Preparation of Polyfunctional Arylmagnesium Reagents Bearing a Triazene Moiety. A new Carbazole Synthesis

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Supporting Information

General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes used to transfer reagents and solvent were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC).

Preparation of the reagent *i*-PrMgCl·LiCl:

Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an Ar-flushed flask and THF (25 mL) was added. A solution of *i*-PrCl (100 mmol) in THF (25 mL) was slowly added at rt. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at rt. The grey solution of *i*-PrMgCl·LiCl was transferred to another flask under Ar and removed in this way from excess of magnesium. A yield of ca. 95-98 % of *i*-PrMgCl·LiCl is obtained.

General Procedure A for the Preparation of 1-(2,6-dibromophenylazo)pyrrolidine (2a).¹

A solution of 2,6-dibromoaniline (4.6 g, 18.1 mmol) in 7.2 mL of conc. HCl was cooled in an ice bath while a solution of NaNO₂ (1.3 g, 19.0 mmol) in 40 mL of cold water was added dropwise. The resulting solution of the diazonium salt was stirred at 0 °C for 30 min and then

added at once to a solution of pyrrolidine (2.6 g, 36.2 mmol) and K_2CO_3 (12.5 g, 90.5 mmol) in 1:2 acetonitrile/water (25 mL). The reaction mixture was stirred for 30 min at 0 °C and was extracted with CH_2Cl_2 (3×50 mL). The organic layer was washed twice with brine, dried ($MgSO_4$), filtered, and concentrated by evaporation. The crude product was purified by flash chromatography over silica gel giving the pure product **2a** (5.7 g, 95 %) as a yellow liquid. 1H NMR ($CDCl_3$, 300 MHz): 7.50 (d, $J = 8.0$ Hz, 2 H), 6.82 (t, $J = 8.0$ Hz, 1 H), 3.93 (br s, 2 H, CH_2N), 3.71 (br s, 2 H, CH_2N), 2.05 (br s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): 148.1, 132.3, 126.5, 117.9, 51.2, 46.6, 24.0, 23.6; IR (film): 3065, 2950, 2974, 2873, 1922, 1865, 1666, 1548, 1416, 1339, 1260, 970 cm^{-1} ; MS (EI, 70 ev), m/z (%): 333 (M^+ , 14 %), 263 (69 %), 235 (100 %), 168 (6 %), 154 (12 %), 75 (16 %); HRMS (EI): calcd. for $C_{10}H_{11}Br_2N_3$: 330.9320, found: 330.9318.

General Procedure B for the preparation of triazene (3a). To a solution of 1-(2,6-dibromophenylazo)pyrrolidine (**2a**) (333 mg, 1.0 mmol) in THF (0.25 mL) was slowly added *i*-PrMgCl·LiCl (0.55 mL, 1.1 mmol, 2.0 M in THF) at −40 °C. The reaction temperature was gradually increased to −15 °C. After 4 h, a complete conversion to the Grignard reagent (**1a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Allyl bromide (2.0 mmol) in THF (1 mL) was added and the reaction mixture was warmed up to rt and quenched as usual. The aqueous phase was extracted with ether (3×10 mL). The organic layers were washed with brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 19:1) yielded the pure product **3a** (229 mg, 78 % yield) as a pale yellow oil. 1H NMR ($CDCl_3$, 300 MHz): 7.43 (dd, $J = 1.3, 8.0$ Hz, 1 H), 7.11 (dd, $J = 1.3, 7.5$ Hz, 1 H), 6.91 (t, $J = 7.7$ Hz, 1 H), 5.79-5.92 (m, 1 H), 4.94-5.04 (m, 2 H), 3.79 (br s, 4 H, CH_2N), 2.03 (br s, 4 H, CH_2N); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.6, 148.3, 137.0, 134.5, 131.1, 129.0, 125.8, 117.3, 115.6, 36.4, 23.8; IR (film): 3058, 2975, 2872, 1736, 1637, 1560, 1421, 1336, 1210, 1160, 1107, 1027, 995, 913, 859 cm^{-1} ; MS (EI, 70 ev): 295 (M^+ , ^{81}Br , 2 %), 293 (M^+ , ^{79}Br , 2 %), 279 (2 %), 264 (2 %), 250 (2 %), 223 (11 %), 208 (4 %), 186 (4 %), 130 (5 %), 116 (100 %), 102 (4 %), 83 (9 %), 63 (5 %); HRMS (EI): calcd. for $C_{13}H_{16}BrN_3$: 293.0528, found: 293.0545.

General Procedure C for the preparation of triazene (3b). To a solution of 1-(2,6-dibromophenylazo)pyrrolidine (**2a**) (999 mg, 3.0 mmol) in THF (0.7 mL) was slowly added *i*-PrMgCl·LiCl (1.6 mL, 3.3 mmol, 2.0 M in THF) at $-40\text{ }^{\circ}\text{C}$. The reaction temperature was gradually increased to $-15\text{ }^{\circ}\text{C}$. After 4 h, a complete conversion to the Grignard reagent (**1a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. CuCN·2LiCl (3 mL, 3.0 mmol, 1.0 M in THF) was added at $-30\text{ }^{\circ}\text{C}$ and the reaction mixture was stirred for 30 min. Benzoyl chloride (4.5 mmol) in THF (1 mL) was added and the reaction mixture was stirred for 1 h at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was warmed up to rt and stirred again for 1 h before the addition of aq. NH_3 (5 mL). The aqueous phase was extracted with ether ($2 \times 30\text{ mL}$). The organic fractions were washed with brine (30 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 3:1) yielded the pure product **3b** (881 mg, 82 %) as a white solid; m.p.: $113.5\text{--}114.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 7.74 (dd, $J = 1.3, 8.0\text{ Hz}$, 1 H), 7.58–7.66 (m, 2 H), 7.28–7.46 (m, 4 H), 7.09 (t, $J = 8.0\text{ Hz}$, 1 H), 3.47 (br s, 2 H, CH_2N), 3.22 (br s, 2 H, CH_2N), 1.60–1.80 (m, 4 H); ^{13}C NMR (CDCl_3 , 75 MHz): 196.4, 147.8, 137.5, 134.9, 132.6, 132.1, 128.9, 128.8, 128.2, 125.6, 119.2, 50.5, 46.9, 23.6, 23.2; IR (KBr): 2974, 2950, 2863, 1664, 1596, 1581, 1450, 1395, 1364, 1303, 1273, 1259, 1225, 1156, 1129, 1071, 949 cm^{-1} ; MS (EI, 70 eV): 359 (M^+ , ^{81}Br , 3 %), 357 (M^+ , ^{79}Br , 3 %), 289 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{81}Br , 19 %), 287 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{79}Br , 19 %), 180 (100 %), 166 (3 %), 152 (39 %), 139 (1 %), 126 (1 %), 105 (21 %), 77 (26 %), 51 (5 %); HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{16}\text{BrN}_3\text{O}$: 357.0477, found: 357.0445.

General Procedure D for the preparation of triazene (3d). To a solution of 1-(2,6-dibromophenylazo)pyrrolidine (**2a**) (999 mg, 3.0 mmol) in THF (0.7 mL) was slowly added *i*-PrMgCl·LiCl (1.6 mL, 3.3 mmol, 2.0 M in THF) at $-40\text{ }^{\circ}\text{C}$. The reaction temperature was

gradually increased to $-15\text{ }^{\circ}\text{C}$. After 4 h, a complete conversion to the Grignard reagent (**1a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. $\text{CuCN}\cdot 2\text{LiCl}$ (3.0 mmol, 3 mL, 1.0 M in THF) was added at $-30\text{ }^{\circ}\text{C}$ and the reaction mixture was stirred for 30 min. 3-Iodo-cyclohex-2-enone (3.0 mmol) in THF (1.5 mL) was added and the reaction mixture was stirred continuously for 3 h at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was gradually warmed up to rt and stirred again for 1 h before the addition of aq. NH_3 (5 mL). The aqueous phase was extracted with ether ($2 \times 30\text{ mL}$). The organic fractions were washed with brine (30 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:1.5) yielded the pure product **3d** (835 mg, 80 %) as a white solid; m.p.: $101.5\text{--}102.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 7.56 (dd, $J = 1.5, 8.0\text{ Hz}$, 1 H), 7.06 (dd, $J = 1.5, 7.5\text{ Hz}$, 1 H), 6.96 (t, $J = 7.7\text{ Hz}$, 1 H), 6.00 (s, 1 H), 3.81 (br s, 2 H, CH_2N), 3.66 (br s, 2 H, CH_2N), 2.34–2.42 (m, 3 H), 1.90–2.10 (m, 7 H); ^{13}C NMR (CDCl_3 , 75 MHz): 199.4, 164.0, 146.7, 134.8, 133.4, 128.6, 127.9, 125.7, 118.9, 51.1, 46.7, 37.5, 30.6, 23.9, 23.5, 23.2; IR (KBr): 2975, 2948, 2873, 1663, 1408, 1346, 1317, 1244, 1210, 1188, 962 cm^{-1} ; MS (EI, 70 ev): 349 (M^+ , ^{81}Br , 4 %), 347 (M^+ , ^{79}Br , 4 %), 279 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{81}Br , 8 %), 277 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{79}Br , 8 %), 251 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, ^{81}Br , 12 %), 249 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, ^{79}Br , 12 %), 142 (100 %), 128 (27 %), 114 (27 %); HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{18}\text{BrN}_3\text{O}$: 347.0633, found: 347.0662

Triazene (3c) was prepared from 1-(2,6-dibromophenylazo)pyrrolidine (**2a**) (999 mg, 3.0 mmol) according to the general procedure **C** and yielding the pure product **3c** (887 mg, 85 %). A yellow solid; m.p.: $124.0\text{--}125.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 7.69 (dd, $J = 1.3, 8.0\text{ Hz}$, 1 H), 7.44–7.50 (m, 1 H), 7.32 (dd, $J = 1.3, 7.5\text{ Hz}$, 1 H), 7.03 (t, $J = 7.8\text{ Hz}$, 1 H), 6.84 (d, $J = 3.5\text{ Hz}$, 1 H), 6.40 (dd, $J = 1.8, 3.5\text{ Hz}$, 1 H), 3.56 (br s, 2 H, CH_2N), 3.46 (br s, 2 H, CH_2N), 1.85 (br s, 2 H, CH_2), 1.79 (br s, 2 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 184.1, 152.6, 147.8, 145.7, 135.1, 131.6, 128.4, 125.3, 119.3, 117.4, 111.9, 50.7, 46.8, 23.7, 23.4; IR (KBr): 3132, 2972, 2875, 1647, 1566, 1466, 1399, 1366, 1312, 1224, 1130, 1012, 973 cm^{-1} ; MS (EI, 70 ev): 349 (M^+ , ^{81}Br , 11 %), 347 (M^+ , ^{79}Br , 11 %), 279 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{81}Br , 57 %), 277 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, ^{79}Br , 57 %), 251 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, ^{81}Br , 100 %), 249 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, ^{79}Br , 100 %), 170 (23 %); HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{14}\text{BrN}_3\text{O}_2$: 347.0269, found: 347.0274.

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Triazene (2b)² was prepared from 2,6-dibromotoluidine (4.8 g, 18.1 mmol) according to the general procedure **A** and yielding the pure product **2b** (5.7 g, 90 %). A pale brown solid; m.p.: 52.5-53.0 °C (lit.³ 53 °C). ¹H NMR (CDCl₃, 300 MHz): 7.33 (s, 2 H), 3.91 (br s, 2 H, CH₂N), 3.70 (br s, 2 H, CH₂N), 2.26 (s, 3 H), 2.04 (br s, 4 H, CH₂CH₂); ¹³C NMR (CDCl₃, 75 MHz): 145.6, 136.7, 132.8, 117.3, 51.1, 46.4, 23.7, 20.2; MS (EI, 70 ev): 347 (M⁺, ⁷⁹Br+⁸¹Br, 20 %), 277 (M-C₄H₈N, ⁷⁹Br+⁸¹Br, 76 %), 249 (M-C₄H₈N-N₂, ⁸¹Br, 100 %), 170 (⁸¹Br, 34 %), 168 (⁷⁹Br, 34 %), 89 (36 %).

Triazene (3e) was prepared from **2b** (1.1 g, 3.0 mmol) according to the general procedure **C** and yielding the pure product **3e** (930 mg, 82 %). An orange solid; m.p.: 124.0-124.6 °C. ¹H NMR (CDCl₃, 300 MHz): 7.44 (s, 1 H), 6.93 (s, 1 H), 3.82 (br s, 2 H, CH₂N), 3.71 (br s, 2 H, CH₂N), 2.32-2.48 (m, 1 H), 2.28 (s, 3 H), 2.00 (br s, 4 H, CH₂), 1.04-2.12 (m, 10 H); ¹³C NMR (CDCl₃, 75 MHz): 193.8, 144.6, 135.7, 134.8, 134.2, 128.2, 119.0, 51.2, 50.4, 47.2, 29.2, 25.9, 25.8, 24.0, 23.6, 20.4; IR (KBr): 2934, 2848, 1688, 1597, 1446, 1409, 1340, 1313, 1260, 1210, 1150, 1117, 997 cm⁻¹; MS (EI, 70 ev): 379 (M⁺, ⁸¹Br, 6 %), 377 (M⁺, ⁷⁹Br, 6 %), 309 (M-C₄H₈N, ⁸¹Br, 28 %), 307 (M-C₄H₈N, ⁷⁹Br, 28 %), 201 (⁸¹Br, 100 %), 199 (⁷⁹Br, 100 %), 185 (⁸¹Br, 22 %), 183 (⁷⁹Br, 22 %), 173 (⁸¹Br, 19 %), 171 (⁷⁹Br, 19 %); HRMS (EI): calcd. for C₁₈H₂₄BrN₃O: 377.1103, found: 377.1080.

Ethyl 4-amino-3-iodobenzoate.⁴ To a solution of iodine (5.1 g, 20.0 mmol) in ethanol (100 mL) was added Ag₂SO₄ (6.2 g, 20.0 mmol) and ethyl 4-aminobenzoate (3.3 g, 20.0 mmol). The reaction was stirred at rt for 1 h, filtered and the solvent evaporated. The residue was diluted in CH₂Cl₂, extracted with aqueous Na₂S₂O₃ solution and dried (MgSO₄). The crude product was purified by column chromatography on silica gel (pentane:ether = 9:1) giving the pure product (5.35 g, 92 %) as an off-white powder; m.p.: 82.6-83.0 °C (lit.⁴ 83 °C). ¹H NMR (CDCl₃, 300 MHz): 8.30 (d, *J* = 1.8 Hz, 1 H), 7.79 (dd, *J* = 1.8, 8.4 Hz, 1 H), 6.67 (d, *J* = 8.4 Hz, 1 H), 4.47 (br s, 2 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz): 165.3, 150.6, 140.9, 131.1, 121.5, 113.1, 82.1, 60.6, 14.3; IR (KBr): 3457, 3364, 2981, 2903, 1688, 1612, 1591, 1288, 1250 cm⁻¹; MS (EI, 70 ev), *m/z* (%): 291 (M⁺, 82 %), 263 (30 %), 246 (100 %), 218 (9 %), 91 (27 %); HRMS (EI): calcd. for C₉H₁₀INO₂: 290.9756, found: 290.9710.

Triazene (2c) was prepared from ethyl 4-amino-3-iodobenzoate (5.3 g, 18.1 mmol) according to the general procedure **A** and yielding the pure product **2c** (5.9 g, 88 %). A brown powder; m.p.: 128.5-130.0 °C. ¹H NMR (CDCl₃, 300 MHz): 8.48 (d, *J* = 1.8 Hz, 1 H), 7.90 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.37 (d, *J* = 8.4 Hz, 1 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.93 (br s, 2 H, CH₂N), 3.73 (br s, 2 H, CH₂N), 2.02 (br s, 4 H, CH₂), 1.35 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz): 165.3, 153.8, 140.6, 130.0, 127.8, 116.5, 95.5, 60.9, 51.2, 47.5, 23.9, 23.4, 14.3; IR (KBr): 2967, 2875, 1694, 1588, 1552, 1374, 1305, 1267, 1244, 1108, 1029, 905 cm⁻¹; MS (EI, 70 ev), *m/z* (%): 373 (M⁺, 31 %), 303 (M-C₄H₈N, 50 %), 275 (M-C₄H₈N-N₂, 100 %), 247 (50 %), 229 (38 %); HRMS (EI): calcd. for C₁₃H₁₆IN₃O₂: 373.0287, found: 373.0249.

General Procedure E for the preparation of triazene (3f). To a solution of triazene (**2c**) (187 mg, 0.5 mmol) in THF (0.5 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.53 mmol, 2.05 M in THF) at $-40\text{ }^{\circ}\text{C}$. The reaction mixture was continuously stirred at $-40\text{ }^{\circ}\text{C}$ for 40 min. A complete conversion to the Grignard reagent (**1c**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. CuCN·2LiCl (0.5 mmol, 0.5 mL, 1.0 M in THF) was added dropwise at $-40\text{ }^{\circ}\text{C}$ and then the reaction mixture was slowly warmed up to $-30\text{ }^{\circ}\text{C}$ over 30 min. Benzoyl chloride (0.75 mmol) in THF (0.1 mL) was added and the mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 1 h and then warmed up to rt and stirred again for 1 h before the addition of aq. NH_3 (2 mL). The aqueous phase was extracted with diethyl ether ($2 \times 10\text{ mL}$). The organic fractions were washed with brine (10 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:1) yielded the pure product **3f** (137 mg, 78 %) as yellow crystals; m.p.: $102.3\text{--}103.5\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 8.06–8.16 (m, 2 H), 7.64–7.74 (m, 2 H), 7.40–7.56 (m, 2 H), 7.28–7.38 (m, 2 H), 4.34 (q, $J = 7.1\text{ Hz}$, 2 H), 3.68 (br s, 2 H, CH_2N), 3.05 (br s, 2 H, CH_2N), 1.72–1.84 (m, 4 H, CH_2), 1.36 (t, $J = 7.1\text{ Hz}$, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 197.5, 166.1, 152.9, 138.3, 132.9, 132.2, 132.0, 130.5, 129.3, 128.1, 126.6, 119.0, 60.9, 50.9, 46.5, 23.7, 23.2, 14.3; IR (KBr): 3064, 2983, 2889, 1709, 1662, 1601, 1394, 1312, 1241, 1126, 1026 cm^{-1} ; MS (EI, 70 eV), m/z (%): 351 (M^+ , 13 %), 281 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, 43 %), 253 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, 33 %), 225 (30 %), 181 (100 %), 152 (63 %), 105 (47 %), 77 (37 %); HRMS (EI): calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3$: 351.1583, found: 351.1571.

Triazene (3g) was prepared from **2c** (187 mg, 0.5 mmol) according to the general procedure E and yielding the pure product **3g** (147 mg, 86 %). A light brown powder; m.p.: $113.8\text{--}115.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 8.02–8.12 (m, 2 H), 7.50–7.58 (m, 2 H), 6.92 (d, $J = 3.5\text{ Hz}$, 1 H), 6.45 (dd, $J = 1.8, 3.5\text{ Hz}$, 1 H), 4.33 (q, $J = 7.1\text{ Hz}$, 2 H), 3.77 (br s, 2 H, CH_2N), 3.30 (br s, 2 H, CH_2N), 1.82–1.94 (m, 4 H, CH_2), 1.34 (t, $J = 7.1\text{ Hz}$, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 193.6, 184.7, 165.9, 153.4, 153.0, 146.2, 132.3, 132.2, 130.1, 126.3, 118.8, 118.5, 112.0, 60.9, 51.1, 46.6, 23.8, 23.3, 14.3; IR (KBr): 3118, 2982, 2878, 1709, 1643, 1604, 1567 cm^{-1} .

1467, 1405, 1266, 1243, 1178, 1030, 979 cm^{-1} ; MS (EI, 70 eV), m/z (%): 341 (M^+ , 16 %), 296 (13 %), 271 ($M-C_4H_8N$, 63 %), 243 ($M-C_4H_8N-N_2$, 100 %), 215 (91 %), 187 (31 %), 159 (44 %), 95 (69 %); HRMS (EI): calcd. for $C_{19}H_{23}N_3O_3$: 341.1376, found: 341.1348.

Triazene (3h) was prepared from **2c** (187 mg, 0.5 mmol) according to the general procedure **E** and yielding the pure product **3h** (136 mg, 80 %). Yellow crystals; m.p.: 118.5-119.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.94 (dd, $J = 1.8, 8.4$ Hz, 1 H), 7.85 (d, $J = 1.8$ Hz, 1 H), 7.49 (d, $J = 8.4$ Hz, 1 H), 6.12 (s, 1 H), 4.34 (q, $J = 7.1$ Hz, 2 H), 3.94 (br s, 2 H, CH_2N), 3.61 (br s, 2 H, CH_2N), 2.76 (t, $J = 6.0$ Hz, 2 H), 2.47 (t, $J = 6.0$ Hz, 2 H), 1.94-2.16 (m, 6 H), 1.3337 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 200.0, 166.3, 163.8, 151.7, 135.1, 130.6, 129.8, 128.6, 126.6, 116.7, 60.9, 51.2, 46.9, 38.6, 31.2, 23.9, 23.5, 23.4, 14.3; IR (KBr): 2948, 2879, 1704, 1668, 1596, 1397, 1311, 1242, 1133, 1028, 965 cm^{-1} ; MS (EI, 70 eV), m/z (%): 341 (M^+ , 4 %), 296 (17 %), 257 (100 %), 215 (48 %), 197 (43 %), 143 (43 %), 128 (85 %), 56 (43 %); HRMS (EI): calcd. for $C_{19}H_{23}N_3O_3$: 341.1739, found: 341.1702.

4-amino-3-iodobenzonitrile. To a solution of iodine (5.1 g, 20.0 mmol) in ethanol (100 mL) was added Ag_2SO_4 (6.2 g, 20.0 mmol) and 4-aminobenzonitrile (2.4 g, 20.0 mmol). The reaction was stirred at rt for 1 h, filtered and the solvent was evaporated. The residue was diluted in CH_2Cl_2 , extracted with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution and dried (MgSO_4). The crude product was purified by column chromatography on silica gel (pentane:ether = 9:1) to give the pure product (4.6 g, 95 %) as a light brown powder; m.p.: 94.0-95.5 °C (lit.⁵ 94-97 °C). ^1H NMR (CDCl_3 , 300 MHz): 7.85 (d, $J = 1.8$ Hz, 1 H), 7.35 (dd, $J = 1.8, 8.4$ Hz, 1 H), 6.68 (d, $J = 8.4$ Hz, 1 H), 4.64 (br s, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz): 150.6, 142.7, 133.2, 118.3,

113.5, 101.6, 81.8; IR (KBr): 3456, 3349, 3202, 3070, 3050, 2216, 1623, 1589, 1498, 1407, 1328, 1197, 1162 cm^{-1} ; MS (EI, 70 eV), m/z (%): 244 (M^+ , 100 %), 117 (44 %), 90 (28 %).

Triazene (2d) was prepared from 4-amino-3-iodobenzonitrile (4.4 g, 18.1 mmol) according to the general procedure **A** and yielding the pure product **2d** (5.5 g, 90 %). A brown powder; m.p.: 159.0-159.8 °C. ^1H NMR (CDCl_3 , 300 MHz): 8.07 (d, $J = 1.8$ Hz, 1 H), 7.50 (dd, $J = 1.8, 8.4$ Hz, 1 H), 7.40 (d, $J = 8.4$ Hz, 1 H), 3.97 (t, $J = 6.5$ Hz, 2 H, CH_2N), 3.75 (t, $J = 6.5$ Hz, 2 H, CH_2N), 1.96-2.18 (m, 4 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 154.0, 142.7, 132.3, 118.0, 117.0, 108.9, 95.6, 51.5, 47.8, 23.9, 23.4; IR (KBr): 2974, 2954, 2865, 2219, 1585, 1375, 1307, 1273 cm^{-1} ; MS (EI, 70 eV), m/z (%): 326 (M^+ , 24 %), 256 ($M - \text{C}_4\text{H}_8\text{N}$, 48 %), 228 ($M - \text{C}_4\text{H}_8\text{N} - \text{N}_2$, 100 %), 101 (24 %); HRMS (EI): calcd. for $\text{C}_{11}\text{H}_{11}\text{IN}_4$: 326.0028, found: 326.0005.

Triazene (3i) was prepared from **2d** (187 mg, 0.5 mmol) according to the general procedure **E** and yielding the pure product **3i** (131 mg, 86 %). A yellow powder; m.p.: 157.8-159.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.62-7.72 (m, 4 H), 7.53-7.59 (m, 1 H), 7.44-7.52 (m, 1 H), 7.31-7.40 (m, 2 H), 3.69 (t, $J = 6.2$ Hz, 2 H), 3.04 (t, $J = 6.2$ Hz, 2 H), 1.74-1.85 (m, 4 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 196.1, 152.6, 137.7, 134.1, 133.8, 132.8, 132.6, 129.2, 128.2, 119.5, 118.8, 107.6, 51.5, 46.7, 23.6, 23.1; IR (KBr): 2947, 2874, 2222, 1665, 1594, 1393, 1310, 1267, 1120, 966 cm^{-1} ; MS (EI, 70 eV), m/z (%): 304 (M^+ , 20 %), 234 ($M - \text{C}_4\text{H}_8\text{N}$,

65 %), 206 (M-C₄H₈N-N₂, 100 %), 178 (85 %), 151 (50 %), 105 (55 %), 77 (50 %); HRMS (EI): calcd. for C₁₈H₁₆N₄O: 304.1324, found: 304.1321.

Triazene (3j) was prepared from **2d** (187 mg, 0.5 mmol) according to the general procedure **C** and yielding the pure product **3j** (125 mg, 85 %). A brown powder; m.p.: 161.0-161.6 °C. ¹H NMR (CDCl₃, 400 MHz): 7.52-7.66 (m, 4 H), 6.96 (d, *J* = 3.4 Hz, 1 H), 6.48 (dd, *J* = 1.8, 3.4 Hz, 1 H), 3.79 (br s, 2 H, CH₂N), 3.29 (br s, 2 H, CH₂N), 1.86-1.94 (m, 4 H, CH₂); ¹³C NMR (CDCl₃, 100 MHz): 183.2, 153.0, 152.8, 146.5, 134.3, 133.2, 132.5, 119.2, 119.0, 118.7, 112.2, 107.3, 51.3, 46.8, 23.7, 23.2; IR (KBr): 3126, 2991, 2953, 2876, 2216, 1653, 1598, 1567, 1465, 1392, 1311, 1269, 1230, 1102, 1018 cm⁻¹; MS (EI, 70 ev), *m/z* (%): 294 (M⁺, 8 %), 224 (M-C₄H₈N, 38 %), 196 (M-C₄H₈N-N₂, 100 %), 168 (13 %), 140 (46 %), 95 (33 %); HRMS (EI): calcd. for C₁₆H₁₄N₄O₂: 294.1117, found: 294.1125.

Triazene (2e)⁶ was prepared from 4-iodoaniline (4.0 g, 18.1 mmol) according to the general procedure **A** and yielding the pure product **22** (5.0 g, 92 %). Brown crystals; m.p.: 111.5-111.9 °C. ¹H NMR (CDCl₃, 300 MHz): 7.57-7.62 (m, 2 H), 7.13-7.18 (m, 2 H), 3.75 (br s, 4 H, CH₂N), 1.99 (br s, 4 H, CH₂); ¹³C NMR (CDCl₃, 75 MHz): 151.0, 137.7, 122.3, 89.0, 23.7; IR (KBr): 2978, 2936, 2868, 1637, 1477, 1417, 1389, 1339, 1313, 1259, 1219, 828 cm⁻¹; MS (EI, 70 ev), *m/z* (%): 301 (M⁺, 33 %), 231 (M-C₄H₈N, 67 %), 203 (M-C₄H₈N-N₂, 100 %), 76 (28 %); HRMS (EI): calcd. for C₁₀H₁₂IN₃: 301.0076, found: 301.0088.

Triazene (3k) was prepared from **2e** (151 mg, 0.5 mmol) according to the general procedure **E** and yielding the pure product **3k** (105 mg, 90 %). An off-white powder; m.p.: 52.5-53.5 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.34 (d, $J = 8.4$ Hz, 2 H), 7.24 (d, $J = 8.4$ Hz, 2 H), 4.52 (t, $J = 6.7$ Hz, 1 H), 3.75 (br s, 4 H, CH_2N), 2.12 (s, 1 H), 1.93-2.04 (m, 4 H, CH_2), 1.63-1.86 (m, 2 H), 0.87 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 150.8, 141.3, 126.5, 120.2, 75.7, 31.7, 23.7, 10.1 cm^{-1} ; IR (KBr): 3143, 2972, 2930, 2873, 1636, 1408, 1342, 1318, 1262, 1222, 1156, 1097, 844 cm^{-1} ; MS (EI, 70 ev), m/z (%): 233 (M^+ , 28 %), 163 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, 40 %), 135 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, 100 %), 117 (47 %), 91 (24 %); HRMS (EI): calcd. for $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}$: 233.1528, found: 233.1527.

Triazene (3l) was prepared from **2e** (151 mg, 0.5 mmol) according to the general procedure **E** and yielding the pure product **3l** (118 mg, 88 %). Yellow crystals; m.p.: 136.0-137.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.98 (d, $J = 8.8$ Hz, 2 H), 7.66 (d, $J = 1.8$ Hz, 1 H), 7.47 (d, $J = 8.8$ Hz, 2 H), 7.20 (d, $J = 3.5$ Hz, 1 H), 6.55 (dd, $J = 1.8, 3.5$ Hz, 1 H), 3.92 (br s, 2 H, CH_2N), 3.70 (br s, 2 H, CH_2N), 2.02 (br s, 4 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 181.7, 155.0, 152.6, 146.6, 133.4, 130.6, 120.1, 119.8, 112.0, 23.7; IR (KBr): 3136, 2978, 2953, 2924, 2874, 1626, 1597, 1561, 1466, 1421, 1394, 1310, 1143, 951 cm^{-1} ; MS (EI, 70 ev), m/z (%): 269 (M^+ , 13 %), 199 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, 35 %), 171 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, 100 %), 115 (47 %), 95 (47 %); HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$: 269.1164, found: 269.1153.

General Procedure F for the preparation of compound (4a). Triazene **3a** (162 mg, 0.55 mmol) was dissolved in freshly distilled iodomethane (3 mL) and heated in a sealed tube at 120 °C for 24 h. The reaction mixture was cooled, diluted with dichloromethane, and filtered through a pad of Celite and silica gel. Concentration and purification of the crude product by column chromatography (pentane:ether = 19:1) provided **4a** (147 mg, 83 %) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz): 7.48 (dd, *J* = 2.2, 7.1 Hz, 1 H), 7.06-7.18 (m, 2 H), 5.84-6.02 (m, 1 H), 5.02-5.20 (m, 2 H), 3.56-3.64 (m, 2 H); ¹³C NMR (CDCl₃, 75 MHz): 146.4, 135.3, 131.2, 130.6, 129.2, 127.6, 117.1, 107.9, 47.4; IR (film): 3078, 2978, 2917, 1639, 1573, 1552, 1434, 1402, 1009, 918 cm⁻¹; MS (EI, 70 ev): 324 (M⁺, ⁸¹Br, 46 %), 322 (M⁺, ⁷⁹Br, 46 %), 243 (8 %), 116 (100 %), 89 (19 %); HRMS (EI): calcd. for C₉H₈BrI: 321.8854, found: 321.8844.

General Procedure G for the preparation of compound (4b). To a solution containing the triazene **3b** (100 mg, 0.28 mmol) in CH₂Cl₂ (0.3 mL) was added trimethylsilyl iodide (112 mg, 0.56 mmol). The mixture was stirred at 40 °C for 20 min. The progress of the reaction was monitored by TLC. After the reaction mixture was cooled to rt, 5 % sodium bicarbonate solution (7 mL) was added. The reaction mixture was extracted with CH₂Cl₂ (2 × 10 mL). The organic layers were combined, washed with water, and dried (MgSO₄). The solvent was removed under reduced pressure, and the crude residue was purified by chromatography on a silica gel column (pentane:ether = 4:1) giving the pure product **4b** (95 mg, 88 %) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz): 7.75-7.81 (m, 2 H), 7.72 (dd, *J* = 1.6, 7.8 Hz, 1 H), 7.55-7.64 (m, 1 H), 7.40-7.44 (m, 2 H), 7.30 (t, *J* = 7.8 Hz, 1 H), 7.13 (dd, *J* = 1.6, 7.8 Hz, 1 H); ¹³C NMR (CDCl₃, 75 MHz): 196.4, 148.0, 134.8, 133.9, 133.4, 131.7, 130.4, 129.3, 128.8, 126.0, 99.2; IR (film): 3060, 1673, 1595, 1580, 1450, 1392, 1314, 1297, 1198, 1178, 1015, 944 cm⁻¹; MS (EI, 70 ev): 388 (M⁺, ⁸¹Br, 45 %), 386 (M⁺, ⁷⁹Br, 45 %), 311 (M-C₆H₅, ⁸¹Br, 16 %), 309 (M-C₆H₅, ⁷⁹Br, 16 %), 283 (M-C₆H₅-CO, ⁸¹Br, 8 %), 281 (M-C₆H₅-CO, ⁷⁹Br, 8 %), 180 (18 %), 105 (100 %), 77 (45 %); HRMS (EI): calcd. for C₁₃H₈BrIO: 385.8803, found: 385.8787.

Compound (4c) was prepared from **3c** (97 mg, 0.28 mmol) according to the general procedure **G** and yielding the pure product **4c** (72 mg, 68 %). A Brown oil. ^1H NMR (CDCl_3 , 300 MHz): 7.72 (dd, $J = 1.3, 7.5$ Hz, 1 H), 7.68 (d, $J = 1.5$ Hz, 1 H), 7.29 (t, $J = 7.5$ Hz, 1 H), 7.21 (dd, $J = 1.3, 7.5$ Hz, 1 H), 7.01 (d, $J = 3.5$ Hz, 1 H), 6.55 (dd, $J = 1.5, 3.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz): 183.7, 150.6, 148.3, 146.7, 133.9, 131.8, 129.2, 126.1, 121.9, 112.8, 99.6; IR (KBr): 3130, 2919, 2850, 1658, 1560, 1461, 1393, 1307, 1177, 1026, 962 cm^{-1} ; MS (EI, 70 ev), m/z (%): 378 (M^+ , ^{81}Br , 100 %), 376 (M^+ , ^{79}Br , 100 %), 251 (M-I, ^{81}Br , 20 %), 249 (M-I, ^{79}Br , 20 %), 114 (16 %), 95 (68 %); HRMS (EI): calcd. for $\text{C}_{11}\text{H}_6\text{BrIO}_2$: 375.8596, found: 375.8589.

Compound (4d) was prepared from **3d** (191 mg, 0.55 mmol) according to the general procedure **F** and yielding the pure product **4d** (180 mg, 87 %). An off-white powder; m.p.: 107.0-107.7 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 7.58 (dd, $J = 1.5, 7.7$ Hz, 1 H), 7.21 (t, $J = 7.7$ Hz, 1 H), 6.98 (dd, $J = 1.5, 7.7$ Hz, 1 H), 5.88 (t, $J = 1.8$ Hz, 1 H), 2.44-2.60 (m, 4 H), 2.14-2.28 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz): 199.2, 165.3, 149.0, 132.1, 131.3, 129.5, 128.8, 125.6, 102.6, 37.2, 20.9, 23.0; IR (KBr): 3054, 2941, 2864, 1660, 1435, 1391, 1344, 1302, 1248, 1187, 1130, 962 cm^{-1} ; MS (EI, 70 ev), m/z (%): 378 (M^+ , ^{81}Br , 100 %), 376 (M^+ , ^{79}Br , 100 %), 251 (M-I, ^{81}Br , 11 %), 249 (M-I, ^{79}Br , 11 %), 223 (^{81}Br , 36 %), 221 (^{79}Br , 36 %), 195 (^{81}Br , 61 %), 193 (^{79}Br , 61 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{10}\text{BrIO}$: 375.8960, found: 375.8931.

Compound (4e) was prepared from triazene **3f** (98 mg, 0.28 mmol) according to the general procedure **G** and yielding the pure product **4e** (77 mg, 72 %). A brown oil. ^1H NMR (CDCl_3 ,

300 MHz): 8.00 (d, $J = 8.0$ Hz, 1 H), 7.90 (d, $J = 2.0$ Hz, 1 H), 7.75-7.82 (m, 3 H), 7.54-7.64 (m, 1 H), 7.45 (t, $J = 8.0$ Hz, 2 H), 4.35 (q, $J = 7.1$ Hz, 2 H), 1.34 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 196.4, 165.4, 144.7, 140.0, 135.2, 134.0, 131.5, 130.4, 130.0, 128.9, 128.7, 98.2, 61.5, 14.2; IR (film): 3063, 2981, 1716, 1674, 1590, 1450, 1367, 1241, 1107, 1016, 963 cm^{-1} ; MS (EI, 70 eV), m/z (%): 380 (M^+ , 59 %), 335 (11 %), 303 (24 %), 275 (8 %), 253 (7 %), 105 (100 %), 77 (34 %); HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{13}\text{IO}_3$: 379.9909, found: 379.9905.

Compound (4f) was prepared from triazene **3g** (95mg, 0.28 mmol) according to the general procedure **G** and yielding the pure product **4f** (81 mg, 78 %). A brown oil. ^1H NMR (CDCl_3 , 300 MHz): 7.97-8.03 (m, 2 H), 7.79 (dd, $J = 2.0, 8.2$ Hz, 1 H), 7.69 (s, 1 H), 7.05 (d, $J = 3.5$ Hz, 1 H), 6.58 (dd, $J = 1.8, 3.5$ Hz, 1 H), 4.35 (q, $J = 7.1$ Hz, 2 H), 1.36 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 183.3, 165.3, 151.0, 148.3, 143.4, 140.3, 132.0, 130.4, 129.2, 122.0, 112.8, 98.5, 61.6, 14.2; IR (film): 3130, 2982, 2930, 1722, 1659, 1590, 1563, 1462, 1387, 1284, 1248, 1187, 1109, 1016 cm^{-1} ; MS (EI, 70 eV), m/z (%): 370 (M^+ , 100 %), 342 (10 %), 325 (56 %), 303 (17 %), 275 (11 %), 243 (8 %), 95 (83 %); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{11}\text{IO}_4$: 369.9702, found: 369.9694.

Compound (4g) was prepared from triazene **3h** (188 mg, 0.55 mmol) according to the general procedure **F** and yielding the pure product **4g** (155 mg, 76 %). A brown oil. ^1H NMR (CDCl_3 , 300 MHz): 7.94 (d, $J = 8.2$ Hz, 1 H), 7.74 (d, $J = 2.0$ Hz, 1 H), 7.65 (dd, $J = 2.0, 8.2$ Hz, 1 H), 5.95 (t, $J = 1.8$ Hz, 1 H), 4.36 (q, $J = 7.1$ Hz, 2 H), 2.46-2.64 (m, 4 H), 2.16-2.28 (m, 2 H), 1.38 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 199.1, 165.6, 163.8, 146.0, 139.8, 130.8, 130.2, 129.5, 128.3, 101.3, 61.5, 37.2, 30.8, 23.0, 14.3; IR (film): 2980, 2940,

1722, 1681, 1587, 1454, 1291, 1239, 1107, 1015, 962 cm^{-1} ; MS (EI, 70 eV): 370 (M^+ , 100 %), 342 (16 %), 325 (18 %), 215 (55 %), 187 (95 %); HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{15}\text{IO}_3$: 370.0066, found: 370.0079.

Compound (4h) was prepared from triazene **3i** (85 mg, 0.28 mmol) according to the general procedure **G** and yielding the pure product **4h** (65 mg, 70 %). A yellow powder; m.p.: 127.0-128.0 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 8.06 (d, $J = 8.0$ Hz, 1 H), 7.75 (d, $J = 8.0$ Hz, 2 H), 7.60-7.68 (m, 1 H), 7.38-7.53 (m, 4 H); ^{13}C NMR (CDCl_3 , 75 MHz): 195.0, 145.8, 140.9, 134.6, 134.4, 133.5, 131.0, 130.4, 129.0, 117.4, 112.4, 98.4; IR (KBr): 3056, 2228, 1670, 1592, 1450, 1294, 1255, 1180, 1020 cm^{-1} ; MS (EI, 70 eV), m/z (%): 333 (M^+ , 63 %), 256 (15 %), 228 (10 %), 206 (6 %), 105 (100 %), 77 (38 %); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_8\text{INO}$: 332.9651, found: 332.9673.

Compound (4i) was prepared from triazene **3j** (82 mg, 0.28 mmol) according to the general procedure **G** and yielding the pure product **4i** (74 mg, 82 %). A brown powder; m.p.: 105.0-105.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 8.02 (d, $J = 8.4$ Hz, 1 H), 7.66 (s, 1 H), 7.57 (d, $J = 2.0$ Hz, 1 H), 7.37 (dd, $J = 2.0, 8.4$ Hz, 1 H), 7.08 (d, $J = 3.7$ Hz, 1 H), 6.57 (dd, $J = 2.0, 3.7$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz): 193.7, 181.8, 148.7, 144.3, 141.1, 133.9, 131.3, 122.2, 117.3, 113.1, 112.3, 98.7; IR (KBr): 3143, 3129, 2232, 1646, 1563, 1461, 1400, 1303, 1082, 1033 cm^{-1} ; MS (EI, 70 eV), m/z (%): 323 (M^+ , 98 %), 256 (18 %), 228 (12 %), 196 (18 %), 140 (12 %), 95 (100 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_6\text{INO}_2$: 322.9443, found: 322.9414.

Compound (4j) was prepared from triazene **3k** (128 mg, 0.55 mmol) according to the general procedure **F** and yielding the pure product **4j** (114 mg, 85 %). White crystals; m.p.: 69.5-69.8 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.58 (d, $J = 8.4$ Hz, 2 H), 7.05 (d, $J = 8.4$ Hz, 2 H), 6.14-6.36 (m, 2 H), 1.86 (d, $J = 5.3$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 137.5, 130.0, 127.6, 126.8, 91.6, 18.5; IR (KBr): 3020, 2956, 2926, 2905, 1655, 1580, 1482, 1441, 1395, 1001, 966 cm^{-1} ; MS (EI, 70 ev): 244 (M^+ , 100 %), 117 (44 %), 91 (14 %); HRMS (EI): calcd. for $\text{C}_9\text{H}_9\text{I}$: 243.9749, found: 243.9756.

Compound (4k) was prepared from triazene **3l** (148 mg, 0.55 mmol) according to the general procedure **F** and yielding the pure product **4k** (148 mg, 90 %). A brown solid; m.p.: 63.4-64.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.80-7.86 (m, 2 H), 7.65-7.71 (m, 3 H), 7.22 (d, $J = 3.5$ Hz, 2 H), 6.57 (dd, $J = 1.8, 3.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz): 193.6, 152.1, 147.2, 137.7, 136.4, 130.7, 120.5, 112.3, 100.3; IR (KBr): 3129, 1636, 1582, 1464, 1392, 1312, 1176, 1006, 950 cm^{-1} ; MS (EI, 70 ev): 298 (M^+ , 100 %), 270 (13 %), 231 (63 %), 203 (21 %), 115 (17 %), 95 (33 %); HRMS (EI): calcd. for $\text{C}_{11}\text{H}_7\text{IO}_2$: 297.9491, found: 297.9505.

General Procedure H for the preparation of triazene (5a). To a solution of 1-(2,6-dibromophenylazo)pyrrolidine (**2a**) (999 mg, 3.0 mmol) in THF (0.75 mL) was slowly added *i*-PrMgCl·LiCl (1.6 mL, 3.3 mmol, 2.0 M in THF) at -40 °C. The reaction temperature was gradually increased to -15 °C. After 4 h, a complete conversion to the Grignard reagent (**1a**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. ZnBr (3.0 mmol, 3.0 mL, 1.0 M in THF) was added at -20 °C and the reaction mixture was slowly warmed to -5 °C. After 1 h, the zinc reagent was transferred to a solution of tetrakis(triphenylphosphine)palladium (116 mg, 0.1 mmol) and 1, 2-diiodobenzene (1.2 g, 3.3

mmol) in THF (3.5 mL). The reaction mixture was heated under reflux for 3 h. The mixture was cooled and quenched as usual. The aqueous phase was extracted with ether (2×30 mL). The organic fractions were washed with brine (50 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 9:1) yielded the pure product **5a** (1.2 g, 88 %) as a yellow solid; m.p.: 64.4-65.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.80 (d, $J = 7.7$ Hz, 1 H), 7.62 (dd, $J = 1.8, 7.7$ Hz, 1 H), 7.25 (t, $J = 7.7$ Hz, 1 H), 7.14 (dd, $J = 1.8, 7.7$ Hz, 1 H), 7.06 (dd, $J = 1.8, 7.7$ Hz, 1 H), 7.01 (t, $J = 7.7$ Hz, 1 H), 6.91 (t, $J = 7.7$ Hz, 1 H), 5.30-3.50 (m, 4 H, CH_2N), 1.81 (br s, 4 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 147.2, 145.7, 138.2, 138.1, 132.7, 131.1, 129.9, 127.8, 127.1, 125.1, 118.5, 100.3, 23.7; IR (KBr): 3055, 2972, 2871, 1557, 1415, 1316, 1220, 1010 cm^{-1} ; MS (EI, 70 ev): 457 (M^+ , ^{81}Br , 9 %), 455 (M^+ , ^{79}Br , 9 %), 387 (M- $\text{C}_4\text{H}_8\text{N}$, ^{81}Br , 31 %), 385 (M- $\text{C}_4\text{H}_8\text{N}$, ^{79}Br , 31 %), 359 (M- $\text{C}_4\text{H}_8\text{N}-\text{N}_2$, ^{81}Br , 81 %), 357 (M- $\text{C}_4\text{H}_8\text{N}$, ^{79}Br , 81 %), 278 (39 %), 230 (61 %), 151 (100 %); HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{15}\text{BrIN}_3$: 454.9494, found: 454.9533.

General Procedure I for the preparation of 1-bromo-9H-carbazole (6a). To a solution of compound (**5a**) (228 mg, 0.5 mmol) in THF (0.25 mL) was slowly added *i*-PrMgCl·LiCl (0.26 mL, 0.53 mmol, 2.0 M in THF) at -40 °C. The reaction mixture was continuously stirred at -40 °C. After 1 h, isopropyl iodide resulting from the I/Mg exchange was evaporated *in vacuo* (evaporation was done twice, 1 h for each time). Then the mixture was heated to 55 °C for 2 h after the addition of fresh THF (1.5 mL). The mixture was cooled to rt and quenched as usual. The aqueous phase was extracted with ether (2×5 mL). The organic fractions were washed with brine (5 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 32:1) yielded the pure product **6a** (92 mg, 75 %) as a white solid; m.p.: 121.5-122.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 8.18 (br s, 1 H, N-H), 7.99 (q, $J = 8.0$ Hz, 2 H), 7.53 (d, $J = 8.0$ Hz, 1 H), 7.40-7.46 (m, 2 H), 7.19-7.28 (m, 1 H), 7.09 (t, $J = 8.0$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz): 139.1, 138.1, 127.9, 126.5, 124.6, 123.6, 120.8, 120.5, 120.1, 119.3, 111.0, 104.1; IR (KBr): 3409, 3051, 2962, 2919, 1603, 1496, 1454, 1424, 1320, 1136, 754 cm^{-1} ; MS (EI, 70 ev): 247 (M^+ , ^{81}Br , 100 %), 245 (M^+ , ^{79}Br , 100 %), 166 (45 %), 139 (23 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_8\text{BrN}$: 244.9840, found: 244.9836.

Triazene (5b) was prepared from triazene **2c** (1.1 g, 3.0 mmol) according to the general procedure **H** and yielding the pure product **5b** (1.1 g, 80 %). A yellow solid; m.p.: 89.0-89.5 °C. ^1H NMR (CDCl_3 , 300 MHz): 8.02 (dd, $J = 2.0, 8.0$ Hz, 1 H), 7.82-7.89 (m, 2 H), 7.54 (d, $J = 8.0$ Hz, 1 H), 7.34 (t, $J = 8.0$ Hz, 1 H), 7.27 (d, $J = 2.0$ Hz, 1 H), 6.98 (t, $J = 8.0$ Hz, 1 H), 4.34 (q, $J = 7.1$ Hz, 2 H), 3.85 (br s, 2 H, CH_2N), 3.31 (br s, 2 H, CH_2N), 1.91 (br s, 4 H, CH_2), 1.36 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 166.5, 151.8, 145.3, 138.5, 138.3, 131.8, 130.6, 130.1, 128.2, 127.4, 126.2, 116.4, 100.6, 60.7, 50.9, 46.5, 23.9, 23.4, 14.3; IR (KBr): 2974, 2921, 2874, 1698, 1601, 1310, 1264, 1231, 1106, 1011 cm^{-1} ; MS (EI, 70 ev): 449 (M^+ , 10 %), 404 (7 %), 379 (12 %), 351 (100 %), 323 (38 %), 307 (37 %), 196 (21 %), 152 (38 %); HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{20}\text{IN}_3\text{O}_2$: 449.0600, found: 449.0561.

9H-Carbazole-3-carboxylic acid ethyl ester (6b) was prepared from compound **5b** (225 mg, 0.5 mmol) according to the general procedure **I** and yielding the pure product **6b** (84 mg, 70 %). A yellow solid; m.p.: 161.8-163.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 8.78 (s, 1 H), 8.40 (br s, 1 H, N-H), 8.05-8.13 (m, 2 H), 7.33-7.42 (m, 3 H), 7.20-7.27 (m, 1 H), 4.41 (q, $J = 7.1$ Hz, 2 H), 1.41 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 194.2, 167.5, 142.3, 139.9, 127.4, 126.5, 123.3, 122.8, 121.7, 120.6, 120.2, 110.9, 110.1, 60.7, 14.5; IR (KBr): 3297, 2980, 2902, 1686, 1603, 1336, 1266, 1101, 1034, 911 cm^{-1} ; MS (EI, 70 ev): 239 (M^+ , 86 %), 224 (11 %), 211 (31 %), 194 (100 %), 166 (46 %), 139 (31 %); HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: 239.0946, found: 239.0926.

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