Intramolecular Cyclization of Vinyldiazoacetates as a Versatile Route to Pyrazoles

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General Remarks

The starting materials were purchased from Merck, Alfa Aesar, Acros Organics, Fluorochem or TCI and used without further purification. The solvents if needed were dried according to standard conditions. For column chromatography and TLC (SiO₂, 60M, pore size 0.04 – 0.063 mm), products of Machery-Nagel were used. The TLC-glass-plates DURASIL consisted of a 0.25 mm layer of silica 60 with Fluorescence indicator UV254. TLCs were checked under UV-light (254 nm or 365 nm) and stained with an aq. KMnO₄-solution or PMA-stain. All ¹H and ¹³C NMR spectra were measured with a BRUKER 250 (¹³C), BRUKER Fourier 300 (¹H, ¹³C), BRUKER Avance I 400 spectrometer (¹H, ¹³C) or BRUKER Avance III HD 500 spectrometer (¹H, ¹³C). The chemical shift of each signal was registered in ppm. For ¹H and ¹³C measurements, the chemical shift refers to TMS reference signal at 0 ppm. As an internal standard, the remaining protons or respectively the carbons of the corresponding deuterated solvent were used (CDCl₃, 7.26 ppm (¹H NMR), 77.16 ppm (¹³C NMR), DMSO-d₆, 2.50 ppm (¹H NMR), 39.51 ppm (¹³C NMR), MeOD, 4.78 ppm, 3.31 ppm (¹H NMR), 49.15 ppm (¹³C NMR) and MeCN-d₃, 1.94 ppm (¹H NMR), 118.26 ppm and 1.32 ppm (¹³C NMR)). High-resolution mass spectra (HRMS) were measured with EI or ESI ionisation. A chromatographic purification was performed before characterization of each compound. The Thermo Q-Exactive plus device for ESI-mass spectra was coupled to a binary UHPLC system. For EI-measurement, a GC-system was coupled to the Thermo Q-Exactive GC device. IR spectra were measured using the Shimadzu IR-Affinity-1 (FTIR) device.
General procedure A

A suspension of aldehyde (1.0 eq) and the Wittig salt (2-carboxyethyl) tri-phenylphosphonium bromide (1.1 eq) in THF (0.25 M) was cooled to 0 °C and slowly added a freshly prepared solution of KO\textsubscript{t}Bu (2.0 eq) in THF (0.5 M) over a period of 1 hour. After complete addition of the KO\textsubscript{t}Bu-solution the resulting mixture was stirred a further hour at 0 °C. The cooling bath was then removed and the mixture was stirred at RT overnight. After addition of sat. NaHCO\textsubscript{3}-solution, the mixture was extracted with diethyl ether (3 x 150 mL), the organic layer was washed with water (2 x 50 mL) and the aqueous layer collected and acidified with 6M HCl to pH 1. Then, the acidified aqueous layer was extracted with ethyl acetate (3 x 150 mL). The combined organic layer was dried over MgSO\textsubscript{4} and the solvent was evaporated. The product was used without further purification.\[1\]

A suspension of the raw carboxylic acid (1.0 eq), Cs\textsubscript{2}CO\textsubscript{3} (0.5 eq) and MeI (2.0 eq) in 150 mL acetone was heated to 80 °C for 3 h. Silica gel was added and the solvent evaporated. The product was purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether) and isolated as yellow to orange oil.\[2\]

A solution of ρ-ABSA (1.5 eq) and ester (1.0 eq) in dry acetonitrile (0.1 M) at 0 °C under a N\textsubscript{2}-atmosphere was slowly added DBU (2.0 eq) over a period of 30 min. After the addition was completed, the mixture was allowed to warm to RT overnight. Then the reaction mixture was quenched by addition of sat. NH\textsubscript{4}Cl-solution. The aqueous layer was washed with ethyl acetate (3 x 150 mL), dried over MgSO\textsubscript{4} and purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether). The products were isolated as orange or red solids or oils.\[3\]

General procedure B

A solution of vinyl diazo compound (1.0 eq) in benzotrifluoride (1.2 M) was heated to reflux until complete consumption of the vinyl diazo compound (<10 min). Silica gel was then added and the solvent evaporated. The product was purified by column chromatography (50 – 70% v/v% ethyl acetate/petrol ether) and isolated as off-white solid.
Synthesis of β,γ-unsaturated Esters

Methyl (E)-4-phenylbut-3-enoate (3a)

A mixture of cinnamic alcohol (1.0 eq), formic acid (3.0 eq), acetic anhydride (3.0 eq), Tris(dibenzylideneacetone)dipalladium(0) (0.5 mol-%) and Xantphos (2 mol-%) was suspended in toluene (15 mL) and heated to 80 °C for 12 h. The mixture was filtered through a short silica pad and washed with ethyl acetate.[5] The conversion to methyl ester 3a was performed according to general procedure A and yielded a yellow oil in 70% yield. Analytical data matches the literature.[5]

\[ ^1H \text{ NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.44 - 7.23 \text{ (m, 5H), 6.53 (d, } J = 15.9 \text{ Hz, 1H), 6.41 - 6.27 \text{ (m, 1H), 3.75 (s, 3H), 3.29 (dd, } J = 7.0, 0.9 \text{ Hz, 2H).} \]

Methyl (E)-4-(p-tolyl)but-3-enoate (3b)

The compound was prepared according to general procedure A with an isolated yield of 42%. Analytical data matches the literature.[6]

\[ ^1H \text{ NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.68 - 7.41 \text{ (m, 9H), 6.57 (d, } J = 15.9 \text{ Hz, 1H), 6.47 - 6.31 \text{ (m, 1H), 3.77 (s, 3H), 3.32 (dd, } J = 6.7, 0.8 \text{ Hz, 2H).} \]

Methyl (E)-4-[(1,1′-biphenyl)-4-yl]but-3-enoate (3c)

The compound was prepared according to general procedure A with an isolated yield of 40%. Analytical data matches the literature.[7]

\[ ^1H \text{ NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.68 - 7.41 \text{ (m, 9H), 6.57 (d, } J = 15.9 \text{ Hz, 1H), 6.47 - 6.31 \text{ (m, 1H), 3.77 (s, 3H), 3.32 (dd, } J = 6.7, 0.8 \text{ Hz, 2H).} \]

Methyl (E)-4-(naphthalen-2-yl)but-3-enoate (3d)

The compound was prepared according to general procedure A with an isolated yield of 62%. Analytical data matches the literature.[8]

\[ ^1H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.70 - 7.43 \text{ (m, 9H), 6.57 (d, } J = 15.8 \text{ Hz, 1H), 6.46 (dt, } J = 15.9, 7.1 \text{ Hz, 1H), 3.77 (s, 3H), 3.35 (dd, } J = 7.0, 1.2 \text{ Hz, 2H).} \]

Methyl (E)-5-phenylpent-3-enoate (3e)

A mixture of 2-phenylacetaldehyde (7.5 mmol, 1.0 eq) and malonic acid (11.25 mmol, 1.5 eq) was added triethylamine (10 mL) and heated to reflux for 16 h. The reaction mixture was then diluted with water and extracted with diethyl ether (3 x 100 mL). The combined organic layer was washed with water and brine, dried over MgSO₄ and concentrated in vacuo.[9] The crude carboxylic acid was converted to the methyl ester according to general procedure A. The compound was isolated as colourless oil with a yield of 50%. Analytical data matches the literature.[10]

\[ ^1H \text{ NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.37 - 7.30 \text{ (m, 2H), 7.28 - 7.20 \text{ (m, 3H), 5.84 - 5.61 \text{ (m, 2H), 3.73 (s, 3H), 3.43 (d, } J = 5.9 \text{ Hz, 2H), 3.12 (d, } J = 6.0 \text{ Hz, 2H).} \]

Methyl (E)-4-(4-allylphenyl)but-3-enoate (3f)

The compound was prepared according to general procedure A with an isolated yield of 36%.

\[ ^1H \text{ NMR} (300 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.44 - 7.08 \text{ (m, 5H), 6.54 - 6.19 \text{ (m, 3H), 3.76 - 3.70 \text{ (m, 3H), 3.41 - 3.30 \text{ (m, 1H), 3.30 - 3.23 \text{ (m, 2H), 1.94 - 1.86 \text{ (m, 2H).} } \text{IR (ν in cm}^{-1}): 1954.93 \text{ (w), 1735.93 (vs).} \text{HR-MS: Calc. mass for } C_{16}H_{20}O_2: [M + Na] = 239.1048, found: 239.1042.} \]

Methyl (E)-4-(p-methoxyphenyl)but-3-enoate (3g)

The compound was prepared according to general procedure A with an isolated yield of 47%. Analytical data matches the literature. Analytical data matches the literature.[11]

\[ ^1H \text{ NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \]

\[ 7.34 (d, } J = 8.6 \text{ Hz, 2H), 6.87 (d, } J = 8.6 \text{ Hz, 2H), 6.51 - 6.41 \text{ (m, 1H), 6.18 (dt, } J = 15.8, 7.1 \text{ Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.26 (dd, } J = 7.0, 1.0 \text{ Hz, 2H).} \]
Methyl (E)-4-(3-methoxyphenyl)but-3-enoate (3h)

The compound was prepared according to general procedure A with an isolated yield of 55%. Analytical data matches the literature.\[12\]

\[\text{H NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.29 - 7.21 \text{ (m, 1H)}, \ 7.03 - 6.91 \text{ (m, 2H)}, \ 6.82 \text{ (dd, } J = 8.1, 1.9 \text{ Hz, 1H)}, \ 6.50 \text{ (d, } J = 15.9 \text{ Hz, 1H)}, \ 6.39 - 6.26 \text{ (m, 1H)}, \ 3.83 \text{ (s, 3H)}, \ 3.74 \text{ (s, 3H)}, \ 3.28 \text{ (dd, } J = 6.8, 0.7 \text{ Hz, 2H}).\]

Methyl (E)-4-(2-methoxyphenyl)but-3-enoate (3i)

The compound was prepared according to general procedure A with an isolated yield of 56%. Analytical data matches the literature.\[6\]

\[\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.46 \text{ (dd, } J = 7.6, 1.5 \text{ Hz, 1H}), \ 7.26 - 7.19 \text{ (m, 1H)}, \ 6.98 - 6.83 \text{ (m, 3H)}, \ 6.34 \text{ (dt, } J = 15.9, 7.1 \text{ Hz, 1H)}, \ 3.83 \text{ (s, 3H)}, \ 3.71 \text{ (s, 3H)}, \ 3.29 \text{ (dd, } J = 7.0, 1.5 \text{ Hz, 2H}).\]

Methyl (E)-4-(4-fluorophenyl)but-3-enoate (3j)

The compound was prepared according to general procedure A with an isolated yield of 38%. Analytical data matches the literature.\[7\]

\[\text{H NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.46 - 7.31 \text{ (m, 2H)}, \ 7.10 - 6.97 \text{ (m, 2H)}, \ 6.48 \text{ (d, } J = 15.9 \text{ Hz, 1H)}, \ 6.32 - 6.17 \text{ (m, 1H)}, \ 3.74 \text{ (s, 3H)}, \ 3.27 \text{ (dd, } J = 7.0, 0.9 \text{ Hz, 2H}).\]

Methyl (E)-4-(2-fluorophenyl)but-3-enoate (3k)

The compound was prepared according to general procedure A with an isolated yield of 50%. Analytical data matches the literature.\[6\]

\[\text{H NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.55 - 7.43 \text{ (m, 1H)}, \ 7.25 - 7.17 \text{ (m, 1H)}, \ 7.15 - 7.04 \text{ (m, 2H)}, \ 6.68 \text{ (d, } J = 16.1 \text{ Hz, 1H)}, \ 6.49 - 6.34 \text{ (m, 1H)}, \ 3.75 \text{ (s, 3H)}, \ 3.31 \text{ (dd, } J = 7.1, 0.9 \text{ Hz, 2H}).\]

Methyl (E)-4-(4-chlorophenyl)but-3-enoate (3l)

The compound was prepared according to general procedure A with an isolated yield of 40%. Analytical data matches the literature.\[6\]

\[\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.33 - 7.28 \text{ (m, 4H)}, \ 6.46 \text{ (d, } J = 16.0 \text{ Hz, 1H)}, \ 6.29 \text{ (dt, } J = 16.0 \text{ Hz, 8.0 Hz, 1H)}, \ 3.74 \text{ (s, 1H)}, \ 3.27 \text{ (dd, } J = 8.0, 0.8 \text{ Hz, 2H}).\]

Methyl (E)-4-(4-bromophenyl)but-3-enoate (3m)

The compound was prepared according to general procedure A with an isolated yield of 55%. Analytical data matches the literature.\[6\]

\[\text{H NMR} (250 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.51 - 7.40 \text{ (m, 2H)}, \ 7.26 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, \ 6.50 - 6.40 \text{ (m, 1H)}, \ 6.40 - 6.25 \text{ (m, 1H)}, \ 3.75 \text{ (s, 3H)}, \ 3.27 \text{ (d, } J = 6.2 \text{ Hz, 2H}).\]

Methyl (E)-4-(4-iodophenyl)but-3-enoate (3n)

The compound was prepared according to general procedure A with an isolated yield of 43%. Analytical data matches the literature.\[6\]

\[\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.65 \text{ (br d, } J = 8.2 \text{ Hz, 2H)}, \ 7.12 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, \ 6.48 - 6.39 \text{ (m, 1H)}, \ 6.37 - 6.28 \text{ (m, 1H)}, \ 3.74 \text{ (s, 3H)}, \ 3.26 \text{ (d, } J = 6.7 \text{ Hz, 2H}).\]

Methyl (E)-4-(2,4,6-trichlorophenyl)but-3-enoate (3o)

The compound was prepared according to general procedure A with an isolated yield of 53%.

\[\text{H NMR} (300 \text{ MHz, CDCl}_3) \delta \text{ ppm } 7.36 \text{ (s, 2H)}, \ 6.99 \text{ (dt, } J = 15.7, 6.2 \text{ Hz, 1H}), \ 5.75 \text{ (dt, } J = 15.7, 1.8 \text{ Hz, 1H)}, \ 3.81 \text{ (dd, } J = 6.2, 1.7 \text{ Hz, 2H)}, \ 3.73 \text{ (s, 3H)}. \ \text{C NMR} (101 \text{ MHz, CDCl}_3) \delta \text{ ppm } 166.56 \text{ (s), } 142.87 \text{ (s), } 136.10 \text{ (s), } 133.47 \text{ (s), } 132.41 \text{ (s), } 128.29 \text{ (s), } 122.56 \text{ (s), } 51.57 \text{ (s), } 33.23 \text{ (s)}. \ \text{IR} (\nu \text{ in cm}^{-1}): 2954.95 \text{ (w), } 1716.65 \text{ (vs)}. \ \text{HR-MS}: \text{Calc. mass for } \text{C}_{11}\text{H}_{11}\text{Cl}_{3}\text{O}_{2}: [M] = 277.9668, \text{found: } 277.9665.\]
Methyl (E)-4-(2-furanyl)but-3-enoate (3p)

The compound was prepared according to general procedure A with an isolated yield of 51%. Analytical data matches the literature.\[^{11}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.35 (s, 1H), 6.39 – 6.31 (m, 2H), 6.27 – 6.20 (m, 2H), 3.73 (s, 3H), 3.23 (d, \(J = 8.0\) Hz, 2H).

Methyl (E)-4-(thiophen-2-yl)but-3-enoate (3q)

The compound was prepared according to general procedure A with an isolated yield of 65%. Analytical data matches the literature.\[^{11}\]

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.20 – 7.14 (m, 1H), 6.99 – 6.93 (m, 2H), 6.65 (d, \(J = 15.7\) Hz, 1H), 6.15 (dt, \(J = 15.6, 7.2\) Hz, 1H), 3.75 (s, 3H), 3.25 (dd, \(J = 7.2, 1.4\) Hz, 2H).

Methyl (E)-4-(4-(trifluoromethyl)phenyl)but-3-enoate (3r)

The compound was prepared according to general procedure A with an isolated yield of 34%. Analytical data matches the literature.\[^{7}\]

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.65 – 7.55 (m, 2H), 7.55 – 7.44 (m, 2H), 6.60 – 6.37 (m, 2H), 3.76 (s, 3H), 3.32 (d, \(J = 6.4\) Hz, 2H).

Methyl (E)-4-(2,4-bis(trifluoromethyl)phenyl)but-3-enoate (3s)

The compound was prepared according to general procedure A with an isolated yield of 42%. Analytical data matches the literature.\[^{6}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.82 – 7.74 (m, 3H), 6.64 – 6.46 (m, 2H), 3.77 (s, 3H), 3.37 – 3.31 (m, 2H).

Methyl (E)-4-(4-methoxy-4-oxobut-1-en-1-yl)benzoate (3t)

The compound was prepared according to general procedure A with an isolated yield of 28%. Analytical data matches the literature.\[^{1}\]

\(^1\)H NMR 8.00 (d, \(J = 8.4\) Hz, 2H), 7.44 (d, \(J = 8.2\) Hz, 2H), 6.60 – 6.38 (m, 2H), 3.93 (s, 3H), 3.75 (s, 3H), 3.30 (d, \(J = 6.2\) Hz, 2H).

Benzyl but-3-enoate (3u)

The raw carboxylic acid (1.0 eq) was added benzyl alcohol (1.5 eq) and p-toluenesulfonic acid (5 mol-%). Toluene (50 mL) was added and the resulting mixture heated to reflux overnight. Silica gel was added and the solvent evaporated.\[^{13}\] The product was purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether) and isolated as yellow oil in 85% yield. Analytical data matches the literature.\[^{14}\]

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.40 (s, 5H), 6.08 – 5.90 (m, 1H), 5.26 – 5.21 (m, 1H), 5.21 – 5.15 (m, 3H), 3.19 (dt, \(J = 6.9, 1.4\) Hz, 2H).

Methyl (E)-oct-3-enoate (3v)

The compound was prepared according to general procedure A with an isolated yield of 69%. Analytical data matches the literature.\[^{15}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 5.60 – 5.48 (m, 2H), 3.68 (s, 3H), 3.03 (d, \(J = 5.5\) Hz, 2H), 2.03 (dd, \(J = 6.4, 6.0\) Hz, 2H), 1.40 – 1.26 (m, 4H), 0.89 (t, \(J = 7.2\) Hz, 3H).

Methyl (E/Z)-5,5-dimethylhex-3-enoate (3w)

The compound was prepared according to general procedure A with an isolated yield of 77%. Analytical data matches the literature.\[^{6}\]

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 6.95 (dt, \(J = 15.6, 7.8\) Hz, 1H), 5.77 (br d, \(J = 15.4\) Hz, 1H), 5.52 – 5.33 (m, 2H), 3.68 (s, 2H), 3.65 (s, 3H), 3.21 (d, \(J = 6.8\) Hz, 2H), 2.05 (br d, \(J = 7.9\) Hz, 1H), 1.07 (s, 9H), 0.97 – 0.86 (m, 6H).
**tert-Butyl (E)-4-(p-toly1)but-3-enoate (3y)**

Commercially available (E)-4-phenylbut-3-enoic acid (1.0 eq) was added dry MgCl₂ (0.1 eq) and Di-tert-butyl-dicarbonate (1.3 eq) and dissolved in tert-butanol (2.0 eq). The reaction mixture was stirred at 50 °C for several days until the starting material was completely consumed (TLC control). Water was added and the aqueous layer washed with ethyl acetate (3 x 150 mL). The combined organic layer was dried over MgSO₄ and the solvent was evaporated. The crude product was purified by column chromatography (10% v/v% ethyl acetate/petrol ether) and isolated as yellow oil in 82% yield. Analytical data matches the literature.⁶

**Benzyl (E)-4-phenylbut-3-enoate (3z)**

The raw carboxylic acid (1.0 eq) was added benzyl alcohol (1.5 eq) and p-toluene sulfonic acid (5 mol%). Toluene (50 mL) was added and the resulting mixture heated to reflux overnight. Silica gel was added and the solvent evaporated. The product was purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether) and isolated as yellow oil in 82% yield.⁷

**Perfluorophenyl)methyl (E)-4-phenylbut-3-enoate (3aa)**

The raw carboxylic acid (1.0 eq) was added benzyl alcohol (1.5 eq) and p-toluene sulfonic acid (5 mol%). Toluene (50 mL) was added and the resulting mixture heated to reflux overnight. Silica gel was added and the solvent evaporated. The product was purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether) and isolated as yellow oil in 76% yield. Analytical data matches the literature.⁸

**4-Bromobenzyl (E)-4-(4-bromophenyl)but-3-enoate (3ab)**

The raw carboxylic acid (1.0 eq) was added benzyl alcohol (1.5 eq) and p-toluene sulfonic acid (5 mol%). Toluene (50 mL) was added and the resulting mixture heated to reflux overnight. Silica gel was added and the solvent evaporated. The product was purified by column chromatography (5 – 20% v/v% ethyl acetate/petrol ether) and isolated as yellow oil in 82% yield.

**Methyl (E)-3-Methyl-4-phenylbut-3-enoate (3ad)**

The compound was prepared according to general procedure A with an isolated yield of 91%. Analytical data matches the literature.⁹
Methyl (E)-4,4-diphenylbut-3-enoate (3ae)

The compound was prepared according to general procedure A with an isolated yield of 93%.

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm 7.30 – 7.26 (m, 3H), 7.23 – 7.20 (m, 2H), 7.12 – 7.10 (m, 3H), 6.99 – 6.96 (m, 2H), 6.60 (s, 1H), 3.65 (s, 3H), 3.52 (d, J = 1.0 Hz, 2H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ ppm 172.55 (s), 140.90 (s), 137.51 (s), 135.95 (s), 131.42 (s), 130.06 (s), 129.50 (s), 128.80 (s), 128.29 (s), 127.70 (s), 52.80 (s), 46.49 (s).

IR (ν in cm$^{-1}$): 1728.22 (vs), 1338.60 (m), 1195.87 (m), 1168.86 (m), 779.24 (m), 694.37 (s).

HR-MS: Calc. mass for C$_{17}$H$_{16}$O$_2$: [M + H] = 253.1223, found: 253.1218.

(Z)-2-benzylidenesuccinic acid (P-3af)

Sodium (170 mmol) was dissolved in dry methanol (ca. 120 mL) at 0 °C. The solution was allowed to warm to RT and added a solution of diethyl succinate (184 mmol, 2.0 eq) in dry methanol. The mixture was heated to reflux and added a solution of benzaldehyde (94 mmol, 1.0 eq) in dry methanol. After heating for further 5 h to reflux, NaOH (450 mmol) in water (90 mL) was added and the reaction mixture further heated overnight. After allowing the mixture to allow to RT, the solvent was evaporated, the residue dissolved in water (50 mL) and washed with ethyl acetate (120 mL). The aqueous layer was added conc. HCl to pH 1. The precipitate was filtered, washed with water (50 mL) and dried in vacuum. The yellow solid resulted in 66% yield. Analytical data matches the literature.[18]

$^1$H NMR (300 MHz, MeOD) δ ppm 7.90 (s, 1H), 7.45 – 7.33 (m, 5H), 3.49 (s, 2H).

Dimethyl (Z)-2-benzylidenesuccinate (3af)

(Z)-2-Benzylidenesuccinic acid (48 mmol) was dissolved in methanol (250 mL) and added conc. H$_2$SO$_4$ (3 mL). The mixture was heated to reflux overnight.[19] After evaporation of the solvent, the residue was added sat. NaHCO$_3$-solution and extracted with ethyl acetate (3 x 100 mL). The combined organic layer was dried over MgSO$_4$ and the solvent was evaporated. After purification by column chromatography (10% v/v% ethyl acetate/petrol ether) the product was isolated as yellow oil in 79% yield. Analytical data matches the literature.[20]

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm 7.89 (s, 1H), 7.40 – 7.29 (m, 5H), 3.80 (s, 3H), 3.73 – 3.68 (m, 3H), 3.53 (s, 2H).

3-Styrenepentane-2,4-dione (P-3ai)

Acetylacetone (1.1 eq) and phenyl acetaldehyde (1.0) were stirred in piperidine (5 mL) for 24 h at r. t. Then, the reaction mixture was diluted with DCM (30 mL) and washed with 5% HCl (30 mL) and water (30 mL). The organic layer was dried over anhydrous MgSO$_4$, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography (10% v/v% ethyl acetate/petrol ether) and isolated as red-brown oil in 28% yield. Analytical data matches the literature.[21]

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 16.86 (s, 1H), 7.54 – 7.29 (m, 5H), 6.81 (d, J = 16.1 Hz, 1H), 6.47 (d, J = 16.1 Hz, 1H), 2.27 (s, 6H).

1-Phenyl-1-en-4-one (3ai)

Dione P-3ai (1.0 eq) was added zinc(II)acetate (0.02 eq) and suspended in anhydrous methanol (100 mL). The mixture was heated to reflux for 24 h. The solvent was removed under reduced pressure and the crude product distilled to obtain 3ai as yellow oil in 88% yield. Analytical data matches the literature.[22]

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.41 – 7.37 (m, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.27 – 7.22 (m, 1H), 6.47 (d, J = 16.1 Hz, 1H), 6.39 – 6.26 (m, 1H), 3.30 (d, J = 7.0 Hz, 2H), 2.17 (s, 3H).
Synthesis of Vinyldiazoacetates

Methyl (E)-2-diazo-4-phenylbut-3-enoate (1a)

The compound was prepared from ester 3a according to general procedure A with an isolated yield of 72%. Analytical data matches the literature.[23]

\[ \text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) ppm 7.37 – 7.16 (m, 5H), 6.46 (d, \( J = 16.3 \) Hz, 1H), 6.19 (d, \( J = 16.3 \) Hz, 1H), 3.84 (s, 3H).

Methyl (E)-2-diazo-4-(p-tolyl)but-3-enenoate (1b)

The compound was prepared from ester 3b according to general procedure A with an isolated yield of 87%. Analytical data matches the literature.[6]

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) ppm 7.28 (br d, \( J = 8.2 \) Hz, 2H), 7.15 (d, \( J = 8.2 \) Hz, 2H), 6.44 (d, \( J = 16.1 \) Hz, 1H), 6.19 (d, \( J = 16.1 \) Hz, 1H), 3.88 (s, 3H).

Methyl (E)-4-((1,1'-biphenyl)-4-yl)-2-diazobut-3-enenoate (1c)

The compound was prepared from ester 3c according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.[24]

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) ppm 8.14 – 8.06 (m, 1H), 7.89 – 7.85 (m, 1H), 7.78 (d, \( J = 8.2 \) Hz, 1H), 7.66 – 7.63 (m, 1H), 7.55 – 7.46 (m, 3H), 7.04 (d, \( J = 15.8 \) Hz, 1H), 6.57 (d, \( J = 16.1 \) Hz, 1H), 3.91 (s, 3H).

Methyl (E)-2-diazo-4-(naphthalen-2-yl)but-3-enenoate (1d)

The compound was prepared from ester 3d according to general procedure A with an isolated yield of 63%. Analytical data matches the literature.[24]

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) ppm 7.37 – 7.20 (m, 7H), 5.89 (d, \( J = 15.8 \) Hz, 1H), 5.51 (dt, \( J = 15.7, 7.1 \) Hz, 1H), 3.83 (s, 3H), 3.54 (d, \( J = 7.0 \) Hz, 2H), \[ \text{C NMR (101 MHz, CDCl}_3 \] \( \delta \) ppm 165.89 (s), 148.44 (s), 139.97 (s), 128.57 (s), 126.32 (s), 123.92 (s), 121.46 (s), 113.29 (s), 52.15 (s), 39.17 (s). \[ IR (\nu \text{ in cm}^{-1}) \]: 2900.94 (w), 2075.41 (vs), 1697.36 (vs). \[ HR-MS \]: Calc. mass for C_{10}H_{12}N_2O_2: [M + Na] = 239.0796, found: 239.0795.

Methyl (E)-2-diazo-5-phenylpent-3-enenoate (1e)

The compound was prepared from ester 3e according to general procedure A with an isolated yield of 52%.

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) ppm 7.37 – 7.20 (m, 7H), 5.89 (d, \( J = 15.8 \) Hz, 1H), 5.51 (dt, \( J = 15.7, 7.1 \) Hz, 1H), 3.83 (s, 3H), 3.54 (d, \( J = 7.0 \) Hz, 2H). \[ ^13C NMR (101 MHz, CDCl}_3 \] \( \delta \) ppm 165.89 (s), 148.44 (s), 139.97 (s), 128.57 (s), 126.32 (s), 123.92 (s), 121.46 (s), 113.29 (s), 52.15 (s), 39.17 (s). \[ IR (\nu \text{ in cm}^{-1}) \]: 2900.94 (w), 2075.41 (vs), 1697.36 (vs). \[ HR-MS \]: Calc. mass for C_{10}H_{12}N_2O_2: [M + Na] = 239.0796, found: 239.0795.

Methyl (E)-4-(4-allylphenyl)-2-diazobut-3-enenoate (1f)

The compound was prepared from ester 3f according to general procedure A with an isolated yield of 26%.

\[ \text{H NMR (250 MHz, CDCl}_3 \] \( \delta \) ppm 7.38 – 7.32 (m, 2H), 7.28 – 7.04 (m, 2H), 6.52 – 6.13 (m, 3H), 5.18 – 5.07 (m, 1H), 3.86 (s, 3H), 3.49 – 3.36 (m, 1H), 2.03 – 1.86 (m, 2H). \[ ^13C NMR (63 MHz, CDCl}_3 \] \( \delta \) ppm 166.49 (s), 137.71 (s), 135.68 (s), 131.60 (s), 129.61 (s), 127.06 (s), 126.80 (s), 124.04 (s), 116.81 (s), 112.11 (s), 53.21 (s), 40.81 (s). \[ IR (\nu \text{ in cm}^{-1}) \]: 2954.83 (w), 2075.41 (vs), 1701.22 (vs). \[ HR-MS \]: Calc. mass for C_{14}H_{16}N_2O_2: [M + Na] = 265.0953, found: 265.0951.

Methyl (E)-4-(4-methoxyphenyl)-2-diazobut-3-enenoate (1g)

The compound was prepared from ester 3g according to general procedure A with an isolated yield of 60%. Analytical data matches the literature.[24]

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) ppm 7.33 – 7.29 (m, 2H), 6.90 – 6.86 (m, 2H), 6.32 (d, \( J = 16.1 \) Hz, 1H), 6.17 (d, \( J = 16.4 \) Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H).
Methyl (E)-2-diazo-4-(3-methoxyphenyl)-but-3-enoate (1h)
The compound was prepared from ester 3h according to general procedure A with an isolated yield of 67%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.30 – 7.22 (m, 1H), 6.97 (d, \(J = 7.9\) Hz, 1H), 6.91 (t, \(J = 1.8\) Hz, 1H), 6.79 (dd, \(J = 8.2\), 2.1 Hz, 1H), 6.50 (d, \(J = 16.1\) Hz, 1H), 6.19 (d, \(J = 16.4\) Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H).

Methyl (E)-2-diazo-4-(2-methoxyphenyl)-2-diazo-but-3-enoate (1i)
The compound was prepared from ester 3i according to general procedure A with an isolated yield of 41%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.71 (d, 2H), 7.36 (dt, 1H), 7.07 (t, 2H), 4.03 (s, 3H), 3.96 (s, 3H).

Methyl (E)-2-diazo-4-(4-fluorophenyl)-but-3-enoate (1j)
The compound was prepared from ester 3j according to general procedure A with an isolated yield of 58%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.35 – 7.29 (m, 2H), 7.05 – 6.97 (m, 2H), 6.39 (d, \(J = 16.1\) Hz, 1H), 6.17 (d, \(J = 16.4\) Hz, 1H), 3.86 (s, 3H).

Methyl (E)-2-diazo-4-(2-fluorophenyl)-but-3-enoate (1k)
The compound was prepared from ester 3k according to general procedure A with an isolated yield of 53%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 7.37 – 7.29 (m, 2H), 7.05 – 6.99 (m, 2H), 6.40 (d, \(J = 15.9\) Hz, 1H), 6.18 (d, \(J = 15.9\) Hz, 1H), 3.87 (s, 3H).

Methyl (E)-4-(4-chlorophenyl)-2-diazo-but-3-enoate (1l)
The compound was prepared from ester 3l according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.33 – 7.28 (m, 4H), 6.47 (d, \(J = 16.0\) Hz, 1H), 6.16 (d, \(J = 16.0\) Hz, 1H), 3.87 (s, 3H).

Methyl (E)-4-(4-bromophenyl)-2-diazo-but-3-enoate (1m)
The compound was prepared from ester 3m according to general procedure A with an isolated yield of 78%. Analytical data matches the literature.\[^7\]
\[^1^H\] NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 7.48 – 7.41 (m, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H), 6.49 (d, \(J = 16.3\) Hz, 1H), 6.15 (d, \(J = 16.3\) Hz, 1H), 3.87 (s, 3H).

Methyl (E)-2-diazo-4-(4-iodophenyl)-but-3-enoate (1n)
The compound was prepared from ester 3n according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.\[^6\]
\[^1^H\] NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 7.64 (d, \(J = 8.4\) Hz, 2H), 7.10 (d, \(J = 8.4\) Hz, 2H), 6.51 (d, \(J = 16.3\) Hz, 1H), 6.13 (d, \(J = 16.3\) Hz, 1H), 3.88 (s, 3H).
Methyl (E)-2-diazo-4-(2,4,6-trichlorophenyl)but-3-enoate (1o)

The compound was prepared from ester 3o according to general procedure A with an isolated yield of 47%.

\[
\text{H NMR} \ (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.37 \ (s, 2H), 6.77 \ (d, J = 16.7 \text{ Hz}, 1H), 6.30 – 6.20 \ (m, 1H), 3.89 \ (s, 3H). \]

\[
\text{C NMR} \ (63 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 107.61 \ (s), 65.98 \ (s), 122.08 \ (s), 120.37 \ (s), 116.26 \ (s), 111.55 \ (s), 53.36 \ (s). \]

IR (\(\tilde{\nu}\) in \text{cm}^{-1}): 2984.50 \ (w), 2079.26 \ (vs), 1708.93 \ (vs), 1111.00 \ (s). \]

HR-MS: Calc. mass for \(\text{C}_{11}\text{H}_{7}\text{Cl}_3\text{N}_2\text{O}_2\): [M + Na] = 326.9471, found: 326.9471.

Methyl (E)-2-diazo-4-(furan-2-yl)but-3-enoate (1p)

The compound was prepared from ester 3p according to general procedure A with an isolated yield of 49%. Analytical data matches the literature.[24]

\[
\text{H NMR} \ (300 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.38 – 7.37 \ (m, 1H), 6.45 – 6.38 \ (m, 2H), 6.21 – 6.13 \ (m, 2H), 3.87 \ (s, 3H). \]

Methyl (E)-2-diazo-4-(thiophen-2-yl)but-3-enoate (1q)

The compound was prepared from ester 3q according to general procedure A with an isolated yield of 58%. Analytical data matches the literature.[24]

\[
\text{H NMR} \ (300 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.16 \ (d, J = 5.0 \text{ Hz}, 1H), 6.99 – 6.94 \ (m, 1H), 6.94 – 6.90 \ (m, 1H), 6.43 \ (d, J = 16.0 \text{ Hz}, 1H), 6.28 \ (d, J = 15.6 \text{ Hz}, 1H), 3.86 \ (s, 3H). \]

Methyl (E)-2-diazo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (1r)

The compound was prepared from ester 3r according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.[25]

\[
\text{H NMR} \ (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.63 – 7.54 \ (m, 2H), 7.51 – 7.43 \ (m, 2H), 6.65 \ (d, J = 16.3 \text{ Hz}, 1H), 6.26 \ (d, J = 16.3 \text{ Hz}, 1H), 3.90 \ (s, 3H). \]

Methyl (E)-4-(2,4-bis(trifluoromethyl)phenyl)-2-diazobut-3-enoate (1s)

The compound was prepared from ester 3s according to general procedure A with an isolated yield of 49%. Analytical data matches the literature.[26]

\[
\text{H NMR} \ (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.80 – 7.68 \ (m, 3H), 6.73 \ (d, J = 16.3 \text{ Hz}, 1H), 6.32 \ (d, J = 16.3 \text{ Hz}, 1H), 3.92 \ (s, 3H). \]

Methyl (E)-4-(3-diazo-4-methoxy-4-oxobut-1-en-1-yl)benzoate (1t)

The compound was prepared from ester 3t according to general procedure A with an isolated yield of 46%. Analytical data matches the literature.[27]

\[
\text{H NMR} \ (250 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 8.01 \ (d, J = 8.4 \text{ Hz}, 2H), 7.43 \ (d, J = 8.4 \text{ Hz}, 2H), 6.67 \ (d, J = 16.3 \text{ Hz}, 1H), 6.26 \ (d, J = 16.3 \text{ Hz}, 1H), 3.94 \ (s, 3H), 3.90 \ (s, 3H). \]

Benzyl 2-diazobut-3-enoate (1u)

The compound was prepared from ester 3u according to general procedure A with an isolated yield of 46%. Analytical data matches the literature.[28]

\[
\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 7.40 \ (s, 5H), 6.23 \ (dd, J = 17.4, 11.0 \text{ Hz}, 1H), 5.29 \ (s, 2H), 5.16 \ (d, J = 11.1 \text{ Hz}, 1H), 4.91 \ (d, J = 17.3 \text{ Hz}, 1H). \]

\[
\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta \text{ ppm} \ 137.37 \ (s), 135.33 \ (s), 129.27 \ (s), 128.45 \ (s), 122.08 \ (s), 116.26 \ (s), 111.55 \ (s), 53.36 \ (s). \]

IR (\(\tilde{\nu}\) in \text{cm}^{-1}): 2083.12 \ (s), 1701.22 \ (vs). HR-MS: Calc. mass for \(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\): [M] = 202.0742, found: 202.074.
Methyl (E)-2-diazooct-3-enoate (1v)

The compound was prepared from ester 3v according to general procedure A with an isolated yield of 65%. Analytical data matches the literature.\[6\]

\[
{\text{H NMR}} \quad \text{(300 MHz, CDCl}_3) \; \delta \text{ ppm 5.73 (dt, } J = 15.8, 1.4 \text{ Hz, 1H), 5.32 (dt, } J = 15.8, 7.0 \text{ Hz, 1H), 2.21 - 2.13 (m, 2H), 3.80 (s, 3H), 1.38 - 1.31 (m, 4H), 0.93 - 0.89 (m, 3H).}
\]

Methyl (E/Z)-2-diazooct-5,5-dimethylhex-3-enoate (1w)

The compound was prepared from ester 3w according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.\[6\]

\[
{\text{H NMR}} \quad \text{(400 MHz, CDCl}_3) \; \delta \text{ ppm 5.81 (d, } J = 15.8 \text{ Hz, 1H), 5.67 (d, } J = 12.0 \text{ Hz, 1H), 5.58 (d, } J = 12.3 \text{ Hz, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 2.06 (dd, } J = 7.9, 1.2 \text{ Hz, 2H), 1.14 - 1.07 (m, 9H), 0.93 (s, 9H).}
\]

Ethyl (E)-2-diazooct-4-phenylbut-3-enoate (1x)

A solution of E-2-bromostyrene (1.0 eq) and ethyl diazoacetate (1.3 eq) was added tetrakis(triphenylphosphin)palladium(0) (5 mol-%), silver(I)carbonate (0.5 eq) and triethylamine (1.3 eq) in dry toluene. The mixture was stirred at RT for 5 hours, filtered through a short silica pad and washed with ethyl acetate. The crude product was purified by column chromatography (10% v/v% ethyl acetate/petrol ether). The products was isolated red solid with 77% yield.\[7\]

\[
{\text{H NMR}} \quad \text{(250 MHz, CDCl}_3) \; \delta \text{ ppm 7.40 (d, } J = 15.9 \text{ Hz, 1H), 6.18 (d, } J = 16.3 \text{ Hz, 1H), 4.35 (q, } J = 7.1 \text{ Hz, 2H), 1.36 (t, } J = 7.9 \text{ Hz, 2H), 1.14 - 1.07 (m, 9H), 0.93 (s, 9H).}
\]

tert-Butyl (E)-2-diazooct-4-(p-tolyl)but-3-enoate (1y)

The compound was prepared from ester 3y according to general procedure A with an isolated yield of 65%. Analytical data matches the literature.\[8\]

\[
{\text{H NMR}} \quad \text{(400 MHz, CDCl}_3) \; \delta \text{ ppm 7.15 (d, } J = 8.2 \text{ Hz, 2H), 7.11 (d, } J = 8.2 \text{ Hz, 2H), 6.43 (d, } J = 16.4 \text{ Hz, 1H), 6.17 (d, } J = 16.4 \text{ Hz, 1H), 2.36 (s, 3H), 1.57 (s, 9H).}
\]

Benzyl (E)-2-diazooct-4-phenylbut-3-enoate (1z)

The compound was prepared from ester 3z according to general procedure A with an isolated yield of 68%. Analytical data matches the literature.\[9\]

\[
{\text{H NMR}} \quad \text{(250 MHz, CDCl}_3) \; \delta \text{ ppm 7.53 (d, } J = 15.8 \text{ Hz, 1H), 7.29 - 7.20 (m, 2H), 7.46 (m, 2H), 6.46 (d, } J = 16.3 \text{ Hz, 1H), 6.24 (d, } J = 16.3 \text{ Hz, 1H), 5.42 (s, 2H).}
\]

(Perfluorophenyl)methyl (E)-2-diazooct-4-phenylbut-3-enoate (1aa)

The compound was prepared from ester 3aa according to general procedure A with an isolated yield of 11%. Analytical data matches the literature.\[6\]

\[
{\text{H NMR}} \quad \text{(250 MHz, CDCl}_3) \; \delta \text{ ppm 7.39 - 7.33 (m, 4H), 7.29 - 7.20 (m, 1H), 6.46 (d, } J = 16.3 \text{ Hz, 1H), 6.24 (d, } J = 16.7 \text{ Hz, 1H), 5.42 (s, 2H).}
\]

4-Bromobenzyl (E)-4-(4-bromophenyl)-2-diazoct-3-enoate (1ab)

The compound was prepared from ester 3ab according to general procedure A with an isolated yield of 86%.

\[
{\text{H NMR}} \quad \text{(400 MHz, CDCl}_3) \; \delta \text{ ppm 7.55 - 7.53 (m, 2H), 7.46 (m, 2H), 7.29 - 7.27 (m, 2H), 7.23 - 7.21 (m, 2H), 6.49 (d, } J = 15.9 \text{ Hz, 1H), 6.17 (d, } J = 16.1 \text{ Hz, 1H), 5.26 (s, 2H).}
\]

\[
{\text{C NMR}} \quad \text{(63 MHz, CDCl}_3) \; \delta \text{ ppm 165.60 (s), 136.57 (s), 135.49 (s), 132.97 (s), 132.73 (s), 131.11 (s), 130.91 (s), 128.23 (s), 123.52 (s), 122.93 (s), 121.76 (s), 112.93 (s), 67.09 (s).}
\]

\[
{\text{IR (}\nu\text{ in cm}^{-1})}: 2943.37 (w), 2071.55 (vs), 1701.22 (vs), 1068.56 (s).}
\]

\[
{\text{HR-MS: Calc. mass for } \text{C}_{17}\text{H}_{22}\text{Br}_{2}\text{N}_{2}\text{O}_{2}: [M + Na] = 433.9266, found: 433.9259.}
\]

12
Dimethyl (Z)-2-benzylidene-3-diazosuccinate (1af)

The compound was prepared from diester 3af according to general procedure A, using TsN₃ as diazotransfer reagent instead of p-ABSA, resulting in an isolated yield of 45%. Analytical data matches the literature.[29]

\[ ^1H \text{NMR (300 MHz, CDCl}_3 \delta \text{ ppm 7.73 (s, 1H), 7.51 – 7.35 (m, 5H), 3.85 (s, 3H), 3.73 – 3.64 (m, 3H).} \]

Ethyl 2-diazo-3-oxobutanoate (P-1ag)

The compound was prepared from ethyl 3-oxobutanoate according to general procedure A with an isolated yield of 71%. Spectral data matches the literature.[30]

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ ppm 4.22 (q, } J = 7.1 \text{ Hz, 2H), 2.39 (s, 3H), 1.26 (t, } J = 7.1 \text{ Hz, 3H).} \]

Ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazo-3-enoate (1ag)

A solution of ethyl 2-diazo-3-oxobutanoate P-1ag (1.0 eq) in anhydrous DCM was added triethylamine (1.2 eq) and cooled to 0 °C. Then, the reaction mixture was slowly added tert-Butyldimethylsilyl triflate and the temperature maintained for 20 min. Afterwards, the reaction mixture was allowed to warm to rt and stirred for 1 h. The mixture was poured into a separatory funnel, washed with water (3 x 100 mL) and brine (50 mL). The combined organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure, resulting in an orange oil with a yield of 96%. Spectral data matches the literature.[30]

\[ ^1H \text{NMR (300 MHz, CDCl}_3 \delta \text{ ppm 5.02 (d, } J = 2.0 \text{ Hz, 1H), 4.28 (q, } J = 7.1 \text{ Hz, 2H), 4.26 (d, } J = 5.2 \text{ Hz, 1H), 1.32 (t, } J = 7.1 \text{ Hz, 3H), 0.94 (s, 9H), 0.25 (s, 6H).} \]

(E)-2-Diazo-4-(p-tolyl)but-3-enoic acid (1ah)

This compound was synthesized by basic ester hydrolysis of the corresponding methyl ester 3b with KOH (3.0 eq) in a mixture of water and methanol (4:1).[31] Therefore, the reaction mixture was stirred 18 h at RT. After evaporation of the solvents, the residue was dissolved in a mixture of water and DCM (1:1). The organic layer was discarded while the aqueous layer was acidified with 1M HCl to pH 1. The aqueous layer was extracted with diethyl ether (3 x 50 mL), dried over MgSO₄ and the solvent was evaporated. During the evaporation of the solvent, a white precipitate of pyrazol 2ah was formed. Therefore, the vinyldiazo compound 1ah could only be obtained as a mixture with pyrazol 2ah. Due to the rapid conversion, \(^{13}\)C-NMR and HR-MS data could not be obtained.

\[ ^1H \text{NMR (300 MHz, CDCl}_3 \delta \text{ ppm 7.29 (s, 2H), 7.15 (d, } J = 8.0 \text{ Hz, 2H), 6.45 – 6.36 (m, 1H), 6.25 – 6.17 (m, 1H), 2.35 (s, 3H).} \]

\[ \text{IR (v in cm}^{-1}) \text{: 2900 - 2553 (m), 2083.12 (s), 1674.21 (vs).} \]

(E)-3-Diazo-5-phenylpent-4-eno-2-one (1ai)

The compound was prepared from vinyl ketone 3ai according to general procedure A with an isolated yield of 21%. Analytical data matches the literature.[1]

\[ ^1H \text{NMR (250 MHz, CDCl}_3 \delta \text{ ppm 7.45 – 7.31 (m, 5H), 6.60 (br d, } J = 16.3 \text{ Hz, 1H), 6.24 (d, } J = 16.1 \text{ Hz, 1H), 2.38 (s, 3H).} \]

Methyl (E)-2-diazo-4-phenylpent-3-enoate (1aj)

The compound was prepared from ester 3aj according to general procedure A with an isolated yield of 78%. Analytical data matches the literature.[32]

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ ppm 7.48 – 7.43 (m, 2H), 7.40 – 7.30 (m, 3H), 6.03 (d, } J = 0.9 \text{ Hz, 1H), 3.86 (s, 3H), 2.13 (d, } J = 1.2 \text{ Hz, 3H).} \]
Methyl (Z)-2-diazohex-3-enoate (1ak)

Commercially available (Z)-3-hexenyl (Z)-3-hexenoate was stirred with KOH (4.0 eq) in a mixture of methanol and water (50 mL, 4 : 1) for 24 h at r. t. After evaporation of the solvent, the residue was dissolved in a mixture of water and DCM (1:1). The organic layer was discarded while the aqueous layer was acidified with 1M HCl to pH 1. The aqueous layer was extracted with diethyl ether (3 x 50 mL), dried over MgSO₄ and the solvent was evaporated. Methylation was performed according to procedure A. The resulting methyl (Z)-hex-3-enoate was used for the next step without further purification. The compound 7y was prepared from methyl (Z)-hex-3-enoate according to general procedure A with an isolated yield of 52%. Analytical data matches the literature.[6]

¹H NMR (250 MHz, CDCl₃) δ ppm 5.62 – 5.47 (m, 2H), 3.82 (s, 3H), 2-09 (qt, J = 7.4 Hz, 2H), 1.04 (t, J = 7.5 Hz, 3H).
Synthesis of Pyrazols

Spectral characterization of pyrazoles is complicated by the existence of tautomers and strongly depends on the solvent in which the spectra were recorded. Numerous reports demonstrate that C3, C4 and C5 of the pyrazoles may appear as weak broad peaks in $^{13}$C NMR in CDCl$_3$.[33] In polar aprotic solvents like d6-DMSO, the equilibrium between tautomers proceeds at lower rates which allows for observation of tautomers and causes doubling of the peaks.[34] We report $^1$H NMR spectra for all compounds as a proof of purity and selected $^{13}$C NMR, $^{19}$F and $^{29}$Si NMR spectra. Unambiguous confirmation of structure has been obtained by X-ray crystallography for several compounds which are shown at the end of the supporting information document.

**Methyl 5-phenyl-1H-pyrazole-3-carboxylate (2a)**

![Methyl 5-phenyl-1H-pyrazole-3-carboxylate (2a)](image)

The compound was prepared from vinyldiazo compound 1a according to general procedure B with an isolated yield of 94%. Analytical data matches the literature.[35] $^1$H NMR (250 MHz, CDCl$_3$) δ ppm 7.89 – 7.76 (m, 2H), 7.51 – 7.37 (m, 3H), 7.14 (s, 1H), 3.97 (s, 3H).

**Methyl 5-(p-tolyl)-1H-pyrazole-3-carboxylate (2b)**

![Methyl 5-(p-tolyl)-1H-pyrazole-3-carboxylate (2b)](image)

The compound was prepared from vinyldiazo compound 1b according to general procedure B with an isolated yield of 92%. $^1$H NMR (600 MHz, MeCN-d$_3$) δ ppm 11.72 (br s, 1H), 7.69 (m, 2H), 7.31 (m, 2H), 7.09 (br s, 1H), 3.91 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ ppm 162.97 (s), 151.78 (s), 144.23 (s), 144.00 (s), 138.62 (s), 137.64 (s), 134.78 (s), 130.37 (s), 129.74 (s), 129.49 (s), 128.80 (s), 126.70 (s), 126.13 (s), 125.72 (s), 105.91 (s), 104.90 (s), 52.42 (s), 51.92 (s), 21.27 (s). IR (v in cm$^{-1}$): 3209.55 (m), 2954.95 (m), 1724.36 (s). HR-MS: Calc. mass for C$_{12}$H$_{12}$N$_2$O$_2$: [M + Na] = 239.0796, found: 239.0808.

**Methyl 5-[[1,1'-biphenyl]-4-yl]-1H-pyrazole-3-carboxylate (2c)**

![Methyl 5-[[1,1'-biphenyl]-4-yl]-1H-pyrazole-3-carboxylate (2c)](image)

The compound was prepared from vinyldiazo compound 1c according to general procedure B with an isolated yield of 77%. $^1$H NMR (400 MHz, DMSO-d$_6$) δ ppm 14.12 - 14.03 (m, 1H), 7.97 - 7.92 (m, 2H), 7.79 - 7.72 (m, 4H), 7.50 - 7.27 (m, 4H), 3.89 - 3.85 (m, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ ppm 162.94 (s), 159.92 (s), 151.39 (s), 144.38 (s), 143.58 (s), 140.62 (s), 140.00 (s), 139.72 (s), 134.98 (s), 132.23 (s), 129.45 (s), 128.22 (s), 127.90 (s), 127.44 (s), 127.05 (s), 126.34 (s), 106.30 (s), 105.46 (s), 52.49 (s), 51.99 (s). IR (v in cm$^{-1}$): 3232.70 (m), 2924.09 (w), 1724.36 (s).

**Methyl 5-(naphthalen-2-yl)-1H-pyrazole-3-carboxylate (2d)**

![Methyl 5-(naphthalen-2-yl)-1H-pyrazole-3-carboxylate (2d)](image)

The compound was prepared from vinyldiazo compound 1d according to general procedure B with an isolated yield of 78%. $^1$H NMR (600 MHz, MeCN-d$_3$) δ ppm 11.91 (br s, 1H), 8.33 (br s, 1H), 8.00 - 7.94 (m, 4H), 7.59 - 7.56 (m, 2H), 7.28 (br s, 1H), 3.94 (s, 3H). IR (v in cm$^{-1}$): 3232.70 (m), 2924.09 (w), 1724.36 (s). HR-MS: Calc. mass for C$_{15}$H$_{14}$N$_2$O$_2$: [M + Na] = 301.0953, found: 301.0956.

**Methyl 5-benzyl-1H-pyrazole-3-carboxylate (2e)**

![Methyl 5-benzyl-1H-pyrazole-3-carboxylate (2e)](image)

The compound was prepared from vinyldiazo compound 1e according to general procedure B with an isolated yield of 64%. $^1$H NMR (600 MHz, MeCN-d$_3$) δ ppm 11.37 (br s, 1H), 7.36 - 7.34 (m, 2H), 7.29 - 7.26 (m, 3H), 6.55 (s, 1H), 4.05 (s, 3H), IR (v in cm$^{-1}$): 3197.98 (m), 2854.65 (w), 1716.65 (vs).

HR-MS: Calc. mass for C$_{12}$H$_{12}$N$_2$O$_2$: [M] = 216.0899, found: 216.0892.
Methyl 5-(4-allylphenyl)-1H-pyrazole-3-carboxylate (2f)

The compound was prepared from vinyldiazo compound 1f according to general procedure B with an isolated yield of 93%.

\(^1\)H NMR (600 MHz, DMSO-d₆) \(\delta\) ppm 14.08 - 13.92 (m, 1H), 7.89 - 7.75 (m, 2H), 7.49 - 6.35 (m, 4H), 6.00 - 5.06 (m, 4H), 6.00 - 5.06 (m, 1H), 3.87 - 3.83 (m, 3H). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3240.41 (m), 2854.65 (w), 1728.22 (s). HR-MS: Calc. mass for C₁₉H₁₈N₂O₂: [M] = 293.1284, found: 293.1285.

Methyl 5-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (2g)

The compound was prepared from vinyldiazo compound 1g according to general procedure B with an isolated yield of 69%.

\(^1\)H NMR (600 MHz, MeCN-d₃) \(\delta\) ppm 11.82 (br s, 1H), 7.73 - 7.72 (m, 2H), 7.05 - 7.03 (m, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 13C NMR (101 MHz, DMSO-d₆) \(\delta\) ppm 163.02 (s), 159.97 (s), 159.57 (s), 151.65 (s), 144.21 (s), 143.88 (s), 134.74 (s), 127.28 (s), 127.05 (s), 125.78 (s), 121.50 (s), 114.93 (s), 114.57 (s), 105.56 (s), 140.40 (s), 55.70 (s), 55.59 (s), 52.42 (s), 51.90 (s). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3194.12 (w), 2951.09 (w), 1724.36 (s). HR-MS: Calc. Mass for C₁₂H₁₀NO₃: [M + Na] = 255.0746, found: 255.0748.

Methyl 5-(3-methoxyphenyl)-1H-pyrazole-3-carboxylate (2h)

The compound was prepared from vinyldiazo compound 1h according to general procedure B with an isolated yield of 69%.

\(^1\)H NMR (600 MHz, MeCN-d₃) \(\delta\) ppm 11.82 (br s, 1H), 7.41 - 7.36 (m, 3H), 7.15 (br s, 1H), 6.99 - 6.97 (m, 1H), 3.92 (s, 3H), 3.89 (s, 3H). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3244.27 (w), 2958.80 (w), 1728.22 (s). HR-MS: Calc. mass for C₁₂H₁₀N₂O₃: [M + Na] = 255.0746, found: 255.0747.

Methyl 5-(2-methoxyphenyl)-1H-pyrazole-3-carboxylate (2i)

The compound was prepared from vinyldiazo compound 1i according to general procedure B with an isolated yield of 76%.

\(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) ppm 11.57 (br s, 1H), 7.71 (dd, J = 7.7, 1.6 Hz, 1H), 7.40 - 7.32 (m, 1H), 7.19 (s, 1H), 7.12 - 7.03 (m, 2H), 4.04 (s, 3H), 3.97 (s, 3H). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3305.99 (m), 2947.23 (w), 1732.08 (s). HR-MS: Calc. mass for C₁₂H₁₀N₂O₃: [M + Na] = 255.0746, found: 255.0743.

Methyl 5-(4-fluorophenyl)-1H-pyrazole-3-carboxylate (2j)

The compound was prepared from vinyldiazo compound 1j according to general procedure B with an isolated yield of 74%.

\(^1\)H NMR (600 MHz, MeCN-d₃) \(\delta\) ppm 7.85 - 7.83 (m, 2H), 7.23 - 7.21 (m, 2H), 7.12 (br s, 1H), 3.92 (s, 3H). 13C NMR (101 MHz, DMSO-d₆) \(\delta\) ppm 163.39 (s), 162.89 (s), 161.77 (s), 159.87 (s), 150.85 (s), 144.34 (s), 143.03 (s), 134.98 (s), 129.69 (s), 128.07 (s), 128.02 (s), 127.76 (s), 127.71 (s), 125.54 (s), 116.60 (s), 116.45 (s), 116.12 (s), 115.98 (s), 52.49 (s), 51.97 (s). 19F NMR (377 MHz, CDCl₃) \(\delta\) ppm -112.92 (s, 1F). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3136.25 (m), 2943.37 (w), 1724.36 (s), 1238.30 (vs). HR-MS: Calc. mass for C₁₂H₁₀F₂N₂O₃: [M] = 220.0648, found: 220.0644.

Methyl 5-(2-fluorophenyl)-1H-pyrazole-3-carboxylate (2k)

The compound was prepared from vinyldiazo compound 1k according to general procedure B with an isolated yield of 77%.

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) ppm 7.86 (br t, J = 7.3 Hz, 1H), 7.43 - 7.32 (m, 1H), 7.28 - 7.19 (m, 3H), 3.99 (s, 3H). 19F NMR (377 MHz, CDCl₃) \(\delta\) ppm -115.75 (s, 1F). IR (\(\tilde{\nu}\) in cm\(^{-1}\)): 3170.97 (m), 2858.51 (m), 1728.22 (s), 1246.02 (s). HR-MS: Calc. mass for C₁₂H₁₀F₂N₂O₃: [M] = 220.0648, found: 220.0644.
Methyl 5-(4-chlorophenyl)-1H-pyrazole-3-carboxylate (2l)
The compound was prepared from vinyldiazo compound 1l according to general procedure B with an isolated yield of 72%.

^1H NMR (600 MHz, DMSO-d_6) δ ppm 14.10 (br s, 1H), 7.88 - 7.87 (m, 2H), 7.51 (br m, 2H), 7.32 (br s, 1H), 3.85 (s, 3H). IR (~ in cm^-1): 3136.25 (s), 1728.22 (s), 1485.19 (s), 1242.16 (vs), 1195.87 (s), 1138.00 (s), 1091.71 (s), 1006.84 (vs), 825.53 (vs), 779.24 (s), 732.95 (m). HR-MS: Calc. mass for C_{11}H_{13}NO_2: [M+H] = 237.0425, found: 237.0429.

Methyl 5-(4-bromophenyl)-1H-pyrazole-3-carboxylate (2m)
The compound was prepared from vinyldiazo compound 1m according to general procedure B with an isolated yield of 73%.

^1H NMR (600 MHz, DMSO-d_6) δ ppm 14.16 - 14.03 (m, 1H), 7.84 - 7.79 (m, 2H), 7.68 - 7.62 (m, 2H), 7.38 - 7.27 (m, 1H), 3.87 - 3.83 (m, 3H). ^13C NMR (151 MHz, DMSO-d_6) δ ppm 162.82 (s), 159.81 (s), 150.65 (s), 144.41 (s), 142.86 (s), 135.09 (s), 132.49 (s), 132.14 (s), 127.78 (s), 122.25 (s), 121.48 (s), 106.41 (s), 105.83 (s), 52.54 (s), 52.02 (s). IR (~ in cm^-1): 3217.50 (m), 2954.63 (w), 1685.79 (s), 1076.28 (m). HR-MS: Calc. mass for C_{11}H_{13}BrNO_2: [M] = 279.9847, found: 279.9844.

Methyl 5-(4-iodophenyl)-1H-pyrazole-3-carboxylate (2n)
The compound was prepared from vinyldiazo compound 1n according to general procedure B with an isolated yield of 77%.

^1H NMR (600 MHz, DMSO-d_6) δ ppm 14.15 - 14.02 (m, 1H), 7.85 - 7.78 (m, 2H), 7.70 - 7.63 (m, 2H), 7.37 - 7.25 (m, 1H), 3.87 - 3.83 (m, 3H). ^13C NMR (151 MHz, DMSO-d_6) δ ppm 162.82 (s), 159.80 (s), 150.81 (s), 144.38 (s), 143.04 (s), 138.31 (s), 137.97 (s), 135.06 (s), 132.67 (s), 128.36 (s), 127.79 (s), 106.36 (s), 105.72 (s), 95.37 (s), 94.41 (s), 52.54 (s), 52.01 (s). IR (~ in cm^-1): 3224.98 (m), 1685.79 (s). HR-MS: Calc. mass for C_{11}H_{13}I_{1}NO_2: [M + Na] = 350.9606, found: 350.9607.

Methyl 5-(2,4,6-trichlorophenyl)-1H-pyrazole-3-carboxylate (2o)
The compound was prepared from vinyldiazo compound 1o according to general procedure B with an isolated yield of 73%.

^1H NMR (250 MHz, CDCl_3) δ ppm 7.45 (s, 2H), 6.97 (s, 1H), 3.97 (s, 3H). ^13C NMR (101 MHz, DMSO-d_6) δ ppm 162.65 (s), 159.68 (s), 146.29 (s), 143.68 (s), 136.81 (s), 136.40 (s), 136.31 (s), 136.00 (s), 134.86 (s), 134.27 (s), 131.36 (s), 128.79 (s), 128.62 (s), 127.52 (s), 110.59 (s), 109.90 (s), 52.59 (s), 52.04 (s). IR (~ in cm^-1): 3248.13 (s), 2920.23 (w), 1701.22 (vs), 1018.41 (s). HR-MS: Calc. mass for C_{11}H_{13}Cl_3NO_2: [M] = 303.9573, found: 303.9565.

Methyl 5-(furan-2-yl)-1H-pyrazole-3-carboxylate (2p)
The compound was prepared from vinyldiazo compound 1p according to general procedure B with an isolated yield of 80%.

^1H NMR (300 MHz, CDCl_3) δ ppm 11.62 (br s, 1H), 7.47 (dd, J = 0.9 Hz, 0.7 Hz 1H), 7.02 (s, 1H), 6.74 (dd, J = 1.7 Hz, 0.6 Hz 1H), 6.49 (dd, J = 1.7 Hz, 1.8 Hz, 1H), 3.94 (s, 1H). ^13C NMR (101 MHz, DMSO-d_6) δ ppm 162.68 (s), 159.66 (s), 148.33 (s), 144.45 (s), 144.17 (s), 144.08 (s), 143.92 (s), 143.07 (s), 135.55 (s), 134.62 (s), 112.38 (s), 112.02 (s), 108.24 (s), 106.87 (s), 105.66 (s), 104.17 (s), 52.56 (s), 52.03 (s). IR (~ in cm^-1): 3062.96 (br, m), 1728.22 (vs), 1489.05 (m), 1249.87 (vs), 1226.73 (s), 1002.98 (s), 752.24 (s), 732.95 (s). HR-MS: Calc. mass for C_{11}H_{13}NO_2S: [M + H] = 192.0529, found: 192.0530.

Methyl 5-(thiophen-2-yl)-1H-pyrazole-3-carboxylate (2q)
The compound was prepared from vinyldiazo compound 1q according to general procedure B with an isolated yield of 68%.

^1H NMR (400 MHz, CDCl_3) δ ppm 11.13 (br s, 1H), 7.40 - 7.33 (m, 2H), 7.12 - 7.09 (m, 1H), 7.04 (s, 1H), 3.97 (s, 3H). ^13C NMR (151 MHz, DMSO-d_6) δ ppm 162.70 (s), 159.75 (s), 147.40 (s), 144.23 (s), 138.47 (s), 136.07 (s), 134.91 (s), 130.65 (s), 128.64 (s), 128.22 (s), 127.24 (s), 125.80 (s), 125.12 (s), 105.81 (s), 105.29 (s), 52.55 (s), 52.05 (s). IR (~ in cm^-1): 3128.54 (m), 2873.94 (m), 1724.36 (s). HR-MS: Calc. mass for C_{9}H_{8}N_{2}O_{2}S: [M + Na] = 231.0204, found: 231.0204.
Methyl 5-(4-(trifluoromethyl)phenyl)-1H-pyrazole-3-carboxylate (2r)

The compound was prepared from vinyldiazocompound 1r according to general procedure B with an isolated yield of 79%.

\[ \text{IR (in cm}^{-1}\text{)}: 3205.69 (w), 2958.80 (w), 1728.22 (m). \]

\[ \text{HR-MS: Calc. mass for C}_{12}H_{9}F_{3}N_{2}O_{2}: [M] = 270.0616, \text{found: 270.0611.} \]

Methyl 5-(2,4-bis(trifluoromethyl)phenyl)-1H-pyrazole-3-carboxylate (2s)

The compound was prepared from vinyldiazocompound 1s according to general procedure B with an isolated yield of 70%.

\[ \text{IR (in cm}^{-1}\text{)}: 3182.55 (w), 2954.95 (m), 1724.36 (s). \]

\[ \text{HR-MS: Calc. mass for C}_{13}H_{9}F_{3}N_{2}O_{2}: [M] = 338.0490, \text{found: 338.0482.} \]

Methyl 5-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3-carboxylate (2t)

The compound was prepared from vinyldiazocompound 1t according to general procedure B with an isolated yield of 78%.

\[ \text{IR (in cm}^{-1}\text{)}: 3205.69 (w), 2958.80 (w), 1728.22 (m). \]

\[ \text{HR-MS: Calc. mass for C}_{13}H_{9}F_{3}N_{2}O_{2}: [M] = 338.0490, \text{found: 338.0482.} \]

Benzyl 1H-pyrazole-3-carboxylate (2u)

The compound was prepared from vinyldiazocompound 1u according to general procedure B with an isolated yield of 56%.

\[ \text{IR (in cm}^{-1}\text{)}: 3128.54 (m), 2846.93 (m), 1720.50 (vs). \]

\[ \text{HR-MS: Calc. mass for C}_{10}H_{10}N_{2}O: [M + Na] = 283.0695, \text{found: 283.0700.} \]

Methyl 5-butyl-1H-pyrazole-3-carboxylate (2v)

The compound was prepared from vinyldiazocompound 1v according to general procedure B with an isolated yield of 48%.

\[ \text{IR (in cm}^{-1}\text{)}: 3182.55 (w), 2954.95 (m), 1724.36 (vs). \]

\[ \text{HR-MS: Calc. mass for C}_{9}H_{10}N_{2}O: [M] = 182.1055, \text{found: 182.1050.} \]

Ethyl 5-phenyl-1H-pyrazole-3-carboxylate (2x)

The compound was prepared from vinyldiazocompound 1x according to general procedure B with an isolated yield of 78%. Analytical data matches the literature.[36]
**tert-Butyl 5-(p-tolyl)-1H-pyrazole-3-carboxylate (2y)**

The compound was prepared from vinyl diazo compound 1y according to general procedure B with an isolated yield of 82%.

**^1H NMR** (300 MHz, CDCl₃) δ ppm 10.63 (br s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 2.40 (s, 3H), 1.63 (s, 9H). **^13C NMR** (151 MHz, DMSO-d₆) δ ppm 161.83 (s), 158.84 (s), 151.61 (s), 145.71 (s), 143.70 (s), 138.48 (s), 137.56 (s), 136.32 (s), 130.51 (s), 129.99 (s), 126.28 (s), 125.67 (s), 105.49 (s), 104.71 (s), 80.73 (s), 55.37 (s), 28.35 (s), 21.27 (s). **IR** (υ in cm⁻¹): 3113.11 (w), 2978.09 (m), 1712.79 (s).

**51-Benzyl-1H-pyrazole-3-carboxylate (2z)**

The compound was prepared from vinyl diazo compound 1z according to general procedure B with an isolated yield of 76%.

**^1H NMR** (300 MHz, CDCl₃) δ ppm 11.04 – 10.60 (m, 1H), 7.79 – 7.72 (m, 2H), 7.49 – 7.37 (m, 8H), 7.16 (s, 1H), 5.41 (s, 2H). **^13C NMR** (101 MHz, DMSO-d₆) δ ppm 162.31 (s), 159.35 (s), 151.80 (s), 144.28 (s), 144.01 (s), 136.70 (s), 136.23 (s), 134.86 (s), 133.09 (s), 129.53 (s), 129.17 (s), 129.97 (s), 128.86 (s), 128.67 (s), 128.55 (s), 128.39 (s), 125.85 (s), 106.39 (s), 105.50 (s), 66.59 (s), 66.03 (s). **IR** (υ in cm⁻¹): 3194.12 (m), 3020.53 (m), 1728.22 (vs).

**Methyl 4-(perfluorophenyl)methyl 1H-pyrazole-3-carboxylate (2aa)**

The compound was prepared from vinyl diazo compound 1aa according to general procedure B with an isolated yield of 85%.

**^1H NMR** (400 MHz, DMSO-d₆) δ ppm 14.31 - 14.02 (m, 1H), 7.86 - 7.80 (m, 2H), 7.49 - 7.21 (m, 4H), 5.45 (s, 2H). **^19F NMR** (377 MHz, CDCl₃) δ ppm -141.41 (dd, J = 22.6, 7.5 Hz, 2F), -151.86 (t, J = 22.6 Hz, 2F), -161.22 (dt, J = 18.9, 7.5, 3.8 Hz, 1F). **IR** (υ in cm⁻¹): 3282.84 (s), 1697.36 (vs), 1253.73 (s). **HR-MS**: Calc. mass for C₁₇H₁₅F₄N₂O₂: [M + Na] = 368.0584, found: 368.0576.

**4-Bromobenzyl 5-(4-bromophenyl)-1H-pyrazole-3-carboxylate (2ab)**

The compound was prepared from vinyl diazo compound 1ab according to general procedure B with an isolated yield of 74%.

**^1H NMR** (600 MHz, MeCN-d₃) δ ppm 11.92 (br s, 1H), 7.74 (br m, 2H), 7.65 - 7.60 (m, 4H), 7.45 - 7.44 (m, 2H), 5.36 (s, 2H). **^13C NMR** (101 MHz, DMSO-d₆) δ ppm 162.10 (s), 159.14 (s), 150.72 (s), 144.24 (s), 142.97 (s), 136.11 (s), 134.94 (s), 132.48 (s), 132.31 (s), 132.12 (s), 131.90 (s), 130.68 (s), 128.06 (s), 127.83 (s), 122.29 (s), 121.88 (s), 121.75 (s), 121.51 (s), 106.71 (s), 106.01 (s), 65.88 (s), 65.31 (s). **IR** (υ in cm⁻¹): 3255.84 (m), 2862.36 (w), 1693.50 (vs), 1072.42 (m). **HR-MS**: Calc. mass for C₁₇H₁₂Br₂N₂O₂: [M + Na] = 433.9266, found: 433.9264.

**Methyl 4-methyl-5-phenyl-1H-pyrazole-3-carboxylate (2ad)**

The compound directly cyclized upon diazotransfer of ester 1ad with an isolated yield of 45% with respect to the starting material.

**^1H NMR** (400 MHz, CDCl₃) δ ppm 7.60 – 7.58 (m, 2H), 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 1H), 3.96 (s, 3H), 2.46 (s, 3H). **^13C NMR** (101 MHz, CDCl₃) δ ppm 161.63 (s), 131.40 (s), 128.76 (s), 128.32 (s), 127.88 (s), 118.03 (s), 51.91 (s), 29.73 (s), 9.67 (s). **IR** (υ in cm⁻¹): 2441.88 (br, m), 1728.22 (s), 1165.00 (vs), 1006.84 (s), 887.26 (m). **HR-MS**: Calc. mass for C₁₇H₁₂N₂O₂: [M] = 216.0899, found: 216.0893.
Methyl 4,5-diphenyl-1H-pyrazole-3-carboxylate (2ae)

The compound directly cyclized upon diazotransfer of ester 1ae with an isolated yield of 36% with respect to the starting material.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ ppm 7.39 – 7.35 (m, 5H), 7.33 – 7.28 (m, 5H), 3.83 (s, 3H).} \]

Dimethyl 5-phenyl-1H-pyrazole-3,4-dicarboxylate (2af)

The compound was prepared from vinyldiazo compound 1af according to general procedure B with an isolated yield of 62%. Analytical data matches the literature.\[37\]

\[ \text{1H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ ppm 7.78 (d, } J = 1.5 \text{ Hz, 1H), 7.64 – 7.59 (m, 1H), 7.53 – 7.50 (m, 1H), 7.41 – 7.37 (m, 2H), 3.86 (s, 3H), 3.73 (s, 3H).} \]

Ethyl 4-((tert-butyldimethylsilyl)oxy)-1H-pyrazole-3-carboxylate (2ag)

The compound was prepared from vinyldiazo compound 1ag according to general procedure B with an isolated yield of 51%.

\[ \text{1H NMR (600 MHz, MeCN-d}_3\text{) } \delta \text{ ppm 10.94 (br s, 1H), 7.05 (s, 1H), 4.12 (q, } J = 7.1 \text{ Hz, 2H), 1.14 (t, } J = 7.1 \text{ Hz, 3H), 0.80 (s, 9H), 0.00 (s, 6H).} \]

5-(p-Tolyl)-1H-pyrazole-3-carboxylic acid (2ah)

The compound was prepared from vinyldiazo compound 1ah and already reacted to the corresponding pyrazole 2ah during evaporation of the solvent. Thus, a light orange solid could be isolated in 95% with respect to the starting material. Analytical data matches the literature.\[38\]

\[ \text{1H NMR (300 MHz, MeOD) } \delta \text{ ppm 7.64 (d, } J = 8.2 \text{ Hz, 2H), 7.26 (d, } J = 8.1 \text{ Hz, 2H), 7.07 (s, 1H), 2.38 (s, 3H).} \]

1-(5-Phenyl-1H-pyrazol-3-yl)ethan-1-one (2ai)

The compound was prepared from vinyldiazo compound 1ai according to general procedure B with an isolated yield of 64%. Analytical data matches the literature.\[33d\]

\[ \text{1H NMR (250 MHz, CDCl}_3\text{) } \delta \text{ ppm 11.57 – 10.46 (m, 1H), 7.77 (d, } J = 7.0 \text{ Hz, 2H), 7.53 – 7.43 (m, 3H), 7.11 (s, 1H), 2.64 (s, 3H).} \]
References

Copies of Spectra

Esters 3

Methyl (E)-5-phenylpent-3-enoate (3e)

Methyl (E)-4-(4-allylphenyl)but-3-enoate (3f)
Methyl (E)-4-(2,4,6-trichlorophenyl)but-3-enoate (3o)
Benzyl but-3-enoate (3u)

4-Bromobenzyl (E)-4-(4-bromophenyl)but-3-enoate (3ab)
Methyl (E)-3-Methyl-4-phenylbut-3-enoate (3ad)
Methyl (E)-4,4-diphenylbut-3-enoate (3ae)
(Z)-2-Benzylidenesuccinic acid (P-3af)

Dimethyl (Z)-2-benzylidenesuccinate (3af)
Vinyl diazo Compounds 1

Methyl (E)-2-diazo-5-phenylpent-3-enoate (1e)
Methyl (E)-4-(4-allylphenyl)-2-diazobut-3-enoate (1f)
Methyl (E)-2-diazo-4-(2,4,6-trichlorophenyl)but-3-enoate (10)
Benzyl 2-diazo-3-enoate (1u)

Ethyl (E)-2-diazo-4-phenylbut-3-enoate (1x)
4-Bromobenzyl \((E)\)-4-(4-bromophenyl)-2-diazobut-3-enoate (1ab)
Dimethyl (Z)-2-benzylidene-3-diazosuccinate (1af)

Ethyl 2-diazo-3-oxobutanoate (P-1ag)
Ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (1ag)

(E)-2-Diazo-4-(p-tolyl)but-3-enoic acid (1ah)
Pyrazoles 2

Spectral characterization of pyrazoles is complicated by the existence of tautomers and strongly depends on the solvent in which the spectra were recorded. Numerous reports demonstrate that C3, C4 and C5 of the pyrazoles may appear as weak broad peaks in $^{13}$C NMR in CDCl$_3$.[33] In polar aprotic solvents like d$_6$-DMSO, the equilibrium between tautomers proceeds at lower rates which allows for observation of tautomers and causes doubling of the peaks.[34] We report 1H NMR spectra for all compounds as a proof of purity and selected $^{13}$C NMR, $^{19}$F and $^{29}$Si NMR spectra. Unambiguous confirmation of structure has been obtained by X-ray crystallography for several compounds which are show at the end of the supporting information document.

Methyl 5-phenyl-1H-pyrazole-3-carboxylate (2a)
Methyl 5-(p-tolyl)-1H-pyrazole-3-carboxylate (2b)
Methyl 5-[[1,1'-biphenyl]-4-yl]-1H-pyrazole-3-carboxylate (2c)
Methyl 5-(naphthalen-2-yl)-1H-pyrazole-3-carboxylate (2d)

Methyl 5-benzyl-1H-pyrazole-3-carboxylate (2e)
Methyl 5-(4-allylphenyl)-1H-pyrazole-3-carboxylate (2f)

Methyl 5-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (2g)
Methyl 5-(3-methoxyphenyl)-1H-pyrazole-3-carboxylate (2h)
Methyl 5-(2-methoxyphenyl)-1H-pyrazole-3-carboxylate (2l)
Methyl 5-(4-fluorophenyl)-1H-pyrazole-3-carboxylate (2j)
Methyl 5-(2-fluorophenyl)-1H-pyrazole-3-carboxylate (2k)
Methyl 5-(4-chlorophenyl)-1H-pyrazole-3-carboxylate (2l)
Methyl 5-(4-bromophenyl)-1H-pyrazole-3-carboxylate (2m)
Methyl 5-(4-iodophenyl)-1H-pyrazole-3-carboxylate (2n)
Methyl 5-(2,4,6-trichlorophenyl)-1H-pyrazole-3-carboxylate (2o)
Methyl 5-(furan-2-yl)-1H-pyrazole-3-carboxylate (2p)
Methyl 5-(thiophen-2-yl)-1H-pyrazole-3-carboxylate (2q)
Methyl 5-(4-(trifluoromethyl)phenyl)-1H-pyrazole-3-carboxylate (2r)
Methyl 5-(2,4-bis(trifluoromethyl)phenyl)-1H-pyrazole-3-carboxylate (2s)

VK-103_2 10 1 "C:\Users\ACER\Desktop\Valente Kerndi"
Methyl 5-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-3-carboxylate (2t)
Benzyl 1H-pyrazole-3-carboxylate (2u)
Methyl 5-butyl-1H-pyrazole-3-carboxylate (2v)
Ethyl 5-phenyl-1H-pyrazole-3-carboxylate (2x)
tert-Butyl 5-(p-tolyl)-1H-pyrazole-3-carboxylate (2y)
Benzyl 5-phenyl-1H-pyrazole-3-carboxylate (2z)
(Perfluorophenyl)methyl 5-phenyl-1H-pyrazole-3-carboxylate (2aa)
4-Bromobenzyl 5-(4-bromophenyl)-1H-pyrazole-3-carboxylate (2ab)
Methyl 4-methyl-5-phenyl-1H-pyrazole-3-carboxylate (2ad)
Methyl 4,5-diphenyl-1H-pyrazole-3-carboxylate (2ae)
Dimethyl 5-phenyl-1H-pyrazole-3,4-dicarboxylate (2af)

Ethyl 4-((tert-butyldimethylsilyl)oxy)-1H-pyrazole-3-carboxylate (2ag)
5-\((p\text{-Tolyl})\text{-1H-pyrazole-3-carboxylic acid (2ah)}\)

1-(5-\text{Phenyl-1H-pyrazol-3-yl})\text{ethan-1-one (2ai)}
Crystallographic data

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[39-41]

The structures were solved by direct methods (SHELXS[42]) and refined by full-matrix least squares techniques against Fo2.[43] All hydrogen atoms were located by difference Fourier synthesis and refined isotropically.

All non-hydrogen atoms were refined anisotropically.[44]

Crystallographic data as well as structure solution and refinement details are summarized in Table 4. XP (SIEMENS Analytical X-ray Instruments, Inc.1994) was used for structure representations.

Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1986463 for 1r, CCDC-1986464 for 2m, and CCDC-1986465 2n. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Table 1: Crystal data and refinement details for the X-ray structure determinations.

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<th>Compound</th>
<th>1r</th>
<th>2m</th>
<th>2n</th>
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<tr>
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<tr>
<td>fw (g∙mol⁻¹)</td>
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<td>-140(2)</td>
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<td>P b c a</td>
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<td>a/Å</td>
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<td>c/Å</td>
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<td>S</td>
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<td>CCDC No.</td>
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a) Definition of the R indices: R1 = (Σ ||Fo|-|Fc||)/Σ Fo;

wR2 = [Σ[w(Fo²-Fc²)²]/Σ[w(Fo²)²]]¹/² with w⁻¹ = □²(Fo²) + (aP)² + bP; P = [2Fo² + Max(Fo²)]/3;
b) S = [Σ[w(Fo²-Fc²)²]/(Nc-Nh)]¹/².
Structure of 1r
Structure of 2m
Structure of 2n