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# Facile synthesis of oligo anilines as permanent hair dyes: How chemical modifications impart colour and avoid toxicity

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Figure S1 (A). <sup>1</sup>HNMR spectrum of compound 1 (PPD 1).







		Mass	Spect	um	Sm	nartF	orm	ula Report		
Analysis Info								Acquisition Date	5/24/2	018 3:00:07 PM
Analysis Name	D:\Data\Che	m\2018 Sa	amples\201	805\05	24-1\	PPD-1.d	Í.			
Method	YCH-50-500	.m						Operator	defaul	t user
Sample Name	PPD-1							Instrument / Ser#	micrO	TOF-Q II 10269
Comment	Dr Wu Jie									
Acquisition Pa	rameter									
Source Type	ESI		Ion Polar	ty		Positive		Set Nebulizer		2.0 Bar
Focus	Not active		Set Capil	lary		4500 V		Set Dry Heat	er	200 °C
Scan Begin	50 m/z		Set End F	Plate Of	fset	-500 V		Set Dry Gas		6.0 l/min
Scan End	700 m/z		Set Collis	ion Cell	RF	100.0 V	'pp	Set Divert Va	lve	Waste
vleas.m/z #	Formula	m/z	err [ppm]	rdb	e <sup>-</sup> C	onf N-	Rule			
200.1185 1	C 12 H 14 N 3	200.1182	-1.5	7.5	even		ok			



Figure S1 (C). HRMS spectrum of compound 1 (PPD 1).



Figure S2 (A). <sup>1</sup>HNMR spectrum of compound 6 (PPD 2).



Figure S2 (B). <sup>13</sup>CNMR spectrum of compound 6 (PPD 2).

		M	ass S	pectrur	n Si	martFo	rmu	la Report		
Analysis In	fo							Acquisition Date	5/24/2018 4:4	3:15 PM
Analysis Na	me	D:\Data\Chem\2	018 Samp	les\201805	0524-	NPPD-14.d				
Method		YCH-50-500.m						Operator	default user	
Sample Nan	ne	PPD-14						Instrument / Ser#	micrOTOF-Q	10269
Comment		Dr Wu Jie								
Acquisition	P	arameter								
Source Type		ESI	1	on Polarity		Positive		Set Nebulizer	2.0 B	ar
Focus		Not active	:	Set Capillary		4500 V		Set Dry Heate	er 200 °	С
Scan Begin		50 m/z	1	Set End Plate	Offset	-500 V		Set Dry Gas	6.0 l/	min
Scan End		700 m/z		Set Collision (	Cell RF	100.0 Vp	р	Set Divert Va	lve Wast	e
leas. m/z	#	Formula	m/z	err [ppm]	rdb	e <sup>-</sup> Conf	N-Rule	9		
411.1931	1	C 26 H 25 N 3 O 2	411.1941	2.4	16.0	odd	0	k		



Figure S2(C). HRMS spectrum of compound 6 (PPD 2).



Figure S3 (A). <sup>1</sup>HNMR spectrum of compound 7 (PPD 3).



Figure S3 (B). <sup>13</sup>CNMR spectrum of compound 7 (PPD 3).

		M	ass S	pectrur	n Si	mart⊦c	ormu	lla Report		
Analysis Info	,							Acquisition Date	5/24/2018 4:2	25:57 PM
Analysis Nam	ie	D:\Data\Chem\	2018 Samp	les\201805	0524-	1\PPD-11.d	l)	•		
Method		YCH-50-500.m	0.					Operator	default user	
Sample Name	e	PPD-11						Instrument / Ser#	micrOTOF-Q	II 10269
Comment		Dr Wu Jie								
Acquisition I	Par	ameter								
Source Type		ESI	l.	on Polarity		Positive		Set Nebulizer	2.0 8	Bar
Focus		Not active	5	Set Capillary		4500 V		Set Dry Heat	er 200	°C
Scan Begin		50 m/z	5	Set End Plate	Offset	-500 V		Set Dry Gas	6.01	min
Scan End		700 m/z	5	Set Collision (	Cell RF	100.0 Vp	p	Set Divert Va	lve Was	te
Meas. m/z #	I	Formula	m/z	err [ppm]	rdb	e <sup>-</sup> Conf	N-Rule	e		
469.1747 1	(	26 H 23 N 5 O 4	469.1745	-0.5	18.0	odd	0	k		



Figure S3(C). HRMS spectrum of compound 7 (PPD 3).



Figure S4 (A). <sup>1</sup>HNMR spectrum of compound 8 (PPD 4).



Figure S4 (B). <sup>13</sup>CNMR spectrum of compound 8 (PPD 4).

	M	ass Sp	ectrur	n Sr	martFo	mula	Report		
Analysis Info						Acc	uisition Date	5/24/201	8 4:33:11 PM
Analysis Name	D:\Data\Chem\	2018 Sample	s\201805	0524-1	I\PPD-12.d	,			
Method	YCH-50-500.m					Op	erator	default u	ser
Sample Name	PPD-12					Inst	trument / Ser#	micrOTC	F-Q II 10269
Comment	Dr Wu Jie								
Acquisition Pa	arameter								
Source Type	ESI	lon	Polarity		Positive		Set Nebulizer		2.0 Bar
Focus	Not active	Se	t Capillary		4500 V		Set Dry Heate	er	200 °C
Scan Begin	50 m/z	Se	t End Plate	Offset	-500 V		Set Dry Gas		6.0 l/min
Scan End	700 m/z	Se	t Collision (	Cell RF	100.0 Vpp		Set Divert Va	lve	Waste
Meas. m/z #	Formula	m/z	[mqq] rre	rdb	e <sup>-</sup> Conf I	N-Rule			
439.2253 1	C 28 H 29 N 3 O 2	439.2254	0.3	16.0	odd	ok			



Figure S4(C). HRMS spectrum of compound 8 (PPD 4).



Figure S5 (A) <sup>1</sup>HNMR spectrum of compound 9 (PPD 5).



#### Figure S5 (B). <sup>13</sup>CNMR spectrum of compound 9 (PPD 5).

		Mass	Spectr	um	Smai	rtForm	ula Report		
Analysis Info							Acquisition Date	5/24/2018 4	:38:43 PM
Analysis Name	D:\Data\Che	m\2018 Sa	mples\201	805\05	24-1\PPD	0-13.d			
Method	YCH-50-500	.m					Operator	default user	
Sample Name	PPD-13						Instrument / Ser#	micrOTOF-0	Q II 10269
Comment	Dr Wu Jie								
Acquisition Pa	arameter								
Source Type	ESI		Ion Polari	ty	Po	sitive	Set Nebulizer	2.0	Bar
Focus	Not active		Set Capill	ary	45	00 V	Set Dry Heate	er 200	0°C
Scan Begin	50 m/z		Set End F	late Of	fset -50	00 V	Set Dry Gas	6.0	) I/min
Scan End	700 m/z		Set Collis	ion Cell	RF 10	0.0 Vpp	Set Divert Va	lve Wa	iste
Meas.m/z #	Formula	m/z	err [ppm]	rdb	e <sup>-</sup> Cont	N-Rule			
407.2363 1	C 28 H 29 N 3	407.2356	-1.7	16.0	odd	ok			



Figure S5(C). HRMS spectrum of compound 9 (PPD 5).



Figure S6 (A). <sup>1</sup>HNMR spectrum of compound 12 (PPD 6).



Figure S6 (B). <sup>13</sup>C NMR spectrum of compound 12 (PPD 6).

	Ν	lass S	Spectru	m S	martF	orm	ula Report		
Analysis Info							Acquisition Date	5/24/20	18 3:28:21 PM
Analysis Name	D:\Data\Chen	n\2018 San	nples\20180	5\0524-	1\PPD-4.	d			
Method	YCH-50-500.	n				-	Operator	default i	user
Sample Name	PPD-4						Instrument / Ser#	micrOT	OF-Q II 10269
Comment	Dr Wu Jie								
Acquisition Pa	rameter								
Source Type	ESI		Ion Polarity		Positiv	e	Set Nebulizer		2.0 Bar
Focus	Not active		Set Capillan	1	4500 \	1	Set Dry Heate	r	200 °C
Scan Begin	50 m/z		Set End Pla	e Offset	-500 V	'	Set Drv Gas		6.0 l/min
Scan End	700 m/z		Set Collision	Cell RF	100.0	Vpp	Set Divert Val	ve	Waste
Meas.m/z #	Formula	m/z	err [ppm]	rdb	∋ Conf	N-Rule			
209.1650 1	C 12 H 21 N 2 O	209.1648	-0.7	3.5	even	ok			



Figure S6(C). HRMS spectrum of compound 12 (PPD 6).



Figure S7 (A). <sup>1</sup>HNMR spectrum of compound 13 (PPD 7).



Figure S7 (B). <sup>13</sup>C NMR spectrum of compound 13 (PPD 7).

		Ν	Mass S	Spectru	m S	Sn	nartF	orm	ula Report		
Analysis Inf	io								Acquisition Date	5/24/2	018 3:23:57 PM
Analysis Nar	ne	D:\Data\Chen	n\2018 San	nples\20180	5\052	4-1	PPD-3.	d			
Method		YCH-50-500.	m	•					Operator	defau	lt user
Sample Nam	ne	PPD-3							Instrument / Ser#	micrO	TOF-Q II 10269
Comment		Dr Wu Jie									
Acquisition	Pa	arameter									
Source Type		ESI		Ion Polarity			Positiv	/e	Set Nebulizer	· ·	2.0 Bar
Focus		Not active		Set Capillar	Y		4500	V	Set Dry Heate	er	200 °C
Scan Begin		50 m/z		Set End Pla	te Offs	ət	-500 V	1	Set Dry Gas		6.0 l/min
Scan End		700 m/z		Set Collision	n Cell F	۲F	100.0	Vpp	Set Divert Va	ve	Waste
Aleas.m/z #	¥	Formula	m/z	err [ppm]	rdb	e	Conf	N-Rule			
237.1958	1	C 14 H 25 N 2 O	237.1961	1.6	3.5	ev	ren	ok			



Figure S7(C). HRMS spectrum of compound 13 (PPD 7).



Figure S8 (A). <sup>1</sup>HNMR spectrum of compound 15 (PPD 8).



Figure S8 (B). <sup>13</sup>CNMR spectrum of compound 15 (PPD 8).

#### Mass Spectrum SmartFormula Report

Analysis Info							Acquisition Date	5/24/20	)18 3:32:00 PM	
Analysis Name Method Sample Name Comment	lethod YCH-50-500.m ample Name PPD-5 comment Dr Wu Jie coulisition Parameter ource Type ESI			5\0524	l-1\PPD-5.c	1	Operator Instrument / Ser#	default micrOT	user OF-Q II 10269	
Acquisition Pa	arameter									_
Source Type Focus Scan Begin Scan End	ESI Not active 50 m/z 700 m/z		lon Polarity Set Capillan Set End Pla Set Collision	/ te Offse i Cell R	Positive 4500 V et -500 V F 100.0 V	e /pp	Set Nebulizer Set Dry Heat Set Dry Gas Set Divert Va	er Ive	2.0 Bar 200 °C 6.0 l/min Waste	
Meas. m/z # 300.2073 1	Formula C 18 H 26 N 3 O	m/z 300.2070	err [ppm] -0.9	rdb 7.5	e Conf even	N-Rule ok				



Figure S8(C). HRMS spectrum of compound 15 (PPD 8).



Figure S9 (A).<sup>1</sup>HNMR spectrum of compound 17 (PPD 9).



Figure S9 (B).<sup>13</sup>C NMR spectrum of compound 17 (PPD 9).

17

#### Mass Spectrum SmartFormula Report

Analysis Info	D:\Data\Chem	02018 San	∟16 d	Acquisition Date	6/21/2018	6:20:50 PM		
Method Sample Name Comment	YCH-50-500.n PPD-16 Dr Wu Jie	n	ipies 201000.00	21416	-10.4	Operator Instrument / Ser#	default us micrOTOI	er Q II 10269
Acquisition P	arameter							
Source Type Focus Scan Begin Scan End	APCI Not active 50 m/z 600 m/z		lon Polarity Set Capillary Set End Plate Of Set Collision Cell	fset - RF	Positive 1500 V 500 V 100.0 Vpp	Set Nebulizer Set Dry Heat Set Dry Gas Set Divert Va	er 2	3.0 Bar 200 °C 4.0 l/min Waste
Meas. m/z # 293.2587 1	Formula C 18 H 33 N 2 O	m/z 293.2587	err [ppm] rdt 0.1 3.5	e C even	onf N-Rule ok			



Figure S9(C). HRMS spectrum of compound 17 (PPD 9).



Figure S10 (A).<sup>1</sup>HNMR spectrum of compound 20 (PPD 10).



Figure S10 (B).<sup>13</sup>C NMR spectrum of compound 20 (PPD 10).

20

		Mass	Spectr	um	Sn	nart	Form	ula Report		
Analysis Info								Acquisition Date	5/24	/2018 3:12:47 PM
Analysis Name	D:\Data\Che	em\2018 Sa	amples\201	805\05	24-1	PPD-2	2.d			
Method	YCH-50-50	).m						Operator	defa	ult user
Sample Name	PPD-2							Instrument / Ser#	micr	OTOF-Q II 10269
Comment	Dr Wu Jie									
Acquisition Pa	rameter									
Source Type	ESI		Ion Polari	ly .		Posit	ive	Set Nebulize	er	2.0 Bar
Focus	Not active	e	Set Capill	arv		4500	V	Set Dry Hea	ter	200 °C
Scan Begin	50 m/z		Set End F	late Of	fset	-500	v	Set Dry Gas		6.0 l/min
Scan End	700 m/z		Set Collisi	on Cel	RF	100.0	Vpp	Set Divert V	alve	Waste
vleas.m/z #	Formula	m/z	err [ppm]	rdb	e <sup>-</sup> (	Conf	N-Rule			
290.1518 1	C 18 H 18 N 4	290.1526	2.9	12.0	odd		ok			



Figure S10(C). HRMS spectrum of compound 20 (PPD 10).



Figure S11 (A). <sup>1</sup>HNMR spectrum of compound 21 (PPD 11).



Figure S11 (B). <sup>13</sup>C NMR spectrum of compound 21(PPD 11).

		Mass	Spectr	um	Sn	nart	Form	ula Report			
Analysis Info								Acquisition Date	5/24/2	2018 3:58:0	7 PM
Analysis Name	D:\Data\Che	m\2018 Sa	mples\201	805\05	24-1	PPD-	B.d				
Method	YCH-50-500	m					0.000.0	Operator	defau	lt user	
Sample Name	PPD-8							Instrument / Ser#	micrO	TOF-Q II 1	0269
Comment	Dr Wu Jie										
Acquisition Pa	rameter										
Source Type	ESI		Ion Polari	ty		Posi	tive	Set Nebulizer		2.0 Bar	
Focus	Not active		Set Capill	ary		4500	v	Set Dry Heat	er	200 °C	
Scan Begin	50 m/z		Set End F	late Of	fset	-500	v	Set Dry Gas		6.0 l/min	
Scan End	700 m/z		Set Collis	on Cell	RF	100.	0 Vpp	Set Divert Va	lve	Waste	
Meas. m/z #	Formula	m/z	err [ppm]	rdb	e_ (	Conf	N-Rule				
381.1952 1	C 24 H 23 N 5	381.1948	1.2	16.0	odd		ok				



Figure S11(C). HRMS spectrum of compound 21 (PPD 11).



Figure S12 (A). <sup>1</sup>HNMR spectrum of compound 28 (PPD 12).



Figure S12 (B).<sup>13</sup>C NMR spectrum of compound 28 (PPD 12).

Mass Spectrum SmartFormula Report									
Analysis Info							Acquisition Date	5/24	/2018 4:17:00 PM
Analysis Name	D:\Data\Chei	m\2018 Sa	mples\201	805\05	24-1\P	PD-9.d			
Method	YCH-50-500.	.m	9997.• 9999945 53689488				Operator	defa	ult user
Sample Name	PPD-9						Instrument / Ser#	micr	OTOF-Q II 10269
Comment	Dr Wu Jie								
Acquisition Pa	rameter								
Source Type	ESI		Ion Polari	ty		Positive	Set Nebulize	)r	2.0 Bar
Focus	Not active		Set Capill	ary		4500 V	Set Dry Hea	ter	200 °C
Scan Begin	50 m/z		Set End F	late Of	set	-500 V	Set Dry Gas		6.0 l/min
Scan End	700 m/z		Set Collis	on Cell	RF	100.0 Vpp	Set Divert V	alve	Waste
vleas.m/z #	Formula	m/z	err (ppm)	rdb	e C	onf N-Ru	le		
303.1731 1	C 20 H 21 N 3	303.1730	-0.4	12.0	odd		ok		



#### Figure S12(C). HRMS spectrum of compound 28(PPD 12).



Figure S13 (A). <sup>1</sup>HNMR spectrum of compound 29 (PPD 13).



Figure S13 (B).<sup>13</sup>C NMR spectrum of compound 29 (PPD 13).

Н

29

			Mass	Spectr	um	Sma	tForm	ula Report	
Analysis Info				Acquisition Date	5/24/2018 4:21:55 PM				
Analysis N Method Sample Na Comment	ame	<ul> <li>D:\Data\Che</li> <li>YCH-50-500</li> <li>PPD-10</li> <li>Dr Wu Jie</li> </ul>	em\2018 Sa ).m	amples\201	805\05	24-1\PP[	0-10.d	Operator Instrument / Ser#	default user micrOTOF-Q II 10269
Acquisitio	n P	arameter							
Source Type	э	ESI		Ion Polar	ty	Po	sitive	Set Nebulize	2.0 Bar
Focus		Not active		Set Capill	ary	45	00 V	Set Dry Heat	er 200 °C
Scan Begin		50 m/z		Set End F	Plate Of	fset -54	V 00	Set Dry Gas	6.0 l/min
Scan End		700 m/z		Set Collis	ion Cell	RF 10	0.0 Vpp	Set Divert Va	ive Waste
Neas. m/z	#	Formula	m/z	err (ppm)	rdb	e <sup>-</sup> Cont	N-Rule		
394.2157	1	C 26 H 26 N 4	394.2152	-1.3	16.0	odd	ok		



Figure S13(C). HRMS spectrum of compound 29(PPD 13).



Figure S14 (A). <sup>1</sup>HNMR spectrum of Bandrowski's base.



Figure S14 (B). <sup>13</sup>CNMR of spectrum of Bandrowski's base.

# Mass Spectrum SmartFormula Report Acquisition Date 5/24/2018 4:59:38 PM D:\Data\Chem\2018 Samples\201805\0524-1\BB.d

Method Sample Name	YCH-50-500.m BB			Operator de Instrument / Ser# mi	fault user crOTOF-Q II 10269
Comment	Dr Wu Jie				
Acquisition Pa	rameter				
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	700 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste
Meas. m/z #	Formula	m/z err [ppm] rdb e	Conf N-Rule		

319.1663 1 C 18 H 19 N 6 319.1666 0.8 12.5 even ok

Analysis Info

Analysis Name



Figure S14(C). HRMS spectrum of Bandrowski's base.

#### 1. Hair Dyeing

**Figure S15**. Hair colors obtained from PPD derivatives 1, 6, 7, 8, 10, PTD and ME-PPD with the oxidant  $H_2O_2$  (formulation B) and the coupler resorcinol (formulation C)



Brown

Black

Brown

Black



Figure S16: Nuance stability analysis of the PPD-1 upon repeated washing over 4 weeks.

**Table S2**. Hair color measurements following dyeing with PPD derivatives in formulations A(no oxidant), B (with oxidant  $H_2O_2$ ) and C (with coupling agent resorcinol)

Derivatives		L*	$L_0$	<i>a*</i>	$a_0$	<b>b</b> *	$\boldsymbol{b_0}$	$\Delta E$	$\Delta H$
	Natural hair		9		0		1		
PPD	А	57		0		30		56.1	29
	В	9		1		1		1	0
	С	14		1		3		5.5	2.2
PPD 1	А	9		1		1		1	1
	В	9		1		1		1	1
	С	9		1		1		1	1
PPD 6	А	16		7		0		9.9	7.1
	В	9		1		1		1	1
	С	13		6		2		7.3	6.1
PPD 7	А	17		13		2		15.3	13.0
	В	9		1		1		1	1
	С	9		1		1		1	1
PPD 8	А	9		0		1		0	0
	В	9		1		1		1	1
	С	11		1		2		2.4	1.4
PPD 10	А	22		4		1		13.6	4
	В	35		5		0		26.5	5.1
	С	49		8		8		41.4	10.6
PTD	А	58		0		30		56.9	29.0
	В	14		1		3		5.4	2.2
	С	9		1		1		1	0
ME-PPD	A	58		0		30		56.9	29.0
	В	15		1		3		6.3	2.2
	С	9		1		1		1	0

Derivatives	Week 1	$\Delta E$	$\Delta H$
PPD	А	56.1	29
	В	1	0
	С	5.5	2.2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	Α	9.9	7.1
	В	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	В	1	l
	<u> </u>	1	<u> </u>
PPD 8	A	0	0
	B	1	
	<u> </u>	2.4	1.4
PPD 10	A	13.0	4
	Б С	20.5	3.1 10.6
DTD	<u> </u>	56.0	20.0
TID	R	54	29.0
	D C	1	0
ME-PPD	<u> </u>	56.9	29.0
ME ITD	B	63	2.2
	Č	1	0
Derivatives	Week 3	$\Lambda E$	ΛН
Derivatives PPD	Week 3 A	Δ <u>E</u> 56.1	<u>ΔΗ</u> 29
Derivatives PPD	Week 3 A B	ΔΕ 56.1 1	<u>AH</u> 29 0
Derivatives PPD	A B C	ΔE 56.1 1 5.5	<u>AH</u> 29 0 2.2
PPD 1	A B C A	ΔΕ 56.1 1 5.5 1	ΔΗ 29 0 2.2 1
PPD PPD 1	Week 3 A B C A B	<u>ΔΕ</u> 56.1 1 5.5 1 1	ΔH 29 0 2.2 1 1
PPD PPD 1	Week 3 A B C A B C	<u>ΔΕ</u> 56.1 1 5.5 1 1 1	ΔH 29 0 2.2 1 1 1 1
PPD 1 PPD 6	Week 3 A B C A B C A	<u>ΔΕ</u> 56.1 1 5.5 1 1 1 9.9	ΔH 29 0 2.2 1 1 1 7.1
PPD 1 PPD 6	Week 3 A B C A B C A B	<u>ΛΕ</u> 56.1 1 5.5 1 1 1 9.9 1	ΔH 29 0 2.2 1 1 1 1 7.1 1
PPD 1 PPD 6	Week 3 A B C A B C A B C	<u>ΛΕ</u> 56.1 1 5.5 1 1 1 9.9 1 7.3	ΔH           29           0           2.2           1           1           7.1           1           6.1
PPD 1 PPD 6 PPD 7	Week 3 A B C A B C A B C A	$     \begin{array}{r} \underline{AE} \\             56.1 \\             1 \\             5.5 \\             1 \\             1 \\         $	XH           29         0           2.2         1           1         1           7.1         1           6.1         13.0
PPD 1 PPD 6 PPD 7	Week 3 A B C A B C A B C A B B C	<u>ΛΕ</u> 56.1 1 5.5 1 1 1 9.9 1 7.3 15.3 1	ΔH           29         0           2.2         1           1         1           7.1         1           6.1         13.0           1         1
PPD 1 PPD 6 PPD 7 PPD 0	Week 3 A B C A B C A B C A B C C	<u>ΛΕ</u> 56.1 1 5.5 1 1 1 9.9 1 7.3 15.3 1 1	ΔH           29         0           2.2         1           1         1           7.1         1           6.1         13.0           1         1
PPD 1 PPD 6 PPD 7 PPD 8	Week 3 A B C A B C A B C A B C A A B C	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ 29 \\ 0 \\ 2.2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 6.1 \\ 13.0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1$
Derivatives       PPD       PPD 1       PPD 6       PPD 7       PPD 8	Week 3 A B C A B C A B C A B C A B C A B C	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ 29 \\ 0 \\ 2.2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 6.1 \\ 13.0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 4 \\ 1 \\ 4 \\ 1 \\ 4 \\ 1 \\ 4 \\ 1 \\ 4 \\ 1 \\ 1$
Derivatives       PPD       PPD 1       PPD 6       PPD 7       PPD 8       PPD 10	Week 3 A B C A B C A B C A B C A B C	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 12.6 \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ 29 \\ 0 \\ 2.2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 7.1 \\ 1 \\ 6.1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1.4 \\ 4 \end{array}$
DerivativesPPDPPD 1PPD 6PPD 7PPD 8PPD 10	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A A A B C A A B C A A B C A A B C A A A B C A A A B B C A A A A	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 6.1 \\ 1 \\ 1 \\ 3.0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1.4 \\ 4 \\ 5 \\ 1 \end{array}$
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 8 PPD 10	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ 29 \\ 0 \\ 2.2 \\ 1 \\ 1 \\ 1 \\ 1 \\ \hline 1 \\ 6.1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1.4 \\ 4 \\ 5.1 \\ 10 \\ 6 \end{array}$
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 8 PPD 10 PTD	Week 3 A B C A B C A B C A B C A B C A B C A B C A A B C A A B C A A A B C A A B C A A A B C A A B C A A B C A A A B C A A A B C A A B C A A A B C A A B C A A A B C A A A B C A A A B C A A A A	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ 56.9 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1$
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 7 PPD 8 PPD 10 PTD	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A A B B C A A B C A A B B C A A B C A A B A B	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ 56.9 \\ 5.4 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1$
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 7 PPD 8 PPD 10 PTD	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A A B B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B A A B C A A B B C A A B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C C C A A B B C C A A B B C C C A A B B C C C A A B B C C C A A A B B C C C A A B B C C C A A A B B C C C A A B B C C C A A A A	$\begin{array}{c c} \underline{AE} \\ \hline 56.1 \\ 1 \\ 5.5 \\ \hline 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ \hline 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ \hline 13.6 \\ 26.5 \\ 41.4 \\ \hline 56.9 \\ 5.4 \\ 1 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1$
DerivativesPPDPPD 1PPD 6PPD 7PPD 7PPD 8PPD 10PTDME-PPD	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A A B C A A B C A A B C A A B C A A B C A A A B C A A B C A A A B C A A B C A A B C A A A B C A A B C A A B C A A A B C A A B C A A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A A B C A A B C A A B C A A B C A A B C A A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B C A A B A A B C A A B C A A B C A A B C A A B C A A B C A A A B C A A B C A A A B C A A A B C A A A B C A A A B C A A A B C A A A B C A A A B C A A A B C A A A B C C A A A B C C A A A B C C A A A A	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ 56.9 \\ 5.4 \\ 1 \\ 56.9 \\ 50.9$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ $
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 7 PPD 8 PPD 10 PTD ME-PPD	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A A B B C A A B C A A B B C A A B C A A B B C A A B B C A A B B C A A B B C A A B B C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A A B B C C A A A B B C C A A B A B	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ 56.9 \\ 5.4 \\ 1 \\ 56.9 \\ 6.3 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1$
Derivatives PPD PPD 1 PPD 6 PPD 7 PPD 8 PPD 10 PTD ME-PPD	Week 3 A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A B C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A B B C C A A A B B C C A A B B C C C A A B B C C C A A A B B C C C A A B B C C C A A B B C C C A A B B C C C A A A B C C C A A A B B C C C A A A A	$\begin{array}{c c} \underline{AE} \\ 56.1 \\ 1 \\ 5.5 \\ 1 \\ 1 \\ 1 \\ 9.9 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 7.3 \\ 15.3 \\ 1 \\ 1 \\ 0 \\ 1 \\ 2.4 \\ 13.6 \\ 26.5 \\ 41.4 \\ 56.9 \\ 5.4 \\ 1 \\ 56.9 \\ 6.3 \\ 1 \\ \end{array}$	$\begin{array}{c} \underline{\lambda H} \\ \underline{29} \\ 0 \\ \underline{2.2} \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 1$

### Table S3. Stability study analysis of Hair dyes on hair.

Derivatives	Week 2	$\Delta E$	$\Delta H$
PPD	А	56.1	29
	В	1	0
	С	5.5	2.2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	А	9.9	7.1
	В	1	1
	С	7.3	6.1
PPD 7	А	15.3	13.0
	В	1	1
	С	1	1
PPD 8	А	0	0
	В	1	1
	С	2.4	1.4
PPD 10	А	13.6	4
	В	26.5	5.1
	С	41.4	10.6
PTD	А	56.9	29.0
	В	5.4	2.2
	С	1	0
ME-PPD	А	56.9	29.0
	В	6.3	2.2
	С	1	0

Derivatives	Week 4	$\Delta E$	$\Delta H$
PPD	А	56.1	29
	В	1	0
	С	5.5	2.2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	А	9.9	7.1
	В	1	1
	С	7.3	6.1
PPD 7	А	15.3	13.0
	В	1	1
	С	1	1
PPD 8	А	0	0
	В	1	1
	С	2.4	1.4
PPD 10	А	13.6	4
	В	26.5	5.1
	С	41.4	10.6
PTD	А	56.9	29.0
	В	5.4	2.2
	С	1	0
ME-PPD	А	56.9	29.0
	В	6.3	2.2
	С	1	0

Derivatives	Month 1	$\Delta E$	$\Delta H$
PPD	А	56.1	29
	В	1	0
	С	5.5	2.2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	А	9.9	7.1
	В	1	1
	С	7.3	6.1
PPD 7	А	15.3	13.0
	В	1	1
	С	1	1
PPD 8	А	0	0
	В	1	1
	С	2.4	1.4
PPD 10	А	13.6	4
	В	26.5	5.1
	С	41.4	10.6
PTD	А	56.9	29.0
	В	5.4	2.2
	С	1	0
ME-PPD	А	56.9	29.0
	В	6.3	2.2
	С	1	0

Derivatives	Month 2	$\Delta E$	$\Delta H$
PPD	A	55.2	28
	В	1	0
	С	5.2	2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	А	9.2	7
	В	1	1
	С	6.8	6
PPD 7	А	14.8	12.5
	В	1	1
	С	1	1
PPD 8	А	0	0
	В	1	1
	С	2.2	1.4
PPD 10	А	13.3	3.5
	В	26.1	5
	С	41.0	10
PTD	А	56.9	29.0
	В	5.4	2.2
	С	1	0
ME-PPD	Α	56.9	29.0
	В	6.3	2.2
	С	1	0

Derivatives	Month 3	$\Delta E$	$\Delta H$	Derivatives
PPD	Α	55.2	28	PPD
	В	1	0	
	С	5.2	2	
PPD 1	Α	1	1	PPD 1
	В	1	1	
	С	1	1	
PPD 6	Α	9.2	7	PPD 6
	В	1	1	
	С	6.8	6	
PPD 7	Α	14.8	12.5	PPD 7
	В	1	1	
	С	1	1	
PPD 8	Α	0	0	PPD 8
	В	1	1	
	С	2.2	1.4	
PPD 10	Α	13.3	3.5	PPD 10
	В	26.1	5	
	С	41.0	10	
PTD	Α	56.9	29.0	PTD
	В	5.4	2.2	
	С	1	0	
ME-PPD	Α	56.9	29.0	ME-PPD
	В	6.3	2.2	
	С	1	0	

Derivatives	Month 6	$\Delta E$	$\Delta H$
PPD	А	55.2	28
	В	1	0
	С	5.2	2
PPD 1	А	1	1
	В	1	1
	С	1	1
PPD 6	А	9.2	7
	В	1	1
	С	6.8	6
PPD 7	А	14.8	12.5
	В	1	1
	С	1	1
PPD 8	А	0	0
	В	1	1
	С	2.2	1.4
PPD 10	А	13.3	3.5
	В	26.1	5
	С	41.0	10
PTD	А	56.9	29.0
	В	5.4	2.2
	С	1	0
ME-PPD	А	56.9	29.0
	В	6.3	2.2
	С	1	0