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# Iron(III)-catalyzed aerobic oxidation for the synthesis of 1-benzoxazolyl-*o*-carboranes

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ABSTRACT

A $FeCl_3$ catalyzed tandem condensation/cyclization/aerobic oxidation process for synthesis of 1-benzoxazolyl-*o*-carboranes has been developed. The degradation of *o*-carborane in the presence of aza-/oxa-nucleophiles was completely suppressed, and a series of 1-benzoxazolyl-*o*-carboranes, 1-benzothiazolyl-*o*-carborane and 1-benzimidazolyl-*o*-carborane have been synthesized with good to excellent yields. This work offers a general protocol for synthesis of 1-benzoxazolyl-*o*-carboranes, which has important reference for synthesis of aromatic heterocycle-carborane derivatives and promote its applications in miscellaneous areas.



## 1. Introduction

Carboranes are a class of carbon-boron molecular clusters with three dimensional aromaticity, which have proved to be the key framework in designing pharmaceuticals for boron neutron capture therapy (BNCT) due to its high boron content as well as synthetic flexibility [1-9] Additionally, the nitrogen or oxygen containing carborane derivatives have also found extensive applications in functional materials [10-16], coordination chemistry and organometallic chemistry [17-22].

Benzoxazoles are a kind of important building blocks in bioactive natural products, pharmaceutical, agrochemical industries and functional materials [23-27]. Based on the three dimensional aromaticity of carborane analogues to benzene, employing benzoxazole unit into the carborane would offer a class of potential synthons in designing drug candidates and molecular imaging regents for targeted radionuclide therapy [28-33].

For synthesis of 1-benzoxazolyl-*o*-carborane, the insertion of C-H bond of benzoxazole into in situ formed carboryne has been developed in Xie's group, and kinds of electron rich aromatic heterocycles were well compatible with this transformation [34] (Scheme 1, a). Later, the *closo*-dodecaborate fused oxazoles and *nido*-carborane fused oxazoles have been synthesized via intramolecular oxidative cyclization of corresponding amides by Duttwyler and our group [35-36], respectively (Scheme 1, b and c). However, the methods for synthesis of *closo*-dodecaborate amides and 9-amide-*o*-carboranes are still a tedious subject as the partial degradation of carborane would occur in the presence of aza-nucleophiles [37-40].

In connection with our continued interest in selective functionalization of *o*-carboranes [41-51], we envisioned to synthesis the 1-benzoxazolyl-*o*-carborane from 1-formyl-*o*-carborane and 2-aminophenol via tandem condensation/cyclization/oxidation process (Scheme 1, d). As the *o*-carborane could be degraded to *nido*-carborane in the presence of aza-/oxa-nucleophiles [37-40], therefore, the condensation of 1-formyl-*o*-carborane with 2-aminophenol to form the Schiff base and the following cyclization should be a fast reaction, and a mild oxidant is needed to facilitate the oxidation dehydrogenation to form 1-benzoxazolyl-*o*-carborane. With this proposal, we consider an aerobic oxidation should be the optimal protocol to accomplish such a transformation [52-56]. Herein, we are pleased to present the $FeCl_3$ catalyzed tandem condensation/cyclization/aerobic oxidation process for synthesis of 1-benzoxazolyl-*o*-carboranes.

## 2. Material and methods

### 2.1. Generals

1a-1h were synthesized according to literature methods [57-58]. Other materials were purchased from Acros, J&K and Al-

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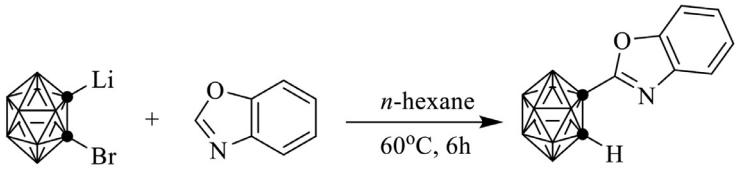
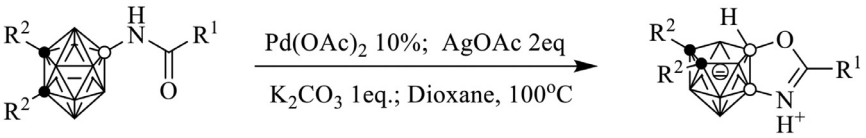
**Previous works**

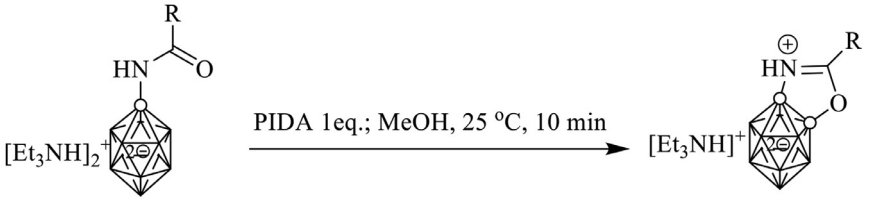
**a**) Synthesis of 1-benzoxazolyl-*o*-carborane via C-H insertion of *o*-carboryne




**b**) Synthesis of *nido*-carborane fused oxazoles via deboronation/cyclization of 9-amide-*o*-carboranes

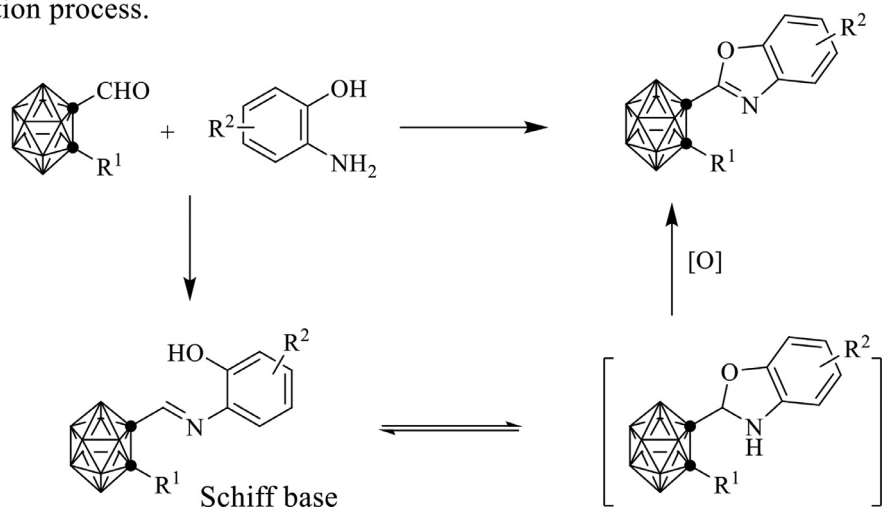



**c**) Synthesis of *closo*-dodecaborate fused oxazoles via cyclization of *closo*-dodecaborate amides




**This work**

**d**) Synthesis of 1-benzoxazolyl-*o*-carboranes via condensation/aerobic oxidation process.



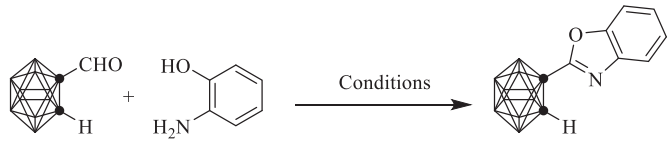

**Scheme 1.** Strategies for synthesis of benzoxazole-carborane derivatives.

addin, and used as received unless otherwise specified. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum ether was 60-90 °C. $^{1}$H NMR, $^{13}$C{$^{1}$H} and $^{11}$B{$^{1}$H} NMR spectra were recorded on the Bruker 600MHz instruments. All $^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra data are reported in ppm relative to tetramethylsilane (TMS) as internal standard, and $^{11}$B{$^{1}$H} NMR spectra data are referenced to external $BF_3$•$Et_2O$.

*2.2. General procedure for synthesis of 1-formyl-2-R-o-carboranes (1a-1h)*

To a 100 mL Schlenk flask were added 1-R-*o*-carborane (5 mmol), $Et_2O$ (30 mL) and cooled to -78°C. Then *n*-BuLi (5.5 mmol, 1.6 M in hexane, 3.4 mL) was added by syringe and the resulting mixture was stirred for 1h at -78°C. Subsequently, methyl formate (2 mL) was added into the mixture and stirred for 2h. The reaction was quenched with diluted HCl (3M, 2 mL) at -78 °C and slowly warmed to room temperature. The mixture was extracted with

**Table 1**
Optimized conditions for synthesis of 1-benzoxazolyl-*o*-carborane [a]




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

| entry | catalyst | solvent | atmosphere | yield(%)[b] |
|---|---|---|---|---|
| 1 | $FeCl_3$ | toluene | Air | 75 |
| 2 | $FeCl_3$ | toluene | Ar | 15 |
| 3 | $FeCl_3$ | toluene | $O_2$ | 65 |
| 4 | - | toluene | Air | 0 |
| 5 | $FeCl_3$ | toluene | Air | 19[c] |
| 6 | $FeCl_3$ | DCE | Air | 0 |
| 7 | $FeCl_3$ | dioxane | Air | 31 |
| 8 | $NiCl_2$ | toluene | Air | 57 |
| 9 | $CuCl_2$ | toluene | Air | 54 |
| 10 | $Cu(OTf)_2$ | toluene | Air | 65 |
| 11 | $FeCl_3$ | toluene | Air | 80[d] |

[a] All reactions were carried out with 0.2 mmol 1a, 0.22 mmol 2a, 10 mol % catalyst and 1 mL solvent at 110°C for 24 h.
[b] Isolated yields.
[c] Reacted at 80°C.
[d] With 0.2 mmol 2a.

EtOAc for three times (3 × 50 mL) and the combined organic pahse was dried over anhydrous $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on 200-300 mesh silica gel with petroleum ether:EtOAc = 20:1~10:1.

### *2.3. General procedure for synthesis of 3a-3k (Take 3a as an example)*

To a 10 mL dried flask were sequentially added 1-formyl-*o*-carborane (1a, 34.4 mg, 0.2 mmol), toluene (1 mL), 2-aminophenols (2a, 0.2 mmol) and $FeCl_3$ (3.4 mg, 0.02 mmol) under air atmosphere and stirred at 110 °C for 24h. Then the mixture was cooled to room temperature and filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with *n*-hexane/EtOAc=100:1 (v/v) as eluent and gave 3a with 80% yield (41.5mg). $^1$H NMR (600 MHz, $CDCl_3$, *ppm*): $\delta$ 7.72-7.70 (d, 1H, $J$ = 12Hz), 7.57-7.55 (d, 1H, $J$ = 12Hz), 7.46-7.39 (m, 2H), 4.49 (s, 1H, Cage C-*H*); $^{13}$C{1H} NMR (150 MHz, $CDCl_3$, *ppm*): $\delta$ 156.0, 151.3, 140.2, 126.8, 125.7, 120.7, 111.1, 65.1, 59.0; 11B{1H} NMR (192 MHz, $CDCl_3$, *ppm*): $\delta$ -2.1(2B), -8.5 (2B), -10.7 (2B), -11.5 (2B), -12.9 (2B); HRMS: calculated for $C_9B_{10}H_{14}NO^-$ $(M\text{-}H)^-$ 260.2084, found 260.2087.

### *2.4. General procedure for synthesis of 4a-4g (Take 4a as an example)*

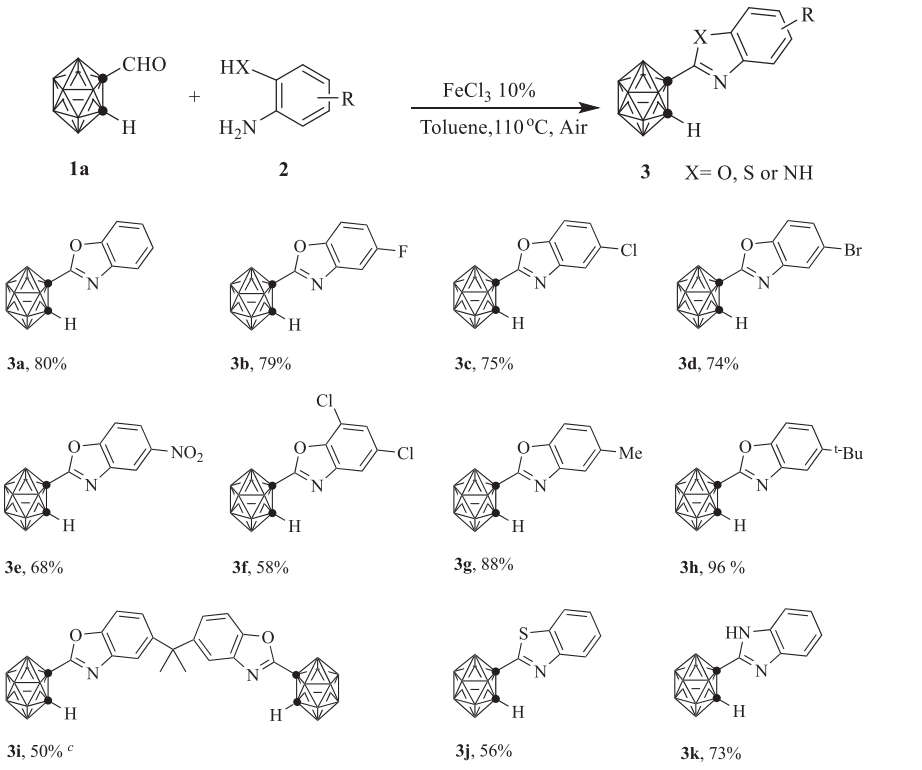
To a 10 mL dried flask were sequentially added 1-formyl-2-methyl-*o*-carborane (1b, 0.2 mmol), toluene (1 mL), 2-aminophenol (2a, 0.2 mmol, 22 mg) and $FeCl_3$ (3.4 mg, 0.02 mmol) under air atmosphere and stirred at 110 °C for 12h, then 20 mol % $AgNO_3$ was added and reacted for another 12h. Then the mixture was cooled to room temperature and filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether/EtOAc=100:1 (v/v) as eluent and gave 4a with 98% yield (54mg). $^1$H NMR (600 MHz, $CDCl_3$, *ppm*): $\delta$ 7.81-7.80 (d, 1H, $J$ = 6Hz), 7.60-7.59 (d, 1H, $J$ = 6Hz), 7.49-7.47 (dd, 1H, $J$ = 6Hz), 7.44-7.42 (dd, 1H, $J$ = 6Hz), 1.99 (s, 3H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *ppm*): $\delta$ 154.6, 151.3, 140.6, 127.2, 125.6, 121.2, 111.2, 77.4, 69.8, 23.8; $^{11}$B{$^1$H} NMR (192 MHz, $CDCl_3$, *ppm*): $\delta$ -1.3 (2B), -6.7 (2B), -12.3 (6B); HRMS: calculated for $C_{10}B_{10}H_{17}NO^-$ $(M\text{-}H)^-$ 274.2241, found 274.2241.

## 3. Results and discussion

To evaluate the feasibility of this tandem transformation, 1-formyl-*o*-carborane and 2-aminophenol were selected as model substrates to screening conditions. After many efforts, we found the tandem condensation/cyclization/oxidation process could be accomplished in the presence of 10 mol % $FeCl_3$ in toluene at 110°C for 24h under air atmosphere, and gave the desired 1-benzoxazolyl-*o*-carborane with 75% yield (Table 1, entry 1). Control experiments demonstrated the $FeCl_3$ was essential for this reaction, and the oxygen in air was the terminal oxidant and displayed more efficiency than pure oxygen (Table 1, entries 1-4). The reaction temperature was a key factor for this transformation, when the reaction was carried out at 80°C, the expected product was only obtained with 19% yield (Table 1, entry 5). Further studies indicated the toluene was more favorable for this reaction than 1,2-dichloroethane (DCE) and dioxane (Table 1, entries 6-7). When the reaction was performed with nickel or copper salts, the desired product was generated with moderate yield (Table 1, entries 8-10), this result indicated that the $FeCl_3$ was the optimal catalyst for this transformation [59]. To our delight, when the loading amount of 2-aminophenol was reduced to equivalent with 1-formyl-*o*-carborane, the corresponding product could be enhanced to 80% yield (Table 1, entry 11), this result demonstrated the *o*-carborane would be degraded with excess 2-aminophenol.

With the optimal reaction conditions in hand (Table 1, entry 11), the scope of 2-aminophenols were then examined. As can be seen from Table 2, the 2-aminophenols substituted with electron donating group or electron withdrawing group were all compatible with this transformation well and gave the expected products with good to excellent yields (3a-3h). When the reaction was conducted with 2,2-bis(3-amino-4-hydroxylphenyl)propane, the desired product was obtained with 50% yield (3i). Furthermore, the *o*-aminothiophenol and *o*-phenylenediamine were also applicable

**Table 2**
Synthesis of 1-benzoxazolyl-*o*-carboranes from 1-formyl-*o*-carborane with 2-aminophenols[a,b]




[a] All reactions were carried out with 0.2 mmol **1a**, 0.2 mmol 2-aminophenols, 10 mol% $FeCl_3$ and 1 mL toluene at 110°C for 24 h under air atmosphere.
[b] Isolated yields. [c] 0.5 equivalent (0.1 mmol) of 2,2-bis(3-amino-4-hydroxylphenyl)propane was used.

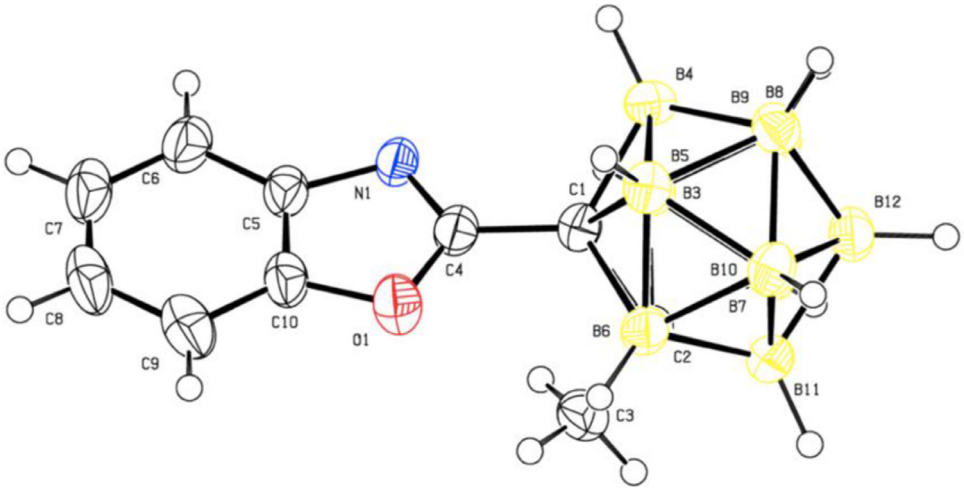
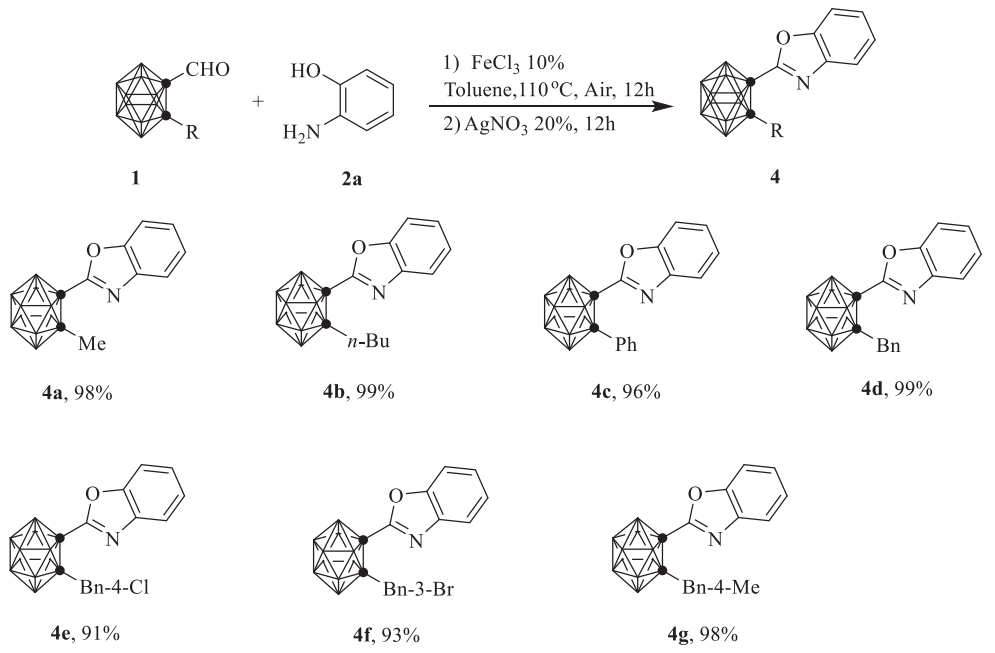



**Fig. 1.** Crystal structure of 4a

to this transformation and the corresponding 1-benzothiazolyl-*o*-carborane and 1-benzimidazolyl-*o*-carborane were afforded with 56% and 73% yields, respectively (3j-3k).

Subsequently, the scope of 1-formyl-2-R-*o*-carboranes was then explored. To our surprise, when the 1-formyl-2-methyl-*o*-carborane was subjected to the standard conditions, the reaction was proceed very sluggish, and only gave the desired product with 31% yield. Meanwhile, a large amount of Schiff base intermediate (Scheme 1, d) was isolated and characterized by $^1$H NMR. To address this problem, some co-oxidants were examined (SI, Table S1). After many efforts, we found when the reaction was carried out under standard conditions for 12h, 20 mol % $AgNO_3$ was added to the reaction mixture for additional 12h could facilitate the cyclization/oxidation process and gave the expected product with 98% yield (4a). Meanwhile, the exact structure of 4a was unambiguously confirmed by X-ray crystallographic analysis [60] (Figure 1). Under the improved conditions, the alkyl, aryl and benzyl substituted 1-formyl-2-R-*o*-carboranes were compatible with this transformation well and generate the expected products with excellent yields (Table 3, 4b-4g). For this result, we consider the $AgNO_3$ would be a co-oxidant to accelerate the oxidative dehydrogenation process.

**Table 3**
Synthesis of 1-benzoxazolyl-*o*-carboranes from 1-formyl-2-R-*o*-carboranes with 2-aminophenol[a,b]




[a] All reactions were carried out with 0.2 mmol 1-formyl-2-R-*o*-carboranes, 0.2 mmol 2-aminophenol, 10 mol % $FeCl_3$ and 1 mL solvent at 110°C for 12 h under air atmosphere, then 20 mol% $AgNO_3$ was added and reacted for another 12 h.
[b] Isolated yields.

Based on the experimental results and previous works for aerobic oxidation [61-64], the $FeCl_3$ promoted condensation of 2-aminophenol with 1-formyl-*o*-carborane should take place first. Then the $FeCl_3$ catalyzed addition of *ortho*-hydroxy to the Schiff base would give the benzoxazoline intermediate, which would be further oxidized into benzoxazole *in situ* under air atmosphere with iron catalyst (Scheme 1, d). For 1-formyl-2-R-*o*-carboranes, the electron donating effect and steric hindrance of R group at C2 would restrain the forming of benzoxazoline intermediate, the $AgNO_3$ would be a co-oxidant to accelerate the oxidative dehydrogenation of benzoxazoline to benzoxazole.

## 4. Conclusions

In conclusion, we have developed a $FeCl_3$ catalyzed tandem condensation/cyclization/aerobic oxidation process for synthesis of 1-benzoxazolyl-*o*-carboranes, and the degradation of *o*-carborane was completely suppressed. A series of 1-benzoxazolyl-*o*-carboranes, 1-benzothiazolyl-*o*-carborane and 1-benzimidazolyl-*o*-carborane have been synthesized with good to excellent yields. This work offers a general and facile protocol for synthesis of 1-benzoxazolyl-*o*-carboranes, which has important reference for synthesis of aromatic heterocycle-carborane derivatives and promote its applications in miscellaneous areas.

## Declaration of Competing Interest

The authors declare no competing financial interests.

## Acknowledgment

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121881.

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