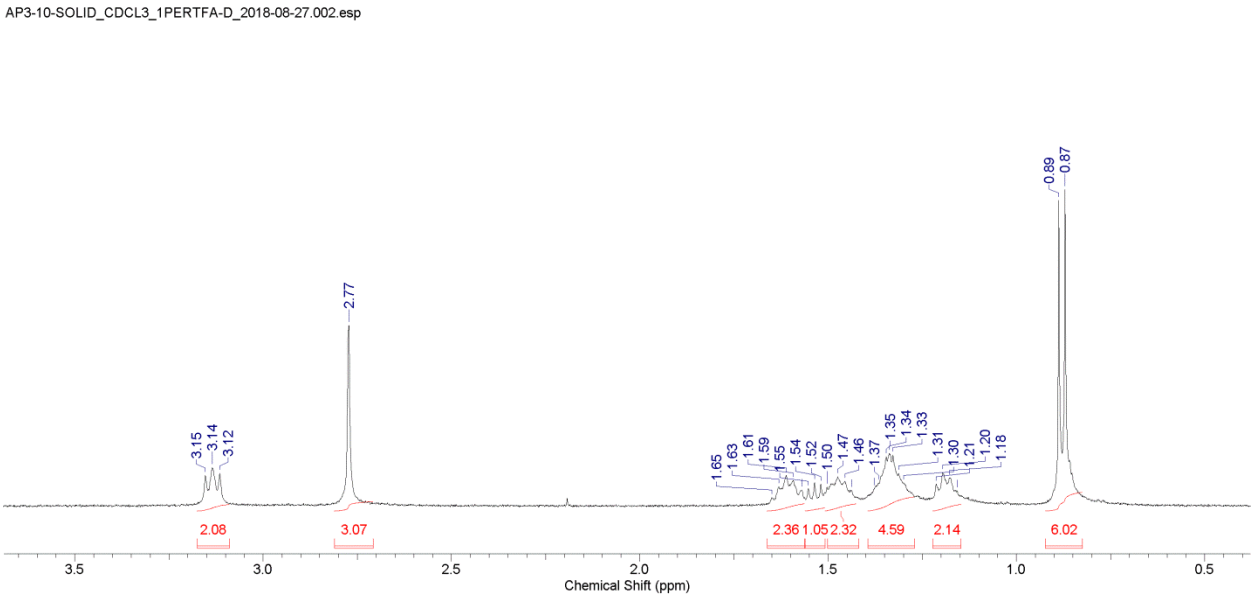
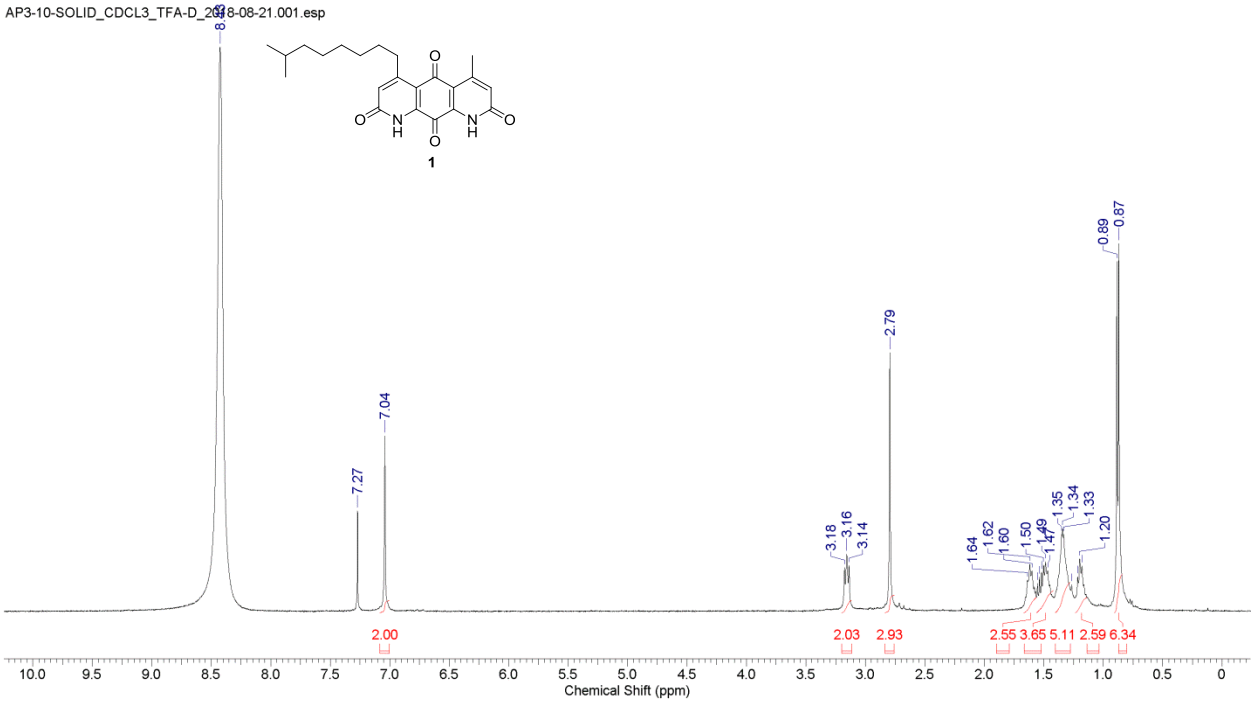
^{1}H NMR of diazaquinomycin H (**1**) in 1% $CF_3CO_2D/CDCl_3$



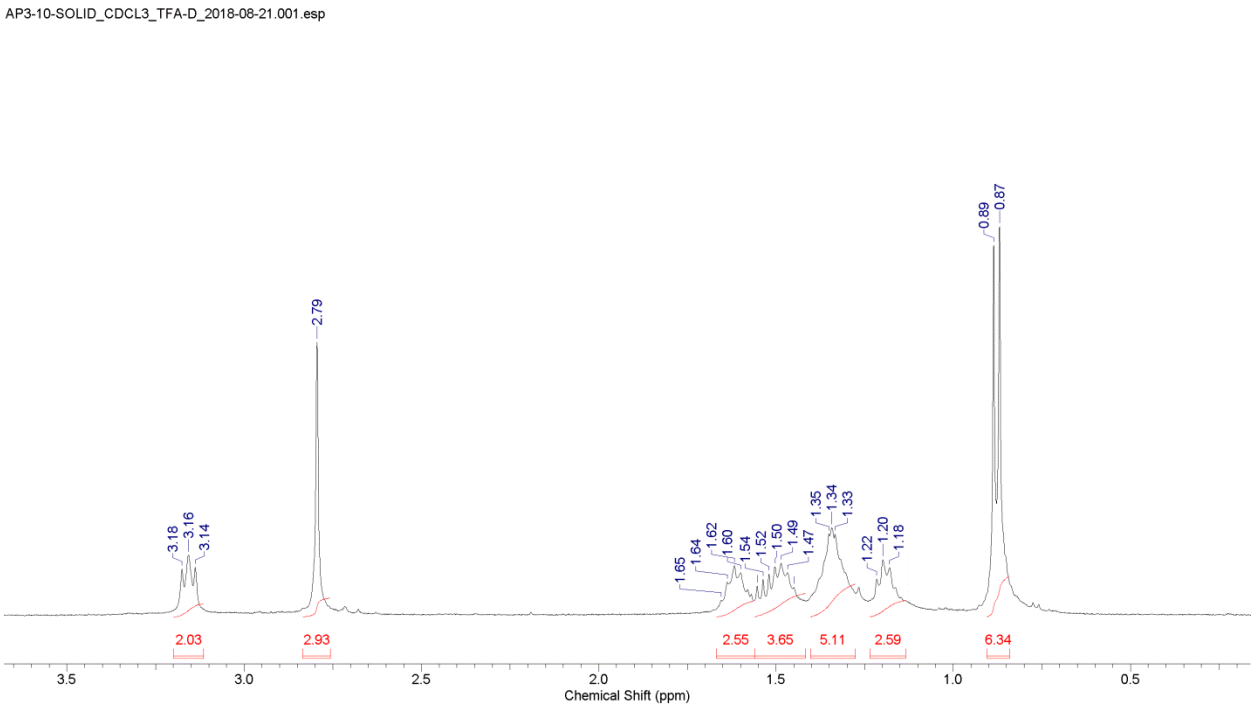
Zoomed ^{1}H NMR of **1** in 1% $CF_3CO_2D/CDCl_3$



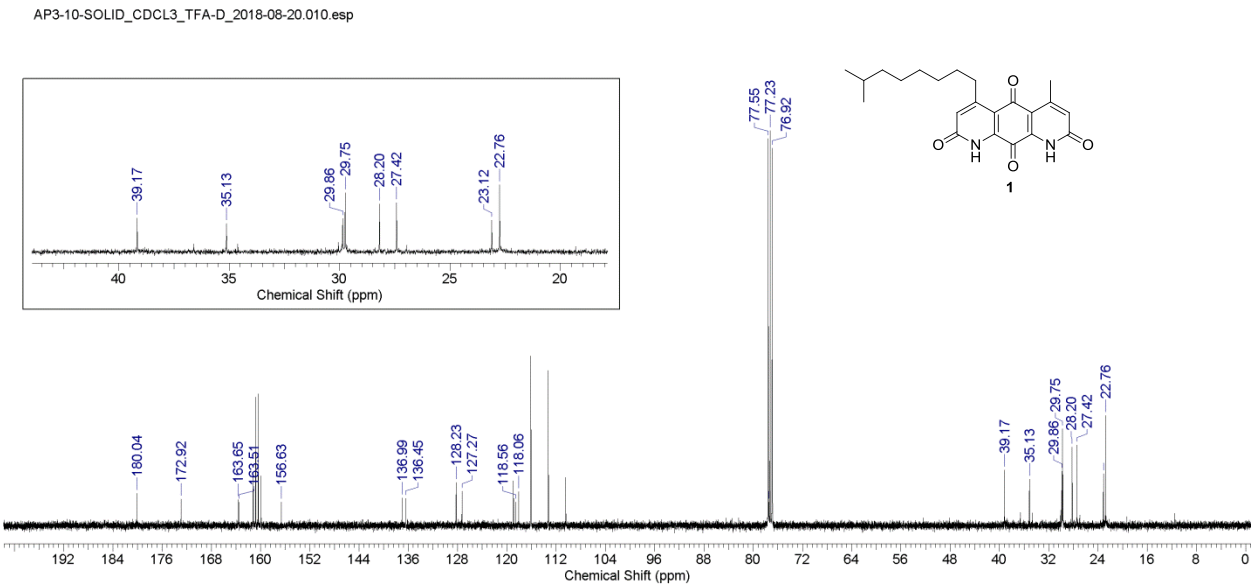
^{1}H NMR of **1** in 2% $CF_3CO_2D/CDCl_3$



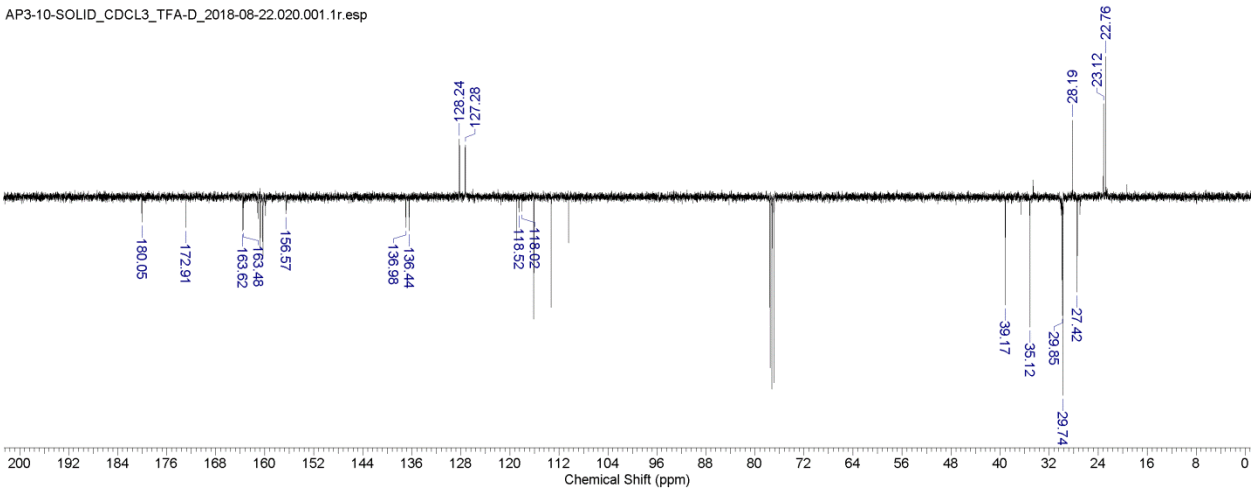
Zoomed ^{1}H NMR of **1** in 2% $CF_3CO_2D/CDCl_3$



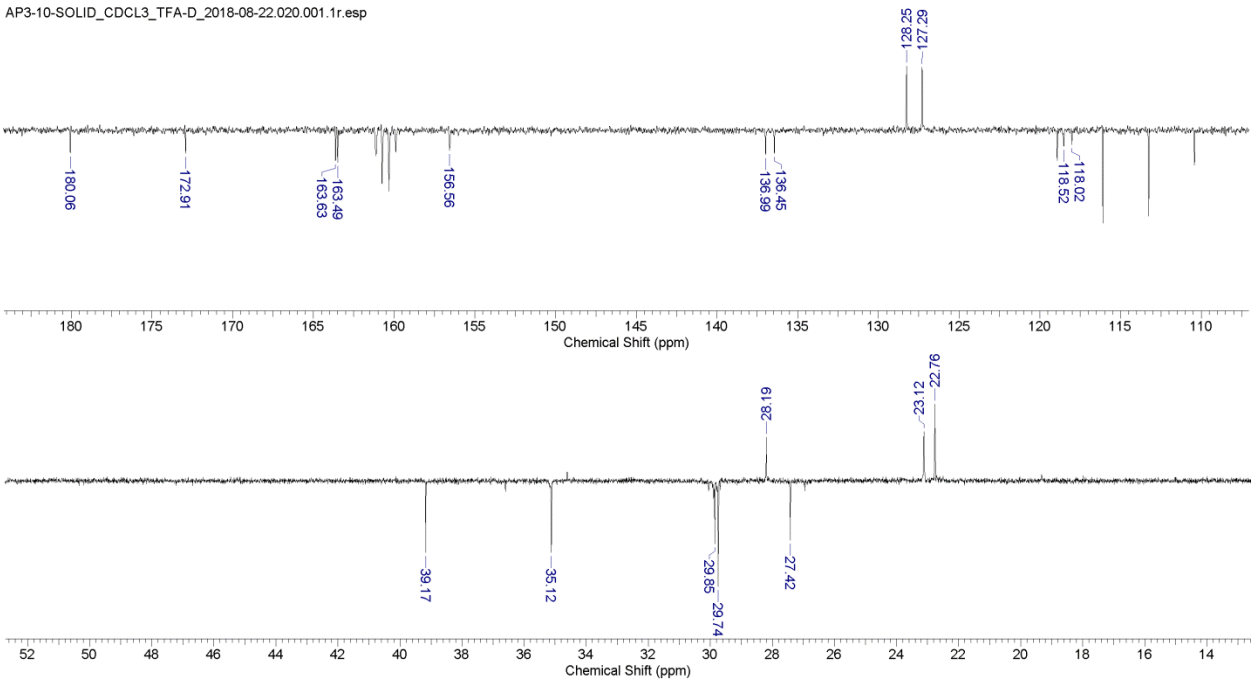
^{13}C NMR of **1** in 2% $CF_3CO_2D/CDCl_3$



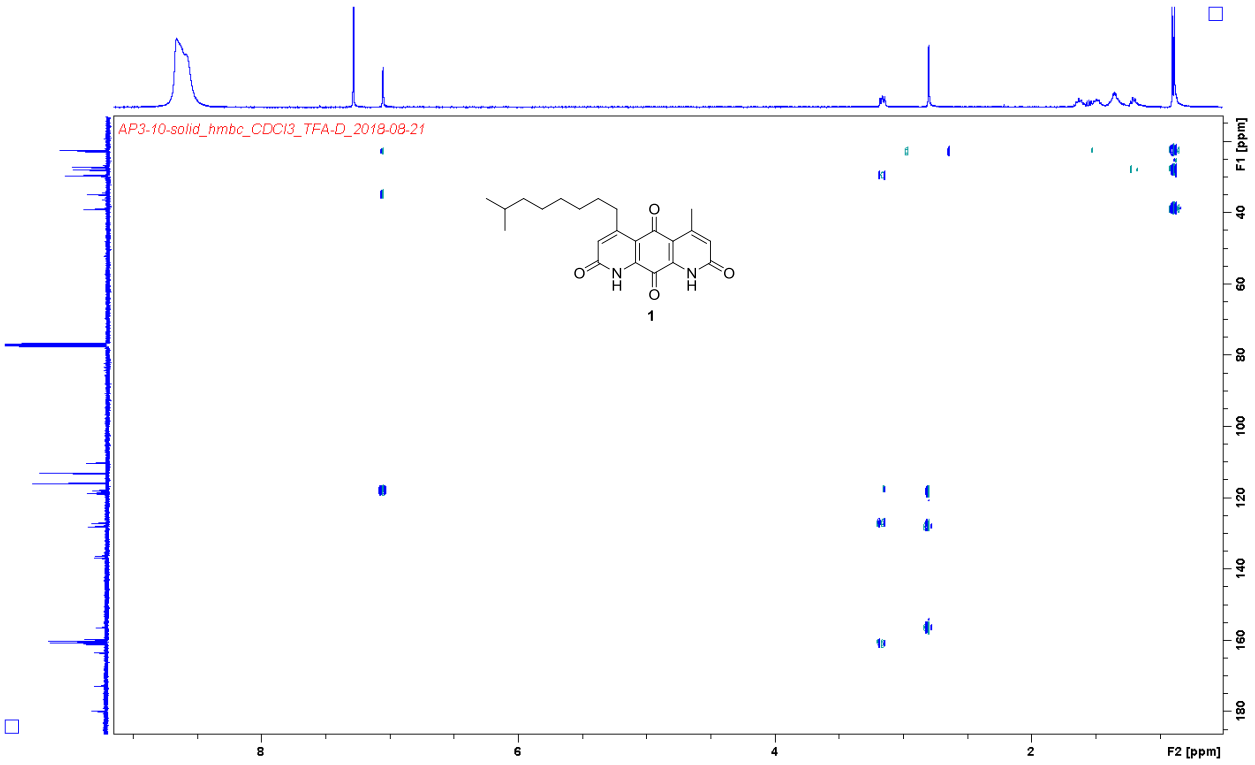
DEPTQ of **1** in 2% $CF_3CO_2D/CDCl_3$



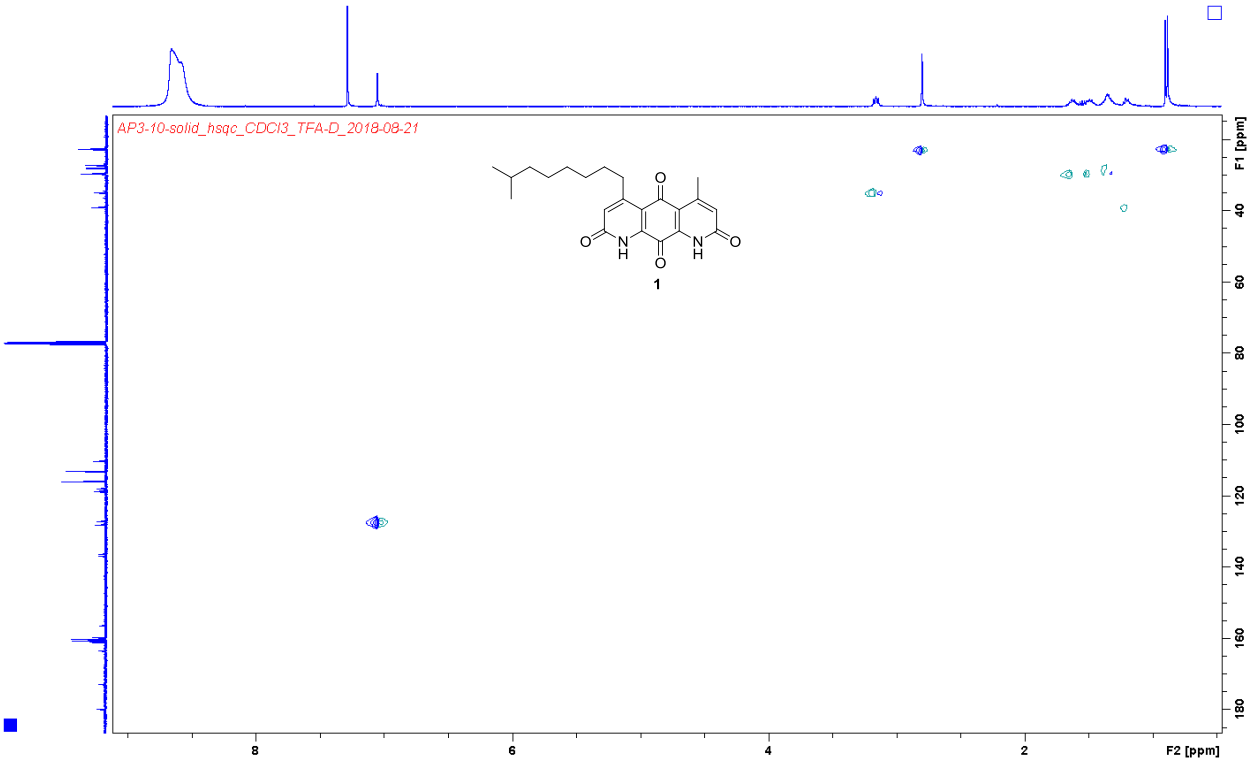
Zoomed DEPTQ regions of **1** in 2% $CF_3CO_2D/CDCl_3$



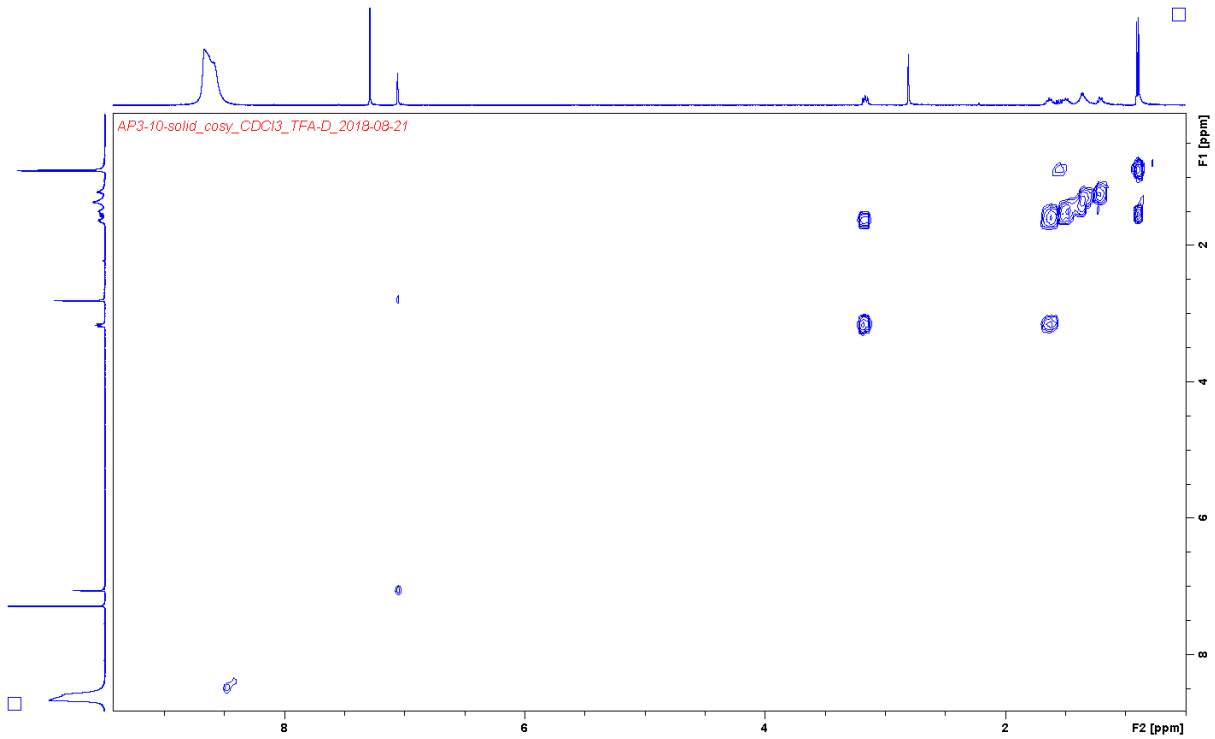
HMBC of **1** in 2% $CF_3CO_2D/CDCl_3$



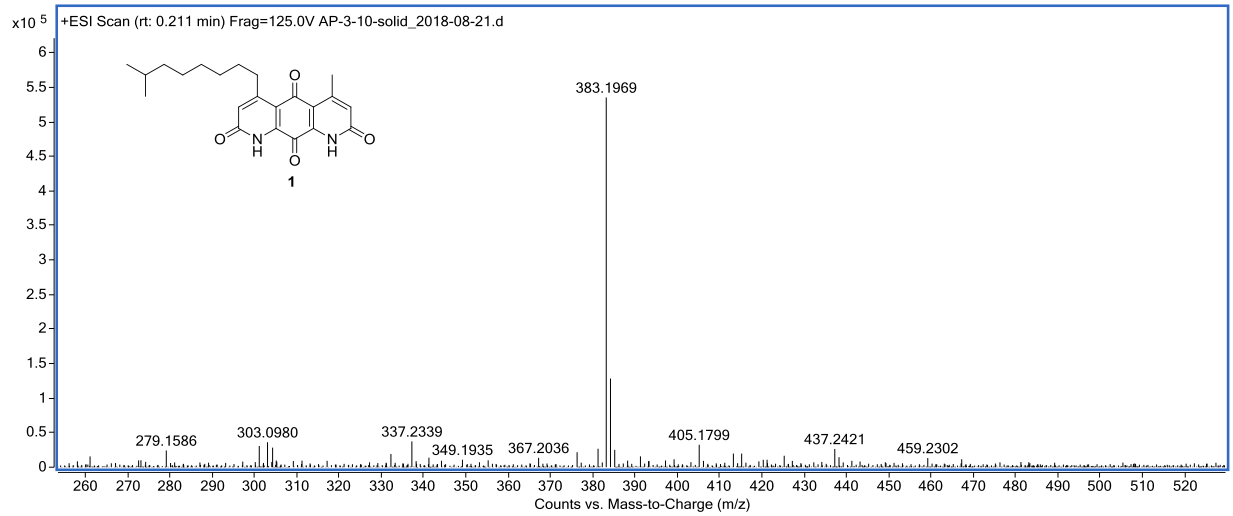
HSQC of **1** in 2% $CF_3CO_2D/CDCl_3$



COSY of **1** in 2% $CF_3CO_2D/CDCl_3$



HRMS of **1**


+ESI Scan (rt: 0.211 min) Frag=125.0V AP-3-10-solid_2018-08-21.d
x10 5
383.1969
279.1586
303.0980
337.2339
349.1935
367.2036
405.1799
437.2421
459.2302
Counts vs. Mass-to-Charge (m/z)
1

HPLC chromatogram of **1**

==== Shimadzu LCsolution Analysis Report ====

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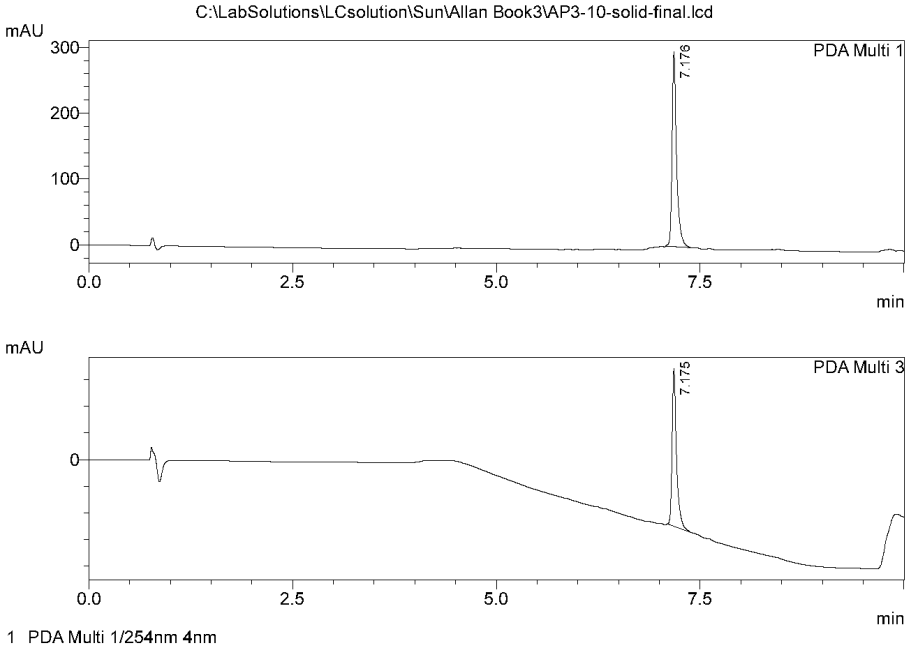


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

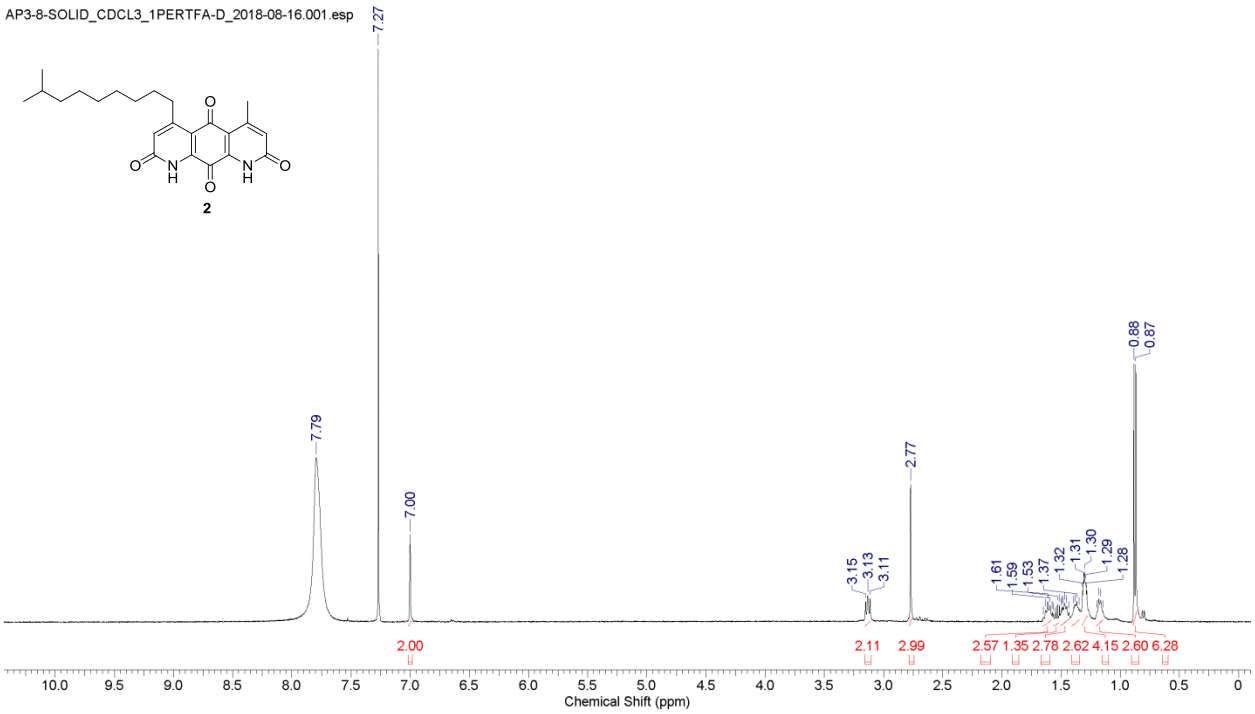
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.176	1122896	290447	100.000	100.000
Total		1122896	290447	100.000	100.000

PeakTable

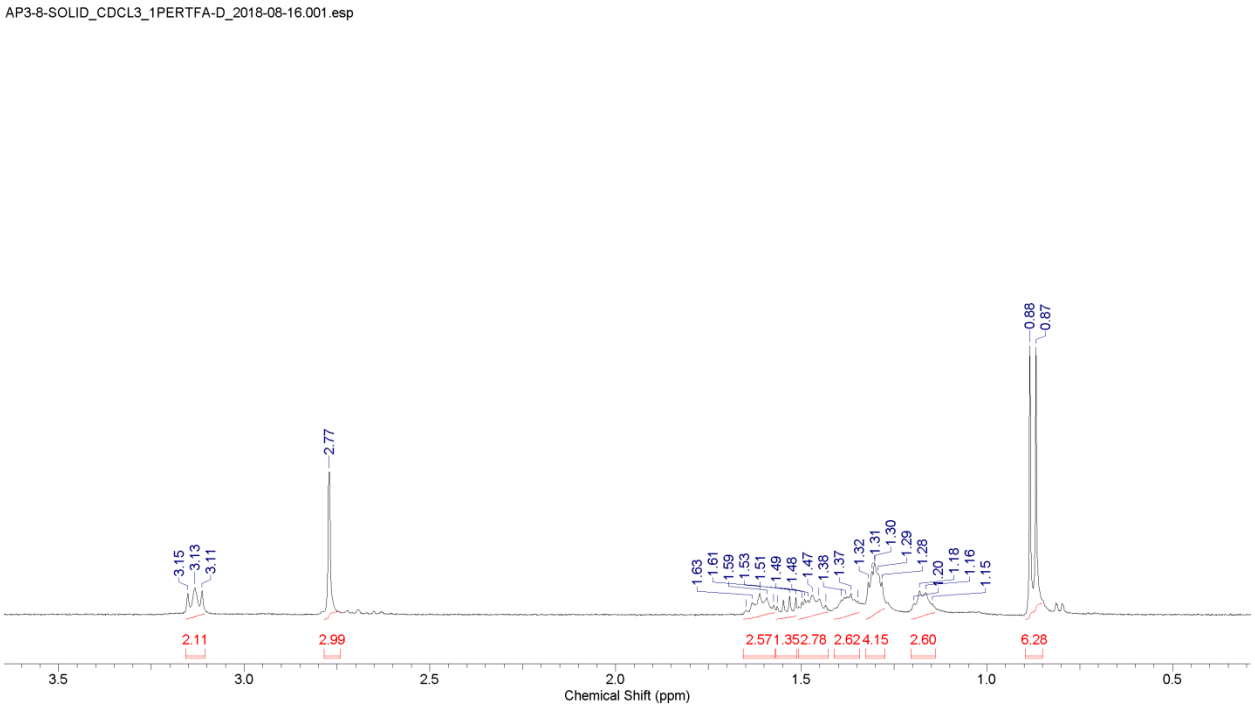
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.175	1101613	295726	100.000	100.000
Total		1101613	295726	100.000	100.000

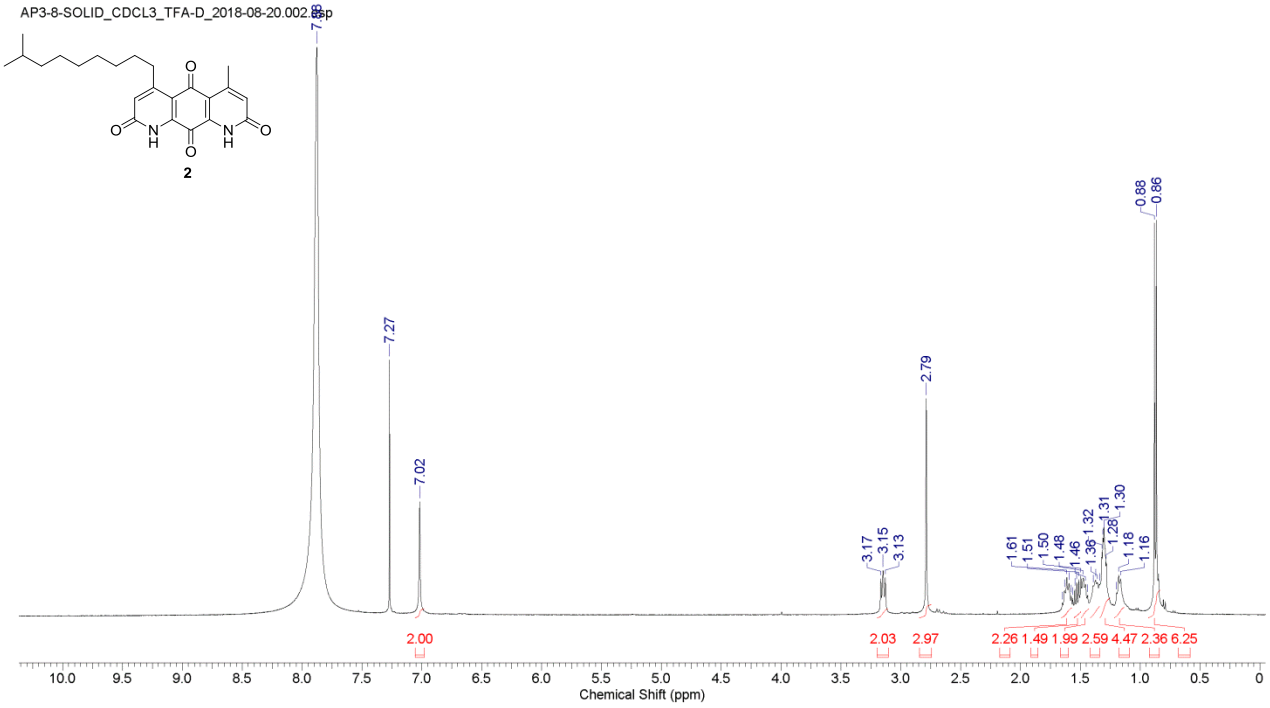
^{1}H NMR of diazaquinomycin J (**2**) in 1% $CF_3CO_2D/CDCl_3$



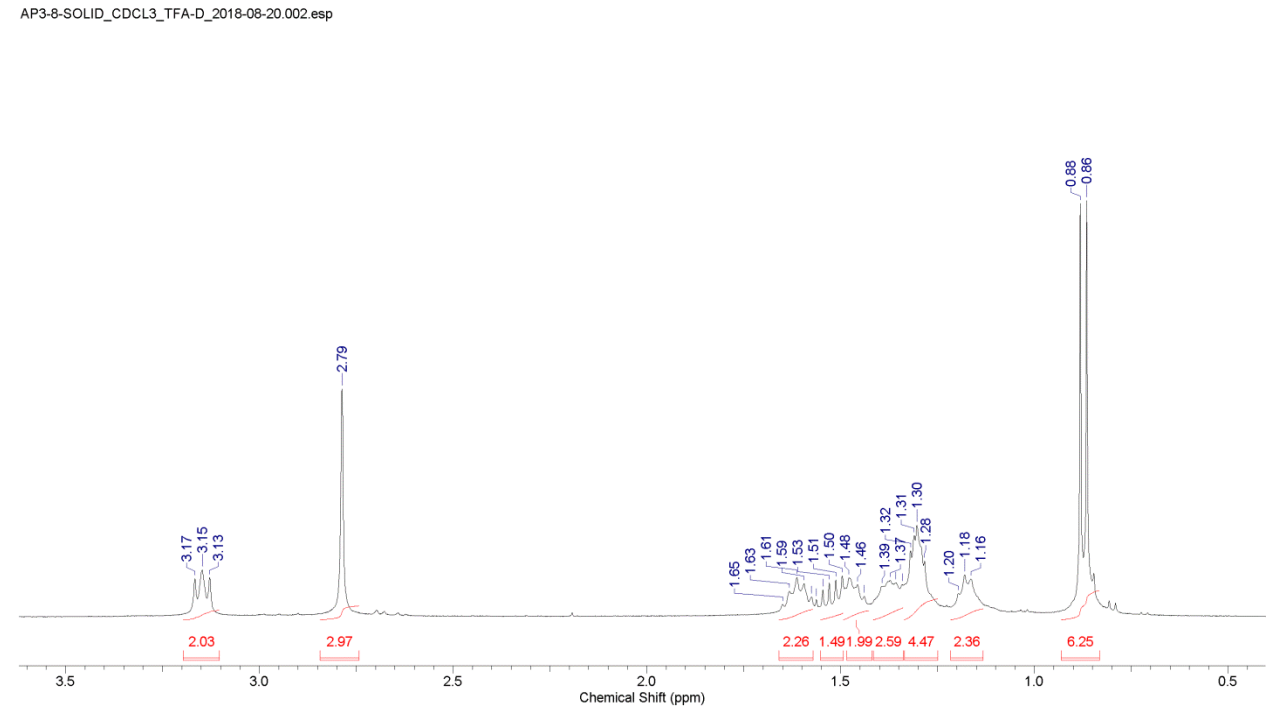
Zoomed ^{1}H NMR of **2** in 1% $CF_3CO_2D/CDCl_3$



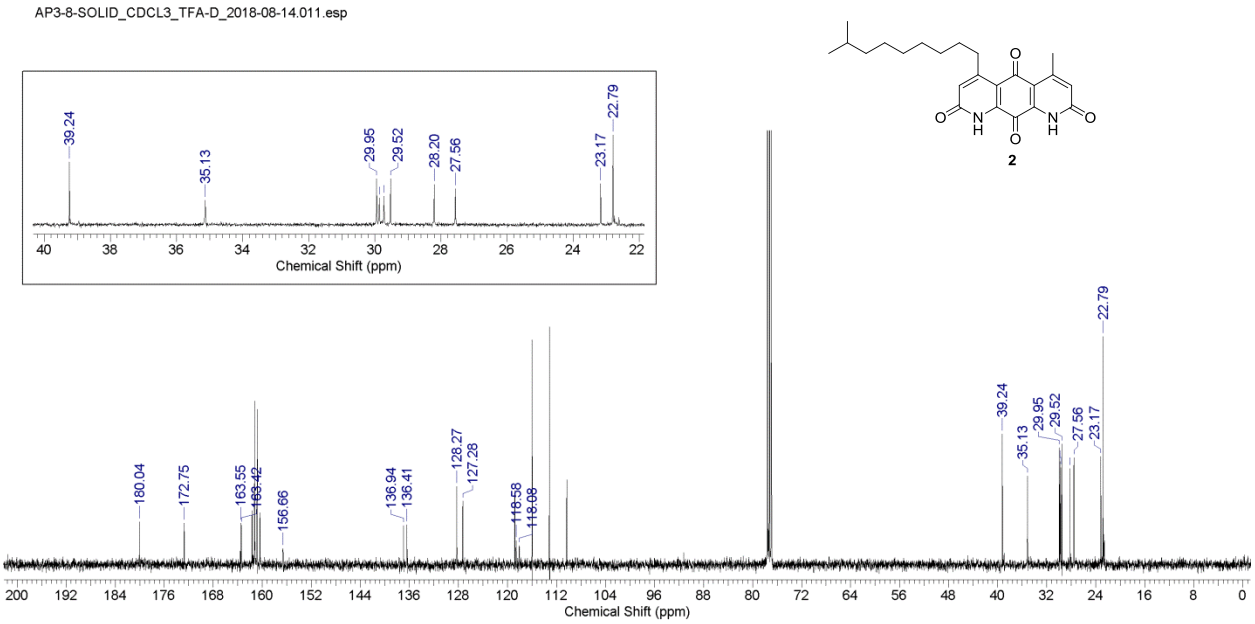
^{1}H NMR of **2** in 2% $CF_3CO_2D/CDCl_3$



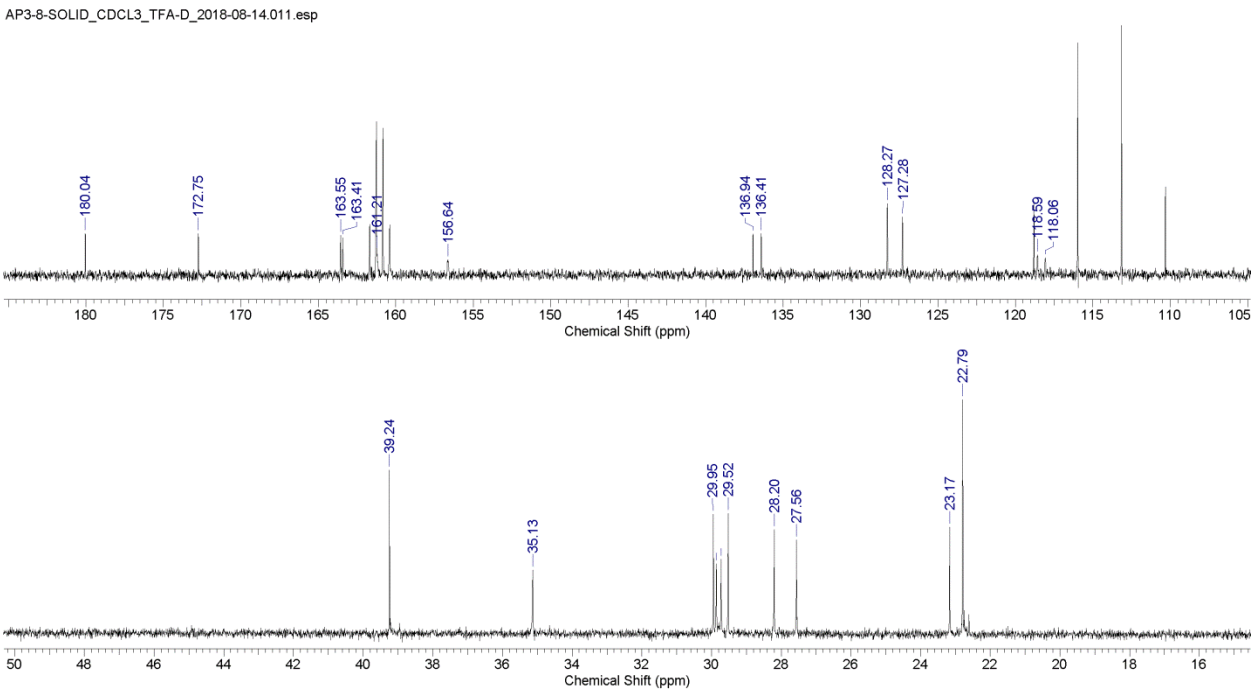
Zoomed ^{1}H NMR of **2** in 2% $CF_3CO_2D/CDCl_3$



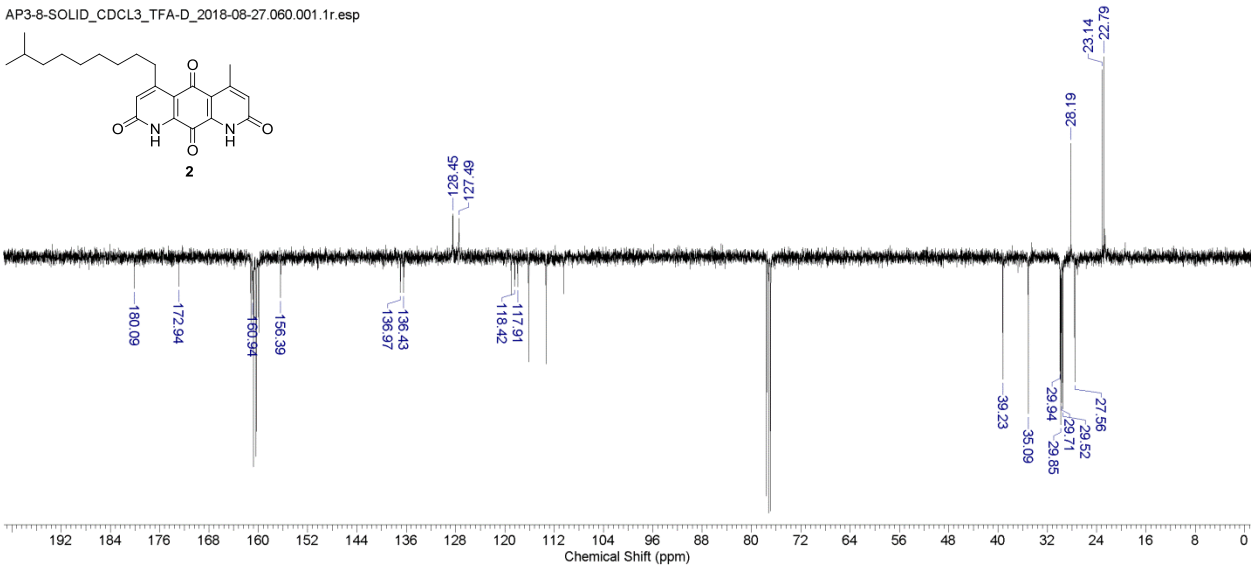
^{13}C NMR of **2** in 2% $CF_3CO_2D/CDCl_3$



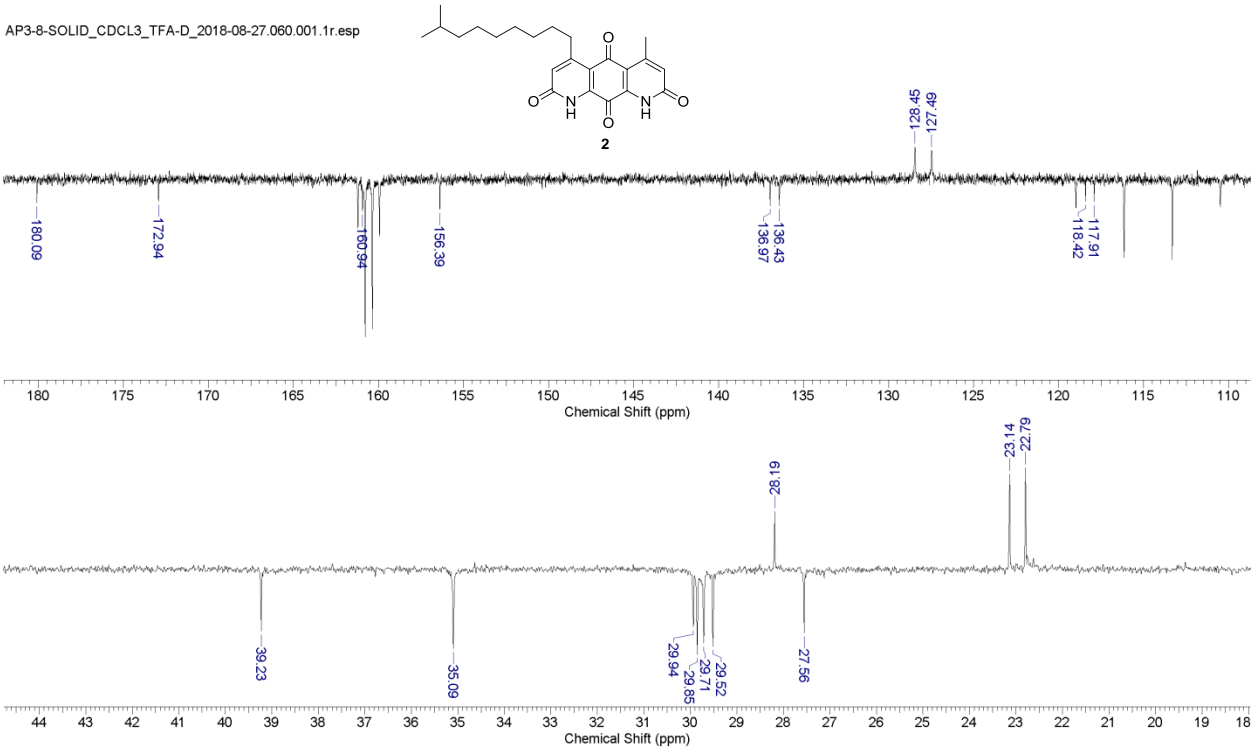
Zoomed ^{13}C NMR regions of **2** in 2% $CF_3CO_2D/CDCl_3$



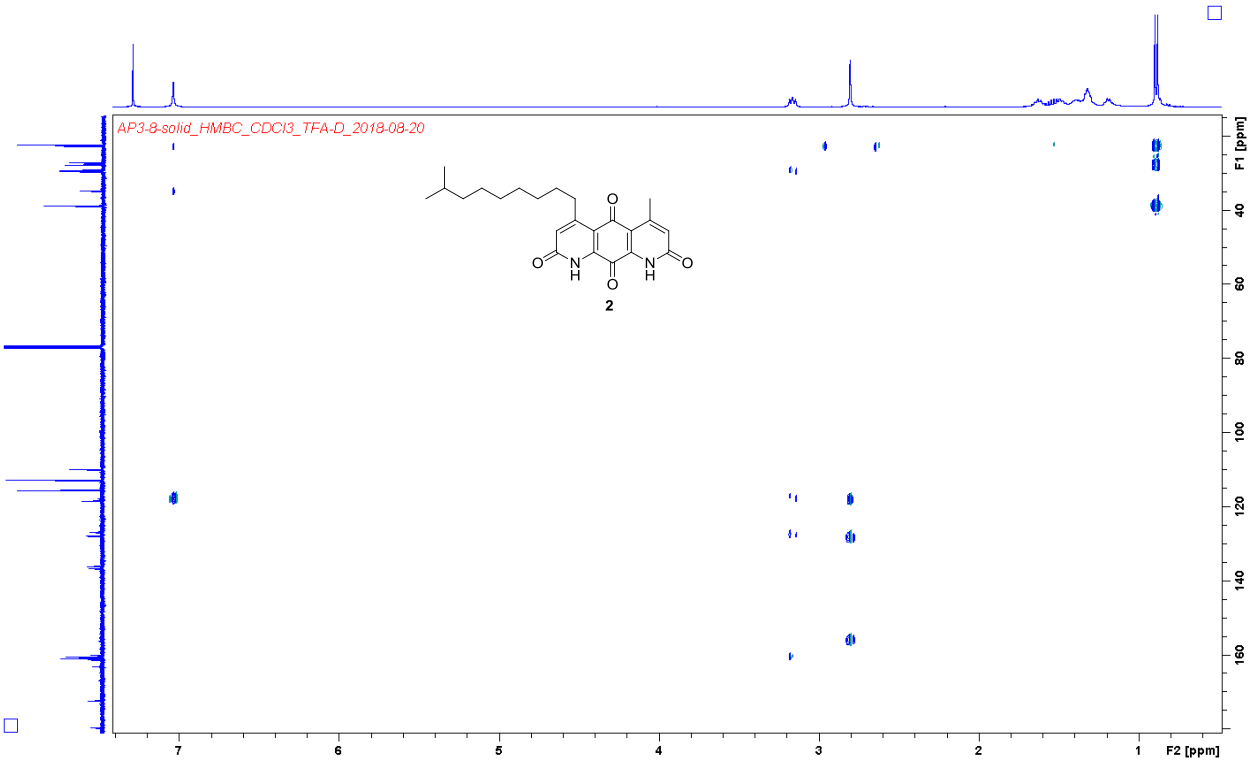
DEPTQ of **2** in 2% $CF_3CO_2D/CDCl_3$



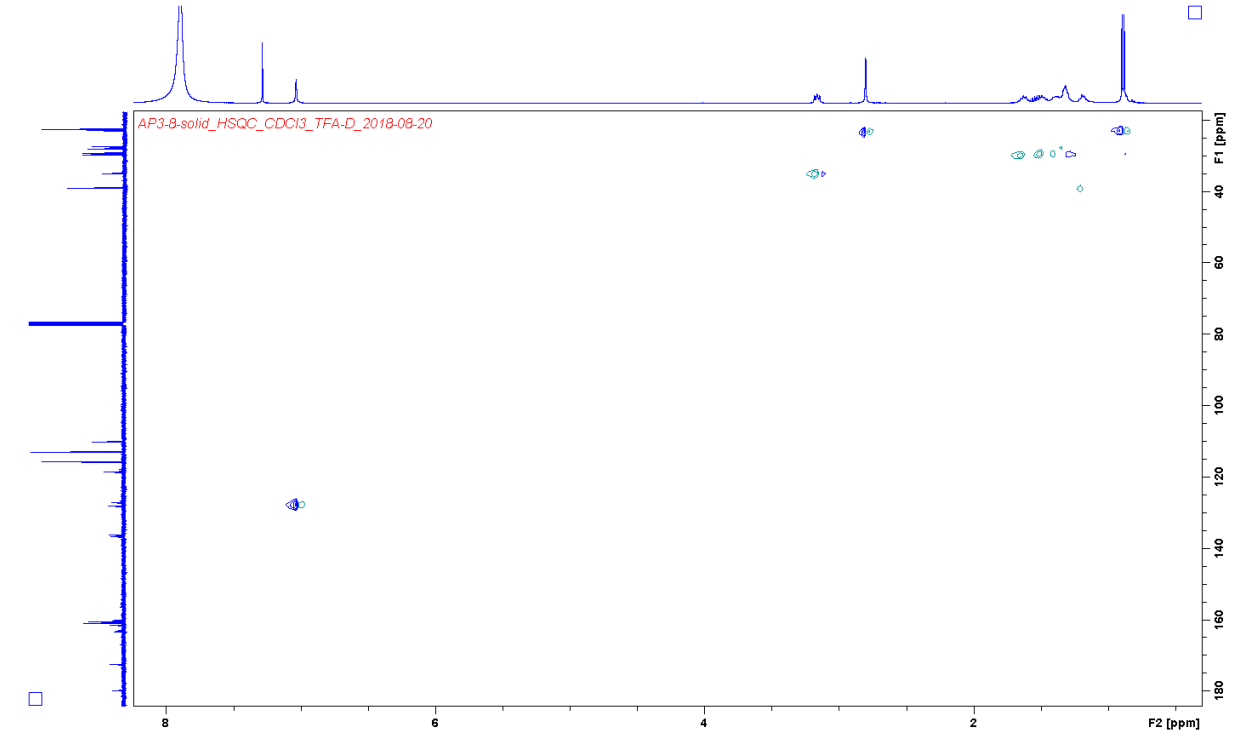
Zoomed DEPTQ regions of **2** in 2% $CF_3CO_2D/CDCl_3$



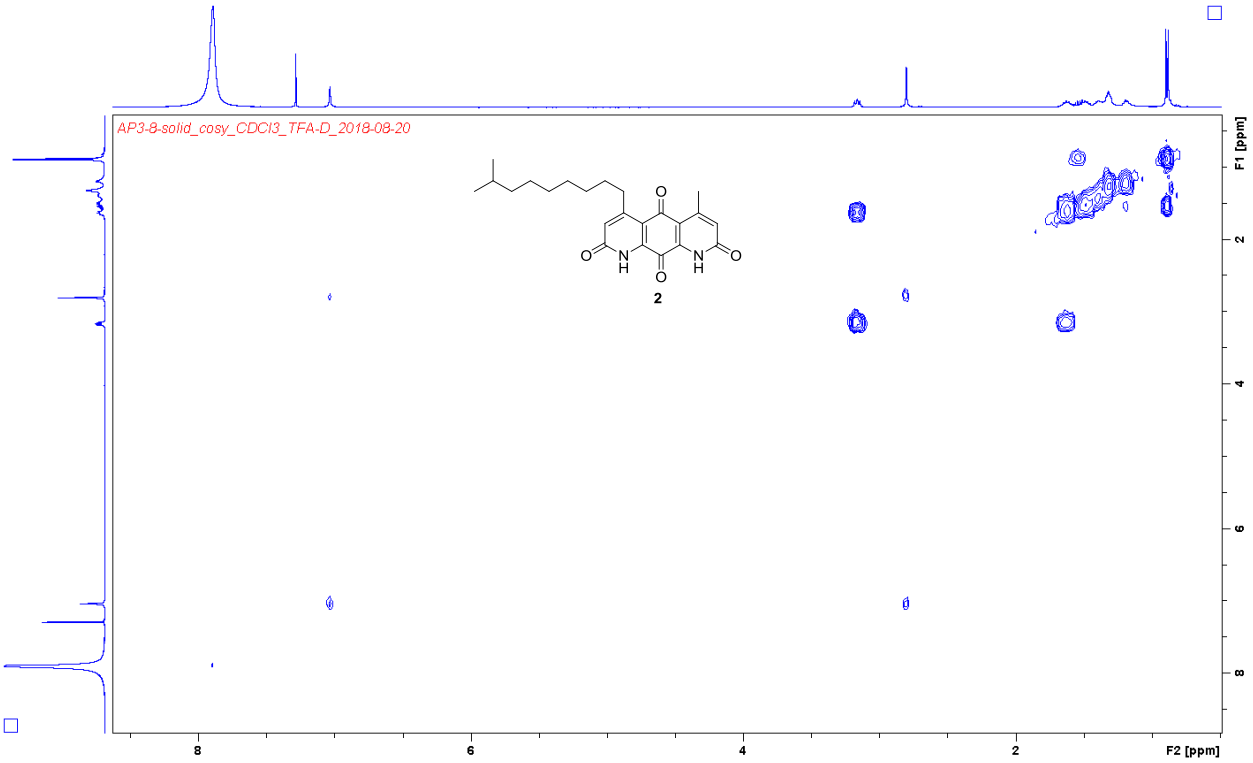
HMBC of **2** in 2% $CF_3CO_2D/CDCl_3$



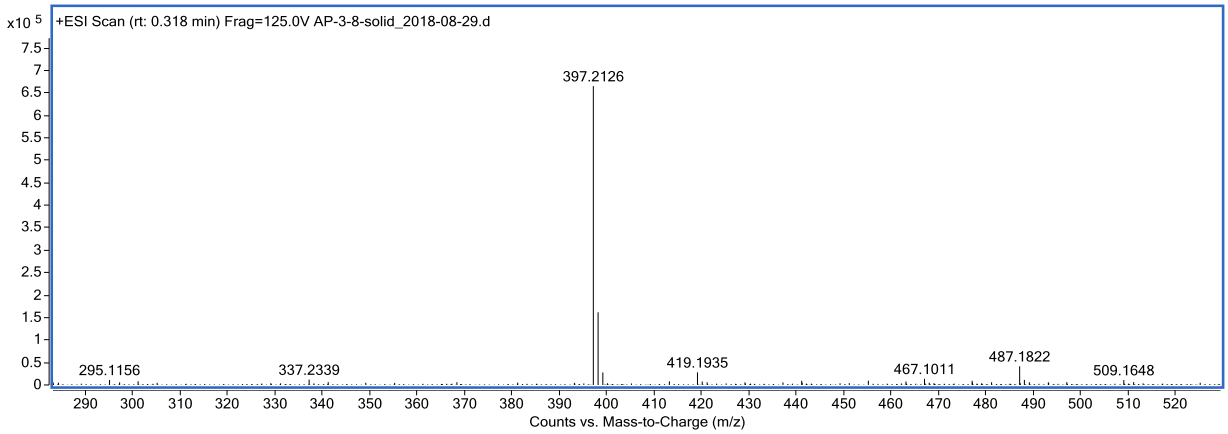
HSQC of **2** in 2% $CF_3CO_2D/CDCl_3$



COSY of **2** in 2% $CF_3CO_2D/CDCl_3$



HRMS of **2**



HPLC chromatogram of **2**

==== Shimadzu LCsolution Analysis Report ====

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Injection Volume	: 10 uL
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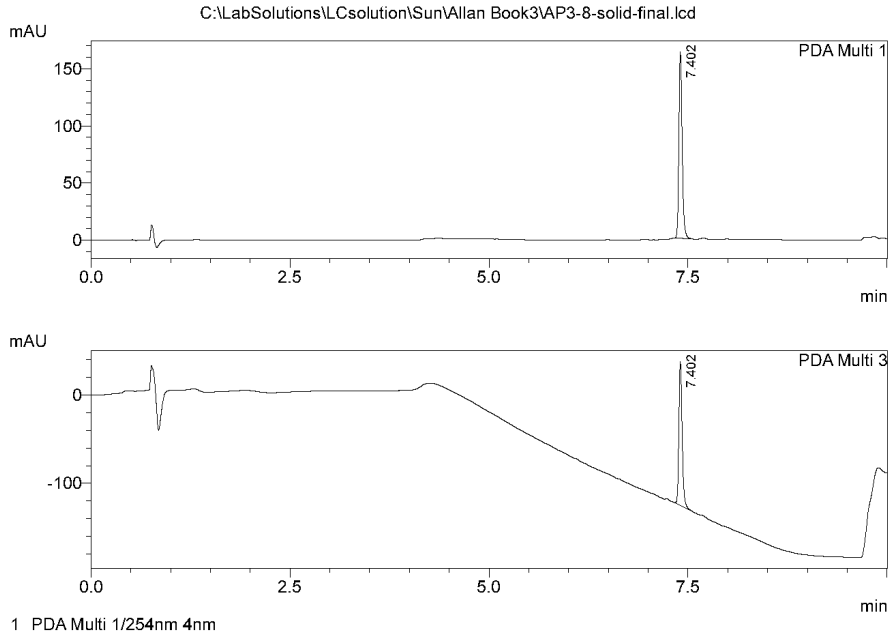


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

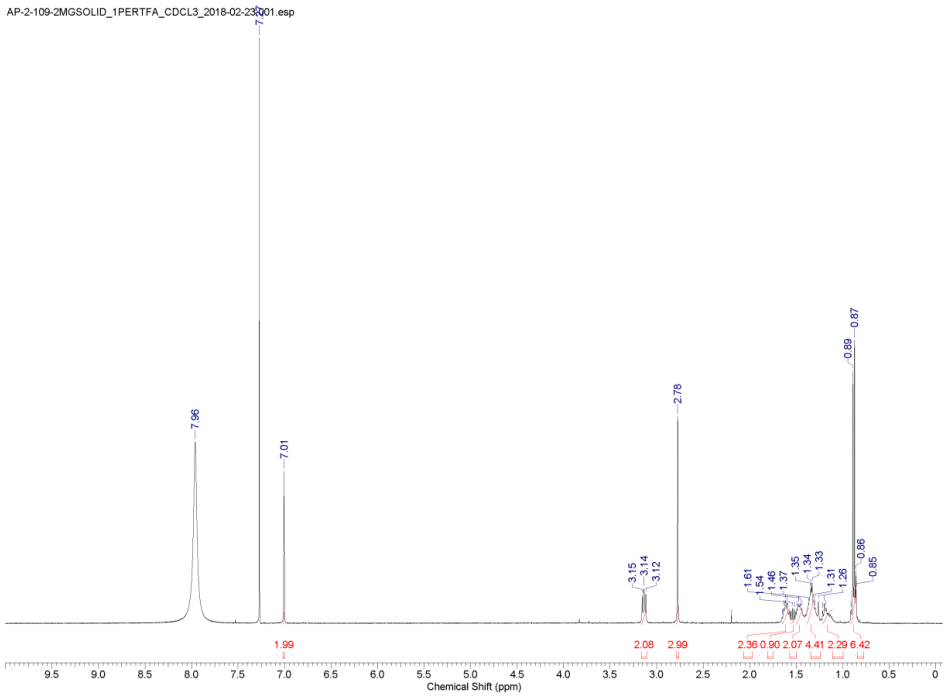
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.402	460879	160511	100.000	100.000
Total		460879	160511	100.000	100.000

PeakTable

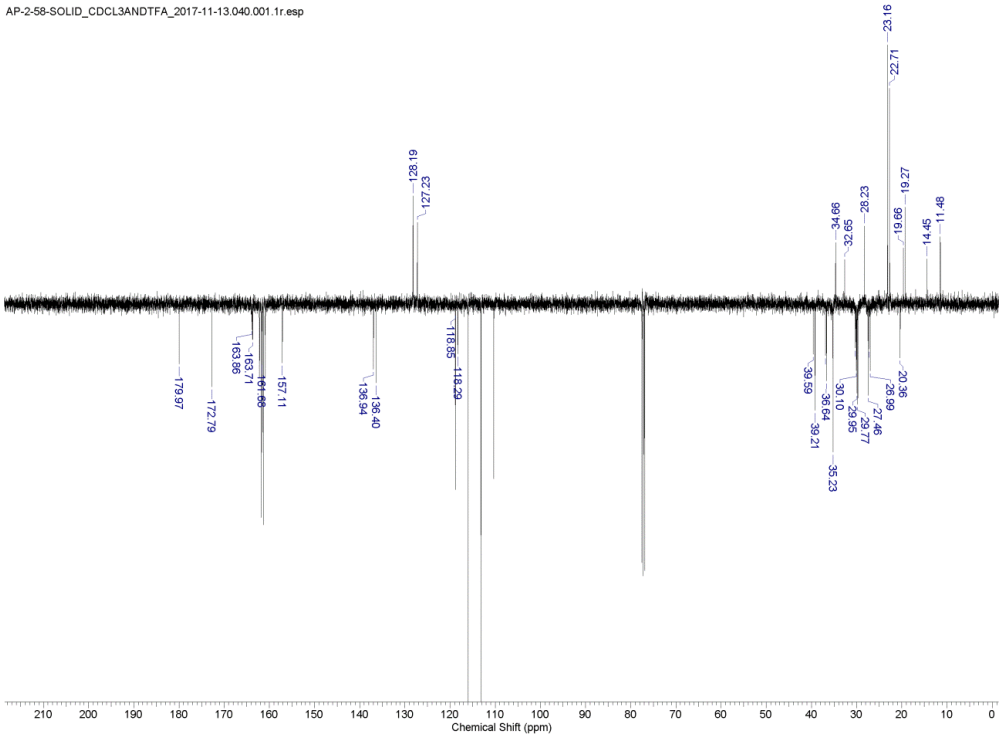
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.402	456057	162479	100.000	100.000
Total		456057	162479	100.000	100.000

^{1}H NMR of isomeric mixture of **1** in 1% $CF_3CO_2D/CDCl_3$



DEPTQ of isomeric mixture of **1** in 2% $CF_3CO_2D/CDCl_3$



HPLC chromatogram of isomeric mixture of **1**

==== Shimadzu LCsolution Analysis Report ====

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Vail #	: 29
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Batch File Name	:
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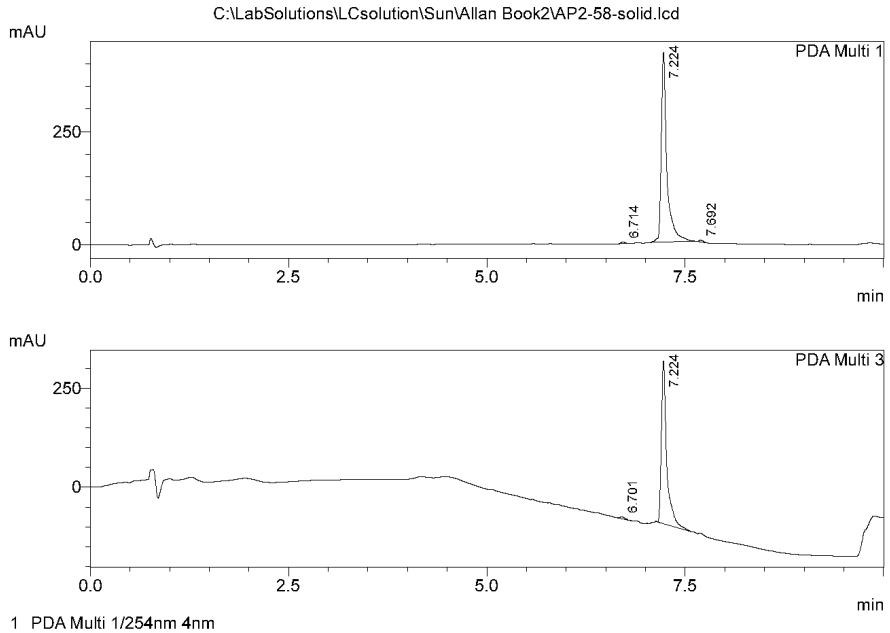


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

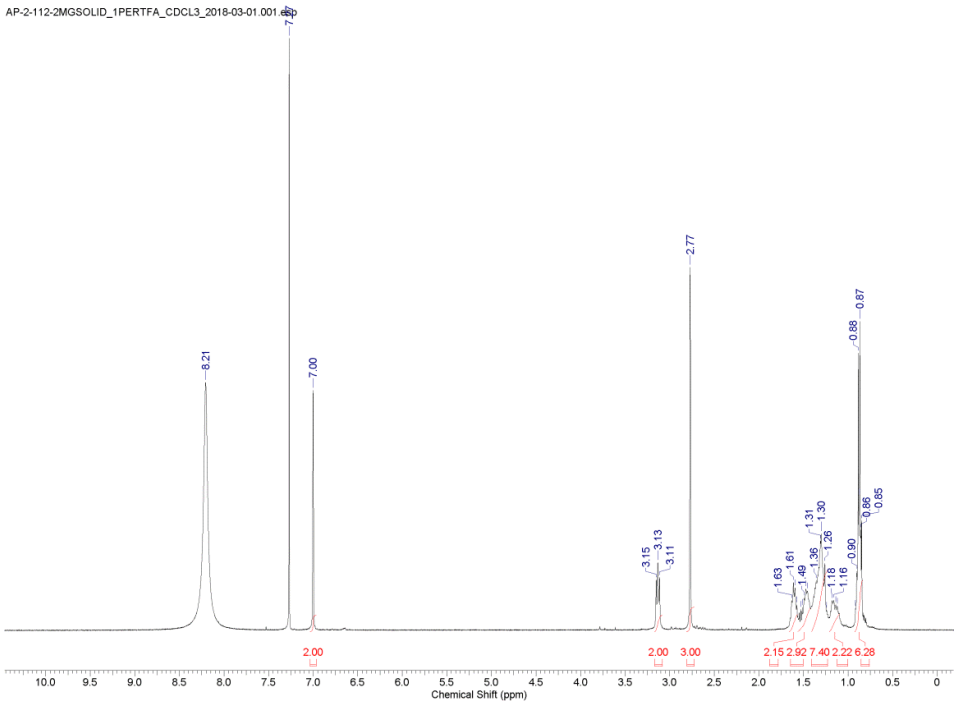
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.714	14341	3874	0.687	0.922
2	7.224	2060504	412745	98.726	98.239
3	7.692	12257	3526	0.587	0.839
Total		2087102	420145	100.000	100.000

PeakTable

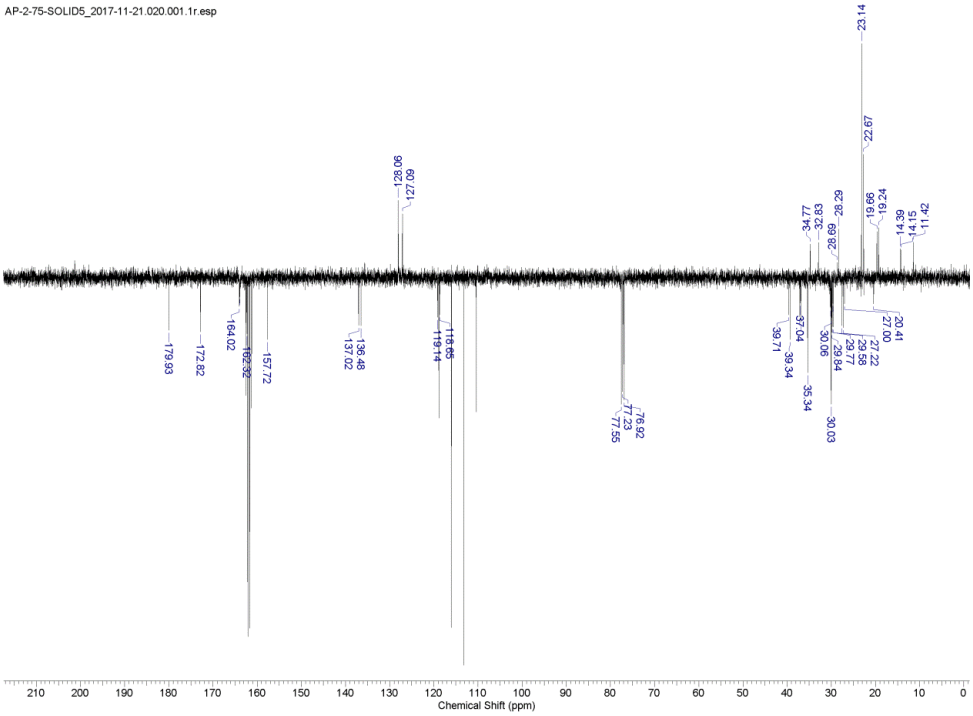
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.701	19557	4926	1.011	1.189
2	7.224	1915543	409538	98.989	98.811
Total		1935099	414464	100.000	100.000

^{1}H NMR of isomeric mixture of **2** in 1% $CF_3CO_2D/CDCl_3$



DEPTQ of isomeric mixture of **2** in 2% $CF_3CO_2D/CDCl_3$



HPLC chromatogram of isomeric mixture of **2**

==== Shimadzu LCsolution Analysis Report ====

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Vail #	: 5
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Method File Name	: SDQ gradient.lcm
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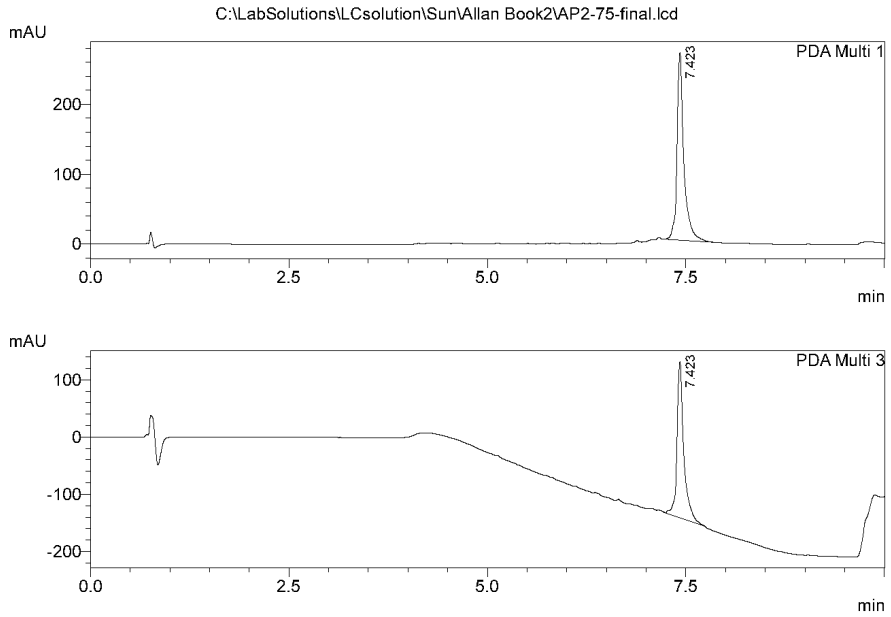


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

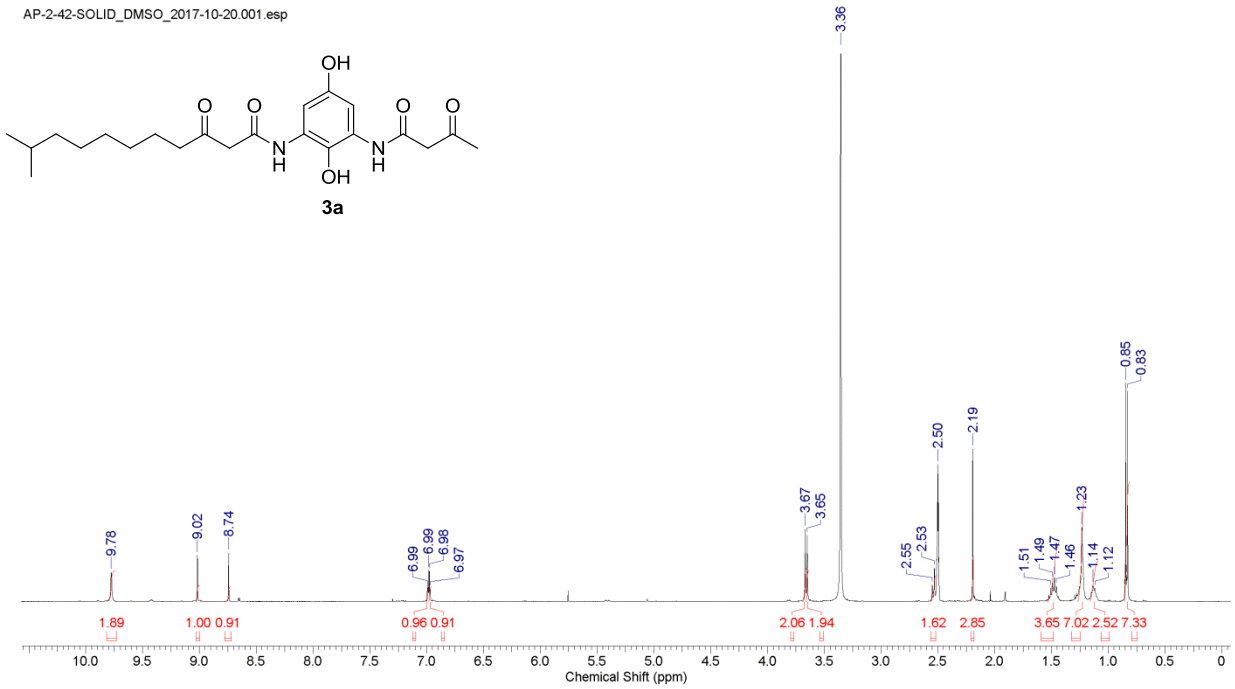
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.423	1605067	266756	100.000	100.000
Total		1605067	266756	100.000	100.000

PeakTable

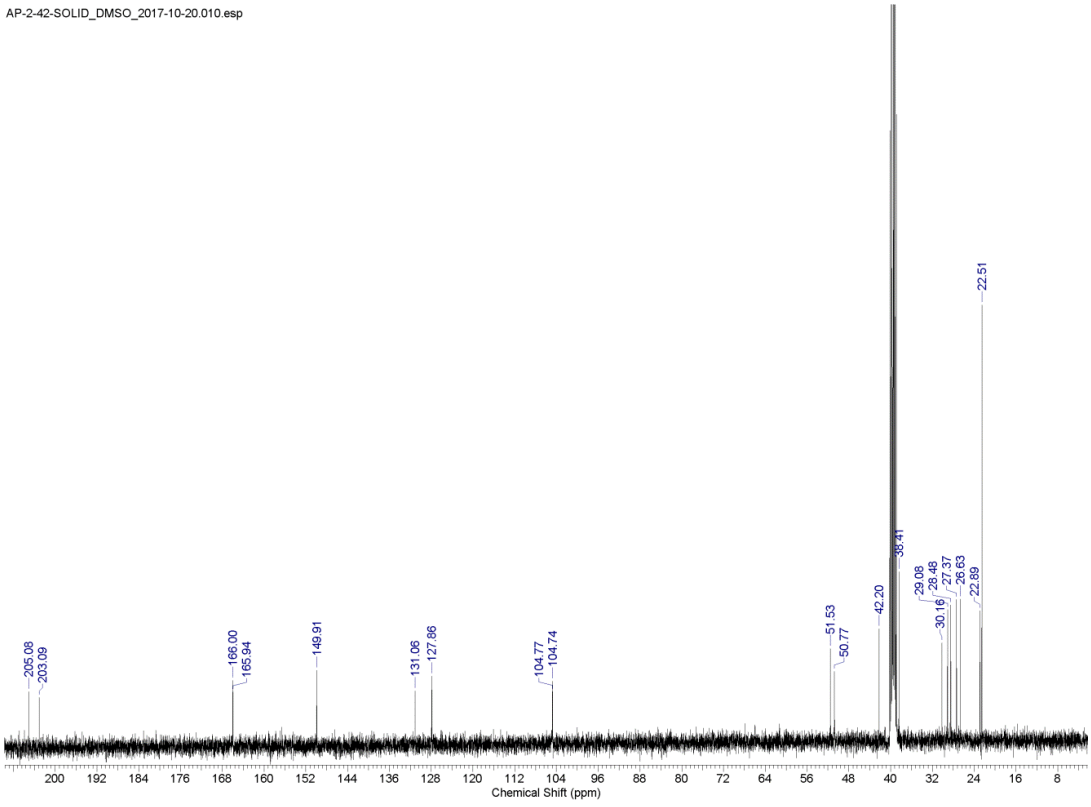
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.423	1610373	272185	100.000	100.000
Total		1610373	272185	100.000	100.000

^{1}H NMR of **3a** in DMSO-d_6



^{13}C NMR of **3a** in DMSO-d_6



HPLC chromatogram of **3a**

==== Shimadzu LCsolution Analysis Report ====

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Vail #	: 5
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Method File Name	: SDQ gradient.lcm
Batch File Name	:
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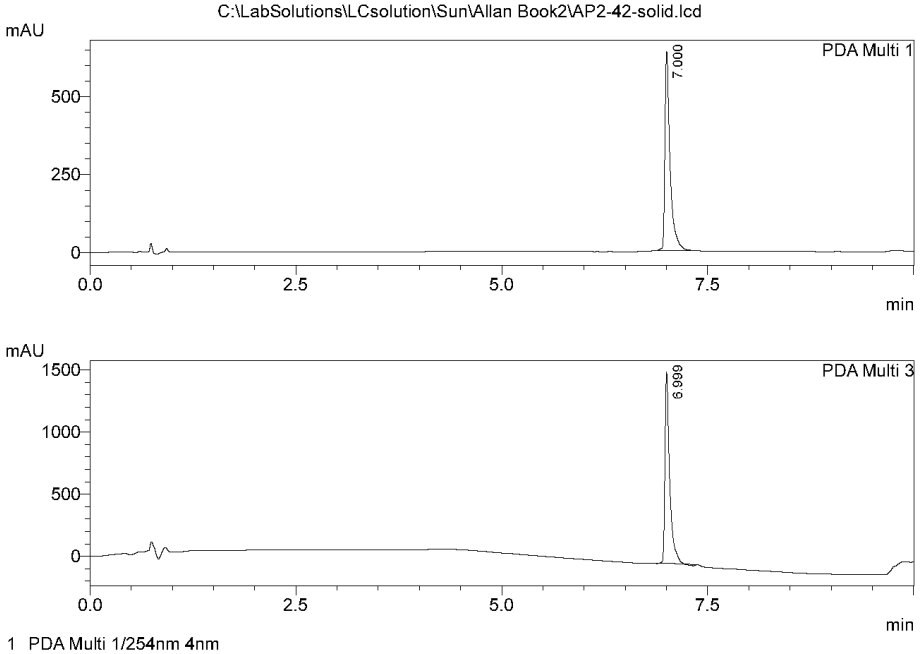


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

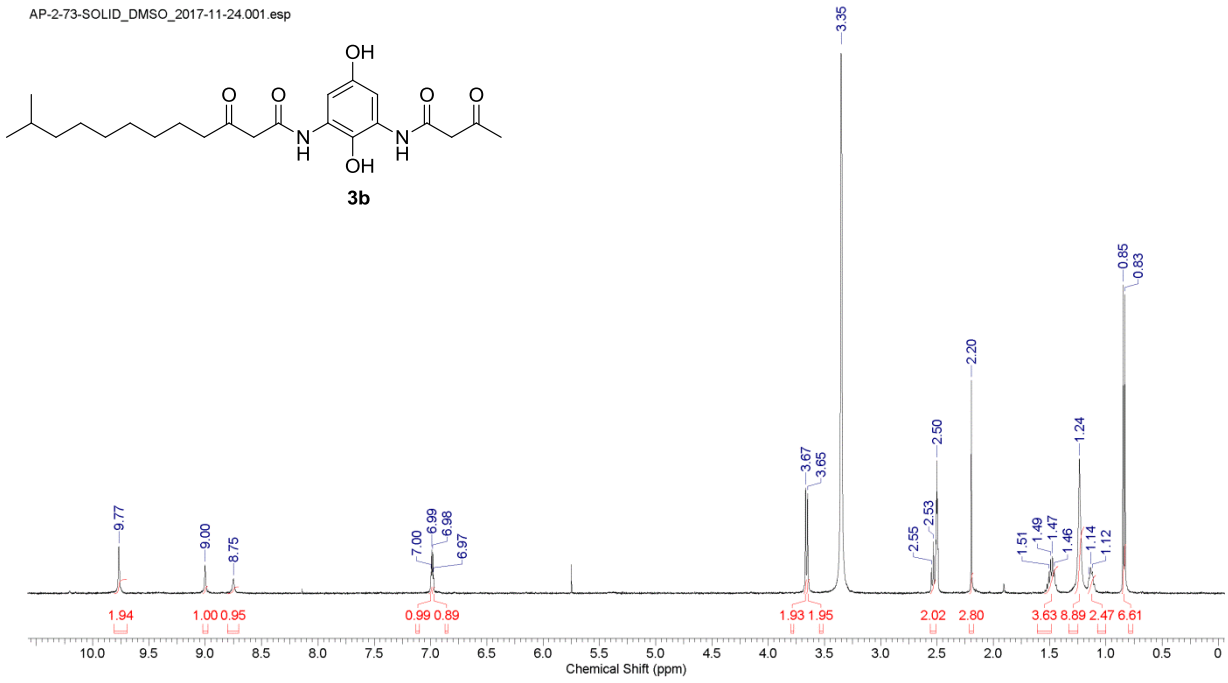
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.000	2764659	627841	100.000	100.000
Total		2764659	627841	100.000	100.000

PeakTable

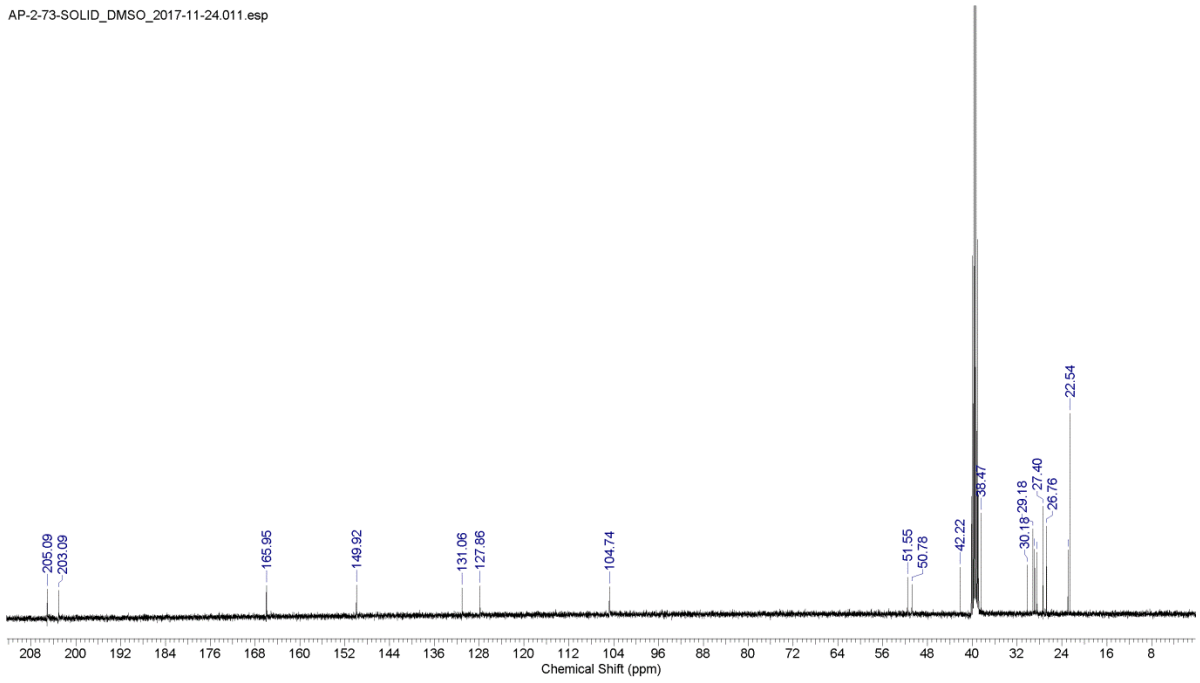
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.999	5979700	1537220	100.000	100.000
Total		5979700	1537220	100.000	100.000

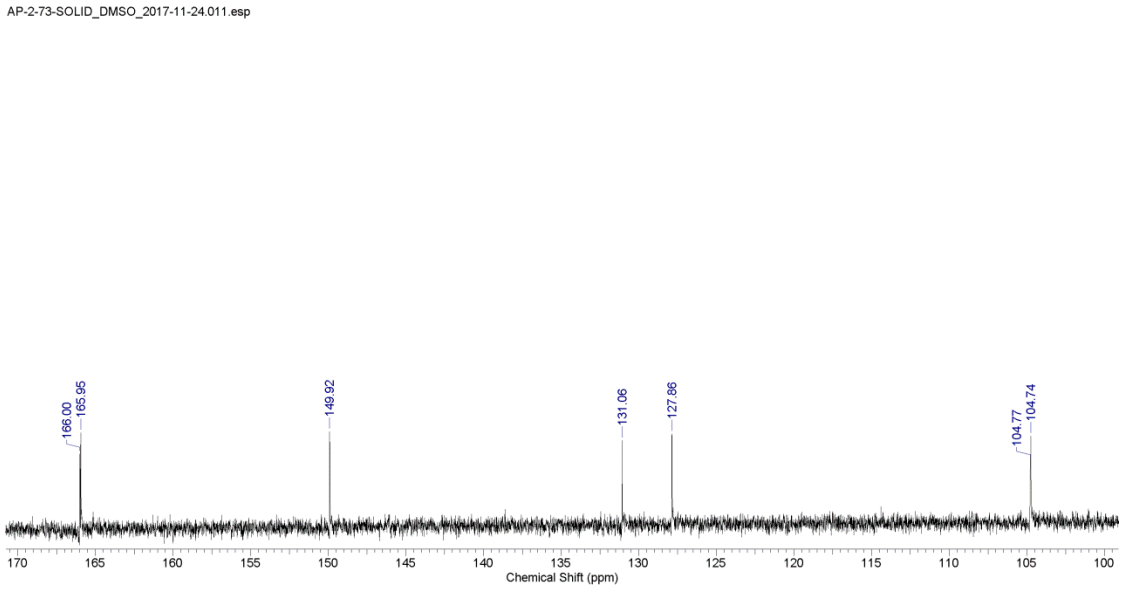
^{1}H NMR of **3b** in DMSO-d_6



^{13}C NMR of **3b** in DMSO-d_6



Zoomed ^{13}C NMR region of **3b** in DMSO-d_6



HPLC chromatogram of **3b**

==== Shimadzu LCsolution Analysis Report ====

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Vail #	: **4**
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Method File Name	: SDQ gradient.lcm
Batch File Name	:
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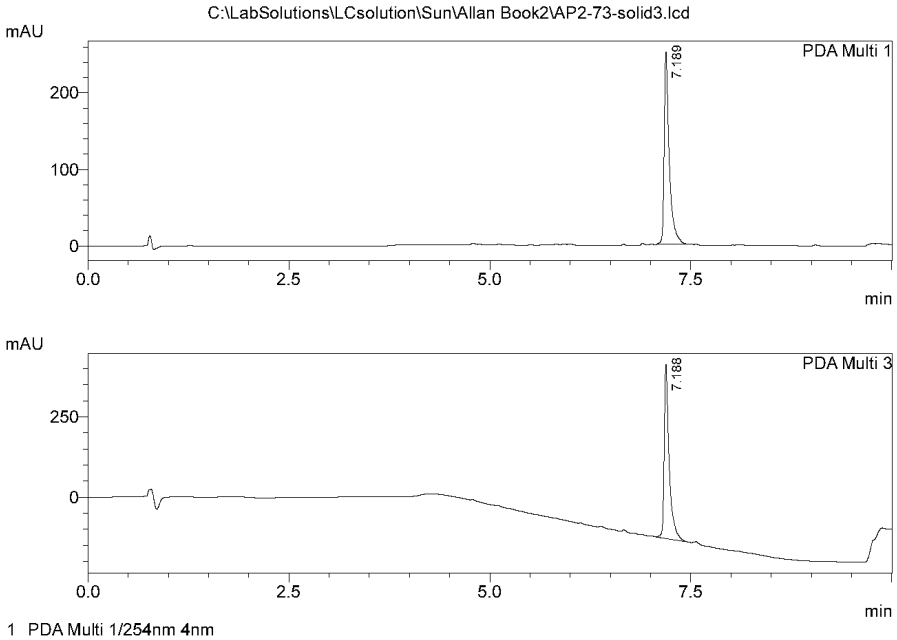


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

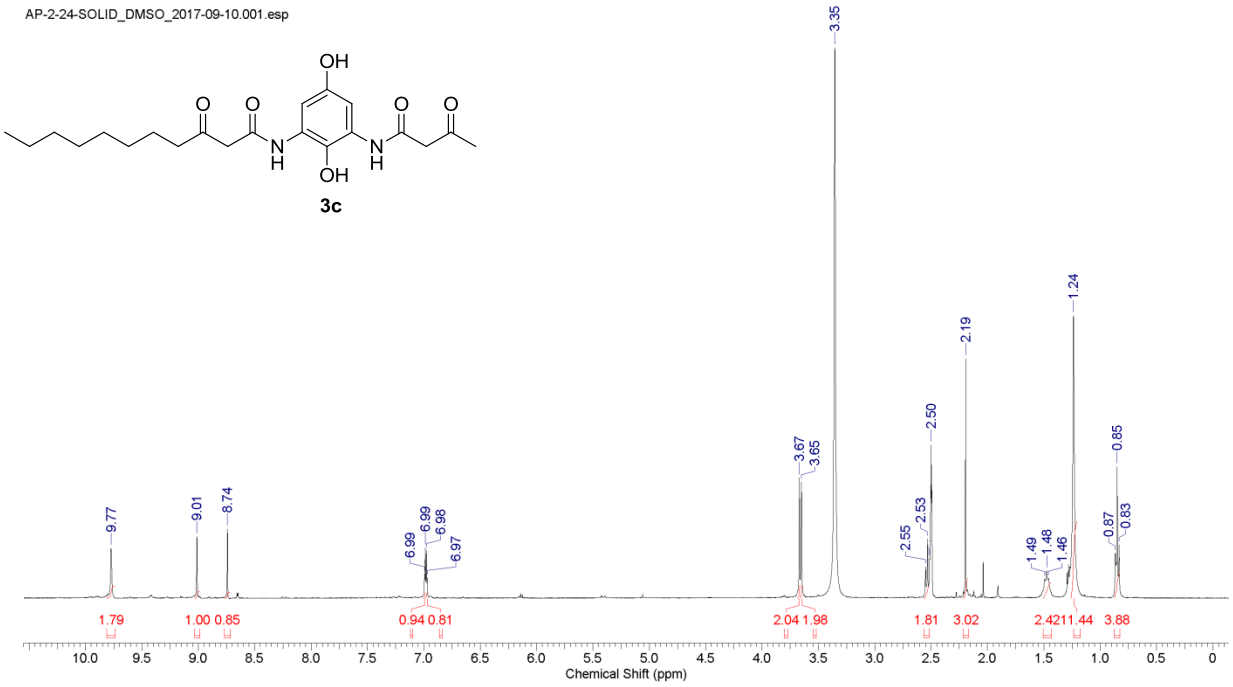
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.189	1093894	250366	100.000	100.000
Total		1093894	250366	100.000	100.000

PeakTable

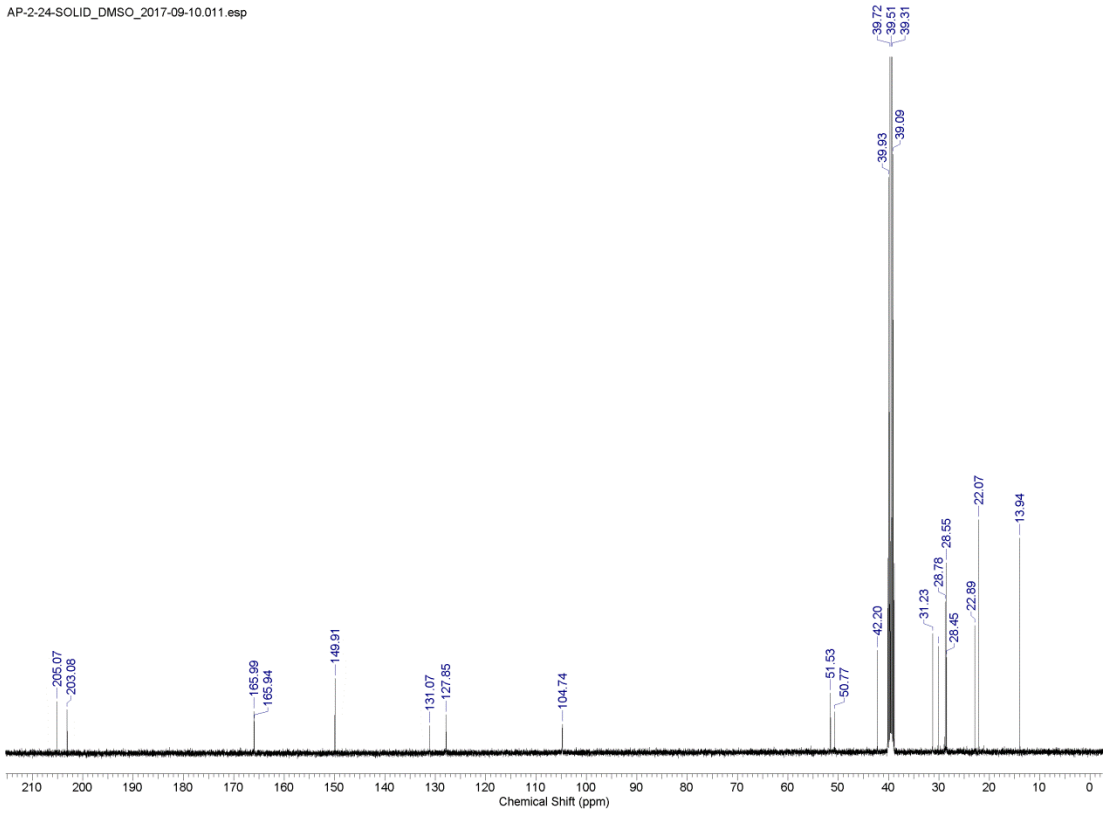
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.188	2309138	540481	100.000	100.000
Total		2309138	540481	100.000	100.000

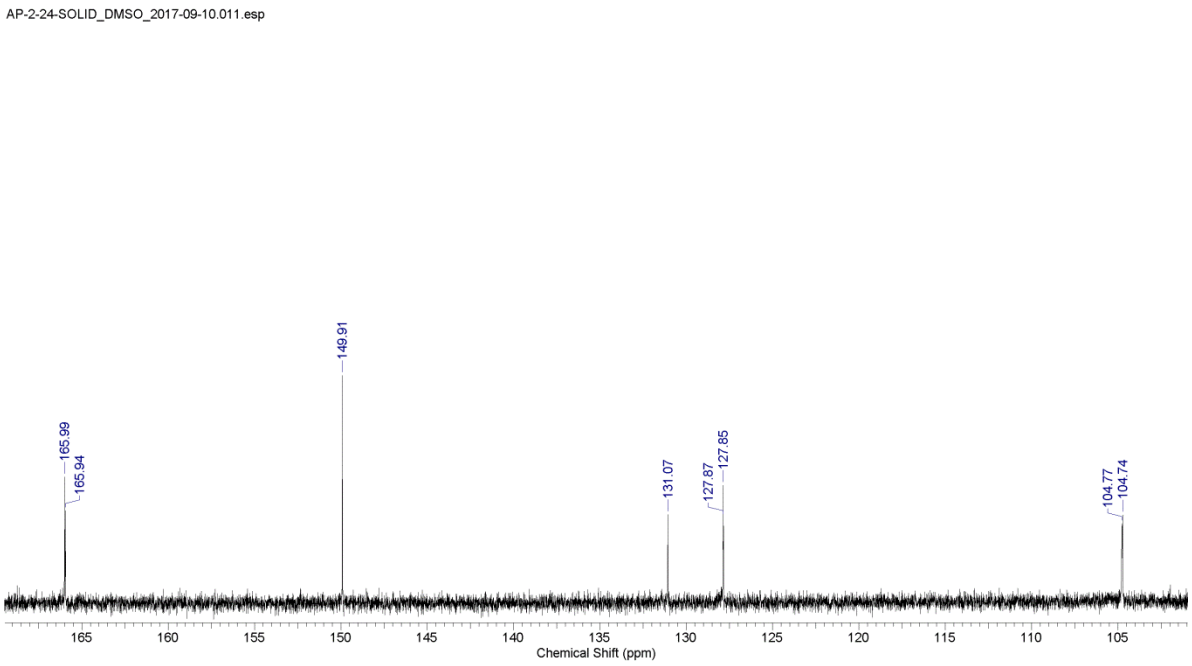
^{1}H NMR of **3c** in DMSO-d_6



^{13}C NMR of **3c** in DMSO-d_6



Zoomed ^{13}C NMR region of **3c** in DMSO-d_6



HPLC chromatogram of **3c**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-32-final
Tray#	: 1
Vail #	: 7
Injection Volume	: 10 uL
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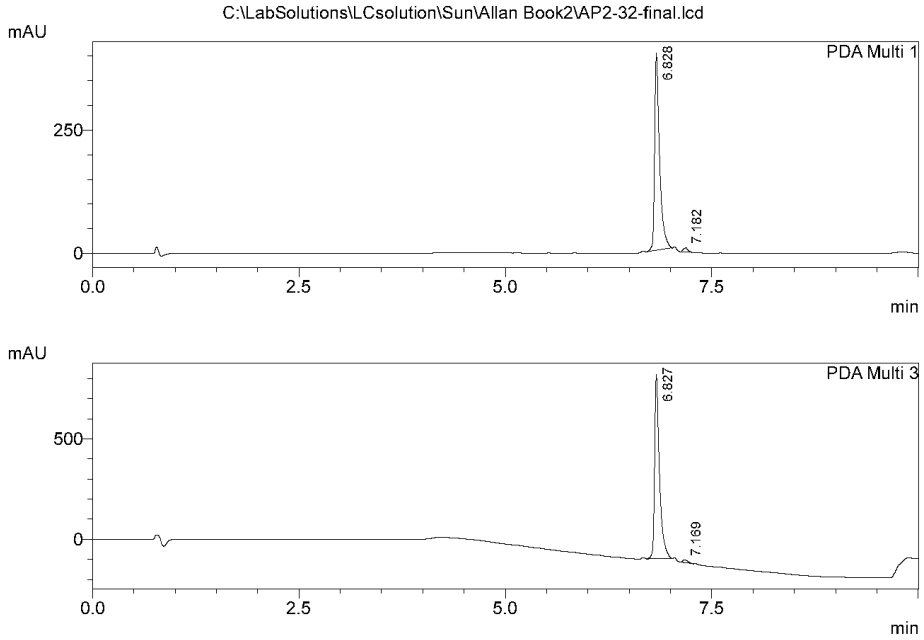


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

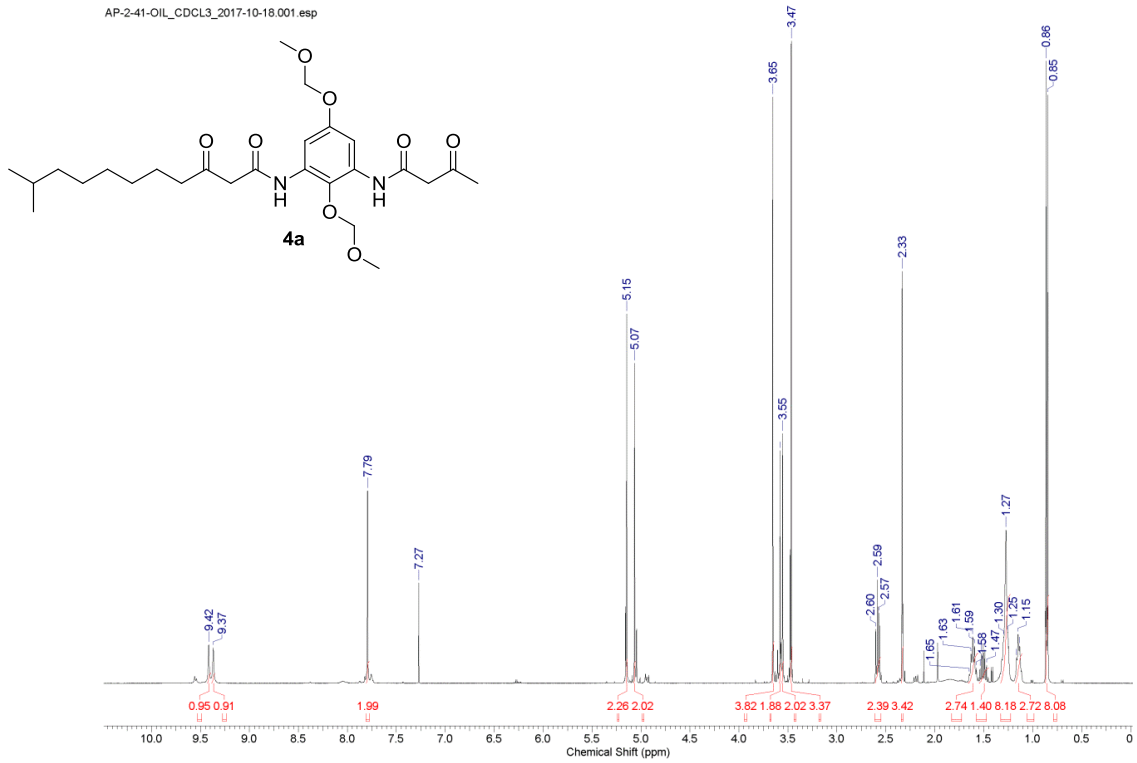
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.828	1674093	397679	98.300	97.997
2	7.182	28956	8128	1.700	2.003
Total		1703049	405807	100.000	100.000

PeakTable

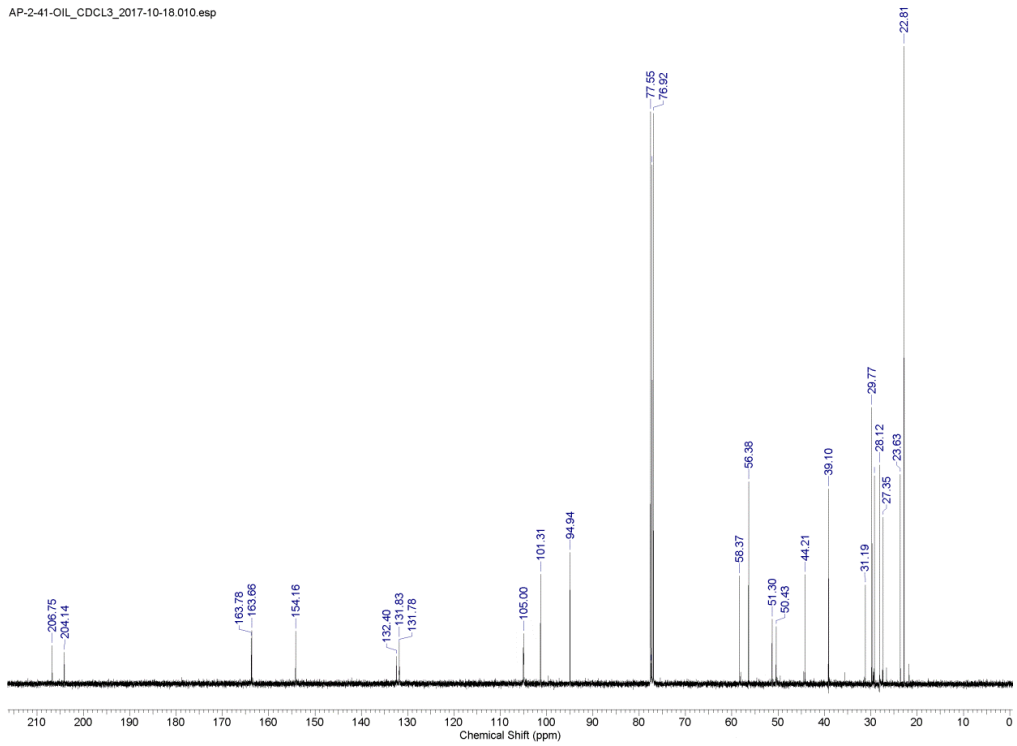
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.827	3727835	916367	98.538	98.634
2	7.169	55328	12695	1.462	1.366
Total		3783164	929062	100.000	100.000

^{1}H NMR of **4a** in $CDCl_3$



^{13}C NMR of **4a** in $CDCl_3$



HPLC chromatogram of **4a**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-41-final
Tray#	: 1
Vail #	: 2
Injection Volume	: 10 uL
Data File Name	: AP2-41-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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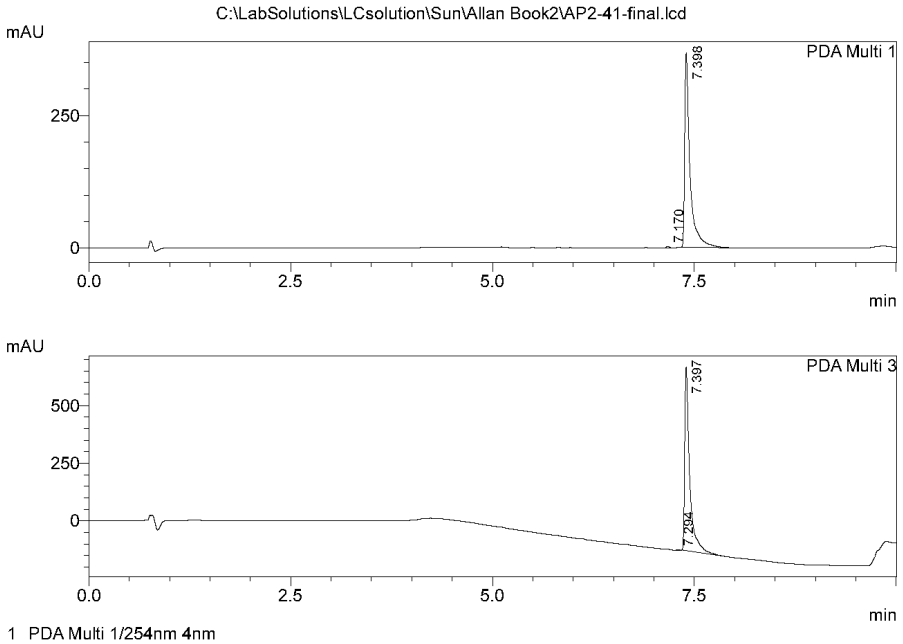


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

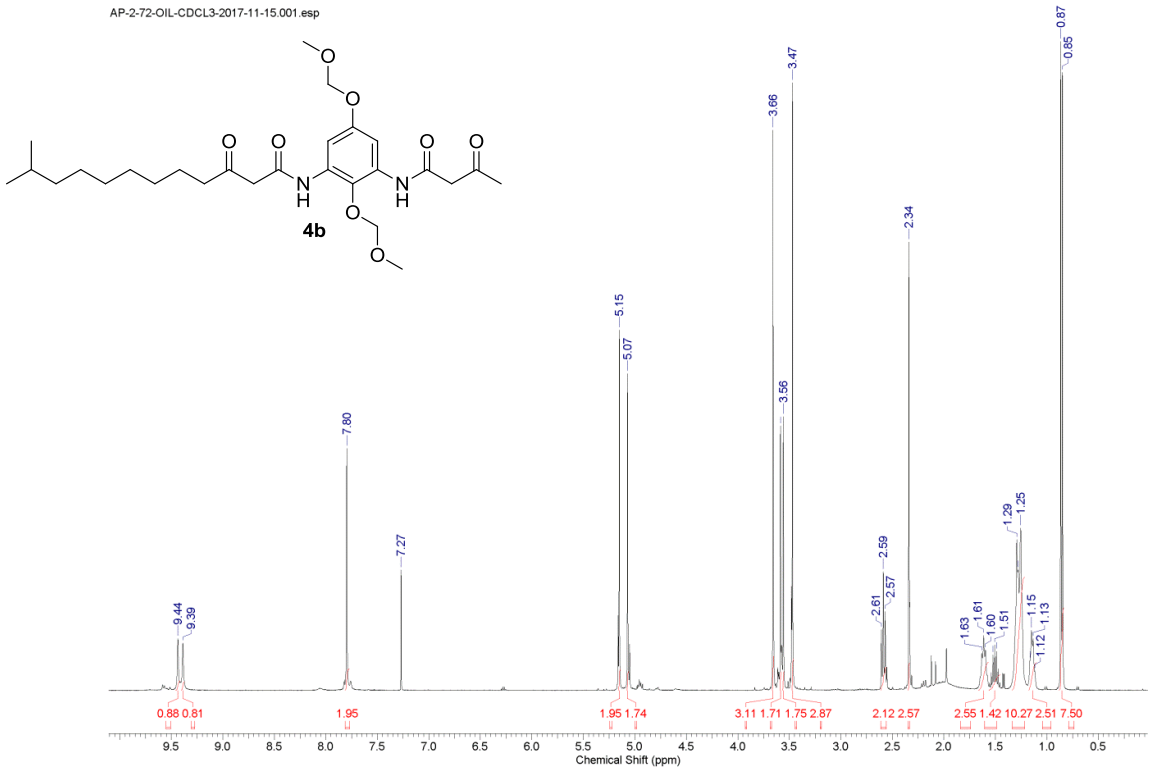
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.170	7066	2700	0.421	0.737
2	7.398	1670190	363779	99.579	99.263
Total		1677256	366479	100.000	100.000

PeakTable

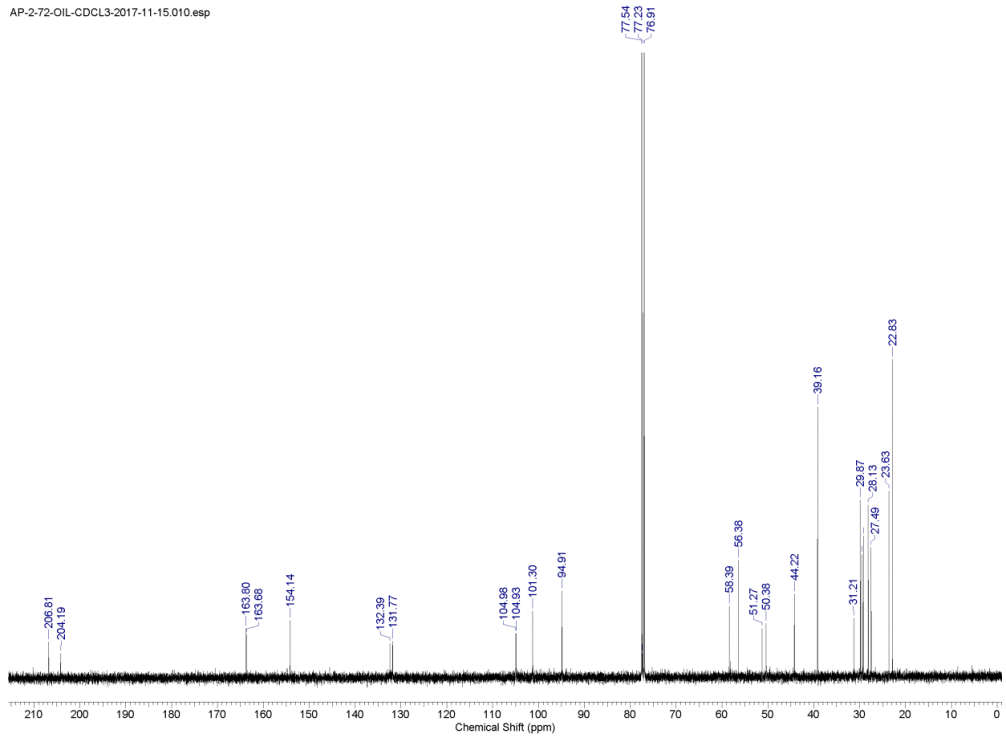
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.294	8244	3492	0.241	0.437
2	7.397	3405385	795190	99.759	99.563
Total		3413629	798682	100.000	100.000

^{1}H NMR of **4b** in $CDCl_3$



^{13}C NMR of **4b** in $CDCl_3$



HPLC chromatogram of **4b**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-72-final
Tray#	: 1
Vail #	: 3
Injection Volume	: 10 uL
Data File Name	: AP2-72-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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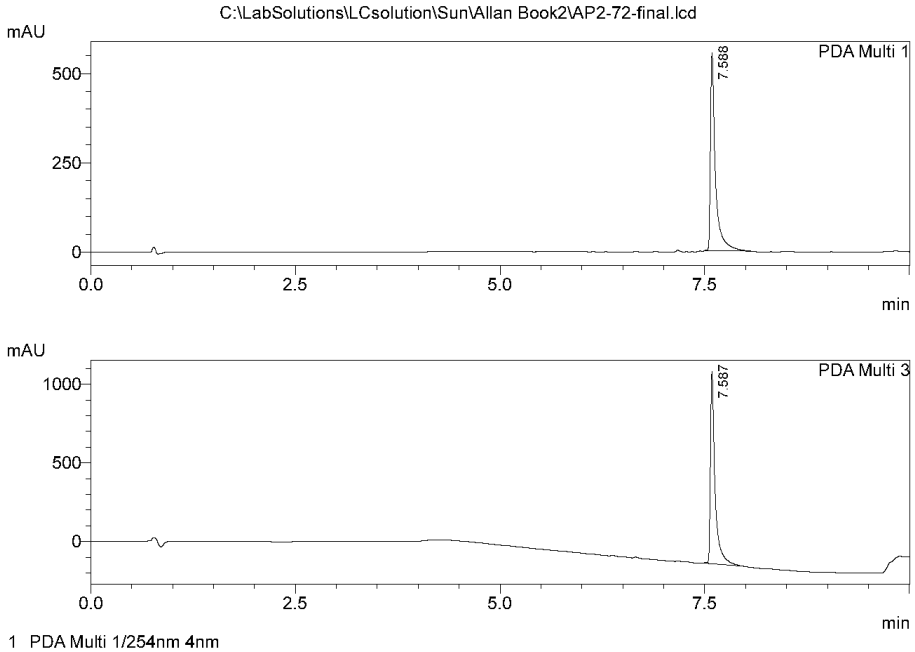


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

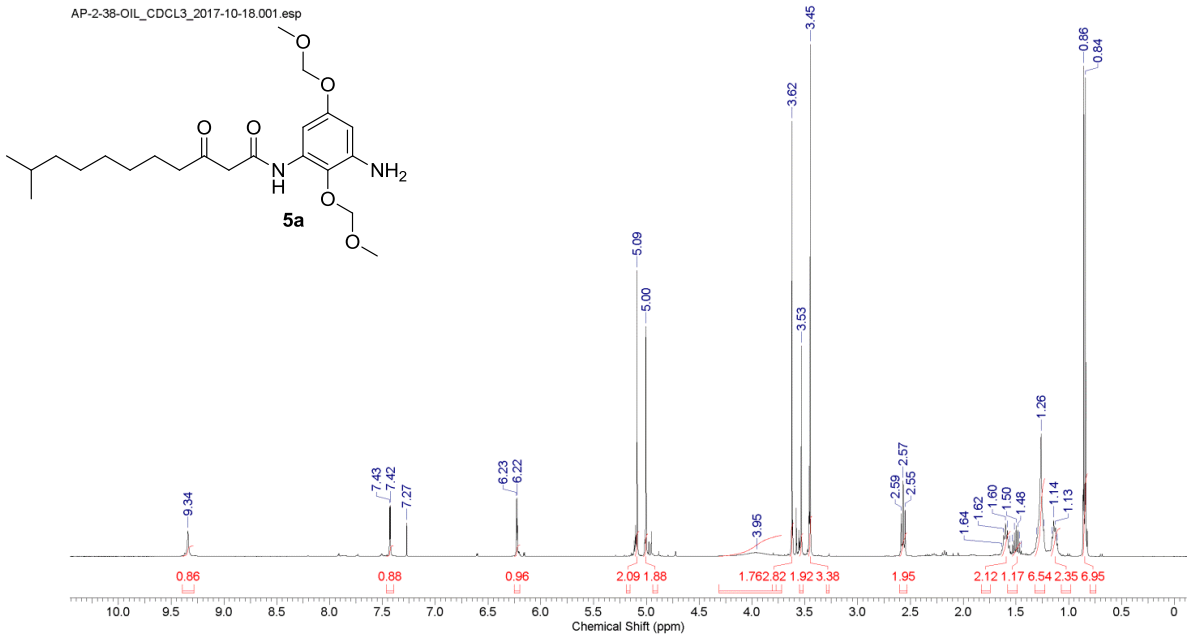
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.588	2348682	552430	100.000	100.000
Total		2348682	552430	100.000	100.000

PeakTable

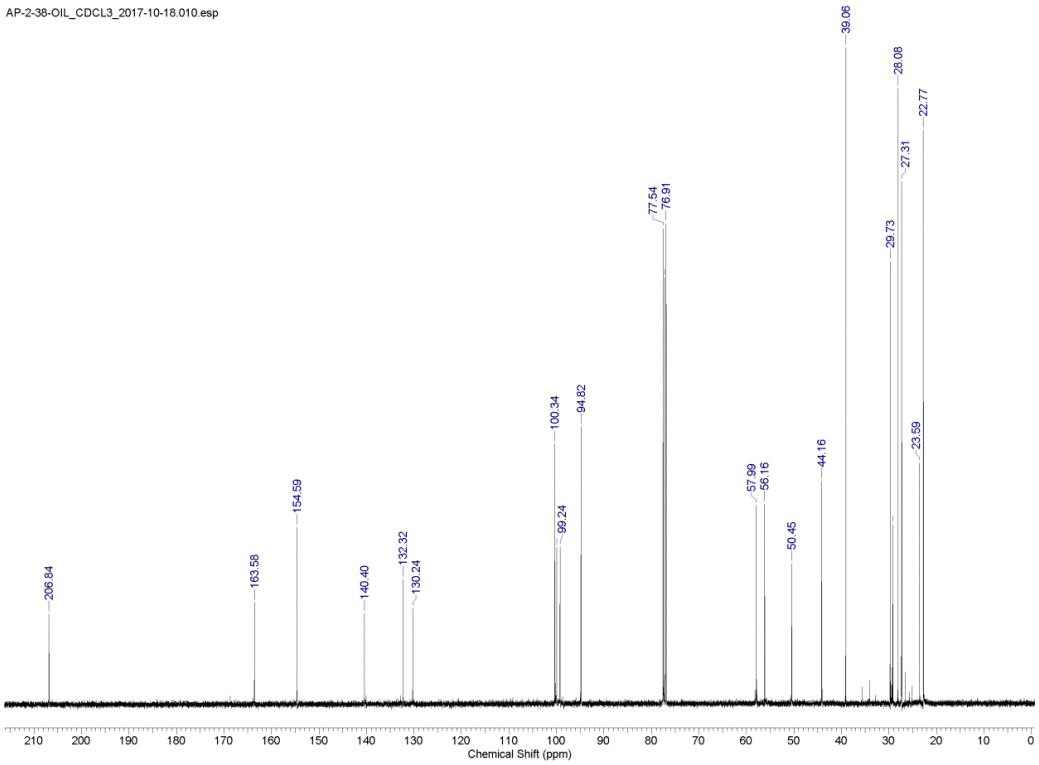
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.587	4775447	1222038	100.000	100.000
Total		4775447	1222038	100.000	100.000

^{1}H NMR of **5a** in $CDCl_3$



^{13}C NMR of **5a** in $CDCl_3$



HPLC chromatogram of **5a**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-38-final
Tray#	: 1
Vail #	: 2
Injection Volume	: 10 uL
Data File Name	: AP2-38-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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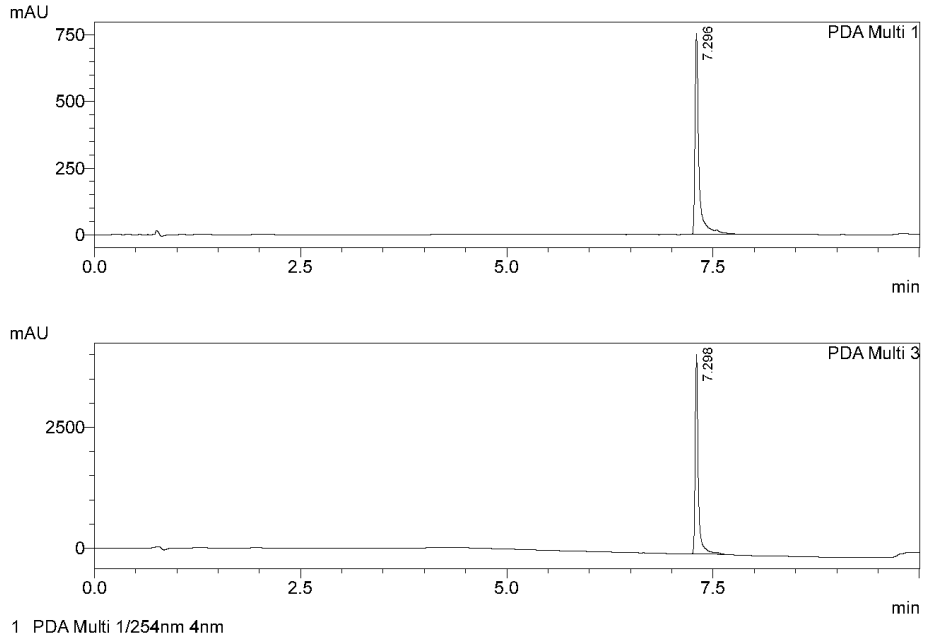


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

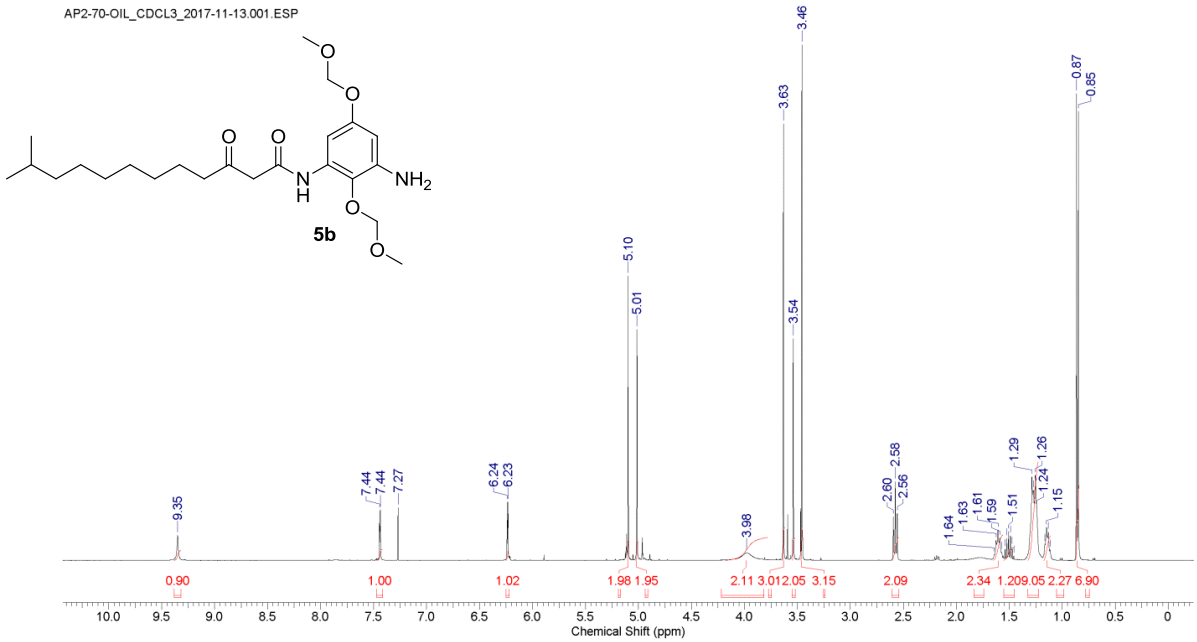
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.296	2485159	730190	100.000	100.000
Total		2485159	730190	100.000	100.000

PeakTable

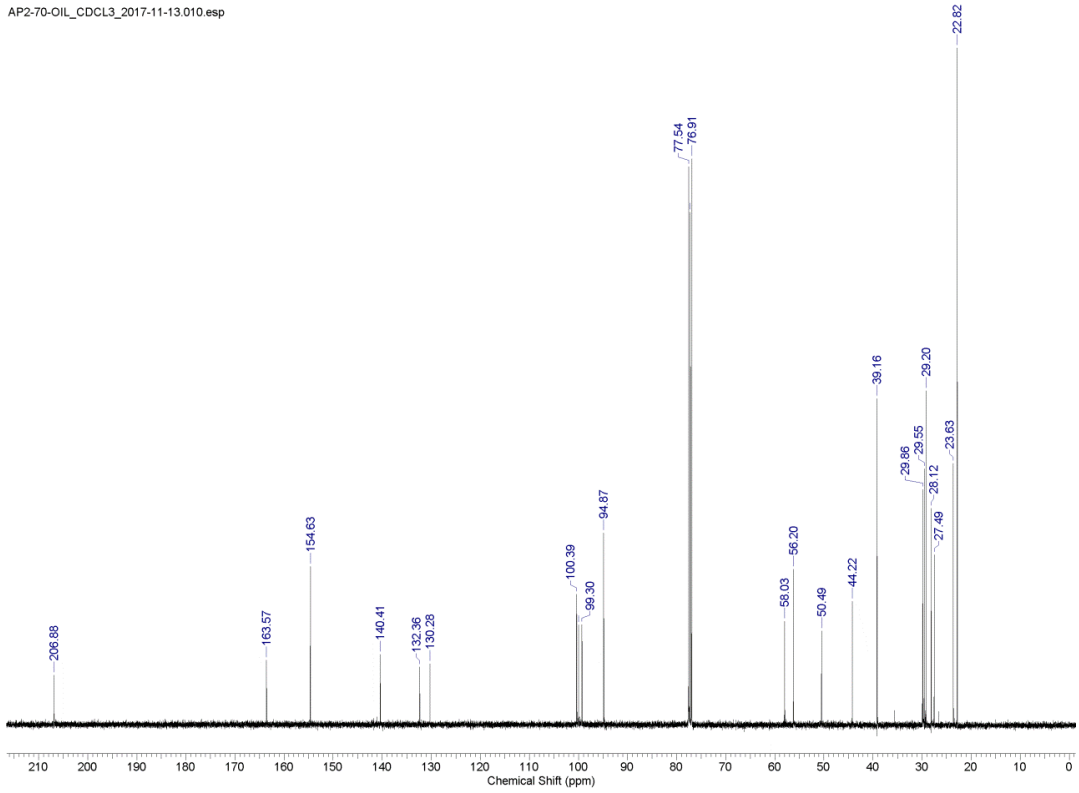
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.298	10862190	4122074	100.000	100.000
Total		10862190	4122074	100.000	100.000

^{1}H NMR of **5b** in $CDCl_3$



^{13}C NMR of **5b** in $CDCl_3$



HPLC chromatogram of **5b**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-70-final
Tray#	: 1
Vail #	: 3
Injection Volume	: 10 uL
Data File Name	: AP2-70-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 11/13/2017 3:25:57 PM

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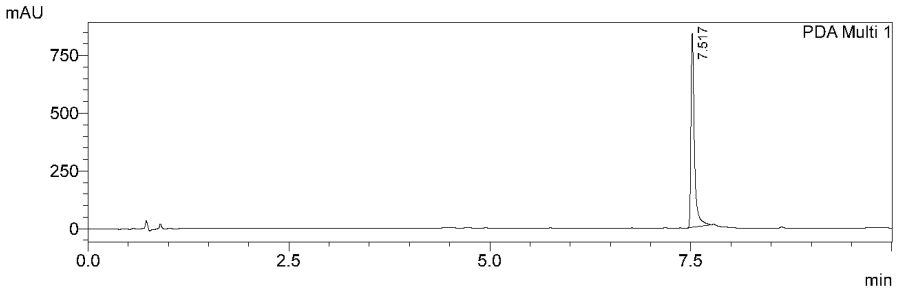
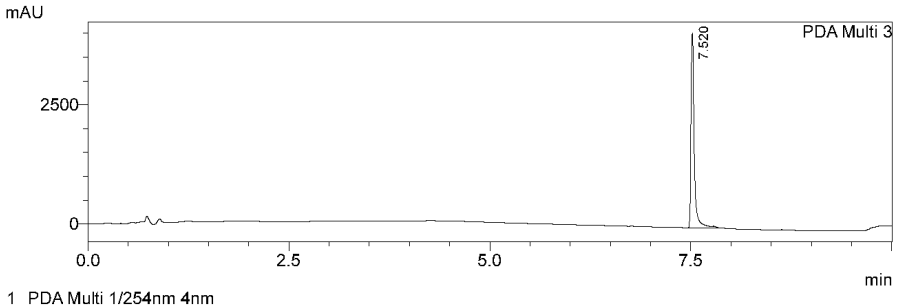




1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

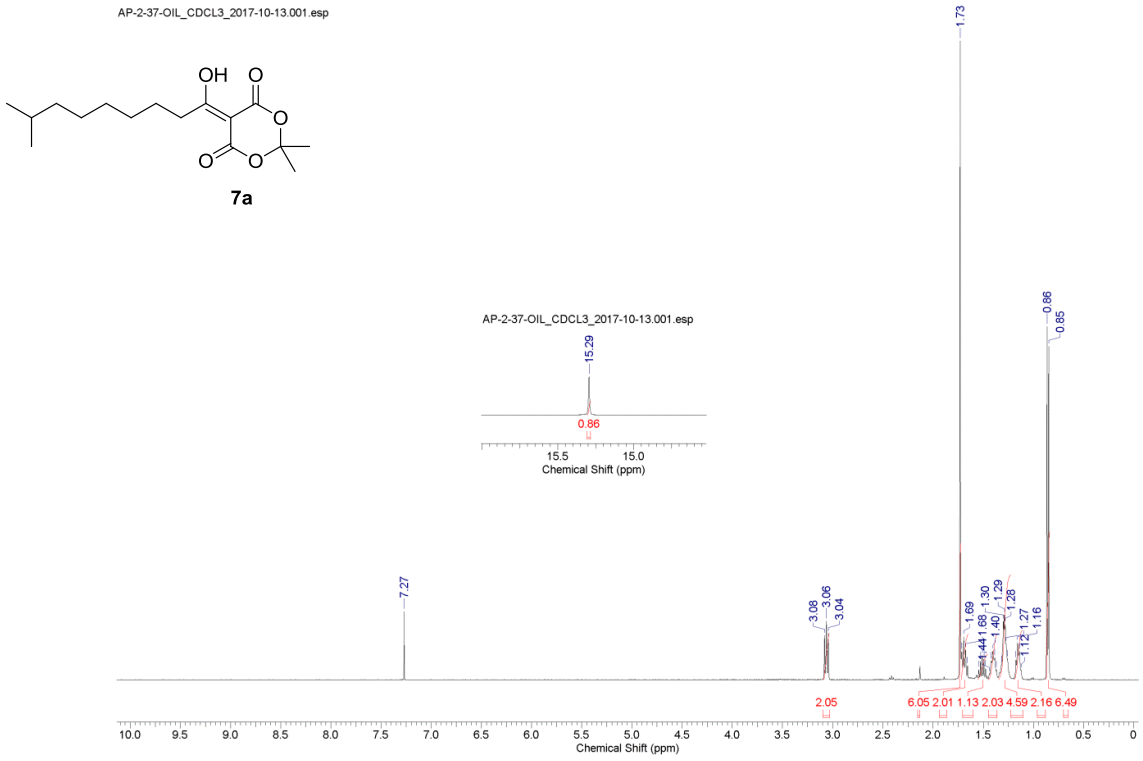
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.517	2492122	836477	100.000	100.000
Total		2492122	836477	100.000	100.000

PeakTable

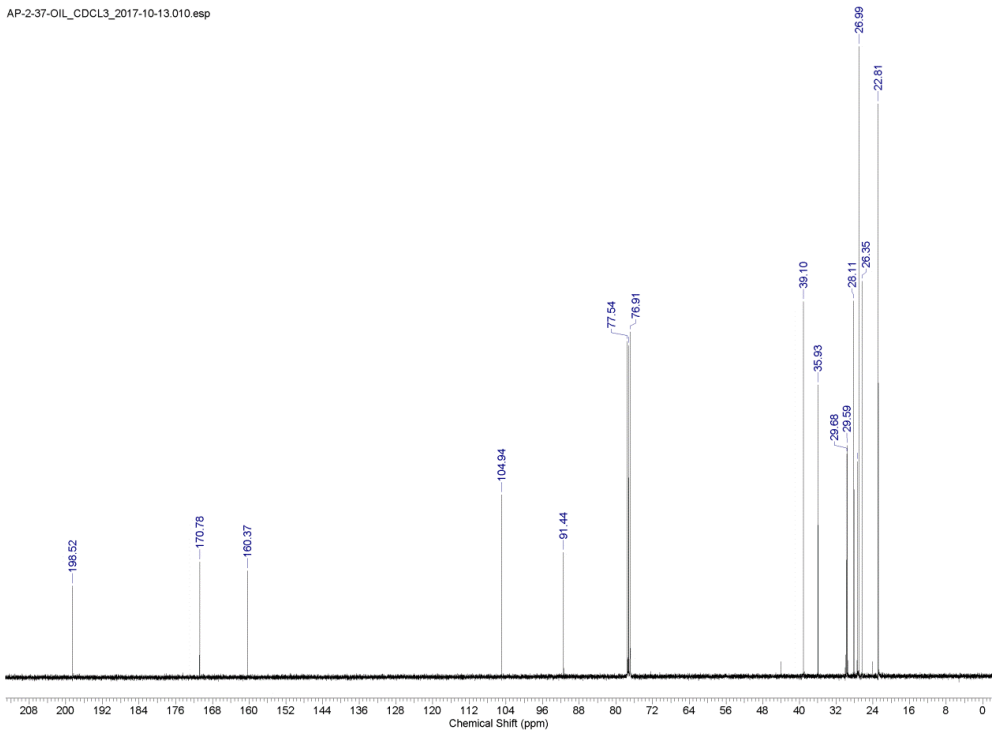
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.520	11403672	4080893	100.000	100.000
Total		11403672	4080893	100.000	100.000

^{1}H NMR of **7a** in $CDCl_3$



^{13}C NMR of **7a** in $CDCl_3$



HPLC chromatogram of **7a**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-37-final
Tray#	: 1
Vail #	: 3
Injection Volume	: 10 uL
Data File Name	: AP2-37-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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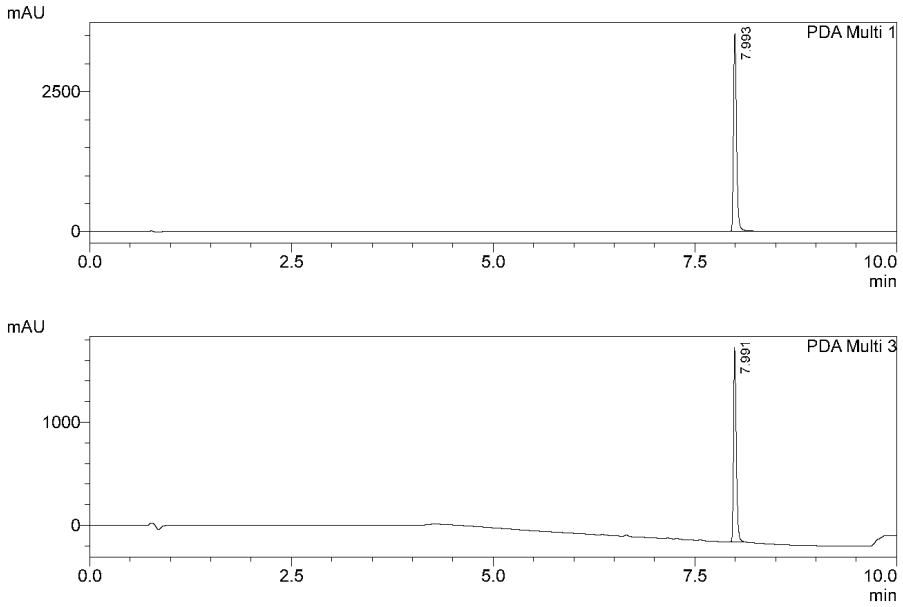


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

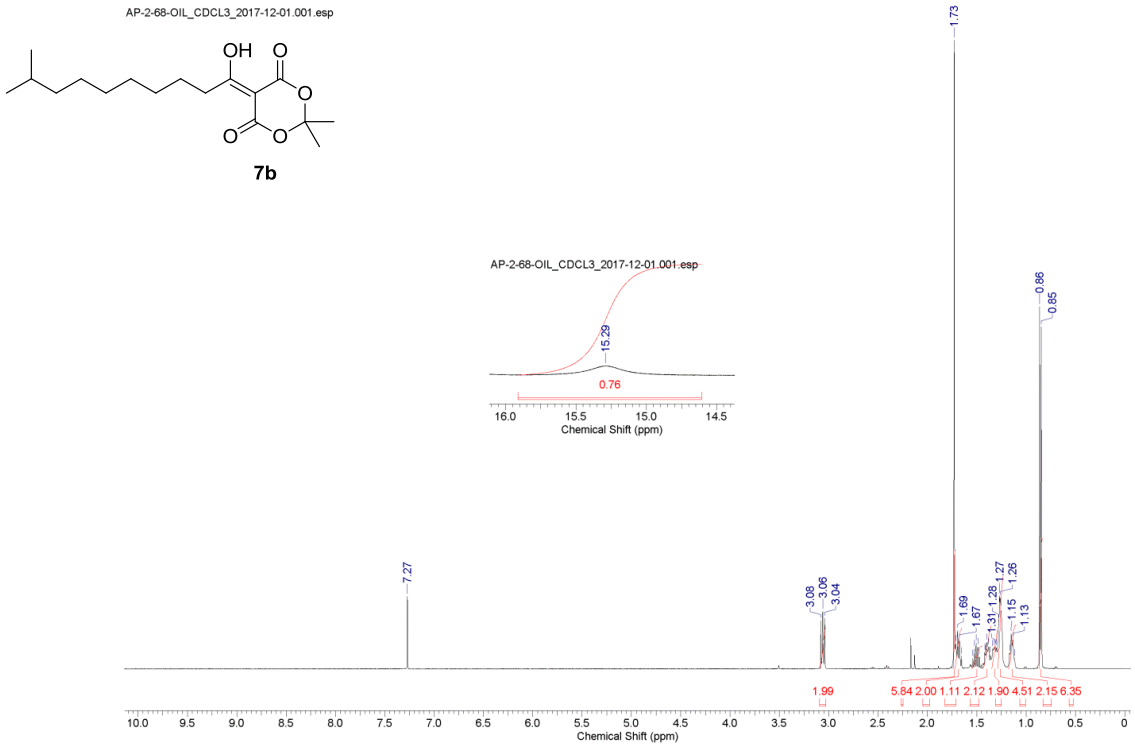
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.993	9032305	3440371	100.000	100.000
Total		9032305	3440371	100.000	100.000

PeakTable

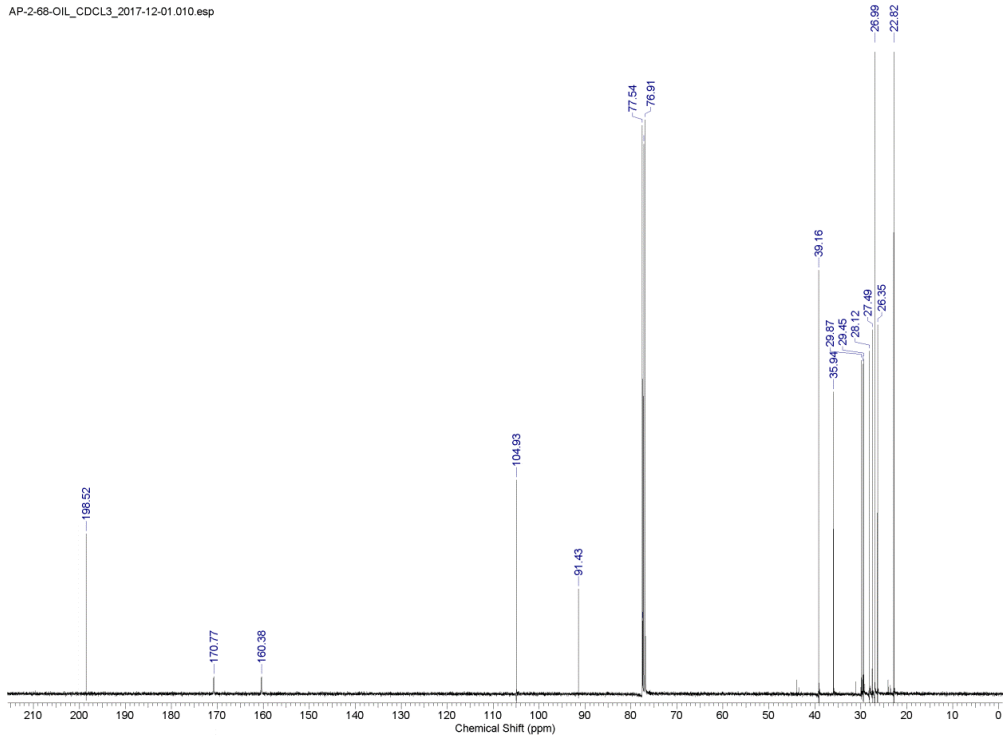
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.991	4248607	1884835	100.000	100.000
Total		4248607	1884835	100.000	100.000

^{1}H NMR of **7b** in $CDCl_3$



^{13}C NMR of **7b** in $CDCl_3$



HPLC chromatogram of **7b**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Allan Book2\AP2-68-final.lcd

Sample Name	: AP2-68-final
Tray#	: 1
Vail #	: 11
Injection Volume	: 10 uL
Data File Name	: AP2-68-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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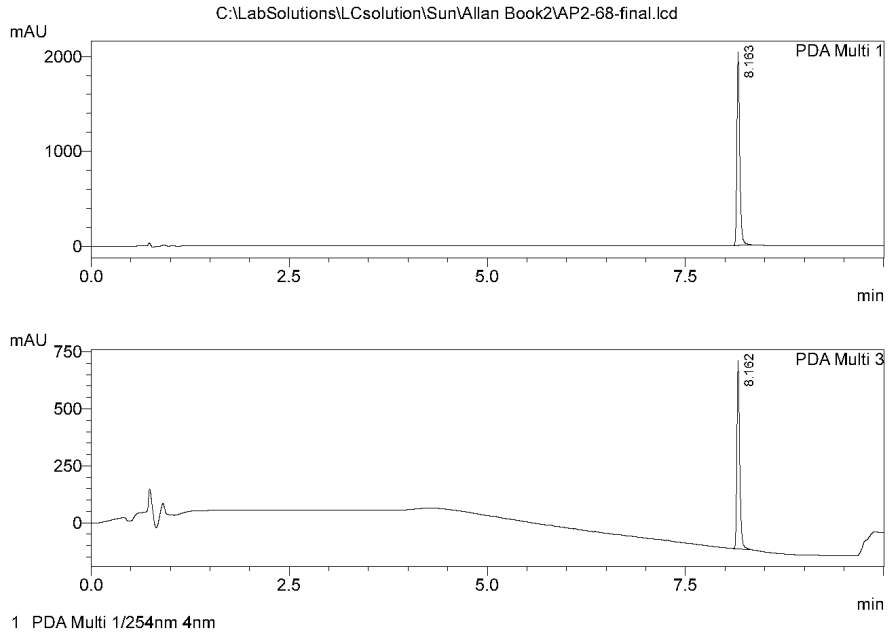


1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

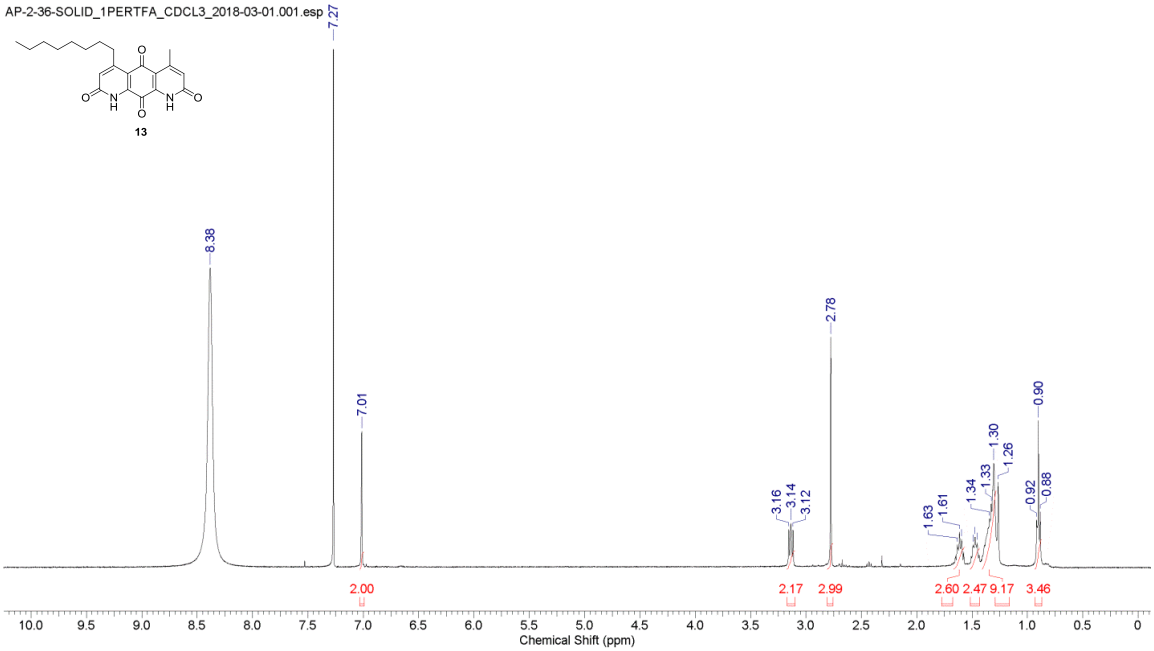
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.163	5084993	2007085	100.000	100.000
Total		5084993	2007085	100.000	100.000

PeakTable

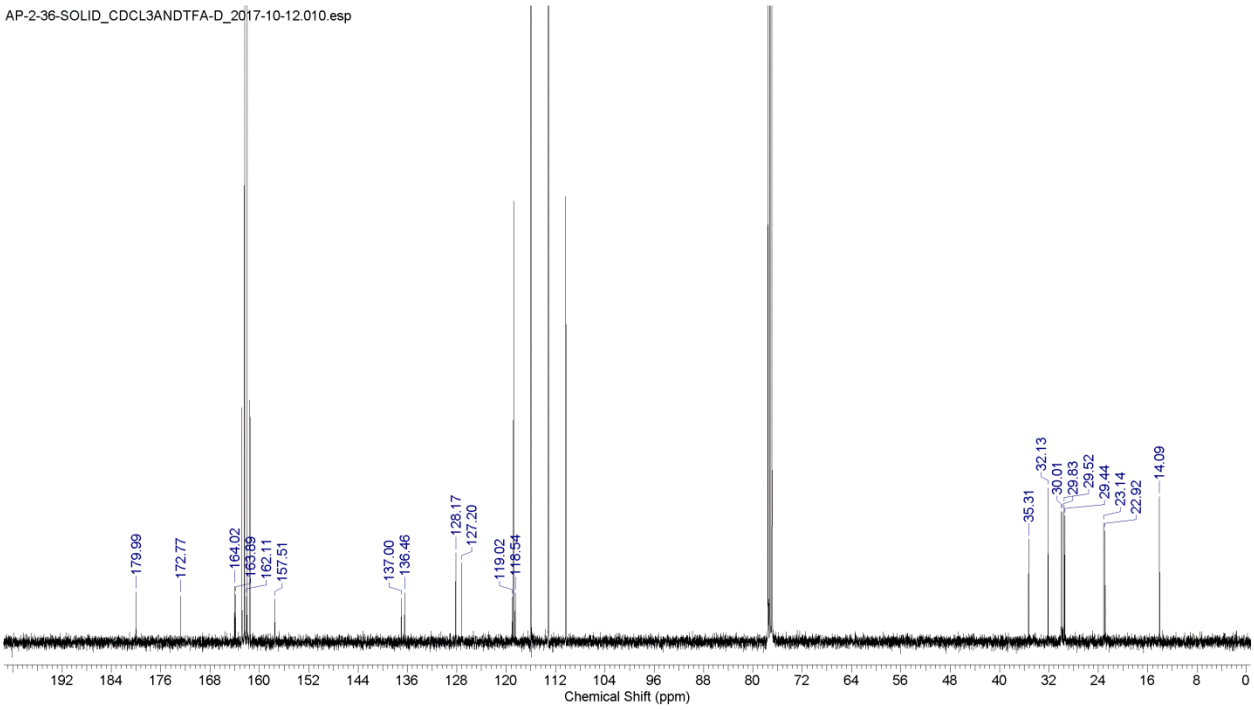
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.162	2045199	825208	100.000	100.000
Total		2045199	825208	100.000	100.000

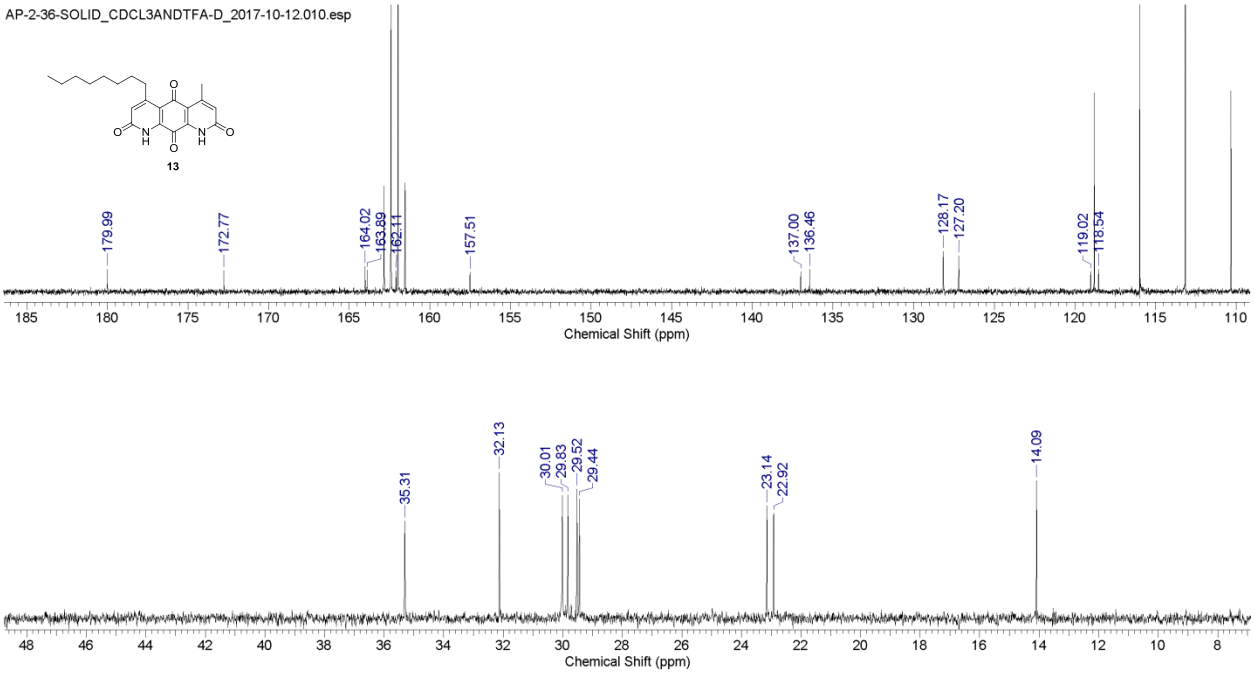
^{1}H NMR of **13** in 1% $CF_3CO_2D/CDCl_3$



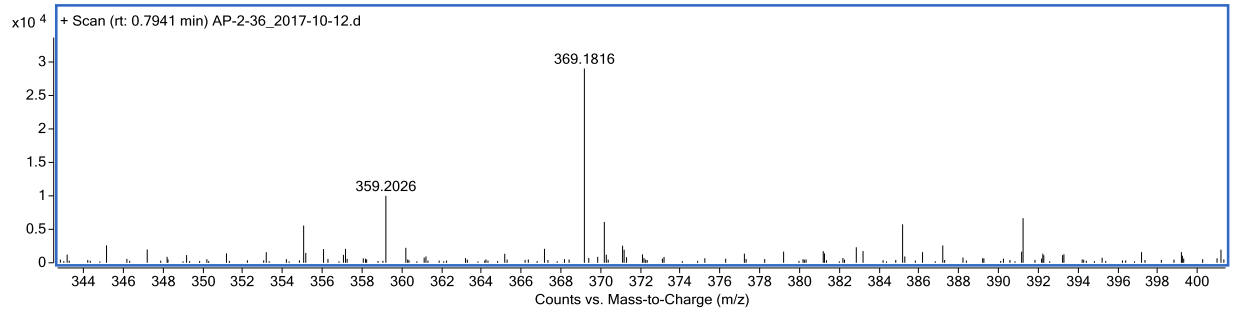
^{13}C NMR of **13** in 2% $CF_3CO_2D/CDCl_3$



Zoomed ^{13}C NMR regions of **13** in 2% $CF_3CO_2D/CDCl_3$



HRMS of **13**



HPLC chromatogram of **13**

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: AP2-36-final
Tray#	: 1
Vail #	: 1
Injection Volume	: 10 uL
Data File Name	: AP2-36-final.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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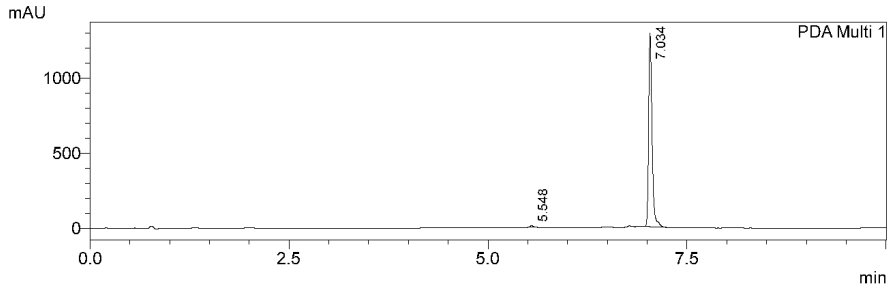
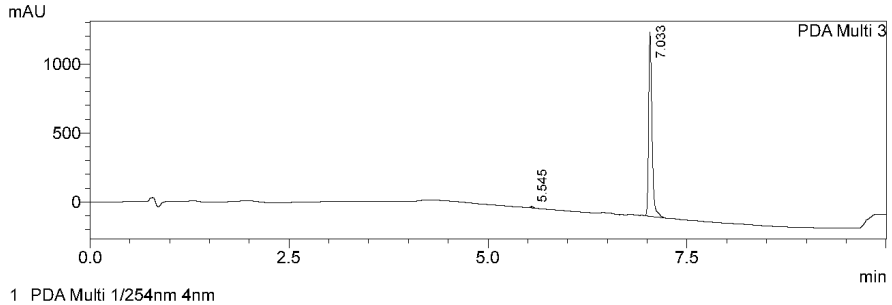
C:\LabSolutions\LCsolution\Sun\Allan Book2\AP2-36-final.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

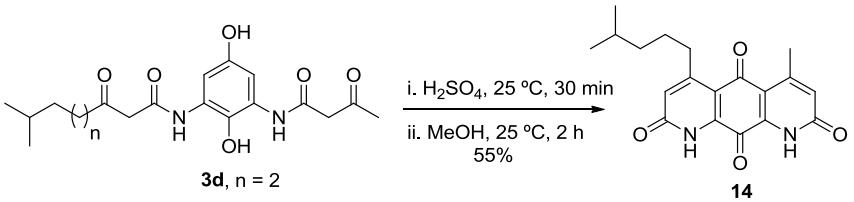
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.548	29880	11511	0.773	0.897
2	7.034	3837809	1271762	99.227	99.103
Total		3867689	1283273	100.000	100.000

PeakTable

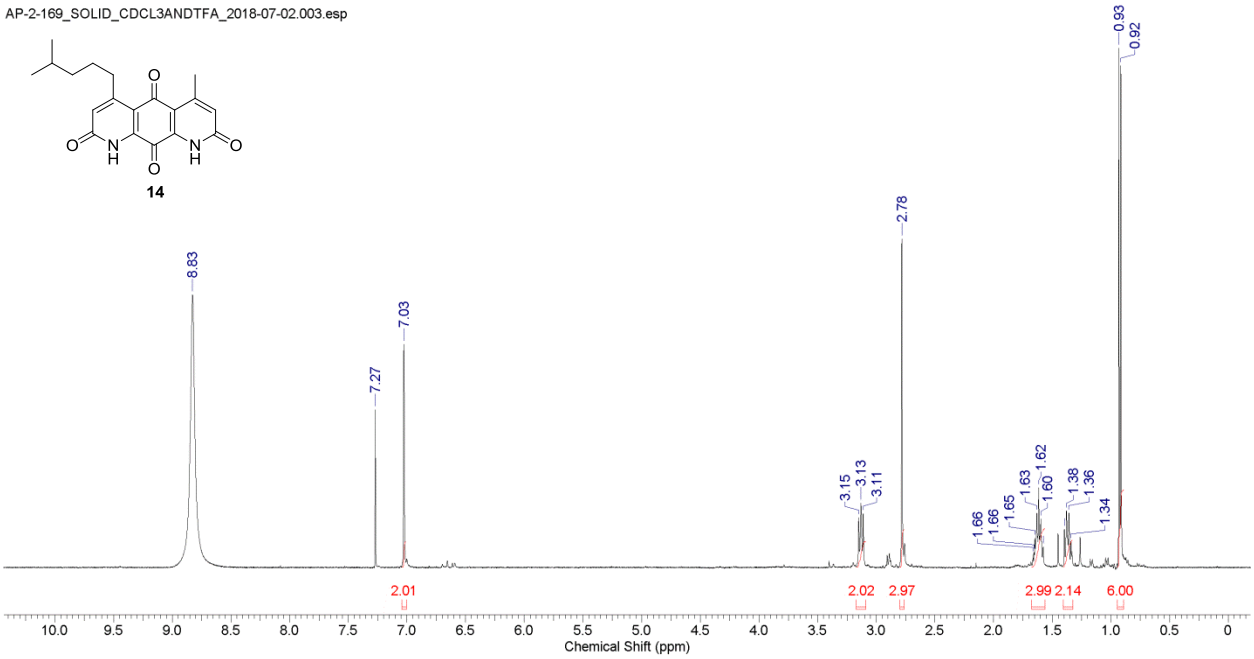
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.545	30189	11069	0.768	0.824
2	7.033	3902002	1332447	99.232	99.176
Total		3932191	1343517	100.000	100.000

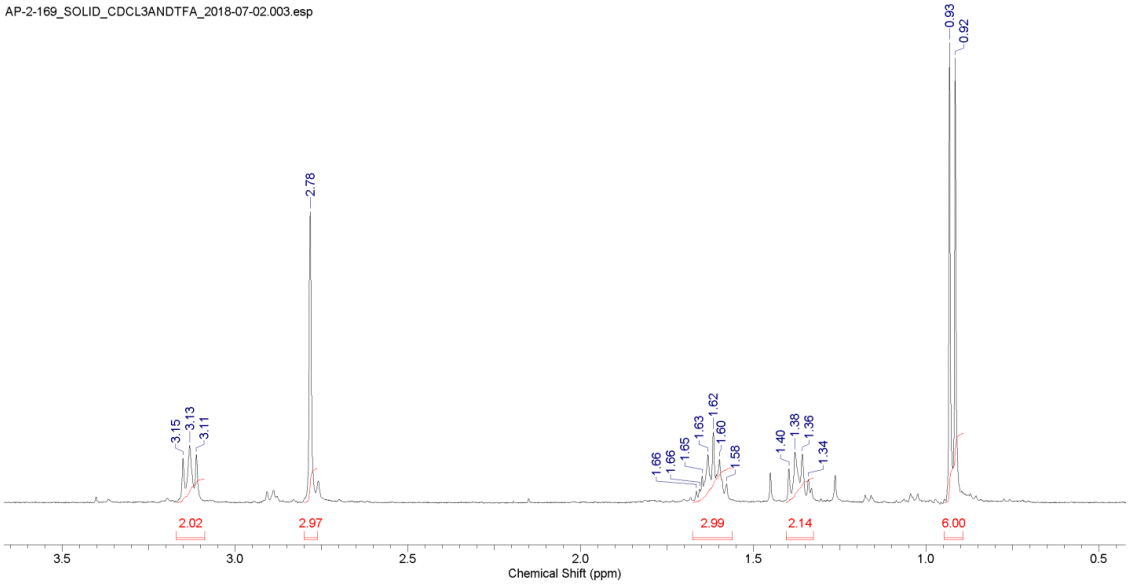


Scheme S1 Synthesis of **14** with a shorter branched side chain.

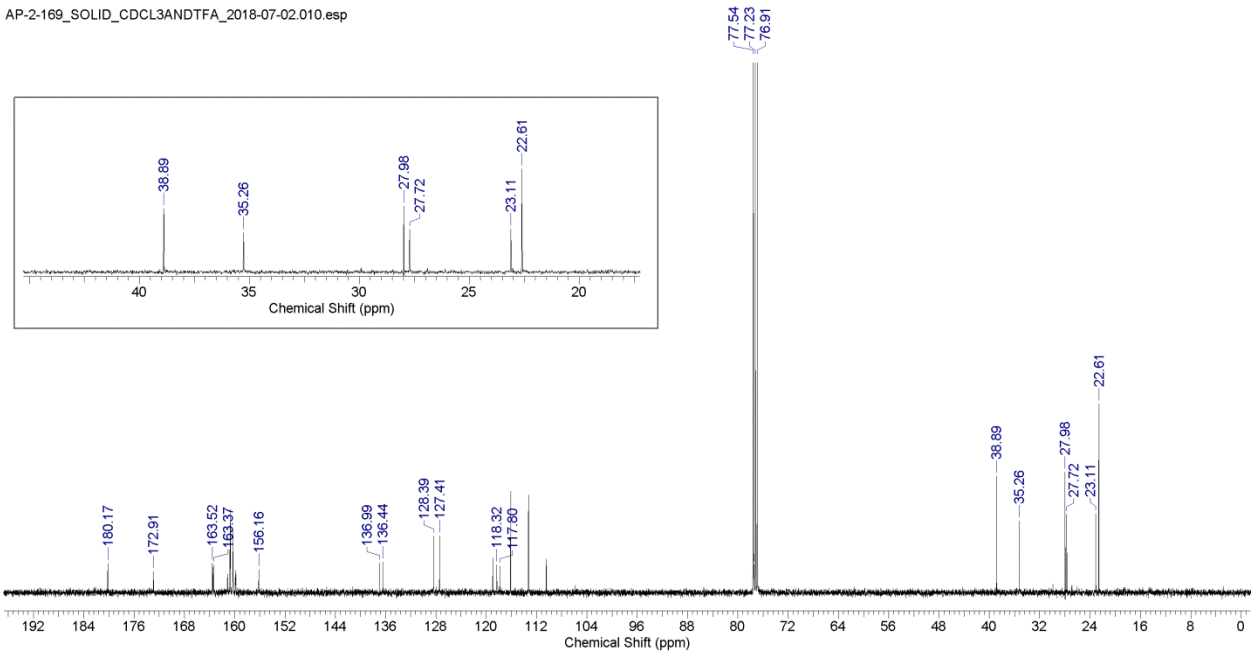
^{1}H NMR of **14** in 2% $CF_3CO_2D/CDCl_3$



Zoomed ^{1}H NMR of **14** in 2% $CF_3CO_2D/CDCl_3$



^{13}C NMR of **14** in 2% $CF_3CO_2D/CDCl_3$



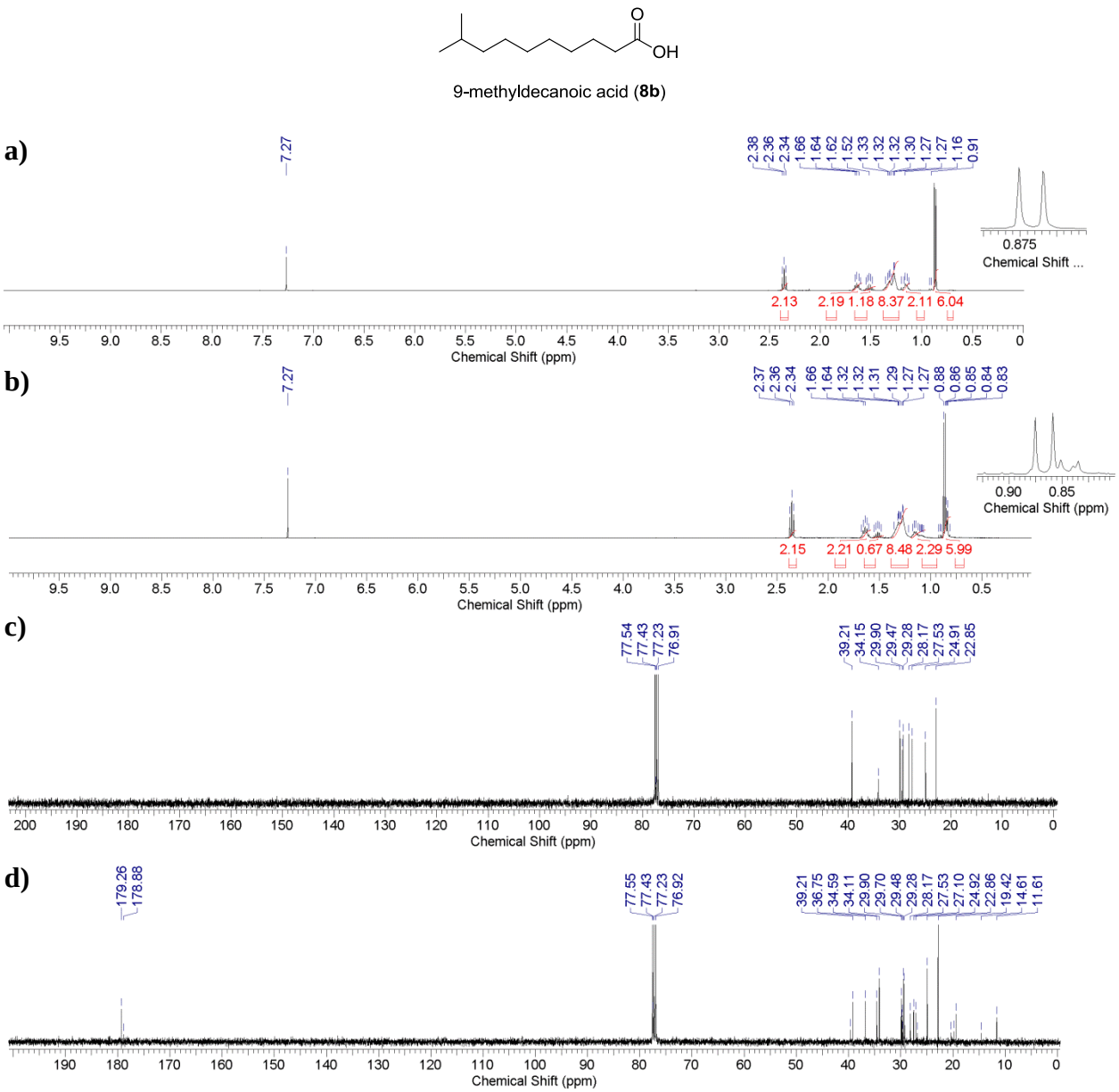


Fig. S1 a) ^{1}H NMR spectrum of 9-methyldecanoic acid; b) ^{1}H NMR spectrum of 9-methyldecanoic acid after stirring 30 min in conc. H_2SO_4 at room temperature; c) ^{13}C NMR spectrum of 9-methyldecanoic acid; d) ^{13}C NMR spectrum of 9-methyldecanoic acid after stirring 30 min in conc. H_2SO_4 at room temperature. All NMR spectra were taken in $CDCl_3$.

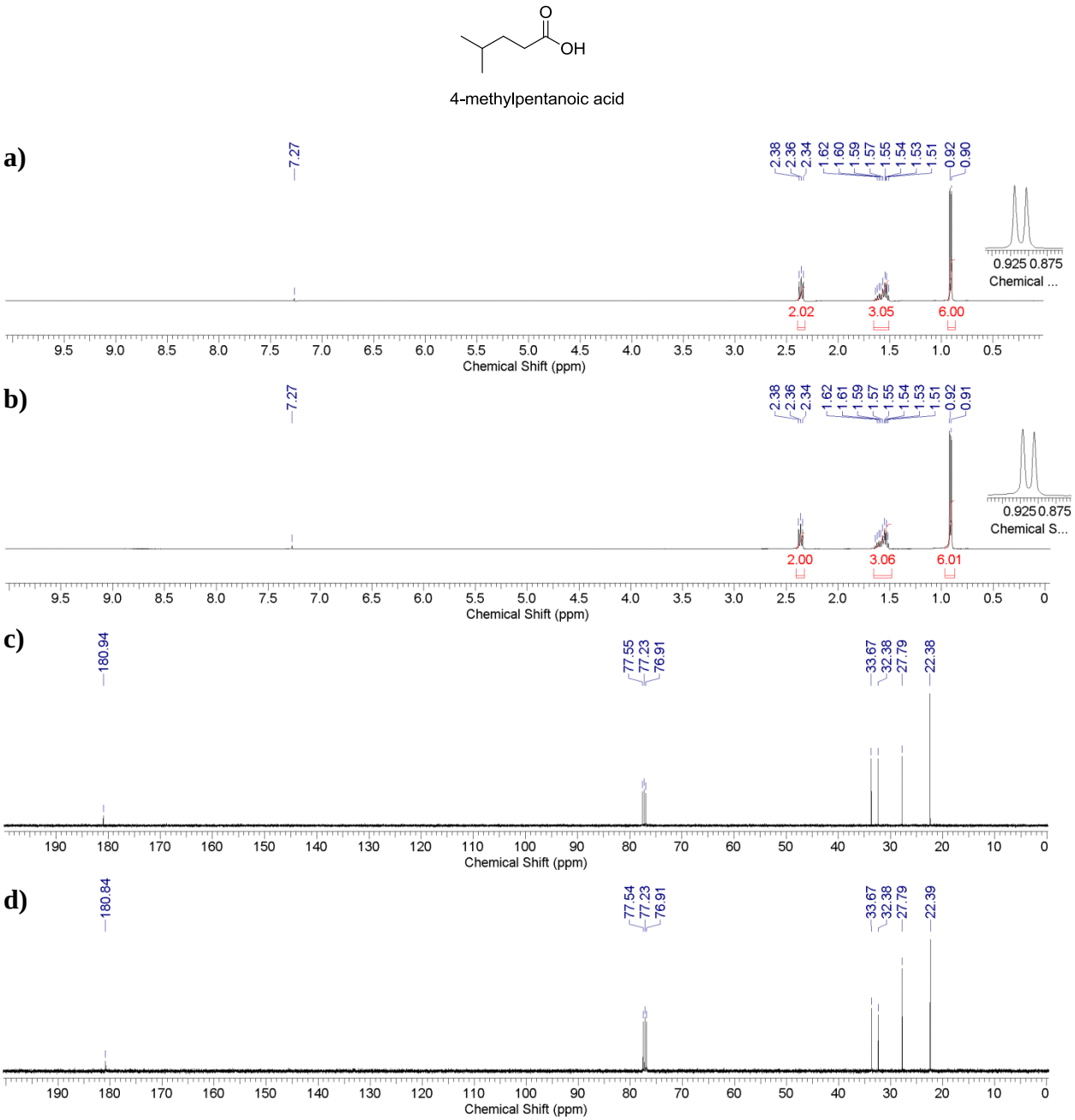


Fig. S2 a) ^{1}H NMR spectrum of 4-methylpentanoic acid; b) ^{1}H NMR spectrum of 4-methylpentanoic acid after stirring 18 h in conc. H_2SO_4 at room temperature; c) ^{13}C NMR spectrum of 4-methylpentanoic acid; d) ^{13}C NMR spectrum of 4-methylpentanoic acid after stirring 18 h in conc. H_2SO_4 at room temperature. All NMR spectra were taken in $CDCl_3$.

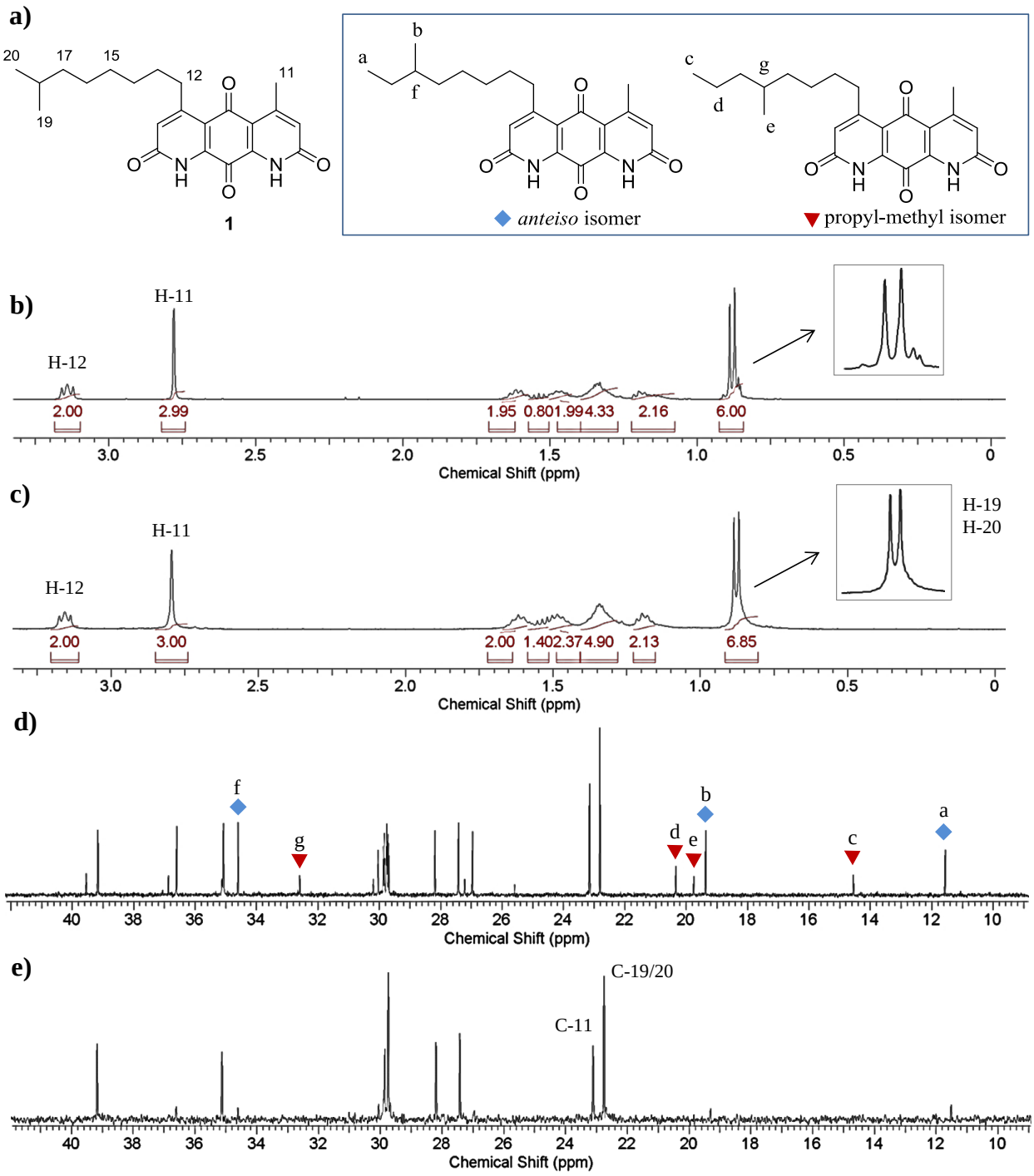


Fig. S3 a) Structures of diazaquinomycin H (**1**) and proposed isomers. b) Zoomed ^{1}H NMR spectrum of isomeric mixture of **1**; c) Zoomed ^{1}H NMR spectrum of pure synthetic diazaquinomycin H (**1**); d) Zoomed ^{13}C NMR spectrum of isomeric mixture of **1**; e) Zoomed ^{13}C NMR spectrum of pure synthetic diazaquinomycin H (**1**).

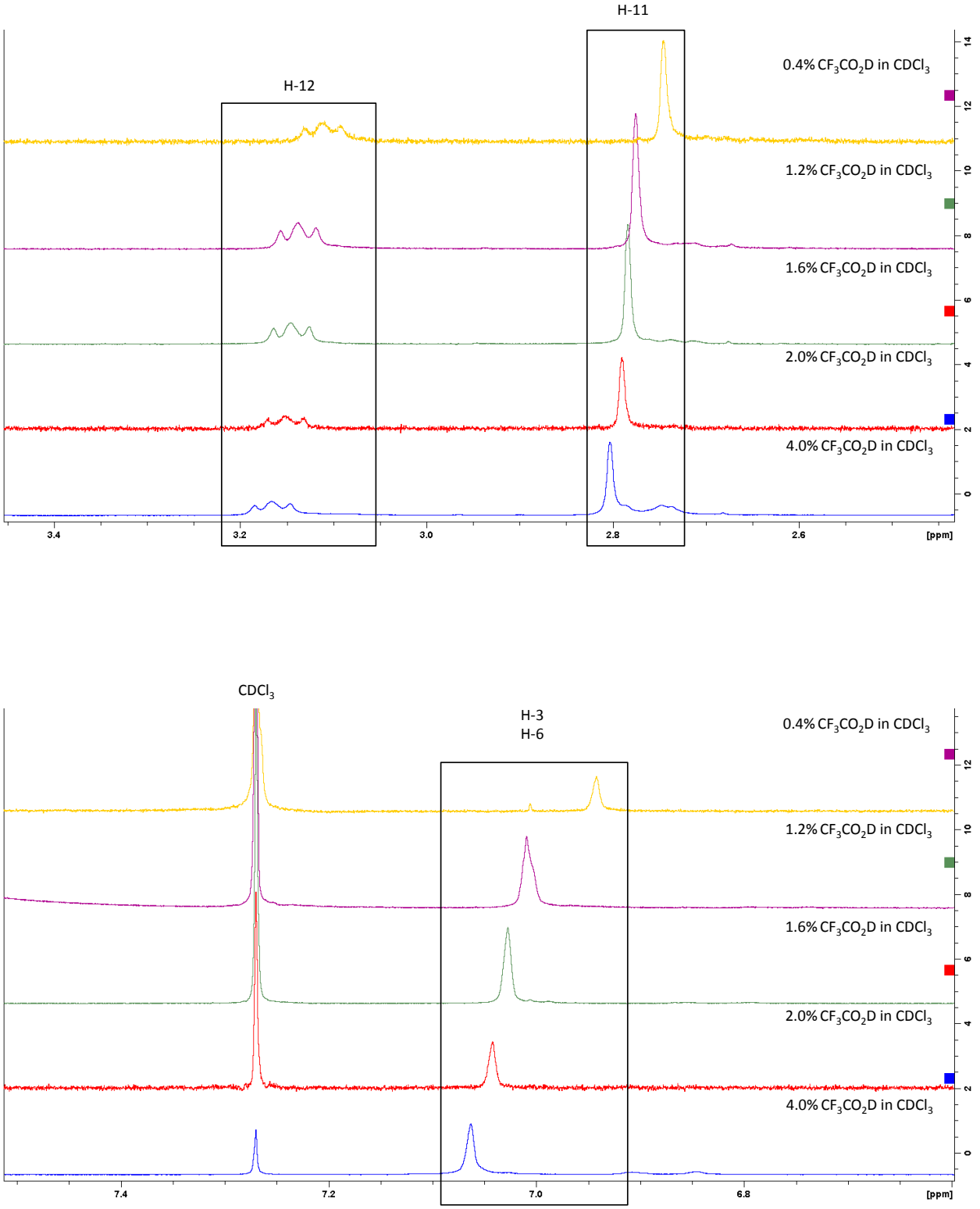


Fig. S4 Zoomed ^{1}H NMR of isomeric mixture of **2** in $CDCl_3$ with varying concentrations of CF_3CO_2D.