Supporting Information

Self-Assembly of a Tellurotungstate Skeleton Inlaid with Ce(III) for Efficient Photocatalytic Synthesis of Quinazolines

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Table of Contents

1. General Information

Materials and Methods

All reagents were obtained from commercial sources and used without further purification.

The FT-IR spectrum was obtained by using a Fourier transform infrared (FT-IR) (4000-500 cm^{-1}) spectrometer (Thermo Nicolet iS5) at 0.5 cm^{-1} resolution and 16 scans. Thermogravimetric analyses (TGA) were performed under an N_2 atmosphere on Mettler-Toledo TGA/SDTA 851^e thermal analyzer from 30 to 800 °C. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature. Inductively coupled plasma optical emission spectrum (ICP-OES) data were obtained on an Agilent 725 ICP-OES spectrometer. The solid-state ultraviolet diffuse reflection spectrum was acquired on a UV-8000 ultraviolet and visible spectrophotometer equipping an integrating sphere (Shanghai Metash Instruments Co., Ltd). The GC analysis was performed on Agilent 7890B equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector. The GC-MS were recorded on Agilent 7890B-7000D.

X-ray Crystallography

The single crystal X-ray diffraction data were collected on Bruker D8 Smart Apex II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were collected by *ω*-scan and reduced on *APEX 3* and a multi-scan absorption correction was applied.[1] The structures were solved and refined on *Olex2* using the *SHELX* package.[2] Parameters of the crystal data collection and refinement are given in Table S1. The CCDC number is 2504253.

2. Experimental

Synthesis of Ce_8

To a 1 M pH = 4.8 NaAc/HAc buffer, $Na_2WO_4 \cdot 2H_2O$ (6 mmol, 1.9791 g), $(CH_3)_2NH_2Cl$ (12 mmol, 0.9785 g), Na_2TeO_3 (0.6 mmol, 0.1329 g), KCl (0.8 mmol, 0.3 g), and squaric acid (0.3 mmol, 0.034 g) were sequentially dissolved, and stirring for several minutes until the solution is clear. The solution was adjusted to pH = 4.5 using dilute HCl and stirred for 10 min. $CeCl_3 \cdot 6H_2O$ (0.6 mmol, 0.2235 g) was subsequently added into the solution and the pH was adjusted to 3.8 after the solids were completely dissolved. The obtained yellow solution was heated and stirred at 90°C for one hour. Then the solution is filtered after it has cooled completely, and yellow crystalline blocks are obtained after a few days (31.5% yield based on W). Elemental analysis found (calc. %): K, 0.81 (0.78); Te, 4.07 (4.06); Ce, 4.48 (4.45); W, 64.21 (64.29). FT-IR (cm^{-1}): 3388 (m), 3145 (m), 2794 (w), 1625 (m), 1461 (w), 1415 (w), 1017 (w), 947 (s), 828 (vs), 776 (vs), 679 (vs).

Typical procedure of the photocatalysis reaction

2-Aminobenzylamine (0.2 mmol), benzaldehyde (0.3 mmol), **Ce_8** (0.2 mol%), and propylenecarbonate (1 mL) were sequentially added to a 25 mL Schlenk flask equipped with a PTFE-coated magnetic stir bar. Subsequently, under an oxygen atmosphere, the reaction flask was placed under irradiation from a 10 W, 465 nm LED light source and stirred at room temperature for 10 h. At the end of the reaction, the mixture was purified by column chromatography (petroleum ether/EtOAc) to obtain the desired product. The substrate expansion of benzaldehyde was carried out under optimal reaction conditions and the resulting product was purified by column chromatography (petroleum ether/EtOAc).

3. Characterization

Table S1. Crystallographic data and structure refinement of **Ce_8** (SQUEEZE).

CCDC	2504253
Empirical formula	$Ce_8K_5O_{336}Te_8W_{88}$
Formula weight	23892.06
Temperature (K)	296.30
Crystal system	tetragonal
Space group	$I4_1/a$
a (Å)	38.599(4)
b (Å)	38.599(4)
c (Å)	27.820(7)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	41448(12)
F (000)	40700.0
Z	4
ρ_{calcd} (g·cm^{-3})	3.829
μ (mm^{-1})	25.855
Crystal size (mm^3)	0.22 × 0.18 × 0.16
2θ range for data collection (°)	3.61 to 49.998
Index ranges	$-45 \le h \le 45$, $-45 \le k \le 45$, $-33 \le l \le 33$
Reflections collected	174270
Independent reflections	18251 [Rint = 0.1056, Rsigma = 0.0557]
Restraints	MoKα (λ = 0.71073)
Parameter	1033
GOOF on F^2	1.079
R_1[a] [$I \ge 2\sigma(I)$]	0.0707, wR2 =
wR_2[b] (all data)	0.1723
Largest diff. peak/hole (e Å^{-3})	4.11/-1.43

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $^bwR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S2. Bond valence calculations for Ce and W atoms in **Ce_8**.

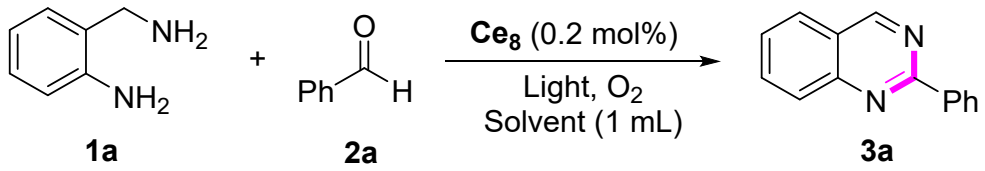
Atom	BVS	Valence	Atom	BVS	Valence
Ce1	3.13	+3	Te1	3.73	+4
Ce2	3.13	+3	Te2	3.64	+4
W1	5.82	+6	W12	5.78	+6
W2	6.12	+6	W13	6.10	+6
W3	5.95	+6	W14	5.68	+6
W4	6.06	+6	W15	6.04	+6
W5	5.75	+6	W16	5.97	+6
W6	6.02	+6	W17	6.08	+6
W7	5.89	+6	W18	5.95	+6
W8	5.99	+6	W19	5.82	+6
W9	5.80	+6	W20	5.84	+6
W10	6.17	+6	W21	5.82	+6
W11	6.39	+6	W22	6.07	+6

Bond valence sum (BVS) analysis: The BVS values (V*i*) of metal atoms were calculated using the following equation:[3]

$$V_i = \Sigma \exp[(r_0 - r_{ij})/B] \qquad (1)$$

where r_0 is the bond valence parameter for a given atom pair, r_{ij} is the bond length between atoms *i* and *j* obtained from the crystal structure.

Table S3 Optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Solvent	Light source (nm)	Time (h)	Yield (%)[b]
1	EA	465	8	80
2	DMC	465	8	73
3	PC	465	8	87
4	H_2O	465	8	56
5	EtOH	465	8	60
6	PC	365	8	67
7	PC	390	8	75
8	PC	420	8	79
9	PC	440	8	83
10	PC	White LED	8	62
11	PC	465	6	75
12	PC	465	10	93
13	PC	465	12	92
14[c]	PC	465	10	75
15[d]	PC	465	10	81
16[e]	PC	465	10	91

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), solvent (1 mL), **Ce_8** (0.2 mol%), at room temperature under the irradiation of 10 W LED and O_2 atmosphere for 8 h; [b] The yields were determined by GC with biphenyl as the internal standard. [c] **1a** (0.2 mmol), **2a** (0.2 mmol). [d] **Ce_8** (0.1 mol%). [e] **Ce_8** (0.3 mol%).

Table S4 Comparison of the present catalytic system with other catalysts for this reaction.

Entry	Catalyst (mol%)	Oxidant	Time (h)	Temperature (°C)	Solvent	Yield (%)	TON	Ref
1	**Ce_8 (0.2)**	**O_2**	**10**	**rt**	**PC**	**93**	**465**	**This work**
2	rose bengal (0.5)	O_2	12	rt	DMF	88	176	4
3	Aminoquinolate B,B-diphenyl (1.0)	O_2	10	rt	NMP	80	80	5
4	Fe-Fe_3C@NC-800 (4)	H_2O_2	12	100	THF	96	24	6
5	CuCl (5)	O_2	6	80	MeCN	95	19	7
6	-	IBX	6	rt	MeCN	88	-	8

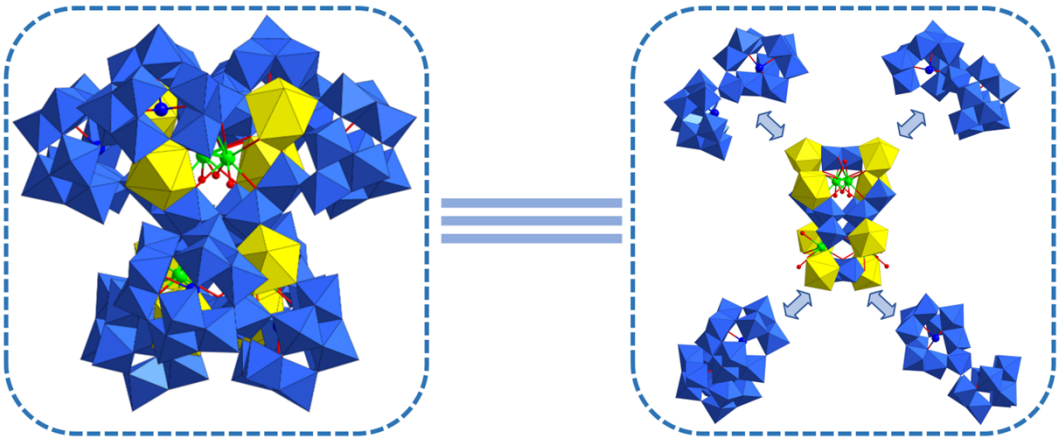


Figure S1. **Ce_8** can be decomposed into $\{Te_2W_{19}\}$ units at different coordinates and $\{C_8W_{12}\}$ units.

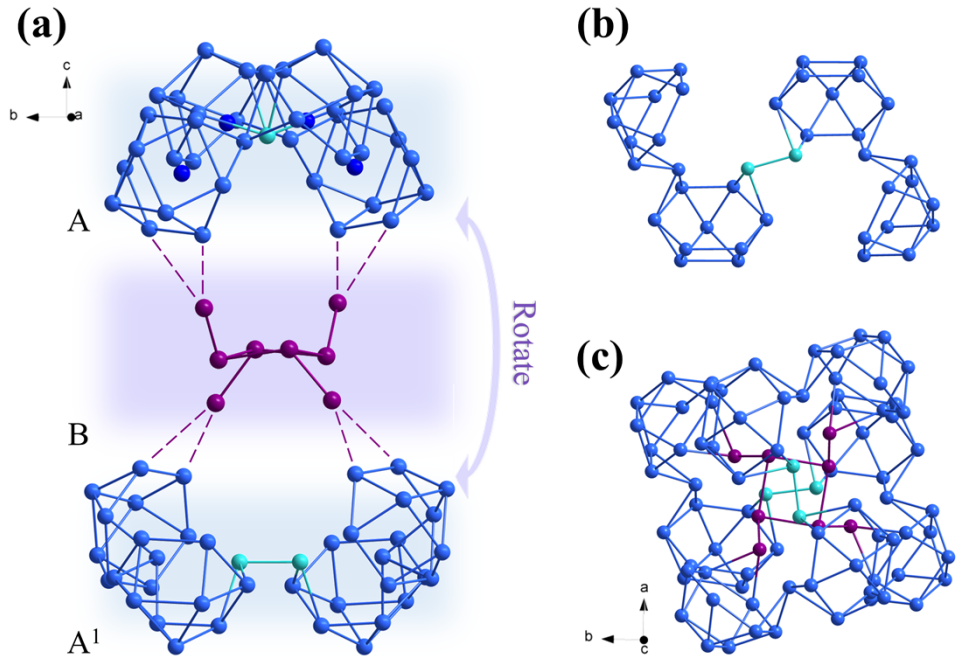


Figure S2. (a) W atomic framework of the A-B-A^1 layer; (b) Framework of A layer; (c) view in the c-axis direction.

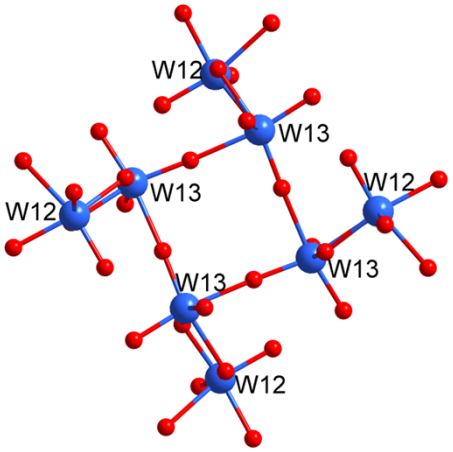


Figure S3. Ball stick model of $\{W_8\}$.

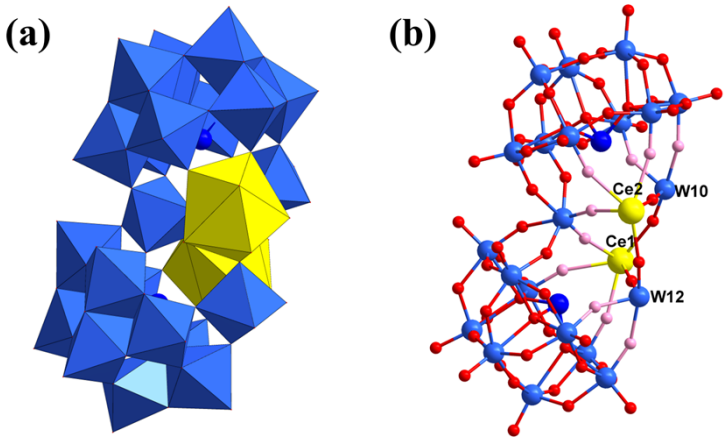


Figure S4. (a) Block diagram of the connection between $\{Ce_8W_{12}\}$ cluster and $\{Te_2W_{19}\}$; (b) Ball stick model of S4a, the pink oxygen atoms are bridge-linked oxygen atoms between the $\{Ce_8W_{12}\}$ cluster and $\{Te_2W_{19}\}$.

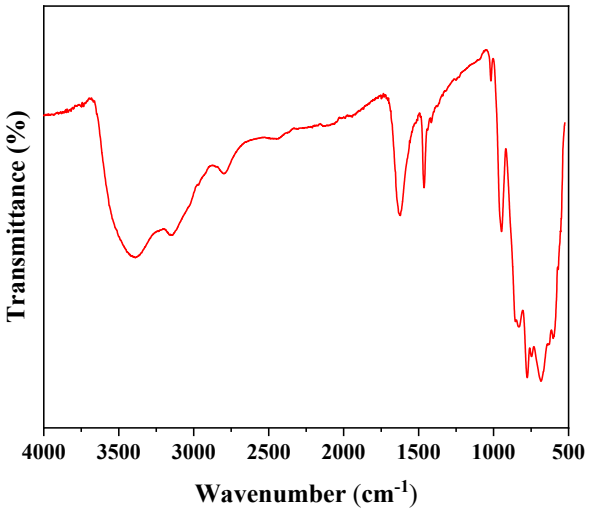


Figure S5 FT-IR spectra of **Ce_8**.

The broad absorption peak at about 3388 cm^{-1} is attributed to the ν(O–H) stretching vibration of water and the bending vibration adsorption of water appears at about 1625 cm^{-1}. The ν(N–H) and ν(C–H) stretching vibrations appear at about 3145 cm^{-1} and 2794 cm^{-1}. The peaks that appear in the range of 500 to 1000 cm^{-1} can be attributed to the stretching vibrations of ν(W-O_t), ν(Te–O), ν(W–O_b) and ν(W–O_c), and the absorption peaks appearing at 947, 828, 776 and 679cm^{-1}, respectively.

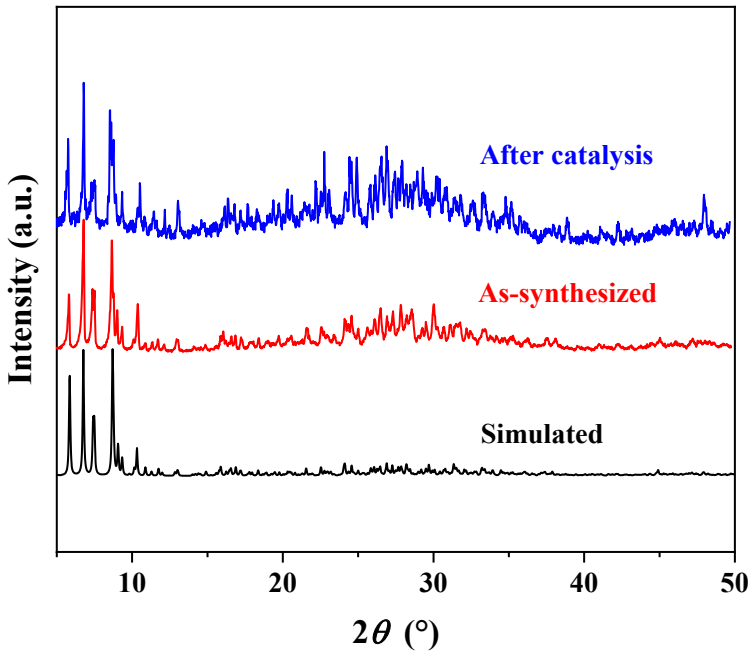


Figure S6 PXRD curves of **Ce_8**.

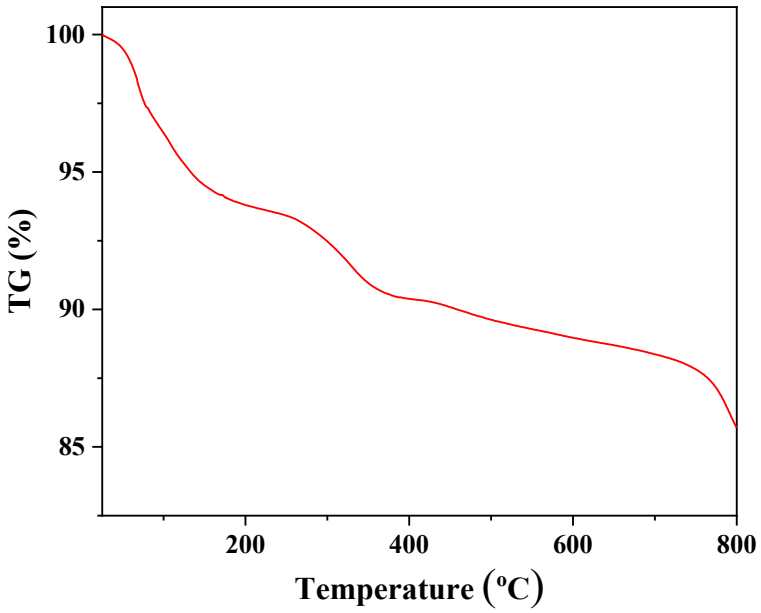


Figure S7 TGA curve of **Ce_8**.

Thermalgravimetric analysis of was performed on the crystalline samples under N_2 atmosphere from 25-800 °C. The weight loss at 234 °C is about 6.47%, which is corresponding to the loss of 73 water molecules (5.2%) and 7 $[(CH_3)_2NH_2]^+$ ions (1.27%).

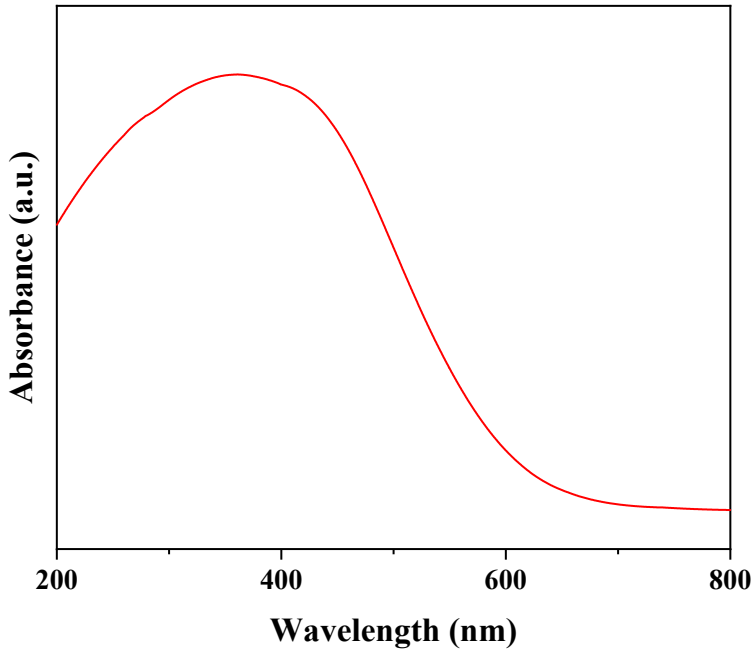
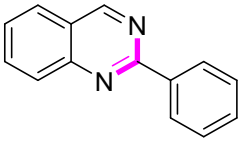


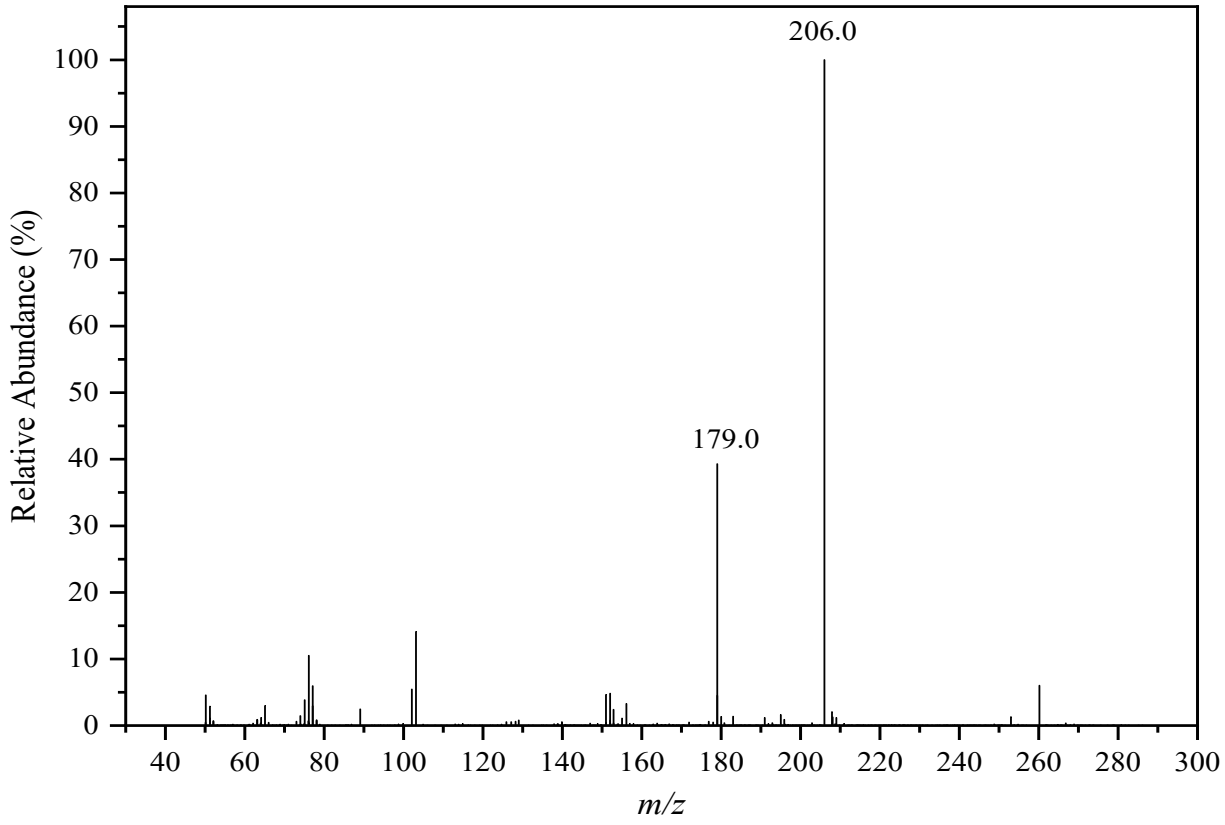
Figure S8 UV-vis diffuse reflection spectra of **Ce_8**.

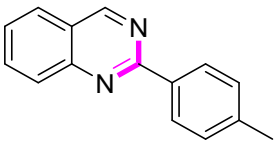
4. Characterization of Products[4]



2-phenylquinazoline (3a)

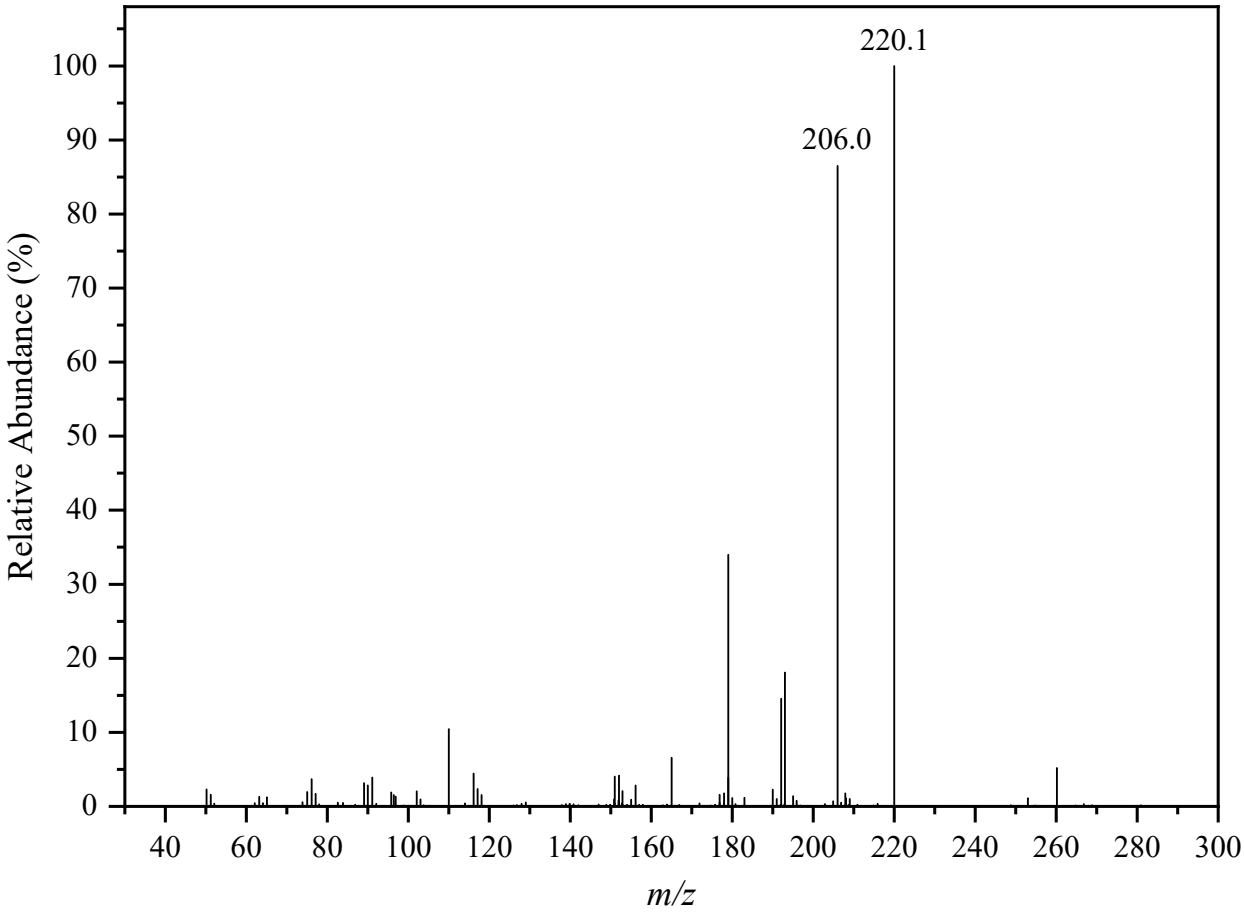
EI-MS: $C_{14}H_{10}N_2$, m/z (%) = 206.0 (100.0%) [M+].

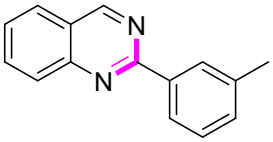




2-(p-tolyl)quinazoline (3b)

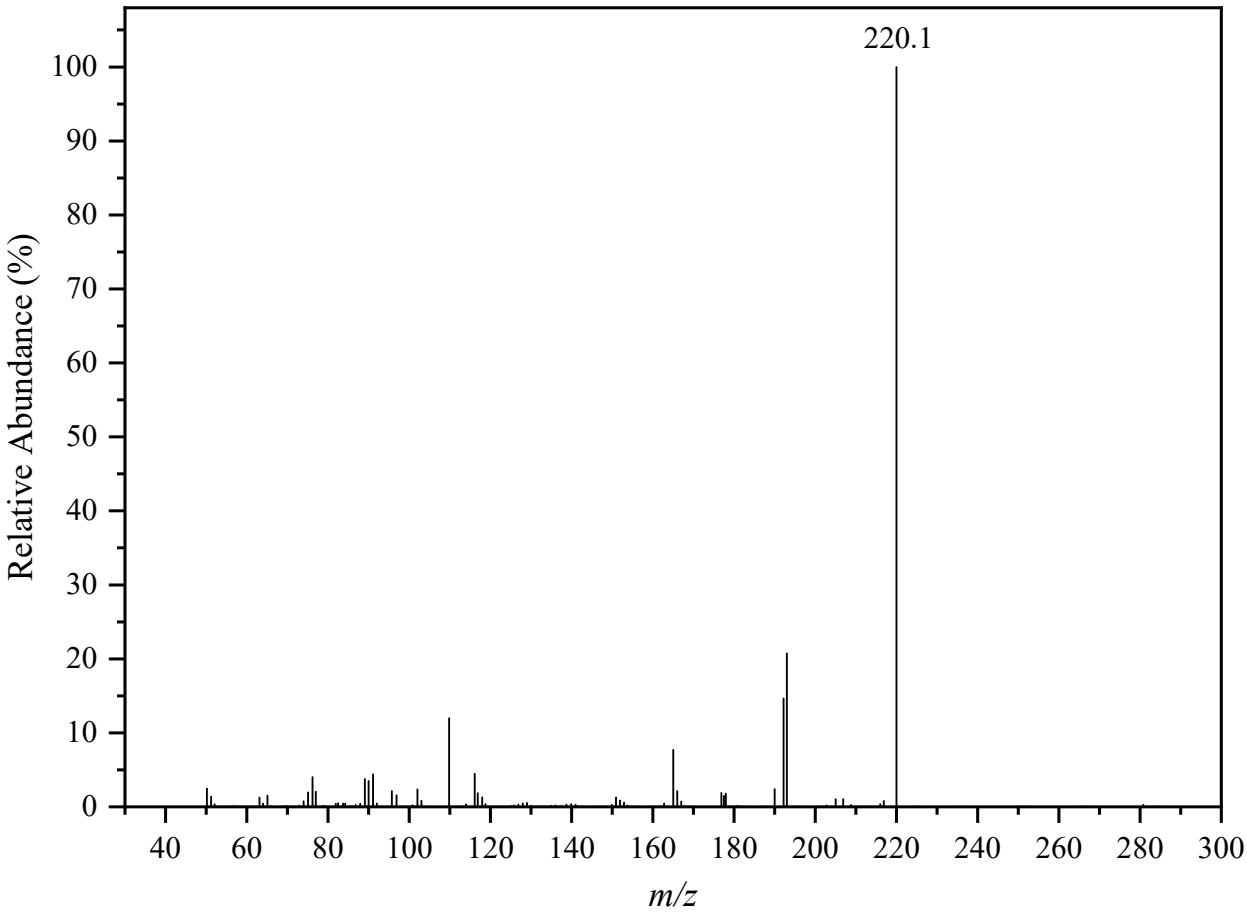
EI-MS: $C_{15}H_{12}N_2$, m/z (%) = 220.1 (100.0%) [M+].

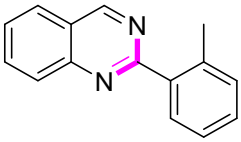




2-(m-tolyl)quinazoline (3c)

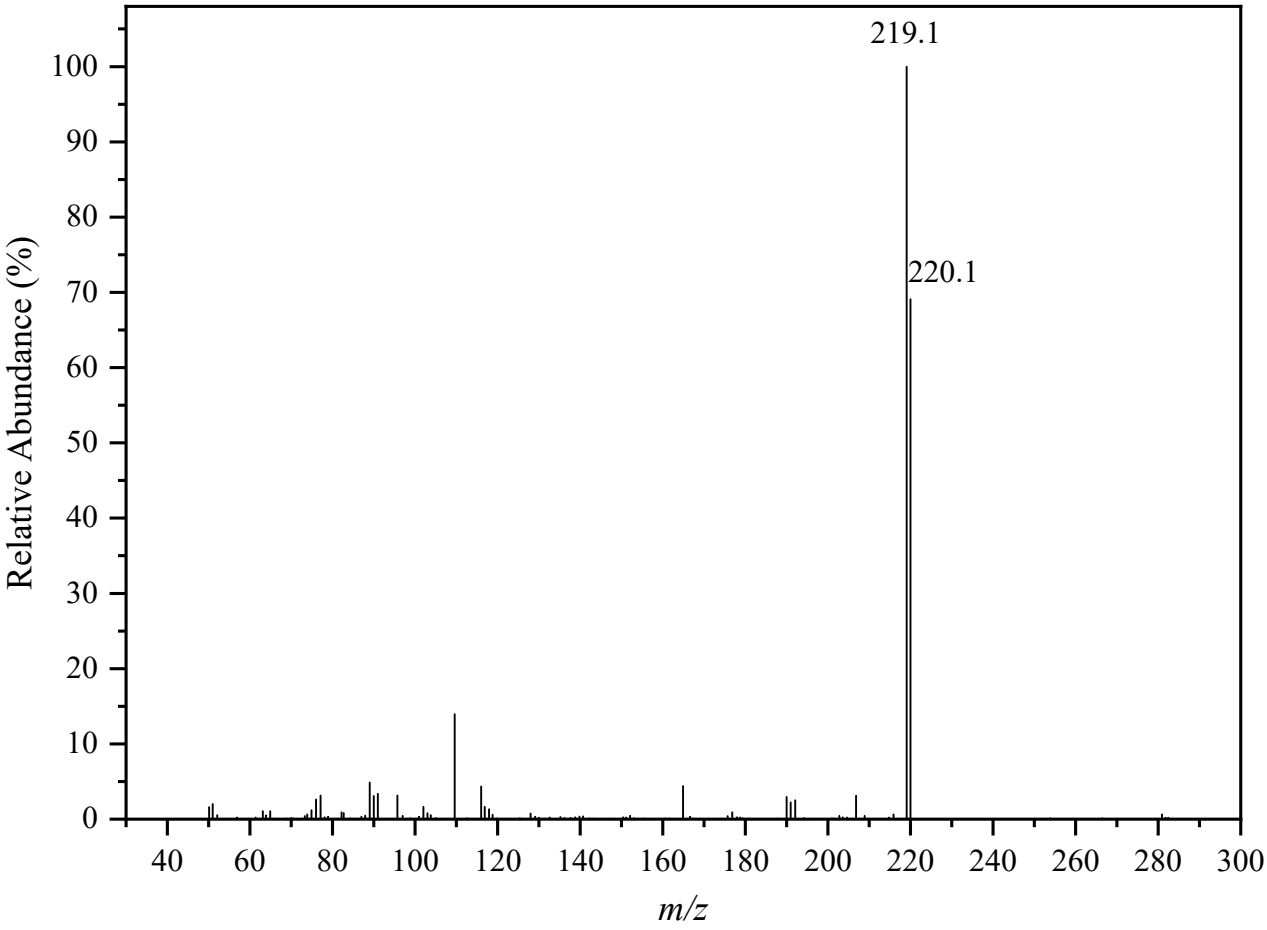
EI-MS: $C_{15}H_{12}N_2$, m/z (%) = 220.1 (100.0%) [M+].

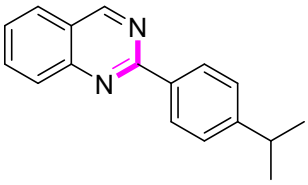




2-(o-tolyl)quinazoline (3d)

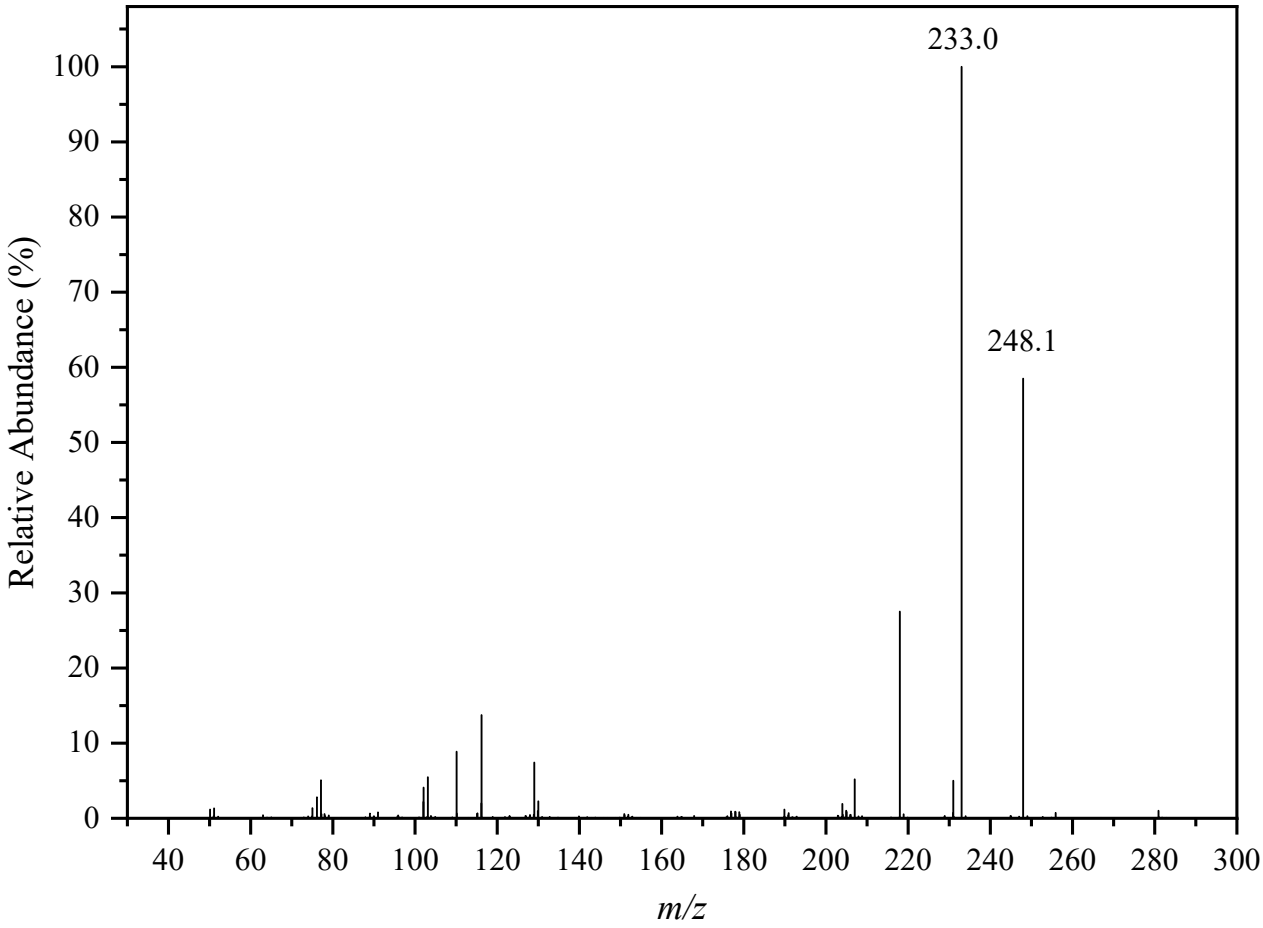
EI-MS: $C_{15}H_{12}N_2$, m/z (%) = 220.1 (69.1%) [M+].

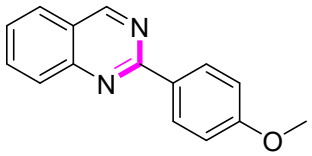




2-(4-isopropylphenyl)quinazoline (3e)

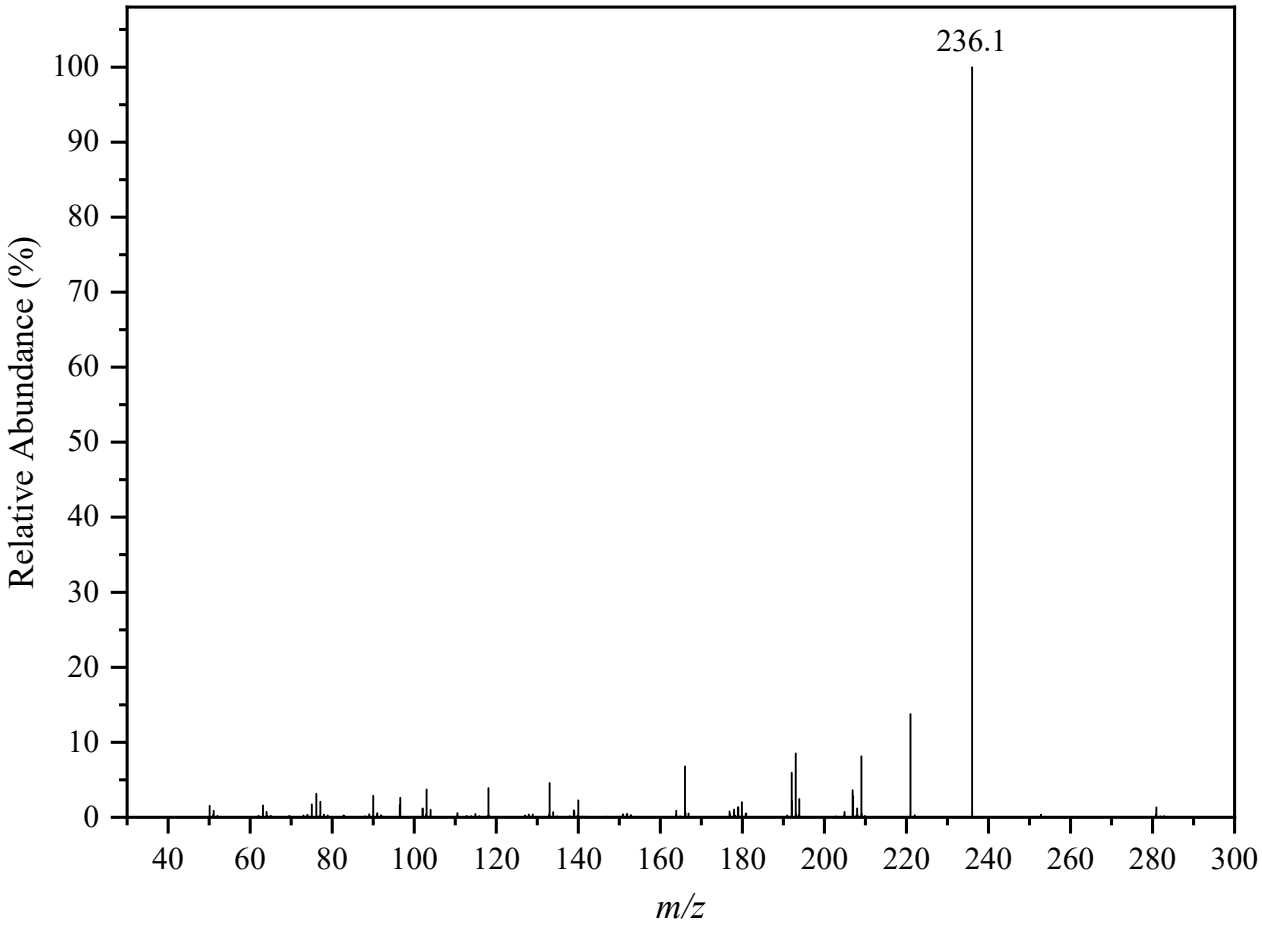
EI-MS: $C_{17}H_{16}N_2$, m/z (%) = 248.1 (58.5%) [M+].

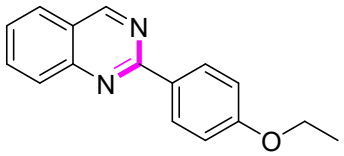




2-(4-methoxyphenyl)quinazoline (3f)

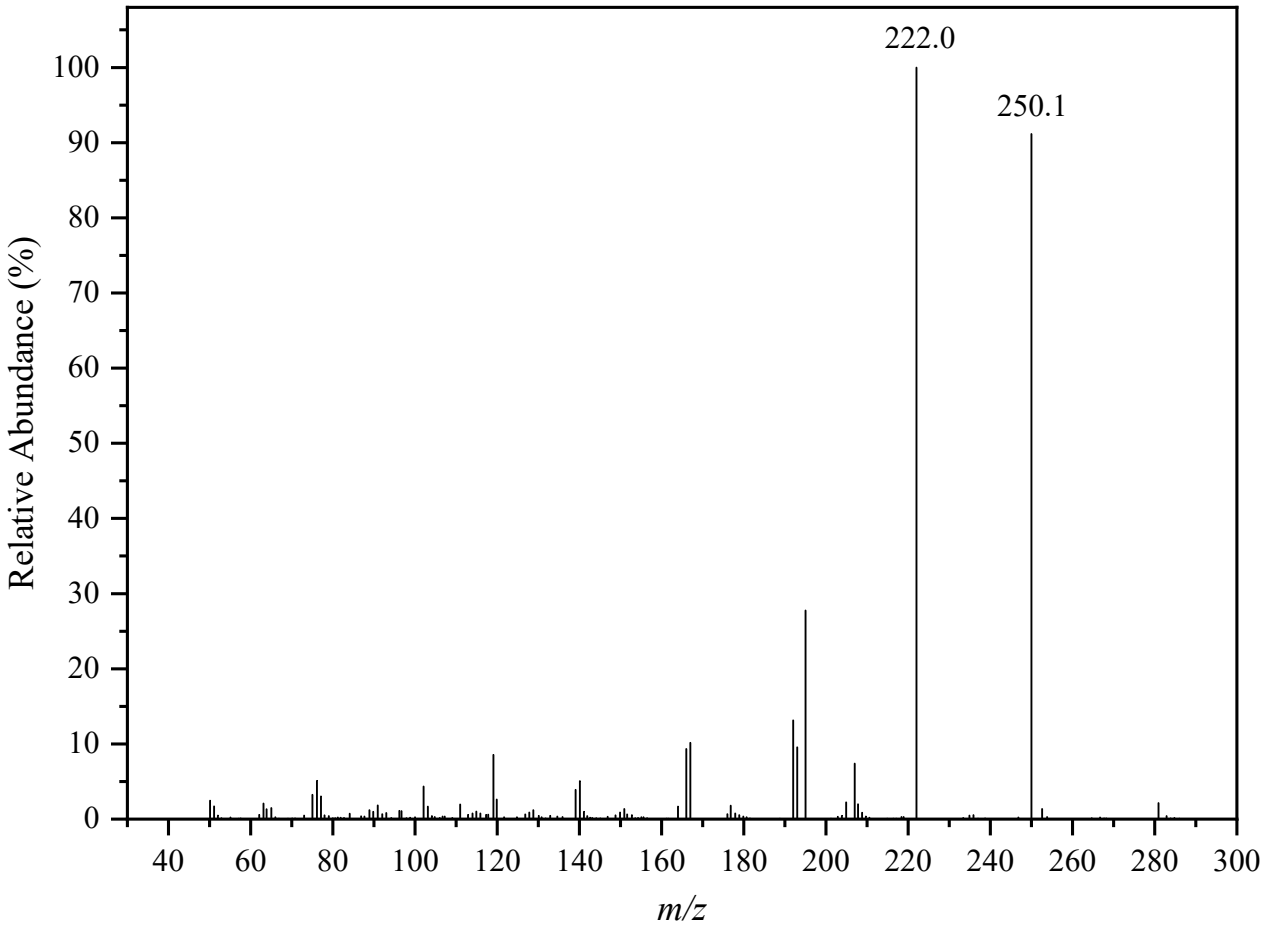
EI-MS: $C_{15}H_{12}N_2O$, m/z (%) = 236.1 (100.0%) [M+].

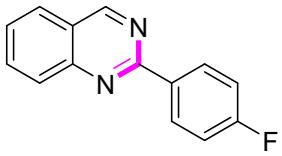




2-(4-ethoxyphenyl)quinazoline (3g)

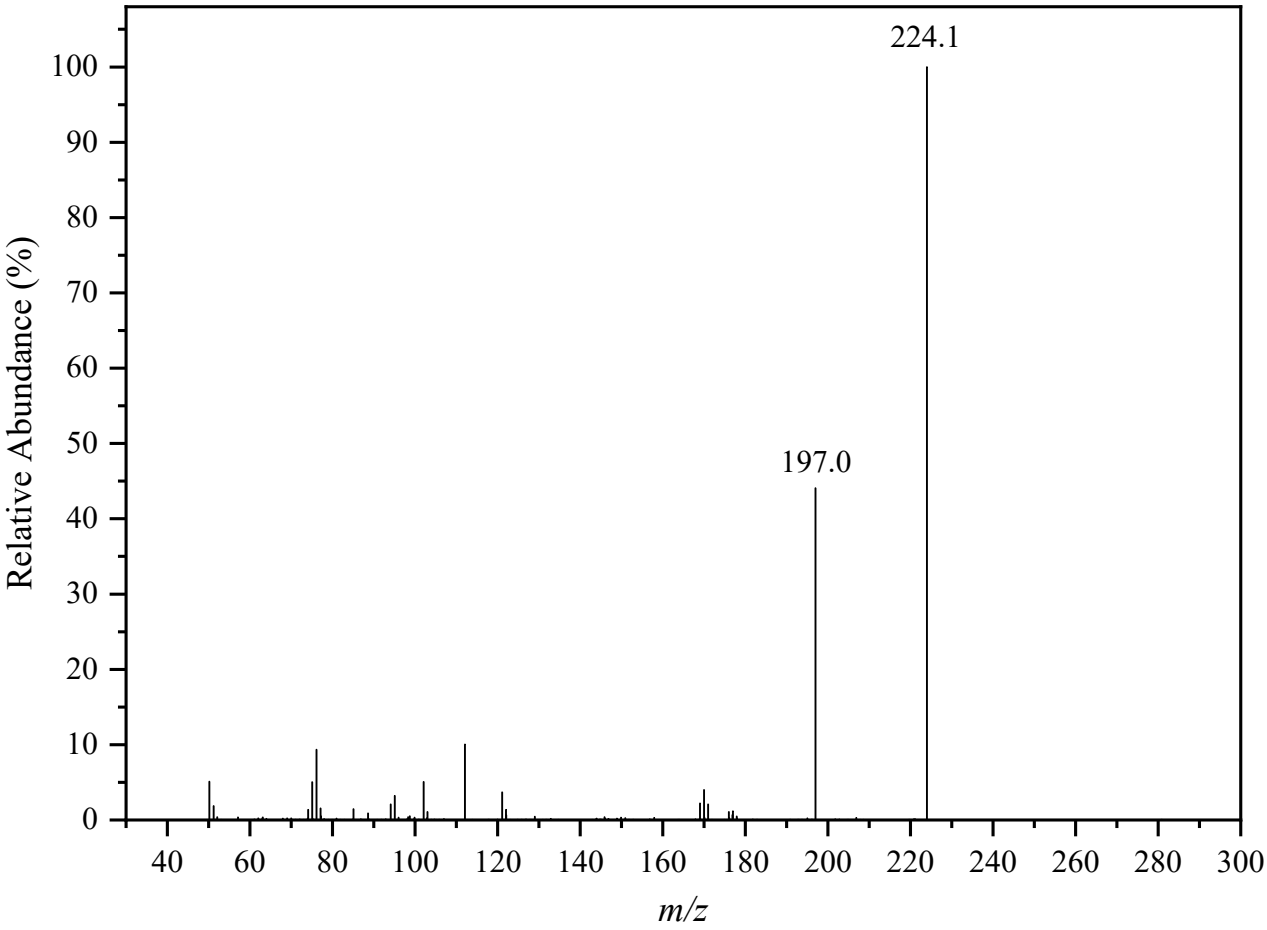
EI-MS: $C_{16}H_{14}N_2O$, m/z (%) = 250.1 (91.1%) [M+].

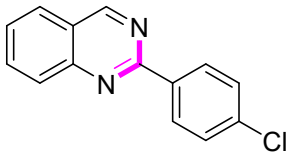




2-(4-fluorophenyl)quinazoline (3h)

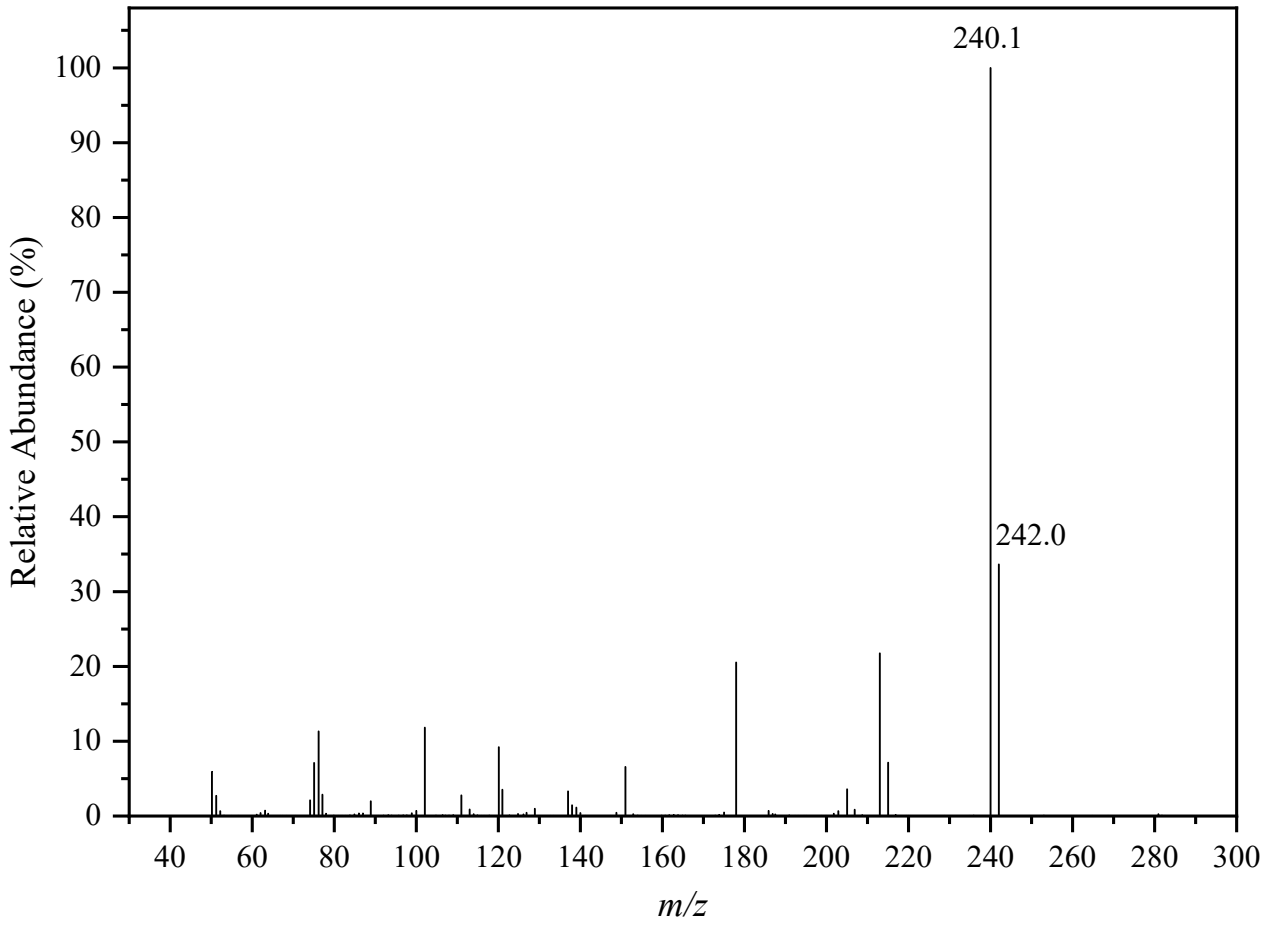
EI-MS: $C_{14}H_9FN_2$, m/z (%) = 240.1 (100.0%) [M+].

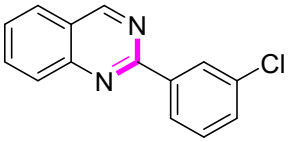




2-(4-chlorophenyl)quinazoline (3i)

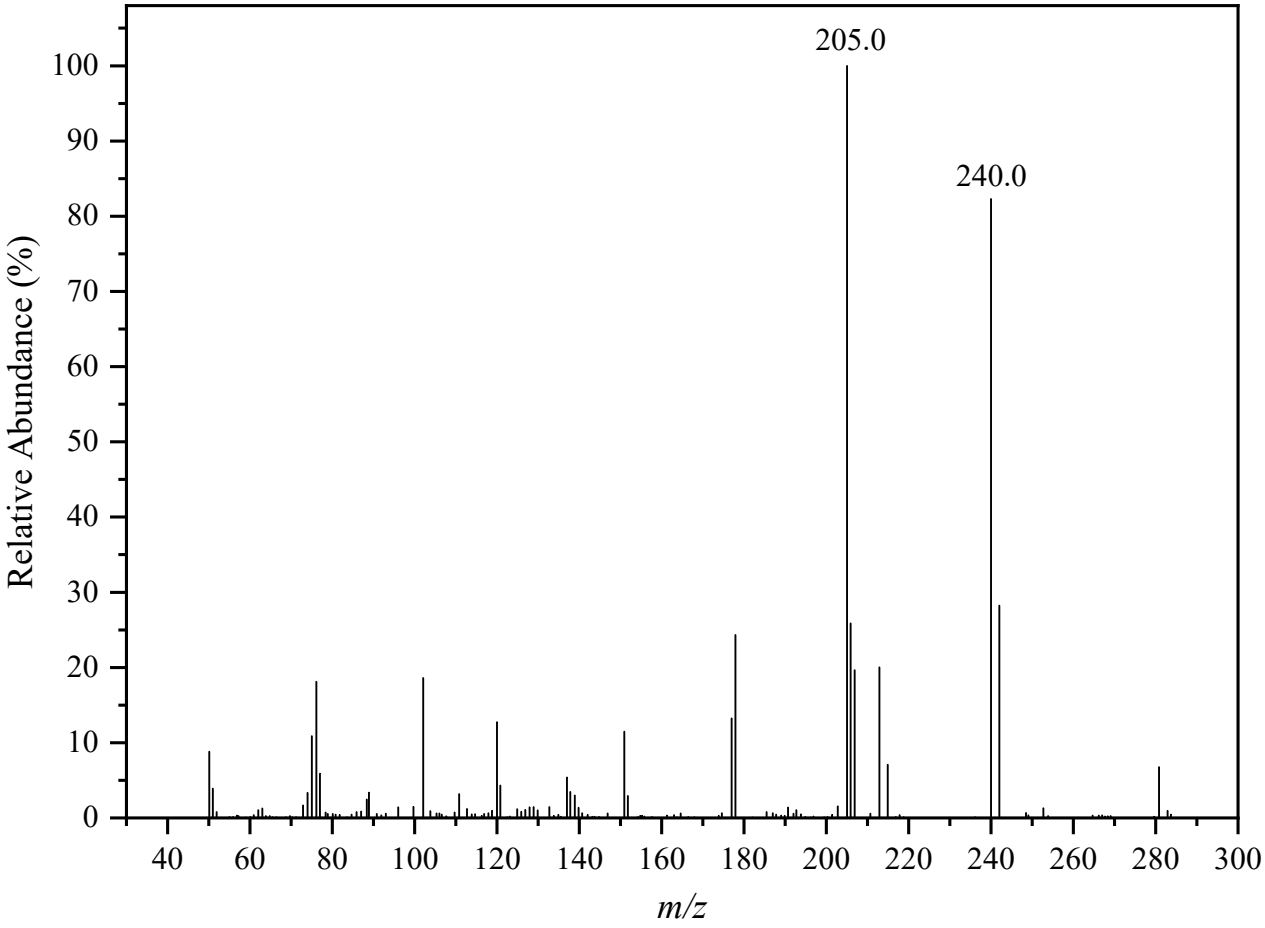
EI-MS: $C_{14}H_9ClN_2$, m/z (%) = 240.1 (100.0%) [M+].

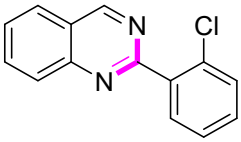




2-(3-chlorophenyl)quinazoline (3j)

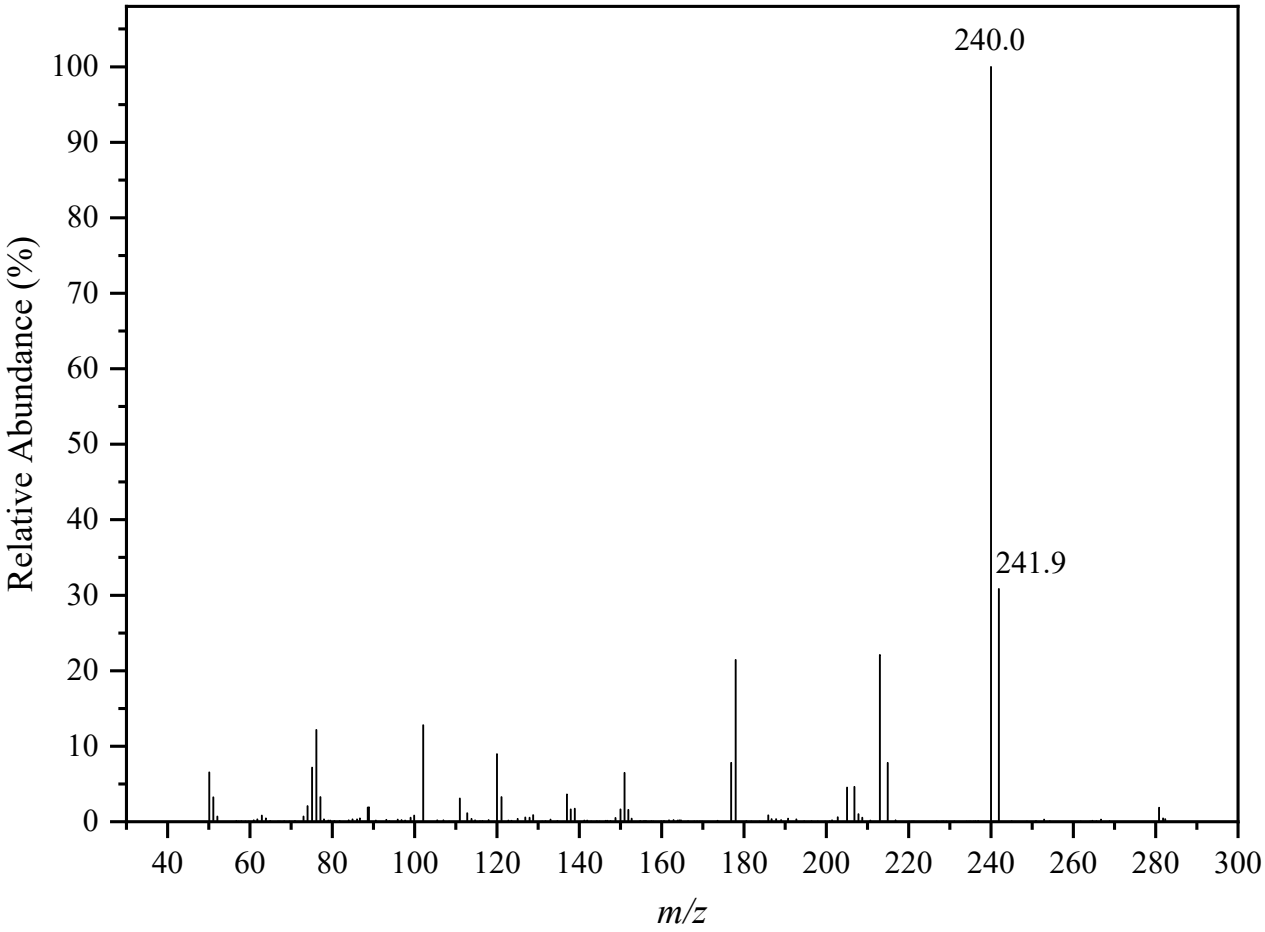
EI-MS: $C_{14}H_9ClN_2$, m/z (%) = 240.0 (82.3%) [M+].

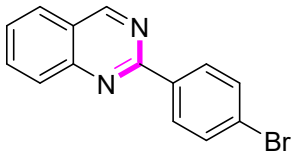




2-(2-chlorophenyl)quinazoline (3k)

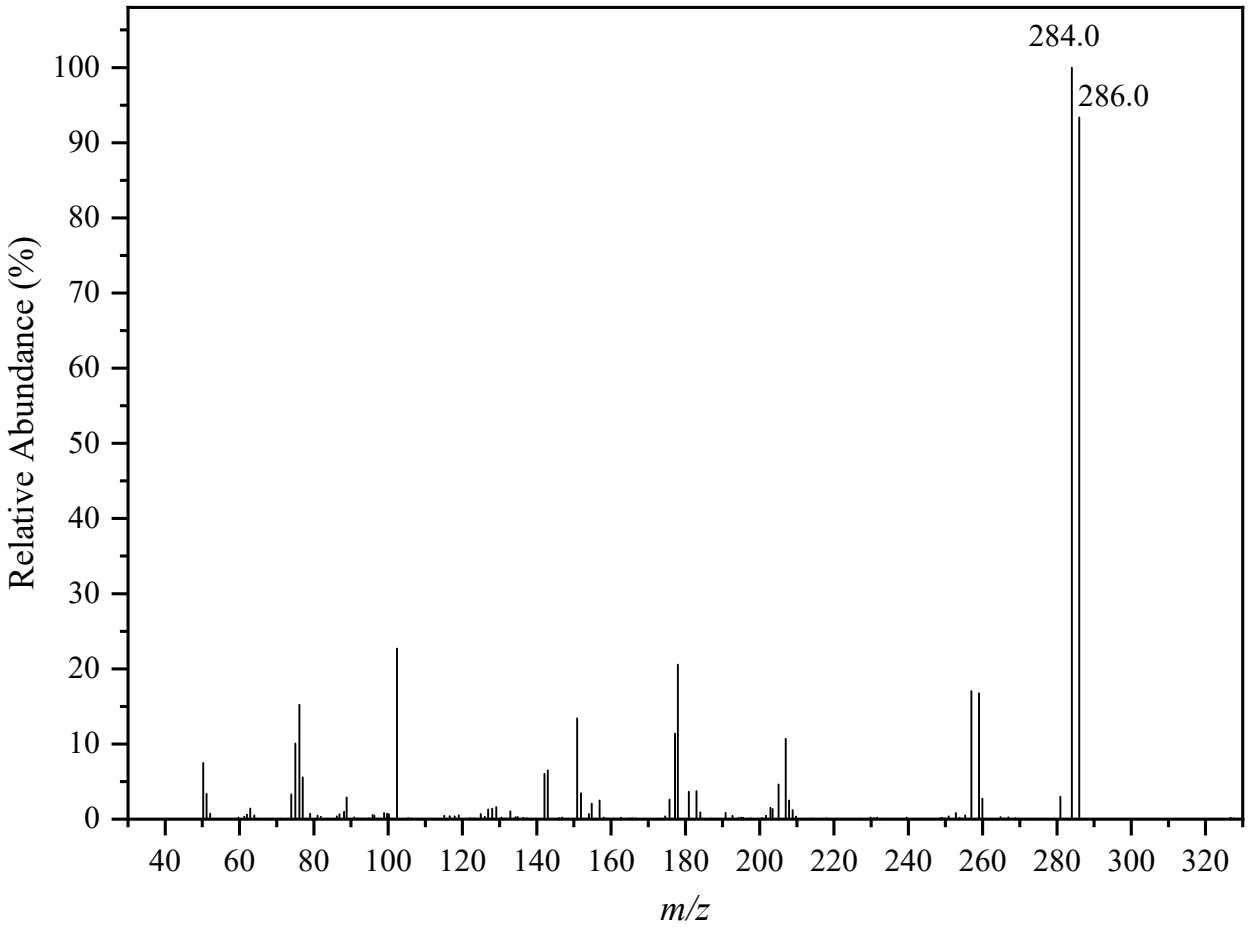
EI-MS: $C_{14}H_9ClN_2$, m/z (%) = 240.0 (100.0%) [M+].

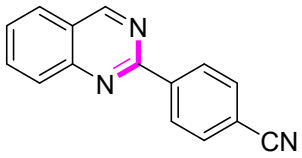




2-(4-bromophenyl)quinazoline (3l)

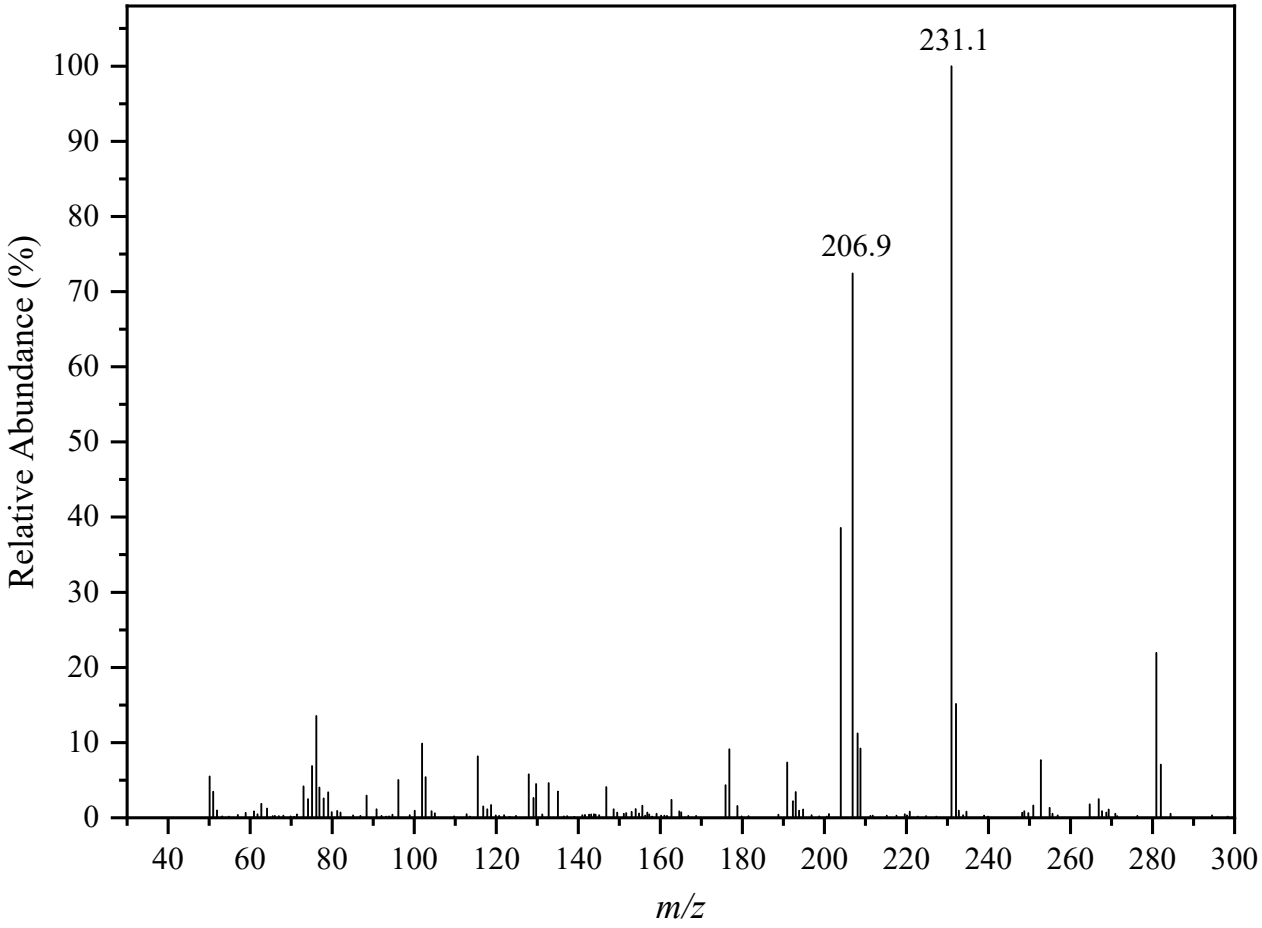
EI-MS: $C_{14}H_9BrN_2$, m/z (%) = 284.0 (100.0%) [M+].

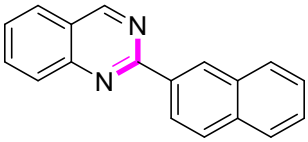




4-(quinazolin-2-yl)benzonitrile (3m)

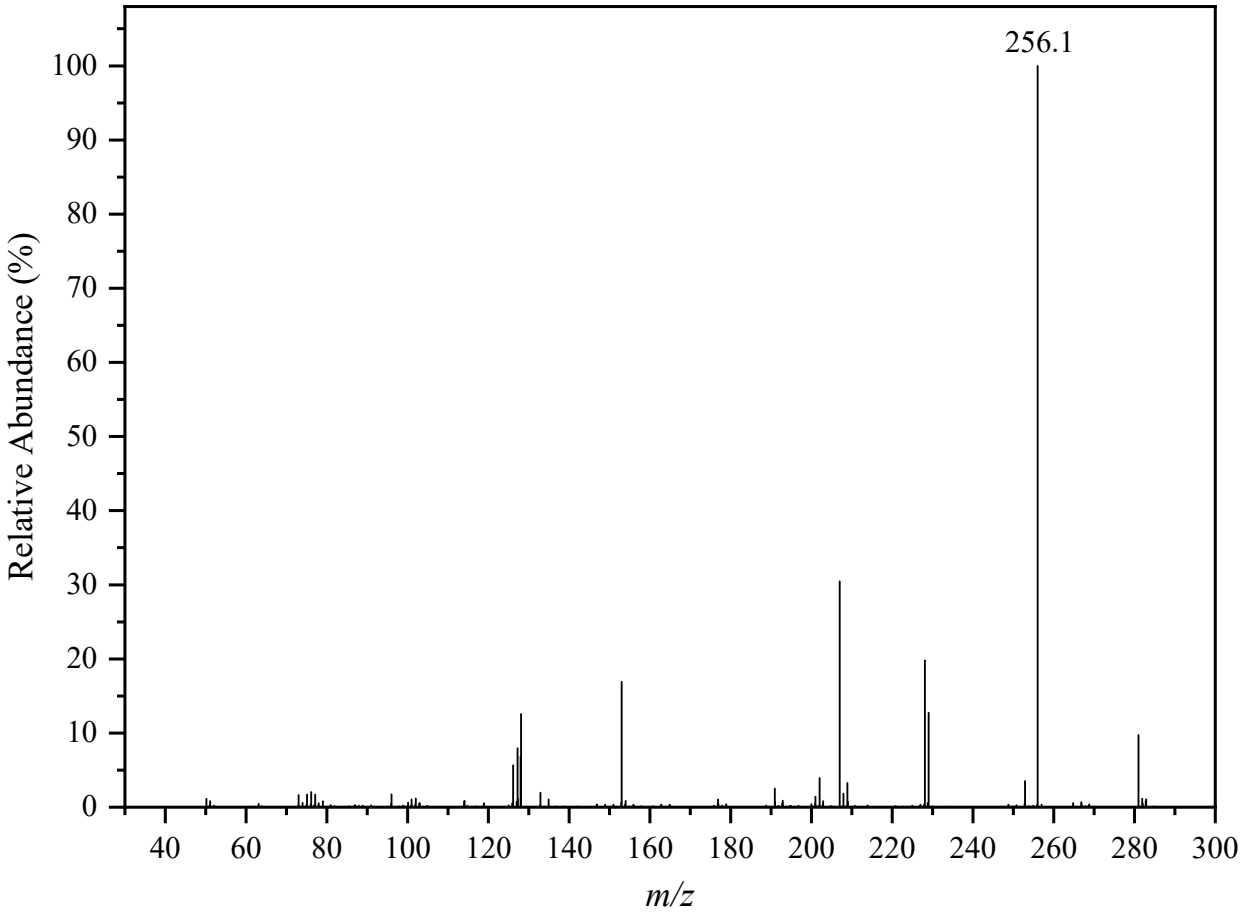
EI-MS: $C_{15}H_9N_3$, m/z (%) = 231.1 (100.0%) [M+].

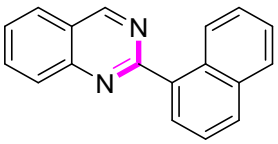




2-(naphthalen-2-yl)quinazoline (3n)

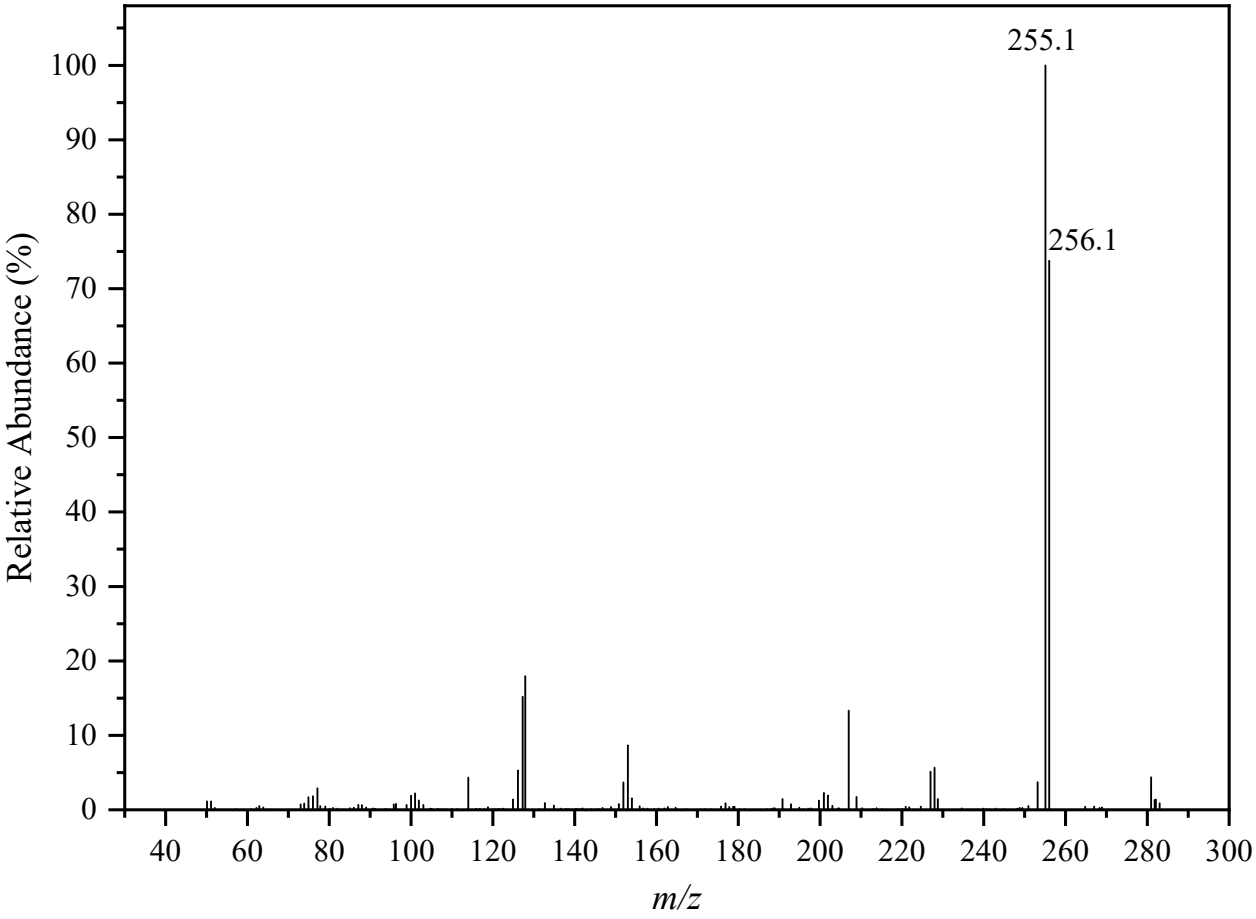
EI-MS: $C_{18}H_{12}N_2$, m/z (%) = 256.1 (100.0%) [M+].





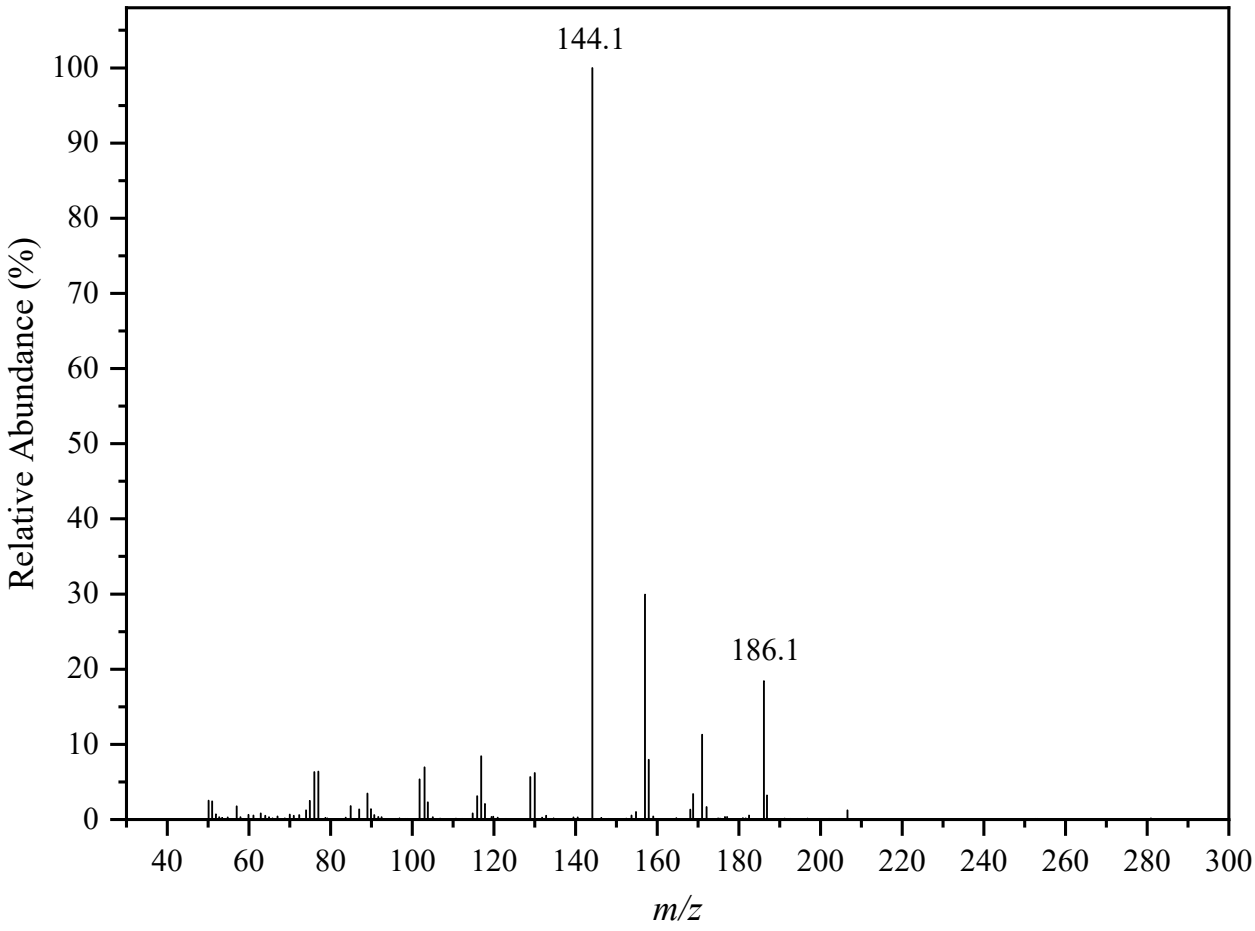
2-(naphthalen-1-yl)quinazoline (3o)

EI-MS: $C_{18}H_{12}N_2$, m/z (%) = 256.1 (73.7%) [M+].



2-butylquinazoline (3p)

EI-MS: $C_{12}H_{14}N_2$, m/z (%) = 186.12 (30.0%) [M+].



5. Notes and References

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