

# Synthesis of a Dual Clickable Fullerene Platform and its Use for the Construction of Dissymmetric BODIPY-[60]Fullerene-DistyrylBODIPY Triad

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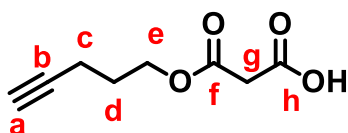
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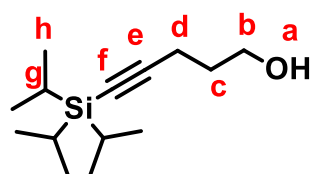
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### Synthesis of pent-4-ynyl mono malonate

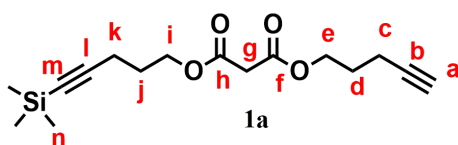


In a round bottomed flask, Meldrum acid (6.07 g, 42 mmol) and 4-pentyn-1-ol (3.5 g, 42 mmol) were added. The reaction mixture is stirred overnight at 80°C, and then evaporated under reduced pressure. After purification by column chromatography on silica gel (SiO<sub>2</sub>, chloroform/methanol, 100/3) 6.5 g of an orange liquid was obtained (yield= 77 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=1.86 (q, J=6 Hz, 2H; H<sub>d</sub>), 1.96 (t, J=2.6 Hz, 1H; H<sub>a</sub>), 2.27 (td, J=6 Hz, J=3 Hz, 2H; H<sub>c</sub>), 3.42 (s, 2H; H<sub>g</sub>), 4.26 (t, J=6 Hz, 2H; H<sub>e</sub>), 10.32 ppm (s, 1H; H<sub>OH</sub>).

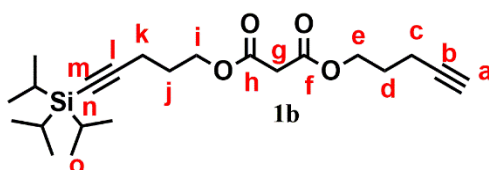
### Synthesis of 5-(tri-iso-propyl)pent-4-yn-1-ol



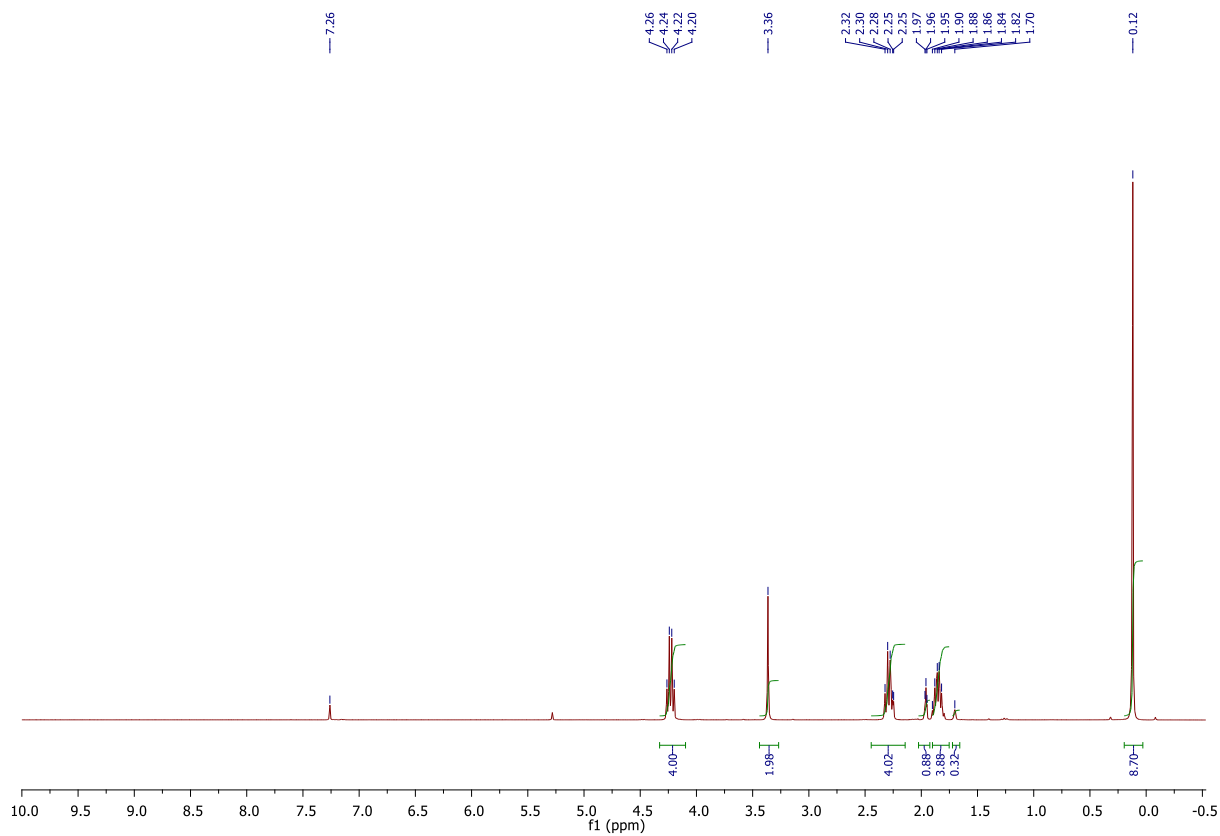
In a round bottomed flask 4-pentyn-1-ol (3 g, 35.7 mmol) was solubilized in 65 mL of THF under argon. Then 37 mL of 2 M solution of ethylmagnesium chloride in THF (6.65 g, 74.9 mmol) were added dropwise during 30 minutes at 0°C. The reaction mixture was stirred under reflux for 12 hours. After cooling down to room temperature, triisopropylsilyl chloride (7.63 mL; 35.7 mmol) in 35 mL of THF was added during 15 minutes. The reaction mixture was then refluxed for 6 hours. After cooling down to room temperature, an aqueous solution of (H<sub>2</sub>SO<sub>4</sub> 10%) was added to the flask and the mixture was extracted with 30 mL (x3) of Et<sub>2</sub>O. The organic phase was dried with MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. After purification by column chromatography on silica gel (cyclohexane/ethyl acetate 9/1), 6.5 g of a yellow oil was obtained (yield= 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=1.05-1.06 (bs, 21H; H<sub>g</sub>, H<sub>h</sub>), 1.70-1.85 (m, 3H; H<sub>a</sub>, H<sub>c</sub>), 2.38 (t, J=6.8 Hz, 2H; H<sub>d</sub>), 3.78 ppm (m, 2H; H<sub>b</sub>).



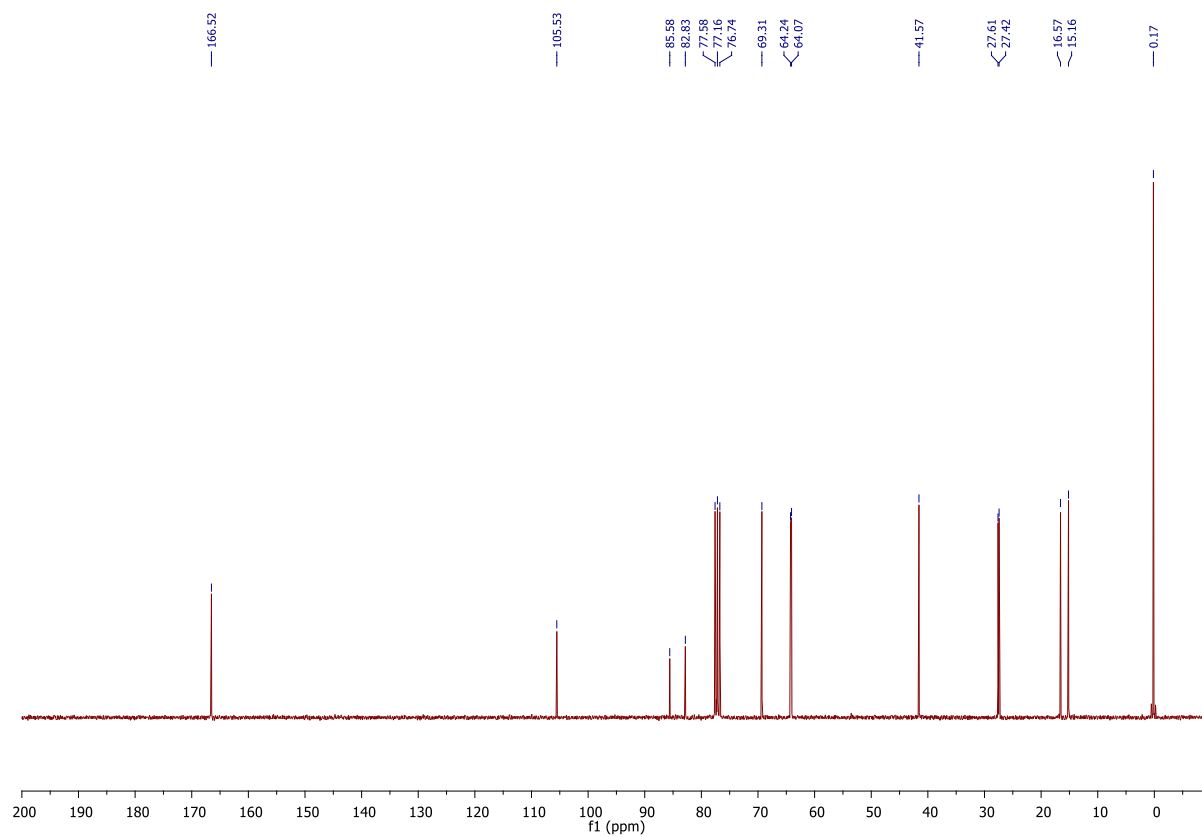
**Figure S1.** Structure and numbering of compound **1a** used for <sup>1</sup>H and <sup>13</sup>C NMR signal assignments



**Figure S2.** Structure and numbering of compound **1b** used for <sup>1</sup>H and <sup>13</sup>C NMR signal assignments



**Figure S3.**  $^1\text{H}$  NMR of compound **1a**



**Figure S4.**  $^{13}\text{C}$  NMR of compound **1a**

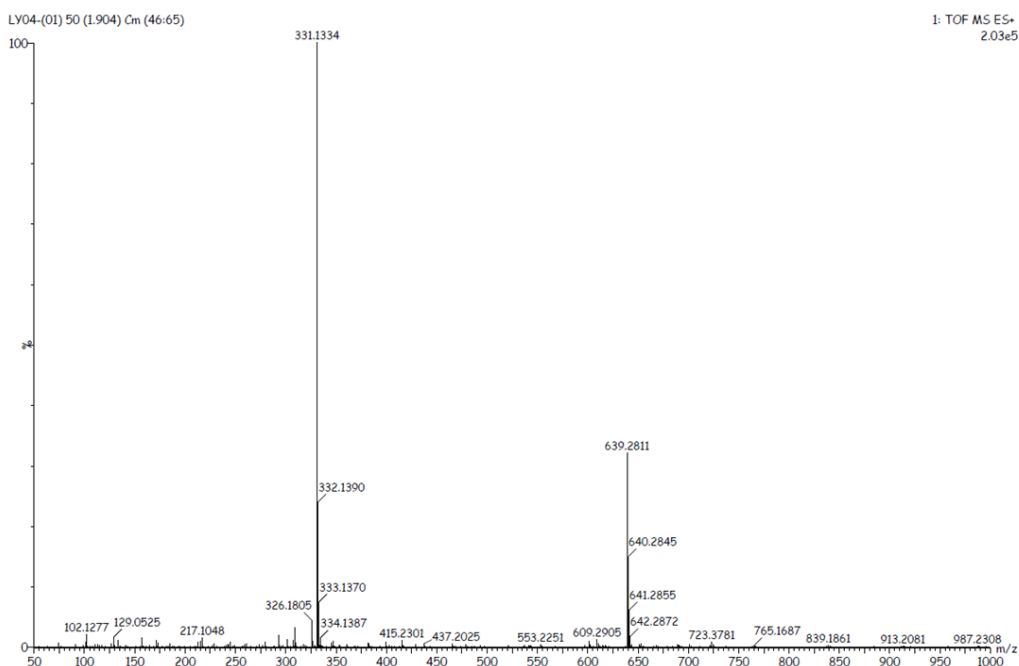


Figure S5. Mass spectrum of compound **1a**

Elemental Composition Report

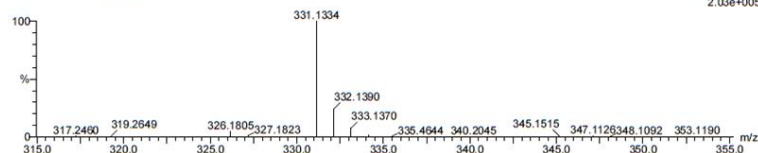
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Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
 4575 formula(e) evaluated with 14 results within limits (all results (up to 1000) for each mass)  
 Elements Used:  
 C: 0-100 H: 0-150 N: 0-10 O: 0-10 Na: 0-1 Si: 0-10  
 Aurelle DAMOND  
 Infusion - dilution 1000  
 LY04-(01) 50 (1.904) Cm (46:65)

08-Jun-2018  
 1: TOF MS ES+  
 2.03e+005



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
331.1334	331.1342	-0.8	-2.4	5.5	445.8	0.1	C16 H24 O4 Na Si
	331.1339	-0.5	-1.5	9.5	448.4	2.7	C14 H19 N6 O2 Si
	331.1325	0.9	2.7	4.5	449.8	4.1	C13 H23 N2 O6 Si
	331.1346	-1.2	-3.6	1.5	451.9	6.2	C8 H24 N6 O3 Na Si2
	331.1334	0.0	0.0	13.5	453.3	7.6	C22 H19 O3
	331.1330	0.4	1.2	0.5	453.8	8.1	C5 H23 N8 O5 Si2
	331.1338	-0.4	-1.2	12.5	454.1	8.3	C21 H23 S12
	331.1342	-0.8	-2.4	2.5	455.8	10.1	C9 H20 N6 O6 Na
	331.1346	-1.2	-3.6	4.5	455.9	10.2	C15 H28 O Na Si3
	331.1330	0.4	1.2	3.5	456.1	10.4	C12 H27 N2 O3 Si3
	331.1326	0.8	2.4	1.5	457.0	11.2	C6 H19 N8 O8
	331.1350	-1.6	-4.8	0.5	457.7	12.0	C7 H28 N6 Na Si4
	331.1334	0.0	0.0	-0.5	458.0	12.3	C4 H27 N8 O2 Si4
	331.1334	0.0	0.0	2.5	459.1	13.4	C11 H31 N2 Si5

Figure S6. Elemental composition report of compound **1a**

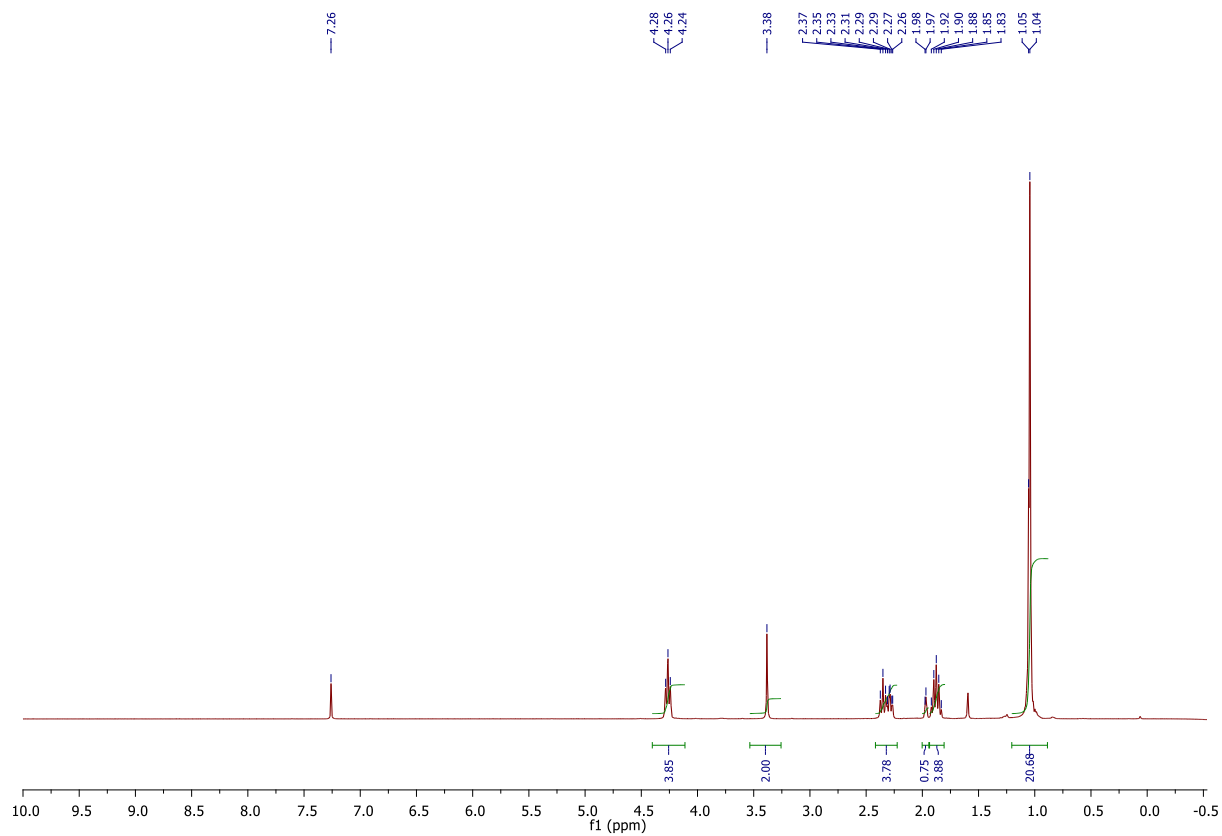


Figure S7.  $^1\text{H}$  NMR of compound **1b**

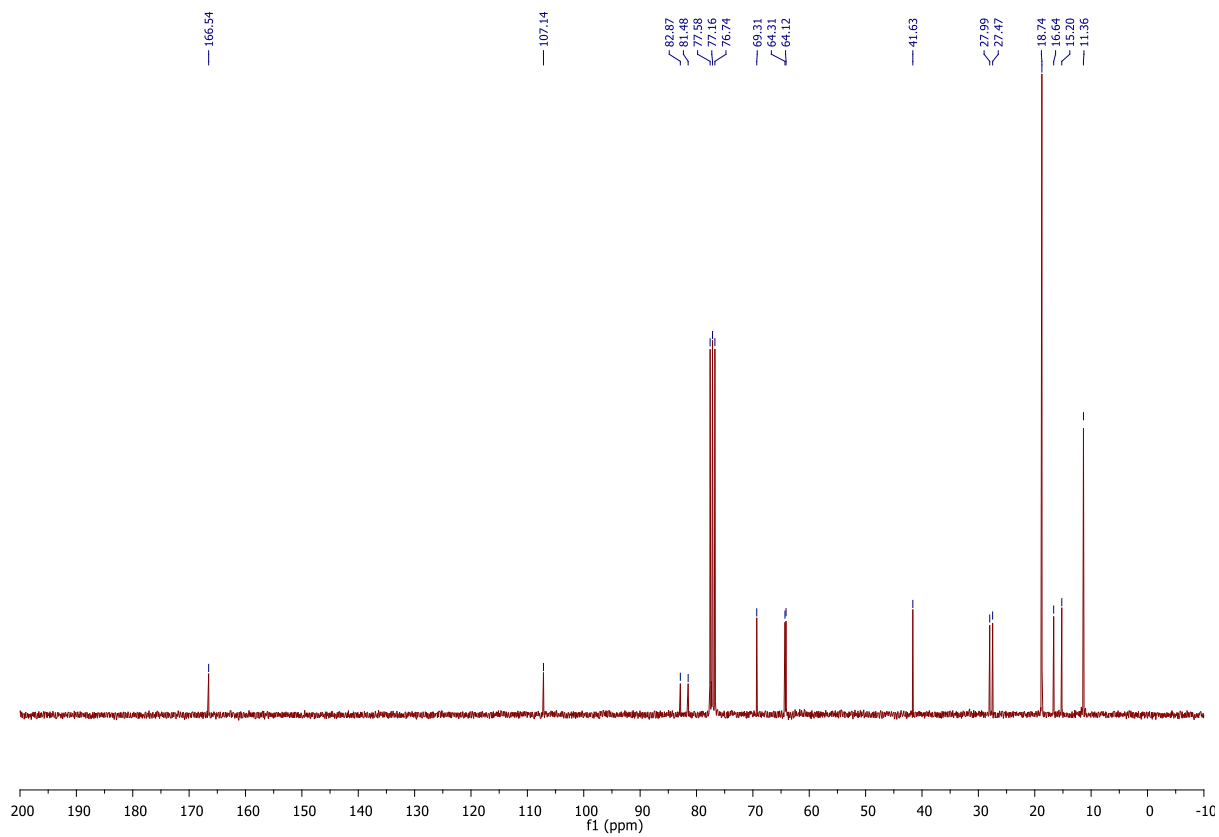
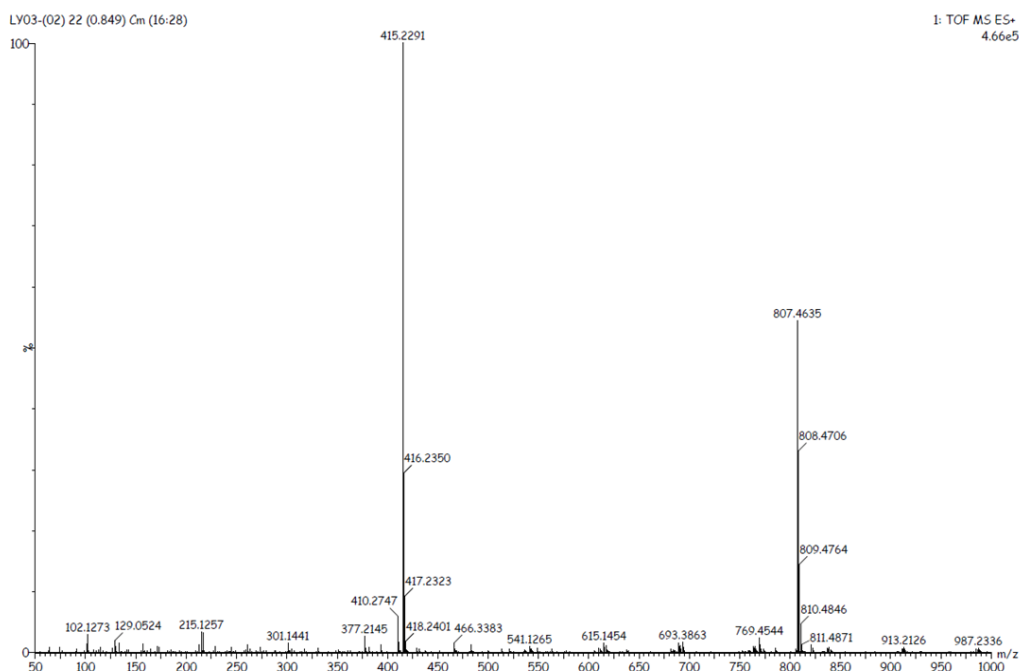


Figure S8.  $^{13}\text{C}$  NMR of compound **1b**



**Figure S9.** Mass spectrum of compound **1b**

**Elemental Composition Report**

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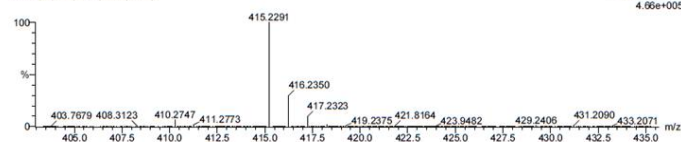
**Single Mass Analysis**

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
 7898 formula(e) evaluated with 20 results within limits (all results (up to 1000) for each mass)  
 Elements Used:  
 C: 0-100 H: 0-150 N: 0-10 O: 0-10 Si: 0-10 Na: 0-1

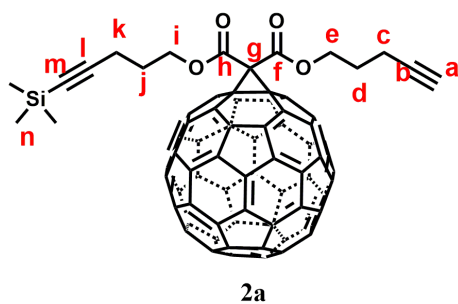
Aurélien DAMOND  
 Infusion - posHM  
 LY03-(02) 22 (0.849) Cm (16:28)

08-Jun-2018  
 1: TOF MS ES+  
 4.66e+005

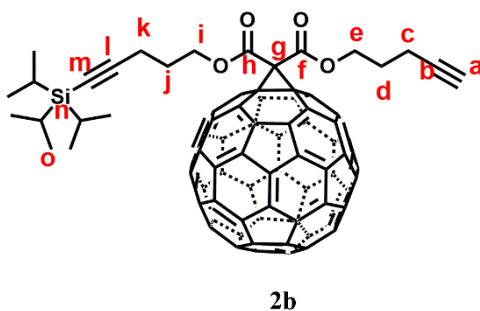


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
415.2291	415.2281	1.0	2.4	5.5	478.1	0.4	C22 H36 O4 S1 Na
415.2305	-1.4	-3.4	8.5	479.7	1.9		C24 H35 O4 S1
415.2278	1.3	3.1	9.5	480.2	2.4		C20 H31 N6 O2 S1
415.2294	-0.3	-0.7	10.5	480.9	3.2		C23 H32 N4 S1 Na
415.2285	0.6	1.4	1.5	482.6	4.9		C14 H36 N6 O3 S12
415.2309	-1.8	-4.3	4.5	482.9	5.1		Na C16 H35 N6 O3 S12
415.2296	-0.5	-1.2	-0.5	483.3	5.5		C15 H39 N2 O7 S12
415.2273	1.8	4.3	13.5	486.1	8.3		C28 H31 O3
415.2277	1.4	3.4	12.5	486.5	8.7		C27 H35 S12
415.2308	-1.7	-4.1	1.5	487.5	9.7		C19 H36 O8 Na
415.2305	-1.4	-3.4	5.5	487.6	9.9		C17 H31 N6 O6
415.2292	-0.1	-0.2	0.5	487.7	9.9		C16 H35 N2 O10
415.2309	-1.8	-4.3	7.5	487.7	9.9		C23 H39 O S13
415.2285	0.6	1.4	4.5	487.9	10.1		C21 H40 O S13 Na
415.2294	-0.3	-0.7	7.5	488.0	10.2		C16 H28 N10 O2 Na
415.2281	1.0	2.4	2.5	488.3	10.5		C15 H32 N6 O6 Na
415.2300	-0.9	-2.2	-1.5	489.3	11.5		C14 H43 N2 O4 S14
415.2289	0.2	0.5	0.5	489.5	11.7		C13 H40 N6 S14 Na
415.2273	1.8	4.3	-0.5	489.8	12.1		C10 H39 N8 O2 S14
415.2273	1.8	4.3	2.5	491.2	13.4		C17 H43 N2 S15

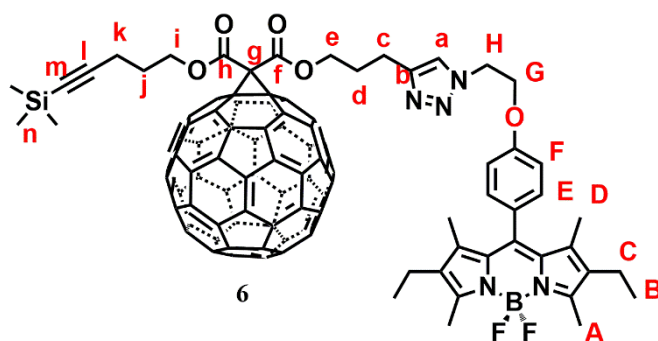
**Figure S10.** Elemental composition report of compound **1b**



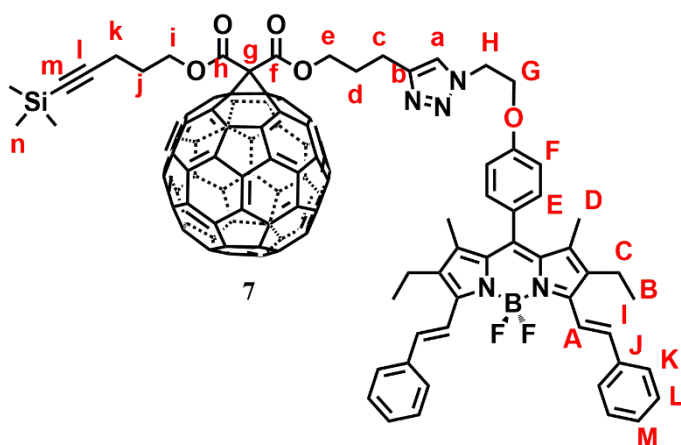
**Figure S11.** Structure and numbering of compound **2a** used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments



**Figure S12.** Structure and numbering of compound **2b** used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments



**Figure S13.** Structure and numbering of compound **6** used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments



**Figure S14.** Structure and numbering of compound **7** used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments

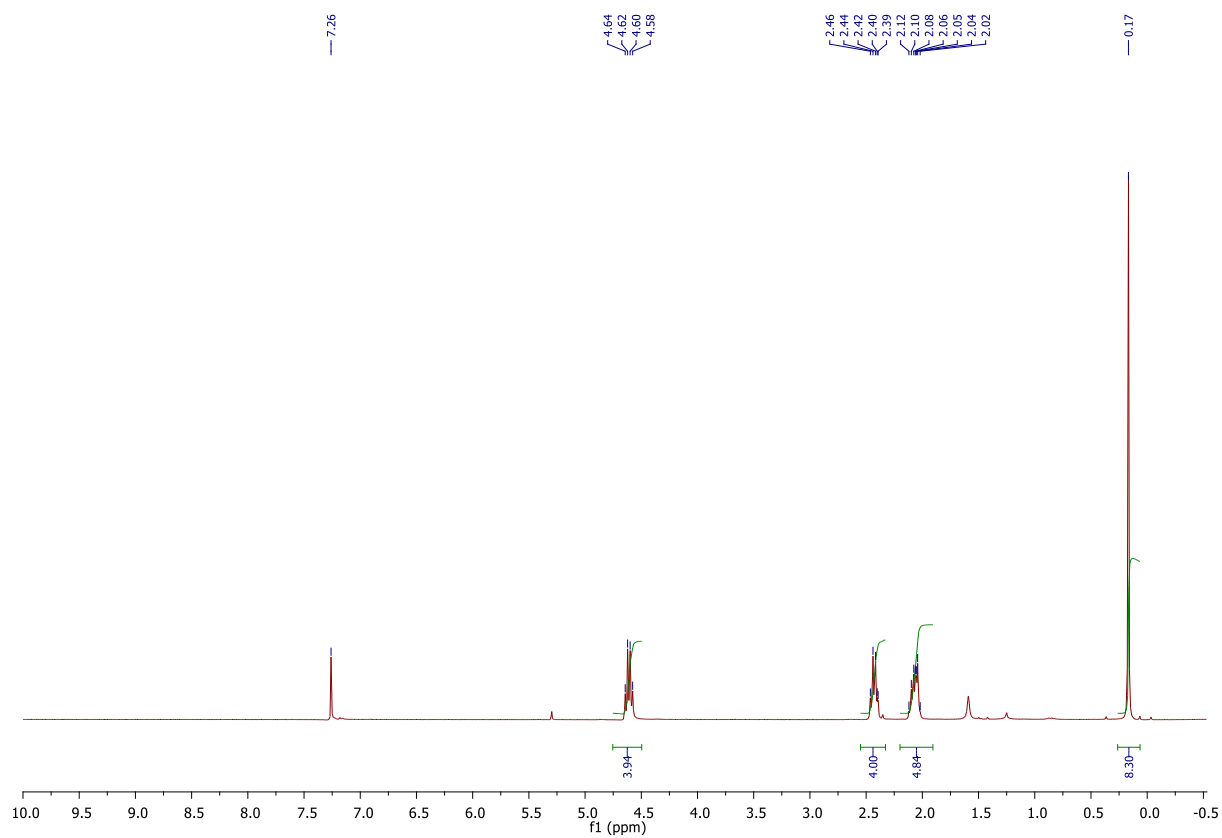


Figure S15. <sup>1</sup>H NMR of compound 2a

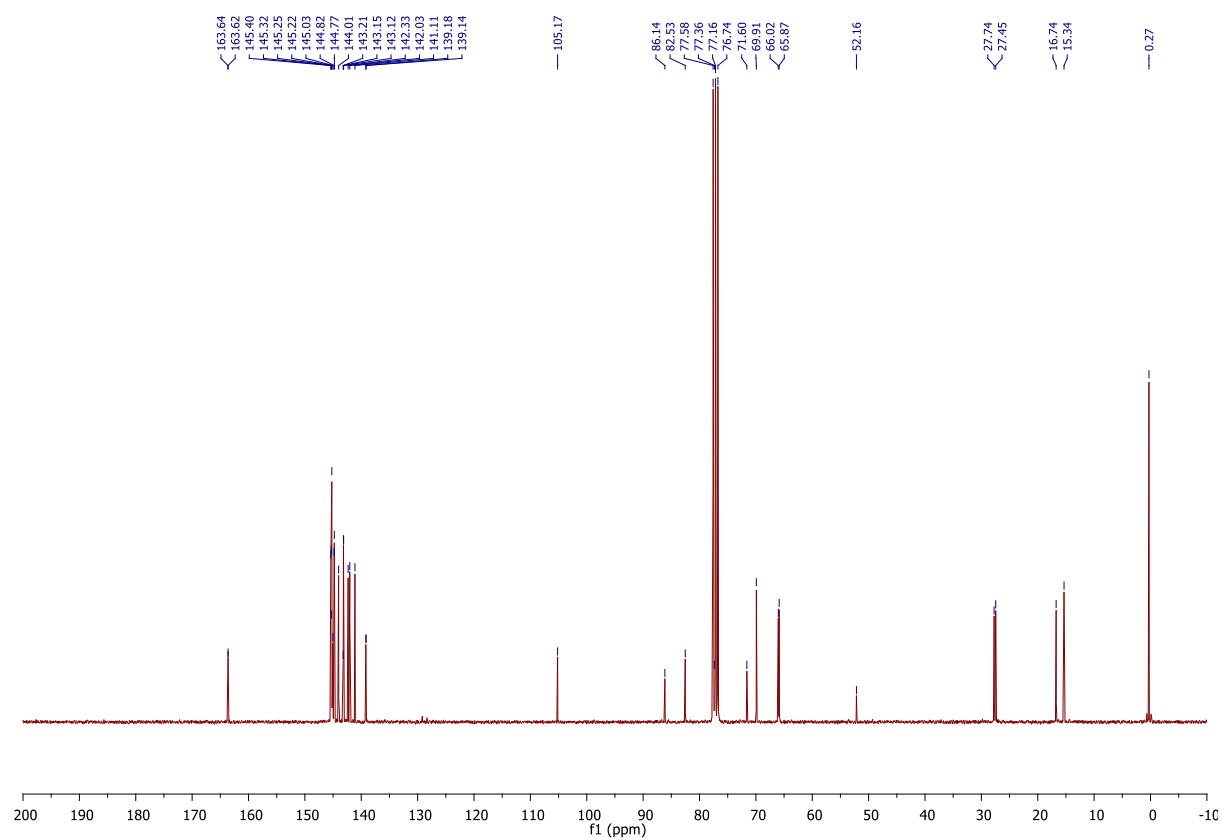


Figure S16. <sup>13</sup>C NMR of compound 2a



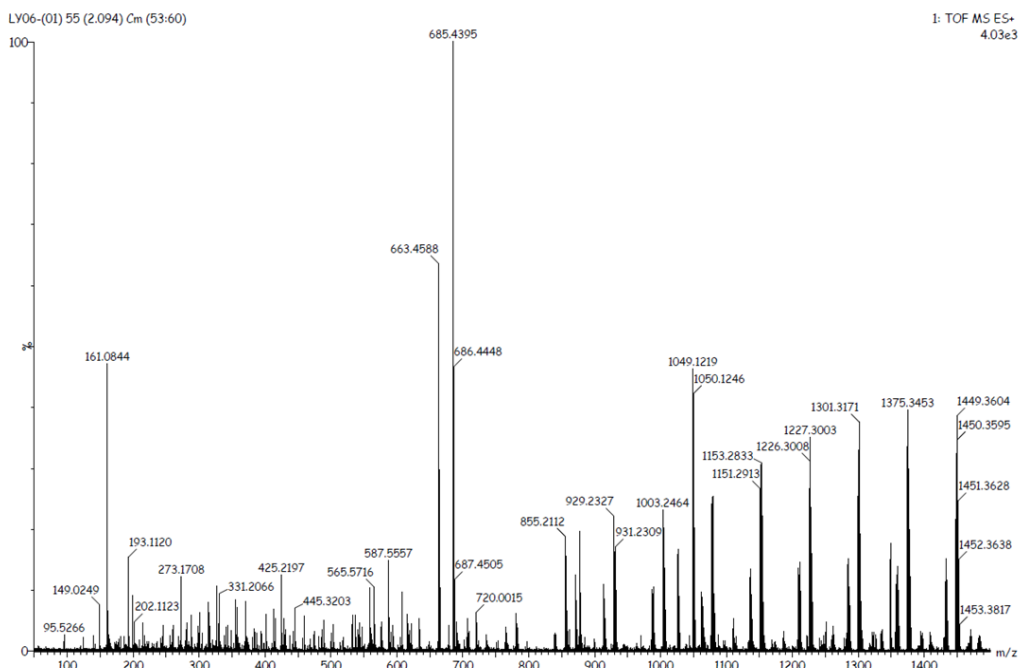


Figure S17. Mass spectrum of compound 2a

Elemental Composition Report

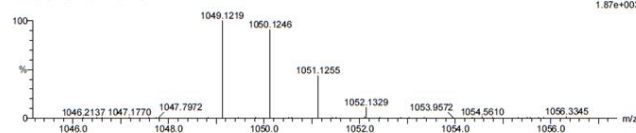
Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 3

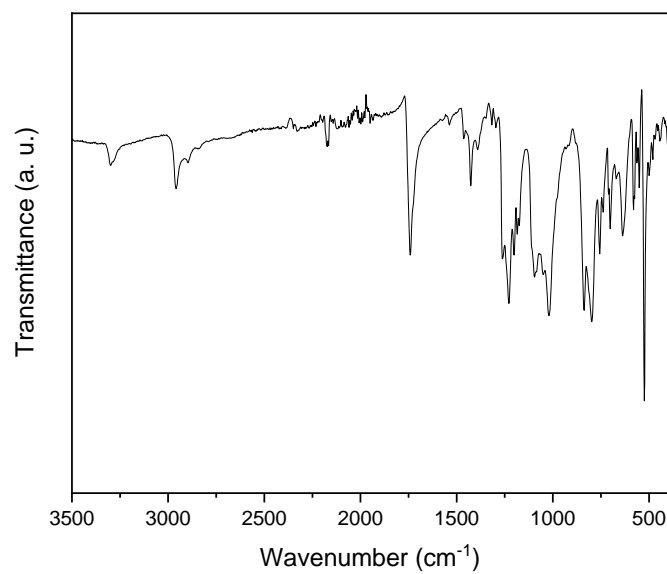
Monoisotopic Mass, Even Electron Ions  
2733 formula(e) evaluated with 25 results within limits (all results (up to 1000) for each mass)  
Elements Used:  
C: 0-100 H: 0-150 O: 0-10 Na: 0-1 Si: 0-10  
Aurélien DAMOND  
Infusion - Dilution 100 (SM = 3.3 mg/mL) - manual quad  
LV06-(01) 55 (2.094) Cm (53:60)

14-Jun-2018  
1: TOF MS ES+  
1.87e+003

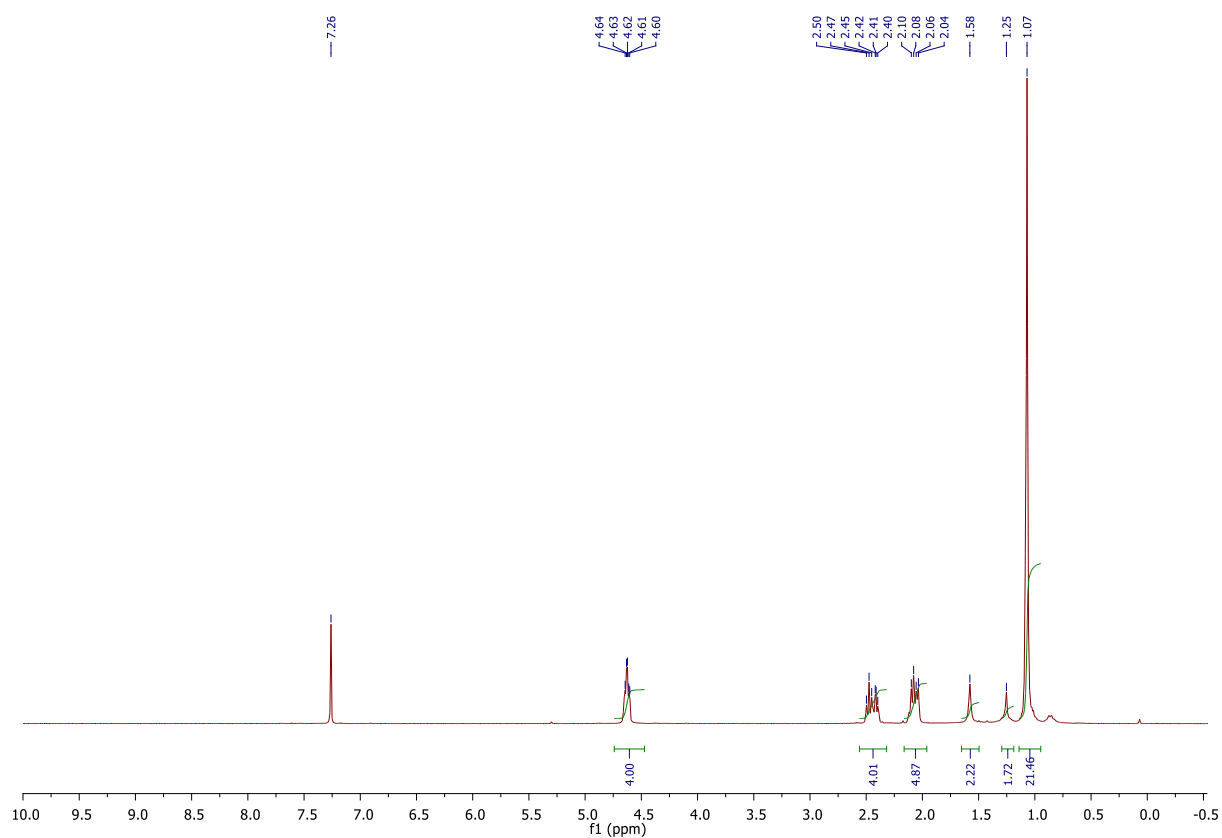


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1049.1219	1049.1209	1.0	1.0	69.5	63.9	0.8	C78 H21 O4 Si
	1049.1185	3.4	3.2	66.5	64.4	1.3	C76 H22 O4 Na Si
	1049.1217	0.2	0.2	61.5	65.1	2.1	C72 H26 O5 Na Si2
	1049.1178	4.1	3.9	74.5	65.3	2.2	C82 H17 O3
	1049.1241	-2.2	-2.1	64.5	66.9	3.8	C74 H25 O5 Si2
	1049.1244	-2.5	-2.4	57.5	67.4	4.3	C69 H26 O9 Na Si
	1049.1268	-4.9	-4.7	60.5	67.8	4.7	C71 H25 O9 Si
	1049.1236	-1.7	-1.6	65.5	68.2	5.2	C75 H21 O8
	1049.1248	-2.9	-2.8	56.5	68.4	5.3	C68 H30 O6 Na Si3
	1049.1212	0.7	0.7	62.5	68.4	5.4	C73 H22 O8 Na
	1049.1213	0.6	0.6	68.5	69.5	6.4	C77 H25 O Si3
	1049.1182	3.7	3.5	73.5	69.9	6.8	C81 H21 Si2
	1049.1221	-0.2	-0.2	60.5	69.9	6.8	C71 H30 O2 Na Si4
	1049.1189	3.0	2.9	65.5	70.0	7.0	C75 H26 O Na Si3
	1049.1245	-2.6	-2.5	63.5	71.1	8.0	C73 H29 O5 Si4
	1049.1252	-3.3	-3.1	55.5	71.8	8.7	C67 H34 O3 Na Si5
	1049.1218	0.1	0.1	39.5	72.5	9.4	C53 H45 O9 Si8
	1049.1225	-0.6	-0.6	31.5	72.7	9.7	C47 H50 O10 Na Si9
	1049.1249	-3.0	-2.9	34.5	73.3	10.3	C49 H49 O10 Si9
	1049.1186	3.3	3.1	44.5	73.5	10.4	C57 H41 O8 Si7
	1049.1194	2.5	2.4	36.5	73.5	10.5	C51 H46 O9 Na Si8
	1049.1222	-0.3	-0.3	38.5	73.6	10.5	C52 H49 O6 Si10
	1049.1256	-3.7	-3.5	54.5	73.6	10.5	O66 H38 Na Si7
	1049.1198	2.1	2.0	35.5	74.5	11.5	C50 H50 O6 Na Si10
	1049.1191	2.8	2.7	43.5	74.7	11.6	C56 H45 O5 Si9

Figure S18. Elemental composition report of compound 2a



**Figure S19.** IR spectrum of compound **2a**



**Figure S20.** <sup>1</sup>H NMR of compound **2b**

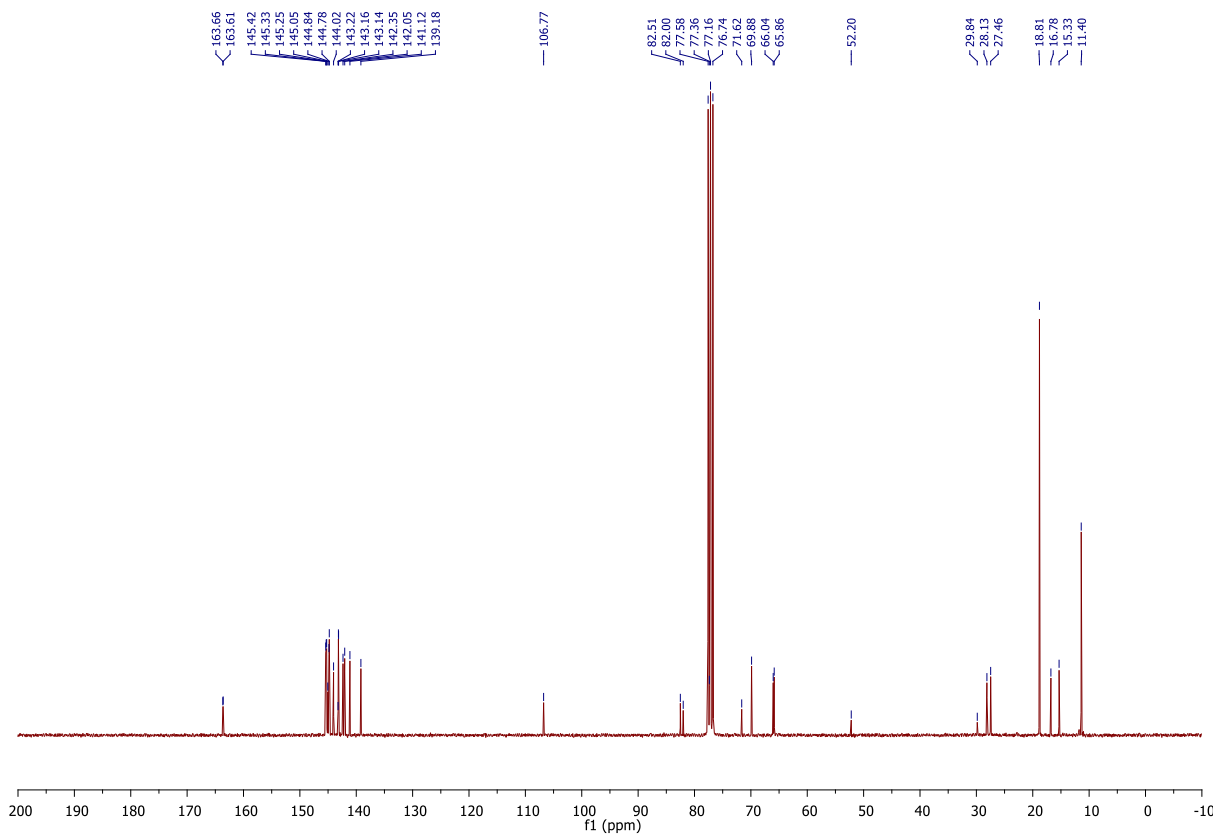


Figure S21. <sup>13</sup>C NMR of compound **2b**

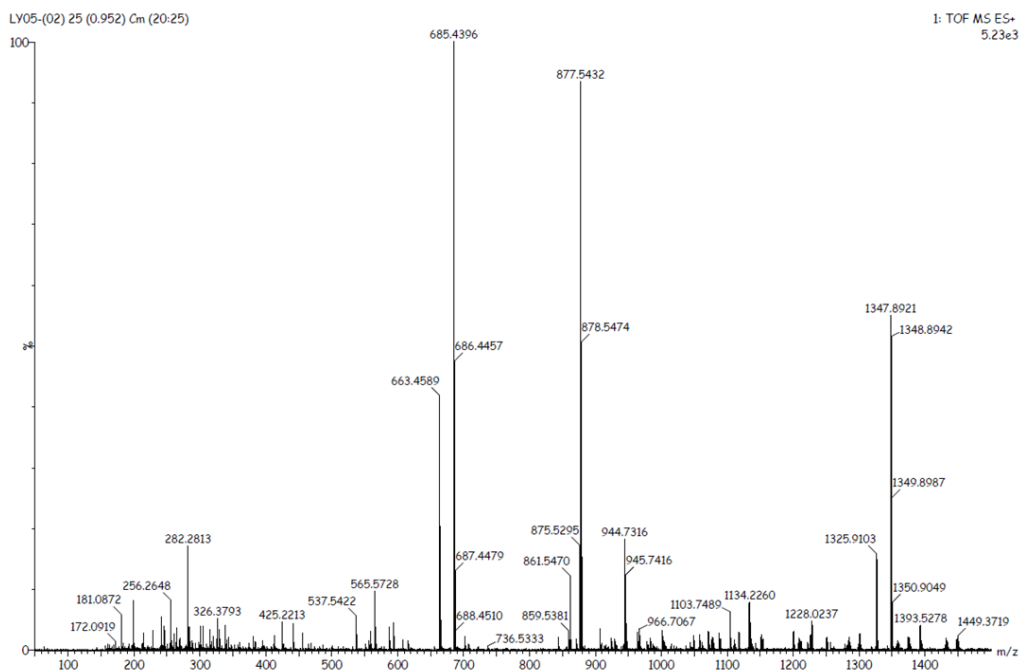


Figure S22. Mass spectrum of compound **2b**

## Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions

2930 formula(e) evaluated with 117 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-150 O: 0-10 Na: 0-1 Si: 0-10

Auricle DAMOND

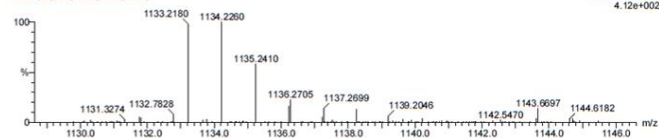
Infusion - Dilution 20 - manual quad

LY05-002.25 (0.952) Cm (20.25)

14-Jun-2018

1: TOF MS ES+

4.12e+002



Minimum:

Maximum: 5.0 20.0 100.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1133.2180	1133.2269	-8.9	-7.9	78.5	110.2	1.9	C92 H29
	1133.2277	-9.7	-8.6	70.5	110.3	2.0	C86 H34 O Na Si
	1133.2148	3.2	2.8	69.5	110.6	2.4	C84 H33 O4 Si
	1133.2245	-6.5	-5.7	75.5	110.7	2.5	C90 H30 Na
	1133.2301	-12.1	-10.7	73.5	110.7	2.5	C88 H33 O Si
	1133.2124	5.6	4.9	66.5	111.0	2.7	C82 H34 O4 Na Si
	1133.2359	-17.9	-15.8	64.5	111.4	3.1	C81 H37 O6 Si
	1133.2117	6.3	5.6	74.5	111.6	3.4	C88 H29 O3
	1133.2335	-15.5	-13.7	61.5	111.6	3.4	C79 H38 O6 Na Si
	1133.2207	-2.7	-2.4	60.5	111.7	3.4	C77 H37 O9 Si
	1133.2238	-5.8	-5.1	55.5	112.0	3.7	C73 H41 O10 Si2
	1133.2214	-3.4	-3.0	52.5	112.1	3.8	C71 H42 O10 Na Si2
	1133.2156	2.4	2.1	61.5	112.2	4.0	C78 H38 O5 Na Si2
	1133.2367	-18.7	-16.5	56.5	112.5	4.2	C75 H42 O7 Na Si2
	1133.2183	-0.3	-0.3	57.5	112.5	4.2	C75 H38 O9 Na Si
	1133.2180	0.0	0.0	64.5	112.6	4.3	C80 H37 O5 Si2
	1133.2328	-14.8	-13.1	49.5	112.6	4.3	C85 H33 O5
	1133.2308	-12.8	-11.3	65.5	112.7	4.4	C82 H38 O2 Na Si2
	1133.2093	6.7	7.7	71.5	112.8	4.5	C86 H30 O3 Na
	1133.1996	18.4	16.2	65.5	112.8	4.5	C80 H33 O7 Si
	1133.2391	-21.1	-18.6	59.5	113.0	4.7	C77 H41 O7 Si2
	1133.2332	-15.2	-13.4	68.5	113.2	4.9	C84 H37 O2 Si2
	1133.2304	-12.4	-10.9	66.5	113.3	5.0	C83 H34 O5 Na

Figure S23. Elemental composition report of compound 2b

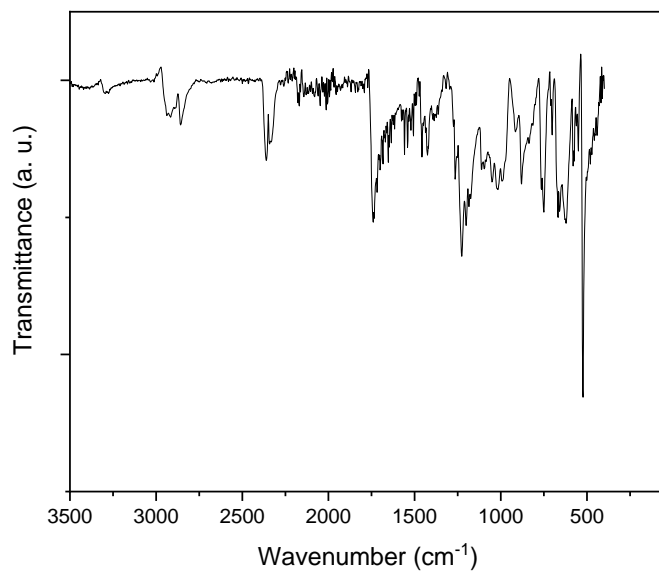
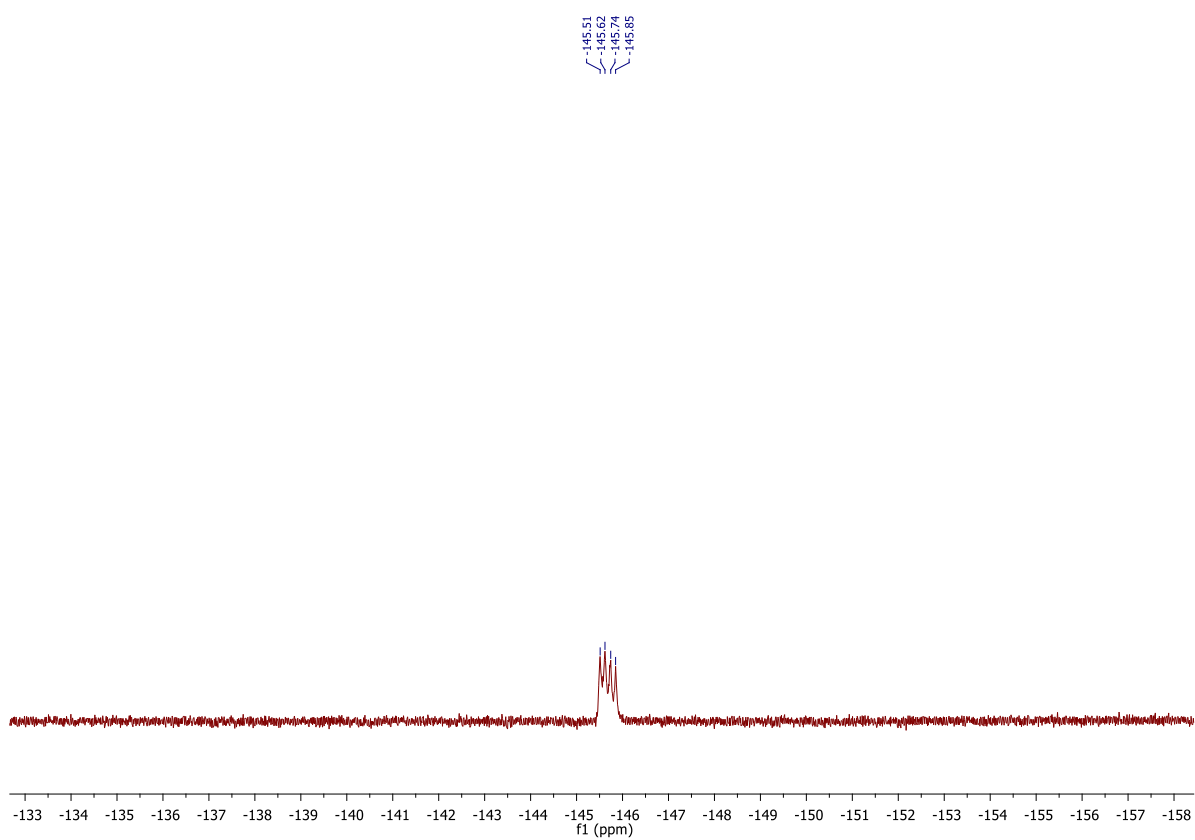
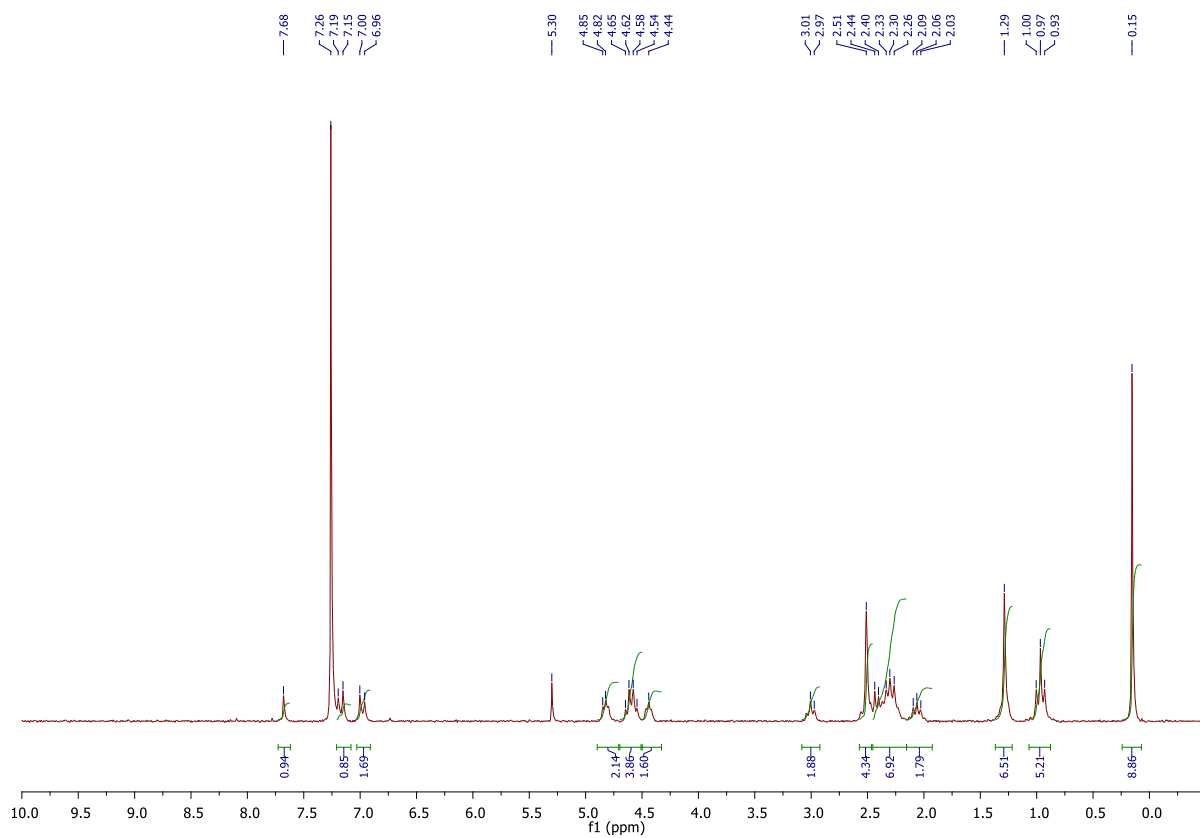


Figure S24. IR spectrum of compound 2b



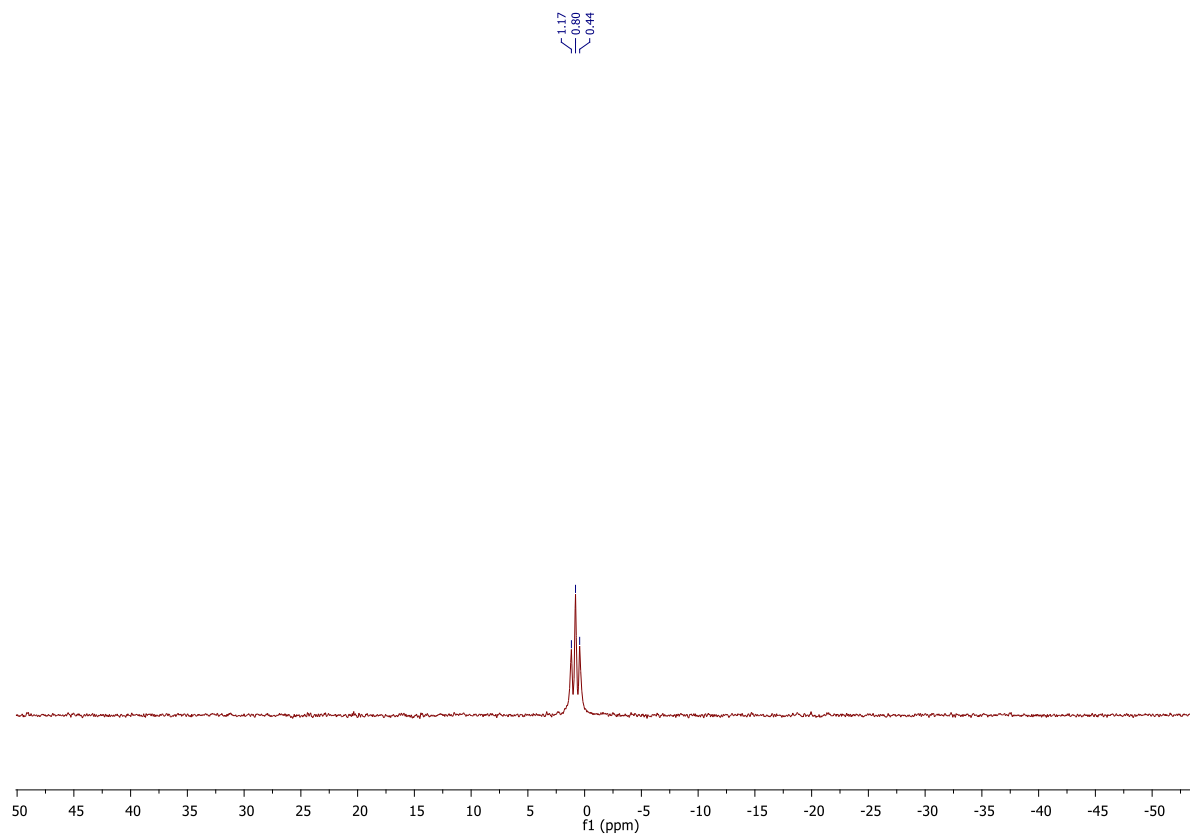


Figure S27. <sup>11</sup>B NMR of compound 6

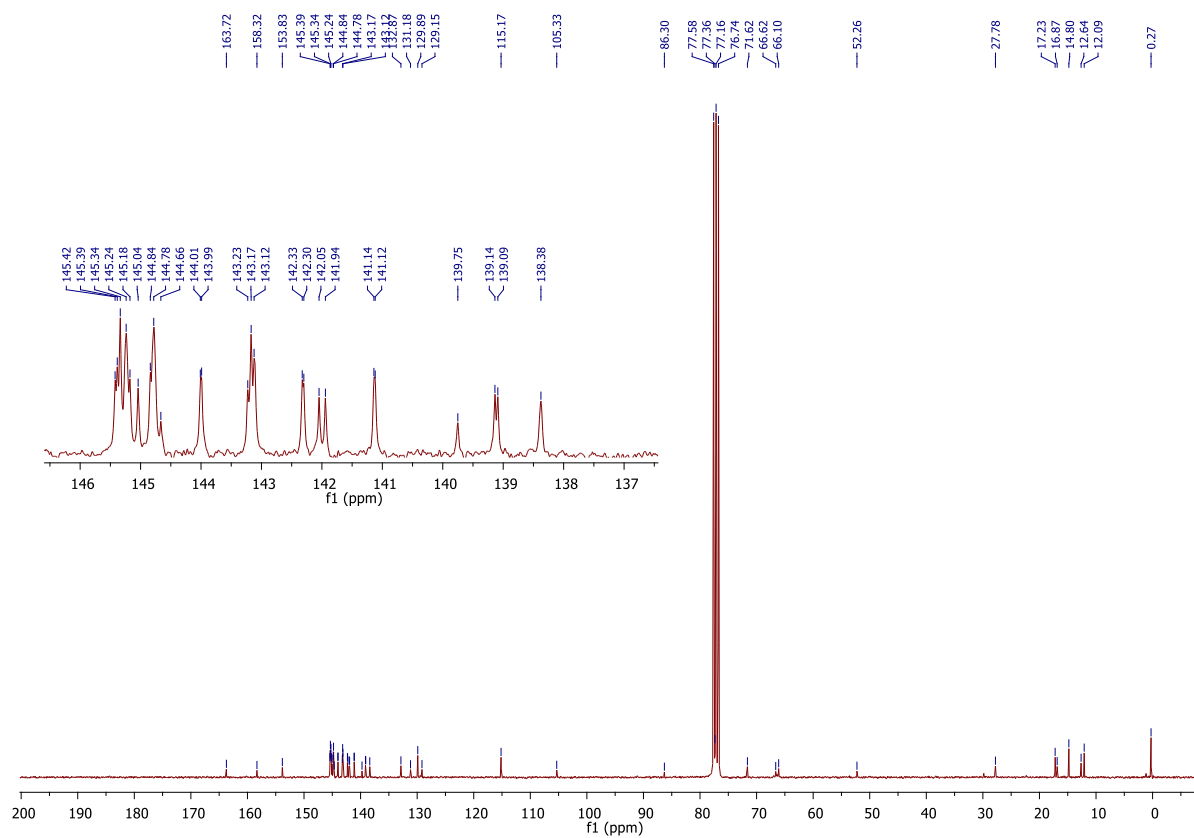


Figure S28. <sup>13</sup>C NMR of compound 6 with a zoom in the 138-146 ppm region.

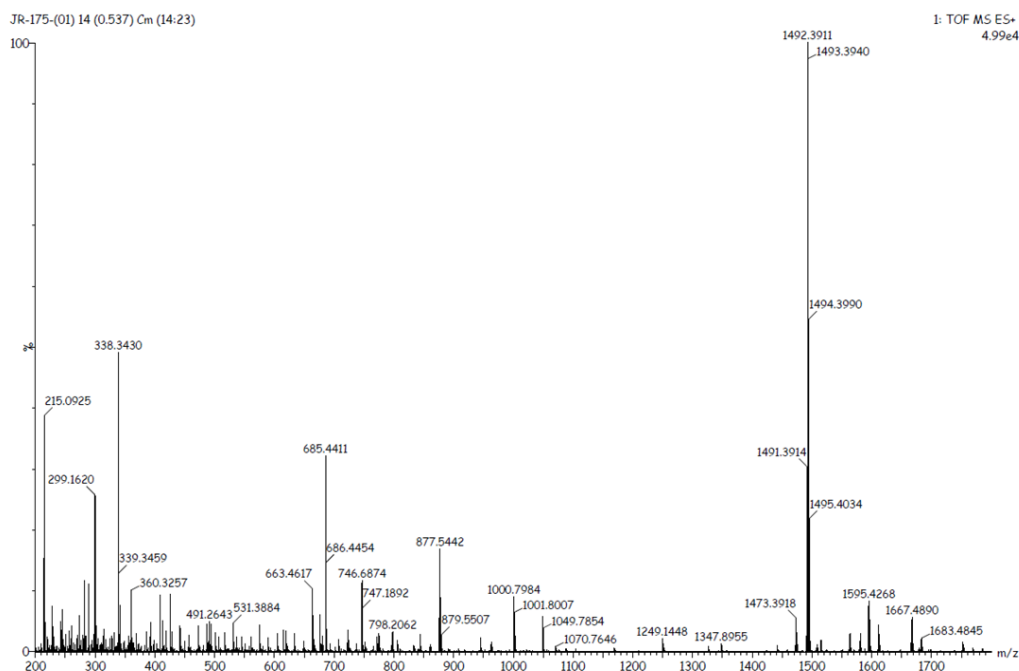


Figure S29. Mass spectrum of compound 6

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions

56169 formulae evaluated with 583 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-101 H: 0-80 B: 0-1 N: 0-10 O: 0-10 F: 0-3 Si: 0-10

Lab: RADIAN

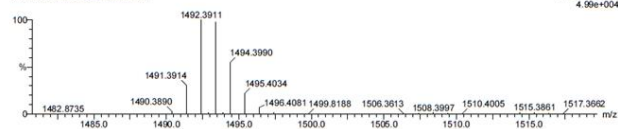
Infusion: dilution 1000

JR-175-(01) 14 (0.537) Cm (14:23)

10Dec2018

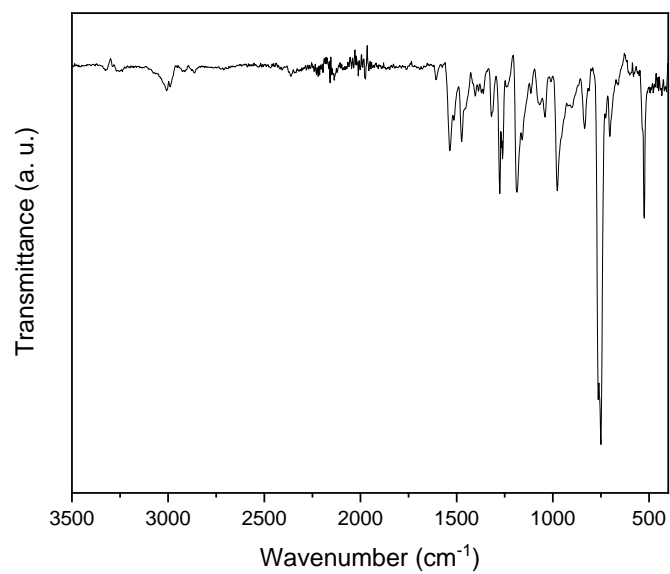
1: TOF MS ES+

4.99e+004

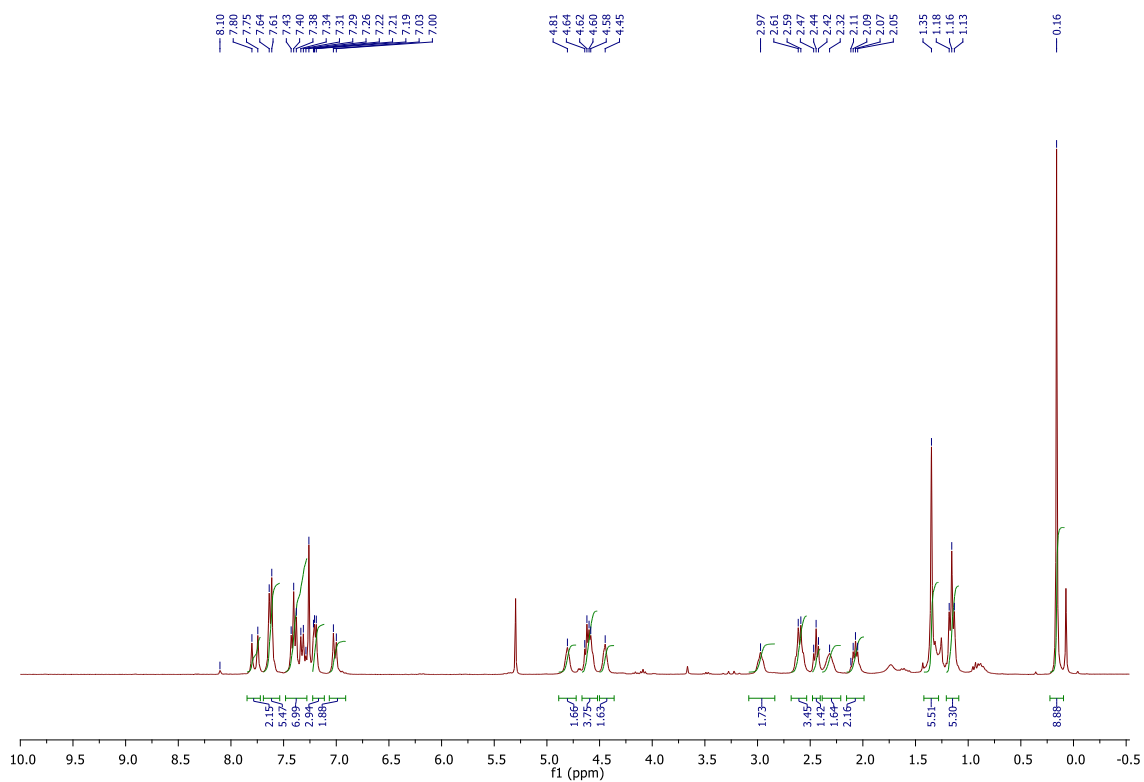


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1492.3911	1492.3985	-7.4	-5.0	76.5	406.8	17.3	C101 H59 B N3 O7 S12
1492.3876	1492.3876	3.5	2.3	73.5	412.8	23.2	C101 H60 N O7 P2 S12
1492.3985	1492.3985	-7.4	-5.0	74.5	399.8	10.2	C101 H56 N3 O9 F2
1492.3861	1492.3861	5.0	3.4	78.5	406.1	16.5	C101 H54 B N5 O2 F3 S12
1492.3910	1492.3910	0.1	0.1	80.5	398.0	8.4	C101 H49 N9 O3 F3 S15
1492.3861	1492.3861	5.0	3.4	75.5	415.7	26.1	C101 H64 B N O2 F S15
1492.3844	1492.3844	6.7	4.5	74.5	393.2	3.6	C101 H54 B N O9 F3 S13
1492.3910	1492.3910	0.1	0.1	77.5	416.4	26.8	C101 H59 N5 O3 F S13
1492.3861	1492.3861	5.0	3.4	73.5	416.6	27.0	C101 H61 N O4 F3 S13
1492.3910	1492.3910	0.1	0.1	82.5	406.0	16.4	C101 H52 B N9 O F S12
1492.3876	1492.3876	3.5	2.3	75.5	413.6	24.0	C101 H63 B N O5 S14
1492.3892	1492.3892	1.9	1.3	73.5	407.5	17.9	C101 H59 N O10 F S1
1492.3877	1492.3877	3.4	2.3	78.5	400.5	10.9	C101 H53 B N5 O5 F2 S1
1492.3893	1492.3893	1.8	1.2	78.5	392.9	3.3	C101 H52 B N5 O8 F C101 H70 N S17
1492.3893	1492.3893	1.8	1.2	74.5	423.9	34.3	C101 H60 N5 F2 S14
1492.3894	1492.3894	1.7	1.1	77.5	419.2	29.6	C101 H50 B N7 O4 F3
1492.3969	1492.3969	-5.8	-3.9	79.5	391.8	2.2	

Figure S30. Elemental composition report of compound 6



**Figure S31.** IR spectrum of compound **6**



**Figure S32.**  $^1\text{H}$  NMR of compound **7**



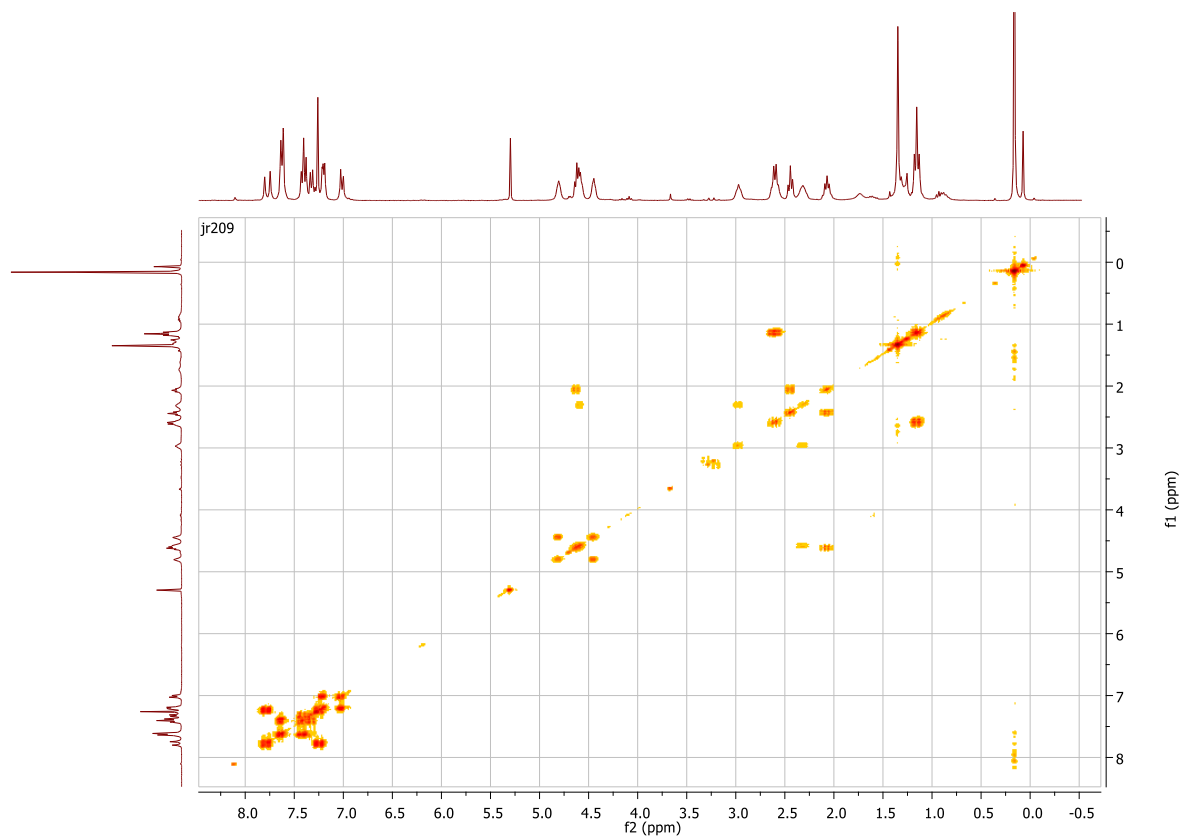


Figure S33. COSY of compound 7

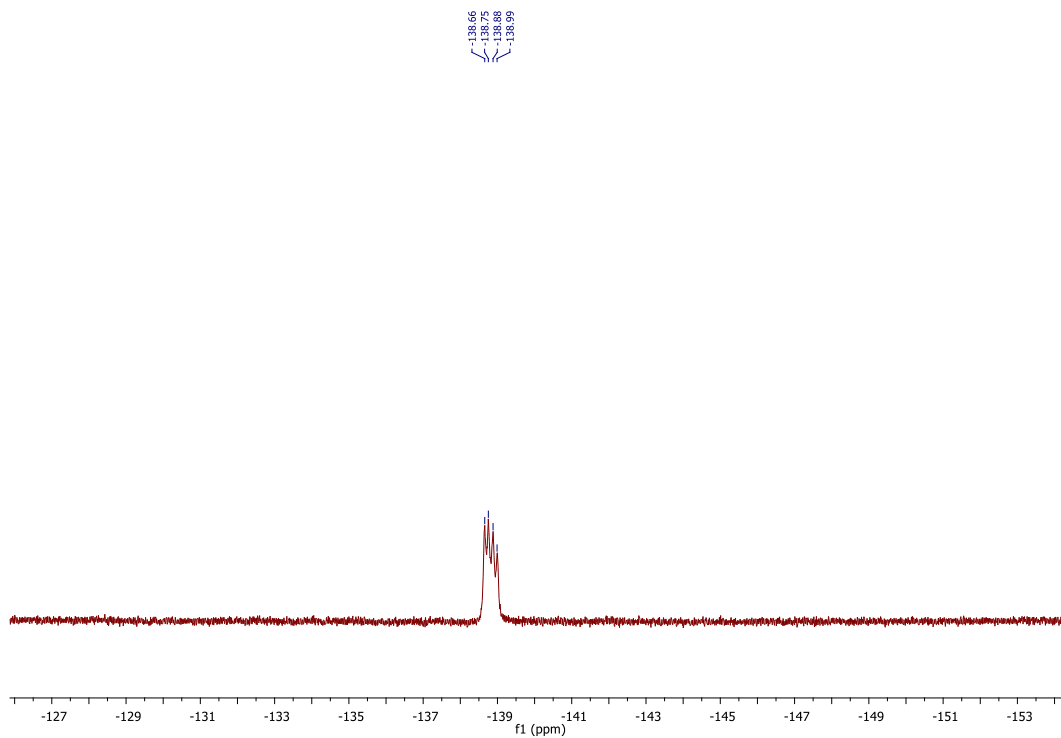


Figure S34.  $^{19}\text{F}$  NMR of compound 7

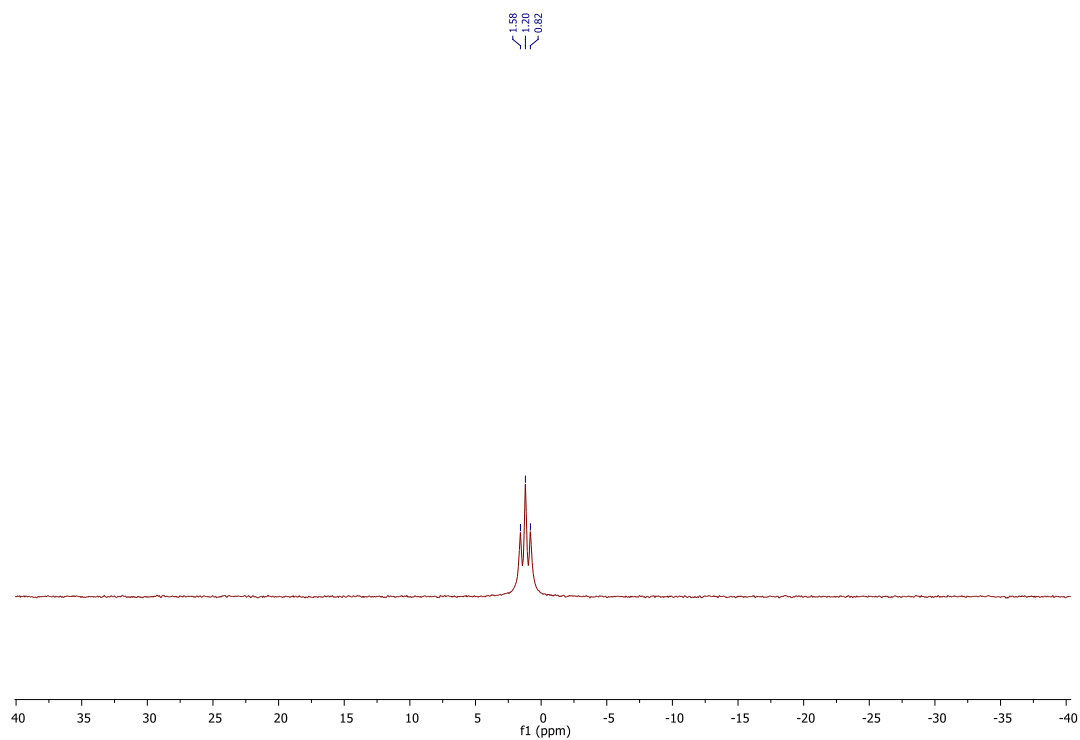


Figure S35.  $^{11}\text{B}$  NMR of compound 7

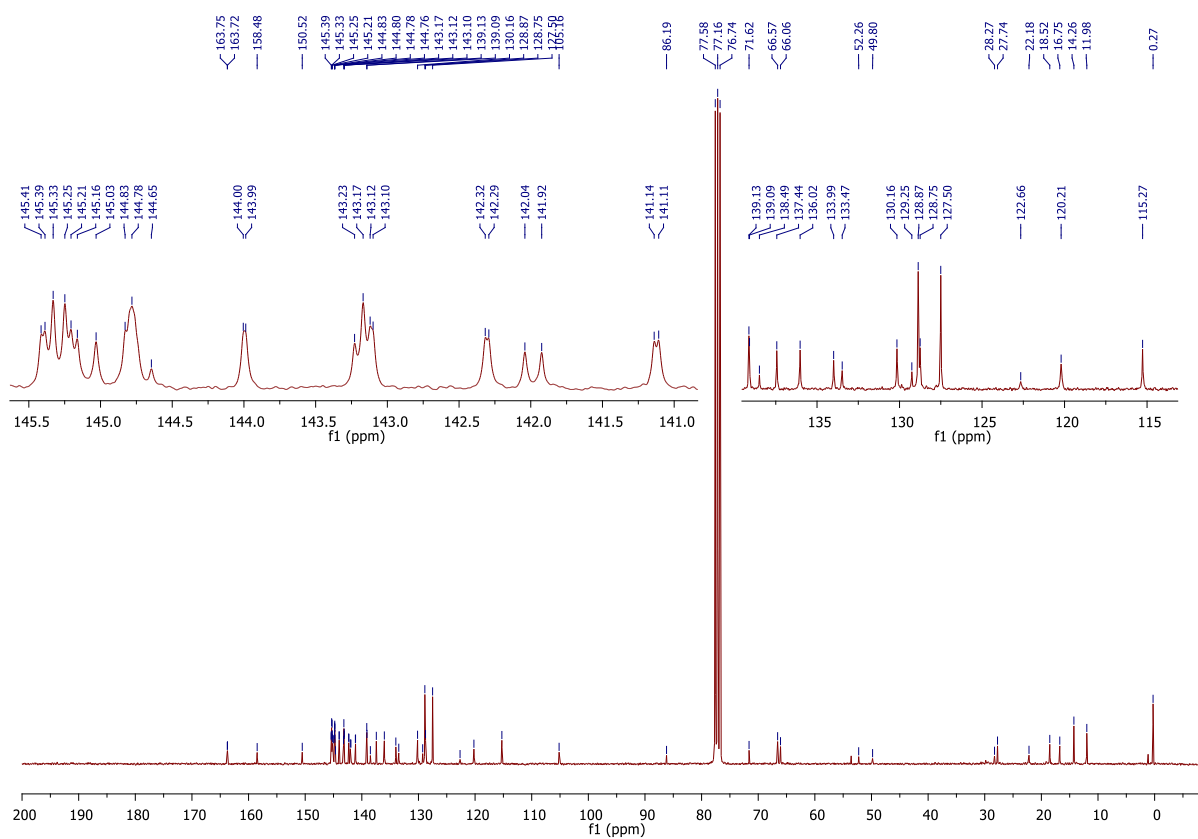


Figure S36.  $^{13}\text{C}$  NMR of compound 7 with a zoom in the 115-146 ppm region.

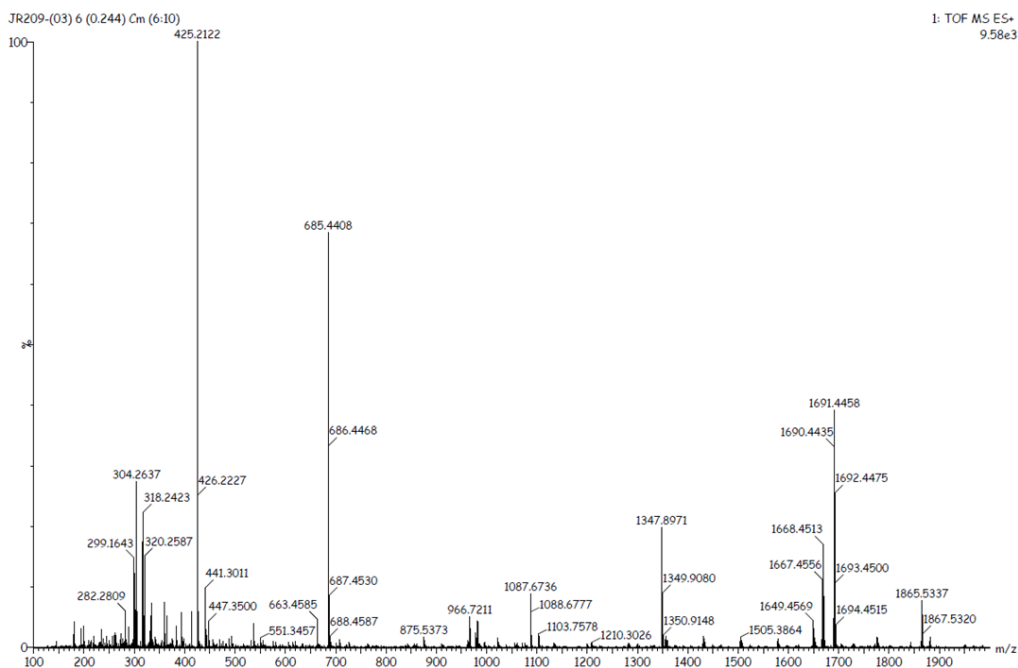


Figure S37. Mass spectrum of compound 7

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 150.0  
 Element prediction: C11  
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions  
 13694 formulae evaluated with 165 results within limits (all results (up to 1000) for each mass)  
 Elements Used:

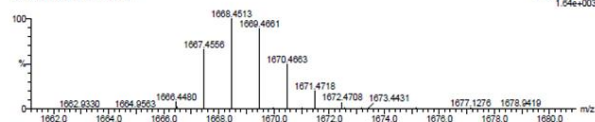
C: 0-115 H: 0-150 O: 0-10 N: 0-10 F: 0-3 Si: 1-1

Jad RABAH

20-Feb-2019

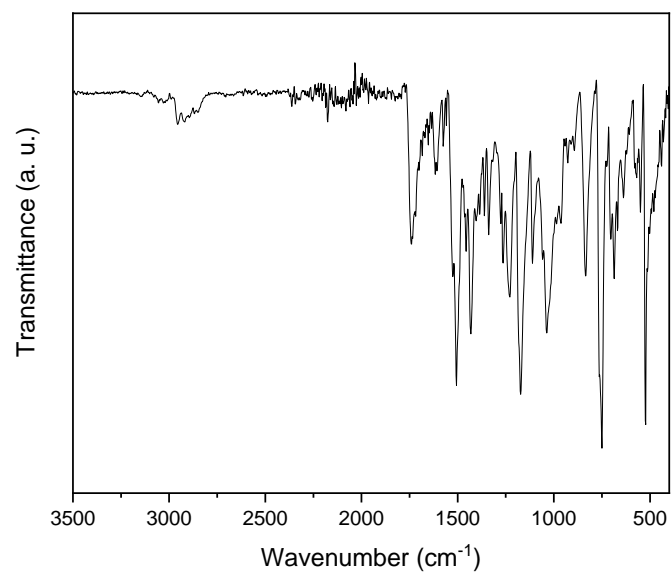
Infusion - dilution 200 - manual quad - ancienne calib

1: TOF MS ES+  
 1.64e+003

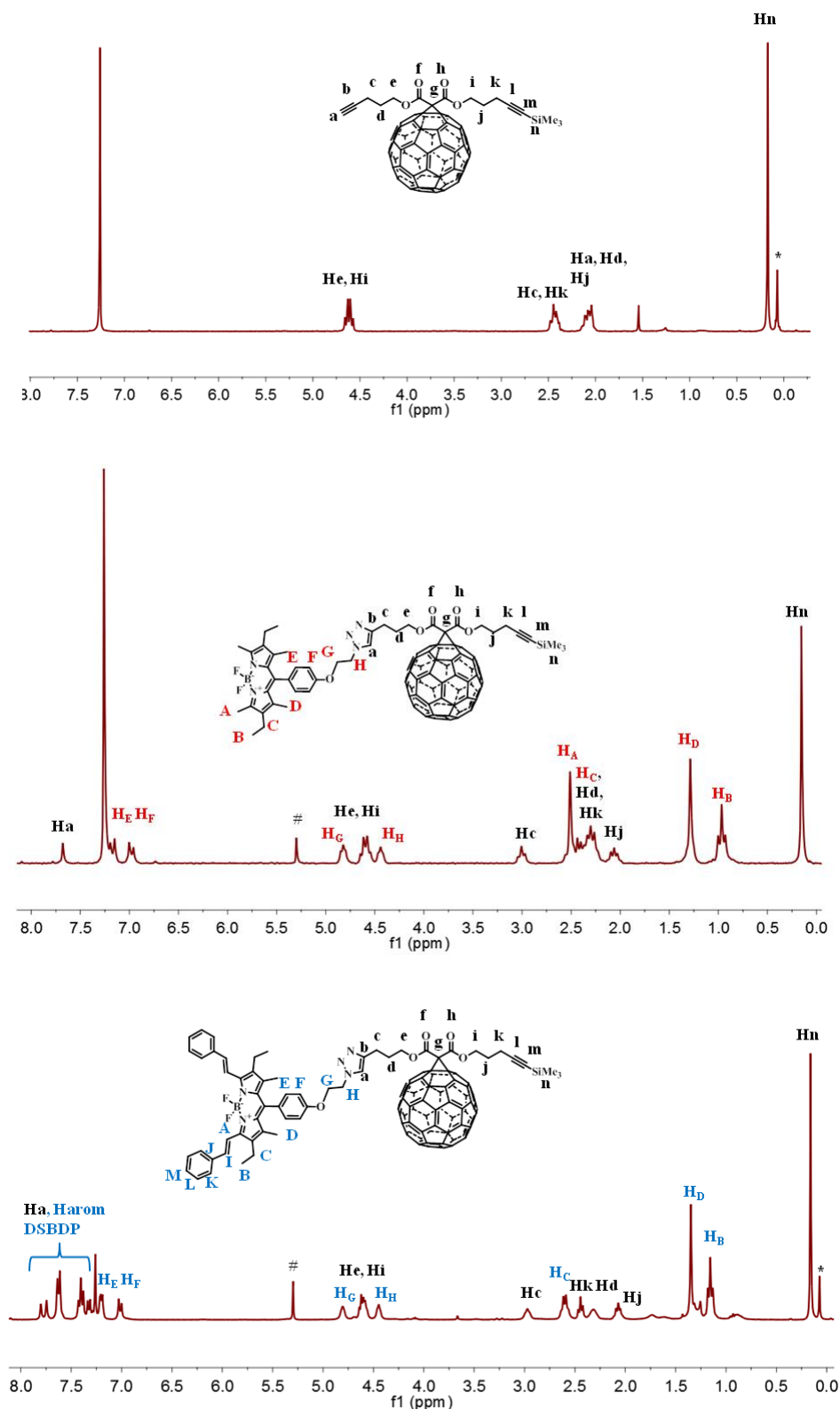


Mass	Calc. Mass	mDa	PPM	DBE	1-FIT	1-FIT (Norm)	Formula
1666.4480	1666.4466	3.4	2.0	94.0	41.8	5.0	C115 H54 O8 N3 N9 P3 S1
	1666.4461	1.9	3.1	89.0	41.5	4.7	C115 H60 O8 N5 O5 P2 S1
	1666.4546	-6.6	-4.0	88.5	42.6	5.8	C115 H62 O8 N5 O6 P S1
	1666.4459	2.1	1.3	84.0	41.5	4.7	C115 H65 O8 N9 O9 P2 S1
	1666.4400	8.0	4.8	85.0	43.2	6.4	C115 H64 N2 O8 P2 S1
	1666.4499	-1.9	-1.1	89.5	41.4	4.6	C115 H59 O8 N6 O3 P3 S1
	1666.4423	5.7	3.4	88.5	42.5	5.7	C115 H61 O8 N4 O7 P S1
	1666.4526	-4.6	-2.8	90.0	41.9	5.1	C115 H60 N8 O3 P2 S1
	1666.4558	-7.8	-4.7	88.5	43.0	6.2	C115 H60 O8 N3 N4 O4 P3 S1
	1666.4482	-0.2	-0.1	87.5	41.3	4.5	C115 H62 O8 N3 N2 O8 P S1
	1666.4444	3.6	2.2	87.0	41.8	5.0	C115 H63 O8 N3 N O10 S1
	1666.4497	-1.7	-1.0	84.5	41.4	4.6	C115 H64 N3 N O7 P3 S1
	1666.4434	4.6	2.8	94.0	42.1	5.3	C115 H56 N3 N10 O2 P S1
	1666.4438	4.2	2.5	85.5	42.0	5.2	C115 H63 N3 O6 P3 S1
	1666.4508	-2.8	-1.7	88.0	41.5	4.7	C115 H63 N3 N4 O8 S1

Figure S38. Elemental composition report of compound 7

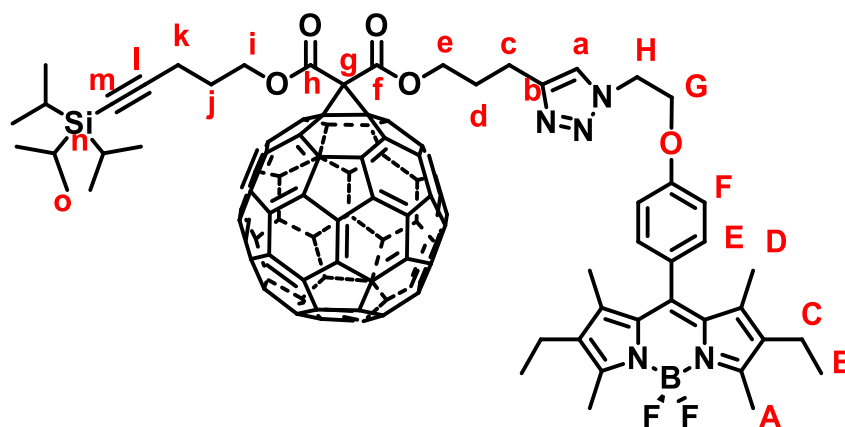


**Figure S39.** IR spectrum of compound **7**



**Figure S40.** <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, 25°C) recorded for: Top) Methanofullerene building block **2a**. Center) BDP-C<sub>60</sub> dyad **6**. Bottom) DSBDP-C<sub>60</sub> dyad **7**. The peaks labeled with hash and asterisk are due to residual CH<sub>2</sub>Cl<sub>2</sub> and H grease.

### Compound 6-bis



To a 25 mL flask under argon was added compound **2b** (100 mg, 0.09 mmol) in dry DCM (13 mL). Argon was then bubbled through the solution for 30 minutes, then BDP-N<sub>3</sub> **4** (50 mg, 0.108 mmol), DIPEA (15  $\mu$ L, 0.09 mmol), and CuBr (13 mg, 0.09 mmol) were added. The mixture was stirred for 4 hours at room temperature under argon. Then, the solution was washed two times with 20 mL of an aqueous solution of EDTA (0.05 M), then with 20 mL of water. The organic phase was dried over anhydrous MgSO<sub>4</sub>, then filtered, and finally concentrated under reduced pressure. After purification by column chromatography on silica gel (DCM/Et<sub>2</sub>O 100/5), 120 mg of a red solid was obtained (yield= 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =0.97 (t, J=7.5 Hz, 6H; H<sub>B</sub>), 1.06-1.07 (bs, 21 H; H<sub>n</sub>, H<sub>o</sub>), 1.29 (s, 6H; H<sub>D</sub>), 2.02-2.14 (m, 2H; H<sub>j</sub>), 2.25-2.32 (m, 6H; H<sub>C</sub>, H<sub>d</sub>), 2.45-2.51 (m, 8H; H<sub>k</sub>, H<sub>A</sub>), 2.96 (t, J=7.1 Hz, 2H; H<sub>c</sub>), 4.43 (bs, 2H; H<sub>H</sub>), 4.57 (t, J=6.1 Hz, 2H; H<sub>e</sub> or H<sub>i</sub>), 4.65 (t, J= 6.1 Hz, 2H; H<sub>i</sub> or H<sub>e</sub>), 4.79 (bs, 2H; H<sub>G</sub>), 6.99 (d, J=8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.16 (d, J=8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.61 ppm (s, 1H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =11.4 (C<sub>n</sub>), 12.1 (C<sub>D</sub>), 12.6 (C<sub>A</sub>), 14.8 (C<sub>B</sub>), 16.8 (C<sub>k</sub>), 17.2 (C<sub>C</sub>), 18.8 (C<sub>o</sub>), 22.1 (C<sub>c</sub>), 28.1, 28.2 (C<sub>d</sub>, C<sub>j</sub>), 49.8 (C<sub>H</sub>), 52.2 (C<sub>g</sub>), 66.0, 66.5 (C<sub>e</sub>, C<sub>i</sub>), 66.4 (C<sub>G</sub>), 71.6 (C<sub>sp3-C60</sub>), 82.0 (C<sub>m</sub>), 106.7 (C<sub>l</sub>), 115.1 (C<sub>E</sub> or C<sub>F</sub>), 122.7 (C<sub>a</sub>), 129.1 (C<sub>BDP</sub>, C<sub>sp2</sub>), 129.9 (C<sub>E</sub> or C<sub>F</sub>), 131.1, 132.9, 138.3 (C<sub>BDP</sub>, C<sub>sp2</sub>), 139.0, 139.1 (C<sub>60</sub>, C<sub>sp2</sub>), 141.10, 140.13, 141.9, 142.0, 142.30, 142.34, 143.10, 143.13, 143.17, 143.20, 143.22, 143.9, 144.0, 144.70, 144.77, 144.80, 144.85, 145.0, 145.1, 145.23, 145.27, 145.28, 145.34, 145.39, 145.43 (C<sub>60</sub>, C<sub>sp2</sub>), 153.8, 158.4 (C<sub>BDP</sub>, C<sub>sp2</sub>), 163.70, 163.76 ppm (C<sub>f</sub>, C<sub>h</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$ =-145.66 ppm (q, J= 34.4 Hz); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>):  $\delta$ =0.80 ppm (t, J= 34.5 Hz); IR:  $\tilde{\nu}$  = 1742 cm<sup>-1</sup> (C=O), 524 (C<sub>60</sub>); HRMS (ESI): m/z calcd for C<sub>107</sub>H<sub>65</sub>BN<sub>5</sub>O<sub>5</sub>F<sub>2</sub>Si: 1575.4852 [M+H]<sup>+</sup>; found: 1575.4779.

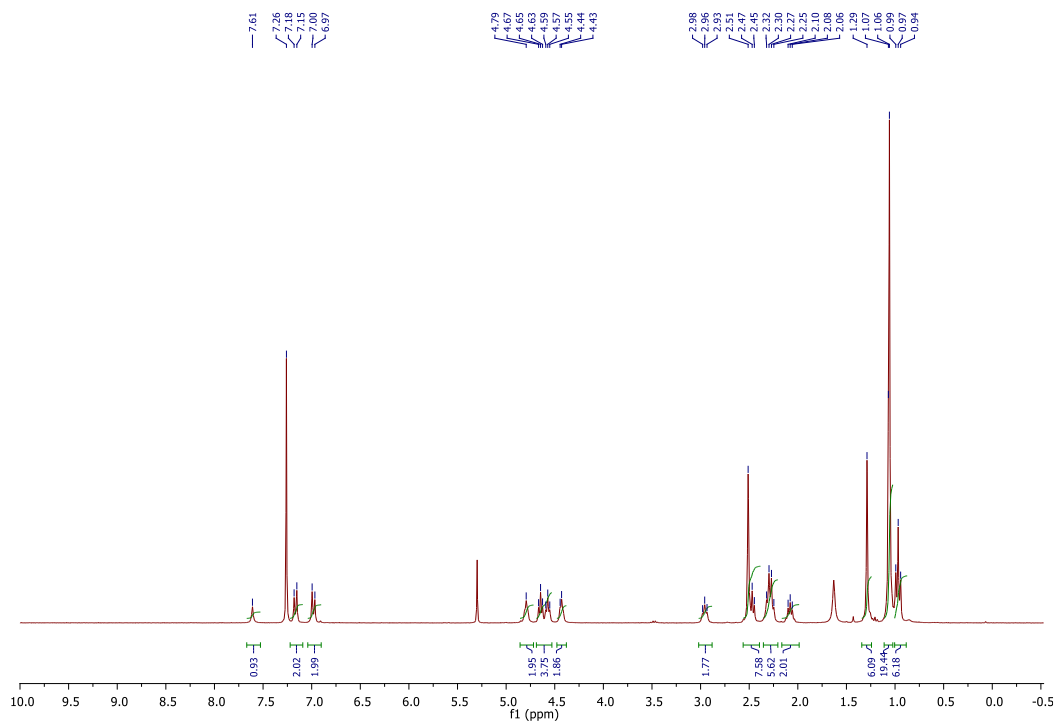


Figure S41.  $^1\text{H}$  NMR of compound **6-bis**

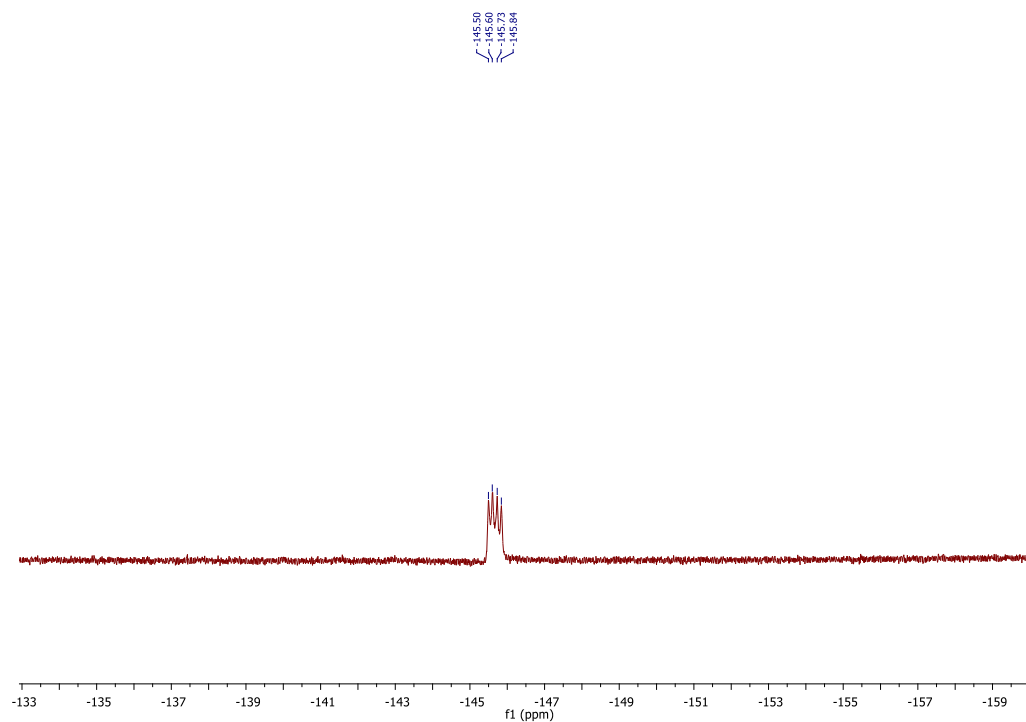
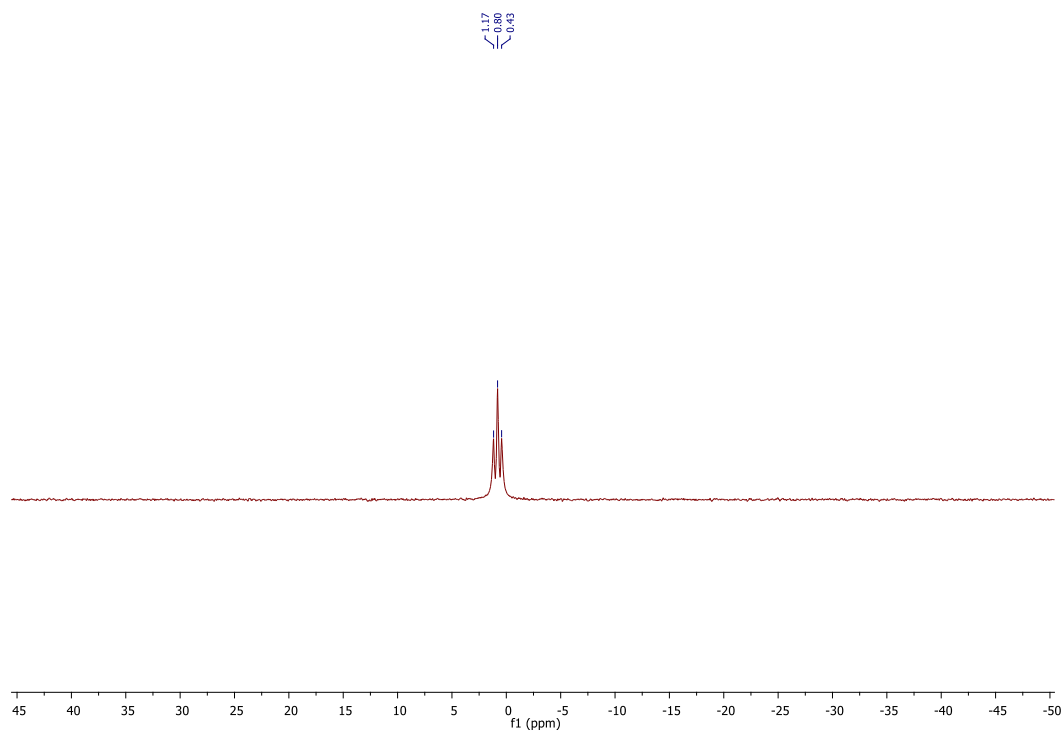
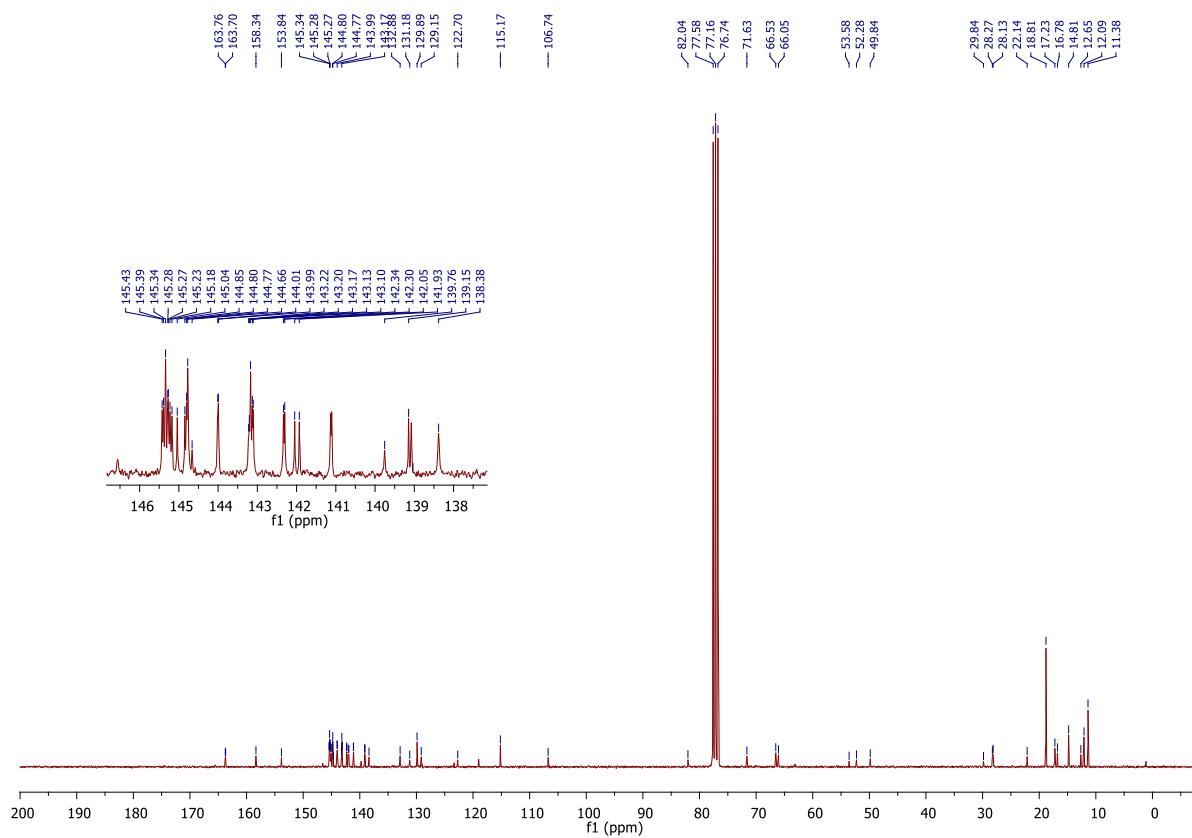


Figure S42.  $^{19}\text{F}$  NMR of compound **6-bis**

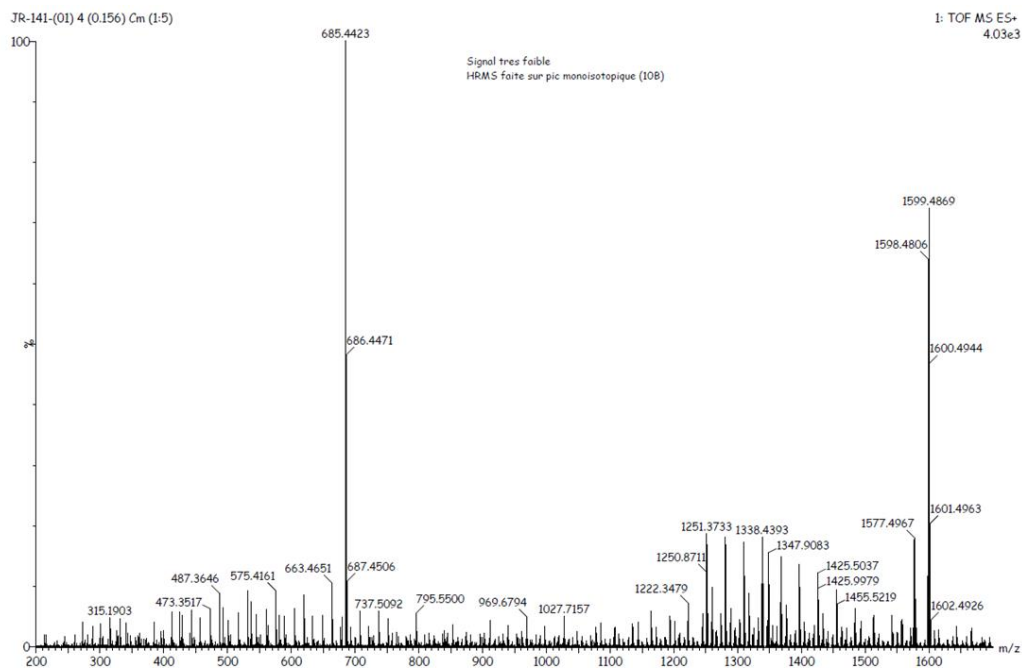


**Figure S43.**  $^{11}\text{B}$  NMR of compound **6-bis**



**Figure S44.**  $^{13}\text{C}$  NMR of compound **6-bis** with a zoom in the 138-146 ppm region.





**Figure S45.** Mass spectrum of compound **6-bis**

**Elemental Composition Report**

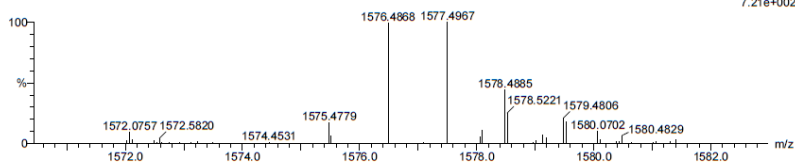
Page 1

**Single Mass Analysis**

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 100.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 5

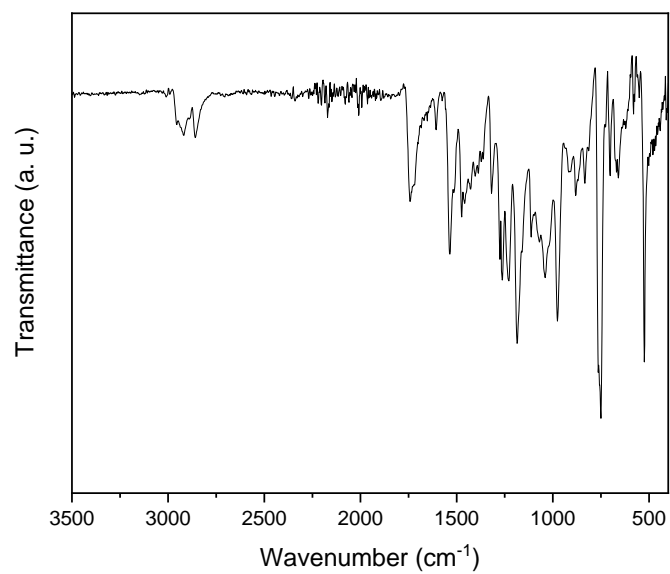
Monoisotopic Mass, Even Electron Ions  
 39 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:  
 C: 107-107 H: 65-65 10B: 0-1 11B: 0-1 N: 5-5 O: 0-10 F: 0-4 Si: 0-1  
 Jad RABAH  
 Infusion - dilution 200  
 JR-141-(01) 4 (0.156) Cm (1:5)

11-Dec-2018  
 1: TOF MS ES+  
 7.21e+002



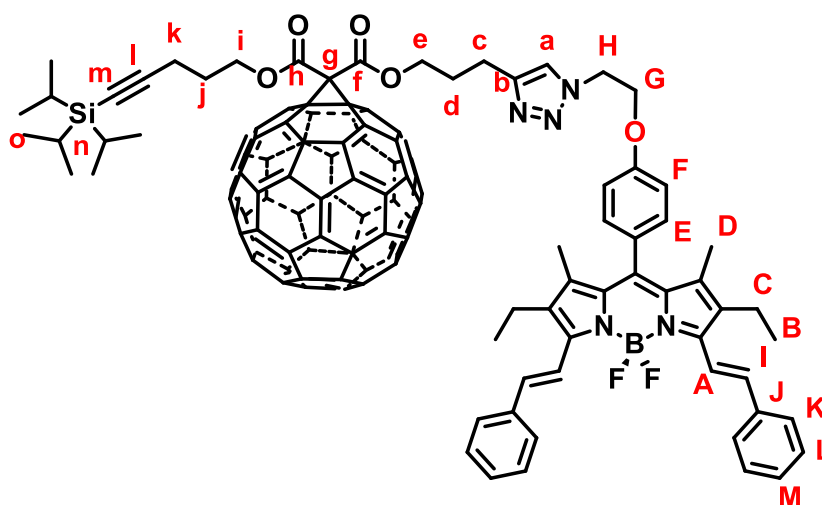
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1575.4779	1575.4852	-7.3	-4.6	78.5	108.1	0.0	C107 H65 10B N5 O5 F2 Si

**Figure S46.** Elemental composition report of compound **6-bis**

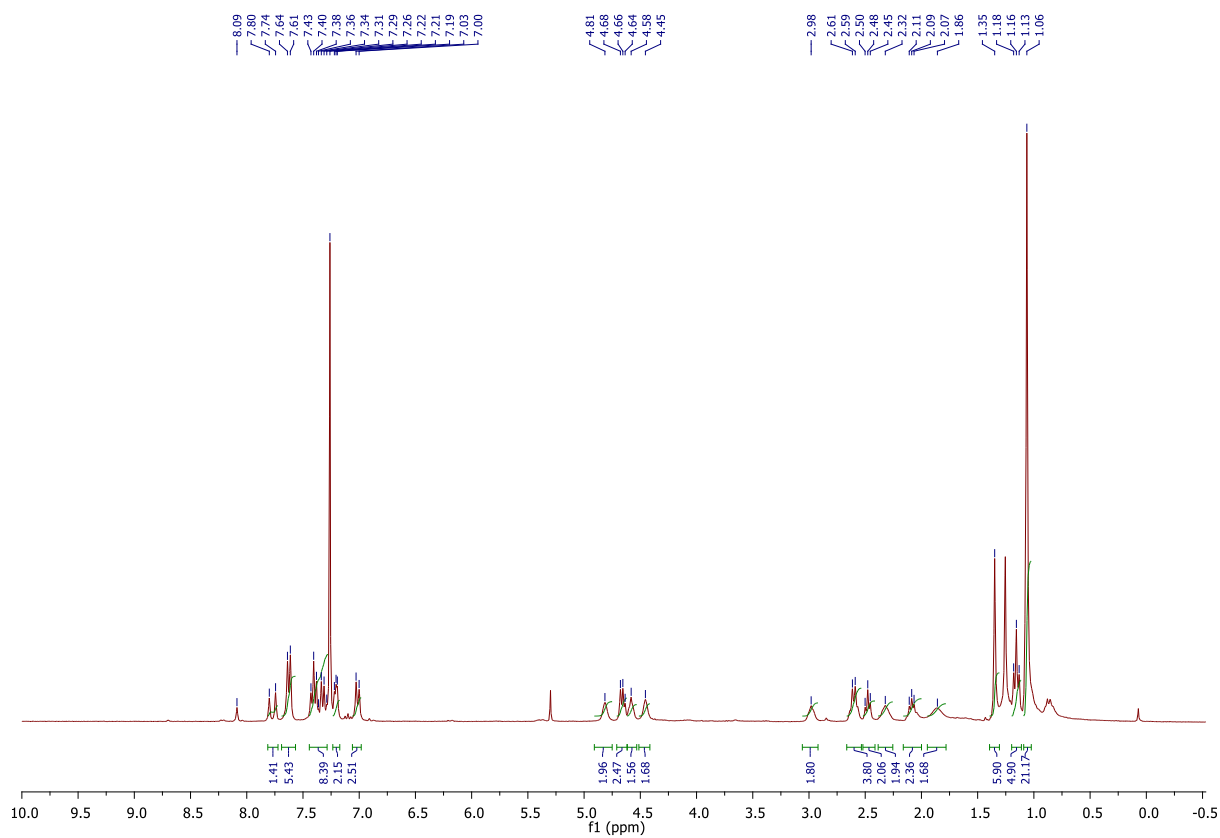


**Figure S47.** IR spectrum of compound **6-bis**

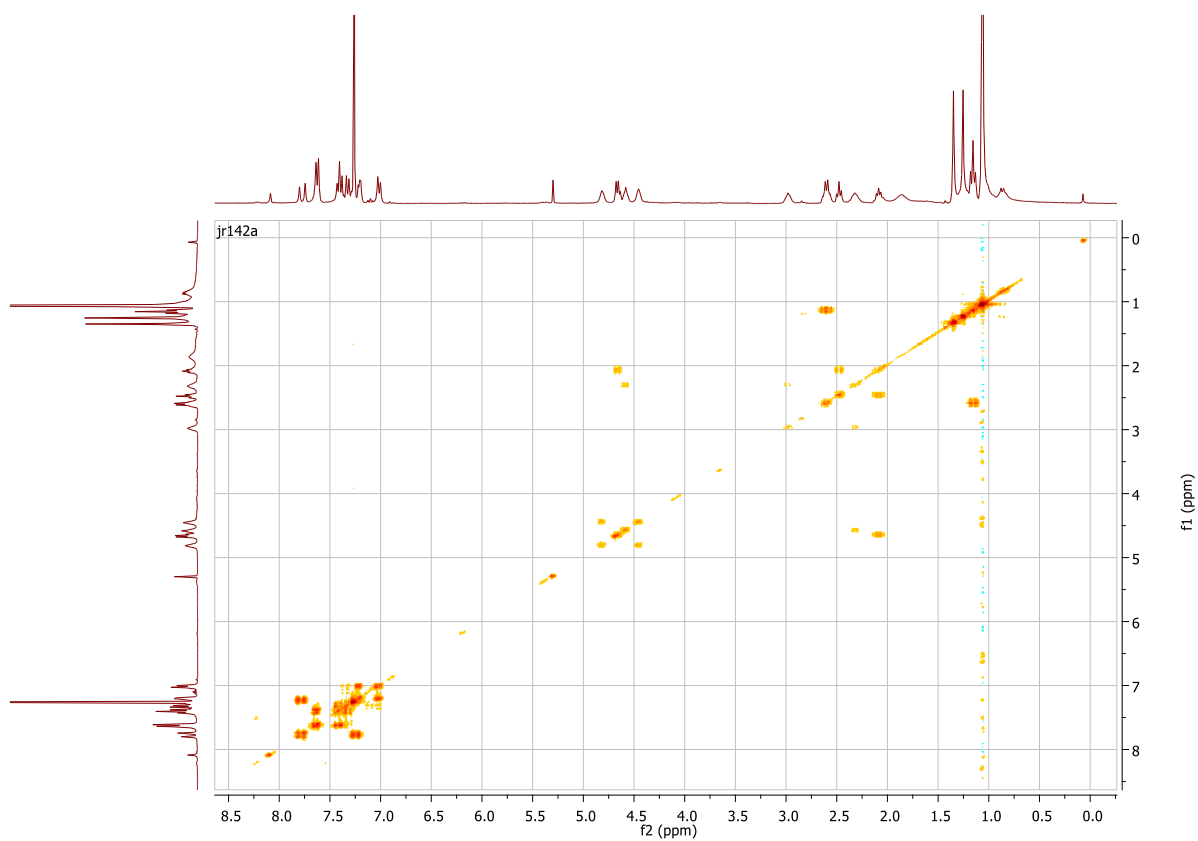
Compound 7-bis



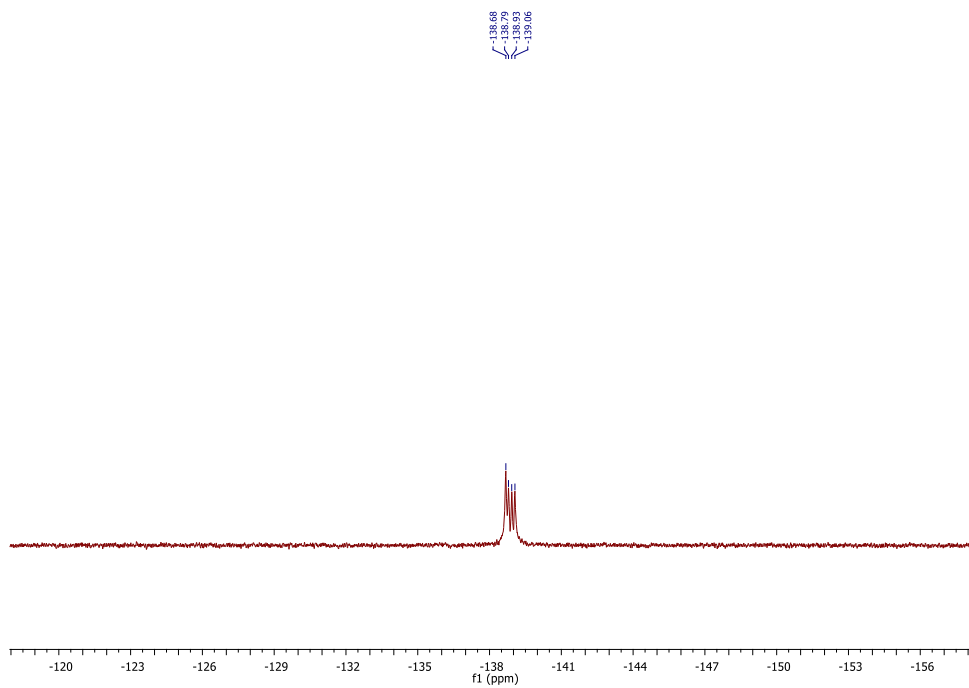
To a 25 mL flask under argon was added compound **2b** (80 mg, 0.071 mmol) in dry DCM (10 mL). Argon was bubbled through the solution for 30 minutes, then DSBDP-N<sub>3</sub> **5** (55 mg, 0.087 mmol), DIPEA (13  $\mu$ L, 0.075 mmol), and CuBr (11 mg, 0.08 mmol) were added. The mixture was stirred for 4 hours at room temperature under argon. Then, the solution was washed two times with 20 mL of an aqueous solution of EDTA (0.05 M), then with 20 mL of water. The organic phase dried over anhydrous MgSO<sub>4</sub>, then filtered, and finally concentrated under reduced pressure. After purification by column chromatography on silica gel (DCM/Et<sub>2</sub>O), 67 mg of a blue solid was obtained (yield= 55%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =1.06-1.07 (bs, 21 H; H<sub>n</sub>, H<sub>o</sub>), 1.16 (t, J=7.5 Hz, 6H; H<sub>B</sub>), 1.35 (s, 6H; H<sub>D</sub>), 2.07-2.11 (m, 2H; H<sub>j</sub>), 2.32 (bs, 2H; H<sub>d</sub>), 2.48 (t, J=6.8 Hz, 2H; H<sub>k</sub>), 2.53-2.66 (q, J=7.5 Hz, 4H; H<sub>C</sub>), 2.98 (bs, 2H; H<sub>c</sub>), 4.45 (bs, 2H; H<sub>H</sub>), 4.58 (bs, 2H; H<sub>e</sub> or H<sub>i</sub>), 4.67 (m, 2H; H<sub>e</sub> or H<sub>i</sub>), 4.81 (bs, 2H; H<sub>G</sub>), 7.01 (d, J=8.5 Hz, 2H; H<sub>E</sub> or H<sub>F</sub>), 7.19-7.22 (m, 3H; H<sub>E</sub> or H<sub>F</sub>, H<sub>dist</sub>), 7.26-7.43 (m, 6H, H<sub>BDP-arom</sub>), 7.62 (m, 5H, H<sub>BDP-arom</sub>, H<sub>a</sub>), 7.77 ppm (d, 2H, H<sub>dist</sub>, J= 16.8 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =11.4 (C<sub>n</sub>), 12.0 (C<sub>D</sub>), 14.2 (C<sub>B</sub>), 16.8 (C<sub>k</sub>), 18.5 (C<sub>C</sub>), 18.8 (C<sub>o</sub>), 22.1 (C<sub>c</sub>), 28.1, 28.2 (C<sub>d</sub>, C<sub>j</sub>), 49.9 (C<sub>H</sub>), 52.3 (C<sub>g</sub>), 66.0, 66.52 (C<sub>e</sub>, C<sub>i</sub>), 66.57 (C<sub>G</sub>), 71.6 (C<sub>sp3-C60</sub>), 82.06 (C<sub>m</sub>), 106.7 (C<sub>i</sub>), 115.2 (C<sub>E</sub> or C<sub>F</sub>), 119.0 (C<sub>dist</sub>), 120.2 (C<sub>a</sub>), 123.3, 127.5, 128.7, 128.8 (C<sub>BDP</sub>, C<sub>arom</sub>), 129.3 (C<sub>BDP</sub>, C<sub>sp2</sub>), 129.8 (C<sub>E</sub> or C<sub>F</sub>), 130.1, 133.4, 134.0, 136.0, 137.4, 138.4 (C<sub>BDP</sub>, C<sub>sp2</sub>), 139.0, 139.1 (C<sub>60</sub>, C<sub>sp2</sub>), 141.12, 141.14, 141.9, 142.0, 142.31, 142.34, 143.13, 143.18, 144.0, 144.7, 144.81, 144.85, 145.0, 145.1, 145.23, 145.27, 145.3, 145.40, 145.43 (C<sub>60</sub>, C<sub>sp2</sub>), 150.5, 158.4 (C<sub>BDP</sub>, C<sub>sp2</sub>), 163.71, 163.77 ppm (C<sub>f</sub>, C<sub>h</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$ =-138.86 ppm (q, J= 34.4 Hz); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>):  $\delta$ =2.61 ppm (t, J= 34.5 Hz); IR:  $\tilde{\nu}$  = 1742 cm<sup>-1</sup> (C=O), 525 (C<sub>60</sub>); HRMS (ESI): m/z calcd for C<sub>121</sub>H<sub>73</sub>BN<sub>5</sub>O<sub>3</sub>F<sub>2</sub>Si: 1752.5442 [M+H]<sup>+</sup>; found: 1752.5480.



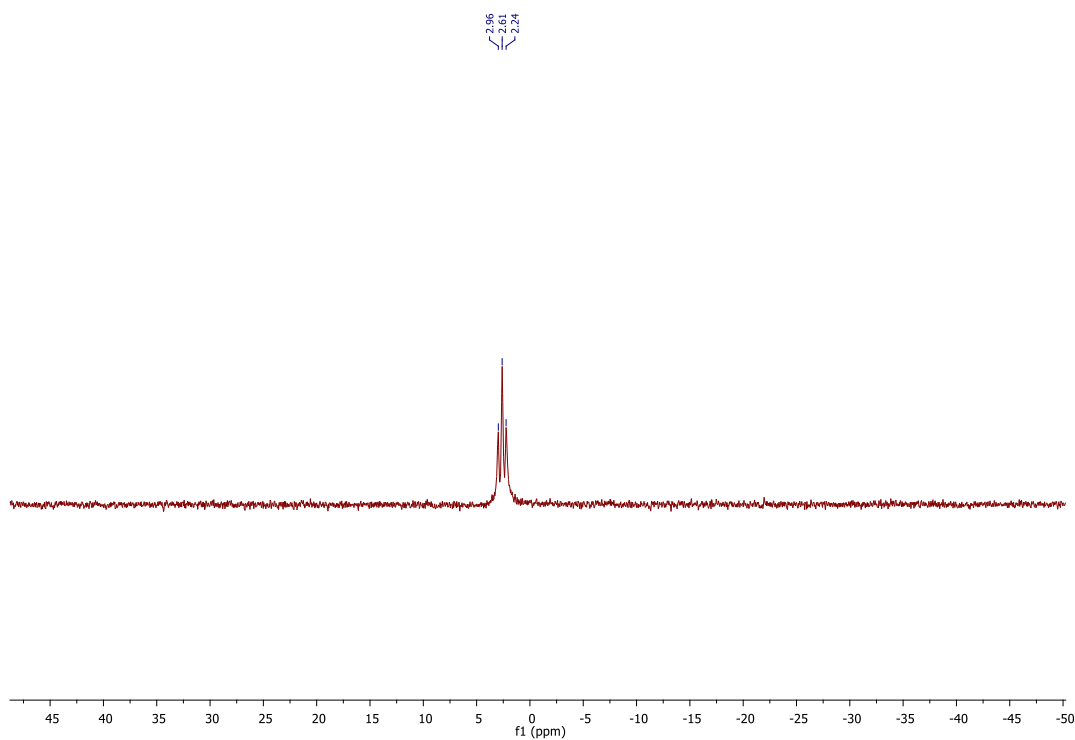
**Figure S48.**  $^1\text{H}$  NMR of compound **7-bis**, the singlet peak at 8.09 ppm is assigned to an impurity



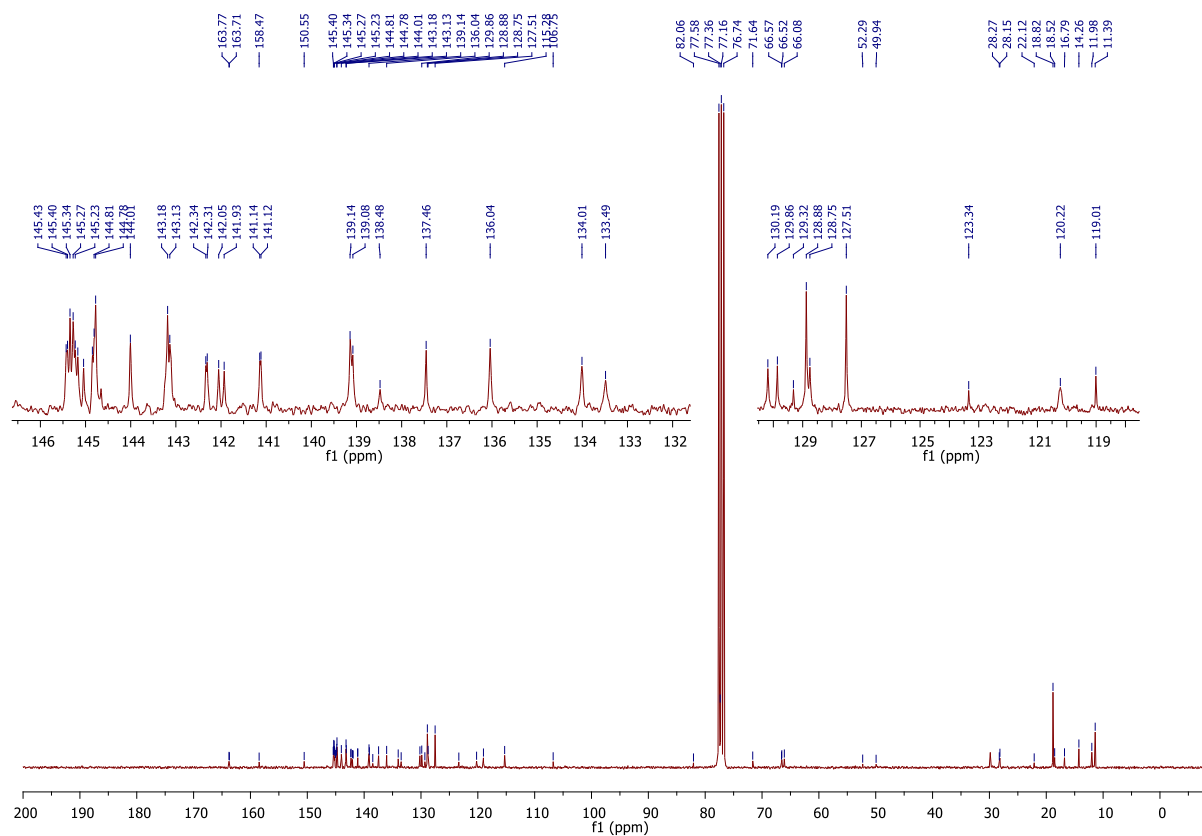
**Figure S49.** COSY of compound **7-bis**



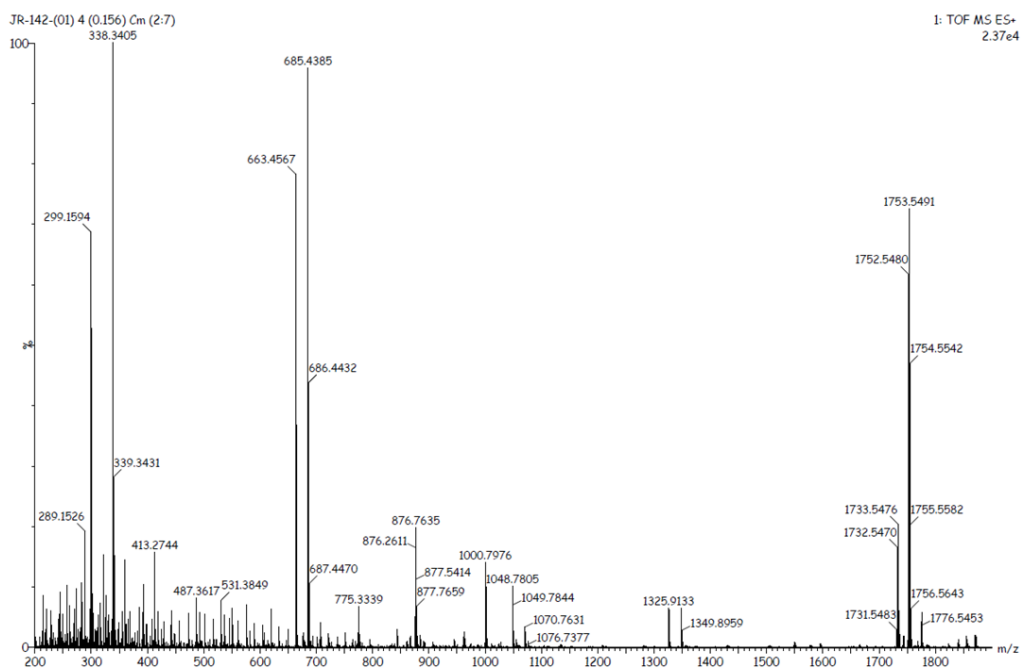
**Figure S50.**  $^{19}\text{F}$  NMR of compound 7-bis



**Figure S51.**  $^{11}\text{B}$  NMR of compound 7-bis



**Figure S52.** <sup>13</sup>C NMR of compound **7-bis** with a zoom in the 119-146 ppm region.



**Figure S53.** Mass spectrum of compound **7-bis**

## Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element predictor: Cliff

Number of isotope peaks used for i-FIT = 8

Monoisotopic Mass, Even Electron Ions  
15267 formula(e) evaluated with 416 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-121 H: 70-90 B: 0-1 N: 0-10 O: 0-10 F: 0-3 Si: 0-10

Jad RABAH

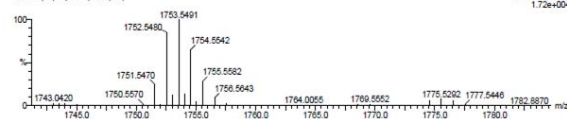
10-Dec-2018

Infusion - dilution 1000

t: TOF MS ES+

JR-142(01)4 (0.100) Cn(2,7)

1.72e+004



Mass	Calc. Mass	ΔDa	PPM	DBE	1-FIT	1-FIT (Norm)	Formula
1752.5480	1752.5399	8.1	4.6	89.5	218.2	10.7	C121 H71 N7 O7 F
	1752.5567	-8.7	-5.0	90.5	221.3	13.8	C121 H79 B N7 S14
	1752.5567	-8.7	-5.0	88.5	223.7	15.2	C121 H76 N7 O2 F2
	1752.5441	3.9	2.2	83.5	222.2	14.8	S12
	1752.5441	3.9	2.2	85.5	220.1	12.6	C121 H80 N O7 F2
	1752.5441	3.9	2.2	86.5	220.0	12.5	S12
	1752.5518	-3.8	-2.2	86.5	220.0	12.5	C121 H81 B N3 O F2
	1752.5458	2.2	1.3	88.5	209.7	2.3	S14
	1752.5458	2.2	1.3	84.5	227.3	19.8	C121 H72 B N5 O8 F
	1752.5534	-5.4	-3.1	84.5	219.9	12.4	C121 H90 N S17
	1752.5534	-5.4	-3.1	86.5	219.2	11.7	C121 H77 N3 O6 F3
	1752.5534	-5.4	-3.1	86.5	219.2	11.7	S1
	1752.5534	-5.4	-3.1	86.5	219.2	11.7	C121 H80 B N3 O4 F
	1752.5566	-8.6	-4.9	85.5	226.9	19.4	S13
	1752.5426	5.4	3.1	88.5	217.2	9.7	C121 H86 N3 O2 S15
	1752.5426	5.4	3.1	88.5	217.2	9.7	C121 H74 B N5 O2
	1752.5426	5.4	3.1	83.5	224.5	17.1	F3 S12
	1752.5534	-5.4	-3.1	89.5	211.5	4.0	C121 H81 N O4 F3
	1752.5534	-5.4	-3.1	89.5	211.5	4.0	S13
	1752.5426	5.4	3.1	85.5	221.4	13.9	C121 H70 B N7 O4
	1752.5459	2.1	1.2	87.5	225.0	17.5	F3
	1752.5442	3.8	2.2	88.5	214.0	6.5	C121 H84 B N O2 F
	1752.5442	3.8	2.2	88.5	214.0	6.5	S15
	1752.5457	2.3	1.3	83.5	219.2	11.7	C121 H80 N5 F2 S14
	1752.5457	2.3	1.3	83.5	219.2	11.7	C121 H73 B N5 O5
	1752.5457	2.3	1.3	83.5	219.2	11.7	F2 S1
	1752.5457	2.3	1.3	83.5	219.2	11.7	C11 H79 N O10 F
	1752.5457	2.3	1.3	83.5	219.2	11.7	S1

Figure S54. Elemental composition report of compound 7-bis

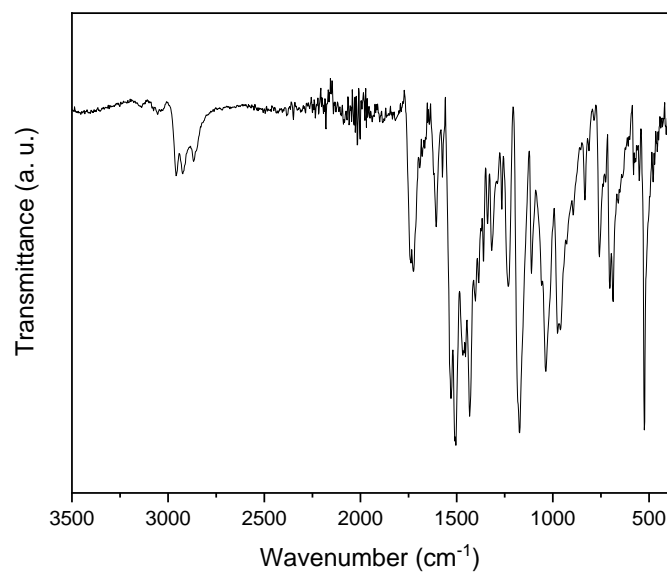
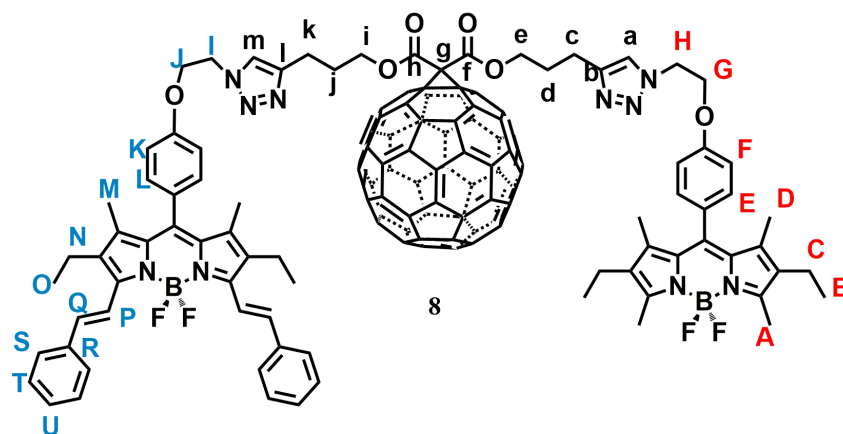
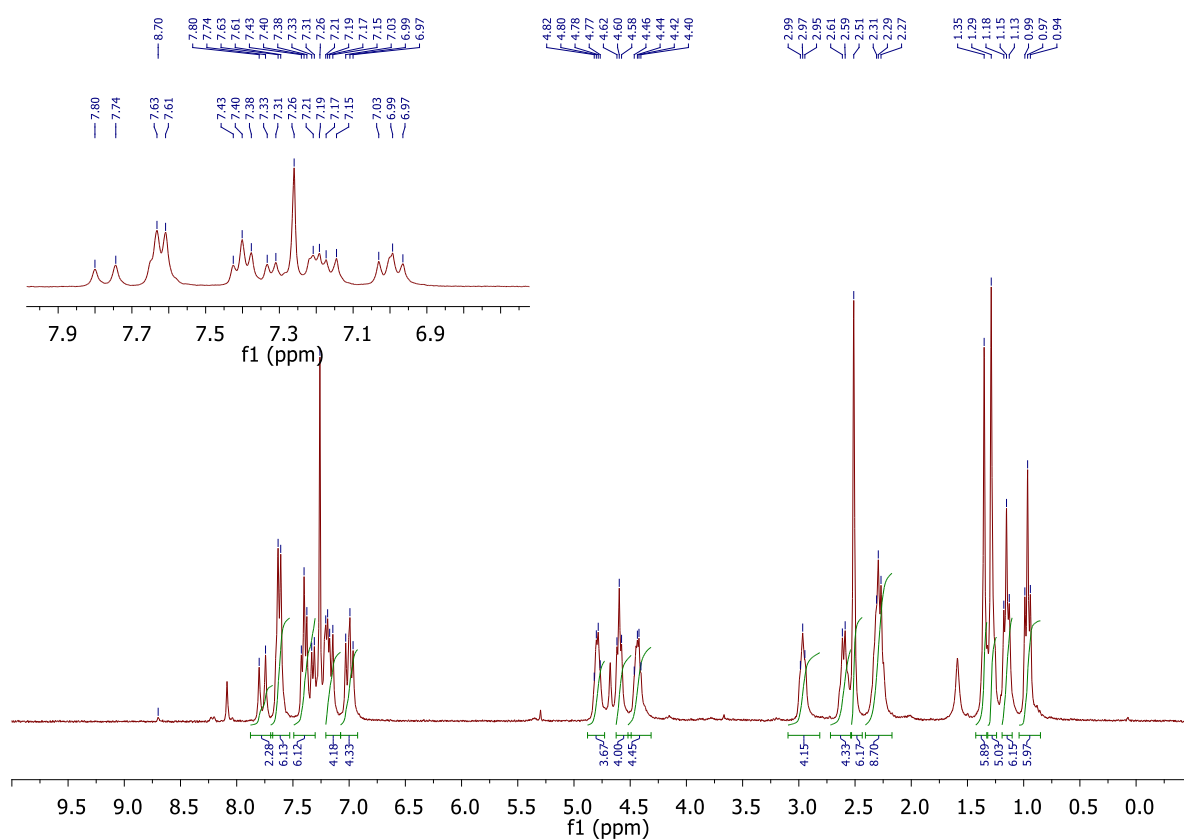


Figure S55. IR spectrum of compound 7-bis

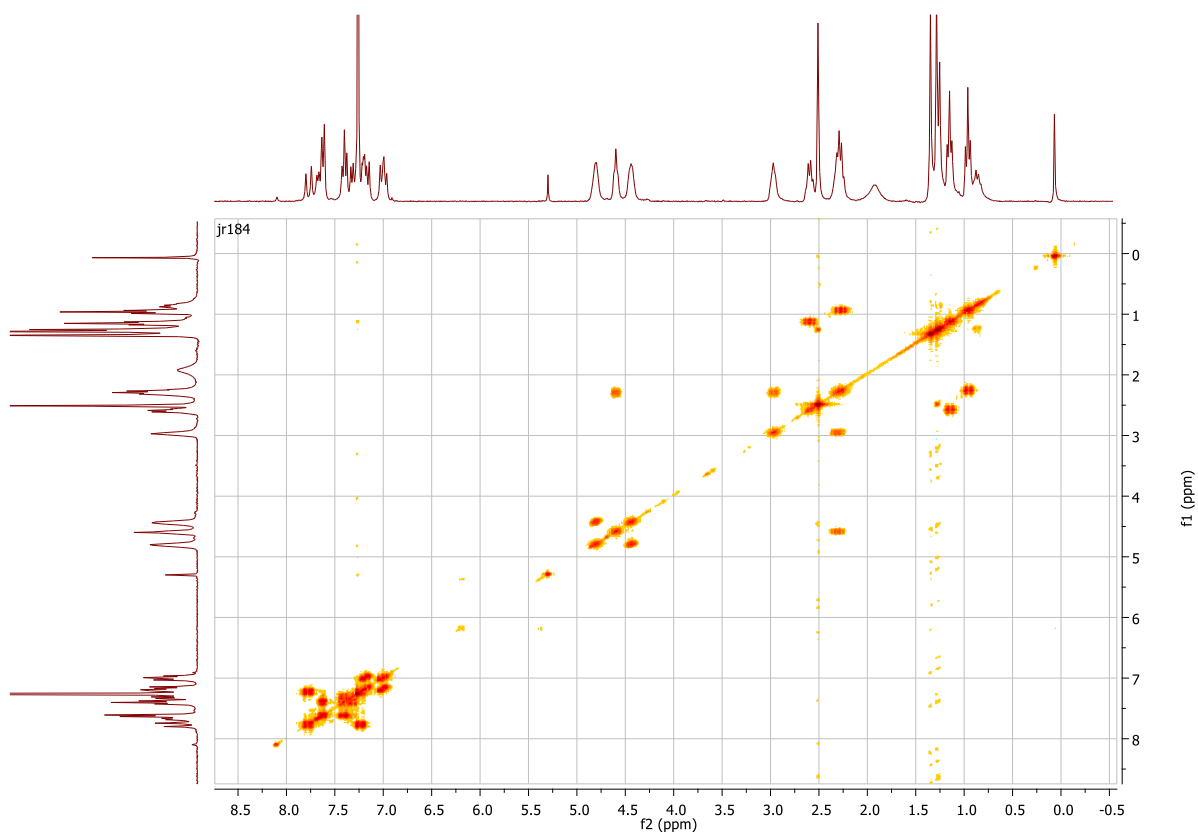


**Figure S56.** Structure and numbering of compound **8** used for  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments

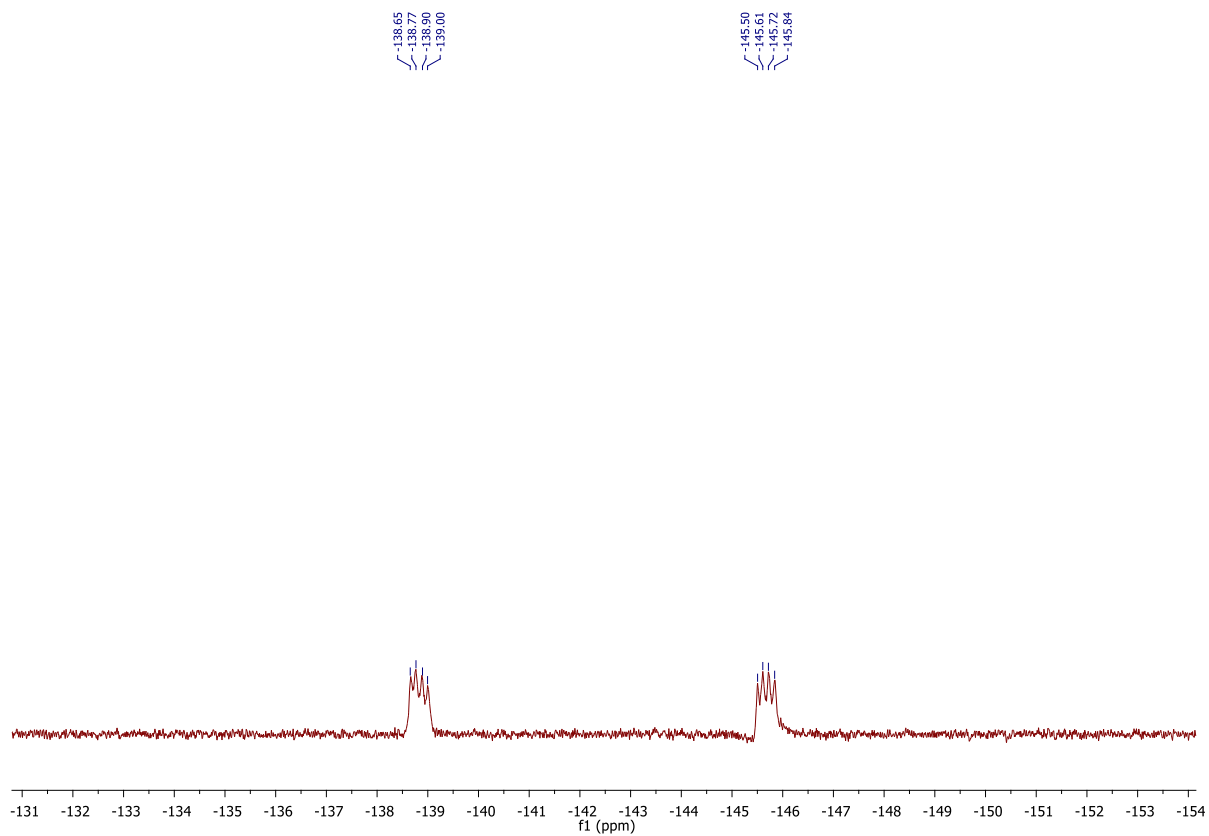


**Figure S57.**  $^1\text{H}$  NMR of compound **8** with a zoom in the 6.50-8.00 ppm region. The singlet peaks at 4.67 ppm and 8.09 ppm are assigned to impurities.





**Figure S58.** COSY of compound **8**



**Figure S59.**  $^{19}\text{F}$  NMR of compound **8**

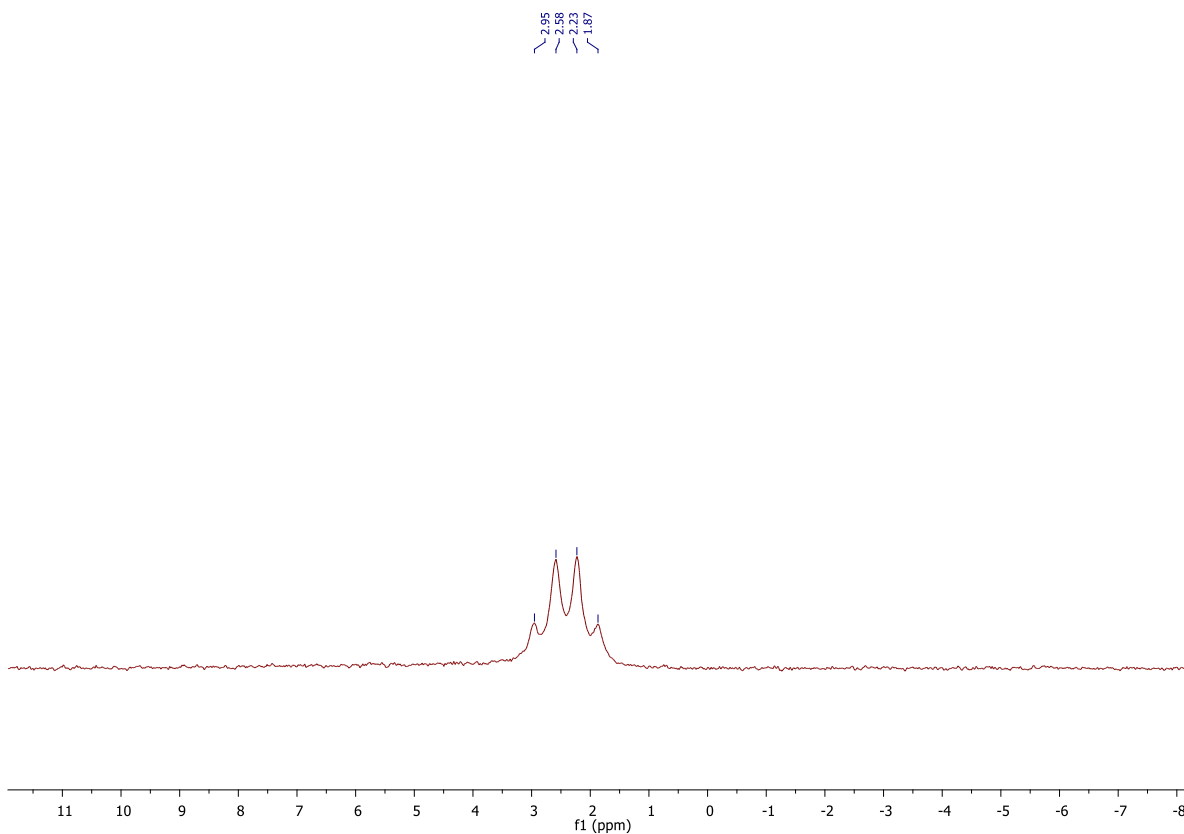


Figure S60.  $^{11}\text{B}$  NMR of compound **8**

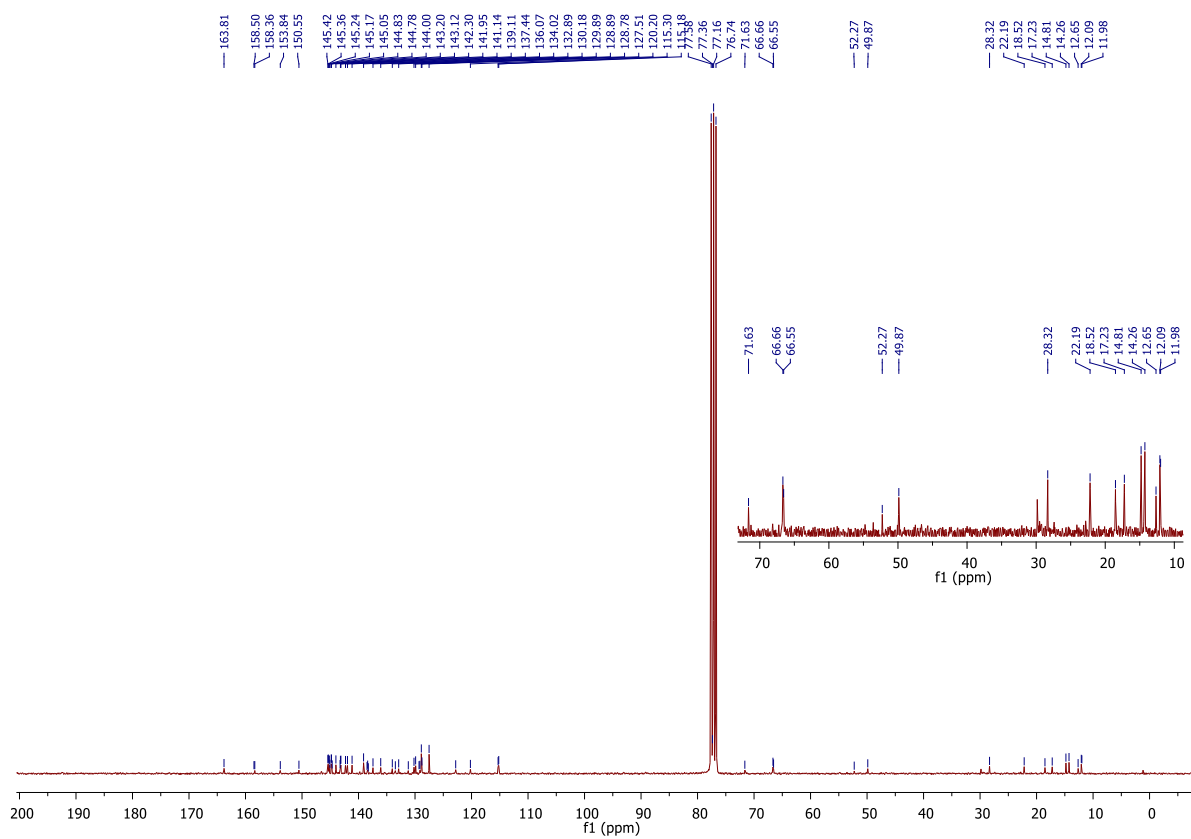
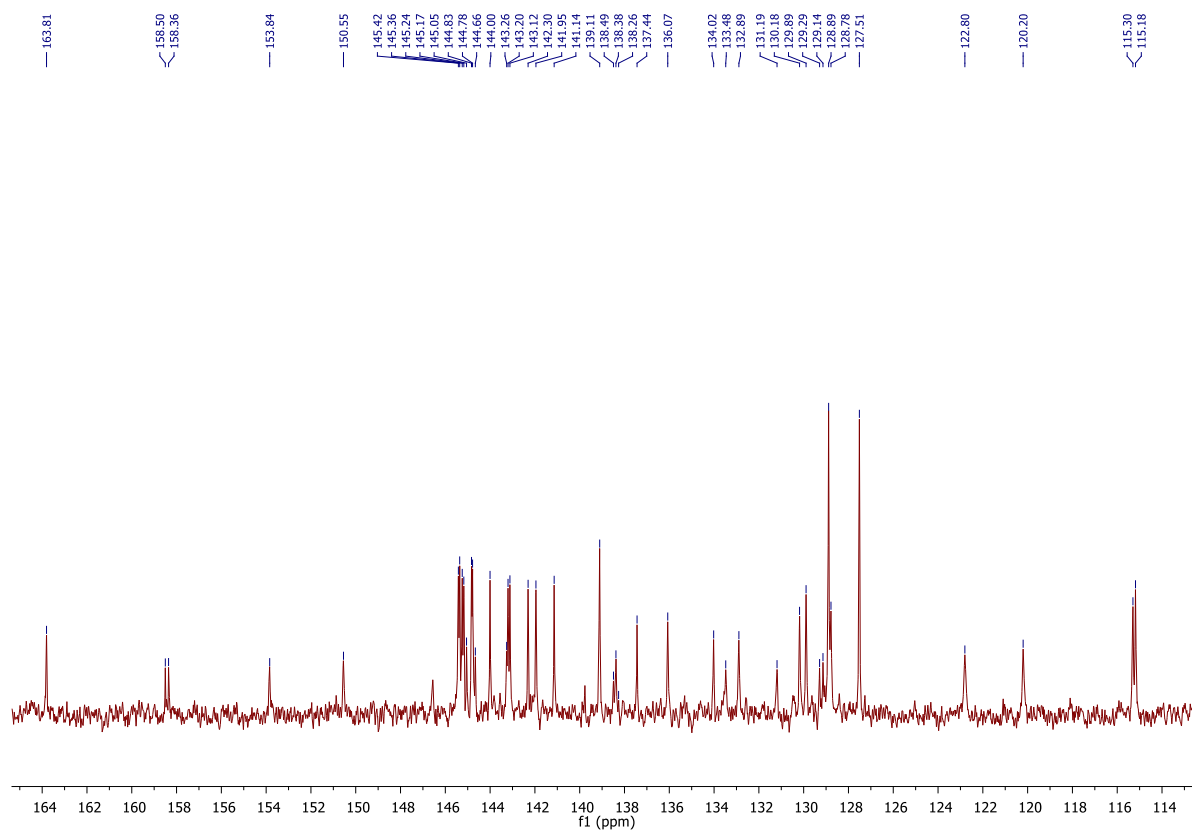
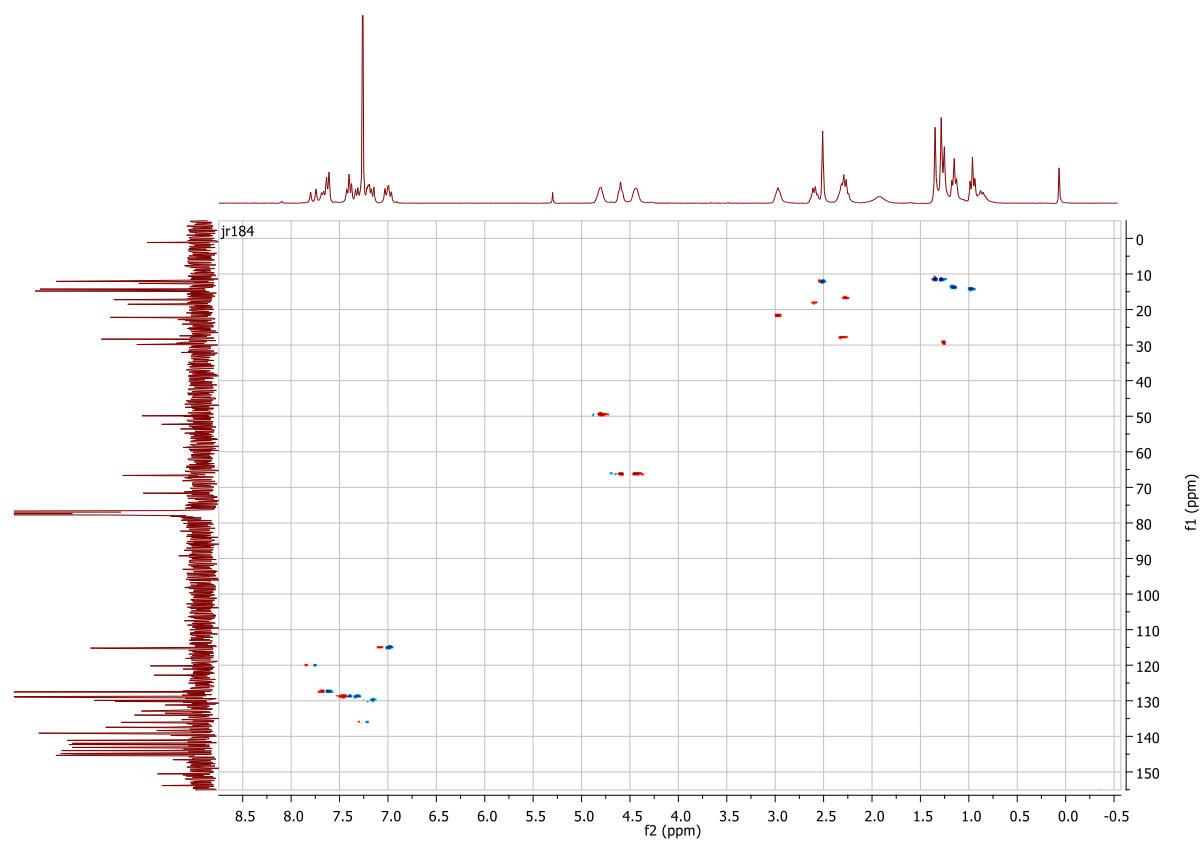


Figure S61.  $^{13}\text{C}$  NMR of compound **8** with a zoom in the 12-72 ppm region.



**Figure S62.**  $^{13}\text{C}$  NMR of compound **8** (zoom in the 110-170 ppm region)



**Figure S63.** HSQC of compound **8**

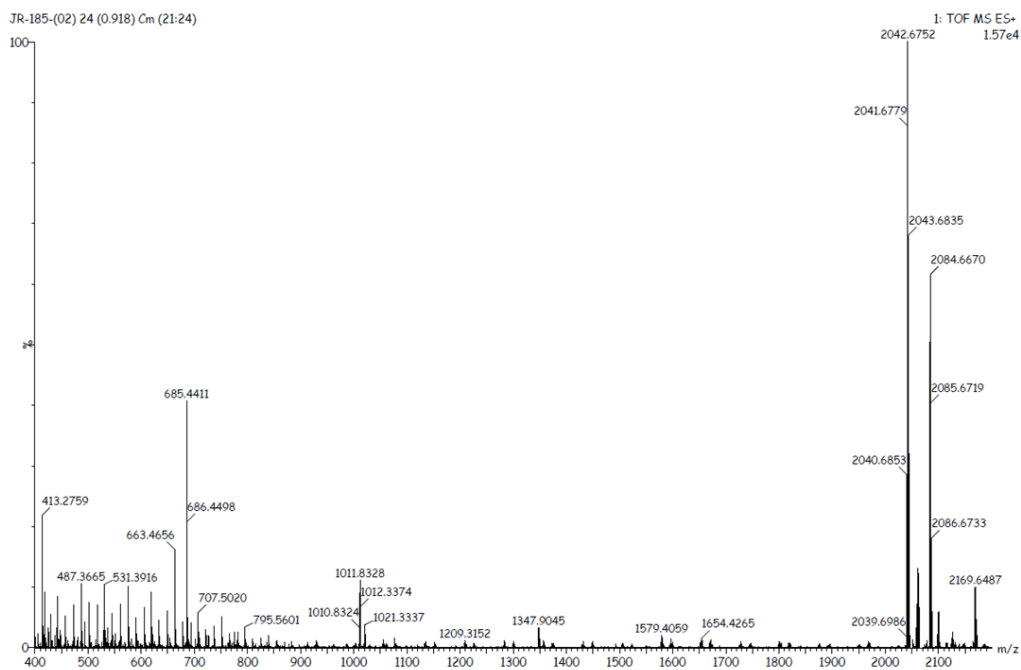


Figure S64. Mass spectrum of compound 8

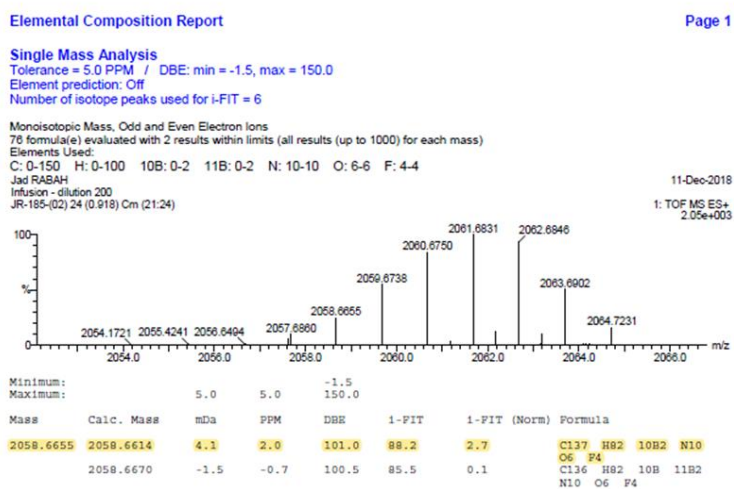
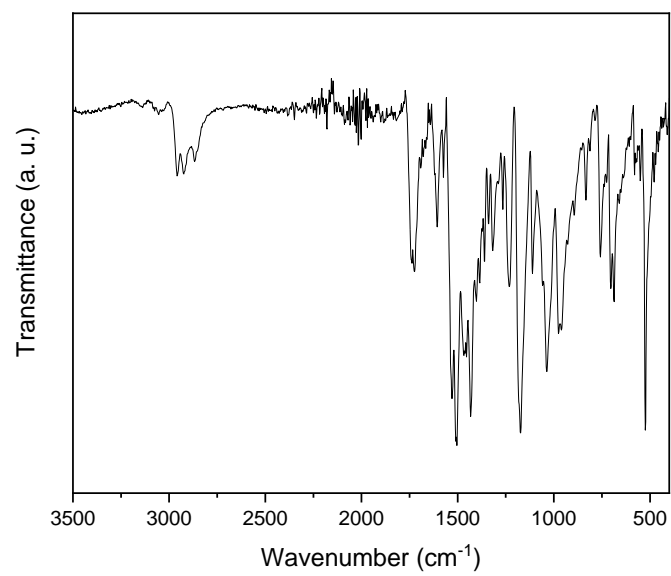
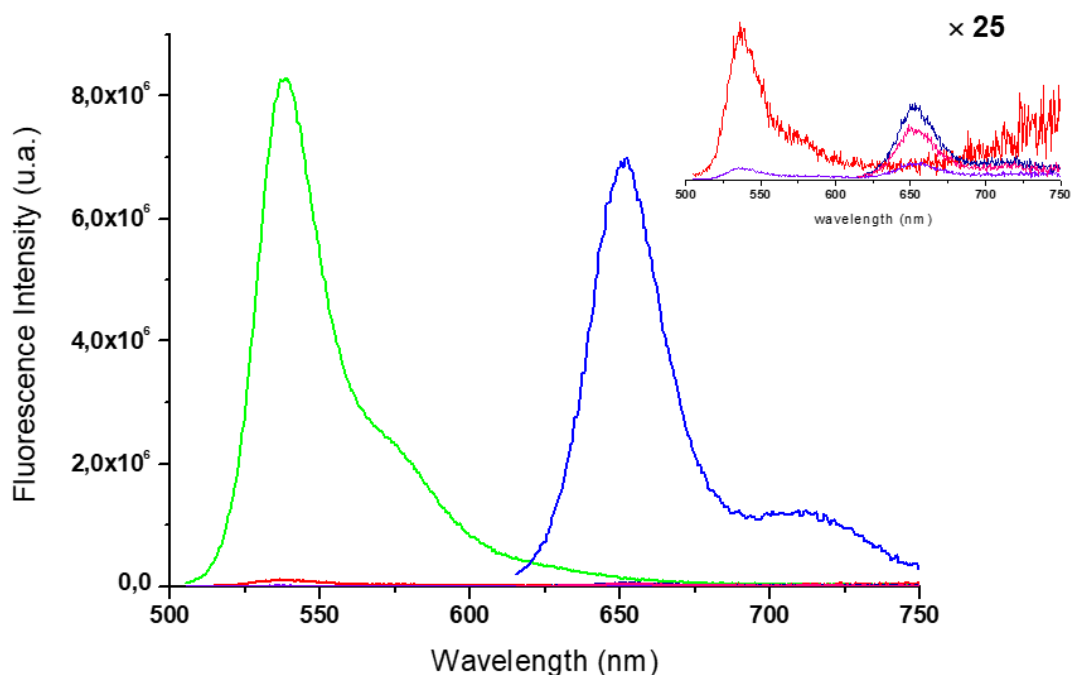


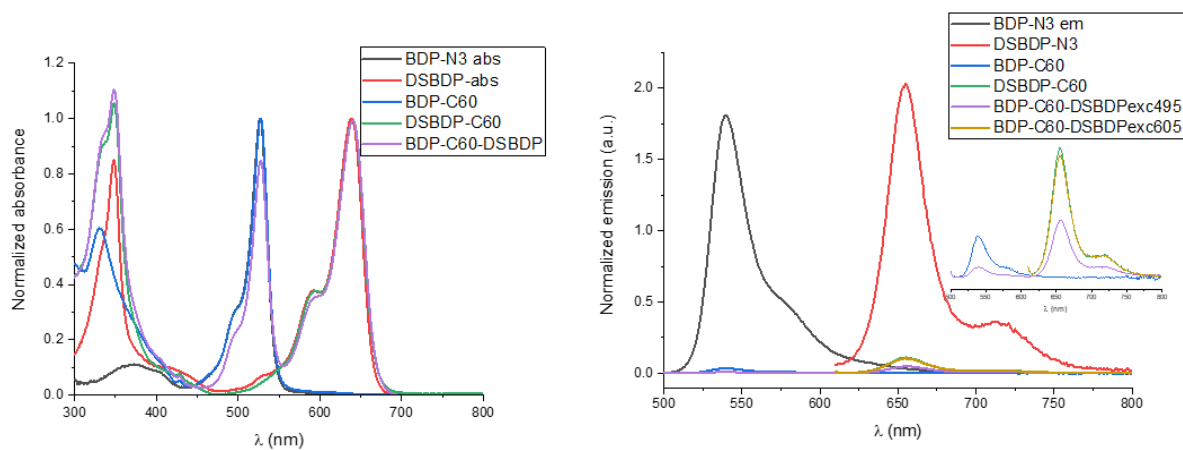
Figure S65. Elemental composition report of compound 8



**Figure S66.** IR spectrum of compound **8**



**Figure S67.** Emission spectra in dichloromethane of BDP-N<sub>3</sub> **4** (green,  $\lambda_{exc}$ = 495 nm), DSBDP-N<sub>3</sub> **5** (blue,  $\lambda_{exc}$ = 605 nm), BDP-C<sub>60</sub> **6** (red,  $\lambda_{exc}$ = 495 nm), DSBDP-C<sub>60</sub> **7** (navy blue,  $\lambda_{exc}$ = 605 nm), and DSBDP-C<sub>60</sub>-BDP **8** (violet,  $\lambda_{exc}$ = 495 nm ; pink,  $\lambda_{exc}$ = 605 nm).

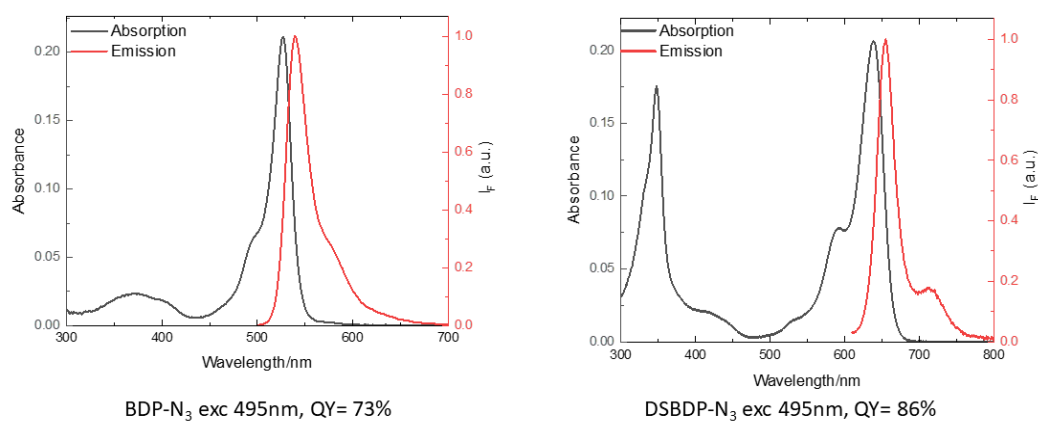


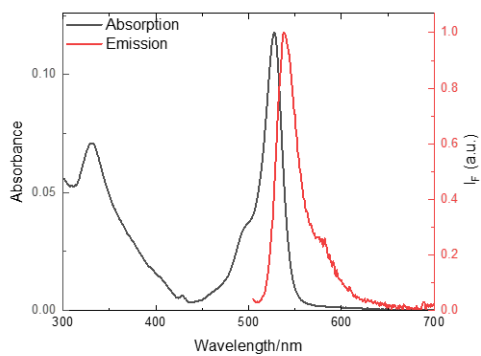
**Figure S68.** Normalized absorption and emission spectra in toluene of BDP-N<sub>3</sub> **4** (black,  $\lambda_{exc}$ = 495 nm), DSBDP-N<sub>3</sub> **5** (red,  $\lambda_{exc}$ = 605 nm), BDP-C<sub>60</sub> **6** (blue,  $\lambda_{exc}$ = 495 nm), DSBDP-C<sub>60</sub> **7** (green,  $\lambda_{exc}$ = 605 nm), and DSBDP-C<sub>60</sub>-BDP **8** (violet,  $\lambda_{exc}$ = 495 nm ; orange,  $\lambda_{exc}$ = 605 nm).

**Table S1.** Absorption and fluorescence data of compounds **4-8** in toluene

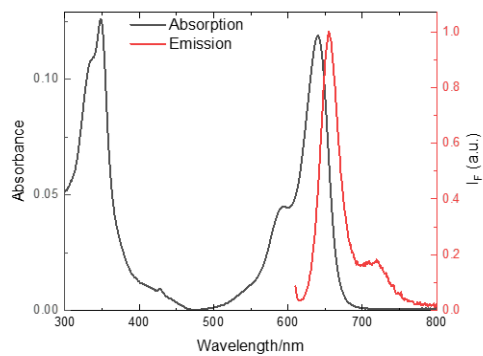
Compound	$\lambda_{\max}$ abs, nm	$\lambda_{\max}$ em, nm	$\phi_F$ , %
BDP-N <sub>3</sub> <b>4</b>	525	535 <sup>a</sup>	73 <sup>c</sup>
BDP-C <sub>60</sub> <b>6</b>	525	535 <sup>a</sup>	1.4 <sup>c</sup>
DSBDP-N <sub>3</sub> <b>5</b>	637	650 <sup>b</sup>	86 <sup>d</sup>
DSBDP-C <sub>60</sub> <b>7</b>	637	650 <sup>b</sup>	4.8 <sup>d</sup>
BDP-C <sub>60</sub> -DSBDP <b>8</b>	525, 637	535 <sup>a</sup> , 650 <sup>b</sup>	0.4 <sup>c</sup> , 2.3 <sup>d</sup> 4.6 <sup>e</sup>

<sup>a</sup>  $\lambda_{\text{exc}}=495\text{nm}$ , <sup>b</sup>  $\lambda_{\text{exc}}=605\text{nm}$ , <sup>c</sup> Reference: Rhodamine 6G ref ( $\lambda_{\text{exc}} = 495 \text{ nm}$ ,  $\lambda_{\text{em}} = 535$ ,  $\phi = 95\%$  in ethanol), <sup>d</sup> Reference:  $[\text{Ru}(\text{bpy})_3]^{2+}$  used as standard ( $\lambda_{\text{exc}} = 495 \text{ nm}$ ,  $\lambda_{\text{em}} = 637 \text{ nm}$   $\phi = 4.2\%$  in water) <sup>e</sup> Reference: Oxazine-1 ( $\lambda_{\text{exc}} = 605 \text{ nm}$ ,  $\lambda_{\text{em}} = 637 \text{ nm}$ ,  $\phi = 11\%$  in ethanol)

**Figure S69.** Steady state absorption and emission of BDP-N<sub>3</sub> **4** and DSBDP-N<sub>3</sub> **5** in toluene.

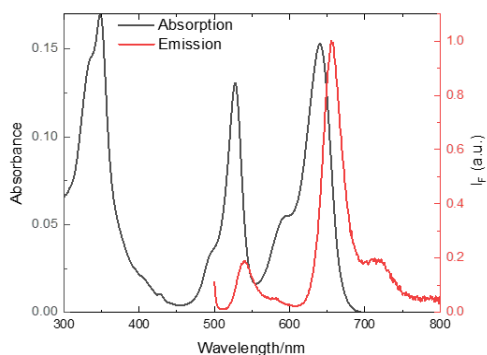


BDP-C60 exc 495nm, QY= 1.4%

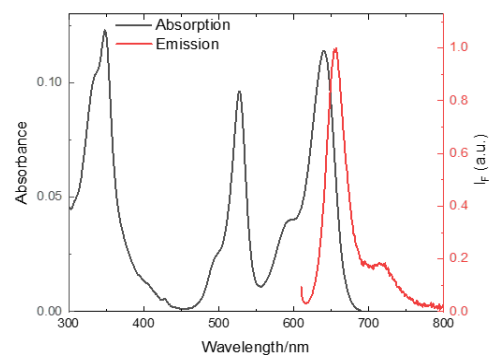


DSBDP-C60 exc 495nm, QY= 4.8%

**Figure S70.** Steady state absorption and emission of BDP-C<sub>60</sub> **6** and DSBDP-C<sub>60</sub> **7** in toluene.



BDP-C60-DSBDP  
exc 495nm em BDP, QY= 0.4%  
exc 495nm, em DSBDP, QY= 2.3%



BDP-C60-DSBDP exc 605nm, QY= 4.6%

**Figure S71.** Steady state absorption and emission of BDP-C<sub>60</sub>-DSBDP **8** in toluene.