Cyclopentannulation and Cyclodehydrogenation of Isomerically Pure 5,11-Dibromo-Anthradithiophenes leading to Contorted Aromatics

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1. UV-Vis Photooxidation

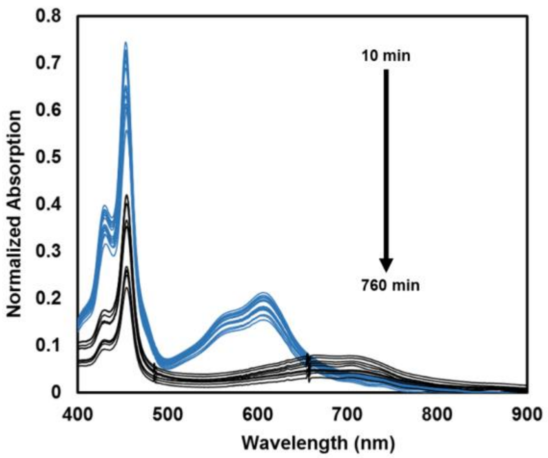


Figure S1. Photodegradation of CP-pentacene **3** (black) and **11** (blue) at 15 μM in oxygenated THF over 760 min.

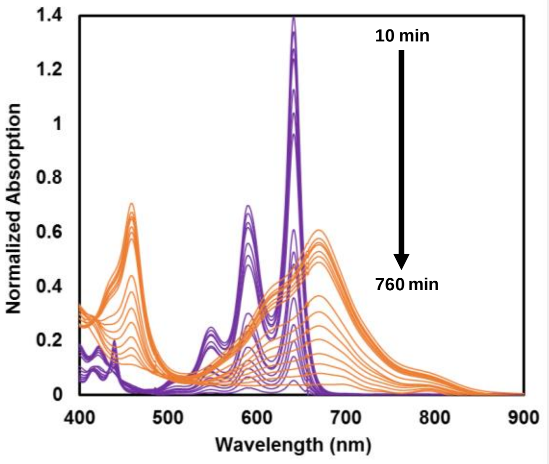


Figure S2. Photodegradation of TIPS-pentacene **TIPS-Pentacene** (purple) and **4** (orange) at 15 μM in oxygenated THF over 760 min.

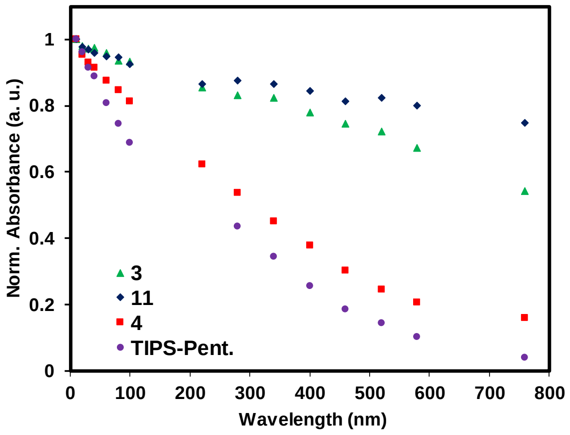


Figure S3. **P**hotodegradation of **3**, **11**, **4**, and TIPS-pentacene in THF (15 μM).

2. DFT Calculated HOMO and LUMO Contours

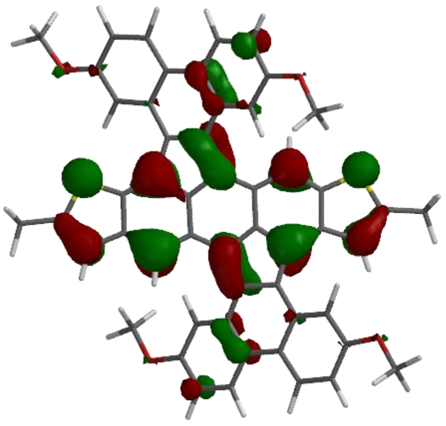


Figure S4. The B3LYP/6-311g(d,p) DFT calculated HOMO contour of **4**.

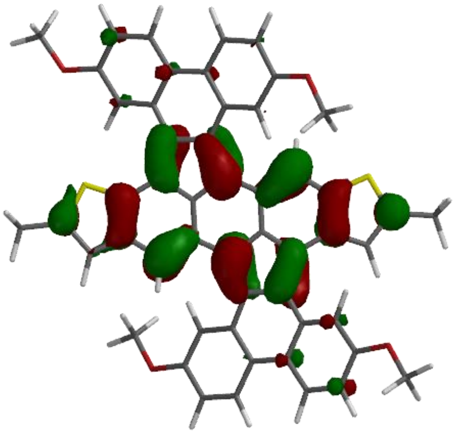
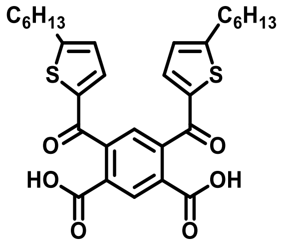


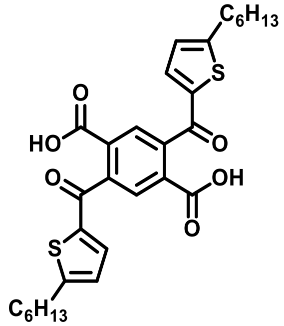
Figure S5. The B3LYP/6-311g(d,p) DFT calculated LUMO contour of **4**.

2. Experimental Procedures

Unless otherwise noted, all reagents were used as received and all reactions were carried out under an argon atmosphere. Column chromatography was performed on a chromatographing system with normal phase silica columns. ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz station at room temperature, unless otherwise noted.



5a

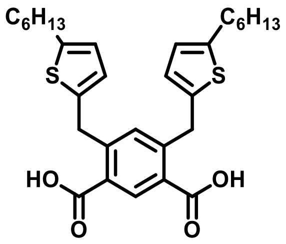


5b

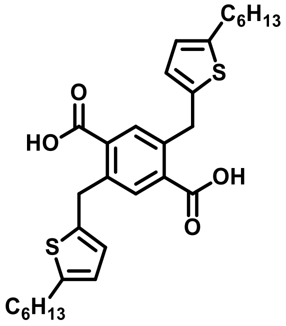
4,6-i(5-hexylthiophene-2-carbonyl)isophthalic Acid (5a) and 2,5-di(5-hexylthiophene-2-carbonyl)terephthalic Acid (5b): To the mixture of pyromellitic dianhydride (2.53 g, 11.6 mmol) and $AlCl_3$ (6.19 g, 46.4 mmol) in 1,2-dichloroethane (80 ml) was added 2-hexylthiophene (3.9 g, 23.2 mmol) slowly at 0 °C and stirred for 1 h. The reaction mixture was then heated to reflux overnight. After cooling, the reaction was transferred into ice water containing conc. HCl and extracted with $CHCl_3$. The combined organic extracts were evaporated in vacuo to give a beige solid as a mixture of meta-/para-isomers (5.1 g, 79%). The meta-/para-isomers are formed in a ratio of ca. 1:1 determined by NMR spectroscopy. The isomers were separated by taking advantage of the solubility characteristics in 80% acetic acid. The para-isomer is less soluble in 80% acetic acid and precipitated on recrystallization. The meta-isomer could be obtained from the filtrate by removing the solvents or by precipitating by adding water to the filtrate. In some cases, the recrystallization process did not fully purify a given isomer. If this was the case, the compound was carried forward to **7a** or **7b** where column chromatography could separate out the minor isomer.

5a: ^{1}H NMR (400 MHz, DMSO) δ 13.62 (bs, 1H), 8.45 (s, 1H), 7.59 (s, 1H), 7.20 (d, *J* = 3.8 Hz, 2H), 6.92 (d, *J* = 3.8 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 4H), 1.61 (m, 2H), 1.26 (s, 6H), 0.84 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 187.07, 166.12, 156.84, 144.02, 141.20, 136.40, 136.04, 131.51, 127.06, 126.86, 31.24, 30.30, 28.56, 22.45, 14.50, 14.17. LRMS (ES+) 553.1 HRMS: (ESI) m/z for $C_{30}H_{33}O_6S_2$ calc: 553.1719, found 553.1721.

5b: ^{1}H NMR (400 MHz, DMSO) δ 13.75 (s, 2H), 7.93 (s, 2H), 7.30 (d, *J* = 3.7 Hz, 2H), 6.98 (d, *J* = 3.6 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 4H), 1.65 (m,4H), 1.30 (s, 12H), 0.87 (t, *J* = 6.3 Hz, 6H).



6a

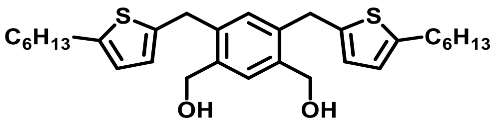


6b

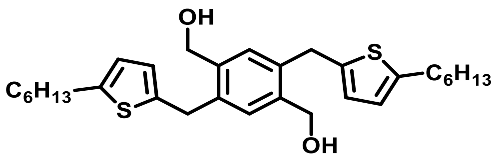
4,6-Bis((5-hexylthiophen-2-ylmethyl)isophthalic Acid (6a) and 2,5-Bis(5-hexylthiophen-2-ylmethyl)terephthalic Acid (6b): Each compound (1.62 g, 2.92 mmol of **5a**, 1.55 g, 2.79 mmol of **5b**) was dissolved in concentrated ammonium hydroxide, and zinc powder (20 equiv.) was added. The reaction mixture was then refluxed for 2 days with additional concentrated ammonium hydroxide added several times to maintain the solvent level. The cooled reaction mixture was poured into cold water and acidified with diluted HCl, filtered to remove zinc and extracted with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate and concentrated to give each product (1.45 g, 94% of **6a**, 1.43 g, 97% of **6b**) as a colorless solid.

6a: ^{1}H NMR (400 MHz, DMSO) δ 13.15 (s, 2H), 8.33 (s, 1H), 7.38 (s, 1H), 6.57 (s, 4H), 4.47 (s, 4H), 2.65 (t, *J* = 7.5 Hz, 4H), 1.52 (m, 4H), 1.25 (m, 6H), 0.84 (t, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 148.44, 144.87, 139.31, 126.14, 125.40, 125.23, 123.55, 123.37, 34.29, 32.11, 31.58, 31.02, 30.46, 30.17, 29.88, 28.83, 22.57, 14.61, 14.25, 13.88. HRMS: (ESI) m/z for $C_{30}H_{39}O_4S_2$ calc: 527.2290, found 527.2284.

6b: ^{1}H NMR (400 MHz, DMSO) δ 13.18 (s, 2H), 8.31 (s, 2H), 7.36 (s, 2H), 6.56 (s, 4H), 4.46 (s, 4H), 2.63 (t, *J* = 7.5 Hz, 4H), 1.50 (m, 4H), 1.23 (s, 8H), 0.82 (t, *J* = 6.3 Hz, 6H).



7a

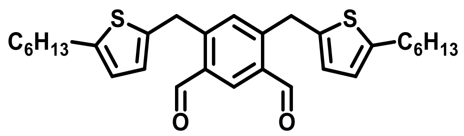


7b

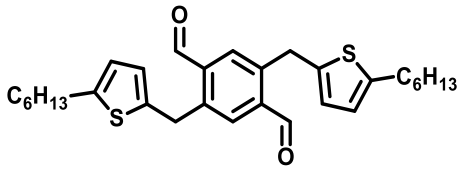
(4,6-Bis(5-hexylthiophen-2-ylmethyl)-1,3-phenylene)-dimethanol (7a) and (2,5-Bis(5-hexylthiophen-2-ylmethyl)-1,4-phenylene)-dimethanol (7b): To a solution of lithium aluminum hydride (6 equiv) in dry ether, each compound (924 mg, 1.75 mmol of **6a**, or 1.06 g, 2.00 mmol of **6b**) was added slowly at 0 °C. The reaction mixture was then stirred at room temperature overnight under argon. The reaction was then quenched by cautiously adding water and enough 10% HCl to dissolve the inorganic salts. The organic phase was collected and aqueous phase was extracted with diethyl ether. The combined organic layers were washed with water and dried over sodium sulfate and evaporated. The residue was purified by column chromatography with silica gel using 60% ethyl acetate in hexane to give each product (605 mg (69%) of **7a** as a beige solid, 800 mg (80%) of **7b** as a gray solid). The Rf values of each isomer on TLC plate were different when eluted with 60% ethyl acetate in hexane; Rf (**7a**) = 0.6 and Rf (**7b**) = 0.7. Column chromatography could be used at this stage if small impurities of a minor isomer was carried through the synthesis.

7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.16 (s, 1H), 6.54 (d, *J* = 3.4 Hz, 2H), 6.49 (d, *J* = 3.3 Hz, 2H), 4.68 (s, 4H), 4.14 (s, 4H), 2.70 (t, *J* = 7.7 Hz, 4H), 1.61 (p, *J* = 7.7 Hz, 4H), 1.29 (s, 6H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 144.61, 140.98, 137.82, 137.28, 124.53, 124.33, 123.52, 123.36, 32.83, 32.16, 31.60, 31.06, 30.48, 30.17, 29.86, 28.84, 22.59, 14.28, 13.91. HRMS: (ESI) m/z for $C_{30}H_{43}O_2S_2$ calc: 499.2626, found 499.2245.

7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 6.54 (d, *J* = 3.4 Hz, 2H), 6.51 (d, *J* = 3.4 Hz, 2H), 4.68 (s, 4H), 4.15 (s, 4H), 2.70 (m, 4H), 1.60 (m, 4H), 1.29 (s, 12H), 0.87 (t, *J* = 6.9 Hz, 6H).



8a

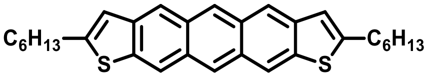


8b

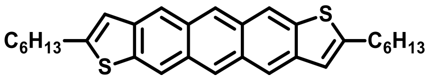
4,6-bis((5-hexylthiophen-2-yl)methyl)isophthalaldehyde (8a) and 2,5-bis((5-hexylthiophen-2-yl)methyl)terephthalaldehyde (8b): A solution of each compound (534 mg, 1.07 mmol of **7a**, 600 mg, 1.20 mmol of **7b**) in dry pyridine was added slowly to a suspension of chromium(VI) oxide (10 equiv) and dry pyridine. After stirring for 4 h at room temperature, the reaction mixture was filtered and washed with diethyl ether. The filtrate was washed with 10% HCl and 10% sodium carbonate solution successively. The combined organic layers were dried over sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel using 50% dichloromethane in hexane to give each product (202 mg (38%) of **8a** as pale yellow oil, 300 mg (50%) of **8b** as pale yellow oil).

8a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 2H), 7.81 (s, 2H), 6.55 (d, *J* = 3.5 Hz, 4H), 4.55 (s, 4H), 2.71 (t, *J* = 7.6 Hz, 4H), 1.63 (m, 4H), 1.30 (s, 6H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 190.97, 190.73, 148.05, 145.34, 138.75, 136.89, 136.29, 134.49, 134.12, 132.56, 125.47, 125.28, 123.74, 123.55, 33.15, 32.84, 31.55, 30.13, 28.79, 22.55, 14.25, 13.87. HRMS (ESI): m/z for $C_{30}H_{39}O_2S_2$ calc: 495.2391, found 495.2390.

8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 2H), 7.81 (s, 2H), 6.55 (dd, *J* = 7.7, 3.4 Hz, 4H), 4.54 (s, 4H), 2.70 (m, 4H), 1.59 (m, 4H), 1.28 (s, 12H), 0.87 (t, *J* = 6.8 Hz, 6H).



9a

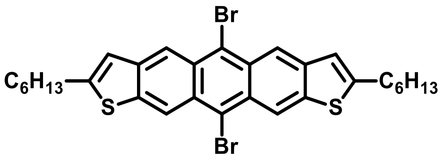


9b

2,8-dihexylanthra[2,3-b:7,6-b']dithiophene (9a) and 2,8-dihexylanthra[2,3-b:6,7-b']dithiophene (9b): To the solution of each compound (500 mg, 1.01 mmol of **8a**, 400 mg, 0.81 mmol of **8b**) in dry dichloromethane was added $BF_3.OEt_2$ (2 equiv) under argon. The reaction mixture was stirred at 30 ^{0}C for 1 h. After the reaction, dichloromethane was mostly removed by rotovap and methanol was added to the concentrated solution. The yellow solid was filtered and washed with excess methanol and dichloromethane to give each isomer (422 mg (91%) of **9a** as orange solid; 360 mg (97%) of **9b** as orange solid).

9a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.52 (s, 1H), 8.39 (s, 2H), 8.29 (s, 2H), 7.02 (s, 2H), 2.85 (d, *J* = 6.8 Hz, 4H), 1.75 (s, 4H), 1.33 (d, *J* = 4.6 Hz, 12H), 1.02 – 0.70 (m, 6H). Too insoluble for ^{13}C NMR. HRMS (ESI): m/z for $C_{30}H_{35}S_2$ calc: 459.2180, found 459.2175.

9b: ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.61 (s, 2H), 8.42 (s, 2H), 8.32 (s, 2H), 7.07 (s, 2H), 2.95 (t, *J* = 7.4 Hz, 4H), 2.95 (m, 4H), 1.84 (m, 4H) 1.40 (s, 12H), 0.95 (t, *J* = 6.9 Hz, 6H).



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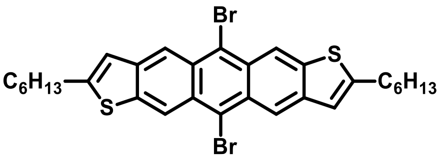
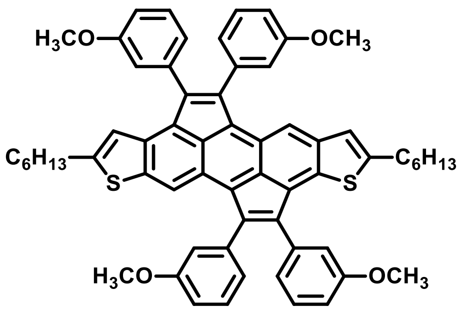


10b

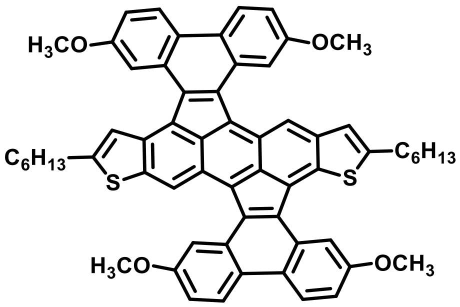
5,11-dibromo-2,8-dihexylanthra[2,3-b:7,6-b']dithiophene (10) and 5,11-dibromo-2,8-dihexylanthra[2,3-b:6,7-b']dithiophene (10b): To the solution of each compound (50 mg, 0.11 mmol of **9a**; 50 mg, 0.17 mmol of **9b**) that was sonicated in 100 mL chloroform for >40 min was added N-bromosuccinimide (2.1 equiv) and stirred for 1 h at room temperature in the dark. The reaction mixture was transferred into separation funnel with water (50 mL), the organic layer was washed with water (50 mL) and brine solution (50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to give each isomer (63 mg, 93% of **10** as red solid; 65 mg, 95% of **10b** as red solid).

10: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.88 (s, 1H), 7.14 (s, 2H), 2.96 (t, *J* = 7.4 Hz, 4H), 1.84 (p, *J* = 7.4 Hz, 4H), 1.42 (s, 12H), 0.93 (t, *J* = 6.6 Hz, 6H). Too insoluble for ^{13}C NMR. HRMS (ESI): m/z for $C_{30}H_{33}Br_2S_2$ calc: 615.0390, found 615.0370.

10b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 2H), 8.79 (s, 2H), 7.08 (s, 2H), 2.92 (t, *J* = 7.5 Hz, 4H), 1.79 (m, 4H), 1.44 (s, 4H), 1.35 (m, 8H), 0.91 (t, *J* = 6.7 Hz, 6H).

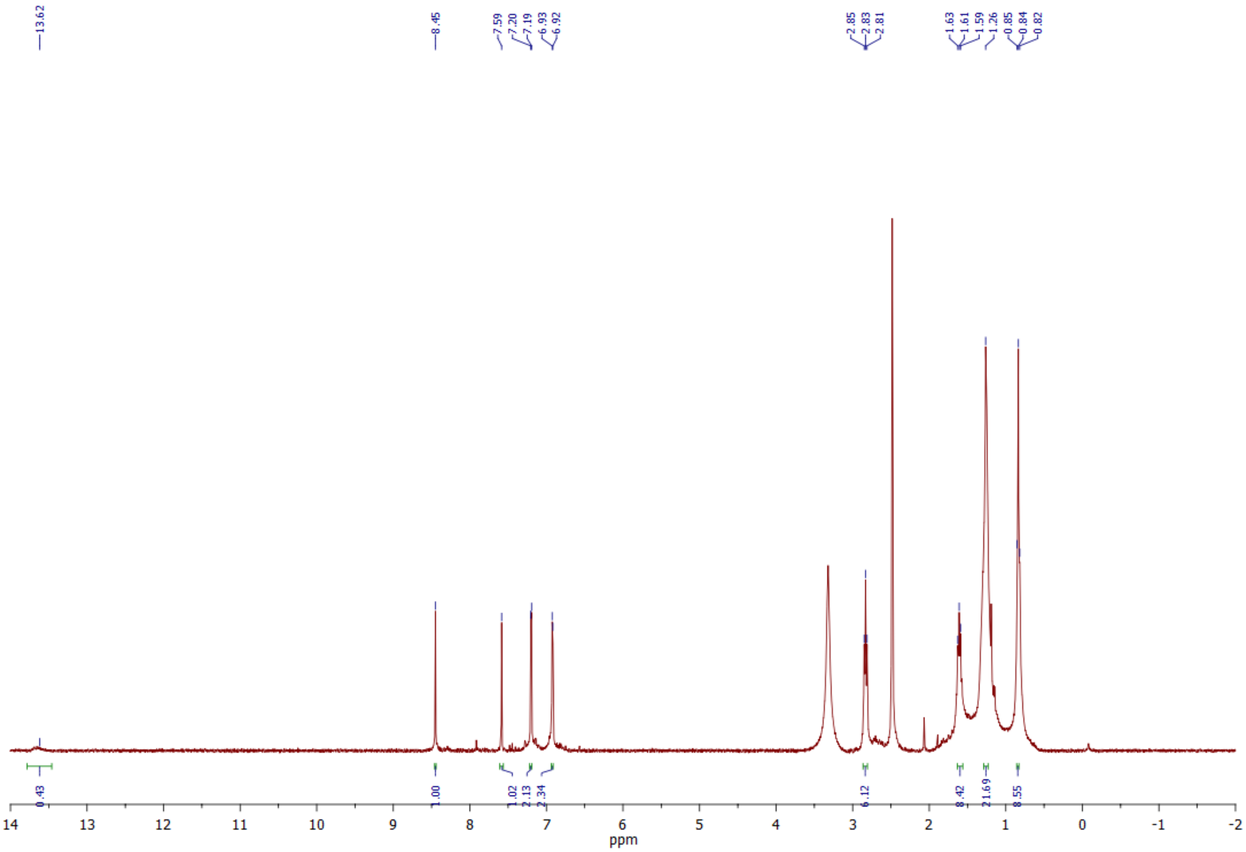


4,10-dihexyl-1,2,7,8-tetrakis(3-methoxyphenyl)cyclopenta[6,7]aceanthryleno[4,3-b:8,9-b']dithiophene (11): In a glove box, 3,3’-dimethoxy,1,1’-diphenyl acetylene (85.0 mg, 0.357 mmol), **10** (100 mg, 0.162 mmol), Pd$_2$(dba)$_3$ (14.8 mg, 0.016 mmol), P(o-Tol)$_3$ (7.4 mg, 0.024 mmol), KOAc (80.0 mg, 0.811 mmol), LiCl (13.7 mg, 0.324 mmol), toluene (4 ml) and DMF (4 ml) were combined in a sealed tube and stirred overnight at 130 ^{0}C. The reaction mixture was cooled to room temperature and poured into 120 ml methanol and filtered. The solid was washed with methanol and purified by column chromatography with 0→20% DCM:Hexane to give 58 mg (39%) of **11** as a green solid. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.24 (s, 1H), 8.09 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 1.2 Hz, 2H), 7.09 (d, *J* = 13.0 Hz, 2H), 7.02 (dt, *J* = 6.0, 2.6 Hz, 4H), 6.93 (m, 3H), 6.88 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 2.82 (dd, *J* = 14.1, 6.9 Hz, 4H), 1.69 (m, 4H), 1.28 (s, 12H), 0.90 (m, 6H). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 159.40, 159.35, 159.24, 155.74, 149.53, 145.04, 143.56, 139.73, 139.61, 139.52, 139.34, 138.77, 138.70, 138.46, 138.39, 137.88, 137.12, 136.64, 135.24, 132.07, 131.02, 129.15, 129.05, 128.96, 128.84, 123.86, 123.65, 123.55, 123.48, 123.20, 123.10, 122.75, 122.11, 120.30, 119.21, 119.14, 118.10, 116.34, 116.30, 115.73, 115.36, 113.64, 113.26, 113.21, 113.15, 77.58, 77.08, 55.24, 55.22, 55.15, 31.68, 31.49, 31.07, 30.25, 30.20, 29.69, 28.79, 28.71, 22.54, 22.52, 13.81. LRMS (ES+) 931.4 HRMS: (ESI-MS) m/z for C$_{62}$H$_{58}$O$_4$S$_2$ calc: 931.3855, found 931.3887.



2,14-dihexyl-5,10,17,22-tetramethoxytetrabenzo[4,5:6,7:11,12:13,14]rubiceno[2,3-b:10,9-b']dithiophene (4): In a round bottom flask **11** (40 mg, 0.043 mmol) was dissolved in 50 ml of CH_2Cl_2. To this mixture $FeCl_3$ (42 mg, 0.258 mmol) in 0.5ml of CH_3NO_2 was added drop wise under Ar. The reaction mixture was stirred at room temperature overnight. The solvent was reduced to 5 ml by rotovap and methanol (30 ml) was added and the mixture was stirred for 20 min. The product was collected by filtration and washed with methanol. The collected solid was subjected to silica gel chromatography 0→20% DCM:Hexane to give 16.2 mg (41%) of **4** as a bright green solid. ^{1}H NMR ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.38 (s, 1H), 9.20 (s, 1H), 8.57 (d, *J* = 9.7 Hz, 4H), 8.53 (d, *J* = 2.5 Hz, 1H), 8.36 (m, 2H), 8.09 (d, *J* = 2.5 Hz, 1H), 7.99 (s, 1H), 7.28 (m, 4H), 7.19 (s,1H), 4.17 (s, 3H), 4.06 (s, 3H), 3.99 (s, 3H), 3.97 (s, 3H), 3.08 (t, *J* =7.7 Hz 2H), 3.00 (t, *J* = 7.6 Hz 2H), 1.88 (m, 4H), 1.27 (s, 8H), 0.94 (m, 4H), 0.89 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 157.58, 154.99, 148.36, 144.27, 143.15, 137.16, 136.44, 136.12, 135.99, 135.29, 134.94, 133.58, 130.97, 129.31, 129.04, 128.92, 128.82, 128.55, 126.02, 125.73, 125.64, 125.37, 124.88, 124.75, 124.62, 122.06, 121.04, 120.95, 120.76, 116.70, 116.47, 116.33, 116.01, 108.47, 108.26, 107.40, 106.90, 55.96, 55.33, 32.09, 31.92, 31.63, 30.97, 30.79, 30.21, 29.68, 29.36, 29.06, 28.95, 22.69, 22.63, 22.59, 13.88. HRMS: (MALDI) m/z for $C_{62}H_{54}O_4S_2$ calc: 926.3458, found 926.300.

Compound 5a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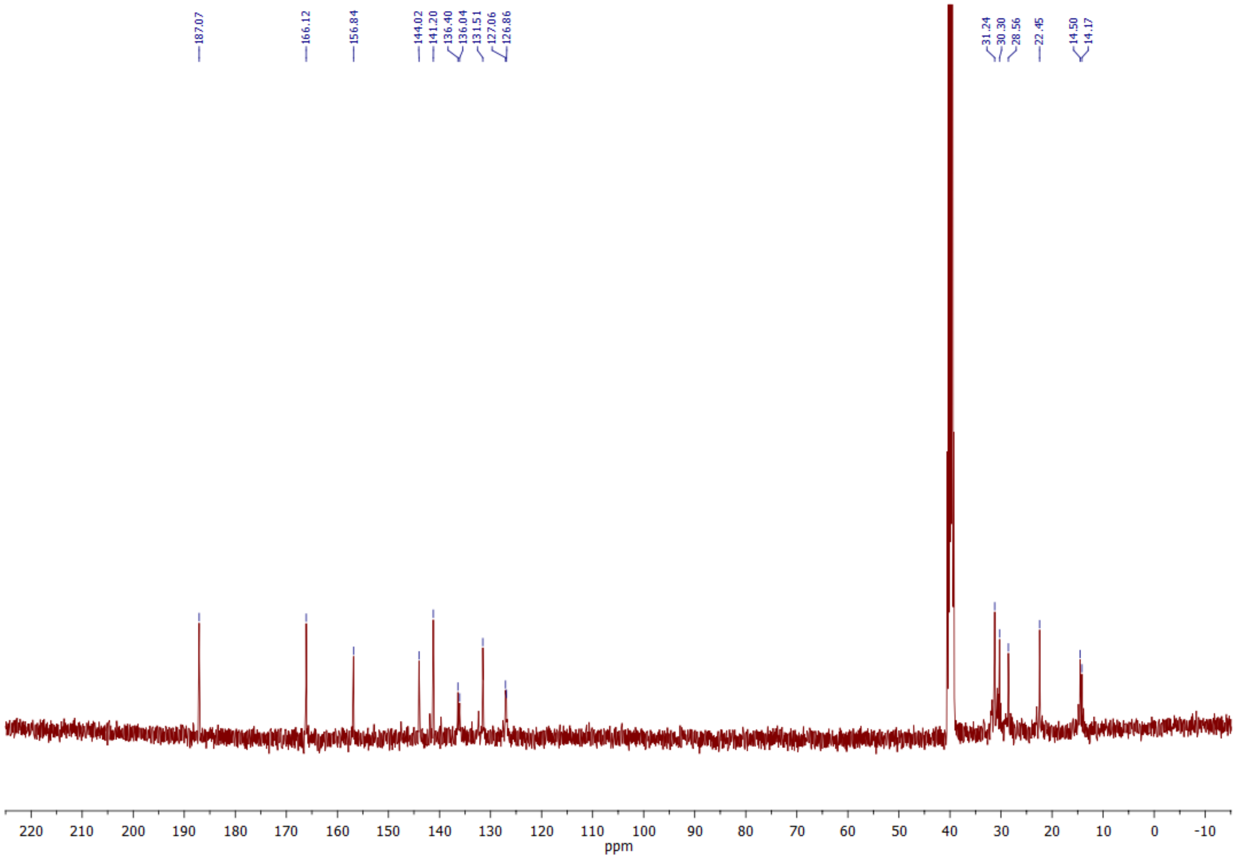
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22.45
14.50
14.17
220
210
200
190
180
170
160
150
140
130
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110
100
90
80
70
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50
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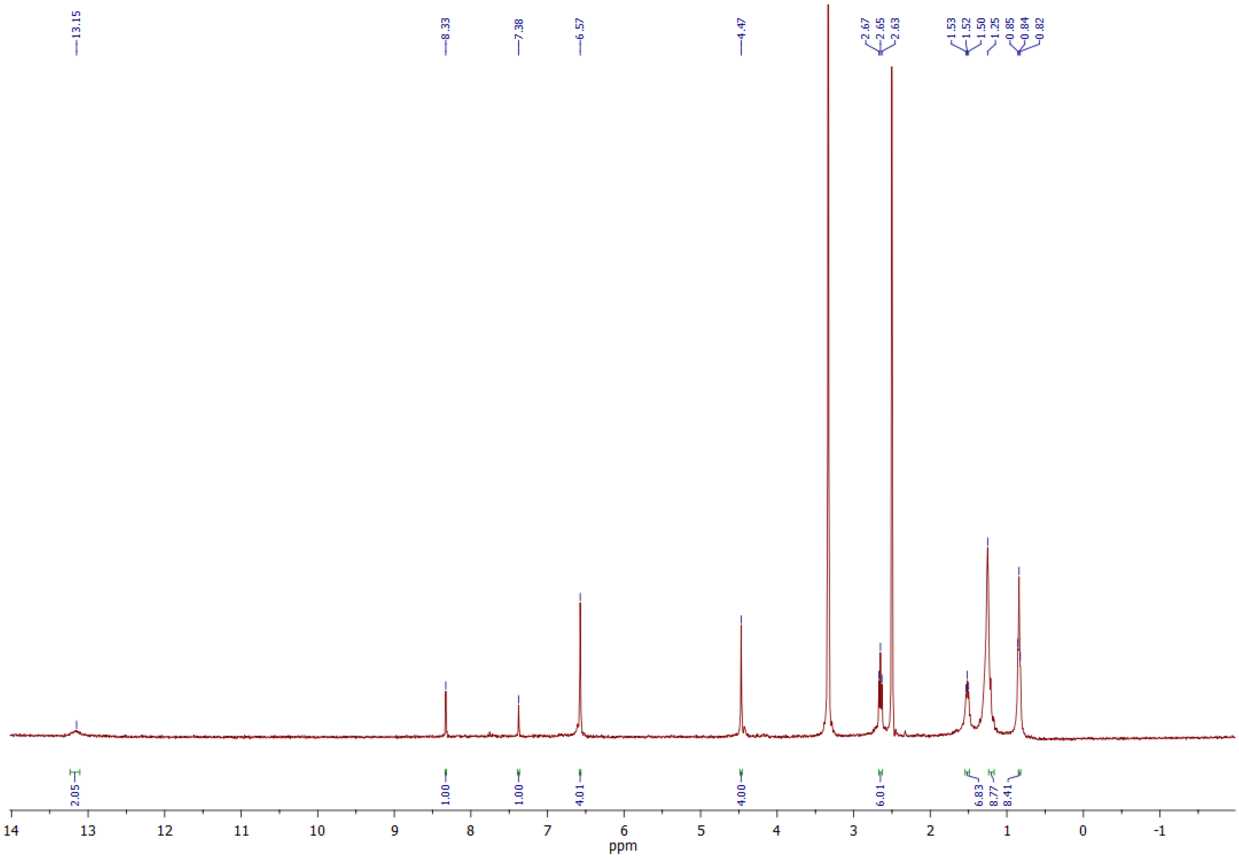
30
20
10
0
-10
ppm

Compound 6a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8.33
7.38
6.57
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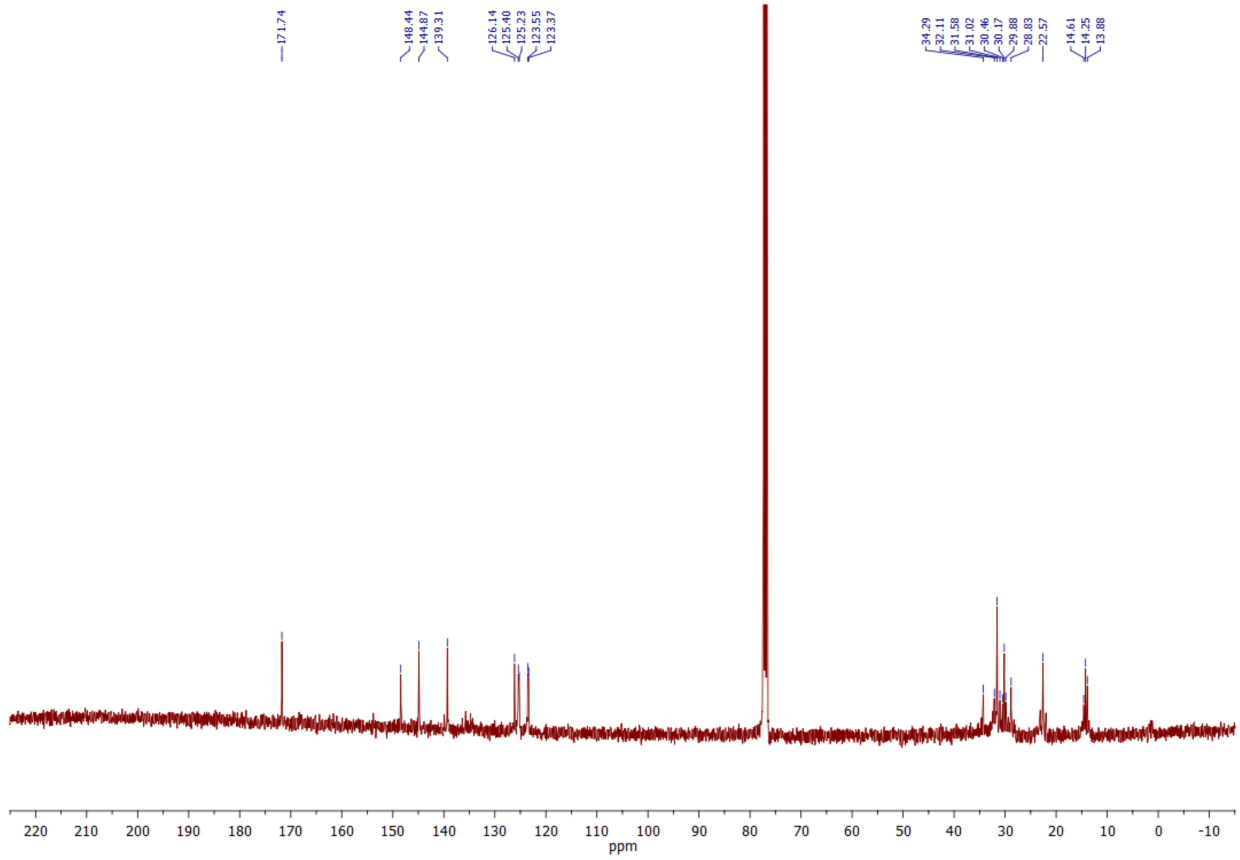
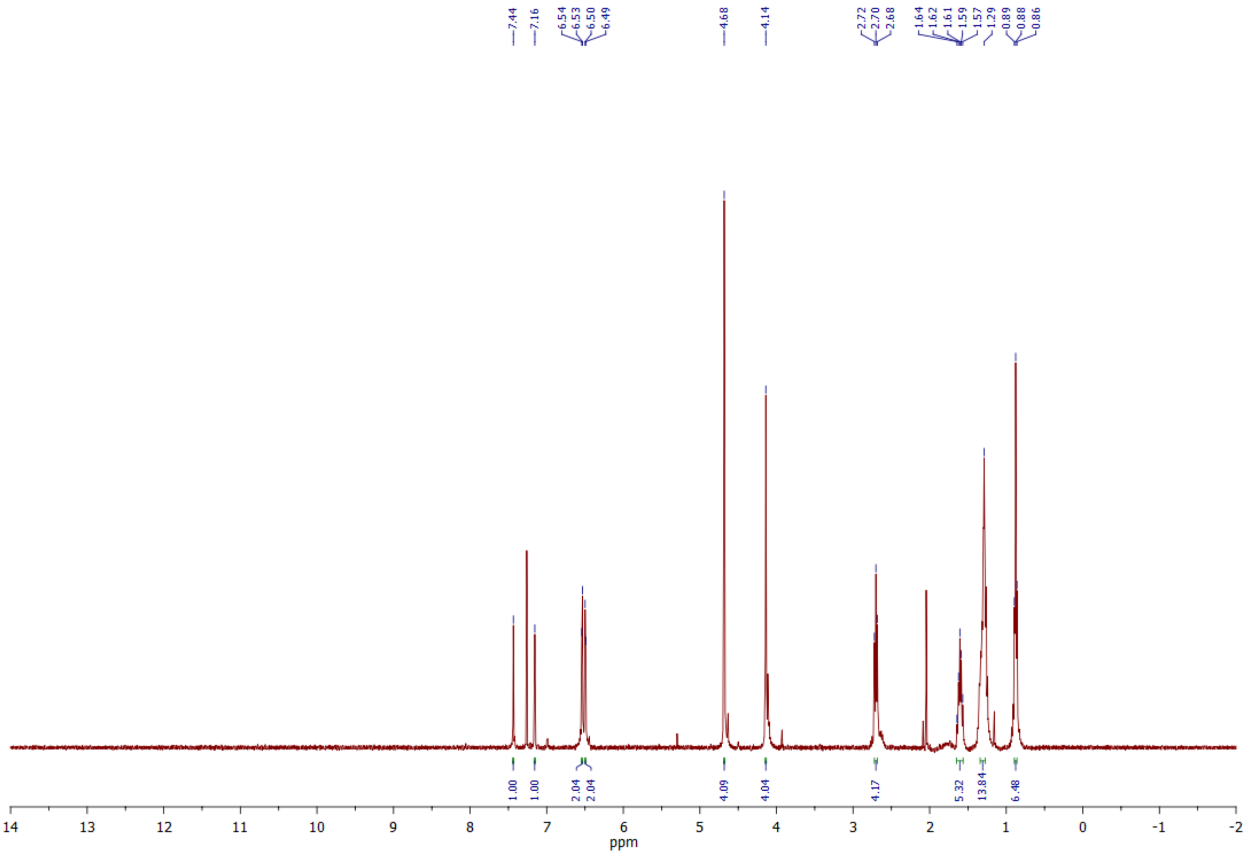
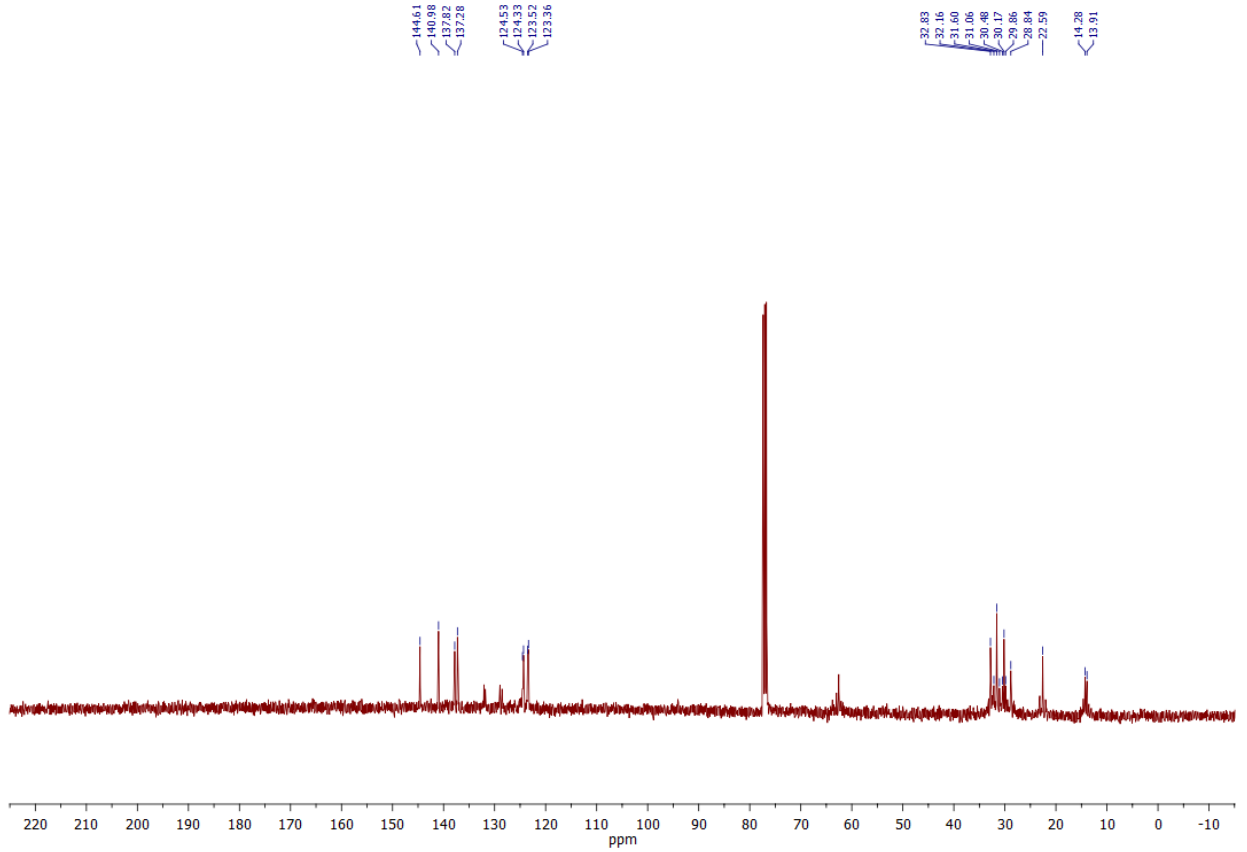
2.67
2.65
2.63
1.53
1.52
1.50
1.25
0.85
0.84
0.82
2.05
1.00
1.00
4.01
4.00
6.01
6.83
8.77
8.41
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


171.74
148.44
144.87
139.31
126.14
125.40
125.23
123.55
123.37
34.29
32.11
31.58
31.02
30.46
30.17
29.88
28.83
22.57
14.61
14.25
13.88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

Compound 7a


7.44
7.16
6.54
6.53
6.50
6.49
4.68
4.14
2.72
2.70
2.68
1.64
1.62
1.61
1.59
1.57
1.29
0.89
0.88
0.86
1.00
1.00
2.04
2.04
4.09
4.04
4.17
5.32
13.84
6.48
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


144.61
140.98
137.82
137.28
124.53
124.33
123.52
123.36
32.83
32.16
31.60
31.06
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30.17
29.86
28.84
22.59
14.28
13.91
220
210
200
190
180
170
160
150
140
130
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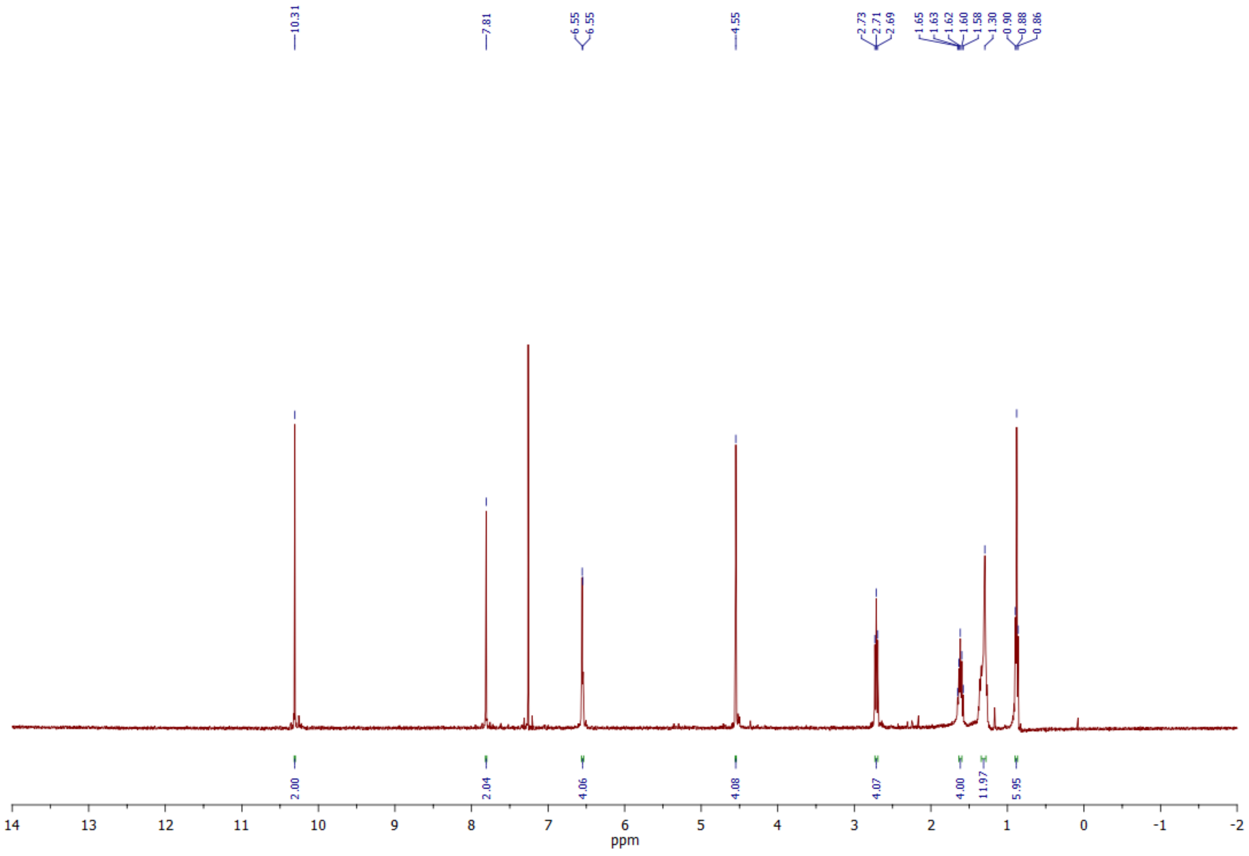
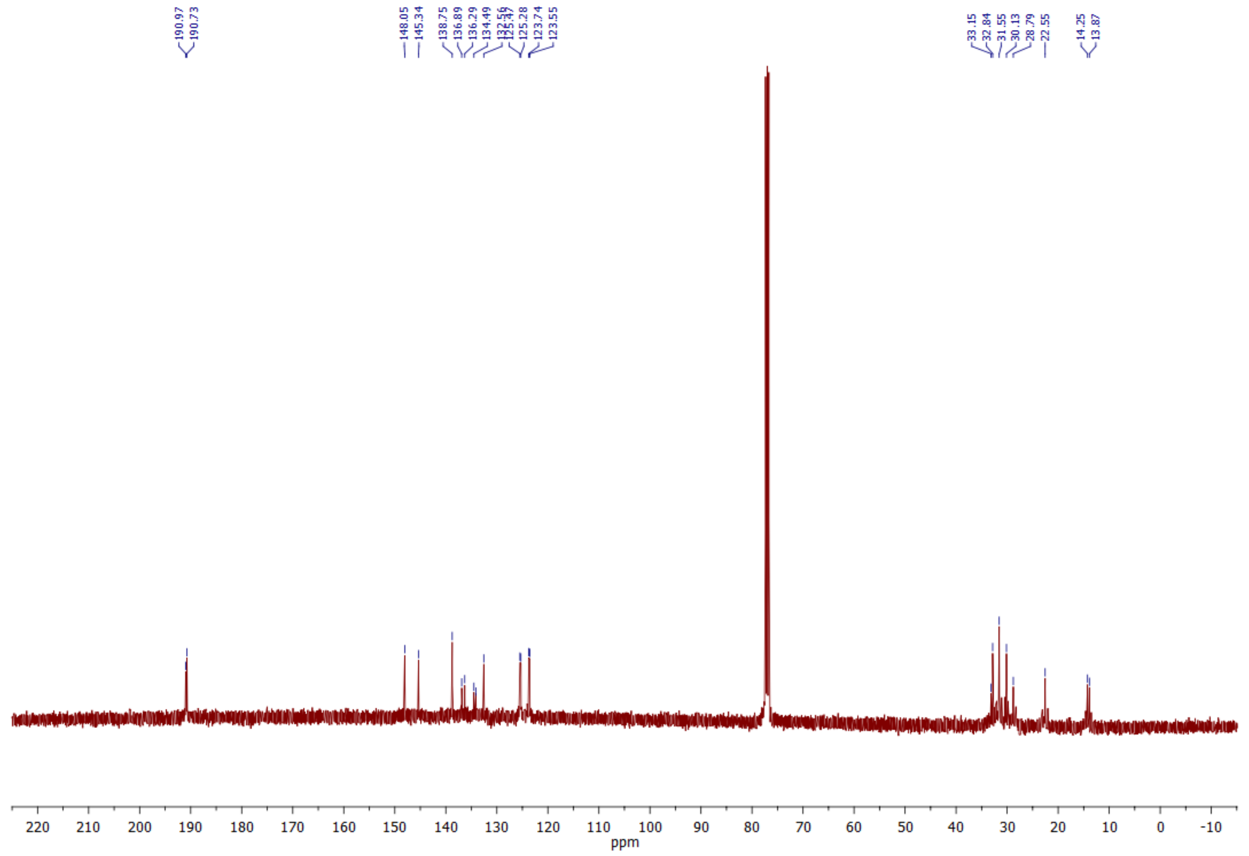
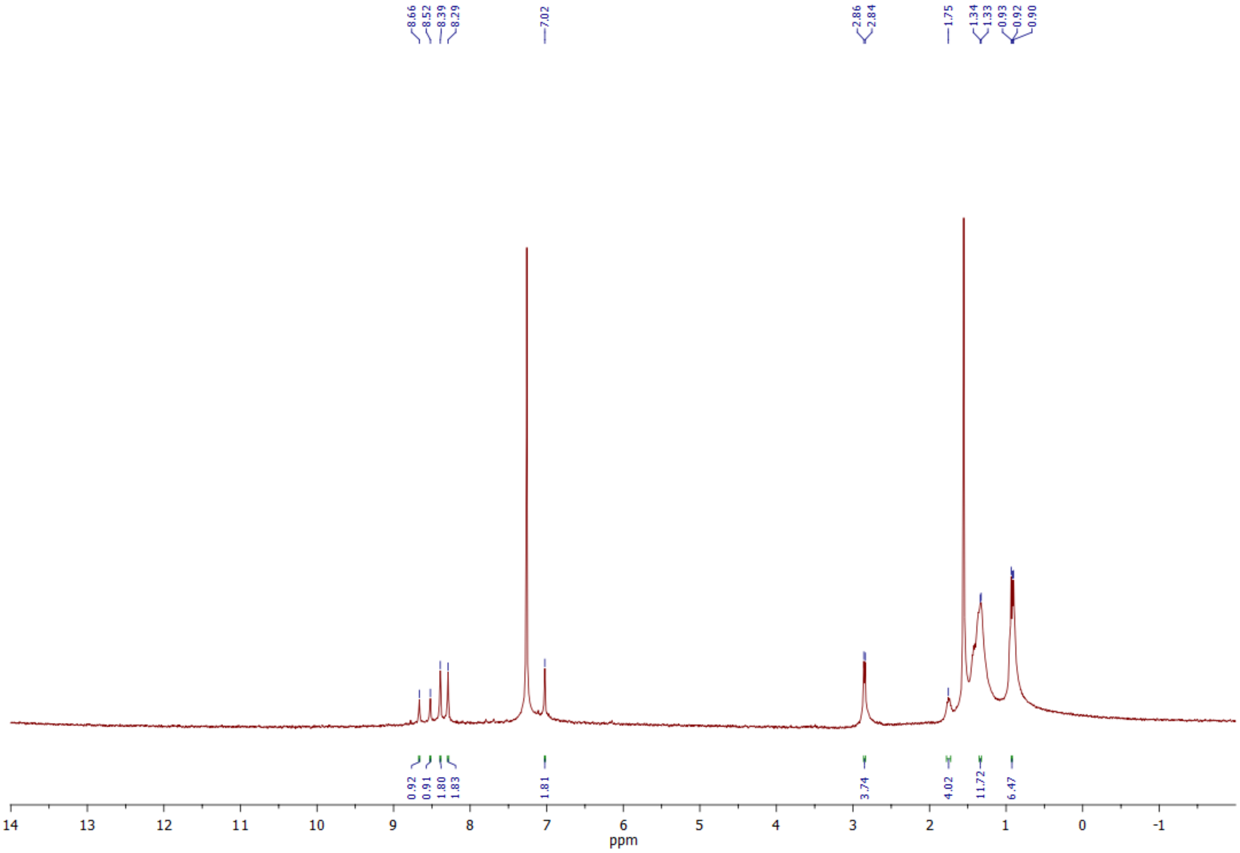
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

Compound 8a

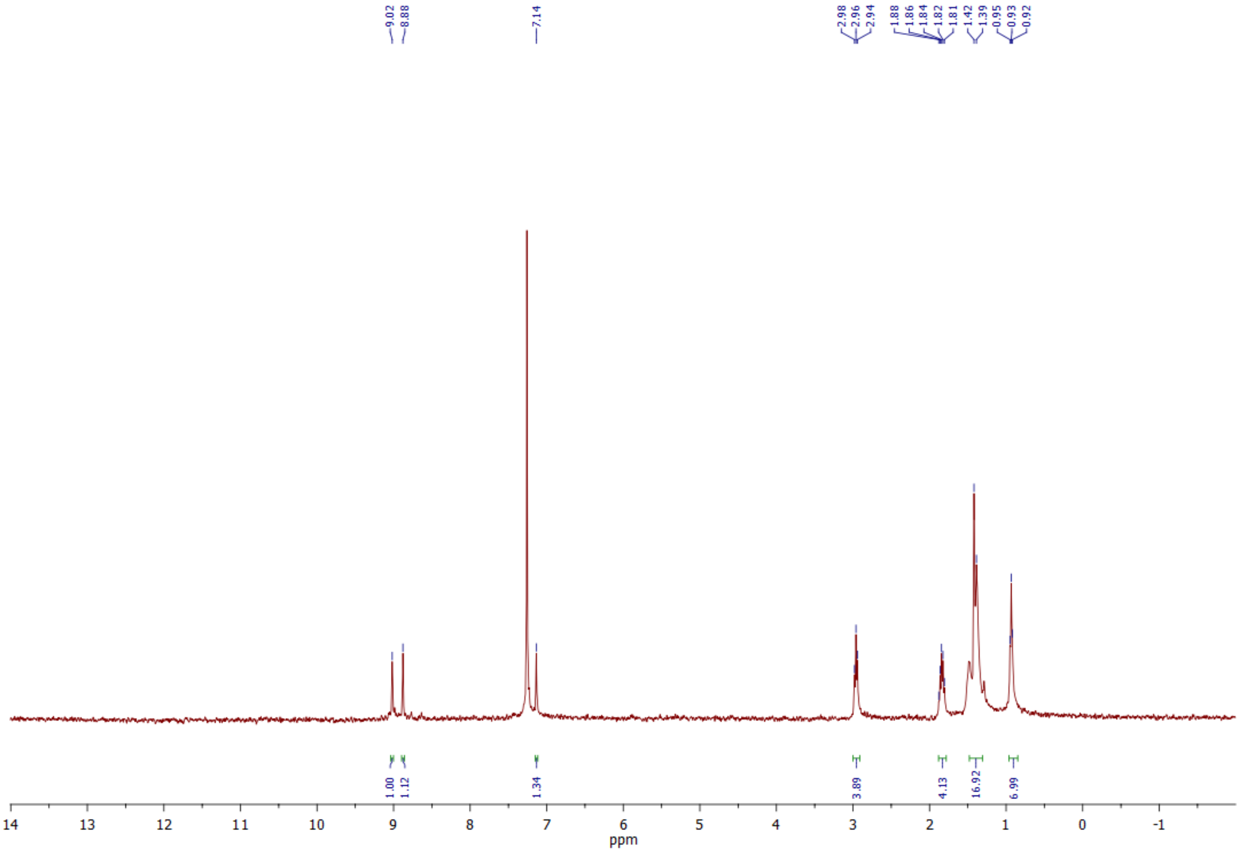

10.31
7.81
6.55
6.55
4.55
2.73
2.71
2.69
1.65
1.63
1.62
1.60
1.58
1.30
0.90
0.88
0.86
2.00
2.04
4.06
4.08
4.07
4.00
11.97
5.95
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


190.97
190.73
148.05
145.34
138.75
136.89
136.29
134.49
132.56
125.47
125.28
123.74
123.55
33.15
32.84
31.55
30.13
28.79
22.55
14.25
13.87
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

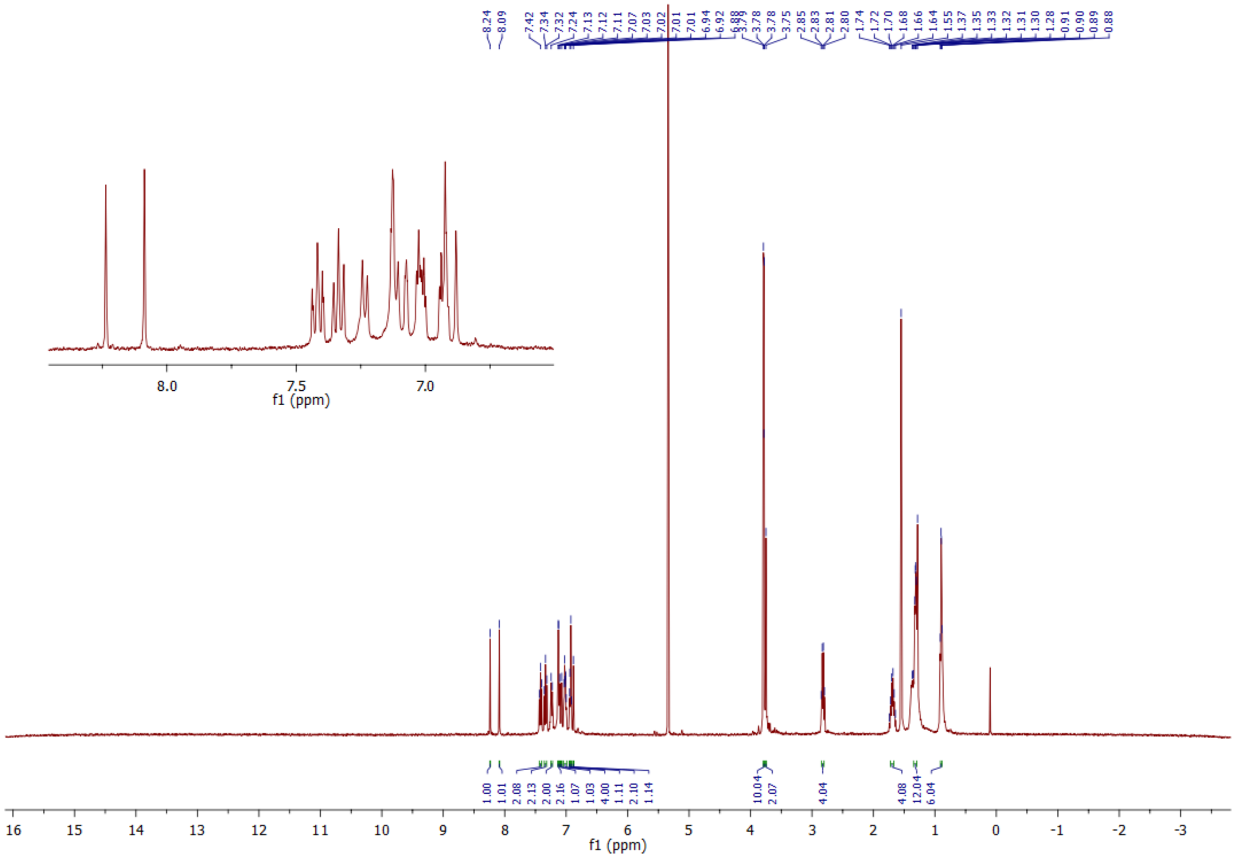
Compound 9a

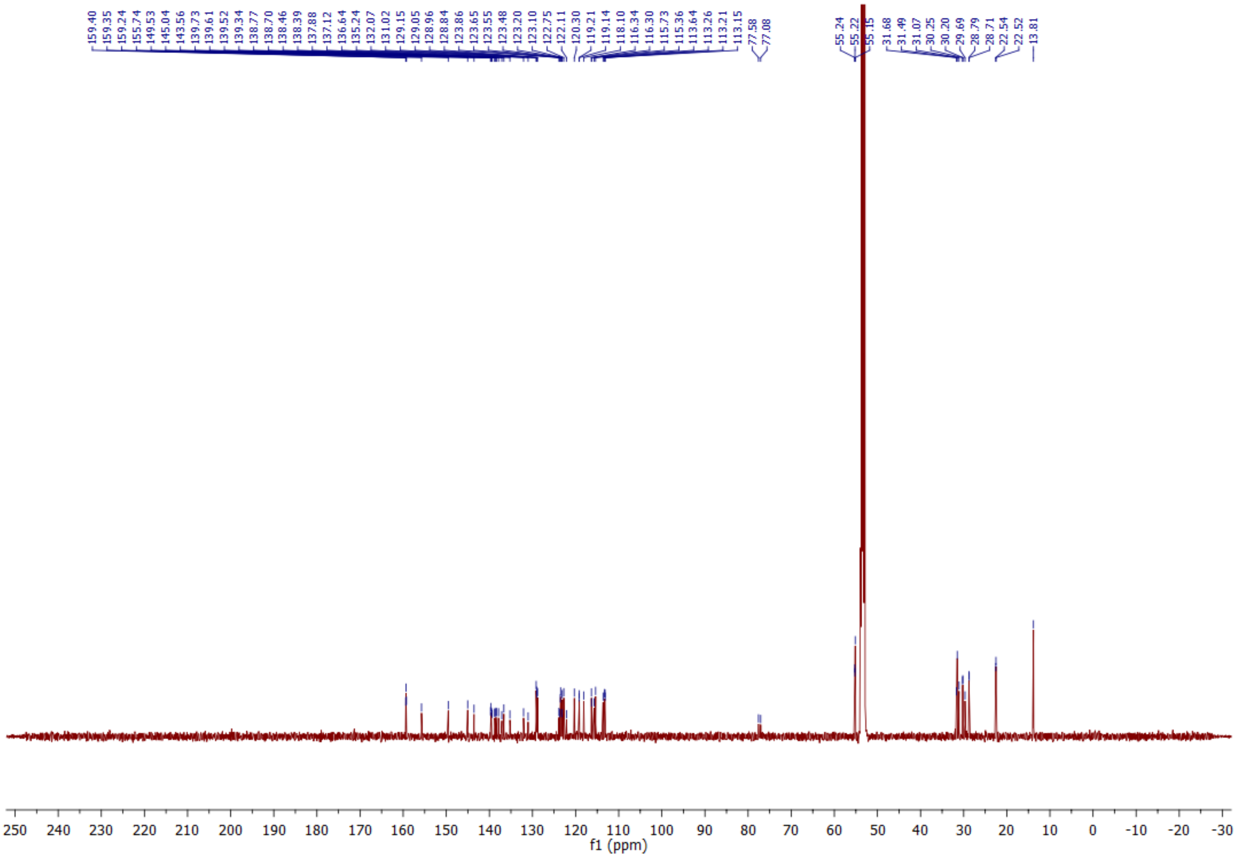


Compound 10



Compound 11


8.24
8.09
7.42
7.34
7.32
7.24
7.13
7.12
7.11
7.07
7.03
7.02
7.01
7.01
6.94
6.92
6.88
3.79
3.78
3.78
3.75
2.85
2.83
2.81
2.80
1.74
1.72
1.70
1.68
1.66
1.64
1.55
1.37
1.35
1.33
1.32
1.31
1.30
1.28
0.91
0.90
0.89
0.88
8.0
7.5
7.0
f1 (ppm)
1.00
1.01
2.08
2.13
2.00
2.16
1.07
1.03
4.00
1.11
2.10
1.14
10.04
2.07
4.04
4.08
12.04
6.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


159.40
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145.04
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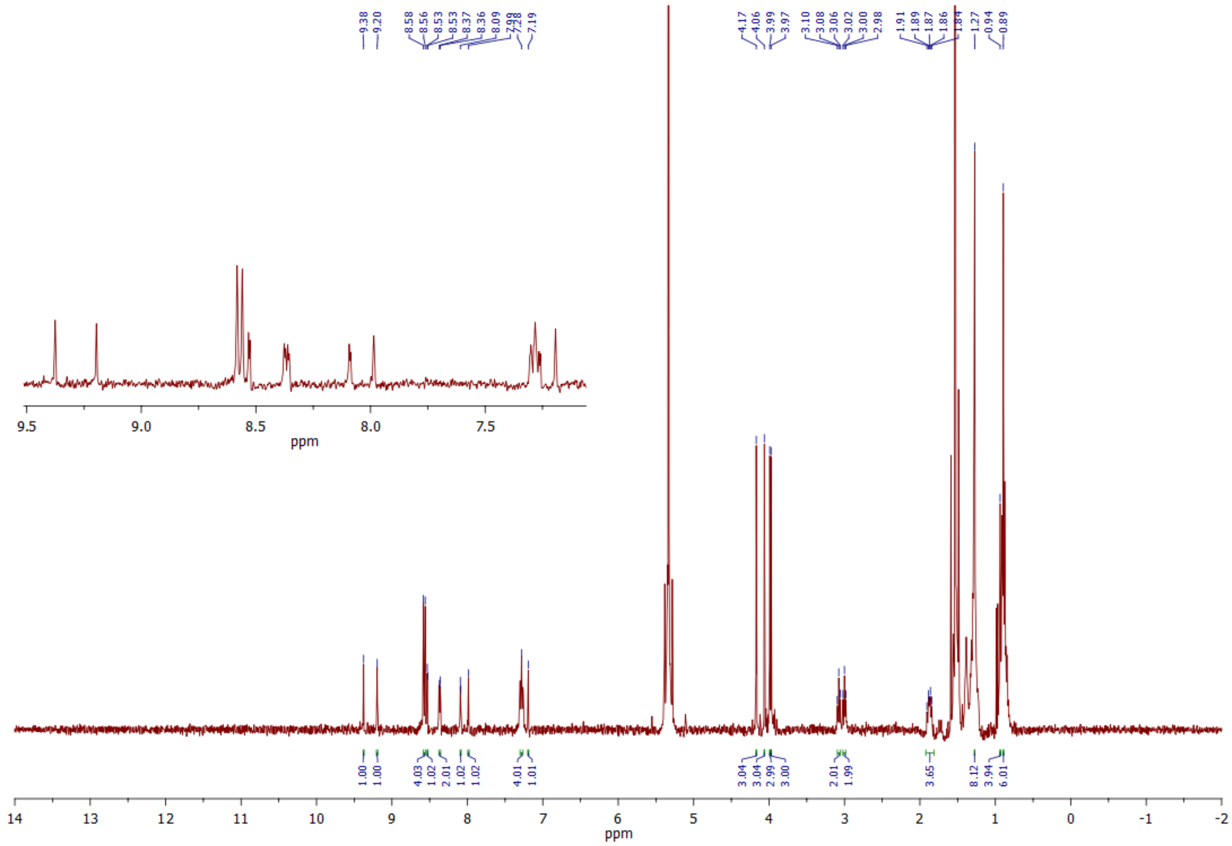
139.73
139.61
139.52
139.34
138.77
138.70
138.46
138.39
137.88
137.12
136.64
135.24
132.07
131.02
129.15
129.05
128.96
128.84
123.86
123.65
123.55
123.48
123.20
123.10
122.75
122.11
120.30
119.21
119.14
118.10
116.34
116.30
115.73
115.36
113.64
113.26
113.21
113.15
77.58
77.08
55.24
55.22
55.15
31.68
31.49
31.07
30.25
30.20
29.69
28.79
28.71
22.54
22.52
13.81
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

Compound 4


9.38
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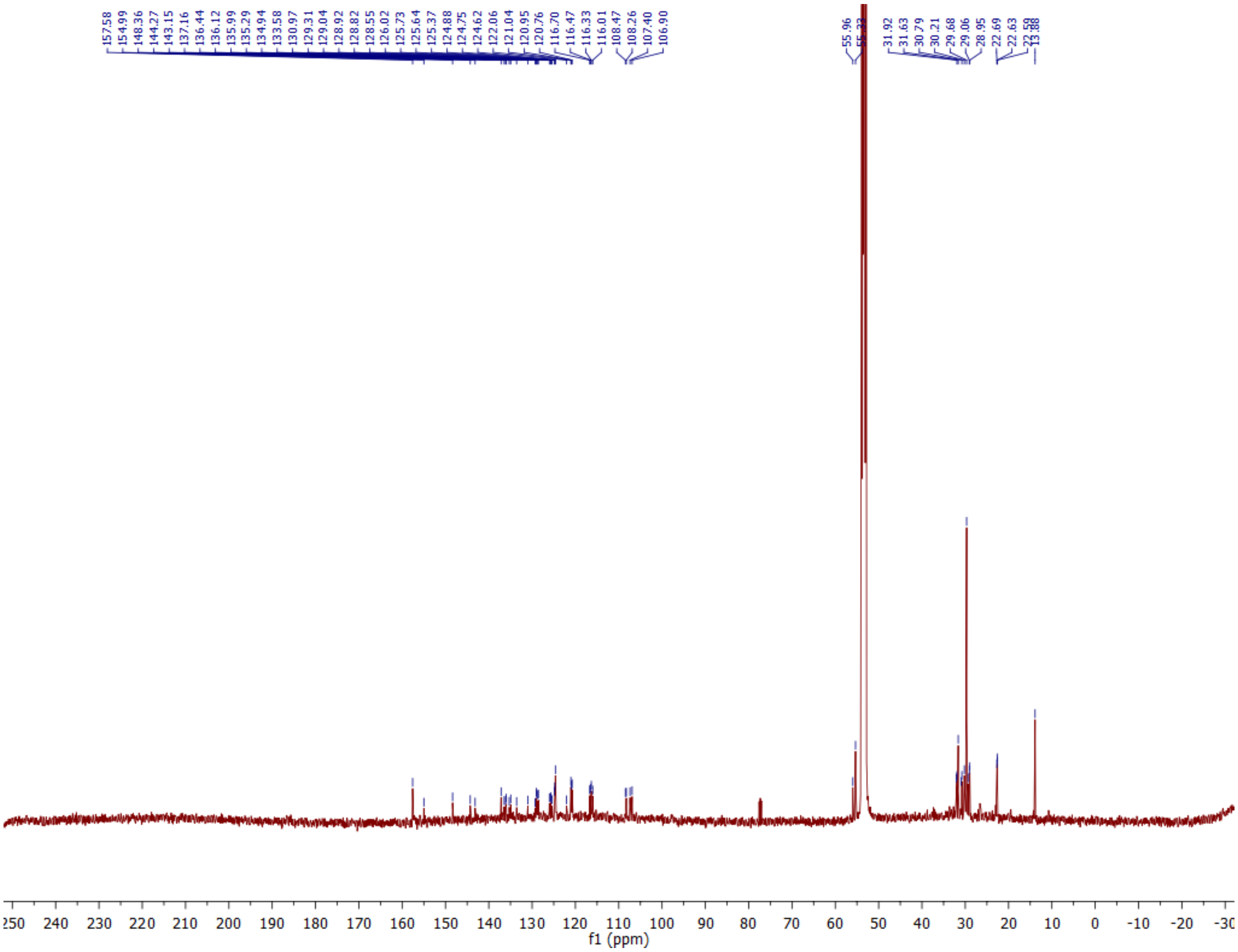
8.56
8.53
8.53
8.37
8.36
8.09
7.99
7.28
7.19
4.17
4.06
3.99
3.97
3.10
3.08
3.06
3.02
3.00
2.98
1.91
1.89
1.87
1.86
1.84
1.27
0.94
0.89
9.5
9.0
8.5
8.0
7.5
ppm
1.00
1.00
4.03
1.02
2.01
1.02
1.02
4.01
1.01
3.04
3.04
2.99
3.00
2.01
1.99
3.65
8.12
3.94
6.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


157.58
154.99
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143.15
137.16
136.44
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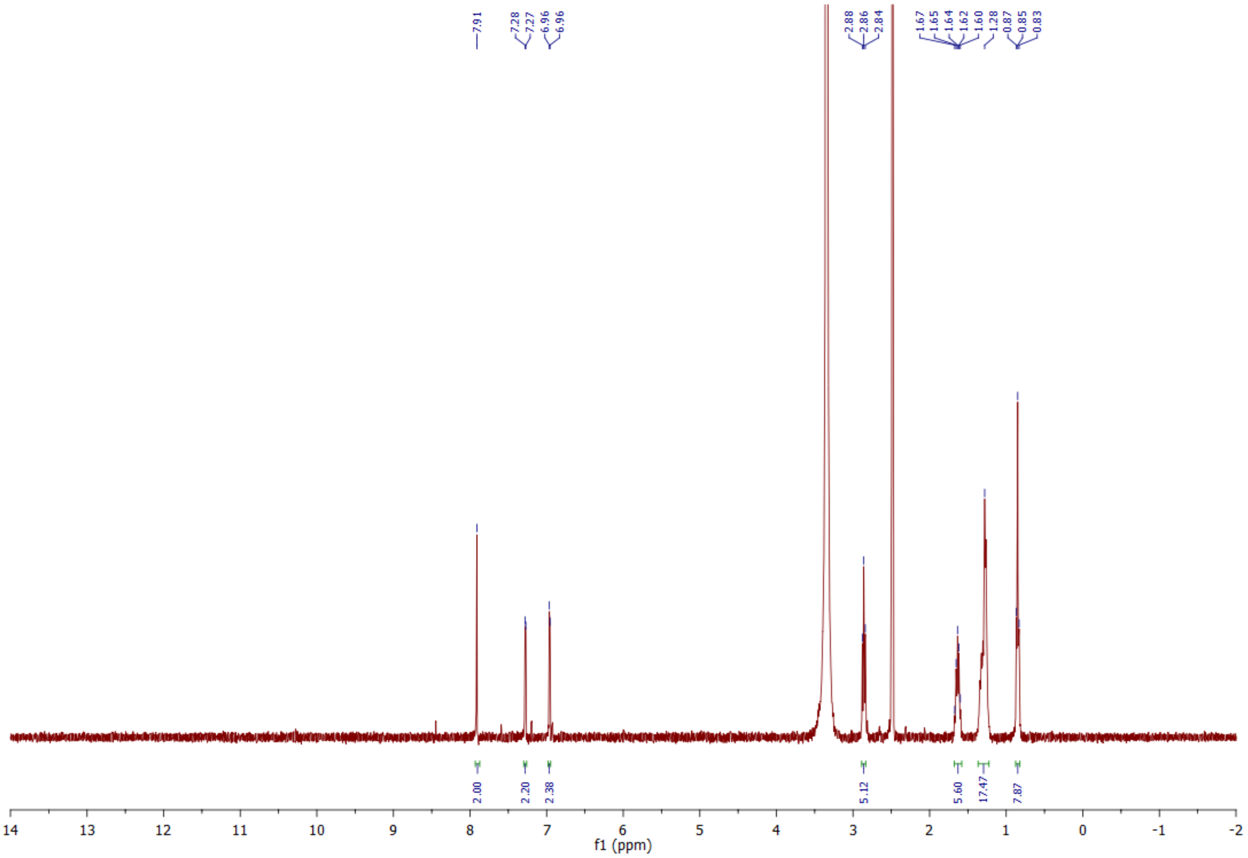
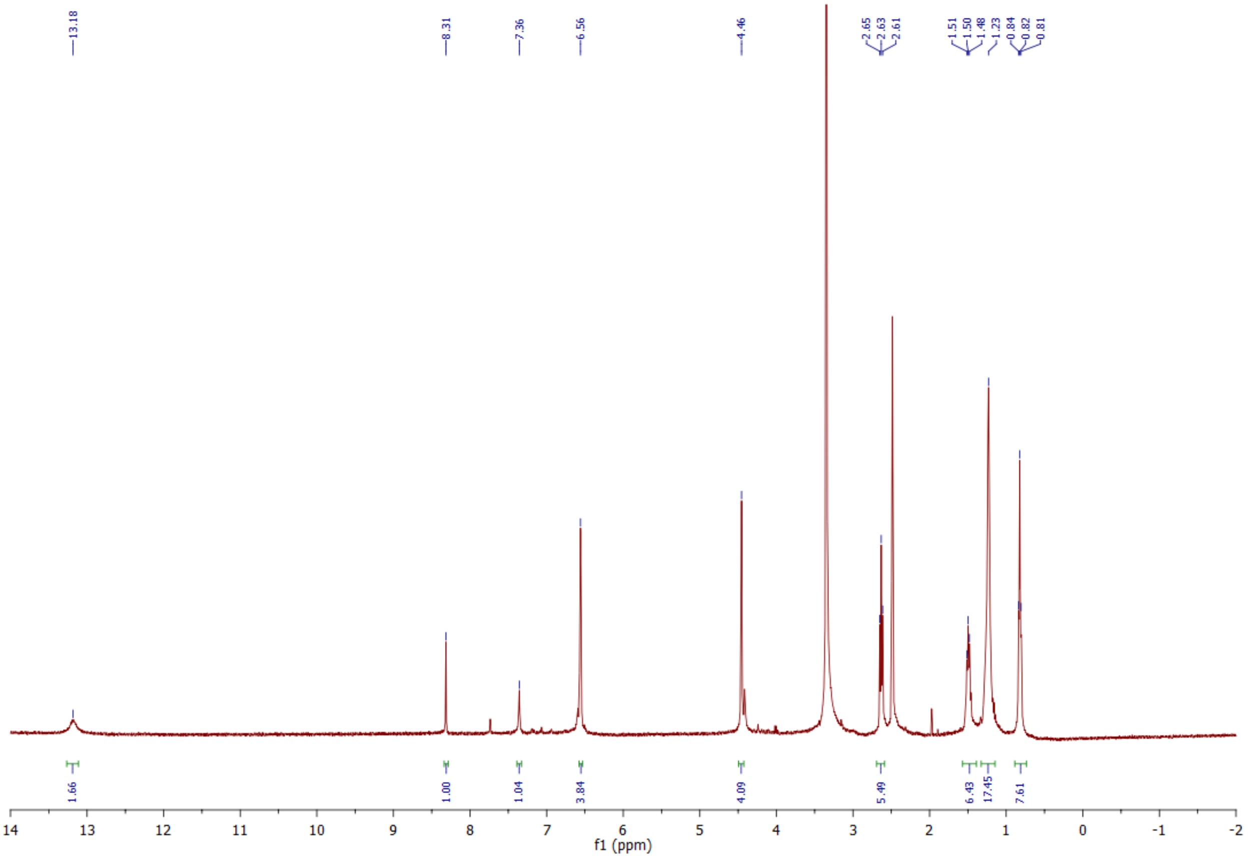
135.99
135.29
134.94
133.58
130.97
129.31
129.04
128.92
128.82
128.55
126.02
125.73
125.64
125.37
124.88
124.75
124.62
122.06
121.04
120.95
120.76
116.70
116.47
116.33
116.01
108.47
108.26
107.40
106.90
55.96
55.33
31.92
31.63
30.79
30.21
29.68
29.06
28.95
22.69
22.63
22.59
13.88
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

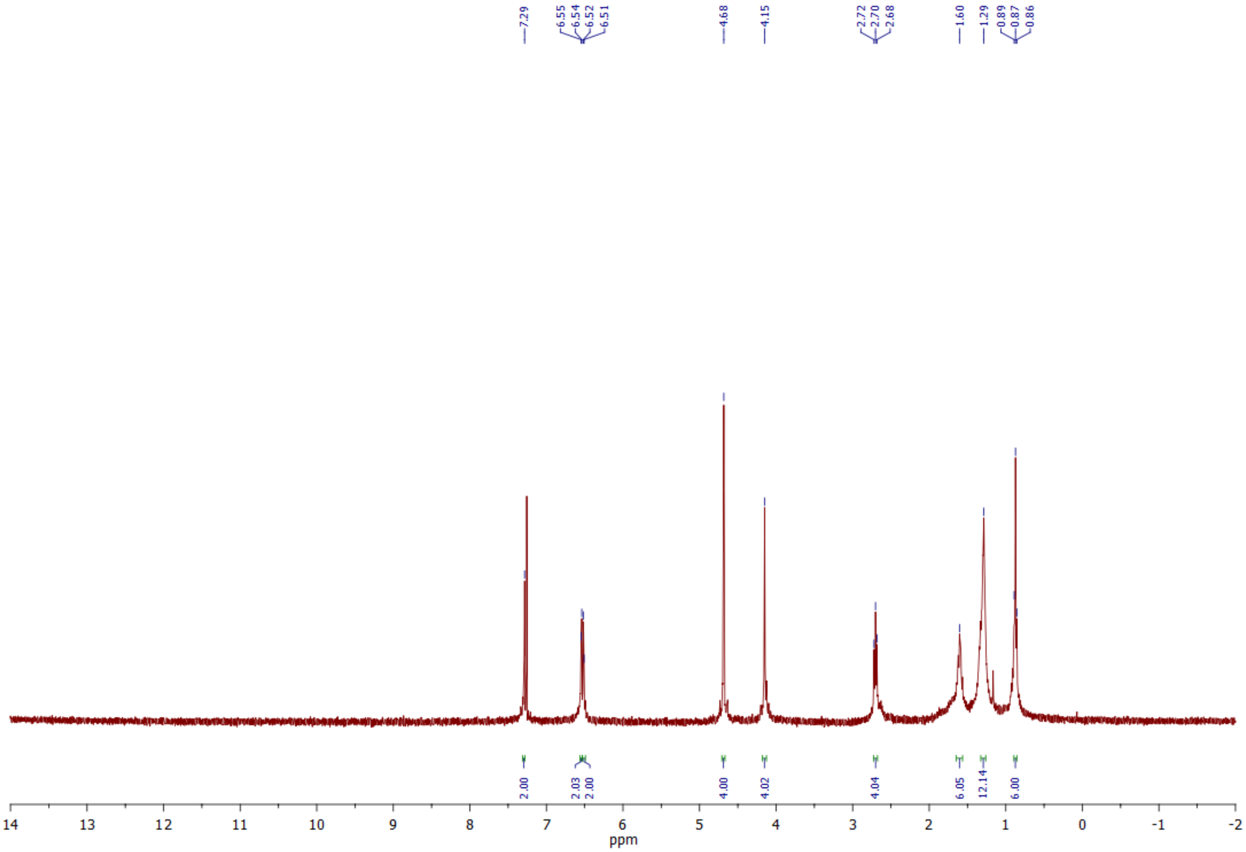
Compound 5b



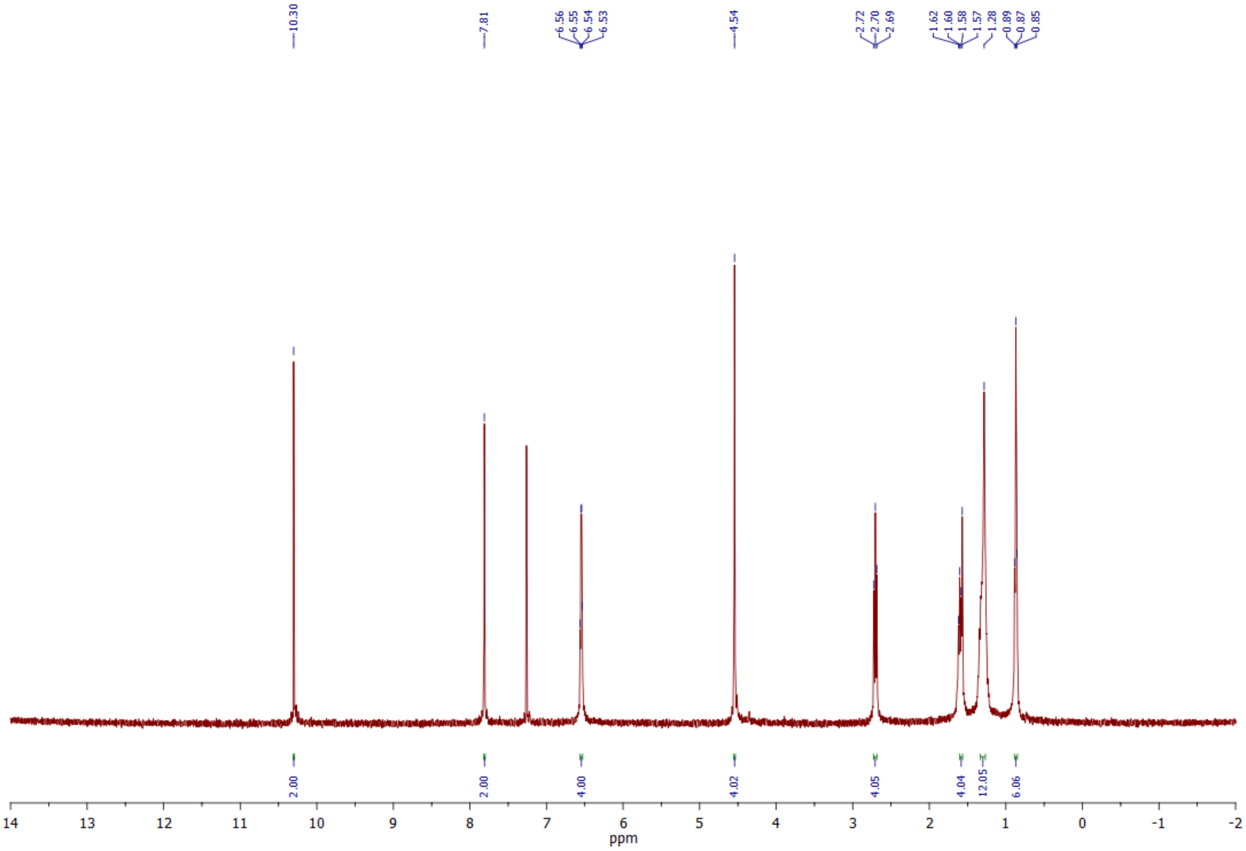
Compound 6b



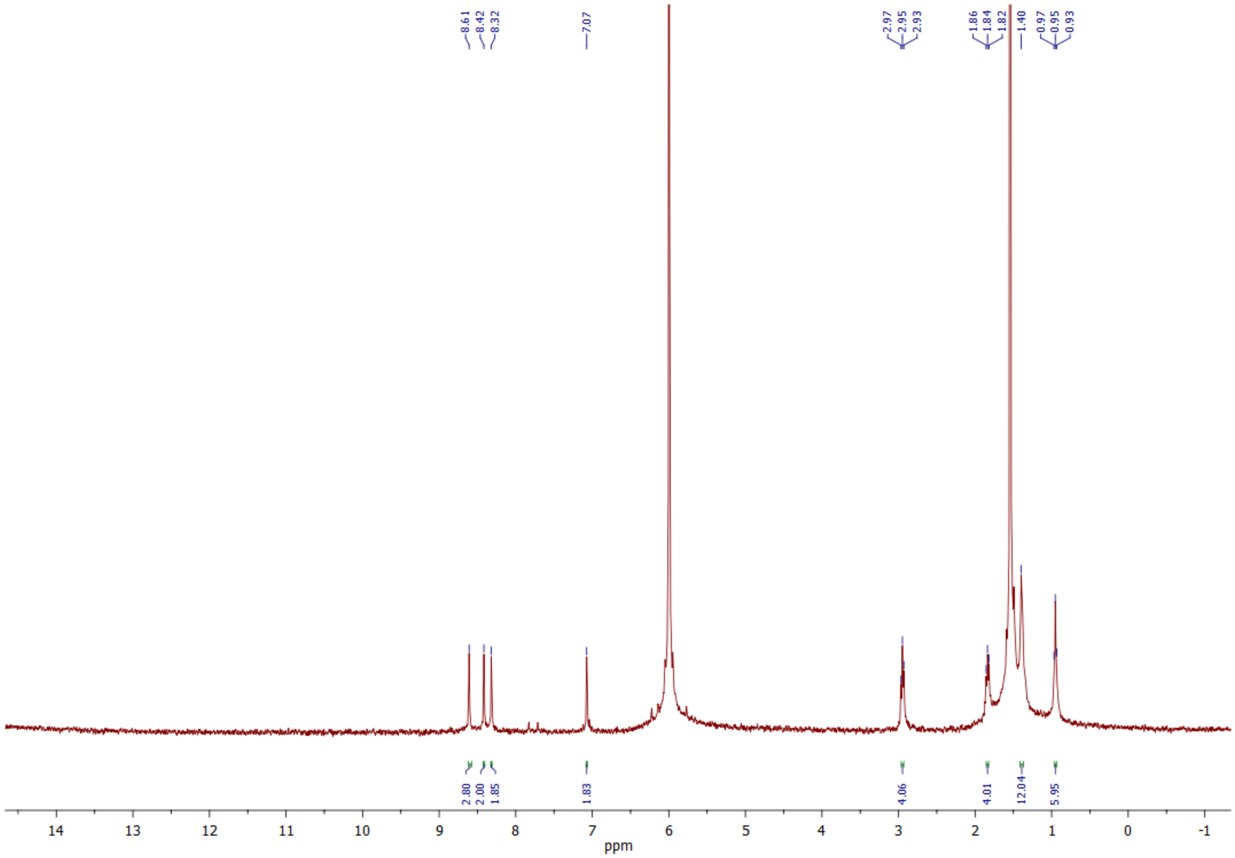
Compound 7b



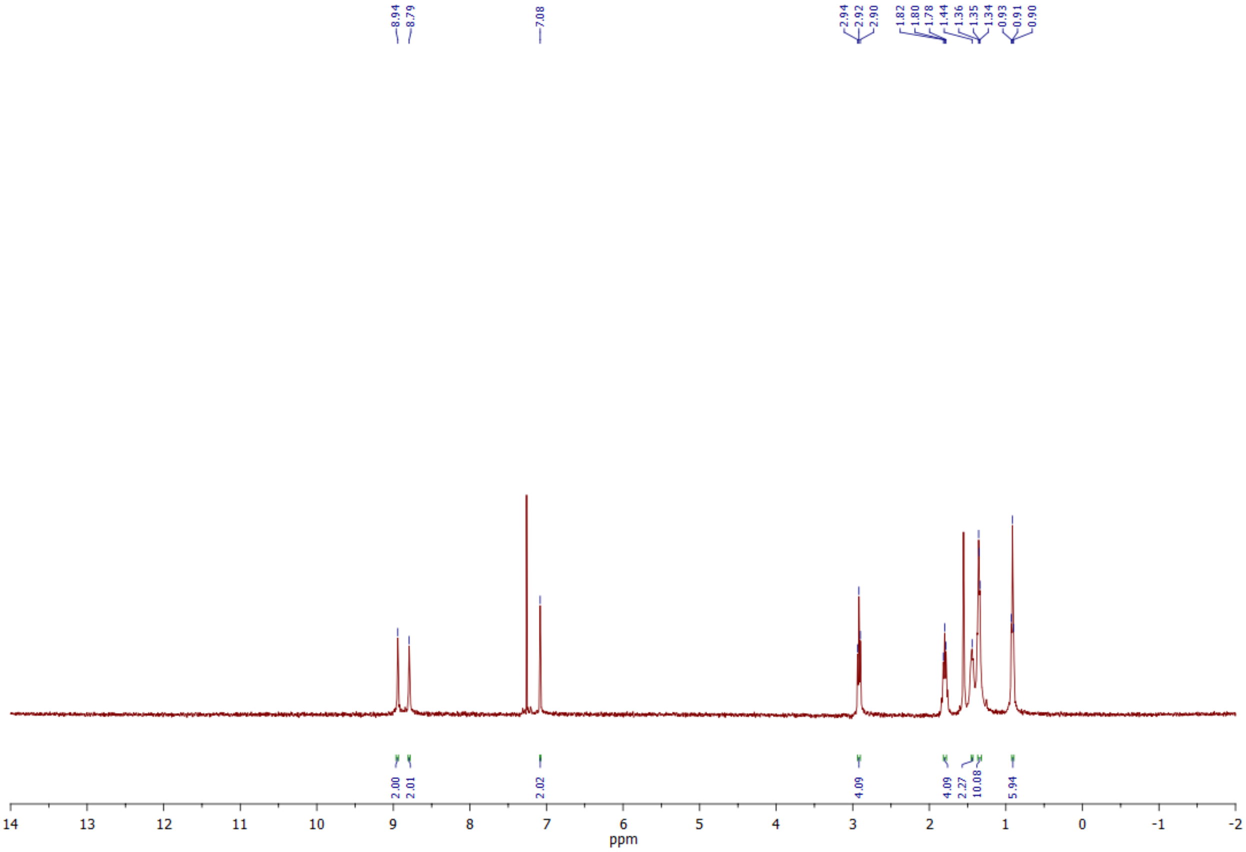
Compound 8b



Compound 9b



Compound 10b



DFT Calculated Structure of 4

SPARTAN '10 Quantum Mechanics Program: (PC/x86) Release 1.1.0v4

Job type: Single point.
Method: RB3LYP
Basis set: 6-311+G**
Number of shells: 498
Number of basis functions: 1496
Multiplicity: 1

SCF total energy: -3099.3578421 hartrees

C	-1.737856	-2.860011	-1.048893
C	-2.749052	-2.002702	-0.833831
C	-2.478022	-0.756356	-0.415765
C	-1.188857	-0.408617	-0.309018
C	-0.156977	-1.263600	-0.414847
C	-0.458412	-2.499250	-0.856368
C	-1.091045	0.913087	-0.096849
C	0.140172	1.416051	0.121397
C	1.183452	0.564059	0.044362
C	1.061018	-0.758851	-0.140361
C	0.448346	2.657345	0.532922
C	1.730074	3.000899	0.718689
C	2.754601	2.151088	0.536536
C	2.483656	0.877432	0.192329
S	-2.182288	-4.171851	-1.536674
C	-3.614468	-3.854679	-1.629863
C	-3.877267	-2.603257	-1.228657
C	2.161820	4.203109	1.113617
C	3.495685	4.165963	1.203665
S	4.010193	2.827851	0.886771
C	2.294794	-1.274387	0.038225
C	3.189107	-0.263638	0.002479
C	-3.192706	0.338640	-0.102104
C	-2.354818	1.393502	-0.157529
C	-4.485132	0.510921	0.225904
C	2.709438	-2.532306	0.289667
C	4.499240	-0.554813	-0.145992
C	-2.885386	2.627439	-0.277303
C	-5.242029	-0.523292	0.634491
C	-6.536500	-0.436823	0.987501
C	-7.048341	0.805896	0.957199
C	-6.298199	1.863844	0.613002
C	-4.997386	1.759997	0.269982
C	-4.205933	2.813054	-0.044984
C	-4.667569	4.077435	-0.137143
C	-3.890839	5.100017	-0.517992
C	-2.603843	4.924819	-0.856537
C	-2.157811	3.659761	-0.745141

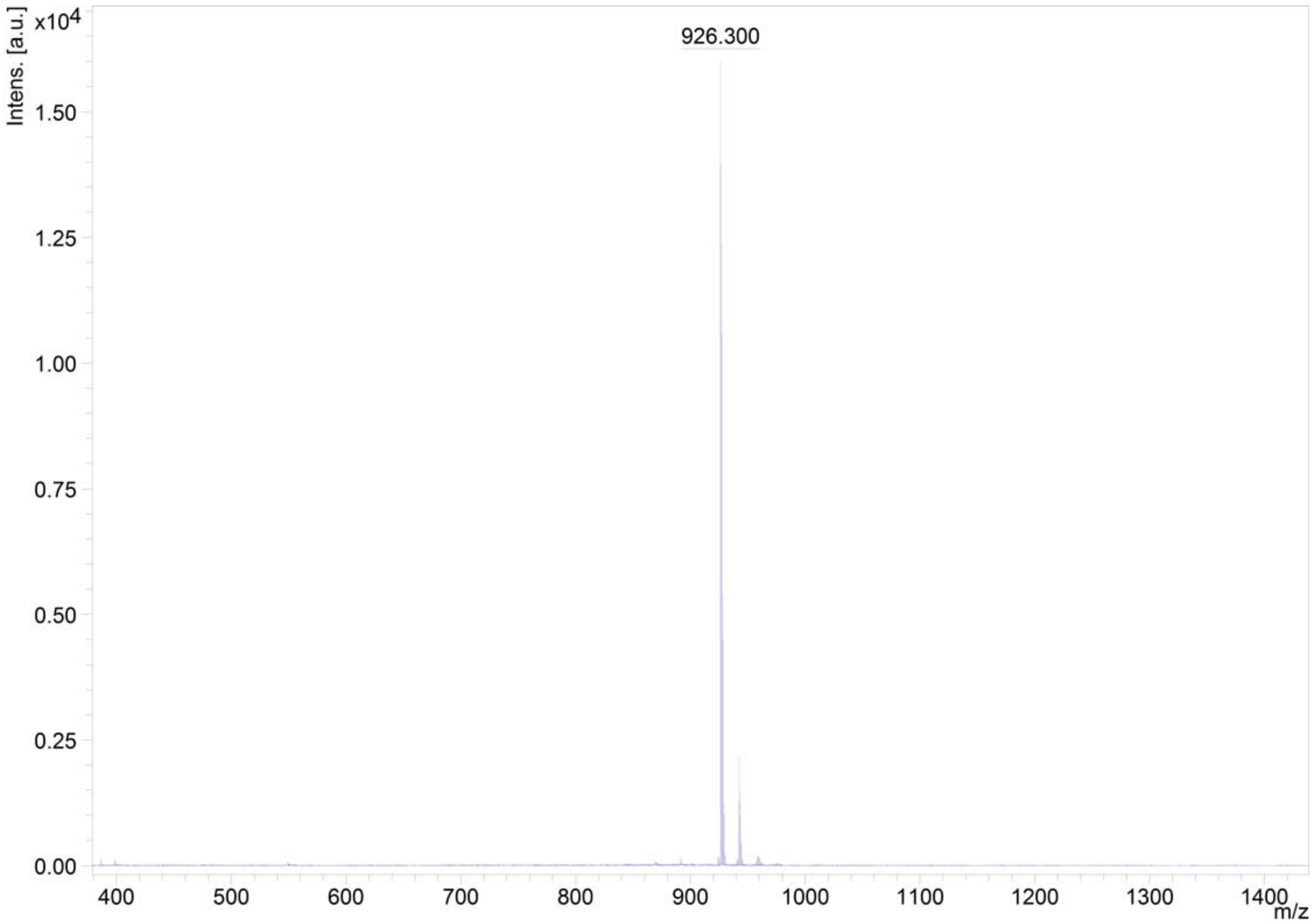
C	4.026821	-2.823401	0.225419
C	4.374900	-4.109692	0.436632
C	3.486688	-5.049684	0.786571
C	2.191591	-4.761815	0.976804
C	1.862055	-3.477862	0.742446
C	5.412081	0.373207	-0.491450
C	6.734641	0.166844	-0.626907
C	7.133574	-1.096191	-0.413028
C	6.243744	-2.062611	-0.147569
C	4.918088	-1.836828	-0.035825
C	-4.644452	-4.820742	-2.150167
C	4.365087	5.330958	1.588867
O	7.558159	1.221068	-0.946285
C	8.953032	1.025664	-0.897576
O	1.348650	-5.752314	1.422558
C	0.014277	-5.428823	1.737720
O	-1.885174	6.002449	-1.316385
C	-0.568235	5.801275	-1.774874
O	-7.197993	-1.570092	1.393051
C	-8.486136	-1.440150	1.948389
H	0.339337	-3.211687	-1.118864
H	-0.315426	3.399990	0.797166
H	-4.880243	-2.163369	-1.282945
H	1.534134	5.080961	1.316055
H	-4.794687	-1.519377	0.763282
H	-8.094872	0.991796	1.246798
H	-6.825402	2.827513	0.663600
H	-5.715030	4.352698	0.056444
H	-4.329177	6.110038	-0.602133
H	-1.145849	3.453543	-1.117507
H	5.408983	-4.477621	0.375627
H	3.833010	-6.081414	0.974340
H	0.836054	-3.183187	0.995814
H	5.095236	1.388486	-0.751070
H	8.195859	-1.376854	-0.487384
H	6.696995	-3.058983	-0.034841
H	-5.663574	-4.371789	-2.141700
H	-4.422859	-5.119241	-3.200929
H	-4.684512	-5.739403	-1.521656
H	4.960148	5.107428	2.503451
H	3.755021	6.238121	1.802679
H	5.067288	5.593853	0.764003
H	9.441953	2.001227	-1.119863
H	9.270923	0.295672	-1.675771
H	9.263894	0.705325	0.122006
H	-0.488043	-6.358640	2.088923
H	-0.521650	-5.069514	0.832997
H	-0.020113	-4.681882	2.563127
H	-0.172398	6.785046	-2.111677
H	-0.562982	5.108098	-2.645518

H	0.078149	5.433914	-0.946665
H	-8.825460	-2.452862	2.261239
H	-8.454096	-0.787929	2.850544
H	-9.200512	-1.056427	1.185895

D:\Mass Spec Lab users_2018\04_2018\wh-66-3-2nd col\0_D14\1\1SRef

Comment 1 Kyle Plunkett

Comment 2 DHB



m/z	S/N	Quality Fac.	Res.	Intens.	Area
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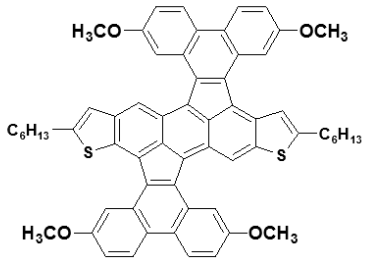
942.308	165	1591	9123	2340	446



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