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Rhodium-Catalyzed Oxidative 1:1, 1:2, and 1:4 Coupling Reactions of Phenylazoles with Internal Alkynes through the Regioselective Cleavages of Multiple C−H Bonds

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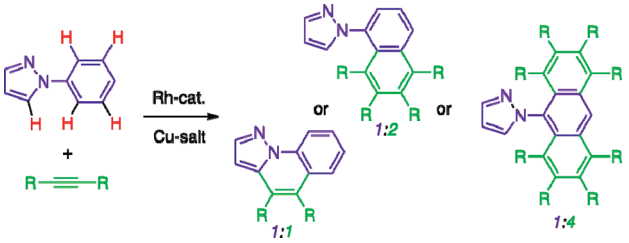

The direct oxidative coupling of phenylazoles with internal alkynes proceeds efficiently in the presence of a rhodium catalyst and a copper oxidant accompanied by double or quadruple C−H bond cleavages. Thus, as a representative example, 4,5-diphenylpyrazolo[1,5-*a*]quinoline, 1-(1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole, and 1-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)pyrazole can be obtained selectively through the coupling of 1-phenylpyrazole and diphenylacetylene in 1:1, 1:2, and 1:4 manners, respectively. The reactions preferentially take place at the electron-deficient sites on the aromatic substrates. A comparison of reactivities of variously substituted and deuterated substrates sheds light on the mechanism of C−H bond cleavage steps. The reaction pathway is highly dependent on reaction conditions employed, especially on the nature of solvent. The influence of solvation of a key rhodacycle intermediate has been investigated computationally. In addition, some of the condensed aromatic products have been found to exhibit intense fluorescence in the solid state.

Introduction

Selective syntheses of substituted polycyclic aromatic and heteroaromatic compounds have become increasingly important because these reactions have been finding increasing application as π-conjugated functional materials.[1] Among modern potential strategies to prepare condensed aromatics is the transition-metal-promoted or -catalyzed homologation, such as benzene to naphthalene and naphthalene to anthracene, of a given aromatic substrate with two alkyne molecules (eq 1).[2] Thus, the catalytic transformations of difunctionalized (X ≠ H, Y ≠ H)[2,3] and more readily available monofunctionalized aromatic substrates (X ≠ H, Y = H)[4] have been developed. While a further straightforward and challenging

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(2) (a) Lin, C.-H.; Lin, K.-H.; Pal, B.; Tsou, L.-D. *Chem. Commun.* **2009**, 803. (b) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-I. *J. Org. Chem.* **2006**, *71*, 7967. (c) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (d) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876.

(3) X = Y = halogen: (a) Huang, W.; Zhou, X.; Kanno, K.-I.; Takahashi, T. *Org. Lett.* **2004**, *6*, 2429. X = OTf, Y = $SiMe_3$: (b) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944. (d) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (e) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659.

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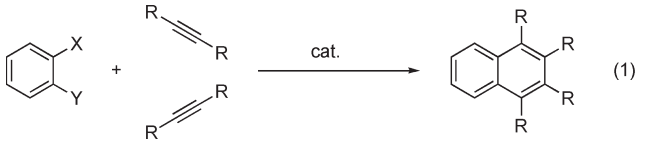
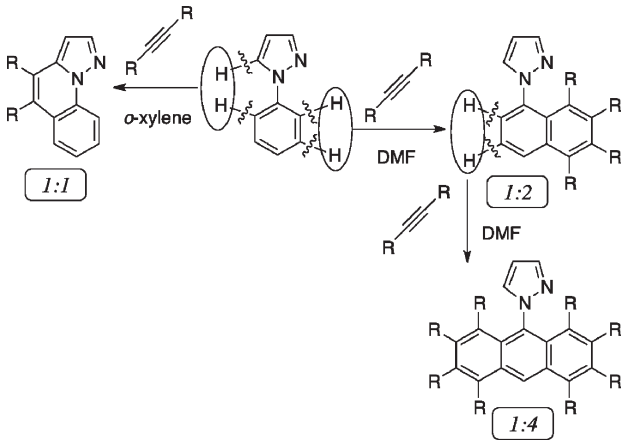
strategy may be the coupling via double C−H bond cleavages (X = Y = H), there has been, to our knowledge, so far no effective catalytic example of such a homologation.[5]



Meanwhile, one of the most promising methods for a catalytic C−H bond activation is to utilize the proximate effect by coordination of a functional group in a given substrate to the metal center of a catalyst.[6] As such examples, we have demonstrated regioselective aromatic C−H arylation and vinylation directed by hydroxyl,[4j,7] carboxyl,[4g−i,8] amide,[9] and imino functions[10] under Pd, Rh, or Ir catalysis. In the course of our further study of the directed C−H functionalization, it has been found that phenylazoles regioselectively couple with internal alkynes in a 1:2 manner via double C−H bond cleavages under rhodium catalysis, achieving the direct homologation to lead to naphthylazoles.[11] Furthermore, under appropriate reaction conditions, these substrates also underwent 1:1 and 1:4 coupling reactions selectively accompanied by the cleavages of two and four C−H bonds, respectively, to give condensed (hetero)aromatic products (Scheme 1). The detailed results obtained with respect to these coupling reactions are described herein.

SCHEME 1. 1:1, 1:2, and 1:4 Couplings of 1-Phenylpyrazole with Alkynes



Results and Discussion

1:2 Coupling of Phenylazoles with Alkynes. When 1-phenylpyrazole (**1a**) (0.5 mmol), as a typical azole, was treated with diphenylacetylene (**2a**) (1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in DMF at 80 °C for 6 h under N_2,[12] 1-(1,2,3,4-tetraphenylnaphthalen-5-yl)-pyrazole (**3a**) was formed as a 1:2 coupling product in 63% yield (entry 1, Table 1). The use of an increased amount of **1a** (1 mmol) enhanced the yield to 87% (entry 2). At 60 °C, the reaction efficiency was somewhat reduced (entry 3). Addition of $C_5H_2Ph_4$ (1,2,3,4-tetraphenyl-1,3-cyclopentadiene, 0.04 mmol) as ligand improved the yield up to 93% (entry 4).[13] $C_5H_3Ph_3$ (1,2,4-triphenyl-1,3-cyclopentadiene) and C_5HPh_5 (1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene) were less effective than $C_5H_2Ph_4$ (entries 5 and 6). The reaction using $[RhCl(cod)]_2$ in place of $[Cp^*RhCl_2]_2$ was sluggish (entry 7). $[Cp^*IrCl_2]_2$ did not show any catalytic activity (entry 8).

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(5) Coupling of benzene with alkynes using a stoichiometric amount of Pd was reported. Naphthalene yields based on Pd were less than 20%. See ref 4e.

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(7) For example, see: (a) Mochida, S.; Shimizu, M.; Hirano, K.; Satoh, T.; Miura, M. *Chem. Asian J.* **2010**, *5*, 847. (b) Shimizu, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem. Asian J.* **2008**, *3*, 881. (c) Nakano, M.; Satoh, T.; Miura, M. *J. Org. Chem.* **2006**, *71*, 8309. (d) Terao, Y.; Wakui, H.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem.* **2003**, *68*, 5236. (e) Terao, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2001**, *123*, 10407. (f) Nishinaka, Y.; Satoh, T.; Miura, M.; Nomura, M.; Matsui, H.; Yamaguchi, C. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1727. (g) Satoh, T.; Inoh, J.-I.; Kawamura, Y.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2239.

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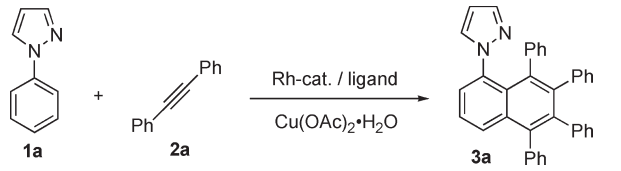
(10) (a) Fukutani, T.; Umeda, N.; Hirano, K.; Satoh, T.; Miura, M. *Chem. Commun* **2009**, 5141. (b) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.

(11) Preliminary communication: (a) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. Later, a Pd-catalyzed version without chelation-control was reported: (b) Wu, Y.-T.; Huang, K.-H.; Shin,; Wu, T.-C. *Chem.—Eur. J.* **2008**, *14*, 6697.

(12) The catalyst system of Rh-complex/Cp-ligand/Cu-oxidant has been developed for related oxidative annulation reactions by our group. See refs 4i−4k, 7a,7b, 8a,8e, 9a, 10a, and 11a. Recently, this system was successfully employed for the oxidative coupling reactions of 2-phenylpyridines, 2-phenylindoles, amides, and imines with alkynes and alkenes: (a) Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565. (b) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982. (c) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585. (d) Morimoto, K.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 2068. (e) Guimond, N.; Gouliaras, C.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6908. (f) Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492. (g) Guimond, N.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, *131*, 12050. (h) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414. (i) Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474.

(13) A similar effect was also observed in the reaction of triarylmethanols with alkynes. See ref 4j.

TABLE 1. 1:2 Coupling of 1-Phenylpyrazole (1a) with Diphenylacetylene (2a)[a]



entry	Rh cat.	ligand	temp (°C)	yield of **3a**[b]
1[c]	$[Cp^*RhCl_2]_2$		80	63
2	$[Cp^*RhCl_2]_2$		80	87
3	$[Cp^*RhCl_2]_2$		60	41
4	$[Cp^*RhCl_2]_2$	$C_5H_2Ph_4$	80	93 (93)
5	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	80	73
6	$[Cp^*RhCl_2]_2$	C_5HPh_5	80	78
7	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	80	37
8	$[Cp^*IrCl_2]_2$	$C_5H_2Ph_4$	80	0

[a]Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), Rh cat. (0.01 mmol), ligand (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), DMF (5 mL) under N_2 for 6 h. [b]GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c]**1a** (0.5 mmol) was used.

Table 2 summarizes the results for the coupling employing a number of phenylazoles and internal alkynes in the presence of the $[Cp^*RhCl_2]_2/C_5H_2Ph_4$ catalyst system. The reactions of **1a** with diarylacetylenes **2b**−**d** proceeded efficiently to produce the corresponding 1-(1,2,3,4-tetraarylnaphthalen-5-yl)pyrazoles **3b**−**d** in good yields (entries 1−3). In contrast, the reaction with 4-octyne gave only a trace amount of coupling product. The reaction efficiency could not be improved by using AgOAc, $AgOCOCF_3$, and Ag_2CO_3 as oxidants in place of $Cu(OAc)_2 \cdot H_2O$. Meanwhile, 1-phenyl-1-hexyne (**2e**) efficiently coupled with **1a** to give 1-(1,4-dibutyl-2,3-diphenylnaphthalen-5-yl)pyrazole (**3e**) predominantly, along with a small amount of an unidentified, inseparable isomer (entry 4). From the reaction of 1-phenyl-1- propyne (**2f**) with **1a**, 1-(1,4-dimethyl-2,3-diphenylnaphthalen-5-yl)pyrazole (**3f**) was obtained in a moderate yield (entry 5). The couplings of 1-(2-methylphenyl)- (**1b**) and 1-(3-methylphenyl)pyrazoles (**1c**) with **2a** took place effectively to afford 1-(6- or 7-methyl-1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole **3g** and **3h** in good yields (entries 6 and 7). While 1-(4-methylphenyl)pyrazole did not react at all, which may be due to steric reasons, 1-(4-fluorophenyl)pyrazole (**1d**) smoothly coupled with **2a** within 45 min to afford product **3i** in 97% isolated yield (entry 8). 1-Phenyl-3-methylpyrazole (**1e**) and 1-phenyl-3,5-dimethylpyrazole (**1f**) also underwent the coupling with **2a** to produce the corresponding 1-naphthylpyrazoles **3j** and **3k** in good yields (entries 9 and 10). Not only phenylpyrazoles but also phenylbenzimidazole **1g** and -pyridine **1h** were found to react with **2a** to give naphthylbenzimidazole **3l** and naphthylpyridine **3m**, respectively (entries 11 and 12).

1:4 Coupling of Phenylazoles with Alkynes. Treatment of 1-phenylpyrazoles with an excess amount of diphenylacetylene (**2a**) using the catalyst system of $[Cp^*RhCl_2]_2/C_5H_2Ph_4/Cu(OAc)_2 \cdot H_2O$ gave the corresponding 1:4 coupling products selectively through the cleavages of four C−H bonds. Thus, **1a** (0.125 mmol) reacted with **2a** (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol), $C_5H_2Ph_4$ (0.04 mmol), and $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) at 100 °C in DMF to furnish 1-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)pyrazole (**4a**) in 74% isolated yield (entry 1, Table 3). 3-Methyl-1-phenylpyrazole (**1e**) and 3,5-dimethyl-1-phenylpyrazole (**1f**) also

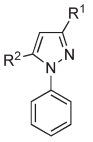
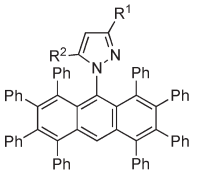
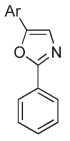
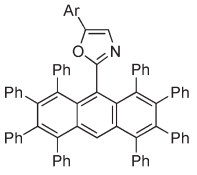
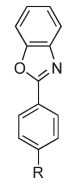
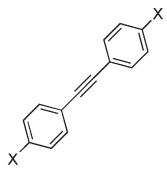
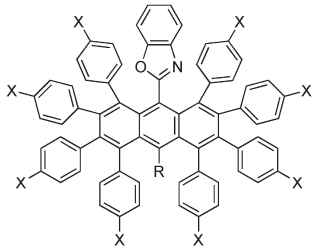
TABLE 2. 1:2 Coupling of Phenylazoles 1 with Alkynes 2[a]

entry	1	2	time (h)	product, % yield[b]
1	**1a**	**2b**: X = Me	6	**3b**: X = Me, 80 (79)
2		**2c**: X = OMe	8	**3c**: X = OMe, (76)
3		**2d**: X = Cl	6	**3d**: X = Cl, (79)
4		**2e**: R = Bu	6	**3e**: R = Bu, 97 (72)[c]
5		**2f**: R = Me	6	**3f**: R = Me, 36 (20)
6	**1b**: R^1 = Me; R^2 = R^3 = H	**2a**	6	**3g**: R^1 = Me; R^2 = R^3 = H, (98)
7	**1c**: R^2 = Me; R^1 = R^3 = H		6	**3h**: R^2 = Me; R^1 = R^3 = H, (88)
8	**1d**: R^3 = F; R^1 = R^2 = H		0.75	**3i**: R^3 = F; R^1 = R^2 = H, (97)
9	**1e**: R^1 = Me; R^2 = H	**2a**	3	**3j**: R^1 = Me; R^2 = H, (87)
10	**1f**: R^1 = R^2 = Me		1	**3k**: R^1 = R^2 = Me, 99 (97)
11	**1g**	**2a**	6	**3l**, (77)
12[d]	**1h**	**2a**	6	**3m**, 61 (51)

[a]Reaction conditions: **1** (1 mmol), **2** (1 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $C_5H_2Ph_4$ (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), DMF (5 mL) at 80 °C under N_2. [b]GC yield based on the amount of **2** used. Value in parentheses indicates yield after purification. [c]Contaminated with an isomer (**3e**/isomer = 94:6). [d]$[Cp^*RhCl_2]_2$ (0.02 mmol) and $C_5H_2Ph_4$ (0.08 mmol) were used.

underwent the 1:4 coupling with **2a** to form the corresponding 1-anthrylpyrazoles **4b** and **4c**, respectively. Similar anthracene derivatives were also obtained from 5-aryl-2-phenyloxazoles **1i**−**m** via the double homologation. Further reaction on the aryl moiety at their 5-position of the oxazoles could not be observed at all. Similarly, the reactions of 2-phenylbenzoxazole (**1n**) and 2-(4-fluorophenyl)benzoxazole

TABLE 3. 1:4 Coupling of Phenylazoles 1 with Alkynes 2[a]

entry	1	2	product, % yield[b]
			
1	**1a**: $R^1 = R^2 = H$	**2a**	**4a**: $R^1 = R^2 = H$, 74
2	**1e**: $R^1 = Me$; $R^2 = H$		**4b**: $R^1 = Me$; $R^2 = H$, 67
3	**1f**: $R^1 = R^2 = Me$		**4c**: $R^1 = R^2 = Me$, 52
			
4	**1i**: Ar = Ph	**2a**	**4d**: Ar = Ph, 75
5	**1j**: Ar = 2-MeC_6H_4		**4e**: Ar = 2-MeC_6H_4, 53
6	**1k**: Ar = 1-naphthyl		**4f**: Ar = 1-naphthyl, 51
7	**1l**: Ar = 4-$MeOC_6H_4$		**4g**: Ar = 4-$MeOC_6H_4$, 22
8	**1m**: Ar = 4-$CF_3C_6H_4$		**4h**: Ar = 4-$CF_3C_6H_4$, 50
			
9	**1n**: R = H	**2a**: X = H	**4i**: R = X = H, 53
10	**1o**: R = F	**2a**: X = H	**4j**: R = F; X = H, 74
11	**1n**: R = H	**2d**: X = Cl	**4k**: R = H; X = Cl, 68

[a]Reaction conditions: **1** (0.125 mmol), **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $C_5H_2Ph_4$ (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol), DMF (3 mL) at 100 °C under N_2 for 6 h. [b]Isolated yield based on the amount of **1** used.

(**1o**) with diaryacetylene **2a**,**d** proceeded efficiently to produce 2-(1,2,3,4,5,6,7,8-octaarylanthracen-9-yl)benzoxazole derivatives **4i**−**k**.

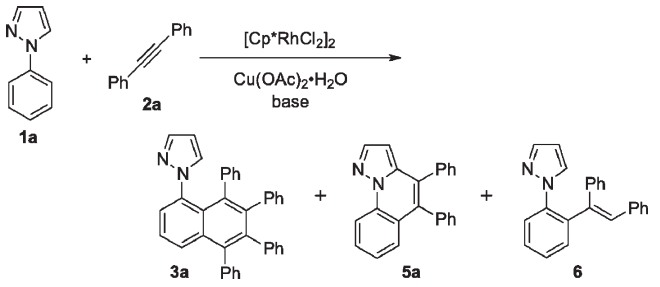
The thus-obtained anthrylazole derivatives **4** showed solid-state fluorescence in a range of 470−530 nm (Figure S1, Supporting Information). Among them, anthryloxazoles **4d**−**f** exhibited a relatively strong emission compared to a typical emitter, coumarin 153, by a factor of ca. 4. Moreover, anthrylbenzoxazole **4i** was found to exhibit more intense luminescence (λ_{emis} 477 nm), and the intensity is at least 6.5 times stronger than that of coumarin 153. Remarkably, the solid-state fluorescence quantum efficiency (Φ) of **4i** measured absolutely was 66 ± 2%.

1:1 Coupling of 1-Phenylpyrazoles with Alkynes. As described above, the aromatic homologation selectively takes place upon treatment of phenylpyrazoles with alkynes using the catalyst system of $[Cp^*RhCl_2]_2/C_5H_2Ph_4/Cu(OAc)_2 \cdot H_2O$ in DMF. It has also been found that the reactions of these substrates in *o*-xylene give considerable amounts of 1:1 coupling products, pyrazolo[1,5-*a*]quinolines **5**, in addition to naphthalenes **3**. Thus, 1-phenylpyrazole (**1a**) reacted with **2a** in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol), $C_5H_2Ph_4$ (0.04 mmol), and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) at 80 °C in *o*-xylene to give **3a** and 4,5-diphenylpyrazolo-[1,5-*a*]quinoline (**5a**) in 19% and 14% yields, respectively (entry 1, Table 4). The yield of **5a** decreased in *n*-octane, 1,4-dioxane, and acetonitrile (entries 2−4). The desired product **5a** could be obtained in a same yield in *o*-xylene even in the absence of $C_5H_2Ph_4$ (entry 5). In these cases, significant amounts of a nonoxidative 1:1 coupling product, 1-[2-(1,2-diphenylethenyl)phenyl]pyrazole (**6**), were also formed in addition to **3a** and **5a**.[14] Interestingly, addition of K_2CO_3 suppressed the formation of **3a** and **6** completely and slightly increased the yield of **5a** (entry 6). At 150 °C, **5a** was obtained in 34% yield (entry 7). Among bases examined, Na_2CO_3 gave the best result to improve the yield of **5a** up to 81% (entry 11).

Since nitrogen-containing polycyclic heteroaromatics such as **5a** have attracted considerable attention because of their photochemical, electrochemical, and biological

(14) For recent examples of hydroarylation of alkynes, see: (a) Schipper, D. J.; Hutchinson, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6910 and references therein. (b) Shibata, Y.; Otake, Y.; Hirano, M.; Tanaka, K. *Org. Lett.* **2009**, *11*, 689. (c) Katagiri, T.; Mukai, T.; Satoh, T.; Hirano, K.; Miura, M. *Chem. Lett.* **2009**, *38*, 118. (d) Mukai, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 6410. (e) Cheng, K.; Yao, B.; Zhao, J. *Org. Lett.* **2008**, *10*, 5309. (f) Tsuchikama, K.; Kasagawa, M.; Hashimoto, Y.; Endo, K.; Shibata, T. *J. Organomet. Chem.* **2008**, *693*, 3939. (g) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 3645. (h) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 2448. (i) Lim, Y.-G.; Lee, K.-H.; Koo, B. T.; Kang, J.-B. *Tetrahedron Lett.* **2001**, *42*, 7609. See also ref 6d,6e,6p.

TABLE 4. Reaction of 1-Phenylpyrazole (1a) with Diphenylacetylene (2a) in *o*-Xylene[a]



					yield[b] (%)		
entry	base	solvent	temp (°C)	time (h)	**3a**	**5a**	**6**
1[c]		*o*-xylene	80	6	19	14	36
2[c]		*n*-octane	80	6	21	tr	26
3[c]		1,4-dioxane	80	6	39	5	3
4[c]		acetonitrile	80	6	20	0	0
5		*o*-xylene	80	6	11	14	44
6	K_2CO_3	*o*-xylene	80	6	0	24	0
7	K_2CO_3	*o*-xylene	150	2	0	34	tr
8	Cs_2CO_3	*o*-xylene	150	2	0	tr	tr
9	Li_2CO_3	*o*-xylene	150	2	tr	67	11
10	$NaHCO_3$	*o*-xyIene	150	2	6	52	tr
11	Na_2CO_3	*o*-xy]ene	150	2	tr	81 (78)	tr

[a]Reaction conditions: **1a** (1 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), base (1 mmol) in *o*-xylene (3 mL) under N_2. [b]GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c]**2a** (1 mmol) was used in the presence of $C_5H_2Ph_4$ (0.04 mmol).

properties,[15] the scope of the reaction was next explored. Table 5 summarizes the results for the 1:1 coupling of substituted 1-phenylpyrazoles **1** with various internal alkynes **2**. The methyl-, methoxy-, and chloro-substituted diphenylacetylenes **2b**−**d** reacted with **1a** to form the corresponding pyrazoloquinolines **5b**−**d** in 56−81% yields (entries 1−3). A dialkylacetylene, 4-octyne (**2g**), also underwent the reaction with **1a** to give 4,5-dipropylpyrazolo[1,5-*a*]quinoline (**5e**), albeit with a lower yield (entry 4). From the reactions of unsymmetrical 1-phenyl-1-hexyne (**2e**) and 1-phenyl-1-propyne (**2f**) with **1a**, 5-alkyl-4-phenylpyrazolo[1,5-*a*]quinolines **5f** and **5g** were produced predominantly along with minor amounts of their isomers (entries 5 and 6). While the reaction of 1-(2-methylphenyl)pyrazole (**1b**) with **2a** was somewhat sluggish (entry 7), those of 1-(3-methylphenyl)- (**1c**) and 1-(4-methylphenyl)pyrazoles (**1p**) proceeded efficiently even under relatively mild conditions using a half amount of Na_2CO_3 (0.5 mmol) at 130 °C to afford the corresponding pyrazoloquinolines **5i** and **5j**, respectively (entries 8 and 9). Under similar conditions, the reactions of 1-(4-substituted phenyl)pyrazoles **1q**−**s** proceeded smoothly to form **5k**−**m** in 63−88% yields (entries 10−12).

In contrast to **1c**, other 1-(3-substituted phenyl)pyrazoles **1t**−**v** reacted with **2a** to give regioisomeric mixtures of the corresponding 1:1 coupling products (**5** and **5′**). In the case

TABLE 5. 1:1 Coupling of 1-Phenylpyrazoles 1 with Alkynes 2[a]

entry	**1**	**2**	product, % yield[b]
1	**1a**	**2b**: X = Me	**5b**: X = Me, 81 (81)
2		**2c**: X = OMe	**5c**: X = OMe, 63 (51)
3		**2d**: X = Cl	**5d**: X = Cl, 56 (33)
4		**2g**: $R^1 = R^2 = Pr$	**5e**: $R^1 = R^2 = Pr$, (25)
5		**2e**: $R^1 = Bu$; $R^2 = Ph$	**5f**: $R^1 = Bu$; $R^2 = Ph$, (55)[c]
6		**2f**: $R^1 = Me$; $R^2 = Ph$	**5g**: R^1=Me; $R^2 = Ph$, (37)[d]
7[e]	**1b**: $R^1 = Me$; $R^2 = R^3 = H$	**2a**	**5h**: $R^1 = Me$; $R^2 = R^3 = H$, (47)
8[e]	**1c**: $R^2 = Me$; $R^1 = R^3 = H$		**5i**: $R^2 = Me$; $R^1 = R^3 = H$, (72)
9[e]	**1p**: $R^3 = Me$; $R^1 = R^2 = H$		**5j**: $R^3 = Me$; $R^1 = R^2 = H$, (76)
10[e]	**1q**: $R^3 = OMe$; $R^1 = R^2 = H$		**5k**: $R^3 = OMe$; $R^1 = R^2 = H$, (63)
11[e]	**1r**: $R^3 = Cl$; $R^1 = R^2 = H$		**5l**: $R^3 = Cl$; $R^1 = R^2 = H$, (88)
12[e]	**1s**: $R^3 = CF_3$; $R^1 = R^2 = H$		**5m**: $R^3 = CF_3$; $R^1 = R^2 = H$, (74)
13[e]	**1t**: $R^2 = Cl$	**2a**	**5n** / **5'n**: $R^2 = Cl$, (77) [13:1]
14[e]	**1u**: $R^2 = F$		**5o** / **5'o**: $R^2 = F$, (98) [1:10]
15[e]	**1v**: $R^2 = OMe$		**5p** / **5'p**: $R^2 = OMe$, (57) [1:1.3]
16	**1e**	**2a**	**5q**, (39)

[a]Reaction conditions: **1** (1 mmol), **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), Na_2CO_3 (1 mmol), *o*-xylene (3 mL) at 150 °C under N_2 for 2 h. [b]GC yield based on the amount of **2** used. Value in parentheses indicates yield after purification. [c]Contaminated with an isomer (**5f**/isomer = 92:8). [d]Contaminated with an isomer (**5g**/isomer = 81:19). [e]With Na_2CO_3 (0.5 mmol) at 130 °C.

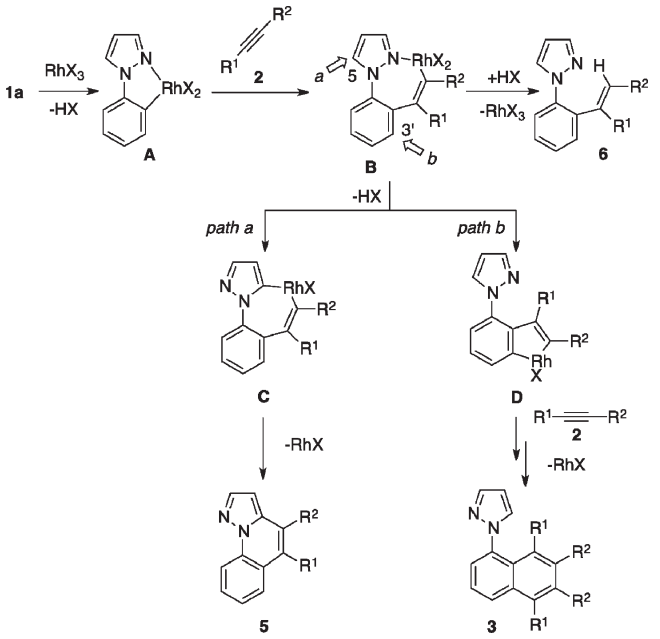
with *m*-chloro-substituted **1t**, the cyclization occurred at the less hindered *ortho*-position predominantly (entry 13). Meanwhile, *m*-fluoro-substituted **1u** reacted at the more hindered position to form **5′o** preferentially (entry 14). In the case of *m*-methoxy-substituted **1v**, comparable amounts of **5p** and **5′p** were obtained. It was reported that similar regioselectivity was observed in the palladium-catalyzed intramolecular arylation[16] as well as the ruthenium-catalyzed *ortho*-alkylation of ketones.[6n,17] The reaction of

(15) See, for example: (a) Abet, V.; Nuñez, A.; Mendicuti, F.; Burgos, C.; Alvarez-Builla, J. *J. Org. Chem.* **2008**, *73*, 8800. (b) Parenty, A. D. C.; Song, Y.-F.; Richmond, C. J.; Cronin, L. *Org. Lett.* **2007**, *9*, 2253. (c) Gondek, E.; Kityk, I. V.; Danel, A.; Wisla, A.; Sanetra, J. *Synth. Met.* **2006**, *156*, 1348. (d) Bersuker, I. B.; Bahceci, S.; Boggs, J. E.; Pearlman, R. S. *J. Comput.-Aided Mol. Des.* **1999**, *13*, 419. (e) Tomoda, H.; Hirano, T.; Saito, S.; Mutai, T.; Araki, K. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1327. (f) Barrio, J. R.; Sattsangi, P. D.; Gruber, B. A.; Dammann, L. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 7408.

(16) (a) Garcia-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880. (b) Garcia-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066.

(17) Sonoda, M.; Kakiuchi, F.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 3117.

SCHEME 2. Plausible Mechanism for the Reaction of 1a with 2



1-phenyl-3-methylpyrazole (**1e**) with **2a** under the standard conditions gave the corresponding pyrazoloquinoline **5q** (entry 16).

Reaction Mechanism. A plausible mechanism for the reaction of **1a** with alkyne **2**, through directed metalation involving rhodacycle intermediates **A**−**D**,[18] is illustrated in Scheme 2 as the representative (neutral ligands are omitted). In the first step, coordination of the 2-N atom of **1a** to a Rh^{III} species appears to be the key for the regioselective C−H bond cleavage[19] to afford **A**. Then, alkyne insertion into the C−Rh bond of **A** may occur to form a common intermediate **B**. In the cases using unsymmetrical alkynes **2e** and **2f**, Rh tends to add on the sp carbon bearing a phenyl group, as in other related oxidative couplings reported previously.[4k,7b,8a,9a,10a] Interaction between Rh and the phenyl group may direct the coordination and insertion steps of such alkynes. In DMF, **B** undergoes the second cyclorhodation at the 3′-position of 1-phenyl ring (path b) to form **D**, and the subsequent second alkyne insertion and reductive elimination take place to produce a 1:2 coupling product **3**. The resulting $Rh^{I}X$ species is oxidized by the added copper(II) salt to regenerate $Rh^{III}X_3$. In the 1:4 coupling, the second homologation may proceed by the same mechanism to form **4**. In *o*-xylene, on the other hand, there seem to be at least two additional pathways from **B**. One of them involves C−H bond cleavage at the 5-position of the pyrazolyl ring (path a) forming a seven-membered rhodacycle intermediate **C** and the subsequent reductive elimination to give **5**. Another route occurs via protonolysis of the C−Rh bond of **B** by HX to form **6**.[20] The latter pathway can be eliminated effectively by the addition of a suitable base such as Na_2CO_3.

For providing further mechanistic information, competitive reactions of (d_0-phenyl)pyrazole (**1a**-d_0) and (d_5-phenyl)-pyrazole (**1a**-d_5) with **2a** were conducted under 1:1 and 1:2 coupling conditions (see the Supporting Information). In the early stage of these reactions, significant primary isotopic effects of 3.4 and 4.6 were observed for the 1:1 and 1:2 couplings, respectively, which suggests that the rate-determining step in each case involves C−H(D) bond cleavage.

Jones et al. reported that a trifluoromethyl-substituted phenylimine underwent cyclometalation by $[Cp^*RhCl_2]_2$ or $[Cp^*IrCl_2]_2$ 10 times slower than the corresponding methoxy-substituted one, which is consistent with an electrophilic activation mechanism.[12e] In our case, however, such a deactivation effect by electron-withdrawing groups was not observed (entry 8, Table 2; entry 10, Table 3; and entries 11−14, Table 5). Actually, the reactions involving the cleavage of C−H bonds adjacent to a fluoro substituent took place rather efficiently. Such substituent effects, including the regioselectivity in the 1:1 coupling of 1-(3-substituted phenyl)pyrazoles **1t**−**v** with **2a** (entries 13−15, Table 5), appear to be roughly similar to those observed in cyclopalladation via a proton-abstraction mechanism,[16,21,22] rather than those in electrophilic cyclorhodation and -iridation.[12e,g,23]

Theoretical Studies of the Metalation. As described above, the regioselectivity of metalation of the present Rh-catalysis is highly dependent on the nature of solvent. To shed more light on the observation, a computational study of the rhodacycles was carried out using RISM-SCF-SEDD, which is a hybrid method of quantum chemistry and statistical mechanics for molecular liquid. The method has been successfully applied to a wide range of chemical reactions in solution. Different from PCM, the method enables us to explicitly treat solvent molecule. However, highly accurate quantum chemical computation can be employed with reasonable computational costs because of the analytically described nature of RISM theory. It is our intent here to only describe the brief summary of the theory. More lengthy discussions of the theory can be found in the literature.[24]

The influence of the rhodacycle was studied with the model system **B** (Scheme 2, X = Cp and OAc, $R^1 = R^2 =$ H). All of the species have been optimized at the B3LYP level in the gas phase, and the influence of the solvent (DMF) was considered through RISM-SCF-SEDD single-point

(18) The stoichiometric reactions of some palladacycles with alkynes to give naphthalenes were reported: (a) Dupont, J.; Pfeffer, M.; Rotteveel, M. A. *Organometallics* **1989**, *8*, 1116. (b) Dupont, J.; Pfeffer, M.; Daran, J.-C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421. (c) Reference 4d.

(19) Catalytic functionalizations involving N-directed C−H activation of 1-phenylpyrazoles have been reported. Acylation: (a) Asaumi, T.; Matsuo, T.; Fukuyama, T.; Ie, Y.; Kakiuchi, F.; Chatani, N. *J. Org. Chem.* **2004**, *69*, 4433. (b) Asaumi, T.; Chatani, N.; Matsuo, T.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **2003**, *68*, 7538. Arylation: (c) Oi, S.; Sakamoto, H.; Funayama, R.; Inoue, Y. *Chem. Lett.* **2008**, *37*, 994. (d) Ackermann, L.; Althammer, A.; Born, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2619. (e) Shabashov, D.; Daugulis, O. *Org. Lett.* **2005**, *7*, 3657Vinylation: (f) Umeda, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7094.

(20) A similar mechanism has been proposed for the Ru-catalyzed coupling of 2-phenylpyridine with alkynes (see ref 14e). However, the participation of another sequence involving oxidative addition of C−H bond to Rh^{I} species followed by alkyne insertion into the formed Rh−H bond cannot be excluded.

(21) Pascual, S.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *Tetrahedron* **2008**, *64*, 6021.

(22) (a) Lafrance, M.; Lapointe, D.; Fagnou, K. *Tetrahedron* **2008**, *64*, 6015. (b) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 10848. (c) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496. (d) Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754.

(23) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210.

(24) (a) *Continuum Solvation Models in Chemical Physics*; Mennucci, B., Cammi, R., Eds.; John Wiley & Sons: Chichester, UK, 2007. (b) *Molecular Theory of Solvation, Understanding Chemical Reactivity*; Hirata, F., Ed.: Kluwer Academic: Dordrecht, Netherlands, 2003. (c) *Computational Biochemistry and Biophysics*; Becker, O. M., MacKerell, A. D., Jr., Roux, B., Watanabe, M., Eds.; Marcel Dekker: New York, 2001.

TABLE 6. Relative Free Energy of Each Species in Scheme 2[a]

media	path a: B + Cl^-	path a: **5** + $[CpRhCl]^-$ + AcOH	path a: **5** + [CpRh(AcOH)] + Cl^-
gas (*o*-xylene)	0.0	−17.1	−3.3
DMF	0.0	7.8	16.1

media	path b: B + C_2H_2 + Cl^-	path b: **3** + $[CpRhCl]^-$ + AcOH	path b: **3** + [CpRh(AcOH)] + Cl^-
gas (*o*-xylene)	0.0	−53.9	−40.2
DMF	0.0	−27.1	−18.7

[a]All of the energies are given in kcal/mol, and the DMF energies are obtained by GF methods.

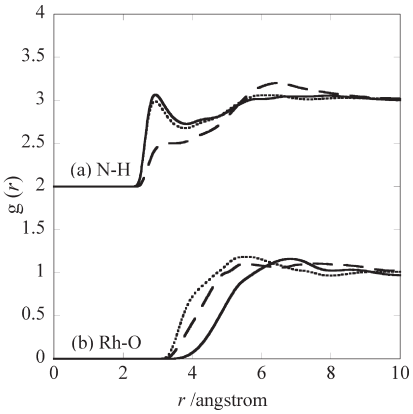


FIGURE 1. Radial distribution functions between (a) the nitrogen of pyrazole and hydrogen of DMF in **B** (dashed line), **5** (solid line), and **3** (dotted line) and (b) the rhodium center and oxygen site of DMF in **B** (dashed line), $[CpRhCl]^-$ (solid line), and [CpRh(AcOH)] (dotted line).

calculations on the gas-phase-optimized geometries. The standard gas-phase computations are used as a substitute for the reaction in *o*-xylene. The reaction mechanisms of both path a and path b from **B** were studied. Here we briefly summarize only the essential part of the computations, and the full description will be reported elsewhere.

The obtained relative free energy of species **B**, **5**, and **3** are summarized, Table 6. This shows that both path a and path b are exothermic in *o*-xylene (gas phase), but path a is endothermic in DMF. This is fully consistent with the experimental results. The essential difference between the two environments is attributed to the change in solvation free energy.

In the RISM-SCF-SEDD method, the solvation structure is described through radial distribution functions (RDFs). We analyzed the RDFs because the first-solvation-shell effects between solvent and the nitrogen of pyrazole and the coordination of solvent to Rh might be responsible for the product selectivity. Since the essential differences in free energy are seen in the products, we analyzed the reactant **B** and the products **5**, **3**, $[CpRhCl]^-$, and [CpRh(AcOH)]. The RDFs of species **B**, **5**, and **3** between the solute nitrogen and solvent hydrogen atoms are shown in Figure 1a. The sharp peaks around 3.0 Å correspond to hydrogen bonding between the nitrogen of pyrazole and the DMF hydrogen. The broad peak located around 6.4 Å is the hydrogen atom of DMF distant from nitrogen. This indicates that the free nitrogen of pyrazole both in **5** and **3** forms a hydrogen bond, but it is relatively weak because the height is slightly lower than a typical one.[25] The RDFs between the solute Rh and solvent oxygen in **B**, $[CpRhCl]^-$, and [CpRh(AcOH)] are shown in Figure 1b. The peaks positioned around 5.5 and 6.8 Å are associated to the oxygen atom of DMF. This indicates that the Rh center of catalysis is not directly coordinated with the oxygen of DMF in all species against our better instincts.

Conclusions

We have demonstrated that multiply substituted polycyclic aromatic and heteroaromatic compounds can be constructed efficiently by the oxidative 1:1, 1:2, and 1:4 coupling reactions of phenylazoles with internal alkynes in the presence of a rhodium catalyst and a copper oxidant. Substrates bearing electron-withdrawing groups underwent the couplings more smoothly, which is consistent with a proton-abstraction mechanism for the C−H bond cleavage steps by Rh^{III} species. A computational study has been carried out to shed further light on the dependence of the reaction pathway on the nature of solvent. The present procedure appears to be highly useful for the straightforward synthesis of various functionalized π-conjugated molecules. Actually, some of products exhibit intense fluorescence in the solid state. Studies are underway toward the further development of this chemistry.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC−MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

1-Arylpyrazoles **1b**−**d**, **1p**−**v**, **1a**-d_5,[26] 1-methyl-2-phenylbenzimidazole **1g**,[27] 5-aryl-2-phenyloxazoles **1j**−**m**,[28,29] 2-arylbenzoxazole **1o**,[28] and diarylacetylenes **2b**−**d**[30] were prepared according to published procedures. Other starting materials were commercially available.

The fluorescence analysis of some products was carried out with the samples recrystallized from hexane−toluene or hexane−dichloromethane and then crashed.[31]

General Procedure for 1:2 Coupling of Phenylazoles with Alkynes. To a 20 mL two-necked flask were added phenylazole **1** (1 mmol), internal alkyne **2** (1 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg), $C_5H_2Ph_4$ (0.04 mmol, 14.8 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 199 mg), dibenzyl (ca. 50 mg) as internal standard, and DMF (5 mL). The resulting mixture was stirred under N_2 at 80 °C. GC and GC−MS analyses of the mixture confirmed formation of **3**. After cooling, the reaction mixture was poured into H_2O (100 mL) containing ethylenediamine (2 mL), extracted with dichloromethane (100 mL), washed with H_2O (100 mL, three times), and dried over $CaCl_2$. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate as eluant.

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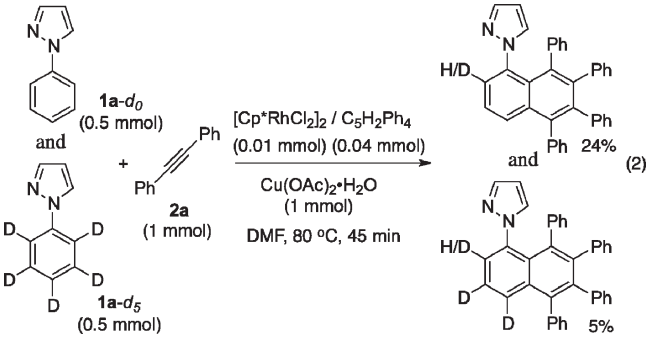
General Procedure for 1:4 Coupling of Phenylazoles with Alkynes. To a 20 mL two-necked flask were added phenylazole **1** (0.125 mmol), internal alkyne **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg), $C_5H_2Ph_4$ (0.04 mmol, 14.8 mg), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol, 100 mg), and DMF (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 6 h. After cooling, the reaction mixture was poured into H_2O (100 mL) containing ethylenediamine (2 mL), extracted with dichloromethane (100 mL), washed with H_2O (100 mL, three times), and dried over $CaCl_2$. The product **4** was isolated by thin-layer chromatography on silica gel using hexane−ethyl acetate as eluant.

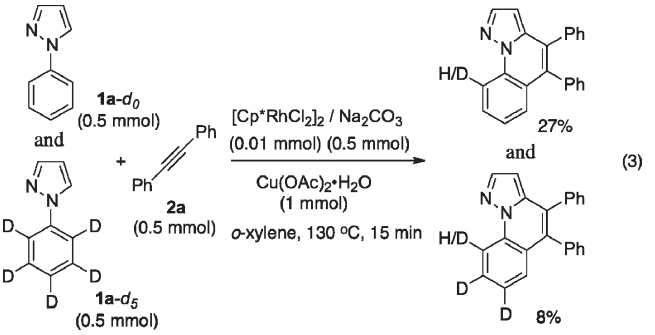
General Procedure for 1:1 Coupling of 1-Phenylpyrazoles with Alkynes. To a 20 mL two-necked flask were added 1-phenylpyrazole **1** (1 mmol), internal alkyne **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.2 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 199 mg), Na_2CO_3 (1 mmol, 106 mg), dibenzyl (ca. 50 mg) as internal standard, and *o*-xylene (3 mL). The resulting mixture was stirred under N_2 at 150 °C. GC and GC−MS analyses of the mixture confirmed formation of **5**. After cooling, the reaction mixture was poured into H_2O (100 mL) containing ethylenediamine (2 mL), extracted with dichloromethane (100 mL), washed with H_2O (100 mL, three times), and dried over $CaCl_2$. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate as eluant and subsequent Kugelrohr distillation (50 °C, 0.01 mmHg) to remove unreacted phenylpyrazole **1**.

Synthesis of (d_5-Phenyl)pyrazole (1a-d_5). (d_5-Phenyl)pyrazole (**1a**-d_5) was prepared according to the published procedure.[26] To a 20 mL two-necked flask were added pyrazole (3 mmol), d_5-bromobenzene (2 mmol), Cu_2O (0.1 mmol), Cs_2CO_3 (4 mmol), salicylaldoxime (0.4 mmol), and CH_3CN (1.2 mL). The resulting mixture was stirred under N_2 at 65 °C for 24 h. After cooling, the reaction mixture was poured into 1 N HCl aq (100 mL), extracted with Et_2O (100 mL), washed with H_2O (100 mL), and dried over Na_2SO_4. The product **1a**-d_5 was isolated by column chromatography on silica gel using hexane−ethyl acetate (99:1) as eluant (179.1 mg, 60%): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, J = 1.8, 2.2 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.92 (d, J = 2.2 Hz, 1H).

Competitive Reactions under 1:2 Coupling Conditions. To a 20 mL two-necked flask were added (d_0-phenyl)pyrazole (**1a**-d_0) (0.5 mmol), (d_5-phenyl)pyrazole (**1a**-d_5) (0.5 mmol), diphenylacetylene (**2a**) (1 mmol), $Cu(OAc)_2-H_2O$ (1 mmol), $C_5H_2Ph_4$ (0.04 mmol), dibenzyl (ca. 50 mg) as internal standard, and DMF (5 mL). The resulting mixture was stirred under N_2 at 80 °C for 45 min (eq 2). After cooling, the reaction mixture was poured into H_2O (100 mL) containing ethylenediamine (2 mL), extracted with CH_2Cl_2 (100 mL), washed with H_2O (100 mL, three times), and dried over $CaCl_2$. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate (9:1) as eluant (72.3 mg, 29%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (dd, J = 1.8, 2.2 Hz, 1H), 6.61−6.84 (m, 15H), 7.15 (d, J = 2.2 Hz, 1H), 7.19−7.26 (m, 6H), 7.39−7.44 (m, 1.8H), 7.73−7.77 (m, 0.82H). The kinetic isotope effect was determined by ^{1}H NMR: k_H/k_D = 0.82/0.18 = 4.56.



Competitive Reactions under 1:1 Coupling Conditions. To a 20 mL two-necked flask were added (d_0-phenyl)pyrazole (**1a**-d_0) (0.5 mmol), (d_5-phenyl)pyrazole (**1a**-d_5) (0.5 mmol), diphenylacetylene (**2a**) (0.5 mmol), $Cu(OAc)_2-H_2O$ (1 mmol), Na_2CO_3 (0.5 mmol), dibenzyl (ca. 50 mg) as internal standard, and *o*-xylene (3 mL) (eq 3). The resulting mixture was stirred under N_2 at 130 °C for 15 min. After cooling, the reaction mixture was poured into H_2O (100 mL) containing ethylenediamine (2 mL), extracted with Et_2O (100 mL), washed with H_2O (100 mL, three times), and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate (99:1) as eluant and subsequent Kugelrohr distillation (50 °C, 0.01 mmHg) to remove unreacted phenylpyrazole **1** (56.2 mg, 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, J = 2.2 Hz, 1H), 7.16−7.29 (m, 10H), 7.32 (t, J = 7.3 Hz, 0.77H), 7.49 (d, J = 8.4 Hz, 0.77H), 7.65 (t, J = 7.3 Hz, 0.77H), 7.99 (d, J = 2.2 Hz, 1H), 8.68 (d, J = 8.4 Hz, 0.80H); kinetic isotope effect determined by ^{1}H NMR: k_H/k_D = 0.77/0.23 = 3.35.



Computational Details. The calculations were performed with the Gaussian03[32] and GAMESS package[33] at the B3LYP[34] level. Rh was represented by the effective core potential (ECP) from the Stuttgart group and the associated basis set.[35] A 6-31G(d) basis set was used for all the atoms (C,N,O) except for H for 6-31G basis set and for Cl for 6-31+G(d) basis set.[36] The geometry optimizations were performed without any symmetry constraint followed by frequency calculations to confirm that a minimum or a transition state had been reached. The solvation effect from DMF is treated using the RISM-SCF-SEDD[37] as implemented in GAMESS modified by ourselves. The geometries obtained in gas phase were used without further reoptimization within the RISM-SCF-SEDD methodology,

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and the previously reported Lennard-Jones parameters were used.[38]

1-(1,2,3,4-Tetraphenylnaphthalen-5-yl)pyrazole (3a):[11a] mp 173−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (dd, J = 1.8, 2.2 Hz, 1H), 6.63−6.81 (m, 15H), 7.15 (d, J = 2.2 Hz, 1H), 7.22−7.26 (m, 6H), 7.41−7.42 (m, 2H), 7.74−7.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.0, 124.8, 125.0, 125.1, 125.4, 126.2 (overlapped), 126.5, 126.6, 127.5, 127.6 (overlapped), 128.9, 131.0 (overlapped), 131.1, 131.2, 132.3, 134.3, 136.2, 137.9, 138.7, 139.4, 139.6, 139.7, 139.9, 140.2, 140.3, 142.2; HRMS m/z calcd for $C_{37}H_{26}N_2$ (M^+) 498.2096, found 498.2091. Anal. Calcd for $C_{37}H_{26}N_2$: C, 89.13; H, 5.26; N, 5.62. Found: C, 88.91; H, 5.52; N, 5.43.

1-[1,2,3,4-Tetrakis-(4-methylphenyl)naphthalen-5-yl]pyrazole (3b):[11a] mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.31(s, 3H), 5.71(t, J = 2.2 Hz, 1H), 6.48−6.65 (m, 12H), 7.05−7.08 (m, 5H), 7.21−7.22 (m, 1H), 7.35−7.36 (m, 2H), 7.69−7.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.96, 21.00, 21.04, 21.2, 105.6, 124.4, 126.7, 126.9, 127.2, 127.3, 127.7, 128.3, 128.8, 130.8 (overlapped), 131.0, 131.1, 132.3, 134.06, 134.10, 134.4, 134.5, 135.8, 136.1, 136.7, 136.8, 137.3, 137.5, 137.9, 138.5, 139.6, 139.9, 142.3; HRMS m/z calcd for $C_{41}H_{34}N_2$ (M^+) 554.2722, found 554.2719.

1-[1,2,3,4-Tetrakis-(4-methoxyphenyl)naphthalen-5-yl]pyrazole (3c):[11a] mp 107−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 3H), 3.61 (s, 3H), 3.65 (s, 3H), 3.79 (s, 3H), 5.77 (dd, J = 1.8, 2.2 Hz, 1H), 6.32 (d, J = 8.8 Hz, 2H), 6.34 (d, J = 8.8 Hz, 2H), 6.40 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.8 Hz, 2H), 6.63−6.67 (m, 2H), 6.68 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 7.08−7.10 (m, 2H), 7.12 (d, J = 2.2 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.37−7.39 (m, 2H), 7.73−7.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 54.9, 55.09, 55.12, 105.8, 111,85, 111.91, 112.1 (overlapped), 113.1, 124.5, 127.3, 127.6, 128.8, 131.9, 132.06, 132.14, 132.26, 132.30, 132.4, 132.9, 133.1, 134.7, 135.8, 137.8, 138.5, 139.8, 140.0, 142.3, 156.8, 156.9 (overlapped), 158.0; HRMS m/z calcd for $C_{41}H_{34}N_2O_4$ (M^+) 618.2519, found 618.2516.

1-[1,2,3,4-Tetrakis-(4-chlorophenyl)naphthalen-5-yl]pyrazole (3d):[11a] mp 282−283 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd, J = 1.8, 2.2 Hz, 1H), 6.49−6.56 (m, 2H), 6.65−6.71 (m, 4H), 6.76−6.83 (m, 4H), 6.88−6.90 (m, 2H), 7.09−7.11 (m, 2H), 7.15 (d, J = 1.8 Hz, 1H), 7.25−7.28 (m, 3H), 7.41−7.48 (m, 2H), 7.67−7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.3, 125.5, 126.2, 126.6, 127.0, 127.3, 127.8, 128.1, 128.2, 128.7, 131.3, 131.4, 131.7, 131.9 (overlapped), 132.0, 132.1, 132.2, 133.1, 134.2, 135.6, 137.4, 137.8, 137.9, 138.00, 138.03, 138.3, 140.3, 140.6; HRMS m/z calcd for $C_{37}H_{22}Cl_4N_2$ (M^+) 634.0537, found 634.0544. Anal. Calcd for $C_{37}H_{22}Cl_4N_2$: C, 69.83; H, 3.48; N, 4.40. Found: C, 69.87; H, 3.57; N, 4.39.

1-(1,4-Dibutyl-2,3-diphenylnaphthalen-5-yl)pyrazole (3e):[11a] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (t, J = 7.3 Hz, 3H), 0.69−0.79 (m, 5H), 1.02−1.10 (m, 2H), 1.20−1.29 (m, 2H), 1.54−1.59 (m, 3H), 1.90 (s, br, 1H), 2.84 (t, J = 8.1 Hz, 2H), 6.44 (t, J = 2.2 Hz, 1H), 6.92−7.12 (m, 10H), 7.40 (d, J = 7.1 Hz, 1H), 7.53 (d, J = 7.3 Hz,1H), 7.72(d, J = 2.2 Hz, 1H), 7.73 (d, J = 2.2 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 13.6, 22.6, 23.1, 30.2, 30.4, 33.3, 35.4, 106.4, 124.2, 125.7, 125.9, 126.9, 127.1 (overlapped), 127.2, 128.2, 130.0 (overlapped), 131.9, 133.8, 134.6, 134.7, 137.9, 140.1, 140.2, 141.3, 141.5, 142.3; HRMS m/z calcd for $C_{33}H_{34}N_2$ (M^+) 458.2722, found.458.2718.

1-(1,4-Dimethyl-2,3-diphenylnaphthalen-5-yl)pyrazole (3f):[11a] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3H), 2.49 (s, 3H), 6.45 (dd, J = 1.8, 2.2 Hz, 1H), 6.91−7.15 (m, 10H), 7.51 (d, J = 7.4, 1H), 7.58 (dd, J = 7.4, 8.4 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 17.4, 106.5, 124.5, 125.9, 126.0, 126.9, 127.3 (overlapped), 129.1, 129.6, 130.3 (overlapped), 132.5, 134.1, 138.0, 140.1, 140.2, 141.4, 141.7, 142.6; HRMS m/z calcd for $C_{27}H_{22}N_2$ (M^+) 374.1783, found 374.1775.

1-(6-Methyl-1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (3g). mp 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 5.71 (dd, J = 1.8, 2.2 Hz, 1H), 6.57−6.60 (m, 1H), 6.63−6.83 (m, 14H), 6.99 (d, J = 2.2 Hz, 1H), 7.15−7.25 (m, 6H), 7.28 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 105.7, 124.8, 124.9, 125.2, 125.5, 126.0, 126.1, 126.3, 126.4, 126.5 (overlapped), 127.4, 127.6, 128.1, 128.8, 128.9, 130.3, 130.8, 130.97, 130.99, 131.03, 131.06, 131.11, 131.4, 132.4, 133.0, 135.6, 136.0, 137.2, 138.5, 138.7, 139.5, 139.6, 139.8, 140.29, 140.32, 142.4; HRMS m/z calcd for $C_{38}H_{28}N_2$ (M^+) 512.2252, found 512.2254.

1-(7-Methyl-1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (3h). mp 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.70 (d, J = 1.8, 2.2 Hz, 1H), 6.61−6.64 (m, 2H), 6.72−6.84 (m, 13H), 7.12 (d, J = 2.2 Hz, 1H), 7.16−7.29 (m, 7H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 105.9, 125.0, 125.3, 125.6, 126.2, 126.47, 126.50, 127.6 (overlapped), 127.8, 129.7, 131.0 (overlapped), 131.2, 131.3, 132.3, 134.4, 134.7, 135.9, 137.7, 138.1, 139.5, 139.7, 139.76, 139.79, 140.3, 140.5, 141.2; HRMS m/z calcd for $C_{38}H_{28}N_2$ (M^+) 512.2252, found 512.2247.

1-(8-Fluoro-1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (3i). mp 123−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, J = 2.2 Hz, 1H), 6.61−6.82 (m, 15H), 7.05−7.19 (m, 7H), 7.22 (d, J = 1.8 Hz, 1H), 7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.2, 110.7 (d, J = 24.5 Hz), 123.7 (d, J = 8.4 Hz), 124.9 (d, J = 9.9 Hz), 125.2, 125.3, 125.4, 126.1, 126.26, 126.30, 126.4, 126.8, 127.6 (d, J = 9.9 Hz), 129.8, 129.9, 130.9, 131.0, 132.3, 134.3, 135.1 (d, J = 2.3 Hz), 136.5 (d, J = 2.3 Hz), 138.9, 139.5, 139.7, 140.0, 141.4, 141.5 (d, J = 22.9 Hz), 143.1 (d, J = 2.3 Hz), 160.5 (d, J = 261 Hz); HRMS m/z calcd for $C_{37}H_{25}FN_2$ (M^+) 516.2002, found 516.1996.

3-Methyl-1-(1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (3j):[11a] mp169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 5.46 (d, J = 2.2 Hz, 1H), 6.56−6.81 (m, 15H), 7.09 (d, J = 2.6 Hz, 1H), 7.18−7.24 (m, 5H), 7.38−7.40(m, 2H), 7.70−7.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 105.6, 124.7, 124.97, 124.99, 125.3, 125.5, 126.2, 126.5, 126.6, 127.1, 127.6 (overlapped), 127.8, 128.7, 131.0 (overlapped), 131.2, 132.5, 134.4, 136.3, 138.0, 138.6, 139.5, 139.6, 139.7, 140.2, 140.4, 142.0, 148,9; HRMS m/z calcd for $C_{38}H_{28}N_2$ (M^+) 512.2252, found 512.2244. Anal. Calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 89.07; H, 5.65; N, 5.37.

3,5-Dimethyl-1-(1,2,3,4-tetraphenylnaphthalen-5-yl)pyrazole (3k):[11a] mp 201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.02 (s, 3H), 5.18 (s, 1H), 6.50−6.52 (m, 1H), 6.70−6.86 (m, 14H), 7.20−7.29 (m, 6H), 7.39−7.43 (m, 1H), 7.72−7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 13.3, 105.2, 124.7, 125.0, 125.07, 125.10, 125.28, 125.30, 126.1, 126.2, 126.4, 126.5, 126.6, 127.5, 127.6, 128.0, 128.8, 129.5, 130.8, 130.9, 130.98, 131.00, 131.3, 131.4, 131.5, 134.4, 136.4, 138.6, 139.1, 139.60, 139.64, 140.0, 140.3, 140.4, 142.1, 148.1; HRMS m/z calcd for $C_{39}H_{30}N_2$ (M^+) 526.2409, found 526.2406. Anal. Calcd for $C_{39}H_{30}N_2$: C, 88.94; H, 5.74; N, 5.32. Found: C, 88.87; H, 5.98; N, 4.93.

1-Methyl-2-(1,2,3,4-tetraphenylnaphthalen-5-yl)benzimidazole (3l):[11a] mp 198−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 6.24−6.28 (m, 1H), 6.30−6.34 (m,1H), 6.59−6.63 (m, 2H), 6.68−6.94 (m, 12H), 7.10−7.13 (m, 2H), 7.18−7.22 (m, 2H), 7.24−7.27 (m, 3H), 7.44−7.53 (m, 3H), 7.80−7.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 108.6, 119.2, 121.5, 121.8, 124.5, 124.7, 124.8, 125.1, 125.4, 125.7, 126.1, 126.35, 126.42, 126.57, 126.61, 127.5, 127.7, 128.4, 129.0, 129.8, 130.8, 131.0,

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131.08, 131.11, 131.2, 131.25, 131.33, 131.5, 132.5, 133.4, 134.9, 137.7, 138.7, 138.9, 139.6, 139.6, 140.3, 140.4, 141.7, 142.8, 154.2; HRMS *m*/*z* calcd for $C_{42}H_{30}N_2$ (M^+) 562.2409, found 562.2407.

2-(1,2,3,4-Tetraphenylnaphthalen-5-yl)pyridine (3m): mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62−6.80 (m, 16H), 6.93 (d, J = 7.7 Hz, 1H), 7.14−7.23 (m, 6H), 7.39 (d, J = 5.5 Hz, 2H), 7.70 (dd, J = 4.8, 5.2 Hz, 1H), 8.23 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.1, 124.7, 124.9, 125.1, 125.2 (overlapped), 126.1, 126.35, 126.42, 127.43, 128.0, 130.0, 130.7, 131.0 (overlapped), 131.4, 131.9, 132.9, 133.7, 134.9, 137.8, 138.6, 139.1, 139.9, 140.1, 140.5, 140.6, 140.8, 141.1, 148.1, 161.8; HRMS *m*/*z* calcd for $C_{39}H_{27}N$ (M^+) 509.2143, found 509.2148.

1-(1,2,3,4,5,6,7,8-Octaphenylanthlacen-9-yl)pyrazole (4a): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (t, J = 1.8 Hz, 1H), 6.46−6.54 (m, 4H), 6.55−6.65 (m, 8H), 6.66−6.86 (m, 20H), 6.94−7.06 (m, 8H), 7.09 (d, J = 7.4 Hz, 2H), 8.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.2, 124.6, 124.8, 124.9, 125.3, 126.0, 126.1, 126.15, 126.20, 126.5, 127.1, 127.3, 129.0, 129.1, 130.7, 130.8, 130.9, 131.0, 131.1, 131.2, 131.7, 133.2, 135.6, 135.8, 138.4, 139.0, 139.3, 140.3, 140.49, 140.52, 142.7; HRMS *m*/*z* calcd for $C_{65}H_{44}N_2$ (M^+)852.3504, found 852.3520.

3-Methyl-1-(1,2,3,4,5,6,7,8-octaphenylanthlacen-9-yl)pyrazole (4b): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3H), 4.34 (d, J = 2.2 Hz, 1H), 6.50−6.60 (m, 7H), 6.61−6.84 (m, 24H), 6.95−7.04 (m, 8H), 7.07 (d, J = 7.3 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 105.2, 124.5, 124.78, 124.80, 125.1, 125.3, 126.0, 126.16, 126.19, 126.5 (overlapped), 127.1, 127.2, 128.7, 129.0, 130.8, 130.96, 130.98, 131.2 131.5, 131.8, 133.3, 135.8, 136.5, 138.3, 139.0, 139.2, 140.4, 140.6, 142.5, 149.0; HRMS *m*/*z* calcd for $C_{66}H_{46}N_2$ (M^+)866.3661, found 866.3649. Anal. Calcd for $C_{66}H_{46}N_2$: C, 91.42; H, 5.35; N, 3.23. Found: C, 91.33; H, 5.38; N, 3.32.

3,5-Dimethyl-1-(1,2,3,4,5,6,7,8-octaphenylanthlacen-9-yl)-pyrazole (4c): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 3H), 1.83 (s, 3H), 4.16 (s, 1H), 6.46−6.84 (m, 30H), 6.93−7.03 (m, 8H), 7.04−7.09 (m, 2H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 31.6, 106.2, 124.5, 124.6, 124.8, 124.9, 125.3, 126.0, 126.2, 126.5, 127.1, 127.2, 128.4, 129.1, 129.9, 130.95, 130.96, 130.98, 131.2, 131.5, 131.8, 131.9, 135.7, 138.3, 138.35, 138.37, 139.0, 140.4, 140.6, 142.1, 142.7, 148.6; HRMS *m*/*z* calcd for $C_{67}H_{48}N_2$ (M^+) 880.3817, found 880.3824.

2-(1,2,3,4,5,6,7,8-Octaphenylanthracen-9-yl)-5-phenyloxazole (4d): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 6.45−6.48 (m, 2H), 6.51−6.56 (m, 6H), 6.62−6.70 (m, 10H), 6.75−6.81 (m, 11H), 6.98−7.10 (m, 13H), 7.18−7.22 (m, 1H), 7.24−7.29 (m, 2H), 8.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.20, 122.22, 123.5, 124.3, 124.6, 124.8, 125.3, 125.8, 126.1, 126.2, 126.5, 127.16, 127.21, 128.2, 128.7, 130.3, 130.9, 131.0, 131.1, 131.2, 131.97, 131.99, 137.0 (overlapped), 138.3, 138.5, 139.0, 139.1, 140.4, 140.6, 142.6, 150.7, 158.8; ESI-MS *m*/*z* calcd for $C_{71}H_{47}NO$ (M + H) 930.3736, found 930.3703.

5-(2-Methylphenyl)-2-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)oxazole (4e): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 3H), 6.08 (s, 1H), 6.41 (t, J = 7.3 Hz, 2H), 6.48−6.58 (m, 7H), 6.64−6.72 (m, 10H), 6.75−6.83 (m, 11H), 6.98−7.07 (m, 10H), 7.10−7.13 (m, 2H), 7.14−7.19 (m, 1H), 7.35 (d, J = 7.7 Hz, 1H), 8.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 122.2, 124.7, 124.8, 125.3, 125.5, 125.8, 126.1, 126.2, 126.3, 126.5, 126.79, 126.82, 127.2, 127.6, 130.3, 130.6, 130.9, 131.0, 131.1, 131.2, 131.9, 132.0, 133.7, 137.0, 138.3, 138.5, 139.0, 139.1, 140.4, 140.6, 142.6, 149.9, 158.1; HRMS *m*/*z* calcd for $C_{72}H_{49}NO$ (M^+) 943.3814, found 943.3820.

5-(Naphthalen-1-yl)-2-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)oxazole (4f:). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 6.40 (t, J = 7.3 Hz, 2H), 6.47−6.57 (m, 7H), 6.65−6.84 (m, 21H), 6.98−7.09 (m, 10H), 7.39 (d, J = 6.2 Hz, 2H), 7.43−7.49 (m, 3H), 7.82−7.86 (m, 1H), 7.89−7.94 (m, 1H), 8.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.0, 124.8, 125.0, 125.1, 125.3, 125.5, 125.6, 125.65, 125.69, 125.9, 126.0, 126.1, 126.3, 126.5, 127.2, 128.1, 128.6, 128.8, 130.2, 130.3, 130.8, 131.0, 131.1, 131.3, 131.9, 132.0, 133.9, 136.9, 138.4, 138.5, 139.0, 139.2, 140.4, 140.6, 142.6, 149.6, 158.9; HRMS *m*/*z* calcd for $C_{75}H_{49}NO$ (M^+) 979.3814, found 979.3808.

5-(4-Methoxyphenyl)-2-(1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)oxazole (4g): mp 199−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 5.95 (s, 1H), 6.47 (t, J = 7.0 Hz, 3H), 6.52−6.59 (m, 6H), 6.63−6.72 (m, 10H), 6.74−6.85 (m, 13H), 6.98−7.07 (m, 12H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 113.7, 121.7, 122.2, 124.6, 124.8, 125.3, 125.80, 125.83, 126.1, 126.2, 126.5, 127.2, 130.2, 130.5, 130.9, 131.0, 131.1, 131.2, 131.98, 132.02, 137.0, 138.3, 138.5, 139.0, 139.1, 140.4, 140.7, 142.5, 150.7, 158.1, 158.8; HRMS *m*/*z* calcd for $C_{72}H_{49}NO_2$ (M^+) 959.3763, found 959.3773.

2-(1,2,3,4,5,6,7,8-Octaphenylanthracen-9-yl)-5-(4-trifluoromethylphenyl)oxazole (4h): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (s, 1H), 6.45 (t, J = 7.0 Hz, 3H), 6.50−6.60 (m, 6H), 6.62−6.72 (m, 10H), 6.75−6.83 (m, 11H), 6.98−7.07 (m, 10H), 7.17 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 8.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.7, 124.1 (d, J = 270 Hz), 124.2, 124.7, 124.9, 125.2, 125.3 (d, J = 3.8 Hz), 125.4, 125.8, 126.2, 126.3, 126.5, 127.2, 128.9 (d, J = 32.6 Hz), 130.6, 130.8, 131.0, 131.1, 131.2, 131.87, 131.92, 132.0, 136.7, 138.4, 138.6, 138.9, 139.2, 140.3, 140.5, 142.8, 149.3, 160.0; HRMS *m*/*z* calcd for $C_{72}H_{46}F_3NO$ (M^+) 997.3531, found 997.3557.

2-(1,2,3,4,5,6,7,8-Octaphenylanthlacen-9-yl)benzoxazole (4i):[11a] mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (t, J = 7.7 Hz, 2H), 6.28 (dd, J = 7.7, 8.0 Hz, 4H), 6.54−6.56 (m, 4H), 6.63 (d, J = 8.4 Hz, 4H), 6.67−6.68 (m, 6H), 6.73−6.82 (m, 11H), 6.89−6.94 (m, 2H), 6.97−7.06 (m, 11H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.6, 119.7, 121.8, 122.9, 123.7, 124.1, 125.0, 125.1, 125.4, 126.2, 126.3, 126.6, 127.3, 130.6, 131.0, 131.1, 131.2, 131.3, 131.7, 131.8, 136.9, 138.51, 138.53, 138.6, 139.0, 140.4, 140.6, 141.4, 142.9, 149.8, 161.3; HRMS *m*/*z* calcd for $C_{69}H_{45}NO$ (M^+) 903.3501, found 903.3499.

2-(10-Fluoro-1,2,3,4,5,6,7,8-octaphenylanthracen-9-yl)benzoxazole (4j): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (t, J = 7.3 Hz, 2H), 6.30 (dd, J = 7.7, 8.0 Hz, 4H), 6.49 (d, J = 7.7 Hz, 4H), 6.59−6.70 (m, 14H), 6.79−6.83 (m, 7H), 6.92−7.04 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.5, 117.6 (d, J = 6.9 Hz), 119.7, 119.9 (d, J = 9.2 Hz), 123.1, 124.0, 124.5, 125.1, 125.27, 125.34, 125.8, 126.3, 126.5, 126.8, 129.8, 129.9, 130.7, 131.1, 131.8, 133.48, 133.51, 134.6, 136.6, 138,3, 139.7, 140.1, 140.3, 141.37, 141.40 (d, J = 5.4 Hz), 142.9, 149.8, 158.0 (d, J = 276 Hz), 161.1; HRMS *m*/*z* calcd for $C_{69}H_{44}FNO$ (M^+) 921.3407, found 921.3431.

2-[1,2,3,4,5,6,7,8-Octakis-(4-chlorophenyl)anthracen-9-yl]benzoxazole (4k): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (d, J = 8.1 Hz, 4H), 6.45 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 6.66 (d, J = 8.4 Hz, 4H), 6.75 (d, J = 8.4 Hz, 4H), 6.88 (d, J = 8.4 Hz, 4H), 6.92−6.94 (m, 5H), 7.10−7.18 (m, 7H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3, 119.5, 122.2, 124.3, 125.5, 125.9, 127.1, 127.5, 127.9, 130.4, 131.1, 131.45, 131.54, 131.7, 131.82, 131.84, 132.1, 132.3, 132.4, 133.4, 136.28, 136.33, 136.5, 137.5, 137.8, 137.9, 138.0, 140.7, 141.8, 149.5, 160.4; ESI-MS *m*/*z* calcd for $C_{69}H_{37}Cl_8NO$ (M + H) 1176.0461, found 1176.0431. Anal. Calcd for $C_{69}H_{37}Cl_8NO$: C, 70.25; H, 3.16; N, 1.19. Found: C, 69.86; H, 3.35; N, 1.37.

4,5-Diphenylpyrazolo[1,5-*a*]quinoline (5a): mp 214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J = 2.2 Hz, 1H), 7.17−7.30 (m, 10H), 7.34 (t, J = 7.5, 8.0 Hz,1H), 7.50 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 7.5, 8.0 Hz, 1H), 8.00 (d, J = 2.2 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.0, 115.4, 124.1, 124.6, 127.3, 127.4, 127.9, 128.0 (overlapped), 129.00, 129.03, 130.0, 131.1, 134.0, 134.2, 136.8, 137.0, 139.2, 141.2; HRMS *m*/*z* calcd for $C_{23}H_{16}N_2$ (M^+) 320.1313, found 320.1311. Anal. Calcd for

$C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74. Found: C, 86.04; H, 4.99; N, 8.79.

4,5-Bis(4-methylphenyl)pyrazolo[1,5-*a*]quinoline (5b): mp 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.35 (s, 3H), 6.36 (d, J = 1.8 Hz, 1H), 7.04−7.13 (m, 8H), 7.32 (dd, J = 7.0, 8,4 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 6.4, 7.0 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 100.9, 115.4, 124.42, 124.44, 128.0, 128.7 (overlapped), 128.8, 129.0, 129.9, 131.0, 133.8, 133.9, 134.1, 134.2, 136.8, 136.9, 139.5, 141.1; HRMS m/z calcd for $C_{25}H_{20}N_2$ (M^+) 348.1626, found 348.1628.

4,5-Bis(4-methoxyphenyl)pyrazolo[1,5-*a*]quinoline (5c): mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.81 (s, 3H), 6.38 (d, J = 1.8 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.33 (dd, J = 7.0, 8.4 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 7.0, 7.9 Hz, 1H), 7.99 (d, J = 1.8 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 55.2, 100.9, 113.47, 113.51, 115.4, 124.46, 124.52, 127.9, 128.75, 128.81, 129.1, 129.5, 131.2, 132.2 (overlapped), 133.6, 134.1, 139.6, 141.1, 158.7; HRMS m/z calcd for $C_{25}H_{20}N_2O_2$ (M^+) 380.1525, found 380.1534.

4,5-Bis(4-chlorophenyl)pyrazolo[1,5-*a*]quinoline (5d): mp 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (d, J = 2.2 Hz, 1H), 7.10−7.17 (m, 4H), 7.24−7.28 (m, 2H), 7.29−7.33 (m, 2H), 7.36 (d, J = 7.5, 7.7 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 8.01 (d, J = 2.2 Hz, 1H), 8.68 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.0, 115.6, 123.7, 124.8, 127.6, 128.0, 128.51, 128.53, 129.4, 131.3, 132.3, 133.0, 133.6, 133.7, 134.2, 135.0, 135.2, 138.7, 141.4; HRMS m/z calcd for $C_{23}H_{14}Cl_2N_2$ (M^+) 388.0534, found 388.0529.

4,5-Dipropylpyrazolo[1,5-*a*]quinoline (5e): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05−1.12 (m, 6H), 1.66−1.74 (m, 4H), 2.85 (t, J = 6.1 Hz, 2H), 2.95 (t, J = 6.1 Hz, 2H), 6.54 (d, J = 2.2 Hz, 1H), 7.44 (t, J = 7.0 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 2.2 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.50, 14.52, 23.0, 23.9, 29.8, 32.1, 98.2, 115.8, 123.5, 124.4, 124.9, 127.4, 127.9, 131.3, 134.0, 139.4, 140.9; HRMS m/z calcd for $C_{17}H_{20}N_2$ (M^+) 252.1626, found 252.1621.

5-Butyl-4-phenylpyrazolo[1,5-*a*]quinoline (5f): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.9 Hz, 3H), 1.23−1.34 (m, 2H), 1.54−1.63 (m, 2H), 2.81 (t, J = 8.3 Hz, 2H), 6.07 (d, J = 2.2 Hz, 1H), 7.36−7.39 (m, 2H), 7.42−7.53 (m, 4H), 7.67 (t, J = 7.4 Hz, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.9, 28.4, 33.0, 100.1, 115.9, 123.2, 124.6, 125.6, 127.8, 128.6, 128.7, 128.8, 129.4, 132.5, 134.5, 137.6, 139.7, 140.9; HRMS m/z calcd for $C_{21}H_{20}N_2$ (M^+) 300.1626, found 300.1636.

5-Methyl-4-phenylpyrazolo[1,5-*a*]quinoline (5g): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.06 (d, J = 2.2 Hz, 1H), 7.29−7.43 (m, 6H), 7.56−7.60 (m, 1H), 7.81 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 100.0, 115.6, 124.2, 124.6, 125.4, 127.5, 127.7, 127.9, 128.5, 128.8, 129.7, 134.1, 137.6, 139.5, 140.9; HRMS m/z calcd for $C_{18}H_{14}N_2$ (M^+) 258.1157, found 258.1147.

4,5-Diphenyl-9-methylpyrazolo[1,5-*a*]quinoline (5h): mp 174−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24 (s, 3H), 6.32 (d, J = 2.2 Hz, 1H), 7.13−7.30 (m, 11H), 7.33 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 100.0, 123.8, 125.8, 126.1, 127.1, 127.2, 127.88, 127.91, 128.3, 129.0, 130.0, 131.0, 132.5, 133.6, 134.4, 137.2, 137.5, 140.1, 140.5; HRMS m/z calcd for $C_{24}H_{18}N_2$ (M^+) 334.1470, found 334.1467. Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.06; H, 5.45; N, 8.30.

4,5-Diphenyl-8-methylpyrazolo[1,5-*a*]quinoline (5i): mp 190−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 6.35 (d, J = 2.2 Hz, 1H), 7.13−7.30 (m, 11H), 7.38 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 100.7, 115.3, 121.8, 126.1, 127.17, 127.23, 127.8, 127.88, 127.90, 127.91, 130.1, 131.1, 133.9, 134.0, 136.9, 137.1, 139.3, 139.7, 141.1; HRMS m/z calcd for $C_{24}H_{18}N_2$ (M^+) 334.1470, found 334.1475.

4,5-Diphenyl-7-methylpyrazolo[1,5-*a*]quinoline (5j): mp 219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.34 (d, J = 2.2 Hz, 1H), 7.15−7.31 (m, 11H), 7.49 (dd, J = 1.8, 8.4 Hz, 1H), 7.97 (d, J = 2.2 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 100.7, 115.3, 124.1, 127.2, 127.3, 127.4, 127.90, 127.91, 129.0, 130.0, 130.4, 131.1, 132.3, 133.8, 134.2, 136.9, 137.1, 138.9, 140.9; HRMS m/z calcd for $C_{24}H_{18}N_2$ (M^+) 334.1470, found 334.1464.

4,5-Diphenyl-7-methoxypyrazolo[1,5-*a*]quinoline (5k): mp 199−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.34 (d, J = 2.2 Hz, 1H), 6.92 (d, J = 2.9 Hz, 1H), 7.17−7.31 (m, 11H), 7.95 (d, J = 2.2 Hz, 1H), 8.61 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 100.7, 110.1, 116.8, 117.4, 125.3, 127.32, 127.33, 127.9, 128.0, 129.1, 129.5, 130.0, 131.0, 133.6, 136.8, 137.1, 138.5, 140.6, 156.5; HRMS m/z calcd for $C_{24}H_{18}N_2O$ (M^+) 350.1419, found 350.1423. Anal. Calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 7.99. Found: C, 82.04; H, 5.14; N, 7.93.

7-Chloro-4,5-diphenylpyrazolo[1,5-*a*]quinoline (5l): mp 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, J = 2.2 Hz, 1H), 7.15−7.18 (m, 2H), 7.19−7.27 (m, 5H), 7.28−7.34 (m, 3H), 7.46 (d, J = 2.2 Hz, 1H), 7.61 (dd, J = 2.2, 9.2 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 8.63 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.4, 117.0, 125.4, 127.1, 127.58, 127.61, 128.0, 128.2, 129.2, 129.9, 130.26, 130.32, 131.0, 132.6, 133.1, 136.0, 136.6, 139.1, 141.5; HRMS m/z calcd for $C_{23}H_{15}ClN_2$ (M^+) 354.0924, found 354.0920.

4,5-Diphenyl-7-trifluoromethylpyrazolo[1,5-*a*]quinoline (5m): mp 171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, J = 2.2 Hz, 1H), 7.16−7.19 (m, 2H), 7.20−7.28 (m, 5H), 7.29−7.35 (m, 3H), 7.79 (d, J = 2.2 Hz, 1H), 7.89 (dd, J = 2.2, 8.8 Hz, 1H), 8.05 (d, J = 2.2 Hz, 1H), 8.79 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.8, 116.3, 123.9, 124.1 (q, J = 273 Hz), 125.3 (q, J = 4.6 Hz), 125.4 (q, J = 1.5 Hz), 126.7 (q, J = 33 Hz), 127.7, 127.8, 128.1, 128.3, 129.8, 130.5, 131.0, 133.7, 135.72 (q, J = 4.6 Hz), 135.73 (q, J = 1.5 Hz), 136.5, 139.7, 142.2; HRMS m/z calcd for $C_{24}H_{15}F_3N_2$ (M^+) 388.1187, found 388.1190. Anal. Calcd for $C_{24}H_{15}F_3N_2$: C, 74.22; H, 3.89; N, 7.21. Found: C, 74.03; H, 3.81; N, 7.12.

8-Chloro-4,5-diphenylpyrazolo[1,5-*a*]quinoline (5n): mp 184−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J = 2.2 Hz, 1H), 7.13−7.31 (m, 11H), 7.41 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 8.69 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.3, 115.4, 122.6, 125.1, 127.47, 127.50, 128.0, 128.1, 129.2, 129.3, 129.9, 131.0, 133.5, 134.5, 135.1, 136.3, 136.6, 139.4, 141.7; HRMS m/z calcd for $C_{23}H_{15}ClN_2$ (M^+) 354.0924, found 354.0922.

4,5-Diphenyl-6-fluoropyrazolo[1,5-*a*]quinoline (5′o): mp 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (d, J = 2.2 Hz, 1H), 7.00 (dd, J = 8.1, 12.4 Hz, 1H), 7.13−7.23 (m, 10H), 7.58 (dt, J = 5.1, 8.1 Hz, 1H), 7.97 (d, J = 2.2 Hz, 1H), 8.52 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.5, 111.6 (d, J = 22.9 Hz), 111.7 (d, J = 3.8 Hz), 113.5 (d, J = 11.5 Hz), 126.8, 127.2, 127.3, 127.8, 129.6 (d, J = 10.0 Hz), 129.8, 129.85, 120.91, 130.3, 130.5 (d, J = 26.7 Hz), 135.4 (d, J = 26.7 Hz), 136.4, 138.6 (d, J = 4.6 Hz), 139.2, 141.7, 150.8 (d, J = 257 Hz); HRMS m/z calcd for $C_{23}H_{15}FN_2$ (M^+) 338.1219, found 338.1222.

4,5-Diphenyl-8-methoxypyrazolo[1,5-*a*]quinoline (5p): mp 195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, 3H), 6.36 (d, J = 2.2 Hz, 1H), 6.94 (dd, J = 2.6, 9.2 Hz, 1H), 7.15−7.19 (m, 2H), 7.20−7.24 (m, 5H), 7.25−7.29 (m, 3H), 7.40 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 2.2 Hz, 1H), 8.12 (d, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 97.1, 100.5, 114.7, 117.9, 126.3, 127.15, 127.20, 127.88, 127.90, 129.4, 130.2, 131.1, 134.0, 135.3, 136.9, 137.1, 139.7, 141.3, 160.6; HRMS m/z calcd for $C_{24}H_{18}N_2O$ (M^+) 350.1419, found 350.1418.

4,5-Diphenyl-6-methoxypyrazolo[1,5-*a*]quinoline (5′p): mp 181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (s, 3H), 6.20 (d, J = 2.2 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 7.05−7.20 (m, 10H), 7.61 (t, J = 8.4 Hz, 1H), 7.96 (d, J = 2.2 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 100.6, 107.2, 108.5, 114.3, 125.7, 126.5, 127.0, 127.7, 129.4, 129.7, 129.8, 130.2, 132.6, 135.6, 137.2, 139.2, 140.9, 141.4, 158.0; HRMS m/z calcd for $C_{24}H_{18}N_2O$ (M^+) 350.1419, found 350.1417.

2-Methyl-4,5-diphenylpyrazolo[1,5-*a*]quinoline (5q): mp 168−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 6.15 (s, 1H), 7.16−7.31 (m, 11H), 7.47 (d, J = 8.4 Hz,1H), 7.63 (t, J = 7.7 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 100.6, 115.2, 123.7, 124.0, 127.2, 127.3, 127.87, 127.90, 127.91, 128.6, 128.9, 130.0, 131.1, 133.9, 134.0, 136.9, 137.2, 140.1, 151.2; HRMS m/z calcd for $C_{24}H_{18}N_2$ (M^+) 334.1470, found 334.1480.

1-[2-(1,2-Diphenylvinyl)phenyl]pyrazole (6): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (t, J = 2.2 Hz, 1H), 6.65 (s, 1H), 6.93−6.96 (m, 2H), 7.01−7.13 (m, 8H), 7.38−7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.2, 126.7, 126.9, 127.1, 127.8, 127.9, 128.1, 128.4, 129.3, 129.5, 130.7, 130.8, 131.6, 137.1, 139.0, 139.2, 139.95, 139.99, 140.1; HRMS m/z calcd for $C_{23}H_{18}N_2$ (M^+) 322.1470, found 322.1464.

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