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Synthesis of polyfunctional indoles and related heterocycles mediated by cesium and potassium bases

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Abstract—A general preparation of 2-substituted indoles starting from functionalized 2-alkynylanilines has been developed. This base mediated reaction has also been used to synthesize the heterocyclic core of the marine alkaloid hinckdentine A. Furthermore the reaction was successfully adapted to the solid phase. Benzofurans and isoindolones could also be prepared with this method.

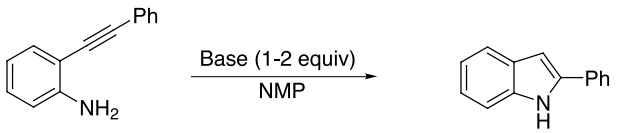
1. Introduction

Heterocycles have a central position in organic chemistry, because of the useful properties of many members of these compounds.[1] Numerous methods have been developed for their synthesis. Ring closure reactions in which a new carbon–heteroatom bond is formed is a common approach. Specifically, the intramolecular addition of a nitrogen functionality to an alkyne or an alkene is a valuable strategy. In general, the additions of heteroatom-centered nucleophiles to unsaturated carbon–carbon bonds are important reactions. They often require harsh reaction conditions if the carbon–carbon double bond or triple bond is not sufficiently polarized.[2] The intramolecular version of such an addition is usually considerably faster. Thus, the hydroamination of styrene derivatives has provided an elegant access to indolines.[3] Transition metal catalysis facilitates the addition reaction, especially for nitrogen nucleophiles.[4] Palladium salts have proven to efficiently catalyze the inter- and intramolecular addition of amines to alkynes and alkenes.[5,6] The metal catalyzed preparation of indoles starting from 2-alkynylanilines or from derivatives thereof represents a useful synthesis of this class of heterocycles.[7–9]

Recently, we reported that substituted anilines and heterocyclic amines add to phenylacetylene in *N*-methylpyrrolidinone (NMP) in the presence of catalytic amounts of $CsOH{\cdot}H_2O$,[10] leading to functionalized enamines.[11] The high thermodynamic basicity of $CsOH{\cdot}H_2O$ in NMP, combined with a high kinetic acidity resulting in fast reactions,[12] allows the performance of catalytic reactions. Although the intermolecular addition of amines to phenylacetylene or styrene requires high temperatures (90–120°C), we envisioned that the intramolecular addition should proceed under much milder conditions. $CsOH{\cdot}H_2O$ has been found to catalyze the ring closure of 2-alkynylanilines of type **1** to the indoles of type **2**. A screening of related bases showed that more soluble bases in NMP, such as CsO*t*-Bu, KO*t*-Bu or KH, efficiently mediate the cyclization of 2-(2-phenylethynyl)aniline (**1a**) to 2-phenyl-1*H*-indole (**2a**). The reaction occurs at room temperature within a few hours (Table 1).

Herein, we wish to report the scope of this new synthesis of indoles and related heterocycles in solution and on solid support. The method was also applied to the short synthesis of the heterocyclic core of hinckdentine A (**3**).[13] This unusual marine alkaloid is of interest due to its potential cataleptogenic activity.

Table 1. Na, K or Cs base mediated cyclizations



1a **2a**

Base	Temperature (°C)	Time (h)	Yield (%)[a]
NaH	60	8	<5
NaOEt	80	15	66
KO*t*-Bu	25	4	79
KH	25	5	72
$CsOH{\cdot}H_2O$	90	5	68
CsO*t*-Bu	25	5	71

[a] Isolated yield of analytically pure **2a**.

Keywords: indoles; heterocycles; cesium and potassium bases; cyclization.

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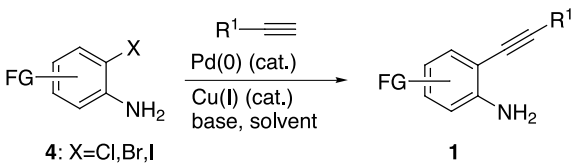
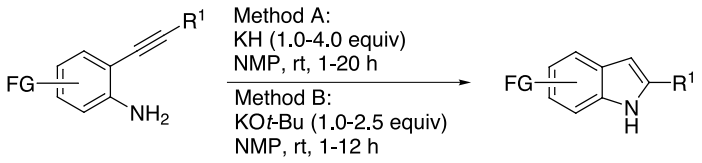
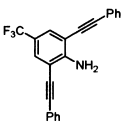
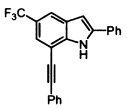
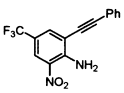
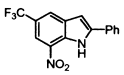
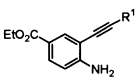
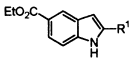
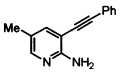
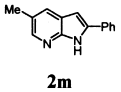
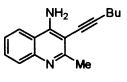
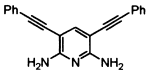
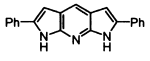


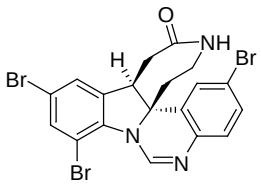
Scheme 1.

Table 2. Functionalized indoles **2a**–**p** obtained by 5-*endo*-dig-cyclization of 2-alkynylanilines **1a**–**p** in the presence of potassium bases



Entry	Alkynylaniline **1**	Indole **2**	Method	Yield (%)[a]
				
1	**1a**: R^1=Ph	**2a**: R^1=Ph	A (B)	72 (79)
2	**1b**: R^1=Bu	**2b**: R^1=Bu	A (B)	76 (78)
3	**1c**: R^1=H	**2c**: R^1=H	B	62
4	**1d**: R^1=1-cyclohexenyl	**2d**: R^1=1-cyclohexenyl	A	67
5	**1e**: R^1=2-thienyl	**2e**: R^1=2-thienyl	A	70
6	**1f**: R^1=2-thiazol	**2f**: R^1=2-thiazol	A	61
7	**1g**: R^1=3-chloropropyl	**2g**: R^1=3-cyclopropyl	A	75
8	**1h**: R^1=2-aminophenyl	**2h**: R^1=2-aminophenyl	A	82
9	 **1i**	 **2i**	A	80
10	 **1j**	 **2j**	A	51
				
11	**1k**: R^1=Ph	**2k**: R^1=Ph	A	78
12	**1l**: R^1=1-cyclohexenyl	**2l**: R^1=1-cyclohexenyl	A	72
13	 **1m**	 **2m**	A	72
14	 **1n**	 **2n**	A	74
15[b]	 **1o**	 **2o**	B	84
16[c]	 **1p**	 **2p**	B	95

[a] Isolated yield of analytically pure product.
[b] 80°C.
[c] 80°C, DMSO was used as solvent.



3

2. Results and discussion

2-Alkynylanilines of type **1** required for the cyclization step were obtained by a Sonogashira cross-coupling reaction with 2-halogenoanilines **4** (Scheme 1).[14]

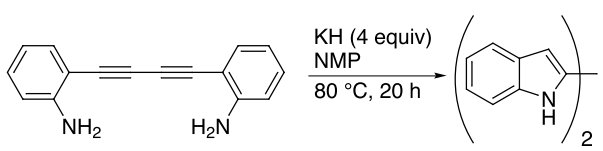
Several variations of the reaction conditions proved to give satisfactory results (40–96%, see Section 4). The iodo-, bromo- or chloroaniline derivatives **4** were either commercially available or prepared by standard halogenation methods.[15] In the case of 2-amino-aryl iodides, the cross-coupling proceeds at rt (1–20 h), whereas for the 2-amino-aryl bromides the reaction mixture has to be heated to 80°C for several hours.

2-Alkynylanilines **1** are conveniently treated with KH (Method A, 1.0–4.0 equiv.) or KO*t*-Bu (Method B, 1.0–2.5 equiv.) in NMP at rt for 1–20 h. A fast cyclization reaction occurs to give the indoles **2a**–**p** in good to excellent yields (see Table 2).

Various substituents R^1 can be attached to the alkyne such as heterocycles, a chloroalkyl or an aminophenyl substituent (entries 1–8 of Table 2). The mild reaction conditions, allowing the performance of the ring closures at rt, assure a broad functional group compatibility. Various substituents can also be attached to the aromatic ring (NO_2, CO_2Et, CF_3, alkynyl group; entries 9–12). Interestingly, various functionalized pyridines and quinolines can be used as the template ring for the cyclization reaction (entries 13–16).

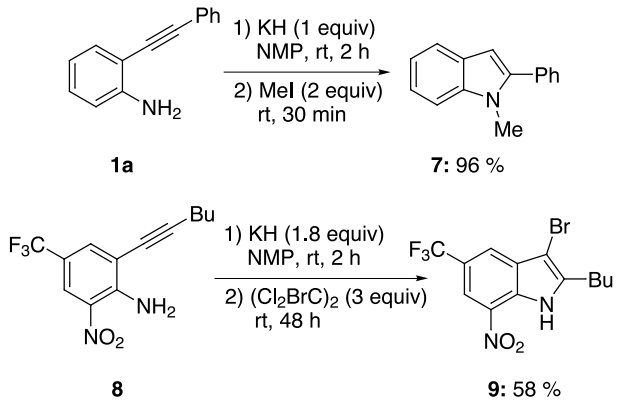
The symmetrical diaminodiyne derivative **5**[16] also readily undergoes the cyclization under standard conditions (KH (4 equiv.), 80°C, 20 h), affording the *bis*-indole **6** in 70% yield (Scheme 2).

It is also possible to prepare 1,2- and 2,3-disubstituted indoles by using this base mediated 5-*endo*-dig-cyclization[17] (Scheme 3). For example, **1a** can be cyclized to the ambivalent indole anion of **2a**, which can be trapped at the nitrogen with MeI (2 equiv., rt, 30 min) affording 1-methyl-2-phenyl-1*H*-indole (**7**) in very good yield (96%). In contrast, the indole anion derived from **8** reacts with 1,2-



5 **6:** 70 %

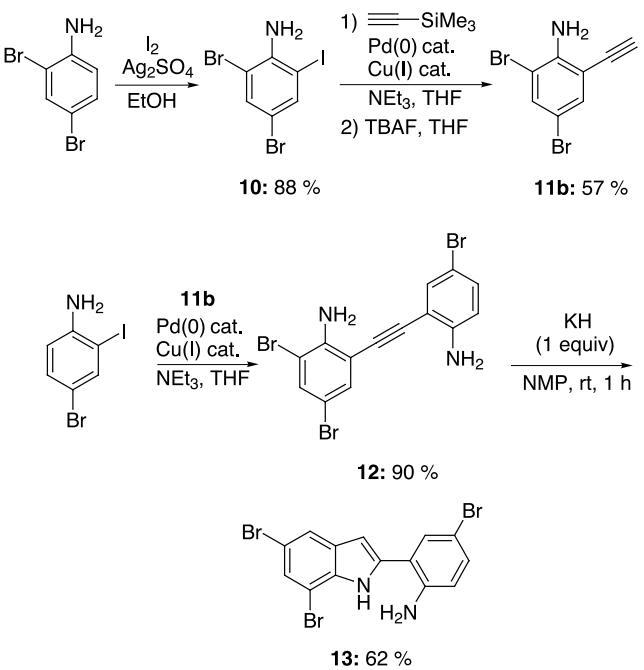
Scheme 2.



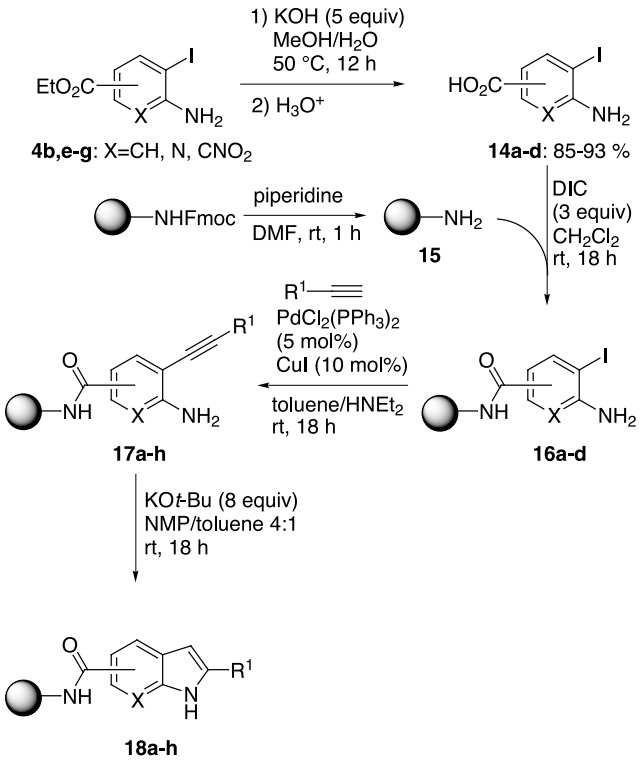
Scheme 3.

dibromotetrachloroethane (3 equiv., rt, 48 h) at C-3 to give 3-bromo-7-nitro-2-phenyl-5-(trifluoromethyl)-1*H*-indole (**9**) in 58% yield.

This ring closure procedure has been successfully applied to prepare the skeleton of hinckdentine A (**3**). Thus, the iodination of 2,4-dibromoaniline with Ag_2SO_4/I_2[18] in ethanol furnishes the expected aryl iodide **10** in 88% yield (Scheme 4). After a Sonogashira cross-coupling with trimethylsilylacetylene ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (5 mol%), NEt_3 (3 equiv.), THF, rt, 3 h, **11a**: 67%) and desilylation (TBAF, THF, rt, 1 h, 85%) the functionalized alkyne **11b** is obtained in 57% overall yield. A second Sonogashira cross-coupling with 4-bromo-2-iodoaniline[19] affords the cyclization precursor **12** in 90% yield ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (5 mol%), NEt_3 (3 equiv.), THF, rt, 3 h). Treatment of **12** with KH (1 equiv., rt, 1 h) results in a regioselective ring closure providing as sole product the indole **13** in 62% yield. This regioselectivity is best explained by assuming that the most acidic amino group is selectively deprotonated and undergoes the ring closure to **13**.



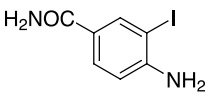
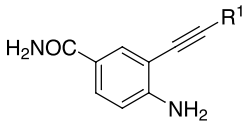
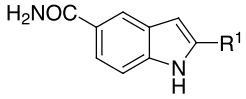
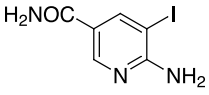
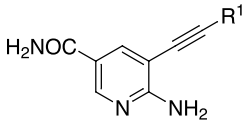
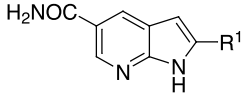
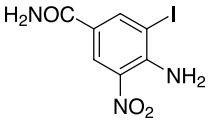
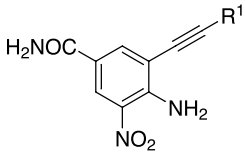
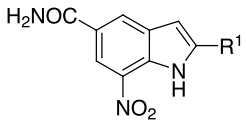
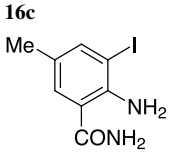
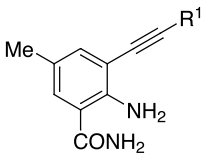
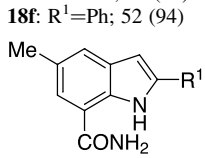
Scheme 4.



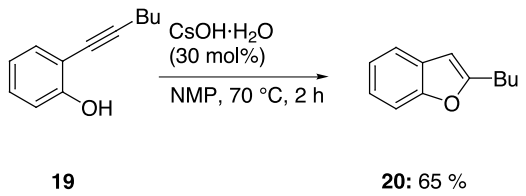
Scheme 5.

The new indole synthesis can also be performed on solid phase.[20] We chose the Rink-MBHA-resin as the solid support, because the amide functionality used as the linker should be stable under the reaction conditions of the Sonogashira cross-coupling reaction and the base mediated cyclization. First, a range of ethyl arylamino esters were iodinated *ortho* to the amine using I_2/Ag_2SO_4 to provide iodoamino esters **4b**, **e**–**g** in good yields (75–82%, see Section 4). Saponification with KOH in MeOH/H_2O yielded the carboxylic acid-precursors **14a**–**d** (85–95%) for the attachment to the deprotected Rink-MBHA-resin **15**, which was in turn synthesized from commercially available Rink-MBHA-resin by treatment with piperidine in DMF (Scheme 5). In the presence of excess **14** (3 equiv.) and diisopropylcarbodiimide (DIC, 3 equiv.) the formation of polymer bound amides **16a**–**d** was possible in very good yields and HPLC-purities (Table 3). Sonogashira reaction of **16** under standard reaction conditions afforded the immobilized 2-alkynylamines **17a**–**h** in nearly quantitative yields and high purities. For the cyclization of **17a**–**h** to the polymer bound indoles **18** an excess of KO*t*-Bu (8 equiv.) in NMP/toluene (4:1) was used. It is important to add toluene to the resin, because the polymer has to swell to enhance the reactivity for the ring closure. Under these conditions the reactions were performed at rt and gave in most cases **18a**–**h** in good yields and purities (Table 3).

Table 3. Solid phase supported synthesis of indoles **18a**–**h**

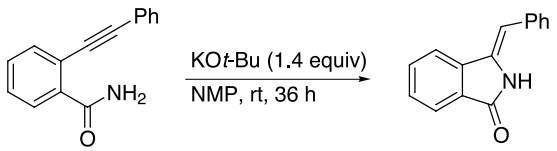
Entry	Amide **16**; yield (%)[a], (purity (%))[b]	Alkynylaniline **17**; yield (%)[a], (purity (%))[b]	Indole **18**; yield (%)[a], (purity (%))[b]
			
1	**16a**: 95 (96)[c]	**17a**: R^1=Bu; 95 (94)[c]	**18a**: R^1=Bu; 93 (85)
2	**16a**	**17b**: R^1=1-cyclohexenyl; 93 (93)[c]	**18b**: R^1=1-cyclohexenyl; 92 (92)
			
3	**16b**: 79 (98)[c]	**17c**: R^1=Bu; 95 (96)[c]	**18c**: R^1=Bu; 97 (93)
4	**16b**	**17d**: R^1=Ph; 94 (98)[c]	**18d**: R^1=Ph; 96 (99)
			
5	**16c**: 94 (98)[c]	**17e**: R^1=Bu; 97 (99)	**18e**: R^1=Bu; 54 (89)
6	**16c**	**17f**: R^1=Ph; 98 (99)	**18f**: R^1=Ph; 52 (94)
			
7	**16d**: 98 (97)[c]	**17g**: R^1=Bu; 96 (99)[c]	**18g**: R^1=Bu; 88 (81)
8	**16d**	**17h**: R^1=Ph; 99 (97)[c]	**18h**: R^1=Ph; 86 (88)

[a] Yields of cleaved products.
[b] Determined by HPLC (see Section 4) after cleavage.
[c] Isolated as its TFA-salt.



19 **20:** 65 %

Scheme 6.



21 **22:** 68 %

Scheme 7.

2-Alkynylphenols, such as **19**, can also undergo a base catalyzed 5-*endo*-dig-cyclization (Scheme 6).[21] $CsOH·H_2O$ in NMP is an efficient catalyst (30 mol%) for this transformation. The reaction proceeds at 70°C in 2 h leading to the benzofuran **20** in 65% yield.

2-Alkynylbenzamides, for example **21**, also undergo a smooth cyclization in the presence of KO*t*-Bu (1.4 equiv., rt, 36 h) furnishing the 5-membered heterocycle **22** as the sole product in 68% yield (Scheme 7).[22]

3. Conclusion

In summary, we have developed a base mediated cyclization of various 2-alkynylanilines leading to indoles and related aza-heterocycles. The cyclization reaction proceeds under mild reaction conditions (mostly at rt) and is compatible with the presence of various important functional groups. For the first time, it was possible to prepare the brominated heterocyclic core of hinckdentine A by using this new base mediated 5-*endo*-dig-cyclization. The reactions have also been applied to the solid phase with excellent yields and purities. Furthermore, benzofurans and isoindolones can be synthesized with satisfactory results by the new method.

4. Experimental

4.1. General methods

Unless otherwise indicated, all reactions were carried out under an argon atmosphere. THF was distilled from sodium/benzophenone, toluene from sodium, NMP, CH_2Cl_2, DMF and DMSO from CaH_2. Reactions in solution were monitored by thin-layer chromatography (TLC) and gas chromatography (GC) analysis of worked up reaction aliquots. Analytical TLC was performed using Merck silica gel (60 F-254) plates (0.25 mm) precoated with a fluorescent indicator. Column chromatography was carried out on silica gel 60 (70–230 mesh). NMR data were recorded on 300 and 600 MHz NMR spectrometers from Bruker. IR spectra were performed with a Nicolet 510 FT-IR-spectrometer. The ionization method used for mass spectroscopy was electron impact ionization (EI, 70 eV). Conversions of solid phase supported reactions and purities were determined by HPLC using a RP 18 (125 mm×3 mm) column with $MeCN/H_2O$ mixtures (5–100% MeCN, 0.1% TFA, 0.8 mL/min) at 254 nm in 20 min. Melting points are uncorrected.

4.2. Starting materials

The following starting materials were prepared according to literature procedures: 4-bromo-2-iodoaniline,[19] ethyl 6-aminonicotinate,[23] ethyl 4-amino-3-nitrobenzoate,[24] ethyl 2-amino-5-methylbenzoate,[25] 2-(1-hexynyl)phenol,[21] 2-(phenylethynyl)benzamide.[22]

4.2.1. Typical procedure A: 2-iodo-6-nitro-4-(trifluoromethyl)aniline (4a). To a solution of iodine (10.64 g, 42.0 mmol) in ethanol (300 mL) was added silver(I)sulfate (13.09 g, 42.0 mmol) and 2-nitro-4-(trifluoromethyl)aniline (6.18 g, 30.0 mmol). The reaction mixture was stirred at rt for 36 h, filtered and the solvent evaporated. The residue was diluted in CH_2Cl_2, extracted with aqueous $Na_2S_2O_3$ solution and dried ($MgSO_4$). The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to give **4a** (7.99 g, 24.0 mmol, 80%) as a yellow-orange solid. Mp: 101–102°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.41–8.39 (m, 1H), 8.06 (d, J=2.1 Hz, 1H), 6.96 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.9, 141.5 (q, J=3.3 Hz), 130.4, 124.7 (q, J=4.3 Hz), 124.2, 120.6, 87.2. IR (KBr): 3463 (s), 3351 (s), 3096 (w), 1633 (s), 1578 (m), 1519 (m), 1455 (s), 1342 (s), 1298 (s), 1252 (s), 1123 (s), 765 (w), 720 (w), 658 (m). *m/z* (EI,%): 332 (M^+, 100), 286 (14), 274 (10), 159 (84), 140 (14). HRMS: calcd for $C_7H_4F_3IN_2O_2$ 331.9270, found 331.9272.

4.2.2. Ethyl 4-amino-3-iodobenzoate (4b).[26] The reaction was carried out according to typical procedure A with iodine (5.08 g, 20.0 mmol), silver(I)sulfate (6.24 g, 20.0 mmol) and ethyl 4-aminobenzoate (3.30 g, 20.0 mmol) in ethanol (100 mL) at rt for 30 min. Column chromatographic purification on silica gel (pentane/ether 9:1) yielded **4b** (5.48 g, 18.8 mmol, 94%) as an off-white powder. Mp: 83°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.25 (d, J=1.8 Hz, 1H), 7.73 (dd, J=8.4, 1.8 Hz, 1H), 6.62 (d, J=8.4 Hz, 1H), 4.43 (s, br, 2H), 4.24 (q, J=7.1 Hz, 2H), 1.28 (t, J=7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=165.7, 151.0, 141.3, 131.3, 121.9, 113.5, 82.5, 61.1, 14.8. IR (KBr): 3661 (m), 1687 (s), 1612 (s), 1590 (m), 1286 (s), 1248 (s). *m/z* (EI,%): 291 (80), 263 (31), 246 (100), 218 (9), 91 (16).

4.2.3. 3-Iodo-2-methyl-4-quinolinylamine (4c). A solution of *N*-iodosuccinimide (1.73 g, 7.7 mmol) in DMF (10 mL) was added to a solution of 2-methyl-4-quinolinylamine (1.11 g, 7.0 mmol) in DMF (20 mL) at −30°C over 15 min. The reaction mixture was warmed up to rt, stirred for 7 h and then poured into cold water. The aqueous layer was extracted with ether and the combined organic layers were washed with aqueous $Na_2S_2O_3$ solution and brine and dried ($MgSO_4$). The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **4c** (0.78 g, 2.8 mmol, 39%) as an orange solid. Mp: 208–210°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.30 (d, J=8.4 Hz, 1H), 7.75–7.70 (m, 1H), 7.65–7.58 (m, 1H), 7.42–7.35 (m, 1H), 6.75 (s, br, 2H), 2.71 (s, 3H). ^{13}C NMR

(DMSO-d_6, 75 MHz): δ=158.8, 150.8, 146.7, 129.4, 127.9, 124.1, 122.3, 116.2, 77.4, 30.8. IR (KBr): 3435 (m), 3292 (m), 3149 (m), 1636 (vs), 1571 (s), 1493 (s), 1393 (m), 758 (s). *m/z* (EI,%): 284 (M^+, 100), 157 (15), 130 (12), 89 (5). HRMS: calcd for $C_{10}H_9IN_2$ 283.9810, found 283.9812.

4.2.4. 3,5-Diiodo-2,6-pyridinediamine (4d). A solution of *N*-iodosuccinimide (4.93 g, 22.0 mmol) in DMF (30 mL) was added to a solution of 2,6-pyridinediamine (1.09 g, 10.0 mmol) in DMF (20 mL) at −30°C over 1 h. The cooling bath was removed and the reaction mixture was stirred for 1 h and then poured into cold water. The resulting precipitate was filtered, washed with water and pentane, dissolved in methanol and dried ($MgSO_4$). Evaporation of the solvents in vacuo afforded **4d** (3.09 g, 8.6 mmol, 86%) as a grey solid. Mp: 202–204°C (decomp.). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=7.74 (s, 1H), 5.73 (s, br, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=156.9, 153.7, 60.1. IR (KBr): 3410 (vs), 3302 (m), 3193 (w), 1621 (s), 1601 (s), 1559 (m), 1439 (s), 1428 (s), 741 (m). *m/z* (EI,%): 361 (M^+, 100), 207 (6), 107 (20), 80 (9). HRMS: calcd for $C_5H_5I_2N_3$ 360.8573, found 360.8566.

4.2.5. Ethyl 6-amino-5-iodonicotinate (4e). The reaction was carried out according to typical procedure A with iodine (10.58 g, 41.7 mmol), silver(I)sulfate (12.95 g, 41.7 mmol) and ethyl 6-aminonicotinate (4.98 g, 30.0 mmol) in ethanol (300 mL) at rt for 18 h. The crude product was recrystallized from ethanol to afford **4e** (6.57 g, 22.5 mmol, 75%) as a yellow-brown solid. Mp: 162°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.51 (d, *J*=2.1 Hz, 1H), 8.48 (d, *J*=2.1 Hz, 1H), 6.80 (s, br, 2H), 4.26 (q, *J*=7.2 Hz, 2H), 1.28 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=162.6, 157.7, 149.4, 144.2, 115.8, 78.9, 60.9, 14.0. IR (KBr): 3325 (s), 3158 (s), 2904 (s), 1720 (vs), 1660 (vs), 1472 (m), 1372 (s), 1311 (s), 1270 (vs), 1055 (s), 887 (m), 760 (s), 642 (s). *m/z* (EI,%): 292 (M^+, 90), 264 (44), 247 (100), 119 (11), 92 (22), 65 (12). HRMS: calcd for $C_8H_9IN_2O_2$ 292.9709, found 292.9715.

4.2.6. Ethyl 4-amino-3-iodo-5-nitrobenzoate (4f). The reaction was carried out according to typical procedure A with iodine (10.65 g, 42.0 mmol), silver(I)sulfate (13.10 g, 42.0 mmol) and ethyl 4-amino-3-nitrobenzoate (6.30 g, 30.0 mmol) in ethanol (150 mL) at rt for 36 h. Column chromatographic purification on silica gel (CH_2Cl_2 100%) yielded **4f** (8.19 g, 24.3 mmol, 81%) as a yellow-orange solid. Mp: 136°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.83 (d, *J*=2.1 Hz, 1H), 8.53 (d, *J*=2.1 Hz, 1H), 7.01 (s, br, 2H), 4.36 (q, *J*=7.2 Hz, 2H), 1.39 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=163.7, 146.4, 145.8, 130.8, 129.1, 120.1, 86.5, 61.5, 14.3. IR (KBr): 3459 (s), 3346 (s), 3084 (m), 2980 (m), 1715 (s), 1620 (s), 1510 (s), 1450 (m), 1334 (s), 1268 (vs), 1141 (s), 756 (s), 717 (m), 677 (m). *m/z* (EI,%): 336 (M^+, 100), 308 (53), 291 (95), 262 (12), 245 (25), 135 (10), 118 (14), 90 (21), 63 (11). HRMS: calcd for $C_9H_9IN_2O_4$ 335.9607, found 335.9603.

4.2.7. Ethyl 2-amino-3-iodo-5-methylbenzoate (4g). The reaction was carried out according to typical procedure A with iodine (3.53 g, 13.9 mmol), silver(I)sulfate (4.30 g, 13.8 mmol) and ethyl 2-amino-5-methylbenzoate (1.79 g, 10.0 mmol) in ethanol (60 mL) at rt for 18 h. Column chromatographic purification on silica gel (CH_2Cl_2 100%) yielded **4g** as a dark brown oil (2.50 g, 8.2 mmol, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.69 (d, *J*=2.1 Hz, 1H), 7.64 (d, *J*=2.1 Hz, 1H), 6.19 (s, br, 2H), 4.33 (q, *J*=7.2 Hz, 2H), 2.20 (s, 3H), 1.38 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=167.3, 147.5, 144.6, 131.7, 126.6, 111.0, 86.3, 60.7, 19.7, 14.3. IR (KBr): 3649 (m), 3023 (m), 1698 (s), 1614 (s), 1588 (m), 1281 (s), 1247 (s). *m/z* (EI,%): 305 (M^+, 100), 277 (6), 259 (92), 230 (8), 105 (11), 77 (10). HRMS: calcd for $C_{10}H_{12}INO_2$ 304.9913, found 304.9910.

4.2.8. 2,4-Dibromo-6-iodoaniline (10). The reaction was carried out according to typical procedure A with iodine (7.81 g, 30.8 mmol), silver(I)sulfate (9.60 g, 30.8 mmol) and 2,4-dibromoaniline (7.02 g, 28.0 mmol) in ethanol (150 mL) at rt for 3 h. Column chromatographic purification on silica gel (pentane/ether 1:1 to ether 100%) yielded **10** (9.22 g, 24.5 mmol, 88%) as a red solid. Mp: 112°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.67 (d, *J*=2.0 Hz, 1H), 7.51 (d, *J*=2.0 Hz, 1H), 4.58 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=143.4, 139.8, 134.7, 109.3, 107.0, 82.6. IR (KBr): 3402 (vw), 3305 (w), 3064 (vw), 1610 (vs), 1555 (m), 1532 (m), 1447 (vs), 1377 (m), 1055 (m), 860 (vs), 704 (m). *m/z* (EI,%): 377 (M^+, 100), 250 (22), 170 (11), 90 (9). HRMS: calcd for $C_6H_4Br_2IN$ 374.7755, found 374.7748.

4.2.9. Typical procedure B: 2-(phenylethynyl)aniline (1a).[6f] 2-Iodoaniline (15.00 g, 68.5 mmol), CuI (0.65 g, 3.4 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (2.39 g, 3.4 mmol, 5 mol%) were suspended in THF (275 mL) under argon. NEt_3 (28.6 mL, 205.5 mmol) and phenylacetylene (9.09 g, 89.0 mmol) were successively added and the reaction mixture was stirred at rt for 2 h. The reaction mixture was diluted with Et_2O and filtered through Celite. After evaporation of the solvents, the crude product was purified by column chromatography on silica gel (pentane/ether 4:1 to 1:1) to give **1a** as a yellow solid (12.79 g, 66.2 mmol, 96%). Mp: 89–90°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.58–7.51 (m, 2H), 7.42–7.32 (m, 4H), 7.18–7.11 (m, 1H), 6.77–6.69 (m, 2H), 4.22 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=147.8, 132.1, 131.4, 129.7, 128.4, 128.2, 123.3, 118.0, 114.3, 107.9, 94.7, 85.9. IR (KBr): 3460 (s), 3368 (s), 3064 (m), 2206 (w), 1616 (m), 1496 (m), 1456 (m), 756 (vs), 751 (vs), 692 (m). *m/z* (EI,%): 193 (M^+, 100), 165 (35), 139 (5), 115 (3), 90 (12), 63 (3).

4.2.10. Typical procedure C: 2-(1-hexynyl)aniline (1b).[21b,27] CuI (28 mg, 0.15 mmol, 5 mol%), $PdCl_2$ (26 mg, 0.15 mmol, 5 mol%) and PPh_3 (78 mg, 0.30 mmol, 10 mol%) were suspended in NEt_3 (6 mL) under argon. 2-iodoaniline (0.657 g, 3.00 mmol) and 1-hexyne (0.410 g, 5.00 mmol) were successively added and the reaction mixture was stirred at rt for 24 h. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to give **1b** (0.421 g, 2.43 mmol, 81%) as yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.31–7.25 (m, 1H), 7.15–7.07 (m, 1H), 6.71 (d, *J*=7.7 Hz, 2H), 4.11 (s, br, 2H), 2.51 (t, *J*=7.0 Hz, 2H), 1.72–1.47 (m, 4H), 1.00 (t, *J*=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=147.6, 132.0, 128.7, 117.8, 114.1, 108.9, 95.7, 76.9, 31.0, 22.0, 19.3, 13.6.

4.2.11. 2-Ethynylaniline (1c).[28] To a solution of 2-[(trimethyl-silyl)ethynyl]aniline (3.20 g, 16.9 mmol) in

THF (20 mL) was slowly added TBAF (1 M in THF, 19 mL, 19.0 mmol). After 30 min at rt, water was added to the reaction mixture, the aqueous layer was extracted with ether and dried ($MgSO_4$). Column chromatography on silica gel (pentane/ether 4:1) yielded **1c** (1.83 g, 15.6 mmol, 92%) as a yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.36 (dd, J=8.0, 1.9 Hz, 1H), 7.20–7.13 (m, 1H), 6.74–6.66 (m, 2H), 4.26 (s, br, 2H), 3.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=148.5, 132.5, 130.0, 117.7, 114.2, 106.5, 82.4, 80.6. IR (neat): 3471 (m), 3379 (m), 3280 (s), 3031 (w), 2096 (m), 1615 (vs), 1491 (vs), 1455 (s), 1316 (s), 1259 (m), 1158 (m), 751 (vs). m/z (EI,%): 117 (M^+, 100), 90 (47), 74 (3), 63 (12), 51 (4). HRMS: calcd for C_7H_8N 117.0578, found 117.0580.

4.2.12. 2-(1-Cyclohexen-1-ylethynyl)aniline (1d). The reaction was carried out according to typical procedure C with 2-iodoaniline (1.095 g, 5.00 mmol), 1-ethynyl-1-cyclohexene (0.742 g, 7.00 mmol), CuI (19 mg, 0.10 mmol, 1 mol%), $PdCl_2$ (18 mg, 0.10 mmol, 1 mol%) and PPh_3 (52 mg, 0.20 mmol, 2 mol%) in NEt_3 (10 mL) at rt for 24 h. Column chromatographic purification on silica gel (CH_2Cl_2 100%) yielded **1d** (0.795 g, 4.05 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.29 (dd, J=7.8, 1.4 Hz, 1H), 7.14–7.07 (m, 1H), 6.73–6.66 (m, 2H), 6.23 (m, 1H), 4.19 (s, br, 2H), 2.31–2.23 (m, 2H), 2.21–2.13 (m, 2H), 1.76–1.59 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=147.4, 134.7, 131.8, 129.0, 120.6, 117.7, 114.1, 108.4, 96.6, 83.0, 29.4, 25.7, 22.3, 21.4.

4.2.13. 2-(2-Thienylethynyl)aniline (1e).[7] The reaction was carried out according to typical procedure C with 2-bromothiophene (0.766 g, 4.70 mmol), 2-ethynylaniline (0.500 g, 4.27 mmol), CuI (32 mg, 0.17 mmol, 4 mol%), $PdCl_2$ (30 mg, 0.17 mmol, 4 mol%) and PPh_3 (89 mg, 0.34 mmol, 8 mol%) in NEt_3 (10 mL) at 80°C for 14 h. Column chromatographic purification on silica gel (pentane/ether 9:1) yielded **1e** (0.789 g, 3.96 mmol, 93%) as a yellow solid. Mp: 60–62°C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.35 (d, J=7.8 Hz, 1H), 7.31–7.25 (m, 2H), 7.15 (t, J=7.7 Hz, 1H), 7.02 (t, J=4.5 Hz, 1H), 6.77–6.68 (m, 2H), 4.25 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ=147.8, 132.1, 131.7, 129.9, 127.2, 127.1, 123.3, 118.0, 114.4, 107.5, 89.5, 87.6. IR (KBr): 3475 (s), 3378 (s), 3070 (vw), 2196 (w), 1611 (s), 1489 (s), 1314 (m), 753 (s), 703 (vs). m/z (EI,%): 199 (M^+, 100), 171 (10), 154 (9), 127 (5), 77 (2). HRMS: calcd for $C_{12}H_9NS$ 199.0456, found 199.0442.

4.2.14. 2-(1,3-Thiazol-2-ylethynyl)aniline (1f). The reaction was carried out according to typical procedure C with 2-bromothiazole (0.615 g, 3.75 mmol), 2-ethynylaniline (0.399 g, 3.41 mmol), CuI (19 mg, 0.10 mmol, 3 mol%), $PdCl_2$ (38 mg, 0.10 mmol, 3 mol%) and PPh_3 (54 mg, 0.20 mmol, 6 mol%) in NEt_3 (20 mL) at 80°C for 2 h. Column chromatographic purification on silica gel (pentane/ether 9:1) yielded **1f** (0.491 g, 2.45 mmol, 72%) as an orange-brown solid. Mp: 102–103°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.85 (s, br, 1H), 7.40–7.31 (m, 2H), 7.15 (dt, J=9.0, 2.3 Hz, 1H), 6.70–6.65 (m, 2H), 4.45 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=148.8, 148.6, 143.3, 132.4, 130.9, 120.7, 117.7, 114.4, 105.3, 91.2, 87.3. IR (KBr): 3378 (w), 3318 (m), 3106 (mw), 2204 (vs), 1636 (s), 1498 (s), 1457 (s), 1320 (m), 1093 (s), 751 (s), 730 (s). m/z (EI,%): 200 (M^+, 100), 173 (6), 142 (27), 115 (17), 58 (28). HRMS: calcd for $C_{11}H_8N_2S$ 200.0408, found 200.0409.

4.2.15. 2-(5-Chloro-1-pentynyl)aniline (1g). The reaction was carried out according to typical procedure B with 2-iodo-aniline (1.095 g, 5.00 mmol), 5-chloro-1-pentyne (0.615 g, 6.00 mmol), NEt_3 (2.1 mL, 15.00 mmol), CuI (48 mg, 0.25 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (175 mg, 0.25 mmol, 5 mol%) in THF (25 mL) at rt for 4 h. Column chromatographic purification on silica gel (pentane/ether 4:1) yielded **1g** (0.825 g, 4.26 mmol, 85%) as a red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.28–7.23 (m, 1H), 7.13–7.07 (m, 1H), 6.71–6.65 (m, 2H), 4.15 (s, br, 2H), 3.73 (t, J=6.4 Hz, 2H), 2.68 (t, J=6.8 Hz, 2H), 2.07 (quint, J=6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=147.7, 132.0, 129.0, 117.8, 114.1, 108.3, 93.3, 78.0, 43.7, 31.4, 17.0. IR (neat): 3471 (m), 3377 (m), 2959 (w), 1614 (vs), 1493 (vs), 1456 (s), 1308 (m), 751 (s), 652 (w). m/z (EI,%): 193 (M^+, 60), 156 (37), 130 (100), 103 (16), 77 (18). HRMS: calcd for $C_{11}H_{12}ClN$ 193.0658, found 193.0669.

4.2.16. 2-[(2-Aminophenyl)ethynyl]phenylamine (1h).[29] The reaction was carried out according to typical procedure B with 2-iodoaniline (0.657 g, 3.00 mmol), 2-ethynylaniline (0.422 g, 3.60 mmol), NEt_3 (2.1 mL, 15.00 mmol), CuI (29 mg, 0.15 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol, 5 mol%) in THF (15 mL) at rt for 3 h. Column chromatographic purification on silica gel (pentane/ethyl acetate 1:1) yielded **1h** (0.506 g, 2.43 mmol, 81%) as a light brown solid. Mp: 140–142°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.37 (dd, J=8.0, 1.6 Hz, 2H), 7.19–7.12 (m, 2H), 6.77–6.70 (m, 4H), 4.28 (s, br, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=147.6, 132.0, 129.7, 118.0, 114.4, 108.1, 91.1. IR (KBr): 3452 (m), 3360 (m), 3058 (w), 1609 (s), 1497 (s), 1456 (s), 1309 (m), 759 (vs). m/z (EI,%): 208 (M^+, 100), 180 (12), 152 (4), 104 (9), 89 (8), 77 (4). HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.0989.

4.2.17. 2,6-Bis(phenylethynyl)-4-(trifluormethyl)aniline (1i). The reaction was carried out according to typical procedure C with 2,6-dibromo-4-(trifluoromethyl)aniline (0.230 g, 0.72 mmol), phenylacetylene (0.221 g, 2.16 mmol), CuI (7.6 mg, 0.04 mmol, 5.5 mol%), $PdCl_2$ (7.1 mg, 0.04 mmol, 5.5 mol%) and PPh_3 (21 mg, 0.08 mmol, 11 mol%) in NEt_3 (10 mL) at 80°C for 15 h. Column chromatographic purification on silica gel (pentane/ether 9:1) yielded **1i** (0.271 g, 0.75 mmol, 75%) as a yellow solid. Mp: 107–109°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.61 (s, br, 2H), 7.59–7.53 (m, 4H), 7.44–7.36 (m, 6H), 5.22 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=150.8, 131.6, 129.2, 129.2, 129.2, 129.1, 128.8, 128.5, 125.8, 122.4, 122.2, 119.7, 119.2, 107.4, 96.0, 84.0. IR (KBr): 3451 (s), 3292 (m), 3143 (m), 2925 (w), 1631 (s), 1566 (m), 1469 (s), 1238 (m), 758 (s), 691 (m). m/z (EI,%): 361 (M^+, 100), 291 (10), 263 (5), 146 (5), 77 (1). HRMS: calcd for $C_{23}H_{14}F_3N$ 361.1078, found 361.1113.

4.2.18. Typical procedure D: 2-nitro-6-(phenylethynyl)-4-(trifluoromethyl)aniline (1j). 2-Iodo-6-nitro-4-(trifluoromethyl)aniline (0.994 g, 3.00 mmol), CuI (12 mg, 0.03 mmol, 2 mol%) and $PdCl_2(PPh_3)_2$ (22 mg, 0.03 mmol, 1 mol%) were suspended in toluene (6 mL)

under argon. $HNEt_2$ (6 mL) and phenylacetylene (0.449 g, 4.40 mmol) were successively added and the reaction mixture was stirred at rt for 2 h. The reaction was quenched by addition of NH_4Cl solution and water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried ($MgSO_4$). Evaporation of the solvents under reduced pressure and column chromatographic purification of the crude product on silica gel (pentane/ethyl acetate 4:1) afforded **1j** (0.790 g, 2.58 mmol, 86%) as an orange-red solid. Mp: 120–121°C. ^1H NMR ($CDCl_3$, 300 MHz): δ=8.18 (s, 1H), 8.01 (s, 1H), 7.83–7.75 (m, 2H), 7.57–7.42 (m, 3H), 6.74 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 142.2, 132.0, 131.4, 131.1, 130.1, 129.3, 128.6, 128.4, 127.9, 127.7, 123.7 (q, J=3.9 Hz), 114.6 (q, J=3.9 Hz), 95.3, 84.8. IR (KBr): 3469 (m), 3398 (m), 2956 (w), 1640 (w), 1529 (m), 1356 (m), 1264 (m), 1097 (m), 1048 (w), 895 (w). *m/z* (EI,%): 306 (M^+, 100), 287 (36), 276 (11), 229 (38), 206 (20), 77 (13). HRMS: calcd for $C_{15}H_9F_3N_2O_2$ 306.0616, found 306.0611.

4.2.19. Ethyl 4-amino-3-(phenylethynyl)benzoate (1k). The reaction was carried out according to typical procedure D with ethyl 4-amino-3-iodobenzoate (0.875 g, 3.00 mmol), phenylacetylene (0.458 g, 4.50 mmol), CuI (11 mg, 0.06 mmol, 2 mol%) and $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol, 1 mol%) in $HNEt_2$ (6 mL) and toluene (6 mL) at rt for 2 h. Column chromatographical purification on silica gel (pentane/ethyl acetate 4:1) afforded **1k** (0.781 g, 2.94 mmol, 98%) as a white solid. Mp: 94–95°C. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.99 (d, J=1.8 Hz, 1H), 7.72 (dd, J=8.4 Hz, 1.8 Hz, 1H), 7.44–7.39 (m, 2H), 7.26–7.21 (m, 3H), 6.58 (d, J=8.4 Hz, 1H), 4.65 (s, br, 2H), 4.22 (q, J=7.2 Hz, 2H), 1.26 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=166.1, 151.4, 134.2, 131.4, 131.3, 128.4, 128.3, 122.8, 119.6, 113.2, 106.9, 95.0, 84.8, 60.4, 14.3. IR (KBr): 3459 (m), 3353 (m), 2982 (w), 2200 (w), 1698 (s), 1626 (s), 1596 (m), 1504 (m), 1365 (m), 1336 (m), 1253 (s), 1143 (m), 1100 (w), 1030 (w), 760 (m), 690 (w). *m/z* (EI,%): 265 (M^+, 36), 247 (100), 220 (63), 189 (78), 165 (23). HRMS: calcd for $C_{17}H_{15}NO_2$ 265.1103, found 265.1097.

4.2.20. Ethyl 4-amino-3-(1-cyclohexen-1-ylethynyl)-benzoate (1l). The reaction was carried out according to typical procedure C with ethyl 4-amino-3-iodobenzoate (0.875 g, 3.00 mmol), 1-ethynyl-1-cyclohexene (0.479 g, 4.50 mmol), CuI (11 mg, 0.06 mmol, 2 mol%) and $PdCl_2$-$(PPh_3)_2$ (21 mg, 0.03 mmol, 1 mol%) in $HNEt_2$ (6 mL) and toluene (6 mL) at rt for 2 h. Column chromatographic purification on silica gel (pentane/ethyl acetate 4:1) afforded **1l** (0.599 g, 2.22 mmol, 74%) as a white solid. Mp: 82–83°C. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.95 (d, J=2.1 Hz, 1H), 7.75 (dd, J=8.4, 2.1 Hz, 1H), 6.63 (d, J=8.4 Hz, 1H), 6.21–6.16 (m, 1H), 4.65 (s, br, 2H), 4.29 (q, J=7.1 Hz, 2H), 2.25–2.18 (m, 2H), 2.16–2.08 (m, 2H), 1.71–1.55 (m, 4H), 1.34 (t, J=7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=166.1, 151.2, 135.3, 133.9, 130.8, 120.4, 119.4, 112.9, 107.5, 97.0, 82.0, 60.3, 29.3, 25.6, 22.2, 21.3, 14.3. IR (KBr): 3469 (m), 3358 (m), 2933 (w), 2180 (w), 1692 (s), 1620 (s), 1504 (w), 1367 (w), 1292 (m), 1242 (s), 1130 (w), 1023 (w), 768 (w). *m/z* (EI,%): 269 (M^+, 100), 241 (66), 224 (17), 196 (29), 189 (41), 168 (25). HRMS: calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1411.

4.2.21. 5-Methyl-3-(phenylethynyl)-2-pyridinylamine (1m). The reaction was carried out according to typical procedure C with 3-bromo-5-methyl-2-pyridinylamine (0.160 g, 0.86 mmol), phenylacetylene (0.175 g, 1.71 mmol), CuI (8.1 mg, 0.04 mmol, 5 mol%), $PdCl_2$ (7.6 mg, 0.04 mmol, 5 mol%) and PPh_3 (22 mg, 0.09 mmol, 10 mol%) in NEt_3 (10 mL) at 80°C for 18 h. Column chromatographic purification on silica gel (pentane/ethyl acetate 1:1) yielded **1m** (0.141 g, 0.68 mmol, 79%) as a brown solid. Mp: 94–96°C. ^1H NMR ($CDCl_3$, 300 MHz): δ=7.77 (s, 1H), 7.45–7.36 (m, 2H), 7.34–7.30 (m, 1H), 5.00 (s, br, 2H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=156.9, 147.8, 140.4, 131.3, 128.4, 128.3, 122.7, 122.2, 102.6, 95.1, 84.6, 17.1. IR (KBr): 3451 (s), 3292 (m), 3143 (m), 2925 (w), 1631 (s), 1566 (m), 1469 (s), 1238 (m), 758 (s), 691 (m). *m/z* (EI,%): 208 (M^+, 100), 192 (5), 180 (8), 152 (5), 104 (5), 91 (1), 77 (2). HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.0995.

4.2.22. 2-(Phenylethynyl)-3-pyridinylamine (1n). The reaction was carried out according to typical procedure C with 2-chloro-3-pyridinylamine (3.86 g, 30.0 mmol), phenylacetylene (6.63 g, 60.0 mmol), CuI (0.23 g, 1.2 mmol, 4 mol%), $PdCl_2$ (0.21 g, 1.2 mmol, 4 mol%) and PPh_3 (0.63 g, 2.4 mmol, 8 mol%) in NEt_3 (60 mL) at 80°C for 20 h. Column chromatographic purification on silica gel (pentane/ethyl acetate 9:1 to 1:1) yielded **1n** (0.388 g, 2.00 mmol, 40%) as a yellow-brown solid. Mp: 125°C. ^1H NMR ($CDCl_3$, 300 MHz): δ=8.04–7.89 (m, 1H), 7.60–7.41 (m, 2H), 7.38–7.19 (m, 3H), 6.94 (m, 2H), 4.30 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.4, 139.8, 131.6, 128.7, 128.3, 123.8, 122.2, 121.0, 94.7, 85.1. IR (KBr): 3434 (m), 3296 (m), 3169 (m), 1615 (s), 1580 (m), 1490 (m), 1462 (s), 1445 (vs), 1263 (m), 800 (m), 753 (s), 685 (m). *m/z* (EI,%): 194 (M^+, 100), 166 (8), 139 (4), 115 (2), 77 (2). HRMS: calcd for $C_{13}H_{10}N_2$ 194.0844, found 194.0836.

4.2.23. 3-(1-Hexynyl)-2-methyl-4-quinolinylamine (1o). The reaction was carried out according to typical procedure B with 3-iodo-2-methyl-4-quinolinylamine (0.450 g, 1.58 mmol), 1-hexyne (0.195 g, 2.38 mmol), NEt_3 (0.66 mL, 4.75 mmol), CuI (15 mg, 0.08 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (56 mg, 0.08 mmol, 5 mol%) in THF (8 mL) at rt for 20 h. Column chromatographic purification on silica gel (pentane/ethyl acetate 1:1) yielded **1o** (0.331 g, 1.39 mmol, 87%) as a yellow-orange solid. Mp: 152–154°C. ^1H NMR (CD_3OD, 300 MHz): δ=7.93 (d, J=8.4 Hz, 1H), 7.67 (d, J=8.2 Hz, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.31 (t, J=7.6 Hz, 1H), 2.55 (s, 3H), 2.51 (t, J=6.9 Hz, 2H), 1.64–1.40 (m, 4H), 0.92 (t, J=7.2 Hz, 3H). ^{13}C NMR (CD_3OD, 75 MHz): δ=160.7, 154.0, 147.1, 131.0, 130.1, 129.9, 128.2, 125.5, 122.9, 102.4, 75.5, 32.3, 24.1, 23.2, 20.3, 14.0. IR (KBr): 3410 (m), 3304 (w), 3092 (m), 2958 (w), 1649 (vs), 1568 (s), 1497 (s), 1442 (s), 1376 (m), 768 (m). *m/z* (EI,%): 238 (M^+, 70), 223 (17), 209 (32), 195 (100), 182 (10), 167 (11), 127 (8), 77 (8). HRMS: calcd for $C_{16}H_{18}N_2$ 238.1470, found 238.1461.

4.2.24. 3,5-Bis(phenylethynyl)-2,6-pyridinediamine (1p). The reaction was carried out according to typical procedure B with 3,5-diiodo-2,6-pyridinediamine (1.99 g, 5.54 mmol), phenylacetylene (1.698 g, 16.62 mmol), NEt_3 (3.9 mL,

27.7 mmol), CuI (53 mg, 0.28 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (194 mg, 0.28 mmol, 5 mol%) in THF (40 mL) at rt for 1 h. Column chromatographic purification on silica gel (pentane/CH_2Cl_2 1:1 to CH_2Cl_2 100% to CH_2Cl_2/MeOH 99:1) yielded **1p** (1.54 g, 4.98 mmol, 90%) as a yellow-orange solid. Mp: 165–167°C. ^{1}H NMR (DMSO-d_6, 300 MHz): 7.63–7.50 (m, 4H), 7.46 (s, 1H), 7.43–7.25 (m, 6H), 6.33 (s, br, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=158.9, 143.3, 130.7, 128.3, 127.5, 123.4, 92.4, 89.6, 86.1. IR (KBr): 3490 (s), 3380 (s), 3049 (w), 2192 (s), 1605 (vs), 1536 (s), 1490 (s), 1464 (s), 1378 (m), 1316 (m), 750 (s), 690 (s). *m/z* (EI,%): 309 (M^+, 100), 281 (4), 264 (3), 205 (6). HRMS: calcd for $C_{21}H_{15}N_3$ 309.1266, found 309.1255.

4.2.25. 2-[4-(2-Aminophenyl)-1,3-butadiynyl]phenylamine (5).[16] $Cu(OAc)_2{\cdot}H_2O$ (1.597 g, 8.00 mmol) was dissolved in pyridine (15 mL) and methanol (15 mL). After addition of 2-ethynylaniline (0.469 g, 4.00 mmol), the reaction mixture was stirred at rt for 24 h. The solution was treated with water, the organic layer separated and the aqueous layer extracted with ether. The combined organic layers were washed with aqueous $CuSO_4$ solution, water and dried ($MgSO_4$). Column chromatographic purification on silica gel (pentane/ether 4:1 to 1:1) yielded **5** (0.360 g, 1.55 mmol, 77%) as a yellow-orange solid. Mp: 126–128°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.37 (dd, *J*=7.7, 1.6 Hz, 2H), 7.19–7.13 (m, 2H), 6.73–6.66 (m, 4H), 4.25 (s, br, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=149.4, 133.0, 130.6, 117.9, 114.4, 106.2, 79.7, 79.0. IR (KBr): 3444 (m), 3324 (m), 3025 (w), 2132 (m), 1621 (vs), 1487 (s), 1455 (s), 1317 (s), 749 (m), 736 (s). *m/z* (EI,%): 232 (M^+, 100), 204 (38), 176 (4), 151 (2), 128 (2), 102 (3), 89 (4). HRMS: calcd for $C_{16}H_{12}N_2$ 232.1000, found 232.0973.

4.2.26. 2-(1-Hexynyl)-6-nitro-4-(trifluoromethyl)aniline (8). The reaction was carried out according to typical procedure C with 2-bromo-6-nitro-4-(trifluoromethyl)aniline (0.470 g, 1.65 mmol), 1-hexyne (0.164 g, 2.00 mmol), CuI (19 mg, 0.10 mmol, 6 mol%), $PdCl_2$ (18 mg, 0.10 mmol, 6 mol%) and PPh_3 (53 mg, 0.20 mmol, 12 mol%) in NEt_3 (5 mL) at rt for 20 h. Column chromatographic purification on silica gel (pentane/CH_2Cl_2 1:4) yielded **8** (0.389 g, 1.35 mmol, 82%) as an orange solid. Mp: 106–107°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.23 (s, 1H), 8.04 (s, 1H), 6.88 (s, br, 2H), 2.85 (t, *J*=7.5 Hz, 2H), 1.74 (quint, *J*=7.5 Hz, 2H), 1.42 (sext, *J*=7.5 Hz, 2H), 0.96 (t, *J*=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.4, 140.7 (q, *J*=3.9 Hz), 130.2, 128.5, 124.9 (q, *J*=3.9 Hz), 124.7, 121.9, 97.6, 84.2, 30.2, 22.3, 19.5, 13.8. IR (KBr): 3476 (m), 3350 (s), 3101 (w), 2212 (w), 1630 (s), 1589 (w), 1530 (m), 1456 (m), 1349 (s), 1281 (vs), 1124 (s), 757 (m). *m/z* (EI,%): 286 (M^+, 100), 267 (42), 256 (13), 229 (22), 206 (31). HRMS: calcd for $C_{13}H_{13}F_3N_2O_2$ 286.0929, found 286.0917.

4.2.27. 2,4-Dibromo-6-[(trimethylsilyl)ethynyl]aniline (11a). The reaction was carried out according to typical procedure B with 2,4-dibromo-6-iodoaniline (8.00 g, 21.2 mmol), trimethylsilylacetylene (2.51 g, 25.5 mmol), NEt_3 (8.9 mL, 63.7 mmol), CuI (0.20 g, 1.1 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (0.75 g, 1.1 mmol, 5 mol%) in THF (100 mL) at rt for 3 h. Column chromatographic purification on silica gel (pentane 100%) yielded **11a** (4.91 g, 14.1 mmol, 67%) as a yellow-orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.46 (d, *J*=2.2 Hz, 1H), 7.34 (d, *J*=2.2 Hz, 1H), 4.65 (s, 2H), 0.08 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.0, 135.0, 133.5, 110.0, 108.6, 108.0, 102.2, 99.5, −0.1. IR (neat): 3485 (m), 3384 (m), 2959 (m), 2153 (m), 1606 (s), 1456 (vs), 1250 (s), 899 (vs), 845 (vs), 760 (s), 700 (s). *m/z* (EI,%): 347 (M^+, 100), 332 (96), 251 (23), 236 (15), 171 (33), 139 (13), 73 (27). HRMS: calcd for $C_{11}H_{13}Br_2NSi$ 344.9184, found 344.9160.

4.2.28. 2,4-Dibromo-6-ethynylaniline (11b). 2,4-Dibromo-[(6-tri-methylsilyl)ethynyl]aniline (4.89 g, 14.1 mmol) was dissolved in THF (30 mL). After addition of TBAF (1 M in THF, 15.5 mL, 15.5 mmol), the reaction mixture was stirred at rt for 1 h. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and washed with water. The combined aqueous layers were extracted with CH_2Cl_2 and the combined organic layers dried ($MgSO_4$). Recrystallisation from pentane/CH_2Cl_2 yielded **11b** (3.30 g, 12.0 mmol, 85%) as a brown solid. Mp: 132–133°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.50 (d, *J*=2.2 Hz, 1H), 7.37 (d, *J*=2.2 Hz, 1H), 4.68 (s, 2H), 3.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.3, 135.5, 135.4, 133.9, 108.7, 108.0, 84.2, 78.7. IR (KBr): 3428 (s), 3319 (s), 3290 (vs), 2101 (vw), 1614 (vs), 1456 (vs), 1232 (w), 866 (s), 668 (s), 617 (s). *m/z* (EI,%): 275 (M^+, 100), 194 (25), 115 (65), 88 (14), 62 (10). HRMS: calcd for $C_8H_5Br_2N$ 272.8789, found 272.8758.

4.2.29. 2-[(2-Amino-5-bromophenyl)ethynyl]-4,6-dibromo-phenylamine (12). The reaction was carried out according to typical procedure B with 4-bromo-2-iodoaniline (1.000 g, 3.40 mmol), 2,4-dibromo-6-ethynylaniline (1.100 g, 4.00 mmol), NEt_3 (1.4 mL, 10.10 mmol), CuI (32 mg, 0.17 mmol, 5 mol%) and $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol, 5 mol%) in THF (6 mL) at rt for 3 h. The crude product was purified by recrystallisation from acetone/water and yielded **12** (1.459 g, 3.28 mmol, 97%) as a brown solid. Mp: 140–142°C. ^{1}H NMR (acetone-d_6, 300 MHz): δ=7.57 (d, *J*=2.2 Hz, 1H), 7.55 (d, *J*=2.2 Hz, 1H), 7.49 (d, *J*=2.4 Hz, 1H), 7.21 (dd, *J*=8.7, 2.4 Hz, 1H), 6.76 (d, *J*=8.7 Hz, 1H), 5.47 (s, 2H), 5.40 (s, 2H). ^{13}C NMR (acetone-d_6, 75 MHz): δ=149.1, 145.8, 134.9, 134.3, 133.8, 133.1, 116.3, 110.2, 108.4, 108.3, 106.9, 106.9, 92.2, 90.1. IR (KBr): 3414 (vs), 3337 (vs), 3052 (m), 2196 (w), 1612 (vs), 1485 (vs), 1454 (s), 1414 (m), 1305 (w), 1278 (w), 1246 (w), 1227 (w), 862 (w), 812 (m), 693 (m). *m/z* (EI,%): 446 (M^+, 100), 366 (7), 286 (60), 205 (28), 177 (9), 142 (9), 89 (8). HRMS: calcd for $C_{14}H_9Br_3N_2$ 441.8316, found 441.8339.

4.3. Indoles

4.3.1. Typical procedure E: 2-phenyl-1*H*-indole (2a).[6f] KO*t*-Bu (117 mg, 1.05 mmol) was dissolved under argon in NMP (2.5 mL). A solution of 2-(phenylethynyl)aniline (97 mg, 0.50 mmol) in NMP (2.5 mL) was added dropwise at rt and the reaction mixture was stirred for 4 h. The reaction was quenched with water, extracted with ether and dried ($MgSO_4$). The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2a** (77 mg, 0.40 mmol, 79%) as an off-white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.22 (s, br, 1H), 7.58–7.53 (m, 3H), 7.37–7.23 (m, 3H), 7.15–7.02 (m, 3H), 6.74 (s, br, 1H). ^{13}C

NMR ($CDCl_3$, 75 MHz): δ=138.3, 137.2, 132.8, 129.7, 129.4, 128.1, 125.6, 122.8, 121.1, 120.7, 111.3, 100.4. *m/z* (EI,%): 194 (32), 193 (M^+, 100), 192 (28), 192 (12), 190 (9), 166 (9), 165 (45), 164 (8), 163 (6), 139 (5), 97 (11), 96 (6), 90 (10), 89 (14).

4.3.2. 2-Butyl-1*H*-indole (2b).[21b,27] The reaction was carried out according to typical procedure E with KO*t*-Bu (110 mg, 0.98 mmol) and 2-(1-hexynyl)aniline (86 mg, 0.50 mmol) in NMP (5 mL) at rt for 12 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2b** (77 mg, 0.39 mmol, 78%) as an off-white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.61 (s, br, 1H), 7.43 (dd, *J*=7.5, 0.9 Hz, 1H), 7.14 (dd, *J*=7.2, 0.6 Hz, 1H), 7.02–6.97 (m, 2H), 6.13 (s, 1H), 2.60 (t, *J*=7.5 Hz, 2H), 1.61–1.55 (m, 2H), 1.35–1.27 (m, 2H), 0.86 (t, *J*=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=139.0, 134.8, 127.8, 119.8, 118.7, 118.5, 109.3, 98.3, 30.2, 26.9, 21.4, 12.8. *m/z* (EI,%): 174 (14), 173 (M^+, 100), 172 (7), 158 (17), 145 (6), 144 (40), 143 (13), 131 (13), 130 (88), 129 (3), 128 (6), 118 (5), 117 (8), 115 (7), 105 (3), 103 (3), 102 (18), 101 (8). HRMS: calcd for $C_{12}H_{15}N$ 173.1204, found 173.1202.

4.3.3. 1*H*-Indole (2c). The reaction was carried out according to typical procedure E with KO*t*-Bu (112 mg, 1.00 mmol) and 2-ethynylaniline (59 mg, 0.50 mmol) in NMP (5 mL) at rt for 4 h. The crude product was purified by column chromatography on silica gel (pentane/CH_2Cl_2 7:3) to afford **2c** (36 mg, 0.31 mmol, 62%) as an off-white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.92 (s, br, 1H), 7.83 (dd, *J*=7.5, 0.9 Hz, 1H), 7.42–7.30 (m, 3H), 7.20–7.18 (m, 1H), 6.71–6.69 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=136.3, 128.3, 124.8, 122.1, 121.3, 120.3, 111.2, 103.0. *m/z* (EI,%): 118 (28), 117 (M^+, 100), 116 (25), 91 (10), 90 (90), 89 (73), 88 (5), 87 (5), 64 (9), 63 (27), 62 (13), 58 (10), 51 (6), 50 (6).

4.3.4. Typical procedure F: 2-(1-cyclohexen-1-yl)-1*H*-indole (2d).[30] KH (48 mg, 1.20 mmol) was dissolved under argon in NMP (2.5 mL). A solution of 2-(1-cyclohexen-1-ylethynyl)aniline (99 mg, 0.50 mmol) in NMP (2.5 mL) was added dropwise at rt and the reaction mixture was stirred for 8 h. The reaction was quenched with water, and the mixture extracted with ether and dried ($MgSO_4$). The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2d** (66 mg, 0.33 mmol, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.98 (s, br, 1H), 7.46 (dd, *J*=7.8, 0.6 Hz, 1H), 7.20 (dd, *J*=8.1, 0.9 Hz, 1H), 7.03–6.95 (m, 2H), 6.35 (s, br, 1H), 6.02 (m, 1H), 2.39–2.35 (m, 2H), 2.17–2.14 (m, 2H), 1.72–1.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=139.9, 136.6, 129.6, 129.4, 123.0, 122.4, 120.8, 120.1, 110.8, 99.1, 26.5, 25.9, 23.0, 22.6. *m/z* (EI,%): 198 (20), 197 (99), 196 (34), 182 (18), 180 (11), 170 (10), 169 (49), 168 (100), 167 (40), 143 (18), 130 (24), 118 (12), 117 (72), 115 (12), 77 (11). HRMS: calcd for $C_{14}H_{15}N$ 197.1204, found 197.1201.

4.3.5. 2-(2-Thienyl)-1*H*-indole (2e).[31] The reaction was carried out according to typical procedure F with KH (80 mg, 2.00 mmol) and 2-(2-thienylethynyl)aniline (199 mg, 1.00 mmol) in NMP (10 mL) at rt for 4 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2e** (139 mg, 0.70 mmol, 70%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.07 (s, br, 1H), 7.50 (d, *J*=7.5 Hz, 1H), 7.23–6.96 (m, 6H), 6.63 (d, *J*=1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=136.9, 136.0, 132.8, 129.5, 128.3, 125.0, 124.4, 123.0, 121.0, 120.9, 111.2, 100.9. *m/z* (EI,%): 199 (M^+, 100), 171 (5), 154 (5), 140 (1), 127 (2), 99 (3), 89 (1). HRMS: calcd for $C_{12}H_9NS$ 199.0456, found 199.0442.

4.3.6. 2-(1,3-Thiazol-2-yl)-1*H*-indole (2f). The reaction was carried out according to typical procedure F with KH (80 mg, 2.00 mmol) and 2-(1,3-thiazol-2-ylethynyl)aniline (200 mg, 1.00 mmol) in NMP (10 mL) at rt for 3 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2f** (122 mg, 0.61 mmol, 61%) as an orange-yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=9.81 (s, br, 1H), 7.86–7.83 (m, 1H), 7.41 (dd, *J*=8.1, 1.2 Hz, 1H), 7.40–7.27 (m, 3H), 7.13 (t, *J*=7.8 Hz, 1H), 7.06 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=160.3, 141.7, 135.9, 130.4, 127.5, 122.8, 120.2, 119.4, 117.3, 110.5, 102.3. *m/z* (EI,%): 200 (M^+, 100), 155 (4), 142 (12), 115 (4), 89 (2). HRMS: calcd for $C_{11}H_8N_2S$ 200.0408, found 200.0391.

4.3.7. 2-Cyclopropyl-1*H*-indole (2g).[32] The reaction was carried out according to typical procedure F with KH (132 mg, 3.29 mmol) and 2-(5-chloro-1-pentynyl)aniline (291 mg, 1.50 mmol) in NMP (15 mL) at rt for 6 h. The crude product was purified by column chromatography on silica gel (pentane/ether 19:1) to afford **2g** (177 mg, 1.13 mmol, 75%) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.80 (s, br, 1H), 7.43–7.38 (m, 1H), 7.20–7.14 (m, 1H), 7.06–6.92 (m, 2H), 6.09–6.04 (m, 1H), 1.91–1.80 (m, 1H), 0.91–0.80 (m, 2H), 0.71–0.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.7, 135.7, 128.7, 121.0, 119.7, 119.7, 110.2, 97.7, 8.8, 7.2. IR (neat): 3307 (m), 3012 (w), 1678 (vs), 1609 (s), 1451 (s), 754 (vs). *m/z* (EI,%): 157 (M^+, 100), 130 (81), 115 (4), 103 (5), 77 (7). HRMS: calcd for $C_{11}H_{11}N$ 157.0891, found 157.0891.

4.3.8. 2-(1*H*-Indol-2-yl)aniline (2h).[13b] The reaction was carried out according to typical procedure F with KH (80 mg, 2.00 mmol) and 2-[(2-aminophenyl)ethynyl]-phenylamine (208 mg, 1.00 mmol) in NMP (10 mL) at rt for 3 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **2h** (171 mg, 0.82 mmol, 82%) as a white pale brown solid. Mp: 152–154°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=11.21 (s, br, 1H), 7.53 (d, *J*=7.8 Hz, 1H), 7.42–7.33 (m, 2H), 7.12–7.04 (m, 2H), 7.03–6.96 (m, 1H), 6.83 (dd, *J*=8.3, 1.0 Hz, 1H), 6.72–6.65 (m, 2H), 5.17 (s, br, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=145.5, 136.2, 136.0, 128.7, 128.5, 128.2, 120.9, 119.6, 118.9, 116.7, 116.4, 115.6, 111.0, 99.8. IR (KBr): 3379 (m), 3304 (m), 1615 (s), 1491 (s), 1456 (s), 1298 (m), 808 (s), 741 (s). *m/z* (EI,%): 208 (M^+, 100), 180 (5), 117 (6), 104 (38), 89 (24), 77 (16). HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.0989.

4.3.9. 2-Phenyl-7-(phenylethynyl)-5-(trifluoromethyl)-1*H*-indole (2i). The reaction was carried out according to typical procedure F with KH (30 mg, 0.75 mmol) and 2,6-bis(phenylethynyl)-4-(trifluoromethyl)aniline (100 mg, 0.28 mmol) in NMP (5 mL) at rt for 14 h. The crude product was purified by column chromatography on silica

gel (pentane/ether 9:1) to afford **2i** (80 mg, 0.22 mmol, 80%) as a yellow solid. Mp: 145–146°C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ=8.93 (s, br, 1H), 7.92 (s, br, 1H), 7.80–7.74 (m, 2H), 7.70–7.62 (m, 3H), 7.54–7.40 (m, 6H), 6.97 (m, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ=140.3, 138.6, 131.8, 131.3, 129.2, 129.0, 128.7, 128.6, 128.5, 125.6, 123.0, 122.6, 122.2, 122.1, 118.5 (q), 106.7, 101.2, 94.5, 84.0. IR (KBr): 3465 (vs), 1630 (s), 1490 (m), 1367 (s), 1317 (m), 1282 (s), 1111 (s), 749 (s). *m/z* (EI,%): 361 (M^+, 100), 342 (3), 291 (4). HRMS: calcd for $C_{23}H_{14}F_3N$ 361.1078, found 361.1064.

4.3.10. 7-Nitro-2-phenyl-5-(trifluoromethyl)-1*H*-indole (2j). The reaction was carried out according to typical procedure F with KH (72 mg, 1.80 mmol) and 2-nitro-6-(phenylethynyl)-4-trifluoromethyl)aniline (306 mg, 1.00 mmol) in NMP (5 mL) at rt for 2 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2j** (157 mg, 0.51 mmol, 51%) as a yellow solid. Mp: 181–182°C. ^{1}H NMR ($CDCl_3$/DMSO-d_6, 300 MHz): δ=10.31 (s, br, 1H), 8.31 (s, 1H), 8.14 (s, 1H), 7.74–7.68 (m, 2H), 7.51–7.36 (m, 3H), 6.97 (d, *J*=2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 75 MHz): δ=142.5, 132.3, 131.6, 131.5, 130.3, 129.5, 128.6, 128.3, 128.1, 127.7, 125.7, 123.5 (q, *J*=3.9 Hz), 114.5 (q, *J*=3.9 Hz), 100.6. IR (KBr): 3414 (m), 2925 (w), 1636 (w), 1524 (m), 1332 (s), 1309 (s), 1269 (m), 1167 (m), 1122 (m), 1085 (w), 894 (w), 758 (m), 588 (w). *m/z* (EI,%): 306 (M^+, 100), 287 (37), 276 (14), 206 (31). HRMS: calcd for $C_{15}H_9F_3N_2O_2$ 306.0616, found 306.0611.

4.3.11. Ethyl 2-phenyl-1*H*-indole-5-carboxylate (2k). The reaction was carried out according to typical procedure F with KH (72 mg, 1.80 mmol) and ethyl 4-amino-3-(phenylethynyl)benzoate (265 mg, 1.00 mmol) in NMP (5 mL) at rt for 2 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2k** (207 mg, 0.78 mmol, 78%) as a white solid. Mp: 184–185°C. ^{1}H NMR ($CDCl_3$/DMSO-d_6, 300 MHz): δ=11.01 (s, br, 1H), 8.26 (s, 1H), 7.76–7.70 (m, 3H), 7.37–7.30 (m, 3H), 7.22 (t, *J*=7.2 Hz, 1H), 6.78 (d, *J*=1.4 Hz, 1H), 4.29 (q, *J*=7.2 Hz, 2H), 1.33 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 75 MHz): δ=167.2, 139.4, 139.2, 131.6, 128.3, 128.0, 127.2, 124.9, 122.5, 122.4, 121.2, 110.4, 99.4, 59.8, 13.9. IR (KBr): 3332 (s), 2985 (w), 1686 (vs), 1612 (m), 1461 (w), 1369 (m), 1330 (m), 1296 (m), 1262 (s), 1177 (s), 1096 (w), 1027 (w), 762 (s), 696 (w). *m/z* (EI,%): 265 (M^+, 100), 250 (6), 237 (37), 220 (60), 192 (32), 165 (18), 110 (6), 95 (8). HRMS: calcd for $C_{17}H_{15}NO_2$ 265.1103, found 265.1101.

4.3.12. Ethyl 2-(1-cyclohexen-1-yl)-1*H*-indole-5-carboxylate (2l). The reaction was carried out according to typical procedure F with KH (72 mg, 1.80 mmol) and ethyl 4-amino-3-(1-cyclohexen-1-ylethynyl)benzoate (269 mg, 1.00 mmol) in NMP (5 mL) at rt for 2 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **2l** (194 mg, 0.72 mmol, 72%) as a white solid. Mp: 192–193°C. ^{1}H NMR ($CDCl_3$/ DMSO-d_6, 300 MHz): δ=10.06 (s, br, 1H), 8.13 (s, 1H), 7.66 (dd, *J*=8.7, 1.5 Hz, 1H), 7.19 (d, *J*=8.7 Hz, 1H), 6.31 (d, *J*=1.5 Hz, 1H), 6.19–6.16 (m, 1H), 4.22 (q, *J*=7.2 Hz, 2H), 2.34–2.27 (m, 2H), 2.13–2.06 (m, 2H), 1.69–1.49 (m, 4H), 1.26 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 75 MHz): δ=167.5, 141.1, 139.1, 128.4, 127.9, 123.4, 122.5, 122.4, 120.9, 109.9, 98.6, 59.9, 25.5, 25.1, 22.1, 21.8, 14.1. IR (KBr): 3370 (s), 2937 (w), 1683 (s), 1610 (w), 1471 (w), 1367 (w), 1310 (s), 1258 (m), 1166 (m), 1095 (w), 768 (m). *m/z* (EI,%): 269 (M^+, 100), 254 (5), 241 (19), 224 (20), 196 (20), 168 (20), 154 (5), 105 (4). HRMS: calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1413.

4.3.13. 5-Methyl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (2m). The reaction was carried out according to typical procedure F with KH (40 mg, 1.00 mmol) and 5-methyl-3-(phenylethynyl)-2-pyridinylamine (100 mg, 0.48 mmol) in NMP (5 mL) at rt for 1 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **2m** (72 mg, 0.35 mmol, 72%) as a white solid. Mp: 252–253°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=11.98 (s, br, 1H), 8.09–8.04 (m, 1H), 7.95–7.89 (m, 2H), 7.70 (s, 1H), 7.45 (t, *J*=7.6 Hz, 1H), 7.36–7.29 (m, 1H), 6.82 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=148.2, 143.6, 138.2, 131.6, 128.8, 127.7, 127.5, 125.1, 124.3, 120.7, 96.4, 18.0. IR (KBr): 3436 (s), 3152 (w), 2914 (w), 1637 (m), 1484 (w), 1456 (m), 1281 (m), 753 (vs), 690 (m). *m/z* (EI,%): 208 (M^+, 100), 180 (6), 152 (4), 104 (6). HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.0995.

4.3.14. 2-Phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (2n).[33] The reaction was carried out according to typical procedure F with KH (42 mg, 1.05 mmol) and 2-(phenylethynyl)-3-pyridinylamine (100 mg, 0.52 mmol) in NMP (5 mL) at rt for 1 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **2n** (74 mg, 0.38 mmol, 74%) as a yellow solid. Mp: 254–255°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=11.78 (s, br, 1H), 8.32 (dd, *J*=4.6, 1.3 Hz, 1H), 7.96–7.91 (m, 2H), 7.77–7.73 (m, 1H), 7.54–7.46 (m, 1H), 7.41–7.34 (m, 1H), 7.13–7.05 (m, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=146.9, 142.8, 140.8, 131.5, 129.8, 128.9, 128.2, 125.3, 118.0, 116.5, 99.1. IR (KBr): 3436 (vs), 3058 (vw), 1634 (m), 1460 (m), 1416 (s), 1278 (m), 763 (m). *m/z* (EI,%): 194 (M^+, 100), 166 (9), 139 (4), 128 (2), 102 (3), 97 (6). HRMS: calcd for $C_{13}H_{10}N_2$ 194.0844, found 194.0839.

4.3.15. 2-Butyl-4-methyl-1*H*-pyrrolo[3,2-*c*]quinoline (2o). The reaction was carried out according to typical procedure F with KH (48 mg, 1.20 mmol) and 3-(1-hexynyl)-2-methyl-4-quinolinylamine (190 mg, 0.80 mmol) in NMP (8 mL) at 80°C for 6 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:2 to ethyl acetate 100%) to afford **2o** (171 mg, 0.82 mmol, 82%) as an orange-yellow solid. Mp: 198–200°C (decomp.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=10.46 (s, br, 1H), 8.11 (d, *J*=8.3 Hz, 1H), 8.06 (d, *J*=8.3 Hz, 1H), 7.48 (t, *J*=7.5 Hz, 1H), 7.40 (t, *J*=7.1 Hz, 1H), 6.48 (s, 1H), 2.98–2.80 (m, 5H), 1.73 (quint, *J*=7.5 Hz, 2H), 1.39 (sext, *J*=7.4 Hz, 2H), 0.91 (t, *J*=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=153.8, 143.2, 139.5, 134.7, 128.4, 126.1, 124.9, 121.1, 119.9, 117.0, 100.1, 31.5, 27.9, 22.3, 22.3, 13.8. IR (KBr): 3430 (s), 3056 (w), 2955 (m), 2928 (m), 1596 (m), 1568 (m), 1514 (m), 1366 (vs), 762 (s). *m/z* (EI,%): 238 (M^+, 53), 195 (100), 167 (6), 154 (3), 127 (4), 77 (2). HRMS: calcd for $C_{16}H_{18}N_2$ 238.1470, found 238.1472.

4.3.16. 2,6-Diphenyl-1,7-dihydrodipyrrolo[2,3-*b*:3,2-*e*]pyridine (2p). The reaction was carried out according to

typical procedure E with KO*t*-Bu (281 mg, 2.50 mmol) and 3,5-bis(phenylethynyl)-2,6-pyridinediamine (309 mg, 1.00 mmol) in DMSO (15 mL) at 80°C for 4 h. The reaction mixture was treated with cold water and the resulting precipitate was filtered, dissolved in THF and dried ($MgSO_4$). Evaporation of the solvents in vacuo yielded **2p** (295 mg, 0.95 mmol, 95%) as a brown solid. Mp: 330–332°C (decomp.). ^{1}H NMR (THF-d_8, 300 MHz): δ=10.65 (s, br, 2H), 7.95 (s, 1H), 7.82 (d, J=8.5 Hz, 4H), 7.39 (t, J=7.8 Hz, 4H), 7.23 (t, J=7.2 Hz, 2H), 6.81 (d, J=2.2 Hz, 2H). ^{13}C NMR (THF-d_8, 75 MHz): δ=149.7, 137.6, 134.4, 129.8, 128.0, 126.0, 120.0, 119.4, 98.3. IR (KBr): 3436 (s), 3247 (m), 1602 (m), 1547 (w), 1348 (m), 1245 (m), 751 (vs), 692 (m). *m/z* (EI,%): 309 (M^+, 100), 281 (3), 205 (5), 155 (11). HRMS: calcd for $C_{21}H_{15}N_3$ 309.1266, found 309.1258.

4.3.17. 2,2′-Bisindolyl (6).[34] The reaction was carried out according to typical procedure F with KH (97 mg, 2.41 mmol) and 2-[4-(2-aminophenyl)-1,3-butadiynyl]-phenylamine (140 mg, 0.60 mmol) in NMP (5 mL) at 80°C for 20 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **6** (97 mg, 0.42 mmol, 70%) as a red-brown solid. Mp: 292–294°C (decomp.). ^{1}H NMR (acetone-d_6, 300 MHz): δ=10.69 (s, br, 1H), 7.60–7.50 (m, 1H), 7.44–7.39 (m, 1H), 7.16–7.09 (m, 1H), 7.07–7.00 (m, 1H), 6.96–6.93 (m, 1H). ^{13}C NMR (acetone-d_6, 75 MHz): δ=139.2, 133.4, 131.0, 123.8, 122.0, 121.6, 112.8, 100.5. IR (KBr): 3400 (vs), 3050 (w), 2532 (w), 1617 (w), 1442 (m), 1342 (s), 778 (m), 751 (vs). *m/z* (EI,%): 232 (M^+, 100), 204 (15), 176 (3), 116 (10), 89 (6).

4.3.18. 1-Methyl-2-phenyl-1*H*-indole (7).[35] The reaction was carried out according to typical procedure F with KH (0.420 g, 10.35 mmol) and 2-(phenylethynyl)aniline (2.00 g, 10.35 mmol) in NMP (50 mL) at rt for 2 h. Then MeI (2.94 g, 20.70 mmol) was slowly added and the reaction mixture was stirred for 30 min. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 1:1) to afford **7** (2.07 g, 10.00 mmol, 96%) as a red-brown solid. ^{1}H NMR (acetone-d_6, 300 MHz): δ=7.77–7.50 (m, 9H), 6.71 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (acetone-d_6, 75 MHz): δ=143.2, 140.4, 134.7, 133.1, 131.0, 130.4, 130.0, 129.6, 123.3, 122.0, 121.4, 111.6, 103.2, 32.4. IR (KBr): 3400 (vs), 3050 (w), 2532 (w), 1617 (w), 1442 (m), 1342 (s), 778 (m), 751 (vs). *m/z* (EI,%): 207 (M^+, 100), 190 (4), 178 (8), 165 (10), 102 (6), 89 (3), 77 (3).

4.3.19. 3-Bromo-2-butyl-7-nitro-5-(trifluoromethyl)-1*H*-indole (9). The reaction was carried out according to typical procedure F with KH (72 mg, 1.80 mmol) and 2-nitro-6-(1-hexynyl)-4-(trifluoromethyl)aniline (287 mg, 1.00 mmol) in NMP (5 mL) at rt for 2 h. $(Cl_2BrC)_2$ (977 mg, 3.00 mmol) was added and the reaction mixture was stirred at rt for 48 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 100%) to afford **9** (213 mg, 0.58 mmol, 58%) as a yellow solid. Mp: 126–127°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=9.90 (s, br, 1H), 8.38 (s, 1H), 8.08 (s, 1H), 2.92 (t, J=7.5 Hz, 2H), 1.76 (quint, J=7.5 Hz, 2H), 1.45 (sext, J=7.5 Hz, 2H), 0.99 (t, J=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.1, 132.1, 131.5, 129.5, 125.5, 123.2 (q, J=3.7 Hz), 122.5, 116.1 (q, J=3.7 Hz), 92.2, 30.7, 26.5, 22.3, 13.7. IR (KBr): 3407 (m), 2959 (w), 1638 (w), 1521 (s), 1340 (s), 1310 (m), 1263 (s), 1188 (m), 1123 (s), 1113 (s), 1049 (w), 894 (w). *m/z* (EI,%): 366 (M^+, 23), 347 (4), 323 (37), 277 (20), 243 (100), 196 (22), 176 (10). HRMS: calcd for $C_{13}H_{12}BrF_3N_2O_2$ 364.0034, found 364.0027.

4.3.20. 4-Bromo-2-(5,7-dibromo-1*H*-indol-2-yl)aniline (13). The reaction was carried out according to typical procedure F with KH (18 mg, 0.45 mmol) and 2-[(2-amino-5-bromophenyl)ethynyl]-4,6-dibromophenylamine (200 mg, 0.45 mmol) in NMP (5 mL) at rt for 1 h. The crude product was purified by column chromatography on silica gel (pentane/ethyl acetate 4:1) to afford **13** (124 mg, 0.28 mmol, 62%) as a light brown solid. Mp: 140–142°C. ^{1}H NMR (acetone-d_6, 300 MHz): δ=7.57 (d, J=2.2 Hz, 1H), 7.55 (d, J=2.2 Hz, 1H), 7.49 (d, J=2.4 Hz, 1H), 7.21 (dd, J=8.7, 2.4 Hz, 1H), 6.76 (d, J=8.7 Hz, 1H), 5.47 (s, 2H), 5.40 (s, 2H). ^{13}C NMR (acetone-d_6, 75 MHz): δ=149.1, 145.8, 134.9, 134.3, 133.8, 133.1, 116.3, 110.2, 108.4, 108.3, 106.9, 106.8, 92.2, 90.1. IR (KBr): 3414 (vs), 3337 (vs), 3052 (m), 2196 (w), 1612 (vs), 1485 (vs), 1454 (s), 1414 (m), 1305 (w), 1278 (w), 1246 (w), 1227 (w), 880 (w), 862 (w), 812 (m), 693 (m). *m/z* (EI,%): 446 (M^+, 100), 366 (7), 286 (60), 205 (28), 177 (9), 142 (9), 89 (8). HRMS: calcd for $C_{14}H_9Br_3N_2$ 441.8316, found 441.8339.

4.4. Starting materials for solid phase reactions

4.4.1. Typical procedure G: 4-amino-3-iodobenzoic acid (14a).[36] Ethyl 4-amino-3-iodobenzoate (1.57 g, 5.39 mmol) and KOH (1.47 g, 26.20 mmol) were dissolved in MeOH/H_2O 3:1 (80 mL) and stirred at 50°C for 12 h. The reaction mixture was then acidified to pH ≈6 by addition of conc. H_2SO_4 and the MeOH was distilled off under reduced pressure. The aqueous layer was extracted with ethyl acetate and the combined organic layers dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue dried in vacuo to give **14a** (1.35 g, 5.13 mmol, 95%) as a white solid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.33 (d, J=1.5 Hz, 1H), 7.81 (dd, J=8.4, 1.5 Hz, 1H), 6.78 (d, J=8.4 Hz, 1H), 4.89 (s, br, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=168.5, 152.1, 140.2, 133.3, 120.0, 114.5, 86.6.

4.4.2. 6-Amino-5-iodonicotinic acid (14b). The reaction was carried out according to typical procedure G with ethyl 6-amino-5-iodonicotinate (1.46 g, 5.00 mmol) and KOH (1.45 g, 25.84 mmol) in MeOH/H_2O 3:1 (80 mL) at 50°C for 12 h. After workup **14b** (1.13 g, 4.28 mmol, 85%) was isolated as a white solid. Mp: 302–303°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.51 (d, J=1.8 Hz, 1H), 8.48 (d, J=1.8 Hz, 1H), 6.71 (s, br, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=168.3, 156.4, 149.1, 144.7, 116.9, 79.3. IR (KBr): 3308 (s), 3143 (s), 2624 (w), 1688 (vs), 1658 (m), 1383 (s), 1311 (s), 1270 (s), 1051 (s), 882 (m), 640 (s), 575 (s). *m/z* (EI,%): 264 (M^+, 89), 247 (100), 119 (18), 92 (35), 65 (15). HRMS: calcd for $C_6H_5IN_2O_2$ 263.9396, found 263.9388.

4.4.3. 4-Amino-3-iodo-5-nitrobenzoic acid (14c). The reaction was carried out according to typical procedure G with ethyl 4-amino-3-iodo-5-nitrobenzoate (1.68 g, 5.00 mmol) and KOH (1.40 g, 24.95 mmol) in MeOH/H_2O 3:1 (80 mL) at 50°C for 12 h. After workup **14c** (1.43 g,

4.64 mmol, 93%) was isolated as a yellow solid. Mp: 278–279°C. ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=8.58 (d, J=2.1 Hz, 1H), 8.49 (d, J=2.1 Hz, 1H), 7.16 (s, br, 2H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ=169.8, 145.0, 142.5, 131.1, 126.7, 123.1, 88.7. IR (KBr): 3400 (s), 3341 (s), 3081 (m), 1698 (s), 1615 (s), 1510 (s), 1450 (m), 1398 (m), 1371 (m), 1334 (s), 1268 (vs), 1141 (s), 1026 (m), 865 (m), 714 (m), 677 (m), 478 (m). m/z (EI,%): 308 (M$^+$, 59), 291 (100), 262 (12), 245 (31), 135 (12), 118 (15), 90 (22), 63 (13). HRMS: calcd for $C_7H_5IN_2O_4$ 307.9294, found 307.9291.

4.4.4. 2-Amino-3-iodo-5-methylbenzoic acid (14d).[37] The reaction was carried out according to typical procedure G with ethyl 2-amino-3-iodo-5-methylbenzoate (1.58 g, 5.18 mmol) and KOH (1.42 g, 25.31 mmol) in MeOH/H$_2$O 3:1 (80 mL) at 50°C for 12 h. After workup **14d** (1.30 g, 4.69 mmol, 90%) was isolated as a white solid. Mp: 196–197°C. ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=7.74 (d, J=2.1 Hz, 1H), 7.61 (d, J=2.1 Hz, 1H), 6.24 (s, br, 2H), 2.22 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ=170.2, 146.8, 144.0, 131.7, 126.5, 111.8, 86.4, 19.9. IR (KBr): 3512 (m), 3031 (m), 1681 (s), 1611 (s), 1584 (m), 1285 (s), 1249 (s). m/z (EI,%): 277 (M$^+$, 34), 259 (100), 230 (9), 105 (16), 77 (12). HRMS: calcd for $C_8H_8INO_2$ 276.9600, found 276.9591.

4.4.5. Deprotection of rink-MBHA-resin (15). In a 250 mL flask Rink-MBHA-resin (15.00 g, 0.55 mmol Fmoc/g, 8.25 mmol) was suspended in DMF (100 mL) and piperidine (50 mL) was added. The reaction mixture was shaken at rt for 1 h, then the polymer was filtered, washed sequentially three times with DMF, MeOH and CH_2Cl_2 and finally three times with CH_2Cl_2 and dried overnight at 55°C to give the deprotected resin **15** (12.85 g, max. 0.63 mmol NH$_2$/g, 8.10 mmol).

4.4.6. Typical procedure H: cleavage from rink-MBHA-resin. In a 2 mL syringe with a filter plate the polymer was shaken with TFA/CH_2Cl_2 (1:1, ca. 1 mL) at rt for 30 min, the reaction mixture was filtered and the polymer was washed with CH_2Cl_2. The solvent was evaporated and the residue dried in vacuo at rt and then at 50°C.

4.4.7. Typical procedure I: polymer bound and cleaved 4-amino-3-iodobenzamide (16a). In a 25 mL flask deprotected Rink-MBHA-resin (2.000 g, 1.26 mmol) was suspended in CH_2Cl_2 (15 mL) and treated with 4-amino-3-iodobenzoic acid (1.010 g, 3.84 mmol) and DIC (0.483 g, 3.84 mmol). The reaction mixture was shaken at rt for 18 h, then the polymer was filtered, washed sequentially three times with THF, DMF and MeOH and finally three times with CH_2Cl_2 and dried at 55°C overnight. The resin (0.100 g) was treated according to typical procedure H and yielded **16a** (13.6 mg, 0.052 mmol, 95% as its TFA-salt) as a light brown solid. HPLC (254 nm): t_R=10.4 min (96%). ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=8.00 (s, br, 1H), 7.94 (d, J=2.1 Hz, 1H), 7.47 (s, br, 1H), 7.39 (dd, J=8.7, 2.1 Hz, 1H), 6.59 (d, J=8.7 Hz, 1H), 5.95 (s, br, 3H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ=169.7, 148.7, 139.8, 136.5, 119.3, 116.7, 75.5. m/z (EI,%): 262 (M$^+$, 38), 246 (100), 218 (11), 91 (18). HRMS: calcd for $C_7H_7IN_2O$ 261.9603, found 261.9596.

4.4.8. Polymer bound and cleaved 6-amino-5-iodonicotinamide (16b). The reaction was carried out according to typical procedure I with 6-amino-5-iodonicotinic acid (1.003 g, 3.80 mmol), DIC (0.479 g, 3.80 mmol) and deprotected Rink-MBHA-resin (2.000 g, 1.26 mmol) in DMF (15 mL) at rt for 18 h. The resin (0.100 g) was treated according to typical procedure H and yielded **16b** (11.3 mg, 0.043 mmol, 79% as its TFA-salt) as a light brown solid. HPLC (254 nm): t_R=2.8 min (98%). ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=8.48 (d, J=1.8 Hz, 1H), 8.41 (d, J=1.8 Hz, 1H), 6.53 (s, br, 3H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ=165.3, 156.7, 148.8, 143.9, 116.4, 78.5. m/z (EI,%): 263 (M$^+$, 77), 247 (100), 119 (20), 92 (32), 65 (12). HRMS: calcd for $C_6H_6IN_3$ 262.9556, found 262.9547.

4.4.9. Polymer bound and cleaved 4-amino-3-iodo-5-nitrobenzamide (16c). The reaction was carried out according to typical procedure I with 4-amino-3-iodo-5-nitrobenzoic acid (1.170 g, 3.80 mmol), DIC (0.480 g, 3.80 mmol) and deprotected Rink-MBHA-resin (2.000 g, 1.26 mmol) in CH_2Cl_2 (15 mL) at rt for 18 h. The resin (0.100 g) was treated according to typical procedure H and yielded **16c** (15.4 mg, 0.050 mmol, 94%) as a yellow solid. HPLC (254 nm): t_R=9.9 min (98%). ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=8.62 (d, J=2.1 Hz, 1H), 8.52 (d, J=2.1 Hz, 1H), 8.07 (s, br, 1H), 7.34 (s, br, 3H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): 164.8, 146.0, 144.2, 130.1, 126.3, 122.7, 88.0. m/z (EI,%): 307 (M$^+$, 72), 291 (100), 262 (18), 245 (25), 135 (9), 118 (13), 90 (22). HRMS: calcd for $C_7H_6IN_3O_3$ 306.9454, found 306.9458.

4.4.10. Polymer bound and cleaved 2-amino-3-iodo-5-methylbenzamide (16d). The reaction was carried out according to typical procedure I with 2-amino-3-iodo-5-methylbenzoic acid (1.053 g, 3.80 mmol), DIC (0.477 g, 3.79 mmol) and deprotected Rink-MBHA-resin (2.000 g, 1.26 mmol) in CH_2Cl_2 (15 mL) at rt for 18 h. The resin (0.100 g) was treated according to typical procedure H and yielded **16d** (14.6 mg, 0.050 mmol, 98% as its TFA-salt) as a light brown solid. HPLC (254 nm): t_R=11.9 min (97%). ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ=7.88 (s, br, 1H), 7.57 (d, J=1.2 Hz, 1H), 7.45 (d, J=1.2 Hz, 1H), 7.25 (s, br, 1H), 4.69 (s, br, 3H), 2.13 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ=170.5, 146.4, 142.0, 129.6, 125.6, 115.2, 86.7, 19.2. m/z (EI,%): 276 (M$^+$, 42), 260 (100), 230 (12), 105 (14), 77 (11). HRMS: calcd for $C_8H_9IN_2O$ 275.9760, found 275.9763.

4.4.11. Typical procedure J: polymer bound and cleaved 4-amino-3-(1-hexynyl)benzamide (17a). In a 10 mL Schlenk flask under argon were placed polymer bound **16a** (300 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol, 5 mol%) and CuI (3.0 mg, 0.016 mmol, 10 mol%). Toluene (3 mL) was added and the reaction mixture was stirred for 5 min. $HNEt_2$ (3 mL) and 1-hexyne (66 mg, 0.80 mmol) were added successively and the solution was stirred at rt for 18 h. The polymer was filtered, washed sequentially three times with THF, DMF and MeOH, finally three times with CH_2Cl_2 and dried at 55°C overnight. The resin (100 mg) was treated according to typical procedure H and yielded **17a** (16.7 mg, 0.051 mmol, 95% as its TFA-salt) as a light brown oil. HPLC (254 nm): t_R=12.7 min (94%). ^{1}H NMR (DMSO-d$_6$, 300 MHz):

δ=8.06 (s, br, 1H), 7.91 (d, *J*=2.1 Hz, 1H), 7.73 (dd, *J*=8.4, 2.1 Hz, 1H), 7.40 (s, br, 1H), 6.71 (d, *J*=8.4 Hz, 1H), 4.78 (s, br, 3H), 2.83 (t, *J*=7.5 Hz, 2H), 1.73 (quint, *J*=7.5 Hz, 2H), 1.44 (sext, *J*=7.5 Hz, 2H), 0.98 (t, *J*=7.5 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=167.5, 151.4, 135.3, 131.1, 121.2, 119.8, 107.7, 96.8, 83.9, 29.7, 26.5, 22.3, 13.7. *m/z* (EI,%): 216 (M^+, 49), 200 (77), 160 (100), 144 (34), 128 (25). HRMS: calcd for $C_{13}H_{16}N_2O$ 216.1263, found 216.1258.

4.4.12. Polymer bound and cleaved 4-amino-3-(1-cyclohexen-1-ylethynyl)benzamide (17b). The reaction was carried out according to typical procedure J with polymer **16a** (300 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol, 5 mol%), CuI (3.0 mg, 0.016 mmol, 10 mol%) and 1-ethynyl-1-cyclohexene (86 mg, 0.8 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17b** (17.3 mg, 0.049 mmol, 93% as its TFA-salt) as a light brown oil. HPLC (254 nm): t_R=13.7 min (93%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.07 (s, br, 1H), 7.95 (d, *J*=2.1 Hz, 1H), 7.75 (dd, *J*=8.4, 2.1 Hz, 1H), 7.43 (s, br, 1H), 6.65 (d, *J*=8.4 Hz, 1H), 6.21–6.15 (m, 1H), 4.65 (s, br, 3H), 2.25–2.17 (m, 2H), 2.14–2.06 (m, 2H), 1.70–1.53 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=167.5, 151.4, 135.3, 133.2, 131.1, 121.2, 119.8, 113.9, 107.7, 96.8, 83.9, 29.2, 25.5, 22.3, 21.4. *m/z* (EI,%): 240 (M^+, 100), 224 (27), 196 (29), 160 (22). HRMS: calcd for $C_{15}H_{16}N_2O$ 240.1263, found 240.1261.

4.4.13. Polymer bound and cleaved 6-amino-5-(1-hexynyl)nicotinamide (17c). The reaction was carried out according to typical procedure J with polymer **16b** (300 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (4.9 mg, 0.007 mmol, 5 mol%), CuI (2.7 mg, 0.014 mmol, 10 mol%) and 1-hexyne (56 mg, 0.68 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17c** (13.8 mg, 0.042 mmol, 95% as its TFA-salt) as a light brown oil. HPLC (254 nm): t_R=9.8 min (96%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.51 (s, br, 1H), 7.97 (s, 1H), 7.72 (s, br, 1H), 7.60 (s, 1H), 6.82 (s, br, 3H), 2.96 (t, *J*=7.5 Hz, 2H), 1.76 (quint, *J*=7.5 Hz, 2H), 1.49 (sext, *J*=7.5 Hz, 2H), 1.00 (t, *J*=7.5 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=167.6, 157.4, 150.2, 143.8, 139.1, 131.2, 94.6, 85.8, 30.1, 26.6, 22.4, 13.8. *m/z* (EI,%): 217 (M^+, 62), 201 (100), 161 (87), 145 (47), 129 (32). HRMS: calcd for $C_{12}H_{15}N_3O$ 217.1215, found 217.1211.

4.4.14. Polymer bound and cleaved 6-amino-5-(phenylethynyl)nicotinamide (17d). The reaction was carried out according to typical procedure J with polymer **16b** (300 mg, 0.130 mmol), $PdCl_2(PPh_3)_2$ (4.9 mg, 0.007 mmol, 5 mol%), CuI (2.7 mg, 0.014 mmol, 10 mol%) and phenylacetylene (68 mg, 0.67 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17d** (15.3 mg, 0.044 mmol, 94% as its TFA-salt) as a light brown solid. HPLC (254 nm): t_R=10.0 min (98%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.52 (s, br, 1H), 8.03 (s, 1H), 7.75 (s, br, 1H), 7.58 (d, *J*=7.5 Hz, 1H), 7.33–7.27 (m, 2H), 7.19–7.08 (m, 3H), 6.81 (s, br, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=167.7, 157.8, 154.1, 152.0, 143.9, 140.6, 131.7, 130.2, 129.3, 126.3, 96.9, 79.8. *m/z* (EI,%): 237 (M^+, 45), 221 (100), 161 (56), 145 (35), 129 (27), 77 (21). HRMS: calcd for $C_{14}H_{11}N_3O$ 237.0902, found 237.0898.

4.4.15. Polymer bound and cleaved 4-amino-3-(1-hexynyl)-5-nitrobenzamide (17e). The reaction was carried out according to typical procedure J with polymer **16c** (300 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol, 5 mol%), CuI (3.0 mg, 0.016 mmol, 10 mol%) and 1-hexyne (79 mg, 0.96 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17e** (12.9 mg, 0.049 mmol, 97%) as a yellow solid. HPLC (254 nm): t_R=14.2 min (99%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.57 (d, *J*=1.5 Hz, 1H), 8.05 (d, *J*=1.5 Hz, 1H), 8.01 (s, br, 1H), 7.41 (s, br, 2H), 7.33 (s, br, 1H), 2.54 (t, *J*=3.6 Hz, 2H), 1.58 (quint, *J*=3.6 Hz, 2H), 1.45 (sext, *J*=3.6 Hz, 2H), 0.93 (t, *J*=3.6 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=165.3, 146.7, 136.4, 130.5, 125.6, 120.8, 112.0, 99.1, 74.5, 29.9, 21.4, 18.6, 13.4. *m/z* (EI,%): 261 (M^+, 66), 244 (100), 231 (19), 217 (18), 199 (11), 182 (20). HRMS: calcd for $C_{13}H_{15}N_3O_3$ 261.1113, found 261.1120.

4.4.16. Polymer bound and cleaved 4-amino-3-nitro-5-(phenylethynyl)benzamide (17f). The reaction was carried out according to typical procedure J with polymer **16c** (300 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol, 5 mol%), CuI (3.0 mg, 0.016 mmol, 10 mol%) and phenylacetylene (79 mg, 0.77 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17f** (14.0 mg, 0.035 mmol, 98%) as a yellow solid. HPLC (254 nm): t_R=14.1 min (99%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.64 (s, 1H), 8.23 (s, 1H), 8.06 (s, br, 1H), 7.72–7.68 (m, 2H), 7.62 (s, br, 2H), 7.47–7.45 (m, 3H), 7.38 (s, br, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=165.2, 146.6, 137.2, 131.6, 130.8, 129.1, 128.6, 126.4, 121.6, 121.0, 111.0, 96.5, 83.5. *m/z* (EI,%): 281 (72), 264 (100), 251 (13), 246 (51), 205 (14), 181 (20), 77 (16). HRMS: calcd for $C_{15}H_{11}N_3O_3$ 281.0800, found 281.0809.

4.4.17. Polymer bound and cleaved 2-amino-3-(1-hexynyl)-5-methylbenzamide (17g). The reaction was carried out according to typical procedure J with polymer **16d** (300 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol, 5 mol%), CuI (3.0 mg, 0.016 mmol, 10 mol%) and 1-hexyne (69 mg, 0.84 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17g** (17.9 mg, 0.052 mmol, 96% as its TFA-salt) as a light brown oil. HPLC (254 nm): t_R=15.6 min (99%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=7.79 (s, br, 1H), 7.38 (s, 1H), 7.16 (s, br, 1H), 7.09 (s, 1H), 5.67 (s, br, 3H), 2.47 (t, *J*=3.6 Hz, 2H), 2.13 (s, 3H), 1.54 (quint, *J*=3.6 Hz, 2H), 1.43 (sext, *J*=3.6 Hz, 2H), 0.91 (t, *J*=3.6 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.7, 147.4, 134.9, 129.0, 122.9, 114.2, 109.3, 96.0, 76.7, 30.3, 21.4, 19.6, 18.5, 13.4. *m/z* (EI,%): 230 (M^+, 60), 214 (100), 186 (24), 173 (22), 151 (27). HRMS: calcd for $C_{14}H_{18}N_2O$ 230.1419, found 230.1425.

4.4.18. Polymer bound and cleaved 2-amino-5-methyl-3-(phenylethynyl)benzamide (17h). The reaction was carried out according to typical procedure J with polymer **16d** (300 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (5.5 mg, 0.008 mmol,

5 mol%), CuI (3.0 mg, 0.016 mmol, 10 mol%) and phenylacetylene (85 mg, 0.83 mmol) in toluene/$HNEt_2$ (1:1, 6 mL) at rt for 18 h. The resin (100 mg) was treated according to typical procedure H and yielded **17h** (19.4 mg, 0.053 mmol, 99% as its TFA-salt) as a light brown solid. HPLC (254 nm): t_R=15.5 min (97%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=7.84 (s, br, 1H), 7.60 (d, J=3.0 Hz, 2H), 7.47 (s, 1H), 7.44–7.38 (m, 3H), 7.26 (s, 1H), 7.22 (s, br, 1H), 6.65 (s, br, 3H), 2.18 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.9, 162.2, 147.8, 135.2, 131.2, 130.2, 128.5, 128.4, 123.1, 122.6, 114.4, 108.0, 94.5, 86.0, 19.6. *m/z* (EI,%): 250 (M^+, 57), 234 (100), 205 (31), 173 (19), 150 (34), 77 (18). HRMS: calcd for $C_{16}H_{14}N_2O$ 250.1106, found 250.1118.

4.5. Indoles prepared on solid phase

4.5.1. Typical procedure K: polymer bound and cleaved 2-butyl-1*H*-indole-5-carboxamide (18a). 17a (150 mg, 0.08 mmol) was placed under argon in a 10 mL Schlenk flask. Toluene (1 mL) was added and the polymer was allowed to swell for 5 min. Then KO*t*-Bu (67 mg, 0.60 mmol), dissolved in NMP (4 mL), was added dropwise to the reaction mixture and was then stirred at rt for 18 h. Toluene (3 mL) was added and the polymer was filtered and first washed three times with toluene/NMP/MeOH (9:1:1). Then the resin was washed sequentially three times with THF, DMF and MeOH, finally three times with CH_2Cl_2 and dried at 55°C overnight. For determination of the HPLC-purity and the polymer loading typical procedure H was used. Cleaved **18a** (15.4 mg, 0.071 mmol, 93%) was isolated as a light brown oil. HPLC (254 nm): t_R=12.9 min (85%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=10.01 (s, br, 1H), 8.10 (s, 1H), 7.88 (s, br, 1H), 7.64 (dd, J=8.7, 1.5 Hz, 1H), 7.42 (s, br, 1H), 7.21 (d, J=8.7 Hz, 1H), 6.39 (d, J=1.5 Hz, 1H), 2.87 (t, J=7.5 Hz, 2H), 1.77 (quint, J=7.5 Hz, 2H), 1.45 (sext, J=7.5 Hz, 2H), 0.95 (t, J=7.5 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.8, 142.0, 139.6, 127.9, 123.5, 122.4, 120.7, 110.4, 101.5, 30.1, 26.5, 22.3, 13.8. *m/z* (EI,%): 216 (M^+, 100), 199 (31), 184 (45), 137 (21). HRMS: calcd for $C_{13}H_{16}N_2O$ 216.1263, found 216.1256.

4.5.2. Polymer bound and cleaved 2-(1-cyclohexen-1-yl)-1*H*-indole-5-carboxamide (18b). The reaction was carried out according to typical procedure K with **17b** (150 mg, 0.07 mmol) and KO*t*-Bu (66 mg, 0.59 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, typical procedure H was used to give **18b** (16.2 mg, 0.067 mmol, 92%) as a light brown solid. HPLC (254 nm): t_R=13.9 min (92%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=10.01 (s, br, 1H), 8.10 (s, 1H), 7.96 (s, br, 1H), 7.64 (dd, J=8.7, 1.5 Hz, 1H), 7.41 (s, br, 1H), 7.21 (d, J=8.7 Hz, 1H), 6.33 (d, J=1.5 Hz, 1H), 6.19–6.15 (m, 1H), 2.33–2.25 (m, 2H), 2.14–2.06 (m, 2H), 1.68–1.47 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.9, 142.0, 139.7, 128.2, 127.9, 123.4, 122.5, 122.4, 120.7, 110.4, 98.5, 25.5, 25.1, 22.3, 21.7. *m/z* (EI,%): 240 (M^+, 100), 224 (27), 212 (38), 208 (16), 196 (20), 140 (20), 154 (5), 105 (4). HRMS: calcd for $C_{15}H_{16}N_2O$ 240.1263, found 240.1260.

4.5.3. Polymer bound and cleaved 2-butyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carboxamide (18c). The reaction was carried out according to typical procedure K with **17c** (150 mg, 0.06 mmol) and KO*t*-Bu (57 mg, 0.51 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, typical procedure H was used to give **18c** (13.3 mg, 0.057 mmol, 92%) as a light brown solid. HPLC (254 nm): t_R=10.2 min (93%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.54 (s, br, 1H), 8.15 (s, 1H), 7.75 (s, br, 1H), 7.71 (d, J=7.5 Hz, 1H), 6.62 (d, J=6.9 Hz, 1H), 2.98 (t, J=7.5 Hz, 2H), 1.79 (quint, J=7.5 Hz, 2H), 1.51 (sext, J=7.5 Hz, 2H), 1.03 (t, J=7.5 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=168.2, 157.7, 150.5, 143.1, 139.7, 131.5, 127.8, 98.6, 30.3, 26.8, 22.4, 13.9. *m/z* (EI,%): 217 (M^+, 38), 201 (100), 173 (12), 138 (33). HRMS: calcd for $C_{12}H_{15}N_3O$ 217.1215, found 217.1212.

4.5.4. Polymer bound and cleaved 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine-5-carboxamide (18d). The reaction was carried out according to typical procedure K with **17d** (150 mg, 0.06 mmol) and KO*t*-Bu (56 mg, 0.50 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, typical procedure H was used to give **18d** (14.0 mg, 0.059 mmol, 96%) as a white solid. HPLC (254 nm): t_R=11.0 min (99%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.55 (s, br, 1H), 8.20 (s, 1H), 7.78 (s, br, 1H), 7.72 (d, J=7.5 Hz, 1H), 7.27–7.21 (m, 2H), 7.15–7.05 (m, 3H), 6.78 (d, J=6.9 Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=168.0, 158.2, 154.3, 151.1, 143.4, 140.0, 131.6, 129.3, 128.7, 127.9, 125.8, 98.3. *m/z* (EI,%): 237 (M^+, 41), 221 (100), 192 (51), 137 (39). HRMS: calcd for $C_{14}H_{11}N_3O$ 237.0902, found 237.0900.

4.5.5. Polymer bound and cleaved 2-butyl-7-nitro-1*H*-indole-5-carboxamide (18e). The reaction was carried out according to typical procedure K with **18e** (150 mg, 0.08 mmol) and KO*t*-Bu (66 mg, 0.59 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, the cleaved indole was purified by filtration (silica gel, CH_2Cl_2/ethyl acetate 1:1) to give **18e** (10.6 mg, 0.041 mmol, 54%) as a yellow solid. HPLC (254 nm): t_R=14.1 min (89%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.52 (s, 1H), 8.40 (s, 1H), 8.10 (s, br, 1H), 7.32 (s, br, 1H), 6.83 (s, 1H), 2.94 (t, J=7.5 Hz, 2H), 1.76 (quint, J=7.5 Hz, 2H), 1.49 (sext, J=7.5 Hz, 2H), 1.01 (t, J=7.5 Hz, 3H). *m/z* (EI,%): 261 (M^+, 46), 244 (100), 242 (52), 231 (9), 217 (12), 199 (14), 182 (27). HRMS: calcd for $C_{13}H_{15}N_3O_3$ 261.1113, found 261.1108.

4.5.6. Polymer bound and cleaved 7-nitro-2-phenyl-1*H*-indole-5-carboxamide (18f). The reaction was carried out according to typical procedure K with **17f** (150 mg, 0.08 mmol) and KO*t*-Bu (67 mg, 0.60 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, the cleaved indole was purified by filtration (silica gel, CH_2Cl_2/ethyl acetate 1:1) to give **18f** (10.9 mg, 0.039 mmol, 52%) as a yellow solid. HPLC (254 nm): t_R=13.9 min (94%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=8.62 (s, 1H), 8.51 (s, 1H), 8.10 (s, br, 1H), 7.95–7.87 (m, 2H), 7.52–7.37 (m, 3H), 7.31 (s, br, 1H), 7.08 (s, 1H). *m/z* (EI,%): 281 (65), 264 (100), 251 (11), 246 (57), 181 (31). HRMS: calcd for $C_{15}H_{11}N_3O_3$ 281.0800, found 281.0795.

4.5.7. Polymer bound and cleaved 2-butyl-5-methyl-1*H*-indole-7-carboxamide (18g). The reaction was carried out

according to typical procedure K with **17g** (150 mg, 0.08 mmol) and KO*t*-Bu (68 mg, 0.61 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, typical procedure H was used to give **18g** (15.8 mg, 0.069 mmol, 88%) as light-brown solid. HPLC (254 nm): t_R=15.0 min (81%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=10.12 (s, br, 1H), 7.77 (s, br, 1H), 7.56 (s, 1H), 7.30 (s, 1H), 7.14 (s, br, 1H), 6.49 (s, 1H), 2.50 (t, J=3.6 Hz, 2H), 2.13 (s, 3H), 1.57 (quint, J=3.6 Hz, 2H), 1.45 (sext, J=3.6 Hz, 2H), 0.93 (t, J=3.6 Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.3, 146.6, 134.1, 128.8, 124.5, 122.9, 114.3, 109.9, 102.7, 29.5, 21.1, 19.4, 18.3, 13.6. *m/z* (EI,%): 230 (M^+, 45), 214 (100), 186 (14), 151 (27). HRMS: calc. for $C_{14}H_{18}N_2O$ 230.1419, found 230.1420.

4.5.8. Polymer bound and cleaved 5-methyl-2-phenyl-1*H*-indole-7-carboxamide (18h). The reaction was carried out according to typical procedure K with **17h** (150 mg, 0.08 mmol) and KO*t*-Bu (68 mg, 0.61 mmol) in NMP/toluene (4:1, 5 mL) at rt for 18 h. After workup, typical procedure H was used to give **18h** (17.1 mg, 0.069 mmol, 86%) as a light-brown solid. HPLC (254 nm): t_R=14.9 min (88%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ=10.15 (s, br, 1H), 7.82 (s, br, 1H), 7.72–7.64 (m, 2H), 7.60 (s, 1H), 7.37–7.31 (m, 3H), 7.26 (s, 1H), 7.21 (s, br, 1H), 6.40 (d, J=1.5 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ=170.1, 162.5, 147.9, 135.2, 131.0, 130.4, 128.2, 128.0, 125.0, 124.1, 122.6, 115.3, 108.9, 19.6. *m/z* (EI,%): 250 (M^+, 48), 234 (100), 205 (46), 150 (31). HRMS: calcd for $C_{16}H_{14}N_2O$ 250.1106, found 250.1106.

4.5.9. 2-Butyl-1-benzofuran (20).[21] To a suspension of $CsOH{\cdot}H_2O$ (26 mg, 0.15 mmol) in NMP (2.5 mL) was added at rt a solution of 2-(1-hexynyl)phenol (87 mg, 0.50 mmol) in NMP (2.5 mL). The reaction mixture was heated to 70°C for 2 h. Standard work up and column chromatographic purification on silica gel (CH_2Cl_2 100%) afforded **20** (56 mg, 0.325 mmol, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.40–7.31 (m, 2H), 7.16–7.08 (m, 2H), 6.28 (s, 1H), 2.68 (t, J=7.5 Hz, 2H), 1.68–1.60 (m, 2H), 1.38–1.31 (m, 2H), 0.87 (t, J=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=158.7, 153.6, 128.0, 122.0, 121.3, 119.1, 109.7, 100.7, 28.8, 27.1, 21.3, 12.8. *m/z* (EI,%): 174 (M^+, 81), 159 (34), 145 (33), 132 (14), 131 (100), 115 (16), 103 (12), 77 (18).

4.5.10. (3*Z*)-3-Benzylidene-2,3-dihydro-1*H*-isoindol-1-one (22).[22] The reaction was carried out according to typical procedure E with KO*t*-Bu (78 mg, 0.70 mmol) and 2-(phenylethynyl)benzamide (110 mg, 0.50 mmol) in NMP (5 mL) at rt for 36 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ether 4:1) to afford **22** (74 mg, 0.34 mmol, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.72 (s, br, 1H), 7.61 (dd, J=7.5, 0.9 Hz, 1H), 7.66 (dd, J=6.9, 0.9 Hz, 1H), 7.52 (t, J=7.5 Hz, 1H), 7.43–7.31 (m, 5H), 7.26–7.17 (m, 1H), 6.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=169.7, 138.7, 135.3, 133.4, 132.6, 129.6, 129.5, 129.1, 129.0, 128.0, 123.9, 120.2, 106.5. *m/z* (EI,%): 222 (21), 221 (M^+, 100), 220 (41), 193 (36), 192 (10), 165 (40), 130 (14), 110 (11), 102 (16), 96 (12), 95 (20), 91 (22), 90 (26), 89 (31), 83 (15), 77 (12), 76 (30), 75 (10), 63 (15), 51 (11), 50 (12). HRMS: calcd for $C_{15}H_{11}NO$ 221.0841, found 221.0831.

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