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5-Hydroxypent-2-enenitriles as precursors toward dihydropyranones, dienenitriles and functionalized naphthalenes

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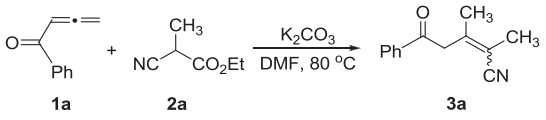
ABSTRACT

5-Hydroxypent-2-enenitriles were found to be precursors toward several classes of compounds with synthetic and biological interests. To be specific, upon treatment with sulfuric acid in dichloromethane and depending on the configuration of the C–C double bond and the nature of substituents attached on the C–C double bond, 5-hydroxypent-2-enenitriles could afford 5,6-dihydropyran-2-ones, 2,4-dienenitriles, or functionalized naphthalenes through *intramolecular* Pinner reaction, β-elimination or *intramolecular* Friedel–Crafts reaction, respectively.

1. Introduction

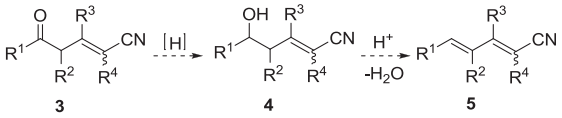
As part of our recent studies on functionalized allenes,[1] we have developed a synthetic pathway toward δ-oxo-α,β-unsaturated nitrile (**3**) via the tandem reaction of 1,2-allenic ketone (**1**) with α-substituted cyanoacetate (**2**) (Scheme 1).[1b]



1a **2a** **3a**

Scheme 1. Synthesis of δ-oxo-α,β-unsaturated nitrile (**3a**).

As both carbonyl and cyano groups are exceptionally versatile in organic transformations, we expected δ-oxo-α,β-unsaturated nitriles (**3**) to serve as valuable precursors toward compounds with synthetic and biological interests. In this regard, 2,4-dienenitriles emerged as attractive targets since they are not only essential building blocks of biologically active natural products, but also intermediates to high-electron affinity polymers used to produce light emitting diodes (LEDs).[2–4] Hence, we hypothesized a synthetic method toward 2,4-dienenitrile (**5**) starting from δ-oxo-α,β-unsaturated nitrile (**3**) and intermediating with 5-hydroxypent-2-enenitrile (**4**) as shown in Scheme 2.

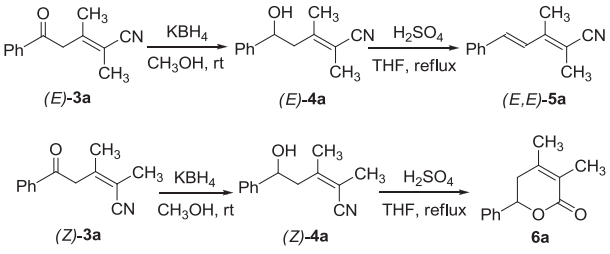


3 **4** **5**

Scheme 2. Proposed synthesis of 2,4-dienenitrile (**5**) from **3**.

2. Results and discussion

To check the feasibility of the envisioned pathway to 2,4-dienenitrile (**5**), (*E*)-5-hydroxy-2,3-dimethyl-5-phenylpent-2-enenitrile ((*E*)-**4a**), prepared through reduction of (*E*)-2,3-dimethyl-5-oxo-5-phenylpent-2-enenitrile ((*E*)-**3a**),[1b] was treated with H_2SO_4 in THF under reflux for 8 h. To our delight, it gave the expected (2*E*,4*E*)-2,3-dimethyl-5-phenylpenta-2,4-dienenitrile ((*E*,*E*)-**5a**) in a yield of 84% (Scheme 3). However, when (*Z*)-5-hydroxy-2,3-dimethyl-5-phenylpent-2-enenitrile ((*Z*)-**4a**) was subjected to similar



Scheme 3. Formation of (*E*,*E*)-**5a** from (*E*)-**3a** and **6a** from (*Z*)-**3a**.

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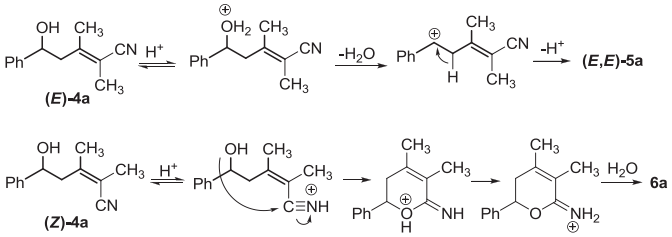
conditions, the corresponding (2*Z*,4*E*)-2,3-dimethyl-5-phenylpenta-2,4-dienenitrile ((*Z*,*E*)-**5a**) was formed only in trace amount. Instead, 5,6-dihydro-3,4-dimethyl-6-phenylpyran-2-one (**6a**) was isolated in a yield of 66% (Scheme 3).

Plausible pathways accounting for the formation of (*E*,*E*)-**5a** and **6a** were described in Scheme 4. While an acid-promoted dehydration of (*E*)-**4a** affords (*E*,*E*)-**5a**, an alternative reaction pathway featured with an *intramolecular* Pinner reaction[5] occurs with (*Z*)-**4a** resulting in the formation of **6a**.

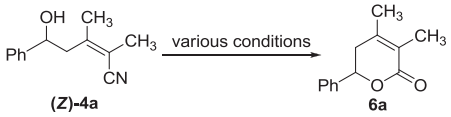


Scheme 4. Plausible pathways toward (*E*,*E*)-**5a** and **6a**.

Literature searching revealed that 5,6-dihydropyran-2(1*H*)-one is a privileged structural scaffold frequently found in both natural products and pharmaceutical agents.[6] This promoted us to carry out thorough studies on the transformation of (*Z*)-**4a** with the aim to develop it into a novel synthetic method toward 5,6-dihydropyran-2(1*H*)-ones.

Thus, the reaction of (*Z*)-**4a** toward **6a** was optimized with regard to solvents and acidic promoters and the results were included in Table 1. With H_2SO_4 as the catalyst, the choice of solvent turned out to be essential to the proceeding of the reaction. Among commonly used solvents, such as THF, DMF, CH_3CN, EtOH, toluene, CH_2Cl_2, and H_2O, CH_2Cl_2 appeared to be the most efficient in mediating this tandem process. Of the acidic catalysts screened, H_2SO_4 exhibited the highest catalytic activity. Finally, the optimal conditions were identified as follows: treating (*Z*)-**4a** with 1 equiv of H_2SO_4 in CH_2Cl_2 under reflux for 3 h. Under such conditions, **6a** was obtained in a yield of 75%.

Table 1
Optimization for the formation of **6a** from (*Z*)-**4a**[a]

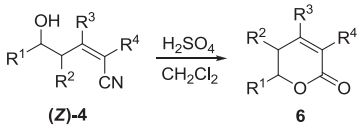


Entry	Catalyst	Solvent	*T* (°C)	*t* (h)	Yield[b] (%)
1	H_2SO_4	THF	Reflux	10	66
2	H_2SO_4	DMF	80	10	Trace
3	H_2SO_4	CH_3CN	Reflux	5	66
4	H_2SO_4	EtOH	Reflux	10	58
5	H_2SO_4	Toluene	80	10	22
6	*H_2SO_4*	*CH_2Cl_2*	*Reflux*	*3*	*75*
7	H_2SO_4	H_2O	80	10	NR
8	$BF_3\cdot Et_2O$	CH_2Cl_2	Reflux	10	70
9	CF_3CO_2H	CH_2Cl_2	Reflux	15	63

[a] Reaction conditions: **4a** (0.5 mmol), acid (0.5 mmol), solvent (5 mL).
[b] Isolated yield.

With the optimized conditions in hand, we then examined the scope and generality of the synthetic procedure toward **6**. The results included in Table 2 show that most of the substrates studied undergo the *intramolecular* Pinner reaction smoothly to afford the corresponding 5,6-dihydropyran-2(1*H*)-ones (**6**) with moderate to good yields. Notably, the reactions are compatible with a variety of functional groups such as chloro, bromo, fluoro, trifluoromethyl, allyl, and benzyl groups. By varying the substituents attached on different positions of the substrates, diversely substituted 5,6-dihydropyran-2(1*H*)-ones could be obtained.

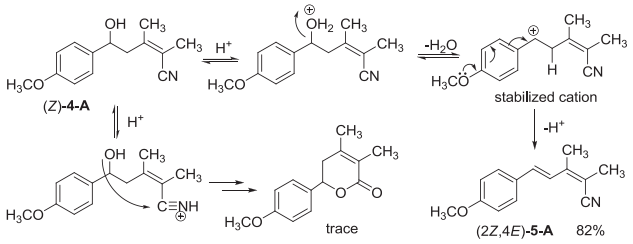
Table 2
Scope of the reaction leading to 6 from (*Z*)-**4**[a]



Entry	R^1	R^2	R^3	R^4	Products	Yield[b] (%)
1	C_6H_5	H	CH_3	CH_3	**6a**	75
2	*m*-ClC_6H_4	H	CH_3	CH_3	**6b**	81
3	*p*-ClC_6H_4	H	CH_3	CH_3	**6c**	85
4	*m*-BrC_6H_4	H	CH_3	CH_3	**6d**	78
5	*p*-BrC_6H_4	H	CH_3	CH_3	**6e**	86
6	*m*-$CH_3C_6H_4$	H	CH_3	CH_3	**6f**	72
7	*p*-$CF_3C_6H_4$	H	CH_3	CH_3	**6g**	88
8	C_6H_5	H	CH_3	Bn	**6h**	68
9	*m*-ClC_6H_4	H	CH_3	Bn	**6i**	80
10	*p*-BrC_6H_4	H	CH_3	Bn	**6j**	79
11	*p*-$CH_3C_6H_4$	H	CH_3	Bn	**6k**	51
12	C_6H_5	H	CH_3	Allyl	**6l**	72
13	*p*-FC_6H_4	H	CH_3	Allyl	**6m**	79
14	*p*-$CF_3C_6H_4$	H	CH_3	Allyl	**6n**	86
15	C_6H_5	CH_3	CH_3	CH_3	**6o**	80
16	4-BrC_6H_4	CH_3	CH_3	CH_3	**6p**	82
17	C_6H_5	H	CH_3	Ph	**6q**	68
18	3-ClC_6H_4	H	CH_3	Ph	**6r**	73
19	4-ClC_6H_4	H	CH_3	Ph	**6s**	78
20	4-BrC_6H_4	H	CH_3	Ph	**6t**	85
21	3-$CH_3C_6H_4$	H	CH_3	Ph	**6u**	51
22	4-$CH_3C_6H_4$	H	CH_3	Ph	**6v**	48
23	4-$CF_3C_6H_4$	H	CH_3	Ph	**6w**	90
24	4-BrC_6H_4	CH_3	CH_3	Ph	**6x**	86
25	CH_3	H	Bn	CH_3	**6y**	81
26	CH_3	H	Bn	Bn	**6z**	76
27	Ph	H	Bn	CH_3	**6aa**	72

[a] Reaction conditions: **4** (0.5 mmol), H_2SO_4 (0.5 mmol), CH_2Cl_2 (5 mL), reflux, 3 h.
[b] Isolated yield.

It is also noted, however, for substrate with strong electron-donating group on the phenyl ring of R^1, namely (*Z*)-5-hydroxy-5-(4-methoxyphenyl)-2,3-dimethylpent-2-enenitrile ((*Z*)-**4-A**), the reaction mainly give the corresponding dehydration product, (2*Z*,4*E*)-5-(4-methoxyphenyl)-2,3-dimethylpenta-2,4-dienenitrile ((2*Z*,4*E*)-**5-A**, Scheme 5). The expected 5,6-dihydropyran-2(1*H*)-one was formed only in trace amount. It might be explained by the stabilizing effect of the electron-donating methoxy group on the proposed cationic intermediate toward 2,4-dienenitrile. The increased stability of the cation intermediate makes the dehydration more favored than the competing *intramolecular* Pinner reaction.

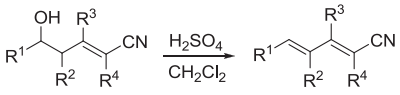


Scheme 5. Dehydration favored with electron-donating effect.

Having established a new protocol for the preparation of 5,6-dihydropyran-2(1*H*)-ones (**6**) from (*Z*)-5-hydroxypent-2-enenitrile ((*Z*)-**4**), we moved our focus back to the synthesis of (2*E*,4*E*)-2,4-dienenitriles ((*E*,*E*)-**5**) from (*E*)-5-hydroxypent-2-enenitrile ((*E*)-**4**). Optimization study with (*E*)-**4a** as a model substrate turned out that treatment of (*E*)-**4a** with 1 equiv of H_2SO_4 in CH_2Cl_2 under reflux for 2 h afforded (*E*,*E*)-**5a** in 86% yield.

The scope and generality of the synthetic strategy toward 2,4-dienenitriles (**5**) were then studied and the results were listed in Table 3. Generally, good to excellent yields of (2*E*,4*E*)-2,4-dienenitriles were observed and the reaction was found to be compatible with various functional groups including the electron-deficient trifluoromethyl and the electron-rich methoxy groups, thus resulting a general and efficient approach toward 2,4-dienenitrile derivatives.

Table 3
Scope of the reaction leading to (*E*,*E*)-**5** from (*E*)-**4**[a]

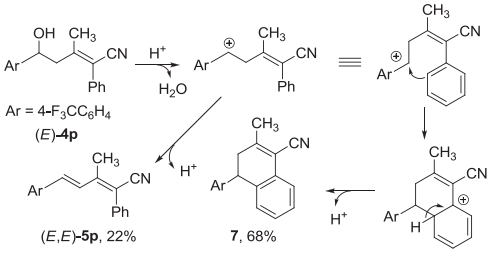


(*E*)-**4** (*E*,*E*)-**5**

Entry	R^1	R^2	R^3	R^4	Products	Yield[b] (%)
1	C_6H_5	H	CH_3	CH_3	**5a**	86
2	*m*-ClC_6H_4	H	CH_3	CH_3	**5b**	88
3	*p*-ClC_6H_4	H	CH_3	CH_3	**5c**	92
4	*m*-BrC_6H_4	H	CH_3	CH_3	**5d**	91
5	*p*-BrC_6H_4	H	CH_3	CH_3	**5e**	93
6	*m*-$CH_3C_6H_4$	H	CH_3	CH_3	**5f**	82
7	*p*-$CH_3OC_6H_4$	H	CH_3	CH_3	**5g**	86
8	*p*-$CF_3C_6H_4$	H	CH_3	CH_3	**5h**	85
9	C_6H_5	H	CH_3	Bn	**5i**	83
10	*m*-ClC_6H_4	H	CH_3	Bn	**5j**	86
11	*p*-BrC_6H_4	H	CH_3	Bn	**5k**	85
12	C_6H_5	H	CH_3	Allyl	**5l**	82
13	*p*-FC_6H_4	H	CH_3	Allyl	**5m**	88
14	*p*-$CF_3C_6H_4$	H	CH_3	Allyl	**5n**	85
15	C_6H_5	CH_3	CH_3	CH_3	**5o**	81

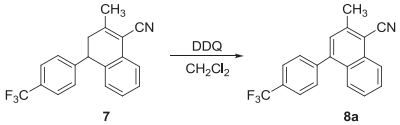
[a] Reaction conditions: **4** (0.5 mmol), H_2SO_4 (0.5 mmol), CH_2Cl_2 (5 mL), reflux.
[b] Isolated yield.

To further extend the scope of the above reaction, (*E*)-5-hydroxy-3-methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)pent-2-enenitrile ((*E*)-**4p**), with a phenyl group on the α-position of the cyano, was treated with H_2SO_4 in CH_2Cl_2. Interestingly, it gave 2-methyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalene-1-carbonitrile (**7**) as a major product rather than the expected (2*E*,4*E*)-3-methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)-penta-2,4-dienenitrile ((*E*,*E*)-**5p**). A mechanism rationalizing the formation of **7** featured with an *intramolecular* Friedel–Crafts reaction is depicted in Scheme 6.



Scheme 6. A plausible pathway for the formation of **7**.

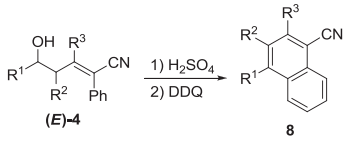
In following studies, we found that upon treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), compound **7** underwent an oxidative aromatization to give 2-methyl-4-(4-(trifluoromethyl) phenyl)-1-naphthonitrile (**8a**) in 87% yield (Scheme 7).



Scheme 7. Oxidative aromatization of **7** with DDQ.

It is well known that naphthalene skeleton occurs in many biologically important natural products and building blocks for the synthesis of pharmaceuticals and polycyclic aromatic electronic materials.[7,8] To date, several efficient methods for the synthesis of substituted naphthalenes have been reported.[9] In spite of their success, some of these synthetic methods still suffer from expensive catalysts, harsh reaction conditions or low efficiency. Based on the above facts, we proceeded to study the feasibility of a one-pot preparation of **8a** directly from (*E*)-**4p**. For this purpose, (*E*)-**4p** was firstly treated with H_2SO_4 in refluxing CH_2Cl_2 for 2 h. Then DDQ was added and the mixture was stirred under reflux for another 4 h. Separation of the resulting mixture gave **8a** in a total yield of 63%. The generality and limitation of the one-pot process leading to α-aryl naphthalene (**8**) was then studied. We found that a variety of (*E*)-5-hydroxypent-2-enenitriles with a phenyl group on the α-position of the cyano participated in this reaction to give the corresponding α-aryl naphthalenes in moderate yields (Table 4). It is notable that this sequence of reactions provides an attractive alternative to cross-coupling protocols in some cases for the preparation of biaryls, including the 1,1′-binaphthyl-4-carbonitrile (**8h**, entry 8).

Table 4
Scope of the one-pot synthesis of α-aryl naphthalenes (**8**)[a]

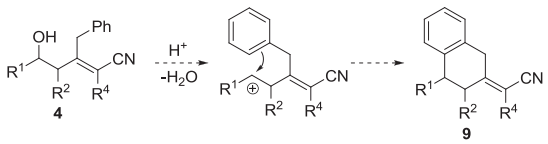


(*E*)-**4** **8**

Entry	R^1	R^2	R^3	Products	Yield[b] (%)
1	4-$CF_3C_6H_4$	H	CH_3	**8a**	63
2	3-ClC_6H_4	H	CH_3	**8b**	52
3	4-ClC_6H_4	H	CH_3	**8c**	53
4	4-BrC_6H_4	H	CH_3	**8d**	56
5	3-$CH_3C_6H_4$	H	CH_3	**8e**	42
6	4-$CH_3C_6H_4$	H	CH_3	**8f**	40
7	C_6H_5	H	CH_3	**8g**	61
8	1-Naphthyl	H	CH_3	**8h**	35
9	4-BrC_6H_4	CH_3	CH_3	**8i**	62

[a] Reaction conditions: **4** (0.5 mmol), H_2SO_4 (0.5 mmol), CH_2Cl_2 (5 mL), reflux, 2 h; then DDQ (0.5 mmol), reflux, 4 h.
[b] Isolated yield.

In a further aspect, inspired by the reaction of (*E*)-5-hydroxypent-2-enenitriles with a phenyl group on the α-position of cyano affording α-substituted 3,4-dihydronaphthalenes (**7**), we envisioned that tetrahydronaphthalene (**9**)[10–13] might be obtained from (*E*)-5-hydroxypent-2-enenitriles having a benzyl group on the β-position of cyano via an *intramolecular* Friedel–Crafts reaction as shown in Scheme 8.

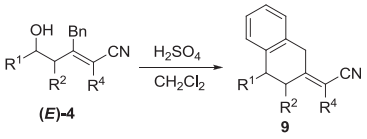


Scheme 8. Proposed synthesis of tetrahydronaphthalene (**9**).

In deed, when (*E*)-3-benzyl-5-hydroxy-2-methylhex-2-ene nitrile was treated with H_2SO_4 in CH_2Cl_2, the expected 2-(4-methyl-3,4-dihydronaphthalen-2(1*H*)-ylidene)propanenitrile (**9a**) was obtained in a yield of 56%. The success of this strategy was further demonstrated by the reactions with other substrates and the results were shown in Table 5.

Finally, since effective separation of (*E*)-**3** and (*Z*)-**3** or (*E*)-**4** and (*Z*)-**4** usually requires considerable efforts due to their structural similarity, the feasibility of one-pot preparation of (2*E*,4*E*)-**5a** and **6a** by

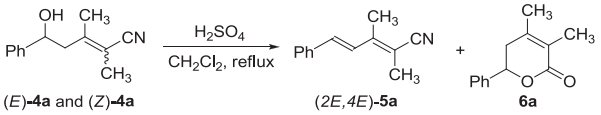
Table 5
Synthesis of 2-methylene-1,2,3,4-tetrahydronaphthalene (**9**)[a]



Entry	R^1	R^2	R^4	Products	Yield[b] (%)
1	CH_3	H	CH_3	**9a**	56
2	CH_3	H	Bn	**9b**	53
3	CH_3	H	Ph	**9c**	43
4	Ph	H	CH_3	**9d**	48

[a] Reaction conditions: **4** (0.5 mmol), H_2SO_4 (0.5 mmol), CH_2Cl_2 (5 mL), reflux, 3 h.
[b] Isolated yield.

using a mixture of (*E*)-**4a** and (*Z*)-**4a** as substrates was investigated. To our delight, treating a mixture of (*E*)-**4a** and (*Z*)-**4a**, obtained through the reduction of a mixture of (*E*)-**3a** and (*Z*)-**3a**, with H_2SO_4 in CH_2Cl_2 resulted in efficient formation of (2*E*,4*E*)-**5a** and **6a** (Scheme 9). In addition, these two products were separated conveniently as they are remarkably different in their structural characteristics.



Scheme 9. One-pot preparation of (2*E*,4*E*)-**5a** and **6a** from **4a**.

3. Conclusion

In conclusion, novel synthetic methods for the preparation of 5,6-dihydropyran-2(1*H*)-ones, 2,4-dienenitriles, and functionalized naphthalenes via acid-promoted reactions of 5-hydroxypent-2-enenitriles with various substitution patterns have been developed. Notable features of the results reported herein include: (1) various kinds of target compounds could be obtained from substrates originated from the same reaction; (2) different transformations could be performed under almost equally mild conditions without using any noble catalysts. In addition, a mixture of *E*/*Z* isomers of 5-hydroxypent-2-enenitrile could be used directly and two different kinds of products can be obtained conveniently from the corresponding *E* or *Z* isomer via a one-pot procedure. With the above-described advantages, these synthetic methods are expected to find wide applications in synthetic, medicinal chemistry, and related areas.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. High-resolution mass spectra (HRMS) were performed on a time-of-flight (ESI-TOF) mass spectrometer. Melting points were measured with a micro melting point apparatus. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F_{254} 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm). δ-Oxo-α,β-unsaturated nitriles (**3**) were prepared based on our previously published procedure.[1b] 5-Hydroxypent-2-enenitriles (**4**) were obtained by reduction of the corresponding δ-oxo-α,β-unsaturated nitriles (**3**) with KBH_4 in methanol at ambient temperature.

4.2. Typical procedure for the preparation of (2*E*,4*E*)-2,3-dimethyl-5-phenylpenta-2,4-dienenitrile ((2*E*,4*E*)-5a) (Table 3)

To a flask containing (*E*)-5-hydroxy-2,3-dimethyl-5-phenylpent-2-enenitrile (101 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added H_2SO_4 (27 μL, 0.5 mmol). The solution was stirred under reflux. Upon completion, the reaction was quenched with aqueous Na_2CO_3. The resulting mixture was extracted with ethyl acetate (5 mL×3). The combined organic phases were washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to give (2*E*,4*E*)-2,3-dimethyl-5-phenylpenta-2,4-dienenitrile ((2*E*,4*E*)-**5a**) in a yield of 86% (79 mg, 0.43 mmol). Other (2*E*,4*E*)-2,4-dienenitrile derivatives were obtained in a similar manner.

*4.2.1. (2E,4E)-2,3-Dimethyl-5-phenylpenta-2,4-dienenitrile (**5a**).* Yield: 79 mg, 86%. White solid, mp: 104–105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 3H), 2.28 (s, 3H), 6.88 (d, *J*=16.0 Hz, 1H), 7.11 (d, *J*=16.0 Hz, 1H), 7.32–7.40 (m, 3H), 7.49 (d, *J*=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 18.5, 105.9, 120.8, 123.8, 127.2, 128.9, 129.0, 135.2, 136.2, 147.9. IR (KBr) ν=2919, 2211, 1531, 772 cm^{-1}; MS: *m*/*z* 184 $(MH)^+$. HRMS calcd for $C_{13}H_{14}N$: 184.1126 [M+H], found: 184.1134.

*4.2.2. (2E,4E)-5-(3-Chlorophenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5b**).* Yield: 95 mg, 88%. White solid, mp: 91–93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.26 (s, 3H), 6.80 (d, *J*=16.0 Hz, 1H), 7.09 (d, *J*=16.0 Hz, 1H), 7.26–7.35 (m, 3H), 7.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.0, 18.5, 107.0, 120.5, 125.0, 125.5, 126.8, 128.8, 130.1, 133.6, 134.8, 138.0, 147.4. IR (KBr) ν=2924, 2201, 1510, 957, 780 cm^{-1}; MS: *m*/*z* 218 $(MH)^+$. HRMS calcd for $C_{13}H_{13}ClN$: 218.0737 [M+H], found: 218.0745.

*4.2.3. (2E,4E)-5-(4-Chlorophenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5c**).* Yield: 100 mg, 92%. White solid, mp: 122–124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.27 (s, 3H), 6.83 (d, *J*=16.0 Hz, 1H), 7.08 (d, *J*=16.0 Hz, 1H), 7.33 (d, *J*=7.2 Hz, 2H), 7.41 (d, *J*=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 18.4, 106.5, 120.6, 124.3, 128.3, 129.1, 133.8, 134.68, 134.71, 147.5. IR (KBr) ν=2923, 2202, 1487, 814 cm^{-1}; MS: *m*/*z* 218 $(MH)^+$. HRMS calcd for $C_{13}H_{13}ClN$: 218.0737 [M+H], found: 218.0729.

*4.2.4. (2E,4E)-5-(3-Bromophenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5d**).* Yield: 119 mg, 91%. White solid, mp: 112–114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.26 (s, 3H), 6.78 (d, *J*=16.0 Hz, 1H), 7.08 (d, *J*=16.0 Hz, 1H), 7.23 (t, *J*=8.0 Hz, 1H), 7.38 (d, *J*=7.6 Hz, 1H), 7.43 (d, *J*=7.6 Hz, 1H), 7.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.0, 18.4, 107.1, 120.4, 123.0, 125.1, 125.9, 129.8, 130.3, 131.7, 133.5, 138.3, 147.3. IR (KBr) ν=2924, 2204, 779 cm^{-1}; MS: *m*/*z* 262 $(MH)^+$. HRMS calcd for $C_{13}H_{13}BrN$: 262.0231 [M+H], found: 262.0235.

*4.2.5. (2E,4E)-5-(4-Bromophenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5e**).* Yield: 122 mg, 93%. White solid, mp: 156–157 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 3H), 2.27 (s, 3H), 6.80 (d, *J*=16.0 Hz, 1H), 7.08 (d, *J*=16.0 Hz, 1H), 7.34 (d, *J*=8.4 Hz, 2H), 7.48 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 18.5, 106.5, 120.6, 122.9, 124.4, 128.6, 132.0, 133.9, 135.1, 147.6. IR (KBr) ν=2918, 2203, 1502, 819 cm^{-1}; MS: *m*/*z* 262 $(MH)^+$. HRMS calcd for $C_{13}H_{13}BrN$: 262.0231 [M+H], found: 262.0238.

*4.2.6. (2E,4E)-5-(3-Methylphenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5f**).* Yield: 81 mg, 82%. Syrup; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 6.86 (d, *J*=15.6 Hz, 1H), 7.09–7.16 (m, 2H), 7.27–7.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 18.5, 21.4, 105.7, 120.8, 123.6, 124.4, 127.9, 128.8, 129.9, 135.4, 136.1, 138.5, 148.0. IR (KBr) ν=2919, 1328, 785 cm^{-1}; MS: *m*/*z* 198 $(MH)^+$. HRMS calcd for $C_{14}H_{16}N$: 198.1283 [M+H], found: 198.1276.

*4.2.7. (2E,4E)-5-(4-Methoxyphenyl)-2,3-dimethylpenta-2,4-dienenitrile (**5g**).* Yield: 92 mg, 86%. White solid, mp: 86–88 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.07 (s, 3H), 2.26 (s, 3H), 3.83 (s, 3H), 6.82 (d,

J=15.6 Hz, 1H), 6.89 (d, J=8.0 Hz, 2H), 6.97 (d, J=16.0 Hz, 1H), 7.42 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.8, 18.4, 55.3, 104.6, 114.3, 120.1, 121.8, 128.6, 129.0, 134.8, 148.1, 160.4. IR (KBr) ν=2929, 2197, 1252, 805 cm^{-1}; MS: m/z 214 $(MH)^+$. HRMS calcd for $C_{14}H_{16}NO$: 214.1232 [M+H], found: 214.1238.

*4.2.8. (2E,4E)-2,3-Dimethyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienenitrile (**5h**).* Yield: 107 mg, 85%. White solid, mp: 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.12 (s, 3H), 2.29 (s, 3H), 6.90 (d, J=16.0 Hz, 1H), 7.18 (d, J=16.0 Hz, 1H), 7.57 (d, J=8.4 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.0, 18.4, 107.6, 120.3, 125.75, 125.78, 126.1, 127.3, 130.3, 133.5, 139.6, 147.2. IR (KBr) ν=2928, 2201, 1324, 827 cm^{-1}; MS: m/z 252 $(MH)^+$. HRMS calcd for $C_{14}H_{13}F_3N$: 252.1000 [M+H], found: 252.0995.

*4.2.9. (2E,4E)-2-Benzyl-3-methyl-5-phenylpenta-2,4-dienenitrile (**5i**).* Yield: 108 mg, 83%. White solid, mp: 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 3.83 (s, 2H), 7.00 (d, J=16.0 Hz, 1H), 7.29–7.42 (m, 9H), 7.50 (d, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.8, 35.5, 110.6, 120.1, 123.7, 127.0, 127.3, 128.4, 128.87, 128.94, 129.2, 136.1, 136.2, 137.5, 148.4. IR (KBr) ν=2928, 2206, 760 cm^{-1}; MS: m/z 260 $(MH)^+$. HRMS calcd for $C_{19}H_{18}N$: 260.1439 [M+H], found: 260.1448.

*4.2.10. (2E,4E)-2-Benzyl-5-(3-chlorophenyl)-3-methylpenta-2,4-dienenitrile (**5j**).* Yield: 126 mg, 86%. White solid, mp: 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 3.82 (s, 2H), 6.90 (d, J=16.0 Hz, 1H), 7.25–7.38 (m, 9H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.9, 35.5, 111.6, 119.9, 124.9, 125.5, 127.0, 127.1, 128.4, 128.9, 129.0, 130.2, 134.7, 134.9, 137.2, 137.9, 147.9. IR (KBr) ν=2931, 2203, 705 cm^{-1}; MS: m/z 294 $(MH)^+$. HRMS calcd for $C_{19}H_{17}ClN$: 294.1050 [M+H], found: 294.1058.

*4.2.11. (2E,4E)-2-Benzyl-5-(4-bromophenyl)-3-methylpenta-2,4-dienenitrile (**5k**).* Yield: 144 mg, 85%. White solid, mp: 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 3.80 (s, 2H), 6.89 (d, J=16.0 Hz, 1H), 7.23–7.36 (m, 8H), 7.49 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.8, 35.5, 111.1, 120.0, 123.2, 124.3, 127.1, 128.3, 128.6, 128.9, 132.1, 134.8, 135.0, 137.2, 148.1. IR (KBr) ν=3023, 2206, 1486, 723 cm^{-1}; MS: m/z 338 $(MH)^+$. HRMS calcd for $C_{19}H_{17}BrN$: 338.0544 [M+H], found: 338.0547.

*4.2.12. (2E,4E)-2-Allyl-3-methyl-5-phenylpenta-2,4-dienenitrile (**5l**).* Yield: 86 mg, 82%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 3.20–3.22 (m, 2H), 5.18–5.22 (m, 2H), 5.84–5.92 (m 1H), 6.93 (d, J=16.0 Hz, 1H), 7.12 (d, J=15.6 Hz, 1H), 7.31–7.40 (m, 3H), 7.47 (d, J=7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.7, 33.8, 109.1, 117.5, 119.9, 123.7, 127.2, 128.9, 129.1, 133.2, 135.8, 136.1, 148.6. IR (KBr) ν=2933, 2210, 910, 768 cm^{-1}; MS: m/z 210 $(MH)^+$. HRMS calcd for $C_{15}H_{16}N$: 210.1283 [M+H], found: 210.1286.

*4.2.13. (2E,4E)-2-Allyl-5-(4-fluorophenyl)-3-methylpenta-2,4-dienenitrile (**5m**).* Yield: 100 mg, 88%. Yellow solid, mp: 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 3.18–3.20 (m, 2H), 5.17–5.21 (m, 2H), 5.83–5.89 (m 1H), 6.88 (d, J=16.0 Hz, 1H), 7.00–7.08 (m, 3H), 7.43–7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.7, 33.7, 109.1, 115.9, 116.1, 117.6, 119.9, 123.4, 128.86, 128.94, 132.30, 132.33, 133.1, 134.5, 148.4, 161.8, 164.4. IR (KBr) ν=2931, 2198, 912, 823 cm^{-1}; MS: m/z 228 $(MH)^+$. HRMS calcd for $C_{15}H_{15}FN$: 228.1189 [M+H], found: 228.1187.

*4.2.14. (2E,4E)-2-Allyl-3-methyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienenitrile (**5n**).* Yield: 118 mg, 85%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 3.21–3.23 (m, 2H), 5.18–5.22 (m, 2H), 5.83–5.89 (m, 1H), 6.93 (d, J=15.6 Hz, 1H), 7.18 (d, J=16.0 Hz, 1H), 7.56 (d, J=8.0 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.7, 33.8, 110.8, 117.8, 119.6, 125.8, 125.9, 127.3, 131.2, 132.9, 134.0, 139.5, 147.9. IR (KBr) ν=2929, 2201, 915, 822 cm^{-1}; MS: m/z 278 $(MH)^+$. HRMS calcd for $C_{16}H_{15}F_3N$: 278.1157 [M+H], found: 278.1152.

*4.2.15. (2E,4E)-2,3,4-Trimethyl-5-phenylpenta-2,4-dienenitrile (**5o**).* Yield: 80 mg, 81%. White solid, mp: 114–115 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.57 (s, 3H), 1.92 (s, 3H), 2.11 (s, 3H), 6.40 (s, 1H), 7.16–7.22 (m, 3H), 7.29–7.33 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 16.7, 21.2, 23.1, 104.7, 119.6, 127.5, 127.6, 127.7, 129.0, 136.0, 136.7, 155.7. IR (KBr) ν=2921, 2210, 772 cm^{-1}; MS: m/z 198 $(MH)^+$. HRMS calcd for $C_{14}H_{16}N$: 198.1283 [M+H], found: 198.1288.

*4.2.16. (2E,4E)-3-Methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienenitrile (**5p**).* Yield: 35 mg, 22%. White solid, mp: 161–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.50 (s, 3H), 6.98 (d, J=16.0 Hz, 1H), 7.14 (d, J=16.0 Hz, 1H), 7.38–7.47 (m, 7H), 7.56 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.0, 114.3, 119.2, 125.7, 125.8, 127.3, 127.5, 127.8, 128.7, 128.8, 129.0, 129.4, 129.9, 130.3, 133.4, 134.2, 139.4, 148.6. IR (KBr) ν=2929, 2195, 822, 766 cm^{-1}; MS: m/z 314 $(MH)^+$. HRMS calcd for $C_{19}H_{15}F_3N$: 314.1157 [M+H], found: 314.1166.

4.3. Typical procedure for the preparation of 5,6-dihydro-3,4-dimethyl-6-phenylpyran-2-one (6a) (Table 2)

To a flask containing (*Z*)-5-hydroxy-2,3-dimethyl-5-phenylpent-2-enenitrile (101 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added H_2SO_4 (27 μL, 0.5 mmol). The solution was stirred under reflux. Upon completion, the reaction was quenched with aqueous Na_2CO_3. The resulting mixture was extracted with ethyl acetate (5 mL×3). The combined organic phases were washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to give 5,6-dihydro-3,4-dimethyl-6-phenylpyran-2-one (**6a**) in a yield of 75% (76 mg, 0.38 mmol). Other 5,6-dihydropyran-2-one derivatives were obtained in a similar manner.

*4.3.1. 3,4-Dimethyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (**6a**).* Yield: 76 mg, 75%. White solid, mp: 98–99 °C (lit.[6i] 97–97.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 1.97 (s, 3H), 2.40–2.45 (m, 1H), 2.66–2.74 (m, 1H), 5.32–5.36 (m, 1H), 7.31–7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 38.2, 122.4, 126.0, 128.4, 128.5, 138.9, 148.6, 166.2. IR (KBr) ν=2919, 1692, 1293, 772 cm^{-1}; MS: m/z 203 $(MH)^+$. HRMS calcd for $C_{13}H_{15}O_2$: 203.1072 [M+H], found: 203.1077.

*4.3.2. 3,4-Dimethyl-6-(3-chloro)phenyl-5,6-dihydro-2H-pyran-2-one (**6b**).* Yield: 96 mg, 81%. White solid, mp: 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.89 (s, 3H), 1.94 (s, 3H), 2.37–2.42 (m, 1H), 2.56–2.64 (m, 1H), 5.24–5.28 (m, 1H), 7.23–7.26 (m, 3H), 7.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 38.0, 122.3, 124.1, 126.1, 128.4, 129.9, 134.4, 140.9, 148.7, 165.9. IR (KBr) ν=2917, 1700, 786 cm^{-1}; MS: m/z 237 $(MH)^+$. HRMS calcd for $C_{13}H_{14}ClO_2$: 237.0682 [M+H], found: 237.0678.

*4.3.3. 3,4-Dimethyl-6-(4-chloro)phenyl-5,6-dihydro-2H-pyran-2-one (**6c**).* Yield: 100 mg, 85%. White solid, mp: 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 1.96 (s, 3H), 2.38–2.43 (m, 1H), 2.60–2.68 (m, 1H), 5.28–5.32 (m, 1H), 7.32–7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 38.1, 122.5, 127.3, 128.7, 134.1, 137.4, 148.4, 165.9. IR (KBr) ν=2925, 1711, 814 cm^{-1}; MS: m/z 237 $(MH)^+$. HRMS calcd for $C_{13}H_{14}ClO_2$: 237.0682 [M+H], found: 237.0676.

*4.3.4. 3,4-Dimethyl-6-(3-bromo)phenyl-5,6-dihydro-2H-pyran-2-one (**6d**).* Yield: 110 mg, 78%. White solid, mp: 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 1.96 (s, 3H), 2.40–2.44 (m, 1H),

2.60–2.68 (m, 1H), 5.27–5.31 (m, 1H), 7.21–7.26 (m, 1H), 7.30 (d, J=7.6 Hz, 1H), 7.44 (d, J=7.2 Hz, 1H), 7.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 38.1, 122.5, 122.6, 124.5, 129.0, 130.2, 131.4, 141.1, 148.5, 165.8. IR (KBr) ν=2920, 1701, 780 cm^{-1}; MS: m/z 281 $(MH)^+$. HRMS calcd for $C_{13}H_{14}BrO_2$: 281.0177 [M+H], found: 281.0186.

*4.3.5. 3,4-Dimethyl-6-(4-bromo)phenyl-5,6-dihydro-2H-pyran-2-one (**6e**).* Yield: 121 mg, 86%. White solid, mp: 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 1.91 (s, 3H), 2.33–2.38 (m, 1H), 2.53–2.60 (m, 1H), 5.21–5.25 (m, 1H), 7.20 (d, J=8.4 Hz, 2H), 7.42 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 38.0, 122.2, 122.3, 127.7, 131.6, 138.0, 148.8, 165.9. IR (KBr) ν=2919, 1711, 1135, 819 cm^{-1}; MS: m/z 281 $(MH)^+$. HRMS calcd for $C_{13}H_{14}BrO_2$: 281.0177 [M+H], found: 281.0183.

*4.3.6. 3,4-Dimethyl-6-(3-methyl)phenyl-5,6-dihydro-2H-pyran-2-one (**6f**).* Yield: 78 mg, 72%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 1.95 (s, 3H), 2.33 (s, 3H), 2.37–2.42 (m, 1H), 2.62–2.70 (m, 1H), 5.26–5.30 (m, 1H), 7.10–7.16 (m, 2H), 7.21–7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.5, 20.2, 21.4, 38.2, 122.3, 123.0, 126.6, 128.4, 129.1, 138.2, 138.8, 148.9, 166.3. IR (KBr) ν=2928, 1708, 785 cm^{-1}; MS: m/z 217 $(MH)^+$. HRMS calcd for $C_{14}H_{17}O_2$: 217.1229 [M+H], found: 217.1236.

*4.3.7. 3,4-Dimethyl-6-(4-(trifluoromethyl)phenyl)-5,6-dihydro-2H-pyran-2-one (**6g**).* Yield: 119 mg, 88%. White solid, mp: 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.91 (s, 3H), 1.96 (s, 3H), 2.42–2.47 (m, 1H), 2.59–2.67 (m, 1H), 5.36–5.40 (m, 1H), 7.50 (d, J=7.6 Hz, 2H), 7.60 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.4, 20.1, 38.0, 122.5, 122.6, 125.3, 125.48, 125.51, 126.2, 130.3, 130.6, 142.9, 148.5, 165.7. IR (KBr) ν=2918, 1693, 1330, 836 cm^{-1}; MS: m/z 271 $(MH)^+$. HRMS calcd for $C_{14}H_{14}F_3O_2$: 271.0946 [M+H], found: 271.0952.

*4.3.8. 3-Benzyl-4-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (**6h**).* Yield: 95 mg, 68%. White solid, mp: 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 3H), 2.48–2.53 (m, 1H), 2.75–2.83 (m, 1H), 3.74–3.90 (m, 2H), 5.36–5.39 (m, 1H), 7.18–7.30 (m, 5H), 7.32–7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 32.3, 38.3, 77.5, 126.0, 126.1, 126.4, 128.3, 128.4, 128.6, 138.7, 139.6, 150.2, 165.7. IR (KBr) ν=2918, 1698, 770 cm^{-1}; MS: m/z 279 $(MH)^+$. HRMS calcd for $C_{19}H_{19}O_2$: 279.1385 [M+H], found: 279.1388.

*4.3.9. 3-Benzyl-6-(3-chlorophenyl)-4-methyl-5,6-dihydro-2H-pyran-2-one (**6i**).* Yield: 125 mg, 80%. White solid, mp: 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.04 (s, 3H), 2.46–2.51 (m, 1H), 2.68–2.75 (m, 1H), 3.73–3.88 (m, 2H), 5.30–5.34 (m, 1H), 7.18–7.32 (m, 8H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.7, 32.3, 38.1, 76.7, 124.1, 126.2, 126.3, 128.3, 128.5, 128.6, 128.8, 130.0, 134.5, 139.4, 140.7, 150.4, 165.4. IR (KBr) ν=3026, 2937, 1703, 724 cm^{-1}; MS: m/z 313 $(MH)^+$. HRMS calcd for $C_{19}H_{18}ClO_2$: 313.0995 [M+H], found: 313.0988.

*4.3.10. 3-Benzyl-6-(4-bromophenyl)-4-methyl-5,6-dihydro-2H-pyran-2-one (**6j**).* Yield: 141 mg, 79%. White solid, mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 3H), 2.46–2.51 (m, 1H), 2.69–2.76 (m, 1H), 3.73–3.88 (m, 2H), 5.31–5.35 (m, 1H), 7.17–7.27 (m, 7H), 7.50 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 32.3, 38.2, 122.4, 126.1, 126.5, 127.6, 128.3, 128.5, 131.7, 137.8, 139.4, 150.0, 165.4. IR (KBr) ν=2925, 1712, 1123, 819 cm^{-1}; MS: m/z 357 $(MH)^+$. HRMS calcd for $C_{19}H_{18}BrO_2$: 357.0490 [M+H], found: 357.0479.

*4.3.11. 3-Benzyl-4-methyl-6-p-tolyl-5,6-dihydro-2H-pyran-2-one (**6k**).* Yield: 75 mg, 51%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 3H), 2.37 (s, 3H), 2.45–2.51 (m, 1H), 2.75–2.82 (m, 1H), 3.75–3.90 (m, 2H), 5.33–5.37 (m, 1H), 7.18–7.30 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 21.2, 32.3, 38.3, 77.5, 126.0, 126.1, 126.3, 128.3, 128.5, 129.2, 135.8, 138.2, 139.6, 150.4, 165.9. IR (KBr) ν=2928, 1710, 1118, 815 cm^{-1}; MS: m/z 293 $(MH)^+$. HRMS calcd for $C_{20}H_{21}O_2$: 293.1542 [M+H], found: 293.1552.

*4.3.12. 3-Allyl-4-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (**6l**).* Yield: 82 mg, 72%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97 (s, 3H), 2.42–2.47 (m, 1H), 2.67–2.75 (m, 1H), 3.10–3.24 (m, 2H), 5.00–5.06 (m, 2H), 5.32–5.36 (m, 1H), 5.81–5.88 (m, 1H), 7.26–7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 30.9, 38.3, 77.7, 115.2, 124.6, 126.0, 128.4, 128.5, 134.9, 138.8, 150.5, 165.5. IR (KBr) ν=2930, 1699, 773 cm^{-1}; MS: m/z 229 $(MH)^+$. HRMS calcd for $C_{15}H_{17}O_2$: 229.1229 [M+H], found: 229.1221.

*4.3.13. 3-Allyl-6-(4-fluorophenyl)-4-methyl-5,6-dihydro-2H-pyran-2-one (**6m**).* Yield: 97 mg, 79%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.00 (s, 3H), 2.41–2.47 (m, 1H), 2.70–2.77 (m, 1H), 3.11–3.25 (m, 2H), 5.02–5.07 (m, 2H), 5.33–5.36 (m, 1H), 5.82–5.88 (m, 1H), 7.05–7.09 (m, 2H), 7.37–7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.1, 30.9, 38.4, 77.1, 115.3, 115.4, 115.6, 124.8, 127.8, 127.9, 134.5, 134.8, 150.3, 165.4. IR (KBr) ν=2931, 1711, 825 cm^{-1}; MS: m/z 247 $(MH)^+$. HRMS calcd for $C_{15}H_{16}FO_2$: 247.1134 [M+H], found: 247.1122.

*4.3.14. 3-Allyl-4-methyl-6-(4-(trifluoromethyl)-phenyl)-5,6-dihydro-2H-pyran-2-one (**6n**).* Yield: 127 mg, 86%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.00 (s, 3H), 2.47–2.52 (m, 1H), 2.66–2.74 (m, 1H), 3.11–3.24 (m, 2H), 5.01–5.06 (m, 2H), 5.41–5.45 (m, 1H), 5.79–5.89 (m, 1H), 7.53 (d, J=8.4 Hz, 2H), 7.64 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 30.8, 38.2, 76.8, 115.4, 124.8, 125.6, 126.2, 134.7, 142.7, 150.2, 165.0. IR (KBr) ν=2931, 1693, 838 cm^{-1}; MS: m/z 297 $(MH)^+$. HRMS calcd for $C_{16}H_{16}F_3O_2$: 297.1102 [M+H], found: 297.1108.

*4.3.15. 3,4,5-Trimethyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (**6o**).* Yield: 86 mg, 80%. White solid, mp: 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (d, J=7.2 Hz, 3H), 1.88 (s, 6H), 2.68 (t, J=6.8 Hz, 1H), 5.05 (d, J=6.4 Hz, 1H), 7.27–7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.8, 15.9, 18.2, 39.5, 83.1, 122.1, 126.6, 128.2, 128.4, 138.8, 152.2, 165.3. IR (KBr) ν=2911, 1699, 771 cm^{-1}; MS: m/z 217 $(MH)^+$. HRMS calcd for $C_{14}H_{17}O_2$: 217.1229 [M+H], found: 217.1222.

*4.3.16. 6-(4-Bromophenyl)-3,4,5-trimethyl-5,6-dihydro-2H-pyran-2-one (**6p**).* Yield: 121 mg, 82%. White solid, mp: 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (d, J=7.2 Hz, 3H), 1.83 (s, 6H), 2.60 (t, J=6.8 Hz, 1H), 4.97 (d, J=6.8 Hz, 1H), 7.12 (d, J=8.4 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.7, 15.8, 18.3, 39.4, 82.3, 122.0, 122.2, 128.4, 131.5, 137.9, 152.3, 165.1. IR (KBr) ν=2918, 1698, 770 cm^{-1}; MS: m/z 295 $(MH)^+$. HRMS calcd for $C_{14}H_{16}BrO_2$: 295.0334 [M+H], found: 295.0341.

*4.3.17. 4-Methyl-3,6-diphenyl-5,6-dihydro-2H-pyran-2-one (**6q**).* Yield: 90 mg, 68%. White solid, mp: 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.91 (s, 3H), 2.60–2.65 (m, 1H), 2.86–2.93 (m, 1H), 5.53–5.57 (m, 1H), 7.32–7.48 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.2, 77.8, 126.1, 127.7, 128.1, 128.5, 128.6, 128.9, 130.0, 134.6, 138.7, 151.4, 164.9. IR (KBr) ν=2915, 1701, 773 cm^{-1}; MS: m/z 265 $(MH)^+$. HRMS calcd for $C_{18}H_{17}O_2$: 265.1229 [M+H], found: 265.1232.

*4.3.18. 6-(3-Chlorophenyl)-4-methyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**6r**).* Yield: 109 mg, 73%. White solid, mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88 (s, 3H), 2.58–2.83 (m, 2H), 5.47–5.50 (m, 1H), 7.24 (d, J=6.8 Hz, 2H), 7.32–7.40 (m, 6H), 7.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.0, 77.0, 124.2, 126.2, 127.8, 128.2, 128.60, 128.64, 130.01, 130.04, 134.4, 134.5, 140.8, 151.7, 164.6.

IR (KBr) ν=3058, 2909, 1703, 788 cm^{-1}; MS: *m*/*z* 299 $(MH)^+$. HRMS calcd for $C_{18}H_{16}ClO_2$: 299.0839 [M+H], found: 299.0838.

*4.3.19. 6-(4-Chlorophenyl)-4-methyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**6s**).* Yield: 116 mg, 78%. White solid, mp: 128–130 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 2.58–2.63 (m, 1H), 2.80–2.87 (m, 1H), 5.49–5.53 (m, 1H), 7.23–7.25 (m, 2H), 7.32–7.41 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.1, 127.4, 127.8, 128.2, 128.8, 129.9, 134.3, 134.4, 137.2, 151.3, 164.6. IR (KBr) ν=2922, 1703, 827 cm^{-1}; MS: *m*/*z* 299 $(MH)^+$. HRMS calcd for $C_{18}H_{16}ClO_2$: 299.0839 [M+H], found: 299.0832.

*4.3.20. 6-(4-Bromophenyl)-4-methyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**6t**).* Yield: 146 mg, 85%. White solid, mp: 149–150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 2.58–2.63 (m, 1H), 2.78–2.82 (m, 1H), 5.49–5.52 (m, 1H), 7.22–7.24 (m, 2H), 7.34–7.40 (m, 5H), 7.52–7.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.1, 122.4, 127.7, 127.8, 128.2, 128.8, 130.0, 131.8, 134.4, 137.8, 151.4, 164.6. IR (KBr) ν=2916, 1699, 826 cm^{-1}; MS: *m*/*z* 343 $(MH)^+$. HRMS calcd for $C_{18}H_{16}BrO_2$: 343.0334 [M+H], found: 343.0349.

*4.3.21. 4-Methyl-3-phenyl-6-m-tolyl-5,6-dihydro-2H-pyran-2-one (**6u**).* Yield: 71 mg, 51%. White solid, mp: 116–118 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.91 (s, 3H), 2.39 (s, 3H), 2.59–2.64 (m, 1H), 2.85–2.93 (m, 1H), 5.50–5.54 (m, 1H), 7.18 (d, *J*=7.2 Hz, 1H), 7.25–7.42 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 21.5, 38.3, 77.9, 123.1, 126.7, 127.7, 128.1, 128.5, 128.8, 129.2, 130.0, 134.6, 138.4, 138.6, 151.4, 164.9. IR (KBr) ν=2930, 1708, 771 cm^{-1}; MS: *m*/*z* 279 $(MH)^+$. HRMS calcd for $C_{19}H_{19}O_2$: 279.1385 [M+H], found: 279.1381.

*4.3.22. 4-Methyl-3-phenyl-6-p-tolyl-5,6-dihydro-2H-pyran-2-one (**6v**).* Yield: 67 mg, 48%. White solid, mp: 129–130 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3H), 2.38 (s, 3H), 2.58–2.63 (m, 1H), 2.85–2.92 (m, 1H), 5.50–5.53 (m, 1H), 7.21–7.26 (m, 4H), 7.32–7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 21.5, 38.2, 77.8, 126.0, 127.7, 128.1, 128.8, 129.3, 130.0, 134.6, 135.7, 138.3, 151.4, 165.0. IR (KBr) ν=2922, 1698, 718 cm^{-1}; MS: *m*/*z* 279 $(MH)^+$. HRMS calcd for $C_{19}H_{19}O_2$: 279.1385 [M+H], found: 279.1376.

*4.3.23. 4-Methyl-3-phenyl-6-(4-(trifluoromethyl)- phenyl)-5,6-dihydro-2H-pyran-2-one (**6w**).* Yield: 150 mg, 90%. White solid, mp: 123–124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 2.63–2.68 (m, 1H), 2.82–2.89 (m, 1H), 5.60–5.63 (m, 1H), 7.24 (d, *J*=6.8 Hz, 1H), 7.35–7.43 (m, 3H), 7.60 (d, *J*=8.0 Hz, 2H), 7.68 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 38.2, 76.9, 125.6, 125.7, 126.2, 127.9, 128.2, 128.9, 129.9, 134.2, 142.6, 151.2, 164.4. IR (KBr) ν=2947, 2867, 1710, 1130, 836, 701 cm^{-1}; MS: *m*/*z* 333 $(MH)^+$. HRMS calcd for $C_{19}H_{16}F_3O_2$: 333.1102 [M+H], found: 333.1089.

*4.3.24. 6-(4-Bromophenyl)-4,5-dimethyl-3-phenyl-5,6-dihydro-2H-pyran-2-one (**6x**).* Yield: 153 mg, 86%. White solid, mp: 138–140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.26 (d, *J*=6.8 Hz, 3H), 1.79 (s, 3H), 2.80–2.84 (m, 1H), 5.21 (d, *J*=6.8 Hz, 1H), 7.15 (d, *J*=7.2 Hz, 2H), 7.26–7.39 (m, 5H), 7.53 (d, *J*=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.9, 19.7, 39.7, 82.5, 122.4, 127.8, 128.2, 128.4, 128.6, 129.9, 131.7, 134.7, 137.7, 155.0, 163.8. IR (KBr) ν=2921, 1711, 1010, 697 cm^{-1}; MS: *m*/*z* 357 $(MH)^+$. HRMS calcd for $C_{19}H_{18}BrO_2$: 357.0490 [M+H], found: 357.0498.

*4.3.25. 4-Benzyl-3,6-dimethyl-5,6-dihydro-2H-pyran-2-one (**6y**).* Yield: 88 mg, 81%. Syrup; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.32 (d, *J*=6.0 Hz, 3H), 2.06 (s, 3H), 2.15–2.20 (m, 2H), 3.54–3.67 (m, 2H), 4.38–4.42 (m, 2H), 7.14 (d, *J*=7.2 Hz, 1H), 7.26–7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.8, 20.6, 35.1, 39.5, 73.0, 122.9, 126.9, 128.6, 128.9, 137.0, 150.2, 166.8. IR (KBr) ν=3020, 2926, 1708, 708 cm^{-1}; MS: *m*/*z* 217 $(MH)^+$. HRMS calcd for $C_{14}H_{17}O_2$: 217.1229 [M+H], found: 217.1226.

*4.3.26. 3,4-Dibenzyl-6-methyl-5,6-dihydro-2H-pyran-2-one (**6z**).* Yield: 111 mg, 76%. Syrup; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.33 (d, *J*=6.4 Hz, 3H), 2.15–2.25 (m, 2H), 3.68 (s, 2H), 3.89–3.99 (m, 2H), 4.41–4.46 (m, 1H), 7.01–7.03 (m, 2H), 7.18–7.31 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 32.2, 35.1, 39.6, 72.9, 126.2, 126.7, 127.0, 128.3, 128.5, 128.78, 128.85, 136.6, 139.8, 152.0, 166.4. IR (KBr) ν=3024, 2929, 1709, 706 cm^{-1}; MS: *m*/*z* 293 $(MH)^+$. HRMS calcd for $C_{20}H_{21}O_2$: 293.1542 [M+H], found: 293.1546.

*4.3.27. 4-Benzyl-3-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-one (**6aa**).* Yield: 100 mg, 72%. White solid, mp: 112–113 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.14 (s, 1H), 2.36–2.42 (m, 1H), 2.52–2.60 (m, 1H), 3.62–3.71 (m, 2H), 5.28–5.32 (m, 1H), 7.14 (d, *J*=7.6 Hz, 2H), 7.24–7.35 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.9, 35.8, 39.6, 78.0, 123.3, 126.0, 127.0, 128.4, 128.5, 128.6, 128.9, 136.8, 138.7, 150.2, 166.4. IR (KBr) ν=3025, 2932, 1700, 708 cm^{-1}; MS: *m*/*z* 279 $(MH)^+$. HRMS calcd for $C_{19}H_{19}O_2$: 279.1385 [M+H], found: 279.1375.

4.4. Typical procedure for the preparation of 7

To a flask containing (*E*)-5-hydroxy-3-methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)pent-2-enenitrile (166 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added H_2SO_4 (27 μL, 0.5 mmol). The solution was stirred under reflux. Upon completion, the mixture was neutralized with aqueous Na_2CO_3, and then extracted with ethyl acetate (5 mL×3). The combined organic phases were washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:20) to give 2-methyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalene-1-carbonitrile (**7**) in a yield of 68% (107 mg, 0.34 mmol).

*4.4.1. 2-Methyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydrona-phthalene-1-carbonitrile (**7**).* Yield: 107 mg, 68%. Syrup; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.69–2.86 (m, 2H), 4.24 (t, *J*=7.6 Hz, 1H), 6.86 (d, *J*=7.2 Hz, 1H), 7.19–7.24 (m, 3H), 7.34 (t, *J*=7.6 Hz, 1H), 7.56–7.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.4, 38.2, 42.7, 109.6, 116.2, 124.9, 125.7, 127.9, 128.4, 128.6, 129.2, 129.6, 134.6, 146.9, 152.9. MS: *m*/*z* 314 $(MH)^+$. HRMS calcd for $C_{19}H_{15}F_3N$: 314.1157 [M+H], found: 314.1158.

4.5. Typical procedure for the one-pot preparation of 8a (Table 4)

To a flask containing (*E*)-5-hydroxy-3-methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)pent-2-enenitrile (166 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added H_2SO_4 (27 μL, 0.5 mmol). The solution was stirred under reflux. Upon complete consumption of the starting material as indicated by TLC analysis, DDQ (114 mg, 0.5 mmol) was added. The mixture was stirred under reflux. Upon completion, the mixture was filtered through Celite and the filter cake was washed twice with CH_2Cl_2 (5 mL). The combined filtrate was neutralized with aqueous Na_2CO_3, and then extracted with ethyl acetate (5 mL×3). The combined organic phases were washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:20) to give 2-methyl-4-(4-(trifluoromethyl)-phenyl)-1-naphthonitrile (**8a**) in a yield of 63% (98 mg, 0.32 mmol). Other naphthalene-1-carbonitriles were obtained in a similar manner.

*4.5.1. 2-Methyl-4-(4-(trifluoromethyl)phenyl)-1-naphthonitrile (**8a**).* Yield: 98 mg, 63%. White solid, mp: 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.80 (s, 3H), 7.35 (s, 1H), 7.52 (t, J=7.6 Hz, 1H), 7.59 (d, J=7.6 Hz, 2H), 7.70 (t, J=7.6 Hz, 1H), 7.78–7.80 (m, 3H), 8.30 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 109.5, 116.9, 125.38, 125.45, 125.49, 126.2, 127.0, 128.6, 128.7, 129.4, 130.1, 130.6, 133.2, 142.3, 142.8, 143.4. IR (KBr) ν=2921, 2216, 818 cm^{-1}; MS: m/z 312 $(MH)^+$. HRMS calcd for $C_{19}H_{13}F_3N$: 312.1000 [M+H], found: 312.1011.

*4.5.2. 4-(3-Chlorophenyl)-2-methyl-1-naphthonitrile (**8b**).* Yield: 72 mg, 52%. White solid, mp: 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.78 (s, 3H), 7.34 (s, 2H), 7.45–7.46 (m, 3H), 7.51 (t, J=8.0 Hz, 1H), 7.67 (t, J=7.6 Hz, 1H), 7.84 (d, J=8.8 Hz, 1H), 8.27 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 109.2, 117.1, 125.3, 126.4, 126.9, 127.9, 128.3, 128.6, 128.7, 129.4, 129.7, 129.8, 133.2, 134.5, 140.9, 142.3, 143.4. IR (KBr) ν=3059, 2921, 2218, 799, 765 cm^{-1}; MS: m/z 278 $(MH)^+$. HRMS calcd for $C_{18}H_{13}ClN$: 278.0737 [M+H], found: 278.0745.

*4.5.3. 4-(4-Chlorophenyl)-2-methyl-1-naphthonitrile (**8c**).* Yield: 74 mg, 53%. White solid, mp: 148–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.78 (s, 3H), 7.33 (s, 1H), 7.39 (d, J=8.4 Hz, 2H), 7.48–7.52 (m, 3H), 7.68 (t, J=7.6 Hz, 1H), 7.84 (d, J=8.4 Hz, 1H), 8.27 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 109.0, 117.1, 125.3, 126.4, 126.8, 128.5, 128.68, 128.74, 129.5, 131.0, 133.3, 134.3, 137.5, 142.3, 143.7. IR (KBr) ν=2923, 2218, 813 cm^{-1}; MS: m/z 278 $(MH)^+$. HRMS calcd for $C_{18}H_{13}ClN$: 278.0737 [M+H], found: 278.0743.

*4.5.4. 4-(4-Bromophenyl)-2-methyl-1-naphthonitrile (**8d**).* Yield: 90 mg, 56%. White solid, mp: 164–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.78 (s, 3H), 7.32–7.34 (m, 3H), 7.51 (t, J=7.6 Hz, 1H), 7.64–7.70 (m, 3H), 7.83 (d, J=8.4 Hz, 1H), 8.28 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 109.1, 117.1, 122.5, 125.3, 126.4, 126.8, 128.5, 128.6, 129.5, 131.3, 131.7, 133.3, 138.0, 142.3, 143.7. IR (KBr) ν=2946, 2210, 819 cm^{-1}; MS: m/z 322 $(MH)^+$. HRMS calcd for $C_{18}H_{13}BrN$: 322.0231 [M+H], found: 322.0241.

*4.5.5. 2-Methyl-4-m-tolyl-1-naphthonitrile (**8e**).* Yield: 54 mg, 42%. White solid, mp: 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 2.78 (s, 3H), 7.25–7.51 (m, 6H), 7.66 (t, J=7.6 Hz, 1H), 7.92 (d, J=8.4 Hz, 1H), 8.28 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 21.5, 108.5, 117.3, 125.2, 126.5, 126.8, 126.9, 128.3, 128.6, 128.9, 129.8, 130.3, 133.3, 138.2, 139.1, 142.3, 145.2. IR (KBr) ν=2931, 2218, 810 cm^{-1}; MS: m/z 258 $(MH)^+$. HRMS calcd for $C_{19}H_{16}N$: 258.1283 [M+H], found: 258.1282.

*4.5.6. 2-Methyl-4-p-tolyl-1-naphthonitrile (**8f**).* Yield: 52 mg, 40%. White solid, mp: 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 2.78 (s, 3H), 7.32–7.37 (m, 5H), 7.48 (t, J=7.6 Hz, 1H), 7.66 (t, J=7.6 Hz, 1H), 7.93 (d, J=7.6 Hz, 1H), 8.27 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.26, 21.29, 108.4, 117.3, 125.2, 126.5, 126.8, 128.3, 128.7, 129.2, 129.6, 129.8, 133.3, 136.2, 138.0, 142.3, 145.1. IR (KBr) ν=2959, 2918, 2214, 1286, 834 cm^{-1}; MS: m/z 258 $(MH)^+$. HRMS calcd for $C_{19}H_{16}N$: 258.1283 [M+H], found: 258.1273.

*4.5.7. 2-Methyl-4-phenyl-1-naphthonitrile (**8g**).* Yield: 74 mg, 61%. White solid, mp: 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.79 (s, 3H), 7.36 (s, 1H), 7.45–7.54 (m, 6H), 7.67 (t, J=7.6 Hz, 1H), 7.91 (d, J=8.4 Hz, 1H), 8.28 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 108.6, 117.2, 125.2, 126.6, 126.8, 128.1, 128.4, 128.5, 128.7, 129.67, 129.74, 133.3, 139.1, 142.3, 145.1. IR (KBr) ν=3053, 2921, 2217, 766, 704 cm^{-1}; MS: m/z 244 $(MH)^+$. HRMS calcd for $C_{18}H_{14}N$: 244.1126 [M+H], found: 244.1136.

*4.5.8. 3-Methyl-1,1′-binaphthyl-4-carbonitrile (**8h**).* Yield: 52 mg, 35%. White solid, mp: 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (s, 3H), 7.33–7.36 (m, 3H), 7.45–7.54 (m, 4H), 7.60–7.67 (m, 2H), 7.99 (d, J=8.0 Hz, 1H), 8.02 (d, J=8.0 Hz, 1H), 8.36 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 109.1, 117.3, 125.1, 125.4, 126.0, 126.2, 126.5, 126.7, 127.3, 127.6, 128.4, 128.5, 128.7, 129.7, 131.0, 132.2, 133.0, 133.5, 136.8, 142.4, 143.7. IR (KBr) ν=3055, 2918, 2219, 804 cm^{-1}; MS: m/z 294 $(MH)^+$. HRMS calcd for $C_{22}H_{16}N$: 294.1283 [M+H], found: 294.1285.

*4.5.9. 4-(4-Bromophenyl)-2,3-dimethyl-1-naphthonitrile (**8i**).* Yield: 104 mg, 62%. White solid, mp: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 2.74 (s, 3H), 7.10 (d, J=8.4 Hz, 2H), 7.33 (d, J=8.4 Hz, 1H), 7.39 (t, J=8.0 Hz, 1H), 7.57 (t, J=7.6 Hz, 1H), 7.66 (d, J=8.0 Hz, 2H), 8.20 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.0, 20.1, 109.7, 117.6, 121.9, 124.9, 126.6, 126.8, 127.5, 131.0, 131.2, 131.3, 131.9, 133.1, 137.8, 142.0, 142.6. IR (KBr) ν=2952, 2211, 817, 770 cm^{-1}; MS: m/z 336 $(MH)^+$. HRMS calcd for $C_{19}H_{15}BrN$: 336.0388 [M+H], found: 336.0382.

4.6. Typical procedure for the preparation of 2-(4-methyl-3,4-dihydronaphthalene-2(1*H*)-ylidene)propanenitrile (9a) (Table 5)

To a flask containing (*E*)-3-benzyl-5-hydroxy-2-methylhex-2-enenitrile (108 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added H_2SO_4 (27 μL, 0.5 mmol). The solution was stirred under reflux. Upon completion, the reaction was quenched with aqueous Na_2CO_3 and the mixture was extracted with ethyl acetate (5 mL×3). The combined organic phases were washed with brine, dried, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to give 2-(4-methyl-3,4-dihydronaphthalene-2(1*H*)-ylidene) propanenitrile (**9a**) in a yield of 56% (55 mg, 0.28 mmol). Other 2-methylene-1,2,3,4-tetrahydronaphthalenes were obtained in a similar manner.

*4.6.1. (Z)-2-(4-Methyl-3,4-dihydronaphthalen-2(1H)-ylidene)propanenitrile (**9a**).* Yield: 55 mg, 56%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (d, J=6.8 Hz, 3H), 1.93 (s, 3H), 2.29–2.35 (m, 1H), 2.62–2.67 (m, 1H), 3.02–3.07 (m, 1H), 3.71–4.01 (m, 2H), 7.18–7.26 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.7, 20.2, 33.2, 35.9, 37.2, 102.5, 119.4, 125.8, 126.56, 126.63, 128.0, 134.0, 141.4, 154.8. IR (KBr) ν=2962, 2209, 1309, 758 cm^{-1}; MS: m/z 198 $(MH)^+$. HRMS calcd for $C_{14}H_{16}N$: 198.1283 [M+H], found: 198.1276.

*4.6.2. (Z)-2-(4-Methyl-3,4-dihydronaphthalen-2(1H)-ylidene)-3-phenylpropanenitrile (**9b**).* Yield: 73 mg, 53%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.35 (d, J=7.2 Hz, 3H), 2.48–2.54 (m, 1H), 2.78–2.84 (m, 1H), 3.05–3.10 (m, 1H), 3.61–3.71 (m, 2H), 3.83–4.10 (m, 2H), 7.22–7.39 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 33.3, 35.5, 36.1, 37.4, 107.6, 118.8, 126.0, 126.7, 126.8, 127.0, 128.2, 128.4, 128.8, 133.7, 137.3, 141.3, 155.6. IR (KBr) ν=3062, 2963, 2209, 758 cm^{-1}; MS: m/z 274 $(MH)^+$. HRMS calcd for $C_{20}H_{20}N$: 274.1596 [M+H], found: 274.1605.

*4.6.3. (Z)-2-(4-Methyl-3,4-dihydronaphthalen-2(1H)-ylidene)-2-phenylacetonitrile (**9c**).* Yield: 56 mg, 43%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (d, J=6.8 Hz, 3H), 2.45–2.50 (m, 1H), 2.70–2.75 (m, 1H), 2.96–3.01 (m, 1H), 3.96–4.19 (m, 2H), 7.22–7.26 (m, 4H), 7.31–7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.7, 33.7, 36.6, 37.1, 110.0, 118.5, 126.2, 126.6, 126.7, 128.3, 128.3, 128.4, 128.7, 128.8, 129.0, 129.1, 133.3, 141.3, 157.2. IR (KBr) ν=3061, 2960, 2213, 759, 699 cm^{-1}; MS: m/z 260 $(MH)^+$. HRMS calcd for $C_{19}H_{18}N$: 260.1439 [M+H], found: 260.1442.

*4.6.4. (Z)-2-(4-phenyl-3,4-dihydronaphthalen-2(1H)-ylidene)propanenitrile (**9d**).* Yield: 62 mg, 48%. Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68 (s, 3H), 2.83–2.86 (m, 2H), 3.84–4.29 (m, 3H), 6.91 (d,

J=7.6 Hz, 1H), 7.08 (d, J=7.6 Hz, 2H), 7.12–7.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.4, 36.2, 37.3, 45.5, 103.1, 119.4, 126.6, 126.8, 127.1, 128.2, 128.3, 128.4, 128.6, 134.6, 138.8, 143.2, 153.5. IR (KBr) ν=3055, 2953, 2212, 760 cm^{-1}; MS: m/z 260 $(MH)^+$. HRMS calcd for $C_{19}H_{18}N$: 260.1439 [M+H], found: 260.1441.

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Supplementary data

The X-ray crystal structures of **5e**, **6b**, **8i** and the copies of ^{1}H and ^{13}C NMR spectra of **5a**–**5p**, **6a**–**6aa**, **7**, **8a**–**8i**, and **9a**–**9d**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.118.

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