

Supporting Information

Vitamin B1-Catalyzed Aerobic Oxidative Esterification of Aromatic Aldehydes with Alcohols

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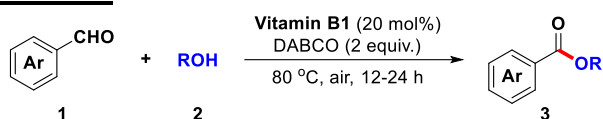
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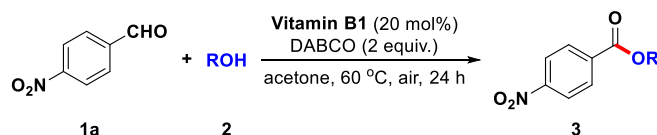
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air atmosphere using undistilled solvent. Melting points were recorded on an Electrothermal digital melting point apparatus. ^1H , ^{19}F , and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance or Joel 300 or 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedure of Vitamin B1-catalyzed aerobic oxidative esterification for the synthesis of products 3

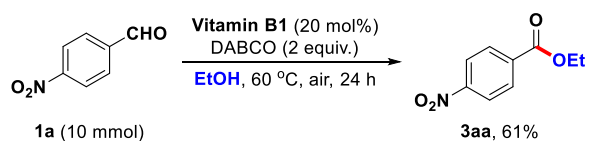


Method 1: A solution of aldehyde (1 mmol), vitamin B1 (60.2 mg, 0.2 mmol), and triethylenediamine (DABCO, 224.3 mg, 2 mmol) in alcohol (2 mL) was stirred at 80 °C under air for 12-24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 2/1) as eluent to afford the pure products 3.



Method 2: A solution of 4-nitrobenzaldehyde (453.4 mg, 3 mmol), alcohol (1 mmol), vitamin B1 (60.2 mg, 0.2 mmol), and triethylenediamine (DABCO, 224.3 mg, 2 mmol) in acetone (2 mL) was stirred at 60 °C under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 2/1) as eluent to afford the pure products 3.

General procedure for the scale-up synthesis of product 3aa

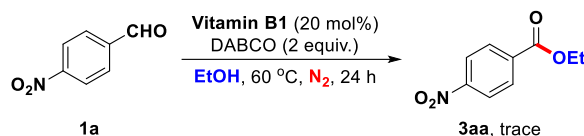


A solution of 4-nitrobenzaldehyde (1.51 g, 10 mmol), vitamin B1 (601.6 mg, 2 mmol), and triethylenediamine (DABCO, 2.24 g, 20 mmol) in EtOH (20 mL) was stirred at 80 °C under air for

24 h. The reaction solvent was removed under reduced pressure, then the reaction mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 2/1) as eluent to afford the pure products **3aa** (1.19 g, 61% yield).

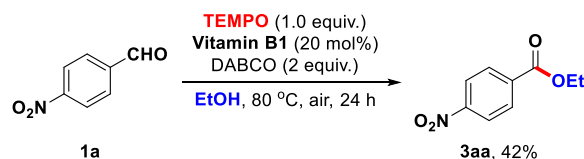
Mechanistic studies

1) Under N_2 atmosphere



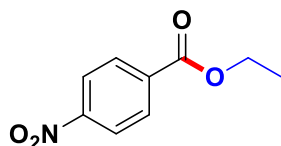
A solution of 4-nitrobenzaldehyde (151.1 mg, 1 mmol), vitamin B1 (60.2 mg, 0.2 mmol), and triethylenediamine (DABCO, 224.3 mg, 2 mmol) in EtOH (2 mL) was stirred at 80 °C under N_2 for 24 h. **Only trace amounts of desired products 3aa were observed. This result suggested that O_2 is important for the desired esterification.**

2) Radical trapping experiment



A solution of 4-nitrobenzaldehyde (151.1 mg, 1 mmol), vitamin B1 (60.2 mg, 0.2 mmol), triethylenediamine (DABCO, 224.3 mg, 2 mmol), and 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 156.3 mg, 1 mmol) in EtOH (2 mL) was stirred at 80 °C under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 20/1) as eluent to afford the pure product **3aa** (82.0 mg, 42% yield). **This result suggested that radical intermediate was not involved in the reaction.**

Characterization data for products

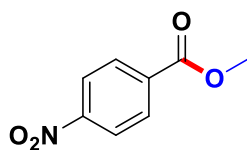


Ethyl 4-nitrobenzoate (3aa)^[1]: Yield = 65% (126.9 mg). Orange solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.28 (d, J = 8.5 Hz, 2H), 8.21 (d, J = 8.6 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 164.6, 150.4, 135.8, 130.6, 123.4, 61.9, 14.2 ppm.

HRMS m/z: calcd for C₉H₁₀NO₄ [M+H]⁺ 196.0604, found: 196.0610.

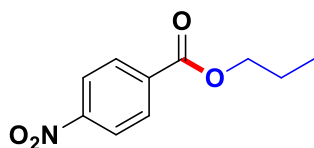


Methyl 4-nitrobenzoate (3ab)^[1]: Yield = 63% (114.1 mg). Orange solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.32 – 8.26 (m, 2H), 8.24 – 8.17 (m, 2H), 3.97 (s, 3H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 165.1, 150.5, 135.4, 130.7, 123.5, 52.8 ppm.

HRMS m/z: calcd for C₈H₈NO₄ [M+H]⁺ 182.0448, found: 182.0453.

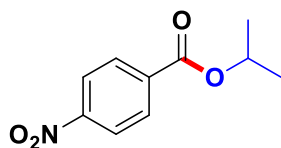


Propyl 4-nitrobenzoate (3ac)^[2]: Yield = 52% (108.8 mg). Orange solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.32 – 8.25 (m, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 4.33 (t, *J* = 6.7 Hz, 2H), 1.82 (h, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 164.7, 150.4, 135.8, 130.6, 123.5, 67.4, 22.0, 10.4 ppm.

HRMS m/z: calcd for C₁₀H₁₂NO₄ [M+H]⁺ 210.0761, found: 210.0766.

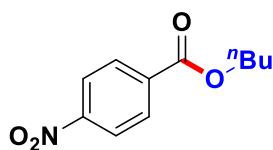


Isopropyl 4-nitrobenzoate (3ad)^[3]: Yield = 53% (110.9 mg). Orange solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.27 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 2H), 5.28 (hept, *J* = 6.3 Hz, 1H), 1.40 (d, *J* = 6.3 Hz, 6H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 164.1, 150.4, 136.2, 130.6, 123.4, 69.7, 21.8 ppm.

HRMS m/z: calcd for C₁₀H₁₂NO₄ [M+H]⁺ 210.0761, found: 210.0765.

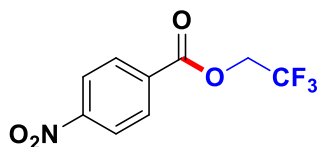


Butyl 4-nitrobenzoate (3ae)^[2]: Yield = 59% (131.7 mg). Orange solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.6 Hz, 2H), 4.38 (t, *J* = 6.6 Hz, 2H), 1.78 (p, *J* = 6.9 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 164.7, 150.4, 135.8, 130.6, 123.5, 65.8, 30.6, 19.2, 13.7 ppm.

HRMS m/z: calcd for C₁₁H₁₄NO₄ [M+H]⁺ 224.0917, found: 224.0923.



2,2,2-Trifluoroethyl 4-nitrobenzoate (3af)^[4]: Yield = 18% (44.8 mg). Light orange solid.

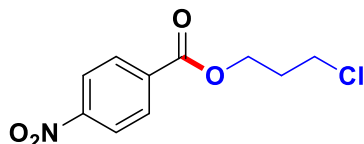
¹H NMR (400 MHz, Chloroform-*d*): δ 8.36 – 8.32 (m, 2H), 8.29 – 8.25 (m, 2H), 4.77 (q, *J* = 8.3

Hz, 2H) ppm.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -73.45 (t, J = 8.2 Hz, 3F).

¹³C NMR (101 MHz, Chloroform-*d*): δ 163.1, 151.0, 133.6, 131.2, 123.8, 122.8 (q, J = 275.4 Hz), 61.3 (q, J = 36.7 Hz) ppm.

HRMS m/z : calcd for C₉H₇F₃NO₄ [M+H]⁺ 250.0322, found: 250.0327.

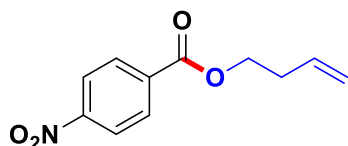


3-Chloropropyl 4-nitrobenzoate (3ag)^[5]: Yield = 59% (143.7 mg). Light yellow oil.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.33 – 8.25 (m, 2H), 8.23 – 8.17 (m, 2H), 4.54 (t, J = 6.1 Hz, 2H), 3.70 (t, J = 6.3 Hz, 2H), 2.27 (p, J = 6.2 Hz, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.5, 150.6, 135.3, 130.7, 123.6, 62.7, 41.0, 31.4 ppm.

HRMS m/z : calcd for C₁₀H₁₁ClNO₄ [M+H]⁺ 244.0371, found: 244.0377.

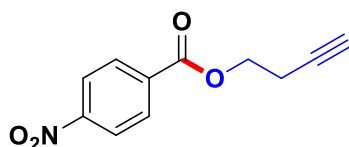


But-3-en-1-yl 4-nitrobenzoate (3ah)^[6]: Yield = 45% (99.5 mg). Orange oil.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.27 – 8.21 (m, 2H), 8.19 – 8.13 (m, 2H), 5.89 – 5.76 (m, 1H), 5.20 – 5.04 (m, 2H), 4.39 (t, J = 6.6 Hz, 2H), 2.56 – 2.46 (m, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.5, 150.4, 135.6, 133.6, 130.6, 123.4, 117.6, 64.7, 32.9 ppm.

HRMS m/z : calcd for C₁₁H₁₂NO₄ [M+H]⁺ 222.0761, found: 222.0766.

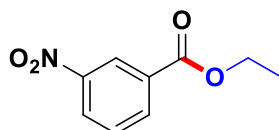


But-3-yn-1-yl 4-nitrobenzoate (3ai)^[7]: Yield = 44% (96.4 mg). Orange solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.30 – 8.25 (m, 2H), 8.24 – 8.18 (m, 2H), 4.50 – 4.40 (m, 2H), 2.73 – 2.65 (m, 2H), 2.04 (t, J = 2.7 Hz, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.3, 150.5, 135.2, 130.7, 123.5, 79.6, 70.3, 63.3, 18.9 ppm.

HRMS m/z : calcd for C₁₁H₁₀NO₄ [M+H]⁺ 220.0604, found: 220.0611.

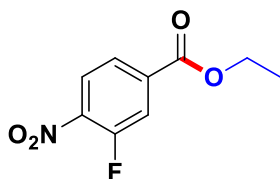


Ethyl 3-nitrobenzoate (3ba)^[8]: Yield = 50% (97.6 mg). Light white solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.87 – 8.77 (m, 1H), 8.43 – 8.29 (m, 2H), 7.67 – 7.59 (m, 1H), 4.48 – 4.37 (m, 2H), 1.45 – 1.38 (m, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.4, 148.2, 135.2, 132.1, 129.5, 127.2, 124.4, 61.9, 14.2 ppm.

HRMS m/z : calcd for C₉H₁₀NO₄ [M+H]⁺ 196.0604, found: 196.0610.



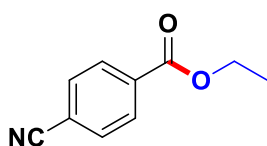
Ethyl 3-fluoro-4-nitrobenzoate (3ca): Yield = 47% (100.2 mg). Orange oil.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.15 – 8.03 (m, 1H), 8.00 – 7.85 (m, 2H), 4.42 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H) ppm.

¹⁹F NMR (377 MHz, Chloroform-*d*): δ -116.58 ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 163.5, 155.0 (d, J = 263.7 Hz), 139.8 (d, J = 7.7 Hz), 137.0 (d, J = 7.7 Hz), 126.1 (d, J = 2.7 Hz), 125.4 (d, J = 2.7 Hz), 119.6 (d, J = 22.2 Hz), 62.3, 14.1 ppm.

HRMS m/z : calcd for C₉H₉FNO₄ [M+H]⁺ 214.0510, found: 214.0516.

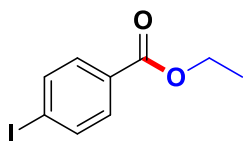


Ethyl 4-cyanobenzoate (3da)^[9]: Yield = 40% (70.1 mg). White solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.17 – 8.08 (m, 2H), 7.77 – 7.68 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.9, 134.2, 132.1, 130.0, 118.0, 116.2, 61.7, 14.2 ppm.

HRMS m/z : calcd for C₁₀H₁₀NO₂ [M+H]⁺ 176.0706, found: 176.0712.

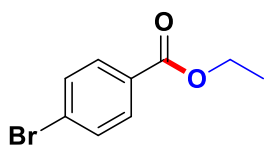


Ethyl 4-iodobenzoate (3ea)^[9]: Yield = 33% (91.1 mg). Yellow oil.

¹H NMR (401 MHz, Chloroform-*d*): δ 7.84 – 7.68 (m, 4H), 4.36 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 166.1, 137.6, 131.0, 129.9, 100.5, 61.2, 14.3 ppm.

HRMS m/z : calcd for C₉H₁₀IO₂ [M+H]⁺ 276.9720, found: 276.9725.

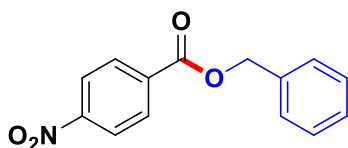


Ethyl 4-bromobenzoate (3fa)^[9]: Yield = 25% (57.3 mg). Yellow solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 7.95 – 7.87 (m, 2H), 7.60 – 7.54 (m, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 165.9, 131.6, 131.1, 129.4, 127.9, 61.2, 14.3 ppm.

HRMS m/z : calcd for C₉H₁₀BrO₂ [M+H]⁺ 228.9859, found: 228.9864.

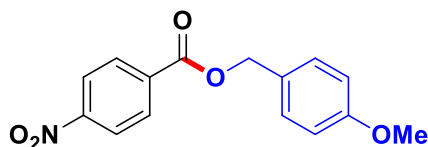


Benzyl 4-nitrobenzoate (3aj)^[5]: Yield = 60% (159.2 mg). Yellow solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.30 – 8.18 (m, 4H), 7.49 – 7.32 (m, 5H), 5.40 (s, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.5, 150.5, 135.4, 135.2, 130.8, 128.7, 128.6, 128.4, 123.5, 67.6 ppm.

HRMS m/z: calcd for C₁₄H₁₂NO₄ [M+H]⁺ 258.0761, found: 258.0766.

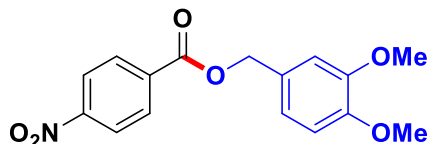


4-methoxybenzyl 4-nitrobenzoate (3ak)^[10]: Yield = 65% (186.7 mg). Yellow solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 – 8.24 (m, 2H), 8.23 – 8.18 (m, 2H), 7.42 – 7.37 (m, 2H), 6.96 – 6.88 (m, 2H), 5.34 (s, 2H), 3.82 (s, 3H) ppm.

¹³C NMR (75 MHz, Chloroform-*d*): δ 164.6, 159.9, 150.4, 135.6, 130.7, 130.4, 127.2, 123.5, 114.0, 67.5, 55.3 ppm.

HRMS m/z: calcd for C₁₅H₁₄NO₅ [M+H]⁺ 288.0866, found: 288.0872.

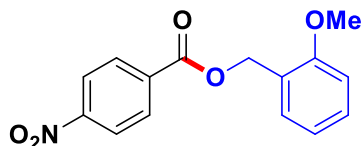


3,4-Dimethoxybenzyl 4-nitrobenzoate (3al): Yield = 71% (225.3 mg). Yellow solid. M.p. = 105.3-106.8 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.22 – 8.09 (m, 4H), 7.02 – 6.91 (m, 2H), 6.83 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.3, 150.2, 149.1, 148.8, 135.3, 130.5, 127.4, 123.2, 121.4, 111.7, 110.8, 67.5, 55.6, 55.6 ppm.

HRMS m/z: calcd for C₁₆H₁₆NO₆ [M+H]⁺ 318.0972, found: 318.0977.

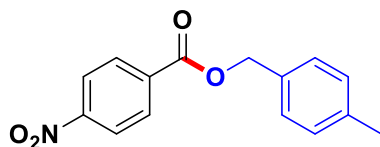


2-Methoxybenzyl 4-nitrobenzoate (3am): Yield = 72% (206.8 mg). White solid. M.p. = 77.3-78.4 °C.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.30 – 8.15 (m, 4H), 7.44 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.45 (s, 2H), 3.86 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.5, 157.5, 150.3, 135.6, 130.6, 129.9, 129.7, 123.4, 123.3, 120.3, 110.4, 63.0, 55.3 ppm.

HRMS m/z: calcd for C₁₅H₁₄NO₅ [M+H]⁺ 288.0866, found: 288.0872.



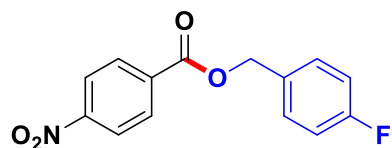
4-Methylbenzyl 4-nitrobenzoate (3an)^[11]: Yield = 62% (168.2 mg). White solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.27 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.35 (d,

$J = 7.7$ Hz, 2H), 7.22 (d, $J = 7.7$ Hz, 2H), 5.36 (s, 2H), 2.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.5, 150.4, 138.6, 135.5, 132.2, 130.7, 129.4, 128.6, 123.5, 67.6, 21.2 ppm.

HRMS m/z : calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 272.0917, found: 272.0923.



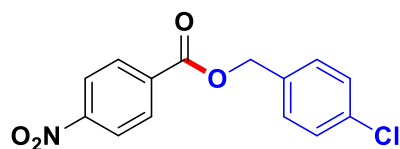
4-Fluorobenzyl 4-nitrobenzoate (3ao)^[11]: Yield = 65% (178.8 mg). White solid.

^1H NMR (401 MHz, Chloroform-*d*): δ 8.31 – 8.26 (m, 2H), 8.25 – 8.18 (m, 2H), 7.49 – 7.39 (m, 2H), 7.13 – 7.02 (m, 2H), 5.37 (s, 2H) ppm.

^{19}F NMR (377 MHz, Chloroform-*d*): δ -112.71 ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.5, 162.8 (d, $J = 245.9$ Hz), 150.6, 135.3, 131.1 (d, $J = 3.2$ Hz), 130.8, 130.5 (d, $J = 8.2$ Hz), 123.6, 115.7 (d, $J = 21.5$ Hz), 66.9 ppm.

HRMS m/z : calcd for $\text{C}_{14}\text{H}_{11}\text{FNO}_4$ $[\text{M}+\text{H}]^+$ 276.0667, found: 276.0672.

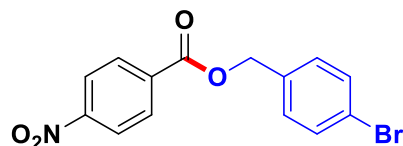


4-chlorobenzyl 4-nitrobenzoate (3ap)^[11]: Yield = 64% (186.7 mg). White solid.

^1H NMR (401 MHz, Chloroform-*d*): δ 8.31 – 8.25 (m, 2H), 8.24 – 8.19 (m, 2H), 7.42 – 7.34 (m, 4H), 5.36 (s, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.4, 150.6, 135.2, 134.6, 133.7, 130.8, 129.8, 128.9, 123.6, 66.8 ppm.

HRMS m/z : calcd for $\text{C}_{14}\text{H}_{11}\text{ClNO}_4$ $[\text{M}+\text{H}]^+$ 292.0371, found: 292.0377.

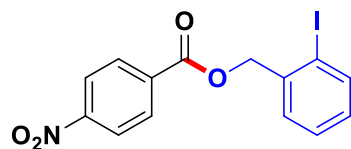


4-Bromobenzyl 4-nitrobenzoate (3aq)^[12]: Yield = 55% (184.9 mg). White solid.

^1H NMR (401 MHz, Chloroform-*d*): δ 8.32 – 8.26 (m, 2H), 8.25 – 8.18 (m, 2H), 7.56 – 7.51 (m, 2H), 7.36 – 7.30 (m, 2H), 5.35 (s, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.5, 150.5, 135.4, 135.2, 130.8, 128.7, 128.6, 128.4, 123.5, 67.6 ppm.

HRMS m/z : calcd for $\text{C}_{14}\text{H}_{11}\text{BrNO}_4$ $[\text{M}+\text{H}]^+$ 335.9866, found: 335.9872.



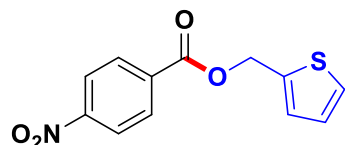
2-Iodobenzyl 4-nitrobenzoate (3ar): Yield = 52% (199.2 mg). White solid. M.p. = 108.5-109.1 °C.

^1H NMR (401 MHz, Chloroform-*d*): δ 8.34 – 8.22 (m, 4H), 7.95 – 7.87 (m, 1H), 7.50 – 7.45 (m, 1H), 7.42 – 7.36 (m, 1H), 7.12 – 7.03 (m, 1H), 5.42 (s, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.4, 150.7, 139.9, 137.8, 135.4, 131.0, 130.5, 130.2,

128.6, 123.7, 99.0, 71.3 ppm.

HRMS m/z: calcd for C₁₄H₁₁INO₄ [M+H]⁺ 383.9727, found: 383.9733.

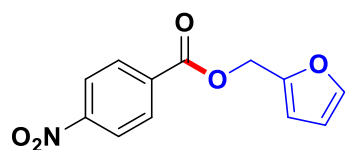


Thiophen-2-ylmethyl 4-nitrobenzoate (3as): Yield = 64% (169.5 mg). White solid. M.p. = 102.4-103.1 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.30 – 8.15 (m, 4H), 7.36 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.19 (d, *J* = 4.3 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.55 (s, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.4, 150.6, 137.0, 135.3, 130.9, 128.8, 127.3, 127.0, 123.5, 61.8 ppm.

HRMS m/z: calcd for C₁₂H₁₀NO₄S [M+H]⁺ 264.0325, found: 264.0331.

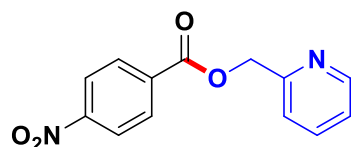


Furan-2-ylmethyl 4-nitrobenzoate (3at): Yield = 63% (156 mg). Light yellow solid. M.p. = 74.9-75.8 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.28 – 8.23 (m, 2H), 8.23 – 8.18 (m, 2H), 7.45 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.54 – 6.50 (m, 1H), 6.39 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.34 (s, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.3, 150.5, 148.7, 143.6, 135.2, 130.8, 123.4, 111.4, 110.7, 59.2 ppm.

HRMS m/z: calcd for C₁₂H₁₀NO₅ [M+H]⁺ 248.0553, found: 248.0559.

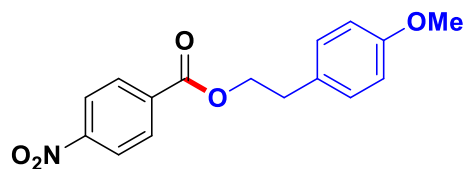


Pyridin-2-ylmethyl 4-nitrobenzoate (3av): Yield = 69% (178 mg). White solid. M.p. > 200 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.65 – 8.60 (m, 1H), 8.32 – 8.24 (m, 4H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 – 7.26 (m, 1H), 5.51 (s, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.4, 155.0, 150.6, 149.7, 136.9, 135.2, 130.9, 123.6, 123.2, 122.1, 68.0 ppm.

HRMS m/z: calcd for C₁₃H₁₁N₂O₄ [M+H]⁺ 259.0713, found: 259.0719.

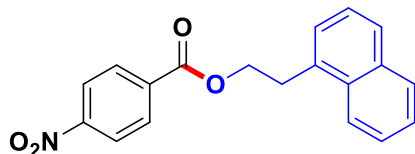


4-Methoxyphenethyl 4-nitrobenzoate (3aw): Yield = 66% (198.9 mg). White solid. M.p. = 112.3-113.0 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.28 (dd, *J* = 8.9, 2.2 Hz, 2H), 8.22 – 8.11 (m, 2H), 7.19 (dd, *J* = 8.7, 2.2 Hz, 2H), 6.92 – 6.79 (m, 2H), 4.54 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.04 (t, *J* = 7.0 Hz, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.6, 158.4, 150.5, 135.6, 130.6, 129.8, 129.3, 123.5, 114.0, 66.5, 55.2, 34.2 ppm.

HRMS *m/z*: calcd for C₁₆H₁₆NO₅ [M+H]⁺ 302.1023, found: 302.1028.

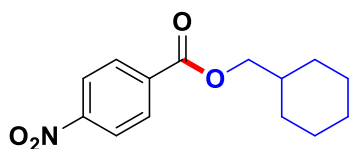


2-(Naphthalen-1-yl)ethyl 4-nitrobenzoate (3ax): Yield = 58% (186.4 mg). White solid. M.p. = 146.6-147.0 °C.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 – 8.23 (m, 2H), 8.18 – 8.11 (m, 3H), 7.92 – 7.86 (m, 1H), 7.82 – 7.76 (m, 1H), 7.61 – 7.49 (m, 2H), 7.47 – 7.41 (m, 2H), 4.72 (t, *J* = 7.2 Hz, 2H), 3.58 (t, *J* = 7.2 Hz, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.7, 150.5, 135.5, 133.9, 133.3, 132.0, 130.7, 128.9, 127.7, 127.1, 126.3, 125.8, 125.5, 123.5, 123.5, 65.9, 32.1 ppm.

HRMS *m/z*: calcd for C₁₉H₁₆NO₄ [M+H]⁺ 322.1074, found: 322.1079.

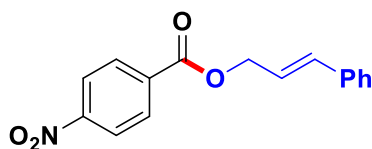


Cyclohexylmethyl 4-nitrobenzoate (3ay): Yield = 46% (121.1 mg). White solid. M.p. = 49.3-51.2 °C.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.29 – 8.22 (m, 2H), 8.21 – 8.14 (m, 2H), 4.16 (dd, *J* = 6.3, 2.0 Hz, 2H), 1.83 – 1.66 (m, 5H), 1.34 – 1.14 (m, 4H), 1.11 – 0.98 (m, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.7, 150.4, 135.8, 130.6, 123.5, 70.9, 37.1, 29.6, 26.2, 25.6 ppm.

HRMS *m/z*: calcd for C₁₄H₁₈NO₄ [M+H]⁺ 264.1230, found: 264.1236.



Cinnamyl 4-nitrobenzoate (3az)^[13]: Yield = 62% (175.6 mg). White solid.

¹H NMR (401 MHz, Chloroform-*d*): δ 8.24 – 8.15 (m, 4H), 7.40 – 7.35 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 6.71 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.35 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.97 (dd, *J* = 6.6, 1.3 Hz, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.4, 150.4, 135.8, 135.4, 135.1, 130.6, 128.6, 128.2, 126.6, 123.4, 122.2, 66.4 ppm.

HRMS *m/z*: calcd for C₁₆H₁₄NO₄ [M+H]⁺ 284.0917, found: 284.0923.

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^1H , ^{19}F , and ^{13}C NMR spectra of products

