Supporting Information
for
An unusual thionyl chloride-promoted C–C bond formation to obtain 4,4′-bipyrazolones

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Experimental details and compound characterization

1. General
Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). IR spectra (KBr pellets) were recorded on a PerkinElmer FTIR spectrum 1000 spectrophotometer and are reported in wave numbers (cm⁻¹). ¹H, ¹³C and ¹⁵N NMR spectra were recorded with a Bruker Avance III 400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, 40 MHz for ¹⁵N), a Bruker Avance 500 spectrometer (500 MHz for ¹H, 125 MHz for ¹³C, 50 MHz for ¹⁵N) and a Varian UnityPlus 300 spectrometer (300 MHz for ¹H, 75 MHz for ¹³C) at 297 K using “directly” detecting broadband observe (BBFO) probes. The center of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (¹H in CDCl₃), δ 2.49 ppm (¹H in DMSO-d₆), δ 77.0 ppm (¹³C in CDCl₃) and δ 39.5 ppm (¹³C in DMSO-d₆). ¹⁵N NMR spectra (gs-HMBC) were referenced against neat, external nitromethane. Digital resolutions were 0.2 Hz/data point in the ¹H NMR spectra and 0.3 Hz/data point in the ¹³C NMR spectra. For column chromatographic separations Merck Kieselgel 60 (70–230 mesh) was used. Light
petroleum refers to the fraction with boiling point 40–65 °C. Elemental analyses were performed at the Microanalytical Laboratory, University of Vienna. Yields are not optimized.

General procedure for the preparation of 5-hydroxypyrazole-4-carboxylates 1a–f

K₂CO₃ (1.38 g, 10 mmol; when the corresponding hydrazine hydrochloride was employed 2.76 g, 20 mmol K₂CO₃ were applied) was dissolved in 75 mL of H₂O and then the appropriate hydrazine (hydrochloride) (10 mmol) was added. Diethyl (ethoxymethylene)malonate (or dimethyl (methoxymethylene)malonate in the synthesis of 1b) (10 mmol) was added dropwise to the reaction mixture and the whole was refluxed for 2 h. Then the mixture was cooled to room temperature and extracted with 3 × 25 mL of EtOAc. For further procedure see below.

Ethyl 5-hydroxy-1-phenyl-1H-pyrazole-4-carboxylate (1a)

The aqueous phase was acidified with 6 N HCl to pH ≈ 2, the formed precipitate was filtered off, washed with water and recrystallized from aqueous EtOH. Yield: 1.97 g (85%), colorless crystals; mp 113 °C (aq EtOH) (lit. [1] mp: 118 °C). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 1.39 (t, ³J = 7.1 Hz, 3H, CH₃), 4.37 (q, ³J = 7.1 Hz, 2H, CH₂), 7.32 (m, 1H, Ph H-4), 7.46 (m, 2H, Ph H-3,5), 7.77 (s, 1H, H-3), 7.80 (m, 2H, Ph H-2,6), 9.40 (br s, 1H, OH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 14.3 (CH₃), 60.7 (CH₂), 95.1 (C-4), 121.3 (Ph C-2,6), 127.1 (Ph C-4), 129.1 (Ph C-3,5), 137.5 (Ph C-1), 138.4 (C-3), 156.7 (C-5), 166.4 (CO). ¹⁵N NMR (50 MHz, CDCl₃): δ (ppm) −185.1 (N-1), −100.8 (N-2).

Methyl 5-hydroxy-1-phenyl-1H-pyrazole-4-carboxylate (1b) [2]

The aqueous phase was acidified with 6 N HCl to pH ≈ 2, the formed precipitate was filtered off, washed with water and recrystallized from aqueous MeOH. Yield: 1.86 g (85%), brownish crystals; mp 158–159 °C (aq MeOH). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.90 (s, 3H, Me), 7.33 (m, 1H, Ph H-4), 7.47 (m, 2H, Ph H-3,5), 7.77 (s, 1H, H-3), 7.80 (m, 2H, Ph H-2,6), 9.70 (br s, 1H, OH). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 51.6 (CH₃), ¹J = 147.6 Hz, 94.9 (C-4, ²JC₄,H₃ = 9.7 Hz), 121.3 (Ph C-2,6), 127.1 (Ph C-4), 129.1 (Ph C-3,5), 137.5 (Ph C-1), 138.4 (C-3, ¹J = 191.6 Hz), 156.6 (C-5, ²JC₅,H₃ = 4.4 Hz), 166.7 (CO, ³JC₉,O,Me = 4.1 Hz). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −184.9 (N-1), −100.5 (N-2). MS: m/z (%) = 218 [M]+ (24), 186 (100), 118 (22), 91 (60), 77 (45). HRMS (ESI): calcd. for C₁₁H₁₁N₂O₃⁺ [M+H]+ 219.0764; found 219.0765.

Ethyl 1-(4-bromophenyl)-5-hydroxy-1H-pyrazole-4-carboxylate (1c)

From reaction of diethyl (ethoxymethylene)malonate (2.16 g, 10 mmol), (4-bromophenyl)-hydrazine hydrochloride (2.23 g, 10 mmol) and K₂CO₃ (2.76 g, 20 mmol). After acidification with 6N HCl to pH ≈ 2 the mixture was extracted with 3 × 20 mL of EtOAc, the combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was recrystallized from aqueous MeOH. Yield: 2.28 g (73%), yellowish crystals, mp 152–153 °C (aq MeOH) (lit. [3] 153–154 °C). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.39 (t, ³J = 7.1 Hz, 3H, CH₃), 4.37 (q, ³J = 7.1 Hz, 2H, CH₂), 7.58
(m, 2H, Ph H-3,5), 7.71 (m, 2H, Ph H-2,6), 7.76 (s, 1H, H-3), 9.88 (br s, 1H, OH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.3 (CH$_3$, $^1J = 127.3$ Hz, $^2J = 2.6$ Hz), 60.9 (CH$_2$, $^1J = 148.1$ Hz, $^2J = 4.5$ Hz), 95.3 (C-4, $^2J_{C4,H3} = 9.5$ Hz), 120.5 (Ph C-4), 122.5 (Ph C-2,6), 132.2 (Ph C-3,5), 136.6 (Ph C-1), 138.6 (C-3, $^1J = 191.8$ Hz), 156.8 (C-5, $^2J_{C5,H3} = 4.5$ Hz), 166.3 (CO). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$ (ppm) –166.9 (N-1), –101.5 (N-2). MS: $m/z$ (%) = 310/312 [M]$^+$ (8/9), 264/266 (98/100), 169/171 (26/24), 155/157 (20/19). HRMS (ESI): calced. for C$_2$H$_7$BrN$_2$O$_3$Na$^+$ [M+Na]$^+$ 332.9845; found 332.9847.

Ethyl 1-(3,4-dichlorophenyl)-5-hydroxy-1H-pyrazole-4-carboxylate (1d)

From reaction of diethyl (ethoxymethylenemalonate (2.16 g, 10 mmol), (3,4-dichlorophenyl)hydrazine hydrochloride (2.13 g, 10 mmol) and K$_2$CO$_3$ (2.76 g, 20 mmol). After acidification with 6N HCl to pH $\approx 2$ the formed precipitate was filtered off, washed with water and recrystallized from aqueous EtOH. Yield: 2.29 g (76%), yellow crystals, mp 152–154 °C (aq EtOH). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.39 (t, $^3J = 7.1$ Hz, 3H, CH$_3$), 4.38 (q, $^3J = 7.1$ Hz, 2H, CH$_2$), 7.52 (dd, $^3J = 0.3$ Hz, 1H, Ph H-5), 7.73 (dd, $^3J = 8.8$ Hz, $^1J = 2.5$ Hz, 1H, Ph H-6), 7.76 (s, 1H, H-3), 8.01 (dd, $^3J = 2.5$ Hz, $^2J = 0.3$ Hz, 1H, Ph H-2), 9.80 (br s, 1H, OH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.3 (CH$_3$, $^1J = 127.3$ Hz, $^2J_{CH3,CH2} = 2.6$ Hz), 61.0 (CH$_2$, $^1J = 148.2$ Hz, $^2J_{CH2,CH3} = 4.5$ Hz), 95.5 (C-4, $^2J_{C4,H3} = 9.6$ Hz), 119.8 (Ph-C6), 122.6 (Ph-C2), 130.7 (Ph C-5, $^1J = 169.4$ Hz), 130.7 (Ph C-4), 133.2 (Ph-C3), 136.9 (Ph-C1), 138.9 (C-3, $^1J = 192.1$ Hz), 157.0 (C-5, $^3J_{C5,H3} = 4.6$ Hz), 166.2 (CO, $^2J_{CO,CH2} = 3.2$ Hz). $^{15}$N NMR (50 MHz, CDCl$_3$): $\delta$ (ppm) –188.3 (N-1), –102.0 (N-2). IR (KBrs): 3415 (OH), 1711 (C=O) cm$^{-1}$. MS: $m/z$ (%) = 300/302/304 [M]$^+$ (9/6/1), 254/256/258 (100/78/9). HRMS (ESI): calced. for C$_2$H$_7$BrN$_2$O$_3$Na$^+$ [M+Na]$^+$ 322.9961; found 322.9962. Anal. Calcd for C$_2$H$_7$BrN$_2$O$_3$Na$^+$: C, 47.86; H, 3.35; N, 9.30, found: C, 47.96; H, 3.31; N, 9.28.

Ethyl 5-hydroxy-1-methyl-1H-pyrazole-4-carboxylate (1e)

Methylhydrazine (1.38 g, 30 mmol) was added to diethyl (ethoxymethylenemalonate (6.49 g, 30 mmol) in ethanol (50 mL) at 0 °C and the mixture was refluxed overnight. The solvent was removed under reduced pressure, the residue was washed with light petroleum and recrystallized from aqueous MeOH. Yield: 3.25 g (64%), colorless crystals, mp 134–135 °C (aq MeOH) (lit. [4] 138–139 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.33 (t, $^3J = 7.1$ Hz, 3H, CH$_3$), 3.64 (s, 3H, 1-Me), 4.29 (q, $^3J = 7.1$ Hz, 2H, CH$_2$), 7.56 (s, 1H, H-3), 7.98 (br s, 1H, OH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.3 (CH$_3$), 33.3 (1-Me), 60.3 (CH$_2$), 94.0 (C-4), 137.5 (C-3), 156.4 (C-5), 165.8 (CO). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$ (ppm) –202.4 (N-1), –100.0 (N-2).

Ethyl 1-tert-butyl-5-hydroxy-1H-pyrazole-4-carboxylate (1f)

From reaction of diethyl (ethoxymethylenemalonate (2.16 g, 10 mmol), tert-butylhydrazine hydrochloride (1.25 g, 10 mmol) and K$_2$CO$_3$ (2.76 g, 20 mmol). After acidification with 6 N HCl to pH $\approx 2$ the mixture was extracted with 3 × 20 mL of EtOAc, the combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under reduced pressure. Yield: 0.96 g (45%), colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.34 (t, $^3J = 7.1$ Hz, 3H, CH$_3$), 1.60 (s, 9H, CH$_3$), 4.31 (q, $^3J = 7.1$ Hz, 2H, CH$_2$), 7.52 (s, 1H, H-3), 9.50 (br s, 1H, OH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 14.4 (CH$_3$, $^1J = 127.1$ Hz, $^J_{CH3,CH2} = 2.6$ Hz), 28.5 (C(CH$_3$)$_3$), 59.4 (C(CH$_3$)$_3$), 60.3 (CH$_2$, $^1J = 147.8$ Hz, $^J_{CH2,CH3} = 4.5$ Hz), 94.6 (C-4, $^J_{C4,H3} = 9.7$ Hz), 135.7 (C-3, $^1J = 190.3$ Hz), 157.1 (C-5, $^3J_{C5,H3} = 4.3$ Hz), 166.7 (CO). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$ (ppm) –174.3 (N-1), –102.3 (N-2). MS: $m/z$ (%)
were present. The residual oil crystallized on standing. Recrystallization from cyclohexane/light petroleum afforded pink crystals, mp 98 °C (aq EtOH) (lit.[6] 114–115 °C). 

**Yield:** The title compound was obtained in 80% yield.

**Diethyl benzoylmalonate,** 2.64 g, 10 mmol was dissolved in 10 mL of acetic acid at room temperature. A solution of phenylhydrazine (4.33 g, 40 mmol) in 10 mL of 70% acetic acid was added dropwise. The reaction mixture was stirred for 2 days, during this time a precipitate formed. The precipitate was filtered off, washed with water and air dried to afford the title compound which was used in the next reaction step without further purification.

**Yield:** 2.76 g (90%), colorless crystals, mp 98–99 °C (lit.[7] 98 °C).

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**Yield:** 2.76 g (90%), colorless crystals, mp 98–99 °C (lit.[7] 98 °C).

**Ethyl 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carboxylate (1h).**

To a solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (13.94 g, 80 mmol) in dioxane (70 mL) was added ethyl chloroformate (8.68 g, 80 mmol) and the solvent was removed under reduced pressure. After refluxing for 45 min the mixture was cooled and 5% HCl (≈ 200 mL until pH ≈ 3) was added. The mixture was cooled and the precipitated crystals were filtered off. The dried crude product was recrystallized from EtOH/H₂O 4:1. Yield: 7.69 g (39%), pink crystals, mp 120–122 °C (aq EtOH) (lit.[6] 114–115 °C). 

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**Yield:** 2.76 g (90%), colorless crystals, mp 98–99 °C (lit.[7] 98 °C).

**Ethyl 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carboxylate (1h).**

To a solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (13.94 g, 80 mmol) in dioxane (70 mL) was added ethyl chloroformate (8.68 g, 80 mmol) and the solvent was removed under reduced pressure. After refluxing for 45 min the mixture was cooled and 5% HCl (≈ 200 mL until pH ≈ 3) was added. The mixture was cooled and the precipitated crystals were filtered off. The dried crude product was recrystallized from EtOH/H₂O 4:1. Yield: 7.69 g (39%), pink crystals, mp 120–122 °C (aq EtOH) (lit.[6] 114–115 °C). 

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**Ethyl 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carboxylate (1h).**

To a solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (13.94 g, 80 mmol) in dioxane (70 mL) was added ethyl chloroformate (8.68 g, 80 mmol) and the solvent was removed under reduced pressure. After refluxing for 45 min the mixture was cooled and 5% HCl (≈ 200 mL until pH ≈ 3) was added. The mixture was cooled and the precipitated crystals were filtered off. The dried crude product was recrystallized from EtOH/H₂O 4:1. Yield: 7.69 g (39%), pink crystals, mp 120–122 °C (aq EtOH) (lit.[6] 114–115 °C). 

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**Ethyl 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carboxylate (1h).**

To a solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (13.94 g, 80 mmol) in dioxane (70 mL) was added ethyl chloroformate (8.68 g, 80 mmol) and the solvent was removed under reduced pressure. After refluxing for 45 min the mixture was cooled and 5% HCl (≈ 200 mL until pH ≈ 3) was added. The mixture was cooled and the precipitated crystals were filtered off. The dried crude product was recrystallized from EtOH/H₂O 4:1. Yield: 7.69 g (39%), pink crystals, mp 120–122 °C (aq EtOH) (lit.[6] 114–115 °C). 

**Yield:** 7.69 g (39%), pink crystals, mp 120–122 °C (aq EtOH) (lit.[6] 114–115 °C).
afforded 1.71 g (74%) of colorless crystals, mp 77–78 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 1.29 (t, 3J = 7.1 Hz, 6H, CH3), 4.27 (dq, 2J = 10.7 Hz, 3J = 7.1 Hz, 2H, OCH2), 4.33 (dq, 3J = 10.7 Hz, 1J = 7.1 Hz, 2H, OCH2), 7.19 (m, 2H, Ph H-4), 7.35 (m, 4H, Ph H-3,5), 7.75 (m, 4H, Ph H-2,6), 8.14 (s, 2H, pyrazole H-3). 13C NMR (125 MHz, CDCl3): δ (ppm) 13.8 (CH3), 1J = 127.8 Hz, 2J_{CH3,CH2} = 2.6 Hz), 64.0 (CH2, 1J = 149.5 Hz, 2J_{CH2,CH3} = 4.4 Hz), 66.1 (pyrazole C-4, 2J_{CH3,CH2} = 9.6 Hz), 119.3 (Ph C-2,6), 126.1 (Ph C-4), 128.9 (Ph C-3,5), 137.0 (Ph C-1), 147.3 (pyrazole C-3, 1J = 209.6 Hz), 163.4 (ester CO, 3J_{CO,CH3} = 3.4 Hz), 163.9 (pyrazole C-5, 3J_{CH3,CH2} = 3.0 Hz). 15N NMR (50 MHz, CDCl3): δ (ppm) −192.3 (N-1), −42.8 (N-2). IR (KBr): 1714 (C=O), 1754 (ester CO) cm⁻¹. ESI-MS: m/z (%) = 463 [M+H]+ (100). Anal. Calcd for C24H22N4O6Na+: C, 62.33; H, 4.79; N, 12.12; found: C, 62.39; H, 4.89; N, 12.18. HRMS (ESI): calcd. for C24H22N4O6Na+: [M+Na]+ 485.1432; found 485.1431.

Dimethyl 5,5'-dioxo-1,1'-diphenyl-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3b)

The remaining residue was purified by column chromatography (SiO2, CH2Cl2/light petroleum 3:1, v/v). Yield: 1.93 g (89%), yellowish crystals, mp 132–134 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 3.85 (s, 6H, OCH3), 7.19 (m, 2H, Ph-4), 7.35 (m, 4H, Ph H-3,5), 7.75 (m, 4H, Ph H-2,6), 8.13 (s, 2H, H-5). 13C NMR (100 MHz, CDCl3): δ (ppm) 54.5 (OCH3, 1J = 148.2 Hz), 65.9 (pyrazole C-4, 2J_{CH3,CH2} = 9.7 Hz), 119.3 (Ph C-2,6), 126.1 (Ph C-4), 128.9 (Ph C-3,5), 137.0 (Ph C-1), 147.0 (pyrazole C-3, 1J = 209.6 Hz), 164.0 (ester CO, 3J_{CO,CH3} = 4.1 Hz), 163.7 (pyrazole C-5, 3J_{CH3,CH2} = 2.9 Hz). 15N NMR (40 MHz, CDCl3): δ (ppm) −191.9 (N-1), −42.0 (N-2). ESI-MS: m/z (%) = 435 [M+H]+ (100). HRMS (ESI): calcd. for C_{22}H_{18}N_{4}O_{6}Na+: [M+Na]+ 457.1119; found 457.1122.

Diethyl 1,1'-bis(4-bromophenyl)-5,5'-dioxo-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3c)

The remaining residue was thoroughly washed with n-hexane and dried in vacuo. Yield: 2.24 g (72%), yellowish crystals, mp 44–45 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 1.28 (t, 3J = 7.1 Hz, 6H, CH3), 4.28 (dq, 2J = 10.7 Hz, 3J = 7.1 Hz, 2H, OCH2), 4.35 (dq, 3J = 10.7 Hz, 1J = 7.1 Hz, 2H, OCH2), 7.47 (m, 2H, Ph H-3,5), 7.66 (m, 4H, Ph H-2,6), 8.12 (s, 2H, H-3). 13C NMR (100 MHz, CDCl3): δ (ppm) 13.8 (CH3, 1J = 127.8 Hz, 2J_{CH3,CH2} = 2.6 Hz), 64.2 (CH2, 1J = 149.7 Hz, 2J_{CH2,CH3} = 4.4 Hz), 66.1 (pyrazole C-4, 2J_{CH3,CH2} = 9.5 Hz), 119.2 (Ph C-4), 120.6 (Ph C-2,6), 132.0 (Ph C-3,5), 136.0 (Ph C-1), 147.6 (pyrazole C-3, 1J = 209.9 Hz), 163.1 (ester CO, 3J_{CO,CH3} = 3.4 Hz), 163.9 (C-5, 3J_{CH3,CH2} = 2.9 Hz). 15N NMR (40 MHz, CDCl3): δ (ppm) −193.5 (N-1), −43.8 (N-2). ESI-MS: m/z (%) = 621 [M+H]+ (33), 540 (29), 500 (430), 499 (92), 482 (31), 484 (100), 321 (95). HRMS (ESI): calcd. for C_{24}H_{20}Br_{2}N_{4}O_{6}Na+: [M+Na]+: 640.9642; found: 640.9630.

Diethyl 1,1'-bis(3,4-dichlorophenyl)-5,5'-dioxo-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3d)

The remaining residue was purified by column chromatography (SiO2, CH2Cl2/light petroleum 7:3, v/v). Yield: 1.86 g (62%), colorless crystals, mp 51–54 °C. 1H NMR (300 MHz, CDCl3): δ (ppm) 1.30 (t, 3J = 7.1 Hz, 6H, CH3), 4.28 (dq, 2J = 10.8 Hz, 3J = 7.1 Hz, 2H, OCH2), 4.35 (dq, 3J = 10.8 Hz, 1J = 7.1 Hz, 2H, OCH2), 7.41 (d, 3J = 8.9 Hz, 2H, Ph H-5),
7.68 (dd, $^3J = 8.9$ Hz, $^4J = 2.6$ Hz, 2H, Ph H-6), 7.97 (d, $^4J = 2.6$ Hz, 2H, Ph H-2), 8.14 (s, 2H, pyrazole H-3). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) 13.9 (CH$_3$), $^1J = 127.8$ Hz, $^2J_{CH,CH} = 2.6$ Hz), 64.4 (OCH$_2$), $^1J = 149.8$ Hz, $^2J_{CH2,CH3} = 4.4$ Hz), 66.2 (pyrazole C-4, $^2J_{CH3H} = 9.6$ Hz), 117.9 (Ph C-6), 120.6 (Ph C-2), 129.6 (Ph C-4), 130.6 (Ph C-5), 133.0 (Ph C-3), 136.2 (Ph C-1), 147.8 (pyrazole C-3, $^1J = 210.3$ Hz), 162.8 (ester CO), $^3J_{CO,CH2} = 3.4$ Hz), 163.9 (pyrazole C-5, $^3J_{CS,CH3} = 3.0$ Hz). $^{15}$N NMR (50 MHz, CDCl$_3$): $\delta$ (ppm) $-194.5$ (N-1), $-44.7$ (N-2). IR (KBr): 1717 (C=O), 1750 (ester CO) cm$^{-1}$. ESI-MS: $m/z$ (%) = 601 [M+H]$^+$ (100), 598 (78). Anal. Calcd for C$_{24}$H$_{18}$Cl$_2$N$_4$O$_6$Na: C, 48,02; H, 3,02; N, 9,33; found: C, 48,11; H, 3,04; N, 9.25. HRMS (ESI): calcd. for C$_{24}$H$_{18}$Cl$_2$N$_4$O$_6$Na$^+$ [M+Na]$^+$:620.9873; found: 620.9868.

Diethyl 1,1'-dimethyl-5,5'-dioxo-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3e).

The remaining residue was purified by column chromatography (SiO$_2$, EtOAc/light petroleum = 1:1, v/v). Yield: 1.124 g (66%) colorless crystals, mp 129−130 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.25 (t, $^3J = 7.1$ Hz, 6H, CH$_3$), 3.27 (s, 6H, 1-Me), 4.21 (dd, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 2H, OCH$_2$), 4.23 (dq, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 2H, OCH$_2$), 7.83 (s, 2H, H-3). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 13.8 (CH$_3$), $^1J = 127.7$ Hz, $^2J_{CH,CH2} = 2.7$ Hz), 31.8 (1-Me, $^1J = 140.8$ Hz), 63.6 (OCH$_2$), $^1J = 149.4$ Hz, $^2J_{CH2,CH3} = 4.4$ Hz), 64.4 (pyrazole C-4, $^2J_{CH3H} = 9.7$ Hz), 146.7 (pyrazole C-3, $^1J = 209.1$ Hz), 163.6 (ester CO, $^3J_{CO,CH2} = 3.4$ Hz), 165.8 (pyrazole C-5, $^3J_{CS,CH3} = 2.8$ Hz, $^3J_{CS,NCH3} = 2.3$ Hz). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$ (ppm) $-209.4$ (N-1), $-40.0$ (N-2). ESI-MS: $m/z$ (%) = 339 [M+H]$^+$ (100). HRMS (ESI): calcd. for C$_{14}$H$_{18}$N$_4$O$_6$Na$^+$ [M+Na]$^+$:361.1119; found 361.1121.

Diethyl 1,1'-di-tert-butyl-5,5'-dioxo-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3f).

The remaining residue was thoroughly washed with n-hexane. Yield: 1.33 g (63%) colorless crystals, mp 80−81 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.23 (t, $^3J = 7.1$ Hz, 6H, ester CH$_3$), 1.44 (s, 18H, CH$_3$), 4.10−4.35 (m, 4H, CH$_2$), 7.71 (s, 2H, pyrazole H-3). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 13.8 (ester CH$_3$), $^1J = 127.6$ Hz, $^2J_{CH,CH2} = 2.7$ Hz), 27.8 (CH$_3$), $^1J = 127.6$ Hz, $^2J_{CH,CH2} = 3.4$ Hz), 58.3 (C(CH$_3$)$_3$), 63.1 (OCH$_2$), $^1J = 149.2$ Hz, $^2J_{CH2,CH3} = 4.4$ Hz), 65.8 (pyrazole C-4, $^2J_{CH3H} = 9.7$ Hz), 145.1 (pyrazole C-3, $^1J = 208.2$ Hz), 164.0 (ester CO, $^3J_{CO,CH2} = 3.3$ Hz), 165.9 (pyrazole C-5, $^3J_{CS,CH3} = 2.8$ Hz). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$ (ppm) $-184.2$ (N-1), $-40.1$ (N-2). MS: $m/z$ (%) = 422 [M]$^+$ (9), 407 (18), 231 (16), 166 (33), 165 (30), 151 (30), 111 (37), 110 (65), 57 (100), 56 (21), 41 (40). HRMS (ESI): calcd. for C$_{20}$H$_{30}$N$_4$O$_6$Na$^+$ [M+Na]$^+$: 445.2058; found: 445.2063.

Diethyl 1,1'-dibenzyl-5,5'-dioxo-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3g).

The remaining residue was recrystallized from aqueous EtOH. Yield: 2.06 g (84%) colorless crystals, mp 106−107 °C (aq EtOH). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.18 (t, $^3J = 7.1$ Hz, 6H, CH$_3$), 4.18 (dd, $^2J = 10.7$ Hz, $^3J = 7.1$ Hz, 2H, OCH$_2$), 4.21 (dd, $^2J = 10.7$ Hz, $^3J = 7.1$ Hz, 2H, OCH$_2$), 4.66 (A-part of an AB-system, $^2J_{AB} = 15.2$ Hz, 2H, NCH$_2$), 4.80 (A-part of an AB-system, $^2J_{AB} = 15.2$ Hz, 2H, NCH$_2$), 7.23 (m, 4H, Ph H-2,6), 7.29 (m, 6H, Ph H-3,4,5), 7.86 (s, 2H, pyrazole H-3). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 13.7 (CH$_3$), $^1J = 127.7$ Hz, $^2J_{CH,CH2} = 2.6$ Hz), 48.4 (NCH$_2$), $^1J = 140.8$ Hz), 63.6 (OCH$_2$), $^1J = 149.4$ Hz, $^2J_{CH2,CH3} = 4.4$ Hz), 64.0 (pyrazole C-4, $^2J_{CH3H} = 9.8$ Hz), 127.77 (Ph C-3,6), 127.79 (Ph C-4), 128.5 (Ph C-3,5), 135.5 (Ph C-1), 146.7 (pyrazole C-3, $^1J = 209.2$ Hz), 163.6 (ester CO, $^3J_{CO,CH2} = 3.3$ Hz), 165.6 (pyrazole C-5, $^3J_{CS,CH3} = 2.7$ Hz, $^3J_{CS,NCH3} = 2.7$ Hz). $^{15}$N NMR (40 MHz, CDCl$_3$): $\delta$.
Diethyl 3,3'-dimethyl-5,5'-dioxo-1,1'-diphenyl-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3h)

The residue was purified by column chromatography (SiO₂, EtOAc/light petroleum = 7:3, v/v). Yield: 1.79 g (73%), colorless crystals, mp 56–57 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.30 (t, ³J = 7.1 Hz, 6H, CH₃), 2.55 (s, 6H, 3-Me), 4.25 (dq, ³J = 10.7 Hz, ³J = 7.1 Hz, 2H, OCH₂), 4.38 (dq, ²J = 10.7 Hz, ³J = 7.1 Hz, 2H, OCH₂), 7.15 (m, 2H, Ph H-4), 7.32 (m, 4H, Ph H-3,5), 7.73 (m, 4H, Ph H-2,6). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 13.9 (CH₃), 127.6 Hz, ²JCH₃,CH₂ = 2.6 Hz), 19.4 (3-Me, ¹J = 130.8 Hz), 63.4 (OCH₂, ¹J = 149.3 Hz, ²JCH₂,CH₃ = 4.4 Hz), 67.8 (pyrazole C-4), 7.15 (m, 2H, NPh H-1), −57.8 (N-1), −54.1 (N-2). IR (KBr): 1716 (C=O), 165.6 (CO), 1753 (ester CO), 3423 (OH). Yield: 2 g (64%). Anal. Calcd for C₃₆H₄₅N₅O₅: C, 63.75; H, 5.28; N, 11.52. HRMS (ESI): calcd. for C₃₆H₄₅N₅O₅ [M+H]⁺ 641.1925: found 641.1925.

Diethyl 5,5'-dioxo-1,1',3,3'-tetraphenyl-1,1',5,5'-tetrahydro-4H,4'H-[4,4'-bipyrazole]-4,4'-dicarboxylate (3i)

The remaining residue was thoroughly washed with n-hexane and dried in vacuo. Yield: 2.30 g (75%), colorless crystals, mp 66–68 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.28 (t, ³J = 7.1 Hz, 6H, CH₃), 4.38 (q, ³J = 7.1 Hz, 4H, OCH₂), 7.15 (m, 2H, NPh H-4), 7.16 (m, 2H, CPh H-4), 7.19 (m, 4H, CPh H-3,5), 7.27 (m, 4H, NPh H-3,5), 7.55 (m, 4H, NPh H-2,6), 7.67 (m, 4H, CPh H-2,6). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 13.7 (CH₃), 63.5 (OCH₂), 65.0 (pyrazole C-4), 119.1 (NPh C-2,6), 125.6 (NPh C-4), 128.2 (CPh C-3,5), 128.3 (CPh C-2,6), 128.4 (NPh C-3,5), 130.20 (CPh C-1), 130.22 (CPh C-4), 136.8 (NPh C-1), 153.0 (pyrazole C-3), 162.1 (ester CO), 165.6 (pyrazole C-5). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −189.9 (N-1), −53.7 (N-2). MS: m/z (%): 614 [M+Na]⁺ (12), 307 (61), 263 (23), 262 (100), 233 (79), 129 (31), 91 (41), 77 (100). HRMS (ESI): calcd. for C₃₆H₃₀N₄O₅Na⁺ [M+Na]⁺ 637.2058; found 637.2057.

5-Hydroxy-1-phenyl-1H-pyrazole-4-carboxyrazide (5)

A suspension of ethyl 5-hydroxy-1-phenyl-1H-pyrazole-4-carboxylate (1a) (2.32 g, 10 mmol) in 5 mL of 85% hydrazine hydrate was heated at 105° for 4 h. After evaporation of the solvents under reduced pressure a yellowish, viscous oil was obtained which was purified by column chromatography (SiO₂, CH₂Cl₂). Yield: 1.40 g (64%), yellow crystals, mp 38–40 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.86 (br s together with H₂O, NH₂), 6.97 (m, 1H, Ph H-4), 7.27 (m, 2H, Ph H-3,5), 7.44 (s, 1H, pyrazole H-3), 8.08 (m, 2H, Ph H-2,6), 9.16 (s, 1H, NH). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 93.9 (C-4), 117.7 (Ph C-2,6), 122.1 (Ph C-4), 128.2 (Ph C-3,5), 139.4 (pyrazole C-3), 141.6 (Ph C-1), 164.0 (pyrazole C-5), 166.1 (CO). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −332.0 (NH₂), −264.8 (NH), −184.4 (N-1), −98.4 (N-2). HRMS (ESI): calcd. for C₁₀H₁₀N₄O₂Na⁺ [M+Na]⁺ 241.0696; found 241.0695.
4-Chloro-4-(dichloromethyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (7).

The corresponding 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde (6) (2.02 g, 10.0 mmol) [8] and SOCl₂ (7.25 mL, 11.9 g, 100 mmol) were heated under reflux for 3 h. Then the excess SOCl₂ was removed under reduced pressure, toluene (ca. 10 mL) was added, and the solvent was removed under reduced pressure. The remaining residue was washed with n-hexane and dried in vacuo. Yield: 0.68 g (23%) yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 2.43 (s, 1H, 5-Me), 5.99 (s, 1H, CHCl₂), 7.25 (m, 1H, Ph H-4), 7.43 (m, 2H, Ph H-3,5), 7.86 (m, 2H, Ph H-2,6), 13C NMR (100 MHz, CDCl₃): δ (ppm) 15.1 (5-Me), 66.5 (C-4), 70.0 (CHCl₂), 119.0 (Ph C-2,6), 126.1 (Ph C-4), 129.1 (Ph C-3,5), 136.9 (Ph-1), 154.8 (C-5), 165.9 (C-3). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −197.6 (N-2), −55.9 (N-1). MS: m/z (%) = 290/292/294/296 [M]+ (23/22/6/1), 207 (57), 77 (100), 51 (33). HRMS (ESI): calcd. for C₁₁H₉Cl₃N₂O⁺ [M+Na]+ 312.9673; found: 312.9665.

Reaction of 1a with sulfuryl chloride

Ethyl 5-hydroxy-1-phenyl-1H-pyrazole-4-carboxylate (1a) (0.65 g, 2.8 mmol) was added to sulfuryl chloride (4.04 mL, 50 mmol) and the solution was refluxed for 3 h. The reaction mixture was cooled and 10 mL of toluene was added. The solvent was evaporated under reduced pressure and the residue was subjected to flash chromatography (CH₂Cl₂/light petroleum = 1:1, v/v).

Ethyl 4-chloro-1-(4-chlorophenyl)-5-oxo-4,5-dihydro-1H-pyrazole-4-carboxylate (8)

Yield: 228 mg (27%), yellowish crystals, mp 42–43 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.32 (t, 3J = 7.1 Hz, 3H, CH₃), 4.35 (q, 3J = 7.1 Hz, 2H, OCH₂), 7.40 (m, 2H, Ph H-3,5), 7.51 (s, 1H, H-3), 7.82 (m, 2H, Ph H-2,6). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 13.9 (CH₃), 63.3 (pyrazole C-4), 64.7 (OCH₂), 120.1 (Ph C-2,6), 129.2 (Ph C-3,5), 131.6 (Ph C-4), 135.5 (Ph C-1), 145.8 (pyrazole C-3), 161.1 (ester CO), 164.4 (pyrazole C-5). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −197.5 (N-1), −44.3 (N-2). MS: m/z (%) = 300/302/304 [M]+ (5/3/0.5), 198 (32), 196 (32), 139 (26), 113 (21), 111 (65), 107 (28), 97 (34), 85 (28), 83 (24), 79 (44), 77 (33), 75 (40), 71 (54), 69 (41), 67 (25), 63 (26), 62 (23), 57 (100), 56 (25), 55 (64), 53 (33), 51 (24), 50 (23), 43 (76), 41 (50). HRMS (ESI): calcd. for C₁₂H₁₀Cl₂N₂O⁺[M+Na]+ 322.9961; found 322.9969.

4,4-Dichloro-2-(4-chlorophenyl)-2,4-dihydro-3H-pyrazol-3-one (9)

Yield: 266 mg (36%), light red crystals, mp 38–40 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.41 (m, 2H, Ph H-3,5), 7.63 (s, 1H, pyrazole H-3), 7.80 (m, 2H, Ph H-2,6). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 70.7 (pyrazole C-4), 120.0 (Ph C-2,6), 129.3 (Ph C-3,5), 131.8 (Ph C-4), 135.1 (Ph C-1), 146.8 (pyrazole C-3), 163.2 (pyrazole C-5). ¹⁵N NMR (40 MHz, CDCl₃): δ (ppm) −203.5 (N-1), −54.9 (N-2). MS: m/z (%) = 262/264/266/268 [M]+ (32/31/10/1), 229 (29), 227 (44), 200 (22), 198 (70), 196 (72), 139 (41), 132 (26), 113 (33), 111 (100), 97 (37), 79 (38), 77 (30), 75 (48), 63 (31), 62 (32), 61 (21), 60 (21), 51 (27), 50 (31), 43 (24).

General procedure for the preparation of pyrazoles 10

A suspension of diester 3 (2.0 mmol), EtOH (5 mL), and 35% aq KOH (5 mL) was refluxed for 3 h. The deep colored solution was concentrated under reduced pressure and acidified with
conc. HCl. Then the solution was cooled in the refrigerator for 30 min, the formed precipitate was filtered off, washed with water (3 x 10 mL) and dried.

1,1'-Diphenyl-1H,1'H-[4,4'-bipyrazole]-5,5'-dial (10a) [9]

Yield: 0.59 g (93%), reddish crystals; mp 191–202 °C. [1H NMR (300 MHz, DMSO-d6): δ (ppm) 3.73 (br s, OH, together with trace H2O), 7.31 (m, 2H, Ph H-4), 7.50 (m, 4H, Ph H-3.5), 7.75 (m, 4H, Ph H-2.6), 7.96 (s, 2H, pyrazole H-3). 13C NMR (75 MHz, DMSO-d6): δ (ppm) 97.5* (C-4), 120.8 (Ph C-2.6), 126.2 (Ph C-4), 129.1 (Ph C-3.5), 136.9 (Ph C-1), 133.7* (C-3), 155.4* (C-5); *broad or very broad signal. IR (KBr): 3406 cm⁻¹. MS: m/z (%) = 318 [M+] (52), 97 (75), 77 (100). Anal. Calcd for C18H14N4O2: 0.4 H2O; C, 66.41; H, 4.58; N, 17.21. Found: C, 66.14; H, 4.38; N, 16.98. HRMS (ESI): calcd. for C18H14N4O2+ [M+H]+ 319.1190; found 319.1191.

1,1'-Bis(4-bromophenyl)-1H,1'H-[4,4'-bipyrazole]-5,5'-dial (10c)

Yield: 0.62 g (65%); reddish crystals; mp 270–290 °C. [1H NMR (400 MHz, DMSO-d6): δ (ppm) 7.68 (m, 4H, Ph H-3.5), 7.73 (m, 4H, Ph H-2.6), 7.97 (s, 2H, pyrazole H-3). 13C NMR (100 MHz, DMSO-d6): δ (ppm) 97.3 (C-4), 118.4 (Ph C-4), 122.3 (Ph C-2.6), 132.0 (Ph C-3.5), 134.4 (C-3, J = 187.5 Hz), 136.3 (Ph C-1), 155.6 (C-5). 15N NMR (40 MHz, DMSO-d6): δ (ppm) -196.2 (N-1); N-2 was not found. ESI-MS: m/z (%) = 477 [M+H]+ (100), 475 (47). HRMS (ESI): calcd. for C18H13Br2N4O2+ [M+H]+ 474.9400; found 474.9401.

1,1'-Bis(3,4-dichlorophenyl)-1H,1'H-[4,4'-bipyrazole]-5,5'-dial (10d)

Yield: 0.84 g (92%); reddish crystals; mp 228–230 °C. [1H NMR (300 MHz, DMSO-d6): δ (ppm) 7.50 (br s, 2H, OH), 7.70 (d, 3J = 8.9 Hz, 2H, Ph H-5), 7.80 (dd, 3J = 8.9 Hz, 4J = 2.4 Hz, 2H, Ph H-6), 7.99 (s, 2H, pyrazole H-3), 8.04 (d, 4J = 2.4 Hz, 2H, Ph H-2). 13C NMR (75 MHz, DMSO-d6): δ (ppm) 97.4 (C-4), 119.7 (Ph C-6), 121.2 (Ph C-2), 127.8 (Ph C-4), 130.9 (Ph C-5), 131.4 (Ph C-3), 135.0 (C-3, J = 188.0 Hz), 136.7 (Ph C1), 155.7 (C-5). 15N NMR (50 MHz, DMSO-d6): δ (ppm) -197.8 (N-1); N-2 was not found. IR (KBr): 3425 (OH) cm⁻¹. MS: m/z (%) = 459 (45), 457 [M+H]+ (100), 455 (75), 255 (42). HRMS (ESI): calcd. for C18H11Cl4N4O2+ [M+H]+ 454.9631; found 454.9626.

3,3'-Dimethyl-1,1'-diphenyl-1H,1'H-[4,4'-bipyrazole]-5,5'-dial (10h)

Yield: 0.60 g, 87%; reddish crystals; mp 290–330 °C. (lit. [10] mp > 300 °C). [1H NMR (300 MHz, DMSO-d6): δ (ppm) 2.16 (s, 6H, 3-Me), 7.21 (m, 2H, Ph H-4), 7.44 (m, 4H, Ph H-3.5), 7.78 (m, 4H, Ph H-2.6), 11.40 (br s, 2H, OH). 13C NMR (75 MHz, DMSO-d6): δ (ppm) 13.3* (3-Me), 95.0* (C-4), 119.9* (Ph C-2.6), 124.9* (Ph C-4), 128.8* (Ph C-3.5), 138.1* (Ph C-1), 146.8* (C-3); C-5 was not found; *broad or very broad signal. IR (KBr): 3426 (OH) cm⁻¹. MS (ESI): m/z (%) = 348 (26), 347 [M+H]+ (100). Anal. Calcd for C20H18N4O2: 0.5 H2O; C, 67.59; H, 5.39; N, 15.76; found: C, 67.78; H, 5.18; N, 15.79. HRMS (ESI): calcd. for C20H19N4O2+ [M+H]+ 347.1503; found 347.1504.
X-ray analysis of compound 3a

The X-ray intensity data was measured on a Bruker-Nonius KappaCCD diffractometer equipped with graphite monochromator, Mo K/α INCOATEC micro focus sealed tube and Cryostream 700 cooling device. The structure was solved by direct method and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fitted to the peaks of the difference synthesis as well as calculated geometrically and refined with a riding model. The following software was used: DENZO and HKL SCALEPEAK software package [11] using a narrow-frame algorithm for frame integration, no absorption correction due to small absorption coefficient, SIR-92 [12] for structure solution, refinement molecular diagrams and graphical user-interface, maXus [13] for refinement and graphical user-interface, Platon [14] for symmetry check and Cg(Pi-Ring) interactions calculations. Experimental data and CCDC-code can be found in Table S1. Crystal data, data collection parameters, and structure refinement details are given in Tables S2 and S3. Molecular structure in “Ortep View” is displayed in Figure S1 and arrangement of enantiomers in the crystal is displayed in Figure S2.

**Table S1:** Experimental parameter and CCDC-Code.

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**Figure S1:** Asymmetric unit of compound 3a (4S,4'S enantiomer), drawn with 50% displacement ellipsoids.
Figure S2: Arrangement of enantiomers $4R,4'R$ and $4S,4'S$ in the crystal of 3a, drawn with 50% displacement ellipsoids.

Table S2: Sample and crystal data of compound 3a.

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</tr>
<tr>
<td>Abs. correction type</td>
<td>no absorption correction</td>
<td>F(000) [e$^{-}$]</td>
<td>484</td>
</tr>
</tbody>
</table>

Table 3. Data collection and structure refinement of compound 3a.

<table>
<thead>
<tr>
<th>Index ranges</th>
<th>-13 ≤ h ≤ 14, -13 ≤ k ≤ 14, -12 ≤ l ≤ 15</th>
<th>Theta range for data collection [$^\circ$]</th>
<th>2.0 to 28.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflections number</td>
<td>5319</td>
<td>Data / restraints / parameters</td>
<td>4245/0/307</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Least squares matrix: full</td>
<td>Final R indices</td>
<td>all data</td>
</tr>
<tr>
<td>Function minimized</td>
<td>$\Sigma w(F_o^2 - F_c^2)^2$</td>
<td></td>
<td>R1 = 0.068, wR2 = 0.294</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.028</td>
<td></td>
<td>l&gt;3$\sigma$(l)</td>
</tr>
<tr>
<td>Largest diff. peak and hole [e Å$^3$]</td>
<td>0.48/-0.53</td>
<td>Weighting scheme</td>
<td>w=1/($\sigma^2(F_o^2)+0.10000F_c^2$)</td>
</tr>
</tbody>
</table>


References


