Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for:

Synthesis and Study of Electrochemical and Optical Properties of Substituted Perylenemonoimides in Solutions and on Solid Surfaces

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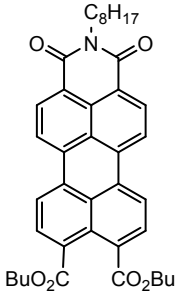
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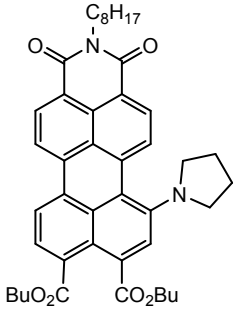
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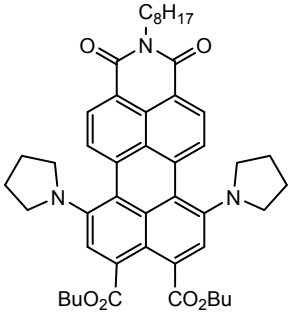
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CO2Bu

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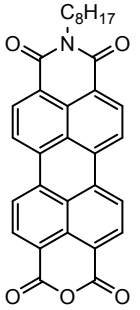
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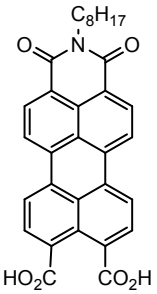
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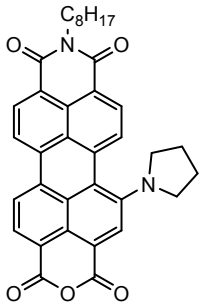
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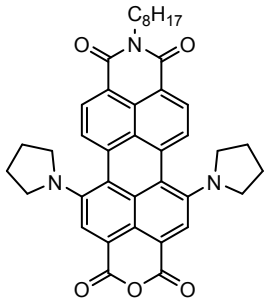
O
O
N
O
O
O

6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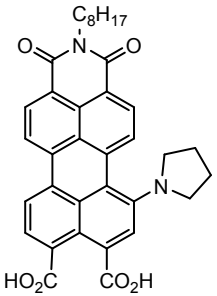
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O
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HO2C
CO2H

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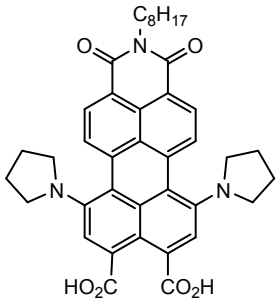
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O
O
N
N
HO2C
CO2H

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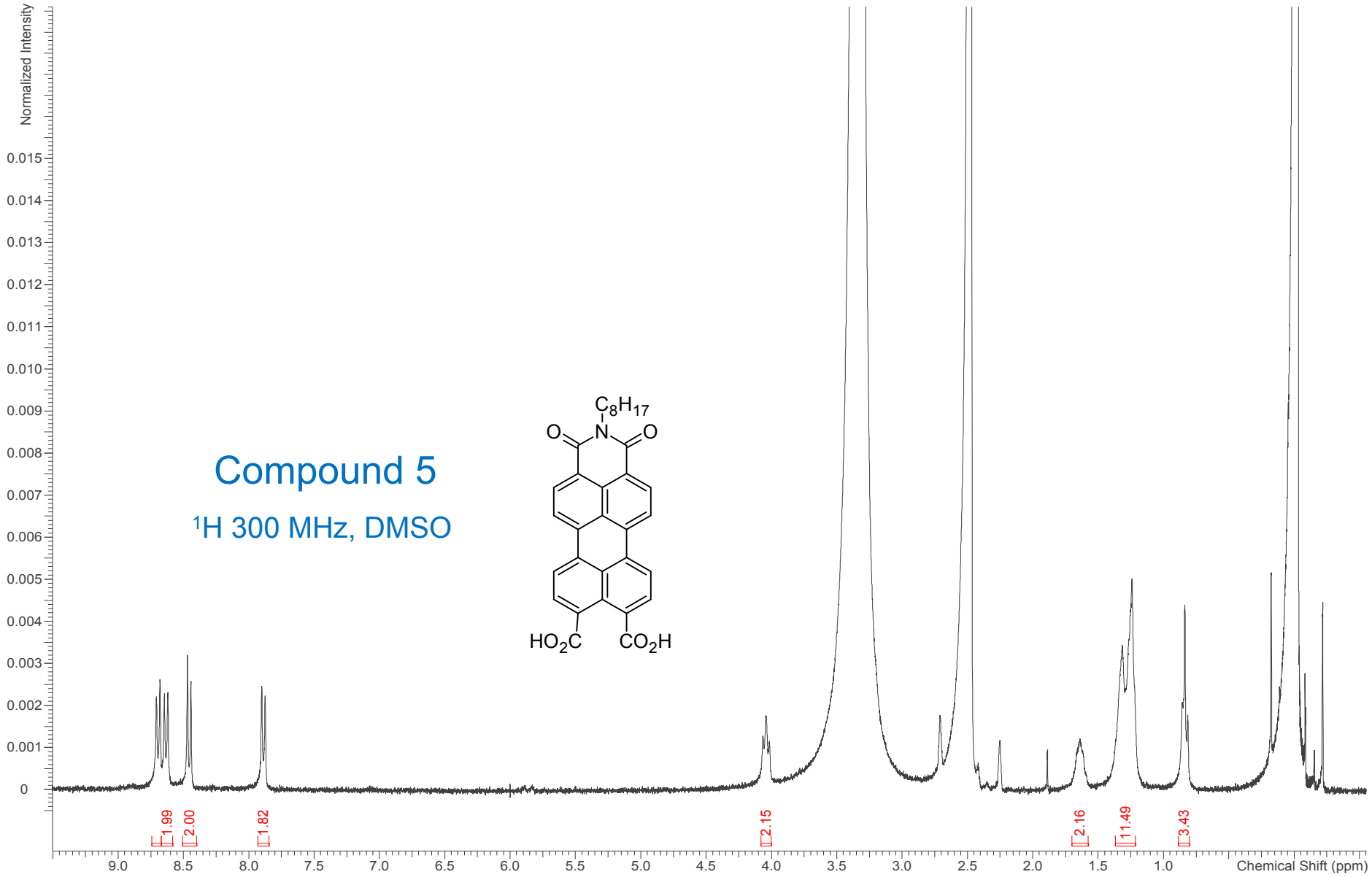
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N
O
HO2C
CO2H
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0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
1.99
2.00
1.82
2.15
2.16
11.49
3.43
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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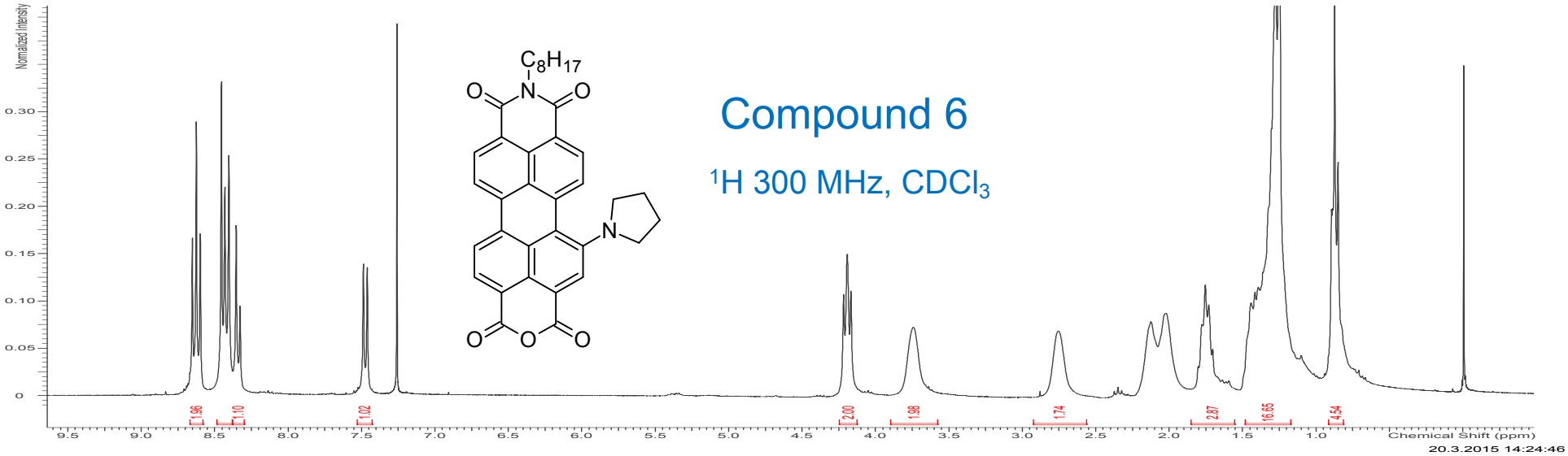
2.0
1.5
1.0
Chemical Shift (ppm)



Compound 6

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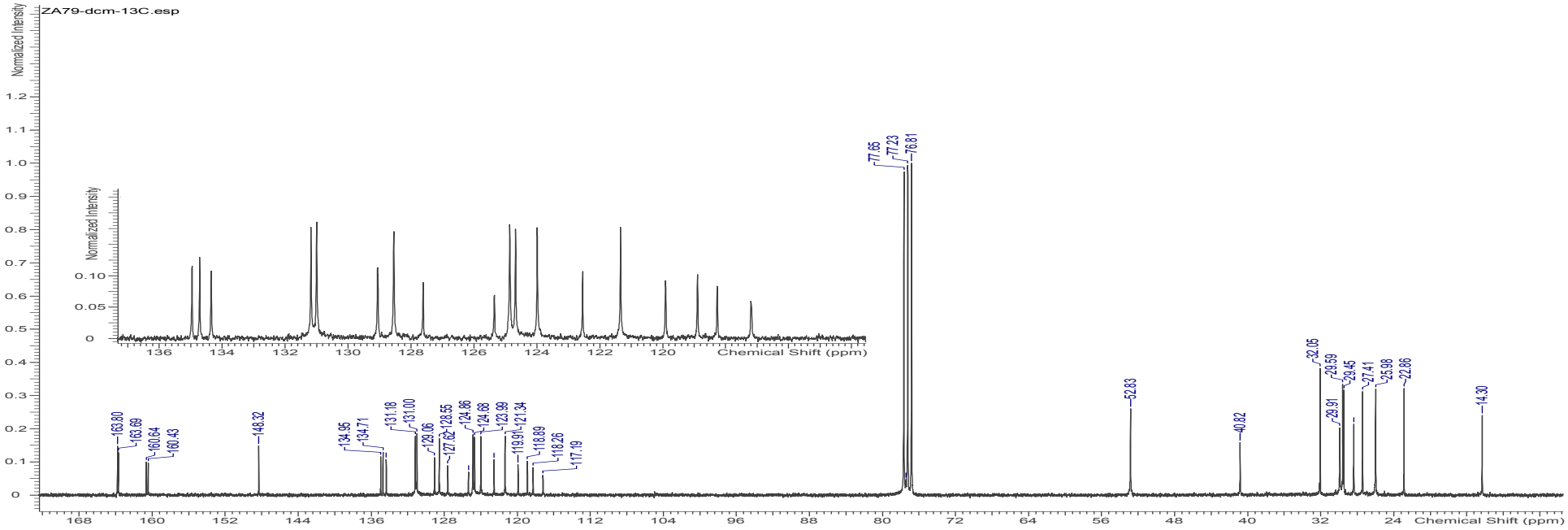

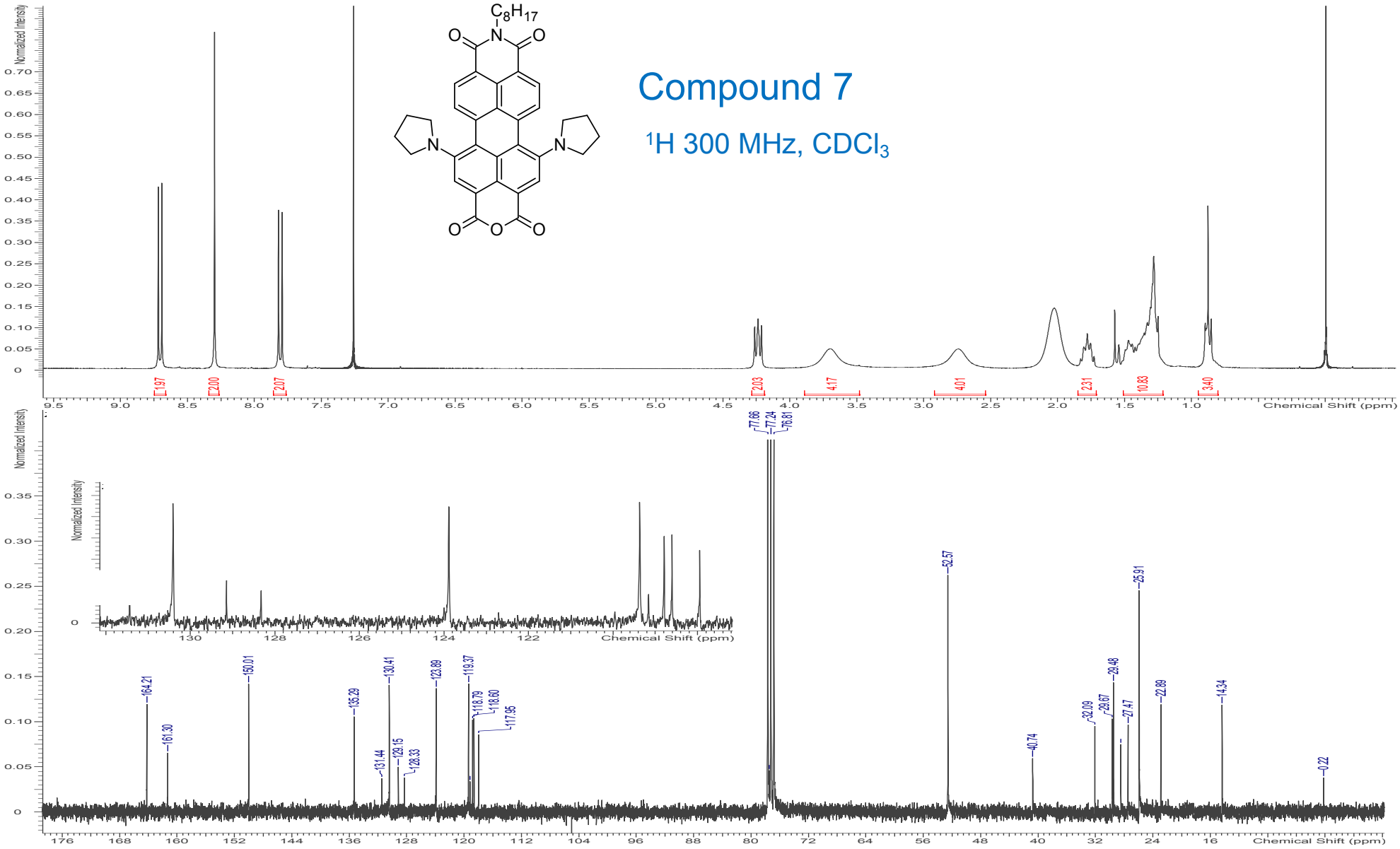
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Normalized Intensity
Chemical Shift (ppm)
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2.03
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4.01
2.31
10.83
3.40
77.66
77.24
76.81
52.57
25.91
164.21
161.30
150.01
135.29
131.44
130.41
129.15
128.33
122.89
119.37
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118.60
117.95
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32.09
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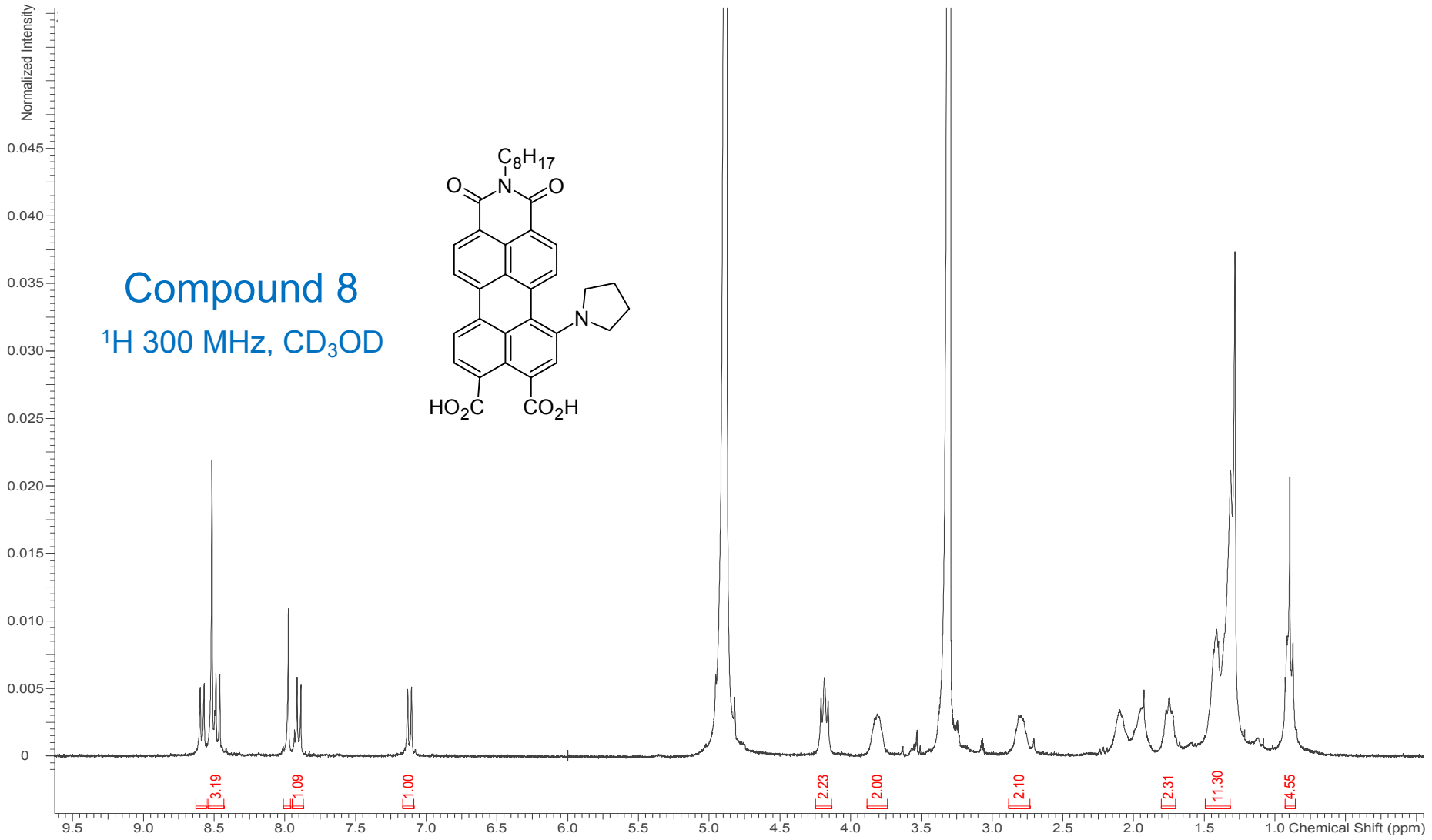
29.48
27.47
22.89
14.34
0.22


Compound 8
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C_8H_{17}
O
N
O
N
HO_2C
CO_2H
Normalized Intensity
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0.030
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0.020
0.015
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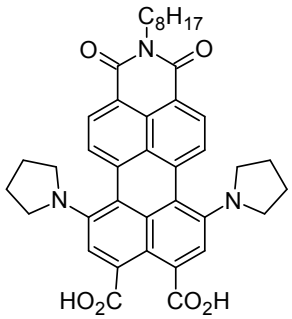
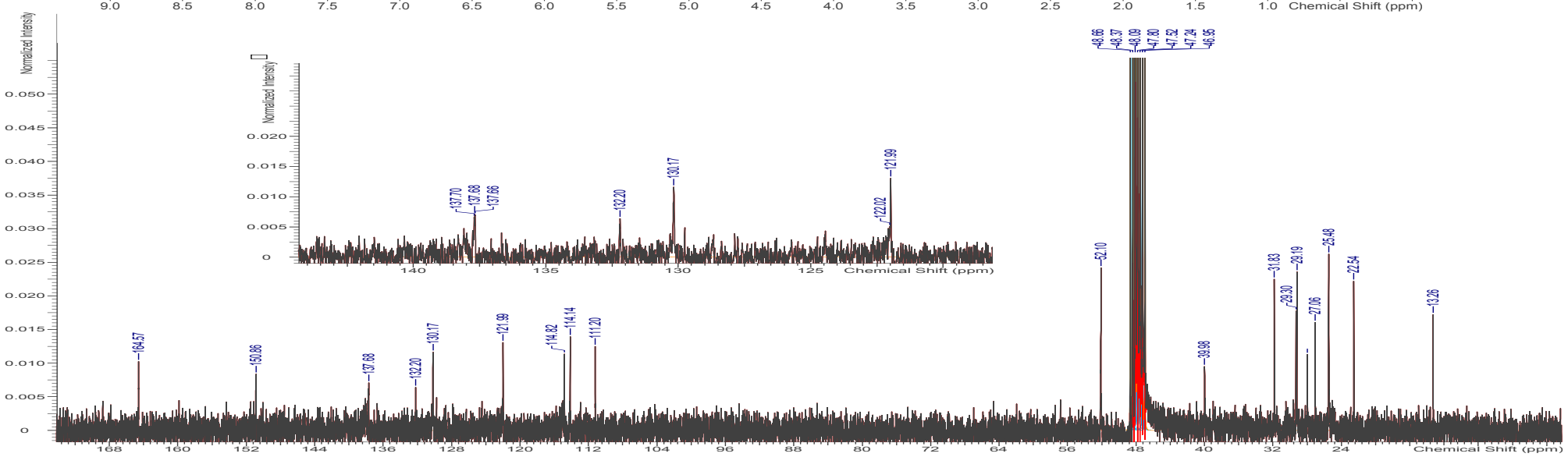
0.005
0
3.19
1.09
1.00
2.23
2.00
2.10
2.31
11.30
4.55
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 Chemical Shift (ppm)

Compound 9

^{1}H 300 MHz, CD_3OD





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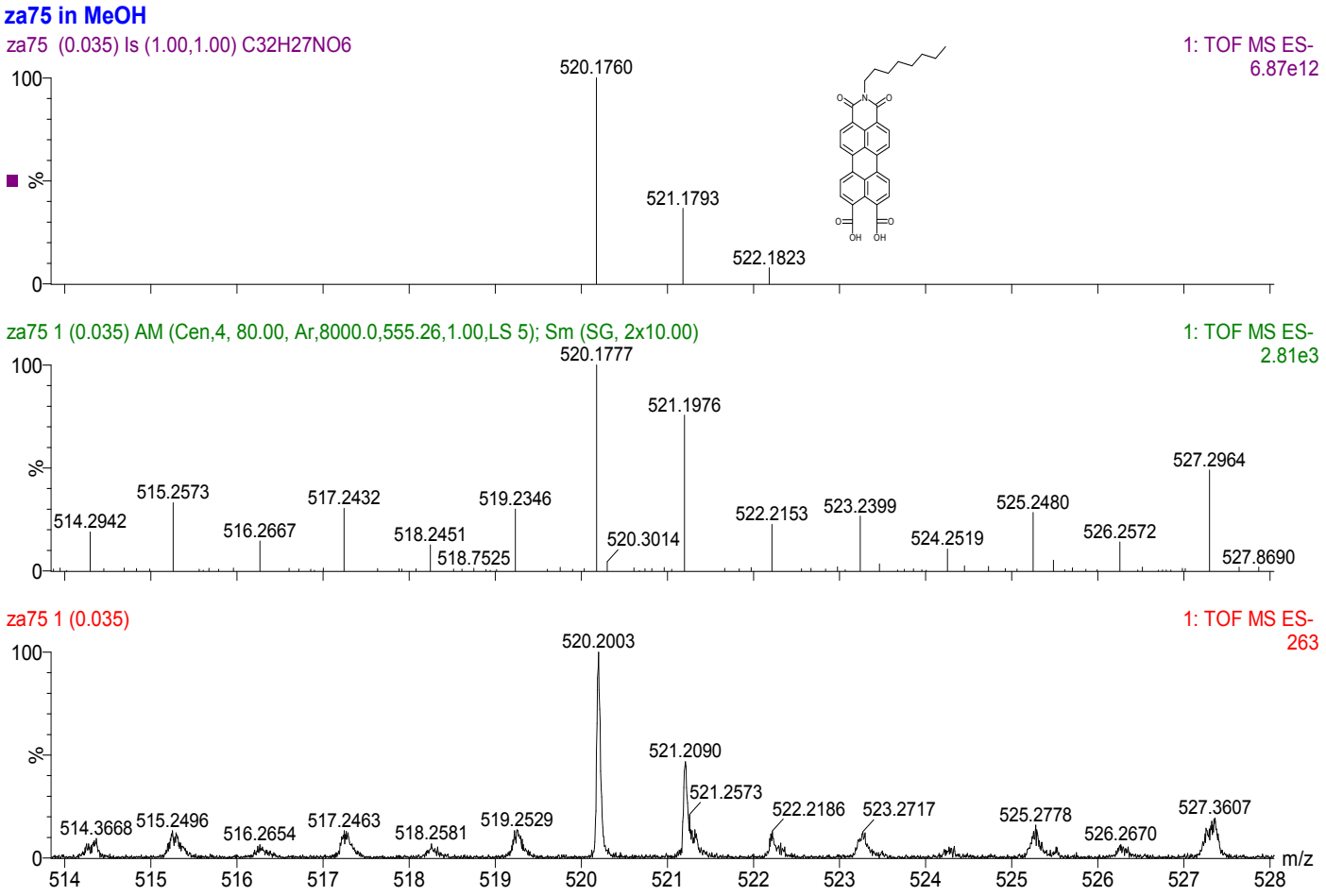
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100
%
0
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521.1793
522.1823
za75 1 (0.035) AM (Cen,4, 80.00, Ar,8000.0,555.26,1.00,LS 5); Sm (SG, 2x10.00)
1: TOF MS ES-
2.81e3
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523.2399
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za75 1 (0.035)
1: TOF MS ES-
263
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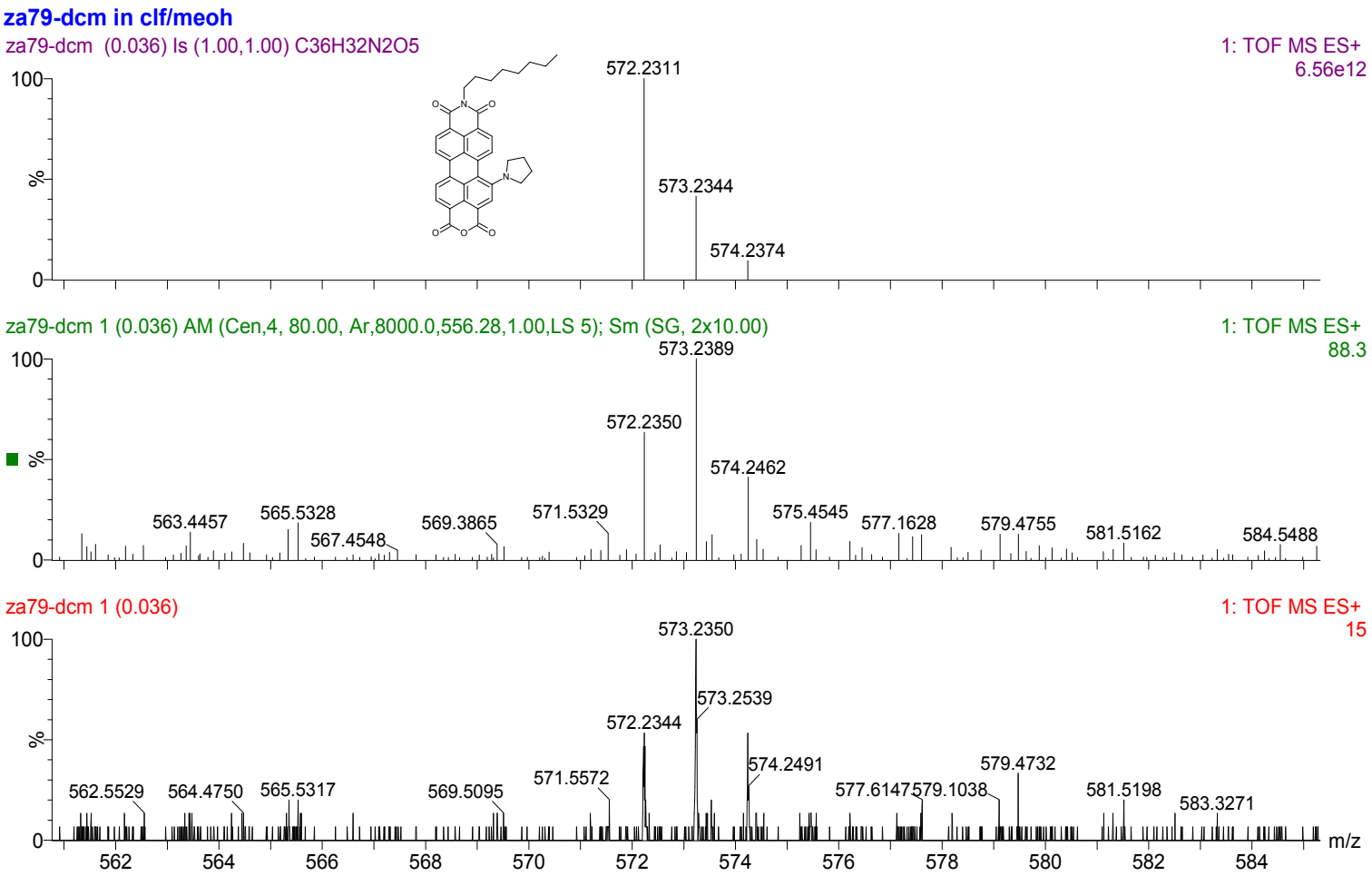
m/z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%
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573.2344
574.2374
za79-dcm 1 (0.036) AM (Cen,4, 80.00, Ar,8000.0,556.28,1.00,LS 5); Sm (SG, 2x10.00)
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569.3865
571.5329
575.4545
577.1628
579.4755
581.5162
584.5488
za79-dcm 1 (0.036)
1: TOF MS ES+
15
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573.2539
572.2344
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569.5095
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579.4732
581.5198
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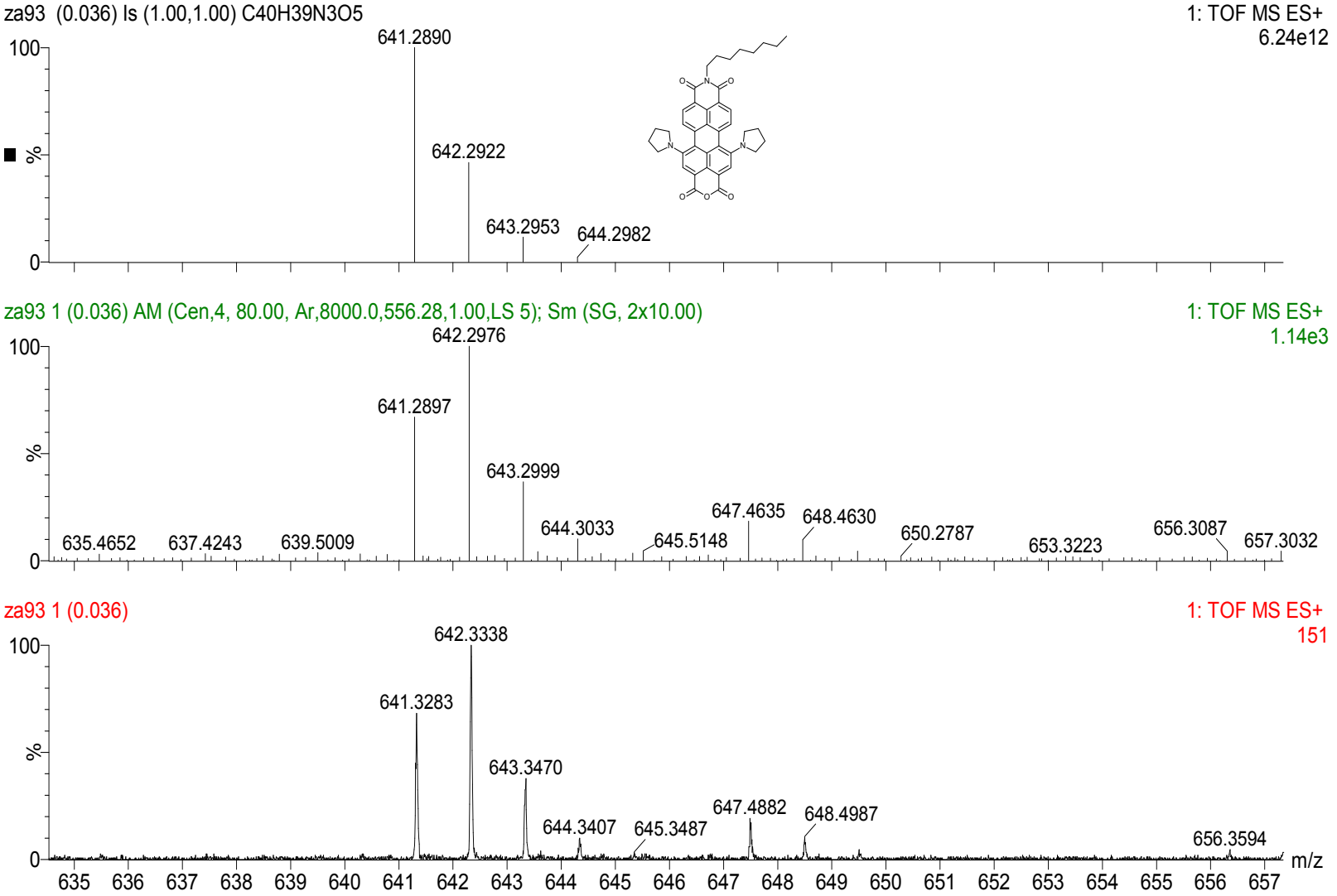
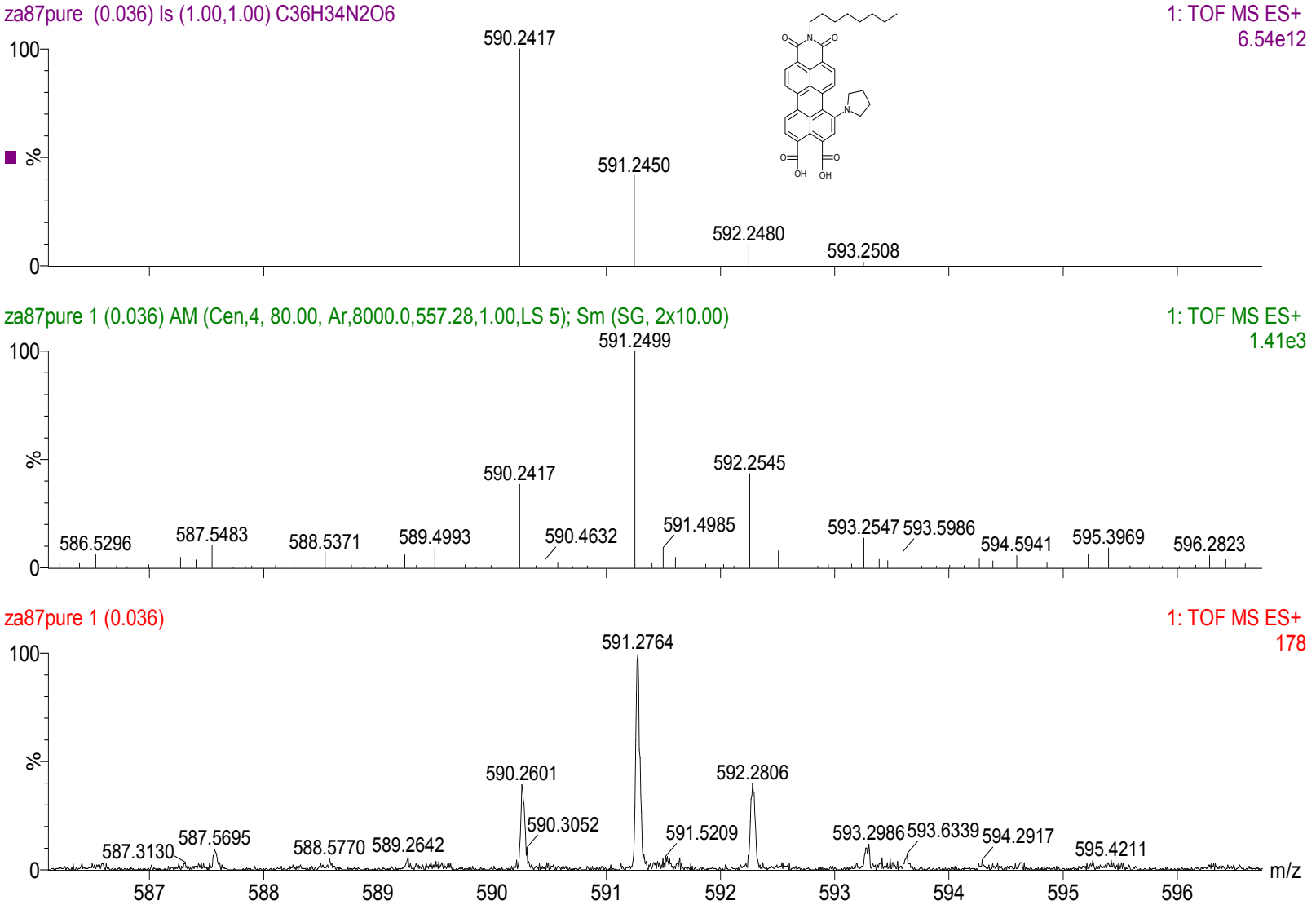
576
578
580
582
584
m/z

za93 in clf/meoh



za87pure in clf/meoh



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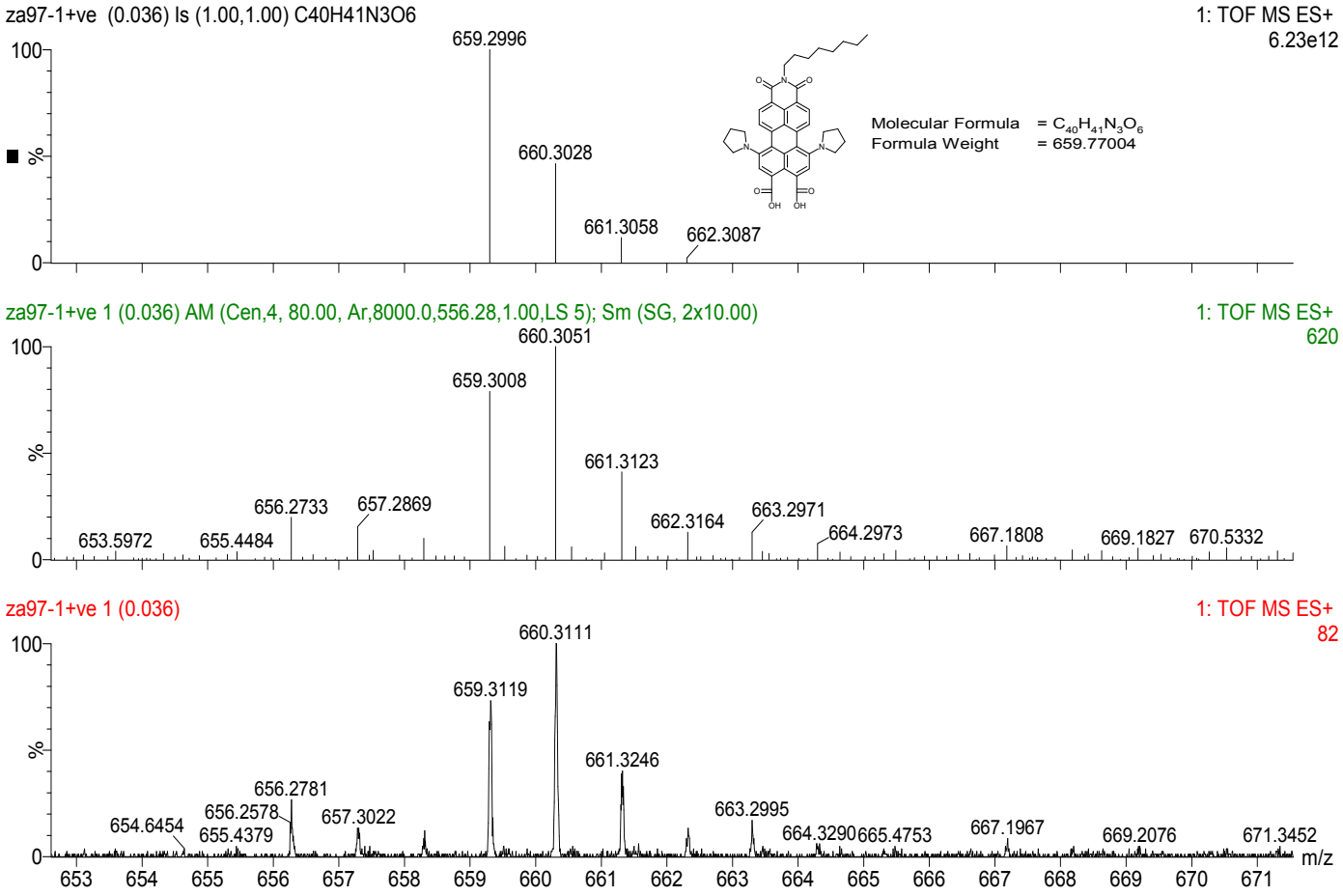

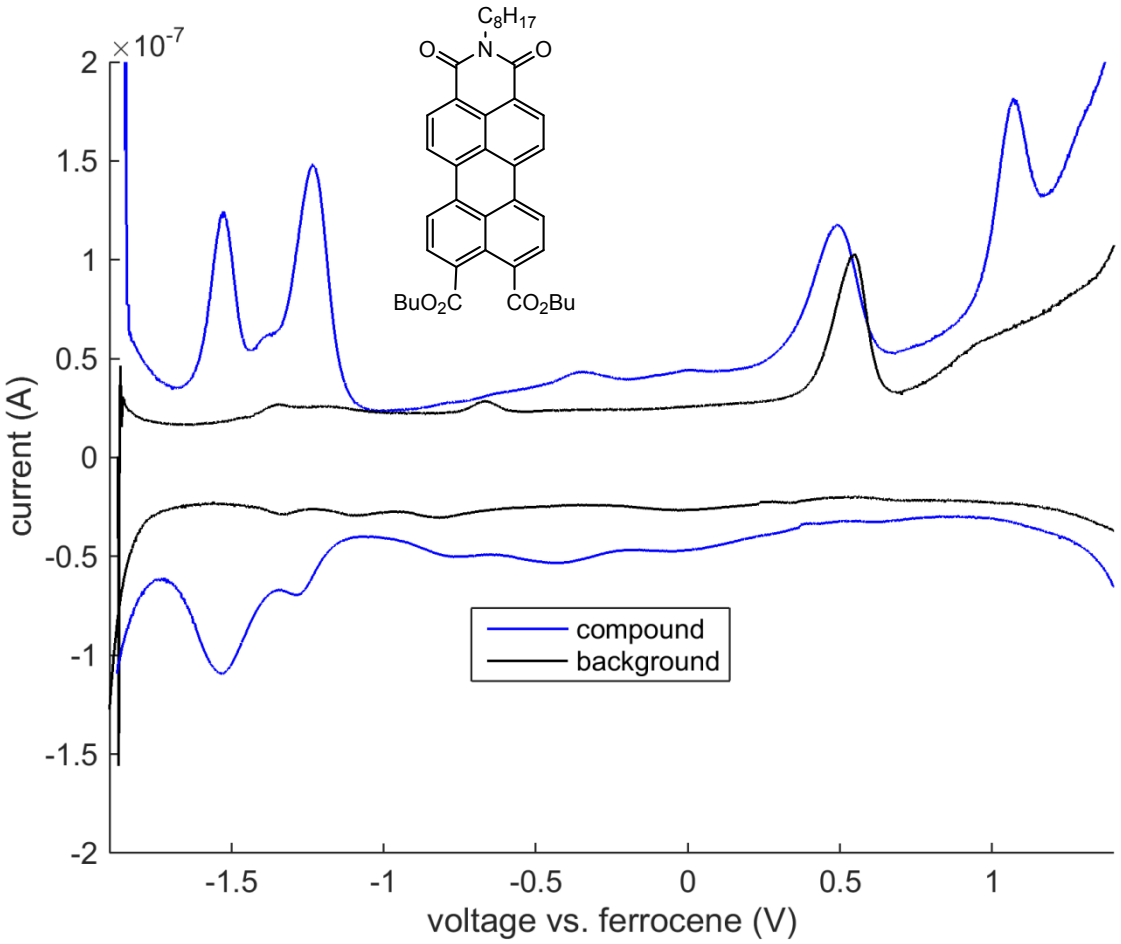

Figure S1. *DPV Voltammogram of compound* ***1*** *vs ferrocene*

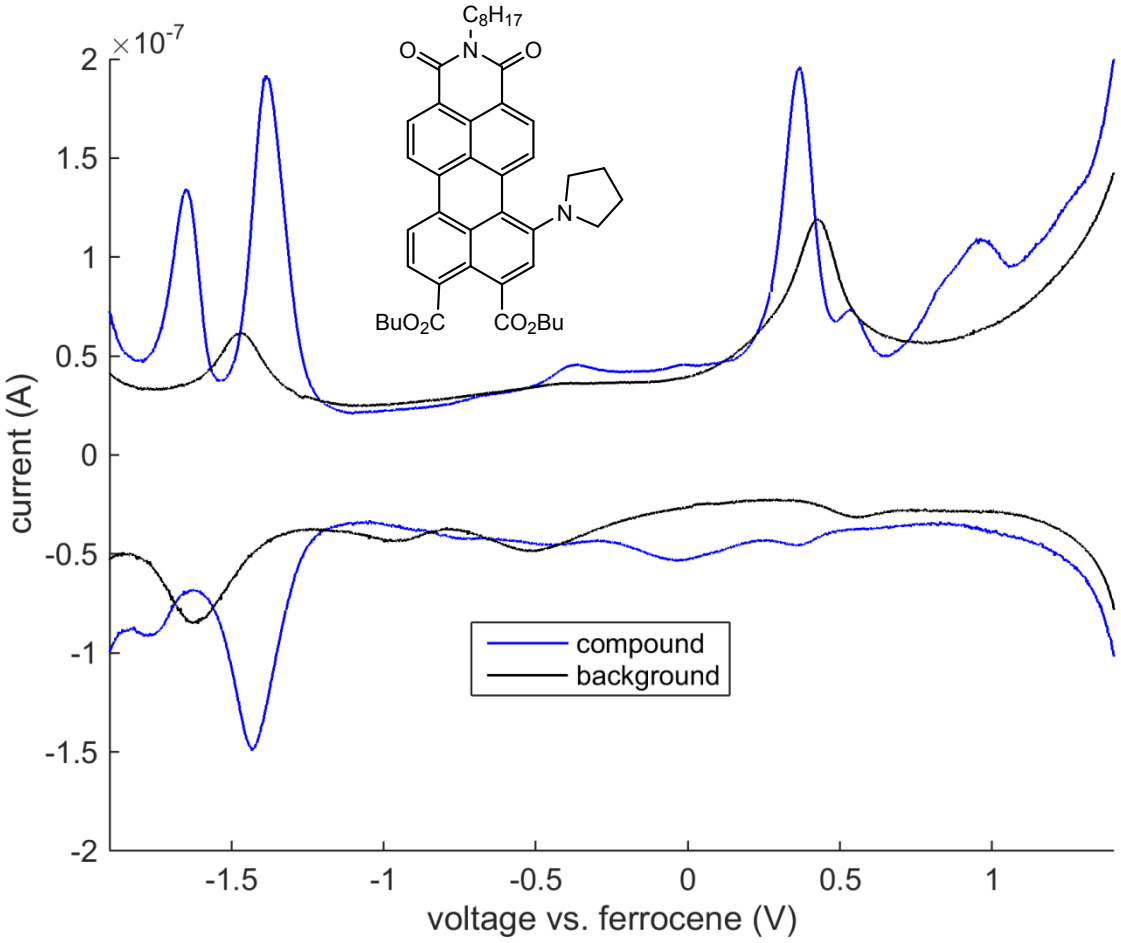

Figure S2. *DPV Voltammogram of compound* ***2*** *vs ferrocene*

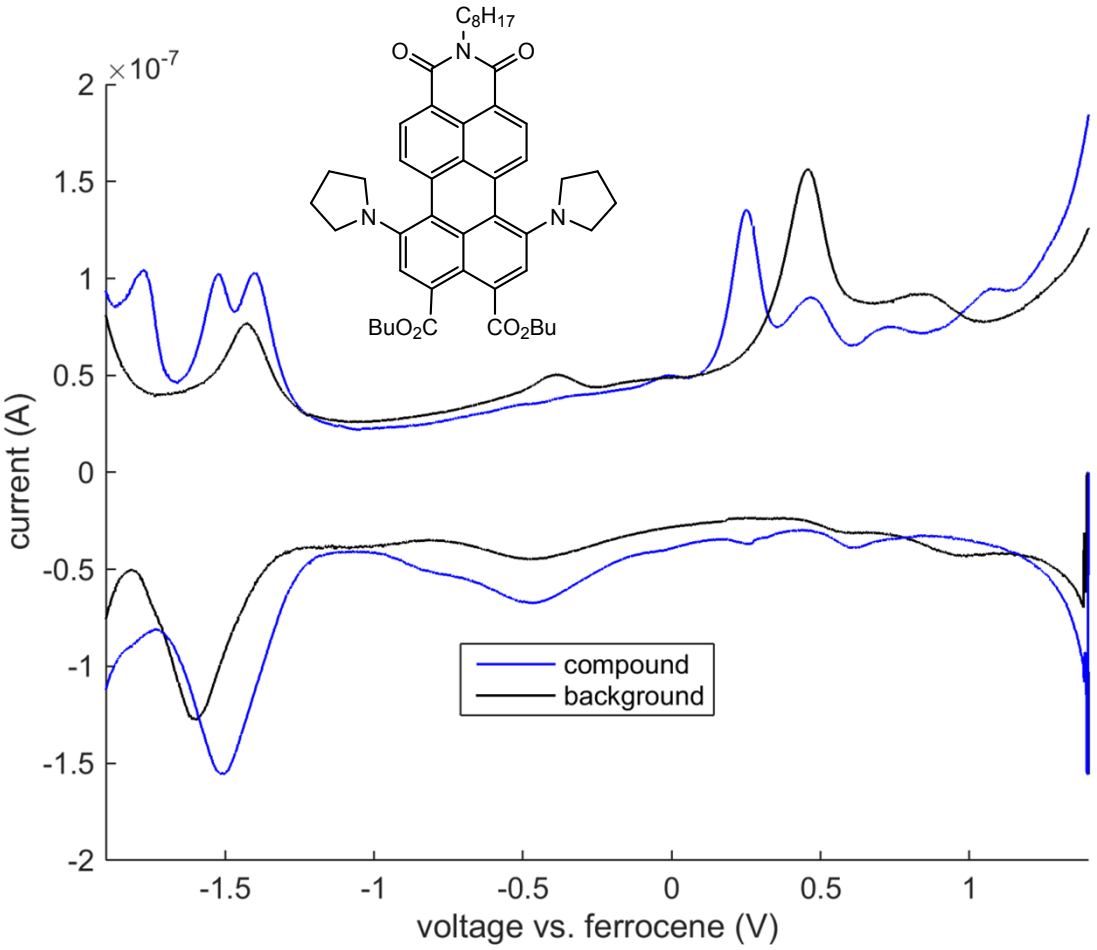

Figure S3. *DPV Voltammogram of compound* ***3*** *vs ferrocene*

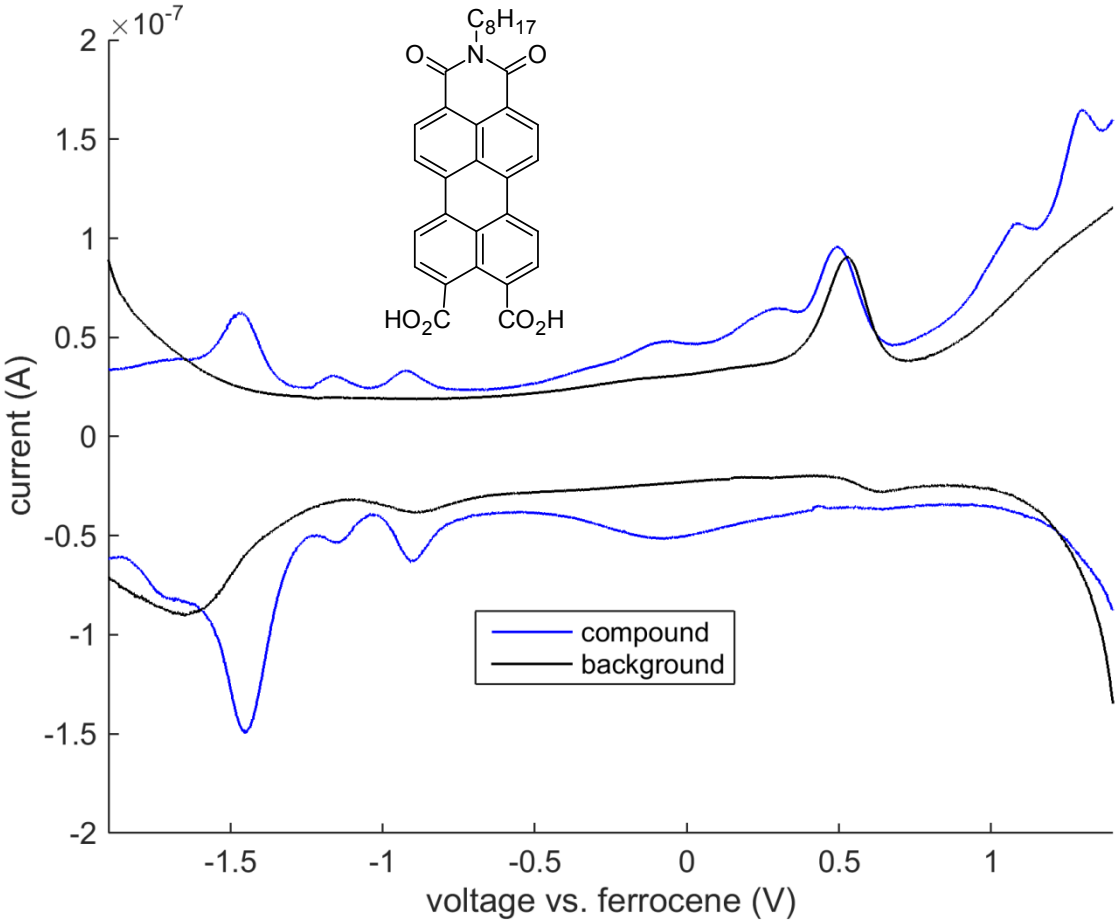

Figure S4. *DPV Voltammogram of compound* ***5*** *vs ferrocene*

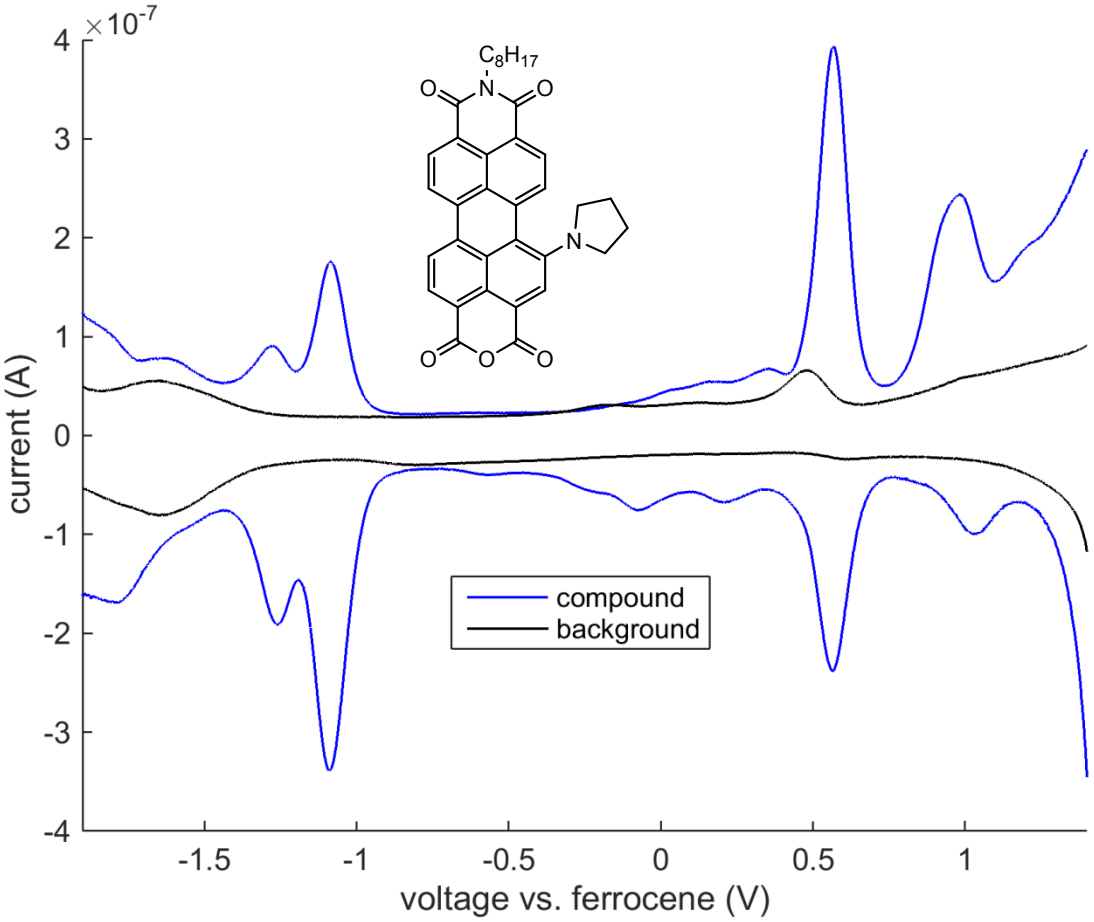

Figure S5. *DPV Voltammogram of compound* ***6*** *vs ferrocene*

Computational energies

Table S1 *Energies E (in eV) of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the molecular models of compounds* ***1–3*** [a] *and the corresponding HOMO–LUMO gap energies* $E_{(L-H)}$ *calculated at various levels of density functional theory (DFT).*

	1			**2**			**3**		
Functional/ basis set	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**	$\Delta E_{(L-H)}$ **(eV)**	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**	$\Delta E_{(L-H)}$ **(eV)**	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**	$\Delta E_{(L-H)}$ **(eV)**
B3LYP/									
6-31G(d)	-5.7359	-3.0752	2.66	-5.2039	-2.7380	2.47	-4.9316	-2.4665	2.47
6-311+G(d,p)	-6.0671	-3.4551	2.61	-5.5142	-3.0980	2.42	-5.2429	-2.8180	2.42
6-311++G(d,p)	-6.0668	-3.4545	2.61	-5.5139	-3.0978	2.42	-5.2426	-2.8178	2.42
M062X/									
6-31G(d)	-6.8810	-2.3780	4.50	-6.3082	-2.0556	4.25	-6.0290	-1.7894	4.24
6-311++G(d,p)	-7.1452	-2.7056	4.44	-6.5460	-2.3614	4.18	-6.2671	-2.0833	4.18

[a]In the models of **1**–**3** the octyl- and butyl chains have been replaced by the CH_3 groups.

Table S2 *Total energies E_{TOT} (in Hartree) of the molecular models of compounds **1–3**[a] and the relative energies (in kJ/mol) between the 1,7- and 7,12-substituted isomers calculated at various levels of density functional theory (DFT).*

	1 *neutral*	**1** *radical anion*	**2** *neutral*	**2** *radical anion*	**3** *1, 7-substituted*	**3** *7, 12-substituted*	**3** *7, 12-substituted-1, 7-substituted*
Functional/ basis set	E_{TOT} **(Hartree)**						**Δ*E*** **(kJ/mol)**
B3LYP/							
6-31G(d)	-1545.3166772	-1545.3886086	-1756.7009631	-1756.7641427	-1968.0837178	-1968.0828523	+2.27
6-311+G(d,p)	-1545.7127660	-1545.8005522	-1757.1509143	-1757.2291864	-1968.5868644	-1968.5861952	+1.76
6-311++G(d,p)	-1545.7130325	-1545.8008173	-1757.1512723	-1757.2295545	-1968.5873005	-1968.5866379	+1.74
M062X/							
6-31G(d)	-1544.7220569	-1544.7951974	-1756.0187827	-1756.0829605	-1967.3141574	-1967.3133058	+2.24
6-311++G(d,p)	-1545.1285063	-1545.2150818	-1756.4815679	-1756.5583731	-1967.8028771	-1967.8319400	-76.3 = the 7,12-substituted model is thermo-dynamical-ly more stable than the 1,7-substituted model

[a]In the models of **1**–**3** the octyl- and butyl chains have been replaced by the CH_3 groups. No imaginary frequencies were found after geometry optimization at the B3LYP/6-31G(d) level of theory.

Computational atomic charges

Molecular structures have been visualized using the ChemCraft 1.7 program.[1]

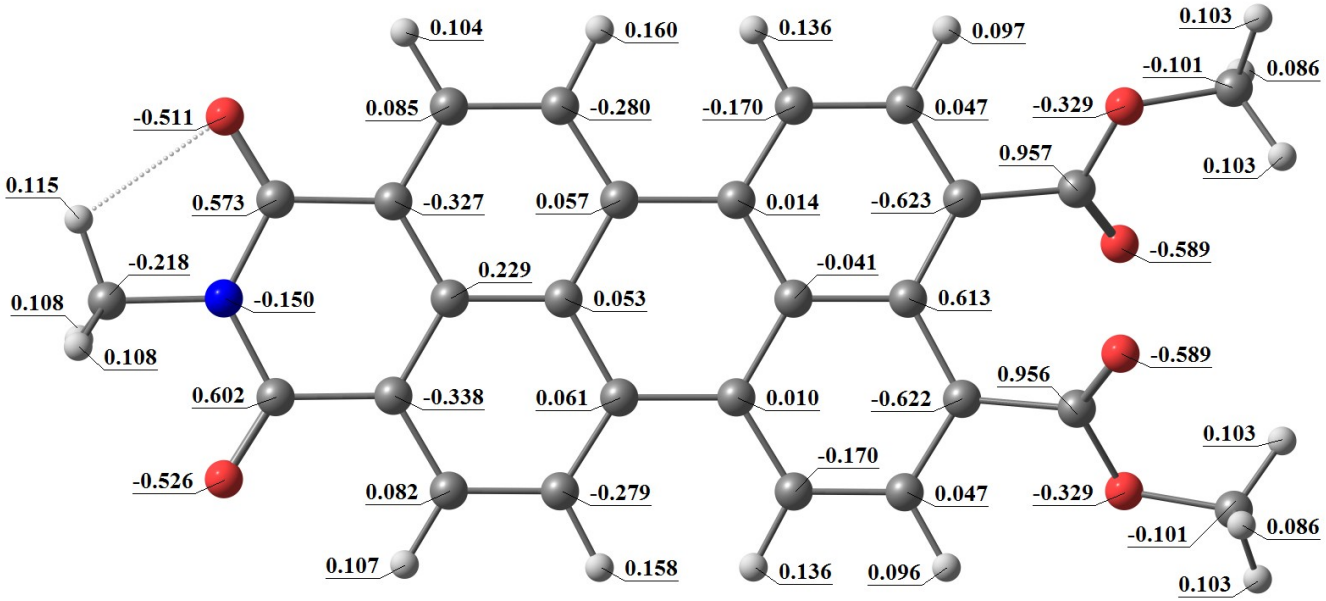

Figure S6*. Atomic charges of model* ***1*** *(neutral) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

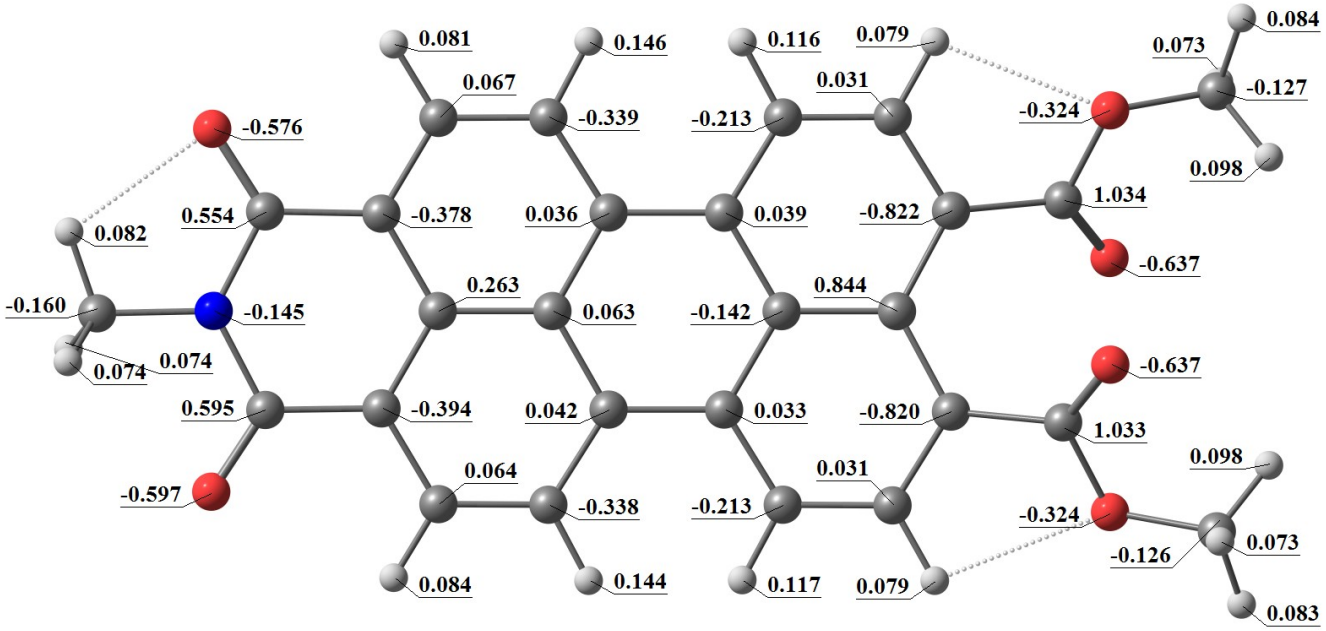

Figure S7*. Atomic charges of model* ***1*** *(radical anion) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

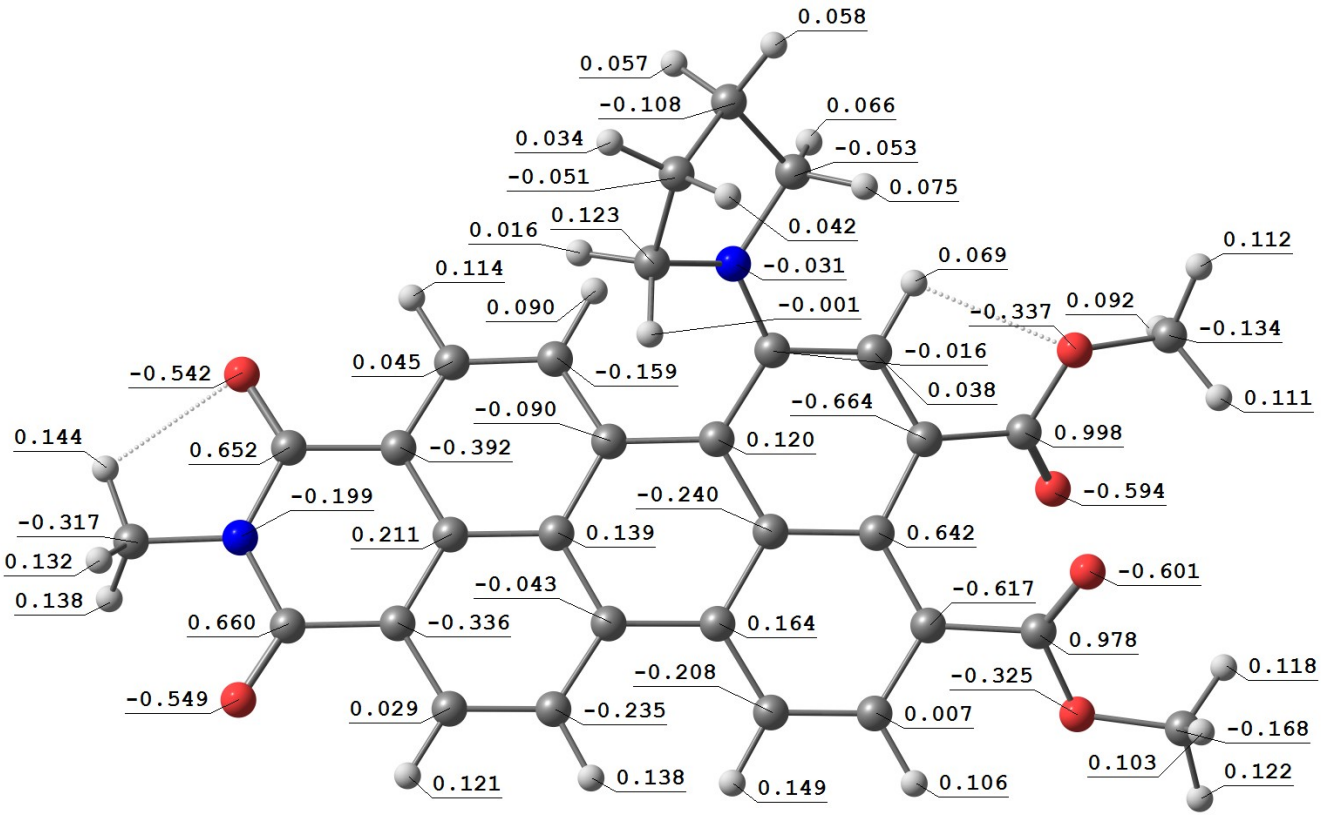

Figure S8. *Atomic charges of model* ***2*** *(neutral) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

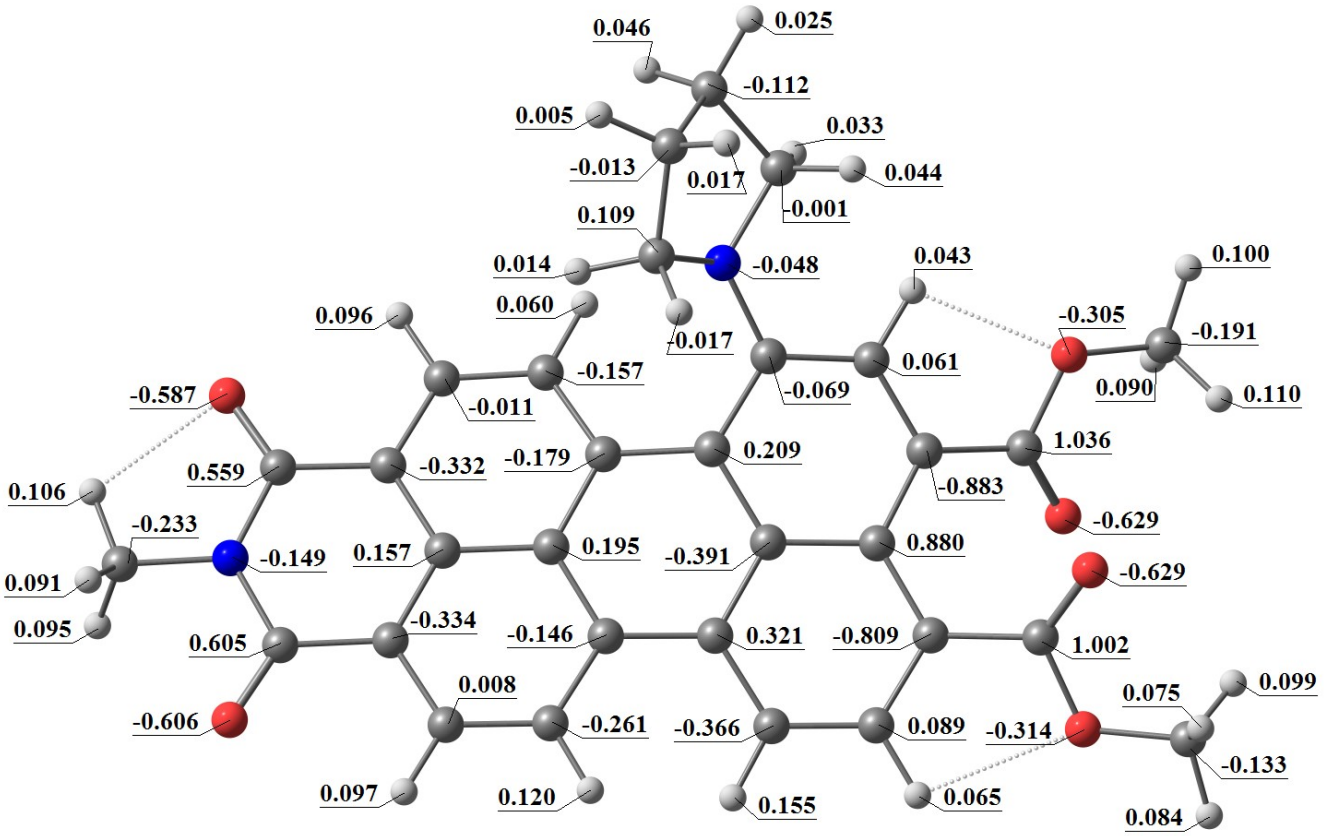

Figure S9. *Atomic charges of model* ***2*** *(radical anion) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

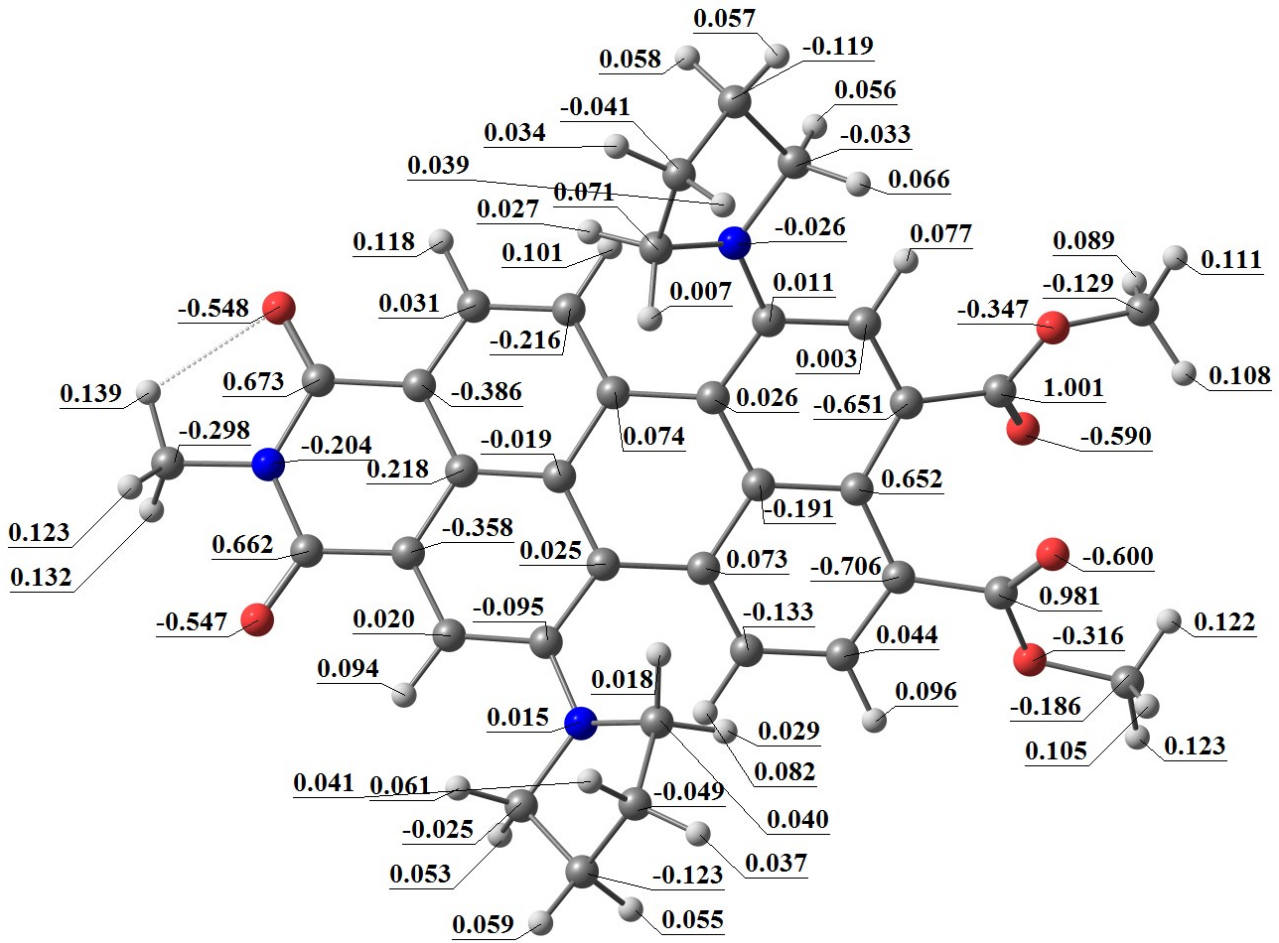

Figure S10. *Atomic charges of model* ***3*** *(neutral, 1,7-substituted isomer) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

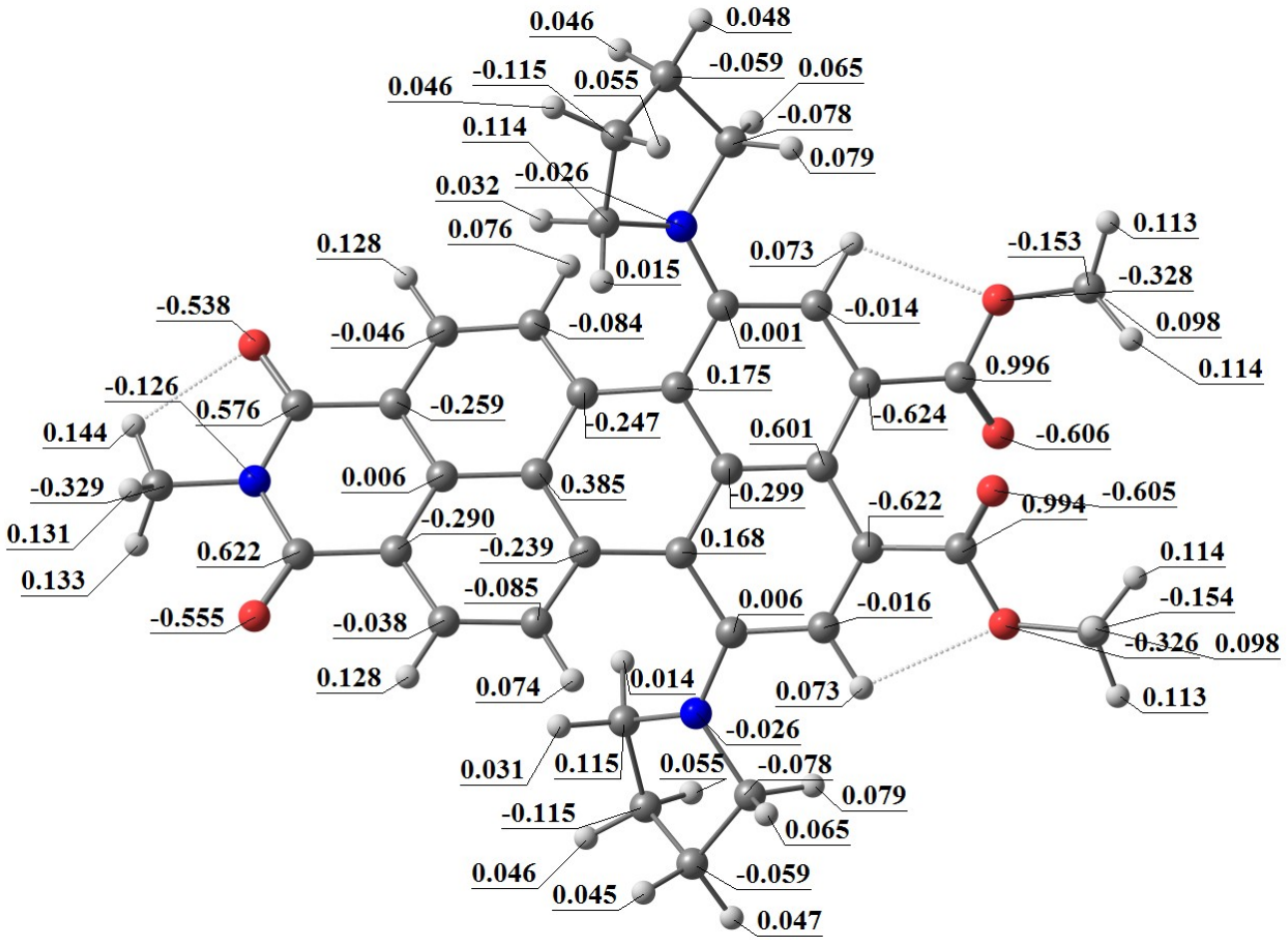

Figure S11. *Atomic charges of model* ***3*** *(neutral, 7,12-substituted isomer) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

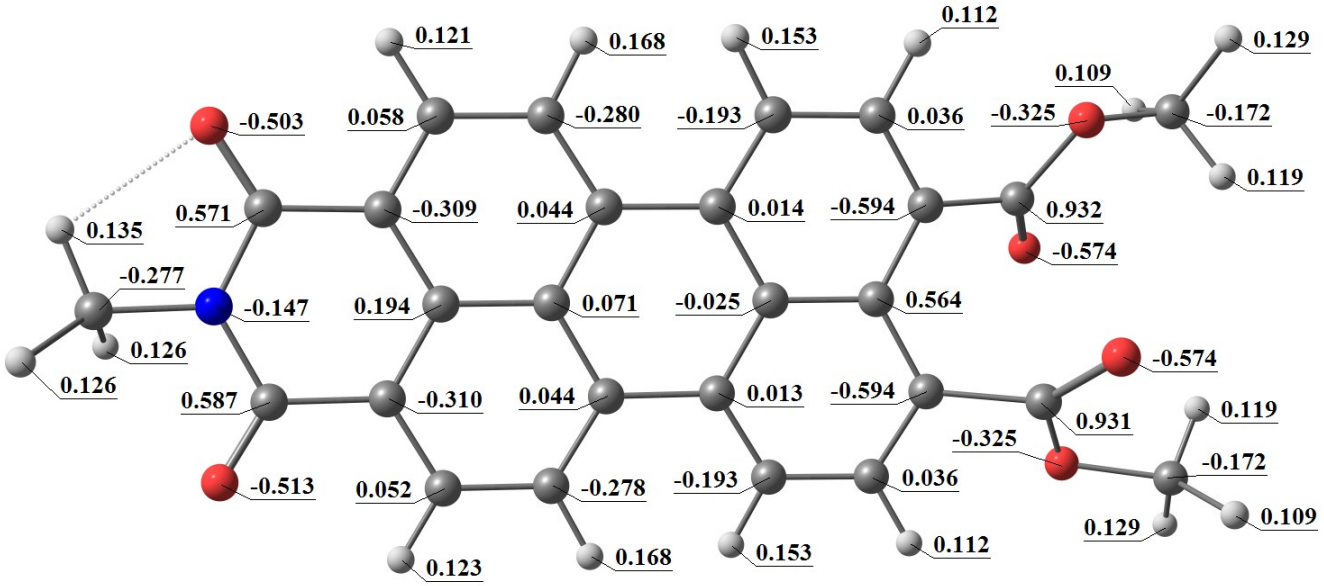

Figure S12. *Atomic charges of model* ***1*** *(neutral) computed with the Merz–Kollman (M-K) method at the M062X/6-311++G(d,p)// M062X/6-311++G(d,p) level of theory.*

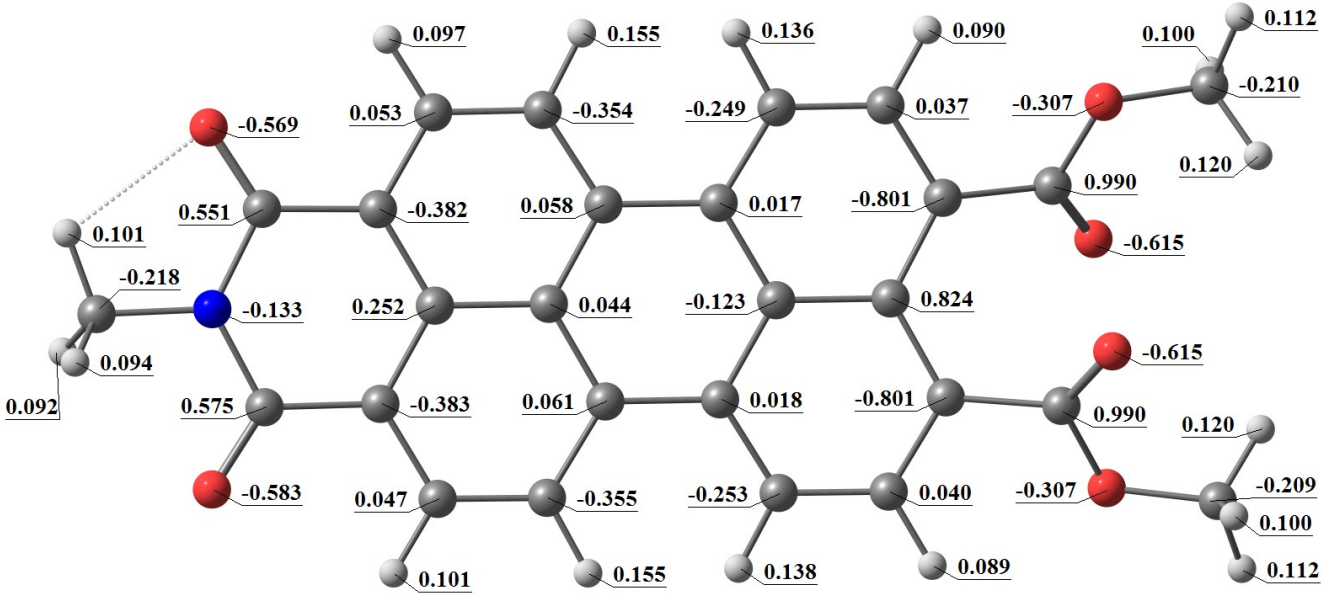

Figure S13. *Atomic charges of model* ***1*** *(radical anion) computed with the Merz–Kollman (M-K) method at the M062X/6-311++G(d,p)// M062X/6-311++G(d,p) level of theory.*

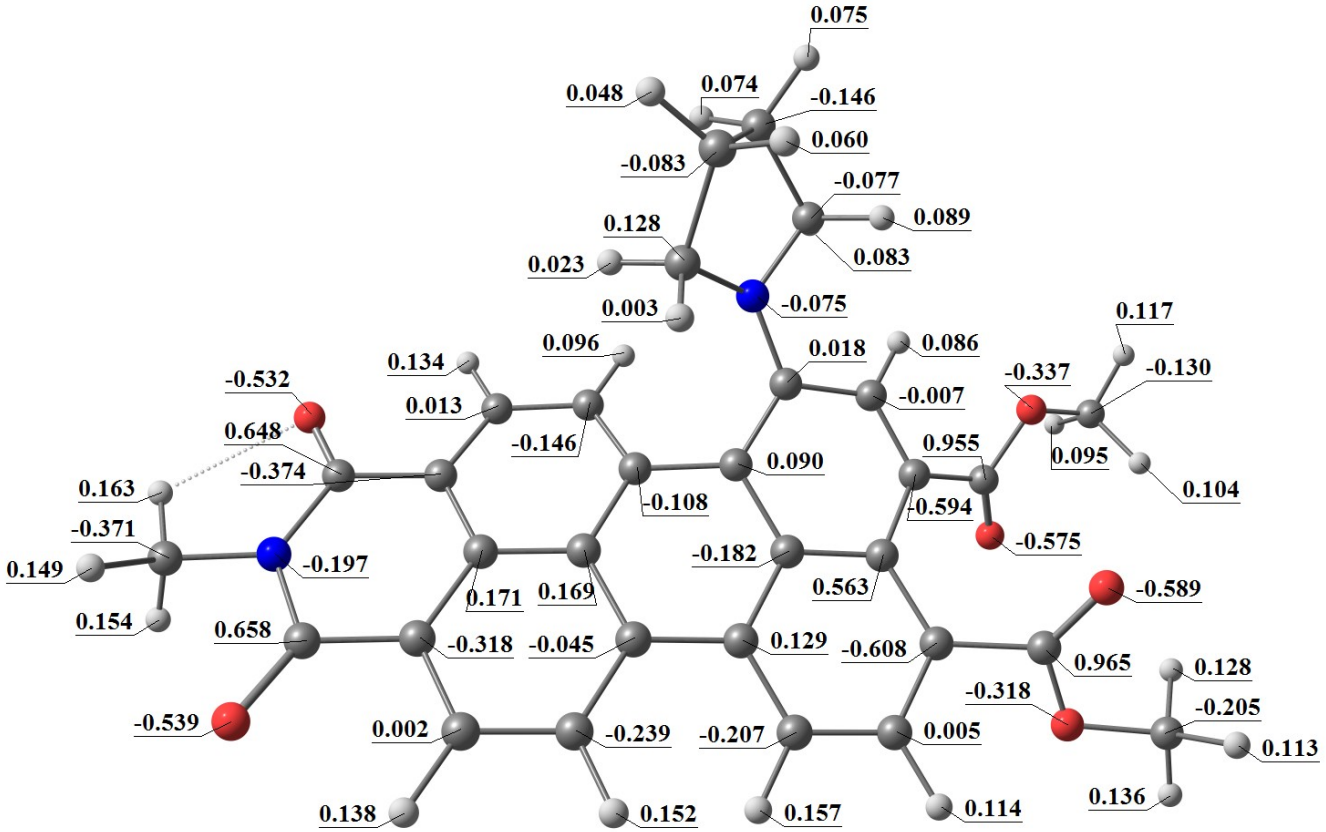

Figure S14. *Atomic charges of model* ***2*** *(neutral) computed with the Merz–Kollman (M-K) method at the M062X/6-311++G(d,p)// M062X/6-311++G(d,p) level of theory.*

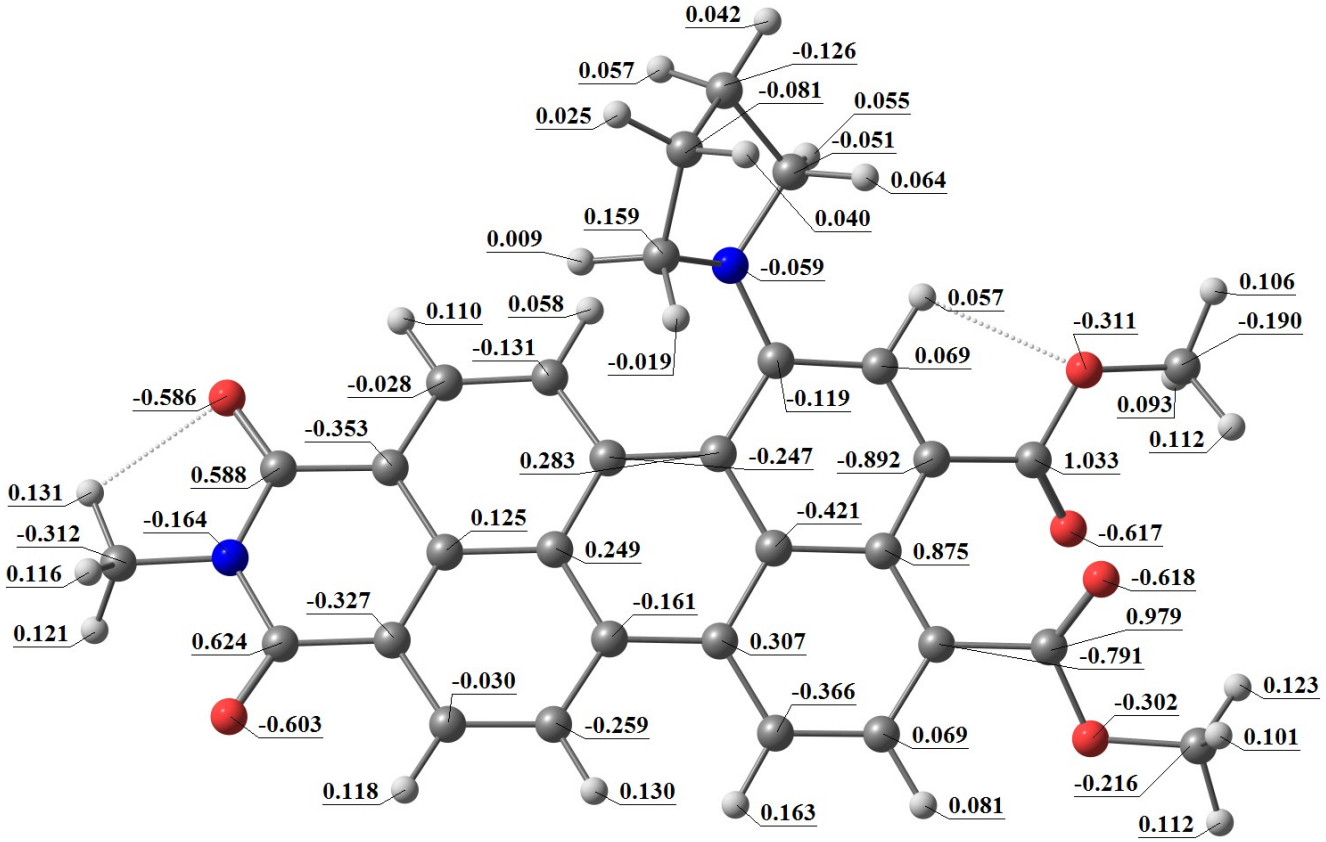

Figure S15. *Atomic charges of model* ***2*** *(radical anion) computed with the Merz–Kollman (M-K) method at the M062X/6-311++G(d,p)// M062X/6-311++G(d,p) level of theory.*

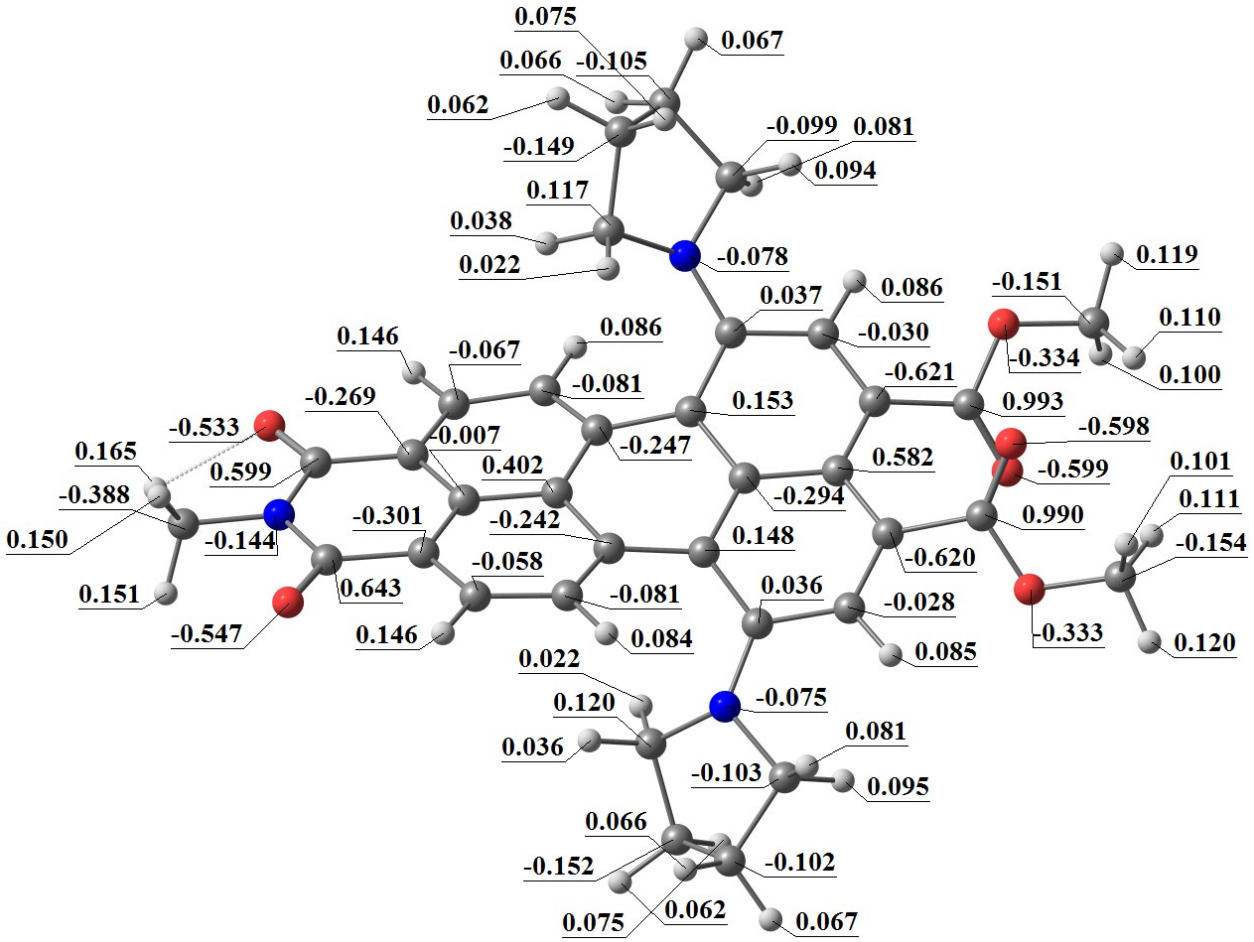

Figure S16. *Atomic charges of model* ***3*** *(neutral, 1,7-substituted isomer) computed with the Merz–Kollman (M-K) method at the M062X/6-311++G(d,p)// M062X/6-311++G(d,p) level of theory.*

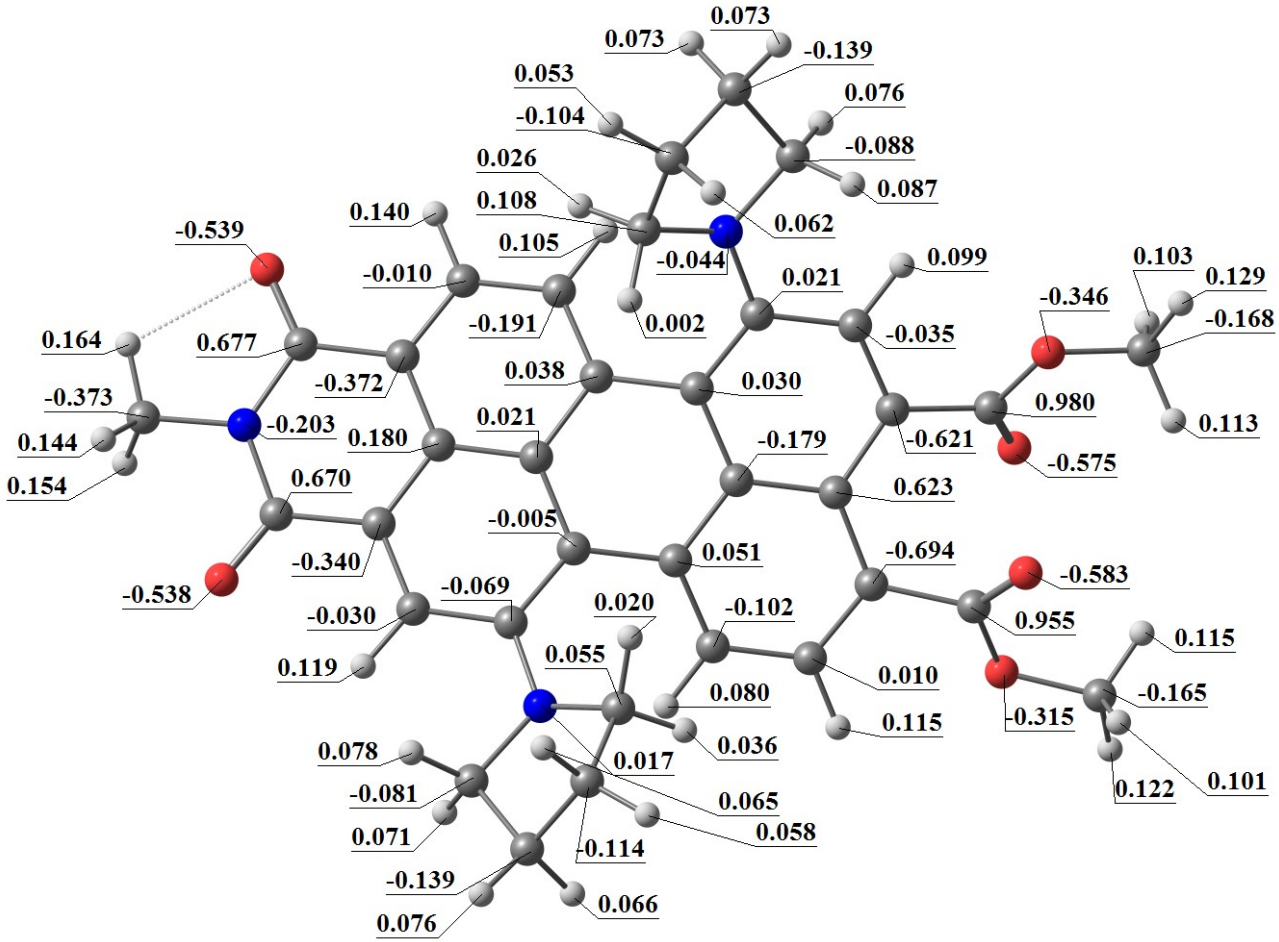

Figure S17*. Atomic charges of model* ***3*** *(neutral, 7,12-substituted isomer) computed with the Merz–Kollman (M-K) method at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

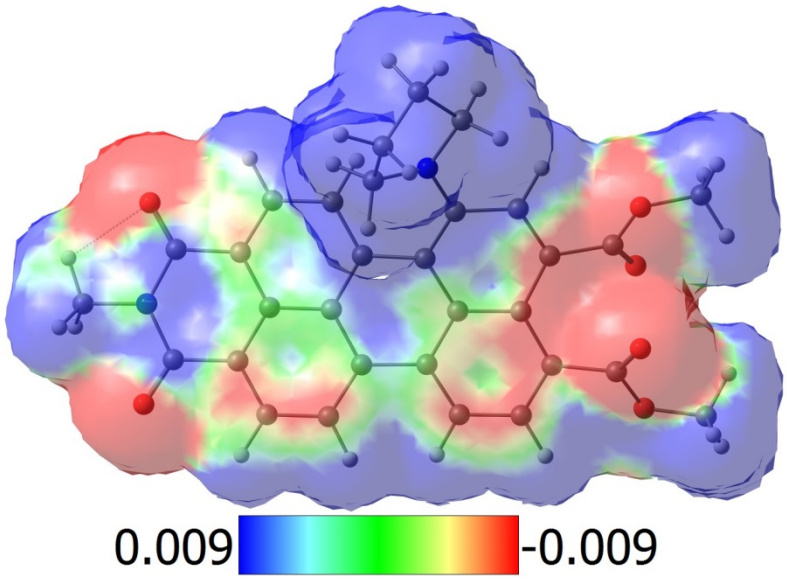

Figure S18. *Electrostatic potential surface of model* ***2*** *(neutral, substitution at 7 position) showing the electronegative areas in red. Electrostatic potential map tells which areas (red) are more prone to an electrophilic attack. Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

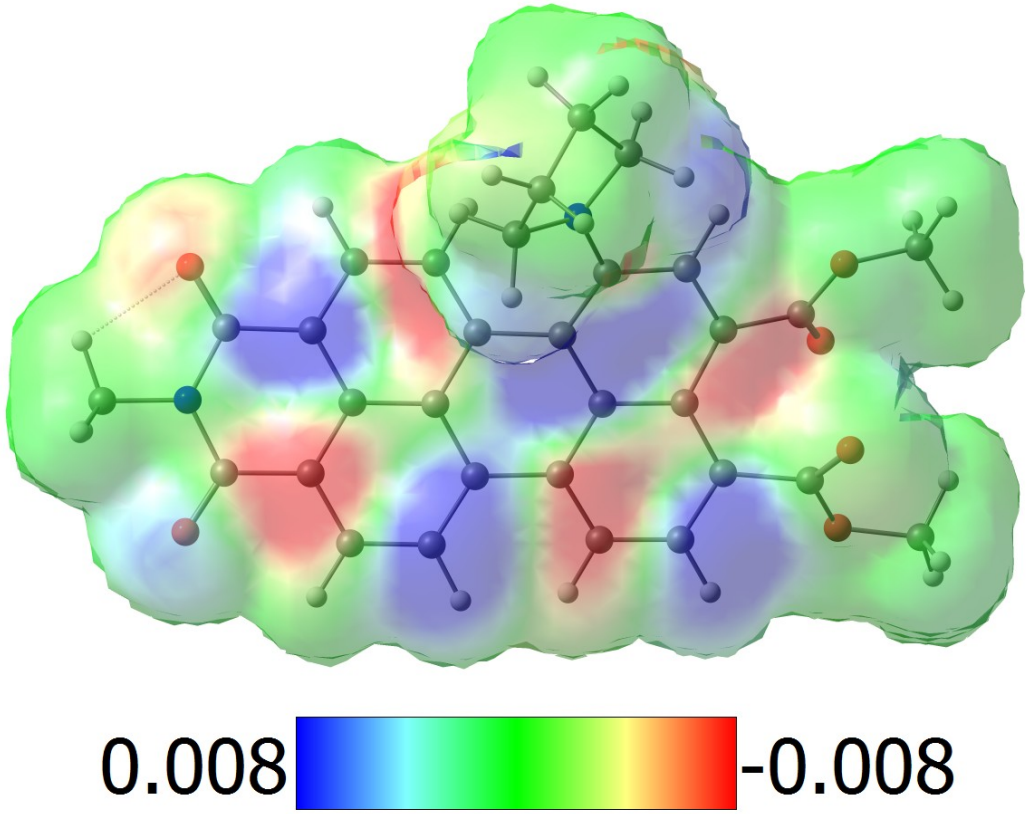

Figure S19. *Electron density together with the HOMO orbital of model* ***2*** *(neutral, substitution at 7 position) showing the positions prone to an electrophilic attack. Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

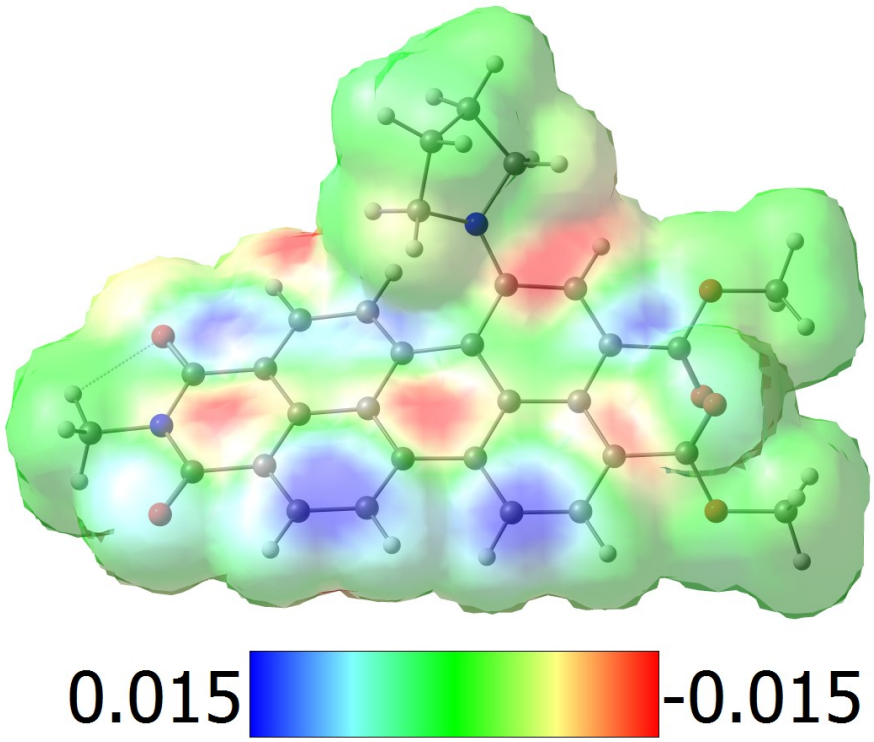

Figure S20. *Electron density together with the LUMO orbital of model* ***2*** *(neutral, substitution at 7 position) showing the the positions prone to a nucleophilic attack. These areas may accept electrons due to an empty orbital. Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

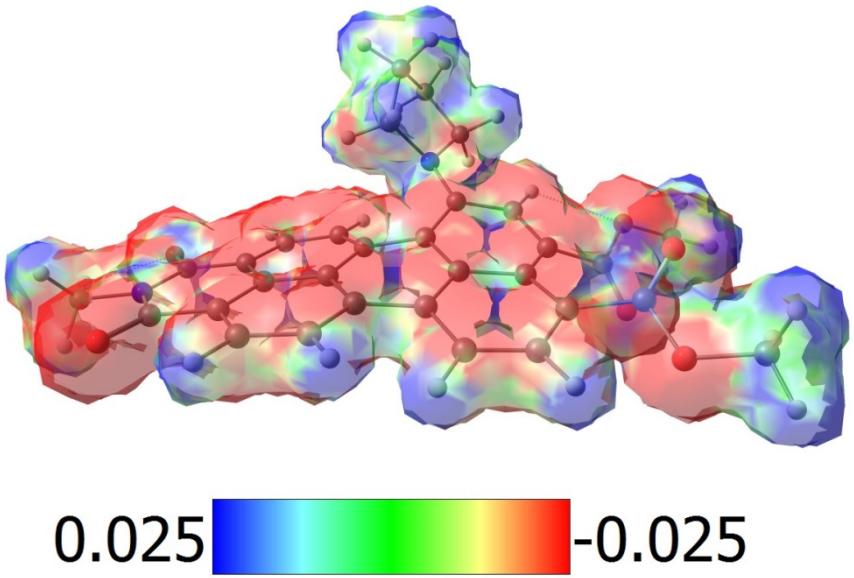

Figure S21. *Electrostatic potential surface of model* ***2*** *(radical anion, substitution at 7 position) showing the electronegative areas in red. Electrostatic potential map tells which areas (red) are more prone to an electrophilic attack. Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

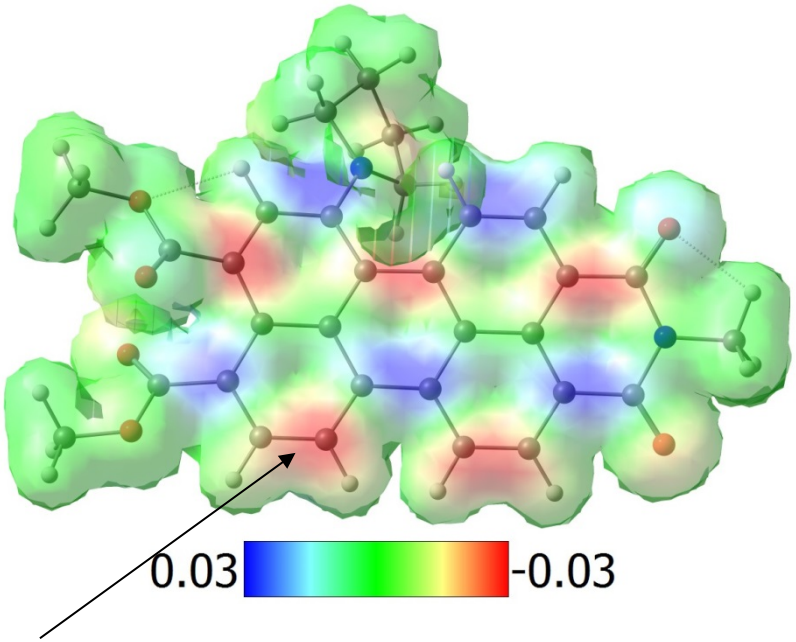

Figure S22. *Electron density map and the HOMO of the model* ***2*** *(radical anion, substitution at 7 position) showing the positions prone to an electrophilic attack. The arrow indicates the 12-position.Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.*

References for Supporting Information and for the Figure 1 inside the main article.

1. http://www.chemcraftprog.com