Supporting Information

The effect of enhanced π-π interactions and tail branching on azobenzene surfactant self-assembly

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Critical packing parameter *P* calculation

The critical packing parameter (P) was calculated following a previously established procedure.[1] Initially, molecular structures were drawn using Chem3D, and their 3D geometries were optimized via the built-in MM2 force field. The tail group length was then measured using Chem3D's internal measuring tool. The betaine head group was removed to isolate the tail volume, and the optimized tail structures were exported as .sdf files. These files were submitted to the Molecular Volume Calculator provided by the Supercomputing Facility for Bioinformatics and Computational Biology at IIT Delhi [https://scfbio-iitd.res.in/Sanjeevini/Molecular-volume-calculator.php] to obtain the tail volumes for both *cis* and *trans* isomers. The minimum interfacial area per betaine head group was obtained from reported experimental values from the literature. Using the calculated tail volume and length along with the estimated head group area, the critical packing parameter (P) for each azo-surfactant was determined using the standard formula.

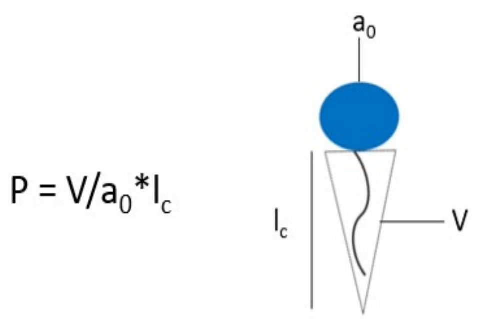


Figure S1: Critical packing parameter (P), where V is the volume of the hydrophobic tail, a_o is surface area of head, and l_c is the length of the hydrophobic tail.

Table S1: Critical packing parameter *P* calculation

Surfactant	a_o (Å²)	V_{trans} (Å³)	V_{cis} (Å³)	$l_{c(trans)}$ Å	$l_{c(cis)}$ Å	P_{trans}	P_{cis}
n-BDAP	55.5	250.35	250.00	16.8	12.2	0.27	0.37
iso-BDAP	55.5	250.29	248.73	14.7	10.4	0.31	0.43
t-BDAP	55.5	250.10	249.62	14.6	12.6	0.31	0.36
n-BDAN	55.5	289.43	288.98	16.7	13.1	0.31	0.40
iso-BDAN	55.5	289.35	288.78	14.6	11	0.36	0.47
t-BDAN	55.5	289.07	287.82	13.2	12.2	0.39	0.42

Photoisomerisation and kinetic studies

UV–vis spectroscopy was used to evaluate the photo-isomerisation and thermal stability behaviour of the azo-surfactants 0.1 M solutions of *n*-BDAN, *iso*-BDAN, *t*-BDAN and *n*-BDAP. The *trans*-rich photostationary state (PSS*)* was achieved through thermal relaxation by heating the sample solution to 50 ºC, followed by storage in the dark until it cooled to room temperature. Upon irradiation at 365 nm, rapid photoisomerisation to a *cis*-rich state occurred, reaching equilibrium within 5 minutes. Complete conversion to the *cis*-isomer is limited by spectral overlap between the π→π (*trans*) and n→π* (*cis*) transitions. The *cis*-isomer fraction (P_{cis}) was calculated using the change in absorbance at 386, 387, 392 or 348 nm for *n*-BDAN, *iso*-BDAN, *t*-BDAN or *n*-BDAP respectively, using the following equation. Relaxation back to *trans*-dominant PSS was monitored by UV-Vis spectroscopy in the dark, at the wavelengths noted in Fig. S2.

$$Pcis = Ai - Af \div Ai * 100$$

where P_{cis} is the proportion of the *cis* isomer present, A_i is the absorbance noted in Fig. S2 before UV irradiation, and A_f is the absorbance after UV irradiation.

The relaxation processes for all surfactants followed first-order reaction kinetics, which is consistent with a unimolecular process driven by light absorption.[2, 3] The rate constants, determined from the linear fit of $\ln(A_t/A_0)$ vs time, as well as the half-lives, are noted in Table S2.

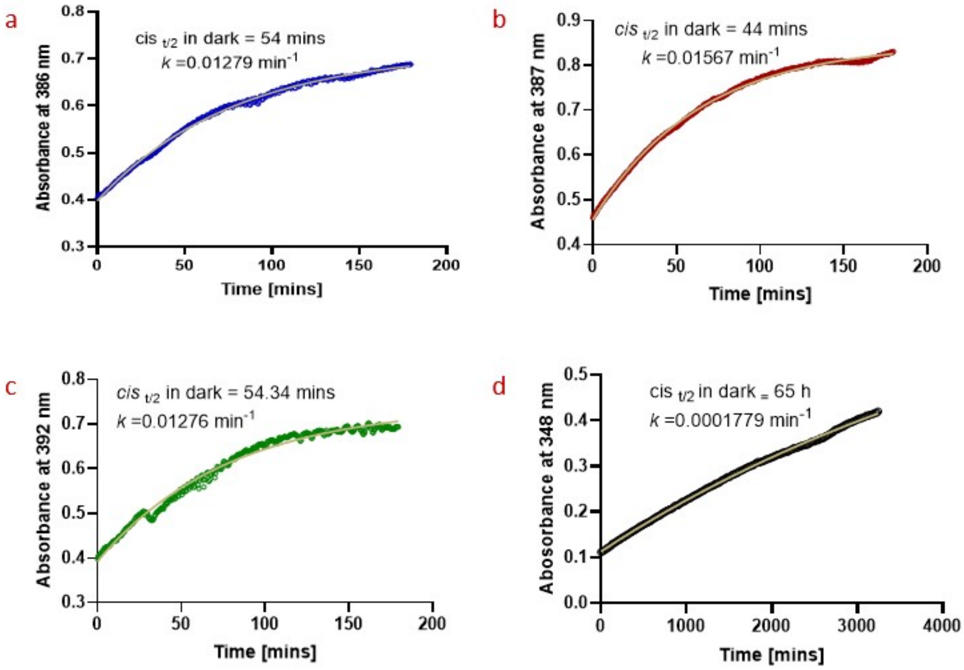


Figure S2: Change in absorbance of samples after irradiation at 365 nm a) *n*-BDAN b) *iso*-BDAN c) *tert*-BDAN d) *n*-BDAP

Table S2: Thermal relaxation kinetic data

Surfactant	**Rate constant (*k*) (min^{-1})**	**$t_{1/2}$ (min)**
n-BDAN	0.013	54.2
iso-BDAN	0.016	44.2
tert-BDAN	0.013	54.3
n-BDAP	0.00018	3896 (65 h)

The reversibility of photoresponsiveness of 0.1 M *n*-BDAN under alternating UV (365 nm) and visible light irradiation is shown in Fig. S3. Illumination with UV This reversible switching between the *trans*- and *cis*-rich PSS over five successive irradiation cycles demonstrate excellent cyclability; however, a slight decrease in absorbance of the *trans* band after repeated cycling indicates formation of a new steady-state equilibrium that is less *trans*-rich than the initial *trans* state.

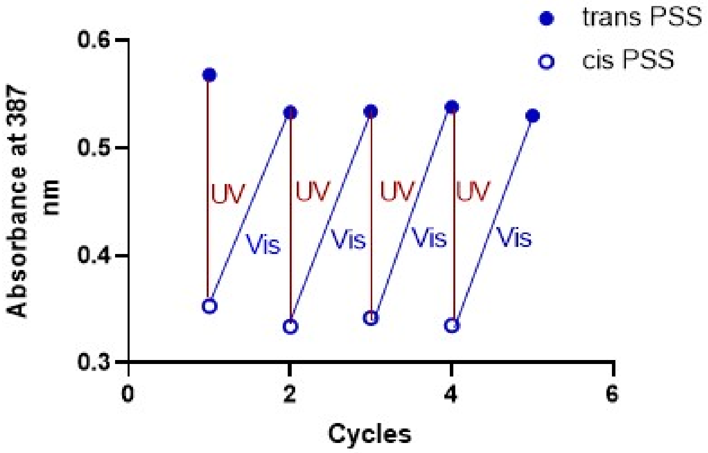


Figure S3: Photocyclability of *n*-BDAN

SANS fitting parameter

The SANS patterns collected for *n*-BDAN were analysed using the built-in models from SASView 4.4.0 (https://www.sasview.org). Both models were fit using a scattering length density (SLD) of 1.37 for the micelle core and 6.3 for the D_2O solvent. The detailed fitting parameters are provided in Table S3.

Table S3: SANS Fitting parameters

Sample	Model	Cylinder length/ Polar radius (Å)	Cylinder radius/ Equatorial radius (Å)	Axis ratio	Background (1/cm)	Scale
***trans n*-BDAN**	Flexible elliptical cylinder	~2600	18	1.8	0.0007	0.0024
***cis n*-BDAN**	Elliptical Cylinder	678	18	1.8	0.0035	0.008

*Kuhn length for *trans* n-BDAN is >1000 Å

Rheology

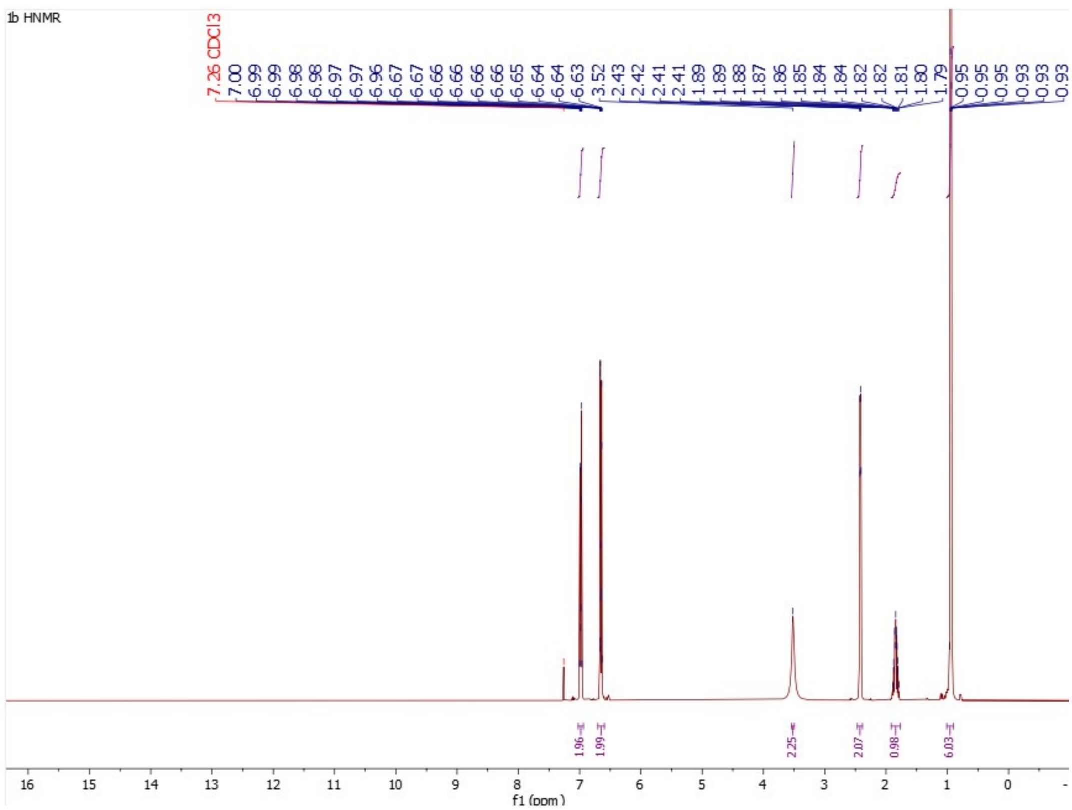
Triplicate rheological measurements were performed on a representative 1 wt.% n-BDAP sample to evaluate experimental reproducibility. The mean values and corresponding standard deviations for viscosity, storage modulus, loss modulus, and relaxation time are summarised in Table S4.

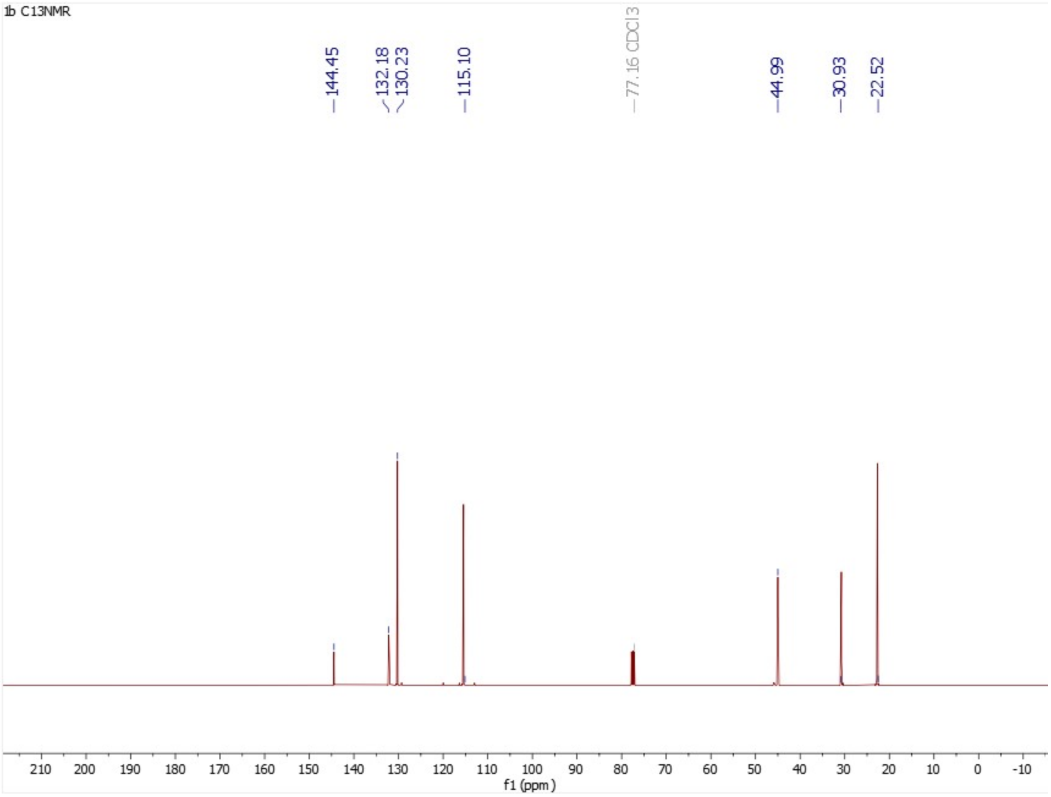
Table S4. Mean ± SD from triplicate rheological measurements of 1 wt.% n-BDAP.

Parameter	Mean	SD	Unit
Viscosity	1.20×10^{3}	$\pm$ 30.9	mPa·s
Storage modulus *(G')*	1.4×10^{-3}	$\pm 7.3 \times 10^{-4}$	Pa
Loss modulus *(G'')*	1.3×10^{-3}	$\pm 8.3 \times 10^{-4}$	Pa
Relaxation time (τ)	0.66	$\pm$ 0.49	S

NMR Spectra

1b

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132.18
130.23
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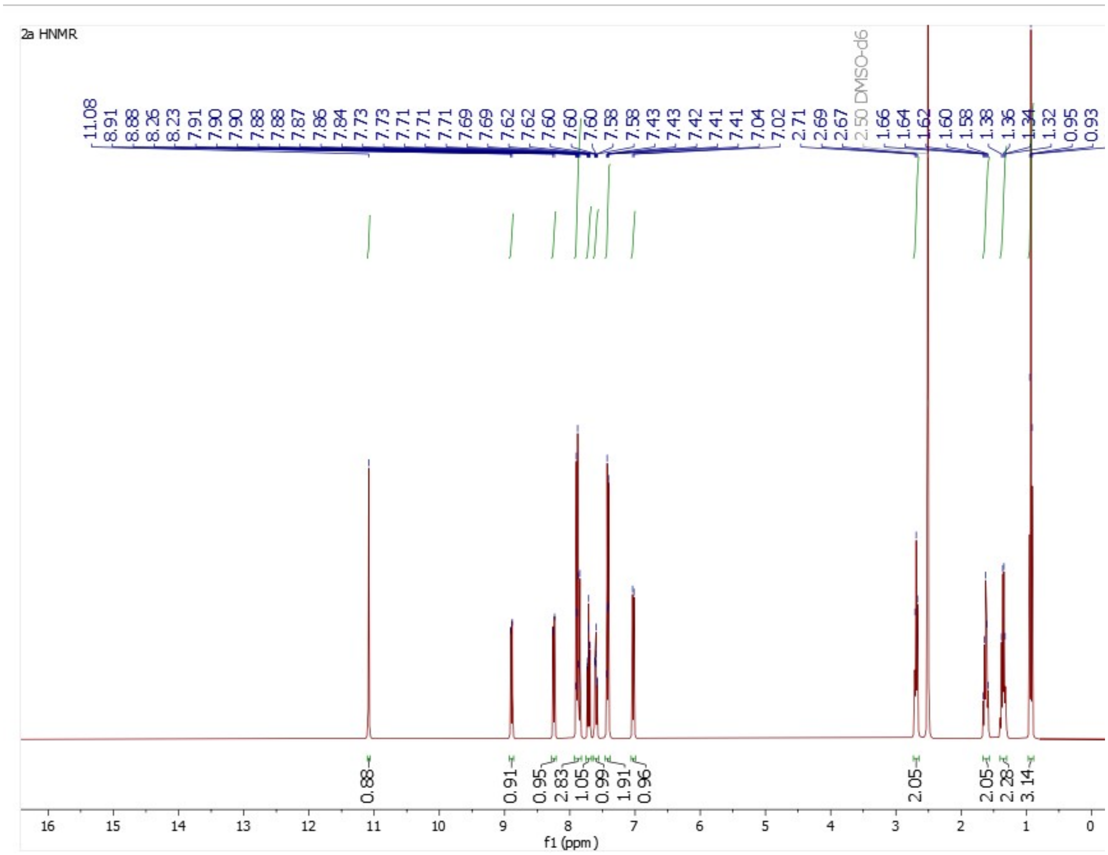
44.99
30.93
22.52
f1 (ppm)

2a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8.88
8.26
8.23
7.91
7.90
7.88
7.88
7.87
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7.73
7.73
7.71
7.71
7.71
7.69
7.62
7.62
7.60
7.60
7.60
7.58
7.58
7.43
7.43
7.42
7.41
7.41
7.04
7.02
2.71
2.69
2.67
2.50 DMSO-d6
1.66
1.64
1.62
1.60
1.58
1.38
1.36
1.34
1.32
0.95
0.93
0.88
0.91
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1.05
0.99
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0.96
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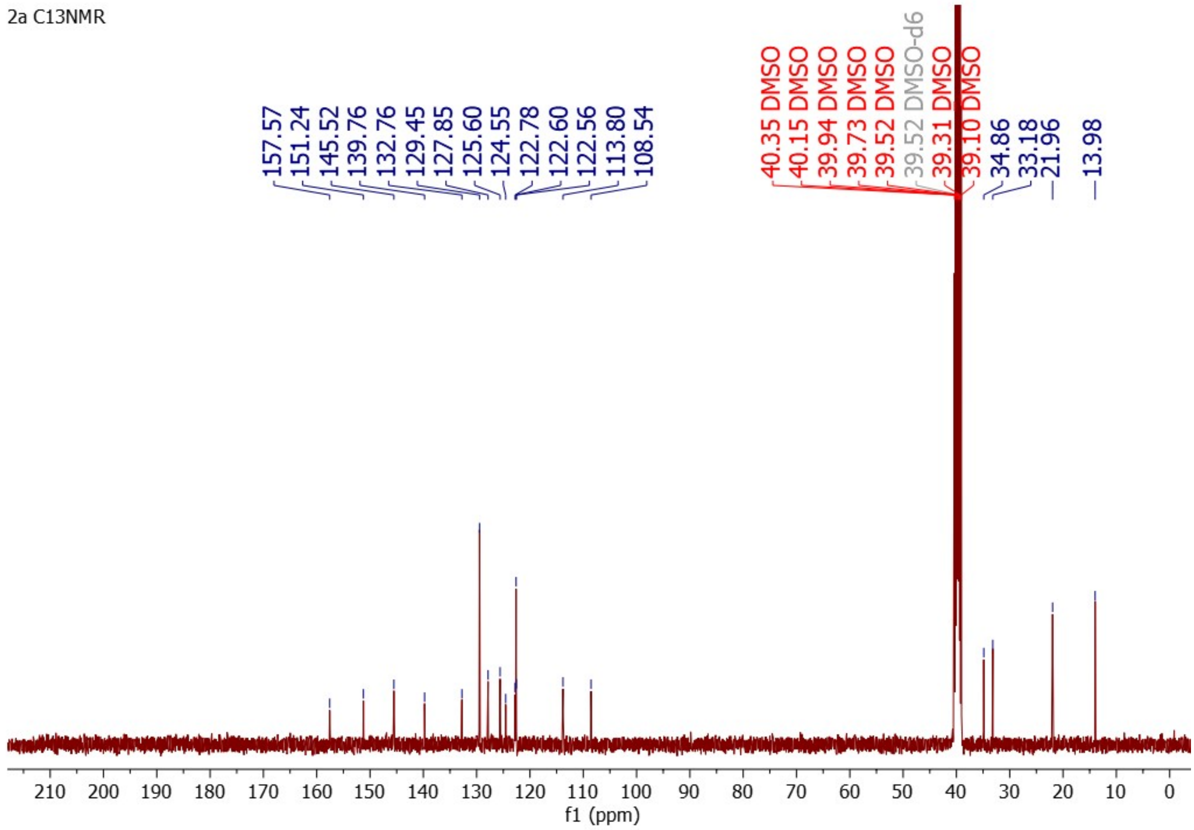
2.05
2.28
3.14
f1 (ppm)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127.85
125.60
124.55
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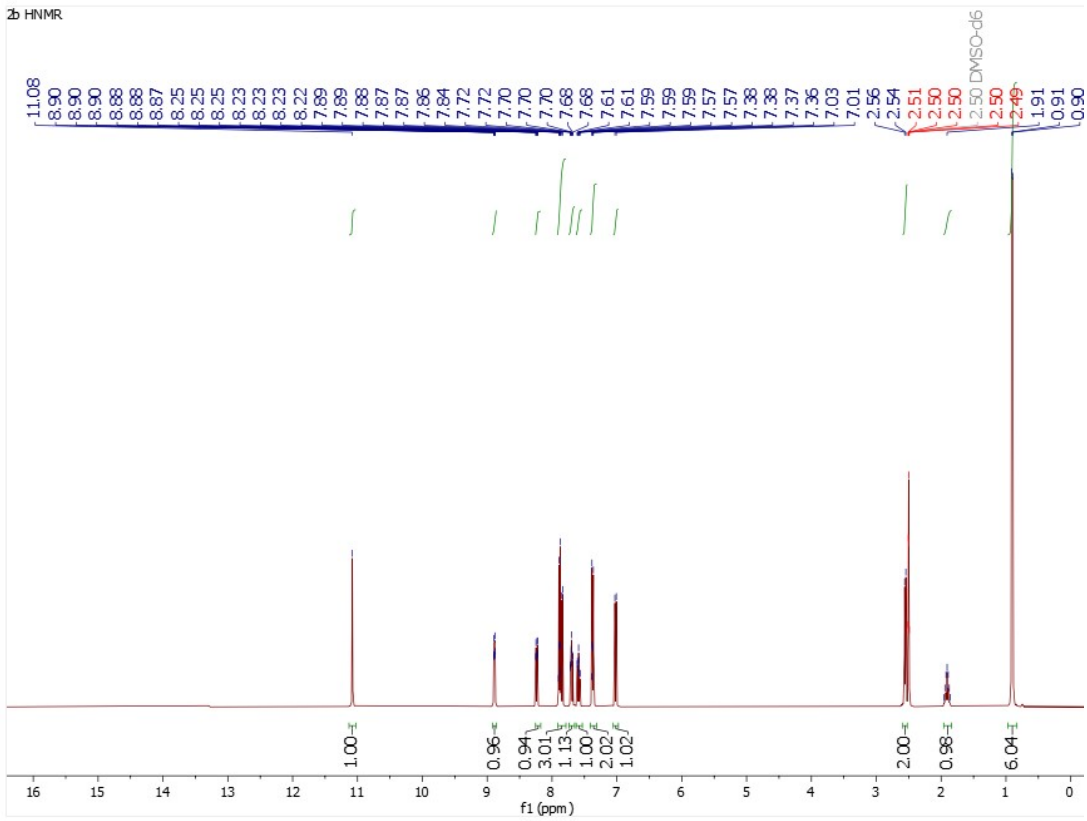
122.60
122.56
113.80
108.54
40.35 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.52 DMSO-d6
39.31 DMSO
39.10 DMSO
34.86
33.18
21.96
13.98
f1 (ppm)

2b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8.90
8.90
8.88
8.88
8.87
8.25
8.25
8.25
8.23
8.23
8.23
8.22
7.89
7.89
7.88
7.87
7.87
7.86
7.84
7.72
7.72
7.70
7.70
7.68
7.68
7.61
7.61
7.59
7.59
7.57
7.57
7.38
7.38
7.37
7.36
7.03
7.01
2.56
2.54
2.51
2.50
2.50 DMSO-d6
2.50
2.50
2.49
1.91
0.91
0.90
1.00
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1.00
2.02
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2.00
0.98
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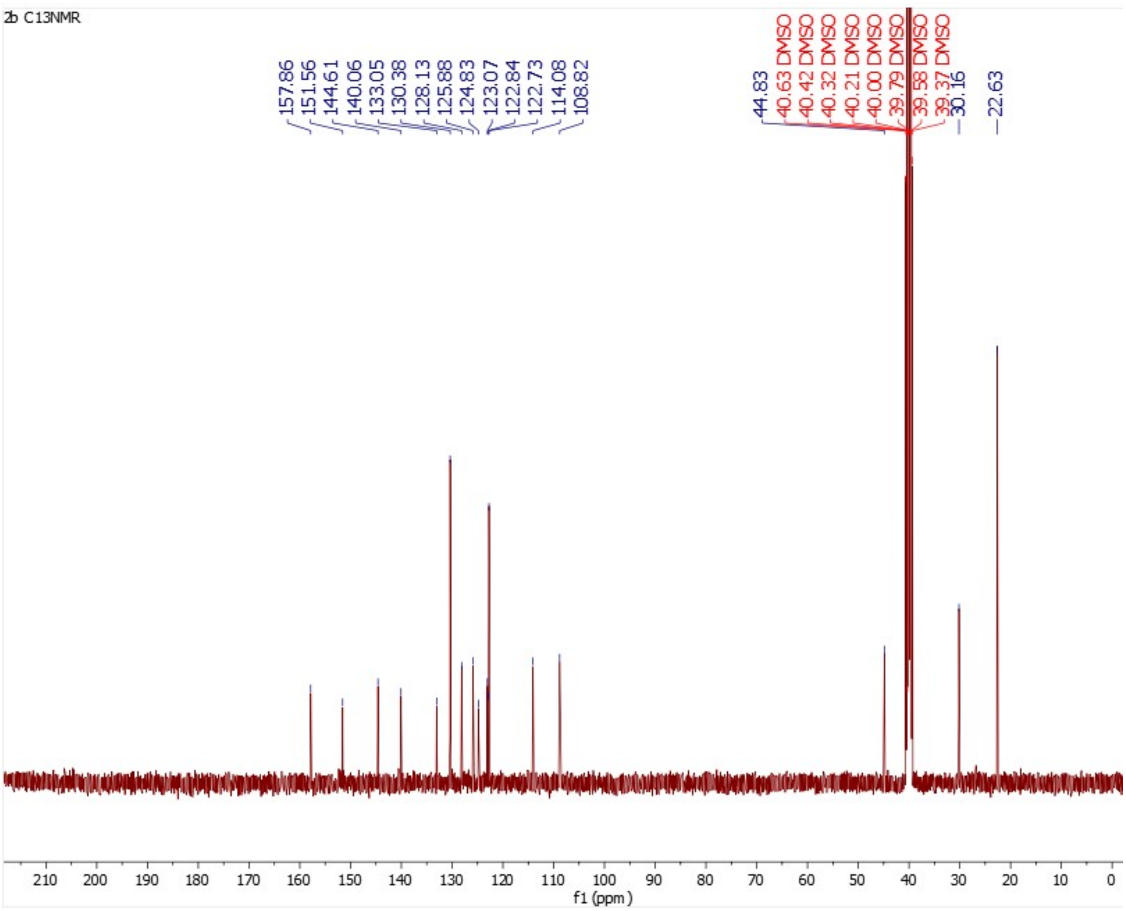
f1 (ppm)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133.05
130.38
128.13
125.88
124.83
123.07
122.84
122.73
114.08
108.82
44.83
40.63 DMSO
40.42 DMSO
40.32 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
30.16
22.63
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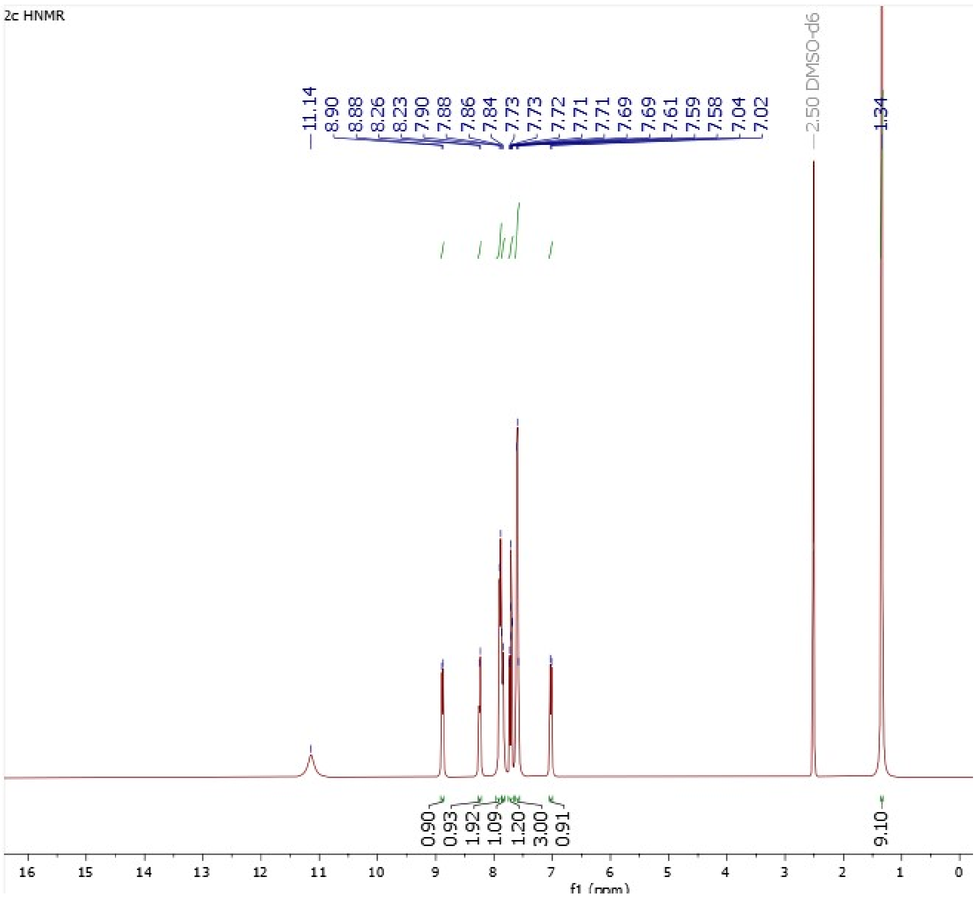
f1 (ppm)

2c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8.90
8.88
8.26
8.23
7.90
7.88
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7.84
7.73
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7.72
7.71
7.71
7.69
7.61
7.59
7.58
7.04
7.02
2.50 DMSO-d6
1.34
0.90
0.93
1.92
1.09
1.20
3.00
0.91
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14
13
12
11
10
9
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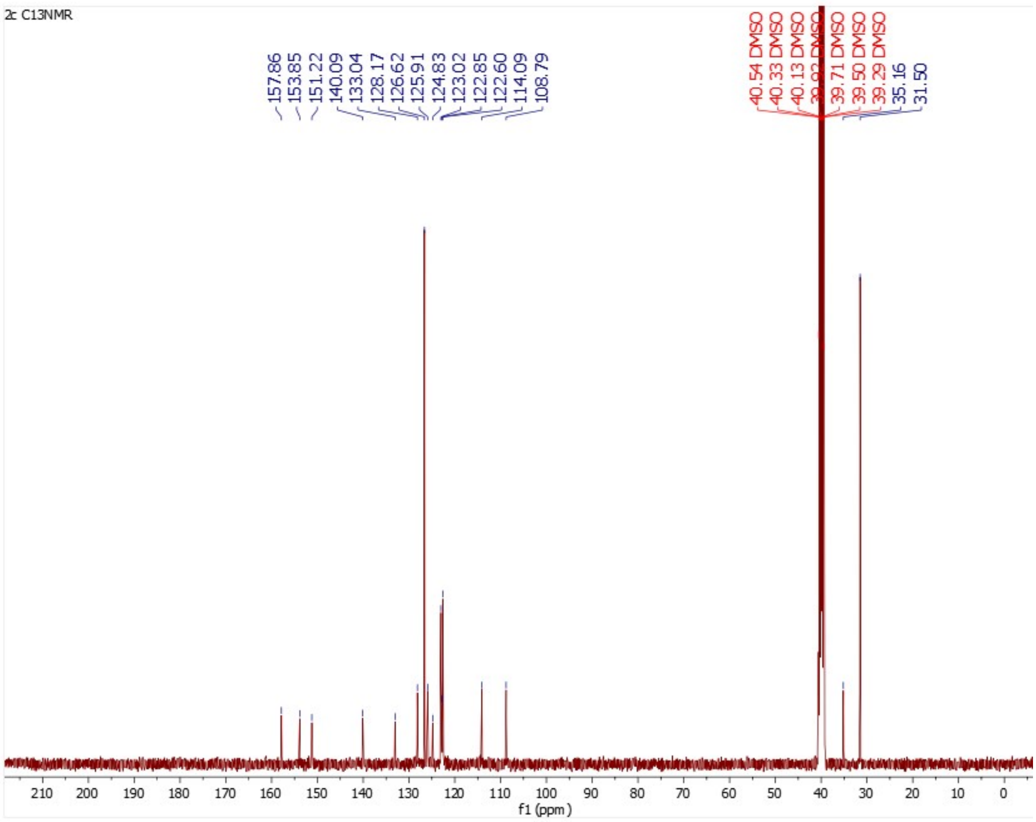
7
6
5
4
3
2
1
0
f1 (ppm)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128.17
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122.60
114.09
108.79
40.54 DMSO
40.33 DMSO
40.13 DMSO
39.92 DMSO
39.71 DMSO
39.50 DMSO
39.29 DMSO
35.16
31.50
210
200
190
180
170
160
150
140
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110
100
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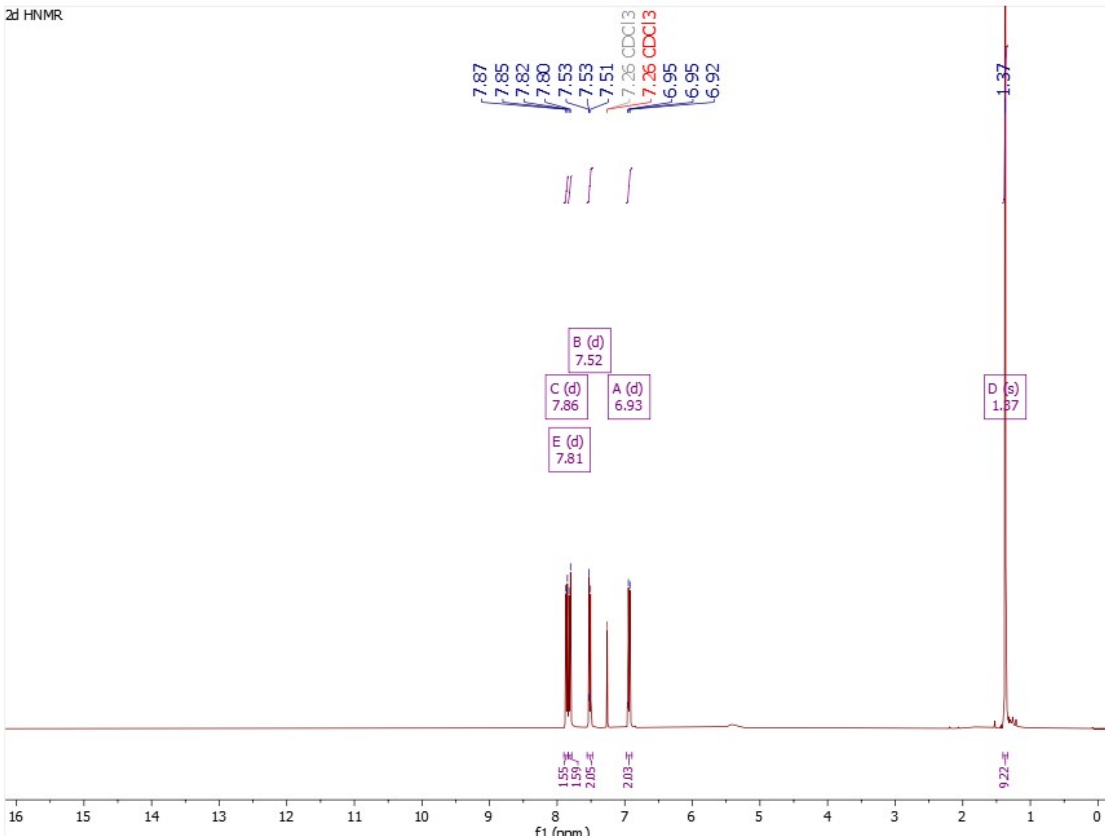
50
40
30
20
10
0
f1 (ppm)

2d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7.85
7.82
7.80
7.53
7.53
7.51
7.26 CDCl3
7.26 CDCl3
6.95
6.95
6.92
1.37
B (d)
7.52
C (d)
7.86
A (d)
6.93
E (d)
7.81
D (s)
1.37
1.55
1.59
2.05
2.03
9.22
16
15
14
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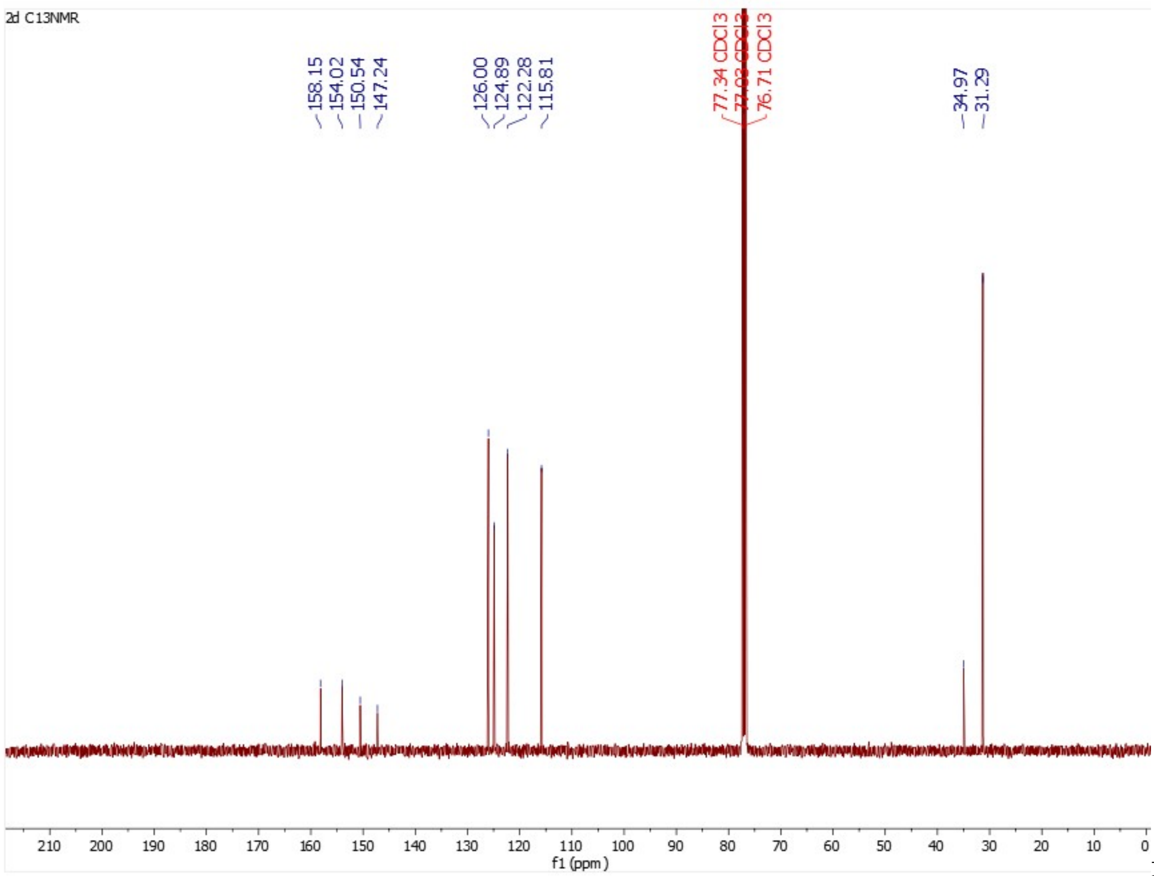
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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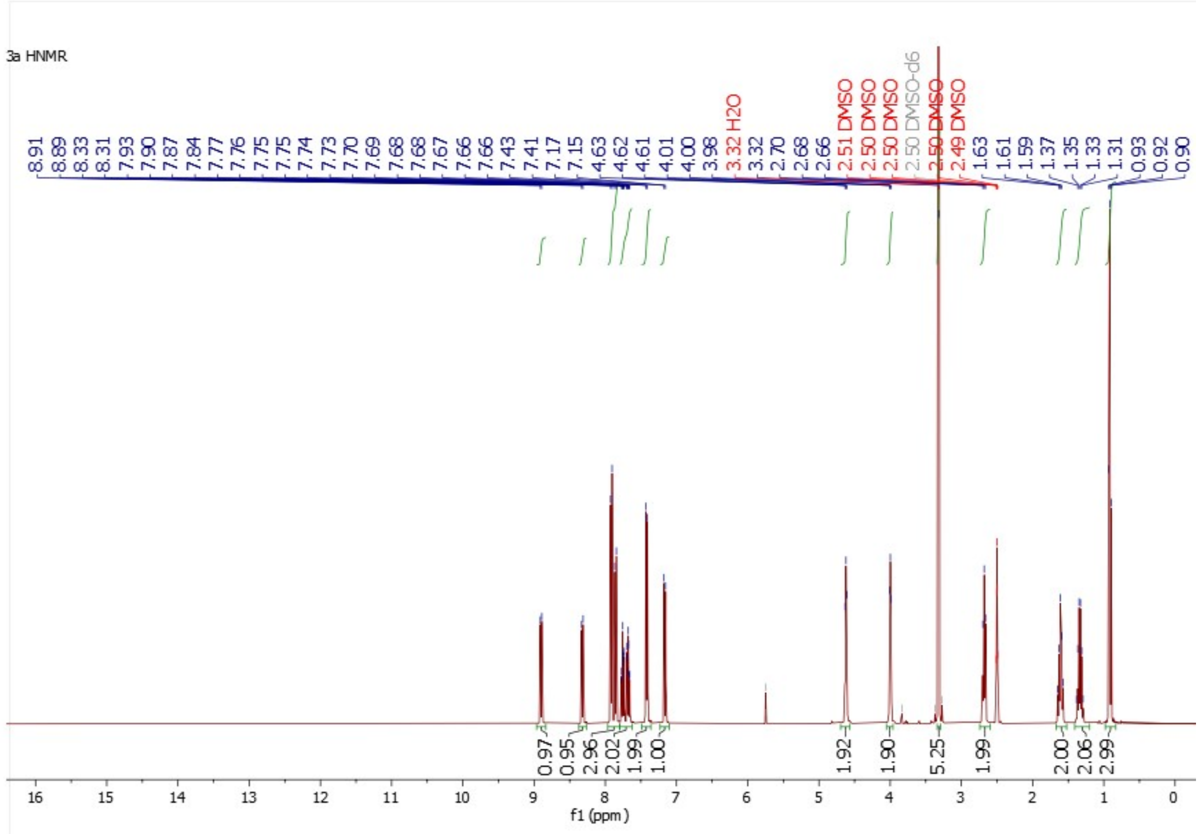
126.00
124.89
122.28
115.81
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
34.97
31.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

f

3a



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3.32 H2O
3.32 2.70 2.68 2.66
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.49 DMSO
1.63 1.61 1.59 1.37 1.35 1.33 1.31 0.93 0.92 0.90
0.97 0.95 2.96 2.02 1.99 1.00 1.92 1.90 5.25 1.99 2.00 2.06 2.99
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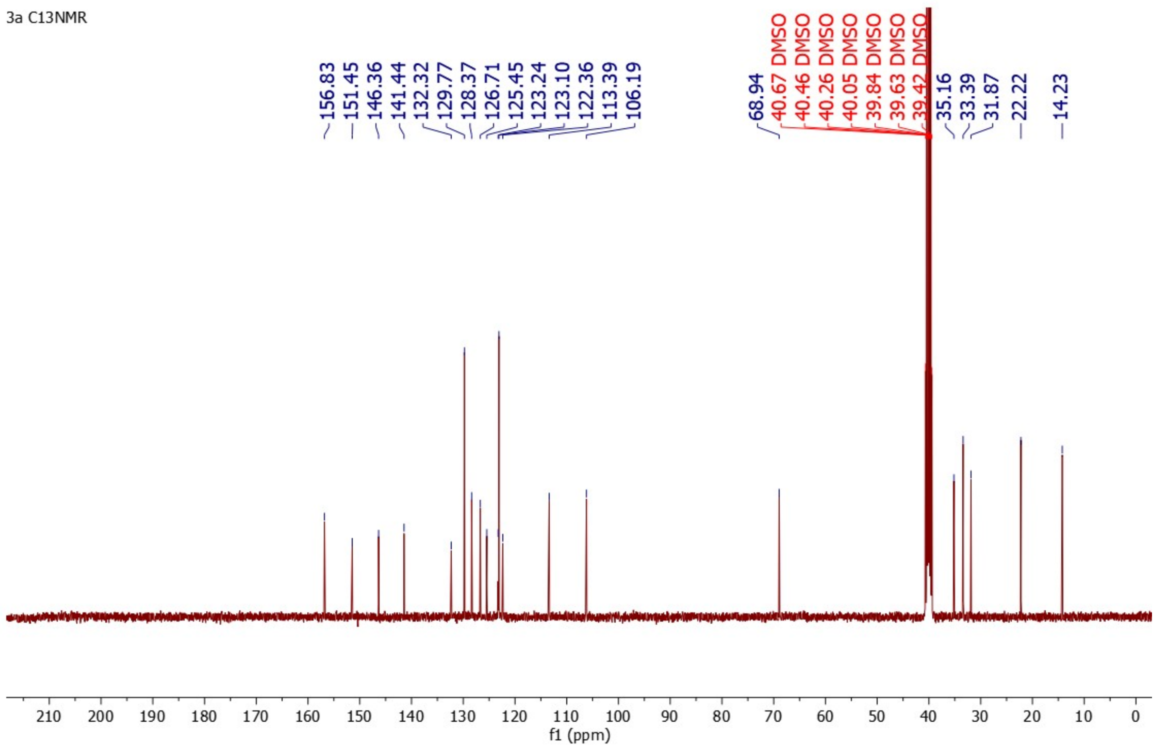
f1 (ppm)



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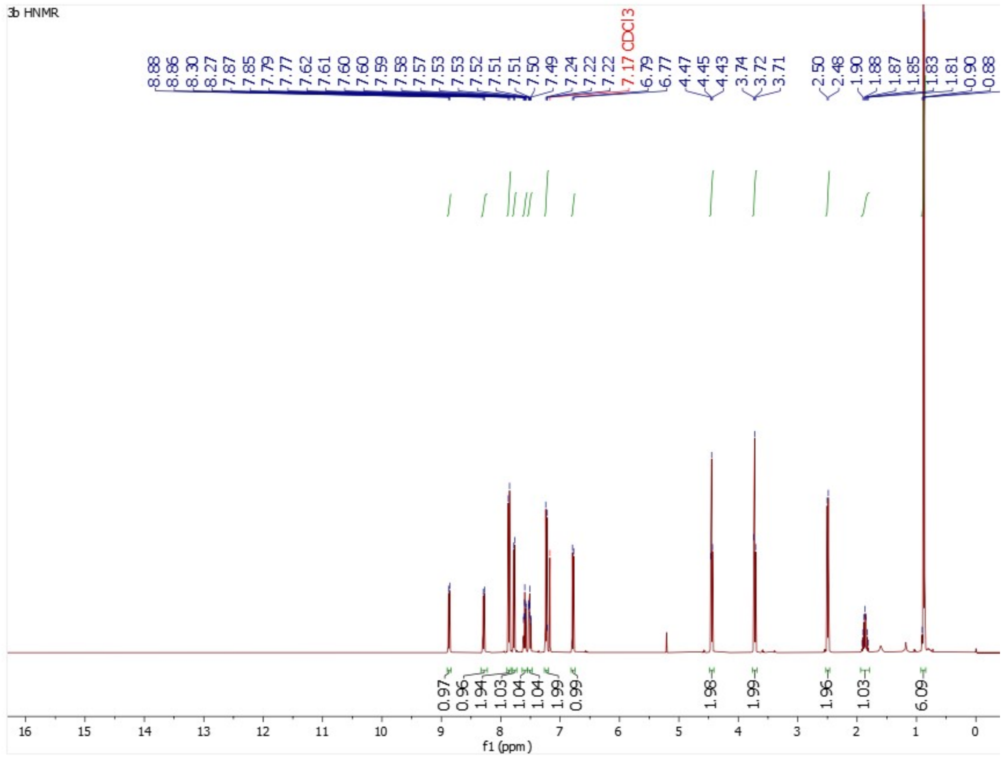
68.94
40.67 DMSO
40.46 DMSO
40.26 DMSO
40.05 DMSO
39.84 DMSO
39.63 DMSO
39.42 DMSO
35.16 33.39 31.87 22.22 14.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3b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7.60
7.59
7.58
7.57
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.24
7.22
7.22
7.17 CDCl3
6.79
6.77
4.47
4.45
4.43
3.74
3.72
3.71
2.50
2.48
1.90
1.88
1.87
1.85
1.83
1.81
0.90
0.88
0.97
0.96
1.94
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1.04
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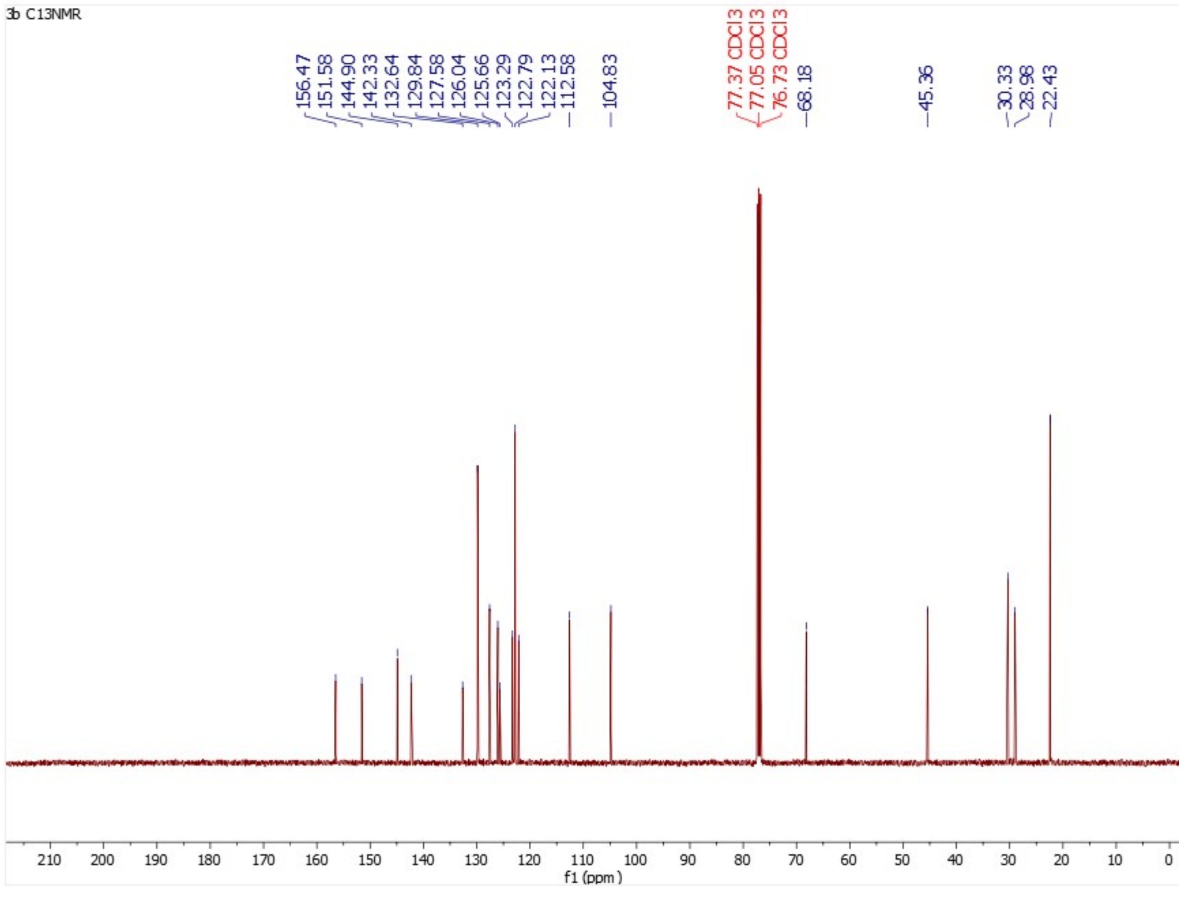
1.96
1.03
6.09
f1 (ppm)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122.13
112.58
104.83
77.37 CDCl3
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76.73 CDCl3
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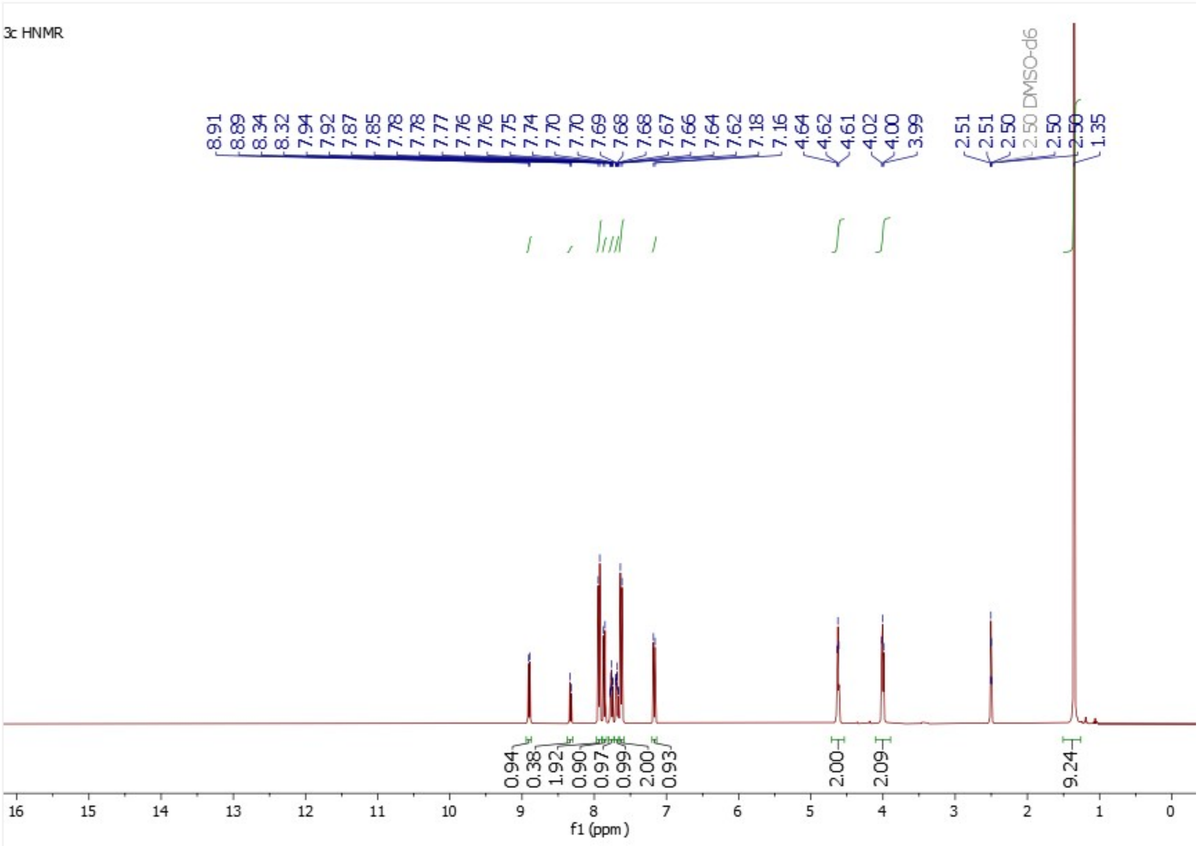
30.33
28.98
22.43
f1 (ppm)

3c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7.76
7.76
7.75
7.74
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.64
7.62
7.18
7.16
4.64
4.62
4.61
4.02
4.00
3.99
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2.51
2.50
2.50 DMSO-d6
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2.50
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0.93
2.00
2.09
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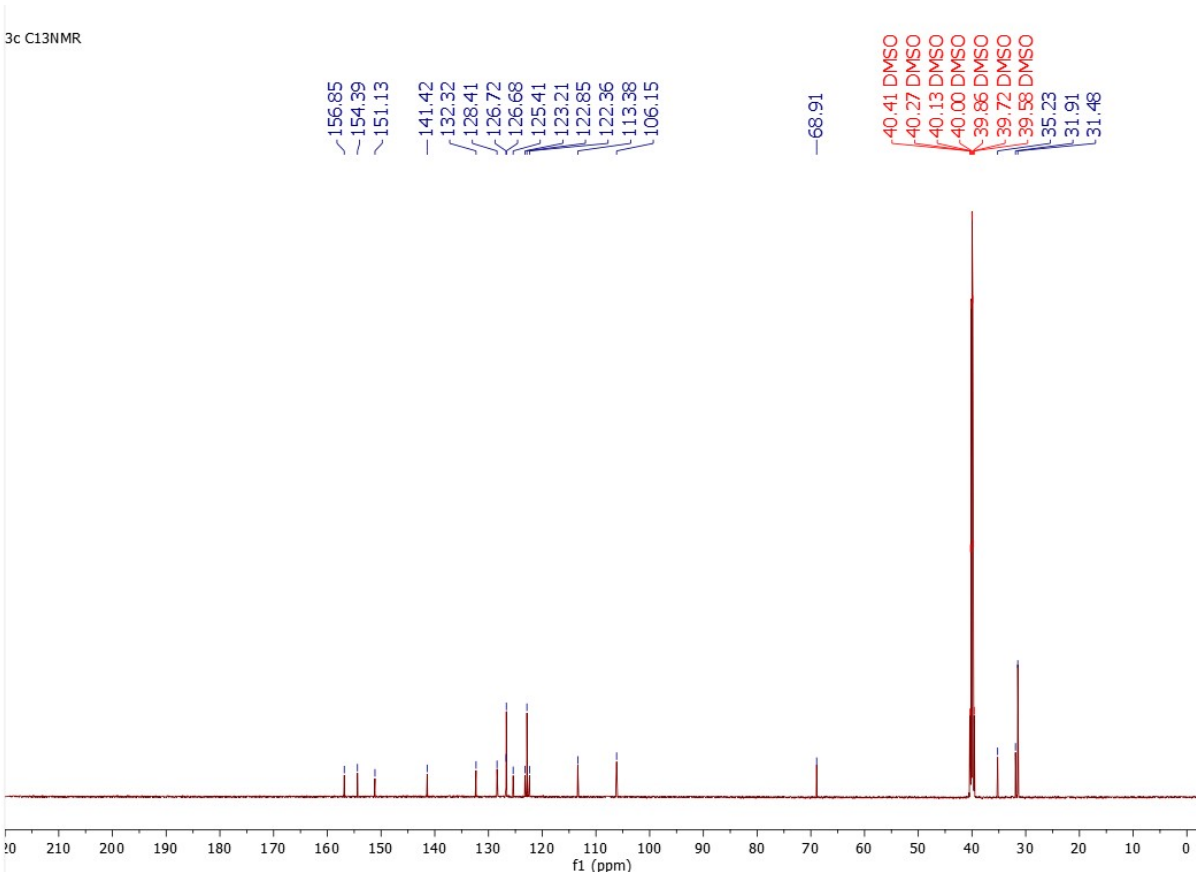
f1 (ppm)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122.85
122.36
113.38
106.15
68.91
40.41 DMSO
40.27 DMSO
40.13 DMSO
40.00 DMSO
39.86 DMSO
39.72 DMSO
39.58 DMSO
35.23
31.91
31.48
210
200
190
180
170
160
150
140
130
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110
100
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80
70
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50
40
30
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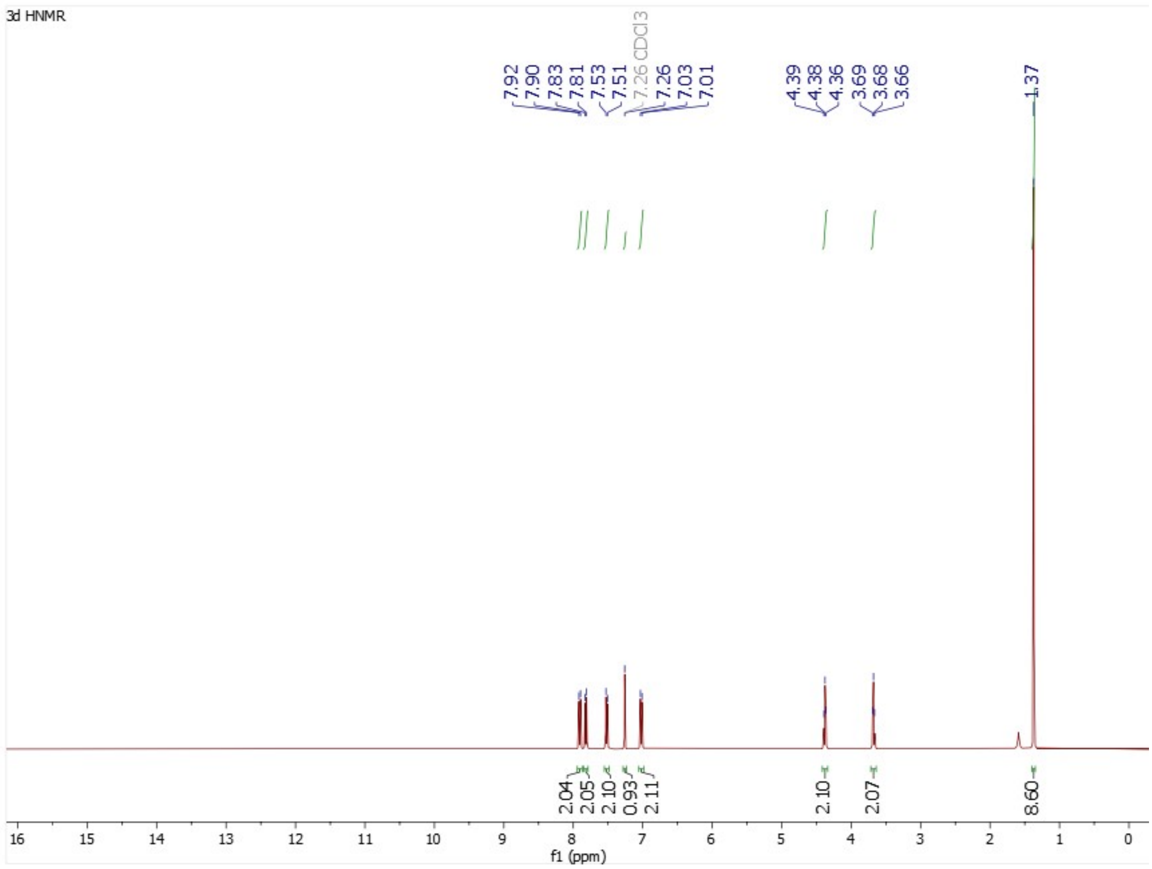
10
0
f1 (ppm)

3d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7.26 CDCl3
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7.01
4.39
4.38
4.36
3.69
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2.10
2.07
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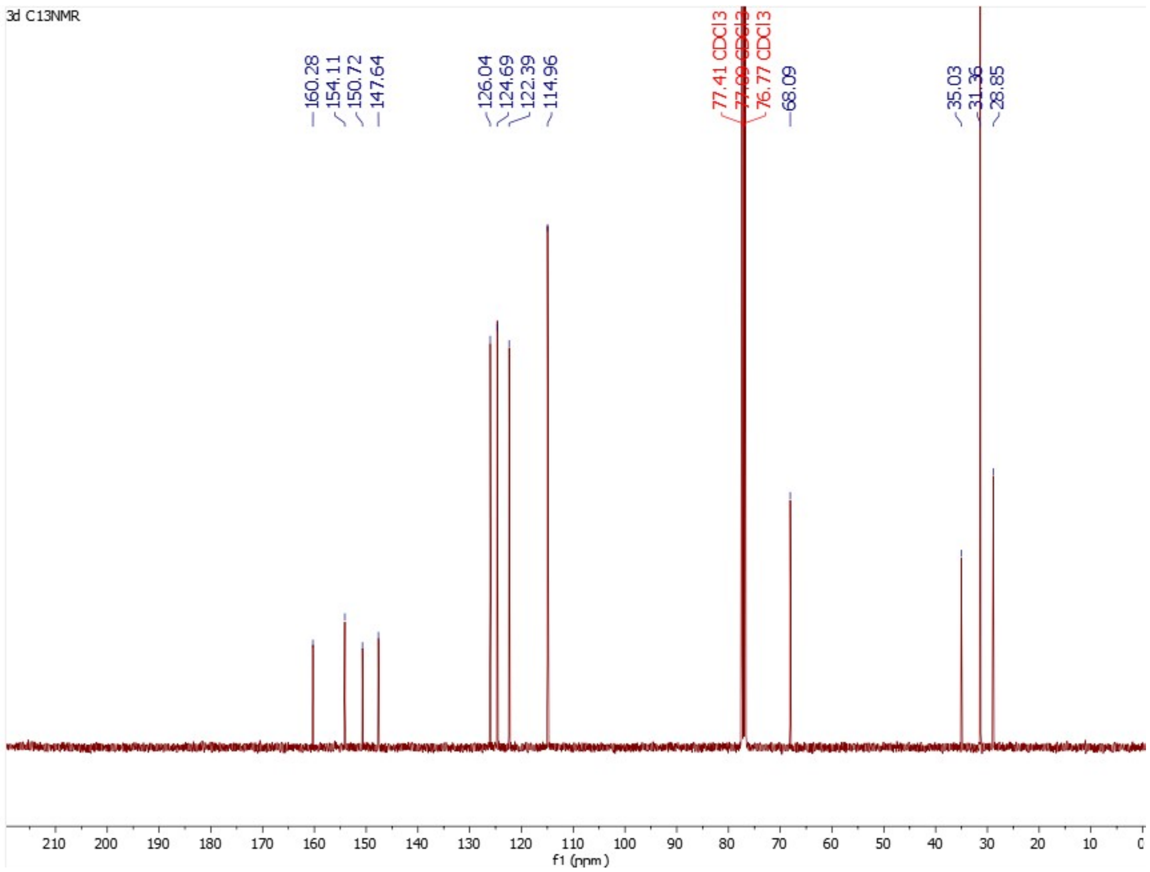
f1 (ppm)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122.39
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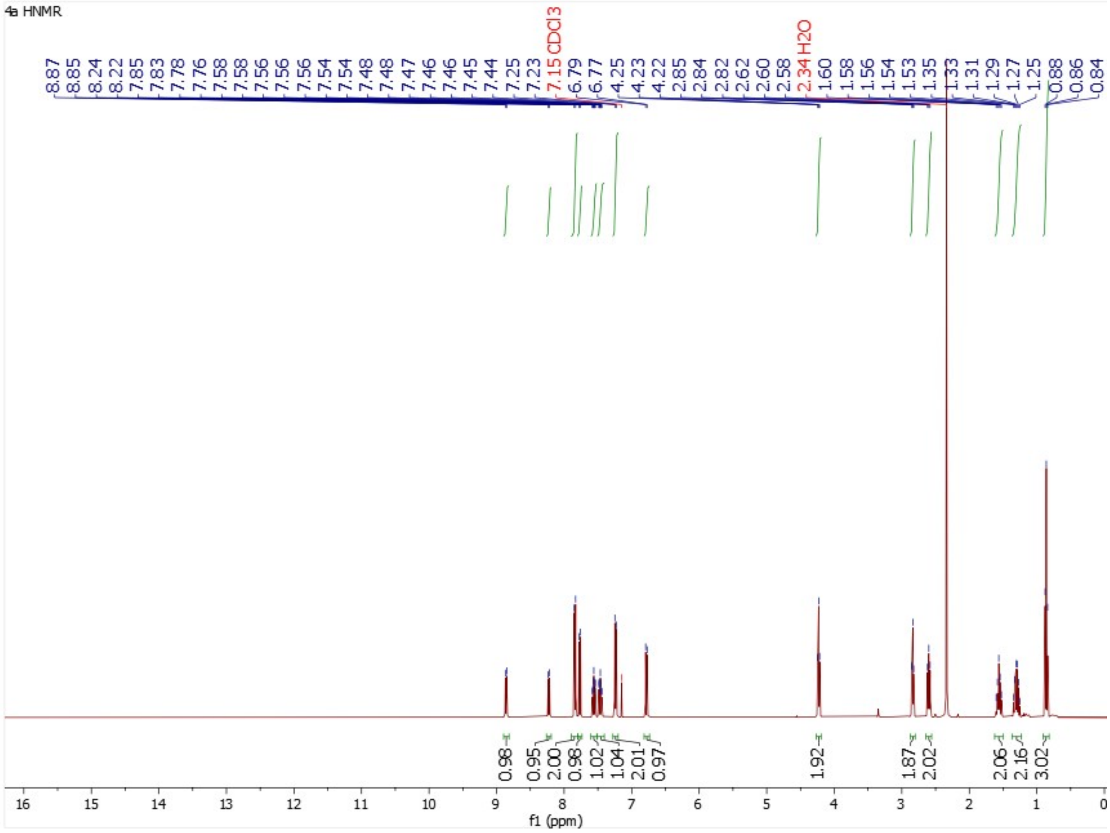
76.77 CDCl3
68.09
35.03
31.36
28.85
f1 (ppm)

4a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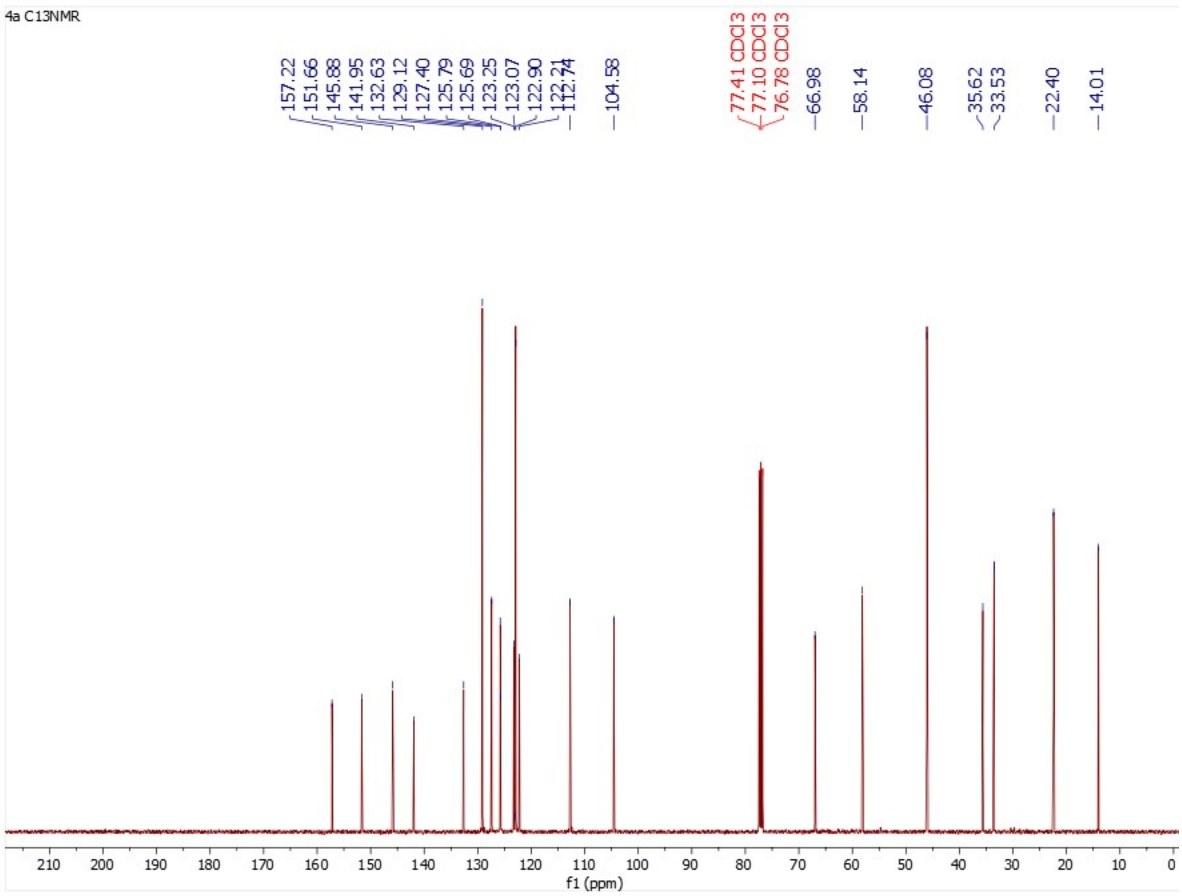
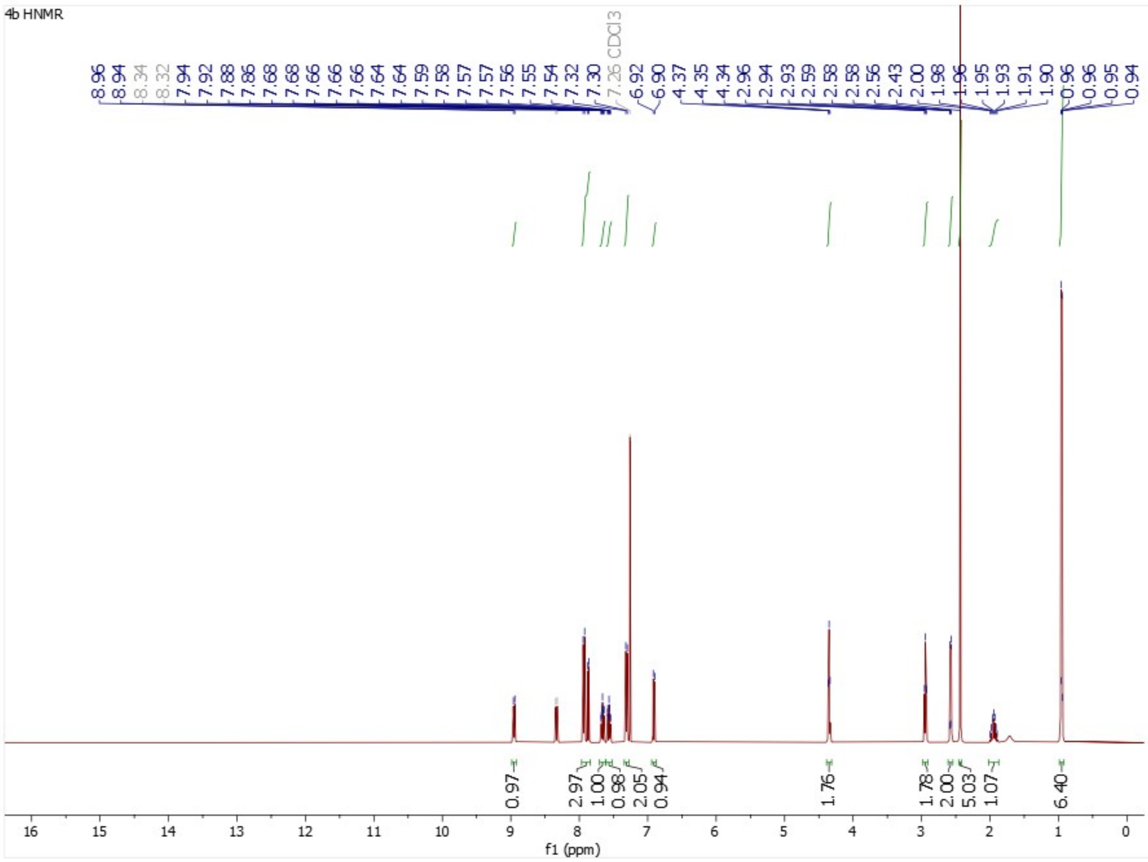
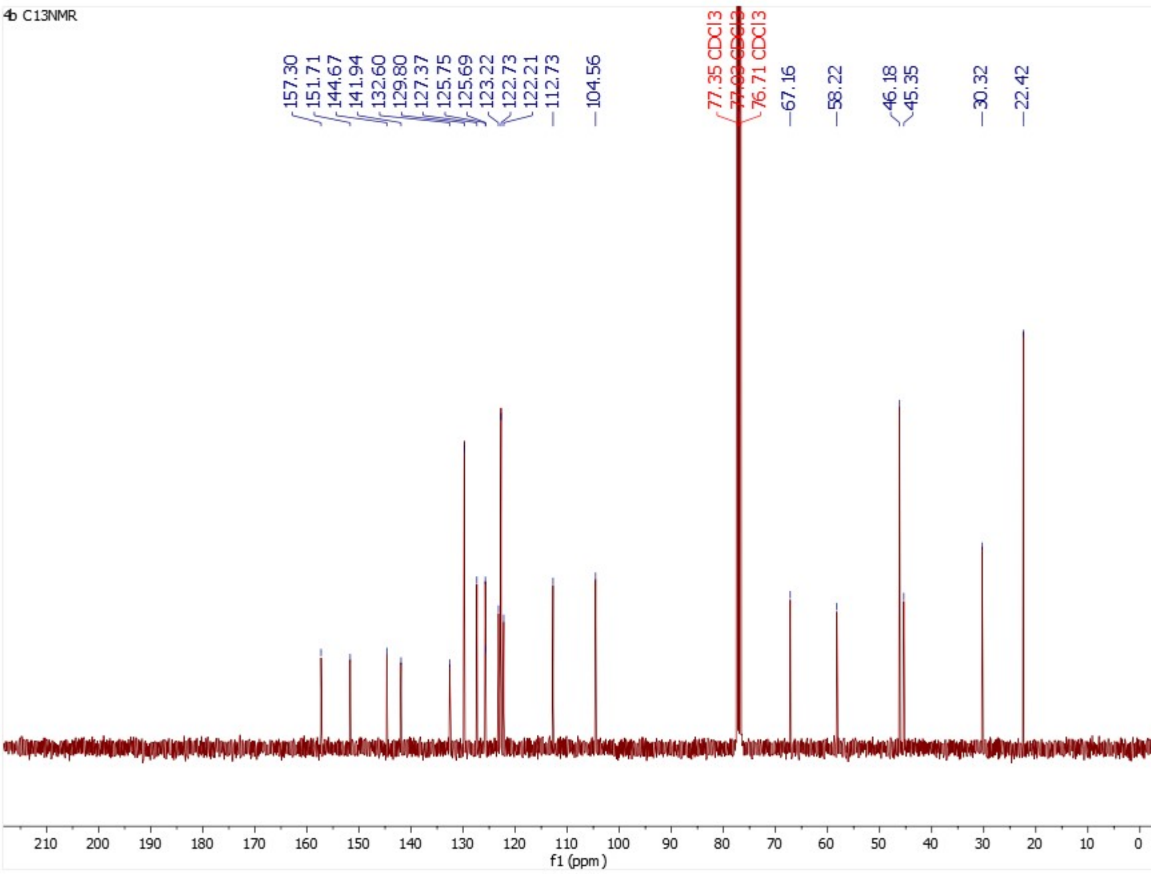
7.56
7.54
7.54
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.25
7.23
7.15 CDCl3
6.79
6.77
4.25
4.23
4.22
2.85
2.84
2.82
2.62
2.60
2.58
2.34 H2O
1.60
1.58
1.56
1.54
1.53
1.35
1.33
1.31
1.29
1.27
1.25
0.88
0.86
0.84
0.98
0.95
2.00
0.98
1.02
1.04
2.01
0.97
1.92
1.87
2.02
2.06
2.16
3.02
f1 (ppm)

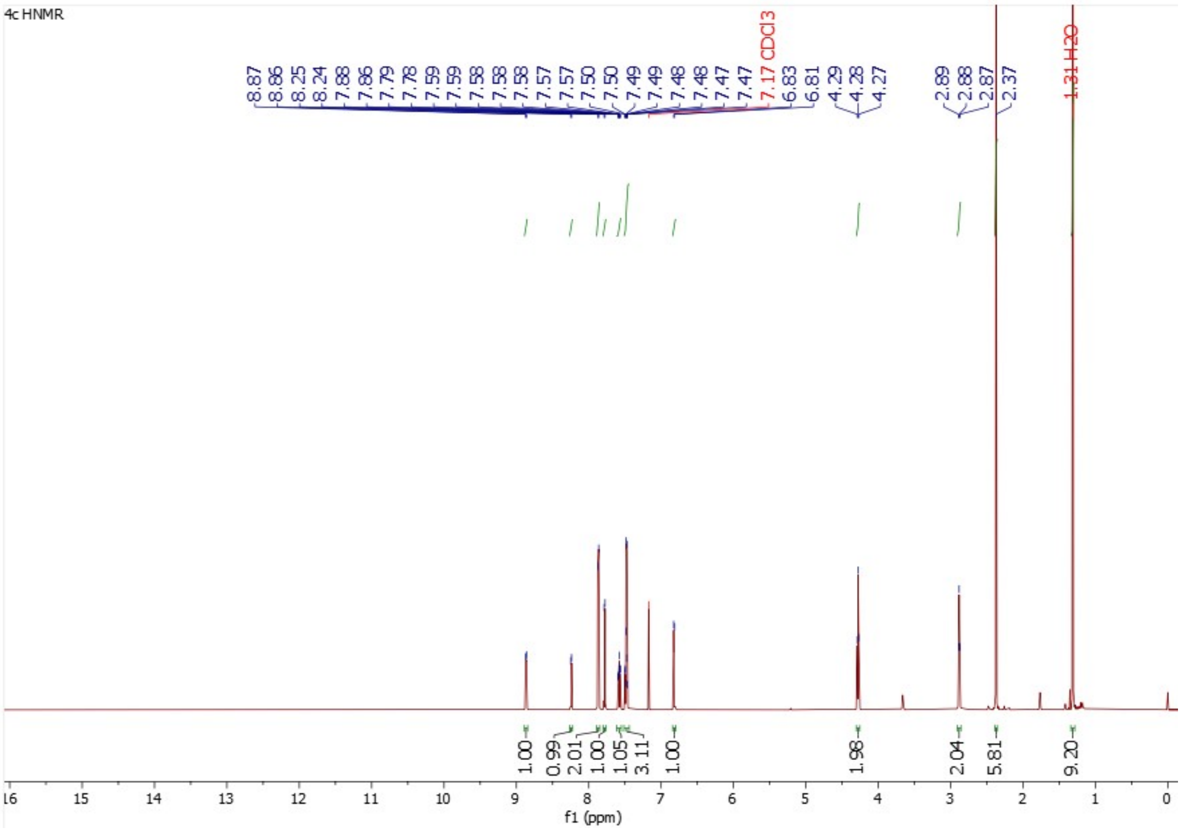

4a C13NMR
157.22
151.66
145.88
141.95
132.63
129.12
127.40
125.79
125.69
123.25
123.07
122.90
122.21
112.74
104.58
77.41 CDCl3
77.10 CDCl3
76.78 CDCl3
66.98
58.14
46.08
35.62
33.53
22.40
14.01
f1 (ppm)

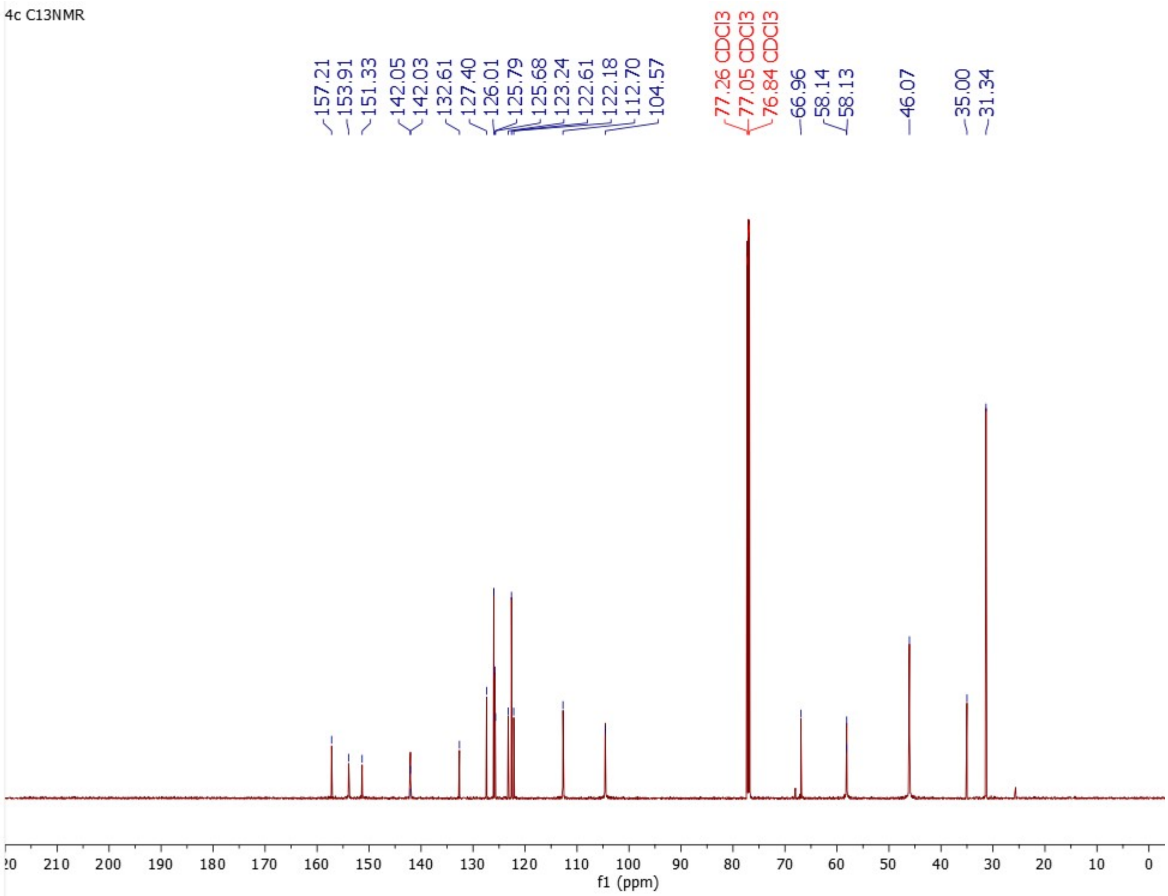
4b


4b HNMR
8.96
8.94
8.34
8.32
7.94
7.92
7.88
7.86
7.68
7.68
7.66
7.66
7.66
7.64
7.64
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.32
7.30
7.26 CDCl3
6.92
6.90
4.37
4.35
4.34
2.96
2.94
2.93
2.59
2.58
2.58
2.56
2.43
2.00
1.98
1.96
1.95
1.93
1.91
1.90
0.96
0.96
0.95
0.94
0.97
2.97
1.00
0.98
2.05
0.94
1.76
1.78
2.00
5.03
1.07
6.40
f1 (ppm)

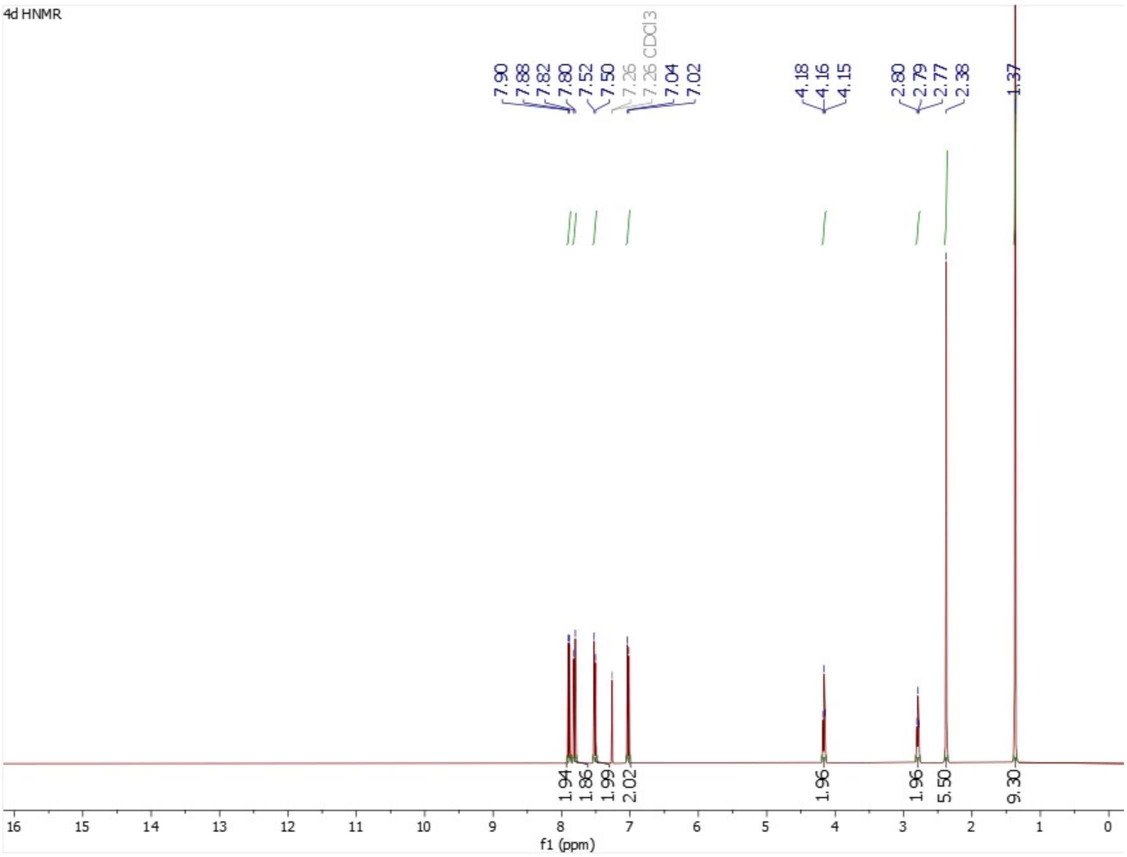

4b C13NMR
157.30
151.71
144.67
141.94
132.60
129.80
127.37
125.75
125.69
123.22
122.73
122.21
112.73
104.56
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
67.16
58.22
46.18
45.35
30.32
22.42
f1 (ppm)

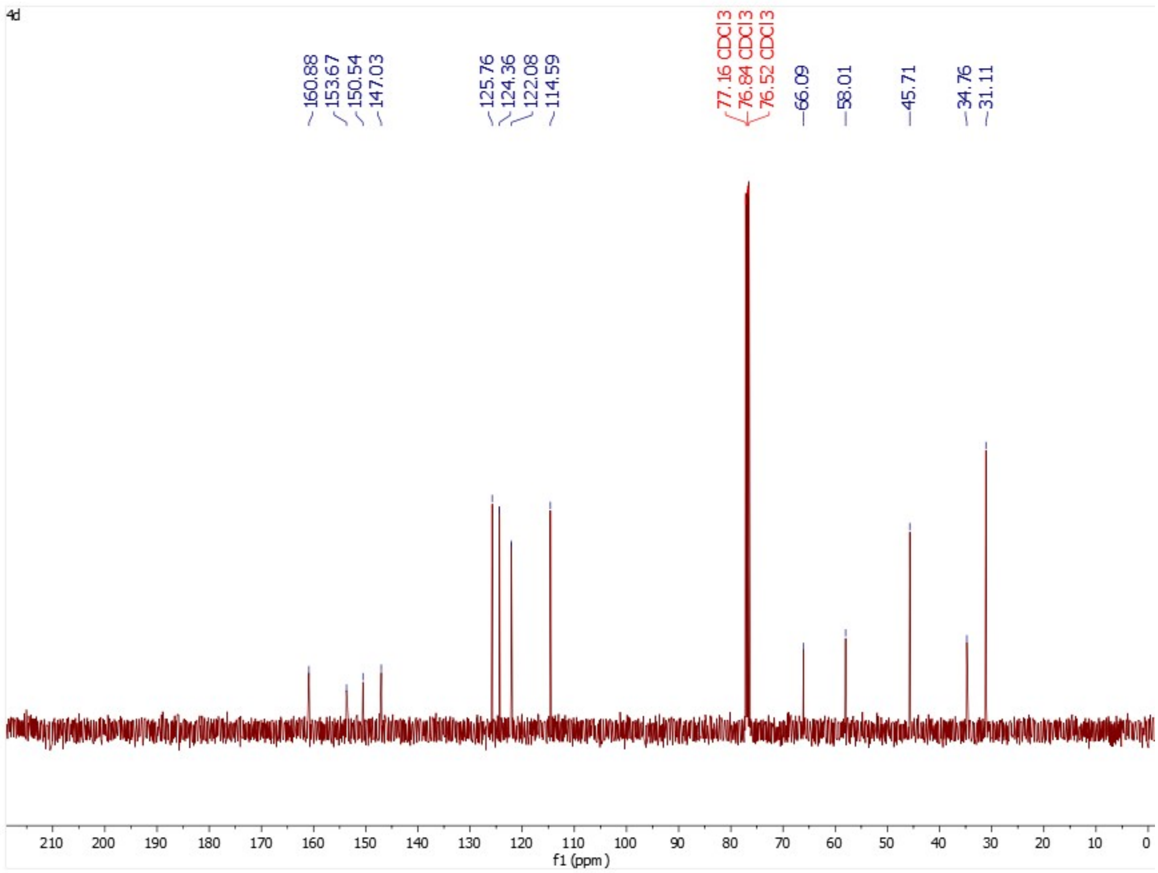
4c


4c HNMR
8.87
8.86
8.25
8.24
7.88
7.86
7.79
7.78
7.59
7.59
7.58
7.58
7.58
7.57
7.57
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.17 CDCl3
6.83
6.81
4.29
4.28
4.27
2.89
2.88
2.87
2.37
1.31 H2O
1.00
0.99
2.01
1.00
1.05
3.11
1.00
1.98
2.04
5.81
9.20
f1 (ppm)

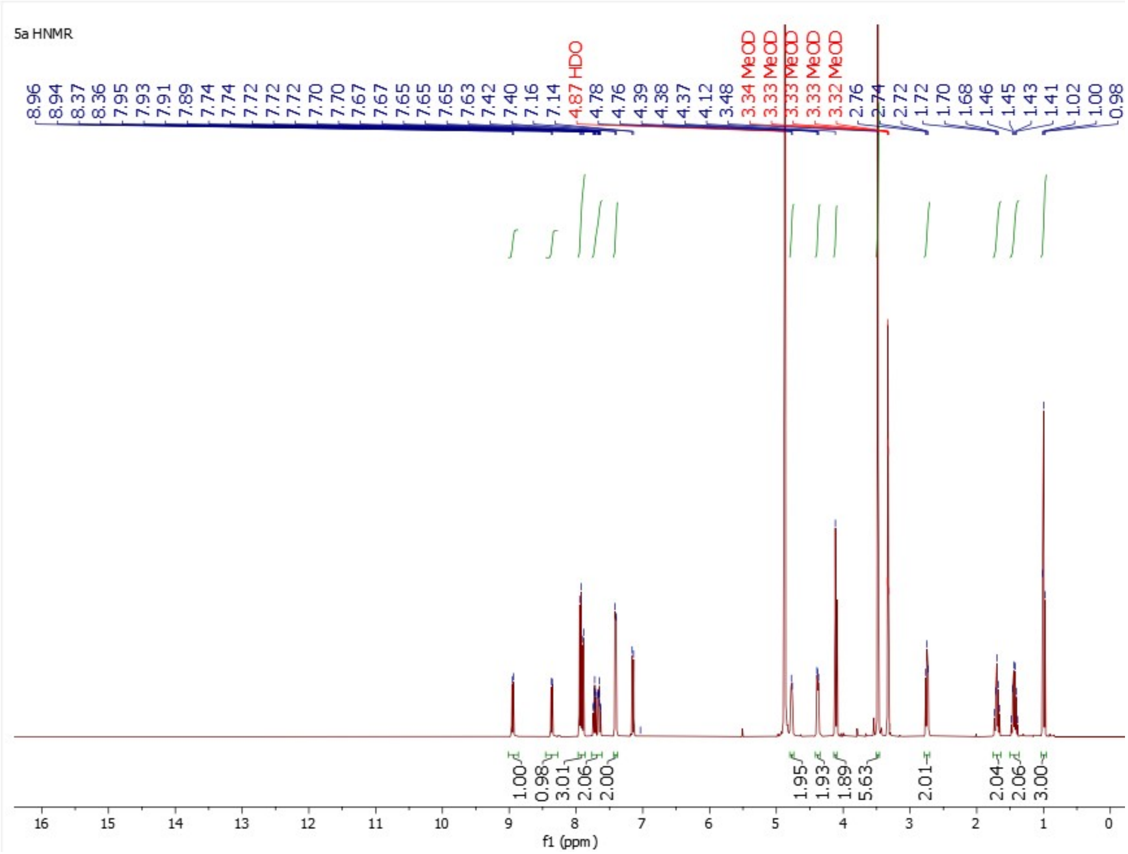

4c C13NMR
157.21
153.91
151.33
142.05
142.03
132.61
127.40
126.01
125.79
125.68
123.24
122.61
122.18
112.70
104.57
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
66.96
58.14
58.13
46.07
35.00
31.34
f1 (ppm)

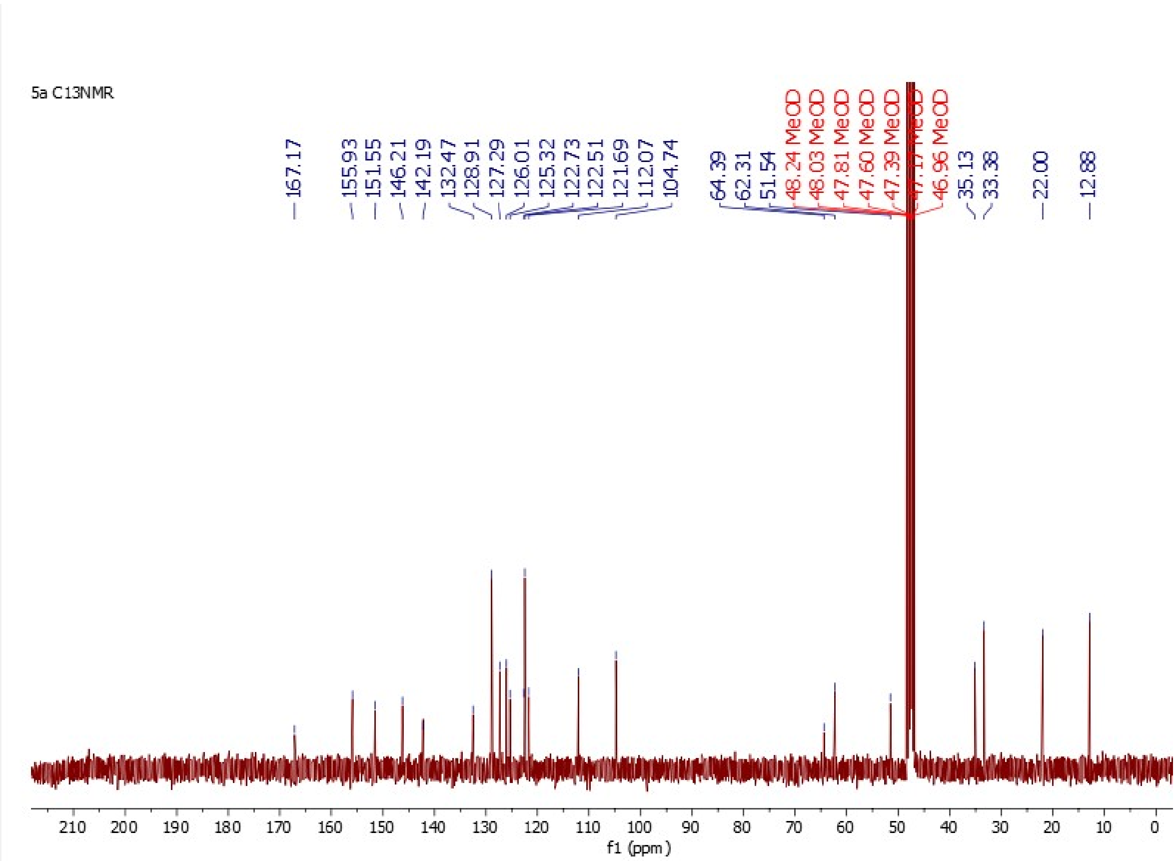
4d


4d HNMR
7.90
7.88
7.82
7.80
7.52
7.50
7.26
7.26 CDCl3
7.04
7.02
4.18
4.16
4.15
2.80
2.79
2.77
2.38
1.37
1.94
1.86
1.99
2.02
1.96
1.96
5.50
9.30
f1 (ppm)

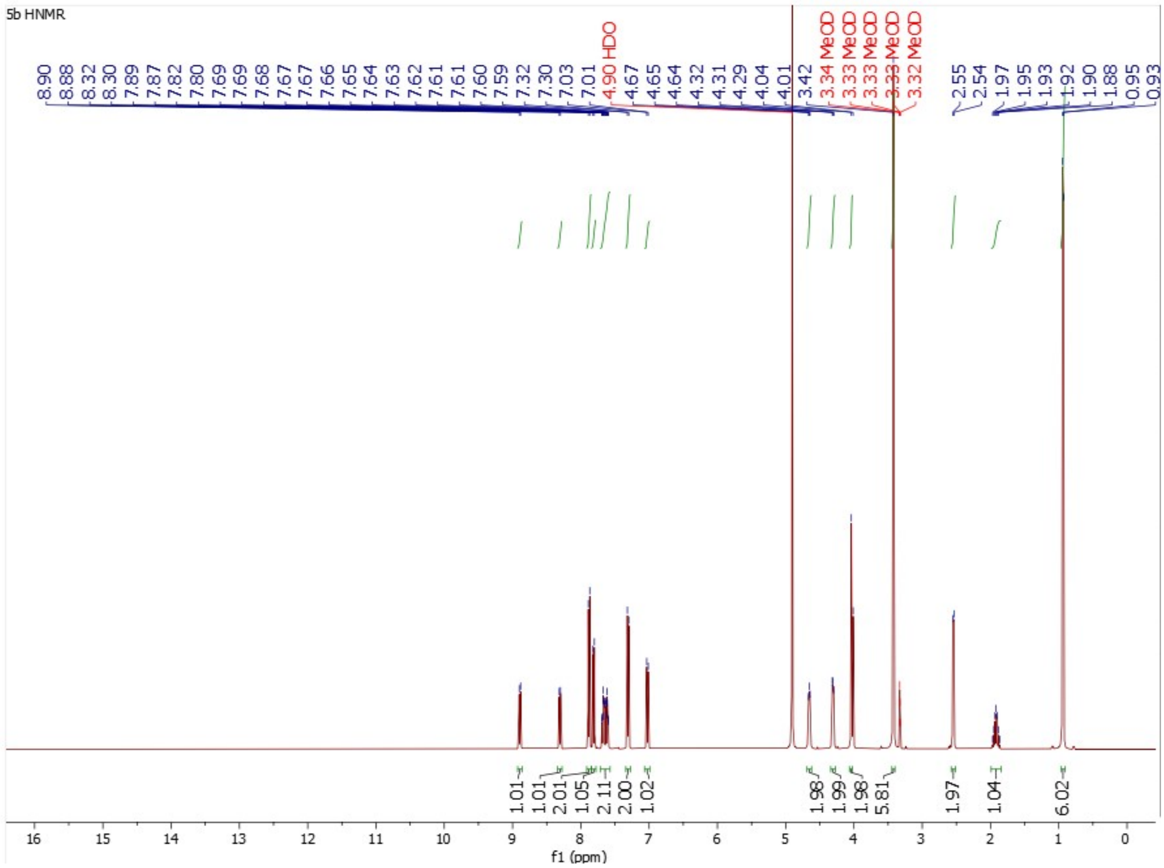

4d
160.88
153.67
150.54
147.03
125.76
124.36
122.08
114.59
77.16 CDCl3
76.84 CDCl3
76.52 CDCl3
66.09
58.01
45.71
34.76
31.11
f1 (ppm)

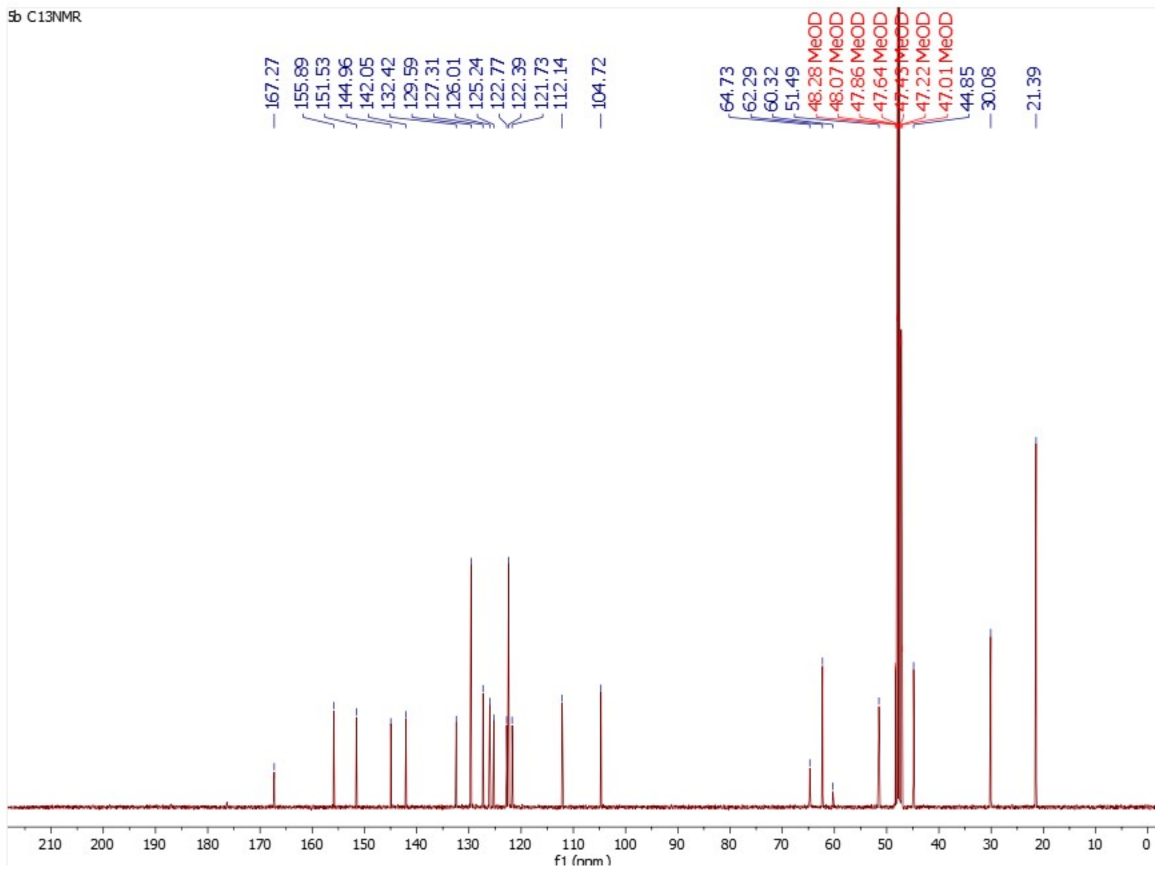
5a


5a HNMR
8.96
8.94
8.37
8.36
7.95
7.93
7.91
7.89
7.74
7.72
7.72
7.72
7.70
7.67
7.67
7.65
7.65
7.65
7.63
7.42
7.40
7.16
7.14
4.87 HDO
4.78
4.76
4.39
4.38
4.37
4.12
3.48
3.34 MeOD
3.33 MeOD
3.33 MeOD
3.33 MeOD
3.32 MeOD
2.76
2.74
2.72
1.72
1.70
1.68
1.46
1.45
1.43
1.41
1.02
1.00
0.98
1.00
0.98
3.01
2.06
2.00
1.95
1.93
1.89
5.63
2.01
2.04
2.06
3.00
f1 (ppm)

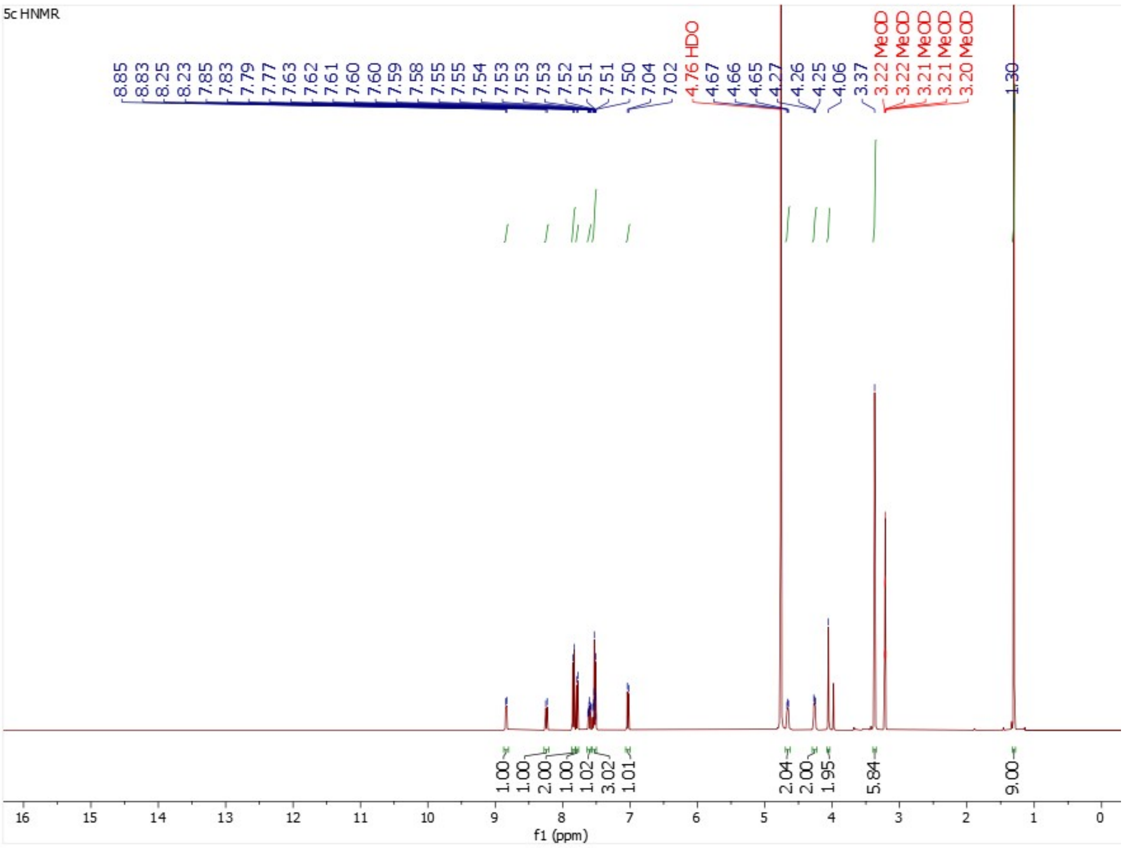

5a C13NMR
167.17
155.93
151.55
146.21
142.19
132.47
128.91
127.29
126.01
125.32
122.73
122.51
121.69
112.07
104.74
64.39
62.31
51.54
48.24 MeOD
48.03 MeOD
47.81 MeOD
47.60 MeOD
47.39 MeOD
47.17 MeOD
46.96 MeOD
35.13
33.38
22.00
12.88
f1 (ppm)

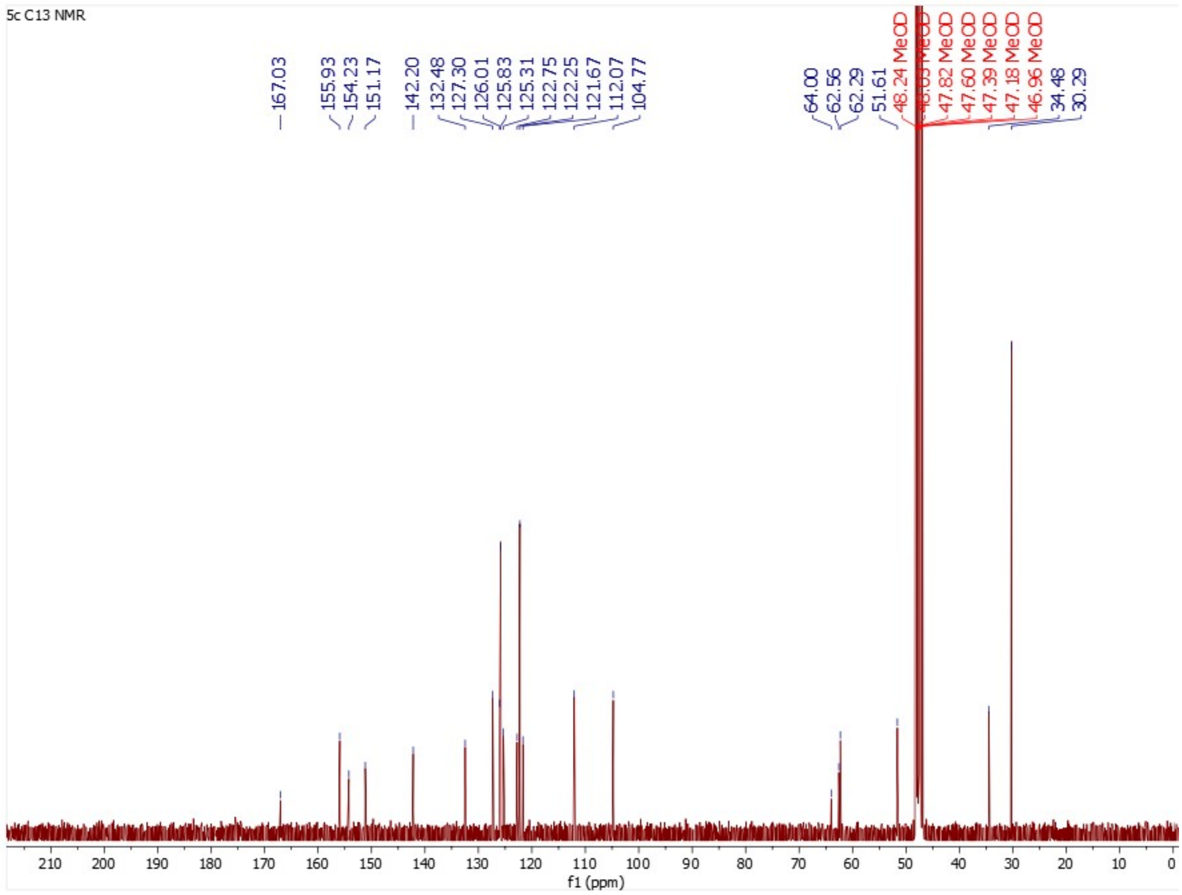
5b



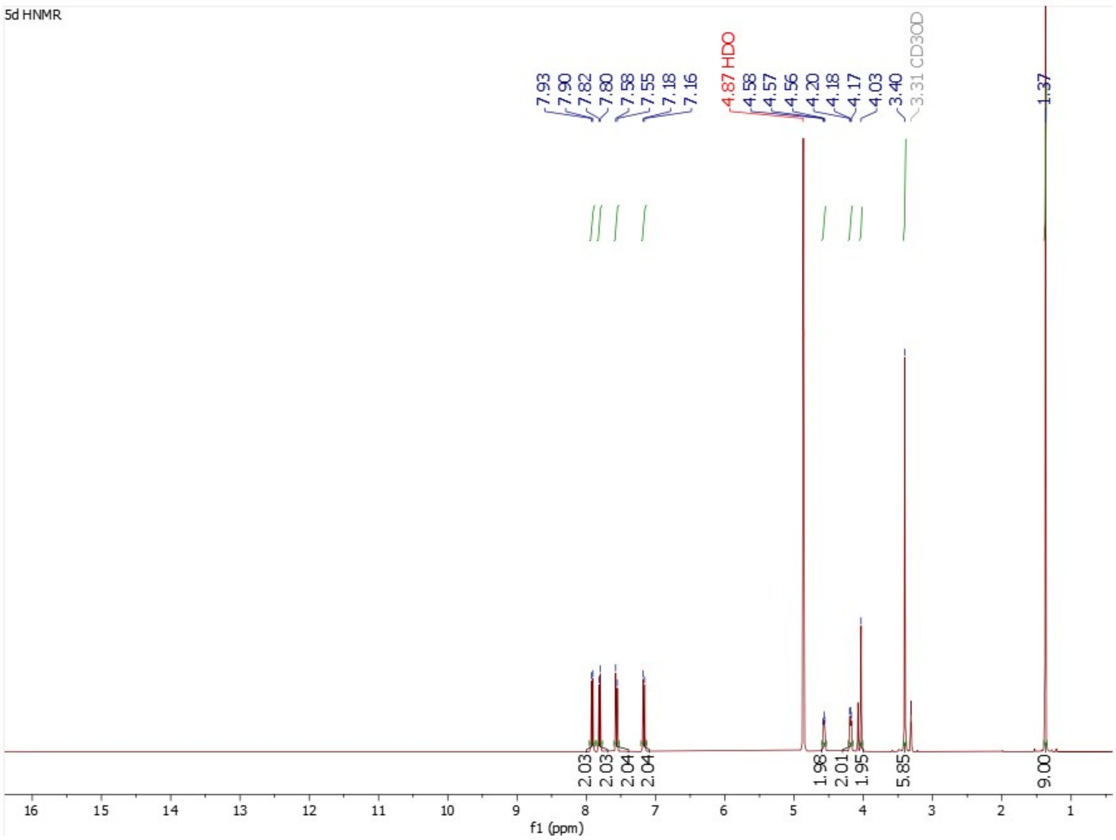


5c

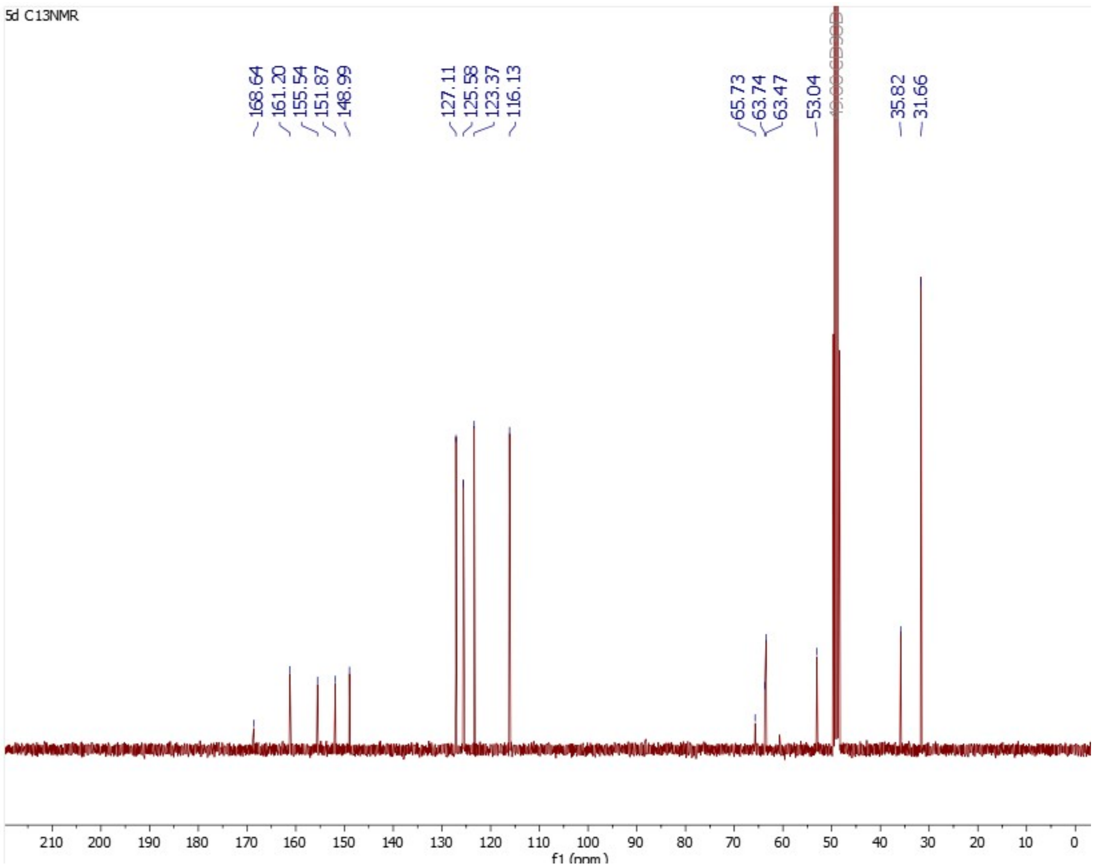




5d



5d HNMR
7.93
7.90
7.82
7.80
7.58
7.55
7.18
7.16
4.87 HDO
4.58
4.57
4.56
4.20
4.18
4.17
4.03
3.40
3.31 CD3OD
1.37
2.03
2.03
2.04
2.04
1.98
2.01
1.95
5.85
9.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)



5d C13NMR
168.64
161.20
155.54
151.87
148.99
127.11
125.58
123.37
116.13
65.73
63.74
63.47
53.04
35.82
31.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

References

1. Butler, C. S.; Giles, L. W.; Sokolova, A. V.; de Campo, L.; Tabor, R. F.; Tuck, K. L., Structure–Performance Relationships for Tail Substituted Zwitterionic Betaine–Azobenzene Surfactants. *Langmuir* **2022**.
2. Zimmerman, G.; Chow, L.-Y.; Paik, U.-J., The photochemical isomerization of azobenzene. *Journal of the American Chemical Society* **1958,** *80* (14), 3528-3531.
3. Beharry, A. A.; Woolley, G. A., Azobenzene photoswitches for biomolecules. *Chemical Society Reviews* **2011,** *40* (8), 4422-4437.