

## Electronic supplementary information

# PALLADIUM-CATALYZED ALLYLATION OF $\alpha$ -(*o*-CARBORAN-1-YL)ACETOPHENONE WITH ALLYL CARBONATES

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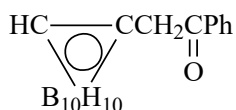
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## Experimental section

### General information

The NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400.13 MHz for  $^1\text{H}$  NMR, 100.62 MHz for  $^{13}\text{C}$  NMR, and 128.38 MHz for  $^{11}\text{B}$  NMR. The chemical shifts ( $\delta$ ) were relative to TMS for  $^1\text{H}$  and  $^{13}\text{C}$ ,  $\text{BF}_3 \cdot \text{OEt}_2$  for  $^{11}\text{B}$ . The data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants ( $J$ , Hz). The elemental analyses were performed using a Carlo-Erba CE-1106 elemental analyzer. The melting points were determined with an Electrothermal 1002 MEL-TEMP® capillary melting point apparatus and were uncorrected. All reactions were carried out in an argon atmosphere. All solvents were purified (dried and distilled) prior to use according to the standard methods. Allyl ethyl carbonate, dppe, and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  were purchased from a commercial source (Aldrich). 1-Bromomethyl-*o*-carborane [1] and cinnamyl methyl carbonate [2] were synthesized according to the published procedures.

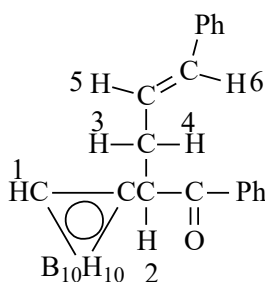
### Syntheses and characterization



**[(*o*-Carboranyl-1)methyl] phenyl ketone (1).** A small amount of dibromoethane was added to magnesium turnings (0.045 mol, 1.08 g) in diethyl ether, and then 1-(bromomethyl)-*o*-carborane (0.0253 mol, 6.00 g) was added dropwise. The mixture was refluxed for 30 min. After cooling, a

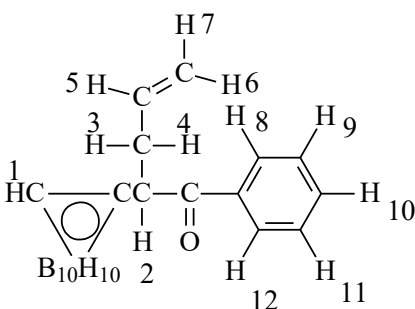
solution of benzaldehyde (0.027 mol, 2.7 mL) in absolute ether was added dropwise, and the mixture was refluxed for 20 min. After cooling to room temperature, an aqueous solution of HCl was added until pH = 6, and the mixture was extracted with ether. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate, and evaporated to dryness. Then absolute ether (17 mL) was added to the reaction mixture, and the chromium mixture (30.6 mL  $\text{H}_2\text{O}$  + 7.66 mL  $\text{H}_2\text{SO}_4$  + 7.40 g  $\text{K}_2\text{Cr}_2\text{O}_7$ ) was added dropwise. The reaction mixture was refluxed for 4 h. After cooling, the mixture was poured into water and extracted with ether. The organic layer was separated, washed with water, aq.  $\text{Na}_2\text{CO}_3$ , and again with water. After distilling off the solvent, the residue was recrystallized from hexane, the precipitated white crystals were filtered off and dried

under vacuum. The target product was obtained as colorless crystals. Yield: 4.13 g (62%). Mp: 54–57 °C [3].



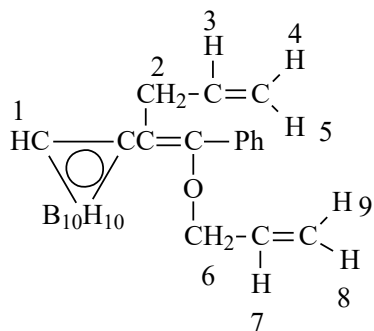
**2-(*o*-Carboranyl-1)-1,5-diphenylpenten-4-one-1 (4).** THF (10 mL) was added to Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.015 g, 0.015 mmol). Then dppe (0.026 g, 0.065 mmol) was added in small portions upon stirring until the solution became light yellow. [(*o*-Carboranyl-1)methyl] phenyl ketone (0.26 g, 1 mmol) and methyl (3-phenylpropen-2-yl-1)carbonate (0.38 g, 0.33 mL, 2 mmol) were added to the resulting mixture. The reaction mixture was stirred for 3 h. After distilling off the solvent, the residue was dissolved in a

mixture of chloroform–petroleum ether (1:1), filtered through silica gel (2 cm), and the silica gel pad was washed with a mixture of chloroform–petroleum ether (1:1). The filtrate was evaporated, and the resulting yellow oil was recrystallized from petroleum ether to give the target product as light-brown crystals. Yield: 0.267 g (71%). Mp: 120–121 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.85 (m, 2H) (H(3,4)); 4.23 (s, 1H) (H(1)); 4.55 (dd, 1H, <sup>3</sup>J<sub>2,3</sub> = 9.6, <sup>3</sup>J<sub>2,4</sub> = 5.8) (H(2)); 5.83 (m, 1H) (H(5)); 6.44 (d, 1H, <sup>3</sup>J<sub>5,6</sub> = 15.7) (H(6)); 7.10 (dd, 2H, *J* = 7.4, 1.9) + 7.24 (m, 3H) (Ph-CH); 7.54 (t, 2H, *J* = 7.7) + 7.68 (t, 1H, *J* = 7.4) + 7.94 (d, 2H, *J* = 7.6) (Ph-CO) ppm. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>): δ -2.71 (1B); -4.07 (1B); -8.89 (2B); -9.95 (2B); -12.77 (5B) ppm. IR (cm<sup>-1</sup>, KBr): 1353, 1447, 1594 (Ph), 1671 (C=O), 2603 (B-H), 3079 (C-H). Anal. Calcd for C<sub>19</sub>H<sub>26</sub>B<sub>10</sub>O: C, 60.06; H, 6.44; B, 28.59. Found: C, 60.30; H, 6.88; B, 28.59%.



**2-(*o*-Carboranyl-1)-1-phenylpenten-4-one-1 (5).** THF (10 mL) was added to Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.015 g) and then dppe (0.03 g, 0.075 mmol) was added in small portions upon stirring until the solution became light yellow. [(*o*-Carboranyl-1)methyl] phenyl ketone (0.26 g, 1 mmol) and allyl ethyl carbonate (1 mmol) were added to the resulting mixture. The reaction mixture was stirred for 1 h. After distilling off the solvent, the residue was dissolved in a chloroform–petroleum ether (1:1) mixture,

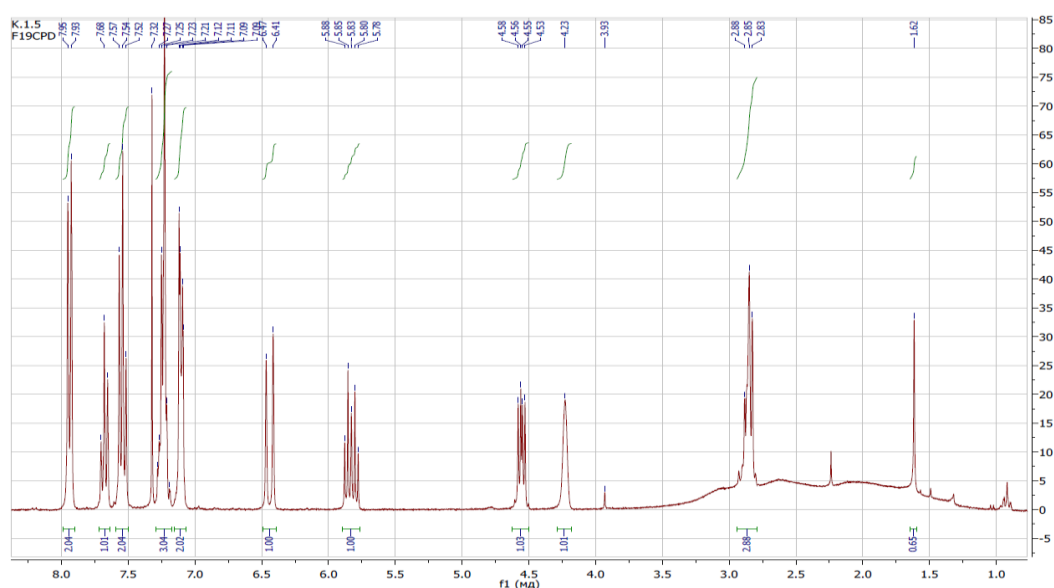
filtered through silica gel (2 cm), and the silica gel pad was washed with chloroform–petroleum ether (1:1). The filtrate was evaporated and the resulting yellow oil was purified by column chromatography on silica gel (eluent: petroleum ether–dichloromethane (3:1)) to give the target product as colorless crystals. Yield: 0.071 g (24%). Mp: 49–51 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.65 (m, 2H) (H(3,4)); 4.12 (s, 1H) (H(1)); 4.43 (dd, 1H, <sup>3</sup>J<sub>2,3</sub> = 10.7, <sup>3</sup>J<sub>2,4</sub> = 4.8) (H(2)); 4.83 (br. d, 1H) (H(6)); 5.06 (m, 1H) (H(7)), 5.47 (m, 1H) (H(5)); 7.54 (m, 2H) + 7.67 (m, 1H) + 7.91 (m, 2H) (H(8–12)) ppm. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>): δ -2.73 (1B); -4.17 (1B); -8.87 (2B); -9.95 (2B); -12.50 (5B) ppm. IR (cm<sup>-1</sup>, KBr): 1447, 1596 (Ph), 1671 (C=O), 2591 (B-H), 3076 (C-H). Anal. Calcd for C<sub>16</sub>H<sub>26</sub>B<sub>10</sub>O: C, 51.64; H, 7.28; B, 35.78. Found: C, 56.41; H, 7.27; B, 35.95%.



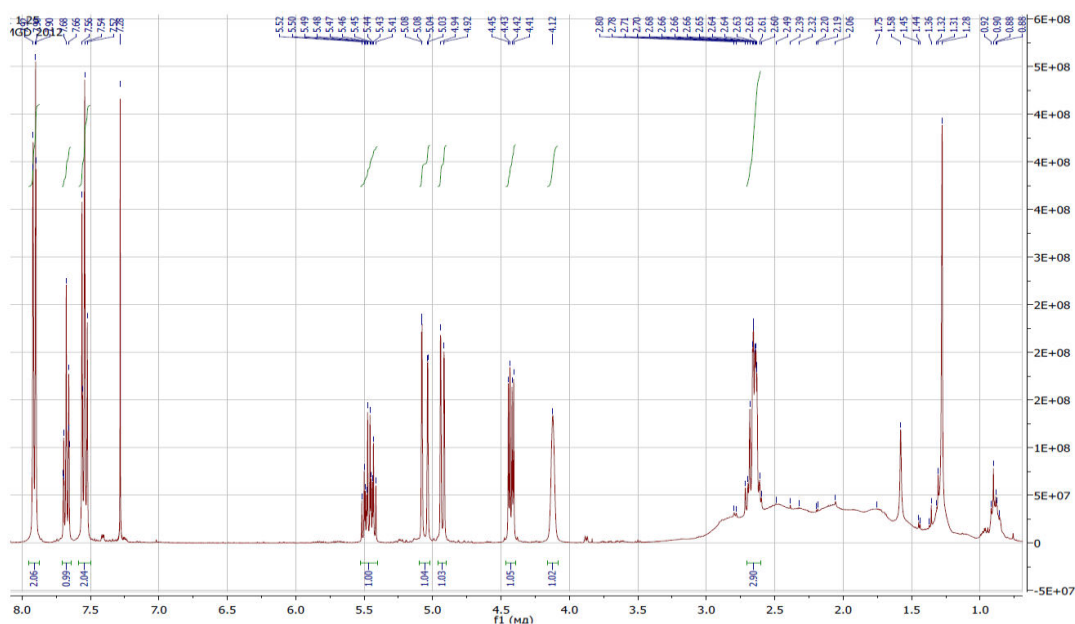
**(Z)-2-(*o*-Carboranyl-1)-1-[(propen-2-yl)oxy]-1-phenylpentadiene-1,4 (6).** THF (10 mL) was added to Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.015 g) and then dppe (0.03 g, 0.075 mmol) was added in small portions upon stirring until the solution became light yellow. Then [(*o*-carboranyl-1)methyl] phenyl ketone (0.26 g, 1 mmol) and allyl ethyl carbonate (0.38 g, 0.37 mL, 3 mmol) were added to the resulting mixture. The reaction mixture was stirred for 3 h. After distilling off the solvent, the residue was dissolved in a chloroform–petroleum ether (1:1) mixture, filtered through silica

gel (2 cm), and the silica gel pad was washed with chloroform–petroleum ether (1:1). The filtrate was evaporated, and the resulting yellow oil was purified by column chromatography on silica gel (eluent: petroleum ether–dichloromethane (3:1)) to give the target product as colorless crystals. Yield: 0.048 g (16%). Mp: 69–70 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.60–3.20 (m, 10 H) ( $\text{B}_{10}\text{H}_{10}$ ); 2.79 (m, 2H) (H(2)); 3.88 (m, 2H) (H(6)); 4.79 (m, 1H) (H(5)); 4.98 (m, 1H) (H(4)); 5.13 (s, 1H) (H(1)); 5.20–5.24 (m, 2H) (H(8+9)); 5.7 (m, 1H) (H(3)); 5.83 (m, 1H) (H(7)); 7.25 (m, 2H) + 7.41 (m, 3H) (Ph) ppm.  $^{11}\text{B}$  NMR (128.38 MHz,  $\text{CDCl}_3$ ):  $\delta$  -2.70 (1B); -4.07 (1B); -8.89 (2B); -9.95 (2B); -12.76 (5B) ppm.  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  37.39 ( $\text{CH}_2$ ); 61.60 ( $1\text{C}_{\text{Cb}}$ ); 70.71 ( $\text{CH}_2$ ); 75.64 ( $\text{C}_\alpha$ ); 110.42 ( $1\text{C}_{\text{Cb}}$ ); 116.25 ( $=\text{CH}_2$ ); 118.22 ( $=\text{CH}_2$ ); 128.57 (2C, *m*-Ph); 129.14 (2C, *o*-Ph); 129.40 (2C, *p*-Ph); 132.30 ( $\text{CH}_2\text{-CH}=\text{CH}_2$ ); 133.45 ( $\text{C}_{\text{ips}}$ , Ph); 155.53 ( $\text{C}=\text{O}$ ) ppm. IR ( $\text{cm}^{-1}$ , KBr): 1444, 1599 (Ph), 2578 (B–H), 3083 (C–H). Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{B}_{10}\text{O}$ : C, 56.12; H, 7.6; B, 31.6. Found: C, 56.12; H, 7.61; B, 31.59%.

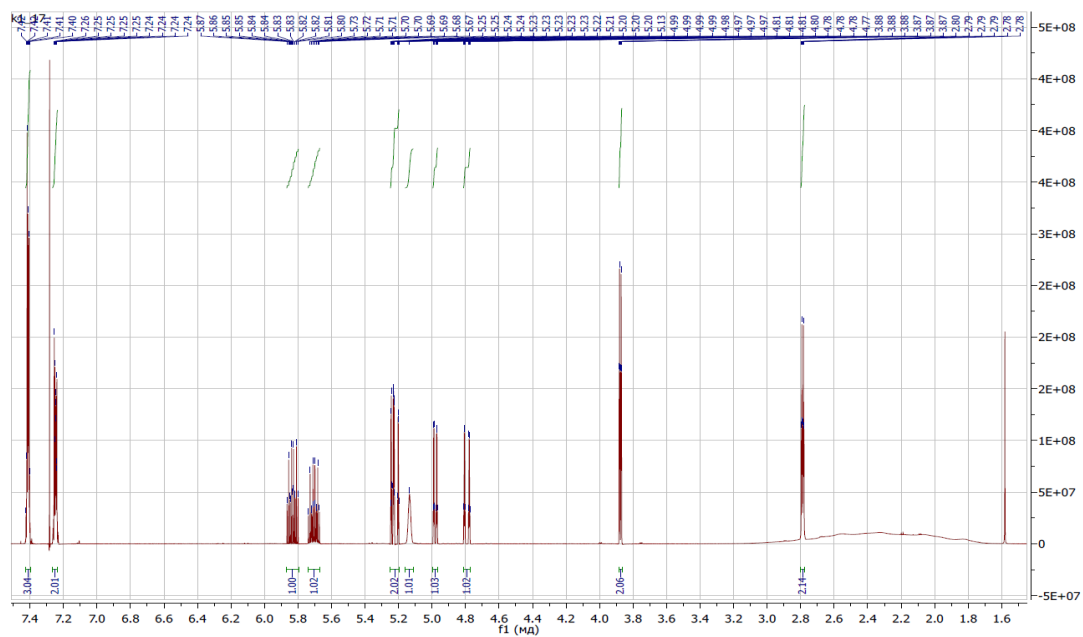
### NMR spectra of the products



**Figure S1.**  $^1\text{H}$  NMR spectrum of 2-(*o*-carboranyl-1)-1,5-diphenylpenten-4-one-1 4.



**Figure S2.**  $^1\text{H}$  NMR spectrum of 2-(*o*-carboranyl-1)-1-phenylpenten-4-one-1 5.



**Figure S3.**  $^1\text{H}$  NMR spectrum of (Z)-2-(*o*-carboranyl-1)-1-[(propen-2-yl)oxy]-1-phenylpentadiene-1,4 **6**.

## X-ray crystallography

X-ray diffraction data for **6** were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ,  $\omega$ -scans). Using Olex2 [4], the structure was solved with the ShelXT [5] structure solution program using Intrinsic Phasing and refined with the XL [6] refinement package using the Least-Squares minimization against  $F^2$  in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of the BH groups were located from the difference Fourier synthesis, while positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation in the riding model. The crystal data and structure refinement parameters are given in Table S1. CCDC 2387674 contains the supplementary crystallographic information for **6**.

**Table S1.** Crystal data and structure refinement parameters for **6**

<b>6</b>	
Formula unit	C <sub>16</sub> H <sub>26</sub> B <sub>10</sub> O
Formula weight	342.47
Crystal system	Orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Z	4
a, $\text{\AA}$	9.5776(8)
b, $\text{\AA}$	10.5433(9)
c, $\text{\AA}$	19.7974(17)
$\alpha$ , $^\circ$	90
$\beta$ , $^\circ$	90
$\gamma$ , $^\circ$	90
V, $\text{\AA}^3$	1999.1(3)
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.138
Linear absorption, $\mu$ (cm <sup>-1</sup> )	0.6
F(000)	720
$2\Theta_{\text{max}}$ , $^\circ$	50
Reflections measured	13773
Independent reflections	3515
Observed reflections [ $I > 2\sigma(I)$ ]	3334
Parameters	260
R1	0.0461
wR2	0.1202
GOOF	1.042
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e $\text{\AA}^{-3}$ )	0.371/-0.556

## References

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