Electronic Supplementary Material (ESI) for New Journal of Chemistry.

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

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Supplementary Information

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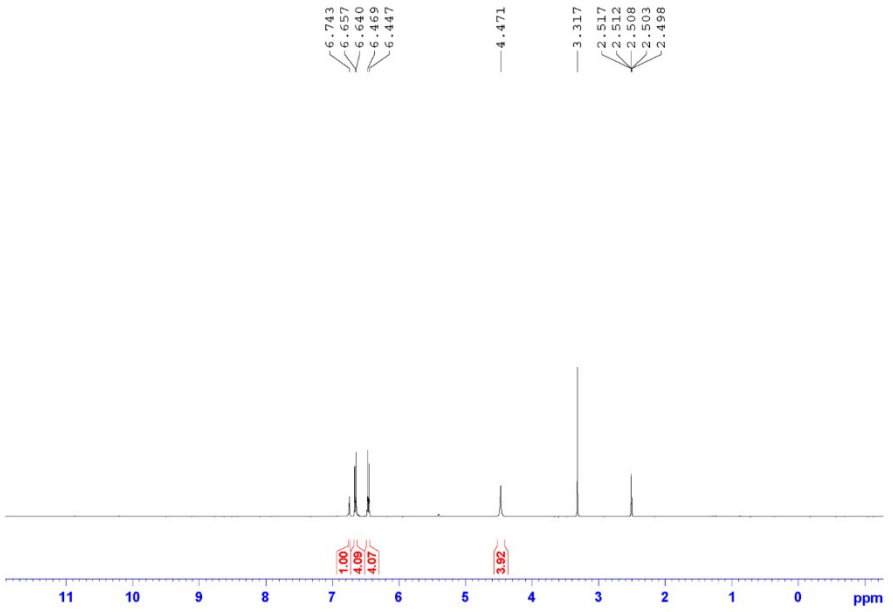


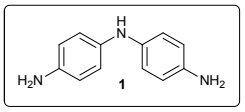
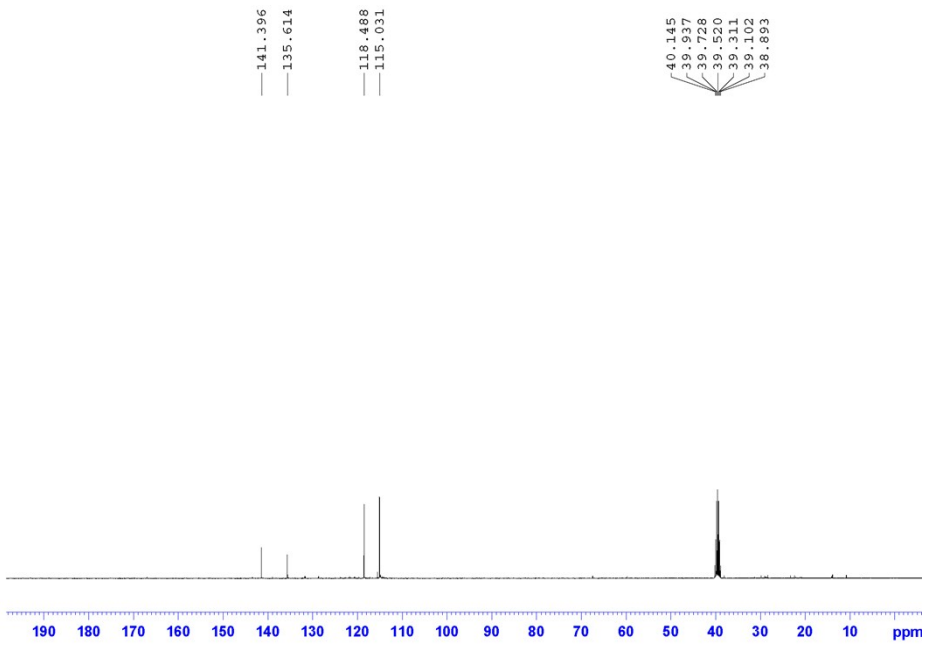


Figure S1 (A). [1]HNMR spectrum of compound **1** (PPD 1).



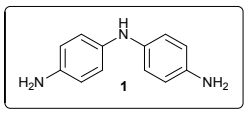


Figure S1 (B). ^{13}CNMR spectrum of compound **1** (PPD 1).

Mass Spectrum SmartFormula Report

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Comment	Dr Wu Jie		

Acquisition Parameter

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Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
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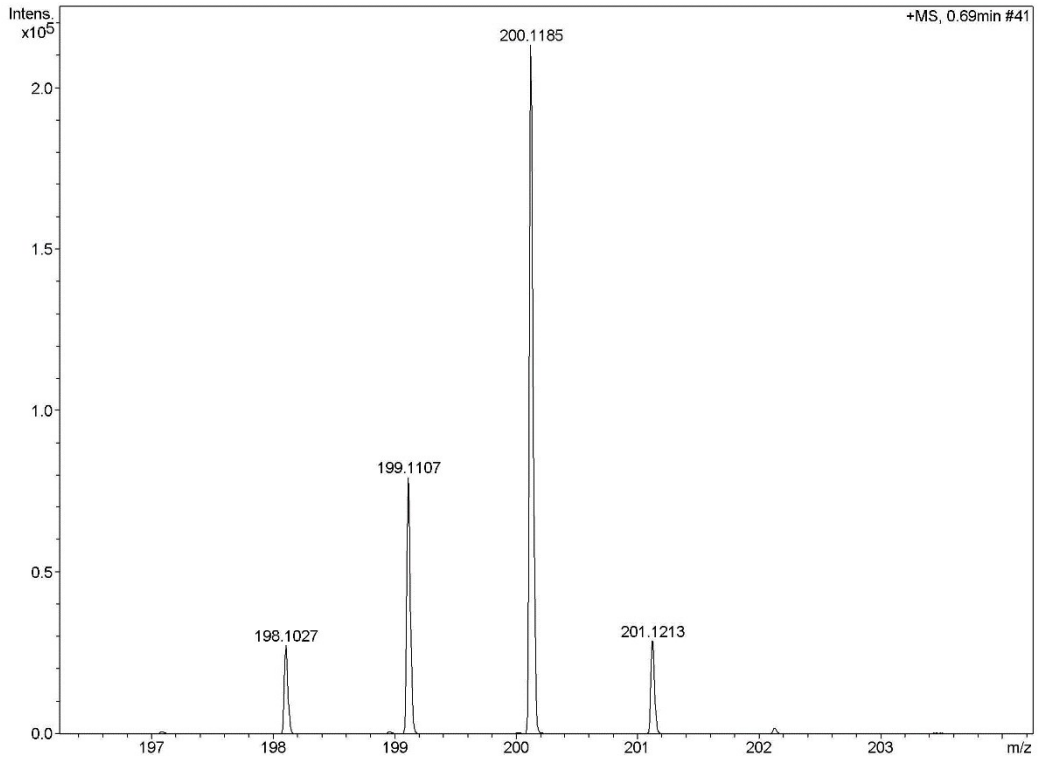

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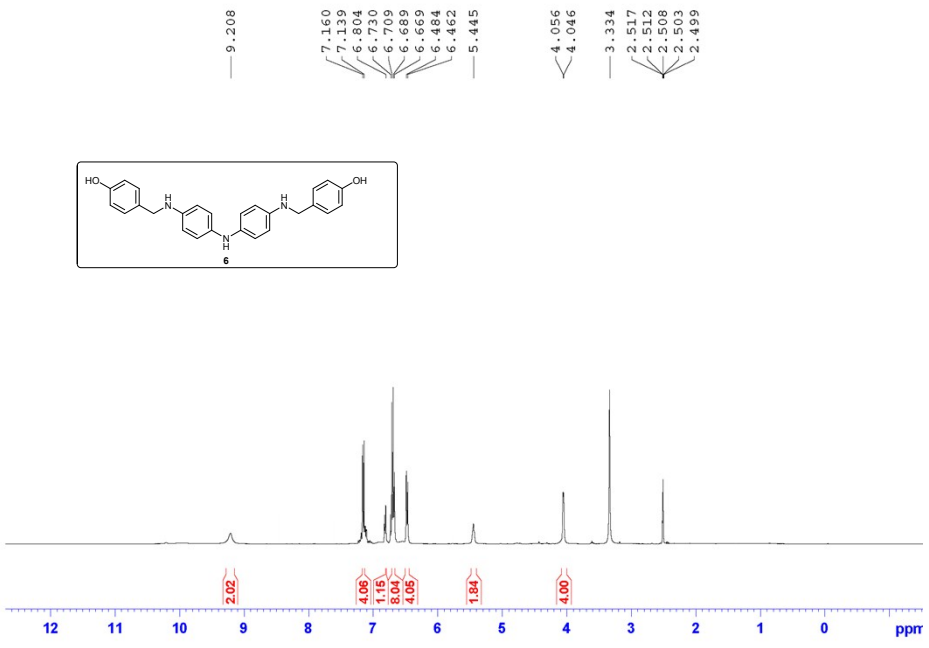
Figure S1 (C). HRMS spectrum of compound **1** (PPD 1).



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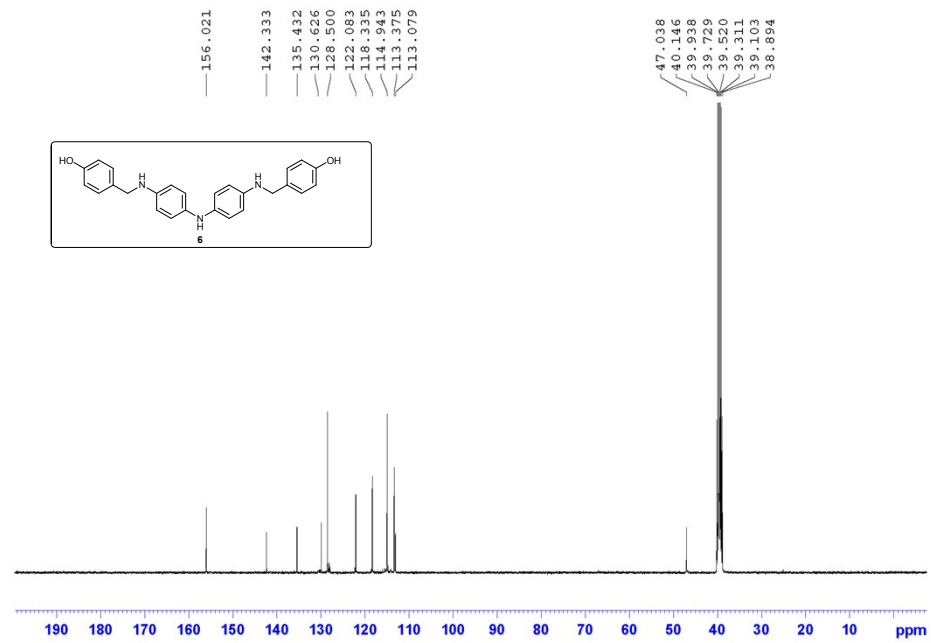

Figure S2 (B). [13]CNMR spectrum of compound **6** (PPD 2).

Mass Spectrum SmartFormula Report

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Comment	Dr Wu Jie		

Acquisition Parameter

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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
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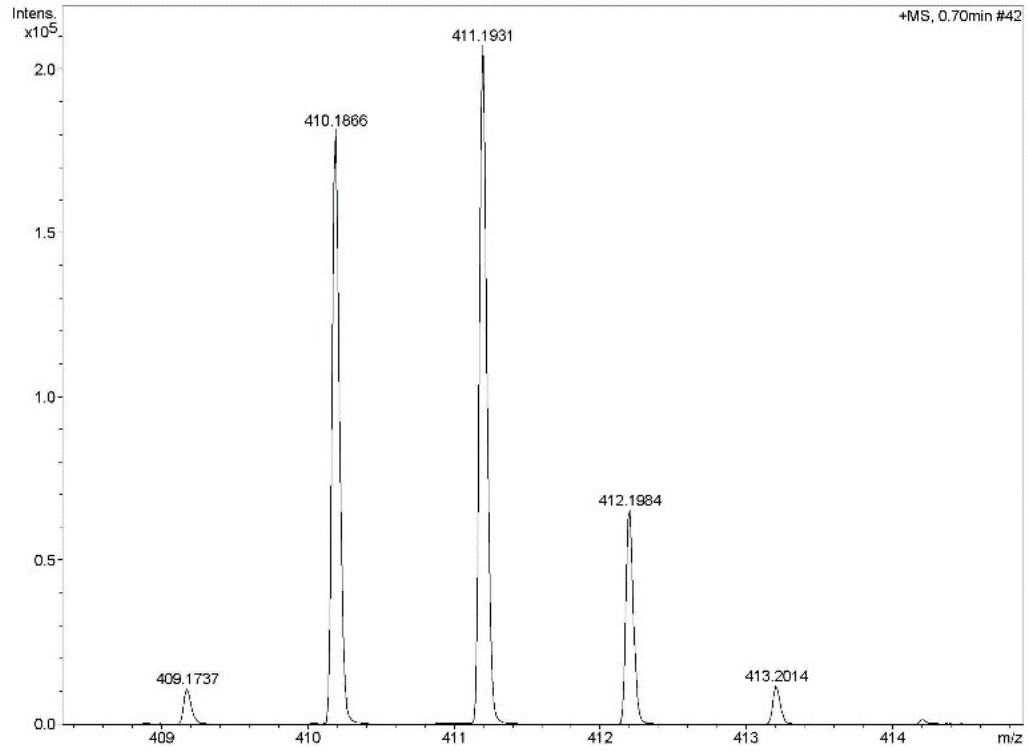

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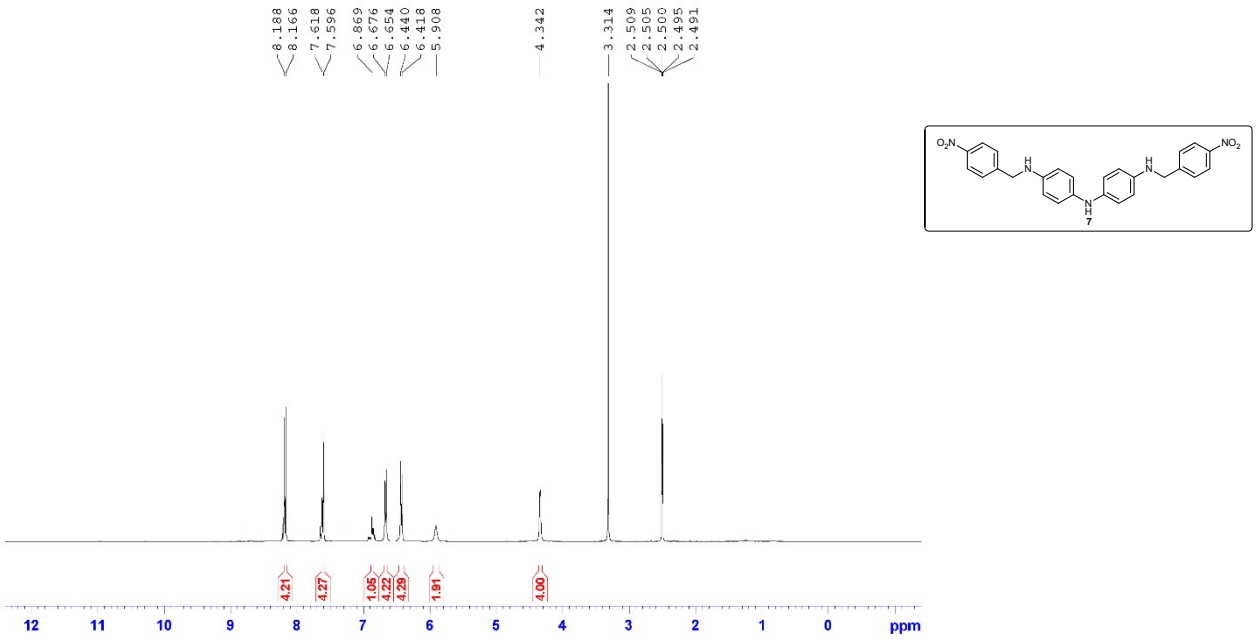
Figure S2(C). HRMS spectrum of compound **6** (PPD 2).



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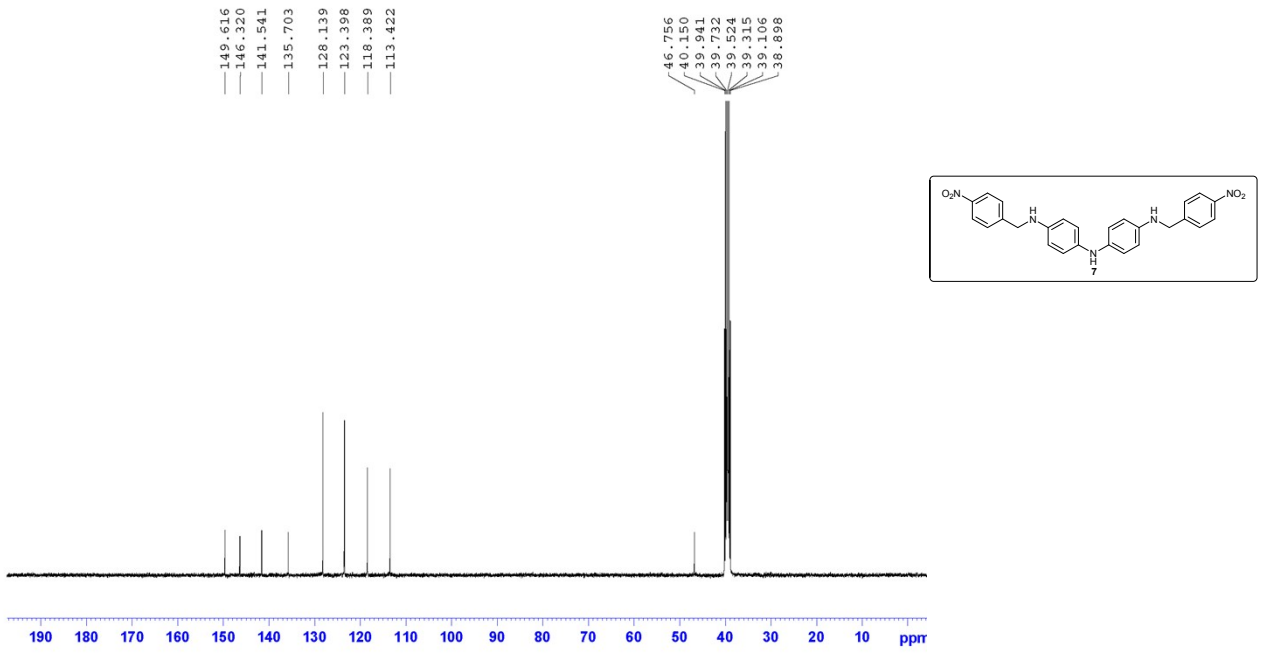

Figure S3 (B). [13]CNMR spectrum of compound **7** (PPD 3).

Mass Spectrum SmartFormula Report

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Comment	Dr Wu Jie		

Acquisition Parameter

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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
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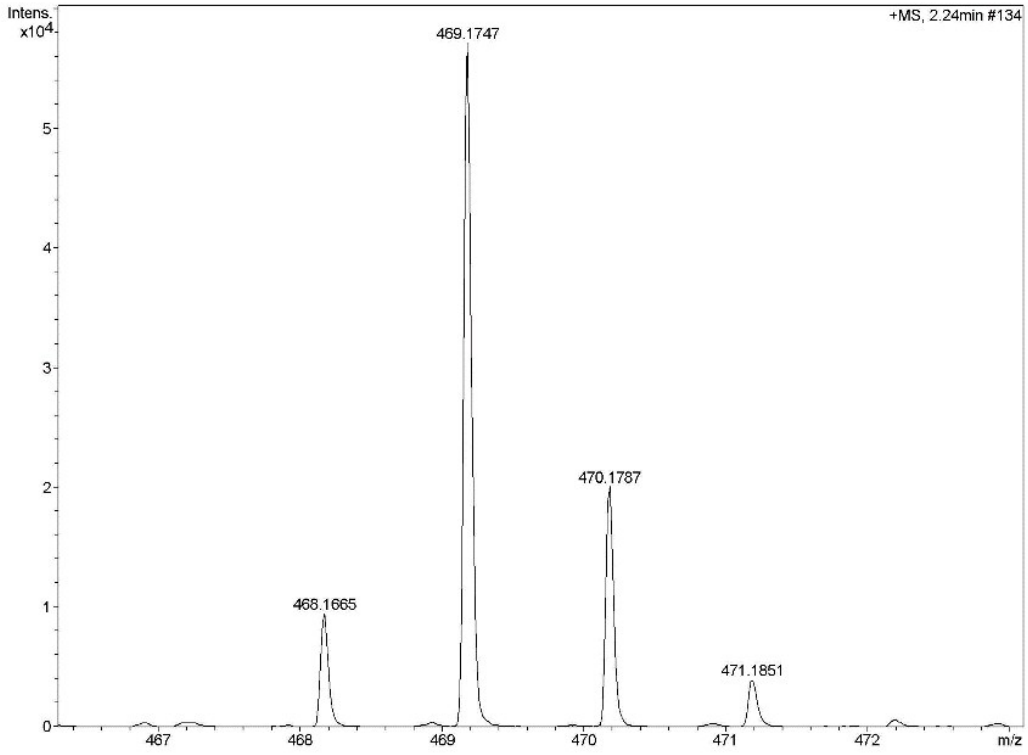

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Figure S3(C). HRMS spectrum of compound **7** (PPD 3).

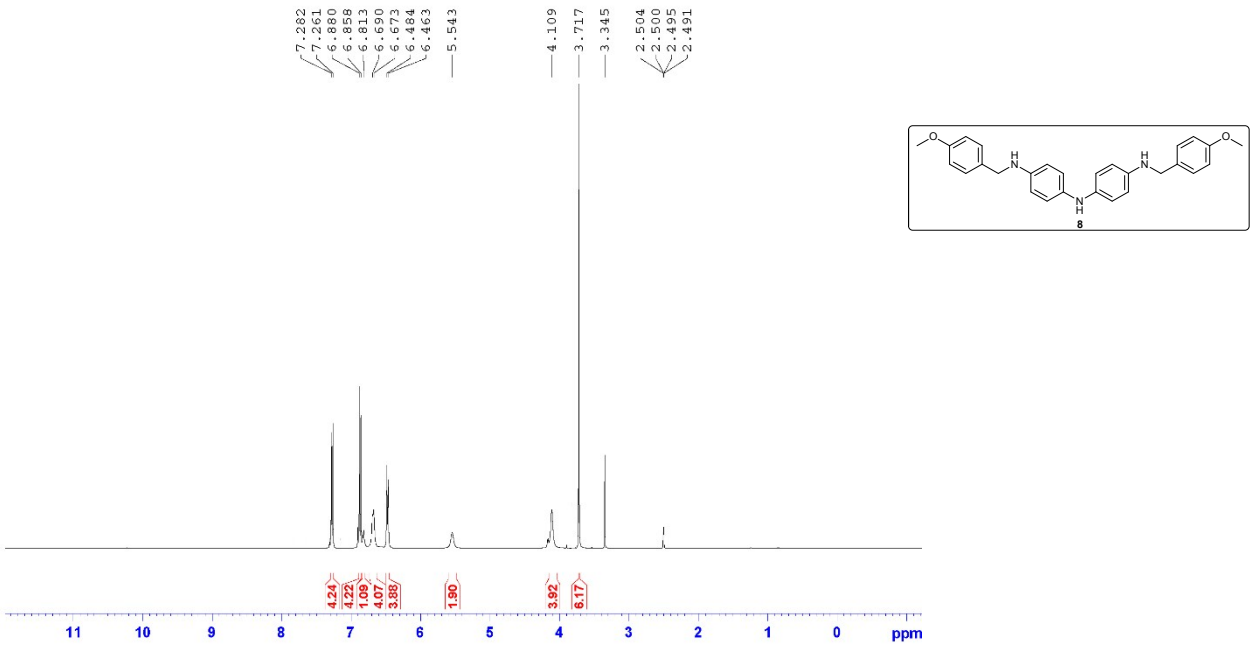

Figure S4 (A). [1]HNMR spectrum of compound **8** (PPD 4).

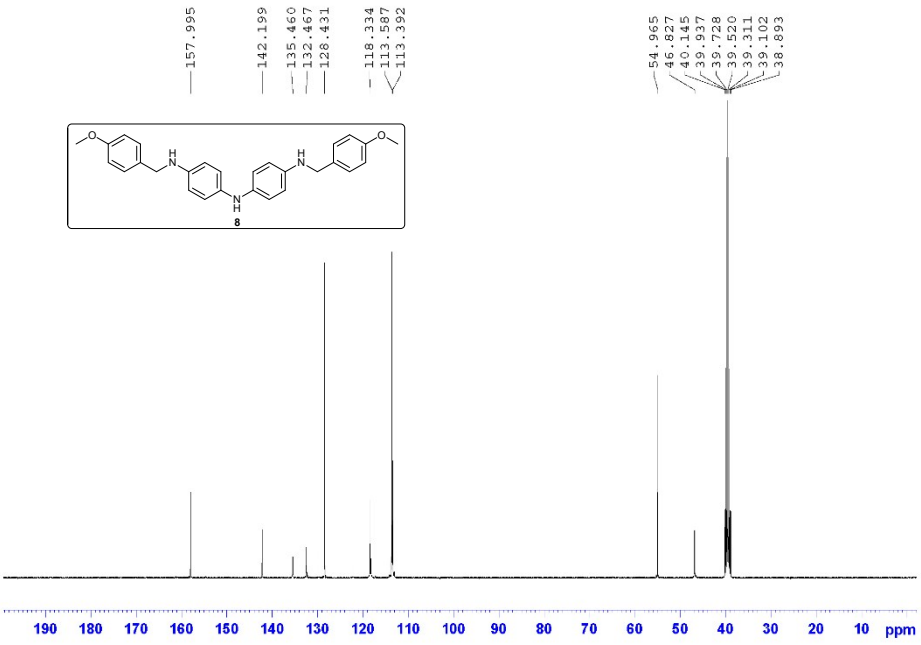

Figure S4 (B). [13]CNMR spectrum of compound **8** (PPD 4).

Mass Spectrum SmartFormula Report

Analysis Info

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Comment	Dr Wu Jie		

Acquisition Parameter

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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
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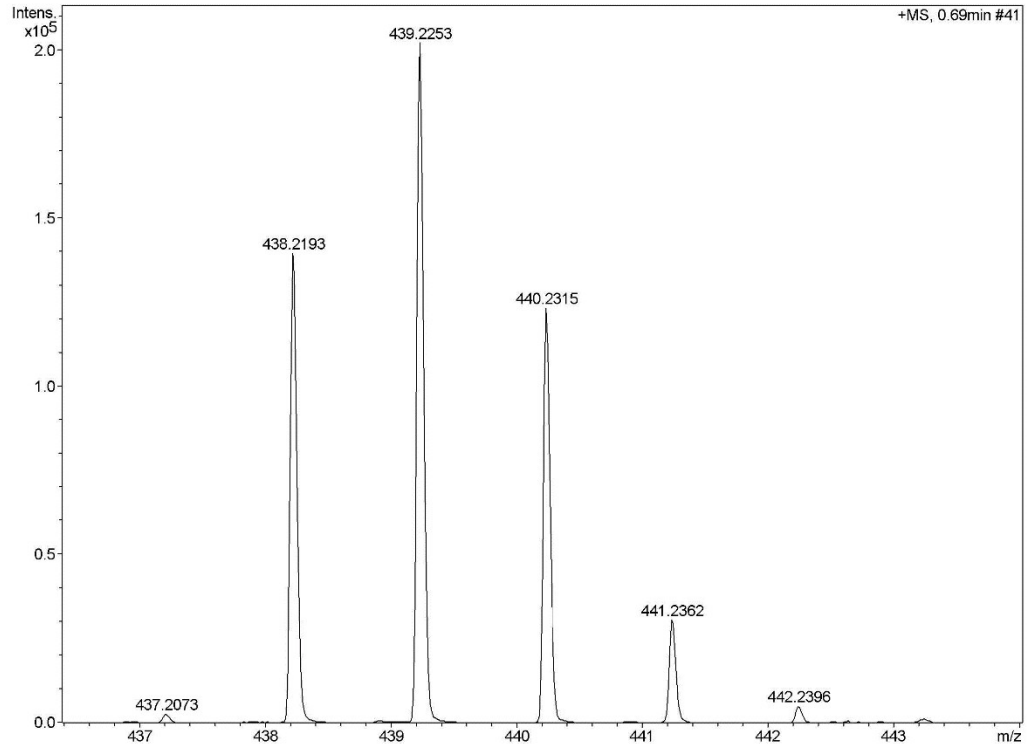

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Figure S4(C). HRMS spectrum of compound **8** (PPD 4).

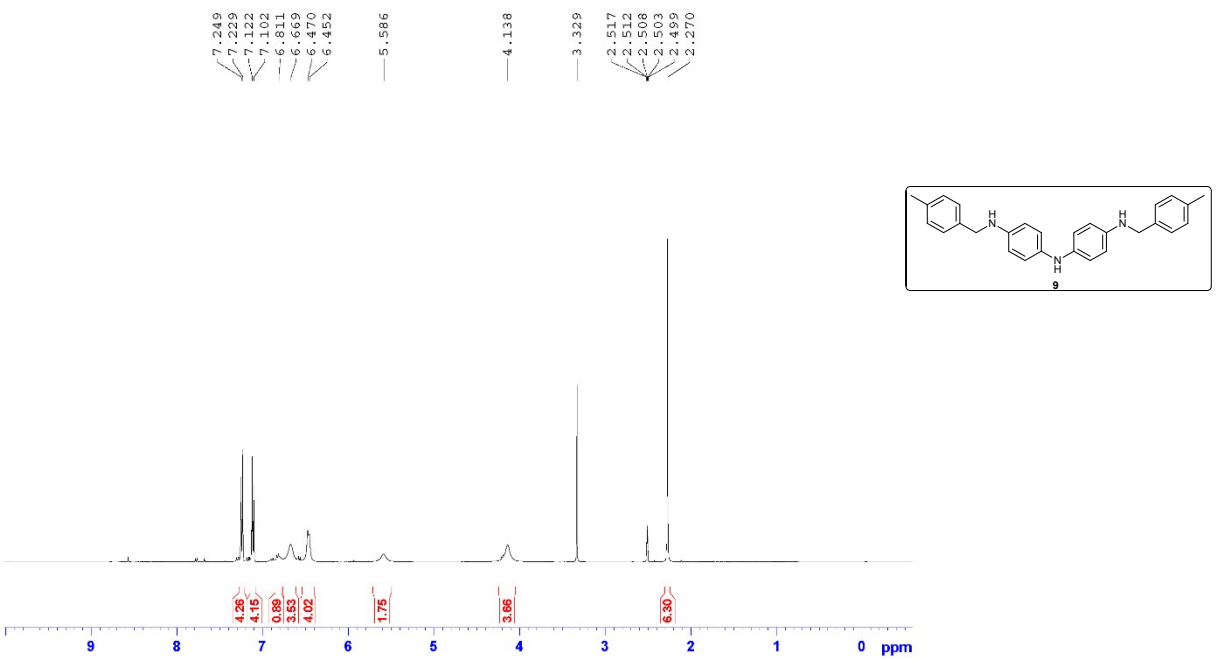

Figure S5 (A) [1]HNMR spectrum of compound **9** (PPD 5).

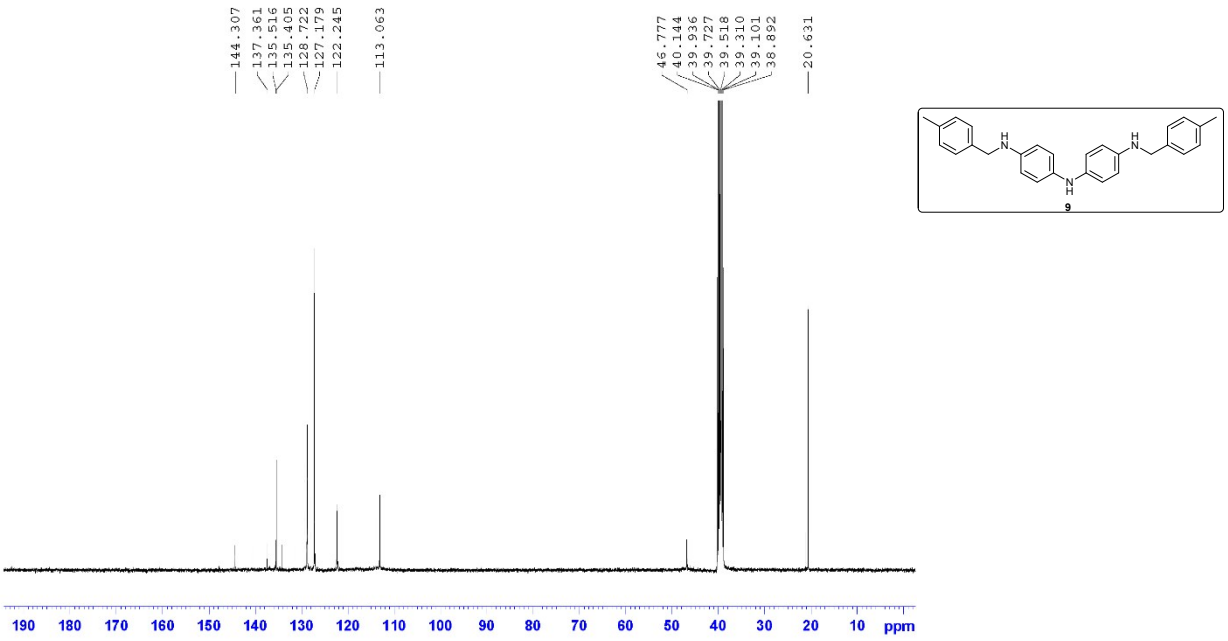

Figure S5 (B). ^{13}CNMR spectrum of compound **9** (PPD 5).

Mass Spectrum SmartFormula Report

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Comment	Dr Wu Jie		

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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
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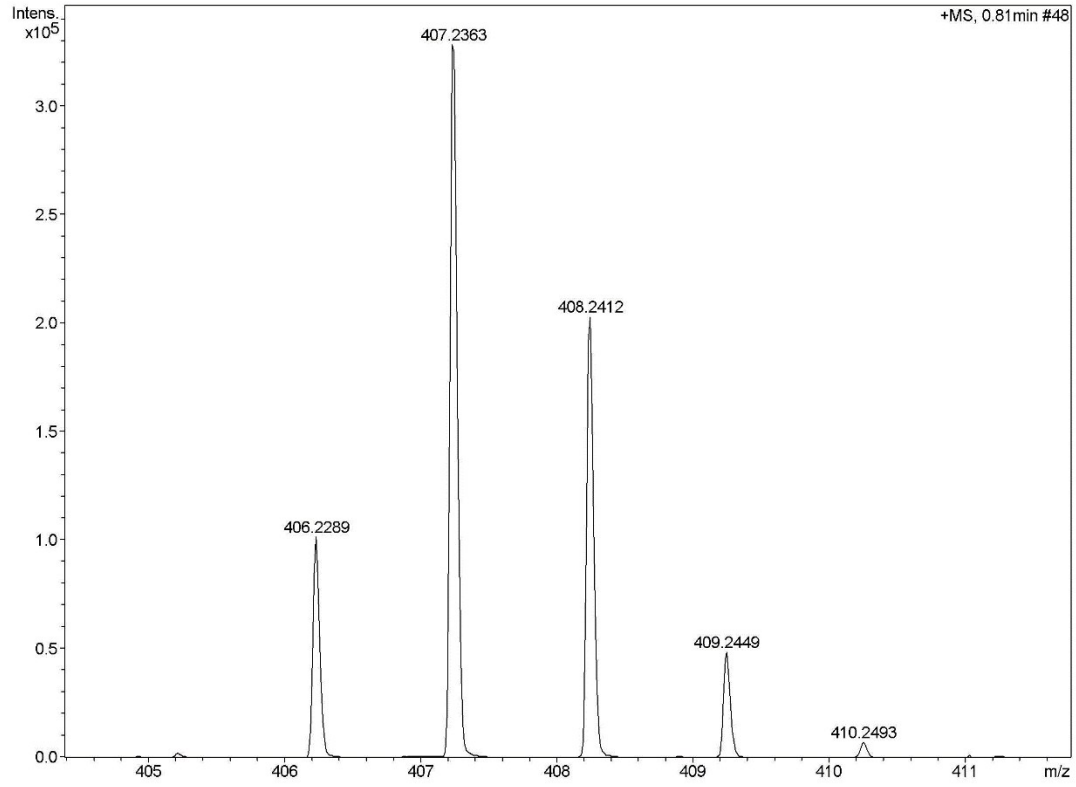

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Figure S5(C). HRMS spectrum of compound **9** (PPD 5).

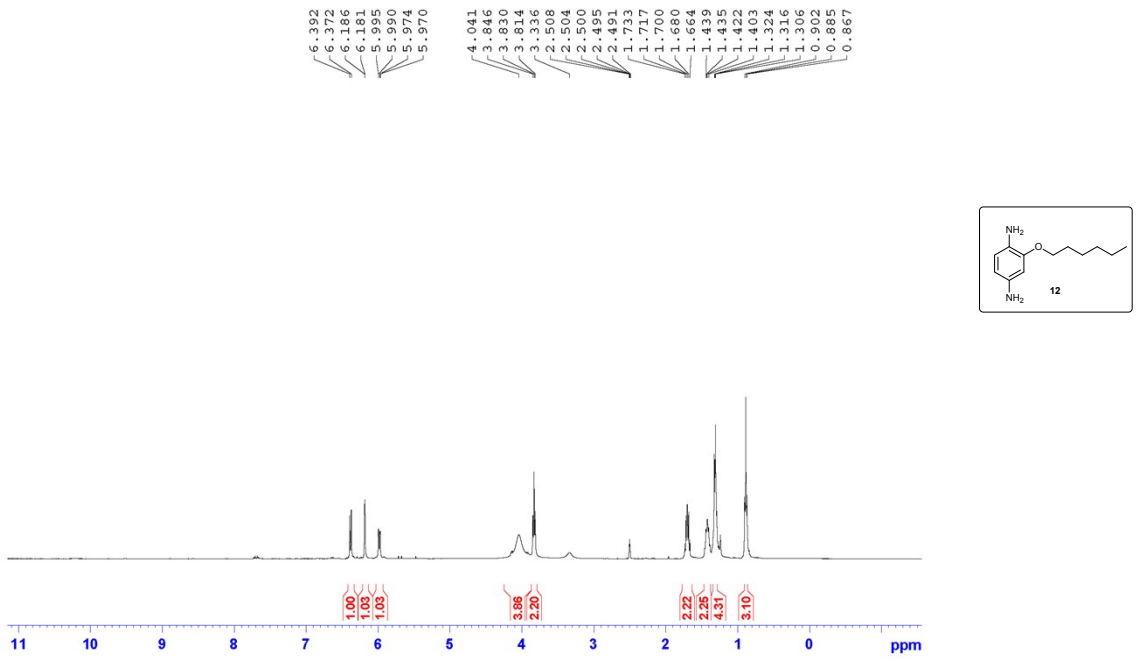

Figure S6 (A). [1]HNMR spectrum of compound **12** (PPD 6).

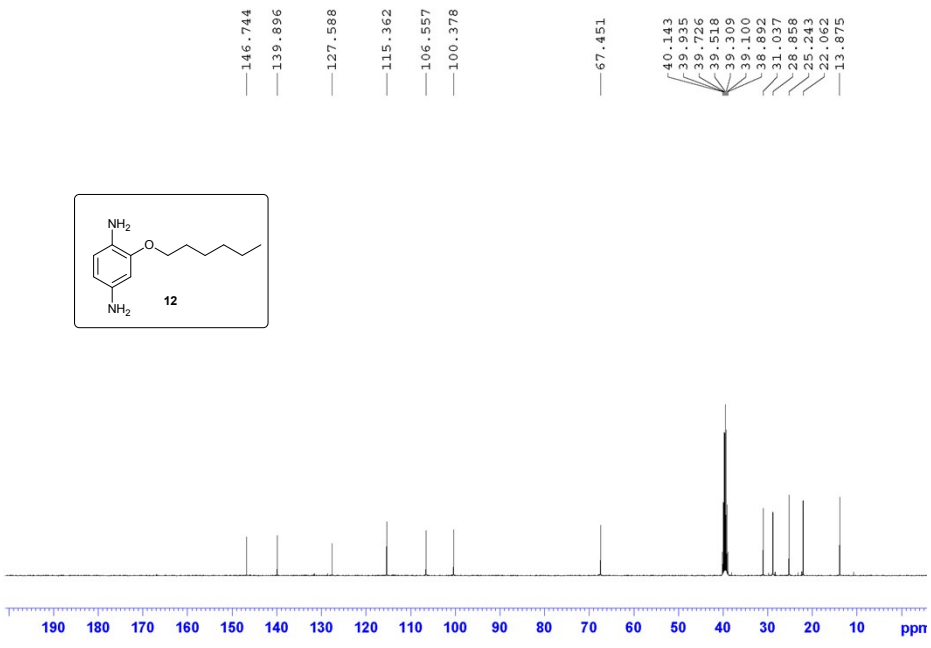

Figure S6 (B). [13]C NMR spectrum of compound **12** (PPD 6).

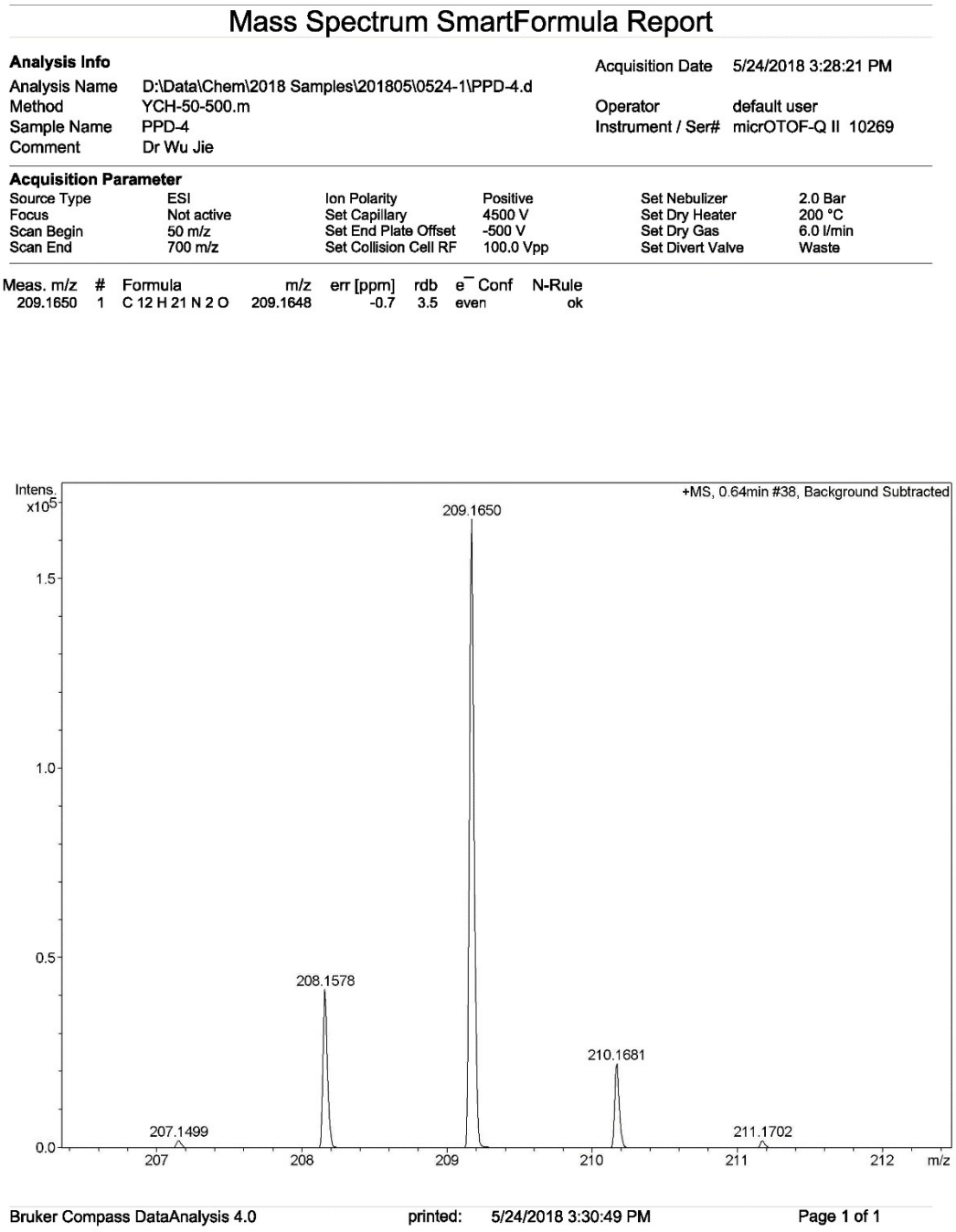

Figure S6(C). HRMS spectrum of compound **12** (PPD 6).

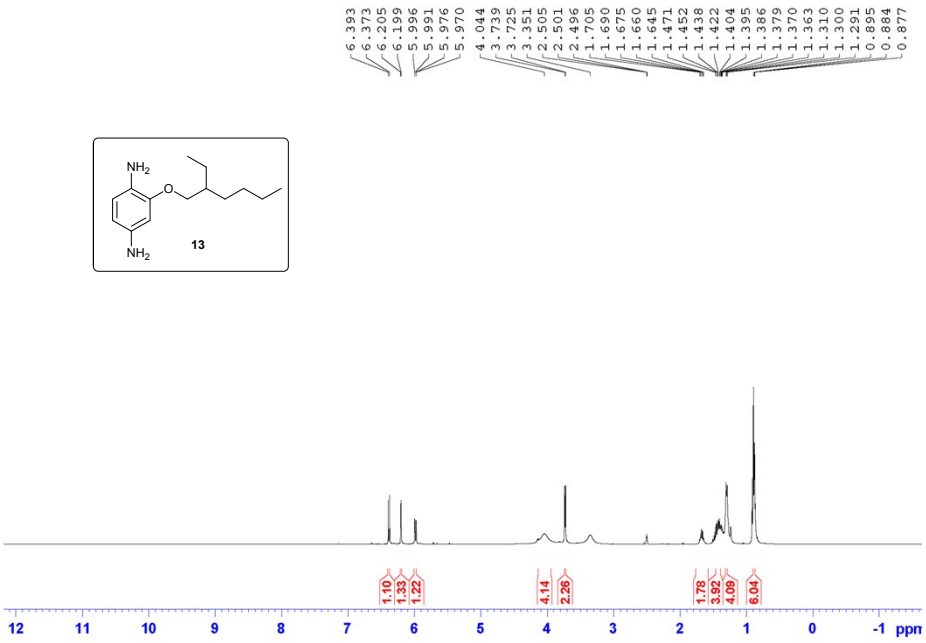

Figure S7 (A). [1]HNMR spectrum of compound **13** (PPD 7).

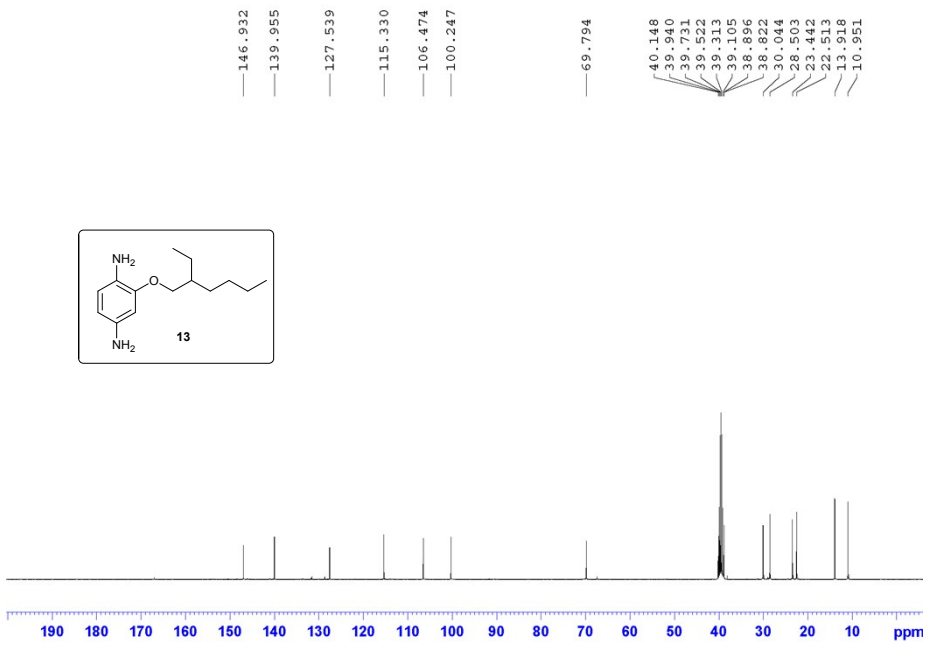

Figure S7 (B). [13]C NMR spectrum of compound **13** (PPD 7).

Mass Spectrum SmartFormula Report

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Comment	Dr Wu Jie		

Acquisition Parameter

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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
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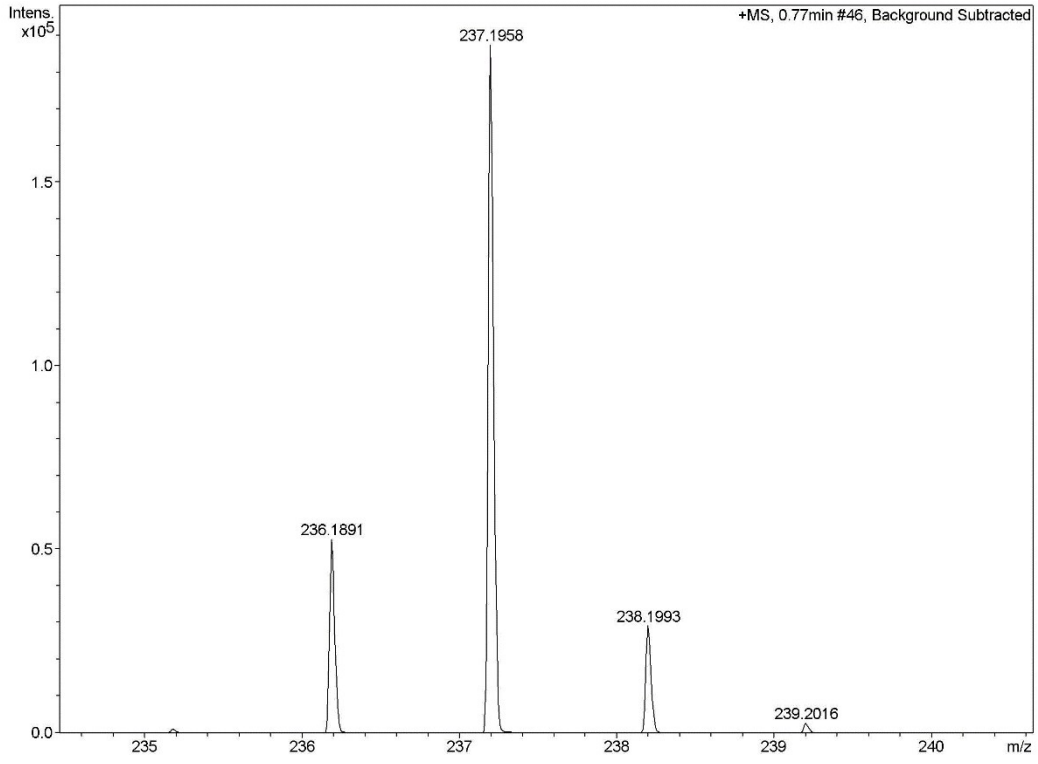

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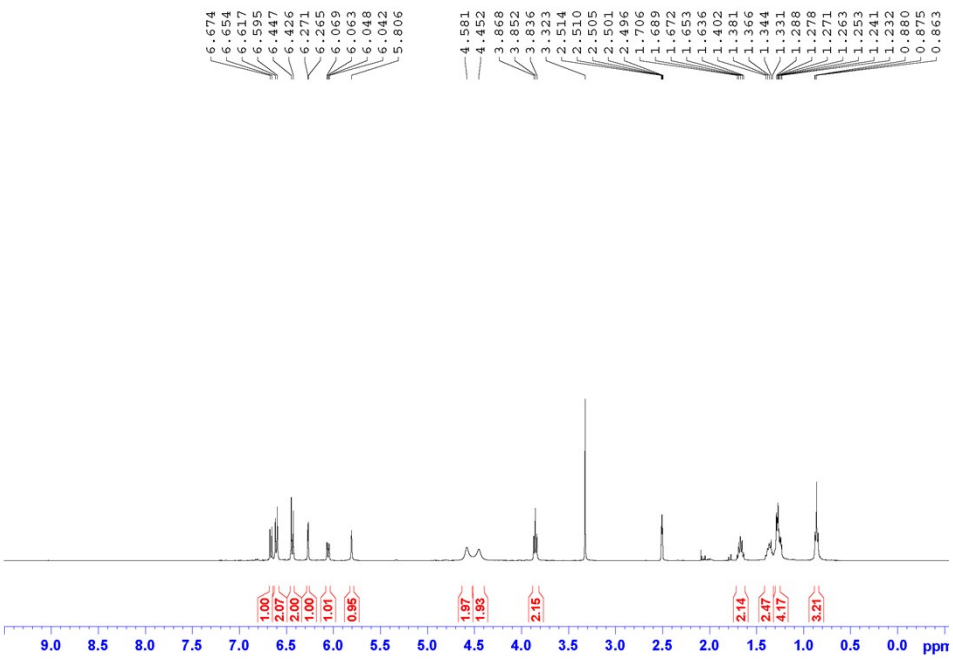
Figure S7(C). HRMS spectrum of compound **13** (PPD 7).



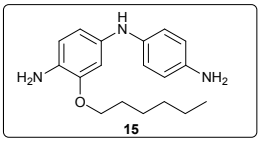
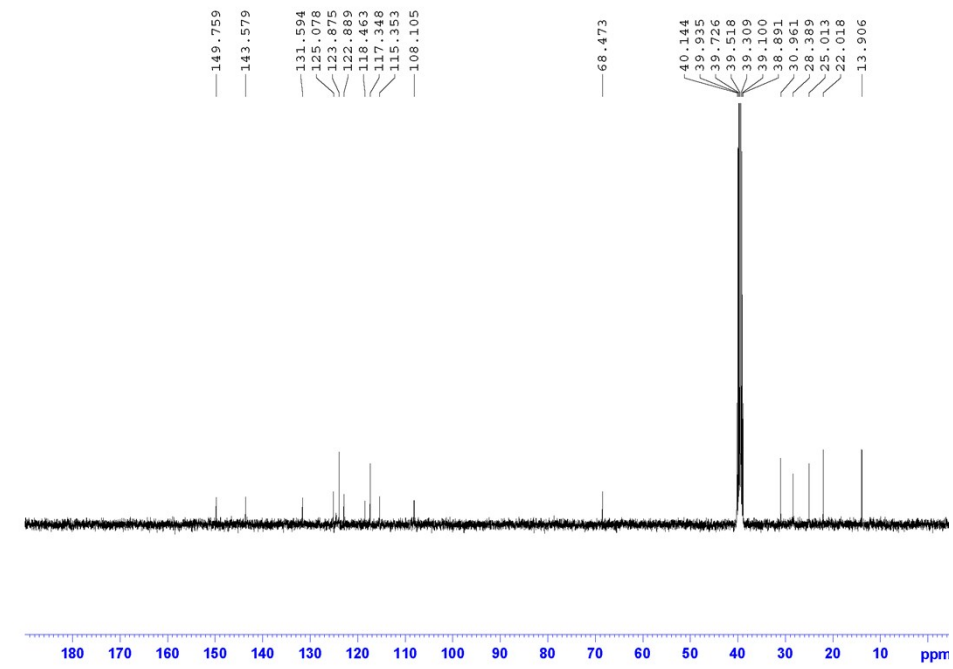


Figure S8 (A). [1]HNMR spectrum of compound **15** (PPD 8).



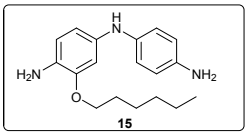


Figure S8 (B). [13]CNMR spectrum of compound **15** (PPD 8).

Mass Spectrum SmartFormula Report

Analysis Info

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Comment	Dr Wu Jie		

Acquisition Parameter

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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
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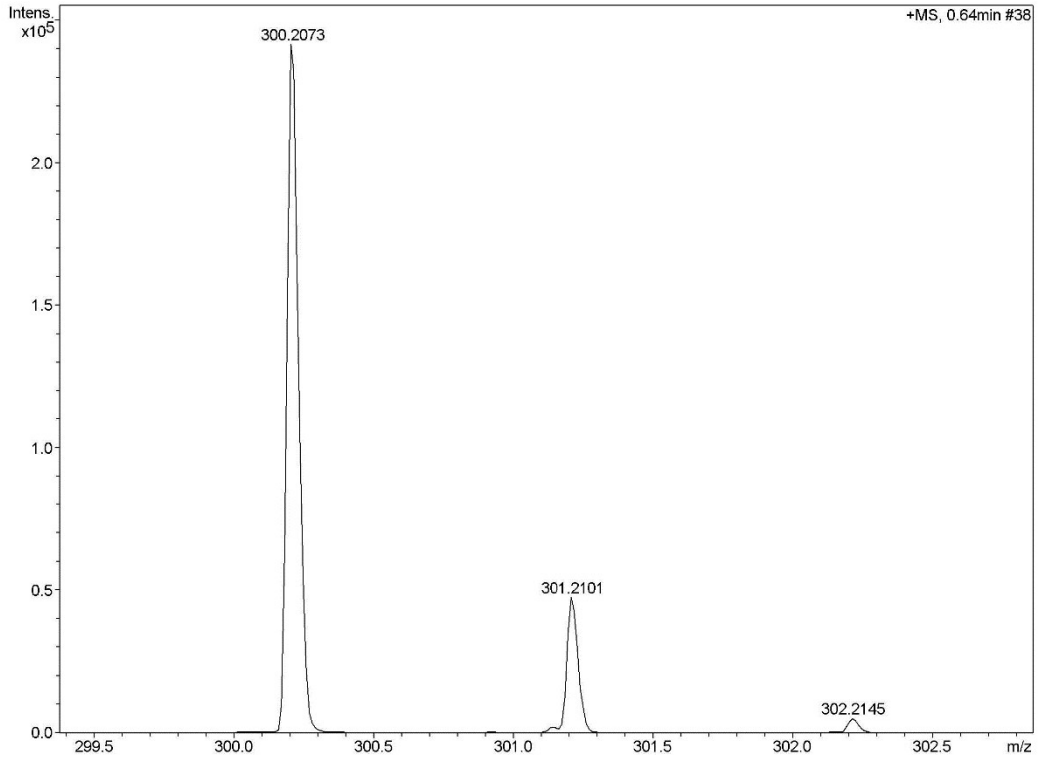

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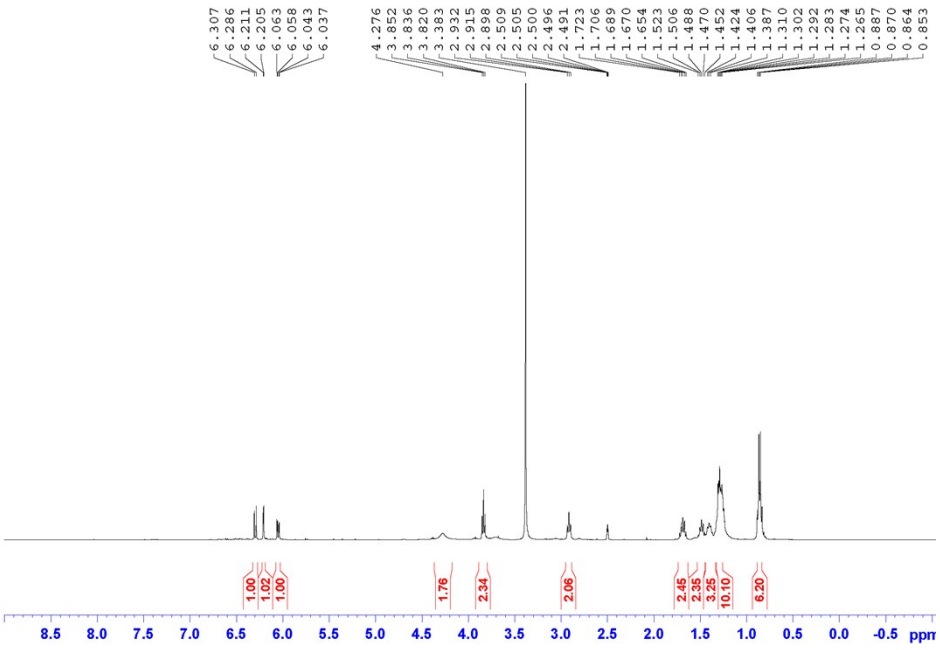
Figure S8(C). HRMS spectrum of compound **15** (PPD 8).



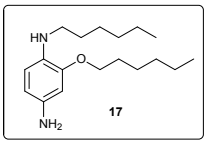


Figure S9 (A).[1]HNMR spectrum of compound **17** (PPD 9).

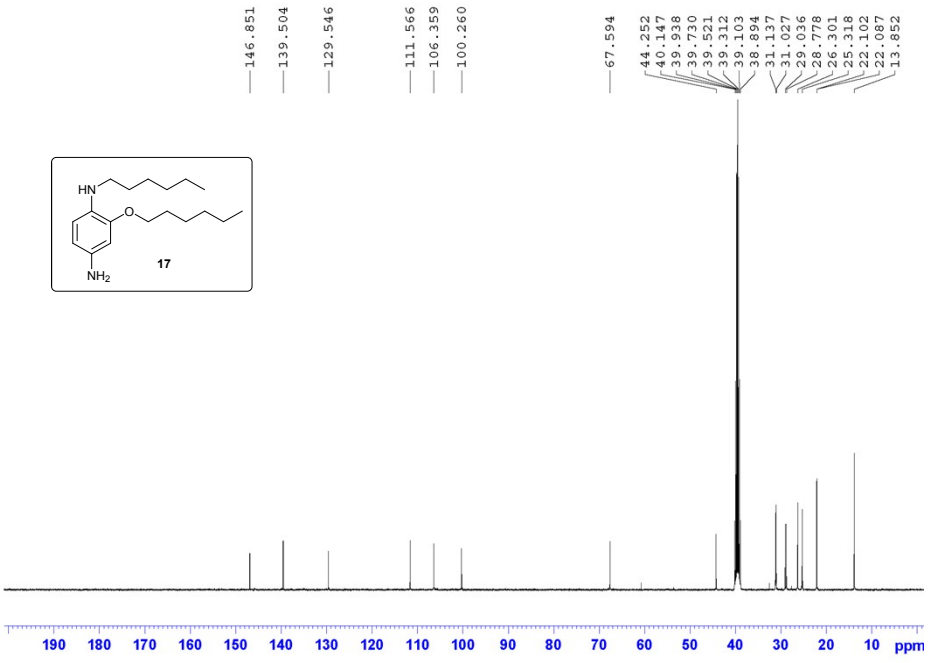


Figure S9 (B).[13]C NMR spectrum of compound **17** (PPD 9).

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	PPD-16	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	600 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
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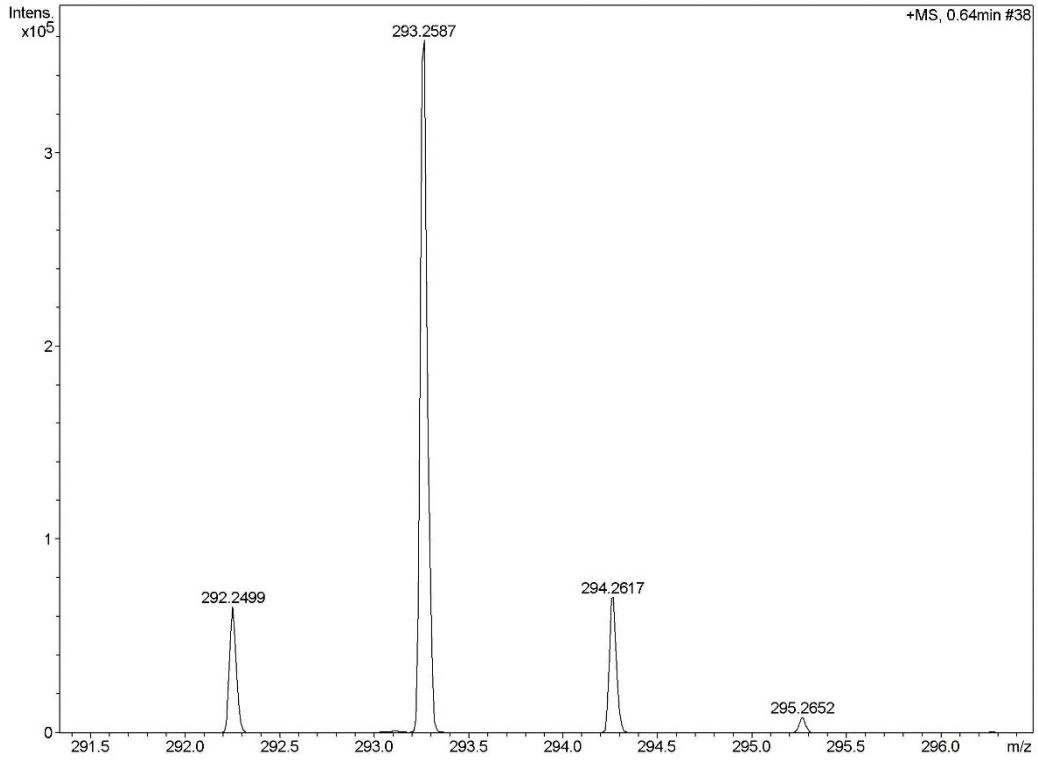

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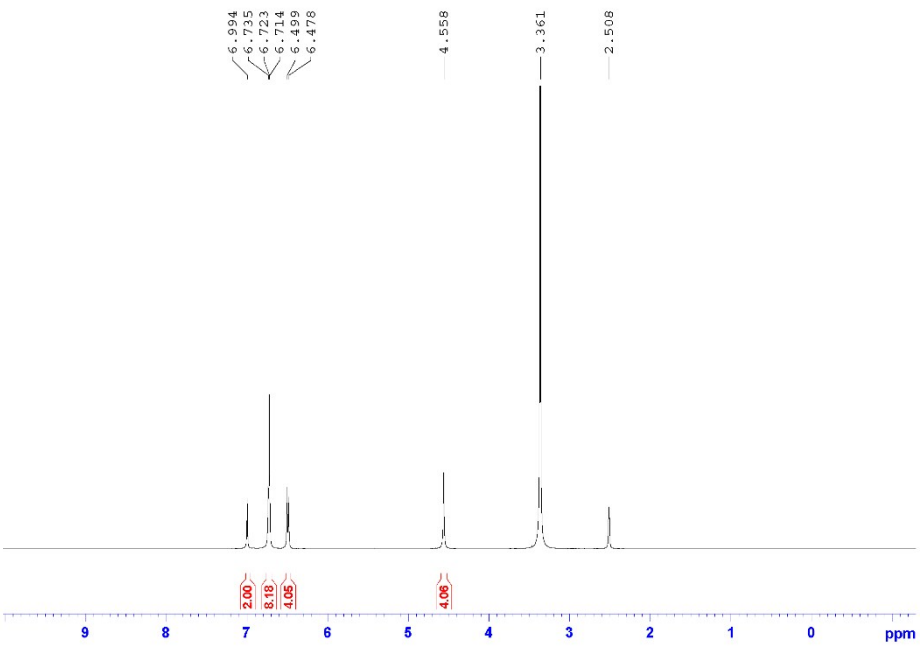
Figure S9(C). HRMS spectrum of compound **17** (PPD 9).



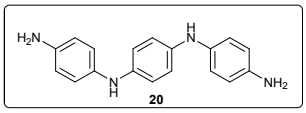
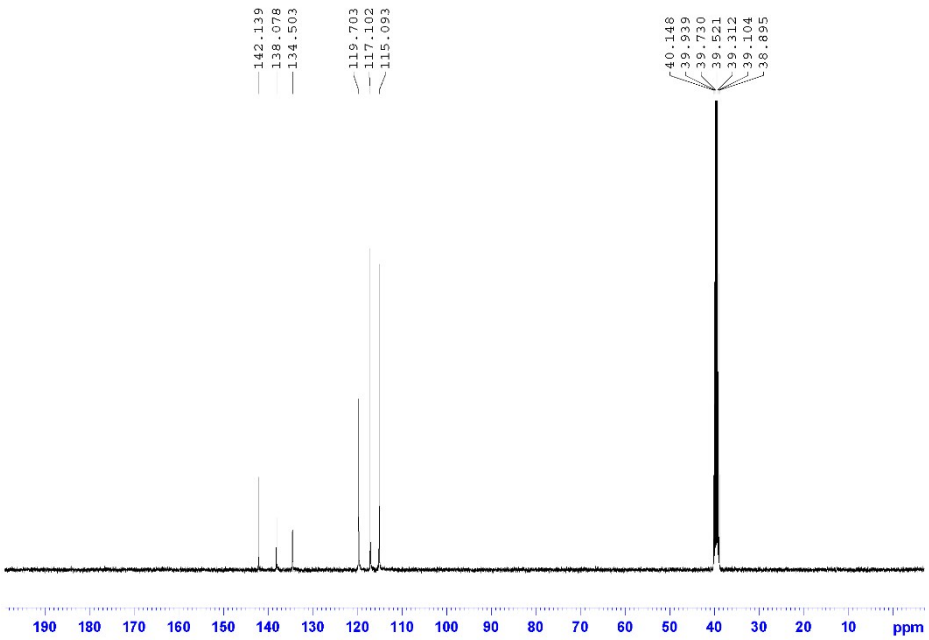


Figure S10 (A).[1]HNMR spectrum of compound **20** (PPD 10).



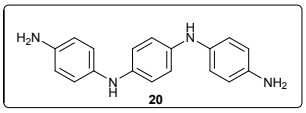


Figure S10 (B).[13]C NMR spectrum of compound **20** (PPD 10).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524-1\PPD-2.d	Acquisition Date	5/24/2018 3:12:47 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	PPD-2	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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
290.1518	1	C 18 H 18 N 4	290.1526	2.9	12.0	odd	ok

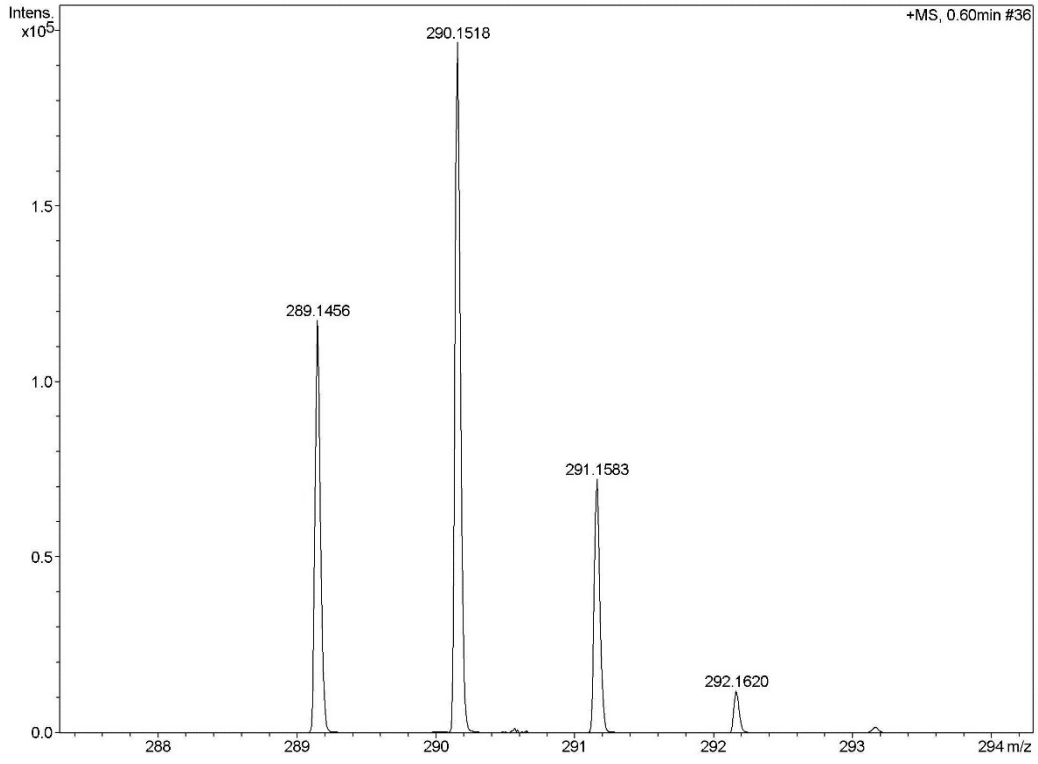


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Figure S10(C). HRMS spectrum of compound **20** (PPD 10).

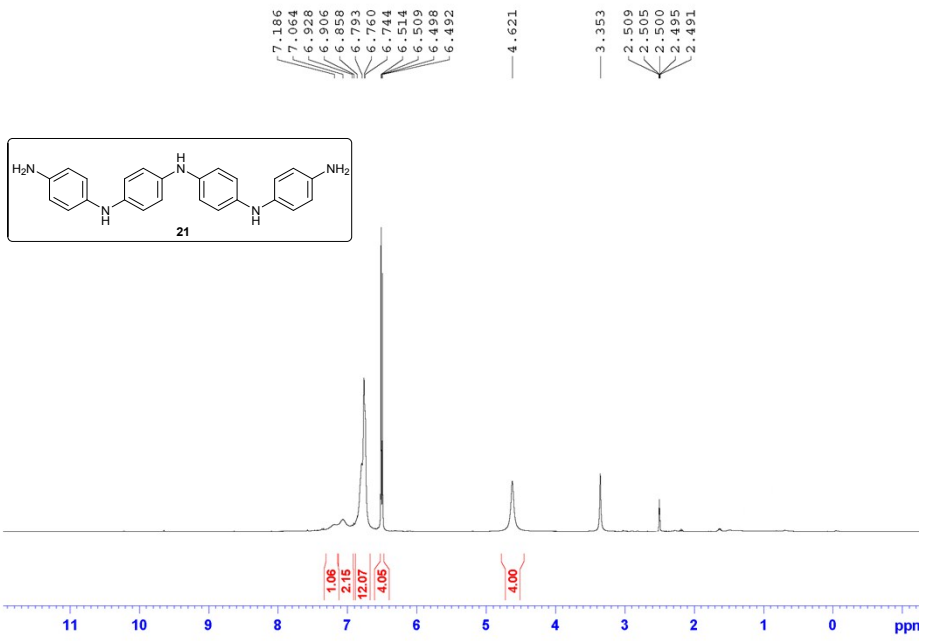

Figure S11 (A). [1]HNMR spectrum of compound **21** (PPD 11).

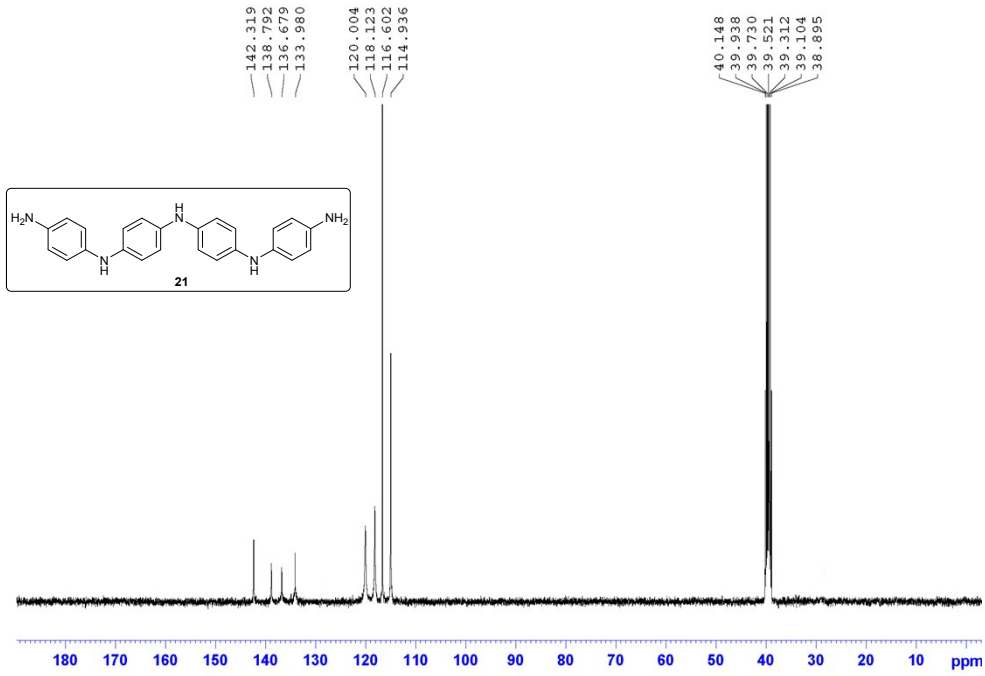

Figure S11 (B). [13]C NMR spectrum of compound **21**(PPD 11).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524-1\PPD-8.d	Acquisition Date	5/24/2018 3:58:07 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	PPD-8	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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
381.1952	1	C 24 H 23 N 5	381.1948	-1.2	16.0	odd	ok

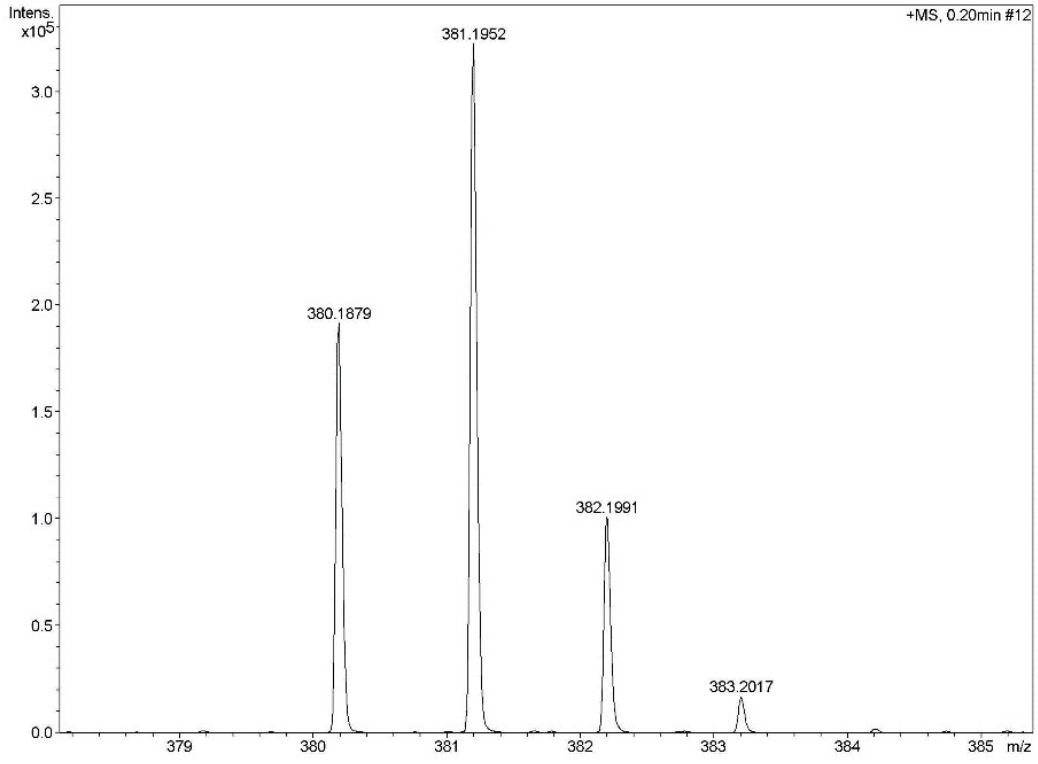

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Figure S11(C). HRMS spectrum of compound **21** (PPD 11).

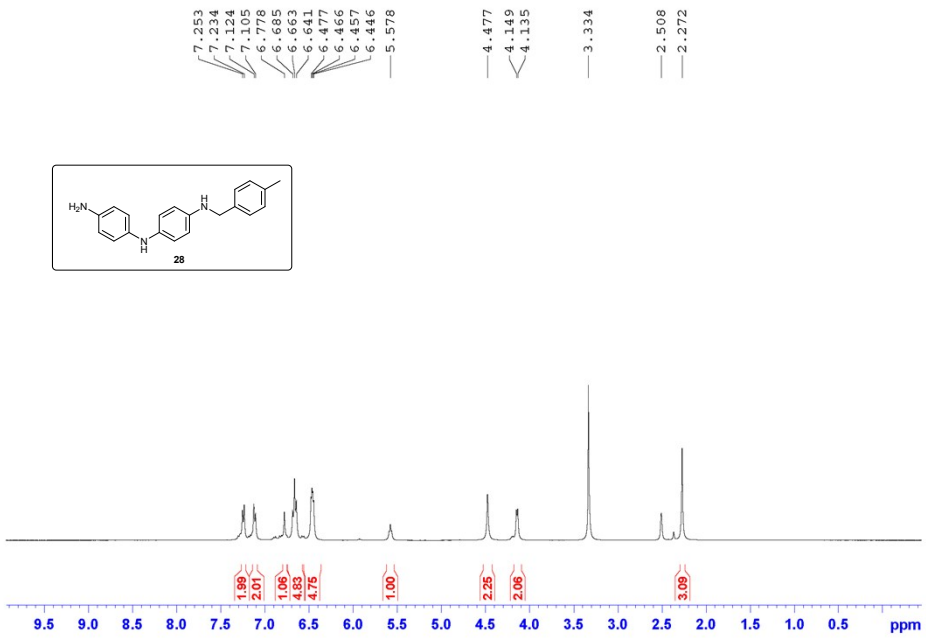
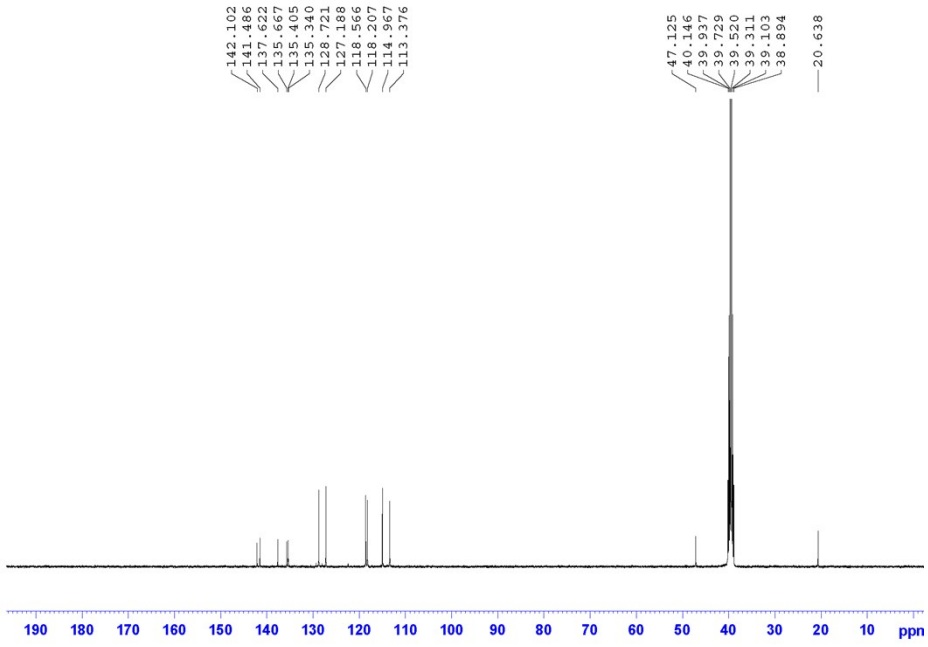


Figure S12 (A). [1]HNMR spectrum of compound **28** (PPD 12).



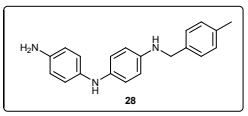


Figure S12 (B).[13]C NMR spectrum of compound **28** (PPD 12).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524-1\PPD-9.d	Acquisition Date	5/24/2018 4:17:00 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	PPD-9	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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
303.1731	1	C 20 H 21 N 3	303.1730	-0.4	12.0	odd	ok

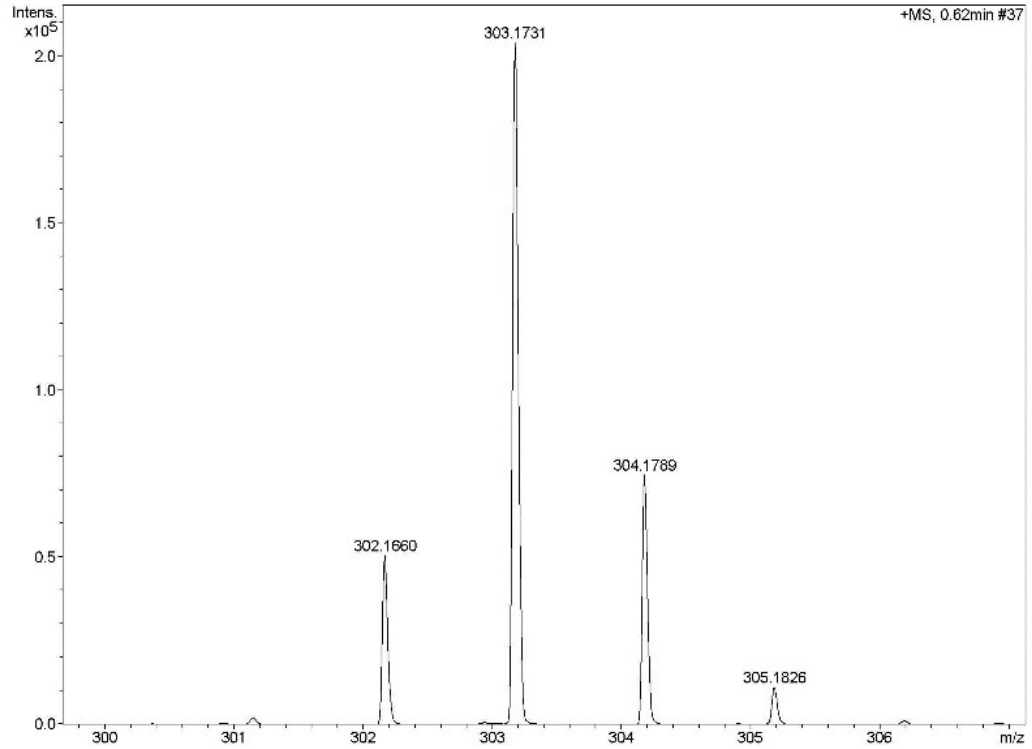


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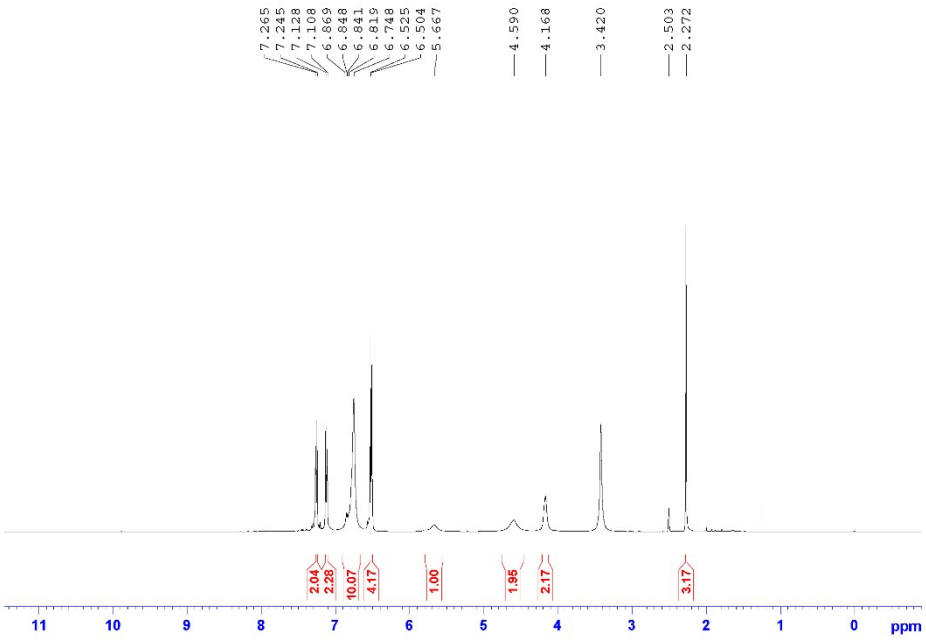
Figure S12(C). HRMS spectrum of compound **28**(PPD 12).



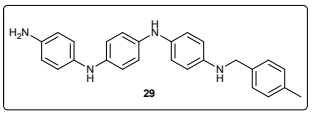


Figure S13 (A). [1]HNMR spectrum of compound **29** (PPD 13).

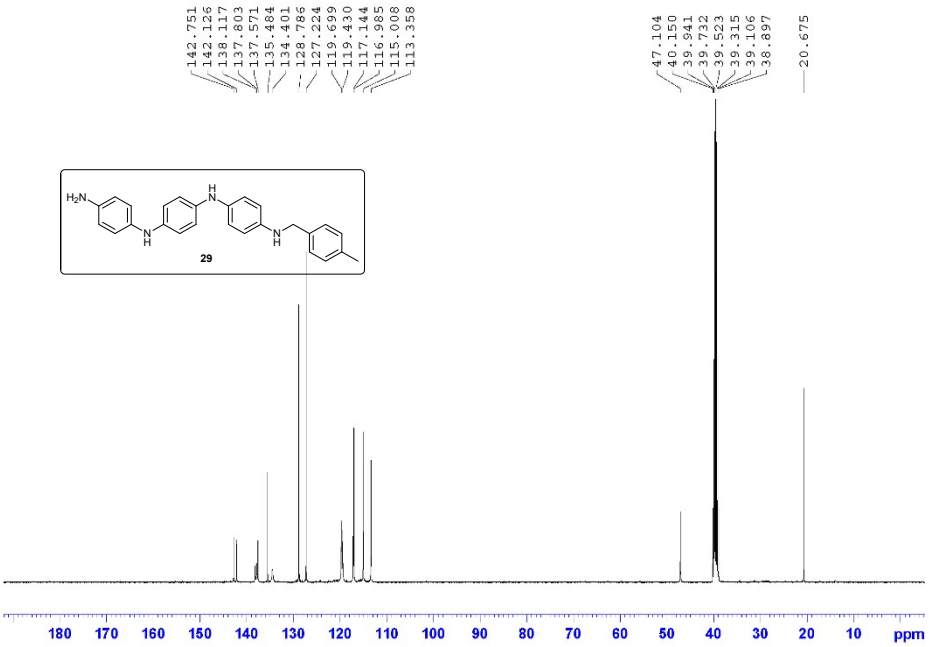


Figure S13 (B).[13]C NMR spectrum of compound **29** (PPD 13).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524-1\PPD-10.d	Acquisition Date	5/24/2018 4:21:55 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	PPD-10	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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
394.2157	1	C 26 H 26 N 4	394.2152	-1.3	16.0	odd	ok

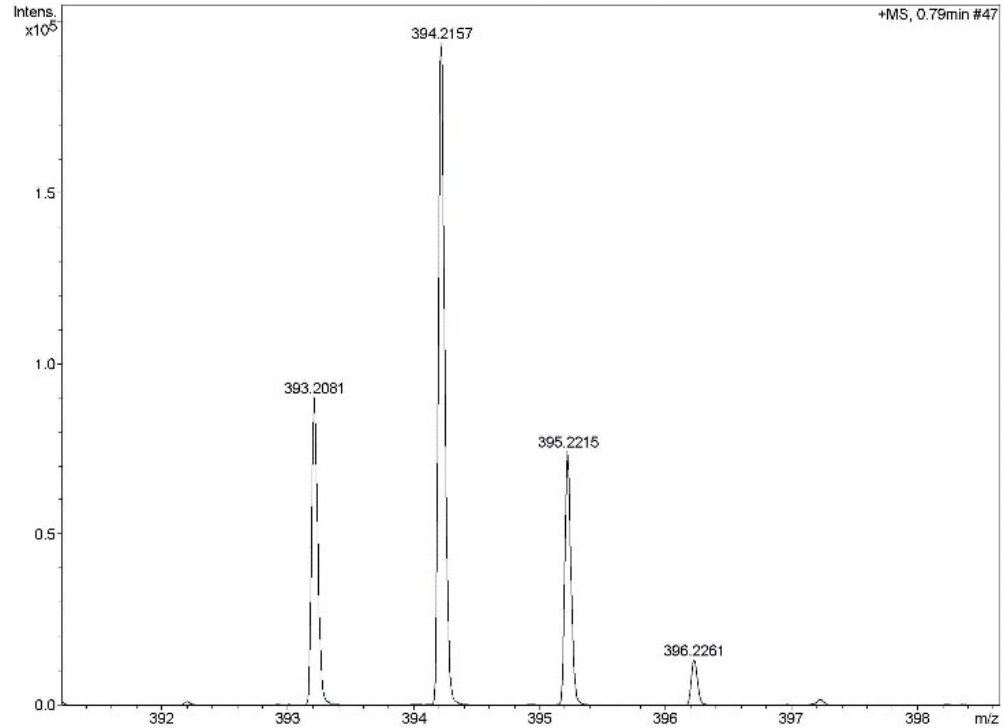


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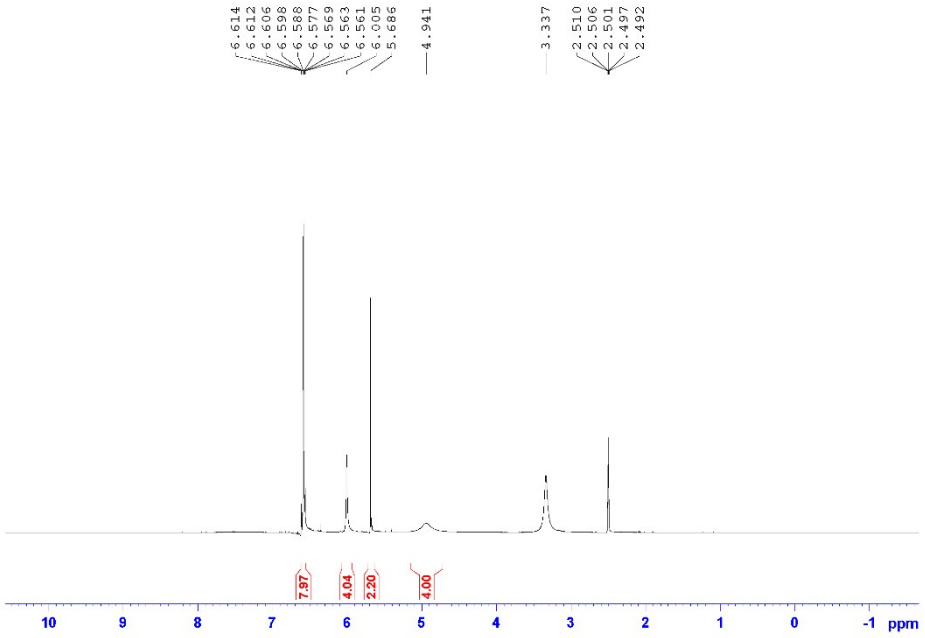
Figure S13(C). HRMS spectrum of compound **29**(PPD 13).



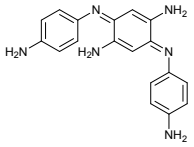
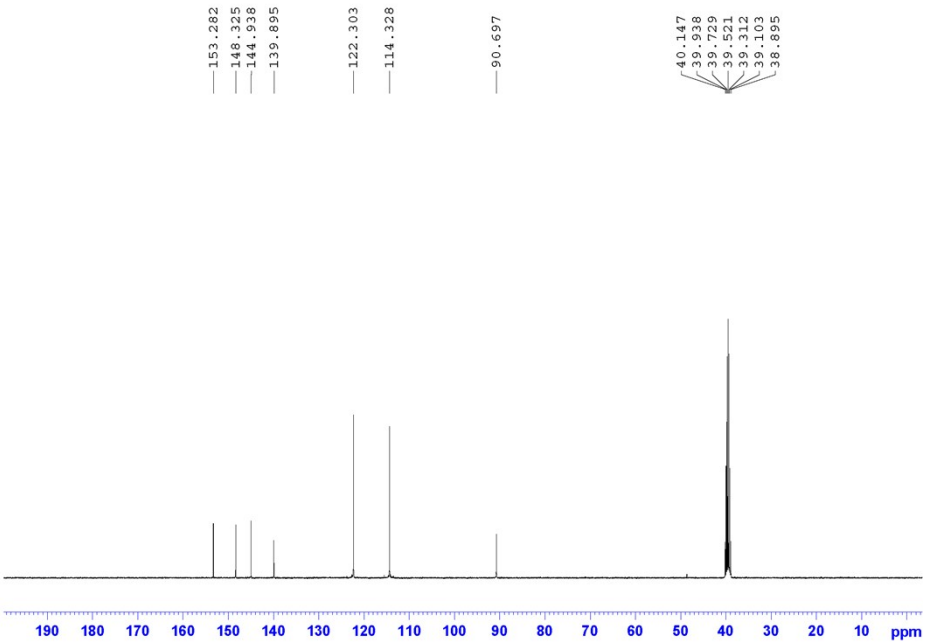


Figure S14 (A). [1]HNMR spectrum of Bandrowski's base.



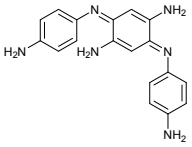


Figure S14 (B). [13]CNMR of spectrum of Bandrowski's base.

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chem\2018 Samples\201805\0524-1\BB.d	Acquisition Date	5/24/2018 4:59:38 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	BB	Instrument / Ser#	micrOTOF-Q II 10269
Comment	Dr Wu Jie		

Acquisition Parameter

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

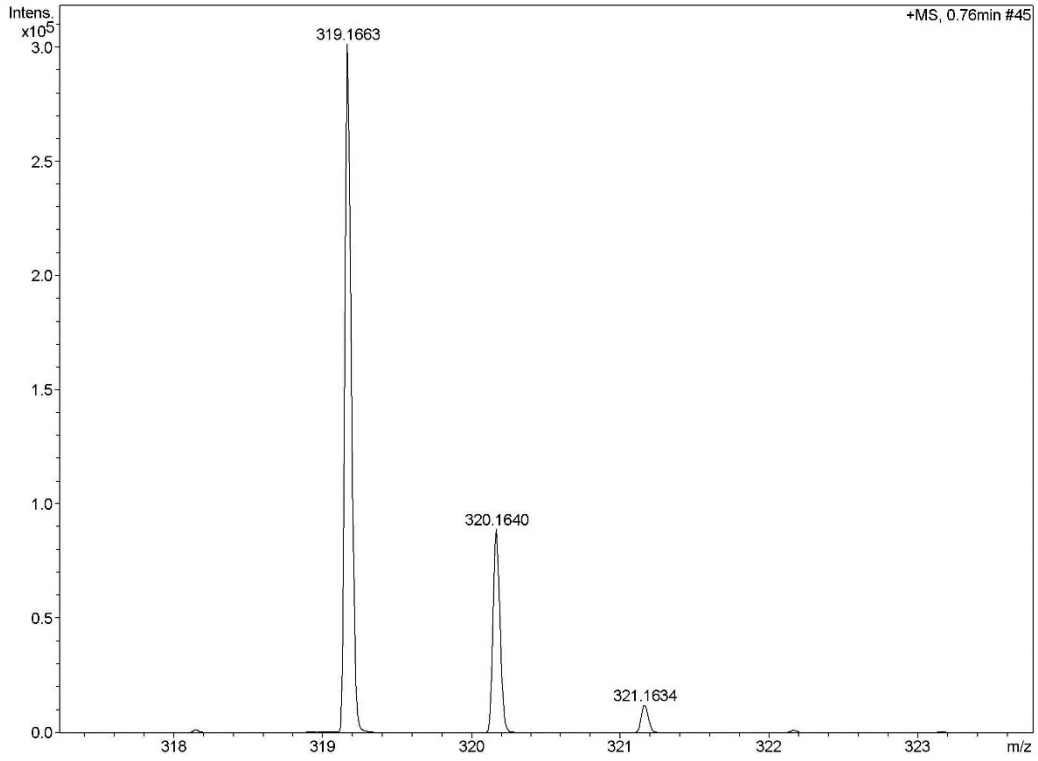


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Figure S14(C). HRMS spectrum of Bandrowski's base.

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)

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	a^*	a_0	b^*	b_0	ΔE	ΔH
	Natural hair		9		0		1		
PPD	A	57		0		30		56.1	29
	B	9		1		1		1	0
	C	14		1		3		5.5	2.2
PPD 1	A	9		1		1		1	1
	B	9		1		1		1	1
	C	9		1		1		1	1
PPD 6	A	16		7		0		9.9	7.1
	B	9		1		1		1	1
	C	13		6		2		7.3	6.1
PPD 7	A	17		13		2		15.3	13.0
	B	9		1		1		1	1
	C	9		1		1		1	1
PPD 8	A	9		0		1		0	0
	B	9		1		1		1	1
	C	11		1		2		2.4	1.4
PPD 10	A	22		4		1		13.6	4
	B	35		5		0		26.5	5.1
	C	49		8		8		41.4	10.6
PTD	A	58		0		30		56.9	29.0
	B	14		1		3		5.4	2.2
	C	9		1		1		1	0
ME-PPD	A	58		0		30		56.9	29.0
	B	15		1		3		6.3	2.2
	C	9		1		1		1	0

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

Derivatives	Week 1	**Δ*E***	**Δ*H***
PPD	A	56.1	29
	B	1	0
	C	5.5	2.2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.9	7.1
	B	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.4	1.4
PPD 10	A	13.6	4
	B	26.5	5.1
	C	41.4	10.6
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	Week 2	**Δ*E***	**Δ*H***
PPD	A	56.1	29
	B	1	0
	C	5.5	2.2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.9	7.1
	B	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.4	1.4
PPD 10	A	13.6	4
	B	26.5	5.1
	C	41.4	10.6
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	Week 3	**Δ*E***	**Δ*H***
PPD	A	56.1	29
	B	1	0
	C	5.5	2.2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.9	7.1
	B	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.4	1.4
PPD 10	A	13.6	4
	B	26.5	5.1
	C	41.4	10.6
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	Week 4	**Δ*E***	**Δ*H***
PPD	A	56.1	29
	B	1	0
	C	5.5	2.2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.9	7.1
	B	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.4	1.4
PPD 10	A	13.6	4
	B	26.5	5.1
	C	41.4	10.6
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	Month 1	**Δ*E***	**Δ*H***
PPD	A	56.1	29
	B	1	0
	C	5.5	2.2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.9	7.1
	B	1	1
	C	7.3	6.1
PPD 7	A	15.3	13.0
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.4	1.4
PPD 10	A	13.6	4
	B	26.5	5.1
	C	41.4	10.6
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	Month 2	**Δ*E***	**Δ*H***
PPD	A	55.2	28
	B	1	0
	C	5.2	2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.2	7
	B	1	1
	C	6.8	6
PPD 7	A	14.8	12.5
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.2	1.4
PPD 10	A	13.3	3.5
	B	26.1	5
	C	41.0	10
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0

Derivatives	**Month 3**	**Δ*E***	**Δ*H***
PPD	**A**	**55.2**	**28**
	B	**1**	**0**
	C	**5.2**	**2**
PPD 1	**A**	**1**	**1**
	B	**1**	**1**
	C	**1**	**1**
PPD 6	**A**	**9.2**	**7**
	B	**1**	**1**
	C	**6.8**	**6**
PPD 7	**A**	**14.8**	**12.5**
	B	**1**	**1**
	C	**1**	**1**
PPD 8	**A**	**0**	**0**
	B	**1**	**1**
	C	**2.2**	**1.4**
PPD 10	**A**	**13.3**	**3.5**
	B	**26.1**	**5**
	C	**41.0**	**10**
PTD	**A**	**56.9**	**29.0**
	B	**5.4**	**2.2**
	C	**1**	**0**
ME-PPD	**A**	**56.9**	**29.0**
	B	**6.3**	**2.2**
	C	**1**	**0**

Derivatives	Month 6	Δ***E***	Δ***H***
PPD	A	55.2	28
	B	1	0
	C	5.2	2
PPD 1	A	1	1
	B	1	1
	C	1	1
PPD 6	A	9.2	7
	B	1	1
	C	6.8	6
PPD 7	A	14.8	12.5
	B	1	1
	C	1	1
PPD 8	A	0	0
	B	1	1
	C	2.2	1.4
PPD 10	A	13.3	3.5
	B	26.1	5
	C	41.0	10
PTD	A	56.9	29.0
	B	5.4	2.2
	C	1	0
ME-PPD	A	56.9	29.0
	B	6.3	2.2
	C	1	0