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TBAB-mediated radical 5-*exo-trig ipso*-cyclization of 2-arylbenzamide for the synthesis of spiro[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione

Guanyinsheng Qiu* [a,b], Zhi-Feng Chen[b], Wenlin Xie[c], and Hongwei Zhou*[b]

Dedication ((optional))

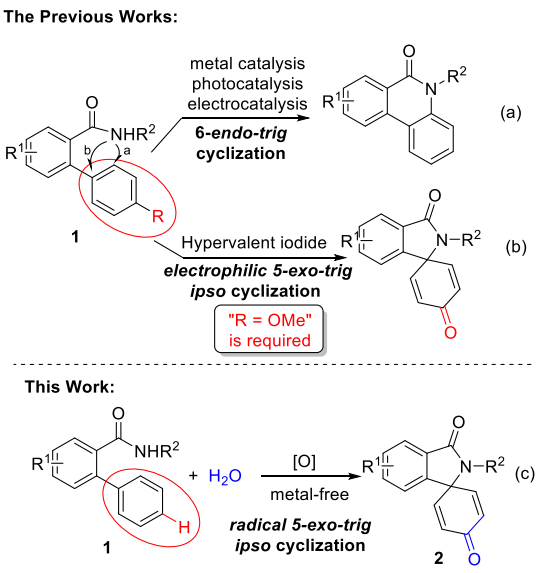
Abstract: A TBAB-mediated radical 5-*exo-trig ipso*-cyclization of *N*-aryl-2-arylbenzamide is described herein for the synthesis of spiro[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione. The transformation proceeds regioselectively and provides the final products with high efficiency and a broad reaction scope. Mechanism studies show the use of TBAB as an additive is pivotal for the reaction. In the process, *para*-bromination of *N*-aryl group, 5-*exo-tri ipso*-cyclization of *N*-aryl-2-arylbenzamide nitrogen radical and sequential aromatization is involved.

Introduction

Quaternary carbon center is ubiquitous in many natural products and useful archirectures.[1] To date, its synthetic methodology development attracted continuous interests of chemists.[2] Among them, *ipso*-cyclization dearomatizative reaction was recognized as one of powerful strategies to construct cyclic quaternary carbon center.[3]

2-arylbenzamide was a versatile synthons towards *N*-heterocyclic compounds.[4] Basically, 6-*endo-trig* cyclization of 2-arylbenzamide was well recognized. To the best of our knowledge, transitional metal-catalyzed[5] or nonmetal reagent-mediated C-H bond functionalization[6] enabled this 6-*endo-trig* cyclization of 2-arylbenzamide to produce various phenanthridin-6(5*H*)-one derivatives. Considering high importance of phenanthridin-6(5*H*)-one[7] and limitation of the previous protocols, sequential chemistry was focused intensively on 6-*endo-trig* cyclization of 2-arylbenzamide under photocatalysis[8] and electrocatalysis[9] (Scheme 1a). Distinctively, the photo/electron-induced 6-*endo-trig* cyclization of 2-arylbenzamide involved an amidy *N*-radical intermediate[10]. It is noteworthy that amidy nitrogent radical-based 6-*endo-trig* cyclization of 2-arylbenzamide was not unprecedent.[11,12] Thereotically, an amidyl nitriogen radical-based 5-*exo-trig ipso*-cyclization of 2-arylbenzamide seemed plausible. This model of cyclization could construct a cyclic quaternary carbon center. However, it is surprising to find that amidy nitrogent radical-based 5-*exo-trig ipso*-cyclization of 2-arylbenzamide remains rare in the past decades.[12] The success of the reported example resorted to the use of 2-(4-methoxylphenyl)benzamide as the substrate. Serveral years ago, few examples on electrophilic 5-*exo-trig ipso*-cyclization of 2-(4-methoxylphenyl)benzamide have been reported towards a series of *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-diones. [13] According to these findings from Kita and co-workers, electrophilic 5-*exo-trig ipso*-cyclization of 2-arylbenzamide was subject to limitation of substrates. Basically, the *para*-methoxyl group in 2-aryl of 2-arylbenzamide was always required for electrophilic 5-*exo-trig ipso*-cyclization (Scheme 1b). Inspired by what mentioned above, this paper would like to discolse our endeavor on radical 5-*exo-trig ipso*-cyclization of 2-arylbenzamide **1** for the synthesis of *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-diones **2**, an important synthetic building block for many useful molecules (Scheme 1c) [14]. Our primary aim in this paper was to expand nitrogen radical-based oxidative 5-*exo-trig ipso*-cyclization to 2-arylbenzamides without the required substituent methoxyl group. Furthermore, we envisioned that this radical 5-*exo-trig ipso*-cyclization of 2-arylbenzamides could worked well under metal-free conditions, and water in the reaction could be incorporated into carbonyl group of the products **2**.

Scheme 1. Proposed route for the synthesis of *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-diones.



Results and Discussion

In light of our previous results in oxone chemistry,[15] our preliminary trial was conducted in the presence of 2.0 equiv of oxone and 3.0 equiv of K_2CO_3 in H_2O (entry 2, Table 1).

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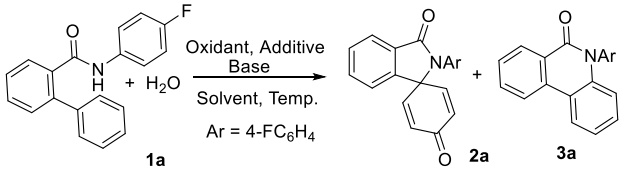
Presented as the previous result using $K_2S_2O_8$ (entry 1, Table 1)[12], a combination of oxone/K_2CO_3 could not realize *5-exo-trig ipso*-cyclization of 2-arylbenzamides.We inferred that the above noted negative result was ascribed to the electrophilic nature of amidyl nitrogen radical. To adjust electrophilicity of amidyl nitrogen radical, 2.0 equiv of *tetra-n*-butylammonium bromide (TBAB) was added as an additive. To our delight, the model reaction of *N*-(4-fluorophenyl)-2-phenylbenzamide 1a in water afforded a desired *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione 2a in a 35% isolated yield (entry 3, Table 1). Oxidative 6-*endo-trig* cyclization product 3a was not detected. Encouraged by the above result, we then optimized other result-affecting factors.

Table 1 Initial studies on oxidative 6-*endo-dig* radical cyclization of 2-alkynylbenzamide for the synthesis of 1-imine-isocoumarins [a,b]

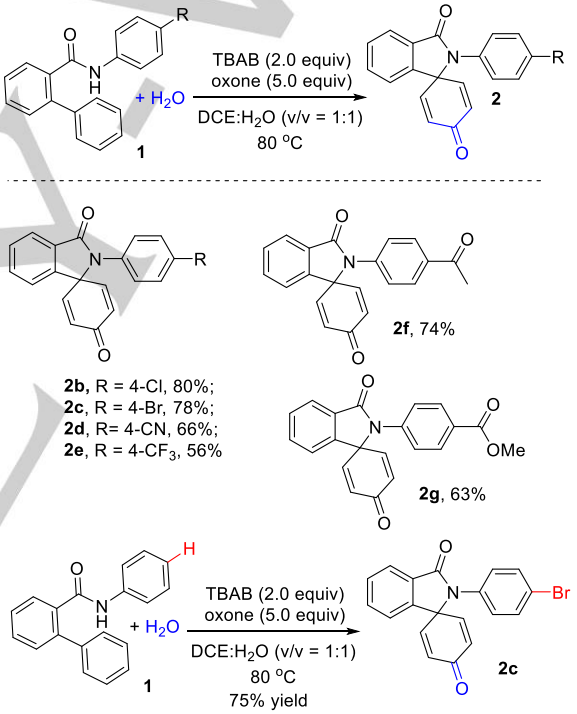


Entry	Additive	Oxidant (2.0 eq.)	Base	Solvent	Yield of **2a** (%)[a,b]
1	/	$K_2S_2O_8$	K_2CO_3	H_2O	nd
2	/	oxone	K_2CO_3	H_2O	nd
3	TBAB	oxone	K_2CO_3	H_2O	35
4	TBAB	oxone	K_2CO_3	DCE:H_2O (v/v, 1:1)	60
5	TBAB	oxone	K_2CO_3	THF:H_2O (v/v, 1:1)	36
6	TBAB	oxone	K_2CO_3	MeCN:H_2O (v/v, 1:1)	20
7	TBAB	oxone	K_2CO_3	DCE	trace
8[c]	TBAB	oxone	K_2CO_3	DCE:H_2O (v/v, 1:1)	75
9[c,d]	TBAB	oxone	K_2CO_3	DCE:H_2O (v/v, 1:1)	42
10[c]	TBAB	oxone	/	DCE:H_2O (v/v, 1:1)	78
11[c,e]	TBAB	oxone	/	DCE:H_2O (v/v, 1:1)	65
12[c,f]	TBAB	oxone	/	DCE:H_2O (v/v, 1:1)	49

[a] Isolated yield based on 2-alkynylbenzamide **1a**. [b] Standard conditions: 2-alknylbenzamide **1a** (0.2 mmol), TBAB (2.0 equiv), oxone (2.0 equiv), base (3.0 equiv), solvent (4 mL), 80 °C, overnight. [c] 5.0 equiv oxone was used. [d]1.0 equiv TBAB was used. [e] Reaction temperature = 100 °C. [f] Reaction temperature = 50 °C. TBAB = *n-tetra*-butyl ammonium bromide; oxone = $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$

Considering solubility of substrate in solvent, the sequential trials were carried out in a mixed solvent with various organic solvents. As illustrated in Table 1, it seemed that the mixed solvent DCE:H_2O was favorable for the reaction efficiency, leading to the desired product **2a** in 60% yield (entry 4, Table 1). Other solvents MeCN:H_2O and THF:H_2O provided inferior results (entries 5-6, Table 1). Pure 1,2-dichloroethane (DCE) without mixing water just offered a trace ammount of the desired product **2a** (entry 7, Table 1). This outcome supported our assumption that oxygen atom of carbonyl group in product **2** probably came from water. To increase loading of oxone to 5.0 equiv improve the reaction yield to 75% (entry 8, Table 1). However, decrease of TBAB ammount made a negative effect on the reaction (entry 9, Table 1). A control experiment without base K_2CO_3 implied that the use of K_2CO_3 did not make a significant impact on, providing the desired molecule **2a** in a similar yield (entry 10, Table 1). Further reaction temperature screening seemed that both increase of temperature and descrease of temperature were unfavorable for the reactions (entries 11-12, Table 1). As such, we got the optimized conditions: 2.0 equiv of TBAB, 5.0 equiv of oxone, DCE: H_2O (v/v = 1:1) as solvent, and 80 °C.

Scheme 2. Reaction scope oxidative 5-*exo-trig* radical *ipso*-cyclization of 2-phenylbenzamide: Effect of *N*-protecting group [a]



[a] isolated yield based on 2-phenylbenzamide **1**

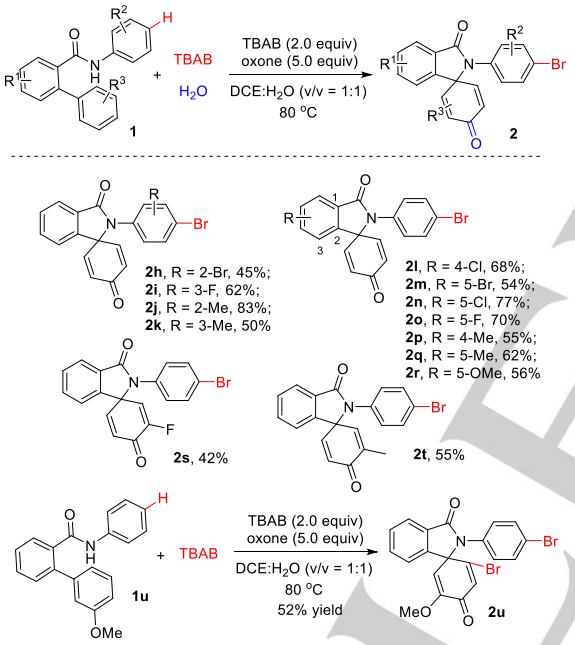
With optimized conditions in hand (entry 10, Table1), we then explored the reaction scope. The results were presented in Scheme 2. A series of spiro[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione 2 was achieved accordingly. As illustrated in Table 2, the substituents R in *N*-aryl protecting groups could replaced with chloro, bromo, ketone, and ester. To our delight, the corresponding products **2b-2g** were achieved in 56-80% yields.

Interestingly, the result from the reaction of *N*-phenyl-2-phenylbenzamide showed a *para*-bromination happened to *N*-phenyl protecting group,[4b,6c] and the reaction gave rise to the product **2c** in 75% yield. Considering synthetic versatility of bromo group, all the the sequential reactions employed the

substrates with *N*-phenyl protecting group, wishing to introduce bromo atom in the product **2**.

As presented in Scheme 3, a series of bromo-containing *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione **2** was afforded accordingly. From the results, the steric effect and electron effect of the substituents R^1 did not make significant impact on the outcomes, leading to the corresponding products **2l-2r** in 54-77% yields. The reaction of the substrate **1s** with the substituent fluoro at R^3 gave rise to the desired product **2s** in a moderate yield, while the reaction of the substrate **1t** with the substituent methyl at R^3 provided the expected product **2t** in a 55% yield. Interestingly, the methoxyl group at R^3 was also compatible for the reaction, offering a dibrominative product **2u** in 52% yield.

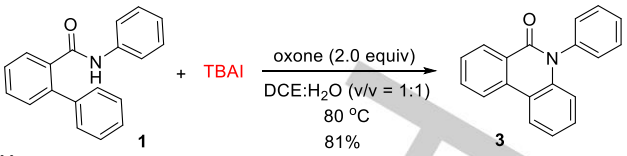
Scheme 3. Reaction scope on oxidative 6-*exo-trig* radical ipso-cyclization of 2-arylbenzamide.[a]



[a] Isolated yield based on 2-phenylbenzamide **1**.

During reaction conditions optimization, it was found that the use of *tetra-n*-butylammonium iodide (TBAI) as an additive afforded a *6-endo-trig* cyclization product phenanthridin-6(5*H*)-one **3** in a reasonable yield. By reducing the loading of oxone to 2.0 equiv, the yield of the reaction of *N*-phenyl-2-phenylbenzamide was further improved, providing the desired phenanthridin-6(5*H*)-one **3** in 81% yield (Scheme 4).

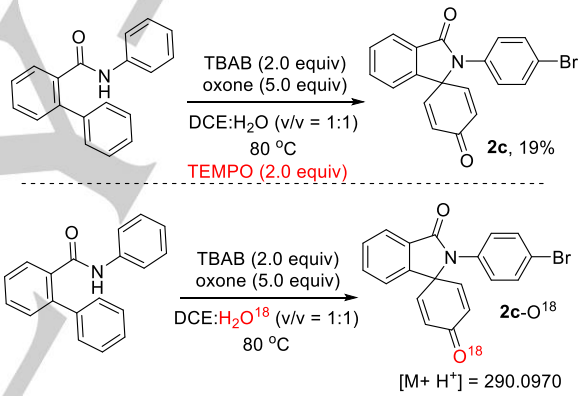
Scheme 4. Reaction scope oxidative 5-*exo-dig* radical cyclization of 2-trimethylsilylethynylbenzamide. [a]



[a] isolated yield based on 2-phenylbenzamide **1**

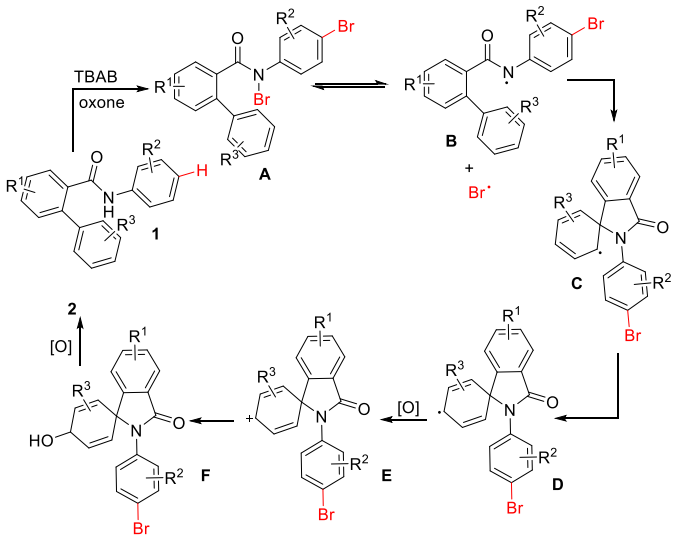
To gain insight into mechanism, two control experiments were conducted in Scheme 5. To clarify the radical process, the reaction with TEMPO as an additive was carried out. The reaction was greatly retarded, resulting in **2a** in 19% yield. However, we did not detect any radical-trapped species. Additionally, wishing to clarify where the carbonyl oxygen of the product came, we run the reaction of *N*-phenyl-2-phenylbenzamide in the presence of DCE:H_2O^{18} as solvent. As expected, oxygen-18 atom was detected in the product **2c** after analysing its EI-MS spectrum. This result probably supported our assumption that water has been incorporated into carbonyl of the product **2**.

Scheme 5. Control experiments



In light of forementioned results, a plausible mechanism was proposed in Scheme 6. In the process, in the presence of TBAB and oxone 2-arylbenzamide was oxidized into dibrominative 2-arylbenzamide **A**. It is believed that the formation of the intermediate **A** was pivotal for the reaction. The intermediate **A** then ocurred to convert into 2-arylbenzamide nitrogen radical **B** and bromo radical. A 5-*exo-trig ipso*-cyclization happened to the intermediate **B**, producing a sprio radical species **C**. The following radical migration and oxidation provided a sprio cation species **E**, which was trapped by water to obtain an intermediate **F**. Oxidation of the intermediate **F** gave rise to the desired products **2**. For a whole process, the use of TBAB as an additive was very important. From results on blank experiments using TBAI and other bromide source as additives and descrease of TBAB loading, it should be convinced that the use of TBAB probably changed electrophilicity nature of amidyl nitrogen radical.[10a, 12]

Scheme 6. Proposed pathway for the designed reaction



Conclusion

We have developed a TBAB-mediated oxidative cyclization of 2-aryllbenzamide for a series of *spiro*[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-diones. The transformation was regioselective in a fashion of *5-exo-trig ipso*-cyclization and provided the final products with high efficiency and a broad reaction scope. However, it was surprising to find that *N*-alkyl protecting group in 2-arylbenzamide was not compatible for the reaction. Mechanism studies showed the use of TBAB as an additive was pivotal for the reaction. The use of TBAB as an additive not only stabilized the resulting 2-arylbenzamide nitrogen radical intermediate, but also probably changed electrophilicity nature of amidyl nitrogen radical.

Experimental Section

General procedure for the synthesis of compound 2: *N*-aryl-2-arylbenzamides **1** (0.2 mmol), TBAB (2 equiv), Oxone (5 equiv) were added to a test tube, and then co-solvent DCE:H_2O (v/v =1:1, 4 mL) was added. The mixture was stirred at 80 ^oC for 14 h. The reaction was quenched with water and extracted three times with ethyl acetate. The organic phase is dried over anhydrous sodium sulfate, evaporation of the solvent and purification by flash column chromatograph provided the desired product **2**.

General procedure for the synthesis of compound 3: *N*-aryl-2-arylbenzamides **1** (0.2 mmol), TBAI (2 equiv), Oxone (2 equiv), K_2CO_3 (3 equiv) were added to a test tube, and then co-solvent DCE: H_2O (v/v =1:1, 4 mL) was added. The mixture was stirred at 100 ^oC for 14 h. The reaction was quenched with water and extracted three times with ethyl acetate. The organic phase is dried over anhydrous sodium sulfate, evaporation of the solvent and purification by flash column chromatograph provided the desired product **3**.

2'-(4-fluorophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2a**) (White solid, 47.6 mg, 78%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 1H), 7.64-7.59 (m, 2H), 7.39-7.35 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 9.9 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.36 (s), 167.67 (s), 161.73 (d, $^1J_{CF}$ = 250 Hz), 160.36 (s), 147.44 (s), 141.01 (s), 133.32 (s), 132.04 (s), 131.46 (s), 130.53 (d, $^3J_{CF}$ = 8.2 Hz), 128.04 (d, $^3J_{CF}$ = 8.6 Hz), 125.18 (s), 122.82 (s), 116.27 (d, $^4J_{CF}$ = 2.3 Hz), 66.71 (s); HRMS (ESI) calcd for $C_{19}H_{13}FNO_2$+: 306.0925 ($M+H^+$), found: 306.0926

2'-(4-chlorophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2b**) (White solid, 51.5 mg, 80%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 10.0 Hz, 2H), 6.43 (d, *J* = 10.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.28 (s), 167.52 (s), 147.66 (s), 140.86 (s), 134.96 (s), 133.44 (s), 133.03 (s), 131.41 (s), 130.92 (s), 130.15 (s), 129.46 (s), 126.60 (s), 125.21 (s), 122.80 (s), 66.75 (s); HRMS (ESI) calcd for $C_{19}H_{13}ClNO_2$+: 322.0629 ($M+H^+$), found: 322.0637

2'-(4-bromophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2c**) (Yellow solid, 57.1 mg, 78%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 1H), 7.66-7.60 (m, 2H), 7.48 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.26 (d, *J* = 6.7 Hz, 1H), 6.79 – 6.66 (m, 2H), 6.46-6.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.26 (s), 167.47 (s), 147.69 (s), 140.83 (s), 135.55 (s), 133.46 (s), 132.44 (s), 131.41 (s), 130.92 (s), 130.17 (s), 126.72 (s), 125.23 (s), 122.79 (s), 120.94 (s), 66.72 (s); HRMS (ESI) calcd for $C_{19}H_{13}BrNO_2$+: 366.0124 ($M+H^+$), found: 366.0142

4-(3',4-dioxospiro[cyclohexa[2,5]diene-1,1'-isoindolin]-2'-yl)benzonitrile (**2d**) (White solid, 41.2 mg, 66%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.56 (m, 4H), 7.27 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.71 (m, 2H), 6.57 – 6.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.95 (s), 167.46 (s), 148.05 (s), 141.37 (s), 140.41 (s), 134.06 (s), 133.23 (s), 131.08 (s), 130.99 (s), 130.40 (s), 125.49 (s), 122.92 (s), 122.78 (s), 118.26 (s), 109.61 (s), 66.89 (s); HRMS (ESI) calcd for $C_{20}H_{13}N_2O2$+: 313.0972 ($M+H^+$), found: 313.0936

2'-(4-(trifluoromethyl)phenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2e**) (Yellow solid, 39.8 mg, 56%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 1H), 7.77 – 7.58 (m, 6H), 7.29-7.25 (m, 1H), 6.82 – 6.72 (m, 2H), 6.56 – 6.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.15 (s), 167.54 (s), 147.95 (s), 140.64 (s), 133.75 (s), 131.24 (s), 130.97 (s), 130.27 (s), 126.46 (s), 126.42 (s), 125.38 (s), 123.91 (s), 122.79 (s), 66.85 (s); HRMS (ESI) calcd for $C_{20}H_{13}F_3NO_2$+: 356.0893 ($M+H^+$), found: 356.0877

2'-(4-acetylphenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2f**) (White solid, 48.7 mg, 74%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.95 (m, 3H), 7.72 – 7.66 (m, 2H), 7.66 – 7.56 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 9.9 Hz, 2H), 6.49 (d, *J* = 9.9 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.81 (s), 184.18 (s), 167.50 (s), 148.18 (s), 141.32 (s), 140.60 (s), 134.93 (s), 133.74 (s), 131.34 (s), 130.87 (s), 130.25 (s), 129.50 (s), 125.36 (s), 123.19 (s), 122.78 (s), 66.92 (s), 26.57 (s); HRMS (ESI) calcd for $C_{21}H_{16}NO_3$+: 330.1125 (M+H$^+$), found: 330.1129

methyl 4-(3',4-dioxospiro[cyclohexa[2,5]diene-1,1'-isoindolin]-2'-yl)benzoate (**2g**) (White solid, 43.5 mg, 63%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 2H), 8.01 – 7.95 (m, 1H), 7.69 – 7.55 (m, 4H), 7.28-7.23 (m, 1H), 6.77 (d, *J* = 10.1 Hz, 2H), 6.48 (d, *J* = 10.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.20 (s), 167.49 (s), 166.19 (s), 148.18 (s), 141.15 (s), 140.62 (s), 133.69 (s), 131.38 (s), 130.84 (s), 130.71 (s), 130.23 (s), 128.13 (s), 125.34 (s), 123.18 (s), 122.77 (s), 66.92 (s), 52.23 (s); HRMS (ESI) calcd for $C_{21}H_{16}NO4$+: 346.1074 (M+H$^+$), found: 346.1084

2'-(2,4-dibromophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2h**) (Yellow solid, 40.1 mg, 45%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 1H), 7.89-7.84 (m, 1H), 7.70 – 7.55 (m, 2H), 7.45 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.02-6.92 (m, 1H), 6.82 – 6.71 (m, 1H), 6.45 (dd, *J* = 10.0, 1.8 Hz, 1H), 6.33 (dd, *J* = 10.1, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.27 (s), 166.62 (s), 146.51 (s), 144.77 (s), 141.97 (s), 136.68 (s), 133.75 (s), 133.43 (s), 131.73 (s), 131.50 (s), 131.00 (s), 130.77 (s), 130.17 (s), 125.47 (s), 123.64 (s), 122.91 (s), 67.21 (s); HRMS (ESI) calcd for $C_{19}H_{12}Br_2NO_2$+: 443.9229 (M+H$^+$), found: 443.9229

2'-(4-bromo-3-fluorophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2i**) (White solid, 47.6 mg, 62%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.55 – 7.43 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 8.7, 1.5 Hz, 1H), 6.74 (d, *J* = 10.0 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.07 (s), 167.36 (s), 159.28 (d, $^1J_{CF}$ = 247 Hz), 147.72 (s), 140.59 (s), 137.35 (s), 133.73 (d, *J* = 5.0 Hz), 131.10 (d, *J* = 3.4 Hz), 130.28 (s), 125.34 (s), 122.79 (s), 120.55 (d, *J* = 3.6 Hz), 112.93 (s), 112.67 (s), 107.17 (s), 106.96 (s), 66.80 (s); HRMS (ESI) calcd for $C_{19}H_{12}BrFNO_2$+: 384.0030 (M+H$^+$), found: 384.0036

2'-(4-bromo-2-methylphenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2j**) (Yellow solid, 63.1 mg, 83%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.7 Hz, 1H), 7.70 – 7.53 (m, 2H), 7.47-7.46 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.61 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.25 (s), 166.90 (s), 147.20 (s), 144.83 (s), 141.97 (s), 139.37 (s), 134.49 (s), 133.21 (s), 133.07 (s), 131.70 (s), 131.07 (s), 130.60 (s), 130.15 (s), 129.80 (s), 125.30 (s), 122.89 (s), 67.06 (s), 18.87 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2$+: 380.0281 (M+H$^+$), found: 380.0283

2'-(4-bromo-3-methylphenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2k**) (Yellow solid, 38.0 mg, 50%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.9 Hz, 1H), 7.70 – 7.55 (m, 2H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.36-7.35 (m, 1H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.44 (d, *J* = 10.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.38 (s), 167.56 (s), 147.65 (s), 140.90 (s), 139.23 (s), 135.39 (s), 133.38 (s), 133.08 (s), 131.49 (s), 130.88 (s), 130.14 (s), 128.05 (s), 125.23 (s), 124.30 (s), 123.86 (s), 122.80 (s), 66.73 (s), 23.19 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2$+: 380.0281 (M+H$^+$), found: 380.0273

2'-(4-bromophenyl)-6'-chlorospiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2l**) (Yellow solid, 54.5 mg, 68%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.1 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.24 (s, 1H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.86 (s), 166.41 (s), 146.74 (s), 142.66 (s), 139.90 (s), 135.12 (s), 132.54 (s), 131.36 (s), 130.85 (s), 129.77 (s), 126.88 (s), 126.40 (s), 123.22 (s), 121.31 (s), 66.21 (s); HRMS (ESI) calcd for $C_{19}H_{12}BrClNO_2$+: 399.9734 (M+H$^+$), found: 399.9730

5'-bromo-2'-(4-bromophenyl)spiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2m**) (Yellow solid, 48.1 mg, 54%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.74 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 9.9 Hz, 2H), 6.44 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.94 (s), 165.98 (s), 146.82 (s), 139.64 (s), 136.51 (s), 135.08 (s), 133.26 (s), 132.54 (s), 131.22 (s), 128.29 (s), 126.85 (s), 124.46 (s), 124.38 (s), 121.37 (s), 66.42 (s); HRMS (ESI) calcd for $C_{19}H_{12}Br_2NO_2$+: 443.9229 (M+H$^+$), found: 443.9215

2'-(4-bromophenyl)-5'-chlorospiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2n**) (Brown solid, 61.7 mg, 77%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.64 – 7.54 (m, 1H), 7.53 – 7.43 (m, 2H), 7.36 – 7.27 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.75 – 6.64 (m, 2H), 6.49 – 6.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.97 (s), 166.12 (s), 146.90 (s), 139.09 (s), 136.65 (s), 135.10 (s), 133.70 (s), 133.04 (s), 132.53 (s), 131.20 (s), 126.88 (s), 125.23 (s), 124.13 (s), 121.37 (s), 66.38 (s); HRMS (ESI) calcd for $C_{19}H_{12}BrClNO_2$+: 399.9734 (M+H$^+$), found: 399.9718

2'-(4-bromophenyl)-5'-fluorospiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2o**) (Yellow solid, 53.8 mg, 70%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.2, 2.3 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.35 – 7.28 (m, 3H), 7.24 (dd, *J* = 8.3, 4.1 Hz, 1H), 6.71 (d, *J* = 10.1 Hz, 2H), 6.44 (d, *J* = 10.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.03 (s), 166.31 (d, *J* = 3.4 Hz), 163.56 (d, $^1J_{CF}$ = 250 Hz), 147.13 (s), 136.27 (d, *J* = 2.4 Hz), 135.19 (s), 133.57 (d, *J* = 9.0 Hz), 132.53 (s), 131.07 (s), 126.86 (s), 124.68 (d, *J* = 8.7 Hz), 121.33 (s), 121.09 (s), 111.95 (d, *J* = 24 Hz), 66.30 (s); HRMS (ESI) calcd for $C_{19}H_{12}BrFNO_2$+: 384.0030 (M+H$^+$) found: 384.0022

2'-(4-bromophenyl)-6'-methylspiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2p**) (Yellow solid, 41.8mg, 55%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 9.7 Hz, 2H), 6.48 (d, *J* = 9.7 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.22 (s), 167.85 (s), 145.31 (s), 138.28 (s), 135.62 (s), 134.51 (s), 134.41 (s), 132.49 (s), 132.24 (s), 131.71 (s), 130.31 (s), 129.15 (s), 122.99 (s), 122.02 (s), 66.00 (s), 16.73 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2$+: 380.0281 (M+H$^+$), found: 380.0283

2'-(4-bromophenyl)-5'-methylspiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2q**) (Yellow solid, 47.1 mg, 62%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.52 – 7.39 (m, 3H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 10.1 Hz, 2H), 6.42 (d, *J* = 10.0 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.36 (s), 167.60 (s), 147.97 (s), 140.67 (s), 137.93 (s), 135.70 (s), 134.49 (s), 132.39 (s), 131.52 (s), 130.71 (s), 126.59 (s), 125.36 (s), 122.49 (s), 120.78 (s), 66.55 (s), 21.41 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2$+: 380.0281 (M+H$^+$), found: 380.0257

2'-(4-bromophenyl)-5'-methoxyspiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2r**) (Yellow solid, 44.4mg, 56%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.18-7.12 (m, 2H), 6.69 (d, *J* = 9.9 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.35 (s), 167.45 (s), 161.49 (s), 147.93 (s), 135.65 (s), 132.92 (s), 132.42 (s), 132.36 (s), 130.64 (s), 126.61 (s), 123.70 (s), 121.94 (s), 120.89 (s), 107.67 (s), 66.32 (s), 55.94 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_3$+: 396.0230 (M+H$^+$), found: 396.0232

2'-(4-bromophenyl)-3-fluorospiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2s**) (Yellow solid, 32.3 mg, 42%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 1H), 7.69-7.60 (m, 2H), 7.52 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.27 (dd, *J* = 9.1, 2.1 Hz, 2H), 6.74 (d, *J* = 9.9 Hz, 1H), 6.44 (dd, *J* = 9.8, 7.0 Hz, 1H), 6.29 (dd, *J* = 11.2, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.27 (d, *J* = 22 Hz), 167.14 (s), 154.36 (d, *J* = 270 Hz), 148.55 (d, *J* = 2.5 Hz), 140.35 (s), 134.86 (s), 133.65 (s), 132.69 (s), 131.13 (s), 130.51 (s), 129.82 (d, *J* = 4.1 Hz), 127.60 (s), 125.49 (s), 123.45 (d, *J* = 14.2 Hz), 122.70 (s), 121.73 (s), 67.79 (s); HRMS (ESI) calcd for $C_{19}H_{12}BrFNO_2$+: 384.0030 (M+H$^+$) found: 384.0034

2'-(4-bromophenyl)-3-methylspiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2t**) (Gray solid, 41.8 mg, 55%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.64-7.55 (m, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.19 (m, 1H), 6.70 (dd, *J* = 9.8, 3.0 Hz, 1H), 6.48 (d, *J* = 3.0, 1.5 Hz, 1H), 6.44 (d, *J* = 9.8 Hz, 1H), 1.94 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.10 (s), 167.51 (s), 147.51 (s), 142.60 (s), 141.44 (s), 137.98 (s), 135.69 (s), 133.32 (s), 132.38 (s), 131.41 (s), 130.69 (s), 129.92 (s), 126.62 (s), 125.14 (s), 122.68 (s), 120.75 (s), 67.17 (s), 15.95 (s); HRMS (ESI) calcd for $C_{20}H_{15}BrNO_2$+: 380.0281 (M+H$^+$), found: 380.0295

2-bromo-2'-(4-bromophenyl)-3-methoxyspiro[cyclohexa[2,5]diene-1,1'-isoindoline]-3',4-dione (**2u**) (Yellow solid, 48 mg, 51%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 1H), 7.68-7.59 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.88 (s, 1H), 5.75 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.90 (s), 167.53 (s), 151.69 (s), 147.71 (s), 142.83 (s), 134.73 (s), 133.71 (s), 132.50 (s), 131.48 (s), 130.36 (s), 127.15 (s), 125.13 (s), 121.86 (s), 121.28 (s), 114.35 (s), 71.28 (s), 55.75 (s); HRMS (ESI) calcd for $C_{20}H_{14}Br_2NO_3$+: 473.9335 (M+H$^+$), found: 473.9333

5-phenylphenanthridin-6(5H)-one (**3**) (White solid, 35.7 mg, 66%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.53 (m, 1H), 8.37 – 8.29 (m, 2H), 7.86 – 7.77 (m, 1H), 7.62 (t, *J* = 7.5 Hz, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 6.73 – 6.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.72 (s), 139.16 (s), 138.28 (s), 134.00 (s), 132.83 (s), 130.20 (s), 129.09 (s), 129.02 (s), 128.78 (s), 128.13 (s), 125.85 (s), 122.98 (s), 122.65 (s), 121.78 (s), 119.03 (s), 117.03 (s)

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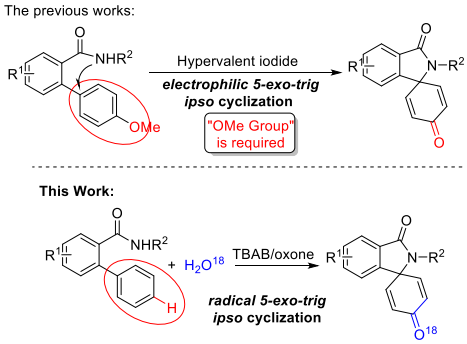

TBAB-mediated radical 5-exo-trig ipso-cyclization of 2-arylbenzamide for the synthesis of spiro[cyclohexane-1,1'-isoindoline]-2,5-diene-3',4-dione

Guanyinsheng Qiu, Zhi-Feng Chen, Wenlin Xie, and Hongwei Zhou

Radical ipso-cyclization: a TBAB-mediated radical 5-*exo-trig ipso*-cyclization of *N*-aryl-2-arylbenzamide is described in this paper.