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Highly Site-Selective Direct C–H Bond Functionalization of Unactivated Arenes with Propargyl α -Aryl- α -diazooacetates via Scandium Catalysis

Balu S. Navale,^a Debasish Laha,^a Subhrashis Banerjee,^{b,c} Kumar Vanka,^{b,c} and Ramakrishna G. Bhat^{a*}

Abstract: Highly chemo- and regio-selective C–H bond functionalization of unactivated arenes with propargyl α -aryl- α -diazooacetates is developed using scandium catalysis. Variety of unactivated, mildly deactivated and electronically activated arenes are functionalized using this protocol. We have explored the novel combination of scandium triflate and propargyl α -aryl- α -diazooacetate as catalyst-reagent system for the effective C–H bond functionalization. The protocol avoids the use of expensive catalysts and practicality of the protocol has been demonstrated by the gram scale synthesis of very useful α -diarylacetates including antispasmodic drug-adephenine.

Catalytic C–H bond functionalization is one of the most important and viable methods for the synthesis of complex organic molecules.^[1] Developing catalytic methods for the chemo- and regioselective C–H bond functionalization is highly desirable but challenging task for the synthetic community. Substituted arenes are widespread and present in various biologically active compounds, and drug molecules.^[2] Owing to the importance the chemo- and regioselective C–H bond functionalization of arenes are highly desirable to access different bioactive compounds in minimum number of steps. Aromatic C–H bond functionalization using α -diazocarbonyl compounds is one of the important approaches to access substituted arenes.^[3] As the α -diazocarbonyl compounds can be easily prepared from readily available starting materials, the use of α -diazocarbonyl compounds in aromatic C–H bond functionalization made remarkable progress over the years.^[3,4,9] Efforts have been made to make this method more practical with modifying catalysts, α -diazocarbonyl reagents for the aromatic C–H bond functionalization. The transition metal complexes of rhodium,^[4] gold,^[5] copper,^[6] and iron^[7] have been widely used for the aromatic C–H bond functionalization reactions with α -diazocarbonyl compounds. Recently Pérez and co-workers utilized manganese catalyst for the aromatic C–H bond functionalization using α -diazocarbonyl compounds.^[8] Likewise, transition metal-free C–H bond functionalization reactions of electron rich arenes have been also explored.^[9] Recently, Yu et al. reported a highly chemoselective C–H bond functionalization of phenols with α -aryl- α -diazooacetates by exploring the gold catalysis.^[5d] Interestingly, under the reaction conditions, C–H insertion occurred exclusively, and the O–H insertion product was not obtained. This was the first protocol wherein; the unprotected phenols were effectively functionalized by using α -aryl- α -diazooacetates and gold catalyst and this transformation proved to be highly *para* selective. In 2014, Shi and co-workers reported the ligand-controlled gold-catalyzed C–H bond functionalization of electronically activated arenes with α -aryl- α -diazooacetates (Fig 1 A).^[5e] Various electronically rich arenes

underwent the C–H bond functionalization reaction with the α -aryl- α -diazooacetates in the presence of gold catalyst to afford corresponding desired α -diarylacetates. However, this method had a limited substrate scope as the protocol worked only with the electronically activated arenes. In 2017, Zhang and co-workers reported the *para* selective C–H alkylation of arenes with 2,2,2-trifluoroethyl α -aryl- α -diazooesters via gold catalysis (Fig 1B).^[5f] However, the C–H alkylation of benzene and unactivated arenes worked only with 2,2,2-trifluoroethyl α -(4-trifluoromethyl)-phenyl- α -diazooacetate. The presence of electron withdrawing group such as trifluoromethyl on the aryl group of diazoester (*p*-position) was found to be essential for this transformation. Very recently, Shi and co-workers developed another method for the C–H bond functionalization of arenes with α -aryl- α -diazooacetates in the presence of gold catalyst-triphenylphosphine gold(I) trifluoromethanesulfonate (Fig 1 C).^[5g] In this protocol they used α -aryl- α -diazooacetates containing electron deactivating substituents such as halogens on the phenyl ring. These substituents proved to be important for the chemoselectivity and site-selectivity of the transformation. The desired products α -diarylacetates were obtained in good to excellent yields. Although gold catalysts have been well explored for the synthesis of α -diarylacetates, however, usually they are expensive, and not all of these gold catalysts are commercially available.^[5] The synthesis of α -diarylacetates using unactivated arenes and electronically deactivated arenes by modifying the catalyst and modulating the diazocarbonyl reagent system electronically remains an interesting and challenging task for the synthetic chemists.^[5f,5g] Also, it would be highly interesting and challenging to explore the C–H bond functionalization of unactivated arenes with α -phenyl- α -diazooacetates or aryl diazoesters containing unsubstituted phenyl group. It would also be interesting to tap the potential of the unexplored early transition metal-based catalysts for the site selective C–H bond functionalization of unactivated arenes.

Previous Work: Gold Catalysis

Present Work: Scandium catalysis

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Fig. 1. C–H functionalization of arenes with diazoacetates

Some of the late transition metals have been explored for the C–H bond functionalization for their efficiency. Interestingly, to the best of our knowledge, early transition elements have been seldom explored in the literature for the C–H bond functionalization. However, the synergistic combination of reagent and catalyst is very crucial for the effective C–H bond functionalization. As a part of our ongoing efforts to explore the diazocarbonyl compounds for the effective C–H bond functionalization using early transition elements, we planned to explore the suitable combination of the catalyst and the modified diazocarbonyl reagent. We believed that the reagents with suitable electronic properties may be necessary for the effective C–H bond functionalization using early transition metal catalysts. Herein, we report the novel scandium catalyzed C–H bond functionalization of unactivated arenes and mildly deactivated arenes with propargyl α -aryl- α -diazooacetates as new robust reagents to synthesize useful and biologically important α -diarylacetate compounds in good to excellent yields (Fig 1 D).

Table 1. Optimization of the reaction conditions^[a-d]

1: R = Ethyl
1a': R = Allyl
1a'': R = CH₂CF₃
1a: R = Propargyl

2a (as solvent)

3

Entry	Catalyst	R	Time [h]	Temp [°C]	Yield ^[b,c,d] [%]
1	Rh ₂ (OAc) ₄	Ethyl	12	rt	DC
2	Rh ₂ (OAc) ₄	Ethyl	4	80	DC
3	Cu(OTf) ₂	Ethyl	12	rt	DC
4	Cu(OTf) ₂	Ethyl	4	80	trace
5	(ArO) ₃ PAuNTf ₂	Ethyl	12	rt	DC
6	Sc(OTf) ₃	Ethyl	12	rt	NR ^d
7	Sc(OTf) ₃	Ethyl	12	80	21%
8	LAuPhCNSbF ₆	Ethyl	12	rt	NR
9	LAuPhCNSbF ₆	Ethyl	12	80	trace
10	Sc(OTf) ₃	Allyl	12	80	33%
11	Sc(OTf) ₃	CH ₂ CF ₃	8	80	52%
12*	LAuPhCNSbF ₆	CH ₂ CF ₃	20 min	rt	8%
13	Sc(OTf) ₃	Propargyl	12	rt	NR
14	Sc(OTf) ₃	Propargyl	8	80	70%
15	Cu(OTf) ₂	Propargyl	12	80	trace
16	(ArO) ₃ PAuNTf ₂	Propargyl	12	rt	DC
17	(ArO) ₃ PAuNTf ₂	Propargyl	4	80	DC
18	Rh ₂ (OAc) ₄	Propargyl	12	rt	DC
19	Dichloro(<i>p</i> -cymene) ruthenium(II) dimer	Propargyl	12	rt	DC
20	In(OTf) ₃	Propargyl	12	rt	NR
21	In(OTf) ₃	Propargyl	12	80	47%
22	Bi(OTf) ₃	Propargyl	12	rt	NR
23	Bi(OTf) ₃	Propargyl	12	rt	10%
24	Y(OTf) ₃	Propargyl	12	80	20%
25	Yb(OTf) ₃	Propargyl	12	80	trace
26	FeCl ₃ ·6H ₂ O	Propargyl	12	rt	NR
27	FeCl ₃ ·6H ₂ O	Propargyl	12	80	19%
28	Triflic acid	Propargyl	12	rt	21%
29	Triflic acid	Propargyl	12	80	23%
30	No Catalyst	Propargyl	12	80	NR

[a] Reaction conditions: a solution of α -aryl- α -diazooacetate **1** (0.5 mmol, 1 equiv.) in 1 mL benzene was added to a solution of catalyst (5 mol%) and benzene **2a** (1.5 mL) under inert atmosphere; the reaction was monitored by TLC. [b] Isolated yield after purification by column chromatography. [c] DC- decomposed, [d] NR- no reaction, **L** = (2,4-*t*-Bu₂C₆H₃O)₃P. ***1a** was completely consumed in 20 min.

In order to explore the feasibility of the proposed strategy, we commenced our study using ethyl α -phenyl- α -diazooacetate **1a'** and benzene **2a** as the model substrates in presence of various metal catalysts at room temperature to refluxing conditions (80 °C) in dry benzene (entries 1-7, Table 1). Rhodium, copper and gold catalysts found to be ineffective for the C–H bond functionalization of benzene at room temperature as well as at refluxing conditions (entries 1-5, Table 1). Later, when we used catalytic amount (5 mol%) of Sc(OTf)₃ for this transformation at room temperature, the starting material ethyl α -phenyl- α -diazooacetate **1a'** remained intact even after prolonged reaction time (12 h, entry 6, Table 1). Interestingly, the reaction of ethyl α -phenyl- α -diazooacetate **1a'** and benzene **2a** in the presence of catalytic amount of Sc(OTf)₃ (5 mol%) at elevated temperature (80 °C), afforded the desired C–H bond functionalization product ethyl 2,2-diphenylacetate **3a'a** in 31% yield (entry 7, Table 1). Later, reaction of ethyl α -phenyl- α -diazooacetate **1a'** and benzene **2a** in presence of gold catalyst under rt to elevated temperature did afford the desired product (Table 1, entries 8,9). Encouraged by this preliminary result (entry 7), we synthesized allyl α -phenyl- α -diazooacetate **1a''**. The treatment of allyl α -phenyl- α -diazooacetate **1a''** with benzene **2a** in presence of catalytic amount of Sc(OTf)₃ (5 mol%) in dry benzene at 80 °C afforded the desired product allyl 2,2-diphenylacetate **3a''a** in slightly improved yield in comparison to the ethyl α -phenyl- α -diazooacetate **1a'** (33%, Table 1, entry 10). Further, we planned to explore the reactivity of 2,2,2-trifluoroethyl α -phenyl- α -diazooacetate **1a'''** under scandium catalysis. Gratifyingly, the reaction of **1a'''** and **2a** in presence of Sc(OTf)₃ (5 mol%) at 80 °C afforded the desired product **3a'''a** in 52% yield (Table 1, entry 11). However, surprisingly, reaction of 2,2,2-trifluoroethyl α -phenyl- α -diazooacetate **1a'''** and benzene under the reported gold catalysis furnished the desired product in poor yield (Table 1, entry 12).

The Initial results of the scandium catalyzed C–H bond functionalization proved to be encouraging. However, based on our initial observations, we hypothesized that ethyl/allyl/2,2,2-trifluoroethyl α -phenyl- α -diazooacetate reagents (**1a'**, **1a''** and **1a'''**) may be relatively less reactive (donor/acceptor type α -diazo acetates) to afford the desired products α -diarylacetates **3** in higher yields. Also, the catalytic activity of scandium triflate and low reactivity of unactivated arene such as benzene **2a** towards C–H bond functionalization may be the other prime cause of lower yields of **3a'a** and **3a''a**. It is known in the literature that propargyl moiety is a weakly electron-withdrawing group^{13a} and in this regard, we planned to explore the effect of propargyl group in C–H bond functionalization of unactivated arenes. To explore the feasibility and to enhance the reactivity of α -aryl- α -diazooacetate towards the C–H bond functionalization, we synthesized the propargyl α -phenyl- α -diazooacetate **1a** containing electron withdrawing^{13a} propargyl group as an ester part that can be removed after the functionalization.

To validate our hypothesis, we planned to explore the reactivity of propargyl α -phenyl- α -diazooacetate **1a**. The reaction of **1a** with benzene **2a** in presence of Sc(OTf)₃ at room temperature did afford the desired product (Table 1, entry 13). Gratifyingly, the reaction of propargyl α -phenyl- α -diazooacetate **1a** and benzene **2a** afforded the desired C–H bond functionalization product propargyl 2,2-diphenylacetate **3aa** in 70% yield in the presence of Sc(OTf)₃ (5 mol%) at 80 °C in 8 h (entry 14, Table 1). Further we planned to explore the reactivity of **1a** in presence of different metal catalysts at room temperature to elevated temperature in dry benzene **2a** (Table 1, entries 15-27). It is interesting to note copper as well as gold catalysts were found to be unsuccessful in affording the desired product (Table 1, entries 15-17). Rhodium as well ruthenium catalysts also found to be ineffective for the desired direct C–H bond functionalization of benzene **2a** (Table 1, entries 18-19). The reaction of benzene **2a** with propargyl α -phenyl- α -diazooacetate **1a** in the presence of other metal catalysts afforded the direct C–H bond functionalization product **3aa** either in low or moderate yields, in some cases starting materials

remained intact (Table 1, entries 20-27). We observed that the most of the catalysts were found to be ineffective to catalyse the desired transformation. In few cases the reactions led to the decomposition of the reagent. Also, varying the reaction temperatures from rt to 80 °C did not influence the outcome of the reaction in most of the cases. In order to confirm the role Sc(OTf)₃ as a catalyst and to rule out the possible formation of trace amount of triflic acid in situ by the hydrolysis of Sc(OTf)₃ if any due to the moisture and its subsequent catalysis, we carried out the reaction of **1a** and **2a** in presence of catalytic amount triflic acid (Table 1, entries 28-29). However, the desired product **3aa** was formed in poor yields. The C–H bond functionalization did not work in the absence of catalyst Sc(OTf)₃ (Table 1, entry 30).

Scheme 1. Scope of Diazoacetates and Arenes

optimum solvent by affording the desired product **3aa** in 72% yield at 80 °C in 4 h (Appendix-I, Entry 4, ESI). However, the polar solvents such as DMF and acetonitrile found to be disadvantageous (entries 5-6, Appendix-I). Solvents such as ethyl acetate, nitromethane, and dichloromethane afforded the desired product **3aa** in low to moderate yields (Appendix I, entries 1-3, ESI). We also observed that the lower catalyst loading of Sc(OTf)₃ (2.5 mol%) afforded the desired product **3aa** in moderate yield in 8 h (Appendix-I, entry 7, ESI).

We further looked into the possible effect of co-catalyst in this transformation. We screened two different silver co-catalysts along with the Sc(OTf)₃ to optimize the reaction (Appendix-II, ESI). Interestingly, both AgSbF₆ and AgOTf found to be ineffective and led to the formation of the desired product **3aa** in lower yields (Appendix-II, entry 1-5, ESI). However, the reaction worked smoothly in the absence of co-catalyst to afford the desired product **3aa** in good yield (72% yield, Appendix-II entry 6, ESI). This very important to note that C–H bond functionalization of benzene and unactivated arenes is quite challenging and many efforts have been made earlier by different strategies. Further, the molecular structure of the compound **3aa** was unambiguously confirmed by single crystal X-ray analysis.^[14] Based on comprehensive screening propargyl α -phenyl- α -diazoacetate **1a**, benzene **2a** (10 equiv.), Sc(OTf)₃ (2.5 mol%) at 80 °C under inert atmosphere proved to be the optimum reaction condition.

Having optimized the reaction conditions, we then focussed our attention to explore the reagent scope of this C–H bond functionalization protocol using unactivated arene such as benzene **2a** with different the propargyl α -aryl- α -diazoacetate reagents **1**. Benzene **2a** reacted with propargyl α -aryl- α -diazoacetates (**1a-1f**, **1h**, **1j**) smoothly to afford the desired products (**3aa-3fa**, **3ha**, **3ja**) in excellent yields (up to 97% yield, Scheme 1). Propargyl α -aryl- α -diazoacetates (**1b-1f**) with weak electron-withdrawing substituents on the phenyl ring proved to be very good reagents for the C–H bond functionalization of benzene **2a** to afford the desired products (**3ba-3fa**) in good to excellent yields (up to 97% yield, Scheme 1). While the α -aryl- α -diazoacetates (**1h**, **1j**) with electron-donating substituents on the phenyl ring greatly reduced the reactivity of propargyl α -aryl- α -diazoacetates towards the C–H bond functionalization under the optimum reaction conditions to afford the desired products (**3ha**, **3ja**) in lower yields (Scheme 1). These observations indicated that electron-withdrawing substituents on the phenyl ring of propargyl α -aryl- α -diazoacetates play a major role in tuning the reactivity of the reagent. Propargyl α -aryl- α -diazoacetates found to be most suitable reagents for the effective C–H bond functionalization of an unactivated arene **2a** in presence Sc(OTf)₃.

After the initial success on the C–H bond functionalization of an unactivated arene such as benzene, we turned our attention to explore the relatively more challenging mildly deactivated arenes. Gratifyingly, the reactions of fluorobenzene **2b** with different propargyl α -aryl- α -diazoacetates (**1a**, **1b**, **1c**) under the optimal reaction conditions afforded the corresponding desired products (**3ab**, **3bb**, **3cb**) in moderate yields with good regioselectivity (up to 54% yield, up to 91:9 p:o ratio, Scheme 1). Likewise, the chlorobenzene **2c** reacted smoothly with propargyl α -aryl- α -diazoacetates (**1b**, **1c**) under the optimal reaction conditions to furnish the corresponding desired products (**3bc**, **3cc**) in moderate yields with very good regioselectivity (up to 52% yield, up to 90:10 p:o ratio, Scheme 1).

Later, we planned to explore the reactivity of electron rich arenes. Mildly activated arene such as toluene **2d** reacted with propargyl α -aryl- α -diazoacetates (**1a-1b**) under the optimal reaction conditions to afford the corresponding desired products (**3ad-3bd**) in good yields with good regioselectivity (up to 84% yield, up to 80:20 p:o ratio, Scheme 1). *o*-Xylene **2e** and *p*-xylene **2f** reacted smoothly with propargyl α -aryl- α -diazoacetates (**1a-1b**) under the optimal reaction conditions to afford the corresponding desired products (**3ae-3be**, **3af-3bf**) in good to excellent yields (up to 94% yield, Scheme 1). Mesitylene (**2g**),

Encouraged by the initial success, we screened the reaction in different solvents at varying temperature and catalytic loading of Sc(OTf)₃ to optimize the synthesis of desired product **3aa** in highest yield (Appendix-I, ESI). Dichloroethane proved to be the

when treated with propargyl α -aryl- α -diazooacetates (**1a-1d**) under optimal reaction condition, furnished the corresponding products (**3ag-3dg**) in excellent yields (up to 98% yield, Scheme 1). Under the optimal reaction conditions, the activated arene such as anisole **2h** reacted smoothly with the propargyl α -aryl- α -diazooacetate **1b** to afford the corresponding desired product **3bh** in very good yield. Activated arene such as 1,4-dimethoxybenzene **2i** reacted with different propargyl α -aryl- α -diazooacetates (**1a-1d**, **1g**) to afford the corresponding desired products (**3ai-3di**, **3gi**) in excellent yields (up to 96%, Scheme 1) under the optimized reaction conditions. Highly activated arene such as 1,3,5-trimethoxybenzene **2j** reacted smoothly with propargyl α -aryl- α -diazooacetates (**1a**, **1b**, **1g**) to furnish the corresponding C–H bond functionalization products (**3aj**, **3bj**, **3gj**) in very good to excellent yields (up to 92%, Scheme 1). 1,3-Benzodioxole **2k** also reacted smoothly with various propargyl α -aryl- α -diazooacetates (**1a,1b**, **1h**, **1i**) under the optimal reaction conditions to afford the corresponding desired C–H functionalized products (**3ak**, **3bk**, **3hk**, **3ik**) in moderate to excellent yields with excellent regioselectivity (up to 94% yield, up to 99:1 *p*:*o* ratio, Scheme 1).

Scheme 2. Gram-scale synthesis of α -diarylacetates

It is significant to note that C–H bond functionalization of 1,3-benzodioxole **2k** worked smoothly with α -(4-methoxyphenyl)- α -diazooacetate **1i**, unlike the previous procedure.^[5e] Even the heteroaromatic arene such as 2,5-dimethylfuran **2l**, when treated with propargyl α -aryl- α -diazooacetate **1b** under the optimal reaction conditions afforded the C–H functionalization product **3bl** in 60% yield (see Scheme 1). We demonstrated the robustness of this protocol using different arenes and propargyl α -aryl- α -diazooacetates. It is also very significant to note that

To demonstrate the practicality and the generality of the protocol, we further explored this protocol for the gram scale synthesis of few α -diarylacetates. Reactions of propargyl α -aryl- α -diazooacetates (**1a**, **1c**, **1e**, and **1b**) and arenes (**2a** and **2i**) on a gram scale afforded the corresponding α -diarylacetates (**3aa**, **3ca**, **3ea**, **3bi**) in very good yields under the optimal reaction conditions (up to 88% yield, Scheme 2). The protocol proved to be very effective on a gram scale and found to be reproducible. Later, the hydrolysis of propargyl α -diarylacetates (**3aa**, **3ca**, **3ea**) was carried out using LiOH.H₂O (2.5 equiv.) in ethanol-tetrahydrofuran-water (1:1:1) mixture at room temperature in 1 h, to furnish the corresponding α -diarylacids (**4aa**, **4ca**, and **4ea**) in excellent yields (up to 96% yield, Scheme 3). The easy removal of propargyl group under mild condition proved to be useful for the further synthetic transformations.

Further, in order to demonstrate the applicability of this protocol, we explored the synthesis of biologically active adiphene **21** on a gram scale. Adiphene is a nicotinic receptor inhibitor, used as an antispasmodic drug.^[12] The C–H bond functionalization of benzene **2a** with propargyl α -phenyl- α -diazooacetate **1a** in the presence of catalytic amount of Sc(OTf)₃ (5 mol%) afforded the corresponding product **3aa**. This was further utilized for the synthesis of adiphene **4** in two steps in good yield ((85%, Scheme 4).

Scheme 4. Gram-scale synthesis of Adiphene-An antispasmodic drug

Figure 2: Mechanistic investigation. I: Expected interaction of scandium metal with alkyne. II: Possible mechanism for the C–H bond functionalization of benzene under Scandium-catalysis. III: Electrophilicity measurement employing Fukui function indices. IV: The energy profile for the reaction of propargyl -(4-bromophenyl)- α -diazooacetate with benzene, with the scandium triflate [Sc(OTf)₃] catalyst. Energies are in kcal/mol.

substrates containing C(sp³)–H bonds (benzylic C–H) underwent chemo-selective arene C–H bond functionalization exclusively.^[13b-13d]

After successfully demonstrating the practicability of the protocol, we further planned to understand the reaction pathway. In order to understand whether or not the C–H bond cleavage of benzene is a rate-determining step in this reaction, we carried

out kinetic isotope effect studies. The studies indicated that cleavage of the C–H bond of benzene was not a rate-determining step ($K_H/K_D = 1$, see Appendix III, ESI). Further, to confirm whether or not the direct [1,2]-H shift from benzene takes place in this transformation, we carried out another controlled experiment (see Appendix III, ESI). This result indicated that 48% of direct [1,2]-D shift from the deuterated benzene occurred in this transformation. The third controlled experiment in D_2O (5 equiv.) indicated that there was no direct proton exchange of **3ba** with D_2O under the optimized reaction conditions (see Appendix III, ESI).

In order to have further insight into the mechanism, computational calculations have been performed in detail using density functional theory (DFT) at the PBE/TZVP level of theory. We also calculated the Fukui function indices to investigate the electrophilicity of the carbon where the diazo moiety (carbene precursor) is attached. The turn over frequency (TOF) has also been calculated to compare the activity for different groups associated with the ester carbon of α -aryl- α -diazoacetates. Based on the experimental results, previous literature reports^[15] and quantum chemical calculations that we have carried out the plausible catalytic cycle has been depicted in Figure 2.

At first the Hirshfield population of carbene carbon of different alkyl α -(*p*-bromophenyl)- α -diazoacetates has been calculated to get insight on the electrophilic diazoacetate. Based on the Fukui function indices, the diazo carbon of propargyl α -(*p*-bromophenyl)- α -diazoacetate was found to be the most electrophilic ($F^+ = 0.064785$). As this preliminary result attained our hypothesis, we further sought to optimize the interaction of propargyl α -aryl- α -diazoacetate with $Sc(OTf)_3$ to investigate the most stable conformation. We optimized different interactions of $Sc(OTf)_3$ with ester oxygen(s) and acetylenic moiety of the propargyl group α -aryl- α -diazoacetate (see ESI, Appendix-IV, Figure-1). We have also looked into the all possible modes of interactions of $Sc(OTf)_3$ with the propargyl ester moiety. It is proposed that propargyl α -(*p*-bromophenyl)- α -diazoacetate **1b** interacts with scandium triflate to form an intermediate **int-I** (scandium triflate-coordinated complex) via an energetically favourable anti-fashion ($\Delta G = -10.9$ kcal/mol) as shown in Fig. 2 (II and IV). This intermediate **int-I** further reacts with benzene at an elevated temperature (80 °C) to furnish an energetically feasible ($\Delta G = -29.5$ kcal/mol) zwitterionic intermediate **int-II** via high energy transition state **TS-I** ($\Delta G = 33.4$ kcal/mol). This step found to be highly favourable by the extrusion of thermodynamically stable dinitrogen (Fig. 2 II and IV). The intermediate **int-II** finally affords the highly stable product **3ba** ($\Delta G = -42.7$ kcal/mol) via the transition state **TS-II** ($\Delta G = 18.0$ kcal/mol) by the abstraction of proton and regenerating the catalyst.

Further we calculated the Hirshfield population of carbene carbon of different $Sc(OTf)_3$ -bounded alkyl α -(*p*-bromophenyl)- α -diazoacetates. Based on the Fukui function indices, the diazo carbon of propargyl α -(*p*-bromophenyl)- α -diazoacetate- $Sc(OTf)_3$ complex was the most electrophilic ($F^+ = 0.038369$) (for more details, see ESI, Appendix-IV). This result unambiguously supports that propargyl moiety on α -aryl- α -diazoester enhances the electrophilicity of the diazocarbon and thus significantly increases the reactivity towards the nucleophilic arenes. This computational result is in accordance with the experimental result wherein we observed that propargyl α -(*p*-bromophenyl)- α -diazoacetate reacted smoothly affording the desired product **3ba** in higher yield than that of trifluorethyl α -(*p*-bromophenyl)- α -diazoacetate (see Table 1, entries 11 and 14 for comparison). Thermodynamics and kinetics calculations have also been calculated for the other groups that have been experimentally studied with the $Sc(OTf)_3$ catalyst. The turnover frequency (TOF) has also been calculated and compared for all the energy profiles associated with the different groups (see ESI, Appendix-IV). All these results are in accordance with the experimental observations. The TOF calculations suggest that the reaction of propargyl α -aryl- α -diazoacetates with $Sc(OTf)_3$ will give the product with highest efficiency. This shows that there is a

definite role of the propargyl group in activating the arene efficiently.

In conclusions, we have developed novel scandium catalyzed chemo highly- and regioselective C–H bond functionalization of unactivated arenes and mildly deactivated arenes with propargyl α -aryl- α -diazoacetates as a new reagent. The combination of catalyst- $Sc(OTf)_3$ and reagent-propargyl α -aryl- α -diazoacetate worked synergistically and this was further evident from the computational studies. The practicability of this protocol demonstrated on a gram scale. The protocol has been successfully applied for the gram scale synthesis of biologically active adiphenine an antispasmodic drug.

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Conflicts of interest

There are no conflicts to declare.

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Page No. – Page No.

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Highly Site-Selective Direct C–H Bond Functionalization of Unactivated Arenes with Propargyl α -Aryl- α -diazoacetates via Scandium Catalysis

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1. General.....	S2
2. General procedure A for the synthesis of Propargyl esters.....	S2-S6
3. General procedure B for the synthesis of α -aryl- α diazoacetates.....	S7-S12
4. General Procedure C1 for optimization of reaction conditions.....	S12
5. General Procedure C2 for screening of solvents and Appendix-I.....	S13
6. General procedure C3 for screening of co-catalyst and Appendix-II.....	S14
7. General procedure D for synthesis of α -diarylacetates.....	S14-S34
8. General procedure E for gram-scale synthesis of α -diarylacetates.....	S35-S37
9. General procedure F for the deprotection of propargyl group.....	S37-S38
10. Procedure for gram-scale synthesis of Adiphenine: antispasmodic drug.....	S39-S40
11. Mechanistic Investigations	
Appendix-III (studies of kinetic isotopic effect).....	S40-S41
Appendix-IV (Computational studies).....	S42-S49
12. References.....	S49
13. Copies of ¹ H and ¹³ C NMR spectra.....	S50-S119
14. Crystal data of compound 3aa	S120-S121

1. General

Unless otherwise noted, all reactions were carried out with distilled and dried solvents using oven-dried glassware. All the reagents were purchased from commercial sources and used as received unless otherwise indicated. Thin-layer chromatography (TLC) was performed using silica gel 60 GF₂₅₄ precoated aluminum backed plates (2.5 mm) with detection by UV light. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ and DMSO-d₆. Chemical shifts in ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard or from the residual solvent peak as internal standard and *J* values are given in Hz. ¹³C NMR spectra are reported as δ in ppm downfield from tetramethylsilane and relative to the signal of chloroform-d and DMSO-d₆. ¹³C NMR spectra were recorded with complete proton decoupling. Mass samples were analyzed by high-resolution mass spectrometry (HRMS) using ESI TOF. FT-IR spectra were obtained using a FT-IR spectrophotometer as neat and reported in cm⁻¹. Melting points were measured in an open glass capillary and values are uncorrected.

2. General procedure A for the synthesis of propargyl esters

To the stirred solution of 2-phenylacetic acid **4a** (2.72 g, 20 mmol) in DMF (15 mL) was added propargyl bromide solution 80% in toluene (3.57 g, 24 mmol) and K₂CO₃ (5.53 g, 40 mmol). The reaction mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC. The reaction mixture was filtered through celite, and the filtrate was diluted with water (30 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with cold water and brine solution. The extract was dried over anhydrous Na₂SO₄ and filtered. The filtrate was evaporated under vacuum and the crude product was purified using column chromatography over silica gel to afford product **6a** as colourless liquid (3.34 g, 96% yield).¹

Prop-2-yn-1-yl 2-phenylacetate (**6a**):

Compound **6a** was synthesized following the general procedure (A). The product was obtained as pale yellow liquid (3.34 g, 96% yield): $R_f = 0.35$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3288, 2946, 2128, 1737, 1605, 1496, 1446, 1333, 1239, 1136, 999, 938, 760, 697; ^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.19 (m, 5H), 4.69 (d, $J = 2.5$ Hz, 2H), 3.68 (s, 2H), 2.47 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 133.5, 129.4, 128.8, 127.4, 77.6, 75.2, 52.5, 41.1; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_{10}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 197.0578, Found: 197.0576.

Prop-2-yn-1-yl 2-(4-bromophenyl)acetate (6b):

Compound **6b** was synthesized following the general procedure (A). The product was obtained as white solid (4.657 g, 92% yield): $R_f = 0.35$ petroleum ether/EtOAc (95:5); m.p.: 41-43 °C; IR (neat) cm^{-1} : 3288, 3032, 2946, 2128, 1737, 1605, 1239, 1136, 831, 760, 697, 639; ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 4.70 (d, $J = 2.5$ Hz, 2H), 3.63 (s, 2H), 2.48 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.4, 131.9, 131.2, 129.7, 121.5, 77.4, 75.3, 52.6, 40.4; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_{10}\text{BrO}_2$ ($\text{M} + \text{H}$) $^+$: 252.9864, Found: 252.9871.

Prop-2-yn-1-yl 2-(4-chlorophenyl)acetate (6c):

Compound **6c** was synthesized following the general procedure (A). The product was obtained as viscous liquid (3.964 g, 95% yield): $R_f = 0.3$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3293, 2948, 2129, 1738, 1597, 1492, 1371, 1143, 1091, 938, 807, 758, 676, 641; ^1H NMR (400 MHz, DMSO-d_6): δ 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 4.72 (d, $J = 2.5$ Hz, 2H), 3.75 (s, 2H), 3.55 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.1, 133.0, 131.6, 131.2, 128.2, 78.2, 77.7, 52.1, 39.0; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_{10}\text{ClO}_2$ ($\text{M} + \text{H}$) $^+$: 209.0369, Found: 209.0365.

Prop-2-yn-1-yl 2-(4-fluorophenyl)acetate (6d):

Compound **6d** was synthesized following the general procedure (A). The product was obtained as colourless liquid (3.611 g, 94% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 2948, 2129, 1739, 1606, 1510, 1222, 1140, 937, 826, 785, 681, 643; ^1H NMR (400 MHz, DMSO- d_6): δ 7.38 – 7.28 (m, 2H), 7.20 – 7.11 (m, 2H), 4.71 (d, J = 2.5 Hz, 2H), 3.73 (s, 2H), 3.54 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 170.3, 161.2 (d, J = 242.8 Hz), 131.3 (d, J = 8.1 Hz), 130.1 (d, J = 3.1 Hz), 115.0 (d, J = 21.3 Hz), 78.3, 77.7, 52.0, 38.8; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_9\text{FNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 215.0484, Found: 215.0490.

Prop-2-yn-1-yl 2-(3,4-dichlorophenyl)acetate (6e):

Compound **6e** was synthesized following the general procedure (A). The product was obtained as colourless liquid (4.473 g, 92% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 2948, 2130, 1738, 1133, 1026, 998, 877, 820, 781, 743, 637; ^1H NMR (400 MHz, CDCl_3): δ 7.44 – 7.35 (m, 2H), 7.13 (dd, J = 8.3, 2.1 Hz, 1H), 4.71 (d, J = 2.5 Hz, 2H), 3.63 (s, 2H), 2.50 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 133.5, 130.9, 129.8, 125.7, 125.4, 122.8, 77.4, 75.6, 52.6; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_9\text{Cl}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 242.9980, Found: 242.9984.

Prop-2-yn-1-yl 2-(3,5-difluorophenyl)acetate (6f):

Compound **6f** was synthesized following the general procedure (A). The product was obtained as colourless liquid (3.909 g, 93% yield): $R_f = 0.35$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3299, 3094, 2951, 2130, 1741, 1626, 1306, 1120, 994, 936, 850, 787, 667, 642; ^1H NMR (400 MHz, CDCl_3): δ 6.91 – 6.79 (m, 2H), 6.75 (m, 1H), 4.72 (d, $J = 2.5$ Hz, 2H), 3.65 (s, 2H), 2.50 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 163.1 (dd, $J = 248.7, 12.9$ Hz), 136.9 (t, $J = 9.8$ Hz), 113.5 – 111.6 (m), 103.1 (t, $J = 25.2$ Hz), 77.3, 75.4, 52.8, 40.6 (t, $J = 2.0$ Hz); HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_9\text{FNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 215.0484, Found: 215.0490.

Prop-2-yn-1-yl 2-(naphthalen-2-yl)acetate (6g):

Compound **6g** was synthesized following the general procedure (A). The product was obtained as white solid (4.261 g, 95% yield): $R_f = 0.3$ petroleum ether/EtOAc (95:5); m.p.: 50-51°C; IR (neat) cm^{-1} : 3288, 3055, 2311, 2129, 1736, 1509, 1325, 1135, 946, 900, 857, 748, 679, 636; ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.78 (m, 3H), 7.74 (s, 1H), 7.54 – 7.29 (m, 3H), 4.71 (d, $J = 2.5$ Hz, 2H), 3.83 (s, 2H), 2.47 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.8, 133.6, 132.7, 131.0, 128.5, 128.2, 127.83, 127.80, 127.4, 126.3, 126.0, 77.7, 75.2, 52.5, 41.3; HRMS (ESI TOF): Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 225.0916, Found: 225.0908.

Prop-2-yn-1-yl 2-(p-tolyl)acetate (6h):

Compound **6h** was synthesized following the general procedure (A). The product was obtained as pale yellow liquid (3.539 g, 94% yield): $R_f = 0.35$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3288, 2945, 2129, 1740, 1515, 1241, 1141, 1005, 938, 808, 774, 682, 644; ^1H

NMR (400 MHz, CDCl₃): δ 7.17 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.68 (d, J = 2.5 Hz, 2H), 3.63 (s, 2H), 2.47 (t, J = 2.5 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.0, 137.0, 130.5, 129.4, 129.3, 77.7, 75.1, 52.4, 40.7, 21.2; HRMS (ESI TOF): Calculated for C₁₂H₁₃O₂ (M + H)⁺: 189.0916, Found: 189.0912.

Prop-2-yn-1-yl 2-(4-methoxyphenyl)acetate (6i):

Compound **6i** was synthesized following the general procedure (A). The product was obtained as colourless liquid (3.88 g, 95% yield): R_f = 0.5 petroleum ether/EtOAc (80:20); IR (neat) cm⁻¹: 3285, 2948, 2128, 1736, 1511, 1242, 1138, 1025, 938, 819, 780, 682, 643; ¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.17 (m, 2H), 6.89 – 6.83 (m, 2H), 4.68 (d, J = 2.5 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 2H), 2.47 (t, J = 2.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 159.0, 130.4, 125.6, 114.2, 77.7, 75.1, 55.4, 52.4, 40.2; HRMS (ESI TOF): Calculated for C₁₂H₁₂NaO₃ (M + Na)⁺: 227.0684, Found: 227.0685.

Prop-2-yn-1-yl 2-(3,5-dimethoxyphenyl)acetate (6j):

Compound **6j** was synthesized following the general procedure (A). The product was obtained as colourless liquid (4.263 g, 91% yield): R_f = 0.25 petroleum ether/EtOAc (90:10); IR (neat) cm⁻¹: 3282, 2946, 2127, 1739, 1597, 1201, 1142, 1061, 941, 835, 782, 683, 651; ¹H NMR (400 MHz, CDCl₃): δ 6.44 (d, J = 2.2 Hz, 2H), 6.37 (t, J = 2.2 Hz, 1H), 4.69 (d, J = 2.5 Hz, 2H), 3.77 (s, 6H), 3.60 (s, 2H), 2.48 (t, J = 2.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 161.0, 135.5, 107.4, 99.5, 77.6, 75.1, 55.4, 52.4, 41.3; HRMS (ESI TOF): Calculated for C₁₃H₁₅O₄ (M + H)⁺: 235.0970, Found: 235.0971.

3. General procedure B for the synthesis of α -aryl- α -diazoacetates

To the stirred solution propargyl 2-phenylacetate **6a** (1.74 g, 10 mmol) in 15 mL, acetonitrile was added 4-acetamidobenzenesulfonyl azide (2.88 g, 12 mmol) and DBU (2.24 mL, 15 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for 16 h at room temperature. The reaction was quenched with saturated NH_4Cl , and the product was extracted with diethyl ether (30 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . The extract was filtered, and the filtrate was evaporated under vacuum. The crude product was purified using column chromatography over silica gel to afford α -aryl- α -diazoacetates **1a** as orange solid (1.934 g, 84% yield).²

Prop-2-yn-1-yl 2-diazo-2-phenylacetate (**1a**):

Compound **1a** was synthesized following the general procedure (B). The product was obtained as Orange solid (1.521 g, 76% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); m.p.: 41-43 °C; IR (neat) cm^{-1} : 3295, 3062, 2948, 2085, 1696, 1597, 1497, 1240, 1143, 1017, 950, 752, 682, 637; ^1H NMR (400 MHz, CDCl_3): δ 7.50 – 7.46 (m, 2H), 7.44 – 7.36 (m, 2H), 7.24 – 7.15 (m, 1H), 4.88 (d, J = 2.5 Hz, 2H), 2.52 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.4, 129.1, 126.2, 125.1, 124.1, 77.7, 75.3, 52.3; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_8\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$)⁺: 223.0483, Found: 223.0478.

Ethyl 2-diazo-2-phenylacetate (**1a'**):

Compound **1a'** was synthesized following the general procedure (B). The product was obtained as orange liquid (1.522 g, 80% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 2984, 2081, 1696, 1597, 1496, 1387, 1286, 1156, 1094, 979, 823, 688; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.45 (m, 2H), 7.41 – 7.35 (m, 2H), 7.20 – 7.15 (m, 1H), 4.33 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 129.0, 125.9, 125.8, 124.1, 61.1, 14.6; HRMS (ESI TOF): Calculated for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$)⁺: 213.0639, Found: 213.0631.

Allyl 2-diazo-2-phenylacetate (**1a''**):

Compound **1a''** was synthesized following the general procedure (B). The product was obtained as orange liquid (1.516 g, 75% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3028, 2952, 2085, 1700, 1598, 1497, 1242, 1151, 1043, 1012, 929, 753, 694; ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.47 (m, 2H), 7.41 – 7.34 (m, 2H), 7.21 – 7.15 (m, 1H), 5.98 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.36 (dq, J = 17.2, 1.5 Hz, 1H), 5.27 (ddd, J = 10.4, 2.6, 1.3 Hz, 1H), 4.84 – 4.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.9, 132.3, 129.1, 126.0, 125.6, 124.2, 118.5, 65.6; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$ (M)⁺: 202.0742, Found: 202.0760.

2,2,2-trifluoroethyl 2-diazo-2-phenylacetate (**1a'''**):

Compound **1a'''** was synthesized following the general procedure (B). The product was obtained as orange solid (1.48 g, 76% yield): R_f = 0.55 petroleum ether/EtOAc (95:5); m.p.: 55-57 °C; IR (neat) cm^{-1} : 3067, 2985, 2099, 1719, 1502, 1413, 1355, 1288, 1245, 1170, 1078, 972, 758, 692, 570; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.50 – 7.39 (m, 4H), 7.26 –

7.21 (m, 1H), 4.66 (q, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.32, 129.23, 126.53, 124.61, 124.20, 123.05 (q, $J = 277.5$ Hz), 63.56, 60.41 (q, $J = 36.9$ Hz). ^{19}F NMR (377 MHz, CDCl_3): δ (ppm) -73.94. **HRMS (ESI TOF)**: Calculated for $\text{C}_{10}\text{H}_8\text{F}_3\text{N}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 245.0528, Found: 245.0534.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-diazoacetate (1b):

Compound **1b** was synthesized following the general procedure (B). The product was obtained as orange solid (2.261 g, 81% yield): $R_f = 0.45$ petroleum ether/EtOAc (95:5); m.p.: 57-59 °C; IR (neat) cm^{-1} : 3294, 2948, 2085, 1695, 1488, 1336, 1236, 1144, 1030, 999, 948, 813, 678, 632; ^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.47 (m, 2H), 7.38 – 7.33 (m, 2H), 4.87 (d, $J = 2.3$ Hz, 2H), 2.52 (t, $J = 2.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.0, 132.2, 125.5, 124.4, 119.7, 77.6, 75.5, 52.5; **HRMS (ESI TOF)**: Calculated for $\text{C}_{11}\text{H}_8\text{BrN}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 278.9769, 280.9749, Found: 278.9722, 280.9739.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-diazoacetate (1c):

Compound **1c** was synthesized following the general procedure (B). The product was obtained as orange solid (1.736 g, 74% yield). $R_f = 0.35$ petroleum ether/EtOAc (95:5); m.p.: 61-63 °C; IR (neat) cm^{-1} : 3295, 2949, 2086, 1697, 1492, 1336, 1276, 1237, 1146, 1093, 1005, 820, 734, 680, 637; ^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 4.87 (d, $J = 2.5$ Hz, 2H), 2.52 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.1, 131.9, 129.3, 125.3, 123.8, 77.6, 75.4, 52.5; **HRMS (ESI TOF)**: Calculated for $\text{C}_{11}\text{H}_7\text{ClN}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 257.0094, Found: 257.0097.

Prop-2-yn-1-yl 2-diazo-2-(4-fluorophenyl)acetate (1d):

Compound **1d** was synthesized following the general procedure (B). The product was obtained as yellow solid (1.833 g, 84% yield). R_f = 0.3 petroleum ether/EtOAc (95:5); m.p.: 62-64 °C; IR (neat) cm^{-1} : 3298, 2950, 2086, 1696, 1508, 1339, 1286, 1233, 1145, 1033, 829, 683, 642; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.38 (m, 2H), 7.17 – 7.02 (m, 2H), 4.87 (d, J = 2.5 Hz, 2H), 2.52 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.4, 161.3 (d, J = 246.7 Hz), 126.1 (d, J = 8.0 Hz), 120.9 (d, J = 3.2 Hz), 116.2 (d, J = 22.0 Hz), 77.7, 75.4, 52.4; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_7\text{FN}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 241.0389, Found: 241.0384.

Prop-2-yn-1-yl 2-diazo-2-(3,4-dichlorophenyl)acetate (1e):

Compound **1e** was synthesized following the general procedure (B). The product was obtained as orange solid (2.206 g, 82% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); m.p.: 52-54 °C; IR (neat) cm^{-1} : 3297, 2950, 2090, 1698, 1589, 1475, 1274, 1149, 1039, 956, 884, 815, 736, 680, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, J = 2.3 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.28 (dd, J = 8.6, 2.4 Hz, 1H), 4.87 (d, J = 2.6 Hz, 2H), 2.53 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 133.5, 130.9, 129.8, 125.7, 125.4, 122.8, 77.4, 75.6, 52.6; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_6\text{Cl}_2\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 290.9704, Found: 290.9701.

Prop-2-yn-1-yl 2-diazo-2-(3,5-difluorophenyl)acetate (1f):

Compound **1f** was synthesized following the general procedure (B). The product was obtained as orange solid (1.842 g, 78% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); m.p.:

36-38 °C; IR (neat) cm^{-1} : 3301, 3099, 2953, 2094, 1704, 1623, 1589, 1479, 1445, 1269, 1124, 1067, 987, 926, 839, 741, 669, 641; ^1H NMR (400 MHz, CDCl_3): δ 7.26 – 6.82 (m, 2H), 6.65-6.59 (m, 1H), 4.88 (d, $J = 2.5$ Hz, 2H), 2.54 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.5 (dd, $J = 247.8, 13.7$ Hz), 163.3, 129.2 (t, $J = 11.5$ Hz), 106.7 – 106.2 (m), 101.2 (t, $J = 25.5$ Hz), 77.3, 75.6, 52.6; HRMS (ESI TOF): Calculated for $\text{C}_{11}\text{H}_6\text{F}_2\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 259.0294, Found: 259.0281.

Prop-2-yn-1-yl 2-diazo-2-(naphthalen-2-yl)acetate (1g):

Compound **1g** was synthesized following the general procedure (B). The product was obtained as pale orange solid (1.927 g, 77% yield). $R_f = 0.35$ petroleum ether/EtOAc (95:5); m.p.: 82-84 °C; IR (neat) cm^{-1} : 3291, 3057, 2947, 2083, 1698, 1323, 1248, 1147, 1121, 1038, 895, 852, 812, 736, 680, 639; ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 1.7$ Hz, 1H), 7.92 – 7.69 (m, 3H), 7.58 – 7.37 (m, 3H), 4.91 (d, $J = 2.5$ Hz, 2H), 2.53 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.5, 133.7, 131.7, 128.9, 127.8, 127.8, 126.8, 126.0, 122.8, 122.3, 121.9, 77.7, 75.4, 52.4; HRMS (ESI TOF): Calculated for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 273.0640, Found: 273.0640.

Prop-2-yn-1-yl 2-diazo-2-(p-tolyl)acetate (1h):

Compound **1h** was synthesized following the general procedure (B). The product was obtained as orange solid (1.392 g, 65% yield): $R_f = 0.35$ petroleum ether/EtOAc (95:5); m.p.: 52-54 °C; IR (neat) cm^{-1} : 3293, 2947, 2084, 1699, 1567, 1514, 1242, 1154, 1037, 949, 811, 771, 735, 680, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.36 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 4.86 (d, $J = 2.5$ Hz, 2H), 2.51 (t, $J = 2.5$ Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.7, 136.1, 129.9, 124.3, 121.8, 77.8, 75.2, 52.3, 21.1; HRMS (ESI TOF): Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 237.0640, Found: 237.0635.

Prop-2-yn-1-yl 2-diazo-2-(4-methoxyphenyl)acetate (**1i**):

Compound **1i** was synthesized following the general procedure (B). The product was obtained as dark orange solid (1.934 g, 84% yield): R_f = 0.3 petroleum ether/EtOAc (95:5); m.p.: 68-69 °C; IR (neat) cm^{-1} : 3289, 2949, 2837, 2081, 1694, 1609, 1573, 1510, 1240, 1142, 1022, 949, 825, 735, 680, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.30 (m, 2H), 7.09 – 6.81 (m, 2H), 4.86 (d, J = 2.4 Hz, 2H), 3.81 (s, 3H), 2.51 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.0, 158.3, 126.2, 116.5, 114.8, 77.8, 75.2, 55.5, 52.3; HRMS (ESI TOF): Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{NaO}_3$ ($\text{M} + \text{Na}$) $^+$: 253.0589, Found: 253.0584.

Prop-2-yn-1-yl 2-diazo-2-(3,5-dimethoxyphenyl)acetate (**1j**):

Compound **1j** was synthesized following the general procedure (B). The product was obtained as yellow solid (1.822 g, 70% yield): R_f = 0.25 petroleum ether/EtOAc (95:5); m.p.: 91-93 °C; IR (neat) cm^{-1} : 3254, 2946, 2839, 2075, 1703, 1594, 1454, 1383, 1324, 1272, 1154, 1035, 954, 926, 830, 736, 672; ^1H NMR (400 MHz, CDCl_3): δ 6.67 (d, J = 2.2 Hz, 2H), 6.30 (t, J = 2.2 Hz, 1H), 4.86 (d, J = 2.5 Hz, 2H), 3.80 (s, 6H), 2.52 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.2, 161.3, 127.3, 102.1, 98.4, 77.7, 75.3, 55.5, 52.3; HRMS (ESI TOF): Calculated for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_4$ ($\text{M} + \text{Na}$) $^+$: 283.0695, Found: 283.0695.

4. General Procedure C1 for optimization of reaction conditions

A mixture of 5 mol% of catalyst and 1.5 mL of benzene **2a** was stirred at room temperature in a dried 25 mL two-necked RB flask under an inert atmosphere for 5 minutes. Then α -aryl- α -diazoacetate **1** (0.5 mmol) in 1 mL of benzene was added to above reaction mixture dropwise over 5 minutes, and then the reaction mixture was stirred at room temperature or refluxed at 80 °C over 4-12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The

crude product obtained was purified by column chromatography over silica gel to furnish the product **3**.

5. General procedure C2 for screening of solvents

In a dried 25 mL RB flask, Sc(OTf)₃ (2.5-5 mol%), propargyl α -phenyl- α -diazoacetate **1a** (0.1 g, 0.5 mmol) and benzene **2a** (0.45 mL, 5 mmol) were added in 2.5 mL of solvent at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 72-80 °C over 4-12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **3aa** (see Appendix-I).

Appendix-I Screening of solvents^{a-c}

Entry	Solvent	Sc(OTf) ₃ (mol%)	Temp (°C)	Time (h)	Yield ^{b,c} (%)
1	EtOAc	5	78	8	39
2	Nitromethane	5	80	4	45
3	DCM	5	72	12	48
4	DCE	5	80	4	72
5	DMF	5	80	12	NR
6	Acetonitrile	5	80	12	NR
7	DCE	2.5	80	8	40
8	THF	-	-	-	-

^aReaction conditions: propargyl α -phenyl- α -diazoacetate **1a** (0.5 mmol, 1 equiv.), Sc(OTf)₃ (5 mol%), and benzene **2a** (5 mmol, 10 equiv.) was added in solvent (2.5 mL) under inert atmosphere and reaction mixture was refluxed at 72-80 °C; the reaction was monitored by TLC. ^bIsolated yield after purification by column chromatography. ^cNR- no reaction.

6. General procedure C3 for screening of co-catalyst

In a dried 25 mL RB flask, $\text{Sc}(\text{OTf})_3$ (2.5-5 mol%), co-catalyst (0-5 mol%), propargyl α -phenyl- α -diazoacetate **1a** (0.1 g, 0.5 mmol) and benzene **2a** (0.45 mL, 5 mmol) was added in 2.5 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 2-12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **3aa** (see Appendix-II).

Appendix-II Screening of co-catalyst^{a-c}

Entry	Solvent	$\text{Sc}(\text{OTf})_3$ (mol%)	Co-catalyst (mol%)	Time (h)	Yield (%) ^{b,c} 3aa
1	DCE	2	AgSbF_6 (5)	4	20
2	DCE	5	AgSbF_6 (5)	2	40
3	DCE	1	AgSbF_6 (5)	12	10
4	DCE	5	AgOTf (5)	12	DC
5	DCE	2	AgOTf (5)	12	DC
6	DCE	5	-	4	72

^aReaction conditions: propargyl α -phenyl- α -diazoacetate **1a** (0.5 mmol, 1 equiv.), benzene **2a** (5 mmol, 10 equiv.), Catalyst (1-5 mol%) and co-catalyst (5 mol%) was added in DCE (2.5 mL) under inert atmosphere and reaction mixture was refluxed at 80 °C; the reaction was monitored by TLC. ^bIsolated yield after purification by column chromatography. ^cDC- decomposed.

7. General procedure D for synthesis of α -diarylacetates

In a dried 25 mL RB flask, $\text{Sc}(\text{OTf})_3$ (12.3 mg, 5 mol%), propargyl α -phenyl- α -diazoacetate **1a** (0.1 g, 0.5 mmol) and benzene **2a** (0.45 mL, 5 mmol) was added in 2.5 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained

was purified by column chromatography over silica gel to furnish the desired product **3aa** (0.09 g, 72% yield).

Prop-2-yn-1-yl 2,2-diphenylacetate (3aa):

Compound **3aa** was synthesized following the general procedure (D). The product was obtained as white solid (0.09 g, 72% yield): R_f = 0.5 petroleum ether/EtOAc (95:5); m.p.: 46-48 °C; IR (neat) cm^{-1} : 3289, 3031, 2941, 2126, 1739, 1598, 1494, 1448, 1370, 1220, 1181, 1080, 997, 739, 694, 638, 564; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.12 (m, 10H), 5.07 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 2.46 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 138.3, 128.8, 128.7, 127.5, 77.4, 75.3, 56.8, 52.7; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{14}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 273.0891, Found: 273.0891.

Ethyl 2,2-diphenylacetate (3a'a):

Compound **3a'a** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.037 g, 31% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3029, 2984, 1730, 1598, 1493, 1452, 1148, 1093, 1025, 961, 697, 633, 561; ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.29 (m, 8H), 7.28 – 7.22 (m, 2H), 5.01 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 138.9, 128.7, 128.7, 127.3, 61.3, 57.3, 14.3; HRMS (ESI TOF): Calculated for $\text{C}_{16}\text{H}_{16}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 263.1048, Found: 263.1042.

Allyl 2,2-diphenylacetate (3a''a):

Compound **3a''a** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.042 g, 33% yield): R_f = 0.6 petroleum ether/EtOAc (95:5); IR(neat) cm^{-1} : 3029, 2942, 2109, 1734, 1648, 1494, 1450, 1184, 1145, 1083, 989, 931, 740, 700, 624, 559; ^1H NMR (400 MHz, CDCl_3): δ 7.38 – 7.17 (m, 10H), 5.89 (ddt, J = 15.4, 10.4, 5.7 Hz, 1H), 5.22 (ddq, J = 15.4, 10.4, 1.4 Hz, 1H), 5.05 (s, 1H), 4.65 (dt, J = 5.7, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.3, 138.8, 132.0, 128.8, 128.7, 127.4, 118.6, 65.9, 57.2; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{16}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 275.1048, Found: 275.1044.

2,2,2-trifluoroethyl 2,2-diphenylacetate (3a'''a):

Compound **3a'''a** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.063 g, 52% yield): R_f = 0.6 petroleum ether/EtOAc (95:5); IR(neat) cm^{-1} : 3032, 2945, 1758, 1497, 1451, 1408, 1282, 1170, 1137, 1047, 976, 845, 741, 702, 646, 561. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.36 – 7.24 (m, 10H), 5.12 (s, 1H), 4.51 (q, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 171.15, 137.78, 128.88, 128.64, 127.75, 122.98 (q, J = 277.4 Hz), 60.82 (q, J = 36.7 Hz), 56.61. ^{19}F NMR (377 MHz, CDCl_3): δ (ppm) -73.57. HRMS (ESI TOF): Calculated for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 295.0946, Found: 295.0941.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-phenylacetate (3ba):

Compound **3ba** was synthesized following the general procedure (D). The product was obtained as white solid (0.122 g, 74% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); m.p.: 104-106 °C; IR (neat) cm^{-1} : 3292, 3032, 2940, 2126, 1739, 1597, 1488, 1271, 1368, 1139, 1002, 810, 746, 694, 639, 579; ^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.43 (m, 2H), 7.36 – 7.25 (m, 5H), 7.22 – 7.17 (m, 2H), 5.02 (s, 1H), 4.85 – 4.62 (m, 2H), 2.48 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 137.8, 137.3, 131.9, 130.5, 128.9, 128.6, 127.8, 121.7, 77.3, 75.5, 56.2, 52.9; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{14}^{81}\text{BrO}_2$ ($\text{M} + \text{H}$) $^+$: 331.0157, Found: 331.0144.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-phenylacetate (3ca):

Compound **3ca** was synthesized following the general procedure (D). The product was obtained as white solid (0.114 g, 80% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); m.p.: 83-85 °C; IR (neat) cm^{-1} : 3293, 3033, 2127, 1739, 1598, 1490, 1272, 1222, 1138, 1001, 813, 751, 691, 636, 550; ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.24 (m, 9H), 5.03 (s, 1H), 4.79 – 4.69 (m, 2H), 2.47 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.0, 138.4, 137.7, 132.0, 130.4, 128.7, 128.5, 128.3, 127.3, 78.1 (for 2-C), 54.5, 52.6; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{ClNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 307.0502, Found: 307.0505.

Prop-2-yn-1-yl 2-(4-fluorophenyl)-2-phenylacetate (3da):

Compound **3da** was synthesized following the general procedure (D). The product was obtained as white solid (0.094 g, 70% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); m.p.: 65-67 °C; IR (neat) cm^{-1} : 3293, 3064, 2130, 1739, 1604, 1506, 1448, 1370, 1276, 1182, 1137, 996, 809, 732, 692, 636; ^1H NMR (400 MHz, CDCl_3): δ 7.38 – 7.25 (m, 7H), 7.09 – 6.92 (m, 2H), 5.05 (s, 1H), 4.78 – 4.67 (m, 2H), 2.47 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 162.2 (d, J = 246.3 Hz), 138.2, 134.1 (d, J = 3.3 Hz), 130.4 (d, J = 8.1 Hz), 128.9, 128.6, 127.7, 115.6 (d, J = 21.5 Hz), 77.4, 75.4, 56.0, 52.8; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{14}\text{FO}_2$ ($\text{M} + \text{H}$) $^+$: 269.0978, Found: 269.0980.

Prop-2-yn-1-yl 2-(3,4-dichlorophenyl)-2-phenylacetate (3ea):

Compound **3ea** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.136 g, 85% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 3071, 2948, 2124, 1743, 1596, 1470, 1269, 1145, 1028, 907, 772, 702; ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 2.2 Hz, 1H), 7.41 – 7.26 (m, 6H), 7.16 (dd, J = 8.3, 2.2 Hz, 1H), 5.00 (s, 1H), 4.80 – 4.69 (m, 2H), 2.49 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.0, 138.4, 137.2, 132.8, 131.8, 130.7, 130.6, 129.1, 128.5, 128.2, 128.0, 75.6 (for 2-C), 55.8, 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 341.0112, Found: 341.0099.

Prop-2-yn-1-yl 2-(3,5-difluorophenyl)-2-phenylacetate (3fa):

Compound **3fa** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.139 g, 97% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3297, 3091, 2130, 1742, 1623, 1597, 1495, 1450, 1302, 1219, 1146, 1119, 1026, 987, 848, 770, 697; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.27 (m, 5H), 6.98 – 6.79 (m, 2H), 6.71 (tt, J = 8.8, 2.3 Hz, 1H), 5.01 (s, 1H), 4.92 – 4.48 (m, 2H), 2.49 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.8, 163.1 (dd, J = 248.8, 12.8 Hz), 142.0 (t, J = 9.2 Hz), 137.0, 129.1, 128.6, 128.1, 112.11 – 111.55 (m), 103.1 (t, J = 25.3 Hz), 77.4, 75.6, 56.2 (t, J = 1.9 Hz), 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 287.0884, Found: 287.0888.

Prop-2-yn-1-yl 2-phenyl-2-(*p*-tolyl)acetate (3ha):

Compound **3ha** was synthesized following the general procedure (D). The product was obtained as white solid (0.02 g, 15% yield): R_f = 0.5 petroleum ether/EtOAc (95:5); m.p.: 88-90 °C; IR (neat) cm^{-1} : 3290, 3028, 2927, 2128, 1742, 1509, 1448, 1370, 1221, 1182, 1141, 999, 731, 695; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.24 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.03 (s, 1H), 4.73 (d, J = 2.5 Hz, 2H), 2.45 (t, J = 2.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 138.5, 137.2, 135.4, 129.5, 128.7, 128.66, 128.6, 127.4, 77.5, 75.3, 56.4, 52.7, 21.2; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{16}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 287.1048, Found: 287.1040.

Prop-2-yn-1-yl 2-(3,5-dimethoxyphenyl)-2-phenylacetate (3ja):

Compound **3ja** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.026 g, 17% yield): R_f = 0.5 petroleum ether/EtOAc (80:20); IR (neat) cm^{-1} : 3284, 2936, 2841, 2128, 1740, 1595, 1460, 1298, 1201, 1143, 1062, 999, 938, 834, 761; ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.22 (m, 5H), 6.48 (d, J = 2.2 Hz, 2H), 6.37 (t, J = 2.2 Hz, 1H), 4.99 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 3.75 (s, 6H), 2.46 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 161.0, 140.3, 138.0, 128.7, 128.7, 127.6, 107.0, 99.4, 77.5, 75.3, 56.9, 55.4, 52.7; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{19}\text{O}_4$ ($\text{M} + \text{H}^+$): 311.1283, Found: 311.1287.

Prop-2-yn-1-yl 2-(4-fluorophenyl)-2-phenylacetate (3ab):

Compound **3ab** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer ($p:o$ = 91:9), $p:o$ ratio determined by ^1H NMR. The product was obtained as viscous colourless liquid (0.054 g, 40% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3294, 3071, 2945, 2125, 1742, 1604, 1506, 1447, 1370, 1279, 1227, 1144, 1001, 816, 733, 695, 641, 560; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.18 (m, 7H), 7.13 – 6.85 (m, 2H), 5.05 (s, 1H), 4.73 (dd, J = 2.4, 1.0 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 162.2 (d, J = 246.3 Hz), 138.1, 134.1 (d, J = 2.9 Hz), 130.4 (d, J = 8.0 Hz), 128.9, 128.5, 127.7, 115.6 (d, J = 21.3 Hz), 77.3, 75.4, 55.9, 52.8; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{14}\text{FO}_2$ ($\text{M} + \text{H}^+$): 269.0978, Found: 269.0988.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(4-fluorophenyl)acetate (3bb):

Compound **3bb** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 91:9), *p:o* ratio determined by ^1H NMR. The product was obtained as semisolid (0.090 g, 52% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 3060, 2130, 1741, 1603, 1504, 1438, 1369, 1273, 1227, 1144, 950, 822, 760, 683, 641; ^1H NMR (400 MHz, CDCl_3): δ 7.50 – 7.41 (m, 2H), 7.30 – 7.22 (m, 2H), 7.21 – 7.13 (m, 2H), 7.07 – 6.94 (m, 2H), 4.99 (s, 1H), 4.74 (dd, J = 3.8, 2.5 Hz, 2H), 2.48 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.3, 162.3 (d, J = 246.9 Hz), 137.2, 133.6 (d, J = 3.3 Hz), 132.0, 130.3, 130.2, 121.8, 115.8 (d, J = 21.6 Hz), 77.2, 75.5, 55.4, 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{BrFO}_2$ ($\text{M} + \text{H}$) $^+$: 347.0083, Found: 347.0092.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-(4-fluorophenyl)acetate (3cb):

Compound **3cb** was synthesized following the general procedure (B). The product was obtained as a major product *para*-isomer (*p:o* = 91:9), *p:o* ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.082 g, 54% yield). R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3297, 2947, 2130, 1741, 1602, 1439, 1270, 1227, 1143, 1093, 1005, 823, 762, 683, 641; ^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.16 (m, 6H), 7.15 – 6.90 (m, 2H), 5.01 (s, 1H), 4.73 (d, J = 2.5 Hz, 2H), 2.48 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.3, 163.0 (d, J = 246.8 Hz), 136.6, 133.7, 133.6 (d, J = 3.3 Hz), 130.3 (d, J = 8.1 Hz), 129.9, 129.0, 115.8 (d, J = 21.6 Hz), 77.2, 75.5, 55.3, 52.9; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{ClFO}_2$ ($\text{M} + \text{H}$) $^+$: 303.0588, Found: 303.0595.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(4-chlorophenyl)acetate (3bc):

Compound **3bc** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 90:10), *p:o* ratio determined by ^1H NMR. The product was obtained as viscous colourless liquid (0.091 g, 50% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3294, 2946, 2130, 1740, 1591, 1488, 1369, 1301, 1183, 1142, 1088, 1006, 954, 807, 761, 681, 638; ^1H NMR (400 MHz, CDCl_3): δ 7.50 – 7.43 (m, 2H), 7.34 – 7.14 (m, 6H), 4.98 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 2.49 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.0, 136.8, 136.2, 133.8, 132.0, 130.3, 130.0, 129.1, 121.9, 77.4, 75.6, 55.5, 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{BrClO}_2$ ($\text{M} + \text{H}$) $^+$: 362.9787, Found: 362.9785.

Prop-2-yn-1-yl 2,2-bis(4-chlorophenyl)acetate (3cc):

Compound **3cc** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 89:11), *p:o* ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.083 g, 52% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 2947, 2130, 1740, 1594, 1489, 1369, 1268, 1141, 1090, 1003, 954, 905, 808, 762, 681, 637; ^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.28 (m, 4H), 7.25 – 7.18 (m, 4H), 5.00 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 2.48 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 136.3, 133.8, 130.0, 129.1, 77.2, 75.6, 55.4, 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 319.0293, Found: 319.0305.

Prop-2-yn-1-yl (S)-2-phenyl-2-(p-tolyl)acetate (3ad):

Compound **3ad** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 80:20), *p:o* ratio determined by ^1H NMR. The product was obtained as viscous colourless liquid (0.111 g, 84% yield): R_f = 0.5 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3290, 2925, 2124, 1743, 1603, 1501, 1449, 1371, 1306, 1275, 1219, 1142, 999, 806, 732, 696, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.45 – 6.99 (m, 9H), 5.03 (s, 1H), 4.73 (d, J = 2.4 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 138.5, 137.2, 135.3, 129.5, 128.7, 128.7, 128.6, 127.5, 77.4, 75.3, 56.4, 52.7, 21.2; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{16}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 287.1048, Found: 287.1054.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(p-tolyl)acetate (3bd):

Compound **3bd** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 78:22), *p:o* ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.144 g, 84% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3291, 3025, 2945, 2130, 1739, 1592, 1487, 1441, 1369, 1270, 1219, 1073, 1002, 951, 809, 754, 680, 638; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.37 (m, 2H), 7.28 – 7.03 (m, 6H), 4.98 (s, 1H), 4.82 – 4.65 (m, 2H), 2.46 (t, J = 2.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.5, 137.6, 137.5, 134.8, 131.8, 130.4, 129.6, 128.4, 121.6, 77.4, 75.4, 55.8, 52.8, 21.2; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{16}\text{BrO}_2$ ($\text{M} + \text{H}$) $^+$: 343.0334, Found: 343.0330.

Prop-2-yn-1-yl 2-(3,4-dimethylphenyl)-2-phenylacetate (3ae):

Compound **3ae** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer ($p:o = 84:16$), $p:o$ ratio determined by ^1H NMR. The product was obtained as white solid (0.124 g, 89% yield): $R_f = 0.5$ petroleum ether/EtOAc (95:5); m.p.: 88-90 °C; IR (neat) cm^{-1} : 3287, 3027, 2934, 2126, 1740, 1601, 1497, 1448, 1371, 1207, 1137, 1079, 997, 815, 695, 637, 573; ^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.21 (m, 5H), 7.11 – 7.02 (m, 3H), 5.01 (s, 1H), 4.79 – 4.68 (m, 2H), 2.46 (t, $J = 2.5$ Hz, 1H), 2.30 – 2.15 (m, 6H) (for 2- CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 138.6, 137.0, 135.9, 135.7, 130.0, 129.9, 128.7, 128.7, 127.4, 126.0, 77.6, 75.2, 56.4, 52.7, 20.0, 19.5; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{19}\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 279.1385, Found: 279.1387.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(3,4-dimethylphenyl)acetate (3be):

Compound **3be** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer ($p:o = 83:17$), $p:o$ ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.161 g, 90% yield): $R_f = 0.5$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3293, 2939, 2123, 1744, 1590, 1490, 1446, 1371, 1272, 1145, 1073, 1007, 949, 818, 762, 681, 641, 568; ^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.39 (m, 2H), 7.21 – 6.99 (m, 5H), 4.95 (s, 1H), 4.79 – 4.66 (m, 2H), 2.52 – 2.41 (m, 1H), 2.29 – 2.12 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 137.6, 137.2, 136.2, 135.2, 131.8, 130.4, 130.1, 129.7, 125.9, 121.5, 77.4, 75.4, 55.8, 52.8, 20.0, 19.5; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{18}\text{BrO}_2$ ($\text{M} + \text{H}$) $^+$: 357.0490, Found: 357.0487.

Prop-2-yn-1-yl 2-(2,5-dimethylphenyl)-2-phenylacetate (3af):

Compound **3af** was synthesized following the general procedure (D). The product was obtained as white solid (0.12 g, 86% yield): R_f = 0.5 petroleum ether/EtOAc (95:5); m.p.: 79-81 °C; IR (neat) cm^{-1} : 3289, 2929, 2126, 1740, 1606, 1498, 1447, 1370, 1273, 1213, 1141, 996, 946, 812, 736, 692, 637, 578; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.14 (m, 5H), 7.09 – 6.95 (m, 3H), 5.22 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 2.46 (t, J = 2.5 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 137.6, 136.3, 135.8, 133.4, 130.7, 129.1, 128.8, 128.7, 128.3, 127.4, 77.6, 75.2, 53.5, 52.7, 21.3, 19.5; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{18}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 301.1204, Found: 301.1209.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(2,5-dimethylphenyl)acetate (3bf):

Compound **3bf** was synthesized following the general procedure (D). The product was obtained as white solid (0.168 g, 94% yield): R_f = 0.5 petroleum ether/EtOAc (95:5); m.p.: 115-117 °C; IR (neat) cm^{-1} : 3292, 2930, 2123, 1743, 1613, 1491, 1445, 1370, 1315, 1213, 1149, 1074, 1007, 813, 761, 679, 641; ^1H NMR (400 MHz, CDCl_3): δ 7.61 – 7.33 (m, 2H), 7.19 – 6.94 (m, 5H), 5.16 (s, 1H), 4.90 – 4.64 (m, 2H), 2.48 (t, J = 2.5 Hz, 1H), 2.30 (s, 3H), 2.21 (s, 3H); ^{13}C NMR ((100 MHz, CDCl_3): δ 171.8, 136.7, 136.1, 135.8, 133.3, 131.8, 130.9, 130.8, 128.59, 128.58, 121.5, 77.4, 75.3, 53.0, 52.8, 21.2, 19.4; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{BrNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 379.0310, Found: 379.0305.

Prop-2-yn-1-yl 2-mesityl-2-phenylacetate (3ag):

Compound **3ag** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.135 g, 92% yield): $R_f = 0.5$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3286, 2922, 2125, 1742, 1608, 1489, 1448, 1371, 1271, 1154, 1000, 943, 853, 734, 693, 569; ^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.20 (m, 3H), 7.15 – 7.08 (m, 2H), 6.90 (s, 2H), 5.42 (s, 1H), 4.79–4.68 (m, 2H), 2.43 (t, $J = 2.5$ Hz, 1H), 2.29 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 137.6, 137.1, 136.5, 131.9, 130.1, 128.8, 128.3, 127.0, 77.8, 75.0, 52.5, 50.8, 21.0 (for two type of carbons); HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{20}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 315.1361, Found: 315.1365.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-mesitylacetate (3bg):

Compound **3bg** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.182 g, 98% yield): $R_f = 0.45$ petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3292, 2949, 2120, 1743, 1611, 1486, 1447, 1159, 1075, 1005, 946, 878, 778, 679, 634; ^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.35 (m, 2H), 7.06 – 6.97 (m, 2H), 6.91 (s, 2H), 5.33 (s, 1H), 4.89 – 4.57 (m, 2H), 2.44 (t, $J = 2.4$ Hz, 1H), 2.30 (s, 3H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 137.5, 137.4, 135.5, 131.4, 131.4, 130.6, 130.1, 121.1, 77.6, 75.2, 52.6, 50.1, 21.0, 20.9; HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{19}\text{BrNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 393.0466, Found: 393.0452.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-mesitylacetate (3cg):

Compound **3cg** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.154 g, 94% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3293, 2923, 2123, 1742, 1610, 1489, 1448, 1268, 1159, 1093, 1008, 848, 775, 681, 635; ^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.21 (m, 2H), 7.10 – 7.03 (m, 2H), 6.91 (s, 2H), 5.35 (s, 1H), 4.78– 4.68(m, 2H), 2.43 (t, J = 2.5 Hz, 1H), 2.30 (s, 6H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 137.5, 137.3, 135.0, 132.9, 131.5, 130.2, 130.1, 128.5, 77.6, 75.1, 52.6, 50.1, 21.0, 20.9; HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{19}\text{ClNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 349.0971, Found: 349.0966.

Prop-2-yn-1-yl 2-(4-fluorophenyl)-2-mesitylacetate (3dg):

Compound **3dg** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.148 g, 95% yield): R_f = 0.45 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3293, 2924, 2122, 1743, 1606, 1509, 1452, 1372, 1273, 1227, 1158, 1004, 847, 799, 681, 639; ^1H NMR (400 MHz, CDCl_3): δ 7.14 – 7.07 (m, 2H), 7.02 – 6.94 (m, 2H), 6.92 (s, 2H), 5.36 (s, 1H), 4.83 – 4.64 (m, 2H), 2.44 (t, J = 2.5 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 161.9 (d, J = 245.6 Hz), 137.5, 137.3, 132.1 (d, J = 3.2 Hz), 131.8, 130.4 (d, J = 7.9 Hz), 130.1, 115.1 (d, J = 21.4 Hz), 77.7, 75.1, 52.6, 50.0, 21.0, 20.9; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{19}\text{FNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 333.1267, Found: 333.1268.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(4-methoxyphenyl)acetate (3bh):

Compound **3bh** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 74:26), *p:o* ratio determined by ^1H NMR. The product was obtained as (0.169 g, 94% yield). R_f = 0.3 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3290, 2946, 2838, 2309, 2126, 1899, 1739, 1504, 1368, 1297, 1147, 1007, 815, 681; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.38 (m, 2H), 7.31 – 7.12 (m, 4H), 6.94 – 6.80 (m, 2H), 4.96 (s, 1H), 4.78 – 4.65 (m, 2H), 3.78 (s, 3H), 2.46 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 159.1, 137.7, 131.8, 131.0, 130.3, 129.7, 121.6, 114.3, 77.4, 75.4, 55.4, 55.3, 52.8; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{16}\text{BrO}_3$ ($\text{M} + \text{H}$) $^+$: 359.0283, Found: 359.0275.

Prop-2-yn-1-yl 2-(2,5-dimethoxyphenyl)-2-phenylacetate (3ai):

Compound **3ai** was synthesized following the general procedure (D). The product was obtained as white solid (0.149 g, 96% yield): R_f = 0.4 petroleum ether/EtOAc (80:20); m.p.: 74–76 °C; IR (neat) cm^{-1} : 3286, 2945, 2836, 2126, 1741, 1595, 1496, 1455, 1369, 1277, 1219, 1145, 1026, 947, 807, 699, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.24 (m, 5H), 6.82–6.74 (m, 2H), 6.61 (d, J = 2.9 Hz, 1H), 5.30 (s, 1H), 4.79–4.66 (m, 2H), 3.78 (s, 3H), 3.68 (s, 3H), 2.44 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.1, 153.6, 151.3, 137.0, 129.2, 128.8, 128.6, 127.6, 116.2, 112.5, 111.4, 77.9, 74.9, 56.2, 55.7, 52.5, 51.0; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{19}\text{O}_4$ ($\text{M} + \text{H}$) $^+$: 311.1283, Found: 311.1277.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(2,5-dimethoxyphenyl)acetate (3bi):

Compound **3bi** was synthesized following the general procedure (D). The product was obtained as white solid (0.175 g, 90% yield): R_f = 0.45 petroleum ether/EtOAc (80:20); m.p.: 97-99 °C; IR (neat) cm^{-1} : 3289, 2944, 2837, 2126, 1741, 1593, 1494, 1222, 1148, 1010, 945, 806, 712, 641, 537; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.42 (m, 2H), 7.23 – 7.17 (m, 2H), 6.86 – 6.73 (m, 2H), 6.62 (d, J = 2.8 Hz, 1H), 5.25 (s, 1H), 4.78 – 4.67 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.45 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 153.6, 151.1, 136.3, 131.9, 130.9, 128.0, 121.6, 115.9, 112.7, 111.5, 77.7, 75.1, 56.2, 55.8, 52.6, 50.4; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{BrO}_4$ (M) $^+$: 388.0310, Found: 388.0305.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-(2,5-dimethoxyphenyl)acetate (3ci):

Compound **3ci** was synthesized following the general procedure (D). The product was obtained as white solid (0.159 g, 92% yield): R_f = 0.45 petroleum ether/EtOAc (80:20); m.p.: 98-99 °C; IR (neat) cm^{-1} : 3290, 2947, 2836, 2125, 1741, 1595, 1494, 1278, 1222, 1174, 1095, 1014, 806, 755, 709, 639, 539; ^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 6.85 – 6.74 (m, 2H), 6.62 (d, J = 2.8 Hz, 1H), 5.27 (s, 1H), 4.78 – 4.67 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.45 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 153.7, 151.2, 135.8, 133.5, 130.6, 128.9, 128.1, 115.9, 112.8, 111.6, 77.7, 75.0, 56.2, 55.8, 52.6, 50.3; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{ClNaO}_4$ ($\text{M} + \text{Na}$) $^+$: 367.0713, Found: 367.0710.

Prop-2-yn-1-yl 2-(2,5-dimethoxyphenyl)-2-(4-fluorophenyl)acetate (3di):

Compound **3di** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.156 g, 95% yield): R_f = 0.35 petroleum ether/EtOAc (85:15); IR (neat) cm^{-1} : 3291, 2948, 2838, 2122, 1744, 1603, 1503, 1457, 1369, 1280, 1226, 1153, 1040, 844, 808, 712, 642; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.25 (m, 2H), 7.07 – 6.96 (m, 2H), 6.78 (dt, J = 8.8, 5.8 Hz, 2H), 6.61 (d, J = 2.8 Hz, 1H), 5.27 (s, 1H), 4.78 – 4.66 (m, 2H), 3.77 (s, 3H), 3.69 (s, 3H), 2.45 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 162.2 (d, J = 245.8 Hz), 153.6, 151.1, 132.9 (d, J = 3.2 Hz), 130.8 (d, J = 8.2 Hz), 128.4, 115.8 (d, J = 18.1 Hz), 115.5, 112.6, 111.5, 77.7, 75.0, 56.1, 55.7, 52.5, 50.2; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{FNaO}_4$ ($\text{M} + \text{Na}$) $^+$: 351.1009, Found: 351.1000.

Prop-2-yn-1-yl 2-(2,5-dimethoxyphenyl)-2-(naphthalen-2-yl)acetate (3gi):

Compound **3gi** was synthesized following the general procedure (D). The product was obtained as white solid (0.151 g, 84% yield): R_f = 0.45 petroleum ether/EtOAc (80:20); m.p.: 91-93 $^{\circ}\text{C}$; IR (neat) cm^{-1} : 3287, 2945, 2837, 2125, 1740, 1597, 1497, 1455, 1369, 1222, 1148, 1032, 863, 808, 750, 709, 644; ^1H NMR (400 MHz, CDCl_3): δ 7.87 – 7.73 (m, 4H), 7.52 – 7.40 (m, 3H), 6.84 – 6.75 (m, 2H), 6.63 (d, J = 3.0 Hz, 1H), 5.47 (s, 1H), 4.82 – 4.69 (m, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.45 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.1, 153.6, 151.3, 134.5, 133.6, 132.8, 128.6, 128.5, 128.1, 128.0, 127.7, 127.3, 126.3, 126.1, 116.3, 112.6, 111.4, 77.9, 75.0, 56.2, 55.8, 52.6, 51.1; HRMS (ESI TOF): Calculated for $\text{C}_{23}\text{H}_{20}\text{NaO}_4$ ($\text{M} + \text{Na}$) $^+$: 383.1259, Found: 383.1262.

Prop-2-yn-1-yl 2-phenyl-2-(2,4,6-trimethoxyphenyl)acetate (3aj):

Compound **3aj** was synthesized following the general procedure (D). The product was obtained as white solid (0.157 g, 92% yield): R_f = 0.35 petroleum ether/EtOAc (80:20); m.p.: 121-123 °C; IR (neat) cm^{-1} : 3281, 2937, 2842, 2127, 1741, 1597, 1496, 1420, 1337, 1195, 1114, 1002, 949, 864, 814, 746, 696, 664; ^1H NMR ((400 MHz, CDCl_3)): δ 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 6.14 (s, 2H), 5.33 (s, 1H), 4.77 – 4.64 (m, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 2.38 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 160.7, 158.2, 138.7, 129.4, 128.1, 126.8, 109.2, 90.9, 78.5, 74.2, 55.9, 55.4, 52.0, 45.8; HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{21}\text{O}_5$ ($\text{M} + \text{H}$) $^+$: 341.1389, Found: 341.1398.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(2,4,6-trimethoxyphenyl)acetate (3bj):

Compound **3bj** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.176 g, 84% yield): R_f = 0.3 petroleum ether/EtOAc (80:20); IR(neat) cm^{-1} : 3287, 2943, 2841, 2121, 1743, 1600, 1460, 1420, 1195, 1157, 1061, 1009, 950, 814, 759, 668, 634; ^1H NMR (400 MHz, CDCl_3): δ 7.41 – 7.33 (m, 2H), 7.26 – 7.17 (m, 2H), 6.13 (s, 2H), 5.27 (s, 1H), 4.75 – 4.64 (m, 2H), 3.79 (s, 3H), 3.77 (s, 6H), 2.39 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 160.8, 158.1, 137.8, 131.2, 131.1, 120.7, 108.6, 90.9, 78.3, 74.4, 55.8, 55.4, 52.1, 45.2; HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{20}\text{BrO}_5$ ($\text{M} + \text{H}$) $^+$: 419.0494, Found: 419.0494.

Prop-2-yn-1-yl 2-(naphthalen-2-yl)-2-(2,4,6-trimethoxyphenyl)acetate (3gj):

Compound **3gj** was synthesized following the general procedure (D). The product was obtained as white solid (0.166 g, 85% yield): R_f = 0.25 petroleum ether/EtOAc (80:20); m.p.: 99-101 °C; IR (neat) cm^{-1} : 3285, 2941, 2842, 2122, 1741, 1598, 1499, 1458, 1422, 1154, 1115, 1026, 950, 857, 812, 751, 662; ^1H NMR (400 MHz, CDCl_3): δ 7.80 – 7.72 (m, 3H), 7.67 (s, 1H), 7.55 (dd, J = 8.5, 1.8 Hz, 1H), 7.42 – 7.36 (m, 2H), 6.16 (s, 2H), 5.50 (s, 1H), 4.82 – 4.66 (m, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 2.40 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 160.8, 158.3, 136.3, 133.4, 132.6, 128.1, 128.0, 127.9, 127.6, 125.6, 125.5, 109.0, 91.0, 78.5, 77.4, 74.3, 55.9, 55.5, 52.1, 46.0; HRMS (ESI TOF): Calculated for $\text{C}_{24}\text{H}_{23}\text{O}_5$ ($\text{M} + \text{H}$) $^+$: 391.1545, Found: 391.1546.

Prop-2-yn-1-yl 2-(benzo[d][1,3]dioxol-5-yl)-2-phenylacetate (3ak):

Compound **3ak** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer ($p:o$ = 90:10), $p:o$ ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.138 g, 94% yield): R_f = 0.55 petroleum ether/EtOAc (80:20); IR(neat) cm^{-1} : 3288, 3027, 2895, 2126, 1739, 1490, 1444, 1367, 1239, 1138, 1032, 997, 930, 807, 735, 694, 643; ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.25 (m, 5H), 6.85 – 6.71 (m, 3H), 5.93 (d, J = 3.9 Hz, 2H), 4.98 (s, 1H), 4.73 (d, J = 2.6 Hz, 2H), 2.50 – 2.43 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 148.0, 147.1, 138.4, 132.1, 128.8, 128.5, 127.6, 122.1, 109.3, 108.4, 101.3, 77.4, 75.4, 56.3, 52.8; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{14}\text{NaO}_4$ ($\text{M} + \text{Na}$) $^+$: 317.0790, Found: 317.0778.

Prop-2-yn-1-yl 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-bromophenyl)acetate (3bk):

Compound **3bk** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 92:8), *p:o* ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.175 g, 94% yield): R_f = 0.6 petroleum ether/EtOAc (80:20); IR (neat) cm^{-1} : 3290, 2896, 2126, 1738, 1606, 1487, 1442, 1301, 1238, 1140, 1031, 1002, 931, 800, 760, 676, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.39 (m, 2H), 7.24 – 7.13 (m, 2H), 6.82 – 6.69 (m, 3H), 5.94 (s, 2H), 4.92 (s, 1H), 4.78 – 4.68 (m, 2H), 2.48 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 148.1, 147.2, 137.4, 131.9, 131.5, 130.3, 122.0, 121.7, 109.1, 108.5, 101.4, 77.3, 75.5, 55.7, 52.9; HRMS (ESI TOF): Calculated for $\text{C}_{18}\text{H}_{13}\text{BrNaO}_4$ ($\text{M} + \text{Na}$) $^+$: 394.9895, Found: 394.9894.

Prop-2-yn-1-yl 2-(benzo[d][1,3]dioxol-5-yl)-2-(p-tolyl)acetate (3hk):

Compound **3hk** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 98:2), *p:o* ratio determined by ^1H NMR. The product was obtained as white solid (0.094 g, 61% yield): R_f = 0.6 petroleum ether/EtOAc (80:20); m.p.: 59-61 $^\circ\text{C}$; IR (neat) cm^{-1} : 3288, 2894, 2779, 2129, 1739, 1611, 1489, 1441, 1306, 1241, 1185, 1140, 1034, 997, 932, 808, 755, 681; ^1H NMR (400 MHz, CDCl_3): δ 7.23 – 7.16 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.86 – 6.78 (m, 1H), 6.78 – 6.69 (m, 2H), 5.92 (s, 2H), 4.94 (s, 1H), 4.72 (d, J = 2.5 Hz, 2H), 2.46 (t, J = 2.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 148.0, 147.0, 137.3, 135.4, 132.3, 129.5, 128.4, 122.0, 109.2, 108.3, 101.2, 77.5, 75.3, 56.0, 52.7, 21.2; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{O}_4$ ($\text{M} + \text{H}$) $^+$: 309.1127, Found: 309.1127.

Prop-2-yn-1-yl 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-methoxyphenyl)acetate (3ik):

Compound **3ik** was synthesized following the general procedure (D). The product was obtained as a major product *para*-isomer (*p:o* = 99:1), *p:o* ratio determined by ^1H NMR. The product was obtained as colourless liquid (0.089 g, 55% yield): R_f = 0.5 petroleum ether/EtOAc (80:20); IR (neat) cm^{-1} : 3287, 2904, 2124, 1740, 1610, 1501, 1443, 1367, 1246, 1143, 1034, 933, 807, 760, 683, 637; ^1H NMR (400 MHz, CDCl_3): δ 7.24 – 7.19 (m, 2H), 6.88 – 6.82 (m, 2H), 6.80 (s, 1H), 6.77 – 6.70 (m, 2H), 5.91 (s, 2H), 4.93 (s, 1H), 4.72 (d, J = 2.5 Hz, 2H), 3.77 (s, 3H), 2.47 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.1, 159.0, 148.0, 147.0, 132.5, 130.5, 129.6, 121.9, 114.2, 109.2, 108.3, 101.2, 77.5, 75.3, 55.5, 55.4, 52.7; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{O}_5$ ($\text{M} + \text{H}^+$): 325.1076, Found: 325.1092.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(2,5-dimethylfuran-3-yl)acetate (3bl):

Compound **3bl** was synthesized following the general procedure (D). The product was obtained as colourless liquid (0.104 g, 60% yield): R_f = 0.5 petroleum ether/EtOAc (80:20); IR (neat) cm^{-1} : 3296, 2924, 2126, 1742, 1583, 1487, 1222, 1146, 1079, 1003, 935, 805, 762, 677, 640; ^1H NMR (400 MHz, CDCl_3): δ 7.44 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 5.98 (s, 1H), 4.75 (s, 1H), 4.71 (dd, J = 2.5, 1.9 Hz, 2H), 2.47 (t, J = 2.5 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 150.1, 146.9, 137.3, 131.8, 129.9, 121.5, 116.4, 106.8, 77.3, 75.4, 52.8, 47.3, 13.6, 11.8; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{16}\text{BrO}_3$ ($\text{M} + \text{H}^+$): 347.0283, Found: 347.0290.

8. General procedure E for gram-scale synthesis of α -diarylacetates

In a dried 100 mL RB flask, $\text{Sc}(\text{OTf})_3$ (0.184 g, 5 mol%), propargyl α -phenyl- α -diazoacetate **1a** (1.5 g, 1 equiv.) and benzene **2a** (6.7 mL, 10 equiv.) was added in 25 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **3aa** as white solid (1.31 g, 70% yield).

Prop-2-yn-1-yl 2,2-diphenylacetate (**3aa**):

Compound **3aa** was synthesized following the general procedure (E). The product was obtained as white solid (1.31 g, 70% yield); R_f = 0.5 petroleum ether/EtOAc (95:5); m.p.: 46–48 °C; IR (neat) cm^{-1} : 3289, 3031, 2941, 2126, 1739, 1598, 1494, 1448, 1370, 1220, 1181, 1080, 997, 739, 694, 638, 564; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.12 (m, 10H), 5.07 (s, 1H), 4.74 (d, J = 2.5 Hz, 2H), 2.46 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 138.3, 128.8, 128.7, 127.5, 77.4, 75.3, 56.8, 52.7; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{14}\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 273.0891, Found: 273.0891.

Prop-2-yn-1-yl 2-(4-chlorophenyl)-2-phenylacetate (3ca):

Compound **3ca** was synthesized following the general procedure (E). The product was obtained as white solid (1.31 g, 72% yield): R_f = 0.4 petroleum ether/EtOAc (95:5); m.p.: 83-85 °C; IR (neat) cm^{-1} : 3293, 3033, 2127, 1739, 1598, 1490, 1272, 1222, 1138, 1001, 813, 751, 691, 636, 550; ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.24 (m, 9H), 5.03 (s, 1H), 4.79 – 4.69 (m, 2H), 2.47 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.0, 138.4, 137.7, 132.0, 130.4, 128.7, 128.5, 128.3, 127.3, 78.1 (for 2-C), 54.5, 52.6; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{13}\text{ClNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 307.0502, Found: 307.0505.

Prop-2-yn-1-yl 2-(3,4-dichlorophenyl)-2-phenylacetate (3ea):

Compound **3ea** was synthesized following the general procedure (E). The product was obtained as colourless liquid (1.46 g, 82% yield): R_f = 0.35 petroleum ether/EtOAc (95:5); IR (neat) cm^{-1} : 3295, 3071, 2948, 2124, 1743, 1596, 1470, 1269, 1145, 1028, 907, 772, 702; ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 2.2 Hz, 1H), 7.41 – 7.26 (m, 6H), 7.16 (dd, J = 8.3, 2.2 Hz, 1H), 5.00 (s, 1H), 4.80 – 4.69 (m, 2H), 2.49 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.0, 138.4, 137.2, 132.8, 131.8, 130.7, 130.6, 129.1, 128.5, 128.2, 128.0, 75.6 (for 2-C), 55.8, 53.0; HRMS (ESI TOF): Calculated for $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{NaO}_2$ ($\text{M} + \text{Na}$) $^+$: 341.0112, Found: 341.0099.

Prop-2-yn-1-yl 2-(4-bromophenyl)-2-(2,5-dimethoxyphenyl)acetate (3bi):

Compound **3bi** was synthesized following the general procedure (E). The product was obtained as white solid (1.84 g, 88% yield): R_f = 0.45 petroleum ether/EtOAc (80:20); m.p.: 97-99 °C; IR (neat) cm^{-1} : 3289, 2944, 2837, 2126, 1741, 1593, 1494, 1222, 1148, 1010, 945, 806, 712, 641, 537; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.42 (m, 2H), 7.23 – 7.17 (m, 2H), 6.86 – 6.73 (m, 2H), 6.62 (d, J = 2.8 Hz, 1H), 5.25 (s, 1H), 4.78 – 4.67 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.45 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 153.6, 151.1, 136.3, 131.9, 130.9, 128.0, 121.6, 115.9, 112.7, 111.5, 77.7, 75.1, 56.2, 55.8, 52.6, 50.4; HRMS (ESI TOF): Calculated for $\text{C}_{19}\text{H}_{17}\text{BrO}_4$ (M) $^+$: 388.0310, Found: 388.0305.

9. General procedure F for the deprotection of propargyl group

A mixture of diarylacetate **3aa** (1.25 g, 1 equiv.) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.524 g, 2.5 equiv.) was taken in 100 mL RB flask & 30 mL solvent (THF: MeOH: H_2O = 1:1:1) was added in above mixture under open atmosphere. The reaction mixture was stirred at room temperature over 1 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was acidified by using 3 N HCl and adjusted to pH 2-3. The crude product was extracted by using ethyl acetate. Solvent was removed under reduced pressure & crude product was purified by column chromatography over silica gel (100-200 mesh size) to furnish the product **4aa** as a white solid (1.01 g, 95% yield).

2,2-Diphenylacetic acid (4aa):

Compound **4aa** was synthesized following the general procedure (F). The product was obtained as white solid (1.01 g, 95% yield). $R_f = 0.5$ petroleum ether/EtOAc (70:30); m.p.: 147-149 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.16 (m, 10H), 5.04 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 178.9, 138.0, 128.8 (for two carbon), 127.6, 57.1; IR (neat) cm^{-1} : 3027, 2910, 1699, 1494, 1451, 1411, 1306, 1218, 1031, 934, 737, 698, 635; HRMS (ESI TOF): Calculated for $\text{C}_{14}\text{H}_{13}\text{O}_2$ ($\text{M} + \text{H}$) $^+$: 213.0916, Found: 213.0917.

2-(4-Chlorophenyl)-2-phenylacetic acid (4ca):

Compound **4ca** was synthesized following the general procedure (F). The product was obtained as white solid (1.02 g, 94% yield). $R_f = 0.25$ petroleum ether/EtOAc (80:20); m.p.: 117-119 °C; IR (neat) cm^{-1} : 3029, 2695, 1704, 1599, 1491, 1452, 1408, 1280, 1213, 1091, 1015, 930, 812, 749, 700, 663; ^1H NMR ((400 MHz, CDCl_3): δ 7.39 – 7.20 (m, 9H), 5.01 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 178.6, 137.5, 136.4, 133.7, 130.2, 129.0 (for 2 Carbons), 128.7, 127.9, 56.4; HRMS (ESI TOF): Calculated for $\text{C}_{14}\text{H}_{11}\text{ClNaO}_2$ ($\text{M} + \text{Na}$) $^+$: 269.0345, Found: 269.0342.

2-(3,4-Dichlorophenyl)-2-phenylacetic acid (4ea):

Compound **4ea** was synthesized following the general procedure (F). The product was obtained as white solid (1.06 g, 96% yield). R_f = 0.30 petroleum ether/EtOAc (75:25); m.p.: 118-121 °C; IR (neat) cm^{-1} : 3028, 1706, 1596, 1560, 1469, 1404, 1274, 1214, 1136, 1032, 917, 816, 755, 705; ^1H NMR (400 MHz, CDCl_3): δ 7.45 – 7.29 (m, 7H), 7.18 (dd, J = 8.4, 2.1 Hz, 1H), 5.00 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 178.0, 138.0, 136.9, 132.9, 132.0, 130.8, 130.7, 129.1, 128.6, 128.2, 128.2, 56.1. HRMS (ESI TOF): Calculated for $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{O}_2$ ($\text{M} + \text{Na}$) $^+$: 302.9956, Found: 302.9948.

10. Procedure for gram-scale synthesis of Adiphenine: antispasmodic drug

A mixture of 2,2-diphenylacetic acid **4aa** (0.9 g, 1 equiv.), sodium carbonate (2.25 g, 5 equiv.) and diethyl amine (8.8 mL, 20 equiv.) was stirred in 30 mL of DCE at room temperature in 100 mL RB flask under inert atmosphere for 5 minutes. The reaction mixture was refluxed at 80 °C over 16 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The residue was diluted with water (30 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with cold water and brine and dried over Na_2SO_4 , filtered and the filtrate was evaporated under vacuum. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **21** obtained as colourless liquid (1.12 g, 85% yield).

2-(Diethylamino)ethyl 2,2-diphenylacetate (**21**):

The compound **21** was obtained as colourless liquid (1.12 g, 85% yield). R_f = 0.30 petroleum ether/EtOAc (75:25); IR (neat) cm^{-1} : 2969, 2805, 1735, 1597, 1496 1447, 1304, 1189, 1149, 1079, 1020, 741, 697. ^1H NMR (400 MHz, CDCl_3): δ 7.38 – 7.20 (m, 10H), 5.03 (s, 1H), 4.22 (t, J = 6.2 Hz, 2H), 2.68 (t, J = 6.2 Hz, 2H), 2.50 (q, J = 7.2 Hz, 4H), 0.97 (t, J = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 138.8, 128.8, 128.7, 127.3, 63.6, 57.3, 51.1, 47.7, 12.0; HRMS (ESI TOF): Calculated for $\text{C}_{20}\text{H}_{26}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$: 312.1964, Found: 312.1969.

11. Mechanistic investigations:

Appendix-III: Studies of Kinetic isotopic effect:

Reaction-A: In a dried 25 mL RB flask, $\text{Sc}(\text{OTf})_3$ (12.3 mg, 5 mol%), propargyl α -(4-bromophenyl)- α -diazoacetate **1b** (0.140 g, 1 equiv., 0.5 mmol), benzene **2a** (0.223 mL, 5 equiv., 2.5 mmol) and benzene-d₆ **2a-d** (0.222 mL, 5 equiv., 2.5 mmol) were added in 2.5 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **3ba-d₁**.

Reaction-B: In a dried 25 mL RB flask, Sc(OTf)₃ (12.3 mg, 5 mol%), propargyl α -(4-bromophenyl)- α -diazoacetate **1b** (0.140 g, 1 equiv., 0.5 mmol) and benzene-d₆ **2a-d** (0.443 mL, 10 equiv., 5 mmol) were added in 2.5 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel to furnish the desired product **3ba-d₂**.

Reaction-C: In a dried 25 mL RB flask, Sc(OTf)₃ (12.3 mg, 5 mol%), Prop-2-yn-1-yl 2-(4-bromophenyl)-2-phenylacetate **3ba** (0.165 g, 1 equiv., 0.5 mmol) and deuterium oxide (0.045 mL, 5 equiv., 2.5 mmol) were added in 2.5 mL of DCE at room temperature under inert atmosphere. Then the reaction mixture was refluxed at 80 °C over 2.5 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography over silica gel. The product **3ba** was obtained as one and only product.

Appendix-IV: Computational Studies:

The calculations have been carried out with Turbomole 7.2 [1,2] using the TZVP basis set [3]. Geometry optimizations were performed using the Perdew, Burke, and Ernzerhof functional (PBE) [4]. Dispersion corrections [5] have been included in all the calculations. The resolution of identity (RI) [6] along with the multipole accelerated RI (marij) [7] approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent corrections have also been included in all the calculations using the cosmo model [8], with epsilon (ϵ) = 10.4, employed to model the solvent dichloroethane, which has been employed experimentally to study the reaction involved. Local reactivity is described in terms of the Fukui function, which represents the change of the electronic density in a given point of the molecule with respect to the change in the number of electrons. The Fukui function is usually the correct reactivity indicator for predicting the reaction mechanism. [9-11] These descriptors are useful to evaluate the relevant sites in a molecule where nucleophilic or electrophilic attack can take place[12]. The efficiency of the catalytic cycle for the reaction mechanism investigated has been calculated with the AUTOF [13,14] program by employing the “Energetic Span Model” (ESM), developed by Shaik and co-workers [15-17]. This has been done for all the free energy profiles discussed in the manuscript. The turnover frequency (TOF) calculations take into account the principal rate-determining transition state, as well

as the potentially rate-influencing transition states and intermediates during the catalysis process. In most cases, the TOF is calculated from the TOF-determining transition state (TDTS), the TOF-determining intermediate (TDI), and from the reaction energy, ΔG_r as shown below:

$$\text{TOF} = \frac{k_B T}{h} e^{-\Delta E / RT}$$

$$\Delta E = \text{TDTS} - \text{TDI} \quad \text{if TDTS appears after TDI}$$

$$\Delta E = \text{TDTS} - \text{TDI} - \Delta G_r \quad \text{if TDTS appears before TDI}$$

This model has been employed to calculate the TOFs for the free energy profiles obtained for the mechanisms in the solvent phase discussed in the manuscript. This model can also be employed for stoichiometric reactions, where the TOF would correspond to the efficiency of the reaction.

Results and Discussion (computational approach)

At first, we looked into the electrophilicity of the carbon center with the diazo functional group, by employing the Fukui function indices. The highest electrophilicity at the incoming carbene carbon was seen for the case when the ester carbon had a propargyl group attached to it, in comparison to other groups (see Table 1).

Table 1. Fukui function indices at the carbene carbon for different reactant complexes.

Reactant complex	Hirshfield population for Neutral Species at Carbene Carbon	Hirshfield population for cationic species at Carbene Carbon	Hirshfield population for anionic species at Carbene Carbon	Electrophilicity(F^+) at Carbene Carbon
Propargyl α -Aryl- α -diazoacetate	-0.001580	0.091116	-0.066365	0.064785
2,2,2-trifluoro ethyl α -Aryl- α -diazoacetate	0.000779	0.088683	-0.062377	0.063156

Allyl α -Aryl- α - diazoacetate	-0.003877	0.092164	-0.066856	0.062979
Ethyl α -Aryl- α - diazoacetate	-0.003250	0.092229	-0.064495	0.061245
Propargyl α -Aryl- α -diazoacetate- Sc(OTf) ₃ complex	0.013038	0.069141	-0.025331	0.038369
2,2,2-trifluoro ethyl α -Aryl- α - diazoacetate- Sc(OTf) ₃ complex	0.015817	0.070922	-0.020496	0.036313
Allyl α -Aryl- α - diazoacetate- Sc(OTf) ₃ complex	0.011210	0.069464	-0.02327	0.03448
Ethyl α -Aryl- α - diazoacetate- Sc(OTf) ₃ complex	0.011551	0.076957	-0.021929	0.033480

To look into the reaction mechanism, we first optimized the propargyl α -aryl- α -diazoacetate with Sc(OTf)₃ to investigate the most stable conformation in which Sc(OTf)₃ would interact with the different oxygens of the propargyl α -aryl- α -diazoacetate (see Figure 1). It was found that Sc(OTf)₃ interacts with the carbonyl oxygen in an *anti* fashion to the diazo group with an interaction energy (**Int1**) of -10.0 kcal/mol (see Figure 1).

Figure 1. The energy profile for different conformations of interactions of propargyl α -(4-bromophenyl)- α -diazoacetate with scandium triflate (Sc(OTf)₃) catalyst. Energies are in kcal/mol.

Figure 2. The energy profile for the reaction of propargyl α -(4-bromophenyl)- α -diazoacetate with benzene, with the scandium triflate ($\text{Sc}(\text{OTf})_3$) catalyst. Energies are in kcal/mol.

After the $\text{Sc}(\text{OTf})_3$ interacts with the carbonyl oxygen of the propargyl α -aryl- α -diazoacetate, the arene approaches and interacts with the carbene carbon of the propargyl α -aryl- α -diazoacetate, removing the diazo as dinitrogen, with a free energy (**TS1**) of 33.4 kcal/mol (see Figure 2). The free energy for the transition state is acceptable for the experimental conditions employed (temperature of 80 °C). The arene forms a complex (**Int2**) with an interaction energy of -21.5 kcal/mol. At this point, the arene aromatizes (**TS2**) with a free energy of 18.0 kcal/mol to form the product (see Figure 2). The product is stable by 42.7 kcal/mol (see Figure 2). Thermodynamics and kinetics calculations have also been calculated for the other groups that have been experimentally studied with the $\text{Sc}(\text{OTf})_3$ catalyst (see Figure 3-5). The turnover frequency (TOF) has also been calculated and compared for all the energy profiles associated with the different groups (see Table 2).

Figure 3. The energy profile for the reaction of 2,2,2-Trifluoroethyl α -(4-bromophenyl)- α -diazoacetate with benzene, with the scandium triflate [Sc(OTf)₃] catalyst. Energies are in kcal/mol.

Figure 4. The energy profile for the reaction of allyl α -(4-bromophenyl)- α -diazoacetate with benzene, with the scandium triflate ($\text{Sc}(\text{OTf})_3$) catalyst. Energies are in kcal/mol.

Figure 5. The energy profile for the reaction of ethyl α -(4-bromophenyl)- α -diazoacetate with benzene, with the scandium triflate ($\text{Sc}(\text{OTf})_3$) catalyst. Energies are in kcal/mol.

Table 2. TOFs obtained for the different reactions with the $\text{Sc}(\text{OTf})_3$ catalyst.

Reaction	TOF (h^{-1})
Propargyl α -Aryl- α -diazoacetate + $\text{Sc}(\text{OTf})_3$	8.6×10^{-12}
2,2,2-trifluoroethyl α -Aryl- α -diazoacetate + $\text{Sc}(\text{OTf})_3$	2.4×10^{-13}
Allyl α -Aryl- α -diazoacetate + $\text{Sc}(\text{OTf})_3$	7.4×10^{-15}
Ethyl α -Aryl- α -diazoacetate + $\text{Sc}(\text{OTf})_3$	1.9×10^{-16}

The TOF calculations suggest that the reaction of propargyl α -aryl- α -diazoacetates with Sc(OTf)₃ will give the product with highest efficiency. This shows that there is a definite role of the propargyl group in activating the arene efficiently.

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13. Copies of ^1H and ^{13}C NMR spectra

14. Crystal data of compound 3aa

Bond precision:	C-C = 0.0025 Å	Wavelength=0.71073	
Cell:	a=6.234 (3)	b=24.681 (9)	c=9.003 (3)
	alpha=90	beta=95.074 (10)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1379.8 (10)	1379.8 (9)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C17 H14 O2	?	
Sum formula	C17 H14 O2	C17 H14 O2	
Mr	250.28	250.28	
Dx, g cm ⁻³	1.205	1.205	
Z	4	4	
Mu (mm ⁻¹)	0.078	0.078	
F000	528.0	528.0	
F000'	528.25		
h, k, lmax	8, 33, 12	8, 32, 12	
Nref	3527	3493	
Tmin, Tmax	0.985, 0.988	0.667, 0.746	
Tmin'	0.985		

Correction method= # Reported T Limits: Tmin=0.667
Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.990 Theta(max)= 28.575

R(reflections)= 0.0496 (2311) wR2(reflections)= 0.1164 (3493)

S = 1.005 Npar= 172

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