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An effective organocatalytic preparation of both 1,3-diketones and nitriles from alkynones with oximes as hydroxide source

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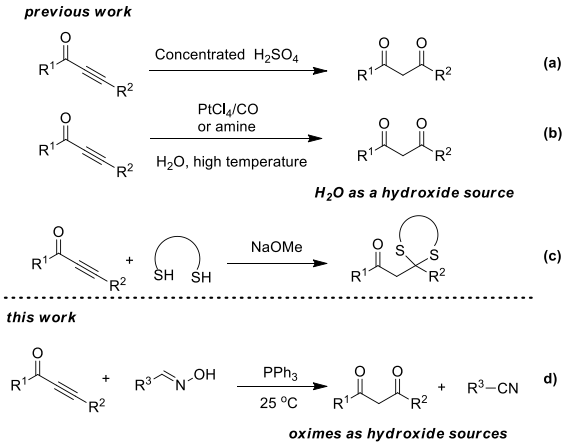
An effective phosphine-catalyzed protocol has been established for the synthese of 1,3-diketones and nitriles from alkynones with oximes as hydroxide surrogate. This method features the use of phosphine catalyst , compatibility with various functional groups and ambient temperature, which makes this approach very practical. Plausible mechanism was proposed.

Introduction

1,3-Diketones have recently attracted much attentions due to their uses as versatile synthetic precursors, bioactive molecules, bidentate ligands and luminescent materials.[1-2] Because of their importance, a variety of synthetic methods have been developed to construct this useful scaffold. The typical approach is the classical Claisen condensation reaction through a hard enolate using a strong base.[3] Due to the strong basic conditions, these reactions are not applicable to substrates containing base-sensitive functionality. This limitation was subsequently overcome by using soft enolate system to coupling the two carbonyl compounds.[4] In addition, 1,3-diketones can be also synthesized by the oxidation of *β*-hydroxyketones,[5] the decarboxylative coupling strategy,[6] and organo-[7] and metal catalysis.[8] Although above methodologies are favorable, they usually suffer from the limitations, such as use of a strong base, oxidant, high temperature or metal catalysts. On the other hand, nitriles are also important structural units existing in natural products and bioactive molecules.[9] Common methods for the syntheses of nitrile, such as the Sandmeyer reaction, [10] dehydration of amine,[11] dehydration of primary amides [12] and others, [13] have been reported. However, those methodologies usually suffer from poor reactivity, harsh reaction conditions, narrow substrate tolerance or use of metal catalysts. Therefore, the development of simple, efficient and metal-free synthetic approach with high activity and broad substrate scope for both syntheses of 1,3-diketones and nitriles under mild conditions is still a challenging but attractive task.



Scheme 1 Synthesis of 1,3-diketones and protected 1,3-diketones from alkynones.

As we all knew, alkynones as important structural motifs have been widely studied due to their convenient synthesis by the Sonogashira coupling of terminal alkynes with acyl chlorides[14] and functionalized transformations to valuable cyclic compounds.[15] It is noteworthy that a tactical approach for synthesis of 1,3-diketones by hydration of alkynones were described.[16] However, due to use of concentrated sulfuric acid (H_2SO_4) , platinum(IV) chloride ($PtCl_4$) or amines as catalysts, this method somewhat suffer from narrow substrate scope and high temperature (Scheme 1a-b). Additionally, Ley and coworkers reported an interesting work for the synthese of a versatile masked 1,3-diketone from the conjugate addition of dithiols to alkynones with the strong base NaOMe (Scheme 1c). Recently, Fier and Maloney reported an excellent work for the synthesis of phenols from aryl halides using benzaldehyde oxime as a hydroxide surrogate, meanwhile benzaldehyde oxime was transformed into benzonitrile.[17] Base on above mechanistic and experimental insights, we speculate if 1,3-diketones and nitriles were both obtained from alkynones with oximes as hydroxide surrogates by choosing appropriate metal-free base catalysts under

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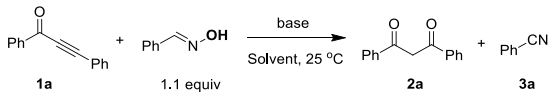
mild conditions (room temperature). Intrigued by the development of a convenient and simple access to 1,3-diketones, nitriles and as a continuation of our interests in the applications of alkynones,[18] herein we wish to report our active results, in which a variety of alkynones and oximes were smoothly transformed to the corresponding 1,3-diketones and nitriles in the presence of a simple and efficient metal-free catalyst. This catalytic system showed wide substrate scope and a series of functionalized 1,3-diketones and nitriles were successfully obtained in moderate to excellent yields (Scheme 1d).

Results and discussion

Table 1. Optimization of reaction conditions [a]



Entry	Base (equiv.)	Solvent	Yield (%)	
			2a[b]	**3a**[c]
1	DABCO (0.2)	CH_2Cl_2	-	-
2	DMAP (0.2)	CH_2Cl_2	19	17
3	DBU (0.2)	CH_2Cl_2	43	40
4	PPh_3 (0.2)	CH_2Cl_2	95	91
5	K_2CO_3 (0.2)	CH_2Cl_2	trace	trace
6	Cs_2CO_3 (0.2)	CH_2Cl_2	23	20
7[d]	PPh_3 (0.1)	CH_2Cl_2	88	85
8	PPh_3 (0.2)	DMF	52	50
9	PPh_3 (0.2)	DMSO	63	61
10	PPh_3 (0.2)	THF	17	15
11	PPh_3 (0.2)	1,4-dioxane	trace	trace
12	PPh_3 (0.2)	CH_3CN	83	79
13	PPh_3 (0.2)	DCE	91	87
14[e]	-	CH_2Cl_2	-	-
15[f]	PPh_3 (0.2)	CH_2Cl_2	-	-
16[g]	PPh_3 (0.2)	CH_2Cl_2	87	84

[a]Reaction conditions: **1a** (0.3 mmol), 0.33 mmol benzaldehyde oxime, PPh_3 (0.06 mmol), 1.5 mL solvent, 25 °C, 3 h, N_2. [b]Isolated yield for product **2a**. [c]Yield determined by ^{1}H-NMR spectroscopy for product **3a**, using 1,3,5-trimethoxybenzene as an internal standard. [d]6 h. [e]The reaction was conducted without PPh_3. [f]The reaction was conducted without benzaldehyde oxime. [g]Under open air atmosphere. DABCO = 1,4-diazabicyclo[2.2.2]octane; DMAP = 4-dimethylaminopyridine ; DBU = 1,8-diaza bicyclo[5.4.0]undec-7-ene; PPh_3 = triphenylphosphine; CH_2Cl_2 = dichloromethane, DMF = N,N-dimethylfo rmamide; DMSO = dimethyl sulfoxide; CH_3CN = acetonitrile; DCE = 1,2-dichloroethane.

To validate this hypothesis, we choose 1,3-diphenylprop-2-yn-1-one **1a** and benzaldehyde oxime as model substrates to investigate the optimal conditions and the experimental results are listed in Table 1. Since products **2a** and **3a** were both obtained almost in equalyields, we only discussed the results for product **2a**. When 0.2 equivalent amount of DABCO as catalyst in CH_2Cl_2 under room temperature was used, no desired product **2a** was obtained (Table 1, entry 1). Then, treatment of **1a** with organic base of DMAP or DBU under same conditions, product **2a** was obtained in 19% or 43% yields, respectively (Table 1, entries 2-3). To our delight, the desired product **2a** was obtained in 95% yield when PPh_3 as catalyst (Table 1, entry 4). When inorganic bases such as K_2CO_3 or Cs_2CO_3 were used as catalysts, inferior results were observed (Table 1, entries 5-6). Those results demonstrated that the properties of base show an obvious effect on this transformation. Even the reaction time was prolonged to 6 h, a decreased yield of **2a** was observed when the loading of PPh_3 was lowered from 0.2 to 0.1 equiv. (Table 1, entry 7). **2a** was obtained in moderate yield in DMSO or DMF (Table 1, entries 8-9). Other solvents such as THF or 1,4-dioxane gave low or trace yields (Table 1, entries 10-11). While CH_3CN and DCE gave better results (Table 1, entries 12-13). However, the reaction failed to give without PPh_3 or benzaldehyde oxime, which demonstrated that both of PPh_3 and benzaldehyde oxime are necessary for this reaction. Additionally, when the reaction was conducted out under open-air condition, the yield is slightly lower than the yield under N_2 condition (Table 1, entry 16). This may be attributed to partial oxidation of triphenylphosphine (PPh_3) to triphenylphosphine oxide ($O=PPh_3$). Thus, the optimal reaction conditions were obtained: 0.3 mmol **1a**, 1.1 equiv. benzaldehyde oxime, 20 mol% PPh_3 as a catalyst in CH_2Cl_2 at room temperature.

With the optimized reaction conditions, the scope of various alkynones with benzaldehyde oximes were further investigated. This metal-free catalytic system showed high generality and a series of 1,3-diketones were obtained in moderate to good yields, as shown in Table 2. For alkynones, common functional substituents including alkyl, ether, halo, and even a cyano group at *ortho*, *meta*, or *para* positions of the aryl groups, were all tolerated (Table 2, entries 3, 5, 8, 10–13, 15-17, 19, 21-24 and 28). Notably, naphthyl and heteroaromatic alkynones were also compatible under similar reaction conditions (Table 2, entries 25–27). Still, cinnamyl substrate **1w** gave the corresponding product **2w** in 43% yield. When 3-aryl substituted alkynones with different electron-rich, electron-withdrawing groups and heteroaromatic derivative were used as substrates, the reactions proceeded smoothly to generate the desired products (Table 2, entries 2, 4, 6-7, 9, 14, 18, 20 and 30-31). Additionally, the substrate bearing 3-*n*-butyl-substitution could also provide the desired product **2z**, albeit in a lower yield (Table 2, entry 32). Unfortunately, the developed protocol failed to produce **2aa** and **2ab**, when alkyl-substituted substrates **1aa** and **1ab** were used (Table 2, entry 33-34).

A variety of aromatic and aliphatic aldehyde oximes were also employed, the desired products **3** all gave in good to high yields (Table 3). Aromatic aldehyde oximes, with electron-withdrawing or election-donating groups at the 2, 3, and 4 positions of the aryl ring, were all tolerated, affording the corresponding nitriles in good to excellent yields (**3a**–**3k**). Aliphatic aldehyde oximes including 2-phenylacetaldehyde oxime and dodecanal oxime were also effective hydroxide source for the reaction.

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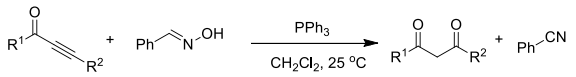
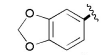
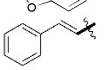
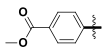
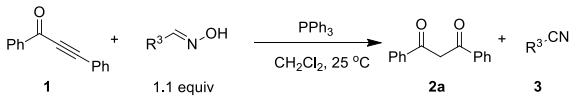
Table 2. Scope of alkynones [a]



Entry	R^1	R^2		T (h)	Yield (%)	
					2[b]	**3a**[c]
1	C_6H_5	C_6H_5	**1a**	3	95 (**2a**)	90
2	C_6H_5	4-MeC_6H_4	**1b**	12	80 (**2b**)	78
3	4-MeC_6H_4	C_6H_5	**1b'**	8	92 (**2b**)	88
4	C_6H_5	4-$OMeC_6H_4$	**1c**	12	65 (**2c**)	62
5	4-$OMeC_6H_4$	C_6H_5	**1c'**	12	82 (**2c**)	79
6	C_6H_5	4-EtC_6H_4	**1d**	9	61 (**2d**)	59
7	C_6H_5	3-MeC_6H_4	**1e**	5	86 (**2e**)	83
8	3-MeC_6H_4	C_6H_5	**1e'**	5	85 (**2e**)	82
9	C_6H_5	4-^{t}BuC_6H_4	**1f**	5	85 (**2f**)	81
10	4-^{t}BuC_6H_4	C_6H_5	**1f'**	5	70 (**2f**)	66
11	2-MeC_6H_4	C_6H_5	**1g**	5	78 (**2g**)	75
12	3-$OMeC_6H_4$	C_6H_5	**1h**	5	74 (**2h**)	72
13	2-$OMeC_6H_4$	C_6H_5	**1i**	5	86 (**2i**)	82
14	C_6H_5	4-ClC_6H_4	**1j**	3	89 (**2j**)	86
15	4-ClC_6H_4	C_6H_5	**1j'**	3	88 (**2j**)	84
16	3-ClC_6H_4	C_6H_5	**1k**	3	89 (**2k**)	86
17	2-ClC_6H_4	C_6H_5	**1l**	3	90 (**2l**)	88
18	C_6H_5	4-FC_6H_4	**1m**	3	91 (**2m**)	87
19	4-FC_6H_4	C_6H_5	**1m'**	3	86 (**2m**)	83
20	C_6H_5	4-$CF_3C_6H_4$	**1n**	3	80 (**2n**)	78
21	4-BrC_6H_4	C_6H_5	**1o**	5	61 (**2o**)	60
22	3-BrC_6H_4	C_6H_5	**1p**	5	56 (**2p**)	54
23	2-BrC_6H_4	C_6H_5	**1q**	3	80 (**2q**)	78
24	4-CNC_6H_4	C_6H_5	**1r**	5	96 (**2r**)	91
25	1-naphthyl	C_6H_5	**1s**	5	90 (**2s**)	86
26	2-thienyl	C_6H_5	**1t**	10	72 (**2t**)	68
27	2-furanyl	C_6H_5	**1u**	5	74 (**2u**)	70
28		C_6H_5	**1v**	15	75 (**2v**)	73
29		C_6H_5	**1w**	24	43 (**2w**)	40
30	C_6H_5		**1x**	5	68 (**2x**)	64
31	C_6H_5	3-pyridyl	**1y**	5	73 (**2y**)	68
32	C_6H_5	^{n}Bu	**1z**	5	26 (**2z**)	24
33	Me	C_6H_5	**1aa**	3	- (**2aa**)	-
34	$C_6H_5CH_2$	C_6H_5	**1ab**	3	- (**2ab**)	-

[a]Reaction conditions: **1a** (0.3 mmol), 0.33 mmol benzaldehyde oxime, PPh_3 (0.06 mmol), 1.5 mL CH_2Cl_2. [b]Isolated yield for product **2**. [c]Yield determined by ^{1}H-NMR spectroscopy for product **3a** using 1,3,5-trimethoxybenzene as an internal standard.

Table 3. Scope of aromatic and aliphatic aldehyde oximes [a]



Entry	R^3	T (h)	Yield (%)	
			2a[b]	**3**[c]
1	C_6H_5	3	95	90 (**3a**)
2	4-MeC_6H_4	3	87	85 (**3b**)
3	2-MeC_6H_5	3	86	83 (**3c**)
4	4-^{i}PrC_6H_4	3	92	89 (**3d**)
5	4-$OMeC_6H_5$	3	90	88 (**3e**)
6	4-$NMe_2C_6H_4$	3	95	94 (**3f**)
7	4-ClC_6H_4	3	90	89 (**3g**)
8	2-BrC_6H_5	3	88	85 (**3h**)
9	4-$CF_3C_6H_4$	3	85	82 (**3i**)
10	4-$NO_2C_6H_5$	5	87	85 (**3j**)
11		3	95	93 (**3k**)
12	1-naphthyl	24	81	78 (**3l**)
13	$C_6H_5CH_2$	5	88	85 (**3m**)
14	$CH_3(CH_2)_9CH_2$	5	89	86 (**3n**)

[a]Reaction conditions: **1a** (0.3 mmol), 0.33 mmol oximes, PPh_3 (0.06 mmol), 1.5 mL CH_2Cl_2. [b]Isolated yield. [c]Yield determined by ^{1}H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard.

To explore the reaction mechanism, control experiment was carried out (Scheme 2). To exclude the hydration of substrates **1**, no product **2a** was obtained when H_2O in place of benzaldehyde oxime under the standard conditions (Scheme 2). Base on the above results and literature precedent in the catalytic transformation of alkynones using phosphines as catalysts,[19] a plausible mechanism was proposed in Scheme 3. When substrate is firstly activated by PPh_3, an addition reaction takes place to form intermediate **A**. On the other hand, the intermediate **B** is produced by the proton transfer reaction of oximes to substrates **1**. Finally, after elimination of nitriles **3**, the product **2** are released together with the regenerated catalyst PPh_3 to finish the catalyst cycle. Furthermore, ESI-HRMS detection of the reaction mixture of **1a** and benzaldehyde oxime as substrates after 0.5 h was conducted to capture the information of reaction intermediates. Fortunately, the species of m/z for the intermediates **A**, **B**, product **2a** and benzonitrile **3a** were observed, and the values were consistent with the theoretical calculation (R^1 = Ph, R^2 = Ph; calcd for $[M_A+H]^+$ = 469.1716, found: 469.1711; calcd for $[M_B+H]^+$: 328.1332, found: 328.1324; calcd for $[M_{2a}+H]^+$: 225.0910, found: 225.0908; R^3 = Ph, calcd for $[M_{3a}+H]^+$: 104.0495, found: 104.0498; see Fig. S1 in the ESI†for details).

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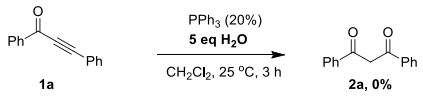
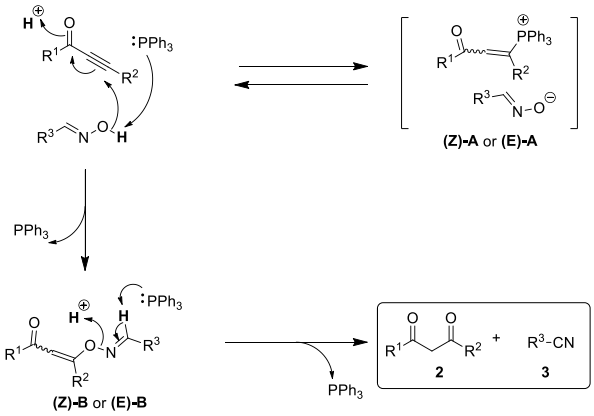
Additionally, since the methyl characteristic peak in the NMR spectrum in 4-methylbenzaldehyde oxime having, it was chosen to react with substrate **1a** for monitoring the reaction course by ^{1}H NMR spectroscopy. From the changes of ^{1}H NMR spectroscopy, substrate **1a** and 4-methylbenzaldehyde oxime were continuously consumed gradually, and the peak intensity of the product **2a** and 4-methylbenzonitrile **3b** were constantly raised (see Fig. S2 in the ESI† for details).



Scheme 2 Control experiments.



Scheme 3 Possible mechanism for the reaction of alkynones with oximes.

Conclusions

In summary, we have demonstrated a simple and efficient metal-free approach for the synthese of 1,3-diketones and nitriles from alkynones with oximes as hydroxide sources in a one-pot manner under mild conditions. A variety of functionalized 1,3-diketones and nitriles can be obtained in moderate to excellent yields, which are both useful building blocks toward organic synthesis. The plausible mechanism of this reaction was suggested and supported by control experiments, ESI-HRMS detection and ^{1}H NMR monitoring. Further efforts are currently ongoing to use oximes as hydroxide surrogates for more synthetic applications.

Experimental

Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere. NMR spectra were recorded with tetramethylsilane as the internal standard. NMR spectra were recorded on a BrukerAvanceII400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) was measured using a Nicolet NEXUS FT-IR spectrophotometer. Tetrahydrofuran and 1,4-dioxane were distilled from sodium/benzophenone under N_2 atmosphere. Acetonitrile was distilled from phosphorus pentoxide under N_2 atmosphere. CH_2Cl_2, DCE, DMSO and DMF were distilled from calcium hydride under N_2 atmosphere. Substrates **1** were prepared by the Sonogashira coupling of terminal alkynes with acyl chlorides.[14]

*General Procedure for Synthesis of Products **2** and **3***

General Procedure: A 10 mL oven-dried Schlenck tube was successively charged with 0.30 mmol alkynones **1**, 0.33 mnol benzaldehyde oxime, 0.06 mmol PPh_3 and 1.5 mL CH_2Cl_2. The tube was sealed and the reaction mixture was stirred at room temperature for 3-24 h. After completion of this reaction, solvent was moved by the rotary evaporator and the resulting mixture was diluted with ethyl acetate (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether /EtOAc) to give products **2** and **3**.

*NOTE: All the products **2** are existed in keto-enol equilibrium and the enol forms dominate.*

1,3-Diphenylpropane-1,3-dione (2a):[6,8c] white solid (95% yield); mp 74.5−76.3 °C (lit.[20a] mp 76−77 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.98 (s, 1H), 8.02–8.00 (m, 4H), 7.57–7.54 (m, 2H), 7.49 (t, *J* = 7.2 Hz, 4H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 185.7, 135.5, 132.5, 128.7, 127.2, 93.2.

1-Phenyl-3-(p-tolyl)propane-1,3-dione (2b):[6b] white solid (**1b** as substrate for 80% yield; **1b'** as substrate for 92% yield); mp 79.9.5−81.0 °C (lit.[20a] mp 80−81.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.92 (s, 1H), 8.04–7.95 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.51–7.49 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 2.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 185.3, 143.4, 135.7, 133.0, 132.4, 129.5, 128.8, 127.4, 127.2, 93.0, 21.8.

1-(4-Methoxyphenyl)-3-phenylpropane-1,3-dione (2c):[6,8c] white solid (**1c** as substrate for 65% yield; **1c'** as substrate for 82% yield); mp 128.7−129.5 °C (lit.[20a] mp 127-128 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.99 (s, 1H), 8.00–7.97 (m, 4H), 7.57–7.46 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.80 (s, 1H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.3, 184.2, 163.4, 135.7, 132.3, 129.5, 128.8, 128.4, 127.1, 114.1, 92.5, 55.6.

1-(4-Ethylphenyl)-3-phenylpropane-1,3-dione (2d): slight yellow solid (61% yield); mp: 49.5-51.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.94 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 2.73 (q, *J* = 7.8 Hz, 2H), 1.28 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 185.3, 149.6, 135.7, 133.2, 132.4, 128.7, 128.3, 127.5, 127.2, 93.0, 29.0, 15.3; IR (KBr, cm^{-1}): 2968, 2931, 2868, 1600, 1512, 1471, 1299, 1226; HRMS (ESI-TOF) calcd for $C_{17}H_{17}O_2^+$ ([M+H]$^+$): 253.1223, found:

253.1224.

1-Phenyl-3-(m-tolyl)propane-1,3-dione (2e):[6b] light brown oil (**1e** as substrate for 86% yield; **1e'** as substrate for 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.87 (s, 1H), 8.01–7.99 (m, 2H), 7.81–7.78 (m, 2H), 7.58-7.54 (m, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.40–7.37 (m, 2H), 6.85 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 185.8, 138.6, 135.7, 135.7, 133.4, 132.5, 128.8, 128.7, 127.9, 127.3, 124.5, 93.3, 21.6.

1-(4-(Tert-butyl)phenyl)-3-phenylpropane-1,3-dione (2f):[8e] white solid (**1f** as substrate for 85% yield; **1f'** as substrate for 70% yield); mp 94.6−96.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.91 (s, 1H), 8.00–7.98 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.57-7.47 (m, 5H), 6.85 (s, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.0, 185.5, 156.4, 135.8, 132.9, 132.4, 128.8, 127.3, 127.2, 125.8, 93.1, 35.2, 31.3.

1-Phenyl-3-(o-tolyl)propane-1,3-dione (2g):[20b] slight yellow oil (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.56 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.45 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.19-7.15 (m, 2H), 6.44 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.6, 185.1, 137.2, 136.8, 135.4, 132.6, 131.6, 130.9, 128.8, 128.4, 127.3, 125.9, 97.4, 20.8.

1-(3-Methoxyphenyl)-3-phenylpropane-1,3-dione (2h):[6] white solid (74% yield); mp 57.9−58.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.86 (s, 1H), 8.04–7.94 (m, 2H), 7.61– 7.52 (m, 3H), 7.48 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.84 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.0, 185.5, 160.0, 137.2, 135.5, 132.6, 129.8, 128.8, 127.3, 119.7, 118.7, 112.2, 93.4, 55.6.

1-(2-Methoxyphenyl)-3-phenylpropane-1,3-dione (2i):[6] white solid (86% yield); enol/ ketone = 91:9; mp 62.2−64.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.88 (s, 1H), 7.98-7.94 (m, 3H), 7.56–7.44 (m, 4H), 7.16 (s, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 185.9, 184.3, 158.6, 136.1, 133.2, 132.3, 130.4, 128.7, 127.3, 125.0, 120.9, 111.8, 98.6, 55.9.

1-(4-Chlorophenyl)-3-phenylpropane-1,3-dione (2j):[6a] white solid (**1j** as substrate for 89% yield; **1j'** as substrate for 88% yield); mp 84.6−86.1 °C (lit.[20a] mp 82.5-84 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.80 (s, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.93 (t, *J* = 6.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.53–7.39 (m, 4H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 185.9, 184.6, 138.8, 135.4, 134.1, 132.7, 129.1, 128.8, 128.6, 127.3, 93.1.

1-(3-Chlorophenyl)-3-phenylpropane-1,3-dione (2k):[3b] brick-red solid (89% yield); mp 65.2−66.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): δ 16.73 (s, 1H), 8.00–7.95 (m, 3H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.53–7.48 (m, 3H), 7.43 (t, *J* = 8.0 Hz, 1H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 184.2, 137.5, 135.3, 135.1, 132.8, 132.4, 130.1, 128.9, 127.4, 125.4, 93.4.

1-(2-Chlorophenyl)-3-phenylpropane-1,3-dione (2l):[3b] brown solid (90% yield); mp 50.2−51.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.34 (s, 1H), 7.97–7.95 (m, 2H), 7.68 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.56 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.50–7.47 (m, 3H), 7.39 (dtd, *J* = 14.4, 7.2, 1.6 Hz, 2H), 6.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.0, 184.7, 136.4, 135.1, 132.8, 131.9, 131.8, 130.9, 130.2, 128.9, 127.4, 127.1, 98.5.

1-(4-Fluorophenyl)-3-phenylpropane-1,3-dione (2m):[6b] white solid (**1m** as substrate for 86% yield; **1m'** as substrate for 85%); mp 78.0−79.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.85 (s, 1H), 8.03–7.97 (m, 4H), 7.58–7.54 (m, 1H), 7.51–7.47 (m, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 185.2, 165.5, (d, $J_{C\text{-}F}$ = 252.4 Hz), 135.4, 132.6, 132.0 (d, $J_{C\text{-}F}$ = 3.0 Hz),, 129.7 (d, $J_{C\text{-}F}$ = 9.1 Hz), 128.8, 127.2, 115.9 (d, $J_{C\text{-}F}$ = 21.8 Hz), 92.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -106.3 (dd, $J_{C\text{-}F}$ = 4.8, 1.9 Hz).

1-Phenyl-3-(4-(trifluoromethyl)phenyl)propane-1,3-dione (2n):[6,8c] white solid (80% yield); mp 96.3−97.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.72 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.2, 183.5, 138.9, 135.4, 133.9 (d, $J_{C\text{-}F}$ = 32.5 Hz),133.0, 128.9, 127.6, 127.5, 125.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (d, $J_{C\text{-}F}$ = 270.9 Hz), 93.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.0.

1-(4-Bromophenyl)-3-phenylpropane-1,3-dione (2o):[6] light yellow solid (61% yield); mp 91.4−93.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.80 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.1, 184.7, 135.5, 134.6, 132.8, 132.1, 128.9, 128.8, 127.4, 127.3, 93.1.

1-(3-Bromophenyl)-3-phenylpropane-1,3-dione (2p):[6a] light yellow solid (56% yield); mp 66.7−67.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.73 (s, 1H), 8.11 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 184.2, 137.7, 135.3, 135.3, 132.9, 130.4, 130.3, 128.9, 127.4, 125.8, 123.1, 93.4.

1-(2-Bromophenyl)-3-phenylpropane-1,3-dione (2q):[6a] light brown oil (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.24 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.6, 1.6 Hz, 1H), 6.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.7, 184.1, 138.6, 134.9, 134.0, 132.8, 131.8, 130.1, 128.8, 127.6, 127.4, 120.3, 98.3.

4-(3-Oxo-3-phenylpropanoyl)benzonitrile (2r):[6a] white solid (96% yield); mp 154.0−155.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.67 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.7, 182.4, 139.5, 135.3, 133.2, 132.6, 129.0, 127.7, 127.5, 118.2, 115.6, 94.1.

1-(Naphthalen-1-yl)-3-phenylpropane-1,3-dione (2s):[6a] white solid (90% yield); mp 49.3−50.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.82 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.00–7.98 (m, 3H), 7.93–7.91 (m, 1H), 7.83 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.62–7.47 (m, 6H), 6.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.7, 184.6, 135.2, 135.1, 134.0, 132.7, 131.9, 130.3, 128.8, 128.7, 127.5, 127.3,

127.2, 126.5, 125.7, 124.9, 98.3.

1-Phenyl-3-(thiophen-2-yl)propane-1,3-dione (2t):[6] yellow solid (72% yield); mp 80.1−81.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.29 (s, 1H), 7.95–7.93 (m, 2H), 7.81 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 4.0 Hz, 1H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 183.1, 181.0, 142.4, 134.6, 132.7, 132.4, 130.5, 128.8, 128.5, 127.0, 93.3.

1-(Furan-2-yl)-3-phenylpropane-1,3-dione (2u):[6b] light brown solid (74% yield); mp 68.2−69.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.19 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.61 (s, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 3.2 Hz, 1H), 6.77 (s, 1H), 6.59 (dd, *J* = 3.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.7, 177.8, 151.2, 146.2, 134.9, 132.5, 128.8, 127.1, 115.9, 112.8, 92.9.

1-(Benzo[d][1,3]dioxol-5-yl)-3-phenylpropane-1,3-dione (2v):[6] white solid (75% yield); mp 83.2−84.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.89 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.60 (dd, *J* = 8.0, 1.6Hz, 1H), 7.50–7.47 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 6.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 183.9, 151.6, 148.4, 135.5, 132.4, 130.3, 128.8, 127.1, 123.1, 108.4, 107.4, 102.0, 92.7.

(E)-1,5-Diphenylpent-4-ene-1,3-dione (2w):[6] bright yellow solid (43% yield); mp 104.3−106.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.14 (s, 1H), 7.97–7.95 (m, 2H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.58–7.54 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43–7.38 (m, 3H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 189.5, 179.6, 140.2, 136.4, 135.2, 132.7, 130.2, 129.1, 128.8, 128.2, 127.5, 123.5, 97.8.

Methyl 4-(3-oxo-3-phenylpropanoyl)benzoate (2x):[6a] white solid (68% yield); mp 124.2−125.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.75 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.05–7.99 (m, 4H), 7.60–7.56 (m, 1H), 7.53-7.49 (m, 2H), 6.89 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.3, 183.6, 166.4, 139.4, 135.6, 133.4, 132.9, 130.0, 128.9, 127.5, 127.2, 94.0, 52.6.

1-Phenyl-3-(pyridin-3-yl)propane-1,3-dione (2y):[8e] light yellow solid (73% yield); mp 121.6−122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.70 (s, 1H), 9.19 (d, *J* = 1.6 Hz, 1H), 8.77 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.28–8.25 (m, 1H), 8.00-7.98 (m, 2H), 7.61–7.56 (m, 1H), 7.53–7.49 (m, 2H), 7.44 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 6.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.6, 183.6, 153.0, 148.6, 135.2, 134.7, 133.0, 131.4, 128.9, 127.4, 123.7, 93.6.

1-Phenylheptane-1,3-dione (2z):[4] light yellow oil (26% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.20 (s, 1H), 7.89–7.878 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47–7.42 (m, 2H), 6.17 (s, 1H), 2.45–2.41 (m, 2H), 1.67 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.40 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): δ 197.1, 183.6, 135.2, 132.3, 128.7, 127.1, 96.2, 39.1, 28.1, 22.5, 13.9.

Benzonitrile (3a):[13] colorless oil (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66–7.64 (m, 1H), 7.63–7.57 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 132.9, 132.2, 129.2, 118.9, 112.6.

4-Methylbenzonitrile (3b):[13] colorless oil (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.8, 132.1, 129.9, 119.2, 109.3, 21.9.

2-Methylbenzonitrile (3c): [13] colorless oil (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.0, 132.7, 132.6, 130.3, 126.3, 118.2, 112.9, 20.5.

4-Isopropylbenzonitrile (3d):[13] colorless oil (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.5, 132.3, 127.4, 119.3, 109.7, 34.5, 23.6.

4-Methoxybenzonitrile (3e):[13] colorless oil (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.9, 134.0, 119.3, 114.8, 104.0, 55.6.

4-(Dimethylamino)benzonitrile (3f):[13] white solid (94% yield); mp 74.6−75.9 °C (lit.[13c] mp 75-76 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 (dd, *J* = 9.4, 2.3 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.5, 133.3, 120.7, 111.4, 97.2, 39.9.

4-Chlorobenzonitrile (3g):[13] white solid (89% yield); mp 91.2−92.8 °C (lit.[13c] mp 91-93 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.6, 133.4, 129.7, 118.0, 110.9.

2-Bromobenzonitrile (3h):[13] white solid (85% yield); mp 51.6−52.8 °C (lit.[13j] mp 52-54 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69–7.64 (m, 2H), 7.48–7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.4, 134.0, 133.3, 127.7, 125.3, 117.2, 115.9.

4-(Trifluoromethyl)benzonitrile (3i):[13] colorless oil (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.6 (q, J_{C-F} = 33.4 Hz), 132.8, 126.3 (q, J_{C-F} = 3.7 Hz), 123.2 (q, J_{C-F} = 3.7 Hz), 117.5, 116.2 (d, J_{C-F} = 1.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.6.

4-Nitrobenzonitrile (3j):[13] white solid (85% yield); mp 147.5−149.1 °C (lit.[13e] mp 148-149 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.37–8.34 (m, 2H), 7.91–7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.1, 133.6, 124.4, 118.4, 116.9.

2-Bromo-4,5-dimethoxybenzonitrile (3k):[13] white solid (93% yield); mp 114.1−115.8 °C (lit.[13m] mp 113 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.06 (s, 1H), 7.04 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.3, 148.6, 117.7, 117.6, 115.6, 115.4, 106.9, 56.6, 56.5.

1-Naphthonitrile (3l):[13] colorless oil (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.91 (t, *J* = 7.0 Hz, 2H), 7.68 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.62 (dd, *J* = 11.1,

3.9 Hz, 1H), 7.55–7.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 133.3, 132.9, 132.6, 132.3, 128.7, 128.6, 127.6, 125.1, 124.9, 117.8, 110.2.

2-Phenylacetonitrile (3m):[13] colorless oil (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40–7.32 (m, 5H), 3.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 130.0, 129.2, 128.1, 128.0, 118.0, 23.6.

Dodecanenitrile (3n):[13] colorless oil (86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.32 (t, *J* = 7.1 Hz, 2H), 1.71–1.59 (m, 2H), 1.43 (dd, *J* = 14.6, 7.0 Hz, 2H), 1.30-1.26 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 119.9, 32.0, 29.7, 29.6, 29.4, 29.4, 28.9, 28.8, 25.5, 22.8, 17.2, 14.2.

Conflicts of interest

There are no conflicts to declare.

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