



Supporting Information: experimental procedures and spectroscopic data for compounds 1, 2, 3a, 3b, 5, 9a, 9b, 10, 11, 12a, 12b, 13a, 13b, 14, 18-23.

1-(4-Nitrophenyl)-3-Isopropyl-4-ethylpyrazole (3a) and 1-(4-nitrophenyl)-3-ethyl-5-isopropylpyrazole (3b). To a solution of 2-isopropyl-4-ethylpyrazole (**3**) (11.3 g, 82.0 mmol) in dry DMSO (30 mL) was added *tert*-BuOK (10.0 g, 89.9 mmol) under nitrogen. After 10 min, 4-fluoronitrobenzene (9.1 mL, 86.0 mmol) was added. The mixture was heated to 75°C and kept at this temperature for 1 hour, it was then cooled to room temperature and quenched with water and extracted with ethyl acetate. The extract was dried over MgSO₄ and filtered. The filtrate was concentrated and the residue was chromatographed on silica gel (hexane/ethyl acetate, 15:1) to give pyrazole **3a** (9.27 g, 44%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) 8.32, 7.69 (ABq, J = 9.0 Hz, 4 H, ArH), 6.17 (s, 1 H, py H-4), 3.03 (m, 1 H, CH(CH₃)₂), 2.78 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.33 (d, J = 6.5 Hz, 6 H, CH(CH₃)₂), 1.30 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 161.4, 146.6, 146.0, 145.7, 125.0, 124.4, 104.5, 28.4, 23.0, 20.9, 13.4. MS m/e 260 (100, MH⁺). HRMS calcd for C₁₄H₁₇N₃O₂ 259.1321, found 259.1319. Continuous elution (hexane/ethyl acetate, 10:1) yielded pyrazole **3b** (9.10 g, 43%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) 8.34, 7.66 (ABq, J = 9.0 Hz, 4 H, ArH), 6.16 (s, 1 H, py H-4), 3.15 (m, 1 H, CH(CH₃)₂), 2.70 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.30 (t, J = 7.5 Hz, 3 H, CH₂CH₃), 1.25 (d, J = 6.5 Hz, 6 H, CH(CH₃)₂). ¹³C NMR (400 MHz, CDCl₃) 156.9, 151.9, 146.4, 145.8, 125.5, 125.0, 103.9, 26.1, 23.5, 21.0, 14.0. MS m/e 260 (100, MH⁺). HRMS calcd for C₁₄H₁₇N₃O₂ 259.1321, found 259.1320.

2-(Tetrahydropyran-2-yloxy)methyl-4-ethylpyrazole (5). To a solution of 1-(tetrahydropyran-2-yloxy)-2-hexyn-4-one (28.4 g, 0.14 mol) in THF (200 mL) was added hydrazine monohydrate (8.3 mL, 0.17 mol) at 0°C and the mixture was stirred at room temperature overnight. The solution was then concentrated and the residue was taken up in ethyl acetate and washed with water. The organic was dried over Na₂SO₄ and concentrated to give pyrazole **5** as a colorless oil. (28.0 g, 93%). ¹H NMR (400 MHz, CDCl₃) 11.96 (bs, 1 H, NH), 6.08 (s, 1 H, H-4), 4.76, 4.57 (ABq, J = 8.1 Hz, 2 H, OCH₂), 4.73 (m, 1 H, OCHO), 3.91 (m, 1 H, OCH₂), 3.53 (m, 1 H, OCH₂), 2.67 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.88-1.50 (m, 6 H, (CH₂)₃), 1.25 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 102.9, 98.2, 62.5, 62.2, 32.0, 30.9, 25.8, 23.0, 20.2, 19.7, 14.5, 13.9. MS m/e 211 (100, MH⁺). HRMS calcd for C₁₁H₁₈N₂O₂ 210.1368, found 210.1369.

1-(4-Nitrophenyl)-3-hydroxymethyl-5-ethylpyrazole (12a). To a solution of pyrazole **5** (270 g, 1.29 mol) in dry THF (2500 mL) was added *tert*-BuOK (144 g, 1.30 mol) under nitrogen. After 10 min, 4-fluoronitrobenzene (181 g, 0.13 mol) was added. The mixture was heated to reflux for 10 hour, the solvent was then removed under vacuum. The residue was taken up in ethyl acetate and washed with water. The organic was dried over MgSO₄ and filtered. The filtrate was treated with active carbon (3.0 g, Notrit, Neutral) at reflux for 10 min and filtered through a pad of Celite. The filtrate was concentrated to give a crude 7:1 mixture of **5a** and **5b**, which was dissolved in 10:1 mixture of methanol and water (175 mL) and *p*-toluenesulfonic acid (1.2 g, 6.4 mmol) was added. The solution was stirred at room temperature for 12 hours and concentrated. The residue was taken up in ethyl acetate and washed with water. The organic was dried over MgSO₄,

filtered and concentrated to a crude solid. Recrystallization from hexane/ethyl acetate gave **12a** (156 g, 45%). mp: 151-152°C. ¹H NMR (400 MHz, CDCl₃) 8.38, 7.70 (ABq, J = 9.0 Hz, 4 H, ArH), 6.37 (s, 1 H, py H-4), 4.78 (s, 2 H, CH₂OH), 2.81 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.33 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 154.4, 147.4, 146.6, 145.2, 125.2, 124.9, 105.7, 59.4, 20.8, 13.4. MS m/e 248 (100, M⁺+H). Anal. calcd for C₁₂H₁₃N₃O₃: C, 58.29; H, 5.30; N, 16.99. found: C, 58.46; H, 5.25; N, 16.99. A small amount of minor isomer, 1-(4-Nitrophenyl)-3-ethyl-5-hydroxymethylpyrazole (**12b**), was isolated from the mother liquor. mp: 107-108°C. ¹H NMR (400 MHz, CDCl₃) 8.37; 7.98 (ABq, J = 9.0 Hz, 4 H, ArH), 6.40 (s, 1 H, py H-4), 4.75 (s, 2 H, CH₂OH), 2.76 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 2.05 (bs, 1 H, OH), 1.34 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 157.1, 146.2, 145.0, 143.1, 125.2, 123.7, 109.1, 55.6, 21.8, 14.0. MS m/e 248 (100, MH⁺). Anal. calcd for C₁₂H₁₃N₃O₃: C, 58.29; H, 5.30; N, 16.99. found: C, 58.48; H, 5.28; N, 16.93.

1-(4-Aminophenyl)-3-methyl-5-ethylpyrazole (2). To a solution of **12a** (50.0 g, 0.20 mol) in acetic acid (300 mL) was added 10% Pd/C (5.0 g, 50% wet) and concentrated HCl (2 mL). The mixture was subjected to par-shaker under 40 psi H₂ overnight. It was then filtered through a pad of *Celite* and the filtrate was concentrated. The residue was taken up in ethyl acetate and washed with aqueous Na₂CO₃ and water, dried over MgSO₄ and concentrated a crude solid. Recrystallization from a hexane/ethyl acetate to give **2** (37 g, 92%) as a white solid. mp: 101-102°C. ¹H NMR (400 MHz, CDCl₃) 7.14, 6.68 (ABq, J = 9.0 Hz, 4 H, ArH), 5.96 (s, 1 H, py H-4), 3.50 (bs, 2 H, NH₂), 2.55 (q, J = 7.7 Hz, 2 H, CH₂CH₃), 2.29 (s, 3H, CH₃), 1.16 (t, J = 7.7 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 148.2, 146.0, 131.2, 126.8, 115.0, 103.9, 19.5, 13.6, 13.2. MS m/e 202 (100, MH⁺). Anal. calcd for C₁₂H₁₅N₃: C, 71.61; H, 7.51. found: C, 71.50; H, 7.57.

1-(4-Nitrophenyl)-3-(1-hydroxyethyl)-5-ethylpyrazole (9a). The procedure described for **9a** was used. Yield: 62%. mp: 127-128°C. ¹H NMR (400 MHz, CDCl₃) 8.38, 7.71 (ABq, J = 8.8 Hz, 4 H, ArH), 6.33 (s, 1 H, py H-4), 5.03 (q, J = 6.5 Hz, 1 H, CHOH), 2.81 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 2.36 (bs, 1 H, OH), 1.61 (d, J = 6.5 Hz, 3H, CHCH₃), 1.34 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 158.7, 147.3, 146.4, 145.3, 125.1, 124.8, 104.0, 65.2, 23.7, 20.9, 13.4. MS m/e 262 (100, MH⁺). Anal. calcd for C₁₃H₁₅N₃O₃: C, 59.76; H, 5.79; N, 16.09. found: C, 59.96; H, 5.70; N, 15.96. A small amount of minor isomer, 1-(4-Nitrophenyl)-3-ethyl-5-(1-hydroxyethyl)pyrazole (**9b**), was isolated from the mother liquor. mp: 140-141°C. ¹H NMR (400 MHz, CDCl₃) 8.37, 7.96 (ABq, J = 9.0 Hz, 4 H, ArH), 6.41 (s, 1 H, py H-4), 4.92 (q, J = 6.5 Hz, 1 H, CHOH), 2.75 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.67 (d, J = 6.5 Hz, 3H, CHCH₃), 1.33 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 156.9, 147.5, 146.4, 145.2, 105.4, 61.6, 23.6, 21.9, 14.0. MS m/e 262 (100, MH⁺). Anal. calcd for C₁₃H₁₅N₃O₃: C, 59.76; H, 5.79; N, 16.09. found: C, 59.87; H, 5.79; N, 16.10.

1-(4-Nitrophenyl)-3-acetyl-5-ethylpyrazole (10). To a solution of alcohol **9a** (3.30 g, 12.6 mmol) in CH₂Cl₂ (50 mL) was added MnO₂ (3.30 g) and the mixture was stirred at reflux for 5 hours and filtered. The filtrate was concentrated. The light yellow solid was washed with 10:1 mixture of hexane and ethyl acetate to give **10** (2.31 g, 91%). mp: 93-95°C. ¹H NMR (400 MHz, CDCl₃) 8.43, 7.76 (ABq, J = 9.0 Hz, 4 H, ArH), 6.85 (s, 1 H,

py H-4), 2.80 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 2.67 (s, 3 H, CH_3CO), 1.34 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 194.5, 152.6, 148.2, 147.2, 144.7, 125.7, 125.2, 106.8, 26.7, 20.6, 13.2. MS m/e 260 (100, MH^+). Anal. calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3$: C, 60.22; H, 5.05; N, 16.21. found: C, 59.85; H, 5.00; N, 15.92.

1-(4-Nitrophenyl)-3-isopropenyl-5-ethylpyrazole (11). To a solution of methyltriphenylphosphonium bromide (3.47 g, 9.72 mmol) in THF (20 mL) was added 1 M $\text{KO}t\text{-Bu}$ in THF (9.73 mL, 9.73 mmol) followed by ketone **10** (2.10 g, 8.10 mmol). The mixture was stirred at room temperature for 4 hours and concentrated. The residue was triturated with toluene and filtered. The filtrate was concentrated to give a crude solid. Recrystallization from hexane/ethyl acetate gave **11** as a white solid (1.46 g, 70%). mp: 61–63°C. ^1H NMR (400 MHz, CDCl_3) 8.38, 7.74 (ABq, $J = 9.0$ Hz, 4 H, ArH), 6.49 (s, 1 H, py H-4), 5.61 (s, 1 H, vinyl H), 5.21 (s, 1 H, vinyl H), 2.81 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 2.21 (s, 3 H, CH_3), 1.33 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 154.7, 147.0, 146.3, 137.1, 113.9, 104.5, 20.9, 20.4, 14.6. MS m/e 258 (100, MH^+). Anal. calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$: C, 65.35; H, 5.88; N, 16.33. found: C, 65.56; H, 5.72; N, 16.10.

1-(4-Aminophenyl)-3-isopropyl-5-ethylpyrazole (1). To a solution of **11** (1.25 g, 4.86 mmol) in methanol (20 mL) was added 10% Pd/C (0.1 g, 50% wet). The mixture was subjected to par-shaker under 10 psi H_2 for 1 hour. It was then filtered through a pad of *Celite* and the filtrate was concentrated to give **1** (1.10 g, 99%) as a white solid. mp: 88–89°C. ^1H NMR (400 MHz, CDCl_3) 7.15, 6.68 (ABq, $J = 9.0$ Hz, 4 H, ArH), 6.05 (s, 1 H, py H-4), 3.75 (bs, 2 H, NH_2), 2.95 (m, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.49 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 1.33 (d, $J = 6.5$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.20 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 159.0, 146.9, 146.1, 131.2, 127.2, 115.2, 101.0, 28.3, 23.5, 20.1, 13.5. MS m/e 230 (100, MH^+). Anal. calcd for $\text{C}_{14}\text{H}_{19}\text{N}_3$: C, 73.32; H, 8.35. found: C, 73.16; H, 8.12.

1-(4-Nitrophenyl)-3-(1-hydroxyethyl)-5-isopropylpyrazole (13a). The procedure described for **9a** was used. Yield: 56%. ^1H NMR (400 MHz, CDCl_3) 8.35, 7.65 (ABq, $J = 9.0$ Hz, 4 H, ArH), 6.27 (s, 1 H, py H-4), 4.97 (q, $J = 6.4$ Hz, 1 H, CHOH), 3.11 (m, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.40 (bs, 1 H, OH), 1.46 (d, $J = 6.4$ Hz, 3 H, CHCH_3), 1.25 (d, $J = 6.7$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (400 MHz, CDCl_3) 158.1, 152.0, 145.1, 125.4, 124.7, 101.5, 64.9, 25.8, 23.3, 23.0. MS m/e 276 (100, MH^+). A small amount of minor isomer, 1-(4-Nitrophenyl)-3-isopropyl-5-(1-hydroxyethyl)pyrazole (**13b**), was isolated by chromatography on silica gel (hexane/ethyl acetate, 3:1). ^1H NMR (400 MHz, CDCl_3) 8.37, 7.96 (ABq, $J = 9.0$ Hz, 4 H, ArH), 6.41 (s, 1 H, py H-4), 4.92 (q, $J = 6.5$ Hz, 1 H, CHOH), 2.75 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 1.67 (d, $J = 6.5$ Hz, 3 H, CHCH_3), 1.33 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 160.9, 147.0, 146.0, 144.0, 126.1, 124.6, 124.5, 115.5, 103.5, 61.2, 27.9, 23.1, 22.6, 22.5. MS m/e 276 (100, MH^+).

1-(4-Aminophenyl)-3-ethyl-5-isopropylpyrazole (14). The procedure for **2** was used. mp: 93–94°C. ^1H NMR (400 MHz, CDCl_3) 7.14, 6.68 (ABq, $J = 9.0$ Hz, 4 H, ArH), 5.98 (s, 1 H, py H-4), 3.65 (bs, 2 H, NH_2), 2.90 (m, 1 H, $\text{CH}(\text{CH}_3)_2$), 2.65 (q, $J = 7.6$ Hz, 2 H, CH_2CH_3), 1.27 (t, $J = 7.6$ Hz, 3 H, CH_2CH_3), 1.14 (d, $J = 6.5$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C

NMR (400 MHz, CDCl₃) 154.1, 151.0, 146.2, 131.2, 127.4, 115.0, 100.2, 25.4, 23.5, 21.5, 13.8. MS m/e 230 (100, MH⁺). Anal. calcd for C₁₄H₁₉N₃: C, 73.32; H, 8.35. found: C, 73.30; H, 8.39.

2-(Tetrahydropyran-2-yloxy)-2-methyl-3-heptyn-5-one (18). To a solution of terminal acetylene **16** (83.8 g, 0.50 mol) in dry THF (1.2 L) was added 2.5 M n-BuLi in hexane (219 mL, 0.55 mol) over 30 min at -30°C. The solution was stirred at -30°C for 30 min and N,O-dimethylpropionamide (**17**) (58.4 g, 0.5 mol) was added. The mixture was allowed to warm to 0°C over 1 hour and quenched with water. The layers were separated. The organic was concentrated to a low volume and the aqueous layer was extracted with MTBE. The combined organics were washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by high vacuum distillation to give **18** (68.4 g, 61%). bp: 90-105°C (0.4 mmHg). ¹H NMR (400 MHz, CDCl₃) 5.05 (m, 1 H, OCHO), 3.99 (m, 1 H, OCH₂), 3.55 (m, 1 H, OCH₂), 2.62 (q, J = 7.5 Hz, 2 H, COCH₂), 1.93-1.55 (m, 6 H, (CH₂)₃), 1.62 (s, 3 H, CH₃), 1.58 (s, 3 H, CH₃), 1.19 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 188.8, 96.6, 94.5, 83.0, 71.0, 63.7, 39.2, 32.2, 30.0, 29.7, 25.7, 20.6, 8.4. The compound is not stable and used directly after distillation.

2-[1-(Tetrahydropyran-2-yloxy)-1-methyl]ethyl-4-ethylpyrazole (19). To a solution of propargyl ketone **18** (60.0 g, 0.27 mol) in THF (500 mL) was added hydrazine monohydrate (15.6 mL, 0.32 mol) at 0°C and the mixture was stirred at room temperature overnight. The solution was then concentrated and the residue was taken up in ethyl acetate and washed with water. The organic was dried over Na₂SO₄ and concentrated to give pyrazole **19** as a colorless oil. (63.0 g, 99%). ¹H NMR (400 MHz, CDCl₃) 6.00 (s, 1 H, py H-4), 4.60 (m, 1 H, OCHO), 3.99 (m, 1 H, OCH₂), 3.47 (m, 1 H, OCH₂), 2.69 (q, J = 7.5 Hz, 2 H, CH₂CH₃), 1.88-1.54 (m, 6 H, (CH₂)₃), 1.60 (s, 6 H, (CH₃)₂), 1.30 (t, J = 7.5 Hz, 3 H, CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) 101.0, 95.9, 74.9, 64.3, 32.7, 30.0, 27.8, 25.6, 21.3, 20.9, 13.9. MS m/e 239 (100, MH⁺). HRMS calcd for C₁₃H₂₂N₂O₂ 238.1691, found 238.1683.

1-(4-Nitrophenyl)-3-(1-hydroxy-1-methyl)ethyl-5-ethylpyrazole (21). To a solution of pyrazole **19** (63.0 g, 0.27 mol) in dry DMSO (160 mL) was added tert-BuOK (31.5 g, 0.28 mol) under nitrogen. After 10 min, 4-fluoronitrobenzene (28 mL, 0.27 mol) was added. The mixture was heated to 70°C and kept at this temperature for 1 hour, it was then cooled to room temperature and quenched with water and extracted with ethyl acetate. The extract was dried over MgSO₄ and filtered. The filtrate was treated with active carbon (5.0 g, notrit A alkaline) at reflux for 10 min and filtered through a pad of celite. The filtrate was concentrated to give a crude **20**, which was used for the next step without purification. The forgoing crude **20** was dissolved in 10:1 mixture of methanol and water (500 mL) and p-toluenesulfonic acid (2.5 g, 13 mmol) was added. The solution was stirred at room temperature for 30 min and concentrated. The residue was taken up in ethyl acetate and washed with water. The organic was dried over MgSO₄, filtered and concentrated to a crude **21** (73.3 g, 99%), which was subjected to hydrogenation without purification. A small amount of sample was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1). ¹H NMR (400 MHz, CDCl₃) 8.26, 7.65 (ABq, J = 9.0 Hz, 4

H, ArH), 6.26 (s, 1 H, py H-4), 3.23 (bs, 1 H, OH), 2.75 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 1.26 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 161.9, 147.1, 146.2, 145.4, 125.0, 124.6, 103.8, 70.0, 30.8, 20.9, 14.5, 13.3. MS m/e 276 (100, MH^+). HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2$ 275.1269, found 275.1265.

1-(4-Aminophenyl)-3-isopropyl-5-ethylpyrazole (1). To a solution of crude **21** (73.3 g, 0.27 mol) in acetic acid (1.0 L) was added 10% Pd/C (7.0 g, 50% wet). The mixture was subjected to par-shaker under 40 psi H_2 overnight. It was then filtered through a pad of celite and the filtrate was concentrated. The residue was taken up in ethyl acetate and washed with aqueous Na_2CO_3 and water, dried over MgSO_4 and concentrated to afford a crude **1** (59.0 g, 95%) as a light brown solid. A small amount of sample was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1). mp: 88-89°C

3-tert-Butyl-5-ethylpyrazole (22). To a solution of 2,2-dimethyl-3,5-heptandione (1.75 g, 11.2 mmol) in ethanol (20 mL) was added hydrazine monohydrate (0.7 mL, 13.4 mmol) and the mixture was stirred at room temperature for 2 hours. The solution was then quenched with water and extracted with ethyl acetate. The extract was dried over MgSO_4 concentrated. The crude solid was recrystallized in 5:1 mixture of hexane and ethyl acetate to give pyrazole (**22**) as a white solid. (1.57 g, 92%). mp: 150-152°C. ^1H NMR (400 MHz, CDCl_3) 11.49 (bs, 1 H, NH), 5.92 (s, 1 H, H-4), 2.68 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 1.35 (s, 9 H, $(\text{CH}_3)_3$), 1.26 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 99.4, 30.9, 13.9. MS m/e 153 (100, MH^+). Anal. calcd for $\text{C}_9\text{H}_{16}\text{N}_2$: C, 71.00; H, 10.60. found: C, 71.52; H, 10.55.

1-(4-Nitrophenyl)-3-tert-butyl-5-ethylpyrazole (23). The procedure described for **3a** was used. Yield: 96%. ^1H NMR (400 MHz, CDCl_3) 8.30, 7.70 (ABq, $J = 9.0$ Hz, 4 H, ArH), 6.22 (s, 1 H, py H-4), 2.79 (q, $J = 7.5$ Hz, 2 H, CH_2CH_3), 1.37 (s, 9 H, $(\text{CH}_3)_3$), 1.31 (t, $J = 7.5$ Hz, 3 H, CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) 164.1, 146.4, 145.9, 125.0, 124.3, 104.3, 32.6, 30.7, 21.0, 13.4. MS m/e 274 (100, MH^+). Anal. calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$: C, 65.91; H, 7.01; N, 15.37. found: C, 66.34; H, 7.12; N, 15.59.