Supporting Information

•-Nitro xanthates as olefin precursors

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General Considerations

Commercial reagents were used as received without further purification. All products were purified by flash column chromatography using silica gel SDS 60 C.C. 40-63. NMR spectra were recorded in CDCl₃ with TMS as an internal standard at ambient temperature on a Bruker AMX400 operating at 400 MHz for ¹H and 100 MHz for ¹³C. Infrared Absorption spectra were recorded as a solution in CCl₄ with a Perkin-Elmer 1600 Fourier Transform Spectrophotometer. Mass spectra were recorded using an HP 5989B mass spectrometer. Melting points were determined on a Reichert microscope apparatus and are uncorrected.

Experimental Section

Compounds **1a**¹, **1c** were synthesized according to literature procedures.² Compound **1b** is commercially available.

Synthesis of nitroolefins

General Procedure

The aldehyde (*X* mmol), the nitro compound (*X* mmol), 3 drops of acetic acid and 3 drops of *n*-butylamine in toluene (*X*/2 mL) were refluxed in a Dean-Stark apparatus.² Upon complete transformation (TLC monitoring), the reaction mixture was cooled to room temperature then concentrated *in vacuo*. The crude residue was either recrystallized or purified by flash chromatography.

Compound **1d**

¹ We thank Dr Joëlle Prunet (Ecole Polytechnique) for a gift of this nitroolefin.

² Jones, G. *Org. React.* **1967**, *15*, 204-599.

According to the general procedure, 1-nitromethylcyclohexene³ (2.82 g, 20.0 mmol, 1.0 equiv) and 3,4,5-trimethoxybenzaldehyde (3.90 g, 20.0 mmol, 1.0 equiv) were refluxed for 2h in toluene (10 mL). Recrystallization from methanol gave compound **1d** (4.08g, *E/Z* : 2/1, 64%) as bright yellow needles (mp 89°C). ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 7.85 (s, 0.66H), 6.92 (s, 1.32H), 6.50 (s, 0.68H), 6.25 (s, 0.34H), 6.00 (bs, 0.66H), 5.84 (bs, 0.34H), 3.90 (s, 2H), 3.87 (s, 4H), 3.84 (s, 1H), 3.81 (s, 2H), 2.28-2.19 (m, 4H), 1.87-1.80 (m, 2H), 1.79-1.72 (m, 2H). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) (*E* isomer only) 153.2, 150.9, 140.4, 134.6, 132.8, 129.6, 126.9, 109.0, 61.0, 56.2, 27.3, 25.7, 22.6, 21.6. IR (ν_{max}, cm⁻¹) (CCl₄) 3003, 2936, 2834, 1635, 1579, 1523, 1506, 1463, 1419, 1313, 1244, 1133, 1008. MS (CI, NH₃) *m/z* [MNH₄]⁺=336, [MH]⁺=320. **Analysis** Calcd for C₁₇H₂₁NO₅ C(63.94), H(6.63), found C(63.82), H(6.69).

Compound **1e**

According to the general procedure, 2-(3'-benzyloxy-4'-methoxyphenyl)-1-nitroethane⁴ (5.74 g, 20.0 mmol, 1.0 equiv) and *p*-cyanobenzaldehyde (2.60 g, 20 mmol, 1.0equiv) were refluxed for 4h in toluene (10 mL). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **1e** (6.86 g, 81%) as a dark yellow solid, which was used directly in the next step. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 8.21 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 6.4 Hz, 2H), 7.38 (t, *J* = 6.4 Hz, 2H), 7.32 (t, *J* = 6.4 Hz, 1H), 6.83 (d, *J* = 6.6 Hz, 1H), 6.73 (d, *J* = 2.2 Hz, 1H), 6.62 (dd, *J* = 2.2, 6.6 Hz, 1H), 5.14 (s, 2H), 4.16 (s, 2H), 3.86 (s, 3H). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) 152.1, 150.1, 147.6, 137.0, 136.6, 132.8, 130.0, 128.6, 128.3, 128.0, 127.3, 119.2, 118.0, 114.3, 113.8, 111.7, 70.9, 56.1, 32.4. IR (ν_{max}, cm⁻¹) (CCl₄) 2957, 2231, 1741, 1606, 1532, 1513, 1264, 1238, 1142. MS (CI, NH₃) *m/z* [MNH₄]⁺=418.

³ (a) Tamura, R.; Sato, M.; Oda, D. *J. Org. Chem.* **1986**, *51*, 4368-4375. (b) Barton, D. H. R. ; Motherwell, W. B. M.; Zard, S. Z. *Bull. Soc. Chim. Fr.(II)* **1983**, 61.

⁴ Bhattacharjya, A.; Mukhopadhyay, R.; Pakrachi, S. C. *Synthesis*, **1985**, 886-887.

COc1cc(ccc1OC(=O)c2ccccc2)CC(=C)C3=CC=CC=C3

Synthesis of β -nitro xanthates

To a solution vinyl nitro compound (X mmol) in glacial acetic acid ($2X$ mL) at 0°C under N_2 atmosphere, was added potassium *O*-ethyl xanthate ($4X$ mmol) portionwise. The reaction was stirred at room temperature until total consumption of the starting material. If the stirring became difficult because of precipitation of the product, then X mL of glacial acetic acid were added to the solution. The reaction was quenched by adding a saturated solution of citric acid ($4X$ mL).

Compound **2a**

Following the general procedure, to a solution of nitro compound **1a** (1.07 g, 4.84 mmol, 1.0 equiv) in acetic acid (9 mL) was added potassium *O*-ethyl xanthate (3.10 g, 19.36 mmol, 4.0 equiv) of at 0°C. The reaction was stirred for 1h. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **2a** (1.52 g, 92%) as a pale yellow oil, which was used directly in the next step without further purification. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 7.34-7.18 (m, 5H), 4.85-4.51 (m, 5H, OCH₂CH₃), 4.38 (m, 1H), 2.74 (ddd, *J* = 7.8, 10.1, 17.9 Hz, 1H), 2.67 (ddd, *J* = 7.1, 10.2, 17.9 Hz, 1H), 2.09-1.77 (m, 5H), 1.46 (t, *J* = 7.8 Hz). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) 212.5, 211.6, 141.4, 141.1, 128.4, 128.2, 126.0, 125.9, 78.2, 77.3, 70.8, 70.6, 68.9, 68.2, 44.6, 44.4, 39.2, 39.0, 38.6, 38.0, 31.8, 31.6, 13.6. IR (ν_{max}, cm⁻¹) (CCl₄) 3623, 3027, 2937, 1556, 1371, 1227, 1112, 1057, 908. MS (CI, NH₃) *m/z* [MNH₄]⁺=361, [MH]⁺=344.

Compound **2b**

Following general procedure, to a solution of the commercially available nitroolefin **1b** (8.55 g, 30.0 mmol, 1.0 equiv) in acetic acid (60mL) was added potassium *O*-ethyl xanthate (19.20g, 120 mmol, 4.0 equiv) at 0°C. The reaction was stirred for 1h. Precipitation (water) gave compound **2b** (10.6 g, 87%) as a white solid, which was used directly in the next step without further purification. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 7.44 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.93-6.84 (m, 3H), 5.37 (dd, *J* = 5.1, 10.4 Hz, 1H), 5.13 (s, 2H), 5.03 (dd, *J* = 5.1, 13 Hz, 1H), 4.79 (dd, *J* = 10.4, 13 Hz, 1H), 4.67 (q, *J* = 7.1 Hz, 2H), 3.57 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) 210.7, 150.2, 148.4, 136.4, 128.5, 127.9, 127.4, 126.8, 126.2, 113.9, 111.9, 77.6, 71.2, 70.5, 55.8, 50.0, 13.6. IR (ν_{max}, cm⁻¹) (CCl₄) 2957, 2933, 2836, 1558, 1517, 1370, 1263, 1230, 1142, 1110, 1050. MS (CI, NH₃) *m/z* [MNH₄]⁺=425, [MH]⁺=408, [MH-HSC(S)OEt]⁺=286, [MH-HNO₂-HSC(S)OEt]⁺=240.

Compound **2c**

Following the general procedure, to a solution of commercially available nitroolefin **1c** (5.06 g, 20.0 mmol, 1.0 equiv) in acetic acid (40 mL) was added potassium *O*-ethyl xanthate (12.80 g 80.0 mmol, 1.0 equiv) at 0°C. The

reaction was stirred for 2h. Recrystallization (petroleum ether-ethyl acetate) gave compound **2c** (6.30 g, 5/2 mixture of diastereoisomers, 84%) as white needles (mp 79-80°C; petroleum ether-ethyl acetate). **¹H NMR** (δ , ppm) (CDCl₃, 400 MHz) (major diastereoisomer) 6.49 (s, 2H), 5.39 (d, J = 8.8 Hz, 1H), 5.02 (dq, J = 6.7, 8.8 Hz, 1H), 4.65 (q, J = 7.1 Hz, 2H), 3.82 (s, 6H), 3.80 (s, 3H), 1.75 (d, J = 6.7 Hz, 3H), 1.45 (d, J = 8.8 Hz, 3H). **¹³C NMR** (δ , ppm) (CDCl₃, 100 MHz) (major diastereoisomer) 210.6, 153.5, 138.2, 131.8, 105.3, 86.5, 71.0, 60.9, 57.1, 57.1, 17.5, 13.8. **IR** ($\nu_{\max}$, cm⁻¹) (CCl₄) 2994, 2938, 2837, 1589, 1557, 1509, 1463, 1421, 1355, 1330, 1232, 1133, 1110, 1048, 1010. **MS** (CI, NH₃) m/z [MNH₄]⁺=393, [MH]⁺=376, [MH-HSC(S)OEt]⁺=254, [MH-NO₂-SC(S)OEt]⁺=209. **Analysis** Calcd for C₁₅H₂₁NO₆S₂ C(47.98), H(5.64), found C(47.93), H(5.68).

Compound **2d**

Following the general procedure, to a solution of nitroolefin **1d** (1.59 g, 5.0 mmol, 1.0 equiv) in acetic acid (10 mL) was added potassium *O*-ethyl xanthate (3.20 g, 20.0 mmol, 4.0 equiv) at 0°C. The reaction was stirred for 1h. Recrystallization (methanol) gave compound **2d** (1.19 g, only major isomer crystallized, 54%) as white crystals (mp 114-116; methanol). **¹H NMR** (δ , ppm) (CDCl₃, 400 MHz) (major diastereoisomer) 6.58 (s, 2H), 6.16 (bs, 1H), 5.52 (d, J = 6.0 Hz, 1H), 5.28 (d, J = 6.0 Hz, 1H), 4.62 (dq, J = 7.5, 10.7 Hz, 1H), 4.56 (dq, J = 7.5, 10.7 Hz, 1H), 3.85 (s, 6H), 3.80 (s, 3H), 2.19-2.09 (m, 4H), 1.69-1.54 (m, 4H), 1.37 (t, J = 7.5 Hz, 3H). **¹³C NMR** (δ , ppm) (CDCl₃, 100 MHz) (major diastereoisomer) 210.0, 153.0, 137.9, 134.9, 132.7, 130.1, 105.5, 96.4, 70.6, 60.7, 56.1, 53.54, 25.5, 23.5, 22.1, 21.4, 13.5. **IR** ($\nu_{\max}$, cm⁻¹) (CCl₄) 2938, 2836, 1590, 1556, 1508, 1463, 1422, 1229, 1133, 1110, 1048, 1010. **MS** (CI, NH₃) m/z [MH-NO₂-SC(S)OEt]⁺=275. **Analysis** Calcd for C₂₀H₂₇NO₆S₂ C(54.40), H(6.16), found C(54.31), H(6.09).

Compound **2e**

Following the general procedure, to a solution of nitroolefin **1e** (4.00 g, 10.0 mmol, 1.0 equiv) in acetic acid (20 mL) was added potassium *O*-ethyl xanthate (6.40 g, 40.0 mmol, 4.0 equiv) at 0°C. The reaction was stirred for 2h. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **2e** (4.18 g, 77/23 mixture of diastereoisomers, 80%) as white solid. **¹H NMR** (δ, ppm) (CDCl₃, 400 MHz) 7.66 (d, *J* = 8.5 Hz, 0.46H), 7.63 (d, *J* = 8.2 Hz, 1.54H), 7.46-7.43 (m, 4H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.62 (dd, *J* = 2.1, 8.1 Hz, 1H), 5.43 (d, *J* = 10.0 Hz, 0.77H), 5.34 (d, *J* = 6.5 Hz, 0.23H), 5.12 (s, 2H), 5.10-5.02 (m, 1H), 4.66 (adq, *J* = 2.0, 7.1 Hz, 1.54H), 4.58 (m, 0.46H), 3.86 (s, 2.31H), 3.81 (s, 0.69H), 3.45 (dd, *J* = 3.2, 14.7 Hz, 0.77H), 3.29 (dd, *J* = 10.4, 14.7 Hz, 0.77H), 3.27 (dd, *J* = 8.9, 14.0 Hz, 0.23H), 3.04 (dd, *J* = 5.7, 14.0 Hz, 0.23H), 1.43 (t, *J* = 7.1 Hz, 2.31H), 1.32 (t, *J* = 7.1 Hz, 0.69H). **¹³C NMR** (δ, ppm) (CDCl₃, 100 MHz) 209.0, 149.9, 147.9, 142.1, 141.4, 132.7, 129.2, 128.6, 128.0, 127.3, 121.0, 118.2, 114.3, 114.2, 112.8, 112.3, 92.6, 92.5, 71.5, 71.3, 71.1, 56.1, 55.6, 55.1, 38.1, 37.8, 13.8. **IR** (ν_{max}, cm⁻¹) (CCl₄) 2930, 2358, 1559, 1515, 1463, 1366, 1269, 1236, 1142, 1111, 1045. **MS** (CI, NH₃) *m/z* [MNH₄-SC(S)OEt]⁺=419, [MNH₄-NO₂-SC(S)OEt]⁺=373.

Compound **2f**

Following general procedure, to a solution of nitroolefin **1f** (0.508 g, 1.50 mmol, 1.0 equiv) in acetic acid (3 mL) was added potassium *O*-ethyl xanthate (0.960 g, 6.0 mmol, 4.0 equiv) at 0°C. The reaction was stirred for 1h. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **2f** (588 mg, 64/36 mixture of diastereoisomers 85%) as a white powder (mp 80-82; petroleum ether-dichloromethane). **¹H NMR** (δ, ppm) (CDCl₃, 300 MHz) 7.46-7.29 (m, 5H), 6.82 (d, *J* = 8.1Hz, 1H), 6.73 (d, *J* = 8.1Hz, 1H), 6.71 (s, 1H), 5.12 (s, 2H), 5.08 (m, 0.36H), 5.00 (ddd, *J* = 3.3, 6.6, 11.9Hz, 0.64H), 4.67 (q, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 3.83 (m, 0.36H), 3.66 (dd, *J* = 6.6, 10.4 Hz, 0.64H), 3.40 (dd, *J* = 11.9, 14.7 Hz, 0.36H), 3.36 (dd, *J* = 11.9, 14.7 Hz, 0.64H), 3.20 (dd, *J* = 11.9, 3.2 Hz, 0.64H), 3.12 (dd, *J* = 3.2, 14.7 Hz, 0.36H), 1.45 (t, *J* = 7.0 Hz, 1.92H), 1.40 (t, *J* = 7.0 Hz, 1.08H), 1.18-1.02 (m, 1H), 1.44-0.32 (m, 4H). **¹³C NMR** (δ, ppm) (CDCl₃, 75 MHz) 213.2, 149.9, 149.1, 137.8, 129.5, 128.8, 128.7, 128.3, 122.6, 122.5, 115.7, 115.6, 110.8, 94.0, 92.9, 72.0, 71.7, 58.6, 57.5, 56.9, 38.1, 37.0, 14.7, 14.0, 13.5, 9.7, 7.7, 5.1, 4.9. **IR** (ν_{max}, cm⁻¹) (CCl₄) 3003, 2905, 2835, 1555, 1516, 1442, 1365, 1262, 1229, 1141, 1111, 1050, 1028. **MS** (CI, NH₃) *m/z* [MNH₄]⁺=479, [MH]⁺=462. **Analysis** Calcd for C₂₃H₂₇NO₅S₂ C(59.85), H(5.90), found C(59.81), H(5.94).

General procedure (from adducts derived from the Henry reaction)

To a solution of the acetylated Henry adduct (X mmol) in a 9/1 mixture of acetonitrile and acetic acid ($2X$ mL) was added potassium *O*-ethyl xanthate ($1.2X$ mmol) portionwise, at 0°C under N_2 atmosphere. The reaction was stirred at room temperature until complete consumption of the starting material (TLC). The reaction was then quenched with a saturated solution of citric acid ($2X$ mL).

The reaction mixture was extracted with dichloromethane ($3 \times 8X$ mL), and the organic layer was washed with water ($4X$ mL), saturated solution of NaHCO_3 ($4X$ mL) and brine ($2X$ mL). The organic layer was dried over MgSO_4 , concentrated *in vacuo* and purified by flash chromatography.

Compound **2g**

To a solution of TBAF (630 mg, 2.00 mmol, 0.4 equiv) in THF (5 mL) was added 2-(3'-benzyloxy-4'-methoxyphenyl)-1-nitroethane⁴ (1.435 g, 5.00 mmol, 1.0 equiv) at 0°C . Isobutyraldehyde (0.410 mL, 4.50 mmol, 0.9 equiv) and triethylamine (0.627 mL, 4.50 mmol, 0.9 equiv) were sequentially added to the bright red solution. To this solution was added a solution of *tert*-butyldimethylsilyl chloride (1.13 g, 7.50 mmol, 1.5 equiv) in THF (5 mL) at 0°C . The reaction mixture was allowed to warm up to room temperature for 30 min. The suspension was filtrated and the filtrate diluted with water (20 mL) and a 3/1 mixture of petroleum ether and ether (100 mL). The organic layer was washed with water (20 mL). The solvent was removed *in vacuo* and the syrupy residue directly used in the next step.

The residue was dissolved in dichloromethane (10 mL) and acetic anhydride (0.942 mL, 10.0 mmol, 2.0 equiv) and DMAP (30 mg) were added sequentially at room temperature. After stirring for 2 h at room temperature the reaction was quenched with water (10 mL). The reaction mixture was extracted with dichloromethane (2×10 mL) and the combined organic layers were washed with water (10 mL) and brine (10 mL). The solvent was evaporated and the crude acetylated Henry adduct was used in the next step.

Following the general procedure, to a solution of this compound in acetonitrile (9 mL) and acetic acid (1 mL) was added potassium *O*-ethyl xanthate (0.720 g, 6.0 mmol, 1.2 equiv) at 0°C . The reaction was stirred overnight. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 97/3) gave compound **2g** (927 mg, 68/32 mixture of diastereoisomers, 40%) as a pale yellow oil, which was used directly in the next step without further purification. ^1H NMR (δ , ppm) (CDCl_3 , 400 MHz) 7.43-7.27 (m, 5H), 6.79 (d, J = 8.8 Hz, 1H), 6.68-6.60 (m, 2H), 5.11 (s, 2H), 4.82 (dt, J = 2.9, 11.0 Hz, 0.68H), 4.71 (q, J = 7.1 Hz, 2H), 4.63 (ddd, J = 7.1, 14.1, 19.2 Hz, 0.32H), 4.50 (dd, J = 3.1, 10.5 Hz, 0.68H), 4.23 (dd, J = 5.1, 6.3 Hz, 0.32H), 3.87 (s, 3H), 3.39-3.34 (m, 1H), 3.26-3.17 (m, 1H), 2.52 (m, 0.32H), 2.00 (m, 0.32H), 1.48 (t, J = 7.1 Hz, 2.04H), 1.40 (t, J = 7.1 Hz, 0.96H), 1.14 (d, J = 6.6 Hz, 0.96H), 1.08 (d, J = 6.7 Hz, 2.04H), 1.05 (d, J = 6.6 Hz, 0.96H), 0.97 (d, J = 6.7 Hz, 0.96H). ^{13}C NMR (δ , ppm) (CDCl_3 , 100 MHz) 212.2, 149.8, 147.6, 143.3, 128.6, 128.4,

127.9, 127.3, 120.9, 114.2, 112.4, 92.6, 90.6, 71.2, 71.1, 70.9, 59.4, 58.3, 56.1, 38.3, 37.6, 29.2, 28.3, 20.6, 19.6, 13.8. **IR** (ν_{max} , cm^{-1}) (CCl_4) 2964, 2358, 1550, 1515, 1463, 1368, 1335, 1264, 1228, 1142, 1111, 1046. **MS** (Cl^- , NH_3) m/z $[\text{MNH}_4]^+ = 481$, $[\text{MNH}_4\text{-HSC(S)OEt}]^+ = 359$.

Aldehyde

2-(3'-benzyloxy-4'-methoxyphenyl)-1-nitroethane⁴ (5.30 g, 18.6 mmol, 1.0 equiv) was added to solution of sodium methoxide (302 mg, 5.60 mmol, 0.3 equiv) in dry methanol (20 mL) at room temperature. A solution of freshly distilled acrolein (1.38 mL, 20.4 mmol, 1.1 equiv) in methanol (20 mL) was slowly added (over 20 minutes) to the solution at -55°C . The reaction mixture was allowed to warm up to -10°C over 2h. It was concentrated *in vacuo* and rapidly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) to give aldehyde (1.46 g, 23%) as colorless solid. This compound was used directly in the next step. **¹H NMR** (δ , ppm) (CDCl_3 , 400 MHz) 9.76 (s, 1H), 7.43 (d, $J = 6.4$ Hz, 2H), 7.38 (t, $J = 6.4$ Hz, 2H), 7.32 (t, $J = 6.4$ Hz, 1H), 6.83 (d, $J = 6.4$ Hz, 1H), 6.73 (d, $J = 2.0$ Hz, 1H), 6.62 (dd, $J = 2.0, 6.4$ Hz, 1H), 5.12 (s, 2H), 4.73 (dddd, $J = 7.3, 7.3, 7.3, 7.3$ Hz, 1H), 3.88 (s, 3H), 3.21 (dd, $J = 7.3, 16.8$ Hz, 1H), 3.04 (dd, $J = 7.3, 16.8$ Hz, 1H), 2.59 (m, 2H), 2.19 (q, $J = 7.3$ Hz, 2H). **¹³C NMR** (δ , ppm) (CDCl_3 , 100 MHz) 199.7, 149.8, 147.6, 136.9, 128.6, 128.1, 127.9, 127.3, 121.1, 114.1, 112.4, 88.9, 71.0, 56.1, 39.8, 39.7, 25.5.

Compound 2h

To a solution of the aldehyde (961 mg, 2.80 mmol, 1.0 equiv) in nitromethane (10 mL), was added triethylamine (0.975 mL, 7.0 mmol, 2.5 equiv) at room temperature. After stirring for 1h, the reaction mixture was concentrated under reduced pressure. The crude residue was diluted with dichloromethane (6 mL) and acetic anhydride (0.565 mL, 6.0 mmol, 2.1 equiv) and DMAP (30 mg) were added sequentially at room temperature. After stirring for 2h, the reaction was quenched with water (10 mL). The reaction mixture was extracted with dichloromethane (2x10 mL). The organic layers were combined and washed with water (10 mL) and brine (10 mL). The solvent was evaporated and the crude acetylated Henry adduct was used in the next step.

Following general procedure, to a solution of this compound in acetonitrile (4.5 mL) and acetic acid (0.5 mL) was added potassium *O*-ethyl xanthate (0.530 g, 3.36 mmol, 1.2 equiv) at 0°C . The reaction was stirred overnight. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 8/2) gave

compound **2h** (928mg, 1/1 mixture of diastereoisomers, 69%) as a pale brown oil, which was used directly in the next step without further purification. **¹H NMR** (δ , ppm) (CDCl_3 , 400 MHz) 7.43 (d, $J = 7.0$ Hz, 2H), 7.37 (t, $J = 7.0$ Hz, 2H), 7.31 (t, $J = 7.0$ Hz, 2H), 6.81 (d, $J = 8.1$ Hz, 1H), 6.66 (bs, 1H), 6.62 (bd, $J = 8.1$ Hz, 1H), 5.13 (s, 2H), 4.77-4.65 (m, 4H), 4.55 (dd, $J = 6.0, 7.9$ Hz, 1H), 4.52 (dd, $J = 6.0, 7.9$ Hz, 1H), 4.29 (m, 1H), 3.88 (s, 3H), 3.22 (dd, $J = 5.9, 8.0$ Hz, 0.5H), 3.20 (dd, $J = 5.9, 8.0$ Hz, 0.5H), 2.98 (dd, $J = 5.8, 11.4$ Hz, 0.5H), 2.96 (dd, $J = 5.8, 11.4$ Hz, 0.5H), 2.43-1.68 (m, 4H), 1.44 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (δ , ppm) (CDCl_3 , 100 MHz) 211.1, 149.6, 147.4, 136.8, 128.4, 127.8, 127.1, 120.8, 113.8, 112.1, 89.1, 88.9, 77.6, 77.4, 71.0, 70.9, 70.8, 55.9, 46.5, 46.4, 39.5, 39.3, 30.0, 29.6, 27.3, 27.1, 13.6. **IR** (ν_{max} , cm^{-1}) (CCl_4) 2933, 1591, 1556, 1515, 1371, 1264, 1231, 1111, 1051, 908.

Compound **2i**

To a solution of β -nitro xanthate **2e** (1.66 g, 3.06 mmol, 1.0 equiv) and formaldehyde (0.848 mL, 12.2 mmol, 4.0 equiv, 37% solution in water) in THF (6 mL), were sequentially added potassium *O*-ethyl xanthate (0.24 g, 1.53 mmol, 0.5 equiv) and acetic acid (0.14 mL, 1.53 mmol, 0.5 equiv). The solution was stirred for 5 days and quenched with a saturated solution of citric acid (10 mL). The reaction mixture was extracted with dichloromethane (3x10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL). The organic layer was dried over MgSO_4 , concentrated *in vacuo* and the crude residue purified by flash chromatography on silica gel (petroleum ether/ethyl acetate : 7/3) to give compound **2i** (675 mg, 55/45 mixture of diastereoisomers, 40%) as a white solid, which was used directly in the next step without further purification. **¹H NMR** (δ , ppm) (CDCl_3 , 400 MHz) 7.67-7.56 (m, 4H), 7.42-7.27 (m, 4H), 6.78-6.53 (m, 3H), 5.84 (s, 0.90H), 5.67 (s, 1.10H), 5.11 (s, 2H), 4.65-4.58 (m, 2H), 3.88 (m, 1.10), 3.82 (s, 1.35H), 3.81 (s, 1.65H), 3.65 (d, $J = 14.2$ Hz, 0.55H), 3.62 (m, 0.90), 3.41 (d, $J = 14.3$ Hz, 0.45H), 3.31 (d, $J = 14.3$ Hz, 0.45H), 2.94 (d, $J = 14.2$ Hz, 0.55H), 2.43 (bs, 0.45H), 2.40 (bs, 0.55H), 1.38 (t, $J = 7.1$ Hz, 1.35H), 1.37 (t, $J = 7.1$ Hz, 1.65H). **¹³C NMR** (δ , ppm) (CDCl_3 , 100 MHz) 211.2, 149.6, 147.9, 141.6, 141.5, 132.4, 132.2, 131.1, 128.6, 128.0, 127.3, 122.4, 118.4, 113.8, 113.5, 113.1, 112.4, 96.0, 89.9, 71.5, 71.1, 70.9, 63.5, 60.1, 58.4, 58.0, 56.0, 40.8, 39.9, 13.8. **IR** (ν_{max} , cm^{-1}) (CCl_4) 3605, 2936, 2231, 1545, 1515, 1463, 1364, 1264, 1232, 1146, 1111, 1047. **MS** (CI, NH_3) m/z [$\text{MNH}_4\text{-SC(S)OEt-CH}_2\text{OH}$] $^+$ =419.

Compound **2j**

To a solution of commercially available β -nitrostyrene (2.85 g, 10.0 mmol, 1.0 equiv) and formaldehyde (3.7 mL, 50.0 mmol, 5.0 equiv, 37% solution in water) in THF (20 mL), were sequentially added potassium *O*-ethyl xanthate (2.40g, 15.0 mmol, 1.5 equiv) and acetic acid (0.85 mL, 15.0 mmol, 1.5 equiv) at room temperature. The solution was stirred for 5 days and quenched with a saturated solution of citric acid (20 mL). The reaction mixture was extracted with dichloromethane (3x20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL). The solvents were removed under reduced pressure. The crude residue was dissolved in dichloromethane (20 mL) and to that solution was added acetic anhydride (3.77 mL, 40 mmol, 4.0 equiv) and DMAP (50 mg). After stirring for 2h at room temperature, the reaction was quenched with water (20 mL). The reaction mixture was extracted with dichloromethane (2x20 mL). The organic layers were combined, washed with water (20 mL), brine (20 mL) and dried over MgSO_4 . The solvent was evaporated and the crude diacetylated adduct was purified by flash chromatography. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 7/3) gave compound **2j** (2.58 g, 47%) as a pale orange oil, which was used directly in the next step without further purification. $^1\text{H NMR}$ (δ , ppm) (CDCl_3 , 400 MHz) 7.41 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.4 Hz, 2H), 7.29 (t, J = 8.4 Hz, 1H), 6.80 (bs, 2H), 6.73 (s, 1H), 5.66 (s, 1H), 5.13 (d, J = 12.4 Hz, 1H), 5.11 (d, J = 12.4 Hz, 1H), 5.13 (d, J = 12.0 Hz, 1H), 4.60 (dq, J = 7.1, 10.6 Hz, 1H), 4.56 (dq, J = 7.1, 10.6 Hz, 1H), 4.47 (s, 2H), 4.34 (d, J = 12.0 Hz, 1H), 3.86 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (δ , ppm) (CDCl_3 , 100 MHz) 211.7, 139.4, 150.1, 147.9, 136.5, 128.6, 127.9, 127.2, 126.4, 122.3, 114.8, 111.3, 92.1, 71.2, 71.0, 62.2, 60.9, 55.8, 20.7, 20.6, 13.6. **IR** (ν_{max} , cm^{-1}) (CCl_4) 2957, 1759, 1555, 1516, 1367, 1226, 1144, 1111, 1046, 908. **MS** (CI, NH_3) m/z $[\text{MNH}_4]^+$ =569.

Radical elimination

General Procedure

To a solution of β -nitro xanthate (X mmol) in refluxing degassed 1,2-dichloroethane ($5X$ mL) was added dilauroyl peroxide (DLP; $1.5X$ mmol) under N_2 atmosphere. The reaction was stirred at reflux for 90min and DLP ($1.5X$ mmol) was added once again. After a further 90 min at reflux, the reaction was cooled to room temperature, concentrated under reduced pressure and the crude residue purified by flash chromatography.

Compound **3a**

According to the above general procedure, to a solution of compound **2a** (490 mg, 1.42 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (7 mL) was added DLP (2x852 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **3a** (155 mg, 62%) as a colorless oil.⁵

Compound **3c**

According to the general procedure, to a solution of compound **2c** (375 mg, 1.00 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (5 mL) was added DLP (2x597 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **3c** (156 mg, *E/Z* 10:1; 75%) as a colorless oil.⁶

Compound **3d**

According to the general procedure, to a solution of compound **2d** (441 mg, 1.00 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (5 mL) was added DLP (2x597 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 95/5) gave compound **3d** (145 mg, 53%) as a colorless oil. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 6.68 (d, *J* = 16.1 Hz, 1H), 6.37 (s, *J* = 16.1 Hz, 1H), 5.91 (bt, *J* = 4Hz, 1H), 3.88 (s, 6H), 3.84 (s, 3H), 2.31-2.17 (m, 4H), 1.77-1.49 (m, 4H). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) 153.3, 140.4, 133.9, 132.2, 130.9, 124.6, 103.2, 61.0, 56.1, 29.6, 26.2, 24.6, 22.5. IR (ν_{max}, cm⁻¹) (CCl₄) 2936, 1697, 1582, 1506, 1463, 1417, 1331, 1239, 1132, 1010. MS (CI, NH₃) *m/z* [MNH₄]⁺=292.

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⁶ Büchi, G.; Chu, P.-S. *J. Am. Chem. Soc.* **1981**, *103*, 2718-2721.

Compound **3e**

According to the general procedure, to a solution of compound **2e** (522 mg, 1.00 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (5 mL) was added DLP (2x597 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **3e** (266 mg, 75%) as white needles (mp 99-100°C; ethyl acetate-petroleum ether). **¹H NMR** (δ , ppm) (CDCl₃, 400 MHz) 7.57 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 1.9 Hz, 1H), 6.72 (dd, J = 1.9, 8.1 Hz, 1H), 6.52 (dd, J = 6.3, 15.8 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 5.16 (s, 2H), 3.90 (s, 3H), 3.52 (d, J = 6.3 Hz). **¹³C NMR** (δ , ppm) (CDCl₃, 100 MHz) 149.7, 146.9, 141.9, 137.1, 133.8, 132.3, 128.5, 127.8, 127.2, 126.6, 120.6, 119.0, 114.3, 112.5, 111.2, 71.2, 56.0, 39.9. **IR** (ν_{max} , cm⁻¹) (CCl₄) 2927, 2228, 1741, 1648, 1605, 1513, 1463, 1265, 1231, 1140, 1038, 968. **MS** (CI, NH₃) m/z [[MNH₄]⁺=373, [MH]⁺=356. **Analysis** Calcd for C₂₄H₂₁NO₂ C(81.10), H(5.96), found C(80.85), H(5.98).

Compound **3f**

According to method A, to a solution of compound **2f** (580 mg, 1.25 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (6.0 mL) was added DLP (2x750 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **3f** (231 mg, 3/1 mixture of *E/Z* isomers 63%) as a white solid. **¹H NMR** (δ , ppm) (CDCl₃, 400 MHz) 7.46 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.75 (s, 1H), 6.74 (d, J = 7.7 Hz, 1H), 5.58 (dt, J = 6.8, 15.1 Hz, 0.75H), 5.44 (dt, J = 7.6, 10.3 Hz, 0.25H), 5.14 (s, 2H), 5.00 (dd, J = 8.6, 15.1 Hz, 0.75H), 4.86 (dd, J = 10.3, 10.3 Hz, 0.25H), 3.87 (s, 3H), 3.43 (d, J = 7.6 Hz, 0.5H), 3.21 (d, J = 6.8 Hz, 1.5H), 1.63 (m, 0.25H), 1.36 (m, 0.75H), 0.77 (m, 0.5H), 0.66 (m, 1.5H), 0.38 (m, 0.5H), 0.32 (m, 1.5H). **¹³C NMR** (δ , ppm) (CDCl₃, 100 MHz) 148.1, 148.0, 137.4, 135.2, 134.9, 133.9, 133.6, 128.5, 127.8, 127.4, 126.8, 121.0, 120.8, 114.8, 114.6, 112.0, 71.0, 56.2, 38.3, 33.3, 13.5, 9.7, 6.5, 6.0. **IR** (ν_{max} , cm⁻¹) (CCl₄) 3005, 2931, 2906, 2833, 1698, 1605, 1589, 1513, 1463, 1441, 1309, 1263, 1231, 1189, 1137, 1025, 961. **MS** (CI, NH₃) m/z [MNH₄]⁺=312. **Analysis** Calcd for C₂₀H₂₂O₂ C(81.60), H(7.53), found C(81.16), H(7.45).

Compound **3g**

According to the general procedure, to a solution of compound **2g** (462 mg, 1.00 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (5 mL) was added DLP (2x597 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 95/5) gave compound **3g** (168mg, 7/1 mixture of *E/Z* isomers 57%) as a colorless oil. **¹H NMR** (δ , ppm) (CDCl₃, 300 MHz) 7.45 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 1H), 6.65 (dd, *J* = 1.9, 8.1 Hz, 1H), 5.54-5.49 (m, 2H), 5.14 (s, 2H), 3.89 (s, 3H), 3.35 (d, *J* = 7.0 Hz, 0.25H), 3.26 (d, *J* = 4.2 Hz, 1.75H), 2.72 (m, 0.12H), 2.31 (m, 0.88H), 1.01 (d, *J* = 6.8 Hz). **¹³C NMR** (δ , ppm) (CDCl₃, 75 MHz) 149.6, 146.4, 139.2, 137.5, 134.4, 128.6, 127.8, 127.3, 125.9, 120.3, 114.3, 112.4, 71.2, 56.0, 39.6, 31.0, 22.8. **IR** (ν_{max} , cm⁻¹) (CCl₄) 2926, 2870, 1741, 1702, 1513, 1464, 963. **MS** (CI, NH₃) *m/z* [MH-HCH₂-phenyl]⁺=206.

Compound **3h**

According to method A, to a solution of compound **2h** (508 mg, 1.0 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (5.0 mL) was added DLP (597 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 9/1) gave compound **3h** (230 mg, 54%) as a white solid. **¹H NMR** (δ , ppm) (CDCl₃, 400 MHz) 7.43 (t, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 1.9 Hz, 1H), 6.63 (dd, *J* = 1.9, 8.1 Hz, 1H), 5.72 (ddt, *J* = 6.4, 10.2, 17.0 Hz, 1H), 5.13 (s, 2H), 5.05 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 4.69 (dddd, *J* = 1.9, 5.8, 8.5, 8.5 Hz, 1H), 3.87 (s, 3H), 3.19 (dd, *J* = 8.5, 14.2 Hz), 2.97 (dd, *J* = 5.8, 14.2 Hz), 2.16-2.06 (m, 3H), 1.82 (m, 1H). **¹³C NMR** (δ , ppm) (CDCl₃, 75 MHz) 149.8, 147.6, 137.1, 135.9, 128.6, 128.5, 127.9, 127.3, 121.1, 116.7, 114.2, 112.5, 89.3, 71.0, 56.1, 39.8, 32.4, 29.9. **IR** (ν_{max} , cm⁻¹) (CCl₄) 2927, 2854, 1552, 1514, 1464, 1377, 1266, 1234, 1142, 1038. **MS** (CI, NH₃) *m/z* [MNH₄]⁺=359. **Analysis** Calcd for C₂₀H₂₃NO₄ C(70.36), H(6.79), found C(70.18), H(6.93).

Compound **3i**

According to the general procedure, to a solution of compound **2i** (238 mg, 0.42 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (2.0 mL) was added DLP (2x250 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 7/3) gave compound **3i** (136 mg, 4/1 mixture of *Z/E* isomers 82%) as a white solid. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) (4/1 mixture of *Z/E* isomers) 7.62 (d, *J* = 8.3 Hz, 1.6H), 7.62 (d, *J* = 8.3 Hz, 1.6H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 1.6H), 7.38 (d, *J* = 8.3 Hz, 1.6H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 0.8H), 6.82 (d, *J* = 1.9 Hz, 0.8H), 6.81 (d, *J* = 8.1 Hz, 0.2H), 6.80 (s, 0.2H), 6.76 (dd, *J* = 1.9, 8.1 Hz, 0.8H), 6.68 (d, *J* = 1.9 Hz, 0.2H), 6.64 (dd, *J* = 1.9, 8.1 Hz, 0.2H), 6.47 (s, 0.8H), 5.15 (s, 1.6H), 5.14 (s, 0.4H), 4.19 (s, 1.6H), 4.18 (s, 0.4H), 3.89 (s, 2.4H), 3.84 (s, 0.6H), 3.60 (bs). ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) (*Z* isomer only) 7.62 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 6.76 (dd, *J* = 1.9, 8.1 Hz, 1H), 6.47 (s, 1H), 5.15 (s, 2H), 4.19 (s, 2H), 3.89 (s, 3H), 3.60 (s). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) (*Z* isomer only) 149.7, 146.9, 141.9, 137.1, 133.8, 132.3, 128.5, 127.8, 127.2, 126.6, 120.6, 119.0, 114.3, 112.5, 111.2, 71.2, 56.0, 39.9. IR (ν_{max}, cm⁻¹) (CCl₄) 3632, 2930, 2229, 1605, 1512, 1463, 1417, 1379, 1262, 1228, 1140, 1024, 908. MS (CI, NH₃) *m/z* [MNH₄]⁺=401, [MH]⁺=386. **Analysis** Calcd for C₂₅H₂₃NO₃ C(77.90), H(6.01), found C(78.15), H(6.21).

Compound **3j**

According to method A, to a solution of compound **2j** (370 mg, 0.67 mmol, 1.0 equiv) in refluxing degassed 1,2-dichloroethane (3.3 mL) was added DLP (2x400 mg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate : 8/2) gave compound **3j** (185 mg, 72%) as a colorless oil. ¹H NMR (δ, ppm) (CDCl₃, 400 MHz) 7.43 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.89-6.83 (m, 3H), 6.73 (s, 1H), 5.14 (s, 2H), 4.74 (s, 3H), 4.70 (s, 3H), 3.89 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H). ¹³C NMR (δ, ppm) (CDCl₃, 100 MHz) 170.1, 149.4, 147.7, 136.8, 134.5, 129.4, 128.5, 127.9, 127.2, 122.2, 114.4, 114.4, 111.4, 70.8, 66.7, 60.7, 55.9, 21.0, 20.9. IR (ν_{max}, cm⁻¹) (CCl₄) 3033, 2931, 2836, 1743, 1602, 1580, 1514, 1368, 1232, 1140, 1025, 973. MS (CI, NH₃) *m/z* [MNH₄]⁺=402, 326[MH-HOAc]⁺, [MH-2x(HOAc)]⁺=266. **Analysis** Calcd for C₂₂H₂₄O₆ C(68.74), H(6.29), found C(68.55), H(6.37).