Supporting information

A straightforward access to new amides of the melanin precursor 5,6-dihydroxyindole-2-carboxylic acid and characterization of the properties of the pigments thereof

Table of contents

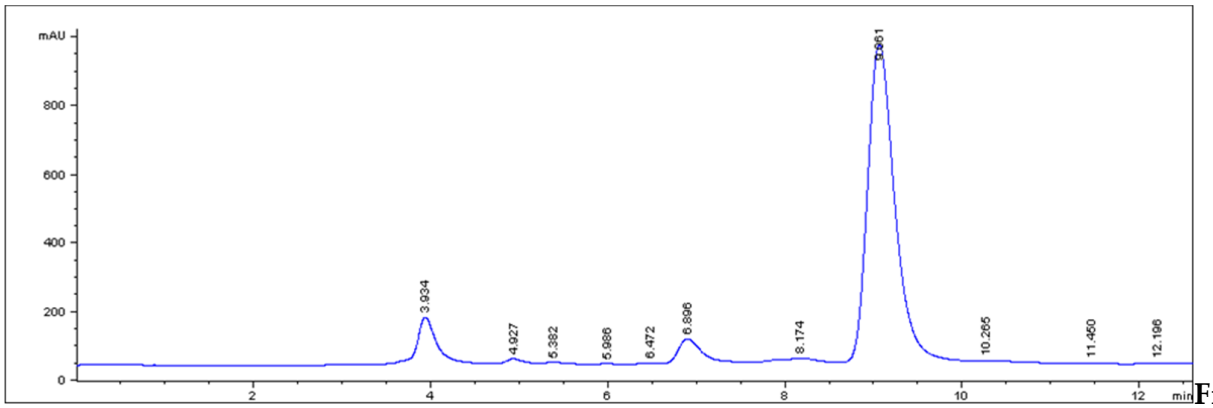

Figure S1. HPLC profile of the amidation reaction of DAICA at 10 min after addition of HATU (λ = 300 nm).

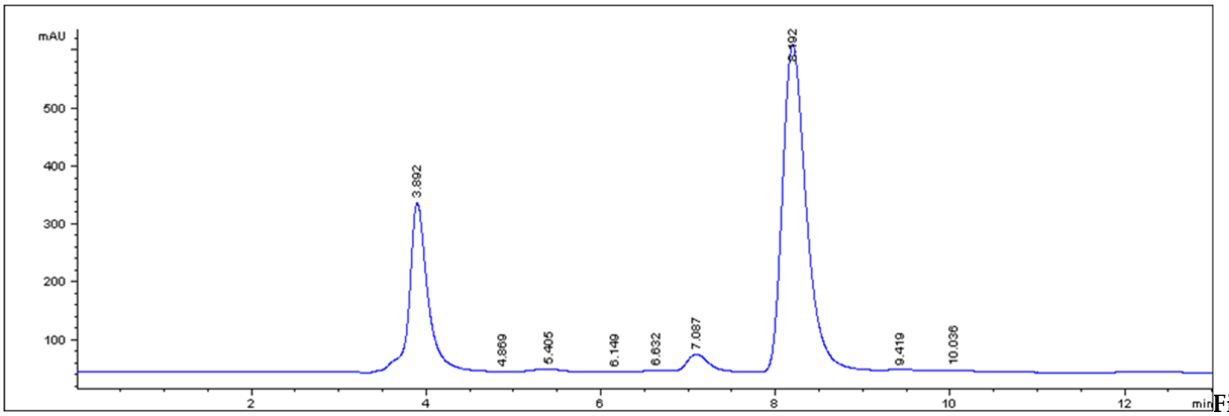

Figure S2. Chromatogram of the course of the amidation reaction at 5 minutes after addition of 1-butanamine (λ = 300 nm).

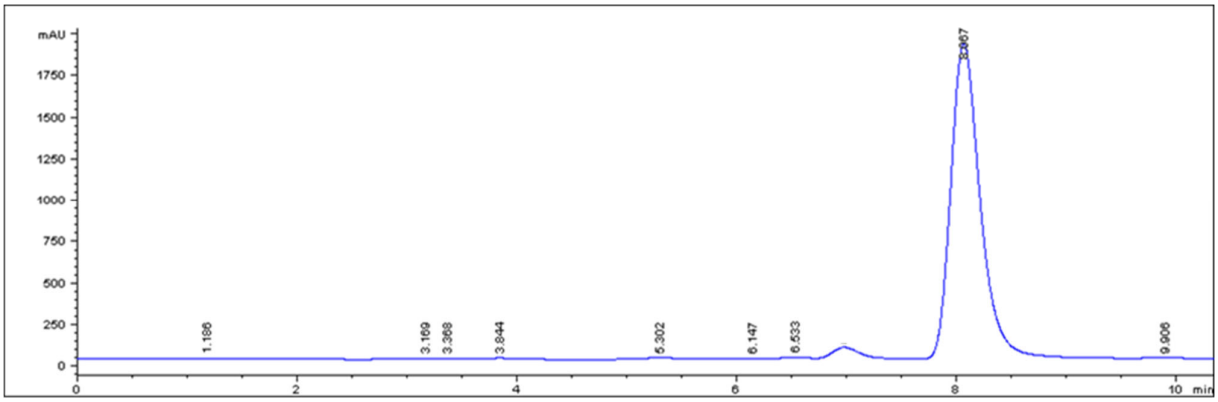

Figure S3. HPLC profile of DAICA butanamide after purification (λ = 300 nm).

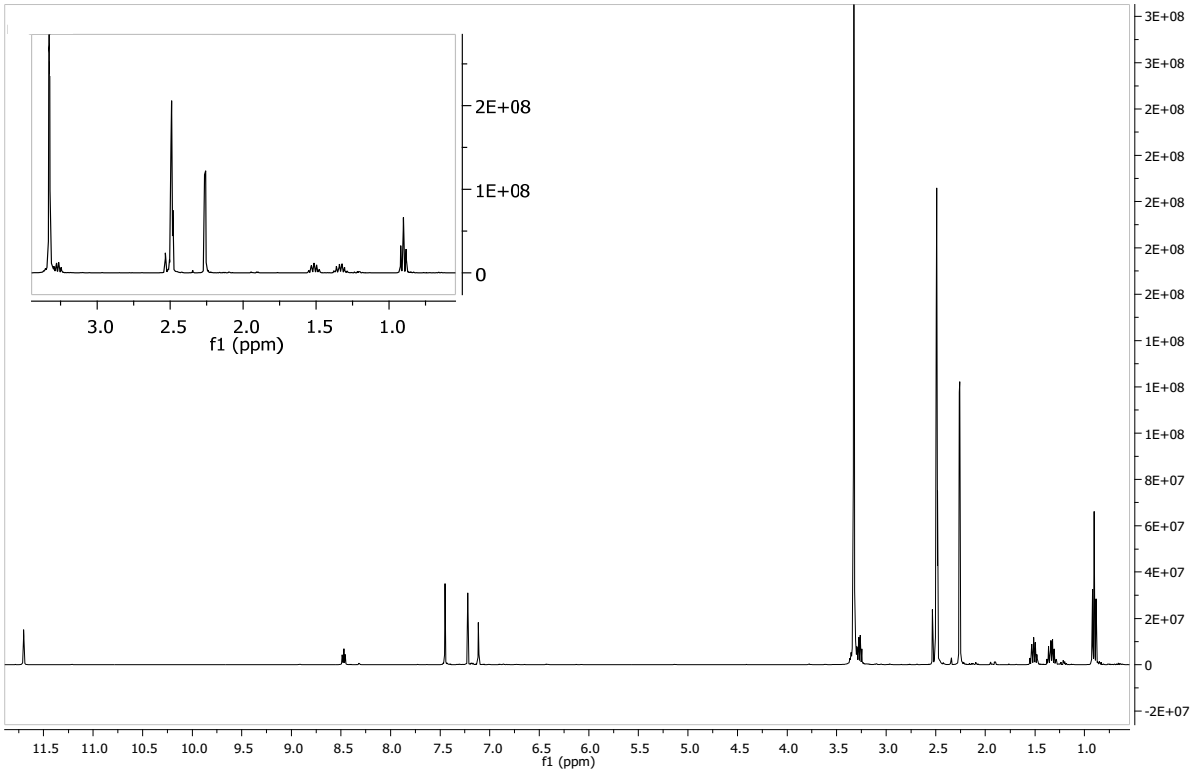

Figure S4. ^{1}H NMR spectrum of *N*-butane-5,6-diacetoxy-1*H*-indole-2-carboxamide (**1)** (DMSO-d_6).

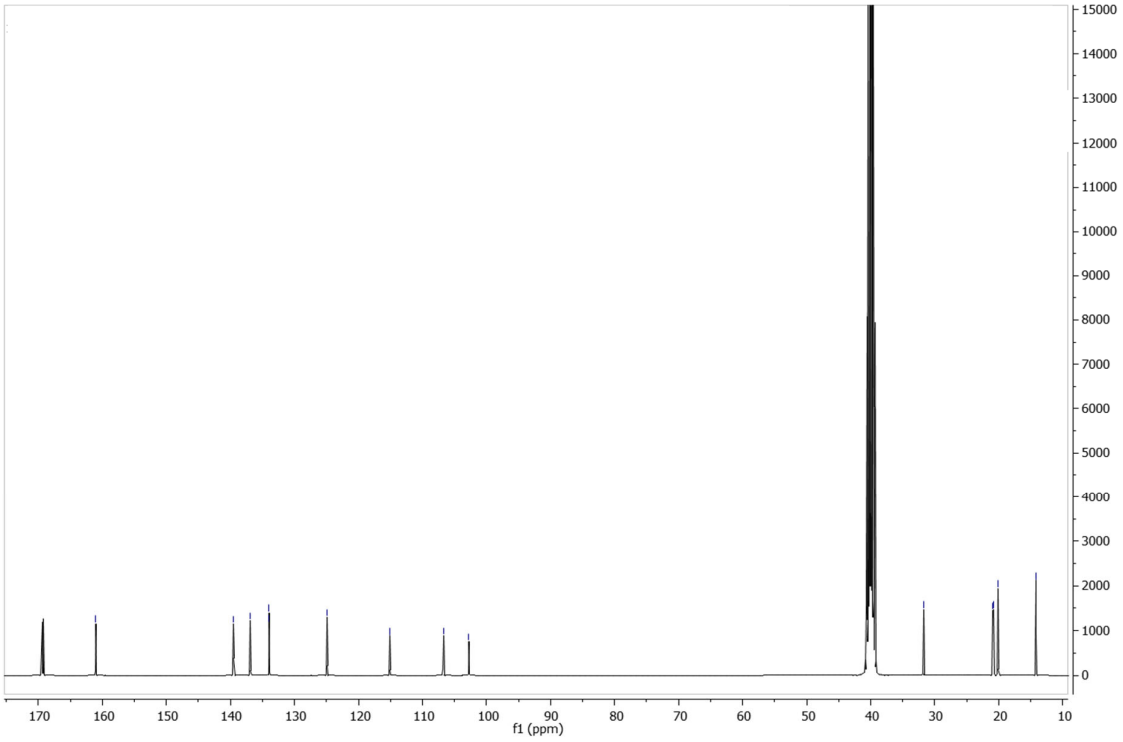

Figure S5. ^{13}C NMR spectrum of *N*-butane-5,6-diacetoxy-1*H*-indole-2-carboxamide (**1)** (DMSO-d_6).

Table S1. NMR spectral data (ppm) for **1***.

	^{1}H (J, Hz)	^{13}C
CH$_3$CH$_2$CH$_2$CH$_2$NH	0.90(t,7.2)	14.3
CH$_3$**CH$_2$**CH$_2$CH$_2$NH	1.33(s,7.2)	20.1
CH$_3$CH$_2$**CH$_2$**CH$_2$NH	1.51(quint, 7.6)	31.8
CH$_3$COO-5 indole	2.25(s)	20.8
CH$_3$COO-6 indole	2.26(s)	20.9
CH$_3$CH$_2$CH$_2$**CH$_2$**NH	3.21(m)	39.3
CH-3 indole	7.14(dd, 0.8, 2.0)	102.8
CH-4 indole	7.45(d, 0.8)	106.7
CH-7 indole	7.21(bs)	115.2
CH$_2$**NH**CO	8.47(t,5.8)	
NH indole	11.74(bs)	
C9 indole		124.9
C2 indole		133.9
C8 indole		134.0
C6 indole		136.9
C5 indole		139.5
NH**C**O		161.0
CH$_3$**C**OO-5 indole		169.2
CH$_3$**C**OO-6 indole		169.3

*Resonance assignment based on 2D NMR spectra (not shown).

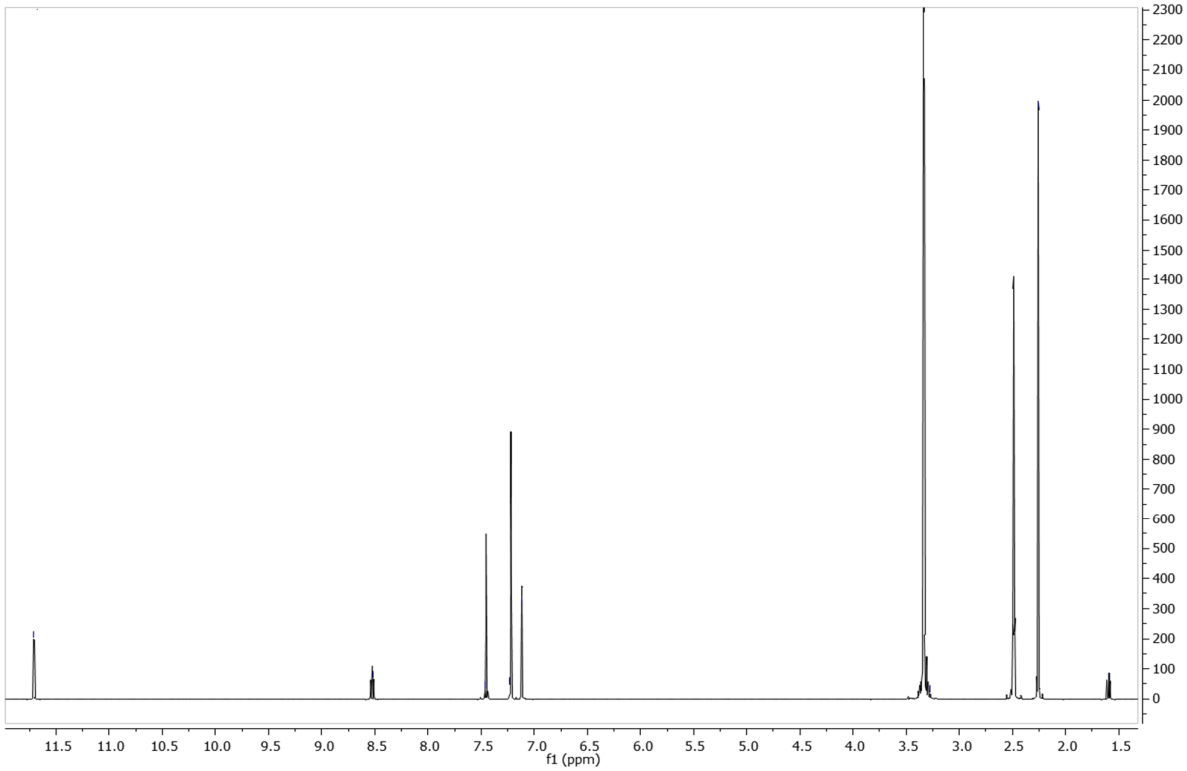

Figure S6. ^{1}H NMR spectrum *N,N'*-(butane-1,4-diyl)bis(5,6-diacetoxy-1*H*-indole-2-carboxamide) (**2**) (DMSO-d$_6$).

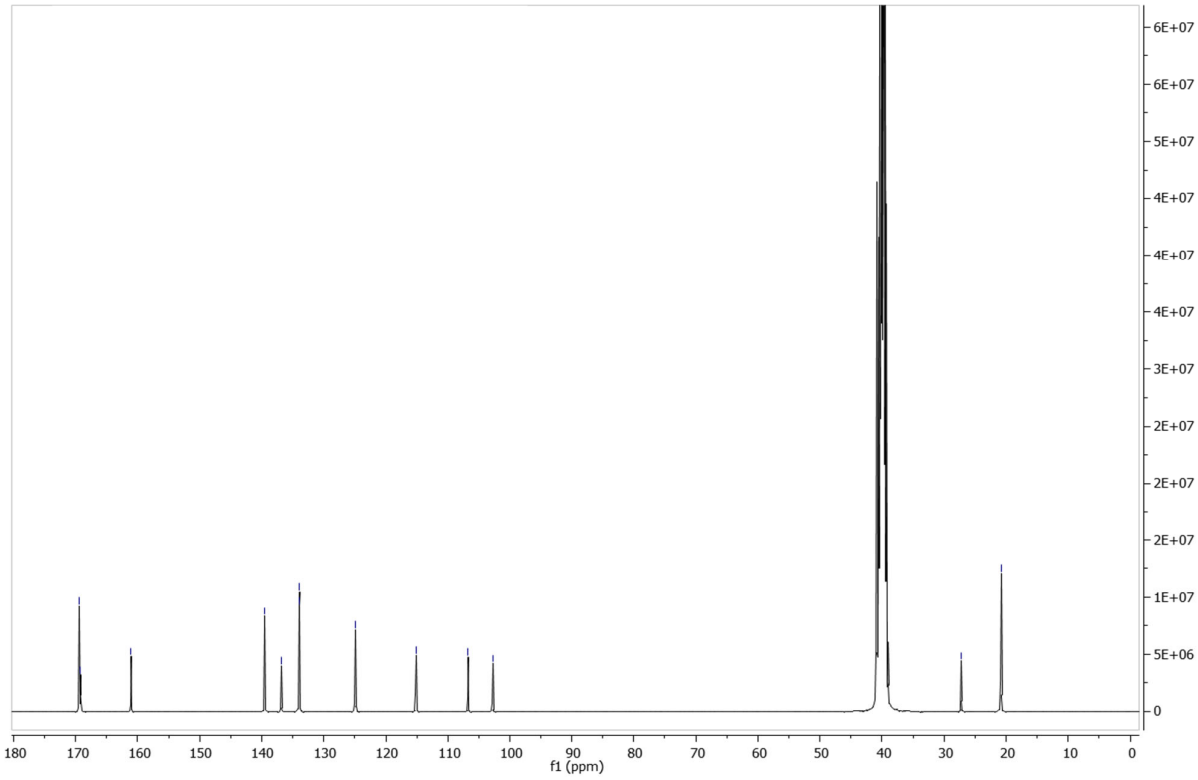

Figure S7. ^{13}C NMR spectrum *N,N′*-(butane-1,4-diyl)bis(5,6-diacetoxy-1*H*-indole-2-carboxamide) (**2**) (DMSO-d_6).

Table S2. NMR spectral data (ppm) for **2.**

	^{1}H (J, Hz)	^{13}C
$NHCH_2\underline{\mathbf{CH_2}}CH_2CH_2NH$	1.58(t,8.0)	27.2
$\underline{\mathbf{CH_3}}COO$-5 indole	2.25(s)	20.8
$\underline{\mathbf{CH_3}}COO$-6 indole	2.26(s)	20.9
$NH\underline{\mathbf{CH_2}}CH_2CH_2CH_2NH$	3.32(m)	39.8
CH-3 indole	7.12(dd, 0.8, 2.4)	102.8
CH-4 indole	7.45(d, 0.8)	106.7
CH-7 indole	7.21(bs)	115.2
$CH_2\underline{\mathbf{NH}}CO$	8.51(t,6.0)	
NH indole	11.72(bs)	
C9 indole		124.9
C2 indole		133.9
C8 indole		134.0
C6 indole		136.9
C5 indole		139.5
$NH\underline{\mathbf{C}}O$		161.0
$CH_3\underline{\mathbf{C}}OO$-5 indole		169.2
$CH_3\underline{\mathbf{C}}OO$-6 indole		169.4

*Resonance assignment based on 2D NMR spectra (not shown)

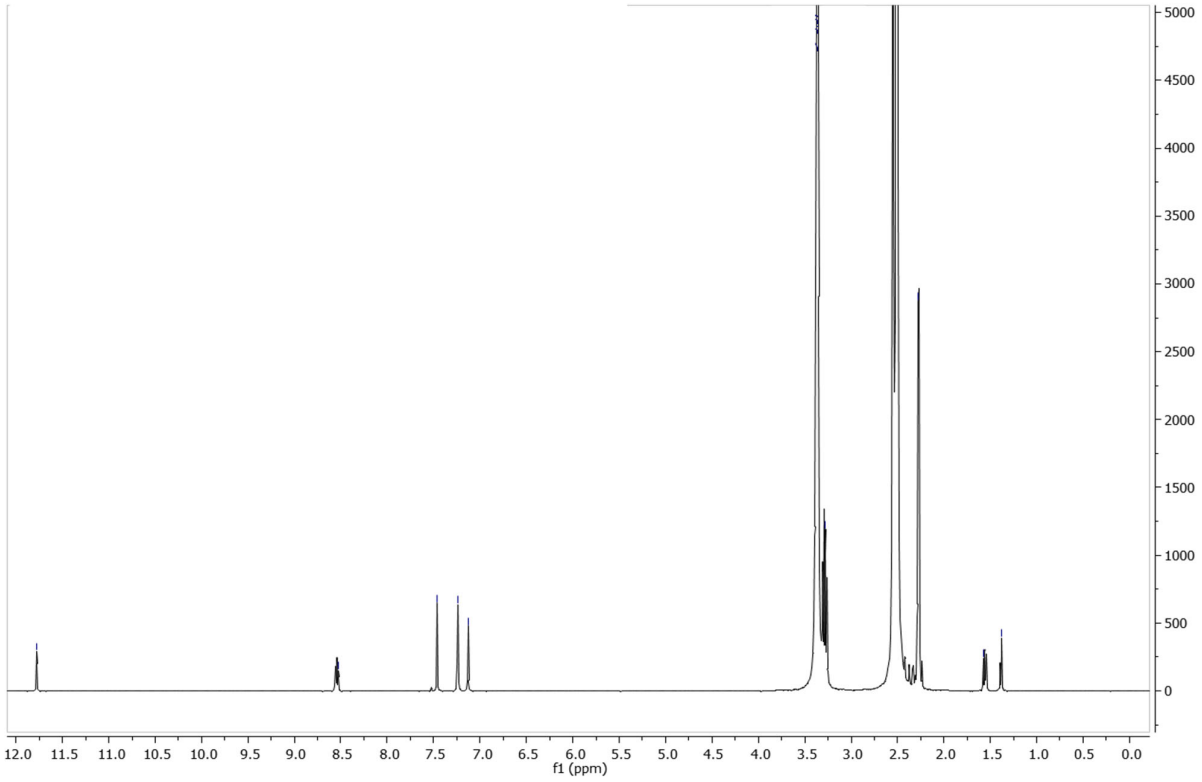

Figure S8. ^{1}H NMR spectrum of *N,N′*-(hexane-1,6-diyl)bis(5,6-diacetoxy-1*H*-indole-2-carboxamide) (**3)** (DMSO-d_6).

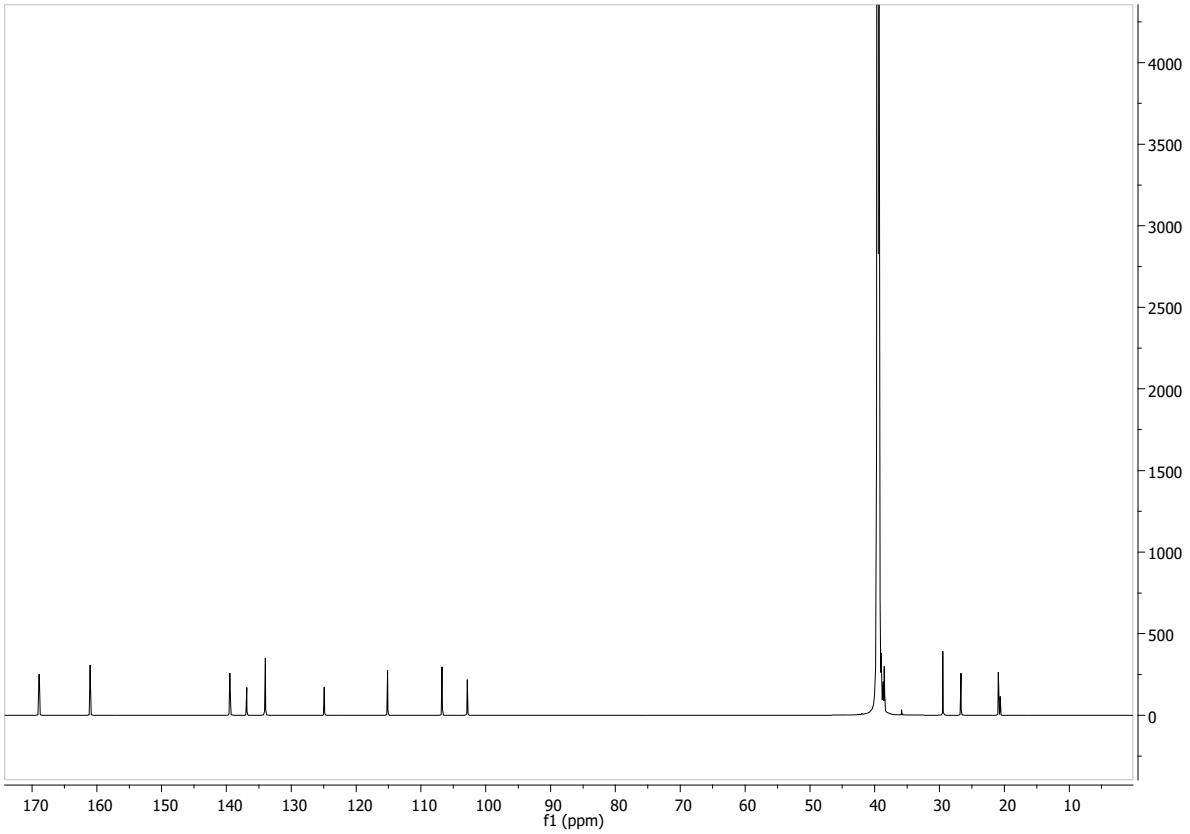

Figure S9. ^{13}C NMR spectrum of *N,N'*-(hexane-1,6-diyl)bis(5,6-diacetoxy-1*H*-indole-2-carboxamide) **(3)** (DMSO-d_6).

Table S3. NMR spectral data (ppm) for **3.**

	^{1}H (J, Hz)	**^{13}C**
$NHCH_2CH_2$**CH_2**$CH_2CH_2CH_2NH$	1.37(m)	26.7
$NHCH_2$**CH_2**$CH_2CH_2CH_2CH_2NH$	1.56(m)	29.6
CH_3COO-5 indole	2.25(s)	20.8
CH_3COO-6 indole	2.26(s)	20.9
NH**CH_2**$CH_2CH_2CH_2CH_2CH_2NH$	3.32(m)	39.3
CH-3 indole	7.12(bs)	102.8
CH-4 indole	7.45(bs)	106.5
CH-7 indole	7.22(bs)	115.2
CH_2**NH**CO	8.51(t,6)	
NH indole	11.72(bs)	
C9 indole		124.9
C2 indole		133.9
C8 indole		134.0
C6 indole		136.8
C5 indole		139.3
NH**C**O		161.0
CH_3**C**OO-5 indole		169.2
CH_3**C**OO-6 indole		169.4

*Resonance assignment based on 2D NMR spectra (not shown)

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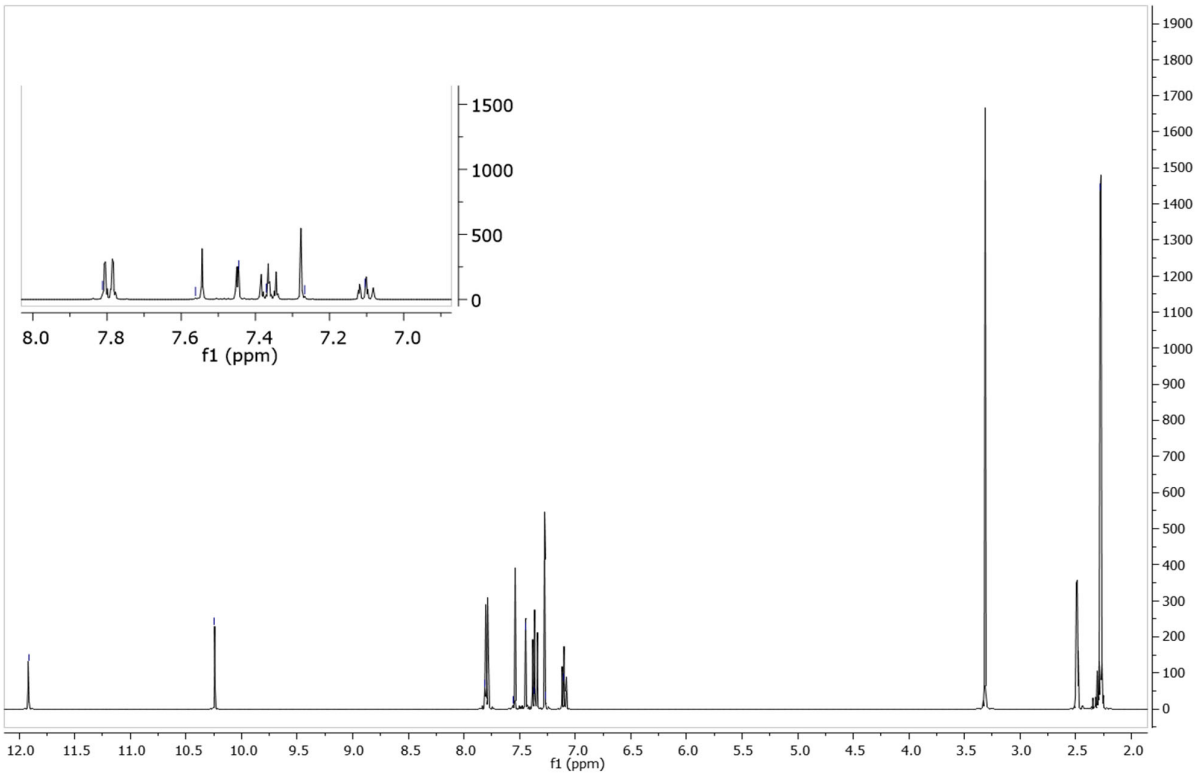

Figure S10. ^{1}H NMR spectrum of 5,6-diacetoxy-*N*-phenyl-1*H*-indole-2-carboxamide of DHICA (**4**) (DMSO-d_6).

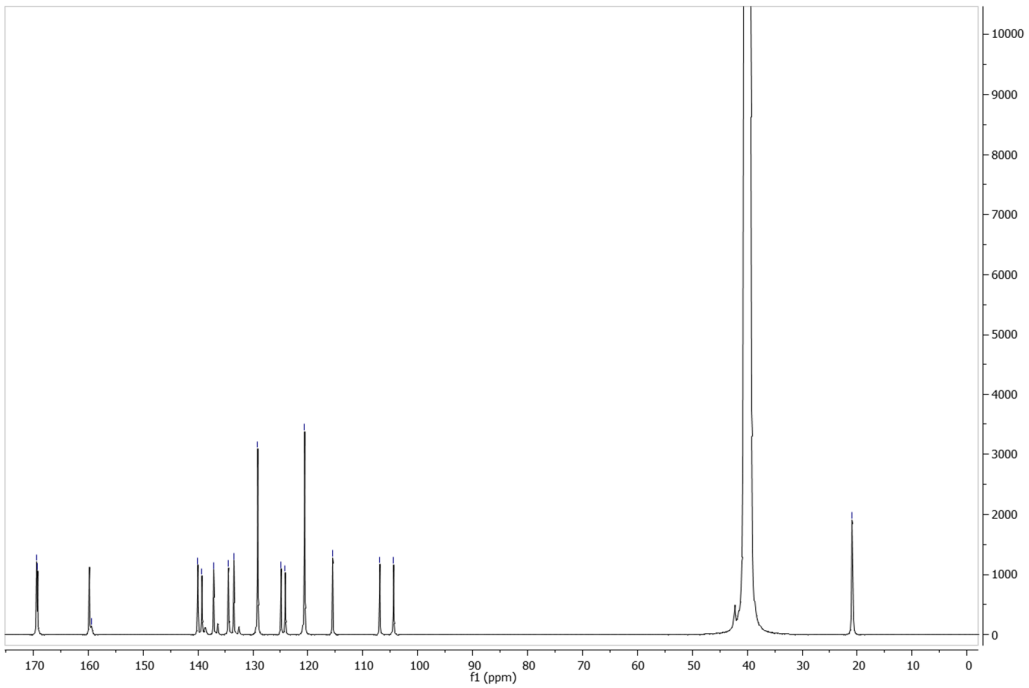

Figure S11. ^{13}C NMR spectrum of 5,6-diacetoxy-*N*-phenyl-1*H*-indole-2-carboxamide of DHICA (**4**) (DMSO-d_6).

Table S4. NMR spectral data (ppm) for **4.**

	^{1}H (J, Hz)	^{13}C
CH$_3$COO-5 indole	2.27(s)	20.8
CH$_3$COO-6 indole	2.28(s)	20.9
CH-aniline	7.10(t,8.0)	124.1
CH-7 indole	7.27(t,0.8)	106.8
CH-aniline	7.37(t,8.0)	120.6
CH-3 indole	7.44(dd, 2.4,0.8)	104.4
CH-4 indole	7.55(bs)	115.4
CH-aniline	7.88(d,2.0)	129.2
aniline **NH**CO	10.24(s)	
NH indole	11.92(bs)	
C9 indole		124.5
C2 indole		133.4
C8 indole		134.5
C6 indole		137.1
C5 indole		139.3
C aniline		140.0
NH**C**O		159.9
CH$_3$**C**OO-5 indole		169.2
CH$_3$**C**OO-6 indole		169.4

*Resonance assignment based on 2D NMR spectra (not shown)

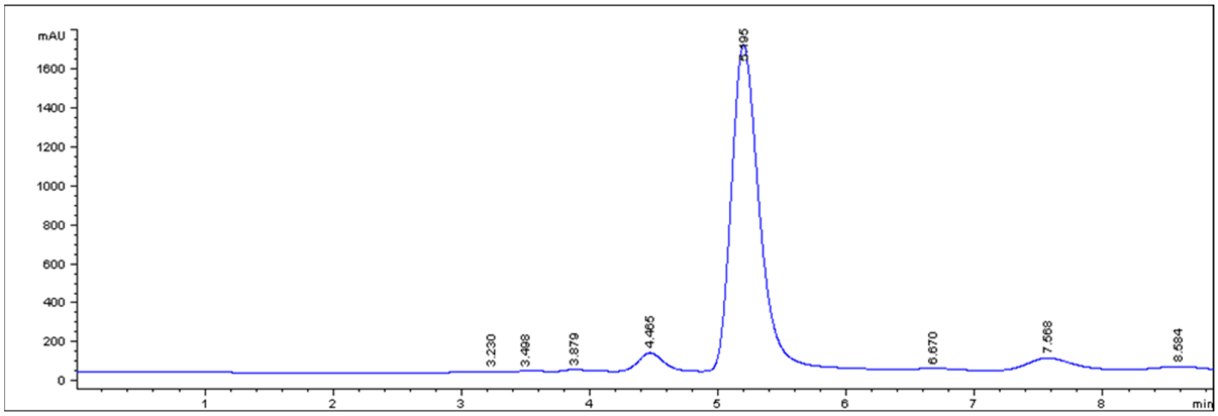

Figure S12. Chromatogram of deacetylated **1** (λ = 300 nm).

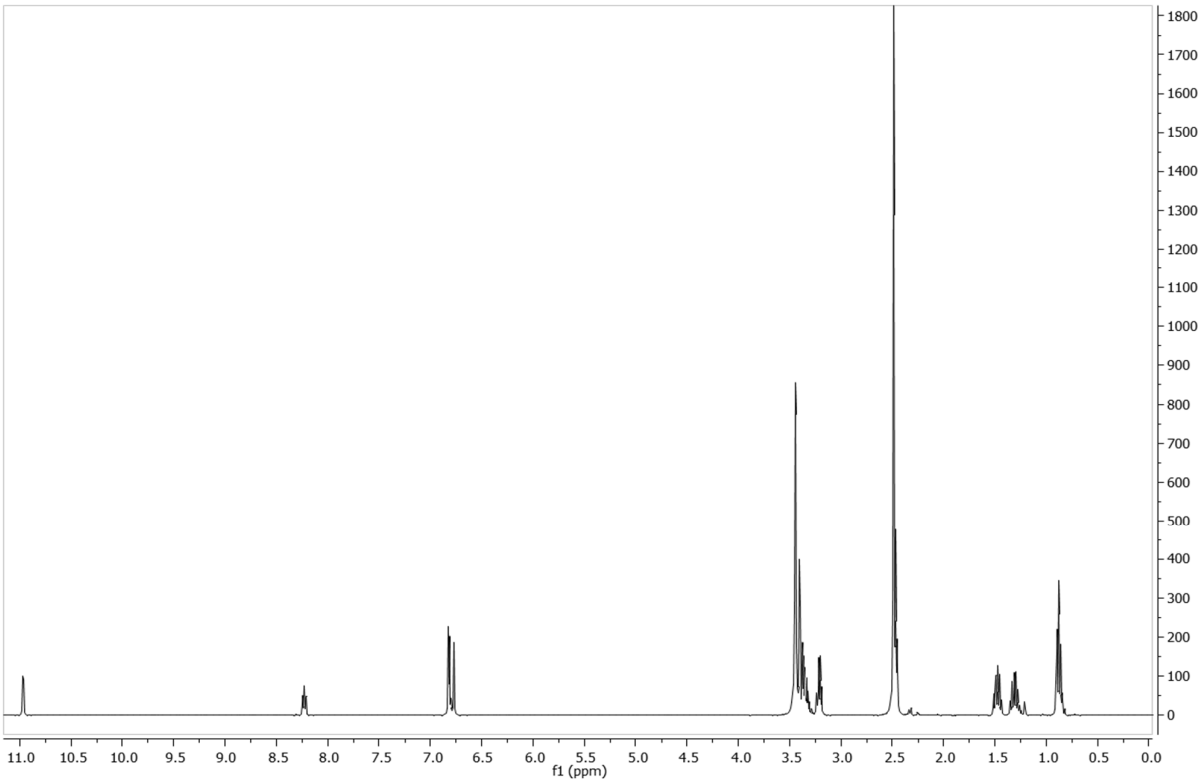

Figure S13. ^{1}H NMR spectrum of deacetylated **1** (DMSO-d_6).

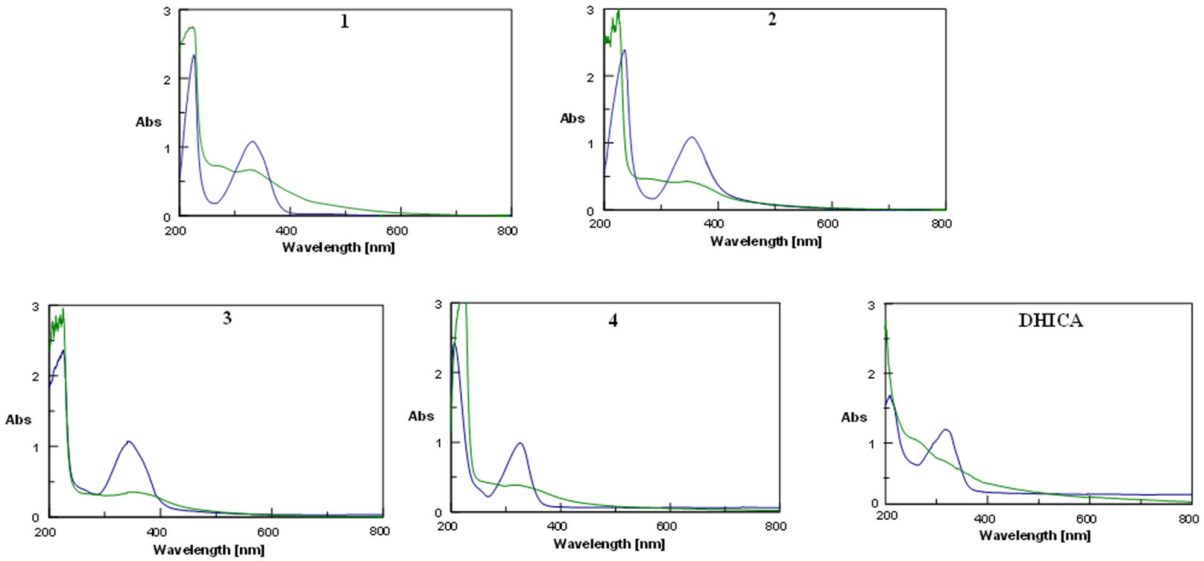

Figure S14. UV-Vis spectrophotometric monitoring of the course of the aerial oxidation of DHICA carboxyamides at t 0 h (blu), t24 h (green).

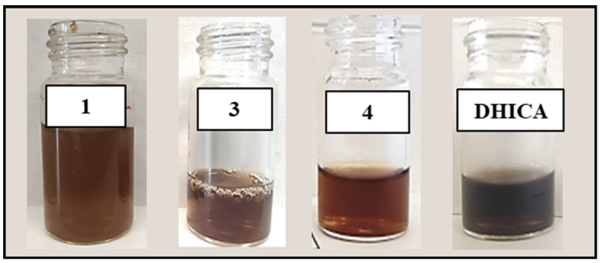

Figure S15. Digital photos of pigments as obtained from DHICA carboxyamides in carbonate buffer at pH 9 after 24 h under stirring.

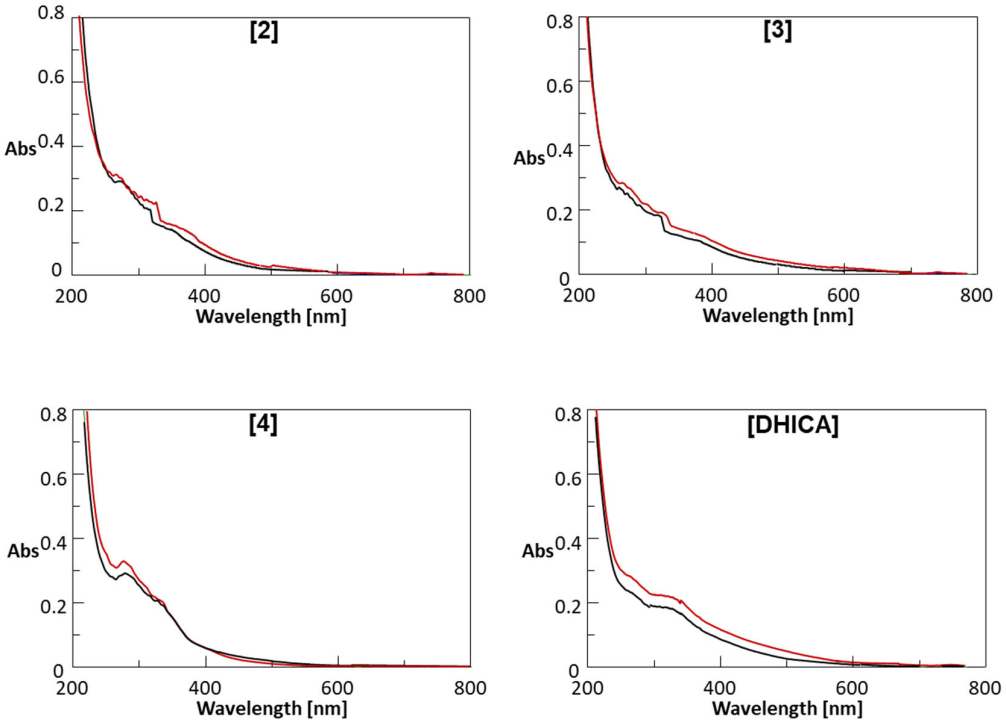

Figure S16. UV-vis spectrum prior and after filtration of the ethanol solution (1mg/mL) of carboxamides and DHICA.