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Eco-friendly synthesis of benzoxazepine and malonamide derivatives in aqueous media

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A special, efficient and reusable heterogeneous catalytic system is reported for the one-pot three-component synthesis of a series of malonamide and 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepine derivatives in the presence of a heterogeneous material composed of MCM-48/$H_5PW_{10}V_2O_{40}$ in aqueous media and at room temperature. The products were identified using physical data (melting points) by comparison with those reported in the literature. Also, the structures of the new compounds were characterized by means of infrared, ^1H NMR, ^{13}C NMR and CHN analyses. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: MCM-48/$H_5PW_{10}V_2O_{40}$; malonamide; 2,3,4,5-tetrahydrobenzo[*b*][1,4] oxazepine; green chemistry

Introduction

Heterocyclic chemistry is one of the most significant branches in organic chemistry.[1] The increasing applications of catalyst-based synthetic procedures in emerging industries have been favoured by the continuous innovations observed over the last decade for various catalytic processes.[2] Catalysts based on heteropolyacids (HPAs) and related compounds, especially those comprising the strongest Keggin-type HPAs, represent a field in which new and promising developments are being achieved in both technology and academia.[3] The main disadvantages of HPAs lie in their water-solubility, low surface area, recycling and difficult recovery which always limit their practical applications.[4]\ Heterogeneous catalysts offer high atom efficiency, higher surface area, easy product purification, lower coordinating sites, and simple and efficient recovery and reusability.

MCM-48 is a class of mesoporous silica tube-like materials with consistent-sized three-dimensional mesoporous structure. This combination has led to them being of interest as sorbents and solid supports in catalysis.[5]

The benzo[*b*][1,4]oxazepine derivatives show various forms of bioactivity such as allergic bronchitis, treating of bronchial asthma,[6] anxiolytic activity, antidepressive,[7] antihistaminic and antiserotoninergic[8] effects, anticancer activity against breast cancer cells[9] and progesterone receptor agonists.[10] The common methods for the syntheses of benzo[*b*][1,4]oxazepines involve *N*-alkylation of *N*-methylanthranilic acid with an α-chloroacid[11] and *N*-alkylation of 2-aminobenzhydrol, in the presence of ethanolic sodium solution.[12] Also, a single-step synthesis of benzoxazepines has been reported in which *N*-tosyl-1,3-aminoalcohols were treated with bromoethylsulfonium salts, through vinyl sulfonium salt formation, which upon intramolecular cyclization provide 1,4-benzoxazepines.[13]

Malonamide derivatives are some of the most important goals in synthetic chemistry because they display a number of interesting properties in various fields.[14] These compounds have some important applications such as effective liquid–liquid extractants,[15] poncoments in peptidomimetic substances,[16] excellent ionophores,[17] bidentate chelates and monomers in the nylon family.[18]

Shaabani *et al.* have reported novel routes for the synthesis of benzoxazepine and malonamide derivatives in the absence of catalyst in CH_2Cl_2 as solvent and long reaction times using isocyanide-based multicomponent reactions.[19] Herein, we report a highly versatile, eco-friendly and efficient one-pot three-component heterogeneous protocol for the synthesis of benzoxazepine and malonamide derivatives in the presence of a catalytic amount of MCM-48/$H_5PW_{10}V_2O_{40}$ in water as solvent at room temperature (Scheme 1).

Results and discussion

Low-angle powder X-ray diffraction (XRD) was used to study the calcined mesoporous structure of MCM-48. This compound shows an intense peak assigned to reflections at (100) and two low-intensity peaks at (110) and (200), which correspond to a significant degree of long-range ordering in the structure and well-ordered hexagonal pore system. The (100) reflection of MCM-48 is still observed after loading with $H_5PW_{10}V_2O_{40}$ (Fig. 1(a)). However, modification of MCM-48 with $H_5PW_{10}V_2O_{40}$ results in a loss of crystalline order, as is evidenced by a significant decrease in diffraction intensities.

This observation confirms that the mesoporous structure of MCM-48 remains almost unchanged upon $H_5PW_{10}V_2O_{40}$ loading. According to scanning electron microscopy (SEM) images (Figs. 1 (b) and (c)), the morphology of MCM-48 surface tends to be rougher after immobilization of $H_5PW_{10}V_2O_{40}$, which confirms the successful loading of the HPA on MCM-48.

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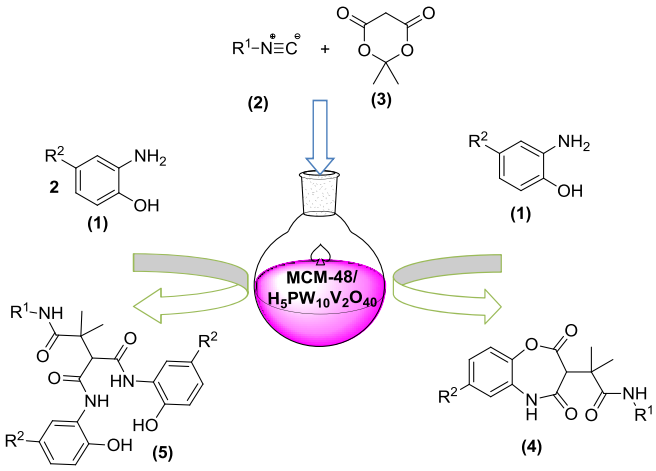
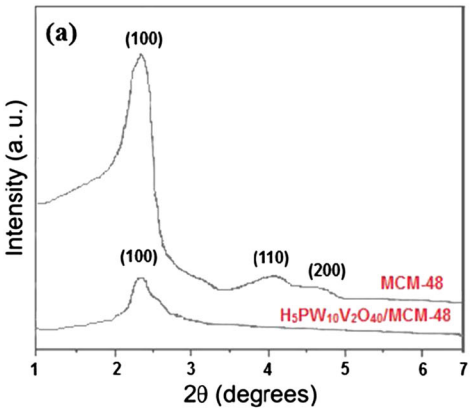
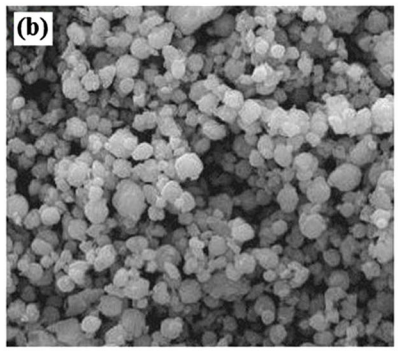


Scheme 1. Synthesis of 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepine and malonamide derivatives.





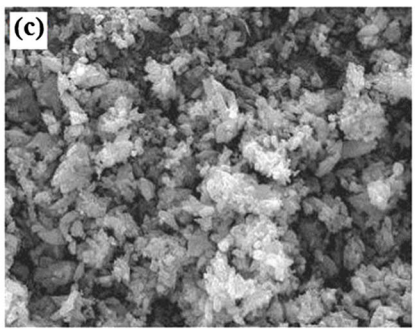


Figure 1. (a) Low-angle XRD patterns of calcined MCM-48 and MCM-48/H5PW $_{10}$V $_2$O $_{40}$. SEM images of (b) MCM-48 and (c) MCM-48/H $_5$PW $_{10}$V $_2$O $_{40}$.

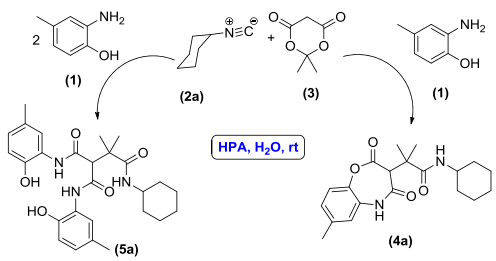
A comparative study was carried out using the reaction of one or two equivalents of 2-amino-4-methylphenol with cyclohexylisocyanide and Meldrum's acid as a model system with various vanadium-substituted tungsten heteropolyacid (HPW) catalysts, solvents and catalyst quantities.

In a pilot experiment, the catalytic activity of H $_5$PW $_{10}$V $_2$O $_{40}$ was compared with that of other vanadium-substituted HPW catalysts in the preparation of compounds **4a** and **5a** (Table 1). The results indicate that the substitution of one and two vanadium atoms instead of W(VI) and Mo(VI) in H $_3$PM $_{12}$O $_{40}$ leads to an enhancement in the catalytic activity of HPW. Also, H $_5$PW $_{10}$V $_2$O $_{40}$ is a little more active than H $_5$PMo $_{10}$V $_2$O $_{40}$. The catalytic activity of H $_5$PW $_{10}$V $_2$O $_{40}$ could be due to coordination geometry of the metaloxo complex species and the far distance of the vanadyl oxygen double bond from the heteropolyanion. This geometry exposes the vanadyl species at the surface of the heteropolyanion, which might be involved in the catalytic cycle. This consideration has to be taken into account for the assessment of the catalytic activity of H $_5$PW $_{10}$V $_2$O $_{40}$ and the role of vanadium in the catalytic system.[20]

The effect of solvent was also examined for the reaction mentioned above, and the results indicate that the solvent has an effect on the reaction (Table 2). Performing the reaction of one or two equivalents of 2-amino-4-methylphenol with cyclohexylisocyanide and Meldrum's acid in various protic and aprotic solvents reveals that polar solvents are more efficient than nonpolar solvents, and preferentially water as the reaction solvent (Table 2).

According to expectations, the catalytic efficiency should be influenced by the amount of catalyst. Thus, a set of experiments was conducted using various amounts of MCM-48/H $_5$PW $_{10}$V $_2$O $_{40}$ in the reaction of one or two equivalents of 2-amino-4-methylphenol with cyclohexylisocyanide and Meldrum's acid in water as solvent at room temperature (Table 3). The optimum

Table 1. Effect of type of vanadium-substituted HPA catalyst in the synthesis of 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepine and malonamide derivatives[a]



HPA	Amount (mol%)	Time (min)	Yield of **4a** (%)[b]	Yield of **5a** (%)[b]
H $_5$PW $_{10}$V $_2$O $_{40}$	0.5	120	78	82
H $_7$SiW $_9$V $_3$O $_{40}$	0.5	120	70	72
H $_5$PMo $_{10}$V $_2$O $_{40}$	0.5	120	77	80
H $_5$SiW $_9$Mo $_2$VO $_{40}$	0.5	120	79	81
HPA/MCM-48	0.05 g	120	91	95
CuSO $_4$		120	39	44
CuSO $_4$/SiO $_2$		120	53	58

[a]Reaction conditions: 2-amino-4-methylphenol (**1**, 1.00 or 2.00 mmol), cyclohexylisocyanide (**2a**, 1.00 mmol), Meldrum's acid (**3**, 1.00 mmol) and HPA in water as solvent at room temperature.

[b]Isolated yields.

Table 2. Influence of solvent on yield of **4a** and **5a**[a]

Entry	Solvent	Time (min)	Yield of **4a** (%)[b]	Yield of **5a** (%)[b]
1	Water	120	86	91
2	Ethanol	120	93	95
3	Acetonitrile	120	89	89
4	Toluene	120	38	46
5	Dichloromethane	120	87	92
6	Chloroform	120	85	88
7	Tetrahydrofuran	120	79	81

[a]Reaction conditions: 2-amino-4-methylphenol (**1**, 1.00 mmol or 2.00 mmol), cyclohexylisocyanide (**2a**, 1.00 mmol), Meldrum's acid (**3**, 1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.10 g), solvent (3.00 ml), at room temperature.

[b]Isolated yields.

amount of catalyst is 0.05 g resulting in 86 and 91% yields of compounds **4a** and **5a**, respectively. Lower amounts of catalyst result in a decrease in the efficacy of the reaction, while higher amounts lead to complete conversion in the same reaction time.

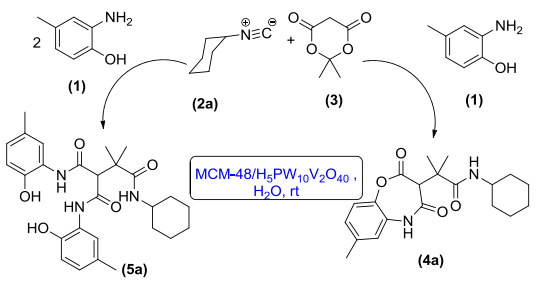
The generality of the process was studied using a range of isocyanides and 2-aminophenol derivatives for the synthesis of **4a**–**h** and **5a**–**h** in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$ (Table 4).

Recovery/reuse is one of the important properties of catalysts. It is observed that the MCM-48/$H_5PW_{10}V_2O_{40}$ catalytic activity stays almost unaltered even after four recovery/reutilization cycles. Therefore, the catalyst was recovered from the reaction between 2-amino-4-methylphenol, Meldrum's acid and cyclohexylisocyanide by filtration. Thereby, the stability of MCM-48/$H_5PW_{10}V_2O_{40}$ after successive cycles of recovery/reuse was assessed (Table 5).

The changes in the morphology of MCM-48/$H_5PW_{10}V_2O_{40}$ after use were determined using XRD and Fourier transform infrared spectroscopy. As can be seen in Fig. 2, the structure of the recycled catalyst does not change and a very slight decrease in the reaction yield may be due to the covering of the surface of catalyst by impurities. Therefore, MCM-48/$H_5PW_{10}V_2O_{40}$ can be considered as a promising material for the adsorption of HPAs for catalytic purposes.

Finally, a reasonable mechanism is proposed for the synthesis of **4a**–**h** by means of the HPA $H_5PW_{10}V_2O_{40}$ immobilized on MCM-48 (Scheme 2). First, Meldrum's acid **3** is protonated by MCM-48/$H_5PW_{10}V_2O_{40}$ and the intermediate **7** is formed from condensation between molecules of **1** and **3** and releasing a molecule of acetone. Then, intermediate **8** is obtained from the reaction of intermediate **7** with acetone undergoing a Knoevenagel condensation. On the basis of the well-established chemistry of reactions of isocyanides, intermediate **9** is formed by nucleophilic attack of isocyanide **2** on intermediate **8**, followed by nucleophilic attack of an H_2O molecule on the activated nitrilium moiety to produce compound **10**. Finally, tautomerization of compound **10** leads to the formation of products **4a**–**h**, as shown in Scheme 2.[21]

Table 3. Effect of amount of MCM-48/$H_5PW_{10}V_2O_{40}$ on reaction of 2-amino-4-methylphenol with cyclohexylisocyanide and Meldrum's acid[a]



Entry	Catalyst amount (g)	Time (min)	Yield of **4a** (%)[b]	Yield of **5a** (%)[b]
1	0.01	120	30	25
2	0.03	120	68	60
3	0.05	120	86	91
4	0.07	120	95	92
5	0.1	120	97	96

[a]Reaction conditions: 2-amino-4-methylphenol (**1**, 1.00 mmol or 2.00 mmol), cyclohexylisocyanide (**2a**, 1.00 mmol), Meldrum's acid (**3**, 1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ in water as solvent at room temperature.

[b]Isolated yields.

Conclusions

A highly efficient and environmentally friendly method is presented for the synthesis of 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepine and malonamide derivatives in the presence of a catalytic amount of MCM-48/$H_5PW_{10}V_2O_{40}$ in aqueous media and at room temperature which led to excellent yields. Easy workup, low cost, short reaction time, easy recyclability of the catalyst with no loss in its activity and using mild reaction condition are some advantages of the method presented. The experimental procedure for this reaction is remarkably simple and requires no toxic organic solvents or inert atmosphere.

Experimental

Preparation of $H_5PW_{10}V_2O_{40}\cdot 30H_2O$[22]

$NaVO_3$ (6.1 g, 50 mmol) was dissolved in 50 ml of boiling water and mixed with Na_2HPO_4 (1.78 g, 12.5 mmol). After the resulting solution was cooled to room temperature, concentrated sulfuric acid (2.5 ml, 17 M, 43 mmol) was added to give a red solution. Sodium tungstate dehydrate ($Na_2WO_4\cdot 2H_2O$, 41.2 g, 125 mmol) was dissolved in 50 ml of water and was added to the red solution with vigorous stirring, followed by the slow addition of concentrated sulfuric acid (21 ml, 17 M, 357 mmol).[21] Extraction of the solution with diethyl ether (160 ml), foll\owed by evaporation in air, afforded $H_5PW_{10}V_2O_{40}$ as a crystalline, orange-red solid (yield, 75%).

Synthesis of MCM-48 using Hydrothermal Method[23]

n-Hexadecyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, template) was dissolved in deionized water, and sodium hydroxide and tetraethoxysilane (TEOS) were added. The molar composition of the gel was 1 M TEOS/0.25 M Na_2O/0.65 M $C_{16}H_{33}(CH_3)_3NBr$/62 M H_2O. The solution was stirred for about 1 h, charged into a polypropylene bottle and then heated at 383 K for 4 days. The product was filtered, washed with water and calcined at 823 K for 8 h.

Table 4. Synthesis of 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepine derivatives (**4a–h**) and malonamide derivatives (**5a–h**) in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$[a]

Product	R_1	R_2	Time (min)	Yield (%)[b]	M.p. (°C)	
					Found	Reported
4a	*c*-Hex	4-CH_3	120	86	249–251	—
4b	*c*-Hex	4-Cl	140	85	228–230	228–230[23a]
4c	*t*-Bu	H	160	83	152–153	151–153[23a]
4d	*t*-Bu	4-CH_3	130	88	227–229	227–229[23a]
4e	1,1,3,3-Tetramethylbutyl	H	140	87	213–215	214–216[23a]
4f	*c*-Hex	H	150	90	170–172	169–171[23a]
4g	2,6-Dimethylphenyl	H	130	91	220–223	—
4h	2,6-Dimethylphenyl	4-CH_3	110	92	264–267	—
5a	*c*-Hex	4-CH_3	120	91	221–223	220–222[23a]
5b	1,1,3,3-Tetramethylbutyl	4-CH_3	130	90	227–229	227–229[23a]
5c	2,6-Dimethylphenyl	H	160	89	243–245	242–244[23a]
5d	2,6-Dimethylphenyl	4-CH_3	110	88	233–235	233–235[23a]
5e	4-Methylphenylsulfonyl	H	140	85	172–174	172–174[23a]
5f	4-Methylphenylsulfonyl	4-CH_3	140	89	150–153	151–153[23a]
5g	*c*-Hex	4-Cl	140	84	245–247	—
5h	*t*-Bu	4-CH_3	130	82	215–218	—

[a]Reaction conditions: 2-amino-4-methylphenol (**1**, 1.00 mmol or 2.00 mmol), cyclohexylisocyanide (**2**, 1.00 mmol), Meldrum's acid (**3**, 1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ in water as solvent at room temperature.
[b]Isolated yields.

Table 5. Reusability of the catalyst for the synthesis of **4a** and **5a**[a]

Compound	Cycle	0	First	Second	Third	Fourth
4a	Time (min)	120	120	120	120	120
	Yield (%)[b]	86	84	82	81	79
5a	Time (min)	120	120	120	120	120
	Yield (%)[b]	91	90	88	86	84

[a]Reaction conditions: 2-amino-4-methylphenol (**1**, 1.00 mmol or 2.00 mmol), cyclohexylisocyanide (**2**, 1.00 mmol), Meldrum's acid (**3**, 1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ in water as solvent at room temperature.
[b]Isolated yields.

Preparation of MCM-48/$H_5PW_{10}V_2O_{40}$[24]

MCM-48/$H_5PW_{10}V_2O_{40}$ was prepared by mixing dried MCM-48 (2 g) with a solution of $H_5PW_{10}V_2O_{40}{\cdot}30H_2O$ (0.50 g) in the minimum amount of deionized water. The resulting mixture was stirred continuously with a magnetic stirrer for 17 h. After removal of water, the solid powder was first dried at 100°C for 6–7 h, then dried at 150°C for 3 h.

General procedure for preparation of malonamide derivatives 4a–h

An intimate mixture isocyanide derivatives (1.00 mmol), Meldrum's acid (1.00 mmol), 2-aminophenol derivatives (1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.05 g) was reacted in water (3.00 ml) as solvent at room temperature for appropriate times. After completion of reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 1:1), ethanol (3 ml) was added to the reaction mixture which was then heated at 60°C. Catalyst was removed by filtration and the filtrate solution was crystallized to give pure crystalline products **4a–h**.

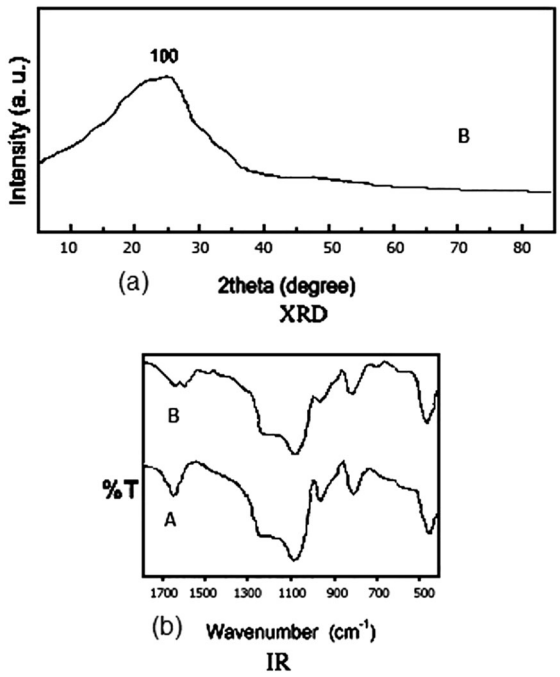
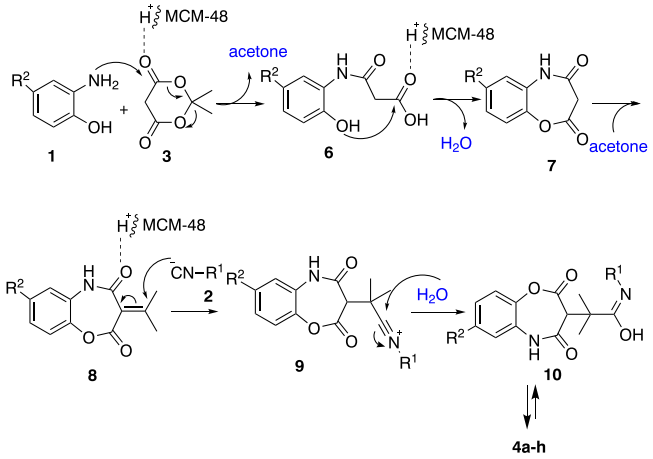


Figure 2. (a) XRD pattern and (b) infrared spectra. A: MCM-48/$H_5PW_{10}V_2O_{40}$ before reaction; B: MCM-48/$H_5PW_{10}V_2O_{40}$ after recycling.

General procedure for preparation of 2,3,4,5-tetrahydrobenzo[*b*][1,4]oxazepines 5a–h

An intimate mixture of isocyanide derivatives (1.00 mmol), Meldrum's acid (1.00 mmol), 2-aminophenol derivatives (2.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.05 g) was reacted in water (3.00 ml) as solvent at room temperature for appropriate times After completion of reaction, as indicated by TLC (ethyl



Scheme 2. Possible mechanism for the preparation of products 4a–h catalysed by MCM-48/H5PW10V2O40.

acetate–*n*-hexane, 1:1), ethanol (3 ml) was added to the reaction mixture which was then heated at 60°C. Catalyst was removed by filtration and the filtrate solution was crystallized to give pure crystalline products **5a**–**h**.

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