Facile, mild and efficient synthesis of azines using phosphonic dihydrazide

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**Supplemental Materials**

**Table S 1: Crystal Structure and Data Refinement Parameters for Compound 3c.**

|  |  |
| --- | --- |
| **Compound** | **3c** |
| Formula  | C18H16Cl4N6 |
| Formula weight  | 458.17 |
| Temperature / K | 296(2) |
| Wavelength / Å | 0.71073 |
| Crystal system  | Triclinic |
| Space group  | Pī |
| a / Å | 3.9485(4)  |
| b / Å | 5.9999(9) |
| c / Å | 20.956(3) |
|  | 86.279(11). |
|  | 86.751(9) |
|  | 89.561(10) |
| V / Å3 | 494.61(11) |
| Z | 1 |
| Dcalc / Mgm-3 | 1.538 |
| μ (mm-1) | 0.616 |
| Crystal size / mm3 | 0.218 x 0.115 x 0.104 |
| Reflections collected | 3847 |
| Independent  | 2275 |
| R(int) | 0.0185 |
| Goodness-of-fit on F2 | 1.063 |
| R1 [I>2σ(I)] | 0.0434 |
| wR2 [I>2σ(I)] | 0.0964 |
| R1 (all data) | 0.0616 |
| wR2 (all data) | 0.1071 |
| Extinction coefficient | n/a |
| Largest diff. peak, hole / e.Å-3 | 0.204, -0.232  |

**Table S 2: Crystal Structure and Data Refinement Parameters for Compound 3d.**

|  |  |
| --- | --- |
| **Compound** | **3d** |
| Formula  | C18H16Br2Cl2N6 |
| Formula weight  | 547.09 |
| Temperature / K | 296(2) |
| Wavelength / Å | 1.54184 |
| Crystal system  | Monoclinic |
| Space group  | P21/n |
| a / Å | 4.0227(2) |
| b / Å | 5.8986(3) |
| c / Å | 42.9459(14) |
|  | 90 |
|  | 89.732(4) |
|  | 90 |
| V / Å3 | 1019.02(8) |
| Z | 2 |
| Dcalc / Mgm-3 | 1.783 |
| μ (mm-1) | 7.605 |
| Crystal size / mm3 | 0.117 x 0.102 x 0.061 |
| Reflections collected | 6382 |
| Independent  | 2023 |
| R(int) | 0.0350 |
| Goodness-of-fit on F2 | 1.095 |
| R1 [I>2σ(I)] | 0.0445 |
| wR2 [I>2σ(I)] | 0.1154 |
| R1 (all data) | 0.0510 |
| wR2 (all data) | 0.1210 |
| Extinction coefficient | n/a |
| Largest diff. peak, hole / e.Å-3 | 0.461, -0.391 |

**Table S 3: Crystal Structure and Data Refinement Parameters for Compound 5b.**

|  |  |
| --- | --- |
| **Compound** | **5b** |
| Formula  | C30H26Br2N6S2 |
| Formula weight  | 694.51 |
| Temperature / K | 293(2) |
| Wavelength / Å | 0.71073 |
| Crystal system  | Orthorhombic |
| Space group  | Pbcn |
| a / Å | 23.2644(18) |
| b / Å | 9.9839(8) |
| c / Å | 12.7550(8) |
|  | 90 |
|  | 90 |
|  | 90 |
| V / Å3 | 2962.6(4) |
| Z | 4 |
| Dcalc / Mgm-3 | 1.557 |
| μ (mm-1) | 2.909 |
| Crystal size / mm3 | 0.476 x 0.100 x 0.065 |
| Reflections collected | 12975 |
| Independent  | 3734 |
| R(int) | 0.0404 |
| Goodness-of-fit on F2 | 1.066 |
| R1 [I>2σ(I)] | 0.0493 |
| wR2 [I>2σ(I)] | 0.1174 |
| R1 (all data) | 0.1036 |
| wR2 (all data) | 0.1425 |
| Extinction coefficient | n/a |
| Largest diff. peak, hole / e.Å-3 | 0.550, -0.821 |

**Table S 4: Crystal Structure and Data Refinement Parameters for Compound 10a.**

|  |  |
| --- | --- |
| **Compound** | **10a** |
| Formula  | C20H16N2O2 |
| Formula weight  | 316.35 |
| Temperature / K | 296(2) |
| Wavelength / Å | 0.71073 |
| Crystal system  | Monoclinic |
| Space group  | C2/c |
| a / Å | 19.6760(9) |
| b / Å | 6.3340(2) |
| c / Å | 25.3640(11) |
|  | 90 |
|  | 96.466(4) |
|  | 90 |
| V / Å3 | 3141.0(2) |
| Z | 8 |
| Dcalc / Mgm-3 | 1.338 |
| μ (mm-1) | 0.088 |
| Crystal size / mm3 | 0.304 x 0.180 x 0.117 |
| Reflections collected | 13456 |
| Independent  | 3916 |
| R(int) | 0.0289 |
| Goodness-of-fit on F2 | 1.076 |
| R1 [I>2σ(I)] | 0.0514 |
| wR2 [I>2σ(I)] | 0.1356 |
| R1 (all data) | 0.0642 |
| wR2 (all data) | 0.1469 |
| Extinction coefficient | 0.0012(3) |
| Largest diff. peak, hole / e.Å-3 | 0.203, -0.166  |

**Table S 5: Crystal Structure and Data Refinement Parameters for Compound 10b.**

|  |  |
| --- | --- |
| **Compound** | **10b** |
| Formula  | C20H18N4 |
| Formula weight  | 314.38 |
| Temperature / K | 296(2) |
| Wavelength / Å | 0.71073 |
| Crystal system  | Monoclinic |
| Space group  | P21/c |
| a / Å | 7.3795(3) |
| b / Å | 10.3392(4) |
| c / Å | 21.6783(10) |
|  | 90 |
|  | 98.336(4) |
|  | 90 |
| V / Å3 | 1636.54(12) |
| Z | 4 |
| Dcalc / Mgm-3 | 1.276 |
| μ (mm-1) | 0.078 |
| Crystal size / mm3 | 0.319 x 0.183 x 0.142 |
| Reflections collected | 13592 |
| Independent  | 4092 |
| R(int) | 0.0310 |
| Goodness-of-fit on F2 | 1.062 |
| R1 [I>2σ(I)] | 0.0551 |
| wR2 [I>2σ(I)] | 0.1457 |
| R1 (all data) | 0.0766 |
| wR2 (all data) | 0.1626 |
| Extinction coefficient | n/a |
| Largest diff. peak, hole / e.Å-3 | 0.194, -0.193 |

**Table S 6: Crystal Structure and Data Refinement Parameters for Compound 12.**

|  |  |
| --- | --- |
| **Compound** | **12** |
| Formula  | C16H10N4O2 |
| Formula weight  | 290.28 |
| Temperature / K | 296(2) |
| Wavelength / Å | 1.54184 |
| Crystal system  | Trigonal |
| Space group  | R3̅ H |
| a / Å | 24.7517(5) |
| b / Å | 24.7517(5) |
| c / Å | 5.64860(10) |
|  | 90 |
|  | 90 |
|  | 120 |
| V / Å3 | 2996.96(13) |
| Z | 9 |
| Dcalc / Mgm-3 | 1.448 |
| μ (mm-1) | 0.824 |
| Crystal size / mm3 | 0.553 x 0.052 x 0.039 |
| Reflections collected | 6861 |
| Independent  | 1336 |
| R(int) | 0.0309 |
| Goodness-of-fit on F2 | 1.069 |
| R1 [I>2σ(I)] | 0.0406 |
| wR2 [I>2σ(I)] | 0.1129 |
| R1 (all data) | 0.0441 |
| wR2 (all data) | 0.1175 |
| Extinction coefficient | n/a |
| Largest diff. peak, hole / e.Å-3 | 0.271, -0.177 |

**Table S 7: Bond lengths [Å] and selected angles [°] of compound 3c.**

|  |  |
| --- | --- |
| C(1)-C(2) 1.379(3) | C(1)-C(6) 1.384(3) |
| C(1)-N(1) 1.390(3) | C(2)-C(3) 1.380(3) |
| C(3)-C(4) 1.377(3) | C(4)-C(5) 1.370(3) |
| C(4)-Cl(1) 1.741(2) | C(5)-C(6) 1.375(3) |
| C(7)-N(2) 1.270(2) | C(7)-C(8) 1.465(3) |
| C(7)-Cl(2) 1.742(2) | C(8)-N(3) 1.283(3) |
| C(8)-C(9) 1.490(3) | N(1)-N(2) 1.340(2) |
| N(3)-N(3)#1 1.402(3) | N(2)-C(7)-C(8) 120.87(18) |
| N(2)-C(7)-Cl(2) 121.14(15) | C(8)-C(7)-Cl(2) 117.99(15) |
| N(3)-C(8)-C(7) 116.29(18) | N(3)-C(8)-C(9) 126.13(18) |
| C(7)-C(8)-C(9) 117.57(17) | N(2)-N(1)-C(1) 120.32(17) |
| C(7)-N(2)-N(1) 120.60(17) | C(8)-N(3)-N(3)#1 112.9(2) |
| #1 -x+1,-y+1,-z |

**Table S 8: Bond lengths [Å] and selected angles [°] of compound 3d.**

|  |  |
| --- | --- |
| C(1)-C(6) 1.385(6) | C(1)-C(2) 1.391(5) |
| C(1)-N(1) 1.396(5) | C(2)-C(3) 1.379(6) |
| C(3)-C(4) 1.369(6) | C(4)-C(5) 1.386(5) |
| C(4)-Br(1) 1.908(4) | C(5)-C(6) 1.378(5) |
| C(7)-N(2) 1.265(5) | C(7)-C(8) 1.470(5) |
| C(7)-Cl(1) 1.749(4) | C(8)-N(3) 1.284(5) |
| C(8)-C(9) 1.493(6) | N(1)-N(2) 1.334(4) |
| N(3)-N(3)#1 1.410(6) | N(2)-C(7)-C(8) 121.2(3) |
| N(2)-C(7)-Cl(1) 121.3(3) | C(8)-C(7)-Cl(1) 117.5(3) |
| N(3)-C(8)-C(7) 116.2(3) | N(3)-C(8)-C(9) 126.5(3) |
| C(7)-C(8)-C(9) 117.2(3) | N(2)-N(1)-C(1) 120.4(3) |
| N(2)-N(1)-H(1) 119.8 | C(8)-N(3)-N(3)#1 112.5(4) |
| #1 -x-1,-y,-z |

**Table S 9: Bond lengths [Å] and selected angles [°] of compound 5b.**

|  |  |
| --- | --- |
| C(1)-N(1) 1.383(4) | C(1)-C(2) 1.384(5) |
| C(1)-C(6) 1.392(4) | C(2)-C(3) 1.371(4) |
| C(3)-C(4) 1.380(5) | C(4)-C(5) 1.371(5) |
| C(4)-Br(1) 1.901(3) | C(5)-C(6) 1.372(5) |
| C(7)-N(2) 1.281(4) | C(7)-C(8) 1.470(4) |
| C(7)-S(1) 1.789(3) | C(8)-N(3) 1.283(4) |
| C(8)-C(9) 1.493(4) | C(10)-C(11) 1.380(5) |
| C(10)-C(15) 1.388(5) | C(10)-S(1) 1.769(3) |
| C(11)-C(12) 1.364(5) | C(12)-C(13) 1.366(6) |
| C(13)-C(14) 1.374(6) | C(14)-C(15) 1.378(5) |
| N(1)-N(2) 1.339(4) | N(3)-N(3)#1 1.397(5) |
| N(2)-C(7)-C(8) 117.6(3) | N(2)-C(7)-S(1) 122.7(2) |
| C(8)-C(7)-S(1) 119.7(2) | N(3)-C(8)-C(7) 116.4(3) |
| N(3)-C(8)-C(9) 125.0(3) | C(7)-C(8)-C(9) 118.6(3) |
| N(2)-N(1)-C(1) 120.1(3) | C(7)-N(2)-N(1) 120.6(3) |
| C(8)-N(3)-N(3)#1 113.1(3) | C(10)-S(1)-C(7) 101.63(15) |
| #1 -x+2,-y+1,-z-1 |

**Table S 10: Bond lengths [Å] and selected angles [°] of compound 10a.**

|  |  |
| --- | --- |
| C(1)-C(2) 1.343(2) | C(1)-O(1) 1.378(2) |
| C(1)-C(9) 1.454(2) | C(2)-C(3) 1.417(2) |
| C(3)-C(4) 1.392(2) | C(3)-C(5) 1.396(2) |
| C(4)-C(8) 1.377(2) | C(4)-O(1) 1.3767(18) |
| C(5)-C(6) 1.375(3) | C(6)-C(7) 1.394(3) |
| C(7)-C(8) 1.375(3) | C(9)-N(1) 1.284(2) |
| C(9)-C(10) 1.500(2) | C(11)-C(12) 1.497(2) |
| C(12)-N(2) 1.285(2) | C(12)-C(13) 1.455(2) |
| C(13)-C(14) 1.351(2) | C(13)-O(2) 1.3816(18) |
| C(14)-C(15) 1.426(2) | C(15)-C(16) 1.389(2) |
| C(15)-C(17) 1.399(2) | C(16)-O(2) 1.3733(18) |
| C(16)-C(20) 1.381(2) | C(17)-C(18) 1.375(3) |
| C(18)-C(19) 1.386(3) | C(19)-C(20) 1.380(3) |
| N(1)-N(2) 1.3933(18) | N(1)-C(9)-C(1) 117.38(15) |
| N(1)-C(9)-C(10) 126.19(15) | C(1)-C(9)-C(10) 116.38(14) |
| N(2)-C(12)-C(13) 117.67(14) | N(2)-C(12)-C(11) 125.25(14) |
| C(13)-C(12)-C(11) 117.05(14) | C(14)-C(13)-O(2) 111.24(13) |
| C(14)-C(13)-C(12) 130.87(15) | O(2)-C(13)-C(12) 117.84(13) |
| C(9)-N(1)-N(2) 114.57(14) | C(12)-N(2)-N(1) 113.90(13) |

**Table S 11: Bond lengths [Å] and selected angles [°] of compound 10b.**

|  |  |
| --- | --- |
| C(1)-N(1) 1.357(3) | C(1)-C(2) 1.372(3) |
| C(2)-C(3) 1.444(3) | C(2)-C(9) 1.452(2) |
| C(3)-C(5) 1.395(3) | C(3)-C(4) 1.405(3) |
| C(4)-N(1) 1.373(3) | C(4)-C(8) 1.390(3) |
| C(5)-C(6) 1.379(3) | C(6)-C(7) 1.391(3) |
| C(7)-C(8) 1.365(3) | C(9)-N(2) 1.292(2) |
| C(9)-C(10) 1.500(2) | C(11)-N(3) 1.294(2) |
| C(11)-C(14) 1.453(2) | C(11)-C(12) 1.502(2) |
| C(13)-N(4) 1.357(2) | C(13)-C(14) 1.376(2) |
| C(14)-C(15) 1.444(2) | C(15)-C(17) 1.400(2) |
| C(15)-C(16) 1.408(2) | C(16)-N(4) 1.374(2) |
| C(16)-C(20) 1.396(2) | C(17)-C(18) 1.383(3) |
| C(18)-C(19) 1.397(3) | C(19)-C(20) 1.375(3) |
| N(2)-N(3) 1.405(2) | N(2)-C(9)-C(2) 116.85(16) |
| N(2)-C(9)-C(10) 124.40(17) | C(2)-C(9)-C(10) 118.74(17) |
| N(3)-C(11)-C(14) 117.02(15) | N(3)-C(11)-C(12) 123.71(16) |
| C(14)-C(11)-C(12) 119.27(15) | C(1)-N(1)-C(4) 109.72(17) |
| C(9)-N(2)-N(3) 114.22(14) | C(11)-N(3)-N(2) 113.36(14) |

**Table S 12: Bond lengths [Å] and selected angles [°] of compound 12.**

|  |  |
| --- | --- |
| C(1)-O(1) 1.2183(17) | C(1)-N(1) 1.3573(17) |
| C(1)-C(2) 1.5225(18) | C(2)-N(2) 1.2870(17) |
| C(2)-C(3) 1.4558(18) | C(3)-C(5) 1.388(2) |
| C(3)-C(4) 1.4044(18) | C(4)-C(8) 1.3758(19) |
| C(4)-N(1) 1.3991(17) | C(5)-C(6) 1.385(2) |
| C(6)-C(7) 1.386(2) | C(7)-C(8) 1.391(2) |
| N(2)-N(2)#1 1.404(2) | C(2)-N(2)-N(2)#1 111.86(14) |
| #1 -x+1,-y,-z |



Figure S 1: 1H NMR spectrum of compound **3a**



Figure S 2: 13C NMR Spectrum of compound **3a**

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Figure S 3: 1H NMR Spectrum of compound **5b**

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Figure S 4: 13C NMR Spectrum of compound **5b**

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Figure S 5: 1H NMR Spectrum of compound **6a**

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Figure S 6: 13C NMR Spectrum of compound **6a**

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Figure S 7: 1H NMR Spectrum of compound **7b**

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Figure S 8: 13C NMR Spectrum of compound **7b**



Figure S 9: 1H NMR Spectrum of compound **10e**



Figure S 10: 1H NMR Spectrum of compound **10e**



Figure S 11: 13C NMR Spectrum of compound **10e**