Supporting Information

## A Vinylic Rosenmund-von Braun Reaction: Practical Synthesis of Acrylonitriles

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## **General Information.**

All reactions were carried out in oven-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials.

All solvents were reagent grade. THF was freshly distilled from sodium/benzophenone under argon, DMF and dichloromethane were distilled under argon over calcium hydride. Dry diethyl ether was bought over molecular sieves in AcroSeal<sup>®</sup> bottles from Acros Organics. Cyclohexene was purified by distillation at atmospheric pressure before use. Copper(I) iodide (99,999% purity) was purchased from Aldrich and all other reagents were used as supplied.

Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kieselgel  $60F_{254}$  plates. Flash chromatography and filtrations were performed with silica gel 60 (particle size 40-63  $\mu$ m) supplied by Merck. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise mentioned.

Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Brucker 300 MHz spectrometer. Internal reference of  $\delta_{\rm H}$  7.26 was used for CDCl<sub>3</sub>. Data are presented as follows: chemical shift (in ppm on the  $\delta$  scale relative to  $\delta_{\rm TMS}$  =0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, m = multiplet, br. = broad, app. = apparent), coupling constants (J/Hz) and integration. Carbon-13 NMR spectra were recorded at 75 MHz using CDCl<sub>3</sub> ( $\delta_{\rm C}$  77.16) as internal reference.

Melting points were recorded on Wagner & Munz Kofler bench. Infrared spectra were recorded on a Brucker Alpha Spectrometer (ATR). High-resolution mass-spectra were obtained on a Waters QTogf API US or Thermo Finnigan MAT 95XP. Optical rotations were recorded on an Atago AP-100 automatic polarimeter at 589 nm and reported as follows:  $[\alpha]_D^{25}$ , concentration (*c* in g/100 mL), and solvent.

S2

## **Experimental Procedures and Characterization Data:**

# 11j

(Z)-1-(2-Iodovinyl)-4-methylbenzene 11j. This compound was synthesized based on a previously reported procedure.<sup>S1</sup> To a cooled (0 °C) solution of borane dimethylsulfide complex (820 µL, 8.6 mmol) in diethyl ether (8 mL) was added freshly distilled cyclohexene (1.7 mL, 17.1 mmol) dropwise. After appearance of a white precipitate, the suspension was stirred at 0 °C for 15 minutes and at rt for 1 hour. The suspension was then quickly concentrated under reduced pressure, the remaining solid was suspended in pentane (8 mL) and the resulting suspension was cooled to 0 °C before adding 1-(iodoethynyl)-4-methylbenzene<sup>S2</sup> (2.0 g, 8.1 mmol) dropwise. After complete disappearance of the precipitate, the solution was warmed to rt, treated with glacial acetic acid (495 µL, 8.9 mmol) and stirred for an additional 3 hours. Ethanolamine was next added in two portions, a first one (200 µL, 3.3 mmol) to initiate the precipitation and then the second one (770 μL, 12.7 mmol). The resulting suspension was stirred for 5 minutes and filtered over a short plug of silica (washed with 75 mL of pentane) and the filtrate was finally concentrated under reduced pressure to afford the desired iodoalkene 11j (1.9 g, 7.8 mmol, 96%, Z/E: 5/95) as a colorless oil which could be used without further purification; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.55 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 8.6 Hz, 1H), 2.36 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 138.5, 133.9, 129.0, 128.5, 126.3, 78.4, 21.6; IR (ATR): ν<sub>max</sub> 2920, 1614, 1508, 1305, 844, 819 cm<sup>-1</sup>.

## **Unreported Starting Materials**

<sup>&</sup>lt;sup>S1</sup> Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. J. Org. Chem. **1989**, 54, 6064.

<sup>&</sup>lt;sup>s2</sup> Yan, J.; Li, J.; Cheng, D. Synlett **2007**, 2442.



(*E*)-1-lododec-1-ene 11k. This compound was synthesized based on a previously reported procedure.<sup>53</sup> Diisobutylaluminium hydride (1M solution in hexane, 22.0 mL, 22.0 mmol) was added dropwise at rt to a solution of 1-decyne (3.8 mL, 21.0 mmol) in hexane (50 mL) under argon. The reaction mixture was then stirred at 50 °C for 2 hours, cooled to rt and concentrated under vacuum. The resulting colorless oil was diluted in THF (50 mL) and a solution of iodine (5.3 g, 21.0 mmol) in THF (20 mL) was then added dropwise at -78 °C. The resulting mixture was then stirred at rt for 16h and quenched by addition of 20 mL of a 1M aqueous solution of hydrochloric acid. The layers were separated and the aqueous layer was extracted with diethyl ether. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was purified by filtration over a short plug of silica (cyclohexane) to afford the desired vinyl iodide (2.4 g, 9.1 mmol, 43%, *Z/E* > 5/95) as a colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  6.51 (dt, *J* = 14.3 and 7.1 Hz, 1H), 5.97 (dt, *J* = 14.3 and 1.4 Hz, 1H), 2.04 (qd, *J* = 7.2 and 1.4 Hz, 2H), 1.36-1.26 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  147.0, 74.4, 36.2, 32.0, 29.5, 29.4, 29.1, 28.5, 22.8, 14.3; IR (ATR): v<sub>max</sub> 2955, 2924, 2853, 1457, 1208, 945 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>10</sub>H<sub>19</sub>I [M]<sup>+</sup> 266.0531, found 266.0526.



(Z)-1-benzyloxy-3-iodo-2-methylprop-2-ene 11p. Sodium hydride (60 wt% in mineral oil, 264 mg, 6.6 mmol) was added portionwise at 0 °C to a solution of (Z)-3-iodo-2-methylprop-2-en-1-ol<sup>S4</sup> (584 mg, 3.0 mmol) in THF (6 mL) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1 hour, treated with benzyl bromide (780  $\mu$ L, 6.6 mmol), stirred at rt for an additional 20

<sup>&</sup>lt;sup>S3</sup> Peterson, M. A.; Polt, R. Synth. Commun. **1992**, 22, 477.

<sup>&</sup>lt;sup>S4</sup> Prepared in two steps from ethyl propiolate according to the procedures described in the following articles: (a) Marek, I.; Meyer, C.; Normant, J.-F. *Org. Synth.* **1997**, *74*, 194. (b) Beruben, D.; Marek, I.; Normant, J.-F.; Platzer, N. J. Org. Chem. **1995**, *60*, 2488.

hours and hydrolyzed carefully by slow addition of 20 mL of a saturated aqueous solution of sodium hydrogencarbonate. The layers were separated and the aqueous layer was extracted with diethyl ether. Combined organic layer were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate: 9/1) to afford the desired benzylic ether **11p** (548 mg, 1.9 mmol, 63%, Z/E > 95/5) as a colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.37-7.30 (m, 5H), 6.08 (s, 1H), 4.50 (s, 2H), 4.17 (s, 2H), 1.97 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  144.4, 138.2, 128.5, 127.9, 127.8, 76.2, 75.0, 72.3, 22.0; IR (ATR): v<sub>max</sub> 3031, 2912, 2854, 1540, 1496, 1093, 1073, 735, 696 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>11</sub>H<sub>13</sub>IO [M]<sup>+</sup> 288.0011, found 288.0006.



(*Z*)-2-Iodo-1-methoxymethoxy-3-phenylprop-2-ene 11r. To a cooled (0 °C) solution of (*Z*)-2-iodo-3-phenylprop-2-en-1-ol<sup>S5</sup> (1.5 g, 5.8 mmol), 4-dimethylaminopyridine (70 mg, 0.6 mmol), diisopropylethylamine (2.9 mL, 17.3 mmol) in dichloromethane (11.5 mL) was added dropwise chloromethyl methylether (870  $\mu$ L, 9.0 mmol). The reaction mixture was stirred for 3 days at rt before being diluted with 15 mL of water. The layers were separated and the aqueous layer was extracted with diethyl ether. Combined organic layer were dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was finally purified by flash chromatography on silica gel (cyclohexane/ethyl: acetate 9/1) to afford the desired protected alcohol **11r** (1.4 g, 4.4 mmol, 77%, Z/E > 95/5) as a yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.56-7.53 (m, 2H), 7.32-7.40 (m, 3H), 7.11 (s, 1H), 4.75 (s, 2H), 4.42 (d, *J* = 1.3 Hz, 2H), 3.45 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$ 137.2, 135.8, 128.8, 128.3, 128.2, 101.8, 95.4, 76.5, 55.9; IR (ATR): v<sub>max</sub> 2885, 1491, 1445, 1149, 1105, 1027, 749, 695 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>11</sub>H<sub>13</sub>IO<sub>2</sub> [M]<sup>+</sup> 303.9960, found 303.9957.

<sup>&</sup>lt;sup>S5</sup> This compound was prepared in two steps from cinnamaldehyde according to the procedures described in: (a) Hashmi, A. S. K.; Häffner, T.; Rudolf, M.; Rominger, F. *Eur. J. Org. Chem.* **2011**, 667. (b) Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. C. *J. Chem. Soc., Perkin Trans.* **1 2002**, 58.

## Experimental Procedures and Characterization Data: Copper-Catalyzed Cyanation of Alkenyl Iodides.

#### **General procedure**

A 10 mL round bottom flask was charged with the alkenyl iodide (1.0 mmol), copper iodide (19 mg, 0.1 mmol) and 1,10-phenanthroline (39 mg, 0.2 mmol). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Distilled DMF (1.2 mL) was added and the mixture was stirred at room temperature for 5 minutes. Tri-*n*-butylamine (310  $\mu$ L, 1.3 mmol) and acetone cyanohydrin<sup>S6</sup> (110  $\mu$ L, 1.2 mmol) were then successively added and the reaction mixture was heated at 110 °C until complete conversion (typically 16-24 hours). The resulting solution was cooled to rt and diluted with 50 mL of diethyl ether and 50 mL of water. The organic layer was successively washed with 50 mL of water and 50 mL of brine, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography on silica gel to afford the desired acrylonitrile.



(*E*)-3-(4-Methoxyphenyl)acrylonitrile 12a. Yield: 72% (115 mg, 0.72 mmol, *Z/E*: 5/95). Solvent system for flash chromatography: cyclohexane/dichloromethane: 30/70. White solid. This compound has been previously reported.<sup>S7</sup>

 <sup>&</sup>lt;sup>S6</sup> Cyanide containing waste can be decontaminated using a solution of sodium hypochlorite in water, see Lunn, G.;
Sansone, E. B. *Destruction of Hazardous Chemicals in the Laboratory*, 2<sup>nd</sup> Ed., Wiley & Sons: New-York, 1994, 133.
<sup>S7</sup> Sharma, D.; Kumar, S.; Shil, A. K.; Guha, N. R.; Bandna; Das, P. *Tetrahedron Lett.* **2012**, *53*, 7044.



(*E*)-3-[4-(Trifluoromethyl)phenyl]acrylonitrile 12b. Yield: 58% (115 mg, 0.58 mmol, Z/E > 5/95). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. White solid. This compound has been previously reported.<sup>S8</sup>



(*E*)-3-(4-Chlorophenyl)acrylonitrile 12c. Yield: 77% (126 mg, 0.77 mmol, Z/E > 5/95). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. White solid. This compound has been previously reported.<sup>S9</sup>



(*E*)-3-(4-Bromophenyl)acrylonitrile 12d. Prepared according to the general procedure using 2.2 eq. of acetone cyanohydrin and 2.3 eq. of tri-*n*-butylamine. Yield: 73% (152 mg, 0.73 mmol, Z/E > 5/95). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Yellow solid. This compound has been previously reported.<sup>S10</sup>

<sup>&</sup>lt;sup>S8</sup> Qin, C.; Jiao, N.; J. Am. Chem. Soc. **2010**, 132, 15893.

<sup>&</sup>lt;sup>59</sup> Peppe, C.; de Azevedo Mello, P.; Pavão das Chagas, R. J. Organomet. Chem. **2006**, 691, 2335.

<sup>&</sup>lt;sup>S10</sup> Ruan, J.; Li, X.; Saidi, O.; Xiao, J. J. Am. Chem. Soc. **2008**, 130, 2124.



(*E*)-Cinnamonitrile 12e. Yield: 82% (531 mg, 4.10 mmol, Z/E > 5/95) starting from 5 mmol of alkenyl iodide 11e. Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Yellow oil. This compound has been previously reported.<sup>59</sup>



(*E*)-3-(Naphthalen-2-yl)acrylonitrile 12f. Yield: 96% (172 mg, 0.96 mmol, Z/E > 5/95). No purification needed. Brown solid. This compound has been previously reported.<sup>58</sup>



(*Z*)-3-(4-Methoxyphenyl)acrylonitrile 12g. Yield: 52% (83 mg, 0.52 mmol, *Z*/*E*: 9/1). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Orange oil. This compound has been previously reported.<sup>59</sup>



(Z)-3-(2-Methoxyphenyl)acrylonitrile 12h. Yield: 85% (135 mg, 0.85 mmol, Z/E > 95/5). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Brown solid. This compound has been previously reported.<sup>S11</sup>



(*Z*)-Cinnamonitrile 12i. Yield: 75% (94 mg, 0.75 mmol, *Z*/*E*: 95/5). Solvent system for flash chromatography: cyclohexane/dichloromethane: 50/50. Yellow oil. This compound has been previously reported.<sup>59</sup>



(*Z*)-3-(*p*-Tolyl)acrylonitrile 12j. Yield: 57% (81 mg, 0.57 mmol, Z/E > 95/5). Solvent system for flash chromatography: cyclohexane 100% then cyclohexane/ethyl acetate: 90/10. Colorless oil. This compound has been previously reported.<sup>S9</sup>

<sup>&</sup>lt;sup>S11</sup> Fang, F.; Li, Y.; Tian, S.-K. Eur. J. Org. Chem. **2011**, 1084.



(*E*)-Undec-2-enenitrile 12k. Yield: 73% (121 mg, 0.73 mmol, *Z/E* > 5/95). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 95/5. Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.10 (td, *J* = 6.9 and 16.3 Hz, 1H), 5.31 (dt, *J* = 16.3 and 1.6 Hz, 1H), 2.21 (qd, *J* = 7.1 and 1.5 Hz, 2H), 1.46-1.27 (m, 12H), 0.88 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  156.3, 117.7, 99.7, 33.5, 31.9, 29.4, 29.3, 29.1, 27.7, 22.8, 14.2; IR (ATR): v<sub>max</sub> 2955, 2926, 2855, 2223, 1633, 1465, 968, 723 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>11</sub>H<sub>9</sub>N [M]<sup>+</sup> 165.1517, found 165.1520.



(*E*)-4-Phenylbut-2-enenitrile 12I. Yield: 39% (56 mg, 0.39 mmol, Z/E > 5/95). Solvent system for flash chromatography: petroleum ether/ethyl acetate: 90/10. Yellow solid. This compound has been previously reported.<sup>S12</sup>



(*Z*)-Non-2-enenitrile 12m. Yield: 47% (64 mg, 0.47 mmol, Z/E > 95/5). Solvent system for flash chromatography: cyclohexane 100% then cyclohexane/ethyl acetate: 90/10. Colorless oil. This compound has been previously reported.<sup>S9</sup>

<sup>&</sup>lt;sup>S12</sup> Zhang, Z.; Liebeskind, L. S. Org. Lett. **2006**, *8*, 4331.



(*Z*)-4-(*tert*-Butyldimethylsilyloxy)but-2-enenitrile 12n. Yield: 59% (117 mg, 0.59 mmol, *Z/E* > 95/5). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Red oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.55 (dt, *J* = 11.3 and 5.6 Hz, 1H), 5.37 (dt, *J* = 11.3 and 1.8 Hz, 1H), 4.48 (dd, *J* = 5.6 and 1.8 Hz, 2H), 0.91 (s, 9H), 0.11 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 115.4, 98.7, 62.3, 25.9, 18.4, -5.2; IR (ATR): v<sub>max</sub> 2955, 2931, 2858, 2221, 1662, 1472, 1256, 1108, 837, 778 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>10</sub>H<sub>19</sub>NOSi [M]<sup>+</sup> 197.1236, found 197.1234.



(*Z*)-4-(*tert*-Butyldimethylsilyloxy)-3-methylbut-2-enenitrile 12o. Yield: 79% (168 mg, 0.79 mmol, *Z/E* > 95/5). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 95/5. Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  5.15 (s, 1H), 4.40 (s, 2H), 1.95 (s, 3H), 0.91 (s, 12H), 0.11 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  164.0, 116.1, 94.6, 64.6, 25.9, 20.4, 18.4, -5.2; IR (ATR): v<sub>max</sub> 2955, 2930, 2858, 2220, 1472, 1256, 1195, 1103, 838, 778 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>11</sub>H<sub>21</sub>NOSi [M]<sup>+</sup> 211.1392, found 211.1388.



(*Z*)-4-Benzyloxy-3-methylbut-2-enenitrile 12p. Yield: 74% (138 mg, 0.74 mmol, *Z/E* > 95/5). Solvent system for flash chromatography: cyclohexane/ethyl acetate: 90/10. Brown oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (s, 5H), 5.27 (s, 1H), 4.54 (s, 2H), 4.29 (s, 2H), 2.00 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  161.3, 137.5, 128.6, 128.1, 127.9, 116.0, 97.1, 73.1, 71.0, 20.8; IR (ATR): v<sub>max</sub> 3032, 2859, 2219, 1637, 1454, 1098, 1072, 739, 698 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>12</sub>H<sub>13</sub>NO [M]<sup>+</sup> 187.0997, found 187.1002.



**2-Methyleneoctanenitrile 12q.** Yield: 41% (56 mg, 0.41 mmol); isolated as a mixture of the desired compound **12q** and (*E*)-non-2-enenitrile in a 94/6 ratio. Solvent system for flash chromatography: cyclohexane 100% and then cyclohexane/ethyl acetate: 90/10. Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  5.81 (s, 1H), 5.69 (s, 1H), 2.24 (dd, *J* = 7.6 Hz, 2H), 1.57-1.49 (m, 2H), 1.34-1.25 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  130.1, 123.5, 118.4, 34.7, 31.5, 28.4, 27.6, 22.6, 14.1; IR (ATR): v<sub>max</sub> 2956, 2929, 2859, 2223, 1622, 1458, 1101, 953 cm<sup>-1</sup>; EIHRMS *m*/*z* calcd for C<sub>9</sub>H<sub>15</sub>N [M]<sup>+</sup> 137.1204, found 137.1208.



(*E*)-2-[(Methoxymethoxy)methyl]-3-phenylacrylonitrile 12r. Yield: 66% (135 mg, 0.66 mmol, *Z/E* > 5/95). Solvent system for flash chromatography: petroleum ether/ethyl acetate: 90/10. Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.80-7.77 (m, 2H), 7.42-7.44 (m, 3H), 7.18 (s, 1H), 4.73 (s, 2H), 4.32 (s, 2H), 3.44 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  145.3, 133.1, 130.8, 129.2, 129.0, 117.8, 108.1, 95.8, 68.6, 55.9; IR (ATR): v<sub>max</sub> 2947, 2214, 1213, 1149, 1103, 1045, 1004, 923, 753, 691 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub> [M]<sup>+</sup> 203.0946, found 203.0952.



(2*E*,2'*E*)-3,3'-(1,3-Phenylene)diacrylonitrile 14. Yield: 50% (47 mg, 0.25 mmol, *EZ/EE* 1/9) starting from 0.5 mmol of substrate 13. Solvent system for flash chromatography: petroleum ether/ethyl acetate: 95/5 and then 90/10. White solid; Mp: 198 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.54-7.38 (m, 6H), 5.94 (d, *J* = 16.6 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  149.3, 134.6, 130.1, 129.5, 126.5, 117.7, 98.3; IR (ATR): v<sub>max</sub> 2928, 2213, 1619, 1177, 968, 780, 679 cm<sup>-1</sup>; EIHRMS *m/z* calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> [M]<sup>+</sup> 180.0687, found 180.0688.

## **Experimental Procedures and Characterization Data:**

# AcO AcO 17

#### Formal Synthesis of Alliarinoside.

**O**-α-Glucopyranosyl-[(Z)-3-iodoprop-2-en-1-ol] 17. This compound was synthesized based on a previously reported procedure.<sup>S13</sup> A 100 mL round bottom flask was charged with peracetyl  $\alpha$ -Dglucopyranosyl bromide 15 (2.2 g, 5.3 mmol), (Z)-3-iodoprop-2-en-1-ol 16 (2.9 g, 16.0 mmol), 500 mg of finely powdered 4Å molecular sieves and dichloromethane (12 mL) under an argon atmosphere. The reaction mixture was stirred at rt for 30 min and silver carbonate (1.6 g, 5.9 mmol) was added in one portion. The flask was covered with aluminium foil and the reaction mixture was stirred at rt for 4 days and then diluted with 70 mL of chloroform. The resulting suspension was filtered over a plug of Celite® and the filtrate was successively washed with 50 mL of an aqueous saturated solution of sodium hydrogencarbonate and 50 mL of brine. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was finally purified by flash chromatography on silica gel (petroleum ether/ethyl acetate: 80/20) to afford the desired compound 17 (1.6 g, 3.2 mmol, 59%) as a yellow oil;  $[\alpha]_D^{25} = +10.0$  (c 1.9, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  6.47-6.36 (m, 2H), 5.20 (t app., J = 9.4 Hz, 1H), 5.09 (t app., J = 9.6 Hz, 1H), 4.99 (dd, J = 9.4 and 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.37-4.24 (m, 3H), 4.15 (dd, J = 12.3 and 2.4 Hz, 1H), 3.71 (ddd, J = 9.8, 4.7 and 2.4 Hz, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H);  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  170.8, 170.4, 169.5 (2C), 137.1, 99.9, 84.7, 73.0, 72.1, 71.9, 71.4, 68.5, 62.0, 20.9 (2C), 20.7 (2C); IR (ATR): v<sub>max</sub> 2954, 1749, 1366, 1217, 1038, 906 cm<sup>-1</sup>; ESIHRMS *m/z* calcd for C<sub>17</sub>H<sub>24</sub>IO<sub>10</sub> [M+H]<sup>+</sup> 515.1414, found 515.1408.

<sup>&</sup>lt;sup>S13</sup> Rodebaugh, R.; Fraser-Reid, B. *Tetrahedron* **1996**, *52*, 7663.



**Peracetyl-alliarinoside 18.** A 250 mL round bottom flask was charged with copper iodide (61 mg, 0.32 mmol), 1,10-phenanthroline (114 mg, 0.63 mmol) and iodoalkene **17** (1.6 g, 3.2 mmol). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Distilled DMF (3.8 mL) was added and the mixture was stirred at rt for 5 minutes. Tri-*n*-butylamine (863 μL, 4.1 mmol) and acetone cyanohydrin (345 μL, 3.8 mmol) were then successively added and the reaction mixture was heated at 110 °C for 24 hours. The resulting solution was cooled to rt and diluted with 150 mL of diethyl ether and 150 mL of water. The organic layer was successively washed with 150 mL of water and 150 mL of brine, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography on silica gel (cyclohexane/ethyl: acetate 50/50) to afford the peracetyl-alliarinoside **18** (764 mg, 1.9 mmol, 59%) as a brown waxy solid. This compound has been previously reported.<sup>514</sup>

<sup>&</sup>lt;sup>514</sup> Haribal, M.; Yang, Z.; Attygalle, A. B.; Renwick, J. A. A.; Meinwald, J. J. Nat. Prod. 2001, 64, 440.

Supporting information

<sup>1</sup>H and <sup>13</sup>C NMR Spectra



















-10 100 90 f1 (ppm) Ó 























S33

















