

SUPPORTING INFORMATION

Synthesis of Functionalized Vinyl Boronates Via Ruthenium-Catalyzed Olefin Cross-Metathesis and Subsequent Conversion to Vinyl Halides

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Table of Contents

| | |
|-------------------------------------------------------------------------------------------------|---------|
| General experimental section | S1 |
| Characterization data for compounds 7 through 21 | S1-S6 |
| Characterization data for compounds 22 through 26 | S6-S7 |
| Characterization data for compounds 27 through 30 | S7-S8 |
| References for supporting information | S8-S9 |
| ¹ H, ¹³ C NMR spectra for compounds 4 through 6 | S10-S15 |
| ¹ H, ¹³ C NMR spectra for compounds 7 through 21 | S16-S47 |
| ¹ H, ¹³ C NMR spectra for compounds 22 through 26 | S48-S57 |
| ¹ H, ¹³ C NMR spectra for compounds 27 through 30 | S58-S65 |

General Experimental Section. NMR spectra were recorded on either a 500 MHz or a 300 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad (br). The reported ¹H NMR and ¹³C NMR data refer to the major olefin isomer (which is identified) except for cases in which the minor isomer showed significantly prominent peaks, in which case both isomers are characterized. It should be noted that, for all vinyl boronates reported, the ¹³C peak for the β -carbon atom is not visible, due to the large quadrupolar effect of the attached boron nucleus.ⁱ

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed with standard potassium permanganate stains. Flash column chromatography was performed using silica gel 60 (230-400 mesh). All commercial chemicals were used as obtained unless noted otherwise. Diethyl ether and dichloromethane were purified and dried by passage through a solvent column.ⁱⁱ

1-Octenylboronic acid (7). The crude product was purified using column chromatography (3:2 hexane:ethyl acetate). ¹H NMR (500 MHz, CDCl₃, ppm): (cyclic trimer, *E*-isomer) δ 6.97 (3H, dt, *J* = 18.0, 6.4 Hz), 5.54 (3H, d, *J* = 18.0 Hz), 2.22 (6H, dt, *J* = 7.0, 7.0 Hz), 1.4 (24H, m), 0.9 (9H, m). (monomeric acid, *E*-isomer): δ 6.52 (1H, dt, 18.0, 6.4 Hz), 5.41 (1H, d, *J* = 17.5 Hz), 4.20 (2H, br), 2.17 (2H, dt, *J* = 7.0, 7.0 Hz), 1.4 (8H, m), 0.9 (3H, m). ¹³C NMR (300 MHz, CDCl₃, ppm): (cyclic trimer, *E*-isomer) δ 158.0, 36.0, 32.0, 29.2, 28.5, 22.9, 14.4. HRMS (EI) calcd. for C₂₄H₄₅B₃O₃: 414.3648, found: 414.3635.

3-(Triisopropyl-silanyl)-1-propenylboronic acid (8). The crude product was purified using column chromatography (7:3 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (cyclic trimer, *E*-isomer) δ 7.10 (3H, dt, J = 17.1, 8.5 Hz), 5.43 (3H, d, J = 17.1 Hz), 1.90 (6H, d, J = 7.8 Hz), 1.082 (54H, s), 1.075 (9H, s). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (cyclic trimer, *E*-isomer) δ 156.1, 21.5, 19.0, 11.4. HRMS (CI) calcd. for $\text{C}_{12}\text{H}_{27}\text{BO}_2\text{Si}$: 242.1873, found: 242.1877; calcd. for $\text{C}_{36}\text{H}_{75}\text{B}_3\text{O}_3\text{Si}_3 + \text{H}$: 673.5382, found: 673.5382.

4,4,5,5-Tetramethyl-2-[3-(triisopropyl-silanyl)-propenyl]-[1,3,2]dioxaborolane (9). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) δ 6.76 (1H, dt, J = 17.7, 8.3 Hz), 5.33 (1H, dt, J = 17.4, 1.1 Hz), 1.81 (2H, dd, J = 8.3, 1.1 Hz), 1.25 (12H, s), 1.06 (18H, s), 1.05 (3H, s). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) δ 153.3, 82.9, 25.0, 21.2, 19.0, 11.3. HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{37}\text{BO}_2\text{Si}$: 324.2656, found: 324.2660.

Acetic acid 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-enyl ester (10). The crude product was purified using column chromatography (4:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) δ 6.60 (1H, dt, J = 17.7, 6.4 Hz), 5.43 (1H, dt, J = 18.0, 1.5 Hz), 4.04 (2H, t, J = 6.5 Hz), 2.17 (2H, ddt, J = 6.7, 6.7, 1.7 Hz), 2.03 (3H, s), 1.65 (2H, m), 1.50 (2H, m), 1.25 (12H, s). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) δ 171.4, 153.9, 83.2, 64.5, 35.4, 28.3, 25.0, 24.7, 21.2. HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{25}\text{BO}_4$: 268.1846, found: 268.1854.

4,4,5,5-Tetramethyl-2-oct-1-enyl-[1,3,2]dioxaborolane (11). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) δ 6.64 (1H, dt, J = 18.3, 6.5 Hz), 5.43 (1H, J = 18.3, 1.7 Hz),

2.16 (2H, dtd, $J = 7.0, 7.0, 1.8$ Hz), 1.4 (8H, m), 1.28 (12H, s), 0.89 (3H, t, $J = 6.9$ Hz).

^{13}C NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) \square 155.1, 83.2, 36.1, 31.9, 29.1, 28.4, 25.0, 22.8, 14.3. HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{27}\text{BO}_2$: 238.2104, found: 238.2109.

2-(2-Cyclopentyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (12a). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) \square 6.62 (1H, dd, $J = 17.9, 7.4$ Hz), 5.37 (1H, dd, $J = 17.7, 1.2$ Hz), 2.5 (1H, m), 1.7 (6H, m), 1.4 (1H, m), 1.28 (12H, s), 1.1 (1H, m). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) \square 159.2, 83.2, 46.4, 32.6, 25.5, 25.0. HRMS (CI) calcd. for $\text{C}_{13}\text{H}_{23}\text{BO}_2$: 222.1791, found: 222.1799.

2-(2-Cyclohexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (12b). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 ppm): (*E*-isomer) \square 6.58 (1H, dd, $J = 18.2, 6.2$ Hz), 5.38 (1H, dd, $J = 18.3, 1.5$ Hz), 2.0 (1H, m), 1.6 (5H, m), 1.27 (12H, s), 1.2 (5H, m). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (*E*-isomer) \square 160.1, 83.2, 43.5, 32.1, 26.4, 26.2, 25.0. HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{25}\text{BO}_2$: 236.1948, found: 236.1956.

2-Cyclopentylidenemethyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (13a). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): \square 5.28 (1H, quint, $J = 2.2$ Hz), 2.53 (2H, t, $J = 7.5$ Hz), 2.37 (2H, t, $J = 6.8$ Hz), 1.65 (4H, m), 1.26 (12H, s). ^{13}C NMR (300 MHz, CDCl_3 , ppm): \square 172.2, 112.5, 82.7, 37.2, 33.5, 27.0, 26.1, 25.1. HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{21}\text{BO}_2$: 208.1635, found: 208.1627.

2-Cyclohexylidenemethyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (13b). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H

NMR (300 MHz, CDCl₃, ppm): δ 5.02 (1H, s), 2.52 (2H, t, *J* = 6.3 Hz), 2.20 (2H, t, *J* = 5.6 Hz), 1.57 (6H, m), 1.26 (12H, s). ¹³C NMR (300 MHz, CDCl₃, ppm): δ 167.2, 82.7, 40.3, 33.4, 28.9, 28.7, 26.6, 25.0. HRMS (EI) calcd. for C₁₃H₂₃BO₂: 222.1791, found: 222.1790.

4,4,5,5-Tetramethyl-2-styryl-[1,3,2]dioxaborolane (14a). The crude product was purified using column chromatography (9:1 hexane:ethyl acetate). ¹H NMR (300 MHz, CDCl₃, ppm): (*E*-isomer) δ 7.50 (2H, dd, *J* = 7.8, 1.5 Hz), 7.41 (1H, d, *J* = 19.2 Hz), 7.3 (3H, m), 6.18 (1H, d, *J* = 18.6 Hz), 1.33 (12H, s). ¹³C NMR (300 MHz, CDCl₃, ppm): (*E*-isomer) δ 149.7, 137.7, 129.1, 128.8, 127.3, 83.6, 25.0. HRMS (EI) calcd. for C₁₄H₁₉BO₂: 230.1478, found: 230.1473.

2-[2-(2-Bromo-phenyl)-vinyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (14b). The crude product was purified using column chromatography (9:1 hexane:ethyl acetate). ¹H NMR (300 MHz, CDCl₃, ppm): (*E*-isomer) δ 7.72 (1H, d, *J* = 18.3 Hz), 7.62 (1H, dd, *J* = 8.0, 1.7 Hz), 7.56 (1H, dd, *J* = 7.8, 1.2 Hz), 7.30 (1H, ddd, *J* = 6.9, 6.9, 0.6 Hz), 7.15 (1H, ddd, *J* = 7.5, 7.5, 1.8 Hz), 6.13 (1H, d, *J* = 18.3 Hz), 1.33 (12H, s). ¹³C NMR (300 MHz, CDCl₃, ppm): (*E*-isomer) δ 147.7, 137.6, 133.3, 130.1, 127.7, 127.5, 124.5, 83.7, 25.0. HRMS (EI) calcd. for C₁₄H₁₈BBrO₂: 308.0583, found: 308.0589.

4,4,5,5-Tetramethyl-2-[2-(3-nitro-phenyl)-vinyl]-[1,3,2]dioxaborolane (14c). The crude product was purified using column chromatography (4:1 hexane:ethyl acetate). ¹H NMR (300 MHz, CD₂Cl₂, ppm): (*E*-isomer) δ 8.32 (1H, s), 8.12 (1H, d, *J* = 8.3 Hz), 7.81 (1H, d, *J* = 7.5 Hz), 7.53 (1H, dd, *J* = 7.8, 7.8 Hz), 7.39 (1H, d, *J* = 18.6 Hz), 6.29 (1H, d, *J* = 18.3 Hz), 1.29 (12H, s). ¹³C NMR (300 MHz, CD₂Cl₂, ppm): (*E*-isomer) δ

149.2, 146.9, 139.8, 133.3, 130.2, 123.7, 122.0, 84.2, 25.2. HRMS (EI) calcd. for $C_{14}H_{18}BNO_4$: 275.1329, found: 275.1330.

2-Methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-but-3-en-2-ol (16). The crude product was purified using column chromatography (7:3 hexane:ethyl acetate). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 6.72 (1H, d, J = 18.0 Hz), 5.61 (1H, d, J = 18.3 Hz), 1.58 (1H, br), 1.32 (6H, s), 1.29 (12H, s). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 160.0, 83.5, 72.0, 29.3, 25.0. HRMS (EI) calcd. for $C_{11}H_{21}BO_3 - CH_3$: 197.1349, found: 197.1348.

Benzoic acid 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-but-3-enyl ester (17). The crude product was purified using column chromatography (9:1 hexane:ethyl acetate). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 8.04 (2H, dd, J = 8.4, 1.5 Hz), 7.56 (1H, tt, J = 7.4, 1.8 Hz), 7.44 (2H, dd, J = 8.1, 6.6 Hz), 6.67 (1H, dt, J = 17.4, 6.3 Hz), 5.61 (1H, dt, J = 18.3, 1.5 Hz), 4.41 (2H, t, J = 6.9 Hz), 2.65 (2H, ddd, J = 6.6, 6.6, 1.2 Hz), 1.28 (12H, s). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 166.8, 149.2, 133.1, 130.5, 129.8, 128.5, 83.4, 63.7, 35.2, 25.0. HRMS (EI) calcd. for $C_{14}H_{25}BO_2$: 302.1689, found: 302.1683.

Benzoic acid 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-allyl ester (19). The crude product was purified using column chromatography (4:1 hexane:ethyl acetate). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 8.08, 2H, d, J = 7.2 Hz), 7.57 (1H, t, J = 7.4 Hz), 7.44 (2H, dd, J = 7.5, 7.5 Hz), 6.74 (1H, dt, J = 18.3, 4.4 Hz), 5.79 (1H, dt, J = 18.3, 2.0 Hz), 4.92 (2H, dd, J = 4.4, 1.7 Hz), 1.28 (12H, s). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) δ 166.3, 146.2, 133.2, 130.2, 129.9, 128.6, 83.7, 65.9, 25.0. HRMS (EI) calcd. for $C_{16}H_{21}BO_4$: 288.1533, found: 288.1534.

2-[3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-allyl]-isoindole-1,3-dione (21).

The crude product was purified using column chromatography (7:3 hexane:ethyl acetate).

¹H NMR (300 MHz, CDCl₃, ppm): (E-isomer) □ 7.85 (2H, dd, *J* = 5.7, 3.3 Hz), 7.72 (2H, dd, *J* = 5.6, 2.9 Hz), 6.59 (1H, dt, *J* = 18.0, 4.4 Hz), 5.48 (1H, dt, *J* = 18.3, 1.7 Hz), 4.39 (2H, dd, *J* = 4.5, 1.5 Hz), 1.23 (12H, s). ¹³C NMR (300 MHz, CDCl₃, ppm): (E-isomer) □ 167.8, 145.3, 134.1, 132.1, 123.4, 83.6, 41.2, 25.0. HRMS (EI) calcd. for C₁₇H₂₀BNO₄: 313.1485, found: 313.1476.

1-Bromo-oct-1-ene (22). The crude product was purified using column chromatography (pure hexanes). ¹H NMR (300 MHz, C₆D₆, ppm): (Z-isomer) □ 5.85 (1H, dt, *J* = 7.2, 1.4 Hz), 5.66 (1H, dt, *J* = 6.9, 6.9 Hz), 2.09 (2H, dtd, *J* = 7.1, 7.1, 1.4 Hz), 1.2 (8H, m), 0.57 (3H, t, *J* = 6.9 Hz). (E-isomer) □ 5.97 (1H, dt, *J* = 13.5, 7.4 Hz), 5.70 (1H, dt, *J* = 13.8, 1.5 Hz), 2.09 (2H, dtd, *J* = 7.1, 7.1, 1.4 Hz), 1.2 (8H, m), 0.57 (3H, t, *J* = 6.9 Hz). ¹³C NMR (300 MHz, CDCl₃, ppm): (Z-isomer) □ 135.2, 107.7, 31.9, 30.0, 29.1, 28.4, 22.9, 14.1. HRMS calcd. for C₈H₁₅Br: 190.0357, found: 190.0360.

Acetic acid 6-bromo-hex-5-enyl ester (23). The crude product was purified using column chromatography (9:1 hexane:ethyl acetate). ¹H NMR (300 MHz, CDCl₃, ppm): (Z-isomer) □ 6.18 (1H, d, *J* = 7.5 Hz), 6.09 (1H, dt, *J* = 6.8, 6.8 Hz), 4.08 (2H, t, *J* = 6.6 Hz), 2.24 (2H, dt, *J* = 7.3, 7.3 Hz), 2.05 (3H, s), 1.7 (2H, m), 1.5 (2H, m). ¹³C NMR (300 MHz, CDCl₃, ppm): (Z-isomer) □ 171.4, 134.5, 108.5, 64.4, 29.5, 28.3, 24.8, 21.2. (E-isomer) □ 137.7, 105.0, 64.3, 32.7, 28.1, 25.2. HRMS (EI) calcd. for C₈H₁₃BrO₂: 220.0099, found: 220.0104

1-(2-Bromo-vinyl)-3-nitro-benzene (24). The crude product was purified using column chromatography (9:1 hexane:ethyl acetate). ¹H NMR (300 MHz, CDCl₃, ppm): (Z-

isomer) δ 8.56 (1H, dd, J = 2.0, 2.0 Hz), 8.20 (1H, dd, J = 8.3, 1.7 Hz), 8.00 (1H, d, J = 7.5 Hz), 7.57 (1H, dd, J = 8.0, 8.0 Hz), 7.15 (1H, d, J = 8.1 Hz), 6.65 (1H, d, J = 8.1 Hz). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (Z-isomer) δ 148.4, 136.7, 134.9, 130.5, 129.4, 123.9, 123.2, 110.0. HRMS (EI) calcd. for $\text{C}_{11}\text{H}_8\text{BrNO}_2$: 226.9582, found: 226.9580.

Benzoic acid 4-bromo-but-3-enyl ester (25). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , ppm): (Z-isomer) δ 8.06 (2H, d, J = 6.6 Hz), 7.58 (1H, t, J = 7.5 Hz), 7.45 (2H, dd, J = 7.7, 7.7 Hz), 6.34 (1H, dt, J = 7.2, 1.2 Hz), 6.24 (1H, dt, J = 6.9, 6.9 Hz), 4.41 (2H, t, J = 6.5 Hz), 2.71 (2H, dtd, J = 6.7, 6.7, 1.4 Hz). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (Z-isomer) δ 166.7, 133.2, 130.6, 130.3, 129.8, 128.9, 110.7, 63.1, 29.8. HRMS (CI) calcd. for $\text{C}_{11}\text{H}_{11}\text{BrO}_2 + \text{H}$: 255.0021, found: 255.0009.

2-(3-Bromo-allyl)-isoindole-1,3-dione (26). The crude product was purified using column chromatography (4:1 hexane:ethyl acetate). Further purification could be obtained via recrystallization from hexanes. ^1H NMR (300 MHz, CDCl_3 , ppm): (Z-isomer) δ 7.87 (2H, dd, J = 5.3, 3.2 Hz), 7.74 (2H, dd, J = 5.6, 3.2 Hz), 6.39 (1H, dt, J = 7.2, 1.7 Hz), 6.24 (1H, dt, J = 6.9, 6.2 Hz), 4.48 (2H, dd, J = 6.2, 1.4 Hz). ^{13}C NMR (300 MHz, CDCl_3 , ppm): (Z-isomer) δ 167.9, 134.3, 132.2, 129.1, 123.6, 111.1, 37.6. HRMS (CI) calcd. for $\text{C}_{11}\text{H}_8\text{BrNO}_2 + \text{H}$: 265.9817, found: 265.9825.

(3-Iodo-allyl)-trisopropyl-silane (27). The crude product was purified using column chromatography (pure hexanes). ^1H NMR (300 MHz, C_6D_6 , ppm): (E-isomer) δ 6.52 (1H, dt, J = 14.4, 8.6 Hz), 5.76 (1H, dt, J = 14.4, 1.3 Hz), 1.67 (2H, dd, J = 8.6, 1.4 Hz), 1.07 (18H, s), 1.06 (3H, s). (Z-isomer) δ 6.25 (1H, dt, J = 7.7, 7.7 Hz), 6.01 (1H, dt, J = 7.2, 1.4 Hz), 1.75 (2H, dd, J = 8.0, 1.4 Hz), 1.10 (21H, s). ^{13}C NMR (300 MHz, CDCl_3 ,

ppm): (*E*-isomer) □ 143.9, 70.7, 20.4, 18.9, 11.2. (*Z*-isomer) □ 139.1, 80.5, 30.0, 19.0, 11.6. HRMS (EI) calcd. for $C_{12}H_{25}SiI$: 324.0770, found: 324.0775.

1-Iodo-oct-1-ene (28). The crude product was purified using column chromatography (19:1 hexane:ethyl acetate). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 6.52 (1H, dt, J = 14.1, 7.1 Hz), 5.98 (1H, dt, J = 14.1, 1.4 Hz), 2.06 (2H, dtd, J = 7.2, 7.2, 1.2 Hz), 1.4 (8H, m), 0.90 (3H, t, J = 6.6 Hz). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 146.9, 74.5, 36.4, 31.9, 28.9, 28.6, 22.9, 14.4. HRMS (CI) calcd. for $C_8H_{15}I$: 238.0218, found: 238.0224.

(2-Iodo-vinyl)-benzene (29). The crude product was purified using column chromatography (pure hexanes). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 7.45 (1H, d, J = 14.7 Hz), 7.3 (5H, m), 6.84 (1H, d, J = 15.0 Hz). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 145.0, 137.7, 128.8, 128.5, 126.1, 76.9. HRMS (CI) calcd. for C_8H_7I : 229.9592, found: 229.9592.

4-Iodo-2-methyl-but-3-en-2-ol (30). The crude product was purified using column chromatography (4:1 hexane:ethyl acetate). 1H NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 6.68 (1H, d, J = 14.1 Hz), 6.34 (1H, d, J = 14.7 Hz), 1.71 (1H, br), 1.31 (6H, s). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): (*E*-isomer) □ 153.1, 75.0, 74.0, 29.5. HRMS (CI) calcd. for C_5H_9IO : 211.9698, found: 211.9696.

References

(i) For similar examples of this phenomenon, see Hall, L. W.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, 97(16), 4527-4531.

(ii) The solvent columns were composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.