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**General Information**

Commercially available reagents were purchased from Sigma-Aldrich or Acros. Chlorobenzene was distilled over P₄O₁₀ and stored over molecular sieves. Commercially unavailable reagents were prepared according to literature procedures:

- 5-[hydroxy((3-chlorophenyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione \(1\alpha\)
- 5-[hydroxy(phenylamino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione \(1\beta\)
- 5-[hydroxy((4-methoxyphenyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione \(1\delta\)
- 5-[hydroxy((4-nitrophenyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione \(1\epsilon\)
- 5-[hydroxy((ethyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione \(1\gamma\)

Iminium salts \(3\alpha-d\). Analytical TLC was performed on aluminum sheets of silica gel UV-254 Merck. Flash chromatography was performed using 40-63 microns of Zeochem silica gel. The \(^1H\), \(^13C\) were recorded on Bruker Avance III HD 400 MHz, chemical shifts (δ) in ppm rel. to internal Me₄Si; coupling constants \(J\) in Hz. High-resolution (HRMS) were recorded on MicroMass Quattro LCT mass spectrometer. Melting points were determined with Warsztat Elektromechaniczny W-wa apparatus and are not corrected.
Experimental Procedures and Characterization Data

5-[Hydroxy((4-methylphenyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione (1c).

To a cooled to 0°C solution of Meldrum’s acid (0.72 g, 5 mmol) in dry DMF (5 ml) was added Et3N (1.4 ml, 10 mmol). The mixture was stirred for 10 min and 4-methylphenylisocyanate (0.665 g, 5 mmol) was added. The stirring was continued for 15 min at 0°C and 1 h at R.T. The reaction mixture was poured into 2 M HCl ice cooled aqueous solution (30 ml). The solid precipitate was filtered and washed with cold water. Crystallization from AcOEt/Hexan gave 0.955 g, 68% yield; mp 134°C.1H NMR (400 MHz, CDCl3): δ 15.65 (s, 1H), 11.10 (s, 1H), 7.36-7.34 (m, 2H), 7.23-7.21 (m, 2H), 2.83 (s, 3H), 1.79 (s, 6H), 169.1, 164.3, 136.5, 132.1. 129.8, 122.2, 105.0, 73.5, 26.3, 20.9. HRMS (ESI-): m/z calcd for C15H19NO3Na [M-H]- 276.0872, found. 276.0877.

5-[Hydroxy((4-fluorophenyl)amino)methylene]-2,2-dimethyl-1,3-dioxo-4,6-dione (1f).

To a cooled to 0°C solution of Meldrum’s acid (0.72 g, 5 mmol) in dry DMF (5 ml) was added Et3N (1.4 ml, 10 mmol). The mixture was stirred for 10 min and 4-fluorophenylisocyanate (0.685 g, 5 mmol) was added. The stirring was continued for 15 min at 0°C and 1 h at R.T. The reaction mixture was poured into 2 M HCl ice cooled aqueous solution (30 ml). The solid precipitate was filtered and washed with cold water. Crystallization from AcOEt/Hexan gave 0.990 g, 65% yield; mp 118-120 °C. 1H NMR (400 MHz, CDCl3): δ 15.65 (s, 1H), 11.10 (s, 1H), 7.36-7.34 (m, 2H), 7.23-7.21 (m, 2H), 2.83 (s, 3H), 1.79 (s, 6H), 169.1, 164.3, 136.5, 132.1. 129.8, 122.2, 105.0, 73.5, 26.3, 20.9. HRMS (ESI-): m/z calcd for C15H15NO3Na [M-H]- 280.0621, found. 280.0622.

Preparation of 2-arylidene malonamides (8aa/8aa’-8gc/8gc’). General Procedure

To a solution of 5-{N-aryl/alkylamino)(hydroxyl)methylene}-2,2-dimethyl-1,3-dioxo-4,6-dione (1a-g) (1 mmol) in dry chlorobenzene (10 ml) was added iminium salts 3a-d (2 mmol). The resulting mixture was stirred and heated to reflux for 2 h. After completion of the reaction, the solvent was removed under vacuum, and the residue was purified with flash chromatography as specified below.

2-benzylidene-N1-(3-chlorophenyl)-N3,N4-dimethylmalonamide (8aa) (8aa’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil;

(E)-isomer (8aa) 0.170 g, 51% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.36 (s, 1 H), 7.80 (s, 1 H), 7.79 (t, J = 2.0 Hz, 1 H), 7.46 (dq, J = 8.0 Hz, J = 0.8 Hz, 1 H), 7.40 (s, 5 H), 7.26 (t, J = 8.0 Hz, 1 H), 7.10 (dq, J = 8.0 Hz, J = 1.2 Hz, 1 H), 3.01 (s, 3 H), 2.64 (s, 3 H), 1.3C NMR (CDCl3, 100 MHz): δ = 169.0, 162.1, 139.6, 138.9, 134.5, 133.7, 130.1, 129.9, 129.3, 128.9, 128.7, 124.4, 120.2, 118.1, 37.8, 34.9; (Z)-isomer (8aa’) 0.144 g, 44% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.15 (s, 1 H), 7.70 (t, J = 2.0 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.38-7.36 (m, 4 H), 7.24 (t, J = 8.0 Hz, 1 H), 7.10 (dq, J = 8.0 Hz, J = 1.2 Hz, 1 H), 2.64 (s, 3 H), 1.26 (s, 3 H), 1.3C NMR (CDCl3, 100 MHz): δ = 169.0, 162.1, 139.6, 138.9, 134.5, 133.7, 130.1, 129.9, 129.3, 128.9, 128.7, 124.4, 120.2, 118.1, 37.8, 34.9; HRMS (ESI-): m/z calcd for C15H15NO3Na [M-H]- 276.0872, found. 276.0877.
N²-(3-chlorophenyl)-N³,N⁴-dimethyl-2-(4-methylbenzylidene)malonamide (8ab), (8ab’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil;

(E)-isomer (8ab) 0.189 g, 55% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.33 (s, 1 H), 7.79-7.78 (m, 2 H), 7.46 (dq, J = 8.0 Hz, J = 0.8 Hz, 1 H), 7.32-7.25 (m, 3 H), 7.22-7.20 (m, 1 H), 7.10 (dq, J = 8.0 Hz, J = 1.2 Hz, 1 H), 3.04 (s, 3 H), 2.68 (s, 3 H), 2.40 (s, 3 H) ¹³C NMR (CDCl₃, 100 MHz): δ = 169.3, 162.2, 140.6, 139.7, 139.0, 134.5, 130.9, 129.9, 129.7, 128.8, 128.1, 124.3, 120.1, 118.0, 37.8, 35.0, 21.5;

(Z)-isomer (8ab’) 0.145 g 42% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.22 (s, 1 H), 7.78 (t, J = 2.0 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 2 H), 7.39 (dq, J = 8.4 Hz, J = 0.8 Hz, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.10 (dq, J = 8.0 Hz, J = 0.8 Hz, 1 H), 6.74 (s, 1 H), 3.27 (s, 3 H), 3.09 (s, 3 H), 2.36 (s, 3 H), ¹³C NMR (CDCl₃, 100 MHz): δ = 169.4, 162.8, 140.0, 138.9, 137.0, 134.6, 131.3, 130.4, 130.0, 129.4, 129.3, 124.4, 120.0, 117.9, 39.7, 35.3, 21.4, HRMS (ESI+): m/z [M + Na]⁺ calc for C₁₉H₁₆Cl₂N₂O₄Na: 365.1033; found: 365.1045.

2-(2-chlorobenzylidene)-N²-(3-chlorophenyl)-N⁴,N⁵-dimethylmalonamide (8ac, 8ac’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2), brown oil, 0.322 g, 89% yield; mixture of (Z) and (E) stereoisomers with ratio 1:1; ¹H NMR (CDCl₃, 400 MHz): δ = 9.72 (s, 0.5 H), 9.44 (s, 0.5 H), 8.02 (s, 0.5 H), 7.81 (t, J = 2.4 Hz, 0.5 H), 7.72 (t, J = 2.5 Hz, 0.5 H), 7.48-7.45 (m, 1.5H), 7.41 (dd, J = 8.0 Hz, J = 1.2 Hz, 0.5 H), 7.37-7.30 (m, 1.5 H), 7.29-7.17 (m, 2.5 H), 7.10 (dq, J = 8.0 Hz, J = 0.8 Hz, 0.5 H), 7.07-7.04 (m, 1H), 3.33 (s, 1.5 H), 3.09 (s, 1.5 H), 2.92 (s, 1.5 H), 2.61 (s, 1.5 H), ¹³C NMR (CDCl₃, 100 MHz): δ = 169.0, 169.4, 161.6, 161.4, 138.9, 138.7, 136.8, 135.0, 134.6, 134.5, 134.4, 133.8, 132.6, 132.5, 132.1, 131.1, 130.3, 129.0, 129.8, 129.7, 129.4, 129.1, 126.9, 126.8, 124.4, 124.3, 120.2, 119.9, 118.0, 117.8, 39.9, 37.8, 35.3, 34.9, HRMS (ESI+): m/z [M + Na]⁺ calc for C₁₉H₁₆Cl₂N₂O₄Na: 385.0487; found: 385.0495. Ratio of stereoisomers was determined based on integration of ¹H NMR spectra.

2-benzylidene-N¹,N⁴-dimethyl-N⁵-phenylmalonamide (8ba), (8ba’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil;

(E)-isomer (8ba) 0.115 g, 39% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.23 (s, 1 H), 7.81 (s, 1 H), 7.66-7.63 (m, 2 H), 7.43-7.34 (m, 7 H), 7.16-7.11 (m, 1 H), 3.02 (s, 3 H), 2.67 (s, 3 H), ¹³C NMR (CDCl₃, 100 MHz): δ = 169.2, 161.9, 139.0, 133.9, 129.9, 129.7, 129.0, 128.9, 128.7, 124.4, 120.1, 37.8, 34.9; (Z)-isomer (8ba’) 0.121 g, 41% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 8.92 (s, 1 H), 7.59-7.53 (m, 4 H), 7.39-7.32 (m, 5 H), 7.15-7.11 (m, 1 H), 6.76 (s, 1 H), 3.29 (s, 3 H), 3.10 (s, 3 H), ¹³C NMR (CDCl₃, 100 MHz): δ =
N\textsuperscript{1},N\textsuperscript{1}-dimethyl-2-(4-methylbenzylidene)-N\textsuperscript{2}-phenylmalonamide (8bb), (8bb\textsuperscript{'})

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil (E)-isomer (8bb) 0.110 g, 35% yield; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ = 9.21 (s, 1 H), 7.78 (s, 1 H), 7.66-7.63 (m, 2 H), 7.38-7.30 (m, 4 H), 7.21-7.19 (m, 2 H), 7.15-7.11 (m, 1 H), 3.04 (s, 3 H), 2.69 (s, 3 H), 2.39 (s, 3 H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ = 169.5, 162.1, 140.4, 139.2, 137.8, 131.0, 129.6, 128.9, 128.8, 128.6, 124.3, 120.1, 37.8, 34.9, 21.4; (Z)-isomer (8bb\textsuperscript{'}) 0.155 g, 50% yield; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ = 8.98 (s, 1 H), 7.60-7.58 (m, 2 H), 7.45-7.43 (m, 2 H), 7.35-7.18 (m, 2 H), 7.17-7.11 (m, 3 H), 6.72 (s, 1 H), 3.27 (s, 3 H), 3.08 (s, 3 H), 2.35 (s, 3 H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ = 169.4, 162.8, 139.7, 137.7, 136.2, 130.7, 130.5, 129.4, 129.3, 128.9, 124.4, 119.9, 39.6, 35.3, 21.4; HRMS (ESI\textsuperscript{+}): m/z [M + Na]\textsuperscript{+} calcd for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}O\textsubscript{2}Na: 331.1422; found: 331.1416.

2-(2-chlorobenzylidene)-N\textsuperscript{1},N\textsuperscript{1}-dimethyl-N\textsuperscript{3}-phenylmalonamide (8bc, 8bc\textsuperscript{'})

Purification by flash column chromatography, (EtOAc/Hex, 1:1), brown oil, 0.242 g, 74% yield; mixture of (Z) and (E) stereoisomers with ratio 1:1; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ = 9.45 (s, 0.5 H), 9.33 (s, 0.5 H), 8.10 (s, 0.5 H), 7.67-7.65 (m, 1 H), 7.57-7.55 (m, 1 H), 7.51 (dd, J = 7.6 Hz, J = 1.6 Hz, 0.5 H), 7.46 (dd, J = 8.0 Hz, J = 1.2 Hz, 0.5 H), 7.41 (dd, J = 8.0 Hz, J = 1.2 Hz, 0.5 H), 7.38-7.28 (m, 3.5 H), 7.27-7.19 (m, 1 H), 7.16-7.08 (m, 1 H), 7.04 (s, 0.5 H), 3.31 (s, 1.5 H), 2.93 (s, 1.5 H), 2.63 (s, 1.5 H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ = 169.2, 168.6, 161.4, 161.2, 137.7, 137.6, 136.6, 134.6, 134.3, 133.8, 132.7, 132.6, 131.6, 130.9, 130.2, 129.9, 129.8, 129.4, 129.1, 129.0, 128.9, 126.9, 126.8, 124.5, 124.4, 120.0, 119.9, 39.8, 37.8, 35.3, 34.9, HRMS (ESI\textsuperscript{+}): m/z [M + Na]\textsuperscript{+} calcd for C\textsubscript{18}H\textsubscript{17}ClN\textsubscript{2}O\textsubscript{2}Na: 351.0876; found: 351.0870. Ratio of stereoisomers was determined based on integration of \textsuperscript{1}H NMR spectra.

2-benzylidene-N\textsuperscript{1},N\textsuperscript{1}-dimethyl-N\textsuperscript{3}-(p-tolyl)malonamide (8ca), (8ca\textsuperscript{'})

Purification by flash column chromatography, (EtOAc/Hex, 1:2:1:1), brown oil; (E)-isomer (8ca) 0.207 g, 67% yield; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ = 9.14 (s, 1 H), 7.79 (s, 1 H), 7.53-7.50 (m, 2 H), 7.42-7.37 (m, 5 H), 7.15-7.13 (m, 2 H), 3.01 (s, 3 H), 2.65 (s, 3 H), 2.33 (s, 3 H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ = 169.2, 161.7, 138.8, 135.2, 134.0, 133.9, 129.9, 129.8, 129.4, 128.8, 128.7, 120.1, 37.8, 34.9, 20.9 (Z)-isomer (8ca\textsuperscript{'}) 0.085 g, 28% yield; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ = 8.78 (s, 1 H), 7.54-7.51 (m, 2 H), 7.47-7.43 (m, 2 H), 7.38-7.33 (m, 3 H), 7.15-7.12 (m, 2 H), 6.74 (s, 1 H), 3.28 (s, 3 H), 3.09 (s, 3 H), 2.33 (s, 3 H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ = 169.2, 162.5, 135.6, 135.0, 134.1, 133.5, 132.0, 129.5, 129.4, 129.3, 128.6, 119.9, 39.6, 35.2, 20.9; HRMS (ESI\textsuperscript{+}): m/z [M + Na]\textsuperscript{+} calcd for C\textsubscript{18}H\textsubscript{26}N\textsubscript{2}O\textsubscript{2}Na: 331.1422; found: 331.1412.
N³-(4-methoxyphenyl)-N¹,N³-dimethyl-2-(4-methylbenzylidene)malonamide (8db), (8db⁺)

Purification by flash column chromatography, (EtOAc/Hex, 1:2:1:1), brown oil;

(E)-isomer (8db) 0.081 g, 24% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.06 (s, 1 H), 7.77 (s, 1 H), 7.57-7.53 (m, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 6.91-6.87 (m, 2 H), 3.81 (s, 3 H), 3.03 (s, 3 H), 2.69 (s, 3 H), 2.39 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.5, 161.8, 156.4, 140.3, 138.8, 131.1, 131.0, 129.6, 128.7, 128.6, 121.7, 114.0, 55.4, 37.8, 34.9, 21.4; (Z)-isomer (8db⁺) 0.110 g, 33% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 8.82 (s, 1 H), 7.51-7.47 (m, 2 H), 7.43 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 6.88-6.84 (m, 2 H), 6.70 (s, 1 H), 3.80 (s, 3 H), 3.27 (s, 3 H), 3.08 (s, 3 H), 2.35 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.5, 162.6, 156.4, 139.7, 135.8, 130.9, 130.8, 130.6, 129.3, 129.1, 121.6, 114.0, 55.4, 39.6, 35.3, 21.3; HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₂₆H₂₇N₂O₂Na: 361.1528; found: 361.1542.

2-(2-chlorobenzylidene)-N¹,N³-dimethyl-Ν²-(4-nitrophenyl)malonamide (8ec, 8ec⁺)

Purification by flash column chromatography, (EtOAc/Hex, 1:1), brown oil, 0.298 g, 80% yield; mixture of (Z) and (E) stereoisomers with ratio 0.37:0.63;

¹H NMR (CDCl₃, 400 MHz): δ = 10.22 (s, 0.37 H), 9.94 (s, 0.63 H), 8.27-8.23 (m, 1.26 H), 8.20-8.16 (m, 0.74 H), 8.13 (s, 0.63 H), 7.86-7.82 (m, 1.26 H), 7.75-7.71 (m, 0.74 H), 7.49 (dd, J = 8.0 Hz, J = 0.8 Hz, 0.63 H), 7.46-7.43 (m, 0.74 H), 7.40-7.22 (m, 2.63 H), 7.13 (s, 0.37 H), 3.37 (s, 1.11 H), 3.14 (s, 1.11 H), 2.94 (s, 1.89 H), 2.62 (s, 1.89 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.0, 168.3, 161.9, 161.8, 143.6, 143.6, 143.5, 143.4, 138.0, 136.8, 134.4, 133.8, 132.3, 131.3, 131.2, 130.6, 130.5, 129.9, 129.6, 129.5, 129.0, 127.0, 126.8, 125.0, 124.9, 119.6, 119.4, 40.0, 37.9, 35.5, 35.0, HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₉H₁₆ClN₂O₂Na: 396.0727; found: 396.0735. Ratio of stereoisomers was determined based on integration of ¹H NMR spectra.

2-benzylidene-N¹-(4-fluorophenyl)-N¹,N³-dimethylmalonamide (8fa), (8fa⁺)

Purification by flash column chromatography, (EtOAc/Hex, 1:2:1:1), brown oil;

(E)-isomer (8fa) 0.165 g, 52% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.27 (s, 1 H), 7.80 (s, 1 H), 7.63-7.58 (m, 2 H), 7.40 (s, 5 H), 7.07-7.01 (m, 2 H), 3.01 (s, 3 H), 2.65 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.2, 161.9, 159.4 (d, J' = 242.1 Hz), 139.2, 133.8 (d, J' = 1.8 Hz), 130.0, 129.4, 128.9, 128.7, 121.8 (d, J' = 7.8 Hz), 115.6 (d, J' = 22.3 Hz), 37.8, 34.9; (Z)-isomer (8fa⁺) 0.20 mg, 39% yield; ¹H NMR (CDCl₃, 400 MHz): δ = 9.05 (s, 1 H), 7.56-7.51 (m, 4 H), 7.40-7.34 (m, 3 H), 7.03-6.99 (m, 2 H), 6.75 (s, 1 H), 3.28 (s, 3 H), 3.08 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.2, 162.6, 159.4 (d, J' = 242.1 Hz), 136.1, 133.7 (d, J' = 1.3 Hz), 133.4, 131.4, 129.5, 129.2, 128.6, 121.7 (d, J' = 7.8 Hz), 115.6 (d, J' = 22.3 Hz), 39.6, 35.3; HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₉H₁₈F₂N₂O₂Na: 335.1172; found: 335.1161.
N-(3-chlorophenyl)-3-phenyl-2-(pyrrolidine-1-carbonyl)acrylamide (8ad), (8ad’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil; (E)-isomer (8ad) 0.150 g, 42% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.50 (s, 1 H), 7.80 (t, J = 2.0 Hz, 1 H), 7.79 (s, 1 H), 7.48-7.44 (m, 3 H), 7.41-7.38 (m, 3 H), 7.26 (t, J = 8.0 Hz, 1 H), 7.10 (dq, J = 8.0 Hz, J = 0.8 Hz, 1 H), 3.55 (s, 2 H), 3.29-3.03 (m, 1 H), 2.91-2.46 (m, 1 H), 1.84-1.53 (m, 4 H), 13C NMR (CDCl3, 100 MHz): δ = 167.3, 162.0, 139.4, 139.0, 134.6, 133.8, 130.5, 130.2, 129.9, 128.9, 128.7, 124.3, 120.1, 118.0, 47.4, 46.0, 25.5, 24.0; (Z)-isomer (8ad’) 0.091 g, 26% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.49 (s, 1 H), 7.80 (t, J = 2.0 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.40 (dq, J = 8.0 Hz, J = 0.8 Hz, 1 H), 7.38-7.34 (m, 3 H), 7.24 (t, J = 8.0 Hz, 1 H), 7.10 (dq, J = 8.0 Hz, J = 1.2 Hz, 1 H), 6.93 (s, 1 H), 3.73 (t, J = 6.4 Hz, 2 H), 3.59 (t, J = 6.4 Hz, 2 H), 2.01-1.95 (m, 4 H), 13C NMR (CDCl3, 100 MHz): δ = 167.4, 162.6, 138.9, 137.9, 134.6, 133.3, 132.0, 129.9, 129.6, 129.4, 128.6, 124.4, 120.0, 117.9, 49.5, 46.3, 26.0, 24.4; HRMS (ESI+): m/z [M + Na]+ calcd for C29H27ClN2O2Na: 377.1033; found: 377.1025.

N-(4-fluorophenyl)-3-phenyl-2-(pyrrolidine-1-carbonyl)acrylamide (8fd), (8fd’)

Purification by flash column chromatography, (EtOAc/Hex, 1:2-1:1), brown oil; (E)-isomer (8fd) 0.153 g, 45% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.40 (s, 1 H), 7.80 (s, 1 H), 7.64-7.60 (m, 2 H), 7.48-7.44 (m, 2 H), 7.42-7.36 (m, 3 H), 7.08-7.02 (m, 2 H), 3.63-3.50 (m, 2 H), 3.63-3.50 (m, 2 H), 3.34-3.10 (m, 1 H), 2.78-2.42 (m, 1 H), 1.88-1.55 (m, 4 H), 13C NMR (CDCl3, 100 MHz): δ = 167.4, 161.8, 159.3 (d, J′ = 242.0 Hz), 139.0, 133.9 (d, J′ = 3.1 Hz), 130.7, 130.1, 128.8, 128.7, 121.8 (d, J′ = 7.8 Hz), 115.6 (d, J′ = 22.4 Hz), 47.3, 46.0, 25.5, 24.0; (Z)-isomer (8fd’) 0.106 g, 31% yield; 1H NMR (CDCl3, 400 MHz): δ = 9.29 (s, 1 H), 7.59-7.52 (m, 4 H), 7.37-7.34 (m, 3 H), 7.05-7.00 (m, 2 H), 6.91 (s, 1 H), 3.74 (t, J = 6.4 Hz, 2 H), 3.59 (t, J = 6.4 Hz, 2 H), 2.02-1.95 (m, 4 H), 13C NMR (CDCl3, 100 MHz): δ = 167.5, 162.5, 159.4 (d, J′ = 242.1 Hz), 137.4, 133.8 (d, J′ = 2.8 Hz), 133.4, 132.3, 129.5, 129.4, 128.5, 121.6 (d, J′ = 7.8 Hz), 115.5 (d, J′ = 22.3 Hz), 49.5, 46.2, 26.0, 24.4; HRMS (ESI+): m/z [M + Na]+ calcd for C29H29F2N2O2Na: 361.1328; found: 361.1320.

2-(2-chlorobenzylidene)-N1-ethyl-N1,N3-dimethylmalonamide (8gc, 8ge’)

Purification by flash column chromatography, (EtOAc/Hex, 2:1), brown oil, 0.249 g, 89% yield; mixture of (E) and (Z) stereoisomers with ratio 3:1; 1H NMR (CDCl3, 400 MHz): δ = 7.98 (s, 0.75 H), 7.49 (dd, J = 7.6 Hz, J = 2.0 Hz, 0.25 Hz), 7.42 (dd, J = 8.0 Hz, J = 1.2 Hz, 0.75 Hz), 7.38 (dd, J = 7.2 Hz, J = 1.6 Hz, 0.63 Hz), 7.34-7.20 (m, 2.75 Hz), 7.10 (brs, 0.75 Hz), 7.02 (brs, 0.25 Hz), 6.90 (s, 0.25 Hz), 3.39 (quint, J = 7.2 Hz, 1.5 Hz), 3.33-3.25 (m, 1.25 Hz), 3.07 (s, 0.75 H), 2.86 (s, 2.25 H), 2.60 (s, 2.25 H), 1.20 (t, J = 7.2 Hz, 2.25 H), 1.11 (t, J = 7.2 Hz, 0.75 Hz), 13C NMR (CDCl3, 100 MHz): δ = 168.9, 168.6, 163.6, 163.0, 135.0, 134.2, 133.7, 133.4, 132.8, 132.7, 132.5, 131.6, 130.5, 130.0, 129.8, 129.7, 129.3, 129.1, 126.8, 126.6, 39.7, 37.7, 35.2, 34.8, 34.7, 34.4, 14.6, 14.4; HRMS (ESI+): m/z [M + Na]+ calcd for C29H27ClN2O2Na: 303.0876; found: 303.0884. Ratio of stereoisomers was determined based on integration of 1H NMR spectra.
$^1$H and $^{13}$C-NMR Spectra
S33
8ad'}
References