Amphiphilic allylation of activated alkenes by allyl acetates and allylstannanes catalyzed by palladium nanoparticles: an easy access to stereodefined substituted cyclohexene derivatives†

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An efficient *vicinal* double allylation of activated alkenes by allyl acetates and allylstannanes catalyzed by palladium nanoparticles, generated *in situ* from palladium(II) chloride, has been demonstrated. Several activated alkenes produce functionalized 1,7-octadiene derivatives in one pot. The additions of substituted allyl acetates are highly regioselective. The Grubbs cyclization of octadiene derivatives gives an easy access to stereodefined substituted cyclohexene derivatives.

Introduction

The concept of amphiphilic behavior of a bis-π-allylpalladium complex, introduced by Yamamoto *et al.*,[1–4] has received remarkable applications in organic synthesis. The bis-allyl palladium intermediate, generated by treatment of allyl chloride and allyltributyl stannane in the presence of $Pd(PPh_3)_2Cl_2$, reacts with activated alkenes in a way where the σ-allyl acts as a nucleophile and the π-allyl group as an electrophile leading to 1,7-octadiene derivatives.[1–3] Subsequently, several modifications of this reaction with variation of allyl sources, activated alkenes and catalyst have been reported by different groups.[5–9] However, the major challenge in this reaction is the control of regiochemistry of the two differently substituted allyl groups as the bis-allylpalladium complex readily undergoes σ–π exchange and thus the nucleo- and electrophilic positions are interchanged.

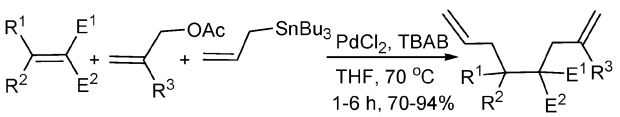
Metal nanoparticles have been the subject of current interest because of their performance as catalysts providing high selectivity, reactivity and improved yields of products.[10–12] In addition, the high surface-to-volume ratio of nanoparticles provides a large number of active sites per unit area compared to their parent metal. As a part of our continuing activities[13–18] on catalysis by palladium nanoparticles we report here a highly regioselective palladium nanoparticles catalyzed amphiphilic allylation of activated alkenes with allyl acetates (unsubstituted and substituted) and allyltributyl stannanes to produce 1,7-octadiene derivatives (Scheme 1).

Results and discussion

To determine the optimum reaction conditions for an efficient reaction a series of experiments were performed for a representative reaction of 2-benzylidenemalononitrile, allyl acetate and allyltri-(*n*-butyl)stannane with variation of reaction parameters such as solvents, palladium salt, stabilizer and temperature. The results are summarized in Table 1. It was found that the reaction proceeded best in THF using $PdCl_2$ and tetra-(*n*-butyl)ammonium bromide which acts as a stabilizer,[19] at 70 °C for 4 h (Table 1, entry 7). The amount of $PdCl_2$ was also optimized to 4 mol%. Nevertheless, the Pd nanoparticles are formed *in situ* by the reduction of $PdCl_2$ with allyl acetate in the reaction mixture under these conditions.[14,16,20,21] It is also apparent from the results in Table 1 (entries 2 and 9) that $PdCl_2$ in solution catalyzes the reaction at 25 °C marginally.

Thus, in a typical experimental procedure a mixture of activated alkene, allyl acetate and allyltri-(*n*-butyl)stannane was heated at 70 °C in the presence of $PdCl_2$ and tetra-(*n*-butyl)ammonium bromide for a certain period of time as required for completion (TLC). The standard work up and purification by column chromatography provided the product.

To find the active catalytic species in the reaction an extract from the reaction of 2-benzylidenemalononitrile, allyl acetate and allyltri-(*n*-butyl)stannane in the presence of TBAB under the standardized reaction conditions after 1 h showed the formation of nanoparticles (5–10 nm) by a TEM (Transmission Electron Microscope) image (Fig. 1). In the absence of TBAB, the nanoparticles undergo agglomerization and form a big cluster as shown in Fig. 2. The identity of nanoparticles as of palladium was established by EDX (Energy Dispersive X-ray) spectra (Fig. 3). A UV spectroscopic study of the reaction mixture before start of the reaction showed the presence of a peak at 418 nm corresponding to Pd(II) and disappearance of this peak with progress of the reaction indicating the formation of Pd(0) (Fig. 4). Nevertheless, Pd(0) nanoparticles are the active catalytic species in this reaction as the reaction was set at 70 °C when Pd nanoparticles are generated and available in the reaction mixture.



Scheme 1 Bis-allylation of activated alkenes.

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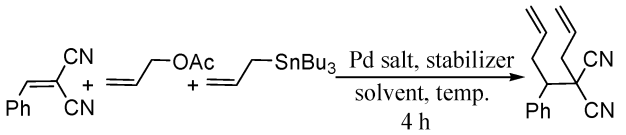
Table 1 Standardization reaction conditions[a]



Entry	Solvent	Pd salt	Stabilizer	Temp/°C	Yield (%)	TON
1	CH_2Cl_2	$PdCl_2$	TBAB	25	0	0
2	Toluene	$PdCl_2$	TBAB	25	12	3
3	Toluene	$PdCl_2$	TBAB	0	0	0
4	Toluene	$PdCl_2$	TBAB	70	56	14
5	EtOH	$PdCl_2$	TBAB	70	50	13
6	H_2O	$PdCl_2$	TBAB	70	25	6
7	**THF**	**$PdCl_2$**	**TBAB**	**70**	**92**	**23**
8	THF	$PdCl_2$	—	70	37	9
9	THF	$PdCl_2$	TBAB	25	18	5
10	THF	$PdCl_2$	TBAB	0	0	0
11	CH_3CN	$PdCl_2$	TBAB	70	82	21
12	DMF	$PdCl_2$	TBAB	70	78	20
13	THF	$PdCl_2$	SDS	70	0	0
14	THF	$PdCl_2$	PEG-6000	70	0	0
15	THF	$Pd(OAc)_2$	TBAB	70	88	22
16	THF	Na_2PdCl_4	TBAB	70	75	19
17	THF	$Pd(NO_3)_2$	TBAB	70	70	18
18	THF	PdNPs[b]	TBAB	70	58	15

[a] Reaction conditions: phenylethylidene malononitrile (1 mmol) allylacetate (3 mmol), allyltributyl stannane (1.2 mmol), Pd salt (4 mol%), stabilizer (1 mmol), solvent (4 mL) were heated at 70 °C. [b] Pd nanoparticles were prepared separately from $PdCl_2$ by reaction with *n*-Bu_3N following a reported procedure;[22] particle size 10–15 nm.

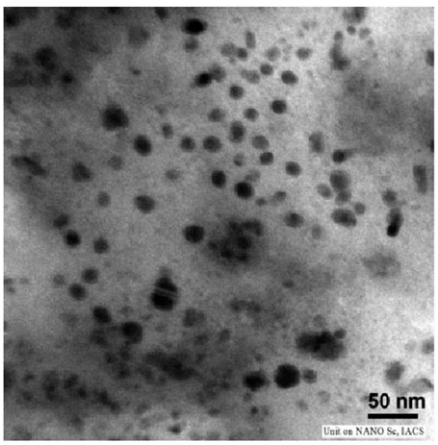


Fig. 1 TEM image of Pd-nanoparticles formed in the reaction mixture in the presence of TBAB.

Several diversely substituted ethylidene malononitriles underwent bis-allylations with allyl acetates and allyltri-(*n*-butyl)stannanes by this procedure to produce the corresponding 1,7-octadiene derivatives. The results are summarized in Table 2. This procedure is compatible with a wide range of substituents including phenyl, electron-donating and electron-withdrawing groups substituted phenyl, naphthyl, furyl, thiophenyl, cyclohexyl, alkyl *etc*. Most significantly, the tetrasubstituted 2-(propan-2-ylidene)malononitrile also (Table 2, entry 15) participated in this reaction giving the corresponding bis-allyl derivatives although in relatively low yields. The reaction of tetrasubstituted alkenes

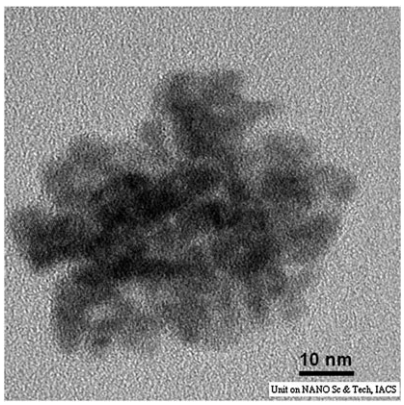


Fig. 2 TEM image of Pd nanoparticles formed in the reaction mixture in the absence of TBAB.

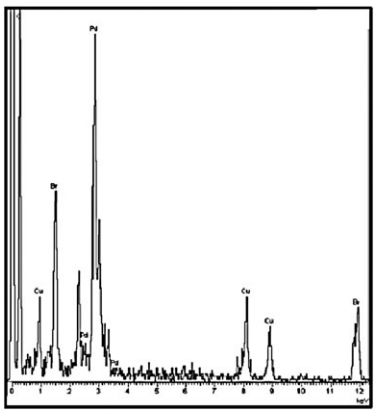


Fig. 3 EDX spectra of Pd nanoparticles.

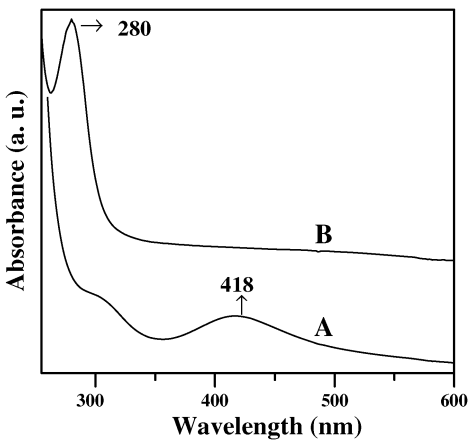
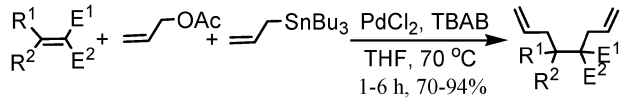


Fig. 4 UV spectra of Pd; A = $PdCl_2$, B = reaction mixture.

is not addressed in any existing methods and Yamamoto *et al.*[1] reported only a trace of product for dimethylethylidene malononitrile even after running the reaction for one week. On the other hand, we have been able to isolate 38% of this product by the present procedure which speaks of its better efficiency. The ethylidene cyanoesters also underwent this reaction (Table 2, entries 16–19) without any difficulty although a mixture of diastereoisomers was obtained. Thus, this protocol provides an easy access to a wide range of

Table 2 Palladium nanoparticles catalyzed double allylation of activated olefins with allyl acetates and allyltributylstannane



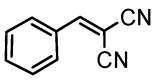
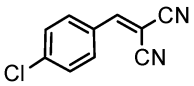
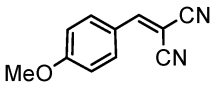
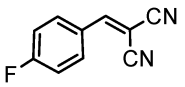
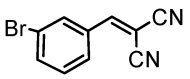
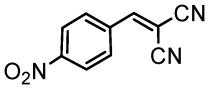
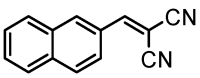
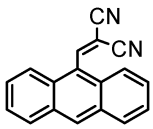
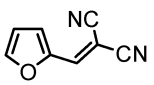
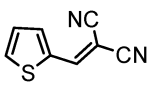
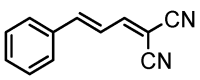
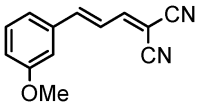
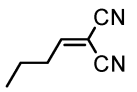
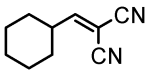
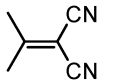
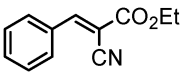
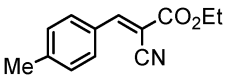
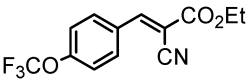
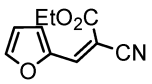
Entry	Olefin	Time/h	Yield of product[a] (%)	Turnover no.	Ref.
1		2.0	92	23	2
2		2.0	94	24	
3		1.5	90	23	1
4		4.0	92	23	
5		2.0	88	22	
6		6.0	70	18	
7		6.0	78	20	
8		6.0	75	19	
9		2.0	91	23	1
10		2.0	90	23	
11		3.0	94	21	
12		2.5	82	21	
13		2.0	88	22	1

Table 2 (*continued*)

Entry	Olefin	Time/h	Yield of product[a] (%)	Turnover no.	Ref.
14		5.0	85	21	
15		15	38	10	
16		6.0	86 (66/34)	22	1
17		5.5	82 (63/37)	21	
18		6.0	80 (71/29)	20	
19		4.5	90 (98/2)	23	1

[a] Yield refers to those of purified isolated products characterized by spectroscopic data (1R, ^{1}H NMR, ^{13}C NMR).

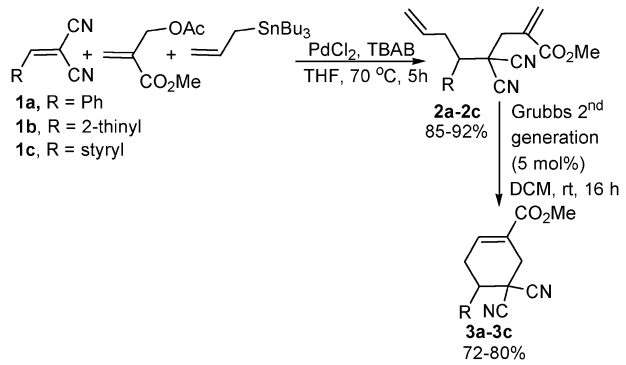
functionalized 1,7-octadiene derivatives which are known to have versatile applications in organic synthesis.[23,24]

To address the issue of regiochemistry a few selected ethylidene malononitriles (Scheme 2, **1a**, **1b**, **1c**) were reacted with methyl 2-(acetoxymethyl)acrylate and allyltri-(*n*-butyl)-stannane by this procedure. Although a single product was obtained in each case, the identity of these isomers (**2a**, **2b**, **2c**) was not established beyond doubt by spectroscopic (^{1}H and ^{13}C NMR) data.

Thus, these products were subjected to ring closing metathesis reaction using Grubbs second generation catalyst to produce the corresponding cyclized derivatives as crystalline solids and XRD analysis[25] confirmed the structures of **3a** and **3b** (Fig. 5) (we failed to get a good single crystal for **3c**). The formation of cyclohexene derivatives **3a**, **3b** and **3c** from **2a**, **2b** and **2c** suggested that the allyl group from the allyl acetates adds to the carbon bearing cyano groups and the allyl moiety from allylstannane to the carbon bonded to the phenyl/alkyl group. The same pattern of regioselectivity was observed in all three (**2a–2c**) reactions.

The substituted cyclohexene derivatives constitute the core unit of many natural products and thus their synthesis is of much importance.[26–28] By utilizing this protocol we have provided an easy access to several stereodefined diversely substituted cyclohexene compounds as illustrated in Scheme 3.

The reactions are, in general, very clean and high yielding. Palladium nanoparticles are generated *in situ* in the reaction mixture. Several functionalities such as Cl, Br, F, OMe, NO_2, OCF_3, CO_2Et and sensitive moieties such as furan and thiophene are compatible with this procedure. The catalyst was



Scheme 2 Allylations with 2-carbomethoxy allyl acetate followed by cyclization.

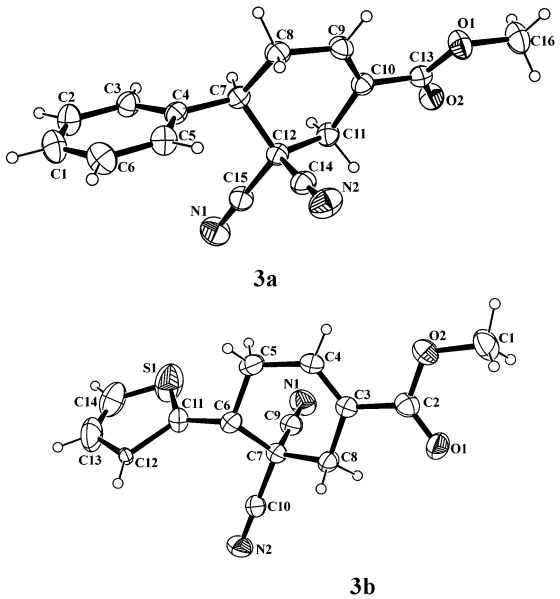
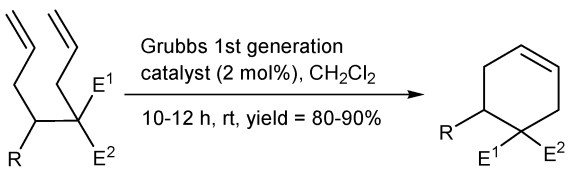


Fig. 5 ORTEP diagrams of the products **3a** and **3b**.



4a, R = Ph, E^1 = CN, E^2 = CN
4b, R = c-C_6H_{11}, E^1 = CN, E^2 = CN
4c, R = styryl, E^1 = CN, E^2 = CN
4d, R = 2-thinyl, E^1 = CN, E^2 = CN
4e, R= n-C_3H_7, E^1 = CN, E^2 = CN
4f, R = 4-Me-C_6H_4, E^1 = CN, E^2 = CO_2Et
4g, R = 4-OCF_3-C_6H_4, E^1 = CN, E^2 = CO_2Et

Scheme 3 Synthesis of cyclohexene derivatives.

recycled for three times with decreasing yield in every cycle (1st run—92%, 2nd run—72%, 3rd run—51%, 4th run—38%) possibly due to agglomerization of Pd nanoparticles after every cycle.[12]

Regarding the mechanism of the reaction it is proposed that allyl acetate undergoes oxidative addition to Pd(0) to produce a π-allylpalladium complex I which then interacts with tributylallyl stannane to give bis-π-allylpalladium complex II. Complex II reacts with the activated alkene to form intermediate III which on reductive elimination provides the product and regenerates Pd(0) (Scheme 4).[1] The involvement of both allyl acetate and allyltri-(*n*-butyl)stannane for a successful reaction, as delineated here, gained support by the fact that when the reaction was carried out in the presence of one equivalent of activated olefin and two equivalents of either allyltributylstannane or allyl acetate, no bis-allylated product was isolated.

For reactions with carbomethoxy-substituted allylic acetates (Scheme 2) it is likely that the relatively nucleophilic allyl moiety coming from the stannane part adds to the electrophilic β-position of ethylidene malononitrile followed by subsequent interaction with the more electrophilic carbon at the other allyl moiety containing electron withdrawing CO_2Me producing the octadienes **2a–2c** regioselectively.[7]

Conclusions

In conclusion, we have developed an efficient one pot procedure for an amphiphilic bis-allylation of activated alkenes by allyl acetates and tributylallyl stannanes to produce functionalized 1,7-octadiene derivatives catalyzed by palladium nanoparticles. We have also successfully utilized the octadienes for the synthesis of stereodefined substituted cyclohexenes. The significant advantages offered by this procedure are use of readily available, moderately active and configurationally stable allyl acetates[29] in place of conventional allyl halides, remarkable regioselectivity for carbomethoxy-substituted allyl acetates, reaction with tetrasubstituted alkene and high yields. This also demonstrates the potential of palladium nanoparticles as efficient catalysts[10–12,30] in organic reactions.

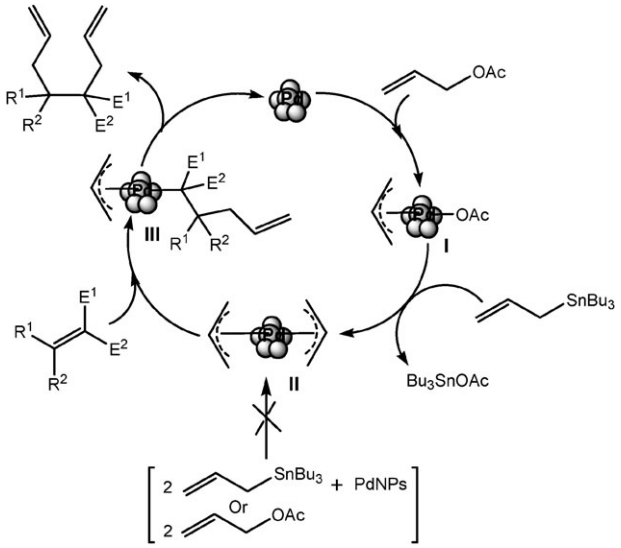
Experimental

General comments

IR spectra were recorded on a Shimadzu 8300 FTIR spectrometer in neat. ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker DPX-300 instrument at 300 MHz and 75 MHz respectively. HRMS were taken on a Microtek Qtof Micro YA263 spectrometer. The suspension of nanoparticles in THF was drop-cast onto a carbon-coated copper grid and TEM image was taken on a JEM-2011 (JEOL) microscope of a dry powder. All commercial reagents were distilled before use.

Representative procedure for the allylation of phenylethylidene malononitrile, allyl acetate and allyltributyl stannane (Table 2, entry 1)

A mixture of 2-benzylidenemalononitrile (154 mg, 1 mmol), allyl acetate (300 mg, 3 mmol), allyltri-(*n*-butyl)stannane (397 mg, 1.2 mmol), $PdCl_2$ (7 mg, 4 mol%), tetra-(*n*-butyl)-ammonium bromide (323 mg, 1 mmol) in THF (4 mL) was heated with stirring at 70 °C under nitrogen for 2 h (TLC). The reaction mixture was extracted with Et_2O, washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent left the



Scheme 4 Possible mechanism for double allylation reaction.

crude product which was purified by column chromatography over silica gel (60–120 mesh) (hexane/ether 97 : 3) to provide 2-allyl-2-(1-phenyl-but-3-enyl) malononitrile as a colorless oil (217 mg, 92%). The spectroscopic data of this compound are in good agreement with those reported.[2] This procedure was followed for all the reactions in Table 2.

A few of these products are known compounds (see references in Table 2) and were easily identified by comparison of their spectroscopic data with those reported. The unknown compounds were properly characterized by their IR, ^{1}H NMR, ^{13}C NMR, HRMS and C, H, N-analysis. These data are given below in order of their entries in Table 2, Scheme 2 and Scheme 3.

2-Allyl-2-[1-(4-chlorophenyl)but-3-enyl]malononitrile [Table 2, entry 2]. Colorless liquid. ν_{max}/cm^{-1} 3084, 2926, 2856, 2249, 1643, 1597, 1495, 1443, 1416, 1096, 991, 929. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.37–2.55 (m, 2H), 2.80–2.90 (m, 2H), 3.08 (dd, J_1 = 11.5 Hz, J_2 = 3.9 Hz, 1H), 4.96–5.09 (m, 2H), 5.29–5.50 (m, 3H), 5.83–5.92 (m, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.0, 40.5, 43.1, 50.6, 114.3, 115.1, 118.9, 123.4, 128.6, 129.5 (2C), 130.4 (2C), 133.1, 133.6, 135.1. Anal Calcd for $C_{16}H_{15}ClN_2$: C 70.98, H 5.58, N 10.35%. Found: C 70.84, H 5.43, N 10.47%.

2-Allyl-2-[1-(4-fluorophenyl)but-3-enyl]malononitrile [Table 2, entry 4]. Colorless liquid. ν_{max}/cm^{-1} 3082, 2984, 2926, 2247, 1643, 1593, 1570, 1477, 1431, 1076, 991, 929. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.39–2.58 (m, 2H), 2.81–2.96 (m, 2H), 3.12 (dd, J_1 = 11.5 Hz, J_2 = 3.3 Hz, 1H), 4.99–5.11 (m, 2H), 5.32–5.56 (m, 3H), 5.84–5.97 (m, 1H), 7.12 (t, J = 8.4 Hz, 2H), 7.33–7.37 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.1, 40.4, 43.2, 50.3, 114.3, 115.1, 116.2 (d, J = 21.4 Hz, 2C), 118.7, 123.3, 128.6, 130.7 (d, J = 8.2 Hz, 2C), 133.2 (2C), 162.9 (d, J = 246.9 Hz). Anal Calcd for $C_{16}H_{15}FN_2$: C 75.57, H 5.95, N 11.02%. Found: C 75.40, H 5.94, N 10.89%.

2-Allyl-2-[1-(3-bromophenyl)but-3-enyl]malononitrile [Table 2, entry 5]. Pale yellow liquid. ν_{max}/cm^{-1} 3084, 2926, 2247, 1643, 1604, 1512, 1441, 1230, 1163, 991. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.38–2.57 (m, 2H), 2.81–2.94 (m, 2H), 3.07 (dd, J_1 = 11.5 Hz, J_2 = 3.9 Hz, 1H), 4.98–5.11 (m, 2H), 5.31–5.53 (m, 3H), 5.84–5.93 (m, 1H), 7.26–7.35 (m, 2H), 7.50 (t, J = 8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.0, 40.4, 42.9, 50.6, 114.1, 114.9, 119.0, 123.1, 123.4, 127.4, 128.5, 130.7, 132.2, 132.3, 132.9, 137.4. Anal Calcd for $C_{16}H_{15}BrN_2$: C 60.97, H 4.80, N 8.89%. Found: C 60.77, H 4.90, N 8.69%.

2-Allyl-2-[1-(4-nitrophenyl)but-3-enyl]malononitrile [Table 2, entry 6]. Pale brown liquid. ν_{max}/cm^{-1} 3084, 2983, 2926, 2856, 2249, 1643, 1606, 1525, 1441, 1350, 1317, 1111, 991, 934. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.40–2.52 (m, 2H), 2.74–2.91 (m, 2H), 3.19 (dd, J_1 = 11.5 Hz, J_2 = 3.8 Hz, 1H), 4.89–5.00 (m, 2H), 5.24–5.38 (m, 3H), 5.74–5.87 (m, 1H), 7.48 (d, J = 8.5 Hz, 2H), 8.17 (d, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 35.6, 40.3, 42.7, 50.3, 113.9, 114.5, 119.4, 123.6, 124.1 (2C), 128.1, 130.2 (2C), 132.3, 142.5, 148.2. Anal Calcd for $C_{16}H_{15}N_3O_2$: C 68.31, H 5.37, N 14.94%. Found: C 68.19, H 5.26, N 14.73%.

2-Allyl-2-[1-(naphthalen-2-yl)but-3-enyl]malononitrile [Table 2, entry 7]. Pale yellow liquid. ν_{max}/cm^{-1} 3061, 3016, 2982, 2926, 2850, 2247, 1642, 1628, 1599, 1441, 1346, 1273, 1170, 991, 929. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.21–2.43 (m, 2H), 2.88 (t, J = 6.9 Hz, 2H), 3.14 (t, J = 7.7 Hz, 1H), 4.78–4.98 (m, 2H), 5.11–5.25 (m, 2H), 5.33–5.44 (m, 1H), 5.69–5.82 (m, 1H), 7.38–7.51 (m, 2H), 7.66–7.85 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.2, 40.5, 43.2, 51.3, 114.6, 115.4, 118.6, 122.7, 123.1, 125.7, 126.7, 126.8, 128.0, 128.8, 128.9, 129.1, 129.2, 132.4, 133.4, 134.6. Anal Calcd for $C_{20}H_{18}N_2$: C 83.88, H 6.34, N 9.78%. Found: C 83.69, H 6.26, N 9.62%.

2-Allyl-2-[1-(anthracen-10-yl)but-3-enyl]malononitrile [Table 2, entry 8]. Pale brown liquid. ν_{max}/cm^{-1} 3069, 3051, 3018, 2955, 2930, 2245, 1670, 1641, 1599, 1452, 1306, 1217, 1033, 929. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.66–2.87 (m, 2H), 3.12–3.32 (m, 2H), 3.49–3.67 (m, 1H), 5.12–5.26 (m, 2H), 5.45–5.69 (m, 2H), 5.86–5.96 (m, 1H), 6.21–6.25 (m, 1H), 7.20–7.35 (m, 3H), 7.47–7.49 (m, 3H), 8.00 (d, J = 8.2 Hz, 2H), 8.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 42.1, 44.4, 45.4, 54.2, 117.7, 119.5, 123.5, 124.6 (2C), 124.9, 125.5 (2C), 125.9, 126.1, 126.4, 126.8, 128.1, 129.2 (2C), 129.3 (2C), 131.6, 134.6, 135.2. Anal Calcd for $C_{24}H_{20}N_2$: C 85.68, H 5.99, N 8.33%. Found: C 85.46, H 5.85, N 8.12%.

2-Allyl-2-[1-(thiophen-2-yl)but-3-enyl]malononitrile [Table 2, entry 10]. Colorless liquid. ν_{max}/cm^{-1} 3084, 2951, 2926, 2249, 1643, 1443, 1149, 1014, 991, 931. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.50–2.55 (m, 2H), 2.80–2.95 (m, 2H), 3.41 (dd, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 1H), 5.01–5.15 (m, 2H), 5.32–5.45 (m, 2H), 5.52–5.62 (m, 1H), 5.85–5.94 (m, 1H), 7.03–7.05 (m, 1H), 7.09–7.11 (m, 1H), 7.32–7.34 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 37.9, 40.1, 43.4, 46.8, 114.1, 114.9, 118.8, 123.2, 126.1, 127.2, 127.7, 128.5, 132.9, 137.1. Anal Calcd for $C_{14}H_{14}N_2S$: C 69.39, H 5.82, N 11.56%. Found: C 69.18, H 5.64, N 11.38%.

2-Allyl-2-[(*E*)-1-phenylhexa-1,5-dien-3-yl]malononitrile [Table 2, entry 11]. Pale yellow liquid. ν_{max}/cm^{-1} 3082, 3028, 2982, 2957, 2852, 2247, 1642, 1494, 1441, 1417, 989, 970. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.40–2.72 (m, 5H), 5.01–5.12 (m, 2H), 5.28–5.36 (m, 2H), 5.45–5.78 (m, 1H), 5.83–5.94 (m, 1H), 6.48 (d, J = 15.7 Hz, 1H), 7.21–7.33 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.0, 40.2, 41.9, 49.2, 114.1, 114.8, 118.6, 123.1, 123.3, 126.6 (2C), 128.7, 128.9, 129.0 (2C), 133.4, 135.4, 137.2. Anal Calcd for $C_{18}H_{18}N_2$: C 82.41, H 6.92, N 10.68%. Found: C 82.26, H 6.74, N 10.76%.

2-Allyl-2-[(*E*)-1-(2-methoxyphenyl)hexa-1,5-dien-3-yl]malononitrile [Table 2, entry 12]. Pale yellow liquid. ν_{max}/cm^{-1} 3007, 2957, 2926, 2872, 2854, 2247, 1601, 1585, 1494, 1454, 1438, 1292, 1262, 1047. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.39–2.48 (m, 2H), 2.68–3.03 (m, 3H), 3.82 (s, 3H), 4.96–5.46 (m, 4H), 5.71–5.90 (m, 2H), 6.52 (d, J = 15.8 Hz, 1H), 6.88–6.94 (m, 3H), 7.26–7.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.3, 40.5, 43.1, 51.3, 55.3, 114.2 (2C), 114.7, 115.4, 118.5, 121.2, 123.1, 128.8, 130.2, 133.4, 136.5, 137.4, 160.0. Anal Calcd for $C_{19}H_{20}N_2O$: C 78.05, H 6.89, N 9.58%. Found: C 77.88, H 6.76, N 9.37%.

2-Allyl-2-(1-cyclohexylbut-3-enyl)malononitrile [Table 2, entry 14]. Colorless liquid. ν_{max}/cm^{-1} 2933, 2856, 2245, 1657, 1543, 1485, 1344, 1261, 989, 933. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.25–1.35 (m, 2H), 1.62–1.93 (m, 8H), 2.15 (broad, 2H), 2.47–2.48 (m, 2H), 2.79 (d, J = 7.1 Hz, 2H), 5.05–5.23 (m, 2H), 5.36–5.45 (m, 2H), 5.87–5.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 25.8, 26.3, 28.2, 30.7, 32.6, 36.9, 40.8, 41.1, 43.1, 48.4, 112.2, 115.3, 117.8, 123.1, 128.8, 136.5. Anal Calcd for $C_{16}H_{22}N_2$: C 79.29, H 9.15, N 11.56%. Found: C 79.01, H 8.99, N 11.38%.

2-Allyl-2-(2-methylpent-4-en-2-yl)malononitrile [Table 2, entry 15]. Colorless liquid. ν_{max}/cm^{-1} 2974, 2936, 2918, 2245, 1663, 1465, 1440, 1390, 1379, 1207, 991, 937. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.21 (s, 6H), 2.32 (d, J = 12.2 Hz, 2H), 2.61 (d, J = 12.3 Hz, 2H), 5.15–5.23 (m, 2H), 5.39–5.45 (m, 2H), 5.45–5.79 (m, 1H), 5.94–5.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 22.5 (2C), 36.5, 40.8, 42.3, 49.1, 114.7 (2C), 120.2, 122.7, 129.7, 131.9. Anal Calcd for $C_{12}H_{16}N_2$: C 76.55, H 8.57, N 14.88%. Found: C 76.35, H 8.41, N 14.68%.

Ethyl 2-allyl-2-cyano-3-*p*-tolylhex-5-enoate (mixture of two isomers) [Table 2, entry 17]. Colorless liquid. ν_{max}/cm^{-1} 3007, 2982, 2926, 2243, 1742, 1641, 1443, 1298, 1225, 1145, 993. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.94 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.1Hz, 3H), 2.29 (s, 3H), 2.33 (s, 3H), 2.37–2.44 (m, 2H), 2.70–2.83 (m, 6H), 3.02–3.17 (m, 2H), 3.88 (q, J = 7.1 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 4.86–5.28 (m, 8H), 5.43–5.49 (m, 2H), 5.76–5.82 (m, 2H), 7.07–7.26 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.6, 14.2, 21.0, 21.1, 34.8, 36.7, 40.5, 41.2, 50.5, 50.9, 55.0, 55.8, 62.2, 62.8, 117.4, 118.0, 118.2, 120.4, 120.9, 128.8 (4C), 129.1 (4C), 129.4, 130.7, 130.8, 133.9, 134.5, 134.7, 134.8, 137.5, 137.9, 167.4, 168.7. Anal Calcd for $C_{19}H_{23}NO_2$: C 76.73, H 7.80, N 4.71%. Found: C 76.55, H 7.63, N 4.67%.

Ethyl 2-allyl-2-cyano-3-(4-(trifluoromethoxy)phenyl)hex-5-enoate (mixture of two isomers) [Table 2, entry 18]. Colorless liquid. ν_{max}/cm^{-1} 3015, 2983, 2933, 2244, 1742, 1510, 1442, 1261, 1225, 1167, 923. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.91 (t, J = 7.0 Hz, 3H), 1.38 (t, J = 7.0 Hz, 3H), 2.41–2.46 (m, 2H), 2.72–2.89 (m, 6H), 3.09–3.18 (m, 2H), 3.88 (q, J = 7.0 Hz, 2H), 4.30 (q, J = 7.0 Hz, 2H), 4.90–5.31 (m, 8H), 5.40–5.51 (m, 2H), 5.77–5.85 (m, 2H), 7.15–7.23 (m, 4H), 7.35–7.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.5, 14.1, 34.8, 36.7, 40.6, 41.2, 50.1, 50.6, 54.7, 55.5, 62.4, 62.9, 117.7, 117.8, 117.9 (2C), 118.7, 120.7 (4C), 120.8, 121.0, 121.2, 122.1, 130.3 (4C), 130.4, 130.5, 134.1, 135.7, 136.5, 148.8, 148.9, 167.2, 168.4. Anal Calcd for $C_{19}H_{20}F_3NO_3$: C 62.12, H 5.49, N 3.81%. Found: C 62.32, H 5.27, N 4.29%.

Methyl 4,4-dicyano-2-methylene-5-phenylhept-6-enoate [Scheme 2, 2a]. Colorless liquid. ν_{max}/cm^{-1} 2957, 2924, 2872, 2854, 2247, 1726, 1634, 1442, 1303, 1163. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.57 (dd, J_1 = 13.9 Hz, J_2 = 0.6 Hz, 1H), 2.88–2.96 (m, 3H), 3.14 (dd, J_1 = 11.2 Hz, J_2 = 4.3 Hz, 1H), 3.77 (s, 3H), 4.94–5.10 (m, 2H), 5.45–5.54 (m, 1H), 5.95 (s, 1H), 6.52 (s, 1H), 7.33–7.41 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.2, 37.1, 43.6, 52.4, 52.5, 114.2, 115.1, 118.6, 129.1 (2C), 129.2 (3C), 131.9, 133.0, 133.4, 135.0, 166.1. HRMS Calcd for $C_{18}H_{18}N_2O_2$ $[M + Na]^+$: 317.1266. Found: 317.1261.

Methyl 4,4-dicyano-2-methylene-5-(thiophen-2-yl)-oct-7-enoate [Scheme 2, 2b]. Colorless liquid. ν_{max}/cm^{-1} 3080, 3003, 2953, 2850, 2247, 1724, 1634, 1441, 1305, 1163. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.72 (d, J = 14.0 Hz, 1H), 2.77–3.01 (m, 3H), 3.48 (dd, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 1H), 3.79 (s, 3H), 5.02–5.16 (m, 2H), 5.52–5.62 (m, 1H), 5.99 (s, 1H), 6.55 (s, 1H), 7.06 (dd, J_1 = 5.1 Hz, J_2 = 3.6 Hz, 1H), 7.12–7.14 (m, 1H), 7.34 (d, J = 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.8, 37.9, 43.9, 48.1, 52.5, 113.9, 114.7, 118.9, 126.3, 127.4, 127.9, 131.9, 132.9 (2C), 137.2, 166.0. HRMS Calcd for $C_{16}H_{16}N_2O_2S$ $[M + Na]^+$: 323.0830. Found: 323.0830.

Methyl 4,4-dicyano-2-methylene-5-styrylhept-6-enoate [Scheme 2, 2c]. Pale yellow liquid. ν_{max}/cm^{-1} 3082, 3028, 3005, 2982, 2912, 2247, 1726, 1631, 1442, 1305, 1163, 970. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.38–2.55 (m, 1H), 2.74–2.81 (m, 2H), 2.95–3.09 (m, 2H), 3.80 (s, 3H), 5.13–5.23 (m, 2H), 5.71–5.76 (m, 1H), 5.97–6.06 (m, 1H), 6.60 (s, 1H), 6.63 (d, J = 15.5 Hz, 1H), 7.34–7.46 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 36.0, 36.9, 42.6, 50.6, 52.5, 113.9, 114.6, 118.7, 123.4, 126.8 (2C), 128.5, 129.0 (2C), 131.9, 133.0, 133.4, 135.5, 137.6, 166.1. HRMS Calcd for $C_{20}H_{20}N_2O_2$ $[M + Na]^+$: 343.1422. Found: 343.1421.

Methyl 5,5-dicyano-4-phenylcyclohex-1-enecarboxylate [Scheme 2, 3a]. White crystalline solid. mp 100–102 °C; ν_{max}/cm^{-1} 3032, 2953, 2850, 2251, 1715, 1659, 1456, 1437, 1278, 1261, 1236, 1105, 1078. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.70–2.75 (m, 1H), 2.86–2.92 (m, 1H), 2.97–3.02 (m, 1H), 3.18–3.28 (m, 1H), 3.27 (d, J = 18 Hz, 1H), 3.75 (s, 3H), 7.17–7.19 (m, 1H), 7.35–7.37 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 29.3, 34.8, 37.2, 45.3, 52.3,

113.9, 114.8, 124.8, 128.1 (2C), 129.2 (2C), 129.4, 136.1, 138.8, 165.2. HRMS Calcd for $C_{16}H_{14}N_2O_2$ $[M + Na]^+$: 289.0953. Found: 289.0955.

Methyl 5,5-dicyano-4-(thiophen-2-yl)cyclohex-1-enecarboxylate [Scheme 2, 3b]. White crystalline solid. mp 84–86 °C. ν_{max}/cm^{-1} 3111, 3022, 2953, 2253, 1715, 1659, 1437, 1383, 1265, 1236, 1103, 1018. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.87–2.93 (m, 2H), 3.03–3.08 (m, 1H), 3.35 (d, J = 18 Hz, 1H), 3.62–3.65 (m, 1H), 3.81 (s, 3H), 7.07 (t, J = 4.5 Hz, 1H), 7.18 (broad, 1H), 7.22 (d, J = 3.5 Hz, 1H), 7.35 (d, J = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 31.0, 33.9, 38.1, 40.9, 52.4, 113.7, 114.8, 124.9, 126.2, 127.5, 127.6, 137.9, 138.1, 165.1. HRMS Calcd for $C_{14}H_{12}N_2O_2S$ $[M + Na]^+$: 295.0517. Found: 295.0514.

Methyl 5,5-dicyano-4-styrylcyclohex-1-enecarboxylate [Scheme 2, 3c]. Colorless low melting solid. ν_{max}/cm^{-1} 3064, 3015, 2946, 2916, 2249, 1728, 1645, 1440, 1365, 1232, 991. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.59–2.79 (m, 2H), 2.94–3.03 (m, 2H), 3.35 (d, J = 17.5 Hz, 1H), 3.84 (s, 3H), 6.15–6.19 (m, 1H), 6.78 (d, J = 15.5 Hz, 1H), 7.17 (broad, 1H), 7.28–7.34 (m, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 28.8, 33.2, 36.3, 43.0, 52.4, 113.8, 115.1, 123.6, 124.7, 126.9 (2C), 128.8 (2C), 128.9, 135.5, 136.8, 137.8, 165.3. HRMS Calcd for $C_{18}H_{16}N_2O_2$ $[M + Na]^+$: 315.1110. Found: 315.1113.

6-Phenylcyclohex-3-ene-1,1-dicarbonitrile [Scheme 3, 5a]. Colorless liquid. ν_{max}/cm^{-1} 3038, 2917, 2849, 2251, 1658, 1604, 1498, 1454, 1435, 1340, 1101. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.52–2.59 (m, 1H), 2.73–2.93 (m, 3H), 3.23–3.29 (m, 1H), 5.69–5.76 (m, 1H), 5.96–6.05 (m, 1H), 7.38–7.51 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 28.7, 35.9, 37.0, 45.8, 114.5, 115.4, 120.2, 127.9, 128.1 (2C), 129.0 (2C), 129.1, 137.2. Anal Calcd for $C_{14}H_{12}N_2$: C 80.74, H 5.81, N 13.45%. Found: C 80.60, H 5.56, N 13.49%.

6-Cyclohexylcyclohex-3-ene-1,1-dicarbonitrile [Scheme 3, 5b]. Colorless liquid. ν_{max}/cm^{-1} 2928, 2854, 2245, 1450, 1435, 1244, 1095, 985. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.06–1.42 (m, 5H), 1.58–2.01 (m, 7H), 2.25 (m, 2H), 2.75–2.90 (m, 2H), 5.58–5.61 (m, 1H), 5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 23.6, 26.2, 26.7, 26.9, 32.0, 36.9, 37.7, 40.2, 43.2, 45.5, 115.4, 115.9, 120.1, 128.5. Anal Calcd for $C_{14}H_{18}N_2$: C 78.46, H 8.47, N 13.07%. Found: C 78.28, H 8.37, N 13.18%.

6-Propylcyclohex-3-ene-1,1-dicarbonitrile [Scheme 3, 5c]. Colorless liquid. ν_{max}/cm^{-1} 2962, 2933, 2876, 2249, 1464, 1435, 1383, 1103. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.98 (t, J = 7.1 Hz, 3H), 1.35–1.56 (m, 4H), 1.87–2.10 (m, 3H), 2.76–2.88 (m, 2H), 5.60–5.65 (m, 1H), 5.84–5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.8, 19.5, 27.2, 34.4, 34.8, 36.4, 39.4, 114.5, 116.1, 120.0, 127.2. HRMS Calcd for $C_{11}H_{14}N_2$ $[M + H]^+$: 175.1230. Found: 175.1236.

6-Styrylcyclohex-3-ene-1,1-dicarbonitrile [Scheme 3, 5d]. Colorless liquid. ν_{max}/cm^{-1} 3037, 2914, 2843, 2249, 1658, 1494, 1433, 968. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.44–2.48 (m, 2H), 2.82–2.93 (m, 3H), 5.66–5.71 (m, 1H), 5.89–5.90 (m, 1H), 6.16–6.24 (m, 1H), 6.76 (d, J = 15.7 Hz, 1H), 7.30–7.47 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 27.9, 34.0, 35.8, 43.4, 114.3, 115.7, 120.3, 124.7, 126.8 (2C), 128.2, 128.5, 128.7 (2C), 129.1, 135.8. HRMS Calcd for $C_{16}H_{14}N_2$ $[M + Na]^+$: 257.1055. Found: 257.1058.

6-(Thiophen-2-yl)cyclohex-3-ene-1,1-dicarbonitrile [Scheme 3, 5e]. Colorless liquid. ν_{max}/cm^{-1} 3042, 2916, 2841, 2249, 1660, 1433, 1248. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.69–2.78 (m, 2H), 2.92–2.99 (m, 2H), 3.63 (t, J = 7.6 Hz, 1H), 5.71–5.74 (m, 1H), 5.95–5.99 (m, 1H), 7.02–7.08 (m, 1H), 7.18–7.26 (m, 1H), 7.28–7.34 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 30.4, 35.2, 37.9, 41.3, 114.3, 115.4, 120.4, 125.8, 127.2, 127.3, 127.4, 139.4. HRMS Calcd for $C_{12}H_{10}N_2S$ $[M + Na]^+$: 237.0462. Found: 237.0463.

Ethyl 1-cyano-6-(4-(trifluoromethoxy)phenyl)cyclohex-3-enecarboxylate (mixture of two isomers) [Scheme 3, 5f]. Colorless liquid. ν_{max}/cm^{-1} 3034, 2982, 2922, 2242, 1742, 1516, 1433, 1367, 1275, 1258, 1230, 1194, 1078. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.81 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 2.31–2.90 (m, 8H), 3.17–3.22 (m, 2H), 3.89 (q, J = 7.1 Hz, 2H), 4.05–4.09 (m, 2H), 5.68–5.96 (m, 4H), 7.05 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.4, 13.8, 28.6, 29.2, 30.0, 34.9, 43.2, 45.2, 46.1, 49.2, 62.6, 62.7, 116.0, 118.0, 118.7, 119.6, 120.8, 121.1 (2C), 121.8 (2C), 122.1, 122.7, 126.8, 126.9 (2C), 129.7 (2C), 129.8, 137.6, 137.8, 148.9, 166.9, 168.3. Anal Calcd for $C_{17}H_{16}F_3NO_3$: C 60.18, H 4.75, N 4.13%. Found: C 60.45, H 4.83, N 4.46%.

Ethyl 1-cyano-6-(furan-2-yl)cyclohex-3-enecarboxylate [Scheme 3, 5g]. Colorless liquid. ν_{max}/cm^{-1} 3038, 2983, 2931, 2906, 2239, 1742, 1502, 1435, 1255, 1224. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.31 (t, J = 7.1 Hz, 3H), 2.46–2.56 (m, 3H), 2.83–2.92 (m, 1H), 3.81–3.83 (m, 1H), 4.22–4.30 (m, 2H), 5.68–5.73 (m, 1H), 5.85–5.89 (m, 1H), 6.17–6.18 (m, 1H), 6.27–6.29 (m, 1H), 7.26 (broad, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.8, 27.6, 28.7, 37.9, 44.9, 62.8, 107.9, 110.4, 119.3, 122.3, 125.1, 141.9, 152.1, 167.0. HRMS Calcd for $C_{14}H_{15}NO_3$ $[M + Na]^+$: 268.0950. Found: 268.0957.

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