Highly Regioselective Nitrile Oxide Dipolar Cycloadditions with *ortho*-Nitrophenyl Alkynes.

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Electronic Supplementary Information: X-Ray Data
**X-ray Crystallography.** Diffraction intensities for rc45a, rc46, rc47, rc63 and rc71a were collected at 173(2) and 193(2) K, respectively, on a Bruker Apex CCD diffractometer using MoKα radiation = 0.71073 Å. Space groups were determined based on systematic absences (rc45a, rc47, rc63 and rc71a) and intensity statistics (rc46). Absorption corrections were applied by SADABS. Structures were solved by direct methods and Fourier techniques and refined on $F^2$ using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. The terminal –NO₂ groups and the Cl atoms in rc45a and rc46 are disordered over two positions in ratios (0.854/0.146 and 0.717/0.283, respectively) corresponding two possible opposite orientations of the groups in the crystal structures. Only one orientation of this group is shown on Fig. 1. The disordered –NO₂ groups in these structures were refined with restrictions; the standard C-N and N-O bond distances were used in the refinement as the targets for corresponding bond distances. All H atoms in rc45a, rc46, rc47 and rc63 were treated in calculated positions in a rigid group model. The H atoms in rc71a were found from the residual density and refined with isotropic thermal parameters. The crystals of rc45a and rc63 have non-centrosymmetrical space groups, but absolute configurations of these compounds have not been determined from the X-ray diffraction data. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.

Crystallographic Data for compound 13b (rc45a): C₁₉H₁₇ClN₂O₃, M = 356.80, 0.22 x 0.14 x 0.06 mm, T = 173 K, orthorhombic, space group $P_{ca}2_1_1$, $a = 13.6753(18)$ Å, $b = 8.3473(11)$ Å, $c = 15.493(2)$ Å, $V = 1768.5(4)$ Å³, $Z = 4$, $D_c = 1.340$ Mg/m³, $\mu = 0.236$ mm$^{-1}$, $F(000) = 744$, $2\theta_{max} = 54.00^\circ$, 9680 reflections, 3413 independent reflections $[R_{int} = 0.0443]$, $R_1 = 0.0541$, wR2 = 0.1323 and GOF = 1.027 for 3413 reflections (244 parameters) with $b$-2$\alpha$(l), $R_1 = 0.0766$, wR2 = 0.1484 and GOF = 1.032 for all reflections, max/min residual electron density +0.253/-0.209 eÅ$^{-3}$. 
Crystallographic Data for Compound 13d (rc46): C\textsubscript{18}H\textsubscript{14}BrClN\textsubscript{2}O\textsubscript{3}, M = 421.67, 0.24 x 0.14 x 0.05 mm, T = 173 K, triclinic, space group P-1, a = 7.1538(6) Å, b = 8.3848(7) Å, c = 15.2827(13) Å, α = 78.938(1)°, β = 87.667(1)°, γ = 75.921(1)°, V = 872.63(13) Å\(^3\), Z = 2, D\(_c\) = 1.605 Mg/m\(^3\), μ = 2.528 mm\(^{-1}\), F(000) = 424, 2θ\(_{\text{max}}\) = 54.00°, 9826 reflections, 3785 independent reflections [R\(_{\text{int}}\) = 0.0246], R1 = 0.0431, wR2 = 0.1072 and GOF = 1.040 for 3785 reflections (243 parameters) with b \(>\) 2σ(I), R1 = 0.0514, wR2 = 0.1128 and GOF = 1.044 for all reflections, max/min residual electron density +0.696/-0.598 eÅ\(^{-3}\).

Crystallographic Data for Compound 13g (rc47): C\textsubscript{19}H\textsubscript{17}ClN\textsubscript{2}O\textsubscript{3}, M = 356.80, 0.38 x 0.32 x 0.18 mm, T = 173 K, monoclinic, space group P\(_{2_1}/c\), a = 15.8541(16) Å, b = 7.1382(7) Å, c = 16.7066(17) Å, β = 114.406(2)°, V = 1721.7(3) Å\(^3\), Z = 4, D\(_c\) = 1.376 Mg/m\(^3\), μ = 0.243 mm\(^{-1}\), F(000) = 744, 2θ\(_{\text{max}}\) = 54.00°, 18222 reflections, 3747 independent reflections [R\(_{\text{int}}\) = 0.0321], R1 = 0.0438, wR2 = 0.1219 and GOF = 1.018 for 3747 reflections (294 parameters) with b \(>\) 2σ(I), R1 = 0.0462, wR2 = 0.1245 and GOF = 1.018 for all reflections, max/min residual electron density +0.783/-0.293 eÅ\(^{-3}\).
Crystallographic Data for Compound 13h (rc63): C_{18}H_{16}N_{2}O_{3}, M = 308.33, 0.38 x 0.19 x 0.12 mm, T = 173 K, orthorhombic, space group Pna2₁, a = 19.125(5) Å, b = 7.3751(19) Å, c = 22.492(6) Å, V = 3172.5(14) Å³, Z = 8, D_c = 1.291 Mg/m³, μ = 0.089 mm⁻¹, F(000) = 1296, 2θ_max = 50.00°, 22732 reflections, 5589 independent reflections \(R_int = 0.0383\), R1 = 0.0521, wR2 = 0.1346 and GOF = 1.012 for 5589 reflections (416 parameters) with h>2σ(h), R1 = 0.0598, wR2 = 0.1442 and GOF = 1.012 for all reflections, max/min residual electron density +0.349/-0.166 eÅ⁻³.
Crystallographic Data for compound 11 (rc71a): C_{16}H_{14}N_{2}O_{4}, M = 298.29, 0.35 x 0.07 x 0.02 mm, T = 193 K, orthorhombic, space group Pnca, a = 12.238(4) Å, b = 8.006(3) Å, c = 28.867(10) Å, V = 2828.3(17) Å³, Z = 8, D_c = 1.401 Mg/m³, μ = 0.102 mm⁻¹, F(000) = 1248, 2θ_{max} = 50.00°, 18841 reflections, 2501 independent reflections [R_{int} = 0.0889], R1 = 0.0641, wR2 = 0.1590 and GOF = 1.062 for 2501 reflections (255 parameters) with $I>2\sigma(I)$, R1 = 0.1151, wR2 = 0.1919 and GOF = 1.062 for all reflections, max/min residual electron density +0.611/-0.332 eÅ⁻³.

References


2. SHELXTL-6.10 "Program for Structure Solution, Refinement and Presentation" BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.