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Carbonylative Alkynylation

Synthesis of Fluorescent 1,3-Diarylpropynones by Carbonylative Alkynylation Reaction Using (Phosphine) (1,2,3-triazol-5-ylidene)palladium Complexes as Catalysts

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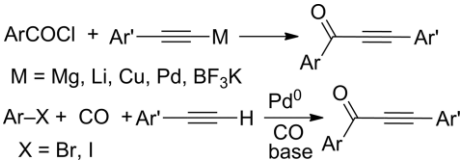
Abstract: The synthesis of a variety of 1,3-diarylpropynones that contain not only substituted phenyl groups but also fluorophoric 1-pyrenyl, 3-carbazolyl, and 1-naphthyl groups was achieved in good to excellent yields by using a carbonylative alkynylation reaction in the presence of *cis*-(Tz)Pd(Cl)$_2$(PPh$_3$) (Tz = 1,2,3-triazol-5-ylidene) as a precatalyst under 1.0 atm of CO. Products resulting from competing Sonogashira coupling reactions, namely 1,2-diarylacetylenes, were not observed. The synthesized ynones exhibit fluorescence not only in solution but also in the solid state. The catalytically active palladium species was recovered and reused for up to three cycles by adsorbing the *cis*-(Tz)Pd(Cl)$_2$(PPh$_3$) precatalyst onto silica gel and carrying out the reaction under heterogeneous conditions.

Introduction

1,3-Diarylpropynones (ynones) are an important class of compounds that are widely used in organic synthesis. They can serve as electrophiles and Diels–Alder dienophiles[1–3] and are crucial intermediates in the synthesis of several heterocyclic compounds.[4] Recently, ynones that exhibit fluorescence emission in the solid state have been reported as useful and important organic materials for applications in photonics.[5,6]

Several methods have been reported for the synthesis of 1,3-diarylpropynones.[7] Among these, stoichiometric reactions that involve the treatment of aroyl chlorides with alkynylmetal compounds (Scheme 1) have been widely used.[8] Alternatively, a catalytic carbonylative alkynylation reaction that involves carbon monoxide as a one-carbon source is an attractive approach that has been studied as well.[9] This reaction involves the palladium(0)-catalyzed carbonylation of aryl iodides in the presence of carbon monoxide and terminal acetylenes (Scheme 1). Despite tremendous advancements in catalytic carbonylative alkynylation reactions for the synthesis of ynones, this method has not been previously used for the synthesis of fluorescent 1,3-diarylpropynones. There is one report, however, for the synthesis of a pyrenyl-substituted ynone by using an electrophilic Friedel–Crafts acylation.[5] Most reports on carbonylative alkynylation reactions, however, deal with the synthesis of 1,3-diphenylpropynones that contain a variety substituted phenyl rings. Moreover, a majority of the carbonylative alkynylation reactions reported so far have employed CO under high pressure.[9]



Scheme 1. Commonly used methods for the synthesis of 1,3-diarylpropynones.

In view of the importance of fluorescent 1,3-diarylpropynones, we have investigated the synthesis of not only phenyl-substituted derivatives but also 1-naphthyl, 1-pyrenyl, and 3-carbazolyl derivatives. N-Heterocyclic carbene–palladium complexes have been widely used in organic synthesis as versatile catalysts for C–C bond-forming reactions.[10] In the present study, we employed a palladium complex that contains both 1,2,3-triazol-5-ylidene (Tz) and phosphine ligands for use in the carbonylative alkynylation reaction. Herein we report the synthesis of fluorescent 1,3-diarylpropynones by employing a carbonylative alkynylation reaction that is catalyzed by the *cis*-(Tz)Pd(Cl)$_2$(PPh$_3$) (**2**) under 1.0 atm of CO. The solution and solid-state fluorescence of the ynones are reported, and the recovery and use of the active recycled catalyst has been demonstrated for up to three cycles.

Results and Discussion

Structures of palladium complexes that have been screened as catalysts for carbonylative alkylation reactions are shown in Figure 1. Complexes **1**–**3** were synthesized (Scheme 2) by using procedures similar to those reported for their imidazolylidene analogues.[11] The synthesis of complex **4** has been previously

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reported by our group.[12] Complexes **2** and **3** were prepared by two different routes that proceed either through intermediate acetonitrile complex **1** or through chloro-bridged dinuclear complex **5** (Scheme 2). The treatment of **1** with triphenylphosphine in CH_2Cl_2 selectively afforded the corresponding *cis* isomer **2**, whereas treatment with tri(*o*-tolyl)phosphine selectively gave the corresponding *trans* isomer **3**. Results identical to those above were obtained when **5** was treated with triphenylphosphine and tri(*o*-tolyl)phosphine, respectively, to afford **2** and **3**. The ^{1}H NMR spectra of **2** and **3** obtained by these two methods were superimposable, which clearly indicates the selective formation of triphenylphosphine complex **2** or tri(*o*-tolyl)phosphine complex **3**. The structures and stereochemistry of **1**–**3** were unambiguously assigned by single-crystal XRD analysis (Figure 2).

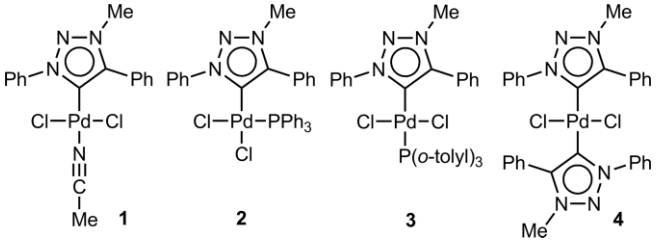
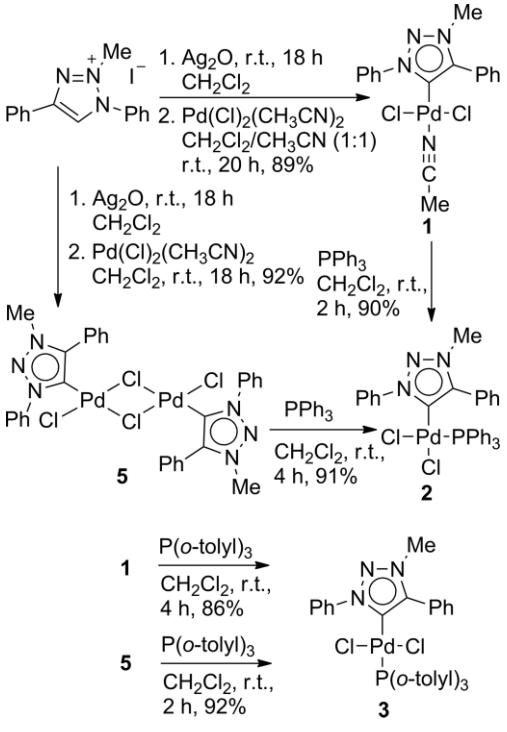
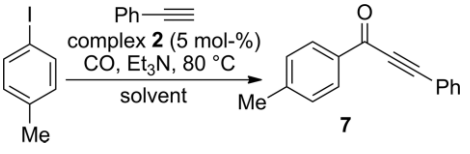


Figure 1. Structure of palladium complexes **1**–**4** screened as catalysts in the carbonylative alkynylation reaction.



Scheme 2. Synthesis of complexes **1**–**3**.

Initially, we investigated the effect of solvent polarity on the carbonylative alkynylation reaction by using complex **2** as the catalyst and *p*-iodotoluene and phenylacetylene as substrates (Scheme 3 and Table 1). The reactions were carried out in various solvents at 80 °C, as there was no reaction at room temperature. In polar solvents such as ethanol and acetonitrile, the reactions did not proceed to yield the desired product, and only starting materials were recovered. In 1,4-dioxane, 1,2-dimethoxyethane, and 1,2-dichloroethane (i.e., solvents of moderate polarity), the reaction did not reach completion after 24 h, and the isolated yield of the corresponding ynone **7** was 51, 40, and 61 %, respectively. When the reaction was carried out in toluene, it went to completion within 18 h to give **7** in an isolated yield of 81 %. In addition to **7**, 1,4-diphenylbuta-1,3-diyne, which resulted from the oxidative coupling of phenylacetylene, was also formed as a byproduct. The Sonogashira coupling product, namely 4-methyltolan, was not obtained in any of these reactions. All of the subsequent reactions were carried out in toluene at 80 °C.



Scheme 3. Carbonylative alkynylation reaction for the screening of solvents.

Table 1. Solvent screening for the carbonylative alkynylation reaction.

Entry	Solvent	Time [h]	Yield [%] of **7**
1	CH_3CN	24	no reaction
2	C_2H_5OH	24	no reaction
3	1,4-dioxane	24	51
4	1,2-dimethoxyethane	24	40
5	1,2-dichloroethane	24	61
6	toluene	18	81

The catalytic reactivity of complexes **1**–**4** in the carbonylative alkynylation reaction of phenylacetylene and 4-iodoanisole in

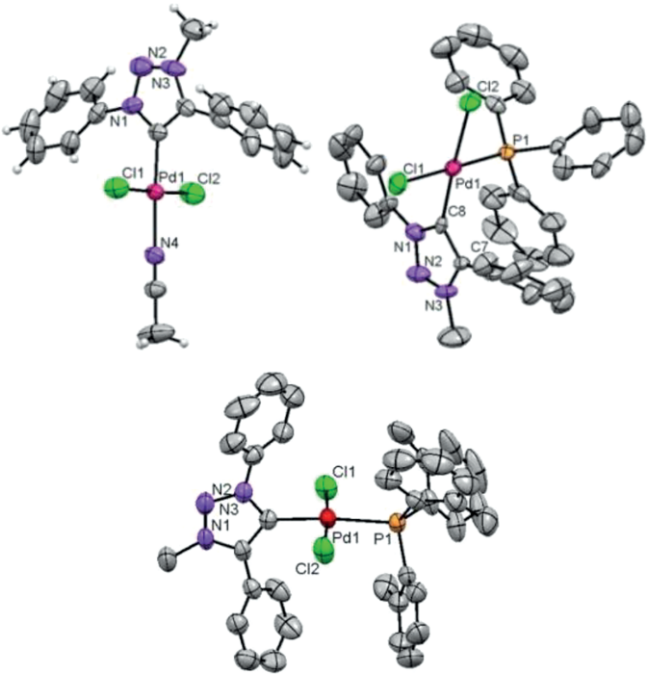


Figure 2. ORTEP representation (50 % probability) of the crystal structures of **1** (top left), **2** (top right) and **3** (bottom).

toluene was studied. The course of the reaction over time was monitored by removing an aliquot from the reaction mixture at various intervals of time (up to 10 h) and then recording its ^{1}H NMR spectrum. The methoxy proton signal of 4-iodoanisole appeared at δ = 3.76 ppm, and that of the carbonylative alkynylation product **11** appeared at δ = 3.89 ppm with good baseline separation in the 400 MHz ^{1}H NMR spectra of the crude product. The percentage conversion into **11** was calculated at various time intervals, and the data obtained by using complexes **2**–**4** as the catalysts are presented in Figure 3. The carbonylative alkynylation reaction did not proceed with complex **1**, as the catalyst and starting materials were recovered after a prolonged reaction time at 80 °C. When complex **4** was used as the catalyst, 30 % conversion was achieved after 10 h, whereas the reaction proceeded smoothly to an extent of 86 % when complexes **2** and **3** were used as catalysts. The catalytic activities of complexes **2** and **3** were nearly the same.

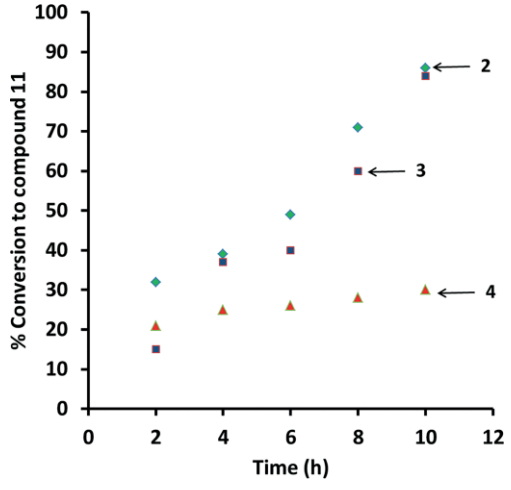
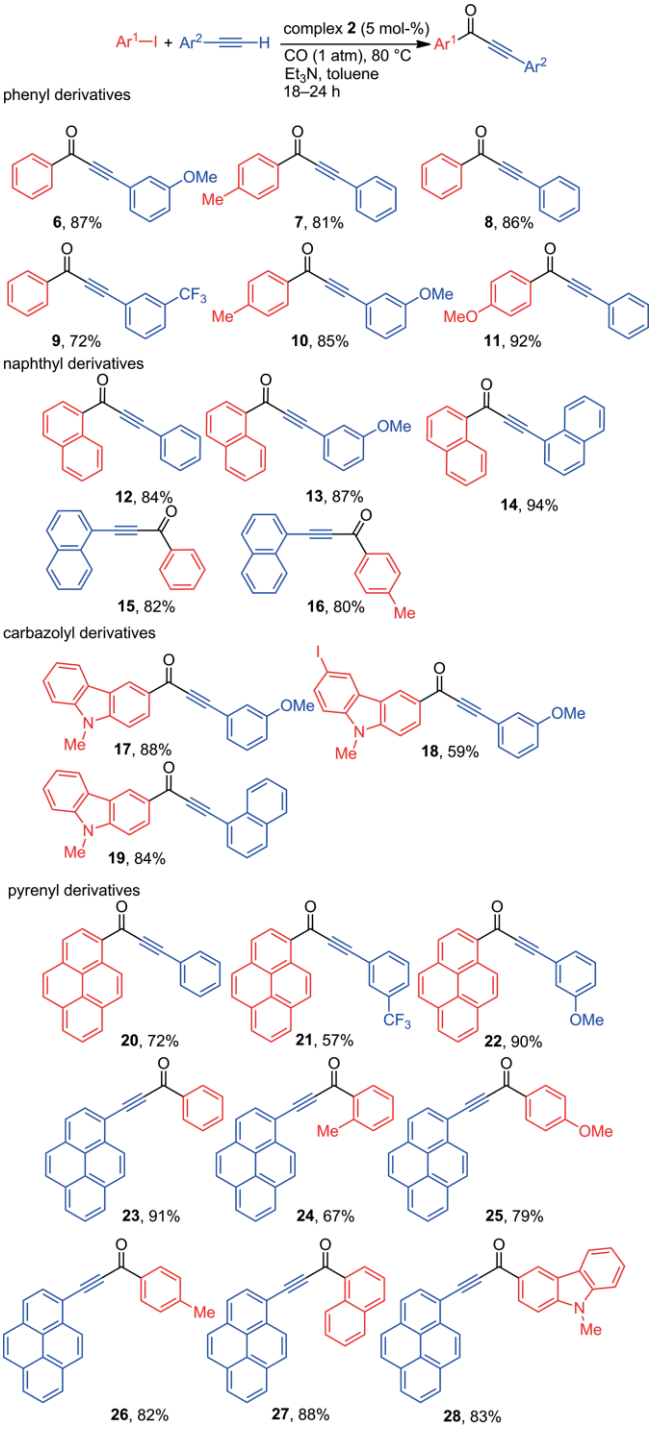


Figure 3. Comparison of the catalytic activity of complexes **2**, **3**, and **4** in the carbonylative alkynylation reaction of 4-iodoanisole and phenylacetylene.

Complex **2** (5 mol-%) was used to investigate the scope of the substrates for the carbonylative alkynylation, with specific emphasis on the synthesis of ynones that not only are substituted phenyl derivatives but also are fluorophores such as 1-naphthyl, 1-pyrenyl, and 3-carbazolyl derivatives. The results are summarized in Scheme 4.

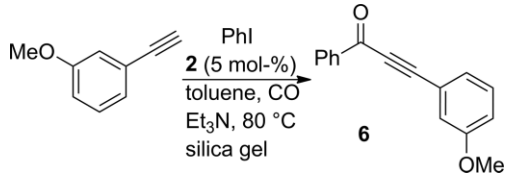
The products of the carbonylative alkynylation reaction, namely the 1,3-diarylpropynones, were formed in good to excellent yields. In all of the reactions, the corresponding Sonogashira coupling product, that is the diarylethyne, was not formed in even trace amounts.[13] This indicates that the carbonylation step is much faster than that of the Sonogashira coupling. Small amounts (<10 %) of the 1,4-diarylbuta-1,3-diynes, however, were observed, presumably from the oxidative dimerization of the excess amounts of the terminal acetylenes. The carbonylated products **6**–**28** were easily isolated by a chromatography on silica gel, and the reported yields are that of the pure product after chromatography. Notably, regioisomeric ynones **12** and **15** as well as **20** and **23** are easily accessible by this method. All of the compounds were thoroughly characterized by spectroscopic methods.



Scheme 4. Synthesis of 1,3-diarylpropynones through a carbonylative alkynylation reaction catalyzed by complex **2**.

After the synthesis of a variety of fluorescent ynones, we focused our attention on recovering and recycling the catalyst. Complex **2** was initially adsorbed onto an excess amount of silica gel (100–200 mesh; 0.025 mmol on 1 g of silica gel, 5 mol-% Pd relative to the substrate), and the carbonylative alkynylation reaction of iodobenzene and (3-methoxyphenyl)acetylene was carried out in toluene at 80 °C in the presence of Et_3N (Scheme 5 and Table 2). The reaction was equally efficient on

silica gel (i.e., under heterogeneous conditions)[14] and reached completion in 18 h to give **6** in 92 % yield. These results are comparable to those of the carbonylative alkynylation reactions that were carried out under homogeneous conditions (Scheme 4). Upon completion of the reaction, the mixture (i.e., toluene layer) was removed by a syringe, and the residue, which was presumably the active catalyst adsorbed onto the silica gel, was rinsed with toluene. The residue was reused as the catalyst in subsequent cycles of the carbonylative alkynylation reaction. This recovered catalyst was used for up to three cycles to give **6** in the second and third cycle of 85 % (after 22 h) and 78 % (after 27 h), respectively (Table 2). We also carried out a hot filtration test, in which the Pd-coated silica was separated from the reaction mixture, and the filtrate was further used for the reaction under reaction conditions similar to those described above. No significant reaction progress, however, was observed over the prolonged period of time. Pd had leached into the toluene layer after each catalytic cycle according to inductively coupled plasma-optical emission spectrometry (ICP-OES). The Pd content in the toluene layer was found to be 0.98 ppm (average of three estimations), and only 0.2 wt.-% of Pd leached out of the reaction mixture during each cycle. On the basis of the above analysis, we concluded that precatalyst **2** and the activated catalyst, which was formed during the reaction, are strongly adsorbed onto the surface of silica gel.



Scheme 5. Carbonylative alkynylation reaction used to demonstrate the recovery and recycling of the catalyst.

Table 2. Recovery and recycling of catalyst by using silica gel support.

Cycle	Time [h]	Yield [%] **6**
1	18	92
2	22	85
3	27	78

The electronic absorption and fluorescence emission spectra of carbazolyl ynones **17** and **19** along with the nine pyrenyl ynones **20**–**28** were recorded in CH_3CN (10^{-5} M; Figure 4; Supporting Information). In a comparison of pyrene, carbazole, and naphthalene, all of which absorb and emit in the UV region,[15] the absorption and fluorescence emission bands of the pyrenyl ynones were bathochromically shifted by 1.1–1.3 eV as a result of the extended conjugation. The absorption bands in the region of 350–450 nm are essentially from the pyrene chromophore.[16] At a concentration of 10^{-5} M, the emission band in the region of 450–550 nm is largely the result of pyrene monomer emission[15] with a weak shoulder beyond 550 nm, which could be from the excimer emission.[16] Notably, the emission from some of these multichromophoric ynones (i.e., **27** and **28**) essentially covers most of the visible region (450–650 nm). Regioisomeric ynones **20** and **23** did not exhibit any large difference in their absorption and emission spectra. Pyrene derivatives **23** and **27** were emissive in the solid state as well. The emission spectra of these derivatives as neat solids are shown in Figure 5. The excimer emission band (approximately 583–590 nm) of these derivatives was more prominent than the monomer band in the solid-state spectra compared with those of the solution spectra. The emission bands were bathochromically shifted by approximately 0.20 eV in the solid state compared with those of the solution spectra. The quantum yield of fluorescence (Φ_f) was measured for compounds **20**–**28** by using quinine sulfate as the reference (Supporting Information) and was found to be in the range of 0.08–0.12 for phenylethynyl pyrene derivatives **20**–**25** and in the range of 0.42–0.43 for naphthyl- and carbazolyl-substituted pyrene derivatives **27** and **28**, respectively.

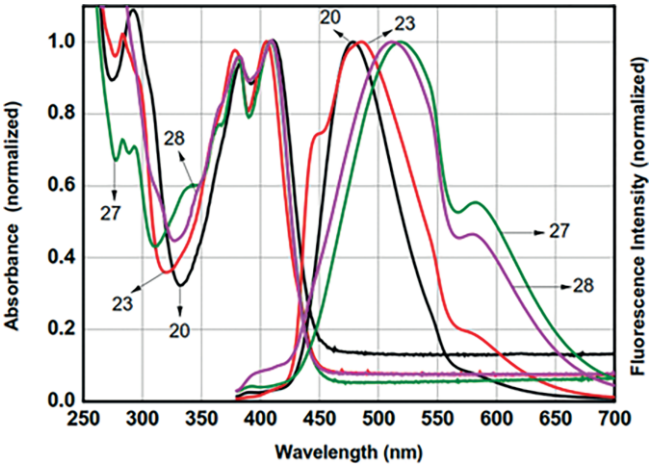


Figure 4. Absorption (left) and fluorescence spectra (λ_{ex} = 370 nm) of regioisomeric ynones **20** and **23** along with ynones **27** and **28** in acetonitrile (10^{-5} M).

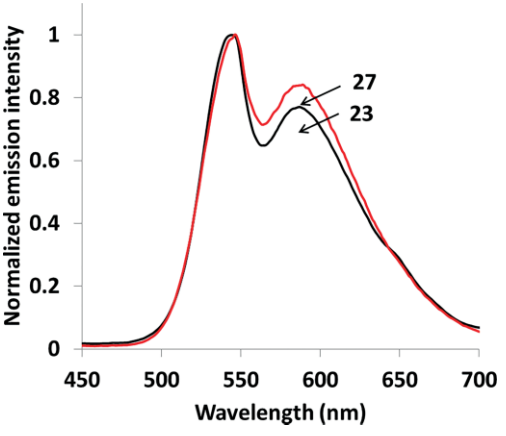


Figure 5. Emission spectra of **23** and **27** in the solid state (λ_{ex} = 372 nm).

Conclusions

The synthesis of several 1,3-diarylpropynones has been accomplished by a carbonylative alkynylation reaction using a (phosphine)(1,2,3-triazol-5-ylidene)palladium complex as a catalyst

under 1.0 atm of CO. The products were obtained in good to excellent yields. Several fluorescent ynones that contain 1-naphthyl, 1-pyrenyl, and 3-carbazolyl chromophores have been synthesized for the first time by using this catalytic carbonylation method. The reactions were very clean, as the usual by-products that could arise from a competing Sonogashira coupling reaction were not observed. This indicates that the carbonylation reaction proceeded much faster than the Sonogashira coupling under these reaction conditions. The feasibility of the recovery and recycling of the catalyst was demonstrated by using silica gel as a solid support to anchor the catalyst precursor. The fluorescent ynones exhibit emission not only in the solution state but also in the solid state, which make them potential candidates for application as organic photonic materials.

Experimental Section

General Procedure for the Carbonylative Alkynylation Reaction: Complex **2** (5 mol-%) was added to an oven-dried Schlenk flask under nitrogen. Dry toluene (5 mL) was added to the flask followed by triethylamine (3 equiv.) and then the aryl iodide (1 equiv.). Finally, arylacetylene (1.5 equiv.) was added to the reaction mixture, and the reaction flask was flushed with a balloon filled with CO (2 ×). The reaction mixture was stirred under CO (balloon) at 80 °C for 18–24 h. The crude reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine solution, dried with sodium sulfate, and concentrated under vacuum. The crude reaction mixture was purified by column chromatography (hexane and ethyl acetate). CCDC 1476176 (for **1**), 1415599 (for **2**), and 1415600 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

3-(3-Methoxyphenyl)-1-(9-methyl-9*H*-carbazol-3-yl)prop-2-yn-1-one (17): The carbonylative alkynylation reaction between 3-iodo-9-methyl-9*H*-carbazole (100 mg, 0.33 mmol) and 1-ethynyl-3-methoxybenzene (62 μL, 0.49 mmol) in the presence of triethylamine (0.13 mL, 0.98 mmol) and complex **2** (11 mg, 0.02 mmol) gave **17** (97 mg, 88 %) as a yellow solid; m.p. 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (m, 1 H), 8.34 (dd, J = 8, 2 Hz, 1 H), 8.12 (dd, J = 8, 1 Hz, 1 H), 7.53–7.49 (m, 1 H), 7.42–7.39 (m, 2 H), 7.33–7.28 (m, 3 H), 7.23–7.22 (m, 1 H), 7.03–7.00 (m, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 159.6, 144.6, 141.9, 129.9, 129.0, 127.9, 126.8, 125.5, 123.4, 123.2, 122.9, 121.7, 120.8, 120.5, 117.7, 117.3, 109.2, 108.3, 92.1, 87.3, 55.5, 29.5 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 3004, 2933, 2832, 2194, 1766, 1619, 1588, 1481, 1430, 1363, 1327, 1252, 1220, 1128, 1042, 1021 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{17}NO_2$ 339.1259; found 339.1252.

1-(6-Iodo-9-methyl-9*H*-carbazol-3-yl)-3-(3-methoxyphenyl)-prop-2-yn-1-one (18): The carbonylative alkynylation reaction between 3,6-diiodo-9-methyl-9*H*-carbazole (100 mg, 0.23 mmol) and 1-ethynyl-3-methoxybenzene (44 μL, 0.35 mmol) in the presence of triethylamine (96 μL, 0.70 mmol) and complex **2** (8 mg, 0.01 mmol) gave **18** (63 mg, 59 %) as a yellow solid; m.p. 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 1 Hz, 1 H), 8.43 (d, J = 6 Hz, 1 H), 8.35 (dd, J = 8, 2 Hz, 1 H), 7.76 (dd, J = 9 Hz, 1 H), 7.42–7.34 (m, 3 H), 7.25–7.19 (m, 2 H), 7.06–7.04 (m, 1 H), 3.87 (s, 3 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 159.6, 144.4, 141.0, 135.1, 129.9, 129.6, 129.4, 128.2, 125.6, 123.8, 121.61, 121.5, 117.6, 117.6, 117.4, 111.2, 108.6, 92.4, 90.1, 83.2, 55.6, 29.6 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2958, 2922, 2854, 2194, 1712, 1616, 1580, 1481, 1445, 1424, 1363, 1327, 1281, 1227, 1192, 1152, 1124, 1042, 1010 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{16}INO_2$ $[M + H]^+$ 466.0304; found 466.0300.

1-(9-Methyl-9*H*-carbazol-3-yl)-3-(naphthalen-1-yl)prop-2-yn-1-one (19): The carbonylative alkynylation reaction between 3-iodo-9-methyl-9*H*-carbazole (100 mg, 0.33 mmol) and 1-ethynylnaphthalene (70 μL, 0.49 mmol) in the presence of triethylamine (0.13 mL, 0.98 mmol) and complex **2** (11 mg, 0.02 mmol) gave **19** (98 mg, 84 %) as a yellow-orange solid; m.p. 95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.10 (d, J = 1 Hz, 1 H), 8.54 (d, J = 9 Hz, 1 H), 8.46 (dd, J = 9, 2 Hz, 1 H), 8.18 (d, J = 8 Hz, 1 H), 8.02–7.98 (m, 2 H), 7.93 (d, J = 9 Hz, 1 H), 7.71–7.68 (m, 1 H), 7.62–7.59 (m, 1 H), 7.57–7.53 (m, 2 H), 7.47 (t, J = 9 Hz, 2 H), 7.34 (dt, J = 8, 1 Hz, 1 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.7, 144.6, 141.9, 133.9, 133.3, 133.0, 131.2, 129.2, 128.7, 127.85, 127.82, 127.7, 127.0, 126.9, 126.1, 125.4, 123.7, 123.2, 123.0, 120.8, 120.5, 118.4, 109.3, 108.4, 92.3, 90.5, 29.5 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2926, 2851, 2194, 1617, 1588, 1499, 1472, 1395, 1363, 1321, 1249, 1195 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{17}NO$ 359.1310; found 359.1312.

3-Phenyl-1-(pyren-1-yl)prop-2-yn-1-one (20):[5] The carbonylative alkynylation reaction between iodopyrene (100 mg, 0.30 mmol) and phenylacetylene (50 μL, 0.46 mmol) in the presence of triethylamine (0.12 mL, 0.91 mmol) and complex **2** (10 mg, 0.01 mmol) gave **20** (73 mg, 72 %) as a yellow solid; m.p. 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (d, J = 9 Hz, 1 H), 9.00 (dd, J = 8, 1 Hz, 1 H), 8.29–8.17 (m, 5 H), 8.08–8.04 (m, 2 H), 7.75 (d, J = 7 Hz, 2 H), 7.52–7.43 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.0, 135.3, 133.1, 131.5, 130.9, 130.7, 130.7, 130.6, 130.5, 128.8, 127.2, 127.0, 126.7, 126.5, 124.9, 124.1, 120.6, 92.4, 89.3 ppm. IR (KBr): $\tilde{\nu}$ = 3050, 2918, 2847, 2194, 1755, 1630, 1613, 1591, 1499, 1484, 1438, 1380, 1317, 1273, 1202, 1117, 1067 cm^{-1}. HRMS (EI): calcd. for $C_{25}H_{14}O$ 330.1045; found 330.1040.

1-(Pyren-1-yl)-3-[3-(trifluoromethyl)phenyl]prop-2-yn-1-one (21): The carbonylative alkynylation reaction between iodopyrene (100 mg, 0.30 mmol) and 1-ethynyl-3-(trifluoromethyl)benzene (66 μL, 0.46 mmol) in the presence of triethylamine (0.12 mL, 0.91 mmol) and complex **2** (10 mg, 0.02 mmol) gave **21** (69 mg, 57 %) as a yellow-orange solid; m.p. 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.57 (d, J = 9 Hz, 1 H), 9.03 (d, J = 8 Hz, 1 H), 8.36–8.25 (m, 5 H), 8.14–8.09 (m, 2 H), 8.00 (s, 1 H), 7.92 (d, J = 8 Hz, 1 H), 7.75 (d, J = 8 Hz, 1 H), 7.60 (t, J = 8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 136.0, 135.7, 131.7, 131.2, 131.1, 131.1, 131.0, 129.7, 129.7, 129.4, 129.0, 127.32, 127.30, 127.1, 127.1, 127.0, 126.7, 125.0, 124.9, 124.2, 124.1, 121.7, 89.97, 89.94 ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2918, 2855, 2358, 2198, 1737, 1630, 1591, 1502, 1430, 1331, 1263, 1120, 1073, 1002 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{13}F_3O$ 398.0918; found 398.0915.

3-(3-Methoxyphenyl)-1-(pyren-1-yl)prop-2-yn-1-one (22): The carbonylative alkynylation reaction between 1-iodopyrene (100 mg, 0.30 mmol) and 1-ethynyl-3-methoxybenzene (58 μL, 0.46 mmol) in the presence of triethylamine (0.12 mL, 0.91 mmol) and complex **2** (10 mg, 0.02 mmol) gave **22** (99 mg, 90 %) as a yellow solid; m.p. 112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.64 (d, J = 9 Hz, 1 H), 8.51 (d, J = 8 Hz, 1 H), 8.31–8.23 (m, 4 H), 8.16 (t, J = 9 Hz, 2 H), 8.08–8.05 (m, 2 H), 7.52 (t, J = 7 Hz, 1 H), 7.45 (t, J = 7 Hz, 1 H), 7.34 (d, J = 7 Hz, 1 H), 2.76 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.0, 140.6, 136.2, 133.8, 133.2, 133.1, 133.0, 132.4, 131.2, 131.1, 131.0, 129.67, 129.61, 127.3, 126.7, 126.6, 126.4, 126.1, 125.2, 124.7, 124.4, 114.3, 94.2, 91.7, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2926, 2832, 2190, 1634, 1613, 1591, 1499, 1484, 1459, 1363, 1313, 1260, 1117,

1046, 1010 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{16}O_2$ 360.1150; found 360.1148.

1-Phenyl-3-(pyren-1-yl)prop-2-yn-1-one (23): The carbonylative alkynylation reaction between iodobenzene (100 mg, 0.49 mmol) and 1-ethynylpyrene (167 mg, 0.76 mmol) in the presence of triethylamine (0.20 mL, 1.47 mmol) and complex **2** (17 mg, 0.02 mmol) gave **23** (147 mg, 91 %) as a yellow solid; m.p. 170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 9 Hz, 1 H), 8.38 (d, J = 7 Hz, 2 H), 8.33 (d, J = 8 Hz, 1 H), 8.29–8.25 (m, 3 H), 8.17 (t, J = 8 Hz, 2 H), 8.08–8.05 (m, 2 H), 7.68 (t, J = 7 Hz, 1 H), 7.59 (t, J = 7 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.2, 137.4, 134.2, 133.8, 133.3, 131.3, 131.2, 130.9, 129.8, 129.7, 128.8, 127.2, 126.7, 126.6, 126.5, 125.1, 124.7, 124.4, 124.1, 114.1, 92.9, 92.7 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2922, 2855, 2194, 1613, 1588, 1495, 1474, 1438, 1395, 1359, 1321, 1256, 1202, 1141, 1120 cm^{-1}. HRMS (EI): calcd. for $C_{25}H_{14}O$ 330.1045; found 330.1040.

3-(Pyren-1-yl)-1-(*o*-tolyl)prop-2-yn-1-one (24): The carbonylative alkynylation reaction between *o*-iodotoluene (100 mg, 0.45 mmol) and 1-ethynylpyrene (154 mg, 0.68 mmol) in the presence of triethylamine (0.19 mL, 1.36 mmol) and complex **2** (15 mg, 0.02 mmol) gave **24** (105 mg, 0.30 mmol, 67 %) as a light yellow solid; m.p. 115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, J = 9 Hz, 1 H), 8.51 (dd, J = 8, 1 Hz, 1 H), 8.29–8.21 (m, 4 H), 8.16–8.11 (m, 2 H), 8.07–8.04 (m, 2 H), 7.51 (dt, J = 7, 1 Hz, 1 H), 7.45 (t, J = 7 Hz, 1 H), 7.34 (d, J = 7 Hz, 1 H), 2.76 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.0, 140.6, 132.2, 133.8, 133.2, 133.1, 133.0, 132.4, 131.19, 131.15, 130.9, 129.6, 129.5, 127.2, 126.7, 126.5, 126.4, 126.1, 125.1, 124.6, 124.4, 124.1, 114.3, 94.2, 91.7, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 2958, 2918, 2847, 2173, 1627, 1594, 1566, 1487, 1455, 1430, 1306, 1270, 1206, 1124, 1010 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{16}O$ 344.1201; found 344.1200.

1-(4-Methoxyphenyl)-3-(pyren-1-yl)prop-2-yn-1-one (25): The carbonylative alkynylation reaction between 4-iodoanisole (100 mg, 0.43 mmol) and 1-ethynylpyrene (145 mg, 0.64 mmol) in the presence of triethylamine (0.17 mL, 1.28 mmol) and complex **2** (14 mg, 0.02 mmol) gave **25** (122 mg, 79 %) as a yellow solid; m.p. 172 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (d, J = 9 Hz, 1 H), 8.36–8.25 (m, 6 H), 8.19–8.17 (m, 2 H), 8.10–8.06 (m, 2 H), 7.06 (d, J = 9 Hz, 2 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.8, 164.6, 133.7, 133.1, 132.1, 131.25, 131.21, 131.0, 130.81, 129.66, 129.62, 127.3, 126.7, 126.6, 126.4, 125.2, 124.7, 124.5, 124.1, 114.4, 114.1, 92.7, 92.0, 55.7 ppm. IR (KBr): 2962, 2922, 2851, 2194, 1613, 1588, 1502, 1481, 1323, 1252, 1224, 1117 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{16}O_2$ 360.1150; found 360.1146.

3-(Pyren-1-yl)-1-(*p*-tolyl)prop-2-yn-1-one (26): The carbonylative alkynylation reaction between 4-iodotoluene (100 mg, 0.45 mmol) and 1-ethynylpyrene (154 mg, 0.68 mmol) in the presence of triethylamine (0.19 mL, 1.36 mmol) and complex **2** (15 mg, 0.02 mmol) gave **26** (128 mg, 82 %) as a yellow solid; m.p. 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, J = 9 Hz, 1 H), 8.34–8.25 (m, 6 H), 8.19–8.16 (m, 2 H), 8.09–8.05 (m, 2 H), 7.38 (d, J = 8 Hz, 2 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 145.3, 135.1, 133.7, 133.2, 131.29, 131.22, 131.0, 129.9, 129.7, 129.65, 129.62, 127.3, 126.7, 126.6, 126.5, 125.2, 124.7, 124.4, 124.1, 114.2, 92.8, 92.4, 22.0 ppm. IR (KBr): $\tilde{\nu}$ = 2962, 2918, 2851, 2180, 1627, 1594, 1570, 1292, 1216, 1166, 1006 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{16}O$ 344.1201; found 344.1200.

1-(Naphthalen-1-yl)-3-(pyren-1-yl)prop-2-yn-1-one (27): The carbonylative alkynylation reaction between 1-iodonaphthalene (100 mg, 0.39 mmol) and 1-ethynylpyrene (134 mg, 0.59 mmol) in the presence of triethylamine (0.16 mL, 1.18 mmol) and complex **2** (13 mg, 0.02 mmol) gave **27** (132 mg, 0.35 mmol, 88 %) as a yellow-orange solid; m.p. 141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (d, J = 8 Hz, 1 H), 8.82 (dd, J = 7, 1 Hz, 1 H), 8.62 (d, J = 9 Hz, 1 H), 8.31–8.03 (m, 9 H), 7.94 (d, J = 8 Hz, 1 H), 7.74–7.59 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.9, 135.1, 134.3, 134.1, 133.8, 133.6, 133.1, 131.1, 130.9, 129.6, 129.5, 129.0, 128.7, 127.2, 126.9, 126.6, 126.5, 126.4, 126.2, 125.1, 124.7, 124.6, 124.4, 124.0, 114.2, 94.3, 91.7 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2918, 2847, 2190, 1634, 1509, 1430, 1327, 1281, 1249, 1216, 1174, 1131, 1103, 1070 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{16}O$ 380.1201; found 380.1205.

1-(9-Methyl-9*H*-carbazol-3-yl)-3-(pyren-1-yl)prop-2-yn-1-one (28): The carbonylative alkynylation reaction between 3-iodo-9-methyl-9*H*-carbazole (100 mg, 0.33 mmol) and 1-ethynylpyrene (110 mg, 0.49 mmol) in the presence of triethylamine (0.13 mL, 0.98 mmol) and complex **2** (11 mg, 0.02 mmol) gave **28** (117 mg, 0.27 mmol, 83 %) as a yellow-orange solid; m.p. 189 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.15 (d, J = 1 Hz, 1 H), 8.77 (d, J = 9 Hz, 1 H), 8.51 (dd, J = 8, 1 Hz, 1 H), 8.37 (d, J = 8 Hz, 1 H), 8.30–8.24 (m, 3 H), 8.21–8.16 (m, 3 H), 8.09–8.07 (m, 2 H), 7.56 (t, J = 8 Hz, 1 H), 7.50–7.45 (m, 2 H), 7.35 (t, J = 8 Hz, 1 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.7, 144.5, 141.9, 133.7, 133.0, 131.2, 131.2, 131.0, 129.5, 129.3, 127.9, 127.3, 126.9, 126.7, 126.5, 126.4, 125.3, 124.7, 124.5, 124.2, 123.6, 123.2, 123.0, 120.8, 120.5, 114.7, 109.3, 108.4, 93.3, 91.8, 29.6 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2855, 2180, 1613, 1588, 1470, 1430, 1359, 1321, 1267, 1117, 1002 cm^{-1}. HRMS (EI): calcd. for $C_{32}H_{19}NO$ 433.1467; found 433.1467.

Supporting Information (see footnote on the first page of this article): Characterization data, copies of ^{1}H and ^{13}C NMR spectra of all new compounds.

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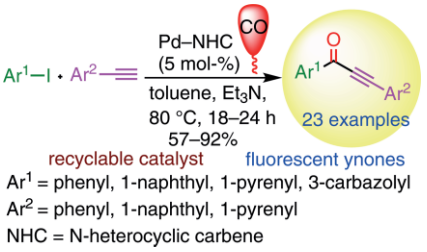

A Pd–N-heterocyclic carbene (Pd–NHC) complex has been used as the catalyst in a carbonylative alkynylation reaction that afforded several fluorescent 1,3-diarylpropynones in high yields.

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