Supporting Information

A One-dimensional Selenotungstate Based on Neodymium and $\{SeO_3\}$ Groups Connecting for Catalytic Synthesis of Imidazoles

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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. Elemental analyses (EA) (C, H, and N) were performed on a Vario EL Cube CHN elemental analyzer. 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 2489933.

2. Experimental

Synthesis of NdSeW

$Na_2WO_4 \cdot 2H_2O$ (6.00 mmol, 1.98 g), Na_2SeO_3 (0.80 mmol, 0.14 g), NH_4Cl (12.00 mmol, 0.32 g), and DL-malic acid (0.30 mmol, 0.04 g) were sequentially dissolved in deionized water (20.00 mL). The solution was adjusted to pH = 4.50 using dilute HCl and stirred for 10 min. $NdCl_3 \cdot 6H_2O$ (0.40 mmol, 0.14 g) was subsequently added to the solution and the pH was adjusted to 4.00 after the solids were completely dissolved. The solution was stirred for another 30 min before being filtered. The clear filtrate was left to evaporate at room temperature. Colorless stick crystals were collected after about five weeks (yield: 31.5% based on W). Elemental analysis (%): C, 0.53; H, 0.74; Na, 4.10; Nd, 4.02; W, 61.38. FT-IR (cm^{-1}): 3407 (m), 3209 (m), 1621 (s), 1576 (s), 1416 (vs), 1193 (w), 1123 (w), 1052 (w), 1016 (w), 957 (vs), 832 (vs), 780 (vs), 684 (vs), 633 (vs).

Synthetic of $(NH_4)_6Na_{18}[Se_6W_{39}O_{141}(H_2O)_3] \cdot 60H_2O$ ($\{Se_6W_{39}\}$)

$Na_2WO_4 \cdot 2H_2O$ (4.0 g, 12.1 mmol), Na_2SeO_3 (0.4 g, 2.31 mmol) and NH_4NO_3 (0.15 g, 1.87 mmol) were dissolved with stirring in 40 ml H_2O. The pH of the solution was then adjusted to 4.0 by 70% HNO_3 and maintained at this value for 5 minutes. The solution was subsequently filtered and the filtrate was collected in a 100 mL conical flask and allowed to stand at 4 °C. Large colourless needle-shaped crystals of **$\{Se_6W_{39}\}$** were collected after two days. Yield: 0.70 g, (19.2 %, based on tungsten). FT-IR (cm^{-1}): 3383 (m), 3229 (m), 1625 (m), 1423 (m), 1118 (w), 943 (m), 882 (m), 750 (vs), 654 (vs), 602 (vs).

Typical procedure of the three-component condensation reaction

To a 4 mL reaction vial, benzaldehydes (**1**, 0.2 mmol), benzils (**2**, 0.2 mmol), ammonium acetate (**3a**, 0.6 mmol), **NdSeW** (0.5 mol%), and EtOH (1 mL) were added. Then the reaction was carried out in screw cap vials with a Teflon seal at 90 °C for 3 h. After the reaction, the mixture was purified by column chromatography (petroleum ether/EtOAc) or recrystallization to afford the desired products. Upon completion of the reaction, the catalyst was collected by centrifugation, washed sequentially three times with ethyl acetate and ethanol, and subsequently regenerated by drying under vacuum at 50 °C for 3 h to be reactivated for further use.

3. Characterization

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

CCDC	2489933
Empirical formula	$C_4H_3Na_{3.5}Nd_{2.5}O_{118}Se_5W_{30}$
Formula weight	8290.43
Temperature (K)	150
Crystal system	monoclinic
Space group	*C*2/c
a (Å)	41.1758(15)
b (Å)	37.6331(14)
c (Å)	25.8350(11)
α (°)	90
β (°)	118.3350(10)
γ (°)	90
V (Å^3)	35237(2)
F (000)	28396.0
Z	8
ρ_{calcd} (g·cm^{-3})	3.126
μ (mm^{-1})	21.332
Crystal size (mm^3)	0.21 × 0.15 × 0.14
2θ range for data collection (°)	3.864 to 52.904
Index ranges	$-51 \le h \le 51$, $-46 \le k \le 47$, $-32 \le l \le 30$
Reflections collected	180974
Independent reflections	36190 [R_{int} = 0.0800, R_{sigma} = 0.0631]
Restraints	0
Parameter	1491
GOOF on F^2	1.021
R_1[a] [$I \ge 2\sigma(I)$]	0.0493
wR_2[b] (all data)	0.1304
Largest diff. peak/hole (e Å^{-3})	3.15/-1.23

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b]$wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S2. Bond valence calculations for Nd and W atoms in **NdSbW**.

Atom	BVS	Valence	Atom	BVS	Valence
Nd1	3.29	+3	W15	5.66	+6
Nd2	3.26	+3	W16	6.48	+6
Nd3	3.01	+3	W17	5.99	+6
W1	6.16	+6	W18	6.00	+6
W2	6.21	+6	W19	6.30	+6
W3	5.92	+6	W20	6.19	+6
W4	5.85	+6	W21	5.93	+6
W5	6.11	+6	W22	6.04	+6
W6	6.09	+6	W23	5.98	+6
W7	6.42	+6	W24	6.37	+6
W8	6.33	+6	W25	5.82	+6
W9	6.29	+6	W26	6.03	+6
W10	6.18	+6	W27	5.86	+6
W11	5.97	+6	W28	6.21	+6
W12	6.10	+6	W29	5.99	+6
W13	6.15	+6	W30	6.23	+6
W14	6.19	+6			

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

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

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. Comparison of the present catalytic system with other heterogeneous catalysts reported before.

Entry	Catalyst	Loading	Time/h	Solvent	T/°C	Yield/%	Ref.
1	**NdSeW**	0.5 mol%	3	EtOH	90	97	This work
2	ZnO/CuI/PPy	20 mg	0.8	Neat	100	95	4
3	Fe_3O_4@SiO_2-imid-PMA	30 mg	1.5	Solvent-free	110	92	5
4	$(CTA)_3$PMo-MMT	50 mg	1	Solvent-free	100	78	6
5	$InCl_3$∽3H_2O	10 mol%	8.3	MeOH	rt	82	7
6	PMO@$ILBF_4$	35 mg	2	EtOH	80	94	8
7	L-proline	15 mol%	9	MeOH	60	90	9
8	Au@RGO	54 mg	6	H_2O	50	93	10

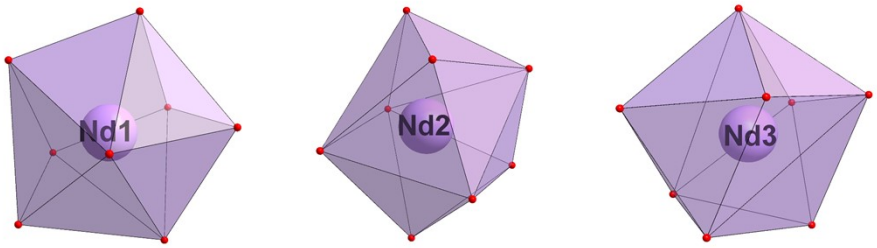


Figure S1. Octahedral coordination of the Nd atom.

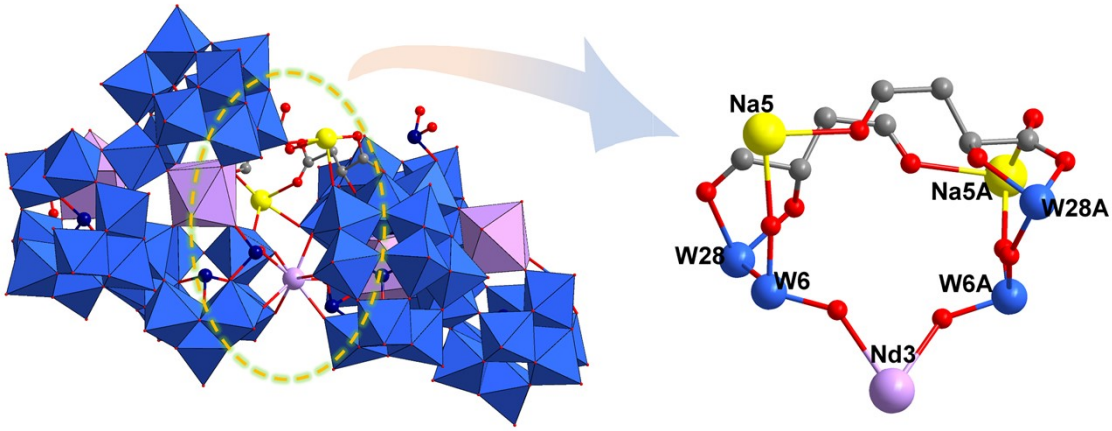


Figure S2. Schematic diagram of the dimer formation of **NdSeW** via bridging.

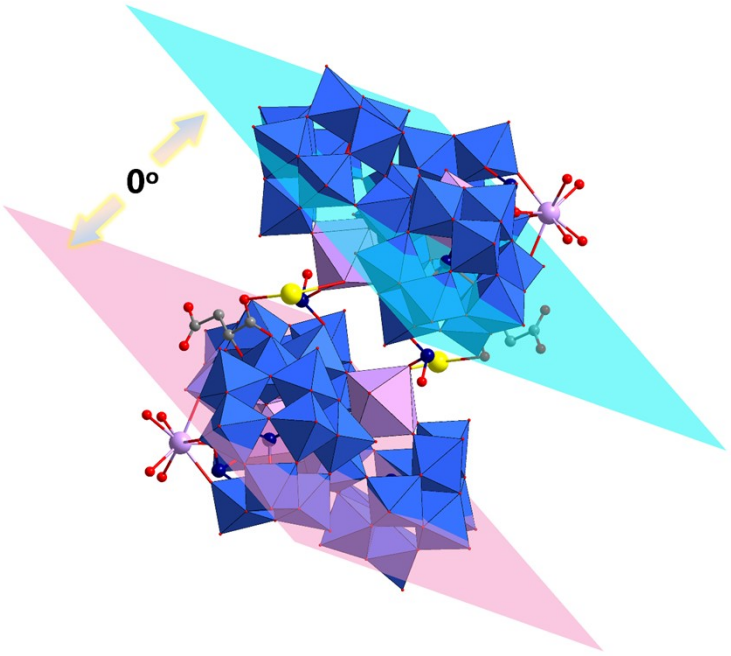


Figure S3. The angle between the dimers of **NdSeW**

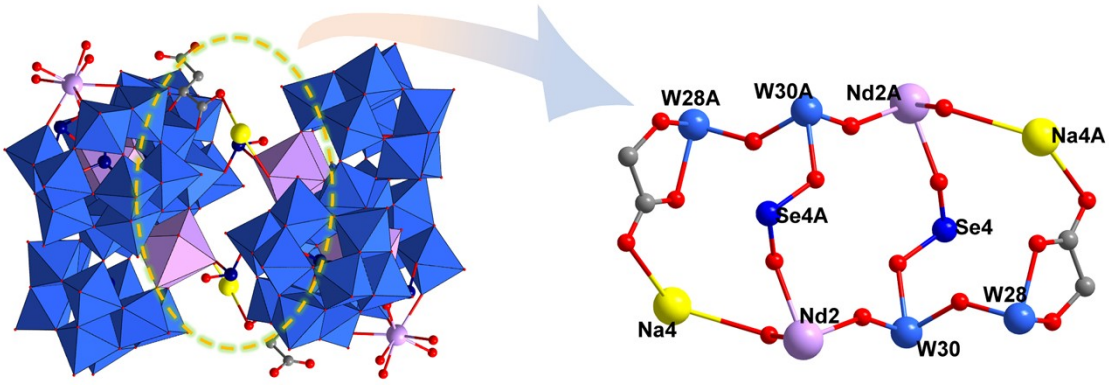


Figure S4 Bridging mode between the dimers of **NdSeW**.

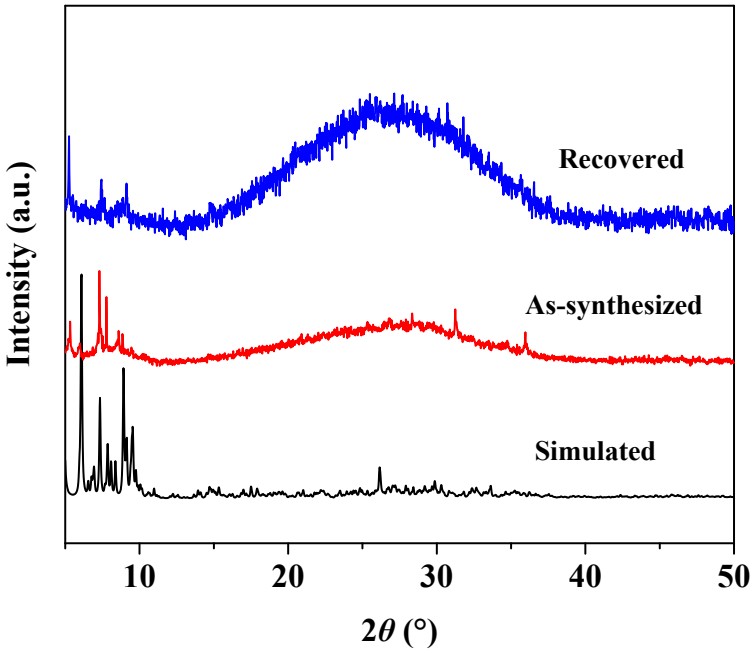


Figure S5 PXRD patterns of **NdSeW**.

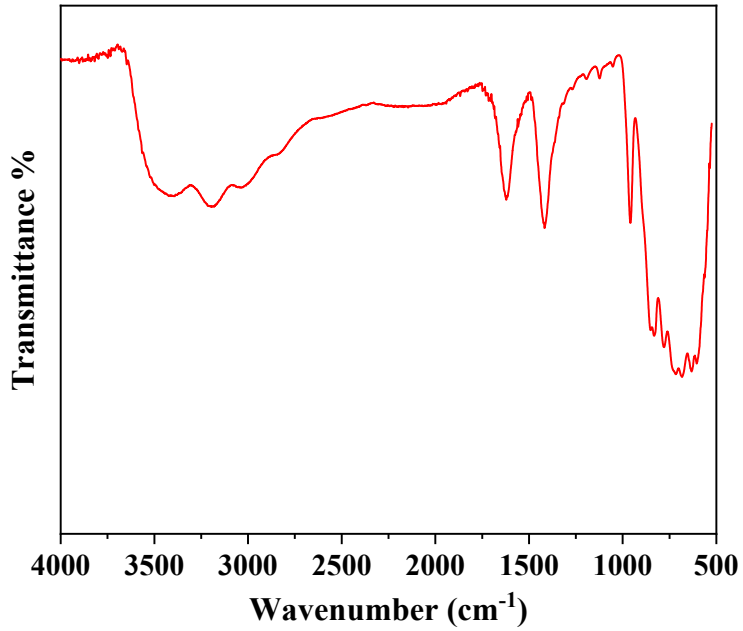


Figure S6 FT-IR spectra of **NdSeW**.

The spectrum showed ν(W–O–W) bridges at 780 and 832 cm^{-1}, terminal ν(W=O) bonds at 957 cm^{-1}, and ν(Se–O) vibrations at 1052 cm^{-1}. Features associated with the DL-malic acid ligand were also discernible, with C=O and C–O stretching vibrations occurring at 1621 and 1416 cm^{-1}, respectively, validating its coordination. Finally, a broad band centered at 3407 cm^{-1} was indicative of O-H stretches from water molecules.

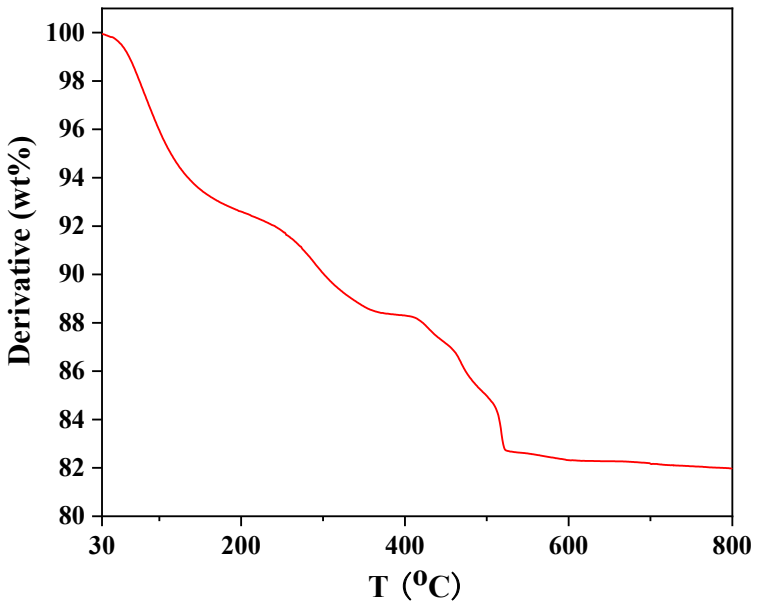


Figure S7 TGA curve of **NdSeW**.

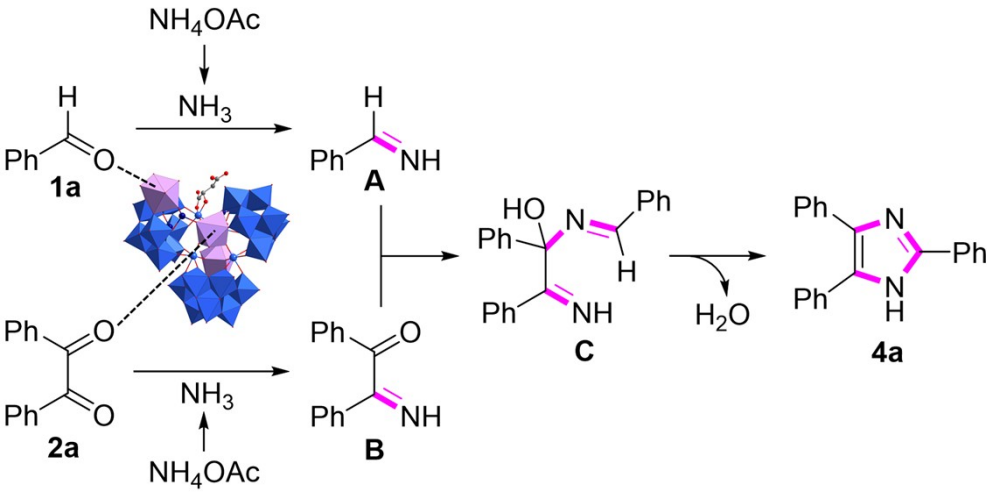
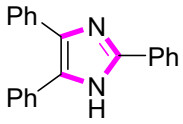


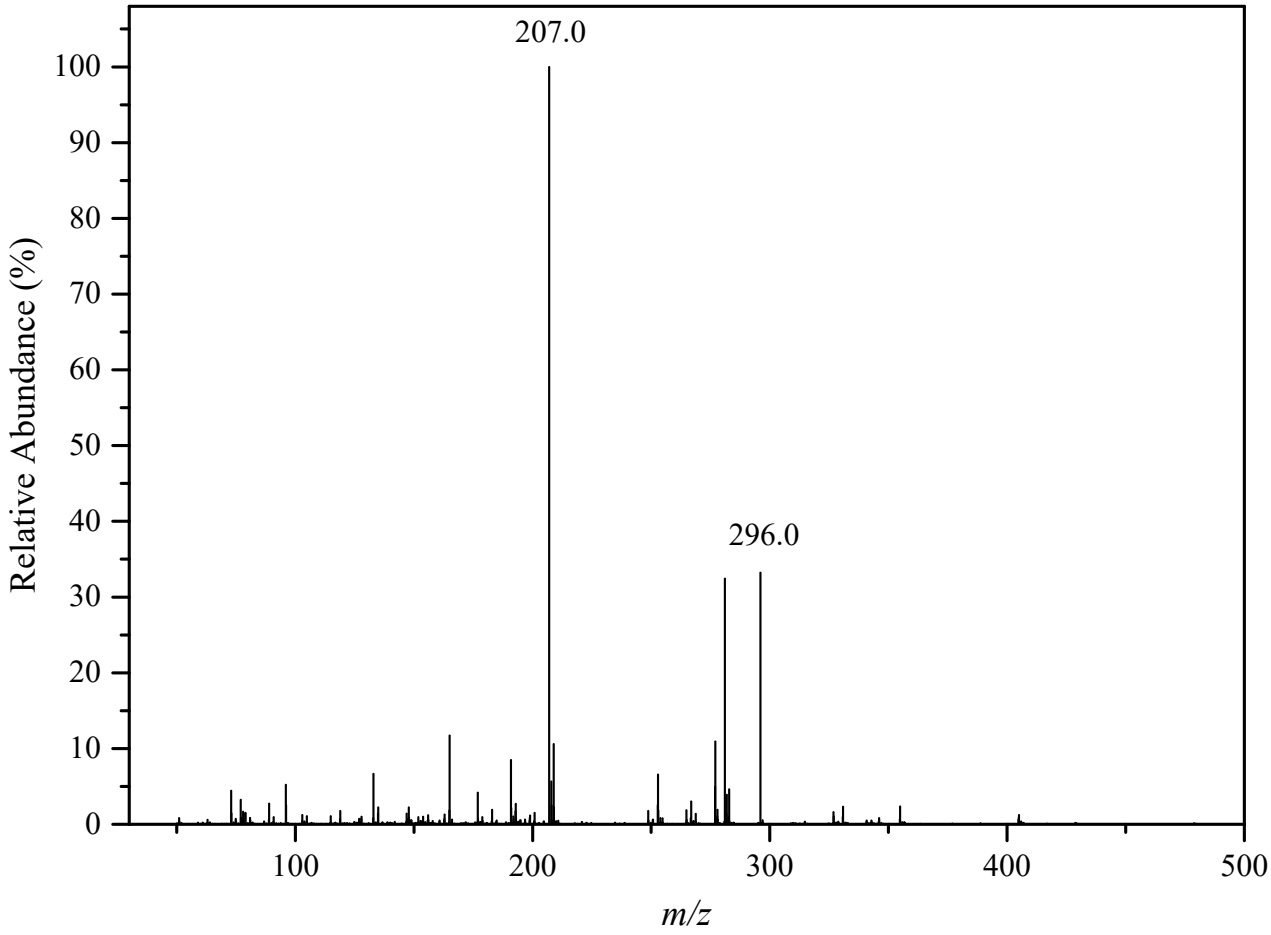
Figure S8 The possible catalytic mechanism.

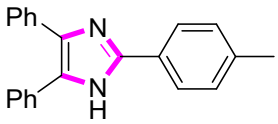
4. Characterization of Products[11]



2,4,5-triphenyl-1*H*-imidazole (4a)

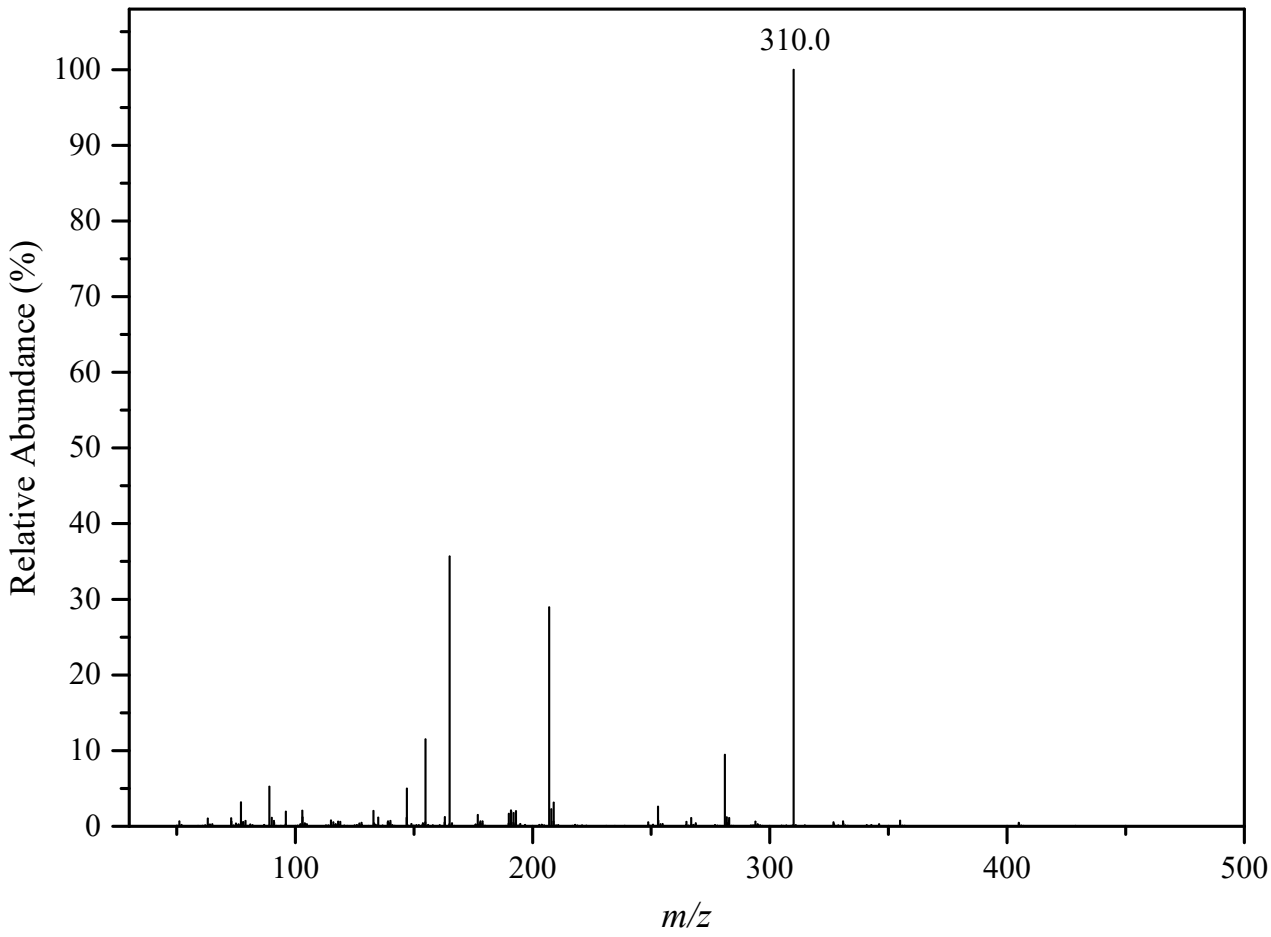
EI-MS: $C_{21}H_{16}N_2$, m/z (%) = 296.0 (33%) [M+].

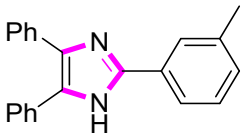




4,5-diphenyl-2-(p-tolyl)-1*H*-imidazole (4b)

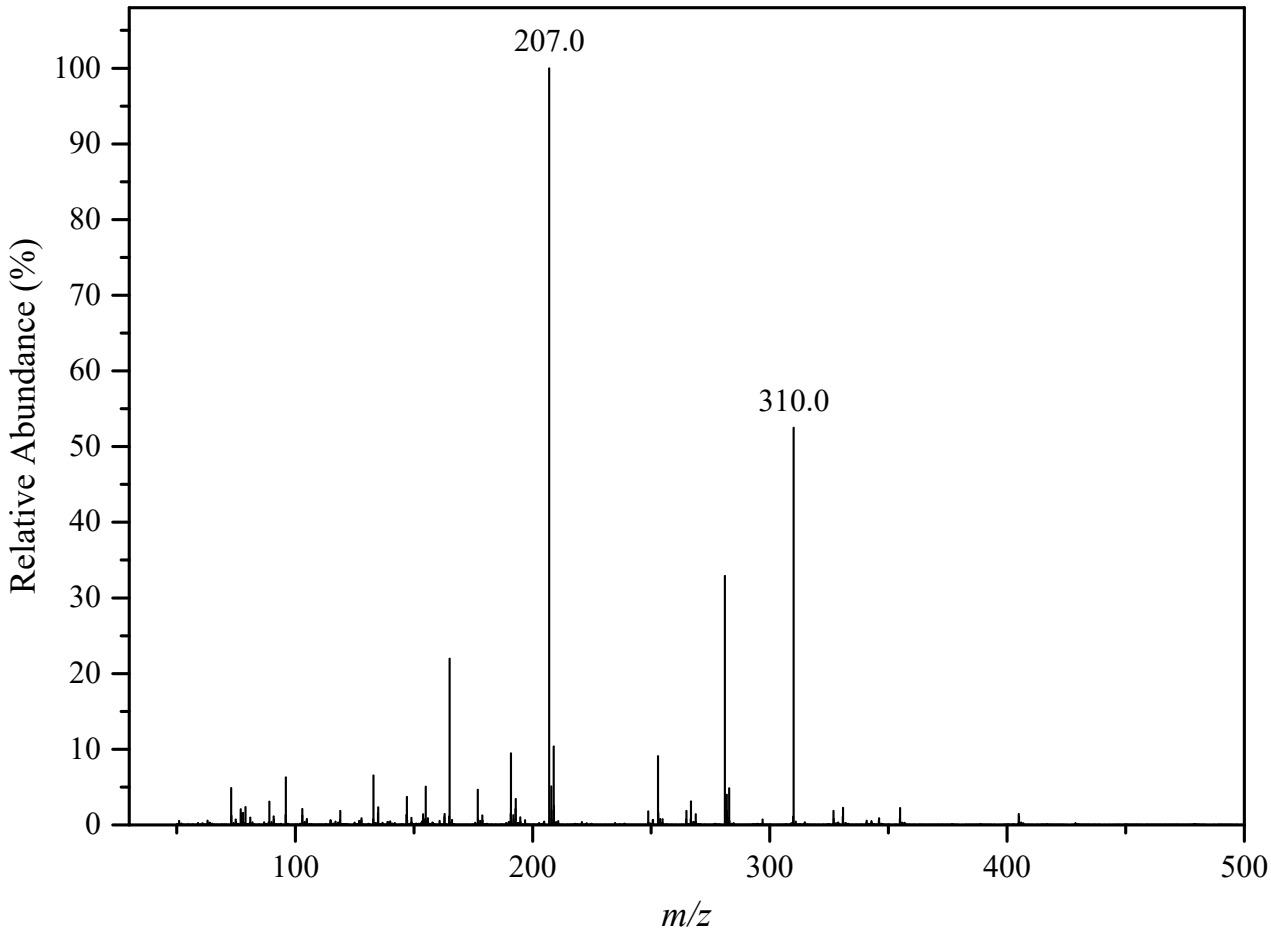
EI-MS: $C_{22}H_{18}N_2$, m/z (%) = 310.0 (100%) [M+].

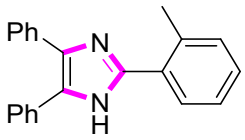




4,5-diphenyl-2-(m-tolyl)-1*H*-imidazole (4c)

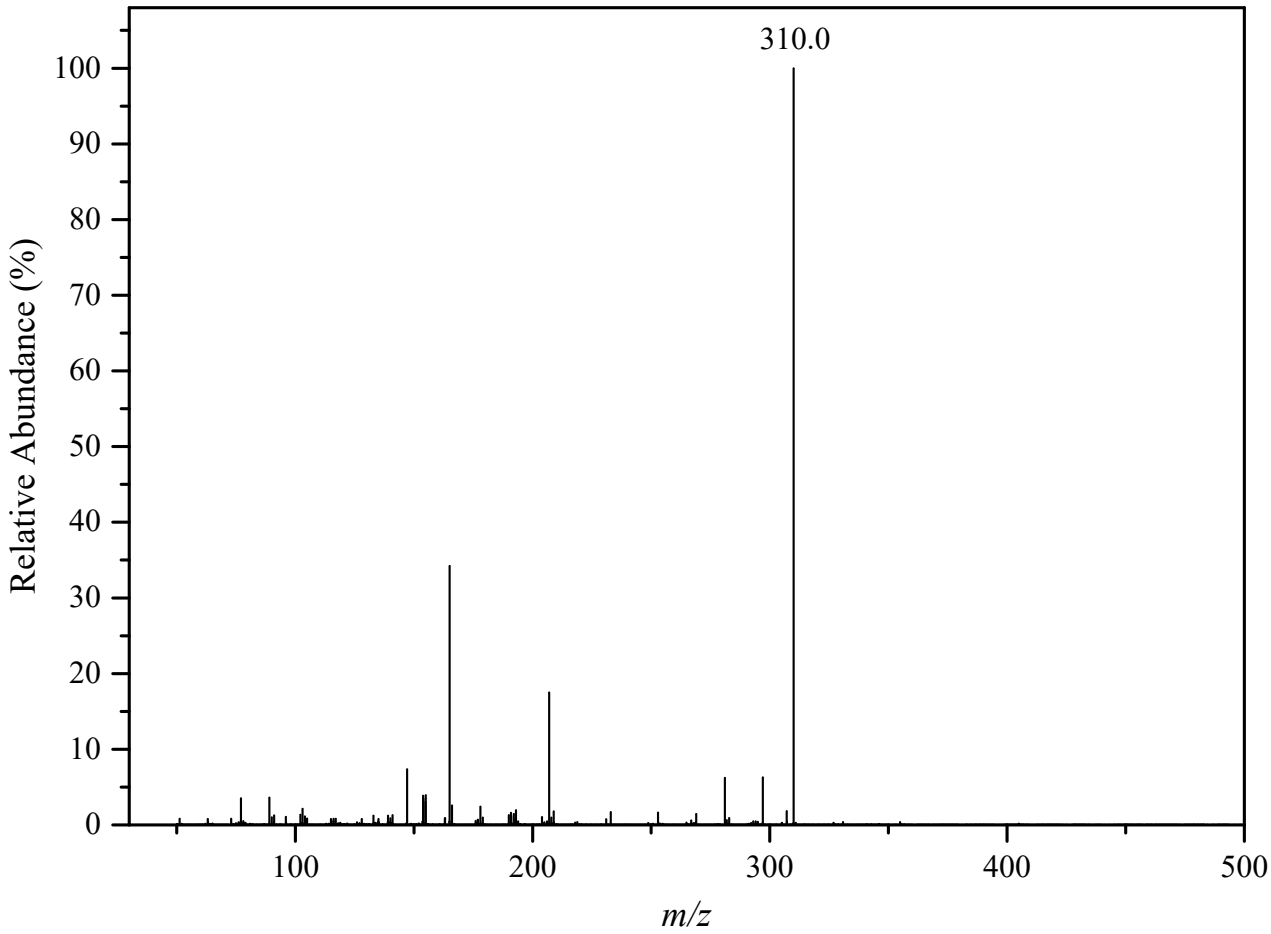
EI-MS: $C_{22}H_{18}N_2$, m/z (%) = 310.0 (52%) [M+].

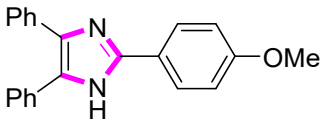




4,5-diphenyl-2-(o-tolyl)-1*H*-imidazole (4d)

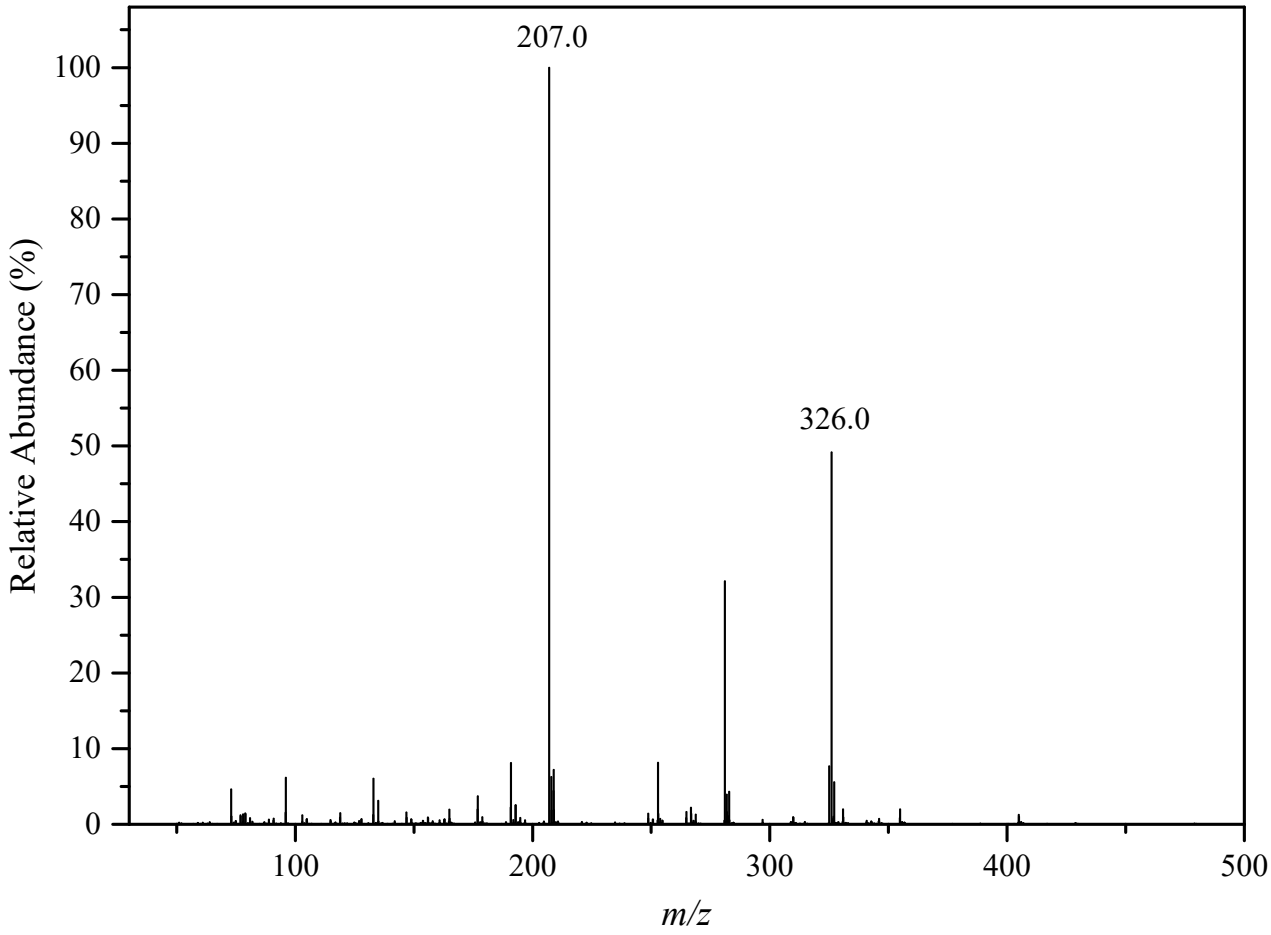
EI-MS: $C_{22}H_{18}N_2$, m/z (%) = 310.0 (100%) [M+].

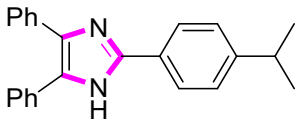




2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (4e)

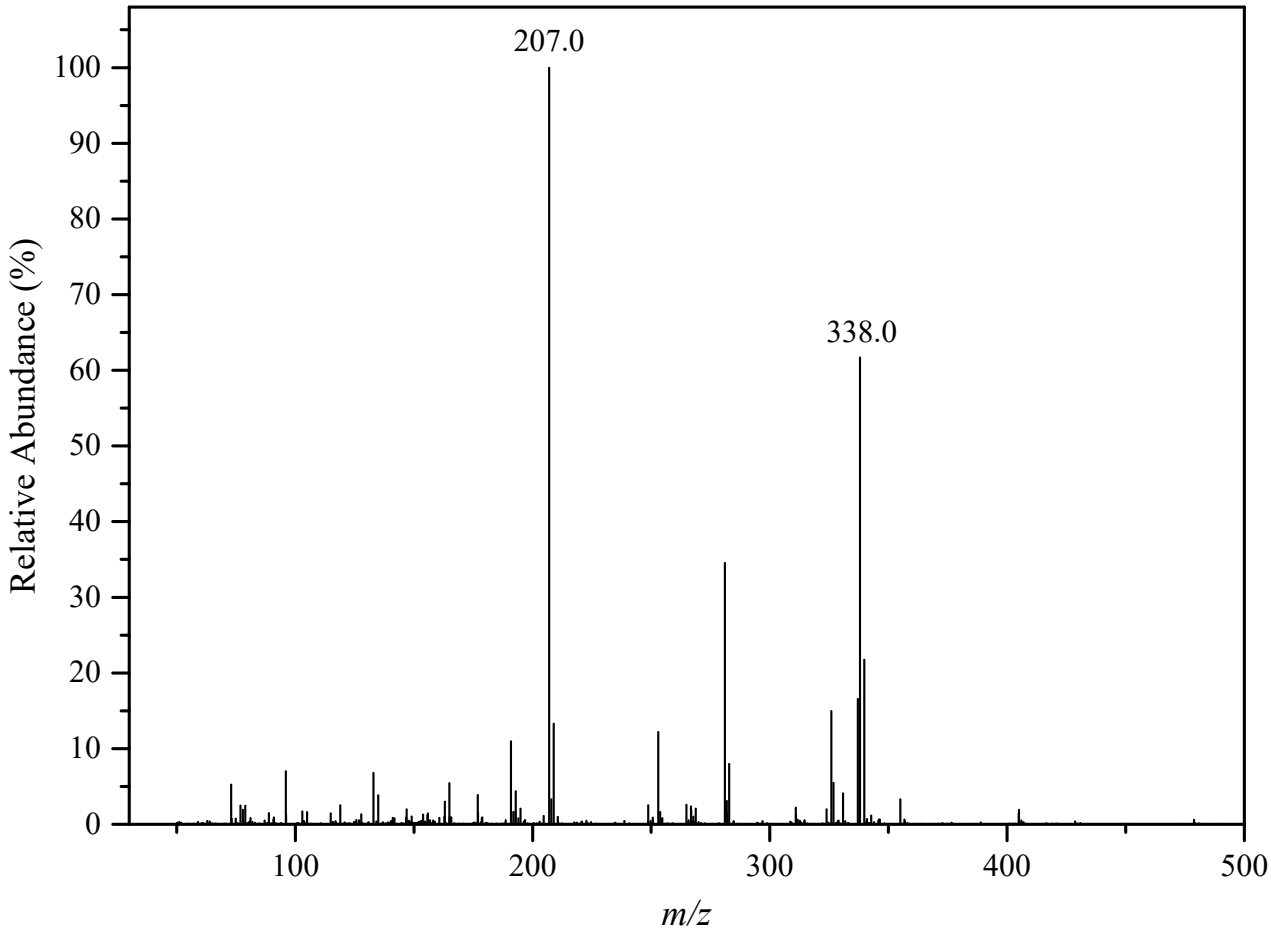
EI-MS: $C_{22}H_{18}N_2O$, m/z (%) = 326.0 (100%) [M+].

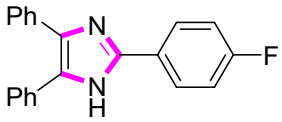




2-(4-isopropylphenyl)-4,5-diphenyl-1*H*-imidazole (4f)

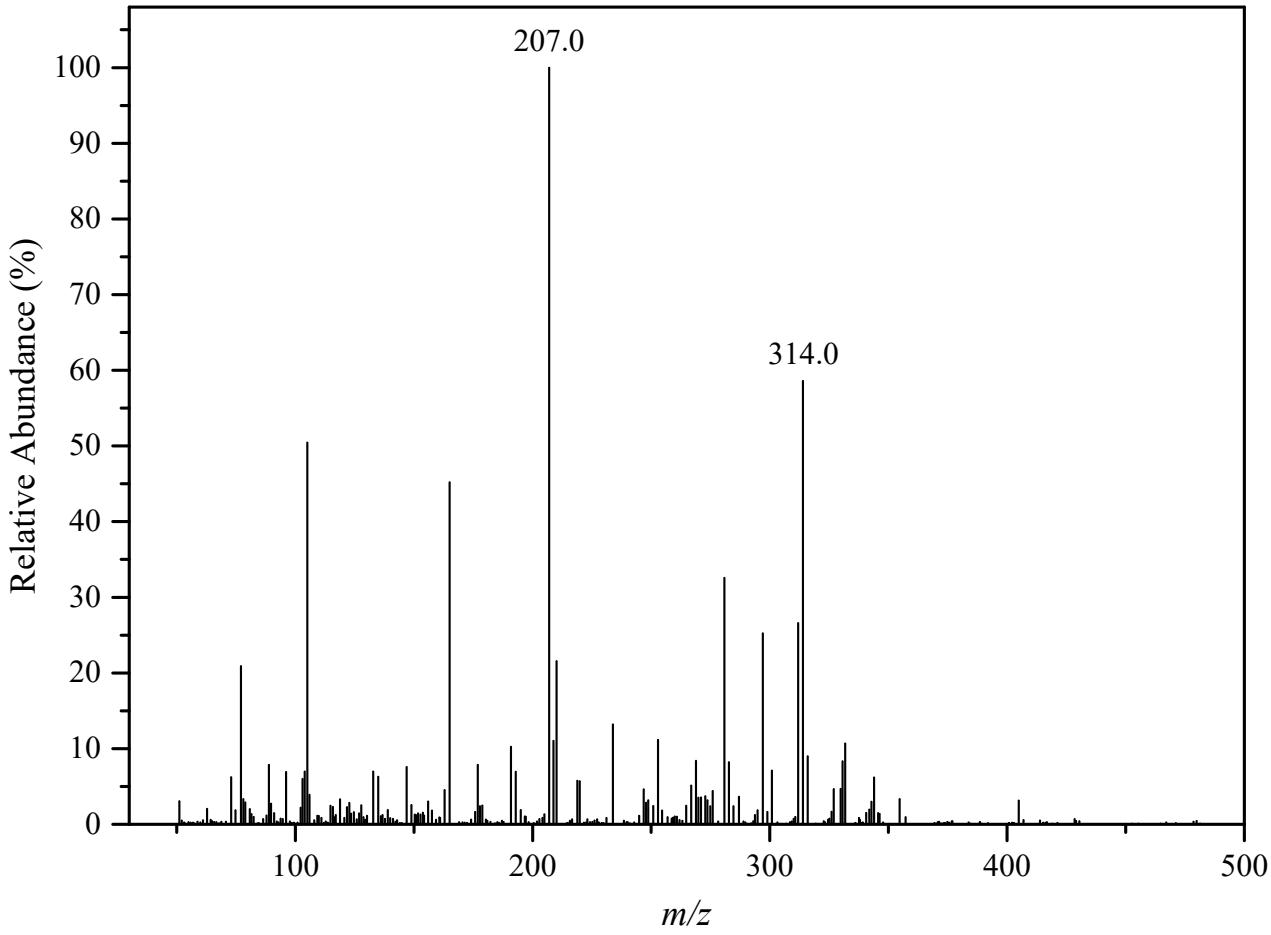
EI-MS: $C_{24}H_{22}N_2$, m/z (%) = 338.0 (62%) [M+].

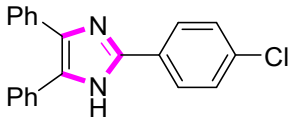




2-(4-fluorophenyl)-4,5-diphenyl-1*H*-imidazole (4g)

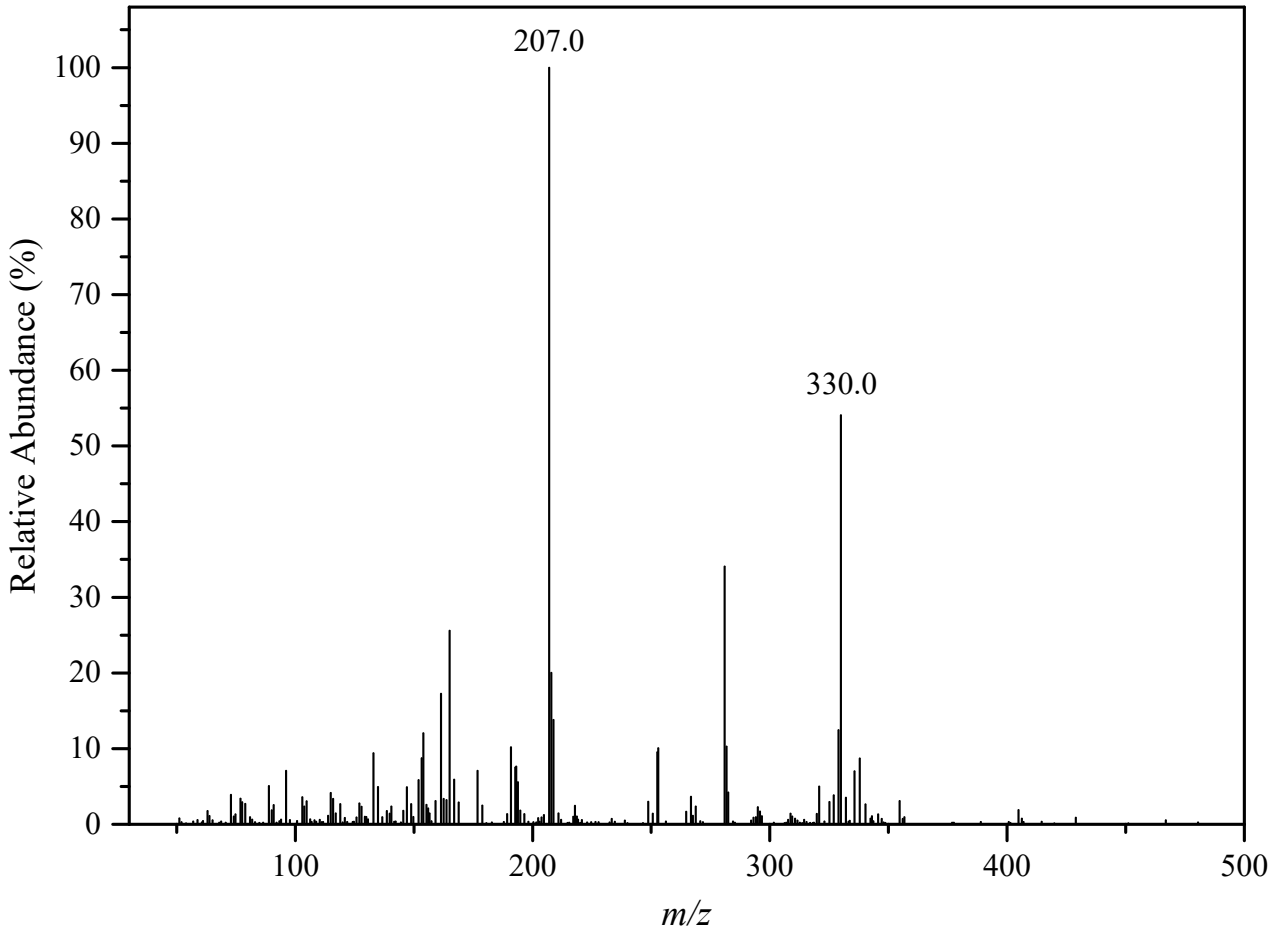
EI-MS: $C_{21}H_{15}FN_2$, m/z (%) = 314.0 (59%) [M+].

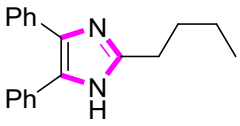




2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (4h)

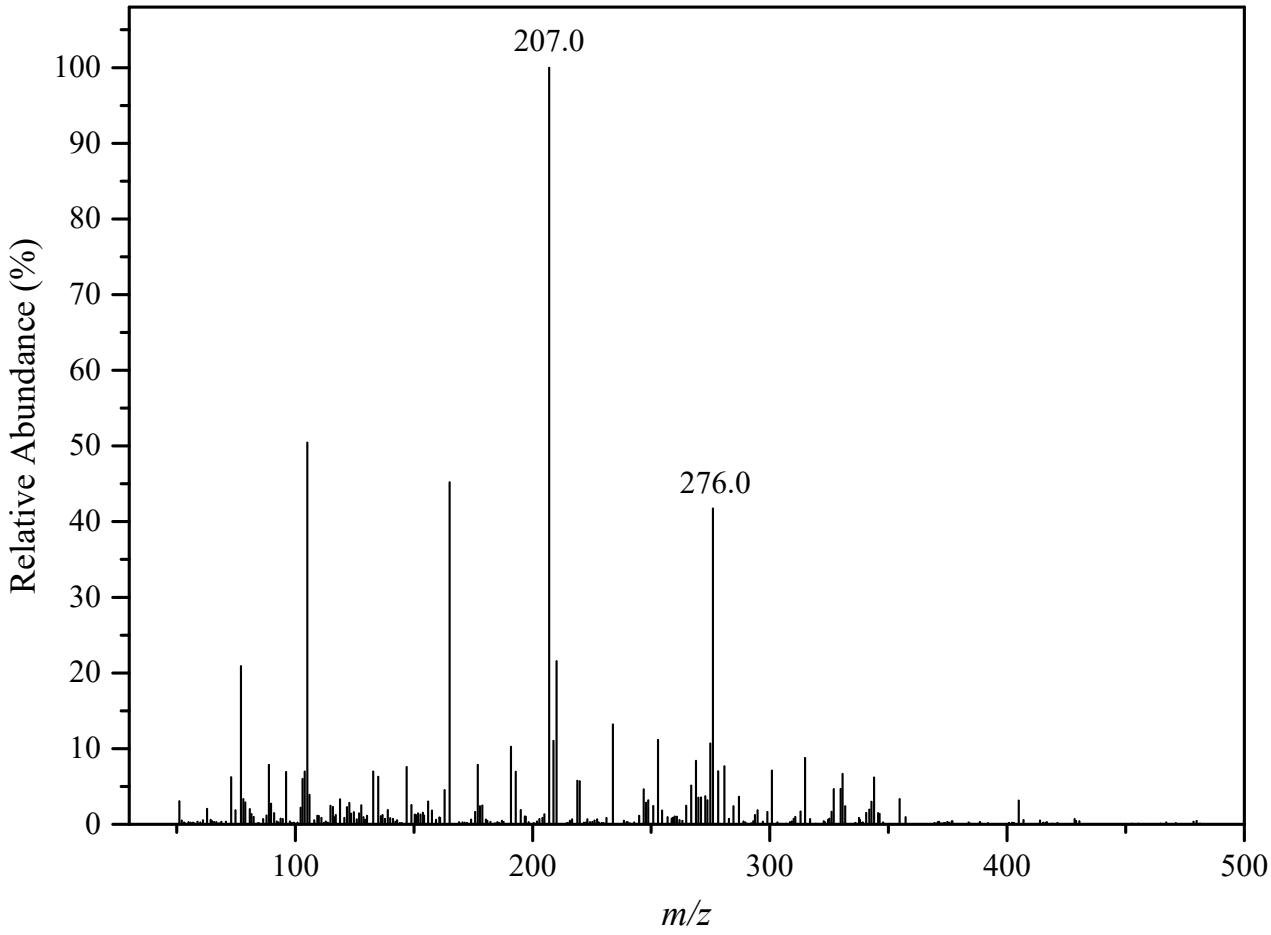
EI-MS: $C_{21}H_{15}ClN_2$, m/z (%) = 330.0 (54%) [M+].

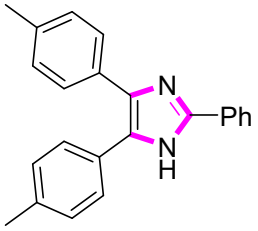




2-butyl-4,5-diphenyl-1*H*-imidazole (4i)

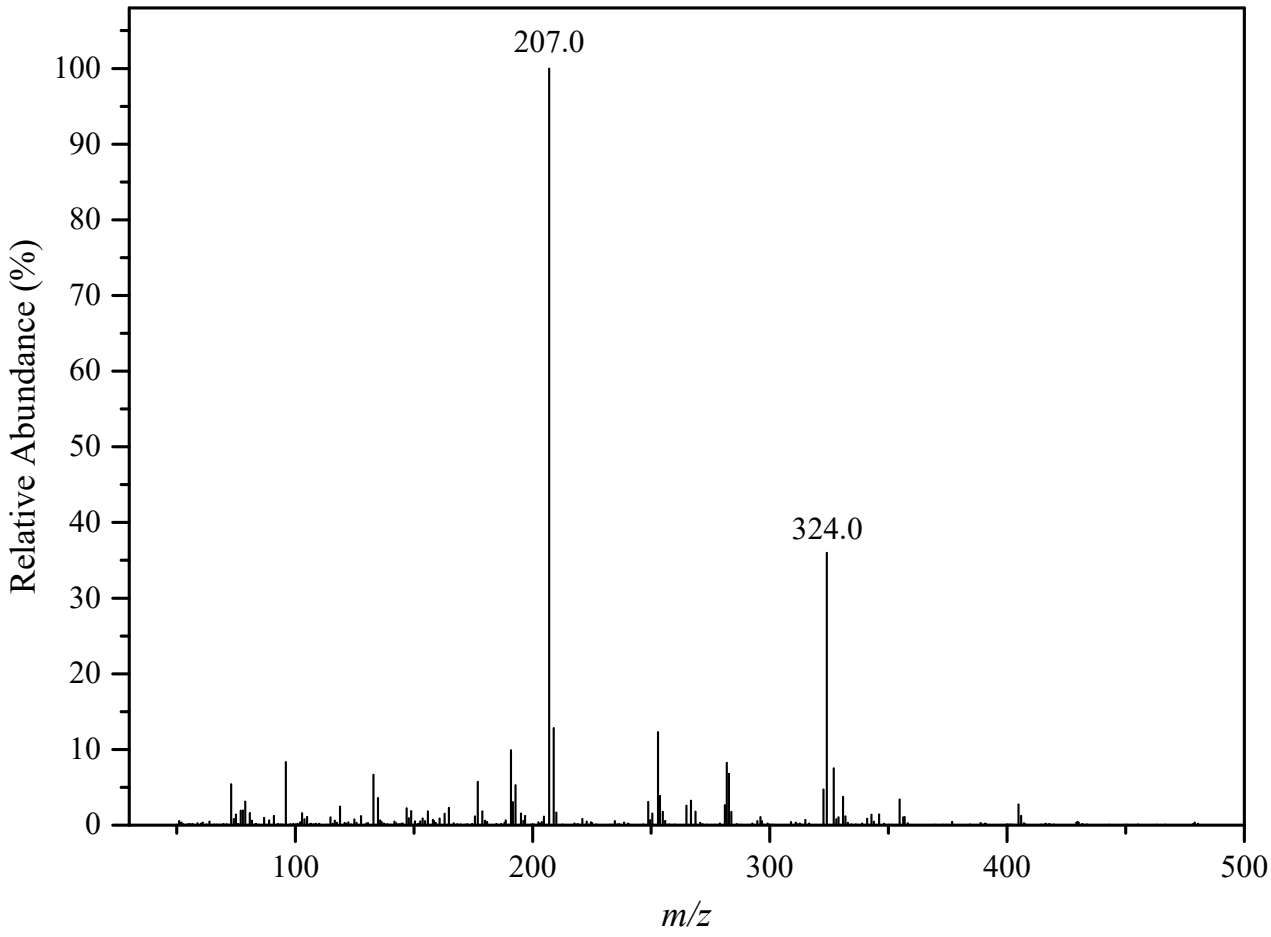
EI-MS: $C_{19}H_{20}N_2$, m/z (%) = 276.0 (42%) [M+].

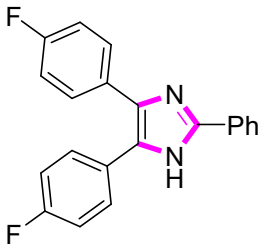




2-phenyl-4,5-di-p-tolyl-1*H*-imidazole (4j)

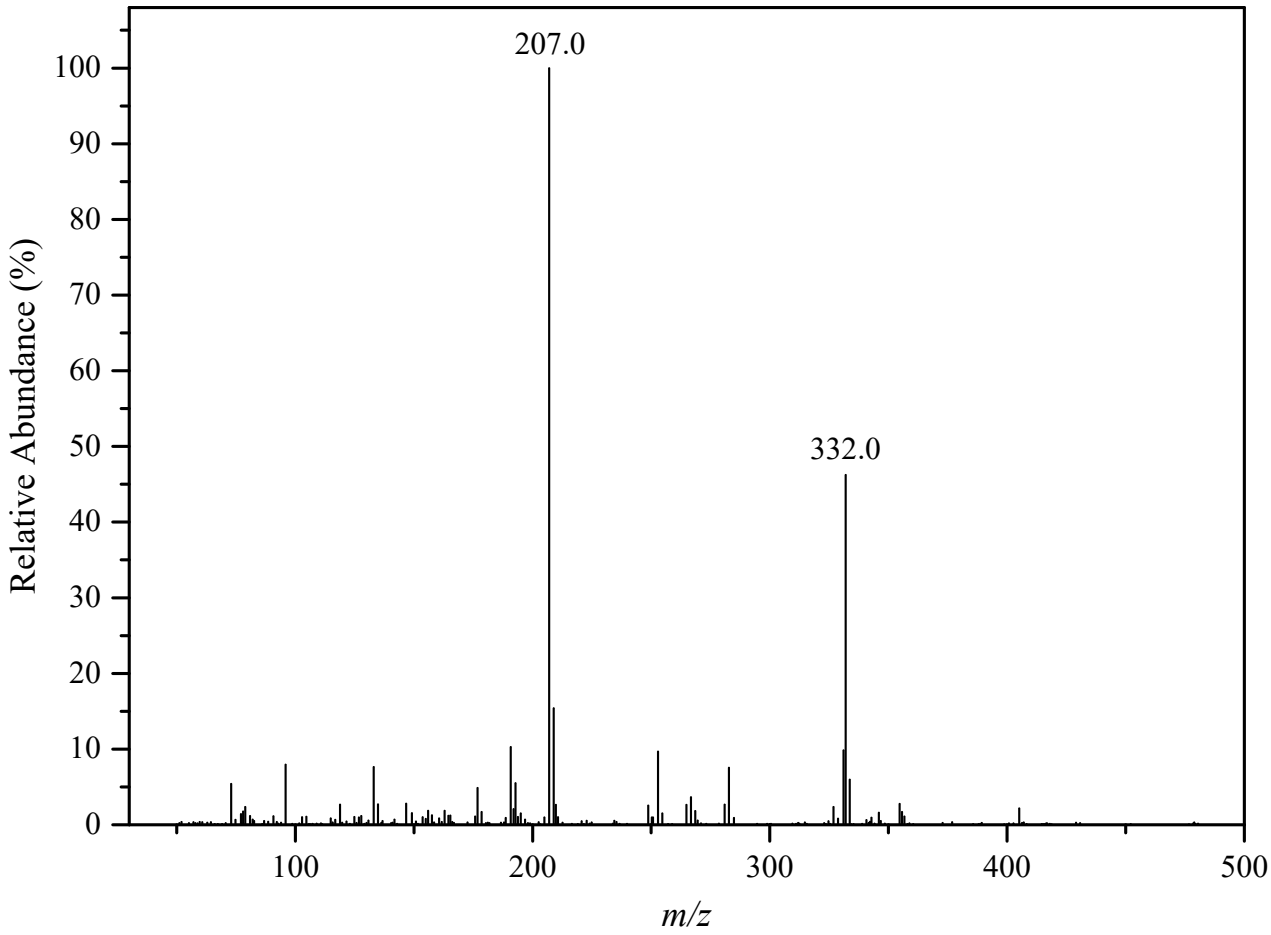
EI-MS: $C_{23}H_{20}N_2$, m/z (%) = 324.0 (36%) [M+].

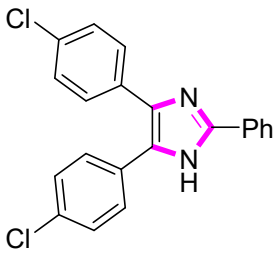




4,5-bis(4-fluorophenyl)-2-phenyl-1*H*-imidazole (4k)

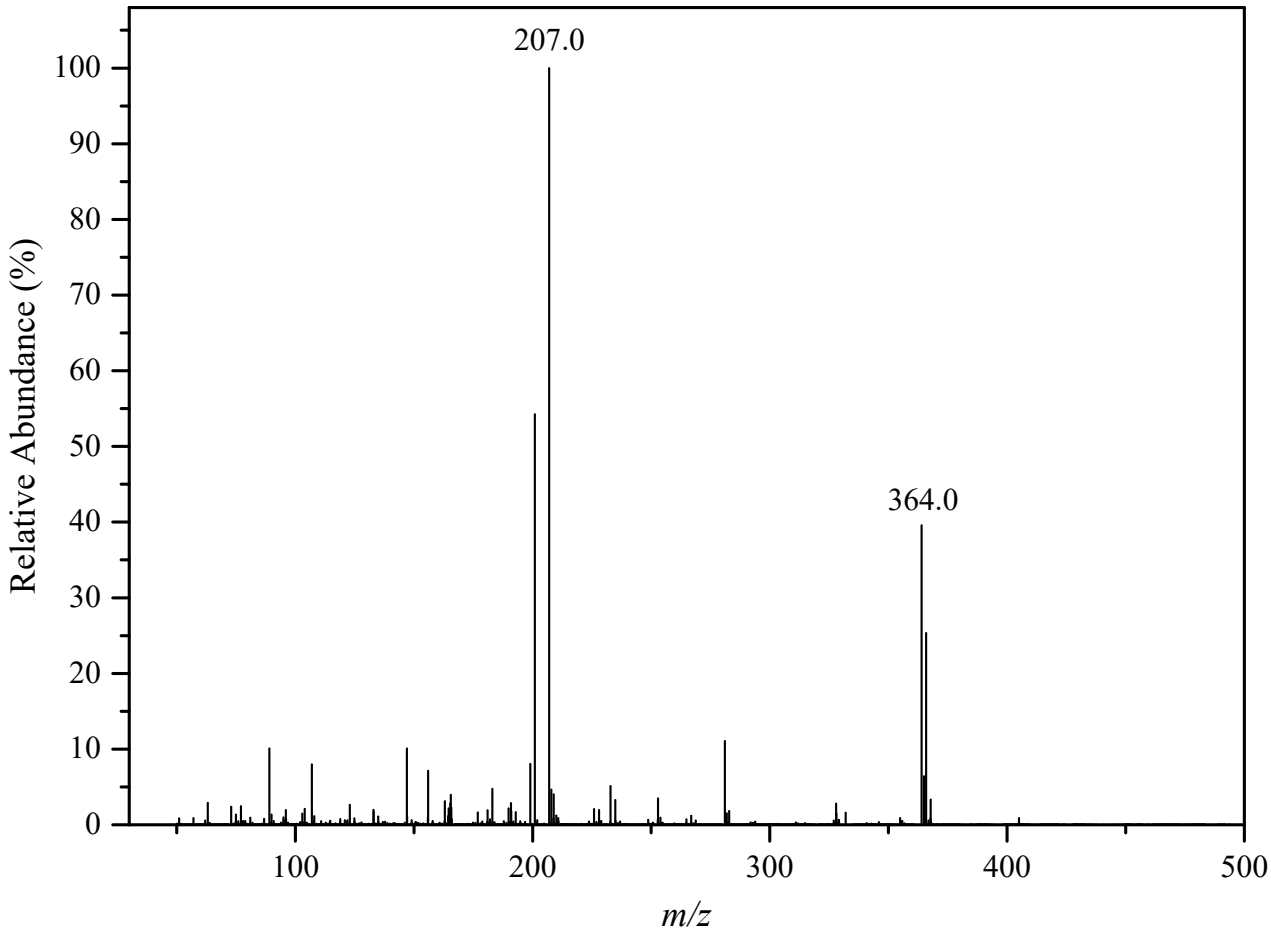
EI-MS: $C_{21}H_{14}F_2N_2$, m/z (%) = 332.0 (46%) [M+].





4,5-bis(4-chlorophenyl)-2-phenyl-1*H*-imidazole (4l)

EI-MS: $C_{21}H_{14}Cl_2N_2$, m/z (%) = 364.0 (40%) [M+].



5. Notes and References

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