Photoredox-Catalyzed Addition of Carbamoyl Radicals to Olefins: A 1,4-Dihydropyridine Approach

Luana Cardinale, Mikhail O. Konev,* and Axel Jacobi von Wangelin*[a]
# Table of Contents

1. General Information.......................................................................................................................... S2
2. Optimization Studies.......................................................................................................................... S3
3. Synthesis of Starting Materials. ........................................................................................................... S4
   3.1 General Procedure A: Synthesis of 4-Amido-1,4-Dihydropyridines............................................. S4
   3.2 General Procedure C: Synthesis of Malononitrile-Condensates ................................................. S6
   3.3 General Procedure D: Synthesis of 1,1-Diarylalkenes................................................................. S10
   3.4 Synthesis of Photocatalysts 3DPAFIPN and 3DPA2FBN......................................................... S11
4. General Procedure E. Carbamoylation Reaction of Olefins ................................................................. S12
   4.1 Characterization of Products........................................................................................................ S13
   4.2 Unsuccessful Substrates................................................................................................................ S19
5. Mechanistic Investigations.................................................................................................................. S20
   5.1 Cyclic Voltammetry and Estimation of Excited State Redox Potential ........................................ S20
   5.2 On/Off Experiments....................................................................................................................... S21
   5.3 Radical Trapping Experiment......................................................................................................... S22
   5.4 Fluorescence Quenching Experiments........................................................................................... S23
   5.5 UV-Vis Experiments....................................................................................................................... S26
6. References............................................................................................................................................ S27
7. NMR Spectra...................................................................................................................................... S28
1. General Information

**Chemicals and solvents:** All reagents (≥96% purity) and solvents (≥99% purity) were purchased from commercial suppliers (Acros, Alfa Aesar, Fisher, Fluka, Merck, Sigma Aldrich, TCI, Th. Geyer) and used as received unless otherwise indicated.

**Reaction setup:** All reactions were carried out in LABSOLUTE 4 mL Screw Neck Vials, 45 x 14.7 mm, clear glass, 1st hydrolytic class unless otherwise stated. Irradiation was performed with EvoluChem™ PhotoRedOx reactor fitted with a 455 nm high-power single LED or 405 nm as specified.

**Nuclear magnetic resonance (NMR) spectroscopy:** $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were used for purity and structure determination of products. NMR spectral data were collected on a Bruker Avance 300 (300 MHz for $^1$H; 75 MHz for $^{13}$C, 282 MHz for $^{19}$F) spectrometer, a Bruker Avance 400 (400 MHz for $^1$H; 100 MHz for $^{13}$C) spectrometer or a Bruker Avance III 600 (600 MHz for $^1$H; 585 MHz for $^{19}$F) spectrometer at 20 °C. Chemical shifts are reported in δ/ppm, coupling constants $J$ are given in Hertz. Solvent residual peaks were used as internal standard for all NMR measurements. The quantification of $^1$H cores was obtained from integrations of appropriate resonance signals. Abbreviations used in NMR spectra: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, bs – broad singlet, dd – doublet of doublet.

**High resolution mass spectrometry (HRMS):** HRMS was carried out by the Central Analytics at the department of chemistry, University of Hamburg. Abbreviations used in MS spectra: M – molar mass of target compound, ESI – electrospray ionization.

**Column chromatography:** TLC was performed on the commercial SiO$_2$-coated aluminum plates (DC60 F254, Merck). Visualization was done by UV light (254 nm). Product yields were determined as isolated yields after flash column chromatography on silica gel (Acros Organics, mesh 35-70, 60 Å pore size).

**UV/VIS absorption spectroscopy:** UV/Vis absorption spectroscopy was performed at room temperature on an Agilent Cary 5000 UV/VIS NIR double beam spectrometer with a 10 mm quartz cuvette.

**Cyclic voltammetry:** CV measurements were performed with a potentiostat galvanostat PGSTAT101 from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a silver/silver(I)chloride reference electrode and N(\(n\)-Bu)$_4$PF$_6$ (0.1 M) as supporting electrolyte. The potentials were achieved relative to the Fc/Fc$^+$ redox couple with ferrocene as external standard.
2. Optimization Studies

![Chemical structure](image)

| Entry | Solvent | PC (mol %) | mmol ratio | Conc. (M) | hv (nm) | Additive | Yield % |
|-------|---------|------------|------------|-----------|---------|----------|---------|
| 1     | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | none     | 80      |
| 2     | DCM     | 2.5        | 1:1.3      | 0.1       | 410     | none     | 77      |
| 3     | DCM     | -          | 1:1.3      | 0.1       | 405     | none     | 60      |
| 4     | CH₃CN   | 2.5        | 1:1.3      | 0.1       | 455     | none     | 65      |
| 5     | DCM degas | 2.5       | 1:1.3      | 0.1       | 455     | none     | 80      |
| 6     | DCM:H₂O (1:1) | 2.5   | 1:1.3      | 0.1       | 455     | none     | 65      |
| 7     | DCM:hexafluoro propanol 2:1 | 2.5 | 1:1.3      | 0.1       | 455     | none     | 52      |
| 8     | DCM dry | 2.5        | 1:1.3      | 0.1       | 455     | none     | 71      |
| 9     | EtOAc   | 2.5        | 1:1.3      | 0.1       | 455     | none     | 14      |
| 10    | DCE     | 2.5        | 1:1.3      | 0.1       | 455     | none     | 50      |
| 11    | CHCl₃   | 2.5        | 1:1.3      | 0.1       | 455     | none     | 14      |
| 12    | DMF     | 2.5        | 1:1.3      | 0.1       | 455     | none     | 50      |
| 13    | DMA     | 2.5        | 1:1.3      | 0.1       | 455     | none     | 60      |
| 14    | DCM     | 1.0        | 1:1.3      | 0.1       | 455     | none     | 67      |
| 15    | DCM     | Mes-Acr 2.5 | 1:1.3  | 0.1       | 455     | none     | 65      |
| 16    | DCM     | 3DPAFBN 2.5 | 1:1.3 | 0.1       | 455     | none     | 78      |
| 17    | DCM     | 2.5        | 1:1.3      | 0.06      | 455     | none     | 76      |
| 18    | DCM     | 2.5        | 1:1.3      | 0.2       | 455     | none     | 76      |
| 19    | DCM     | 2.5        | 1:1.3      | 0.5       | 455     | none     | 73      |
| 20    | DCM     | 2.5        | 1:2        | 0.1       | 455     | none     | 78      |
| 21    | DCM     | 2.5        | 1.5:1      | 0.1       | 455     | none     | 73      |
| 22    | DCM     | 2.5        | 1:1        | 0.1       | 455     | none     | 72      |
| 23    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | Benzophenone 20 mol% | 51      |
| 24    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | 1,4- dicyanobenzene 20 mol% | 89      |
| 25    | DCM     | -          | 1:1.3      | 0.1       | 455     | 1,4- dicyanobenzene 20 mol% | 7       |
| 26    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | Ni(bpy)3(BF4)2 20 mol% | 36      |
| 27    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | K₂HPO₄ 20 mol% | 46      |
| 28    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | Thiophenol 20 mol% | 8       |
| 29    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | TFA 20 mol% | 49      |
| 30    | DCM     | 2.5        | 1:1.3      | 0.1       | 455     | DMAP 20 mol% | 20      |

Table S1. Optimization studies. Reaction run on 0.1 mmol scale following the general procedure D using the dihydropyridine 1a and benzylidenemalononitrile 2a as model substrates in the presence of 3DPAFIPN as photocatalyst. Deviations from standard conditions are highlighted in blue. The yield of 3aa was determined using 1,3,5-trimethoxybenzene as the external standard.
3. Synthesis of Starting Materials.

3.1 General Procedure A: Synthesis of 4-Amido-1,4-Dihydropyridines:

Scheme S1. Synthesis of 4-carbamoyl-1,4-dihydropyridines 1a-c, e.

This procedure was adapted from one reported by Dubur and Uldrikis.¹

A mixture of methyl dichloroacetate (0.72 g, 5.0 mmol) and amine (25 mmol) was heated at 75 °C for 30 minutes in an oil bath, during which the reaction mixture crystallized. The reaction product was a mixture of SI-I and amine hydrochloride that was subsequently used without purification. Ethyl 3-aminocrotonate (1.3 g, 10 mmol) and SI-I (5.0 mmol) were dissolved in glacial acetic acid (10 mL), and the mixture was allowed to stir at room temperature for 20 h. The resultant suspension was diluted with water, the precipitate was removed by filtration, and washed with water to give the corresponding 4-amido-1,4-dihydropyridine.

General Procedure B: Synthesis of 4-Amido-1,4-Dihydropyridines:

Scheme S2. Synthesis of 4-carbamoyl-1,4-dihydropyridines 1d, f, g.

This procedure was adapted from two separate reports by Dubur and Uldrikis and by Duburs.²

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 3-ethyl aminocrotonate (14.9 g, 115 mmol) in glacial acetic acid (5 mL) and the mixture was cooled to 0 °C. A solution of glyoxylic acid (4.6 g, 62 mmol) in glacial acetic acid (20 mL) was then added dropwise to the mixture. The mixture was allowed to warm up to room temperature and stirred overnight. The resulting suspension was then filtered and washed with acetic acid until the yellow color of the washings no longer persisted. The precipitate was collected and 4-carboxy-1,4-dihydropyridine was obtained (4.0 g, 14 mmol, 22% yield).

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with carboxylic acid (1.0 equiv.) SI-II and DCM (0.20 M). Triethylamine (1.2 equiv) was added dropwise to the mixture and the yellow solution was cooled to 0 °C. Isobutylchloroformate (1.2 equiv.) was then added dropwise. After 10 minutes, the mixture was warmed to room temperature and was stirred for 20 minutes upon which the amine was added, and the mixture was stirred overnight. The mixture was then concentrated under reduced pressure and purified by flash column chromatography (eluent: pentane/acetone 70/30).
3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid (SI-II)

\[ \text{EtO}_2\text{C}-\text{CO}_2\text{Et} \]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\), ppm): 11.81 (s, 1H), 8.84 (s, 1H), 4.58 (s, 1H), 4.16 – 4.00 (m, 4H), 2.22 (s, 6H), 1.19 (t, \(J = 7.1\), 6H).

\(^1\)H NMR is consistent with previously published data.\(^3\)

diethyl 2,6-dimethyl-4-(morpholine-4-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1a)

\[ \text{EtO}_2\text{C}-\text{CO}_2\text{Et} \]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\), ppm): 7.17 (s, 1H), 5.01 (s, 1H), 4.27 – 4.07 (m, 4H), 3.97 – 3.87 (m, 2H), 3.79 – 3.70 (m, 2H), 3.70 – 3.55 (m, 4H), 2.24 (s, 6H), 1.28 (t, \(J = 7.1\) Hz, 6H).

\(^1\)H NMR is consistent with previously published data.\(^3\)

diethyl 2,6-dimethyl-4-(piperidine-1-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1b)

\[ \text{EtO}_2\text{C}-\text{CO}_2\text{Et} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): 7.76 (s, 1H), 5.10 (s, 1H), 4.27 – 4.05 (m, 4H), 3.88 – 3.75 (m, 2H), 3.60 – 3.43 (m, 2H), 3.70 – 3.55 (m, 4H), 2.22 (s, 6H), 1.88 – 1.70 (m, 2H), 1.70 – 1.44 (m, 4H), 1.27 (t, \(J = 7.1\) Hz, 6H).

\(^1\)H NMR is consistent with previously published data.\(^4\)

diethyl 4-(4-(ethoxycarbonylpiperazine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c)

\[ \text{EtO}_2\text{C}-\text{CO}_2\text{Et} \]

\(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm): 174.6, 167.5, 155.5, 147.6, 98.9, 61.6, 60.0, 46.6, 42.1, 36.7, 19.5, 14.7, 14.6. HRMS (ESI): \(m/z\) = calcd. for C\(_{21}\)H\(_{31}\)ClN\(_3\)O\(_9\): 438.2235, found: 438.2246.

\(^1\)H NMR is consistent with previously published data.\(^4\)

diethyl 2,6-dimethyl-4-(pyrrolidine-1-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1d)

\[ \text{EtO}_2\text{C}-\text{CO}_2\text{Et} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): 7.66 (s, 1H), 5.03 (s, 1H), 4.29 – 4.03 (m, 6H), 3.99 – 3.78 (m, 2H), 3.74 – 3.34 (m, 6H), 2.21 (s, 6H), 1.26 (apparent t, \(J = 7.2\) Hz, 9H).\(^13\)C NMR (75 MHz, CDCl\(_3\), ppm): 174.6, 167.5, 155.5, 147.6, 98.9, 61.6, 60.0, 46.6, 42.1, 36.7, 19.5, 14.7, 14.6. HRMS (ESI): \(m/z\) = calcd. for C\(_{21}\)H\(_{31}\)ClN\(_3\)O\(_9\): 438.2235, found: 438.2246.

\(^1\)H NMR is consistent with previously published data.\(^4\)
diethyl 4-(benzyl(methyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1e)

Starting from methyl dichloroacetate (0.72 g), N-benzylmethylamine (3.0 g), ethyl 3-aminocrotonate (1.3 g) and following the general procedure A, 1e was isolated by column chromatography on silica (eluent: pentane/acetone, 60:40) as a yellow powder (0.19 g, 10% yield).\(^1\)\(\text{H NMR}\) (300 MHz, CDCl\(_3\), ppm): \(\delta\) 7.76 (s, 1H), 7.32 – 7.13 (m, 5H), 5.07 (s, 1H), 4.59 (s, 2H), 4.25 – 4.02 (m, 4H), 3.29 (s, 3H), 2.24 (s, 6H), 1.21 (t, \(J = 7.1\) Hz, 6H).

\(^1\)H NMR is consistent with previously published data.\(^4\)

diethyl 4-(cyclopropylcarbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f)

Starting from 4-carboxy-1,4-dihydropyridine (0.446 g), NEt\(_3\) (250 µL), cyclopropylamine (130 µL), isobutylchloroformate (230 µL) in DCM and following the general procedure B, 1f was isolated by column chromatography on silica (eluent: pentane/acetone, 70:30) as a pale-yellow powder (0.272 g, 54% yield).\(^1\)\(\text{H NMR}\) (300 MHz, CDCl\(_3\), ppm): \(\delta\) 8.05 (s, 1H), 6.82 (d, \(J = 3.3\) Hz, 1H), 4.49 (s, 1H), 4.17 (qd, \(J = 7.2, 0.9\) Hz, 4H), 2.67 (tq, \(J = 7.4, 3.7\) Hz, 1H), 2.21 (s, 6H), 1.27 (t, \(J = 7.1\) Hz, 6H), 0.76 – 0.68 (m, 2H), 0.47 – 0.39 (m, 2H) ppm.

\(^1\)H NMR is consistent with previously published data.\(^4\)

diethyl 2,6-dimethyl-4-(phenylcarbamoyl)-1,4-dihydropyridine-3,5-dicarboxylate (1g)

Starting from 4-carboxy-1,4-dihydropyridine (0.315 g), NEt\(_3\) (300 µL), aniline (300 mg), isobutylchloroformate (170 mg) in DCM and following the general procedure B, 1g was isolated by column chromatography on silica (eluent: pentane/acetone, 70:30) as a pale-yellow powder (0.168 g, 43% yield).\(^1\)\(\text{H NMR}\) (300 MHz, CDCl\(_3\), ppm): \(\delta\) 8.86 (s, 1H), 7.59 – 7.52 (m, 2H), 7.45 (s, 1H), 7.33 – 7.35 (m, 2H), 7.10 – 7.03 (m, 1H), 4.73 (s, 1H), 4.20 (q, \(J = 7.1\) Hz, 4H), 2.24 (s, 6H), 1.28 (t, \(J = 7.1\) Hz, 6H).

\(^1\)H NMR is consistent with previously published data.\(^4\)

3.2 General Procedure C: Synthesis of Malononitrile-Condensates

The (electron-poor olefins) 2(b-j) used in the present work were prepared following a procedure reported in literature.\(^5\) To a 5 mL round bottom flask the desired aldehyde (1.0 equiv, 3.0 mmol) and the activated methylene (1.0 equiv, 3.0 mmol) were added and suspended in 3 mL of H\(_2\)O. DABCO (10 mol%) was added in one portion to the suspension. Reaction was monitored by TLC. The product precipitated upon formation, the obtained solid was filtered and recrystallized from hot ethanol.

2-(4-chlorobenzylidene)malononitrile (2b)

Starting from 4-chlorobenzaldehyde and following the general procedure C, 2b was obtained as a white powder (450 mg, 80% yield).\(^1\)\(\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 7.91 – 7.80 (m, 2H), 7.73 (s, 1H), 7.58 – 7.48 (m, 2H).

\(^1\)H NMR is consistent with previously published data\(^5\)

2-(4-cyanobenzylidene)malononitrile (2c)

Starting from 4-cyanobenzaldehyde and following the general procedure C, 2c was obtained as a white powder (484 mg, 90% yield).\(^1\)\(\text{H NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 8.03 – 7.95 (m, 2H), 7.90 – 7.75 (m, 3H).

\(^1\)H NMR is consistent with previously published data\(^6\)
2-(4-methoxybenzylidene)malononitrile (2d)

Starting from 4-methoxybenzaldehyde and following the general procedure C, 2d was obtained as a white powder (431 mg, 78% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\)) \(\delta 7.96 – 7.86 \text{ (m, 2H)}, 7.65 \text{ (s, 1H)}, 7.06 – 6.95 \text{ (m, 2H)}, 3.92 \text{ (s, 3H)}.

\(\text{H NMR is consistent with previously published data}^6\)

2-(3-methoxybenzylidene)malononitrile (2e)

Starting from 3-methoxybenzaldehyde and following the general procedure C, 2e was obtained as a white powder (387 mg, 70% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\)) \(\delta 7.75 \text{ (s, 1H)}, 7.53 – 7.38 \text{ (m, 3H)}, 7.17 \text{ (dt, } J = 7.2, 2.4 \text{ Hz, 1H)}, 3.87 \text{ (s, 3H)}.

\(\text{H NMR is consistent with previously published data}^6\)

2-(pentafluorobenzylidene)malononitrile (2f)

Starting from pentafluorobenzaldehyde and following the general procedure C, 2f was obtained as a white powder (658 mg, 90% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\)) \(\delta 7.75 \text{ (q, } J = 1.2 \text{ Hz, 1H)}.

\(\text{F NMR} \text{ (565 MHz, CDCl\(_3\)) } \delta -132.33 \text{ (dt, } J = 19.0, 5.8 \text{ Hz}), -143.34 \text{ (dd, } J = 20.9, 5.6 \text{ Hz}), -157.79 – -158.77 \text{ (m)}.

\(\text{H NMR data are consistent with previously published data}^7\)

2-(pyridin-3-ylmethylene)malononitrile (2g)

Starting from 3-pyridincarboxaldehyde and following the general procedure C, 2g was obtained as a white powder (349 mg, 75% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\), ppm): \(\delta 8.82 \text{ (d, } J = 2.4 \text{ Hz, 1H), 8.76 \text{ (dd, } J = 4.8, 1.6 \text{ Hz, 1H)}, 8.43–8.39 \text{ (m, 1H), 7.75 \text{ (s, 1H)}, 7.45 \text{ (dd, } J = 8.2, 4.8 \text{ Hz, 1H)}.

\(\text{H NMR is consistent with previously published data}^8\)

2-[(5-methylfuran-2-yl)methylene]malononitrile (2h)

Starting from 5-methylfurfural and following the general procedure C, 2h was obtained as a yellow powder (261 mg, 55% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\), ppm): \(\delta 7.37 \text{ (s, 1H), 7.26 \text{ (s, 1H), 6.36–6.35 \text{ (m, 1H)}, 2.46 \text{ (s, 3H)}).

\(\text{H NMR is consistent with previously published data}^9\)

2-(thiophen-2-ylmethylene)malononitrile (2i)

Starting from thiophene-2-carboxaldehyde and following the general procedure C, 2i was obtained as a yellow powder (311 mg, 65% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\), ppm): \(\delta 7.90 – 7.87 \text{ (m, 2H)}, 7.82 – 7.80 \text{ (m, 1H), 7.28 – 7.27 \text{ (m, 1H)}.

\(\text{H NMR is consistent with previously published data}^9\)

2-(cyclohexylmethylene)malononitrile (2j)

Starting from cyclohexylcarboxaldehyde and following the general procedure C, 2j was obtained as a colorless oil (335 mg, 70% yield).\(^1\)\textbf{H NMR} (300 MHz, CDCl\(_3\)) \(\delta 7.15 \text{ (d, } J = 10.5 \text{ Hz, 1H), 2.80 – 2.60 \text{ (m, 1H), 1.83 – 1.67 \text{ (m, 5H), 1.37 – 1.19 \text{ (m, 5H)}}.

\(\text{H NMR is consistent with previously published data}^6\)

\(\text{S7}\)
The following compounds were obtained following literature procedures:

**2-(3,7-dimethyloct-6-en-1-ylidene)malononitrile (2k)**

Starting from citronellal (0.90 mL, 5.0 mmol) and malononitrile (360 mg, 5.5 mmol) and following the literature procedure\(^\text{10}\) 2k was obtained as a colorless oil (0.80 mg, 76% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): δ 7.37 (t, \(J = 8.0\) Hz, 1H), 5.08 (dddd, \(J = 7.1, 5.7, 2.9, 1.5\) Hz, 1H), 2.62 (ddd, \(J = 14.7, 7.7, 5.8\) Hz, 1H), 2.49 (ddd, \(J = 14.7, 8.4, 7.5\) Hz, 1H), 2.04 (m, 2H), 1.88 – 1.77 (m, 1H), 1.72 (s, 3H), 1.63 (s, 3H), 1.42 – 1.30 (m, 2H), 1.00 (d, \(J = 6.7\) Hz, 3H).

\(^1\)H NMR is consistent with previously published data\(^\text{11}\)

**2-benzylidene-1H-indene-1,3(2H)-dione (2l)**

Starting from indandione (440 mg, 3.0 mmol) and benzaldehyde (0.31 mL, 3.0 mmol) and following the literature procedure\(^\text{12}\) 2l was obtained as a beige powder (540 mg, 77% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 8.50 – 8.43 (m, 2H), 8.06 – 7.98 (m, 2H), 7.92 (s, 1H), 7.86 – 7.77 (m, 2H), 7.59 – 7.48 (m, 3H).

\(^1\)H NMR is consistent with previously published data\(^\text{12}\)

**5-benzylidene-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (2m)**

Starting from barbituric acid (1.0 g, 6.5 mmol) and benzaldehyde (0.70 mL, 6.5 mmol) and following the literature procedure\(^\text{12}\) 2m was obtained as a yellow powder (1.3 g, 83% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): δ 8.58 (s, 1H), 8.07 – 8.03 (m, 2H), 7.53 – 7.44 (m, 3H), 3.42 (s, 3H), 3.39 (s, 3H).

\(^1\)H NMR is consistent with previously published data\(^\text{13}\)

**5-benzylidene-2.2-dimethyl-1,3-dioxane-4,6-dione (2n)**

Starting from Meldrum’s acid (1.0 g, 7.0 mmol) and benzaldehyde (0.70 mL, 7.0 mmol) and following the literature procedure\(^\text{12}\) 2n was obtained as a yellow solid (0.89 mg, 55% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): δ 8.42 (s, 1H), 8.06 – 8.02 (m, 2H), 7.56 – 7.45 (m, 3H), 1.81 (s, 6H).

\(^1\)H NMR is consistent with previously published data\(^\text{14}\)

**(E)-3-phenyl-2-(phenylsulphonyl)acrylonitrile (2p)**

Starting from (E)-3-phenyl-2-(phenylsulphonyl)acrylonitrile (270 mg, 1.5 mmol) and benzaldehyde (0.15 mL, 1.5 mmol) and following the literature procedure\(^\text{15}\) procedure 2p was obtained as a white powder (300 mg, 74% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): δ 8.24 (s, 1H), 8.07 – 7.99 (m, 2H), 7.97 – 7.89 (m, 2H), 7.77 – 7.67 (m, 1H), 7.67 – 7.55 (m, 3H), 7.53 – 7.48 (m, 2H).

\(^1\)H NMR is consistent with previously published data\(^\text{15}\)

**(E)-3-(5-chloropyridin-3-yl)-2-(phenylsulphonyl)acrylonitrile (2q)**

Starting from (E)-3-phenyl-2-(phenylsulphonyl)acrylonitrile (270 mg, 1.5 mmol) and 5-Chloro-pyridine-3-carbaldehyde (210 mg, 1.5 mmol) and adapting a literature procedure\(^\text{15}\) procedure 2q was obtained as a white powder (410 mg, 87% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): δ 8.72 (dd, \(J = 2.4, 0.6\) Hz, 1H), 8.21 (s, 1H), 8.09 – 7.99 (m, 2H), 7.82 (dd, \(J = 8.3, 2.5\) Hz, 1H), 7.75 – 7.56 (m, 4H).\(^{13}\)C NMR (75
MHZ, CDCl₃, ppm): δ 149.88, 147.67, 146.70, 137.12, 136.82, 135.72, 134.96, 129.75, 129.05, 127.85, 119.43, 112.34. **HRMS** (ESI): m/z = calcd. for C₁₄H₁₀ClN₂O₂S⁺ [M-H]⁺: 305.0146, found: 305.0133.

**(E)-3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-(phenylsulfonyl)acrylonitrile (2r)**

Starting from (E)-3-phenyl-2-(phenylsulfonyl)acrylonitrile (270 mg, 1.5 mmol) and 3-Methyl-1-phenyl-1H-pyrazole-4-carboxaldehyde (280 mg, 1.5 mmol) and adapting a literature procedure¹⁵ 2r was obtained as a yellow powder (497 mg, 94% yield). **¹H NMR** (300 MHz, CDCl₃, ppm): δ 8.80 (s, 1H), 8.11 (d, J = 0.6 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.71 – 7.55 (m, 5H), 7.47 (ddd, J = 8.0, 7.0, 1.3 Hz, 2H), 7.40 – 7.32 (m, 1H), 2.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃, ppm): δ 153.8, 142.4, 138.7, 138.6, 134.4, 129.7, 129.7, 128.7, 128.3, 128.2, 119.8, 114.6, 114.2, 109.9, 11.8. **HRMS** (ESI): m/z = calcd. for C₁₉H₁₆N₃O₂S⁺ [M-H]⁺: 350.0958, found: 350.0961.
3.3 General Procedure D: Synthesis of 1,1-Diarylalkenes:

This procedure was adapted from one reported by Zhang.\textsuperscript{16} A dry 100 mL round bottom flask equipped with a magnetic stir bar was charged with methyl triphenylphosphonium bromide (3.6 g, 10 mmol, 2.0 equiv) and KO\textsubscript{t}Bu (1.3 g, 12 mmol, 1.2 equiv) followed by THF (20 mL). The resulting yellow suspension was stirred at room temperature for 1 hour. A solution of 1,1-diarylketone (5.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise and the resulting mixture was stirred at 50 °C for 1 hour and allowed to cool down overnight. Next, a saturated solution of NH\textsubscript{4}Cl (25 mL) followed by distilled water (25 mL) were added and the resulting mixture was extracted with EtOAc (3 x 50 mL). The organic phases were combined and dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed under reduced pressure and the residue was further purified by flash chromatography on silica gel to afford the corresponding alkenes.

1-chloro-4-(1-phenylvinyl)benzene (2t)

Starting from 4-chlorobenzophenone (1.08 g) and following the general procedure D, 2t was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 98:2) as a colorless oil (0.80 g, 75% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): δ 7.36–7.31 (m, 9H), 5.50 (bs, 1H), 5.48 (bs, 1H). \textsuperscript{1}H NMR is consistent with previously published data.\textsuperscript{17}

4,4′-(ethene-1,1-diyl)bis(methylbenzene) (2u)

Starting from 4,4′-dimethylbenzophenone (1.05 g) and following the general procedure D, 2u was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 98:2) as a white solid (0.83 g, 80% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): δ 7.26 (apparent d, \(J = 8.1\) Hz, 4H), 7.15 (apparent d, \(J = 8.0\) Hz, 4H), 5.40 (s, 2H), 2.38 (s, 6H). \textsuperscript{1}H NMR is consistent with previously published data.\textsuperscript{17}

2-(1-phenylvinyl)pyridine (2v)

Starting from 2-benzoylpyridine (0.92 g) and following the general procedure D, 2v was isolated by flash chromatography on silica (eluent:pentane/EtOAc, 95:5) as a yellow oil (0.90 g, 99% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): δ 8.56 (ddd, \(J = 4.8, 1.8, 0.9\) Hz, 1H), 7.54 (td, \(J = 7.8, 1.9\) Hz, 1H), 7.31–7.21 (m, 5H), 7.81 (td, \(J = 7.9, 1.1\) Hz, 1H), 7.12 (ddd, \(J = 7.5, 4.8, 1.1\) Hz, 1H), 5.91 (d, \(J = 1.5\) Hz, 1H), 5.52 (d, \(J = 1.5\) Hz, 1H).

\textsuperscript{1}H NMR is consistent with previously published data.\textsuperscript{17}

2-(1-phenylvinyl)thiophene (2w)

Starting from 2-benzoylthiophene (0.70 g) and following the general procedure D on 3.7 mmol scale, 2w was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 98:2) as a colorless oil (0.44 g, 63% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): δ 7.50–7.33 (m, 5H), 7.25 (dd, \(J = 5.1, 1.1\) Hz, 1H), 6.99 (dd, \(J = 5.1, 3.7\) Hz, 1H), 6.92 (dd, \(J = 3.6, 1.1\) Hz, 1H), 5.60 (s, 1H), 5.26 (s, 1H).

\textsuperscript{1}H NMR is consistent with previously published data.\textsuperscript{17}
3.4 Synthesis of Photocatalysts 3DPAFIPN and 3DPA2FBN

The organic photocatalysts 3DPAFIPN and 3DPA2FBN used in this work were synthesized following a literature procedure\textsuperscript{18} on 1.0 mmol scale.

\textbf{2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN)}

\begin{center}
\includegraphics[width=0.2\textwidth]{3DPAFIPN.png}
\end{center}

$^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 7.28–7.23 (m, 14H), 7.08–7.05 (m, 6H), 7.00–6.96 (m, 12H).$^{19}$F NMR (377 MHz, CDCl$_3$, ppm): $\delta$ –121.31 (s, 1F).

Spectroscopic data are consistent with previously published data\textsuperscript{18}

\textbf{2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN)}

\begin{center}
\includegraphics[width=0.2\textwidth]{3DPA2FBN.png}
\end{center}

$^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 7.27–7.22 (m, 13H), 7.04–6.95 (m, 17H).$^{19}$F NMR (377 MHz, CDCl$_3$, ppm): $\delta$ –120.22 (s, 1F).

Spectroscopic data are consistent with previously published data\textsuperscript{18}
4. General Procedure E. Carbamoylation Reaction of Olefins

Scheme S3. Photoredox-mediated carbamoylation of olefins.

To a 4 mL screw cap vial equipped with a stir bar was added dihydropyridines 1 (0.30 mmol, 1.0 equiv), the desired olefin 2 (0.39 mmol, 1.3 equiv), and DCM as solvent (3.0 mL, 0.10 M). The vial was then sealed with a plastic screw cap and placed in an EvoluChemTMPhotoRedOx reactor fitted with a 455 nm high-power single LED ($\lambda_{\text{max}}= 455 \text{ nm}$) with an irradiance of 55 mW/cm$^2$ (the set-up is detailed in Figure S1). After 20 hours of irradiation, the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel to afford the title compound.

General procedure F. Carbamoylation reaction of olefins

To a 4 mL screw cap vial equipped with a stir bar was added dihydropyridines 1 (0.30 mmol, 1.0 equiv), the desired olefin 2 (0.39 mmol, 1.3 equiv), and DCM as solvent (3.0 mL, 0.10 M). The vial was then sealed with a plastic screw cap and placed in an EvoluChemTMPhotoRedOx reactor fitted with a 405 nm high-power single LED ($\lambda_{\text{max}}= 405 \text{ nm}$) with an irradiance of 28 mW/cm$^2$ (the set-up is detailed in Figure S1). After 20 hours of irradiation, the mixture was concentrated under reduced pressure. The yield of product was determined by $^1$H NMR analysis using 1,3,5-trimethoxybenzene as the external standard.

Figure S1. EvoluChemTMPhotoRedOx reactor fitted with a 455 nm high-power single LED
4.1 Characterization of Products

2-(2-morpholio-2-oxo-1-phenylethyl)malononitrile (3aa)

Starting from benzylidenemalonitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3aa was isolated by flash chromatography on silica (gradient: pentane/ EtOAc, from 7:3 to 4:6) as a white solid (59.2 mg, 73% yield). 1H NMR (300 MHz, CDCl3, ppm): δ 7.48–7.43 (m, 3H), 7.37–7.33 (m, 2H), 4.50 (d, J = 8.6 Hz, 1H), 4.30 (d, J = 8.6 Hz, 1H), 3.84–3.67 (m, 2H), 3.58–3.46 (m, 3H), 3.33 (ddd, J = 13.3, 7.5, 3.1 Hz, 1H) 3.15 (ddd, J = 13.4, 5.7, 3.0 Hz, 1H), 3.01 (ddd, J = 11.6, 7.5, 3.0 Hz, 1H).13C NMR (75 MHz, CDCl3, ppm): δ 165.8, 130.2, 130.0, 128.2, 112.4, 111.7, 66.5, 65.8, 50.7, 46.0, 42.9, 27.8. HRMS (ESI): m/z = calcd. for C15H16N2O2+ [M-H]−: 270.1243, found: 270.1236.

2-(1-(4-chlorophenyl)-2-morpholio-2-oxoethyl)malononitrile (3ba)

Starting from 2-((4-chlorobenzylidene)malononitrile 2b (118 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ba was isolated by flash chromatography on silica (gradient: pentane/ EtOAc, from 7:3 to 4:6) as a white solid (75.0 mg, 83% yield). 1H NMR (300 MHz, CDCl3, ppm): δ 7.46–7.43 (m, 2H), 7.32–7.29 (m, 2H), 4.48 (d, J = 8.4 Hz, 1H), 4.28 (d, J = 8.4 Hz, 1H), 3.82–3.66 (m, 2H), 3.63–3.44 (m, 3H), 3.40–3.30 (m, 1H), 3.12 (td, J = 10.6, 10.1, 3.1 Hz, 1H).13C NMR (75 MHz, CDCl3, ppm): δ 165.4, 136.3, 130.4, 130.3, 129.6, 112.1, 111.4, 66.5, 65.9, 49.9, 46.1, 43.0, 27.8. HRMS (ESI): m/z = calcd. for C15H15ClN2O2+ [M-H]−: 304.0853, found: 304.0850.

2-(1-(4-cyanophenyl)-2-morpholio-2-oxoethyl)malononitrile (3ca)

Starting from 2-((4-cyanobenzylidene)malononitrile 2c (115 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ca was isolated by flash chromatography on silica (gradient: pentane/ EtOAc, from 7:3 to 4:6) as a white solid (89.0 mg, 90% yield). 1H NMR (300 MHz, CDCl3, ppm): δ 7.80–7.77 (m, 2H), 7.54–7.51 (m, 2H), 4.53 (d, J = 8.2 Hz, 1H), 4.38 (d, J = 8.3 Hz, 1H), 3.74–3.54 (m, 5H), 3.39–3.32 (m, 1H), 3.18–3.05 (m, 2H).13C NMR (75 MHz, CDCl3, ppm): δ 164.7, 136.8, 133.7, 129.2, 117.5, 114.4, 111.7, 111.1, 66.5, 65.9, 50.2, 46.1, 43.1, 27.6. HRMS (ESI): m/z = calcd. for C16H15N2O2+ [M-H]−: 295.1190, found: 295.1170.

2-(1-(4-methoxyphenyl)-2-morpholio-2-oxoethyl)malononitrile (3da)

Starting from 2-((4-methoxybenzylidene)malononitrile 2d (117 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3da was isolated by flash chromatography on silica (gradient: pentane/ EtOAc, from 7:3 to 4:6) as a colorless gum (30.6 mg, 33% yield). 1H NMR (300 MHz, CDCl3, ppm): δ 7.27–7.24 (m, 2H), 9.96–9.93 (m, 2H), 4.46 (d, J = 8.3 Hz, 1H), 4.26 (d, J = 8.3 Hz, 1H), 3.82 (s, 3H), 3.80–3.67 (m, 2H), 3.56–3.47 (m, 3H), 3.32–3.28 (m, 1H), 3.18–3.12 (m, 1H), 3.09–3.01 (m, 1H).13C NMR (75 MHz, CDCl3, ppm): δ 166.0, 160.6, 129.5, 123.7, 115.3, 112.5, 111.8, 66.5, 65.9, 55.4, 50.1, 46.1, 42.9, 28.0. HRMS (ESI): m/z = calcd. for C16H15N2O2+ [M-H]−: 300.1343, found: 300.1325.

2-(1-(3-methoxyphenyl)-2-morpholio-2-oxoethyl)malononitrile (3ea)

Starting from 2-((3-methoxybenzylidene)malononitrile 2e (117 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ea was isolated by flash chromatography on silica (gradient: pentane/ EtOAc, from 7:3 to 4:6) as a white solid (59.2 mg, 80% yield). 1H NMR (300 MHz, CDCl3, ppm): δ 7.39–7.34 (m, 1H), 6.97–6.85 (m, 3H), 4.50 (d, J = 8.3 Hz, 1H), 4.27 (J = 8.3 Hz, 1H), 3.81 (s, 3H), 3.73–3.68 (m, 2H), 3.56–3.52 (m, 3H), 3.34–3.30 (m, 1H), 3.22–3.14 (m, 1H), 3.11–3.03 (m, 1H).13C NMR (75 MHz, CDCl3, ppm): δ 165.6, 160.5, 113.3, 131.1, 120.4, 115.1, 113.9, 112.4, 111.6, 66.5, 65.9, 55.5, 50.7, 46.1, 43.0, 27.8. HRMS (ESI): m/z = calcd. for C16H15N2O2+ [M-H]−: 300.1343, found: 300.1357.
2-(2-morpholino-2-oxo-1-(perfluorophenyl)ethyl)malononitrile (3fa)

Starting from 2-(pentfluorobenzyliden)e)malononitrile 2f (141 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3fa was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as an orange solid (80.7 mg, 75% yield). \(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): δ 4.80 (d, J = 8.3 Hz, 1H), 4.71 (d, J = 8.3 Hz, 1H), 3.86–3.78 (m, 1H), 3.71–3.51 (m, 4H), 3.45–3.29 (m, 2H), 3.09–3.04 (m, 1H). \(^1^C\) NMR (75 MHz, CDCl\(_3\), ppm): δ 162.6, 111.3, 110.7, 66.5, 65.9, 45.9, 43.5, 40.5, 24.9. \(^1^F\) NMR (565 MHz, CDCl\(_3\), ppm) δ -137.62 – -139.80 (m), -147.70 (t, J = 21.5 Hz), -156.53 – -158.24 (m). HRMS (ESI): m/z = calcld. for C\(_{13}\)H\(_{11}\)F\(_3\)N\(_2\)O\(_4^+\) [M-H]\(^+\): 360.0756, found: 360.0754.

2-(2-morpholino-2-oxo-1-(pyridin-3-yl)ethyl)malononitrile (3ga)

Starting from 2-(pyridin-3-ylmethylene)malononitrile 2g (105 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ga was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a pink solid (70.5 mg, 86% yield). \(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): δ 8.73 (dd, J = 4.8, 1.6 Hz, 1H), 8.68–8.61 (m, 1H), 7.79–7.68 (m, 1H), 7.49–7.38 (m, 1H), 4.54 (d, J = 8.3 Hz, 1H), 4.38 (d, J = 8.3 Hz, 1H), 3.81–3.49 (m, 5H), 3.37–3.34 (m, 1H), 3.14 (m, 1H). \(^1^C\) NMR (75 MHz, CDCl\(_3\), ppm): δ 164.9, 151.5, 149.7, 135.5, 128.1, 124.5, 66.5, 65.9, 47.9, 46.1, 43.1, 27.7. HRMS (ESI): m/z = calcld. for C\(_{14}\)H\(_{13}\)N\(_2\)O\(_4^+\) [M-H]\(^+\): 271.1190, found: 271.1252.

2-(1-(5-methylfuran-2-yl)-2-morpholino-2-oxoethyl)malononitrile (3ha)

Starting from 2-[(5-methylfuran-2-yl)methylene]malononitrile 2h (61.7 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ha was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 5:5) as a brown gum (49.3 mg, 60% yield). \(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): δ 6.35 (d, J = 3.2 Hz, 1H), 6.04–5.96 (m, 1H), 4.57 (d, J = 8.2 Hz, 1H), 4.48 (d, J = 8.2 Hz, 1H), 3.86–3.68 (m, 2H), 3.65–3.51 (m, 3H), 3.43–3.25 (m, 3H), 2.29 (s, 3H). \(^1^C\) NMR (75 MHz, CDCl\(_3\), ppm): δ 163.6, 154.4, 142.8, 112.1, 111.8, 111.5, 107.4, 66.6, 66.1, 46.1, 44.8, 43.1, 26.1, 13.6. HRMS (ESI): m/z = calcld. for C\(_{14}\)H\(_{13}\)N\(_2\)O\(_4^+\) [M-H]\(^+\): 274.1186, found: 274.1207.

2-(2-morpholino-2-oxo-1-(thiophen-2-yl)ethyl)malononitrile (3ia)

Starting from 2-(thiophen-2-ylmethylene)malononitrile 2i (62.5 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ia was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 5:5) as a yellow solid (54.0 mg, 65% yield). \(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): δ 7.40 (dd, J = 5.2, 1.2 Hz, 1H), 7.16 (dd, J = 3.2, 1.2 Hz, 1H), 7.07 (dd, J = 5.2, 3.2 Hz, 1H), 4.67 (d, J = 8.4 Hz, 1H), 4.56 (d, J = 8.4 Hz, 1H), 3.85–3.68 (m, 2H), 3.62–3.52 (m, 3H), 3.47–3.37 (m, 1H), 3.33–3.27 (m, 1H), 3.22–3.14 (m, 1H). \(^1^C\) NMR (75 MHz, CDCl\(_3\), ppm): δ 165.1, 133.1, 128.9, 128.0, 127.9, 112.1, 111.5, 66.4, 65.9, 46.3, 45.6, 43.2, 28.5. HRMS (ESI): m/z = calcld. for C\(_{14}\)H\(_{13}\)N\(_2\)O\(_4^+\) [M-H]\(^+\): 276.0801, found: 276.0547.

2-(1-cyclohexyl-2-morpholino-2-oxoethyl)malononitrile (3ja)

Starting from 2-(cyclohexylmethylene)malononitrile 2j (107 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ja was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a yellowish solid (62.2 mg, 75% yield). \(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): δ 4.26 (d, J = 30.0 Hz, 1H), 3.96–3.88 (m, 1H), 3.73–3.50 (m, 7H), 3.23 (dd, J = 9.0, 6.2 Hz, 1H), 1.99–1.89 (m, 1H), 1.81–1.62 (m, 4H), 1.31–1.07 (m, 6H). \(^1^C\) NMR (75 MHz, CDCl\(_3\), ppm): δ 167.2, 112.1, 67.0, 66.0, 47.2, 46.7, 42.9, 39.4, 30.9, 28.8, 26.1, 25.9, 25.7, 24.1. HRMS (ESI): m/z = calcld. for C\(_{13}\)H\(_{22}\)N\(_2\)O\(_3^+\) [M-H]\(^+\): 276.1707, found: 276.1608.
2-[(4R)-4,8-dimethyl-1-morpholino-1oxonon-7-en-2-yl]malononitrile (3ka)

Starting from 2-(3.7-dimethyloct-6-en-1-ylidene)malononitrile 2k (78.9 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ka was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a yellowish oil (30.0 mg, 32% yield).\(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 5.04 (dt, \(J = 6.9, 1.5\) Hz, 1H), 4.08 (dd, \(J = 9.0, 4.2\) Hz, 1H), 3.87 – 3.83 (m, 1H), 3.76 – 3.49 (m, 6H), 3.40 (t, \(J = 6.4, 2.8\) Hz, 1H), 2.00 – 1.80 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.40 – 1.13 (m, 6H), 0.95 (d, \(J = 6.5\) Hz, 3H).\(^13^C\) NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 168.4, 132.3, 123.7, 112.0, 66.8, 66.5, 46.8, 43.0, 40.5, 38.7, 37.1, 29.8, 26.1, 25.1, 19.7, 19.5, 17.7. HRMS (ESI): \(m/z\) = calcd. for C\(_{19}\)H\(_{26}\)N\(_2\)O\(_2\) [M+H\(^+\)]: 318.2176, found: 318.2165.

2-(2-morpholino-2-oxo-1-phenylethy)-1H-indene-1,3(2H)-dione (3la)

Starting from 2-benzylidene-1H-indene-1,3(2H)-dione 2l (136 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3la was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 5:5) as an orange solid (89.5 mg, 80% yield).\(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 7.97 – 7.92 (m, 2H), 7.84 – 7.71 (m, 2H), 7.45 – 7.28 (m, 5H), 4.85 (d, \(J = 3.4\) Hz, 1H), 3.65 – 3.54 (m, 2H), 3.54 – 3.30 (m, 3H), 3.28 – 3.18 (m, 1H), 3.15 (d, \(J = 3.4\) Hz, 1H), 3.13 – 3.04 (m, 2H).\(^13^C\) NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 199.7, 197.7, 169.2, 143.3, 140.7, 136.1, 135.5, 134.6, 129.0, 128.9, 127.8, 123.1, 122.9, 66.6, 66.0, 55.7, 51.2, 46.5, 42.6. HRMS (ESI): \(m/z\) = calcd. for C\(_{19}\)H\(_{25}\)N\(_2\)O\(_2\) [M+H\(^+\)]: 350.1387, found: 350.1441.

1,3-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)pyridazine-2,4,6-(1H,3H,5H)-trione (3ma)

Starting from 5-benzylidene-1,3-dimethylpyridazine-2,4,6-(1H,3H,5H)-trione 2m (140 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ma was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 2:8) as a yellow solid (56.1 mg, 52% yield).\(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 7.41 – 7.39 (m, 3H), 7.30 – 7.28 (m, 2H), 4.66 (bs, 1H), 3.66 – 3.61 (m, 2H), 3.58 – 3.35 (m, 5H), 3.31 (s, 3H), 3.26 (s, 3H), 3.07 – 3.03 (m, 2H).\(^13^C\) NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 169.3, 169.1, 168.5, 150.9, 131.9, 130.3, 129.2, 128.9, 74.1, 66.6, 66.1, 59.1, 46.6, 42.5, 29.3, 28.9. HRMS (ESI): \(m/z\) = calcd. for C\(_{18}\)H\(_{22}\)N\(_2\)O\(_2\) [M+OH\(^-\)]: 376.1503, found: 376.1503.

2,2-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)-1,3-dioxane-4,6-dione (3na)

Starting from 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione 2n (135 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3na was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 2:8) as a yellow solid (48.7 mg, 47% yield).\(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 7.31–7.29 (m, 5H), 4.88 (d, \(J = 4.2\) Hz, 1H), 3.75 (d, \(J = 4.2\) Hz, 1H), 3.65–3.52 (m, 5H), 3.45–3.38 (m, 1H), 3.21–3.03 (m, 2H), 1.74 (s, 3H), 1.70 (s, 3H). 1H \(^13^C\) NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 168.4, 165.5, 164.1, 135.7, 129.4, 128.7, 127.9, 104.9, 66.7, 66.0, 50.0, 49.6, 46.5, 42.8, 28.2, 27.4. HRMS (ESI): \(m/z\) = calcd. for C\(_{18}\)H\(_{23}\)N\(_2\)O\(_2\) [M+H\(^+\)]: 365.1475, found: 365.1334.

1-morpholino-3,3-bis(phenylsulfonyl)propan-1-one (3oa)

Starting from 1,1-bis(phenylsulfonyl)ethylene (121 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure A, 3oa was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 5:5 to 2:8) as a yellow solid (73.0 mg, 57% yield).\(^1^H\) NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 5.92 – 7.77 (m, 4H), 7.69 – 7.60 (m, 2H), 7.52 – 7.47 (m, 4H), 5.68 (t, \(J = 5.7\) Hz, 1H), 3.75 – 3.48 (m, 8H), 3.25 (d, \(J = 5.7\) Hz, 2H).\(^13^C\) NMR (75 MHz, 300 MHz, CDCl\(_3\), ppm) \(\delta\) 165.7, 138.3, 134.7, 129.4, 129.3, 66.7, 66.5, 46.1, 43.0, 28.5. HRMS (ESI): \(m/z\) = calcd. for C\(_{19}\)H\(_{24}\)N\(_2\)O\(_2\)S\(_2\) [M+H\(^+\)]: 424.0883, found: 424.0878.

S15
4-morpholino-4-oxo-3-phenyl-2-(phenylsulphonyl)butenenitrile (3pa)

Starting from (E)-3-phenyl-2-(phenylsulphonyl)acrylonitrile 2p (105 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3pa was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a white solid (55.4 mg, 48% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 8.05–8.02 (m, 2H), 7.76–7.73 (m, 1H), 7.66–7.61 (m, 2H), 7.39–7.35 (m, 5H), 5.43 (d, J = 8.0 Hz, 1H), 4.68 (d, J = 8.0 Hz, 1H), 3.74–3.49 (m, 6H), 3.39–3.32 (m, 1H), 3.23–3.11 (m, 1H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 166.8, 136.7, 135.3, 133.1, 129.7, 129.6, 129.4, 129.3, 128.6, 112.7, 66.5, 66.0, 60.3, 46.3, 45.6, 43.3. HRMS (ESI): m/z = calcd. for C$_{20}$H$_{15}$N$_2$O$_4$ [M–H]: 385.1217, found: 385.1179.

3-(5-chloropyridin-2-yl)-4-morpholino-4-oxo-2-(phenylsulphonyl)butenenitrile (3qa)

Starting from (E)-3-(5-chloropyridin-3-yl)-2-(phenylsulphonyl)acrylonitrile 2q (119 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3qa was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a brown solid (80.2 mg, 64% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 8.54–8.53 (m, 1H, major), 8.51–8.50 (m, 1H, minor), 8.04–8.01 (m, 2H, major), 7.96–7.93 8m, 2H, minor), 7.66–7.60 (m, 4H major + 4H minor), 7.41 (dd, J = 8.4, 0.7 Hz, 1H minor), 7.36 (dd, J = 8.4, 0.7 Hz, 1H major), 5.46 (d, J = 8.4, 1H major), 4.98 (d, J = 8.4 Hz, 1H minor), 4.97 (d, J = 8.3 Hz, 1H minor), 4.91 (d, J = 8.3 Hz, 1H minor), 3.72–3.26 (m, 8H major + 8H minor).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 165.8 (major), 165.3 (minor), 151.6 (major), 150.8 (minor), 149.2 (major), 148.9 (minor), 137.4 (major), 137.3 (minor), 136.4 (major), 136.0 (minor), 135.5 (major), 135.4 (minor), 132.6 (major), 132.3 (minor), 129.7 (major), 129.6 (minor), 129.5 (minor), 129.4 (major), 123.9 (major), 123.8 (minor), 113.3 (major), 112.7 (major), 66.5 (minor), 66.4 (major), 66.3 (minor), 66.2 (major), 59.6 (minor), 59.0 (major), 48.0 (minor), 47.2 (major), 46.5 (minor), 46.4 (major), 43.5 (major), 43.0 (minor). HRMS (ESI): m/z = calcd. for C$_{19}$H$_{19}$ClN$_2$O$_5$S– [M–H]: 420.0779, found: 420.0717.

3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-4-morpholino-4-oxo-2-(phenylsulphonyl)butenenitrile (3ra)

Starting from (E)-3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-(phenylsulphonyl)acrylonitrile 2r (136 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ra was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 6:4 to 2:8) as a yellow solid (77.3 mg, 87% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 8.07–7.98 (m, 2H), 7.88 (s, 1H), 7.79–7.73 (m, 1H), 7.69–7.57 (m, 4H), 7.41 (dd, J = 8.7, 7.1 Hz, 2H), 7.26–7.24 (m, 1H), 5.27 (d, J = 7.7 Hz, 1H), 4.71 (d, J = 7.6 Hz, 1H), 3.80–3.52 (m, 7H), 3.49–3.30 (m, 1H), 2.42 (s, 3H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 167.5, 148.7, 139.5, 136.4, 135.5, 129.8, 129.5, 129.4, 126.7, 118.8, 113.6, 66.5, 66.2, 46.4, 43.3, 35.9, 23.9, 14.2. HRMS (ESI): m/z = calcd. for C$_{26}$H$_{20}$N$_2$O$_4$S– [M–H]: 465.1591, found: 465.1591.

1-morpholino-3,3-diphenylpropan-1-one (3sa)

Starting from 1,1-diphenylethylene 2s (70.3 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3sa was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 70:30) as a pale-yellow solid (77.3 mg, 87% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.73–7.16 (m, 10H), 4.67 (t, J = 7.6 Hz, 1H), 3.54 (m, 4H), 3.31 (m, 4H), 3.05 (d, J = 7.6 Hz, 2H).

$^1$H NMR is consistent with previously published data$^{19}$

S16
3-(4-chlorophenyl)-1-morpholino-3-phenylpropan-1-one (3ta)

Starting from 1-chloro-4-(1-phenylvinyl)benzene 2t (83.7 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ta was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 70:30) as a pale-yellow solid (82.5 mg, 83% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.35–7.16 (m, 9H), 4.67 (t, $J$ = 7.5 Hz, 1H), 3.67–3.30 (m, 8H), 3.03 (d, $J$ = 7.5 Hz, 2H), 2.29 (s, 6H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 169.6, 141.2, 136.0, 129.2, 127.7, 127.0, 126.7, 124.4, 123.9, 66.8, 66.6, 49.3, 46.9, 46.2, 42.0, 38.7. HRMS (ESI): $m/z$ = calcd. for C$_{19}$H$_{20}$ClN$_2$O$_2$ $^+$ [M-H]$^+$: 324.1598, found: 324.1973.

1-morpholino-3,3-di-p-tolylpropan-1-one (3ua)

Starting from 4,4’-(ethene-1,1-diyl)bis(methylbenzene) 2u (83.7 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3ua was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 70:30) as a white solid (82.5 mg, 83% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.18 (m, 8H), 4.57 (t, $J$ = 7.6 Hz, 2H), 2.29 (s, 6H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 170.4, 162.2, 148.8, 143.5, 136.5, 128.6, 128.7, 127.8, 126.8, 66.8, 66.4, 46.9, 46.2, 42.1, 38.5. HRMS (ESI): $m/z$ = calcd. for C$_{19}$H$_{20}$ClN$_2$O$_2$ $^+$ [M-H]$^+$: 330.1255, found: 330.1254.

1-morpholino-3-phenyl-3-(pyridin-2-yl)propan-1-one (3va)

Starting from 2-(1-phenylvinyl)pyridine 2v (70.7 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3va was isolated by flash chromatography on silica (gradient: pentane/EtOAc, 70:30 to 100% EtOAc) as an orange solid (59.0 mg, 66% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 8.56–8.50 (m, 1H), 7.54 (td, $J$ = 7.7, 1.8 Hz, 1H), 7.36–7.14 (m, 6H), 7.09 (ddd, $J$ = 7.4, 4.9, 1.0 Hz, 1H), 4.75 (dd, $J$ = 8.5, 6.1 Hz, 1H), 3.63–3.34 (m, 9H), 2.90 (dd, $J$ = 15.3, 6.1 Hz, 1H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 170.1, 141.2, 136.0, 129.2, 127.7, 66.8, 66.4, 46.7, 46.2, 42.0, 38.7, 21.0. HRMS (ESI): $m/z$ = calcd. for C$_{19}$H$_{20}$N$_2$O$_2$ $^+$ [M-H]$^+$: 297.1598, found: 297.1633.

1-morpholino-3-phenyl-3-(thiophen-2-yl)propan-1-one (3wa)

Starting from 2-(1-phenylvinyl)thiophene 2w (72.6 mg, 0.390 mmol) and dihydropyridine 1a (109 mg, 0.300 mmol) following the general procedure E, 3wa was isolated by flash chromatography on silica (eluent: pentane/EtOAc, 80:20) as a white solid (35.2 mg, 39% yield).$^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.33–7.19 (m, 5H), 7.15 (dd, $J$ = 1.2 Hz, 1H), 6.92 (dd, $J$ = 5.1, 3.5 Hz, 1H), 6.84 (dt, $J$ = 3.5, 1.0 Hz, 2H), 4.90 (t, $J$ = 7.4 Hz, 1H), 3.65–3.24 (m, 8H), 3.06 (14.7, 7.5 Hz, 2H).$^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 169.3, 148.0, 143.6, 128.7, 127.7, 127.0, 126.7, 124.4, 123.9, 66.8, 66.4, 46.2, 43.2, 42.1, 40.2. HRMS (ESI): $m/z$ = calcd. for C$_{17}$H$_{18}$N$_2$O$_2$S $^+$ [M-H]$^+$: 302.1209, found: 302.1221.
2-[2-oxo-1-phenyl-2-(piperidin-1-yl)ethyl]malononitrile (3ab)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1b (109 mg, 0.300 mmol) following the general procedure E, 3ab was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 5:5) as a yellowish gum (55.6 mg, 70% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.44–7.36 (m, 5H), 4.52 (d, $J = 8.5$ Hz, 1H), 4.34 (d, $J = 8.4$ Hz, 1H), 3.85–3.79 (m, 1H), 3.38–3.32 (m, 1H), 3.22–3.18 (m, 2H), 1.55–1.31 (m, 5H), 0.83 (dq, $J = 12.7$, 6.1 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 165.2, 132.6, 129.7, 129.6, 128.3, 112.7, 112.0, 50.7, 46.8, 43.8, 28.0, 25.5, 24.1. HRMS (ESI): $m/z =$ calcd. for C$_{16}$H$_{18}$N$_2$O$^+$ [M–H]$^-$: 268.1444, found: 268.1456.

Ethyl 4-(3,3-dicyano-2-phenylpropanoyl)piperazine-1-carboxylate (3ac)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1c (131 mg, 0.300 mmol) following the general procedure E, 3ac was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 2:8) as a yellowish solid (78.5 mg, 77% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.47–7.44 (m, 3H), 7.37–7.38 (m, 2H), 4.50 (d, $J = 7.9$ Hz, 1H), 4.33 (dd, $J = 7.9$ Hz, 1H), 4.11 (q, $J = 6.8$ Hz, 2H), 3.93–3.87 (m, 1H), 3.66–3.62 (m, 1H), 3.44–3.41 (m, 1H), 3.25–3.22 (m, 1H), 2.59 (dd, $J = 13.2$, 7.6, 4.1 Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 165.9, 156.1, 132.0, 130.0, 128.2, 112.4, 111.6, 61.8, 50.8, 45.5, 42.5, 27.9, 14.6. HRMS (ESI): $m/z =$ calcd. for C$_{18}$H$_{21}$N$_3$O$_3$ [M–H]$^-$: 341.1608, found: 341.1615.

2-[2-oxo-1-phenyl-2-(pyrrolidin-1-yl)ethyl]malononitrile (3ad)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.39 mmol) and dihydropyridine 1d (76.0 mg, 0.300 mmol) following the general procedure E, 3ad was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 8:2 to 6:4) as a yellowish solid (54.5 mg, 72% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.54–7.29 (m, 5H), 4.55 (d, $J = 8.8$ Hz, 1H), 4.19 (d, $J = 8.8$ Hz, 1H), 3.67–3.35 (m, 3H), 3.02–2.87 (m, 1H), 2.01–1.67 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 165.4, 132.0, 129.72, 129.70, 128.5, 112.6, 111.8, 51.9, 46.7, 46.3, 27.6, 25.9, 24.0. HRMS (ESI): $m/z =$ calcd. for C$_{15}$H$_{17}$N$_2$O$^+$ [M–H]$^-$: 254.1288, found: 254.1286.

$\textit{N}$-benzyl-3,3-dicyano-$\textit{N}$-methyl-2-phenylpropanamide (3ae)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1e (121 mg, 0.300 mmol) following the general procedure E, 3ae was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 5:5) as a yellowish solid (56.5 mg, 62% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.45–7.26 (m, 9H), 7.17–7.14 (m, 1H), 4.63 (s, 2H), 4.36 (d, $J = 8.2$ Hz, 1H), 4.27 (d, $J = 8.2$ Hz, 1H), 2.75 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 167.4, 136.0, 131.8, 129.8, 128.8, 128.4, 127.9, 126.1, 112.6, 111.8, 52.8, 51.7, 51.0, 34.7, 34.6, 28.0. HRMS (ESI): $m/z =$ calcd. for C$_{15}$H$_{16}$N$_2$O$^+$ [M–H]$^-$: 304.1444, found: 304.1449.

3,3-dicyano-$\textit{N}$-cyclopropyl-2-phenylpropanamide (3af)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1f (71.8 mg, 0.300 mmol) following the general procedure E, 3af was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 7:3 to 4:6) as a white solid (76.0 mg, 75% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 7.46–7.35 (m, 5H), 5.81 (s, 1H), 4.60 (d, $J = 7.9$ Hz, 1H), 3.97 (d, $J = 7.9$ Hz, 1H), 2.70 (tq, $J = 7.1$, 3.6 Hz, 1H), 0.83–0.67 (m, 2H), 0.53–0.37 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): δ 168.7, 132.3, 130.0, 129.8, 129.7, 128.6, 112.1, 111.5, 52.7, 26.8, 23.2, 6.8, 6.6. HRMS (ESI): $m/z =$ calcd. for C$_{14}$H$_{14}$N$_3$O$^+$ [M–H]$^-$: 240.1131, found: 240.1152.
3,3-dicyano-N,2-diphenylpropanamide (3ag)

Starting from benzylidenemalononitrile 2a (60.1 mg, 0.390 mmol) and dihydropyridine 1g (112 mg, 0.300 mmol) following the general procedure E, 3ag was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 8:2 to 6:4) as a white solid (60.3 mg, 73% yield).

\[ ^1H \text{NMR} \ (300 \text{ MHz, DMSO-d}_6, \text{ppm}): \delta \]

10.42 (s, 1H), 7.57–7.54 (m, 2H), 7.48–7.42 (m, 5H), 7.34–7.29 (m, 2H), 7.11–7.08 (m, 1H), 5.48 (d, \( J = 7.8 \text{ Hz, 1H} \)), 4.57 (d, \( J = 7.8 \text{ Hz, 1H} \)).

\[ ^{13}C \text{NMR} \ (75 \text{ MHz, DMSO-d}_6, \text{ppm}): \delta \]

166.1, 138.7, 134.4, 129.5, 129.4, 128.9, 124.5, 119.9, 114.0, 113.9, 51.5, 27.0.

\[ \text{HRMS (ESI)}: \ m/z = \text{calcd. for C}_{17}\text{H}_{14}\text{N}_{3}\text{O [M-H]}^-: 276.1137, \text{found:} \ 276.0851.\]

4.2 Unsuccessful Substrates

Figure S2. Unsuccessful substrates under reaction conditions.
5 Mechanistic Investigations

5.1 Cyclic Voltammetry and Estimation of Excited State Redox Potential

Figure S4. Cyclic voltammogram of 1a [0.5 mM] in [0.1 M] TBAPF₆ in CH₃CN. Scan rate 100 mV s⁻¹.

Figure S5. Absorption and emission spectra of a solution of 1a (CH₃CN, 0.15 mM).

Evaluation of the Excited State Potential of 1a

Using the data collected from the cyclic voltammetry studies (Figure S4) and from the absorption/emission spectra (Figure S5) of 1a, the redox potential of the excited state 1a was determined as follow:

\[ E(1a^+/1a^\ast) = E(1a^+/1a) - E_{0-0}(1a^\ast/1a) \] [Eq. 1]
The irreversible peak potential $E_{pa}$ was used for $(1a^*/1a)$ (Figure S4). The zero-zero vibrational state excitation energy $E_{\text{v0}}$ was estimated by the corresponding energy of the wavelength at which emission and absorption overlap that corresponds to 404 nm (Figure S5) which translates into an $E_{\text{v0}}(1a^*/1a)$ of 3.07 eV.

$$E(1a^*/1a^*) = +1.17 \text{ V} - 3.07 \text{ V} = -1.90 \text{ V (vs SCE)}.$$  

5.2 On/Off Experiments.

Following the general procedure E the reaction between dihydropyridine 1a and benzylidenemalononitrile 2a was performed on 0.3 mmol scale. Upon addition of all reagents, the reaction was irradiated alternating intervals of 1 hour irradiation (light on) with 1 hour dark (light off), during a total of 7 hours. Aliquots (100 µL) of the reaction were collected after every hour, combined with 100 µL of a stock solution of 1,3,5-trimethoxybenzene (0.1 mmol, 0.1 M in DCM) as the external standard and analysed by $^1$H NMR to obtain the corresponding yields. As shown in the figure Sx the reaction proceeds only during the irradiation time excluding a possible long-lived radical-chain process.

![Figure S3. Light On/Off experiment.](image-url)
5.3 Radical Trapping Experiment

Following the general procedure, a reaction of dihydropyridine 1a and benzylidemalononitrile 2a on a 0.1 mmol scale in the presence of the radical trapping agent TEMPO (0.1 mmol, 1.0 equiv) was setup. The reaction mixture was sparged with nitrogen and irradiated for 16 h. $^1$H NMR analysis, after the addition of 1,3,5-trimethoxybenzene as the external standard, showed no product formation.
5.4 Fluorescence Quenching Experiments.

Fluorescence measurements were acquired at room temperature using an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer with excitation slits open at 5 nm and emission slit open at 5 nm. Emission quenching of the different samples were done using quartz cuvettes (Precision cell SUPRASIL, Art. No. 117100F-10-40, Hellma Analytics) with argon-purged solvent (DMSO or CH\textsubscript{3}CN). All the prepared solutions were degassed for 8 minutes and successively added to the cuvette using 1 mL gas tight syringe through a rubber septum fitted with an argon balloon. The balloon remained inserted in between quencher additions to prevent oxygen from entering the cuvette.

![Fluorescence quenching results](image)

**Figure S4.** a) Emission of a 3DPAFIPN solution (top blue line, DMSO, 0.09 mM) recorded in presence of increasing amounts of benzylidenemalononitrile 2a as quencher with a $\lambda_{ex} = 380$ nm. Fluorescence intensity was integrated from 450 nm to 700 nm. b) Stern-Volmer plot analysis derived from the data extracted from Figure S4 a. The $K_q$ was determined from Stern-Volmer equation [$K_{sv} = K_q \tau$] using a lifetime of $\tau = 4.2$ ns for 3DPAFIPN\textsuperscript{18}. The resulting $K_q$ for benzylidenemalononitrile 2a was of $2.26 \times 10^9$ L mol\textsuperscript{-1} s\textsuperscript{-1}. 

S23
Figure S5. a) Emission of a 3DPAFIPN solution (top orange line, DMSO, 0.09 mM) recorded in the presence of increasing amounts of dihydropyridine 1a as quencher with a λex = 410 nm. Fluorescence intensity was integrated from 550 nm to 720 nm due to the overlapping with the emission of dihydropyridine 1a. b) Stern-Volmer plot analysis derived from the data extracted from Figure S5 a. The Kq was determined from Stern-Volmer equation and using a lifetime of τ = 4.2 ns for 3DPAFIPN18. The resulting Kq for dihydropyridine 1a was of 9.22 10^{10} L mol^{-1} s^{-1}. 

$I_{0}$ : Fluorescence intensity of 3DPAFIPN
$I$ : Fluorescence intensity in presence of dihydropyridine 1a
$[1a]$ : Concentration of dihydropyridine 1a (mM)
Figure S6. a) Emission of a dihydropyridine 1a solution (top green line, CH$_3$CN, 0.15 mM) recorded in presence of increasing amounts of benzylidenemalononitrile 2a as quencher with a $\lambda_{ex} = 365$ nm. Fluorescence intensity was integrated from 380 nm to 600 nm. b) Stern-Volmer plot analysis derived from the data extracted from Figure S6 a.
5.5 UV-Vis Experiments

**Figure S7.** Absorption spectra of 1a at different concentrations in CH$_3$CN.

**Figure S8.** UV-Vis spectra of benzyldenemalononitrile 2a (orange line, 0.050 M in DCM), dihydropyridine 1a (yellow line, 0.050 M in DCM), and an equimolar mixture of 2a and 1a (grey line, 0.050 M in DCM).
6. References

1. Dubur, G. Ya.; Uldrikis, Ya. R. Synthesis and oxidation of 1,4-dihydroisonicotinic acid derivatives. Chem. Heterocycl. Compd. 1972, 5, 321–323.

2. a) Dubur, G. Ya.; Uldrikis, Ya. R. Preparation of 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydroisonicotinic acid and 3,5-diacetyl-2,6-dimethyl-1,4-dihydroisonicotinic acid and their salts. Chem. Heterocycl. Compd. 1972, 5, 762–763. b) Poikans, J.; Tirzitis, G.; Bisenieks, E.; Uldrikis, J.; Gurevich, V. S.; Mikhailova, I. A.; Duburs, G. Eur. J. Med. Chem. 1994, 29, 325.

3. Wu, D.-H.; Hu, L. 3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid Acta Cryst. 2009, E65, o1748.

4. Alandini, N.; Buzzetti, L.; Favi, G.; Schulte, T.; Candish, L.; Collins, K. D.; Melchiorre, P. Amide Synthesis by Nickel/Photoredox-Catalyzed Direct Carbamyolation of (Hetero)Aryl Bromides Angew. Chem. Int. Ed. 2020, 59, 2–8.

5. Yu, Y.-Q.; Wang, Z.-L. A Simple, Efficient and Green Procedure for Knoevenagel Condensation in Water or under Solvent-free Conditions J. Chin. Chem. Soc. 2013, 60, 288–292.

6. Mona, H.-S.; Hashem, S.; Samane, E. Solvent-free Knoevenagel Condensations over TiO2. Chin. J. Chem. 2007, 25, 1563–1567.

7. Berryman, O.B.; Sather, A.C.; Lledó, A.; Rebek Jr., J. Switchable Catalysis with a Light-Responsive Cavitand. Angew. Chem. Int. Ed. 2011, 50, 9400 –9403.

8. Jimenez, D.-O.; Ferreira, I.-M.; Birolli, W.-G.; Fonseca, L.-P.; Porto, A.-M. Synthesis and Biocatalytic Enediyne Reduction of Knoevenagel Condensation Compounds by the Marine-Derived Fungus Penicillium Citrinum CBMAI 1186. Tetrahedron. 2016, 72, 7317–7322.

9. Altundas, A.; Ayvaz, S.; Logoglu, E. Synthesis and Evaluation of a Series of Aminocyanopyridines as Antimicrobial Agents. Med Chem Res. 2011, 20, 1–8.

10. L.F. Tietze, U. Beifuss, M. Ruther J. Org. Chem. 1989, 54, 3120.

11. Volchoa, K.P.; Kurbakova, S.Yu.; Korchagina, D.V.; Suslova, E.V.; Salakhutdinova, N.F.; Toktarevb, A.V.; Echevskiib, G.V.; Barkhash, V.A. Competing Michael and Knoevenagel Reactions of Terpenoids with Malononitrile on Basic Cs-beta Zeolite. J. M. Catal. A: Chem. 2003, 195, 263–274.

12. He, G.; Wu, C.; Zhou, J.; Yang, Q.; Zhang, C.; Zhou, Y.; Zhang, H.; Liub, H. A Method for Synthesis of 3-hydroxy-1-indanones via Cu-Catalyzed Intramolecular Annulation Reactions. J. Org. Chem. 2018, 83, 13356–13362.

13. Rezende, M.-C.; Almodovar, I. Substituent Electrophilicities in the NMR Spectra of Barbituric Derivatives. Magn. Reson. Chem. 2012, 50, 266–270.

14. Ferreira, J.M.G.O.; de Resende Filho, j.B.M.; Batista, P.K.; Teotonio, E.E.S.; Vale, J.A. Rapid and Efficient Uncatalyzed Knoevenagel Condensations from Binary Mixture of Ethanol and Water. J. Braz. Chem. Soc. 2018, 29 (7), 1382-1387.

15 Pandit, K.S.; Kupwade, R.V.; Chavan, P.V.; Desai, U.V.; Wadgaonkar, P.P; Kodam, K.M. Problem Solving and Environmentally Benign Approach toward Diversity Oriented Synthesis of Novel 2-Amino-3-phenyl (or Alkyl)Sulfonyl 4H-chromenes at Ambient Temperature. ACS Sustainable Chem. Eng.2016, 4, 3450–3464.

16. Yang, H.; Wang, E.; Yang, P.; Lv, H.; Zhang, X. Pyridine-Directed Asymmetric Hydrogenation of 1,1-Diaryalkenones. Org. Lett. 2017, 19, 5062.

17. Zhang, H.-R.; Xiao, C.; Zhang, S.-L.; Zhang, X. Radical C–H Bond Trifluoromethylation of Alkenes by High-Valent Copper(III) Trifluoromethyl Compounds. Adv. Synth. Catal. 2019, 361, 5305.

18. Speckmeier, E.; Fischer, T.G.; Zeitler, K. A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor–Acceptor Cyanohaerenes J. Am. Chem. Soc. 2018, 140, 15353–15365.

19. Koltunov, K.-Y.; Walspurger, S.; Sommer, J. Supercacidic Activation of α,β-Unsaturated Amides and their Electrophilic Reactions. Eur. J. Org. Chem. 2004, 4039-4047.

S27
7. NMR Spectra

$^1\text{H NMR}$ of 3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid (SI-II)

$^1\text{H NMR}$ of diethyl 2,6-dimethyl-4-(morpholine-4-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1a)
$^1$H NMR of diethyl 2,6-dimethyl-4-(piperidine-1-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1b)
$^1$H NMR of diethyl 4-(4-(ethoxycarbonyl)piperazine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c)

$^{13}$C NMR of diethyl 4-(4-(ethoxycarbonyl)piperazine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c)
$^1$H NMR of diethyl 2,6-dimethyl-4-(pyrrolidine-1-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (1d)

$^1$H NMR of diethyl 4-(benzyl(methyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1e)
$^1$H NMR of diethyl 4-(cyclopropylcarbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f)

$^1$H NMR of diethyl 2,6-dimethyl-4-(phenylcarbamoyl)-1,4-dihydropyridine-3,5-dicarboxylate (1g)
$^1$H NMR of 2-(4-chlorobenzylidene)malononitrile (2b)

$^1$H NMR of 2-(4-cyanobenzylidene)malononitrile (2c)
$^1$H NMR of 2-(4-methoxybenzylidene)malononitrile (2d)

$^1$H NMR of 2-(3-methoxybenzylidene)malononitrile (2e)
$^1$H NMR of 2-(pentafluorobenzylidene)malononitrile (2f)

$^{19}$F NMR of 2-(pentafluorobenzylidene)malononitrile (2f)
$^1$H NMR of 2-(pyridin-3-ylmethylene)malononitrile (2g)

$^1$H NMR of 2-[(5-methylfuran-2-yl)methylene]malononitrile (2h)
$^1\text{H NMR}$ of 2-(thiophen-2-ylmethylene) malononitrile ($2i$)

$^1\text{H NMR}$ of 2-(cyclohexylmethylene) malononitrile ($2j$)
$^1$HNM of 2-(3,7-dimethyloct-6-en-1-ylidene)malononitrile (2k)

$^1$HNM of 2-benzylidene-1H-indene-1,3(2H)-dione (2l)
$^1$HNM of 5-benzyldene-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (2m)

$^1$HNM of 5-benzyldene-2,2-dimethyl-1,3-dioxane-4,6-dione (2n)
$^1$H NMR of (E)-3-(5-chloropyridin-3-yl)-2-(phenylsulphonyl)acrylonitrile (2p)
$\text{H NMR of (E)-3-(5-chloropyridin-3-yl)-2-(phenylsulphonyl)acrylonitrile (2q)}$

$\text{C NMR of (E)-3-(5-chloropyridin-3-yl)-2-(phenylsulphonyl)acrylonitrile (2q)}$
$^1$H NMR of (E)-3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-(phenylsulfonyl)acrylonitrile (2r)

$^{13}$C NMR of (E)-3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-(phenylsulfonyl)acrylonitrile (2r)
$^1$H NMR of 1-chloro-4-(1-phenylvinyl)benzene (2t)

$^1$H NMR of 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (2u)
$^1$H NMR of 2-(1-phenylvinyl)pyridine (2v)

$^1$H NMR of 2-(1-phenylvinyl)thiophene (2w)
$^1$H NMR of 3DPAFIPN

$^{19}$F NMR of 3DPAFIPN
$^1$H NMR of 3DPA2FBN

$^{19}$F NMR of 3DPA2FBN
$^{1}H$ NMR of 2-(2-morpholino-2-oxo-1-phenylethyl)malononitrile (3aa)

$^{13}C$ NMR of 2-(2-morpholino-2-oxo-1-phenylethyl)malononitrile (3aa)
$^1$H NMR of 2-(1-(4-chlorophenyl)-2-morpholino-2-oxoethyl)malononitrile (3ba)

$^{13}$C NMR of 2-(1-(4-chlorophenyl)-2-morpholino-2-oxoethyl)malononitrile (3ba)
$^1$H NMR of 2-((4-cyanophenyl)-2-morpholino-2-oxoethyl)malononitrile (3ca)

$^{13}$C NMR of 2-((4-cyanophenyl)-2-morpholino-2-oxoethyl)malononitrile (3ca)
$^1$H NMR of 2-(1-(4-methoxyphenyl)-2-morpholino-2-oxoethyl)malononitrile (3da)

$^{13}$C NMR of 2-(1-(4-methoxyphenyl)-2-morpholino-2-oxoethyl)malononitrile (3da)
$^1$H NMR of 2-(1-(3-methoxyphenyl)-2-morpholino-2-oxoethyl)malononitrile (3ea)

$^{13}$C NMR of 2-(1-(3-methoxyphenyl)-2-morpholino-2-oxoethyl)malononitrile (3ea)
$^{1}$H NMR of 2-(2-morpholino-2-oxo-1-(perfluorophenyl)ethyl)malononitrile (3fa)

$^{13}$C NMR of 2-(2-morpholino-2-oxo-1-(perfluorophenyl)ethyl)malononitrile (3fa)
$^{19}$F NMR of 2-(2-morpholino-2-oxo-1-(perfluorophenyl)ethyl)malononitrile (3fa)
$^1$H NMR of 2-(2-morpholino-2-oxo-1-(pyridin-3-yl)ethyl)malononitrile (3ga)

$^{13}$C NMR of 2-(2-morpholino-2-oxo-1-(pyridin-3-yl)ethyl)malononitrile (3ga)
$^{1}$H NMR of 2-(1-(5-methylfuran-2-yl)-2-morpholino-2-oxoethyl)malononitrile (3ha)

$^{13}$C NMR of 2-(1-(5-methylfuran-2-yl)-2-morpholino-2-oxoethyl)malononitrile (3ha)
\textbf{\textsuperscript{1}H NMR} of 2-(2-morpholino-2-oxo-1-(thiophen-2-yl)ethyl)malononitrile (3ia)

\textbf{\textsuperscript{13}C NMR} of 2-(2-morpholino-2-oxo-1-(thiophen-2-yl)ethyl)malononitrile (3ia)
\( ^1H \text{NMR} \) of \( \text{2-(1-cyclohexyl-2-morpholino-2-oxoethyl)malononitrile (3ja)} \)

\( ^{13}C \text{NMR} \) of \( \text{2-(1-cyclohexyl-2-morpholino-2-oxoethyl)malononitrile (3ja)} \)
$^1$H NMR of 2-[(4R)-4,8-dimethyl-1-morpholino-1oxonon-7-en-2-yl]malononitrile (3ka)

$^{13}$C NMR of 2-[(4R)-4,8-dimethyl-1-morpholino-1oxonon-7-en-2-yl]malononitrile (3ka)
$^1$H NMR of 2-(2-morpholino-2-oxo-1-phenylethyl)-1$H$-indene-1,3(2$H$)-dione (3la)

$^{13}$C NMR of 2-(2-morpholino-2-oxo-1-phenylethyl)-1$H$-indene-1,3(2$H$)-dione (3la)
$^1$H NMR of 1,3-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)pyrimidine-2,4,6-(1H,3H,5H)-trione (3ma)

$^{13}$C NMR of 1,3-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)pyrimidine-2,4,6-(1H,3H,5H)-trione (3ma)
$^1$H NMR of 2,2-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)-1,3-dioxane-4,6-dione (3na)

$^{13}$C NMR of 2,2-dimethyl-5-(2-morpholino-2-oxo-1-phenylethyl)-1,3-dioxane-4,6-dione (3na)
$^1$H NMR of 1-morpholino-3,3-bis(phenylsulfonyl)propan-1-one (3oa)

$^{13}$C NMR of 1-morpholino-3,3-bis(phenylsulfonyl)propan-1-one (3oa)
\( ^{1}H \) NMR of 4-morpholino-4-oxo-3-phenyl-2-(phenylsulphonyl)butenitrile (3pa)

\( ^{13}C \) NMR of 4-morpholino-4-oxo-3-phenyl-2-(phenylsulphonyl)butenitrile (3pa)
$^1$H NMR of 3-(5-chloropyridin-2-yl)-4-morpholino-4-oxo-2-(phenylsulphonyl)butanenitrile (3qa)

$^{13}$C NMR of 3-(5-chloropyridin-2-yl)-4-morpholino-4-oxo-2-(phenylsulphonyl)butanenitrile (3qa)
$^1$H NMR of 3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-4-morpholino-4-oxo-2-(phenylsulfonyl)butanenitrile (3ra)

$^{13}$C NMR of 3-(3-methyl-1-phenyl-1H-pyrazol-4-yl)-4-morpholino-4-oxo-2-(phenylsulfonyl)butanenitrile (3ra)
$^1$H NMR of 1-morpholino-3,3-diphenylpropan-1-one (3sa)
$^1$H NMR of 3-(4-chlorophenyl)-1-morpholino-3-phenylpropan-1-one (3ta)

$^{13}$C NMR of 3-(4-chlorophenyl)-1-morpholino-3-phenylpropan-1-one (3ta)
$^1$H NMR of 1-morpholino-3,3-di-p-tolylpropan-1-one (3ua)

$^{13}$C NMR of 1-morpholino-3,3-di-p-tolylpropan-1-one (3ua)
$^1$H NMR of 1-morpholino-3-phenyl-3-(pyridin-2-yl)propan-1-one (3va)

$^{13}$C NMR of 1-morpholino-3-phenyl-3-(pyridin-2-yl)propan-1-one (3va)
\textbf{H NMR} of 1-morpholino-3-phenyl-3-(thiophen-2-yl)propan-1-one (3wa)

\textbf{C NMR} of 1-morpholino-3-phenyl-3-(thiophen-2-yl)propan-1-one (3wa)

S70
$^1$H NMR of 2-[2-oxo-1-phenyl-2-(piperidin-1-yl)ethyl]malononitrile (3ab)

$^{13}$C NMR of 2-[2-oxo-1-phenyl-2-(piperidin-1-yl)ethyl]malononitrile (3ab)
$^1$H NMR of Ethyl 4-(3,3-dicyano-2-phenylpropanoyl)piperazine-1-carboxylate (3ac)

$^{13}$C NMR of Ethyl 4-(3,3-dicyano-2-phenylpropanoyl)piperazine-1-carboxylate (3ac)
$^1$H NMR of 2-[2-oxo-1-phenyl-2-(pyrrolidin-1-yl)ethyl]malononitrile (3ad)

$^{13}$C NMR of 2-[2-oxo-1-phenyl-2-(pyrrolidin-1-yl)ethyl]malononitrile (3ad)
$^1$H NMR of $N$-benzyl-3,3-dicyano-$N$-methyl-2-phenylpropanamide (3ae)

$^{13}$C NMR of $N$-benzyl-3,3-dicyano-$N$-methyl-2-phenylpropanamide (3ae)
$^1$H NMR of 3,3-dicyano-$N$-cyclopropyl-2-phenylpropanamide (3af)

$^{13}$C NMR of 3,3-dicyano-$N$-cyclopropyl-2-phenylpropanamide (3af)
$^1$H NMR of 3,3-dicyano-N,2-diphenylpropanamide (3ag)

$^{13}$C NMR of 3,3-dicyano-N,2-diphenylpropanamide (3ag)