Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

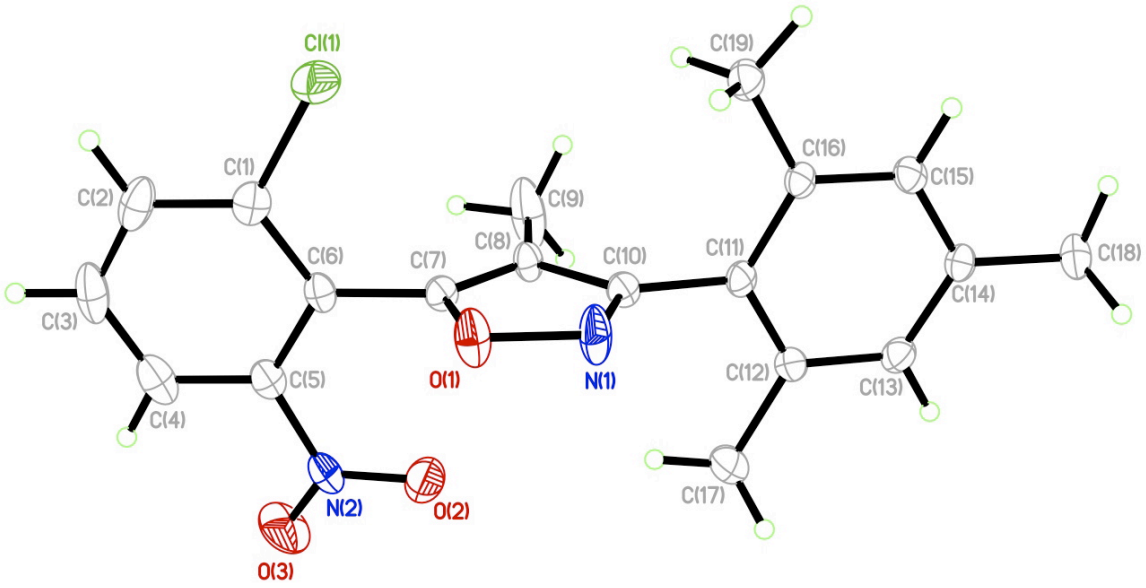
Highly Regioselective Nitrile Oxide Dipolar Cycloadditions with *ortho*-Nitrophenyl Alkynes.

Melissa L. McIntosh, Michael R. Naffziger, Bradley O. Ashburn, Lev N. Zakharov and Rich G. Carter*

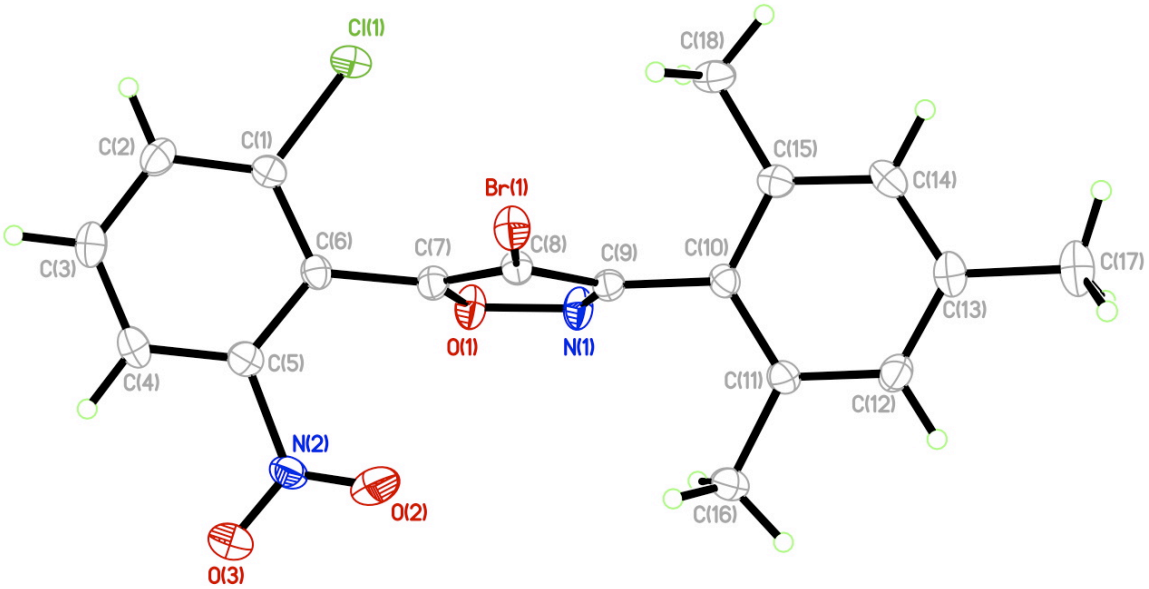
Department of Chemistry, Oregon State University, Corvallis, OR 97331

Electronic Supplementary Information: X-Ray Data

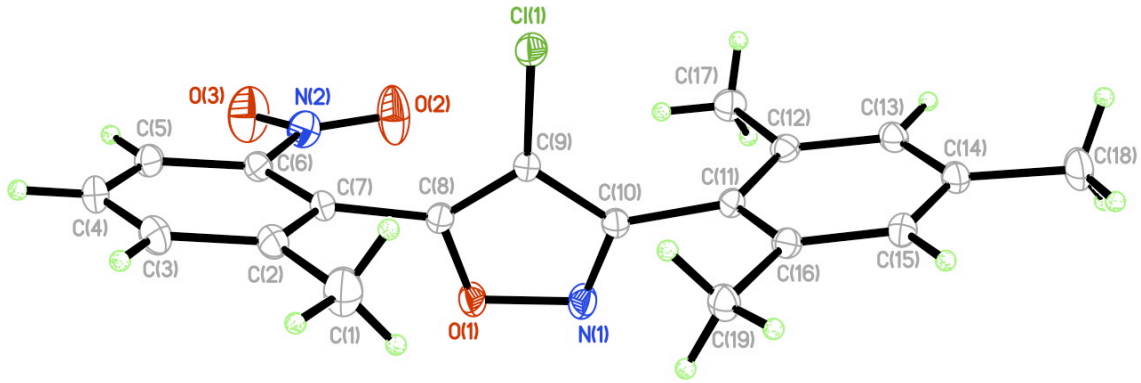
X-ray Crystallography. Diffraction intensities for **rc45a, rc46, rc47, rc63** and **rc71a** were collected at 173(2) and 193(2) K, respectively, on a Bruker Apex CCD diffractometer using MoKα radiation = 0.71073 Å. Space groups were determined based on systematic absences (**rc45a, rc47, rc63** and **rc71a)** and intensity statistics (**rc46)**. Absorption corrections were applied by SADABS[1]. Structures was 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 $-NO_2$ 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 $-NO_2$ 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 form the X-ray diffraction data. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.[2]



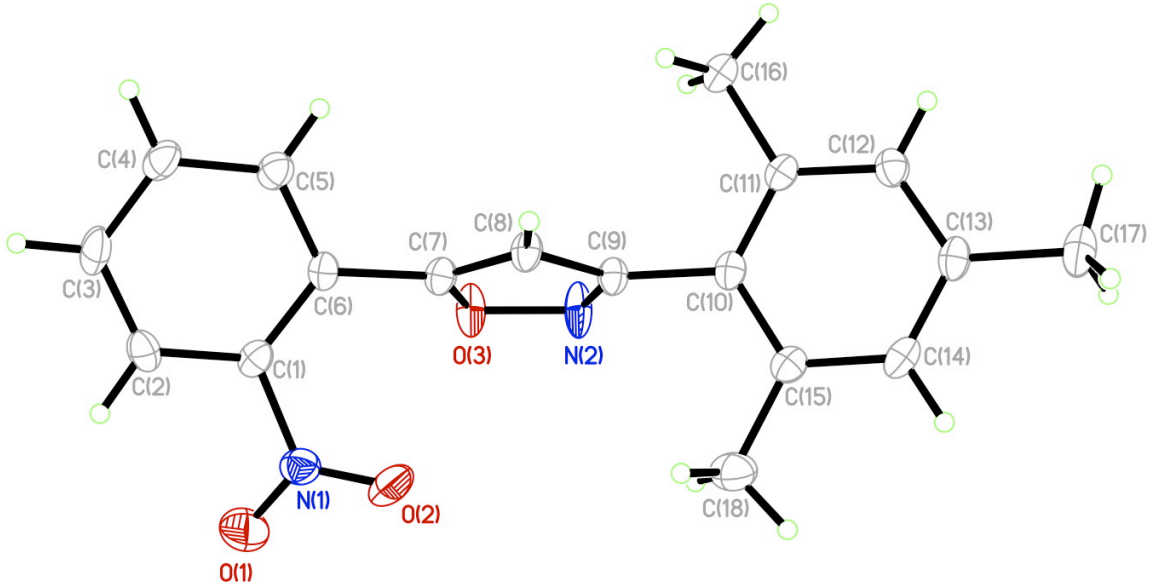
Crystallographic Data for compound ***13b*** *(**rc45a**):* $C_{19}H_{17}ClN_2O_3$, M = 356.80, 0.22 x 0.14 x 0.06 mm, T = 173 K, orthorhombic, space group *Pca*2_1, *a* = 13.6753(18) Å, *b* = 8.3473(11) Å, *c* = 15.493(2) Å, *V* = 1768.5(4) Å^3, *Z* = 4, D_c = 1.340 Mg/m^3, μ = 0.236 mm^{-1}, *F*(000) = 744, $2\theta_{max}$ = 54.00°, 9680 reflections, 3413 independent reflections [R_{int} = 0.0443], R1 = 0.0541, wR2 = 0.1323 and GOF = 1.027 for 3413 reflections (244 parameters) with $I>2\sigma(I)$, R1 = 0.0766, wR2 = 0.1484 and GOF = 1.032 for all reflections, max/min residual electron density +0.253/-0.209 eÅ^{-3}.



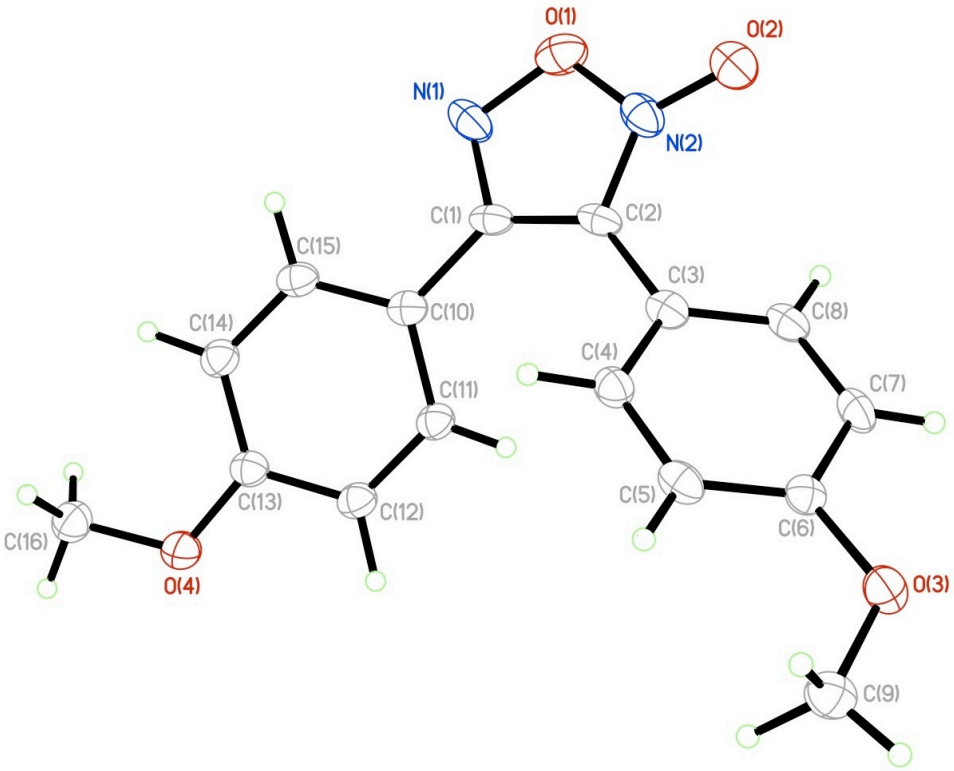
Crystallographic Data for compound ***13d*** *(**rc46**):* $C_{18}H_{14}BrClN_2O_3$, M = 421.67, 0.24 x 0.14 x 0.05 mm, T = 173 K, triclinic, space group *P*-1, *a* = 7.1538(6) Å, *b* = 8.3848(7) Å, *c* = 15.2827(13) Å, α = 78.938(1)°, β = 87.667(1)°, γ = 75.921(1)°, *V* = 872.63(13) Å^3, *Z* = 2, D_c = 1.605 Mg/m^3, μ = 2.528 mm^{-1}, *F*(000) = 424, $2\theta_{max}$ = 54.00°, 9826 reflections, 3785 independent reflections [R_{int} = 0.0246], R1 = 0.0431, wR2 = 0.1072 and GOF = 1.040 for 3785 reflections (243 parameters) with $I>2\sigma(I)$, 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**):* $C_{19}H_{17}ClN_2O_3$, M = 356.80, 0.38 x 0.32 x 0.18 mm, T = 173 K, monoclinic, space group $P2_1/c$, *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, $2\theta_{max}$ = 54.00°, 18222 reflections, 3747 independent reflections [R_{int} = 0.0321], R1 = 0.0438, wR2 = 0.1219 and GOF = 1.018 for 3747 reflections (294 parameters) with $I>2\sigma(I)$, 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**):* $C_{18}H_{16}N_2O_3$, M = 308.33, 0.38 x 0.19 x 0.12 mm, T = 173 K, orthorhombic, space group *Pna*2_1, *a* = 19.125(5) Å, *b* = 7.3751(19) Å, *c* = 22.492(6) Å, *V* = 3172.5(14) Å^3, *Z* = 8, D_c = 1.291 Mg/m^3, μ = 0.089 mm^{-1}, *F*(000) = 1296, $2\theta_{max}$ = 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 $I>2\sigma(I)$, 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**):* $C_{16}H_{14}N_2O_4$, M = 298.29, 0.35 x 0.07 x 0.02 mm, T = 193 K, orthorhombic, space group *Pbca*, *a* = 12.238(4) Å, *b* = 8.006(3) Å, *c* = 28.867(10) Å, *V* = 2828.3(17) Å^3, *Z* = 8, D_c = 1.401 Mg/m^3, μ = 0.102 mm^{-1}, *F*(000) = 1248, $2\theta_{max}$ = 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

1. G. M. Sheldrick, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, 1998.

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