Supporting Information for:

Organocatalytic Mitsunobu Reactions Using 3,5-Dinitrobenzoic Acid

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General Experimental Procedures

All reagents were obtained from the Acros, Aldrich, or Lancaster chemical companies. Tetrahydrofuran was dried using a Solv-Tek purification system employing activated Al₂O₃. Triphenylphosphine was recrystallized from hexane prior to use. Other commercially available reagents were used as received. All reactions were carried out in dry glassware under a N₂ atmosphere, and were monitored by TLC analysis using GF₂₅₄ silica gel coated plates. Column chromatography was carried out using silica gel (300-400 mesh) at increased pressure. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker DRX-300 or DRX-400 spectrometer operating at 300/400 MHz for ¹H and 75/100 MHz for ¹³C analysis. Chemical shift data is expressed in ppm with reference to TMS. Optical rotation data were recorded in CHCl₃ or EtOH on a Perkin Elmer Polarimeter 343 operating at 20 °C for 589 nm. HPLC analyses were carried out using a Waters Delta Prep 4000 chromatography system equipped with the indicated columns.

General Procedure for Catalytic Mitsunobu Reactions

To a solution of 10 (1.98 mmol) and the alcohol substrate (1.8 mmol) in anhydrous THF (11 mL) under a N₂ atmosphere, was added 2 (0.028 mL, 0.18 mmol), and 7 (1.16 g, 3.6 mmol). This was followed by the addition of a solution of 1 (0.94 g, 3.6 mmol) in anhydrous THF (4 mL) slowly by syringe pump (0.25 equiv/h). The reaction mixture was stirred for a total of 16 h and then was diluted with diethyl ether (30 mL). The organic phase was separated and then washed sequentially with saturated aq. NaHCO₃ (2
x 20 mL), and brine (20 mL), dried with Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography.

**Product Characterization Data**

![Structure 12a](image)

**Benzyl 4-nitrobenzoate (12a).**

$^1$H-NMR (400 MHz, CDCl₃) δ 5.40 (s, 2H), 7.26-7.39 (m, 5H), 8.16 (d, 2H, $J = 9$ Hz), 8.28 (d, 2H, $J = 9$ Hz); $^{13}$C-NMR (100 MHz, CDCl₃) δ 67.7, 123.5, 128.4, 128.5, 128.6, 128.7, 130.8, 135.2, 135.4, 150.3, 164.5.

![Structure 12b](image)

**2-Phenylethyl 4-nitrobenzoate (12b).**

$^1$H-NMR (CDCl₃, 300 MHz) δ 3.10 (t, 2H, $J = 6.9$ Hz), 4.59 (t, 2H, $J = 6.9$ Hz), 7.20-7.36 (m, 5H), 8.16 (d, 2H, $J = 8.8$ Hz), 8.28 (d, 2H, $J = 8.8$ Hz); $^{13}$C-NMR (100 MHz, CDCl₃) δ 55.2, 67.5, 114.0, 123.4, 127.3, 130.3, 130.7, 135.6, 150.5, 164.5.

![Structure 12c](image)
3-Phenylpropyl 4-nitrobenzoate (12c). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 2.12-2.16 (m, 2H), 2.80 (t, 2H, $J = 8$Hz), 4.40 (t, 2H, $J = 8$Hz), 7.20-7.29 (m, 5H), 8.15 (d, 2H, $J = 12$Hz), 8.28 (d, 2H, $J = 12$Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 29.9, 32.2, 65.2, 123.3, 126.0, 128.2, 128.4, 130.5, 135.5, 140.8, 150.3, 164.5.

![12d]

4-Methylbenzyl 4-nitrobenzoate (12d). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 2.37 (s, 3H), 5.36 (s, 2H), 7.21 (d, 2H, $J = 8$Hz), 7.34 (d, 2H, $J = 8$Hz), 8.22 (d, 2H, $J = 8$Hz), 8.26 (d, 2H, $J = 8$Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 67.6, 123.4, 128.5, 129.3, 130.7, 132.2, 135.5, 138.5, 150.5, 164.5.

![12e]

3-Nitrobenzyl 4-nitrobenzoate (12e). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 5.50 (s, 2H), 7.62 (t, 1H, $J = 8$Hz), 7.79 (d, 1H, $J = 8$Hz), 8.24-8.33 (m, 6H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 66.1, 123.1, 123.5, 123.6, 129.8, 130.8, 134.1, 134.8, 137.2, 150.7, 164.2.
4-Nitrobenzyl 4-nitrobenzoate (12f). $^1$H-NMR (CDCl$_3$, 300 MHz) δ 5.50 (s, 2H), 7.51 (d, 2H, $J$ = 8 Hz), 7.62 (d, 2H, $J$ = 8 Hz), 8.21-8.33 (m, 4H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 66.0, 123.6, 123.8, 128.6, 130.8, 134.7, 142.3, 150.8, 164.2.

4-Bromobenzyl 4-nitrobenzoate (12g). $^1$H-NMR (400 MHz, CDCl$_3$) δ 5.34 (s, 2H), 7.32 (d, 2H, $J$ = 8.1 Hz), 7.53 (d, 2H, $J$ = 8.1 Hz), 8.23 (d, 2H, $J$ = 12 Hz), 8.27 (d, 2H, $J$ = 12 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 66.8, 122.7, 123.5, 130.0, 130.7, 131.8, 134.1, 135.2, 150.6, 164.3.

3-Methoxybenzyl 4-nitrobenzoate (12h). $^1$H-NMR (CDCl$_3$, 300 MHz) δ 3.83 (s, 3H), 5.37 (s, 2H), 6.90-7.04 (m, 3H), 7.30 (t, 1H, $J$ = 6 Hz), 8.23 (d, 2H, $J$ = 9 Hz), 8.27 (d, 2H, $J$ = 9 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 55.2, 67.4, 113.8, 114.0, 120.5, 123.5, 129.7, 130.7, 135.4, 136.6, 159.8, 164.4.
(S)-3-butynyl 4-nitrobenzoate (12i).  $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 1.67 (d, 3H, $J = 8$Hz), 2.53 (s, 1H), 5.67-5.73 (m, 1H), 8.23 (d, 2H, $J = 12$ Hz), 8.27 (d, 2H, $J = 12$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 61.7, 73.7, 81.4, 123.5, 130.9, 135.1, 150.6, 163.5.

Ethyl (R)-2-((4-nitrobenzoyl)oxy) propionate (12j).  $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 1.29 (t, 3H, $J = 7.1$ Hz), 1.66 (d, 3H, $J = 7.0$ Hz), 4.23 (q, 2H, $J = 7.1$ Hz), 5.35 (q, 1H, $J = 7.0$ Hz), 8.27 (d, 2H, $J = 1.2$ Hz), 8.29 (d, 2H, $J = 1.2$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 16.9, 61.6, 69.9, 123.5, 130.9, 134.8, 150.7, 164.0, 170.1.

Benzyl 3,5-dinitrobenzoate (13a).  $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 5.47 (s, 2H), 7.41-7.47 (m, 5H), 9.16-9.22 (m, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 68.5, 122.4, 128.7, 128.8, 129.0, 129.4, 133.8, 134.5, 148.6, 162.3.
2-Phenylethyl 3,5-dinitrobenzoate (13b). $^1$H-NMR (CDCl$_3$, 300 MHz) δ 3.14 (t, 2H, J = 6Hz), 4.65 (t, 2H, J = 6Hz), 7.27-7.35 (m, 5H), 9.10 (d, 2H, J = 3Hz), 9.21 (t, 1H, J = 3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 34.9, 67.1, 122.3, 126.9, 128.7, 128.8, 129.3, 133.8, 136.9, 148.5, 162.3.

3-Phenylpropyl 3,5-dinitrobenzoate (13c). $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.18-2.12 (m, 2H), 2.81 (t, 2H, J = 7.6Hz), 4.89 (t, 2H, J = 7.6Hz), 7.16-7.28 (m, 5H) 9.08 (d, 2H, J = 3Hz), 9.21 (t, 1H, J = 3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 29.8, 32.3, 66.4, 122.2, 126.1, 128.3, 129.3, 133.8, 140.6, 148.5, 162.4.

4-Methylbenzyl 3,5-dinitrobenzoate (13d). $^1$H-NMR (CDCl$_3$, 400 MHz) δ 2.38 (s, 3H), 5.43 (s, 2H), 7.23 (d, 2H, J = 8Hz), 7.37 (d, 2H, J = 8Hz), 9.15 (d, 2H, J = 4Hz),
9.21 (t, 1H, J = 4Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.2, 68.5, 122.3, 128.9, 129.4, 129.5, 131.5, 133.9, 139.0, 148.6, 162.4.

3-Nitrobenzyl 3,5-dinitrobenzoate (13e). $^1$H-NMR (CDCl$_3$, 300 MHz) δ 5.57 (s, 2H), 7.64 (t, 1H, J = 8Hz), 7.83 (d, 1H, J = 8Hz), 8.27 (d, 1H, J = 8Hz), 8.35 (s, 1H), 9.185 (d, 2H, J = 2Hz), 9.25 (t, 1H, J = 2Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 67.0, 122.7, 123.6, 123.9, 129.5, 130.0, 133.1, 134.6, 136.3, 148.7, 162.2.

4-Nitrobenzyl 3,5-dinitrobenzoate (13f). $^1$H-NMR (CDCl$_3$, 300 MHz) δ 5.57 (s, 2H), 7.65 (d, 2H, J = 8Hz), 8.29 (d, 2H, J = 8Hz), 9.18 (d, 2H, J = 2Hz), 9.25 (t, 1H, J = 2Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 66.9, 122.7, 124.1, 129.1, 129.5, 133.1, 141.4, 148.7, 162.1.
4-Bromobenzyl 3,5-dinitrobenzoate (13g). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 5.42 (s, 2H), 7.36 (d, 2H, $J$ = 8Hz), 7.55 (d, 2H, $J$ = 8Hz), 9.15 (d, 2H, $J$ = 3Hz), 9.22 (t, 1H, $J$ = 3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 67.6, 122.5, 129.4, 130.5, 132.0, 133.4, 133.5, 148.6, 162.3.

3-Methoxybenzyl 3,5-dinitrobenzoate (13h). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 3.83 (s, 3H), 5.44 (s, 2H), 6.92-7.0 (m, 3H), 7.36 (m, 1H), 9.17 (d, 2H, $J$ = 3Hz), 9.22 (t, 1H, $J$ = 3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 55.3, 68.4, 114.2, 114.4, 120.9, 122.4, 129.5, 129.9, 133.7, 135.9, 148.6, 162.3.
(S)-3-butylnyl 3,5-dinitrobenzoate (12i). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 1.41 (d, 3H, $J$ = 9Hz), 2.17 (s, 1H), 5.16-5.26 (m, 1H), 9.15 (d, 2H, $J$ = 3Hz), 9.22 (t, 1H, $J$ = 3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 62.8, 74.4, 80.7, 122.5, 129.5, 133.4, 148.6, 161.4.

![Chemical Structure](image)

Ethyl (R)-2-((3,5-dinitrobenzoyl)oxy) propionate (13j). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 1.31 (t, 3H, $J$ = 9 Hz), 1.72 (d, 3H, $J$ = 6.9 Hz), 4.26 (q, 2H, $J$ = 7.2 Hz), 5.41 (q, 1H, $J$ = 7.2 Hz), 9.20 (d, 2H, $J$ = 2.1Hz), 9.25 (t, 1H, $J$ = 2.1Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 16.8, 61.9, 70.7, 122.6, 129.6, 133.1, 148.6, 161.9, 169.6.
HPLC Data for Products Prepared from 11i

OJ column, 0.7mL/min, 30% IPA in hexane

From racemic 3-butyn-2-ol

4-NBA with butynol
30%IPA, 0.7mL/min
49.88:50.02

From racemic 3-butyn-2-ol

862C
1.01:98.19

3,5-DNBBA with 3-butyn-2-ol
racemic
OJ, 30%IPA, 0.7mL/min
49.88:50.2

From racemic 3-butyn-2-ol

O\text{O}_2N
\text{O}