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Transition-Metal-Free Synthesis of 2-Substituted Benzo[*cd*]Indoles via the Reaction of 1-Halo-8-lithionaphthalenes with Nitriles

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Dedicated to Professor Alexander F. Pozharskii on the occasion of his 85th birthday.

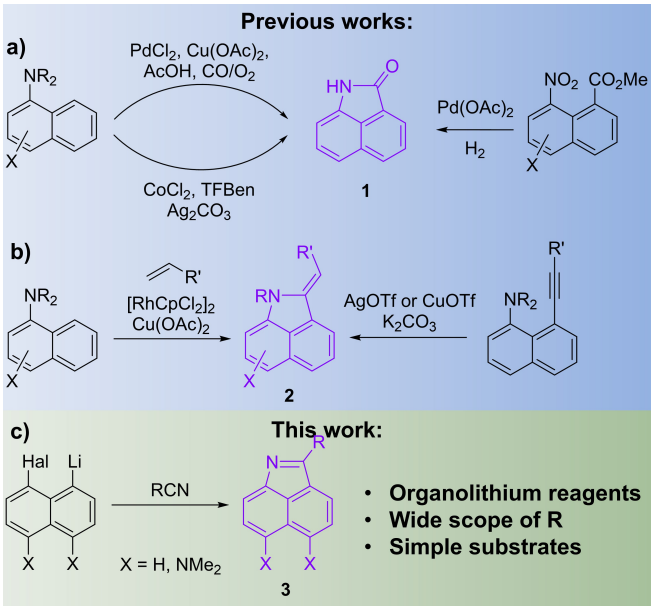
A simple and effective organolithium approach to the synthesis of 2-substituted benzo[*cd*]indoles from *peri*-dihalonaphthalenes and nitriles has been developed. The reaction proceeds via a surprisingly easy intramolecular aromatic nucleophilic substitution facilitated by the "clothespin effect". The discovered transformation provides good isolated yields, allows usage of an extensive range of nitriles, and demonstrates a good substituents tolerance. UV-absorption and NMR spectra of the obtained benzo[*cd*]indoles and their protonated forms demonstrated exclusive protonation to the indole nitrogen atom even in the presence of two NMe_2 groups in positions 5 and 6 (i.e. "proton sponge" moiety).

Introduction

Indoles are a highly prevalent class of heterocyclic systems in nature. They play a crucial role in the structure of proteins, neurotransmitters, hormones, alkaloids, and natural pigments.[1,2] To date, numerous indole-based drugs have emerged, demonstrating their remarkable pharmacophore potential, and it appears that the limits of this potential have not yet been fully explored.[3–6] While indoles have been extensively studied, benzannulated indoles remain less investigated. They can be found in nature e.g. exhibiting various arrangements in alkaloids.[7,8] Benzo[*cd*]indole derivatives are of particular interest due to their remarkable biological activity.[9–14] Thus, benzo[*cd*]indole core serves as a base for such commercial drugs as ergometrine, methysergide, lisuride, ergotamine, pergolide, terguride etc. A number of studies have shown that substituted benzo[*cd*]indoles can inhibit oncogenic thymidylate synthase,[15] exhibit cytotoxicity against tumor cells,[16,17] display neuroprotective activity,[18] and serve as fluorescent probes.[19–21]

The abovementioned naturally leads to the development of new approaches to the synthesis of benzo[*cd*]indoles. Currently known synthetic protocols for the construction of the benzo[*cd*]indole core are based on the usage of transition metal catalysis and hard-to-reach substrates. Thus, the synthesis of indolones **1** involves transition metal-catalyzed transformations of *peri*-disubstituted naphthalenes or 1-napthylamines (Scheme 1a).[22–27] In contrast to indolones **1**, synthesis of 2-substituted benzo[*cd*]indoles **2** is much less developed: known approaches are limited, multistep, require specific substrates or catalysts, and have low functional groups tolerance. (Scheme 1b).[15,28–32]

Despite the grand success of homogeneous catalysis, the high cost of metals like palladium, platinum, and rhodium, along with the need for complex and expensive ligands, as well as challenges in purifying final products from toxic transition



Scheme 1. Some previously published approaches for the synthesis of benzo[*cd*]indoles (a,b) and our new organolithium based approach (c).

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metals, continue to limit its application. On the other hand, the main group organometallics, particularly organolithiums, lack these disadvantages. Consequently, they not only maintain their solid positions as indispensable tools for modern organic synthesis but also open up new possibilities through novel applications discovered in recent years.[33,34] Thus, an effective utilisation of lithionapthalenes for the synthesis of benzo[*de*]isoquinolines, benzo[*h*]quinazolines, and benzo[*g*]indoles has been demonstrated in the past decade.[35–39]

The concept of utilisation of aryllithiums containing a group suitable for nucleophilic substitution is very promising for the heterocyclic moiety annulation. As a development of this concept, we present our simple and effective organometallic approach to the synthesis of 2-substituted benzo[*cd*]indoles based on the interaction of easily available 1-halo-8-lithionaphthalenes with nitriles (Scheme 1c).

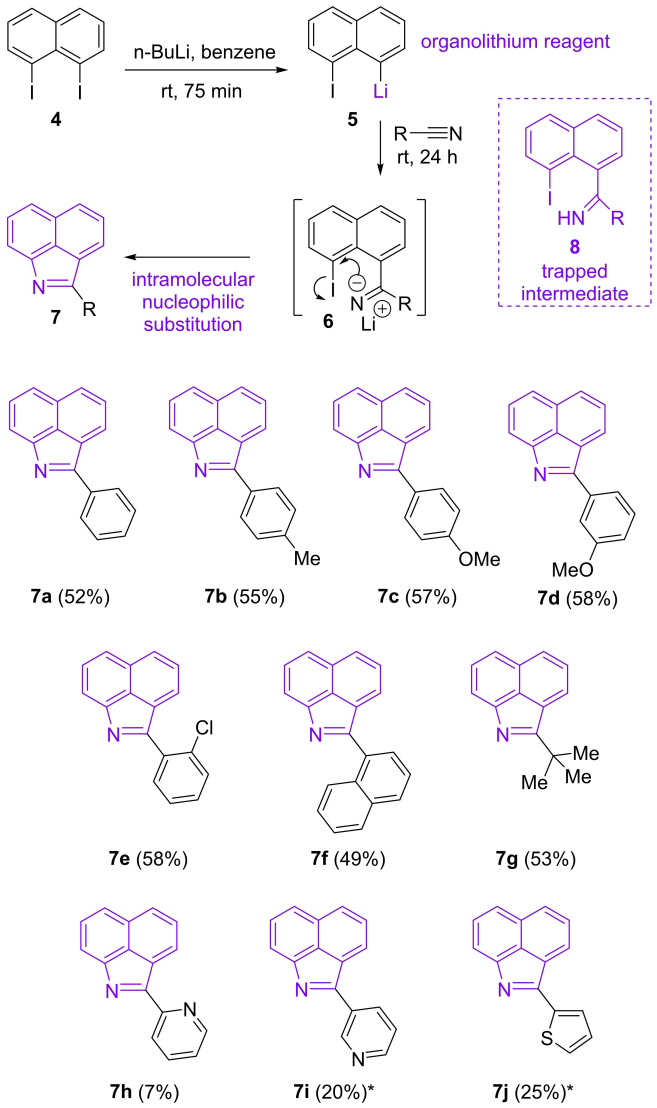
Results and Discussion

We have found that subsequent treatment of readily available *peri*-diiodonaphthalene **4** with one equivalent of *n*-BuLi and nitriles in benzene at room temperature results in the formation of 2-substituted benzo[*cd*]indoles **7** as the only reaction product with good isolated yields (Scheme 2). Benzene was selected since it has low CH-acidity and provides good solubility of diiodonapthalene **4**. Our attempts to utilize even less acidic hexane resulted in lower yields (42% for **7a**): due to the poor solubility of **4**, the reaction is heterogeneous and proceeds with significant tarring. It should be noted that the process is equally effective for the *peri*-dibromonapthalene.

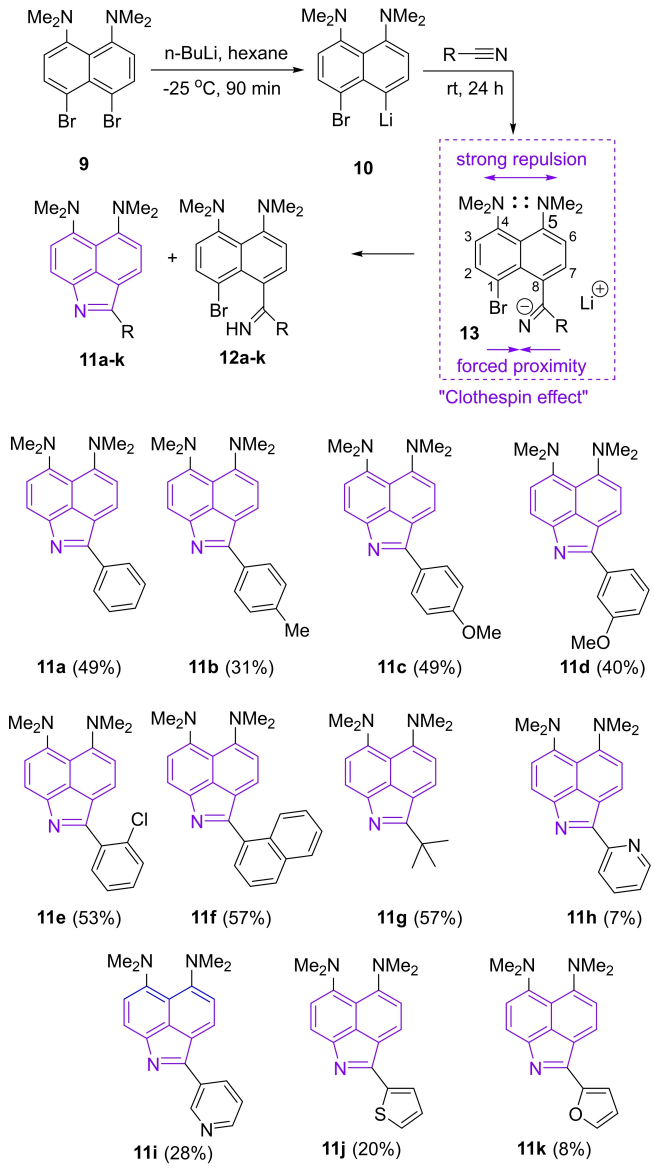
The reaction is tolerant to the presence of various substituents in the nitriles used and works well for pivalonitrile, benzonitriles and cyanonaphthalene. In contrast, the usage of heterocyclic nitriles leads to less satisfying results. Thus, the reaction with 2-pyridinecarbonitrile provides a very low yield of indole **7h** and is accompanied with significant tarring. In the case of 3-pyridinecarbonitrile and 2-thiophenecarbonitrile, chromatographically inseparable mixtures of the corresponding imines **8i,j** and indoles **7i,j** in the ratio 5:1 are formed. Boiling these mixtures in triethylamine completed transformation of **8i,j** to the corresponding benzo[*cd*]indole. While the cyclization of the 2-thienyl-containing **8j** under these conditions proceeds smoothly and quantitively, the transformation of 3-pyridine-substituted **8i** is more difficult and is accompanied by resinification.

Interestingly, the transition to 1,8-dibromo-4,5-bis(dimethylamino)naphthalene **9**, containing strong electron-donating NMe_2 groups, provides similar and, in some cases, better yields – even with the use of heterocyclic nitriles (Scheme 3). For this substrate, hexane was selected as more suitable solvent since utilization of benzene generally provided significant tarring. For instance, the reaction of *in situ* generated lithionaphthalene **10** with *para*-methoxybenzonitrile provides only a 30% yield in benzene vs 49% in hexane. We believe that the high basicity of **10**, typical for the lithioderivatives of 1,8-bis(dimethylamino)naphthalene,[39,40] is facilitated in benzene due to the lesser aggregation. As a result, the nucleophilic addition of **10** to the C≡N triple bond less effectively competes with the deprotonation of CH-bonds of aromatic nitriles. Conveniently, in contrast to **4**, dibromide **9** has excellent solubility in hexane even at low temperatures, providing smooth reactivity and good substituent tolerance. However, due to the poor solubility of ionic intermediates **13** in hexane, in almost all cases in addition to indoles **11** a noticeable amount of imines **12** was isolated after quenching the reaction mixture with water. Increasing the reaction time to 72 hours does not noticeably affect the **11**:**12** ratio.

The mechanism of this discovered reaction appears to be rather straightforward. The initially formed lithionaphthalene **5**(**10**) transforms into a corresponding intermediate **6**(**13**) upon interaction with a nitrile. Due to the proximity of a nucleophilic C=N– moiety and a good leaving group (halogen), the



Scheme 2. Synthesis of benzo[*cd*]indoles via *in situ* generated 1-lithio-8-iodonaphthalene. *After boiling the initially formed mixture of **7** and **8** in triethylamine for 72 hours.

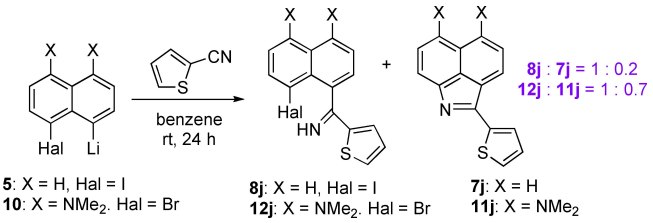


Scheme 3. Interaction of 4-lithium-5-bromo-1,8-bis(dimethylamino)naphthalene **10** with nitriles.

product is furnished by the fast intramolecular nucleophilic substitution. As a result, the electron-withdrawing nature[41] of the used heterocyclic substituents decreases the nucleophilicity of the iminium nitrogen suppressing the cyclisation and allowing the detection of the intermediate in the form of imines **8**(**12**). In the case of the much more reactivebenzonitrile, reducing the reaction time to 2 hours also allows the isolation of a small amount of the imine **8a** (R=Ph).

Interestingly, while the isolated imines **8i,j** are very stable and require prolonged boiling in triethylamine to initiate the transformation into the corresponding benzo[*cd*]indoles (see above), most of the isolated imines **12** (except for **12j,k**) are quite unstable and undergo slow further transformation into the corresponding benzo[*cd*]indoles during purification via chromatography or storing in solutions. This is especially surprising, since imines **12** possess much lesser electrophilicity of their naphthalene core, compared to imines **8**, due to the presence of two electron donating dimethylamino groups and thus should be more stable. Apparently, this unusual behaviour of **12** originates from the fact that the repulsion of the dimethylamino groups in positions 4 and 5 forces the reaction centers in positions 1 and 8 to approach each other, thereby facilitating cyclization. This effect of *peri*-substituents in the naphthalene "proton sponge" series is known as the "clothespin effect".[42] This is well illustrated by the reaction of lithionaphthalenes **5** and **10** with 2-thiophenecarbonitrile in benzene: **10** provides a much better imine:indole ratio (1:0.7) than **5** (1:0.2) (Scheme 4). Altogether, the combination of the rigidity of the naphthalene skeleton, the "clothespin effect", and the elevated nucleophilicity of the C=N-group allow a smooth and effective halogen substitution, even in the presence of electron donating groups in the naphthalene core.

The electronic structure of the obtained benzo[*cd*]indoles is rather peculiar and deserves special discussion. Indoles **7**, bearing no substituents in the naphthalene core, are bright yellow substances with long-wavelength absorption maxima, located in the region of 395–422 nm (see SI). The only exception is *tert*-butyl derivative **7g** with a less extended π-system, which has no absorption maximum over 400 nm. It however displays the residual absorption up to 450 nm (Figure 1, solid blue line). 5,6-Bis(dimethylamino)benzo[*cd*]indoles **11** are red to crimson-colored viscous oils, the long-wavelength absorption bands of which are represented by a shoulder in the



Scheme 4. Interaction of **5** and **10** with 2-thiophenecarbonitrile in benzene.

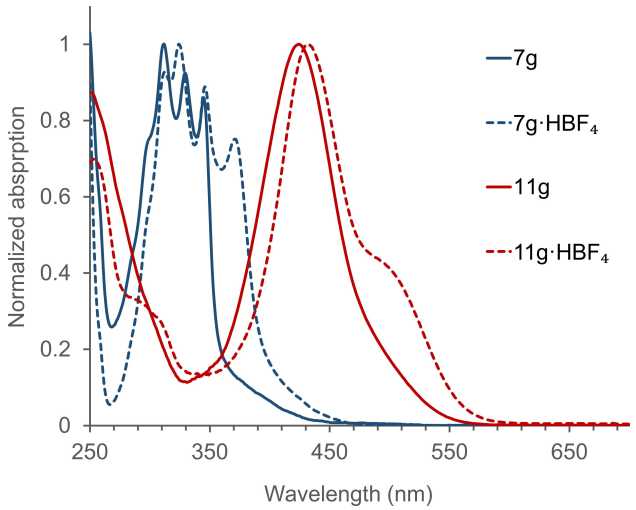
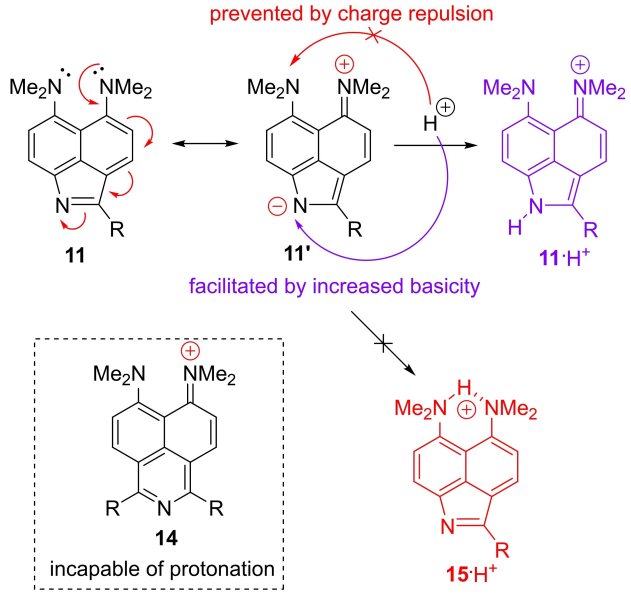


Figure 1. UV-Vis spectra of **7g** and **11g** and their cations **7g**·HBF_4 and **11g**·HBF_4 in MeCN.

region of 500–650 nm (see SI). Such a noticeable bathochromic shift in comparison with benzo[*cd*]indoles **7** is associated with a significant conjugation of the electron-donating NMe_2 group with the aza-group. Similarly to **7g**, indole **11g** bearing *tert*-butyl group exhibits an approximately 30 nm hypsochromic shift of absorption in comparison with other molecules **11** (Figure 1, solid red line).

The protonation of the aza-chromophore of **7** with tetrafluoroboric acid results in the expected bathochromic shift of the absorption maximum (Figure 1, dashed blue line). Surprisingly, the protonation of benzo[*cd*]indoles **11** also results in a bathochromic shift (Figure 1, dashed red line). It is known that the protonation of 1,8-bis(dimethylamino)naphthalenes leads to a noticeable hypsochromic shift of the long-wavelength absorption band due to a disruption of the NMe_2 groups' effective conjugation with the naphthalene system, which is caused by the participation of lone electron pairs of nitrogen in hydrogen bonding.[43–46] With this behavior of **11** in mind, it can be concluded that the protonation does not disrupt the conjugation of the NMe_2 group with the aromatic core.

All of the abovementioned suggests that the acidic proton in **11**·HBF_4 is localized on the indole nitrogen. Indeed, in ^1H NMR spectra (CD_3CN) no signals can be observed at 16–20 ppm – a typical chemical shift region for the protons chelated in the internitrogen space of naphthalene "proton sponges".[47] Instead, the matching signal of an acidic proton appears at ≈11 ppm (10.84 ppm for **11g**·HBF_4) which is very similar to the corresponding chemical shift of **7**·HBF_4 (12.60 for **7g**·HBF_4, see SI). This is rather surprising, since the protonation of "proton sponges" containing a second basic center generally results in the formation of an equilibrating mixture of protonated species with a proton preferably localized in the internitrogen space.[48–50] We believe that the selectivity of the protonation of **11** originates from the abovementioned strong conjugation of the 5-NMe_2 group with an aromatic core: the stabilization of form **11'** boosts the basicity of the indole nitrogen on the one hand, and prevents the protonation of the non-conjugated NMe_2 group by inducing a positive charge in close proximity, on the other hand (Scheme 5). A similar effect was previously observed in the case of cations **14**, where the conjugation of the 1-NMe_2 group with the aromatic system also prevented the protonation of the molecule.[35] Additionally, the abovementioned "clothespin effect" in the case of **11** leads to the decrease of the basicity of the "proton sponge" moiety: the annulation of the 5-membered cycle to the *peri*-positions of 1,8-bis(dimethylamino)naphthalene leads to the increase of the internitrogen distance.[49,51,52] Indeed, performed quantum chemical calculations (for R = *tert*-Bu) have demonstrated that formation of form **15** is thermodynamically less favourable than **11**·H^+: ΔΔG (**11g**·H^+ → **15g**) = +8.0 kcal/mol (Figure 2).



Scheme 5. Protonation of benzo[*cd*]indoles **11**.

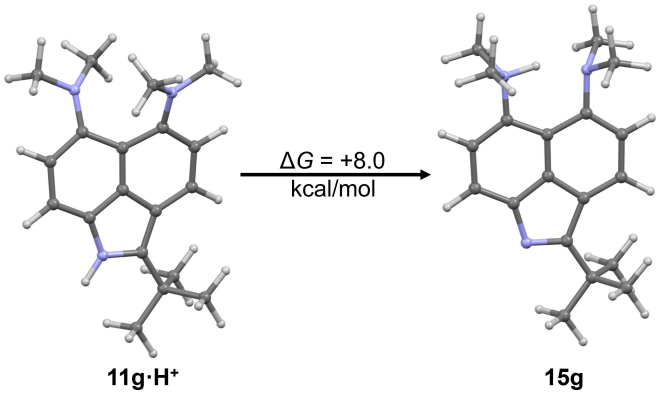


Figure 2. Optimised geometries of **11g**·H^+ and **15g**: proton transfer from indole nitrogen to the internitrogen space of "proton sponge" moiety is thermodynamically unfavourable.

Conclusions

In summary, a new, effective transition-metal-free synthesis of 2-substituted benzo[*cd*]indoles via the interaction of 1-halo-8-lithionaphthalenes with nitriles was developed. The method provides good isolated yields and high substituent tolerance. The reaction proceeds through the intermediate formation of imines, which in some cases can also be isolated. The presence of the NMe_2 groups in positions 4 and 5 of the naphthalene core facilitates the cyclization via the so-called "clothespin effect": the repulsion of dimethylamino groups causes the reactive centers in positions 1 and 8 to approach each other. The obtained 5,6-bis(dimethylamino)benzo[*cd*]indoles demonstrate a strong conjugation of the 5-NMe_2 group with the heteroaromatic core, resulting in the selective protonation of these compounds exclusively to indole nitrogen atom.

Experimental details

General

Hexane and benzene were dried over sodium/benzophenone.

Liquid-state NMR experiments were performed using a Bruker Avance iii NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at the Center for Magnetic Resonance, St. Petersburg State University Research Park. Chemical shifts are referenced to TMS for ^{1}H and ^{13}C.

HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source; methanol was used as the solvent at the Chemical Analysis and Materials Research Centre, St. Petersburg State University Research Park. The instrument was operated in positive mode using an m/z range of 50–1200. The capillary voltage of the ion source was set at 4000 V. The nebulizer gas pressure was 1.0 bar, and the drying gas flow was set to 4.0 L/min.

The UV-vis spectra were measured using UV-3600 spectrometer at the Chemical Analysis and Materials Research Centre, St. Petersburg State University Research Park. All measurements were performed for the solutions of studying compounds in $CHCl_3$ and MeCN.

Computational resources were provided by the Computer Center of Saint-Petersburg University Research Park (http://www.cc.spbu.ru/).

Computational Details

The calculations were carried out using the Gaussian16 software package.[53] Geometry optimizations and harmonic vibrational frequencies calculations were performed at the

B3LYP-GD3BJ/6-311++G(d,p) level of theory.[54,55] The Grimme dispersion correction D3 with Becke-Johnson damping function was included.[56] All structures were checked on the absence of imaginary harmonic vibrational frequencies. Solvent effects were accounted implicitly using the conductor-like polarizable continuum model (CPCM) with dielectric constant value for acetonitrile (ε = 35.688).

Synthesis

*2-Phenylbenzo[cd]indole (**7a**)*: *n*-Butyllithium (1.6 M solution in hexanes, 0.16 mL, 0.26 mmol) was added via syringe to a solution of 1,8-diiodonaphthalene **4** (100 mg, 0.26 mmol) in dry benzene (5 mL) in flame-dried flask under an argon atmosphere at 5 °C. Resulted mixture was stirred for 75 min at the room temperature. A solution of benzonitrile (30 mg, 0.29 mmol) of in dry benzene (2 mL) was added. The reaction mixture was kept at 25 °C for 24 h and treated with water (30 mL). The products were extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried with Na_2SO_4 and filtered off. The solvent was evaporated to dryness. The residue was purified by column chromatography on Al_2O_3 (2×20 cm) with *n*-hexane/Et_2O (5:1, v/v) as the eluent. The yellow fraction with R_f = 0.5 gave **7a** (31 mg, 52%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.62 (m, 3 H), 7.63–7.69 (m, 1 H), 7.71–7.78 (m, 1 H), 7.86 (d, J = 8.2 Hz, 1 H), 7.94 (d, J = 7.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 8.23–8.33 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.9, 126.6, 127.5, 128.4, 129.0(8), 129.1(1), 129.2(6), 129.3(4), 129.4, 130.4, 130.8, 135.1, 135.4, 151.8, 168.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 264 [4.23], 327 [3.82], 350 [3.91], 365 [3.92], 395 [3.46] nm. HRMS (ESI): *m/z* calcd. for $C_{17}H_{12}N^+$ [M+H^+]: 230.0964, found 230.0984. Obtained data is in agreement with previously published.[57]

*(8-Iodonaphthalen-1-yl)(phenyl)methanimine (**8a**)*. When the reaction time for the described above experiment was reduced to 2 hours (instead of 24) the yellow fraction with R_f = 0.6 was collected to yield **8a** (3 mg, 3%) of as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.20 (m, 1 H), 7.35–7.47 (m, 4 H), 7.48–7.53 (m, 1 H), 7.74 (d, J = 7.6 Hz, 2 H), 7.90–7.97 (m, 2 H), 8.22 (dd, J = 7.4, 1.3 Hz, 1 H), 9.74 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 92.5, 125.5, 127.4, 128.4, 129.0, 129.4, 130.0, 130.8, 130.9, 131.3, 135.7, 140.5, 140.6, 142.4, 178.3 ppm. HRMS (ESI): *m/z* calcd. for $C_{17}H_{13}IN^+$ [M+H^+]: 358.0087, found 358.0084.

*2-(p-Tolyl)benzo[cd]indole (**7b**)*: Compound **7b** was obtained similarly to **7a** using *p*-methylbenzonitrile (34 mg, 0.29 mmol). Yellow solid, yield: 35 mg (55%), R_f = 0.3 (*n*-hexane/Et_2O (5:1, v/v)), mp 101–102 °C (*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.64 (dd, J = 8.2, 7.1 Hz, 1 H), 7.72 (dd, J = 8.0, 7.0 Hz, 1 H), 7.82 (d, J = 8.3 Hz, 1 H), 7.90 (d, J = 7.0 Hz, 1 H), 8.04 (d, J = 8.0 Hz, 1 H), 8.20 (d, J = 8.1 Hz, 2 H), 8.24 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 122.5, 126.4, 127.6, 128.4, 129.1, 129.2(3), 129.2(4), 129.4, 129.9, 130.5, 132.1, 135.3, 141.4, 151.5, 168.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 259 [4.12], 310 sh [3.77], 328 [3.84], 351 [3.94], 367 [3.95], 402 [3.60] nm. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}N^+$ [M+H^+]: 244.1121, found 244.1120.

*2-(p-Methoxyphenyl)benzo[cd]indole (**7c**)*: Compound **7c** was obtained similarly to **7a** using *p*-methoxybenzonitrile (38 mg, 0.29 mmol). Yellow oil, yield: 38 mg (57%), R_f = 0.15 (*n*-hexane/Et_2O (5:1, v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.06–7.13 (m, 2 H), 7.64 (dd, J = 8.3, 7.0 Hz, 1 H), 7.73 (dd, J = 8.0, 7.0 Hz, 1 H), 7.82 (d, J = 8.3 Hz, 1 H), 7.92 (d, J = 7.0 Hz, 1 H), 8.06 (d, J = 7.9 Hz, 1 H), 8.27 (d, J = 7.1 Hz, 1 H), 8.29–8.35 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 114.7, 122.1, 126.2, 127.2, 128.0, 128.5, 129.1, 129.3, 129.5, 130.8, 131.0, 134.9, 150.8, 162.4, 167.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 262 [4.14], 327 [3.89], 354 [4.05], 370 [4.09], 416 [3.80] nm. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO^+$ [M+H^+]: 260.1070, found 260.1077.

*2-(m-Methoxyphenyl)benzo[cd]indole (**7d**)*: Compound **7d** was obtained similarly to **7a** using *m*-methoxybenzonitrile (38 mg, 0.29 mmol). Yellow oil, yield: 39 mg (58%), R_f = 0.25 (*n*-hexane/Et_2O (5:1, v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H), 7.08–7.14 (m, 1 H), 7.46–7.52 (m, 1 H), 7.66 (dd, J = 8.3, 7.0 Hz, 1 H), 7.74 (dd, J = 8.0, 7.0 Hz, 1 H), 7.82–7.91 (m, 3 H), 7.97 (d, J = 7.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 8.27 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 113.5, 117.8, 122.0, 123.0, 126.9, 128.1, 128.6, 129.0, 129.2, 129.5, 130.1, 131.0, 134.8, 135.8, 150.7, 160.3, 168.4 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 264 [4.18], 326 [3.86], 353 [3.91], 366 [3.91], 401 [3.55] nm. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO^+$ [M+H^+]: 260.1070, found 260.1068.

*2-(o-Chlorophenyl)benzo[cd]indole (**7e**)*: Compound **7e** was obtained similarly to **7a** using *o*-chlorobenzonitrile (40 mg, 0.29 mmol). Yellow solid, yield: 40 mg (58%), R_f = 0.25 (*n*-hexane/Et_2O (5:1, v/v)), mp 158–159 °C (Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.50 (m, 2 H), 7.57–7.61 (m, 1 H), 7.65–7.73 (m, 2 H), 7.78–7.83 (m, 1 H), 7.91 (d, J = 8.3 Hz, 1 H), 8.01–8.09 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.9, 127.2, 127.5, 128.3, 128.4, 128.5, 129.1, 129.3, 130.7, 131.0, 131.2, 132.1, 133.1, 133.9, 135.4, 150.8, 168.1 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 326 [3.97], 347 [4.00], 359 [3.97], 400 sh [3.38] nm. HRMS (ESI): *m/z* calcd. for $C_{17}H_{11}ClN^+$ [M+H^+]: 264.0575, found 264.0575.

*2-(Naphthalen-1-yl)benzo[cd]indole (**7f**)*: Compound **7f** was obtained similarly to **7a** using α-naphthonitrile (44 mg, 0.29 mmol). Yellow solid, yield: 36 mg (49%), R_f = 0.25 (*n*-hexane/Et_2O (5:1, v/v)), mp 101–102 °C ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.62 (m, 2 H), 7.66 (t, J = 7.7 Hz, 1 H), 7.70–7.77 (m, 2 H), 7.91–7.99 (m, 2 H), 7.99–8.06 (m, 3 H), 8.06–8.15 (m, 2 H), 8.81 (dd, J = 7.0, 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.4, 125.3, 126.5(8), 126.6(2), 127.1, 127.4, 128.2(9), 128.3(4), 128.4, 128.6, 128.7, 129.3, 129.6, 129.9, 131.1, 131.3, 131.7, 134.3, 136.1, 150.7, 169.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 297 [3.91], 310 [3.92], 324 [3.95], 359

[3.97], 406 [3.69] nm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{14}N^+$ [M+H$^+$]: 280.1121, found 280.1122.

*2-(tert-Butyl)benzo[cd]indole (**7g**)*: Compound **7g** was obtained similarly to **7a** using pivalonitrile (24 mg, 0.29 mmol). Yellow oil, yield: 29 mg (53%), R_f=0.4 (*n*-hexane/Et_2O (5:1, v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.64 (s, 9 H), 7.60 (dd, *J*=8.3, 7.0 Hz, 1 H), 7.67 (dd, *J*=8.1, 7.0 Hz, 1 H), 7.80 (d, *J*=8.3 Hz, 1 H), 7.88 (d, *J*=7.0 Hz, 1 H), 8.00 (d, *J*=8.0 Hz, 1 H), 8.12 (d, *J*=7.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=30.4, 37.3, 122.0, 126.2, 127.6, 128.2, 129.0(7), 129.1(4), 129.2, 130.4, 134.4, 149.9, 181.3 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 300 sh [3.80], 315 [3.92], 334 [3.87], 349 [3.85] nm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{16}N^+$ [M+H$^+$]: 210.1277, found 210.1279.

*2-(Pyridin-2-yl)benzo[cd]indole (**7h**)*: Compound **7h** was obtained similarly to **7a** using 2-pyridincarbonitrile (30 mg, 0.29 mmol). Yellow oil, yield: 4 mg (7%), R_f=0.8 (*n*-hexane/Et_2O (2:1, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ=7.44 (ddd, *J*=7.7, 4.9, 1.2 Hz, 1 H), 7.55–7.66 (m, 3 H), 7.71 (dd, *J*=8.2, 7.1 Hz, 1 H), 7.88 (td, *J*=7.7, 1.8 Hz, 1 H), 7.99 (dd, *J*=7.2, 1.3 Hz, 1 H), 8.10 (dd, *J*=8.2, 1.4 Hz, 1 H), 8.29 (dd, *J*=8.3, 1.3 Hz, 1 H), 8.67 (ddd, *J*=4.9, 1.8, 1.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=109.9, 118.7, 124.2, 126.1, 126.2, 127.6, 130.5, 130.7, 131.5, 135.0, 135.1, 137.4(9), 137.5(0), 139.4, 149.8, 159.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 296 sh [3.62], 302 [3.64], 316 sh [3.56], 417 [2.61] nm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{11}N_2^+$ [M+H$^+$]: 231.0917, found 231.0921.

*2-(Pyridin-3-yl)benzo[cd]indole (**7i**)*: Following the preparation method of compound **7a** using 3-pyridincarbonitrile (30 mg, 0.29 mmol) an inseparable mixture of **7i** and **8i** was obtained. This mixture was dissolved in Et_3N (15 mL) and stirred for 72 h under reflux conditions. The solvent was evaporated to dryness. The residue was purified by column chromatography on Al_2O_3 (1×15 cm) with *n*-hexane/Et_2O (1:1, v/v) as the eluent. The yellow fraction with R_f= 0.2 gave **7i** (11 mg, 20%) as a yellow oil. ^{1}H NMR (400 MHz, CD_3CN): δ=7.61 (dd, *J*=8.0, 4.8 Hz, 1 H), 7.77 (dd, *J*=8.3, 7.1 Hz, 1 H), 7.84–7.92 (m, 1 H), 7.99 (d, *J*=7.0 Hz, 1 H), 8.03 (d, *J*=8.3 Hz, 1 H), 8.24 (d, *J*=8.0 Hz, 1 H), 8.46 (d, *J*=7.1 Hz, 1 H), 8.67 (dt, *J*=8.0, 2.0 Hz, 1 H), 8.79 (dd, *J*=4.8, 1.7 Hz, 1 H), 9.54 (d, *J*=2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=124.1, 125.0, 128.2, 128.9, 129.6, 129.8, 130.2, 130.4, 131.7(0), 131.7(3), 135.4, 136.8, 150.5, 152.3, 152.4, 166.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 329 [3.60], 351 [3.68], 365 [3.68], 406 sh [3.13] nm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{11}N_2^+$ [M+H$^+$]: 231.0917, found 231.0917.

*(8-Iodonaphthalen-1-yl)(thiophen-2-yl)methanimine (**8j**)*: *n*-Butyllithium (1.6 M solution in hexanes, 0.16 mL, 0.26 mmol) was added via syringe to a solution of of 1,8-diiodonaphthalene **4** (100 mg, 0.26 mmol) in dry benzene (5 mL) in flame-dried flask under an argon atmosphere at 5 °C. Resulted mixture was stirred for 75 min at the room temperature. A solution of 2-thiophene carbonitrile (31 mg, 0.29 mmol) in dry benzene (2 mL) was added. The reaction mixture was kept at 25 °C for 12 h and the solvent was evaporated to dryness. The residue was purified by column chromatography on Al_2O_3 (2×20 cm) with *n*-hexane/Et_2O (5:1, v/v) as the eluent. The yellow fraction with R_f=0.5 gave **8j** (28 mg, 29%) of as a yellow oil. ^{1}H NMR (400 MHz, CD_3CN): δ=6.74 (d, *J*=3.7 Hz, 1 H), 6.97 (dd, *J*=5.1, 3.6 Hz, 1 H), 7.22 (t, *J*=7.8 Hz, 1 H), 7.48–7.62 (m, 3 H), 7.99–8.10 (m, 2 H), 8.27 (d, *J*=7.4 Hz, 1 H), 9.79 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=92.5, 126.5, 128.2, 128.6, 130.3, 131.0, 131.4, 131.5, 132.0, 132.8, 136.5, 140.3, 143.3, 149.2, 172.3 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{11}INS^+$ [M+H$^+$]: 363.9651, found 363.9648.

*2-(Thiophen-2-yl)benzo[cd]indole (**7j**)*: A solution of imine **8j** (30 mg, 0.08 mmol) in Et_3N (15 mL) was stirred for 72 h under reflux. The solvent was evaporated to dryness to give **7j** (17 mg, 86%) as a yellow oil. ^{1}H NMR (400 MHz, CD_3CN): δ=7.31 (dd, *J*=5.1, 3.7 Hz, 1 H), 7.66 (dd, *J*=8.3, 7.0 Hz, 1 H), 7.72 (dd, *J*=5.0, 1.1 Hz, 1 H), 7.77–7.85 (m, 2 H), 7.90 (d, *J*=8.3 Hz, 1 H), 8.11–8.22 (m, 2 H), 8.45 (d, *J*=7.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=122.8, 127.3, 127.8, 129.6, 129.7(0), 129.7(2), 130.1, 130.4, 130.9, 131.5 (2 C), 135.3, 139.8, 152.7, 162.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 272 [3.99], 330 sh [3.76], 340 [3.78], 357 [3.95], 373 [4.00], 422 [3.73] nm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{10}NS^+$ [M+H$^+$]: 236.0528, found 236.0531.

*5,6-Bis(dimethylamino)-2-phenylbenzo[cd]indole (**11a**)* and *(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(phenyl)methan-imine (**12a**)*: *n*-Butyllithium (1.6 M solution in hexanes, 0.15 mL, 0.24 mmol) was added via syringe to a solution of 4,5-dibromo-1,8-bis(dimethylamino)naphthalene **9** (90 mg, 0.24 mmol) in dry *n*-hexane (8 mL) in flame-dried flask under an argon atmosphere at −25 °C. Resulted mixture was stirred for 90 min at −25 °C. A solution of benzonitrile (28 mg, 0.27 mmol) in dry *n*-hexane (2 mL) was added. The reaction mixture was kept at the room temperature for 24 h and treated with water (30 mL). The products were extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried with Na_2SO_4 and filtered off. The solvent was evaporated to dryness. The residue was purified by column chromatography on Al_2O_3 (2×20 cm) with *n*-hexane/Et_2O (1:1, v/v) as the eluent. The first red-orange fraction with R_f=0.45 gave **12a** (21 mg, 22%) as red viscous oil. The second crimson fraction with R_f=0.2 gave **11a** (37 mg, 49%) as crimson viscous oil.

Compound **12a**. ^{1}H NMR (400 MHz, CD_3CN): δ=2.78–2.85 (m, 12 H), 6.75 (d, *J*=8.2 Hz, 1 H), 6.91 (d, *J*=7.9 Hz, 1 H), 7.15 (d, *J*=7.9 Hz, 1 H), 7.30–7.36 (m, 2 H), 7.38–7.43 (m, 1 H), 7.47 (d, *J*=8.2 Hz, 1 H), 7.56–7.64 (m, 2 H), 9.74 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=43.8, 110.2, 111.7, 112.9, 121.6, 128.9 (2 C), 129.2, 130.4, 131.0, 133.4, 133.9, 141.9, 151.8, 152.6, 179.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 291 [4.07], 455 [3.88], 544 [3.87] nm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{23}{}^{79}BrN_3Na^+$ [M+Na$^+$]: 418.0890, found 418.0894; *m/z* calcd. for $C_{21}H_{23}{}^{81}BrN_3Na^+$ [M+Na$^+$]: 420.0869, found 420.0875.

Compound **11a**. ^{1}H NMR (400 MHz, CD_3CN): δ=2.87 (s, 6 H), 3.00 (s, 6 H), 6.96 (d, *J*=8.0 Hz, 1 H), 7.03 (d, *J*=8.2 Hz, 1 H), 7.41–7.46 (m, 1 H), 7.48–7.54 (m, 2 H), 7.73 (d, *J*=8.0 Hz, 1 H), 8.14 (d, *J*=8.2 Hz, 1 H), 8.16–8.22 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=43.7, 44.0, 113.9, 114.6, 115.3, 124.5, 124.6, 129.1, 129.8, 129.9(7), 129.9(9), 133.0, 136.9, 143.3, 152.9, 156.7, 160.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 282 [4.19], 456 [4.20], 518 sh [3.98] nm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{22}N_3^+$ [M+H$^+$]: 316.1809, found 316.1807.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(p-tolyl)methanimine (**12b**)* and *5,6-Bis(dimethylamino)-2-(p-tolyl)benzo[cd]indole (**11b**)*: Compounds **12b** and **11b** were obtained similarly to **12a** and **11a** using *p*-methylbenzonitrile (32 mg, 0.27 mmol).

Compound **12b**. Red viscous oil, yield: 18 mg (18%), R_f=0.45 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ=2.34 (s, 3 H), 2.77–2.89 (m, 12 H), 6.76 (d, *J*=8.2 Hz, 1 H), 6.91 (d, *J*=7.9 Hz, 1 H), 7.09–7.20 (m, 3 H), 7.41–7.53 (m, 3 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=21.4, 43.8 (2 C), 110.3, 111.6, 112.9, 121.6, 129.3, 129.6, 130.6, 131.0, 133.5, 134.0, 139.1, 141.5, 151.9, 152.7, 179.1 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 295 [4.09], 355 sh [3.80], 456 [3.77], 543 [3.75] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{25}{}^{79}BrN_3^+$ [M+H$^+$]: 410.1227, found 410.1227; *m/z* calcd. for $C_{22}H_{25}{}^{81}BrN_3^+$ [M+H$^+$]: 412.1206, found 412.1214.

Compound **11b**. Crimson viscous oil, yield: 24 mg (31%), R_f=0.25 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ=2.41 (s, 3 H), 2.88 (s, 6 H), 3.01 (s, 6 H), 6.96 (d, *J*=7.9 Hz, 1 H), 7.04 (d, *J*=8.0 Hz, 1 H), 7.29–7.37 (m, 2 H), 7.69 (d, *J*=7.9 Hz, 1 H), 8.02–8.12 (m, 2 H), 8.14 (d, *J*=8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ=21.4, 43.8, 44.0, 113.9, 114.4, 116.2, 124.2, 125.9, 129.0, 129.5,

130.4, 133.5, 134.6, 140.1, 145.0, 152.4, 156.1, 162.0 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 284 [4.28], 454 [4.29], 518 sh [4.06] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{24}N_3^+$ [M + H^+]: 330.1965, found 330.1966.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(p-methoxyphenyl)methanimine (**12c**)* and *5,6-Bis(dimethylamino)-2-(p-methoxyphenyl)benzo[cd]indole (**11c**)*: Compounds **12c** and **11c** were obtained similarly to **12a** and **11a** using *p*-methoxybenzonitrile (36 mg, 0.27 mmol).

Compound **12c**. Red viscous oil, yield: 12 mg (12%), R_f = 0.3 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.76–2.84 (m, 12 H), 3.79 (s, 3 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.82–6.88 (m, 2 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 1 H), 7.50–7.58 (m, 2 H), 9.19 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8 (2 C), 55.8, 110.4, 111.7, 112.9, 114.1, 116.6, 121.6, 122.0, 130.0, 130.5, 133.4, 143.5, 151.9, 152.6, 160.4, 179.0 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 295 [4.11], 358 sh [3.78], 459 [3.98], 527 [3.91] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{25}{}^{79}BrN_3O^+$ [M + H^+]: 426.1176, found 426.1174; *m/z* calcd. for $C_{22}H_{25}{}^{81}BrN_3O^+$ [M + H^+]: 428.1156, found 428.1168.

Compound **11c**. Crimson viscous oil, yield: 41 mg (49%), R_f = 0.1 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.86 (s, 6 H), 2.98 (s, 6 H), 3.85 (s, 3 H), 6.94 (d, *J* = 7.9 Hz, 1 H), 7.01 (d, *J* = 8.1 Hz, 1 H), 7.02–7.07 (m, 2 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 8.10 (d, *J* = 8.1 Hz, 1 H), 8.13–8.20 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.9, 44.1, 56.1, 114.0, 114.4, 115.2, 116.5, 123.8, 126.2, 129.4, 130.2, 130.5, 133.7, 145.3, 152.2, 156.0, 161.6, 161.9 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 259 [4.28], 288 [4.30], 453 [4.32], 522 sh [4.11] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{24}N_3O^+$ [M + H^+]: 346.1914, found 346.1917.

(*8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(m-methoxyphenyl)methanimine (**12d**)* and *5,6-Bis(dimethylamino)-2-(m-methoxyphenyl)benzo[cd]indole (**11d**)*: Compounds **12d** and **11d** were obtained similarly to **12a** and **11a** using *m*-methoxybenzonitrile (36 mg, 0.27 mmol).

Compound **12d**. Red viscous oil, yield: 19 mg (19%), R_f = 0.4 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.81 (s, 6 H), 2.82 (s, 6 H), 3.73 (s, 3 H), 6.76 (d, *J* = 8.3 Hz, 1 H), 6.91 (d, *J* = 7.9 Hz, 1 H), 6.94–6.98 (m, 1 H), 7.02–7.09 (m, 1 H), 7.13–7.25 (m, 3 H), 7.47 (d, *J* = 8.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8 (2 C), 56.0, 110.3, 111.7, 112.8, 114.2 (2 C), 121.7, 130.2, 130.9, 131.4, 133.4, 133.9, 134.7, 151.8, 152.5, 162.2, 178.5 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 349 [3.96], 432 [3.60], 524 [3.43] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{25}{}^{79}BrN_3O^+$ [M + H^+]: 426.1176, found 426.1177; *m/z* calcd. for $C_{22}H_{25}{}^{81}BrN_3O^+$ [M + H^+]: 428.1156, found 428.1174.

Compound **11d**. Crimson viscous oil, yield: 33 mg (40%), R_f = 0.15 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.93 (s, 6 H), 3.05 (s, 6 H), 3.90 (s, 3 H), 6.98–7.04 (m, 2 H), 7.09 (d, *J* = 8.1 Hz, 1 H), 7.44 (t, *J* = 7.9 Hz, 1 H), 7.70–7.76 (m, 2 H), 7.79 (dt, *J* = 7.6, 1.3 Hz, 1 H), 8.19 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8, 43.9, 55.9, 113.6, 113.8, 114.3, 115.9(5), 115.9(9), 121.6, 124.7, 125.6, 129.6, 130.8, 133.4, 138.8, 144.7, 152.8, 156.2, 161.0, 161.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 282 [4.02], 458 [4.05], 526 sh [3.86] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{24}N_3O^+$ [M + H^+]: 346.1914, found 346.1915.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(o-chlorophenyl)methanimine (**12e**)* and *5,6-Bis(dimethylamino)-2-(o-chlorophenyl)benzo[cd]indole (**11e**)*: Compounds **12e** and **11e** were obtained similarly to **12a** and **11a** using *o*-chlorobenzonitrile (37 mg, 0.27 mmol).

Compound **12e**. Red viscous oil, yield: 5 mg (5%), R_f = 0.45 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.80–2.84 (m, 12 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.23–7.29 (m, 1 H), 7.34–7.42 (m, 2 H), 7.46–7.53 (m, 2 H), 10.15 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.6, 44.1, 114.6, 117.2, 123.7, 127.6, 128.2, 128.6, 128.7, 131.0, 131.6, 132.2, 133.5, 133.8, 135.4, 135.5, 155.7, 161.5, 175.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 282 [4.06], 354 [3.59], 453 [4.14], 512 sh [3.94] nm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{22}{}^{79}BrClN_3^+$ [M + H^+]: 430.0681, found 430.0676; *m/z* calcd. for $C_{21}H_{22}{}^{81}BrClN_3^+$ [M + H^+]: 432.0660, found 432.0648.

Compound **11e**. Red viscous oil, yield: 45 mg (53%), R_f = 0.2 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.90 (s, 6 H), 3.00 (s, 6 H), 6.94–7.02 (m, 2 H), 7.39–7.46 (m, 2 H), 7.52–7.62 (m, 1 H), 7.64–7.70 (m, 1 H), 7.71–7.83 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.7, 43.9, 113.5, 114.1, 115.7, 125.4, 126.3, 128.0, 129.3, 130.8, 131.1, 132.5, 133.0, 133.3, 136.5, 144.7, 153.1, 156.3, 161.0 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 276 [4.20], 450 [4.29], 512 sh [3.88] nm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{21}ClN_3^+$ [M + H^+]: 350.1419, found 350.1416.

*5,6-Bis(dimethylamino)-2-(naphthalen-1-yl)benzo[cd]indole (**11f**)*: Compound **11f** was obtained similarly to **11a** using α-naphthonitrile (41 mg, 0.27 mmol). Red viscous oil, yield: 50 mg (57%), R_f = 0.2 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.93 (s, 6 H), 3.03 (s, 6 H), 6.99–7.06 (m, 2 H), 7.48 – 7.58 (m, 2 H), 7.63 (dd, *J* = 8.3, 7.1 Hz, 1 H), 7.77–7.85 (m, 2 H), 7.90 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.95–8.01 (m, 2 H), 8.77–8.89 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8, 44.0, 113.9, 114.4, 116.1, 124.9, 126.4, 127.0, 127.2, 127.4, 128.0, 129.1, 129.2, 129.7(7), 129.7(9), 132.6, 132.8, 134.2, 135.2, 145.2, 152.8, 156.4, 162.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 256 [4.27], 313 sh [4.03], 452 [4.32], 516 sh [4.01] nm. HRMS (ESI): *m/z* calcd. for $C_{25}H_{24}N_3^+$ [M + H^+]: 366.1965, found 366.1971.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(tert-butyl)-methanimine (**12g**)* and *5,6-Bis(dimethylamino)-2-(tert-butyl)benzo[cd]indole (**11g**)*: Compounds **12g** and **11g** were obtained similarly to **12a** and **11a** using pivalonitrile (22 mg, 0.27 mmol).

Compound **12g**. Red oil, yield: 4 mg (4%), R_f = 0.45 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 1.22 (s, 9 H), 2.77–2.83 (m, 12 H), 6.78 (d, *J* = 7.9 Hz, 1 H), 6.90 (d, *J* = 8.2 Hz, 1 H), 7.09 (d, *J* = 7.9 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 9.70 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 27.8, 29.8, 31.3, 31.4, 110.0, 111.5, 112.6, 113.0, 129.0, 129.1, 133.2, 149.7, 151.7, 151.8, 192.3 ppm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{27}{}^{79}BrN_3^+$ [M + H^+]: 376.1383, found 376.1363; *m/z* calcd. for $C_{19}H_{27}{}^{81}BrN_3^+$ [M + H^+]: 378.1363, found 378.1394.

Compound **11g**. Red viscous oil, yield: 41 mg (57%), R_f = 0.35 (*n*-hexane/Et_2O (1:2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 1.52 (s, 9 H), 2.88 (s, 6 H), 3.01 (s, 6 H), 6.92 (d, *J* = 7.8 Hz, 1 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 30.9, 37.2, 44.1, 44.3, 113.8, 114.1, 117.2, 123.0, 126.3, 129.1, 133.8, 144.6, 151.9, 155.6, 175.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 261 [4.04], 307 sh [3.67], 434 [4.17] nm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{26}N_3^+$ [M + H^+]: 296.2121, found 296.2127.

*5,6-Bis(dimethylamino)-2-(pyridin-2-yl)benzo[cd]indole (**11h**)*: Compound **11h** was obtained similarly to **11a** using 2-pyridinecarbonitrile (28 mg, 0.27 mmol). Crimson viscous oil, yield: 5 mg (7%), R_f = 0.5 (*n*-hexane/Et_2O (1:1, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.96 (s, 6 H), 3.07 (s, 6 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 8.2 Hz, 1 H), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1 H), 8.39 (dt, *J* = 8.0, 1.1 Hz, 1 H), 8.68–8.78 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.6, 43.8, 113.7, 114.7, 115.0,

122.5, 124.2, 125.4, 125.6, 132.8, 133.0, 137.4, 143.6, 150.4, 153.7, 156.4, 156.7, 159.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 284 [3.69], 469 [3.85], 534 sh [3.54] nm. HRMS (ESI): *m/z* calcd. for $C_{20}H_{21}N_4^+$ [M + H^+]: 317.1761, found 317.1770.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(pyridin-3-yl)-methanimine (**12i**)* and *5,6-Bis(dimethylamino)-2-(pyridin-3-yl)benzo[cd]indole (**11i**)*: Compounds **12i** and **11i** were obtained similarly to **12a** and **11a** using 3-pyridinecarbonitrile (28 mg, 0.27 mmol).

Compound **12i**. Red viscous oil, yield: 21 mg (22%), R_f = 0.25 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.76–2.87 (m, 12 H), 6.76 (d, *J* = 8.3 Hz, 1 H), 6.91 (d, *J* = 7.9 Hz, 1 H), 7.19 (d, *J* = 7.9 Hz, 1 H), 7.30 (dd, *J* = 8.0, 4.8 Hz, 1 H), 7.46 (d, *J* = 8.3 Hz, 1 H), 7.88–7.97 (m, 1 H), 8.56 (dd, *J* = 4.8, 1.7 Hz, 1 H), 8.66 (d, *J* = 2.3 Hz, 1 H), 9.93 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.7 (2 C), 109.8, 111.6, 112.9, 121.5, 124.0, 129.8, 130.6, 133.5, 133.8, 136.1, 137.4, 150.5, 151.6, 152.0, 153.0, 177.5 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 302 sh [3.90], 358 [3.84], 454 [3.83], 542 [3.78] nm. HRMS (ESI): *m/z* calcd. for $C_{20}H_{21}{}^{79}BrN_4Na^+$ [M + Na^+]: 419.0847, found 419.0847; *m/z* calcd. for $C_{20}H_{21}{}^{81}BrN_4Na^+$ [M + Na^+]: 421.0827, found 421.0819.

Compound **11i**. Crimson viscous oil, yield: 21 mg (28%), R_f = 0.1 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.92 (s, 6 H), 3.04 (s, 6 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 7.08 (d, *J* = 8.1 Hz, 1 H), 7.46 (ddd, *J* = 7.9, 4.8, 0.9 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 8.19 (d, *J* = 8.1 Hz, 1 H), 8.49 (ddd, *J* = 7.8, 2.2, 1.8 Hz, 1 H), 8.61 (dd, *J* = 4.8, 1.7 Hz, 1 H), 9.38 (dd, *J* = 2.3, 0.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.6, 43.8, 113.7, 114.2, 115.5, 124.7, 124.9, 125.3, 129.6, 133.2 (2 C), 135.8, 144.5, 149.9, 150.4, 153.1, 156.5, 158.4 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 279 [4.23], 459 [4.24], 516 sh [3.94] nm. HRMS (ESI): *m/z* calcd. for $C_{20}H_{21}N_4^+$ [M + H^+]: 317.1761, found 317.1766.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(thiophen-2-yl)-methanimine (**12j**)* and *5,6-Bis(dimethylamino)-2-(thiophen-2-yl)benzo[cd]indole (**11j**)*: Compounds **12j** and **11j** were obtained similarly to **12a** and **11a** using 2-thiophenecarbonitrile (29 mg, 0.27 mmol).

Compound **12j**. Orange-brown viscous oil, yield: 31 mg (32%), R_f = 0.3 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.81 (s, 6 H), 2.82 (s, 6 H), 6.68–6.80 (m, 2 H), 6.88–6.96 (m, 2 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 7.43–7.56 (m, 2 H), 9.46 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8 (2 C), 110.2, 111.5, 112.8, 121.6, 128.4, 130.1, 130.2, 130.5, 131.5, 133.5, 133.6, 148.9, 151.9, 152.8, 173.5 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 291 sh [4.07], 356 [3.95], 461 [3.31], 543 [3.34] nm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}{}^{79}BrN_3SNa^+$ [M + Na^+]: 424.0459, found 424.0460; *m/z* calcd. for $C_{19}H_{20}{}^{81}BrN_3SNa^+$ [M + Na^+]: 426.0439, found 426.0447.

Compound **11j**. Crimson viscous oil, yield: 16 mg (20%), R_f = 0.2 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.90 (s, 6 H), 3.03 (s, 6 H), 6.95 (d, *J* = 7.9 Hz, 1 H), 7.07 (d, *J* = 8.1 Hz, 1 H), 7.20 (dd, *J* = 5.1, 3.7 Hz, 1 H), 7.50 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 7.90 (dd, *J* = 3.7, 1.2 Hz, 1 H), 8.21 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.7, 44.0, 113.9, 114.5, 116.0, 124.2, 125.0, 127.7, 128.3, 128.6, 129.2, 133.4, 141.7, 144.9, 152.6, 156.0, 156.4 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 290 [4.24], 461 [4.13], 520 sh [3.93] nm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}N_3S^+$ [M + H^+]: 322.1372, found 322.1375.

*(8-Bromo-4,5-bis(dimethylamino)naphthalen-1-yl)(furan-2-yl)-methanimine (**12k**)* and *5,6-Bis(dimethylamino)-2-(furan-2-yl)benzo[cd]indole (**11k**)*: Compounds **12k** and **11k** were obtained similarly to **12a** and **11a** using 2-furonitrile (25 mg, 0.27 mmol).

Compound **12k**. Crimson viscous oil, yield: 11 mg (12%), R_f = 0.2 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.81 (s, 6 H), 2.82 (s, 6 H), 6.12 (d, *J* = 3.4 Hz, 1 H), 6.44 (dd, *J* = 3.4, 1.8 Hz, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 8.2 Hz, 1 H), 7.62 (dd, *J* = 1.8, 0.8 Hz, 1 H), 9.70 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8 (2 C), 110.4, 111.6, 112.6, 112.9, 114.3, 121.6, 128.7, 130.8, 133.3, 134.2, 145.8, 151.7, 152.9, 154.7, 168.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 253 [4.36], 371 [3.98], 459 sh [3.59], 547 sh [3.36] nm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{21}{}^{79}BrN_3^+$ [M + H^+]: 386.0863, found 386.0869; *m/z* calcd. for $C_{19}H_{21}{}^{81}BrN_3^+$ [M + H^+]: 388.0843, found 388.0847.

Compound **11k**. Crimson viscous oil, yield: 6 mg (8%), R_f = 0.1 (*n*-hexane/Et_2O (1 : 2, v/v)). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.93 (s, 6 H), 3.07 (s, 6 H), 6.67 (dd, *J* = 3.5, 1.8 Hz, 1 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 7.14 (d, *J* = 8.1 Hz, 1 H), 7.19 (d, *J* = 3.5 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 1.8 Hz, 1 H), 8.29 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 43.8, 44.0, 111.0, 113.2, 114.0, 114.8, 115.6, 124.5 (2 C), 124.6, 129.6, 132.5, 145.0 (2 C), 152.8, 153.1, 156.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [(log ε/m^{-1} cm^{-1})]: 291 [3.61], 461 [3.64], 521 sh [3.43] nm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}N_3O^+$ [M + H^+]: 306.1601, found 306.1606.

*2-(tert-Butyl)benzo[cd]indole Hydrogen Tetrafluoroborate (**7g·HBF$_4$**)*: HBF_4 (50% aqueous solution, 15 μL, 0.12 mmol) was added to a solution of **7g** (25 mg, 0.12 mmol) in Et_2O (2 mL). Resulted mixture was stirred for 5 min and the solvent was evaporated to dryness. This gave the desired salt as yellow solid in a quantitative yield. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.77 (s, 9 H), 7.95 (dd, *J* = 8.3, 7.3 Hz, 1 H), 8.13 (t, *J* = 7.7 Hz, 1 H), 8.23 (d, *J* = 7.3 Hz, 1 H), 8.38 (d, *J* = 8.3 Hz, 1 H), 8.74 (d, *J* = 8.0 Hz, 1 H), 8.98 (d, *J* = 7.4 Hz, 1 H), 12.60 (s, 1 H) ppm. UV/Vis (CH_3CN): λ_{max} [(log ε/m^{-1} cm^{-1})]: 312 [3.85], 324 [3.88], 346 [3.83], 371 [3.76] nm.

*5,6-Bis(dimethylamino)-2-(tert-butyl)benzo[cd]indole Hydrogen Tetrafluoroborate (**11g·HBF$_4$**)*: HBF_4 (50% aqueous solution, 13 μL, 0.10 mmol) was added to a solution of **7g** (30 mg, 0.10 mmol) in Et_2O (2 mL). Resulted mixture was stirred for 5 min and the solvent evaporated to dryness. This gave the desired salt as crimson viscous oil (31 mg, 80%). ^{1}H NMR (400 MHz, CD_3CN): δ = 2.68–3.11 (m, 9 H), 3.51 (s, 3 H), 7.20 (d, *J* = 8.7 Hz, 1 H), 7.29 (d, *J* = 9.3 Hz, 1 H), 7.89 (d, *J* = 8.7 Hz, 1 H), 8.37 (d, *J* = 9.3 Hz, 1 H), 10.84 (s, 1 H) ppm. UV/Vis (CH_3CN): λ_{max} [(log ε/m^{-1} cm^{-1})]: 253 [3.87], 295 [3.53], 432 [4.02], 497 sh [3.65] nm.

Supporting Information

NMR and UV/Vis spectra data for obtained compounds can be found in the Supporting Information.

Author Contributions

Semyon V. Tsybulin: investigation (synthesis and characterisation of all compounds), writing – original draft; Mark V. Kaplanskiy: investigation (quantum chemical calculations); Alexander S. Antonov: conceptualization, supervision, writing – review & editing.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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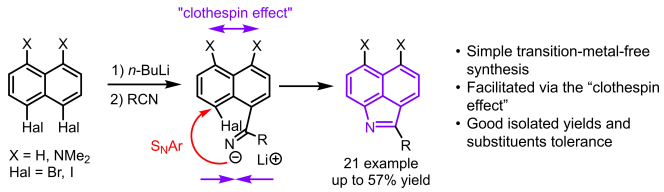

A simple and effective organolithium approach to the synthesis of 2-substituted benzo[*cd*]indoles from *peri*-dihalonaphthalenes and nitriles has been developed. The reaction proceeds via a surprisingly easy intramolecular aromatic nucleophilic substitution facilitated by the "clothespin effect". The discovered transformation provides good yields, allows usage of extensive range of nitriles, and demonstrates a good substituents tolerance.

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Transition-Metal-Free Synthesis of 2-Substituted Benzo[*cd*]Indoles via the Reaction of 1-Halo-8-lithionaphthalenes with Nitriles