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Graphical Abstract

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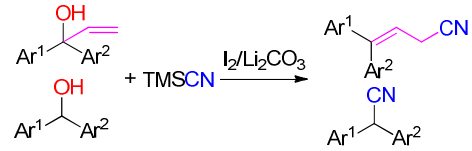

- Mild reaction conditions
- Free of transition metal
- Dual activation
- Highly effective transformation
- Versatile nitriles
- Base promoted strategy

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ABSTRACT

One-step base promoted strategy for cyanation of *α,α*-diaryl alcohols has been developed under mild and transition metal-free conditions. This method provides a straightforward and facile way towards the synthesis of *β,γ*-unsaturated nitriles and *α*-phenylnitiriles from *α*-vinyl carbinols and *α,α*-diaryl methanols, respectively, up to 99% yield. Moreover, various azides and ethers could also be accessed from their respective nucleophiles under standard reaction conditions.

1. Introduction

β,γ-Unsaturated nitriles are not only important compounds in dyes and perfumes but also notably important fragments in natural products and various potential medicinal drugs, for instance, HIV-1 cytopathic drug.[1] Common cyanation methods to synthesize cyanides started from halides[2] and other allylic substituted compounds, such as carbonates and acetates, have been well reported.[3] Except for these common strategies, quite limited publications were reported to achieve *β,γ*-unsaturated nitriles.[4] Whereas, in the last few decades, the direct access to nitriles from relatively easily available alcohols, which are key substrates in carbon chain elongation, attracted much attention. Based on the concept of the Mitsunobu reaction,[5] various one-pot cyanation strategies from alcohols have been developed by utilizing either inorganic nitrile sources, for instance, HCN, NaCN, KCN or using *n*-Bu_4NCN reagent as organic cyanide source.[6] Meanwhile, both metal-free and metal-catalyzed nucleophilic carbocation cyanation of alcohols have also been developed, such as, utilizing $B(C_6F_5)_3$,[7] In(III),[8] montmorillonite,[9] $FeCl_3{\cdot}6H_2O$,[10] and $Zn(OTf)_2$[11] as catalysts. Takemoto *et al.* developed a strategy by using the combined halogen bond donor with trimethylsilyl halide as Lewis acid co-catalyst to achieve the direct dehydroxylative coupling of alcohols with organosilanes.[12]

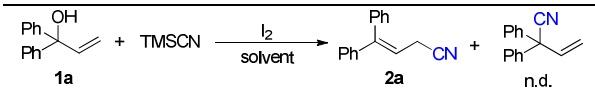
As important as metal Lewis acids, iodine as Lewis acid has extensive applications in organic synthesis especially the functionalization of alcohols as well as alkenes.[13] Iodine-promoted reactions have a great advantage due to the mild reaction conditions, safe handling, easy operation and clean mixture.[14] In the recent years, introduction of cyano motifs to provide useful nitrile complexity in the compounds utilizing both metal and metal-free reagents attracts most of our attention.[15] In this regards, we have successfully employed both elemental iodine and hypervalent iodines to promote intramolecular aminocyanation, aminothiocyanation and other cyanations.[16] Allylic alcohols were used to form C-C, C-O, C-N bonds through nucleophilic substitution procedure in the last two decades.[17] Meanwhile, diarylalkanes are crucial fragment as pharmacologically active compounds.[18] Therefore, in the continuation of our ongoing interest, we envisioned a procedure using *α,α*-diaryl alcohols as substrates via carbocation intermediate direct into nitriles promoted by iodine could be achieved. As expected, a series of both *β,γ*-unsaturated nitriles and *α*-phenylnitiriles from *α*-vinyl carbinols and *α,α*-diaryl methanols were approached successively. Herein, we would like to report iodine-promoted transition metal-free cyanation of diaryl alcohols towards synthesis of versatile nitriles.

2. Results and discussion

The feasibility of the intended transformation was appraised using 1,1-diphenylprop-2-en-1-ol as a model substrate and TMSCN with lower toxicity as cyanide source in the presence of iodine in DCM and results are shown in Table 1. To our delight, the transformation of test substrate proceeds selectively to allylic cyanide **2a** at 35 ^oC in 35% yield and no rearranged benzyl cyanated product was observed (entry 1, Table 1). The benzyl carbocation, more stable and sterically hindered, is harder to be attacked by nucleophile, therefore, it undergoes a rearrangement to less sterically hindered allylic carbocation which is easier to be attacked by cyanide anion, as depicted in Figure 1. Encouraged by this primary result, the efficiencies of several solvents were examined. Firstly, the reaction seems to be sensitive to solvents and only DCE and DCM afforded the desired product **2a** in 20% and 35% yields, respectively (entries 2-6, Table 1). Next, the effect of various amounts of I_2 was investigated and the

decreased yield was observed no matter increasing or decreasing its dosage (entries 7-8, Table 1). After the concentration effect of TMSCN was examined and the best outcome was obtained in 47% yield when 4.5 equivalents of TMSCN was added (entries 9-12, Table 1). In the study of temperature effect, decreased yields of the targeted product were observed in both cases of raising and lowering of temperature (entries 13-14, Table 1). In the end, effects of concentration and reaction time were tested, and it proved to be detrimental to this reaction when the two factors were changed (entries 15-18, Table 1).

Table 1. Optimization of reaction conditions.[a]



Entry	Solvent	TMSCN (eq.)	I_2 (eq.)	*T* (°C)	Yield[b] (%)
1	DCM	3.0	1.8	35	35
2	THF	3.0	1.8	35	trace
3	CH_3OH	3.0	1.8	35	0
4	EA	3.0	1.8	35	trace
5	DCE	3.0	1.8	35	20
6	DMF	3.0	1.8	35	0
7	DCM	3.0	1.5	35	30
8	DCM	3.0	2.0	35	27
9	DCM	2.0	1.8	35	trace
10	DCM	4.0	1.8	35	40
11	DCM	4.5	1.8	35	47
12	DCM	5.0	1.8	35	39
13	DCM	4.5	1.8	25	13
14	DCM	4.5	1.8	40	25
15	DCM	4.5	1.8	35	31[c]
16	DCM	4.5	1.8	35	32[d]
17	DCM	4.5	1.8	35	22[e]
18	DCM	4.5	1.8	35	18[f]

[a] Conditions: **1a** (0.3 mmol), TMSCN (specified), I_2 (specified) in solvent (5 mL) at 35 °C for 5 h.
[b] Yield determined by ^{1}H-NMR using anisole as an internal standard.
[c] 4 mL of DCM.
[d] 6 mL of DCM.
[e] 4 h.
[f] 6 h. n.d. = not detected.

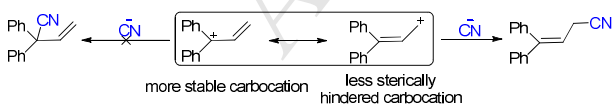
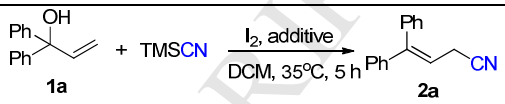


Figure 1. Cyanation favoured rearrangement of carbocation from benzyl to allylic site.

It is well-known that bases are capable of enhancing the reactivity of TMSCN through ionization of TMSCN.[19] Accordingly, diverse bases were subjected under standard reaction conditions and as a result, the expected improvements in yield was noticed (Table 2). A strong organic base such as *t*-BuOK facilitated the transformation and gave a better yield of 54% (entry 1, Table 2). Next, various inorganic bases were analyzed and weak base were found to be capable to increase the reaction yield (entries 2-6, Table 2). The best yield of 80% was provided when 0.2 equivalent of Li_2CO_3 was loaded along with optimized conditions (entry 6, Table 2). In cases of increasing and decreasing the amount of Li_2CO_3, decreased yield of desired product was observed (entries 6-8, Table 2). When the reaction was performed in the dark which excluded the light promoting reaction pathway the yield kept the same with in light (entry 6). Eventually, after detailed experimentation, we were successful to gain optimal dual-activation reaction conditions where iodine activates alcohol substrate to generate carbocation and Li_2CO_3 activates TMSCN to release free cyanide anion.

Table 2. Optimization of Additives.[a]



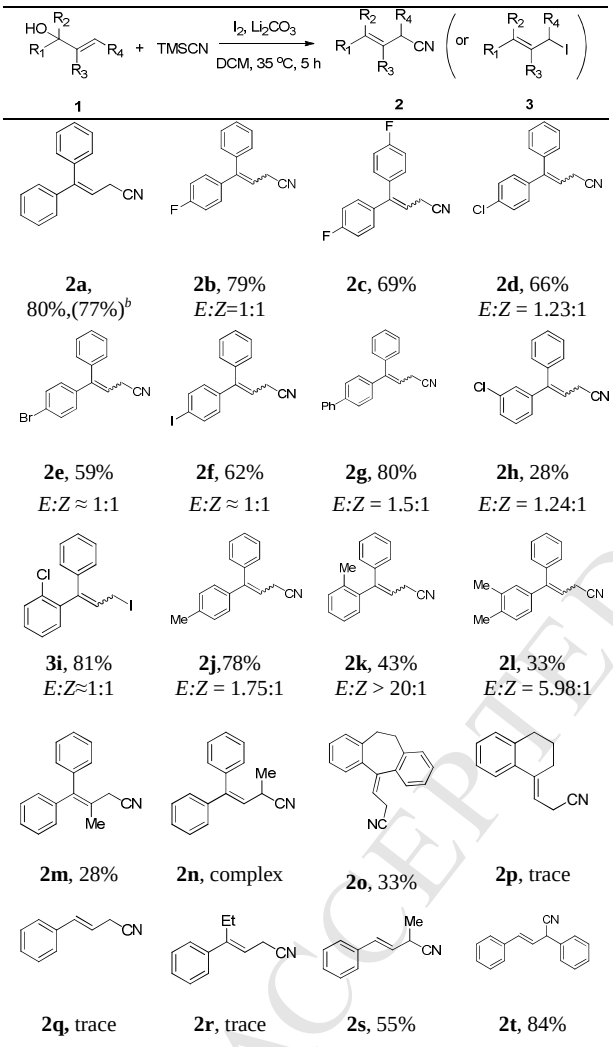
Entry	Additives	Equiv. (eq.)	Yield[b] (%)
1	*t*-BuOK	0.2	54
2	$NaHCO_3$	0.2	63
3	Na_2CO_3	0.2	50
4	K_2CO_3	0.2	62
5	Mn_2CO_3	0.2	63
6	Li_2CO_3	0.2	80 (80)[c]
7	Li_2CO_3	0.1	63
8	Li_2CO_3	0.3	70

[a] Conditions: **1a** (0.3 mmol), TMSCN (4.5 eq.), I_2 (1.8 eq.) and base (specified) in solvent (5 mL) at 35°C for 5 h.
[b] Yield determined by ^{1}H-NMR using anisole as an internal standard.
[c] The reaction was performed in dark condition.

With the optimized conditions in hand, first we turned our attention to explore the scope of diarylallylic alcohols and the results were summarized in Table 3. Several allylic alcohols bearing one or two electron-withdrawing groups were evaluated to study this metal-free transformation and the desired cyanation products under standard conditions were afforded in good to excellent yields with some interesting conversions (**2b-i**). At the outset, electronic effect of various halogens was investigated, as a result, good to excellent outcome was obtained (**2b-f**). Among these, substrates with electronegative substituents gave better yields and a gradual decrease of yield is observed with the increase of size and decrease of electronegativity. After that, space orientation effect of halo-substituted substrates at *ortho*- and *meta*-position was analyzed. As a result, lower yield of *meta*-chloro substrate comparing to *para*- substituted was obtained. It is important to note that *ortho*-chloro substrates responded to this transformation under standard conditions in completely different fashion and gave the rearranged iodinated products **3i** in 81% isolated yields. These results imply the prominent steric influence of same counterparts at different positions on aromatic phenyl ring. Furthermore, the remarkable transformation generality and efficacy was demonstrated in the case of alcohol having an electron donating functional group at *para*-position and **2j** was obtained in 78% yield. However, a decreased yield of targeted product **2k** was found due to the significant steric effect of *ortho*-substitutent. For both electron-donating and electron-withdrawing groups, *para*-substituents seemed to more

favourable than *ortho*- and *meta*- counterparts. Besides mono-substituted substrates, 3,4-dimethyl substituted alcohol also readily gave the desired product **2l** in moderate yield. Quite low stereoselectivity of desired products was observed, with the exception of the strong steric hindrance substrate **1k**. To test the flexibility of the reaction, substrates with substitution at the double bond were tested under the standard conditions, but only **2m** was provided with lower yield of 28% and internal alkene failed to give desired product **2n**. Next, **1o** and **1p** were examined. Only rigid allylic alcohol **1o** provided product **2o** in 33% yield because of conjugation in the cations. Next, *α*-arylallylic alcohols were tested but neither cinnamyl alcohol nor 1-phenylprop-2-en-1-ol works well. Common substrates **1s** and **1t** were employed **2s** and **2t** were obtained in the yields of 55% and 84%, respectively.

Table 3. Scope of cyanation of allylic alcohol.[a]

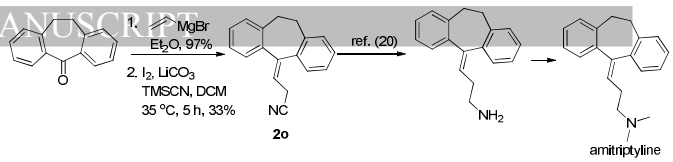


[a] Conditions: **1** (0.3 mmol), TMSCN (1.35 mmol), I_2 (0.54 mmol) and Li_2CO_3 (0.06 mmol) in DCM (5 mL) at 35 °C for 5 h in sealed reaction test tube.

[b] *E*:*Z* ratio of products was determined by ^{1}H NMR or ^{13}C NMR, and *E*- and *Z*- isomers was confirmed by 2D NOESY. [c] Isolated yields.

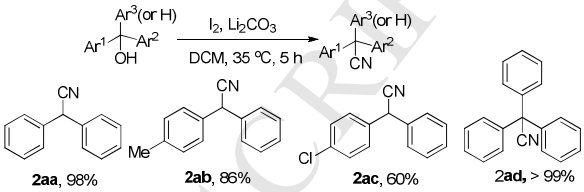
The synthetic utility of this method is amply demonstrated in the alternative formal synthesis of well-known mental disorder drug amitriptyline. The compound **1o** obtained from dibenzosuberone was subjected to this *β,γ*-unsaturated cyanation gave **2o** and followed by a reduction[20] and a substitution to access amitriptyline (Scheme 1).

Scheme 1. Synthetic utility of I_2/Li_2CO_3-promoted cyanation of diarylalcohols protocol in the synthesis ofamitriptyline.



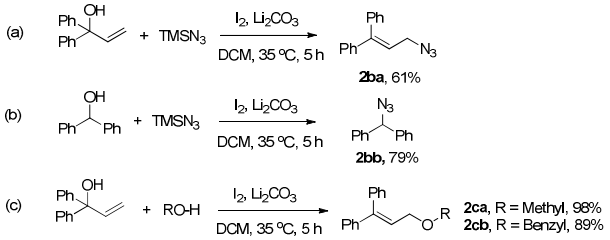
Following above results, we investigated cyanation of phenyl substituted methanols (Scheme 2). As depicted in Scheme 1, several phenyl commuted methanols such as diphenyl or triphenyl could be transformed into cyanation products (**2aa-ad**) up to 99% yield. *Para*-substituted substrates provided the cyanation products in moderate to good yields (**2ab-ac**) and better reactivity of electron-donating substituted derivatives was observed as compared to electron-withdrawing substituted one.

Scheme 2. Cyanation of di- or tri-phenylmethanols.



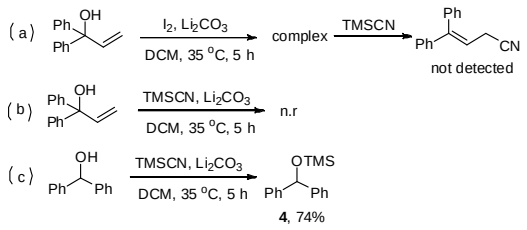
To extend nucleophilic dual activation generality, other trimethylsilyl based nucleophile such as TMS-N_3, -OTf, -CF_3 and -C≡CH were utilized under standard conditions. Among these trimethylsilyl reagents, the only azidation (Scheme 3) of the model substrate was successful and product **2ba** was isolated in 61% while other counterparts found to be ineffectual to give the responding products. Likewisely, the azidated product **2bb** from diphenylmethanol was obtained in a good yield of 79%. Moreover, *β,γ*-unsaturated ethers were assembled when alcohols such as methyl and benzyl alcohol were been chosen as a nucleophilic reagents, in excellent yields of 98% and 89%, respectively.

Scheme 3. Azidation and etherification under the optimal conditions**.**



In an effort to glean insights into the mechanism, some control experiments were conducted. In the absence of either TMSCN or I_2, neither iodide nor cyanide was observed (Scheme 4 (a) and (b)). In the former case, the cyanation did not proceed, even the time was prolonged to 24 h. However, in the later case, TLC analysis showed a complex reaction then TMSCN was added to react for another 5 h and no cyanided product was detected. This suggested that elemental iodine plays a role of Lewis acid to activate the oxygen and as such the C-O bond became readily cleavable meanwhile there was no iodinated intermediates formed. When diphenylmethanol was subjected to this standard conditions only in the absence of I_2, (benzhydryloxy)trimethylsilane was captured and isolated in 74% yield (Scheme 4 (c)), which shows the existence of ether intermediate.

Scheme 4. Control experiments.



Based on the above experiments, a plausible mechanistic pathway is proposed (Figure 3). Initially, substrate reacts with TMSCN to form an intermediate **A** which interacted with iodine to afford intermediate **B**. Subsequent removal of iodine and trimethylsilyl alcohol could give carbocation intermediates which changed to its steady state and coupled with the formed cyanide anion to generate the desired product.

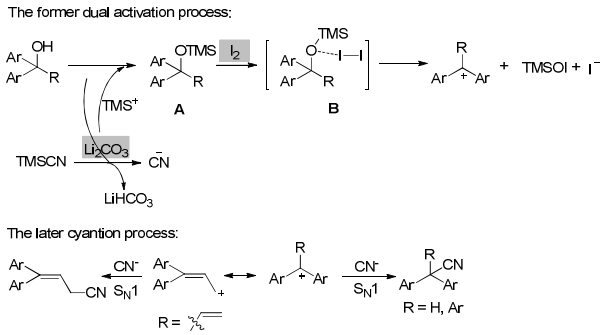


Figure 3. Proposed reaction mechanism.

3. Conclusion

In summary, a straightforward transition metal-free dually activated cyanation for preparation of diaryl substituted *β,γ*-unsaturated nitriles, and *α*-phenylnitiriles from alcohols has been developed. The mechanistic study revealed that elemental iodine plays a role of Lewis acid to activate the oxygen and a possible mechanism has been proposed: iodine activates alcohol and lithium carbonate activates TMSCN. This protocol has successfully been utilized in the concise synthesis of amitriptyline. The easy operation and mild condition make this protocol feasible and practical

4. Experimental section

4.1. General Information

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500 (125) MHz spectrometer at 20-25 ^{o}C. ^{1}H NMR spectra were reported in parts per million using TMS (δ = 0.00 ppm) as an internal standard. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ (δ = 77.2 ppm) as an internal standard. High-resolution mass spectra (HRMS) electrospray ionization (ESI) was carried out on a UPLC-Q-ToF MS spectrometer. All reagents were purchased from commercial suppliers and used as received. Common experiments were conducted in the atmosphere, while the reactions with Grignard reagent were developed in argon. Column chromatography and thin-layer chromatography (TLC) which was used to monitor the reactions were performed on silica gel.

4.2. General procedure for preparation of cyclic, acyclic allylic alcohols, furan-2-yl(phenyl)methanol and phenyl(thiophen-2-yl)methanol.[21]

To a two-necked flask under argon atmosphere loaded with a solution of ketone (5 mmol) in anhydrous THF (5 mL) then under vigorous stirring Grignard reagent (1.0 M in THF, 5.5 mL, 5.5 mmol, 1.1 equiv.) was dropwise added via syringe in ice-bath. The mixture was stirred for 0.5 h in ice bath, then warmed to room temperature and stirred for 2-5 h. After detected by TLC, aqueous NH_4Cl (6 mL) was added to quench the reaction, then the mixture was extracted with EtOAc (5 mL×3). The combined organic layers were dried over anhydrous magnesium. The solvent was removed in vacuo by ratory evaporator. And the crude was purified by chromatography on silica gel to obtain desired allylic alcohols.

4.3. General procedure for the synthesis of aryl methanols [22]

To ice-cold solution of ketone (5 mmol) in methanol (10 mL), sodium borohydride (7 mmol) was slowly added under stirring. Then, the mixture was further stirred for 1-3 h at 0 ^{o}C. After completion of the reaction monitored by TLC, evaporation of the solvent and purified by a short chromatography on silica gel to give alcohols.

4.4. General procedure of this method for synthesizing the desired products (2 and 3)

To a round-bottom flask was charged with compounds **1** (0.3 mmol) in DCM (5 mL), Li_2CO_3 (0.06 mmol), TMSCN (or $TMSN_3$, or RO-H) (1.35 mmol), and I_2 (0.54 mmol) in sequence successively. Then the resulting mixture was stirred under closed conditions at 35 ^{o}C (water bath temperature) for 5h. The reaction was quenched with saturated solution of $Na_2S_2O_3$. The organic phase was separated, and the aqueous layer was extracted with DCM (5 mL × 3). The combined organic solution was dried with Mg_2SO_4 and concentrated in vacuo. The resulting residue was purified by a column chromatography to give the corresponding products.

*4.4.1 4,4-diphenylbut-3-enenitrile (**2a**).* White solid; m.p. 92.0-94.0 ^{o}C; 77% yield, 50.7 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.36 (m, 3H), 7.29 (t, *J* = 4.5 Hz, 3H), 7.23 (t, *J* = 4.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.04 (t, *J* = 7.5 Hz, 1H), 3.15 (d, *J* = 7.5Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 140.9, 138.1, 129.5, 129.0, 128.5, 128.4, 128.3, 127.6, 118.3, 115.6, 18.5; HRMS *(m/z)* calcd for $C_{16}H_{13}NH^{+}$ 220.1121, found 220.1130.

4.4.2 4-(4-fluorophenyl)-4-phenylbut-3-enenitrile (**2b**). *E/Z*= 1:1 White solid; m.p. 91-92 ^{o}C; 79% yield, 56.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.29 (m, 3H), 7.20-7.10 (m, 5H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.00 (dt, *J* = 29.5, 7.0 Hz, 1H) ，3.12 （d, *J* = 7.5 Hz, 2H）. ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 163.6, 161.9, 161.6, 146.8, 146.7, 140.7, 137.9, 137.0 (d, *J* = 3.12 Hz), 134.0 (d, *J* = 3.25 Hz), 131.3 (d, *J* = 8.05 Hz), 129.3 (d, *J* = 7.12 Hz), 129.2 (d, *J* = 50.38 Hz), 128.6, 128.5 (d, *J* = 7.13 Hz), 127.5, 118.1, 118.0, , 116.03, 116.02 (d, *J* = 21.38 Hz), 115.5, 115.4 (d, *J* = 21.50 Hz), 18.48, 18.46; HRMS *(m/z)* calcd for $C_{16}H_{12}FNH^{+}$ 238.1027, found 238.1027.

*4.4.3 4,4-bis(4-fluorophenyl)but-3-enenitrile (**2c**).* Light yellow solid; m.p. 76-78 ^{o}C; 69%, 53.1 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.11 (m, 6H), 6.99 (t, *J* = 8.0 Hz, 3H), 5.99 (t, *J* = 7.0 Hz, 1H), 3.13 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (d, *J* = 31.38 Hz), 161.8 (d, *J* = 31.25 Hz), 145.7, 136.8 (d, J = 3.25 Hz), 133.8 (d, J = 3.38 Hz), 130.29 (d, *J* = 250 Hz), 130.23 (d, *J* = 250 Hz), 118.0, 116.1 (d, *J* = 21.37 Hz), 115.9, 115.5 (d, *J* = 21.50 Hz), 18.5; HRMS (m/z) calcd for $C_{16}H_{11}F_2NH^{+}$ 256.0933, found 256.0936.

*4.4.4 4-(4-chlorophenyl)-4-phenylbut-3-enenitrile (**2d**).* *E*/*Z*= 1.23:1; White solid; m.p. 69-71 °C; 66% yield, 50.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.16 (m, 5H), 7.11 (d, *J* = 1.5 Hz, 1H), 7.07-7.03 (m, 3H), 5.95 (dt, *J* = 12.5, 7.5 Hz, 1H), 3.05 (t, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.59, 146.57, 140.4, 139.3, 137.6, 136.5, 134.35, 134.28, 130.9, 129.4, 129.2, 129.1, 128.8, 128.7, 128.59, 128.55, 128.50, 127.5, 118.05, 117.97, 116.14, 116.10, 18.50, 18.46; HRMS (m/z) calcd for $C_{16}H_{12}ClNH^+$ 254.0731, found 254.0731.

*4.4.5 4-(4-bromophenyl)-4-phenylbut-3-enenitrile (**2e**).* *E*/*Z* ≈ 1:1 White solid; m.p. 59-60 °C; 59% yield, 52.7 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.5 Hz, 1H), 7.44-7.38 (m, 3H), 7.29 (s, 1H), 7.20 (s, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.07 (dd, *J* = 11.5, 8.5 Hz, 2H), 6.03 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.12 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.56, 146.53, 140.3, 139.7, 137.5, 137.0, 132.1, 131.6, 131.2, 129.4, 129.1, 129.0, 128.55, 128.52, 128.47, 127.5, 122.5, 117.96, 117.90, 116.17, 116.11, 18.47, 18.42; HRMS (m/z) calcd for $C_{16}H_{12}BrNH^+$ 298.0226, found 298.0226.

*4.4.6 4-(4-iodophenyl)-4-phenylbut-3-enenitrile (**2f**).* *E*/*Z* ≈ 1:1 White solid; m.p. 66-68 °C; 62% yield, 63.9 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.45-7.37 (m, 2H), 7.31-7.28 (m, 1H), 7.21-7.17 (m, 1H), 7.16-7.13 (m, 1H), 6.97-6.92 (m, 2H), 6.06-6.01 (m, 1H), 3.13 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.6, 140.3, 140.2, 138.1, 137.54, 137.50, 137.4, 131.3, 129.4, 129.3, 129.0, 128.53, 128.50, 128.4, 127.5, 117.93, 117.88, 116.1, 116.0, 94.18, 94.15, 18.5, 18.4; HRMS (m/z) calcd for $C_{16}H_{12}INH^+$ 346.0087, found 346.0086.

*4.4.7 4-phenyl-4-(p-tolyl)but-3-enenitrile (**2g**).* *E*/*Z* = 1.5:1 Light yellow solid; m.p. 152-154 °C; 80% yield, 56.1 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (t, *J* = 9.0 Hz 2H) 7.54 (dd, *J* = 24.5, 7.5 Hz, 2H), 7.47-7.33 (m, 4H), 7.30-7.19 (m, 6H), 6.06 (td, *J* = 14.5, 7.5 Hz, 1H), 3.16 (dd, *J* = 25.0, 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 147.3, 141.17, 141.15, 140.9, 140.56, 140.52, 139.7, 138.1, 137.1, 130.0, 129.6, 129.05, 129.02, 128.98, 128.6, 128.4, 128.3, 128.0, 127.8, 127.66, 127.60, 127.22, 127.20, 127.15, 118.3, 118.2, 115.8, 115.6, 18.6, 18.5; HRMS (m/z) calcd for $C_{22}H_{17}NH^+$ 296.1434, found 296.1440.

*4.4.8 4-(3-chlorophenyl)-4-phenylbut-3-enenitrile (**2h**).* *E*/*Z*= 1.24:1; Light yellow liquid; 28% yield, 21.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.30 (m, 4H), 7.27-7.09 (m, 5H), 6.05 (dd, *J* = 4.5, 2.5 Hz, 1H), 3.14 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 146.4, 142.7, 140.1, 139.9, 137.4, 135.0, 134.5, 130.3, 129.7, 129.47, 129.43, 129.1, 128.64, 128.61, 128.59, 128.55, 128.4, 127.74, 127.66, 127.5, 125.8, 118.0, 117.9, 116.9, 116.4, 18.50, 18.48; HRMS (m/z) calcd for $C_{16}H_{12}ClNH^+$ 254.0731, found 254.0723.

*4.4.9 4-phenyl-4-(p-tolyl)but-3-enenitrile (**2j**).* *E*/*Z* = 1.75:1; Yellow liquid; 78% yield, 56.3 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.36 (m, 2H), 7.27 (s, 1H), 7.22 (d, *J* = 5.5 Hz, 2H), 7.16 (d, *J* = 7.0 Hz, 1H),7.10 (s, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 5.99 (t, *J* = 7.0 Hz, 1H), 3.12 (dd, *J* = 15.5, 7.0 Hz, 2H), 2.36 (d, *J* = 30.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 147.5, 141.1, 138.3, 138.2, 138.1, 138.0, 135.1, 129.6, 129.5, 129.4, 129.2, 128.9, 128.4, 128.23, 128.17, 127.6, 127.4, 118.4, 115.4, 114.7, 21.4, 21.2, 18.5, 18.4; HRMS (m/z) calcd for $C_{17}H_{15}NH^+$ 234.1277, found 234.1285.

*4.4.10 4-phenyl-4-(o-tolyl)but-3-enenitrile (**2k**).* *E*/*Z* > 20:1 White liquid; 43% yield, 30.1 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 6H), 7.24-7.20 (m, 2H), 7.11-7.08 (m, 1H), 6.16 (t, *J* = 7.5 Hz, 1H), 2.97(t, *J* = 5.5 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 139.3, 137.1, 136.4, 130.8, 129.5, 128.6, 128.4, 128.3, 126.6, 126.4, 118.0, 115.6, 19.6, 18.2; HRMS (m/z) calcd for $C_{16}H_{12}ClNH^+$ 234.1277, found 234.1273.

*4.4.11 4-(3,4-dimethylphenyl)-4-phenylbut-3-enenitrile (**2l**).* *E*/*Z* = 5.98:1 White liquid; 33% yield, 24.3 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.34 (m, 2H), 7.29-7.15 (m, 3H), 7.06-6.89 (m, 3H), 5.98 (td, *J* = 7.5, 3.5Hz, 6H), 3.13 (dd, *J* = 20.0, 7.5 Hz, 2H), 2.24 (dd, *J* = 27.0, 17.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 147.6, 141.1, 138.5, 138.4, 137.2, 137.0, 136.7, 136.6, 135.6, 130.5, 130.0, 129.7, 129.5, 128.8, 128.7, 128.4, 128.2, 128.1, 127.6, 126.9, 125.1, 118.4, 115.2, 114.6, 19.94, 19.93, 19.7, 19.6, 18.5, 18.4; HRMS (m/z) calcd for $C_{18}H_{17}NH^+$ 248.1434, found 248.1442.

*4.4.12 3-methyl-4,4-diphenylbut-3-enenitrile (**2m**).* White solid; m.p. 71-73 °C; 28% yield, 16.1 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.21 (m, 6H), 7.16-7.12 (m, 4H), 3.16 (s, 2H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 141.42, 141.36, 129.4, 129.2, 128.7, 128.3, 127.6, 127.3, 123.5, 118.4, 24.6, 19.9.

*4.4.13 3-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)propanenitrile (**2o**).* White solid; m.p. 136-137 °C; 33% yield, 24.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.25-7.14 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 (d, J = 7.0 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 3.32 (dd, *J* = 24.5, 13.5 Hz, 1H), 3.20-3.06 (m, 2H), 2.95 (t, J = 13.0 Hz, 1H), 2.78 (d, *J* = 12.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 139.44, 139.40, 138.2, 137.4, 130.4, 128.7, 128.6, 128.4, 128.1, 127.51, 126.46, 118.2, 117.6, 33.6, 31.9, 18.1.

*4.4.14 (E)-2-methyl-4-phenylbut-3-enenitrile (**2s**).* [23] Colorless oil; 55% yield, 26.1 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (m, 4H), 7.32-7.27 (m, 1H), 6.73 (d, *J* = 15.5 Hz, 1H), 6.09 (dd, *J* = 15.5, 6.0 Hz, 1H), 3.52-3.48 (m, 1H), 1.52 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.8, 132.6, 128.8, 128.3, 126.6, 124.4, 121.0, 28.4, 19.1.

*4.4.15 (E)-2,4-diphenylbut-3-enenitrile (**2t**).* [8] White solid; m.p. 62-64 °C; 84% yield, 55.0 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.21 (m, 10H), 6.79 (d, *J* = 15.5 Hz, 1H), 6.17 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.66 (dd, *J* = 6.5, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.7, 133.4, 129.4, 128.8, 128.6, 127.7, 126.8, 123.4, 118.9, 40.1.

*4.4.16 2,2-diphenylacetonitrile (**2aa**).* White solid; m.p. 67-69 °C; 98% yield, 55.7 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 10H), 5.13 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 129.3, 128.4, 127.8, 119.8, 42.7.

*4.4.17 2-phenyl-2-(p-tolyl)acetonitrile (**2ab**).* White solid; m.p. 52-54 °C; 98% yield, 55.7 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 7.24-7.22 (m, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 5.10 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 136.8, 128.9, 128.4, 127.2, 126.3, 123.8, 122.0, 120.1, 119.8, 119.4, 111.2, 40.3.

*4.4.18 2-(4-chlorophenyl)-2-phenylacetonitrile (**2ac**).* Colorless liquid; 60% yield, 41.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.30 (m, 7H), 7.29-7.24 (m, 2H), 5.11 (s, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5, 134.6, 134.4, 129.5, 129.4, 129.2, 128.6, 127.8, 119.4, 42.1.

*4.4.19 2,2,2-triphenylacetonitrile (**2ad**).* White solid; m.p. 124-126 ^{o}C; > 99% yield, 80.3 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.39 (m, 9H), 7.31-7.28 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 128.9, 128.7, 128.2, 123.6, 57.5.

*4.4.20 (3-azidoprop-1-ene-1,1-diyl)dibenzene (**2ba**).* Light yellow liquid; 61% yield, 43 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.33 (m, 3H), 7.29-7.23 (m, 5H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.17 (t, *J* = 7.5 Hz, 1H), 3.85 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 141.3, 138.5, 129.9, 128.6, 128.4, 128.2, 128.0, 127.8, 49.9; IR (KBr): 2093 cm^{-1}.

*4.4.21 (azidomethylene)dibenzene (**2bb**).* Light yellow liquid; 79% yield, 49.3 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 4H), 7.38-7.34 (m, 6H), 5.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 128.8, 128.2, 127.5, 68.6.

*4.4.22 2,2-bis(4-methoxyphenyl)-2-phenylacetonitrile (**2bc**).* White solid; m.p. 67.2-69 ^{O}C; 99% yield, 97.6 mg; ^{1}H NMR (500 MHz, CDCl3) δ 7.37-7.30 (m, 3H), 7.23-7.21 (m, 2H), 7.13-7.10 (m, 4H), 6.88-6.84 (m, 4H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 159.4, 141.0, 132.7, 130.1, 128.80, 128.76, 128.2, 123.9, 114.1, 56.2, 55.5.

*4.4.23 (3-methoxyprop-1-ene-1,1-diyl)dibenzene (**2ca**).* Colorless liquid; 98% yield, 65.8 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.43 (m, 3H), 7.39-7.34 (m, 5H), 7.29 (d, *J* = 7.0 Hz, 2H), 6.34 (t, *J* = 6.5 Hz, 1H), 4.10 (d, *J* = 6.5 Hz, 2H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 142.0, 139.3, 129.9, 128.3, 127.7, 127.63, 127.60, 125.6, 70.3, 58.2.

*4.4.24 (3-methoxyprop-1-ene-1,1-diyl)dibenzene (**2cb**).* Colorless liquid; 89% yield, 80.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 7H), 7.27-7.22 (m, 6H), 7.17 (d, *J* = 1.5 Hz, 2H), 7.15 (s, 1H), 6.27 (t, *J* = 2.0 Hz, 2H), 4.46 (s, 2H), 4.10 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 142.0, 139.4, 138.5, 129.9, 128.5, 128.3, 128.0, 127.8, 127.73, 127.67, 127.61, 125.7, 72.5, 68.1.

*4.4.25 1-chloro-2-(3-iodo-1-phenylprop-1-en-1-yl)benzene (**3i**).* E/Z ≈ 1:1 Light yellow liquid ; 81% yield, 78 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.37-7.31 (m, 3H), 7.28-7.24 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.54 (t, *J* = 9.0 Hz, 1H), 3.93 (t, *J* = 8.0 Hz, 1H), 3.71 (t, *J* = 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 139.2, 136.7, 134.0, 130.5, 130.2, 129.5, 128.6, 128.2, 127.1, 126.6, 126.3, 4.2; HRMS (m/z) calcd for $C_{15}H_{12}ClINa^{+}$ 376.9564, found 376.9553.

*4.4.26 (benzhydryloxy)trimethylsilane (**4**).* Colorless liquid; 74% yield, 57.2 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 4H), 7.33 (t, *J* = 8.0 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 5.81 (s, 1H), 2.20 (s, 2H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 128.3, 127.2, 126.7, 76.6, 0.28.

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