Supporting Information

Empowering Transition-metal-free Cascade protocol for the green Synthesis of Biaryls and Alkynes

Preet Kamal Walia\textsuperscript{a}, Manoj Kumar\textsuperscript{a} and Vandana Bhalla\textsuperscript{a,*}

\textsuperscript{a}Department of chemistry, UGC Sponsored Centre for Advanced Studies-II, Guru Nanak Dev University, Amritsar-143005, Punjab, INDIA

vanmanan@yahoo.co.in
General Experimental Methods and Materials

Solvents and reagents were purchased from Sigma-Aldrich chemical company and were used without further purification unless otherwise specified. $^1$H NMR and $^{13}$C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer, Bruker (Avance II) FT-NMR-AL 400 MHz and 500 MHz spectrophotometers using CDCl$_3$ and DMSO-d$_6$ as solvents and tetramethylsilane (SiMe$_4$) as internal standards. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant (J/Hz) and integration. A 80 W UV light irradiation source was used for carrying out the photocatalytic reactions.

Common Procedure for the UV-light induced synthesis of aryl iodides:

In a reaction vial, to the solution (4mL) of aryl bromide (0.05g, 1.0 mmol) in H$_2$O/ACN (1:1), 0.062g KI and 135 µl of I$_2$ solution (0.2 M in CH$_3$CN) was added dropwise under aerial conditions (argon free conditions) and the reaction mixture was stirred until there was no more color change. The resultant solution was stirred under UV light at room temperature. TLC was used to monitor the formation of products. The reaction was stopped after 40 h by turning off the lamp. The resulting suspension was quenched with aqueous solution of Na$_2$S$_2$O$_3$ (0.01 M, 25 ml). The final product was isolated by extraction with organic solvent (EtOAc) and was purified by recrystallization using methanol except compound 2a. The compound 2a was isolated by extraction with organic solvent (EtOAc). The EtOAc layer was dried over Na$_2$SO$_4$, the solvent was then removed in vacuo to give compound 2a as colourless liquid.

General procedure for UV-light induced biaryl coupling:

Aryl halide (0.05g, 1.0 mmol), arene (4 mL) and KOtBu (3.0 mmol) were added in sequence to a reaction vial under aerial conditions (argon free conditions). The reaction mixture was stirred under UV light at 30°C. TLC was used to monitor the formation of products. After the completion of the reaction, the lamp was turned off. The final product was isolated by extraction with organic solvent and was purified by recrystallization using methanol.
General procedure for UV-light induced one-pot two-step reaction comprising of aromatic Finkelstein reaction and biaryl coupling:

In a reaction vial, to the solution (4mL) of aryl bromide (0.05g, 1.0 mmol) in H₂O/ACN (1:1), 0.062g KI and 135 µl of I₂ solution (0.2 M in CH₃CN) was added dropwise under aerial conditions (argon free conditions) and the reaction mixture was stirred until there was no more color change. The resultant solution was stirred under UV light at room temperature. TLC was used to monitor the formation of products. After the completion of the reaction, benzene (4 mL) and KOtBu (3 mmol) was charged into the same reaction mixture in the same pot. The formation of the product was monitored by TLC. When the reactants were consumed (after 72 h), the resulting mixture was diluted with ethyl acetate. The organic layer was concentrated in vacuo and purified by recrystallization from methanol.

General procedure for UV-light induced cascade synthesis of biaryls by aromatic Finkelstein reaction and biaryl coupling:

A reaction vial was charged with aryl bromide (0.05g, 1 mmol), ACN/H₂O (1:1), KI (3 mmol), I₂ (0.2M in ACN), arene (benzene/toluene/anisole/nitrobenzene) (4 mL) and KO'Bu (3 mmol) (all in sequence) under under aerial conditions (argon free conditions) in the presence of UV light. The reaction mixture was then stirred at r.t for 40 h in the presence of UV light. The reaction was monitored using TLC (after 40h, TLC of the reaction mixture matches very well with the standard sample) indicating the formation of aryl iodide. The reaction was then continued under UV light irradiation at 30°C. The formation of the final product was monitored by TLC again. When the reactants were consumed (after 72 h), the resulting mixture was diluted with ethyl acetate. The organic layer was concentrated in vacuo and purified by recrystallization from methanol.
General procedure for UV-light induced one-pot two-step reaction comprising of aromatic Finkelstein reaction and Sonogashira coupling:

In a reaction vial, to the solution (4mL) of aryl bromide (0.05g, 1.0 mmol) in H₂O/ACN (1:1), 0.062g KI and 135 µl of I₂ solution (0.2 M in CH₃CN) was added dropwise under aerial conditions (argon free conditions) and the reaction mixture was stirred until there was no more color change. The resultant solution was stirred under UV light at room temperature. TLC was used to monitor the formation of products. After the completion of the reaction, phenylacetylene (3 mmol) and KO'Bu (3 mmol) was charged into the same reaction mixture in the same pot. The formation of the product was monitored by TLC. When the reactants were consumed (after 75 h), the resulting mixture was diluted with ethyl acetate. The organic layer was concentrated in vacuo and purified by recrystallization from methanol.

General procedure for UV-light induced cascade synthesis of alkynes by aromatic Finkelstein reaction and Sonogashira coupling:

A reaction vial was charged with aryl bromide (0.05g, 1 mmol), ACN/H₂O (1:1), KI (3 mmol), I₂ (0.2M in ACN), alkyne (phenylacetylene/ 4-ethynylpyridine) (3 mmol) and KO'Bu (3 mmol) (all in sequence) under under aerial conditions (argon free conditions) in the presence of UV light. The reaction mixture was then stirred at r.t for 40 h in the presence of UV light. The reaction was monitored using TLC (after 40h, TLC of the reaction mixture matches very well with the standard sample) indicating the formation of aryl iodide). The reaction was then continued under UV light irradiation at 30°C. The formation of the final product was monitored by TLC again. When the reactants were consumed, the resulting mixture was diluted with ethyl acetate. The organic layer was concentrated in vacuo and purified by recrystallization from methanol.
Table S1. Control Experiments for the UV light mediated aromatic Finkelstein conversion of 4-bromobenzene to 4-iodobenzene using KI and iodine as shown in Scheme 1.

| Entry | Control Experiments | Yield[\(\%\)] |
|-------|---------------------|----------------|
| 1     | ACN[\(^{b}\)]      | 80             |
| 2     | ACN[\(^{b}\)]      | 73             |
| 3     | H\(_2\)O/ ACN(1:1)[\(^{b}\)] | 70             |
| 4     | H\(_2\)O[\(^{a}\)]  | 35             |
| 5     | H\(_2\)O/ ACN(1:1)[\(^{c}\)] | Negligible     |
| 6     | H\(_2\)O/ ACN(1:1)[\(^{d}\)] | Negligible     |
| 7     | TEMPO               | Negligible     |
| 8     | Benzoquinone        | Negligible     |

\(^{a}\) under inert conditions. \(^{b}\) under aerial conditions. \(^{c}\) under visible light. \(^{d}\) under dark. \(^{e}\) Isolated yields determined after recrystallization.

Table S2. Photocatalytic aromatic Finkelstein reaction for the synthesis of aryl iodides using I\(_2\) and KI in H\(_2\)O/ACN (1:1) at room temperature under aerial conditions using UV light.

| Entry | R  | Product | Time | Yield[\(^{a}\)] |
|-------|----|---------|------|----------------|
| 1     | H  | 2a      | 40 h | 70             |
| 2     | NO\(_2\) | 2b | 52 h | 63             |
| 3     | NH\(_2\) | 2c | 45 h | 66             |
| 4     | COOH | 2d | 58 h | 62             |
| 5     | CH\(_3\) | 2e | 52 h | 69             |
| 6     | OH  | 2f      | 56 h | 64             |
| 7     | OCH\(_3\) | 2g | 55 h | 69             |

\(^{a}\) Isolated yields determined after recrystallization.
**Scheme S1.** Mechanism of photo-induced aromatic Finkelstein reaction, heterolytic approach [path (a) and (b)].
[2a]. [iodobenzene]: (colourless liquid, 0.045g in 70% yield). $^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta = 7.77-7.75$ (m, 2H), 7.39-7.36 (m, 1H), 7.17-7.14 (m, 2H).

[2b]. [1-iodo-4-nitrobenzene]: (yellow solid, 0.038g in 63% yield). $^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta = 7.97$ (d, $J = 5$ Hz, 2H), 7.93 (d, $J = 10$ Hz, 2H).

[2c]. [4-iodoaniline]: (purple solid, 0.042g in 66% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta = 7.41$ (d, $J = 9$ Hz, 2H), 6.46 (d, $J = 6$ Hz, 2H), 3.67 (s, 2H, -NH$_2$).

[2d]. [4-iodobenzoic acid]: (white solid, 0.038g in 62% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta = 13.13$ (s, 1H, -COOH), 7.89 (d, $J = 10$ Hz, 2H), 7.70 (d, $J = 5$ Hz, 2H).

[2e]. [1-iodo-4-methylbenzene]: (white solid, 0.043g in 69% yield). $^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta = 7.59$ (d, $J = 10$ Hz, 2H), 6.95 (d, $J = 10$ Hz, 2H), 2.32 (s, 3H, -CH$_3$).

[2f]. [4-iodophenol]: (white solid, 0.040g in 64% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta = 7.51$ (d, $J = 9$ Hz, 2H), 6.63 (d, $J = 9$ Hz, 2H), 5.57 (s, 1H, -OH).

[2g]. [1-iodo-4-methoxybenzene]: (white solid, 0.043g in 69% yield). $^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta = 7.58$ (d, $J = 10$ Hz, 2H), 6.71 (d, $J = 10$ Hz, 2H), 3.80 (s, 3H, -OCH$_3$).

(1) (a) Liu, W.; Yang, X.; Gao, Y.; Li, C. J. Simple and Efficient Generation of Aryl Radicals from Aryl Triflates: Synthesis of Aryl Boronates and Aryl Iodides at Room Temperature. J. Am. Chem. Soc. 2017, 139, 8621–8627. (b) Leas, D. A.; Dong, Y.; Vennerstrom, J. L.; Stack, D. E. One-Pot, Metal-Free Conversion of Anilines to Aryl Bromides and Iodides. Org. Lett. 2017, 19, 2518–2521. (c) Ji, P.; Manna, K.; Lin, Z.; Feng, X.; Urban, A.; Song, Y.; Lin, W. Single-Site Cobalt Catalysts at New Zr12(µ3-O)$_8$(µ3-OH)$_8$(µ2-OH)$_6$ Metal–Organic Framework Nodes for Highly Active Hydrogenation of Nitroarenes, Nitriles, and Isocy-anides J. Am. Chem. Soc. 2017, 139, 7004–7011. (d) Babu, S. S.; Shanmugam, S. CAN-Supported Chemoselective Oxidative Conversion of α-Aroylketene-(S,S)-acetals to Aryl Carboxylic Acids. ChemistrySelect, 2017, 2, 2330–2334. (e) Li, L.; Liu, W.; Mu, X.; Mi, Z.; Li, C. J. Photo-induced iodination of aryl halides under very mild conditions. doi:10.1038/nprot.2016.125.
Figure S1. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 2a.

Figure S2. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 2b.
Figure S3. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 2c.

Figure S4. $^1$H NMR Spectra (DMSO-d$_6$, 500 MHz, ppm) of compound 2d.
Figure S5. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 2e.

Figure S6. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 2f.
Figure S7. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 2g.

Figure S8. Standard XRD analysis of AgBr.
**Figure S9(A).** Overlay $^1$H NMR spectra showing the consumption of 1-bromo-4-nitrobenzene and formation of 1-iodo-4-nitrobenzene.

**Figure S9(B).** Overlay $^1$H NMR spectra showing the consumption of 1-bromo-4-nitrobenzene and formation of 1-iodo-4-nitrobenzene.
Table S3. UV light mediated biaryl coupling of 4-iodoanisole with benzene using KO'Bu by varying the reaction conditions under aerial conditions as shown in Scheme 3.

| Entry | Reaction Conditions | Yield[^d] (%) |
|-------|---------------------|--------------|
| 1     | KO'Bu[^a]           | 66           |
| 2     | KO'Bu[^b]           | Negligible   |
| 3     | Visible light       | Negligible   |
| 4     | KO'Bu[^c]           | 61           |
| 5     | No UV light at 30°C | No reaction  |
| 6     | K$_3$PO$_4$         | Negligible   |
| 7     | NaOH                | <15%         |
| 8     | KOAc                | Negligible   |
| 9     | TEMPO               | Negligible   |
| 10    | Benzoquinone        | Negligible   |

[^a]: under inert conditions.  
[^b]: under dark.  
[^c]: under aerial conditions.  
[^d]: Isolated yields determined after recrystallization.
**Scheme S2.** Tentative mechanism for the photo-induced transition-metal-free biaryl coupling.

**Figure S10.** Reaction Progress monitored by TLC for the cascade reaction for the synthesis of biaryl (5b) under aerial conditions in the presence of UV light. (a) Conversion of 4-bromotoluene to 4-iodotoluene (dark coloured when kept in iodine chamber). (b) Conversion of 4-iodotoluene to biaryl (5b).
[5a]. [1,1'-biphenyl]: (white solid, 0.019g in 52% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.72-7.69 (m, 2H), 7.62-7.58 (m, 4H), 7.47-7.42 (m, 4H).

[5b]. [4-methyl-1,1'-biphenyl]: (white solid, 0.023g in 62% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.41-7.35 (m, 5H), 7.08-7.04 (m, 4H), 2.33 (s, 3H, CH$_3$).

[5c]. [1,1'-biphenyl]-4-amine]: (brown solid, 0.022g in 59% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.71-7.62 (m, 2H), 7.42-7.31 (m, 5H), 6.47 (d, $J$ = 6 Hz, 2H), 3.66 (s, 2H, NH$_2$).

[5d]. [4-methoxy-1,1'-biphenyl]: (white solid, 0.023g in 61% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.57-7.39 (m, 5H), 7.00-6.94 (m, 4H), 3.84 (s, 3H, OCH$_3$).

[5e]. [3,4-dimethoxy-1,1'-biphenyl]: (off white solid, 0.022g in 54% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.03 (d, $J$ = 3 Hz, 2H), 7.00 (d, $J$ = 3 Hz, 2H), 6.96 (d, $J$ = 3 Hz, 2H), 6.73 (d, $J$ = 9 Hz, 2H), 3.85 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$).

[5f]. [3,4-dimethyl-1,1'-biphenyl]: (off white solid, 0.021g in 54% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.39 (d, $J$ = 9 Hz, 2H), 7.22-7.19 (m, 2H), 7.00-6.90 (m, 4H), 2.35 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$).

[5g]. [4-bromo-1,1'-biphenyl]: (white solid, 0.025g in 61% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.57-7.53 (m, 4H), 7.46-7.39 (m, 5H).

[5h]. [4-nitro-1,1'-biphenyl]: (greenish yellow crystals, 0.025g in 63% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 8.05-8.02 (m, 2H), 7.94-7.91 (m, 2H), 7.87-7.80 (m, 5H).

[5i]. [4,4'-dimethyl-1,1'-biphenyl]: (white solid, 0.021g in 52% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ = 7.58-7.54 (m, 4H), 6.94-6.91 (m, 4H), 2.29 (s, 6H, CH$_3$).

[5j]. [4-methoxy-4'-methyl-1,1'-biphenyl]: (off white solid, 0.024g in 53% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.42-7.37 (m, 4H), 7.08-7.00 (m, 4H), 3.84 (s, 3H, OCH$_3$), 2.11 (s, 3H, CH$_3$).

[5k]. [4,4'-dimethoxy-1,1'-biphenyl]: (off white solid, 0.025g in 55% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ = 7.50-7.43 (m, 4H), 7.18-7.10 (m, 4H), 3.81 (s, 6H, OCH$_3$).
[5l]. [4-fluoro-1,1'-biphenyl]: (white solid, 0.021g in 55% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ = 7.69 (d, $J = 6$ Hz, 2H), 7.36-7.29 (m, 2H), 7.11-7.05 (m, 5H).

[5m]. [4-chloro-1,1'-biphenyl]: (white solid, 0.023g in 59% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ = 7.60-7.64 (m, 4H), 7.51-7.46 (m, 5H).

[5n]. [4-methyl-4'-nitro-1,1'-biphenyl]: (white solid, 0.028g in 57% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ = 8.47 (d, $J = 8$ Hz, 2H), 8.02 – 7.98 (m, 2H), 7.86 – 7.82 (m, 4H), 2.30 (s, 3H, CH$_3$).

[5o]. [4-fluoro-4'-methyl-1,1'-biphenyl]: (white solid, 0.024g in 56% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ = 7.59 – 7.56 (m, 4H), 6.95 – 6.91 (m, 4H), 2.30 (s, 3H, CH$_3$).

[5p]. [4-chloro-4'-methyl-1,1'-biphenyl]: (white solid, 0.025g in 55% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ = 7.65 – 7.62 (m, 4H), 7.57 – 7.52 (m, 4H), 2.30 (s, 3H, CH$_3$).

[5q]. [4-bromo-4'-methyl-1,1'-biphenyl]: (white solid, 0.032g in 57% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ = 7.81 – 7.77 (m, 4H), 7.49 – 7.45 (m, 4H), 2.30 (s, 3H, CH$_3$).

[5r]. [2-bromo-1,1'-biphenyl]: (white solid, 0.025g in 60% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ = 7.67 – 7.64 (m, 1H), 7.43 – 7.40 (m, 1H), 7.05-6.97 (m, 4H), 6.81-6.76 (m, 3H).
Singh, G.; Kumar, M.; Sharma, K.; Bhalla, V. A supramolecular ensemble of a PBI derivative and Cu₂O NPs: potential photocatalysts for the Suzuki and Suzuki type coupling reactions. *Green Chem.* **2016**, *18*, 3278-3285. (b) Cheng, Y.; Gu, X.; Li, P. Visible-Light Photoredox in Homolytic Aromatic Substitution: Direct Arylation of Arenes with Aryl Halides. *Org. Lett.* **2013**, *15*, 2664-2667. (c) Khana, R. I.; Pitchumani, K. A pyridinium modified β-cyclodextrin: an ionic supramolecular ligand for palladium acetate in C–C coupling reactions in water. *Green Chem.* **2016**, *18*, 5518-5528. (d) Wu, W.; Teng, Q.; Chua, Y. Y.; Huynh, H. V.; Duong, H. A. Iron-Catalyzed Cross-Coupling Reactions of Arylmagnesium Reagents with Aryl Chlorides and Tosylates: Influence of Ligand Structural Parameters and Identification of a General N-Heterocyclic Carbene Ligand. *Organometallics.* **2017**, *36*, 2293–2297. (e) Borah, R. K.; Mahanta, A.; Dutta, A.; Bora, U.; Thakur, A. J. A green synthesis of palladium nanoparticles by Sapindus mukorossi seed extract and use in efficient room temperature Suzuki–Miyaura cross-coupling reaction. *Appl Organometal Chem.* **2017**, e3784, doi.org/10.1002/aoc.3784. (f) Luan, Y. X.; Zhang, T.; Yao, W. W.; Lu, K.; Kong, L. Y.; Lin, Y. T.; Ye, M. Amide-Ligand-Controlled Highly para-Selective Arylation of Monosubstituted Simple Arenes with Arylboronic Acids. *J. Am. Chem. Soc.* **2017**, *139*, 1786–1789. (g) Tashiro, M.; Yamato, T. Studies on selective preparation of aromatic compounds.20.Selective preparation of 2-mono- and 2, 2'-disubstituted biphenyl using the tert-butyl group as a positional protective group. *J. Org. Chem.* **1979**, *44*, 3037-3041.
Figure S11. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5a.

Figure S12. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5b.
Figure S13. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5c.

Figure S14. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5d.
Figure S15. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5e.

Figure S16. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5f.
Figure S17. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5g.

Figure S18. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5h.
Figure S19. $^1$H NMR Spectra (CDCl$_3$, 400 MHz, ppm) of compound 5i.

Figure S20. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5j.
Figure S21. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5k.

Figure S22. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5l.
Figure S23. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5m.

Figure S24. $^1$H NMR Spectra (CDCl$_3$, 400 MHz, ppm) of compound 5n.
Figure S25. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5o.

Figure S26. $^1$H NMR Spectra (CDCl$_3$, 400 MHz, ppm) of compound 5p.
Figure S27. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5q.

Figure S28. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of adduct between 4-iodotoluene and TEMPO.
Figure S29. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of residual liquid left after recrystallization of compound 5b.

Figure S30. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 5r.
Figure S31. Mass Spectrum (ESI-MS) of intermediate 2e in one-pot two-step reaction comprising of aromatic Finkelstein reaction and biaryl coupling reaction.
Figure S32. Mass Spectrum (ESI-MS) of intermediate 2a in one-pot two-step reaction comprising of aromatic Finkelstein reaction and Sonogashira-Hagihara coupling reaction.
**Figure S33.** Cascade reaction for the synthesis of alkyne (9a) under aerial conditions in the presence of UV light. Reaction Progress monitored by TLC for the cascade reaction for the synthesis of alkyne (9a) under aerial conditions in the presence of UV light. (a) Conversion of bromobenzene to iodobenzene (slightly dark coloured when kept in iodine chamber). (b) Conversion of iodobenzene to alkyne (9a).

**Scheme S3.** Tentative mechanism for the photo-induced transition metal free cascade Sonogashira-Hagihara coupling reaction.
[9a]. \(^{3a}\) (1,2-diphenylethyne): (white solid, 0.039g in 69% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 7.54\) (d, \(J = 5\)Hz, 2H), 7.52 (d, \(J = 5\)Hz, 2H), 7.36-7.32 (m, 6H).

[9b]. \(^{3b}\) [1-methoxy-4-(phenylethynyl)benzene]: (yellow solid, 0.036g in 65% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 7.55\) (d, \(J = 10\)Hz, 1H), 7.51 (d, \(J = 10\)Hz , 2H), 7.47 (d, \(J = 10\)Hz, 2H), 7.33 (d, \(J = 5\)Hz, 2H), 6.87 (d, \(J = 10\)Hz, 1H), 6.68 (d, \(J = 10\)Hz, 1H), 3.83 (s, 3H, OCH\(_3\)).

[9c]. \(^{3b}\) [1-methyl-4-(phenylethynyl)benzene]: (yellow solid, 0.037g in 66% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 7.52\) (d, \(J = 10\)Hz, 2H), 7.43 (d, \(J = 5\)Hz, 2H), 7.34(d, \(J = 10\)Hz, 2H), 7.15 (d, \(J = 5\)Hz, 2H), 7.01 (d, \(J = 10\)Hz, 1H), 2.37 (s, 3H, CH\(_3\)).

[9d]. \(^{3a}\) [4-(phenylethynyl)aniline]: (brown solid, 0.034g in 61% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 7.50\) (d, \(J = 15\)Hz, 2H), 7.35 -7.30 (m, 5H), 6.64(d, \(J = 10\)Hz, 2H), 3.82 (s, 2H, NH\(_2\)).

[9e]. \(^{3a}\) [1-nitro-4-(phenylethynyl)benzene]: (yellow solid, 0.038g in 70% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 8.23\) (d, \(J = 10\)Hz, 2H), 7.68 (d, \(J = 5\)Hz, 2H), 7.58 -7.56 (m, 2H), 7.41-7.39 (m, 3H).

[9f]. \(^{3e}\) [1,2-dimethoxy-4-(phenylethynyl)benzene]: (yellow solid, 0.031g in 57% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta = 7.02\) (d, \(J = 5\)Hz, 2H), 7.01 (d, \(J = 5\)Hz, 2H), 6.97 (d, \(J = 5\)Hz, 2H), 6.71 (d, \(J = 5\)Hz, 2H), 3.85 (s, 3H, OCH\(_3\)), 3.83 (s, 3H, OCH\(_3\)).

[9g]. \(^{3d}\) [4-(phenylethynyl)pyridine]: (yellow solid, 0.031g in 56% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta = 8.49-8.42\) (m, 2H), 7.58-7.51 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.31 (m, 3H).

[9h]. \(^{3d}\) [3-(phenylethynyl)pyridine]: (yellow solid, 0.031g in 55% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta = 8.79\) (s, 1H), 8.52 (d, \(J = 3\) Hz, 1H), 7.77 (d, \(J = 6\) Hz, 1H), 7.57-7.54 (m, 2H), 7.36-7.30 (m, 4H).
(3) Ibrahim, M. B.; Ali, B. E.; Malik, I.; Fettouhi, M. Synthesis of functionalized alkynes via palladium-catalyzed Sonogashira reactions. Tetrahedron Lett. 2016, 57, 554-558. (b) Gazvoda, M.; Virant, M.; Pevec, A.; Urankar, D.; Bolje, A.; Kocevar, M.; Kosmrlj, J. A mesoionic bis(Py-tzNHC) palladium(II) complex catalyses “green” Sonogashira reaction through an unprecedented mechanism. Chem. Commun. 2016, 52, 1571-1574. (c) Sakaguchi, T.; Tsuzuki, T.; Masuda, T.; Hashimoto, T. Synthesis, gas permeability, and metal-induced gelation of poly(disubstituted acetylene)s having p,m-dimethoxyphenyl and p,m-dihydroxyphenyl groups. Polymer. 2014, 55, 1977-1983. (d) H. Yoneyama, M. Numata, K. Uemura, Y. Usami and S. Harusawa, Transformation of Carbonyl Compounds into Homologous Alkynes under Neutral Conditions: Fragmentation of Tetrazoles Derived from Cyanophosphates. J. Org. Chem., 2017, 82, 5538–5556.
Figure S34. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 9a.

Figure S35. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 9b.
Figure S36. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 9c.

Figure S37. $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 9d.
Figure S38. $^1$H NMR Spectra (CDCl₃, 500 MHz, ppm) of compound 9e.

Figure S39. $^1$H NMR Spectra (CDCl₃, 500 MHz, ppm) of compound 9f.
Figure S40. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 9g.

Figure S41. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 9h.
Figure S42. $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of residual liquid left after recrystallization of compound 9a.