

Supporting information

Facile Synthesis of (*E*)- β -Nitroolefinic Alkoxyamines via Silver-Catalyzed Decarboxylative Nitroaminoxylation of Phenylpropionic Acids

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1. General Information

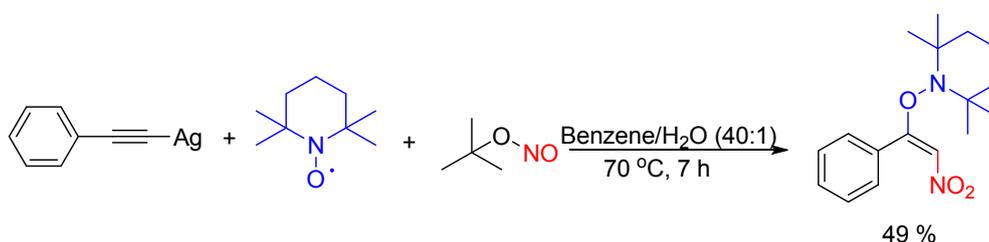
All the reactions were carried out under the air atmosphere condition. Solvents were dried and degassed by standard methods and all alkynes, 4-Acetamido-TEMPO and 4-Hydroxy-2,2,6,6-tetramethyl-piperidinoxy were commercial available. 4-Acetoxy TEMPO¹ and silver phenylacetylide² were synthesized as the literature reported. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were measured in CDCl₃ on 400 MHz or 300 MHz NMR spectrometer with TMS as an internal reference. Products were characterized by comparison of ¹H NMR, ¹³C NMR, LC-MS.

2. General Procedure for Silver-catalyzed Decarboxylative Nitroaminoxylation of Phenylpropionic Acid

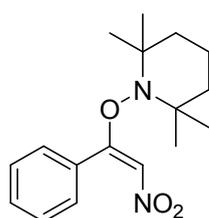
Phenylpropionic acid (0.0439 g), TEMPO (0.3mmol, 0.0469 g) and silver oxide (5 mol %, 0.0035 g) were added to a test tube. Then benzene (2 mL) and *tert*-butylnitrite (2 equiv, 72 μL) was added to the tube in order. The resulting reaction mixture was kept stirring at 70 °C for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

3. Mechanic study

Silver phenylacetylide (0.3mmol, 0.0627 g), TEMPO (0.3mmol, 0.0469 g) and were added to a test tube. Then benzene (2 mL), distilled water (50 μL) and *tert*-butylnitrite (2 equiv, 72 μL) was added to the tube in order. The resulting reaction mixture was kept stirring at 70 °C for 7 h. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford **4a** in 49% yield.

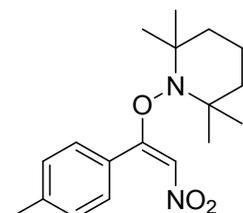


4. Characterization Data of All Products



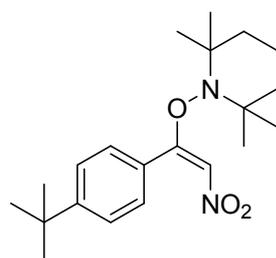
(E)-2,2,6,6-tetramethyl-1-((2-nitro-1-phenylvinyl)oxy)piperidine (4a)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 69.4 mg; m.p. 108-110 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.53-7.47 (m, 5H), 1.68-1.64 (m, 5H), 1.50-1.46 (m, 1H), 1.25 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 131.8, 130.6, 128.3, 128.2, 123.4, 61.6, 39.6, 32.0, 20.7, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{NaO}_3$ 327.1685, found 327.1681.



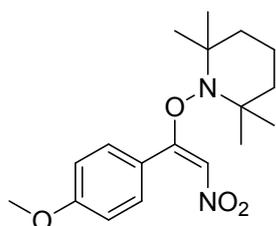
(E)-2,2,6,6-tetramethyl-1-((2-nitro-1-(p-tolyl)vinyl)oxy)piperidine (4b)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 67.6 mg; m.p. 100-102 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.45 (s, 3H), 1.68-1.63 (m, 5H), 1.50-1.45 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 141.0, 129.0, 128.8, 128.2, 123.2, 61.5, 39.6, 32.0, 21.6, 20.7, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{NaO}_3$ 341.1841, found 341.1800.



(E)-1-((1-(4-(tert-butyl)phenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4c)

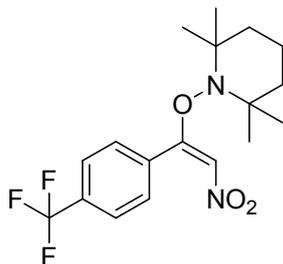
The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.3$); yellow solid, 80.6 mg; m.p. 125-127 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.50-7.42 (m, 4H), 1.68-1.63 (m, 5H), 1.50-1.45 (m, 1H), 1.38 (s, 9H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 154.0, 128.6, 128.2, 125.2, 123.2, 61.5, 39.6, 35.0, 32.0, 31.2, 20.8, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{NaO}_3$ 383.2311, found 383.2285.



(E)-1-((1-(4-methoxyphenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4d)

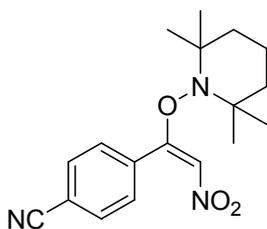
The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.1$); yellow oil, 65.2 mg. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.36 (d, $J = 8.8$ Hz, 2H), 6.88

(d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 1.58-1.53 (m, 5H), 1.39-1.35 (m, 1H), 1.12 (d, $J = 3.6$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 161.6, 130.2, 123.5, 122.9, 113.7, 61.5, 55.4, 39.6, 32.0, 20.7, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{NaO}_4$ 357.1790, found 357.1774.



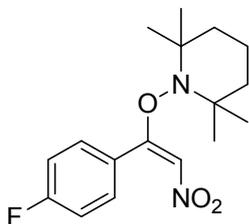
(E)-2,2,6,6-tetramethyl-1-((2-nitro-1-(4-(trifluoromethyl)phenyl)vinyl)oxy)piperidine (4e)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 48.3 mg; m.p. 88-90 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 1.68-1.65 (m, 5H), 1.51-1.46 (m, 1H), 1.25 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 135.5 (d, $J = 1.1$ Hz), 132.32 (d, $J = 32.9$ Hz), 128.6, 125.4 (q, $J = 3.8$ Hz), 124.0, 123.7 (d, $J = 273.6$ Hz), 61.7, 39.6, 32.1, 20.7, 16.6. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ 395.1558, found 395.1561.



(E)-4-(2-nitro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)vinyl)benzonitrile (4f)

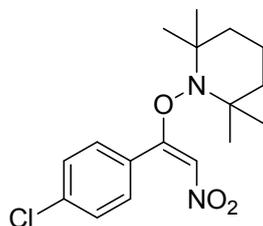
The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 12:1, $R_f = 0.5$); yellow solid, 60.7 mg; m.p. 168-170 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 1.68-1.65 (m, 5H), 1.50-1.47 (m, 1H), 1.24 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 136.4, 132.2, 128.9, 124.2, 118.1, 114.3, 61.8, 39.6, 32.1, 20.7, 16.6. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{23}\text{N}_3\text{NaO}_3$ 352.1637, found 352.1623.



(E)-1-((1-(4-fluorophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4g)

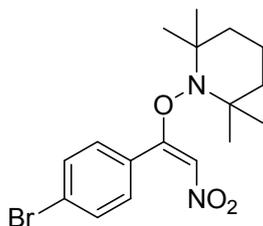
The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 73.1 mg; m.p. 113-115 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.49-7.45 (m, 2H), 7.19-7.13 (m, 2H), 1.68-1.63 (m, 5H), 1.50-1.45 (m, 1H), 1.22 (d, $J = 3.2$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 164.0 (d, $J = 252.3$ Hz), 130.5 (d, $J = 8.8$ Hz), 127.7 (d, $J = 3.6$ Hz),

123.55, 115.6 (d, $J = 22.2$ Hz), 61.6, 39.6, 32.0, 20.7, 16.7. HRMS (TOF MS ESI+) $[M+Na]^+$ calculated for $C_{17}H_{23}FN_2NaO_3$ 345.1590, found 345.1574.



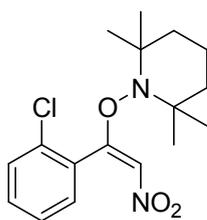
(E)-1-((1-(4-chlorophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4h)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 53.5 mg; m.p. 100-102 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.46-7.39 (m, 4H), 1.68-1.63 (m, 5H), 1.50-1.45 (m, 1H), 1.22 (d, $J = 5.2$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 136.8, 130.2, 129.6, 128.7, 123.7, 61.6, 39.6, 32.0, 20.7, 16.7. HRMS (TOF MS ESI+) $[M+Na]^+$ calculated for $C_{17}H_{23}ClN_2NaO_3$ 361.1295, found 361.1294.



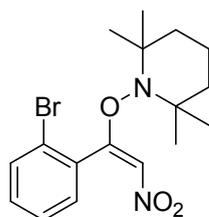
(E)-1-((1-(4-bromophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4i)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 56.9 mg; m.p. 78-80 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 1.58-1.54 (m, 5H), 1.40-1.36 (m, 1H), 1.12 (d, $J = 5.6$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 131.7, 130.7, 129.8, 125.2, 123.7, 61.6, 39.6, 32.0, 20.7, 16.7. HRMS (TOF MS ESI+) $[M+Na]^+$ calculated for $C_{17}H_{23}BrN_2NaO_3$ 405.0790, found 405.0781.



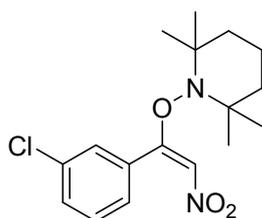
(E)-1-((1-(2-chlorophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4j)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, $R_f = 0.4$); yellow solid, 78.2 mg; m.p. 135-137 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.52-7.50 (m, 1H), 7.46-7.42 (m, 1H), 7.40-7.34 (m, 2H), 1.68-1.61 (m, 5H), 1.48-1.45 (m, 1H), 1.32 (d, $J = 21.6$ Hz, 6H), 1.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 132.7, 132.1, 131.1, 129.8, 129.2, 126.9, 125.0, 61.9, 40.0, 32.2, 20.6, 16.7. HRMS (TOF MS ESI+) $[M+Na]^+$ calculated for $C_{17}H_{23}ClN_2NaO_3$ 361.1295, found 361.1277.



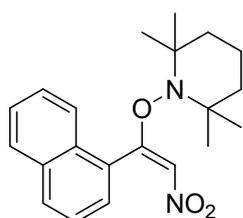
(E)-1-((1-(2-bromophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4k)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, R_f = 0.3); yellow solid, 94.5 mg; m.p. 144-146 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.69-7.67 (m, 1H), 7.45-7.41 (m, 1H), 7.37-7.33 (m, 2H), 1.65 (s, 5H), 1.47-1.44 (m, 1H), 1.40 (s, 3H), 1.28 (s, 3H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 134.2, 133.0, 131.2, 129.4, 127.5, 124.8, 121.8, 62.1, 61.8, 40.2, 39.8, 32.2, 20.6, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{BrN}_2\text{NaO}_3$ 405.0790, found 405.0780.



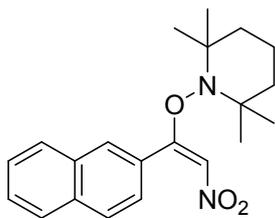
(E)-1-((1-(3-chlorophenyl)-2-nitrovinyl)oxy)-2,2,6,6-tetramethylpiperidine (4l)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, R_f = 0.4); yellow solid, 65.6 mg; m.p. 72-74 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.51-7.48 (m, 1H), 7.43-7.39 (m, 2H), 7.34-7.32 (m, 1H), 1.68-1.64 (m, 5H), 1.51-1.46 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 134.3, 133.5, 130.7, 129.7, 128.1, 126.4, 123.8, 61.7, 39.6, 32.1, 20.7, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{ClN}_2\text{NaO}_3$ 361.1295, found 361.1270.



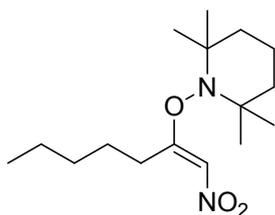
(E)-2,2,6,6-tetramethyl-1-((1-(naphthalen-1-yl)-2-nitrovinyl)oxy)piperidine (4m)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, R_f = 0.3); yellow solid, 32.3 mg; m.p. 178-180 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.02-7.99 (m, 1H), 7.96-7.93 (m, 1H), 7.91-7.89 (m, 1H), 7.60-7.53 (m, 4H), 1.74-1.66 (m, 5H), 1.50-1.48 (m, 1H), 1.40 (s, 6H), 1.26 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 133.2, 130.6, 130.6, 130.4, 128.8, 127.3, 126.4, 126.0, 125.3, 125.0, 123.9, 62.1, 61.4, 39.8, 32.4, 20.7, 16.8. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{NaO}_3$ 377.1841, found 377.1833.



(E)-2,2,6,6-tetramethyl-1-((1-(naphthalen-2-yl)-2-nitrovinyl)oxy)piperidine (4n)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, R_f = 0.3); yellow solid, 75.5 mg; m.p. 106-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (s, 1H), 7.95-7.91 (m, 4H), 7.62-7.52 (m, 3H), 1.70-1.64 (m, 5H), 1.52-1.47 (m, 1H), 1.31 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 134.2, 132.7, 129.3, 128.7, 128.2, 128.1, 127.9, 127.6, 126.7, 125.2, 123.7, 61.6, 39.6, 32.1, 20.8, 16.7. HRMS (TOF MS ESI+) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{NaO}_3$ 377.1841, found 377.1823.



(E)-2,2,6,6-tetramethyl-1-((1-nitrohept-1-en-2-yl)oxy)piperidine (4o)

The product was purified on silica gel column chromatography (petroleum ether/ethyl acetate, 36:1, R_f = 0.5); yellow oil, 40.0 mg. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (s, 1H), 2.81-2.77 (m, 2H), 1.65-1.58 (m, 2H), 1.53-1.48 (m, 6H), 1.38-1.32 (m, 4H), 1.12 (s, 6H), 0.98 (s, 6H), 0.85 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.4, 123.0, 61.2, 39.5, 31.9, 31.9, 31.2, 26.9, 22.3, 20.6, 16.7, 13.9. HRMS (TOF MS CI+) $[\text{M}]^+$ calculated for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_3$ 298.2256, found 298.2254.

5. Reference:

- [1] J. Zakrzewski, *Beilstein J. Org. Chem.* 2012, **8**, 1515–1522.
 [2] B. K. Teo, Y. H. Xu, B. Y. Zhong, Y. K. He, H. Y. Chen, W. Qian, Y. J. Deng and Y. H. Zou, *Inorg. Chem.* 2001, **40**, 6794-6801.

6. Spectral Copies of ^1H and ^{13}C NMR of All Products

