LiO^{t}Bu-Promoted Intramolecular Cycloaddition of 2'-Alkynyl-Biaryl-2-Aldehyde *N*-Tosylhydrazones Approach to 3-Substituted 1*H*-Dibenzo[*e*,*g*]indazoles

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Article

LiO^{t}Bu-Promoted Intramolecular Cycloaddition of 2′-Alkynyl-Biaryl-2-Aldehyde *N*-Tosylhydrazones Approach to 3-Substituted 1*H*-Dibenzo[*e*,*g*]indazoles

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Abstract: A two-step, one-pot synthesis of 3-substituted 1*H*-dibenzo[*e*,*g*]indazoles in good to high yields *via* a LiO^{t}Bu-promoted intramolecular cyclization of 2′-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazones, formed *in situ* by the reactions of 2′-alkynyl-biaryl-2-aldehydes with *p*-methylbenzenesulfonohydrazide was developed. Two kinds of hydrogen bonds forming in several products were observed in DMSO-d_6 solution in ^{1}H NMR spectroscopic data, which were assigned to the formation of solvated products and dimers of products, supported by the studies of density functional theory (DFT).

Keywords: *N*-tosylhydrazones; 1*H*-dibenzo[*e*,*g*]indazoles; intramolecular cycloaddition; lithium *tert*-butoxide; hydrogen bonds

1. Introduction

1,3-dipolar cycloaddition reactions of azides and alkynes as the most important representative reactions in click chemistry and bioorthogonal chemistry, have attracted enormous attention in the past decades [1-5]. Besides azide compounds, diazo compounds as another class of efficient 1,3-dipoles, could also be used in 1,3-dipolar cycloadditions to react with alkynes, providing diverse pyrazole-based skeletons [6,7]. Recently, numerous elegant works involving the cycloadditions between diazo compounds (or their *N*-tosylhydrazone precursors) and alkynes were reported [8-18]. However, the design of *N*-tosylhydrazones for intramolecular 1,3-dipolar cycloadditions to construct π-extended pyrazole-based skeletons is rarely reported.

Indazole-containing derivatives comprising a pyrazole ring represent one of the most important heterocyclic scaffolds in pharmaceutical industry [19-21], which possess a variety of biological activities, such as antimicrobial [22], anti-inflammatory [23] and antiHIV [24] activities. 1*H*-indazole as one of the tautomeric forms of indazole, owns more thermodynamic stability than 2*H*-indazoles. Since the synthesis of 2*H*-dibenzo[*e*,*g*]indazole has been developed [25], we prefer to offer a synthetic method towards 1*H*-dibenzo[*e*,*g*]indazole, the π-extended structure of 1*H*-indazole, to provide more possibilities of indazole-based derivatives in further exploration of pharmaceutical molecules or larger polycyclic aromatic compounds (PACs). In 1975, Jones's group reported a pyrolysis method to prepare 1*H*-dibenzo[*e*,*g*]indazole in quantitative yield from 2′-ethynyl-biaryl-2-aldehyde *N*-tosylhydrazone salt [26] (Scheme 1. a). In 2013, Zhan's group synthesized 3-phenyl-substituted 1*H*-dibenzo[*e*,*g*]indazole (**2a**) in 60% yield from a ring-expansion strategy of 9-(phenylethynyl)-9*H*-fluoren-9-ol [27] (Scheme 1. b). Noted that only one example was reported in each literature, and either high temperature or complicated starting materials were required. Based on our previous studies on the applications of *N*-tosylhydrazones in the cyclizations [28-30], herein we report a one-pot synthetic method towards 3-substituted 1*H*-dibenzo[*e*,*g*]indazoles (**2**) from 2′-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazones, which was optimized to a one-pot two step manner starting from 2′-alkynyl-biaryl-2-aldehydes (**1**) (Scheme 1. c). Also, to clearly explain the ^{1}H NMR result of **2a**, two

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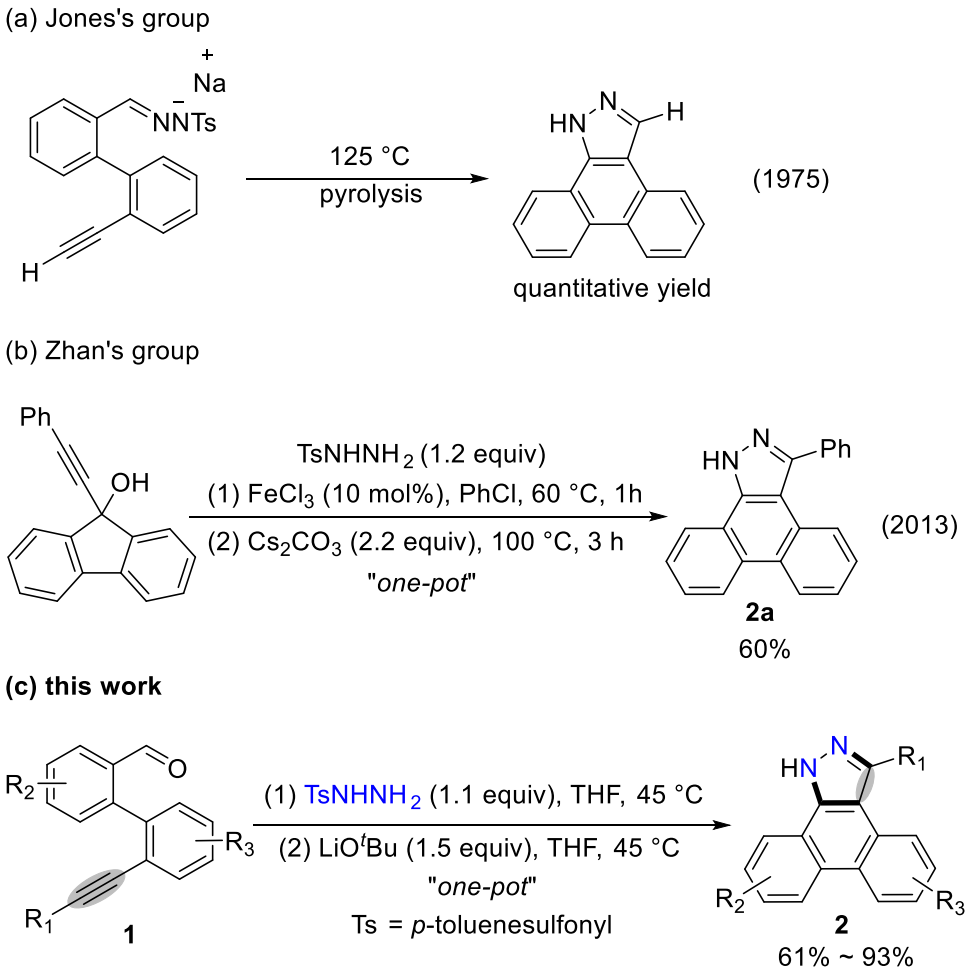
kinds of hydrogen bonds of **2a** in DMSO-d_6 were proposed, which were supported by the studies of density functional theory (DFT) using Gaussian 09 [31].



Scheme 1. The construction of 1*H*-dibenzo[*e*,*g*]indazoles *via* different starting materials.

2. Results and Discussion

Our investigations started from (*E*)-4-methyl-*N*′-((2′-(phenylethynyl)-[1,1′-biphenyl]-2-yl)methylene)benzenesulfonohydrazide (**1a′**), which is easily prepared from 2′-(phenylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1a**) and *p*-methylbenzenesulfonohydrazide (TsNHNH$_2$) in methanol at room temperature. When the reaction of **1a′** (1.0 equiv) and LiO^{t}Bu (1.5 equiv) in tetrahydrofuran (THF) was heated at 100 °C for 2 h, 3-phenyl-1*H*-dibenzo[*e*,*g*]indazole (**2a**) could be isolated from the reaction mixture in 89% yield (entry 1). When the reaction was performed at 50 °C, 45 °C, 35 °C or 25 °C, the yields of **2a** were not significantly decreased except at 25 °C (entries 2-5). Repeating the reaction in THF at 45 °C for 1 h, the yield of **2a** could be maintained in 88% (entry 6). Since **1a′** was prepared in methanol, we examined the reaction of **1a′** in methanol to replace of THF, but the yield of **2a** was decreased to 68% (entry 7). While in THF at 45 °C, the condensation of **1a** and TsNHNH$_2$ was also examined to explore the possibility to develop a two-step, one-pot procedure from **1a** to **2a** in THF, and fortunately, it was found that **1a** could be totally converted into **1a′** after 1 h (monitored by TLC board). Therefore, when LiO^{t}Bu (1.5 equiv) and additional 2.5 mL of THF were added to a reaction mixture of entry 6, **2a** could be also obtained in 88% yield after an additional heating for 1 h. In addition, the structure of **2a** was confirmed by its X-ray diffraction study [32].

Table 1. Optimizing Reaction Conditions of **2a**

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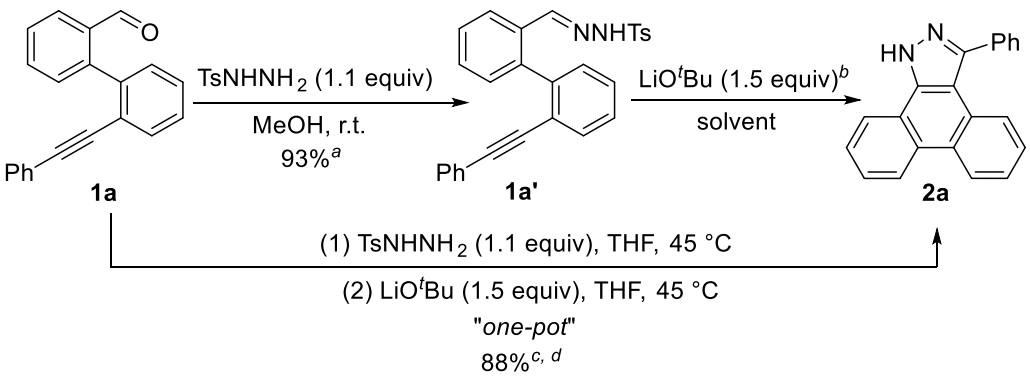

entry [b]	solvent	°C / h	yield of 2a (%) [d]
1	THF	100/2	89
2	THF	50/2	88
3	THF	45/2	88
4	THF	35/2	85
5	THF	25/2	77
6	THF	45/1	88
7	MeOH	45/1	68

[a] Reaction conditions: **1a** (1.5 mmol), $TsNHNH_2$ (1.1 equiv, 1.65 mmol) in 5.0 mL of MeOH at room temperature. [b] Reaction conditions: **1a'** (1.0 mmol), LiO^tBu (1.5 equiv, 1.5 mmol) in 5.0 mL of solvent. [c] Reaction conditions: **1a** (1.0 mmol), $TsNHNH_2$ (1.1 equiv, 1.1 mmol) in 5.0 mL of THF at 45 °C for 1 h, then LiO^tBu (1.5 equiv, 1.5 mmol) and additional 2.5 mL of THF at 45 °C for 1 h. [d] Isolated yields.

We also examined the formation of **2a** with the use of other inorganic bases such as NaO^tBu, KO^tBu, Li_2CO_3, K_2CO_3 and Cs_2CO_3 from **1a**. As shown in Table 2, the use of NaO^tBu and KO^tBu resulted in the formation of **2a** in 81% and 85% yields, respectively (entries 2-3), similar to the yield with the use of LiO^tBu (entry 1). However, with the use of Li_2CO_3, K_2CO_3 and Cs_2CO_3, **2a** formed in 9%-14% (entries 4-6). These results support the proposed mechanism depicted in Scheme 2 (*vide infra*), in which *tert*-butanol anion ($^-O^tBu$) is the main contribution to promote the intramolecular cyclization *via* formation of diazo intermediate **A**.

Table 2. Optimizing Base Conditions of **2a**

entry [a]	base	yield of 2a (%)
1	LiO^tBu	88
2	NaO^tBu	81
3	KO^tBu	85
4	Li_2CO_3	9
5	K_2CO_3	11
6	Cs_2CO_3	14

[a] Reaction conditions: **1a** (1.0 mmol), $TsNHNH_2$ (1.1 equiv, 1.1 mmol) in 5.0 mL of THF at 45 °C for 1 h, then base (1.5 equiv, 1.5 mmol) and additional 2.5 mL of THF at 45 °C for 1 h. The yields were isolated yields.

The scope and limitations of the substrates for the formation of 1*H*-dibenzo[*e*,*g*]indazoles (**2**) are included in Table 3. The intramolecular cycloaddition from starting materials 2'-alkynyl-biaryl-2-aldehydes (**1**) with different substituents in alkynyl groups (R_1) could afford the desired products in 61%-93% yields (**2a-2e**, **2i-2l**). Aromatic alkynyl substrates bearing either electron-donating groups (*p*-methoxy (**1b**), *p*-methyl (**1c**)) or electron-withdrawing groups (*p*-fluoro (**1d**), *p*-chloro (**1e**)) underwent the condensation reactions smoothly to give **2b-2e** in 80%-88% yields. Moreover, pyridyl- (**1i**), thienyl- (**1j**), and silyl- (**1k**) substituted substrates showed good tolerance, providing **2i-2k** in 78%-93% yields. However, the substrate having an alkyl alkynyl group (**1l**) showed a slightly lower reactivity, giving **2l** in 61% yield. In addition, the introduce of methyl (**1f**), chloro (**1g**), and trifluoromethyl (**1h**) groups at the position of R_3 showed the similar reactivity to **1a** to produce **2f-2h** in 83%-86% yields. In the case of the substrate having chloro and silyl groups (**1m**), the corresponding product of 10-chloro-3-(triisopropylsilyl)-1*H*-dibenzo[*e*,*g*]indazole (**2m**) could be also obtained in 82% yield. More interestingly, three pyridyl-fused analogues of **2a**, 3-phenyl-1*H*-benzo[*f*]pyrazolo[3,4-*h*]quinoline (**2n**), 3-phenyl-1H-benzo[*f*]pyrazolo[3,4-*h*]isoquinoline (**2o**), and 3-phenyl-1H-

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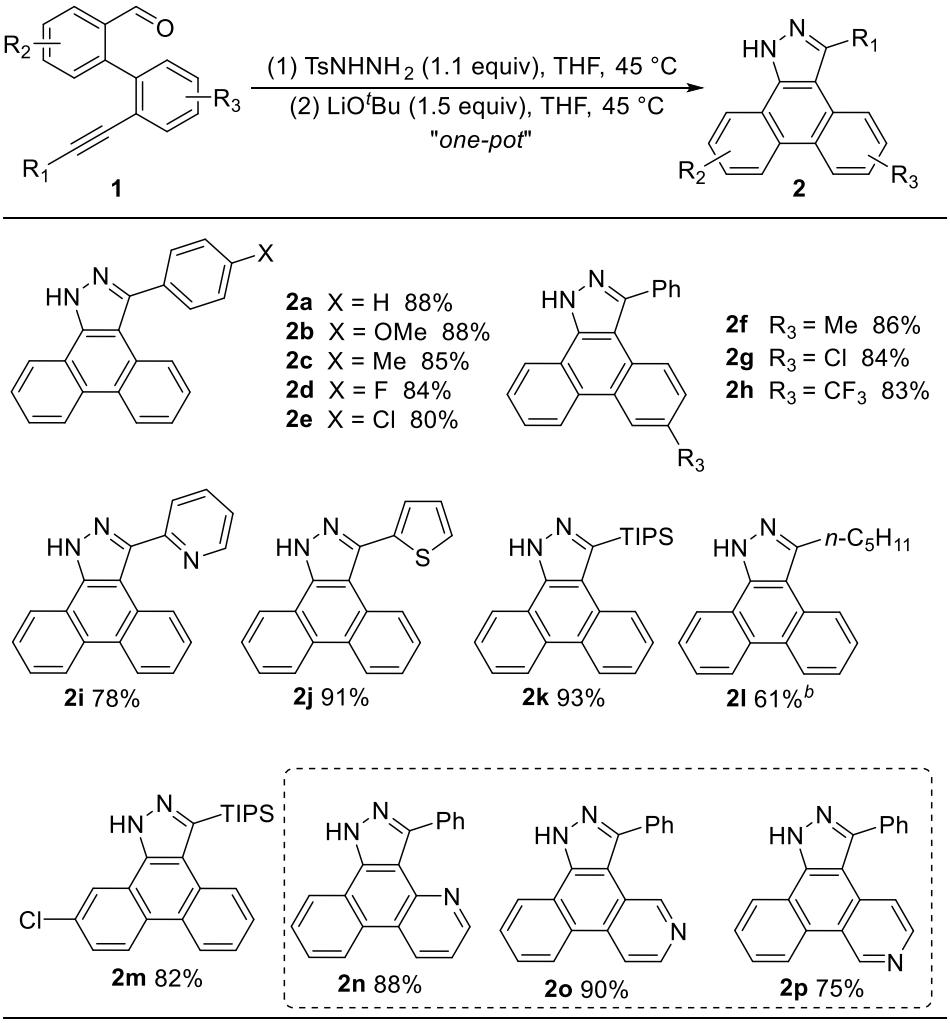
benzo[*h*]pyrazolo[4,3-*f*]isoquinoline (**2p**) were also successfully synthesized in 88%, 90% and 75% yields, respectively.

Table 3. Substrate scope of 2′-alkynyl-biaryl-2-aldehydes [a]



[a] Reaction conditions: **1** (1.0 mmol), $TsNHNH_2$ (1.1 equiv, 1.1 mmol) in 5.0 mL of THF at 45 °C for 1 h, then LiO^tBu (1.5 equiv, 1.5 mmol) and additional 2.5 mL of THF at 45 °C for 1 h. The yields were isolated yields. [b] Reaction condition: **1l** (0.3 mmol), $TsNHNH_2$ (1.1 equiv, 0.33 mmol) in 2.0 mL of THF at 45 °C for 1 h, then LiO^tBu (1.5 equiv, 0.45 mmol) and additional 1.0 mL of THF at 45 °C for 1 h. The yields were isolated yields.

The proposed mechanism of 3-phenyl-1*H*-dibenzo[*e*,*g*]indazole (**2a**) formation is depicted in Scheme 2. In the presence of base, diazo intermediate **A** forms from *N*-tosylhydrazone **1a**, the intramolecular nucleophilic cycloaddition of **B** affords **C**, which takes place the aromatization to give the final product of **2a**.

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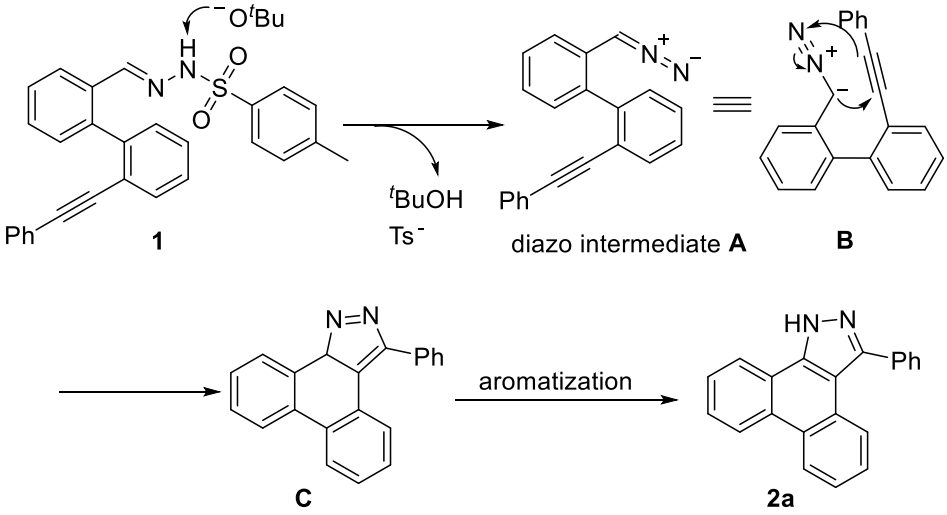

Scheme 2. Proposed mechanism of **2a** formation.

Additionally, in DMSO-d_6 solvent, we notice that the proton nuclear magnetic resonance (NMR) spectra of **2a**, **2d**, **2f**, **2h**, **2i**, **2j**, **2l**, **2n**, **2o** and **2p** appear two kinds of proton peaks assigned to N-H bond are observed, however when $CDCl_3$ was used as deuterium solvent, only one broaden peak of N-H appears, such as **2n** (Figure 1, a). We speculate that **2n**'s N-H appearing in relatively lower field of ^{1}H NMR (DMSO-d_6) spectrum at 14.39 ppm is the proton of N-H with the hydrogen bond forming between **2n** and DMSO-d_6, due to the strong electron-withdrawing effect of DMSO-d_6, and other one appearing at 14.16 ppm is the proton of N-H of **2n** dimer. To clarify and confirm the possibility to easily form **2n**·DMSO-d_6 and **2n** dimer to appear two kinds of N-H signals, we selected **2a** as representative sample to calculate the different energy requirements in two kinds of hydrogen bond formation by density functional theory (DFT) using Gaussian 09 at B3LYP-D3(BJ)/ma-TZVP [33-35] level. Basis set superposition error (BSSE) was corrected by the counterpoise (CP) method of Boys and Bernardi [36]. The calculation results indicate that two kinds of hydrogen bonds form with binding energies of -13.2 kcal/mol for complex-1 (**2a**·DMSO-d_6) and -16.6 kcal/mol for complex-2 (a dimer of **2a**) respectively (Figure 1, b), both are definitely lower than that of the sum of two isolated monomers. Although the formation of **2a** dimer with lower energy than **2a**·DMSO-d_6, the integrated intensity of **2a**·DMSO-d_6 is stronger, due possible to the better solubility of **2a**·DMSO-d_6 in DMSO-d_6.

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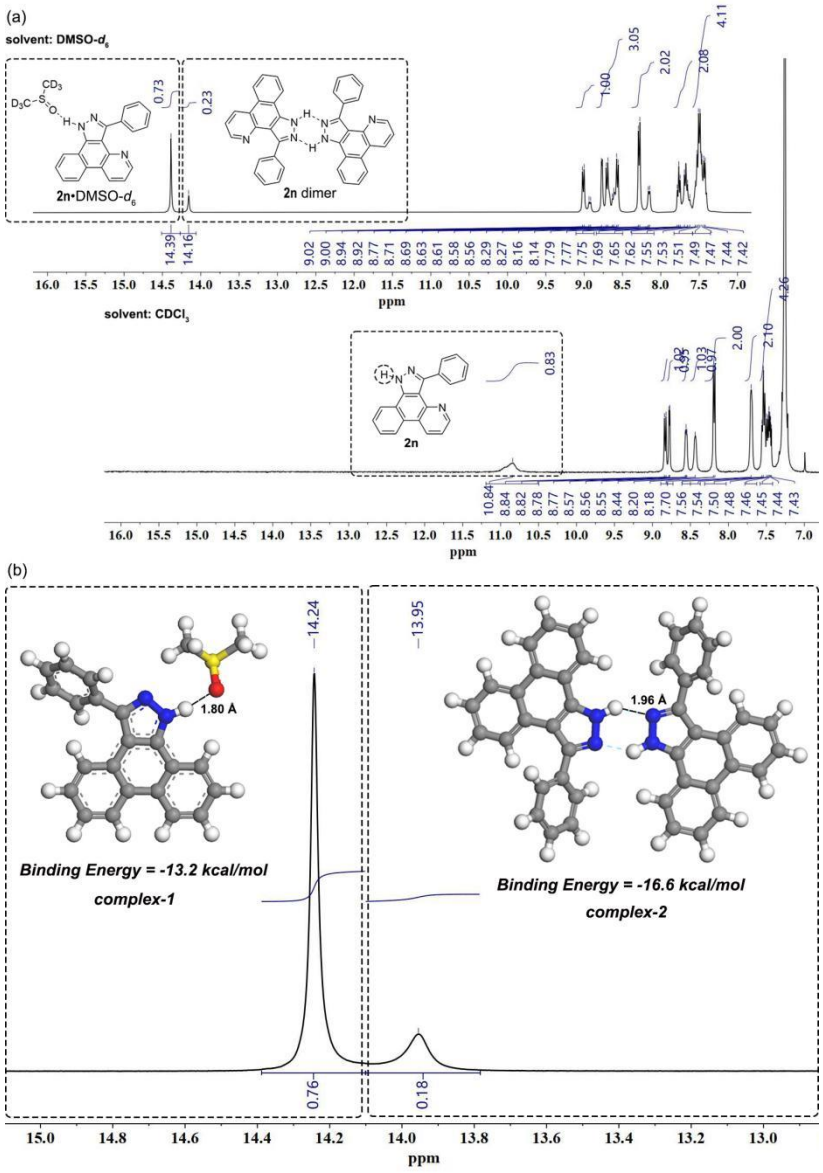

Figure 1. (a) The ^{1}H NMR spectra of **2n** in DMSO-d_6 and $CDCl_3$ respectively. (b)The calculation results of two kinds of hydrogen bonds formed in DMSO-d_6 of **2a**. The calculations were performed using Gaussian 09 at B3LYP-D3(BJ)/ma-TZVP level.

3. Materials and Methods

3.1 General Methods

Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel-coated glass sheets. All yields given referred to isolated yields. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL 400 using $CDCl_3$ or DMSO-d_6 as solvents at 298 K. ^{1}H NMR (400 MHz) chemical shifts (δ) were referenced to internal standard TMS (δ = 0.00 ppm) or internal solvent DMSO-d_6 (δ = 2.50 ppm); ^{13}C{^{1}H} NMR (101 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.52 ppm). High Resolution Mass Spectroscopy (HRMS) spectra were obtained by high-resolution mass spectrometers with electrospray ionization (ESI) source. Single-crystal X-ray diffraction data were obtained from SuperNova diffractometer with Cu K_α radiation at low temperature (173.15 K). All the NMR charts for the prepared starting materials, and the products are reported in the Supplementary Materials.

3.2 Characterization Data of Substrates

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2′-(Phenylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1a**). Pale yellow oil (355 mg, 1.26 mmol, 84%). Rf = 0.40 (PE/EA = 10/1). 1H NMR (400 MHz, Chloroform-d) δ 9.94 (s, 1H), 8.09 (dd, J = 7.8, 1.5 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.25 – 7.22 (m, 4H), 7.17 – 7.15 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 191.95, 144.42, 140.40, 134.34, 133.59, 132.10, 131.40, 130.37, 128.55, 128.37, 128.34, 126.98, 123.83, 122.79, 93.90, 88.30.

2′-((4-Methoxyphenyl)ethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1b**). Yellow oil (332 mg, 1.07 mmol, 71%). R_f = 0.55 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.12 – 7.08 (m, 2H), 6.77 – 6.74 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.92, 159.83, 144.50, 140.08, 134.32, 133.54, 132.83, 131.80, 131.38, 130.27, 128.27, 128.23, 128.18, 126.82, 124.14, 114.85, 114.02, 94.04, 87.12, 55.32. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{22}H_{17}O_2$ 313.1223, found 313.1223.

2′-(p-Tolylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1c**). Pale yellow oil (417 mg, 1.41 mmol, 94%). R_f = 0.50 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.07 – 7.02 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.91, 144.44, 140.25, 138.71, 134.31, 133.53, 131.96, 131.38, 131.26, 130.31, 129.12, 128.34, 128.27, 126.89, 123.99, 119.68, 94.14, 87.70, 21.59.

2′-((4-Fluorophenyl)ethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1d**). Pale yellow oil (333 mg, 1.11 mmol, 74%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.16 – 7.11 (m, 2H), 6.95 – 6.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.86, 162.65 (d, *J* = 249.6 Hz), 144.29, 140.33, 134.31, 133.60, 133.27 (d, *J* = 8.3 Hz), 131.95, 131.36, 130.29, 128.63, 128.34, 126.88, 123.64, 118.84 (d, *J* = 3.6 Hz), 115.67 (d, *J* = 22.2 Hz), 92.80, 88.01. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{21}H_{14}FO$ 301.1023, found 301.1023.

2′-((4-Chlorophenyl)ethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1e**). Pale yellow oil (436 mg, 1.38 mmol, 92%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 8.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.22 – 7.19 (m, 2H), 7.09 – 7.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.90, 144.27, 140.47, 134.60, 134.33, 133.64, 132.58, 132.06, 131.39, 130.37, 128.82, 128.75, 128.42, 128.40, 126.97, 123.52, 121.26, 92.73, 89.25.

5′-Methyl-2′-(phenylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1f**). Pale yellow oil (404 mg, 1.36 mmol, 91%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.08 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.53 – 7.49 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.20 (m, 5H), 7.16 – 7.14 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.00, 144.53, 140.25, 138.78, 134.31, 133.50, 131.94, 131.33, 131.28, 131.11, 129.12, 128.30, 128.20, 126.84, 122.97, 120.82, 93.10, 88.45, 21.57.

5′-Chloro-2′-(phenylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1g**). Pale yellow solid (374 mg, 1.18 mmol, 79%). R_f = 0.40 (PE/EA = 10/1). m.p. 83.7 – 84.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 (td, *J* = 7.4, 1.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.42 – 7.39 (m, 3H), 7.26 – 7.21(m, 4H), 7.16 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.35, 142.86, 142.06, 134.50, 134.25, 133.77, 133.12, 131.39, 131.17, 130.27, 128.83, 128.59, 128.42, 127.30, 122.45, 94.77, 87.27.

2′-(Phenylethynyl)-5′-(trifluoromethyl)-[1,1′-biphenyl]-2-carbaldehyde (**1h**). Pale yellow solid (483 mg, 1.38 mmol, 92%). R_f = 0.40 (PE/EA = 10/1). m.p. 79.5 – 80.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 8.11 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.26 (m, 3H), 7.18 – 7.15 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.09, 142.68, 141.21, 134.30, 133.87, 132.36, 131.56, 131.27, 130.33 (q, *J* = 32.7 Hz), 129.14, 128.99, 128.46, 127.60, 127.54, 126.88 (q, *J* = 3.8 Hz), 125.09 (q, *J* = 3.5 Hz), 123.85 (q, *J* = 273.7 Hz), 122.06, 96.35, 87.08. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.53. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{22}H_{14}F_3O$ 351.0991, found 351.0991.

2′-(Pyridin-2-ylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1i**). Pale yellow solid (378 mg, 1.34 mmol, 89%). R_f = 0.40 (PE/EA = 10/1). m.p. 104.6 – 104.9 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.50 (d, *J* = 3.3 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.66 (td, *J* = 7.5, 1.4 Hz, 1H), 7.55 – 7.39 (m, 6H), 7.15 – 7.11 (m, 1H), 7.00 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.60, 149.85, 143.88, 142.79, 140.57, 136.03, 134.09, 133.50, 132.57, 131.31, 130.26, 129.12, 128.29, 128.26, 127.06, 126.81, 122.83, 122.60, 92.68, 87.76. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{14}NO$ 284.1070, found 284.1069.

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2′-(Thiophen-2-ylethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1j**). Pale yellow oil (363 mg, 1.26 mmol, 84%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 8.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.98 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.88 (dd, *J* = 5.2, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.72, 144.11, 140.17, 134.24, 133.56, 132.06, 131.68, 131.32, 130.38, 128.59, 128.33, 128.29, 127.71, 127.14, 127.08, 123.47, 122.63, 92.02, 87.32. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{19}H_{13}OS$ 289.0682, found 289.0682.

2′-((Triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1k**). White solid (391 mg, 1.08 mmol, 72%). R_f = 0.50 (PE/EA = 10/1). m.p. 68.0 – 68.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.31 – 7.28 (m, 1H), 0.91 (s, 21H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.69, 144.63, 140.73, 134.10, 133.48, 132.78, 131.09, 130.19, 128.36, 128.10, 128.04, 127.07, 123.94, 105.21, 95.72, 18.52, 11.16. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{24}H_{31}OSi$ 363.2139, found 363.2138.

2′-(Hept-1-yn-1-yl)-[1,1′-biphenyl]-2-carbaldehyde (**1l**). Pale yellow oil (99 mg, 0.36 mmol, 24%). R_f = 0.50 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.50 – 7.49 (m, 2H), 7.35 – 7.32 (m, 4H), 7.25 (s, 1H), 2.17 – 2.13 (s, 2H), 1.33 – 1.26 (m, 2H), 1.21 – 1.16 (m, 2H), 1.11 – 1.05 (m, 2H), 0.83 – 0.79 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.01, 144.75, 140.20, 134.19, 133.48, 132.08, 131.21, 130.18, 128.14, 128.04, 127.75, 126.76, 124.57, 95.57, 79.50, 30.83, 27.86, 22.23, 19.34, 14.02. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{20}H_{21}O$ 277.1587, found 277.1587.

4-Chloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-carbaldehyde (**1m**). Pale yellow oil (422 mg, 1.07 mmol, 71%). R_f = 0.50 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 7.98 (d, *J* = 2.6 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.28 (m, 1H), 0.92 (s, 21H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.42, 142.86, 139.53, 135.30, 134.74, 133.38, 132.91, 132.64, 130.08, 128.57, 128.46, 126.95, 124.06, 104.90, 96.42, 18.51, 11.19. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{21}H_{24}ClOSi$ 355.1279, found 355.1278.

2-(2-(Phenylethynyl)pyridin-3-yl)benzaldehyde (**1n**). Pale yellow oil (365 mg, 1.29 mmol, 86%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 8.69 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.30 – 7.19 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.85, 149.76, 142.85, 141.49, 137.52, 136.68, 134.22, 133.75, 131.74, 131.39, 129.18, 128.95, 128.31, 127.74, 122.65, 121.66, 93.72, 87.72. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{20}H_{14}NO$ 284.1070, found 284.1069.

2-(3-(Phenylethynyl)pyridin-4-yl)benzaldehyde (**1o**). Pale yellow oil (386 mg, 1.36 mmol, 91%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.86 (s, 1H), 8.65 (d, *J* = 5.1 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.71 (td, *J* = 7.5, 1.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.34 (d, *J* = 5.1 Hz, 1H), 7.31 – 7.20 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.69, 152.52, 148.75, 147.84, 141.12, 133.85, 131.47, 130.73, 129.36, 129.05, 128.43, 127.84, 124.25, 122.04, 120.65, 96.70, 84.94. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{20}H_{14}NO$ 284.1070, found 284.1069.

2-(4-(Phenylethynyl)pyridin-3-yl)benzaldehyde (**1p**). Pale yellow oil (378 mg, 1.33 mmol, 89%). R_f = 0.40 (PE/EA = 10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.67 – 8.66 (m, 2H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.71 (td, *J* = 7.4, 1.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.19 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.88, 150.23, 149.34, 140.16, 135.03, 134.48, 133.81, 131.67, 131.63, 131.42, 129.48, 129.07, 128.45, 127.78, 125.13, 121.52, 98.27, 85.70. HRMS (ESI IT-TOF) *m*/*z* [M + H]$^+$ Calcd for $C_{20}H_{14}NO$ 284.1070, found 284.1069.

3.3 General Procedure for the Preparation of 1H-dibenzo[e,g]indazoles ***2a-2p***

The mixture of H_2NNHTs (1.1 equiv.), 2′-alkynyl-biaryl-2-aldehydes (**1**, 1.0 equiv.) and THF (5.0 mL) in a 25 mL screw-capped thick-walled Pyrex tube was stirred at 45 °C for 1 h. After the reaction was completed (checked by TLC), LiO^tBu (1.5 equiv.) and additional 2.5 mL of THF was added and then the mixture was stirred at 45 °C for 1 h. After the reaction was completed (checked by TLC), the crude residue was purified by column chromatography on silica gel, eluting with petroleum ether / ethyl acetate (gradient mixture ratio from 5 / 1 to 2 / 1) as eluent to afford product **2a-2p** in 61% - 93% yields.

3.4 Characterization Data of Products

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3-Phenyl-1H-dibenzo[e,g]indazole (**2a**). White solid (259 mg, 0.88 mmol, 88%). R_f = 0.40 (PE/EA = 1/1). m.p. 260.4 – 260.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.24 – 13.95 (s, 1H), 8.78 – 8.71 (m, 2H), 8.55 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.74 – 7.69 (m, 4H), 7.59 – 7.54 (m, 3H), 7.50 – 7.40 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.37, 137.25, 135.45, 129.62, 128.61, 128.32, 127.51, 127.41, 127.13, 124.95, 124.18, 124.07, 122.63, 122.34, 121.00, 112.55.

3-(4-Methoxyphenyl)-1H-dibenzo[e,g]indazole (**2b**). White solid (285 mg, 0.88 mmol, 88%). R_f = 0.40 (PE/EA = 1/1). m.p. 204.2 – 204.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.97 (s, 1H), 8.71 (dd, J = 16.9, 8.1 Hz, 2H), 8.56 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 7.74 – 7.63 (m, 4H), 7.49 – 7.40 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.34, 147.25, 137.27, 130.91, 129.68, 127.45, 127.31, 127.12, 124.87, 124.09, 123.99, 122.67, 122.40, 121.14, 114.02, 112.64, 55.14. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{22}H_{17}N_2O$ 325.1335, found 325.1334.

3-(p-Tolyl)-1H-dibenzo[e,g]indazole (**2c**). White solid (262 mg, 0.85 mmol, 85%). R_f = 0.40 (PE/EA = 1/1). m.p. 199.6 – 200.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.79 (s, 1H), 8.71 (dd, J = 17.1, 8.1 Hz, 2H), 8.57 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.48 – 7.36 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.18, 139.07, 137.85, 131.46, 129.70, 129.49, 129.26, 127.59, 127.49, 127.36, 127.12, 125.64, 124.99, 124.15, 123.99, 122.67, 122.38, 112.36, 20.95. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{22}H_{17}N_2$ 309.1386, found 309.1385.

3-(4-Fluorophenyl)-1H-dibenzo[e,g]indazole (**2d**). White solid (262 mg, 0.84 mmol, 84%). R_f = 0.40 (PE/EA = 1/1). m.p. 235.7 – 236.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.31 – 14.03 (s, 1H), 8.70 – 8.58 (m, 3H), 8.00 (s, 1H), 7.80 – 7.62 (m, 4H), 7.43 – 7.39 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.26 (d, J = 245.1 Hz), 146.41, 137.38, 131.89, 131.77, 131.69, 129.66, 127.48, 127.39, 127.17, 124.93, 124.13, 124.01, 122.60, 122.40, 121.04, 115.55 (d, J = 21.5 Hz), 112.66. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{21}H_{14}FN_2$ 313.1136, found 313.1134.

3-(4-Chlorophenyl)-1H-dibenzo[e,g]indazole (**2e**). White solid (262 mg, 0.80 mmol, 80%). R_f = 0.40 (PE/EA = 1/1). m.p. 265.3 – 265.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.18 (s, 1H), 8.76 (dd, J = 17.0, 8.0 Hz, 2H), 8.53 (dd, J = 7.7, 1.7 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.76 – 7.68 (m, 4H), 7.66 – 7.64 (m, 2H), 7.53 – 7.44 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.83, 138.58, 133.68, 133.32, 131.39, 129.69, 128.73, 127.61, 127.47, 127.40, 127.19, 127.12, 125.05, 124.13, 123.95, 122.64, 122.40, 121.72, 112.52. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{21}H_{14}ClN_2$ 329.0840, found 329.0838.

6-Methyl-3-phenyl-1H-dibenzo[e,g]indazole (**2f**). White solid (265 mg, 0.86 mmol, 86%). R_f = 0.40 (PE/EA = 1/1). m.p. 235.6 – 235.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.22 – 13.93 (s, 1H), 8.76 – 8.52 (m, 3H), 7.94 (d, J = 8.3 Hz, 1H), 7.76 – 7.52 (m, 7H), 7.19 (d, J = 8.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.12, 137.04, 135.60, 134.02, 129.61, 129.51, 128.55, 128.40, 128.23, 127.53, 127.30, 127.19, 124.88, 123.99, 122.59, 122.34, 121.16, 112.64, 21.26. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{22}H_{17}N_2$ 309.1386, found 309.1385.

6-Chloro-3-phenyl-1H-dibenzo[e,g]indazole (**2g**). White solid (276 mg, 0.84 mmol, 84%). R_f = 0.40 (PE/EA = 1/1). m.p. 286.9 – 287.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.77 (s, 1H), 8.73 – 8.69 (m, 2H), 8.51 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.75 – 7.64 (m, 4H), 7.60 – 7.52 (m, 3H), 7.40 (dd, J = 8.6, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 129.86, 129.55, 129.22, 128.74, 128.59, 128.12, 127.49, 127.08, 125.86, 124.32, 124.20, 123.65, 122.33, 111.74. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{21}H_{14}ClN_2$ 329.0840, found 329.0838.

3-Phenyl-6-(trifluoromethyl)-1H-dibenzo[e,g]indazole (**2h**). White solid (300 mg, 0.83 mmol, 83%). R_f = 0.40 (PE/EA = 1/1). m.p. 276.9 – 277.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.29 – 14.10 (s, 1H), 8.88 – 8.84 (m, 1H), 8.72 – 8.65 (m, 1H), 8.55 – 8.47 (m, 1H), 8.07 – 8.02 (m, 1H), 7.71 – 7.51 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.73, 138.05, 135.04, 129.87, 129.58, 128.80, 128.64, 128.45, 128.15, 127.61, 127.08, 126.02, 125.06 (q, J = 31.7 Hz), 124.14, 123.35 (d, J = 6.7 Hz), 122.84, 122.39, 121.13 (d, J = 15.7 Hz), 111.73. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.08. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{22}H_{14}F_3N_2$ 363.1104, found 363.1102.

3-(Pyridin-2-yl)-1H-dibenzo[e,g]indazole (**2i**). White solid (230 mg, 0.78 mmol, 78%). R_f = 0.40 (PE/EA = 1/1). m.p. 209.3 – 209.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.44 – 14.28 (s, 1H), 9.04 – 9.02 (m, 1H), 8.86 (d, J = 4.9 Hz, 1H), 8.79 – 8.58 (m, 3H), 8.06 – 7.97 (m, 2H), 7.78 – 7.67 (m, 2H), 7.52 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.35, 148.81, 147.16, 137.80, 137.04, 129.72, 127.58, 127.54, 127.48, 127.30, 127.05, 125.65, 125.24, 124.34, 124.04, 123.71, 123.15, 122.30, 120.92, 113.53. HRMS (ESI IT-TOF) m/z [M + H]$^+$ Calcd for $C_{20}H_{14}N_3$ 296.1182, found 296.1181.

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3-(Thiophen-2-yl)-1H-dibenzo[e,g]indazole (**2j**). White solid (273 mg, 0.91 mmol, 91%). R_f = 0.40 (PE/EA = 1/1). m.p. 255.4 – 255.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.40 – 14.17 (s, 1H), 8.71 – 8.56 (m, 3H), 8.34 – 8.31 (m, 1H), 7.76 – 7.73 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.32 – 7.30 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.47, 137.44, 136.12, 129.61, 128.07, 127.72, 127.55, 127.30, 127.10, 126.97, 125.19, 124.11, 124.03, 122.65, 122.36, 120.86, 113.25. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{19}H_{13}N_2S$ 301.0794, found 301.0793.

3-(Triisopropylsilyl)-1H-dibenzo[e,g]indazole (**2k**). White solid (348 mg, 0.93 mmol, 93%). R_f = 0.40 (PE/EA = 1/1). m.p. 87.8 – 88.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.12 (s, 1H), 8.75 (d, *J* = 7.6 Hz, 1H), 8.58 – 8.53 (m, 2H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.46 (m, 4H), 1.78 (hept, *J* = 7.5 Hz, 3H), 1.12 (d, *J* = 7.7 Hz, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 130.58, 129.10, 128.79, 127.31, 127.26, 126.54, 126.04, 125.39, 124.01, 123.62, 123.40, 123.21, 18.89, 12.74. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{24}H_{31}N_2Si$ 375.2251, found 375.2251.

3-Pentyl-1H-dibenzo[e,g]indazole (**2l**). White solid (176 mg, 0.61 mmol, 61%). R_f = 0.40 (PE/EA = 1/1). m.p. 188.5 – 188.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.69 – 13.49 (s, 1H), 8.78 – 8.67 (m, 2H), 8.44 (d, *J* = 7.5 Hz, 1H), 8.24 – 8.15 (m, 1H), 7.69 – 7.52 (m, 4H), 3.19 (t, *J* = 7.6 Hz, 2H), 1.82 – 1.80 (m, 2H), 1.42 – 1.32 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.37, 137.15, 129.46, 127.67, 127.32, 127.11, 124.40, 124.08, 123.17, 122.21, 121.17, 112.43, 31.20, 28.96, 27.75, 21.97, 13.94. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{21}N_2$ 289.1699, found 289.1698.

10-Chloro-3-(triisopropylsilyl)-1H-dibenzo[e,g]indazole (**2m**). White solid (335 mg, 0.82 mmol, 82%). R_f = 0.40 (PE/EA = 1/1). m.p. 191.1 – 191.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.96 (s, 1H), 8.68 (s, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.50 (m, 3H), 1.76 (hept, *J* = 7.5 Hz, 3H), 1.15 (d, *J* = 7.6 Hz, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.34, 129.03, 128.72, 128.55, 127.65, 126.94, 125.72, 125.52, 125.10, 124.01, 123.97, 122.83, 18.93, 12.78. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{24}H_{30}ClN_2Si$ 409.1861, found 409.1860.

3-Phenyl-1H-benzo[f]pyrazolo[3,4-h]quinoline (**2n**). White solid (260 mg, 0.88 mmol, 88%). R_f = 0.40 (PE/EA = 1/1). m.p. 265.7 – 266.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.39 – 14.16 (s, 1H), 9.02 – 8.92 (m, 1H), 8.78 – 8.56 (m, 3H), 8.29 – 8.14 (m, 2H), 7.79 – 7.62 (m, 2H), 7.55 – 7.42 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.60, 148.23, 147.43, 145.91, 144.68, 139.95, 139.70, 134.63, 131.70, 130.10, 129.96, 129.66, 128.92, 128.57, 128.08, 127.98, 127.63, 127.49, 126.03, 124.19, 123.89, 123.45, 122.44, 122.31, 120.87, 120.59, 120.16, 113.43, 112.53. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.84 (s, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 8.78 (d, *J* = 4.2 Hz, 1H), 8.57 – 8.55 (m, 1H), 8.44 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 2H), 7.70 (s, 2H), 7.56 – 7.43 (m, 4H) [b]. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{14}N_3$ 296.1182, found 296.1181.

3-Phenyl-1H-benzo[f]pyrazolo[3,4-h]isoquinoline (**2o**). White solid (266 mg, 0.90 mmol, 90%). R_f = 0.40 (PE/EA = 1/1). m.p. 277.9 – 278.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.37 – 14.12 (s, 1H), 9.22 (s, 1H), 8.82 – 8.72 (m, 1H), 8.56 – 8.52 (m, 3H), 7.85 – 7.59 (m, 7H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.96, 145.14, 144.19, 137.71, 135.14, 132.51, 129.63, 129.48, 128.76, 128.57, 127.74, 127.52, 124.76, 122.43, 117.54, 110.61. HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{14}N_3$ 296.1182, found 296.1181.

3-Phenyl-1H-benzo[h]pyrazolo[4,3-f]isoquinoline (**2p**). White solid (221 mg, 0.75 mmol, 75%). R_f = 0.40 (PE/EA = 1/1). m.p. 324.3 – 324.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.46 – 14.20 (s, 1H), 10.06 – 9.95 (m, 1H), 9.04 – 8.87 (m, 1H), 8.56 – 8.48 (m, 2H), 7.86 – 7.55 (m, 8H). HRMS (ESI IT-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{14}N_3$ 296.1182, found 296.1181. The ^{13}C NMR spectroscopic data could not be recorded due to the poor solubility in deuterated solvents, such as DMSO-d_6, $CDCl_3$.

4. Conclusion

In conclusion, the syntheses of 3-substituted 1*H*-dibenzo[*e*,*g*]indazoles in good to high yields have been developed *via* a LiO^{t}Bu-promoted intramolecular cyclization of 2′-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazones under mild conditions, since 2′-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazones were prepared *in situ* by the reactions of 2′-alkynyl-biaryl-2-aldehydes with *p*-methylbenzenesulfono-hydrazide, thus it is a simple and efficient two-step, one-pot procedure. In addition, two kinds of hydrogen bonds were observed in several products in DMSO-d_6 solution in their ^{1}H-NMR spectroscopic data, which are proposed to be the complexes of products with DMSO-d_6, and the dimer of products, respectively. In the case of **2a**, two kinds of hydrogen bonds with different binding energies of -13.2 kcal/mol and -16.6 kcal/mol were disclosed by DFT calculation.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org: the general procedure for the synthesis of starting materials, the copies of NMR charts of new starting materials, and all products, as well as X-ray structural details of **2a**.

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