Highly Enantioselective Direct Michael Addition of Nitroalkanes to Nitroolefins Catalyzed by La(OTf)$_3$/N,N'-Dioxide Complexes

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1. General

$^1$H NMR spectra were recorded on commercial instruments (300 or 400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$, $\delta = 7.26$). Spectra are reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. $^{13}$C NMR spectra were collected on commercial instruments (100 or 75 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl$_3$, $\delta = 77.0$). The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALCEL AS-H, OD-H or CHIRALPAK AD-H column at 210 nm. Optical rotations are measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^T$ (c = g/100 mL, solvent).

Solvents were dried according to standard procedures. Nitroalkanes were obtained from commercial sources and used without further purification. Nitroalkenes were prepared according to the literature procedures.$^{[1]}$ The N,N'-dioxide ligands were prepared according to the methods reported in the literature.$^{[2]}$ Racemic samples of 3a-3n were prepared with 10 mol% Et$_3$N as the catalyst and the nitroalkane as solvent.
2. Characterization of N,N'-Dioxide Ligands

For the characterization of the ligands L1,[2b] L4,[2b] L6,[2c,2d] L7,[2b] and L8,[2e] see literature.

**L2**: white solid; m.p. 176-179 °C; [α]$_{25}^D$ = -110.0 (c = 0.196, in CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 13.12 (s, 2H), 7.50-7.52 (d, $J$ = 8.0 Hz, 4H), 7.27-7.31 (m, 4H), 7.08-7.12 (t, $J$ = 7.6 Hz, 2H), 2.38-2.56 (m, 6H), 2.02-2.07 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 164.8, 137.4, 128.9, 124.4, 120.2, 76.1, 70.1, 61.0, 27.6, 20.4 ppm; ESI-HRMS: calcd for C$_{25}$H$_{33}$N$_4$O$_4$ [M+H$^+$] 439.2340, found 439.2345.

**L3**: white solid; m.p. 166-170 °C; [α]$_{25}^D$ = -89.4 (c = 0.174, in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 13.60 (s, 2H), 7.59-7.61 (d, $J$ = 7.6 Hz, 4H), 7.07-7.10 (t, $J$ = 8.4 Hz, 2H), 3.60-3.65 (dd, $J$ = 10.8, 8.4 Hz, 2H), 3.49-3.54 (t, $J$ = 8.8 Hz, 2H), 3.33-3.41 (m, 2H), 3.16-3.25 (m, 4H), 2.11-2.20 (m, 2H), 1.97-2.06 (m, 2H), 1.78-1.89 (m, 2H), 1.36-1.44 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 165.8, 138.1, 129.1, 124.2, 120.3, 75.9, 67.1, 27.9, 24.3, 23.9, 20.5 ppm; ESI-HRMS: calcd for C$_{25}$H$_{33}$N$_4$O$_4$ [M+H$^+$] 481.2809, found 481.2816.

**L5**: white powder; m.p. 95-99 °C; [α]$_{25}^D$ = -125.0 (c = 0.136, in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 13.49 (s, 2H), 7.49-7.51 (d, $J$ = 8.8 Hz, 4H), 7.22-7.24 (d, $J$ = 8.8 Hz, 4H), 3.61-3.71 (m, 4H), 3.45-3.59 (m, 4H), 3.29-3.36 (dd, $J$ = 9.6, 20.0 Hz, 2H), 2.68-2.76 (m, 2H), 2.49-2.57 (m, 2H), 2.40-2.47 (m, 2H), 2.04-2.12 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 165.3, 136.4, 129.2, 129.1, 121.4, 76.7, 68.2, 65.1, 27.7, 20.5, 20.0 ppm; ESI-HRMS: calcd for C$_{25}$H$_{33}$N$_4$O$_4$ [M+H$^+$] 521.1717, found 521.1721.

3. Typical Procedure for the Synthesis of 1,3-Dinitroalkanes

The mixture of ligand L1 (10.9 mg, 0.024 mmol), La(OTf)$_3$ (11.7 mg, 0.02 mmol) was stirred in CH$_2$Cl$_2$ (0.4 mL) at 30 °C under N$_2$ atmosphere for 30 min to form the complex catalyst. Then nitroethane (29 μL, 0.4 mmol), imidazole (20 μL, c = 1 mol/L in CH$_2$Cl$_2$, 10 mol%) and the β-nitrostyrene (0.2 mmol) in CH$_2$Cl$_2$ (0.6 mL) were sequentially added to the mixture. After stirring at 30 °C for 2.5 d, the reaction mixtures were directly purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:4 to 1:9) to afford the syn/anti mixtures of chiral 1,3-dinitro compounds. After the mixtures of products were analyzed by HPLC analysis, the pure syn diastereoisomers were afforded through another column chromatography separation on silica gel (ethyl acetate/petroleum ether = 1:4 to 1:9) and then the pure syn products were used to $^1$H NMR, $^{13}$C NMR and the determination of optical rotation and melting points.

4. Characterization of the Conjugate Addition Products

**2-Phenyl-1,3-dinitrobutane (3a)**

The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (96% ee) of the syn diastereoisomer and diastereoselectivity (93:7 d.r.) of the reaction were determined by HPLC analysis using a chiral AS-H column (hexane/2-propanol...
90:10, 0.5 mL/min, UV 210 nm, t_r (syn. major) = 51.150 min, t_r (syn. minor) = 58.040 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:5, R_f 0.4) to afford a white solid, m.p. 80-81°C. \([\alpha]^{20}_D\) (syn) = +7.3 (c = 0.11, in CH_2Cl_2). ^1^H NMR (400 MHz, CDCl_3): \(\delta\) 7.38-7.33 (m, 3H), 7.17-7.15 (m, 2H), 5.00-4.92 (m, 2H), 4.83 (dd, \(J = 13.6, 8.4\) Hz, 1H), 4.05-4.00 (m, 1H ), 1.59 (d, \(J = 6.8\) Hz, 3H).

**2-(4-Methylphenyl)-1,3-dinitrobutane (3b).**

The *syn/anti* mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the *syn* diastereoisomer. The ee value (96% ee) of the *syn* diastereoisomer and diastereoselectivity (88:12 d.r.) of the reaction were determined by HPLC analysis using a chiral OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, UV 210 nm, \(t_r\) (syn. minor) = 24.599 min, \(t_r\) (syn. major) = 28.679 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R_f 0.3) to afford a white solid, m.p. 52-53°C. \([\alpha]^{20}_D\) (syn) = +14.7 (c = 0.15, in CH_2Cl_2). ^1^H NMR (400 MHz, CDCl_3): \(\delta\) 7.15 (d, \(J = 8.0\) Hz, 2H), 7.03 (d, \(J = 8.0\) Hz, 2H), 4.97-4.88 (m, 2H), 4.85 (dd, \(J = 13.6, 8.4\) Hz, 1H), 4.00-3.95 (m, 1H ), 2.32 (s, 3H), 1.57 (d, \(J = 6.8\) Hz, 3H).
2-(4-Methoxyphenyl)-1,3-dinitrobutane (3c).

The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (93% ee) of the syn diastereoisomer and diastereoselectivity (86:14 d.r.) of the reaction were determined by HPLC analysis using a chiral AD-H column (hexane/2-propanol 90:10, 0.4 mL/min, UV 210 nm, \( t_r \) (syn. major) = 45.22 min, \( t_r \) (syn. minor) = 47.43 min).

\textit{syn} Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, \( R_f \) 0.2) to afford a white solid. m.p. 75-77°C. \([\alpha]^{20}_D\) (syn) = +11.7 (c = 0.06, in CH\(_2\)Cl\(_2\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.02-6.98 (m, 2H), 6.82-6.79 (m, 2H), 4.87-4.82 (m, 2H), 4.72 (dd, \( J = 13.6, 8.4 \) Hz, 1H), 3.91-3.86 (m, 1H), 3.72 (s, 3H), 1.51 (d, \( J = 6.8 \) Hz, 3H).
2-(3-Methoxyphenyl)-1,3-dinitrobutane (3d).
The syn/anti mixtures of products were analyzed to determine the
diastereoselectivity of the reaction and enantioselectivity of the syn
diastereoisomer. The ee value (97% ee) of the syn diastereoisomer
and diastereoselectivity (84:16 d.r.) of the reaction were determined
by HPLC analysis using a chiral AS-H column (hexane/2-propanol
90:10, 1.0 mL/min, UV 210 nm, t<sub>r</sub> (syn. major) = 51.82 min, t<sub>r</sub> (syn.
minor) = 59.37 min).

<chem>
  \begin{aligned}
    &\text{OMe} \\
    &\text{NO}_2 \\
    &\text{NO}_2 \\
    &\text{3d}
  \end{aligned}
</chem>
syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R<sub>f</sub>
0.2) to afford a gel product. \([\alpha]^{20}_D\) (syn) = +6.3 (c = 0.49, in CH<sub>2</sub>Cl<sub>2</sub>). \(^1\)H NMR (400 MHz,
CDCl<sub>3</sub>): \(\delta\) 7.29-7.25 (m, 1H), 6.87 (dd, J = 8.0, 2.0 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H),
6.68 (t, J = 2.0 Hz, 1H), 4.98-4.89 (m, 2H), 4.81 (dd, J = 13.6, 8.0 Hz, 1H), 4.03-3.99 (m,
1H ), 3.79 (s, 3H), 1.60 (d, J = 6.8 Hz, 3H). \(^1\)C NMR (100 MHz, CDCl<sub>3</sub>): \(\delta\) = 160.1,
135.0, 130.4, 119.9, 114.3, 114.0, 84.0, 76.0, 55.3, 47.3, 16.7. ESI-HRMS: calef for
C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub> [M+Na<sup>+</sup>] 277.0795, found 277.0802.

2-(2-Methoxyphenyl)-1,3-dinitrobutane (3e).
The syn/anti mixtures of products were analyzed to determine the
diastereoselectivity of the reaction and enantioselectivity of the syn
diastereoisomer. The ee value (90% ee) of the syn diastereoisomer
and diastereoselectivity (71:29 d.r.) of the reaction were determined
by HPLC analysis using a chiral OD-H column (hexane/2-propanol
90:10, 1.0 mL/min, UV 210 nm, t<sub>r</sub> (syn. major) = 18.29 min, t<sub>r</sub> (syn. minor) = 32.76 min).

<chem>
  \begin{aligned}
    &\text{OMe} \\
    &\text{NO}_2 \\
    &\text{NO}_2 \\
    &\text{3e}
  \end{aligned}
</chem>
syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R<sub>f</sub>
0.25) to afford a white solid. m.p. 59-61°C. \([\alpha]^{20}_D\) (syn) = -10.0 (c = 0.18, in CH<sub>2</sub>Cl<sub>2</sub>). \(^1\)H NMR (400 MHz,
CDCl<sub>3</sub>): \(\delta\) 7.32-7.27 (m, 1H), 7.05 (dd, J = 8.0, 1.6 Hz, 1H), 6.92-6.88
(m, 2H), 5.21-5.14 (m, 1H), 4.92-4.83 (m, 2H), 4.30 (dd, J = 14.2, 7.6 Hz, 1H ), 3.85 (s,
3H), 1.58 (d, J = 6.8 Hz, 3H).
2-(4-Bromophenyl)-1,3-dinitrobutane (3f).

The *syn/anti* mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the *syn* diastereoisomer. The ee value (96% ee) of the *syn* diastereoisomer and diastereoselectivity (89:11 d.r.) of the reaction were determined by HPLC analysis using a chiral AD-H column (hexane/2-propanol 90:10, 0.4 mL/min, UV 210 nm, tr (*syn* major) = 42.43 min, tr (*syn* minor) = 45.15 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, Rf 0.2) to afford a white solid. m.p. 76-77°C. [α]$_D$ $^{20}$ (syn) = +13.6 (c = 0.11, in CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.51-7.48 (m, 2H), 7.04 (d, $J$ = 8.4 Hz, 2H), 4.96-4.88 (m, 2H), 4.79 (dd, $J$ = 13.6, 8.4 Hz, 1H), 4.02-3.96 (m, 1H), 1.60 (d, $J$ = 6.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 131.5, 131.4, 128.6, 122.4, 82.8, 74.9, 45.9, 15.8.

ESI-HRMS: calcd for C$_{10}$H$_{11}$BrN$_2$O$_4$ [M+H] 302.9986, found 302.9852.
2-(3-Chlorophenyl)-1,3-dinitrobutane (3g).

The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (97% ee) of the syn diastereoisomer and diastereoselectivity (86:14 d.r.) of the reaction were determined by HPLC analysis using a chiral AS-H column (hexane/2-propanol 90:10, 1.0 mL/min, UV 210 nm, t_r (syn. major) = 36.37 min, t_r (syn. minor) = 42.06 min).

**syn** Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R_f 0.25) to afford a white solid. m.p. 82-84°C. [α]^{20}_D (syn) = +8.3 (c = 0.12, in CH2Cl2). ^1H NMR (400 MHz, CDCl₃): δ 7.35-7.28 (m, 2H), 7.17 (d, J = 1.6 Hz, 1H), 7.07-7.04 (m, 1H), 4.98-4.89 (m, 2H), 4.80 (dd, J = 13.6, 8.4 Hz, 1H), 4.04-3.99 (m, 1H ), 1.62-1.60 (d, J = 6.8 Hz, 3H). ^13C NMR (100 MHz, CDCl₃): δ = 134.5, 134.2, 129.6, 128.4, 127.4, 124.9, 82.8, 74.8, 45.9, 15.8. ESI-HRMS: calcd for C₁₀H₁₁ClN₂O₄ [M+Na⁺] 281.0300, found 281.0310.

2-(2-Chlorophenyl)-1,3-dinitrobutane (3h).

The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (96% ee) of the syn diastereoisomer and diastereoselectivity (85:15 d.r.) of the reaction were determined by HPLC analysis using a chiral AD-H column (hexane/2-propanol 98:2, 0.5 mL/min, UV 210 nm, t_r (syn. major) = 57.22 min, t_r (syn. minor) = 62.02 min).

**syn** Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R_f 0.3) to afford a yellow oil. [α]^{20}_D (syn) = -11.1 (c = 0.45, in CH2Cl2). ^1H NMR (400 MHz,
2-(2,4-Dichlorophenyl)-1,3-dinitrobutane (3i).
The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (95% ee) of the syn diastereoisomer and diastereoselectivity (83:17 d.r.) of the reaction were determined by HPLC analysis using a chiral OD-H column (hexane/2-propanol 90:10, 0.7 mL/min, UV 210 nm, t_r (syn. major) = 42.21 min, t_r (syn. minor) = 46.73 min).

syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:4, R_f 0.45) to afford a yellow oil. [α]^{20}_{D} (syn) = -6.9 (c = 0.48, in CH₂Cl₂). ^1H NMR (400 MHz, CDCl₃): δ 7.48 (t, J = 2.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.17-5.10 (m, 1H), 4.94-4.82 (m, 2H), 4.64 (dd, J = 13.6, 6.8 Hz, 1H), 1.65-1.63 (d, J = 6.8 Hz, 3H). ^13C NMR (100 MHz, CDCl₃): δ = 135.7, 135.3, 130.6, 130.0, 129.1, 128.1, 82.8, 74.9, 42.7, 16.6. ESI-HRMS: calcd for C₁₀H₁₀Cl₂N₂O₄ [M+H] 293.0101, found 292.9900.
2-(2-Nitrophenyl)-1,3-dinitrobutane (3j).

The *syn/anti* mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the *syn* diastereoisomer. The ee value (96% ee) of the *syn* diastereoisomer and diastereoselectivity (76:24 d.r.) of the reaction were determined by HPLC analysis using a chiral AS-H column (hexane/2-propanol 90:10, 1.0 mL/min, UV 210 nm, *t*<sub>f</sub> (*syn* major) = 45.47 min, *t*<sub>f</sub> (*syn* minor) = 56.36 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, *R*<sub>f</sub> 0.2) to afford a white solid. m.p. 99-101°C. [α]<sup>20</sup> <sub>D</sub> (*syn*) = +19.2 (c = 0.13, in CH<sub>2</sub>Cl<sub>2</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.65-7.51 (m, 2H), 7.34 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.30 (dt, *J* = 14.8, 6.8 Hz, 1H), 5.03 (dd, *J* = 13.6, 5.2 Hz, 1H), 4.93 (dd, *J* = 13.6, 6.8 Hz, 1H), 4.72 (dd, *J* = 12.8, 6.4 Hz, 1H), 1.73 (d, *J* = 6.4 Hz, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 150.0, 134.0, 130.2, 129.2, 126.1, 83.5, 75.8, 41.6, 17.5. ESI-HRMS: calcd for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O<sub>6</sub> [M+Na<sup>+</sup>] 292.0540, found 292.0547.

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2-(2-Naphthyl)-1,3-dinitrobutane (3k).
The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (92% ee) of the syn diastereoisomer and diastereoselectivity (92:8 d.r.) of the reaction were determined by HPLC analysis using a chiral AD-H column (hexane/2-propanol 90:10, 0.5 mL/min, UV 210 nm, t_r (syn. major) = 51.69 min, t_r (syn. minor) = 57.02 min).

syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R_f 0.35) to afford a yellow oil. [α]_D^20 = -38.8 (c = 0.50, in CH_2Cl_2). ¹H NMR (400 MHz, CDCl_3): δ 8.19 (d, J = 8.4 Hz, 1H), 7.92-7.85 (dd, J = 21.2, 8.4 Hz, 2H), 7.69-7.64 (t, J = 8.4 Hz, 1H), 7.59-7.55 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.33 (dd, J = 7.2, 0.8 Hz, 1H), 5.22-5.15 (m, 2H), 5.01 (dd, J = 6.4, 2.0 Hz, 2H), 1.60 (d, J = 6.4 Hz, 3H).

2-(2-Furyl)-1,3-dinitrobutane (3l).
The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (86% ee) of the syn diastereoisomer and diastereoselectivity (81:19 d.r.) of the reaction were determined by HPLC analysis using a chiral OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, UV 210 nm, t_r (syn. major) = 28.22 min, t_r (syn. minor) = 30.92 min).

syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, R_f 0.35) to afford a yellow oil. [α]_D^20 = +24.3 (c = 0.28, in CH_2Cl_2). ¹H NMR (400 MHz, CDCl_3): δ 7.39 (d, J = 1.6 Hz, 1H), 6.34 (dd, J = 3.2, 2.0 Hz, 1H), 6.27 (d, J = 3.6 Hz, 1H), 4.97-4.81 (m, 3H), 4.25-4.21 (m, 1H), 1.61 (d, J = 6.8 Hz, 3H).
2-styryl-1,3-dinitrobutane (3m).
The syn/anti mixtures of products were analyzed to determine the diastereoselectivity of the reaction and enantioselectivity of the syn diastereoisomer. The ee value (85% ee) of the syn diastereoisomer and diastereoselectivity (81:19 d.r.) of the reaction were determined by HPLC analysis using a chiral OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, UV 210 nm, 
\( t_r \) (syn. major) = 40.088 min, 
\( t_r \) (syn. minor) = 55.685 min).

syn Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:5, \( R_f \) 0.3) to afford a white solid. m.p. 55-57°C. \([\alpha]^{20}_D\) (syn) = +52.7 (c = 0.11, in CH₂Cl₂). \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.36-7.27 (m, 5H), 6.64-6.60 (d, \( J = 15.6 \) Hz, 1H), 5.91 (dd, \( J = 15.6, 9.6 \) Hz, 1H), 4.85-4.79 (m, 1H), 4.77-4.72 (m, 1H), 4.59 (dd, \( J = 13.2, 8.0 \) Hz, 1H), 1.63 (dd, \( J = 6.8, 2.0 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 136.8, 134.3, 127.7, 125.7, 118.7, 82.1, 75.3, 44.6, 15.7. ESI-HRMS: calcd for C₁₂H₁₄N₂O₄ [M+Na⁺] 273.0846, found 273.0852.
2-isopropyl-1,3-dinitrobutane (3n).
The *syn/anti* mixtures of products were analyzed to determine the
diastereoselectivity of the reaction and enantioselectivity of the *syn*
diastereoisomer. The ee value (83% *ee*) of the *syn* diastereoisomer and
diastereoselectivity (78:22 d.r.) of the reaction were determined by
HPLC analysis using a chiral OD-H column (hexane/2-propanol 90:10,
0.4 mL/min, UV 210 nm, *t*<sub>s</sub> (*syn* major) = 31.83 min, *t*<sub>s</sub> (*syn* minor) = 34.08 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:9, *R*<sub>f</sub> 0.4) to afford a yellow oil. [*α*]<sup>20</sup><sub>D</sub> (*syn*) = -3.6 (c = 0.59, in CH<sub>2</sub>Cl<sub>2</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.78 (t, *J* = 6.8 Hz, 1H), 4.52-4.41 (m, 2H), 2.89-2.84 (m, 1H), 1.89-1.82 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 5H), 0.92 (d, *J* = 6.8 Hz, 4H).

2-Phenyl-1,3-dinitropentane (5).
The *syn/anti* mixtures of products were analyzed to determine the
diastereoselectivity of the reaction and enantioselectivity of the *syn*
diastereoisomer. The ee value (95% *ee*) of the *syn* diastereoisomer and
diastereoselectivity (92:8 d.r.) of the reaction were determined by
HPLC analysis using a chiral AS-H column (hexane/2-propanol 90:10,
0.4 mL/min, UV 210 nm, *t*<sub>(syn. minor) = 58.90 min, *t*<sub>(syn. major) = 60.77 min).

*syn* Isomer, purified by flash chromatography (ethyl acetate : petroleum ether = 1:6, *R*<sub>f</sub> 0.3) to afford a white solid. m.p. 54-56°C. [*α*]<sup>20</sup><sub>D</sub> (*syn*) = +10.0 (c = 0.11, in CH<sub>2</sub>Cl<sub>2</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30-7.26 (m, 3H), 7.10-7.07 (m, 2H), 4.85-4.79 (ddd, *J* =
13.4, 6.4, 2.8 Hz, 1H), 4.74-4.68 (m, 2H), 3.97 (dd, $J = 14.4, 6.8$ Hz, 1H), 1.99-1.91 (m, 1H), 1.83-1.75 (m, 1H), 0.95 (dt, $J = 7.2, 2.4$ Hz, 3H).

5. References
6. Copy of NMR Spectra for N,N'-Dioxide Ligand
7. Copy of NMR Spectra for the products
NO2

NO2

S21