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Synthesis of Mono- and Dialkylsubstituted 1,10-Phenanthrolines

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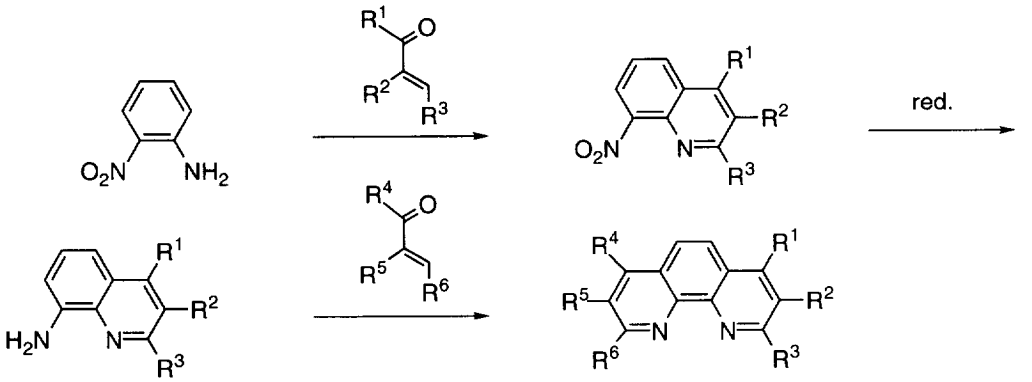
Abstract *:* Starting from o-anisidine, alkylated 8-hydroxyquinolines **2** and 8-aminoquinolines **3** were obtained. From the latter, dialkylsubstituted 1,10-phenanthrolines **5** have been prepared in good yields. Reaction of unsubstituted 8-aminoquinoline under the same conditions, yielded monoalkylated 1,10-phenanthrolines **4**.

INTRODUCTION

Substituted 1,10-phenanthrolines are known as important complexing agents in the analysis of transition metal ions, such as iron(II) and copper(I).[1] In recent years substituted 1,10–phenanthrolines have also been used in homogenous catalysis.[2] A large number of studies on supramolecular assemblies involving 1,10-phenanthroline derivatives, have been made over the last decade. For instance Sauvage prepared the "molecular knot" , Chandler studied crown-ether substituted derivatives, while others have used 1,10-phenanthroline functions in enzyme mimics.[3] Additionally substituted Fe/Ru/Os-phenanthroline complexes have been investigated as potential electron and energy transfer species.[4] An excellent review over the uses and properties of 1,10-phenanthrolines and derivatives has been written by Sammes and Yahioglu.[5]

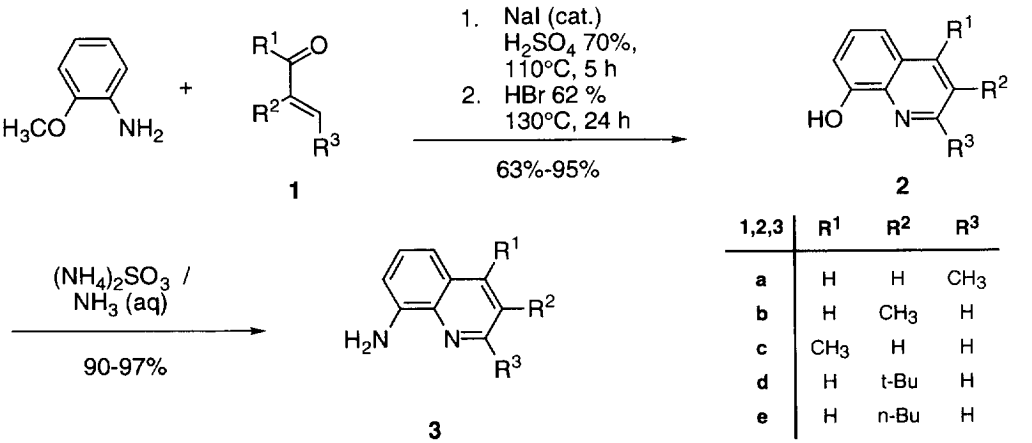
Case and co-workers prepared disubstituted 1,10-phenanthrolines by a three-step synthesis.[6] Condensation of an α,β-unsaturated ketone or aldehyde with o-nitroaniline and reduction of the resulting 8-nitroquinoline gave a monosubstituted 8-aminoquinoline. Condensation of the latter with a second α,β-unsaturated ketone or aldehyde yielded the disubstituted 1,10–phenanthroline, using arsenic acid as the oxidizing agent for the condensations. However, the overall yields for the procedure were generally very low (Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

Recently O'Murchu showed an easy way to condense 3-substituted quinolines from anilines and 2-substituted acroleins with sodium iodide as catalyst.[7] Unfortunately attempts to prepare substituted 8-nitroquinolines under the same conditions proved unsuccessful. Consequently p-anisidine was used to synthesize substituted 8-hydroxyquinolines **2** (Scheme 2).



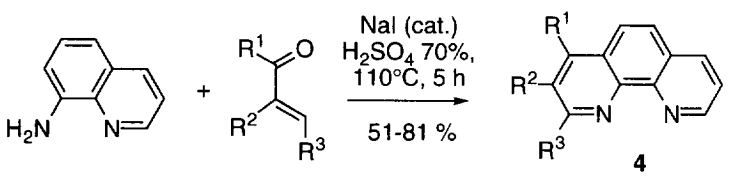
1 **2** **3**

1,2,3	R1	R2	R3
a	H	H	CH_3
b	H	CH_3	H
c	CH_3	H	H
d	H	t-Bu	H
e	H	n-Bu	H

Scheme 2

To examine the generality of this procedure, a series of 2-, 3- and 4-substituted 8–hydroxyquinolines **2** were prepared with unsaturated carbonyl compounds **1** in good yields. The 8–hydroxyquinolines **2** were then transformed to the desired 8–aminoquinolines **3** by the Bucherer reaction[8] in excellent yields.

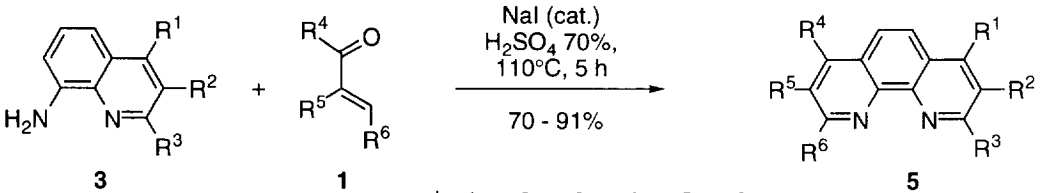
The synthesis of substituted 1,10-phenanthrolines under the condensation conditions described above were subsequently attempted. 2-, 3- and 4-monomethyl-substituted 1,10-phenanthrolines **4** (Scheme 3) can be prepared from commercially available 8–aminoquinoline and crotonic aldehyde **1a**, methacrolein **1b** or methylvinylketone **1c** respectively.



4	R1	R2	R3	Yield (%)
a	H	H	CH_3	55
b	H	CH_3	H	81
c	CH_3	H	H	51

Scheme 3

Similarly a series of disubstituted 1,10-phenanthrolines can be synthesized using the appropriate substituted 8-aminoquinolines and by varying the carbonyl functionalized reagent **1**. Both, symmetrically and unsymmetrically substituted 1,10-phenanthrolines were prepared in yields of up to 70% (Scheme 4). With 8-aminoquinolines **3d** and **3e**, poor solubility was overcome using additional solvent (H_2SO_4 70%). However, working under more dilute conditions decreases the yields dramatically.



5	R1	R2	R3	R4	R5	R6	Yield (%)
a	H	H	CH_3	CH_3	H	H	75
b	H	CH_3	H	H	H	CH_3	70
c	H	CH_3	H	H	CH_3	H	81
d	H	CH_3	H	CH_3	H	H	70
e	H	t-Bu	H	H	t-Bu	H	82
f	H	n-Bu	H	H	n-Bu	H	70
g	H	t-Bu	H	H	CH_3	H	91

Scheme 4

EXPERIMENTAL

^1H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded in $CDCl_3$ on a Varian Gemini 300, using solvent as the internal standard. Chemical shifts are reported in ppm on the δ scale. Mass spectral data were obtained with a VG Instruments 7070E mass spectrometer. The melting points were measured on a Büchi 520 and are uncorrected. All reagents and solvents were obtained from either Fluka Chemie AG or Aldrich and unless otherwise stated used as supplied. 2-tert-Butylacrolein **1d** was prepared by the method of Fujii.[9]

8-Hydroxyquinolines 2a-e, General Procedure :

The unsaturated carbonyl compound **1** (40 mmol) was added over 5 h to a stirred solution of o-anisidine (2.96 g, 24 mmol) and NaI (0.035 g, 0.23 mmol) in H_2SO_4 70% (8.7 ml, 100 mmol) at 110°C. After 1 h at 110 °C the dark brown reaction mixture was cooled to r. t. , poured into 1 M Na_2CO_3 (150 ml) and extracted with CH_2Cl_2 (**2a-2c**, 3 x 100 ml) or diethyl ether (**2d+2e**, 3 x 100 ml). The combined organic layers were extracted with 12 M HCl (5x40 ml), the acidic solution was neutralized (3 M NaOH and 1 M Na_2CO_3) and extracted with CH_2Cl_2. Removal of the solvent in vacuo afforded a brown oil. HBr 62% (50 ml) was added and the resulting mixture refluxed for 30 h, cooled and neutralized (3 M NaOH and 1 M Na_2CO_3) . The yellow suspension was extracted with CH_2Cl_2 (3 x 100 ml) and the combined organic layers dried, treated with charcoal and filtered through silica gel. The silica gel was rinsed with additional CH_2Cl_2 until no product was detectable in the eluent by TLC. Removal of the solvent in vacuo affords the quinolinols in good yields (Table 1) as yellow solids.

Table 1. Yields and Spectroscopic Data of the Prepared 8-Hydroxyquinolines **2** (Scheme 2)

Com-pound	Sub-strate **1**	Yield (%)	mp / (°C) (Lit)	^{1}H NMR ($CDCl_3$ / TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$ / TMS) δ	MS (70 eV) *m/z* (%)
2a	**1a**	95	73-75 (72-73)[10]	2.71 (s, 3H), 7.13 (d, J = 7.3, 1H), 7.22-7.30 (m, 2H), 7.32-7.41 (m, 1H), 8.00 (d, J = 8.5, 1H)	156.8, 151.6, 137.5, 136.1, 126.6, 126.5, 122.6, 117.5, 109.8, 24.8	159 (M^+,100), 131 (73)
2b	**1b**	88	111-114 (112-113)[11]	2.51 (s, 3H), 7.10 (d, J = 7.5, 1H), 7.22-7.25 (m, 1H) 7.38-7.43 (m, 1H), 7.90 (d, J = 1.0, 1H), 8.61 (d, J = 2.0, 1H)	152.2, 149.7, 136.6, 134.8, 131.2, 128.4, 127.7, 117.2, 109.2, 18.7	159 (M^+,100), 131 (82)
2c	**1c**	86	135-137 (138-140)[12]	2.68 (s, 3H), 7.12-7.28 (m, 2H), 7.43-7.45 (m, 2H), 8.61 (d, J = 4.4, 1H)	152.5, 147.3, 144.9, 138.0, 128.4, 127.2, 122.4, 114.0, 109.6, 18.7	159 (M^+,100), 131 (77)
2d	**1d**	67	74-75	1.44 (s, 9H), 7.10 (d, J = 7.5, 1H), 7.28 (d, J = 8.3, 1H) 7.39-7.44 (m, 1H), 8.03 (d, J = 2.3, 1H), 8.88 (d, J = 2.3, 1H)	151.9, 147.3, 144.2, 136.1, 131.1, 128.1, 127.7, 117.7, 109.3, 33.8, 30.9	201 (M^+, 70), 186 (100), 158 (32)[a]
2e	**1e**	91	73-77	0.95 (t, J = 7.3, 3H), 1.33-1.46 (m, 2H), 1.64-1.73 (m, 2H), 2.79 (t, J = 8.0, 2H), 7.10 (d, J = 7.5, 1H), 7.25 (d, J = 8.1, 1H) 7.38-7.43 (m, 1H), 7.89 (d, J = 2.0, 1H), 8.62 (d, J = 2.0, 1H)	152.2, 149.5, 136.8, 136.2, 134.3, 128.5, 127.7, 117.4, 109.3, 33.2, 32.9, 22.2, 13.8	201 (M^+, 100), 158 (80), 130 (59)[b]

[a] HRMS for **2d** : $C_{13}H_{15}NO$ calcd : 201.1154 found : 201.1162
[b] HRMS for **2e** : $C_{13}H_{15}NO$ calcd : 201.1154 found : 201.1161

8-Aminoquinolines 3a-e, General Procedure :

2 (10 mmol (**2a-2c**) or 5 mmol (**2d+2e**)), ammonium sulfite monohydrate $(NH_4)_2SO_3 \cdot H_2O$ (6.7 g, 20 mmol) and ammonia solution 32% (9 ml) were added to a teflon coated autoclave (23 ml capacity, Parr Instrument Company). The mixture was heated at 170°C for 2 days (**2a-2c**) or 7 days (**2d+2e**). After cooling the autoclave was rinsed with water and CH_2Cl_2. The CH_2Cl_2 was separated and the aqueous layer washed twice with CH_2Cl_2 (50 ml). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo. Yields and analytical data are given in Table 2.

Table 2. Yields and Spectroscopic Data of the Prepared 8-Aminoquinolines **3** (Scheme 2)

Compound	Substrate **2**	Yield (%)	mp / (°C) (Lit)	^{1}H NMR ($CDCl_3$ / TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$ / TMS) δ	MS (70 eV) *m/z* (%)
3a	**2a**	95	51-52 (56)[13]	2.71 (s, 3H), 5.0 (bs, 2H), 6.89 (d, J = 7.4 , 1H), 7.11 (d, J = 8.2, 1H), 7.19-7.30 (m, 1H), 7.92 (d, J = 8.3, 1H)	156.0, 143.4, 137.8, 136.0, 126.9, 126.3, 122.1, 115.8, 110.1, 25.2	158 (M^+,100), 131 (22)
3b	**2b**	97	58-60 (70-71)[14]	2.47 (s, 3H), 4.9 (bs, 2H), 6.84 (d, J = 7.5, 1H), 7.05 (d, J = 8.1, 1H) 7.25-7.31 (m, 1H), 7.81 (d, J = 1.0, 1H), 8.59 (d, J = 2.0, 1H)	149.2, 143.8, 136.7, 134.7, 130.6, 128.6, 127.4, 115.4, 109.2, 18.6	158 (M^+,100), 130 (29)
3c	**2c**	96	80-81 (84)[15]	2.62 (s, 3H), 5.0 (bs, 2H), 6.90 (d, J = 7.1, 1H), 7.17 (d, J = 4.4, 1H), 7.24-7.36 (m, 2H), 8.60 (d, J = 4.4, 1H)	146.9, 144.4, 144.2, 138.0, 128.8, 127.0, 122.1, 112.0, 109.9, 18.9	158 (M^+,100), 131 (23)
3d	**2d**	90	50-53	1.43 (s, 9H), 6.86 (d, J = 7.5, 1H), 7.11 (d, J = 8.1, 1H) 7.24-7.33 (m, 1H), 7.96 (d, J = 2.4, 1H), 8.86 (d, J = 2.4, 1H)	146.9, 143.6, 143.4, 136.5, 130.8, 128.4, 127.3, 115.9, 109.4, 33.7, 30.9	200 (M^+, 70), 185 (100), 157 (28)[a]
3e	**2e**	93	oil	0.94 (t, J = 7.3, 3H), 1.32-1.45 (m, 2H), 1.63-1.73 (m, 2H), 2.76 (t, J = 8.0, 2H), 5.0 (bs, 2H), 6.85 (d, J = 7.4, 1H), 7.08 (d, J = 8.2, 1H) 7.26-7.32 (m, 1H), 7.81 (d, J = 2.1, 1H), 8.60 (d, J = 2.1, 1H)	148.8, 143.7, 136.7, 135.5, 134.3, 128.7, 127.4, 115.5, 109.3, 33.2, 32.8, 22.2, 13.8	200 (M^+, 84), 157 (100), 130 (28)

a	HRMS for **3d**	:	$C_{13}H_{16}N_2$	calcd :	200.1313	found :	200.1313
b	HRMS for **3e**	:	$C_{13}H_{16}N_2$	calcd :	200.1313	found :	200.1324

Mono- and Dialkylsubstituted 1,10-Phenanthrolines 4a-c, 5a-g, General Procedure :

The unsaturated carbonyl compound **1** (40 mmol) was added over 5 h to a stirred solution of the 8-aminoquinoline **3** (24 mmol) and NaI (0.035 g, 0.23 mmol) in H_2SO_4 70% (8.7 ml, 100 mmol) at 110°C (In the case of **3d** and **3e** further H_2SO_4 70% was added until the mixture dissolved). After 1 h at 110°C the dark brown reaction mixture was cooled to r. t. , poured into 1 M Na_2CO_3 (100 ml) and extracted with CH_2Cl_2 (3 x 100 ml). The combined organic layers were extracted with 12 M HCl (5x50 ml), the acidic solution was neutralized (3 M NaOH and 1 M Na_2CO_3) and extracted with CH_2Cl_2. Removal of the solvent in vacuo afforded the appropriate 1,10-phenanthroline. The products were purified by filtration through silica gel using CH_2Cl_2 or THF as solvent. Schemata 3 and 4 indicate the yields obtained, Tables 3 and 4 give the analytical data for the respective compounds.

Table 3. Spectroscopic Data of the Prepared Methyl-1,10-phenanthrolines **4** (Scheme 3)

Compound	Substrate **1**	mp / (°C) (Lit)	^{1}H NMR ($CDCl_3$ / TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$ / TMS) δ	MS (70 eV) *m/z* (%)
4a	**1a**	53 (51-52)[16]	2.91 (s, 3H), 7.46 (d, J = 8.2 , 1H), 7.57 (dd, J = 8.1, 4.4, 1H), 7.66 (d, J = 8.8 , 1H), 7.72 (d, J = 8.8 , 1H), 8.07 (d, J = 8.2 , 1H), 8.18 (dd, J = 9.1, 1.8 , 1H), 9.17 (dd, J = 4.4, 1.8 , 1H)	159.5, 150.1, 145.8, 145.5, 136.1, 136.0, 128.7, 126.6, 126.4, 125.3, 123.6, 122.6, 25.7	194 (M^+,100), 166 (14)
4b	**1b**	158-159 (151-152)[14]	2.57 (s, 3H), 7.57 (dd, J = 8.1, 4.4, 1H), 7.69 (d, J = 8.8 , 1H), 7.74 (d, J = 8.8 , 1H), 7.99 (d, J = 2.2 , 1H), 8.20 (dd, J = 8.1, 1.8, 1H), 9.01 (d, J = 2.2 , 1H), 9.15 (dd, J = 4.3, 1.8 , 1H)	151.7, 150.1, 146.1, 144.0, 135.9, 135.2, 132.8, 128.4, 128.1, 126.4, 126.2, 122.6, 18.6	194 (M^+,100), 167 (19)
4c	**1c**	146-150 (144-145)[17]	2.73 (s, 3H), 7.47 (dd, J = 4.4, 0.8, 1H), 7.58 (dd, J = 8.1, 4.3 , 1H), 7.76 (d, J = 9.1 , 1H), 7.95 (d, J = 9.1 , 1H), 8.20 (dd, J = 8.1, 1.8, 1H), 9.01 (d, J = 4.5 , 1H), 9.15 (dd, J = 4.3, 1.7 , 1H)	150.2, 149.7, 146.3, 145.7, 144.4, 135.7, 128.1, 126.0, 125.4, 124.1, 122.8, 122.4, 19.0	194 (M^+,100), 167 (13)

Table 4. Spectroscopic Data of the Prepared Dialkyl-1,10-phenanthrolines **5** (Scheme 4)

Compound	Substrate **1**	Substrate **3**	mp / (°C) (Lit)	^{1}H NMR ($CDCl_3$ / TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS (70 eV) *m/z* (%)
5a	**1a**	**3c**	145-147	2.73 (s, 3H), 2.91 (s, 3H), 7.39 (d, J = 3.8 , 1H), 7.45 (d, J = 8.2, 1H), 7.72 (d, J = 9.0 , 1H), 7.89 (d, J = 9.0 , 1H), 8.07 (d, J = 8.2 , 1H), 9.01 (d, J = 4.5 , 1H)	159.3, 149.6, 145.7, 145.4, 144.1, 135.9, 128.2, 126.1,125.8, 123.7, 123.4, 121.2, 25.7, 19.0	208 (M^+,100)[a]
5b	**1a**	**3b**	122-124	2.55 (s, 3H), 2.91 (s, 3H), 7.43 (d, J = 8.2 , 1H), 7.61 (d, J = 8.8, 1H), 7.67 (d, J = 8.8 , 1H), 7.95 (d, J = 1.9 , 1H), 8.05 (d, J = 8.2 , 1H), 9.01 (d, J = 1.9 , 1H)	159.3, 151.6, 145.6, 143.8, 136.0, 135.2, 132.3, 128.5,126.3, 126.1, 125.1, 123.2, 25.7, 18.6	208 (M^+,100)[b]
5c	**1b**	**3b**	194-196 (209-212)[14]	2.57 (s, 3H), 7.68 (s, 1H), 7.96 (d, J = 1.8, 1H), 8.99 (d, J = 1.7 , 1H)	151.5, 144.2, 135.1, 132.3, 127.9, 126.2, 18.6	208 (M^+,100)
5d	**1c**	**3b**	129-134 (137-138)[14]	2.56 (s, 3H), 2.74 (s, 3H), 7.39 (d, J = 4.5 , 1H), 7.70 (d, J = 9.1, 1H), 7.93 (d, J = 9.1 , 1H), 7.96 (d, J = 1.1 , 1H), 8.98-9.00 (m, 2H)	151.6, 149.5, 145.8, 144.3, 144.1, 134.8, 132.4, 127.8, 127.5, 125.6, 123.6, 122.3, 18.9, 18.5	208 (M^+, 100)
5e	**1d**	**3d**	44-47	1.47 (s, 9H), 7.72 (s, 1H), 8.08 (d, J = 2.5, 1H), 9.21 (d, J = 2.4 , 1H)	149.2, 145.1, 143.8, 131.2, 127.7, 126.5, 33.8, 31.0	292 (M^+, 32), 277 (M^+-CH_3, 100), 262 (20)[c]
5f	**1e**	**3e**	112-115	0.95 (t, J = 7.4, 3H), 1.35-1.49 (m, 2H), 1.68-1.78 (m, 2H), 2.86 (t, J = 7.6, 2H), 7.72 (s, 1H), 7.99 (d, J = 2.0, 1H), 9.02 (d, J = 2.0 , 1H)	151.3, 144.4, 137.1, 134.4, 128.0, 126.2, 33.2, 32.7, 22.2, 13.8	292 (M^+, 30), 249 (M^+-C_3H_7, 100), 206 (M^+-2 C_3H_7, ,25)[d]
5g	**1b**	**3d**	75-80	1.48 (s, 9H), 2.57 (s, 3H), 7.68 (d, J = 8.8 , 1H), 7.73 (d, J = 8.8, 1H), 7.98 (d, J = 1.2 , 1H), 8.11 (d, J = 1.4 , 1H), 9.00 (d, J = 1.2), 9.24 (d, J = 1.4)	151.6, 149.2, 145.0, 144.1, 144.0, 135.0, 132.2, 131.2, 128.0, 127.6, 126.6, 126.0, 33.8, 31.0, 18.6	250 (M^+, 31), 235 (M^+-CH_3, 100), 205 (M^+-3 CH_3, 45)[e]

a	HRMS for **5a**	:	$C_{14}H_{12}N_2$	calcd. :	208.1000	found :	208.1002
b	HRMS for **5b**	:	$C_{14}H_{12}N_2$	calcd. :	208.1000	found :	208.1013
c	HRMS for **5e**	:	$C_{20}H_{24}N_2$	calcd. :	292.1939	found :	292.1941
d	HRMS for **5f**	:	$C_{20}H_{24}N_2$	calcd. :	292.1939	found :	292.1943
e	HRMS for **5g**	:	$C_{17}H_{18}N_2$	calcd. :	250.1470	found :	250.1475

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