

Cs₂CO₃ catalyzed direct aza-Michael addition of azoles to α,β -unsaturated malonates

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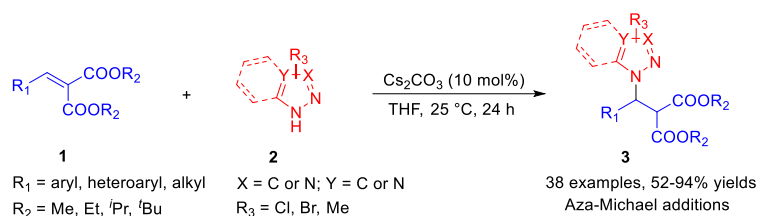
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1. General

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 ; $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, w = wide), coupling constants (Hz) and integration. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 ; $\delta = 77.0$). ESI-HRMS spectra were recorded on a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. Reagents obtained from commercial sources were used without further purification. CH_2Cl_2 were distilled over CaH_2 before use. The THF and other solvents were distilled from sodium benzophenone ketyl before use. Purifications of the products were carried out by flash chromatography.

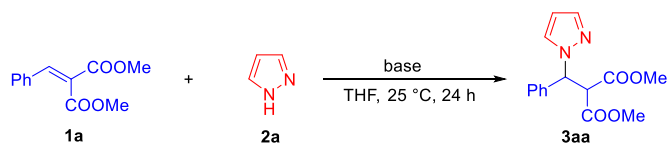
2. Typical procedure for the direct aza-Michael additions



The reactions were performed with α,β -unsaturated malonates **1** (0.50 mmol), azoles **2** (0.75 mmol) and Cs_2CO_3 (0.05 mmol) in THF (0.5 mL) at 25 $^\circ\text{C}$. The reaction mixtures were stirred at 25 $^\circ\text{C}$ for 24 h. Then, the solvents were removed under reduced pressure, and the residues were purified by flash chromatography on silica gel by gradient elution with PE/EA = 8/1 to 3/1 to afford the azole derivatives **3**.

3. Extra condition optimizations for the direct aza-Michael addition

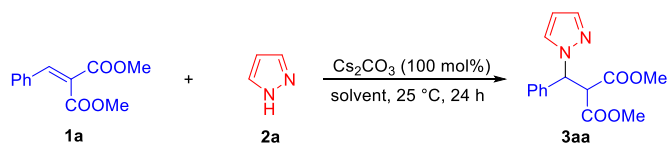
Table 1: Exploring the efficiency of base on the direct aza-Michael addition^[a].



Entry	Base	Yield [%] ^[b]
1	-	0
2	Et ₃ N	Trace
3	DBU	31
4	LiOH•H ₂ O	60
5	K ₃ PO ₄ •7H ₂ O	58
6	Cs₂CO₃	69
7	K ₂ CO ₃	53

[a] Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), base (100 mol %) in THF (1.0 mL) at 25 °C for 24 h. [b] Isolated yield.

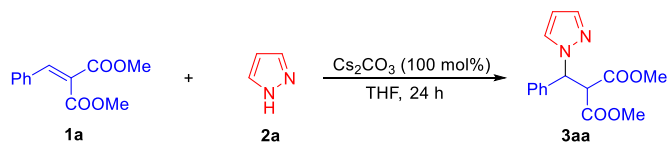
Table 2: Exploring the efficiency of solvent on the direct aza-Michael addition^[a].



Entry	Solvent	Yield [%] ^[b]
1	THF	69
2	CH ₃ OH	-
3	PhCH ₃	62
4	EtOAc	48
5	CH ₂ Cl ₂	61

[a] Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), Cs₂CO₃ (100 mol %) in solvent (1.0 mL) at 25 °C for 24 h. [b] Isolated yield.

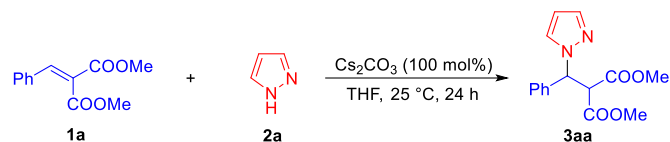
Table 3: Exploring the efficiency of temperature on the direct aza-Michael addition^[a].



Entry	T (°C)	Yield [%] ^[b]
1	0	50
2	25	69
3	30	68
4	40	67
5	50	66

[a] Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), Cs₂CO₃ (100 mol %) in THF (1.0 mL) at the indicated temperature for 24 h. [b] Isolated yield.

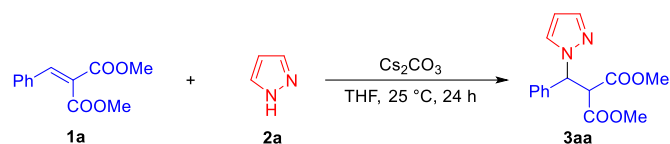
Table 4: Exploring the efficiency of the ratio of substrates on the direct aza-Michael addition^[a].



Entry	Ratio (1a/2a)	Yield [%] ^[b]
1	1.0/3.0	80
2	1.0/2.0	81
3	1.0/1.5	80
4	1.0/1.0	69
5	1.5/1.0	69
6	2.0/1.0	70
7	3.0/1.0	72

[a] Unless otherwise noted, the reactions were performed with **1a**, **2a**, Cs₂CO₃ (100 mol %) in THF (1.0 mL) at 25 °C for 24 h. [b] Isolated yield.

Table 5: Exploring the efficiency of catalyst loading on the direct aza-Michael addition^[a].

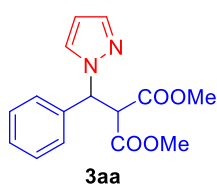


Entry	Cs ₂ CO ₃ (x mol%)	Yield [%] ^[b]
1	0	-
2	1	55
3	5	62
4	10	79
5	20	80
6	50	80
7	100	80

[a] Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), Cs₂CO₃ (x mol %) in THF (1.0 mL) at 25 °C for 24 h. [b] Isolated yield.

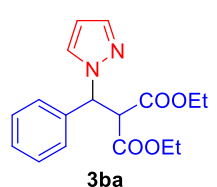
4. Characterization of the aza-Michael products 3

Dimethyl 2-(phenyl(1*H*-pyrazol-1-yl)methyl)malonate 3aa:



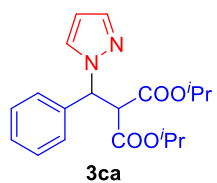
Prepared according to **general procedure**. 83% yield. White solid, m.p.: 98 – 101 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (s, 1H), 7.44 (s, 1H), 7.43 (d, *J* = 6.4 Hz, 2H), 7.33 – 7.24 (m, 3H), 6.18 (s, 1H), 5.93 (d, *J* = 11.2 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 3.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.99, 166.71, 139.59, 137.08, 129.81, 128.71, 128.67, 127.59, 105.84, 64.10, 56.97, 52.92, 52.74 ppm. IR (KBr, thin film): ν_{\max} = 3449, 3151, 3058, 3023, 2970, 2858, 1982, 1734, 1613, 1508, 1441, 1203, 1093, 1053, 1013, 971, 936, 885, 817, 767, 707, 673, 636, 584 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₆N₂O₄[M + H]⁺ m/z 289.1183, Found: m/z 289.1179.

Diethyl 2-(phenyl(1*H*-pyrazol-1-yl)methyl)malonate 3ba:



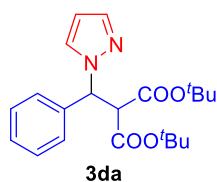
Prepared according to **general procedure**. 68% yield. White solid, m.p.: 127 – 130 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1H), 7.45 (d, *J* = 6.4 Hz, 2H), 7.44 (s, 1H), 7.31 – 7.25 (m, 3H), 6.18 (s, 1H), 5.91 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.11 – 4.06 (m, 2H), 3.98 – 3.92 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.57, 166.33, 139.51, 137.12, 129.72, 128.63, 128.58, 127.76, 105.67, 64.19, 61.83, 61.73, 57.30, 13.83, 13.65 ppm. IR (KBr, thin film): ν_{\max} = 3476, 2968, 1753, 1641, 1528, 1443, 1269, 1153, 1029, 931, 757, 702, 670, 634, 587 cm⁻¹. ES-HRMS Calcd for C₁₇H₂₀N₂O₄[M + Na]⁺ m/z 339.1315, Found: m/z 339.1313.

Diisopropyl 2-(phenyl(1*H*-pyrazol-1-yl)methyl)malonate 3ca:



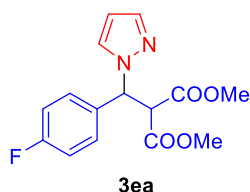
Prepared according to **general procedure**. 67% yield. White solid, m.p.: 73 – 76 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 – 7.43 (m, 4H), 7.32 – 7.24 (m, 3H), 6.17 (s, 1H), 5.89 (d, *J* = 11.6 Hz, 1H), 4.92 (sep, *J* = 6.4 Hz, 1H), 4.80 (sep, *J* = 6.4 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.12, 165.85, 139.45, 137.18, 129.62, 128.56, 128.52, 127.88, 105.54, 69.33, 64.19, 57.63, 21.36, 21.33, 21.26, 21.14 ppm. IR (KBr, thin film): ν_{\max} = 3422, 2993, 2946, 1755, 1650, 1512, 1465, 1387, 1305, 1185, 1101, 1051, 963, 910, 828, 764, 705, 631, 570 cm⁻¹. ES-HRMS Calcd for C₁₉H₂₄N₂O₄[M + H]⁺ m/z 345.1809, Found: m/z 345.1804.

Di-*tert*-butyl 2-(phenyl(1*H*-pyrazol-1-yl)methyl)malonate 3da:



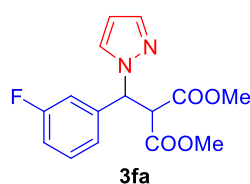
Prepared according to **general procedure**. 69% yield. White solid, m.p.: 118 – 121 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 – 7.43 (m, 4H), 7.32 – 7.24 (m, 3H), 6.17 (s, 1H), 5.79 (d, *J* = 11.2 Hz, 1H), 4.61 (d, *J* = 11.2 Hz, 1H), 1.32 (s, 9H), 1.19 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 165.81, 165.55, 139.31, 137.43, 129.52, 128.44, 127.99, 105.41, 82.06, 82.01, 64.30, 58.98, 27.63, 27.44 ppm. IR (KBr, thin film): ν_{\max} = 3488, 3127, 3074, 3002, 2949, 1752, 1608, 1463, 1332, 1133, 1045, 963, 923, 860, 759, 704, 629, 596, 523 cm⁻¹. ES-HRMS Calcd for C₂₁H₂₈N₂O₄[M + Na]⁺ m/z 395.1941, Found: m/z 395.1939.

Dimethyl 2-((4-fluorophenyl)(1*H*-pyrazol-1-yl)methyl)malonate **3ea**:



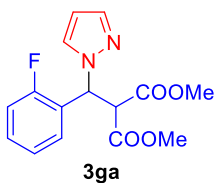
Prepared according to **general procedure**. 84% yield. White solid, m.p.: 113 – 116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (s, 1H), 7.47 – 7.41 (m, 3H), 6.98 (t, *J* = 8.4 Hz, 2H), 6.19 (s, 1H), 5.92 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 3.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.82, 166.65, 163.93, 161.47, 139.81, 133.00, 132.96, 129.83, 129.58, 129.50, 115.71, 115.50, 105.88, 63.34, 57.06, 52.95, 52.81 ppm. IR (KBr, thin film): ν_{\max} = 3456, 3134, 3086, 3032, 2973, 2862, 1770, 1615, 1522, 1442, 1153, 1095, 969, 926, 889, 859, 801, 762, 668, 628, 577 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅FN₂O₄[M + Na]⁺ *m/z* 329.0908, Found: *m/z* 329.0906.

Dimethyl 2-((3-fluorophenyl)(1*H*-pyrazol-1-yl)methyl)malonate **3fa**:



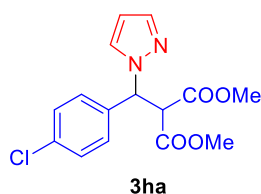
Prepared according to **general procedure**. 73% yield. White solid, m.p.: 139 – 141 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (s, 1H), 7.47 (s, 1H), 7.33 – 7.17 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 5.94 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.73, 166.56, 163.83, 161.36, 139.90, 139.48, 139.42, 130.28, 130.19, 129.94, 123.33, 123.30, 115.85, 125.64, 114.85, 114.63, 106.00, 63.45, 56.85, 53.00, 52.87 ppm. IR (KBr, thin film): ν_{\max} = 3471, 1655, 1506, 1438, 1059, 1010, 981, 946, 875, 807, 760, 708, 677, 626, 581 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅FN₂O₄[M + H]⁺ *m/z* 307.1089, Found: *m/z* 307.1091.

Dimethyl 2-((2-fluorophenyl)(1*H*-pyrazol-1-yl)methyl)malonate **3ga**:



Prepared according to **general procedure**. 66% yield. White solid, m.p.: 115 – 117 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (t, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.30 – 7.20 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 9.2 Hz, 1H), 6.36 (d, *J* = 11.2 Hz, 1H), 6.16 (s, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 3.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.78, 166.31, 161.10, 158.63, 139.96, 130.48, 130.40, 130.08, 128.91, 128.88, 125.45, 124.51, 124.19, 124.06, 115.73, 115.51, 105.65, 56.14, 56.09, 55.80, 52.95, 52.83 ppm. IR (KBr, thin film): ν_{\max} = 3464, 3130, 3055, 2973, 2859, 1945, 1770, 1622, 1596, 1504, 1444, 1397, 1210, 1094, 1052, 1013, 976, 931, 881, 814, 765, 670, 631, 594 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅FN₂O₄[M + Na]⁺ *m/z* 329.0908, Found: *m/z* 329.0906.

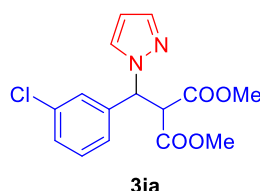
Dimethyl 2-((4-chlorophenyl)(1*H*-pyrazol-1-yl)methyl)malonate **3ha**:



Prepared according to **general procedure**. 92% yield. White solid, m.p.: 114 – 117 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1H), 7.43 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.18 (s, 1H), 5.91 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 3.61 (s, 3H), 3.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.74, 166.57, 139.88, 135.22, 134.64, 129.89, 129.10, 128.85, 105.95, 63.35, 56.97, 52.97, 52.87 ppm. IR (KBr,

thin film): $V_{\max} = 3456, 3131, 3075, 2972, 1768, 1604, 1503, 1443, 1358, 1308, 1152, 1093, 1053, 1016, 972, 929, 858, 795, 757, 668, 632, 587 \text{ cm}^{-1}$. ES-HRMS Calcd for $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_4[\text{M} + \text{Na}]^+$ m/z 345.0613, Found: m/z 345.0611.

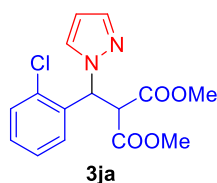
Dimethyl 2-((3-chlorophenyl)(1H-pyrazol-1-yl)methyl)malonate **3ia**:



Prepared according to **general procedure**. 87% yield. White solid, m.p.: 135 – 138 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ (s, 1H), 7.44 (s, 2H), 7.36 – 7.30 (m, 1H), 7.27 – 7.18 (m, 2H), 6.19 (s, 1H), 5.89 (d, $J = 11.2$ Hz, 1H), 4.79 (d, $J = 11.2$ Hz, 1H), 3.61 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.68, 166.52, 139.93, 139.06, 134.42, 129.95, 128.92, 127.86, 125.82, 106.01, 63.43, 56.82, 52.99, 52.88$ ppm. IR (KBr, thin film):

$V_{\max} = 3440, 3135, 3026, 2970, 1759, 1583, 1516, 1485, 1439, 1404, 1361, 1314, 1157, 1093, 1054, 1013, 973, 930, 882, 821, 788, 762, 699, 632, 584 \text{ cm}^{-1}$. ES-HRMS Calcd for $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_4[\text{M} + \text{Na}]^+$ m/z 345.0613, Found: m/z 345.0604.

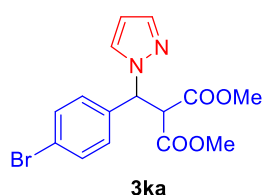
Dimethyl 2-((2-chlorophenyl)(1H-pyrazol-1-yl)methyl)malonate **3ja**:



Prepared according to **general procedure**. 64% yield. Yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.70$ (d, $J = 7.6$ Hz, 1H), 7.54 (s, 1H), 7.46 (s, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.28 – 7.15 (m, 2H), 6.58 (d, $J = 11.2$ Hz, 1H), 6.15 (s, 1H), 4.93 (d, $J = 11.2$ Hz, 1H), 3.61 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.79, 166.21, 140.01, 134.26, 133.64, 130.39, 129.85, 129.78,$

128.87, 127.33, 105.54, 58.97, 55.99, 52.98, 52.84 ppm. IR (KBr, thin film): $V_{\max} = 3462, 3132, 3038, 2975, 1768, 1602, 1520, 1441, 1398, 1362, 1293, 1149, 1094, 1051, 1009, 970, 929, 882, 820, 761, 699, 668, 629, 589 \text{ cm}^{-1}$. ES-HRMS Calcd for $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_4[\text{M} + \text{Na}]^+$ m/z 345.0613, Found: m/z 345.0612.

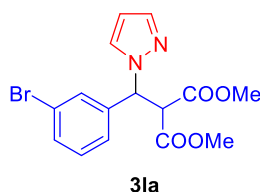
Dimethyl 2-((4-bromophenyl)(1H-pyrazol-1-yl)methyl)malonate **3ka**:



Prepared according to **general procedure**. 74% yield. White solid, m.p.: 115 – 117 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ (s, 1H), 7.43 (s, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 6.19 (s, 1H), 5.89 (d, $J = 11.2$ Hz, 1H), 4.79 (d, $J = 11.2$ Hz, 1H), 3.62 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 166.73, 166.56, 139.91, 136.10, 131.83, 129.89, 129.40, 122.90, 105.97, 63.42, 56.82, 53.01, 52.91$ ppm. IR (KBr,

thin film): $V_{\max} = 3446, 3129, 3073, 3022, 2969, 1764, 1601, 1500, 1440, 1358, 1315, 1152, 1088, 1055, 1017, 970, 927, 880, 837, 790, 758, 713, 665, 633, 589 \text{ cm}^{-1}$. ES-HRMS Calcd for $\text{C}_{15}\text{H}_{15}\text{BrN}_2\text{O}_4[\text{M} + \text{Na}]^+$ m/z 389.0107, Found: m/z 389.0104.

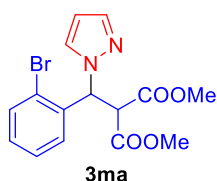
Dimethyl 2-((3-bromophenyl)(1*H*-pyrazol-1-yl)methyl)malonate 3la:



Prepared according to **general procedure**. 71% yield. White solid, m.p.: 108 – 110 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (s, 1H), 7.49 (s, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 5.89 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 3.60 (s, 3H), 3.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.66, 166.50, 139.94, 139.30, 131.84, 130.76, 130.24, 129.97, 126.28, 122.53, 106.02, 63.36,

56.84, 52.99, 52.89 ppm. IR (KBr, thin film): ν_{\max} = 3440, 3135, 3031, 2969, 1759, 1603, 1576, 1516, 1483, 1437, 1403, 1359, 1314, 1089, 1052, 1017, 972, 935, 887, 821, 758, 693, 631, 580 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅BrN₂O₄[M + Na]⁺ m/z 389.0107, Found: m/z 389.0105.

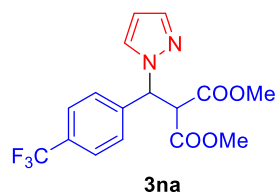
Dimethyl 2-((2-bromophenyl)(1-*H*-pyrazolyl)methyl)malonate 3ma:



Prepared according to **general procedure**. 52% yield. White solid, m.p.: 111 – 114 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.73 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 11.2 Hz, 1H), 6.17 (s, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 3.64 (s, 3H), 3.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.78, 166.19, 140.03,

135.85, 133.13, 130.42, 130.11, 129.08, 127.97, 124.28, 105.53, 61.62, 56.17, 53.00, 52.84 ppm. IR (KBr, thin film): ν_{\max} = 3460, 3159, 3134, 3107, 2974, 1770, 1520, 1439, 1386, 1360, 1292, 1212, 1093, 1053, 1017, 970, 928, 881, 80, 760, 673, 628, 588 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅BrN₂O₄[M + Na]⁺ m/z 389.0107, Found: m/z 389.0105.

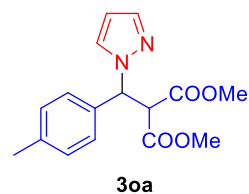
Dimethyl 2-((1*H*-pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methyl)malonate 3na:



Prepared according to **general procedure**. 81% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.46 (s, 1H), 6.20 (s, 1H), 6.00 (d, *J* = 11.2 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 3.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.63, 166.49, 140.96, 140.07, 130.64, 130.62, 130.03, 128.18, 125.68, 125.64, 125.60, 125.57, 125.14, 122.43, 106.07, 63.48,

56.76, 53.00, 52.86 ppm. IR (KBr, thin film): ν_{\max} = 3456, 3156, 2974, 1760, 1630, 1522, 1441, 1404, 1325, 1175, 1118, 1073, 1024, 968, 925, 864, 815, 761, 672, 633, 556 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₅F₃N₂O₄[M + Na]⁺ m/z 379.0876, Found: m/z 379.0876.

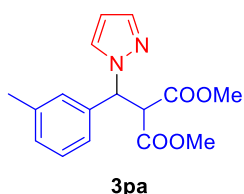
Dimethyl 2-((1*H*-pyrazol-1-yl)(*p*-tolyl)methyl)malonate 3oa:



Prepared according to **general procedure**. 63% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1H), 7.42 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.18 (s, 1H), 5.90 (d, *J* = 11.2 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 3.63 (s, 3H), 3.52 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.07, 166.74, 139.54, 138.51, 134.10, 129.68, 129.36, 127.46, 105.74, 63.88, 56.97, 52.90, 52.76, 21.12 ppm. IR (KBr, thin film): ν_{\max} =

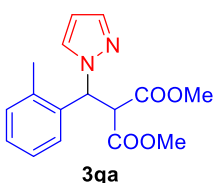
3483, 2968, 1752, 1522, 1443, 1401, 1269, 1155, 1095, 1029, 972, 932, 759, 631, 584 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₄[M + Na]⁺ m/z 325.1159, Found: m/z 325.1157.

Dimethyl 2-((1*H*-pyrazol-1-yl)(*m*-tolyl)methyl)malonate 3pa:



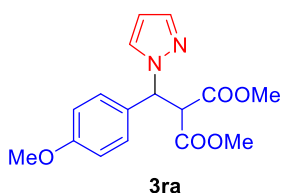
Prepared according to **general procedure**. 91% yield. White solid, m.p.: 104 – 106 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1H), 7.43 (s, 1H), 7.23 (s, 1H), 7.22 – 7.13 (m, 2H), 7.10 – 7.04 (m, 1H), 6.17 (s, 1H), 5.90 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 11.2 Hz, 1H), 3.60 (s, 3H), 3.49 (s, 3H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.01, 166.71, 139.51, 138.35, 137.02, 129.75, 129.47, 128.52, 128.21, 124.58, 105.77, 64.08, 56.93, 52.86, 52.70, 21.37 ppm. IR (KBr, thin film): *V*_{max} = 3484, 2968, 1757, 1651, 1443, 1281, 1156, 1096, 1030, 760, 632, 581 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₄[M + Na]⁺ *m/z* 325.1159, Found: *m/z* 325.1157.

Dimethyl 2-((1*H*-pyrazol-1-yl)(*o*-tolyl)methyl)malonate 3qa:



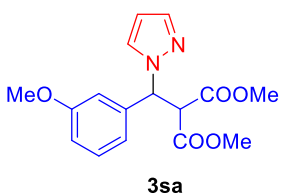
Prepared according to **general procedure**. 55% yield. White solid, m.p.: 84 – 86 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, *J* = 6.8 Hz, 1H), 7.46 (s, 1H), 7.37 (s, 1H), 7.30 – 7.20 (m, 3H), 6.27 (d, *J* = 11.2 Hz, 1H), 6.15 (s, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 3.47 (s, 3H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.27, 166.64, 139.48, 136.26, 134.88, 130.85, 129.48, 128.59, 127.18, 126.46, 105.67, 59.56, 56.51, 52.94, 52.68, 19.44 ppm. IR (KBr, thin film): *V*_{max} = 3468, 3130, 2969, 1741, 1509, 1442, 1400, 1360, 1319, 1248, 1204, 1147, 1094, 1029, 968, 931, 771, 630, 580 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₄[M + Na]⁺ *m/z* 325.1159, Found: *m/z* 325.1157.

Dimethyl 2-((4-methoxyphenyl)(1*H*-pyrazol-1-yl)methyl)malonate 3ra:



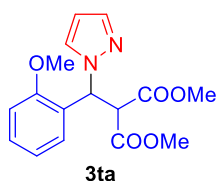
Prepared according to **general procedure**. 77% yield. White solid, m.p.: 95 – 98 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (s, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.17 (s, 1H), 5.88 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 3.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.05, 166.75, 159.68, 139.55, 129.65, 129.16, 128.89, 113.97, 105.70, 63.58, 57.10, 55.17, 52.89, 52.76 ppm. IR (KBr, thin film): *V*_{max} = 3483, 2970, 1751, 1623, 1521, 1444, 1402, 1266, 1181, 1036, 755, 629, 558 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₅[M + Na]⁺ *m/z* 341.1108, Found: *m/z* 341.1106.

Dimethyl 2-((3-methoxyphenyl)(1*H*-pyrazol-1-yl)methyl)malonate 3sa:



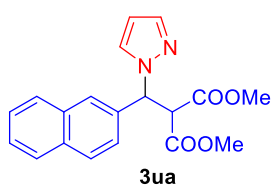
Prepared according to **general procedure**. 87% yield. White solid, m.p.: 88 – 91 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (s, 1H), 7.43 (s, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 5.90 (d, *J* = 11.2 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 3.72 (s, 3H), 3.61 (s, 3H), 3.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.94, 166.66, 159.66, 139.55, 138.58, 129.81, 129.66, 119.75, 114.25, 113.03, 105.85, 63.98, 56.93, 55.14, 52.89, 52.76 ppm. IR (KBr, thin film): *V*_{max} = 3449, 3132, 3048, 2973, 2851, 1735, 1607, 1505, 1402, 1361, 1246, 1091, 1044, 996, 971, 947, 780, 754, 664, 636, 567 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₅[M + Na]⁺ *m/z* 341.1108, Found: *m/z* 341.1108.

Dimethyl 2-((2-methoxyphenyl)(1*H*-pyrazol-1-yl)methyl)malonate 3ta:



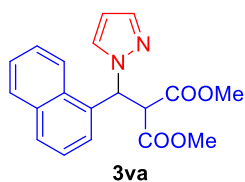
Prepared according to **general procedure**. 65% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.45 (s, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 11.2 Hz, 1H), 6.13 (s, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 3.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.33, 166.72, 156.61, 139.45, 130.07, 129.82, 128.11, 125.07, 120.76, 110.93, 105.08, 56.65, 55.65, 55.61, 52.84, 52.65 ppm. IR (KBr, thin film): V_{\max} = 3481, 1750, 1654, 1441, 1259, 1028, 755, 626, 574 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₅[M + Na]⁺ *m/z* 341.1108, Found: *m/z* 341.1108.

Dimethyl 2-(naphthalen-2-yl(1*H*-pyrazol-1-yl)methyl)malonate 3ua:



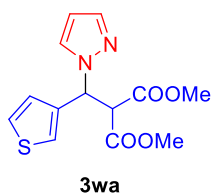
Prepared according to **general procedure**. 75% yield. White solid, m.p.: 129 – 131 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (s, 1H), 7.88 – 7.76 (m, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.50 (s, 1H), 7.48 – 7.42 (m, 2H), 6.21 (s, 1H), 6.17 (d, *J* = 11.2 Hz, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 3.67 (s, 3H), 3.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.05, 166.78, 139.70, 134.57, 133.24, 133.02, 129.95, 128.68, 128.23, 127.67, 127.08, 126.60, 126.43, 124.96, 105.98, 64.27, 56.97, 53.00, 52.81 ppm. IR (KBr, thin film): V_{\max} = 3469, 2965, 1740, 1519, 1436, 1177, 756 cm⁻¹. ES-HRMS Calcd for C₁₉H₁₈N₂O₄[M + Na]⁺ *m/z* 361.1159, Found: *m/z* 361.1157.

Dimethyl 2-(naphthalen-1-yl(1*H*-pyrazol-1-yl)methyl)malonate 3va:



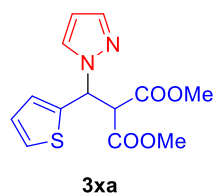
Prepared according to **general procedure**. 88% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.25 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.38 (m, 5H), 6.92 (d, *J* = 11.2 Hz, 1H), 6.16 (s, 1H), 5.05 (d, *J* = 11.2 Hz, 1H), 3.70 (s, 3H), 3.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.37, 166.55, 139.41, 133.91, 132.53, 130.91, 129.66, 129.56, 128.99, 126.93, 125.94, 125.50, 125.24, 122.53, 106.03, 59.24, 56.77, 53.08, 52.70 ppm. IR (KBr, thin film): V_{\max} = 3479, 2971, 1749, 1442, 1258, 797 cm⁻¹. ES-HRMS Calcd for C₁₉H₁₈N₂O₄[M + Na]⁺ *m/z* 361.1159, Found: *m/z* 361.1156.

Dimethyl 2-((1*H*-pyrazol-1-yl)(thiophen-3-yl)methyl)malonate 3wa:



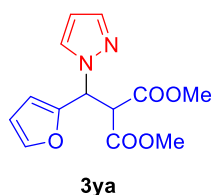
Prepared according to **general procedure**. 84% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (s, 1H), 7.46 (s, 1H), 7.34 (s, 1H), 7.25 – 7.21 (m, 1H), 7.16 – 7.10 (m, 1H), 6.19 (s, 1H), 6.07 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 3.60 (s, 3H), 3.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.79, 139.89, 137.80, 129.92, 126.77, 126.29, 123.79, 105.55, 59.70, 57.25, 52.92, 52.88 ppm. IR (KBr, thin film): V_{\max} = 3459, 3133, 2968, 1734, 1442, 1253, 1093, 1022, 970, 840, 761, 681, 646, 581 cm⁻¹. ES-HRMS Calcd for C₁₃H₁₄N₂O₄S[M + Na]⁺ *m/z* 317.0566, Found: *m/z* 317.0566.

Dimethyl 2-((1*H*-pyrazol-1-yl)(thiophen-2-yl)methyl)malonate **3xa**:



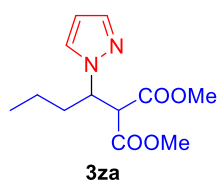
Prepared according to **general procedure**. 81% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (s, 1H), 7.50 (s, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 7.10 (w, 1H), 6.93 – 6.88 (m, 1H), 6.24 (d, *J* = 11.2 Hz, 1H), 6.20 (s, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 3.60 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.50, 166.49, 140.12, 139.33, 129.92, 126.76, 126.57, 126.52, 105.73, 59.64, 58.13, 52.96 ppm. IR (KBr, thin film): V_{\max} = 3469, 3127, 2968, 1739, 1443, 1253, 1091, 1027, 966, 861, 761, 635, 584 cm⁻¹. ES-HRMS Calcd for C₁₃H₁₄N₂O₄S[M + Na]⁺ *m/z* 317.0566, Found: *m/z* 317.0565.

Dimethyl 2-(furan-2-yl(1*H*-pyrazol-1-yl)methyl)malonate **3ya**:



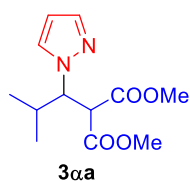
Prepared according to **general procedure**. 76% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 – 7.45 (m, 2H), 7.34 (s, 1H), 7.36 (d, *J* = 3.2 Hz, 1H), 6.31 – 6.28 (m, 1H), 6.19 (s, 1H), 6.08 (d, *J* = 11.2 Hz, 1H), 4.71 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.40, 166.38, 149.59, 142.97, 140.11, 129.82, 110.57, 108.75, 105.73, 57.64, 55.17, 53.03, 52.99 ppm. IR (KBr, thin film): V_{\max} = 3469, 1737, 1638, 1444, 1265, 1228, 767, 759 cm⁻¹. ES-HRMS Calcd for C₁₃H₁₄N₂O₅[M + Na]⁺ *m/z* 301.0795, Found: *m/z* 301.0891.

Dimethyl 2-(1-(1*H*-pyrazol-1-yl)butyl)malonate **3za**:



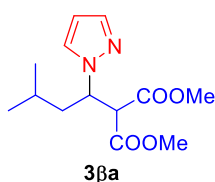
Prepared according to **general procedure**. 85% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (s, 1H), 7.44 (s, 1H), 6.17 (s, 1H), 4.80 (dt, *J*₁ = 11.2 Hz, *J*₂ = 2.8 Hz, 1H), 4.13 (d, *J* = 11.2 Hz, 1H), 3.79 (s, 3H), 3.53 (s, 3H), 2.05 – 2.00 (m, 1H), 1.74 – 1.64 (m, 1H), 1.17 – 0.97 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.42, 167.04, 139.90, 130.69, 104.46, 60.70, 56.94, 52.74, 52.50, 34.64, 18.85, 13.24 ppm. IR (KBr, thin film): V_{\max} = 2978, 1756, 1444, 1284, 985, 770 cm⁻¹. ES-HRMS Calcd for C₁₂H₁₈N₂O₄[M + Na]⁺ *m/z* 277.1159, Found: *m/z* 277.1166.

Dimethyl 2-(2-methyl-1-(1*H*-pyrazol-1-yl)propyl)malonate **3αa**:



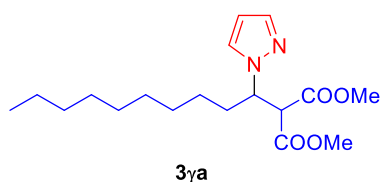
Prepared according to **general procedure**. 92% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (s, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 6.23 (s, 1H), 4.75 (dd, *J*₁ = 10.0 Hz, *J*₂ = 5.6 Hz, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 3.57 (s, 3H), 2.32 – 2.20 (m, 1H), 0.94 (d, *J* = 2.0 Hz, 3H), 0.92 (d, *J* = 2.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.66, 167.10, 139.24, 131.32, 104.47, 65.62, 54.49, 52.89, 52.59, 31.12, 20.15, 17.31 ppm. IR (KBr, thin film): V_{\max} = 3477, 1750, 1444, 1258, 756 cm⁻¹. ES-HRMS Calcd for C₁₂H₁₈N₂O₄[M + Na]⁺ *m/z* 277.1159, Found: *m/z* 277.1163.

Dimethyl 2-(3-methyl-1-(1*H*-pyrazol-1-yl)butyl)malonate **3βa**:



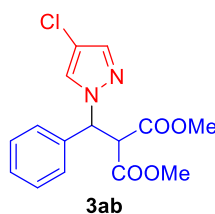
Prepared according to **general procedure**. 60% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (s, 1H), 7.42 (s, 1H), 6.15 (s, 1H), 4.87 (dt, *J*₁ = 10.0 Hz, *J*₂ = 2.4 Hz, 1H), 4.06 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 2.21 – 2.11 (m, 1H), 1.45 – 1.36 (m, 1H), 1.17 – 1.05 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.43, 167.15, 139.97, 130.65, 104.56, 59.20, 57.28, 52.82, 52.61, 41.38, 24.34, 23.25, 20.87 ppm. IR (KBr, thin film): *V*_{max} = 3450, 2973, 1738, 1445, 1248, 1196, 755, 631 cm⁻¹. ES-HRMS Calcd for C₁₃H₂₀N₂O₄[M + Na]⁺ *m/z* 291.1315, Found: *m/z* 291.1324.

Dimethyl 2-(1-(1*H*-pyrazol-1-yl)decyl)malonate **3γa**:



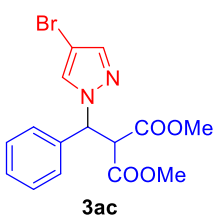
Prepared according to **general procedure**. 74% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (s, 1H), 7.38 (s, 1H), 6.12 (s, 1H), 4.87 (dt, *J*₁ = 10.0 Hz, *J*₂ = 2.8 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 3.74 (s, 3H), 3.48 (s, 3H), 2.11 – 1.98 (m, 1H), 1.74 – 1.64 (m, 1H), 1.25 – 1.10 (m, 14H), 0.82 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.46, 167.08, 139.93, 130.69, 104.47, 60.97, 56.99, 52.75, 52.52, 32.61, 31.73, 29.30, 29.23, 29.11, 28.75, 25.61, 22.54, 13.98 ppm. IR (KBr, thin film): *V*_{max} = 3464, 2940, 1752, 1641, 751 cm⁻¹. ES-HRMS Calcd for C₁₈H₃₀N₂O₄[M + H]⁺ *m/z* 339.2278, Found: *m/z* 339.2291.

Dimethyl 2-((4-chloro-1*H*-pyrazol-1-yl)(phenyl)methyl)malonate **3ab**:



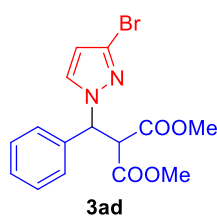
Prepared according to **general procedure**. 68% yield. White solid, m.p.: 136 – 138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.43 (s, 1H), 7.41 (s, 1H), 7.41 – 7.36 (m, 2H), 7.33 – 7.26 (m, 3H), 5.86 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 3.67 (s, 3H), 3.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.84, 166.44, 137.98, 136.41, 129.01, 128.80, 127.84, 127.53, 110.49, 64.58, 56.47, 53.06, 52.82 ppm. IR (KBr, thin film): *V*_{max} = 3471, 3139, 3058, 3022, 2970, 2860, 1736, 1615, 1504, 1441, 1372, 1326, 1263, 1030, 970, 938, 885, 810, 744, 704, 668, 621, 578 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅ClN₂O₄[M + Na]⁺ *m/z* 345.0613, Found: *m/z* 345.0611.

Dimethyl 2-((4-bromo-1*H*-pyrazol-1-yl)(phenyl)methyl)malonate **3ac**:



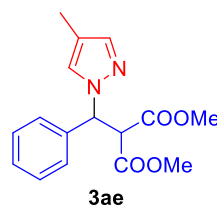
Prepared according to **general procedure**. 77% yield. White solid, m.p.: 121 – 123 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (s, 1H), 7.44 (s, 1H), 7.42 – 7.36 (m, 2H), 7.33 – 7.26 (m, 3H), 5.89 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.81, 166.43, 140.07, 136.43, 130.01, 129.02, 128.80, 127.56, 93.69, 64.53, 56.49, 53.05, 52.82 ppm. IR (KBr, thin film): *V*_{max} = 3473, 3131, 3024, 2971, 2858, 1736, 1613, 1502, 1437, 1387, 1168, 1029, 982, 952, 883, 852, 813, 749, 703, 644, 618, 577 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅BrN₂O₄[M + Na]⁺ *m/z* 389.0107, Found: *m/z* 389.0106.

Dimethyl 2-((3-bromo-1H-pyrazol-1-yl)(phenyl)methyl)malonate 3ad:



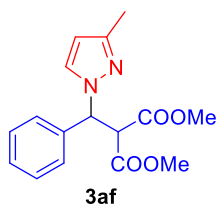
Prepared according to **general procedure**. 55% yield. White solid, m.p.: 113 – 116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.48 – 7.40 (m, 2H), 7.35 (s, 1H), 7.33 – 7.27 (m, 3H), 6.19 (s, 1H), 5.85 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.86, 166.49, 136.23, 132.03, 128.98, 128.75, 127.72, 125.91, 108.81, 64.84, 56.63, 53.01, 52.81 ppm. IR (KBr, thin film): *V*_{max} = 3456, 3132, 3015, 2967, 2856, 1973, 1758, 1613, 1502, 1441, 1337, 1155, 1047, 1013, 966, 930, 870, 814, 754, 703, 669, 639, 563 cm⁻¹. ES-HRMS Calcd for C₁₅H₁₅BrN₂O₄[M + Na]⁺ *m/z* 389.0107, Found: *m/z* 389.0106.

Dimethyl 2-((4-methyl-1H-pyrazol-1-yl)(phenyl)methyl)malonate 3ae:



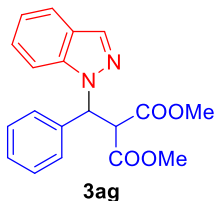
Prepared according to **general procedure**. 94% yield. White solid, m.p.: 93 – 95 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.42 – 7.37 (m, 2H), 7.32 – 7.25 (m, 4H), 7.19 (s, 1H), 5.84 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 3H), 1.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.10, 166.80, 140.02, 137.36, 128.64, 128.62, 128.48, 127.47, 116.39, 63.89, 56.80, 52.91, 52.70, 8.83 ppm. IR (KBr, thin film): *V*_{max} = 3467, 3105, 2972, 1765, 1437, 1270, 1143, 1017, 971, 935, 853, 815, 753, 704, 673, 631, 580 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₄[M + Na]⁺ *m/z* 325.1159, Found: *m/z* 325.1158.

Dimethyl 2-((3-methyl-1H-pyrazol-1-yl)(phenyl)methyl)malonate 3af:



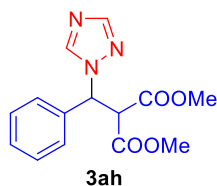
Prepared according to **general procedure**. 81% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.48 – 7.40 (m, 2H), 7.35 (s, 1H), 7.33 – 7.27 (m, 3H), 6.19 (s, 1H), 5.85 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.07, 166.84, 148.70, 137.27, 130.31, 128.59, 128.55, 127.63, 105.45, 63.94, 56.91, 52.82, 52.67, 13.74 ppm. IR (KBr, thin film): *V*_{max} = 3470, 2968, 1764, 1531, 1444, 1314, 1270, 1202, 1093, 1030, 937, 761, 705, 637, 590 cm⁻¹. ES-HRMS Calcd for C₁₆H₁₈N₂O₄[M + Na]⁺ *m/z* 325.1159, Found: *m/z* 325.1153.

Dimethyl 2-((1H-indazol-1-yl)(phenyl)methyl)malonate 3ag:



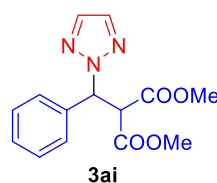
Prepared according to **general procedure**. 52% yield. White solid, m.p.: 112 – 115 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.50 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 11.2 Hz, 1H), 5.10 (d, *J* = 11.2 Hz, 1H), 3.56 (s, 3H), 3.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 167.06, 167.00, 139.58, 136.97, 133.68, 128.65, 128.60, 127.67, 126.58, 124.25, 121.03, 120.99, 109.34, 60.99, 57.02, 52.89, 52.79 ppm. IR (KBr, thin film): *V*_{max} = 3488, 3022, 2967, 1753, 1622, 1504, 1437, 1369, 1325, 1204, 1023, 971, 941, 870, 753, 703, 639, 603 cm⁻¹. ES-HRMS Calcd for C₁₉H₁₈N₂O₄[M + Na]⁺ *m/z* 361.1159, Found: *m/z* 361.1157.

Dimethyl 2-(phenyl(1*H*-1,2,4-triazol-1-yl)methyl)malonate 3ah:



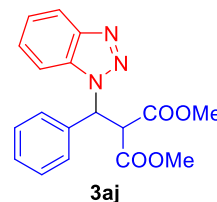
Prepared according to **general procedure**. 71% yield. White solid, m.p.: 148 – 151 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.15 (s, 1H), 7.89 (s, 1H), 7.45 (w, 2H), 7.30 (w, 3H), 6.03 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 3.62 (s, 3H), 3.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.54, 166.09, 151.98, 143.68, 135.38, 129.26, 128.88, 127.86, 62.11, 56.56, 53.13, 52.92 ppm. IR (KBr, thin film): V_{\max} = 3456, 3137, 3005, 2970, 1764, 1508, 1438, 1388, 1312, 1277, 1240, 1201, 1158, 1017, 972, 933, 874, 845, 821, 729, 705, 665, 638, 593 cm⁻¹. ES-HRMS Calcd for C₁₄H₁₅N₃O₄[M + Na]⁺ m/z 312.0955, Found: m/z 312.0952.

Dimethyl 2-(phenyl(2*H*-1,2,3-triazol-2-yl)methyl)malonate 3ai:



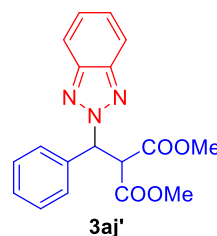
Prepared according to **general procedure**. 61% yield. White solid, m.p.: 116 – 118 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (s, 2H), 7.43 – 7.36 (m, 2H), 7.33 – 7.25 (m, 3H), 6.36 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 3.64 (s, 3H), 3.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.54, 166.13, 135.67, 134.47, 129.02, 128.76, 127.55, 66.84, 56.88, 53.04, 52.87 ppm. IR (KBr, thin film): V_{\max} = 3458, 3142, 3050, 3023, 3000, 2969, 1736, 1503, 1444, 1308, 1206, 1156, 1015, 971, 935, 847, 760, 707, 641, 582 cm⁻¹. ES-HRMS Calcd for C₁₄H₁₅N₃O₄[M + Na]⁺ m/z 312.0955, Found: m/z 312.0952.

Dimethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methyl)malonate 3aj:



Prepared according to **general procedure**. 57% yield. White solid, m.p.: 135 – 138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.99 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.24 (m, 4H), 6.40 (d, *J* = 11.2 Hz, 1H), 5.20 (d, *J* = 11.2 Hz, 1H), 3.59 (s, 3H), 3.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.65, 166.44, 145.95, 135.27, 132.87, 129.22, 128.96, 127.73, 127.64, 124.22, 119.88, 109.66, 61.51, 56.87, 53.12, 52.96 ppm. IR (KBr, thin film): V_{\max} = 3480, 3050, 2970, 1732, 1616, 1499, 1460, 1439, 1372, 1318, 1255, 1120, 1068, 1023, 984, 929, 874, 821, 784, 756, 702, 665, 621, 581 cm⁻¹. ES-HRMS Calcd for C₁₈H₁₇N₃O₄[M + Na]⁺ m/z 362.1111, Found: m/z 362.1108.

Dimethyl 2-((2*H*-benzo[*d*][1,2,3]triazol-2-yl)(phenyl)methyl)malonate 3aj':



Prepared according to **general procedure**. 18% yield. White solid, m.p.: 149 – 152 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.8 Hz, 2H), 7.50 (d, *J* = 6.4 Hz, 2H), 7.35 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 6.64 (d, *J* = 11.6 Hz, 1H), 5.13 (d, *J* = 11.6 Hz, 1H), 3.62 (s, 3H), 3.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.49, 166.09, 144.22, 135.32, 129.24, 128.86, 127.71, 126.50, 118.29, 68.49, 56.93, 53.11, 52.97 ppm. IR (KBr, thin film): V_{\max} = 3462, 2968, 1761, 1505, 1447, 1370, 1309, 1273, 1233, 1184, 1155, 982, 943, 792, 747, 705, 643, 594 cm⁻¹. ES-HRMS Calcd for C₁₈H₁₇N₃O₄[M + Na]⁺ m/z 362.1111, Found: m/z 362.1107.

5. Copy of ^1H NMR and ^{13}C NMR spectra for the products 3

