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铑催化 2-芳基-2*H*-吲唑与硫叶立德的酰甲基化/串联环化反应高效构建 6-芳基吲唑并[2,3-*a*]喹啉类衍生物

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摘要 报道了铑(III)催化2-芳基-2*H*-吲唑与硫叶立德的C—H键活化/环化反应, 有效地合成了6-芳基吲唑并[2,3-*a*]喹啉及其衍生物. 该反应效率高, 官能团兼容性好, 避免了外置氧化剂, 并且副产物仅为二甲基亚砜(DMSO)和水. 此外放大反应证明了该方式在工业上应用的可行性.

关键词 2-芳基-2*H*-吲唑; 硫叶立德; 铑催化; 环化

Rhodium-Catalyzed Tandem Acylmethylation/Annulation Reactions of 2-Aryl-2*H*-indazoles with Sulfoxonium Ylides: Easy Access to 6-Arylindazolo[2,3-*a*]quinolines

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Abstract An efficient synthesis of 6-arylindazolo[2,3-*a*]quinolines starting from 2-aryl-2*H*-indazoles with sulfoxonium ylides via rhodium(III)-catalyzed C—H activation and cyclization reaction has been described. This transformation features high efficiency, tolerates various functional groups, avoids external oxidant and produces dimethyl sulfoxide (DMSO) and H_2O as the sole by-products. In addition, the scale-up reaction demonstrated the practicability of this protocol in industry.

Keywords 2-aryl-2*H*-indazoles; sulfoxonium ylides; rhodium-catalyzed; cyclization

1 Introduction

Heterocyclic frameworks fused π-conjugated systems exhibit important electrochemical and photochemical properties with potential applications as luminescence materials.[1] Particularly, indazolo[2,3-*a*]quinoline is fundamental structural motif in biologically active molecules[2] and organic light-emitting diodes.[3] Considering their immense importance, extensive efforts have been devoted to construct such core.[4] Although the significant progress has been made, the highly functionalized starting materials, excess external oxidants and hash reaction conditions are required. Therefore, it is urgent to explore novel green and efficient catalytic systems to synthesize indazolo[2,3-*a*]-quinolines. In the past decades, the transition metal catalyzed C—H bond functionalization has proved to be a powerful tool for the construction of complex structures due to high atom- and step-economy.[5] Among them, the transition metal-catalyzed C—H bond activation reaction involving directing groups (DGs) could greatly enhance the regioselectivity of the reaction.[6]

However, most of the DGs should be further transformed or removed, which greatly reduced their atom economy.[7] Recently, DGs-involved C—H bond activation tandem cyclization has been well developed.[8] However, the research on transition metal catalyzed C—H bond cyclization of indazoles to synthesize indazolo[2,3-*a*]quinoline and its derivatives is still infancy. In 2012, Punniyamurthy[4f]

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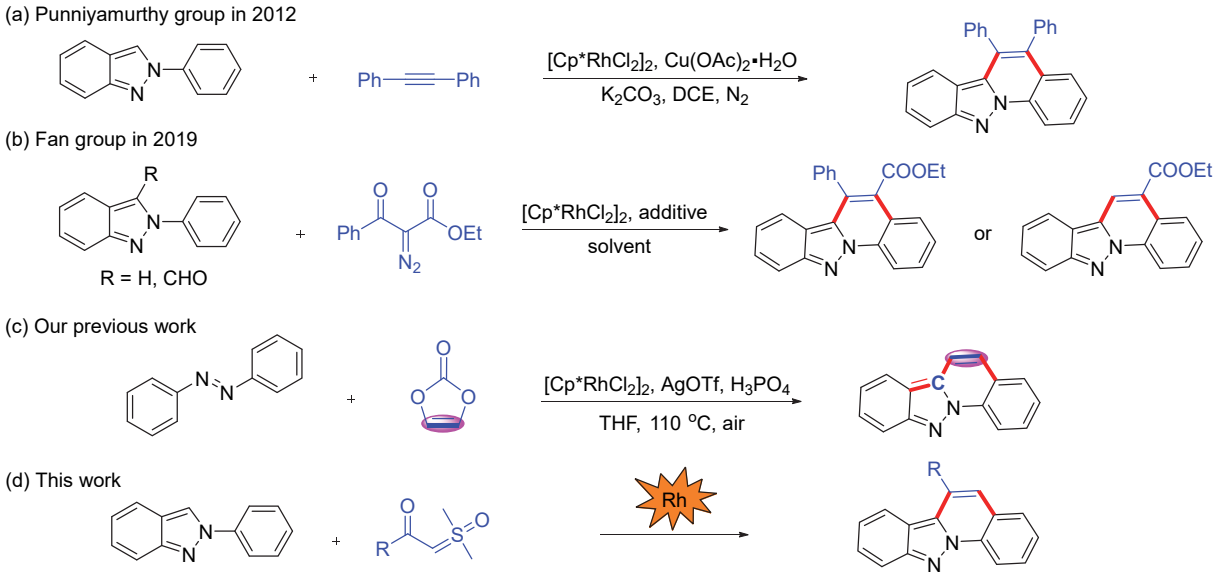


Scheme 1 Transition metal catalyzed C—H cyclization to build indazolo[2,3-*a*]quinolines

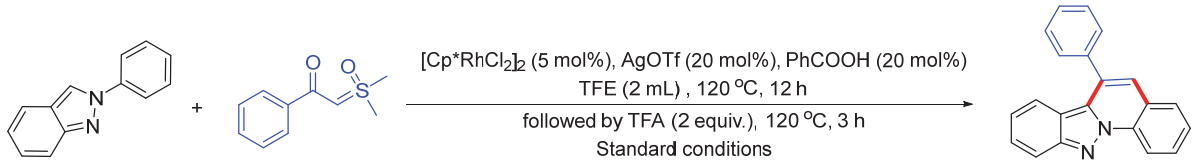
reported a Rh(III)-catalyzed oxidative annulation of 2-aryl-2*H*-indazoles with internal alkynes, leading to the formation of indazolo[2,3-*a*]quinolines (Scheme 1a). The excessive $Cu(OAc)_2$•H_2O as an external oxidant was required to regenerate active metal catalyst. Subsequently, Fan *et. al.*[4g] disclosed Rh(III)-catalyzed oxidant-free [4＋2] or [5＋1] annulation reaction of 2-aryl-2*H*-indazoles starting from *α*-diazo carbonyl compounds and selectively offered 5,6-disubstituted or 5-substitued indazolo[2,3-*a*]quinolines (Scheme 1b). Recently, our group developed rhodium-catalyzed cyclization of azobenzenes with vinylene carbonate via C—H bond activation to construct non-substituted indazolo[2,3-*a*]quinolines (Scheme 1c).[9] The vinylene carbonate (VC) acts as C(1) and C(2) synthons as well as "vinylene transfer" and acylation reagent in this transformation. On the other hand, sulfoxonium ylides, as versatile synthetic precursor, have emerged in C—H functionalization[10] because of its safe and higher coordination affinity with the metal center, leading to easily convert carbonyl compounds and provide the possibility to construct complex molecules through tandem annulation in "one-pot" manner.[11] Inspired by these elegant works, we deduced that the nucleophilicity of indazoles might contribute to tandem annulation with carbonyl compounds to synthesize indazolo[2,3-*a*]quinolines. Based on our research on the construction of heterocyclic compounds,[12] herein, we explored the synthesis of 6-arylindazolo[2,3-*a*]-quinolines via Rh(III)-catalyzed [4＋2] annulation of 2-aryl-2*H*-indazoles with sulfoxonium ylides in one pot (Scheme 1d). This reaction features excellent regioselectivity and tolerance of broad scope. DMSO and water are released as the sole byproducts. Meanwhile, the scale-up reaction demonstrated the practicability of this protocol.

2 Results and discussion

Initially, 2-phenyl-2*H*-indazole (**1a**) and benzoyl sulfoxonium ylide **2a** were chosen as the model substrates to optimize various reaction conditions. The desired 6-phenylindazolo[2,3-*a*]quinoline (**3aa**) was obtained in 83% yield in the presence of $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (20 mol%) and PhCOOH (20 mol%) in trifluoroethanol (TFE, 2 mL) at 120 ℃ for 12 h followed by addition of trifluoroacetate (TFA, 2 equiv.) and continued reaction for 3 h at 120 ℃ (Table 1, Entry 1). In the absence of $[Cp^*RhCl_2]_2$ or AgOTf, the reaction could not work well (Table 1, Entries 2, 3), which indicated that the catalyst and silver salt were essential for the reaction. Subsequently, other transition-metals as the catalyst were investigated (including $[Cp^*Co(CO)I_2]$, $[Cp^*IrCl_2]_2$, $[RuCl_2(p\text{-cymene})Cl_2]_2$ and $Pd(OAc)_2$), and no product was obtained (Table 1, Entries 4～7). Meanwhile, the effect of silver salts was investigated, such as $AgSbF_6$, $AgNTf_2$, PhCOOAg, Ag_2CO_3, CF_3COOAg and $AgBF_4$. While none of them was more effective (Table 1, Entry 8). Investigation of the solvents showed that TFE was superior to DCE, DCM, CH_3CN, THF, DMF, MeOH, HFIP and toluene (Table 1, Entry 9). Then, different acids, including PivOH, HOAc, 1-AdCOOH and TsOH were used instead of PhCOOH, all resulted in the inferior efficiency (Table 1, Entry 10). When the loading of TFA was decreased to 1 equiv., the yield of **3aa** was decreased to 64% (Table 1, Entry 11).

With the optimal reaction conditions in hand, the scope of indazoles was first examined with **2a** as a model substrate. As summarized in Table 2, when indazoles with electron-withdrawing (F, Cl and Br) or electron-donating (MeO) at C(5) or C(6) were examined, the corresponding indazolo[2,3-*a*]quinolines **3aa**～**3ia** were afforded in 60%～84% yields through [4＋2] cyclization. In addition, the 2-phenyl-5-trifluoromethyl-2*H*-indazole was employed in reaction, however, affording the desired product **3ja** in only 30% yield, probably due to its strong electron-withdrawing ability. Meanwhile, this transformation also tolerated COOMe group at C(6), providing the corresponding product **3ka** in moderate yield. Indazole with two methoxy groups at C(5)

Table 1 Optimization of the reaction conditions[a]

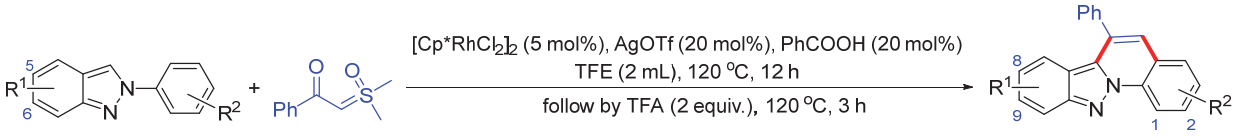


1a **2a** **3aa**

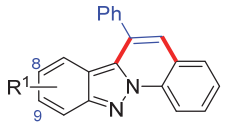
Entry	Variation from standard conditions	Yield[b]/%
1	None	83
2	Without $[Cp^*RhCl_2]_2$	NR
3	Without AgOTf	NR
4	$Cp^*Co(CO)I_2$ instead of $[Cp^*RhCl_2]_2$	NR
5	$[Cp^*IrCl_2]_2$ instead of $[Cp^*RhCl_2]_2$	NR
6	$[RuCl_2(p\text{-cymene})]_2$ instead of $[Cp^*RhCl_2]_2$	NR
7	$Pd(OAc)_2$ instead of $[Cp^*RhCl_2]_2$	NR
8	$AgSbF_6$, $AgNTf_2$, PhCOOAg, Ag_2CO_3, CF_3COOAg, $AgBF_4$ instead of AgOTf	64/68/56/46/64/70
9	DCE, DCM, CH_3CN, THF, DMF, MeOH, HFIP, toluene instead of TFE	52/48/43/NR/NR/63/45/60
10	PivOH, HOAc, 1-AdCOOH, TsOH instead of PhCOOH	52/63/58/54
11	TFA (1 equiv.)	64
12	80 ℃ instead of 120 ℃	42

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (5 mol%), Ag salt (20 mol%), acid (20 mol%), solvent (2 mL), 12 h, 120 ℃ then TFA (2 equiv.), 3 h, 120 ℃. DCE: 1,2-dichloroethane, DCM: dichloromethane, THF: tetrahydrofuran, DMF: *N*,*N*-dimethylformamide, HFIP: hexafluoroisopropanol, TFE: trifluoroethanol, TFA: trifluoroacetic acid, NR: no reaction. [b] Isolated yields.

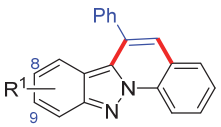
Table 2 Scope of 2-aryl-2*H*-indazoles[a,b]



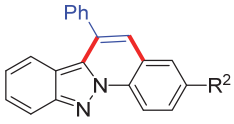
1a-y **2a** **3aa-ya**



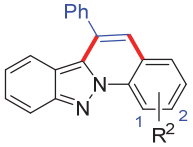
3aa, R^1 = H, 83%/68%[c]; **3ba**, R^1 = 9-F, 73%;
3ca, R^1 = 8-F, 84%; **3da**, R^1 = 9-Cl, 60%;
3ea, R^1 = 8-Cl, 70%; **3fa**, R^1 = 9-Br, 64%;
3ga, R^1 = 8-Br, 75%; **3ha**, R^1 = 9-OMe, 74%;
3ia, R^1 = 8-OMe, 84%



3ja, R^1 = 8-CF_3, 30%
3ka, R^1 = 9-COOMe, 62%
3la, R^1 = 8,9-$(OMe)_2$, 48%



3ma, R^2 = Me, 84%; **3na**, R^2 = OMe, 78%;
3oa, R^2 = F, 80%; **3pa**, R^2 = Cl, 69%;
3qa, R^2 = Br, 55%; **3ra**, R^2 = ^{i}Pr, 54%;
3sa, R^2 = ^{t}Bu, 45%; **3ta**, R^2 = COOMe, 50%;
3ua, R^2 = CF_3, 45%



3va, R^2 = 2-Me, 45%
3wa, R^2 = 2-Cl, 42%
3xa, R^2 = 1-OMe, 62%
3ya, R^2 = 1-F, 45%

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.15 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (20 mol%), PhCOOH (20 mol%), TFE (2 mL), 12 h, 120 ℃, then TFA (2 equiv.), 3 h, 120 ℃. [b] Isolated yields. [c] **1a** (0.97 g) was used.

and C(6) gave the corresponding product **3la** in 48% yield. Subsequently, the effect of R^2 in 2-aryl-2*H*-indazoles was tested. To our delight, when various groups (such as Me, MeO, halogen, *iso*-propyl, *tert*-butyl, COOMe and CF_3) were introduced at the *para*, *meta* and *ortho* position of 2-phenyl unit of **1**, this transformation showed satisfactory tolerance and afforded products **3ma**～**3ya** in moderate to good yields. These results indicated that the electron density and steric hindrance of the 2-phenyl unit had no significant effect on the reaction. To demonstrate the synthetic potential application of the present method, a gram-scale reaction of **1a** with **2a** was performed under the standard reaction conditions, and product **3aa** was obtained in 68% yield.

To further evaluate the scope of this protocol, the scope of sulfoxonium ylides was examined. The results are shown in Table 3. A variety of electron-donating (Me, MeO) or electron-withdrawing (F, Cl, Br and I) groups at the *para* position of the phenyl ring were all well tolerated in this

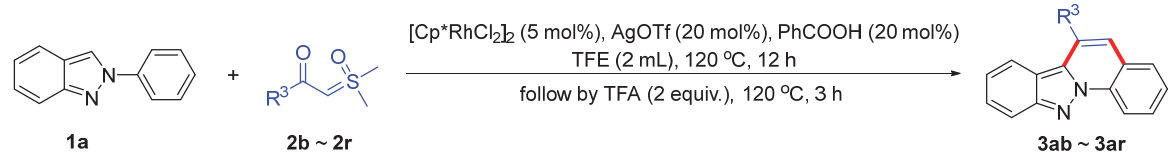
transformation, affording the corresponding products **3ab**～**3ag** in 74%～88% yields. Whereas, the desired products **3ah**～**3ai** were afforded in 65% and 35% yields for *para*-CF_3 and -NO_2 substituted sulfoxonium ylides, respectively, perhaps due to their strong electron-withdrawing ability. In addition, substitutions at the *meta*-position of the benzene ring were also suitable for this reaction, delivering the corresponding products **3aj**～**3ak** in 75%～78% yields. However, sulfoxonium ylides bearing *ortho* Me and Cl provided the corresponding products **3am**～**3an** in 24%～43% yields probably due to the steric hindrance.

The 3,5-dichlorophenylsulfoxonium ylide was coupled with **1a** to provide the corresponding product **3ao** in 80% yield. To our delight, other aromatic rings, such as furan, thiophene and naphthalene, also showed good reactivity, delivering the corresponding products in 43%～64% yields.

To gain insight into the mechanism of this transformation, a series of control experiments were conducted as shown in Scheme 2. The desired product could be obtained in 92% isolated yield by treatment of 2-(2-(2*H*-indazol-2-yl)phenyl)-1-phenylethan-1-one with 2 equiv. of TFA, which further implied that TFA was crucial for the transformation of the intermediate to the final product **3aa** (Scheme 2a). Under the standard reaction conditions, the reaction of **1a** with D_2O afforded **1a-d2** with 30% of deuterium in corporation based on ^1H NMR analysis (see supporting information), which suggested that the step of the C—H bond cleavage might be reversible (Scheme 2b). In addition, the reaction involving **1a-d5** with **2a** gave a kinetic isotope effect (KIE) value of 5.25, indicating that aryl C—H bond cleavage might be involved in the turnover-limiting step (Scheme 2c).

On the basis of the above experimental results and the previous literatures,[4f-4g,8] a plausible mechanistic pathway was proposed in Scheme 3. Firstly, the cationic active species Cp*Rh(III) is generated through treatment of $[Cp^*RhCl_2]_2$ with AgOTf, and can coordinate with **1a** to afford the intermediate **I**. Then, coordination of sulfoxonium ylide with Rh(III) intermediate **I** generates intermediate **II**, which forms a reactive rhodium *α*-oxo carbene species **III** by *α*-elimination of DMSO. Subsequently, the intermediate **III** undergoes migratory insertion of the Rh—C bond to give a

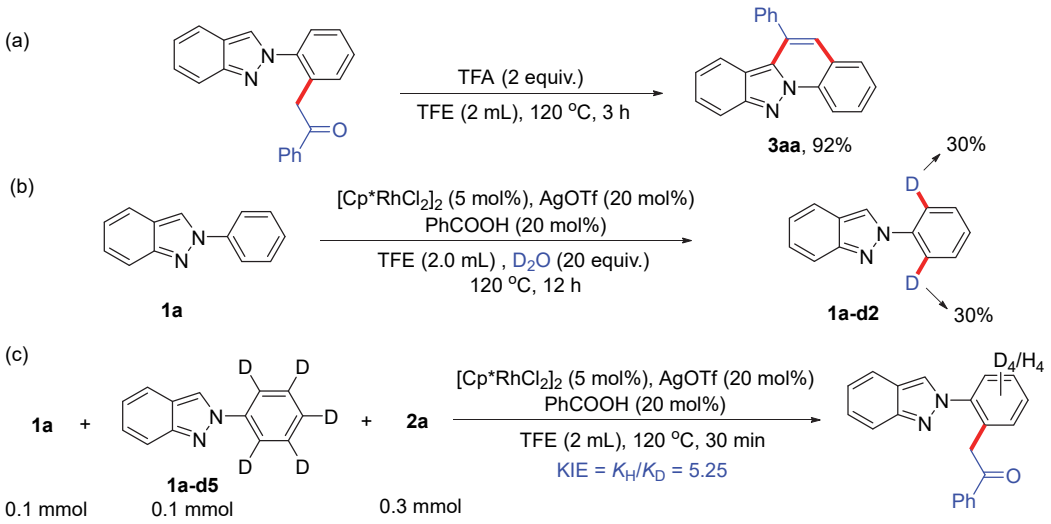
Table 3 Scope of sulfoxonium ylides[a,b]



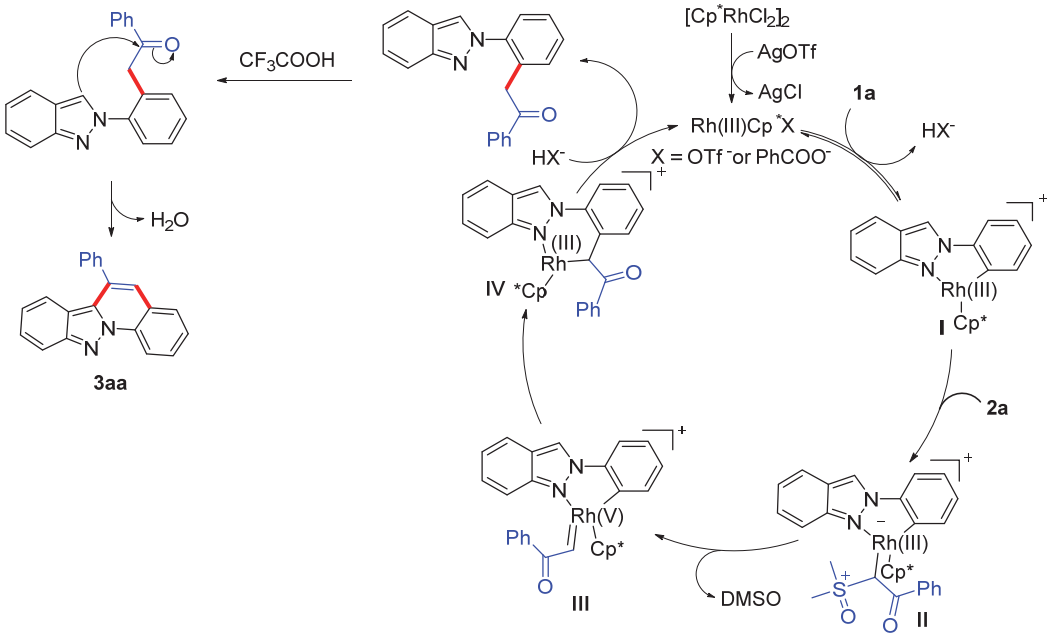
3ab, R^3 = 4-MeC_6H_4, 77%
3ac, R^3 = 4-$MeOC_6H_4$, 85%
3ad, R^3= 4-FC_6H_4, 84%
3ae, R^3 = 4-ClC_6H_4, 88%
3af, R^3 = 4-BrC_6H_4, 76%
3ag, R^3 = 4-IC_6H_4, 74%
3ah, R^3 = 4-$CF_3C_6H_4$, 65%
3ai, R^3 = 4-$NO_2C_6H_4$, 35%

3aj, R^3 = 3-MeC_6H_4, 78%; **3ak**, R^3 = 3-ClC_6H_4, 75%;
3al, R^3 = 3-BrC_6H_4, 77%; **3am**, R^3 = 2-MeC_6H_4, 24%;
3an, R^3 = 2-ClC_6H_4, 43%; **3ao**, R^3 = 3,5-$Cl_2C_6H_3$, 80%
3ap, R^3 = furan-2-yl, 64%; **3aq**, R^3 = thiophen-2-yl, 43%
3ar, R^3 = naphthalen-2-yl, 45%

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (20 mol%), PhCOOH (20 mol%), TFE (2 mL), 12 h, 120 ℃, then TFA (2 equiv.), 3 h, 120 ℃. [b] Isolated yields.



Scheme 2 Control experiment and KIE study



Scheme 3 Proposed reaction mechanism for tandem acylmethylation/annulation reactions of 2-aryl-2*H*-indazoles with sulfoxoium ylides

six-membered rhodacyclic intermediate **IV**. Protonolysis of the Rh—N and Rh—C bonds releases the acylmethylated intermediate and regenerates the active Rh(III) catalyst for next cycle. Finally, the desired product **3aa** is afforded through TFA-mediated intramolecular cyclization and dehydration.

3 Conclusions

In summary, we have developed Rh(III)-catalyzed C—H acylmethylation and TFA-mediated cyclization of 2-aryl-2*H*-indazoles with sulfoxonium ylides to afford indazolo[2,3-*a*]quinoline structural frameworks. The protocol showed good functional group tolerance and high atom economy. In this approach, external oxidants were avoided, and DMSO and water were released as the sole byproduct. The reaction could perform on a gram scale and maintain a relatively good efficiency. Further application of the obtained indazolo[2,3-*a*]quinolones is currently ongoing in our laboratory.

4 Experimental section

4.1 General experimental information

All experiments were carried out under air atmosphere. indazoles **1**[13] and sulfoxonium ylides **2**[14] were prepared according to literatures. All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer and the frequencies for ^{1}H NMR and ^{13}C NMR test are 400 and 100 MHz, respectively. The chemical shifts were reported with TMS as internal standard. Melting points were tested in an X-4A instrument without correcting temperature. High resolution mass spectra (HRMS) were obtained on an Agilent Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI). Liquid Chromatograph Mass Spectrometer (LC-MS) was performed on a 6120-Quadrupole from Agilent Technologies 1260 Infinity.

4.2 General catalytic procedure

To a 15 mL flame-dried tube were added $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTf (5.1 mg, 20 mol%), PhCOOH (2.4 mg, 20 mol%), **1** (0.1 mmol), **2** (0.15 mmol) and TFE (2 mL). The tube was sealed and stirred at 120 ℃ for 12 h. After cooled down to room temperature, TFA (0.2 mmol) was added. Then, the reaction mixture was stirred at 120 ℃ for 3 h. Next, TFE was removed under reduced pressure, H_2O was added and the mixture was extracted with dichloromethane. The extract was washed with brine and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography to provide the product **3** with the elution of mixed petroleum ether/ethyl acetate (V∶V=99∶1).

1-(2-(2*H*-Indazol-2-yl)phenyl)-2-phenylethan-1-one: White solid, isolated yield 76% (23.7 mg). m.p. 112.2～114 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (s, 1H), 7.79 (d, J=7.2 Hz, 2H), 7.64 (d, J=9.1 Hz, 1H), 7.56 (d, J=8.9 Hz, 1H), 7.50～7.44 (m, 4H), 7.41 (d, J=7.3 Hz, 1H), 7.35 (t, J=7.9 Hz, 2H), 7.25 (t, J=9.8 Hz, 1H), 7.06 (t, J=7.3 Hz, 1H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.1, 149.5, 140.3, 136.6, 133.1, 132.3, 131.2, 129.3, 128.5, 128.3, 128.0, 126.5, 126.4, 124.7, 122.2, 122.0, 120.5, 117.7, 41.6. HRMS (ESI) calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1335, found 313.1333.

6-Phenylindazolo[2,3-*a*]quinoline (**3aa**): Yellow-green

solid, isolated yield 83% (24.4 mg). m.p. 187～189 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (d, J=8.8 Hz, 1H), 7.95 (d, J=8.8 Hz, 1H), 7.83 (d, J=7.84 Hz, 1H), 7.73 (t, J=7.3 Hz, 1H), 7.61～7.72 (m, 2H), 7.53～7.55 (m, 4H), 7.45 (t, J=7.0 Hz, 2H), 7.30 (d, J=8.3 Hz, 1H), 6.98 (t, J=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 137.6, 133.8, 132.7, 131.3, 129.2, 129.1, 128.8, 128.7, 128.3, 127.7, 126.3, 125.0, 123.3, 121.8, 120.5, 117.3, 116.8, 116.7. HRMS (ESI) calcd for $C_{21}H_{15}N_2$ $[M+H]^+$ 295.1230, found 295.1232.

9-Fluoro-6-phenylindazolo[2,3-*a*]quinoline (**3ba**): Yellow-green solid, isolated yield 73% (22.7 mg). m.p. 168～171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94 (d, J=8.4 Hz, 1H), 7.93 (d, J=7.8 Hz, 1H), 7.81 (t, J=5.2 Hz, 1H), 7.66～7.22 (m, 3H), 7.61～7.58 (m, 3H), 7.55 (s, 1H), 7.52 (dd, J=10.0, 2.2 Hz, 1H), 7.26 (t, J=6.8 Hz, 1H), 6.78 (td, J=8.8, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.7 (d, J=244 Hz), 149.9 (d, J=13.3 Hz), 137.3, 133.3, 132.2, 131.6, 129.5, 129.1, 128.9 (d, J=2.1 Hz), 128.4, 126.4, 124.8, 124.0, 123.7, 123.5, 117.2, 113.9, 111.5 (d, J=27.5 Hz), 100.0 (d, J=22.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): －111.95 (s). HRMS (ESI) calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1140.

8-Fluoro-6-phenylindazolo[2,3-*a*]quinoline (**3ca**): Yellow-green solid, isolated yield 84% (26.2 mg). m.p. 136～139 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.93 (d, J=8.4 Hz, 1H), 7.93～7.90 (m, 2H), 7.79 (t, J=7.6 Hz, 1H), 7.65～7.58 (m, 6H), 7.48 (s, 1H), 7.26 (td, J=9.2, 2.4 Hz, 1H), 6.89 (dd, J=9.2, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3 (d, J=242 Hz), 146.7, 137.1, 133.5, 132.6, 131.5 (d, J=8.0 Hz), 129.3, 129.0, 128.9 (d, J=1.4 Hz), 128.4, 126.5, 125.0, 123.0, 118.8, 118.5 (d, J=9.3 Hz), 117.1, 116.1, 115.9, 105.0 (d, J=25.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: －120.24 (s). HRMS (ESI) calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1140.

9-Chloro-6-phenylindazolo[2,3-*a*]quinoline (**3da**): Yellow-green solid, isolated yield 60% (19.6 mg). m.p. 188～191 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (d, J=8.8 Hz, 1H), 7.93 (d, J=8.8 Hz, 2H), 7.82 (t, J=7.8 Hz, 1H), 7.66～7.58 (m, 6H), 7.56 (s, 1H), 7.23 (d, J=8.8 Hz, 1H), 6.94 (dd, J=6.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ ＋DMSO) δ: 149.6, 137.0, 133.4, 133.2, 132.2, 131.4, 129.5, 128.9 (2), 128.8, 128.4, 126.6, 124.9, 124.0, 122.9, 121.5, 117.1, 115.4, 115.1. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0843.

8-Chloro-6-phenylindazolo[2,3-*a*]quinoline (**3ea**): Yellow-green solid, isolated yield 70% (22.9 mg). m.p. 235～237 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94 (d, J=8.4 Hz, 1H), 7.90 (q, J=7.6 Hz, 2H), 7.80 (t, J=7.6 Hz, 1H), 7.66～7.59 (m, 6H), 7.52 (s, 1H), 7.40 (dd, J=8.8, 1.2 Hz, 1H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 137.1, 133.3, 132.6, 130.9, 129.5, 129.1, 129.0 (2), 128.8, 128.4, 126.7, 125.8, 125.1, 123.7, 120.6, 118.1, 117.3, 117.2. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0842.

9-Bromo-6-phenylindazolo[2,3-*a*]quinoline (**3fa**): Yellow-green solid, isolated yield 64% (23.8 mg). m.p. 176～179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94 (d, J=8.4 Hz, 1H), 8.10 (s, 1H), 7.92 (d, J=8.0 Hz, 1H), 7.80 (t, J=7.8 Hz, 1H), 7.65～7.57 (m, 6H), 7.54 (s, 1H), 7.16 (d, J=9.2 Hz, 1H), 7.05 (dd, J=8.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 137.2, 133.3, 132.4, 131.6, 129.5, 129.0, 128 (2), 128.4, 126.6, 125.0, 124.1, 124.0, 123.1, 121.8, 119.0, 117.3, 115.4. HRMS (ESI) calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0336.

8-Bromo-6-phenylindazolo[2,3-*a*]quinoline (**3ga**): Yellow-green solid, isolated yield 75% (27.9mg). m.p. 232～235 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94 (d, J=8.4 Hz, 1H), 7.93 (d, J=8.0 Hz, 1H), 7.84～7.79 (m, 2H), 7.66～7.64 (m, 2H), 7.62～7.59 (m, 3H), 7.52 (dd, J=10.0, 2.0 Hz, 2H), 7.46 (d, J=1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 137.0, 133.3, 132.6, 131.2, 130.7, 129.5, 129.1, 129.0 (2), 128.4, 126.7, 125.1, 124.0, 123.8, 118.3, 117.9, 117.3, 113.5. HRMS (ESI) calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0334.

9-Methoxy-6-phenylindazolo[2,3-*a*]quinoline (**3ha**): Yellow-green solid, isolated yield 74% (24.0 mg). m.p. 124～127 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, J=8.4 Hz, 1H), 7.88 (d, J=7.2 Hz, 1H), 7.68 (td, J=7.6 Hz, J=1.2 Hz, 1H), 7.66～7.63 (m, 2H), 7.60～7.54 (m, 4H), 7.48 (s, 1H), 7.22 (d, J=2.0 Hz, 1H), 7.17 (d, J=9.2 Hz, 1H), 6.68 (dd, J=9.2, 2.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 151.0, 133.5, 132.2, 131.5, 129.3, 129.1, 128.8, 128.7, 128.3, 125.8, 124.5, 123.6, 122.6, 116.9, 114.9, 111.9, 94.1, 55.3. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1335, found 325.1339.

8-Methoxy-6-phenylindazolo[2,3-*a*]quinoline (**3ia**): Yellow-green solid, isolated yield 84% (27.3 mg). m.p. 189～192 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, J=8.4 Hz, 1H), 7.87 (t, J=9.2 Hz, 2H), 7.56 (td, J=8.4, 1.2 Hz, 1H), 7.68～7.37 (m, 2H), 7.60～7.55 (m, 4H), 7.42 (s, 1H), 7.17 (dd, J=9.1, 2.4 Hz, 1H), 6.48 (d, J=2.4 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0, 146.0, 137.6, 133.7, 132.7, 130.6, 129.3, 129.0, 128.7, 128.6, 128.3, 126.1, 124.9, 122.0, 121.8, 118.0, 116.9, 116.5, 99.1, 55.1. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1335, found 325.1338.

6-Phenyl-8-(trifluoromethyl)indazolo[2,3-*a*]quinoline (**3ja**): Yellow-green solid, isolated yield 30% (10.8 mg). m.p. 172～175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (d, J=8.4 Hz, 1H), 7.99 (q, J=8.0 Hz, 2H), 7.85 (td, J=7.2, 1.2 Hz, 1H), 7.69～7.61 (m, 9H); ^{13}C NMR (100 MHz, $CDCl^3$) δ: 150.0, 136.8, 133.3, 132.6, 132.4, 129.8, 129.2, 129.0 (d, J=5.8 Hz), 128.5, 126.9, 126.1, 123.7 (q, J=4.2 Hz), 123.2 (q, J=279.0 Hz), 124.6, 123.0 (d, J=2.8 Hz), 122.2 (d, J=31.5 Hz), 120.4 (q, J=4.4 Hz), 117.5 (d, J=4.1 Hz), 115.4. ^{19}F NMR (376 MHz, $CDCl_3$): －61.39 (s). HRMS (ESI) calcd for $C_{21}H_{14}F_3N_2$ $[M+H]^+$ 363.1104, found 363.1107.

Methyl 6-phenylindazolo[2,3-*a*]quinoline-9-carboxylate (**3ka**): Yellow-green solid, isolated yield 62% (21.8 mg). m.p. 225～229 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (d, J=8.4 Hz, 1H), 8.73 (s, 1H), 7.94 (d, J=8.0 Hz, 1H), 7.83 (td, J=7.2, 1.2 Hz, 1H), 7.68～7.59 (m, 7H),

7.56 (s, 1H), 7.35 (d, J=8.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.5, 148.7, 137.2, 133.3, 132.8, 131.3, 129.5, 129.2, 129.1, 129.0, 128.9, 128.4, 126.9, 125.3, 123.7, 121.8, 120.2, 120.1, 118.9, 117.5, 52.3. HRMS (ESI) calcd for $C_{23}H_{17}N_2O_2$ $[M+H]^+$ 353.1285, found 353.1288.

8,9-Dimethoxy-6-phenylindazolo[2,3-*a*]quinoline (**3la**): Yellow-green solid, isolated yield 48% (16.9 mg). m.p. 150～153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, J=8.4 Hz, 1H), 7.87 (d, J=8.0 Hz, 1H), 7.75 (td, J=8.0 Hz, J=1.2 Hz, 1H), 7.68～7.66 (m, 2H), 7.61～7.53 (m, 4H), 7.42 (s, 1H), 6.48 (s, 1H), 4.01 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 146.4, 146.3, 137.6, 133.7, 132.2, 130.7, 129.3, 129.1, 128.7, 128.6, 128.3, 125.5, 124.4, 122.4, 116.5, 110.5, 99.6, 95.3, 56.0, 55.6. HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2$ $[M+H]^+$ 355.1441, found 353.1444.

3-Methyl-6-phenylindazolo[2,3-*a*]quinoline (**3ma**): Yellow-green solid, isolated yield 84% (25.8 mg). m.p. 185～188 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J=8.4 Hz, 1H), 7.95 (d, J=8.8 Hz, 1H), 7.61～7.64 (m, 3H), 7.62～7.55 (m, 4H), 7.48～7.43 (m, 2H), 7.31 (d, J=8.4 Hz, 1H), 6.99 (t, J=7.6 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 137.7, 136.3, 132.6, 131.6, 131.0, 130.9, 129.1, 128.8, 128.7, 127.8, 127.5, 125.1, 123.1, 121.7, 120.3, 117.1, 116.8, 116.5, 21.4. HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1389.

3-Methoxy-6-phenylindazolo[2,3-*a*]quinoline (**3na**): Yellow-green solid, isolated yield 78% (25.2 mg). m.p. 178～180 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (d, J=9.2 Hz, 1H), 7.93 (d, J=8.8 Hz, 1H), 7.66～7.64 (m, 2H), 7.58～7.55 (m, 3H), 7.45 (t, J=8.0 Hz, 1H), 7.41 (s, 1H), 7.38 (dd, J=9.2, 2.7 Hz, 1H), 7.31 (d, J=8.4 Hz, 1H), 7.24 (d, J=2.7 Hz, 1H), 6.99 (td, J=7.0, 0.6 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 149.3, 137.6, 133.2, 130.4, 129.1, 128.8, 128.7, 128.3, 127.4, 126.2, 122.9, 121.6, 120.3, 119.2, 118.8, 116.8, 116.4, 108.5, 55.7. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1335, found 325.1338.

3-Fluoro-6-phenylindazolo[2,3-*a*]quinoline (**3oa**): Yellow-green solid, isolated yield 80% (24.9 mg). m.p. 180～183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (q, J=4.2 Hz, 1H), 7.95 (d, J=8.8 Hz, 1H), 7.67～7.64 (m, 2H), 7.62～7.57 (m, 3H), 7.55 (t, J=2.8 Hz, 1H), 7.52～7.46 (m, 2H), 7.43 (s, 1H), 7.31 (d, J=8.4 Hz, 1H), 7.02 (t, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6 (d, J=247.2 Hz), 149.5, 137.2, 134.0, 130.9, 130.1, 129.0 (d, J=7.2 Hz), 128.9, 127.8, 126.3, 126.2, 122.3 (d, J=3.5 Hz), 121.6, 120.8, 119.5 (d, J=8.9 Hz), 117.8 (d, J=24.8 Hz), 116.9, 116.6, 112.7 (d, J=22.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): −114.66 (s). HRMS (ESI) calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1138.

3-Chloro-6-phenylindazolo[2,3-*a*]quinoline (**3pa**): Yellow-green solid, isolated yield 69% (22.6 mg). m.p. 187～190 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (d, J=9.2 Hz, 1H), 7.93 (d, J=8.8 Hz, 1H), 7.87 (d, J=2.4 Hz, 1H), 7.71 (dd, J=9.2, 2.4 Hz, 1H), 7.66～7.64 (m, 2H), 7.60～7.58 (m, 3H), 7.48 (t, J=7.8 Hz, 1H), 7.39 (s, 1H), 7.29 (d, J=8.4 Hz, 1H), 7.01 (t, J=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 137.1, 134.0, 132.0, 131.8, 131.2, 129.5, 129.0, 128.9, 128.8, 127.9, 127.3, 126.0, 121.9, 121.7, 120.9, 118.9, 116.9, 116.7. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0844.

3-Bromo-6-phenylindazolo[2,3-*a*]quinoline (**3qa**): Yellow-green solid, isolated yield 55% (20.4 mg). m.p. 209～211 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (d, J=8.8 Hz, 1H), 8.05 (d, J=2.0 Hz, 1 H), 7.94 (d, J=8.8 Hz, 1H), 7.86 (dd, J=9.2, 2.0 Hz, 1H), 7.66～7.64 (m, 2H), 7.61～7.58 (m, 3H), 7.48 (td, J=7.8, 1.2 Hz, 1H), 7.39 (s, 1H), 7.30 (d, J=8.4 Hz, 1H), 7.02 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 137.1, 134.0, 132.2, 131.2, 130.4, 129.1, 129.0, 128.9, 128.8, 128.6, 128.0, 126.4, 121.8, 121.7, 121.0, 119.9, 119.1, 116.9, 116.7. HRMS (ESI) calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0337.

3-Isopropyl-6-phenylindazolo[2,3-*a*]quinoline (**3ra**): Yellow-green solid, isolated yield 54% (18.2 mg). m.p. 106～109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, J=8.8 Hz, 1H), 7.95 (d, J=8.8 Hz, 1H), 7.74 (s, 1H), 7.77～7.65 (m, 3H), 7.61～7.56 (m, 3H), 7.50～7.48 (m, 2H), 7.31 (d, J=8.4 Hz, 1H), 6.95 (t, J=7.4 Hz, 1H), 3.32～3.09 (m, 1H), 1.39 (d, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 147.2, 137.7, 132.6, 131.9, 131.0, 129.1, 128.8, 128.7, 128.6, 127.5, 125.2, 125.1, 123.4, 121.7, 120.3, 117.3, 116.7, 116.5, 34.1, 24.1. HRMS (ESI) calcd for $C_{24}H_{21}N_2$ $[M+H]^+$ 337.1699, found 337.1702.

3-(*tert*-Butyl)-6-phenylindazolo[2,3-*a*]quinoline (**3sa**): Yellow-green solid, isolated yield 45% (15.7 mg). m.p. 180～182 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, J=8.2 Hz, 1H), 7.96 (d, J=8.8 Hz, 1H), 7.87～7.85 (m, 2H), 7.67～7.64 (m, 2H), 7.59～7.54 (m, 3H), 7.51 (s, 1H), 7.46 (td, J=7.6, 0.6 Hz, 1H), 7.32 (d, J=8.4 Hz, 1H), 6.99 (td, J=7.4, 0.6 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5 (2), 137.7, 132.5, 131.5, 131.1, 129.1, 128.8, 128.6, 127.6, 127.5, 124.8, 124.1, 123.7, 121.7, 120.3, 117.0, 116.7, 116.5, 34.9, 31.4. HRMS (ESI) calcd for $C_{25}H_{23}N_2$ $[M+H]^+$ 351.1856, found 351.1858.

Ethyl 6-phenylindazolo[2,3-*a*]quinoline-3-carboxylate (**3ta**): Yellow-green solid, isolated yield 50% (18.3 mg). m.p. 211～214 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (d, J=8.8 Hz, 1H), 8.66 (d, J=1.2 Hz, 1H), 8.42 (dd, J=8.8 Hz, J=1.3 Hz, 1H), 7.96 (d, J=8.8 Hz, 1H), 7.69～7.65 (m, 2H), 7.63～7.57 (m, 4H), 7.50 (t, J=7.9 Hz, 1H), 7.32 (d, J=8.8 Hz, 1H), 7.03 (t, J=7.9 Hz, 1H), 4.48 (q, J=7.2 Hz, 2H), 1.48 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 150.0, 137.1, 135.6, 133.6, 132.0, 130.7, 129.5, 129.0, 128.9, 128.8, 128.2, 124.4, 123.2, 121.8, 121.0, 117.4, 116.9, 116.8, 61.5, 14.4. HRMS (ESI) calcd for $C_{24}H_{19}N_2O_2$ $[M+H]^+$ 367.1441, found 367.1439.

6-Phenyl-3-(trifluoromethyl)indazolo[2,3-*a*]quinoline (**3ua**): Yellow-green solid, isolated yield 45% (15.7 mg). m.p. 180～182 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10

(d, J=8.8 Hz, 1H), 8.21 (s, 1H), 8.01～7.95 (m, 2H), 7.68～7.65 (m, 2H), 7.62～7.60 (m, 3H), 7.54～7.49 (m, 2H), 7.32 (d, J=8.4 Hz, 1H), 7.04 (t, J=7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 137.0, 134.8, 134.3, 130.5 (q, J=279.4 Hz), 129.0 (d, J=5.1 Hz), 128.3 (q, J=32.8 Hz), 128.2, 125.9 (q, J=4.2 Hz), 125.6 (q, J=3.6 Hz), 124.5, 122.6, 121.8, 121.3, 118.3, 116.9; ^{19}F NMR (376 MHz, $CDCl_3$): −61.93 (s). HRMS (ESI) calcd for $C_{22}H_{14}F_3N_2$ $[M+H]^+$ 363.1104, found 363.1107.

2-Methyl-6-phenylindazolo[2,3-*a*]quinoline (**3va**): Yellow-green solid, isolated yield 45% (13.8 mg). m.p. 179～183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (s, 1H), 7.95 (d, J=8.4 Hz, 1H), 7.80 (d, J=8.0 Hz, 1H), 7.67～7.64 (m, 2H), 7.60～7.54 (m, 3H), 7.49～7.42 (m, 3H), 7.32 (d, J=8.4 Hz, 1H), 6.99 (t, J=7.4 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 140.2, 137.7, 133.3, 131.7, 131.5, 129.2, 128.8, 128.6, 128.2, 128.1, 127.7, 123.3, 122.8, 121.8, 120.3, 116.9, 116.7, 116.5, 22.1. HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1389.

2-Chloro-6-phenylindazolo[2,3-*a*]quinoline (**3wa**): Yellow-green solid, isolated yield 42% (13.7 mg). m.p. 158～161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (d, J=2.0 Hz, 1H), 7.93 (d, J=8.8 Hz, 1H), 7.80 (d, J=8.4 Hz, 1H), 7.65～7.62 (m, 2H),7.59～7.55 (m, 3H), 7.52 (dd, J=8.4 Hz, J=2.0 Hz, 1H), 7.47 (t, J=7.2 Hz, 1H), 7.48 (s, 1H), 7.29 (d, J=8.2 Hz, 1H), 7.00 (td, J=8.0 Hz, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 137.2, 135.2, 133.7, 132.9, 131.5, 129.5, 129.0, 128.9, 128.8, 128.0, 127.0, 123.3, 122.5, 121.7, 120.9, 117.2, 116.8, 116.7. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0843.

1-Methoxy-6-phenylindazolo[2,3-*a*]quinoline (**3xa**): Yellow-green solid, isolated yield 62% (20.0 mg). m.p. 138～140 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J=8.4 Hz, 1H), 7.66～7.64 (m, 2H), 7.59～7.57 (m, 3H), 7.54～7.52 (m, 2H), 7.48 (s, 1H), 7.45 (t, J=7.6 Hz, 1H), 7.33～7.31 (m, 1H), 7.21 (d, J=8.8 Hz, 1H), 6.98 (t, J=7.2 Hz, 1H), 4.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.5, 149.7, 137.4, 133.0, 132.8, 129.1, 128.8, 128.7, 128.0, 127.1, 126.4, 124.8, 123.8, 121.2, 120.9, 120.7, 117.4, 115.3, 111.7, 57.4. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1335, found 325.1338.

1-Fluoro-6-phenylindazolo[2,3-*a*]quinoline (**3ya**): Yellow-green solid, isolated yield 45% (14.0 mg). m.p. 183～185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, J=8.8 Hz, 1H), 7.70 (t, J=4.2 Hz, 1H), 7.66～7.63 (m, 2H), 7.60～7.58 (m, 3H), 7.55～7.50 (m, 2H), 7.48 (t, J=7.4 Hz, 2H), 7.23 (s, 1H), 7.02 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2 (d, J=257.0 Hz), 150.1 (d, J=4.9 Hz), 137.1, 133.6, 132.5, 129.0 (d, J=6.9 Hz), 128.9, 128.0, 127.7, 126.1 (d, J=8.2 Hz), 124.1, 124.0, 122.9 (d, J=2.4 Hz), 121.3 (d, J=20.8 Hz), 117.3, 116.2 (d, J=20.6 Hz), 115.5; ^{19}F NMR (376 MHz, $CDCl_3$): −117.13 (s). HRMS (ESI) calcd for $C_{22}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1140.

6-(*p*-Tolyl)indazolo[2,3-*a*]quinoline (**3ab**): Yellow-green solid, isolated yield 77% (23.7 mg). m.p. 156～158 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, J=8.4 Hz, 1H), 7.95 (d, J=8.6 Hz, 1H), 7.89 (d, J=8.0 Hz, 1H), 7.77 (td, J=7.8, 1.3 Hz, 1H), 7.60～7.54 (m, 3H), 7.48 (t, J=8.1 Hz, 2H), 7.39～7.37 (m, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 138.6, 134.6, 133.3, 132.8, 131.5, 129.5, 129.1, 129.0, 128.3, 127.7, 126.3, 125.1, 123.2, 121.9, 120.4, 117.3, 116.8, 116.6, 21.5. HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, ound 309.1390.

6-(4-Methoxyphenyl)indazolo[2,3-*a*]quinoline (**3ac**): Yellow-green solid, isolated yield 85% (27.5 mg). m.p. 202～204 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.5 Hz, 1H), 7.96 (d, J=8.7 Hz, 1H), 7.91 (d, J=8.0 Hz, 1H), 7.78 (td, J=7.8, 1.2 Hz, 1H), 7.61 (t, J=8.4 Hz, 3H), 7.49 (td, J=7.8, 0.8 Hz, 2H), 7.41 (d, J=8.4 Hz, 1H), 7.11 (d, J=8.4 Hz, 2H), 7.02 (t, J=7.3 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 149.5, 133.3, 132.5, 131.6, 130.3, 129.9, 129.1, 128.3, 127.7, 126.3, 125.1, 123.2, 121.9, 120.5, 117.3, 116.8, 116.6, 114.1, 55.5. HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1335, found 325.1338.

6-(4-Fluorophenyl)indazolo[2,3-*a*]quinoline (**3ad**): Yellow-green solid, isolated yield 84% (26.2 mg). m.p. 150～153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, J=9.2 Hz, 1H), 7.96 (d, J=8.6 Hz, 1H), 7.89 (d, J=7.5 Hz, 1H), 7.78 (td, J=7.8, 0.8 Hz, 1H), 7.64～7.58 (m, 3H), 7.50～7.46 (m, 2H), 7.30～7.27 (m, 3H), 7.02 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.0 (d, J=248 Hz), 149.5, 133.5 (d, J=3.8 Hz), 133.4, 131.6, 131.2, 130.9, 130.8, 129.4, 128.3, 127.7, 126.4, 124.8, 123.4, 121.5, 120.7, 117.3, 116.7 (d, J=9.2 Hz), 115.8 (d, J=21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): −112.75 (s). HRMS (ESI) calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1140.

6-(4-Chlorophenyl)indazolo[2,3-*a*]quinoline (**3ae**): Yellow-green solid, isolated yield 88% (28.8 mg). m.p. 187～189 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.4 Hz, 1H), 7.97 (d, J=8.7 Hz, 1H), 7.91 (d, J=7.5 Hz, 1H), 7.80 (t, J=8.4 Hz, 1H), 7.63～7.59 (m, 3H), 7.57～7.55 (m, 2H), 7.51～7.48 (m, 2H), 7.33 (d, J=8.5 Hz, 1H), 7.04 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 136.0, 134.8, 133.5, 131.4, 130.9, 130.5, 129.5, 129.1, 128.4, 127.8, 126.5, 124.8, 123.4, 121.5, 120.8, 117.3, 116.8, 116.6. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0842.

6-(4-Bromophenyl)indazolo[2,3-*a*]quinoline (**3af**): Yellow-green solid, isolated yield 76% (28.2 mg). m.p. 187～191 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.2 Hz, 1H), 7.97 (d, J=8.4 Hz, 1H), 7.91 (d, J=7.9 Hz, 1H), 7.80 (td, J=7.2, 1.2 Hz, 1H), 7.72 (dd, J=6.7 Hz, J=2 Hz, 2H), 7.51～7.48 (m, 2H), 7.34 (d, J=8.4 Hz, 1H), 7.05 (t, J=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 136.5, 133.4, 132.0, 131.4, 130.8, 130.7, 129.5, 128.4, 127.8, 126.4, 124.5, 123.3, 123.0, 121.5, 120.8, 117.3, 116.8, 116.6. HRMS (ESI) calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0338.

6-(4-Iodophenyl)indazolo[2,3-*a*]quinoline (**3ag**): Yel-

low-green solid, isolated yield 74% (31 mg). m.p. 165～168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, J=8.4 Hz, 1H), 7.96 (d, J=8.8 Hz, 1H), 7.93～7.89 (m, 3H), 7.80 (td, J=7.9, 1.3 Hz, 1H), 7.61 (t, J=7.6 Hz, 1H), 7.51～7.46 (m, 2H), 7.35 (d, J=8.4 Hz, 1H), 7.05 (t, J=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 138.0, 137.1, 133.5, 131.5, 130.9, 130.7, 129.5, 128.4, 127.8, 126.5, 124.8, 123.3, 121.5, 120.8, 117.3, 116.8, 116.6, 94.6. HRMS (ESI) calcd for $C_{21}H_{14}IN_2$ $[M+H]^+$ 421.0196, found 421.0197.

6-(4-(Trifluoromethyl)phenyl)indazolo[2,3-*a*]quinoline (**3ah**): Yellow-green solid, isolated yield 65% (23.6 mg). m.p. 220～222 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (d, J=8.6 Hz, 1H), 7.98 (d, J=8.8 Hz, 1H), 7.93 (d, J=7.9 Hz, 1H), 7.87～7.80 (m, 5H), 7.64 (t, J=7.6 Hz, 1H), 7.52～7.48 (m, 2H), 7.27 (d, J=8.4 Hz, 1H), 7.05 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 141.2, 133.6, 131.1 (d, J=7.1 Hz), 130.8, 130.5, 129.8, 129.6, 128.5, 127.9, 126.5, 125.8 (q, J=4.6 Hz), 124.7, 123.6, 121.3, 121.0, 117.4, 116.9, 116.5; ^{19}F NMR (376 MHz, $CDCl_3$): −62.42 (s). HRMS (ESI) calcd for $C_{21}H_{14}F_3N_2$ $[M+H]^+$ 363.1104, found 363.1107.

6-(4-Nitrophenyl)indazolo[2,3-*a*]quinoline (**3ai**): Yellow-green solid, isolated yield 35% (11.8 mg). m.p. 203～207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (d, J=8.3 Hz, 1H), 8.47 (dt, J=8.8, 1.8 Hz, 2H), 7.97 (q, J=8.2 Hz, 2H), 7.90～7.83 (m, 3H), 7.66 (t, J=7.6 Hz, 1H), 7.54～7.49 (m, 2H), 7.27 (s, 1H), 7.06 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 148.1, 144.1, 133.7, 130.3, 130.2, 130.1, 130.0, 128.6, 128.0, 126.7, 124.5, 124.2, 123.8, 121.2, 121.0, 117.4, 117.1, 116.3. HRMS (ESI) calcd for $C_{21}H_{14}N_3O_2$ $[M+H]^+$ 340.1081, found 340.1083.

6-(*m*-Tolyl)indazolo[2,3-*a*]quinoline (**3aj**): Yellow-green solid, isolated yield 78% (24 mg). m.p. 137～141 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.8 Hz, 1H), 7.96 (d, J=8.7 Hz, 1H), 7.90 (d, J=8.2 Hz, 1H), 7.78 (td, J=7.8, 1.2 Hz, 1H), 7.60 (t, J=7.6 Hz, 1H), 7.50～7.46 (m, 5H), 7.38～7.34 (m, 2H), 7.01 (t, J=7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 138.5, 137.5, 133.4, 132.9, 131.4, 129.7, 129.4, 129.2, 128.6, 128.3, 127.7, 126.3, 126.2, 125.0, 123.2, 121.8, 120.5, 117.3, 116.8, 116.6, 21.6. HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386. Found 309.1389.

6-(3-Chlorophenyl)indazolo[2,3-*a*]quinoline (**3ak**): Yellow-green solid, isolated yield 75% (24.6 mg). m.p. 171～174 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.4 Hz, 1H), 7.97 (d, J=8.4 Hz, 1H), 7.92 (dd, J=8.0 Hz, J=1.2 Hz, 1H), 7.81 (td, J=7.4, 1.2 Hz, 1H), 7.68 (s, 1H), 7.62 (t, J=7.2 Hz, 1H), 7.57～7.47 (m, 5H), 7.33 (d, J=8.8 Hz, 1H), 7.05 (td, J=7.8, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 139.3, 134.8, 133.5, 131.2, 130.8, 130.1, 129.6, 129.2, 128.9, 128.4, 127.8, 127.4, 126.5, 124.8, 123.4, 121.4, 120.9, 117.3, 116.8, 116.6. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0841.

6-(3-Bromophenyl)indazolo[2,3-*a*]quinoline (**3al**): Yellow-green solid, isolated yield 77% (28.6 mg). m.p. 176～179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=8.4 Hz, 1H), 7.97 (d, J=8.8 Hz, 1H), 7.91 (d, J=6.0 Hz, 1H), 7.84～7.78 (m, 2H), 7.70 (d, J=8.0 Hz, 1H), 7.61 (t, J=7.0 Hz, 2H), 7.51～7.43 (m, 3H), 7.33 (d, J=8.0 Hz, 1H), 7.05 (t, J=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 139.5, 133.5, 132.1, 131.8, 131.1, 130.7, 130.3, 129.6, 128.4, 127.8 (2), 126.5, 124.7, 123.5, 122.8, 121.4, 120.9, 117.3, 116.8, 116.5. HRMS (ESI) calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0337.

6-(*o*-Tolyl)indazolo[2,3-*a*]quinoline (**3am**): Yellow-green solid, isolated yield 24% (7.4 mg). m.p. 158～161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (d, J=8.4 Hz, 1H), 7.94 (t, J=8.1 Hz, 2H), 7.82 (t, J=7.8 Hz, 1H), 7.63 (t, J=8.0 Hz, 1H), 7.50～7.39 (m, 6H), 6.96 (td, J=7.8 Hz, J=0.6 Hz, 1H), 6.83 (d, J=8.5 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 136.9, 136.9, 133.4, 132.0, 131.5, 130.3, 129.7, 129.3, 128.9, 128.4, 127.8, 126.3 (2) , 125.1, 122.9, 121.0, 120.9, 117.3, 117.0, 116.5, 19.7. HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1388.

6-(2-Chlorophenyl)indazolo[2,3-*a*]quinoline (**3an**): Yellow-green solid, isolated yield 43% (14.1 mg). m.p. 150～154 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (d, J=8.5 Hz, 1H), 7.96 (d, J=8.8 Hz, 2H), 7.84 (td, J=8.4 Hz, J=1.2 Hz, 1H), 7.65 (t, J=7.2 Hz, 2H), 7.55 (t, J=7.2 Hz, 3H), 7.48 (t, J=7.2 Hz, 2H), 7.00 (t, J=8.3 Hz, 1H), 6.93 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 136.2, 134.1, 133.6, 131.5, 131.1, 130.3, 130.0, 129.6, 129.5, 128.6, 127.8, 127.3, 126.4, 124.8, 123.7, 120.9, 117.3, 116.8, 116.6. HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0843.

6-(3,5-Dichlorophenyl)indazolo[2,3-*a*]quinoline (**3ao**): Yellow-green solid, isolated yield 80% (28.9 mg). m.p. 247～248 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (d, J=8.8 Hz, 1H), 7.98 (d, J=8.8 Hz, 1H), 7.93 (d, J=8.8 Hz, 1H), 7.83 (td, J=8.4, 1.2 Hz, 1H), 7.58～7.51 (m, 5H), 7.35 (d, J=8.5 Hz, 1H), 7.11 (t, J=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 140.4, 135.5, 133.6, 130.2, 129.9 (2) 128.9, 128.5, 127.9, 127.6, 126.6, 124.5, 123.6, 121.2, 121.1 117.4, 116.9, 116.4. HRMS (ESI) calcd for $C_{21}H_{13}Cl_2N_2$ $[M+H]^+$ 363.0450, found 363.0452.

6-(Furan-2-yl)indazolo[2,3-*a*]quinoline (**3ap**): Yellow-green solid, isolated yield 64% (18.1 mg). m.p. 100～102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (d, J=8.4 Hz, 1H), 7.97 (t, J=8.8 Hz, 2H), 7.90 (d, J=7.3 Hz, 1H), 7.80～7.73 (m, 3H), 7.59 (t, J=7.4 Hz, 1H), 7.53 (t, J=7.2 Hz, 1H), 7.18 (t, J=6.8 Hz, 1H), 6.90 (d, J=3.2 Hz, 1H), 6.68～6.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 149.6, 143.0, 133.7, 130.3, 129.7, 128.5, 127.9, 126.4, 124.5, 122.8, 121.9, 121.8, 120.9, 117.4, 116.7, 116.5, 111.9, 110.0. HRMS (ESI) calcd for $C_{19}H_{12}N_2O$ $[M+H]^+$ 285.1022, found 285.1024.

6-(Thiophen-2-yl)indazolo[2,3-*a*]quinoline (**3aq**): Green solid, isolated yield 43% (12.9 mg). m.p. 145～148 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, J=8.4 Hz, 1H), 7.97 (d, J=8.6 Hz, 1H), 7.91 (d, J=7.7 Hz, 1H), 7.80 (td, J=

8.4, 1.2 Hz, 1H), 7.64～7.49 (m, 5H), 7.45 (dd, *J*=3.3, 1.1 Hz, 1H), 7.28 (t, *J*=4.6 Hz, 1H), 7.08 (t, *J*=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 149.5, 138.1, 133.6, 131.2, 129.7, 128.4, 127.9, 127.8, 127.6, 126.5, 126.4, 125.4, 124.8, 124.6, 121.7, 120.7, 117.3, 116.8, 116.7. HRMS (ESI) calcd for $C_{19}H_{13}N_2S$ $[M+H]^+$ 301.0794, found 301.0794.

6-(Naphthalen-2-yl)indazolo[2,3-*a*]quinoline (**3ar**): Yellow-green solid, isolated yield 45% (15.4 mg). m.p. 178～180 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 9.02 (d, *J*=8.4 Hz, 1H), 8.16 (s, 1H), 8.05 (d, *J*=8.4 Hz, 1H), 8.01～7.94 (m, 4H), 7.84～7.77 (m, 2H), 7.65～7.57 (m, 4H), 7.47 (t, *J*=8.4 Hz, 1H), 7.32 (d, *J*=8.4 Hz, 1H), 6.95 (t, *J*=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 149.6, 135.1, 133.5, 133.4, 133.3, 132.7, 131.4, 129.3, 128.4, 128.3, 128.1, 128.0, 127.7, 127.0, 126.7, 126.4, 125.0, 123.6, 121.8, 120.6, 117.3, 116.8, 116.7. HRMS (ESI) calcd for $C_{25}H_{17}N_2$ $[M+H]^+$ 345.1386, found 345.1387.

Supporting Information Experiments with mechanism studies, ^{1}H NMR ,^{13}C NMR and some ^{19}F NMR spectra of all compounds, and crystallographic data for **3na**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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