


 Cite this: *RSC Adv.*, 2024, 14, 27141

Palladium(II) complexes bearing mesoionic carbene ligands: catalytic application in domino Sonogashira coupling/cyclization reactions for one-pot synthesis of benzofuran and indole derivatives†

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Bioactive heterocycles such as benzofuran and indole derivatives were synthesized from commercially available 2-iodoarenes and alkynes *via* domino Sonogashira coupling followed by cyclization reaction using well-defined palladium PEPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) complexes (**2a** and **2b**). These reactions tolerate a variety of 2-iodoarenes and diversely substituted terminal alkynes, resulting in the corresponding product in moderate to good yields in an open-air atmosphere. In particular, two palladium(II) PEPSI complexes **2a** and **2b** were synthesized in good yields from the reaction of corresponding 1,2,3-triazol-5-ylidene (MIC: mesoionic carbene), PdCl₂, KI, and K₂CO₃ in pyridine at 110 °C and structurally characterized by various spectroscopic techniques including NMR spectroscopy, IR spectroscopy, HRMS and elemental analysis studies. Complex **2b** is also characterized by X-ray crystallography.

 Received 11th May 2024
 Accepted 8th August 2024

DOI: 10.1039/d4ra03485f

rsc.li/rsc-advances

Introduction

Benzofused five-membered heterocyclic scaffolds such as benzofuran and indole derivatives are extensively spread as a common structural skeleton in many biologically active compounds, natural products, and pharmaceuticals.^{1–6} Over the years, considerable effort has been devoted to synthesizing these heterocycles.^{6–10} Synthesis of benzofuran and indole derivatives *via* a domino approach has received more attention than the traditional multistep approach due to its high atom economy, environmentally benign nature, and operational simplicity.^{1,8,11–15} Along these lines, palladium-catalyzed domino Sonogashira coupling/cyclization reaction has emerged as an efficient method for the construction of the benzofuran and indole framework.^{16–19}

N-heterocyclic carbenes (NHCs) have been used as spectator ligands in organometallic chemistry for the past three

decades.^{20–23} Their strong metal-NHC bond-forming tendency and high steric demands have made them much more popular and a good alternative to conventional phosphine ligands.^{20,24} An interesting counterpart of normal NHCs, 1,2,3-triazol-5-ylidene mesoionic carbene (1,2,3-triazolylidene) was first reported by Albrecht and co-workers in 2008.²⁵ In these MICs, only one adjacent electronegative nitrogen atom at the donor site increased the sigma donor ability compared to NHCs.²⁵ Triazolylidenes can be easily synthesized *via* copper-catalyzed Click reaction followed by an alkylation reaction.^{26–28} Several triazolylidene-based transition metal complexes are reported as catalysts in various organic transformations.^{27,29–38} PEPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) themed³⁹ palladium complexes bearing 1,2,3-triazolylidene were reported by Albrecht *et al.* in 2012.⁴⁰

Very few well-defined palladium complexes bearing N-heterocyclic carbene ligands are used as catalysts in domino Sonogashira coupling/cyclization reactions for one-pot synthesis of benzofuran and indole derivatives.^{41–43} Mata and coworkers reported the triazole based N-heterocyclic carbene-palladium complex as catalyst for the synthesis of benzofuran derivatives.⁴¹ Ghosh and coworkers revealed the dipalladium complex stabilized by N-heterocyclic carbene ligand for benzofuran synthesis.⁴² Our group also reported various palladium complexes as catalysts for the synthesis of benzofurans *via* domino Sonogashira coupling and cyclization reactions.^{43,44} Bera and coworkers developed the annellated mesoionic

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† Electronic supplementary information (ESI) available: ¹H and ¹³C{¹H} NMR spectra, HRMS data, X-ray crystallographic data of the complexes, NMR data of catalytic products. CCDC 2336820. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4ra03485f>



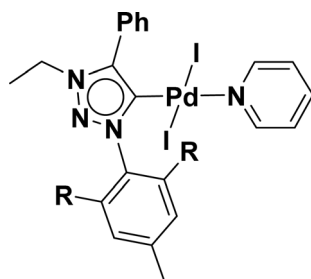
R = H (**2a**), CH₃ (**2b**)

Fig. 1 1,2,3-Triazol-5-ylidene based palladium PEPPSI complexes.

carbene ligand stabilized palladium complexes and explored their catalytic activity for the synthesis of benzofuran, indole, isocoumarin, and isoquinolone derivatives using domino approach.⁷ Herein, we reported the synthesis of 1,2,3-triazol-5-ylidene mesoionic carbene-based palladium PEPPSI complexes, **2a** and **2b** (Fig. 1) and further utilized these catalysts for the synthesis of biologically active benzofuran and indole derivatives *via* domino Sonogashira coupling/cyclization reaction under copper and amine free condition.

Results and discussion

Synthesis and characterization of palladium PEPPSI complexes

The 1,2,3-triazolium triflate ligands **1a** and **1b** were synthesized by AgOTf-assisted *N*-ethylation of corresponding 1,2,3-triazole^{40,45} using ethyl iodide as ethylating reagent (Scheme 1). Formation of triazolium ligands was indicated by the appearance of a quartet peak of two protons which corresponds to triazolium methylene (trz-CH₂-) peak in ¹H NMR spectrum at 4.64 ppm (**1a**) and 4.76 ppm (**1b**), respectively. The 1,2,3-triazolylidene based palladium(II) complexes (**2a** and **2b**) were synthesized with good yield (**2a** = 74%, **2b** = 83%) from the reaction of corresponding triazolium triflate, PdCl₂, K₂CO₃, and KI in pyridine at 110 °C in 5 days using a similar method reported earlier.^{35,46} The disappearance of a singlet of triazolium proton and the presence of a set of additional pyridine peaks in the aromatic region suggest the formation of palladium PEPPSI complexes. The ¹³C{¹H} NMR spectrum of these complexes revealed Pd-C_{carbene} peak at around 134.4 ppm for **2a** and 135.6 ppm for **2b**, respectively. After purification, both the complexes were obtained as pale-yellow solid.

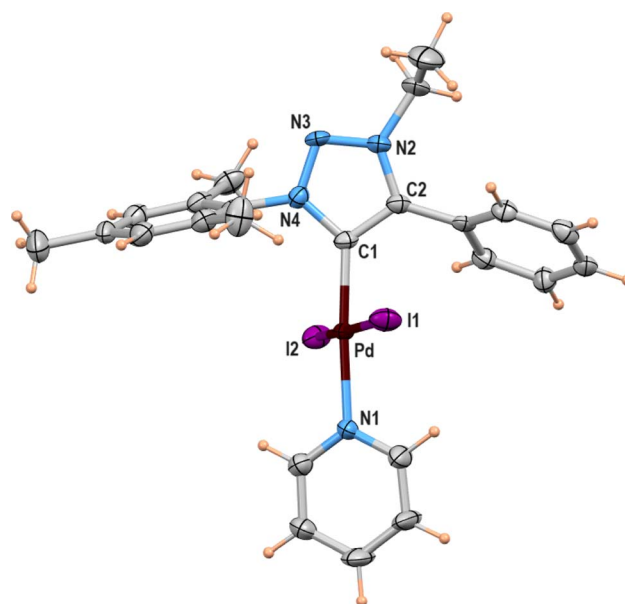
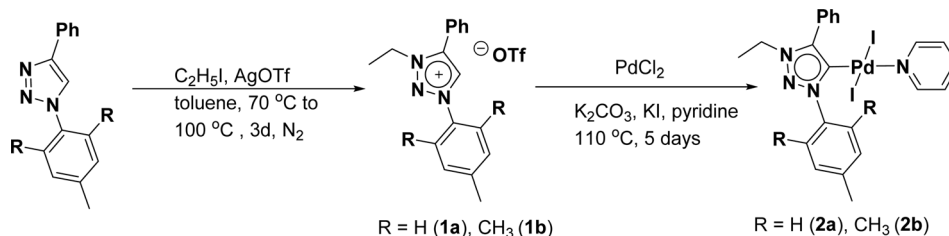


Fig. 2 Molecular structure showing [LPdI₂(pyridine)] (**2b**), ellipsoids are shown at 50% probability level. Only one of the molecules (out of two) present in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) 2.116(5), Pd(1)–C(1) 1.970(5), Pd(1)–I(1) 2.6208(6), Pd(1)–I(2) 2.5973(6), N(1)–Pd(1)–I(1) 92.12(14), N(1)–Pd(1)–I(2) 90.49(14), C(1)–Pd(1)–I(1) 87.90(17), C(1)–Pd(1)–I(2) 88.99(17); Pd(2)–N(5) 2.107(5), Pd(2)–C(25) 1.980(6), Pd(2)–I(3) 2.5801(6), Pd(2)–I(4) 2.6281(6), N(5)–Pd(2)–I(3) 90.93(14), N(5)–Pd(2)–I(4) 88.96(14), C(25)–Pd(2)–I(3) 89.24(16), C(25)–Pd(2)–I(4) 90.91(16).

X-ray structure

A suitable single crystal for X-ray diffraction analysis was obtained for complex **2b** by slow evaporation of solvent from a saturated solution of complex **2b** in acetonitrile at room temperature. The formation of palladium PEPPSI complex **2b** was confirmed by molecular structure analysis, and the geometry of the central palladium metal is found to be slightly distorted square planar in which 1,2,3-triazolylidene ligand located *trans* to pyridine and remaining coordination sites are occupied by iodido donors (Fig. 2). The average Pd–C_{carbene} and Pd–N_{pyridine} bond distances are 1.975(5) and 2.111(5), respectively, which are similar to analogous 1,2,3-triazolylidene ligand-based PEPPSI complexes previously reported in the literature.^{47–49} The average Pd–I bond lengths were also observed as close to the other reported PEPPSI type complexes containing iodide ligands.⁴⁹ The average C_{carbene}–Pd–N_{pyridine} and I–Pd–I bond angles are 174.4 (2)° and 175.96(2)°, respectively, which are closer to the expected 180° for a square planar geometry.

Scheme 1 Synthesis of palladium-PEPPSI complex **2a** and **2b**.

Domino Sonogashira coupling/cyclization reactions

Based on our previous study,^{43,44} 2-iodophenol and phenylacetylene were chosen as model substrates for domino Sonogashira coupling/cyclization reactions. In the optimization experiments, the initial reaction condition included 2-iodophenol (0.50 mmol), phenylacetylene (0.60 mmol), K₂CO₃ (1 mmol), and catalyst **2a** (2 mol%) in DMSO at 110 °C in air. Under this reaction condition, the desired benzofuran was obtained in 81% yield (entry 1, Table 1). Various other bases (entries 2–4, Table 1) and solvents (entries 5 and 6, Table 1) were screened for this reaction, with the result that K₃PO₄ base and DMSO solvent were found to be optimum for this reaction. Reducing the reaction time reduced the product yield to 65% (entry 7, Table 1). There was a negligible decrease in the product yield (83%) at 90 °C (entry 8, Table 1), but it decreased significantly to 41% at 60 °C (entry 9, Table 1). Reducing the catalyst loading to 1 mol% significantly decreases the product yield to 63% (entry 10, Table 1). The reaction with palladium precursor, *i.e.*, Pd(CH₃CN)₂Cl₂ gave a yield of 36% (entry 11, Table 1). In continuation, poor yield of the product was obtained under base-free conditions (entry 12, Table 1), while no reaction was observed in absence of a palladium catalyst (entry 13, Table 1).

With the optimized reaction condition in hand (entry 8), various substituted benzofuran and indole derivatives were synthesized in moderate to good yields from commercially available terminal alkynes and 2-iodoarenes (Table 2). In comparison, benzofuran derivatives were obtained a higher yield (entries 1 to 7, Table 2) with respect to indole derivatives (entries 8 to 14, Table 2). Furthermore, there is not much difference in the catalytic activity of the catalysts **2a** and **2b** under the same reaction conditions was observed.

Under the same reaction condition, (*Z*)-1-benzylidene-1,3-dihydroisobenzofuran derivatives were also synthesized in good yields from 2-iodobenzyl alcohols and terminal alkynes

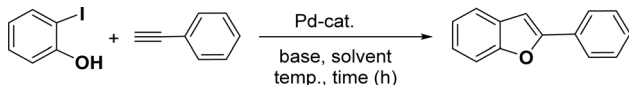
(Table 3). Formation of (*Z*)-1-benzylidene-1,3-dihydroisobenzofuran was confirmed from the presence of a singlet of one proton at δ 5.98 ppm for methine proton and singlet of two protons at δ 5.54 ppm for methylene protons, which matches with the previously reported NMR data.⁵⁰

Based on previous literature reports and experimental observations,^{7,42,44} a plausible reaction mechanism pathway for the Sonogashira coupling/cyclization of 2-iodoarenes and terminal alkynes was proposed in Scheme 2.

Initially, the palladium(II) complex **2b** was reduced to palladium(0) intermediate **A** as an active species. In cycle I, oxidative addition of 2-iodoarene led to the formation of intermediate **B**. This intermediate **B** coordinates with phenylacetylene to form intermediate **C** which is converted to intermediate **D** upon deprotonation of the coordinated phenylacetylene moiety. Next, through reductive elimination of intermediate **D**, 2-(phenylethynyl)arene and intermediate **A** are generated. Now, in cycle II, 2-(phenylethynyl)arene coordinated with intermediate **A** to give intermediate **F**, which is converted to intermediate **G** upon base-assisted deprotonation followed by palladium-assisted 5-*endo*-dig cyclization. Finally, protonolysis of intermediate **G** afforded the desired benzofuran along with the regeneration of intermediate **A**. This procedure yielded intermediates **A** (calcd = 499.1090; found = 499.1196), **B** (calcd = 696.0577; found = 696.0511), **D** (calcd = 670.1924; found = 670.1852), and **E** (calcd = 195.0810; found = 195.0808) detected by high-resolution mass spectrometry (HRMS).

The comparison of catalytic activity of complexes **2a** and **2b** with the previously reported N-heterocyclic carbene-based palladium complexes for the synthesis of benzofuran from the 2-iodophenol and phenylacetylene *via* domino Sonogashira coupling/cyclization reactions was shown in Table 4. Initially, Peris and coworkers reported the domino synthesis of benzofuran *via* Sonogashira coupling/cyclization reactions using 1 mol% of 1,2,4-triazole derived PEPSI complexes under copper- and

Table 1 Optimization of the reaction conditions for the synthesis of 2-arylbenzofuran^a

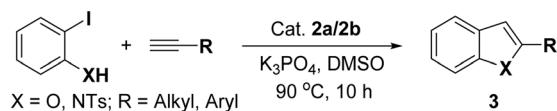


Entry	Catalyst (mol%)	Base	Solvent	Time (h)	Temp. (°C)	% Yield ^b
1	2a (2.0)	K ₂ CO ₃	DMSO	10	110	81
2	2a (2.0)	K ₃ PO ₄	DMSO	10	110	84
3	2a (2.0)	KO ^t Bu	DMSO	10	110	51
4	2a (2.0)	KOH	DMSO	10	110	42
5	2a (2.0)	K ₃ PO ₄	Dioxane	10	110	71
6	2a (2.0)	K ₃ PO ₄	Toluene	10	110	37
7	2a (2.0)	K ₃ PO ₄	DMSO	4	110	65
8	2a (2.0)	K ₃ PO ₄	DMSO	10	90	83
9	2a (2.0)	K ₃ PO ₄	DMSO	10	60	41
10	2a (1.0)	K ₃ PO ₄	DMSO	10	90	63
11	Pd(CH ₃ CN) ₂ Cl ₂ (2.0)	K ₃ PO ₄	DMSO	10	90	36
12	2a (2.0)	—	DMSO	10	90	10 ^c
13	—	K ₃ PO ₄	DMSO	10	90	nr ^d

^a Reaction conditions: 2-iodophenol (0.50 mmol), phenylacetylene (0.60 mmol), 2.0 mol% of catalyst, base (1.00 mmol), and solvent (2 mL).

^b Isolated yield. ^c Without base. ^d Without catalyst. nr = no reaction.



Table 2 Synthesis of benzofuran and indole derivatives via domino Sonogashira coupling/cyclization reactions catalyzed by 2a/2b^a

Entry	2-Iodoarenes	Alkynes	Product	Yield ^b (%)	
				2a	2b
1				83	87
2				80	85
3				68	71
4				76	83
5				71	77
6				64	65
7				63	65
8				65	57
9				48	53
10				35	39
11				46	49
12				40	38



Table 2 (Contd.)

X = O, NTs; R = Alkyl, Aryl

Entry	2-Iodoarenes	Alkynes	Product	Yield ^b (%)	
				2a	2b
13				34	38
14				39	37

^a Reaction conditions: 2-iodoarene derivative (0.50 mmol), alkyne (0.60 mmol), 2.0 mol% of **2a** or **2b**, K₃PO₄ (1.00 mmol), DMSO (2 mL), 90 °C, 10 h.
^b Isolated yield.

Table 3 Synthesis of isobenzofuran derivatives via domino Sonogashira coupling/cyclization reactions catalyzed by **2a/2b**^a

Ar = Aryl

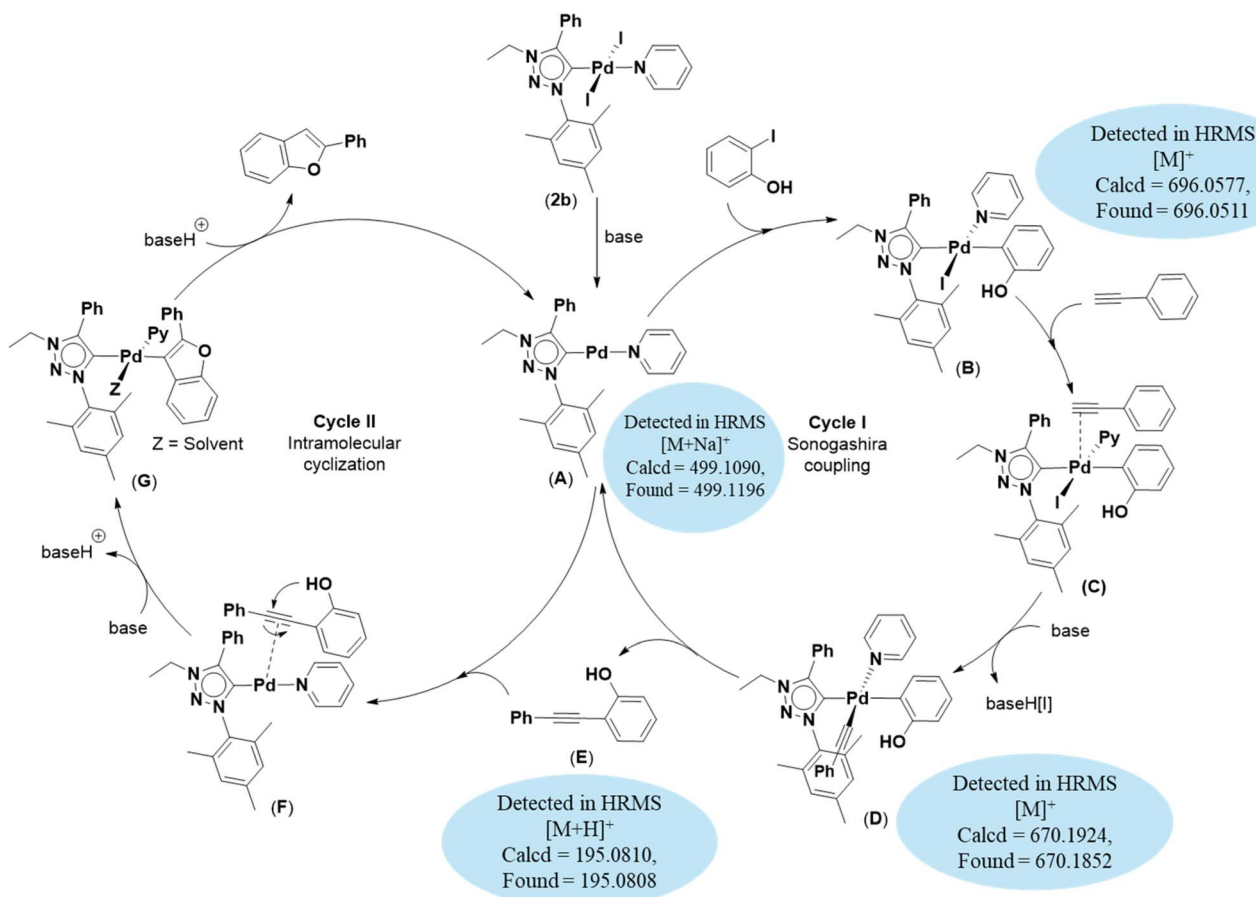
Entry	Iodobenzyl alcohol	Alkyne	Product	Yield ^b (%)	
				2a	2b
1				87	86
2				79	83
3				76	72
4				82	80



Table 3 (Contd.)

Entry	Iodobenzyl alcohol	Alkyne	Product	Yield ^b (%)	
				2a	2b
5				77	80
6				82	83

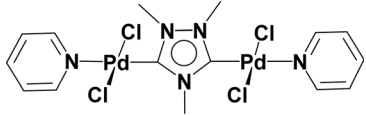
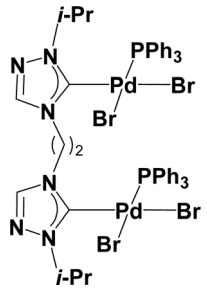
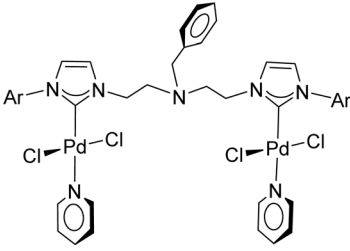
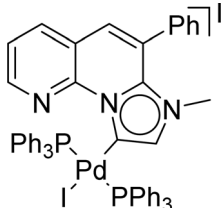
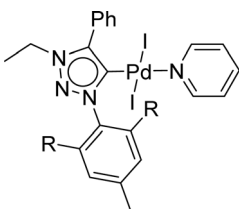
^a Reaction conditions: 2-iodobenzyl alcohol (0.50 mmol), alkyne (0.60 mmol), 2.0 mol% of **2a** or **2b**, K₃PO₄ (1.00 mmol), DMSO (2 mL), 90 °C, 10 h.
^b Isolated yield.



Scheme 2 Proposed mechanism for the synthesis of benzofuran derivatives via domino Sonogashira coupling/cyclization reactions.



Table 4 Comparison with reported well-defined catalysts for domino Sonogashira coupling/cyclization reaction of 2-iodophenol with phenylacetylene for synthesizing 2-phenylbenzofuran

No.	Catalyst	Loading (mol%)	Time (h)	Base/solvent	Temp. (°C)	Yield (%)	Ref.
1		1 mol%	8	CS ₂ CO ₃ /DMSO	80	93	41
2		1 mol%	4	CS ₂ CO ₃ /DMSO	80	81	42
3		0.2 mol%	16	K ₃ PO ₄ /DMSO	90	>99	43
4		2 mol%	2	K ₂ CO ₃ /DMSO	90	100 (GC-MS yield)	7
5		2 mol%	10	K ₃ PO ₄ /DMSO	90	83	This work

2a & 2b

amine-free conditions.⁴¹ Ghosh and coworkers group reported the same catalytic transformation employing 1 mol% of 1,2,4-triazole derived bis-NHC and phosphine ligand-based dipalladium complexes.⁴² Later, our group reported the same domino synthesis of benzofuran using 0.2 mol% of N-heterocyclic carbene ligated bimetallic palladium PEPPSI complexes.⁴³ Recently, Bera group also developed an annellated mesoionic carbene ligand stabilized palladium complex and explored their catalytic activity in benzofuran synthesis *via* domino approach.⁷ Thus, a comparison of the performance with previously reported well-defined N-heterocyclic carbene-based palladium complexes revealed that these types of mesoionic palladium complexes were not as active as other normal N-heterocyclic carbene-based PEPPSI complexes in terms of catalyst loading.

Conclusions

We have reported the preparation and characterization of two 1,2,3-triazolyliene-based palladium PEPPSI complexes **2a** and **2b** and their application in domino Sonogashira coupling/cyclization reactions for the synthesis of benzofuran and indole derivatives. Both PEPPSI-themed palladium complexes were well characterized by spectroscopic techniques. The complex **2b** was characterized by X-ray crystallography. The desired catalytic products were obtained in moderate to good yields with broad substrate scope at 2 mol% catalyst loading. This work further showed the catalytic potential of PEPPSI-themed complexes as effective catalysts for domino Sonogashira coupling/cyclization reactions.



Experimental section

General methods and materials

All manipulations were carried out under an atmosphere of nitrogen or in air. NMR spectra were recorded at 298 K on Bruker 500 MHz and JEOL 400 MHz NMR spectrometer. The chemical shifts of proton and carbon are reported in ppm and referenced using residual proton (7.26 ppm) and carbon signals (77.16 ppm) of CDCl₃.⁵¹ NMR annotations used: br. = broad, d = doublet, m = multiplet, s = singlet, t = triplet, sept = septet. Elemental analyses were performed using Thermo Quest FLASH 2000 SERIES (CHNS) Elemental Analyzer. Mass data are collected from Agilent 6545 LC/Q-ToF spectrometer. Solvents were purchased from commercial suppliers and used without further purification. CCDC-2336820 (2b) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>.[†] Catalytic substrates 2-iodophenol, (2-iodophenyl)methanol, phenylacetylene, 4-ethynyltoluene, 3-ethynyltoluene, 4-ethylphenylacetylene, 4-*tert*-butylphenylacetylene, 4-ethynylanisole, 3-ethynylaniline, prop-2-yn-1-ol, AgOTf, C₂H₅I, and K₃PO₄ were purchased from Sigma-Aldrich and used as received without further purification. 1-(*p*-Tolyl)-4-phenyl-1*H*-1,2,3-triazole,⁴⁵ phenyl-1*H*-1,2,3-triazole,⁴⁰ and *N*-(2-iodophenyl)-4-methylbenzenesulfonamide⁵² were synthesised using literature procedures.

Synthesis of ligand 1a

C₂H₅I (0.955 g, 6.12 mmol), AgOTf (1.57 g, 6.12 mmol) and anhydrous toluene (20 mL) were added in an aluminum foil covered 50 mL round bottom flask. The resulting mixture was heated at 60 °C for 5 hours under nitrogen atmosphere. In another 50 mL round bottom flask, 1-(*p*-tolyl)-4-phenyl-1*H*-1,2,3-triazole (1.20 g, 5.10 mmol) was mixed with anhydrous toluene (10 mL). After 5 hours, the mixture of C₂H₅I and AgOTf was transferred into the triazole containing round bottom flask by glass syringe, and the resulting reaction mixture was heated at 100 °C for 3 days under nitrogen atmosphere. The reaction mixture was cooled to room temperature and was decanted off the solvent. The residue was purified by column chromatography (MeOH/CHCl₃ = 2 : 98), affording the product as a dark brownish solid (1.48 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ 8.97 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.64 (q, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.58 (t, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.7, 142.5, 132.6, 131.8, 130.8, 129.6, 129.6, 126.5, 121.7, 121.4, 47.9, 21.3, 14.1 ppm. IR data (KBr pellet) cm⁻¹: 3094 (w), 2994 (w), 2947 (w), 2923 (w), 1613 (w), 1571 (w), 1518 (w), 1494 (w), 1457 (w), 1378 (w), 1265 (s), 1224 (m), 1153 (s), 1032 (m), 821 (w), 765 (w), 695 (w), 637 (w), 573 (w). HRMS (ESI) calcd for C₁₈H₁₈F₃N₃O₃S⁺ [M + H]⁺ *m/z* 414.1093; found 414.1116.

Synthesis of (1-ethyl-3(*p*-tolyl)5-phenyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl)(pyridin-2-yl) palladium(II) iodide (2a). Ligand 1a (0.349 g, 0.844 mmol), PdCl₂ (0.125 g, 0.704 mmol), KI (0.246 g, 1.48 mmol), K₂CO₃ (0.486 g, 3.52 mmol) and pyridine (4 mL) were added in 50 mL round bottom flask and the reaction mixture was heated at 110 °C for 5 days. The reaction mixture was cooled

down to room temperature and washed with saturated copper sulphate solution (5 × 10 mL) (for the removal of unbounded pyridine) and the organic fraction was extracted in chloroform (3 × 20 mL). Afterwards, the organic fraction was dried on MgSO₄ and filtered on a Celite-pad. The resulting crude product was further purified by column chromatography (20 : 80, EtOAc : petroleum ether), affording desired product as an orange solid (0.366 g, 74%). ¹H NMR (400 MHz, CDCl₃): 8.78 (d, *J* = 8.0 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.60–7.55 (dd, *J* = 14.6, 7.2 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.22–7.15 (m, 2H), 4.34 (q, *J* = 7.3 Hz, 2H), 2.48 (s, 3H), 1.57–1.53 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 153.8, 143.6, 140.1, 137.5, 137.3, 134.4 (MIC-Pd), 130.8, 130, 129.5, 128.8, 127.6, 125.2, 124.2, 46.2, 21.5, 14.7 ppm. IR data (KBr pellet) cm⁻¹: 2984 (w), 1740 (w), 1599 (w), 1509 (w), 1444 (m), 1374 (w), 1291 (m), 1188 (m), 1071 (m), 1019 (m), 815 (m), 764 (s), 692 (s), 595 (w), 519 (w), 475 (w), 421 (w). HRMS (ESI) calcd for C₂₂H₂₂I₂N₄Pd⁺ [M + Na]⁺ *m/z* 724.8867; found 724.8820. Anal. calcd for C₂₂H₂₂I₂N₄Pd: C, 37.61; H, 3.16; N, 7.97; found: C, 37.59; H, 3.12; N, 7.42%.

Synthesis of ligand 1b. C₂H₅I (0.853 g, 5.46 mmol), AgOTf (1.40 g, 5.46 mmol) and anhydrous toluene (20 mL) were added in an aluminum foil covered 50 mL round bottom flask and the mixture was heated at 60 °C for 5 hours under nitrogen atmosphere. In another 50 mL round bottom flask, 1-mesityl-4-phenyl-1*H*-1,2,3-triazole (1.20 g, 4.55 mmol) was suspended in anhydrous toluene (10 mL). After 5 hours, the reaction mixture of C₂H₅I and AgOTf was transferred into the triazole containing round bottom flask by glass syringe, and the resulting reaction mixture was heated at 100 °C for 3 days under nitrogen atmosphere. The reaction mixture was cooled to room temperature and solvent was decanted off. The residue was purified by column chromatography (SiO₂ : MeOH/CHCl₃ = 2 : 98), affording the product as a dark brownish solid (1.61 g, 80%). ¹H NMR (500 MHz, CDCl₃): 8.60 (s, 1H), 7.76 (d, *J* = 6.0 Hz, 2H), 7.55 (s, 3H), 7.02 (s, 2H), 4.76 (q, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 2.08 (s, 6H), 1.58 (t, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 143.8, 142.5, 134.4, 132.0, 131.4, 130.3, 129.89, 129.84, 129.77, 121.5, 48.3, 21.1, 17.2, 14.0 ppm. IR data (KBr pellet) cm⁻¹: 3096 (m), 2924 (w), 2855 (w), 1615 (w), 1459 (w), 1267 (s), 1155 (m), 1030 (m), 637 (w). HRMS (ESI) calcd for C₂₀H₂₂F₃N₃O₃S⁺ [M + H]⁺ *m/z* 442.1406; found 442.1396.

Synthesis of (1-ethyl-3-mesityl-5-phenyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl)(pyridin-2-yl)palladium(II) iodide (2b). Ligand 1b (0.267 g, 0.609 mmol), PdCl₂ (0.090 g, 0.507 mmol), KI (0.176 g, 1.06 mmol), K₂CO₃ (0.351 g, 2.54 mmol) and pyridine (*ca.* 4 mL) were added in 50 mL round bottom flask and the reaction mixture was heated at 110 °C for 5 days. The reaction mixture was cooled down to room temperature and washed with saturated copper sulphate solution (5 × 10 mL) (to remove unbounded pyridine), and the organic fraction was extracted in chloroform. Afterward, the organic fraction was dried on MgSO₄ and filtered on a Celite-pad. The resulting crude product was further purified by column chromatography (EtOAc : petroleum ether = 20 : 80) affording the desired product as an orange solid (0.308 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 8.67–8.65 (m, 2H), 8.00–7.98 (m, 2H), 7.63–7.53 (m, 4H), 7.14–7.11 (m, 2H), 7.05 (s, 2H), 4.42 (q, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 6H), 1.50 (t, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 153.7, 144.7,

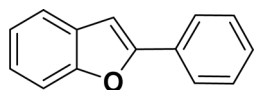


140.3, 137.5, 137.1, 135.7, 135.6 (MIC-Pd), 131.1, 130, 129.5, 128.6, 128.1, 124, 46.1, 21.4, 21.3, 14.8 ppm. IR data (KBr pellet) cm^{-1} : 2921 (w), 1739 (w), 1600 (w), 1442 (m), 1371(m), 1284 (m), 1228 (w), 1174 (m), 1084 (m), 1025 (m), 853 (w), 760 (s), 693 (s), 600 (w), 548 (w), 489 (w). HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{I}_2\text{N}_4\text{Pd}^+$ $[\text{M} + \text{K}]^+$ m/z 768.8919; found 768.8943. Anal. calcd for $\text{C}_{24}\text{H}_{26}\text{I}_2\text{N}_4\text{Pd}$: C, 39.45; H, 3.59; N, 7.67; found: C, 38.90; H, 3.56; N, 7.20. Suitable single crystal for X-ray diffraction analysis of **2b** was obtained by slow evaporation of acetonitrile solution at room temperature.

General procedure for Sonogashira coupling/cyclization reactions of 2-iodoarenes and alkyne

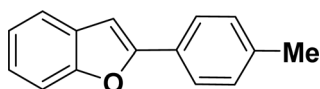
In a reaction vial, 2-iodoarenes (0.50 mmol), phenylacetylene (0.60 mmol), and K_3PO_4 (1.00 mmol) were added. A palladium complex (**2a** or **2b**, 2 mol%) and DMSO (*ca.* 2 mL) were added, and the resulting reaction mixture was heated at 90 °C for 10 hours. The reaction mixture was cooled to room temperature and quenched with water (*ca.* 20 mL). The resulting reaction mixture was extracted with EtOAc (3×20 mL) and dried on anhydrous Na_2SO_4 . Solvent was evaporated under reduced pressure and further purification was done by column chromatography.

2-Phenylbenzofuran (3aa: Table 2, entry 1).⁴⁴



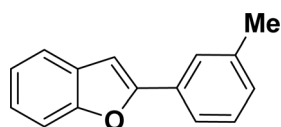
^1H NMR (500 MHz, CDCl_3): δ 7.92–7.87 (m, 2H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.56–7.54 (m, 1H), 7.48–7.45 (m, 2H), 7.40–7.35 (m, 1H), 7.33–7.28 (m, 1H), 7.28–7.23 (m, 1H), 7.04 (s, 1H) ppm.

2-(*p*-Tolyl)benzofuran (3ab: Table 2, entry 2).⁴⁴



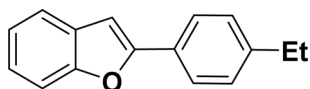
^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.61–7.58 (m, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.31–7.23 (m, 2H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.98 (s, 1H), 2.42 (s, 3H) ppm.

2-(*m*-Tolyl)benzofuran (3ac: Table 2, entry 3).⁴⁴



^1H NMR (500 MHz, CDCl_3): δ 7.76 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.29–7.26 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.06 (s, 1H), 2.48 (s, 3H) ppm.

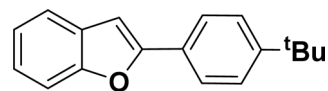
2-(4-Ethylphenyl)benzofuran (3ad: Table 2, entry 4).⁴⁴



^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 7.5$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.37

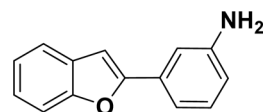
(d, $J = 8.0$ Hz, 2H), 7.34–7.30 (m, 1H), 7.05 (s, 1H), 2.78 (q, $J = 7.0$ Hz, 2H), 1.37 (t, $J = 7.0$ Hz, 3H) ppm.

2-(4-*tert*-Butylphenyl)benzofuran (3ae: Table 2, entry 5).⁴⁴



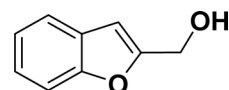
^1H NMR (500 MHz, CDCl_3): δ 7.86 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.28–7.26 (m, 1H), 7.03 (s, 1H), 1.42 (s, 9H) ppm.

3-(Benzofuran-2-yl)aniline (3af: Table 2, entry 6).⁴⁴



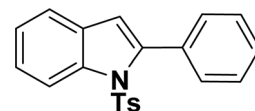
^1H NMR (500 MHz, CDCl_3): δ 7.60 (d, $J = 7.5$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.34–7.21 (m, 5H), 7.00 (s, 1H), 6.70–6.69 (m, 1H), 3.70 (br s, 2H) ppm.

Benzofuran-2-ylmethanol (3ag: Table 2, entry 7).⁴³



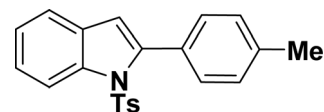
^1H NMR (500 MHz, CDCl_3): δ 7.58 (d, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.37–7.27 (m, 2H), 7.26–7.16 (m, 1H), 6.69 (s, 1H), 4.80 (s, 2H) ppm.

2-Phenyl-1-tosyl-1H-indole (3ah: Table 2, entry 8).¹⁹



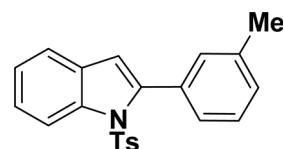
^1H NMR (500 MHz, CDCl_3): δ 8.23 (d, $J_{\text{HH}} = 7.0$ Hz, 1H), 7.42–7.35 (m, 6H), 7.27–7.18 (m, 4H), 6.96–6.95 (m, 2H), 6.46 (s, 1H), 2.20 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 144.6, 142.2, 138.4, 134.9, 132.5, 130.6, 130.4, 129.3, 128.7, 127.6, 126.9, 124.8, 124.4, 120.8, 116.7, 113.6, 21.6 ppm.

2-(4-Tolyl)-1-tosyl-1H-indole (3ai: Table 2, entry 9).⁵³



^1H NMR (500 MHz, CDCl_3): δ 8.22 (d, $J_{\text{HH}} = 8.0$ Hz, 2H), 7.35–7.31 (m, 3H), 7.27–7.24 (m, 1H), 7.21–7.14 (m, 5H), 6.96–6.94 (m, 2H), 6.42 (s, 1H), 2.36 (s, 3H), 2.19 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 144.5, 142.4, 138.7, 138.3, 134.8, 130.7, 130.3, 129.6, 129.2, 128.3, 126.9, 124.7, 124.3, 120.7, 116.8, 113.3, 29.8, 21.5 ppm.

2-(3-Tolyl)-1-tosyl-1H-indole (3aj: Table 2, entry 10).⁵⁴

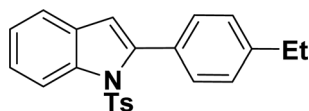


^1H NMR (500 MHz, CDCl_3): δ 8.22 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.35–



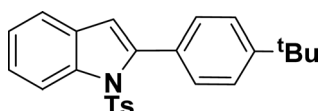
7.34 (m, 1H), 7.27–7.24 (m, 1H), 7.23–7.18 (m, 5H), 7.16–7.15 (m, 2H), 6.96–6.94 (m, 2H), 6.44 (s, 1H), 2.33 (s, 3H), 2.20 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 144.5, 142.4, 138.3, 137.0, 134.9, 132.4, 131.1, 130.6, 129.5, 129.2, 127.55, 127.5, 126.9, 124.7, 124.3, 120.7, 116.7, 113.4, 29.8, 21.6 ppm.

2-(4-Ethylphenyl)-1-tosyl-1H-indole (3ak: Table 2, entry 11).⁵⁵



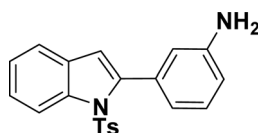
^1H NMR (500 MHz, CDCl_3): δ 8.21 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.33–7.31 (m, 3H), 7.25–7.22 (m, 1H), 7.18–7.15 (m, 5H), 6.93–6.91 (m, 2H), 6.41 (s, 1H), 2.64 (q, $J_{\text{HH}} = 7.0$ Hz, 2H), 2.17 (s, 3H), 1.21 (t, $J_{\text{HH}} = 7.0$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 144.9, 144.5, 142.4, 138.3, 134.8, 130.7, 130.3, 129.8, 129.2, 127.1, 126.9, 124.7, 124.3, 120.6, 116.7, 113.3, 28.8, 21.5, 15.4 ppm.

2-(4-(tert-Butyl)phenyl)-1-tosyl-1H-indole (3al: Table 2, entry 12).⁵⁶



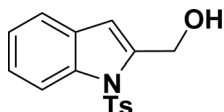
^1H NMR (500 MHz, CDCl_3): δ 8.22 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.35–7.34 (m, 4H), 7.27–7.24 (m, 1H), 7.20–7.16 (m, 4H), 6.96–6.94 (m, 2H), 6.44 (s, 1H), 2.20 (s, 3H), 1.31 (s, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 151.8, 144.5, 142.4, 138.4, 134.8, 130.7, 130.1, 129.5, 129.2, 127.0, 124.7, 124.5, 124.3, 120.7, 116.8, 113.4, 34.8, 31.5, 21.6 ppm.

3-(1-Tosyl-1H-indol-2-yl)aniline (3am: Table 2, entry 13).



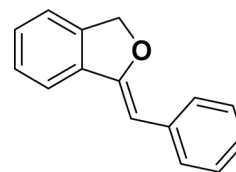
^1H NMR (500 MHz, CDCl_3): δ 8.21 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.34–7.33 (m, 1H), 7.27–7.23 (m, 3H), 7.18–7.14 (m, 1H), 7.12–7.09 (m, 1H), 6.96–6.94 (m, 2H), 6.79–6.77 (m, 1H), 6.75 (s, 1H), 6.67–6.66 (m, 1H), 6.44 (s, 1H), 3.54 (br s, 2H), 2.19 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 145.6, 144.5, 142.5, 138.4, 134.8, 133.4, 130.6, 129.2, 128.5, 127.0, 124.7, 124.3, 120.77, 120.76, 117.4, 116.7, 115.6, 113.3, 21.6 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2\text{S}^+$ [$\text{M} + \text{H}$] $^+$ m/z 363.1169; found 363.1163.

2-Hydromethanene-1-tosyl-1H-indole (3an: Table 2, entry 14).¹⁹



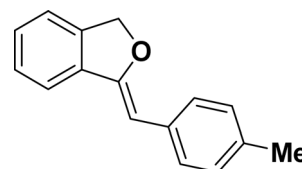
^1H NMR (500 MHz, CDCl_3): δ 7.97 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.63 (d, $J_{\text{HH}} = 8.0$ Hz, 2H), 7.39 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.23–7.19 (m, 1H), 7.17–7.10 (m, 3H), 6.55 (s, 1H), 4.82 (s, 2H), 3.10 (br s, 1H), 2.24 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 145.2, 140.3, 137.1, 135.7, 130, 129.2, 126.5, 125, 123.8, 121.2, 114.4, 111.3, 58.6, 21.6 ppm.

1-[(Z)-Phenylmethylidene]isobenzofuran (4aa: Table 3, entry 1).⁵⁷



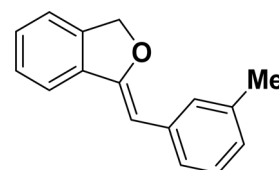
^1H NMR (500 MHz, CDCl_3): δ 7.78–7.77 (m, 2H), 7.60–7.59 (m, 1H), 7.38–7.35 (m, 5H), 7.19–7.16 (m, 1H), 5.98 (s, 1H), 5.54 (s, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 156.3, 139.3, 136.4, 134.9, 128.8, 128.4, 128.1, 127.8, 125.3, 121.2, 120.0, 96.3, 74.9, 29.7 ppm.

1-[(Z)-4-(Methylphenyl)methylidene]isobenzofuran (4ab: Table 3, entry 2).⁵⁷



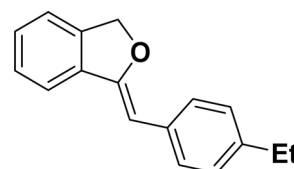
^1H NMR (500 MHz, CDCl_3): δ 7.56–7.54 (m, 2H), 7.47–7.46 (m, 1H), 7.26–7.23 (m, 3H), 7.07–7.06 (m, 2H), 5.84 (s, 1H), 5.42 (s, 2H), 2.26 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 155.7, 139.2, 135.1, 135.0, 133.6, 129.2, 128.6, 128.1, 127.8, 121.2, 119.9, 96.3, 74.9, 21.3 ppm.

1-[(Z)-3-(Methylphenyl)methylidene]isobenzofuran (4ac: Table 3, entry 3).⁵⁰



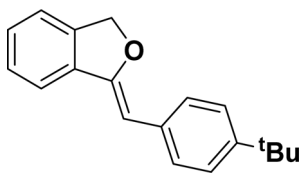
^1H NMR (500 MHz, CDCl_3): δ 7.48–7.44 (m, 3H), 7.26–7.20 (m, 3H), 7.15–7.12 (m, 1H), 6.88–6.87 (m, 1H), 5.82 (s, 1H), 5.40 (s, 2H), 2.28 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 156.2, 139.3, 137.8, 136.3, 135.0, 128.7, 128.5, 128.3, 128.1, 126.2, 125.0, 121.2, 120.0, 96.4, 74.9, 21.6 ppm.

1-[(Z)-4-(Ethylphenyl)methylidene]isobenzofuran (4ad: Table 3, entry 4).⁵⁷

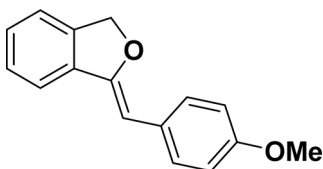


^1H NMR (500 MHz, CDCl_3): δ 7.59–7.57 (m, 2H), 7.48–7.47 (m, 1H), 7.28–7.24 (m, 3H), 7.10–7.08 (m, 2H), 5.85 (s, 1H), 5.42 (s, 2H), 2.56 (q, $J_{\text{HH}} = 7.5$ Hz, 2H), 1.16 (t, $J_{\text{HH}} = 7.5$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 155.7, 141.5, 139.2, 135.1, 133.8, 128.6, 128.1, 128.0, 127.8, 121.2, 119.9, 96.3, 74.8, 28.7, 15.7 ppm.



1-[(Z)-4-(*tert*-Butylphenyl)methylidene]isobenzofuran (4ae):
Table 3, entry 5).

^1H NMR (500 MHz, CDCl_3): δ 7.60–7.58 (m, 2H), 7.47–7.45 (m, 1H), 7.29–7.27 (m, 2H), 7.26–7.21 (m, 3H), 5.85 (s, 1H), 5.40 (s, 2H), 1.24 (s, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 155.9, 148.3, 139.3, 135.1, 133.6, 128.6, 128.1, 127.6, 125.3, 121.2, 120, 96.1, 74.8, 34.6, 31.4 ppm. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{O}^+$ [$\text{M} - \text{H}$] $^+$ m/z 263.1434; Found 263.1432.

1-[(Z)-4-(Methoxyphenyl)methylidene]isobenzofuran (4af):
Table 3, entry 6).⁵⁸

^1H NMR (500 MHz, CDCl_3): δ 7.60–7.59 (m, 2H), 7.45–7.44 (m, 1H), 7.25–7.22 (m, 3H), 6.81–6.80 (m, 2H), 5.82 (s, 1H), 5.41 (s, 2H), 3.73 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 157.5, 154.8, 139, 135.1, 129.3, 129, 128.4, 128.1, 121.2, 119.7, 114, 95.9, 74.7, 55.3 ppm.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the DST-SERB, New Delhi, Grant No. CRG/2023/003598. Om Prakash Joshi thanks Central University of Rajasthan for Infrastructure facility and UGC for the Fellowship.

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