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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 CD_3OD_2 , 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 hold 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 silvl 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.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.02 (dd, 1 H, *J* = 7.7, 1.4 Hz, Ar*H*), 7.97 (m, 1 H, Ar*H*), 7.85 (dd, 1 H, *J* = 8.2, 0.7 Hz, Ar*H*), 7.71 (td, 1 H, *J* = 7.6, 1.2 Hz, Ar*H*); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4; IR v 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

¹H NMR (400 MHz, CDCl₃) δ 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR v 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 **23** corresponded to the literature values.²

1-[Phenylethynyl]-1,2-benziodoxol-3(1*H*)-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_2Cl_2 (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.

² J. P Brand, C. Chevalley, R. Scopelliti, J. Waser, Chem. Eur. J. 2012, 18, 5655.

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 NaHCO₃ (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. NaHCO₃ (100 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by filtration and boiled in CH₃CN (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. ¹H 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). ¹³C 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.⁴

Triisopropylsilyl trimethylsilylacetylene (26)

$$= SiMe_3 \xrightarrow{\ ^n BuLi, \ 'Pr_3SiCl} Me_3Si = Si'Pr_3$$

$$THF$$
25
$$-78^{\circ}C \rightarrow 0^{\circ}C$$

$$Overnight$$

$$26$$

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 MgSO₄, 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.

¹H NMR (400 MHz, CDCl₃) δ 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR v 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

³ C J. Helal, P A. Magriotis, E J. Corey, J. Am. Chem. Soc. **1996**, 118, 10938.

⁴ J. P. Brand, J. Waser, Angew. Chem., Int. Ed. 2010, 49, 7304.

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 CH_2Cl_2 (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, Ar*H*), 8.29 (m, 1 H, Ar*H*), 7.77 (m, 2 H, Ar*H*), 1.16 (m, 21 H, TIPS). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.4, 134.6, 132.3, 131.4, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1. IR v 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1584 (m), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 883 (m), 833 (m), 742 (m), 702 (s), 636 (m); Characterization data of **5b** corresponded to the literature values.⁴

1-[4-Fluorophenylethynyl]-1,2-benziodoxol-3(1*H*)-one (5c)



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-fluorophenyl)ethynyl)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, Ar*H*), 8.29 – 8.16 (m, 1H, Ar*H*), 7.85 – 7.69 (m, 2H, Ar*H*), 7.68 – 7.53 (m, 2H, Ar*H*), 7.17 – 7.05 (m, 2H, Ar*H*). 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)

⁵ K. Jia, F. Zhang, H. Huang, Y. Chen, J. Am. Chem. Soc. 2016, 138, 1514–1517.

⁶ F. Le Vaillant, T. Courant, J. Waser, Angew. Chem. Int. Ed. 2015, 54, 11200–11204.



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 3 h, followed by the drop wise addition of ((4-bromophenyl)ethynyl)trimethylsilane (**27**) (1.17 g, 5.50 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 **5d** (1.0 g, 2.3 mmol, 47%) as a pale yellow solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 – 8.30 (m, 1 H, Ar*H*), 8.30 – 8.13 (m, 1 H, Ar*H*), 7.84 – 7.72 (m, 2 H, Ar*H*), 7.58 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.46 (d, *J* = 8.5 Hz, 2 H, Ar*H*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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.⁶

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



Following a reported procedure,⁵ 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 CH₂Cl₂ (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 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 recrystallized in CH₃CN (ca 20 mL) to afford **5e** (850 mg, 2.04 mmol, 51%) as a pale yellow solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 – 8.38 (m, 1 H, Ar*H*), 8.28 – 8.19 (m, 1 H, Ar*H*), 7.84 – 7.74 (m, 2 H, Ar*H*), 7.74 – 7.65 (m, 4 H, Ar*H*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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.⁷

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

⁷ B. Lu, J. Wu, N. Yoshikai, J. Am. Chem. Soc. 2014, 136, 11598.



Following a slightly modified procedure,⁸ 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_2Cl_2 (20 mL) and stirred vigorously with NaHCO₃ 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_2Cl_2 (2x50 mL). The combined organic layers were washed with sat. NaHCO₃, dried over MgSO₄, 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.45 – 8.40 (m, 1H, Ar*H*), 8.28 – 8.21 (m, 1H, Ar*H*), 7.79 – 7.74 (m, 2H, Ar*H*), 7.56 – 7.48 (m, 2H, Ar*H*), 7.26 – 7.23 (m, 2H, Ar*H*), 2.71 – 2.60 (m, 2H, ArC*H*₂), 1.69 – 1.54 (m, 2H, ArCH₂C*H*₂), 1.40 – 1.27 (m, 4H, C*H*₂C*H*₂CH₃), 0.90 (t, *J* = 6.8 Hz, 3H, CH₂C*H*₃). ¹³C 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 v 3446 (m), 3359 (w), 2349 (w), 1644 (s), 1482 (m), 1327 (m), 1214 (m), 1121 (m), 1034 (m), 840 (s), 753 (m). HRMS (ESI) calcd for C₂₀H₂₀IO₂⁺ [M+H]⁺ 419.0503; found 419.0496.

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



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 ((3-fluorophenyl)ethynyl)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 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

⁸ M. J. Bouma, B. Olofsson, Chem. Eur. J. 2012, 18, 14242 – 14245.

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. ¹H NMR (400 MHz, DMSO- d_6) δ 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 (ddd, 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*). ¹³C NMR (101 MHz, DMSO- d_6)⁹ 166.3, 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. ¹⁹F NMR (376 MHz, (CD₃)₂SO) δ -111.7. IR v 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 C₁₅H₉FIO₂⁺ 366.9626; Found 366.9625.

1-[2-Bromophenylethynyl]-1,2-benziodoxol-3(1*H*)-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 CH₂Cl₂ (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 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 the collected solid was dried under high vacuum to afford **5h** (1.50 g, 3.51 mmol, 70%) as a colorless solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 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*).¹³C NMR (101 MHz, Chloroform-*d*)⁹ δ 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-iodosylbenzoic acid (**23**) (1.19 g, 4.49 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-formylphenyl)ethynyl)trimethylsilane (**33**) (1.00 g, 4.94 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 **5i** (0.80 g, 2.1 mmol, 41%) as a yellow solid.

¹H NMR (400 MHz, DMSO- d_6) δ 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). ¹³C NMR (101 MHz, DMSO- d_6) δ 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-iodobenzonitrile (**34**) (1.00 g, 4.37 mmol, 1.0 equiv) was dissolved in triethylamine (10 mL) (without prior drying). After three freeze-thraw-pump cycles, PdCl₂(PPh₃)₂ (92 mg, 0.13 mmol, 3 mol%) and copper iodide (42 mg, 0.22 mmol, 5 mol%) were added under N₂. 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 CH₂Cl₂ (30 mL), washed with a saturated ammonium chloride solution (30 mL) and water (30 mL). The organic layers were then dried over MgSO₄, filtered and concentrated under vacuum. The resulting oil was purified by column chromatography (pentane/ethyl acetate 25:1) to afford 4-((trimethylsilyl)ethynyl)benzonitrile (**35**) (847 mg, 4.25 mmol, 97%) as a white solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.7 Hz, 2H, Ar*H*), 7.53 (d, *J* = 8.8 Hz, 2H, Ar*H*), 0.26 (s, 9H, SiC*H*₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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)



¹⁰ H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Chen, J. Am. Chem. Soc. 2014, 136, 2280-2283.

¹¹ Y. Feng, C. Xie, W.-L. Qiao, and H.-J. Xu, Org. Lett. **2013**, 15, 936-939.

¹² R. Rahaim and J. Shaw, J. Org. Chem. 2008, 73, 2912–2915.

Following a reported procedure,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 CH₂Cl₂ (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 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 **5**j (865 mg, 2.32 mmol, 64%) as a pale brown solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.34 (d, *J* = 8.2 Hz, 1H, Ar*H*), 8.13 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.99 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.90 (d, *J* = 8.6 Hz, 3H, Ar*H*), 7.81 (t, *J* = 7.3 Hz, 1H, Ar*H*). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.3, 135.3, 133.3, 132.8, 131.9, 131.4, 131.4, 127.8, 125.3, 118.2, 116.4, 112.7, 102.0, 57.4. Consistent with reported data.⁵

PhVBX (14)



Following a reported procedure,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 CH₂Cl₂ (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 NaHCO₃ solution (25 mL) was added and the mixture was stirred for 1 h. The mixture was diluted with CH₂Cl₂ (25 mL) and H₂O (25 mL) and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL) and the combined organic layers were washed with brine, dried (Mg₂SO₄) 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%).

¹H NMR (400 MHz, Methanol- d_4) δ 8.28 (dd, J = 5.8, 3.4 Hz, 1H, Ar*H*), 7.96 (d, J = 15.4 Hz, 1H, Ar*H*), 7.74 (dd, J = 5.9, 3.5 Hz, 1H, Ar*H*), 7.70 (dd, J = 7.5, 3.5 Hz, 4H, Ar*H*), 7.66 (d, J = 8.7 Hz, 1H, Ar*H*), 7.49 (dd, J = 5.1, 2.0 Hz, 3H, Ar*H*). The NMR shifts match the literature data.¹²

¹³ E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. Eur. J.* **2016**, *18*, 16066-16070.

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



Following a reported procedure,¹⁴ 1-hydroxy-1,2-benziodoxol-3-(1*H*)-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.

¹H NMR (CDCl₃, 400 MHz): δ 8.24 (dd, 1 H, *J* = 7.6, 1.6 Hz, Ar*H*), 8.00 (dd, 1 H, *J* = 8.3, 1.0 Hz, Ar*H*), 7.92 (ddd, 1 H, *J* = 8.4, 7.2, 1.6 Hz, Ar*H*), 7.71 (td, 1 H, *J* = 7.3, 1.1 Hz, Ar*H*), 2.25 (s, 3 H, COC*H*₃). ¹³C NMR (CDCl₃, 100 MHz): δ 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-(1*H*)-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 μ L, 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.

¹⁴ P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579.

¹⁵ M. Chen, Z. T. Huang, Q. Y. Zheng, Org. Biomol. Chem. 2015, 13, 8812.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.29 (d, J = 8.3 Hz, 1 H, Ar*H*), 8.13 (dd, J = 7.4, 1.7 Hz, 1 H, Ar*H*), 8.06-7.97 (m, 1 H, Ar*H*), 7.88 (t, J = 7.3 Hz, 1 H, Ar*H*). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 166.7, 136.5, 132.0, 131.9, 130.2, 127.8, 117.5, 87.9. IR v 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.¹⁵

tBu PF_6 38 tBu 40 tBu IrCl₃ C DME/H₂O 2:1 Ethylene glycol, 120 °C. 15 h 180 °C, 15 h tBu CF_3 2 2 39 1

[Ir{dF(CF₃)ppy}₂(dtbpy)]PF₆ (1)

Following a reported procedure,¹⁶ 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-PF₆ salt to precipitate, which was filtered, dried and recrystallized (acetone/ether), affording **1** (117 mg, 0.104 mmol, 78%) as a yellow solid.

¹H NMR (400 MHz, Acetone- d_6) δ 9.01 (d, J = 7.6 Hz, 2H, ArH), 8.64 (dd, J = 8.8, 2.5 Hz, 2H, ArH), 8.47–8.38 (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). ¹H NMR matches the literature data.¹⁶

¹⁶ A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* **2015**, 776, 51–59

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)



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, Ar*H*), 7.8 – 7.6 (m, 8H, Ar*H*), 7.5 (ddd, J = 8.0, 6.6, 1.6 Hz, 2H, Ar*H*), 7.3 (d, J = 7.5 Hz, 2H, Ar*H*), 7.2 (dd, J = 8.4, 1.5 Hz, 4H, Ar*H*), 7.2 – 7.0 (m, 8H, Ar*H*), 6.8 (t, J = 7.8 Hz, 4H, Ar*H*), 6.6 (td, J = 7.6, 1.2 Hz, 2H, Ar*H*). 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-9*H***-carbazole (7b)**

¹⁷ H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234–238.



Following a reported procedure,¹⁸ 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 K₂CO₃ (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.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 6.89 (m, 8H, Ar*H*), 5.46 (bs, 1H, N*H*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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.¹⁸

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.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H, N*H*), 7.66 (dd, *J* = 8.9, 2.5 Hz, 2H, Ar*H*), 7.35 (dd, *J* = 8.8, 4.3 Hz, 2H, Ar*H*), 7.18 (td, *J* = 9.0, 2.5 Hz, 2H, Ar*H*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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.¹⁸

¹⁸ K. L. Woon, Z. N. Nadiah, Z. A. Hasan, A. Ariffin, S.-A. Chen. Dyes and Pigments, 2016, 132, 1-6.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-difluoro-9*H*-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 μ mol, 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). ¹H NMR (400 MHz, DMSO-d⁶) δ 8.34 – 8.27 (m, 2H, Ar*H*), 8.09 (dd, *J* = 9.0, 4.2 Hz, 2H, Ar*H*), 7.81 (dd, *J* = 9.0, 2.6 Hz, 3H, Ar*H*), 7.72 – 7.61 (m, 6H, Ar*H*), 7.45 (dd, *J* = 8.9, 2.6 Hz, 2H), 7.36 (dd, *J* = 9.1, 4.2 Hz, 2H, Ar*H*), 7.15 – 7.05 (m, 4H, Ar*H*), 6.73 – 6.63 (m, 3H, Ar*H*).

¹³C NMR not enough material for recording a clean spectra.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -120.6 (s, 2F), -120.8 (s, 4F), -121.5 (s, 2F). IR (v_{max} , 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 C₅₆H₂₄F₈N₆⁺ 932.1929; Found 932.1955.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-dichloro-9*H*-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/CH₂Cl₂ (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.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.60 (d, *J* = 2.1 Hz, 2H, Ar*H*), 8.15 (d, *J* = 2.1 Hz, 4H, Ar*H*), 8.08 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.87 (dd, *J* = 8.8, 2.1 Hz, 2H, Ar*H*), 7.80 (d, *J* = 2.2 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.8 Hz, 4H, Ar*H*), 7.46 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.32 (dd, *J* = 8.8, 2.2 Hz, 4H, Ar*H*), 6.93 (dd, *J* = 8.8, 2.2 Hz, 2H, Ar*H*). ¹³C 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) calcd for C₅₆H₂₄Cl₈N₆ [M+] 1059.9565; found 1059.9573.

¹H NMR shift in CDCl₃ are consistent with reported data.¹⁹ However, for better solubility and better resolution new ¹H and ¹³C spectra were recorded in DMSO-*d*₆.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-dibromo-9*H*-carbazol-9-yl)isophthalonitrile (4BrCzIPN, 4d)



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-9*H*-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). ¹H 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). ¹³C NMR (101 MHz, DMSO- d_6) δ 145.0, 144.5, 138.6, 137.7, 136.8, 135.9, 130.4, 129.1, 128.0, 124.7, 124.2, 123.9, 123.8, 116.8, 115.0, 114.4, 113.6, 112.9, 112.7, 111.7. NMR matches the literature data.¹⁹

¹⁹ A. Kretzschmar, C. Patze, S. T. Schwaebel, and U. H. F. Bunz J. Org. Chem. **2015**, *80*, 9126–9131.

4. Physical measurement

Spectroscopic characterization

4CzIPN derivatives were studied at 10 μ mol.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.



Figure 2. Zoom on the 250-550 nm region of the UV-Vis spectra of 4CzIPN derivatives in DCM.



Figure 3. Absorbance and emission of 4CzIPN at 10 μ mol.L⁻¹ in DCM.



Figure 4. Absorbance and emission of 4ClCzIPN at 10 μ mol.L⁻¹ in DCM.



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



Figure 6. Absorbance and emission of 4FCzIPN at 10 μ mol.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 μ mol.L⁻¹ in acetonitrile.



Figure 11. Absorbance and emission of 4BrCzIPN at 10 µmol.L⁻¹ in acetonitrile.

Electrochemical measurements

Cyclic Voltammetry (CV) was performed using an Autolab Potentiostat, with a threeelectrode 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_4NPF_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.^{20,19} 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.²¹ Voltammograms 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_pmax , 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.

²⁰ R. Ishimatsu, S. Matsunami, T. Kasahara, J. Mizuno, T. Edura, C. Adachi, K.Nakano and T. Imato, *Angew, Chem, Int. Ed.* **2014**, *53*, 6993-6996.

²¹ J. Davies, N. S. Sheikh and D. Leonori, Angew. Chem. Int. Ed. 2017, 56, 13361–13365.

| Photocatalyst | $E_{1/2}(P/P^{-})$ | $E_{1/2}(P^+/P)$ | E ₀₋₀ | $E_{1/2}(P^+/P^*)$ | $E_{1/2}(P^*/P^-)$ | |
|--|---|---|--|--|--|--|
| 4CzIPN ²² | -1.21 | +1.52 | 2.56 | -1.04 | +1.35 | |
| 4CzIPN _{exp} | -1.05 | +1.68 | 2.64 | -0.96 | +1.59 | |
| 4ClCzIPN | -0.97 | +2.05 | 2.68 | -0.63 | +1.71 | |
| Table 1. Redox potentials of 4CzIPN derivatives in acetonitrile ^a | | | | | | |
| | | | | | | |
| Photocatalyst | E _{1/2} (P/P ⁻) | E _{1/2} (P ⁺ / P) | E ₀₋₀ | E _{1/2} (P ⁺ / P *) | E _{1/2} (P*/P ⁻) | |
| Photocatalyst 4CzIPN | E _{1/2} (P/P ⁻) -1.16 | E _{1/2} (P ⁺ /P) +1.61 | E ₀₋₀ 2.59 | E _{1/2} (P ⁺ /P*) -0.98 | E _{1/2} (P*/P ⁻) +1.43 | |
| Photocatalyst 4CzIPN 4ClCzIPN | E _{1/2} (P/P ⁻) -1.16 -1.11 | E _{1/2} (P ⁺ /P) +1.61 +1.73 | E ₀₋₀ 2.59 2.59 | E _{1/2} (P ⁺ /P*) -0.98 -0.86 | E _{1/2} (P*/P ⁻) +1.43 +1.48 | |
| Photocatalyst 4CzIPN 4ClCzIPN 4BrCzIPN | E _{1/2} (P/P ⁻) -1.16 -1.11 -1.06 | E _{1/2} (P ⁺ /P) +1.61 +1.73 +1.76 | E ₀₋₀ 2.59 2.59 2.58 | E _{1/2} (P ⁺ /P*) -0.98 -0.86 -0.82 | E _{1/2} (P*/P ⁻) +1.43 +1.48 +1.52 | |

Table 2. Redox potentials of 4CzIPN derivatives in DCM^a

^aPotentials 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 4FCzIPN.



Figure 12. Cyclic Voltammetry of 4ClCzIPN in acetonitrile.

²² J. Luo and J. Zhang, ACS Catal. 2016, 6, 873–877.



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.



Table 3. Electrochemical potentials of the oximes in DMF.²³



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

²³ The potassium carboxylate salts were prepared by treatment of the corresponding acids with 1 equivalent of ^tBuOK 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,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-dioxoisoindolin-2-yl)oxy)-2-methylpropanoate (44) (14.1 g, 50.8 mmol, 92% yield) was obtained as a pale brown-colored solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.88 (s, 4H; Ar*H*), 4.13 (q, *J* = 7.1 Hz, 2H; OC*H*₂CH₃), 1.51 (s, 6H, C(*CH*₃)₂), 1.22 (t, *J* = 7.1 Hz, 3H; OCH₂C*H*₃). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 170.0, 164.4, 135.1, 128.6, 123.5, 86.1, 61.4, 22.7, 13.8. IR (vmax, 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 (m), 789 (w), 765 (w), 943 (w), 859 (w).

Ethyl 2-((1,3-dioxoisoindolin-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-

²⁴ L. Jiang, J. Yang, Z. Shumin, Synthesis of Oxoamino-Aliphatic Carboxylic Acids, 1991, CN1051170 (A).

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

¹H NMR (400 MHz, DMSO- d_6 ; the signals corresponding to carboxylic and amine ¹Hs were not resolved) δ 1.46 (s, 6H, *CH*₃). ¹³C NMR (101 MHz, DMSO- d_6) δ 173.6, 82.5, 23.2. IR (v_{max}, cm⁻¹) 3440 (m), 2972 (m), 2897 (m), 2648 (w), 2299 (w), 1719 (s), 1757 (m), 1152 (s), 747 (m), 847 (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 MgSO₄, 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.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.98 (s, 1H, CO₂*H* or CON*H*), 11.91 (s, 1H, CO₂*H* or CON*H*), 7.76 (d, *J* = 7.6 Hz, 2H, Ph*H*), 7.54 (t, *J* = 7.4 Hz, 1H, Ph*H*), 7.45 (t, *J* = 7.6 Hz, 2H, Ph*H*), 4.53 (q, *J* = 6.9 Hz, 1H, *CH*CH₃), 1.40 (d, *J* = 6.9 Hz, 3H, *CH*₃). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 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

²⁵ H. Jiang, A. Studer, Angew. Chem. Int. Ed. 2017, 56, 12273–12276.

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).

¹H NMR (400 MHz, Deuterium Oxide) δ 4.70 (q, J = 6.9 Hz, 1H, *CH*CH₃), 1.46 (t, J = 6.9 Hz, 3H, CH*CH*₃). ¹³C NMR (101 MHz, DMSO- d_6) δ 171.8, 77.1, 16.4. The values for the ¹H-NMR spectrum are in roughly agreement with the data reported in the literature (small differences are likely due to concentration effects).²⁵

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-(aminooxy)-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, CO₂*H*), 3.02 – 2.81 (m, 4H, CH₂CH₂CH₂CH₂C=N), 2.02 (p, *J* = 8.1 Hz, 2H, CH₂CH₂CH₂), 1.50 (s, 6H, *Me*₂). 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-

²⁶ E. M. Dauncey, S. P. Morcillo, J. J. Douglas, N. S. Sheikh, D. Leonori, *Angew. Chem. Int. Ed.* **2018**, *57*, 744–748.

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, CO₂*H*), 4.63 (q, *J* = 7.1 Hz, 1H, OC*H*), 3.09 – 2.77 (m, 4H, C*H*₂CH₂C*H*₂C=N), 2.00 (p, *J* = 8.4 Hz, 2H, CH₂C*H*₂CH₂), 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 (v_{max}, cm⁻¹) 2995 (m), 2934 (m), 2559 (w), 1727 (s), 1689 (m), 1455 (m), 1403 (w), 1330 (m), 1229 (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-1] 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, CO₂*H*), 7.38 - 7.32 (m, 2H, Ph*H*), 7.29 - 7.25 (m, 3H, Ph*H*), 3.64 (p, *J* = 8.4 Hz, 1H, Ph*CH*), 3.50-3.35 (m, 2H, *CH*₂), 3.10 (m, 1H, *CH*₂), 3.06 (ddd, *J* = 7.7, 4.9, 3.4 Hz, 1H, *CH*₂), 1.54 (s, 6H, *CH*₃). 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 (vmax, cm-1) 1694 (w), 1582 (w), 1482 (w), 1420 (w), 1333 (w), 1270 (m), 1214 (w), 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), 3365 (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,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 (elution with only heptane) showed the (almost) complete conversion of the starting material and the formation of a major product. The reaction was therefore stopped and the mixture diluted with diethyl ether (20 mL) and the solids were filtered off through a plug of celite and washed with diethyl ether. The filtrate was then washed with water (2 x 20 mL), sat. aq. NaHCO₃ (4 x 20 mL), and brine; it was then dried over MgSO₄, filtered and concentrated under vacuum. Column chromatography (25 g SiO₂; 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (m, 2H, Ph*H*), 7.35 (m, 1H, Ph*H*), 7.29 (m, 2H, Ph*H*), 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 ¹H-NMR spectrum are in roughly agreement with the data reported in the literature.²⁸

Following a reported procedure, 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 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 9/1) 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 pad of celite. The filtrate was concentrated under reduced pressure, diluted with aq. HCl (1.0 M; 15 mL) and extracted with diethyl ether (3 x 15 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum. The resulting crude oil was submitted to column chromatography (40 g SiO₂; EtOAc in pentane 1 to 20%) to afford 3-methyl-3-phenylcyclobutanone (**52**) (0.438 g, 2.73 mmol, 45% yield) as colorless oil.

Rf (Pentane/EtOAc 9/1) 0.70. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, J = 8.1, 6.9 Hz, 2H, Ph*H*), 7.33 (m, 2H, Ph*H*), 7.27 (m, 1H, Ph*H*), 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 ¹H-NMR spectrum are in roughly agreement with the data reported in the literature ³⁰

²⁷ J. Boivin, E. Fouquet, S. Z. Zard, *Tetrahedron* **1994**, *50*, 1757–1768.

²⁸ W. Cao, I. Erden, R. H. Grow, J. R. Keeffe, J. Song, M. B. Trudell, T. L. Wadsworth, F.-P. Xu, J.-B. Zheng, *Can. J. Chem.* **1999**, 77, 1009–1034.

²⁹ B. D. Johnston, K. N. Slessor, A. C. Oehlschlager, J. Org. Chem 1985, 50, 114-117.

³⁰ H.-J. Xu, F.-F. Zhu, Y.-Y. Shen, X. Wan, Y.-S. Feng, *Tetrahedron* **2012**, *68*, 4145–4151.

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. ¹H NMR (400 MHz, Chloroform-*d*) δ 11.04 (s, 1H, CO₂*H*), 7.38 - 7.32 (m, 2H, Ph*H*), 7.28 - 7.20 (m, 3H, Ph*H*), 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). ¹³C 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 (v_{max}, cm⁻¹) 3608 (w), 2986 (m), 2930 (m), 2567 (w), 2684 (w), 1716 (s), 1593 (m), 1488 (m), 1168 (s), 971 (s), 1297 (m), 1408 (m), 1248 (w), 1371 (m), 730 (s), 872 (m), 909 (s), 699 (s), 749 (m). HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₅H₂₀NO₃⁺ 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). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.40 (s, 1H, CO₂*H*), 7.38 (d, *J* = 7.4 Hz, 1H, N*H*), 4.03 (q, *J* = 7.4 Hz, 1H, C*H*NHBoc), 3.19 – 2.98 (m, 2H, C*H*₂), 2.83 – 2.66 (m, 2H, C*H*₂), 1.39 (s, 9H, N*Boc*), 1.36 (s, 3H, C*Me*₂)., 1.35 (s, 3H, C*Me*₂). ¹³C 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 (v_{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 C₁₃H₂₂N₂NaO₅⁺ [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 anthranylic 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 (icewater bath). Aq. HCl (37% v/v; 0.45 mL, 5.5 mmol, 1.0 equiv) was added via pipette (the reaction mixture darkened from vellowish 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 MgSO₄, filtered and concentrated under vacuum. The resulting crude oil was submitted to column chromatography (25 g SiO₂; 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 - 7.47 (m, 2H, Ar*H*), 7.38 (t, J = 7.5 Hz, 1H, Ar*H*), 7.32 (dd, J = 7.6, 1.0 Hz, 1H, Ar*H*), 4.00 - 3.92 (m, 2H, Ar*CH*₂). ¹³C NMR (101 MHz, Chloroform-*d*) δ 188.7, 151.3, 147.9, 135.2, 128.7, 123.7, 120.6, 52.3.

³¹ M. S. South, L. S. Liebeskind, J. Org. Chem. 1982, 47, 3815–3821.

³² O. Abou-Teim, M. C. Goodland, J. F. W. McOmie, J. Chem. Soc. Perkin Trans. 1 1983, 2659–2662.

The values for the ¹H-NMR spectrum are in roughly agreement with the data reported in the literature.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-methylpropanoic 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. ¹H NMR (400 MHz, Chloroform-*d*; the signals corresponding to the minor isomer are reported in *italics*) δ 10.73 (br s, 1 H, CO₂*H*), 7.42 (dd, *J* = 13.2, 7.3 Hz, 2H, Ar*H*), 7.32 (q, *J* = 9.7, 8.7 Hz, 2H, Ar*H*), 3.91 (s, 2H, Ar*CH*₂), 3.89 (s, 2H, Ar*CH*₂), 1.63 (s, 6H, *CH*₃), 1.59 (s, 6H, *CH*₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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 (v_{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-1]⁺ Calcd for C₁₂H₁₂NO₃⁺ 218.0817; Found 218.0817.

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



Following a modified version of a reported procedure,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. NaHCO₃ (4 x

³³ K. Nishikawa, H. Fukuda, M. Abe, K. Nakanishi, Y. Tazawa, C. Yamaguchi, S. Hiradate, Y. Fujii, K. Okuda, M. Shindo, *Phytochemistry* **2013**, *96*, 223–234.
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-1*H*-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, Ar*H*), 7.34 – 7.30 (m, 2H, Ar*H*), 7.27 (m, 1H, Ar*H*), 4.50 (dd, *J* = 8.0, 1.5, 2H, Ar*CH*₂), 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]⁺ Calcd 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-1*H*-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 reduced pressure, diluted with aq. HCl (1.0 M; 20 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and 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-1*H*-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, Ar*H*), 7.25 - 7.20 (m, 3H, Ar*H*), 4.07 (m, 1H, (CO)*CH*), 4.05 (d, J = 1.3 Hz, 1H, Ar*CH*), 3.61 (m, 1H, *CH*₂), 3.31 (dt, J = 16.9, 1.4 Hz, 1H, *CH*₂), 3.12 (m, 1H, *CH*₂), 2.89 (m, 1H, *CH*₂). 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-1*H*-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 (inseparable 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, CO₂*H*), 7.34 - 7.21 (m, 4H, Ar*H*), 4.09 - 3.88 (m, 1.6H, CH or CH₂), 3.57 (ddd, *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

³⁴ M. D. Lawlor, T. W. Lee, and R. L. Danheiser, J. Org. Chem., 2000, 65, 4375–4384.

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



Starting from oxetanone (60) (85 μ L, 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.77 (s, 1H, CO₂*H*), 5.33 (dd, *J* = 3.7, 2.3 Hz, 2H, CH₂OCH₂), 5.29 (dd, *J* = 3.2, 2.1 Hz, 2H, CH₂OCH₂), 1.51 (s, 6H, *Me*₂). ¹³C NMR (101 MHz, Chloroform-*d*) δ 179.3, 153.8, 81.4, 79.1, 78.9, 23.8. IR (v_{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 C₁₈H₁₅NNa⁺ [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 ¹H NMR (400 MHz, Chloroform-*d*) δ 10.42 (br s, 1H, CO₂*H*), 4.64 (d, *J* = 3.3 Hz, 3H, NC*H*₂), 4.62 (d, *J* = 2.8 Hz, 2H, NC*H*₂), 1.52 (s, 6H, *CH*₃), 1.46 (s, 9H, *CH*₃ in Boc). ¹³C NMR (101 MHz, Chloroform-*d*; *The signals correspondings to the carbons in* α *to the nitrogen are not fully resolved*.) δ 178.6, 156.3, 149.3, 81.5, 80.7, 58.3, 28.3, 23.9. IR (vmax, 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 C₁₂H₂₀N₂NaO₅⁺ 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 MgSO₄, 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 °C. Rf (Pentane/EtOAc 9/1) 0.71. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, J = 8.2 Hz, 2H, Ar*H*), 7.19 (d, J = 7.9 Hz, 2H, Ar*H*), 4.75 (s, 1H, O*H*), 4.63 (t, J = 6.0 Hz, 1H, *CH*OH), 4.44 - 4.34 (m, 2H, N*CH*₂), 4.18 (dd, J = 9.9, 4.4 Hz, 1H, N*CH*₂), 4.02 (dd, J = 11.2, 4.6 Hz, 1H, N*CH*₂), 2.38 (s, 3H, ArCH₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.4, 141.5, 129.9, 129.0, 127.8, 61.4, 51.9, 21.4. IR (vmax, 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 C₁₁H₁₃NNaO₂⁺ 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

³⁵ S. Kasai, T. Kaku, M. Kamaura, *Heterocyclic Compound as Blood RBP4 Lowering Agent*, **2010**, EP2202223 (A1).

organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum. The resulting yellow crude solid was submitted to column chromatography (25 g SiO₂; 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, J = 8.2 Hz, 2H, Ar*H*), 7.25 (m, 2H, Ar*H*), 4.95 (s, 4H, N(*CH*)₂CO), 2.40 (s, 3H, *CH*₃). ¹³C 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) δ 196.0, 171.2, 142.4, 129.6, 129.3, 128.2, 72.4, 21.5. IR (vmax, cm-1) 3054 (m), 1833 (m), 1655 (w), 1550 (w), 1494 (w), 1420 (w), 1383 (w), 1605 (w), 1266 (m), 1205 (w), 1125 (w), 1057 (m), 1008 (m), 909 (w), 940 (w), 736 (s). HRMS (APCI/QTOF) m/z: [M + H]⁺ Calcd for C₁₁H₁₂NO₂⁺ 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 GP2.

M.p. 158.7-163.0 °C. Rf (DCM/EtOAc 9/1) 0.16. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.63 (br s, 1H, CO₂*H*), 7.55 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.23 (d, *J* = 7.9 Hz, 2H, Ar*H*), 4.93 (s, 2H, N*CH*₂), 4.90 (m, 2H, N*CH*₂), 2.39 (s, 3H, Ar*CH*₃), 1.52 (s, 6H, *CH*₃). ¹³C NMR (101 MHz, Chloroform-*d*; in italics are reported the signals corresponding to the same C in either rotamers) δ 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 (vmax, 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-1]⁺ Calcd for C₁₅H₁₇N₂O₄⁺ 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 GP2.

M.p. 53.4 - 55.5°C ¹H NMR (400 MHz, Chloroform-*d*) δ 11.14 (s, 1H, CO₂*H*), 2.55 (t, *J* = 7.5 Hz, 2H, CH₂C=N), 1.80 (p, *J* = 7.1 Hz, 2H, CH₂CH₂C=N), 1.65 (t, *J* = 6.8 Hz, 2H, CH₂CH₂CH₂C=N), 1.49 (s, 6H, CMe₂COOH), 1.16 (s, 6H, CMe₂). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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(2*H*)-ylidene)amino)oxy)propanoic acid (12k)



Starting from 2-methyldihydrofuran-3(2*H*)-one (66) (129 μ L, 1.33 mmol), 2-methyl-2-(((2-methyldihydrofuran-3(2*H*)-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 11.10 (bs, 1H, CO₂*H*), 4.70 (q, *J* = 6.6 Hz, 0.2H, CH₃*CHO*), 4.33 (q, *J* = 6.3 Hz, 0.8H, CH₃*CHO*), 4.14 (td, *J* = 8.6, 4.0 Hz, 0.8H, OCH₂), 4.08 (dd, *J* = 8.3, 5.3 Hz, 0.2H, OCH₂), 3.94 – 3.77 (m, 1H, OCH₂), 2.84 – 2.59 (m, 2H, NCCH₂), 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). ¹³C NMR (101 MHz, CDCl₃; 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, *22.1*, 18.1, *17.0*, *15.9*. IR (v_{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 C₉H₁₅NNaO₄⁺ 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H, CO₂*H*), 4.11 (s, 1.6H, NC*H*₂), 4.06 (s, 0.4H, NC*H*₂), 3.59 (m, 1.6H, NC*H*₂CH₂), 3.38 (dd, *J* = 10.6, 6.0 Hz, 0.4H, NC*H*₂CH₂), 2.79 (t, *J* = 7.8 Hz, 0.6H, NCH₂C*H*₂), 2.71 (t, *J* = 7.5 Hz, 1H, NCH₂C*H*₂), 2.58 (dd, *J* = 8.3, 3.7 Hz, 0.4H, NCH₂C*H*₂), 1.53 – 1.45 (m, 15H, C*H*₃). ¹³C 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, 28.4, 24.3, 24.1, 22.1, 15.9. IR (v_{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 C₁₃H₂₁N₂O₅⁺ 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_2CO_3 (0.11 mmol, 1.1 equiv) and organic dye (4) (0.05 mmol, 0.05 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. 6 µL of CH₂Br₂ 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%).



| entry | catalyst | base | concentration | solvent | time | conversion ^[a] | yield ^[b] |
|-------------------|----------|---|---------------|---------|-----------|---------------------------|----------------------|
| 1 ^[c] | 1 | 1.0 equiv Cs ₂ CO ₃ | 0.05 | DCE | 2 h | >95% | 50% |
| 2 | 2 | 1.0 equiv Cs ₂ CO ₃ | 0.05 | DCE | 2 h | 50% | 20% |
| 3 | 3 | 1.0 equiv Cs ₂ CO ₃ | 0.05 | DCE | 2 h | >95% | 5% |
| 4 | 4a | 1.0 equiv Cs ₂ CO ₃ | 0.05 | DCE | 2 h – 6 h | 60% | 50% |
| 5 | 4a | 1.0 equiv Cs ₂ CO ₃ | 0.10 | DCE | 2 h | 60% | 40% |
| 6 | 4c | 1.0 equiv Cs ₂ CO ₃ | 0.05 | DCE | 2 h | >95% | 70% |
| 7 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 2 h | >95% | 75% |
| 8 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | >95% | 80% |
| 9 | 4b | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | 90% | 75% |
| 10 | 4d | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | 90% | 75% |
| 11 | 4c | 1.1 equiv KHPO ₄ | 0.05 | DCE | 1 h | <10% | <10% |
| 12 | 4c | 1.1 equiv KOAc | 0.05 | DCE | 1 h | >95% | 70% |
| 13 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCM | 1 h | >95% | 80% |
| 14 | 4c | 1.1 equiv K ₂ CO ₃ | 0.025 | DCM | 1 h | >95% | 45% |
| 15 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | THF | 1 h | >95% | 25% |
| 16 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DMF | 1 h | >95% | 55% |
| 17 ^[e] | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | >95% | 70% |
| 18 | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 30 min | >95% | 80% |
| 19 ^[f] | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | >95% | 80% |
| 20 ^[g] | 4c | 1.1 equiv K ₂ CO ₃ | 0.05 | DCE | 1 h | >95% | 80% |

Table 4: PS: photosensitizer. ^[a]Reaction conditions: Using 0.1 mmol **12a** (1 equiv), 0.2 mmol **5a** (2.0 equiv), 5 mol% **4** (0.05 equiv) in DCE (2.0 mL) for 2 h at RT. The conversion of **12a** by NMR is given. The values for reduction potentials are given in volts for catalyst **4** in relation to SCE, in MeCN. ^[b]NMR yield using dibromomethane as internal standard. ^[c] Using 1 mol% of **1**. ^[e] Using 1.5 equiv. of **5a**. ^[f] Using 3.0 mol% of organic dye **4c**. ^[g] Using oxime **48**.

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

³⁶ B. Lu, J. Wu, N. Yoshikai, J. Am. Chem. Soc. **2014**, 136, 11598–11601.



¹H NMR (400 MHz, Chloroform-*d*) δ 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, OCH₂COAr). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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 C₁₅H₁₁IO₃ [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 ¹H NMR. This product could arise from direct alkynylation, before fragmentation of acetone, followed by hydration of the alkyne moiety. We hypothesize that the fragmentation alkynylation 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%).



¹H NMR (400 MHz, Chloroform-*d*) δ 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, CH₂CO), 2.94 (dt, *J* = 16.8, 7.9 Hz, 4H), 1.99 (p, *J* = 8.1 Hz, 2H), 1.60 (s, 6H, CH₃).



Figure 20. Sun spectra during experiment³⁷



Figure 21. Set-up of the sunlight experiment, December 21st 2017.

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 μ L 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 ($15:30 - 18:00, 25-26^{\circ}C$), under sunlight exposition, the conversion was followed by TLC control (DCM/MeOH 9/1). The crude product was analyzed by NMR, using 6 μ L of CH₂Br₂ as internal standard. (**13h**, 90% NMR yield, <10% remaining starting material **12h**). Clean reaction profile.

³⁷ Capture form <u>http://www.meteolausanne.com/soleil-et-uv.html</u>

Reaction performed on 18th 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 μ L of CH₂Br₂ as internal standard. (**13a**, 75% NMR yield, <5% remaining starting material **12a**). Detection of **69** possible by NMR. Clean reaction profile.



Figure 22. Set-up of the sunlight experiment, May 18th 2018.

One-pot procedure:

A solution of cyclobutanone **11** (23 μ l, 0.30 mmol) in DCE (Volume: 1.5 ml) was treated with 2-(aminooxy)-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 μ L 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



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), K_2CO_3 (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-aminoalkynylnitriles were obtained as mixtures of non-resolved rotamers.

6-Phenylhex-5-ynenitrile (13a)



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, Ar*H*), 7.32 – 7.27 (m, 3H, Ar*H*), 2.60 (t, J = 6.8 Hz, 2H, *CH*₂), 2.56 (t, J = 7.2 Hz, 2H, *CH*₂), 1.96 (p, J = 7.0 Hz, 2H, *CH*₂CH₂C≡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-ynenitrile (13b)

³⁸ L.-G. Xie, S. Shaaban, X. Chen, N. Maulide, *Angew.Chem. Int. Ed.* **2016**, *55*, 12864–12867.



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. ¹H NMR (400 MHz, Chloroform*d*) δ 7.43 – 7.35 (m, 4H, Ar*H*), 7.35 – 7.28 (m, 6H, Ar*H*), 3.31 (tt, *J* = 7.7, 6.1 Hz, 1H, C*H*Ph), 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*₂C=C). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.4, 131.5, 128.9, 128.3, 128.1, 127.8, 127.0, 123.0, 118.2, 85.9, 83.5, 41.2, 25.8, 23.2. IR (v_{max}, cm⁻¹) 3065 (w), 3031 (w), 2920 (w), 2251 (w), 1735 (w), 1691 (w), 1600 (w), 1493 (m), 1451 (w), 1427 (w), 1381 (w), 1326 (m), 1225 (w), 1107 (w), 1072 (w), 1030 (w), 915 (w), 847 (w), 758 (s). HRMS (ESI) calcd for C₁₈H₁₅NNa⁺ [M+Na]⁺ 268.1097; found 268.1100.

3-Methyl-3,6-diphenylhex-5-ynenitrile (13c)



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%).

Rf (Pentane/EtOAc 9/1) 0.48. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 - 7.37 (m, 4H, Ph*H*), 7.37 - 7.32 (m, 2H, Ph*H*), 7.31 - 7.27 (m, 4H, Ph*H*), 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). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.4, 131.5, 128.7, 128.2, 128.1, 127.3, 125.6, 123.1, 117.9, 85.5, 84.1, 40.4, 32.5, 29.7, 25.6. IR (vmax, 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 C₁₉H₁₈N⁺ 260.1434; Found 260.1436.

tert-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 2H, Ar*H*), 7.30 – 7.20 (m, 3H, Ar*H*), 4.90 (d, *J* = 8.5 Hz, 1H, N*H*), 4.06 (ddd, *J* = 10.3, 7.9, 4.3 Hz, 1H, BocHNC*H*), 2.84 – 2.62 (m, 4H, N=CC*H*₂CHC*H*₂), 1.39 (s, 9H, *Boc*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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 (v_{max}, 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), 734 (s). HRMS (ESI) calcd for C₁₇H₂₀N₂NaO₂⁺ [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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 1H, Ar*H*), 7.66 (dd, *J* = 7.7, 1.3 Hz, 1H, Ar*H*), 7.61 (td, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.47 (ddt, *J* = 5.4, 2.9, 1.6 Hz, 2H, Ar*H*), 7.42 – 7.34 (m, 1H, Ar*H*), 7.34 – 7.29 (m, 3H, Ar*H*), 4.06 (s, 2H, C*H*₂Ar). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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 (v_{max}, 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)

³⁹ X. Zhang, X. X. and Y. Liu, Chem. Sci., 2016, 7, 5815-5820.



(+/-) 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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 2H, Ar*H*), 7.38 – 7.21 (m, 7H, Ar*H*), 3.56 (dtt, *J* = 7.7, 5.1, 1.2 Hz, 1H, C*H*CH₂CN), 3.43 – 3.27 (m, 1H, C*H*C≡CPh), 3.23 – 3.06 (m, 2H, ArC*H*₂), 2.97 (dd, *J* = 17.0, 5.1 Hz, 1H, C*H*₂CN), 2.86 (dd, *J* = 17.0, 6.5 Hz, 1H, C*H*₂CN). ¹³C 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 (v_{max}, cm⁻¹) 3045 (w), 2918 (w), 2247 (w), 1598 (w), 1489 (m), 1461 (w), 1443 (w), 1423 (w), 1348 (w), 1320 (w), 1233 (w), 1207 (w), 1070 (w), 1022 (w), 913 (w), 754 (s). HRMS (ESI) calcd for C₁₉H₁₅NNa⁺ [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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.43 (m, 2H, ArH), 7.40 – 7.29 (m, 3H, ArH), 4.56 (s, 2H, OCH₂CN), 4.45 (s, 2H, OCH₂C=CPh). ¹³C 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)



<u>0.30 mmol scale</u>: 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).

<u>1 mmol scale</u>: Starting from **12h** (272 mg, 1.00 mmol) and using <u>1 mol %</u> of **4c** (10.6 mg, 10.0 μ mol), 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- d_3) δ 7.46 (m, 2H, Ph*H*), 7.37 (m, 3H, Ph*H*), 4.34 (s, 2H, CH₂), 4.27 (s, 2H, CH₂), 1.49 (s, 9H, *CH₃* in Boc). ¹³C NMR (101 MHz, Acetonitrile- d_3) 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 (vmax, 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, Ar*H*), 7.51 - 7.44 (m, 2H, Ph*H*), 7.39 - 7.32 (m, 3H, Ph*H*), 7.28 (d, J = 7.9 Hz, 2H, Ar*H*), 4.57 (br s, 2H, *CH*₂), 4.50 (br s, 2H, *CH*₂), 2.41 (s, 3H, Ph*CH*₃). 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 (vmax, 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, Ar*H*), 7.32 – 7.20 (m, 3H, Ar*H*), 2.41 (t, *J* = 7.1 Hz, 2H, C*H*₂C≡N), 1.99 – 1.79 (m, 2H, C*H*₂CH₂C≡N), 1.71 – 1.54 (m, 2H, C*H*₂CH₂C=N), 1.32 (s, 6H, C*Me*₂). 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 (v_{max}, cm⁻¹) 2970 (m), 2922 (m), 2872 (w), 2247 (w), 1739 (w), 1687 (w), 1598 (w), 1491 (m), 1467 (m), 1427 (w), 1383 (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, Ar*H*), 7.38 – 7.27 (m, 3H, Ar*H*), 4.47 (q, *J* = 6.6 Hz, 1H, OC*H*CH₃), 4.14 – 3.90 (m, 1H OC*H*₂CH₂), 3.85 – 3.58 (m, 1H, OC*H*₂CH₂), 2.66 (t, *J* = 6.4 Hz, 2H, OCH₂C*H*₂), 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 (v_{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 **121** (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 **131** 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, Ar*H*), 7.32 (dd, J = 5.3, 2.0 Hz, 3H, Ar*H*), 4.36 (m, NC*H*₂C=C), 3.78 – 3.58 (m, 2H, NC*H*₂CH₂), 2.72 (m, 2H, NCH₂C*H*₂), 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 (v_{max}, 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 *p*F-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, Ar*H*), 7.01 (t, J = 8.7 Hz, 2H, Ar*H*), 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 (v_{max}, 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 C₁₆H₁₇FN₂NaO₂⁺ [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 *p*Br-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, Ar*H*), 7.30 (d, J = 8.5 Hz, 2H, Ar*H*), 4.34 (m, C*H*₂NC*H*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 (v_{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 (w), 1248 (s), 1159 (s), 1072 (m), 1012 (m), 963 (w), 909 (w), 863 (m), 828 (m), 770 (m), 740 (m). HRMS (ESI) calcd for C₁₆H₁₇⁷⁹BrN₂NaO₂⁺ [M+Na]⁺ 371.0366; found 371.0362.

tert-Butyl (cyanomethyl)(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)carbamate (130)



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, Ar*H*), 4.52 – 4.16 (m, 4H, C*H*₂NC*H*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 (v_{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 C₁₇H₁₇F₃N₂NaO₂⁺ [M+Na]⁺ 361.1134; found 361.1136.

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



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). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 2H, Ar*H*), 7.17 – 7.04 (m, 2H, Ar*H*), 4.35 (m, 4H, C*H*₂NC*H*₂), 2.59 (t, *J* = 7.8 Hz, 2H, C*H*₂Ph), 1.67 – 1.54 (m, 2H, C*H*₂CH₂Ph), 1.52 (s, 9H, *Boc*), 1.30 (m, 4H, C*H*₂C*H*₂(CH₂)₂Ph), 0.88 (t, *J* = 6.9 Hz, 3H, *Me*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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 (v_{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 C₂₁H₂₈N₂NaO₂⁺ [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 *m*F-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 1H, Ar*H*), 7.25 (dd, J = 7.7, 1.5 Hz, 1H, Ar*H*), 7.16 (dd, J = 9.3, 2.1 Hz, 1H, Ar*H*), 7.07 (td, J = 8.4, 2.4 Hz, 1H, Ar*H*), 4.74 – 4.18 (m, 4H, CH₂NCH₂), 1.54 (s, 8H, *Boc*). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -112.6. IR (v_{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 C₁₆H₁₇FN₂NaO₂⁺ [M+Na]⁺ 311.1166; found 311.1162.

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



Starting from 12h (82 mg, 0.30 mmol, 1.0 equiv) and *o*Br-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 1H, Ar*H*), 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.30 – 7.24 (m, 1H, Ar*H*), 7.19 (td, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 4.52 – 4.32 (m, 4H, C*H*₂NC*H*₂), 1.52 (s, 9H, *Boc*). ¹³C 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, 34.5, 28.2, 28.1, 28.0, 27.9. IR (v_{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 C₁₆H₁₇⁷⁹BrN₂NaO₂⁺ [M+Na]⁺ 371.0366; found 371.0363.

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



Starting from **12a** (51 mg, 0.30 mmol, 1.0 equiv) and *p*F-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H, Ar*H*), 7.04 – 6.94 (m, 2H, Ar*H*), 2.59 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 7.2 Hz, 2H) 1.96 (p, J = 7.0 Hz, 2H, CH₂CH₂CH₂). ¹³C 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. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.4. IR (v_{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 C₁₂H₁₁FN⁺ 188.0870; Found 188.0863.

6-(4-(Trifluoromethyl)phenyl)hex-5-ynenitrile (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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.49 (d, *J* = 8.2 Hz, 2H, Ar*H*), 2.63 (t, *J* = 6.8 Hz, 2H, C*H*₂CC), 2.56 (t, *J* = 7.1 Hz, 2H, C*H*₂CN), 1.98 (p, *J* = 6.9 Hz, 2H, C*H*₂CH₂CN). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.79. IR (v_{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.

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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, J = 8.1 Hz, 2H, Ar*H*), 7.47 (d, J = 8.0 Hz, 2H, Ar*H*), 2.42 (td, J = 7.1, 1.4 Hz, 2H, CH₂CN), 1.89 (ddd, J = 14.5, 8.3, 4.3 Hz, 2H, CH₂CH₂CN), 1.72 – 1.58 (m, 2H, CH₂CMe₂), 1.32 (s, 6H, CMe₂). ¹³C NMR (101 MHz, Chloroform-*d*) δ 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. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.72. IR (v_{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 C₁₆H₁₆F₃N [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 *p*Br-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 2.41 (t, *J* = 7.0 Hz, 2H, C*H*₂CN), 2.05 – 1.77 (m, 2H, C*H*₂CH₂CN), 1.65 – 1.57 (m, 2H, C*H*₂(CH₂)₂CN), 1.30 (s, 6H, C*Me*₂). ¹³C NMR (101 MHz,

⁴⁰ L. Melzig, J. Stemper, P. Knochel *Synthesis*, **2010**, *12*, 2085–2091.

Chloroform-*d*) δ 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 (v_{max} , cm⁻¹) 2970 (s), 2918 (m), 2874 (m), 2354 (w), 2247 (w), 1741 (m), 1677 (w), 1588 (w), 1487 (s), 1465 (m), 1427 (w), 1391 (w), 1368 (w), 1318 (w), 1276 (w), 1227 (m), 1205 (m), 1141 (w), 1072 (s), 1012 (m), 915 (w), 828 (s), 740 (m). HRMS (ESI) calcd for C₁₅H₁₆⁷⁹BrNNa⁺ [M+Na]⁺ 312.0358; found 312.0358.

tert-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.48 – 3.80 (m, 4H, CH₂NCH₂), 1.50 (s, 9H, *Boc*), 1.07 (s, 21H, *TIPS*). ¹³C NMR (101 MHz, Chloroform-*d*, *mixture of not fully resolved rotamers (M=major, m=minor)* δ 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 (v_{max} , 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 C₁₉H₃₄N₂NaO₂Si⁺ [M+Na]⁺ 373.2282; found 373.2287.

tert-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.20 (m, 5H, Ar*H*), 6.77 – 6.68 (m, 0.05H, HC=*CH*Ar, Z isomer), 6.58 (d, *J* = 15.8 Hz, 1H, HC=*CH*Ar, E isomer), 6.11 (dt, *J* = 15.8, 6.6 Hz, 1H, *HC*=*CH*Ar, E isomer), 5.65 (dt, *J* = 11.6, 6.5 Hz, 0.05H, Z isomer, *HC*=*CH*Ar, Z isomer), 4.30 – 3.79 (m, 4H, CH₂), 1.52 (s, 9H, *Boc*). ¹³C NMR (101 MHz, Chloroform-*d*)⁴¹ δ 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 ¹H and ¹³C NMR are not fully resolved.

127.5 (Z), 126.5, 123.2, 116.0, 82.0, 49.2, 34.4, 28.2. IR (v_{max} , cm⁻¹) 2982 (m), 2934 (w), 1830 (w), 1705 (s), 1481 (m), 1455 (m), 1401 (m), 1369 (m), 1252 (s), 1165 (s), 1066 (w), 966 (w), 913 (m), 875 (w), 772 (w), 742 (m). HRMS (ESI) calcd for $C_{16}H_{20}N_2NaO_2^+$ [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 μ L of CH₂Br₂ as internal standard. Integration of peak at 4.42-4.18 ppm (m, 4H, CH₂CN) 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. ¹H NMR (400 MHz, Chloroform-d)⁴² δ 4.42-4.18 (m, 4H, CH₂CN), 1.52 (s, 9H, *Boc*). ¹³C NMR (101 MHz, Chloroform-d) δ 152.6, 114.4, 84.5, 35.5 (brs, non-resolved rotamers), 28.0. IR (v_{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 C₉H₁₃N₃NaO₂⁺ [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 *p*CHO-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.01 (s, 1H, CHO), 7.84 (d, J = 8.3 Hz, 2H, Ar*H*), 7.60 (d, J = 8.3 Hz, 2H, Ar*H*), 4.37 (m, 4H, CH₂NCH₂), 1.52 (s, 9H, *Boc*). ¹³C 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_{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),

⁴² Mixture of non-resolved rotamers.

865 (w), 835 (m), 774 (w), 738 (w). HRMS (ESI) calcd for $C_{17}H_{19}N_2O_3^+$ [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 *p*CN-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. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.3 Hz, 2H, Ar*H*), 7.53 (d, J = 8.4 Hz, 2H, Ar*H*), 4.35 (m, 4H, CH₂NCH₂), 1.52 (s, 9H, *Boc*). ¹³C 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 (v_{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 C₁₇H₁₈N₃O₂⁺ [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.⁴³ 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_{I} - r_{IV} (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_I in the optimized geometries for several different dispersion-corrected DFT methods and experimental crystal structures.

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 software⁴⁴ 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 $IP = E_{P^+} - E_P$ and

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 scaled⁴⁵ 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 radii⁴⁶ 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 $E_{1/2}(P^+/P) = \frac{G_{electron} + G_{P+}^{soln} - G_{P-}^{soln}}{F} - E_{SCE}$ and Reduction potential $E_{1/2}(P/P^-) = \frac{G_{electron} + G_{P-}^{soln} - G_{P-}^{soln}}{F} - E_{SCE}$,

⁴⁴ Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, R.; Gomperts, R.; Stratmann, R. E.; Yazyev, J.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D. Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

⁴⁵ Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factor. *J. Phys. Chem. A* **2007**, *111*, 11683-11700 (PBE0/6-311+G(d,p) scaling factors were adopted).

⁴⁶ (a) Scaling factor α=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 α=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 $G_{electron}$ is the gas-phase Gibbs free energy of an electron, equal under Fermi-Dirac statistics to $-3.632 \text{ kJ mol}^{-1}$, ⁴⁷ G^{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_{SCE} is the absolute potential of SCE in a given solvent (4.429 eV in acetonitrile⁴⁸ and 4.462 eV in dichloromethane⁴⁹).

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 4e.
- 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.

⁴⁷ Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. Theoretical Calculation of Reduction Potentials. In *Organic Electrochemistry: Revised and Expanded*, 5th Edition; Hammerich, O.; Speiser, B., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, **2015**; Chapter 6, pp 231-261.

⁴⁸ Isse, A. A.; Gennaro, A. Absolute Potential of the Standard Hydrogen Electrode and the Problem of Interconversion of Potentials in Different Solvents. *J. Phys. Chem. B* **2010**, *114*, 7894-7899.

⁴⁹ Derived from the 4.927 eV absolute potential of Fc⁺/Fc couple in 1,2-dichloroethane (Namazian, M.; Lin, C. Y.; Coote, M. L. *J. Chem. Theory Comput.* **2010**, *6*, 2721–2725) and the 0.465 eV correction to SCE in dichloromethane (Palmer, J. H. *Iridium corroles: synthesis, properties, and electronic structure.* 2011, Dissertation (Ph.D.), California Institute of Technology).



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.

| | MeCN | | DCM | |
|----|------------------|--------------------|------------------|--------------------|
| | $E_{1/2}(P^+/P)$ | $E_{1/2}(P/P^{-})$ | $E_{1/2}(P^+/P)$ | $E_{1/2}(P/P^{-})$ |
| 4a | 1.56 | -1.29 | 1.67 | -1.29 |
| 4b | 1.67 | -1.18 | 1.79 | -1.18 |
| 4c | 1.76 | -1.10 | 1.87 | -1.09 |
| 4d | 1.89 | -0.83 | 1.98 | -0.85 |

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.

| | Oxidation | | | Reduction | | |
|-----------|-----------|------|------|-----------|------|------|
| | gas phase | MeCN | DCM | gas phase | MeCN | DCM |
| 4a | 7.00 | 5.99 | 6.02 | 1.89 | 3.14 | 3.06 |
| 4b | 7.30 | 6.10 | 6.14 | 2.27 | 3.25 | 3.17 |
| 4c | 7.37 | 6.19 | 6.22 | 2.50 | 3.33 | 3.26 |
| 4d | 7.46 | 6.32 | 6.33 | 2.78 | 3.60 | 3.50 |

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.

| | Ι | II | III | IV | Ι | II | III | IV |
|------------|----------|-------|-------|-------|-------|-------|-------|-------|
| | gas phas | e | | | X-ray | | | |
| 4a | 6.099 | 6.186 | 6.215 | 6.301 | 5.900 | 6.609 | 6.611 | 7.266 |
| 4b | 6.134 | 6.216 | 6.420 | 6.320 | | | | |
| 4c | 5.678 | 5.700 | 6.863 | 7.142 | 5.164 | 6.558 | 8.326 | 9.150 |
| 4d | 4.371 | 4.396 | 7.655 | 8.133 | | | | |
| | DCM | | | | MeCN | | | |
| 4 a | 6.823 | 6.833 | 6.833 | 6.823 | 6.362 | 6.405 | 6.467 | 6.380 |
| 4b | 6.831 | 6.946 | 6.945 | 6.829 | 6.403 | 6.496 | 6.800 | 6.576 |
| 4c | 7.310 | 7.377 | 7.456 | 7.419 | 6.871 | 6.981 | 6.988 | 6.883 |
| 4d | 7.372 | 7.409 | 7.629 | 7.757 | 7.079 | 7.168 | 7.169 | 7.081 |

Table 7. Interatomic distances in the optimized geometries and crystal structures of the studied dyes, in Å.

| | | gas phase | | | | MeCN | DCM |
|------------|---------------------|---|--------------------------------------|---------------------------------------|-----------------------|-----------------------------|------------------------|
| | geometry / state | S^{298} , J mol ⁻¹ K ⁻ | TC^{298} , kJ mol ⁻¹ | <i>ZPVE</i> , kJ mol ⁻¹ | <i>E</i> , Hartree | ΔG^{298}_{solv} , 1 | kcal mol ⁻¹ |
| 4 a | 01/01 | 1118.5401 | 121.3468 | 1888.9644 | -2477.41341 | 23.53 | 5.00 |
| | 01/12 | | | | -2477.15623 | | |
| | 12/12 | 1083.3725 | 119.3373 | 1884.9387 | -2477.15769 | 0.93 | -16.79 |
| | 01/-12 | | | | -2477.47126 | | |
| | -1 2 / -1 2 | 1130.1518 | 122.5092 | 1879.1700 | -2477.47829 | -6.13 | -22.91 |
| 4b | 01/01 | 1264.5510 | 140.0826 | 1718.2348 | -3269.96854 | 25.73 | 5.02 |
| | 01/12 | | | | -3269.70054 | | |
| | 12/12 | 1226.5210 | 137.8545 | 1715.1549 | -3269.70244 | -1.09 | -20.84 |
| | 01/-12 | | | | -3270.04226 | | |
| | -1 2 / -1 2 | 1250.3950 | 139.0590 | 1708.9503 | -3270.04947 | 2.23 | -16.74 |
| 4c | 01/01 | 1361.7109 | 148.6806 | 1687.7816 | -6151.89172 | 31.19 | 8.21 |
| | 01/12 | | | | -6151.62241 | | |
| | 12/12 | 1309.0876 | 146.1016 | 1684.2253 | -6151.62444 | 4.73 | -17.56 |
| | 01/-12 | | | | -6151.97211 | | |
| | -1 2 / -1 2 | 1368.2332 | 149.6635 | 1679.3511 | -6151.97992 | 11.10 | -10.32 |
| 4d | 01/01 | 1399.6969 | 152.0885 | 1675.4331 | -2576.77867 | 30.75 | 6.12 |
| | 01/12 | | | | -2576.50149 | | |
| | 12/12 | 1398.6982 | 152.0594 | 1672.1752 | -2576.50320 | 5.14 | -19.08 |
| | 01/-12 | | | | -2576.86906 | | |
| | -1 2 / -1 2 | 1420.3436 | 153.2410 | 1667.5107 | -2576.87601 | 11.12 | -11.19 |

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.

Geometries

PBE0-D3BJ/def2-SVP optimized geometries of all species in the form of Gaussian archive entries.

4a

| 1\1\GINC-R02-NODE33\FOpt\RPBE1PBE\Gen\C56H32N6\GRYNOVA\29-Mar-2018\0\\ |
|--|
| <pre>#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) EmpiricalDis</pre> |
| persion=GD3BJ Nosymm\\7d.pbe0.freq\\0,1\C,-0.9895476287,1.7956982867,0 |
| .1577610417\C,-0.9405709724,0.5871289508,-0.5675621431\C,0.0320328402, |
| -0.3866227028,-0.2446180109\C,0.9254231072,-0.1533103304,0.8263340783\ |
| C, 0.8188379726, 1.0327410581, 1.5819154901\C, -0.1253755478, 2.0154539372, |
| 1 24261504\C -1 8474119963 2 8503825884 -0 2789436316\N -2 5286246982 |
| 3 7149527223 -0 6400689869\C 1 5987726876 1 1907315413 2 7675422714\N |
| 2 2160760762 1 3167747333 3 73008405551N _0 2063125544 3 1075740656 1 |
| 2765005051/c 0 803265588 4 1553122168 2 080000862/c =1 3151534700 3 |
| 5105055051(C,0.0055555500,4.1555122100,2.0059545002(C,-1.515554755,5. |
| 0132/4/130/2./1304413/3/N, T.0333331000,0.30423022/1, T.0139000303/C, T |
| 1.3080303329,-0.0776010002,-2.893492333(C,-3.2291848422,0.2039849327,- |
| 1.4438943942(N,U.1U995)1499,-1.5/U240803,-U.9/8//22114(C,1.23619/8111, |
| -2.0255929469,-1.6683590399(C,-0.91/5421613,-2.5043/36905,-1.131931123 |
| 1\N,1.8976776859,-1.0929854502,1.16872573\C,3.2804080643,-0.870359939, |
| 1.0585095008\C,1.6820883809,-2.4697891975,1.3064072908\C,-1.013689517, |
| 4.8649731036,3.3083241188\c,0.336301642,5.2070818014,2.910370848\c,3.9 |
| 424194761,-2.1177923859,1.0966762654\C,2.9248639016,-3.135846564,1.253 |
| 1188595\C,-0.446074323,-3.5686128635,-1.932959255\C,0.9311257029,-3.26 |
| 98590982,-2.2634968575\C,-2.6816062944,-0.5228266878,-3.5381020077\C,- |
| 3.7774499589,-0.304347353,-2.6173636543\C,2.0640907889,4.1811759317,1. |
| 4997543296\C,-2.5313571618,2.9744889437,2.9215453774\C,-0.2685627855,- |
| 0.0955801124,-3.524481461\C,-4.014049782,0.5407756458,-0.3296333433\C, |
| 2.4672991609,-1.404198135,-1.8547291528\C,-2.1925872617,-2.513994643,- |
| 0.5741859374\c,3.972471913,0.3200681721,0.852193154\c,0.4873899155,-3. |
| 1531916042,1.5078970884\C,1.1694123233,6.3001104882,3.1611892966\C,5.3 |
| 2837177552.1673473192.0.9398102725\C.2.96176892454.5285916576.1.34 |
| 72327198\C1 29470284184 63910596772 2210622991\C.1 90666070613 |
| 9286276553 -3 0142414851\C -2 5981806377 -1 0514213641 -4 8280658809\ |
| C = 5 1438137943 =0 5836082872 =2 6732916947\C =1 9706850054 5 48686053 |
| 52 4 1141284242/C - 5 9369012534 - 0 3014394591 -1 5658873871/C - 5 37417 |
| 77060 0 2519911355 -0 007994842(c =1 354354032 -1 121146703 -5 446442 |
| 0.062/c _0 2052286708 _0 62010756 _4 8032685313/c _3 0334556344 _3 58 |
| 7469210 - 0.2022200105, -0.0322010135, -1.0032003315(C, -3.023430344, -3.30) |
| 14003510, -0.0001320420(C, -2.303003149, -4.0333404942, -1.1023297303(C, 0.0001320420(C, -2.303003149, -4.0333404942, -1.1023297303(C, 0.0001320(C, 0.0001320(C, 0.0001320(C, 0.000132002))))) |
| 544862/39/,-4.5409081684,1.583/323824(C,1.76243601,-5.223939201,1.49 |
| 51188242 C, 6.0286144517, -0.9819314455, 0.7413211979 C, 5.3544059275, 0.24 |
| 5/963483,0.6960606353(C,2.43/811694/,6.3259614326,2.5916490192(C,2.8/5 |
| /931/63,5.2/92558/2/,1./6/2862439(C,-3.196060981/,4.859834/9/4,4.31242 |
| 64442\C,-3.4688465917,3.6157307526,3.7252511833\H,2.4043044435,3.37582 |
| 90331,0.846558626\H,-2.7429835268,1.9996882411,2.4788288318\H,0.626869 |
| 1873,0.2895448553,-3.0374769488\H,-3.5918798571,0.9707795977,0.5786729 |
| 74\H,-2.540584348,-1.7161934659,0.0811909989\H,3.4629961275,1.28304455 |
| 55,0.8141618743\H,-0.4640429912,-2.6286136979,1.592112844\H,0.82572790 |
| 8,7.1223934501,3.7924498829\H,5.8504331402,-3.1263721955,0.9603636952\ |
| H,3.9143929626,-5.0605369459,1.3017162307\H,-0.9455781504,-5.467418383 |
| 7,-2.8413546519\H,-3.4957512807,-1.4063685499,-5.3388522301\H,-5.57808 |
| 96415,-1.0283782846,-3.5712138056\H,-1.755689553,6.4495615378,4.582905 |
| 1169\H,-7.0076741731,-0.5127747641,-1.5959779757\H,-6.0122213298,0.468 |
| 9087098,0.4514073621\H,-1.2708346875,-1.5435138129,-6.4498438095\H,0.7 |
| 609885367,-0.6897614479,-5.3094775895\H,-4.0360812781,-3.6044767063,-0 |
| .4723428855\H,-3.2631336024,-5.4618672438,-1.9273432125\H,-0.382718238 |
| ,-5.1025318035,1.7121170242\H,1.7774256487,-6.3140245036,1.5564182622\ |
| H,7.1133289102,-1.0051608723,0.6189234319\H.5.9204877684.1.1669426788. |
| 0.5423708617\H,3.1003869749,7.172621156.2.7818380287\H,3.8726946365.5 |
| 3248710285,1.3236573039\H,-3.9541755039.5.3364028645.4.9370510537\H4 |
| .4345938307.3.1373928264.3.9020624503\C.3.42727792062.0827733811 -2 |
| 5992034153\C.3.15651570243.33633782073.1654892817\H.2.6855793475 - |
| 0.4224223307,-1.4357954588\H.1.68762316334 89327544723 4770783149 |
| H. 4. 4091433871, -1. 6250856387, -2. 7370220025\H. 3. 9320468713, -3. 845313054 |
| ,, |

8,-3.7414858151\\Version=ES64L-G09RevD.01\HF=-2477.4133295\RMSD=5.581e
-09\RMSF=2.619e-06\Dipole=0.0985215,-1.5203002,-0.9372358\Quadrupole=1
2.6901939,1.4631831,-14.153377,9.0427375,-14.5658535,13.1607317\PG=C01
[X(C56H32N6)]\\@

4a.cr_opt

1\1\GINC-R05-NODE45\F0pt\UPBE1PBE\Gen\C56H32N6(1+,2)\GRYNOVA\30-Mar-20 18\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empiri calDispersion=GD3BJ Nosymm\\7d.cr_opt.pbe0.freq\\1,2\C,-1.0332589995,1 .8042482481,0.2076430258\C,-0.9688884487,0.6052809693,-0.5251048124\C, 0.0234436722,-0.351424364,-0.2141175419\C,0.9409854974,-0.1118843835,0 .8336854564\C,0.8505857894,1.0791410072,1.5771212029\C,-0.1307218966,2 .043802764,1.2653215978\C,-1.9210584253,2.8349300429,-0.2228175829\N,-2.6380047851,3.6671805688,-0.5900772096\C,1.6623098049,1.2359438357,2. 7400473648\N,2.3179316985,1.3459903217,3.6885011326\N,-0.2071569039,3. 2209070576,1.9926116581\C,0.8282916313,4.1509016155,2.1464024906\C,-1. 3334761848,3.6730873892,2.6911551562\N,-1.8430711683,0.3805869315,-1.5 865467546\C,-1.4549187246,-0.0608878065,-2.8640761991\C,-3.2200443315, 0.1722606418,-1.4440012258\N,0.0980296214,-1.5348710357,-0.9464896302\ C,1.2123890599,-1.9764130407,-1.6572821774\C,-0.9318369161,-2.46360619 3,-1.0889443166\N,1.8977023306,-1.0708292892,1.1567652783\C,3.27721948 21,-0.893248056,0.9913384629\C,1.6401522674,-2.4441522482,1.3138969057 \C,-1.0161281142,4.9069879635,3.3009407938\C,0.3600244878,5.2124903114 ,2.9520202197\C,3.8977913848,-2.1657102167,0.9914470923\C,2.8548115072 ,-3.1501328733,1.199255956\C,-0.4771858468,-3.5187700717,-1.913143167\ C,0.8988348745,-3.2139879408,-2.2654222617\C,-2.5795024897,-0.60176073 01,-3.5194229047\C,-3.7043554612,-0.4551141864,-2.6177324955\C,2.10194 93899,4.1520316712,1.5820167175\C,-2.566800925,3.0507425994,2.87074831 12\C,-0.2131409387,0.0337998517,-3.4817376929\C,-4.0440601649,0.417456 3601,-0.345003248\C,2.4304217648,-1.3318078573,-1.8718585729\C,-2.1868 179686, -2.4847966978, -0.4812635935\C, 3.9983936249, 0.2788609445, 0.76204 52033\C,0.4374978534,-3.0822455432,1.5959016498\C,1.2049937332,6.28461 35441,3.2275088375\C,5.2714878162,-2.2604378724,0.7709879693\C,2.85326 72257,-4.5409991357,1.3108335734\C,-1.3287255508,-4.5803998803,-2.1925 938153\c,1.8554507062,-3.8513337116,-3.0458672231\c,-2.4393573143,-1.1 215921305,-4.8067717719\C,-5.0453429292,-0.8302873335,-2.6930041416\C, -1.9742345726,5.5492476521,4.0812374607\C,-5.87412221,-0.5838496879,-1 .6027561279\C,-5.3758159437,0.0306993175,-0.4426196496\C,-1.185400334, -1.0833151843,-5.413189696\C,-0.0899862089,-0.5028496461,-4.762449516\ C,-3.0284078456,-3.5538678582,-0.7818165753\C,-2.6125864422,-4.5800619 4,-1.6361948852\C,0.453989671,-4.4727910031,1.6885458588\C,1.644221988 ,-5.1949574843,1.5385933778\C,5.9982850698,-1.095000217,0.5473780962\C ,5.3658970325,0.1584521859,0.5409686752\C,2.4934608445,6.2804561053,2. 6923298307\C,2.9315907306,5.2306502568,1.8751364019\C,-3.2236238673,4. 9493171399,4.2419000526\C,-3.5114747894,3.713233083,3.649398356\H,2.44 09345264,3.3472618833,0.9281939856\H,-2.7891579778,2.0782390901,2.4292 953197\H,0.6349946028,0.5126322843,-2.9914249126\H,-3.6716327383,0.900 1562556,0.5586616629\H,-2.5032783371,-1.7095814676,0.2154814838\H,3.52 08151501,1.2587561602,0.7609657913\H,-0.4862218126,-2.5225936561,1.745 8642893\H,0.863240312,7.117368691,3.8451471112\H,5.7650579046,-3.23417 26127,0.7645636149\H,3.7836995012,-5.1058459738,1.2261384177\H,-1.0005 211283,-5.4059458349,-2.8269998015\H,-3.2981428001,-1.5455078481,-5.33 08630381\H,-5.4344328355,-1.3170153694,-3.589372797\H,-1.7497759188,6. 5019814086,4.564642343\H,-6.9271231543,-0.8682511405,-1.6476235604\H,-6.0481586874,0.219048036,0.3966060078\H,-1.0584580748,-1.4907679713,-6 .4178621899\H,0.8779436698,-0.4595793127,-5.2655826257\H,-4.025348706, -3.5850805118,-0.3386504759\H,-3.2931827507,-5.4050951105,-1.854956673 1\H,-0.4789938194,-5.0023919239,1.8909373995\H,1.6259309678,-6.2831402 639,1.6223368202\H,7.0750192471,-1.1523492625,0.3769809179\H,5.9590729 554,1.0587846816,0.3695953029\H,3.1676314036,7.1125389203,2.9034869011 \H,3.9392228758,5.2590620994,1.4563740146\H,-3.9853199111,5.4438793449 ,4.8474397558\H,-4.4914070448,3.2576876905,3.803506706\C,3.379341501,-1.9929615805,-2.6481127628\C,3.1028827866,-3.241172893,-3.2160795334\H ,2.6395010762,-0.343402322,-1.464842955\H,1.6364879719,-4.8070235776,-3.525861701\H,4.3505998652,-1.5231127551,-2.8130564148\H,3.8654755209, -3.7367099187,-3.8199477812\\Version=ES64L-G09RevD.01\HF=-2477.1577432 \S2=0.761223\S2-1=0.\S2A=0.750127\RMSD=7.934e-09\RMSF=3.059e-06\Dipole =0.0846467,-1.7521867,-1.1087699\Quadrupole=12.3496978,12.4080739,-24. 7577717,6.6890391,-12.8964389,35.7003711\PG=C01 [X(C56H32N6)]\\@

4a.ar_opt

1\1\GINC-R05-NODE53\FOpt\UPBE1PBE\Gen\C56H32N6(1-,2)\GRYNOVA\30-Mar-20 18\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empiri calDispersion=GD3BJ Nosymm\\7d.ar opt.pbe0.freq\\-1,2\C,-0.9737363676, 1.8248584848,0.1320625738\C,-0.9332416466,0.5649520609,-0.5920076821\C ,0.0267699684,-0.3959041928,-0.2411736038\C,0.9098992423,-0.1925583104 ,0.829940644\C,0.7901018714,1.0162057514,1.628725514\C,-0.1292607488,1 .9985410115,1.2365076734\c,-1.7979602888,2.8832079191,-0.3123127791\N, -2.4933333272,3.7439928108,-0.6785707939\C,1.5355644143,1.1683251663,2 .81946586\N,2.1670334451,1.2909252934,3.7915456874\N,-0.2078079767,3.1 972849217,1.975500068\C,0.793210186,4.1513340544,2.0752819518\C,-1.301 4217958, 3.6152108402, 2.718432633\N, -1.8469120845, 0.3383177769, -1.63858 90227\C,-1.5258402439,-0.0169947703,-2.9423519083\C,-3.219454194,0.197 1250241,-1.474119406\N,0.1069724154,-1.5938698913,-0.9849056134\C,1.21 51617375,-2.0285807276,-1.6992758565\C,-0.9018448965,-2.5392964847,-1. 1108700918\N,1.9031184073,-1.1377861797,1.1497031061\C,3.2700734481,-0 .9208111136,1.0212498698\C,1.6979382696,-2.4911493077,1.3863350473\C,-1.0026647828, 4.8652526617, 3.3140951543\C, 0.3388568399, 5.2103866973, 2.8 993106213\C,3.9542330469,-2.1543456632,1.1481901155\C,2.9447930917,-3. 1637239137,1.3748157741\C,-0.4392957927,-3.60211263,-1.9243756316\C,0. 9203587244,-3.2794158514,-2.2933447631\C,-2.7006531398,-0.426750287,-3 .6197495598\C,-3.7888154455,-0.2823886559,-2.6792596833\C,2.0550596911 ,4.170652167,1.4823367853\C,-2.521797287,2.9740825977,2.9272401969\C,-0.2834307901,-0.0076278284,-3.5744062742\C,-3.9932853814,0.4143600403, -0.3337500971\C,2.4382560774,-1.3929528628,-1.9039306095\C,-2.16939118 49,-2.561181323,-0.5318881177\C,3.9481629115,0.2687696378,0.7539205428 \C,0.5025103208,-3.1731706085,1.6086593182\C,1.1777804397,6.3025960099 ,3.1382127818\C,5.343155161,-2.1891098083,1.0030143656\C,2.9821261448, -4.549196055,1.5547703651\C,-1.2826884063,-4.6838102284,-2.1890318233\ C,1.890338017,-3.9177894468,-3.0700709051\C,-2.6145385567,-0.863981710 8,-4.944647706\C,-5.1593475919,-0.5470402681,-2.7350328551\C,-1.957329 5355, 5.483826768, 4.1264532919\C, -5.9365438659, -0.3338583117, -1.6012057 327\C,-5.3547273085,0.1427848255,-0.4151937298\C,-1.3725668483,-0.8852 636179,-5.5694637354\C,-0.2217689621,-0.4550428042,-4.8883770236\C,-2. 9933481168,-3.6440732369,-0.8168766521\C,-2.561185232,-4.6943659888,-1 .6416633018\C,0.5642135789,-4.5512013145,1.7756583168\C,1.7891056303,-5.2379821858,1.743570964\c,6.0252631236,-1.0070141167,0.7342361705\c,5 .3302671655,0.2072356192,0.6125020718\C,2.4407102396,6.3242393361,2.55 71587529\C,2.8693543953,5.2680031598,1.7367003278\C,-3.1797111022,4.85 40368327,4.3322477895\C,-3.4534858308,3.6110735856,3.7383983864\H,2.38 5125738,3.3485853349,0.8460894862\H,-2.7313869023,2.0092537127,2.46380 93447\H,0.609617237,0.3297353041,-3.0492970169\H,-3.5410446375,0.78840 80333,0.5853371878\H,-2.5070635647,-1.755626288,0.1187254803\H,3.40762 86179,1.2114688986,0.6634222178\H,-0.4483534359,-2.6419641719,1.637511 9191\H,0.8416175844,7.1270086219,3.7718695917\H,5.8823499441,-3.135722 4127,1.0897462587\H,3.9367405049,-5.0809696733,1.5404126569\H,-0.93799 4755,-5.5087630413,-2.8172218919\H,-3.5119312375,-1.1895614639,-5.4766 006562\H,-5.6099086906,-0.9255315578,-3.6559403757\H,-1.7418040015,6.4 483335022,4.592790905\H,-7.0098419083,-0.535617873,-1.63138651\H,-5.98 34442873,0.3107687022,0.4626073073\H,-1.288274845,-1.2370568069,-6.600 3202829\H,0.7461943861,-0.4765304284,-5.3945405203\H,-3.9993010764,-3. 6668041223,-0.3914712232\H,-3.2349401739,-5.5289033472,-1.8492904781\H ,-0.3640836288,-5.107129218,1.926651832\H,1.8017260687,-6.3228705936,1 .8715251819\H,7.1116363718,-1.0196660071,0.6192201981\H,5.8848635049,1 .1264761449,0.4088405645\H,3.10797662,7.1700986595,2.737960299\H,3.865 6733222,5.3052035617,1.2896529884\H,-3.936256838,5.3278564722,4.961968 8836\H,-4.4205564923,3.1334461,3.9132164541\C,3.3904396973,-2.05148097 61,-2.6734075383\C,3.1262627041,-3.3049440278,-3.247247062\H,2.6455846 128,-0.4155299065,-1.4705910765\H,1.6762793294,-4.8851375256,-3.530944 8477\H,4.3644574583,-1.580086201,-2.8234348394\H,3.8976134996,-3.79836 87637,-3.8431022007\\Version=ES64L-G09RevD.01\HF=-2477.478192\S2=0.767 387\S2-1=0.\S2A=0.750211\RMSD=4.811e-09\RMSF=2.242e-06\Dipole=0.145804 ,-2.1297179,-1.3162405\Quadrupole=11.6009494,-5.0786305,-6.522319,14.8 92257,-22.28218,-2.0937666\PG=C01 [X(C56H32N6)]\\@

1\1\GINC-R02-NODE38\F0pt\RPBE1PBE\Gen\C56H24F8N6\GRYNOVA\29-Mar-2018\0 \\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) EmpiricalD ispersion=GD3BJ Nosymm\\7g.pbe0.freq\\0,1\C,-0.9953756294,1.8140187687 ,0.1687445317\C,-0.9443841409,0.6071760137,-0.5598448135\C,0.029154266 4,-0.3664532075,-0.2372458081\C,0.9229931066,-0.1349251345,0.834581185 2\C,0.8178575073,1.0519322617,1.5894227834\C,-0.1288333474,2.034219321 4,1.2525888076\C,-1.855479451,2.867138876,-0.2660792675\N,-2.543257511 1,3.7280439597,-0.6237134233\C,1.5999443222,1.2088633041,2.7733426482\ N, 2.2247966226, 1.335069013, 3.7406801899\N, -0.2092409169, 3.2148026373, 1 .9868474639\C,0.8058912146,4.1658537472,2.1158285792\C,-1.3219931148,3 .6460427574,2.7133913865\N,-1.8396625402,0.4070438034,-1.6102329044\C, -1.5029806127,-0.0794135726,-2.8800295397\C,-3.2295827649,0.2741508758 ,-1.4454524089\N,0.1069887254,-1.548719578,-0.9721996983\C,1.235741475 4,-2.0099706763,-1.6534490913\C,-0.9177372811,-2.4862887606,-1.1238473 623\N,1.8914670189,-1.0775133439,1.1803220911\C,3.2759447362,-0.862998 249,1.0573684418\C,1.6730880159,-2.457114514,1.2878407469\C,-1.0169453 679,4.8875684946,3.3151670828\C,0.3385011315,5.2190922795,2.9338517448 \c,3.9304632177,-2.1150288683,1.0532185375\c,2.9097280989,-3.129725503 4,1.1956047144\C,-0.4415952483,-3.5566272265,-1.9141806261\C,0.9364010 953, -3.2610998308, -2.2371859116\C, -2.6685411923, -0.556047609, -3.515907 1243\C,-3.7681237053,-0.3283296366,-2.6044043535\C,2.0732388994,4.1916 712113,1.5395199056\C,-2.5464632304,3.0144498314,2.9147728986\C,-0.265 1243871,-0.0965125887,-3.5152474847\C,-4.0260255739,0.5627699726,-0.34 03894622\C,2.4670035187,-1.3903363139,-1.8469675369\C,-2.1944616362,-2 .5011128104,-0.5692980529\C,3.978573209,0.3241383262,0.8685241011\C,0. 4806524276,-3.1439914964,1.4932472965\C,1.1670379958,6.3112802429,3.20 32404292\C,5.3129928594,-2.1832564841,0.8751444869\C,2.9518174559,-4.5 245347892,1.2465198564\C,-1.2785059602,-4.6361377784,-2.2042674452\C,1 .9104881116,-3.9369272067,-2.975024096\C,-2.5886422623,-1.1183007696,-4.7917446053\C,-5.12914778,-0.6303715753,-2.6699612471\C,-1.9680830278 ,5.5249580934,4.1158545591\C,-5.9106697161,-0.3283393198,-1.5662108662 \c,-5.3812354517,0.2555680058,-0.4121676227\c,-1.3395204554,-1.1796374 553,-5.3885018284\C,-0.188826917,-0.6697200083,-4.7786060653\C,-3.0234 873402,-3.5767240438,-0.867130927\C,-2.5623745955,-4.6143038549,-1.683 0941316\C,0.5263442205,-4.5322417888,1.5279012988\C,1.7489987084,-5.19 74334701,1.3920170792\C,5.9996233231,-0.9929365835,0.6964506366\C,5.35 61579062,0.2476905675,0.6879184275\C,2.4328303659,6.3137431911,2.64056 85194\C,2.891041678,5.2811299916,1.8157890565\C,-3.1897788242,4.895589 1985,4.2900351954\C,-3.487231676,3.6578749759,3.7103022745\H,2.4200652 807,3.3909608392,0.8846586603\H,-2.7675378208,2.0415433818,2.473353828 2\H,0.6266524095,0.3149314,-3.0436654165\H,-3.6191653883,1.0192473562, 0.5615081621\H,-2.5498096692,-1.7038259805,0.0824948306\H,3.4823203423 ,1.2942804212,0.8623989829\H,-0.4677446339,-2.6211954154,1.6132742038\ H,0.8465110082,7.145999835,3.8280531536\H,5.8511325931,-3.1319417088,0 .8582773283\H,3.8851953447,-5.0840241635,1.1730553888\H,-0.9508591191, -5.4801579164,-2.8126203853\H,-3.4639811046,-1.5033923591,-5.316216333 5\H,-5.5789814331,-1.100695031,-3.5453543941\H,-1.7743841314,6.4828586 258,4.6003993553\F,-7.2128808967,-0.6062706376,-1.5971213318\H,-6.0512 80325,0.4721810608,0.4210356019\F,-1.2260379021,-1.7271369604,-6.59750 6919\H,0.7613450134,-0.7308906279,-5.3110932316\H,-4.0400508018,-3.626 217491,-0.4743176507\F,-3.3885486052,-5.6248958399,-1.9518923397\H,-0. 3826772257,-5.1208179054,1.6594969999\F,1.7523996325,-6.5291399501,1.4 237850528\F,7.3195400728,-1.0247059735,0.5207928534\H,5.9552200043,1.1 485131963,0.5473924774\F,3.2478024967,7.3398924342,2.8813937113\H,3.89 60209541,5.3529723039,1.3974301881\F,-4.1187968858,5.4801137436,5.0452 693294\H,-4.4658113257,3.2139009201,3.898606169\C,3.4338841717,-2.0721 493749,-2.5767839668\C,3.1492938003,-3.331251773,-3.1140327427\H,2.684 5166861,-0.4020809221,-1.4434103605\H,1.7225976027,-4.9067044924,-3.43 7632215\H,4.4229237785,-1.6407260061,-2.7375210489\F,4.1040365008,-3.9 58530663,-3.8004911927\\Version=ES64L-G09RevD.01\HF=-3269.9685005\RMSD =7.416e-09\RMSF=2.864e-06\Dipole=0.0432976,-0.6677445,-0.4188723\Quadr upole=5.3335757,-3.01749,-2.3160857,7.8542901,-11.6049653,-2.3840731\P G=C01 [X(C56H24F8N6)]\\@

4b.cr_opt

1\1\GINC-R03-NODE57\F0pt\UPBE1PBE\Gen\C56H24F8N6(1+,2)\GRYNOVA\30-Mar-2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empi ricalDispersion=GD3BJ Nosymm\\7g.cr_opt.pbe0.freq\\1,2\C,-1.0363379165 ,1.806482638,0.210846802\C,-0.9728329684,0.6076199303,-0.524726866\C,0 .0234345478,-0.3487140167,-0.2170732941\C,0.9426748143,-0.1084706983,0 .8315511115\c,0.8510873029,1.0830979355,1.5761228891\c,-0.1320157702,2 .0456640538,1.2662161742\C,-1.9242775914,2.839092604,-0.2136577847\N,-2.6429544876, 3.675154691, -0.5690287167\C, 1.6626031824, 1.2441193655, 2.7 382123954\N,2.3199027627,1.365075817,3.6843169951\N,-0.2086406348,3.22 38572052,1.9951748188\C,0.8226804784,4.1568034753,2.1440400778\C,-1.33 16423247,3.6733481926,2.6974468273\N,-1.8509010179,0.3886380803,-1.582 8081925\C,-1.4751725373,-0.0691493169,-2.856912532\C,-3.2343451581,0.2 043906859,-1.4390807607\N,0.0996738788,-1.5298874324,-0.9496197758\C,1 .2227580698,-1.9815622628,-1.6415445188\C,-0.9297998165,-2.4582950056, -1.1012719596\N,1.9007702719,-1.0641174071,1.1587151698\C,3.2838664279 ,-0.8790882344,1.0092325177\C,1.652304535,-2.4401424778,1.2948192833\C ,-1.0175229437,4.910142615,3.3051121961\C,0.3558596644,5.2189892983,2. 951283146\C,3.9110698792,-2.1472534663,0.9983385054\C,2.8710385069,-3. 1395750205,1.1792689754\C,-0.4648798923,-3.5224109271,-1.9089507072\C, 0.9162938536, -3.2249402497, -2.241525111\C, -2.6091625777, -0.5968829894, -3.5073537837\C,-3.730649768,-0.4223492183,-2.6066551851\C,2.095581873 ,4.1670734017,1.5759139775\C,-2.5643538594,3.0508294683,2.8870707296\C ,-0.234755955,-0.0024941099,-3.484200226\C,-4.0575509726,0.4633222466, -0.3433149336\C,2.4454469983,-1.3448702255,-1.8539425846\C,-2.19333064 72,-2.4825216488,-0.5107639992\C,4.0069436456,0.2945845865,0.796654882 1\C,0.4531704462,-3.0953250369,1.5589073153\C,1.188393912,6.2978367039 ,3.2294522987\C,5.2843468781,-2.2474413888,0.7894294619\C,2.8883267935 ,-4.5311332124,1.2620933012\C,-1.3020960784,-4.5927047027,-2.197009472 5\C,1.8742044929,-3.8835079752,-3.0018418528\C,-2.4923788213,-1.134815 7596,-4.7883339578\C,-5.0735781504,-0.7815677505,-2.6911920909\C,-1.96 53461398, 5.5593454402, 4.0890458833\C, -5.8830219748, -0.5102278241, -1.59 56138343\C,-5.3950861705,0.0985859707,-0.4327823083\C,-1.23532376,-1.1 172894124,-5.3799197955\C,-0.1190713504,-0.5505109914,-4.7569826843\C, -3.0302300233, -3.5516625119, -0.8071443582\C, -2.5854546259, -4.573195640 2,-1.6511617868\C,0.4717581298,-4.4840164858,1.6270598867\C,1.67516241 84,-5.1774468761,1.4652651789\C,5.9925448751,-1.0699153203,0.586968304 \c,5.3757470681,0.1872438988,0.5845768262\c,2.468793586,6.2810950828,2 .682367367\C,2.9248671936,5.2439769846,1.8615196521\C,-3.2043141827,4. 9429600228,4.2444785795\C,-3.5093073172,3.7062062616,3.6658200558\H,2. 4384420657,3.3665073731,0.9194878577\H,-2.7893919971,2.0765811972,2.45 16667062\H,0.6252304715,0.4673346097,-3.0066021736\H,-3.6836143435,0.9 427949726,0.5609907995\H,-2.5259146004,-1.7043559496,0.1749084698\H,3. 5320074781,1.2753417539,0.800055687\H,-0.4769635603,-2.5486440502,1.71 51136089\H,0.8715863135,7.1422335176,3.8430619582\H,5.8046793598,-3.20 59533546,0.7686582461\H,3.8075308234,-5.1126479616,1.1798841717\H,-0.9 88677683,-5.4359637624,-2.8139891885\H,-3.342467025,-1.5530646407,-5.3 288980586\H,-5.4944864057,-1.2694677366,-3.5713584642\H,-1.7679866895, 6.5124001814,4.5816042458\F,-7.1629738155,-0.8423703179,-1.6430084694\ H,-6.0882922803,0.2889218573,0.3877897734\F,-1.0873374983,-1.637681643 3,-6.5895860598\H,0.8316109462,-0.5380873977,-5.2919788238\H,-4.035135 4561,-3.6136702117,-0.3873593669\F,-3.4057109083,-5.5733884633,-1.9204 365182\H,-0.4404852063,-5.0511293036,1.8177598238\F,1.6552427962,-6.50 08403783,1.5292925833\F,7.2982203857,-1.1311192722,0.3812460316\H,5.99 3620532,1.0722159763,0.426063512\F,3.2835837646,7.2906031182,2.9339096 462\H,3.9344044143,5.306280231,1.4532540887\F,-4.126211708,5.539552581 7,4.9795975893\H,-4.494619736,3.2741772179,3.8454277917\C,3.4039821797 ,-2.0106370784,-2.6083133617\c,3.1159211854,-3.2658501926,-3.151572318 1\H,2.6558399121,-0.3519333604,-1.4589071772\H,1.6852787473,-4.8434148 55,-3.4843714246\H,4.3843535791,-1.5685469449,-2.7909521259\F,4.049122 9059,-3.878778773,-3.8581075722\\Version=ES64L-G09RevD.01\HF=-3269.702 4267\\$2=0.759945\\$2-1=0.\\$2A=0.750097\RMSD=4.748e-09\RMSF=1.902e-06\Di pole=0.0170982,-0.3266919,-0.1952875\Quadrupole=4.8257543,9.8987292,-1 4.7244835,4.7939198,-9.8689303,23.0664102\PG=C01 [X(C56H24F8N6)]\\@

4b.ar_opt

1\1\GINC-R04-NODE04\F0pt\UPBE1PBE\Gen\C56H24F8N6(1-,2)\GRYNOVA\30-Mar-2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empi ricalDispersion=GD3BJ Nosymm\\7g.ar_opt.pbe0.freq\\-1,2\C,-0.986654514 4,1.8400931536,0.152381176\C,-0.9401608985,0.5838322202,-0.5776005281\ C,0.024899791,-0.3735774594,-0.2318326378\C,0.9118051972,-0.1697836299 ,0.8368559753\C,0.7963720374,1.041030263,1.6327157028\C,-0.1328584037, 2.0181734743,1.249664332\c,-1.8241070597,2.8916138885,-0.2825106528\N, -2.5346774439,3.7441152797,-0.6386686104\C,1.5571072549,1.1985817889,2 .8128493566\N,2.2060568374,1.3269393587,3.7724767338\N,-0.211588877,3. 2152951023,1.9891634516\C,0.791272843,4.1673481192,2.0976330056\C,-1.3 083669996,3.639761307,2.7248223536\N,-1.8480514165,0.3584795839,-1.629 1159466\C,-1.5185274777,-0.0118298956,-2.9268865668\C,-3.2203792446,0. 2014210045,-1.4716630596\N,0.106260385,-1.5692506008,-0.977252827\C,1. 2199845515,-2.0096585747,-1.6795591525\C,-0.8962209016,-2.5222885908,-1.0986150552\N,1.898322055,-1.1209216996,1.1597936685\C,3.2670436813,-0.9226612352,1.0110207991\C,1.6814533697,-2.4773273151,1.3697353319\C, -1.0089143494,4.8885399322,3.3219996988\C,0.3346394106,5.2277221441,2. 9181038339\C,3.9350065804,-2.1686799944,1.0950832944\C,2.917175386,-3. 1673435769,1.3155658512\C,-0.42280145,-3.5936829657,-1.894430205\C,0.9 362070941,-3.2707437427,-2.2566219063\C,-2.6840943682,-0.447433368,-3. 6035506919\C,-3.7770669114,-0.3028172409,-2.6725995112\C,2.0580355781, 4.1883635971,1.515054415\C,-2.5340749655,3.0074146067,2.9299182457\C,-0.2753942539,0.0033867033,-3.5579941948\C,-4.00677964,0.421312379,-0.3 405209687\C,2.4410134805,-1.3720888253,-1.8918312128\C,-2.16655554,-2. 5500901688,-0.5254744258\c,3.9614621223,0.259816601,0.7551038221\c,0.4 831356585, -3.1516249881, 1.6009158038\C, 1.1670883871, 6.323553429, 3.1696 270089\C,5.3209162527,-2.23224866,0.9219067761\C,2.9485587103,-4.55872 85969,1.4579352249\C,-1.2499954655,-4.6904081997,-2.1542840957\C,1.909 3273785,-3.9253925521,-3.017827219\C,-2.5973110066,-0.9049857793,-4.92 29803993\C,-5.143941756,-0.5886571752,-2.7433426737\C,-1.9595301866,5. 5208788031,4.1304797101\C,-5.9079884351,-0.3654106087,-1.6111242427\C, -5.3635983444,0.1310135348,-0.4214840133\C,-1.3494406368,-0.9114939595 ,-5.5202911198\C,-0.1979123875,-0.4609690044,-4.8641333594\C,-2.983312 3044, -3.6411434354, -0.7951404141\c, -2.5204153215, -4.6831992589, -1.6052 740033\C,0.5231631025,-4.5332745952,1.7316250574\C,1.7444057354,-5.212 3641401,1.6502484539\C,5.992581715,-1.0496272276,0.6657538315\C,5.3383 483577,0.1844623853,0.5808503149\C,2.4236667715,6.3227740037,2.5909808 28\C,2.8753325149,5.2814862303,1.772339306\C,-3.1732250289,4.883140723 6,4.3153513435\C,-3.4698208024,3.6451562391,3.7340311583\H,2.395560262 6,3.3692689779,0.8794178668\H,-2.750196723,2.0428780039,2.4696425143\H ,0.6128953294,0.3622844341,-3.0395033105\H,-3.570426021,0.813932557,0. 5781474041\H,-2.5159684093,-1.7427037749,0.1162177308\H,3.4393693215,1 .2150196309,0.6966025175\H,-0.4605841916,-2.6113875376,1.667213867\H,0 .8541682832,7.1609152345,3.795198778\H,5.8712767254,-3.173180842,0.970 0280574\H,3.8783721282,-5.1279356987,1.4146808749\H,-0.9225743583,-5.5 342025053,-2.7633863986\H,-3.4699654093,-1.2545102392,-5.4767960156\H, -5.6098894839,-0.9850448877,-3.6468630391\H,-1.7691342504,6.4825413536 ,4.6094112285\F,-7.2210912633,-0.6318352505,-1.6470461691\H,-6.0261940 104,0.2920344963,0.4304652943\F,-1.2313131012,-1.3566588137,-6.7790230 26\H,0.75516277,-0.4872771651,-5.3948085127\H,-3.9935557439,-3.6979422 345,-0.3868437528\F,-3.3395955028,-5.7157849566,-1.8447803852\H,-0.390 2185711,-5.1085097208,1.8911779883\F,1.7397322667,-6.5468558082,1.7749 332534\F,7.3212731226,-1.0781011308,0.4917572173\H,5.9316552126,1.0793 600774,0.3859973367\F,3.2452693751,7.3576428198,2.814173464\H,3.878587 5752,5.3473071521,1.3482654492\F,-4.1052683011,5.4643947495,5.08295367 53\H,-4.4477159548,3.1994828644,3.9232546215\C,3.4041064624,-2.0334398 011,-2.6432948494\C,3.1302109855,-3.2945463093,-3.1828663508\H,2.64276 9373,-0.3853660879,-1.4777689305\H,1.7314758959,-4.8996289385,-3.47543 42902\H,4.3839805853,-1.5857070412,-2.8160472961\F,4.0863097728,-3.902 9923991,-3.8972129841\\Version=ES64L-G09RevD.01\HF=-3270.0495101\S2=0. 767349\S2-1=0.\S2A=0.750212\RMSD=6.764e-09\RMSF=2.682e-06\Dipole=0.105 092,-1.5068355,-0.9208502\Quadrupole=4.0559236,-9.3811647,5.3252411,13 .5475761,-19.0182082,-17.3027345\PG=C01 [X(C56H24F8N6)]\\@

4c

1\1\GINC-R03-NODE52\FOpt\RPBE1PBE\Gen\C56H24C18N6\GRYNOVA\29-Mar-2018\
0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empirical
Dispersion=GD3BJ Nosymm\\7e.pbe0.freq\\0,1\C,-1.0119548129,1.847041863
4,0.1760975468\C,-0.9569077813,0.6453653636,-0.5602363471\C,0.01469822
37,-0.3289120402,-0.241988213\C,0.8932115893,-0.1141393703,0.847671826
3\C,0.7879561428,1.0688668146,1.6062163759\C,-0.149710367,2.0583584869
,1.2644924748\C,-1.8745957748,2.9006752187,-0.2526028938\N,-2.56535147
13,3.7610682104,-0.6053981975\C,1.5675637383,1.2189775826,2.7928363869
\N,2.1931474486,1.3403208721,3.7602260598\N,-0.222988784,3.2396236287,

2.0000767411\C,0.7986155839,4.1828788956,2.124438606\C,-1.3304066501,3 .6772898062,2.728892209\N,-1.8507646604,0.445823914,-1.6132363596\C,-1 .5110597156,-0.0266564434,-2.8864075911\C,-3.2375255388,0.2993624976,-1.4458810599\N,0.1055699918,-1.4984565815,-0.9984014927\C,1.2672510687 ,-1.9563436199,-1.6217089618\C,-0.8783116119,-2.4847533846,-1.11161411 28\N,1.849494612,-1.0695008455,1.2041498878\C,3.2347261912,-0.88466122 97,1.0389321254\C,1.6022388029,-2.4465383171,1.2685065454\C,-1.0161452 079,4.9168955795,3.3288079817\C,0.3415183458,5.2396533481,2.9427585953 \c,3.8555586767,-2.1506296756,0.9569359828\c,2.8132866978,-3.146350884 8,1.0898390945\C,-0.3331589638,-3.5911038408,-1.8013904354\C,1.0418535 56,-3.2619505554,-2.109017928\C,-2.6730515553,-0.5063265618,-3.5252477 369\C,-3.7735990928,-0.2980751783,-2.6080759934\C,2.0643918892,4.19854 91319,1.5452308798\C,-2.5586242968,3.0546831533,2.9324962591\C,-0.2732 161068,-0.0336175141,-3.5209774048\C,-4.0325853074,0.568970075,-0.3353 654401\C,2.4758400677,-1.2983647719,-1.8278617925\C,-2.1677054851,-2.5 171022528,-0.5896419289\C,3.9590687101,0.2908262458,0.8649005621\C,0.3 995754689,-3.1093731854,1.4857550952\C,1.1788601491,6.3246231887,3.207 7157807\C,5.2215078322,-2.2459250318,0.6959634718\C,2.8089270255,-4.54 00190434,1.0294581861\C,-1.1037302162,-4.7352003154,-2.0061388159\C,2. 0778586374,-3.9594652265,-2.7302028588\C,-2.588609093,-1.058326171,-4. 8042366185\C,-5.129522289,-0.6185494467,-2.6678039154\C,-1.9612095551, 5.5595806124,4.1302942196\C,-5.920658652,-0.3409316802,-1.5582785723\C ,-5.3835821823,0.2448948317,-0.403327316\C,-1.3391376827,-1.1133709712 ,-5.4116166686\C,-0.1928730612,-0.5974618732,-4.7876355325\C,-2.932638 2651,-3.6573903146,-0.8065100724\C,-2.4037541202,-4.7479309222,-1.5125 848957\C,0.3987983495,-4.4966904107,1.4151908065\C,1.5887099267,-5.194 7933145,1.1625204565\C,5.939298405,-1.0686197424,0.5169419787\C,5.3215 138858,0.1871804753,0.6031300587\C,2.4498179784,6.3263533055,2.6444805 962\C,2.8911733012,5.2814953906,1.8182754431\C,-3.1942331515,4.9443493 663,4.3140518854\C,-3.4934142888,3.7043869301,3.7291614971\H,2.4047685 67,3.3950437331,0.8901355879\H,-2.788809379,2.0835962255,2.4915523069\ H, 0.6172575212, 0.3774681091, -3.04634359\H, -3.6281547757, 1.0220760347, 0 .5694571706\H,-2.5811847764,-1.6890689284,-0.0153790756\H,3.4911170207 ,1.2731949134,0.9263022601\H,-0.5258644512,-2.5668878763,1.6782492209\ H, 0.8536786002, 7.1560517118, 3.8343048632\H, 5.7168925099, -3.2131165999, 0.6036973614\H,3.7244532539,-5.1080603519,0.86147931\H,-0.7024960196,-5.6067879549,-2.5245128398\H,-3.4690543829,-1.4440315911,-5.319402014\ H,-5.5643561332,-1.0893981264,-3.550312374\H,-1.7474593109,6.516691758 4,4.607625441\Cl,-7.606702437,-0.7320835221,-1.5940134612\H,-6.0403167 403,0.4491474092,0.4430200048\Cl,-1.1885740033,-1.8199997456,-6.984839 1769\H,0.7645254594,-0.6442095673,-5.3078107914\H,-3.9533982359,-3.712 1041599,-0.426084993\Cl,-3.3937152364,-6.1478502058,-1.7565817535\H,-0 .5317881888,-5.0524224024,1.5362104753\Cl,1.5282342042,-6.9188983474,1 .0129041625\Cl,7.6330669556,-1.1482570465,0.1673243632\H,5.9242542636, 1.0857164287,0.4660868811\Cl,3.5178471861,7.6533518061,2.9569595397\H, 3.8931136647,5.3319179144,1.3904874031\Cl,-4.3930694507,5.7163397468,5 .2969358895\H,-4.4706333651,3.2554531447,3.9105353831\C,3.5035616463,-1.9992003712,-2.4467933305\C,3.3071470581,-3.322695723,-2.8672046879\H ,2.6348571488,-0.2705238997,-1.5022399313\H,1.9418754967,-4.9787630567 ,-3.09329227\H,4.476738734,-1.5299584588,-2.5955915502\Cl,4.633101041, -4.1758850722,-3.5846622458\\Version=ES64L-G09RevD.01\HF=-6151.8917235 \RMSD=7.916e-09\RMSF=3.369e-06\Dipole=0.02181,-0.5642622,-0.3817545\Qu adrupole=5.917381,-3.2476726,-2.6697085,8.0943238,-11.9230946,-2.33270 96\PG=C01 [X(C56H24C18N6)]\\@

4c.cr_opt

1\1\GINC-R05-NODE47\FOpt\UPBE1PBE\Gen\C56H24C18N6(1+,2)\GRYNOVA\30-Mar -2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Emp iricalDispersion=GD3BJ Nosymm\\7e.cr_opt.pbe0.freq\\1,2\C,-1.067432131 4,1.8513633817,0.2006925785\C,-0.9847203248,0.6724550075,-0.5696075881 \C,0.0306999904,-0.2623169593,-0.2900596589\C,0.8864694549,-0.06876254 32,0.8165323059\C,0.7929277903,1.1007459954,1.5857109733\C,-0.17508860 97,2.0781204097,1.2679619584\C,-1.978172628,2.874512165,-0.1996367749\ N,-2.7135202268,3.7021393862,-0.5397341369\C,1.6100628283,1.2352301503 ,2.747498782\N,2.2873188759,1.328670209,3.6825008824\N,-0.2424208709,3 .253608627,2.0033586505\C,0.8027626474,4.1713587336,2.1523202722\C,-1. 3596975877,3.7207335627,2.7023649467\N,-1.8848510935,0.44425422,-1.604 9258272\C,-1.5521310057,0.0699865651,-2.9153204455\C,-3.2573125271,0.2
26005108,-1.4148660046\N,0.1968552256,-1.4050014324,-1.0826269708\C,1. 4082139409,-1.7465182528,-1.6737695476\C,-0.6514804784,-2.5145438428,-1.1144939387\N,1.778281443,-1.091421595,1.1795250906\C,3.1455332473,-1 .0803549763,0.8875021652\C,1.3717812639,-2.4223319841,1.3385104578\C,-1.0286981642,4.9541869466,3.3063802319\C,0.3499400597,5.2421723188,2.9 544209738\C,3.5973929263,-2.4179304277,0.7782594303\C,2.463224384,-3.2 751472262,1.071409487\C,0.064841388,-3.60811954,-1.6574565214\C,1.3808 778938,-3.1151441159,-2.0249638222\C,-2.7075389304,-0.4227275402,-3.55 54399432\C,-3.793626402,-0.3287542024,-2.5991179037\C,2.0786565872,4.1 594596496,1.592961944\c,-2.6038172667,3.1218097102,2.8878559151\c,-0.3 389483923, 0.1901899233, -3.5854653279\C, -4.0345675871, 0.3992586341, -0.2 714526714\C,2.5087348186,-0.9346347476,-1.9535655065\C,-1.946815083,-2 .656554765,-0.6223991419\C,3.9880051581,0.0031957296,0.6438526959\C,0. 1255581609,-2.9170552613,1.7150969396\c,1.1988665421,6.3087708562,3.23 09867019\C,4.8951501585,-2.677661191,0.3561277906\C,2.2859331281,-4.65 59307758,1.0948576917\C,-0.5065809805,-4.8728641816,-1.6706164388\C,2. 5069820866,-3.706218028,-2.5834713726\C,-2.638599106,-0.8592660979,-4. 8779095307\C,-5.1361599387,-0.6971759328,-2.6494345738\C,-1.9700174314 ,5.620675946,4.0836207203\C,-5.9144500181,-0.5115274505,-1.508753023\C ,-5.3724566283,0.027615924,-0.3307524982\C,-1.4103265926,-0.7861191934 ,-5.5307641709\C,-0.2737683724,-0.2567360643,-4.8994684522\C,-2.521899 9471,-3.9218297575,-0.6633277618\C,-1.8029341152,-5.0168542362,-1.1626 576838\C,-0.0448372704,-4.2956259504,1.7403889094\C,1.0147234924,-5.14 81339736,1.3978036643\c,5.7247832786,-1.590063334,0.0699407859\c,5.287 6552877,-0.2654385965,0.2337353683\C,2.4874489333,6.2819513617,2.69337 23721\C,2.9225422665,5.2249831275,1.8782878361\C,-3.2271568527,5.03380 2374,4.2435563334\C,-3.5405548281,3.7958538383,3.6600250143\H,2.416492 0516,3.3492546641,0.9453580974\H,-2.8480510468,2.1527479001,2.45126518 13\H,0.5385515217,0.6295835877,-3.1115113388\H,-3.6260689328,0.8180310 846,0.648423525\H,-2.5013126747,-1.8213412898,-0.1958916618\H,3.648284 4031,1.0328022019,0.7629996084\H,-0.6968196801,-2.2505256561,1.9781232 072\H,0.8783038726,7.1529704198,3.842711402\H,5.260619327,-3.695488956 2,0.2147947124\H,3.1014651676,-5.3438057126,0.8679857603\H,0.036238998 8,-5.7461621291,-2.0340287029\H,-3.5152152602,-1.244942136,-5.39984573 67\H,-5.5754887157,-1.1308241347,-3.5486976879\H,-1.7448815238,6.57279 84251,4.5656710147\C1,-7.5778401488,-0.9587023454,-1.5340717283\H,-6.0 191726904,0.1580245047,0.5376631823\Cl,-1.2814133757,-1.3363865714,-7. 1598600744\H,0.660699031,-0.1897086554,-5.4578948476\H,-3.5345160318,-4.0764443597,-0.2887144366\C1,-2.5157218915,-6.5791476749,-1.124967398 5\H,-1.0091817013,-4.7286047617,2.0074002371\Cl,0.7285594636,-6.846443 2367,1.3382666304\C1,7.312320592,-1.8804317778,-0.521284707\H,5.981979 3091,0.5501799115,0.0281090783\Cl,3.565378877,7.5809749787,3.023207773 5\H,3.9328256417,5.2547588213,1.4689173702\Cl,-4.417579771,5.836956195 8,5.1896211296\H,-4.5304713201,3.3692453446,3.8247765018\C,3.626008636 1,-1.5265000894,-2.5250764046\C,3.6336343892,-2.9031212384,-2.79920344 32\H,2.5026076059,0.132536481,-1.7296660842\H,2.5322654467,-4.76512653 38,-2.8439081559\H,4.516257913,-0.9365464345,-2.7438137836\Cl,5.071520 6501,-3.6185465131,-3.4109608519\\Version=ES64L-G09RevD.01\HF=-6151.62 44985\s2=0.7581\s2-1=0.\s2A=0.750066\RMSD=5.639e-09\RMSF=3.229e-06\Dip ole=0.6000222,-0.5841405,-0.0332361\Quadrupole=7.6779123,13.0273837,-2 0.7052959,2.7303431,-14.2922603,22.5539184\PG=C01 [X(C56H24C18N6)]\\@

4c.ar_opt

1\1\GINC-R05-NODE56\FOpt\UPBE1PBE\Gen\C56H24C18N6(1-,2)\GRYNOVA\30-Mar -2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Emp iricalDispersion=GD3BJ Nosymm\\7e.ar_opt.pbe0.freq\\-1,2\C,-1.02662888 76,1.8750019852,0.1326588217\C,-0.9432344946,0.6392009692,-0.631663899 6\C,0.0264169492,-0.3071129857,-0.3021452524\C,0.8779992938,-0.1350233 551,0.8074245197\C,0.7529191683,1.0644204982,1.6127326969\C,-0.1777991 498,2.0405956161,1.2395647403\C,-1.8811653597,2.9181445064,-0.28459158 53\N,-2.6065547576,3.7636014161,-0.6284909288\C,1.5347837392,1.2184516 317,2.7809320645\N,2.2025608796,1.3397590113,3.7276576414\N,-0.2605256 011,3.2309970008,1.9907739703\C,0.7428654844,4.1805565106,2.1083795214 \C,-1.361001009,3.6521435196,2.7211840076\N,-1.8529909383,0.4132482733 ,-1.6816037149\C,-1.5467294731,0.168698516,-3.0115789487\C,-3.21847312 54,0.2392080723,-1.5095076296\N,0.156447267,-1.479469207,-1.0880071795 \C,1.3506317248,-1.8735340693,-1.6800504536\C,-0.6829983015,-2.5863325 768,-1.0223725934\N,1.8100911949,-1.1334562634,1.1652632803\C,3.167553 5201,-1.0848286065,0.8653867878\C,1.4720298713,-2.4641100754,1.3891306 574\C,-1.0633255993,4.896297484,3.3278555935\C,0.2840575082,5.23664336 04,2.9322782337\C,3.6910535018,-2.4000509675,0.8264933658\C,2.59828863 81, -3.2878730578, 1.1550375614 \ C, 0.0003494854, -3.7169319097, -1.53425937 13\C,1.3043930614,-3.2589503181,-1.9560301242\C,-2.7281200524,-0.19016 20873,-3.7064393738\C,-3.8027106321,-0.1417190112,-2.7419109019\C,2.01 29355567,4.2023193164,1.5336434812\C,-2.59009301,3.0228564038,2.912645 4974\C,-0.3160106432,0.2403087332,-3.6619668369\C,-3.9787162784,0.3506 726562,-0.3449273903\C,2.4703986321,-1.1053709479,-1.9947340493\C,-1.9 699030918,-2.6895425603,-0.4990258771\C,3.9568602249,0.0249163673,0.57 0884859\C,0.2421698593,-3.0019427408,1.7646972691\C,1.1156670103,6.328 4001523,3.1935657978\c,5.0127095023,-2.6115163442,0.4298850438\c,2.467 682916,-4.67805324,1.2136082082\C,-0.597354,-4.9768380013,-1.482047639 8\C,2.4256361843,-3.8999030432,-2.488937973\C,-2.6707683839,-0.5009864 36,-5.0675186388\C,-5.1716682601,-0.4096985955,-2.8102207572\C,-2.0160 410024,5.5240968955,4.1340771154\C,-5.9208334433,-0.2938386187,-1.6461 839997\C,-5.3390210913,0.0812464562,-0.4249650109\C,-1.4359743781,-0.4 449398555,-5.6998433611\C,-0.2684592157,-0.0751592153,-5.0125185697\C, -2.5603819061,-3.9461717104,-0.4633103963\C,-1.8707511581,-5.072973525 1,-0.9365029414\C,0.1220008327,-4.3826892844,1.8279638389\C,1.22004228 58,-5.2026730933,1.5239300848\C,5.7809016323,-1.5019019384,0.102477571 1\C,5.2732901956,-0.1954613684,0.1867953019\C,2.3814897021,6.337176248 8,2.6234093087\C,2.8305567426,5.2920007928,1.8007063414\C,-3.239340180 9,4.8925261221,4.3135285549\C,-3.5293508399,3.6563167334,3.7148031067\ H,2.3553612979,3.3851139356,0.8979016254\H,-2.809814354,2.0648765314,2 .4407710179\H,0.5860239002,0.5326350078,-3.1263091781\H,-3.5192874229, 0.6471692907,0.5986691332\H,-2.4959316461,-1.8193861621,-0.108326661\H ,3.5473010197,1.0342822684,0.6275969559\H,-0.6089844563,-2.3534661884, 1.9730578135\H,0.7884172131,7.1566372696,3.8235871827\H,5.4295576121,-3.6154416394,0.3403765616\H,3.3068414619,-5.3397192226,0.9946623499\H, -0.0755141258, -5.8710625328, -1.8244614684\H, -3.5640909552, -0.783209932 1,-5.6264560013\H,-5.6480322754,-0.7113578029,-3.7441156439\H,-1.81392 88604, 6.482244783, 4.6147758929\Cl, -7.6288049607, -0.6231910929, -1.69476 53649\H,-5.9710184967,0.1641633794,0.4601945123\Cl,-1.3247257941,-0.83 85894979,-7.3912688775\H,0.6792009265,-0.0420173013,-5.5516262263\H,-3 .5653813749,-4.0685925922,-0.057236515\C1,-2.6298718262,-6.6323102135, -0.8149270115\H,-0.8336335125,-4.8444598883,2.0778520383\Cl,0.98987294 76,-6.9270852061,1.5073195886\Cl,7.4160592717,-1.7293881675,-0.4457241 852\H,5.9255690554,0.6433610852,-0.0603210768\Cl,3.4460546942,7.679171 5503,2.9297543828\H,3.8339730331,5.3453605105,1.376410516\Cl,-4.451196 4192,5.6467409157,5.3087565879\H,-4.5059678253,3.2013026349,3.88464521 81\C, 3.5779663509, -1.7472683476, -2.5305758905\C, 3.5545124135, -3.133395 4681,-2.746634039\H,2.4939861706,-0.0355814643,-1.7865783396\H,2.43215 12248, -4.974280583, -2.6769508784\H, 4.4880660708, -1.1889161237, -2.75120 45011\C1,4.9993313418,-3.9085199755,-3.3256089645\\Version=ES64L-G09Re vD.01\HF=-6151.979874\S2=0.767575\S2-1=0.\S2A=0.750219\RMSD=7.128e-09\ RMSF=4.256e-06\Dipole=0.2153552,-1.5497361,-0.8827777\Quadrupole=4.335 4309,-11.535436,7.2000051,14.9557599,-17.0726744,-18.0516664\PG=C01 [X (C56H24C18N6)]\\@

4d

1\1\GINC-R08-NODE07\FOpt\RPBE1PBE\Gen\C56H24Br8N6\GRYNOVA\30-Mar-2018\ 0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Empirical Dispersion=GD3BJ pseudo=read Nosymm\\7f.pbe0.freq\\0,1\C,-1.0460453376 ,1.862909102,0.1737836128\C,-0.9739461744,0.6740272243,-0.5826059837\C ,0.0102655539,-0.2872123607,-0.2831515758\C,0.852214038,-0.0997829243, 0.839194809\C,0.7496391724,1.0753630195,1.6045717565\C,-0.1825083455,2 .0717523613,1.2620250403\C,-1.9335153293,2.9030185698,-0.2375505035\N, -2.6473834924,3.7491415347,-0.5782268894\C,1.5407570818,1.2143459705,2 .7851909895\N,2.184490513,1.3266355764,3.7415458903\N,-0.2444989301,3. 2541439224,1.9970757794\c,0.7934473812,4.1798925909,2.1211308406\c,-1. 346525816, 3.7125942968, 2.7213412763 \N, -1.8753933243, 0.4687089489, -1.62 86971638\C,-1.5463936279,0.0743051744,-2.9290880033\C,-3.2500503208,0. 2700546275,-1.4395399508\N,0.159279857,-1.4249745346,-1.0845600235\C,1 .3730603961,-1.7961647609,-1.6667797286\C,-0.7047677474,-2.5240110239, -1.1234973785\N,1.7612924777,-1.0959967053,1.2232484249\C,3.1406758556 ,-1.0301164835,0.9655313371\C,1.4065226801,-2.4469923146,1.3317730665\ C,-1.0119581303,4.9487955519,3.3175829373\C,0.3518604751,5.2472269871,

2.9339914349\C,3.6464977034,-2.3442387863,0.84804004\C,2.5389979792,-3 .2484614462,1.0799874531\C,-0.012492154,-3.6229717182,-1.6828435372\C, 1.3143161618,-3.158306397,-2.0278125497\C,-2.7101974184,-0.3960771239, -3.5733151784\C,-3.7957803215,-0.2752364441,-2.6229823956\C,2.06149606 65,4.1690618027,1.5466149328\C,-2.5860884645,3.1120299538,2.9223859178 \C,-0.3213763166,0.1384109235,-3.5853556036\C,-4.0243496089,0.45915214 72,-0.2979401403\C,2.5004448795,-1.0182449552,-1.915730777\C,-2.005331 6167,-2.6456803335,-0.6445700891\C,3.9449074909,0.0853529598,0.7568475 881\C,0.1712107671,-2.9998627081,1.6534789519\C,1.2069178384,6.3187301 778,3.1971966125\C,4.9728401922,-2.549389228,0.4695363862\C,2.41054809 96,-4.6378788021,1.0461253646\C,-0.6210266122,-4.8768504083,-1.7346865 89\C,2.443693129,-3.7819824372,-2.561001724\C,-2.6400503017,-0.8567267 915,-4.8892364058\C,-5.145649004,-0.6236893063,-2.671682218\C,-1.94735 93581,5.6108181718,4.1144889793\C,-5.9147399285,-0.4245425966,-1.53083 09877\C,-5.3693565424,0.1087399003,-0.3552617648\C,-1.4039941917,-0.83 04714024,-5.5233034952\C,-0.2553664179,-0.3327245737,-4.8902890142\C,-2.6088116986, -3.8962184574, -0.7121247859\C, -1.9138680897, -4.9944036656 ,-1.2388307034\C,0.0488541702,-4.3834291525,1.6235716982\C,1.152611544 6,-5.178980673,1.2863560684\C,5.7615188195,-1.4308271261,0.2287726635\ C,5.2678527863,-0.1276778679,0.3840617507\C,2.4781618072,6.2927615286, 2.6366668456\C,2.9069561886,5.2383139476,1.817630167\C,-3.1897781771,5 .0152658368,4.2950587439\C,-3.5121984932,3.7802507105,3.7142572936\H,2 .3919740087,3.3551299479,0.8994431554\H,-2.8341563154,2.1456597604,2.4 813595707\H,0.5688466705,0.5390814186,-3.101909268\H,-3.6068861388,0.8 694258878,0.6216099774\H,-2.542647993,-1.8057518603,-0.2055744232\H,3. 5618855063,1.100425959,0.8673522184\H,-0.6872975022,-2.3731954249,1.89 70395171\H,0.8896493709,7.1560868975,3.8201973157\H,5.3730766534,-3.55 40774835,0.3277257679\H,3.2597498887,-5.2807283793,0.8109678352\H,-0.0 926422474,-5.7478001997,-2.1241191676\H,-3.5245951376,-1.229203414,-5. 4074960837\H,-5.585801897,-1.0542682061,-3.5722314324\H,-1.7131057854, 6.5657424422,4.586952867\Br,-7.7523074449,-0.8975115096,-1.5553548943\ H,-6.0073033284,0.2512828546,0.5178960801\Br,-1.2616855629,-1.47245618 25, -7.3034923816\H, 0.6932485153, -0.314538218, -5.428409858\H, -3.6272572 27,-4.0286561023,-0.3442617169\Br,-2.759794299,-6.6925695014,-1.249958 5513\H,-0.9130166783,-4.8537919483,1.829961352\Br,0.8987150833,-7.0516 40154,1.1151258637\Br,7.5512222874,-1.6670554736,-0.3545499315\H,5.928 7245554,0.7217777739,0.2065177272\Br,3.6717704323,7.7289965343,2.97749 32904\H,3.9106538352,5.2631589447,1.3914662331\Br,-4.4898803324,5.8888 946203,5.3674035228\H,-4.4967081841,3.3447388141,3.8896038329\C,3.6180 888185, -1.6408239344, -2.4567290384\C, 3.5887537581, -3.0140052441, -2.738 8389435\H,2.5291186177,0.0433321556,-1.6678671558\H,2.439143548,-4.843 4373224,-2.8122868926\H,4.5316841504,-1.0720986232,-2.6329263306\Br,5. 1818005591,-3.8465748389,-3.3477695507\\Version=ES64L-G09RevD.01\HF=-2 576.7787164\RMSD=3.411e-09\RMSF=3.761e-06\Dipole=-0.0525069,-0.1498629 ,-0.2085434\Quadrupole=4.420551,-4.6488058,0.2282548,8.2778991,-11.174 5657,-5.8325233\PG=C01 [X(C56H24Br8N6)]\\@

4d.cr_opt

1\1\GINC-R03-NODE39\FOpt\UPBE1PBE\Gen\C56H24Br8N6(1+,2)\GRYNOVA\30-Mar -2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Emp iricalDispersion=GD3BJ pseudo=read Nosymm\\7f.cr opt.pbe0.freq\\1,2\C, -1.0630476349,1.8728919291,0.1991275053\C,-0.980181865,0.6954860456,-0 .5724661008\C,0.0261338735,-0.2462273119,-0.2844434916\C,0.8760384982, -0.0587711083,0.827013873\C,0.7828718474,1.1100809639,1.5972464576\C,-0.1778263499,2.0921959004,1.2736767497\C,-1.9704470202,2.8990483672,-0 .2013414531\N,-2.7043020873,3.7285791092,-0.5398505234\C,1.5964633144, 1.2426997853,2.7617834728\N,2.2710482103,1.3354308507,3.6987189167\N,-0.244770197,3.267477255,2.0111876803\C,0.8006643073,4.1841821981,2.160 5469993\C,-1.3611366174,3.7325691604,2.7120744783\N,-1.8736002559,0.47 20220017,-1.6164576409\C,-1.5252737102,0.0823644421,-2.918066211\C,-3. 24252988,0.2288871288,-1.4308844361\N,0.190942487,-1.3905221919,-1.076 3447707\C,1.3994438739,-1.7326448713,-1.6720727985\C,-0.6630945141,-2. 4943002883,-1.1149204388\N,1.7644285801,-1.0854801974,1.1899602752\C,3 .1314374685,-1.0766158646,0.8996119529\C,1.3537701326,-2.4159657654,1. 344081507\C,-1.0293587636,4.9649924836,3.3179205633\C,0.348772541,5.25 34199572,2.9653170947\c,3.5801208229,-2.4152164382,0.7864144947\c,2.44 31739261,-3.2703015667,1.0735922588\C,0.0452197622,-3.5868402774,-1.67 06958536\C,1.3640373038,-3.0983924384,-2.0342915522\C,-2.6652022332,-0

.4477739162,-3.555681555\C,-3.7588187988,-0.3599202475,-2.6077495359\C ,2.0763707989,4.1702458934,1.6011585376\C,-2.6049022209,3.1325397903,2 .89555076\c,-0.3085511417,0.2130995748,-3.5793056166\c,-4.0291336713,0 .4069551758,-0.2947743535\c,2.5034242067,-0.9234285662,-1.9450024105\c ,-1.9583329097,-2.6313034162,-0.6209619749\C,3.9764625432,0.0065543472 ,0.661702389\C,0.1054029227,-2.907958077,1.7162055244\C,1.1998260703,6 .3183594716,3.2439484364\C,4.8783751422,-2.6766424593,0.366285304\C,2. 2603327735,-4.6506905296,1.0846656977\C,-0.5367579299,-4.8468300094,-1 .6985614164\C,2.4886965757,-3.691294588,-2.5943285131\C,-2.5746592754, -0.9149959006,-4.866728514\C,-5.0910671246,-0.7657361606,-2.6557992397 \C,-1.9710476546,5.6297010788,4.0969543565\C,-5.8752408653,-0.58101110 46,-1.5201288236\C,-5.3566965804,-0.0018755711,-0.3515926998\C,-1.3411 25891,-0.8326089009,-5.5066872261\C,-0.2210399104,-0.2645756493,-4.881 6488008\C,-2.5447683895,-3.8910592454,-0.6776105216\C,-1.834301928,-4. 9835225474,-1.192599742\C,-0.0709905169,-4.2868189005,1.7302474797\C,0 .986481144,-5.1380065503,1.3819367591\C,5.7085834341,-1.5889055054,0.0 858364754\C,5.2763929949,-0.2634866108,0.2528357098\C,2.4868511999,6.2 884334054,2.7049486701\C,2.9224797518,5.234068106,1.8884761597\C,-3.22 62334758, 5.0401356448, 4.2550034313\C, -3.5420778921, 3.8046532659, 3.6697 711356\H,2.4128370509,3.3605468145,0.9522348334\H,-2.8488304036,2.1642 781551,2.4569359392\H,0.5546500348,0.682169418,-3.107376514\H,-3.63679 27472,0.8563403146,0.6175551269\H,-2.5040002594,-1.7976700114,-0.18058 09991\H,3.6393280575,1.0365115371,0.7847092393\H,-0.7146628478,-2.2403 837414,1.9836811678\H,0.8758864015,7.1591706071,3.8590083426\H,5.23766 17558,-3.697121226,0.2261119914\H,3.0766905248,-5.3357432235,0.8513310 501\H,0.0023544617,-5.7168521332,-2.0760724308\H,-3.4410252186,-1.3318 84752,-5.3821885057\H,-5.5097902631,-1.2285234763,-3.55070091\H,-1.740 96908, 6.5812767659, 4.5783581697\Br, -7.6820364124, -1.1331161677, -1.5413 975936\H,-6.0061124488,0.1312454161,0.514705534\Br,-1.1703026079,-1.48 33965216,-7.2744269961\H,0.7201284213,-0.1899801283,-5.4282301617\H,-3 .5586045443,-4.036063675,-0.3017933934\Br,-2.6293116091,-6.6897746674, -1.1728804381\H,-1.0398163915,-4.7126215651,1.9936328895\Br,0.66520500 8,-6.9975978942,1.2933813149\Br,7.4473766572,-1.9108910406,-0.56268894 54\H,5.9687055389,0.5555029759,0.0529002153\Br,3.6707316499,7.71086952 89,3.0704851769\H,3.9320193411,5.2575178657,1.4763574973\Br,-4.5300120 669,5.9188861823,5.2966351209\H,-4.5304480346,3.3723368853,3.830540956 9\C,3.6189033075,-1.5164482712,-2.5202415995\C,3.6180475717,-2.8905055 366,-2.8025718257\H,2.5018589424,0.1421887174,-1.7141700505\H,2.504627 7523, -4.7493956867, -2.8597446643\H, 4.5087626327, -0.9236835809, -2.73403 39791\Br,5.1927606227,-3.6793084409,-3.4703604512\\Version=ES64L-G09Re vD.01\HF=-2576.5032234\S2=0.757621\S2-1=0.\S2A=0.750059\RMSD=6.355e-09 \RMSF=4.719e-06\Dipole=0.7213894,-0.7122403,-0.0429002\Quadrupole=8.00 90037,12.4869932,-20.4959968,2.7158059,-14.6119123,21.0889567\PG=C01 [X(C56H24Br8N6)]\\@

4d.ar_opt

1\1\GINC-R08-NODE11\FOpt\UPBE1PBE\Gen\C56H24Br8N6(1-,2)\GRYNOVA\30-Mar -2018\0\\#PBE1PBE/gen SCF=Tight INT(grid=finegrid) OPT IOP(2/17=4) Emp iricalDispersion=GD3BJ pseudo=read Nosymm\\7f.ar opt.pbe0.freq\\-1,2\C ,-1.0251535067,1.8817529787,0.1323267869\C,-0.9398404222,0.6468623161, -0.6324408593\C,0.0266131803,-0.3012799361,-0.2991420682\C,0.874795937 6,-0.1311236906,0.8131886192\C,0.7496654678,1.0687330909,1.617480496\C ,-0.1790993995,2.0451304316,1.2413878428\C,-1.8811958023,2.9244065129, -0.282888181\N,-2.6084657512,3.7690552693,-0.6242351382\C,1.531145708, 1.2248229288,2.7856840447\N,2.1988452578,1.3486915279,3.7319108362\N,-0.2631814096, 3.2356619642, 1.9931952281\C, 0.7377095887, 4.18733701, 2.107 1756016\C,-1.3617872845,3.6513498091,2.7283664618\N,-1.8469075171,0.42 04373946,-1.6850268658\C,-1.5349960532,0.1685000945,-3.0119337781\C,-3 .2122917771,0.2448396822,-1.5160100302\N,0.1554912909,-1.4750268756,-1 .0835258237\C,1.3485759273,-1.8728892753,-1.6741630684\C,-0.6901685301 ,-2.5769014224,-1.021822719\N,1.8077183547,-1.1292985325,1.1705129465\ C,3.1656747503,-1.0758509777,0.8750235422\C,1.4714616239,-2.4608916494 ,1.3890544663\C,-1.0656103683,4.8959286043,3.3352129553\C,0.2791622266 ,5.2409890564,2.9345280363\C,3.6921703793,-2.3897563647,0.8320776575\C ,2.5998948333,-3.2814058011,1.152099414\C,-0.0121364996,-3.7098584904, -1.5356645636\C,1.2961700686,-3.2581355773,-1.9513655075\C,-2.71294325 86,-0.1991556367,-3.7082100355\C,-3.7911543153,-0.1466079673,-2.747701 255\C,2.0050502544,4.2115571905,1.526540843\C,-2.5873908944,3.01624183

9,2.9229552755\C,-0.3015090864,0.2405075919,-3.6570606669\C,-3.9751782 817,0.3625377293,-0.3537233945\C,2.4721599989,-1.1084155187,-1.9844450 787\C,-1.9779994416,-2.6728147385,-0.499308232\C,3.9516291765,0.037864 5215,0.5861621987\C,0.2414299886,-3.0014620183,1.7603686578\C,1.108666 4271,6.3343243598,3.1939678599\C,5.0146461686,-2.5973451829,0.43678882 08\C,2.4699960572,-4.6717717943,1.1943781427\C,-0.617169841,-4.9663765 705,-1.4889789574\C,2.4184857891,-3.9054973379,-2.4732437133\C,-2.6494 429819,-0.5218456276,-5.0658409682\C,-5.1584815989,-0.4206934829,-2.81 85310485\C,-2.0168504462,5.5193432217,4.1459023482\C,-5.9073448031,-0. 2989622315,-1.6553281624\C,-5.3343502249,0.0873394074,-0.4343174985\C, -1.4106741731,-0.466126912,-5.689645879\C,-0.2458370622,-0.0864936335, -5.0047110204\C,-2.5782252477,-3.9251096318,-0.4699347811\C,-1.8929185 946,-5.0518073567,-0.9478743085\C,0.1205197182,-4.3830085495,1.8105983 418\C,1.2205728986,-5.1958104241,1.4973942961\C,5.7774842762,-1.482251 2735,0.1170010415\C,5.2697207176,-0.176697982,0.2041685858\C,2.3708026 399,6.3429596012,2.6166881125\C,2.8224183455,5.3022405966,1.7911139539 \c,-3.2353185961,4.8798035899,4.326894605\c,-3.5269897239,3.6443165047 ,3.7292988851\H,2.3461451196,3.3961535701,0.8878350137\H,-2.8046226726 ,2.057597894,2.4513231596\H,0.5966160298,0.5425825138,-3.12026853\H,-3 .5196050697,0.6678042232,0.5888264063\H,-2.4983933824,-1.8011983789,-0 .1046114049\H,3.5397112595,1.0459683179,0.6464372105\H,-0.6096478535,-2.3550324791,1.9752677859\H,0.7778879345,7.1587374592,3.8271828659\H,5 .4304546877,-3.6017671475,0.3474724084\H,3.312024276,-5.3270216161,0.9 670553007\H,-0.0974138172,-5.8599611977,-1.8365483507\H,-3.5422191005, -0.8114652048,-5.6219348203\H,-5.6266094344,-0.7305728943,-3.754033108 4\H,-1.8118543213,6.4775610444,4.6253025624\Br,-7.7759435733,-0.670642 2309,-1.7117221013\H,-5.9642973406,0.175389647,0.451852903\Br,-1.28155 52623,-0.9162925139,-7.537252751\H,0.7064009435,-0.0515726258,-5.53566 82703\H,-3.585136258,-4.0366699041,-0.0653700898\Br,-2.7370502105,-6.7 541803687,-0.828378179\H,-0.8368115183,-4.8424372257,2.0587442748\Br,0 .9661573002,-7.0828668044,1.4428681364\Br,7.5694309954,-1.7256849254,-0.4815459675\H,5.9162724921,0.6683986902,-0.0362395468\Br,3.5330862845 ,7.8166839704,2.9503116595\H,3.822874887,5.353521732,1.3596317278\Br,-4.5591934778,5.7012125687,5.4252563796\H,-4.4995565169,3.1806221478,3. 8992898701\C,3.5814162655,-1.7549364203,-2.5120386046\C,3.5506956061,-3.1412755013,-2.72166151\H,2.4983773856,-0.0382037182,-1.7788864137\H, 2.4176153446,-4.9808137236,-2.6560981954\H,4.4916716455,-1.1950761822, -2.7287394716\Br,5.1385571934,-4.0021950778,-3.3241236509\\Version=ES6 4L-G09RevD.01\HF=-2576.8759924\S2=0.767544\S2-1=0.\S2A=0.75022\RMSD=3. 895e-09\RMSF=4.653e-06\Dipole=0.1719442,-0.9812473,-0.5723511\Quadrupo 1e=2.5482146,-13.5916034,11.0433888,14.8778283,-15.6018832,-22.4645446 \PG=C01 [X(C56H24Br8N6)]\\@

9. Spectra for new compounds



¹H-NMR (400 MHz, DMSO-*d*₆)



¹⁹F NMR (376 MHz, DMSO-d₆)



| 10 | 0 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | -80 | -90 | -100 | -110 | -120 | -130 | -140 | -150 | -160 | -170 | -180 | -190 | -200 |
|----------|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|------|------|------|
| f1 (ppm) | | | | | | | | | | | | | | | | | | | | | |















1.7

74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 f1 (ppm)



















S90































S101











¹⁹F-NMR (376 MHz, Chloroform-d)




















-80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 fl (ppm)

 $<^{-111.4}_{-111.4}$



























