Supplementary Information for

Metal- and Solvent-free Synthesis of Functionalized Dihydrooxazolo-[3,2-a]indoles by One-pot Tandem Assembly of 3H-Indoles and Propargylic Alcohols

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1. $^1$H and $^{13}$C spectra of the synthesized products 4a-f.................................................................2
   (Z)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetonitrile (4a)...........2
   (Z)-2-(9,9a-trimethyl-9,9a-dihydro-3H-spiro[cyclohexane-1,2-oxazolo[3,2-a]indol-3-ylidene]acetonitrile (4b)...........................................3
   (Z)-2-(9,9a-trimethyl-9,9a-dihydro-3H-spiro[cyclohexane-1,2-oxazolo[3,2-a]indol-3-ylidene]acetonitrile (4c)...........................................4
   (Z)-2-(2-Butyl-9,9a-trimethyl-2-phenyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetonitrile (4d)..................................................................................5
   Methyl (E)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)-1-phenylethan-1-one (4e)........................................................................6
   Methyl (E)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetate (4f)......7

2. $^1$H and $^{13}$C spectra of the synthesized products 5a-e.................................................................................8
   (Z)-2-(9,9a,10a,11,11-Pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)acetonitrile (5a).................................................................8
   2-(9-Ethyl-9,10a,11,11-tetramethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)acetonitrile (5b).................................................................9
   (Z)-2-(10a,11,11-trimethyl-10a,11-dihydro-8H-spiro[benzo[e]oxazolo[3,2-a]indole-9,1’-cyclohexan]-8-ylidene)acetonitrile (5c)........................................10
   (E)-2-(9,9a,10a,11,11-Pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)-1-phenyletan-1-one (5d)..................................................11
   Methyl (E)-2-(9,9a,10a,11,11-pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)acetate (5e).................................................................12

3. X-Ray Diffraction analysis..................................................................................................................13

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1. $^1$H and $^{13}$C spectra of the synthesized products 4a-f

(Z)-2-(2,2,9,9a-pentamethyl-9a-dihydrooxazolo[3,2-a]indol-3(2$H$)-ylidene)acetonitrile (4a)
(Z)-2-(9,9a-trimethyl-9a-dihydro-3H-spirocyclohexane-1,2-oxazolo[3,2-a]indol-3-ylidene)acetonitrile (4b)
(Z)-2-(9,9a-trimethyl-9a-dihydro-3H-spiro[cyclohexane-1,2-oxazolo[3,2-α]indol-3-ylidene]acetonitrile (4c)
(Z)-2-(2-Butyl-9,9a-trimethyl-2-phenyl-9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetonitrile (4d)
Methyl \((E)\)-2-(2,2,9,9,9a-pentamethyl-9a-dihydrooxazolo[3,2-\(a\)]indol-3(2\(H\))-ylidene)-1-phenylethano-1-one (4e)
Methyl (E)-2-(2,2,9,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetate (4f)
2. $^1$H and $^{13}$C spectra of the synthesized products 5a-e

(Z)-2-(9,9,10a,11,11-Pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)acetonitrile (5a)
2-(9-Ethyl-9,10a,11,11-tetramethyl-10a,11-dihydrobenzo[ε]oxazolo[3,2-α]indol-8(9H)-ylidene)acetonitrile (5b)
(Z)-2-(10a,11,11-trimethyl-10a,11-dihydro-8H-spiro[benzo[e]oxazolo[3,2-a]indole-9,1'-'cyclohexan]-8-ylidene)acetonitrile (5c)
(E)-2-(9,9,10a,11,11-Pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)-1-phenyletan-1-one (5d)
Methyl (E)-2-(9,9a,10a,11,11-pentamethyl-10a,11-dihydrobenzo[e]oxazolo[3,2-a]indol-8(9H)-ylidene)acetate (5e)
**X-Ray Diffraction Analysis**

The determination of the unit cell and the data collection for (Z)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetonitrile (4a) was performed on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with MoKα radiation (λ = 0.71073) at 300.0(2) K using the φ-φ scan technique. A specimen of C₁₇H₂₉N₂O₂, approximate dimensions 0.16 mm × 0.26 mm × 0.47 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with P2₁/c space group yielded a total of 29631 reflections to a maximum θ angle of 27.6 (0.81 Å resolution), of which 3441 were independent (completeness = 99%, Rint = 4.10%, Rsig = 3.34%) and 2154 were greater than 2σ(F2). The final cell constants of a = 11.440(3) Å, b = 16.013(5) Å, c = 8.753(3) Å, Z = 4, volume = 1508.8(8) Å³. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.956. The structure was solved and refined using the Bruker SHELXTL Software Package.¹ The H atoms were determined from a difference Fourier synthesis. The unit cell are presented by 2 enantiomers: (R,Z)- and (S,Z)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene) acetonitrile (4a). Relative population of enantiomers is 50:50. A short distance (2.614 Å) between centroid of triple bond and benzene stacking.

![X-ray structure of (Z)-2-(2,2,9,9a-pentamethyl-9,9a-dihydrooxazolo[3,2-a]indol-3(2H)-ylidene)acetonitrile (4a).](image)

The final anisotropic full-matrix least-squares refinement on F2 with 197 variables converged at R1 = 5.29%, for the observed data and wR2 = 14.39% for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was 0.130 e Å⁻³ and the largest hole was −0.160 e Å⁻³. On the basis of the final model, the calculated density was 1.181 g/cm³ and F(000), 576 e.

The determination of the unit cell and the data collection for 2-(10a,11,11-trimethyl-10a,11-dihydro-8H-spiro[benzo[e]oxazolo[3,2-a]indole-9,1’-cyclohexan]-8-ylidene)acetonitrile (5c) was performed at 193.15(2) K using the φ-φ scan technique. A specimen of C₂₃H₃₆N₂O₂, approximate dimensions 0.16 mm × 0.17 mm × 0.19 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell with P2₁/n space group yielded a total of 61494 reflections to a maximum θ angle of 26.8 (0.79 Å resolution), of which 4243 were independent (completeness = 100%, Rint = 4.71%, Rsig = 4.24%) and 7670 were greater than 2σ(F2). The final cell constants of a = 13.988(8) Å, b = 9.586(6) Å, c = 15.003(5) Å, Z= 4, volume = 2008(2) Å³. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.949. The structure was solved and refined using the Bruker SHELXTL Software Package.¹ The H atoms were determined from a difference Fourier synthesis. The unit cell are presented by 2 enantiomers: (R,Z)- and (S,Z)-2-(10a,11,11-trimethyl-10a,11-dihydro-8H-spiro[benzo[e]oxazolo[3,2-a]indole-9,1’-cyclohexan]-8-ylidene)acetonitrile (5c). Relative population of enantiomers is 50:50. Cyclohexane moiety has a chair shape. Acetonitrile and naphthalene groups are sin-oriented. The short distance (2.631 Å) between triple bond of acetonitrile group and naphthalene hydrogen suggests C-H…π stacking.
Figure 2. X-ray structure of 2-(10a,11,11-trimethyl-10a,11-dihydro-8H-spiro[benzo[e]oxazolo[3,2-a]indole-9,1’-cyclohexan]-8-ylidene)acetonitrile (5c). Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F2 with 247 variables converged at R1 = 5.05%, for the observed data and wR2 = 12.90% for all data. The goodness-of-fit was 1.03. The largest peak in the final difference electron density synthesis was 0.17 e⁻/Å³ and the largest hole was −0.15 e⁻/Å³. On the basis of the final model, the calculated density was 1.186 g/cm³ and F(000), 768 e⁻.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 1852755 and 1852754. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.