

## Direct subphthalocyanine conjugation to bombesin vs indirect conjugation to its lipidic nanocarrier

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## Supporting Information

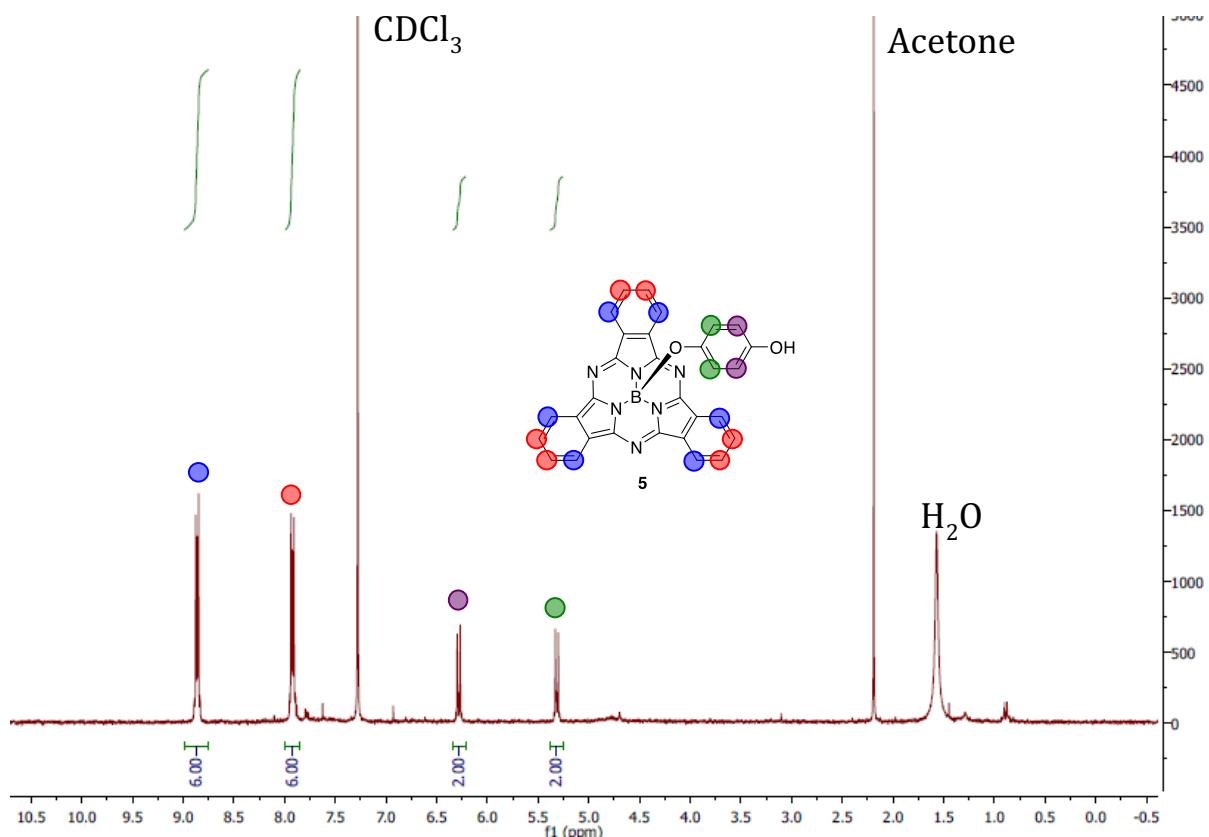


Fig. S1. <sup>1</sup>H NMR spectrum of B-(4-hydroxyphenoxy)[subphthalocyaninato]boron(III) , Sub-phenol (5) (CDCl<sub>3</sub>, 300 MHz, 300K)

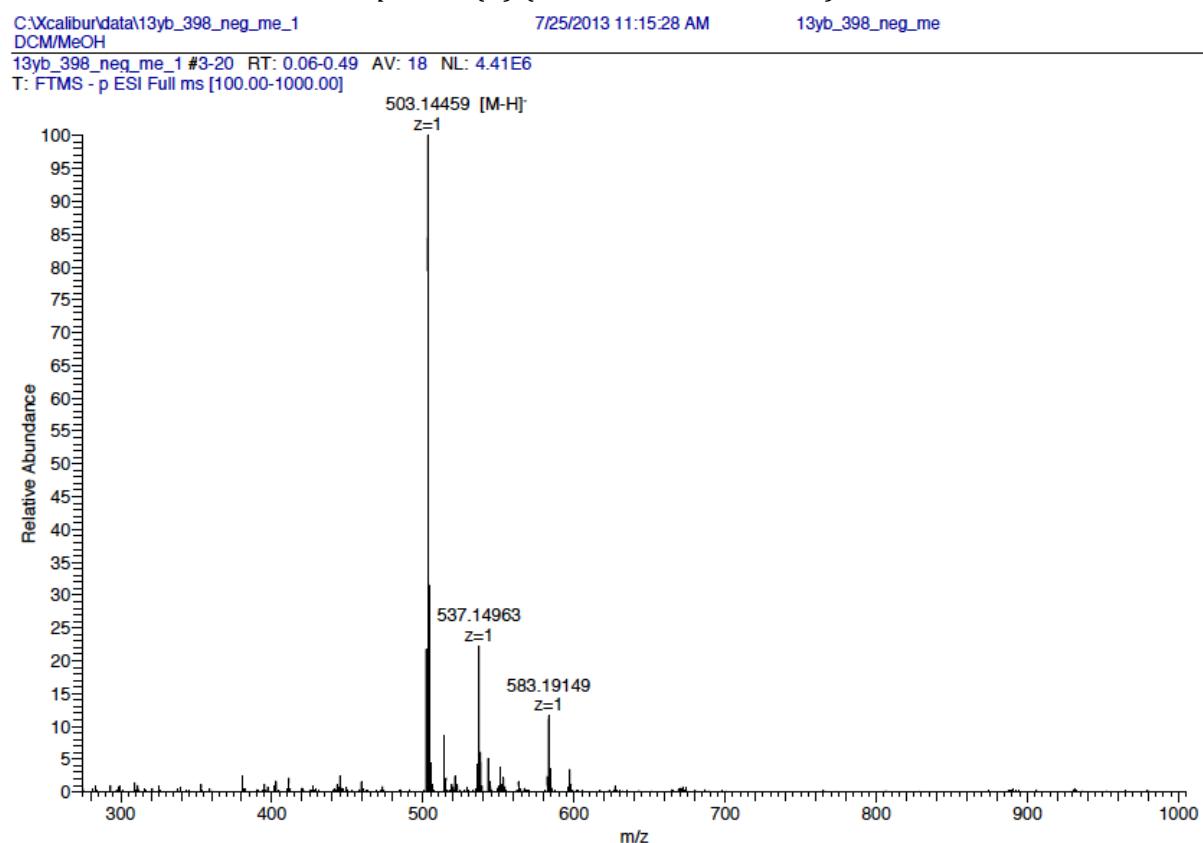
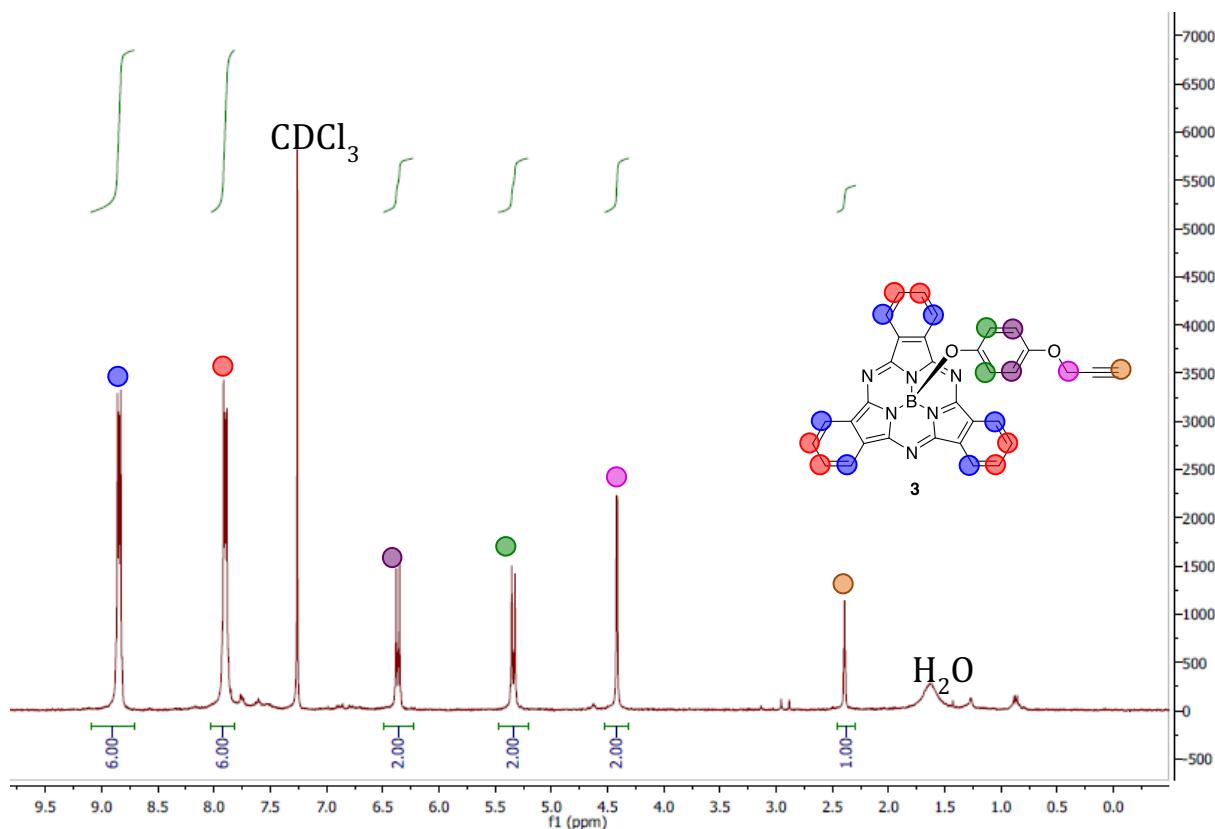
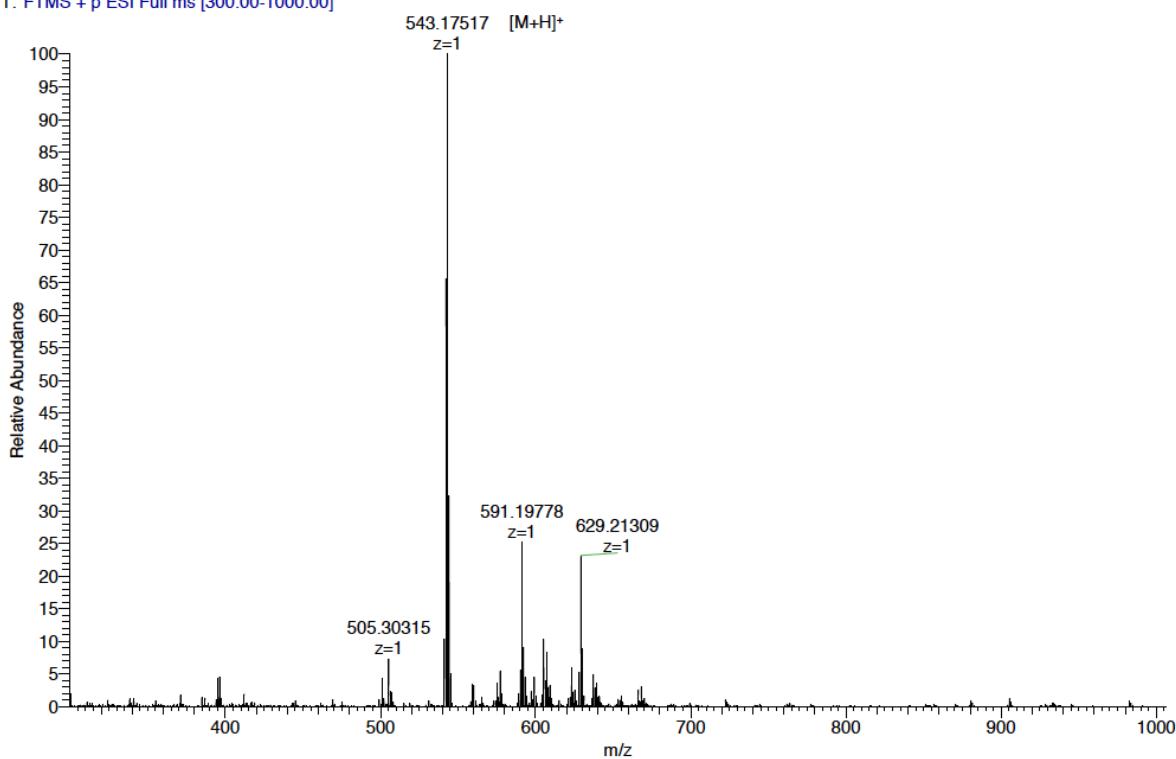


Fig. S2. HR-MS of B-(4-hydroxyphenoxy)[subphthalocyaninato]boron(III) , Sub-phenol (5)



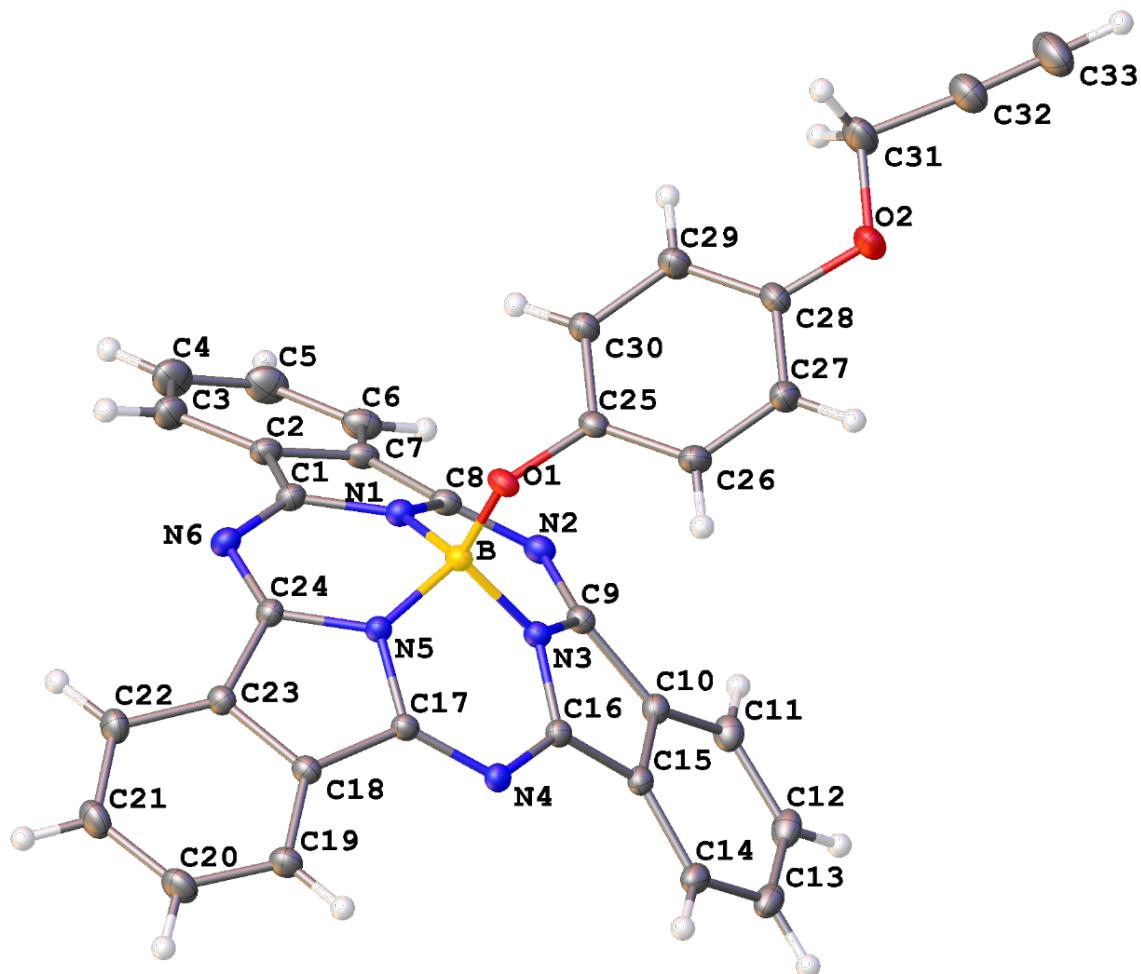
*Fig. S3.*  $^1\text{H}$  NMR spectrum of *B*-(4-propargyloxyphenoxy)[subphthalocyaninato]boron(III) (Sub-alkyne, **3**) ( $\text{CDCl}_3$ , 300 MHz, 300K)

C:\Xcalibur\data\13yb\_400\_me\_1  
DCM/MeOH  
13yb\_400\_me\_1 #3-19 RT: 0.02-0.15 AV: 17 NL: 1.66E7  
T: FTMS + p ESI Full ms [300.00-1000.00]



*Fig. S4.* HR-MS spectrum of *B*-(4-propargyloxyphenoxy)[subphthalocyaninato]boron(III)

## Crystal data for compound 3



*Fig. S5. Crystallographic structure of of B-(4-propargyloxyphenoxy)[subphthalocyaninato]boron(III) (Sub-alkyne, 3)*

Identification code	3
Empirical formula	C <sub>33</sub> H <sub>19</sub> BN <sub>6</sub> O <sub>2</sub>
Formula weight	542.35
Temperature/K	115
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.3797(13)
b/Å	27.177(3)
c/Å	7.8604(8)
α/°	90
β/°	98.193(2)
γ/°	90
Volume/Å <sup>3</sup>	2617.5(5)
Z	4

$\rho_{\text{calc}}$ g/cm <sup>3</sup>	1.376
$\mu/\text{mm}^{-1}$	0.089
F(000)	1120.0
Crystal size/mm <sup>3</sup>	0.32 × 0.2 × 0.17
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	4.476 to 64.414
Index ranges	-18 ≤ h ≤ 18, -40 ≤ k ≤ 40, -11 ≤ l ≤ 11
Reflections collected	76218
Independent reflections	9197 [R <sub>int</sub> = 0.0336, R <sub>sigma</sub> = 0.0203]
Data/restraints/parameters	9197/0/379
Goodness-of-fit on F <sup>2</sup>	1.052
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0480, wR <sub>2</sub> = 0.1217
Final R indexes [all data]	R <sub>1</sub> = 0.0590, wR <sub>2</sub> = 0.1298
Largest diff. peak/hole / e Å <sup>-3</sup>	0.55/-0.28
CCDC	1456530

Table S1. X-ray details related to 3.

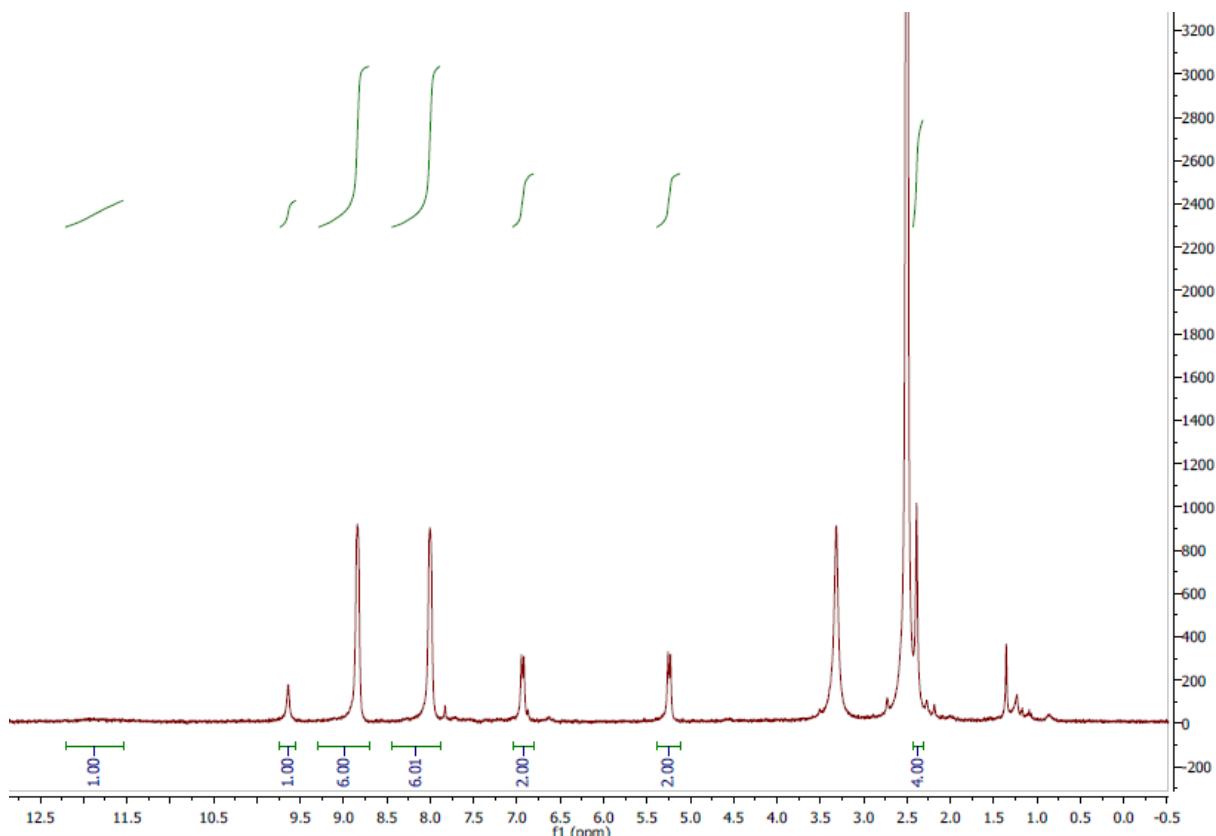


Fig. S6. <sup>1</sup>H NMR spectrum of Sub-acid (6) (CDCl<sub>3</sub>, 300 MHz, 300K)

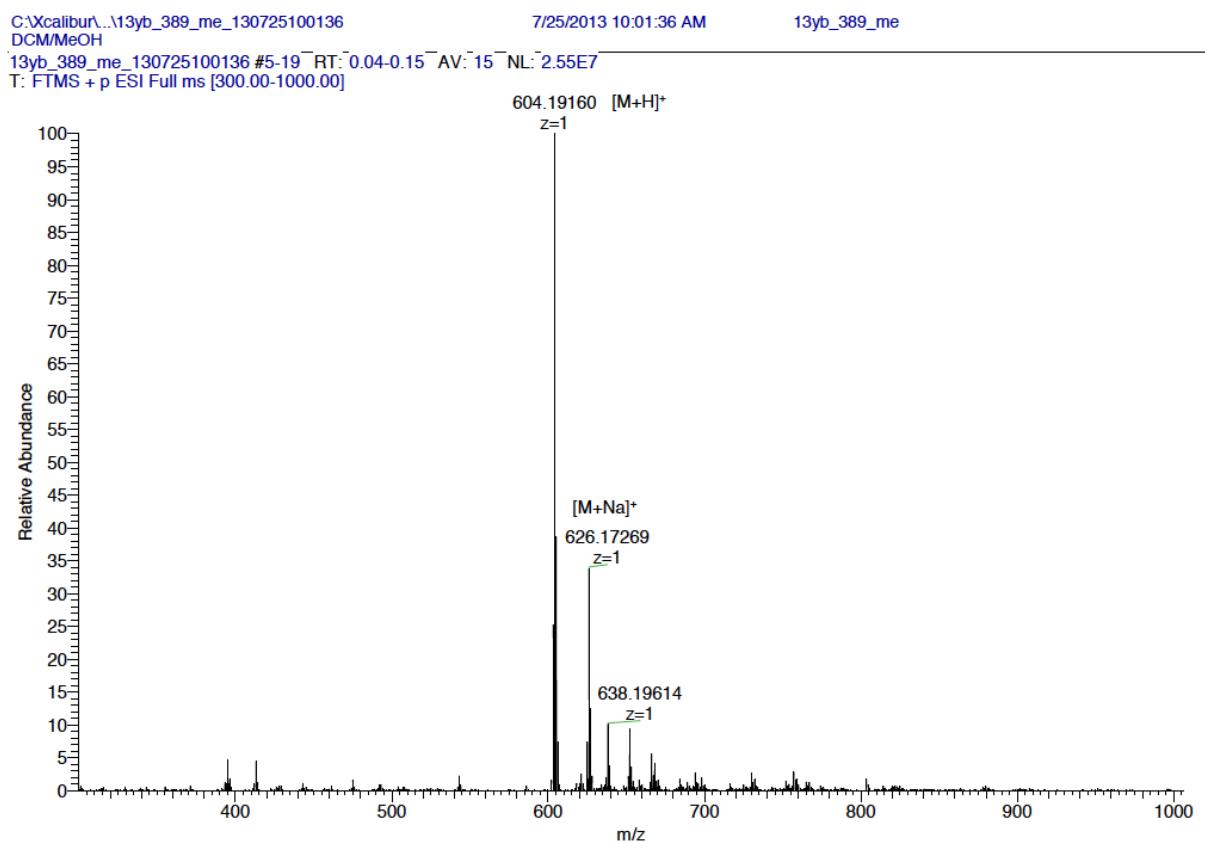


Fig. S7. HR-MS NMR spectrum of Sub-acid (6)

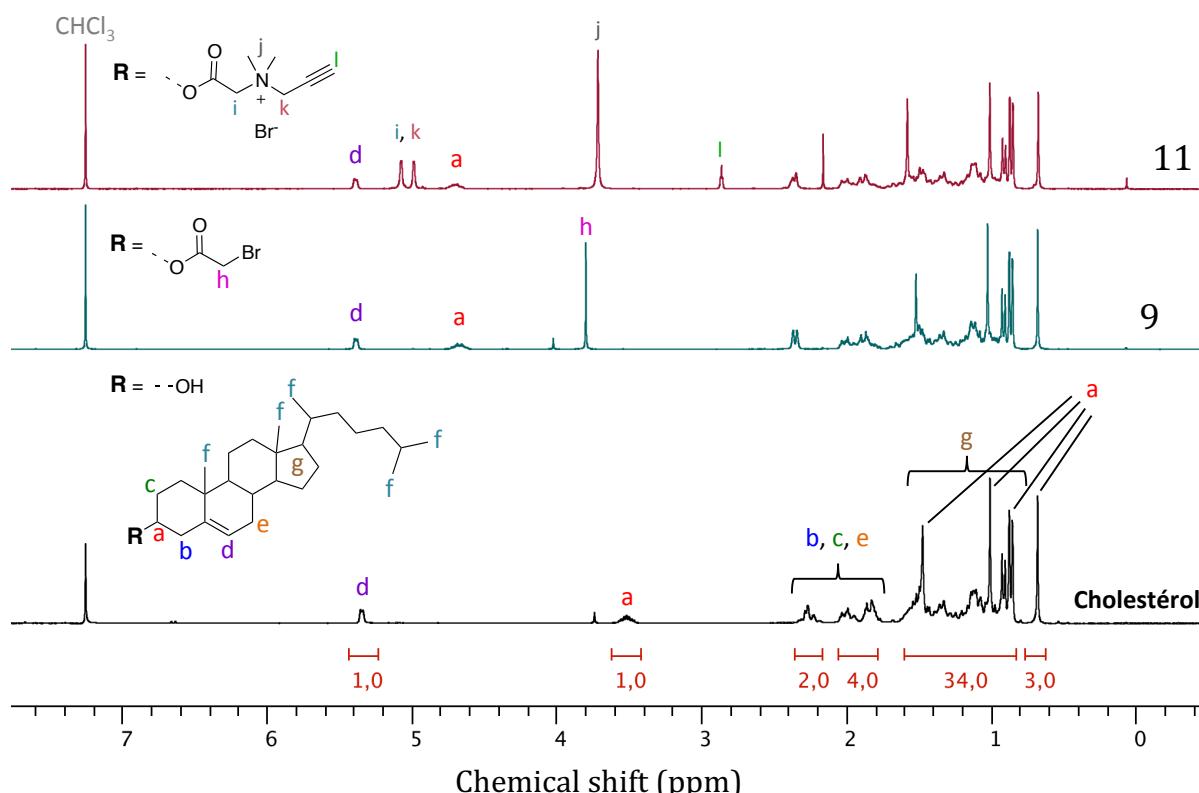
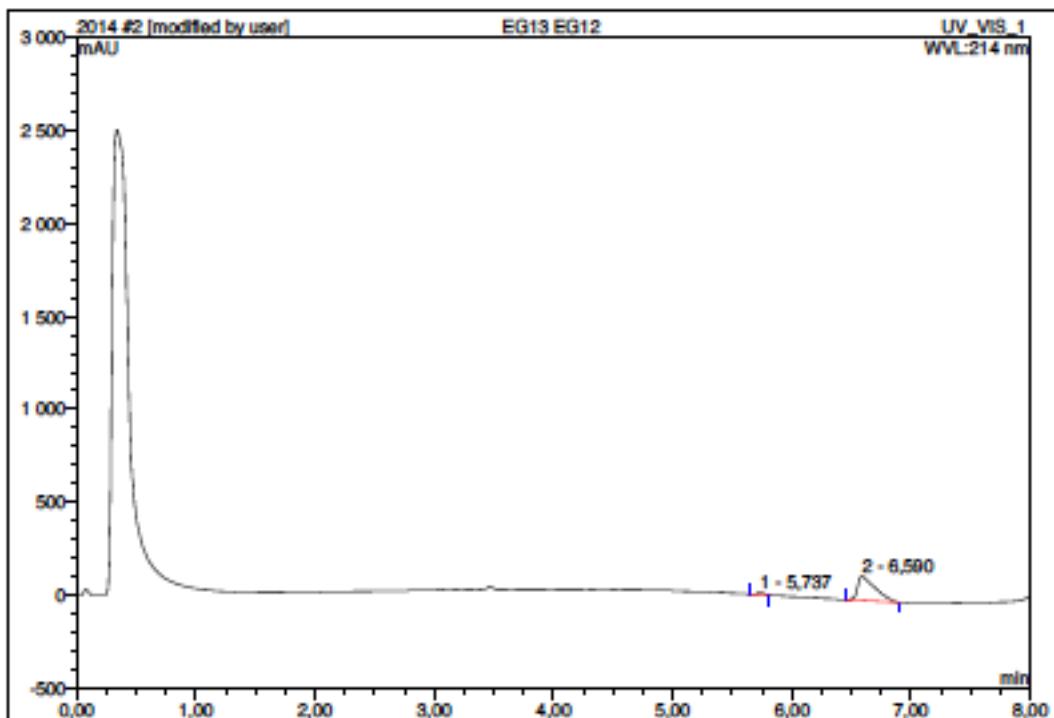


Fig. S8. <sup>1</sup>H NMR spectrum of Cholesteryl (prop-2-ynyl-N,N-dimethylammonium bromide) acetate (11) (CDCl<sub>3</sub>, 300 MHz, 300K)

## 2 EG13 EG12

Sample Name:	EG13 EG12	Injection Volume:	20,0
Vial Number:	62	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214.0
Control Program:	Kinetex C18 50x21 5to100 In 5min 0_5	Bandwidth:	4
Quantif. Method:	Intégration valley to valley	Dilution Factor:	1,0000
Recording Time:	22/5/2014 17:00	Sample Weight:	1,0000
Run Time (min):	8,00	Sample Amount:	1,0000

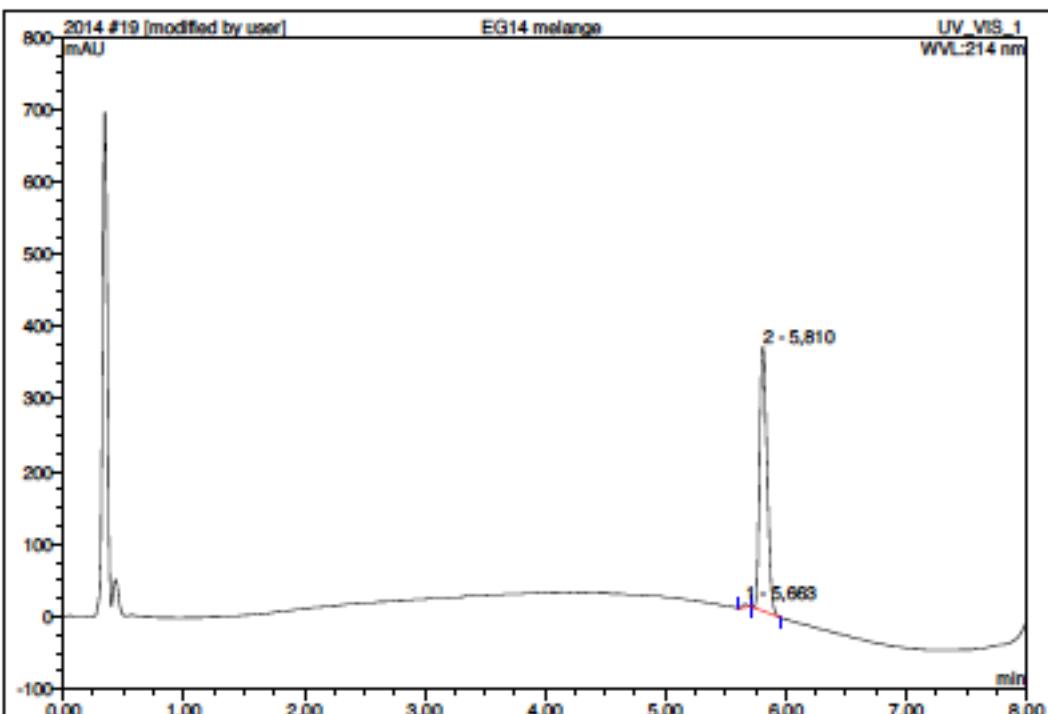


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,74	n.a.	13,804	0,778	3,38	n.a.	BMB <sup>a</sup>
2	6,59	n.a.	131,341	22,320	96,64	n.a.	BMB
Total:			145,145	23,095	100,00	0,000	

Fig. S9. Chromatogram of Cholesteryl (alkyne) – BBN conjugate 1b (click coupling)

## 19 EG14 melange

Sample Name:	EG14 melange	Injection Volume:	20,0
Vial Number:	79	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214.0
Control Program:	Kinetex C18 50x21 5to100 In 5min 0_5	Bandwidth:	4
Quantif. Method:	Intégration valley to valley	Dilution Factor:	1,0000
Recording Time:	28/5/2014 14:40	Sample Weight:	1,0000
Run Time (min):	8,00	Sample Amount:	1,0000

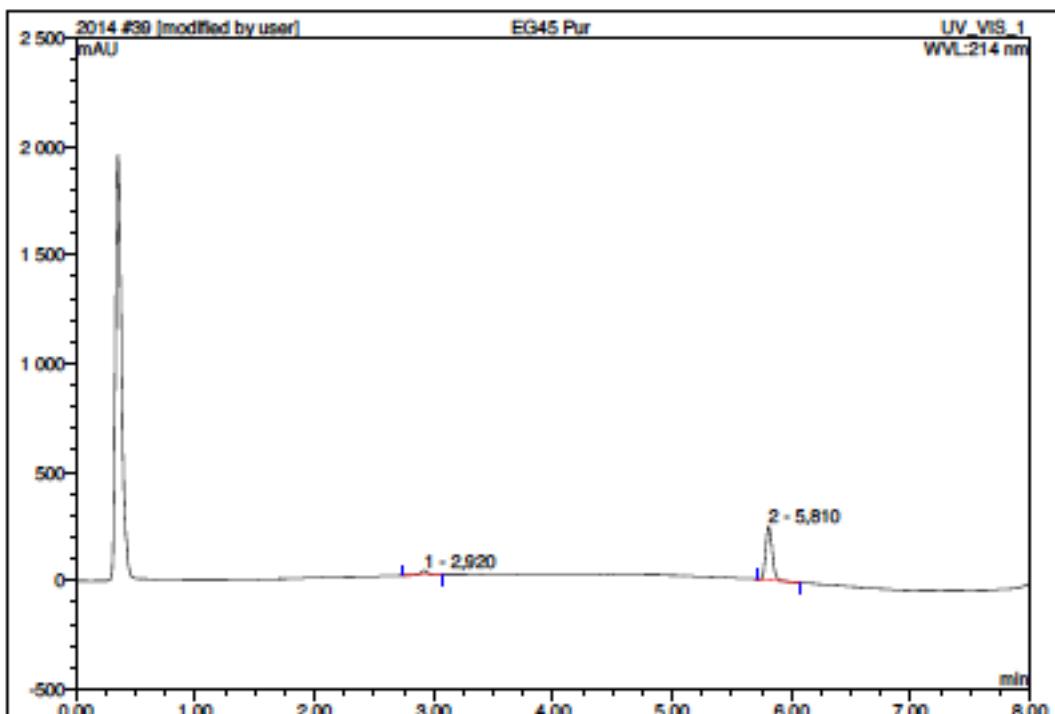


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,66	n.a.	3,982	0,203	0,77	n.a.	BMB <sup>f</sup>
2	5,81	n.a.	365,585	26,115	99,23	n.a.	bMB <sup>f</sup>
<b>Total:</b>			<b>369,568</b>	<b>26,318</b>	<b>100,00</b>	<b>0,000</b>	

Fig. S10. Chromatogram of Cholesteryl( alkyne) – BBN conjugate **1b** (Cu-catalyzed click reaction)

### 39 EG45 Pur

Sample Name:	EG45 Pur	Injection Volume:	20,0
Vial Number:	99	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214.0
Control Program:	Kinetex C18 50x21 5to100 In 5min 0_5	Bandwidth:	4
Quantif. Method:	Intégration valley to valley	Dilution Factor:	1,0000
Recording Time:	17/9/2014 15:38	Sample Weight:	1,0000
Run Time (min):	8,00	Sample Amount:	1,0000

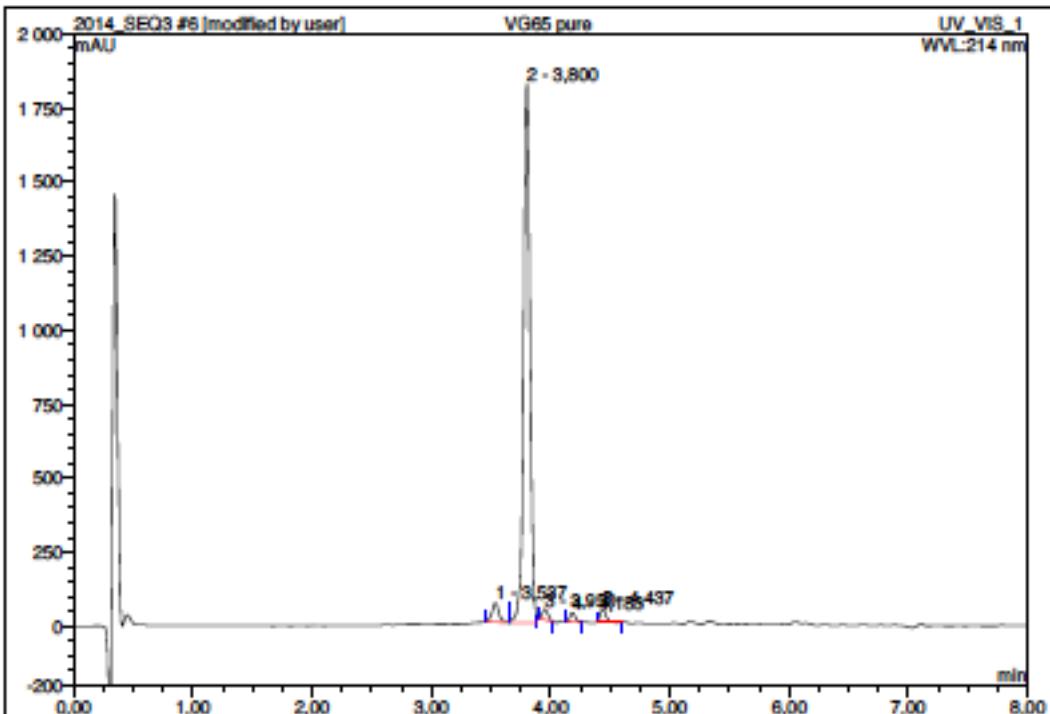


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount %	Type
1	2,92	n.a.	21,841	1,483	8,86	n.a.	BMB <sup>c</sup>
2	5,81	n.a.	247,062	15,644	91,34	n.a.	BMB
Total:			268,924	17,126	100,00	0,000	

Fig. S11. Chromatogram of Cholestryl – BBN conjugate **1a** (copper-free click reaction)

## 6 VG65 pure

Sample Name:	VG65 pure	Injection Volume:	20,0
Vial Number:	66	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214,0
Control Program:	Kinetex C18 50x21 5to100 In 5min 0_5	Bandwidth:	4
Quantif. Method:	Intégration valley to valley	Dilution Factor:	1,0000
Recording Time:	3/6/2014 10:56	Sample Weight:	1,0000
Run Time (min):	8,00	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area	Amount %	Type
1	3,54	n.a.	64,502	4,602	3,73	n.a.	BM <sup>a</sup>
2	3,80	n.a.	1820,619	112,774	91,50	n.a.	M <sup>a</sup>
3	3,95	n.a.	30,395	1,985	1,61	n.a.	BMB <sup>a</sup>
4	4,18	n.a.	31,563	1,817	1,31	n.a.	BMB <sup>a</sup>
5	4,44	n.a.	43,319	2,268	1,84	n.a.	BMB <sup>a</sup>
Total:			1995,399	123,246	100,00	0,000	

Fig. S12. Chromatogram of BCN – BBN conjugate