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Photochemical C–H Activation: Generation of Indole and Carbazole Libraries, and First Total Synthesis of Clausenawalline D

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Abstract: The photolysis of *N*-aryltriazoles and *N*-arylbenzotriazoles leads to indoles and carbazoles, respectively. Because libraries of triazoles can be accessed rapidly, for example by the copper-catalyzed [3+2] cycloaddition reaction between alkynes and azides, this reaction allows the preparation of indoles in a single operation, by the simultaneous photolysis of the precursor library. As an example of such a synthesis of carbazoles, we prepared for the first time clausenawalline D, an antimalarial alkaloid that was recently isolated.

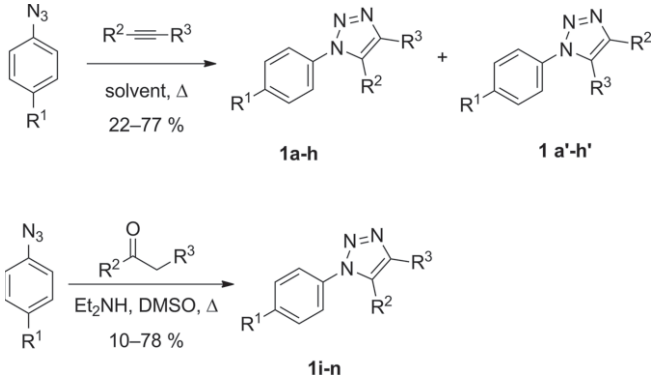
Introduction

C–H activation chemistry has been a spectacular development in the last decade, and was noted as a Holy Grail in chemistry in a landmark special issue of Accounts of Chemical Research in 1995.[1] The use of transition-metal complexes as catalysts of ever-increasing efficiency and selectivity is a major route by which to activate inert C–H bonds. Similarly, radicals, carbenes, and other neutral species with unusual electron distribution are capable of abstracting hydrogen atoms or inserting into inert C–H bonds, and photochemistry is a typical way of generating such reactive species.

Indole is a fundamental heterocyclic motif present in a plethora of biologically active molecules.[2] The importance of this scaffold in organic chemistry has been underlined by the wide range of synthetic methods that have been developed to access it.[3] As a result of the wealth of biological activities displayed by indole derivatives, they are frequently used as building blocks for systematic screening and many combinatorial methods have been reported in recent years.[4] The last decades have shown an explosion of publications on the [3+2] cycloaddition reaction of azides with alkynes,[5,6] with regio-control on terminal substrates in the Cu-catalyzed versus uncatalyzed reaction, and we were interested in the possibility of exploiting the product of this '"click" reaction in the synthesis of indoles. Although much work has been devoted to the properties of triazoles, little has been done on their application in organic synthesis, apart from the detailed work of Katritzky et al.[7] Alkyl-substituted azo compounds frequently undergo dinitrogen extrusion upon photolysis.[8] Based on selected literature precedent, we expected triazoles to undergo a similar process to generate a reactive biradical or its mesomeric carbene form. This could produce an indole ring by a type-I process, as classified by Taber and Tirunahari.[3d] Examples of this reaction have appeared in the literature, with both thermal[9] and photochemical versions reported.[10,11] In this work, we wish to report on our results in this field, which constitute both a proof-of-principle towards a combinatorial approach to indoles by post-assembly photolysis of entire libraries, and a convenient preparative-scale access to variously substituted indoles. As an example of the application of this reaction, we synthesized clausenawalline D, an anti-malarial carbazole alkaloid, by using photo-induced insertion into a C–H bond.

Results and Discussion

Trisubstituted triazoles **1** (Scheme 1) were synthesized by two different routes, by using either an uncatalyzed [3+2] cycloaddition reaction (**1a–1h**, **1c′**–**1h′**) or an amine-catalyzed condensation reaction between an arylazide and a methylene-bearing ketone (**1i–1n**).[12] Thus, triazoles **1a**–**1h**, **1c′**–**1h′** were prepared from anilines by diazotization with *tert*-butyl nitrite at 0 °C, followed by the addition of trimethylsilyl azide and by stirring at



Scheme 1. Preparation of the triazole library.

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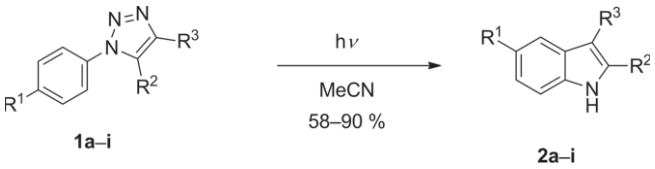
room temperature for 2–3 h in accordance with the procedure reported by Moorhouse and co-workers.[13] The [3+2] cycloaddition reaction was then performed by heating the azide and the alkyne under microwave irradiation or by conventional heating at reflux temperatures in toluene or benzene over several hours. For unsymmetrical alkynes, as expected, ≈ 2:1 regioisomeric mixtures of triazoles were obtained. Because we were interested in having the largest number of triazoles in our library, we did not attempt to improve this ratio. The isomers were separable, and isolated by column chromatography. Triazoles **1i**–**1n** were prepared by treating a mixture of arylazide and a suitable ketone in dimethyl sulfoxide (DMSO) with 5 mol-% diethylamine and by heating to 70 °C for 2–5 d. As these procedures were known, we did not attempt further optimization.

With a library of triazoles in hand, we investigated their behavior under UV irradiation. The library was irradiated for 4 h at 254 nm in open vials in a 48-wells plate with a transilluminator (it is worth pointing out that similar qualitative observations can be done with a simple laboratory TLC UV-lamp). Crude reaction mixtures were analyzed by LC-MS, and vials that revealed the presence of the desired indoles were identified and resynthesized in classic quartz vessels on a ≈ 100 mg scale (Scheme 2, Table 1).



Scheme 2. Photolysis of the triazole library.

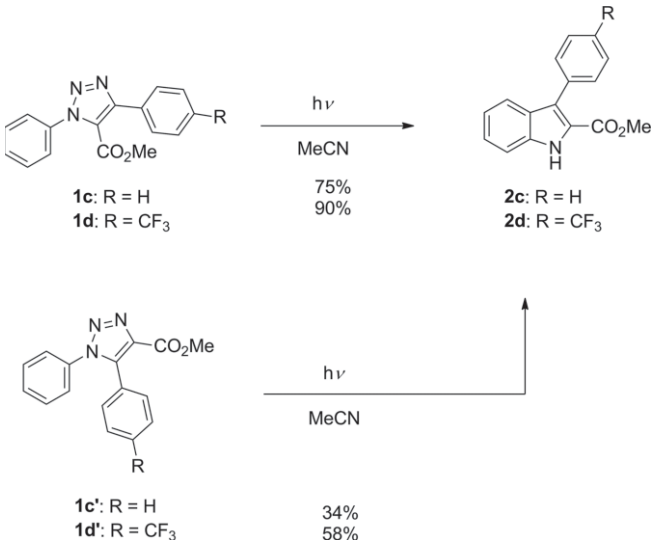
Table 1. Photolysis of the triazole library.

Entry	R^1	R^2	R^3	Indole	Yield [%][a]
1	H	CO_2CH_3	CO_2CH_3	**2a**	67
2	Cl	CO_2CH_3	CO_2CH_3	**2b**	63
3	H	CO_2CH_3	C_6H_5	**2c**	75
4	H	CO_2CH_3	*p*-CF_3-C_6H_4	**2d**	90
5	H	CO_2CH_3	*p*-CH_3O-C_6H_4	**2e**	73
6	OCH_3	CO_2CH_3	C_6H_5	**2f**	88
7	OCH_3	CO_2CH_3	*p*-CH_3O-C_6H_4	**2g**	68
8	OCH_3	CO_2CH_3	*p*-CF_3-C_6H_4	**2h**	80
9	H	C_6H_5	CN	**2i**	78
10	OCH_3	C_6H_5	CN	**2j**	83
11	OCH_3	CF_3	COC_6H_5	**2k**	83
12	H	CF_3	COC_6H_5	**2l**	67
13	OCH_3	CF_3	CO_2Et	**2m**	65
15	H	CF_3	CO_2Et	**2n**	53

[a] Isolated yields. All reactions were carried out in MeCN or *i*PrOH and irradiated at 254 nm.

All trisubstituted triazoles **1a**–**1n** gave indoles in moderate to excellent yields (53–90 %, Table 1). The reaction proceeds best with electron-withdrawing R^2 and R^3 (ester, trifluoromethyl or cyano groups), but a hydrogen atom or an alkyl group shuts it down. We also tested the influence of the solvent, which did not significantly impact the yield on the photolysis of **1d** in a series of standardized experiments (20 mg in 1 mL, 5 h irradiation): MeOH (97 %), MeCN (97 %), PhH (93 %), Me_2CO (98 %), *i*PrOH (>95 %). The [3+2] cycloaddition reaction and the photolysis can also be telescoped. For example, the cycloaddition of phenyl azide with acetylene dimethyldicarboxylate was immediately followed by photolysis to give 35 % of indole **2a** after purification.

Interestingly, the photolysis of regioisomeric mixtures of triazoles led to the formation of *single isomers* of the corresponding indole. To confirm this observation, purified and isomerically well-defined triazoles **1c**/**1c′** and **1d**/**1d′** were individually photolyzed and both gave indoles **2c** (75 % and 34 %) and **2d** (90 % and 58 %), respectively, without observable trace of other regioisomers (Scheme 3). The stark difference in yields may reflect the different stabilities of the azirine intermediates (vide infra). The latter are inherently unstable and may decompose through alternative pathways.



Scheme 3. Regioconvergence in the photolysis.

According to our initial expectation, photoinduced extrusion of dinitrogen should lead to biradical **A**, which would then insert into a nearby C–H bond in a stepwise process (Scheme 4). The regioconvergent transformation of **1c**,**c′** and **1d**,**d′** into **2c** and **2d** contradicts this hypothesis. Mitchell and Rees proposed, for non-phenyl-substituted triazoles, that iminocarbene **B** results from photolysis of **1**, which can undergo C–H insertion to eventually give **C**.[14] Alternatively, **B** can isomerize to **B′** through an intermediate azirine, which then undergoes C–H insertion to form **C′**. In all our cases, we observed that **C′** is obtained regardless of the starting material, which means that supposed carbene intermediate **B′** is either significantly more stable or more reactive than intermediate **B**.

On the basis of this mechanistic depiction, we then attempted to expand the scope of the reaction to the preparation of carbazoles by photolysis of benzotriazoles. The benzotriazole precursor would be accessed from the 1,3 dipolar cycloaddition

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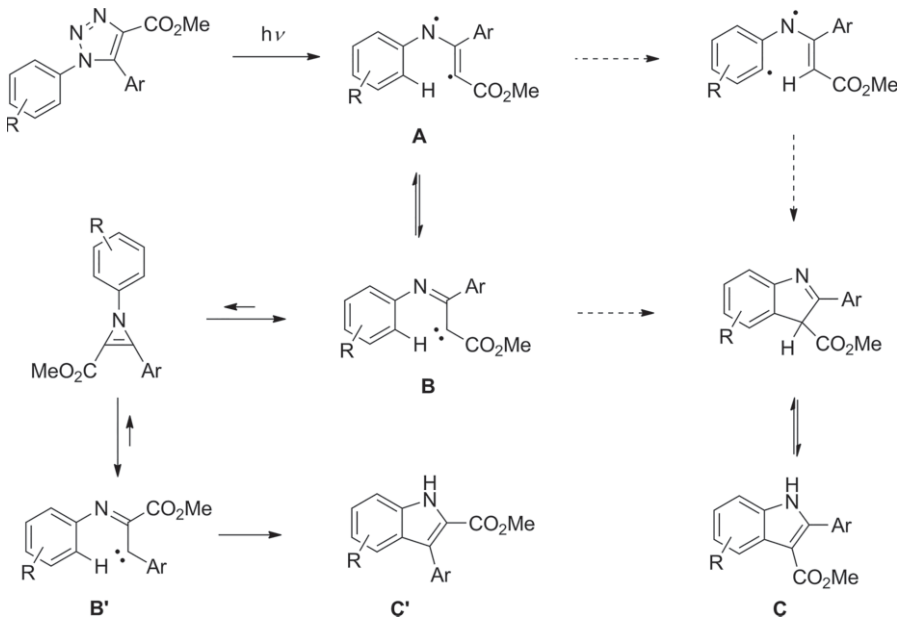
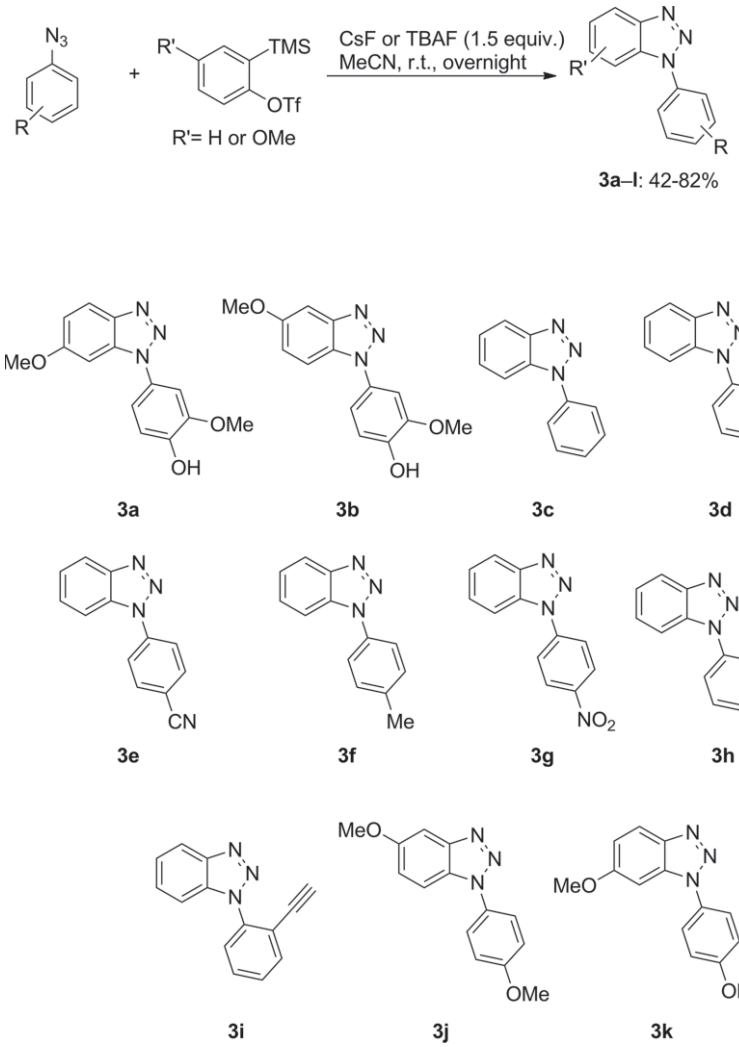
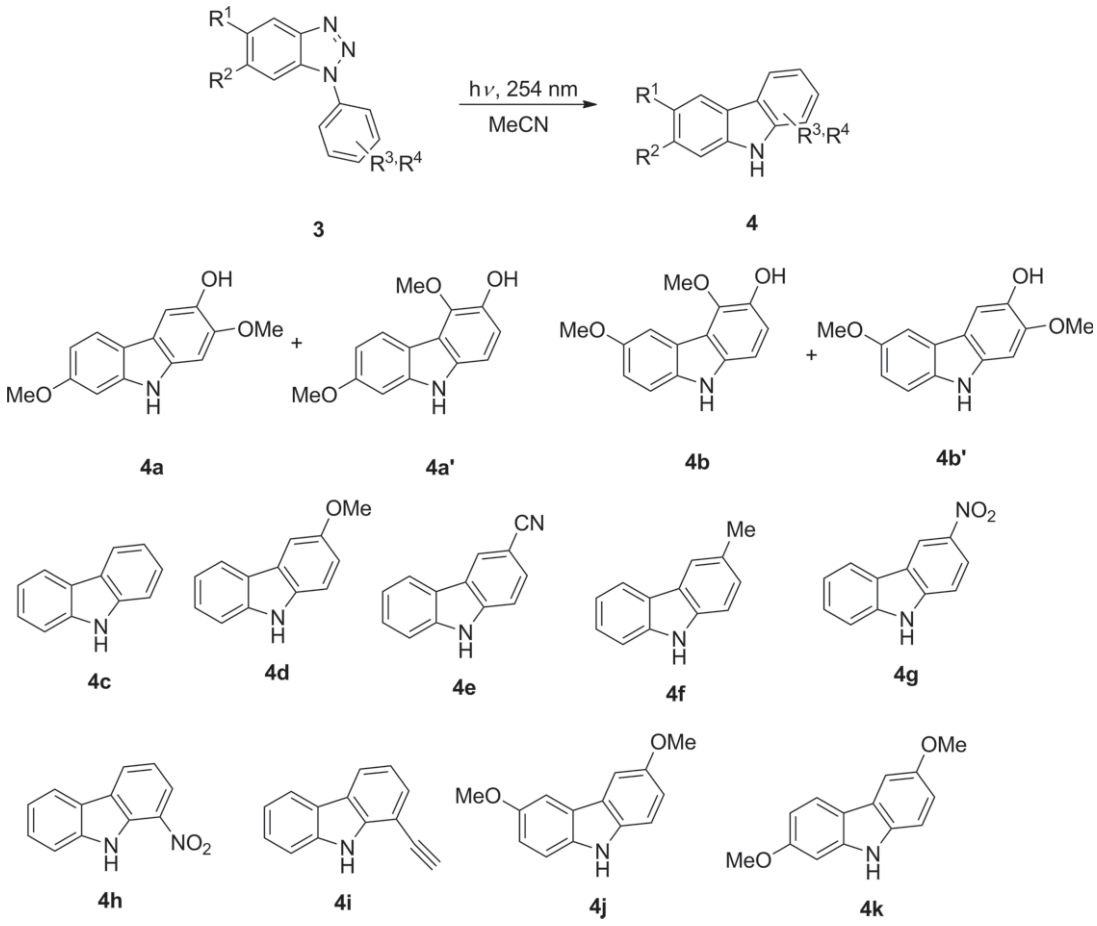


Scheme 4. Mechanistic rationale.



Scheme 5. Preparation of benzotriazole photolysis precursors.



Scheme 6. Preparation of carbazoles by photolysis of benzotriazoles.

between an aromatic azide and benzyne derivative (in situ generated). A process previously developed by Moses et al.,[13c] involves the use of a fluoride to desilylate an aryl triflate (Scheme 5). This room temperature procedure was preferred over the alternative that involved diazotization of an anthranilic acid derivative with *t*BuONO to generate, upon heating, gaseous nitrogen and carbon dioxide; this method caused problems of overpressure and creation of a complex mixture, which made isolation of the desired product in good yield difficult.

Thus, the photolysis of the corresponding benzotriazoles was performed under the same conditions as described above (Scheme 6, Table 2):

All benzotriazoles **3a**–**3k** gave carbazoles in poor to good yields (17–84 %). No general trends in the electronic feature or position of the substituents on the benzotriazole precursor were observed. The yield variation seems more dependent on the relative absorbance of both precursor and product that are in competition during irradiation. It seems that 1-methyl and 1-methoxy substituted carbazoles cannot be generated through this process (no product isolated). In contrast to the formation of indoles, there was a solvent dependence, with acetonitrile remaining the best. Conversion was either slower or non-existent for the other tested solvents (PhH, acetone, *i*PrOH).

Table 2. Photolysis of the benzotriazole library.

Entry	Benzotriazole	Carbazole	Yield [%][a]
1	**3a**	**4a 4a′**	45[b]
2	**3b**	**4b 4b′**	66[b]
3	**3c**	**4c**	39
4	**3d**	**4d**	47
5	**3e**	**4e**	63
6	**3f**	**4f**	32
7	**3g**	**4g**	17
8	**3h**	**4h**	43
9	**3i**	**4i**	22
10	**3j**	**4j**	84
11	**3k**	**4k**	52

[a] Isolated yields. [b] Isolated as 1:1 mixtures of regioisomers.

Contrary to the photochemical synthesis of indoles, the photolysis of benzotriazoles showed no regioconvergence when starting from isomeric precursors. Thus, as shown in Scheme 7, this photolysis is regiospecific according to our experiments (**3j**, **3k**). No azirine, here benzazirine, is expected to form during the process as proposed by Selvarajan et al.[15] If this were the case, we would have observed the formation of regioisomers **4j** and **4k** from precursors **3j** and **3k**, respectively.

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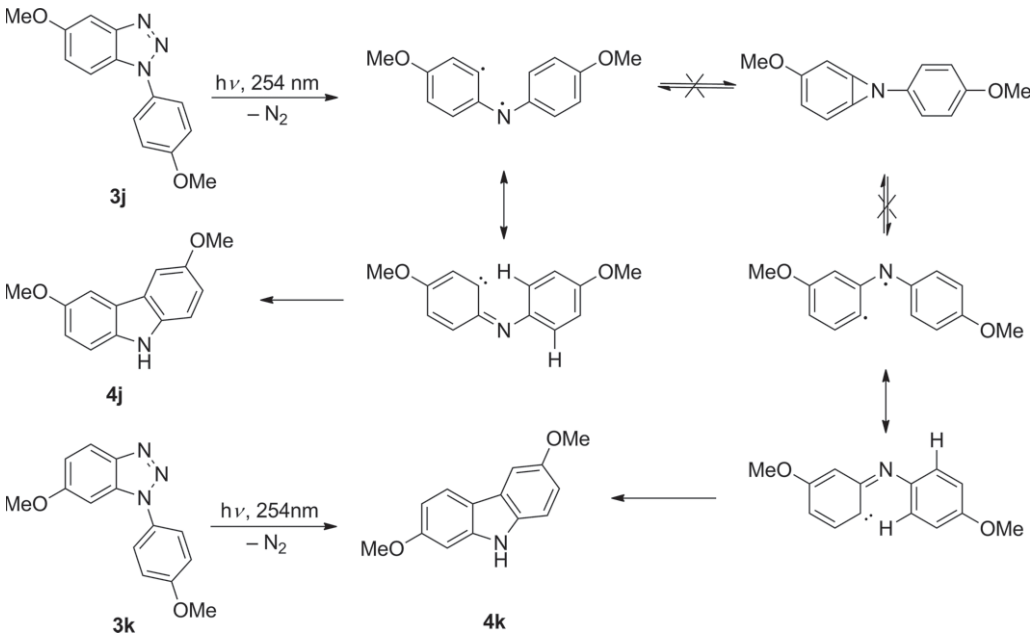

Scheme 7. Regiospecificity of the reaction.

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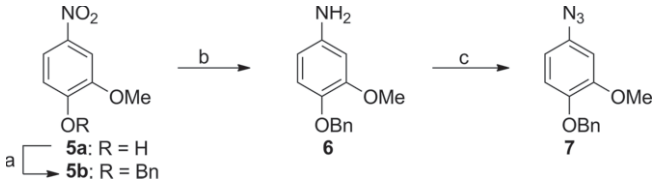
Synthesis of Clausenawalline D

Rutaceae plants are a rich source of carbazole alkaloids. The *clausena* genus of the *Rutaceae* family provides a wide variety of carbazoles alkaloids named *clausenawalline* and classified from A to F.[16] The biological activities of these aromatic compounds against bacteria and cancer generated interest to provide chemical processes to synthesize clausenawallines.[17] Based on the reactions reported above, we envisioned a total synthesis of clausenawalline D in six steps from commercially available 4-nitroguaiacol.

In our retrosynthetic analysis, we planned to obtain the target product photochemically from a benzotriazole precursor (Scheme 8).

The synthesis of the azide precursor (Scheme 9) started with the protection of 4-nitroguaiacol (**5a**) with BnBr to give protected phenol **5b** in 75 % yield.

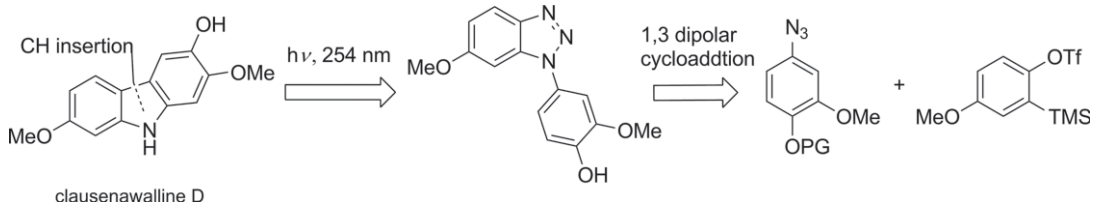
The nitro group was then reduced with tin powder (5 equiv.) in a mixture of acetic acid, water, and ethanol as described by Keller et al.[18] Other reductants were also tried (iron powder and Raney Nickel) with lower yields. Aniline **6** was then treated with *t*BuONO and trimethylsilyl azide ($TMSN_3$) in a Sandmeyer-like reaction to give aromatic azide intermediate **7** in 78 % yield on a gram scale.



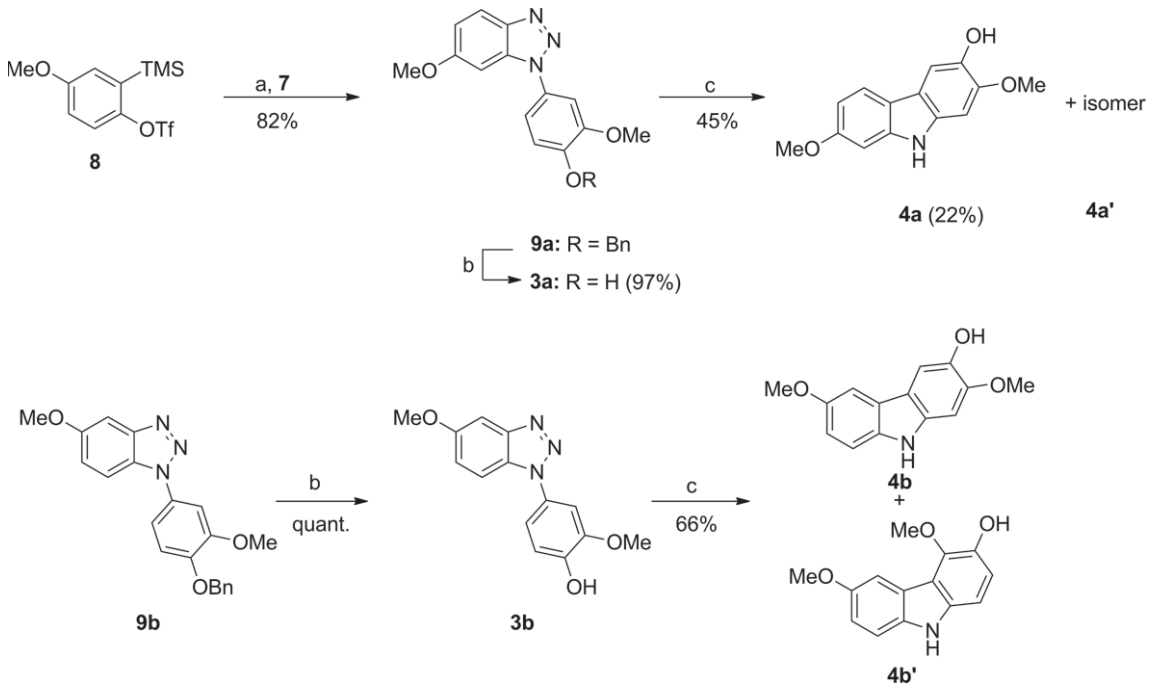
Scheme 9. Preparation of the benzotriazole precursor; reagents and conditions: (a) BnBr, K_2CO_3, MeCN, 3 d, r.t., 75 % (b) Sn (5 equiv.), AcOH/H_2O/EtOH (1:0.5:1), 30 °C, sonication 1–2 h, 66 % (c) *t*BuONO, $TMSN_3$, MeCN, overnight, 78 %.

The next steps dealt with the preparation of the protected benzotriazole precursor and the final photolysis (Scheme 10). This was done by treatment of the isolated aromatic azide with benzyne precursor **8** and a fluoride donor at room temperature. Thus, overnight stirring of a solution in acetonitrile made by mixing the azide and benzyne generated by the addition of tetra-*n*-butylammonium fluoride (TBAF) led to a (1:1) mixture of regioisomers of benzotriazoles **9a** and **9b** in 82 % yield. These products were separable by column chromatography.

Photolysis of precursor **9a** proved to be almost completely photo-inert under 254 nm UV-light. After 48 h of irradiation, no conversion of the starting material was observed, only slight



Scheme 8. Retrosynthetic analysis.



Scheme 10. Total synthesis of clausenawalline D; reagents and conditions: (a) **7** (2 equiv.), TBAF, MeCN [2 M], room temp., overnight, r.r. (1:1). (b) Pd/C (10 % wt.), H_2, EtOH, room temp., overnight. (c) hν: 254 nm, dry and degassed MeCN, room temp., 24 h, r.r. (1:1).

decomposition. However, removal of the protecting group led to a half conversion of the precursor after 24 h exposure to give regioisomers **4a** and **4a′** in a 1:1 mixture. The absence of total conversion of the benzotriazole is probably the result of a common absorbance of the precursor and the final product at the same wavelength. Longer irradiation times led to reduction of the isolated yield and an increase in undesirable side-products. Notably, different protecting groups were tested (TMS and Ac) that showed an inhibition of the photochemical reaction. Suitable precursor **9a** underwent hydrogenolysis of the benzyl protecting group [Pd/C (10 % wt.) and 1 bar H_2] to give unprotected benzotriazole **3a** in 97 % yield. Finally, **3a** was irradiated for 24 h in anhydrous and de-aerated acetonitrile in a Rayonet® photochemical reactor, equipped with 8 UV lamps (254 nm) to give final product **4a** as a (1:1) regioisomer mixture with **4a′**. Chromatographic separation gave pure clausenawalline D (**4a**) in 22 % yield.

The two last steps were also performed on benzotriazole isomer **9b** to give deprotected product **3b** quantitatively. Finally, its photolysis gave regioisomers **4b** and **4b′** in a (1:1) r.r. in 66 % yield. As observed earlier, there was no regioconvergence in the photolysis treatment of benzotriazole precursor **3b**.

Conclusions

This photochemical method for the generation of substituted indoles could be applied to the production of small libraries and therefore be useful for drug discovery. We demonstrated here an easy and rapid way to transform a library of molecules into another library simply by using UV light. The easy experimental setup (HPLC vial) and monitoring setup (HPLC-MS) make this method an efficient tool to test photochemical properties of many molecules in a single experimental procedure. In addition, the relatively mild reaction conditions could potentially solve preparative synthetic problems if sensitive substituents are incompatible with classical indole access routes.

Experimental Section

General Experimental: All starting materials were obtained from standard suppliers and were used without further purification. Thin layer chromatography (TLC) analyses were done with aluminum sheets coated with silica gel 60 $F_2$54. Flash column chromatography was carried out with Brunschwig silica gel 60 Å (32–63 mesh). Commercially available products were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with an FT 300 MHz or FT 360 MHz spectrometer in deuterated chloroform with solvent residual signals used as a reference, unless specified otherwise. Chemical shifts are reported relative to residual solvent protons: chloroform (δ = 7.27 ppm for ^{1}H, δ = 77.0 ppm for ^{13}C); coupling constants are expressed relative to multiplicity: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br. = broad signal). IR spectra were recorded with a FTIR spectrometer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 25 spectrometer. High-resolution ESI mass spectra were measured with a ion-cyclotron FT/MS (4.7 T) spectrometer. Photochemical irradiations were carried out in a Srinivasan-Griffin (Rayonet-RPR-100) photoreactor, in a quartz vessel, with 5 to 8 lamps at 254 nm. Photochemical irradiations of the 48 plates library of triazoles was carried out in a homemade transilluminator with 4 lamps at 254 nm. The routine HPLC-MS measurements were recorded on a UPLC/SQD instrument.

Dimethyl 1-Phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate (1a):[19] To a stirred solution of aniline (0.273 mL, 3 mmol) in MeCN (4 mL) was added *t*BuONO (0.535 mL, 4.5 mmol) at 0 °C in a 2–5 mL micro-

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wave reaction vial. To this solution was added $TMSN_3$ (0.472 mL, 3.6 mmol) dropwise. The solution was stirred 2 h at room temp. At this point, dimethyl but-2-ynedioate (0.443 mL, 3.6 mmol) was added. The vial was capped with an aluminum-Teflon cap and the solution was heated by microwave for 10 min at 130 °C (125 W). The solution was concentrated in vacuo and recrystallized from MeOH to afford **1a** (352 mg, 45 % yield) as a white solid. M.p. 128–131 °C (lit. 124–125 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.60 (m, 5 H); 4.00 (s, 3 H); 3.91 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 160.1 (Cq), 159.4 (Cq), 138.7 (Cq), 135.5 (Cq), 132.5 (Cq), 130.5 (CH), 129.6 (2 CH), 124.2 (2 CH), 53.8 (CH_3), 52.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2956, 1721, 1557, 1498, 1355, 1292, 1239, 1201, 1170, 1093, 1067, 1005, 962, 828, 761, 687 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{12}H_{12}N_3O_4$ [M + H]$^+$ 262.0822; found 262.0823.

Dimethyl 1-(4-Chlorophenyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (1b):[20] 1-Azido-4-chlorobenzene (216 mg, 1.69 mmol) and dimethyl but-2-ynedioate (0.312 mL, 2.54 mmol) were dissolved in MeCN (4 mL) in microwave vial. The mixture was stirred for 6 d at room temp., concentrated in vacuo and recrystallized from MeOH to afford **1b** (203 mg, 40 %) as a white solid. M.p. 135–137 °C (lit. 135 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.49–7.56 (m, 4 H); 4.02 (s, 3 H); 3.94 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 160.0 (Cq), 159.2 (Cq), 138.9 (Cq), 136.7 (Cq), 133.9 (Cq), 132.3 (Cq), 129.9 (2 CH), 125.6 (2 CH), 53.9 (CH_3), 52.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 1718, 1496, 1440, 1305, 1241, 1077, 1000, 829, 535 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{12}H_{11}ClN_3O_4$ [M + H]$^+$ 296.0432; found 296.0432.

Methyl 1,5-Diphenyl-1*H*-1,2,3-triazole-4-carboxylate (1c) and Methyl 1,4-Diphenyl-1*H*-1,2,3-triazole-5-carboxylate (1c′):[21] Methyl 3-phenylpropiolate (642 mg, 4.01 mmol) and azidobenzene (716 mg, 6.01 mmol) were dissolved in benzene (10 mL) and heated at reflux for 48 h. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford desired product **1c** (320 mg, 29 %) and **1c′** (135 mg, 12 %) as white solids. **1c**: M.p. 132–134 °C (lit. 130 °C). R_f = 0.15 (hexane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.28–7.48 (m, 9 H); 3.93 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 161.3 (Cq), 140.9 (Cq), 136.5 (Cq), 135.6 (Cq), 130.1 (2 CH), 129.9 (CH), 129.4 (CH), 129.2 (2 CH), 128.3 (2 CH), 125.4 (Cq), 125.1 (2 CH), 52.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3063, 1725, 1500, 1442, 1432, 1224, 1141, 1070, 998, 925, 819, 762, 691 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{14}N_3O_2$ [M + H]$^+$ 280.1080; found 280.1079. **1c′**: M.p. 108–110 °C (lit. 135 °C). R_f = 0.37 (hexane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.87 (d, J = 6.36 Hz, 2 H); 7.39–7.65 (m, 8 H); 3.74 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 159.8 (Cq), 149.4 (Cq), 136.9 (Cq), 129.9 (CH), 129.6 (CH), 129.1 (2 CH), 128.8 (2 CH), 128.3 (2 CH), 125.4 (Cq), 125.2 (2 CH), 52.6 (CH) ppm. IR (neat): $\tilde{\nu}$ = 3058, 2953, 2923, 2852, 1721, 1554, 1495, 1440, 1297, 1263, 1225, 1150, 993, 764, 697 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{14}N_3O_2$ [M + H]$^+$ 280.1080; found 280.1080.

Methyl 1-Phenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-4-carboxylate (1d) and Methyl 1-Phenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-5-carboxylate (1d′): Methyl 3-[4-(trifluoromethyl)phenyl]propiolate (1.76 g, 7.71 mmol) and azidobenzene (1.38 g, 11.56 mmol) were dissolved in toluene (20 mL) and heated at reflux for 62 h. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **1d** and **1d′** in a 3:2 ratio (2.05 g, 77 %) as pale yellow solids. **1d′**: M.p. 115–117 °C. R_f = 0.4 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.17 Hz, 2 H); 7.76 (d, J = 8.17 Hz, 2 H); 7.42–7.64 (m, 5 H); 3.76 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 159.4, 148.0, 136.7, 133.2, 131.42, 131.0, 130.7, 130.3, 130.1, 129.1, 128.5, 126.0, 125.4, 125.3, 125.25, 125.20, 125.16, 125.13, 122.4, 119.4, 52.7 ppm. IR (neat): $\tilde{\nu}$ = 1724, 1497, 1440, 1326, 1300, 1268, 1228, 1201, 1153, 1105, 1066, 1038, 1023, 994, 852, 815, 785, 773, 696 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{13}F_3N_3O_2$ [M + H]$^+$ 348.0954; found 348.0955. ε_{254nm} (MeCN): 38.86 l/mol cm. **1d**: M.p. 128–130 °C. R_f = 0.17 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.72 Hz, 2 H); 7.36–7.50 (m, 5 H); 7.27–7.33 (m, 3 H); 3.94 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 161.0, 139.4, 136.8, 135.2, 132.2, 131.9, 131.5, 131.1, 130.7, 129.8, 129.4, 129.2, 128.0, 125.3, 125.2, 125.18, 125.14, 125.11, 125.0, 121.9, 118.9, 52.1 ppm. IR (neat): 1727, 1500, 1441, 1326, 1221, 1123, 1067, 998, 846, 763, 690, 618. HRMS (ESI$^+$): calcd. for $C_{17}H_{13}F_3N_3O_2$ [M + H]$^+$ 348.0954; found 348.0953. ε_{254nm} (MeCN): 34.14 l/mol cm.

Methyl 5-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (1e) and Methyl 4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-5-carboxylate (1e′): Azidobenzene (650 mg, 5.46 mmol), methyl 3-(4-methoxyphenyl)propiolate (692 mg, 3.64 mmol) were dissolved in toluene (10 mL) and heated at reflux for 48 h. The solvent was removed under reduce pressure and purified by chromatography (Silica gel, hexane/EtOAc, 2:1) to afford **1e** (298 mg, 26 %) and **1e′** (184 mg, 16 %) as off-white solids. **1e′**: M.p. 100–102 °C. R_f = 0.28 (hexane/EtOAc 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.63 Hz, 2 H); 7.46–7.62 (m, 5 H); 7.02 (d, J = 8.63 Hz, 2 H); 3.89 (s, 3 H); 3.74 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 160.3 (Cq), 160.0 (Cq), 149.5 (Cq), 137.0 (Cq), 130.3 (2 CH), 129.8 (CH), 129.1 (2 CH), 125.2 (2 CH), 124.8 (Cq), 122.0 (Cq), 113.8 (2 CH), 55.3 (CH_3), 52.5 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 1718, 1612, 1497, 1438, 1356, 1248, 1221, 1111, 1017, 989, 846, 760 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{16}N_3O_3$ [M + H]$^+$ 310.1186; found 310.1181. ε_{254nm} (MeCN): 37.48 l/mol cm. **1e**: M.p. 98–100 °C. R_f = 0.12 (Hexane/EtOAc, 2:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.36–7.49 (m, 3 H); 7.28–7.34 (m, 2 H); 7.24 (d, J = 8.6 Hz, 2 H); 6.90 (d, J = 8.6 Hz, 2 H); 3.93 (s, 3 H); 3.83 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 161.4 (Cq), 160.6 (Cq), 140.8 (Cq), 136.1 (Cq), 135.8 (Cq), 131.6 (2 CH), 129.3 (CH), 129.2 (2 CH), 125.1 (2 CH), 117.1 (Cq), 113.8 (2 CH), 55.1 (CH_3), 52.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 1726, 1499, 1441, 1380, 1289, 1217, 1145, 1091, 1008, 839, 776, 696, 614 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{16}N_3O_3$ [M + H]$^+$ 310.1186; found 310.1182. ε_{254nm} (MeCN): 35.9 l/mol cm.

Methyl 1-(4-Methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (1f) and Methyl 1-(4-Methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole-5-carboxylate (1f′): 1-Azido-4-methoxybenzene (0.905 g, 6.07 mmol) and methyl 3-phenylpropiolate (0.597 mL, 4.05 mmol) were dissolved in benzene (10 mL) in a microwave vial and heated to 100 °C for 50 h. The mixture was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 1:0 to 2:1) to afford **1f** (436 mg, 35 %) as a yellow solid and **1f′** (245 mg, 20 %) as a pink solid. **1f′**: M.p. 100–102 °C. R_f = 0.38 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.85 (d, J = 6.8 Hz, 2 H); 7.37–7.57 (m, 5 H); 7.04 (d, J = 8.6 Hz, 2 H); 3.90 (s, 3 H); 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.6 (Cq), 159.9 (Cq), 149.3 (Cq), 129.9 (Cq), 129.8 (Cq), 129.1 (CH), 128.8 (2 CH), 128.3 (2 CH), 126.6 (2 CH), 125.5 (Cq), 114.2 (2 CH), 55.6 (CH_3), 52.6 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3006, 2953, 2838, 1727, 1511, 1487, 1450, 1230, 1224, 1113, 1106, 1017, 836, 768, 699 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{16}N_3O_3$ [M + H]$^+$ 310.1186; found 310.1179. ε_{254nm} (MeCN): 41.4 l/mol cm. **1f**: M.p. 122–124 °C. R_f = 0.13 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.35–7.48 (m, 3 H); 7.28–7.34 (m, 2 H); 7.19 (d, J = 9.1 Hz, 2 H); 6.88 (d, J = 9.1 Hz, 2 H); 3.92 (s, 3 H); 3.82 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4 (Cq), 160.1 (Cq), 140.9 (Cq), 136.3 (Cq), 130.1 (2 CH), 129.8 (CH), 128.6 (Cq), 128.3 (2 CH), 126.5 (2 CH), 125.6 (Cq), 114.3 (2 CH), 55.4 (CH_3), 52.0 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3062, 2949, 2841, 1717, 1515, 1370, 1252, 1223, 1084, 994, 838, 765, 698 cm^{-1}. HRMS (ESI$^+$): calcd. for

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$C_{17}H_{16}N_3O_3$ [M + H]$^+$ 310.1186; found 310.1180. ε_{254nm} (MeCN): 42.94 l/mol cm.

Methyl 1,5-Bis(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (1 g) and Methyl 1,4-Bis(4-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (1g′): 1-Azido-4-methoxybenzene (895 mg, 6.00 mmol) and methyl 3-(4-methoxyphenyl)propiolate (761 mg, 4 mmol) were dissolved in benzene (10 mL) and heated at reflux for 26 h. The solvent was removed under reduced pressure and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **1g** (202 mg, 15 %) and **1g′** (101 mg, 7 %) as brown solids. **1g′**: M.p. 148–150 °C. R_f = 0.25 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.6 Hz, 2 H); 7.43 (d, J = 8.6 Hz, 2 H); 6.87–7.12 (m, 4 H); 3.90 (s, 3 H); 3.89 (s, 3 H); 3.74 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5 (Cq), 160.3 (Cq), 159.9 (Cq), 149.3 (Cq), 130.3 (2 CH), 130.0 (Cq), 126.6 (2 CH), 124.9 (Cq), 122.2 (Cq), 114.2 (2 CH), 113.8 (2 CH), 55.6 (CH_3), 55.3 (CH_3), 52.5 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3009, 2954, 2846, 1729, 1591, 1514, 1446, 1346, 1301, 1248, 1222, 1149, 1097, 1020, 834, 780 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{18}N_3O_4$ [M + H]$^+$ 340.1291; found 340.1291. **1g**: M.p. 152–155 °C. R_f = 0.08 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.22 (dd, J = 11.1, 8.9 Hz, 4 H); 6.90 (d, J = 7.3 Hz, 4 H); 3.93 (s, 3 H), 3.83 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6 (Cq), 160.7 (Cq), 160.1 (Cq), 140.9 (Cq), 136.1 (Cq), 131.7 (2 CH), 128.8 (Cq), 126.6 (2 CH), 117.4 (Cq), 114.4 (2 CH), 113.9 (2 CH), 55.5 (CH_3), 55.2 (CH_3), 52.1 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3012, 2957, 2842, 1716, 1612, 1508, 1444, 1366, 1292, 1252, 1215, 1176, 1067, 1017, 991, 835, 802, 792 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{18}N_3O_4$ [M + H]$^+$ 340.1291; found 340.1291.

Methyl 1-(4-Methoxyphenyl)-5-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-4-carboxylate (1h) and Methyl 1-(4-Methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-5-carboxylate (1h′): 1-Azido-4-methoxybenzene (336 mg, 2.250 mmol) and methyl 3-[4-(trifluoromethyl)phenyl]propiolate (342 mg, 1.5 mmol) were dissolved in benzene (5 mL) and heated at reflux for 60 h. The solvent was removed under reduced pressure and the residue was purified by chromatography (Silica gel, pentane/EtOAc,1:0 to 2:1) to afford **1h** (255 mg, 45 %) and **1h′** (183 mg, 32 %) as brown solids. **1h′**: M.p. 115–117 °C. R_f = 0.33 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.2 Hz, 2 H); 7.75 (d, J = 8.2 Hz, 2 H); 7.44 (d, J = 8.6 Hz, 2 H); 7.05 (d, J = 8.6 Hz, 2 H); 3.91 (s, 3 H); 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (Cq), 159.5 (Cq), 147.9 (Cq), 133.4 (Cq), 131.6 (Cq*), 131.1 (Cq*), 130.7 (Cq*), 130.3 (Cq*), 129.6 (Cq), 129.4 (Cq$^{\#}$), 129.2 (2 CH), 126.6 (2 CH), 126.1 (Cq), 125.8 (Cq$^{\#}$), 125.2 (q, J = 3.85 Hz, CH), 122.2 (Cq$^{\#}$), 118.6 (Cq$^{\#}$), 114.2 (2 CH), 55.6 (CH_3), 52.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3328, 2954, 2844, 1720, 1511, 1441, 1319, 1248, 1225, 1170, 1129, 1095, 1067, 1009, 991, 839, 783 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{15}F_3N_3O_3$ [M + H]$^+$ 378.1060; found 378.1059. **1h**: M.p. 137–139 °C. R_f = 0.12 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.2 Hz, 2 H); 7.44 (d, J = 8.2 Hz, 2 H); 7.17 (d, J = 8.6 Hz, 2 H), 6.89 (d, J = 9.1 Hz, 2 H); 3.91 (s, 3 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.2 (Cq), 160.4 (Cq), 139.5 (Cq), 136.7 (Cq), 132.4 (Cq*), 132.0 (Cq*), 131.5 (Cq*), 131.1 (Cq*), 130.8 (2 CH), 129.4 (Cq), 129.0 (Cq$^{\#}$), 128.1 (CH), 126.6 (2 CH), 125.3 (q, J = 3.48 Hz, CH$^{\&}$), 121.7 (Cq$^{\#}$), 118.1 (Cq$^{\#}$), 114.6 (2 CH), 55.5 (CH_3), 52.2 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3083, 2936, 2842, 1732, 1512, 1320, 1256, 1219, 1162, 1107, 1079, 1065, 838 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{15}F_3N_3O_3$ [M + H]$^+$ 378.1060; found 378.1059.

1,5-Diphenyl-1*H*-1,2,3-triazole-4-carbonitrile (1i): In a microwave vial, azidobenzene (0.812 g, 6.82 mmol) was dissolved in DMSO (6.8 mL). 3-Oxo-3-phenylpropanenitrile (0.66 g, 4.55 mmol) and diethylamine (0.024 mL, 0.227 mmol) were then added. The solution was heated for 24 h at 70 °C. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 9:1) to afford **1i** (0.87 g, 78 %) as a yellow solid. **1i**: M.p. 161–163 °C. R_f = 0.48 (pentane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.54 (m, 6 H); 7.30–7.39 (m, 4 H) ppm. IR (neat): $\tilde{\nu}$ = 2237, 1592, 1494, 1450, 1069, 967, 774, 735, 687 cm^{-1}. Additional data in ref.[12]

1-(4-Methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carbonitrile (1j): In a 25 mL two-necked round bottomed flask, 1-azido-4-methoxybenzene (2 g, 13.41 mmol) was dissolved in DMSO (11.7 mL) and 3-oxo-3-phenylpropanenitrile (1.75 g, 12.06 mmol) was added, followed by diethylamine (1.260 mL, 12.06 mmol). The reaction mixture was stirred at 70 °C in a silicon oil bath for 5 d. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 9:1) to afford **1j** (1.13 g, 34 %) as a beige solid. M.p. 143–145. R_f = 0.31(pentane/EtOAc, 4:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.40–7.55 (m, 3 H); 7.31–7.39 (m, 2 H); 7.23–7.27 (m, 2 H), 6.96 (d, J = 9.1 Hz, 2 H); 3.87 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (Cq), 142.9 (Cq), 130.9 (CH), 129.3 (2 CH), 128.9 (2 CH), 128.1 (Cq), 126.5 (2 CH), 123.4 (Cq), 120.3 (Cq), 114.8 (2 CH), 112.2 (Cq), 55.6 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2239, 1607, 1514, 1457, 1308, 1256, 1153, 1106, 1021, 995, 838, 776, 683 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{13}N_4O$ [M + H]$^+$ 277.1083; found 277.1086.

[1-(4-Methoxyphenyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl](phenyl)methanone (1k): In a 25 mL round-bottomed flask, 1-azido-4-methoxybenzene (1.5 g, 10.06 mmol) was dissolved in DMSO (8.8 mL) and 4,4,4-trifluoro-1-phenylbutane-1,3-dione (1.9 g, 8.79 mmol) was added, followed by diethylamine (0.046 mL, 0.439 mmol). The reaction mixture was stirred at 70 °C in a silicon oil bath for 48 h. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 9:1) to afford **1k** (510 mg, 17 %) as a yellow solid. M.p. 70–73 °C. R_f = 0.46 (pentane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14–8.27 (m, 2 H); 7.64–7.73 (m, 1 H); 7.52–7.61 (m, 2 H); 7.44–7.51 (m, 2 H); 7.02–7.16 (m, 2 H); 3.92 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.3, 161.5, 145.67, 135.8, 134.1, 130.7, 129.7, 129.2, 128.6, 128.06, 126.9, 124.5, 120.9, 117.3, 114.6, 113.7, 55.7 ppm. IR (neat): $\tilde{\nu}$ = 2318, 1664, 1599, 1548, 1514, 1469, 1352, 1250, 1236, 1176, 1116, 1091, 1045, 911, 833, 719 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{13}F_3N_3O_2$ [M + H]$^+$ 348.0954; found 348.0957.

Phenyl[1-phenyl-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl]methanone (1l): In a 25 mL round-bottomed flask, azidobenzene (1.5 g, 12.59 mmol) was dissolved in DMSO (12.6 mL) and 4,4,4-trifluoro-1-phenylbutane-1,3-dione (2.72 g, 12.59 mmol) was added, followed by diethylamine (0.066 mL, 0.630 mmol). The reaction mixture was stirred at 70 °C in a silicon oil bath for 48 h. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 9:1) to afford **1l** (402 mg, 10 %) as a solid. M.p. 75–78 °C. R_f = 0.72 (pentane/EtOAc, 4:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.21 (d, J = 7.7 Hz, 2 H); 7.47–7.81 (m, 8 H) ppm. Additional data in ref.[12]

Ethyl 1-(4-Methoxyphenyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazole-4-carboxylate (1m):[22] In a 25 mL round-bottomed flask,1-azido-4-methoxybenzene (2 g, 13.41 mmol) was dissolved in DMSO (12 mL) and ethyl 4,4,4-trifluoro-3-oxobutanoate (2.16 g, 11.73 mmol) was added, followed by diethylamine (0.061 mL, 0.588 mmol). The reaction mixture was stirred at 70 °C in a silicon oil bath for 5 d. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 8:2) to afford **1m** (450 mg, 12 %) as a yellow solid. M.p. 75–78 °C (lit. 82–83 °C). R_f = 0.47 (pentane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.45 (m, 2 H); 7.00–7.11 (m, 2 H); 4.51 (q, J = 7.2 Hz, 2 H); 3.90 (s, 3

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H); 1.46 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCL_3$): δ = 161.4, 159.0, 139.1, 130.2, 129.7, 129.1, 128.6, 128.0, 126.9, 124.1, 120.5, 116.8, 114.5, 113.4, 62.2, 55.6, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2988, 2942, 2920, 2846, 1737, 1606, 1591, 1513, 1458, 1376, 1351, 1252, 1235, 1178, 1138, 1034, 1016, 835, 752 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{13}H_{13}F_3N_3O_3$ [M + H]$^+$ 316.0903; found 316.0903.

Ethyl 1-Phenyl-5-(trifluoromethyl)-1*H*-1,2,3-triazole-4-carboxylate (1n): In a 25 mL round-bottomed flask, azidobenzene (1.5 g, 12.59 mmol) was dissolved in DMSO (12.6 mL) and ethyl 4,4,4-trifluoro-3-oxobutanoate (2.318 g, 12.59 mmol) was added, followed by diethylamine (0.066 mL, 0.629 mmol). The reaction mixture was stirred at 70 °C in a silicon oil bath for 48 h. The crude mixture was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 9:1) to afford **1n** (490 mg, 14 %) as an oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.53–7.69 (m, 3 H); 7.47 (d, J = 7.3 Hz, 2 H); 4.51 (q, J = 7.0 Hz, 2 H); 1.45 (t, J = 7.0 Hz, 3 H) ppm. Additional data in ref.[12]

Dimethyl 1*H*-Indole-2,3-dicarboxylate (2a):[19] Dimethyl 1-phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate **1a** (99.3 mg, 0.380 mmol) was dissolved in MeCN (13 mL) in a quartz vessel and irradiated at 254 nm for 15 h. The solvent was removed and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2a** (59.4 mg, 67 %) as a solid. M.p. 107–109 °C (lit. 112–113 °C). R_f = 0.25 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.43 (br. s., 1 H); 8.07 (d, J = 8.2 Hz, 1 H); 7.43–7.48 (m, 1 H); 7.36–7.42 (m, 1 H); 7.28–7.32 (m, 1 H); 4.00 (s, 6 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 164.6 (Cq), 161.3 (Cq), 134.8 (Cq), 128.0 (Cq), 126.8 (Cq), 125.9 (CH), 122.7 (CH), 122.6 (CH), 111.9 (CH), 52.7 (CH_3), 51.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3299, 2952, 1722, 1687, 1526, 1438, 1255, 1066, 749, 716 cm^{-1}. 519. HRMS (ESI$^+$): calcd. for $C_{12}H_{11}NO_4Na$ [M + Na]$^+$ 256.0580; found 256.0578.

Dimethyl 5-Chloro-1*H*-indole-2,3-dicarboxylate (2b):[23] Dimethyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **1b** (54.4 mg, 0.184 mmol) was dissolved in MeCN (10 mL) in a quartz vessel and irradiated at 254 nm for 12 h. The solvent was removed and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2b** (31.1 mg, 63 %) as a solid. M.p. 156–158 °C (162–164 °C). R_f = 0.23(pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.28 (br. s., 1 H); 8.08 (s, 1 H); 7.31–7.43 (m, 2 H); 4.01 (s, 3 H); 4.00 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 163.9 (Cq), 161.1 (Cq), 133.0 (Cq), 129.4 (Cq), 128.6 (Cq), 127.7 (Cq), 126.6 (CH), 122.2 (CH), 113.0 (CH), 111.3 (Cq), 52.9 (CH_3), 51.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3325, 2952, 1676, 1524, 1435, 1217, 1179, 1085, 945, 766, 681 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{12}H_{10}ClNO_4Na$ [M + Na]$^+$ 290.0190; found 290.0191.

Methyl 3-Phenyl-1*H*-indole-2-carboxylate (2c): Methyl 1,5-diphenyl-methyl 1,4-diphenyl-1*H*-1,2,3-triazole-5-carboxylate **1c′** (104.5 mg, 0.374 mmol) was dissolved in MeCN (2 mL) and 2-propanol (14 mL) in quartz vessel. The solution was irradiated at 254 nm for 22 h at room temp. The solution was concentrated in vacuo and purified by chromatography (Silica gel, hexane/EtOAc, 4:1 to 2:1) to afford **2c** (70.1 mg, 75 %) as a yellow solid. M.p. 132–135 °C. R_f = 0.23 (hexane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.04 (br. s., 1 H); 7.68 (dd, J = 8.1, 0.8 Hz, 1 H); 7.55–7.64 (m, 2 H), 7.33–7.55 (m, 5 H); 7.18 (ddd, J = 8.1, 6.8, 1.1 Hz, 1 H); 3.85 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5 (Cq), 135.8 (Cq), 133.4 (Cq), 130.5 (2 CH), 127.8 (2 CH), 127.2 (CH), 125.8 (CH), 124.4 (Cq), 122.4 (Cq), 121.7 (CH), 120.9 (CH), 111.7 (CH), 51.8 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3329, 3046, 2947, 1676, 1535, 1492, 1441, 1335, 1251, 1143, 1000, 769, 737, 700, 632 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{13}NO_2Na$ [M + Na]$^+$ 274.0838; found 274.0839.

Methyl 3-[4-(Trifluoromethyl)phenyl]-1*H*-indole-2-carboxylate (2d): Methyl 1-phenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-5-carboxylate **1d′** (105.2 mg, 0.303 mmol) was dissolved in MeCN (7 mL) and *i*PrOH (7 mL) in a quartz vessel and irradiated at 254 nm for 15 h. The solvent was removed and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2d** (87.1 mg, 90 %) as a white solid. M.p. 175–177 °C. R_f = 0.25 (hexane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.06 (br. s., 1 H); 7.66–7.76 (m, 4 H); 7.61 (d, J = 8.2 Hz, 1 H); 7.45–7.51 (m, 1 H); 7.36–7.44 (m, 1 H); 7.20 (t, J = 7.5 Hz, 1 H); 3.85 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.2 (Cq), 137.3 (Cq), 137.3 (Cq), 135.7 (Cq), 130.9 (2 CH), 129.8 (Cq*), 129.8 (Cq$^{\#}$), 129.4 (Cq*), 129.0 (Cq*), 128.6 (Cq*), 127.5 (Cq), 126.1 (CH), 124.8 (q, J = 3.85 Hz, CH), 122.7 (Cq), 122.6 (Cq$^{\#}$), 121.3 (CH), 121.3 (CH), 119.0 (Cq$^{\#}$), 111.9 (CH), 51.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3317, 1692, 1615, 1457, 1320, 1251, 1163, 1119, 1105, 1065, 839, 744, 672 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{12}F_3NO_2Na$ [M + Na]$^+$ 342.0712; found 342.0713.

Methyl 3-(4-Methoxyphenyl)-1*H*-indole-2-carboxylate (2e): Methyl 4-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-5-carboxylate **1e′** (106.6 mg, 0.345 mmol) was dissolved in MeCN (1 mL) and *i*PrOH (14 mL) in a quartz vessel and was irradiated at 254 nm for 40 h. The solvent was removed and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1 to 1:1) to afford the desired product **2e** (71.1 mg, 73 %) as a white solid. M.p. 162–164 °C. R_f = 0.27 (hexane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.94 (br. s., 1 H); 7.66 (d, J = 8.2 Hz, 1 H); 7.51 (d, J = 8.6 Hz, 2 H); 7.42–7.47 (m, 1 H); 7.33–7.41 (m, 1 H); 7.2 (t, J = 7.5 Hz, 1 H); 7.02 (d, J = 8.6 Hz, 2 H); 3.90 (s, 3 H); 3.84 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 162.5 (Cq), 158.8 (Cq), 135.8 (Cq), 131.6 (2 CH), 127.9 (Cq), 125.8 (CH), 125.6 (Cq), 124.2 (Cq), 122.1 (Cq), 121.7 (CH), 120.7 (CH), 113.3 (2 CH), 111.7 (CH), 55.2 (CH_3), 51.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3336, 2949, 1669, 1548, 1496, 1442, 1331, 1240, 1142, 1100, 1030, 991, 825, 767, 652 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{15}NO_3Na$ [M + Na]$^+$ 304.0944; found 304.0941.

Methyl 5-Methoxy-3-phenyl-1*H*-indole-2-carboxylate (2f): Methyl 1-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole-5-carboxylate **1f′** (84 mg, 0.272 mmol) was dissolved in 2-propanol (15 mL) in a quartz vessel. The solution was irradiated at 254 nm for 24 h at room temp. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2f** (67.3 mg, 88 %) as a yellow solid. M.p. 150–152 °C. R_f = 0.59 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.90 (br. s., 1 H); 7.53–7.60 (m, 2 H); 7.49 (t, J = 7.27 Hz, 2 H); 7.31–7.44 (m, 2 H); 6.97–7.10 (m, 2 H); 3.81 (s, 3 H); 3.80 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.4 (Cq), 154.9 (Cq), 133.6 (Cq), 131.1 (Cq), 130.4 (2 CH), 128.0 (2 CH), 127.9 (2 CH), 127.1 (CH), 123.8 (Cq), 122.9 (Cq), 117.6 (CH), 112.7 (CH), 101.4 (CH), 55.7 (CH_3), 51.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3312, 2956, 1676, 1625, 1532, 1485, 1460, 1439, 1245, 1204, 1169, 1141, 1029, 947, 805, 744, 698, 659 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{17}H_{15}NO_3Na$ [M + Na]$^+$ 304.0944; found 304.0941.

Methyl 5-Methoxy-3-(4-methoxyphenyl)-1*H*-indole-2-carboxylate (2g): Methyl 1,4-bis(4-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate **1g′** (112.8 mg, 0.332 mmol) was dissolved in 2-propanol (15 mL) and MeCN (5 mL) in a quartz vessel. The solution was irradiated at 254 nm for 14 h at room temp. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2g** (70.5 mg, 68 %) as a white solid. M.p. 150–152 °C. R_f = 0.49 (pentane/EtOAc, 3:1). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.84 (br. s., 1 H); 7.44–7.56 (m, 2 H); 7.30–7.38 (m, 1 H); 6.95–7.12 (m, 4 H); 3.90 (s, 3 H); 3.82 (s, 3 H); 3.80 (s, 3 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 162.3 (Cq), 158.7 (Cq), 154.8 (Cq), 131.5 (2 CH), 131.1 (Cq), 128.1 (Cq), 125.8 (Cq), 123.7 (Cq), 122.6 (Cq), 117.5

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(CH), 113.4 (2 CH), 112.7 (CH), 101.4 (CH), 55.6 (CH_3), 55.2 (CH_3), 51.7 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3335, 2946, 2834, 1672, 1503, 1438, 1247, 1221, 1176, 1034, 865, 806, 789, 664 cm^{-1}. HRMS (ESI^+): calcd. for $C_{18}H_{18}NO_4$ $[M + H]^+$ 312.1230; found 312.1231.

Methyl 5-Methoxy-3-[4-(trifluoromethyl)phenyl]-1*H*-indole-2-carboxylate (2h): Methyl 1-(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-5-carboxylate **1h'** (129.7 mg, 0.344 mmol) was dissolved in MeCN (10 mL) and *i*PrOH (5 mL) in a quartz vessel and irradiated for 18 h at 254 nm. The solution was concentrated in vacuo and the residue was purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2h** (96 mg, 80 %) as a white solid. M.p. 195–197 °C. R_f = 0.59 (pentane/EtOAc, 3:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.96 (br. s., 1 H); 7.60–7.79 (m, 4 H); 7.37 (d, *J* = 8.9 Hz, 1 H); 7.07 (dd, *J* = 8.9, 2.5 Hz, 1 H); 6.95 (d, *J* = 2.3 Hz, 1 H); 3.83 (s, 3 H); 3.80 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.0 (Cq), 155.3 (Cq), 137.5 (Cq), 137.5 (Cq), 131.0 (Cq), 130.7 (2 CH), 129.8 (Cq*), 129.3 (Cq*), 128.9 (Cq*), 128.5 (Cq*), 127.8 (Cq), 126.2 ($Cq^{\#}$), 124.9 (q, *J* = 3.67 Hz, 2 CH), 123.1 (Cq), 122.6 ($Cq^{\#}$), 122.2 (Cq), 119.0 ($Cq^{\#}$), 117.9 (CH), 112.9 (CH), 100.9 (CH), 55.7 (CH_3), 51.9 (CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3326, 2957, 1666, 1614, 1506, 1461, 1324, 1255, 1222, 1106, 837, 806, 766, 694 cm^{-1}. HRMS (ESI^+): calcd. for $C_{18}H_{14}F_3NO_3Na$ $[M + Na]^+$ 372.0817; found 372.0829.

2-Phenyl-1*H*-indole-3-carbonitrile (2i):[24] 1,5-Diphenyl-1*H*-1,2,3-triazole-4-carbonitrile **1i** (110.4 mg, 0.448 mmol) was dissolved in MeCN (15 mL) in a quartz vessel and irradiated for 14 h at 254 nm. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2i** (76.8 mg, 78 %) as a white solid. M.p. 236–238 °C (lit. 224–226 °C). R_f = 0.29 (pentane/EtOAc, 4:1). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.74 (br. s., 1 H); 7.90 (d, *J* = 7.3 Hz, 2 H); 7.80 (d, *J* = 7.3 Hz, 1 H); 7.44–7.61 (m, 4 H); 7.29–7.40 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $[D_3]$MeCN): δ = 146.0 (Cq), 136.6 (Cq), 131.1 (CH), 130.7 (Cq), 130.4 (2 CH), 129.7 (Cq), 128.1 (2 CH), 125.2 (CH), 123.2 (CH), 119.8 (CH), 117.7 (Cq), 113.3 (CH), 83.7 (Cq) ppm. IR (neat): $\tilde{\nu}$ = 3218, 3194, 2342, 2317, 2221, 1491, 1450, 1425, 1244, 737, 710, 687 cm^{-1}. HRMS (ESI^+): calcd. for $C_{15}H_{11}N_2$ $[M + H]^+$ 219.0916; found 219.0919.

5-Methoxy-2-phenyl-1*H*-indole-3-carbonitrile (2j):[24] In a quartz vessel, 1-(4-methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carbonitrile **1j** (116 mg, 0.420 mmol) was dissolved in MeCN (15 mL) in a quartz vessel and irradiated at 254 nm for 6 h. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 3:1) to afford **2j** (86.8 mg, 83 %) as a white solid. M.p. 247–250 °C (lit. 120–122 °C). R_f = 0.17 (pentane/EtOAc, 5:1). ^1H NMR (360 MHz, $[D_6]$DMSO): δ = 12.48 (s, 1 H); 7.98–7.93 (m, 2 H); 7.65–7.57 (m, 2 H); 7.54 (d, *J* = 7.3 Hz, 1 H); 7.45 (d, *J* = 9.1 Hz, 1 H); 7.08 (d, *J* = 2.3 Hz, 1 H); 6.93 (dd, *J* = 8.9, 2.5 Hz, 1 H); 3.83 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 155.5, 144.5, 130.36, 129.8, 129.5, 129.3, 129.2, 126.8, 117.2, 114.3, 113.6, 99.6, 81.2, 55.4 ppm. IR (neat): $\tilde{\nu}$ = 3204, 2219, 1645, 1591, 1488, 1475, 1449, 1295, 1251, 1218, 1161, 1021, 820, 764, 685, 663 cm^{-1}. HRMS (ESI^+): calcd. for $C_{16}H_{12}N_2ONa$ $[M + Na]^+$ 271.0841; found 271.0845.

[5-Methoxy-2-(trifluoromethyl)-1*H*-indol-3-yl](phenyl)methanone (2k): [1-(4-methoxyphenyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl](phenyl)methanone **1k** (114.9 mg, 0.331 mmol) was dissolved in MeCN (15 mL) in a quartz vessel and irradiated at 254 nm for 100 min. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 4:1) to afford **2k** (87.7 mg, 83 %) as a brown solid. M.p. 143–146 °C. R_f = 0.42 (pentane/EtOAc, 3:1). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.93 (br. s., 1 H); 7.88 (d, *J* = 7.7 Hz, 2 H); 7.58–7.66 (m, 1 H); 7.45–7.53 (m, 2 H); 7.40 (d, *J* = 9.1 Hz, 1 H); 7.03 (d, *J* = 9.1 Hz, 1 H); 6.81 (s, 1 H); 3.67 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 155.8, 139.0, 133.1, 129.6, 129.6, 128.4, 128.2, 127.7, 127.2, 127.1, 126.6, 125.8, 122.3, 118.7, 116.6, 116.4, 116.3, 115.1, 113.2, 102.4, 55.4 ppm. IR (neat): $\tilde{\nu}$ = 3257, 3063, 2957, 2939, 2834, 1630, 1466, 1211, 1164, 1119, 1001, 905, 806, 729, 696 cm^{-1}. HRMS (ESI^+): calcd. for $C_{17}H_{12}F_3NO_2Na$ $[M + Na]^+$ 342.0712; found 342.0710.

Phenyl[2-(trifluoromethyl)-1*H*-indol-3-yl]methanone (2l): Phenyl[1-phenyl-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl]methanone **1l** (121.1 mg, 0.382 mmol) was dissolved in MeCN (15 mL) in a quartz vessel and irradiated at 254 nm for 4.5 h. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 9:1) to afford **2l** (74.8 mg, 67 %) as a white solid. M.p. 142–145 °C. R_f = 0.43 (pentane/EtOAc, 5:1). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.96 (br. s., 1 H); 7.89 (d, *J* = 7.72 Hz, 2 H); 7.58–7.68 (m, 1 H); 7.44–7.55 (m, 3 H); 7.34–7.43 (m, 2 H); 7.14–7.23 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.7, 138.8, 134.5, 133.2, 129.7, 128.4, 127.9, 127.4, 126.9, 126.4, 126.3, 125.9, 125.3, 122.4, 122.4, 121.9, 118.8, 116.9, 115.2, 112.3 ppm. IR (neat): $\tilde{\nu}$ = 3214, 3188, 3155, 3117, 3065, 1624, 1541, 1448, 1380, 1288, 1228, 1180, 1123, 994, 748, 730, 695, 614 cm^{-1}. HRMS (ESI^+): calcd. for $C_{16}H_{10}F_3NONa$ $[M + Na]^+$ 312.0606; found 312.0601.

Ethyl 5-methoxy-2-(trifluoromethyl)-1*H*-indole-3-carboxylate (2m): Ethyl 1-(4-methoxyphenyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazole-4-carboxylate **1m** (101.7 g, 323 mmol) was dissolved in MeCN (15 mL) in a quartz vessel and irradiated at 254 nm for 10 h at 254 nm. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 4:1) to afford **2m** (60.5 g, 65 %) as a white solid. M.p. 143–146 °C. R_f = 0.42 (pentane/EtOAc, 4:1). ^1H NMR (360 MHz, $CDCl_3$): δ = 8.88 (br. s., 1 H); 7.74 (s, 1 H); 7.36 (d, *J* = 8.6 Hz, 1 H); 7.05 (d, *J* = 9.1 Hz, 1 H); 4.44 (q, *J* = 7.0 Hz, 2 H); 3.90 (s, 3 H); 1.44 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 156.4, 129.5, 129.0, 128.8, 128.4, 127.9, 127.6, 125.7, 122.2, 118.6, 116.8, 115.0, 112.9, 107.8 (d, *J* = 2.20 Hz, 1 C) 102.9, 60.6, 55.6, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3280, 2995, 2833, 1681, 1550, 1467, 1439, 1309, 1209, 1166, 1154, 1112, 1032, 845, 824, 713, 637 cm^{-1}. HRMS (ESI^+): calcd. for $C_{13}H_{12}F_3NO_3Na$ $[M + Na]^+$ 310.0661; found 310.0662. X-ray analysis reported in ref.[30]

Ethyl 2-(Trifluoromethyl)-1*H*-indole-3-carboxylate (2n): Ethyl 1-phenyl-5-(trifluoromethyl)-1*H*-1,2,3-triazole-4-carboxylate **1n** (111.3 mg, 0.390 mmol) was dissolved in MeCN (15 mL) and irradiated for 5 h 40 min at 254 nm. The solution was concentrated in vacuo and purified by chromatography (Silica gel, pentane/EtOAc, 9:1) to afford **2n** (53 mg, 53 %) as a pale yellow solid. ^1H NMR (360 MHz, $CDCl_3$): δ = 9.00 (br. s., 1 H); 8.29 (d, *J* = 7.7 Hz, 1 H); 7.45–7.53 (m, 1 H), 7.31–7.45 (m, 2 H); 4.45 (q, *J* = 7.0 Hz, 2 H); 1.45 (t, *J* = 7.0 Hz, 3 H) ppm. Additional data in ref.[31]

1-(Benzyloxy)-2-methoxy-4-nitrobenzene (5b):[25] 2-Methoxy-4-nitrophenol **5a** (1.015 g, 6.00 mmol) was dissolved in acetonitrile (25 mL), and potassium carbonate (1.244 g, 9.00 mmol) was added to the reaction mixture, followed by the addition of (bromomethyl)benzene (1.213 mL, 10.20 mmol) and stirred under an argon atmosphere at room temperature for 3 d. The extent of completion of the reaction was monitored by UPLC-MS analysis. The reaction mixture was quenched with the addition of an equivalent amount of water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water and brine and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified with a flash column chromatography Biotage Isolera system (gradient pentane/EtOAc 5–20 % on 9 CV, 20–65 % on 7 CV, 65–100 % on 1 CV and then 100 % on 2.5 CV) on a Büchi 40 g column to give 1-(benzyloxy)-2-methoxy-4-nitrobenzene (**5b**; 1.16 g, 4.47 mmol, 75 %) as a yellow solid. M.p. 76–79 °C (lit. 80–82 °C). ^1H NMR (360 MHz, $CDCl_3$): δ = 3.92–4.11 (m, 3 H); 5.20–5.38

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(m, 2 H); 6.93 (d, *J* = 8.9 Hz, 1 H); 7.31–7.60 (m, 5 H); 7.77 (d, *J* = 2.7 Hz, 1 H); 7.85 (dd, *J* = 8.9, 2.7 Hz, 1 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 56.3, 71.1, 106.7, 111.7, 117.7, 127.2, 128.4, 128.8, 135.5, 141.6, 149.3, 153.7 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}N_1O_4$ [M + Na]$^+$ 282.0737; found 282.0737. IR (neat): $\tilde{\nu}$ = 3109, 3090, 3010, 2946, 1583, 1501, 1462, 1338, 1270, 1231, 1136, 1089 cm^{-1}.

4-(Benzyloxy)-3-methoxyaniline (6):[25] In accordance with the procedure of Keller et al., to a suspension of 1-(benzyloxy)-2-methoxy-4-nitrobenzene (**5b**; 209.2 mg, 0.807 mmol) in a mixture of acetic acid (4 mL), ethanol (4 mL) and water (2 mL) was added tin powder (479 mg, 4.03 mmol). The resulting suspension was sonicated for 1 h at 30 °C. The reaction mixture was filtered to remove the tin residue, which was washed with EtOAc (10 mL). The filtrate was partitioned with 2 M KOH and the basic layer was further extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (2 × 5 mL) and water (3 × 5 mL), dried with Na_2SO_4, and concentrated under reduced pressure. The crude residue was then purified with a flash column chromatography Biotage Isolera system (gradient pentane/EtOAc 10 % on 6 CV, 10–40 % on 8 CV, 40–75 % on 4 CV, 75–100 % on 1.5 CV and finally 100 % on 3 CV) on a Büchi 40 g column to give 4-(benzyloxy)-3-methoxyaniline (**6**; 122.3 mg, 0.533 mmol, 66 %) as a brown solid. M.p. 65–69 °C (lit. 84.85 °C). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.85 (s, 3 H); 5.05 (s, 2 H); 6.17 (dd, *J* = 8.4, 2.7 Hz, 1 H); 6.33 (d, *J* = 2.5 Hz, 1 H); 6.72 (d, *J* = 8.4 Hz, 1 H); 7.28–7.46 (m, 5 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$): δ = 55.8, 72.4, 100.8, 106.5, 117.0, 127.5, 127.6, 128.3, 137.7, 141.0, 141.4, 150.9 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{16}NO_2$ [M + H]$^+$ 230.1176; found 230.1176. IR (neat): $\tilde{\nu}$ = 3385, 3324, 3274, 3028, 2856, 1596, 1509, 1452, 1284, 1228, 1202, 1025, 838 cm^{-1}.

4-Azido-1-(benzyloxy)-2-methoxybenzene (7): To a solution of 4-(benzyloxy)-3-methoxyaniline (**6**; 715 mg, 3.12 mmol) in acetonitrile (25 mL), *tert*-butyl nitrite (0.556 mL, 4.68 mmol) was added followed by addition of azidotrimethylsilane (0.621 mL, 4.68 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was then quenched with an equivalent amount of water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water and brine and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified with a flash column chromatography Biotage Isolera system (gradient pentane/EtOAc 5–20 % on 9 CV, 20–65 % on 7 CV, 65–100 % on 1 CV and then 100 % on 2.5 CV) on a Büchi 40 g column to give 4-azido-1-(benzyloxy)-2-methoxybenzene (**7**; 617 mg, 2.417 mmol, 78 %) as an orange solid. M.p. 67–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3 H); 5.13 (s, 2 H); 6.52–6.58 (m, 2 H); 6.87 (d, *J* = 9.4 Hz, 1 H); 7.28–7.47 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.0, 71.6, 103.6, 110.5, 115.4, 127.3 (2 C), 127.9, 128.5 (2 C), 133.4, 136.9, 145.5, 150.9 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{16}NO_2$ [M + Na]$^+$ 278.0900; found 278.0903. IR (neat): $\tilde{\nu}$ = 3066, 3000, 2941, 2885, 2837, 2097, 1545, 1503, 1454, 1383, 1298, 1247, 1218, 1147, 989 cm^{-1}.

1-[4-(Benzyloxy)-3-methoxyphenyl]-6-methoxy-1*H*-benzo[*d*][1,2,3]triazole (9b): To a solution of 4-azido-1-(benzyloxy)-2-methoxybenzene (**7**; 13.9 mg, 0.054 mmol) and 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**8**; 0.029 mL, 0.109 mmol) in acetonitrile (0.3 mL), tetrabutylammonium fluoride (0.109 mL, 0.109 mmol) was added and the reaction mixture was stirred under an argon atmosphere at room temperature overnight. Then an equivalent amount of water was added to quench the reaction, which was then extracted with CH_2Cl_2 (3 × 3 mL) and the combined organic layers were washed with $NaHCO_3$ sat. sol., water, and brine, and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified with a flash column chromatography Biotage Isolera system (gradient pentane/EtOAc 5–15 % on 8 CV, 15–100 % on 2 CV and finally 100 % on 4 CV) on a Büchi 40 g column to give 1-[4-(benzyloxy)-3-methoxyphenyl]-5-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**9a**) and 1-[4-(benzyloxy)-3-methoxyphenyl]-6-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**9b**) as a yellow oil (16.1 mg, 0.045 mmol, 82 %) in a 1:1 regioisomer mixture. This was then further separated for analyses with a flash column chromatography Biotage Isolera system (gradient pentane/EtOAc 5–15 % on 8 CV, 15–100 % on 2 CV and finally 100 % on 4 CV) on a Büchi 90 g column to give both separated regioisomers as two white solids. **9a**: M.p. 84–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3 H); 3.98 (s, 3 H); 5.27 (s, 2 H); 6.96 (d, *J* = 2.2 Hz, 1 H); 7.04–7.06 (m, 1 H); 7.07–7.10 (m, 1 H); 7.14–7.19 (m, 1 H); 7.31 (d, *J* = 2.4 Hz, 1 H); 7.33–7.52 (m, 5 H); 7.98 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_3$]MeCN): δ = 57.1, 57.2, 72.1, 92.5, 109.3, 115.3, 116.8, 117.8, 121.6, 129.4 (2 C), 129.5, 129.9 (2 C), 131.7, 135.3, 138.3, 142.6, 149.8, 151.8, 161.9 ppm. HRMS (ESI$^+$): calcd. for $C_{21}H_{19}N_3O_3$ [M + H]$^+$ 362.1499; found 362.1495. IR (neat): $\tilde{\nu}$ = 3071, 3012, 2967, 2916, 2867, 2834, 1512, 1496, 1218 cm^{-1}. **9b**: M.p. 106–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.94 (s, 3 H); 4.00 (s, 3 H); 5.27 (s, 2 H); 7.07 (d, *J* = 8.6 Hz, 1 H); 7.19 (dd, *J* = 2.4, 1.5 Hz, 1 H); 7.21–7.23 (m, 1 H); 7.35 (d, *J* = 2.4 Hz, 1 H); 7.37–7.53 (m, 5 H); 7.59 (dd, *J* = 9.0, 0.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_3$]MeCN): δ = 56.3, 56.6, 71.5, 99.5, 108.4 112.3, 114.6, 115.7, 116.2, 121.1, 128.8 (2 C), 129.4 (2 C), 131.2, 137.7, 142.1, 148.0, 151.2, 158.2, 161.3 ppm. HRMS (ESI$^+$): calcd. for $C_{21}H_{19}N_3O_3$ [M + H]$^+$ 362.1499; found 362.1496. IR (neat): $\tilde{\nu}$ = 3089, 2948, 2914, 2874, 2833, 1600, 1513, 1439, 1215, 1198 cm^{-1}.

2-Methoxy-4-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)phenol (3a): 1-[4-(benzyloxy)-3-methoxyphenyl]-6-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**9a**; 434.8 mg, 1.203 mmol) was dissolved in ethanol (20 mL), then Pd/C (wt. 10 %, 64.0 mg, 0.060 mmol) was added to the reaction mixture, which was purged with a balloon of hydrogen and stirred at room temperature overnight. The reaction mixture was filtered through Celite and washed with ethanol. The solvent was removed under reduced pressure, and the crude residue was then purified by filtration through a pad of silica by using CH_2Cl_2 and then diethylether to afford 2-methoxy-4-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)phenol (**3a**; 315.6 mg, 1.163 mmol, 97 % yield) as a greenish solid. M.p. 123–126 °C. ^{1}H NMR (300 MHz, [D$_3$]MeCN): δ = 3.85 (s, 3 H); 3.93 (s, 3 H); 7.01–7.10 (m, 3 H); 7.18 (dd, *J* = 8.4, 2.3 Hz, 1 H); 7.29 (d, *J* = 2.3 Hz, 1 H); 7.86–7.93 (m, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_3$]MeCN): δ = 56.8, 57.1, 92.1, 108.9, 116.3, 117.4, 117.5, 121.3, 130.2, 135.1, 142.3, 147.9, 149.1, 161.6 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}N_3O_3$ [M + H]$^+$ 272.1030; found 272.1028. IR (neat): $\tilde{\nu}$ = 3479, 1618, 1519, 1448, 1232 cm^{-1}. ε**254** 7598 L mol^{-1} cm^{-1}.

2-Methoxy-4-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)phenol (3b): 1-[4-(benzyloxy)-3-methoxyphenyl]-5-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**9b**; 508.2 mg, 1.406 mmol) was dissolved in ethanol (20 mL) then Pd/C (wt. 10 %, 74.8 mg, 0.070 mmol) was added to the reaction mixture, which was purged with a balloon of hydrogen and stirred at room temperature overnight. The reaction mixture was filtered through Celite and washed with ethanol. The solvent was removed under reduced pressure. The crude mixture was purified by filtration through a pad of silica by using CH_2Cl_2 and then diethylether as solvents to afford 2-methoxy-4-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)phenol (**3b**; 303.5 mg, 1.119 mmol, 80 % yield) as a brown solid. M.p. 97–101 °C. ^{1}H NMR (300 MHz, [D$_3$]MeCN): δ = 3.89 (s, 3 H); 3.92 (s, 3 H); 6.99 (s, 1 H); 7.04 (d, *J* = 8.4 Hz, 1 H); 7.17 (dd, *J* = 2.4, 1.65 Hz, 1 H); 7.18–7.21 (m, 1 H); 7.30 (d, *J* = 2.4 Hz, 1 H); 7.43 (d, *J* = 2.2 Hz, 1 H); 7.61 (dd, *J* = 9.2, 0.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_3$]MeCN): δ = 56.6, 57.1, 99.6, 108.6,

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112.6, 116.2, 117.0, 121.3, 129.2, 130.3, 147.8, 148.1, 149.0, 158.4 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}N_3O_3$ [M + H]$^+$ 272.1030; found 272.1029. IR (neat): $\tilde{\nu}$ = 3092, 2993, 2961, 2837, 1603, 1519, 1206, 1126 cm^{-1}. ε_{254} 12391 L mol^{-1} cm^{-1}.

4,7-Dimethoxy-9*H*-carbazol-3-ol (4a′) and Clausenawalline D (4a):[16] 2-Methoxy-4-(6-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-phenol (**3a**, 78.7 mg, 0.290 mmol) was dissolved in degassed acetonitrile (20 mL) and irradiated for 24 h in a Rayonet reactor at 254 nm. The solvent was then evaporated under reduced pressure and the crude mixture was purified with a flash column chromatography Biotage Isolera system (gradient CH_2Cl_2/Et_2O 5–10 % on 8.5 CV and 10–55 % on 4 CV) to give 4,7-dimethoxy-9*H*-carbazol-3-ol (**4a′**; 16.2 mg, 0.067 mmol, 23 %) as a brown solid and clausenawalline D (**4a**; 15.2 mg, 0.062 mmol, 22 %) as a white solid. **4a**: M.p. 245–248 °C (lit. 247–249 °C). ^{1}H NMR (300 MHz, acetone): δ = 3.83 (s, 3 H); 3.91 (s, 3 H); 6.72 (dd, *J* = 8.5, 2.3 Hz, 1 H); 6.95 (d, *J* = 2.2 Hz, 1 H); 6.97 (s, 1 H); 7.04 (s, 1 H); 7.41 (s, 1 H); 7.78 (d, *J* = 8.6 Hz, 1 H); 9.80 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 55.8, 56.6, 95.3, 95.6, 105.4, 108.2, 120.7, 135.2, 142.1, 147.6, 159.1 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}NO_3$ [M + Na]$^+$ 266.0788; found 266.0790. IR (neat): $\tilde{\nu}$ = 3529, 3390, 2957, 2922, 2852, 1615, 1442, 1270, 1142 cm^{-1}. ε_{254} 14009 L mol^{-1} cm^{-1}. **4a′**: M.p. 151–154 °C. ^{1}H NMR (300 MHz, acetone): δ = 3.85 (s, 3 H); 4.01 (s, 3 H); 6.75–6.80 (m, 1 H); 6.90–6.94 (m, 1 H) 6.96 (d, *J* = 2.2 Hz, 1 H) 7.01–7.06 (m, 1 H) 8.02 (d, *J* = 8.6 Hz, 1 H) 9.93 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, Acetone): δ = 55.8; 60.4; 95.2; 107.0; 108.6; 115.3; 116.4; 117.9; 123.9; 136.4; 142.3; 142.9; 143.3; 159.9 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}NO_3$ [M + Na]$^+$ 266.0788; found 266.0788. IR (neat): $\tilde{\nu}$ = 3402, 2999, 2935, 2833, 2584, 1613, 1500, 1445, 1281, 1197 cm^{-1}. ε_{254} 24943 L mol^{-1} cm^{-1}.

4,6-Dimethoxy-9*H*-carbazol-3-ol (4b′) and 2,6-dimethoxy-9*H*-carbazol-3-ol (4b): 2-Methoxy-4-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)phenol (**2b**, 100 mg, 0.369 mmol) was dissolved in dry acetonitrile (20 mL), placed in a Rayonet reactor equipped with eight 254 nm lamps, and irradiated for 24 h. The solvent was then evaporated, and the crude residue was purified with a flash column chromatography Biotage Isolera system (gradient CH_2Cl_2/Et2O 5–9 % on 6.5 CV) to give 4,6-dimethoxy-9*H*-carbazol-3-ol (**4b**; 26.9 mg, 0.111 mmol, 30 % yield) and 2,6-dimethoxy-9*H*-carbazol-3-ol (**4b′**; 32 mg, 0.132 mmol, 36 % yield) as brown and white solids. **4b**: M.p. 190–195 °C. ^{1}H NMR (300 MHz, acetone): δ = 3.85 (s, 3 H); 3.92 (s, 3 H); 6.89 (dd, *J* = 8.8, 2.6 Hz, 1 H); 7.00 (s, 1 H); 7.04 (s, 1 H); 7.27–7.32 (m, 1 H); 7.48 (s, 1 H); 7.50 (d, *J* = 2.4 Hz, 1 H); 9.72 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 56.2; 56.5; 95.0; 103.2; 105.6; 111.98; 112.03; 113.9; 116.9; 124.8; 136.0; 136.2; 148.8; 154.5 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}NO_3$ [M + Na]$^+$ 266.0788; found 266.0786. IR (neat): $\tilde{\nu}$ = 3400, 1636, 157, 1491, 1465, 1439, 1331, 1283, 1182, 1139, 1022 cm^{-1}. ε_{254} 11367 L mol^{-1} cm^{-1}. **4b′**: ^{1}H NMR (300 MHz, acetone): δ = 3.88 (s, 3 H); 4.04 (s, 3 H); 6.98–7.03 (m, 2 H); 7.05–7.09 (m, 1 H); 7.35 (dd, *J* = 8.8, 0.4 Hz, 1 H); 7.71 (d, *J* = 2.6 Hz, 1 H); 9.87 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 56.2; 60.6; 106.2; 107.2; 107.6; 112.1; 115.3; 117.0; 117.8; 122.9; 136.5; 137.3; 142.8; 154.4 ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{13}NO_3$ [M + Na]$^+$ 266.0788; found 266.0790. IR (neat): $\tilde{\nu}$ = 3404, 2933, 2832, 1685, 1579, 1503, 1483, 1434, 1208, 1162 cm^{-1}. ε_{254} 12473 L mol^{-1} cm^{-1}.

General Procedure for the Synthesis of the Carbazole Library: Benzotriazoles[13c] (50–100 mg) were dissolved in acetonitrile (15 mL) and kept under an argon atmosphere. The reaction mixture was placed in a quartz reactor and irradiated at 254 nm. Conversion into the desired carbazole was monitored by UPLC-MS analysis. The solvent was then removed under reduced pressure and the crude residue was purified with a flash column chromatography with a Biotage Isolera system (gradient pentane/EtOAc 0–40 % on 11 CV, 40–75 % on 5 CV, 75–100 % on 3 CV and finally 100 % EtOAc on 1.5 CV) to give the desired carbazole.

9*H*-Carbazole (4c): The general procedure was followed by using 1-phenyl-1*H*-benzo[*d*][1,2,3]triazole **3c** (100 mg, 0.512 mmol) as precursor to give 9*H*-carbazole **4c** (33 mg, 0.197 mmol, 39 % yield) as a yellow solid. M.p. 244–248 °C. ^{1}H NMR (300 MHz, Acetone): δ = 7.16 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 2 H); 7.30–7.42 (m, 2 H) 7.50 (dt, *J* = 8.1, 0.9 Hz, 2 H); 8.10 (ddt, *J* = 7.8, 1.3, 0.7 Hz, 2 H); 10.36 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 111.8; 119.7; 120.9; 124.0; 126.5 ppm. HRMS (MALDI-TOF): calcd. for $C_{12}H_9N$ 167.0735; found 167.0730. IR (neat): $\tilde{\nu}$ = 3415, 3049, 2543, 1934, 1893, 1867, 1598, 1491, 1449, 1324, 1234, 1205, 1139, 995, 927, 840, 755, 721 cm^{-1}.

3-Methoxy-9*H*-carbazole (4d):[26] The general procedure was followed by using 1-(4-methoxyphenyl)-1*H*-benzo[*d*][1,2,3]triazole **3d** (100 mg, 0.444 mmol) to give 3-methoxy-9*H*-carbazole **4d** (41 mg, 0.208 mmol, 47 % yield) as a pale brown solid. M.p. 149–151 °C (lit. 148–149 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (s, 3 H); 7.04–7.12 (m, 1 H); 7.17–7.26 (m, 1 H); 7.34 (dd, *J* = 8.8, 0.5 Hz, 1 H); 7.39–7.46 (m, 2 H); 7.6 (d, *J* = 2.5 Hz, 1 H); 7.92 (br. s., 1 H); 8.05 (dq, *J* = 7.8, 0.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.1; 103.1; 110.7; 111.3; 115.1; 119.0; 120.2; 123.8; 125.8; 134.3; 140.3; 153.9 ppm. HRMS (MALDI-TOF): calcd. for $C_{13}H_{11}NO$ 197.0841; found 197.0837. IR (neat): $\tilde{\nu}$ = 3399, 3048, 3002, 2844, 1926, 1890, 1626, 1606, 1492, 1474, 1457, 1332, 1293, 1282, 1222, 1197, 1170, 1030, 933, 899, 874, 816, 746, 719, 618 cm^{-1}.

9*H*-Carbazole-3-carbonitrile (4e):[27] The general procedure was followed by using 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzonitrile **3e** (100 mg, 0454 mmol) to give 9*H*-carbazole-3-carbonitrile **4e** (55 mg, 0.286 mmol, 63 % yield) as a pale yellow solid. M.p. 191–199 °C (lit. 184–185 °C). ^{1}H NMR (300 MHz, CD_3CN): δ = 7.29 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H); 7.45–7.54 (m, 1 H); 7.55–7.64 (m, 2 H); 7.65–7.74 (m, 1 H); 8.08–8.19 (m, 1 H); 8.44–8.53 (m, 1 H); 9.8 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 112.3; 112.6; 121.1; 121.4; 122.7; 126.2; 127.9; 129.6 ppm. HRMS (ESI$^+$): calcd. for $C_{13}H_8N_2$ [M + Na]$^+$ 215.0580; found 215.0575. IR (neat): $\tilde{\nu}$ = 3295, 2221, 1627, 1599, 1465, 1406, 1326, 1239, 1223, 1204, 1126, 938, 902, 815, 753, 733, 613 cm^{-1}.

3-Methyl-9*H*-carbazole (4f): The general procedure was followed by using 1-(*p*-tolyl)-1*H*-benzo[*d*][1,2,3]triazole **3f** (100 mg, 0.478 mmol) to give 3-methyl-9*H*-carbazole **4f** (27.4 mg, 0.151 mmol, 32 % yield) as a white solid. M.p. 201–203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 3 H); 7.21–7.26 (m, 1 H); 7.27–7.30 (m, 1 H); 7.33–7.37 (m, 1 H); 7.41–7.45 (m, 2 H); 7.91 (td, *J* = 1.51, 0.76 Hz, 1 H); 7.96 (br. s., 1 H) 8.08 (dq, *J* = 7.7, 0.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4; 110.2; 110.5; 119.2; 120.1; 120.3; 123.2; 123.5; 125.6; 127.2; 128.7; 137.7; 139.8 ppm. HRMS (MALDI-TOF): calcd. for $C_{13}H_{11}N$ 181.0891; found 181.0881. IR (neat): $\tilde{\nu}$ = 3402, 3048, 2912, 2852, 1604, 1492, 1458, 1333, 1292, 1239, 1026, 928, 885, 845, 804, 746, 725 cm^{-1}.

3-Nitro-9*H*-carbazole (4g):[27] The general procedure was followed by using 1-(4-nitrophenyl)-1*H*-benzo[*d*][1,2,3]triazole **3g** (95.9 mg, 0.399 mmol) to give 3-nitro-9*H*-carbazole **4g** (14.1 mg, 0.066 mmol, 17 % yield) as a yellow solid. M.p. 196–202 °C (lit. 213 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.41 (m, 1 H); 7.46–7.50 (m, 1 H); 7.52–7.53 (m, 1 H); 7.54 (dd, *J* = 3.9, 1.0 Hz, 1 H); 8.13–8.19 (m, 1 H); 8.37 (dd, *J* = 9.0, 2.2 Hz, 1 H); 8.45–8.59 (m, 1 H); 9.03 (d, *J* = 2.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.3; 111.3; 117.3; 121.0; 121.2 (2 C); 121.8; 123.2; 127.6; 140.4; 178.7 ppm. HRMS (ESI$^+$): calcd.

for $C_{12}H_8N_2O_2$ [M + Na]$^+$ 235.0478; found 235.0477. IR (neat): $\tilde{\nu}$ = 3294, 3101, 3025, 2919, 2850, 1606, 1582, 1522, 1492, 1473, 1457, 1335, 1279, 1241, 1213, 1193, 1112, 1084, 889, 847, 830, 768, 749, 722, 685, 623 cm^{-1}.

1-Nitro-9*H*-carbazole (4h):[28] The general procedure was followed by using 1-(2-nitrophenyl)-1*H*-benzo[*d*][1,2,3]triazole **3h** (100 mg, 0.416 mol) to give 1-nitro-9*H*-carbazole **4h** (38 mg, 0.179 mmol, 43 % yield) as a yellow solid. M.p. 181–186 °C (lit. 188–189 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.41 (m, 2 H); 7.52–7.63 (m, 2 H); 8.12 (dq, *J* = 7.9, 0.9 Hz, 1 H); 8.33–8.41 (m, 2 H); 10.03 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.6; 118.8; 120.7; 121.3; 122.0; 127.4; 127.5; 127.7; 133.7; 139.7 ppm. HRMS (ESI$^+$): calcd. for $C_{12}H_8N_2O_2$ [M + Na]$^+$ 235.0478; found 235.0479. IR (neat): $\tilde{\nu}$ = 3395, 3038, 1603, 1518, 1457, 1436, 1325, 1279, 1205, 1178, 1143 cm^{-1}.

1-Ethynyl-9*H*-carbazole (4i): The general procedure was followed by using 1-(2-ethynylphenyl)-1*H*-benzo[*d*][1,2,3]triazole **3i** (50 mg, 0.228 mmol) to give 1-ethynyl-9*H*-carbazole **4i** (9.7 mg, 0.051 mmol, 22 % yield) as a pale yellow solid. M.p. 126–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 1 H); 7.21 (t, *J* = 7.7 Hz, 1 H); 7.25–7.31 (m, 2 H); 7.42–7.53 (m, 2 H); 7.58 (dd, *J* = 7.5, 1.0 Hz, 1 H); 8.04–8.13 (m, 2 H); 8.42 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.1; 81.8; 104.3; 110.9; 119.2; 119.9; 120.6; 121.3; 123.1; 123.4; 126.3; 129.1; 139.2; 141.0 ppm. MS (EI): 192.06 (17), 191.03 (M$^{+\cdot}$, 100), 190.04 (31), 164.01 (12), 163.01 (16), 95.4 (10). IR (neat): $\tilde{\nu}$ = 3464, 328, 3061, 2925, 1585, 1493, 1452, 1421, 1316, 1269, 1236, 1215, 1114, 799, 748, 680 cm^{-1}.

3,6-Dimethoxy-9*H*-carbazole (4j):[29] 5-Methoxy-1-(4-methoxyphenyl)-1*H*-benzo[*d*][1,2,3]triazole **3j** (73.9 mg, 0.289 mmol) was dissolved in dry acetonitrile (20 mL), placed in a Rayonet reactor equipped with 254 nm lamps, and irradiated overnight. The solvent was then evaporated and the crude residue was purified with a flash column chromatography Biotage Isolera system (eluent CH_2Cl_2/Et_2O, 95:5) to give 3,6-dimethoxy-9*H*-carbazole **4j** (55.5 mg, 0.244 mmol, 84 % yield) as a white solid. M.p. 105–107 °C (lit. 131–133 °C). ^{1}H NMR (300 MHz, acetone): δ = 3.73 (s, 6 H); 6.87 (dd, *J* = 8.7, 2.5 Hz, 2 H); 7.23 (d, *J* = 8.8 Hz, 2 H); 7.51 (d, *J* = 2.6 Hz, 2 H); 9.80 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 56.2 (2 C); 103.5 (2 C); 112.5 (2 C); 112.6 (2 C); 115.9 (2 C); 136.7 (2 C); 154.4 (2 C) ppm. MS (EI): 228.10 (M$^{+\cdot}$, 38), 227.06 (100), 213.06 (28), 211.98 (77), 184.01 (24), 141.00 (15), 139.92 (10), 113.89 (9), 82.75 (14). IR (neat): $\tilde{\nu}$ = 3417, 3392, 2936, 2536, 1611, 1573, 1481, 1469, 1432, 1201, 1154, 1107, 1026, 820 cm^{-1}.

2,6-Dimethoxy-9*H*-carbazole (4k):[26] 6-Methoxy-1-(4-methoxyphenyl)-1*H*-benzo[*d*][1,2,3]triazole **3k** (68.2 mg, 0.267 mmol) was dissolved in dry acetonitrile (20 mL), placed in Rayonet reactor equipped with 254 nm lamps, and irradiated overnight. The solvent was then evaporated, and the crude mixture was purified with a flash column chromatography Biotage Isolera system (eluent CH_2Cl_2/Et_2O, 95:5) to give 2,6-dimethoxy-9*H*-carbazole **4k** (31.6 mg, 0.139 mmol, 52 % yield) as a pale brown solid. M.p. 156–159 °C (lit. 163–164 °C). ^{1}H NMR (300 MHz, acetone): δ = 3.85 (s, 3 H); 3.86 (s, 3 H); 6.77 (dd, *J* = 8.6, 2.4 Hz, 1 H); 6.94 (dd, *J* = 8.7, 2.5 Hz, 1 H); 6.99 (d, *J* = 2.4 Hz, 1 H); 7.31–7.36 (m, 1 H); 7.57 (d, *J* = 2.4 Hz, 1 H); 7.93 (dd, *J* = 8.6, 0.6 Hz, 1 H); 9.97 (br. s., 1 H) ppm. ^{13}C NMR (75 MHz, acetone): δ = 55.7; 56.2; 95.4; 103.3; 108.6; 112.0; 114.0; 117.9; 121.7; 124.8; 135.8; 143.2; 154.9; 160.1 ppm. MS (EI): 228.10 (M$^{+\cdot}$, 29), 227.08 (100), 213.07 (26), 212.06 (25), 184.04 (45), 169.00 (31), 153.00 (12), 140.99 (28), 139.96 (21), 113.91 (15). IR (neat): $\tilde{\nu}$ = 3459, 3074, 3032, 2938, 2765, 1557, 1522, 1518, 1421, 1382, 1268, 1132, 1036, 871, 736 cm^{-1}.

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