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Transition Metal-Free Catalytic Carboalkoxylation of Styrenes at Room Temperature

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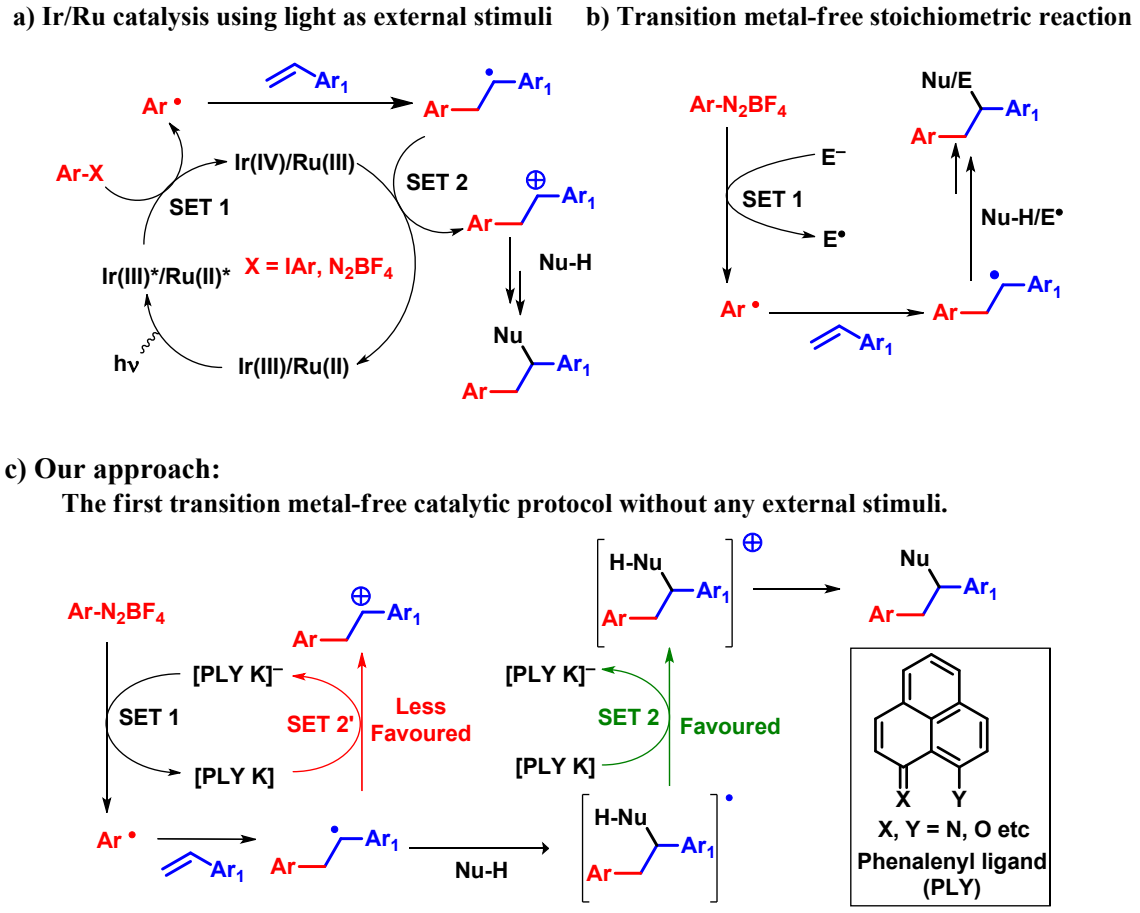
ABSTRACT: Herein, we describe the first transition metal-free catalytic carboalkoxylation of styrenes with aryl diazonium salts by Meerwein addition in the presence of a phenalenyl ligand (PLY) at room temperature without requiring any light stimulation. This three-component reaction allows facile di-functionalization of styrene derivatives with various alcohols (such as 1°, 2° and 3°) as the source of alkoxy group during this transformation. The key intermediates and the transition states involved in this reaction path were unraveled by a series of control experiments coupled with density functional theory (DFT) calculations. The full mechanistic investigations provide an understanding of the selectivity towards carboalkoxylation (Meerwein arylation addition-elimination) in presence of various alcohols over the simple arylation to multiple bond (Meerwein arylation-elimination) reaction.

KEYWORDS: Carboalkoxylation, Transition metal free catalysis, Phenalenyl ligand, Styrene di-functionalization, Meerwein arylation-elimination.

INTRODUCTION:

Over the last decades, a numerous strategies was developed for functionalization of alkenes such as olefin polymerization,[1] hydrosilylation,[2] hydroamination,[3] carboxylation,[4] reductive alkylation, simple arylation[5] etc. Such protocols for functionalization of alkenes are highly important in an extensive range of applications covering medicines, materials and polymer chemistry.[6] In this context, a relatively new methodology has been devised for di-functionalization of alkenes, which involves the formation of two different chemical bonds across the C-C double bond by utilizing three different chemical components.[7-9] In 2010, Toste and co-workers developed a gold catalyzed intermolecular oxyarylation of alkenes by using boronic acid coupling partner in presence of selectfluor oxidant at 50 °C.[10] Later on, Glorius and co-workers introduced an Au-Ru based dual catalyst to perform intramolecular oxyarylation reaction of alkene by using aryl diazonium salt coupling partners in presence of light.[11] Subsequently, research groups of Itoh[12], Greaney[13], and König,[14] have developed the intermolecular oxyarylation of alkene under light stimulation using Ru or Ir based catalyst and diphenyliodinium or aryl diazonium salt as the arylating component (Scheme 1a). All these methods have been carried out by the photoinduced electron transfer from the catalyst to the aryl diazo/iodonium salt coupling partner to generate aryl radical. This aryl radical subsequently attacks the terminal carbon of the alkene to generate a benzylic radical. Subsequently, the benzyl radical regenerates the catalyst by a single electron transfer (SET2) resulting in the formation of a benzylic cation (Scheme 1a). A parallel effort to avoid the transition metal based catalysts was introduced by using an equivalent amount of TEMPONa where TEMPONa and aryl diazonium salt reacted to generate aryl radical which reacted with styrene to provide the corresponding oxyarylated products (Scheme 1b).[15] Further efforts by Heinrich and

co-workers avoiding transition metal based catalysts, described the use of stoichiometric amount of KOAc under heating to accomplish carbohydroxylation of α-methylstyrene.[16]



Scheme 1. (a) Previous work on di-functionalization of styrenes using transition metal based catalysts under light/heat activation. (b) Previous work on transition metal-free stoichiometric reactions on di-functionalization of styrenes. (c) This work describing the first transition metal-free catalysis for carboalkoxylation of styrenes at room temperature without requiring any light stimulation.

In both of these studies, only aryl radical generation was taken care of by a single electron donation from an equivalent amount of electron donor such as TEMPONa/KOAc (Scheme 1b), however

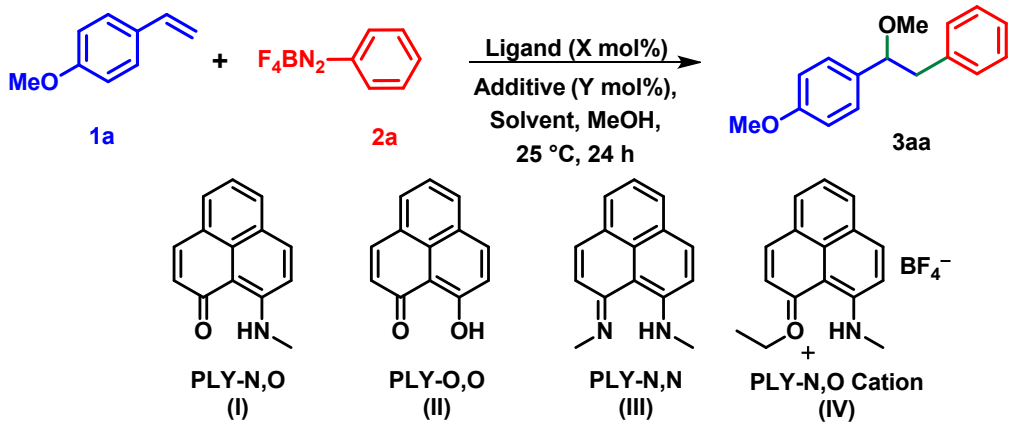
none of these approaches was catalytic. As a result, till date, no report is available which can avoid transition metals to perform this fascinating transformation in a catalytic fashion. The current study documents the first transition metal-free catalytic carboalkoxylation of styrenes under ambient conditions using phenalenyl based radical (Scheme 1c). In recent years, we adopted a strategy to avoid transition metal catalysts utilizing an odd alternant hydrocarbon, phenalenyl which takes advantage of a readily accessible non-bonding molecular orbital (NBMO).[17] Earlier, relatively stable phenalenyl radicals with singly occupied molecular orbital (SOMO), generated by the reduction of phenalenyl cation have been utilized in designing various smart materials by research groups of Haddon[18, 19], Takui[20], Kubo[21], Morita[22] and co-workers. The major advantage of phenalenyl based radical as a catalyst has been argued and demonstrated in a few synthetically important chemical transformations and the topic of using phenalenyl radical in catalysis was recently reviewed.[23] In particular, recent applications of phenalenyl radicals for various catalytic protocols such as C-C coupling[24-25], electrocatalysis in H_2O_2 fuel cell[26], hydrosilylation[27] as well as in spin filtration[28] are worth to mention. In the present study, we used an in-situ generated phenalenyl-K complex based radical as the redox catalyst for carboalkoxylation of different styrenes with both activated and unactivated diazonium salt coupling partners in presence of different alcohols (1^o, 2^o and 3^o) at room temperature without requiring any light stimulation (Scheme 1c). This catalytic transition metal-free approach successfully accomplishes both carboalkoxylation in the presence of alcohol and simple arylation (Meerwein arylation-elimination) in absence of alcohol for the first time. Computational studies with experimental evidences in tandem delineated the underlying mechanistic pathway, which in particular helped us in understanding the origin of selectivity observed towards carboalkoxylation *vs* simple arylation

reaction as a function of alcohol used. DFT calculations were performed to understand the feasibility of single electron transfer (SET) processes involved in the catalytic cycle.

RESULTS AND DISCUSSION:

We started our investigation by optimizing the reaction conditions for methoxyarylation of 4-methoxystyrene (**1a**, 1equiv.) with electronically unbiased phenyl diazoniumtetrafluoroborate (**2a**, 1 equiv.) coupling partner in the presence of PLY-N,O ligand (**I**) and KO^{t}Bu (20 mol%) as a base in DMSO under room temperature for 24 h to afford 38% yield of corresponding methoxyarylated product **3aa** (Table 1, entry 1). By varying the loading of diazonium salt coupling partner (**2a**) from 2 equiv. and 3 equiv., the yield of **3aa** increased to 50% and 64%, respectively (Table 1, entries 4-5). In absence of PLY-N,O, keeping all other conditions unchanged, only 8% of **3aa** formation was noted (Table 1, entry 2). In absence of potassium tertiary butoxide, only less than 5% product formation was observed (Table 1, entry 3). The screening of other solvents and bases did not give any better result (Table 1, entries 6−8). In order to investigate the role of PLY-N,O ligand on the catalytic activity, an identical study was performed using a PLY-O,O (**II**), PLY-N,N (**III**) and PLY-N,O cation (**IV**). It resulted in only 35, 40 and 23% of the methoxyarylated product, respectively (Table 1, entries 9-11). Low ligand and base loading shows lowering down in the yield to 57% and 38% of product **3aa** with the ligand loading 7.5 mol% and 5 mol%, respectively (Table 1, entry 12 and 13). Further, two sets of reaction were performed by varying the amount of methanol (200 μL and 600 μL) which offered 35% and 50% yield of the product **3aa**, respectively (Table 1, entries 14 and 15). When the same reaction was conducted following protocol described in entry 16 and was carried out for 18 h, it resulted in almost similar yield of the methoxyarylated product (**3aa**, 55%).

Table 1. Reaction optimization for methoxyarylation of 4-methoxystyrene with phenyldiazonium tetrafluoroborate salt at room temperature.

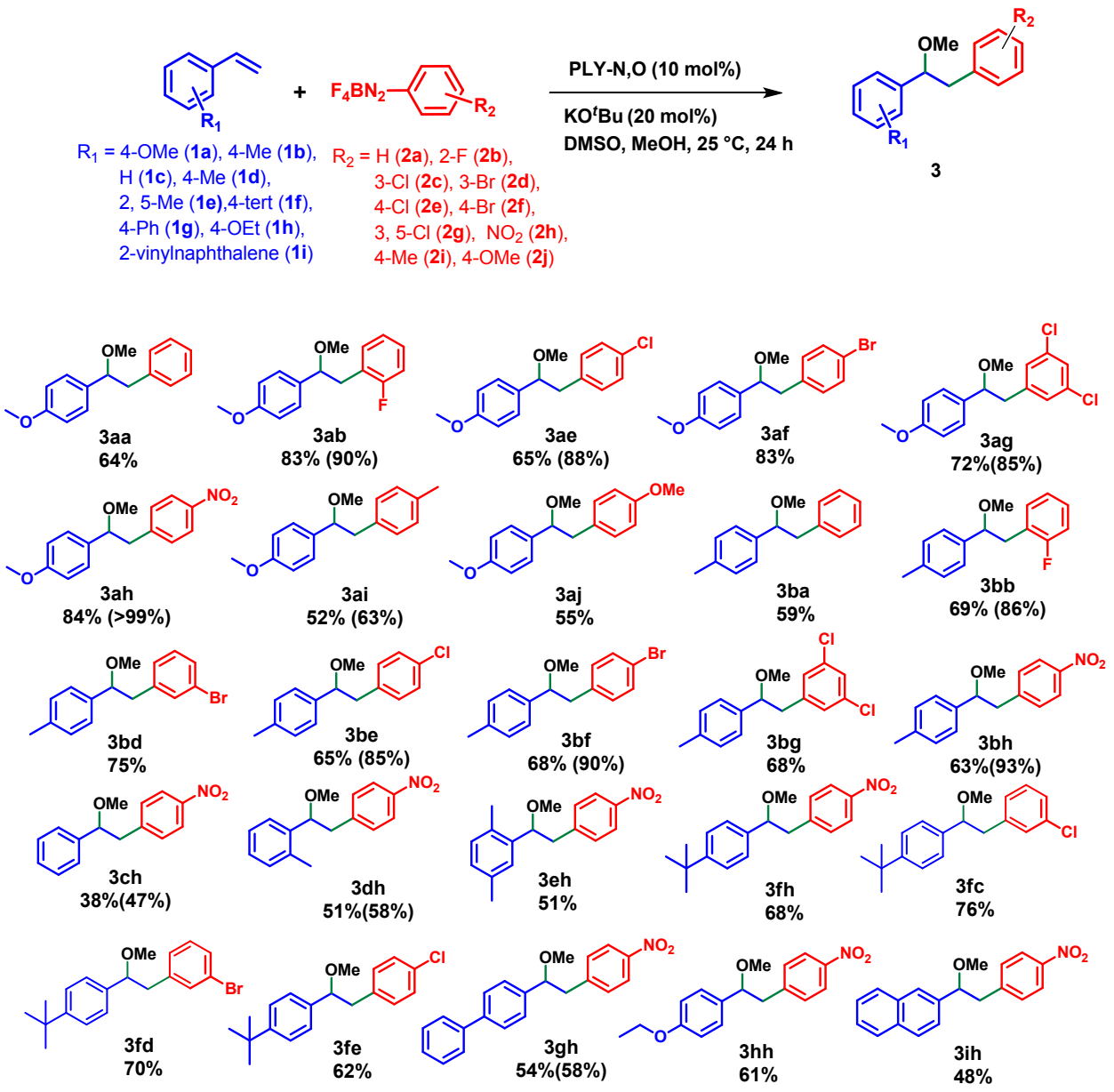


Entry	2a (equiv.)	Ligand (mol%)	Base (mol%)	Solvent	Yield %
1.	1	**I** (10)	KO^{t}Bu(20)	DMSO	38
2.	1	-	KO^{t}Bu(20)	DMSO	8
3.	1	**I** (10)	-	DMSO	5
4.	2	**I** (10)	KO^{t}Bu(20)	DMSO	50
5.	**3**	**I (10)**	**KO^{t}Bu(20)**	**DMSO**	**64**
6.	3	**I** (10)	KO^{t}Bu(20)	DMF	53
7.	3	**I** (10)	KO^{t}Bu(20)	THF	NR
8.	3	**I** (10)	NaO^{t}Bu(20)	DMSO	52
9.	3	**II** (10)	KO^{t}Bu(20)	DMSO	35
10.	3	**III** (10)	KO^{t}Bu(20)	DMSO	40
11.	3	**IV** (10)	K (20)	DMSO	23
12.	3	**I** (7.5)	KO^{t}Bu(15)	DMSO	57
13.	3	**I** (5)	KO^{t}Bu (10)	DMSO	38
14.	3	**I** (10)	KO^{t}Bu (20)	DMSO	35[b]
15.	3	**I** (10)	KO^{t}Bu (20)	DMSO	50[c]
16.	3	**I** (10)	KO^{t}Bu(20)	DMSO	55[d]

[a]Reaction conditions: **1a** (0.24mmol), **2a** (0.72 mmol) and MeOH (0.8 mL), 24 h. [b]The reaction was carried out by using 200 µL MeOH. [c]The reaction was carried out by using 600 µL MeOH. [d]The reaction was continued for 18 h.

From all these different reaction combinations, it can be concluded that the reaction between 4-methoxystyrene (**1a**) and phenyldiazonium tetrafluoroborate salt (**2a**) in presence of 10 mol % of PLY-N,O and 20 mol % of KO^{t}Bu in DMSO for 24 h is the best condition to obtain the maximum yield (64%) of methoxyarylated product **3aa** (Table 1, entry 5).

With this optimized reaction condition, we started investigating the versatility and the reaction scopes of this protocol. Different diazonium salt coupling partners were tested for methoxyarylation of 4-methoxystyrene (**1a**). All the diazonium salts bearing electron withdrawing group (EWG) such as 2-F (**2b**), 4-Cl (**2e**), 4-Br (**2f**), 3,5-dichloro (**2g**), 4-NO_2 (**2h**) afforded good to excellent isolated yields (65-84%) of the corresponding methoxyarylated products (**3ab**-**3ah**) of 4-methoxystyrene (**1a**, Scheme 2). Notably, only diazonium salt coupling partners bearing electron donating group (EDG) such as 4-Me (**2i**), 4-OMe (**2j**) afforded moderate to good yields (52-55%) of the corresponding products (**3ai-3aj**). Using 4-methylstyrene (**1b**), the present protocol delivered good yields (59-75%) of the corresponding carboalkoxylated products (**3ba-3bh**) for various aryl diazonium salt coupling partners. When simple styrene (**1c**) was taken for the carboalkoxylation with 4-nitrophenyldiazonium (**2h**) coupling partner, the isolated yield was reduced to 38% (**3ch**). We performed four different reactions for preparation of carboalkoxylated products, **3aa**, **3ba** and **3aj** in absence of catalyst which afforded 17%, 13%, and 10% product formation, respectively (see ESI, Scheme S2). This indicates that the presence of catalyst is required to obtain satisfactory yield of the carboalkoxylated products.



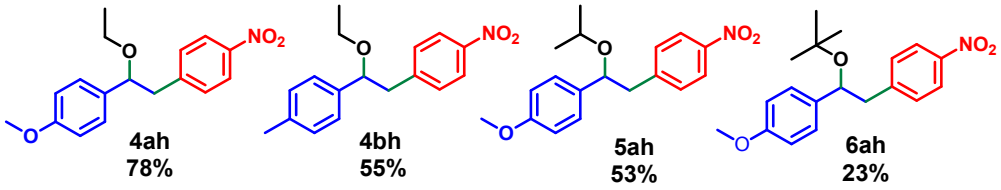
Scheme 2. Transition metal-free methoxyarylation of different styrenes with various diazo coupling partners at room temperature. Reaction conditions: **1a-i** (0.24 mmol), **2a-j** (0.72 mmol), catalyst (0.024 mmol), KO^{t}Bu (0.048 mmol), DMSO (0.8 mL), MeOH (0.8 mL). In the parentheses, conversion by ^{1}H NMR spectroscopy is noted.

Next, the reaction scope was further checked over different styrenes bearing 2-Me (**1d**), 2, 5-Me (**1e**), 4-tertiary butyl (**1f**), 4-Ph (**1g**) and 4-OEt (**1h**) groups, which afforded moderate to good

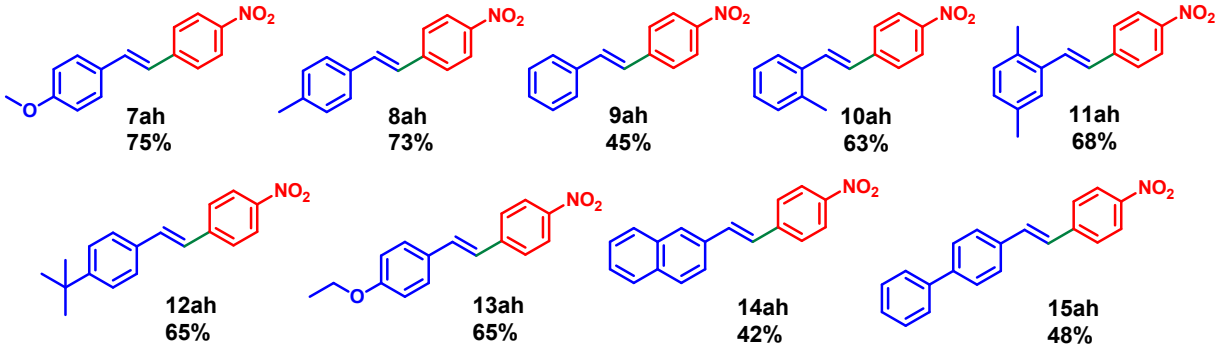
yields (51-76%) of the corresponding methoxyarylated products (**3dh-3hh**). The electron withdrawing group (such as -NO_2, -CN and -F) containing styrenes as well as aliphatic alkene remained unsuccessful for carboalkoxylation reaction under this current protocol (see ESI, Scheme S2).

Polyaromatic styrene such as 2-vinylnaphthalene (**1I**) was also considered for the same reaction with 4-nitrophenyldiazonium salt (**2h**), which delivered 48% isolated yield of the corresponding product **3Ih** (Scheme 2). These results thus demonstrate the applicability of the current protocol for various styrenes. Encouraged by the versatility towards different styrenes and diazonium coupling partners, further we checked the effect of different alcohols (such as 1°, 2° and 3°). Previous reports were limited over the use of mainly primary and secondary alcohols.[10, 12] In this current protocol, different alcohols such as 1°, 2° and 3° were used as the source of alkoxy partner (Scheme 3a). The primary alcohols led to satisfactory yields (52-84%) of the products (Schemes 2 and 3a including **4ah** using ethanol) using 4-methoxystyrene as a coupling partner. When isopropanol was used, moderate yield of the carboalkoxylated compound (**5ah**) was obtained (53%, Scheme 3a) as the major product along with simple arylated product in 7:3 ratio. This ratio of carboalkoxylated product to simple arylated product increased to 1:1 when a tertiary alcohol such as *tert*-butanol was used as the source of alkoxy partner (see later for further details). Apart from the simple arylated product, the *tert*-butoxyarylated product (**6ah**) was obtained in 23% isolated yield, respectively (Scheme 3a). Such significant yield of simple arylated product during the alkoxylation with *tert*-butanol insisted us to check the reaction in absence of any alcohol.

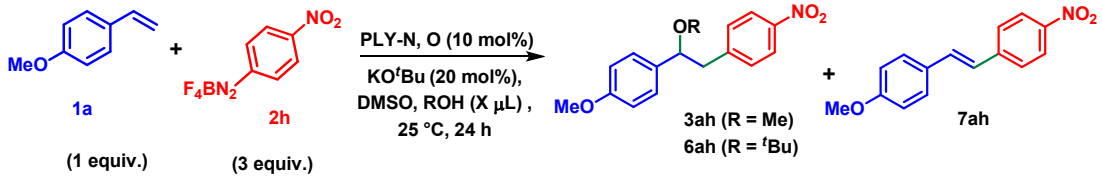
a) In presence of different alcohol.



b) In absence of alcohol (simple arylation).



c)



Entry	ROH (X µL; Y mmol)	Total product formation	3ah or 6ah	7ah
1.	MeOH (200; 4.9)	>99%	74 (**3ah**)	26
2.	MeOH (400; 9.8)	>99%	66 (**3ah**)	34
3.	^{t}BuOH (465; 4.9)	>99%	39 (**6ah**)	61
4.	^{t}BuOH (936; 9.8)	>99%	48 (**6ah**)	52

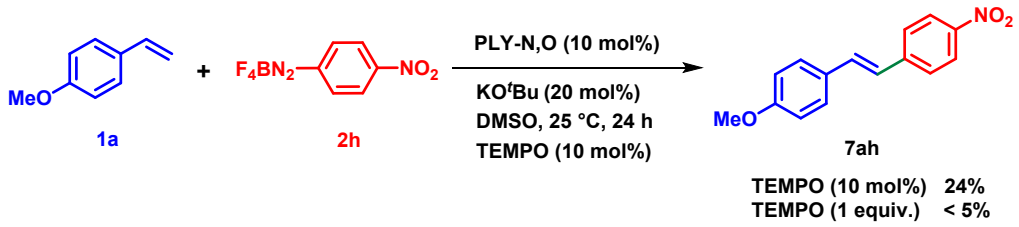
Scheme 3. a) Carboalkoxylation with 1°, 2° and 3° alcohols. Reaction conditions: **1a-b** (0.24 mmol), **2h** (0.72 mmol), catalyst (0.024 mmol), KO^{t}Bu (0.048 mmol), DMSO (0.8 mL), alcohol (0.8 mL); b) Reaction carried out in absence of alcohol. c) Reactions under different concentration of alcohols (MeOH and ^{t}BuOH).

In absence of any alcohol, only simple arylated product **7ah** was found by reaction of 4-methoxystyrene (**1a**) with 4-nitrophenyl diazonium salt coupling partner (**2h**) resulting in 75% isolated yield. Following this observation, different styrenes were considered for this reaction in absence of alcohol to understand if this is a general trend, and we obtained the simple arylated products **7ah-15ah** in moderate to good yields (42%-75%, Scheme 3b). This result establishes efficacy of this catalytic protocol as a common platform for both carboalkoxylation as well as simple arylation reaction. Keeping the above results in mind, it may be concluded that the present transition metal-free catalytic method is versatile towards different sets of styrenes, diazo coupling partners as well as alcohols. To understand the influence of alcohol concentration on the ratio of carboalkoxylation and Meerwein arylation-elimination products, four different sets of reaction were carried out separately maintaining an identical concentration of methanol and *tert*-butanol (Scheme 3c). It may be noticed that the amount of carboalkoxylated product is higher for methanol than that of the *tert*-butanol; for example, 9.8 mmol of ^{t}BuOH resulted in 48:52 ratio of carboalkoxylation and Meerwein arylation-elimination product whereas similar concentration of MeOH resulted in 74:26 ratio for the same (Scheme 3c; see ESI, Figures S1-S4 for details). These results (presented in Scheme 3c) clearly indicate that the ratio of carboalkoxylation and Meerwein arylation-elimination product is not only dependent on the amount of alcohol but also on the nature of alcohol.

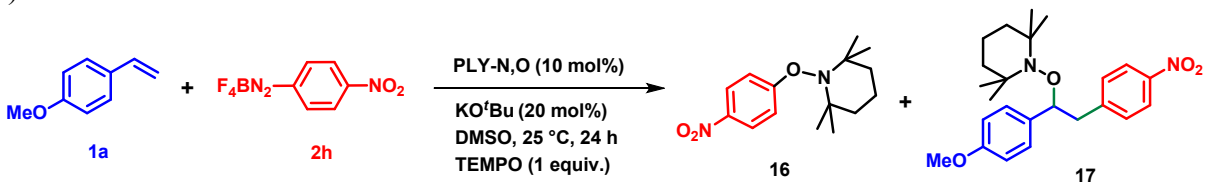
Given an illustrious scope of the reaction, we started to investigate the mechanistic pathway of this reaction. At first, the catalytic reaction was performed in presence of a radical scavenger. The catalytic reaction of 4-methoxystyrene (**1a**) and 4-nitrophenyldiazonium salt coupling partner (**2h**) in presence of 10 mol% of a radical scavenger TEMPO, could slow down the reaction almost

completely (24%, Scheme 4a), while 1 equiv. TEMPO almost completely shuts down the reaction (<5%, Scheme 4a). This observation indicates that this reaction is mediated through radical.

a)



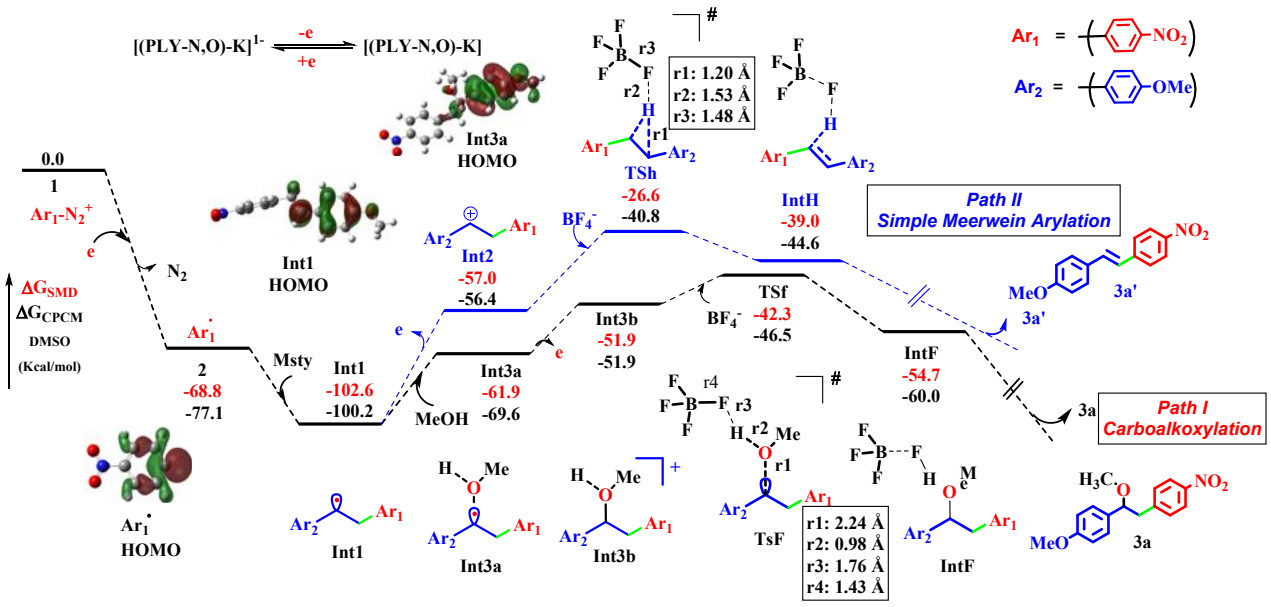
b)



Scheme 4. a) Reaction inhibition in presence of a radical quencher TEMPO. b) Trapping of radical intermediate. Reaction condition: **1a** (0.24 mmol), **2a** (0.72 mmol), catalyst (0.024 mmol), KO^{t}Bu (0.048 mmol), DMSO (0.8 mL), CH_3OH (0.8 mL).

To further confirm this, the stoichiometric version of this reaction using an equivalent amount of TEMPO was investigated by mass spectroscopic measurement, which reveals the molecular peaks at (M+H = 256.6379 (**16**) and 413.8648 (**17**), clearly authenticating the formation of compounds **16** and **17** (Scheme 4b). Furthermore, compound **16** was isolated and characterized with the help of ^{1}H and ^{13}C NMR spectroscopic techniques and matched the spectroscopic data with the previous report.[29] These controlled experiments and the characterization of the trapped intermediates clearly support a radical mediated mechanistic pathway. Moreover, to understand the rate determining step *(r.d.s)* of this reaction, a kinetic isotope effect (KIE) experiment was also conducted for the same methoxyarylation reaction. A series of parallel reactions was carried out using CH_3OH and CD_3OD separately under our catalytic condition for the carboalkoxylation of 4-methoxystyrene

(**1a**) with phenyldiazonium salt (see SI, Scheme S1). The reactions were stopped after different time interval in each case and the product formation was quantified by ^{1}H NMR spectroscopy in presence of an internal standard (4-nitrotoluene). Comparing their rates, the K_H/K_D value was measured as 1.26. This value indicates that O-H bond breaking is not directly involved during the rate determining step (*r.d.s*) of this reaction.

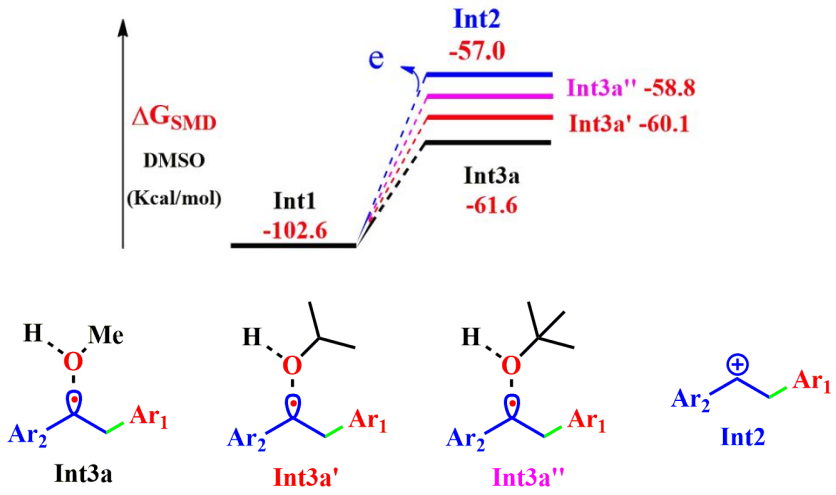


Scheme 5. Calculated energy profile diagram for the methoxyarylation reaction and simple arylation reaction of 4-methoxystyrene with 4-nitrophenyl diazo coupling partner.

Based on the experimental results and detailed DFT calculations (using Gaussian 09[30] at M062X/UM062X level of theory by using 6-311+g(d,p)[31] considering both CPCM[32] and SMD solvent model), a proposed mechanism is outlined in Scheme 5. In our earlier studies, it was demonstrated that PLY-N,O reacts with KO^{t}Bu (1:1) to form a (PLY-N,O)-K complex, which can be reduced by another equivalent of KO^{t}Bu to obtain a monoreduced (PLY-N,O)-K radical anionic

complex.[24] In this work, theoretical calculations reveal an electron transfer from the SOMO of the monoreduced (PLY-N,O)-K radical complex to the anti-bonding orbital of Ar-N_2^+ at ambient condition to generate an aryl radical (Ar$^\bullet$), and the free energy change for formation of such aryl radical is thermodynamically feasible (ΔG = -68.3 Kcal/mol). Further, this radical was also experimentally trapped by a radical quencher TEMPO and characterized by ^1H, ^{13}C NMR and mass spectroscopy (**16**, Scheme 4b). Calculated HOMO of this aryl radical reveals the maximum localization of electron spin density is at the *para*-carbon atom with respect to NO_2 group. This in-situ generated aryl radical next can attack the terminal carbon atom of the 4-methoxystyrene resulting in the formation of a radical intermediate (**Int1**), which was also trapped as **17** by the radical scavenger TEMPO and characterized by mass spectroscopy (Scheme 4b). The **Int1** next can release an electron to regenerate the monoreduced (PLY-N,O)-K radical complex and cationic intermediate (**Int2**). However the calculation suggests such process is slightly more energy demanding (45.6 Kcal/mol) with respect to another reaction pathway involving intermediate **Int3a** (40.7 Kcal/mol), which can be accessed only in presence of an alcohol such as methanol. The access of such less energetic intermediate **Int3a** in presence of methanol explains our results in obtaining selectively carboalkoxylated product (**3a**) over the simple arylation product (**3a'**). This **Int3a** in such case (in presence of methanol for example), can release one electron to generate the cationic carboalkoxylated intermediate (**Int3b**) regenerating the monoreduced (PLY-N,O)-K radical complex. However, it may be noted that the current experimental results are not sufficient to distinguish between these two possible mechanisms and the present mechanistic proposal is drawn on the basis of computational data. The **Int3b** further can interact with BF_4^- through a transition state **TSf** leading to bond cleavage between O-H and B-F while forming a F-H bond (Scheme 6) with calculated thermodynamic parameter of ($\Delta G^{\neq}$ = 9.9 Kcal/mol (SMD)/5.4

Kcal/mol (CPCM), Scheme 5). This step is exothermic in nature by -19 Kcal/mol (Scheme 5). On the other hand, in absence of any alcohol, the same reaction leads to the selective formation of simple arylated product (**3a'**), which can be explained by direct removal of an electron from **Int1** to form a cationic intermediate **Int2**. In presence of BF_4^- ion, a proton abstraction from the I**nt2** results in the formation of product **3a'** through the transition state [**TSh**, 30.1 (SMD)/15.6 (CPCM) Kcal/mol]. This transition state involves the C-H and B-F bond dissociation as well as H-F bond formation (Scheme 5).



Scheme 6. Comparison of the energy levels of corresponding intermediates for different alcohols and simple arylation to understand selectivity of this transformation.

Interestingly, when higher analogue of the alcohol was used instead of methanol, a competition between simple arylation product and carboalkoxylated product was observed. For example, in case of isopropanol, carboalkoxylated and simple arylation products were observed in the ratio of 7:3, whereas *tert*-butanol leads to 1:1 ratio of such products formation. This observation clearly indicates that the choice of alcohol plays a major role in determining selectivity of the process. To understand such selectivity, we resorted to the DFT by calculating the energy of **Int3a**, **Int3a'** and **Int3a''** which are adducts of the radical intermediate (**Int1**) with different alcohols such as

methanol, isopropanol (^{i}PrOH) and *tert*-butanol (^{t}BuOH), respectively. In case of methanol, energy difference between **Int2** and **Int3a** is 4.6 Kcal/mol. This energy gap gradually decreases to 3.1 Kcal/mol (between **Int3a'** and I**nt2**) and 1.8 Kcal/mol (between **Int3a''** and **Int2**) for ^{i}PrOH and ^{t}BuOH, respectively (Scheme 6). As this energy gap decreases, the selectivity towards the carboalkoxylated product also diminishes.

CONCLUSIONS:

In conclusion, we have developed the first transition metal-free catalytic protocol for the carboalkoxylation of styrenes. Various styrenes containing electron donating group and diazonium coupling partners containing both electron donating as well as electron withdrawing groups were successfully screened for this reaction to afford structurally diverse carboalkoxylated products. The present protocol is effective for simple arylation in absence of alcohol as well as it successfully delivers carboalkoxylated products in presence of methanol under ambient conditions, thus representing an operationally convenient and economically attractive alternative to the reported rare metal and light mediated methodologies. The mechanistic pathway of this reaction was proposed by carrying out a detailed density functional theory (DFT)-based investigation of the catalytic cycle in combination with several experimental evidences.

EXPERIMENTAL SECTION:

General considerations.

Solvents were dried using standard methods and freshly distilled prior to use.[33] All chemicals were purchased and used as received. The ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on 400 MHz (JEOL) and 500 MHz (BRUKER) spectrometers in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$, 7.26/77.00) as an internal standard. Chemical shifts (δ) are given in ppm, and *J* values are

given in Hz. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Open-column chromatography and thin-layer chromatography (TLC) were performed on silica gel (Merck silica gel 100-200 mesh) and aluminium oxide active neutral activity I-II (Merck). High-resolution mass spectra (HRMS) were obtained on a BrukermaXis impact and Agilent 6530 Q-TOF mass spectrometer using electron spray ionization mass spectroscopic technique. ESI-mass spectra were taken on a Water Q-TOF micro mass spectrometer. Melting points were measured on a Büchi melting point B-545 apparatus.

All aryldiazonium tetrafluoroborate salts were prepared following the previous literature reports.[34-37]

Reaction procedure for optimization study on methoxyarylation of styrenes (3aa-3ih).

Substituted styrene (0.24 mmol, 1 equiv.), diazocoupling partner (0.72 mmol, 3 equiv.), PLY-N,O (0.024 mmol, 0.1 equiv.), KO^{t}Bu (0.048 mmol, 0.2 equiv.) were taken in a 25 mL quartz tube, DMSO (0.8 mL) and methanol (0.8 mL) were poured into the reaction mixture inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for required time at 25 °C. After completion of the reaction, product was extracted using 30 mL ethyl acetate (EA) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (Merck silica gel 100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products.

General procedure for carboalkoxylation of styrenes (4ah-6ah).

Substituted styrene (0.24 mmol, 1 equiv.), diazocoupling partner (0.72 mmol, 3 equiv.), PLY-N,O (0.024 mmol, 0.1 equiv.), KO^{t}Bu (0.048 mmol, 0.2 equiv.) were taken in a 25 mL pressure tube, DMSO (0.8 mL) and alcohol (0.8 mL) were poured into the reaction mixture inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for 24 h at 25 °C. After completion of the reaction, the product was extracted using 30 mL ethyl acetate (EA) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (Merck silica gel 100-200 mesh) using hexane/EtOAc mixture to yield the pure desired products.

Large scale preparation of 6ah.

4-Vinylanisole (**1a**, 2.4 mmol, 320 µL, 1 equiv.), 4-nitrophenyldiazocoupling partner (**2h**, 7.2 mmol, 1.7 g, 3 equiv.), PLY-N,O (0.24 mmol, 50 mg, 0.1 equiv.), KO^{t}Bu (0.48 mmol, 60 mg, 0.2 equiv.) were taken in a 100 mL pressure tube, DMSO (5 mL) and ^{t}BuOH (5 mL) were poured into the reaction mixture inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for 24 h at 25 °C. After completion of the reaction, the product was extracted using 30 mL ethyl acetate (EA) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on silica gel (Merck silica gel 100-200 mesh) using 1% EtOAc in *n*-hexane mixture to yield the pure desired products. 110 mg (14%) of compound **6ah** was isolated as yellow colored solid.

General Procedure for Meerwein arylation-elimination (7ah-15ah).

Substituted styrene (0.24 mmol, 1 equiv.), diazocoupling partner (0.72 mmol, 3 equiv.), PLY-N,O (0.024 mmol, 0.1 equiv.), KO^{t}Bu (0.048 mmol, 0.2 equiv.) were taken in a 25 mL pressure tube, DMSO (0.8 mL) was poured into the reaction mixture inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for 24 h at 25 °C. After completion of the reaction, product was extracted using 30 mL ethyl acetate (EA) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and crude product was purified by column chromatography on neutral aluminium oxide using hexane/EtOAc mixture to yield the pure desired products.

Physical Properties and Characterization Data of the Synthesized Compounds:

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]benzene (3aa)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 µL, 0.24 mmol, 1 equiv.), phenyldiazonium tetrafluoroborate (138 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as a pale yellow solid (37 mg, 64 %). Data are in accordance with previous literature reports.[13] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.27 – 7.15 (m, 5H), 7.15 – 7.09 (m, 2H), 6.87 (d, J = 8.0 Hz, 2H), 4.29 (m, 1H), 3.82 (s, 3H), 3.18 (s, 3H), 3.15 (dd, J = 16.0, 8.0 Hz, 1H), 2.90 (dd, J = 12.0, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.0, 138.5, 133.6, 129.5, 128.0, 128.0, 126.0, 113.8, 84.6, 56.5, 55.2, 44.7.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-2-fluorobenzene (3ab)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 2-fluorophenyldiazonium tetrafluoroborate (155 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as pale yellow oil (52 mg, 83 %). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.17 (m, 3H), 7.06 – 6.96 (m, 3H), 6.85 (d, J = 8.0 Hz, 2H), 4.33 (t, 1H), 3.80 (s, 3H), 3.22-3.11 (m, 4H), 2.91 (dd, J = 16.0, 8.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 161.3 (d, J = 244.0 Hz), 159.1, 133.5, 131.9 (d, J = 4.0 Hz), 127.8, 125.5 (d, J = 15.0 Hz), 123.6 (d, J = 3.0 Hz), 115.1 (d, J = 22.0 Hz), 113.6, 83.1, 56.6, 55.2, 37.8. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K**)** δ (ppm) −118.2.**HRMS m/z** calcd for $C_{15}H_{14}FO$ (M-MeOH+H): 229.1029, found 229.1038.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-4-chlorobenzene (3ae)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 4-chlorophenyldiazonium tetrafluoroborate (163 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as a brown oil (43 mg, 65%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.19 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 4.23 (m, 1H), 3.81 (s, 3H), 3.16 (s, 3H), 3.09-3.04 (dd, J = 12.0, 4.0 Hz, 1H), 2.84 (dd, J = 12.0, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.1, 136.9, 133.2, 131.8, 130.8, 128.1, 127.9, 113.7, 84.3, 56.4, 55.1, 43.9. **HRMS m/z** calcd for $C_{15}H_{14}ClO$ (M-MeOH+H): 245.0733, found 245.0726.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-4-bromobenzene (3af)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 4-bromophenyldiazonium tetrafluoroborate (194 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as brown oil (64 mg, 83%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.34 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 4.22 (t, 1H), 3.81 (s, 3H), 3.16 (s, 3H), 3.08–3.02 (dd, J = 16.0, 8.0 Hz, 1H), 2.82 (dd, J = 16.0, 8.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.1, 137.5, 133.1, 131.2, 131.1, 128.0, 120.0, 113.7, 84.2, 56.5, 55.2, 44.1. **HRMS m/z** calcd for $C_{16}H_{17}BrNaO_2$ (M+Na): 343.0304, found 343.0289.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-3,5-dichlorobenzene (3ag)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 3,5-dichlorophenyldiazonium tetrafluoroborate (187 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as brown oil (54 mg, 72%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm)7.19 (s, 1H), 7.15 (d, J = 8 Hz, 2H), 7.01 (s, 2H), 6.88 (d, J = 8.0 Hz, 2H), 4.24 (dd, J = 8.0, 4.0 Hz, 1H), 3.82 (s, 3H), 3.15 (s, 3H), 3.02 (dd, J = 16.0, 8.0 Hz, 1H), 2.80 (dd, J = 12.0, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.3, 142.0, 134.3, 132.8, 127.9, 127.8, 126.3, 113.8, 83.6, 56.5, 55.2, 44.1. **HRMS m/z** calcd for $C_{15}H_{13}Cl_2O$ (M-MeOH+H): 279.0343, found 279.0345.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-4-nitrobenzene (3ah)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as yellow solid (58 mg, 84%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.09 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 4.29 (m, 1H), 3.81 (s, 3H), 3.20-3.15 (m, 4H), 2.98 (dd, J = 12.0 Hz, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.3, 146.5, 146.4, 132.6, 130.3, 127.9, 123.3, 113.8, 83.7, 56.5, 55.2, 44.5. **HRMS m/z** calcd for $C_{16}H_{17}NNaO_4$ (M+Na): 310.1050, found 310.1052.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-4-methylbenzene (3ai)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 4-methylphenyldiazonium tetrafluoroborate (148 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as pale yellow oil (33 mg, 52%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.17 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 13.0Hz, 2H), 4.27 (t, J = 16.0 Hz, 1H), 3.82 (s, 3H), 3.18 (s, 3H), 3.10 (dd, J = 12.0, 8.0 Hz, 1H), 2.85 (dd, J = 16.0, 8.0 Hz, 1H), 2.32 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.0, 135.5, 133.7, 129.3, 128.7, 128.0, 127.7, 113.6, 84.7, 56.5, 55.2, 44.3. **HRMS m/z** calcd for $C_{17}H_{20}NaO_2$ (M+Na) :279.1356, found 279.1365.

1-[2-Methoxy-2-(4-methoxyphenyl)ethyl]-4-methoxybenzene (3aj)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv.), 4-methoxyphenyldiazonium tetrafluoroborate (160 mg, 0.72 mmol, 3 equiv.) with methanol (0.8 mL, 83 equiv.). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as yellow solid (36 mg, 55%). m.p.: 63.4 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.13 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.17 (s, 3H), 3.06 (dd, J = 12.0, 4.0 Hz, 1H), 2.81 (dd, J = 16.0, 8.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.1, 158.0, 133.7, 130.7, 130.5, 128.1, 113.7, 113.5, 84.9, 56.6, 55.3, 55.3, 43.9. **HRMS m/z** calcd for $C_{17}H_{20}NaO_3$ (M+Na): 295.1305, found 295.1281.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]benzene (3ba)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), phenyldiazonium tetrafluoroborate (138 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using 0.1% EtOAc in *n*-hexane as a pale yellow solid (32 mg, 59%). Data are in accordance with previous literature reports.[13] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.32–7.17 (m, 9H), 4.36 (m, 1H), 3.24 (s, 3H), 3.17 (dd, J = 16.0, 8.0 Hz, 1H), 2.94 (dd, J = 16.0, 8.0 Hz, 1H), 2.41 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 138.7, 138.6, 137.2, 129.4, 129.0, 128.0, 126.7, 126.1, 84.9, 56.6, 44.8, 21.1.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-2-fluorobenzene (3bb)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 2-fluorophenyldiazonium tetrafluoroborate (155 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as a pale yellow oil (41 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.17 – 7.12 (m, 5H), 7.09 – 7.04 (m, 1H), 7.01-6.96 (m, 2H), 4.35 (t, J = 16.0 Hz, 1H), 3.17 (s, 3H), 3.12 (dd, J = 12.0, 8.0 Hz, 1H), 2.93 (dd, J = 12.0, 4.0 Hz, 1H), 2.34 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$, 298 K) δ (ppm) 161.3 (d, J = 244.0 Hz), 138.4, 137.3, 131.9 (d, J = 5.0 Hz), 129.0, 127.8 (d, J = 8.0 Hz), 126.6, 125.5 (d, J = 15.0 Hz), 123.6 (d, J = 3.0 Hz), 115.0 (d, J = 22.0 Hz), 83.4, 56.7, 37.9, 21.1. **^{19}F {^{1}H} NMR (**470 MHz, $CDCl_3$, 298 K**)** δ (ppm) –118.3. **HRMS m/z** calcd for $C_{16}H_{17}FNaO$ (M+Na): 267.1156, found 267.1153.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-3-bromobenzene (3bd)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 3-bromophenyldiazonium tetrafluoroborate (194 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as brown oil (55 mg, 75%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.33 (d, J = 8.0 Hz, 2H), 7.18–7.08 (m, 5H), 7.04 (d, J = 8.0 Hz, 1H), 4.29 (dd, J = 8.0, 4.0 Hz, 1H), 3.18 (s, 3H), 3.06 (dd, J = 16.0, 8.0 Hz, 1H), 2.85 (dd, J = 12.0, 4.0 Hz, 1H), 2.36 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 141.0, 138.2, 137.4, 132.4, 129.5, 129.2, 129.1, 128.1, 126.6, 122.1, 84.4, 56.6, 44.4, 21.1. **HRMS m/z** calcd for $C_{16}H_{17}BrNaO$ (M+Na): 327.0355, found 327.0356.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-4-chlorobenzene (3be)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 4-chlorophenyldiazonium tetrafluoroborate (163 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as brown oil (40 mg, 65%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.21 (d, J = 8.0 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.04 (d, J = 8.0 Hz, 2H), 4.26 (m, 1H), 3.18 (s, 3H), 3.05 (dd, J = 16.0, 4.0 Hz, 1H), 2.87 (dd, J = 12.0, 4.0 Hz, 1H), 2.36 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 138.1, 137.3, 137.0, 131.8, 130.7, 129.0, 128.0, 126.6, 84.5, 56.5, 44.0, 21.1. **HRMS m/z** calcd for $C_{15}H_{14}Cl$ (M-MeOH+H): 229.0784, found 229.0751.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-4-bromobenzene (3bf)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 4-bromophenyldiazonium tetrafluoroborate (194 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using 1% EtOAc in *n*-hexane as brown oil (50 mg, 68%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.35 (d, J = 8.0 Hz, 2H), 7.13 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 4.24 (m, 1H), 3.16 (s, 3H), 3.04 (dd, J = 12.0, 8.0 Hz, 1H), 2.83 (dd, J = 16.0, 8.0 Hz, 1H), 2.35 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 138.2, 137.6, 137.4, 131.2, 131.1, 129.1, 126.7, 120.0, 84.5, 56.6, 44.1, 21.1. **HRMS m/z** calcd for $C_{15}H_{14}Br$ (M-MeOH+H): 273.0279, found 273.0272.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-3,5-dichlorobenzene (3bg)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 3,5-dichlorophenyldiazonium tetrafluoroborate (187 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as brown oil (48 mg, 68%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.21 – 7.12 (m, 5H), 7.04 (d, J = 4.0 Hz, 2H), 4.26 (dd, J = 8.0, 4.0 Hz, 1H), 3.17 (s, 3H), 3.01 (dd, J = 12.0, 8.0 Hz, 1H), 2.81 (dd, J = 12.0, 4.0 Hz, 1H), 2.36 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 142.1, 137.9, 137.6, 134.3, 129.2, 127.9, 126.5, 126.4, 84.0, 56.7, 44.2, 21.1. **HRMS m/z** calcd for $C_{15}H_{13}Cl_2$ (M-MeOH+H): 263.0394, found 263.0401.

1-[2-Methoxy-2-(4-methylphenyl)ethyl]-4-nitrobenzene (3bh)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as colorless oil (43 mg, 63%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.08 (d, J = 12.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.14-7.08 (m, 4H), 4.30 (m, 1H), 3.18-3.13 (m, 4H), 3.00 (m, 1H), 2.34 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.5, 146.4, 137.6, 137.6, 130.3, 129.1, 126.5, 123.2, 83.9, 56.6, 44.5, 21.1.

1-(2-Methoxy-2-phenylethyl)-4-nitrobenzene (3ch)

Prepared according to general procedure described above by reacting styrene (28μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a yellow solid (24 mg, 38%). Data are in accordance with previous literature reports.[13] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.09 (d, J = 8.0 Hz, 2H), 7.33 – 7.20 (m, 7H), 4.34 (m, 1H), 3.20–3.15 (m, 4H), 3.00 (dd, J = 12.0, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.3, 146.2, 140.7, 130.4, 128.5, 128.0, 126.6, 123.3, 84.2, 56.8, 44.5.

1-[2-Methoxy-2-(2-methylphenyl)ethyl]-4-nitrobenzene (3dh)

Prepared according to general procedure described above by reacting 2-methylstyrene (31 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a palebrownish oil (33 mg, 51%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.08 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.26-7.15 (m, 4H), 7.10 (d, J = 8.0 Hz, 1H), 4.59 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 3.14 (s, 3H), 3.08 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 2.95 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 2.20 (s, 3H). **^{13}C {^{1}H} NMR (**125 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.7, 146.5, 138.8, 135.2, 130.5, 130.3, 127.5, 126.4, 125.9, 123.3, 80.5, 56.7, 43.5, 19.0.

1-[2-Methoxy-2-(2,5-dimethylphenyl)ethyl]-4-nitrobenzene (3eh)

Prepared according to general procedure described above by reacting 2,5-dimethylstyrene (35μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a pale yellow solid (35 mg, 51%). m.p.: 50–52 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.11 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 7.01 (s, 1H), 4.58 (dd, J = 8.0, 4.0 Hz, 1H), 3.16 (s, 3H), 3.12–3.07 (dd, J = 12.0, 8.0 Hz, 1H), 2.95 (dd, J = 12.0, 4.0 Hz, 1H), 2.33 (s, 3H), 2.18 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.7, 146.6, 138.6, 135.9, 132.1, 130.4, 130.2, 128.2, 126.3, 123.3, 80.5, 56.7, 43.6, 21.1, 18.5. **HRMS m/z** calcd for $C_{17}H_{19}NNaO_3$ (M+Na): 308.1257, found 308. 1272.

1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-4-nitrobenzene (3fh)

Prepared according to general procedure described above by reacting 4-tert-butylstyrene (44 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as yellow crystalline solid (51 mg, 68%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 4.0 Hz, 2H), 4.32 (dd, J = 4.0 Hz, 4.0 Hz, 1H), 3.18-3.14 (m, 4H), 2.99 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 1.33 (s, 9H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 151.0, 146.7, 146.6, 137.7, 130.3, 126.3, 125.4, 123.2, 83.9, 56.7, 44.5, 34.5, 31.3. **HRMS m/z** calcd for $C_{19}H_{23}NNaO_3$ (M+Na): 336.1570, found 336.1557.

1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-3-chlorobenzene (3fc)

Prepared according to general procedure described above by reacting 4-tert-butylstyrene (44 μL, 0.24 mmol, 1 equiv), 3-chlorophenyldiazonium tetrafluoroborate (163 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as orange oil (55 mg, 76%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.32 (d, J = 12 Hz, 2H), 7.15 – 7.13 (m, 4H), 7.08 (s, 1H), 6.98 (t, 1H), 4.26 (dd, J = 8.0, 4.0 Hz, 1H), 3.15 (s, 3H), 3.02 (dd, J = 12.0, 8.0 Hz, 1H), 2.82 (dd, J = 16.0, 4.0 Hz, 1H), 1.30 (s, 9H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 150.7, 140.9, 138.2, 133.7, 129.5, 129.2, 127.6, 126.3, 126.3, 125.2, 84.3, 56.8, 44.4, 34.5, 31.4. **HRMS m/z** calcd for $C_{19}H_{23}ClNaO$ (M+Na): 325.1330, found 325.1332.

1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-3-bromobenzene (3fd)

Prepared according to general procedure described above by reacting 4-tert-butylstyrene (44 μL, 0.24 mmol, 1 equiv), 3-bromophenyldiazonium tetrafluoroborate (194 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a pale yellow oil (58 mg, 72%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.35 (d, J = 8.0 Hz, 2H), 7.32 (td, J = 8.0 Hz, 4.0 Hz, 1H), 7.25 (t, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.11-7.06 (m, 2H), 4.28 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 3.18 (s, 3H), 3.03 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 2.84 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 1.33 (s, 9H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 150.7, 141.2, 138.2, 132.4, 129.5, 129.2, 128.1, 126.3, 125.2, 122.1, 84.4, 56.8, 44.4, 34.5, 31.4.

1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-4-chlorobenzene (3fe)

Prepared according to general procedure described above by reacting 4-tert-butylstyrene (44 μL, 0.24 mmol, 1 equiv), 4-chlorophenyldiazonium tetrafluoroborate (163 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as brown orange oil (45 mg, 62%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 4.26 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 3.17 (s, 3H), 3.05 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 2.85 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 1.33 (s, 9H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 150.7, 138.3, 137.3, 131.9, 130.8, 128.1, 126.4, 125.2, 84.5, 56.8, 44.0, 34.5, 31.4.

4-(1-methoxy-2-(4-nitrophenyl)ethyl)-1,1'-biphenyl (3gh)

Prepared according to general procedure described above by reacting 4-vinylbiphenyl (43 mg, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a pale yellow solid (43 mg, 54%). m.p.: 126.9 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm)8.11 (d, J = 8.0 Hz, 2H), 7.61 – 7.57 (m, 4H), 7.47-7.43 (m, 2H), 7.37-7.34 (m, 1H), 7.31-7.28 (m, 4H), 4.40 (dd, J = 8.0, 4.0 Hz, 1H), 3.24-3.18 (m, 4H), 3.04 (dd, J = 16.0, 8.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.6, 146.3, 140.9, 140.6, 139.8, 130.4, 128.8, 127.4, 127.2, 127.1, 127.0, 123.0, 83.9, 56.9, 44.5. **HRMS m/z** calcd for $C_{20}H_{16}NO_2$ (M-MeOH+H): 302.1181, found 302.1166.

1-[2-Methoxy-2-(4-ethoxyphenyl)ethyl]-4-nitrobenzene (3hh)

Prepared according to general procedure described above by reacting 4-ethoxystyrene (36 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as a pale yellow solid (44 mg, 61%). m.p.: 72–74 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.08 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 4.28 (t, J = 16.0 Hz, 1H), 4.03 (q, 2H), 3.20-3.15 (m, 4H), 2.99 (m, 1H), 1.42 (t, J = 12.0 Hz, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 158.7, 146.5, 146.4, 132.4, 130.3, 127.8, 123.2, 114.4, 83.7, 63.4, 56.5, 44.5, 14.8. **HRMS m/z** calcd for $C_{17}H_{19}NNaO_4$ (M+Na): 324.1206, found 324.1214.

2-[1-Methoxy-2-(4-nitrophenyl)ethyl]naphthalene (3ih)

Prepared according to general procedure described above by reacting 2-vinylnaphthalene (37mg, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with methanol (0.8 mL, 83 equiv). The title compound was purified by column chromatography with silica gel using1% EtOAc in *n*-hexane as yellow solid (36 mg, 48%). Data are in accordance with previous literature reports.[12] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.09 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.80 (m, 1H), 7.64 (s, 1H), 7.49 (dd, J = 8.0, 4.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 4.52 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 3.27 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 3.22 (s, 3H), 3.10 (dd, J = 12.0 Hz, 4.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.7, 146.3, 138.2, 133.3, 130.4, 128.6, 127.9, 127.8, 126.4, 126.2, 126.0, 124.2, 123.4, 84.4, 56.9, 44.5.

1-(2-Ethoxy-2-(4-methoxyphenyl)ethyl)-4-nitrobenzene (4ah)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with ethanol (0.8 mL, 58 equiv). The title compound was purified by column chromatography with silica gel using 0.1% EtOAc in *n*-hexane as yellow oil (57 mg, 78%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H) 4.39 (m, 1H), 3.82 (s, 3H), 3.41-3.34 (m, 1H), 3.28-3.17 (m, 2H), 2.98 (dd, J = 16.0, 8.0 Hz, 1H), 1.13 (t, J = 16.0 Hz, 3H). **^{13}C {^{1}H} NMR (**125 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.2, 146.6, 146.5, 133.4, 130.4, 127.7, 123.1, 113.8, 81.8, 64.0, 55.2, 44.7, 15.1. **HRMS m/z** calcd for $C_{17}H_{19}NNaO_4$ (M+Na): 324.1206, found 324.1198.

1-(2-Ethoxy-2-(4-methylphenyl)ethyl)-4-nitrobenzene (4bh)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with ethanol (0.8 mL, 58 equiv). The title compound was purified by column chromatography with silica gel using *n*-hexane as a pale yellow solid (38 mg, 55%). m.p.: 65 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.09 (d, J = 4.0 Hz, 2H), 7.27 (d, J = 4.0 Hz, 2H), 7.14-7.10 (m, 4H), 4.39 (t, J = 8.0 Hz, 1H), 3.38-3.33 (m, 1H), 3.26-3.14 (m, 2H), 2.97 (dd, J = 12.0, 4.0 Hz, 2H), 2.34 (s, 3H), 1.10 (m, 3H). **^{13}C {^{1}H} NMR (**125 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.6, 146.5, 138.4, 137.5, 130.4, 129.1, 126.5, 123.2, 82.1, 64.2, 44.7, 21.1, 15.1. **HRMS m/z** calcd for $C_{17}H_{19}NNaO_3$ (M+Na): 308.1257, found 308.1270.

1-(2-Isopropoxy-2-(4-methoxyphenyl)ethyl)-4-nitrobenzene (5ah)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv), 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv), with 2-propanol (0.8 mL, 10 equiv). The title compound was purified by column chromatography with silica gel using *n*-hexane as yellow oil (40 mg, 53%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.09 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 4.48 (dd, J = 8.0, 4.0 Hz, 1H), 3.81 (s, 3H), 3.42 (m, 1H), 3.11 (dd, J = 16.0, 8.0 Hz, 1H), 2.94 (dd, J = 12.0, 8.0 Hz, 1H), 1.04 (d, J = 8.0 Hz, 3H), 0.96 (d, J = 8.0 Hz, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 159.1, 146.8, 146.5, 134.2, 130.5, 127.7, 123.1, 113.7, 79.2, 68.9, 55.2, 45.2, 23.3, 21.0. **HRMS m/z** calcd for $C_{18}H_{21}NNaO_4$ (M+Na): 338.1363, found 338.1381.

1-(2-Tert-butoxy-2-(4-methoxyphenyl)ethyl)-4-nitrobenzene (6ah)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv) with tertbutanol (0.8 mL, 10 equiv). The title compound was purified by column chromatography with silica gel using *n*-hexane as pale brown oil (18 mg, 23%). **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 4.56 (dd, J = 8.0 Hz, 4.8 Hz, 2H), 3.80 (s, 3H), 2.98-2.86 (m, 2H), 0.92 (s, 9H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 158.6, 147.2, 146.5, 137.3, 130.8, 127.0, 123.0, 113.5, 74.6, 74.3, 55.2, 46.8, 28.4. **HRMS m/z** calcd for $C_{19}H_{23}NNaO_4$ (M+Na) : 352.1519, found 352.1515.

(E)-1-methoxy-4-(4-nitrostyryl)benzene (7ah)

Prepared according to general procedure described above by reacting 4-methoxystyrene (32 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as a pale yellow solid (46 mg, 75%). Data are in accordance with previous literature report.[38] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.20 (d, J = 8.0, 2H), 7.59 (d, J = 8.0, 2H), 7.50 (d, J = 12.0, 2H), 7.22 (d, J= 16.0 Hz, 1H), 7.00 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 160.2, 144.3, 132.9, 128.4, 126.5, 124.1, 124.1, 114.3, 55.3.

(E)-1-methyl-4-(4-nitrostyryl)benzene (8ah)

Prepared according to general procedure described above by reacting 4-methylstyrene (32 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as yellow solid (42 mg, 73%). Data are in accordance with previous literature report.[39] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.20 (d, J = 12.0 Hz, 2H), 7.60 (d, J = 8.0Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.25-7.18 (m, 3H), 7.08 (d, J = 16.0 Hz, 2H), 2.37 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.6, 144.1, 139.0, 133.4, 133.3, 129.6, 126.9, 126.7, 125.3, 124.1, 21.3.

(E)-1-Nitro-4-styrylbenzene (9ah)

Prepared according to general procedure described above by reacting styrene (28 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title

compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as yellow solid (25 mg, 45%). Data are in accordance with previous literature report.[40] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.23 (d, J = 12.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.56(d, J = 8.0 Hz, 2H), 7.42−7.34 (m, 2H), 7.28 (d, J = 16.0 Hz, 2H), 7.15 (d, J = 16.0 Hz, 2H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.8, 143.8, 136.2, 133.3, 128.9, 128.8, 127.0, 126.9, 126.3, 124.1.

(E)-2-Methyl-4'-nitrostilbene (10ah)

Prepared according to general procedure described above by reacting 2-methylstyrene (31 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as yellow solid (36 mg, 63%). Data are in accordance with previous literature report.[41] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.23 (d, J = 8.0, 2H), 7.65–7.63 (m, 3H), 7.52 (d, J = 16, 1H), 7.26–7.23 (m, 3H), 7.04 (d, J = 16.0, 1H), 2.46 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.7, 144.1, 136.4, 135.2, 131.0, 130.7, 128.7, 127.6, 126.9, 126.4, 125.6, 124.1, 19.9.

(E)-2,5-dimethyl-4'-nitrostilbene (11ah)

Prepared according to general procedure described above byreacting 2,5-dimethylstyrene (35 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as a pale yellow solid (42 mg, 68%). m.p.: 108–110 °C. **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.23 (d, J = 12, 2H). 7.64 (d, J = 8.0, 2H), 7.49 (d, J = 16.0, 1H), 7.43 (s, 1H), 7.12-7.02 (m, 3H), 2.42 (s, 3H), 2.37 (s, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298

K) δ (ppm) 146.7, 144.2, 135.8, 135.0, 133.4, 131.2, 130.6, 129.5, 127.2, 126.9, 126.1, 124.1, 21.0, 19.4. **HRMS m/z** calcd for $C_{16}H_{16}NO_2$ (M+H): 254.1181, found 254.1177.

(E)-1-(tert-Butyl)-4-(4-nitrostyryl)benzene (12ah)

Prepared according to general procedure described above by reacting 4-tert-butylstyrene (44 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as yellow solid (44 mg, 65%). Data are in accordance with previous literature reports.[42] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.21 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8 Hz, 2H), 7.50 (d, J = 12 Hz, 2H), 7.43 (d, J = 12 Hz, 2H), 7.27 (d, J = 16.0 Hz, 1H), 7.11 (d, J = 16.0 Hz, 1H), 1.35 (s, 9H). **^{13}C {^{1}H} NMR (**125 MHz, $CDCl_3$, 298 K) δ (ppm) 152.2, 146.6, 144.1, 133.4, 133.2, 126.8, 126.7, 125.8, 125.5, 124.1, 34.8, 31.2.

(E)-4-Ethoxy-4-(4-nitrostyryl)benzene(13ah)

Prepared according to general procedure described above by reacting 4-ethoxystyrene (36 μL, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as a yellow solid (42 mg, 65%). Data are in accordance with previous literature report.[43] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.20 (d, J = 4 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.48(d, J = 8 Hz, 2H), 7.22 (d, J = 12.0 Hz, 1H), 7.00 (d, J = 12.0 Hz, 1H), 6.91 (d, J = 8 Hz, 2H), 4.08 (q, 2H), 1.44 (m, 3H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K) δ (ppm) 159.7, 146.4, 144.3, 133.0, 128.8, 128.4, 126.5, 124.1, 114.9, 63.6, 14.8.

2-[(E)-2-(4-Nitrophenyl)ethenyl]naphthalene (14ah)

Prepared according to general procedure described above by reacting 2-vinylnaphthalene (37 mg, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 2% EtOAc in *n*-hexane as yellow solid (28 mg, 42%). Data are in accordance with previous literature report.[44] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.25 (2H, d, J = 12.0 Hz), 7.92 (s, 1H), 7.87-7.83 (m, 3H,), 7.75 (d, J = 8.0 Hz, 1H), 7.68 (d, d, J = 8.0 Hz, 2H), 7.52-7.49 (m, 2H), 7.44 (d, J = 16 Hz, 1H), 7.27 (d, J = 16.0 Hz, 1H). **^{13}C {^{1}H} NMR (**100 MHz, $CDCl_3$, 298 K**)** δ (ppm) 146.8, 143.9, 133.7, 133.6, 133.5, 128.7, 128.3, 128.0, 127.8, 126.9, 126.7, 126.6,124.3, 123.3.

4-(4-Nitrostyryl)-1,1'-biphenyl (15ah)

Prepared according to general procedure described above by reacting 4-vinylbiphenyl (43 mg, 0.24 mmol, 1 equiv) with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv). The title compound was purified by column chromatography with neutral aluminum oxide using 3% EtOAc in *n*-hexane as a yellow solid (35 mg, 48%). Data are in accordance with previous literature reports.[45] **^{1}H NMR (**400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.20 (d, J = 8.0 Hz, 2H), 7.63-7.58 (m, 7H), 7.43 (t, J = 12.0 Hz, 3H),7.34 (d, J = 8.0 Hz, 1H), 7.24 (d, J= 16.0 Hz, 3H), 7.15 (d, J= 16.0 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 298 K) δ (ppm) 146.3, 143.9, 141.6, 140.3, 135.2, 132.9, 128.9, 127.6, 127.5, 127.5, 127.0, 126.9, 126.3, 124.2.

TEMPO-trapped intermediate 16:

4-Vinylanisole (**1a**, 0.24 mmol, 32 μL, 1 equiv), with 4-nitrophenyldiazonium tetrafluoroborate (171 mg, 0.72 mmol, 3 equiv), PLY-N,O (0.024 mmol, 5 mg, 0.1 equiv), KO^{t}Bu (0.048 mmol, 6

mg, 0.2 equiv), TEMPO (0.24 mmol, 38 mg, 1 equiv.) were taken in a 25 mL pressure tube, DMSO (5 mL) were poured into the reaction mixture inside a nitrogen filled glovebox. The final reaction mixture was allowed to stir for 24 h at 25 °C. After completion of the reaction, the product was extracted using 30 mL ethyl acetate (EA) and dried over anhydrous sodium sulphate. The compound was purified by column chromatography using neutral aluminum oxide in hexaneand obtained as a white solid (16 mg, 24 %). Data are in accordance with previous literature report.[24] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 8.14 (d, J = 12.0 Hz, 2H), 7.47-7.11 (m, 2H), 1.67-1.59 (m, 5H), 1.44-1.42 (m, 1H), 1.23 (s, 6H), 0.98 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 298 K) δ (ppm) 168.6, 141.1, 125.5, 114.1, 60.9, 39.6, 32.2, 20.4, 16.8.

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Author contributions

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Notes

The authors declare no competing financial interest

ASSOCIATED CONTENT:

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:….

KIE experiments, additional experiments, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, Mass spectra and computational details.

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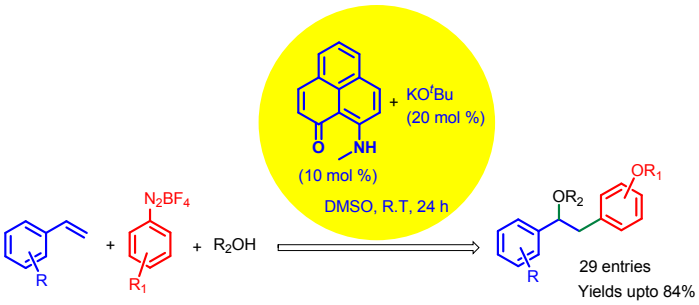

- First transition metal free catalysis
- Multicomponent reaction
- Room temperature
- Low ligand and base loading
- Moderate to good yield