

Supporting information

Sequential photochemistry of dibenzo[*a,e*]dicyclopropa[*c,g*][8]annulene-1,6-dione:
selective formation of didehydrodibenzo[*a,e*][8]annulenes with ultrafast SPAAC
reactivity

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Table S.1 Observed rates of cycloaddition of **5a** with BuN₃ at 25°C.

Azide Concentration (M)	k_{obs} (s ⁻¹)		
0.03	5.121E-4	4.763E-4	4.872E-4
0.04	6.901E-4	6.876E-4	6.779E-4
0.05	7.966E-4	7.566E-4	7.657E-4
0.1	0.00162	0.00160	0.00161
0.15	0.00250	0.00251	0.00247

Table S2. Observed rates of cycloaddition of **3a** with BuN₃ at 25°C.

Azide Concentration (M)	k_{obs} (s ⁻¹)		
3x10 ⁻⁴	0.01226	0.01145	0.01235
4x10 ⁻⁴	0.01442	0.01610	0.01477
4.8x10 ⁻⁴	0.01877	0.01965	0.01965
6x10 ⁻⁴	0.02173	0.02155	0.0214
8x10 ⁻⁴	0.02965	0.02896	0.02934

Table S.3 Observed rates of cycloaddition of **2a** with BuN₃ at 25°C.

Azide Concentration (M)	k_{obs} (s ⁻¹)		
0.0151	9.31E-4	0.00104	0.00112
0.0252	0.00172	0.00176	0.00175
0.0378	0.00243	0.00269	0.00229
0.0503	0.00301	0.00331	0.00394
0.0755	0.00513	0.00461	0.00522

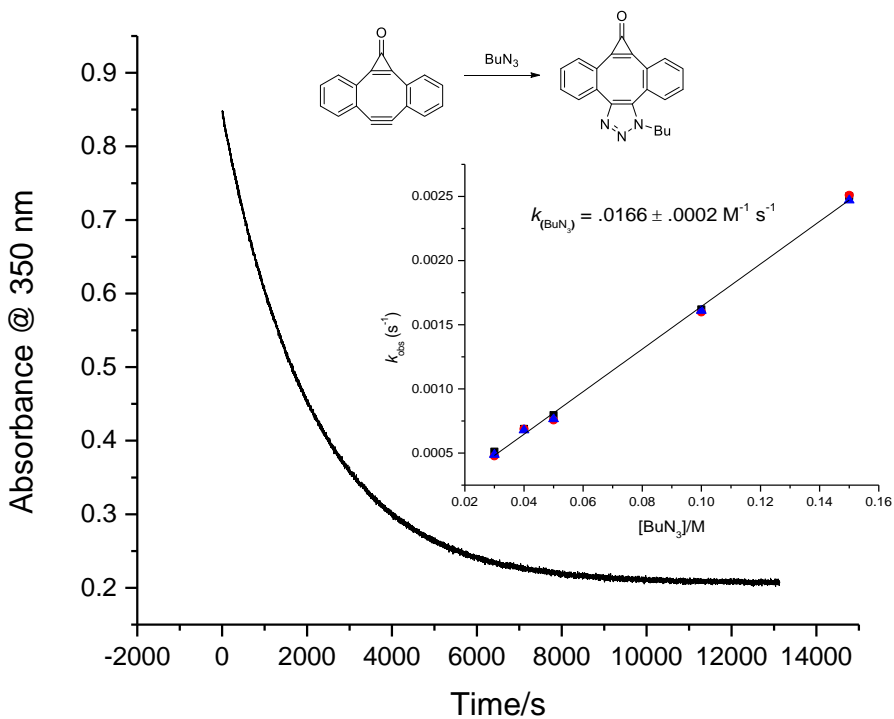


Figure S1. Reaction of 0.088 mM MC-DIBOD (5a) with butyl azide in 1:1 DCM/MeOH at 25°C.

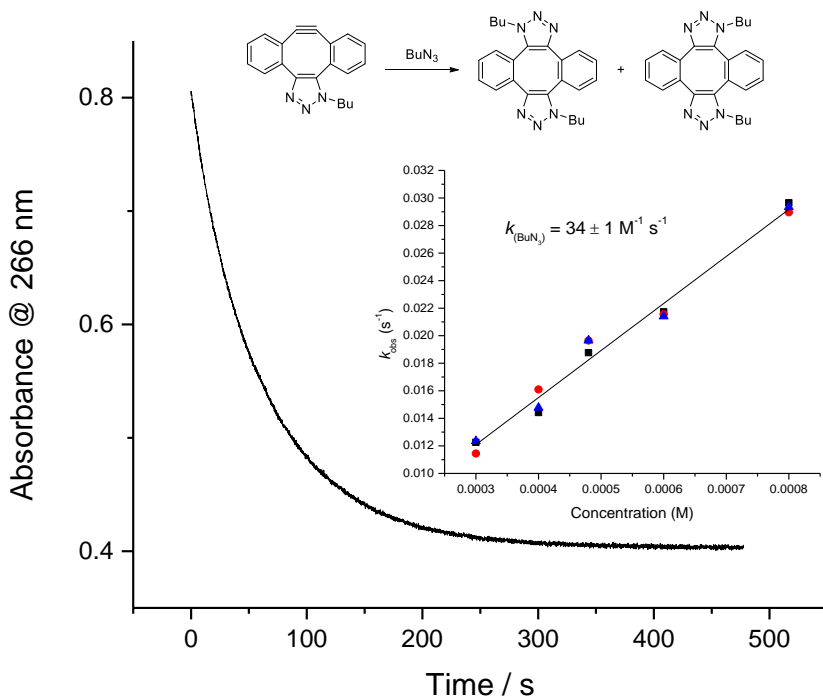


Figure S2. Reaction of 0.029 mM mono-triazole 3a with butyl azide in 1:1 DCM/MeOH at 25°C.

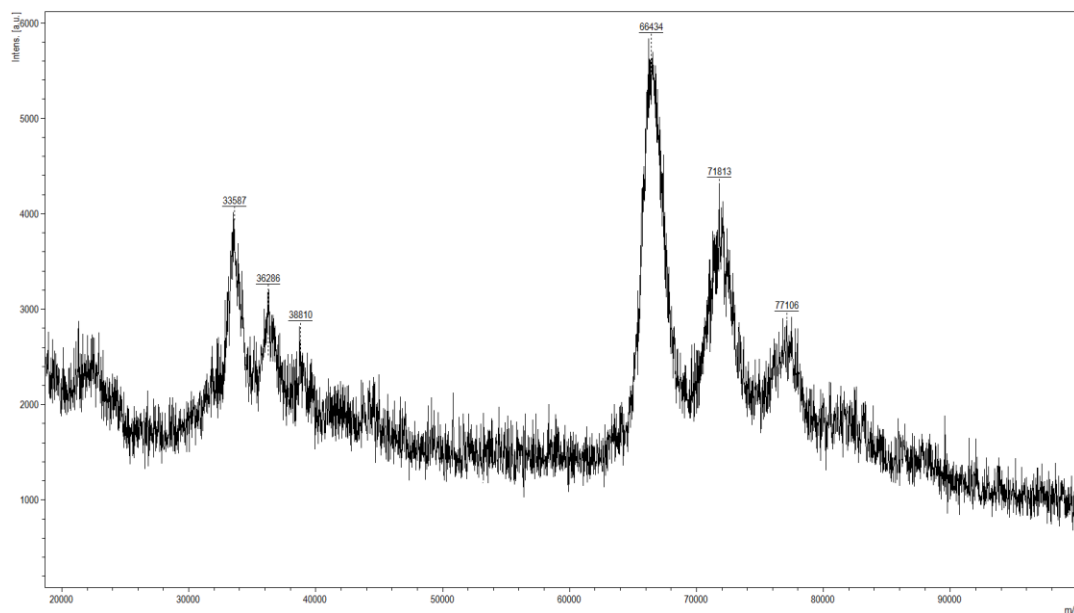


Figure S3. Photo-derivatization of azido-BSA-azide with PEG₅₀₀₀-azide using MC-DIBOD (**5a**).

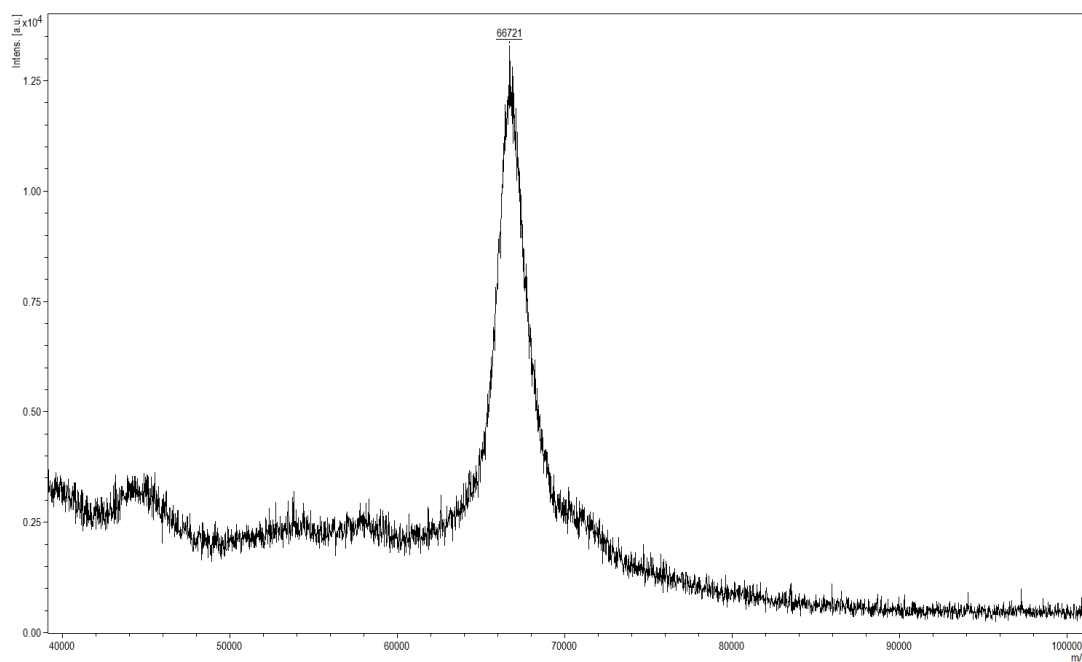


Figure S4. Dark control: azido-BSA-azide incubated with PEG₅₀₀₀-triazole and MC-DIBOD (**5a**) in the dark.

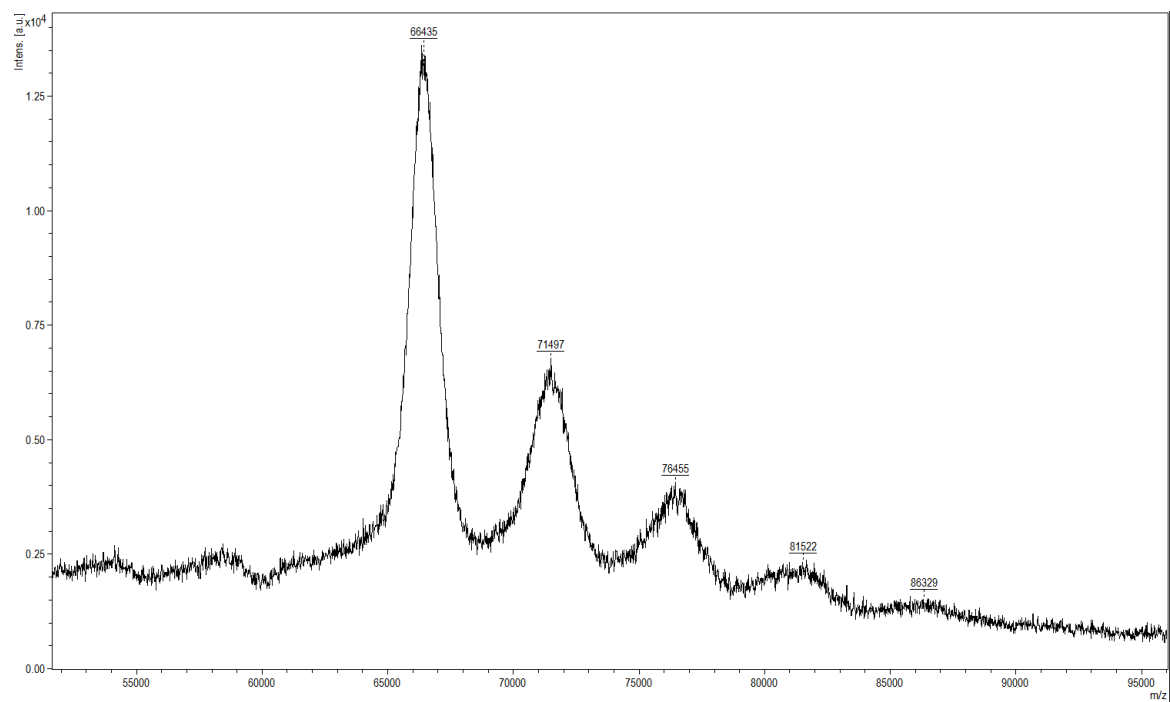
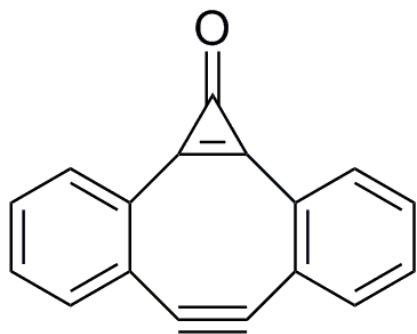
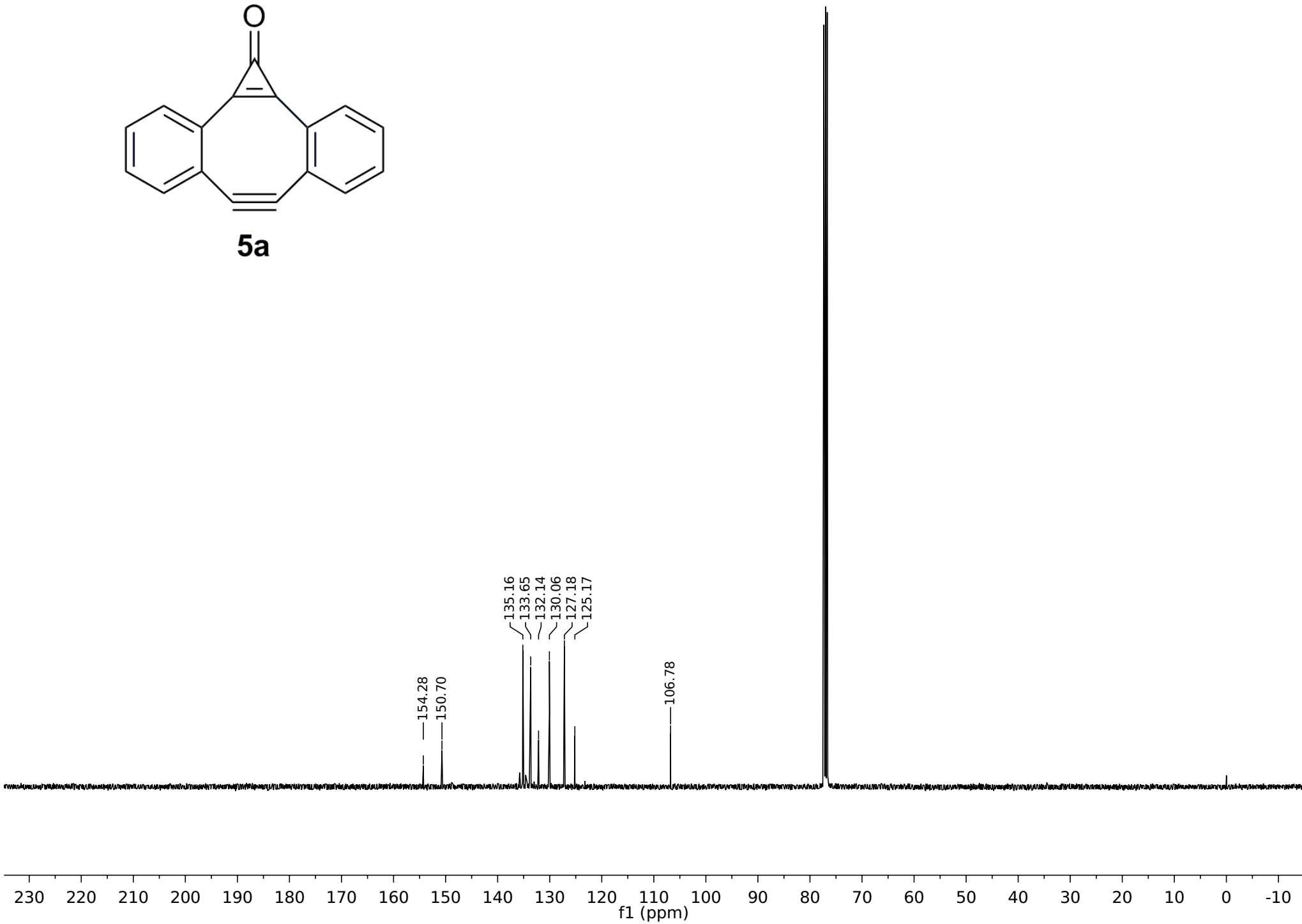
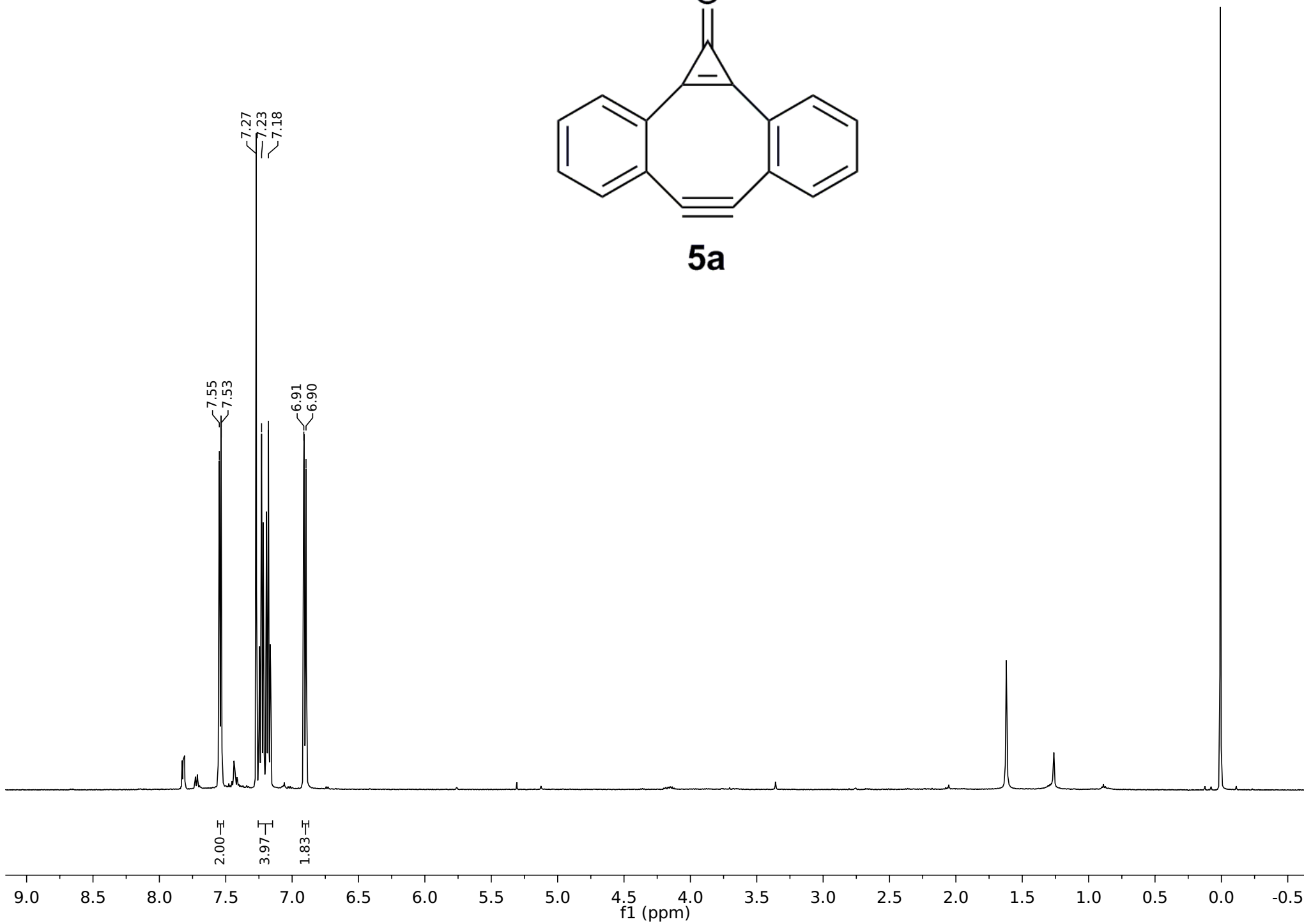
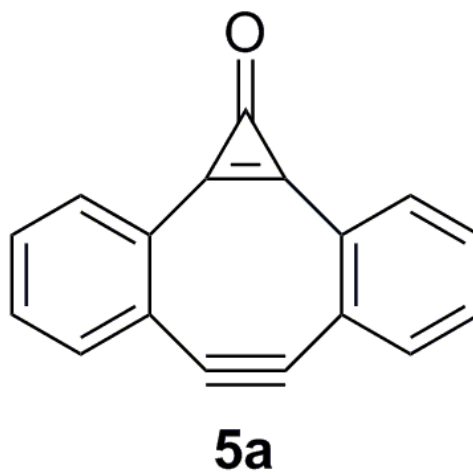


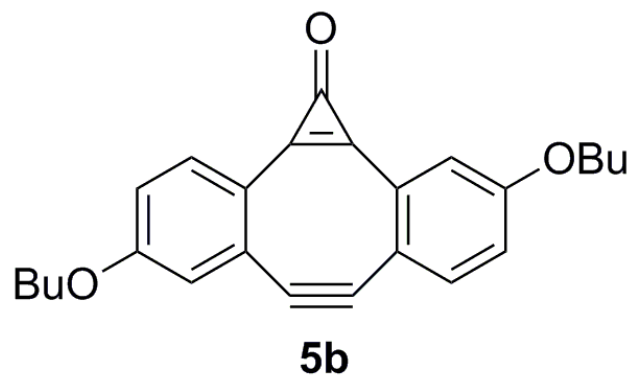
Figure S5. CuAAC-conjugation of azido-BSA with propargyl-PEG₅₀₀₀

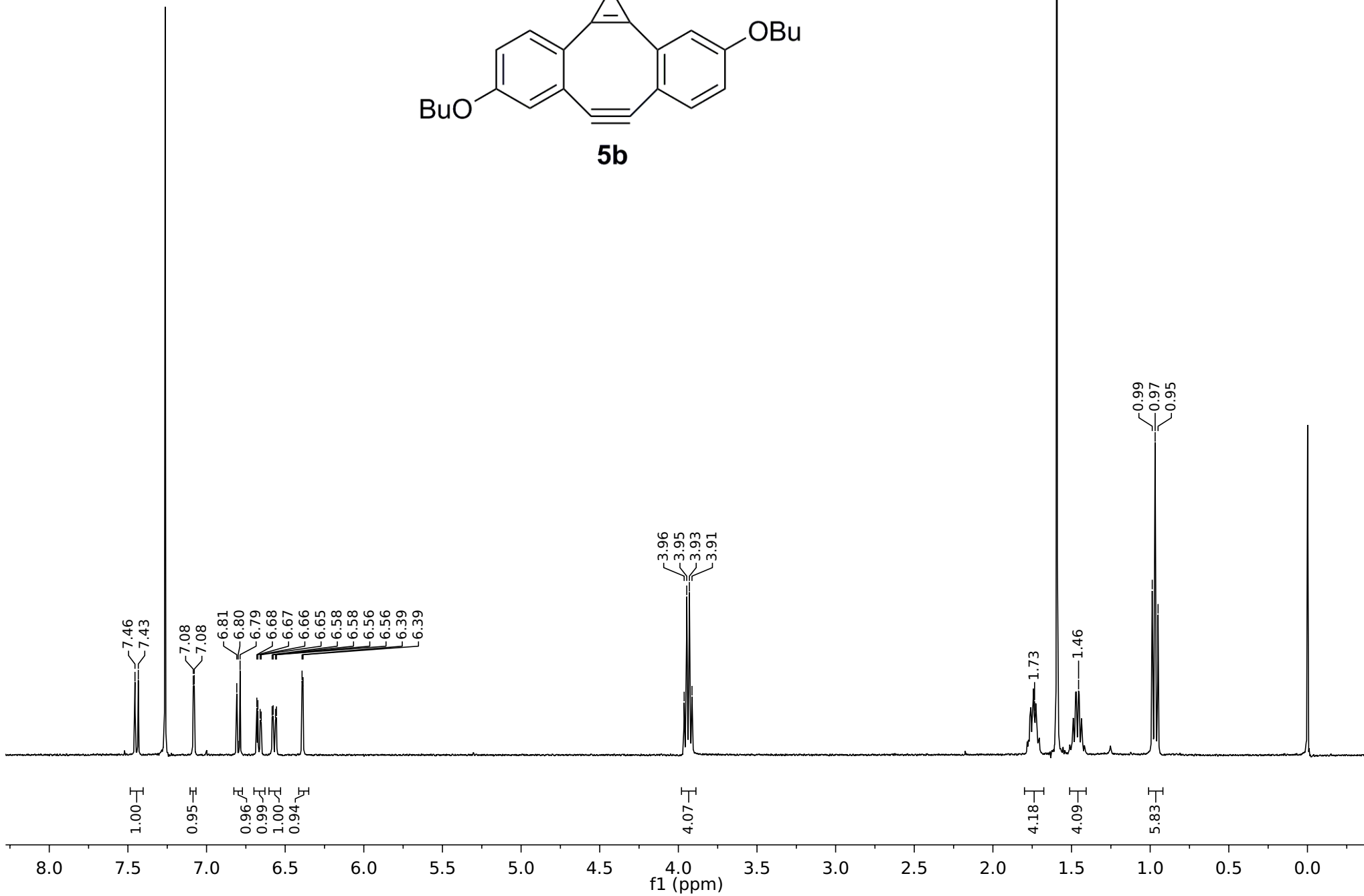
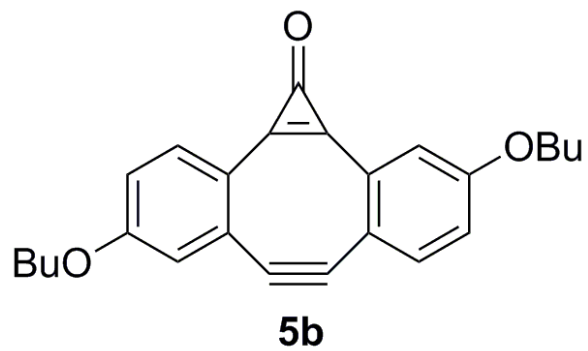


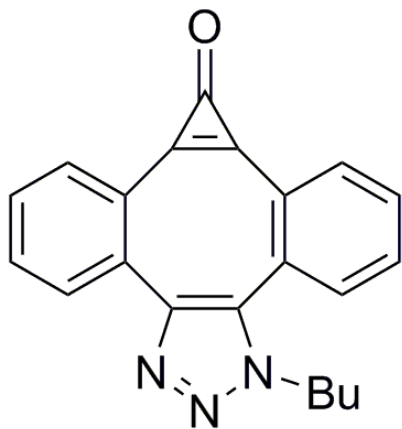
5a



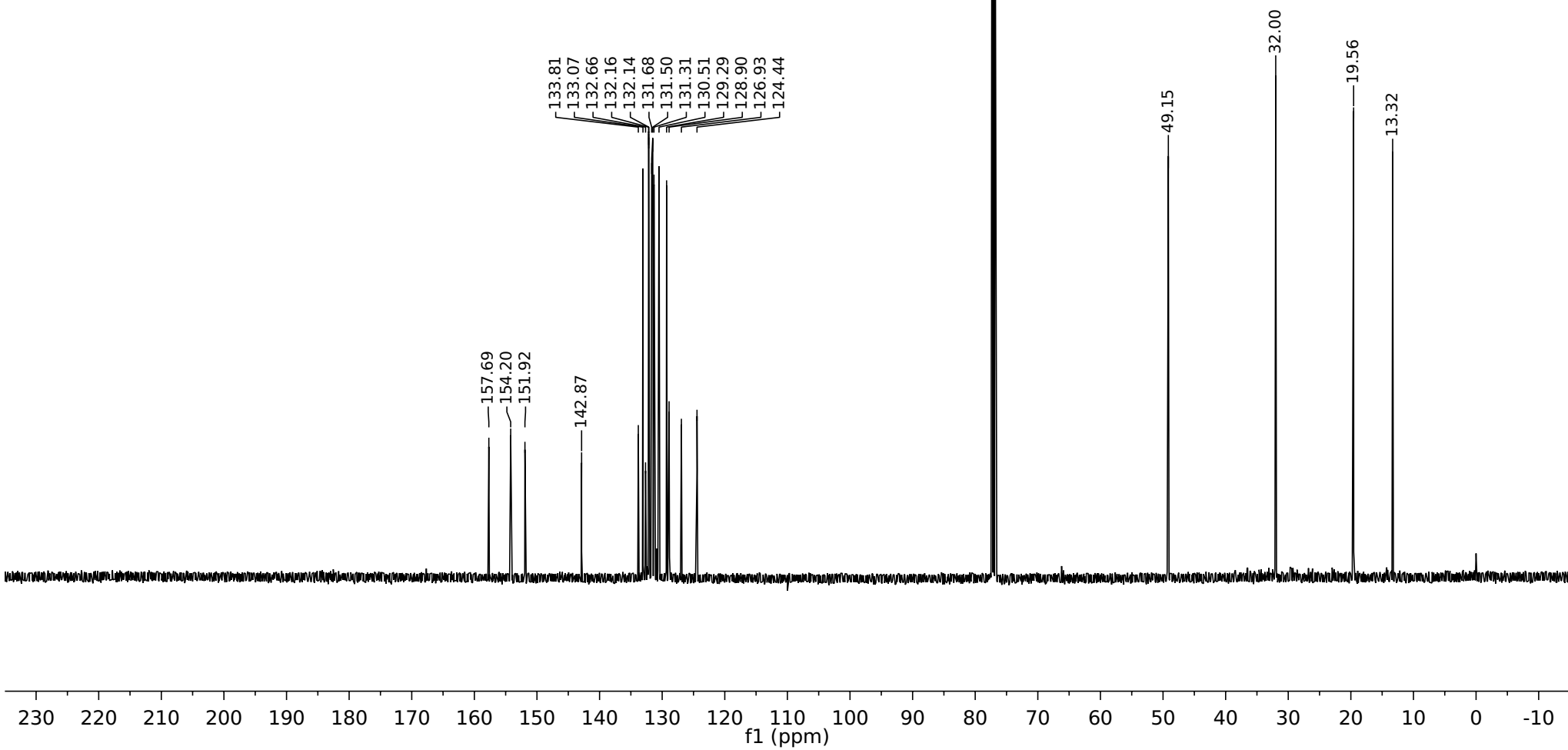


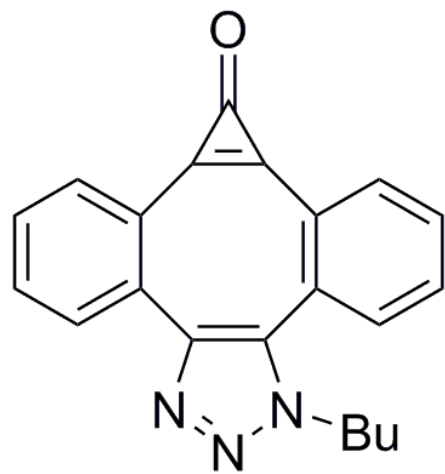




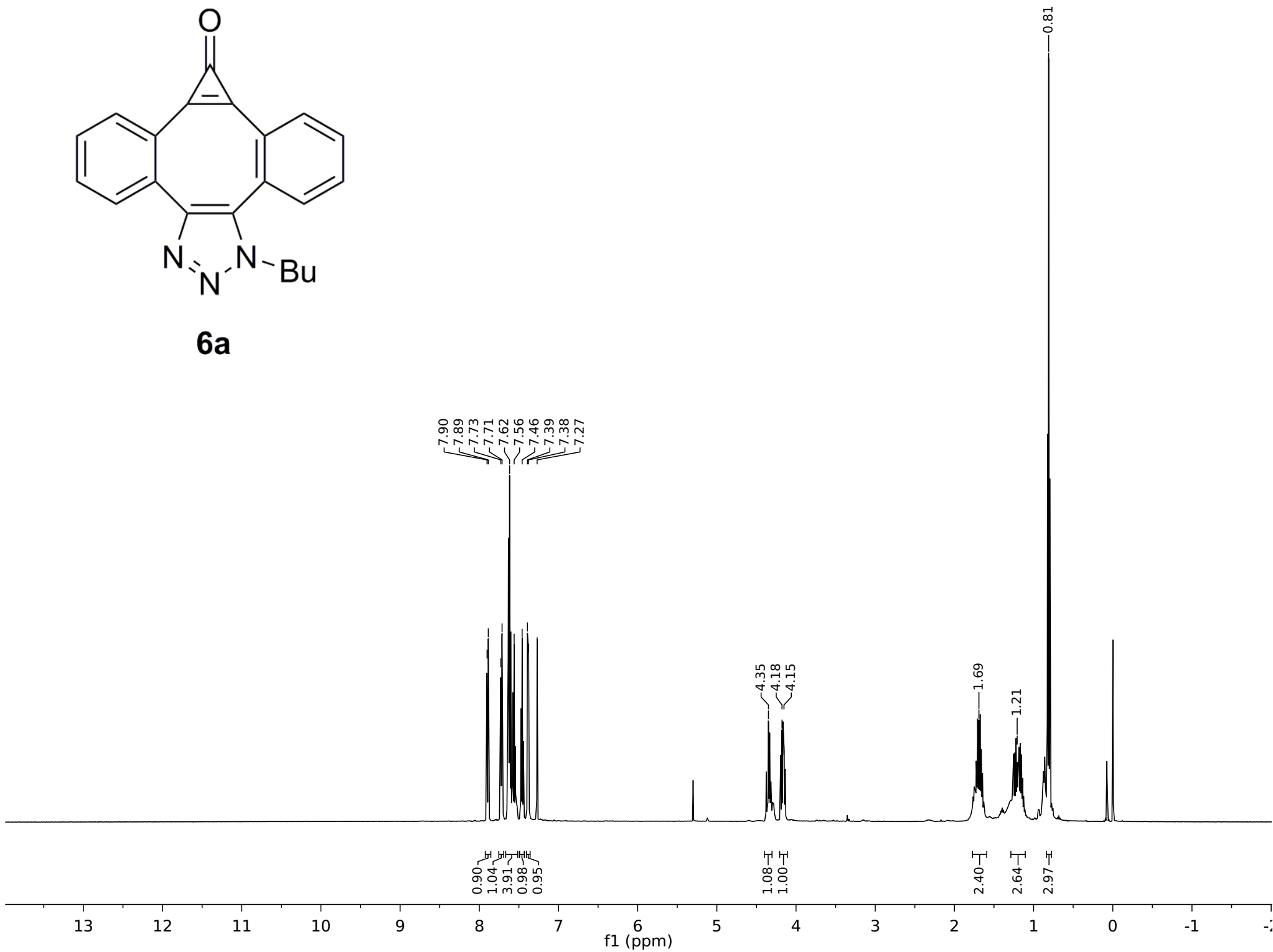


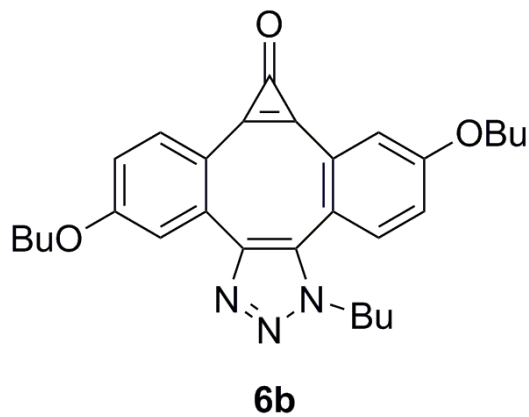
6a



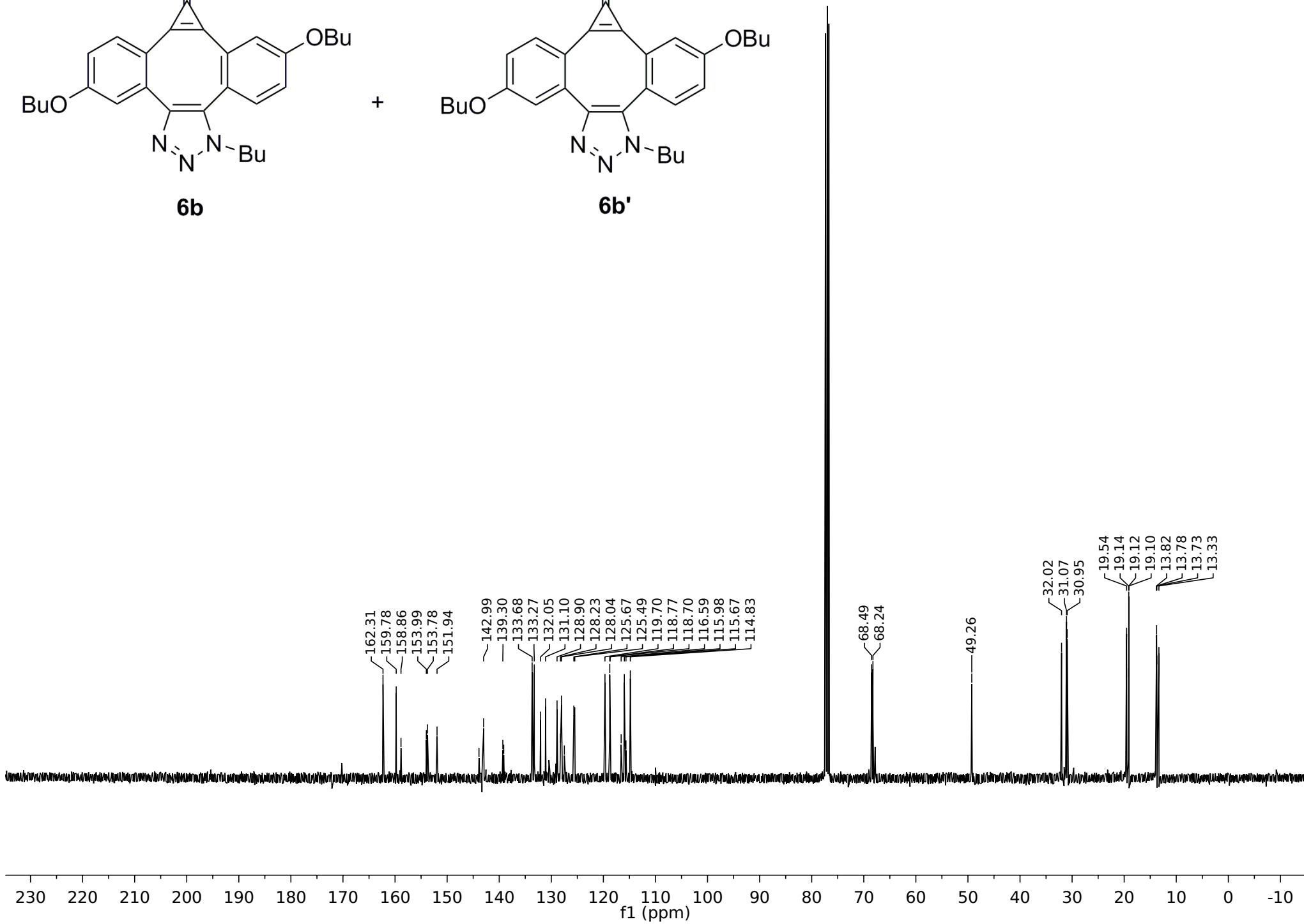
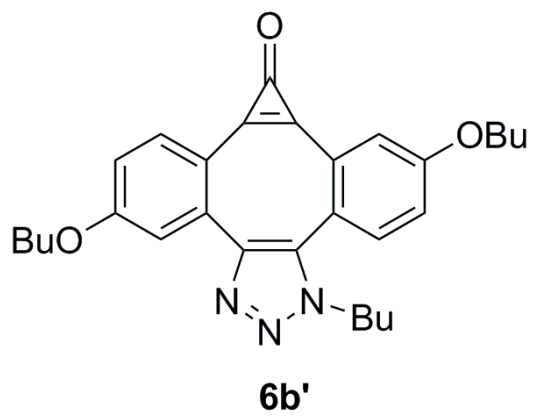


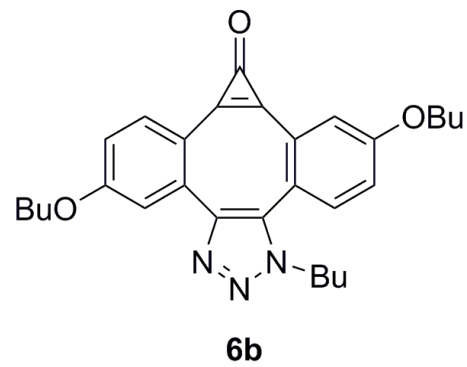
6a



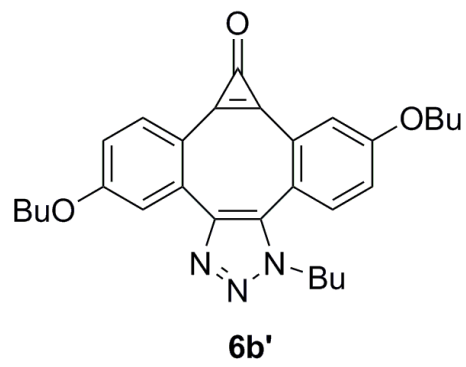


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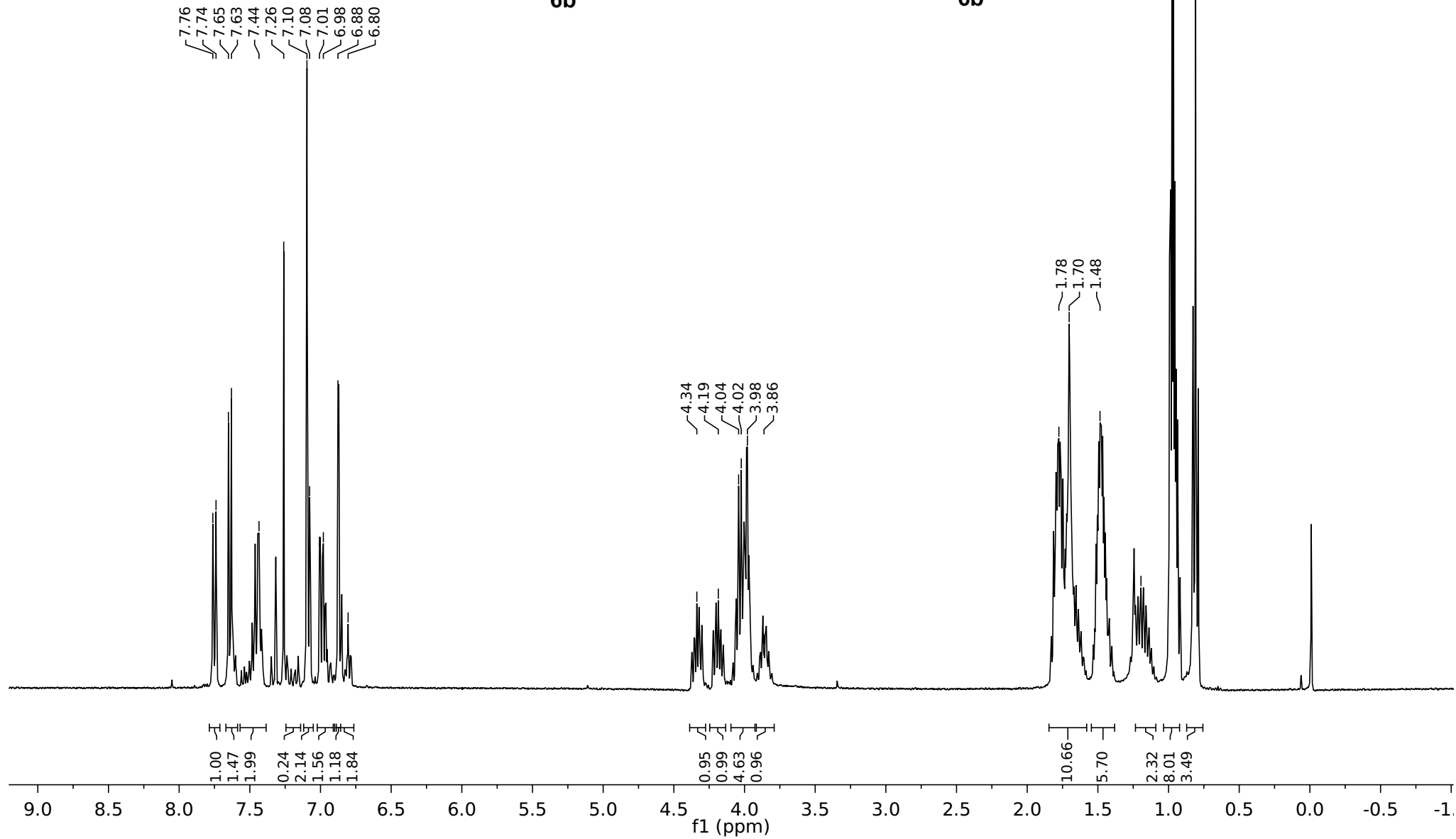


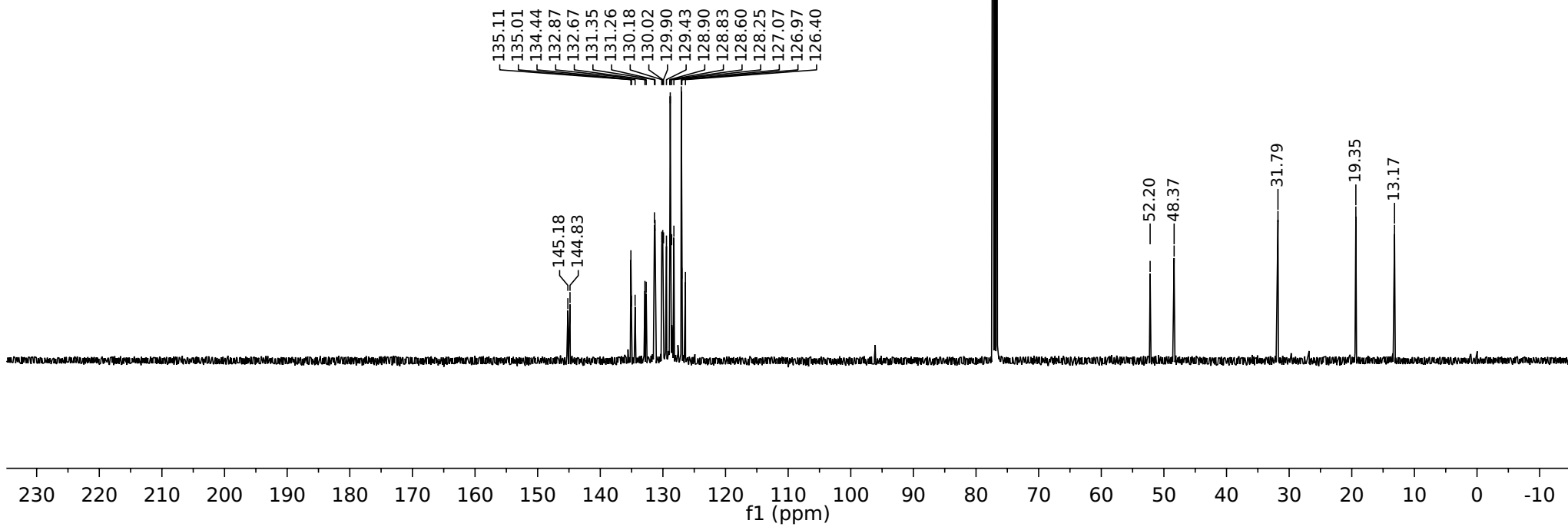
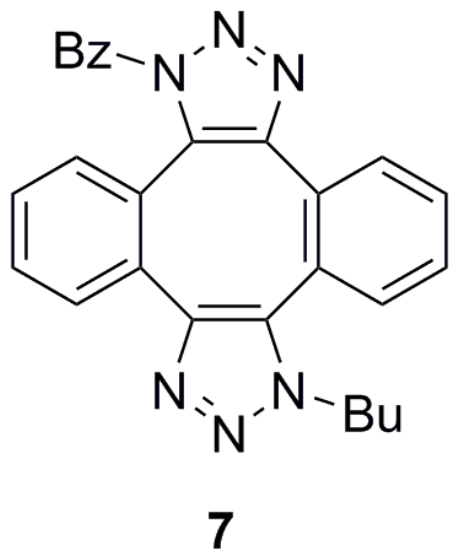
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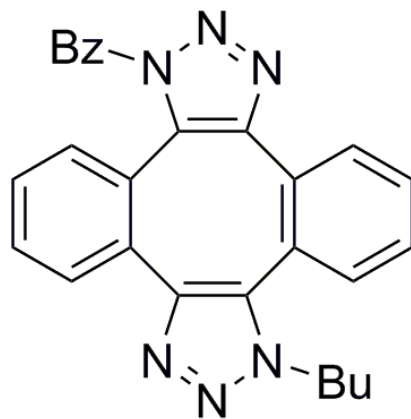


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7.74
7.65
7.63
7.44
7.26
7.10
7.08
7.01
6.98
6.88
6.80

1.20
0.97
0.97
0.81







7

