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# Gold(I) Iodide Catalyzed Sonogashira Reactions

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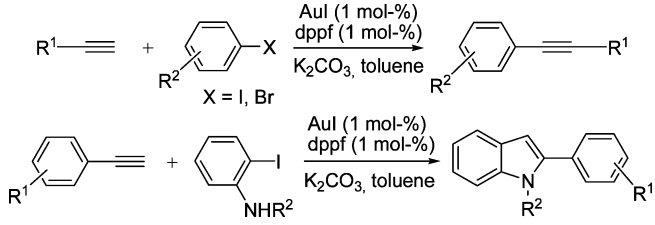
Gold(I) iodide catalyzed Sonogashira reactions have been developed. Terminal alkynes reacted with aryl iodides and bromides smoothly in the presence of AuI (1 mol-%) and dppf (1 mol-%) in toluene to generate the corresponding cross-coupling products in good to excellent yields. Furthermore, aromatic terminal alkynes could also react with 2-iodoaniline to form substituted indoles in excellent yields through a coupling–cyclization reaction sequence under the present reaction conditions.



## Introduction

Gold (and its complexes) catalyzed organic transformations have been a focus of attention in recent years.[1] Gold-mediated organic transformations, such as oxidation of CO,[2] oxidation of alcohols,[3] direct arene functionalization,[4] and carbene insertion into benzene and O–H and N–H bonds,[5] have been developed recently. Both gold(I) and gold(III) species also show unique activities in mediating reactions involving alkynes,[6] alkenes,[7] and allenes.[8] To the best of our knowledge, gold-catalyzed direct carbon–carbon and carbon–heteroatom bond coupling reactions have been less explored. In 2003, Li and his coworkers reported gold(I)-catalyzed three-component coupling reactions of aldehydes, alkynes, and amines.[9] Corma and his coworkers developed Au/$CeO_2$ and $Au^{III}$ Schiff base complex catalyzed homocouplings of phenylboronic acid in 2005,[10] and Corma and his group also developed NHC–gold(I) complexes for the Suzuki reaction in 2006.[11] Sonogashira reactions, that is, the palladium complex/CuI-catalyzed cross-coupling reactions of terminal alkynes with aryl and alkenyl halides, have been widely investigated in the past decades.[12] Palladium, copper, nickel, ruthenium, and indium have been used to catalyze the reactions independently, whereas little attention has been paid to the catalytic activities of silver and gold in Sonogashira reactions. Our group successfully developed silver(I) iodide catalyzed Sonogashira reactions,[13] but coincidentally, while that manuscript was being prepared, a similar strategy appeared. Corma and coworkers also developed gold-catalyzed Sonogashira reactions. They prepared $Au^{I}$ and $Au^{III}$ complexes with a Schiff base and triphenylphosphane ligands, and only four examples (only aryl iodides and aromatic terminal alkynes) were carried out in low yields when they used the $Au^{I}$–Schiff base–$PPh_3$ complex as a catalyst for the Sonogashira reactions.[14] In addition, these kinds of catalyst systems suffer from drawbacks, as they require tedious multistep syntheses. It is desirable to develop a more simple and practical in situ Au/ligand catalyst systems for the Sonogashira reactions.

Herein, we report gold(I) iodide catalyzed Sonogashira reactions of terminal alkynes with aryl iodides and bromides, which generated the corresponding cross-coupling products in good to excellent yields in the presence of AuI (1 mol-%) and dppf (1 mol-%) in toluene. Furthermore, terminal alkynes could also react with 2-iodoaniline to form the substituted indoles through a cross-coupling–cyclization reaction sequence in excellent yields under the present reaction conditions (Scheme 1).




Scheme 1.

## Results and Discussion

Our initial investigation was directed towards exploring the reaction conditions for the cross coupling of *p*-iodoanisole with phenylacetylene catalyzed by gold(I). At first, the effect of several different solvents on the reaction catalyzed by gold(I) iodide was examined, and a significant solvent effect was observed (Table 1). When the reactions were con-

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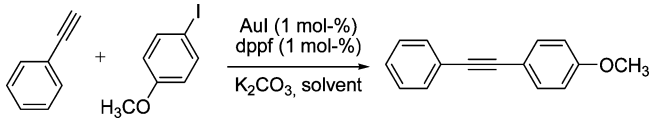
ducted in toluene and xylene, good yields of the products were obtained. The use of dioxane, ethanol, acetonitrile, and water as solvents resulted in middle yields of the products. It is worth noting that no desired cross-coupling product was observed when the reactions were performed in DMF and DMSO (Table 1, Entries 1–12).

Table 1. Effect of solvents on the Sonogashira reaction.[a]



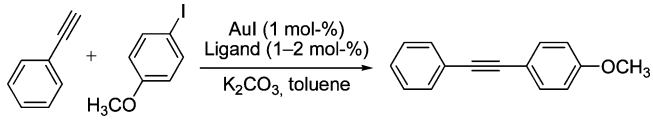

| Entry | Solvent | Temperature [°C] | Yield[b] [%] |
|---|---|---|---|
| 1 | $C_2H_5OH$ | 78 | 52 |
| 2 | $CH_3CN$ | 80 | 50 |
| 3 | THF | 70 | <10 |
| 4 | acetone | 60 | <10 |
| 5 | dioxane | 100 | 50 |
| 6 | DMF | 130 | 0 |
| 7 | DMSO | 130 | 0 |
| 8 | $H_2O$ | 100 | 61 |
| 9 | DMSO/$H_2O$ (1:1) | 120 | 0 |
| 10 | toluene | 130 | 96 |
| 11 | toluene | 90 | 25 |
| 12 | xylene | 130 | 96 |

[a] Phenylacetylene (102 mg, 1.0 mmol), *p*-iodoanisole (234 mg, 1.0 mmol), AuI (3.2 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), $K_2CO_3$ (276 mg, 2.0 mmol) in solvent (2 mL) at the temperature indicated for 24 h. [b] Isolated yields.

We then turned our attention to investigate the ligand effects on the reactions. No reaction occurred in the absence of any ligand (Table 2, Entry 1). Among the ligands tested, 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) proved to be the best of choice, whereas the other phosphane ligands, such as triphenylphosphane ($PPh_3$), tris(2-tolyl)phosphane [P(*o*-tolyl)$_3$], *p*-tolyldiphenylphosphane (*p*-tolyl$PPh_2$), 2,3,2′,3′-tetrahydro-5,5′-bis(1,4-benzodioxin)-6,6′-diylbis-(diphenylphosphane) (Bisbenzodioxanphos), and 2,2′-bis(diphenylphosphanyl)-1,1-binaphthalene (binap) were inferior (Table 2, Entries 5–12). The experimental results also indicated that when P(OMe)$_3$, P(OPh)$_3$, and P(*n*Bu)$_3$ were used as the ligand, yields of less than 10% were obtained (Table 2, Entries 2–4). However, when *N*,*N*-dimethylglycine, 1,4-diazabicyclo[2.2.2]octane (dabco), α,α-bipyridine, 1,10-phenanthroline, and 8-hydroxyquinoline were employed instead of dppf, respectively for the above-mentioned reaction, no cross-coupling product was isolated (Table 2, Entries 13–17). The results also showed that when the mol ratio of dppf to $Au^I$ was less than 1:1, the reaction was not complete, whereas ratios equal to or more than 1:1 provided satisfactory results (Table 2, Entries 10–12).

Also, the effect of several different bases on the Sonogashira reactions catalyzed by gold(I) iodide was investigated. With regard to other reaction conditions, $K_2CO_3$ was found to act as an excellent base. $Na_2CO_3$, $Cs_2CO_3$, $K_3PO_4$, KF, and *t*BuOK were also effective. Other bases, such as KOH and KOAc were substantially less effective. However, pyridine, triethylamine, and piperidine were no longer the effective bases in this catalytic system (Table 3, Entries 1–11).

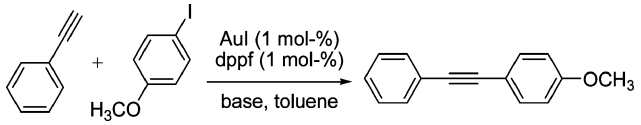
Table 2. Effect of ligands on the Sonogashira reaction.[a]




| Entry | Ligand (amount) | Yield[b] [%] |
|---|---|---|
| 1 | – | 0 |
| 2 | P(OPh)$_3$ (2 mol-%) | <10 |
| 3 | P(OMe)$_3$ (2 mol-%) | <10 |
| 4 | P(*n*Bu)$_3$ (2 mol-%) | <10 |
| 5 | $PPh_3$ (2 mol-%) | 70 |
| 6 | P(*o*-tolyl)$_3$ (2 mol-%) | 64 |
| 7 | (*p*-tolyl)$PPh_2$ (2 mol-%) | 66 |
| 8 | binap (1 mol-%) | 79 |
| 9 | bisbenzodioxanphos (1 mol-%) | 73 |
| 10 | dppf (1 mol-%) | 96 |
| 11 | dppf (2 mol-%) | 96 |
| 12 | dppf (0.5 mol-%) | 68 |
| 13 | *N*,*N*-dimethylglycine (1 mol-%) | 0 |
| 14 | 1,10-phenanthroline (1 mol-%) | 0 |
| 15 | α,α-bipyridine (1 mol-%) | 0 |
| 16 | 8-hydroxyquinoline (1 mol-%) | 0 |
| 17 | dabco (1 mol-%) | 0 |

[a] Phenylacetylene (102 mg, 1.0 mmol), *p*-iodoanisole (234 mg, 1.0 mmol), AuI (3.2 mg, 0.01 mmol), $K_2CO_3$ (276 mg, 2.0 mmol), and ligand (amount indicated) in toluene (2 mL) at 130 °C for 24 h. [b] Isolated yields.

Table 3. Effect of bases on the Sonogashira reaction.[a]




| Entry | Base | Yield [b] [%] |
|---|---|---|
| 1 | $K_2CO_3$ | 96 |
| 2 | $Na_2CO_3$ | 90 |
| 3 | $Cs_2CO_3$ | 92 |
| 4 | $K_3PO_4$ | 82 |
| 5 | KF | 68 |
| 6 | KOAc | 59 |
| 7 | KOH | <10 |
| 8 | *t*BuOK | 65 |
| 9 | pyridine | <5 |
| 10 | triethylamine | <5 |
| 11 | piperidine | <5 |

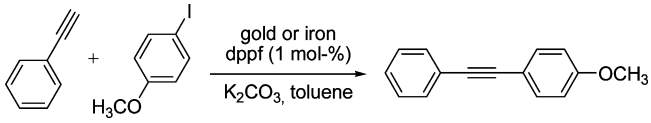
[a] Phenylacetylene (102 mg, 1.0 mmol), *p*-iodoanisole (234 mg, 1.0 mmol), AuI (3.2 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), base (2.0 mmol) in toluene (2 mL) at 130 °C for 24 h. [b] Isolated yields.

Finally, the catalytic activity of gold salts for the reactions was explored. According to our experimental results, $Au^{III}$, $Au^I$, and $Au^0$ were all effective catalysts for Sonogashira reactions in the presence of dppf, and $Au^I$ was the best of choice, which did not agree with the literature[14] (Table 4, Entries 1–15). It is worth noting that homocoupling of the terminal alkynes did not occurred with the use

of our procedure. Recently, iron species also showed high activities in mediating reactions involving alkynes and alkenes.[15] We wondered whether iron had any catalytic activity in the Sonogashira reaction. However, no desired product was isolated when $Fe^{III}$, $Fe^{II}$, or Fe (nanosized powder) was added to the reactions instead of gold (Table 4, Entry 12–14). In addition, no desired product was isolated in the absence of a gold source (Table 4, Entry 15). We also investigated the effect of the amount of AuI. The experimental data indicated that the reaction was not complete when the amount of AuI was less than 1 mol-% at 130 °C for 24 h. When the reaction was carried out under microwave irradiation by using a 650-W microwave oven (Sanle WP 650D at 2450 MHz) at 50% power for 0.5 h, 91% yield of the cross-coupling product was isolated (Table 4, Entry 11). Fortunately, excellent yield of the desired product was observed with 0.5 mol-% of AuI when the reaction time was prolonged (Table 4, Entry 9).

Table 4. Effect of gold and iron sources on the Sonogashira reaction.[a]



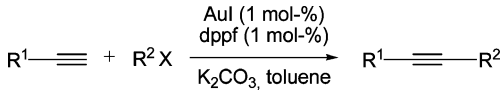

| Entry | Gold or iron source (amount) | Yield[b][%] |
|---|---|---|
| 1 | $AuCl_3$ (1 mol-%) | 90 |
| 2 | $HAuCl_4$ (1 mol-%) | 75 |
| 3 | AuCl (1 mol-%) | 95 |
| 4 | $Au^0$ colloid [c] (1 mol-%) | 55 |
| 5 | $Au^0$ on PVP [c] (1 mol-%) | 20 |
| 6 | AuI (1 mol-%) | 96 |
| 7 | AuI (2 mol-%) | 96 |
| 8 | AuI (0.5 mol-%) | 84 |
| 9 | AuI (0.5 mol-%) | 96[d] |
| 10 | AuI (1 mol-%) | 72[e] |
| 11 | AuI (1 mol-%) | 91[f] |
| 12 | $FeCl_3$ (1 mol-%) | 0 |
| 13 | $FeCl_2$ (1 mol-%) | 0 |
| 14 | nanosized $Fe^0$ (1 mol-%) | 0 |
| 15 | – | 0 |

[a] Phenylacetylene (102 mg, 1.0 mmol), *p*-iodoanisole (234 mg, 1.0 mmol), gold or iron source (amount indicated), dppf (5.5 mg, 0.01 mmol), $K_2CO_3$ (276 mg, 2.0 mmol) in toluene (2 mL) at 130 °C for 24 h. [b] Isolated yields. [c] It was prepared according to the literature.[3b] [d] Reaction time was 48 h. [e] Reaction time was 12 h. [f] The reaction was carried out under microwave irradiation by using a 650-W microwave oven (Sanle WP 650D at 2450 MHz) at 50% power for 0.5 h.

During the course of further optimization of the reaction conditions, when using 1 mol-% of AuI, the reactions were generally completed in a matter of hours, but the time, as expected, was inversely proportional to the temperature. A reaction temperature of 130 °C was found to be optimal. Thus, the optimized reaction conditions for the Sonogashira reactions are: AuI (1 mol-%), dppf (1 mol-%), $K_2CO_3$ (2 equiv.) in toluene at 130 °C for 24 h.

We investigated the coupling reactions by using a variety of aryl iodides and bromides and a wide range of terminal alkynes as the substrates under the optimized reaction conditions, and the results are summarized in Table 5. Electron-neutral, electron-rich, and electron-poor aryl iodides reacted with phenylacetylene very well to generate the corresponding cross-coupling products in excellent yields (Table 5, Entries 1–4, 6–7, 9, and 11–13), whereas the cross coupling did not tolerate *ortho*-substituted aryl iodides (Table 5, Entries 5, 8, and 10). Regardless of their electronic character, both aromatic terminal alkynes and aliphatic terminal alkynes coupled with iodobenzene smoothly to produce the desired products in excellent yields (Table 5, Entries 3 and 14–21). Activated aryl bromides also reacted with phenylacetylene to provide the corresponding products in excellent yields (Table 5, Entries 22–27), but electron-rich aryl bromides, such as *p*-bromoanisole, only afforded the product in poor yield (35%; Table 5, Entry 28).

Table 5. AuI-catalyzed Sonogashira reactions.[a]




| Entry | Alkyne | Organic halide | Yield[b] [%] |
|---|---|---|---|
| 1 | $C_6H_5C{\equiv}CH$ | *p*-$CH_3OC_6H_4I$ | 96 |
| 2 | $C_6H_5C{\equiv}CH$ | *p*-$CH_3C_6H_4I$ | 98 |
| 3 | $C_6H_5C{\equiv}CH$ | $C_6H_5I$ | 99 |
| 4 | $C_6H_5C{\equiv}CH$ | *m*-$CH_3C_6H_4I$ | 92 |
| 5 | $C_6H_5C{\equiv}CH$ | *o*-$CH_3C_6H_4I$ | 35 |
| 6 | $C_6H_5C{\equiv}CH$ | *p*-$CF_3C_6H_4I$ | 99 |
| 7 | $C_6H_5C{\equiv}CH$ | *m*-$CF_3C_6H_4I$ | 91 |
| 8 | $C_6H_5C{\equiv}CH$ | *o*-$CF_3C_6H_4I$ | 42 |
| 9 | $C_6H_5C{\equiv}CH$ | *p*-$FC_6H_4I$ | 99 |
| 10 | $C_6H_5C{\equiv}CH$ | *o*-$FC_6H_4I$ | 45 |
| 11 | $C_6H_5C{\equiv}CH$ | *p*-$NO_2C_6H_4I$ | 99 |
| 12 | $C_6H_5C{\equiv}CH$ | *m*-$NO_2C_6H_4I$ | 91 |
| 13 | $C_6H_5C{\equiv}CH$ | *p*-$CH_3COC_6H_4I$ | 99 |
| 14 | *n*-$C_8H_{17}C{\equiv}CH$ | $C_6H_5I$ | 78 |
| 15 | *n*-$C_8H_{17}C{\equiv}CH$ | $C_6H_5I$ | 92[c] |
| 16 | *n*-$C_6H_{13}C{\equiv}CH$ | $C_6H_5I$ | 82[c] |
| 17 | *p*-$CH_3C_6H_4C{\equiv}CH$ | $C_6H_5I$ | 97 |
| 18 | *p*-$BrC_6H_4C{\equiv}CH$ | $C_6H_5I$ | 98 |
| 19 | *p*-$ClC_6H_4C{\equiv}CH$ | $C_6H_5I$ | 99 |
| 20 | *p*-$FC_6H_4C{\equiv}CH$ | $C_6H_5I$ | 99 |
| 21 | *p*-$C_6H_4C_6H_4C{\equiv}CH$ | $C_6H_5I$ | 95 |
| 22 | $C_6H_5C{\equiv}CH$ | 2-bromopyridine | 91 |
| 23 | $C_6H_5C{\equiv}CH$ | 3-bromopyridine | 79 |
| 24 | $C_6H_5C{\equiv}CH$ | *p*-$NO_2C_6H_4Br$ | 92 |
| 25 | $C_6H_5C{\equiv}CH$ | *m*-$NO_2C_6H_4Br$ | 81 |
| 26 | $C_6H_5C{\equiv}CH$ | *p*-$CNC_6H_4Br$ | 94 |
| 27 | $C_6H_5C{\equiv}CH$ | *p*-$CH_3COC_6H_4Br$ | 93 |
| 28 | $C_6H_5C{\equiv}CH$ | *p*-$CH_3OC_6H_4Br$ | 35[c] |

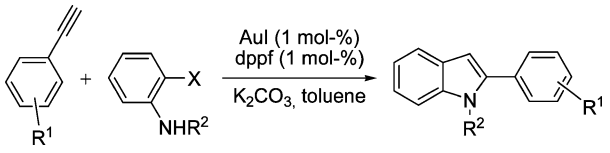
[a] Alkyne (1.0 mmol), organic halide (1.0 mmol), AuI (3.2 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), $K_2CO_3$ (276 mg, 2.0 mmol) in toluene (2 mL) at 130 °C for 24 h. [b] Isolated yields. [c] AuI (0.02 mmol) and dppf (0.02 mmol) were added to the reaction.

We also investigated the application of this coupling–cyclization reaction sequence to the synthesis of substituted indoles, and the results are listed in Table 6. The reaction of *o*-iodoaniline with aromatic terminal alkynes proceeded very well and excellent yields of the desired products were achieved (Table 6, Entries 1–4). However, only a moderate yield of the desired product was obtained for an aliphatic terminal alkyne (Table 6, Entry 5). *N*-substituted *o*-iodoani-

lines, such as *N*-Boc, *N*-*p*-Ts, *N*-Ms, and *N*-acetyl *o*-iodoanilines, also reacted with phenylacetylene to provide the coupling–cyclization reaction products in good yields (Table 6, Entries 7–10). Unfortunately, when *o*-bromoaniline was used as the substrate instead of *o*-iodoaniline, no desired product was obtained (Table 6, Entry 6). However, when *o*-iodophenol was used as the starting material, no desired product was isolated. The mechanism of the gold-catalyzed Sonogashira coupling reaction and the effect of the ligand are not fully clear and further investigation is currently underway in our laboratory.

Table 6. AuI-catalyzed coupling–cyclization reactions of alkynes and *o*-iodoanilines.[a]




| Entry | Alkyne | $R^2$ | X | Yield[b] [%] |
|---|---|---|---|---|
| 1 | $C_6H_5C{\equiv}CH$ | H | I | 99 |
| 2 | $p$-$CH_3C_6H_4C{\equiv}CH$ | H | I | 99 |
| 3 | $p$-$ClC_6H_4C{\equiv}CH$ | H | I | 96 |
| 4 | $p$-$FC_6H_4C{\equiv}CH$ | H | I | 94 |
| 5 | $n$-$C_6H_{13}C{\equiv}CH$ | H | I | 41 |
| 6 | $C_6H_5C{\equiv}CH$ | H | Br | 0 |
| 7 | $C_6H_5C{\equiv}CH$ | Boc | I | 72 |
| 8 | $C_6H_5C{\equiv}CH$ | *p*-Ts | I | 73 |
| 9 | $C_6H_5C{\equiv}CH$ | Ms | I | 60 |
| 10 | $C_6H_5C{\equiv}CH$ | acetyl | I | 79 |

[a] Alkyne (1.0 mmol), *o*-iodoaniline (1.0 mmol), AuI (3.2 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), $K_2CO_3$ (276 mg, 2.0 mmol) in toluene (2 mL) at 130 °C for 24 h. [b] Isolated yields.

## Conclusions

We developed a novel gold(I)-catalyzed Sonogashira coupling reaction. The cross-coupling reactions of terminal alkynes with aryl iodides and aryl bromides generate the corresponding coupling products in good to excellent yields under the present reaction conditions. Furthermore, aromatic terminal alkynes could also react with 2-iodoaniline to form substituted indoles in excellent yields through a coupling–cyclization reaction sequence under the present reaction conditions.

## Experimental Section

**Representative Procedure for the Gold(I) Iodide Catalyzed Sonogashira Reaction:** Phenylacetylene (102 mg, 1.0 mmol), *p*-iodoanisole (234 mg, 1.0 mmol), AuI (3.2 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol) and $K_2CO_3$ (276 mg, 2.0 mmol) were added to a round-bottomed flask containing toluene (2 mL). The reaction mixture was stirred at 130 °C for 24 h. After completion of reaction, the mixture was filtered and washed with diethyl ether (2 × 5 mL). The combined organic phase was dried with $Na_2SO_4$, filtered, and concentrated, and the residue was purified by flash chromatography on silica gel to give 200 mg of (*p*-methoxyphenyl)phenylacetylene (96% yield).

**(4-Methoxyphenyl)phenylacetylene:**[16] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.54–7.44 (m, 4 H, Ar*H*), 7.38–7.32 (m, 3 H, Ar*H*), 6.89 (d, $J$ = 8.4 Hz, 2 H, Ar*H*), 3.83 (s, 3 H, ArO$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 159.6, 133.1, 131.4, 128.4, 127.9, 123.4, 115.4, 113.9, 89.2, 88.1, 55.4 ppm.

**Phenyl-*p*-tolylacetylene:**[17] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.50–7.45 (m, 2 H, Ar*H*), 7.44 (d, $J$ = 8.1 Hz, 2 H, Ar*H*), 7.28–7.22 (m, 3 H, Ar*H*), 7.15 (d, $J$ = 7.8 Hz, 2 H, Ar*H*), 2.31 (s, 3 H, Ar$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 138.2, 131.6, 129.0, 128.1, 128.0, 123.5, 120.0, 89.8, 88.5, 21.5 ppm.

**Diphenylacetylene:**[18] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.58–7.53 (m, 4 H, Ar*H*), 7.35–7.29 (m, 6 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 131.7, 128.5, 128.2, 123.2, 89.5 ppm.

**Phenyl-*m*-tolylacetylene:**[19] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.57–7.53 (m, 2 H, Ar*H*), 7.42–7.29 (m, 5 H, Ar*H*), 7.29–7.16 (m, 2 H, Ar*H*), 2.38 (s, 3 H, Ar$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 138.0, 132.1, 131.6, 129.3, 128.8, 128.4, 128.2, 128.1, 123.4, 123.1, 89.7, 89.1, 21.4 ppm.

**Phenyl-*o*-tolylacetylene:**[20] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.68–7.58 (m, 3 H, Ar*H*), 7.44–7.39 (m, 3 H, Ar*H*), 7.31–7.20 (m, 3 H, Ar*H*), 2.63 (s, 3 H, Ar$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 140.1, 132.8, 131.9, 131.8, 129.6, 129.1, 128.6, 128.5, 128.2, 125.7, 88.5, 81.9, 20.7 ppm.

**(4-Trifluoromethylphenyl)phenylacetylene:**[21] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.64–7.61 (m, 4 H, Ar*H*), 7.59–7.55 (m, 2 H, Ar*H*), 7.39–7.36 (m, 3 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 131.9, 131.8, 129.9 ($J$ = 32.4 Hz), 128.9, 128.5, 127.1 ($J$ = 1.4 Hz), 125.2 ($J$ = 3.9 Hz), 123.9 ($J$ = 270.1 Hz), 122.6, 91.8, 87.9 ppm.

**(3-Trifluoromethylphenyl)phenylacetylene:**[22] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.78–7.73 (m, 1 H, Ar*H*), 7.74–7.63 (m, 1 H, Ar*H*), 7.61–7.51 (m, 3 H, Ar*H*), 7.47–7.42 (m, 1 H, Ar*H*), 7.43–7.32 (m, 3 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 134.8, 131.8, 131.2 (q, $J$ = 32 Hz), 129.7, 128.9, 128.5, 124.8, 124.4, 124.1, 123.9 (q, $J$ = 270 Hz), 122.6, 90.9, 87.9 ppm.

**(2-Trifluoromethylphenyl)phenylacetylene:**[23] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.68–7.61 (m, 2 H, Ar*H*), 7.59–7.54 (m, 2 H, Ar*H*), 7.49–7.42 (m, 1 H, Ar*H*), 7.39–7.32 (m, 4 H, Ar*H*) ppm. MS: $m/z$ (%) = 246 (100) $[M]^+$, 225 (19), 202 (15), 196 (9), 176 (10), 98 (12).

**(4-Fluorophenyl)phenylacetylene:**[24] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.54–7.49 (m, 4 H, Ar*H*), 7.37–7.32 (m, 3 H, Ar*H*), 7.08–7.02 (m, 2 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 162.6 (d, $J$ = 248.0 Hz), 133.5 (d, $J$ = 8.7 Hz), 131.6, 128.3, 123.1, 119.5 (d, $J$ = 5.9 Hz), 115.8 (d, $J$ = 22.8 Hz), 89.1, 88.2 ppm.

**(2-Fluorophenyl)phenylacetylene:**[25] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.58–7.49 (m, 3 H, Ar*H*), 7.34–7.20 (m, 4 H, Ar*H*), 7.12–7.01 (m, 2 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 162.7 (d, $J$ = 250.0 Hz), 133.5, 131.7, 129.9 (d, $J$ = 7.9 Hz), 128.6, 128.4, 123.9 (d, $J$ = 2.9 Hz), 122.9, 115.5 (d, $J$ = 21.0 Hz), 111.9 (d, $J$ = 15.7 Hz), 94.5, 82.8 ppm.

**(4-Nitrophenyl)phenylacetylene:**[26] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.21 (d, $J$ = 8.82 Hz, 2 H, Ar*H*), 7.66 (d, $J$ = 8.70 Hz, 2 H, Ar*H*), 7.58–7.54 (m, 2 H, Ar*H*), 7.39–7.35 (m, 3 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 146.9, 132.1, 131.9, 130.1, 129.3, 128.6, 123.7, 122.0, 94.8, 87.7 ppm.

**(3-Nitrophenyl)phenylacetylene:**[27] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.34 (s, 1 H, Ar*H*), 8.17 (d, $J$ = 8.19 Hz, 1 H, Ar*H*), 7.77 (d, $J$ = 7.86 Hz, 1 H, Ar*H*), 7.55–7.49 (m, 3 H, Ar*H*), 7.34–7.32 (m, 3 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 148.4, 137.3, 131.9, 129.5, 129.1, 128.6, 126.5, 125.3, 122.9, 122.5, 92.1, 86.9 ppm.

**(4-Acetylphenyl)phenylacetylene:**[25] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.95 (d, $J$ = 8.47 Hz, 2 H, Ar*H*), 7.59 (d, $J$ = 8.44 Hz, 2 H, Ar*H*), 7.58–7.54 (m, 2 H, Ar*H*), 7.39–7.35 (m, 3 H, Ar*H*), 2.57 (s, 3 H, CO$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 197.3, 136.2, 131.9, 131.8, 128.9, 128.5, 128.3, 128.1, 122.7, 92.7, 88.8, 26.7 ppm.

**1-Phenyl-1-decyne:**[28] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.44–7.39 (m, 2 H, Ar*H*), 7.29–7.24 (m, 3 H, Ar*H*), 2.39 [t, $J$ = 6.99 Hz, 2 H, $CH_2(CH_2)_6CH_3$], 1.62–1.55 [m, 2 H, $CH_2CH_2(CH_2)_5CH_3$], 1.47–1.29 [m, 10 H, $CH_2CH_2(CH_2)_5CH_3$], 0.89 (t, $J$ = 6.57 Hz, 3 H, $CH_2CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 131.7, 128.1, 127.5, 124.3, 90.1, 80.7, 31.9, 29.2, 29.1, 28.9, 28.8, 22.8, 19.4, 14.0 ppm.

**1-Phenyl-1-octyne:**[29] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.41–7.36 (m, 2 H, Ar*H*), 7.32–7.25 (m, 3 H, Ar*H*), 2.41 [t, $J$ = 6.97 Hz, 2 H, $CH_2(CH_2)_4CH_3$], 1.66–1.52 [m, 2 H, $CH_2CH_2(CH_2)_3CH_3$], 1.53–1.29 [m, 6 H, $CH_2CH_2(CH_2)_3CH_3$], 0.91 (t, $J$ = 6.72 Hz, 3 H, $CH_2CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 131.7, 128.1, 127.5, 124.2, 90.5, 80.7, 31.5, 28.9, 22.6, 19.4, 14.1 ppm.

**(4-Bromophenyl)phenylacetylene:**[24] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.55–7.45 (m, 4 H, Ar*H*), 7.39–7.30 (m, 5 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 133.1, 131.7, 128.6, 128.4, 122.9, 122.6, 122.3, 90.5, 88.4 ppm.

**(4-Chlorophenyl)phenylacetylene:**[30] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.56–7.48 (m, 2 H, Ar*H*), 7.48–7.42 (m, 2 H, Ar*H*), 7.37–7.32 (m, 4 H, Ar*H*), 7.32–7.29 (m, 1 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 134.6, 133.3, 132.1, 129.1, 128.9, 128.8, 123.5, 122.1, 90.6, 88.5 ppm.

**4-(Phenylethynyl)-1,1′-biphenyl:**[27] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.65–7.52 (m, 7 H, Ar*H*), 7.49–7.45 (m, 2 H, Ar*H*), 7.41–7.37 (m, 4 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 140.9, 140.4, 132.1, 131.6, 128.9, 128.4, 128.2, 127.7, 127.0, 123.1, 122.1, 90.0, 89.4 ppm.

**2-(2-Phenylethynyl)pyridine:**[31] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.61 (dd, $J$ = 5.10, 0.90 Hz, 1 H, Py*H*), 7.69–7.58 (m, 3 H, Py*H*), 7.53 (dd, $J$ = 8.10, 0.90 Hz, 1 H, Ar*H*), 7.39–7.35 (m, 3 H, Ar*H*), 7.25–7.17 (m, 1 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 149.9, 143.1, 136.2, 131.9, 128.8, 128.3, 127.1, 122.6, 122.0, 89.2, 88.6 ppm.

**3-(2-Phenylethynyl)pyridine:**[32] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.75–8.71 (m, 1 H, Ar*H*), 8.59–8.53 (m, 1 H, Ar*H*), 7.79–7.72 (m, 1 H, Ar*H*), 7.58–7.53 (m, 2 H, Ar*H*), 7.39–7.33 (m, 3 H, Ar*H*), 7.25–7.21 (m, 1 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 152.3, 148.5, 138.5, 131.7, 128.9, 128.4, 123.1, 122.6, 120.5, 92.8, 86.1 ppm.

**(4-Cyanophenyl)phenylacetylene:**[33] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.68–7.61 (m, 4 H, Ar*H*), 7.58–7.55 (m, 2 H, Ar*H*), 7.44–7.40 (m, 3 H, Ar*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 132.0, 131.8, 129.1, 128.5, 128.2, 122.2, 118.5, 111.4, 93.7, 87.7 ppm.

**2-Phenylindole:**[34] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.26 (br. s, 1 H, N*H*), 7.66–7.63 (m, 3 H, Ar*H*), 7.44–7.27 (m, 4 H, Ar*H*), 7.22–7.10 (m, 2 H, Ar*H*), 6.84 (s, 1 H, 3-indole-*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 137.9, 136.9, 132.3, 129.2, 129.0, 127.8, 125.1, 122.4, 120.6, 120.3, 110.9, 100.1 ppm.

**2-*p*-Tolylindole:**[35] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.28 (br. s, 1 H, N*H*), 7.63 (d, $J$ = 7.64 Hz, 1 H, Ar*H*), 7.56 (d, $J$ = 8.04 Hz, 2 H, Ar*H*), 7.36 (d, $J$ = 7.91 Hz, 1 H, Ar*H*), 7.25 (d, $J$ = 7.91 Hz, 2 H, Ar*H*), 7.18–7.09 (m, 2 H, Ar*H*), 6.79 (s, 1 H, 3-indole-*H*), 2.38 (s, 3 H, Ar$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 138.1, 137.6, 136.7, 129.7, 129.6, 129.3, 125.1, 122.1, 120.5, 120.2, 110.8, 99.4, 21.2 ppm.

**1-Methylsulfonyl-2-phenylindole:**[36] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.12 (d, $J$ = 7.84 Hz, 1 H, Ar*H*), 7.52–7.61 (m, 3 H, Ar*H*), 7.46–7.40 (m, 3 H, Ar*H*), 7.37 (td, $J$ = 7.44, 1.53 Hz, 1 H, Ar*H*), 7.34 (td, $J$ = 7.41, 1.53 Hz, 1 H, Ar*H*), 6.72 (s, 1 H, 3-indole-*H*), 2.74 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.9, 137.9, 131.9, 130.5, 130.1, 128.9, 127.6, 125.1, 124.7, 120.9, 115.9, 113.1, 39.8 ppm.

**1-(*p*-Toluenesulfonyl)-2-phenylindole:**[37] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.25 (d, $J$ = 7.58 Hz, 1 H, Ar*H*), 7.45–7.30 (m, 6 H, Ar*H*), 7.29–7.13 (m, 4 H, Ar*H*), 6.98 (d, $J$ = 8.13 Hz, 2 H, Ar*H*), 6.47 (s, 1 H, 3-indole-*H*), 2.23 (s, 3 H, Ar$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 144.5, 142.3, 138.5, 138.1, 134.5, 130.8, 130.3, 129.3, 126.8, 124.5, 124.1, 120.7, 116.6, 113.1, 21.5 ppm.

**2-(*p*-Fluorophenyl)indole:**[38] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.24 (br. s, 1 H, N*H*), 7.69–7.59 (m, 3 H, Ar*H*), 7.45 (d, $J$ = 8.31 Hz, 1 H, Ar*H*), 7.25–7.10 (m, 4 H, Ar*H*), 6.78 (s, 1 H, 3-indole-*H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 152.5 ($J$ = 250.3 Hz), 137.1, 136.9, 129.3, 128.8, 127.1 ($J$ = 7.6 Hz), 122.6, 120.7, 120.3, 116.4 ($J$ = 20.5 Hz), 111.1, 99.7 ppm.

**2-(*p*-Chlorophenyl)indole:**[39] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.26 (br. s, 1 H, N*H*), 7.64 (d, $J$ = 8.19 Hz, 2 H, Ar*H*), 7.52 (d, $J$ = 8.25 Hz, 2 H, Ar*H*), 7.45–7.38 (m, 3 H, Ar*H*), 7.26–7.10 (m, 2 H, Ar*H*), 6.79 (s, 1 H, 3-indole-*H*) ppm. MS: $m/z$ = 227 $[M]^+$.

**2-Hexyl-1*H*-indole:**[40] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.84 (br. s, 1 H, N*H*), 7.54 (d, $J$ = 7.80 Hz, 1 H, Ar*H*), 7.25 (d, $J$ = 7.86 Hz, 1 H, Ar*H*), 7.16–7.00 (m, 2 H, Ar*H*), 6.25 (s, 1 H, 3-indole-*H*), 2.72 [t, $J$ = 7.65 Hz, 2 H, $CH_2(CH_2)_4CH_3$], 1.69–1.59 [m, 2 H, $CH_2CH_2(CH_2)_3CH_3$], 1.45–1.32 [m, 6 H, $CH_2CH_2(CH_2)_3CH_3$], 0.89 (t, $J$ = 7.53 Hz, 3 H, $CH_2CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 140.1, 136.2, 129.0, 121.3, 119.7, 119.5, 110.3, 99.8, 31.9, 29.5, 29.3, 28.8, 22.9, 14.4 ppm.

**1-(2-Phenyl-1*H*-indol-1-yl)ethanone:**[41] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.38 (d, $J$ = 8.43 Hz, 1 H, Ar*H*), 7.57 (d, $J$ = 7.56 Hz, 1 H, Ar*H*), 7.47–7.39 (m, 5 H, Ar*H*), 7.33 (ddd, $J$ = 8.40, 7.32, 1.38 Hz, 1 H, Ar*H*), 7.21 (dt, $J$ = 7.50, 1.20 Hz, 1 H, Ar*H*), 6.52 (s, 1 H, 3-indole-*H*), 2.02 (s, 3 H, CO$CH_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 171.5, 139.6, 137.6, 134.3, 129.0, 128.8, 128.5, 125.2, 123.7, 120.4, 116.0, 111.6, 27.9 ppm.

***tert*-Butyl 2-phenylindole-1-carboxylate:**[42] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.25 (d, $J$ = 8.40 Hz, 1 H, Ar*H*), 7.58 (d, $J$ = 7.41 Hz, 1 H, Ar*H*), 7.44–7.35 (m, 6 H, Ar*H*), 7.23 (m, 1 H, Ar*H*), 6.51 (s, 1 H, 3-indole-*H*), 1.34 [s, 9 H, $(CH_3)_3$] ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 150.1, 140.3, 137.5, 135.1, 129.0, 128.7, 127.9, 127.3, 124.5, 122.7, 120.2, 115.4, 109.7, 83.6, 27.8 ppm.

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