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6-Arylphenanthridines from Aryl *o*-Biaryl Ketones with 1,1,1,3,3,3-Hexamethyldisilazane and Molecular Iodine

Eiji Kobayashi,[a] Atsushi Kishi,[a] and Hideo Togo*[a]

Keywords: 6-Arylphenanthridine / Ketone / Ketimine / Iodine / Iminyl Radical

Warming treatment of aryl *o*-biaryl ketones with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ in toluene, followed by the reaction with molecular iodine and K_2CO_3 in a mixture of THF and methanol at 60 °C gave the corresponding 6-arylphenanthridines in good to moderate yields. The present reaction is a one-pot method for the preparation of 6-arylphenanthridines from aryl *o*-biaryl ketones through the cyclization of imino-nitrogen-centered radicals that were generated from *N*-iodo aryl *o*-biaryl ketimines formed from the reaction of aryl biaryl ketimines with molecular iodine.

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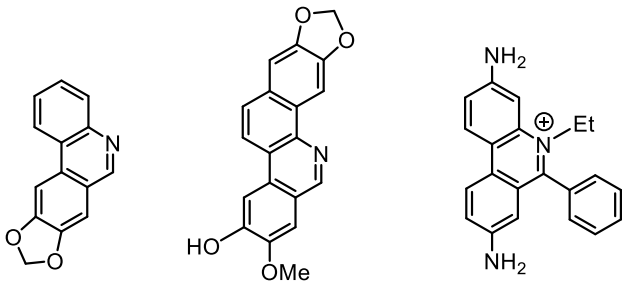
Introduction

Phenanthridines are one of the important nitrogen-containing heteroaromatics because natural products bearing phenanthridine unit are known and phenanthridine derivatives show remarkable biological activities, such as antitumor, antiviral, and antileukemic activities.[1] Typical biologically active phenanthridines, such as trispheridine (DNA intercalator), decarine (DNA intercalator), and ethidium (DNA stain), are shown in Fig. 1.[2]



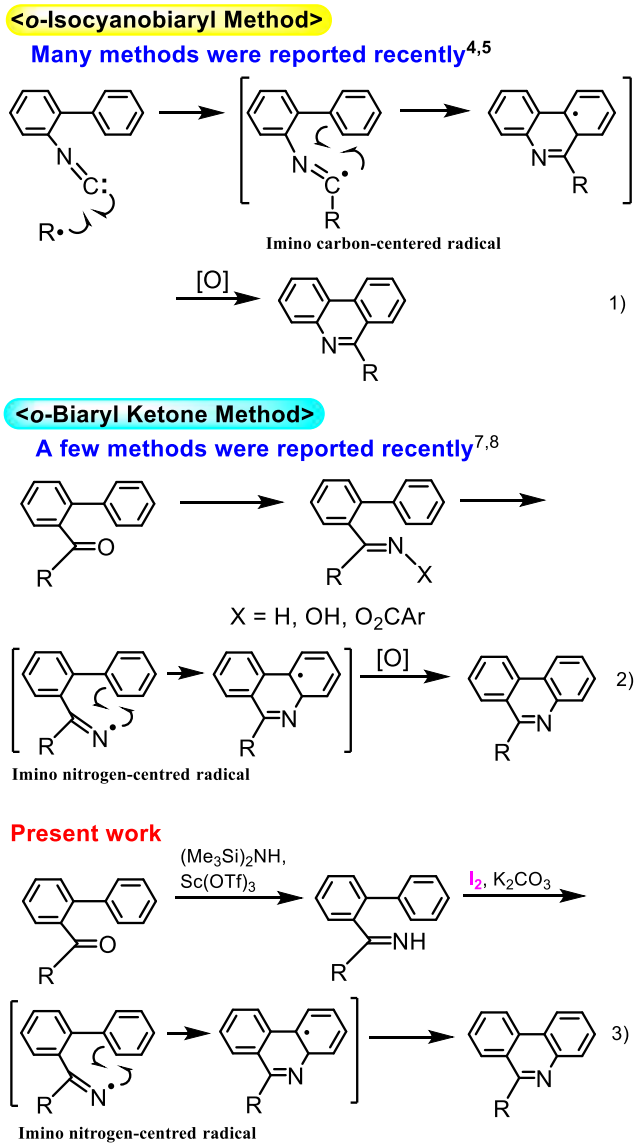
Trispheridine Decarine Ethidium

Fig. 1. Biologically Active Phenanthridines

Synthetic studies of the phenanthridine core have been carried out extensively.[3] Recently, the construction of 6-substituted phenanthridines with *o*-isocyanobiaryls through the formation of imino-carbon-centered radicals and their cyclization onto aromatic rings has become popular (Scheme 1, eq. 1). Recent reports of the construction of 6-substituted phenanthridines with *o*-isocyanobiaryls via imino-carbon-centered radicals are as follows:[4] the preparation of 6-[α-(methoxycarbonyl)alkyl]phenanthridines with Katritzky pyridinium salts in the presence of $Ru(bpy)_2Cl_2$ in acetonitrile under LED irradiation conditions;[4a] the preparation of 6-[dimethyl(trifluoromethyl)]methylphenanthridines with dimethyl(trifluoromethyl)]acetic acid and $(NH_4)_2S_2O_8$ in a mixture of dimethyl sulfoxide and water;[4b] the preparation of 6-methylphenanthridines with (diacetoxyiodo)benzene (DIB), 2-nitropropane, and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in acetonitrile;[4c] the preparation of 6-benzylphenanthridines with toluene, $Fe(acac)_3$, di-*tert*-butyl peroxide (DTBT);[4d] the preparation of 6-(trifluoromethyl)phenanthridines with CF_3SO_2Na and biacetyl under CFL irradiation;[4e] the preparation of 6-(arenesulfonyl)phenanthridines with $ArSO_2Na$, $AgNO_3$, and $K_2S_2O_8$ in DMF;[4f] the preparation of 6-[(dimethyl)(cyano)methyl]phenanthridines with azo[bis(isobutyronitrile)] (AIBN) in toluene;[4g] the preparation of 6-(perfluoroalkyl)phenanthridines with perfluoroalkyl iodides and *N,N,N',N'*-tetraethylethylenediamine in THF under CFL irradiation;[4h] the preparation of 6-alkylphenanthridines with aliphatic carboxylic acids, Ag_2CO_3, and $K_2S_2O_8$ in a mixture of acetonitrile and water;[4i] and the preparation of 6-arylphenanthridines with anilines and *t*-BuONO in benzotrifluoride.[4j] *o*-Isocyanobiaryls could be also used for the preparation of 6-arylphenanthridines with arylbromides and Rh-6G as the catalyst under irradiation with blue LED,[5a] and the preparation of 6-aroylphenanthridines with 2-iodo-2'-isocyano-1,1'-biphenyl, $Pd(OAc)_2$, and CuI as catalysts.[5b] Other recent synthetic approaches for the preparation of phenanthridines are also reported. For example, the preparation of 6-phosphorylated phenanthridines from 2-biaryl isothiocyanates, phosphine oxides, and $Mn(OAc)_3$ in DMF;[6a] the preparation of 6-(trifluoromethyl)phenanthridines from *N*-aryl trifluoromethyl imidoyl chlorides, aryl iodides, $Pd(OAc)_2$, and norbornene in toluene;[6b] the preparation of 6-arylphenanthridines from enediyne acids, *o*-alkynylanilines, $PdCl_2$, and CuI in DMF;[6c] the preparation of 6-aryl- and 6-alkylphenanthridines from *o*-cyanobiaryl and Grignard reagents, followed by the reaction with $Cu(OAc)_2$ under O_2;[6d] the preparation of CF_3S-containing ring-fused phenanthridines from *N*-(*o*-cyanobiaryl)acrylamides and *N*-(trifluoromethylthio)saccharins under visible light irradiation;[6e] the preparation of 6-(trifluoromethyl)phenanthridines from 2-bromophenylboronic acid, fluorinated imidoyl chlorides, and $PdCl_2(Ph_3P)_2$;[6f] and a related reaction for the preparation of nitrogen-containing pyrenes with 2,6-dicyanobiphenyls and Grignard reagents, followed by the reaction with $Co(OAc)_2$ under O_2[6g] are reported.

On the other hand, to the best of our knowledge, studies of the transformation of aryl biaryl ketones into 6-arylphenanthridines are

quite limited, some examples of which are as follows (Scheme 1, eq. 2)[7]: the preparation of 6-alkyl and 6-arylphenanthridines with *o*-acylbiaryls, $TMSN_3$, and TfOH in TFA at 60 °C;[7a] the preparation of 6-unsubstituted phenanthridines with *o*-biarylaldehydes, $ArCO_2NH_2$, and *fac*-Ir(ppy)$_3$ in DMF under visible light irradiation[7b] and with *o*-biarylaldehydes and NH_3 in $(CF_3)_2CHOH$ (HFIP) and CH_3OH under electrochemical conditions.[7c] As indirect methods, the visible light irradiation of *O*-acyl oximes derived from *o*-biaryl ketones in the presence of *fac*-Ir(ppy)$_3$ in DMF at 26 °C gave 6-alkyl and 6-arylphenanthridines,[8a] and the electrochemical treatment of *o*-biaryl methyl ketone oximes in the presence of TEMPO gave 6-methylphenanthridines.[8b] Those reactions[8] proceed through the formation of imino-nitrogen-centered radicals, followed by their cyclization onto aromatic rings to form the phenanthridine core. Based on our previous study for the preparation of 6-alkyl and 6-arylphenanthridines from the reaction of *o*-cyanobiaryls with ArLi, followed by the reaction with water and then molecular iodine,[3] we would like to report herein a one-pot transformation of aryl *o*-biaryl ketones into 6-arylphenanthridines through the formation of the corresponding aryl *o*-biaryl ketimines and the cyclization of the formed imino-nitrogen-centered radicals onto the aromatic ring by the treatment with molecular iodine, as shown in eq. 3 of Scheme 1.

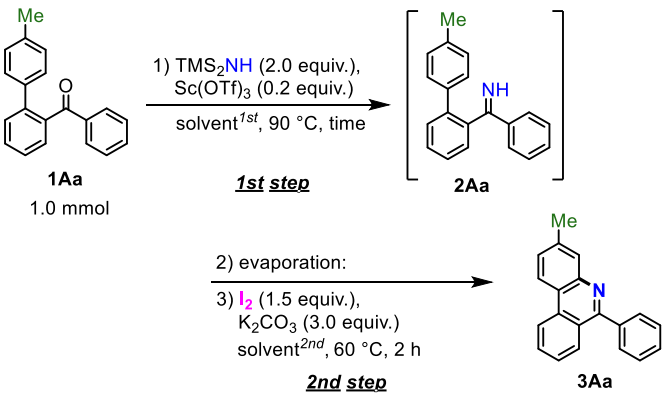


Scheme 1. Construction of Phenanthridine Core

Results and Discussion

The formation of diaryl ketimines in the reaction of diaryl ketones with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ as the catalyst in refluxing toluene is known.[9] Practically, treatment of *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (1.0 mmol) with 1,1,1,3,3,3-hexamethyldisilazane (2.0 equiv.) in the presence of $Sc(OTf)_3$ (0.2 equiv.) without solvent and in toluene (1.0 mL) at 90 °C for 5 h (1st step) gave ketimine **2Aa** in 88% and 90% yields, respectively. Based on those results, treatment of ketone **1Aa** (1.0 mmol) with 1,1,1,3,3,3-hexamethyldisilazane (2.0 equiv.) in the presence of $Sc(OTf)_3$ (0.2 equiv.) without solvent and in toluene (1.0 mL) at 90 °C for 5 h (1st step), followed by the removal of the solvents and the subsequent treatment with molecular iodine (1.5 equiv.) and K_2CO_3 (3.0 equiv.) in a mixture of THF (4.0 mL) and water (4.0 mL) at 60 °C for 2 h (2nd step) gave 3-methyl-6-phenylphenanthridine **3Aa** in 47% and 53% yields, together with ketone **1Aa** in 47% and 35% yields, respectively, as shown in Table 1 (entries 1 and 2). Here, ketone **1Aa** was recovered by hydrolysis of ketimine **2Aa** by quenching of the reaction mixture with sat. aq. Na_2SO_3. Under the same procedure and conditions, the warming treatment of ketimine **2Aa** with molecular iodine (1.5 equiv.) and K_2CO_3 (3.0 equiv.) in a mixture of THF (4.0 mL) and MeOH (4.0 mL), and in MeOH (4.0 mL) at 60 °C for 2 h (2nd step) gave **3Aa** in 63% and 59% yields, together with ketone **1Aa** in 33% and 18% yields, respectively (entries 3, 4). Moreover, treatment of ketone **1Aa** with 1,1,1,3,3,3-hexamethyldisilazane (2.0 equiv.) in the presence of $Sc(OTf)_3$ (0.2 equiv.) in toluene (1.0 mL) at 90 °C for 5 h and 15 h (1st step), followed by removal of the solvent and the subsequent reaction with molecular iodine (1.5 equiv.) and K_2CO_3 (3.0 equiv.) at 60 °C for 2 h in a mixture of THF (2.0 mL) and MeOH (2.0 mL)(2nd step)

Table 1. Optimization for Formation of 3-Methyl-6- phenylphenant hridine **3Aa** from *o*-(*p*-Methylphenyl)phenyl Phenyl ketone **1Aa**.



entry	time (h)	solvent^{1st} (mL)	solvent^{2nd} (mL)	yield (%)
1	5	neat	THF:H_2O = 1:1 (8)	47(47)[a]
2	5	toluene (1)	THF:H_2O = 1:1 (8)	53(35)[a]
3	5	toluene (1)	THF:MeOH = 1:1 (8)	63(33)[a]
4	5	toluene (1)	MeOH (4)	59(18)[a]
5	5	toluene (1)	THF:MeOH = 1:1 (4)	78
6	**15**	**toluene (1)**	**THF:MeOH = 1:1 (4)**	**81**

[a] Yield of recovered **1Aa**

generated **3Aa** in 78% and 81% yields, respectively (entries 5, 6). Thus, entry 6 showed the best result, generating **3Aa** in good yield. As a gram-scale experiment, treatment of ketone **1Aa** (4.0 mmol) under the same procedure and conditions as those of entry 6 gave

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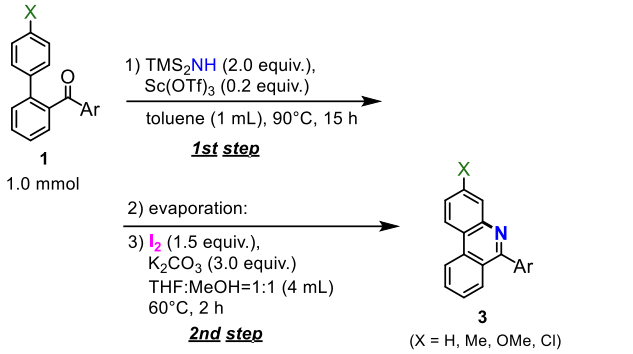
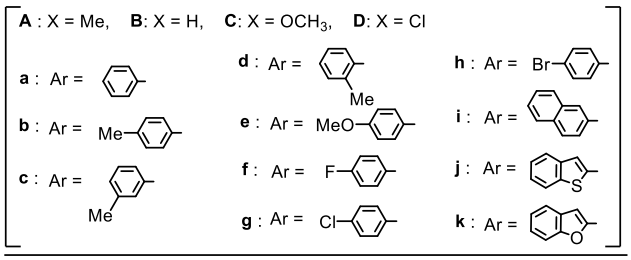
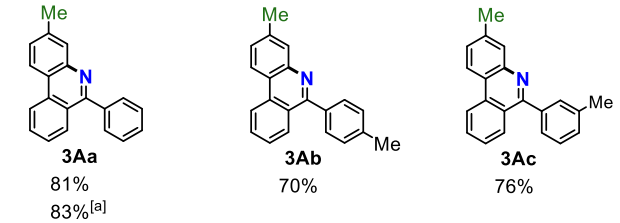
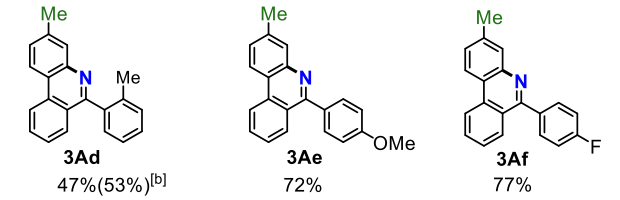
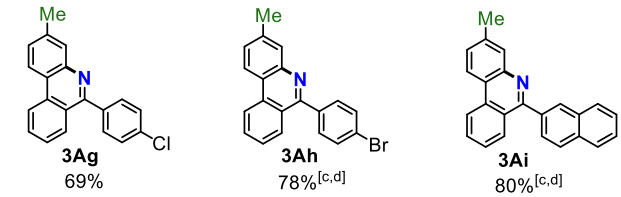
Scheme 2. Transformation of Aryl Biaryl Ketones 1 to 6-Aryl-phenanthridines **3**.

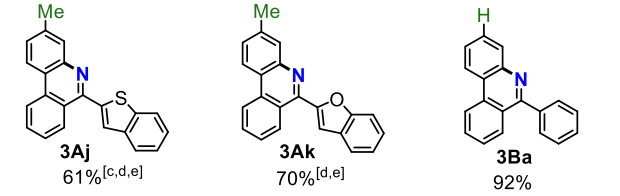


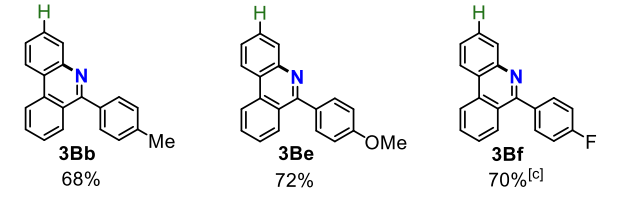


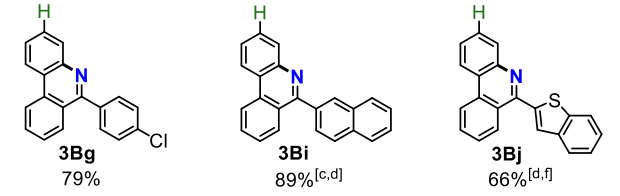


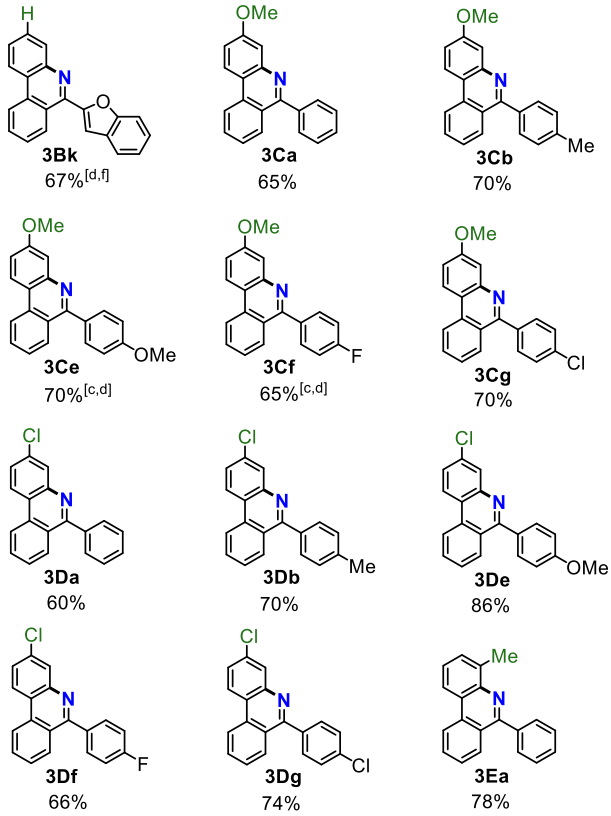












[a] Substrate **1Aa** (4.0 mmol) was used.
[b] Yield of recoverd ketone **1Ad**. Reaction temperature at 1st step reaction was 110 °C.
[c] Reaction temperature at 1st step reaction was 110 °C.
[d] Reaction time at 2nd step reaction was 4 h.
[e] Toluene (4.0 mL) was used as a solvent at 1st step reaction.
[f] Toluene (2.0 mL) was used as a solvent at 1st step reaction.

3-methyl-6-phenylphenanthridine **3Aa** in 83% yield, as shown in Scheme 2.

Based on those results, aryl *o*-(*p*-methylphenyl)phenyl ketones **1A** and aryl *o*-biphenyl ketones **1B**, bearing phenyl (**a**), *p*-methylphenyl (**b**), *m*-methylphenyl (**c**), *o*-methylphenyl (**d**), *p*-methoxyphenyl (**e**), *p*-fluorophenyl (**f**), *p*-chlorophenyl (**g**), *p*-bromophenyl (**h**), 2-naphthyl (**i**), benzothiophen-2-yl (**j**), and benzofuran-2-yl (**k**) groups, were treated with 1,1,1,3,3,3-hexamethyldisilazane (2.0 equiv.) in the presence of $Sc(OTf)_3$ (0.2 equiv.) in toluene (1 mL) at 90 °C for 15 h (1st step), followed by removal of the solvent and the subsequent reaction with molecular iodine (1.5 equiv.) and K_2CO_3 (3.0 equiv.) at 60 °C for 2 h (2nd step) to give 3-methyl-6-arylphenanthridines **3Ab~3Ak**, and 6-arylphenanthridines **3Ba**, **3Bb**, and **3Be~3Bk** in good yields, except **3Ad** in moderate yield, as shown in Scheme 2. Aryl *o*-(*p*-methoxyphenyl)phenyl ketones **1C** and aryl *o*-(*p*-chlorophenyl)phenyl ketones **1D** bearing phenyl (**a**), *p*-methylphenyl (**b**), *p*-methoxyphenyl (**e**), *p*-fluorophenyl (**f**), and *p*-chlorophenyl (**g**), were also treated under the same procedure and conditions to generate the corresponding 6-aryl-3-methoxyphenanthridines **3Ca**, **3Cb**, and **3Ce~3Cg** and 6-aryl-3-chlorophenanthridines **3Da**, **3Db**, and **3De~3Dg** in good to moderate yields, as shown in Scheme 2, respectively. When *o*-(*m*-methylphenyl)phenyl phenyl ketone **1Ea** was used as the substrate under the same procedure and conditions, 4-methyl-6-phenylphenanthridine **3Ea** was obtained as a single product in 78% yield.

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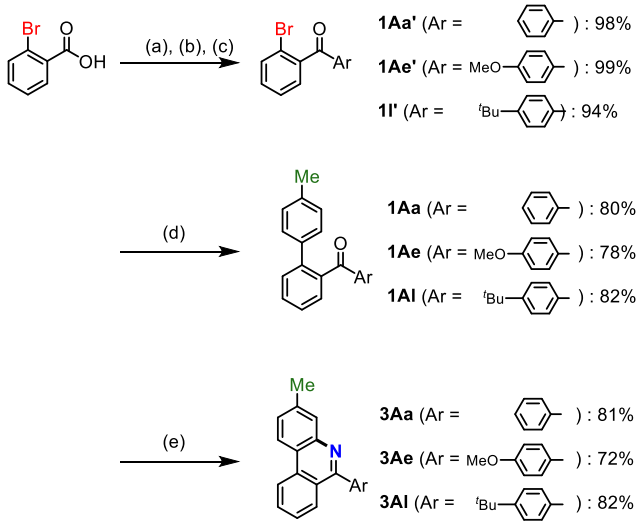
The direct treatment of *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (1.0 mmol) with molecular iodine (4.0 mmol) in aq. NH_3 (3.0 mL) at 60 °C for 15 h did not generate 3-methyl-6-phenylphenanthridine **3Aa** at all and instead, ketone **1Aa** was recovered quantitatively. Thus, the effective and certain formation of ketimine **2Aa** is important. On the other hand, when ethyl *o*-(*p*-methylphenyl)phenyl ketone and *n*-butyl *o*-(*p*-methylphenyl)phenyl ketone were used instead of aryl *o*-biaryl ketones under the same procedure and conditions, 6-ethyl-3-methylphenanthridine and 6-butyl-3-methylphenanthridine were not obtained at all. This is probably because the formed imines isomerized into enamines at the 1st reaction step. Moreover, treatment of *o*-(*p*-methylphenyl)benzaldehyde with 1,1,1,3,3,3-hexamethyldisilazane (2.0 equiv.) in the presence of $Sc(OTf)_3$ (0.2 equiv.) in toluene (1.0 mL) at 90 °C for 15 h (1st step), followed by removal of the solvent and the subsequent reaction with molecular iodine (1.5 equiv.) and K_2CO_3 (3.0 equiv.) at 60 °C for 2 h (2nd step) gave 3-methylphenanthridine only in 20% yield together with *o*-(*p*-methylphenyl)benzonitrile in 75% yield. Thus, the present method is not practical for the preparation of 6-unsubstituted phenanthridines.

Scheme 3. Transformation of *o*-Bromobenzoic Acid to 6- Arylphenant hridines **3** via Aryl Biaryl Ketones

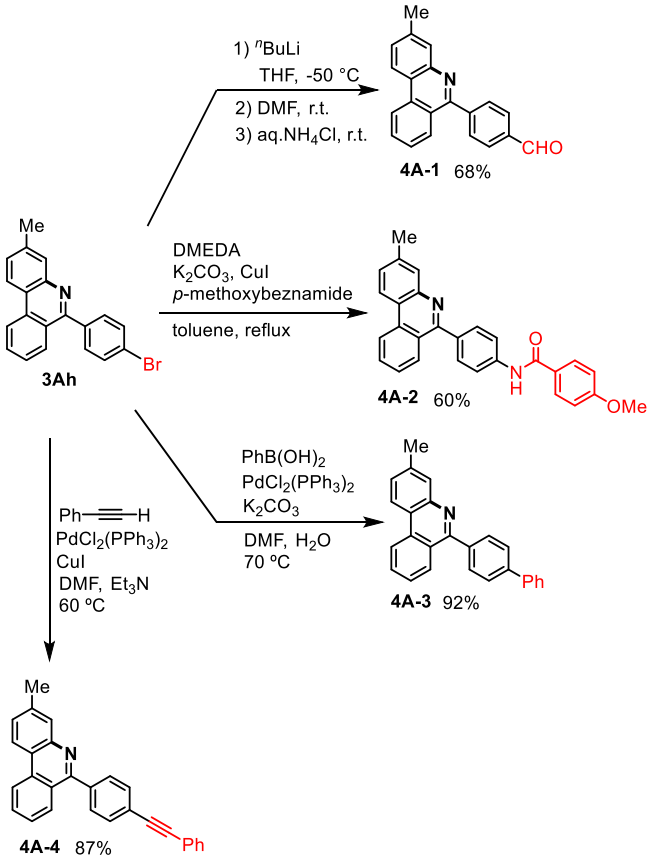


Reaction conditions:
(a) $(COCl)_2$ (1.3 equiv.), DMF (2 drops), CH_2Cl_2 (10 mL), r.t., 2 h
(b) evaporation
(c) **1Aa'** : $AlCl_3$ (1.5 equiv.), Benzene (7.5 mL), 0 °C → r.t., 18 h
1Ac' : $AlCl_3$ (1.3 equiv.), Anisole (1.5 equiv.), CH_2Cl_2 (10 mL), 0 °C → r.t., 5 h
1Aj' : $AlCl_3$ (1.5 equiv.), tButylbenzene (2.5 mL), CH_2Cl_2 (10 mL), 0 °C → r.t., 18 h
(d) 4-Methylphenylboronic Acid (1.2 equiv.), $PdCl_2(PPh_3)_2$ (0.05 equiv.), K_2CO_3 (2.0 equiv.), DMF : H_2O = 5 : 1 (60 mL), 70 °C, 18 h
(e) 1) TMS_2NH (2.0 equiv.), $Sc(OTf)_3$ (0.2 equiv.), toluene (1 mL), 90 °C, 15 h
2) evaporation
3) I_2 (1.5 equiv), K_2CO_3 (3.0 equiv.), THF : MeOH = 1 : 1 (4 mL), 60 °C, 2 h

One of the advantages of the present method for the preparation of 6-arylphenanthridines is that the starting materials, aryl *o*-biaryl ketones, can be obtained easily from the reaction of *o*-aroyl chlorides and arenes in the presence of $AlCl_3$ using the Friedel-Crafts acylation reaction. Thus, treatment of *o*-bromobenzoyl chloride prepared from *o*-bromobenzoic acid and oxalyl chloride, with benzene, anisole, and *t*-butylbenzene in the presence of $AlCl_3$ at room temperature gave the corresponding aryl *o*-bromophenyl ketones **1Aa'**, **1Ae'**, and **1Al'** in 98%, 99%, and 94% yields, respectively, as shown in Scheme 3. Then, aryl *o*-bromophenyl ketones **1Aa'**, **1Ae'**, and **1Al'** were treated with 4-methylphenylboronic acid in the presence of $PdCl_2(Ph_3P)_2$ and K_2CO_3 at 70 °C for 18 h to form aryl *o*-(*p*-methylphenyl)phenyl ketones **1Aa**, **1Ae**, and **1Al** in 80%, 78%, and 82% yields, respectively. The final treatment of aryl *o*-(*p*-methylphenyl)phenyl ketones **1Aa**, **1Ae**, and **1Al** with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ in toluene at 90 °C for 15 h, followed by removal of the solvent and the subsequent reaction with molecular iodine and K_2CO_3 at 60 °C for 2 h gave 6-aryl-3-methyl-phenanthridines **3Aa**, **3Ae**, and **3Al** in 81%, 72%, and 82% yields, respectively.

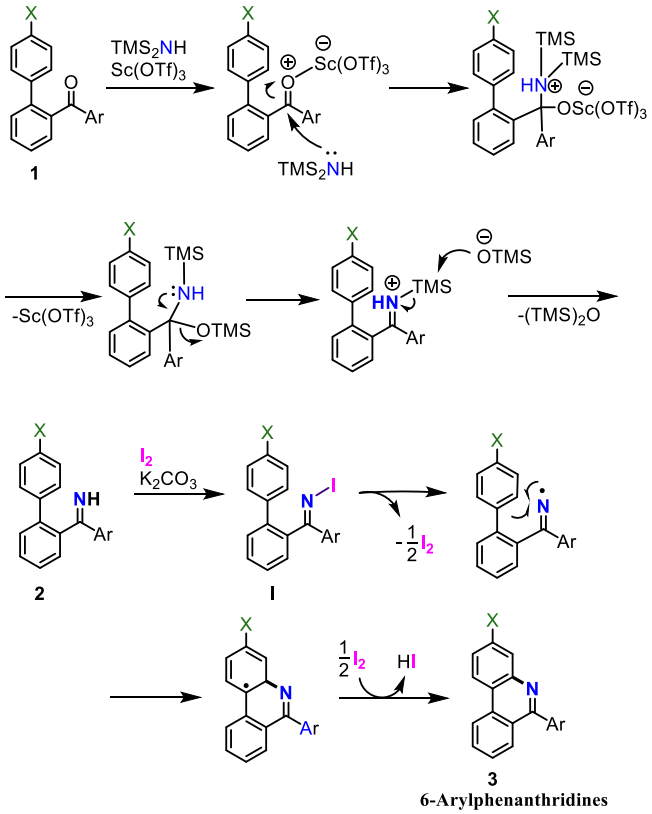
Once 6-arylphenanthridines were obtained, they could be smoothly functionalized. For example, treatment of 6-(4'-bromophenyl)-3-methylphenanthridine **3Ah** with *n*-BuLi (1.1 equiv.) in THF at -50 °C for 0.5 h, followed by the reaction with DMF from -10 °C to room temperature for 1 h, and then with aq. NH_4Cl gave 6-(4'-formylphenyl)-3-methylphenanthridine **4A-1** in 68% yield, as shown in Scheme 4. The reaction of **3Ah** with *p*-methoxybenzamide in the presence of CuI (0.04 equiv.), K_2CO_3, and *N*,*N'*-dimethylethylenediamine (DMEDA) in toluene under refluxing conditions gave *N*-[4'-(3"-methylphenanthridine-6"-yl)phenyl]-4-methoxybenzamide **4A-2** in 60% yield. Treatment of **3Ah** with $PhB(OH)_2$ (1.2 equiv.) and K_2CO_3 in the presence of $PdCl_2(Ph_3P)_2$ (0.04 equiv.) in a mixture of DMF and water at 70 °C for 6 h, and with ethynylbenzene (1.5 equiv.) in the presence of $PdCl_2(Ph_3P)_2$ (0.04 equiv.) and CuI (0.04 equiv.) in a mixture of DMF and Et_3N at 60 °C for 6 h gave 6-(*p*-biphenyl)-3-methylphenanthridine **4A-3** and 3-methyl-6-[(*p*-phenylethynyl)phenyl]phenanthridine **4A-4** in 92% and 87% yields, respectively.

Scheme 4. Derivatization of 6-(4'-Bromophenyl)phenanthridine **3A h**



A possible reaction pathway is shown in Scheme 5. Treatment of aryl *o*-biaryl ketone **1** with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ generates aryl *o*-biaryl ketimine **2**. Aryl *o*-biaryl ketimine **2** reacts with molecular iodine in the presence of K_2CO_3 to form *N*-iodoimine **I**. Once *N*-iodoimine **I** is formed, smooth N-I bond cleavage of *N*-iodoimine **I** occurs to form an iminyl radical that further cyclizes onto the aromatic ring to provide 6-arylphenanthridine **3**. Practically, when the reactions with *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (1.0 mmol) were treated in the presence of 2,6-di-*t*-butyl-*p*-cresol (BHT, 3.0 equiv.) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy radical (4-hydroxy-TEMPO, 3.0 equiv.) at 2nd step reaction under the same procedure and conditions as those of entry 6 in Table 1, yield of 3-methyl-6-phenylphenanthridine **3Aa** was 0% and 12%, together with ketimine **2Aa** in 51% and 78% yields, respectively.

Scheme 5. Possible Reaction Pathway



Conclusions

Treatment of aryl *o*-biaryl ketones with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ in toluene, followed by removal of the solvent and the subsequent reaction with molecular iodine and K_2CO_3 gave 6-arylphenanthridines in one pot in good to moderate yields. The key points of the present reactions are the formation of aryl *o*-biaryl ketimines, their *N*-iodo imines, and imino-nitrogen-centered radicals, and their cyclization onto the *o*-aryl groups in the presence of molecular iodine. Because aryl *o*-biaryl ketones can be obtained from the Friedel-Crafts acylation reaction of arenes with *o*-arylbenzoyl chlorides, we believe that the present method would be useful for the preparation of 6-arylphenanthridines.

Experimental Section

General. ^{1}H NMR spectra were measured on 400 MHz spectrometers. Chemical shifts were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sext = sextet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on 100 MHz spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm, or DMSO-d_6 at 39.5 ppm). Characteristic peaks in the infrared (IR) spectra were recorded in wave number, cm^{-1} on a JASCO FT/IR-4100 spectrometer. Melting points were determined using a Yamato Melting Point Apparatus Model MP-21. High-resolution mass spectra (HRMS) were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Melting points were uncorrected. Thin-layer chromatography (TLC) was performed using 0.25 mm silica gel plates (60F254). The products were purified by column chromatography on neutral silica gel 60N (63-200 mesh).

Typical Procedure for Preparation of Aryl *o*-Biaryl Ketones (1); for 1Aa, 1Ac, 1Ad, 1Ba, 1Ca, and 1Da: PhLi (1.12 M solution in cyclohexane and diethyl ether, 8.93 mL, 10 mmol) was added dropwise to a solution of 2-cyano-4'-methylbiphenyl (1.16 g, 6.0 mmol) in THF (20.0 mL) at −10 °C under Ar atomosphere. After 1 h, the reaction mixture was quenched with aq. HCl (4M, 30.0 mL) and extracted with AcOEt (3 × 80.0 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : EtOAc = 8 : 1) to give *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (998.0 mg, 60%).

Typical Procedure for Preparation of Aryl *o*-Biaryl Ketones (2); for 1Af, 1Ag, 1Ah, 1Ai, 1Aj, 1Ak, 1Bf, 1Bg, 1Bi, 1Bj, and 1Bk: (1) *o*-(*p*-Methylphenyl)benzoic acid (3.184 g, 15 mmol) was dissolved in dry THF (72.0 mL) under Ar atmosphere. $LiAlH_4$ (1.42 g, 37.5 mmol) was slowly added to the solution at 0 °C and then, the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with aq. NaOH solution (2 M, 30.0 mL). The reaction mixture was poured into water (60 mL) and the obtained mixture was filtered. The filtrates were extracted with AcOEt (3 × 60.0 mL). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed to give *o*-(*p*-methylphenyl)benzylalcohol as colorless oil.

(2) MnO_2 (13.04g, 150 mmol) was added to a solution of *o*-(*p*-methylphenyl)benzylalcohol in CH_2Cl_2 (50.0 mL). The resulting suspension was warmed under refluxing conditions overnight. Then, the mixture was filtered through a celite pad and the filtrates were concentrated in vacuo. Purification of the residue by short column chromatography on silica gel (hexane:AcOEt = 10:1) yielded *o*-(*p*-methylphenyl)benzaldehyde (2.06 g, 70%).

(3) *n*-BuLi (1.55 M solution in hexane, 2.13 mL, 3.3 mmol) was added dropwise to a solution of benzo[b]thiophene (0.40 g, 3.0 mmol) in THF (3.0 mL) at −50 °C under Ar atomosphere. After 1 h., *o*-(*p*-methylphenyl)benzaldehyde (0.61 g, 3.1 mmol) in THF (3.0 mL) was added to the mixture. The obtained mixture was gradually warmed to room temperature and stirred for 3 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl. The reaction mixture was extracted with AcOEt (3 × 60.0 mL). The organic layer was washed with brine, dried over Na_2SO_4, and filtered. Removal of the solvent by evaporation gave α-(benzo[b]thiophene-2-yl)-α-[*o*-(*p*-methylphenyl)phenyl]methanol.

(4) MnO_2 (2.61 g, 30 mmol) was added to a solution of α-(benzo[b]thiophene-2-yl)-α-[*o*-(*p*-methylphenyl)phenyl]methanol in CH_2Cl_2 (30.0 mL). The resulting suspension was warmed under refluxing conditions overnight. Then, the mixture was filtered through celite pad and the filtrates were concentrated in vacuo. Purification of the residue by short column chromatography on silica gel (hexane:AcOEt = 10:1) yielded benzo[b]thiophen-2-yl *o*-(*p*-methylphenyl)phenyl ketone **1Aj** (610.8 mg, 62%).

Typical Procedure for Preparation of Aryl *o*-Biphenyl Ketones (3); for 1Ab, 1Ae, 1Bb, 1Be, and 1Cb: (1) To biphenyl-2-carboxylic acid (793.0 mg, 4.0 mmol) in CH_2Cl_2 (10.0 mL) in a 100 mL round-bottom flask was added oxalyl chloride (0.45 mL, 5.2 mmol). Then, DMF (one drop) was added to the mixture and the obtained mixture was stirred at room temperature for 5 h. The resulting mixture was concentrated under reduced pressure to afford *o*-phenylbenzoyl chloride quantitatively.

(2) To a solution of *o*-phenylbenzoyl chloride in CH_2Cl_2 (10.0 mL) was added anisole (125.4 μL, 6.0 mmol) at 0 °C. The mixture was stirred for a few min. Then, anhydrous $AlCl_3$ (693.9 mg, 5.2 mmol) was added and the obtained mixture was stirred for 24 h at room temperature. Then, the reaction mixture was quenched with iced water (~1 g) and extracted with $CHCl_3$ (3 × 60.0 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on neutral silica gel (hexane : AcOEt = 8 : 1) to afford *o*-biphenyl *p*-methoxyphenyl ketone **1Be** (818.9 mg, 71%).

Typical Procedure for Preparation of Aryl *o*-Biphenyl Ketones 1Cb, 1Ce, 1Cf, 1Cg, 1Db, 1De, 1Df, 1Dg, and 1Ea:

(1) To a 200 mL round-bottom flask were added 2-iodobenzoic acid (25.0 g, 100.0 mmol), CH_2Cl_2 (50.0 mL), and oxalyl chloride (9.12 mL, 105 mmol). The mixture was stirred at room temperature for 5 min. Then, DMF (2 drops) was added, and the mixture was stirred at room temperature for 5 h. The resulting mixture was concentrated under reduced pressure to afford 2-iodobenzoyl chloride quantitatively. To a solution of 2-iodobenzoyl chloride in THF (40.0 mL) was added aq.NH_3 (10.0 mL) at r.t., and the mixture was stirred for 2 h. Then, the reaction mixture was quenched with aq. $NaHCO_3$ (100.0 mL) and filtered to give 2-Iodobenzamide (19.8 g, 80%).

(2) To a 200 mL round-bottom flask were added 2-iodobenzamide (19.8 g, 80.0 mmol) and P_2O_5 (12.0 g, 80.0 mmol). The mixture was stirred at 160 °C for 3 h. Then, the reaction mixture was quenched with water (100.0 mL) and extracted with $CHCl_3$ (3 × 80.0 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on neutral silica gel (hexane : AcOEt = 8 : 1) to afford 2-Iodobenzonitrile (14.3 g, 78%).

(3) To a mixture of 2-iodobenzonitrile (2.29 g, 10.0 mmol) and 4-methoxyphenylboronic acid (1.83 g, 12.0 mmol) in DMF (100.0 mL) was added $PdCl_2(PPh_3)_2$ (351.0 mg, 0.5 mmol) under the argon atmosphere. The obtained mixture was stirred for 30 min at room temperature. Then, K_2CO_3 (2.76 g, 20.0 mmol) in H_2O (20.0 mL) was added to the mixture, and the obtained mixture was stirred for 18 h at 70 °C. Water (100.0 mL) was added to the reaction mixture, and the product was extracted with hexane : AcOEt = 4 : 1 (70.0 mL × 3). The organic layer was washed with brine and dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane : EtOAc = 8 : 1) on neutral silica gel to give *o*-(*p*-methoxyphenyl)benzonitrile (1.51 g, 72%).

(4) *n*-BuLi (1.55 M solution in hexane, 2.13 mL, 3.3 mmol) was added dropwise to a solution of 1-bromo-4-chlorobenzene (574.4 mg, 3.0 mmol) in THF (3.0 mL) at −50 °C under Ar atomosphere. After 1 h, *o*-(*p*-methoxyphenyl)benzonitrile (648.7 mg, 3.1 mmol) in THF (3.0 mL) was added, and the obtained mixture was gradually warmed to r.t., and then the reaction mixture was stirred for 0.5 h. Then, the reaction mixture was quenched with 4M HCl (30.0 mL) and extracted with AcOEt (3 × 40.0 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane : EtOAc = 8 : 1) on neutral silica gel to give *p*-chlorophenyl *o*-(*p*-methoxyphenyl)phenyl ketone **1Cg** (697.2 mg, 72%).

Typical Procedure for Preparation of Ary Biaryl Ketones 1 with the Friedel-Crafts Acylation (Scheme 3): (1) To a mixture of *o*-bromobenzoic acid (1.0 g, 5.0 mmol) in CH_2Cl_2 (10.0 mL) was added oxalyl chloride (0.58 mL, 6.5 mmol). The mixture was stirred at room temperature for 5 min. Then, DMF (2 drops) was added to the mixture and the obtained mixture was stirred at room temperature for 2 h. The resulting mixture was evaporated under reduced pressure to afford *o*-bromobenzoyl chloride quantitatively.

A solution of *o*-bromobenzoyl chloride in benzene (7.5 mL) was stirred for a few min at 0 °C. Anhydrous $AlCl_3$ (1.00 g, 7.5 mmol) was added to the mixture and the obtained mixture was stirred for 24 h at room temperature. The reaction mixture was quenched with iced water (~1 g) and extracted with $CHCl_3$ (3 × 40.0 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on neutral silica gel (hexane : AcOEt = 8 : 1) to afford *o*-bromophenyl phenyl ketone **1Aa'** (1.28 g, 98%).

(2) To a mixture of *o*-bromophenyl phenyl ketone **1Aa'** (1.28 g, 4.9 mmol) and *p*-methylphenylboronic acid (0.82 g, 6.0 mmol) in DMF (50.0 mL) was added $PdCl_2(PPh_3)_2$ (0.18 g, 0.25 mmol) under argon atmosphere. The obtained mixture was stirred for 30 min at room temperature. Then, K_2CO_3 (1.38 g, 10.0 mmol) in H_2O (10.0 mL) was added to the mixture, and the obtained mixture was stirred at 70 °C for 18 h. Water (50.0 mL) was added to the reaction mixture, and the product was extracted with a mixture of hexane and AcOEt (4 : 1, 50.0 mL × 3). The organic layer was washed with brine and dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane : EtOAc = 8 : 1) on silica gel to give *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (1.10 g, 80%).

***o*-(*p*-Methylphenyl)phenyl Phenyl Ketone (1Aa)**[10]: white solid; Mp: 82-85 °C; IR (neat) 1659, 1256, 925, 767, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 7.00 (d, 2H, *J* = 8.0 Hz), 7.14 (d, 2H, *J* = 7.4 Hz), 7.25-7.28 (m, 2H), 7.38-7.48 (m, 4H), 7.52-7.55 (m, 1H), 7.65 (d, 2H, *J* = 7.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.8, 128.1, 128.8 (2C), 128.9 (2C), 129.0, 130.0 (2C), 130.1 (2C), 130.5, 132.8, 137.1, 137.3, 137.4, 138.9, 141.2, 198.9; HRMS (ESI) Calcd for $C_{20}H_{17}O$ $[M+H]^+$ = 273.1273, Found = 273.1276.

***o*-(*p*-Methylphenyl)phenyl *p*-Methylphenyl Ketone (1Ab)**[11,12]: white solid; Mp: 148-152 °C; IR (neat) 1659, 1256, 925, 766, 605 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.34 (s, 3H), 7.02 (d, 2H, *J* = 7.7 Hz), 7.11 (d, 2H, *J* = 7.7 Hz), 7.17 (d, 2H, *J* = 8.2 Hz), 7.39-7.48 (m, 3H), 7.52-7.56 (m, 1H), 7.60 (d, 2H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.6, 126.6, 128.5, 128.7 (2C), 128.9 (2C), 129.0, 130.0 (2C), 130.1, 130.2 (2C), 134.8, 137.0, 137.3, 139.1, 141.0, 143.7, 198.4; HRMS (ESI) Calcd for $C_{21}H_{19}O$ $[M+H]^+$ = 287.1430, Found = 287.1426.

***m*-Methylphenyl *o*-(*p*-methylphenyl)phenyl Ketone (1Ac):** white solid; Mp: 142-146 °C; IR (neat) 1662, 1280, 821, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 2.30 (s, 3H), 7.02 (d, 2H, *J* = 8.1 Hz), 7.15 (d, 2H, *J* = 8.1 Hz), 7.19 (d, 1H, *J* = 7.4 Hz), 7.25 (d, 1H, *J* = 7.4 Hz), 7.40-7.57 (m, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.1, 126.6, 127.3, 127.9, 128.6, 128.7 (2C), 128.9 (2C), 130.0, 130.1, 130.3, 133.6, 136.9, 137.2, 137.3, 137.7, 138.9, 141.1, 198.8; HRMS (ESI) Calcd for $C_{21}H_{19}O$ $[M+H]^+$ = 287.1430, Found = 287.1426.

***o*-Methylphenyl *o*-(*p*-methylphenyl)phenyl Ketone (1Ad):** white solid; Mp: 140-145 °C; IR (neat) 1660, 1268, 926, 757, 734 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.43 (s, 3H), 6.98-7.02 (m, 3H), 7.06-7.11 (m, 3H), 7.18-7.23 (m, 2H), 7.39-7.44 (m, 2H) , 7.52-7.56 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 20.8, 20.9, 124.8, 126.7, 128.5 (2C), 128.6 (2C), 129.3, 130.1, 130.5, 130.9, 131.1, 131.2, 136.7, 137.5, 137.7, 139.0, 140.1, 141.6, 200.4; HRMS (ESI) Calcd for $C_{21}H_{19}O$ $[M+H]^+$ = 287.1430, Found = 287.1428.

***p*-Methoxyphenyl *o*-(*p*-Methylphenyl)phenyl Ketone (1Ae)**: white solid; Mp: 130-133 °C; IR (neat) 1658, 1259, 924, 766, 608 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.80 (s, 3H), 6.77 (d, 2H, *J* = 7.5 Hz), 7.02 (d, 2H, *J* = 7.5 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 7.40-7.47 (m, 3H), 7.51-7.55 (m, 1H), 7.67 (d, 2H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 55.4, 113.4 (2C), 126.7, 128.4, 128.7 (2C), 129.0 (2C), 129.9, 130.0, 130.4, 132.4 (2C), 136.9, 137.3, 139.2, 140.7, 163.3, 197.4; HRMS (ESI) Calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ = 303.1379, Found = 303.1376.

***p*-Fluorophenyl *o*-(*p*-Methylphenyl)phenyl Ketone (1Af)**: white solid; Mp: 75-78 °C; IR (neat) 1664, 1259, 924, 768, 603 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 6.94 (d, 2H, *J* = 8.2 Hz), 7.01 (d, 2H, *J* = 8.0 Hz), 7.13 (d, 2H, *J* = 8.2 Hz), 7.42-7.49 (m, 3H), 7.55-7.59 (m, 1H), 7.64-7.69 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.0, 115.2 (d, J_{C-F} = 21.2 Hz, 2C), 126.9, 128.6, 128.8 (2C), 129.0 (2C), 130.0, 130.4, 132.5 (d, J_{C-F} = 8.4 Hz, 2C), 133.7 (d, J_{C-F} = 3.6 Hz), 137.1, 137.2, 138.5, 140.9, 165.4 (d, J_{C-F} = 242.1 Hz), 197.4; HRMS (ESI) Calcd for $C_{20}H_{16}FO$ $[M+H]^+$ = 291.1179, Found = 291.1179.

***p*-Chlorophenyl *o*-(*p*-Methylphenyl)phenyl Ketone (1Ag)**: white solid; Mp: 121-122 °C; IR (neat) 1661, 1258, 923, 767, 653 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 7.02 (d, 2H, *J* = 7.8 Hz), 7.13 (d, 2H, *J* = 7.8 Hz), 7.24 (d, 2H, *J* = 8.8 Hz), 7.42-7.48 (m, 3H), 7.55-7.60 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.9, 128.4 (2C), 128.6, 128.8 (2C), 129.1 (2C), 130.1, 130.5, 131.2 (2C), 135.7, 137.0, 137.3, 138.3, 139.1, 141.0, 197.7; HRMS (ESI) Calcd for $C_{20}H_{16}ClO$ $[M+H]^+$ = 307.0883, Found = 307.0882.

***p*-Bromophenyl *o*-(*p*-Methylphenyl)phenyl Ketone (1Ah)**: white solid; Mp: 125-127 °C; IR (neat) 1661, 1258, 923, 767, 653 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 7.01 (d, 2H, *J* = 7.6 Hz), 7.12 (d, 2H, *J* = 7.6 Hz), 7.39-7.59 (m, 8H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.9, 128.0, 128.6, 128.8 (2C), 129.1 (2C), 130.1, 130.5, 131.3 (2C), 131.4 (2C), 136.1, 137.0, 137.3, 138.3, 141.0, 197.9; HRMS (ESI) Calcd for $C_{20}H_{16}{}^{79}BrO$ $[M+H]^+$ = 351.0379 Found = 351.0379.

***o*-(*p*-Methylphenyl)phenyl β-Naphthyl Ketone((1Ai)**: yellow solid; Mp: 95-97 °C; IR (neat) 1657, 1288, 920, 756, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 6.70 (d, 2H, *J* = 8.1 Hz), 7.19 (d, 2H, *J* = 8.1 Hz), 7.44-7.65 (m, 6H), 7.76-7.82 (m, 3H), 7.87 (d, 1H, *J* = 8.6 Hz), 8.11 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.0, 125.0, 126.5, 126.7, 126.7, 127.6, 128.1, 128.4, 128.4, 128.7 (2C), 129.0 (2C), 129.5, 130.2, 132.2, 132.5, 134.7, 135.4, 137.0, 137.3, 139.0, 141.2, 198.7; HRMS (ESI) Calcd for $C_{24}H_{19}O$ $[M+H]^+$ = 323.1430, Found = 323.1427.

Benzo[b]thiophen-2-yl *o*-(*p*-Methylphenyl)phenyl Ketone (1Aj): orange solid; Mp: 132-135 °C; IR (neat) 1650, 1262, 911, 740, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 7.06 (d, 2H, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 7.6 Hz), 7.34 (t, 1H, *J* = 8.2 Hz), 7.40-7.48 (m, 2H), 7.50-7.53 (m, 2H), 7.56-7.62 (m, 2H), 7.74 (d, 1H, *J* = 8.2 Hz), 7.82 (d, 1H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.0, 122.8, 124.8, 125.9, 126.7, 127.3, 128.3, 128.6 (2C), 129.2 (2C), 130.3, 130.5, 132.7, 137.0, 137.1, 138.2, 138.8, 140.7, 142.9, 144.2, 192.2; HRMS (ESI) Calcd for $C_{22}H_{17}OS$ $[M+H]^+$ = 329.0994, Found = 329.0991.

Benzofuran-2-yl *o*-(*p*-Methylphenyl)phenyl Ketone (1Ak): white solid; Mp: 117-119 °C; IR (neat) 1650, 971, 750 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 7.04 (d, 2H, *J* = 7.6 Hz), 7.12 (s, 1H), 7.22-7.27 (m, 3H), 7.40-7.54 (m, 4H), 7.56-7.64 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.1, 112.5, 116.8, 123.3, 123.8, 126.9, 127.0, 128.3, 128.7, 128.8 (2C), 129.2, 130.4, 130.9, 137.1, 137.3, 137.8, 141.3, 152.7, 156.0,

187.6; HRMS (ESI) Calcd for $C_{22}H_{17}O_2$ $[M+H]^+$ = 313.1222, Found = 313.1221.

***p*-(*tert*-Butyl)phenyl *o*-(*p*-Methylphenyl)phenyl Ketone (1Al)**: white solid; Mp: 118-120 °C; IR (neat) 1664, 1251, 927, 765 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H), 2.25 (s, 3H), 7.02 (d, 2H, *J* = 7.7 Hz), 7.16 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.6 Hz), 7.39-7.48 (m, 3H), 7.54 (t, 1H, *J* = 7.7 Hz), 7.64 (d, 2H, *J* = 8.6 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 20.9, 30.9 (3C), 35.0, 124.9 (2C), 126.4, 128.5, 128.7 (2C), 128.8 (2C), 129.9 (2C), 130.0, 130.0, 134.7, 136.7, 137.3, 138.9, 141.1, 156.3, 198.1; HRMS (ESI) Calcd for $C_{24}H_{25}O$ $[M+H]^+$ = 329.1900, Found = 329.1901.

***o*-Biphenyl Phenyl Ketone (1Ba)**[11]: white solid; Mp: 85-86 °C; IR (neat) 1661, 1260, 927, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13-7.22 (m, 3H), 7.24-7.29 (m, 4H), 7.38-7.53 (m, 4H), 7.56-7.60 (m, 1H), 7.63-7.65 (m, 2H) ; ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 127.0, 127.3, 128.0 (2C), 128.2 (2C), 128.7, 129.0 (2C), 129.9 (2C), 130.0, 130.3, 132.8, 137.3, 138.9, 140.1, 141.1, 198.9; HRMS (ESI) Calcd for $C_{19}H_{15}O$ $[M+H]^+$ = 259.1117, Found = 259.1115.

***o*-Biphenyl *p*-Methylphenyl Ketone (1Bb)**: white solid; Mp: 120-122 °C; IR (neat) 1656, 1254, 925, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 7.08 (d, 2H, *J* = 7.8 Hz), 7.15-7.30 (m, 5H), 7.42-7.49 (m, 3H), 7.52-7.58 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.6, 126.9, 127.2, 128.2 (2C), 128.6, 128.8 (2C), 128.9 (2C), 130.0, 130.1, 130.1 (2C), 134.8, 139.2, 140.2, 140.9, 143.7, 198.3; HRMS (ESI) Calcd for $C_{20}H_{17}O$ $[M+H]^+$ = 273.1273, Found = 273.1273.

***o*-Biphenyl *p*-Methoxyphenyl Ketone (1Be)**[12]: white solid; Mp: 120-122 °C; IR (neat) 1650, 1260, 1147, 745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 6.77 (d, 2H, *J* = 8.8 Hz), 7.15-7.24 (m, 3H), 7.27-7.30 (m, 2H), 7.42-7.49 (m, 3H), 7.52-7.58 (m, 1H), 7.65 (d, 2H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ =55.4, 113.3 (2C), 127.0, 127.3, 128.2 (2C), 128.4, 128.9 (2C), 130.0, 130.0, 130.3, 132.3 (2C), 139.9, 140.2, 140.7, 163.3, 197.3; HRMS (ESI) Calcd for $C_{20}H_{17}O_2$ $[M+H]^+$ = 289.1223, Found = 289.1220.

***o*-Biphenyl *p*-Fluorophenyl Ketone (1Bf)**: white solid; Mp: 68-70 °C; IR (neat) 1662, 1147, 930, 743 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.91 (t, 2H, *J* = 8.6 Hz), 7.14-7.26 (m, 5H), 7.45-7.54 (m, 3H), 7.57-7.67 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 115.2 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 127.2, 127.4, 128.3 (2C), 128.7, 128.9 (2C), 130.0, 130.5, 132.4 (d, $J_{C\text{-}F}$ = 8.6 Hz, 2C), 133.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 138.6, 140.0, 140.9, 165.4 (d, $J_{C\text{-}F}$ = 242.8 Hz), 197.3; HRMS (ESI) Calcd for $C_{19}H_{14}FO$ $[M+H]^+$ = 277.1022, Found = 277.1020.

***o*-Biphenyl *p*-Chlorophenyl Ketone (1Bg)**: white solid; Mp: 115-118 °C; IR (neat) 1660, 1259, 1087, 928, 740 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.15-7.26 (m, 7H), 7.45-7.53 (m, 3H), 7.55 (d, 2H, *J* = 8.6 Hz), 7.56-7.62 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 127.2, 127.5, 128.3 (2C), 128.4 (2C), 128.7, 128.9 (2C), 130.0, 130.6, 131.1 (2C), 135.7, 138.5, 139.1, 139.9, 141.0, 197.6; HRMS (ESI) Calcd for $C_{19}H_{14}ClO$ $[M+H]^+$ = 293.0727, Found = 293.0729.

***o*-Biphenyl *β*-Naphthyl Ketone (1Bi)**: white solid; Mp: 108-110 °C; IR (neat) 1652, 1294, 916, 749, 701 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.08 (t, 1H, *J* = 7.5 Hz), 7.14 (d, 1H, *J* = 7.5 Hz), 7.16 (d, 1H, *J* = 7.5 Hz), 7.30 (d, 2H, *J* = 7.5 Hz), 7.46-7.65 (m, 6H), 7.74-7.86 (m, 4H), 8.07 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 124.9, 126.5, 127.0, 127.3, 127.6, 128.1, 128.2 (2C), 128.4, 128.8, 128.8 (2C), 129.5, 130.1, 130.3, 132.1, 132.5, 134.7, 135.3, 139.0, 140.2, 141.2, 198.6; HRMS (ESI) Calcd for $C_{23}H_{17}O$ $[M+H]^+$ = 309.1273, Found = 309.1272.

Benzo[b]thiophen-2-yl *o*-Biphenyl Ketone (1Bj): yellow solid; Mp: 153-155 °C; IR (neat) 1643, 1291, 755, 700 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (t, 1H, *J* = 7.3 Hz), 7.23-7.26 (m, 2H), 7.32-7.37 (m, 3H), 7.42 (t, 1H, *J* = 7.3 Hz), 7.47-7.55 (m, 3H), 7.59-7.63 (m, 2H), 7.72 (d, 1H, *J* = 8.2 Hz), 7.81 (d, 1H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 122.9, 124.8, 126.0, 127.0, 127.4, 127.5, 128.4, 128.4 (2C), 128.8 (2C), 130.4, 130.6, 132.8, 138.4, 138.8, 140.0, 140.9, 142.9, 144.1, 192.1; HRMS (ESI) Calcd for $C_{21}H_{15}OS$ $[M+H]^+$ = 315.0837, Found = 315.0835.

Benzofuran-2-yl *o*-Biphenyl Ketone (1Bk): yellow solid; Mp: 129-131 °C; IR (neat) 1651, 973, 897, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.12 (s, 1H), 7.15 (t, 1H, *J* = 7.2 Hz), 7.22-7.26 (m, 3H), 7.36 (d, 2H, *J* = 7.2 Hz), 7.41 (t, 1H, *J* = 7.2 Hz), 7.47-7.53 (m, 2H), 7.55 (t, 2H, *J* = 8.0 Hz), 7.61-7.66 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 112.4, 116.6, 123.2, 123.7, 126.8, 127.1, 127.4, 128.3, 128.4 (2C), 128.8 (2C), 128.8, 130.3, 130.9, 137.8, 140.0, 141.3, 152.5, 155.8, 187.4; HRMS (ESI) Calcd for $C_{21}H_{15}O_2$ $[M+H]^+$ = 299.1066, Found = 299.1065.

***o*-(*p*-Methoxyphenyl)phenyl Phenyl Ketone (1Ca)**[10]: white solid; Mp: 88-90 °C; IR (neat) 1651, 1259, 924, 766, 608 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 6.73 (d, 2H, *J* = 8.6 Hz), 7.18 (d, 2H, *J* = 8.6 Hz), 7.26-7.30 (m, 2H), 7.40-7.49 (m, 4H), 7.56 (t, 1H, *J* = 8.2 Hz), 7.65 (d, 2H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 55.0, 113.7 (2C), 126.5, 128.0 (2C), 128.6, 129.8 (2C), 129.9, 130.0 (2C), 130.2, 132.5, 132.8, 137.2, 138.7, 140.6, 158.8, 198.9; HRMS (ESI) Calcd for $C_{20}H_{17}O_2$ $[M+H]^+$ = 289.1222, Found = 289.1220.

***p*-Methylphenyl *o*-(*p*-Methoxyphenyl)phenyl Ketone (1Cb)**: white solid; Mp: 100-102 °C; IR (neat) 1656, 1252, 832, 741 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.73 (s, 3H), 6.75 (d, 2H, *J* = 8.8 Hz), 7.09 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 2H, *J* = 8.8 Hz), 7.39-7.46 (m, 3H), 7.50-7.56 (m, 1H), 7.58 (d, 2H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.7, 55.2, 113.7 (2C), 126.5, 128.5, 128.9 (2C), 129.9, 130.0 (2C), 130.1 (2C), 132.7, 132.7, 134.8, 139.0, 140.5, 143.7, 158.9, 198.6; HRMS (ESI) Calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ = 303.1379, Found = 303.1378.

***o*-(*p*-Methoxyphenyl)phenyl *p*-Methoxyphenyl Ketone (1Ce)**: white solid; Mp: 95-99 °C; IR (neat) 1655, 1250, 1147, 761, 604 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 3.81 (s, 3H) , 6.74-6.79 (m, 4H), 7.21 (d, 2H, *J* = 8.7 Hz) , 7.39-7.46 (m, 3H), 7.53 (t, 1H, *J* = 8.0 Hz), 7.66 (d, 2H, *J* = 8.7 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 55.1, 55.4, 113.4 (2C), 113.7 (2C), 126.5, 128.4, 129.9, 129.9, 130.0 (2C), 130.3, 132.3 (2C), 132.7, 139.1, 140.3, 158.9, 163.3, 197.6; HRMS (ESI) Calcd for $C_{21}H_{19}O_3$ $[M+H]^+$ = 319.1328, Found = 319.1326.

***p*-Fluorophenyl *o*-(*p*-Methoxyphenyl)phenyl Ketone (1Cf)**: yellow oil; IR (neat) 1663, 1596, 1238, 768, 603 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 6.74 (d, 2H, *J* = 8.8 Hz), 6.93 (t, 2H, *J* = 7.8 Hz), 7.16 (d, 2H, *J* = 8.8 Hz), 7.41-7.49 (m, 3H), 7.54-7.59 (m, 1H), 7.62-7.67 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 54.9, 113.7 (2C), 115.1 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 126.6, 128.4, 129.8, 129.9 (2C), 130.3, 132.3, 132.3 (d, $J_{C\text{-}F}$ = 7.8 Hz, 2C), 133.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 138.4, 140.3, 158.9, 165.2 (d, $J_{C\text{-}F}$ = 251.1 Hz), 197.3; HRMS (ESI) Calcd for $C_{20}H_{16}FO_2$ $[M+H]^+$ = 307.1128, Found = 307.1129.

***p*-Chlorophenyl *o*-(*p*-Methoxyphenyl)phenyl Ketone (1Cg)**: yellow solid; Mp: 78-80 °C; IR (neat) 1661, 1516, 1247, 927, 741 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 6.74 (d, 2H, *J* = 8.8 Hz), 7.16 (d, 2H, *J* = 8.6 Hz), 7.23 (d, 2H, *J* = 8.6 Hz), 7.41-7.49 (m, 3H), 7.54-7.59 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 55.1, 113.8 (2C), 126.8, 128.4 (2C), 128.6, 129.9, 130.0 (2C), 130.5, 131.1 (2C), 132.4, 135.6, 138.3, 139.1, 140.5, 159.0, 197.8; HRMS (ESI) Calcd for $C_{20}H_{16}ClO_2$ $[M+H]^+$ = 323.0833, Found = 323.0829.

***o*-(*p*-Chlorophenyl)phenyl Phenyl Ketone (1Da)**: yellow oil; IR (neat) 1662, 1282, 759, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17-7.20 (m, 4H), 7.31 (t, 2H, *J* = 7.7 Hz), 7.44-7.52 (m, 4H), 7.58 (t, 1H, *J* = 7.7 Hz), 7.65 (d, 2H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 127.3, 128.2 (2C), 128.4 (2C), 128.8, 129.9 (2C), 130.0, 130.2 (2C), 130.4, 133.1, 133.5, 137.2, 138.6, 138.8, 139.9, 198.4; HRMS (ESI) Calcd for $C_{19}H_{14}ClO$ $[M+H]^+$ = 293.0728, Found = 293.0725.

***o*-(*p*-Chlorophenyl)phenyl *p*-Methylphenyl Ketone (1Db)**: white solid; Mp: 136-140 °C; IR (neat) 1657, 1258, 831, 768, 681 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 7.12 (d, 2H, *J* = 7.9 Hz), 7.17-7.21 (m, 4H), 7.42-7.48 (m, 3H), 7.52-7.59 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.7, 127.3, 128.4 (2C), 128.7, 129.0 (2C), 130.0, 130.1, 130.1 (2C), 130.2, 133.4, 134.6, 138.7, 139.1, 139.7, 144.1, 198.0; HRMS (ESI) Calcd for $C_{20}H_{16}ClO$ $[M+H]^+$ = 307.0884, Found = 307.0885.

***o*-(*p*-Chlorophenyl)phenyl *p*-Methoxyphenyl Ketone (1De)**: yellow oil; IR (neat) 1655, 1254, 1147, 759 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.80 (d, 2H, *J* = 8.8 Hz), 7.18-7.23 (m, 4H), 7.42-7.48 (m, 3H), 7.52-7.58 (m, 1H) , 7.65 (d, 2H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.5 (2C), 127.3, 128.4 (2C), 128.5, 129.9, 130.1, 130.1, 130.1 (2C), 132.3 (2C), 133.4. 138.7, 139.2, 139.5, 163.5, 197.0; HRMS (ESI) Calcd for $C_{20}H_{16}ClO$ $[M+H]^+$ = 307.0884, Found = 307.0885.

***o*-(*p*-Chlorophenyl)phenyl *p*-Fluorophenyl Ketone (1Df)**: white solid; Mp: 104-106 °C; IR (neat) 1656, 1223, 832, 769, 604 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.97 (t, 2H, *J* = 8.6 Hz), 7.15-7.22 (m, 4H), 7.41-7.51 (m, 3H), 7.55-7.62 (m, 1H), 7.64-7.69 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 127.5, 128.5 (2C), 128.7, 130.0, 130.0, 130.1 (2C), 130.6, 132.5 (d, $J_{C\text{-}F}$ = 8.8 Hz, 2C), 133.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 138.5, 138.5, 139.7, 156.5 (d, $J_{C\text{-}F}$ = 242.6 Hz), 196.9; HRMS (ESI) Calcd for $C_{19}H_{13}ClFO$ $[M+H]^+$ = 311.0634, Found = 311.0635.

***p*-Chlorophenyl *o*-(*p*-Chlorophenyl)phenyl Ketone (1Dg)**: white solid; Mp: 98-100 °C; IR (neat) 1659, 1086, 829, 737 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16-7.22 (m, 4H), 7.27 (d, 2H, *J* = 8.6 Hz), 7.44-7.50 (m, 3H), 7.56-7.61 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 127.5, 128.6 (2C), 128.6 (2C), 128.7, 130.0, 130.1 (2C), 130.7, 131.2 (2C), 133.7, 135.5, 138.3, 138.4, 139.6, 139.7, 197.2; HRMS (ESI) Calcd for $C_{19}H_{13}Cl_2O$ $[M+H]^+$ = 327.0338, Found = 327.0336.

***o*-(*m*-Methylphenyl)phenyl Phenyl Ketone (1Ea)**[10]: white solid; Mp: 80-82 °C; IR (neat) 1665, 1280, 754, 694 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 6.95 (d, 1H, *J* = 8.0 Hz), 7.02-7.09 (m, 3H), 7.25-7.29 (m, 2H), 7.38-7.59 (m, 5H), 7.63 (d, 2H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.2, 126.0, 126.9, 128.0 (2C), 128.0 (2C), 128.1, 128.7, 129.8 (2C), 130.0, 130.3, 132.7, 137.4, 137.7, 138.9, 140.0, 141.2, 198.9; HRMS (ESI) Calcd for $C_{20}H_{17}O$ $[M+H]^+$ = 273.1273, Found = 273.1276.

Typical Procedure for Preparation of 6-Arylphenanthridines 3 from Aryl Biaryl Ketones 1: A toluene (1.0 mL) solution of *o*-(*p*-methylphenyl)phenyl phenyl ketone **1Aa** (272.4 mg, 1.0 mmol), TMS_2NH

(419.2 μL, 2.0 mmol), and $Sc(OTf)_3$ (98.5 mg, 0.2 mmol) in a screw-capped tube (30.0 mL) was heated at 90 °C for 15 h. After removal of the solvent by evaporation, I_2 (380.7 mg, 1.5 mmol) and K_2CO_3 (414.6 mg, 3.0 mmol) were added to a mixture of THF and MeOH (1 : 1, 4.0 mL) solution of the residue. The mixture was stirred at 60 °C for 2 h. The reaction mixture was quenched by sat. aq. Na_2SO_3, and extracted with AcOEt (3 × 60.0 mL). The organic layer was washed with brine and dried over Na_2SO_4. After filtration and removal of the solvent, the residue was treated by short column chromatography on silica gel (hexane:AcOEt = 8:1) to give 3-methyl-6-phenylphenanthridine **3Aa** (218.2 mg, 81%).

Phenyl *o*-(*p*-Methylphenyl)phenyl Ketimine (2Aa): white solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 6.94 (d, 2H, *J* = 7.7 Hz), 7.05 (d, 2H, *J* = 8.2 Hz), 7.28 (t, 2H, *J* = 8.2 Hz), 7.45 (t, 2H, *J* = 7.7 Hz), 7.52 (dd, 1H, *J* = 7.7, 1.1 Hz), 7.60 (td, 1H, *J* = 7.7, 1.1 Hz), 7.69-7.75 (m, 3H), 7.91 (dd, 1H, *J* = 7.7, 1.1 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.0, 127.6, 128.6 (2C), 129.0 (2C), 129.1 (2C), 130.5, 130.7, 130.9, 131.3 (2C), 131.4, 133.3, 135.2, 136.1, 137.8, 143.2, 183.8.

3-Methyl-6-phenylphenanthridine (3Aa): Yield: 218.8 mg (81%); yellow solid; Mp: 110-111 °C; IR (neat) 1559, 1444, 1362, 771, 700, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.50-7.60 (m, 5H), 7.71-7.74 (m, 2H), 7.84 (t, 1H, *J* = 8.4 Hz), 8.05 (s, 1H), 8.09 (d, 1H, *J* = 8.4 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.67 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 121.3, 121.6, 121.9, 124.8, 126.6, 128.3 (2C), 128.5, 128.6, 128.8, 129.6 (2C), 129.8, 130.4, 133.4, 138.9, 139.8, 143.8, 161.2; HRMS (ESI) Calcd for $C_{20}H_{16}N$ $[M+H]^+$ = 270.1277, Found = 270.1274.

3-Methyl-6-(4'-methylphenyl)phenanthridine (3Ab): Yield: 198.5 mg (70%); white solid; Mp: 90-91 °C; IR (neat) 1482, 1360, 1325, 820, 759, 726 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 2.60 (s, 3H), 7.36 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 1H, *J* = 8.8 Hz), 7.57 (t, 1H, *J* = 8.0 Hz), 7.63 (d, 2H, *J* = 8.4 Hz), 7.83 (t, 1H, *J* = 8.0 Hz), 8.03 (s, 1H), 8.12 (d, 1H, *J* = 8.4 Hz), 8.49 (d, 1H, *J* = 8.4 Hz), 8.66 (d, 1H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.3, 21.5, 121.3, 121.6, 121.9, 124.9, 126.5, 128.5, 128.9, 129.0 (2C), 129.6 (2C), 129.8, 130.3, 133.4, 137.0, 138.4, 138.8, 143.9, 161.2; HRMS (ESI) Calcd for $C_{21}H_{18}N$ $[M+H]^+$ = 284.1434, Found = 284.1429.

3-Methyl-6-(3'-methylphenyl)phenanthridine (3Ac): Yield: 215.2 mg (76%); white solid; Mp: 65-68 °C; IR (neat) 1561, 1480, 1361, 768, 729, 709 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 2.60 (s, 3H), 7.33 (d, 1H, *J* = 7.6 Hz), 7.43 (t, 1H, *J* = 7.6 Hz), 7.49-7.60 (m, 4H), 7.83 (t, 1H, *J* = 7.6 Hz), 8.05 (s, 1H), 8.09 (d, 1H, *J* = 8.3 Hz), 8.50 (d, 1H, *J* = 8.3 Hz), 8.66 (d, 1H, *J* = 8.3 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 21.5, 121.3, 121.6, 121.8, 124.9, 126.5, 126.8, 128.0, 128.5, 128.8, 129.3, 129.8, 130.2, 130.3, 133.3, 138.0, 138.8, 139.7, 143.8, 161.3; HRMS (ESI) Calcd for $C_{21}H_{18}N$ $[M+H]^+$ = 284.1434, Found = 284.1429.

3-Methyl-6-(2'-methylphenyl)phenanthridine (3Ad): Yield: 132.0 mg (47%); yellow solid; Mp: 65-66 °C; IR (neat) 1479, 1362, 1328, 768, 745, 727 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3H), 2.61 (s, 3H), 7.33-7.44 (m, 4H), 7.51-7.55 (m, 2H), 7.68 (d, 1H, *J* = 7.7 Hz), 7.83 (t, 1H, *J* = 7.7 Hz), 8.04 (s, 1H), 8.53 (d, 1H, *J* = 8.4 Hz), 8.66 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 19.8, 21.6, 121.4, 121.8, 121.9, 125.5, 125.7, 126.8, 128.5, 128.6, 128.7, 129.2, 129.8, 130.3, 130.5, 133.0, 136.4, 139.0, 139.3, 143.9, 161.9; HRMS (ESI) Calcd for $C_{21}H_{18}N$ $[M+H]^+$ = 284.1434, Found = 284.1432.

6-(4'-Methoxyphenyl)-3-methylphenanthridine (3Ae): Yield: 217.3 mg (72%); yellow solid; Mp: 154-155 °C; IR (neat) 1249, 1173, 1021, 835, 730, 506 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3H), 3.92 (s, 3H), 7.09 (d, 2H, *J* = 8.8 Hz), 7.51 (d, 1H, *J* = 8.8 Hz), 7.59 (t, 1H, *J* = 8.0 Hz), 7.70 (d, 2H, *J* = 8.8 Hz), 7.84 (t, 1H, *J* = 8.0 Hz), 8.03 (s, 1H), 8.14 (d, 1H, *J* = 8.0 Hz), 8.49 (d, 1H, *J* = 8.8 Hz), 8.66 (d, 1H, *J* = 8.0 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 55.4, 113.8 (2C), 121.2, 121.7, 122.0, 124.9, 126.5, 128.4, 128.8, 129.7, 130.3, 131.1 (2C), 132.3, 133.5, 138.9, 144.1, 160.0, 160.8; HRMS (ESI) Calcd for $C_{21}H_{18}NO$ $[M+H]^+$ = 300.1383, Found = 300.1383.

6-(4'-Fluorophenyl)-3-methylphenanthridine (3Af): Yield: 221.2 mg (77%); white solid; Mp: 112-115 °C; IR (neat) 1513, 1220, 1149, 759, 726, 672 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.25 (t, 2H, *J* = 8.5 Hz), 7.53 (d, 1H, *J* = 6.7 Hz), 7.60 (t, 1H, *J* = 6.7 Hz), 7.70-7.75 (m, 2H), 7.85 (t, 1H, *J* = 7.2 Hz), 8.03 (s, 1H), 8.05 (d, 1H, *J* = 8.3 Hz), 8.51 (d, 1H, *J* = 8.6 Hz), 8.67 (d, 1H, *J* = 8.6 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 115.4 (d, J_{C-F} = 21.6 Hz, 2C), 121.3, 121.7, 122.1, 124.8, 126.7, 128.5, 128.8, 129.8, 130.5, 131.6 (d, J_{C-F} = 8.5 Hz, 2C), 133.5, 135.9 (d, J_{C-F} = 2.9 Hz), 139.1, 143.5, 160.1, 163.1 (d, J_{C-F} = 252.8 Hz); HRMS (ESI) Calcd for $C_{20}H_{15}FN$ $[M+H]^+$ = 288.1183, Found = 288.1178.

6-(4'-Chlorophenyl)-3-methylphenanthridine (3Ag): Yield: 211.7 mg (70%); yellow solid; Mp: 170-171 °C; IR (neat) 1479, 1361, 827, 759, 725 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3H), 7.52-7.61 (m, 4H), 7.66-7.69 (m, 2H), 7.82-7.86 (m, 1H), 8.03 (d, 2H, *J* = 9.6 Hz), 8.50 (d, 1H, *J* = 8.8 Hz), 8.66 (d, 1H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 121.3, 121.7, 122.0, 124.6, 126.7, 128.3, 128.6 (2C), 128.8, 129.8, 130.5, 131.1 (2C), 133.4 134.7, 138.2, 139.1, 143.7, 159.8; HRMS (ESI) Calcd for $C_{20}H_{15}ClN$ $[M+H]^+$ = 304.0888, Found = 304.0888.

6-(4'-Bromophenyl)-3-methylphenanthridine (3Ah): Yield: 271.6 mg (78%); yellow solid; Mp: 167-169 °C; IR (neat) 1508, 1227, 833, 724 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.52-7.64 (m, 4H), 7.70 (d, 2H, *J* = 8.6 Hz), 7.85 (t, 1H, *J* = 8.6 Hz), 8.03 (s, 1H), 8.04 (d, 1H, *J* = 8.4 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.67 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.6, 121.4, 121.8, 122.1, 123.0, 124.6, 126.8, 128.4, 128.9, 129.8, 130.6, 131.4 (2C), 131.6 (2C), 133.5, 138.7, 139.2, 143.8, 159.9; HRMS (ESI) Calcd for $C_{20}H_{15}BrN$ $[M+H]^+$ = 348.0383, Found = 348.0378.

3-Methyl-6-(naphthalen-2'-yl)phenanthridine (3Ai): Yield: 255.5 mg (80%); white solid; Mp: 122-125 °C; IR (neat) 1478, 1012, 824, 759, 725 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3H), 7.51-7.60 (m, 4H), 7.84 (d, 1H, *J* = 8.1 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 7.95-7.97 (m, 2H), 8.03 (d, 1H, *J* = 8.4 Hz), 8.08 (s, 1H), 8.14 (d, 1H, *J* = 8.2 Hz), 8.22 (s, 1H), 8.53 (d, 1H, *J* = 8.4 Hz), 8.69 (d, 1H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ =21.5, 121.3, 121.6, 121.9, 124.9, 126.3, 126.4, 126.5, 127.3, 127.7, 127.9, 128.4, 128.6, 128.7, 129.1, 129.8, 130.3, 133.1, 133.2, 133.4, 137.2, 138.9, 143.9, 161.0; HRMS (ESI) Calcd for $C_{24}H_{18}N$ $[M+H]^+$ = 320.1434, Found = 320.1429.

6-(Benzo[b]thiophen-2'-yl)-3-methylphenanthridine (3Aj): Yield: 198.5 mg (61%); white solid; Mp: 118-120 °C; IR (neat) 1484, 861, 763, 679 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.39-7.45 (m, 2H), 7.53 (d, 1H, *J* = 8.3 Hz), 7.69 (t, 1H, *J* = 7.6 Hz), 7.86-7.97 (m, 4H), 8.05 (s, 1H), 8.49 (d, 1H, *J* = 8.3 Hz), 8.64 (d, 1H, *J* = 8.3 Hz) , 8.68 (d, 1H, *J* = 7.6 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 121.2, 121.6, 122.1, 122.2, 124.2, 124.3, 124.4, 125.0, 125.8, 127.0, 127.8, 129.0, 129.8, 130.5, 133.5, 139.0, 140.0, 140.6, 142.8, 143.7, 153.8; HRMS (ESI) Calcd for $C_{22}H_{16}NS$ $[M+H]^+$ = 326.0998, Found = 326.0993.

6-(Benzofuran-2'-yl)-3-methylphenanthridine (3Ak): Yield: 216.6 mg (70%); white solid; Mp: 125-126 °C; IR (neat) 1480, 1154, 837, 748, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3H), 7.33 (t, 1H, *J* = 7.7 Hz), 7.41 (t, 1H, *J* = 7.7 Hz), 7.54 (d, 1H, *J* = 8.5 Hz), 7.57 (s, 1H), 7.69-7.75 (m, 3H), 7.89 (t, 1H, *J* = 8.5 Hz), 8.09 (s, 1H), 8.51 (d, 1H, *J* = 8.5 Hz), 8.69 (d, 1H, *J* = 8.5 Hz) , 8.86 (d, 1H, *J* = 7.7 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 109.4, 111.9, 121.6, 121.7 (2C), 122.1, 123.3, 124.2, 125.3, 127.2, 127.8, 128.3, 129.3, 130.0, 130.7, 133.7, 139.1, 143.8, 149.8, 155.0, 155.5; HRMS (ESI) Calcd for $C_{22}H_{16}NO$ $[M+H]^+$ = 310.1226, Found = 310.1223.

6-(4'-*tert*-Butylphenyl)-3-methylphenanthridine (3Al): Yield: 266.9 mg (82%); white solid; Mp: 70-72 °C; IR (neat) 1482, 1361, 769, 608 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9H), 2.60 (s, 3H), 7.51 (d, 1H, *J* = 8.8 Hz), 7.56-7.60 (m, 3H), 7.68 (d, 2H, *J* = 8.4 Hz), 7.84 (t, 1H, *J* = 7.7 Hz), 8.04 (s, 1H), 8.17 (d, 1H, *J* = 8.8 Hz), 8.50 (d, 1H, *J* = 8.2 Hz), 8.66 (d, 1H, *J* = 8.2 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.5, 31.3 (3C), 34.6, 121.2, 121.6, 121.8, 124.8, 125.3 (2C), 126.4, 128.4, 128.9, 129.4 (2C), 129.8, 130.2, 133.3, 136.9, 138.7, 143.9, 151.5, 161.1; HRMS (ESI) Calcd for $C_{24}H_{24}N$ $[M+H]^+$ = 326.1903, Found = 326.1903.

6-Phenylphenanthridine (3Ba) Yield: 208.4 mg (92%); yellow solid; Mp: 99-101 °C; IR (neat) 1360, 1137, 960, 1758, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51-7.66 (m, 4H), 7.68-7.79 (m, 4H), 7.87 (td, 1H, *J* = 7.6, 1.4 Hz), 8.11 (d, 1H, *J* = 8.4Hz), 8.25 (d, 1H, *J* = 8.4, 1.4 Hz), 8.64 (dd, 1H, *J* = 8.4, 1.4 Hz), 8.72 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 121.8, 122.1, 123.6, 125.1, 126.8, 127.0, 128.3 (2C), 128.6, 128.7, 128.8, 129.6 (2C), 130.2, 130.4, 133.3, 139.7, 143.7, 161.1;HRMS (ESI) Calcd for $C_{19}H_{14}N$ $[M+H]^+$ = 256.1121, Found = 256.1121.

6-(4'-Methylphenyl)phenanthridine (3Bb) Yield: 183.5 mg (68%); white solid; Mp: 80-82 °C; IR (neat) 1357, 960, 822, 754, 726 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.48 (s, 3H), 7.37 (d, 2H, *J* = 8.4 Hz), 7.60-7.71 (m, 4H), 7.75 (td, 1H, *J* = 7.6, 1.4 Hz), 7.86 (td, 1H, *J* = 7.6, 1.1 Hz), 8.14 (d, 1H, *J* = 8.4 Hz), 8.24 (dd, 1H, *J* = 8.4, 1.1 Hz), 8.62 (dd, 1H, *J* = 8.4, 1.4 Hz), 8.71 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.3, 121.8, 122.1, 123.6, 125.2, 126.7, 127.0, 128.7, 128.9, 129.0 (2C), 129.6 (2C), 130.2, 130.4, 133.3, 136.9, 138.5, 143.7, 161.2; HRMS (ESI) Calcd for $C_{20}H_{16}N$ $[M+H]^+$ = 270.1277, Found = 270.1273.

6-(4'-Methoxyphenyl)phenanthridine (3Be): Yield: 185.6 mg (72%); yellow solid; Mp: 144-146 °C; IR (neat) 1509, 1247, 1171, 1028, 828, 759 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 7.09 (d, 2H, *J* = 8.4 Hz), 7.60-7.77 (m, 5H), 7.82 (t, 1H, *J* = 8.4 Hz), 8.16 (d, 1H, *J* = 8.4 Hz), 8.23 (d, 1H, *J* = 8.4 Hz), 8.60 (d, 1H, *J* = 8.4 Hz), 8.70 (d, 1H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.8 (2C), 121.8, 122.1, 123.5, 125.2, 126.6, 127.0, 128.7, 128.8, 130.2, 130.3, 131.1 (2C), 132.2, 133.4, 143.8, 160.3, 160.8; HRMS (ESI) Calcd for $C_{20}H_{16}NO$ $[M+H]^+$ = 286.1226, Found = 286.1227.

6-(4'-Fluorophenyl)phenanthridine (3Bf): Yield: 191.3 mg (70%); white solid; Mp: 118-120 °C; IR (neat) 1508, 1217, 834, 751 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22-7.30 (m, 2H), 7.64 (t, 1H, *J* = 8.1 Hz), 7.69-7.80 (m, 4H), 7.88 (t, 1H, *J* = 8.3 Hz), 8.08 (d, 1H, *J* = 8.3 Hz), 8.23 (d, 1H, *J* = 9.4

Hz), 8.64 (d, 1H, *J* = 8.1 Hz), 8.73 (d, 1H, *J* = 8.3 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 115.3 (d, J_{C-F} = 21.6 Hz, 2C), 121.8, 122.2, 123.6, 125.0, 126.9, 127.1, 128.4, 128.8, 130.2, 130.5, 131.5 (d, J_{C-F} = 8.5 Hz, 2C), 133.3, 135.7 (d, J_{C-F} = 2.8 Hz), 143.6, 160.0, 163.0 (d, J_{C-F} = 248.1 Hz); HRMS (ESI) Calcd for $C_{19}H_{13}FN$ $[M+H]^+$ = 274.1027, Found = 274.1023.

6-(4'-Chlorophenyl)phenanthridine (3Bg): Yield: 227.5 mg (79%); yellow solid; Mp: 151-152 °C; IR (neat) 1359, 1089, 1014, 829, 752, 722 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51-7.56 (m, 2H), 7.62-7.79 (m, 5H), 7.88 (t, 1H, *J* = 7.6 Hz), 8.07 (d, 1H, *J* = 8.8 Hz), 8.23 (d, 1H, *J* = 8.4 Hz), 8.63 (d, 1H, *J* = 8.4 Hz), 8.72 (d, 1H, *J* = 8.8 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 122.0, 122.3, 123.7, 124.4, 127.1, 127.4, 128.4, 128.6 (2C), 128.9, 130.3, 130.6, 131.1 (2C), 133.4, 134.8, 138.1, 143.6, 159.9; HRMS (ESI) Calcd for $C_{19}H_{13}ClN$ $[M+H]^+$ = 290.0731, Found = 290.0728.

6-(Naphthalen-2'-yl)phenanthridine (3Bi): Yield: 271.8 mg (89%); white solid; Mp: 148-151 °C; IR (neat) 758, 741, 724, 681 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55-7.65 (m, 3H), 7.72 (t, 1H, *J* = 7.9 Hz), 7.79 (t, 1H, *J* = 7.9 Hz), 7.86-7.91 (m, 2H), 7.95-7.97 (m, 2H), 8.04 (d, 1H, *J* = 8.6 Hz), 8.16 (d, 1H, *J* = 8.2 Hz), 8.24 (s, 1H), 8.28 (d, 1H, *J* = 7.9 Hz), 8.66 (d, 1H, *J* = 7.9 Hz), 8.74 (d, 1H, *J* = 8.2 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 122.0, 122.2, 123.7, 125.3, 126.4, 126.6, 127.0, 127.2, 127.3, 127.8, 128.1, 128.5, 128.9, 128.9, 129.2, 130.3, 130.6, 133.2, 133.3, 133.5, 137.2, 143.8, 161.2; HRMS (ESI) Calcd for $C_{23}H_{16}N$ $[M+H]^+$ = 306.1277, Found = 306.1274.

6-(Benzo[b]thiophen-2'-yl)phenanthridine (3Bj): Yield: 205.5 mg (66%); orange solid; Mp: 153-156 °C; IR (neat) 1356, 907, 765, 742, 721 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41-7.46 (m, 2H), 7.69-7.80 (m, 3H), 7.87 (s, 1H), 7.90-7.97 (m, 3H), 8.25 (d, 1H, *J* = 8.1 Hz), 8.62 (d, 1H, *J* = 8.1 Hz), 8.67 (d, 1H, *J* = 8.1 Hz), 8.74 (d, 1H, *J* = 8.3 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 121.9, 122.3, 122.4, 123.6, 124.3, 124.5, 124.8, 125.2, 126.0, 127.4, 127.6, 128.0, 129.0, 130.4, 130.8, 133.6, 140.0, 140.7, 142.6, 143.6, 154.1; HRMS (ESI) Calcd for $C_{21}H_{14}NS$ $[M+H]^+$ = 312.0841, Found = 312.0837.

6-(Benzofuran-2'-yl)phenanthridine (3Bk): Yield: 197.9 mg (67%); yellow solid; Mp: 138-140 °C; IR (neat) 1314, 745, 685 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, 1H, *J* = 7.7 Hz), 7.42 (t, 1H, *J* = 7.7 Hz), 7.59 (s, 1H), 7.70-7.79 (m, 5H), 7.92 (t, 1H, *J* = 7.7 Hz), 8.29 (d, 1H, *J* = 9.1 Hz), 8.63 (d, 1H, *J* = 9.1 Hz) , 8.74 (d, 1H, *J* = 7.7 Hz), 8.89 (d, 1H, *J* = 9.1 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 109.6, 111.9, 121.8, 122.0, 122.3, 123.3, 123.9, 124.5, 125.4, 127.5, 127.7, 127.9, 128.3, 129.0, 130.5, 130.7, 133.6, 144.0, 149.8, 154.8, 155.5; HRMS (ESI) Calcd for $C_{21}H_{14}NO$ $[M+H]^+$ = 296.1070, Found = 296.1067.

3-Methoxy-6-phenylphenanthridine (3Ca): Yield: 185.5 mg (65%); yellow solid; Mp: 107-108 °C; IR (neat) 1617, 1203, 1035, 768, 706, 673 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3H), 7.32 (dd, 1H, *J* = 9.2, 2.8 Hz), 7.50-7.59 (m, 4H), 7.66 (d, 1H, *J* = 2.8 Hz), 7.71-7.74 (m, 2H), 7.81 (t, 1H, *J* = 7.8 Hz), 8.06 (d, 1H, *J* = 8.4 Hz), 8.50 (d, 1H, *J* = 9.2 Hz), 8.60 (d, 1H, *J* = 8.0 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.3, 109.7, 117.5, 117.9, 121.4, 122.9, 124.0, 125.7, 128.2 (2C), 128.4, 128.6, 129.5 (2C), 130.3, 133.6, 139.6, 145.1, 160.0, 161.4; HRMS (ESI) Calcd for $C_{20}H_{16}NO$ $[M+H]^+$ = 286.1226, Found = 286.1225.

3-Methoxy-6-(4'-methylphenyl)phenanthridine (3Cb): Yield: 209.6 mg (70%); white solid; Mp: 118-120 °C; IR (neat) 1203, 1039, 821, 760, 721, 599cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 3.98 (s, 3H), 7.32 (dd, 1H, *J* = 9.2, 2.8 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 7.54 (t, 1H, *J* = 8.0 Hz), 7.61-7.65 (m, 3H), 7.81 (t, 1H, *J* = 8.0 Hz), 8.10 (d, 1H, *J* = 8.4 Hz), 8.50 (d, 1H, *J* = 9.0 Hz), 8.59 (d, 1H, *J* = 8.0 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 21.2, 55.3, 109.7, 117.5, 117.7, 121.4, 122.9, 124.1, 125.7, 128.7, 128.9 (2C), 129.4 (2C), 130.2, 133.4, 136.8, 138.2, 145.2, 159.9, 161.5; HRMS (ESI) Calcd for $C_{21}H_{18}NO$ $[M+H]^+$ = 300.1383, Found = 300.1379.

3-Methoxy-6-(4'-methoxyphenyl)phenanthridine (3Ce): Yield: 220.8 mg (70%); white solid; Mp: 141-143 °C; IR (neat) 1607, 1244, 1027, 832, 766 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 3.98 (s, 3H), 7.07-7.11 (m, 2H), 7.31 (dd, 1H, *J* = 8.4, 2.8 Hz), 7.55 (t, 1H, *J* = 7.8 Hz), 7.64 (d, 1H, *J* = 2.4 Hz), 7.68-7.71 (m, 2H), 7.82 (t, 1H, *J* = 7.8 Hz), 8.13 (d, 1H, *J* = 8.4 Hz), 8.50 (d, 1H, *J* = 8.4 Hz), 8.59 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.1, 55.2, 109.6, 113.6 (2C), 117.3, 117.6, 121.4, 122.8, 124.5, 125.6, 128.6, 130.1, 130.9 (2C), 132.1, 133.4, 145.2, 159.8, 159.9, 161.0; HRMS (ESI) Calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$ = 316.1332, Found = 316.1331.

6-(4'-Fluorophenyl)-3-methoxyphenanthridine (3Cf): Yield: 197.2 mg (65%); white solid; Mp: 117-120 °C; IR (neat) 1510, 1218, 1149, 759, 672 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H), 7.23-7.29 (m, 2H), 7.34 (dd, 1H, *J* = 9.1, 2.7 Hz), 7.56 (t, 1H, *J* = 7.6 Hz), 7.64 (d, 1H, *J* = 2.7 Hz), 7.70-7.75 (m, 2H), 7.84 (t, 1H, *J* = 7.6 Hz), 8.04 (d, 1H, *J* = 8.4 Hz), 8.51 (d, 1H, *J* = 9.1 Hz), 8.61 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.6, 109.8, 115.4 (d, J_{C-F} = 21.6 Hz, 2C), 117.8, 118.3, 121.8, 123.2, 124.2, 126.1, 128.6, 130.7, 131.5 (d, J_{C-F} = 8.5 Hz, 2C), 133.7, 135.9 (d, J_{C-F} = 3.8 Hz), 145.3, 160.3, 160.6, 163.1 (d, J_{C-F} = 248.1 Hz); HRMS (ESI) Calcd for $C_{20}H_{15}FNO$ $[M+H]^+$ = 304.1132, Found = 304.1128.

6-(4'-Chlorophenyl)-3-methoxyphenanthridine (3Cg): Yield: 223.9 mg (70%); white solid; Mp: 143-145 °C; IR (neat) 1617, 1204, 1044, 757, 719, 502 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3H), 7.33 (dd, 1H, *J* = 8.4, 2.8 Hz), 7.52-7.69 (m, 6H), 7.84 (t, 1H, *J* = 7.2 Hz), 8.02 (d, 1H, *J* = 8.4 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.61 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.5, 110.0, 117.7, 118.3, 121.7, 123.1, 123.9, 126.1, 128.4 , 128.6 (2C), 130.7, 131.0 (2C), 133.6, 134.8, 138.2, 145.2, 160.2, 160.3; HRMS (ESI) Calcd for $C_{20}H_{15}ClNO[M+H]^+$ = 320.0837, Found = 320.0834.

3-Chloro-6-phenylphenanthridine (3Da): Yield: 173.9 mg (60%); yellow solid; Mp: 132-134 °C; IR (neat) 1443, 1360, 1074, 765, 668 cm^{-1};^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51-7.65 (m, 5H), 7.70-7.75 (m, 2H), 7.87 (t, 1H, *J* = 8.8 Hz), 8.12 (d, 1H, *J* = 9.2 Hz). 8.24 (d, 1H, *J* = 2.4 Hz), 8.53 (d, 1H, *J* = 9.2 Hz), 8.64 (d, 1H, *J* = 8.8 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 122.1, 122.2, 123.3, 125.1, 127.4 (2C), 128.4 (2C), 128.9, 129.0, 129.5, 129.6 (2C), 130.9, 133.0, 134.4, 139.3, 144.4, 162.4; HRMS (ESI) Calcd for $C_{19}H_{13}ClN$ $[M+H]^+$ = 290.0731, Found = 290.0730.

3-Chloro-6-(4'-methylphenyl)phenanthridine (3Db): Yield: 212.7 mg (70%); white solid; Mp: 128-129 °C; IR (neat) 1078, 905, 819, 746, 719, 671 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 7.37 (d, 2H, *J* = 8.0 Hz), 7.65-7.10 (m, 4H), 7.86 (t, 1H, *J* = 8.0 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 8.22 (d, 1H, *J* = 2.0 Hz), 8.52 (d, 1H, *J* = 8.8 Hz), 8.63 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 21.4, 122.0, 122.1, 123.2, 125.1, 127.2, 127.3, 129.1 (3C), 129.4, 129.6 (2C), 130.8, 133.0, 134.3, 136.4, 138.9, 144.4, 162.4; HRMS (ESI) Calcd for $C_{20}H_{15}ClN$ $[M+H]^+$ = 304.0888, Found = 304.0887.

3-Chloro-6-(4'-methoxyphenyl)phenanthridine (3De): Yield: 275.0 mg (86%); white solid; Mp: 133-135 °C; IR (neat) 1360, 1248, 1031, 828, 761, 598 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 7.10 (d, 2H, *J* = 8.8 Hz), 7.61-7.72 (m, 4H), 7.88 (t, 1H, *J* = 8.4 Hz), 8.18 (d, 1H, *J* = 8.4 Hz), 8.21 (d, 1H, *J* = 2.4 Hz), 8.52 (d, 1H, *J* = 8.8 Hz), 8.63 (d, 1H, *J* = 8.4 Hz), $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.3, 113.8 (2C), 121.9, 122.0, 123.2, 125.1, 127.1, 127.2, 129.0, 129.3, 130.7, 131.2 (2C), 131.7, 132.9, 134.2, 144.4, 160.2, 161.9; HRMS (ESI) Calcd for $C_{20}H_{15}ClNO$ $[M+H]^+$ = 320.0837, Found = 320.0836.

3-Chloro-6-(4'-fluorophenyl)phenanthridine (3Df): Yield: 203.1 mg (66%); white solid; Mp: 172-175 °C; IR (neat) 1502, 1208, 826, 736 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24-7.30 (m, 2H), 7.63-7.67 (m, 2H), 7.70-7.75 (m, 2H), 7.89 (t, 1H, *J* = 7.7 Hz), 8.09 (d, 1H, *J* = 8.4 Hz), 8.22 (d, 1H, *J* = 2.0 Hz), 8.53 (d, 1H, *J* = 8.4 Hz), 8.65 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 115.5 (d, J_{C-F} = 21.6 Hz, 2C), 122.2, 122.2, 123.4, 125.0, 127.5, 127.6, 128.8, 129.5, 131.1, 131.6 (d, J_{C-F} = 8.5 Hz, 2C), 133.1, 134.5, 135.4 (d, J_{C-F} = 2.8 Hz), 144.4, 161.3, 163.3 (d, J_{C-F} = 249.0 Hz); HRMS (ESI) Calcd for $C_{19}H_{12}ClFN$ $[M+H]^+$ = 308.0637, Found = 308.0633.

3-Chloro-6-(4'-chlorophenyl)phenanthridine (3Dg): Yield: 239.9 mg (74%); white solid; Mp: 210-212 °C; IR (neat) 1359, 1078, 831, 765, 722 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.72 (d, 2H, *J* = 8.4 Hz), 7.83-7.93 (m, 4H), 8.13 (d, 1H, *J* = 8.4 Hz), 8.19 (t, 1H, *J* = 8.4 Hz), 8.26 (d, 1H, *J* = 2.0 Hz), 8.97 (d, 1H, *J* = 9.2 Hz), 9.02 (d, 1H, *J* = 8.4Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$ and CF_3CO_2H): δ = 121.1, 123.1, 123.2, 123.3, 124.6, 127.4, 130.0 (2C), 130.7, 131.3 (2C), 131.8, 132.2, 133.3, 135.8, 138.1, 139.0, 140.4, 160.6; HRMS (ESI) Calcd for $C_{19}H_{12}Cl_2N$ $[M+H]^+$ = 324.0341, Found = 324.0340.

4-Methyl-6-phenylphenanthridine (3Ea). Yield: 221.1 mg (78%); pale yellow solid; Mp: 108−110 °C; IR (neat) 1566, 1466, 1360, 744, 687, 667 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (s. 3H), 7.50-7.62 (m, 6 H), 7.80-7.84 (m, 3 H), 8.18 (d, 1H, *J* = 8.4 Hz), 8.46 (d, 1H, *J* = 8.0 Hz), 8.69 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 18.4, 119.6, 122.4, 123.4, 124.7, 126.4, 126.8, 128.2 (2C), 128.5, 128.6, 129.4, 130.1, 130.2 (2C), 133.8, 138.2, 140.2, 142.5, 159.2; HRMS (ESI) Calcd for $C_{20}H_{16}N$ [M + H]+ = 270.1277, Found = 270.1278.

Transformation of 6-(4'-Bromophenyl)-3-methylphenanthridine 3Ah (I): *n*-BuLi (1.55 M solution in hexane, 0.71 mL, 1.1 mmol) was added dropwise to a solution of **3Ah** (348.2 mg, 1.0 mmol) in THF (6.0 mL) at -50 °C under Ar atomosphere. After 30 min, DMF (125.4 μL, 1.5 mmol) was added, the obtained mixture was gradually warmed to room temperature, and then the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by sat. aq. NH_4Cl and was extracted with AcOEt (3 × 60.0 mL). The organic layer was washed with brine and dried over Na_2SO_4. After filtration and removal of the solvent, the residue was purified by short column chromatography on silica gel (hexane:AcOEt = 4:1) to give 6-(4'-formylphenyl)-3-methylphenanthridine **4A-1** (202.2 mg, 68%).

6-(4'-Formylphenyl)-3-methylphenanthridine (4A-1): Yield: 202.1 mg (68%); white solid; Mp: 173-175 °C; IR (neat) 1697, 1606, 1209, 830, 762 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3H), 7.54-7.63 (m, 2H),

7.88 (t, 1H, *J* = 8.2 Hz), 7.92 (d, 2H, *J* = 8.2 Hz), 8.00 (d, 1H, *J* = 7.9 Hz), 8.04 (s, 1H), 8.09 (d, 2H, *J* = 8.2 Hz), 8.53 (d, 1H, *J* = 8.2 Hz), 8.70 (d, 1H, *J* = 7.9 Hz), 10.17 (s, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ = 21.7, 121.6, 121.9, 122.3, 124.6, 127.0, 128.3, 129.3, 129.9 (2C), 130.0, 130.6 (2C), 130.9, 133.7, 136.3, 139.4, 143.9, 146.0, 159.8, 192.2; HRMS (ESI) Calcd for $C_{21}H_{16}NO$ $[M+H]^+$ = 298.1227, Found = 298.1224.

Transformation of 6-(4'-Bromophenyl)-3-methylphenanthridine 3Ah (II): To a mixture of **3Ah** (348.2 mg, 1.0 mmol), K_2CO_3 (3.0 mmol, 207.4 mg), CuI (0.04 mmol, 38.4 mg), and DMEDA (0.080 mmol, 40 μL) in toluene (12.0 mL) was added *p*-methoxybenzamide (2.4 mmol, 181.4 mg) under argon atmosphere. The obtained mixture was stirred at 130 °C for 18 h. Then, sat. aq. $NaHCO_3$ (10.0 mL) was added to the reaction mixture, and the product was extracted with $CHCl_3$ (30.0 mL × 3). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : $CHCl_3$ = 1 : 1) to give *N*-[4'-(3"-methylphenanthridin-6"-yl)phenyl]-4-methoxybenzamide **4A-2** (251.1 mg, 60% yield).

***N*-[4'-(3"-Methylphenanthridin-6"-yl)phenyl]-4-methoxybenzamide (4A-2)**: Yield: 251.1 mg (60%); orange solid; Mp: 228-230 °C; IR (neat) 3274, 1645, 1606, 1253, 766, 611 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 3.90 (s, 3H), 7.01 (d, 2H, *J* = 8.8 Hz), 7.52 (d, 1H, *J* = 8.4 Hz), 7.60 (t, 1H, *J* = 7.3 Hz), 7.76-7.92 (m, 7H), 8.04 (s, 1H), 8.15 (d, 1H, *J* = 8.2 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.67 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ = 21.6, 35.5, 114.0 (2C), 119.9 (2C), 121.4, 121.7, 122.0, 124.9, 126.7, 127.0, 128.6, 128.8, 129.0 (2C), 129.8, 130.5, 130.6 (2C), 133.5, 135.8, 138.6, 139.0, 143.9, 160.6, 162.6, 165.3; HRMS (ESI) Calcd for $C_{28}H_{23}N_2O_2$ $[M+H]^+$ = 419.1754, Found = 419.1753.

Transformation of 6-(4'-Bromophenyl)-3-methylphenanthridine 3Ah (III): To a mixture of **3Ah** (348.2 mg, 1.0 mmol) and phenylboronic acid (146.4 mg, 1.2 mmol) in DMF (10.0 mL) was added $PdCl_2(PPh_3)_2$ (280.8 mg, 0.04 mmol) under argon atmosphere. The obtained mixture was stirred at room temperature for 30 min. Then, K_2CO_3 (138.2 mg, 1.0 mmol) in H_2O (2 mL) was added to the mixture, and the obtained mixture was stirred at 70 °C for 5.5. h. Then, water (20.0 mL) was added to the reaction mixture, and the product was extracted with a mixture of hexane and AcOEt (4 : 1, 30.0 mL × 3). The organic layer was washed with brine (30 mL × 2) and dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane/EtOAc = 10:1) on silica gel to give 6-(*p*-biphenyl)-3-methylphenanthridine **4A-3** (317.8 mg, 92% yield).

6-(*p*-Biphenyl)-3-methylphenanthridine (4A-3): Yield: 317.8 mg (92%); yellow solid; Mp: 164-164 °C; IR (neat) 1482, 1361, 847, 758, 727, 687 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.40 (t, 1H, *J* = 7.5 Hz), 7.48-7.55 (m, 3H), 7.62 (t, 1H, *J* = 7.5 Hz), 7.71 (d, 2H, *J* = 7.5 Hz), 7.78-7.88 (m, 5H), 8.10 (s, 1H), 8.19 (d, 1H, *J* = 8.2 Hz), 8.52 (d, 1H, *J* = 8.2 Hz), 8.69 (d, 1H, *J* = 8.2 Hz); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ = 21.5, 121.4, 121.7, 122.0, 124.9, 126.6, 127.1 (2C), 127.2 (2C), 127.5, 128.7, 128.8 (2C), 129.8, 130.2 (2C), 130.5, 132.1, 133.5, 138.8, 139.0, 140.8, 141.5, 143.9, 160.8; HRMS (ESI) Calcd for $C_{26}H_{20}N$ $[M+H]^+$ = 346.1590, Found = 346.1588.

Transformation of 6-(4'-Bromophenyl)-3-methylphenanthridine 3Ah (IV): To a mixture of **3Ah** (348.2 mg, 1.0 mmol), ethynylbenzene (1.5 mmol, 165.0 μL), and CuI (72.0 mg, 0.04 mmol) were added $PdCl_2(PPh_3)_2$ (280.8 mg, 0.04 mmol), DMF (10.0 mL), and Et_3N (2.0 mL) under argon atmosphere. The obtained mixture was stirred at 60 °C for 6 h. Then, water (20.0 mL) was added to the reaction mixture, and the product was extracted with a mixture of hexane and AcOEt (4 : 1, 30.0 mL × 3). The organic layer was washed with brine (30 mL × 2) and dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : EtOAc = 10 : 1) to give 3-methyl-6-[(*p*-phenylethynyl)phenyl]phenanthridine **4A-4** (344.9 mg, 87% yield).

3-Methyl-6-[(*p*-phenylethynyl)phenyl]phenanthridine (4A-4): Yield: 321.4 mg (87%); yellow solid; Mp: 132-134 °C; IR (neat) 1359, 1327, 756, 671, 604 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.34-7.41 (m, 3H), 7.54 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.58-7.62 (m, 3H), 7.71-7.77 (m, 4H), 7.85 (td, 1H, *J* = 7.7, 1.8 Hz), 8.05 (s, 1H), 8.08 (d, 1H, *J* = 7.7 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.67 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ = 21.6, 89.2, 90.4, 121.4, 121.7, 122.1, 123.1, 123.6, 124.7, 126.7, 128.4, 128.4 (2C), 128.6, 128.8, 129.8, 129.8 (2C), 130.6, 131.6 (2C), 131.7 (2C), 133.5, 139.1, 139.7, 143.9, 160.4; HRMS (ESI) Calcd for $C_{28}H_{20}N$ $[M+H]^+$ = 370.1590, Found = 370.1588.

Supporting Information (see footnote on the first page of this article):

Copies of ^{1}H-NMR and ^{13}C-NMR spectra of all aryl *o*-biaryl ketones **1**, ketimine **2Aa**, all 6-arylphenanthridines **3**, and their derivatives **4A-1**~**4A-4**.

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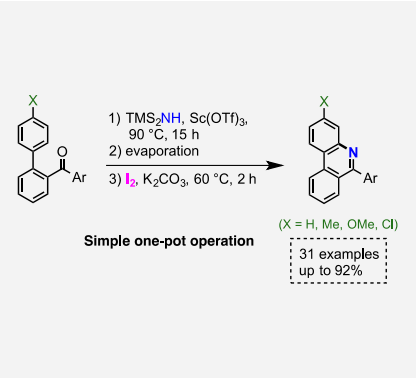
Entry for the Table of Contents ((Please choose one layout.))

Layout 1:

(6-Arylphenanthridines)

Aryl biaryl ketones were transformed into 6-arylphenanthridines efficiently by the reaction with 1,1,1,3,3,3-hexamethyldisilazane in the presence of $Sc(OTf)_3$ in toluene, followed by removal of the solvent and the subsequent reaction with molecular iodine and K_2CO_3 in a mixture of THF and methanol.



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6-Arylphenanthridines from Aryl *o*-Biaryl Ketones with 1,1,1,3,3,3-Hexamethyldisilazane and Molecular Iodine

Keywords: 6-Arylphenanthridine / Ketone / Ketimine / Iodine / Iminyl Radical

Supporting Information

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