Supporting Information
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Supporting information

for

1,3-Dipolar Cycloaddition of Nitrile Imines With Functionalised Acetylenes. Regiocontrolled Sc(OTf)3 Catalyzed Synthesis of 4- and 5-Substituted Pyrazoles.

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Material and Methods: $^1$H NMR and $^{13}$C NMR spectra were recorded using CDCl$_3$ or CD$_3$OD or DMSO solutions at 300, 400 and 600 MHz for $^1$H and 75.46, 100.6 and 150.92 MHz for $^{13}$C. Chemical shifts (δ) are reported in ppm relative to CHCl$_3$ (δ = 7.26 for $^1$H and δ = 77.0 for $^{13}$C ). J values are given in Hz. $^1$H NMR and $^{13}$C NMR spectral assignments were made by DEPT, gCOSY and gHSQC experiments. IR spectra were recorded in solvent as specified. Mass spectra (MS) were obtained with an electrospray ionization source (ESIMS). All the ESIMS spectra were performed using MeOH as the solvent. High Resolution Mass Spectra (HRMS) were recorded on a micromass LCT spectrometer using electrospray (ES$^-$) ionisation techniques. Reactions were conducted in oven-dried (120 °C) glassware under a positive Ar atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes/septum techniques. THF was distilled from sodium/benzophenone just prior to use and stored under Ar. Toluene was distilled from sodium. Et$_2$O was distilled from phosphorus pentoxide. CH$_2$Cl$_2$ was passed through basic alumina and distilled from CaH$_2$ prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with bp 40-60°C. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70-230 mesh). Preparative thick layer chromatography was carried out on glass plates using a 1 mm layer of Merck silica gel 60 Pf 254. All chemicals were used as obtained or purified by distillation as needed.
N-phenylpropionamide (2): to a stirred solution of propiolic acid (16.4 mmol, 1.15 g) and Et₂O (10 mL) at 0 °C was added very slowly dicyclohexylcarbodiimide (DCC) (16.2 mmol, 3.3 5g). Then was added dimethylaminopyridine (0.2 mmol, 23 mg). After 10 minutes a solution of aniline (16.1 mmol, 1.5 g) in Et₂O (15 mL) was added dropwise to the reaction mixture at -10 °C and the system was stirred for other 24h at r.t. The solution was filtered on Celite and washed with HCl 1M (2 x 25 mL) and brine, then the organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to afford the product 2 as a yellow solid (1.60 g, yield 68%). Data in agreement with ref. 16 in the manuscript.

(E/Z)-methyl 2-chloro-2-(2-(4-fluorophenyl) hydrazono) acetate (3a): to a stirred solution of 4-fluoroaniline (22.5 mmol, 2.50 g) in HCl (20 mL) and MeOH (20 mL) at 0 °C was added very slowly NaNO₂ (45 mmol, 3.16 g). The reaction mixture was stirred for 15 minutes then NaOAc was added until pH 5. After that a solution of methyl 2-chloroacetoacetate (22.5 mmol, 2.74 g) in MeOH (10 mL) was added dropwise to the reaction mixture at -10 °C and the system was stirred at r.t. for other 12 h. MeOH was removed under vacuum and Et₂O (80 mL) was added. The solution was washed with NaHCO₃ and with water, then the organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to afford the product 3a as a yellow solid. m.p. = 112-113 °C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.90 (s, 3H, OCH₃), 6.95-7.05 (m, 2H, ArH), 7.15-7.20 (m, 2H, ArH), 8.25 (bs, 1H, NH); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 53.8, 115.85, 116.1, 116.2, 116.3, 116.6, 138.2, 157.7/160.5 (d, J=245, C-F), 160.9; IR (CCl₄): ν = 3442, 3319, 2954, 1737, 1681, 1655, 1562, 1531, 1398, 1072 cm⁻¹; [M+Na]⁺: 253; Anal. Calcd for C9H8ClFN2O2: C, 46.87; H, 3.50; N, 12.15. Found: C, 46.88; H, 3.52; N, 12.14.

(E/Z)-methyl 4-(2-(1-chloro-2-methoxy-2-oxoethylidene)hydrazinyl)benzoate (3b): to a stirred solution of methyl 4-aminobenzoate (22.5 mmol, 3.40 g) in HCl (20 mL) and MeOH (20 mL) at 0 °C was added very slowly NaNO₂ (45 mmol, 3.16 g). The reaction mixture was stirred for 15 minutes then NaOAc was added until pH 5. After that a solution of methyl 2-chloroacetoacetate (22.5 mmol, 2.74 g) in MeOH (10 mL) was added dropwise to the reaction mixture at -10 °C and the system was stirred at r.t. for other 12 h. MeOH was removed under vacuum and Et₂O (80 mL) was added. The solution was washed with NaHCO₃ and with water, then the organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to afford the product 3b as a yellow solid. m.p. = 194-196 °C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.90 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 7.20-7.30 (m, 2H, ArH), 7.95-8.10 (m, 2H, ArH), 8.45 (bs, 1H, NH); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 166.6, 159.8, 145.1, 131.4 (2CH), 124.7, 117.7, 113.9 (2CH), 53.7, 51.9; IR (CCl₄): ν = 3441, 3319, 2953, 1739, 1724, 1681, 1654, 1610, 1559, 1522, 1436, 1398, 1072 cm⁻¹; [M+Na]⁺: 293; Anal. Calcd for C11H11ClN2O4: C, 48.81; H, 4.10; N, 10.35. Found: C, 48.84; H, 4.09; N, 10.33.

(E/Z)-methyl 2-chloro-2-(2-(4-methoxyphenyl)hydrazono)acetate (3c): to a stirred solution of 4-methoxyaniline (22.5 mmol, 2.80 g) in HCl (20 mL) and MeOH (20 mL) at 0 °C was added very slowly NaNO₂ (45 mmol, 3.16 g). The reaction mixture was stirred for 15 minutes then NaOAc was added until pH 5. After that a solution of methyl 2-chloroacetoacetate (22.5 mmol, 2.74 g) in MeOH (10 mL) was added dropwise to the reaction mixture at -10 °C and the system was stirred at r.t. for other 12
h. MeOH was removed under vacuum and Et₂O (80 mL) was added. The solution was washed with NaHCO₃ and with water, then the organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to afford the product 3c as a yellow solid. m.p. = 108-110 °C; ¹H NMR (CDCl₃, 400 MHz): δ= 8.32 (s, 1H, NH), 7.16 (d, 3J(H,H) = 9.0 Hz, 2H, arom.), 6.87 (d, 3J(H,H) = 9.0 Hz, 2H arom.), 3.91 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 160.3, 155.9, 135.3, 115.8 (2CH), 114.7 (2CH), 114.6, 55.5, 53.3; IR (CCl₄): ν = 3441, 3038, 2953, 1735, 1681, 1654, 1517, 1437, 1398, 1073 cm⁻¹; [M+Na]+: 265; Anal. Calcd for C₁₀H₁₁ClN₂O₃: C, 49.50; H, 4.57; N, 11.54. Found: C, 49.52; H, 4.59; N, 11.53.

General procedure for the synthesis of benzoylhydrazines (4a-c): After cooling at 0°C , to a suspension of the hydrazine hydrochloride (1 mmol) and triethylamine (2.55 mmol) in anhydrous tetrahydrofuran (1.8 mL) was added slowly a solution of benzoyl chloride (1.02 mmol) in anhydrous tetrahydrofuran (3.6 mL). After complete addition, the mixture was left to react for 30 minutes then solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (20 mL) and washed with water (4 x 50 mL) and dried over MgSO₄. The crude product was purified by chromatography on silica gel.

N’-(4-fluorophenyl)benzohydrazide (4a): After cooling at 0°C, to a suspension of 4-fluorophenylhydrazine hydrochloride (3.0 g, 17.8 mmol) and triethylamine (6.5 mL, 46 mmol) in anhydrous tetrahydrofuran (30 mL) was added slowly a solution of benzoyl chloride (2.0 mL, 17.8 mmol) in anhydrous tetrahydrofuran (60 mL). After complete addition the mixture was left to react for 30 minutes then solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (4 x 75 mL) and washed with water (4 x 75 mL) and dried over MgSO₄. The crude product was purified by chromatography on silica gel (EtOAc/Light Petroleum 1/3) to give 1.4 g (34%) of N’-(4-fluorophenyl)benzohydrazide as a white solid. m.p. = 140-142 °C; ¹H NMR (CDCl₃, 300 MHz): δ= 8.26 (s, 1H, NH), 7.85-7.79 (m, 2H arom.), 7.59-7.52 (m, 1H arom.), 7.49-7.41 (m, 2H arom.), 6.96-6.82 (m, 4H arom.), 4.95 (br, s, 1H, NH); ¹³C NMR (CD₂OD, 100.6 MHz): δ = 170.2, 158.7 (d, 1J(C,F) = 236.1 Hz), 146.4, 134.1, 129.7 (2CH), 128.4 (2CH), 116.3 (d, 2J(C,F) = 22.6 Hz, 2CH), 115.6 (d, 3J(C,F) = 7.7 Hz, 2CH); ¹⁹F NMR (CD₂OD, 376.3 MHz): δ = −127.7; IR (CHCl₃): ν = 3437, 3336, 1678, 1603, 1582, 1508, 1463, 1443, 1284 cm⁻¹; [M+Na]+: 253; Anal. Calcd for C₁₃H₁₁FN₂O: C, 67.82; H, 4.82; N, 12.17. Found: C, 67.82; H, 4.81; N, 12.15.

methyl 4-(2-benzoylhydrazinyl)benzoate (4b): After cooling at 0°C, to a suspension of methyl 4-hydrazinylbenzoate (rif. 18 in the manuscript, 1.1 g, 6.6 mmol) and triethylamine (1.1 mL, 7.9 mmol) in anhydrous tetrahydrofuran (15 mL) was added slowly a solution of benzoyl chloride (0.77 mL, 6.6 mmol) in anhydrous tetrahydrofuran (30 mL). After complete addition, the mixture was left to react for 30 minutes then solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (100 mL) and washed with water (4 x 25 mL) and dried over MgSO₄. The crude product was purified by chromatography on silica gel (EtOAc/Light Petroleum 1/2) to give 1.4 g (77%) of methyl 4-(2-benzoylhydrazinyl)benzoate as a light yellow solid. m.p. = 163-165 °C; ¹H NMR (CDCl₃, 300 MHz): δ= 8.32 (s, 1H, NH), 7.89-7.81 (m, 4H arom.), 7.56 (t, 3J(H,H) = 7.4 Hz, 1H arom.), 7.45 (t, 3J(H,H) = 7.4 Hz, 2H arom.), 6.83 (d, 3J(H,H) = 8.9 Hz, 2H arom.), 5.20 (br, s, 1H, NH), 3.85 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 100.6 MHz): δ = 167.8, 167.0, 152.0, 132.4, 131.8, 131.2 (2CH), 128.8 (2CH), 127.2 (2CH), 122.3, 112.3 (2CH), 51.7; IR (CHCl₃): ν = 3432, 3338, 2954, 1712, 1685, 1609, 1512, 1466, 1436, 1413, 1285 cm⁻¹.
N'-{(4-methoxyphenyl)benzohydrazide (4c): After cooling at 0°C, to a suspension of 4-methoxyphenylhydrazine hydrochloride (3.0 g, 17.2 mmol) and triethylamine (6.1 mL, 44 mmol) in anhydrous tetrahydrofuran (30 mL) was added slowly a solution of benzoyl chloride (2.0 mL, 17.6 mmol) in anhydrous tetrahydrofuran (60 mL). After complete addition, the mixture was left to react for 30 minutes then solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (300 mL) and washed with water (4 x 75 mL) and dried over MgSO4. The crude product was purified by chromatography on silica gel (EtOAc/Light Petroleum 1/2) to give 1.5 g (35%) of N’-(4-methoxyphenyl)benzohydrazide as a light yellow solid. m.p. = 130-132 °C; 1H NMR (CDCl3, 400 MHz): δ = 8.07 (s, 1H, NH), 7.82 (d, 3J(H,H) = 7.4 Hz, 2H, arom.), 7.55 (t, 3J(H,H) = 7.4 Hz, 1H), 7.46 (t, 3J(H,H) = 7.4 Hz, 2H, arom.), 6.91 (d, 3J(H,H) = 8.9 Hz, 2H arom.), 4.33 (br, s, 1H, NH), 3.75 (s, 3H, OCH3); 13C NMR (CDCl3, 100.6 MHz): δ = 167.8, 154.8, 141.5, 132.3, 132.1, 128.7 (2CH), 127.1 (2CH), 115.7 (2CH), 114.6 (2CH), 55.6; IR (CHCl3): ν = 3439, 3329, 2837, 1676, 1602, 1581, 1509, 1463, 1442, 1411, 1287, 1242 cm⁻¹; 

(E/Z)-N’-(4-fluorophenyl)benzohydrazonoyl chloride (5a): Compound 5a (618 mg, 86%) was obtained as a light yellow solid from N’-(4-fluorophenyl)benzohydrazide following the general procedure (EtOAc/Light Petroleum 1/30). m.p. = 70-72 °C; 1H NMR (CDCl3, 400 MHz): δ = 7.97 (s, 1H, NH), 7.93-7.89 (m, 2H arom.), 7.44-7.34 (m, 3H arom.), 7.16-7.09 (m, 2H arom.), 7.05-6.98 (m, 2H arom.); 13C NMR (CDCl3, 100.6 MHz): δ = 157.8 (d, 1J(C,F) = 238.9 Hz), 139.7, 134.3, 129.3, 128.4 (2CH), 126.4 (2CH), 124.8, 115.9 (d, 2J(C,F) = 22.7 Hz, 2CH), 114.5 (d, 3J(C,F) = 8.1 Hz, 2CH); 19F NMR (CDCl3, 376.3 MHz): δ = −124.2; IR (CHCl3): ν = 3337, 1610, 1587, 1512, 1447, 1410, 1312, 1268 cm⁻¹; [M-H]-: 247; Anal. Calcd for C13H10ClFN2: C, 62.79; H, 4.05; N, 11.26. Found: C, 62.77; H, 4.02; N, 11.25.

(E/Z)-methyl 4-(2-(chloro(phenyl)methylene)hydrazinyl)benzoate (5b): Compound 5b (740 mg, 88%) was obtained as a light yellow solid from methyl 4-(2-benzoylhydrazinyl)benzoate (4b) following the general procedure (EtOAc/Light Petroleum 1/5). m.p. = 160-163 °C; 1H NMR (CDCl3, 300 MHz): δ = 8.26 (s, 1H, NH), 8.01 (d, 3J(H,H) = 8.8 Hz, 2H arom.), 7.97-7.91 (m, 2H arom.), 7.48-7.39 (m, 3H arom.), 7.97 (d, 3J(H,H) = 8.8 Hz, 2H arom.), 3.90 (s, 3H, OCH3); 13C NMR (CDCl3, 100.6 MHz): δ = 166.9, 146.8, 133.9, 131.4 (2CH), 129.7, 128.8 (2CH), 126.8, 126.6 (2CH), 122.5, 112.6 (2CH), 51.7; IR (CHCl3): ν = 3338, 2954, 1711, 1607, 1522, 1482, 1436, 1415, 1284, 1271 cm⁻¹; [M+Na]+: 311; [M-H]: 287; Anal. Calcd for C15H13ClN2O2: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.38; H, 4.51; N, 9.69.

(E/Z)-N’-(4-methoxyphenyl)benzohydrazonoyl chloride (5c): Compound 5c (543 mg, 72%) was obtained as a light yellow solid from N’-(4-
methoxyphenyl)benzohydrazide (4c) following the general procedure (EtOAc/Light Petroleum 1/10). m.p. = 96-98 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.96-7.90\) (m, 2H arom. 1H, NH), 7.44-7.34 (m, 3H arom.), 7.14 (d, \(^3\)I(H,H) = 9.0 Hz, 2H arom.), 6.91 (d, \(^3\)I(H,H) = 9.0 Hz, 2H arom.), 3.81 (s, 3H, OCH\(_3\)); 13C NMR (CDCl\(_3\), 100.6 MHz): \(\delta = 154.5, 137.4, 134.5, 128.9, 128.3\) (2CH), 126.2 (2CH), 123.8, 114.7 (2CH), 114.6 (2CH), 55.6; IR (CHCl\(_3\)): \(\nu = 3336, 2837, 1617, 1600, 1584, 1565, 1514, 1481, 1464, 1446, 1267, 1245\) cm\(^{-1}\); [M-H]: 259; Anal. Calcd for C\(_{14}\)H\(_{13}\)ClN\(_2\)O: C, 64.49; H, 5.03; N, 10.74. Found: C, 64.51; H, 5.05; N, 10.75.

5-benzyl 3-methyl 1-(4-fluorophenyl)-1H-pyrazole-3,5-dicarboxylate and 4-benzyl 3-methyl 1-(4-fluorophenyl)-1H-pyrazole-3,4-dicarboxylate (6a and 7a): Compound 6a/7a were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/6). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (DCM).

5-benzyl 3-methyl 1-(4-fluorophenyl)-1H-pyrazole-3,5-dicarboxylate (6a): m.p. = 123-124 °C; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.95\) (s, 3H, OCH\(_3\)), 5.20 (s, 2H, CH\(_2\)), 7.05-7.15 (m, 2H, ArH), 7.25-7.30 (m, 2H, ArH), 7.35-7.45 (m, 5H, ArH), 7.55 (s, 1H, CH); 13C-NMR (100.6 MHz,, CDCl\(_3\)): \(\delta = 52.3, 67.2, 114.8, 115.4\) (d, \(^2\)J(C,F) = 23.5 Hz, 2CH), 127.8, 128.0 (d, \(^3\)J(C,F) = 8.8 Hz, 2CH), 128.2 (2CH), 128.5 (2CH), 134.2, 134.6, 135.5, 143.3, 157.8, 161.5, 162.5 (d, \(^1\)J(C,F) = 248.5 Hz); 19F-NMR (376.3 MHz, CDCl\(_3\)): \(\delta = -111.4\) (sb, 1F, ArF); IR (CHCl\(_3\)): \(\nu = 2947, 1731, 1513, 1446, 1368, 1275, 1223\); [M+Na\(^+\): 377; Anal. Calcd for C\(_{19}\)H\(_{15}\)FN\(_2\)O\(_4\): C, 64.40; H, 4.27; N, 7.91. Found: C, 64.38; H, 4.26; N, 7.96.

4-benzyl 3-methyl 1-(4-fluorophenyl)-1H-pyrazole-3,4-dicarboxylate (7a): m.p. = 123-124 °C; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.85\) (s, 3H, OCH\(_3\)), 5.30 (s, 2H, CH\(_2\)), 7.10-7.20 (m, 2H, ArH), 7.30-7.45 (m, 5H, ArH), 7.65-7.70 (m, 2H, ArH), 8.35 (s, 1H, CH); \(^13\)C-NMR (100.6 MHz,, CDCl\(_3\)): \(\delta = 52.6, 66.8, 116.2, 116.4\) (d, \(^2\)J(C,F) = 23.7 Hz, 2CH), 121.9 (d, \(^3\)J(C,F) = 8.7 Hz, 2CH), 128.3 (2CH), 128.4 (2CH), 131.8, 134.8, 134.9, 135.4, 144.7, 160.3, 161.9, 162.2 (d, \(^1\)J(C,F) = 248.7 Hz); 19F-NMR (376.3 MHz, CDCl\(_3\)): \(\delta = -113.0\) (sb, 1F, ArF); IR (CHCl\(_3\)): \(\nu = 2947, 1742, 1513, 1477, 1373, 1280, 1223, 1160, 1072\); [M+Na\(^+\): 377; Anal. Calcd for C\(_{19}\)H\(_{15}\)FN\(_2\)O\(_4\): C, 64.40; H, 4.27; N, 7.91. Found: C, 64.39; H, 4.25; N, 7.94.

5-benzyl 3-methyl 1-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3,5-dicarboxylate and 4-benzyl 3-methyl 1-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3,4-dicarboxylate (6b and 7b): Compound 6b/7b were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/2). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (DCM).

5-benzyl 3-methyl 1-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3,5-dicarboxylate (6b): m.p. = 124-126 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.90\) (s, 6H, 2 -OCH\(_3\)), 5.20 (s, 2H, CH\(_2\)), 7.20-7.35 (m, 4H, ArH), 7.40-7.50 (m, 3H, ArH ), 7.55 (s, 1H, CH), 8.05-8.10 (m, 2H, ArH); \(^13\)C-NMR (100.6 MHz,, CDCl\(_3\)): \(\delta = 52.3, 52.4, 67.4, 115.2, 119.4, 126.0\) (2CH), 128.3 (2CH), 128.5 (2CH), 129.9 (2CH), 130.7, 134.4, 134.7, 142.8, 143.8, 157.8, 161.5, 165.8; IR (CHCl\(_3\)): \(\nu = 2999, 1726, 1596, 1508, 1446, 1373, 1316, 1267, 1245\) cm\(^{-1}\); [M-H]: 259; Anal. Calcd for C\(_{14}\)H\(_{13}\)ClN\(_2\)O: C, 64.49; H, 5.03; N, 10.74. Found: C, 64.51; H, 5.05; N, 10.75.
4-benzyl 3-methyl 1-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3,4-dicarboxylate (7b): m.p. = 108-110 °C; 1H-NMR (400 MHz, CDCl3): δ = 3.85 (s, 3H, OCH3), 3.90 (s, 3H, OCH3), 5.30 (s, 2H, CH2), 7.25-7.35 (m, 5H, ArH), 7.80-7.85 (m, 2H, ArH), 8.15-8.20 (m, 2H, ArH), 8.45 (s, 1H, CH); 13C-NMR (100.6 MHz, CDCl3): δ = 52.5, 52.6, 66.3, 116.4, 119.9 (2CH), 128.2 (2CH), 128.3 (2CH), 129.9, 131.8 (2CH), 131.9, 132.1, 135.9, 142.0, 145.6, 160.5, 162.1, 166.0; IR (CHCl3, ν=cm^{-1}): 3009, 1721, 1596, 1524, 1472, 1425, 1332, 1041; [M+Na]+: 417; Anal. Calcd for C21H18N2O6: C, 63.96; H, 4.60; N, 7.10. Found: C, 63.92; H, 4.61; N, 7.12.

5-benzyl 3-methyl 1-(4-methoxyphenyl)-1H-pyrazole-3,5-dicarboxylate and 4-benzyl 3-methyl 1-(4-methoxyphenyl)-1H-pyrazole-3,4-dicarboxylate (6c and 7c): Compound 6c/7c were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/2). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (DCM/Light Petroleum 3/1).

5-benzyl 3-methyl 1-(4-methoxyphenyl)-1H-pyrazole-3,5-dicarboxylate (6c): m.p. = 133-135 °C; 1H-NMR (300 MHz, CDCl3): δ = 3.84 (s, 3H, OCH3), 3.94 (s, 3H, OCH3), 5.22 (s, 2H, CH2), 6.90-6.93 (m, 4H, ArH), 7.32-7.35 (m, 5H, ArH), 7.54 (s, 1H, CH); 13C-NMR (100.6 MHz, CDCl3): δ = 55.6, 55.7, 66.8, 114.7 (2CH), 115.9, 121.9 (2CH), 128.4, 128.5 (2CH), 128.6 (2CH), 131.9, 132.3, 135.7, 144.5, 159.6, 161.4, 162.3; IR (CCl4): ν = 3032, 2955, 1730, 1681, 1655, 1516, 1455, 1372, 1127, 1041 cm^{-1}; [M+H]+: 367; [M+Na]+: 389; Anal. Calcd for C19H16N2O5: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.74; H, 4.55; N, 7.92.

4-benzyl 3-methyl 1-(4-methoxyphenyl)-1H-pyrazole-3,4-dicarboxylate (7c): m.p. = 89-90 °C; 1H-NMR (300 MHz, CDCl3): δ = 3.84 (s, 3H, OCH3), 3.88 (s, 3H, OCH3), 5.32 (s, 2H, CH2), 6.95-6.98 (m, 2H, ArH), 7.34-7.45 (m, 5H, ArH), 7.58-7.61 (m, 2H, ArH), 8.29 (s, 1H, CH); 13C-NMR: (100.6 MHz, CDCl3): δ = 162.4 (d, 1J(C,F) = 248.5 Hz), 158.8, 151.6, 136.4, 135.0, 134.4, 131.9, 128.7 (2CH), 128.6 (2CH), 128.5, 128.4 (2CH), 128.1 (d, 3J(C,F) = 8.8 Hz, 2CH), 125.8 (2CH), 115.5 (d, 3J(C,F) = 23.5 Hz, 2CH), 109.8, 66.9; 19F NMR (CDCl3, 376 MHz): δ = -111.9 (m, 1F, F-F bond).

5-benzyl 1-(4-fluorophenyl)-3-phenyl-1H-pyrazole-5-carboxylate and 5-benzyl 1-(4-fluorophenyl)-3-phenyl-1H-pyrazole-4-carboxylate (8a and 9a): Compound 8a/9a were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/10).

5-benzyl 1-(4-fluorophenyl)-3-phenyl-1H-pyrazole-5-carboxylate (8a): m.p. = 108-110 °C; 1H NMR (CDCl3, 300 MHz): δ = 7.87 (d, 3J(H,H) = 7.2 Hz, 2H arom.), 7.50-7.30 (m, 11H arom.), 7.13 (d, 3J(H,H) = 8.8 Hz, 2H arom.), 5.26 (s, 2H, OCH2); 13C NMR (CDCl3, 100.6 MHz): δ = 162.4 (d, 1J(C,F) = 248.5 Hz), 158.8, 151.6, 136.4, 135.0, 134.4, 131.9, 128.7 (2CH), 128.5, 128.4 (2CH), 128.1 (d, 3J(C,F) = 8.8 Hz, 2CH), 125.8 (2CH), 115.5 (d, 3J(C,F) = 23.5 Hz, 2CH), 109.8, 66.9; 19F NMR (CDCl3,
benzyl 1-(4-fluorophenyl)-3-phenyl-1H-pyrazole-4-carboxylate (9a): m.p. = 109-111 °C; \( \delta = -113.3 \); IR (CHCl\(_3\)): \( \nu = 3000, 1728, 1604, 1514, 1439, 1320, 1279, 1108, 1012 \) cm\(^{-1}\); [M+Na]\(^+\): 395; Anal. Calcd for C\(_{23}\)H\(_{17}\)FN\(_2\)O\(_2\): C, 74.18; H, 4.60; N, 7.52. Found: C, 74.17; H, 4.58; N, 7.50.

benzyl 1-(4-(methoxycarbonyl)phenyl)-3-phenyl-1H-pyrazole-5-carboxylate and benzyl 1-(4-(methoxycarbonyl)phenyl)-3-phenyl-1H-pyrazole-4-carboxylate (8b and 9b): Compound 8b/9b were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/5). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (EtOAc/Light Petroleum 1/10).

benzyl 1-(4-methoxyphenyl)-3-phenyl-1H-pyrazole-5-carboxylate and benzyl 1-(4-methoxyphenyl)-3-phenyl-1H-pyrazole-4-carboxylate (8c and 9c): Compound 8c/9c were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/5).
MHz): $\delta = 159.7, 158.9, 151.2, 135.2, 134.3, 133.4, 132.1, 128.7 (2CH), 128.5 (2CH), 125.8 (2CH), 113.8 (2CH), 109.4, 66.7, 55.5$; IR (CHCl$_3$): $\nu = 2839, 1730, 1606, 1508, 1484, 1445, 1280, 1243, 1104, 1080, 1004$ cm$^{-1}$; [M+Na]$^+$: 407; Anal. Calcd for C$_{24}$H$_{20}$N$_2$O$_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.97; H, 5.22; N, 7.30.

benzyl 1-(4-methoxyphenyl)-3-phenyl-1H-pyrazole-4-carboxylate (9c): m.p. = 96-97 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta =$ 8.41 (s, 1H arom), 7.86-7.82 (m, 2H arom), 7.69-7.64 (m, 2H arom.), 7.44-7.29 (m, 8H arom.), 7.01-6.95 (m, 2H arom.), 5.28 (s, 2H, OCH$_2$), 3.85 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta =$ 162.7, 159.0, 153.9, 136.0, 132.9, 132.3, 132.1, 129.4 (2CH), 128.6, 128.5 (2CH), 128.3 (2CH), 128.2, 127.9 (2CH), 125.8, 121.2 (2CH), 114.6 (2CH), 66.0, 55.6; IR (CHCl$_3$): $\nu = 2840, 1731, 1606, 1508, 1483, 1442, 1281, 1243, 1104, 1082, 1006$ cm$^{-1}$; [M+Na]$^+$: 407; Anal. Calcd for C$_{24}$H$_{20}$N$_2$O$_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.99; H, 5.25; N, 7.29.

methyl 1-(4-fluorophenyl)-5-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate and methyl 1-(4-fluorophenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (10a and 11a): Compound 10a/11a were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc//Light Petroleum 1/6).

methyl 1-(4-fluorophenyl)-5-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (10a): m.p. = 186-188 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 3.95 (s, 3H, OCH$_3$), 7.05-7.20 (m, 3H, ArH), 7.25-7.35 (m, 3H, ArH + CH), 7.40-7.55 (m, 4H, ArH) 8.20 (bs, 1H, NH); $^{13}$C-NMR: (100.6 MHz, CDCl$_3$): $\delta =$ 52.5, 110.6, 115.8 (d, $^2$J(C,F) = 23.9 Hz, 2CH), 120.6 (2CH), 125.2, 127.1 (d, $^2$J(C,F) = 9.1 Hz, 2CH), 129.0 (2CH), 135.2, 136.7, 138.3, 143.2, 156.3, 160.8, 162.9 (d, $^1$J(C,F) = 248.7 Hz); $^{19}$F-NMR (376.3 MHz, CDCl$_3$): $\delta =$ -111.6 (bs, 1F, ArF); IR (CCl$_4$): $\nu =$ 3378, 1677, 1506, 1081; [M+Na]$^+$: 362; Anal. Calcd for C$_{18}$H$_{14}$FN$_3$O$_3$: C, 63.71; H, 4.16; N, 12.36. Found: C, 63.73; H, 4.14; N, 12.32.

methyl 1-(4-fluorophenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (11a): m.p. = 173-174 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 4.10 (s, 3H, OCH$_3$), 7.10-7.22 (m, 3H, ArH), 7.34-7.40 (m, 2H, ArH), 7.70-7.80 (m, 4H, ArH), 8.65 (s, 1H, CH), 11.60 (bs, 1H, NH); $^{13}$C-NMR: (100.6 MHz, CDCl$_3$): $\delta =$ 53.4, 116.7 (d, $^2$J(C,F) = 23.7 Hz, 2CH), 120.1 (2CH), 122.2, 122.3, 124.3 (d, $^3$J(C,F) = 8.8 Hz, 2CH), 128.9 (2CH), 134.7, 134.8, 138.8, 139.1, 158.2, 158.5, 158.6, 160.8, 162.9 (d, $^2$J(C,F) = 243.5 Hz), 165.8; $^{19}$F-NMR (376.3 MHz, CDCl$_3$): $\delta =$ -112.5 (bs, 1F, ArF); IR (CCl$_4$): $\nu =$ 3373, 1664, 1508, 1088; [M+Na]$^+$: 362; Anal. Calcd for C$_{18}$H$_{14}$FN$_3$O$_3$: C, 63.71; H, 4.16; N, 12.36. Found: C, 63.75; H, 4.15; N, 12.34.

methyl 1-(4-(methoxycarbonyl)phenyl)-5-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate and methyl 1-(4-(methoxycarbonyl)phenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (10b and 11b): Compound 10b/11b were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc//Light Petroleum 1/2).
162.9, 165.7; IR (CHCl₃): ν = 3456, 1721, 1597, 1524, 1425, 1041; [M+Na]⁺: 402; Anal. Calcd for C₂₀H₁₇N₃O₅: C, 63.32; H, 4.52; N, 11.06. Found: C, 63.37; H, 4.49; N, 11.07.

methyl 1-(4-(methoxycarbonyl)phenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (11b): m.p. = 186-187 °C; ¹H-NMR (400 MHz, CDCl₃): δ = 4.05 (s, 3H, OCH₃), 4.20 (s, 3H, OCH₃), 7.20-7.60 (m, 4H, ArH + NH), 7.85-7.90 (m, 2H, ArH), 8.25-8.30 (m, 2H, ArH), 8.95 (s, 1H, CH); ¹³C-NMR (100.6 MHz, CDCl₃): δ = 165.8, 165.0, 158.3, 141.7, 139.6, 138.2, 134.6, 131.3 (2CH), 130.0, 129.0 (2CH), 124.4, 124.2, 120.1 (2CH), 119.6 (2CH), 53.5, 52.4; IR (CHCl₃): ν = 3466, 1726, 1597, 1519, 1425, 1041; [M+Na]⁺: 402; Anal. Calcd for C₂₀H₁₇N₃O₅: C, 63.32; H, 4.52; N, 11.06. Found: C, 63.36; H, 4.51; N, 11.09.

methyl 1-(4-methoxyphenyl)-5-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate and methyl 1-(4-methoxyphenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (10c and 11c): Compound 10c/11c were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc//Light Petroleum 1/3).

methyl 1-(4-methoxyphenyl)-5-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (10c): m.p. = 166-168 °C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.74 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 6.78-6.81 (m, 2H, ArH), 7.05-7.11 (m, 1H, ArH), 7.21-7.26 (m, 5H, ArH + CH), 7.47-7.50 (m, 2H, ArH), 8.79 (bs, 1H, NH; ¹³C-NMR: (CDCl₃, 100.6 MHz): δ = 52.2, 55.3, 110.7, 113.8 (2CH), 120.1 (2CH), 124.7, 126.1 (2CH), 128.6 (2CH), 131.9, 137.0, 138.1, 142.4, 156.6, 159.6, 162.0. IR (CHCl₃): ν = 3460, 1722, 1594, 1523, 1420, 1046; [M+Na]⁺: 374; Anal. Calcd for C₁₉H₁₇N₃O₄: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.91; H, 4.84; N, 11.93.

methyl 1-(4-methoxyphenyl)-4-(phenylcarbamoyl)-1H-pyrazole-3-carboxylate (11c): m.p. = 177-179 °C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3H, OCH₃), 4.08 (s, 3H, OCH₃), 6.97-7.16 (m, 3H, ArH), 7.34-7.39 (m, 2H, ArH), 7.63-7.79 (m, 2H, ArH), 8.61 (s, 1H, CH), 11.66 (bs, 1H, NH; ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 165.3, 159.7, 158.7, 138.6, 138.5, 134.6, 132.3, 128.9 (2CH), 124.1, 123.6, 121.9 (2CH), 120.1 (2CH), 114.8 (2CH), 55.6, 53.3; IR (CHCl₃): ν = 3466, 1729, 1592, 1523, 1421, 1042; [M+Na]⁺: 374; Anal. Calcd for C₁₉H₁₇N₃O₄: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.93; H, 4.86; N, 11.94.

1-(4-fluorophenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide and 1-(4-fluorophenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (12a and 13a): Compound 12a/13a were obtained as a white solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc//Light Petroleum 1/4). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (DCM).

1-(4-fluorophenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide (12a): m.p. = 216-218 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.85 (d, 3J(H,H) = 7.4 Hz, 2H arom.), 7.74 (s, 1H, NH), 7.56-7.30 (m, 9H arom.), 7.19-7.09 (m, 4H arom.); ¹³C NMR (CDCl₃, 100.6 MHz): δ = 162.3 (d, 1J(C,F) = 248.9 Hz), 157.3, 151.7, 138.2, 137.0, 136.0, 131.9, 129.2 (2CH), 128.8 (2CH), 128.6 (2CH), 127.1 (d, 3J(C,F) = 9.1 Hz, 2CH), 125.8 (2CH), 125.1, 120.1, 115.9 (d, 2J(C,F) = 22.7 Hz, 2CH), 106.0; ¹⁹F NMR (CDCl₃, 376.3 MHz): δ = -113.3 Hz; IR
(CHCl₃): ν = 3422, 1690, 1600, 1524, 1445, 1385, 1314, 1096 cm⁻¹; [M+Na⁺]: 380; Anal. Calcd for C₂₂H₁₆F₃N₃O: C, 73.94; H, 4.51; N, 11.76. Found: C, 73.93; H, 4.49; N, 11.75.

1-(4-fluorophenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (13a): m.p. = 217-218 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 8.56 (s, 1H arom.), 7.79-7.72 (m, 4H arom.), 7.60-7.55 (m, 3H arom.), 7.42 (s, 1H, NH), 7.30-7.25 (m, 4H arom.), 7.19 (t, 3J(H,H) = 8.7 Hz, 2H arom.), 7.10-7.05 (m, 1H arom.);
¹³C NMR (CDCl₃, 75.3 MHz): δ = 161.6 (d, 1J(C,F) = 246.7 Hz), 160.2, 150.7, 137.5, 131.7, 129.7, 129.4 (2CH), 129.1 (2CH), 128.9 (2CH), 127.8, 124.2, 121.2 (d, 3J(C,F) = 8.8 Hz, 2CH), 119.4 (2CH), 118.6, 116.4 (d, 3J(C,F) = 23.7 Hz, 2CH); ¹⁹F NMR (CDCl₃, 376.3 MHz): δ = -115.0 Hz; IR (CHCl₃): ν = 3422, 1692, 1603, 1522, 1511, 1445, 1383, 1314, 1096 cm⁻¹; [M+Na⁺]: 380; Anal. Calcd for C₂₂H₁₆F₃N₃O: C, 73.94; H, 4.51; N, 11.76. Found: C, 73.92; H, 4.49; N, 11.74.

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide and 1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (12c and 13c): Compound 12c/13c were obtained as a light yellow solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/4). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (EtOAc/DCM 1/17).

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide (12c): m.p. = 226-228 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 8.11 (d, 3J(H,H) = 8.7 Hz, 2H arom.), 7.88-7.82 (m, 3H arom), 7.63 (d, 3J(H,H) = 8.7 Hz, 2H arom.), 7.55-7.30 (m, 7H arom.), 7.17 (t, 3J(H,H) = 7.4 Hz, 1H arom.), 7.11 (s, 1H, NH), 3.92 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 100.6 MHz): δ = 166.2, 157.5, 152.2, 143.2, 138.2, 136.9, 131.7, 130.4 (2CH), 129.6, 129.2 (2CH), 128.8 (2CH), 128.7, 126.3 (2CH), 125.2, 124.4 (2CH), 120.1 (2CH), 106.7, 52.3; IR (CHCl₃): ν = 3422, 2954, 1722, 1691, 1606, 1541, 1524, 1444, 1410, 1360, 1313, 1284, 1244, 1111, 1080, 1011 cm⁻¹; [M+Na⁺]: 420; Anal. Calcd for C₂₄H₁₉N₃O₃: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.51; H, 4.80; N, 10.55.

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (13c): m.p. = 209-210 °C; ¹H NMR (CDCl₃, 300 MHz): δ = 8.69 (s, 1H arom), 8.17 (d, 3J(H,H) = 8.9 Hz, 2H arom.), 7.87 (d, 3J(H,H) = 8.9 Hz, 2H arom.), 7.78-7.72 (m, 2H arom.), 7.61-7.55 (m, 3H arom.), 7.45 (s, 1H, NH), 7.38-7.24 (m, 4H arom.), 7.12-7.05 (m, 1H arom.), 3.95 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 100.6 MHz): δ = 166.0, 160.0, 151.2, 142.2, 137.4, 131.5, 131.4, 131.2 (2CH), 129.8, 129.4 (2CH), 129.2 (2CH), 129.1, 128.9 (2CH), 128.8, 124.3, 119.4 (2CH), 118.6 (2CH), 52.3; IR (CHCl₃): ν = 3421, 2952, 1721, 1690, 1608, 1541, 1524, 1504, 1444, 1410, 1360, 1313, 1284, 1246, 1114, 1080, 1012 cm⁻¹; [M+Na⁺]: 420; Anal. Calcd for C₂₄H₁₉N₃O₃: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.51; H, 4.79; N, 10.55.

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide and 1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (12c and 13c): Compound 12c/13c were obtained as a light yellow solids following the general procedure for the 1,3-DC and separated by chromatography on silica gel (EtOAc/Light Petroleum 1/3). The two regioisomers were further separate by Thick Layer Chromatography on silica gel plates (EtOAc/DCM 1/17).

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-5-carboxamide (12c): m.p. = 214-216 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.87 (d, 3J(H,H) = 7.8 Hz, 2H arom.), 7.56 (s, 1H, NH), 7.52-7.29 (m, 9H arom.), 7.18 (s, 1H arom), 7.14 (t,
$^3$J(H,H) = 7.4 Hz, 1H arom.), 7.00 (d, $^3$J(H,H) = 9.0 Hz, 2H arom.), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 100.6 MHz): δ = 159.9, 157.2, 151.4, 138.4, 137.1, 132.8, 132.1, 129.1 (2CH), 128.8 (2CH), 128.4 (2CH), 126.9 (2CH), 125.8 (2CH), 124.9, 120.0, 114.4 (2CH), 106.3, 55.6; IR (CHCl$_3$): ν = 3417, 2839, 1785, 1601, 1515, 1445, 1314, 1280, 1102, 1085, 1006 cm$^{-1}$; [M+Na]$^+$: 392; Anal. Calcd for C$_{23}$H$_{19}$N$_3$O$_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.80; H, 5.20; N, 11.38.

1-(4-methoxyphenyl)-N,3-diphenyl-1H-pyrazole-4-carboxamide (13c): m.p. = 208-210 °C; $^1$H NMR (CDCl$_3$, 300 MHz): δ = 8.52 (s, 1H arom), 7.77-7.65 (m, 4H arom), 7.60-7.53 (m, 3H arom.), 7.42 (s, 1H, NH), 7.30-7.25 (m, 4H arom.), 7.10-6.97 (m, 3H arom.), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (CDCl$_3$, 75.3 MHz): δ = 160.4, 158.9, 150.2, 137.6, 132.8, 132.0, 131.4, 129.5, 129.1 (2CH), 128.8 (2CH), 124.0, 121.1 (2CH), 119.3 (2CH), 118.0, 114.6 (2CH), 55.6; IR (CHCl$_3$): ν = 3419, 2841, 1782, 1602, 1512, 1445, 1314, 1284, 1106, 1085, 106 cm$^{-1}$; [M+Na]$^+$: 392; Anal. Calcd for C$_{23}$H$_{19}$N$_3$O$_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.79; H, 5.17; N, 11.36.

methyl 1-(4-fluorophenyl)-5-p-tolyl-1H-pyrazole-3-carboxylate and methyl 1-(4-fluorophenyl)-4-p-tolyl-1H-pyrazole-3-carboxylate (14a and 15a): Compound 14a/15a were obtained as a light yellow solids following the general procedure for the 1,3-DC of 1-ethynyl-4-methylbenzene with 3a and separated by Thick Layer Chromatography on silica gel plates (EtOAc/Light Petroleum 1/10). methyl 1-(4-fluorophenyl)-5-p-tolyl-1H-pyrazole-3-carboxylate (14a): m.p. = 153-155 °C; $^1$H NMR (CDCl$_3$, 400 MHz): δ = 7.34-7.28 (m, 2H arom.), 7.15-7.00 (m, 7H arom), 2.35 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 100.6 MHz): δ = 162.8, 162.1 (d, $^1$J(C,F) = 248.5 Hz), 144.9, 144.0, 139.0, 135.7, 129.4 (2CH), 128.6 (2CH), 127.5 (d, $^1$J(C,F) = 8.9 Hz, 2CH), 126.3, 115.9 (d, $^2$J(C,F) = 23.3 Hz, 2CH), 109.6, 52.2, 21.2; $^{19}$F NMR (CDCl$_3$, 376.3 MHz): δ = -113.4; IR (CCl$_3$): ν = 2890, 1726, 1606, 1516, 1503, 1472, 1452, 1270; [M+Na]$^+$: 333; Anal. Calcd for C$_{18}$H$_{15}$FN$_2$O$_2$: C, 69.67; H, 4.87; N, 9.03. Found: C, 69.69; H, 4.89; N, 9.06.

methyl 1-(4-fluorophenyl)-4-p-tolyl-1H-pyrazole-3-carboxylate (15a): yellow sticky oil; $^1$H NMR (CDCl$_3$, 400 MHz): δ = 7.89 (s, 1H arom), 7.78-7.73 (m, 2H arom.), 7.41 (d, $^3$J(H,H) = 8.1 Hz, 2H arom.), 7.25-7.17 (m, 4H arom), 3.92 (s, 3H, OCH$_3$), 2.40 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 100.6 MHz): δ = 162.8, 161.9 (d, $^1$J(C,F) = 247.7 Hz), 140.9, 137.6, 135.7, 129.1 (2CH), 128.9 (2CH), 128.0, 127.9, 127.8, 121.9 (d, $^3$J(C,F) = 8.8 Hz, 2CH), 116.4 (d, $^3$J(C,F) = 23.2 Hz, 2CH), 52.1, 21.6; $^{19}$F NMR (CDCl$_3$, 376.3 MHz): δ = -114.6; IR (CCl$_3$): ν = 2900, 1728, 1605, 1516, 1503, 1469, 1451, 1275; [M+Na]$^+$: 333; Anal. Calcd for C$_{18}$H$_{15}$FN$_2$O$_2$: C, 69.67; H, 4.87; N, 9.03. Found: C, 69.66; H, 4.86; N, 9.02.