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1. General methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 10 ppm, Karl-Fischer titration). NEt₃ and pyridine were distilled under nitrogen from KOH. The solvents were degassed by Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ¹H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation). ¹³C-NMR spectra were recorded with ¹H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, br = broad). High-resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. Reactions were performed in test tubes (1.0 to 10 mL) which were held using a rack for test tubes placed at the center of a crystallization flask. On this flask were attached the blue LEDs (Ruban LED avec câble à extrémités ouvertes Barthelme Y51516414 182405 24 V 502 cm bleu 1 pc(s), bought directly on www.conrad.ch/fr). The distance between the LEDs and the test tubes was approximatively 3 to 4 cm. Long irradiation for more than 2 h resulted in temperature increasing up to 34 °C. UV/Vis spectroscopy was performed on an Agilent Cary 60 UV-Vis and steady-state luminescence spectroscopy was recorded on a Varian Cary Eclipse spectrophotometer.
2. Preparation of Reagents

The synthesis of reagents 2a, 2b, 2i and 16 had already been described before by our group. The procedures are taken from the indicated publications to facilitate reproduction of the results by having all data in the same file. Unless specified, the silyl alkynes are commercially available and used directly as received. Togni reagent I (18) is commercially available and has been used as received (stabilized with 60% of diatomaceous earth).

1-Hydroxy-1,2-benziodoxol-3-(1H)-one (23)

Following a reported procedure,1 NaIO4 (7.24 g, 33.8 mmol, 1.05 equiv) and 2-iodobenzoic acid (22) (8.00 g, 32.2 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product 23 (8.3 g, 31 mmol, 98%) as a colorless solid.

\[
\begin{array}{c}
\text{22} \xrightarrow{\text{NaIO}_4, \text{aq AcOH 30\%}, \text{reflux, 4h}} \text{23}
\end{array}
\]

\(^1\)H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.02 (dd, 1 H, J = 7.7, 1.4 Hz, ArH), 7.97 (m, 1 H, ArH), 7.85 (dd, 1 H, J = 8.2, 0.7 Hz, ArH), 7.71 (td, 1 H, J = 7.6, 1.2 Hz, ArH); \(^13\)C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4; IR ν 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 834 (m), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m); the reported values correspond to the ones in literature.

\(^1\)H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR ν 2959 (m), 2944 (m), 2896 (w), 1464 (w), 1385 (w), 1250 (m), 996 (w), 842 (s), 764 (s), 675 (m), 660 (m). Characterization data of 23 corresponded to the literature values.2

1-[Phenylethynyl]-1,2-benziodoxol-3(1H)-one (Ph-EBX, 5a)

Following a reported procedure,2 trimethylsilyltriflate (1.60 mL, 8.56 mmol, 1.1 equiv) was added dropwise to a stirred solution of 2-iodosylbenzoic Trimethylsilyl triflate (7.50 mL, 41.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (10.0 g, 37.7 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (24) (8.10 mL, 41.5

1. L. Kraszkiewicz, L. Skulski, Arkivoc. 2003, 6, 120.
mmol, 1.1 equiv) (slightly exothermic). The resulting suspension was stirred for 6 h at RT, during this time a white solid was formed. A saturated solution of NaHCO$_3$ (100 mL) was then added and the mixture was stirred vigorously. The resulting suspension was filtered on a glass filter of porosity 4. The two layers of the mother liquors were separated and the organic layer was washed with sat. NaHCO$_3$ (100 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by filtration and boiled in CH$_3$CN (300 mL). The mixture was cooled down, filtered and dried under high vacuum to afford 5a (6.08 g, 17.4 mmol, 46 %) as a colorless solid.

Mp (Dec.) 155 – 160 °C. $^1$H NMR (400 MHz, Chloroform-$d$) (ca 0.03 mmol/ml) δ 8.46 (m, 1 H, ArH), 8.28 (m, 1 H, ArH), 7.80 (m, 2 H, ArH), 7.63 (m, 2 H, ArH), 7.48 (m, 3 H, ArH). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 163.9, 134.9, 132.9, 132.5, 131.6, 131.3, 130.8, 128.8, 126.2, 120.5, 116.2, 106.6, 50.2. Consistent with reported data.  

**Triisopropylsilyl trimethylsilylacetylene (26)**

Following a reported procedure,$^3$ n-butyllithium (2.5 M in hexanes, 12.0 mL, 29.9 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (25) (3.0 g, 30 mmol, 1.0 equiv) in THF (48 mL) at -78 °C. The mixture was then warmed to 0 °C and stirred for 5 min. The mixture was then cooled back to -78 °C and chlorotriisopropylsilane (6.4 mL, 30 mmol, 1.0 equiv) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (40 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 60 mL). The organic layer was washed with water and brine, then dried over MgSO$_4$, filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by Kugelrohr distillation (56-57°C/0.25 mmHg) to yield 26 (7.16 g, 28.0 mmol, 92% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR ν 2959 (m), 2944 (m), 2896 (w), 2867 (m), 1464 (w), 1385 (w), 1250 (m), 996 (w), 842 (s), 764 (s), 675 (m), 660 (m). Characterization data of 26 corresponded to the literature values.$^3$

**1-[(Triiso-propylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one (TIPS-EBX, 5b)**

Following a reported procedure,$^4$ 2-iodosylbenzoic acid (23) (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirrer. After 3

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vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 0 °C. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(triisopropylsilyl)acetylene (26) (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in DCM (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (200 mL) and the aqueous layer was extracted with CH₂Cl₂ (200 mL). The organic layers were combined, washed with a saturated solution of NaHCO₃ (2 x 200 mL), dried over MgSO₄, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (ca 120 mL) afforded 5b (30.1 g, 70.2 mmol, 86%) as colorless crystals.

M. p. (Dec.) 170-176 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.44 (m, 1 H, ArH), 8.29 (m, 1 H, ArH), 7.77 (m, 2 H, ArH), 1.16 (m, 21 H, TIPS). ¹³C NMR (100 MHz, Chloroform-d) δ 166.4, 134.6, 132.3, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1. IR ν 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 833 (m), 742 (m), 636 (m); Characterization data of 5b corresponded to the literature values.

Following a reported procedure,⁵ trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (1.32 g, 5.00 mmol, 1.0 equiv) in CH₂Cl₂ (15 mL) at RT. The resulting suspension was stirred for 1 h, followed by the drop wise addition of ((4-fluorophenylethynyl)trimethylsilane (27) (1.1 mL, 5.5 mmol, 1.1 equiv), which was dissolved in CH₂Cl₂ (1 mL). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO₃ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO₃ (20 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH₃CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford 5c (750 mg, 2.05 mmol, 41%) as a white solid.

¹H NMR (400 MHz, Chloroform-d) δ 8.48 – 8.34 (m, 1H, ArH), 8.29 – 8.16 (m, 1H, ArH), 7.85 – 7.69 (m, 2H, ArH), 7.68 – 7.53 (m, 2H, ArH), 7.17 – 7.05 (m, 2H, ArH). ¹³C NMR (101 MHz, Chloroform-d) δ 166.8, 164.0 (d, J = 253.9 Hz), 135.2 (d, J = 8.8 Hz), 135.0, 132.6, 131.7, 131.50, 126.4, 116.9 (d, J = 3.6 Hz), 116.4 (d, J = 22.4 Hz), 116.3, 105.5, 50.5. Consistent with reported data.⁶

1-[4-Bromophenylethynyl]-1,2-benziodoxol-3(1H)-one (5d)

Following a reported procedure, trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (1.32 g, 5.00 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) at RT. The resulting suspension was stirred for 3 h, followed by the dropwise addition of ((4-bromophenyl)ethynyl)trimethylsilane (27) (1.17 g, 5.50 mmol, 1.1 equiv), which was dissolved in CH$_2$Cl$_2$ (1 mL). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO$_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO$_3$ (20 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH$_3$CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford 5d (1.0 g, 2.3 mmol, 47%) as a pale yellow solid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.51 – 8.30 (m, 1 H, ArH), 8.30 – 8.13 (m, 1 H, ArH), 7.84 – 7.72 (m, 2 H, ArH), 7.58 (d, $J = 8.5$ Hz, 2 H, ArH), 7.46 (d, $J = 8.5$ Hz, 2 H, ArH). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.6, 135.1, 134.3, 132.7, 132.3, 131.9, 131.4, 126.3, 125.7, 119.6, 116.3, 105.4, 52.1. Consistent with reported data.

1-[4-Trifluoromethylphenylethynyl]-1,2-benziodoxol-3(1H)-one (5e)

Following a reported procedure, trimethylsilyl triflate (0.80 mL, 4.4 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (1.06 g, 4.00 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of trimethyl[(4-(trifluoromethyl)phenyl)ethynyl]silane (29) (1.07 g, 4.40 mmol, 1.1 equiv). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO$_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO$_3$ (20 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystallized in CH$_3$CN (ca 20 mL) to afford 5e (850 mg, 2.04 mmol, 51%) as a pale yellow solid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.46 – 8.38 (m, 1 H, ArH), 8.28 – 8.19 (m, 1 H, ArH), 7.84 – 7.74 (m, 2 H, ArH), 7.74 – 7.65 (m, 4 H, ArH). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.6, 135.0, 133.0, 132.6, 132.2 (q, $J_{C,F} = 33.0$ Hz), 131.7, 131.2, 126.3, 125.7 (q, $J_{C,F} = 3.6$ Hz), 124.4, 123.4 (q, $J_{C,F} = 272.6$ Hz), 116.1, 104.2, 53.7; Consistent with reported data.

1-((4-Pentylphenyl)ethynyl)-1,2-benziodoxol-3(1H)-one (5f)

Following a slightly modified procedure, in a sealed tube, 2-iodobenzoic acid (22) (1.00 g, 4.03 mmol, 1.0 equiv), 4-methylbenzenesulfonic acid (775 mg, 4.03 mmol, 1.0 equiv) and mCPBA (994 mg, 4.44 mmol, 1.1 equiv) were suspended in DCE:TFE 1:1 (12 mL) and stirred for 1 h at 55 °C. After 1 h, 1-ethynyl-4-pentylbenzene (30) (1.1 mL, 5.6 mmol, 1.4 equiv) was added and the reaction was stirred at 55 °C for 24 h. After 24 h, the solvent was evaporated and the residue was redissolved in CH$_2$Cl$_2$ (20 mL) and stirred vigorously with NaHCO$_3$ sat. (30 mL). After 1 h, the reaction mixture was transferred into a separating funnel and the layers were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (2x50 mL). The combined organic layers were washed with sat. NaHCO$_3$, dried over MgSO$_4$, filtered and concentrated under vacuum. The resulting solid was boiled in MeCN (20 mL), then filtered and the collected solid was further purified by column chromatography using pure ethyl acetate. Trituration in pentane afforded 5f (191 mg, 0.457 mmol, 11%) as a pale yellow solid.

M.p. (Dec.) 104-107 °C. $^1$H NMR (400 MHz, Chloroform-d) δ 8.45 – 8.40 (m, 1H, ArH), 8.28 – 8.21 (m, 1H, ArH), 7.79 – 7.74 (m, 2H, ArH), 7.56 – 7.48 (m, 2H, ArH), 7.26 – 7.23 (m, 2H, ArH), 2.71 – 2.60 (m, 2H, ArCH$_2$), 1.69 – 1.54 (m, 2H, ArCH$_2$CH$_2$), 1.40 – 1.27 (m, 4H, CH$_2$CH$_2$CH$_3$), 0.90 (t, J = 6.8 Hz, 3H, CH$_3$CH$_2$). $^{13}$C NMR (101 MHz, Chloroform-d) δ 166.6, 146.7, 135.0, 133.0, 132.6, 131.7, 131.5, 129.0, 126.3, 117.7, 116.4, 107.4, 49.4, 36.2, 31.5, 31.0, 22.6, 14.1. IR ν 3446 (m), 3359 (w), 2349 (w), 1644 (s), 1482 (m), 1121 (m), 1034 (m), 840 (s), 753 (m). HRMS (ESI) calcd for C$_{20}$H$_{20}$IO$_2$ $^+ [M+H]^+$ 419.0503; found 419.0496.

1-[3-Fluorophenylethynyl]-1,2-benziodoxol-3(1H)-one (5g)

Following a reported procedure, trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (1.32 g, 5.00 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) at RT. The resulting suspension was stirred for 1 h, followed by the drop wise addition of (3-fluorophenylethynyl)trimethylsilane (31) (1.1 mL, 5.5 mmol, 1.1 equiv). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO$_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO$_3$ (20 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH$_3$CN (20 mL).
The mixture was cooled down, filtered and the collected solid was dried under high vacuum to afford 5g (787 mg, 2.15 mmol, 43%) as a colorless solid.

M.p. (Dec.) 160-164 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.33 (dd, $J = 8.2$, 0.8 Hz, 1H, Ar$H$), 8.13 (dd, $J = 7.4$, 1.7 Hz, 1H, Ar$H$), 7.91 (dd, $J = 8.2$, 7.2, 1.7 Hz, 1H, Ar$H$), 7.81 (td, $J = 7.3$, 0.9 Hz, 1H, Ar$H$), 7.64 – 7.59 (m, 1H, Ar$H$), 7.58 – 7.53 (m, 2H, Ar$H$), 7.47 – 7.37 (m, 1H, Ar$H$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 166.3, 161.8 (d, $J = 245.6$ Hz), 135.3, 131.9, 131.3, 131.2 (d, $J = 8.7$ Hz), 129.0 (d, $J = 2.9$ Hz), 127.7, 122.4 (d, $J = 9.6$ Hz), 119.2 (d, $J = 23.4$ Hz), 118.1 (d, $J = 21.1$ Hz), 116.4, 102.5 (d, $J = 3.3$ Hz), 53.8. $^{19}$F NMR (376 MHz, (CD$_3$)$_2$SO) $\delta$ -111.7. IR $\nu$ 3477 (w), 3334 (w), 2380 (w), 1644 (s), 1457 (m), 1339 (w), 1252 (w), 1146 (m), 946 (w), 840 (w), 753 (m), 2143 (w). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_9$FIO$_2$ 366.9626; Found 366.9625.

1-[2-Bromophenylethynyl]-1,2-benziodoxol-3(1H)-one (5h)

Following a reported procedure,$^6$ trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (1.32 g, 5.00 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) at RT. The resulting suspension was stirred for 3 h, followed by the drop wise addition of ((2-bromophenyl)ethynyl)trimethylsilane (32) (1.17 g, 5.50 mmol, 1.1 equiv). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO$_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO$_3$ (20 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH$_3$CN (20 mL). The mixture was cooled down, filtered and the collected solid was dried under high vacuum to afford 5h (1.50 g, 3.51 mmol, 70%) as a colorless solid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.44 (td, $J = 7.3$, 2.1 Hz, 2 H, Ar$H$), 7.84 – 7.74 (m, 2 H, Ar$H$), 7.68 (d, $J = 1.1$ Hz, 1 H, Ar$H$), 7.61 (dd, $J = 7.6$, 1.7 Hz, 1 H, Ar$H$), 7.36 (m, 2 H, Ar$H$).$^{13}$C NMR (101 MHz, Chloroform-$d$)$^9$ $\delta$ 166.6, 135.2, 134.7, 133.0, 132.7, 131.8, 131.3, 127.6, 126.8, 126.4, 123.2, 116.5, 104.3, 55.4. Consistent with reported data.$^6$

1-((4-Formylphenyl)ethynyl)-1,2-benziodoxol-3(1H)-one (5i)

$^9$ One carbon is not resolved.
Following a reported procedure, \(^{10}\) trimethylsilyl triflate (0.89 mL, 4.9 mmol, 1.1 equiv) was added to a suspension of 2-iodobenzoic acid (23) (1.19 g, 4.49 mmol, 1.0 equiv) in \(\text{CH}_2\text{Cl}_2\) (15 mL) at RT. The resulting suspension was stirred for 1 h, followed by the drop wise addition of ((4-formylphenyl)ethynyl)trimethylsilane (33) (1.00 g, 4.94 mmol, 1.1 equiv), which was dissolved in \(\text{CH}_2\text{Cl}_2\) (1 mL). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO\(_3\) (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO\(_3\) (20 mL), dried over MgSO\(_4\), filtered and evaporated under reduced pressure. The resulting solid was boiled in CH\(_3\)CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford 5i (0.80 g, 2.1 mmol, 41%) as a yellow solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 10.08 (s, 1H, CHO), 8.35 (d, \(J = 9.1\) Hz, 1H, ArH), 8.14 (dd, \(J = 7.4, 1.7\) Hz, 1H, ArH), 8.02 (d, \(J = 8.5\) Hz, 2H, ArH), 7.96 – 7.88 (m, 3H, ArH), 7.82 (t, \(J = 7.3\) Hz, 1H, ArH). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 192.6, 166.3, 136.7, 135.3, 133.2, 131.9, 131.4, 129.8, 127.7, 126.1, 116.4, 102.9, 56.6. Consistent with reported data.\(^{7}\)

**Trimethyl((4-cyanophenyl)ethynyl)silane (35)**

Following a slight modification of the reported procedure,\(^{11}\) 4-iodobenzoitrile (34) (1.00 g, 4.37 mmol, 1.0 equiv) was dissolved in triethylamine (10 mL) (without prior drying). After three freeze-thaw-pump cycles, PdCl\(_2\)(PPh\(_3\))\(_2\) (92 mg, 0.13 mmol, 3 mol%) and copper iodide (42 mg, 0.22 mmol, 5 mol%) were added under N\(_2\). After the addition of ethynyltrimethylsilane (25) (1.2 mL, 8.7 mmol, 2 equiv) the green suspension was stirred at RT for 3 h. The reaction mixture was concentrated under vacuum, dissolved in \(\text{CH}_2\text{Cl}_2\) (30 mL), washed with a saturated ammonium chloride solution (30 mL) and water (30 mL). The organic layers were then dried over MgSO\(_4\), filtered and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/ethyl acetate 25:1) to afford 4-((trimethylsilyl)ethyl)benzonitrile (35) (847 mg, 4.25 mmol, 97%) as a white solid.

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.59 (d, \(J = 7.8\) Hz, 2H, ArH), 7.53 (d, \(J = 8.8\) Hz, 2H, ArH), 0.26 (s, 9H, SiC\(_3\)H\(_3\)). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 132.6, 132.1, 128.1, 118.6, 111.9, 103.1, 99.7, -0.12. Consistent with reported data.\(^{12}\)

**1-[4-Cyanophenylethynyl]-1,2-benziodoxol-3(1H)-one (5j)**

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Following a reported procedure,\textsuperscript{5} trimethylsilyl triflate (0.73 mL, 4.0 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (23) (963 mg, 3.65 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (12 mL) at RT. The resulting suspension was stirred for 1 h, followed by the drop wise addition of ((4-cyanophenyl)ethynyl)trimethylsilane (35) (800 mg, 4.01 mmol, 1.1 equiv), which was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (1 mL). The resulting suspension was stirred for 6 h at RT. A saturated solution of NaHCO\textsubscript{3} (20 mL) was then added and the mixture was stirred vigorously for 30 minutes, the two layers were separated and the organic layer was washed with sat. NaHCO\textsubscript{3} (20 mL), dried over MgSO\textsubscript{4}, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH\textsubscript{3}CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford 5j (865 mg, 2.32 mmol, 64%) as a pale brown solid.\textsuperscript{5}

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \(\delta\) 8.34 (d, \(J = 8.2\) Hz, 1H, Ar\textit{H}), 8.13 (dd, \(J = 7.4, 1.7\) Hz, 1H, Ar\textit{H}), 7.99 (d, \(J = 8.6\) Hz, 2H, Ar\textit{H}), 7.90 (d, \(J = 8.6\) Hz, 3H, Ar\textit{H}), 7.81 (t, \(J = 7.3\) Hz, 1H, Ar\textit{H}).\textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \(\delta\) 166.3, 135.3, 133.3, 132.8, 131.9, 131.4, 127.8, 125.3, 118.2, 116.4, 112.7, 102.0, 57.4. Consistent with reported data.\textsuperscript{5}

PhVBX (14)

Following a reported procedure,\textsuperscript{13} mCPBA (1.25 g, 5.50 mmol, 1.1 equiv) was added to a solution of 2-iodobenzoic acid (22) (1.25 g, 5.00 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (25 mL). The reaction mixture was cooled to 0 °C and trifluoromethanesulfonic acid (0.66 mL, 7.5 mmol, 1.5 equiv) was added at this temperature before being stirred at r.t for 15 min. The reaction mixture was again cooled to 0 °C over 10 min and (E)-styrylboronic acid (36) (1.0 g, 7.0 mmol, 1.4 equiv) and the mixture was stirred at r.t for 1 h. A saturated NaHCO\textsubscript{3} solution (25 mL) was added and the mixture was stirred for 1 h. The mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} (25 mL) and H\textsubscript{2}O (25 mL) and the layers were separated. The aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 50 mL) and the combined organic layers were washed with brine, dried (Mg\textsubscript{2}SO\textsubscript{4}) and filtered. The solvent was removed under reduced pressure. The crude mixture contained a lot of impurities, so purification by column chromatography over silica gel (DCM with 2 to 10% Acetone) afforded 500 mg of pure Ph-VBX 14 as off white crystalline solid (29%).

\textsuperscript{1}H NMR (400 MHz, Methanol-\textit{d}_4) \(\delta\) 8.28 (dd, \(J = 5.8, 3.4\) Hz, 1H, Ar\textit{H}), 7.96 (d, \(J = 15.4\) Hz, 1H, Ar\textit{H}), 7.74 (dd, \(J = 5.9, 3.5\) Hz, 1H, Ar\textit{H}), 7.70 (dd, \(J = 7.5, 3.5\) Hz, 4H, Ar\textit{H}), 7.66 (d, \(J = 8.7\) Hz, 1H, Ar\textit{H}), 7.49 (dd, \(J = 5.1, 2.0\) Hz, 3H, Ar\textit{H}). The NMR shifts match the literature data.\textsuperscript{12}

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (37)

Following a reported procedure, 14 1-hydroxy-1,2-benziodoxol-3-(1H)-one (23, 10.3 g, 39.1 mmol, 1.00 equiv.) was suspended in acetic anhydride (35 mL) and heated to reflux for 30 minutes. The resulting clear, slightly yellow solution was slowly let to warm up to room temperature and then cooled to 0 °C for 30 minutes. The white suspension was filtered and the filtrate was again cooled to 0 °C for 30 minutes. The suspension was once again filtered and the combined two batches of solid product were washed with hexane (2 x 20 mL) and dried in vacuo affording 37 (10.8 g, 35.3 mmol, 90%) as a white solid.

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 8.24 (dd, 1H, J = 7.6, 1.6 Hz, \text{ArH}), 8.00 (dd, 1H, J = 8.3, 1.0 Hz, \text{ArH}), 7.92 (ddd, 1H, J = 8.4, 7.2, 1.6 Hz, \text{ArH}), 7.71 (td, 1H, J = 7.3, 1.1 Hz, \text{ArH}), 2.25 (s, 3H, COCH}_3). \]
\[ \text{C NMR (CDCl}_3, 100 MHz): \delta 176.5, 168.2, 136.2, 133.3, 131.4, 129.4, 129.1, 118.4, 20.4. \]

The values of the NMR spectra are in accordance with reported literature data. 14

1-Cyano-1,2-benziodoxol-3-(1H)-one (16)

Following a reported procedure, 15 1-acetoxy-1,2-benziodoxol-3-(1H)-one (37, 11.8 g, 38.6 mmol, 1.00 eq.) was dissolved under nitrogen in dry dichloromethane (200 mL). Trimethylsilyl cyanide (TMS-CN, 10 mL, 77 mmol, 2.00 eq.) was added via syringe to the clear colorless solution over a five minute time period, followed by trimethylsilyl trifluoromethanesulfonate (TMS-OTf, 70 µL, 0.39 mmol, 0.01 equiv.). Precipitation occurred within 5 min and the reaction mixture was stirred at room temperature and under nitrogen for 30 min to ensure the completion of the reaction. The resulting thick white suspension was diluted with hexane (5 mL) before being filtered and the solid was washed with hexane (3 x 20 mL) and dried in vacuo affording 17 (10.3 g, 37.7 mmol, 98%) as a white solid.

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$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.29 (d, $J = 8.3$ Hz, 1 H, ArH), 8.13 (dd, $J = 7.4$, 1.7 Hz, 1 H, ArH), 8.06-7.97 (m, 1 H, ArH), 7.88 (t, $J = 7.3$ Hz, 1 H, ArH). $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 166.7, 136.5, 132.0, 131.9, 127.8, 117.5, 87.9. IR ν 3157 (w), 3093 (w), 2160 (w), 1629 (s), 1562 (m), 1439 (m), 1321 (s), 1298 (s), 1148 (m), 839 (m), 747 (s). The characterization data is in accordance with reported literature values.  

$\mathrm{[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6}$ (1)  

Following a reported procedure, heteroleptic iridium 1 was synthesized in two steps.  

In a 25 mL tube were placed iridium(III) chloride (170 mg, 0.540 mmol, 1.0 equiv) and 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (38) (315 mg, 1.20 mmol, 2.26 equiv) in a 2:1 v:v mixture of 2-methoxyethanol/water (12 mL) to give a dark purple solution. The mixture was degassed with Ar (Ar bubbling for 10 min) and heated at 120 °C overnight to afford an orange suspension. The reaction mixture was cooled down and filtered. The precipitate was washed with water (3 x 10 mL) and dried under vacuum to afford (39) as a yellow solid (246 mg, 0.170 mmol, 62%), which was directly used for the next step without further purification.  

In a 25 mL tube were added the chloro-bridged dimer (39) (100 mg, 0.670 mmol, 1.0 equiv) and 4,4’-di-tert-butyl-2,2’-bipyridine (40) (39.7 mg, 0.148 mmol, 2.2 equiv) in ethylene glycol (4 mL) to give a yellow suspension. The mixture was heated at 150 °C overnight. The mixture was cooled and washed with hexane (3 x 40 mL) and the ethylene glycol layer was heated to 85 °C for 5 min to remove residual hexane. An aqueous saturated ammonium hexafluorophosphate solution was added, causing the iridium-PF$_6$ salt to precipitate, which was filtered, dried and recrystallized (acetone/ether), affording 1 (117 mg, 0.104 mmol, 78%) as a yellow solid.  

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 9.01 (d, $J = 7.6$ Hz, 2H, ArH), 8.64 (dd, $J = 8.8$, 2.5 Hz, 2H, ArH), 8.45-8.38 (m, 4H, ArH), 8.31 (d, $J = 5.3$ Hz, 2H, ArH), 8.00 (s, 2H, ArH), 7.81 (t, $J = 8$ Hz, 2H, ArH), 6.87 (ddd, $J = 12.7$, 9.3, 2.3 Hz, 2H, ArH), 5.98 (dd, $J = 8.5$, 2.3 Hz, 2H, ArH). $^1$H NMR matches the literature data.  

3. Library of organic dyes: 4CzIPN derivatives

General procedure 1:
Sodium hydride (60% suspension in mineral oil, 8.0 equiv) was added slowly to a stirred solution of substituted-carbazole 7a-d (5.0 equiv) in dry THF (0.05 M) under a nitrogen atmosphere at room temperature. After 30 min, 2,4,5,6-tetrafluoroisophthalonitrile 6 (0.179 g, 0.895 mmol, 1.0 equiv) was added. After stirring at room temperature for 15 h, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The crude product was purified by recrystallization from hexane/CH₂Cl₂ then filtered. The brown liquid filtrate was concentrated and recrystallized as before. The combined solid were then purified by column chromatography on silica gel with DCM/Hexane.

2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN, 4a)

Following the general procedure 1 and starting from 9H-carbazole 7a (1.67 g, 10.0 mmol, 5.0 equiv), sodium hydride (0.60 g, 15 mmol, 7.5 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile 6 (0.40 g, 2.0 mmol) in 40 mL of THF. Recrystallization (Hexanes/CH₂Cl₂ (1:1, 90 mL)) afforded the crude product as a yellow powder. Column chromatography afforded 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4a) was obtained as a bright yellow crystalline solid (1.14 g, 1.45 mmol, 73% yield).

Rf (Hexane/DCM 1/1) = 0.29. (yellow spot on TLC). ¹H NMR (400 MHz, Chloroform-d) δ 8.2 (d, J = 7.7 Hz, 2H, ArH), 7.8 – 7.6 (m, 8H, ArH), 7.5 (ddd, J = 8.0, 6.6, 1.6 Hz, 2H, ArH), 7.3 (d, J = 7.5 Hz, 2H, ArH), 7.2 (ddd, J = 8.4, 1.5 Hz, 4H, ArH), 7.2 – 7.0 (m, 8H, ArH), 6.8 (t, J = 7.8 Hz, 4H, ArH), 6.6 (td, J = 7.6, 1.2 Hz, 2H, ArH). ¹³C NMR (101 MHz, Chloroform-d) δ 145.2, 144.6, 140.0, 138.2, 136.9, 134.7, 127.0, 125.8, 124.9, 124.7, 124.5, 123.8, 122.4, 121.9, 121.4, 121.0, 120.4, 119.6, 116.3, 111.6, 109.9, 109.5, 109.4. ¹H NMR shift in CDCl₃ are consistent with reported data.¹⁷

3,6-Difluoro-9H-carbazole (7b)

Following a reported procedure, a mixture of anhydrous Cu(OAc)\(_2\) (182 mg, 1.00 mmol, 0.2 equiv), benzoic acid (611 mg, 5.00 mmol, 1.0 equiv), 4-fluoroaniline (42) (556 mg, 5.00 mmol, 1.0 equiv), 4-fluorophenylboronic acid (41) (2.10 g, 15.0 mmol, 3.0 equiv) and K\(_2\)CO\(_3\) (61 mg, 5.0 mmol, 1.0 equiv) in ethyl acetate (15 mL) was heated at 80 °C for 4 hours. The crude mixture was concentrated under vacuum and purified by column chromatography (pentane/ethyl acetate 1:1) to afford bis(4-fluorophenyl)amine (43) (184 mg, 0.897 mmol, 18%) as a sticky black oil.

\(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.03 – 6.89 (m, 8H, ArH), 5.46 (bs, 1H, NH). \(^{13}C\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 157.9 (d, \(J = 239.9\) Hz), 139.6, 119.5 (d, \(J = 7.7\) Hz), 116.0 (d, \(J = 22.4\) Hz). NMR matches the literature data.

A mixture of bis(4-fluorophenyl)amine (43) (159 mg, 0.775 mmol, 1.0 equiv), Pd(OAc)\(_2\) (174 mg, 0.775 mmol, 1.0 equiv) in glacial acetic acid (14 mL) was heated at reflux for 30 minutes. The reaction mixture was filtered through celite, which was subsequently washed with sodium bicarbonate (3 X 40 mL) and ethyl acetate (3 X 40 mL). The filtrate was concentrated under vacuum and purified by column chromatography (pentane/ethyl acetate 5:1) to afford 3,6-difluoro-9H-carbazole (7b) (115 mg, 5.66 mmol, 73%) as a pale brown solid.

\(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.98 (s, 1H, NH), 7.66 (dd, \(J = 8.9, 2.5\) Hz, 2H, ArH), 7.35 (dd, \(J = 8.8, 4.3\) Hz, 2H, ArH), 7.18 (td, \(J = 9.0, 2.5\) Hz, 2H, ArH). \(^{13}C\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 157.3 (d, \(J = 235.9\) Hz), 136.8, 123.5 (dd, \(J = 9.5, 4.3\) Hz), 114.4 (d, \(J = 25.7\) Hz), 111.5 (d, \(J = 8.9\) Hz), 106.1 (d, \(J = 23.8\) Hz). NMR matches the literature data.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-difluoro-9H-carbazol-9-yl)isophthalonitrile (4FCzIPN, 4b)

Following the general procedure 1 and starting from 3,6-difluoro-9H-carbazole (7b) (105 mg, 0.517 mmol, 5.0 equiv), sodium hydride (33 mg, 0.83 mmol, 8.0 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile 6 (20.7 mg, 0.103 mmol) in 2 mL of THF, (2r,4s,5r)-2,4,5,6-tetrakis(3,6-difluoro-9H-carbazol-9-yl)isophthalonitrile (4b) was obtained as a bright yellow crystalline solid (10 mg, 11 µmol, 10 % yield) after recrystallization in acetone (5 mL) and column chromatography using pure dichloromethane.

Rf (Hexane/DCM 1/1) = 0.23. (yellow spot on TLC). \(^1\)H NMR (400 MHz, DMSO-d\(^6\)) \(\delta\) 8.34 – 8.27 (m, 2H, ArH), 8.09 (dd, \(J = 9.0, 4.2\) Hz, 2H, ArH), 7.81 (dd, \(J = 9.0, 2.6\) Hz, 3H, ArH), 7.72 – 7.61 (m, 6H, ArH), 7.45 (dd, \(J = 8.9, 2.6\) Hz, 2H), 7.36 (dd, \(J = 9.1, 4.2\) Hz, 2H, ArH), 7.15 – 7.05 (m, 4H, ArH), 6.73 – 6.63 (m, 3H, ArH).

\(^{13}\)C NMR not enough material for recording a clean spectra.

\(^{19}\)F NMR (376 MHz, DMSO-d\(^6\)) \(\delta\) -120.6 (s, 2F), -120.8 (s, 4F), -121.5 (s, 2F). IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3670 (w), 2985 (s), 2897 (s), 2367 (w), 2330 (w), 1725 (w), 1464 (m), 1395 (m), 1233 (m), 1183 (m), 1071 (s), 859 (m), 753 (w). HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C\(_{56}\)H\(_{24}\)F\(_{8}\)N\(_{6}\)\(^+\) 932.1929; Found 932.1955.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile (4ClCzIPN, 4c)

Following the general procedure 1 and starting from 3,6-dichloro-9H-carbazole 7c (1.10 g, 4.47 mmol, 5.0 equiv), sodium hydride (0.286 g, 7.16 mmol, 8.0 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile 6 (0.179 g, 0.895 mmol) in 18 mL of THF. Recrystallization
(Hexanes/CH$_2$Cl$_2$ (1:2, 80 mL)) gave 900 mg of yellow powder, then second recrystallization gave 325 mg of brown powder. Column chromatography of the combined solid afforded (2r,4s,5r)-2,4,5,6-tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile (4c) was obtained as a bright yellow crystalline solid (830 mg, 0.780 mmol, 87 % yield).

Rf (Hexane/DCM 1/1) = 0.25. (yellow spot on TLC). Mp: >240°C, turned dark yellow, decomp.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.60 (d, $J$ = 2.1 Hz, 2H, ArH), 8.15 (d, $J$ = 2.1 Hz, 4H, ArH), 8.08 (d, $J$ = 8.8 Hz, 2H, ArH), 7.87 (dd, $J$ = 8.8, 2.1 Hz, 2H, ArH), 7.80 (d, $J$ = 2.2 Hz, 4H, ArH), 6.93 (dd, $J$ = 8.8, 2.2 Hz, 2H, ArH).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 145.0, 144.5, 138.5, 137.4, 136.5, 135.8, 134.5, 127.8, 127.0, 126.4, 125.7, 125.3, 124.2, 123.8, 123.3, 121.6, 120.9, 120.3, 116.8, 112.6, 112.5, 112.3, 111.7. HRMS (ESI) calced for C$_{56}$H$_{24}$Cl$_8$N$_6$ [M+] 1059.9565; found 1059.9573.

$^1$H NMR shift in CDCl$_3$ are consistent with reported data. However, for better solubility and better resolution new $^1$H and $^{13}$C spectra were recorded in DMSO-d$_6$.

Following the general procedure 1 and starting from 3,6-dibromo-9H-carbazole 7d (1.00 g, 3.08 mmol, 5.0 equiv), sodium hydride (0.197 g, 4.92 mmol, 8.0 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile 6 (0.123 g, 0.615 mmol) in 12 mL of THF, (2r,4s,5r)-2,4,5,6-tetrakis(3,6-dibromo-9H-carbazol-9-yl)isophthalonitrile (4d) was obtained as a bright yellow crystalline solid (562 mg, 0.396 mmol, 64 % yield) after recrystallization in acetone (15 mL) and column chromatography using pure dichloromethane.

Rf (Hexane/DCM 1/1) = 0.43. (yellow spot on TLC). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.74 (d, $J$ = 1.8 Hz, 2H, ArH), 8.30 (d, $J$ = 2.0 Hz, 4H, ArH), 8.04 – 7.99 (m, 4H, ArH), 7.96 (dd, $J$ = 8.6, 1.9 Hz, 2H, ArH), 7.64 (d, $J$ = 8.8 Hz, 4H, ArH), 7.47 – 7.35 (m, 6H, ArH), 7.05 (dd, $J$ = 8.8, 2.0 Hz, 2H, ArH). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 145.0, 144.5, 138.6, 137.4, 136.5, 135.8, 134.5, 127.8, 127.0, 126.4, 125.7, 125.3, 124.2, 123.8, 123.3, 121.6, 120.9, 120.3, 116.8, 112.6, 112.5, 112.3, 111.7. NMR matches the literature data. 

4. Physical measurement

Spectroscopic characterization

4CzIPN derivatives were studied at 10 µmol.L\(^{-1}\) in acetonitrile and dichloromethane. Absorbance was recorded between 200 and 800 nm. The excitation wavelength for fluorescence was 360 nm.

![Figure 1: UV-Vis spectra of 4CzIPN derivatives in DCM.](image1)

![Figure 2. Zoom on the 250-550 nm region of the UV-Vis spectra of 4CzIPN derivatives in DCM.](image2)
Figure 3. Absorbance and emission of 4CzIPN at 10 μmol.L⁻¹ in DCM.

Figure 4. Absorbance and emission of 4ClCzIPN at 10 μmol.L⁻¹ in DCM.
Figure 5. Absorbance and emission of 4BrCzIPN at 10 μmol.L⁻¹ in DCM.

Figure 6. Absorbance and emission of 4FCzIPN at 10 μmol.L⁻¹ in DCM.
Figure 7. UV-Vis spectra of 4CzIPN derivatives in acetonitrile.

Figure 8. Zoom on the 250-550 nm region of the UV-Vis spectra of 4CzIPN derivatives in acetonitrile.
Figure 9. Absorbance and emission of 4CzIPN at 10 µmol.L\(^{-1}\) in acetonitrile.

Figure 10. Absorbance and emission of 4ClCzIPN at 10 µmol.L\(^{-1}\) in acetonitrile.
Cyclic Voltammetry (CV) was performed using an Autolab Potentiostat, with a three-electrode cell configuration: a glassy carbon electrode as the working electrode, Pt wire as a counter electrode and an Ag/AgCl (KCl, 3M) electrode as the reference electrode. Bu$_4$NPF$_6$ was employed as the electrolyte (0.1 M) and ferrocene was added as the internal standard.

For comparison, 4ClCzIPN (7e) was studied in the same conditions as previous reports on 4CzIPN, at 1mM in degassed acetonitrile. All 4CzIPN derivatives were studied in 1 mM solutions in degassed DCM at a scan rate of 0.1 V/s, to ensure solubility. Measures on 4FCzIPN were performed on a 0.5 mM solution due to the quantity of available material.

5 mM solutions of the oximes were prepared in degassed DMF to ensure solubility. The influence of the solvent on the redox properties of similar substrates has been studied by Leonori and coworkers. Voltaammograms were recorded at 4 different scan rates from 0.1 V/s to 1V/s. In the absence of reversible behaviour, the formal oxidation or reduction potentials were estimated with the $E_p$ max, introducing a ~50 mV approximation. In the case of the oximes, determination of the potentials was achieved at 1 V/s, the highest scan rate.

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\[ E_{1/2}(P/P^-) = E_{1/2}(P^+/P) - E_{0,0} \]
\[ E_{1/2}(P^*/P^-) = E_{0,0} + E_{1/2}(P/P^-) \]

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<th>( E_{0,0} )</th>
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Table 1. Redox potentials of 4CzIPN derivatives in acetonitrile

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<th>Photocatalyst</th>
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<th>( E_{1/2}(P^+/P) )</th>
<th>( E_{0,0} )</th>
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Table 2. Redox potentials of 4CzIPN derivatives in DCM

Potentials in V vs SCE, wavelength in nanometers. The excitation energy \( E_{0,0} \) was estimated by the point of intersection of the normalized absorbance and emission signals. \( E_{1/2}(P^+/P^*) = E_{1/2}(P^+/P) - E_{0,0} \) and \( E_{1/2}(P^*/P^-) = E_{0,0} + E_{1/2}(P/P^-) \).

It worth to be noted that measured values were significantly different from previous reports, both in cyclic voltammetry and in the estimation of \( E_{0,0} \), likely due to difference of approximation methods (Table 1). However, in the conditions of this study, an anodic and cathodic shift were measured for 4ClCzIPN in acetonitrile in comparison to 4CzIPN. This confirmed our hypothesis regarding the influence of electron-withdrawing substituents on the carbazole moieties. Results in DCM were in alignment, with anodic and cathodic shifts measured for 4BrCzIPN and 4FCzIPN.

Figure 12. Cyclic Voltammetry of 4ClCzIPN in acetonitrile.

Figure 13. Cyclic Voltammetry of 4CzIPN in DCM.

Figure 14. Cyclic Voltammetry of 4ClCzIPN in DCM.
Figure 15. Cyclic Voltammetry of 4BrCzIPN in DCM.

Figure 16. Cyclic Voltammetry of 4FCzIPN in DCM.
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Table 3. Electrochemical potentials of the oximes in DMF.\textsuperscript{23}

Figure 17. Cyclic Voltammetry of 12a' in DMF.

\textsuperscript{23} The potassium carboxylate salts were prepared by treatment of the corresponding acids with 1 equivalent of \textsuperscript{t}BuOK in ethanol for 2h, followed by concentration under vacuum.
Figure 18. Cyclic Voltammetry of 12j⁺ in DMF.

Figure 19. Cyclic Voltammetry of 12h⁺ in DMF.
5. Synthesis of the activating reagents for carbonyl substrates

2-(Aminooxy)-2-methylpropanoic acid hydrochloride (10)

Following a reported procedure,\textsuperscript{24} N-hydroxyphthalimide (8) (9.00 g, 55.2 mmol, 1.0 equiv) was suspended in DMF (21.6 mL). The suspension was heated to 50 °C, leading to the complete dissolution of the solid to provide a clear bright yellow solution. Ethyl 2-bromo-2-methylpropanoate 9 (9.4 mL, 66 mmol, 1.2 equiv) was then added, followed by triethylamine (10.9 mL, 78.0 mmol, 1.42 equiv). The addition of triethylamine resulted in the darkening of the solution from yellow-green to dark red. The mixture was then stirred at 90 °C. After 45 minutes, the formation of a solid and the decoloration of the mixture to orange-red was noticed. After 5 hours since the beginning of the reaction, heating was stopped and the brown mixture was allowed to cool down to room temperature. The mixture was then poured onto ice (150 g) in a 500 mL becher and stirred until the ice had melted completely. The bright red liquid was then filtered off to furnish a solid, which was washed with two portions of water (50 mL each) and dried under high vacuum for 5 hours. Ethyl 2-(((1,3-dioxoisindolin-2-yl)oxy)-2-methylpropanoate (44) (14.1 g, 50.8 mmol, 92% yield) was obtained as a pale brown-colored solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) δ 7.88 (s, 4H; ArH), 4.13 (q, \textit{J} = 7.1 Hz, 2H; OCH\textsubscript{2}CH\textsubscript{3}), 1.51 (s, 6H, C(CH\textsubscript{3})\textsubscript{2}), 1.22 (t, \textit{J} = 7.1 Hz, 3H; OCH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) δ 170.0, 164.4, 135.1, 128.6, 123.5, 86.1, 61.4, 22.7, 13.8. IR (\textit{\nu}_{\text{max}}, \text{cm}^{-1}) 2992 (w), 2943 (w), 2899 (w), 1796 (m), 1735 (s), 1611 (w), 1371 (m), 1470 (m), 1451 (w), 1353 (m), 1297 (m), 706 (s), 1137 (m), 1183 (s), 1240 (w), 1082 (w), 1024 (m), 974 (m), 876 (w), 789 (w), 765 (w), 943 (w), 859 (w).

Ethyl 2-(((1,3-dioxoisindolin-2-yl)oxy)-2-methylpropanoate (44) (11.95 g, 43.10 mmol, 1.0 equiv) was suspended in aq. HCl (6.0 N; 71.8 mL, 431 mmol, 10.0 equiv). The pale brown suspension was stirred, while being heated to 90 °C. The solids were initially almost completely dissolved; after 2-3 hours, an off-white solid started to precipitate. After 4 hours, heating was stopped and the mixture was allowed to cool down to room temperature. The reaction flask was stored at 4 °C overnight. After 16 hours, the solids were filtered off, washed with water, and dried in the air. Side product phthalic acid (7.04 g, 42.4 mmol, 98% yield) was collected as pale brown solid.

The collected pale yellow clear aqueous solution was concentrated under reduced pressure. The resulting pale yellow solid was further dried at 65 °C under vacuum for 3 hours. It was then suspended in EtOAc (41 mL) and EtOH (1.8 mL) and the mixture was stirred at reflux for 20 minutes. It was then allowed to slowly cool down to room temperature and then further to -20 °C for 20 hours. This led to the precipitation of a crystalline colorless solid that was collected by filtration and washed with EtOAc/Pentane (30/10 mL) and pentane (20 mL). 2-

(Aminooxy)-2-methylpropanoic acid hydrochloride 10 (6.32 g, 40.6 mmol, 94%) was obtained as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$; the signals corresponding to carboxylic and amine $^1$Hs were not resolved) $\delta$ 1.46 (s, 6H, CH$_3$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 173.6, 82.5, 23.2. IR ($\nu_{\text{max}}$, cm$^{-1}$) 3440 (m), 2972 (m), 2897 (m), 2648 (w), 2299 (w), 1719 (s), 1757 (m), 1152 (s), 747 (m), 940 (m), 996 (m), 1052 (m), 1252 (m), 1202 (m), 1401 (w), 1507 (w), 1339 (w).

The NMR spectra match the ones obtained from a commercially available batch: 1 g supplied by ABCR, cat. number AB456479 (lot 1371225).

2-(Aminooxy)propanoic acid hydrochloride (43)

Following a reported procedure,$^{25}$ N-hydroxybenzamide 45 (6.08 g, 44.3 mmol, 1.0 equiv) and finely ground NaOH (5.32 g, 133 mmol, 3.0 equiv) were suspended in absolute EtOH (66 mL). To the resulting thick, off-white suspension, 2-bromopropanoic acid (4.1 mL, 44 mmol, 1.0 equiv) was added slowly via syringe under stirring. This resulted in the conversion of the homogeneous suspension into a pale brown solution, which was then heated to 80 °C. Once this temperature was reached, the mixture looked again as a homogeneous, off-white suspension, which was stirred overnight. The mixture was then concentrated under reduced pressure to provide a solid residue, which was dissolved in water (90 mL). The resulting aqueous solution was washed once with diethyl ether (100 mL) and then acidified by careful addition of aq. HCl (37 % w/w) until pH = 1. It was then extracted with EtOAc (3 x 100 mL) and the combined organic layers were dried over MgSO$_4$, filtered and concentrated under vacuum to provide an off-white solid. Recrystallization from hexane (50 mL) and EtOAc (100 mL) afforded 2-(benzamidooxy)propanoic acid (46) (7.08 g, 33.9 mmol, 76% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.98 (s, 1H, CO$_2$H or CONH), 11.91 (s, 1H, CO$_2$H or CONH), 7.76 (d, $J = 7.6$ Hz, 2H, PhH), 7.54 (t, $J = 7.4$ Hz, 1H, PhH), 7.45 (t, $J = 7.6$ Hz, 2H, PhH), 4.53 (q, $J = 6.9$ Hz, 1H, CHCH$_3$), 1.40 (d, $J = 6.9$ Hz, 3H, CH$_3$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 188.2, 173.0, 165.3, 131.9, 128.5, 127.4, 78.8, 16.6.

2-(Benzamidooxy)propanoic acid (46) (7.08 g, 33.8 mmol, 1.0 equiv) was suspended in acetic acid (20.5 mL). Aq. HCl (5.0 M; 68 mL, 34 mmol, 10 equiv) was then added and the mixture was heated to reflux (110 °C), which resulted in the formation of a pale yellow, clear solution. The latter was refluxed for 18 hours. It was then allowed to cool down to room temperature. This led to the precipitation of a crystalline solid (benzoic acid), which was filtered off. The resulting solution was stored at 4 °C overnight, which permitted the precipitation of a further amount of benzoic acid. Upon removal of the latter (4.13 g, 33.8 mmol, 100% yield) through filtration, the so-obtained clear solution was concentrated under vacuum. The resulting wet solid was further dried under vacuum at 60 °C for 3 hours. It was then refluxed in a mixture of

EtOAc (30 mL) and EtOH (1.5 mL) for 20 minutes, filtered, washed with pentane, and dried in the air. 2-(Aminooxy)propanoic acid hydrochloride (47) was obtained as a colorless solid (4.15 g, 29.3 mmol, 87% yield).

$^1$H NMR (400 MHz, Deuterium Oxide) $\delta$ 4.70 (q, $J = 6.9$ Hz, 1H, $\text{CHCH}_3$), 1.46 (t, $J = 6.9$ Hz, 3H, $\text{CHCH}_2$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 171.8, 77.1, 16.4. The values for the $^1$H-NMR spectrum are in roughly agreement with the data reported in the literature (small differences are likely due to concentration effects).
6. Synthesis of oxime starting materials

General Procedure 2 (GP2)
Following a reported procedure,26 a solution of ketone (1.0 equiv) in MeOH (0.20 M) was treated with 2-(aminoxy)-2-methylpropanoic acid hydrochloride (10) (1.2 equiv), sodium acetate (2.4 equiv) and heated to reflux until complete by TLC analysis (4.5 – 6.0 hours). The mixture was then allowed to cool to room temperature and aq. Na₂CO₃ (2.0 M) was added. In some cases, the addition of a small volume of water was necessary to achieve the complete dissolution of the solids. The resulting aqueous solution was extracted once with Et₂O and the organic layer was washed with aq. Na₂CO₃ (2.0 M; 2 x). The combined aqueous extracts were then acidified by careful addition of aq. HCl solution (30% v/v) until pH < 2, and extracted with DCM (3 x). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuum to provide the pure product.

2-((Cyclobutylideneamino)oxy)-2-methylpropanoic acid (12a)

Starting from commercially available cyclobutanone (11) (0.0930 mg, 0.100 mL, 1.33 mmol), 2-methyl-2-(((3-phenylcyclobutylidene)amino)oxy)propanoic acid (12a) was obtained as a pale yellow solid (0.202 g, 1.18 mmol, 90% yield), upon following the GP2.

M.p. 103.6-105.9°C ¹H NMR (400 MHz, Chloroform-d) δ 10.26 (s, 1H, CO₂H), 3.02 – 2.81 (m, 4H, CH₂CH₂CH₂C=N), 2.02 (p, J = 8.1 Hz, 2H, CH₂CH₂CH₂), 1.50 (s, 6H, Me₂). ¹³C NMR (101 MHz, Chloroform-d) δ 178.5, 161.5, 80.7, 31.8, 31.3, 24.1, 14.5. NMR shifts consistent with literature data.26

2-((Cyclobutylideneamino)oxy)propanoic acid (48)

Starting from commercially available cyclobutanone (11) (0.0930 mg, 0.100 mL, 1.33 mmol), using 47 as activating reagent (226 mg, 1.60 mmol, 1.2 equiv), 2-methyl-2-(((3-...
phenylcyclobutylidene)amino)oxy)propanoic acid (48) was obtained as a pale yellow solid (0.150 g, 0.954 mmol, 72% yield), upon following the GP2.

M.p. 55.6-57.2°C ¹H NMR (400 MHz, Chloroform-d) δ 11.51 (s, 1H, CO₂H), 4.63 (q, J = 7.1 Hz, 1H, OCH₂), 3.09 – 2.77 (m, 4H, CH₂CH₂CH₂C=N), 2.00 (p, J = 8.4 Hz, 2H, CH₂CH₂CH₂), 1.47 (d, J = 7.1 Hz, 3H, Me). ¹³C NMR (101 MHz, Chloroform-d) δ 178.7, 161.4, 76.5, 31.6, 31.3, 16.8, 14.5. IR (νmax cm⁻¹) 2995 (m), 2934 (m), 2559 (w), 1727 (s), 1689 (m), 1455 (m), 1403 (w), 1330 (m), 1189 (m), 1131 (s), 1099 (s), 1044 (m), 972 (m), 943 (m), 911 (m), 873 (s), 736 (m). HRMS (ESI) calcd for C₇H₁₀NO₃ [M+H·] 156.0661; found 156.0659.

2-Methyl-2-(((3-phenylcyclobutylidene)amino)oxy)propanoic acid (12b)

Starting from commercially available 3-phenylcyclobutanone (49) (0.200 g, 1.30 mmol), 2-methyl-2-(((3-phenylcyclobutylidene)amino)oxy)propanoic acid (12b) was obtained as a pale yellow solid (0.295 g, 1.19 mmol, 92% yield), upon following the GP2.

M.p. 90-93.5 °C. Rf (Pentane/EtOAc 5/1) 0.31. ¹H NMR (400 MHz, Chloroform-d) δ 10.33 (br s, 1H, CO₂H), 7.38 - 7.32 (m, 2H, PhH), 7.29 - 7.25 (m, 3H, PhH), 3.64 (p, J = 8.4 Hz, 1H, PhCH), 3.50-3.35 (m, 2H, CH₂), 3.10 (m, 1H, CH₂), 3.06 (ddd, J = 7.7, 4.9, 3.4 Hz, 1H, CH₂), 1.54 (s, 6H, CH₃). ¹³C NMR (101 MHz, Chloroform-d) δ 176.7, 158.9, 143.6, 128.7, 126.7, 126.4, 81.1, 39.7, 38.9, 32.9, 24.2, 24.2. IR (νmax, cm⁻¹) 1694 (w), 1582 (w), 1482 (w), 1420 (w), 1333 (w), 1270 (m), 1127 (m), 1071 (w), 1009 (m), 940 (m), 909 (m), 834 (m), 747 (s), 2835 (w), 2754 (w), 3115 (w), 3739 (w), 3651 (w), 3552 (w), 3253 (w). HRMS (ESI/QTOF) m/z: [M + Na⁺] Calcd for C₁₄H₁₇NNaO₃⁺ 270.1101; Found 270.1109.

2-Methyl-2-(((3-methyl-3-phenylcyclobutylidene)amino)oxy)propanoic acid (12c)
Following a modified version of a reported procedure,\textsuperscript{27} zinc powder (1.61 g, 24.6 mmol, 4.0 equiv) was suspended in diethyl ether (32 mL) under inert atmosphere. After the addition of alpha-methylstyrene (50) (0.80 mL, 6.1 mmol, 1.0 equiv), a solution of trichloroacetyl chloride (1.4 mL, 12 mmol, 2.0 equiv) in diethyl ether (16 mL) was also added drop-wise over a period of 40-45 minutes. During this time, the mixture was irradiated with ultrasound, while being maintained at a temperature < 25 °C by using a water bath and adding ice when necessary. Once the addition was completed, the mixture was kept under sonication for another 4 hours. The reaction then started suddenly: the reaction mixture became darker, from colorless to yellow and then to orange-brown. Consumption of zinc powder also became evident. Ultrasound irradiation was continued for another hour. At this point, TLC analysis (pentane/EtOAc 9/1) showed that full conversion was achieved, in roughly agreement with the data reported in the literature \textsuperscript{(d, 2H, Ph) Rf (Pentane/EtOAc 9/1) 0.70. \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.43 (m, 2H, PhH), 7.35 (m, 1H, PhH), 7.29 (m, 2H, PhH), 4.00 (dd, \(J = 16.3\), 1.0 Hz, 1H, (CO)CH\(_2\)), 3.09 (d, \(J = 16.4\) Hz, 1H, (CO)CH\(_2\)), 1.67 (d, \(J = 0.9\) Hz, 3H, CH\(_3\)). The values for the \(\textsuperscript{1}H\)-NMR spectrum are in roughly agreement with the data reported in the literature.\textsuperscript{28}

Following a reported procedure,\textsuperscript{29} zinc powder (2.00 g, 30.6 mmol, 5.0 equiv) and ammonium chloride (0.817 g, 15.3 mmol, 2.5 equiv) were suspended in MeOH (8.7 mL). A solution of 2,2-dichloro-3-methyl-3-phenylcyclobutanone (51) (1.40 g, 6.11 mmol, 1.0 equiv) in MeOH (8.7 mL) was added to the suspension under stirring, at such a rate to prevent the reaction mixture from refluxing (ca 15 minutes). Once the addition was finished, the mixture was stirred at 70 °C for 3 hours. After this time, TLC analysis (pentane/EtOAc 9/1) showed that full conversion was achieved, with formation of a major product. The mixture was then allowed to cool down to room temperature and the solids were filtered off through a plug of celite. The filtrate was then washed with water (2 x 20 mL), sat. aq. NaHCO\(_3\) (4 x 20 mL), and brine; it was then dried over MgSO\(_4\), filtered and concentrated under vacuum. Column chromatography (25 g SiO\(_2\); EtOAc in Pentane 2 to 10%) furnished 2,2-dichloro-3-methyl-3-phenylcyclobutanone (51) (1.41 g - 85% pure, 5.23 mmol, 85% yield) as pale orange oil.

Rf (pentane/EtOAc 9/1) 0.70. \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.39 (dd, \(J = 8.1\), 6.9 Hz, 2H, PhH), 7.33 (m, 2H, PhH), 7.27 (m, 1H, PhH), 3.49 (d, \(J = 19.2\) Hz, 2H, (CO)CH\(_2\)), 3.13 (d, \(J = 19.3\) Hz, 2H, (CO)CH\(_2\)), 1.62 (s, 3H, CH\(_3\)). The values for the \(\textsuperscript{1}H\)-NMR spectrum are in roughly agreement with the data reported in the literature.\textsuperscript{30}


Starting from 3-methyl-3-phenylcyclobutanone (52) (0.438 g, 2.73 mmol), 2-methyl-2-(((3-methyl-3-phenylcyclobutylidene)amino)oxy)propanoic acid (12c) was obtained as a colorless solid (0.440 g, 1.68 mmol, 62% yield), upon following the GP2.

M.p. 112.6-114.6 °C. Rf (Pentane/EtOAc 4/1) 0.43. $^1$H NMR (400 MHz, Chloroform-$d$) δ 11.04 (s, 1H, CO$_2$H), 7.38 - 7.32 (m, 2H, PhH), 7.28 - 7.20 (m, 3H, PhH), 3.30 (dd, $J$ = 9.9, 3.0 Hz, 1H, CH$_2$), 3.26 (dd, $J$ = 10.6, 2.9 Hz, 1H, CH$_2$), 3.10 (dt, $J$ = 16.7, 3.2 Hz, 1H, CH$_2$), 3.00 (dt, $J$ = 16.1, 3.2 Hz, 1H, CH$_2$), 1.54 (s, 3H, CH$_3$), 1.53 (s, 3H, CH$_3$), 1.52 (s, 3H, CH$_3$).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 179.0, 157.1, 148.6, 128.5, 126.1, 125.2, 80.8, 44.8, 44.2, 38.0, 30.9, 24.1, 24.1. IR ($\nu_{\max}$, cm$^{-1}$) 3608 (w), 2986 (m), 2930 (m), 2567 (w), 2684 (w), 1716 (s), 1593 (m), 1488 (m), 1297 (m), 1408 (m), 1248 (w), 1231 (s), 872 (m), 730 (m). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{20}$NO$_3$ 262.1438; Found 262.1442.

2-(((3-((tert-Butoxycarbonyl)amino)cyclobutylidene)amino)oxy)-2-methylpropanoic acid (12d)

Starting from tert-butyl (3-oxocyclobutyl)carbamate (53) (0.25 g, 1.28 mmol) the product 12d was obtained as a white solid (0.360 g, 1.23 mmol, 98%), upon following the GP2.

M.p. 171.6-175.5°C (decomp). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.40 (s, 1H, CO$_2$H), 7.38 (d, $J$ = 7.4 Hz, 1H, NH), 4.03 (q, $J$ = 7.4 Hz, 1H, CH$_2$NHBoc), 3.19 - 2.98 (m, 2H, CH$_2$), 2.83 - 2.66 (m, 2H, CH$_2$), 1.39 (s, 9H, NBoc), 1.36 (s, 3H, CMe$_2$), 1.35 (s, 3H, CMe$_2$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 175.0, 154.7, 153.3, 80.1, 78.0, 38.8, 28.2, 24.0 (2C). IR ($\nu_{\max}$, cm$^{-1}$) 3361 (w), 2986 (m), 2936 (w), 1715 (s), 1693 (s), 1524 (m), 1457 (w), 1395 (m), 1368 (m), 1278 (m), 1254 (m), 1163 (s), 1070 (w), 1006 (w), 968 (m), 915 (m), 873 (m), 824 (w), 782 (w), 738 (m). HRMS (ESI) calcd for C$_{13}$H$_{22}$N$_2$NaO$_5$ $^{+}$ [M + Na]$^+$ 309.1421; found 309.1424.
2-((Bicyclo[4.2.0]octa-1,3,5-trien-7-ylideneamino)oxy)-2-methylpropanoic acid (12e)

Following a reported procedure,\(^{31}\) anthranilyc acid (54) (0.75 g, 5.5 mmol, 1.0 equiv) was dissolved in absolute EtOH (8.2 mL). Under stirring, the solution was cooled to 0 °C (ice-water bath). Aq. HCl (37% v/v; 0.45 mL, 5.5 mmol, 1.0 equiv) was added via pipette (the reaction mixture darkened from yellowish to brown), followed by ice-cold isopentyl nitrite (1.25 mL, 9.30 mmol, 1.7 equiv). Stirring was continued at 0 °C for 10 minutes. During this time, the mixture converted into a pink-yellow suspension. Diethyl ether (8.2 mL) was then added and stirring was continued at the same temperature for another 5 minutes. The formed solid was then collected by filtration and washed with ether (2 x 8.0 mL) (behind an anti-blast shield: the dry product is reported explosive!). The obtained pale yellow solid was immediately suspended in DCE (12.1 mL). Propylene oxide (0.77 mL, 11 mmol, 2.0 equiv) and 1,1-dichloroethene (3.6 mL, 45 mmol, 8.2 equiv) were then added by syringe. The mixture was then heated to reflux over a period of 20 hours: during this time, the suspension turned from pale yellow to dark orange-brown, and a gentle release of gas was observed. It was then allowed to cool down to room temperature and a brown solid was removed through filtration over a pad of celite, which was washed with several portions of DCM. The filtrate was concentrated under reduced pressure to give an orange-brown crude oil, which was used directly in the following step, without further purification.

Following a reported procedure,\(^{32}\) the crude oil obtained from the previous step was diluted with EtOH (9.3 mL) and water (2.3 mL). Silver nitrate (1.91 g, 11.2 mmol, 2.05 equiv) was then added in small portions. The resulting suspension was heated at 90 °C under stirring for 4 hours: this resulted in the mixture darkening to grey-black. The solids were then removed by filtration through a pad of celite, which was washed with several portions of EtOH. The filtrate was concentrated under reduced pressure, diluted with water (15 mL), and extracted with diethyl ether (3 x 30 mL). The combined organic extracts were washed with brine, dried over MgSO\(_4\), filtered and concentrated under vacuum. The resulting crude oil was submitted to column chromatography (25 g SiO\(_2\); DCM in Pentane 6 to 50%) to furnish bicyclo[4.2.0]octa-1,3,5-trien-7-one (56) (0.458 g, 3.88 mmol, 71% yield) as a colorless solid.

Rf (Pentane/DCM 3/1) 0.38. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.55 - 7.47 (m, 2H, ArH), 7.38 (t, \(J = 7.5\) Hz, 1H, ArH), 7.32 (dd, \(J = 7.6, 1.0\) Hz, 1H, ArH), 4.00 - 3.92 (m, 2H, ArCH\(_2\)). \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 188.7, 151.3, 147.9, 135.2, 128.7, 123.7, 120.6, 52.3.


The values for the $^1$H-NMR spectrum are in roughly agreement with the data reported in the literature.\textsuperscript{33}

Starting from bicyclo[4.2.0]octa-1,3,5-trien-7-one (56) (0.200 g, 1.69 mmol), 2-((bicyclo[4.2.0]octa-1,3,5-trien-7-ylideneamino)oxy)-2-methylproanoic acid (12e) was obtained as a colorless solid (mixture of E and Z isomers; 0.195 g, 0.889 mmol, 52% yield), upon following the GP2.

M.p. 120-125.2 °C. Rf (pentane/EtOAc 4/1) 0.38. $^1$H NMR (400 MHz, Chloroform-$d$; the signals corresponding to the minor isomer are reported in italics) $\delta$ 10.73 (br s, 1 H, CO$_2$H), 7.42 (dd, $J = 13.2$, 7.3 Hz, 2H, ArH), 7.32 (q, $J = 9.7$, 8.7 Hz, 2H, ArH), 3.91 (s, 2H, ArCH$_2$), 3.89 (s, 2H, ArCH$_2$), 1.63 (s, 6H, CH$_3$), 1.59 (s, 6H, CH$_3$). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 178.3, 178.2, 154.7, 152.2, 145.6, 144.6, 140.7, 139.3, 132.2, 131.7, 128.3, 128.2, 123.3, 123.2, 123.0, 120.0, 81.5, 81.4, 39.6, 39.4, 24.2, 24.2. IR ($\nu_{\text{max}}$, cm$^{-1}$) 3009 (m), 2922 (m), 2816 (m), 2660 (m), 2548 (w), 1713 (s), 1595 (w), 1557 (w), 1476 (w), 1364 (w), 1302 (m), 1177 (s), 965 (s), 915 (s), 828 (m), 766 (s). HRMS (ESI/QTOF) m/z: [M + H-I]$^+$ Calcd for C$_{12}$H$_{12}$NO$_3$ $^+$ 218.0817; Found 218.0817.

2-Methyl-2-((2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-ylidene)amino)oxy)propanoic (12f)

Following a modified version of a reported procedure,\textsuperscript{27} zinc powder (1.00 g, 15.3 mmol, 2.0 equiv) was suspended in diethyl ether (40 mL) under inert atmosphere. After the addition of indene (57) (0.90 mL, 0.89 mmol, 1.0 equiv), a solution of trichloroacetyl chloride (1.3 mL, 11 mmol, 1.5 equiv) in diethyl ether (20 mL) was also added drop-wise over a period of 40-45 minutes. During this time, the mixture was irradiated with ultrasound, while being maintained at a temperature < 25 °C by using a water bath and adding ice when necessary. Once the addition was completed, ultrasound irradiation was continued for one additional hour. Suddenly, an exothermal process started leading the grey suspension to rapidly turn to brown. After another 15 minutes, TLC analysis (pentane/EtOAc 8/1) showed the complete conversion of the starting material. The reaction was therefore stopped, the mixture diluted with diethyl ether (20 mL), and the solids were filtered off through a pad of celite, and washed with diethyl ether. The filtrate was then washed with water (2 x 20 mL), sat. aq. NaHCO$_3$ (4 x

20 mL, and brine; it was then dried over MgSO₄, filtered and concentrated under vacuum. Column chromatography (50 g SiO₂; EtOAc in pentane 1 to 25%) furnished 2,2-dichloro-2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one as an off-white solid (58) (0.832 g, 3.66 mmol, 48% yield).

Rf (pentane/EtOAc 9/1) 0.71. ¹H NMR (400 MHz, Chloroform-d) δ 7.44 (m, 1H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.27 (m, 1H, ArH), 4.50 (dd, J = 8.0, 1.5, 2H, ArCH₂), 3.40 (dd, J = 16.9, 1.4, 1H, CH), 3.20 (dd, J = 16.7, 8.0, 1H, CH). ¹³C NMR (101 MHz, Chloroform-d) δ 197.6, 143.5, 137.6, 129.3, 128.7, 127.5, 125.5, 88.3, 59.3, 58.9, 34.4. HRMS (LTQ-Orbitrap) m/z: [M]+ Caled for C₁₁H₈Cl₂O⁺ 225.9947; Found 225.9951.

Following a reported procedure,²⁹ zinc powder (1.01 g, 15.4 mmol, 5.0 equiv) and ammonium chloride (0.412 g, 7.71 mmol, 2.5 equiv) were suspended in MeOH (4.0 mL). A solution of 2,2-dichloro-2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one (0.700 g, 3.08 mmol, 1.0 equiv) in MeOH (10 mL) was added to the suspension under stirring, at such a rate to prevent it from refluxing (ca. 15 minutes). Once the addition was finished, the mixture was stirred at 70 °C for 3 hours. After this time, TLC analysis (pentane/EtOAc 9.5/0.5) showed that full conversion was achieved. The mixture was then allowed to cool down to room temperature and the solids were filtered off through a pad of celite. The filtrate was concentrated under vacuum. The resulting crude oil was submitted to column chromatography (25 g SiO₂; EtOAc in pentane 2 to 20%) to provide 2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one (59) (0.330 g, 2.09 mmol, 68% yield) as colorless oil.

Rf (Pentane/EtOAc 9/1) 0.52. ¹H NMR (400 MHz, Chloroform-d) δ 7.30 (m, 1H, ArH), 7.25 - 7.20 (m, 3H, ArH), 4.07 (m, 1H, (CO)CH), 4.05 (d, J = 1.3 Hz, 1H, ArCH), 3.61 (m, 1H, CH₂), 3.31 (d, J = 16.9, 1.4 Hz, 1H, CH₂), 3.12 (m, 1H, CH₂), 2.89 (m, 1H, CH₂). ¹³C NMR (101 MHz, Chloroform-d; the signal for one aromatic carbon is not resolved) δ 212.3, 144.5, 143.0, 127.4, 125.4, 125.0, 62.8, 55.6, 36.6, 34.0. The reported values are in agreement with the characterization data reported in the literature.³⁴

Starting from 2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one (59) (0.330 g, 2.09 mmol), 2-methyl-2-(((2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-ylidene)amino)oxy)propanoic (12f) was obtained as a crystalline, colorless solid (insoluble mixture of E and Z isomers; 0.160 g, 0.617 mmol, 30% yield), upon following the GP2.

Rf (Pentane/EtOAc 7/1) 0.25. ¹H NMR (400 MHz, Chloroform-d) δ 11.71 (s, 1H, CO₂H), 7.34 - 7.21 (m, 4H, ArH), 4.09 - 3.88 (m, 1.6H, CH or CH₂), 3.57 (dd, J = 17.3, 2.2, 1.1 Hz, 0.4H, CH or CH₂), 3.48 - 3.35 (m, 1H CH or CH₂), 3.33 - 3.21 (m, 1.6H, CH or CH₂), 2.86 (dt, J = 17.2, 3.1 Hz, 0.6H, CH), 2.74 (dt, J = 16.8, 3.4 Hz, 0.4H, CH), 1.59 (s, 1.2H, CH₃), 1.56 (s, 1.2H CH₃), 1.51 (s, 1.8H, CH₃), 1.50 (s, 1.8H, CH₃). ¹³C NMR (101 MHz, Chloroform-d; the signals corresponding to the minor isomer are reported in italics) δ 179.9, 179.8, 163.0, 161.6, 144.8, 144.7, 143.4, 143.3, 127.1, 127.1, 127.1, 127.0, 125.1, 124.9, 124.8, 124.7, 80.6, 80.6, 47.5, 47.2, 40.6, 39.7, 39.7, 39.5, 37.1, 34.8, 24.2, 24.1, 23.9, 23.6. The reported values are in agreement with the characterization data reported in the literature.²⁶

Footnote:
2-Methyl-2-((oxetan-3-ylideneamino)oxy)propanoic acid (12g)

Starting from oxetanone (60) (85 µL, 1.3 mmol. 1.0 equiv), 2-Methyl-2-((oxetan-3-ylideneamino)oxy)propanoic acid 12g was obtained as a colorless solid (55 mg, 0.32 mmol, 24%), upon following the GP2.

M.p. 86.2-89.8 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.77 (s, 1H, CO$_2$H), 5.33 (dd, $J$ = 3.7, 2.3 Hz, 2H, CH$_2$OCH$_2$), 5.29 (dd, $J$ = 3.2, 2.1 Hz, 2H, CH$_2$OCH$_2$), 1.51 (s, 6H, Me$_2$). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 179.3, 153.8, 81.4, 79.1, 78.9, 23.8. IR ($\nu_{\text{max}}$, cm$^{-1}$) 2989 (m), 2944 (w), 2664 (w), 2559 (w), 1741 (s), 1469 (w), 1383 (w), 1366 (w), 1294 (w), 1278 (w), 1227 (m), 1189 (s), 1157 (s), 1074 (w), 1050 (w), 984 (s), 957 (s), 861 (m), 788 (w), 740 (m). HRMS (ESI) calcd for C$_{18}$H$_{15}$NNa$^+$ [M+Na]$^+$ 268.1097; found 268.1100.

2-(((1-(tert-Butoxycarbonyl)azetidin-3-ylidene)amino)oxy)-2-methylpropanoic acid (12h)

Starting from commercially available tert-butyl 3-oxoazetidine-1-carboxylate (61) (0.275 g, 1.61 mmol), 2-(((1-(tert-butoxycarbonyl)azetidin-3-ylidene)amino)oxy)-2-methylpropanoic acid (12h) was obtained as a colorless solid (0.404 g, 1.48 mmol, 92% yield), upon following the GP2.

M.p. 145.8-148.6 °C. Rf (Pentane/EtOAc 5/1) 0.26 $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.42 (br s, 1H, CO$_2$H), 4.64 (d, $J$ = 3.3 Hz, 3H, NCH$_3$), 4.62 (d, $J$ = 2.8 Hz, 2H, NCH$_2$), 1.52 (s, 6H, CH$_3$), 1.46 (s, 9H, CH$_3$ in Boc). $^{13}$C NMR (101 MHz, Chloroform-$d$; The signals correspondings to the carbons in $\alpha$ to the nitrogens are not fully resolved.) $\delta$ 178.6, 156.3, 149.3, 81.5, 80.7, 58.3, 28.3, 23.9. IR ($\nu_{\text{max}}$, cm$^{-1}$) 2991 (w), 2928 (w), 2554 (w), 1694 (s), 1464 (w), 1414 (s), 1370 (m), 1302 (m), 1171 (s), 1127 (s), 965 (s), 871 (m), 766 (m). HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for C$_{12}$H$_{20}$N$_2$NaO$_5$$^+$ 295.1264; Found 295.1261.
2-Methyl-2-(((1-(4-methylbenzoyl)azetidin-3-ylidene)amino)oxy)propanoic acid (12i)

Following a reported procedure,\(^{35}\) 3-hydroxyazetidine hydrochloride (62) (1.72 g, 15.7 mmol, 1.0 equiv) and 4-methylbenzoyl chloride (2.1 mL, 16 mmol, 1.0 equiv) were dissolved in a 3:2 mixture of water and ethyl acetate (86 mL). Potassium carbonate (10.9 g, 79.0 mmol, 5.0 equiv) was added at room temperature and the resulting heterogeneous mixture was stirred vigorously for 18 hours. The organic layer was the separated and concentrated under reduced pressure. The resulting residue was dissolved in a 2:1 mixture of THF and methanol (27 mL) and stirred with aq. sodium hydroxide (1.0 M; 7.0 mL) at room temperature. After 1 hour, the reaction mixture was concentrated under reduced pressure, and the resulting residue was partitioned between EtOAc and water. The organic layer was separated, washed with brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure to provide (3-hydroxyazetidin-1-yl)(\(p\)-tolyl)methanone (63) (96% pure; 2.54 g, 12.7 mmol, 81% yield) as a colorless solid.

M.p. 117.9-121.3 \(^\circ\)C. Rf (Pentane/EtOAc 9/1) 0.71. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.47 (d, \(J = 8.2\) Hz, 2H, Ar\(H\)), 7.19 (d, \(J = 7.9\) Hz, 2H, Ar\(H\)), 4.75 (s, 1H, OH), 4.63 (t, \(J = 6.0\) Hz, 1H, \(\text{CHOH}\)), 4.44 - 4.34 (m, 2H, \(\text{NCH}_2\)), 4.18 (dd, \(J = 9.9, 4.4\) Hz, 1H, \(\text{NCH}_2\)), 4.02 (dd, \(J = 11.2, 4.6\) Hz, 1H, \(\text{NCH}_2\)), 2.38 (s, 3H, Ar\(CH\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 170.4, 141.5, 129.9, 129.0, 127.8, 61.4, 51.9, 21.4. IR (\(\nu\max\), cm\(^{-1}\)) 3251 (w), 2949 (w), 1722 (s), 1605 (m), 1556 (m), 1439 (m), 1279 (s), 1180 (m), 1106 (m), 1038 (w), 971 (w), 847 (m), 755 (s), 743 (m). HRMS (ESI/QTOF) m/z: [M + Na\(^+\)] Calcd for C\(_{11}\)H\(_{13}\)NNaO\(_2\)\(^+\) 214.0838; Found 214.0841.

(3-Hydroxyazetidin-1-yl)(\(p\)-tolyl)methanone (63) (1.70 g, 8.89 mmol, 1.0 equiv) was dissolved in DMSO (34.2 mL). Triethylamine (10.2 mL, 73.8 mmol, 8.3 equiv) was then added at room temperature, followed by solution of pyridine-sulfur trioxide-complex (10.1 g, 62.2 mmol, 7.0 equiv) in DMSO (34.2 mL). The resulting mixture was stirred at room temperature for 1.5 hours, slowly turning from colorless to pale orange. The mixture was poured into iced water (120 mL) and extracted with ethyl acetate (3 x 70 mL). The combined

organic layers were washed with brine, dried over MgSO\(_4\), filtered, and concentrated under vacuum. The resulting yellow crude solid was submitted to column chromatography (25 g SiO\(_2\); EtOAc in DCM, 3 to 30%) to afford 1-(4-methylbenzoyl)azetidin-3-one (64) (0.836 g, 4.42 mmol, 50% yield) as a pale yellow solid.

M.p. 130.3-134.0 °C. Rf (DCM/EtOAc 9/1) 0.45. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.60 (d, \(J = 8.2\) Hz, 2H, ArH), 7.25 (m, 2H, ArH), 4.95 (s, 4H, \(N(CH)\_2\)CO), 2.40 (s, 3H, \(CH\_3\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\); the signal reported in italics is barely resolved due to the existence of the compound as a mixture of two rotamers) \(\delta\) 196.0, 171.2, 142.4, 129.6, 129.3, 128.2, 72.4, 21.5. IR (\(\nu\)max, cm\(^{-1}\)) 3054 (m), 1833 (m), 1655 (w), 1550 (w), 1494 (w), 1420 (w), 1383 (w), 1605 (w), 1266 (m), 1205 (w), 1057 (m), 1008 (m), 940 (w), 736 (s).

HRMS (APCI/QTOF) m/z: [M + H]\(^+\) Calcd for C\(_{11}\)H\(_{12}\)NO\(_2\) 190.0863; Found 190.0863.

Starting from 1-(4-methylbenzoyl)azetidin-3-one (64) (0.500 g, 2.64 mmol), 2-methyl-2-(((1-(4-methylbenzoyl)azetidin-3-ylidene)amino)oxy)propanoic acid (12i) was obtained as a colorless solid (95% pure; mixture of rotamers; 0.606 g, 2.09 mmol, 79% yield), upon following the GP 2.

M.p. 158.7-163.0 °C. Rf (DCM/EtOAc 9/1) 0.16. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 9.63 (br s, 1H, CO\(_2\)H), 7.55 (d, \(J = 8.2\) Hz, 2H, ArH), 7.23 (d, \(J = 7.9\) Hz, 2H, ArH), 4.93 (s, 2H, NCH\(_2\)), 4.90 (m, 2H, NCH\(_2\)), 2.39 (s, 3H, ArCH\(_3\)), 1.52 (s, 6H, CH\(_3\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\); in italics are reported the signals corresponding to the same C in either rotamers) \(\delta\) 178.5, 178.3, 171.1, 148.5, 142.2, 129.5, 129.2, 128.0, 81.7, 61.5, 58.1, 23.9, 21.5. IR (\(\nu\)max, cm\(^{-1}\)) 3054 (w), 1735 (w), 1562 (w), 1531 (w), 1433 (w), 1371 (w), 1266 (m), 1162 (w), 1094 (w), 1026 (w), 866 (w), 736 (s). HRMS (ESI/QTOF) m/z: [M + H-\(\text{H}^+\)] Calcd for C\(_{15}\)H\(_{17}\)N\(_2\)O\(_4\) 289.1188; Found 289.1186.

\((E)-2-(((2,2-Dimethylcyclopentylidene)amino)oxy)-2-methylpropanoic\) acid (12j)

Starting from 2,2-dimethylcyclopentanone (65) (0.243 g, 2.16 mmol), \((E)-2-(((2,2-dimethylcyclopentylidene)amino)oxy)-2-methylpropanoic\) acid (12j) was obtained as a colorless solid (0.455 g, 2.13 mmol, 99% yield), upon following the GP 2.

M.p. 53.4 - 55.5°C \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 11.14 (s, 1H, CO\(_2\)H), 2.55 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)C=N), 1.80 (p, \(J = 7.1\) Hz, 2H, CH\(_2\)CH\(_2\)C=N), 1.65 (t, \(J = 6.8\) Hz, 2H, CH\(_2\)CH\(_2\)CH\(_2\)C=N), 1.49 (s, 6H, \(CMe\_2\)COOH), 1.16 (s, 6H, \(CMe\_2\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 176.0, 175.5, 81.2, 42.8, 40.7, 27.8, 26.4, 24.4, 20.8. NMR shifts consistent with literature data.\(^{26}\)
2-Methyl-2-(((2-methyldihydrofuran-3(2H)-ylidene)amino)oxy)propanoic acid (12k)

Starting from 2-methyldihydrofuran-3(2H)-one (66) (129 µL, 1.33 mmol), 2-methyl-2-(((2-methyldihydrofuran-3(2H)-ylidene)amino)oxy)propanoic acid (12k) was obtained as a colorless oil (inseparable mixture of E and Z isomers in 8:2 ratio; 0.227 g, 1.13 mmol, 85% yield), upon following the GP2.

Rf (DCM/EtOAc 9/1) 0.29. $^1$H NMR (400 MHz, Chloroform-d) δ 11.10 (bs, 1H, CO$_2$H), 4.70 (q, $J$ = 6.6 Hz, 0.2H, CH$_3$CHO), 4.33 (q, $J$ = 6.3 Hz, 0.8H, CH$_3$CHO), 4.14 (td, $J$ = 8.6, 4.0 Hz, 0.8H, OCH$_2$), 4.08 (dd, $J$ = 8.3, 5.3 Hz, 0.2H, OCH$_2$), 3.94 – 3.77 (m, 1H, OCH$_2$), 2.84 – 2.59 (m, 2H, NCH$_2$CH$_3$), 1.53 (s, 6H, CH$_3$), 1.41 (d, $J$ = 6.7 Hz, 0.6H, CH$_3$), 1.35 (d, $J$ = 6.4 Hz, 2.4H, CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$; the signals corresponding to the minor isomer are reported in italics) δ 178.6, 178.4, 166.6, 165.6, 81.3, 80.8, 74.5, 73.2, 65.9, 65.7, 30.5, 28.5, 24.3, 23.9, 18.1, 15.9. IR ($\nu_{max}$, cm$^{-1}$) 2986 (m), 2887 (m), 2363 (w), 1722 (s), 1470 (w), 1371 (m), 1285 (w), 1174 (s), 1069 (m), 977 (m), 853 (m), 743 (w).

HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M + Na]$^+$ Calcd for C$_9$H$_{15}$NNaO$_4$ 224.0893; Found 224.0892.

2-(((1-((tert-Butoxycarbonyl)pyrrolidin-3-ylidene)amino)oxy)-2-methylpropanoic acid (12l)

Starting from tert-butyl 3-oxopyrrolidine-1-carboxylate (67) (0.246 g, 1.33 mmol), 2-(((1-((tert-butoxycarbonyl)pyrrolidin-3-ylidene)amino)oxy)-2-methylpropanoic acid (12l) was obtained as a colorless solid (inseparable mixture of rotamers of E and Z isomers in 8:2 ratio; 0.247 g, 0.863 mmol, 65% yield), upon following the GP2.

M.p. 90.4-103.2 °C. Rf (DCM/MeOH 9.5/0.5) 0.39. $^1$H NMR (400 MHz, Chloroform-d) δ 9.93 (s, 1H, CO$_2$H), 4.11 (s, 1.6H, NCH$_2$), 4.06 (s, 0.4H, NCH$_2$), 3.59 (m, 1.6H, NCH$_2$CH$_3$), 3.38 (dd, $J$ = 10.6, 6.0 Hz, 0.4H, NCH$_2$CH$_3$), 2.79 (t, $J$ = 7.8 Hz, 0.6H, NCH$_2$CH$_3$), 2.71 (t, $J$ = 7.5 Hz, 1H, NCH$_2$CH$_3$), 2.58 (dd, $J$ = 8.3, 3.7 Hz, 0.4H, NCH$_2$CH$_3$), 1.53 – 1.45 (m, 15H, CH$_3$). $^{13}$C NMR (101 MHz, Chloroform-d) δ 178.5, 177.4, 161.1, 158.0, 154.4, 154.3, 81.3, 80.8, 80.1, 46.1, 28.4, 28.4, 24.3, 24.1, 22.1, 15.9. IR ($\nu_{max}$, cm$^{-1}$) 2992 (w), 2943 (w), 1704 (s), 1427 (m), 1168 (s), 977 (m), 897 (m), 767 (w). HRMS (ESI/QTOF) m/z: [M + H-1]$^+$ Calcd for C$_{13}$H$_{21}$N$_2$O$_5$ 285.1450; Found 285.1453.
7. Decarboxylative ring opening / alkynylation cascade

Optimization of the reaction:

Dry DCE was freeze-dried before using (3 cycles) and kept under argon. Dry degassed DCE (2.0 mL, 0.05 M) was added in a flame dried 5.0 mL test tube containing a teflon coated stirring bar, the oxime **12** (0.10 mmol, 1.0 equiv), EBX reagent **5** (0.20 mmol, 2.0 equiv), K$_2$CO$_3$ (0.11 mmol, 1.1 equiv) and organic dye **4** (0.05 mmol, 0.05 equiv) under N$_2$. The reaction mixture was irradiated using blue light LEDs for 1 h at rt. The reaction mixture was filtered over celite, eluting with pentane/DCM (2:1), and evaporated under reduced pressure. 6 µL of CH$_2$Br$_2$ was added as internal standard for NMR yield. Purification was performed only under optimized conditions to obtain isolated yield. The crude product was purified by preparative TLC (Heptane/Ethyl Acetate 85/15) directly without any further work-up affording 6-phenylhex-5-ynenitrile as a yellowish oil in two cases (entry 8, average of two experiments, 87%, and entry 19, 82%).
Control experiments without light or catalyst showed no reactivity, whereas only 5% were observed in the crude NMR when no base was added in the reaction mixture.

**2-Oxo-2-phenylethyl 2-iodobenzoate (68)**

A side product was identified as 2-oxo-2-phenylethyl 2-iodobenzoate. It seems to be formed via a decomposition pathway of Ph-EBX in presence of either water or oxygen, possibly catalyzed by photoredox, however the mechanism is still unclear. The NMR shifts match the literature data.\(^{36}\)

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.07 (dd, $J = 7.8, 1.7$ Hz, 1H, Ar$H$), 8.03 (dd, $J = 7.9, 1.1$ Hz, 1H, Ar$H$), 7.97 (d, $J = 7.1$ Hz, 2H, Ar$H$), 7.67 – 7.59 (m, 1H, Ar$H$), 7.52 (t, $J = 7.7$ Hz, 2H, Ar$H$), 7.46 (td, $J = 7.6, 1.2$ Hz, 1H, Ar$H$), 7.20 (td, $J = 7.7, 1.7$ Hz, 1H, Ar$H$), 5.60 (s, 2H, OCH$_2$COAr). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 191.7, 165.7, 141.4, 134.1, 134.0, 133.9, 133.1, 131.7, 128.9, 128.0, 127.8, 94.5, 66.7. HRMS (ESI) calcd for C$_{15}$H$_{11}$IO$_3$ [M$^+$] 365.9747; found 365.9752.

**Sunlight experiments**

Reaction performed on 21st December, 2017

Starting from 12a (17.1 mg, 0.10 mmol, 1.0 equiv), the reaction mixture was stirred for 2 h outdoors (12:15 – 14:15), under sunlight exposition. The crude product was purified by preparative TLC (pentane/Ethyl acetate 9:1) to afford 13a (5.6 mg, 0.033 mmol, 33%, (45% NMR yield)) as a pale yellow oil. The conversion was low, around 50%. Interestingly, the formation of 69 was observed by NMR, in greater amount than usual. Its structure is assumed according to $^1$H NMR. This product could arise from direct alkylation, before fragmentation of acetone, followed by hydration of the alkyne moiety. We hypothesize that the fragmentation alkylation reaction is temperature dependent as the outside temperature was around 4 °C at the time of the experiment. It is noteworthy that variable amounts of this side-product were observed in most of the reactions, albeit in low yield (<10%).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.96 – 7.86 (m, 2H, Ar$H$), 7.66 – 7.56 (m, 1H, Ar$H$), 7.49 (dt, $J = 8.7, 6.8$ Hz, 3H, Ar$H$), 5.38 (s, 2H, CH$_2$CO), 2.94 (dt, $J = 16.8, 7.9$ Hz, 4H), 1.99 (p, $J = 8.1$ Hz, 2H), 1.60 (s, 6H, CH$_3$).
Reactions performed on 17th May, 2018

Starting from 12a (17 mg, 0.10 mmol, 1.0 equiv), the reaction mixture was stirred for 1 h outdoors (15:30 – 16:30, 25-26°C), under sunlight exposition. The crude product was analyzed by NMR, using 6 µL of CH₂Br₂ as internal standard. (13a, 55% NMR yield, 20% remaining starting material 12a). Detection of 69 possible by NMR.

Starting from 12h (24 mg, 0.10 mmol, 1.0 equiv), the reaction mixture was stirred for 2 h30 outdoors (15:30 – 18:00, 25-26°C), under sunlight exposition, the conversion was followed by TLC control (DCM/MeOH 9/1). The crude product was analyzed by NMR, using 6 µL of CH₂Br₂ as internal standard. (13h, 90% NMR yield, <10% remaining starting material 12h). Clean reaction profile.

Reaction performed on 18\textsuperscript{th} May, 2018

Starting from 12a (17 mg, 0.10 mmol, 1.0 equiv), the reaction mixture was stirred for 2 h outdoors (15:30 – 17:30, 25-26°C), under sunlight exposition. The crude product was analyzed by NMR, using 6 µL of CH\textsubscript{2}Br\textsubscript{2} as internal standard. (13a, 75% NMR yield, <5% remaining starting material 12a). Detection of 69 possible by NMR. Clean reaction profile.

\textbf{One-pot procedure:}

A solution of cyclobutanone 11 (23 µl, 0.30 mmol) in DCE (Volume: 1.5 ml) was treated with 2-(aminoxy)-2-methylpropanoic acid hydrochloride 10 (51 mg, 0.33 mmol, 1.1 equiv.), anhydrous potassium acetate (65 mg, 0.66 mmol, 2.2 equiv.) and heated to reflux until complete by TLC analysis (6 h). The mixture was allowed to cool to room temperature and (2r,4s,5r)-2,4,5,6-tetrakis(3,6-dichloro-9H-carbazol-9-yl)isophthalonitrile 4c (16 mg, 0.015 mmol, 0.05 equiv.) and PhEBX 5a (209 mg, 0.600 mmol, 2.0 equiv.) were added, along with 4 mL of DCE. The reaction mixture was then stirred for 1h under irradiation with Blue LEDs without water or cooling system.
After 1h, the mixture was diluted with 5mL of pentane/DCM (2:1) and filtered over celite, using pentane/DCM (2:1, 50mL) to wash. The yellow solution was then concentrated under reduced pressure. 18 µL of CH₂Br₂ was added as internal standard. (72% NMR yield). The crude NMR Isolation of pure compound 13a was possible by column chromatography starting from full pentane then 20:1 pentane/EA (Rf 0.40), with 71% isolated yield.

**General procedure for the oxidative ring opening / alkynylation cascade**

![Chemical structure](image)

Dry DCE was freeze-dried (3 cycles) before using and kept under argon. Dry degassed DCE (6.0 mL) was added in a flame dried 14.0 mL test tube containing a teflon coated stirring bar, the oxime (0.30 mmol, 1.0 equiv), EBX reagent 5 (0.60 mmol, 2.0 equiv), K₂CO₃ (0.33 mmol, 1.1 equiv) and organic dye (4c) (0.009 mmol, 0.03 equiv) under N₂. The reaction mixture was irradiated using blue light LEDs for 1 h at rt. The reaction mixture was filtered over celite, eluting with pentane/DCM (2:1), and evaporated under reduced pressure. The crude product was purified by column chromatography directly without any further work-up. **Note:** α-α-aminoalkynlnitriles were obtained as mixtures of non-resolved rotamers.

**6-Phenylhex-5-yenitride (13a)**

![Chemical structure](image)

Starting from 12a (51 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13a as light yellow oil (40 mg, 0.24 mmol, 79%).

Rf (Heptane/Ethyl Acetate = 85:15) 0.40. 1H NMR (400 MHz, Chloroform-d) δ 7.40 (dtd, J = 5.5, 4.1, 2.4 Hz, 2H, ArH), 7.32 – 7.27 (m, 3H, ArH), 2.60 (t, J = 6.8 Hz, 2H, CH₂), 2.56 (t, J = 7.2 Hz, 2H, CH₂), 1.96 (p, J = 7.0 Hz, 2H, CH₂CH₂C≡C). 13C NMR (101 MHz, Chloroform-d) δ 131.5, 128.3, 128.0, 123.2, 119.2, 86.9, 82.4, 24.6, 18.5, 16.2. The reported values are in agreement with the characterization data reported in the literature. 38

**3,6-Diphenylhex-5-yenitride (13b)**

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Starting from **12b** (74 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (**5a**) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford **13b** as colorless solid (44 mg, 0.18 mmol, 60%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.40. Mp: 49.2 – 51.5 °C. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.43 – 7.35 (m, 4H, ArH), 7.35 – 7.28 (m, 6H, ArH), 2.96 (dd, $J = 16.8, 6.2$ Hz, 1H, CH$_2$), 2.89 (dd, $J = 6.9, 3.2$ Hz, 2H, CH$_2$), 2.83 (dd, $J = 16.7, 7.7$ Hz, 1H, CH$_2$C≡C). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 140.4, 131.5, 128.9, 128.1, 127.8, 127.0, 123.0, 118.2, 85.9, 83.5, 41.2, 25.8, 23.2. IR ($\nu_{\text{max}}$, cm$^{-1}$) 3065 (w), 3031 (w), 2920 (w), 1735 (w), 1691 (w), 1493 (m), 1451 (w), 1381 (w), 1326 (m), 1225 (m), 1207 (w), 1072 (w), 1030 (w), 915 (w), 847 (w), 758 (s).

HRMS (ESI) calcd for C$_{18}$H$_{15}$NNa$^+$$ [M+Na]^+$ 268.1097; found 268.1100.

Starting from **12c** (78 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (**5a**) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford **13c** as pale yellow oil colorless oil (31.9 mg, 0.123 mmol, 41%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.46 – 7.37 (m, 4H, PhH), 7.37 - 7.32 (m, 2H, PhH), 7.31 - 7.27 (m, 4H, PhH), 2.93 (d, $J = 16.7$ Hz, 1H, CH$_2$), 2.91 (m, 2H, CH$_2$), 2.86 (d, $J = 16.9$ Hz, 1H, CH$_2$), 1.68 (s, 3H, CH$_3$). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 143.4, 131.5, 128.7, 128.2, 127.1, 127.3, 125.6, 123.1, 117.9, 85.5, 84.1, 40.4, 32.5, 29.7, 25.6. IR ($\nu_{\text{max}}$, cm$^{-1}$) 3054 (w), 2986 (w), 2912 (w), 2844 (w), 2252 (w), 1957 (w), 1883 (w), 1747 (w), 1698 (w), 1599 (w), 1494 (m), 1445 (m), 1383 (w), 1328 (w), 1266 (w), 1131 (w), 1069 (w), 1026 (w), 958 (w), 909 (m), 847 (w), 755 (s). HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{18}$N$^+$ 260.1434; Found 260.1436.

**3-Methyl-3,6-diphenylhex-5-yenitrile (13c)**

Starting from **12d** (78 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (**5a**) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford **13d** as tert-Butyl (1-cyano-5-phenylpent-4-yn-2-yl)carbamate (13d)

$^{t}$-Butyl (1-cyano-5-phenylpent-4-yn-2-yl)carbamate (13d)
Starting from 12d (86 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography ((Pentane/Ethyl Acetate = 15:1 to 8:2) to afford 13d as light yellow oil (68 mg, 0.24 mmol, 80%).

Rf (Pentane/Ethyl Acetate = 8:2) 0.25. \(^1^H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.37 – 7.30 (m, 2H, ArH), 7.30 – 7.20 (m, 3H, ArH), 4.90 (d, \(J = 8.5\) Hz, 1H, NH), 4.06 (ddd, \(J = 10.3, 7.9, 4.3\) Hz, 1H, BocHNC\(\text{H}_2\)), 2.84 – 2.62 (m, 4H, \(\text{N} = \text{CCH}_2\text{CHCH}_2\)), 1.39 (s, 9H, Boc). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 154.7, 131.6, 128.4, 128.3, 122.5, 116.9, 84.3, 83.3, 80.5, 46.3, 28.2, 24.5, 22.5. IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3341 (m), 2978 (m), 2251 (w), 1693 (s), 1516 (s), 1499 (s), 1423 (w), 1368 (m), 1254 (m), 1163 (s), 1050 (m), 1024 (m), 915 (m), 867 (w), 758 (s). HRMS (ESI) calcd for C\(_{17}\)H\(_{20}\)N\(_2\)NaO\(_2\) \(+ [M+Na]^+\) 307.1417; found 307.1422.

### 2-(3-Phenylprop-2-yn-1-yl)benzonitrile (13e)

Starting from 12e (66 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13e as light yellow oil (26 mg, 0.12 mmol, 40%).

Rf (Heptane/Ethyl Acetate = 85:15) 0.33. \(^1^H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.81 – 7.73 (m, 1H, ArH), 7.66 (dd, \(J = 7.7, 1.3\) Hz, 1H, ArH), 7.61 (td, \(J = 7.7, 1.4\) Hz, 1H, ArH), 7.47 (ddt, \(J = 5.4, 2.9, 1.6\) Hz, 2H, ArH), 7.42 – 7.34 (m, 1H, ArH), 7.34 – 7.29 (m, 3H, ArH), 4.06 (s, 2H, \(\text{CH}_2\text{Ar}\)). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 140.5, 133.1, 132.7, 131.7, 129.1, 128.3, 128.2, 127.3, 123.0, 117.4, 111.9, 84.8, 84.0, 24.6. IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3061 (w), 2366 (w), 2225 (m), 1600 (w), 1489 (m), 1447 (w), 1415 (w), 1332 (w), 1284 (w), 1211 (w), 1171 (w), 1094 (w), 1068 (w), 1030 (w), 961 (w), 913 (w), 760 (s), 734 (w). The reported values are in agreement with the characterization data reported in the literature.\(^{39}\)

### 2-(trans-2-(Phenylethynyl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (13f)

Starting from 12f (78 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13f as light yellow oil (50 mg, 0.19 mmol, 65%).

Rf (Pentane/Ethyl Acetate = 10:1) 0.3. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.49 – 7.40 (m, 2H, ArH), 7.38 – 7.21 (m, 7H, ArH), 3.56 (dtt, $J = 7.7, 5.1, 1.2$ Hz, 1H, CHCH$_2$CN), 3.43 – 3.27 (m, 1H, CH=CPh), 3.23 – 3.06 (m, 2H, ArCH$_2$), 2.97 (dd, $J = 17.0, 5.1$ Hz, 1H, CH$_2$CN), 2.86 (dd, $J = 17.0, 6.5$ Hz, 1H, CH$_2$CN). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 141.5, 141.2, 131.6, 128.3, 128.1, 128.0, 127.2, 124.7, 123.0, 118.0, 89.5, 82.5, 48.0, 38.6, 37.5, 20.5. IR (ν$_{max}$, cm$^{-1}$) 3045 (w), 2918 (w), 2247 (w), 1598 (w), 1489 (m), 1461 (w), 1423 (w), 1348 (w), 1320 (w), 1233 (w), 1207 (w), 1070 (w), 1022 (w), 913 (w), 754 (s).

HRMS (ESI) calcd for C$_{19}$H$_{15}$NNa$^+$ [M+Na$^+$] 280.1097; found 280.1098. By analogy with compounds isolated from the work of Zard (with methyl acrylate)$^{24}$ and Leonori (with fluorine),$^{23}$ the major diastereoisomer is the $trans$ compound.

2-((3-Phenylprop-2-yn-1-yl)oxy)acetonitrile (13g)

Starting from 12g (17 mg, 0.10 mmol, 1.0 equiv) and Ph-EBX (5a) (70 mg, 0.20 mmol, 2.0 equiv), the crude product was purified by preparative TLC (Pentane/Ethyl Acetate = 9:1) to afford 13g as colorless oil (17 mg, 0.99 mmol, 99%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.38. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.51 – 7.43 (m, 2H, ArH), 7.40 – 7.29 (m, 3H, ArH), 4.56 (s, 2H, OCH$_2$CN), 4.45 (s, 2H, OCH$_2$C=CPh). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 131.8, 129.0, 128.4, 121.7, 115.6, 88.6, 82.0, 58.9, 54.1. The reported values are in agreement with the characterization data reported in the literature.$^{35}$

*tert*-Butyl (cyanomethyl)(3-phenylprop-2-yn-1-yl)carbamate (13h)

s550
0.30 mmol scale: Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1 to 9:1) to afford 13h as yellow oil (82 mg, 0.29 mmol, 97%, 96% purity).

1 mmol scale: Starting from 12h (272 mg, 1.00 mmol) and using 1 mol % of 4c (10.6 mg, 10.0 µmol), the crude product was purified by column chromatography (pentane/DCM/EtOAc 7/3/0 to 4/6/0 to 3/7/0.5) to afford 13h as yellow, viscous oil (0.178 g, 0.658 mmol, 66% yield).

Rf (pentane/DCM 1/1) 0.28. ¹H NMR (400 MHz, Acetonitrile-d₃) δ 7.46 (m, 2H, PhH), 7.37 (m, 3H, PhH), 4.34 (s, 2H, CH₂), 4.27 (s, 2H, CH₂), 1.49 (s, 9H, CH₃ in Boc). ¹³C NMR (101 MHz, Acetonitrile-d₃) δ 155.0, 132.4, 129.7, 129.5, 123.3, 117.6, 85.1, 84.5, 82.7, 38.7, 36.1, 28.3. IR (νmax, cm⁻¹) 2986 (w), 1704 (s), 1476 (w), 1451 (m), 1402 (s), 1371 (m), 1248 (s), 1162 (s), 1131 (m), 971 (w), 872 (m), 761 (m), 1026 (w). HRMS (ESI/QTOF) m/z: [M + Na]⁺ Calcd for C₁₆H₁₈N₂NaO₂⁺ 293.1260; Found 293.1263.

N-(Cyanomethyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzamide (13i)

Starting from 12i (87 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/DCM/EtOAc 3/7/0 to 2/8/1) to afford 13i as yellow solid (39.4 mg, 0.137 mmol, 46%).

M.p. 54.0-57.0 °C (it melts to form a viscous oil). Rf (DCM/EtOAc 96/4) 0.54. ¹H NMR (400 MHz, Chloroform-d) δ 7.50 (d, J = 8.2 Hz, 2H, ArH), 7.51 - 7.44 (m, 2H, PhH), 7.39 - 7.32 (m, 3H, PhH), 7.28 (d, J = 7.9 Hz, 2H, ArH), 4.57 (br s, 2H, CH₂), 4.50 (br s, 2H, CH₂), 2.41 (s, 3H, PhCH₃). ¹³C NMR (101 MHz, Chloroform-d) δ 171.2, 141.6, 131.8, 130.3, 129.4, 129.0, 128.4, 127.5, 121.7, 115.3, 86.3, 81.8, 40.3, 33.5, 21.5. IR (νmax, cm⁻¹) 2986 (w), 3060 (w), 1741 (w), 1661 (w), 1451 (w), 1396 (w), 1260 (w), 1143 (w), 909 (s), 730 (s), 1001 (w). HRMS (ESI/QTOF) m/z: [M + Na]⁺ Calcd for C₁₉H₁₆N₂NaO⁺ 311.1155; Found 311.1155.
5,5-Dimethyl-7-phenylhept-6-ynenitrile (13j)

Starting from **12j** (64 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (**5a**) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford **13j** as light yellow oil (49 mg, 0.23 mmol, 77%).

**Rf** (Pentane/Ethyl Acetate = 9:1) 0.33. **1H NMR** (400 MHz, Chloroform-**d**)** δ** 7.43 – 7.34 (m, 2H, ArH), 7.32 – 7.20 (m, 3H, ArH), 2.41 (t, **J** = 7.1 Hz, 2H, CH₂C≡N), 1.99 – 1.79 (m, 2H, CH₂CH₂C≡N), 1.71 – 1.54 (m, 2H, CH₂CH₂CH₂C≡N), 1.32 (s, 6H, CMe₂). **13C NMR** (101 MHz, Chloroform-**d**)** δ** 131.5, 128.1, 127.6, 123.5, 119.6, 95.8, 81.1, 42.2, 31.4, 29.2, 21.8, 17.5. **IR** (**ν** max, cm⁻¹) 2970 (m), 2922 (m), 2872 (w), 2247 (w), 1739 (w), 1687 (w), 1598 (w), 1491 (m), 1467 (m), 1427 (w), 1368 (w), 1316 (m), 1276 (w), 1205 (m), 1141 (w), 1072 (w), 917 (w), 754 (s). **HRMS** (ESI) calcd for C₁₅H₁₇NNa⁺ [M+Na]⁺ 234.1253; found 234.1247.

3-((4-Phenylbut-3-yn-2-yl)oxy)propanenitrile (13k)

Starting from **12k** (60 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (**5a**) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Chloroform/Pentane = 8:2 then 9:1) to afford **13k** as light yellow oil (39 mg, 0.20 mmol, 65%).

**Rf** (Chloroform/Pentane = 9:1) 0.35. **1H NMR** (400 MHz, Chloroform-**d**)** δ** 7.50 – 7.38 (m, 2H, ArH), 7.38 – 7.27 (m, 3H, ArH), 4.47 (q, **J** = 6.6 Hz, 1H, OCH₂), 4.14 – 3.90 (m, 1H OCH₂CH₂), 3.85 – 3.58 (m, 1H, OCH₂CH₂), 2.66 (t, **J** = 6.4 Hz, 2H, OCH₂CH₂), 1.59 – 1.43 (m, 3H, Me). **13C NMR** (101 MHz, Chloroform-**d**)** δ** 131.7, 128.5, 128.3, 122.2, 117.8, 87.8, 85.7, 66.3, 63.1, 22.0, 18.9. **IR** (**ν** max, cm⁻¹) 3057 (w), 2991 (w), 2936 (w), 2878 (w), 2251 (w), 1731 (w), 1598 (w), 1491 (w), 1445 (w), 1415 (w), 1375 (w), 1330 (m), 1258 (w), 1223 (w), 1107 (s), 1070 (m), 1038 (w), 941 (w), 917 (w), 760 (s). **HRMS** (ESI) calcd for C₁₃H₁₃NNaO⁺ [M+Na]⁺ 222.0889; found 222.0885.

tert-Butyl (2-cyanoethyl)(3-phenylprop-2-yn-1-yl)carbamate (13l)
Starting from 12l (86 mg, 0.30 mmol, 1.0 equiv) and Ph-EBX (5a) (0.21 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 9:1 then 8:2) to afford 13l as light yellow oil (26 mg, 0.090 mmol, 30%).

Rf (Pentane/Ethyl Acetate = 8:2) 0.33. 1H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.38 (m, 2H, ArH), 7.32 (dd, J = 5.3, 2.0 Hz, 3H, ArH), 4.36 (m, NCH2C≡C), 3.78 – 3.58 (m, 2H, NCH2CH2), 2.72 (m, 2H, NCH2CH2), 1.51 (s, 9H, Boc). 13C NMR (101 MHz, Chloroform-d) δ 154.6, 131.7, 128.6, 128.4, 122.4, 118.1, 99.8, 84.0, 81.5, 43.3, 38.6, 28.3, 17.0. IR (νmax, cm⁻¹) 3660 (w), 2980 (m), 2904 (w), 2364 (w), 1703 (s), 1582 (w), 1459 (w), 1409 (m), 1369 (m), 1326 (w), 1250 (m), 1165 (s), 1127 (m), 1068 (m), 961 (w), 913 (m), 867 (w), 760 (m), 736 (w). HRMS (ESI) calcd for C17H21N2O2+ [M+H]+ 285.1598; found 285.1595.

tert-Butyl (cyanomethyl)(3-(4-fluorophenyl)prop-2-yn-1-yl)carbamate (13m)

Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and pF-Ph-EBX (5c) (0.22 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 13m as light yellow oil (72 mg, 0.25 mmol, 83%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.38. 1H NMR (400 MHz, Chloroform-d) δ 7.43 (dd, J = 8.7, 5.5 Hz, 2H, ArH), 7.01 (t, J = 8.7 Hz, 2H, ArH), 4.34 (m, 4H, CH2NCH2), 1.51 (s, 9H, Boc). 13C NMR (101 MHz, Chloroform-d) δ 162.7 (d, J = 250.0 Hz), 153.4 (br s), 133.7 (d, J = 8.5 Hz), 118.1 (d, J = 3.5 Hz), 115.7, 115.64 (d, J = 22.2 Hz), 84.4, 82.6, 82.1, 37.1, 34.6, 28.1. 19F NMR (376 MHz, Chloroform-d) δ -110.1. IR (νmax, cm⁻¹) 3672 (w), 2984 (m), 2940 (w), 2904 (w), 2360 (w), 1705 (s), 1602 (m), 1508 (s), 1479 (w), 1449 (m), 1397 (m), 1368 (m), 1340 (w), 1248 (s), 1159 (s), 1129 (m), 1052 (w), 966 (w), 909 (w), 865 (m), 839 (s), 816 (w), 774 (w), 740 (w). HRMS (ESI) calcd for C16H17FNNaO2+ [M+Na]+ 311.1166; found 311.1169.

tert-Butyl (3-(4-bromophenyl)prop-2-yn-1-yl)(cyanomethyl)carbamate (13n)
Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and pBr-PhEBX (5d) (0.26 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 13n as light yellow oil (63 mg, 0.18 mmol, 60%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.34. 1H NMR (400 MHz, Chloroform-d) δ 7.45 (d, J = 8.5 Hz, 2H, ArH), 7.30 (d, J = 8.5 Hz, 2H, ArH), 4.34 (m, CH$_2$NCH$_2$), 1.52 (s, 9H, Boc). 13C NMR (101 MHz, Chloroform-d) δ 153.2 (br), 133.2, 131.7, 123.7, 121.0, 115.7, 84.4 (br), 83.6, 82.7, 37.2, 34.7, 28.2. IR (ν$_{max}$, cm$^{-1}$) 2980 (m), 2940 (w), 2906 (w), 2362 (w), 1749 (m), 1703 (s), 1588 (w), 1485 (m), 1451 (w), 1397 (m), 1368 (m), 1338 (m), 1248 (m), 1159 (m), 1072 (m), 1012 (m), 963 (w), 909 (w), 863 (m), 828 (m), 770 (m), 740 (m). HRMS (ESI) calcd for C$_{16}$H$_{17}$BrN$_2$NaO$_2$ $[M+Na]^+$ 371.0366; found 371.0362.

**tert-Butyl (cyanomethyl)(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)carbamate (13o)**

Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and pCF$_3$-Ph-EBX (5e) (0.25 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 13o as light yellow oil (62 mg, 0.18 mmol, 61%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.38. 1H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.48 (m, 4H, ArH), 4.52 – 4.16 (m, 4H, CH$_2$NCH$_2$), 1.52 (s, 9H, Boc). 13C NMR (101 MHz, Chloroform-d) δ 153.4, 132.0, 130.4 (q, J = 32.7 Hz), 125.9 (app s), 125.3 (q, J = 3.9 Hz), 123.8 (q, J = 272.2 Hz), 115.6, 85.0, 84.0, 82.8, 37.2, 34.6, 28.1. 19F NMR (376 MHz, Chloroform-d) δ -62.9. IR (ν$_{max}$, cm$^{-1}$) 2984 (w), 2362 (w), 1707 (s), 1616 (w), 1479 (w), 1449 (m), 1401 (m), 1368 (w), 1324 (s), 1248 (s), 1163 (s), 1127 (s), 1068 (s), 1018 (w), 968 (w), 941 (w), 901 (w), 865 (m), 845 (s), 770 (w), 720 (w). HRMS (ESI) calcd for C$_{18}$H$_{17}$F$_3$N$_2$NaO$_2^+$ [M+Na]$^+$ 361.1134; found 361.1136.

**tert-Butyl (cyanomethyl)(3-(4-pentylphenyl)prop-2-yn-1-yl)carbamate (13p)**

Starting from 8p (n-C$_3$H$_{11}$, 85 mg, 0.33 mmol, 1.0 equiv) and p-C$_6$H$_5$Br-EBX (5a) (0.25 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 13p as light yellow oil (67 mg, 0.18 mmol, 60%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.35. 1H NMR (400 MHz, Chloroform-d) δ 7.46 (d, J = 8.5 Hz, 2H, ArH), 7.36 (d, J = 8.5 Hz, 2H, ArH), 4.40 (m, CH$_2$NCH$_2$), 1.52 (s, 9H, Boc). 13C NMR (101 MHz, Chloroform-d) δ 153.4, 132.0, 130.4 (q, J = 32.7 Hz), 125.9 (app s), 125.3 (q, J = 3.9 Hz), 123.8 (q, J = 272.2 Hz), 115.6, 85.0, 84.0, 82.8, 37.2, 34.6, 28.1. 19F NMR (376 MHz, Chloroform-d) δ -62.9. IR (ν$_{max}$, cm$^{-1}$) 2984 (w), 2362 (w), 1707 (s), 1616 (w), 1479 (w), 1449 (m), 1401 (m), 1368 (w), 1324 (s), 1248 (s), 1163 (s), 1127 (s), 1068 (s), 1018 (w), 968 (w), 941 (w), 901 (w), 865 (m), 845 (s), 770 (w), 720 (w). HRMS (ESI) calcd for C$_{18}$H$_{17}$F$_3$N$_2$NaO$_2^+$ [M+Na]$^+$ 361.1134; found 361.1136.
Starting from **12h** (24 mg, 0.10 mmol, 1.0 equiv) and \( pC_5H_{11}\)-Ph-EBX (5f) (84 mg, 0.20 mmol, 2.0 equiv), the crude product was purified by preparative TLC (Pentane/Ethyl Acetate = 85:15) to afford **13p** as light yellow oil (20 mg, 0.060 mmol, 59%).

Rf 0.50 (Pentane/Ethyl Acetate = 85:15). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \( \delta \) 7.42 – 7.27 (m, 2H, ArH), 7.17 – 7.04 (m, 2H, ArH), 4.35 (m, 4H, \( CH_2NCCH_2 \)), 2.59 (t, \( J = 7.8 \) Hz, 2H, \( CH_2Ph \)), 1.67 – 1.54 (m, 2H, \( CH_2CH_2Ph \)), 4.35 (m, 4H, \( CH_2CH_2(\text{CH}_2)_2Ph \)), 0.88 (t, \( J = 6.9 \) Hz, 3H, \( Me \)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \( \delta \) 153.6, 144.0, 131.7, 128.5, 119.2, 115.7, 85.7, 82.5, 81.6, 37.1, 35.8, 34.4, 31.4, 30.9, 28.2, 22.5, 14.0. IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 3670 (w), 2970 (m), 2930 (m), 2870 (w), 2364 (w), 1709 (s), 1510 (w), 1447 (m), 1399 (m), 1368 (w), 1248 (s), 1165 (s), 1127 (m), 1062 (w), 966 (w), 943 (w), 911 (w), 865 (w), 770 (w), 736 (w). HRMS (ESI) calcd for \( C_{21}H_{28}N_2NaO_2^+ \) [M+Na\(^+\)] 363.2043; found 363.2042.

**tert-Butyl (cyanomethyl)(3-(3-fluorophenyl)prop-2-yn-1-yl)carbamate (13q)**

Starting from **12h** (82 mg, 0.30 mmol, 1.0 equiv) and mF-Ph-EBX (5g) (0.22 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford **13q** as light yellow oil (42 mg, 0.15 mmol, 49%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.38. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \( \delta \) 7.36 – 7.27 (m, 1H, ArH), 7.25 (dd, \( J = 7.7, 1.5 \) Hz, 1H, ArH), 7.16 (dd, \( J = 9.3, 2.1 \) Hz, 1H, ArH), 7.07 (td, \( J = 8.4, 2.4 \) Hz, 1H, ArH), 4.74 – 4.18 (m, 4H, \( CH_2NCCH_2 \)), 1.54 (s, 8H, Boc). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \( \delta \) 162.2 (d, \( J = 246.8 \) Hz), 153.3, 130.0 (d, \( J = 8.6 \) Hz), 127.6 (d, \( J = 3.1 \) Hz), 123.9 (d, \( J = 9.5 \) Hz), 118.5 (d, \( J = 22.9 \) Hz), 116.1 (d, \( J = 21.2 \) Hz), 115.6, 84.2, 83.4, 82.7, 37.1, 34.6, 28.1. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \( \delta \) -112.6. IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 2980 (m), 2936 (w), 2906 (w), 1707 (s), 1610 (m), 1582 (m), 1483 (m), 1445 (m), 1399 (s), 1368 (m), 1248 (s), 1165 (s), 1127 (m), 1080 (w), 1004 (w), 964 (w), 945 (w), 907 (w), 867 (m), 788 (m), 732 (w). HRMS (ESI) calcd for \( C_{16}H_{17}FN_2NaO_2^+ \) [M+Na\(^+\)] 311.1166; found 311.1162.

**tert-Butyl (3-(2-bromophenyl)prop-2-yn-1-yl)(cyanomethyl)carbamate (13r)**

Starting from **12h** (24 mg, 0.10 mmol, 1.0 equiv) and \( pC_5H_{11}\)-Ph-EBX (5f) (84 mg, 0.20 mmol, 2.0 equiv), the crude product was purified by preparative TLC (Pentane/Ethyl Acetate = 85:15) to afford **13r** as light yellow oil (20 mg, 0.060 mmol, 59%).

Rf 0.50 (Pentane/Ethyl Acetate = 85:15). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \( \delta \) 7.42 – 7.27 (m, 2H, ArH), 7.17 – 7.04 (m, 2H, ArH), 4.35 (m, 4H, \( CH_2NCCH_2 \)), 2.59 (t, \( J = 7.8 \) Hz, 2H, \( CH_2Ph \)), 1.67 – 1.54 (m, 2H, \( CH_2CH_2Ph \)), 4.35 (m, 4H, \( CH_2CH_2(\text{CH}_2)_2Ph \)), 0.88 (t, \( J = 6.9 \) Hz, 3H, \( Me \)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \( \delta \) 153.6, 144.0, 131.7, 128.5, 119.2, 115.7, 85.7, 82.5, 81.6, 37.1, 35.8, 34.4, 31.4, 30.9, 28.2, 22.5, 14.0. IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 3670 (w), 2970 (m), 2930 (m), 2870 (w), 2364 (w), 1709 (s), 1510 (w), 1447 (m), 1399 (m), 1368 (w), 1248 (s), 1163 (s), 1127 (m), 1062 (w), 966 (w), 943 (w), 911 (w), 865 (w), 770 (w), 736 (w). HRMS (ESI) calcd for \( C_{16}H_{17}FN_2NaO_2^+ \) [M+Na\(^+\)] 311.1166; found 311.1162.
Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and oBr-Ph-EBX (5h) (0.26 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 9:1) to afford 13r as light yellow oil (50 mg, 0.14 mmol, 48%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.25. ^1^H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.54 (m, 1H, ArH), 7.47 (dd, J = 7.7, 1.7 Hz, 1H, ArH), 7.30 – 7.24 (m, 1H, ArH), 7.19 (td, J = 7.8, 1.7 Hz, 1H, ArH), 4.52 – 4.32 (m, 4H, CH_2NCH_2), 1.52 (s, 9H, Boc). ^13^C NMR (101 MHz, Chloroform-d; one carbon signal is not resolved) δ 153.7, 133.5, 132.4, 130.0, 127.2, 125.6, 124.3, 115.7, 87.1, 82.7, 37.0, 28.2, 28.1, 28.0, 27.9. IR (ν_max, cm^-1) 2980 (m), 2934 (w), 1705 (s), 1473 (m), 1445 (m), 1397 (s), 1368 (m), 1248 (s), 1159 (s), 1129 (m), 1054 (w), 1026 (w), 968 (w), 943 (w), 911 (w), 865 (m), 758 (s).

HRMS (ESI) calcd for C_{16}H_{17}BrN_2NaO_2^+ [M+Na]^+ 371.0366; found 371.0363.

6-(4-Fluorophenyl)hex-5-yenenitrile (13s)

Starting from 12a (51 mg, 0.30 mmol, 1.0 equiv) and pF-Ph-EBX (5c) (0.22 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13s as light yellow oil (50.1 mg, 0.214 mmol, 71%, 80% purity). NMR analysis identified 64 as the impurity. A sample was purified by preparative TLC (DCM/toluene 1:1) for characterization.

Rf (DCM/toluene 1/1) 0.43. ^1^H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.34 (m, 2H, ArH), 7.04 – 6.94 (m, 2H, ArH), 2.59 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 7.2 Hz, 2H) 1.96 (p, J = 7.0 Hz, 2H, CH_2CH_2CH_2). ^13^C NMR (101 MHz, Chloroform-d) δ 162.3 (d, J = 240 Hz), 133.4 (d, J = 8.4 Hz), 119.3, 119.1, 115.5 (d, J = 22.0 Hz), 86.6, 81.4, 24.6, 18.5, 16.3. ^19^F NMR (376 MHz, Chloroform-d) δ -111.4. IR (ν_max, cm^-1) 2980 (m), 2906 (w), 2363 (w), 2252 (w), 1741 (w), 1704 (w), 1599 (w), 1507 (s), 1433 (w), 1223 (m), 1069 (m), 841 (s), 749 (w). HRMS (ESI/QTOF) m/z: [M + H]^+ Calcd for C_{16}H_{12}FBrNaO_2^+ 395.0517; Found 395.0510.

6-(4-(Trifluoromethyl)phenyl)hex-5-yenenitrile (13t)

Starting from 12a (51 mg, 0.30 mmol, 1.0 equiv) and pCF_3-Ph-EBX (5e) (0.25 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13u as light yellow oil (54 mg, 0.23 mmol, 76%).
Rf (Chloroform/Pentane = 9:1) 0.40. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.56 (d, $J = 8.2$ Hz, 2H, ArH), 7.49 (d, $J = 8.2$ Hz, 2H, ArH), 2.63 (t, $J = 6.8$ Hz, 2H, CH$_2$CC), 2.56 (t, $J = 7.1$ Hz, 2H, CH$_2$CN), 1.98 (p, $J = 6.9$ Hz, 2H, CH$_3$CH$_2$CN). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 131.8, 129.8 (q, $J = 32.6$ Hz), 127.0 (q, $J = 1.2$ Hz), 125.2 (q, $J = 3.8$ Hz), 123.9 (q, $J = 272.1$ Hz), 119.0, 89.6, 81.2, 24.4, 18.5, 16.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -62.79.

IR ($\nu_{\text{max}}$, cm$^{-1}$) 2946 (w), 2251 (w), 1616 (w), 1431 (w), 1409 (w), 1324 (s), 1167 (m), 1125 (s), 1068 (m), 1018 (w), 915 (w), 845 (m), 760 (w), 738 (w). Consistent with reported data.\(^{40}\)

5,5-Dimethyl-7-(4-(trifluoromethyl)phenyl)hept-6-ynenitrile (13u)

Starting from 12j (64 mg, 0.30 mmol, 1.0 equiv) and pCF$_3$-Ph-EBX (5e) (0.25 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13u as light yellow oil (28 mg, 0.10 mmol, 33%).

Rf (Chloroform/Pentane = 9:1) 0.42. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.53 (d, $J = 8.1$ Hz, 2H, ArH), 7.47 (d, $J = 8.0$ Hz, 2H, ArH), 2.42 (td, $J = 7.1$, 1.4 Hz, 2H, CH$_2$CN), 1.89 (ddd, $J = 14.5$, 8.3, 1.4 Hz, 2H, CH$_2$CH$_2$CN), 1.72 – 1.58 (m, 2H, CMe$_2$). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 131.8, 129.4 (q, $J = 32.7$ Hz), 127.4, 125.1 (q, $J = 3.9$ Hz), 123.9 (q, $J = 272.1$ Hz), 119.6, 98.6, 80.0, 42.0, 31.5, 29.0, 21.8, 17.5. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -62.72. IR ($\nu_{\text{max}}$, cm$^{-1}$) 2974 (m), 2918 (w), 2876 (w), 2358 (w), 2245 (w), 1713 (w), 1616 (w), 1455 (w), 1405 (w), 1326 (s), 1246 (w), 1169 (m), 1127 (s), 1109 (m), 1068 (m), 1018 (w), 845 (m), 740 (w). HRMS (ESI) calcd for C$_{16}$H$_{16}$F$_3$N [M$^+$] 279.1235; found 279.1234.

7-(4-Bromophenyl)-5,5-dimethylhept-6-ynenitrile (13v)

Starting from 12j (64 mg, 0.30 mmol, 1.0 equiv) and pBr-Ph-EBX (5d) (0.26 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1) to afford 13v as light yellow oil (30 mg, 0.10 mmol, 34%).

Rf (Pentane/Ethyl Acetate = 9:1) 0.35. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.45 – 7.37 (m, 2H, ArH), 7.25 – 7.19 (m, 2H, ArH), 2.41 (t, $J = 7.0$ Hz, 2H, CH$_2$CN), 2.05 – 1.77 (m, 2H, CH$_2$CH$_2$CN), 1.65 – 1.57 (m, 2H, CH$_2$(CH$_2$)$_2$CN), 1.30 (s, 6H, CMe$_2$). $^{13}$C NMR (101 MHz,
Chloroform-\(d\) \(\delta\) 133.0, 131.4, 122.5, 121.8, 119.6, 97.1, 80.1, 42.1, 31.4, 29.1, 21.8, 17.5. IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 2970 (s), 2918 (m), 2874 (m), 2354 (w), 2247 (w), 1741 (m), 1677 (w), 1588 (w), 1487 (s), 1427 (w), 1391 (w), 1368 (w), 1318 (w), 1276 (w), 1227 (m), 1205 (m), 1141 (w), 1072 (s), 915 (w), 828 (s), 740 (m).

HRMS (ESI) calcd for \(\text{C}_{15}\text{H}_{16}\text{BrNNa}^{+}[\text{M+Na}]^{+}\) 312.0358; found 312.0358.

\(t_{\text{er}}t\)-Butyl (cyanomethyl)(3-(triisopropylsilyl)prop-2-yn-1-yl)carbamate (13w)

Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and TIPS-EBX (5b) (0.26 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1 to 10:1) to afford 13w as light yellow oil (37 mg, 0.11 mmol, 35%).

Rf (Heptane/Ethyl Acetate = 85:15) 0.4. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 4.48 – 3.80 (m, 4H, \(\text{CH}_{2}\text{NCH}_{2}\)), 1.50 (s, 9H, \(\text{Boc}\)), 1.07 (s, 21H, \(\text{TIPS}\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)), mixture of not fully resolved rotamers (\(M=\text{major}\), \(m=\text{minor}\)) \(\delta\) 153.7 (br s), 153.3 (br s), 115.5, 100.4, 87.6 (br s), 87.0 (br s), 82.4, 37.6 (br s), 37.2 (br s), 34.0 (br s), 29.7 (m), 28.1 (M), 18.5 (M), 17.7 (m), 12.3 (m), 11.0 (M). IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3668 (w), 2944 (s), 2896 (s), 2866 (s), 2362 (w), 2177 (w), 1461 (m), 1395 (s), 1368 (m), 1248 (s), 1165 (s), 1129 (w), 1074 (m), 1012 (s), 917 (w), 883 (m), 865 (m), 826 (w), 772 (w), 738 (w). HRMS (ESI) calcd for \(\text{C}_{19}\text{H}_{34}\text{N}_{2}\text{NaO}_{2}\text{Si}^{+}[\text{M+Na}]^{+}\) 373.2282; found 373.2287.

\(t_{\text{er}}t\)-Butyl cinnamyl(cyanomethyl)carbamate (15)

Starting from 12h (27 mg, 0.10 mmol, 1.0 equiv) and Ph-VBX (14) (70 mg, 0.20 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 20:1 to 10:1) to afford 15 as light yellow oil (14 mg, 0.051 mmol, 51%).

Rf (Heptane/Ethyl Acetate = 85:15) 0.4. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.41 – 7.20 (m, 5H, ArH), 6.77 – 6.68 (m, 0.05H, \(\text{HC=CHAr}\), Z isomer), 6.58 (d, \(J = 15.8\) Hz, 1H, \(\text{HC=CHAr}\), E isomer), 6.11 (dt, \(J = 15.8, 6.6\) Hz, 1H, \(\text{HC=CHAr}\), E isomer), 5.65 (dt, \(J = 11.6, 6.5\) Hz, 0.05H, Z isomer, \(\text{HC=CHAr}\), Z isomer), 4.30 – 3.79 (m, 4H, \(\text{CH}_{2}\)), 1.52 (s, 9H, \(\text{Boc}\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(^{41}\) \(\delta\) 154.0, 136.0, 134.4, 128.6, 128.4 (Z), 128.1,

\(^{41}\) 13:1 E:Z mixture, in which the peaks of the Z isomer in \(^1\)H and \(^{13}\)C NMR are not fully resolved.
127.5 (Z), 126.5, 123.2, 116.0, 82.0, 49.2, 34.4, 28.2. IR ($v_{\text{max}}$, cm$^{-1}$) 2982 (m), 2934 (w), 1830 (w), 1705 (s), 1481 (m), 1455 (m), 1252 (s), 1165 (s), 1066 (w), 966 (w), 913 (m), 875 (w), 772 (w), 742 (m). HRMS (ESI) calcd for C$_{16}$H$_{20}$N$_2$NaO$_2$ [M+Na]$^+$ 295.1417; found 295.1421.

**tert-Butyl bis(cyanomethyl)carbamate (17)**

Starting from 12h (27 mg, 0.10 mmol, 1.0 equiv) and CBX (16) (55 mg, 0.20 mmol, 2.0 equiv), irradiation for 14 h, the crude product was analyzed by NMR using 6 µL of CH$_2$Br$_2$ as internal standard. Integration of peak at 4.42-4.18 ppm (m, 4H, C$_2$H$_2$CN) revealed 51% NMR yield. The crude was then purified by preparative TLC (Heptane/Ethyl Acetate = 7:3) to afford 17 as light yellow oil (6.1 mg, 0.031 mmol, 31%).

Rf (Heptane/Ethyl Acetate = 70:30) 0.45. $^1$H NMR (400 MHz, Chloroform-d) $^4$δ 4.42-4.18 (m, 4H, C$_2$H$_2$CN), 1.52 (s, 9H, Boc). $^{13}$C NMR (101 MHz, Chloroform-d) $^5$δ 152.6, 114.4, 84.5, 35.5 (brs, non-resolved rotamers), 28.0. IR ($v_{\text{max}}$, cm$^{-1}$) 2988 (w), 2933 (w), 2255 (w), 1829 (w), 1712 (s), 1454 (m), 1398 (s), 1373 (m), 1256 (s), 1164 (s), 1139 (m), 942 (m), 911 (m), 868 (m), 776 (m), 739 (m). HRMS (ESI) calcd for C$_9$H$_{13}$N$_3$NaO$_2$ [M+Na]$^+$ 218.0900; found 218.0892.

**tert-Butyl (cyanomethyl)(3-(4-formylphenyl)prop-2-yn-1-yl)carbamate (70)**

Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and pCHO-Ph-EBX (5i) (0.23 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 70 as light yellow oil (25 mg, 0.080 mmol, 27%, 95% purity).

Rf (Chloroform/Pentane = 9:1) 0.20. $^1$H NMR (400 MHz, Chloroform-d) δ 10.01 (s, 1H, CHO), 7.84 (d, $J = 8.3$ Hz, 2H, ArH), 7.60 (d, $J = 8.3$ Hz, 2H, ArH), 4.37 (m, 4H, C$_2$H$_2$NCH$_2$), 1.52 (s, 9H, Boc). $^{13}$C NMR (101 MHz, Chloroform-d) δ 191.4, 153.3 (br s), 135.8, 132.3, 129.6, 128.3, 115.6, 86.5, 84.5, 82.8, 37.3, 34.7, 28.2. IR ($v_{\text{max}}$, cm$^{-1}$) 3670 (w), 2982 (m), 2902 (w), 2733 (w), 1703 (s), 1604 (m), 1562 (w), 1447 (w), 1399 (m), 1368 (w), 1302 (w), 1250 (m), 1207 (w), 1163 (m), 1131 (w), 1074 (w), 1052 (w), 1014 (w), 964 (w), 911 (w).

$^4$δ Mixture of non-resolved rotamers.
865 (w), 835 (m), 774 (w), 738 (w). HRMS (ESI) calcd for C$_{17}$H$_{19}$N$_2$O$_3$ $^+$ [M+H]$^+$ 299.1390; found 299.1395.

**tert-Butyl (cyanomethyl)(3-(4-cyanophenyl)prop-2-yn-1-yl)carbamate (71)**

Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and pCN-Ph-EBX (5j) (0.22 g, 0.60 mmol, 2.0 equiv), the crude product was purified by column chromatography (Pentane/Ethyl Acetate = 15:1 to 9:1) to afford 71 as light yellow oil (31 mg, 0.11 mmol, 35%).

Rf (Chloroform/Pentane = 9:1) 0.15. $^1$H NMR (400 MHz, Chloroform-d) δ 7.61 (d, J = 8.3 Hz, 2H, ArH), 7.53 (d, J = 8.4 Hz, 2H, ArH), 4.35 (m, 4H, CH$_2$NCH$_2$), 1.52 (s, 9H, Boc). $^{13}$C NMR (101 MHz, Chloroform-d) δ 153.4 (br s), 132.3, 132.1, 127.0, 118.3, 115.6, 112.1, 87.0, 83.8, 82.9, 37.3, 35.0, 28.2. IR (ν$_{max}$, cm$^{-1}$) 2982 (m), 2908 (m), 2366 (w), 2230 (m), 1706 (s), 1608 (w), 1503 (w), 1449 (m), 1399 (m), 1368 (m), 1250 (s), 1161 (s), 1129 (m), 1052 (m), 911 (w), 845 (m), 770 (w), 738 (m). HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_3$O$_2$ $^+$ [M+H]$^+$ 296.1394; found 296.1384.
8. Computational details

Geometries of all species were optimized using several different DFT methods and dispersion corrections. All methods give comparable results indicating that, compared to rather symmetric species 4a and 4b, molecules 4c and 4d feature noticeable distortion of the carbazole moiety in the 4th position of the central ring (Figure 23). This distortion is equally observed in the gas-phase optimized geometries and in the experimental crystal structures. The likely cause of this feature is the halogen…halogen bonding between the halogen atoms of the neighbor carbazole moieties, absent/insignificant in 4a and 4b but increasingly pronounced in 4c and 4d, as exemplified by the corresponding interatomic distances. Similar intermolecular interaction also causes distortion of the 1-carbazole ring in the crystal of 4c. This hypothesis is supported by the fact (i) that distortion is almost entirely lifted in solution and (ii) is absent in the optimized structures of dyes, analogous to 4c and 4d, but with halogens selectively removed from the carbazole moieties in either the 4th and or the 3rd and 5th positions of the central ring.

Figure 23. X-ray structures of dyes 4a (A) and 4c (B). Interhalogen distances in 4c are labelled as \( r_f - r_{II} \) (dotted pink lines). (C) Interhalogen distance \( r_I \) in the optimized geometries of the studied dyes in the gas phase (PBE0-D3BJ/def2-SVP) and dichloromethane solution (PCM-UAKS/PBE0/6-31G(d)). (D) Shortest interhalogen distances \( r_f \) in the optimized geometries for several different dispersion-corrected DFT methods and experimental crystal structures.

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43 a) Crystal structure of 4a is deposit to CCDC under number 1052646 (YUGDOV), see S. Wang, Y. Zhang, W. Chen, J. Wei, Y. Liu and Y. Wang, Chem. Commun., 2015, 51, 11972. b) Crystal structure of 4c is available at CCDC under number 1838186.
Electronic energies of the studied molecules were computed at the PBE0-D3BJ/def2-SVP level using Gaussian 09 software\(^{44}\) and including LANL2DZ effective core potential for bromine atoms. Using the `stable=opt` keyword ensured stability of the wavefunction for all species. Gas-phase vertical and adiabatic ionization potentials and electron affinities were computed as follows:

**Ionization potential**

\[
IP = E_{p^+} - E_p
\]

**Electron affinity**

\[
EA = E_p - E_{p^-},
\]

where \(E_p\) is the electronic energy of the neutral (parent) compound, \(E_{p^+}\) is the electronic energy of its radical cation and \(E_{p^-}\) of its radical anion, in eV.

Gas-phase entropies and thermal corrections at 25°C were computed at the PBE0-D3BJ/def2-SVP level under the harmonic oscillator approximation in conjunction with the optimized geometries and scaled\(^{45}\) frequencies. Gas-phase Gibbs free energies at 25°C were computed using Gibbs fundamental equation. Gibbs free energies of solvation in acetonitrile (MeCN) and dichloromethane (DCM) were computed in conjunction with geometries, relaxed in solution, using the polarizable continuum model with scaled UAKS radii\(^{46}\) at the PBE0/6-31G(d) level of theory. These computations include the solvent-solute dispersion and repulsion interaction energies and the solute cavitation energy. Free energies of each species in solution were computed as the sum of the corresponding gas-phase free energy and the free energy of solvation. The phase change correction term cancels out in the computation of redox potentials.

RedOx potentials of the investigated systems in their ground states relative to the saturated calomel electrode (SCE) in a given solvent were computed as follows:

**Oxidation potential**

\[
E_{1/2}(P^+/P) = \frac{g_{\text{electron}} + g_{P^+}^{\text{solv}} - g_{P}^{\text{solv}}}{F} - E_{\text{SCE}}\]

**Reduction potential**

\[
E_{1/2}(P/P^-) = \frac{g_{\text{electron}} + g_{P^-}^{\text{solv}} - g_{P}^{\text{solv}}}{F} - E_{\text{SCE}},
\]


\(^{46}\) (a) Scaling factor \(\alpha=1.45\) is used for MeCN, see Gryn’ova, G.; Barakat, J. M.; Blinco, J. P.; Bottle, S. E.; Coote, M. L. Computational Design of Cyclic Nitroxides as Efficient Redox Mediators for Dye-Sensitized Solar Cells. *Chem. Eur. J.* 2012, 18, 7582-7593. (b) Scaling factor \(\alpha=1.30\) is used for DCM, see Luque, F. J.; Zhang, Y.; Alemán, C.; Bachs, M.; Gao, J.; Orozco, M. J. *Phys. Chem. 1996, 100, 4269-4276.*
where $G_{\text{electron}}$ is the gas-phase Gibbs free energy of an electron, equal under Fermi-Dirac statistics to $-3.632$ kJ mol$^{-1}$, $G_{\text{soln}}$ are the Gibbs free energies of the neutral compound (P), its cation radical ($P^+$) and anion radical ($P^-$) in solution, $F$ is the Faraday constant equal to $96.485$ kJ V$^{-1}$, $E_{\text{SCE}}$ is the absolute potential of SCE in a given solvent (4.429 eV in acetonitrile$^{48}$ and 4.462 eV in dichloromethane$^{49}$).

Results. Computed redox energetics (Figure 24) indicate that one-electron removal becomes harder (higher $E_{1/2}(P^+/P)$) and one-electron addition becomes easier (higher $E_{1/2}(P/P^-)$) in the order of $4a < 4b < 4c < 4d$, i.e. $H < F < Cl < Br$ substituents in the $3'$ and $6'$ (i.e., para-) positions in carbazole rings. A possible explanation of the observed trends is as follows:

- Upon oxidation/ionization, an electron is removed from the peripheral carbazole moieties (Figure 25), in which the stronger resonance donors, such as Cl and Br, stabilize the formed radical cation better. This is reflected in the average Hirshfeld spin densities of the hydrogen and halogen atoms in the $3'$ and $6'$ positions in the carbazole rings: 0.002 on H-atoms in $4a$, 0.010 on F in $4b$, 0.019 on Cl in $4c$ and 0.023 on Br in $4d$.

- Upon reduction, an electron is added to the lowest unoccupied molecular orbital (LUMO), located mostly on the central isophthalonitrile ring (Figure 25). It also involves the carbazole moieties in the 4 and 6 positions of the isophthalonitrile ring and is potentially stabilized by them to a greater extent in the case of Cl and Br substituents (resonance donors) compared to H and F.

Figure 24. Computed oxidation and reduction potentials vs. SCE at 25 °C in acetonitrile and dichloromethane.


Figure 25. Molecular structures of the parent dyes (P) and their HOMO and LUMO plots (isovalue 0.02), as well as the spin densities and electrostatic potential maps (isovalue 0.001) of the products of one-electron addition (P−) and removal (P+), all at the PBE0/def2-SVP level.

Table 5. Computed oxidation and reduction potentials in acetonitrile, N,N-dimethylformamide and dichloromethane vs. SCE at 25 °C (based on PBE0-D3BJ/def2-SVP gas-phase Gibbs free energies and PCM-UAKS/PBE0/6-31G(d) Gibbs free energies of solvation). All values are in eV.

<table>
<thead>
<tr>
<th></th>
<th>MeCN</th>
<th>DCM</th>
</tr>
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<tr>
<td></td>
<td>(E_{1/2}(P^-/P))</td>
<td>(E_{1/2}(P/P^+))</td>
</tr>
<tr>
<td>4a</td>
<td>1.56</td>
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</tr>
<tr>
<td>4b</td>
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<tr>
<td>4c</td>
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<tr>
<td>4d</td>
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<td>-0.83</td>
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Table 6. Computed Gibbs free energies (PBE0-D3BJ/def2-SVP) of oxidation and reduction at 25 °C in the gas phase and solution (PCM-UAKS/PBE0/6-31G(d)). All values are in eV.

<table>
<thead>
<tr>
<th></th>
<th>Oxidation gas phase</th>
<th>Reduction gas phase</th>
<th>MeCN</th>
<th>DCM</th>
<th>MeCN</th>
<th>DCM</th>
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<tr>
<td>4a</td>
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<td>7.00</td>
<td>5.99</td>
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<tr>
<td>4b</td>
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<td>6.10</td>
<td>6.14</td>
<td>2.27</td>
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<tr>
<td>4c</td>
<td>7.37</td>
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<td>6.22</td>
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<td>3.33</td>
</tr>
<tr>
<td>4d</td>
<td>7.46</td>
<td>7.46</td>
<td>6.32</td>
<td>6.33</td>
<td>2.78</td>
<td>3.60</td>
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<td>DCM</td>
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<tr>
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<tr>
<td></td>
<td>S(^{298}), J mol(^{-1}) K(^{-1})</td>
<td>TC(^{298}), kJ mol(^{-1})</td>
<td>ZPVE, kJ mol(^{-1})</td>
<td>E, Hartree</td>
<td>(\Delta G^{298}_{\text{solv}}), kcal mol(^{-1})</td>
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Table 7. Interatomic distances in the optimized geometries and crystal structures of the studied dyes, in Å.

Table 8. Computed gas-phase entropies, thermal corrections, zero-point vibrational energies and electronic energies (PBE0-D3BJ/def2-SVP) and Gibbs free energies of solvation (PCM-UAKS/PBE0/6-31G(d)) for all studied species.
4a_cr_opt

\( |C56H32N6(1+,2)\rangle \)
9. Spectra for new compounds

$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, DMSO-$d_6$)

$^{13}$C-NMR (101 MHz, DMSO-$d_6$)
$^{19}$F NMR (376 MHz, DMSO-$d_6$)
$^{1}$H-NMR (400 MHz, DMSO-$d_6$)

$^{19}$F NMR (376 MHz, DMSO-$d_6$)
$^{1}$H-NMR (400 MHz, DMSO-$d_6$)

$^{13}$C-NMR (101 MHz, DMSO-$d_6$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

![NMR spectrum of 12b]

$^{13}$C-NMR (101 MHz, Chloroform-$d$)

![NMR spectrum of 12b]
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

12d

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

12e

$^{13}$C-NMR (101 MHz, Chloroform-$d$)

12e
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-d)

$^{13}$C-NMR (101 MHz, Chloroform-d)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^{1}H$-NMR (400 MHz, Chloroform-$d$)

![NMR Spectrum for $^{1}H$-NMR]

$^{13}C$-NMR (101 MHz, Chloroform-$d$)

![NMR Spectrum for $^{13}C$-NMR]
\textbf{\(1^H\)-NMR (400 MHz, Chloroform-\textit{d})}

\begin{align*}
\text{Ph} & \\
\text{NH\text{Boc}} & \\
\text{13d} & \\
\end{align*}

\textbf{\(1^3C\)-NMR (101 MHz, Chloroform-\textit{d})}

\begin{align*}
\text{Ph} & \\
\text{NH\text{Boc}} & \\
\text{13d} & \\
\end{align*}
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

(+/-) 13f

$^{13}$C-NMR (101 MHz, Chloroform-$d$)

(+/-) 13f
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Acetonitrile-$d_6$)

$^{13}$C-NMR (101 MHz, Acetonitrile-$d_6$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^{19}\text{F-NMR (376 MHz, Chloroform-}d\text{)}$
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^{19}$F-NMR (376 MHz, Chloroform-$d$)
**S111**

**1H-NMR (400 MHz, Chloroform-d)**

![1H-NMR spectrum](image)

**13C-NMR (101 MHz, Chloroform-d)**

![13C-NMR spectrum](image)
$^{1}H$-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^{19}$F-NMR (376 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-d)

$^{13}$C-NMR (101 MHz, Chloroform-d)
$^{19}$F NMR (376 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^{19}$F-NMR (376 MHz, Chloroform-\textit{d})
$^1$H-NMR (400 MHz, Chloroform-$d$)

![NMR spectrum](image)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)

![NMR spectrum](image)
$^{19}$F-NMR (376 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-\textit{d})

\begin{center}
\includegraphics[width=\textwidth]{1H-NMR.png}
\end{center}

$^{13}$C-NMR (101 MHz, Chloroform-\textit{d})

\begin{center}
\includegraphics[width=\textwidth]{13C-NMR.png}
\end{center}
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)
$^1$H-NMR (400 MHz, Chloroform-$d$)

$^{13}$C-NMR (101 MHz, Chloroform-$d$)