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Communication

An original one-pot approach to boronic esters using the titanium-catalyzed reaction of cyclic olefins with alkyldichloroboranes

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ABSTRACT

Boronic esters (dicycloheptylalkylboronates, dicyclooctylalkylboronates, dicyclododecylalkylboronates, dibicyclo[2.2.1]hept-2-ylalkylboronates) are produced with yields ranging from moderate to excellent (52–96%) by the reaction between cyclic olefins (cycloheptene, *cis*-cyclooctene, *cis/trans*-cyclododecene, norbornene) and alkyldichloroboranes (alkyl = Et, *n*-Pent) in the presence of metallic magnesium and the Cp_2TiCl_2 catalyst with subsequent addition of water.

1. Introduction

Recently we have carried out direct cycloboration of α-olefins with the boron halogenides in the presence of Mg and Cp_2TiCl_2 catalyst to afford appropriate 1,2-substituted boriranes [1]. In order to widen the application scope of this reaction, we have performed the cycloboration involving cyclic olefins. It was quite unexpected for us to isolate the boronic esters as products of this reaction after water treatment. Boronic esters are highly valuable compounds, which have found extensive applications in organic and medicinal chemistry [2]. Moreover, they are an attractive class of synthetic intermediates, because of their unique properties as mild organic Lewis acids, together with their stability and easy of handling [3].

In this paper, we report on boronic esters produced by the interaction between cyclic olefins (cycloheptene, *cis*-cyclooctene, *cis/trans*-cyclododecene, norbornene) and alkyldichloroboranes (alkyl = Et, *n*-Pent) under Cp_2TiCl_2 catalysis with subsequent addition of water.

2. Results and discussion

In continuation of our research into the catalytic cycloboration of unsaturated compounds, we have performed the reaction between cyclic olefins (cyclohexene, cycloheptene, *cis*-cyclooctene, cyclododecene (*cis/trans* = 3:1), norbornene) and alkyldichloroboranes (alkyl = Et, *n*-Pent) in the presence of magnesium metal (a chlorine ion acceptor) and Cp_2TiCl_2 catalyst under optimized reaction conditions (olefin: [B]: [Mg]: [Ti] = 1: 2: 2: 0.2, THF, 50 °C for 5 h, then ~ 22–25 °C for 16 h) (Scheme 1).

We have expected that these cycloboration reactions represent the direct pathway to annelated boriranes **1** and **2** (Fig. 1). However, it was not possible to isolate these compounds.

Thus, in ^{13}C NMR spectra of samples taken from the reaction masses after completion of the reactions with the participation of $EtBCl_2$ and cyclic olefins, instead of signals expected for symmetric annelated structures **1** and **2** (Fig. 1), much more signals are observed, which suggests the formation of a mixture of products. The presence of the broadened signals in the 69–75 ppm region indicates the incorporation of the oxygen atom through the B-C bond of the resulting boron-containing compounds.

Probably, the organoboron products of the reaction are extremely sensitive to trace amounts of oxygen and moisture. We have assumed that the addition of excess water to the reaction mass would facilitate the complete conversion of the resulting

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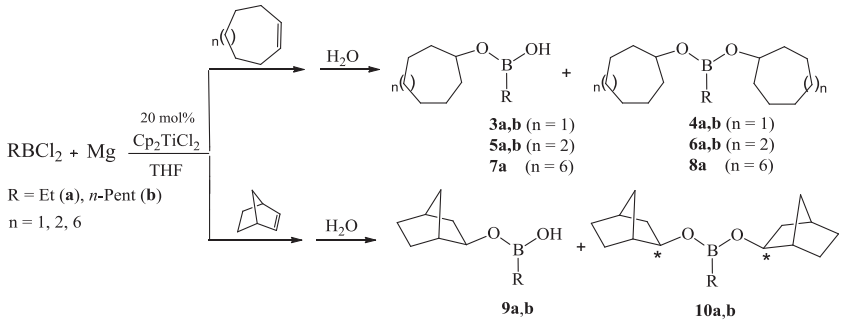


Scheme 1. Cp_2TiCl_2-catalyzed reaction of cyclic olefins with $RBCl_2$ (R = Et, *n*-Pent) after addition of water.

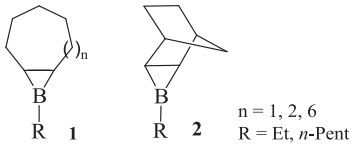


Fig. 1. Proposed structures of boriranes from the Ti-catalyzed cycloboration reaction between cyclic olefins and $RBCl_2$.

organoboron products to oxygen-containing organoboron products. Indeed, the NMR spectra of the reaction masses after the treatment with water have become much simpler (See *SI*, page 2, 3 and 5, 6). This allowed us to identify the formation of a mixture of boronic esters **3a,b** and **4a**,**b**, **5a**,**b** and **6a**,**b**, **7a** and **8a** (Scheme 1). In ^{11}B NMR spectra of the reaction mass after water treatment the signal of the boron atom was observed at ~31 ppm.

The Ti-catalyzed reaction between cyclic olefins and $EtBCl_2$ has certain limitations associated with the ring size of cyclic olefins. Thus, we could not involve cyclohexene in the above reaction. 2-Ethyl-1,2-oxaborinane (Fig. 2) was identified as the major product formed in this reaction as the result of the interaction between $EtBCl_2$ and THF. Reactions of boranes with tetrahydrofuran are well known in the literature [4].

Obviously, the precursors for derivatives of boronic acids **3a**,**b**, **5a**,**b**, **7a**, and **9a**,**b** are chloro(cycloalkyl)alkylboranes **11a**,**b**, **12a**,**b**, **13a** and bicyclo[2.2.1]hept-2-yl(chloro)alkylboranes **14a**,**b** (Scheme 2). These organoboron compounds undergo autoxidation [5] and hydrolysis [6], thus converting to cycloheptyl(cyclooctyl, cyclododecyl) hydrogen alkylboronates **3a**,**b**, **5a**,**b**, **7a** and bicyclo[2.2.1]hept-2-yl hydrogen alkylboronates **9a**,**b**, respectively.

Boronates **4a**,**b**, **6a**,**b**, **8a** and **10a**,**b** can be consider as the products from the condensation of compounds **3a**,**b**, **5a**,**b**, **7a** and **9a**,**b**. A probable route for the formation of boronates is shown in Scheme 3 on the example of transformation of compounds **5a,b** to dicyclooctylalkylboronates **6a,b**.

After vacuum distillation of the reaction mixtures, boronic esters **4a**,**b**, **6a,b** and **10a**,**b** were obtained with high yields (86–96%). The smallest yield of boronic ester **8a** (52%) was observed in the Ti-catalyzed reaction between cyclododecene and $EtBCl_2$. Along with **8a**, in this reaction, 2-ethyl-1,2-oxaborinane is formed (Fig. 2).

The presence of two cycloheptyl(cyclooctyl, cyclododecyl) or norbornyl moieties is confirmed by the ratio of the integral

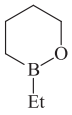
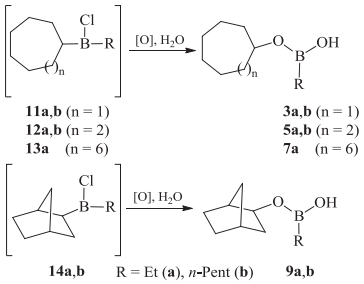
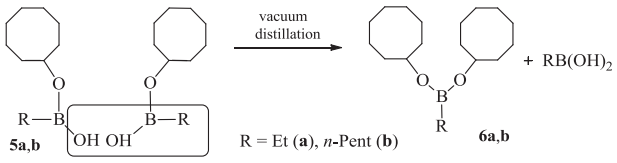


Fig. 2. 2-Ethyl-1,2-oxaborinane, the product of the reaction between $EtBCl_2$ and THF.



Scheme 2. Precursors for derivatives of boronic acids **3a**,**b**, **5a,b, 7a** and **9a**,**b**.



Scheme 3. Probable route for the formation of boronates **6a**,**b** from compounds **5a**,**b**.

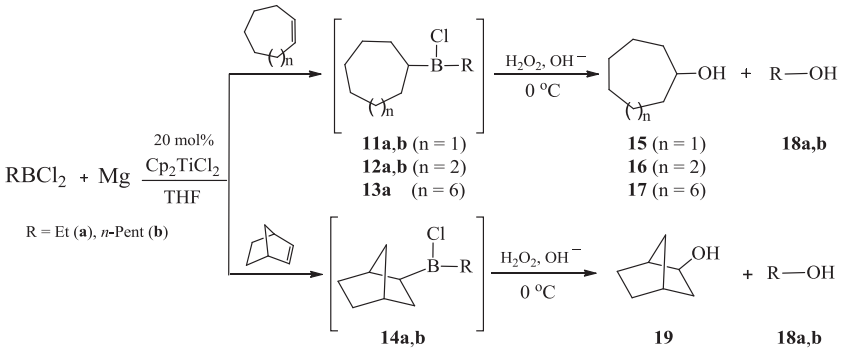
intensities of the signals attributed to alkyl (Et, *n*-Pent) and cycloheptyl(cyclooctyl, cyclododecyl) or norbornyl fragments in ^1H NMR spectra of compounds **4a**,**b**, **6a**,**b**, **8a** and **10a**,**b**. It should be noted that in the ^{13}C NMR spectra of dibicyclo[2.2.1]hept-2-ylalkylboronates **10a**,**b**, diastereomeric splitting of a number of signals is observed due to the interaction between two asymmetric centers in the boronate molecule (See *SI*, pages 9–10).

Apparently, annelated boriranes, **1** and **2** were not produced in the Cp_2TiCl_2-catalyzed reactions of cyclic olefins with $RBCl_2$. The absence of the expected diols and the formation of exclusively monools **15**–**19** after oxidation of the reaction mixtures with H_2O_2/NaOH additionally evidence for this fact and findings (Scheme 4).

The previously proposed mechanism for the Ti-catalyzed cycloboration of α-olefins with boron chlorides with the participation of titanacyclopropane intermediates [1d], does not explain the formation of esters as well as the formation of monoalcohols after oxidation.

Theoretically calculations of thermodynamic and activation parameters for the transmetallation of titanium cyclopropane intermediate as the key step of the model reaction between cyclohexene and $EtBCl_2$ in the presence of metallic magnesium and Cp_2TiCl_2 catalyst have demonstrated high activation barriers and the thermodynamic unfavorability of this process (see *SI* p. 11).

Apparently, other catalytically active Ti-containing species participate in the reaction between alkyldichloroboranes and cyclic olefins. We can assume that titanium hydride complexes are the key intermediates in this reaction, leading to precursors **11a,b,**



Scheme 4. Cp_2TiCl_2-catalyzed reaction of cyclic olefins (cycloheptene, *cis*-cyclooctene, *cis/trans*-cyclododecene, norbornene) with $RBCl_2$ (R = Et, *n*-Pent) after addition H_2O_2/NaOH.

12a,b, 13a and **14a,b**, from which boronic esters are formed after oxidation and hydrolysis. Probably, intermediate titanium hydride complexes are the result of the reaction between the titanocene "Cp_2Ti", formed under the reaction conditions in the presence of metallic magnesium, and tetrahydrofuran [7]. To gain a deeper understanding of the nature of the active species involved in this catalytic reaction, further investigations are needed to perform.

3. Conclusion

In summary, we have elaborated the original one-pot method for producing boronic esters, namely dicycloheptylalkylboronates, dicyclooctylalkylboronates, and dibicyclo[2.2.1]hept-2-ylalkylboronates, with yields from good to excellent (86–96%) via the reaction of cyclic olefins such as cycloheptene, *cis*-cyclooctene and norbornene with $RBCl_2$ (R = Et, *n*-Pent) in the presence of the Cp_2TiCl_2 catalyst with subsequent addition of water. The Ti-catalyzed reaction between cyclic olefins and $RBCl_2$ has certain limitations associated with the ring size of cyclic olefins. Yields of dicyclododecylalkylboronates derived from dodecene did not exceed 52%. Cyclic olefins with small rings (*e.g.* cyclohexene) do not give boronic esters at all.

4. Experimental section

All reactions were carried out using standard Schlenk techniques. Commercially available cyclic olefins (cycloheptene, norbornylene, *cis*-cyclooctene, *cis/trans*-cyclododecene), BCl_3 (1 M solution in hexane), Et_3B and Cp_2TiCl_2 (Acros Organics, Aldrich) were used. THF employed were pre-dried over KOH, refluxed over sodium-wire for 2 h and distilled from $LiAlH_4$ in a stream of argon. Reactions with organometallic compounds were performed in a dry argon flow.

The ^1H, ^{13}C, ^{11}B and 2D homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were measured in $CDCl_3$ on a Bruker Avance-400 spectrometer [400.13 (^1H), 100.62 (^{13}C), 128.33 (^{11}B) MHz]. Chemical shifts (δ) are given in ppm relative to TMS, and the coupling constants (J) in Hz. ^1H and ^{13}C NMR shifts were referenced to internal solvent resonances and reported in parts per million (ppm) relative to Me_4Si. ^{11}B NMR spectra were referenced to an external standard of $BF_3 \cdot Et_2O$. In the ^{13}C NMR spectra of boron compounds, signals of carbon atoms bonded to boron atoms, occur as broadened ones, obviously, due to quadrupole broadening effect of the boron nuclei [8].

The treatment of the reaction mixture with H_2O_2 was done under alkaline conditions as described in Refs. [1,9]. Spectral and physical characteristics of compounds **15**–**17**, **18b**, **19** have been reported Refs. [10].

*4.1. Synthesis of dicycloheptylethylboronate (**4a**), dicycloheptylpentylboronate (**4b**), dicyclooctylethylboronate (**6a**), dicyclooctylpentylboronate (**6b**), dicyclododecylethylboronate (**8a**), dibicyclo[2.2.1]hept-2-ylethylboronate (**10a**), dibicyclo[2.2.1]hept-2-ylpentylboronate (**10b**)*

4.1.1. General procedure

A glass reactor (50 mL), under a dry argon atmosphere at 0°C, was charged under stirring with Cp_2TiCl_2 (2 mmol, 0.498 g), magnesium (powder) (20 mmol, 0.486 g), THF (30 mL), the corresponding cyclic olefin (10 mmol) and $EtBCl_2$ (or *n*-$PentBCl_2$) (12 mmol). $EtBCl_2$ was synthesized according to the methods as described in Ref. [11]. *n*-$PentBCl_2$ was synthesized according to the method as described in Ref. [12]. The temperature was raised to 50°C and the mixture was stirred 5 h. Then reaction mixture was cooled to room temperature (~22–25 °C) and was stirred for additional 16 h. Then to a reaction mixture water (2 mL) was added and the mixture was stirred for 3 h. The organic layer was separated, the aqueous layer was extracted with diethyl ether (2 × 10 mL), extracts were combined with the organic phase. The solvent was evaporated and the residue was distilled under reduced pressure.

*4.1.1.1. Spectral date for dicycloheptylethylboronate **4a**.* Yellow oil liquid, bp 150 °C (5 mm). Yield: 94% (1.25 g, 4.7 mmol). IR spectrum, ν, cm^{-1}: 2927, 2858, 2687, 1655, 1608, 1461, 1336, 1221, 1172, 1108, 1025, 913, 834, 821, 762. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.72$ (q, 2H, B-CH_2-CH_3, $J = 7.9$ Hz), 0.93 (t, 3H, B-CH_2-CH_3, $J = 7.6$ Hz), 1.35–1.45 (m, 4H, cycloheptyl), 1.52–1.73 (m, 16H, cycloheptyl), 1.75–1.85 (m, 4H, cycloheptyl), 4.22–4.28 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): $\delta = 5.77$ (br* B-CH_2-CH_3), 8.27 (B-CH_2-CH_3), 22.83, 28.18, 36.67, 72.67. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 30.65$.

*4.1.1.2. Spectral date for dicycloheptylpentylboronate **4b**.* Yellow oil liquid, bp 152 °C (1 mm). Yield: 90% (1.39 g, 4.5 mmol). IR spectrum, ν, cm^{-1}: 2911, 2830, 2718, 1428, 1380, 1300, 1210, 1195, 1170, 1107, 1005, 955, 830, 797, 720, 685. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.71$ (t, 2H, B–CH_2, $J = 7.8$ Hz), 0.90 (t, 3H, CH_3, $J = 6.9$ Hz), 1.23–1.42 (m, 6H, 3CH_2, alkyl), 1.42–1.52 (m, 4H, 4CH, cycloheptyl), 1.55–1.84 (m, 20H, 12CH, 4CH_2, cycloheptyl), 4.20–4.30 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 13.90 (br*, B–CH_2, alkyl), 14.18 (alkyl), 22.64 (alkyl), 23.05 (cycloheptyl), 24.20 (alkyl), 28.27 (cycloheptyl), 34.97 (alkyl), 36.73 (cycloheptyl), 72.65 (O–CH). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 31.99$.

*4.1.1.3. Spectral date for dicyclooctylethylboronate **6a**.* Yellow oil liquid, bp 160 °C (5 mm). Yield: 96% (1.41 g, 4.8 mmol). IR spectrum,

ν, cm^{-1}: 2923, 2854, 2695, 1712, 1466, 1447, 1390, 1342, 1311, 1263, 1216, 1181, 1117, 1053, 991, 908, 845, 805, 762, 736, 706, 677, 648. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.72$ (q, 2H, B-C<u>H</u>$_2$-CH$_3$, $J = 7.6$ Hz), 0.93 (t, 3H, B-CH$_2$-C<u>H</u>$_3$, $J = 7.8$ Hz), 1.45–1.60 (m, 16H, cyclooctyl), 1.60–1.80 (m, 12H, cyclooctyl), 4.22–4.27 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): $\delta = 5.92$ (br*, B-<u>C</u>H$_2$-CH$_3$), 8.27 (B-CH$_2$-<u>C</u>H$_3$), 22.81, 25.38, 27.41, 34.15, 72.23. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 30.76$.

4.1.1.4. Spectral date for dicyclooctylpentylboronate ***6b***. Yellow oil liquid, bp 171 °C (1 mm). Yield: 92% (1.55 g, 4.6 mmol). IR spectrum, ν, cm^{-1}: 2902, 2838, 2704, 1455, 1400, 1385, 1312, 1260, 1205, 1171, 1125, 998, 975, 831, 800, 766, 727, 680, 650. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.70$ (t, 2H, B–CH$_2$, $J = 7.8$ Hz), 0.89 (t, 3H, CH$_3$, $J = 6.8$ Hz), 1.24–1.42 (m, 6H, 3CH$_2$, alkyl), 1.42–1.62 (m, 16H, 4CH, 6CH$_2$, cyclooctyl), 1.65–1.78 (m, 12H, 4CH, 4CH$_2$, cyclooctyl), 4.17–4.32 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 13.50 (br*, B–CH$_2$, alkyl), 14.09 (alkyl), 22.58 (alkyl), 22.80 (cyclooctyl), 24.16 (alkyl), 25.39 (cyclooctyl), 27.43 (cyclooctyl), 34.13 (cyclooctyl), 34.90 (alkyl), 72.23 (O–CH). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 31.36$.

* In the ^{13}C NMR spectra of boron compounds, signals of carbon atoms bonded to boron atoms, occur as broadened ones, obviously, due to quadrupole broadening effect of the boron nuclei [8].

4.1.1.5. Spectral date for dicyclododecylethylboronate ***8a***. Yellow oil liquid, bp 178 °C (0.1 mm). Yield: 52% (1.06 g, 2.6 mmol). IR spectrum, ν, cm^{-1}: 2927, 2863, 1694, 1577, 1543, 1482, 1415, 1333, 1222, 1076, 1049, 906, 797, 763, 717, 600. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.75$ (q, 2H, B-C<u>H</u>$_2$-CH$_3$, $J = 6.7$ Hz), 0.92 (t, 3H, B-CH$_2$-C<u>H</u>$_3$, $J = 8.0$ Hz), 1.25–1.50 (m, 28H, cyclododecyl), 1.51–1.75 (m, 16H, cyclododecyl), 3.97–4.08 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 5.34 (br*, B-<u>C</u>H$_2$-CH$_3$), 7.90 (B-CH$_2$-<u>C</u>H$_3$), 20.91, 23.22, 23.40, 23.76, 24.16, 32.38, 69.38. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 30.64$.

4.1.1.6. Spectral date for dibicyclo[2.2.1]hept-2-ylethylboronate ***10a***. Yellow oil liquid, bp 140 °C (5 mm). Yield: 90% (1.18 g, 4.5 mmol). IR spectrum, ν, cm^{-1}: 2916, 2900, 2859, 2831, 2189, 1470, 1430, 1388, 1335, 1263, 1233, 1201, 1150, 1113, 1063, 980, 855, 790, 760, 726, 695, 670. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.73$ (q, 2H, B–CH$_2$, $J = 8.1$ Hz), 0.87–0.95 (m, 3H, B-CH$_2$-C<u>H</u>$_3$), 1.00–1.12 (m, 4H, 4CH), 1.25–1.52 (m, 8H, 4CH, 2CH$_2$), 1.57–1.67 (m, 4H, 4CH), 2.12 (br.s, 2H, 2CH), 2.23 (br.s, 2H, 2CH), 3.85–4.15 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): $\delta = 5.43$ (br*, B–CH$_2$), 7.94 (8.00) (B-CH$_2$-<u>C</u>H$_3$), 24.33, 28.41, 34.78, 35.38, 42.23 (42.30), 43.70 (43.75), 75.25. ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 30.94$.

4.1.1.7. Spectral date for dibicyclo[2.2.1]hept-2-ylpentylboronate ***10b***. Yellow oil liquid, bp 145 °C (1 mm). Yield: 86% (1.31 g, 4.3 mmol). IR spectrum, ν, cm^{-1}: 2910, 2850, 2828, 2190, 1450, 1425, 1398, 1359, 1300, 1269, 1235, 1160, 1107, 1065, 970, 875, 795, 750, 699, 660, 637. ^1H NMR ($CDCl_3$, in ppm, 400.13 MHz): $\delta = 0.65$–1.00 (m, 5H, B–CH$_2$, CH$_3$), 1.04–1.21 (m, 22H, 5CH$_2$, 12CH), 2.05–2.25 (m, 4H, 4CH), 3.70–3.85 (m, 2H, 2CH–O). ^{13}C NMR ($CDCl_3$, in ppm, 100.62 MHz): δ = 14.03 (alkyl), 15.89 (br*, B–CH$_2$, alkyl), 22.42 (22.52) (alkyl), 23.72 (23.83) (alkyl), 24.28, 28.36, 34.78, 34.83 (alkyl), 35.35, 42.25 (42.32), 43.73 (43.77), 75.24 (75.30). ^{11}B NMR ($CDCl_3$, in ppm, 128.33 MHz): $\delta = 30.96$.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.07.019.

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