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One-Pot Approach for the Synthesis of Bis-indole-1,4-disubstituted-1,2,3-triazoles

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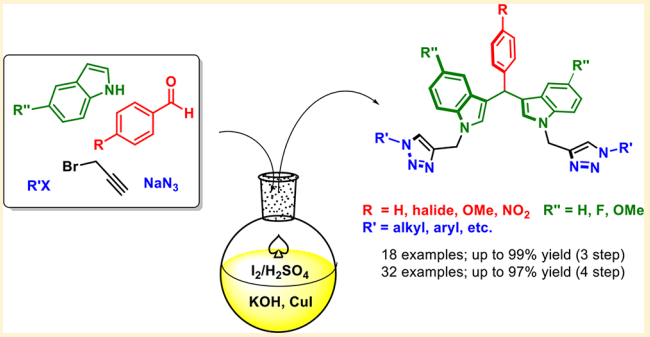
Supporting Information

ABSTRACT: A new strategy for the synthesis of bis-indoletriazoles was developed using a sequential one-pot four-step procedure via I_2 and H_2SO_4−SiO_2 catalyzed Friedel−Crafts reactions of indole with aldehyde followed by *N*-alkylation with propargyl bromide, azidation, and copper(I)-catalyzed azide alkyne cycloaddition (CuAAC). The reaction proceeded smoothly at room temperature in a short time, and a series of bis-indoletriazoles were obtained in good to excellent yields proving the generality of this one-pot methodology.



INTRODUCTION

Indole and triazole are important structural ring systems in pharmacological and agrochemical compounds with various biological properties.[1] Recently, bis-indole has received considerable attention in medicinal chemistry as a main structural scaffold of bioactive natural products and synthetic drugs.[2] Combination of indole or bis-indole and triazole into a single compound for improving the biological efficacy or libraries of analogues for structure−activity studies has been reported.[3] These synthetic compounds exhibited a broad spectrum of biological activities including antitubercular, antiadipogenic, antibacterial, and anticancer activities (Figure 1).[4−8]

Despite the structural diversity and the variety of biological activities observed in indoletriazole compounds, no convenient approach to the synthesis has been disclosed. The previous synthesis reported by Perumal[3] employed separated steps for their preparation which are both time and cost consuming. Therefore, this work aimed to develop an efficient strategy to complete an entire multistep sequence in a single pot for the synthesis of bis-indoletriazoles eliminating the need for workup and product isolation between successive synthetic steps.

The synthesis of bis-indole-1,4-disubstituted-1,2,3-triazoles derivatives was designed via Friedel−Crafts reactions, *N*-propargylation, azidation, and the CuAAC reaction as a sequential one-pot four-step reaction resulting in a high-yielding, scalable, and convergent approach.

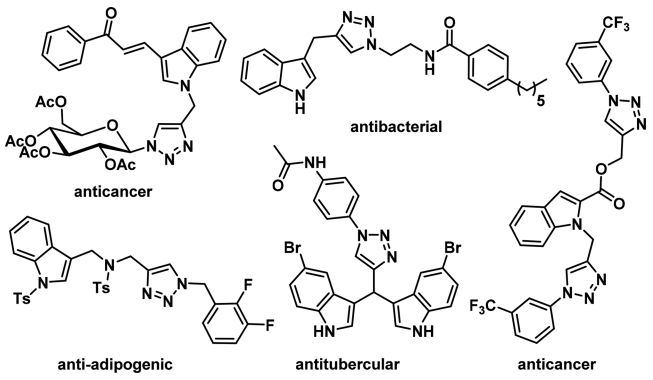


Figure 1. Structure of bioactive compounds containing indole and triazole moieties.

RESULTS AND DISCUSSION

First a possible one-pot three-step method was investigated for preparing bisindole-triazole by screening Brønsted and Lewis acids as catalysts for Friedel−Crafts reactions of indole **1a** (2.2 equiv) and *p*-chlorobenzaldehyde **2a** in acetonitrile for in situ generation of bisindole (Table 1). Then the *N*-propargylation step was carried out with propargyl bromide for 1 h using KOH as a base in the presence of acetonitrile to give products in high yield. Changing to other bases such as NaOH or NaH gave a low yield of product. In the same pot, copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction of the resulting *N*-propargylindole with benzyl azide for 1 h at room temperature was carried out to obtain product **3a**.

In the screening of an acid and a Lewis acid in the Friedel−Crafts step,[9] molecular iodine (I_2) was initially investigated and

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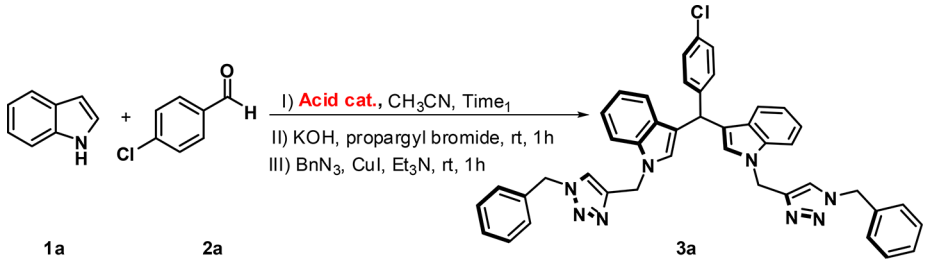
Table 1. Optimization Studies for the Synthesis of 3a via a One-Pot Three-Step Reaction



Entry	Acid cat. (equiv)	$Time_1$ (min)	Yield (%)[a]
1	I_2 (0.2)	20	58
2	$ZnCl_2$ (0.2)	20	23
3	$FeCl_3$ (0.2)	24 (h)	48
4	$Bi(OTf)_3$ (0.2)	30	90
5[b]	H_2SO_4–SiO_2	20	66
6[b]	Amberlyst 15	60	95
7[b]	**H_2SO_4–SiO_2/I_2 (0.15)**	**15**	**98**
8[b]	H_2SO_4–SiO_2/$ZnCl_2$ (0.15)	30	39
9[b]	H_2SO_4–SiO_2/$FeCl_3$ (0.15)	15	82
10[c]	$KHSO_4$ (1.0)	60	58

[a]Reaction conditions: **1a** (0.44 mmol), **2a** (0.2 mmol), KOH (1.9 mmol), CuI (0.06 mmol), propargyl bromide (0.6 mmol), Et_3N (0.6 mmol), BnN_3 (0.6 mmol), and CH_3CN (0.6 mL). [b]Amount of acid catalyst (H_2SO_4–SiO_2 or Amberlyst 15) = 20 mg. [c]Using $KHSO_4$ in MeOH (Perumal's conditions),[3] no reaction was observed in the second step.

the first step reaction was completed within 20 min affording the desired product **3a** in 58% yield after *N*-propargylation and click reactions (Table 1, entry 1). Using $ZnCl_2$, $FeCl_3$, or H_2SO_4–SiO_2[19] as catalyst, low to moderate yields of product were obtained (entries 2, 3 ,and 5). By changing the catalyst to $Bi(OTf)_3$ and Amberlyst 15, the yield of **3a** was increased to 90–95% (entries 4 and 6); however, the reaction with Amberlyst 15 required longer reaction times. Using H_2SO_4 supported on Silica gel mixed with 15 mol % Lewis acid had improved the reaction efficiency compared with the reaction without H_2SO_4–SiO_2 (entries 5 and 7–9). H_2SO_4–SiO_2/I_2 was found to be the most effective catalyst producing **3a** with a 98% yield in a short reaction time (entry 7). On the basis of these findings, entry 7 was selected as an optimal condition for synthesizing other analogues. It should be noted that the reaction failed to give the desired product in our one-pot procedure when employing Perumal's conditions ($KHSO_4$ as the Lewis acid in MeOH).[3] Applying $KHSO_4$ as the Lewis acid to our one-pot process gave a 58% yield of product. When aliphatic aldehydes such as propanal were employed as the substrate instead of aromatic aldehydes under the conditions in entry 7, the reaction gave a 28% yield of product.

With the optimized reaction conditions, a range of aromatic aldehydes and alkyl azides were investigated. The results are summarized in Table 2, and a variety of aldehyde derivatives **2a–2e** bearing either electron-donating groups such as 4-methoxy and electron-withdrawing groups such as 4-chloro, 4-fluoro, and 4-nitro at the *para* position of benzaldehyde gave the desired products **3a–3e** in 17–98% yields. Benzaldehyde **2b**, 4-Cl-benzaldehydes **2a**, and 4-F-benzaldehydes **2c** gave excellent yields of bisindole-triazole products. Electron-donating groups (*p*-methoxybenzaldehyde) exhibited a slightly lower reactivity in the Friedel–Crafts step to afford **3d** in 78% yield after stirring for 60 min. In contrast the strong functionalized electron-deficient aldehyde **2e** was smoothly reacted with indole **1a** in the first step (with observation on TLC) but gave low reactivity with propargyl bromide in the *N*-propargylation step which led to **3e** in poor yield.

A variety of organoazides bearing substituted benzyl, ether, and esters functionalized with alkyl, long chain aliphatic alkyl, and tetra-*O*-acetyl-glucosyl groups were investigated, and the reactions generally proceeded smoothly, affording the corresponding products **3f–3r** in good to excellent yields. With these successful results for the one-pot three-step Friedel–Crafts *N*-propargylation and CuAAC reactions for the synthesis of bis-indole-1,4-disubstituted-1,2,3-triazole derivatives, the next step was to extend the procedure to a one-pot four-step reaction. This can better utilize the reactions by reducing the process in preparing the exposure-azides by in situ preparation from corresponding alkyl halides and sodium azide in the reactor.[10–15] The results are shown in Table 3.

The optimal conditions for the one-pot four-step synthesis of bisindoletriazole were studied, and it was found that including the additional step of azidation required the solvent to be changed to DMF in the final step. DMF proved to be the best choice over acetonitrile, THF, water, and PEG-400, providing a high yield of product in a short reaction time. Moreover, using alkyl halide in the azidation step was found to give yields of bisindoletriazole products **4a–4f** higher than in the case of alkyl mesylate as shown in Table 3.

A range of aldehydes, indoles, and alkyl halides were examined using the one-pot four-step reaction, and the results are summarized in Table 4. Using benzyl bromide in the azidation step, a variety of substituted benzaldehydes were investigated and they similarly gave good yields of benzyl-triazole-bisindoles **4a** and **4i–4l** as the one-pot three-step method in Table 1 except nitrobenzaldehyde **2e**.

Next, a range of substituted methoxy- and fluoro-benzaldehydes were studied together with a number of substituted benzyl bromides, and compounds **4m–4s** were obtained in high yields. Using aliphatic bromide in the azidation step such as *n*-butyl and *n*-octyl bromide, compounds **4t–4y** were produced in moderate to high yields. Fluoroindole

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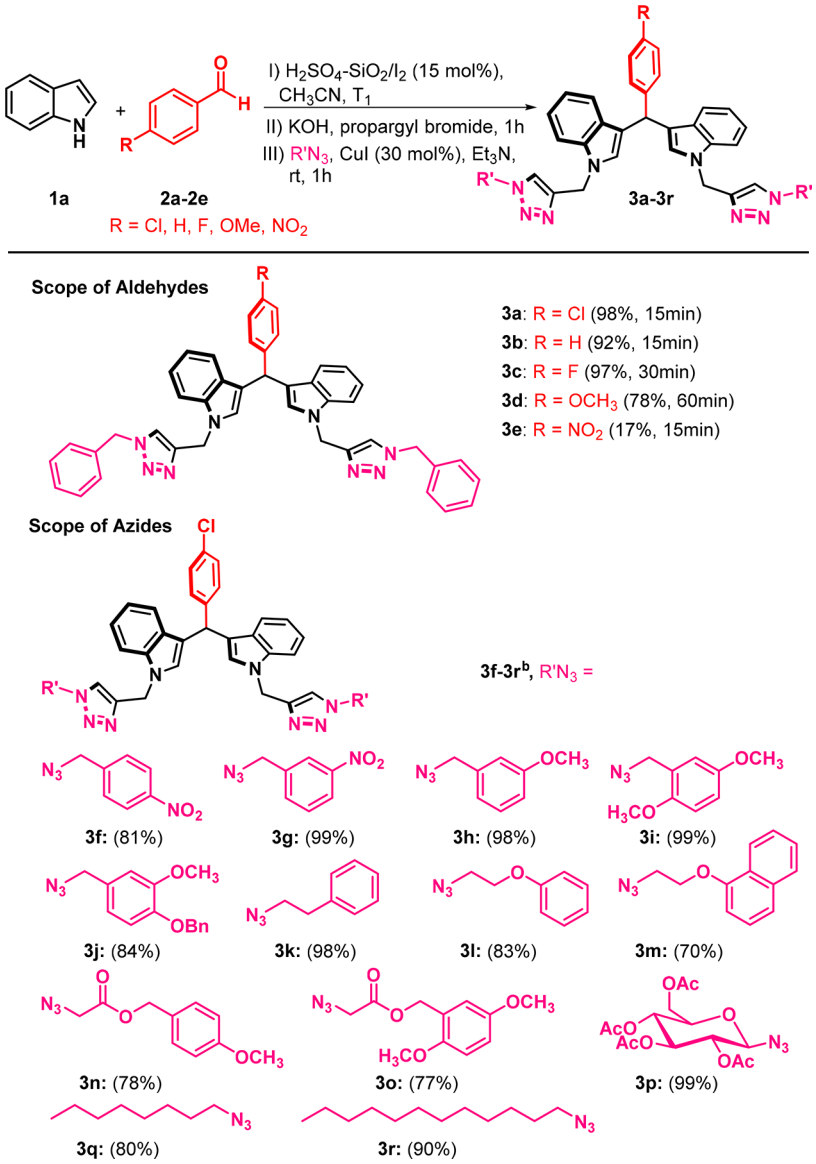
Table 2. Range of Aldehydes and Alkyl Azides Studied



[a]Reaction conditions: **1a** (0.44 mmol), aldehyde (0.2 mmol), KOH (1.9 mmol), propargyl bromide (0.6 mmol), CuI (0.06 mmol), Et_3N (0.6 mmol), R′N_3 (0.6 mmol), and CH_3CN (0.6 mL). [b]T_1 = 15 min.

and methoxyindole were also investigated and performed well to yield the corresponding products **4z**–**4cc** in good to excellent yields under the one-pot conditions.

Furthermore, the one-pot four-step reaction is applicable for the synthesis of bis-indole tetra-triazoles and tetraindole-tetratriazole derivatives[16−18] (Schemes 1 and 2). The reaction of *p*-chlorobenzaldehyde **2a** and 5-hydroxyindole **1d** smoothly proceeded by using the one-pot procedure to give **5** in good yields. When indole was treated with terephthalaldehyde under the optimized conditions, tetraindole-tetratriazole **7** was obtained in good yields proving the efficiency of the one-pot method.

CONCLUSIONS

An efficient protocol was developed for the sequential one-pot four-step synthesis of bis-indole-1,4-disubstituted-1,2,3-triazoles from Friedel–Crafts reactions using H_2SO_4–SiO_2/I_2 as a Lewis acid catalyst, N-propargylation, and azides generated in situ from alkyl halides and sodium azide followed by the final step click reaction. The reactions gave high yields of product under mild conditions and are compatible with many functional groups, which can save time and cost and only requires chromatographic purification of the final product, making this process even more user-friendly and safe.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a BRUKER AVANC 400 and 100 MHz instrument. All spectra were measured in $CDCl_3$ solvent, and chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ(^{1}H), 7.26; δ(^{13}C), 77.0 ppm) as an internal standard. Data are reported as follows; chemical shift (multiplicity, integrated intensity or assignment, coupling constants in Hz, assignment). High-resolution mass spectra (HRMS) data were obtained with a Finnigan MAT 95. Infrared spectra were determined on a PERKIN ELMER

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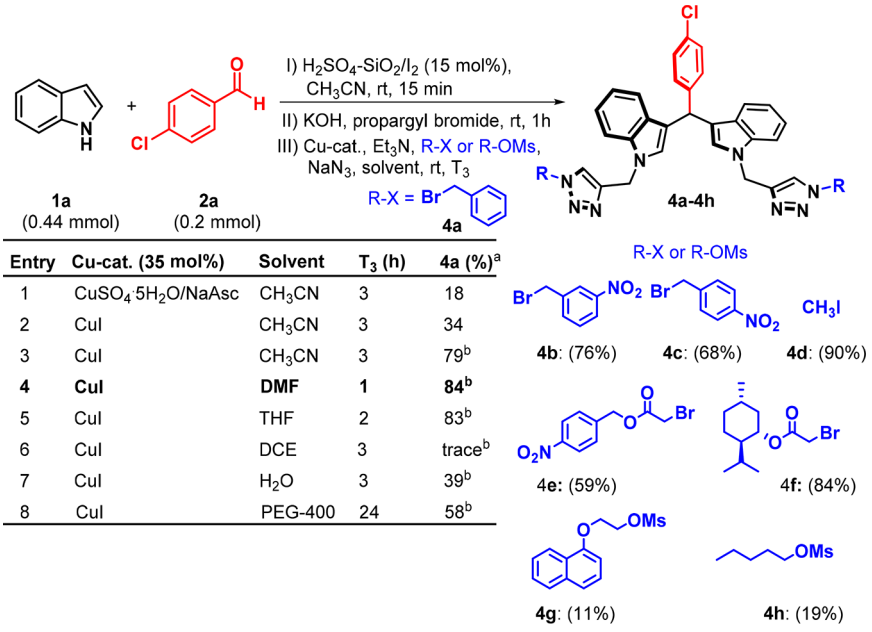
Table 3. Optimization Studies for the Synthesis of 4a via the One-Pot Four-Step Reaction



Entry	Cu-cat. (35 mol%)	Solvent	T_3 (h)	4a (%)[a]
1	$CuSO_4 \cdot 5H_2O$/NaAsc	CH_3CN	3	18
2	CuI	CH_3CN	3	34
3	CuI	CH_3CN	3	79[b]
4	**CuI**	**DMF**	**1**	**84[b]**
5	CuI	THF	2	83[b]
6	CuI	DCE	3	trace[b]
7	CuI	H_2O	3	39[b]
8	CuI	PEG-400	24	58[b]

[a]Reaction conditions: KOH (1.9 mmol), propargyl bromide, Et_3N, BnBr, NaN_3 (0.6 mmol), and CH_3CN (0.6 mL). [b]Mix of benzyl bromide and NaN_3 in solvent previously added to reaction.

FT/IR-2000S spectrophotometer and are reported in wavenumber (cm^{-1}). Analytical thin-layer chromatography (TLC) was conducted on precoated TLC plates; silica gel 60F-254 [E. Merck, Darmstadt, Germany]. Silica gel columns for open-column chromatography utilized silica gel 60 PF254 [E. Merck, Darmstadt, Germany]. Melting points were measured using a Melting point apparatus (Griffin) and are uncorrected. Sulfuric acid immobilized on silica gel (H_2SO_4–SiO_2) was prepared according to the literature procedure.[18]

General Procedure for One-Pot Three-Step Bis-indole Triazole Derivatives. For the first step, a stirred solution of indole **1** (1.1 mmol) in CH_3CN (1 mL) was mixed with the aldehyde **2** (0.5 mmol). Then I_2 powder (9.5 mg, 0.075 mmol) and H_2SO_4–SiO_2 (20 mg) were added while the stirring was continued at room temperature. TLC showed the conversion was complete. In the second step, KOH (266.5 mg, 4.75 mmol) and propargyl bromide (0.1 mL, 1.5 mmol) were added at room temperature, and the stirring was continued for 1 h. The reaction mixture was filtered to remove salt, and the solvent of the filtrate was evaporated to dryness. The reaction mixture was then redissolved in CH_3CN (1 mL). Finally, alkyl azide (1.5 mmol), CuI (33.3 mg, 0.175 mmol), and Et_3N (0.2 mL, 1.5 mmol) were added to the reaction mixture and stirred at room temperature for 1 h. After completion of the reaction, it was quenched with saturated cool aqueous $Na_2S_2O_3$ (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was collected and washed with water (3 × 5 mL), then dried with anhydrous Na_2SO_4, filtered, and evaporated in *vacuo*. The crude product was purified by silica gel column chromatography (SiO_2, 40–50% EtOAc/*n*-Hexane as eluent) to afford bis-indole-1,4-disubstituted-1,2,3-triazoles **3**.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 3a. 98% yield (0.1365 g) as a pink solid; mp 182–183 °C; R_f = 0.13 (40% EtOAc/*n*-Hexane); IR (KBr): 3135, 3052, 2922, 2851, 1634, 1489, 1466, 1332, 804, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 10H), 7.20–7.12 (m, 10H), 7.07 (s, 2H), 6.94 (t, J = 7.6 Hz, 2H), 6.59 (s, 2H), 5.79 (s, 1H), 5.40 (s, 4H), 5.29 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 142.2, 136.5, 134.4, 131.7, 129.8, 128.9, 128.6, 128.3, 127.8, 127.4, 127.1, 121.8, 121.5, 119.8, 119.1, 118.4, 109.6, 53.9, 41.8, 39.4; HRMS (ESI) m/z $C_{43}H_{35}ClN_8$ $(M + H)^+$ calcd 699.2751, found 699.2752.

3,3′-(Phenylmethylene)-bis-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 3b.[3] CAS Number 1174761-01-3; 92% yield (0.1220 g) as a pink solid; mp 94–96 °C; R_f = 0.48 (50% EtOAc/*n*-Hexane); IR (KBr): 3135, 3054, 2923, 2851, 1611, 1480, 1466, 1332, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 12H), 7.23–7.12 (m, 9H), 7.05 (s, 2H), 6.92 (t, J = 7.6 Hz, 2H), 6.59 (s, 2H), 5.82 (s, 1H), 5.40 (s, 4H), 5.30 (s, 2H), 5.29 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 143.6, 136.5, 134.4, 128.9, 128.6, 128.5, 128.2, 127.8, 127.6, 127.1, 126.1, 121.7, 121.6, 119.9, 119.0, 118.9, 109.5, 53.9, 41.9, 40.0.

3,3′-(4-Fluorophenylmethylene)-bis-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 3c. 97% yield (0.1530 g) as a pink solid; mp 102–103 °C; R_f = 0.54 (50% EtOAc/*n*-Hexane); IR (KBr): 3135, 3052, 2922, 2851, 1634, 1506, 1466, 1332, 1221, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.25 (m, 10H), 7.21–7.09 (m, 8H), 7.04 (s, 2H), 6.91 (t, J = 7.6 Hz, 2H), 6.88 (t, J = 8.8 Hz, 2H), 6.55 (s, 2H), 5.77 (s, 1H), 5.38 (s, 4H), 5.27 (s, 2H), 5.26 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 243.0 Hz), 144.9, 139.4 (d, J = 3.0 Hz), 136.5, 134.4, 129.8 (d, J = 8.0 Hz), 128.9, 128.5, 127.7, 127.4, 127.0, 121.8, 121.5, 119.8, 119.0, 118.7, 114.8 (d, J = 21.0 Hz), 109.5, 53.9, 41.8, 39.2; HRMS (ESI) m/z $C_{43}H_{35}FN_8Na$ $(M + Na)^+$ calcd 705.2866, found 705.2870.

3,3′-(4-Methoxyphenylmethylene)-bis-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 3d.[3] CAS Number 1174761-04-6; 78% yield 0.1240 g) as an orange solid; mp 153–155 °C; R_f = 0.38 (50% EtOAc/*n*-Hexane); IR (KBr): 3137, 3052, 2923, 2851, 1610, 1509, 1465, 1331, 1265, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 10H), 7.20–7.10 (m, 8H), 7.05 (s, 2H), 6.92 (t, J = 7.6 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 6.58 (s, 2H), 5.77 (s, 1H), 5.40 (s, 4H), 5.30 (s, 2H), 5.29 (s, 2H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.8, 145.2, 136.6, 135.8, 134.4, 129.4, 128.9, 128.6, 127.8, 127.4, 127.0, 121.7, 121.5, 120.0, 119.3, 118.9, 113.5, 109.5, 55.0, 53.9, 41.9, 39.1.

3,3′-(4-Nitrophenylmethylene)-bis-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 3e. 17% yield (0.0247 g) as a yellow solid; mp 181–182 °C; R_f = 0.22 (50% EtOAc/*n*-Hexane); IR (KBr): 3133, 3054, 2923, 2852, 1660, 1497, 1519, 1466, 1344, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.37–7.28 (m, 10H), 7.20–7.15 (m, 6H), 7.12 (s, 2H), 6.96 (t, J = 7.2 Hz, 2H), 6.63 (s, 2H), 5.92 (s, 1H), 5.42 (s, 4H), 5.30 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.6, 146.5, 144.9, 136.6,

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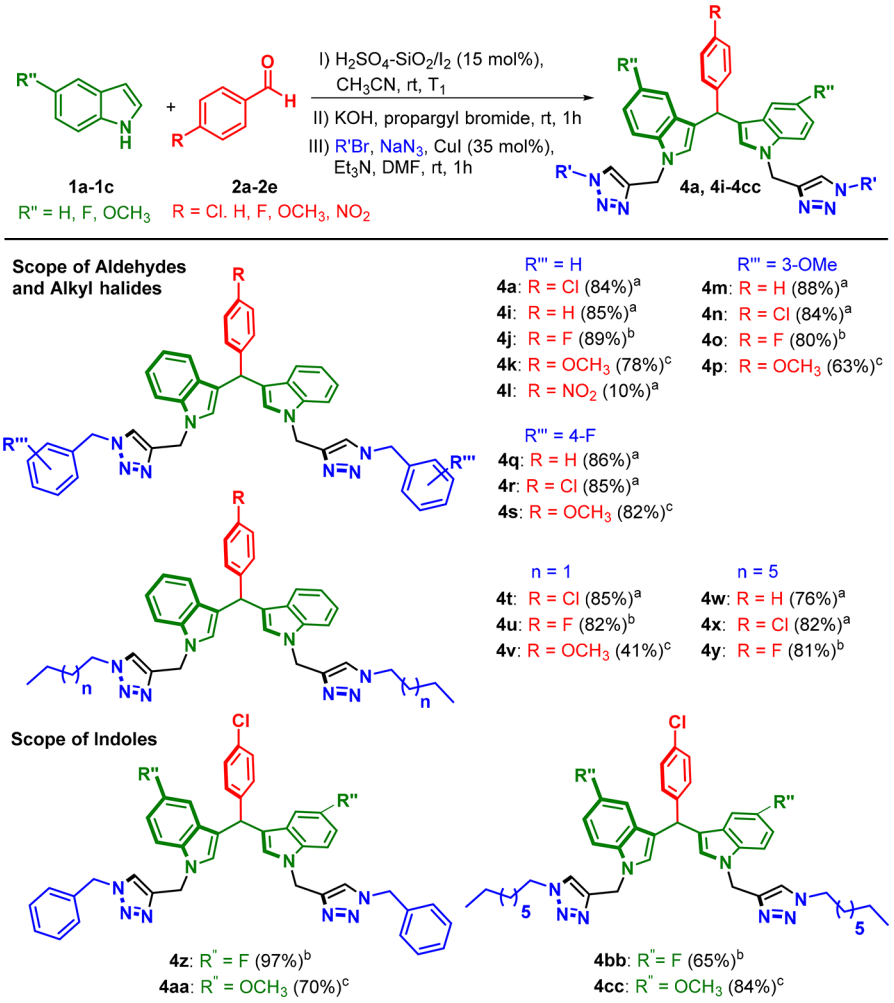
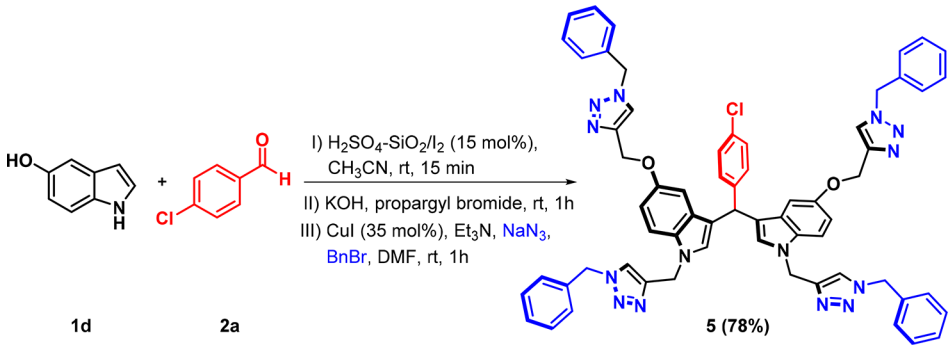
Table 4. Range of Aldehydes, Indoles, and Alkyl Halides Studied



[a]T_1 = 15 min. [b]T_1 = 30 min. [c]T_1 = 60 min.

Scheme 1. One-Pot Four-Step Synthesis of 5 Using 5-Hydroxyindole



134.4, 129.3, 129.1, 128.8, 127.9, 127.3, 127.2, 123.6, 122.2, 121.6, 119.6, 119.4, 117.4, 109.7, 54.1, 42.0, 40.0; HRMS (ESI) *m*/*z* $C_{43}H_{35}N_9O_2Na$ (M + Na)$^+$ calcd 732.2811, found 732.2808.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(4-nitrobenzyl)-1,2,3-triazol-4-yl)methyl) 3f. 81% yield (0.1278 g) as a red solid; mp 109−111 °C; R_f = 0.05 (40% EtOAc/*n*-Hexane); IR (KBr): 3127, 3042, 2922, 2851, 1609, 1489, 1522, 1466, 1347, 804, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.8 Hz, 4H), 7.33−7.26 (m, 8H), 7.23−7.10 (m, 8H), 6.93 (t, J = 7.6 Hz, 2H), 6.65 (s, 2H), 5.79 (s, 1H), 5.48 (s, 4H), 5.30 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9, 145.4, 142.2, 141.4, 136.5, 131.8, 129.8, 128.4, 128.3, 127.5, 127.1, 124.1, 122.0, 121.9, 119.9, 119.2, 118.6, 109.5, 52.9, 41.8, 39.4; HRMS (ESI) *m*/*z* $C_{43}H_{33}ClN_{10}O_4Na$ (M + Na)$^+$ calcd 811.2272, found 811.2278.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(3-nitrobenzyl)-1,2,3-triazol-4-yl)methyl) 3g. 99% yield (0.1570 g) as a pink solid; mp 105−108 °C; R_f = 0.06 (40% EtOAc/*n*-Hexane); IR (KBr): 3137, 3053, 2925, 2852, 1612, 1530, 1465, 1350, 806, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−8.16 (m, 2H), 8.05 (s, 2H), 7.57−7.50 (m, 4H), 7.32 (t, J = 7.6 Hz, 4H), 7.23−7.12 (m, 8H), 6.95 (t, J = 7.2 Hz, 2H), 6.63 (s, 2H), 5.80 (s, 1H), 5.53 (s, 4H), 5.32 (brs, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 145.4, 142.2, 136.5, 133.8, 131.7, 130.1, 129.8, 128.3, 127.4, 127.1, 123.6,

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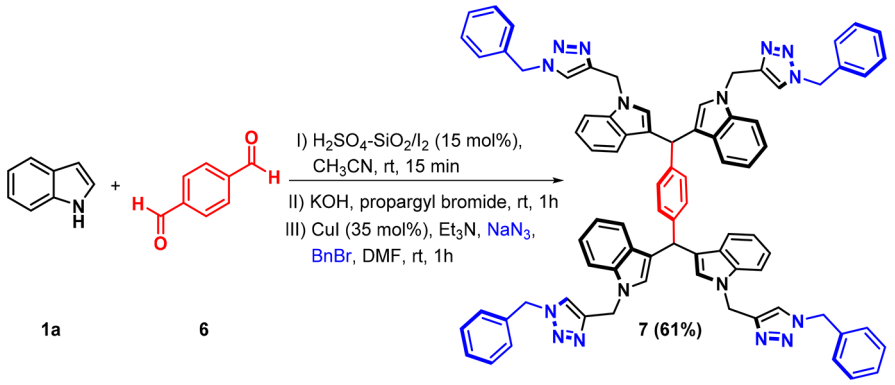
Scheme 2. One-Pot Four-Step Synthesis of 7 Using Terephthalaldehyde



122.6, 121.9, 119.8, 119.2, 118.6, 109.5, 52.8, 41.7, 39.4; HRMS (ESI) m/z $C_{43}H_{33}ClN_{10}O_4Na$ $(M + Na)^+$ calcd 811.2272, found 811.2282.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(3-methoxybenzyl)-1,2,3-triazol-4-yl)methyl) 3h. 98% yield (0.1485 g) as a pink solid; mp 98−100 °C; R_f = 0.14 (50% EtOAc/*n*-Hexane); IR (KBr): 3135, 3052, 2923, 2851, 1602, 1490, 1465, 1332, 1264, 777, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.20 (brs, 4H), 7.15 (t, J = 7.6 Hz, 2H), 7.11 (s, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.87 (dd, J = 8.4, 1.6 Hz, 2H), 6.76 (t, J = 7.6 Hz, 2H), 6.70 (brs, 2H), 6.62 (s, 2H), 5.81 (s, 1H), 5.36 (s, 4H), 5.29 (s, 4H), 3.73 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 145.0, 142.2, 136.5, 135.8, 131.7, 130.1, 129.8, 128.3, 127.5, 127.1, 121.9, 121.6, 120.0, 119.8, 119.1, 118.4, 114.0, 113.4, 109.6, 55.2, 53.9, 41.9, 39.4; HRMS (ESI) m/z $C_{45}H_{39}ClN_8O_2Na$ $(M + Na)^+$ calcd 781.2782, found 781.2777.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(2,3-dimethoxybenzyl)-1,2,3-triazol-4-yl)methyl) 3i. 99% yield (0.1692 g) as a pink solid; mp 94−95 °C; R_f = 0.17 (50% EtOAc/*n*-Hexane); IR (KBr): 3139, 3053, 2923, 2851, 1613, 1505, 1465, 1331, 1228, 808, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.20 (s, 4H), 7.17−7.11 (m, 4H), 6.94 (t, J = 7.6 Hz, 2H), 6.83 (dd, J = 8.8, 2.0 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.66 (brs, 2H), 6.61 (s, 2H), 5.80 (s, 1H), 5.39 (s, 4H), 5.29 (s, 4H), 3.67 (s, 6H), 3.64 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 151.1, 144.5, 142.4, 136.6, 131.7, 129.9, 128.3, 127.5, 127.2, 123.6, 122.0, 121.8, 119.8, 119.1, 118.3, 115.8, 114.7, 111.7, 109.7, 55.7, 55.6, 49.1, 42.0, 39.5; HRMS (ESI) m/z $C_{47}H_{43}ClN_8O_4Na$ $(M + Na)^+$ calcd 841.2993, found 841.2997.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(4-benzyloxy-3-methoxybenzyl)-1,2,3-triazol-4-yl)methyl) 3j. 84% yield (0.1627 g) as a red solid; mp 94−95 °C; R_f = 0.15 (40% EtOAc/*n*-Hexane); IR (KBr): 3139, 3053, 2923, 2851, 1633, 1515, 1466, 1332, 1265, 784, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.27 (m, 14H), 7.20 (s, 4H), 7.14 (t, J = 7.6 Hz, 2H), 7.08 (s, 2H), 6.94 (t, J = 7.2 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.74−6.67 (m, 4H), 6.60 (s, 2H), 5.79 (s, 1H), 5.31 (s, 4H), 5.28 (s, 4H), 5.13 (s, 4H), 3.76 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.0, 148.5, 145.0, 142.3, 136.7, 136.6, 131.8, 129.9, 128.5, 128.3, 127.9, 127.5, 127.3, 127.2, 121.9, 121.4, 120.5, 119.9, 119.1, 118.4, 113.9, 111.5, 109.6, 71.0, 56.0, 53.9, 42.0, 39.5; HRMS (ESI) m/z $C_{59}H_{51}ClN_8O_4Na$ $(M + Na)^+$ calcd 993.3619, found 993.3629.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-phenylethyl-1,2,3-triazol-4-yl)methyl) 3k. 98% yield (0.1489 g) as a pink solid; mp 83−85 °C; R_f = 0.16 (40% EtOAc/*n*-Hexane); IR (KBr): 3136, 3057, 2924, 2853, 1612, 1488, 1465, 1333, 804, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8.8 Hz, 4H), 7.24 (s, 4H), 7.20−7.12 (m, 8H), 7.02−6.94 (m, 6H), 6.85 (s, 2H), 6.60 (s, 2H), 5.82 (s, 1H), 5.27 (brs, 4H), 4.45 (t, J = 7.0 Hz, 4H), 3.09 (t, J = 7.2 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 142.3, 136.8, 136.6, 131.8, 129.9, 128.7, 128.5, 128.4, 127.6, 127.2, 127.0, 121.9, 119.9, 119.2, 118.4, 109.6, 51.6, 42.0, 39.5, 36.6; HRMS (ESI) m/z $C_{45}H_{39}ClN_8Na$ $(M + Na)^+$ calcd 749.2884, found 749.2887.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-phenoxyethyl-1,2,3-triazol-4-yl)methyl) 3l. 83% yield (0.1252 g) as a pink solid; mp 92−94 °C; R_f = 0.17 (50% EtOAc/*n*-Hexane); IR (KBr): 3140, 3052, 2923, 2851, 1599, 1489, 1466, 1333, 1242, 790, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 6H), 7.27−7.13 (m, 10H), 7.00 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.2 Hz, 2H), 6.72 (d, J = 8.4 Hz, 4H), 6.64 (s, 2H), 5.83 (s, 1H), 5.31 (s, 4H), 4.62 (t, J = 4.8 Hz, 4H), 4.26 (t, J = 4.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.6, 144.6, 142.3, 136.6, 131.7, 129.9, 129.5, 128.3, 127.5, 127.2, 122.8, 121.9, 121.6, 119.9, 119.1, 118.5, 114.5, 109.6, 66.0, 49.6, 41.9, 39.4; HRMS (ESI) m/z $C_{45}H_{39}ClN_8O_2Na$ $(M + Na)^+$ calcd 781.2782, found 781.2779.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-naphthyloxyethyl-1,2,3-triazol-4-yl)methyl) 3m. 45% yield (0.0767 g) as a red solid; mp 106−108 °C; R_f = 0.04 (50% EtOAc/*n*-Hexane); IR (KBr): 3133, 3053, 2923, 2851, 1632, 1581, 1464, 1333, 1269, 794, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.48−7.42 (m, 4H), 7.37−7.27 (m, 10H), 7.16−7.07 (m, 6H), 6.96 (t, J = 7.6 Hz, 2H), 6.69 (d, J = 7.6 Hz, 2H), 6.61 (s, 2H), 5.74 (s, 1H), 5.28 (s, 4H), 4.71 (t, J = 4.8 Hz, 4H), 4.39 (t, J = 4.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 144.9, 142.2, 136.6, 134.4, 131.7, 129.9, 128.3, 127.6, 127.5, 127.2, 126.6, 125.6, 125.6, 125.2, 122.6, 122.0, 121.3, 121.2, 120.0, 119.2, 118.5, 109.5, 105.0, 66.3, 49.7, 41.9, 39.4; HRMS (ESI) m/z $C_{53}H_{43}ClN_8O_2Na$ $(M + Na)^+$ calcd 881.3095, found 881.3087.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(4-methoxybenzyldiacetyl)-1,2,3-triazol-4-yl)methyl) 3n. 78% yield (0.1352 g) as a pink solid; mp 78−79 °C; R_f = 0.10 (50% EtOAc/*n*-Hexane); IR (KBr): 3140, 3052, 2934, 2838, 1751, 1614, 1516, 1465, 1333, 1249, 804, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.24−7.22 (m, 8H), 7.19 (s, 2H), 7.16 (t, J = 7.5 Hz, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.86 (d, J = 8.4 Hz, 4H), 6.64 (s, 2H), 5.83 (s, 1H), 5.34 (s, 2H), 5.33 (s, 2H), 5.10 (s, 4H), 5.02 (s, 4H), 3.79 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 159.9, 145.0, 142.3, 136.5, 131.7, 130.3, 129.8, 128.3, 127.4, 127.1, 126.5, 123.0, 121.9, 119.8, 119.1, 118.6, 114.0, 109.5, 67.7, 55.1, 50.6, 41.7, 39.3; HRMS (ESI) m/z $C_{49}H_{43}ClN_8O_6Na$ $(M + Na)^+$ calcd 897.2892, found 897.2899.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(2,3-dimethoxybenzyldiacetyl)-1,2,3-triazol-4-yl)methyl) 3o. 77% yield (0.1434 g) as a pink solid; mp 95−96 °C; R_f = 0.07 (50% EtOAc/*n*-Hexane); IR (KBr): 3143, 3053, 2922, 2851, 1754, 1633, 1505, 1466, 1333, 1223, 805, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 4H), 7.26−7.22 (m, 6H), 7.16 (t, J = 7.2 Hz, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.86−6.79 (m, 6H), 6.65 (s, 2H), 5.83 (s, 1H), 5.35 (s, 2H), 5.34 (s, 2H), 5.20 (s, 4H), 5.06 (s, 4H), 3.76 (s, 6H), 3.74 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 153.4, 151.8, 145.3, 142.2, 136.6, 131.8, 130.0, 128.4, 127.6, 127.2, 123.6, 123.1, 122.0, 119.9, 119.2, 118.8, 116.2, 114.5, 111.6, 109.6, 63.5, 56.0, 55.7, 50.8, 41.9, 39.4; HRMS (ESI) m/z $C_{51}H_{47}ClN_8O_8Na$ $(M + Na)^+$ calcd 957.3103, found 957.3101.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(β-tetraacetylglucose)-1,2,3-triazol-4-yl)methyl) 3p. 99% yield

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(0.2326 g) as a red solid; mp 122−124 °C; R_f = 0.10 (50% EtOAc/*n*-Hexane); IR (KBr): 3138, 3054, 2926, 2853, 1755, 1613, 1489, 1466, 1368, 1224, 805, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.40 (s, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.31−7.22 (m, 4H), 7.20 (t, J = 7.2 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 6.71 (s, 1H), 6.68 (s, 1H), 5.85 (s, 1H), 5.79 (d, J = 8.8 Hz, 2H), 5.40−5.30 (m, 8H), 5.21 (t, J = 9.6 Hz, 2H), 4.27 (ddd, J = 12.8, 8.4, 5.2 Hz, 2H), 4.11 (brd, J = 12.4 Hz, 2H), 3.96 (brdd, J = 10.0, 3.6 Hz, 2H), 2.05 (s, 6H), 2.04 (s, 6H), 2.02 (s, 3H), 2.00 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 169.3, 168.7, 168.7, 145.5, 145.4, 142.3, 136.6, 136.6, 131.8, 130.0, 128.4, 127.7, 127.6, 127.3, 122.0, 120.3, 120.2, 120.0, 119.99, 119.3, 119.28, 118.7, 118.66, 109.6, 109.56, 85.6, 85.57, 75.2, 75.1, 72.6, 70.1, 70.0, 67.7, 67.6, 61.5, 61.47, 41.9, 41.8, 39.5, 20.6, 20.5, 19.9, 19.8; HRMS (ESI) m/z $C_{57}H_{59}ClN_8O_{18}Na$ $(M + Na)^+$ calcd 1201.3534, found 1201.3534.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-octhyl-1,2,3-triazol-4-yl)methyl) 3q. 80% yield (0.1183 g) as a red oil; R_f = 0.36 (40% EtOAc/*n*-Hexane); IR (KBr): 3133, 3053, 2925, 2854, 1633, 1488, 1466, 1332, 804, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25−7.22 (m, 4H), 7.18 (t, J = 7.6 Hz, 2H), 7.10 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.65 (s, 2H), 5.84 (s, 1H), 5.33 (s, 4H), 4.22 (t, J = 7.2 Hz, 4H), 1.84−1.79 (m, 4H), 1.27−1.24 (m, 20H), 0.87 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 142.2, 136.5, 131.6, 129.8, 128.2, 127.4, 127.1, 121.8, 121.3, 119.7, 119.0, 118.3, 109.5, 50.2, 41.9, 39.4, 31.5, 30.0, 28.8, 28.7, 26.2, 22.4, 13.9; HRMS (ESI) m/z $C_{45}H_{55}ClN_8Na$ $(M + Na)^+$ calcd 765.4136, found 765.4135.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-dodecyl-1,2,3-triazol-4-yl)methyl) 3r. 90% yield (0.1532 g) as a brown oil; R_f = 0.35 (30% EtOAc/*n*-Hexane); IR (KBr): 3133, 3055, 2925, 2854, 1614, 1489, 1466, 1333, 803, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.09 (s, 2H), 7.00 (t, J = 7.2 Hz, 2H), 6.64 (s, 2H), 5.84 (s, 1H), 5.33 (s, 4H), 4.22 (t, J = 7.2 Hz, 4H), 1.80 (quin., J = 7.6 Hz, 4H), 1.24 (brs, 36H), 0.88 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.5, 142.3, 136.6, 131.8, 129.9, 128.3, 127.5, 127.2, 121.9, 121.3, 119.8, 119.1, 118.4, 109.6, 50.3, 42.0, 39.5, 31.8, 30.1, 29.5, 29.4, 29.3, 29.2, 28.9, 26.4, 14.0; HRMS (ESI) m/z $C_{53}H_{71}ClN_8Na$ $(M + Na)^+$ calcd 877.5388, found 877.5384.

General Procedure for One-Pot Four-Step Bis-indole Triazoles Derivatives. In the first step, a stirred solution of indole **1** (1.1 mmol) in CH_3CN (1 mL) was mixed with aldehyde **2** (0.5 mmol), I_2 powder (9.5 mg, 0.075 mmol), and H_2SO_4−SiO_2 (20 mg) at room temperature. TLC showed the conversion was complete. In the second step, KOH (266.5 mg, 4.75 mmol) and propargyl bromide (0.1 mL, 1.5 mmol) were added at room temperature, and the stirring was continued for 1 h. The reaction mixture was filtered to remove salt, and the solvent of the filtrate was evaporated to dryness. The reaction mixture was redissolved in DMF (0.50 mL). A solution of NaN_3 (97.5 mg, 1.5 mmol) and alkyl halide **3** (1.5 mmol) in DMF (0.5 mL) was added while stirring at room temperature. Finally, CuI (33.3 mg, 0.175 mmol), Et_3N (0.2 mL, 1.5 mmol), and solution of alkyl azide were added and stirring was continued at room temperature for 1 h. After completion of the reaction, it was quenched with saturated cool aqueous $Na_2S_2O_3$ and extracted with ethyl acetate (3 × 10 mL). The organic phase was collected and washed with water (3 × 5 mL), then dried with anhydrous Na_2SO_4, filtered, and evaporated in *vacuo*. The crude product was purified by silica gel column chromatography (SiO_2, 40−50% EtOAc/Hexane as eluent) to afford bis-indole-1,4-disubstituted-1,2,3-triazoles **4**.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-methyl-1,2,3-triazol-4-yl)methyl) 4d. 90% yield (0.1999 g) as a brown solid; mp 97−99 °C; R_f = 0.03 (50% EtOAc/*n*-Hexane); IR (KBr): 3138, 3052, 2922, 2851, 1633, 1488, 1466, 1333, 804, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.6 Hz, 4H), 7.25−7.21 (m, 4H), 7.18 (t, J = 7.6 Hz, 2H), 7.10 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.64 (s, 2H), 5.83 (s, 1H), 5.32 (s, 2H), 5.31 (s, 2H), 3.97 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 142.2, 136.5, 131.7, 129.8, 128.3, 127.4, 127.1, 122.5, 121.8, 119.8, 119.1, 118.4, 109.5, 41.8, 39.4, 36.5; HRMS (ESI) m/z $C_{31}H_{27}ClN_8Na$ $(M + Na)^+$ calcd 569.1945, found 569.1942.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(4-nitroxybenzyldiacetyl)-1,2,3-triazol-4-yl)methyl) 4e. 59% yield (0.2651 g) as a red solid; mp 98−100 °C; R_f = 0.10 (50% EtOAc/*n*-Hexane); IR (KBr): 3144, 3055, 2922, 2851, 1759, 1608, 1522, 1489, 1466, 1347, 1195, 805, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.25−7.20 (m, 6H), 7.14 (t, J = 7.2 Hz, 2H), 6.97 (t, J = 7.6 Hz, 2H), 6.44 (s, 2H), 5.83 (s, 1H), 5.34 (s, 2H), 5.33 (s, 2H), 5.25 (s, 4H), 5.12 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.8, 147.6, 145.0, 142.3, 141.4, 136.4, 131.6, 129.8, 128.4, 128.2, 127.4, 127.0, 123.7, 123.1, 121.8, 119.8, 119.1, 118.5, 109.5, 66.0, 50.4, 41.6, 39.2; HRMS (ESI) m/z $C_{47}H_{37}ClN_{10}O_8Na$ $(M + Na)^+$ calcd 927.2382, found 927.2379.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(menthyldiacetyl)-1,2,3-triazol-4-yl)methyl) 4f. 84% yield (0.3846 g) as a red solid; mp 112−113 °C; R_f = 0.15 (30% EtOAc/*n*-Hexane); IR (KBr): 3139, 3054, 2956, 2870, 1746, 1613, 1489, 1465, 1334, 1220, 803, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.27−7.22 (m, 6H), 7.18 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 6.65 (s, 2H), 5.83 (s, 1H), 5.36 (s, 4H), 5.02 (t, J = 4.5 Hz, 4H), 4.74 (td, J = 10.8, 4.4 Hz, 2H), 1.96 (brd, J = 12.0 Hz, 2H), 1.77−1.62 (m, 8H), 1.34 (brt, J = 12.0 Hz, 2H), 1.10−0.99 (m, 2H), 0.97 (d, J = 11.6 Hz, 6H), 0.86 (d, J = 6.8 Hz, 6H), 0.71 (d, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 145.0, 142.2, 136.5, 131.7, 129.9, 128.3, 127.5, 127.1, 123.0, 121.9, 119.8, 119.1, 118.5, 109.6, 76.8, 50.8, 46.6, 41.8, 40.5, 39.4, 33.8, 31.2, 26.1, 23.2, 21.8, 20.6, 16.2; HRMS (ESI) m/z $C_{53}H_{63}ClN_8O_4Na$ $(M + Na)^+$ calcd 933.4558, found 933.4569.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-penthyl-1,2,3-triazol-4-yl)methyl) 4h. 19% yield (0.0635 g) as a red solid; mp 77−79 °C; R_f = 0.10 (30% EtOAc/*n*-Hexane); IR (KBr): 3134, 3054, 2927, 2856, 1614, 1489, 1466, 1333, 804, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 4H), 7.18 (t, J = 8.0 Hz, 2H), 7.10 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.64 (s, 2H), 5.84 (s, 1H), 5.33 (brs, 4H), 4.22 (t, J = 7.2 Hz, 4H), 1.81 (quin., J = 7.6 Hz, 4H), 1.35−1.26 (m, 8H), 0.87 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.6, 142.3, 136.6, 131.8, 129.9, 128.4, 127.5, 127.2, 121.1, 121.4, 119.9, 119.1, 118.5, 109.6, 50.3, 42.0, 39.5, 29.8, 28.4, 22.0, 13.8; HRMS (ESI) m/z $C_{39}H_{43}ClN_8Na$ $(M + Na)^+$ calcd 681.3197, found 681.3207.

3,3′-(Phenylmethylene)-bis-indole-((1-(3-methoxybenzyl)-1,2,3-triazol-4-yl)methyl) 4m. 88% yield (0.3193 g) as a pink solid; mp 87−89 °C; R_f = 0.16 (40% EtOAc/*n*-Hexane); IR (KBr): 3138, 3054, 2923, 2851, 1602, 1492, 1466, 1323, 1265, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 6H), 7.27−7.19 (m, 5H), 7.14 (t, J = 7.2 Hz, 2H), 7.08 (s, 2H), 6.93 (t, J = 7.6 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 7.6 Hz, 2H), 6.69 (brs, 2H), 6.62 (s, 2H), 5.84 (s, 1H), 5.35 (s, 4H), 5.28 (s, 4H), 3.73 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 145.2, 143.7, 136.6, 135.9, 130.1, 128.5, 128.2, 127.7, 127.2, 126.1, 121.8, 121.6, 120.0, 119.0, 114.1, 113.4, 109.5, 55.2, 53.9, 42.0, 40.0; HRMS (ESI) m/z $C_{45}H_{40}N_8O_2Na$ $(M + Na)^+$ calcd 747.3172, found 747.3180.

3,3′-(4-Fluorophenylmethylene)-bis-indole-((1-(3-methoxybenzyl)-1,2,3-triazol-4-yl)methyl) 4o. 80% yield (0.2966 g) as a pink solid; mp 91−92 °C; R_f = 0.10 (50% EtOAc/*n*-Hexane); IR (KBr): 3136, 3052, 2922, 2851, 1602, 1506, 1466, 1332, 1265, 1221, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.27−7.19 (m, 4H), 7.14 (t, J = 7.6 Hz, 2H), 7.08 (s, 2H), 6.94 (t, J = 8.0 Hz, 2H), 6.91 (t, J = 8.8 Hz, 2H), 6.86 (dd, J = 8.0, 2.0 Hz, 2H), 6.75 (d, J = 7.6 Hz, 2H), 6.69 (brs, 2H), 6.59 (s, 2H), 5.80 (s, 1H), 5.37 (s, 4H), 5.29 (s, 4H), 3.73 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1 (d, J = 243.0 Hz), 159.8, 144.9, 139.3 (d, J = 3.0 Hz), 136.5, 135.8, 129.9, 129.8 (d, J = 8.0 Hz), 127.4, 127.0, 121.7, 121.6, 119.8, 119.77, 119.0, 118.7, 114.8 (d, J = 21.0 Hz), 113.9, 113.4, 109.5, 55.0, 53.7, 41.7, 39.2; HRMS (ESI) m/z $C_{45}H_{39}FN_8O_2Na$ $(M + Na)^+$ calcd 765.3078, found 765.3075.

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3,3′-(4-Methoxyphenylmethylene)-bis-indole-((1-(3-methoxybenzyl)-1,2,3-triazol-4-yl)methyl) 4p. 63% yield (0.2376 g) as an orange solid; mp 89−91 °C; R_f = 0.16 (50% EtOAc/*n*-Hexane); IR (KBr): 3137, 3053, 2923, 2851, 1603, 1509, 1466, 1332, 1264, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.26−7.22 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 8.0 Hz, 2H), 7.06 (s, 2H), 6.92 (t, J = 7.6 Hz, 2H), 6.86 (dd, J = 8.4, 2.0 Hz, 2H), 6.80−6.73 (m, 4H), 6.68 (brs, 2H), 6.59 (s, 2H), 5.77 (s, 1H), 5.37 (s, 4H), 5.30 (s, 2H), 5.29 (s, 4H), 3.78 (s, 3H), 3.72 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 157.9, 145.2, 136.6, 135.9, 135.8, 130.1, 129.4, 127.7, 127.1, 121.7, 121.6, 120.0, 119.95, 119.4, 119.0, 114.1, 113.6, 113.4, 109.5, 55.2, 55.1, 53.9, 42.0, 39.2; HRMS (ESI) m/z $C_{46}H_{42}N_8O_3Na$ (M + Na)$^+$ calcd 777.3278, found 777.3272.

3,3′-(Phenylmethylene)-bis-indole-((1-(4-fluorobenzyl)-1,2,3-triazol-4-yl)methyl) 4q. 86% yield (0.3019 g) as a pink solid; mp 103−104 °C; R_f = 0.16 (40% EtOAc/*n*-Hexane); IR (KBr): 3134, 3054, 2923, 2851, 1608, 1509, 1465, 1332, 1225, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.12 (m, 15H), 7.04 (s, 2H), 7.02 (t, J = 8.4 Hz, 4H), 6.93 (t, J = 7.2 Hz, 2H), 6.60 (s, 2H), 5.82 (s, 1H), 5.37 (s, 4H), 5.30 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 246.0 Hz), 145.4, 143. 7, 136.6, 130.2 (d, J = 3.0 Hz), 129.8 (d, J = 8.0 Hz), 128.5, 128.2, 127.7, 127.2, 126.2, 121.8, 121.5, 120.0, 119.1, 119.06, 116.4 (d, J = 21.0 Hz), 109.5, 53.3, 42.0, 40.0; HRMS (ESI) m/z $C_{43}H_{34}F_2N_8Na$ (M + Na)$^+$ calcd 723.2772, found 723.2779.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-(4-fluorobenzyl)-1,2,3-triazol-4-yl)methyl) 4r. 85% yield (0.3109 g) as a pink solid; mp 96−98 °C; R_f = 0.10 (40% EtOAc/*n*-Hexane); IR (KBr): 3127, 3054, 2921, 2850, 1644, 1510, 1466, 1332, 1224, 785, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8.0 Hz, 4H), 7.21−7.13 (m, 10H), 7.08 (s, 2H), 7.02 (t, J = 8.8 Hz, 4H), 6.95 (t, J = 7.6 Hz, 2H), 6.60 (s, 2H), 5.79 (s, 1H), 5.37 (s, 4H), 5.30 (brs, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 247.0 Hz), 145.2, 142.3, 136.6, 131.8, 130.3 (d, J = 3.0 Hz), 129.9, 129.8 (d, J = 8.0 Hz), 128.4, 127.5, 127.1, 121.9, 121.5, 119.9, 119.2, 118.5, 116.0 (d, J = 22.0 Hz), 109.6, 53.3, 41.9, 39.5; HRMS (ESI) m/z $C_{43}H_{33}ClF_2N_8Na$ (M + Na)$^+$ calcd 757.2382, found 757.2395.

3,3′-(4-Methoxyphenylmethylene)-bis-indole-((1-(4-fluorobenzyl)-1,2,3-triazol-4-yl)methyl) 4s. 82% yield (0.3480 g) as an orange solid; mp 96−97 °C; R_f = 0.18 (50% EtOAc/*n*-Hexane); IR (KBr): 3133, 3052, 2927, 2852, 1609, 1509, 1465, 1332, 1247, 1225, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 8.5 Hz, 4H), 7.20−7.11 (m, 8H), 7.05 (s, 2H), 7.02 (t, J = 8.4 Hz, 4H), 6.93 (t, J = 7.2 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 6.60 (s, 2H), 5.77 (s, 1H), 5.36 (s, 4H), 5.29 (brs, 4H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 247.0 Hz), 157.9, 145.4, 136.6, 135.8, 130.3 (d, J = 3.0 Hz), 129.8 (d, J = 8.0 Hz), 129.4, 127.7, 127.1, 121.8, 121.5, 120.0, 119.4, 119.0, 116.0 (d, J = 22.0 Hz), 113.6, 109.5, 55.1, 53.3, 42.0, 39.2; HRMS (ESI) m/z $C_{44}H_{36}F_2N_8O$ Na (M + Na)$^+$ calcd 753.2878, found 753.2881.

3,3′-(4-Chlorophenylmethylene)-bis-indole-((1-buthyl-1,2,3-triazol-4-yl)methyl) 4t. 85% yield (0.2933 g) as a brown solid; mp 82−83 °C; R_f = 0.14 (40% EtOAc/*n*-Hexane); IR (KBr): 3135, 3051, 2924, 2852, 1633, 1489, 1466, 1332, 804, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.09 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.64 (s, 2H), 5.84 (s, 1H), 5.33 (brs, 4H), 4.23 (t, J = 7.2 Hz, 4H), 1.79 (quin., J = 7.6 Hz, 4H), 1.29 (sex., J = 7.6 Hz, 4H), 0.92 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.4, 142.2, 136.5, 131.6, 129.8, 128.2, 127.4, 127.1, 121.8, 121.3, 119.7, 119.0, 118.3, 109.5, 49.8, 41.8, 39.4, 31.9, 19.4, 13.2; HRMS (ESI) m/z $C_{37}H_{39}ClN_8Na$ (M + Na)$^+$ calcd 653.2884, found 653.2887.

3,3′-(4-Fluorophenylmethylene)-bis-indole-((1-buthyl-1,2,3-triazol-4-yl)methyl) 4u. 82% yield (0.2656 g) as a pink solid; mp 82−83 °C; R_f = 0.18 (40% EtOAc/*n*-Hexane); IR (KBr): 3135, 3051, 2924, 2851, 1633, 1506, 1466, 1332, 1220, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 4H), 7.29−7.26 (m, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.09 (s, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.95 (t, J = 8.4 Hz, 2H), 6.63 (s, 2H), 5.85 (s, 1H), 5.33 (s, 4H), 4.23 (t, J = 7.2 Hz, 4H), 1.79 (quin., J = 7.6 Hz, 4H), 1.29 (sex., J = 7.2 Hz, 4H), 0.92 (t, J = 7.6 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 242.0 Hz), 144.4, 139.4 (d, J = 3.0 Hz), 136.6, 129.8 (d, J = 8.0 Hz), 127.5, 127.1, 121.8, 121.3, 119.8, 119.0, 118.7, 114.8 (d, J = 21.0 Hz), 109.5, 49.9, 41.8, 39.2, 32.0, 19.5, 13.2; HRMS (ESI) m/z $C_{37}H_{39}FN_8Na$ (M + Na)$^+$ calcd 637.3179, found 637.3179.

3,3′-(4-Methoxyphenylmethylene)-bis-indole-((1-buthyl-1,2,3-triazol-4-yl)methyl) 4v. 41% yield (0.1278 g) as an orange solid; mp 80−81 °C; R_f = 0.20 (50% EtOAc/*n*-Hexane); IR (KBr): 3134, 3053, 2926, 2853, 1610, 1509, 1465, 1332, 1247, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.06 (s, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.64 (s, 2H), 5.82 (s, 1H), 5.33 (brs, 2H), 5.32 (brs, 2H), 4.22 (t, J = 7.6 Hz, 4H), 3.78 (s, 3H), 1.78 (quin., J = 7.6 Hz, 4H), 1.28 (sex., J = 7.6 Hz, 4H), 0.91 (t, J = 7.6 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 144.8, 136.7, 135.9, 129.5, 127.7, 127.2, 121.8, 121.3, 120.1, 119.4, 119.0, 113.6, 109.5, 55.2, 50.1, 42.1, 39.2, 32.1, 19.6, 13.4; HRMS (ESI) m/z $C_{38}H_{42}N_8ONa$ (M + Na)$^+$ calcd 649.3379, found 649.3383.

3,3′-(Phenylmethylene)-bis-indole-((1-octhyl-1,2,3-triazol-4-yl)methyl) 4w. 76% yield (0.2695 g) as a red oil; R_f = 0.27 (40% EtOAc/*n*-Hexane); IR (KBr): 3133, 3056, 2927, 2856, 1613, 1493, 1466, 1333, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 4H), 7.29−7.21 (m, 3H), 7.16 (t, J = 7.6 Hz, 2H), 7.06 (s, 2H), 6.98 (t, J = 7.2 Hz, 2H), 6.65 (s, 2H), 5.87 (s, 1H), 5.33 (s, 4H), 4.21 (t, J = 7.2 Hz, 4H), 1.83−1.78 (m, 4H), 1.26−1.24 (m, 20H), 0.87 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.6, 143.6, 136.5, 128.5, 128.1, 127.6, 127.2, 126.1, 121.7, 121.3, 119.9, 118.9, 109.5, 50.2, 41.9, 40.0, 31.5, 30.0, 28.8, 28.7, 26.2, 22.4, 13.9; HRMS (ESI) m/z $C_{45}H_{56}N_8Na$ (M + Na)$^+$ calcd 731.4526, found 731.4518.

3,3′-(4-Fluorophenylmethylene)-bis-indole-((1-octhyl-1,2,3-triazol-4-yl)methyl) 4y. 81% yield (0.2372 g) as a red oil; R_f = 0.34 (40% EtOAc/*n*-Hexane); IR (KBr): 3133, 3054, 2927, 2856, 1602, 1506, 1466, 1333, 1221, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 4H), 7.29−7.27 (m, 2H), 7.17 (t, J = 7.2 Hz, 2H), 7.09 (s, 2H), 7.00 (t, J = 7.2 Hz, 2H), 6.95 (t, J = 8.4 Hz, 2H), 6.64 (s, 2H), 5.85 (s, 1H), 5.33 (brs, 4H), 4.21 (t, J = 7.2 Hz, 4H), 1.84−1.78 (m, 4H), 1.26−1.24 (m, 20H), 0.87 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 243.0 Hz), 144.6, 139.4 (d, J = 3.0 Hz), 136.6, 129.9 (d, J = 8.0 Hz), 127.5, 127.2, 121.8, 121.4, 119.9, 119.0, 118.8, 114.9 (d, J = 21.0 Hz), 109.6, 50.3, 42.0, 39.3, 31.6, 30.1, 28.9, 28.8, 26.3, 22.5, 14.0; HRMS (ESI) m/z $C_{45}H_{55}FN_8Na$ (M + Na)$^+$ calcd 749.4431, found 749.4434.

3,3′-(4-Chlorophenylmethylene)-bis-5-fluoro-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 4z. 97% yield (0.1419 g) as a pink solid; mp 133−135 °C; R_f = 0.36 (40% EtOAc/*n*-Hexane); IR (KBr): 3132, 3066, 2924, 2853, 1620, 1488, 1455, 1321, 1270, 796, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 6H), 7.24−7.16 (m, 10H), 7.10 (s, 2H), 6.91−6.86 (m, 4H), 6.62 (s, 2H), 5.63 (s, 1H), 5.43 (s, 4H), 5.28 (s, 2H), 5.27 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.5 (d, J = 233.0 Hz), 144.8, 141.5, 134.4, 133.3, 132.1, 129.8, 129.0, 128.7, 128.7, 128.6, 127.9, 127.7 (d, J = 9.0 Hz), 121.5, 118.0 (d, J = 5.0 Hz), 110.5 (d, J = 6.0 Hz), 110.4 (d, J = 23.0 Hz), 104.7 (d, J = 23.0 Hz), 54.1, 42.2, 39.5; HRMS (ESI) m/z $C_{43}H_{33}ClF_2N_8Na$ (M + Na)$^+$ calcd 757.2382, found 757.2384.

3,3′-(4-Chlorophenylmethylene)-bis-5-methoxy-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 4aa. 70% yield (0.2667 g) as a pink solid; mp 133−135 °C; R_f = 0.15 (40% EtOAc/*n*-Hexane); IR (KBr): 3132, 3066, 2924, 2853, 1620, 1488, 1455, 1321, 1270, 796, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.31 (m, 6H), 7.22 (d, J = 8.8 Hz, 2H), 7.20−7.16 (m, 8H), 7.09 (s, 2H), 6.82 (dd, J = 8.8, 2.4 Hz, 2H), 6.72 (dd, J = 2.4 Hz, 2H), 6.72 (s, 1H), 6.58 (s, 2H), 5.68 (s, 1H), 5.41 (s, 4H), 5.25 (s, 2H), 5.24 (s, 2H), 3.65 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.8, 145.2, 142.2, 134.5, 132.0, 131.8, 129.9, 129.0, 128.7, 128.4, 128.0, 127.9, 121.6, 117.8, 111.7, 110.4, 102.3, 55.9, 54.1, 42.2, 39.5; HRMS (ESI) m/z $C_{45}H_{39}ClN_8O_2Na$ (M + Na)$^+$ calcd 781.2782, found 781.2788.

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3,3′-(4-Chlorophenylmethylene)-bis-5-fluoro-indole-((1-octhyl-1,2,3-triazol-4-yl)methyl) 4bb. 65% yield (0.1008 g) as a yellow oil; R_f = 0.45 (40% EtOAc/*n*-Hexane); IR (KBr): 3135, 3080, 2927, 2856, 1623, 1488, 1456, 1321, 1182, 795, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.22 (m, 6H), 7.11 (s, 2H), 6.92−6.88 (m, 4H), 6.67 (s, 2H), 5.67 (s, 1H), 5.34 (d, J = 16.0 Hz, 2H), 5.29 (d, J = 16.0 Hz, 2H), 4.24 (t, J = 7.2 Hz, 4H), 1.83−1.80 (m, 4H), 1.26−1.24 (m, 20H), 0.86 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5 (d, J = 234.0 Hz), 144.3, 141.5, 133.3, 132.1, 129.8, 128.7, 128.5, 127.7 (d, J = 9.0 Hz), 121.3, 117.9 (d, J = 5.0 H), 110.5 (d, J = 9.0 Hz), 110.3 (d, J = 26.0 Hz), 104.7 (d, J = 24.0 Hz), 50.4, 42.3, 39.6, 31.6, 30.1, 28.9, 28.8, 26.3, 22.5, 14.0; HRMS (ESI) m/z $C_{45}H_{53}ClF_2N_8Na$ $(M + Na)^+$ calcd 801.3947, found 801.3951.

3,3′-(4-Chlorophenylmethylene)-bis-5-methoxy-indole-((1-octhyl-1,2,3-triazol-4-yl)methyl) 4cc. 84% yield (0.1340 g) as a pink solid; mp 142−143 °C; R_f = 0.41 (40% EtOAc/*n*-Hexane); IR (KBr): 3133, 3080, 2927, 2855, 1621, 1488, 1452, 1318, 1217, 798, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.23 (m, 6H), 7.10 (s, 2H), 6.83 (dd, J = 8.8, 2.0 Hz, 2H), 6.75 (d, J = 1.6 Hz, 2H), 6.62 (s, 2H), 5.71 (s, 1H), 5.29 (brs, 4H), 4.22 (t, J = 7.6 Hz, 4H), 3.68 (s, 6H), 1.82−1.79 (m, 4H), 1.26−1.24 (m, 20H), 0.87 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.7, 144.6, 142.2, 132.0, 131.8, 129.9, 128.4, 128.0, 127.9, 121.3, 117.8, 111.6, 110.4, 102.3, 55.9, 50.3, 42.3, 39.6, 31.6, 30.2, 29.0, 28.8, 26.4, 22.5, 14.0; HRMS (ESI) m/z $C_{47}H_{59}ClN_8O_2Na$ $(M + Na)^+$ calcd 825.4347, found 825.4341.

3,3′-(4-Chlorophenylmethylene)-bis-5-(1-benzyl-1,2,3-triazol-4-yl-methyl)-indole-((1-benzyl-1,2,3-triazol-4-yl)methyl) 5. According to the general one-pot four-step procedure, a stirred solution of indole **1d** (146.5 mg, 1.1 mmol) in CH_3CN (1 mL) was mixed with aldehyde **2a** (70.0 mg, 0.5 mmol). In the second step, KOH (266.5 mg, 4.75 mmol) and propargyl bromide (0.2 mL, 2.5 mmol) were added at room temperature, and the stirring was continued for 1 h. NaN_3 (162.5 mg, 2.5 mmol), benzyl bromide (0.3 mL, 2.5 mmol), CuI (66.6 mg, 0.35 mmol), and Et_3N (0.4 mL, 2.5 mmol) were added in the final step. The crude product was purified by silica gel column chromatography (SiO_2, 40% EtOAc/*n*-Hexane as eluent) to give product **5** as a brown solid (417.8 mg, 78%); mp 108−110 °C; R_f = 0.24 (40% EtOAc/*n*-Hexane); IR (KBr): 3137, 3064, 2924, 2853, 1619, 1487, 1456, 1329, 1195, 798, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 7.33−7.30 (m, 12H), 7.24−7.19 (m, 6H), 7.17−7.13 (m, 10H), 6.83 (dd, J = 8.8, 2.0 Hz, 2H), 6.80 (d, J = 2.0 Hz, 2H), 6.58 (s, 2H), 5.62 (s, 1H), 5.45 (s, 4H), 5.37 (s, 4H), 5.23 (s, 4H), 4.98 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 144.9, 144.8, 142.1, 134.6, 134.6, 132.3, 131.7, 129.9, 129.0, 128.98, 128.7, 128.6, 128.4, 128.0, 127.9, 122.5, 121.7, 117.8, 112.4, 110.4, 104.0, 63.0, 54.1, 54.0, 42.1, 39.6; HRMS (ESI) m/z $C_{63}H_{53}ClN_{14}O_2Na$ $(M + Na)^+$ calcd 1095.4062, found 1095.4058.

General Procedure for One-Pot Four-Step Compound 7. In the first step, a stirred solution of indole **1a** (117.2 mg, 1.0 mmol) in CH_3CN (0.6 mL) was mixed with terephthalaldehyde **6** (26.8 mg, 0.2 mmol), I_2 powder (10.2 mg, 0.08 mmol), and H_2SO_4−SiO_2 (20 mg) at room temperature. TLC showed the conversion was complete. In the second step, KOH (238.4 mg, 4.25 mmol) and propargyl bromide (0.1 mL, 1.3 mmol) were added at room temperature, and the stirring was continued for 1 h. The reaction mixture was filtered to remove salt, and the solvent of the filtrate was evaporated to dryness. The reaction mixture was redissolved in DMF (0.50 mL). A solution of NaN_3 (84.5 mg, 1.3 mmol) and benzyl bromide (0.2 mL, 1.3 mmol) in DMF (0.5 mL) was added while stirring at room temperature. Finally, CuI (30.5 mg, 0.16 mmol), Et_3N (0.2 mL, 1.3 mmol), and solution of benzyl azide were added, and stirring was continued at room temperature for 1 h. After completion of the reaction, it was quenched with saturated cool aqueous $Na_2S_2O_3$ (10 mL) and extracted with dichloromethane (3 × 10 mL). The organic phase was collected and washed with water (3 × 5 mL), then dried with anhydrous Na_2SO_4, filtered, and evaporated in *vacuo*. The crude product was purified by silica gel column chromatography (SiO_2, 70% EtOAc/*n*-Hexane as eluent) to afford product 7 as a pink solid (170.6 mg, 61%); mp 221−222 °C; R_f = 0.23 (70% EtOAc/*n*-Hexane); IR (KBr): 3131, 3056, 2923, 2851, 1699, 1497, 1465, 1333, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 18H), 7.15−7.11 (m, 18H), 7.04 (s, 4H), 6.91 (t, J = 7.2 Hz, 4H), 6.60 (s, 4H), 5.79 (s, 2H), 5.34 (s, 8H), 5.27 (s, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 141.5, 136.4, 134.4, 128.8, 128.4, 128.4, 127.6, 127.6, 127.0, 121.6, 119.9, 119.0, 118.8, 109.5, 53.7, 41.7, 39.6; HRMS (ESI) m/z $C_{80}H_{66}N_{16}Na$ $(M + Na)^+$ calcd 1273.5554, found 1273.5542.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02056.

^1H and $^{13}C\{^1H\}$ NMR spectra for the synthesized compounds (PDF)

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Notes

The authors declare no competing financial interest.

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