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Ytterbium pentafluorobenzoate as a novel fluorous Lewis acid catalyst in the synthesis of 2,4-disubstituted quinolines

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ABSTRACT

A series of simple, efficient, stable and recoverable rare earth metal pentafluorobenzoates [RE(Pfb)$_3$] have been synthesized for the first time. A highly efficient and environmentally friendly synthesis of 2,4-disubstituted quinolines catalyzed by Yb(Pfb)$_3$ via one-pot reaction of aldehydes, alkynes and amines under solvent-free conditions has been explored.

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1. Introduction

The chemistry of rare earth metals has been under extensive investigations for the last decades owing to their rich structural information of rare earth metal complexes and wide applications in organic chemistry.[1] However, most rare earth complexes' structures are too complicated to be easily characterized, and they are extremely unstable in air and water, making the applications of these complexes far from being an exact science.[2] Because of the unique properties of fluorous ligands in electronics, thermally controlled miscibility and interfacial activities, polyfluorinated complexes as catalysts have been well recognized, especially in field of fluorous biphasic catalysis (FBC).[3] Generally, these catalysts have advantages of high activity, low catalytic use and strong water-tolerated ability. In most cases, the catalysts could be recoverable. Importantly, some fluorous catalysts could also be used directly in organic solvent or solvent-free system. In these cases the fluorous catalysts can be dissolved with organic solvents or substrates directly at high temperature and be easily separated when reaction is finished. In this endeavour, the design and synthesis of metal catalyst coordinated by perfluoroalkylated anion is of great importance.

Rare earth metal triflates,[4] which represent the classic fluorous Lewis acid catalysts, have the advantages of high activity, catalytic use, recoverability, especially strong water-tolerated ability, while the traditional Lewis acid catalysts, like $TiCl_4$, $AlCl_3$, BF_4, etc., are easily decomposed or deactivated in the presence of even a small amount of water and need stoichiometric use. Rare earth metal triflates are so powerful that it has become a common practice to test rare earth metal triflates in both the known and some new reactions in the last few decades.[5] Therefore, to develop a new type of fluorous rare earth metal Lewis acid catalyst, which is simple, stable, efficient, well-characterized, and as powerful as rare earth metal triflates, is of obvious interest.

Quinoline and their derivatives occurring in a large number of biologically active natural products attract much attention.[6] Due to their widely biological activities, the synthesis of quinolines has been extensively researched over the years. Kuninobu and co-workers[7] have explored an important methodology that provided an access to synthesis of 2,4-disubstituted quinoline derivatives from simple starting materials using CuCl and AgOTf as catalysts. This methodology has been improved greatly by Wang and co-workers,[8] although it still took a long reaction time (1.5–4 days). Tu co-workers[9] have utilized a single catalyst $FeCl_3$ to promote the one-pot reaction of aldehydes, alkynes and amines affording 2,4-disubstituted quinolines. But the catalyst loading is not satisfactory and the catalyst cannot be recycled. Very recently, a microwave-assisted methodology promoted by a solid acid catalyst was also developed for this transformation.[10] Further investigations are still needed for this transformation, especially to build an environmentally friendly methodology of one-pot reaction catalyzed by a single catalyst, which is catalytic use and reusable.

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2. Results and discussion

Herein, we have synthesized a series of air-stable and water-tolerated rare earth metal pentafluorobenzoates [RE(Pfb)$_3$] for the first time. These complexes have been prepared from pentafluorobenzoic acid and excess rare earth metal oxides at reflux in water and THF (H_2O/THF=1/4) for 24 h. Crystals suitable for X-ray analyses were grown from a solution of ytterbium pentafluorobenzoate in dioxane/hexane. X-ray crystal structure analyses revealed a coordination polymer structure of $[Yb(C_6F_5COO)_3(H_2O)_2]_n \cdot 2n$ diox (Fig. 1). In the crystal structure, each Yb(III) atom is coordinated to eight O atoms, donated by a chelating pentafluorobenzoate, four bridging pentafluorobenzoates and two terminal water molecules. Thus a coordination polymer with a chain structure is formed by the linkage of the bridging carboxylates.[11]

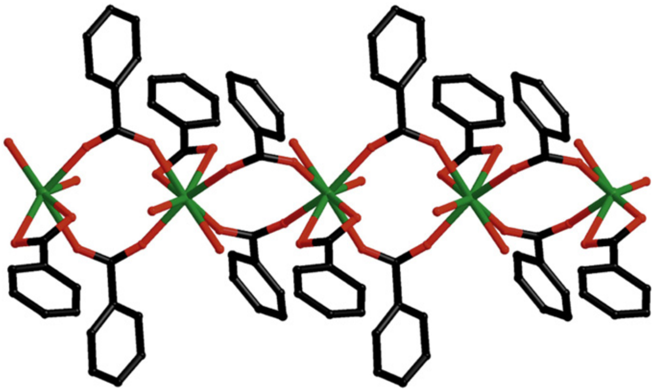


Fig. 1. A chain structure of $[Yb(C_6F_5COO)_3(H_2O)_2]_n \cdot 2n$ diox: green, Yb; red, O; black, C. Lattice dioxane molecules, fluorine and hydrogen atoms are omitted for clarity.

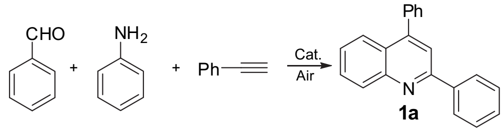
The RE(Pfb)$_3$ are very stable in air and water-tolerated just as RE(OTf)$_3$. The peaks of 794.8431(100%) (^{12}C21, ^{16}O6, ^{19}F15, ^{23}Na, ^{139}La) and 795.8478(18.36%) (^{12}C20, ^{13}C, ^{16}O6, ^{19}F15, ^{23}Na, ^{139}La) were found in lanthanum pentafluorobenzoate's electrospray ionization mass spectrometry (methanol as solvent). Thermogravimetry-differential thermal analysis (TG-DTA) shows that Yb(Pfb)$_3$ loses two molecules of crystallization water at about 130 °C, and the dehydrated complex is decomposed at about 400 °C. The thermal stability of the complex up to 400 °C is probably essential to further applications. The spectrogram was provided in Supplementary data.

As an extension of our contributions in the field of rare earth metal Lewis acid mediated one-pot reaction synthesis,[12] we hope Yb(Pfb)$_3$ could promote the one-pot reaction of aldehydes, alkynes and amines affording 2,4-disubstituted quinolines efficiently. As shown in Table 1, a mixture of aniline, benzaldehyde, phenylacetylene and 10 mol % of Yb(Pfb)$_3$ were stirred in refluxing 1,2-dichloroethane for 24 h. To our delight, the desired product **1a** was isolated in 45% yield successfully. Then the effect of the solvent on the reaction was examined. Toluene was found to be the best solvent, with which the product was obtained in 82% yield (Table 1, entries 1–4). Recently, solvent-free condition is highly demanded in the context of green chemistry. So we tried to carry out the reaction without solvent.

Very exciting, the desired product was obtained in 90% yield with 12 h heating at 80 °C.

To prove our catalyst's superiority, the reaction was catalyzed by Yb(OTf)$_3$ as comparison and the desired product was afforded in 60% yield. Some other rare earth metal pentafluorobenzoates were also tested for this reaction (Table 1, entries 7–8). Interestingly, all other tested rare earth metal pentafluorobenzoates showed no catalytic activity for this reaction except scandium. Sc(Pfb)$_3$ revealed extremely excellent catalytic activity affording the desired product in 95% yield. However, considering the high price of scandium, further investigations for Yb(Pfb)$_3$ catalyzing the one-pot reaction were still conducted. We found the best catalyst loading was 2 mol %, and the catalyst could be recycled and reused for three times without significant loss of activity (Table 1, entry 9). To evaluate the background reaction, a mixture of benzaldehyde, aniline and phenylacetylene was stirred in one-pot under solvent-free conditions without catalyst. Trace product was detected after 48 h reaction. We also did not detect any desired product in the cases of some traditional Lewis acids as catalyst in the solvent-free conditions (Table 1, entries 11–13), even if the temperature was increased to 110 °C.

Table 1
The one-pot synthesis of 2,4-diphenylquinoline under various experimental conditions[a]

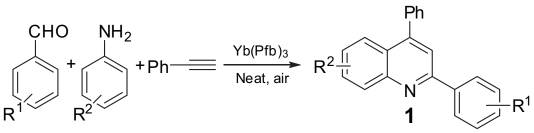


Entry	Cat.	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	Yb(Pfb)$_3$	CH_2ClCH_2Cl	Reflux	24	45
2	Yb(Pfb)$_3$	$PhCH_3$	Reflux	24	82
3	Yb(Pfb)$_3$	CH_2Cl_2	35	48	10
4	Yb(Pfb)$_3$	EtOH	Reflux	48	Trace
5	Yb(Pfb)$_3$	None	80	12	90
6	Yb(OTf)$_3$	None	80	12	60
7	M(Pfb)$_3$[c]	None	80	12	Trace
8	Sc(Pfb)$_3$	None	80	12	95
9	Yb(Pfb)$_3$[d]	None	80	12	88 (90, 88, 87)[e]
10	None	None	80	48	Trace
11	$FeCl_3$	None	110	48	Trace
12	$AlCl_3$	None	110	48	Trace
13	$ZnCl_3$	None	110	48	Trace

[a] A mixture of aniline (1 mmol), benzaldehyde (1 mmol), phenylacetylene (1.5 mmol) and catalyst (10 mol %) were stirred one-pot either with solvent (2 mL) or not.
[b] Isolated yields.
[c] M=La, Sm, Eu, Dy.
[d] The catalyst loading was 2 mol %.
[e] The catalyst was recycled and reused for three times.

As shown in Table 2, the substrate scope of one-pot reaction of aldehydes, alkynes and amines affording 2,4-disubstituted quinolines catalyzed by 2 mol % of Yb(Pfb)$_3$ under solvent-free conditions

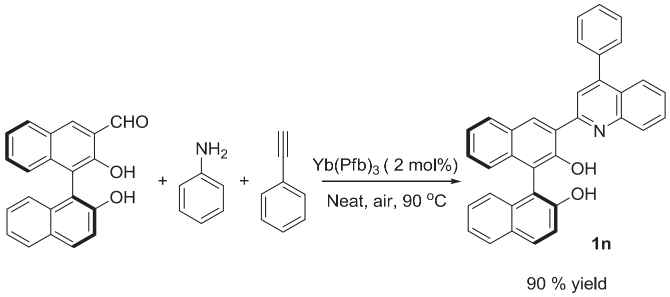
Table 2
Scope of one-pot synthesis of 2,4-disubstituted quinolines catalyzed by Yb(Pfb)$_3$[a]



Entry	R^1	R^2	Temp (°C)	Product	Yield[b] (%)
1	H	H	80	**1a**	88
2	H	4-OCH_3	80	**1b**	90
3	H	4-CH_3	80	**1c**	92
4	H	4-F	80	**1d**	89
5	H	4-Cl	80	**1e**	92
6	H	3-Cl	80	**1f**	65
7	H	2-Cl	80	**1g**	75
8	4-CH_3	H	80	**1h**	89
9	4-OCH_3	H	80	**1i**	91
10	4-Cl	H	80	**1j**	62
11	4-NO_2	H	120	**1k**	70
12	2-NO_2	H	120	**1l**	63
13	3-NO_2	H	120	**1m**	Trace

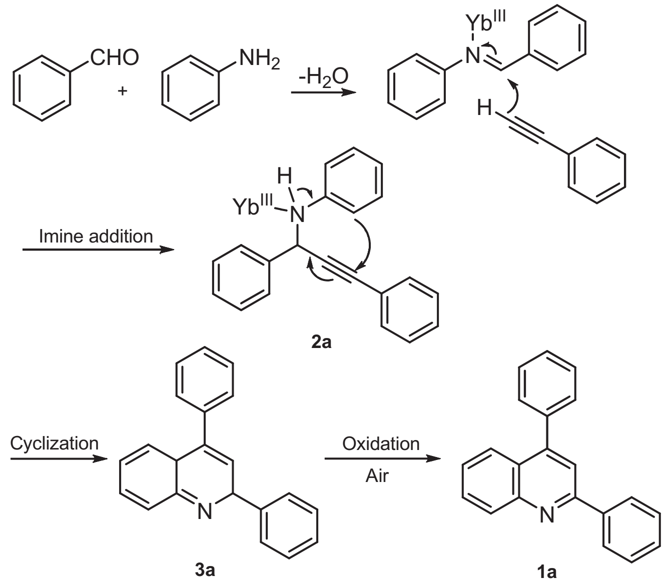
[a] A mixture of amine (1 mmol), aldehyde (1 mmol), phenylacetylene (1.5 mmol) and Yb(Pfb)$_3$ (2 mol %) were stirred one-pot for 12 h without solvent.
[b] Isolated yields.

was examined. Both electron-deficient and electron-rich 4-substitutied anilines provided excellent yields (Table 2, entries 2–5). But *ortho* and *meta* substituted anilines are not the suitable substrates for this protocol (Table 2, entries 6–7). Electron-rich aldehydes reacted with aniline and phenylacetylene very smoothly in excellent yields (Table 2, entries 8 and 9). Several electron-deficient aromatic aldehydes need harsher conditions (120 °C heating), and 3-nitrobenzaldehyde could not afford the desired product. Aliphatic aldehydes are not suitable substrates for this reaction. It is noteworthy that a potential chiral ligand **1n** was obtained in excellent yield (Scheme 1). The application of this easily-prepared chiral ligand, which has the advantages of good stereoselectivity and ability of complex with metals, is under further investigation in our laboratory.

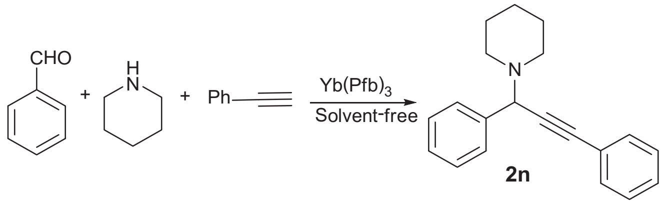


Scheme 1. One-pot synthesis of (*S*)-3-(4-phenylquinolin-2-yl)-1,1′-binaphthyl-2,2′-diol as a potential chiral ligand.

According to the above results, our proposed mechanism of the one-pot synthesis of 2,4-diphenylquinolines is depicted in Scheme 2. The mechanism of the reaction catalyzed by $Yb(Pfb)_3$ might be similar with the reaction catalyzed by other Lewis acids, like $AuCl_3$, $FeCl_3$. However, Yb^{III} may perform better catalytic activity on both processes of imine addition and cyclization, and the water in the reaction system cannot make the catalyst deactivate or decompose. The intermediate **2a** was failed to be isolated. But in the case of piperidine, the corresponding propargylamine **2n** was obtained in 85% yield (Scheme 3). We believe that **2a** is an important intermediate, and this one-pot reaction undergoes domino imine formation, imine addition, cyclization and oxidation.



Scheme 2. The proposed mechanism of one-pot synthesis of 2,4-diphenylquinoline catalyzed by $Yb(Pfb)_3$.



Scheme 3. The corresponding propargylamine was obtained in the case of piperidine.

3. Conclusion

In summary, we have synthesized a series of rare earth metal pentafluorobenzoates from the direct reaction of pentafluorobenzoic acid and RE_2O_3 for the first time. The ytterbium pentafluorobenzoate showed excellent Lewis acid ability in catalyzing one-pot synthesis of 2,4-disubstituted quinoline derivatives. The methodology has the advantages of good to excellent yields, readily available starting materials, solvent-free during the reaction process, catalytic use and reuse of catalyst. The $RE(Pfb)_3$ are well-characterized, simple, efficient, water-tolerated, air and thermal stable, with potential wide range of applications in Lewis acid catalysis and green chemistry.

4. Experimental section

4.1. Synthesis and characterization of rare earth metal pentafluorobenzoates

A series of rare earth metal pentafluorobenzoates was prepared from pentafluorobenzoic acid and excess rare earth oxides in water and THF (H_2O/THF=1/4) at reflux for 24 h. More water was added to dilute the suspension when the reaction finished. The filtrate obtained from high speed centrifugal separation was collected and removed the solvent. Then water was added again to redissolve it, and the resulting solution was filtered carefully. The white powders were obtained after the filtrates were collected and dried at 120 °C in vacuum for 4 h.

The Inductively Coupled Plasma spectrometry (ICP) of ytterbium pentafluorobenzoate showed the content of Yb as 21.9% (the theoretical value is 21.5%). It was supported that the expected metal–ligand ratio (Yb/C_6F_5COO) was 1/3. Compared with the ^{19}F NMR of pentafluorobenzoic acid, Nd and Gd pentafluorobenzoates' ^{19}F NMR showed all peaks were shifted to low field for about 3 ppm, and the peaks of the two F atoms near the carboxyl were split to double-peaks. Rare earth metal pentafluorobenzoates' infrared spectrums (IR) showed the pentafluorobenzoic acid's two strong absorption peaks $\nu_{C=O}$ (3000 cm^{-1}), ν_{O-H} (1716 cm^{-1}) all disappeared. The peaks of 794.8431(100%) ($^{12}C21$, $^{16}O6$, $^{19}F15$, ^{23}Na, ^{139}La) and 795.8478(18.36%) ($^{12}C20$, ^{13}C, $^{16}O6$, $^{19}F15$, ^{23}Na, ^{139}La) were found in lanthanum pentafluorobenzoate's electrospray ionization mass spectrometry (ESI-MS) clearly illustrating its structure is $La(C_6F_5COO)_3$.

4.2. General procedure for synthesis of 1a–l

A mixture of amine (1 mmol), aldehyde (1 mmol), phenylacetylene (1.5 mmol) and ytterbium pentafluorobenzoate (2 mol %) was stirred one-pot without solvent at 80 °C or 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and washed by CH_2Cl_2. The residue is the catalyst that can be directly used in next cycle reaction. The organic layer was concentrated in vacuo, purified by chromatography affording the desired product **1a–l** (EtOAc/Petroleum ether=1:20 to 1:10). When the catalyst had good solubility with the substrates at room temperature, the reaction mixture was extracted by CH_2Cl_2 and H_2O. The organic layer was dried with Na_2SO_4, concentrated in vacuo, purified by chromatography affording the desired product. The water layer, which contains the catalyst, was dried in vacuo. The catalyst was then recovered and reused for next reaction.

4.3. The ^{1}H and ^{13}C spectrum of the desired product

*4.3.1. 2,4-Diphenylquinoline (**1a**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.58 (m, 9H), 7.75 (t, J=7.2 Hz, 1H), 7.85 (s, 1H), 7.93 (d, J=8.4 Hz, 1H), 8.23 (d, J=7.2 Hz, 2H), 8.28 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.93, 149.20, 148.88, 139.71, 138.46, 130.19, 129.61, 129.55, 129.38, 128.88, 128.53, 128.44, 127.63, 126.37, 125.82, 125.88, 119.39. HRMS, M$^+$, found 281.1203, $C_{21}H_{15}N$ requires 281.1204.

*4.3.2. 6-Methoxy-2,4-diphenylquinoline (**1b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.20 (d, J=2.4 Hz, 1H), 7.39–7.47 (m, 2H), 7.50–7.60 (m, 7H), 7.79 (s, 1H), 8.15–8.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.86, 154.62, 147.81, 145.00, 139.80, 138.81, 131.67, 129.44, 129.05, 128.86, 128.77, 128.42, 127.37, 126.71, 121.88, 119.66, 103.73, 55.45. HRMS, M$^+$, found 311.1310, $C_{22}H_{17}NO$ requires 311.1310.

*4.3.3. 6-Methyl-2,4-diphenylquinoline (**1c**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.37–7.54 (m, 9H), 7.62 (s, 1H), 7.73 (s, 1H), 8.12–8.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.07, 148.54, 147.55, 139.85, 138.75, 136.36, 131.89, 130.00, 129.68, 129.29, 128.92, 128.70, 128.42, 127.61, 125.83, 124.52, 119.49, 115.34, 21.94. HRMS, M$^+$, found 295.1359, $C_{22}H_{17}N$ requires 295.1361.

*4.3.4. 6-Fluoro-2,4-diphenylquinoline (**1d**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.59 (m, 10H), 7.85 (s, 1H), 8.18–8.20 (m, 2H), 8.25 (dd, J=5.2, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ d (161.84, 159.38), d (156.33, 156.30), d (148.72, 148.67), 145.98, 139.38, 138.00, d (132.63, 132.55), 129.45, 129.40, 128.91, 128.82, 128.68, 127.49, d (126.59, 126.49), 119.88, d (119.82, 119.57), d (109.20, 108.97). HRMS, M$^+$, found 299.1112, $C_{21}H_{14}FN$ requires 299.1110.

*4.3.5. 6-Chloro-2,4-diphenylquinoline (**1e**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.60 (m, 8H), 7.68 (dd, J=2.4, 9.2 Hz, 1H), 7.84 (s, 1H), 7.88 (d, J=2.4 Hz, 1H), 8.17–8.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.08, 148.45, 147.26, 139.22, 137.78, 132.23, 131.77, 130.46, 129.62, 129.48, 128.93, 128.85, 128.74, 127.56, 126.51, 124.51, 120.04. HRMS, M$^+$, found 315.0815, $C_{21}H_{14}ClN$ requires 315.0815.

*4.3.6. 7-Chloro-2,4-diphenylquinoline (**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J=7.6, 8.4 Hz, 1H), 7.47–7.58 (m, 8H), 7.82 (dd, J=1.2, 8.4 Hz, 1H), 7.86 (dd, J=1.2, 7.6 Hz, 1H), 7.91 (s, 1H), 8.32–8.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.81, 149.76, 144.96, 139.08, 138.16, 134.45, 129.84, 129.71, 129.61, 128.94, 128.71, 128.66, 127.76, 127.35, 125.97, 124.87, 119.73. HRMS, M$^+$, found 315.0815, $C_{21}H_{14}ClN$ requires 315.0815.

*4.3.7. 8-Chloro-2,4-diphenylquinoline (**1g**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J=2.4, 9.2 Hz, 1H), 7.47–7.59 (m, 8H), 7.82 (s, 1H), 7.84 (d, J=8.8 Hz, 1H), 8.18–8.20 (m, 2H), 8.24 (d, J=2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.87, 149.34, 149.23, 139.19, 137.96, 135.46, 129.71, 129.50, 129.01, 128.91, 128.76, 128.69, 127.62, 127.22, 127.08, 124.25, 119.41. HRMS, M$^+$, found 315.0817, $C_{21}H_{14}ClN$ requires 315.0815.

*4.3.8. 4-Phenyl-2-p-tolylquinoline (**1h**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.29 (d, J=8.0 Hz, 2H), 7.39–7.42 (m, 1H), 7.45–7.51 (m, 5H), 7.65–7.70 (m, 1H), 7.77 (s, 1H), 7.86 (d, J=8.4 Hz, 1H), 8.08 (d, J=8 Hz, 2H), 8.22 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.90, 149.10, 148.93, 139.49, 138.57, 136.91, 130.15, 129.66, 129.54, 129.35, 128.66, 128.45, 127.56, 126.23, 125.78, 125.70, 119.26, 21.45. HRMS, M$^+$, found 295.1360, $C_{22}H_{17}N$ requires 295.1361.

*4.3.9. 2-(4-Methoxyphenyl)-4-phenylquinoline (**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 7.06 (d, J=8.8 Hz, 2H), 7.43–7.47 (m, 1H), 7.52–7.57 (m, 5H), 7.70–7.74 (m, 1H), 7.79 (s, 1H), 7.89 (d, J=8.4 Hz, 1H), 8.17–8.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.87, 156.47, 149.03, 148.85, 138.55, 132.25, 129.93, 129.59, 129.47, 128.94, 128.60, 128.38, 125.99, 125.65, 125.55, 118.93, 114.25, 55.41. HRMS, M$^+$, found 311.1311, $C_{22}H_{17}NO$ requires 311.1310.

*4.3.10. 2-(4-Chlorophenyl)-4-phenylquinoline (**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.56 (m, 8H), 7.73–7.78 (m, 2H), 7.91 (d, J=8.0 Hz, 1H), 8.16 (d, J=8.4 Hz, 2H), 8.23 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.55, 149.44, 148.79, 138.27, 138.05, 135.58, 130.01, 129.72, 129.55, 129.03, 128.85, 128.65, 128.52, 126.56, 125.85, 125.71, 118.92. HRMS, M$^+$, found 315.0817, $C_{21}H_{14}ClN$ requires 315.0815.

*4.3.11. 2-(4-Nitrophenyl)-4-phenylquinoline (**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.57 (m, 6H), 7.75–7.79 (m, 1H), 7.82 (s, 1H), 7.93 (d, J=8 Hz, 2H), 8.25 (d, J=8.4 Hz, 1H), 8.30–8.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.97, 149.85, 148.82, 148.31, 145.36, 137.93, 130.36, 130.07, 129.55, 128.77, 128.27, 127.37, 126.17, 125.79, 123.97, 119.05. HRMS, M$^+$, found 326.1057, $C_{21}H_{14}N_2O_2$ requires 326.1055.

*4.3.12. 2-(2-Nitrophenyl)-4-phenylquinoline (**1l**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.45 (m, 8H), 7.54–7.57 (m, 1H), 7.64–7.68 (m, 2H), 7.86–7.90 (m, 2H), 8.14 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.18, 149.35, 149.30, 148.54, 137.72, 135.67, 132.75, 131.67, 130.11, 129.93, 129.65, 129.52, 128.71, 127.20, 125.79, 124.55, 120.80. HRMS, M$^+$, found 326.1055, $C_{21}H_{14}N_2O_2$ requires 326.1055.

*4.3.13. (S)-2,2′-Dihydroxy-1,1′-binaphthyl-3-carbaldehyde(**1n**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41(br, 1H), 8.91 (s, 1H), 8.16 (s, 1H), 7.86–7.98 (m, 4H), 7.44–7.14 (m, 15H), 5.11 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.03, 155.53, 152.78, 151.52, 147.79, 135.78, 135.69, 133.60, 133.44, 131.44, 130.18, 129.56, 129.48, 129.38, 129.16, 128.44, 128.33, 127.91, 127.58, 127.51, 126.63, 124.86, 124.77, 124.22 (two signals overlapped), 124.07, 123.40, 121.43, 121.25, 117.80, 117.75, 114.36, 114.00. HRMS, [M+1]$^+$, found 490.1790, $C_{35}H_{23}NO_2$ requires 490.1807.

*4.3.14. 1-(1,3-Diphenylprop-2-ynyl)piperidine (**2n**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43–1.47 (m, 2H), 1.56–1.64 (m, 4H), 2.57 (t, J=4.8 Hz, 4H), 4.80 (s, 1H), 7.29–7.38 (m, 6H), 7.51–7.54 (m, 2H), 7.64 (d, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.58, 131.82, 128.56, 128.28, 128.06 (two signals overlap), 127.46, 123.35, 87.84, 86.08, 62.40, 50.72, 26.18, 24.44. HRMS, M$^+$, found 275.1676, $C_{20}H_{21}N$ requires 275.1674.

4.3.15. Gadolinium pentafluorobenzoate [Ga(Pfb)$_3$]. ^{19}F NMR (470 MHz DMSO) δ 140.44 (s, 2F), 155.76 (s, 1F), 163.46 (s, 2F).

4.3.16. Neodymium pentafluorobenzoate [Nd(Pfb)$_3$]. ^{19}F NMR (470 MHz DMSO) δ 140.13–140.43 (m, 2F), 155.73 (s, 1F), 163.44 (s, 2F).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.09.004.

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