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Photocatalytic $E \rightarrow Z$ Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity

Jan B. Metternich, Denis G. Artiukhin, Mareike C. Holland, Maximilian von Bremen-Kühne, Johannes Neugebauer* and Ryan Gilmour**

Institute for Organic Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany.

KEYWORDS. Biomimetic; Mechanism; Photocatalysis; Flavin.

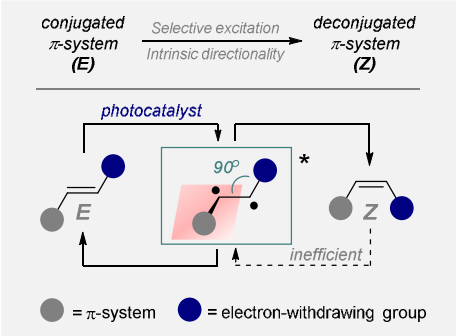
ABSTRACT: Iteratively executed with exquisite spatial and temporal control, the selective isomerization of polarized alkenes underpins a plethora of complex biological processes ranging from natural product biosynthesis through to the mammalian visual cycle. However, *Nature's* proficiency conceals the inherent difficulties in replicating this *contra*-thermodynamic transformation in the laboratory. Recently, we disclosed the first highly *Z*-selective isomerization of polarized alkenes, employing the cinnamoyl chromophore as a retinal surrogate under UV-irradiation (402 nm) with (–)-riboflavin (vitamin B_2) as an inexpensive, organic photocatalyst (*J. Am. Chem. Soc*. **2015**, *137*, 11254–11257). This study was inspired by the propensity of crystalline (–)-riboflavin in the eyes of vertebrae to invert the intrinsic directionality of retinal isomerization. Herein, we extend this methodology to include a bio-inspired, catalytic $E \rightarrow Z$ isomerization of α,β-unsaturated nitriles, thereby mimicking the intermediate Opsin-derived, protonated Schiff base in the visual cycle with simple polarized alkenes. Replacement of the iminium motif by a cyano group is well tolerated and gives an additional degree of versatility for post-

isomerization functionalization. Broad substrate scope is demonstrated (up to 99:1 *Z*:*E*) together with evidence of mechanistic dichotomy via both singlet and triplet energy transfer mechanisms. Kinetic studies, temperature dependent photostationary state correlations and investigation of substituent-based electronic perturbation of the alkene identified polarization combined with increased *Z*-isomer activation barriers as the selectivity governing factors in catalysis. This investigation demonstrates the importance of internal structural preorganization on photostationary composition and explicates the augmented *Z*-selectivity upon hydrogen-alkyl exchange at the *β*-position of the alkene.

Introduction

Conceptualizing and consolidating biological structure – function interplay in a laboratory paradigm has become a hallmark of contemporary organocatalysis.[1] Inimitable in the mimesis of enzymatic catalysis,[2] this discipline's legacy is the platform to translate Nature's intricate reactivity modes into robust, practical chemical methods.[3] This juxtaposition, forged as traditional boundaries in the natural sciences coalesce,[4] ensures that rigorous mechanistic interrogation of biological catalysis continues to inspire and inform this expansive discipline. Unsurprisingly, the most celebrated covalent and non-covalent organocatalysts share common structural resemblances with the more complex biological ensembles from which they are inspired. This has resulted in structure-function relationships that have been definitively classified and are now widely exploited by practitioners of organic synthesis. With the emergent success of organic photocatalysis[5] comes the opportunity to capitalize on the rich tapestry of biological photosystems and thus utilize Nature's blueprints for reaction design. In contrast to covalent and non-covalent organocatalysis, establishing structure-based comparisons to biology in photochemistry is more challenging: This can be attributed to the sensitivity of biological photosystems when altered, or removed from the natural environment of the host protein.

Scheme 1 Conceptual framework for photocatalytic isomerization of polarized alkenes.



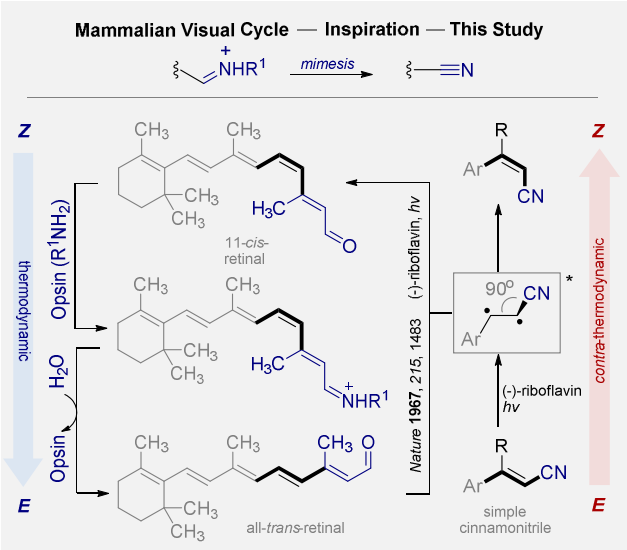
Nonetheless, the conceptual foundations of a variety of biological phenomena are adaptable and have been successfully translated to small molecule catalysis. Proton-coupled electron transfer (PCET), ubiquitous in enzymatic redox catalysis, beautifully exemplifies this notion.[6] As part of a broader interest in acyclic conformational control,[7] we recently became interested in the structural and photochemical prerequisites for retinal isomerization in the vertebrate visual cycle.[8] This curiosity arose from what was perceived to be a strategic gap in the catalysis ordnance, namely general strategies to realize the selective contra-thermodynamic $E \rightarrow Z$ isomerization of polarized alkenes using inexpensive small molecule photo-organocatalysts. This fundamental transformation has significant appeal both in terms of atom economy,[9] and in accessing configurationally defined alkenes for subsequent application in stereospecific transformations.[10] Bio-inspired organic photocatalysis offers a unique paradigm to redress this balance,[5] by amalgamating established photochemical activation modes with the structural and mechanistic precedents found in biology.

Laboratory precedent: It is pertinent to note that a survey of existing alkene isomerization catalysts reveals a rich body of literature describing positional isomerization, in contrast to the limited reports pertaining to geometric isomerization:[11] In both scenarios, transition metal complexes predominate. Organometallic catalysts based on Ir(III) have also proven to be highly effective in the photocatalytic isomerization of styrenyl derivatives as reported by Weaver and co-workers.[12] This latter example is particularly noteworthy on account of the efficiency and selectivity of catalysis, and reiterates the potential of photochemical activation modes in addressing the strategic gap in catalytic *Z*-selective

alkene isomerization. Despite this seminal report, the historic mechanistic delineation of the *E* to *Z*-isomerization of simple alkenes has remained relatively unutilized in small molecule catalyst design. Detailed investigations by Hammond,[13] Arai[14] and others,[15] carefully delineated the sensitized isomerization mechanisms of various stilbenes, styrenes and fumarates.[16] Whilst these important works provide valuable guidelines, scope, yields and translation to catalysis are conspicuously absent. Due to the nature of the experiments performed, stoichiometric quantities of organic sensitizers were routinely employed. Furthermore, examples of polarized, non-symmetrical alkenes are not disclosed despite their synthetic versatility. Many of these limitations also persist in the photochemical isomerization of alkenes facilitated by stoichiometric Lewis acids.[17]

It was envisaged that by integrating the stoichiometric sensitization paradigm delineated in the mid-20th century for non-polarized alkenes, with pioneering studies on the visual cycle from around the same time period,[18] that a theoretical framework could be constructed to facilitate the *Z*-selective isomerization of activated alkenes from the more abundant *E*-configured precursors. Conceptually, this would require an initial, substrate-selective sensitization of the starting material to confer directionality (Scheme 1). This would result from biasing the sensitization efficiency (catalyst-substrate > catalyst-product), and could likely be pre-determined at a structural level by perturbation of the inherent π-system following the catalysis event. This is achievable by inducing non-bonding interactions in the product *Z*-alkene to reduce conjugation and thereby alter the photophysical signature. Since the ephemeral intermediate generated by photocatalyst activation lacks the initial π-bond, an orthogonal arrangement of the substituent is preferred such that the system may collapse to either the *E*- or *Z*-isomer. Under a substrate-selective activation regime, iterative excitation would logically favor formation of the *Z*-isomer. Photochemical activation would thus mitigate the risk of microscopic reversibility and the formation of thermodynamic mixtures.

Scheme 2 Reaction design considerations. Left: the *Z*→*E* photoisomerization of retinal. Center: Qualitative report that (–)-riboflavin photocatalyzes the reverse reaction. Right: A bio-inspired catalytic, *Z*-selective isomerization of cinnamonitriles.



Precedence in biology: In vertebrae, 11-*cis*-retinal is isomerized, via the protonated Opsin-derived Schiff base, by retinal-isomerase to furnish all-*trans*-retinal (Scheme 2, left).[19] Iteratively performed with exquisite spacial and temporal efficiency, this process is the ultimate blueprint for photocatalyst-based alkene isomerization, but with one obvious caveat: In the visual cycle, the *Z*→*E* direction is favored in the photochemical process. However, a study from Walker and Radda in the 1960s, reported that crystalline (–)-riboflavin (vitamin B2), present in the eyes of various mammals and fish, facilitates the contra-thermodynamic *E*→*Z* isomerization of retinal (Scheme 2, center).[18] Although of a qualitative nature, this important study contained two critical details: (i) That an inexpensive, and commercially available co-factor can function as an effective *Z*-selective isomerization catalyst of a polarized alkene, and (ii) that by virtue of its location in the eye, a photocatalytic mechanism was likely operational. This important observation led to the conceptual framework for a generic photocatalytic isomerization of polarized alkene as summarized in Scheme 1.

Results and Discussion

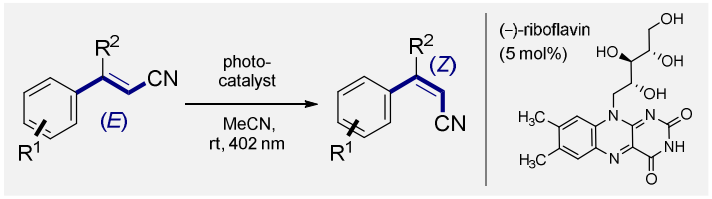
This laboratory recently reported that (–)-riboflavin is an efficient, inexpensive photocatalyst for the isomerization of α,β-unsaturated carbonyl compounds under UV-irradiation (402 nm) with low photocatalyst loadings (5 mol%).[20] By extension, the transformation can also be telescoped to generate coumarins directly from (*E*)-cinnamic acids via two discrete photochemical activation modes.[21] Thus, it has been possible to augment the synthetic virtuosity of flavins in organocatalysis to complement existing redox[22,23] cycloaddition[24] and halogenation processes.[25] In order to augment the scope of this bio-inspired transformation, a detailed mechanistic interrogation of catalysis was devised using cinnamonitrile as a model system. This versatile scaffold provides the requisite polarized olefin / chromophore and mimics the Opsin-derived Schiff base that undergoes isomerization in the visual cycle. Moreover, the nitrile group acts as a masked amine in this oxidized form and thereby alleviates the risk of competing, physical or chemical quenching mechanisms. This organocatalytic approach would complement the existing work of Weaver and co-workers using Ir(III) catalysis, to provide rapid entry to *Z*-configured allylic amine precursors.[12]

It was envisaged that the catalysis activation mode would not be adversely affected by the carbonyl to nitrile substitution in the substrate, such that the generic (*E*)-cinnamonitrile π-system would likely match the excitation energy of (–)-riboflavin. Moreover, selectivity enhancement would be possible by introduction of a β-substituent, thereby inducing non-bonding interactions in the product isomer. This would necessary tilt the π-system, leading to deconjugation and thus diminish activation efficiency (Scheme 2, right).

Expanding Substrate Scope: As a starting point for catalysis, commercially available cinnamonitrile **1** and (–)-riboflavin (5 mol%) were dissolved in MeCN and irradiated at 402 nm (Table 1). Gratifyingly, it was possible to recover the material quantitatively by simple filtration through a silica plug. Analysis by ^{1}H NMR spectroscopy confirmed a *Z*:*E* ratio 63:37 thereby providing an initial proof of concept. To substantiate the proposal that a β-substituent (R^2) would enhance selectivity by augmenting strain in the

product, a series of substituted cinnamonitriles were prepared (**2**-**10**) and submitted to standard photocatalysis conditions. As expected, this led to a significant improvement in the geometric ratios with excellent material recovery.

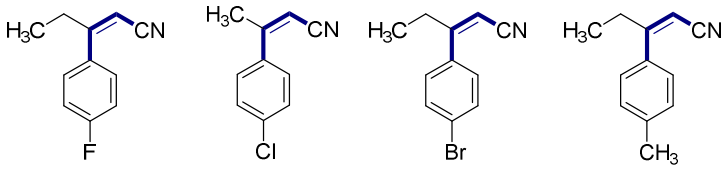
Table 1 The (–)-riboflavin-catalyzed isomerization of cinnamonitriles[a]



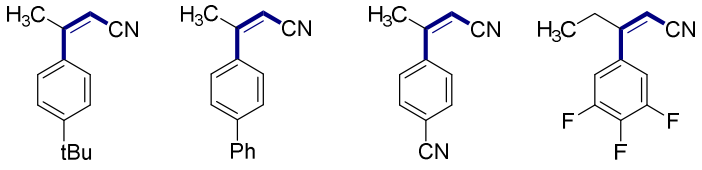
R_2 =	**1**	H	quant.	63:37
	2	Me	quant.	91:9
	3	Et	quant.	97:3
	4	*n*Pr	quant.	96:4
	5	*n*Bu	quant.	96:4
	6	*i*Pr	88%	96:4
	7	*i*Bu	quant.	95:5
	8	*cy*Pr	85%	95:5
	9	*t*Bu	quant.	8:92
	10	F	90%	45:55[b]

R_2 =	**11**	H	quant.	62:38
	12	Me	quant.	91:9
	13	Et	quant.	97:3
	14	*n*Pr	quant.	96:4
	15	*n*Bu	quant.	96:4

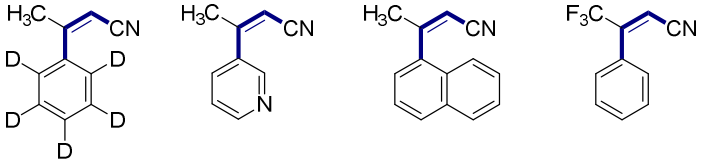
R_2 =	**16**	H	quant.	44:56
	17	Me	quant.	81:19
	18	Et	quant.	91:9
	19	*n*Pr	quant.	90:10
	20	*n*Bu	quant.	90:10



21 quant. 96:4 | **22** quant. 88:12 | **23** quant. 95:5 | **24** quant. 95:5



25 quant. 89:11 | **26** quant. 70:30 | **27** quant. 86:14 | **28** quant. 96:4



29 quant. 91:9 | **30** 82% 91:9 | **31** quant. 91:9 | **32** 88% 7:93[b]

[a] Standard reaction conditions: Reactions were performed with 0.1 mmol substrate (*E*:*Z* >20:1) at ambient temperature in MeCN using 5 mol% catalyst loading under 12 hours of UV-light irradiation (402 nm). *Z*:*E* ratios reported are the average of two experiments and were determined by ^{1}H NMR spectroscopy and HPLC analysis. [b] N.B. product *Z*:*E* ratio is inverted to reflect the higher IUPAC priority of F than C.

Installation of the methyl group (**2**) led to a *Z*:*E* ratio of 91:9 as determined by ^{1}H NMR spectroscopy, and this could be increased further to *Z*:*E* 97:3 when R^2 = Et (**3**). Extending the chain length to R^2 = *n*Pr (**4**) and R^2 = *n*Bu (**5**) led to a plateau in selectivity (*Z*:*E* 96:4). This was also observed in the branched cases where R^2 = *i*Pr (**6**) and R^2 = *i*Bu (**7**) led to *Z*:*E* ratios of 96:4 and 95:5, respectively. Substrate **8** where R^2 = *cy*Pr also gave a *Z*:*E* ratio of 95:5. Interestingly, isomerization of the *t*Bu derivative **9** proved to be challenging with only traces of the *Z*-isomer having been detected (*Z*:*E* 2:98). This is likely a consequence of 1,3-allylic strain in the starting material thus rotating the phenyl ring of the plane: This would disrupt conjugation of the chromophore π-system and renders substrate activation challenging. In contrast, substrates **2**-**8** contain at least one methine proton at the α-carbon of the substituent to minimize this unfavorable interaction. As a control experiment, the fluorinated species **10** was investigated and behaved in a comparable manner to **1**. To explore the influence of electronically modulating the aryl unit, a series of *p*-CF_3 and *p*-OMe derivatives were subjected to catalysis conditions. The *Z*:*E* selectivities obtained with substrates **11**-**15** were found to be identical to those of **1**-**5** (*p*-H): (R^2 = H, **11**, *Z*:*E* 62:38; Me, **12**, *Z*:*E* 91:9; Et, **13**, *Z*:*E* 97:3; *n*Pr, **14**, *Z*:*E* 96:4; *n*Bu, **15**, *Z*:*E* 96:4). A slight deviation in selectivity was observed in the *p*-OMe derivatives **16**-**20** when compared with the parent series **1**-**5**: *p*-OMe (R^2 = H, **16**, *Z*:*E* 44:56; Me, **17**, *Z*:*E* 81:19; Et, **18**, *Z*:*E* 91:9; *n*Pr, **19**, *Z*:*E* 90:10; *n*Bu, **20**, *Z*:*E* 90:10). The origin of selectivity required clarification. Further examination of the substrate scope revealed a general tolerance for electron deficient (**21** – **23**, **27** and **28**; up to *Z*:*E* 96:4) and electron rich substituents (**24**, **25** up to *Z*:*E* 95:5). Heterocyclic aromatic substrates (**30** *Z*:*E* 91:9) as well as larger π-systems (**26** *Z*:*E* 70:30 and **31** *Z*:*E* 91:9) were well tolerated with good to excellent selectivities. Furthermore, deuterium-hydrogen exchange was not observed for per-deuterated substrates (**29**) giving some mechanistic insight. Finally, the installation of a trifluoromethyl group at the *β*-carbon was well tolerated, albeit with a slight impact on yield (**32**).

Mechanistic Delineation: Having established substrate scope and the decisive influence of the *β*-substituent in governing stereoselectivity, efforts were focused on experimental mechanistic interrogation of this transformation. This study, together with the initial photocatalytic isomerization

based on the cinnamoyl motif, provided a rich body of data from which to probe catalysis activation and the influence of internal structural preorganization on the photostationary composition. As a working model, the diffusion controlled energy transfer mechanism summarized in Scheme 3 was considered.[13]

Scheme 3 Postulated, diffusion controlled, collisional energy transfer mechanism for the photocatalytic isomerization of activated alkenes with (–)-riboflavin (RF): $S_{(E)}$ *E*-alkene; $S_{(Z)}$ *Z*-alkene; $S_{(T)}$ twisted intermediate; [RF··S]* exciplex.[13]

$$^{1}RF \xrightarrow[402\ nm]{k_1} {}^{1}RF^* \quad (1)$$

$$^{1}RF^* \xrightarrow[ISC]{k_2} {}^{3}RF^* \quad (2)$$

$$^{1/3}RF^* + {}^{1}S_{(E)} \xrightarrow{k_3} {}^{1/3}[RF\cdot\cdot S]^* \xrightarrow{k_4} {}^{1}RF + {}^{1/3}S_{(E)}^* \quad (3)$$

$$^{1/3}S_{(E)}^* \xrightarrow{k_5} {}^{1/3}S_{(T)}^* \quad (4)$$

$$^{1/3}S_{(T)}^* \xrightarrow{k_6} {}^{1}S_{(E)} \quad (5)$$

$$^{1/3}S_{(T)}^* \xrightarrow{k_7} {}^{1}S_{(Z)} \quad (6)$$

$$^{1/3}RF^* + {}^{1}S_{(Z)} \xrightarrow{k_8} {}^{1/3}[RF\cdot\cdot S]^* \xrightarrow{k_9} {}^{1}RF + {}^{1/3}S_{(T)}^* \quad (7)$$

$$^{1/3}S_{(Z)}^* \xrightarrow{k_{10}} {}^{1/3}S_{(T)}^* \quad (8)$$

Initiation of the photocatalytic isomerization reaction would occur by direct excitation of (–)-riboflavin to the first excited singlet state at 402 nm (eq. 1), opening up the possibility of intersystem crossing to the corresponding triplet state (eq. 2). Energy transfer subsequently results from collisional interactions, likely proceeding via exciplex formation, between the excited photosensitizer ($^{1/3}$RF*) and the ground-state substrate $S_{(E)}$ (eq. 3). Immediate relaxation to the twisted excited alkene $S_{(T)}$ is described by the reaction rates k_5, respectively (eq. 4). Deactivation of the twisted intermediate results in statistical formation (k_6 vs k_7) of the ground state *E*- and *Z*-configured alkenes. The photostationary state composition (*E*/*Z* ratio) would consequently be determined by the $E \rightarrow Z$ isomerization reaction rates compared to the inverse process ($k_3 + k_4 + k_5$ versus $k_8 + k_9 + k_{10}$). This gives rise to the question of the

selectivity determining step. In our initial study,[20] correlation of the triplet energy (E_T) of the photocatalyst[26] with isomerization selectivity reinforced the working hypothesis that isomer-selective energy transfer was operational ($k_3 >> k_8$). To explore the dependence on the alkene substitution pattern, Stern-Volmer fluorescence quenching experiments of (–)-riboflavin with substrates **1** (R^2=H), **2** (R^2=Me) and **3** (R^2=Et) were performed (Figure 1). Inspection of this plot, and comparison with the *Z*:*E* selectivities reported in Table 1, shows that selectivity does not correlate with quenching efficiency (full details in the SI). The following trend was noted: **2** (R^2 = Me) > **1** (R^2 = H) > **3** (R^2 = Et).

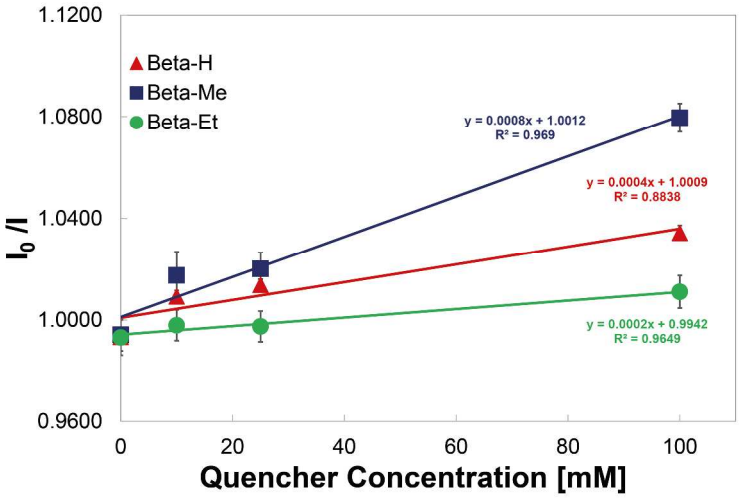


Figure 1 Stern-Volmer fluorescence quenching of (–)-riboflavin using substrates **1**, **2** and **3**.

In contrast to many popular transition-metal photocatalysts (e.g. Ru/Ir), phosphorescence of (–)-riboflavin is not directly observed upon excitation.3 Thus a more important observation from the Stern-Volmer experiment is the interaction between the singlet excited state of the photocatalyst (S_1) and the substrate. This is not consistent with initial proposal invoking only triplet energy transfer as the activation mode.

Confronted with the possibility of mechanistic dichotomy, additional quenching experiments were considered to elucidate the nature of energy transfer. Initially, azulene was investigated as a quencher in a model transformation (**2**, Figure 2) on account of its ability to quench both the singlet and triplet states. Its quenching ability is known to be susceptible to changes in solvent effects, particularly

viscosity, making it a strategically useful tool in delineating photochemical mechanisms.[27] It was observed that the addition of azulene to the reaction in MeCN caused a severe decrease in photostationary state *Z*-selectivity, and clear conclusions regarding the activation mode could not be extrapolated. This may be due to the low singlet and triplet state energies of azulene.[28]

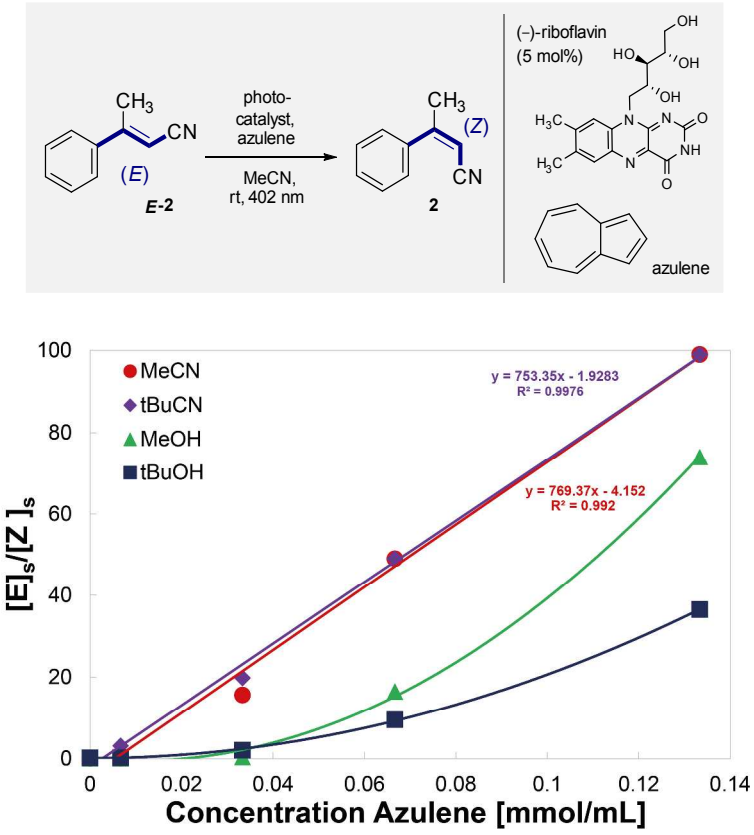
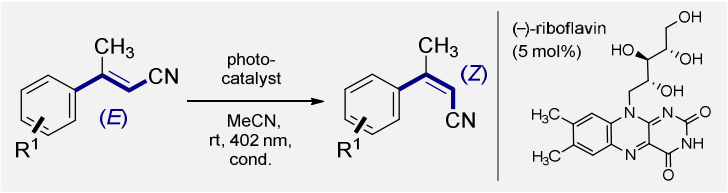


Figure 2 Exploring solvent dependence on the relationship between photostationary state product composition and azulene concentration.

Table 2. Investigating the oxygen effect on the photostationary state composition[a]



Conditions	Yield	Time (h)	*Z*:*E* ratio
Air atmosphere	quant.	12	91:9
Argon atmosphere	quant.	12	92:8
O_2 atmosphere	quant.	12	91:9

[a] Standard reactions conditions: Reactions were performed with 0.1 mmol substrate (*E*:*Z* >20:1) at room temperature with UV-light irradiation (402 nm) under the atmosphere indicated. *Z*:*E* ratios are the average of two experiments and were determined by ^{1}H NMR spectroscopy and HPLC analysis.

Switching to the comparably viscous solvent pivalonitrile, did little to influence the quenching rate. When employing polar protic solvents such as methanol and *t*-butanol, a significantly lower non-linear quenching phenomenon was observed. This non-linear behavior in protic solvents may be attributable to solvation of (–)-riboflavin, and thus disruption of the well-described charge-transfer complexes that form between azulene and flavins.[29] The appearance of a clear viscosity effect in protic solvents is in line with a diffusion controlled, collisional singlet energy transfer mediated reaction.[27]

To interrogate the involvement of a triplet activation pathway further, the effect of oxygen on selectivity was examined (Table 2 and Figure 3). Oxygen is a highly efficient triplet quencher and thus the rigorous presence or absence of oxygen would allow the question of a triplet pathway to be addressed.[30] Comparison of reactions performed under argon, oxygen and air atmospheres are summarized in Table 2. Intriguingly, the reaction selectivity proved to be oxygen independent, reinforcing the Stern-Volmer analysis such that our mechanistic interpretation gravitated towards the notion of mechanistic (spin

multiplicity) dichotomy. Whilst the selectivity of catalysis was unaffected, the efficiency of the transformation was inextricably linked.

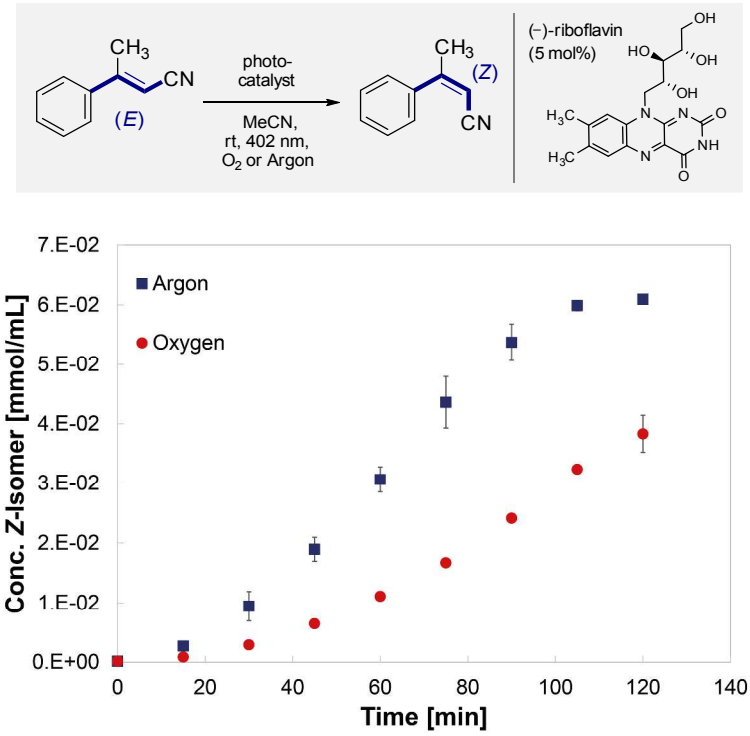


Figure 3 Oxygen effect on reaction rate of the isomerisation of **2**.

Rigorous exclusion of oxygen (Ar atmosphere) resulted in almost quantitative formation of the desired *Z*-isomer after only 2 h. In contrast, the oxygen saturated solution significantly inhibits productive isomerization with only ca. 50% conversion observed after 2 h (Fig. 3). This observation may explain the absence of an oxygen effect on the photostationary state after 12 h.

Overall, these quenching studies converge on two conceivable activation pathways: The first implicates singlet energy transfer from (–)-riboflavin to the starting material to generate the singlet excited alkene. Following efficient intersystem crossing (ISC) based on spin-orbit coupling with the nitrile non-bonding orbitals to generate the triplet state. A second scenario invokes both singlet and triplet energy transfer from (–)-riboflavin to furnish a mixture of triplet and singlet excited state alkene. Since the singlet alkene would likely undergo intersystem crossing to the corresponding triplet alkene, a common

intermediate would derive from both excitation pathways. This finding renders the isomerization of activated cinnamoyl and cinnamonitrile derived alkenes mechanistically distinct from those of the electron rich systems studied in the mid-1960s. Furthermore, this series of quenching experiments eliminated the possibility that the initial excitation event from the photocatalyst to the alkene was selectivity determining (Figure 1). Initially, it was postulated that the directionality of catalysis would have a structural basis, and that the avoidance of non-bonding interactions would dominate selectivity. To support this supposition, and explore a likely correlation between the *β*-substituent and the *Z*-isomer molar fraction, the Taft steric parameter was considered as a descriptor (Figure 4).[31] Since the activated alkenes explored in this study (EWG=CN) behaved in an analogous manner to the cinnamoyl containing esters and amides reported in the initial communication, a set of distinct substrate classes was employed in this analysis. In the case of the cinnamonitriles, the influence of the para-substituent was also addressed by comparing *p*-H with *p*-CF_3 and *p*-OMe. To probe a tentative correlation between steric size and *Z*-selectivity in catalysis, a series of sub-structures were prepared with varying R^2 substituents and are indicated as follows: a = *β*-H, b = *β*-Me, c = *β*-Et, d = β-*n*Pr, e = *β*-*n*Bu (Figure 4, A and B). A plot of the respective Taft parameter versus photostationary state *Z*-isomer molar fraction revealed a linear correlation for R^2 = H (**1**), Me (**2**) and Et (**3**) (Figure 4, upper left; A). At this point, the *Z*-selectivity plateaued, as previously noted during the establishment of catalysis scope. This trend was found to persist in all of the substrate groups studied when R^2 = Et. Figure 4B shows the linear area of the Taft parameter / photostationary state *Z*-isomer molar fraction correlation.

To explore the structural origins of isomerization selectivity further, computational analysis of the substrate in MeCN was performed (Figure 4 C).[32] From this theoretical study, it was possible to extrapolate the C_1-C_2-C_3-C_4 torsion angle and, by extension the extent to which the R^2 substituent twists and deconjugates the π-system prior to photocatalyst activation. Again, this analysis was performed with the substrate classes described above and showed a clear and consistent trend linking torsion angle and Taft steric parameter. This may be considered as the manifestation of 1,3-allylic strain ($A^{1,3}$) between R^2 and the *ortho*-proton of the aryl ring.

Full computational details of the computational analysis are provided in the supporting information. Expectedly, an increase in the aryl-alkene torsion angle resulted from systematically replacing R^2 = H by Me and then Et. As observed in both catalysis experiments and also in the Taft correlation, the Et substituent appears to be a plateau and further size augmenting of the R^2 had little effect (R^2 = Et, *n*Pr, *n*Bu).

Finally, a correlation of the torsion angle and the photostationary state *Z*-isomer molar fraction was considered (Figure 4 D). This revealed a direct linear relationship over all of the *β*-substituted alkenes (**2** – **6**, **12** – **15**, **17** – **20**, **44** – **47** and esters).[20] These data indicate that the conformation of the ground state starting material influences the photostationary state composition. This notion is further reinforced by consideration of starting materials that lack this conformational constraint. Contrastingly, these *β*-unsubstituted substrates (**1**, **11**, **16**, **43**, and methyl cinnamate, R^2 = H) exhibit very different photostationary state compositions (*Z*:*E* ratios), whilst having comparable torsional angles (for full details see SI). General inspection of the computed Z-isomer conformations revealed that the *β*-unsubstituted products have planar π-systems and can thus be re-excited by the photocatalyst. The *β*-substituted substrates, on the other hand, are fully deconjugated (torsional angle 33-55°) and thus cannot undergo photocatalyst activation (for full details see SI). This subtle structural effect is thus a major determinant in endowing the process with an intrinsic directionality and is ultimately responsible for high *Z*-selectivities observed with activated alkenes. Whilst the origin of selectivity can be broadly interpreted at the structural level, R^2 = Et is conspicuous in all of these analyses and remains an anomaly. Evidently, a simple steric model based on ground state conformation is insufficient to account for selectivity and it is likely that an interplay of several factors is operational.

Cognizant of the intrinsic flexibility of the substrates in this study, a series of bicyclic probes were synthesized to minimize conformational freedom (Table 3; **33**-**36**). It was envisaged that this may be addressed by simply pre-organizing the chromophore through an alkyl tether. This would simultaneously preserve the planarity of the π-system and mimic the steric footprint of the Et

substituent. It would also, however, subtly contract the C_1-C_2-C_3-C_4 torsional angle in the product (5-ring **33** > 6-ring **34** > 7-ring **35** > 8-ring **36**) thereby forcing the π-system to deconjugate, and thus augmenting unfavorable non-bonding interactions (Table 3). The selectivities summarized in Table 3 proved to be instructive in confirming the importance of this interaction in ensuring directionality. Whilst low to mediocre selectivities were measured for **33** and **34** (*Z*:*E* 46:54 and 66:34, respectively), a substantial increase was noted for the seven- and eight- membered ring containing substrates leading to **35** and **36** (*Z*:*E* 97:3 and 99:1, respectively). Based on these empirical observations, two possibilities appeared reasonable to account for the selectivity in the acyclic cases summarized in Table 1, and required further exploratory studies: i) The first is the assumption that deconjugation of the alkene and the phenyl ring must occur in the excited state. This is reminiscent of a "hula-twist"-type isomerization mechanism,[33] which would require rotation of the aromatic ring during the isomerization event (see Scheme 3, k_4 and k_8), resulting in higher excited state activation barriers for less pre-organized systems such as 1 (torsion angle, φ = 0°), or ii) As proposed by Hammond and co-workers for stilbene isomerization, substitution could potentially yield a "deeper", more stabilized excited state with higher lifetimes and therefore more productive transitions from the *E*- to *Z*-isomer.[13c,34]

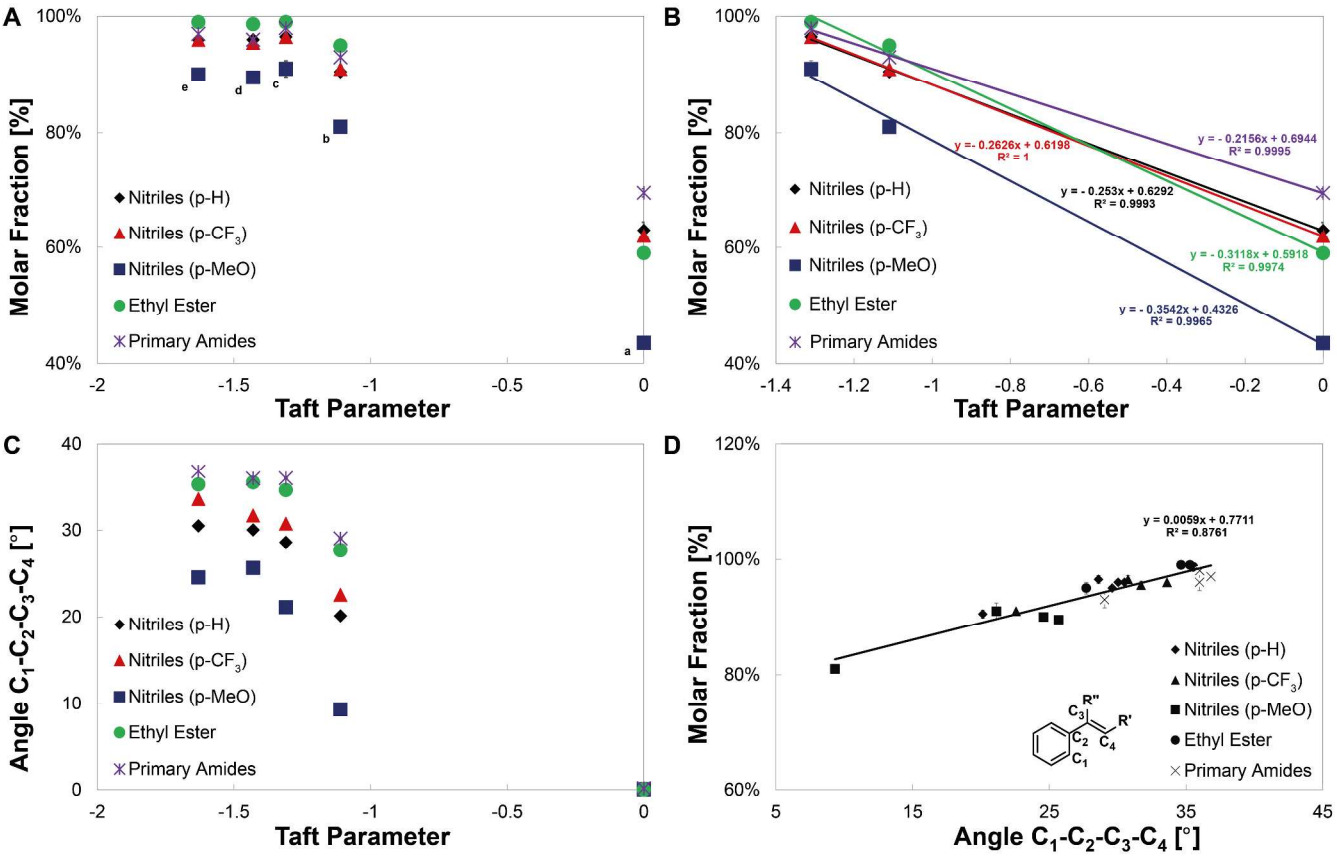


Figure 4 (A) Correlation of Taft parameter and photostationary state Z-isomer molar fraction, (B) Linear area of Taft parameter and photostationary state Z-isomer molar fraction correlation, (C) Correlation of Taft parameter and calculated aryl-alkene torsional angle, (D) Correlation of calculated aryl-alkene torsional angle and photostationary state Z-isomer molar fraction of *β*-substituted alkenes. (a = *β*-H, b = *β*-Me, c = *β*-Et, d = *β*-*n*Pr, e = *β*-*n*Bu)

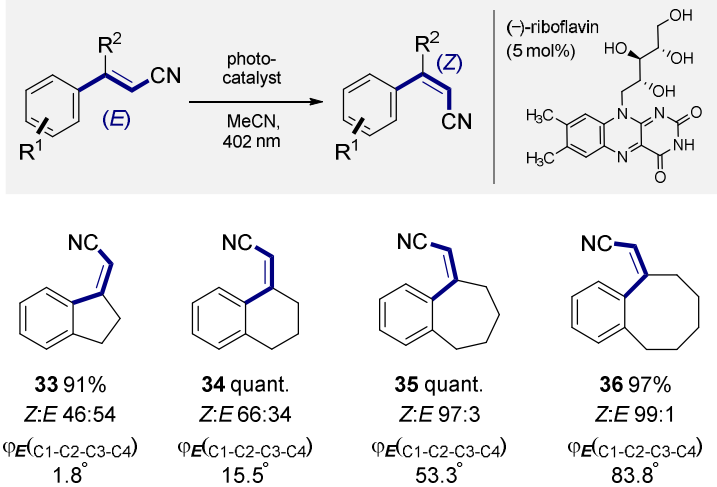
It was reasoned that since rotational barriers are temperature dependent, activation parameters derived from an Eyring analysis might provide an insight into the excited state rotational processes. Ultimately, this may lead to a fuller understanding of the origins of selectivity. An Eyring analysis of the isomerization of various substituted *α*,*β*-unsaturated nitriles (R^2 = H, Me, Et, *n*Pr, *n*Bu, **1**-**5**) was therefore attempted. To that end, the catalytic isomerization was performed at various temperatures and monitored by HPLC-UV under internal standard calibration. Unfortunately, the kinetic data extrapolated showed a complex reaction order, and

thus exact reaction rates and activation parameters could not be derived. As might be expected, a significant enhancement in the reaction rate was observed with increasing temperature. This implicates longer excited state lifetimes and faster state and rotational transitions (see SI for full details). Approaching this same issue from a slightly different perspective led us to determine the effect of temperature on the photostationary state composition. This, in turn, would allow the existence of activation barriers in the isomerization process to be derived. All reactions were performed at 30 °C and 50 °C, and the photostationary state product composition was analyzed by HPLC-UV (Table 4).

As summarized in Table 4, the photostationary state composition of the unsubstituted alkene **1** is slightly enriched with *Z*-isomer at 50 °C compared to 30 °C, suggesting an activation barrier for the transition from *E*-**1** → *Z*-**1**. This observation is fully in line with Hammond and co-workers mechanistic investigation on electron rich stilbene isomerization.[13c] Interestingly, for the polarized alkenes bearing a substituent at R^2, the quotient is notably reduced on account of the increased *E*-isomer molar fraction at higher temperatures.

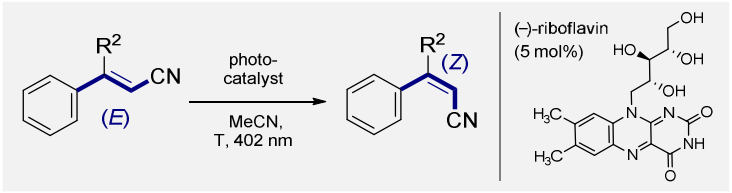
This contrasting behavior indicates a higher activation barrier for the transition from the *Z*- → *E*-isomer. Considering the torsional angle range between φ = 40.7° and 43.5° for **2**, **3**, **4** and **5**, respectively, an in-plane rotation of the aromatic ring is necessary to achieve conjugation and consequently allow catalyst excitation of the *Z*-isomer. Conversely, the unsubstituted *Z*-isomer (R^2 = H) is fully conjugated (φ = 0 °C) and thus the rotational barrier for the *E*- to *Z*-isomer transition must proceed via an excited state process.

Table 3 The (–)-riboflavin-catalyzed isomerization of cyclic α,β-unsaturated nitriles[a]



[a] Standard reaction conditions: Reactions were performed with 0.1 mmol substrate (*E*:*Z* >20:1) at ambient temperature in MeCN using 5 mol% catalyst loading under 12 hours of UV-light irradiation (402 nm). *Z*:*E* ratios are the average of two experiments and were determined by ^{1}H NMR spectroscopy analysis.

Table 4 Temperature effect on photostationary state composition[a]



R^2	30 °C	50 °C	$[E/Z]_{30°C}$
	Z:*E*	*Z*:*E*	$[E/Z]_{50°C}$
H (**1**)	53.9 : 46.1	57.1 : 42.9	1.137
Me (**2**)	88.1 : 11.9	86.6 : 13.4	0.873
Et (**3**)	95.2 : 4.8	93.9 : 6.1	0.788
nPr (**4**)	93.9 : 6.1	92.7 : 7.3	0.820
nBu (**5**)	94.0 : 6.0	92.7 : 7.3	0.816

[a] Standard reaction conditions: Reactions were performed with 0.1 mmol substrate (*E*:*Z* >20:1) at the specified temperature under 12 hours of UV-light irradiation (402 nm) and an air atmosphere. *Z*:*E* ratios are the average of two experiments and were determined by HPLC analysis.

A correlation of the ratio of temperature dependent photostationary states, reflecting the activation barriers for isomerization, with the photostationary state composition at room temperature showed a linear relationship (Figure 5). This observation, which is distinct from the mechanistic nuances of stilbene isomerization, demonstrates that the selectivity and directionality of isomerization catalysis has a structural origin. Ultimately, the presence or absence of R^2 is significant in determining the activation barrier for the forward and reverse transformations, and in turn in governing the *E*/*Z* selectivity quotient.

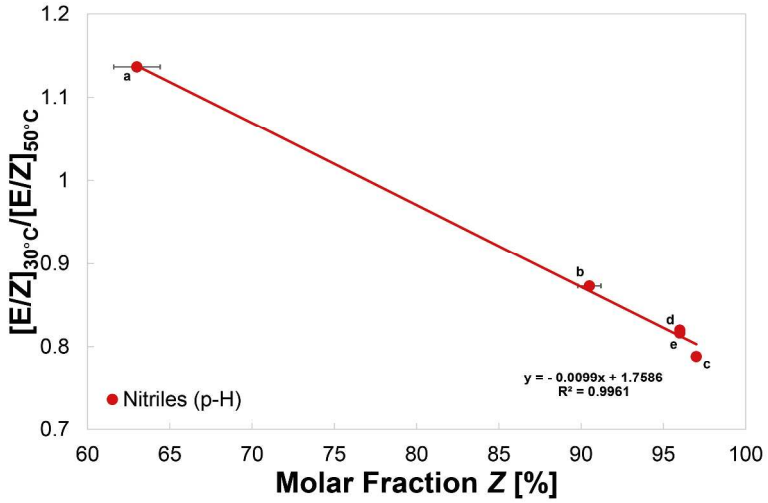


Figure 5 Correlation of ratio of photostationary state composition at 30 °C and 50 °C with photostationary state composition at room temperature; ; a = *β*-H, b = *β*-Me, c = *β*-Et, d = *β*-nPr, e = *β*-nBu.

Whilst it seems reasonable that increased activation barriers for the transition from *Z*- to *E*-isomer should augment the photostationary state *Z*-isomer molar fraction, the torsion angle data

does not satisfactorily account for deviation in the selectivities observed for R^2 = Et (**3**), *n*Pr (**4**) and *n*Bu (**5**). It is therefore likely that a secondary temperature dependent effect, such as excited state stability, must be considered to fully describe the origin of selectivity. Consequently, the second hypothesis was considered. The previous reports by Saltiel *et al.* reported notably enhanced lifetimes of excited state stilbene following substitution of one C(sp^2)-H of the alkene by a methyl group.[34] It logically follows that a direct consequence of extended lifetimes would be a more productive *E*- to *Z*-isomerization.

Since the steric effect of the substituent alone could be discarded based on previous experiments, the electronic contribution of substitution on the alkene was considered. It was envisaged that comparison of the ^{13}C-shifts of the alkene carbon atoms would give direct quantification of electronic changes (Figure 6). Moreover, since conformational changes and orbital hybridization (cf. Figure 4C) also manifest themselves in NMR shift behavior, this spectroscopic approach was appealing.[35] Gratifyingly, a direct linear correlation between the ^{13}C shift difference ($\Delta\delta$ [ppm]) of the β- and α-carbon atoms and the logarithm of the *Z*/*E* ratio was observed (Figure 6).

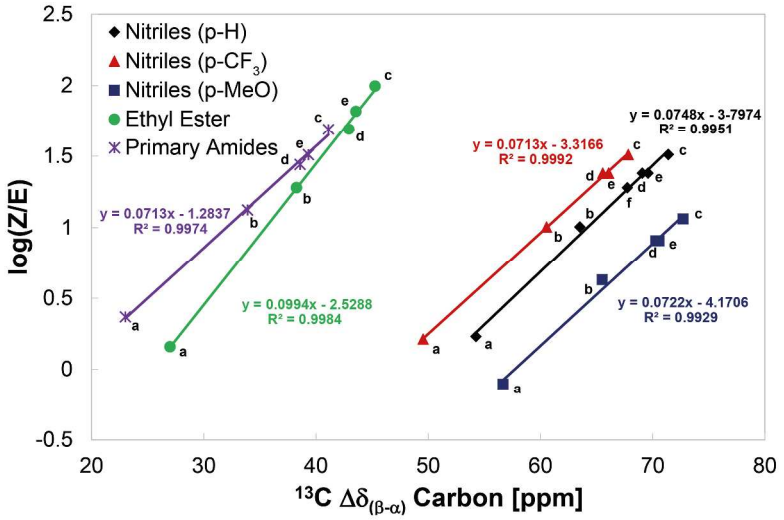


Figure 6 Correlation of ^{13}C shift β-α carbon shift difference $\Delta\delta$ with photostationary state *Z*/*E* selectivity (^{13}C shifts were determined in $CDCl_3$; a = β-H, b = β-Me, c = β-Et, d = β-*n*Pr, e = β-*n*Bu, f = β-*i*Bu).

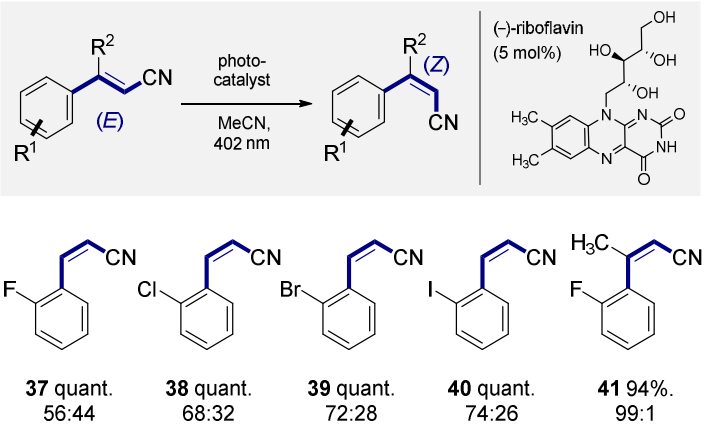
These data indicate that selectivity increases directly with the electron deficiency of the β-carbon (i.e. polarization influences selectivity). An intrinsic consequence of lowering electron density on the β-carbon atom is to enhance polarization of the alkene unit. Considering the zwitterionic contribution to the excited state, stabilization by polarization of the double bond would explain the prolonged lifetimes observed for methyl substituted stilbenes and can be logically extended to the cinnamoyl scaffold. Furthermore, polarization of the alkene by decreasing π-conjugation and substituent effects logically results in an increased bond length and thus lower barrier for rotation around the central carbon-carbon double bond.[35a,b] A selectivity model invoking two aspects is therefore postulated and includes: (i) alkene polarization, resulting in extended excited state alkene lifetimes and lower rotational barriers for *E*- to *Z*-isomerization processes, and (ii) increased activation barriers for the inverse *Z*- to *E*-isomer transitions.

To explore the implications of utilizing the aryl-alkene torsional angle to enhance alkene polarization, and thereby increase *Z*-selectivity, the effect of *ortho*-substitution was explored. Halogenation provides a convenient handle by systematically increasing steric congestion but maintaining the electronic signature of the substrate. A series of structurally modified E-isomers were synthesized (**37**-**41**) and exposed to the standard reaction conditions (Table 5).

A clear trend linking *Z*-selectivity with increasing halogen size was noted. Whilst introduction of an *ortho*-fluorine substituent resulted in a slight decrease in selectivity (**37**, 56:44), chlorine **38**, bromine **39** and iodine **40** substitution led to a significant increase in *Z*-selectivity (68:32, 72:28

and 74:26, respectively). Combining effects by adding a *β*-methyl substituent in the case of **41** furnished a *Z*:*E* ratio of 99:1 (cf. 91:9 for **2**).

Table 5. Effect of *ortho*-substitution on *Z*-isomer selectivity.[a]



[a] Standard reaction conditions: Reactions were performed with 0.1 mmol substrate (*E*:*Z* >20:1) at ambient temperature in MeCN using 5 mol% catalyst loading under 12 hours of UV-light irradiation (402 nm). *Z*:*E* ratios are the average of two experiments and were determined by ^{1}H NMR spectroscopy analysis.

Conclusions

The ubiquity of *Z*-selective alkene isomerization in *Nature* belies the intrinsic challenges of replicating this process in a catalysis paradigm. Consequently, a general solution to this rudimentary process remains visibly absent from the catalysis arsenal. Close inspection of a seminal report describing the qualitative isomerization of retinal in fish and mammals by (–)-riboflavin allowed crucial data to be distilled and translated to address this conspicuous absence in the organocatalysis armory.

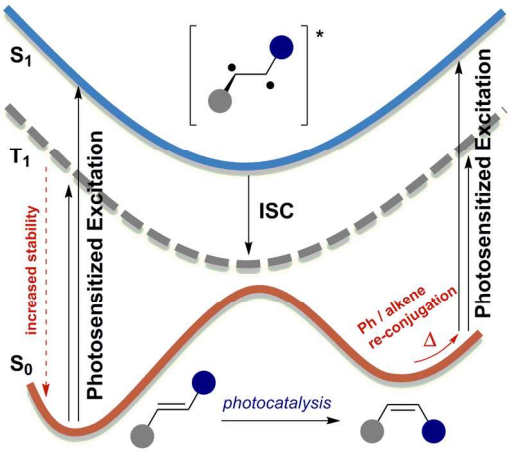


Figure 7 Photochemical activation and origin of selectivity in the (–)-riboflavin catalyzed isomerization of polarized alkenes.

Reinterpretation of the biological photosystem facilitated the development of a highly *Z*-selective, catalytic isomerization of activated alkenes based on the cinnamoyl and cinnamonitrile chromophores. By replacing retinal by a truncated chromophore, the degree of π-conjugation in the starting material and product is determined by the alkene geometry and the avoidance of non-bonding interactions; this results in a selective excitation manifold whereby only the substrate and photocatalyst undergo efficient energy transfer: This ensured directionality in the reaction design by circumventing microscopic reversibility and the inevitable product distributions that result under thermal / non-irradiative conditions.

The optimized transformation proved to be highly efficient (*Z*:*E* up to 99:1), quantitative and operationally simple requiring only filtration. It also validated the synthetic utility of (–)-riboflavin as a powerful antenna for photocatalytic transformations. Moreover, in the case of cinnamonitriles, the masked amine mitigates the risk of physical and chemical quenching that often inhibits photochemical processes involving amines. In addition to expanding substrate

scope, this study intended to delineate both the photocatalyst activation mechanism and the origin of selectivity for a range of substrate classes. A combination of Stern-Volmer quenching experiments and secondary external quencher effects were informative in this regard. Evidence of mechanistic dichotomy has been demonstrated whereby both singlet and triplet energy intermediates are operational and likely converge on a common species. The scenario invoking exclusive singlet energy transfer to the alkene followed by ISC to the triplet state cannot be fully discounted. In contrast to previous studies detailing the stoichiometric isomerization of electron rich alkenes, this complexity in substrate activation arises from the polarized nature of the alkene. It is likely that the non-bonding orbitals of the electron withdrawing carbonyl and nitrile units facilitate intersystem crossing (El Sayed's Rule) thus rendering catalysis efficient. The polarized nature of the alkene unit is also intimately linked to the origin of selectivity. Conformational analysis of the *E*- and *Z*-isomers demonstrated a clear effect of aryl-alkene torsional preorganization on the photostationary composition. Kinetic studies, temperature dependent photostationary state correlations and investigation of substituent-based electronic perturbation of the alkene identified polarization combined with increased Z-isomer activation barriers as the selectivity governing factors in catalysis (Figure 7).

Experimental Section

All chemicals were purchased as reagent grade and used without further purification. Solvents for purification (extraction and chromatography) were purchased as technical grade and distilled on the rotary evaporator prior to use. For column chromatography SiO_2 (40-63 μm for Flash-Chromatography, VWR Chemicals) was used as stationary phase. Analytical thin layer chromatography (TLC) was performed on aluminum foil pre-coated with SiO_2-60 F254 (Merck) and visualized with a UV-lamp (254 nm) and $KMnO_4$ solution. Concentration *in vacuo* was performed at ~10 mbar and 45 °C, drying at ~10^{-2} mbar and room temperature. NMR spectra were measured by the NMR service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a Bruker AV300, Agilent DD2 500 or an Agilent DD2 600 spectrometer at room temperature. The chemical shifts are referenced to the residual solvent peak as internal standard. The resonance multiplicity is abbreviated as: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), sext (sextet), sep (septet), m (multiplet) and b (broad).

Assignments of unknown compounds are based on DEPT, COSY (HH and FF), HMBC, HSQC and NOESY spectra. Alkene configuration is assigned based on coupling constants and NOESY spectra. Melting points were measured on a Büchi B-545 melting-point apparatus in open capillaries. IR spectra were recorded on a Perkin-Elmer 100 FT-IR spectrometer, selected adsorption bands are reported in wavenumbers (cm^{-1}) and intensities are reported as: w (weak), m (medium), s (strong) and b (broad). High-resolution mass spectra (HR ESI with microTOF/orbitrap or Quad detection) were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. Isomerization reactions were performed utilising a ACULED VHL (ACL01-SC-UUUU-E05-C01-L-0000) by LED Solutions (emission spectrum see SI Figure S1). The forward current per chip was set to 350 mA, the resulting forward voltage was 14 V while the resulting radiant flux was 1150 mW. Further isomerization reactions were performed utilizing a set-up of 4 Winger WEPUV3-S2 UV Power LED Star (Schwarzlicht) 1.2 W lamps (emission spectrum see SI Figure S2). The forward current per chip was set to 700 mA, the resulting forward voltage was 3.4 V while the resulting radiant flux was 1200 mW. The distance between the reaction vessels and the UV-lamp was set at approximately 0.5 cm for all reactions.

Preparation of the starting materials

(E)-3-phenylacryl acid, *(E)*-3-phenylbut-2-enoic acid, *(E)*-3-phenylpent-2-enoic acid, *(E)*-3-phenylhex-2-enoic acid, ethyl cinnamate (***E*-53**), ethyl (*E*)-3-phenylbut-2-enoate (***E*-54**), ethyl (*E*)-3-phenylpent-2-enoate (***E*-55**), ethyl (*E*)-3-phenylhex-2-enoate (***E*-55**), ethyl (*Z*)-phenylacrylate (**53**), ethyl (*Z*)-3-phenylbut-2-enoate (**54**), ethyl (*Z*)-3-phenylpent-2-enoate (**55**) and ethyl (*Z*)-3-phenylhex-2-enoate (**56**) were synthesized according to our previous procedure.[20,21]

Synthesis of *N*-Methoxy-*N*-methyl-4-(trifluoromethyl)benzamide (48) 4-Trifluoromethyl-benzoic acid (2.30 g, 9.85 mmol, 1.0 eq.) was dissolved in DMF (100 mL) before *N,O*-dimethylhydroxylamine (1.00 g, 10.4 mmol, 1.1 eq.), EDCI·HCl (1.99 g, 10.4 mmol, 1.1 eq.) and Et_3N (1.45 mL, 10.4 mmol, 1.1 eq.) were added. The resulting white suspension was stirred for 18 h at room temperature, the DMF was removed under high vacuum and the resulting residue was dissolved in EtOAc (30 mL), washed with sat. $NaHCO_3$ solution (aq., 20 mL) and brine (20 mL), before the organic phase was dried over $MgSO_4$. The solvent was removed in vacuum. Purification by column chromatography (SiO_2, 25% EtOAc/ cyclohexane) yielded the product **48** as a colourless oil (1.15 g, 50%). R_f = 0.42 (EtOAc/cyclohexane 2:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 7.8 Hz, 2H; H5), 7.65 (d, J = 8.0 Hz, 2H; H6), 3.51 (s, 3H; H1), 3.36 (s, 3H; H2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6 (C3), 137.7 (q, J_{CF} = 1.2 Hz; C4), 132.3 (q, J_{CF} = 32.5 Hz; C7), 128.6 (C5), 125.1 (q, J_{CF} = 3.8 Hz; C6), 123.8 (q, J_{CF} = 272.4 Hz; C8), 61.3 (C1), 33.4 (C2) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.00 ppm; IR (ATR): ῡ = 2966(w), 2941(w), 2352(w), 1645(m), 1620(m), 1578(w), 1516(w), 1462(w), 1407(w), 1383(w), 1322(s). 1260(w), 1215(w), 1165(m), 1122(s), 1111(s), 1069(s), 1019(s), 980(w), 889(w), 851(m), 797(m), 779(m), 764(m), 701(m), 662(w) cm^{-1}; GC-EI-MS (Quad): m/z: 233.2 ([M], calcd. for $C_{10}H_{10}F_3NO_2$: 233.1902); analytical data in agreement with literature.[36]

Synthesis of 1-(4-(Trifluoromethyl)phenyl)butan-1-one (49) 48 (412 mg, 1.8 mmol, 1.0 eq.) was dissolved in dry THF (10 mL) under Argon, the solution was cooled to 0 °C before *n*PrMgCl (2.7 mL, 5.4 mmol, 3.0 eq.) was added dropwise. The mixture was gradually warmed to room temperature over 3 h and the resulting suspension was added to 1 N HCl (30 mL). The aqueous phase was extracted with EtOAc (3x 15 mL), the combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by column chromatography (SiO_2, 20% EtOAc/ cyclohexane) yielded the product **49** as a colourless oil (342 mg, 88%). R_f = 0.78 (EtOAc/cyclohexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 – 7.96 (m, 2H; H6), 7.79 – 7.69 (m, 2H; H7), 2.97 (t, J = 7.3 Hz, 2H; H3), 1.79 (sext, J = 7.4 Hz, 2H; H2), 1.02 (t, J = 7.4 Hz, 3H; H1) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.5 (C4), 139.9 (C5), 134.4 (q, J_{CF} = 32.6 Hz; C8), 128.5 (C6), 125.8 (q, J_{CF} = 3.8 Hz; C7), 123.8 (q, J_{CF} = 272.7 Hz; C9), 40.9 (C3), 17.7 (C2), 13.9 (C1) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.10 ppm; IR (ATR): ῡ = 2963(m), 1698(w) 1513(w), 1410(w), 1326(m), 1259(s), 1210(w), 1172(w), 1066(s), 1015(s), 864(m), 796(s), 703(w), 662(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 239.0655 ([M+Na]$^+$, calcd. for $C_{11}H_{11}F_3ONa^+$: 239.0660); analytical data in agreement with literature.[37]

Synthesis of 1-(4-(Trifluoromethyl)phenyl)pentan-1-one (50) 48 (466 mg, 2 mmol, 1.0 eq.) was dissolved in dry THF (10 ml) under Argon, the solution was cooled to 0 °C before *n*BuMgCl (3 mL, 6 mmol, 3.0 eq.) was added dropwise. The mixture was gradually warmed to rt over 3 h and the resulting suspension was added to 1 N HCl (30 mL). The aqueous phase was extracted with EtOAc (3x 15 mL), the combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by column chromatography (SiO_2, 20% EtOAc/ cyclohexane) yielded the product **50** as a colourless oil (395 mg, 86%).R_f = 0.78 (EtOAc/cyclohexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dq, J = 7.9, 0.9 Hz, 2H; H7), 7.73 (m, 2H; H8), 3.09 – 2.88 (t, J = 7.4 Hz, 2H; H4), 1.73 (p, J = 7.4 Hz, 2H; H3), 1.42 (tq, J = 14.8, 7.3 Hz, 2H; H2), 0.96 (t, J = 7.3 Hz, 3H; H1) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.6 (C5), 139.9 (C6), 134.4 (q, J_{CF} = 32.6 Hz; C9), 128.5 (C7), 125.8 (q, J_{CF} = 3.8 Hz; C8), 123.8 (q, J_{CF} = 272.6 Hz; C10), 38.8 (C4), 26.4 (C3), 22.6 (C2), 14.1 (C1) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.09 ppm; IR (ATR): ῡ = 2980(w), 2965(w), 2934(w), 2863(w), 1680(s), 1580(w), 1511(w), 1468(w), 1411(m), 1384(w), 1320(s), 1308(s), 1269(m), 1203(m), 1165(s), 1126(s), 1110(s), 1015(m), 979(m), 924(w), 904(w), 852(s), 799(m), 756(m), 726(m), 676(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 253.0819 ([M+Na]$^+$, calcd. for $C_{12}H_{13}F_3ONa^+$: 253.0816); analytical data in agreement with literature.[38]

Synthesis of 7,8,9,10-Tetrahydrobenzo[8]annulen-5(6*H*)-one (51)[39] 6-Phenylhexanoic acid (500 mg, 2.6 mmol, 1.0 eq.) was dissolved in DCM (10 ml) and the solution was cooled to 0 °C before oxalyl chloride (0.446 mL, 5.2 mmol, 2.0 eq.) was added. The resulting mixture was gradually warmed to rt and stirred for 14 h at this temperature before being concentrated *in vacuo*. The residue was dissolved in DCM (25 mL) under Argon and the solution was added to a suspension of $AlCl_3$ (1386 mg, 10.4 mmol, 4.0 eq.) in dry DCM (125 mL) under Argon over 3 h. The reaction mixture was stirred for 17.5 h, washed with sat. NH_4Cl solution (aq., 50 mL) and

dried over $MgSO_4$ before being concentrated *in vacuo*. Purification by column chromatography (SiO_2, 10% EtOAc/ cyclohexane) yielded the product **51** as a colourless oil (340 mg, 75%). R_f = 0.35 (EtOAc/cyclohexane 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H; H8), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H, H10), 7.27 (td, *J* = 7.6, 1.4 Hz, 1H; H9), 7.18 (dd, *J* = 7.7, 1.2 Hz, 1H; H11), 3.08 – 3.00 (m, 2H; H1), 2.96 – 2.89 (m, 2H; H5), 1.90 – 1.75 (m, 4H; H2/4), 1.57 – 1.49 (m, 2H; H3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.7 (C6), 140.1 (C12), 140.0 (C7), 131.6 (C10), 131.1 (C11), 127.7 (C8), 126.5 (C9), 44.3 (C5), 34.5 (C1), 28.0 (C2), 25.3 (C3), 24.2 (C4) ppm; IR (ATR): ϑ̃ = 2928(m), 2854(w), 1664(s), 1597(m), 1485(w), 1485(w), 1444(m), 1344(w), 1328(w), 1305(m), 1287(m), 1255(s), 1185(m), 1158(m), 1132(m), 1115(m), 1040(m), 999(m), 997(m), 947(w), 914(w), 896(w), 787(m), 774(m), 751(s), 716(w), 673(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 197.0943 ([M+Na]$^+$, calcd. for $C_{12}H_{14}ONa^+$: 197.0937).

(*E*)-3-Phenylhept-2-enoic acid (52) 42 (400 mg, 1.72 mmol, 1.0 eq.) was dissolved in NaOH-solution (3.44 mL, aq. 1.0 N, 3.44 mmol, 2.0 eq.) and EtOH (2.5 mL). The resulting mixture was stirred at room temperature for 24 h before the pH was adjusted to pH 1 with HCl (aq., 1.0 M). The aqueous phase was extracted with EtOAc (3x 5 mL), the combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by column chromatography (SiO_2, 10 – 30% Et_2O/*n*-pentane) yielded the product **52** as a white amorphous solid (93 mg, 27%). R_f = 0.1 (Et_2O/*n*-pentane 1:9); M.p.: 52.5 – 53.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.43 (m, 2H; H9), 7.41 – 7.37 (m, 3H; H10/11), 6.06 (d, *J* = 0.5 Hz, 1H; H2), 3.14 – 3.11 (m, 2H; H4), 1.45 – 1.40 (m, 2H; H5), 1.36 (ddd, *J* = 14.8, 7.4, 1.3 Hz, 2H; H6), 0.88 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 170.3 (C1), 164.0 (C3), 141.4 (C8), 129.3 (C11), 128.7 (C10), 126.9 (C9), 116.2 (C2), 31.3 (C5), 31.1 (C4), 22.9 (C6), 14.0 (C7) ppm; IR (ATR): ϑ̃ = 3059(w), 2954(m), 2927(m), 2870(m), 2751(w), 2690(w), 2600(w), 1683(s), 1612(s), 1576(m), 1497(w), 1464(w), 1448(m), 1407(m), 1378(w), 1349(w), 1304(m), 1279(m), 1250(w), 1211(s), 1162(w), 1119(w), 1107(w), 1081(W), 1029(w), 1000(w), 987(w), 924(m), 871(m), 832(w), 767(m), 722(m), 703(s), 693(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 227.1045 ([M+Na]$^+$, calcd. for $C_{13}H_{16}O_2Na^+$: 227.1043); analytical data in agreement with literature.[40]

General Procedure A for the preparation of *α,β*-unsaturated carbonyl compounds

NaH (60% in mineral oil, 1.1 eq.) was dissolved in dry THF, the mixture was cooled to 0 °C, diethylcyanomethylphosphonoacetate (1.05 eq.) was added dropwise to the solution before the resulting solution was stirred for 1 h at 0 °C. The specified aromatic ketone (1.0 eq.) was added to the reaction mixture, before the mixture was stirred for 1 h at 0 °C and subsequently being gradually warmed to room temperature. The resulting mixture was stirred until full conversion (by TLC) or for 24 h before water and Et_2O were added. The organic phase was separated, the aqueous phase was extracted with Et_2O (3x), the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, specified combination of Et_2O/*n*-pentane).

(*E*)-3-Phenylbut-2-enenitrile (*E*-2) Prepared according to General Procedure **A**, acetophenone (5 mmol) was converted to ***E*-2** in 24 h yielding a colourless oil (521 mg, 73%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.39 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.48 – 7.45 (m, 2H; H6), 7.43 – 7.40 (m, 3H; H7/8), 5.62 (q, *J* = 1.1 Hz, 1H; H2), 2.47 (d, *J* = 1.1 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.9 (C3), 138.4 (C5), 130.4 (C8), 128.9 (2C; C7), 126.0 (2C; C6), 117.7 (C1), 95.7 (C2), 20.3 (C4) ppm; IR (ATR): ϑ̃ = 3062(w), 2981(w), 2213(s), 2116(w), 1991(w), 1608(m), 1575(m), 1496(w), 1446(m), 1381(m), 1333(w), 1261(w), 1159(w), 1079(w), 1027(w), 1001(w), 921(w), 826(w), 756(s), 691(s), 658(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 166.0648 ($[M+Na]^+$, calcd. for $C_{10}H_9NNa^+$: 166.0627); analytical data in agreement with literature.[41]

(*E*)-3-Phenylpent-2-enenitrile (*E*-3)[42] Prepared according to General Procedure **A**, propiophenone (4 mmol) was converted to ***E*-3** in 24 h yielding a colourless oil (314 mg, 50%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.7 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.41 (m, 5H; H7-9), 5.49 (s, 1H; C2), 2.90 (q, *J* = 7.6 Hz, 2H; C4), 1.13 (t, *J* = 7.6 Hz, 3H; C5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.5 (C3), 137.5 (C6), 130.2 (C9), 129.0 (2C; C8), 126.4 (2C; C7), 117.4 (C1), 95.1 (C2), 27.4 (C4), 13.4 (C5) ppm; IR (ATR): ϑ̃ = 3060(w), 2975(w), 2938(w), 2877(w), 2213(m), 1603(m), 1574(m), 1495(w), 1465(m), 1445(m), 1378(w), 1342(w), 1308(w), 1284(w), 1235(w), 1159(w), 1081(w), 1030(w), 1001(w), 907(w), 829(m), 806(w), 760(s), 695(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 180.0786 ($[M+Na]^+$, calcd. for $C_{11}H_{11}NNa^+$: 180.0784).

(*E*)-3-Phenylhex-2-enenitrile (*E*-4) Prepared according to General Procedure A, butyrophenone (4 mmol) was converted to ***E*-4** in 24 h yielding a colourless oil (363 mg, 53%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.72 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.39 (m, 5H; H8-10), 5.52 (s, 1H; H2), 2.92 – 2.83 (m, 2H; H4), 1.51 (sext, *J* = 7.4 Hz, 2H; H5), 0.95 (t, *J* = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.1 (C3), 137.8 (C7), 130.1 (C10), 129.0 (2C; C9), 126.4 (2C; C8), 117.6 (C1), 96.0 (C2) 35.9 (C4), 21.9 (C5), 13.7 (C6) ppm; IR (ATR): ϑ̃ = 3060(w), 2962(m), 2933(w), 2873(w), 2214(m), 1679(w), 1603(m), 1574(w), 1494(w), 1457(m), 1445(m), 1381(w), 1335(w), 1255(w), 1213(w), 1159(w), 1081(w), 1031(w), 1001(w), 918(w), 878(w), 829(m), 784(w), 758(s), 695(s), 657(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 194.0946 ($[M+Na]^+$, calcd. for $C_{12}H_{13}NNa^+$: 194.0940); analytical data in agreement with literature.[41]

(*E*)-3-Phenylhept-2-enenitrile (*E*-5) Prepared according to General Procedure **A**, valerophenone (4 mmol) was converted to ***E*-5** in 24 h yielding a colourless oil (482 mg, 65%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.72 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.40 (m, 5H; H9-11), 5.50 (s, 1H; H2), 2.90 (t, *J* = 7.4 Hz, 2H; H4), 1.50 – 1.42 (m, 2H; H5), 1.41 – 1.35 (m, 2H; H6), 0.90 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.3 (C3), 137.9 (C8), 130.1 (C11), 129.0 (2C; C10), 126.4 (2C; C9), 117.6 (C1), 95.8 (C2), 33.8 (C4), 30.7 (C5), 22.5 (C6), 13.9 (C7) ppm; IR

(ATR): ῡ = 3061(w), 2957(m), 2931(m), 2862(w), 2213(m), 2099(w), 1603(m), 1573(w), 1495(w), 1446(m), 1380(w), 1343(w), 1380(w), 1343(w), 1262(w), 1190(w), 1158(w), 1105(w), 1079(w), 1030(w), 1001(w), 955(w), 927(w), 828(m), 758(s), 729(w), 695(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 208.1100 ($[M+Na]^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1097); analytical data in agreement with literature.[43]

(*E*)-4-Methyl-3-phenylpent-2-enenitrile (*E*-6) Prepared according to General Procedure **A**, isobutyrophenone (4 mmol) was converted to ***E*-6** in 24 h yielding a colourless oil (483 mg, 71%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.81 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.33 (m, 3H; H8/9), 7.26 – 7.20 (m, 2H; H7), 5.26 (s, 1H; H2), 3.34 (hept, *J* = 7.0 Hz, 1H; H4), 1.25 (d, *J* = 7.0 Hz, 6H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.3 (C3), 139.0 (C6), 129.1 (C9), 128.5 (2C; C8), 127.2 (2C; C7), 116.9 (C1), 96.6 (C2), 34.7 (C4), 21.3 (2C; C5) ppm; IR (ATR): ῡ = 3057(w), 2969(m), 2934(w), 2875(w), 2216(m), 1597(w), 1574(w), 1492(w), 1463(m), 1443(w), 1388(w), 1366(w), 1242(w), 1167(w), 1105(w), 1078(w), 1030(w), 1001(w), 927(w), 883(w), 830(m), 764(s), 697(s), 665(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 194.0946 ($[M+Na]^+$, calcd. for $C_{12}H_{13}NNa^+$: 194.0940); analytical data in agreement with literature.[44]

(*E*)-5-Methyl-3-phenylhex-2-enenitrile (*E*-7) Prepared according to General Procedure **A**, isovalerophenone (4 mmol) was converted to ***E*-7** in 24 h yielding a colourless oil (284.5 mg, 38%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.7 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.38 (m, 5H; H8-10), 5.52 (s, 1H; H2), 2.78 (d, *J* = 7.3 Hz, 2H; H4), 1.72 (hept, *J* = 6.9 Hz, 1H; H5), 0.93 (d, *J* = 6.7 Hz, 6H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.5 (C3), 138.5 (C7), 130.1 (C10), 129.0 (2C; C9), 126.5 (2C; C8), 117.7 (C1), 96.7 (C2), 42.9 (C4), 27.7 (C5), 22.3 (2C; C6) ppm; IR (ATR): ῡ = 3059(w), 2957(m), 2933(w), 2870(w), 2213(m), 2099(w), 1604(m), 1573(w), 1494(w), 1465(m), 1446(m), 1386(w), 1369(w), 1342(w), 1284(w), 1264(w), 1219(w), 1167(w), 1125(w), 1080(w), 1030(w), 1001(w), 923(w), 826(m), 774(m), 756(s), 696(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 208.1094 ($[M+Na]^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1102); analytical data in agreement with literature.[41]

(*E*)-3-Cyclopropyl-3-phenylacrylonitrile (*E*-8) Prepared according to General Procedure **A**, cyclopropylphenylketone (4 mmol) was converted to ***E*-8** in 24 h yielding a colourless oil (475 mg, 70%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.6 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.37 – 7.31 (m, 3H; H8/9), 7.28 – 7.23 (m, 2H; H7), 5.34 (d, *J* = 0.8 Hz, 1H; H2), 2.18 – 2.12 (m, 1H; H4), 1.05 – 1.01 (m, 2H; H5), 0.73 – 0.69 (m, 2H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.8 (C3), 137.4 (C6), 129.3 (C9), 128.4 (2C; C8), 127.4 (2C; C7), 117.4 (C1), 96.3 (C2), 16.3 (C4), 7.6 (2C; C5) ppm; IR (ATR): ῡ = 3059(w), 3012(w), 2213(m), 1896(w), 1668(w), 1591(m), 1574(w), 1492(m), 1444(m), 1427(w), 1384(w), 1318(w), 1241(w), 1176(w), 1099(w), 1059(w), 1031(m), 1001(w),

939(m), 898(w), 869(w), 820(m), 760(s), 734(w), 703(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 192.0776 ($[M+Na]^+$, calcd. for $C_{12}H_{11}NNa^+$: 192.07849.

(*E*)-4,4-Dimethyl-3-phenylpent-2-enenitrile (*E*-9) Prepared according to General Procedure **A**, 2,2,2-trimethylacetophenone (4 mmol) was converted to ***E*-9** in 24 h yielding a white solid (174 mg, 24%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.8 (Et_2O/*n*-pentane 1:9); M.p.: 60.7 – 61.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.31 (m, 3H; H8/9), 7.08 – 7.05 (m, 2H; H7), 5.22 (s, 1H; H2), 1.33 (s, 9H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.5 (C3), 141.6 (C6), 128.0 (2C; C8), 127.9 (C9), 127.1 (2C; C7), 117.3 (C1), 97.5 (C2), 37.8 (C4), 30.3 (3C; C5) ppm; IR (ATR): ῡ = 3081(w), 3027(w), 2968(m), 2907(w), 2870(w), 2292(w), 2213(m), 1957(w), 1884(w), 1809(w), 1759(w), 1684(w), 1609(m), 1595(m), 1575(w), 1488(m), 1479(m), 1461(m), 1398(m), 1364(m), 1214(m), 1072(m), 1029(w), 1010(w), 1000(w), 938(w), 915(w), 849(m), 837(m), 763(s), 698(s), 685(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 208.1100 ($[M+Na]^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1097).

(*Z*)-3-Fluoro-3-phenylacrylonitrile (*E*-10)[45] 3-phenyl-2-propynenitrile (127 mg, 1 mmol, 1.0 eq.) and AgF (253 mg, 2 mmol, 2.0 eq.) were dissolved with H_2O (0.1 mL) and MeCN (2 mL) under Argon. The resulting mixture was stirred at 80 °C for 24 h before being cooled to room temperature, filtered over celite and eluted with EtOAc. The resulting mixture was concentrated *in vacuo* and purification by column chromatography (SiO_2, 1-5% Et_2O/*n*-pentane) yielded the product ***E*-10** as a clear oil (80 mg, 54%). R_f = 0.44 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 – 7.60 (m, 2H; H5), 7.58 – 7.53 (m, 1H; H7), 7.47 (m, 2H; H6), 5.43 (d, J = 32.6 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.7 (d, J_{CF} = 275.1 Hz; C3), 132.8 (C7), 129.3 (d, J_{CF} = 2.2 Hz, 2C; C6), 128.6 (d, J_{CF} = 24.7 Hz; C4), 125.5 (d, J_{CF} = 7.6 Hz, 2C; C5), 113.6 (d, J_{CF} = 3.2 Hz; C1), 76.7 (d, J_{CF} = 16.0 Hz; C2) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -88.67 (d, J = 32.6 Hz) ppm; IR (ATR): ῡ = 3081(w), 2223(m), 1645(s), 1600(w), 1578(w), 1494(w), 1330(m), 1292(m), 1187(w), 1071(m), 1026(w), 1001(w), 972(w), 923(w), 833(m), 758(s), 687(s), 662(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 170.0380 ($[M+Na]^+$, calcd. for $C_9H_6FNNa^+$: 170.0382).

(*E*)-3-(4-(Trifluoromethyl)phenyl)acrylonitrile (*E*-11) Prepared according to General Procedure **A**, 4-trifluoromethylbenzaldehyde (4 mmol) was converted to ***E*-11** in 24 h yielding a off-white solid (126 mg, 16%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.3 (Et_2O/*n*-pentane 1:9); M.p.: 97.1 – 97.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.3 Hz, 2H; H6), 7.57 (d, J = 8.2 Hz, 2H; H5), 7.44 (d, J = 16.7 Hz, 1H; H3), 5.99 (d, J = 16.7 Hz, 1H; H2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.9 (C3), 136.8 (C4), 132.9 (q, J_{CF} = 32.8 Hz; C7), 127.7 (2C; C5), 126.3 (q, J_{CF} = 3.8 Hz, 2C; C6), 123.7 (q, J_{CF} = 272.4 Hz; C8), 117.5 (C1), 99.4 (C2) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.01 ppm; IR (ATR): ῡ = 3570(w), 3031(w), 2644(w), 2283(w), 2220(m), 1950(w), 1927(w), 1910(w), 1811(w), 1623(m), 1580(w), 1519(w), 1415(m), 1320(s), 1275(m), 1214(m), 1194(w), 1154(m),

1106(s), 1065(s), 1015(m), 979(m), 970(s), 954(m), 861(m), 852(m), 838(m), 813(s), 761(m), 733(m), 657(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.0348 ($[M+Na]^+$, calcd. for $C_{10}H_6F_3NNa^+$: 220.0345); analytical data in agreement with literature.[46]

(*E*)-3-(4-(Trifluoromethyl)phenyl)but-2-enenitrile (*E*-12) Prepared according to General Procedure **A**, 4-trifluoromethylacetophenone (4 mmol) was converted to ***E*-12** in 24 h yielding an off-white solid (577 mg, 68%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.37 (Et_2O/*n*-pentane 1:9); M.p.: 41.2 – 42.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 – 7.65 (m, 2H; H7), 7.59 – 7.55 (m, 2H; H6), 5.67 (q, J = 1.1 Hz, 1H; H2), 2.49 (d, J = 1.1 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.5 (C3), 141.9 (C5), 132.1 (q, J_{CF} = 33.1 Hz; C8), 126.4 (2C; C6), 126.0 (q, J_{CF} = 3.8 Hz, 2C; C7), 123.8 (q, J_{CF} = 272.3 Hz; C9), 117.0 (C1), 97.9 (C2), 20.4 (C4) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.96 ppm; IR (ATR): ῡ = 3071(w), 2990(w), 2215(m), 1927(w), 1804(w), 1675(w), 1614(w), 1577(w), 1442(w), 1415(m), 1384(w), 1322(s), 1262(w), 1201(m), 1155(m), 1110(s), 1087(s), 1067(s), 1014(s), 971(w), 958(m), 923(w), 850(m), 816(s), 749(m), 739(m), 662(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 234.0510 ($[M+Na]^+$, calcd. for $C_{11}H_8F_3NNa^+$: 234.0501).

(*E*)-3-(4-(Trifluoromethyl)phenyl)pent-2-enenitrile (*E*-13) Prepared according to General Procedure **A**, 4-trifluoromethylpropiophenone (4 mmol) was converted to ***E*-13** in 24 h yielding a colourless oil (518 mg, 57%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.67 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 – 7.62 (m, 2H; H8), 7.52 (m, 2H; H7), 5.53 (s, 1H; H2), 2.92 (q, J = 7.6 Hz, 2H; H4), 1.12 (t, J = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.1 (C3), 141.1 (C6), 132.0 (q, J_{CF} = 32.8 Hz; C9), 126.9 (2C; C7), 126.0 (q, J_{CF} = 3.8 Hz, 2C; C8), 123.9 (q, J = 272.2 Hz; C10), 116.7 (C1), 97.3 (C2), 27.6 (C4), 13.2 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.94 ppm; IR (ATR): ῡ = 3064(w), 2979(w), 2941(w), 2881(w), 2217(m), 2105(w), 1611(w) 1575(w), 1467(w), 1410(m), 1381(w), 1324(s), 1168(m), 1119(s), 1068(s), 1016(m), 908(w), 855(m), 822(m), 784(w), 744(w), 733(w), 659(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 248.0667 ($[M+Na]^+$, calcd. for $C_{12}H_{10}F_3NNa$: 248.0658).

(*E*)-3-(4-(Trifluoromethyl)phenyl)hex-2-enenitrile (*E*-14) Prepared according to General Procedure **A**, 4-trifluoromethylbutyrophenone (1.04 mmol) was converted to ***E*-14** in 24 h yielding a colourless oil (138 mg, 58%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.47 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 – 7.63 (m, 2H; H9), 7.54 – 7.46 (m, 2H; H8), 5.56 (s, 1H; H2), 2.92 – 2.84 (t, J = 7.5 Hz, 2H; H4), 1.50 (sext, J = 7.4 Hz, 2H; H5), 0.96 (t, J = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.7 (C3), 141.4 (q, J_{CF} = 1.2 Hz; C7), 132.0 (q, J_{CF} = 32.9 Hz; C10), 126.9 (2C; C8), 126.0 (q, J_{CF} = 3.8 Hz, 2C; C9), 123.9 (q, J_{CF} = 272.3 Hz; C11), 116.9 (C1), 98.1 (C2), 36.0 (C4), 21.7 (C5), 13.7 (C6) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.94 ppm; IR (ATR): ῡ = 3056(w), 2965(w), 2877(w), 2218(m), 1611(m), 1574(w), 1460(w), 1410(m), 1383(w), 1324(s), 1168(m), 1123(s), 1069(s), 1015(m), 878(w), 856(w), 821(m), 761(w), 745(w),

661(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 262.0830 ($[M+Na]^+$, calcd. for $C_{13}H_{12}F_3NNa$: 262.0814).

(*E*)-3-(4-(Trifluoromethyl)phenyl)hept-2-enenitrile (*E*-15) Prepared according to General Procedure **A**, 4-trifluoromethylvalerophenone (1.86 mmol) was converted to ***E*-15** in 24 h yielding a colourless oil (146 mg, 58%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.65 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.73 – 7.63 (m, 2H; H10), 7.55 – 7.47 (m, 2H; H9), 5.54 (s, 1H; H2), 2.90 (t, *J* = 7.3 Hz, 2H; H4), 1.47 – 1.41 (m, 2H; H5), 1.41 – 1.34 (m, 2H; H6), 0.91 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.9 (C3), 141.5 (C8), 131.98 (q, J_{CF} = 32.7 Hz; C11), 126.9 (2C; C9), 126.1 (q, J_{CF} = 3.7 Hz, 2C; C10), 123.9 (q, J_{CF} = 272.2 Hz; C12), 116.9 (C1), 97.9 (C2), 34.0 (C4), 30.5 (C5), 22.5 (C6), 13.8 (C7) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.93 ppm; IR (ATR): ϑ = 2960(w), 2933(w), 2865(w), 2217(w), 1611(w), 1574(w), 1461(w), 1410(w), 1382(w), 1324(s), 1262(w), 1168(m), 1126(s), 1069(s), 1016(m), 955(w), 925(w), 854(m), 821(m), 752(w), 661(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 276.0988 ($[M+Na]^+$, calcd. for $C_{14}H_{14}F_3NNa$: 276.0971).

(*E*)-3-(4-Methoxyphenyl)acrylonitrile (*E*-16) Prepared according to General Procedure **A**, anisaldehyde (4 mmol) was converted to ***E*-16** in 24 h yielding a white solid (538 mg, 84%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.19 (Et_2O/*n*-pentane 1:9); M.p.: 63.3 – 63.9 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (m, 2H; H5), 7.30 (m, 1H; H3), 6.88 (dq, *J* = 8.4, 1.7 Hz, 2H; H6), 5.68 (m, 1H; H2), 3.81 (dt, *J* = 3.0, 1.9 Hz, 3H; H8) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.2 (C7), 150.2 (C3), 129.2 (2C; C5), 126.5 (C4), 118.8 (C1), 114.7 (2C; C6), 93.5 (C2), 55.6 (C8) ppm; IR (ATR): ϑ = 3058(w), 3029(w), 2973(w), 2955(w), 2937(w), 2901(w), 2843(w), 2214(m), 1783(w), 1616(m), 1600(s), 1569(m), 1509(s), 1459(m), 1440(m), 1421(m), 1334(w), 1311(m), 1298(w), 1250(s), 1174(s), 1134(m), 1021(s), 985(s), 964(m), 943(m), 845(s), 827(m), 820(m), 806(s), 770(m), 720(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 182.0550 ($[M+Na]^+$, calcd. for $C_{10}H_9NONa^+$: 182.0576); analytical data in agreement with literature.[46]

(*E*)-3-(4-Methoxyphenyl)but-2-enenitrile (*E*-17) Prepared according to General Procedure **A**, 4-methoxyacetophenone (4 mmol) was converted to ***E*-17** in 24 h yielding an off-white solid (548 mg, 79%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.22 (Et_2O/*n*-pentane 1:9); M.p.: 57.4 – 58.7 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.49 – 7.40 (m, 2H; H6), 6.91 (d, *J* = 8.9 Hz, 2H; H7), 5.55 (q, *J* = 1.0 Hz, 1H; H2), 3.84 (s, 3H; H9), 2.44 (d, *J* = 1.0 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.5 (C8), 158.9 (C3), 130.6 (C5), 127.5 (2C; C6), 118.2 (C1), 114.3 (2C; C7), 93.4 (C2), 55.6 (C9), 20.2 (C4) ppm; IR (ATR): ϑ = 3069(w), 3022(w), 2975(w), 2937(w), 2910(w), 2834(w), 2202(m), 1839(w), 1600(m), 1573(m), 1512(s), 1455(m), 1440(m), 1433(m), 1419(m), 1375(m), 1336(w), 1311(w), 1297(m), 1272(m), 1246(s), 1182(s), 1175(s), 1119(m), 1086(w), 1052(w), 1023(s), 956(w), 940(w), 925(w), 833(m), 819(s), 799(s), 743(m), 720(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z:

196.0735 ([M+Na]$^+$, calcd. for $C_{11}H_{11}NONa^+$: 196.0738); analytical data in agreement with literature.[41]

(*E*)-3-(4-Methoxyphenyl)pent-2-enenitrile (*E*-18) Prepared according to General Procedure **A**, 4-methoxypropiophenone (4 mmol) was converted to ***E*-18** in 24 h yielding a colourless oil (340 mg, 45%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.4 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.35 (m, 2H; H7), 6.94 – 6.88 (m, 2H; H8), 5.43 (s, 1H; H2), 3.84 (s, 3H; H10), 2.87 (q, *J* = 7.6 Hz, 2H; H4), 1.14 (t, *J* = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.7 (C3), 161.4 (C9), 129.5 (C6), 127.9 (2C; C7), 117.9 (C1), 114.4 (2C; C8), 93.0 (C2), 55.5 (C10), 27.2 (C4), 13.7 (C5) ppm; IR (ATR): ῡ = 2973(m), 2937(w), 2840(w), 2210(m), 2060(w), 1980(w), 1678(m), 1599(s), 1572(m), 1512(s), 1463(m), 1418(m), 1377(w), 1352(w), 1297(m), 1255(s), 1234(s), 1183(s), 1103(m), 1066(m), 1030(s), 985(m), 908(w), 843(m), 802(m), 719(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 210.0900 ([M+Na]$^+$, calcd. for $C_{12}H_{13}NONa^+$: 210.0889).

(*E*)-3-(4-Methoxyphenyl)hex-2-enenitrile (*E*-19) Prepared according to General Procedure **A**, 4-methoxybutyrophenone (1 mmol) was converted to ***E*-19** in 24 h yielding a colourless oil (153 mg, 76%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.40 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 – 7.33 (m, 2H; H8), 6.96 – 6.88 (m, 2H; H9), 5.46 (d, *J* = 0.8 Hz, 1H; H2), 3.84 (d, *J* = 0.8 Hz, 3H; H11), 2.87 – 2.78 (m, 2H; H4), 1.52 (sext, *J* = 7.5 Hz, 2H; H5), 0.96 (t, *J* = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1 (C3), 161.3 (C10), 129.9 (C7), 127.9 (2C; C8), 118.1 (C1), 114.4 (2C; C9), 93.9 (C2), 55.5 (C11), 35.7 (C4), 22.1 (C5), 13.8 (C6) ppm; IR (ATR): ῡ = 2962(m), 2933(w), 2873(w), 2840(w), 2210(m), 1597(s), 1568(m), 1512(s), 1459(m), 1442(m), 1419(w), 1381(w), 1354(w), 1293(m), 1251(s), 1220(m), 1182(s), 1121(w), 1110(w), 1031(s), 878(w), 842(m), 813(s), 723(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 224.1044 ([M+Na]$^+$, calcd. for $C_{13}H_{15}NONa^+$: 224.1046).

(*E*)-3-(4-Methoxyphenyl)hept-2-enenitrile (*E*-20)[47] Prepared according to General Procedure **A**, 4-methoxyvalerophenone (2 mmol) was converted to ***E*-20** in 24 h yielding a colourless oil (262 mg, 61%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.35 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.35 (m, 2H; H9), 6.95 – 6.88 (m, 2H; H10), 5.44 (s, 1H; H2), 3.84 (d, *J* = 0.5 Hz, 2H; H12), 2.85 (t, *J* = 7.5 Hz, 2H; H4), 1.50 – 1.44 (m, 2H; H5), 1.42 – 1.35 (m, 2H; H6), 0.91 (t, *J* = 7.3 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.4 (C3), 161.3 (C11), 129.9 (C8), 127.9 (2C; C9), 118.1 (C1), 114.4 (2C; C10), 93.6 (C2), 55.5 (C12), 33.6 (C4), 31.0 (C5), 22.6 (C6), 13.9 (C7) ppm; IR (ATR): ῡ = 2957(m), 2932(m), 2872(w), 2840(w), 2210(m), 1596(s), 1569(m), 1512(s), 1461(m), 1442(m), 1418(w), 1380(w), 1342(w), 1286(m), 1250(s), 1182(s), 1114(w), 1031(s), 841(m), 811(s), 736(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 238.1212 ([M+Na]$^+$, calcd. for $C_{14}H_{17}NONa^+$: 238.1202).

(*E*)-3-(4-Fluorophenyl)pent-2-enenitrile (*E*-21)[42] Prepared according to General Procedure **A**, 4-fluoropropiophenone (4 mmol) was converted to ***E*-21** in 24 h yielding a colourless oil (402 mg, 57%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.48 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 – 7.36 (m, 2H; H7), 7.13 – 7.06 (m, 2H; H8), 5.45 (s, 1H; H2), 2.88 (q, *J* = 7.6 Hz, 2H; H4), 1.12 (t, *J* = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.3 (C3), 163.9 (d, J_{CF} = 250.9 Hz; C9), 133.5 (d, J_{CF} = 3.4 Hz; C6), 128.4 (d, J_{CF} = 8.4 Hz, 2C; C7), 117.3 (C1), 116.1 (d, J_{CF} = 21.7 Hz, 2C; C8), 95.1 (d, J_{CF} = 1.6 Hz; C2), 27.5 (C4), 13.4 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -110.5 (tt, *J*HF = 8.4, 5.2 Hz) ppm; IR (ATR): ῡ = 3060(w), 2977(m), 2940(w), 2879(w), 2214(m), 1897(w), 1602(s), 1587(m), 1509(s), 1467(m), 1411(w), 1379(w), 1338(w), 1306(w), 1285(w), 1231(s), 1163(s), 1100(w), 1066(w), 1013(w), 909(w), 848(m), 817(s), 719(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 198.0697 ([M+Na]$^+$, calcd. for $C_{11}H_{10}FNNa^+$: 198.0689).

(*E*)-3-(4-Chlorophenyl)but-2-enenitrile (*E*-22) Prepared according to General Procedure **A**, 4-chloroacetophenone (4 mmol) was converted to ***E*-22** in 24 h yielding a colourless oil (476 mg, 57%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.50 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.36 (m, 4H; H6/7), 5.60 (q, *J* = 1.1 Hz, 1H; H2), 2.45 (d, *J* = 1.1 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.5 (C3), 136.7 (C5), 136.5 (C8), 129.2 (2C; C7), 127.3 (2C; C6), 117.4 (C1), 96.2 (C2), 20.3 (C4) ppm; IR (ATR): ῡ = 3061(w), 2980(w), 2212(m), 1916(w), 1791(w), 1685(w), 1606(m), 1589(m), 1564(w), 1505(w), 1490(m), 1437(w), 1409(m), 1380(w), 1331(w), 1275(w), 1260(w), 1234(w), 1191(w), 1092(m), 1012(m), 967(w), 952(w), 923(w), 845(m), 809(s), 782(m), 711(w), 691(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 200.0236 ([M+Na]$^+$, calcd. for $C_{10}H_8ClNNa^+$: 200.0237); analytical data in agreement with literature.[41]

(*E*)-3-(4-Bromophenyl)pent-2-enenitrile (*E*-23) Prepared according to General Procedure **A**, 4-bromopropiophenone (4 mmol) was converted to ***E*-23** in 24 h yielding a white solid (655 mg, 69%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.48 (Et_2O/*n*-pentane 1:9); M.p.: 38.6 – 39.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 – 27.52 (m, 2H; H8), 7.30 – 7.27 (m, 2H; H7), 5.48 (s, 1H; H2), 2.87 (q, *J* = 7.6 Hz, 2H; H4), 1.11 (t, *J* = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.2 (C3), 136.3 (C6), 132.3 (2C; C8), 128.0 (2C; C7), 124.6 (C9), 117.1 (C1), 95.7 (C2), 27.3 (C4), 13.4 (C5) ppm; IR (ATR): ῡ = 3068(w), 3056(w), 2972(w), 2934(w), 2876(w), 2208(m), 1911(w), 1884(w), 1796(w), 1603(m), 1583(m), 1559(w), 1489(m), 1461(m), 1448(m), 1399(m), 1377(w), 1335(w), 1308(w), 1278(w), 1229(w), 1188(w), 1116(w), 1100(w), 1076(m), 1065(m), 1056(m), 1036(w), 1008(m), 965(w), 902(m), 845(m), 832(m), 801(s), 754(m), 715(w), 666(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 257.9895 ([M+Na]$^+$, calcd. for $C_{11}H_{10}BrNNa^+$: 257.9889).

(*E*)-3-(*p*-Tolyl)pent-2-enenitrile (*E*-24) Prepared according to General Procedure **A**, 4-methylpropiophenone (4 mmol) was converted to ***E*-24** in 24 h yielding a colourless oil (360 mg, 53%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane).

R_f = 0.41 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 2H; H7), 7.23 – 7.19 (m, 2H; H8), 5.47 (s, 1H; H2), 2.88 (q, *J* = 7.6 Hz, 2H; H4), 2.38 (s, 3H; H10), 1.13 (t, *J* = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3 (C3), 140.5 (C9), 134.5 (C6), 129.7 (2C; C8), 126.3 (2C; C7), 117.7 (C1), 94.1 (C2), 27.2 (C4), 21.4 (C10), 13.5 (C5) ppm; IR (ATR): ῡ = 3031(w), 2976(w), 2938(w), 2877(w), 2212(m), 1909(w), 1599(m), 1568(w), 1512(w), 1466(m), 1409(w), 1378(w), 1341(w), 1308(w), 1285(w), 1236(w), 1215(w), 1191(w), 1102(w), 1058(w), 1040(w), 1019(w), 908(w), 838(w), 801(s), 716(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 194.0950 ($[M+Na]^+$, calcd. for $C_{12}H_{13}NNa^+$: 194.0940).

(*E*)-3-(4-(*tert*-Butyl)phenyl)but-2-enenitrile (*E*-25) Prepared according to General Procedure **A**, 4-*tert*-butylpropiophenone (4 mmol) was converted to ***E*-25** in 24 h yielding a white solid (253 mg, 32%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.41 (Et_2O/*n*-pentane 1:9); M.p.: 97.9 – 98.4 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.44 – 7.40 (m, 4H; H6/7), 5.61 (q, *J* = 1.1 Hz, 1H; H2), 2.46 (d, *J* = 1.0 Hz, 3H; H4), 1.34 (s, 9H; H10) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.6 (C3), 153.9 (C8), 135.4 (C5), 125.9 (2C; C6/7), 125.8 (2C; C6/7), 118.0 (C1), 94.7 (C2), 31.3 (C10), 20.2 (C4) ppm; IR (ATR): ῡ = 3065(w), 3043(w), 2967(m), 2907(w), 2870(w), 2211(s), 1943(w), 1918(w), 1894(w), 1806(w), 1670(w), 1599(s), 1559(w), 1524(w), 1510(m), 1477(w), 1463(m), 1444(m), 1416(m), 1406(w), 1393(m), 1364(m), 1333(w), 1274(s), 1204(w), 1115(m), 1082(w), 1048(w), 1023(w), 1015(m), 924(w), 837(s), 815(s), 781(w), 738(m), 695(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 222.1259 ($[M+Na]^+$, calcd. for $C_{14}H_{17}NNa^+$: 222.1253).

(*E*)-3-([1,1'-Biphenyl]-4-yl)but-2-enenitrile (*E*-26) Prepared according to General Procedure **A**, 4-[1,1'-biphenyl]-acetophenone (4 mmol) was converted to ***E*-26** in 24 h yielding a white solid (74 mg, 8%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.37 (Et_2O/*n*-pentane 1:9); M.p.: 134.7 – 136.6 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.67 – 7.62 (m, 2H; H7), 7.62 – 7.59 (m, 2H; H10), 7.57 – 7.53 (m, 2H; H6), 7.50 – 7.45 (m, 2H; H11), 7.43 – 7.37 (m, 1H; H12), 5.68 (q, *J* = 1.1 Hz, 1H; H2), 2.51 (d, *J* = 1.0 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3 (C3), 143.3 (C8), 140.0 (C9), 137.1 (C5), 129.1 (2C; C11), 128.1 (C12), 127.6 (2C; C7), 127.2 (2C; C10), 126.5 (2C; C6), 117.8 (C1), 95.4 (C2), 20.3 (C4) ppm; IR (ATR): ῡ = 3080(w), 3037(w), 2997(w), 2211(m), 2164(w), 2118(w), 1990(w), 1915(w), 1886(w), 1837(w), 1764(w), 1689(w), 1598(m), 1581(m), 1555(w), 1485(m), 1437(m), 1408(m), 1381(m), 1343(w), 1331(w), 1283(w), 1253(w), 1219(w), 1165(w), 1141(w), 1077(w), 1044(w), 1003(m), 963(w), 919(w), 846(m), 826(m), 811(s), 764(s), 721(s), 690(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 242.0942 ($[M+Na]^+$, calcd. for $C_{16}H_{13}NNa^+$: 242.0940); analytical data in agreement with literature.[48]

(*E*)-4-(1-Cyanoprop-1-en-2-yl)benzonitrile (*E*-27) Prepared according to General Procedure **A**, 4-cyanoacetophenone (4 mmol) was converted to ***E*-27** in 24 h yielding a white solid (303 mg, 45%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.11 (Et_2O/*n*-pentane 1:9); M.p.: 136.5 – 137.9 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.73 –

7.69 (m, 2H; H7), 7.58 – 7.54 (m, 2H; H6), 5.68 (q, J = 1.1 Hz, 1H; H2), 2.49 (d, J = 1.1 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.8 (C3), 142.6 (C5), 132.8 (2C; C7), 126.7 (2C; C6), 118.2 (C9), 116.8 (C1), 113.9 (C8), 98.8 (C2), 20.3 (C4) ppm; IR (ATR): ῡ = 3067(w), 2999(w), 2227(m), 2213(m), 1926(w), 1801(w), 1667(w), 1608(m), 1557(w), 1505(w), 1441(w), 1411(m), 1380(w), 1335(w), 1315(w), 1280(w), 1261(w), 1212(w), 1183(w), 1134(w), 1080(w), 1014(w), 959(w), 922(w), 849(w), 815(s), 721(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 191.0570 ([M+Na]$^+$, calcd. for $C_{11}H_8N_2Na^+$: 191.0580); analytical data in agreement with literature.[41]

(*E*)-3-(3,4,5-Trifluorophenyl)pent-2-enenitrile (*E*-28) Prepared according to General Procedure **A**, 3,4,5-trifluoropropiophenone (4 mmol) was converted to ***E*-28** in 24 h yielding a white solid (308 mg, 34%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.56 (Et_2O/*n*-pentane 1:9); M.p.: 54.1 – 54.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.09 – 7.03 (m, 2H; H7), 5.47 (s, 1H; H2), 2.83 (q, J = 7.6 Hz, 2H; H4), 1.13 (t, J = 7.6 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.1 (q, J_{CF} = 2.1 Hz; C3), 151.6 (ddd, J_{CF} = 251.8, 10.1, 4.2 Hz, 2C; C8), 140.8 (dt, J_{CF} = 256.6, 15.3 Hz; C9), 133.7 – 133.4 (m; C6), 116.40 (C1), 111.4 – 110.8 (m, 2C; C7), 97.4 (d, J_{CF} = 1.7 Hz; C2), 27.4 (C4), 13.2 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -131.80 – -133.19 (m, 2F; F8), -157.07 (tt, J_{HF} = 20.3, 6.4 Hz; F9) ppm; IR (ATR): ῡ = 3076(w), 2987(w), 2951(w), 2887(w), 2214(m), 2163(w), 2013(w), 1762(w), 1623(m), 1603(m), 1558(w), 1529(s), 1466(m), 1445(m), 1431(s), 1381(m), 1366(s), 1338(m), 1286(w), 1271(w), 1262(w), 1245(m), 1221(m), 1195(w), 1126(w), 1099(w), 1070(m), 1052(s), 1039(s), 997(w), 975(w), 879(s), 824(s), 766(s), 708(m), 669(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 234.0470 ([M+Na]$^+$, calcd. for $C_{11}H_8F_3N$: 234.0501).

(*E*)-3-(Phenyl-d$_5$)but-2-enenitrile (*E*-29) Prepared according to General Procedure **A**, acetophenone-d$_5$ (4 mmol) was converted to ***E*-29** in 24 h yielding a colourless oil (468 mg, 79%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.39 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.62 (q, J = 1.1 Hz, 1H; H2), 2.47 (d, J = 1.1 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.8 (C3), 138.2 (C5), 130.8 – 129.3 (m; C8), 128.8 – 127.9 (m, 2C; C6/7), 126.1 – 125.2 (m, 2C; C6/7), 117.7 (C1), 95.6 (C2), 20.3 (C1) ppm; IR (ATR): ῡ = 3066(w), 2923(w), 2277(w), 2213(s), 1682(w), 1605(m), 1538(w), 1440(m), 1393(w), 1378(m), 1337(w), 1307(w), 1224(m), 1056(w), 1006(w), 960(w), 920(w), 837(m), 817(m), 764(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 171.0944 ([M+Na]$^+$, calcd. for $C_{10}H_4D_5NNa^+$: 171.0947).

(*E*)-3-(Pyridin-3-yl)but-2-enenitrile (*E*-30) Prepared according to General Procedure **A**, 3-acetylpyridine (4 mmol) was converted to ***E*-30** in 24 h yielding a pale yellow solid (269 mg, 47%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.05 (Et_2O/*n*-pentane 1:9); M.p.: 48.6 – 51.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 – 8.72 (m, 1H; H9), 8.65 (dd, J = 4.8, 1.6 Hz, 1H; H8), 7.75 (ddd, J = 8.0, 2.5, 1.6 Hz, 1H; H6), 7.35 (ddd, J = 8.0, 4.8, 0.9 Hz, 1H; H7), 5.66 (q, J = 1.1 Hz, 1H; H2), 2.49 (d, J = 1.1 Hz, 3H;

H4) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.8 (C3), 151.3 (C8), 147.1 (C9), 134.0 (C5), 133.3 (C6), 123.6 (C7), 116.9 (C1), 97.5 (C2), 20.2 (C4) ppm; IR (ATR): ϑ̃ = 3060(w), 3043(w), 2997(w), 2930(w), 2211(s), 1963(w), 1951(w), 1923(w), 1884(w), 1737(w), 1603(m), 1571(m), 1486(w), 1443(m), 1415(s), 1383(m), 1336(w), 1279(w), 1228(w), 1203(w), 1145(w), 1095(w), 1039(w), 1019(m), 995(w), 959(w), 984(w), 833(m), 798(s), 703(s), 663(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 167.0588 ([M+Na]$^+$, calcd. for $C_9H_8N_2Na^+$: 167.0585); analytical data in agreement with literature.[44]

(*E*)-3-(Naphthalen-1-yl)but-2-enenitrile (*E*-31) Prepared according to General Procedure **A**, 1-acetonaphthone (4 mmol) was converted to ***E*-31** in 24 h yielding a white solid (519 mg, 67%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.67 (Et_2O/*n*-pentane 1:9); M.p.: 51.2 – 51.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 – 7.83 (m, 3H; H10/8/13), 7.58 – 7.50 (m, 2H; H11/12), 7.47 (dd, *J* = 8.3, 7.0 Hz, 1H; H7), 7.29 (dd, *J* = 7.0, 1.2 Hz, 1H; H6), 5.47 (q, *J* = 1.2 Hz, 1H; H2), 2.56 (d, *J* = 1.2 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.4 (C3), 138.7 (C5), 133.8 (C9), 129.9 (C14), 129.4 (C8), 128.8 (C10), 127.0 (C12), 126.5 (C11), 125.2 (C7), 124.8 (C13), 124.5 (C6), 116.9 (C1), 100.3 (C2), 23.9 (C4) ppm; IR (ATR): ϑ̃ = 3058(w), 3043(w), 2980(w), 2959(w), 2217(m), 2166(w), 1965(w), 1939(w), 1851(w), 1826(w), 1786(w), 1717(w), 1692(w), 1650(w), 1623(m), 1616(m), 1588(m), 1578(m), 1507(m), 1430(s), 1395(m), 1373(m), 1337(w), 1316(m), 1247(m), 1207(m), 1188(w), 1163(w), 1140(w), 1128(w), 1067(w), 1029(m), 1014(m), 984(w), 971(m), 956(w), 918(w), 868(w), 846(s), 829(m), 803(s), 791(m), 774(s), 743(m), 723(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 216.0793 ([M+Na]$^+$, calcd. for $C_{14}H_{11}NNa$: 216.0784); analytical data in agreement with literature.[44]

(*Z*)-4,4,4-Trifluoro-3-phenylbut-2-enenitrile (*E*-32) Prepared according to General Procedure **A**, 2,2,2-trifluoroacetophenone (4 mmol) was converted to ***E*-32** in 24 h yielding a colourless oil (153 mg, 19%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.52 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (ddt, *J* = 8.1, 6.4, 1.6 Hz, 1H; H8), 7.49 – 7.42 (m, 4H; H7/6), 5.94 (s, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.8 (q, J_{CF} = 31.7 Hz; C3), 131.7 (C5), 131.4 (C8), 129.2 (2C; C7), 127.7 (d, J_{CF} = 1.2 Hz, 2C; C6), 121.5 (q, J_{CF} = 276.9 Hz; C4), 113.4 (d, J_{CF} = 1.5 Hz; C1), 103.5 (q, J_{CF} = 3.6 Hz; C2) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -61.54 ppm; IR (ATR): ϑ̃ = 3054(w), 2228(w), 1624(w), 1577(w), 1496(w), 1448(w), 1386(w), 1367(m), 1318(w), 1283(w), 1180(s), 1135(s), 1082(m), 1031(m), 1002(w), 916(m), 858(m), 763(m), 696(m), 663(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.0346 ([M+Na]$^+$, calcd. for $C_{10}H_6F_3NNa^+$: 220.0345); analytical data in agreement with literature.[49]

(*E*)-2-(2,3-Dihydro-1*H*-inden-1-ylidene)acetonitrile (*E*-33)[50] Prepared according to General Procedure **A**, indanone (4 mmol) was converted to ***E*-33** in 24 h yielding a white solid (325 mg, 52%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.36 (Et_2O/*n*-pentane 1:9); M.p.: 69.9 – 70.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (dt,

J = 7.8, 0.9 Hz, 1H; H10), 7.40 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H; H8), 7.38 – 7.35 (m, 1H; H7), 7.30 – 7.26 (m, 1H; H9), 5.65 (t, *J* = 2.4 Hz, 1H; H2), 3.16 – 3.06 (m, 4H; H4/5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.5 (C3), 149.7 (C6), 138.2 (C11), 131.8 (C8), 127.3 (C9), 126.0 (C7), 121.7 (C10), 118.3 (C1), 85.9 (C2), 31.5 (C4), 30.0 (C5) ppm; IR (ATR): ῡ = 3049(m), 3021(w), 2955(w), 2918(w), 2851(w), 2823(w), 2205(s), 1963(w), 1922(w), 1884(w), 1852(w), 1812(w), 1697(w), 1618(s), 1599(m), 1471(m), 1463(m), 1439(m), 1419(m), 1338(m), 1297(m), 1264(m), 1211(w), 1179(w), 1152(m), 1093(w), 1058(w), 1024(w), 1004(w), 984(w), 955(w), 943(w), 870(w), 831(m), 748(s), 765(m), 702(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 178.0647 ([M+Na]$^+$, calcd. for $C_{11}H_9NNa$: 178.0633).

(*E*)-2-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)acetonitrile (*E*-34)[51] Prepared according to General Procedure **A**, α-tetralone (4 mmol) was converted to ***E*-34** in 24 h yielding a white solid (360 mg, 53%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.36 (Et_2O/*n*-pentane 1:9); M.p.: 62.1 – 63.7 °C; ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.61 – 7.56 (m, 1H; H11), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H; H9), 7.25 – 7.17 (m, 2H; H8/10), 5.76 (t, *J* = 1.6 Hz, 1H; H2), 2.93 – 2.83 (m, 4H; H4/6), 2.01 – 1.87 (m, 2H; H5) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 159.6 (C3), 140.2 (C7), 132.3 (C12), 131.2 (C9), 130.1 (C8), 127.0 (C10), 124.7 (C11), 118.4 (C1), 91.3 (C2), 31.4 (C4), 30.6 (C6), 23.3 (C5) ppm; IR (ATR): ῡ = 3069(w), 3023(w), 2945(s), 2871(w), 2831(w), 2204(m), 1969(w), 1937(w), 1907(w), 1853(w), 1714(w), 1608(w), 1591(s), 1488(m), 1458(m), 1427(m), 1365(m), 1335(w), 1308(w), 1285(w), 1266(w), 1234(w), 1199(w), 1149(w), 1124(w), 1075(w), 1057(w), 1038(w), 986(w), 957(w), 916(w), 880(w), 868(w), 855(w), 828(s), 795(w), 754(s), 731(m), 723(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 192.0796 ([M+Na]$^+$, calcd. for $C_{12}H_{11}NNa$: 192.0784).

(*E*)-2-(6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-ylidene)acetonitrile (*E*-35)[52] Prepared according to General Procedure **A**, 2-benzosuberone (4 mmol) was converted to ***E*-35** in 24 h yielding an off-white solid (378 mg, 50%) after purification by column chromatography (SiO_2, - 5 % EtOAc/cyclohexane). R_f = 0.55 (EtOAc/cyclohexane 1:9); M.p.: 27.0 – 27.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (td, *J* = 7.5, 1.4 Hz, 1H; H10), 7.21 (td, *J* = 7.5, 1.4 Hz, 1H; H11), 7.15 (ddd, *J* = 7.5, 1.4, 0.6 Hz, 1H; H9), 7.14 (dd, *J* = 7.5, 1.6 Hz, 1H; H12), 5.34 (d, *J* = 0.8 Hz, 1H; H2), 2.81 – 2.74 (m, 4H; H4/7), 1.88 (p, *J* = 5.9 Hz, 2H; H5), 1.84 – 1.78 (m, 2H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.1 (C3), 140.4 (C13), 139.9 (C8), 129.7 (C9), 129.5 (C10), 127.3 (C12), 126.7 (C11), 117.1 (C1), 96.9 (C2), 34.8 (C7), 33.8 (C4), 27.8 (C5), 26.7 (C6) ppm; IR (ATR): ῡ = 3056(w), 2926(m), 2856(m), 2352(w), 2214(m), 2109(w), 1998(w), 1608(m), 1482(w), 1447(m), 1345(w), 1304(w), 1261(w), 1176(w), 1160(w), 1103(w), 1041(w), 946(w), 909(w), 868(w), 838(m), 758(s), 720(m), 661(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 206.0944 ([M+Na]$^+$, calcd. for $C_{13}H_{13}NNa$: 206.0940).

(*E*)-2-(7,8,9,10-Tetrahydrobenzo[8]annulen-5(6*H*)-ylidene)acetonitrile (*E*-36) Prepared according to General Procedure **A**, **51** (1.7 mmol) was converted to ***E*-36** in 24 h yielding an off-white solid (180 mg, 53%) after purification by column chromatography (SiO_2, - 5 %

EtOAc/cyclohexane). R_f = 0.70 (EtOAc/cyclohexane 1:9); M.p.: 28.3 – 29.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 (td, J = 7.5, 1.4 Hz, 1H; H11), 7.20 (td, J = 7.5, 1.3 Hz, 1H; H12), 7.16 (dd, J = 7.6, 1.2 Hz, 1H; H10), 6.95 (dd, J = 7.5, 1.4 Hz, 1H; H13), 5.23 (m, 1H; H2), 2.81 – 2.74 (m, 2H; H4), 2.68 – 2.64 (m, 2H; H8), 1.72 – 1.65 (m, 2H; H7), 1.65 – 1.60 (m, 2H; H5), 1.52 – 1.44 (m, 2H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.6 (C3), 140.0 (C14), 139.3 (C9), 129.3 (C10), 128.8 (C11), 126.2 (C12), 126.1 (C13), 116.7 (C1), 98.3 (C2), 39.4 (C4), 32.3 (C8), 31.1 (C7), 26.7 (C6), 25.7 (C5) ppm; IR (ATR): ῡ = 3067(w), 3014(w), 2932(m), 2861(m), 2215(m), 2084(w), 1615(m), 1597(w), 1446(m), 1356(w), 1317(w), 1271(w), 1234(w), 1192(w), 1159(w), 1109(w), 1069(w), 1043(w), 987(w), 949(w), 896(w), 835(m), 764(s), 709(m), 659(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.1103 ([M+Na]$^+$, calcd. for $C_{14}H_{15}NNa$: 220.1097).

(*E*)-3-(2-Fluorophenyl)acrylonitrile (*E*-37) Prepared according to General Procedure **A**, 2-fluorobenzaldehyde (5 mmol) was converted to ***E*-37** in 24 h yielding a colourless oil (512 mg, 70%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.5 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 (d, J_{CF} = 16.8 Hz, 1H; H3), 7.46 – 7.42 (m, 1H; H9), 7.42 – 7.39 (m, 1H; H7), 7.19 (td, J = 7.5, 1.1 Hz, 1H; H8), 7.13 (ddd, J = 10.9, 8.3, 1.1 Hz, 1H, H6), 6.03 (dd, J = 16.8, 0.9 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.2 (d, J_{CF} = 254.9 Hz; C5), 143.8 (d, J_{CF} = 2.4 Hz; C3), 132.8 (d, J = 8.9 Hz; C7), 128.8 (d, J_{CF} = 2.6 Hz; C9), 124.9 (d, J_{CF} = 3.7 Hz; C8), 121.8 (d, J_{CF} = 11.4 Hz; C4), 118.1 (C1), 116.6 (d, J_{CF} = 21.7 Hz; C6), 99.4 (d, J_{CF} = 9.0 Hz; C2) ppm.; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -114.20 (ddd, J_{HF} = 11.1, 7.3, 5.2 Hz) ppm; IR (ATR): ῡ = 3065(w), 2219(m), 1923(w), 1802(w), 1622(m), 1611(m), 1578(w), 1487(s), 1457(s), 1323(w), 1288(m), 1268(w), 1248(w), 1233(s), 1203(m), 1191(m), 1155(w), 1112(w), 1098(m), 1034(w), 967(s), 883(w), 862(m), 828(w), 797(m), 756(s), 719(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 170.0397 ([M+Na]$^+$, calcd. for C_9H_6FNNa: 170.0382); analytical data in agreement with literature.[53]

(*E*)-3-(2-Chlorophenyl)acrylonitrile (*E*-38) Prepared according to General Procedure **A**, 2-chlorobenzaldehyde (5 mmol) was converted to ***E*-38** in 24 h yielding a white solid (307 mg, 38%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.52 (Et_2O/*n*-pentane 1:9); M.p.: 40.4 – 40.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, J = 16.7 Hz, 1H; H3), 7.54 (dd, J = 7.8, 1.7 Hz, 1H; H9), 7.44 (dd, J = 7.9, 1.3 Hz, 1H; H8), 7.37 (td, J = 7.7, 1.7 Hz, 1H; H7), 7.31 (dddd, J = 7.9, 7.3, 1.4, 0.6 Hz, 1H; H6), 5.91 (d, J = 16.7 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.7 (C3), 134.7 (C5), 132.1 (C7), 131.9 (C4), 130.5 (C8), 127.5 (C6), 127.0 (C9), 117.8 (C1), 99.1 (C2) ppm; IR (ATR): ῡ = 3218(w), 3066(w), 2905(w), 2215(m), 1966(w), 1933(w), 1904(w), 1853(w), 1817(w), 1799(w), 1709(w), 1665(w), 1615(m), 1593(m), 1565(w), 1474(m), 1438(s), 1323(w), 1287(m), 1262(w), 1209(m), 1161(w), 1132(m), 1053(m), 1040(s), 1023(m), 1002(w), 966(s), 875(w), 859(w), 849(w), 829(m), 764(m), 745(s), 701(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 186.0079 ([M+Na]$^+$, calcd. for C_9H_6ClNNa: 186.0086); analytical data in agreement with literature.[54]

(*E*)-3-(2-Bromophenyl)acrylonitrile (*E*-39) Prepared according to General Procedure **A**, 2-bromobenzaldehyde (5 mmol) was converted to ***E*-39** in 24 h yielding a pale yellow solid (270 mg, 26%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.55 (Et_2O/*n*-pentane 1:9); M.p.: 57.3 – 58.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 16.6, 0.7 Hz, 1H; H3), 7.68 – 7.60 (m, 1H; H8), 7.52 (dd, *J* = 7.8, 1.7 Hz, 1H; H9), 7.35 (dddd, *J* = 7.9, 7.4, 1.3, 0.6 Hz, 1H; H6), 7.28 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H; H7), 5.86 (d, *J* = 16.6 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.2 (C3), 133.8 (C8), 133.7 (C4), 132.3 (C7), 128.1 (C6), 127.2 (C9), 124.9 (C5), 117.7 (C1), 99.3 (C2) ppm; IR (ATR): ῡ = 3212(w), 3083(w), 3068(m), 3037(w), 2896(w), 2219(s), 1961(w), 1923(w), 1790(w), 1699(w), 1667(w), 1615(m), 1587(m), 1563(m), 1466(m), 1435(s), 1305(w), 1289(w), 1281(w), 1255(w), 1206(m), 1163(m), 1116(w), 1048(m), 1026(s), 997(m), 980(w), 958(s), 851(w), 829(w), 743(s), 705(m), 670(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 229.9583 ([M+Na]$^+$, calcd. for C_9H_6BrNNa: 229.9581); analytical data in agreement with literature.[55]

(*E*)-3-(2-Iodophenyl)acrylonitrile (*E*-40) Prepared according to General Procedure **A**, 2-iodobenzaldehyde (5 mmol) was converted to ***E*-40** in 24 h yielding a yellow solid (356 mg, 28%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.56 (Et_2O/*n*-pentane 1:9); M.p.: 79.0 – 79.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H; H6), 7.66 (dd, *J* = 16.5, 0.5 Hz, 1H; H3), 7.48 (dd, *J* = 7.9, 1.6 Hz, 1H; H9), 7.39 (dddd, *J* = 7.8, 7.3, 1.1, 0.6 Hz, 1H; H8), 7.16 – 7.07 (m, 1H; H7), 5.79 (d, *J* = 16.5 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.9 (C3), 140.4 (C6), 137.0 (C4), 132.3 (C7), 128.9 (C8), 126.8 (C9), 117.6 (C1), 100.6 (C5), 99.4 (C2) ppm; IR (ATR): ῡ = 3052(w), 2214(m), 1963(w), 1925(w), 1783(w), 1608(m), 1580(m), 1558(w), 1460(m), 1432(m), 1312(w), 1295(w), 1278(m), 1250(w), 1206(m), 1165(w), 1109(w), 1048(w), 1016(m), 958(s), 945(m), 864(w), 848(w), 825(w), 746(s), 703(m), 657(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 277.9445 ([M+Na]$^+$, calcd. for C_9H_6INNa: 277.9443; analytical data in agreement with literature.[56]

(*E*)-3-(2-Fluorophenyl)but-2-enenitrile (*E*-41) Prepared according to General Procedure **A**, 2-fluoroacetophenone (4 mmol) was converted to ***E*-41** in 24 h yielding a colourless oil (438 mg, 68%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.74 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.35 (m, 1H; H8), 7.31 (td, *J* = 7.7, 1.8 Hz, 1H; H10), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H; H9), 7.11 (ddd, *J* = 11.3, 8.2, 1.2 Hz, 1H; H7), 5.62 (q, *J* = 1.2 Hz, 1H; H2), 2.46 (td, *J* = 1.3, 0.8 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.9 (d, J_{CF} = 251.7 Hz; C6), 156.1 (d, J_{CF} = 1.9 Hz; C3), 131.5 (d, J_{CF} = 8.9 Hz; C8), 129.0 (d, J_{CF} = 3.0 Hz; C10), 127.1 (dd, J_{CF} = 12.2, 1.1 Hz; C5), 124.6 (d, J_{CF} = 3.5 Hz; C9), 117.0 (C1), 116.7 (d, J_{CF} = 22.7 Hz; C7), 99.9 (d, J_{CF} = 6.9 Hz; C2), 21.5 (d, J_{CF} = 3.5 Hz; C4) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.87 (ddtd, J_{HF} = 13.0, 8.2, 3.1, 1.6 Hz) ppm; IR (ATR): ῡ = 3066(w), 2217(m), 1610(m), 1575(w), 1488(s), 1449(s), 1383(w), 1332(w), 1274(w), 1251(w), 1223(m), 1209(m), 1158(w), 1115(m), 1078(w), 1036(w), 946(w), 864(w), 823(s), 759(s), 727(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 184.0539 ([M+Na]$^+$, calcd. for $C_{10}H_8FNNa$: 184.0538); analytical data in agreement with literature.[44]

Ethyl (*E*)-3-Phenylhept-2-enoate (*E*-42) Prepared according to General Procedure **A**, valerophenone (4 mmol) was converted to ***E*-42** with triethyl phosphonoacetate in 24 h yielding a colourless oil (241 mg, 26%) after purification by column chromatography (SiO_2, 1 - 5 % Et_2O/*n*-pentane). R_f = 0.72 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 – 7.41 (m, 2H; H11), 7.39 – 7.34 (m, 3H; H12/13), 6.02 (d, *J* = 1.0 Hz, 1H; H4), 4.21 (qd, *J* = 7.2, 1.0 Hz, 2H; H2), 3.13 – 3.08 (m, 2H; H6), 1.45 – 1.34 (m, 4H; H7/8), 1.31 (td, *J* = 7.1, 1.0 Hz, 3H; H1), 0.88 (td, *J* = 7.1, 1.0 Hz, 3H; H9) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.7 (C3), 161.0 (C5), 141.7 (C10), 128.9 (C13), 128.6 (2C; C12), 126.8 (2C; C11), 117.4 (C4), 59.9 (C2), 31.3 (C7), 30.9 (C6), 22.9 (C8), 14.5 (C1), 14.0 (C9) ppm; IR (ATR): ῡ = 2957(w), 2930(w), 2060(w), 1712(s), 1623(m), 1576(w), 1493(w), 1446(w), 1369(m), 1349(w), 1297(w), 1267(m), 1161(s), 1117(m), 1096(m), 1046(m), 1018(w), 949(w), 915(w), 874(m), 770(m), 728(w), 696(m), 670(w), 660(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 255.1364 ([M+Na]$^+$, calcd. for $C_{15}H_{20}O_2Na^+$: 255.1364); analytical data in agreement with literature.[57]

Cinnamamide (*E*-43) (*E*)-3-phenylacrylic acid (296 mg, 2.0 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 (8.0 mL) and DMF (0.001 mL) under Argon, the solution was cooled to 0 °C and $SOCl_2$ (1.8 mL, 2.4 mmol, 1.2 eq.) was added dropwise. The resulting mixture was gradually warmed to room temperature before being stirred at rt for 6 h. NH_3 (1.36 mL, 28% in H_2O, 20.0 mmol, 10.0 eq.) was added and the resulting mixture was stirred for 24 h at room temperature before HCl (4 mL, 1 M) was added. The aqueous phase was extracted with CH_2Cl_2 (3x 10 mL), the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, 10 - 50 % EtOAc/cyclohexane) to yield the product ***E*-43** as an off-white solid (248 mg, 84%). R_f = 0.10 (EtOAc/cyclohexane 1:1); M.p.: 148.0 – 149.0 °C; ^{1}H NMR (600 MHz, MeOD-d_4): δ = 7.60 – 7.58 (m, 2H; H5), 7.58 (d, *J* = 16.0 Hz, 1H; H3), 7.45 – 7.36 (m, 3H; H6/7), 6.67 (d, *J* = 15.9 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, MeOD-d_4): δ = 170.9 (C1), 142.7 (C3), 136.2 (C4), 130.9 (C7), 130.0 (2C; C6), 128.9 (2C; C5), 121.4 (C2) ppm; IR (ATR): ῡ = 3371(m), 3162(m), 3085(w), 3030(w), 2779(w), 1952(w), 1880(w), 1752(w), 1660(s), 1634(m), 1606(s), 1579(m), 1493(m), 1450(m), 1397(s), 1317(m), 1288(m), 1246(m), 1201(m), 1072(w), 1002(w), 986(w), 967(s), 940(m), 862(m), 847(w), 788(m), 758(m), 692(s), 671(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 170.0577 ([M+Na]$^+$, calcd. for $C_9H_9NONa^+$: 170.0576); analytical data in agreement with literature.[58]

(*E*)-3-Phenylbut-2-enamide (*E*-44) (*E*)-3-phenylbut-2-enoic acid (200 mg, 1.2 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 (5.0 mL) and DMF (0.005 mL) under Argon, the solution was cooled to 0 °C and $SOCl_2$ (1.1 mL, 1.5 mmol, 1.25 eq.) was added dropwise. The resulting mixture was gradually warmed to room temperature before being stirred at rt for 6 h. NH_3 (0.85 mL, 28% in H_2O, 12.5 mmol, 10.4 eq.) was added and the resulting mixture was stirred for 24 h at room temperature before HCl (2.5 mL, 1 M) was added. The aqueous phase was extracted with CH_2Cl_2 (3x 10 mL), the combined organic phases were dried over $MgSO_4$, concentrated in *vacuo* and purified by column chromatography (SiO_2, 10 - 50 %

EtOAc/cyclohexane) to yield the product ***E*-44** as an off-white solid (98 mg, 51%). R_f = 0.18 (EtOAc/cyclohexane 1:1); M.p.: 119.0 – 120.0 °C; ^{1}H NMR (400 MHz, MeOD-d_4): δ = 7.49 – 7.44 (m, 2H; H6), 7.39 – 7.27 (m, 3H; H7/8), 6.20 (q, *J* = 1.3 Hz, 1H; H2), 2.47 (d, *J* = 1.4 Hz, 3H; H4) ppm; ^{13}C NMR (101 MHz, MeOD-d_4): δ = 172.1 (C1), 152.3 (C3), 143.9 (C5), 129.7 (C8), 129.5 (2C; C7), 127.2 (2C; C6), 120.4 (C2), 17.8 (C4) ppm; IR (ATR): $\tilde{\upsilon}$ = 3373(m), 3177(m), 3060(w), 3038(w), 2955(w), 2923(w), 2769(w), 2262(w), 1957(w), 1893(w), 1797(w), 1649(s), 1608(s), 1576(m), 1495(w), 1447(m), 1396(m), 1372(s), 1321(m), 1236(m), 1192(m), 1167(w), 1154(w), 1127(m), 1073(m), 1029(m), 1000(w), 965(w), 920(w), 897(m), 855(s), 836(w), 802(m), 759(s), 698(s), 672(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 184.0745 ([M+Na]$^+$, calcd. for $C_{10}H_{11}NONa^+$: 184.0733); analytical data in agreement with literature.[59]

(*E*)-3-Phenylpent-2-enamide (*E*-45)[60] (*E*)-3-phenylpent-2-enoic acid (438 mg, 2.5 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 (10.0 mL) and DMF (0.015 mL) under Argon, the solution was cooled to 0 °C and $SOCl_2$ (2.2 mL, 3 mmol, 1.2 eq.) was added dropwise. The resulting mixture was gradually warmed to room temperature before being stirred at room temperature for 6 h. NH_3 (1.7 mL, 28% in H_2O, 25.0 mmol, 10.0 eq.) was added and the resulting mixture was stirred for 24 h at room temperature before HCl (5 mL, 1 M) was added. The aqueous phase was extracted with CH_2Cl_2 (3x 10 mL), the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, 10 - 50 % EtOAc/cyclohexane) to yield the product ***E*-45** as an off-white solid (391 mg, 89%). R_f = 0.24 (EtOAc/cyclohexane 1:9); M.p.: 102.0 – 104.0 °C; ^{1}H NMR (600 MHz, MeOD-d_4): δ = 7.48 – 7.45 (m, 2H; H7), 7.42 – 7.34 (m, 3H; H8/H9), 6.11 (d, *J* = 1.0 Hz, 1H; H2), 3.12 (qd, *J* = 7.6, 1.0 Hz, 2H; H4), 1.03 (td, *J* = 7.4, 0.8 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, MeOD-d_4): δ = 171.7 (C1), 159.1 (C3), 142.8 (C6), 129.6 (2C; C8/C9), 129.5 (2C; C8/C9), 27.7 (C7), 120.1 (C2), 24.6 (C4), 13.9 (C5) ppm.; IR (ATR): $\tilde{\upsilon}$ = 3333(m), 3209(m), 2964(m), 2932(w), 2872(w), 1667(m), 1642(s), 1588(s), 1496(w), 1462(m), 1447(m), 1400(s), 1330(m), 1263(m), 1080(m), 1027(w), 886(m), 769(s), 694(s), 677(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 198.0905 ([M+Na]$^+$, calcd. for $C_{11}H_{13}NONa^+$: 198.0889).

(*E*)-3-Phenylhex-2-enamide (*E*-46)[60] (*E*)-3-phenylhex-2-enoic acid (170 mg, 0.90 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 (4.00 mL) and DMF (0.007 mL) under Argon, the solution was cooled to 0 °C and $SOCl_2$ (0.80 mL, 1.07 mmol, 1.2 eq.) was added dropwise. The resulting mixture was gradually warmed to room temperature before being stirred at room temperature for 6 h. NH_3 (0.67 mL, 25% in H_2O, 9.00 mmol, 10.0 eq.) was added and the resulting mixture was stirred for 24 h at room temperature before HCl (2 mL, 1 M) was added. The aqueous phase was extracted with CH_2Cl_2 (3x 5 mL), the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, 10 - 50 % EtOAc/*n*-pentane) to yield the product ***E*-46** as an off-white solid (128 mg, 75%). R_f = 0.06 (Et_2O/*n*-pentane 1:9); M.p.: 98.7 – 99.1 °C; ^{1}H NMR (600 MHz, MeOD-d_4): δ = 7.47 – 7.45 (m, 2H; H8), 7.41 – 7.37 (m, 2H; H9), 7.37 – 7.34 (m, 1H; H10), 6.13 (d, *J* = 0.6 Hz, 1H;

H2), 3.15 – 3.07 (m, 2H; H4), 1.56 – 1.32 (m, 2H; H5), 0.92 (t, J = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, MeOD-d_4): δ = 171.8 (C1), 157.6 (C3), 143.2 (C7), 129.5 (2C; C9), 129.5 (C10), 127.7 (2C; C8), 120.9 (C2), 33.2 (C4), 23.2 (C5), 14.2 (C6) ppm; IR (ATR): ῡ = 3356(w), 3261(w), 3090(w), 3055(w), 2966(w), 2927(w), 2871(w), 2541(m), 2382(m), 2358(m), 2296(w), 1943(w), 1801(w), 1641(s), 1602(s), 1576(m), 1515(w), 1499(m), 1465(m), 1453(m), 1405(s), 1363(s), 1292(w), 1261(w), 1241(w), 1216(w), 1157(m), 1101(w), 1080(w), 1089(w), 1034(w), 1000(w), 956(w), 891(m), 876(m), 851(w), 794(w), 762(s), 736(m), 724(m), 685(s), 662(m) cm^{-1}; HR-ESI-MS (Orbitrap): m/z: 212.10441 ([M+Na]$^+$, calcd. for $C_{12}H_{15}NONa^+$: 212.10459).

(*E*)-3-Phenylhept-2-enamide (*E*-47) 52 (80 mg, 0.40 mmol, 1.0 eq.) was dissolved in dry CH_2Cl_2 (2.00 mL) and DMF (0.007 mL) under Argon, the solution was cooled to 0 °C and $SOCl_2$ (0.07 mL, 0.96 mmol, 2.4 eq.) was added dropwise. The resulting mixture was gradually warmed to room temperature before being stirred at room temperature for 6 h. NH_3 (2.00 mL, 0.4 M in THF, 0.80 mmol, 2.0 eq.) was added and the resulting mixture was stirred for 24 h at room temperature before HCl (2 mL, 1 M) was added. The aqueous phase was extracted with CH_2Cl_2 (3x 5 mL), the combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, 10 - 50 % EtOAc/*n*-pentane) to yield the product ***E*-47** as an off-white solid (15 mg, 18%). R_f = 0.06 (Et_2O/*n*-pentane 1:9); M.p.: 84.4 – 84.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.38 (m, 2H; H9), 7.38 – 7.33 (m, 3H; H10/11), 5.94 (t, J = 0.6 Hz, 1H; H2), 3.15 – 3.07 (m, 2H; H4), 1.43 – 1.31 (m, 4H; H5/6), 0.89 – 0.82 (m, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.4 (C1), 158.2 (C3), 141.9 (C8), 128.6 (C11), 128.6 (2C; C10), 126.8 (2C; C9), 118.9 (C2), 31.2 (C4), 30.6 (C5), 22.9 (C6), 14.0 (C7) ppm.; IR (ATR): ῡ = 3390(m), 3307(w), 3189(m), 3059(w), 2957(w), 2923(w), 2871(w), 2858(w), 1660(s), 1601(s), 1576(m), 1497(w), 1449(m), 1401(m), 1379(m), 1332(m), 1284(m), 1243(m), 1158(w), 1121(w), 1105(w), 1080(w), 1033(w), 999(w), 962(w), 885(m), 865(w), 828(w), 762(s), 728(m), 692(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 226.1207 ([M+Na]$^+$, calcd. for $C_{13}H_{17}NONa^+$: 226.1202); analytical data in agreement with literature.[59]

Isomerisation of α,β-unsaturated carbonyl compounds

General Procedure B for the isomerisation of α,β-unsaturated carbonyl compounds

The specified α,β-unsaturated nitrile (0.100 mmol, 1.0 eq.) and (-)-riboflavin (1.9 mg, 0.005 mmol, 0.05 eq.) were dissolved in MeCN (1.5 mL) before being stirred for 12 h under UV-light irradiation. The residual catalyst was removed by filtration over a SiO_2-plug, subsequent elution of the products with Et_2O (5 mL) and concentration *in vacuo* yielded the mixture of the *Z*- and *E*-isomer. The yield was determined by mass recovery based on NMR-purity and the *E*-/*Z*-isomer ratio was determined by integration of the ^{1}H NMR spectra.

(*Z*)-3-Phenylacrylonitrile (1) Prepared according to General Procedure **B**, cinnamonitrile (13 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **1** in 12 h yielding a clear oil (13 mg, quant.; *Z*:*E* 62:38) after filtration over a SiO_2-plug. R_f = 0.38 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz,

$CDCl_3$): δ = 7.91 – 7.73 (m, 2H; H5), 7.45 (m, 3H; H6/7), 7.13 (d, *J* = 12.1 Hz, 1H; H3), 5.45 (d, *J* = 12.1 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.8 (C3), 133.7 (C4), 131.1 (C7), 129.1 (2C; C5), 129.0 (2C; C6), 117.5 (C1), 95.2 (C2) ppm.; IR (ATR): ῡ = 3069(w), 2215(m), 1697(w), 1611(m), 1575(w), 1495(m), 1448(m), 1339(w), 1323(w), 1306(w), 1233(w), 1180(w), 1078(w), 1030(w), 1001(w), 972(w), 944(w), 919(w), 776(s), 734(w), 712(m), 689(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 152.0469 ([*M*+Na]$^+$, calcd. for $C_9H_7NNa^+$: 152.0476); analytical data in agreement with literature.[61]

(*Z*)-3-Phenylbut-2-enenitrile (2) Prepared according to General Procedure **B**, ***E*-2** (15 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **2** in 12 h yielding a clear oil (15 mg, quant.; *Z*:*E* 91:9) after filtration over a SiO_2-plug. R_f = 0.35 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 – 7.51 (m, 2H; H6), 7.43 (m, 3H; H7/8), 5.40 (q, *J* = 1.7 Hz, 1H; H2), 2.29 (t, *J* = 2.0 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.1 (C3), 138.0 (C5), 130.0 (C8), 128.8 (2C; C7), 127.2 (2C; C6), 117.7 (C1), 95.6 (C2), 24.8 (C4) ppm; IR (ATR): ῡ = 3058(w), 2979(w), 2215(m), 1886(w), 1611(m), 1573(w), 1495(w), 1437(m), 1378(w), 1358(w), 1214(w), 1159(w), 1080(w), 1027(m), 1001(w), 919(w), 806(m), 766(s), 736(m), 697(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 166.0631 ([*M*+Na]$^+$, calcd. for $C_{10}H_9NNa^+$: 166.0627); analytical data in agreement with literature.[62]

(*Z*)-3-Phenylpent-2-enenitrile (3) Prepared according to General Procedure **B**, ***E*-3** (16 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **3** in 12 h yielding a clear oil (16 mg, quant.; *Z*:*E* 97:3) after filtration over a SiO_2-plug. R_f = 0.4 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 – 7.39 (m, 5H; H7-9), 5.37 (t, *J* = 1.5 Hz, 1H; H2), 2.60 (qd, *J* = 7.4, 1.5 Hz, 2H; H4), 1.08 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.4 (C3), 137.8 (C6), 129.6 (C9), 128.8 (2C; C8), 127.3 (2C; C7), 117.7 (C1), 94.6 (C2), 31.3 (C4), 12.3 (C5) ppm; IR (ATR): ῡ = 3060(w), 2973(w), 2938(w), 2876(w), 2216(m), 1614(m), 1573(w), 1496(w), 1461(m), 1443(m), 1419(w), 1370(w), 1310(w), 1208(w), 1086(w), 1049(w), 1029(w), 1002(w), 937(w), 916(w), 827(m), 775(s), 735(m), 699(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 180.0786 ([M+Na]$^+$, calcd. for $C_{11}H_{11}NNa^+$: 180.0784); analytical data in agreement with literature.[44]

(*Z*)-3-Phenylhex-2-enenitrile (4)[63] Prepared according to General Procedure **B**, ***E*-4** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **4** in 12 h yielding a clear oil (17 mg, quant.; *Z*:*E* 97:3) after filtration over a SiO_2-plug. R_f = 0.46 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 – 7.50 (m, 5H; H8-10), 5.50 (t, *J* = 1.3 Hz, 1H; H2), 2.68 (td, *J* = 7.4, 1.3 Hz, 2H; H4), 1.57 (sext, *J* = 7.4 Hz, 2H; H5), 1.04 (t, *J* = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.0 (C3), 137.6 (C7), 129.7 (C10), 128.8 (2C; C9), 127.4 (2C; C8), 117.6 (C1), 95.5 (C2), 40.2 (C4), 21.0 (C5), 13.5 (C6) ppm; IR (ATR): ῡ = 3058(w), 2961(m), 2933(m), 2873(w), 2216(m), 1612(m), 1573(w), 1495(w), 1457(w), 1443(m), 1381(w), 1335(w), 1209(w), 1070(w), 1031(w), 920(w), 868(w), 792(m), 780(m), 768(m), 730(w), 699(s), 663(w) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 194.0948 ([*M*+Na]$^+$, calcd. for $C_{12}H_{13}NNa^+$: 194.0940).

(*Z*)-3-Phenylhept-2-enenitrile (5)[64] Prepared according to General Procedure **B**, ***E*-5** (18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **5** in 12 h yielding a clear oil (18 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.5 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 – 7.38 (m, 5H; H9-11), 5.37 (t, *J* = 1.3 Hz, 1H; H2), 2.59 – 2.55 (m, 2H; H4), 1.41 – 1.36 (m, 2H; H5), 1.36 – 1.29 (m, 2H; H6), 0.88 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3 (C3), 137.7 (C8), 129.7 (C11), 128.8 (2C; C10), 127.4 (2C; C9), 117.7 (C1), 95.3 (C2), 38.0 (C4), 29.9 (C5), 22.2 (C6), 13.8 (C7) ppm; IR (ATR): ῡ = 3058(w), 2958(m), 2932(m), 2872(w), 2216(m), 1612(m), 1573(w), 1495(w), 1466(w), 1443(m), 1416(w), 1379(w), 1209(w), 1158(w), 1104(w), 1070(w), 1027(w), 1002(w), 920(w), 818(m), 777(s), 747(w), 729(m), 697(s), 659(w) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 208.1100 ([*M*+Na]$^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1097).

(*Z*)-4-Methyl-3-phenylpent-2-enenitrile (6) Prepared according to General Procedure **B**, ***E*-6** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **6** in 12 h yielding a clear oil (15 mg, 88%; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.5 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 – 7.38 (m, 3H; H8/9), 7.35 – 7.32 (m, 2H; H7), 5.35 (d, *J* = 1.4 Hz, 1H; H2), 2.85 (heptd, *J* = 6.8, 1.4 Hz, 1H; H4), 1.10 (d, *J* = 6.8 Hz, 6H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.5 (C3), 138.3 (C6), 129.3 (C9), 128.7 (2C; C8), 127.4 (2C; C7), 117.7 (C1), 94.4 (C2), 35.9 (C4), 21.3 (2C; C5) ppm; IR (ATR): ῡ = 3054(w), 2987(m), 2931(w), 2870(w), 2215(m), 1611(w), 1573(w), 1495(w), 1465(m) 1443(m), 1386(w), 1368(m), 1332(w), 1211(w), 1166(w), 1109(w), 1084(w), 1060(w), 1028(w), 1001(w), 920(w), 879(w), 839(w), 795(m), 778(m), 700(s), 666(w) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 194.0945 ([*M*+Na]$^+$, calcd. for $C_{12}H_{13}NNa^+$: 194.0940); analytical data in agreement with literature.[44]

(*Z*)-5-Methyl-3-phenylhex-2-enenitrile (7) Prepared according to General Procedure **B**, ***E*-7** (19 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **7** in 12 h yielding a clear oil (20 mg, quant.; *Z*:*E* 95:5) after filtration over a SiO_2-plug. R_f = 0.52 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.39 (m, 5H; H8-10), 5.36 (t, *J* = 1.2 Hz, 1H; H2), 2.45 (dd, *J* = 7.3, 1.2 Hz, 2H; H4), 1.60 (thept, *J* = 7.3, 6.7 Hz, 1H; H5), 0.87 (d, *J* = 6.7 Hz, 6H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.3 (C3), 137.5 (C7), 129.7 (C10), 128.8 (2C; C9), 127.5 (2C; C8), 117.6 (C1), 96.3 (C2), 47.6 (C4), 26.8 (C5), 22.3 (C6) ppm; IR (ATR): ῡ = 3060(w), 2967(m), 2932(w), 2874(w), 2217(m), 1611(m), 1573(w), 1495(w), 1465(m), 1443(m), 1387(w), 1359(w), 1310(w), 1164(w), 1105(w), 1076(w), 1007(w), 978(w), 919(w), 864(w), 819(m), 774(s), 735(m), 701(s), 666(w), 658(w) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 208.1097 ([*M*+Na]$^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1097); analytical data in agreement with literature.[65]

(*Z*)-3-Cyclopropyl-3-phenylacrylonitrile (8) Prepared according to General Procedure **B**, ***E*-8** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **8** in 12 h yielding a clear oil (15 mg, 85%; *Z*:*E* 95:5) after filtration over a SiO_2-plug. R_f = 0.32 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 – 7.45 (m, 2H; H7), 7.44 – 7.39 (m, 3H; H8/9), 5.21 (d, *J* = 0.8 Hz, 1H; H2), 1.78 (ttd, *J* = 8.3, 5.2, 0.8 Hz, 1H; H4), 1.06 – 0.95 (m, 2H; H5), 0.74 – 0.70 (m, 2H; H5) ppm;

^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.0 (C3), 137.3 (C6), 129.6 (C9), 128.6 (2C; C8), 127.7 (2C; C7), 117.8 (C1), 92.3 (C2), 18.7 (C4), 8.9 (2C; C5) ppm; IR (ATR): ϑ̃ = 3080(w), 3059(w), 3009(w), 2214(m), 1969(w), 1899(w), 1820(w), 1775(w), 1608(m), 1598(m), 1572(m), 1487(w), 1454(w), 1443(m), 1425(w), 1389(w), 1313(w), 1224(m), 1176(w), 1156(w), 1120(w), 1112(w), 1076(w), 1064(m), 1044(w), 1025(m), 1010(w), 978(m), 923(w), 889(w), 860(m), 835(m), 808(m), 770(s), 730(s), 698(s), 657(m) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 192.0776 ([*M*+Na]$^+$, calcd. for $C_{12}H_{11}NNa^+$: 192.0784); analytical data in agreement with literature.[66]

(*Z*)-4,4-Dimethyl-3-phenylpent-2-enenitrile (9) Prepared according to General Procedure **B**, ***E*-9** (19 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **9** in 12 h yielding a white solid (19 mg, quant.; *Z*:*E* 8:92) after filtration over a SiO_2-plug. R_f = 0.39 (Et_2O/*n*-pentane 1:9); M.p.: 78.3 – 79.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.36 (m, 3H; H8/9), 7.14 – 7.10 (m, 2H; H7), 5.52 (s, 1H; H2), 1.15 (s, 9H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 176.0 (C3), 137.9 (C6), 128.3 (C9), 128.3 (2C; C8), 128.0 (2C; C7), 117.2 (C1), 96.9 (C2), 37.9 (C4), 28.9 (3C; C5) ppm; IR (ATR): ϑ̃ = 3070(w), 3032(w), 2970(m), 2907(w), 2872(w), 2217(m), 1982(w), 1958(w), 1885(w), 1812(w), 1764(w9, 1672(w), 1614(m), 1593(m), 1575(w), 1520(w), 1483(m), 1463(w), 1444(w), 1389(w), 1364(m), 1336(w), 1250(m), 1202(w), 1179(w), 1163(w), 1075(m), 1029(w), 1002(w), 970(m), 917(w), 855(w), 837(s), 807(m), 774(m), 717(s), 699(s), 685(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 208.1105 ([*M*+Na]$^+$, calcd. for $C_{13}H_{15}NNa^+$: 208.1097).

(*E*)-3-Fluoro-3-phenylacrylonitrile (10) Prepared according to General Procedure **B**, ***E*-10** (14 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **10** in 12 h yielding a clear oil (13 mg, 90%; *Z*:*E* 45:55) after filtration over a SiO_2-plug. R_f = 0.89 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 – 7.94 (m, 2H; H5), 7.59 – 7.53 (m, 1H; H7), 7.53 – 7.49 (m, 2H; H6), 5.35 (d, *J* = 14.6 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.8 (d, J_{CF} = 267.0 Hz; C3), 132.7 (C7), 129.1 (d, J_{CF} = 1.8 Hz, 2C; C6), 128.54 (d, J_{CF} = 25.1 Hz; C4), 127.3 (d, J_{CF} = 8.0 Hz, 2C; C5), 115.6 (d, J_{CF} = 20.8 Hz; C1), 79.1 (d, J_{CF} = 48.4 Hz; C2) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -84.27 (d, *J* = 14.6 Hz) ppm; IR (ATR): ϑ̃ = 3063(w), 2224(m), 1896(w), 1641(s), 1601(w), 1575(w), 1496(w), 1447(w), 1357(s), 1195(s), 1112(m), 1096(m), 1075(m), 1026(w), 1001(w), 925(w), 801(m), 769(s), 748(w), 688(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 170.0382 ([M+Na]$^+$, calcd. for $C_9H_6FNNa^+$: 170.0376).

(*Z*)-3-(4-(Trifluoromethyl)phenyl)acrylonitrile (11) Prepared according to General Procedure **B**, ***E*-11** (19 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **11** in 12 h yielding a clear oil (19 mg, quant.; *Z*:*E* 62:38) after filtration over a SiO_2-plug. R_f = 0.24 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.88 (m, 2H; H5), 7.75 – 7.67 (m, 2H; H6), 7.19 (d, *J* = 12.1 Hz, 1H; H3), 5.61 (d, *J* = 12.1 Hz, 1H; H2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.2 (C3), 136.8 (q, J_{CF} = 1.2 Hz; C4), 132.54 (q, J_{CF} = 33.0 Hz; C7), 129.3 (2C; C5), 126.1 (q, J_{CF} = 3.8 Hz, 2C; C6), 123.74 (q, J_{CF} = 272.8 Hz; C8), 116.8 (C1), 98.1 (C2) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.03 ppm; IR (ATR): ϑ̃ = 3070(w), 2917(w), 2218(w), 1619(w), 1572(w), 1419(w), 1398(w), 1322(s), 1234(w), 1168(m), 1117(s), 1068(s), 1016(m), 974(w),

850(m), 814(w), 758(w), 728(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.0361 ($[M+Na]^+$, calcd. for $C_{10}H_6F_3NNa$: 220.0345); analytical data in agreement with literature.[67]

(*Z*)-3-(4-(Trifluoromethyl)phenyl)but-2-enenitrile (12) Prepared according to General Procedure **B**, ***E*-12** (22 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **12** in 12 h yielding a clear oil (22 mg, quant.; *Z*:*E* 91:9) after filtration over a SiO_2-plug. R_f = 0.18 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.72 – 7.68 (m, 2H; H7), 7.65 – 7.61 (m, 2H; H6), 5.50 (q, *J* = 1.6 Hz, 1H; H2), 2.30 (d, *J* = 1.6 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.7 (C3), 141.6 (q, J_{CF} = 1.3 Hz; C5), 131.8 (q, J_{CF} = 32.8 Hz; C8), 127.6 (2C; C6), 125.9 (q, J_{CF} = 3.8 Hz, 2C; C7), 123.9 (q, J_{CF} = 272.2 Hz; C9), 117.0 (C1), 97.5 (C2), 24.7 (C4) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.97 ppm; IR (ATR): ῡ = 3046(w), 2987(w), 2219(w), 1927(w), 1615(w), 1572(w), 1518(w), 1441(w), 1410(w), 1381(w), 1321(s), 1166(m), 1113(s), 1088(m), 1063(s), 1032(m), 1015(m), 846(s), 809(w), 722(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 234.0503 ($[M+Na]^+$, calcd. for $C_{11}H_8F_3NNa^+$: 234.0501).

(*Z*)-3-(4-(Trifluoromethyl)phenyl)pent-2-enenitrile (13) Prepared according to General Procedure **B**, ***E*-13** (23 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **13** in 12 h yielding a clear oil (23 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.21 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.73 – 7.69 (m, 2H; H8), 7.56 – 7.52 (m, 2H; H7), 5.46 (t, *J* = 1.6 Hz, 1H; H2), 2.61 (qd, *J* = 7.4, 1.6 Hz, 2H; H4), 1.10 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.0 (C3), 141.4 (C6), 131.6 (q, J_{CF} = 32.9 Hz; C9), 127.8 (2C; C7), 125.9 (q, J_{CF} = 3.8 Hz, 2C; C8), 123.9 (q, J_{CF} = 272.2 Hz; C10), 117.0 (C1), 96.3 (C2), 31.3 (C4), 12.2 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -63.97 ppm; IR (ATR): ῡ = 3055(w), 2975(w), 2944(w), 2882(w), 2218(m), 1938(w), 1818(w), 1615(m), 1574(w), 1515(w), 1463(m), 1445(w), 1405(m), 1382(w), 1322(s), 1289(w), 1249(w), 1214(w), 1190(w), 1163(s), 1115(s), 1108(s), 1065(s), 1046(m), 1012(m), 980(w), 963(w), 935(w), 851(m), 843(m), 835(m), 796(m), 754(w), 720(m), 658(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 248.0668 ($[M+Na]^+$, calcd. for $C_{12}H_{10}F_3NNa$: 248.0658.

(*Z*)-3-(4-(Trifluoromethyl)phenyl)hex-2-enenitrile (14) Prepared according to General Procedure **B**, ***E*-14** (24 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **14** in 12 h yielding a clear oil (24 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.21 (Et_2O/*n*-pentane); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.72 – 7.64 (m, 2H; H9), 7.54 (m, 2H; H8), 5.46 (t, *J* = 1.4 Hz, 1H; H2), 2.56 (td, *J* = 7.4, 1.4 Hz, 2H; H4), 1.58 – 1.39 (m, 2H; H5), 0.92 (t, *J* = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.6 (C3), 141.2 (q, J_{CF} = 1.3 Hz; C7), 131.6 (q, J_{CF} = 32.8 Hz; C10), 127.9 (2C; C8), 125.9 (q, J_{CF} = 3.8 Hz, 2C; C9), 123.9 (q, J_{CF} = 272.4 Hz; C11), 117.0 (C1), 97.1 (C2), 40.2 (C4), 20.9 (C5), 13.5 (C6) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.92 (d, *J* = 0.9 Hz) ppm; IR (ATR): ῡ = 2965(w), 2936(w), 2876(w), 2220(w), 1614(w), 1574(w), 1459(w), 1408(w), 1382(w), 1323(s), 1167(m), 1125(s), 1071(m), 1017(m), 849(m), 818(w), 780(w), 746(w), 721(w), 665(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 262.0797 ($[M+Na]^+$, calcd. for $C_{13}H_{12}F_3NNa$: 262.0814).

(*Z*)-3-(4-(Trifluoromethyl)phenyl)hept-2-enenitrile (15) Prepared according to General Procedure **B**, ***E*-15** (25 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **15** in 12 h yielding a clear oil (25 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.58 (EtOAc/cyclohexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 – 7.64 (m, 2H; H10), 7.56 – 7.50 (m, 2H; H9), 5.46 (t, *J* = 1.4 Hz, 1H; H2), 2.61 – 2.56 (m, 2H; H4), 1.41 – 1.36 (m, 2H; H5), 1.36 – 1.29 (m, 2H; H6), 0.89 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.9 (C3), 141.3 (q, J_{CF} = 1.3 Hz; C8), 131.6 (q, J_{CF} = 32.8 Hz; C11), 127.9 (2C; C9), 125.9 (q, J_{CF} = 3.7 Hz, 2C; C10), 123.9 (q, J_{CF} = 272.3 Hz; C12), 117.0 (C1), 97.0 (C2), 38.0 (C4), 29.7 (C5), 22.2 (C6), 13.8 (C7) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.91 ppm; IR (ATR): ῡ = 2962(w), 2918(w), 2850(w), 2220(w), 1615(w), 1575(w), 1462(w), 1409(w), 1323(m), 1258(m), 1166(m), 1066(s), 1015(s), 847(m), 788(s), 721(m), 703(m), 661(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 276.0990 ($[M+Na]^+$, calcd. for $C_{14}H_{14}F_3NNa$: 276.0971).

(*Z*)-3-(4-Methoxyphenyl)acrylonitrile (16) Prepared according to General Procedure **B**, ***E*-16** (16 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **16** in 12 h yielding an off-white solid (16 mg, quant.; *Z*:*E* 43:57) after filtration over a SiO_2-plug. R_f = 0.15 (Et_2O/*n*-pentane 1:9); M.p.: 57.7 – 59.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 – 7.77 (m, 2H; H5), 7.04 (d, *J* = 12.1 Hz, 1H; H3), 6.97 – 6.92 (m, 2H; H6), 5.29 (d, *J* = 12.1 Hz, 1H; H2), 3.86 (s, 3H; H8) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.8 (C7), 148.2 (C3), 131.1 (2C; C5), 126.7 (C4), 118.1 (C1), 114.4 (2C; C6), 92.1 (C2), 55.6 (C8) ppm; IR (ATR): ῡ = 3212(w), 3059(w), 3028(w), 2967(w), 2933(w), 2907(w), 2841(w), 2212(m), 1945(w), 1901(w), 1779(w), 1617(m), 1601(m), 1569(m), 1510(m), 1463(m), 1452(m), 1422(m), 1336(w), 1311(m), 1298(w), 1275(m), 1248(s), 1174(s), 1113(m), 1025(s), 972(s), 942(w), 843(s), 806(s), 767(m), 720(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 182.0581 ($[M+Na]^+$, calcd. for $C_{10}H_9NONa$: 182.0582).

(*Z*)-3-(4-Methoxyphenyl)but-2-enenitrile (17) Prepared according to General Procedure **B**, ***E*-17** (18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **17** in 12 h yielding a clear oil as an inseparable mixture of the *E*- and *Z*-isomer (19 mg, quant.; *Z*:*E* 81:19) after filtration over a SiO_2-plug. R_f = 0.23 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 – 7.55 (m, 2H; H6), 6.97 – 6.93 (m, 2H; H7), 5.30 (q, *J* = 1.5 Hz, 1H; H2), 3.84 (s, 3H; H9), 2.26 (d, *J* = 1.4 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.0 (C8), 160.1 (C3), 130.2 (C5), 128.9 (2C; C6), 118.3 (C1), 114.1 (2C; C7), 93.7 (C2), 55.5 (C9), 24.7 (C4) ppm; IR (ATR): ῡ = 2970(w), 2940(w), 2211(m), 2083(w), 1603(s), 1571(w), 1512(s), 1441(m), 1377(m), 1297(m), 1255(s), 1182(s), 1120(w), 1029(m), 836(s), 808(m), 730(w), 678(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 196.0740 ($[M+Na]^+$, calcd. for $C_{11}H_{11}NONa$: 196.0738).

(*Z*)-3-(4-Methoxyphenyl)pent-2-enenitrile (18) Prepared according to General Procedure **B**, ***E*-18** (19 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **18** in 12 h yielding a clear oil (19 mg, quant.; *Z*:*E* 92:8) after filtration over a SiO_2-plug. R_f = 0.21 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.43 (m, 2H; H7), 6.97 – 6.93 (m, 2H; H8), 5.29 (t, *J* = 1.4 Hz, 1H; H2), 3.84 (s, 3H; H10), 2.58 (qd, *J* = 7.4, 1.4 Hz, 2H; H4), 1.08 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR

(151 MHz, $CDCl_3$): δ = 166.6 (C3), 160.8 (C9), 129.8 (C6), 128.9 (2C; C7), 118.3 (C1), 114.1 (2C; C8), 93.1 (C2), 55.5 (C10), 31.1 (C4), 12.6 (C5) ppm; IR (ATR): ῡ = 2970(w), 2937(w), 2839(w), 2213(m), 1605(s), 1570(w), 1511(s), 1462(m), 1416(w), 1368(w), 1294(m), 1251(s), 1211(w), 1180(s), 1118(w), 1029(s), 981(w), 932(w), 835(s), 806(m), 738(w), 676(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 210.0900 ($[M+Na]^+$, calcd. for $C_{12}H_{13}NONa$: 210.0889).

(*Z*)-3-(4-Methoxyphenyl)hex-2-enenitrile (19) Prepared according to General Procedure **B**, ***E*-19** (20 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **19** in 12 h yielding a clear oil (20 mg, quant.; *Z*:*E* 90:10) after filtration over a SiO_2-plug. R_f = 0.36 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.8 Hz, 2H; H8), 6.98 – 6.90 (m, 2H; H9), 5.29 (t, *J* = 1.3 Hz, 1H; H2), 3.84 (s, 3H; H11), 2.63 – 2.36 (m, 2H; H4), 1.43 (sext, *J* = 7.4 Hz, 2H; H5), 0.90 (t, *J* = 7.4 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.3 (C3, obscured by gHMBC), 160.8 (C10), 129.7 (C7), 129.0 (2C; C8), 118.2 (C1, obscured by gHMBC), 114.2 (2C; C9), 94.0 (C2), 55.5 (C11), 40.1 (C4), 21.3 (C5), 13.6 (C6) ppm; IR (ATR): ῡ = 2961(m), 2933(w), 2873(w), 2839(w), 2212(m), 1670(w), 1606(s), 1512(s), 1461(m), 1415(w), 1372(w), 1295(m), 1253(s), 1180(s), 1116(w), 1032(m), 837(s), 808(m), 677(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 224.1049 ($[M+Na]^+$, calcd. for $C_{13}H_{15}NONa$: 224.1046).

(*Z*)-3-(4-Methoxyphenyl)hept-2-enenitrile (20) Prepared according to General Procedure **B**, ***E*-20** (22 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **20** in 12 h yielding a clear oil (22 mg, quant.; *Z*:*E* 90:10) after filtration over a SiO_2-plug. R_f = 0.33 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.42 (m, 2H; H9), 6.97 – 6.91 (m, 2H; H10), 5.29 (t, *J* = 1.3 Hz, 1H; H2), 3.84 (s, 3H; H12), 2.61 – 2.50 (m, 2H; H4), 1.41 – 1.35 (m, 2H; H5), 1.35 – 1.28 (m, 2H; H6), 0.88 (t, *J* = 7.2 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.5 (C3), 160.8 (C11), 129.8 (C8), 129.0 (2C; C9), 118.2 (C1), 114.2 (2C; C10), 93.8 (C2), 55.5 (C12), 37.8 (C4), 30.2 (C5), 22.3 (C6), 13.9 (C7) ppm; IR (ATR): ῡ = 2957(m), 2927(m), 2858(w), 2213(m), 1738(w), 1606(s), 1574(w), 1512(s), 1463(m), 1415(w), 1374(w), 1295(m), 1253(s), 1212(w), 1180(s), 1118(m), 1029(m), 836(s), 807(m), 750(w), 681(w), 658(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 238.1206 ($[M+Na]^+$, calcd. for $C_{14}H_{17}NONa$: 238.1202).

(*Z*)-3-(4-Fluorophenyl)pent-2-enenitrile (21)[42] Prepared according to General Procedure **B**, ***E*-21** (18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **21** in 12 h yielding a clear oil (18 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.46 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.42 (m, 2H; H7), 7.15 – 7.09 (m, 2H; H8), 5.37 (t, *J* = 1.5 Hz, 1H; H2), 2.58 (qd, *J* = 7.4, 1.5 Hz, 2H; H4), 1.08 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.2 (C3), 163.4 (d, J_{CF} = 249.9 Hz; C9), 133.7 (d, J_{CF} = 3.4 Hz; C6), 129.4 (d, J_{CF} = 8.4 Hz, 2C; C7), 117.6 (C1), 115.9 (d, J_{CF} = 21.8 Hz, 2C; C8), 94.9 (C2), 31.3 (C4), 12.3 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.12 (tt, *J* = 8.5, 5.3 Hz) ppm; IR (ATR): ῡ = 3051(w), 2974(w), 2938(w), 2217(m), 1897(w), 1603(m), 1509(s), 1462(w), 1420(w), 1368(w), 1302(w), 1227(s), 1162(m), 1104(m), 1049(w), 1014(w), 933(w), 841(s), 734(w),

690(w), 677(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 198.0689 ($[M+Na]^+$, calcd. for $C_{11}H_{10}FNNa$: 198.0689).

(*Z*)-3-(4-Chlorophenyl)but-2-enenitrile (22) Prepared according to General Procedure **B**, ***E*-22** (18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **22** in 12 h yielding a clear oil (18 mg, quant.; *Z*:*E* 87:13) after filtration over a SiO_2-plug. R_f = 0.44 (Et_2O/*n*-pentane 1:9); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 – 7.47 (m, 2H; H6), 7.43 – 7.39 (m, 2H; H7), 5.41 (q, *J* = 1.5 Hz, 1H; H2), 2.27 (d, *J* = 1.5 Hz, 3H; H4) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.7 (C3), 136.4 (C5), 136.0 (C8), 129.1 (2C; C7), 128.6 (2C; C6), 117.4 (C1), 96.2 (C2), 24.7 (C4) ppm; IR (ATR): ϑ̃ = 2979(w), 2918(w), 2216(m), 1899(w), 1611(m), 1596(m), 1491(s), 1440(m), 1397(m), 1378(w), 1357(w), 1271(w), 1214(w), 1097(s), 1030(m), 1013(s), 835(s), 765(m), 720(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 200.0238 ($[M+Na]^+$, calcd. for $C_{10}H_8ClNNa$: 200.0243); analytical data in agreement with literature.[44]

(*Z*)-3-(4-Bromophenyl)pent-2-enenitrile (23) Prepared according to General Procedure **B**, ***E*-23** (24 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **23** in 12 h yielding a white solid (24 mg, quant.; *Z*:*E* 95:5) after filtration over a SiO_2-plug. R_f = 0.28 (Et_2O/*n*-pentane 1:9); M.p.: 63.6 – 66.6 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.59 – 7.53 (m, 2H; H8), 7.34 – 7.30 (m, 2H; H7), 5.38 (t, *J* = 1.5 Hz, 1H; H2), 2.56 (td, *J* = 7.4, 1.5 Hz, 2H; H4), 1.07 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.1 (C3), 136.6 (C6), 132.1 (2C; C8), 129.0 (2C; C7), 124.0 (C9), 117.4 (C1), 95.2 (C2), 31.1 (C4), 12.3 (C5) ppm; IR (ATR): ϑ̃ = 3064(w), 2980(w), 2971(w), 2937(w), 2911(w), 2892(w), 2819(w), 2209(s), 1903(w), 1787(w), 1668(w), 1609(m), 1587(m), 1486(m), 1457(m), 1418(m), 1396(m), 1372(w), 1309(w), 1273(w), 1206(w), 1181(w), 1153(w), 1109(w), 1075(m), 1010(m), 957(w), 939(m), 844(s), 833(s), 826(s), 769(m), 755(s), 712(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 257.9901 ($[M+Na]^+$, calcd. for $C_{11}H_{10}BrNNa$: 257.9889).

(*Z*)-3-(*p*-Tolyl)pent-2-enenitrile (24) Prepared according to General Procedure **B**, ***E*-24** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **24** in 12 h yielding a clear oil (18 mg, quant.; *Z*:*E* 95:5) after filtration over a SiO_2-plug. R_f = 0.7 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.38 – 7.33 (m, 2H; H7), 7.25 – 7.20 (m, 2H; H8), 5.33 (t, *J* = 1.5 Hz, 1H; H2), 2.58 (qd, *J* = 7.4, 1.5 Hz, 2H; H4), 2.38 (d, *J* = 0.7 Hz, 3H; H10), 1.08 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.4 (C3), 139.9 (C9), 134.8 (C6), 129.5 (2C; C8), 127.3 (2C; C7), 118.0 (C1), 94.0 (C2), 31.2 (C4), 21.5 (C10), 12.5 (C5) ppm; IR (ATR): ϑ̃ = 3059(w), 3033(w), 2983(w), 2972(m), 2940(w), 2914(w), 2894(w), 2819(w), 2210(s), 1922(w), 1810(w), 1667(w), 1606(s), 1564(w), 1510(m), 1456(m), 1419(m), 1369(m), 1309(m), 1265(w), 1206(w), 1187(w), 1119(m), 1086(w), 1039(w), 1019(w), 994(w), 958(w), 940(m), 848(s), 839(s), 823(s), 768(m), 716(m), 691(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 194.0939 ($[M+Na]^+$, calcd. for $C_{12}H_{13}NNa$: 194.0940).

(*Z*)-3-(4-(*tert*-Butyl)phenyl)but-2-enenitrile (25) Prepared according to General Procedure **B**, ***E*-25** (20 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **25** in 12 h yielding a white solid (20 mg, quant.; *Z*:*E* 89:11) after filtration over a SiO_2-plug. R_f = 0.38 (Et_2O/*n*-pentane 1:9); M.p.: 66.8 – 67.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 – 7.50 (m, 2H; H6), 7.47 – 7.42 (m, 2H; H7), 5.36 (q, *J* = 1.5 Hz, 1H; H2), 2.27 (d, *J* = 1.5 Hz, 3H; H4), 1.34 (s, 9H; H10) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.7 (C3), 153.4 (C9), 135.0 (C5), 127.0 (2C; C6), 125.7 (2C; C7), 118.0 (C1), 94.7 (C2), 35.0 (C9), 31.3 (3C; C10), 24.7 (C4) ppm; IR (ATR): ṽ = 3086(w), 3042(w), 2960(m), 2904(w), 2867(w), 2211(m), 1921(w), 1800(w), 1683(w), 1611(m), 1591(w), 1513(w), 1478(w), 1465(w), 1440(w), 1405(w), 1394(w), 1378(w), 1363(m), 1271(m), 1217(w), 1200(w), 1128(w), 1117(m), 1078(w), 1050(w), 1022(w), 1015(m), 972(w), 957(w), 937(w), 927(w), 841(s), 828(s), 797(m), 748(w), 704(w), 667(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 222.1245 ([M+Na]$^+$, calcd. for $C_{14}H_{17}NNa$: 222.1253).

(*Z*)-3-([1,1'-Biphenyl]-4-yl)but-2-enenitrile (26) Prepared according to General Procedure **B**, ***E*-26** (22 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **26** in 12 h yielding a clear oil (22 mg, quant.; *Z*:*E* 70:30) after filtration over a SiO_2-plug. R_f = 0.42 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 – 7.64 (m, 4H; H6/7), 7.64 – 7.60 (m, 2H; H10), 7.50 – 7.44 (m, 2H; H11), 7.38 (ddt, *J* = 8.0, 6.8, 1.3 Hz, 1H; H12), 5.43 (q, *J* = 1.5 Hz, 1H; H2), 2.32 (d, *J* = 1.5 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.4 (C3), 142.9 (C8), 140.3 (C9), 136.8 (C5), 129.0 (2C; C11), 128.0 (C12), 127.7 (2C; C7), 127.4 (2C; C6), 127.3 (2C; C10), 117.8 (C1), 95.4 (C2), 24.7 (C4) ppm; IR (ATR): ṽ = 2961(m), 2933(w), 2874(w), 2216(m), 1737(w), 1612(m), 1573(w), 1495(w), 1457(w), 1443(m), 1416(w), 1380(w), 1336(w), 1243(w), 1210(w), 1068(w), 920(w), 866(w), 792(m), 779(m), 768(m), 749(w), 731(w), 699(s), 666(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 242.09375 ([M+Na]$^+$, calcd. for $C_{16}H_{13}NNa$: 242.09402).

(*Z*)-4-(1-Cyanoprop-1-en-2-yl)benzonitrile (27)[41] Prepared according to General Procedure **B**, ***E*-27** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **27** in 12 h yielding a white solid (18 mg, quant.; *Z*:*E* 86:14) after filtration over a SiO_2-plug. R_f = 0.08 (Et_2O/*n*-pentane 1:9); M.p.: 59.0 – 60.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 – 7.71 (m, 2H; H7), 7.65 – 7.59 (m, 2H; H6), 5.52 (q, *J* = 1.5 Hz, 1H; H2), 2.30 (d, *J* = 1.6 Hz, 3H; H4) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.1 (C3), 142.4 (C5), 132.7 (2C; C7), 128.0 (2C; C6), 118.3 (C9), 116.7 (C1), 113.7 (C8), 98.1 (C2), 24.5 (C4) ppm; IR (ATR): ṽ = 3092(w), 3038(w), 2965(w), 2234(m), 2214(m), 1981(w), 1943(w), 1818(w), 1666(w), 1608(m), 1552(w), 1509(m), 1444(w), 1407(m), 1380(m), 1362(m), 1320(w), 1301(w), 1277(w), 1218(w), 1185(w), 1122(w), 1084(w), 1051(w), 1021(m), 982(w), 960(w), 892(w), 847(s), 838(s), 735(w), 703(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 191.0584 ([M+Na]$^+$, calcd. for $C_{11}H_8N_2Na$: 191.0580).

(*Z*)-3-(3,4,5-Trifluorophenyl)pent-2-enenitrile (28) Prepared according to General Procedure **B**, ***E*-28** (21 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **28** in 12 h yielding a clear oil (21 mg, quant.; *Z*:*E* 96:4) after filtration over a SiO_2-plug. R_f = 0.19 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600

MHz, $CDCl_3$): δ = 7.11 – 7.06 (m, 2H; H3), 5.43 (t, *J* = 1.6 Hz, 1H; H2), 2.54 (qd, *J* = 7.4, 1.6 Hz, 2H; H4), 1.09 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.9 (q, J_{CF} = 1.8 Hz; C3), 151.4 (ddd, J_{CF} = 251.9, 10.2, 4.2 Hz, 2C; C8), 140.43 (dt, J_{CF} = 255.3, 15.1 Hz; C9), 133.80 – 133.43 (m; C6), 116.6 (C1), 112.1 (dd, J_{CF} = 17.3, 5.0 Hz, 2C; C7), 96.7 (C2), 31.1 (C4), 12.1 (C5) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -130.86 – -133.93 (m; 2F, F8), -158.01 (tt, *J* = 20.4, 6.4 Hz, 1F; F9) ppm; IR (ATR): ῡ = 3076(w), 3059(w), 2981(w), 2917(w), 2849(w), 2221(m), 1740(w), 1613(m), 1530(s), 1522(s), 1465(m), 1431(m), 1417(m), 1391(m), 1378(s), 1339(m), 1291(w), 1268(w), 1232(m), 1218(m), 1169(w), 1124(w), 1078(w), 1039(s), 955(w), 907(w), 884(w), 861(s), 842(s), 792(w), 765(s), 707(m), 661(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 234.0477 ($[M+Na]^+$, calcd. for $C_{11}H_8F_3NNa^+$: 234.0501).

(*Z*)-3-(Phenyl-d$_5$)but-2-enenitrile (29) Prepared according to General Procedure **B**, ***E*-29** (15 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **29** in 12 h yielding a clear oil (15 mg, quant.; *Z*:*E* 91:9) after filtration over a SiO_2-plug. R_f = 0.34 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.40 (q, *J* = 1.5 Hz, 1H; H2), 2.29 (d, *J* = 1.5 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.0 (C3), 137.8 (C5), 129.5 (m; C8), 128.7 – 127.9 (m, 2C; C6/7), 127.1 – 126.3 (m, 2C; C6/7), 117.7 (C1), 95.6 (C2), 24.8 (C4) ppm; IR (ATR): ῡ = 2979(w), 2918(w), 2214(s), 1610(m), 1536(w), 1437(m), 1402(w), 1377(m), 1322(m), 1191(m), 1064(w), 1024(w), 958(w), 840(m), 829(s), 805(s), 772(w), 701(w), 673(w), 658(m) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 171.0946 ($[M+Na]^+$, calcd. for $C_{10}H_4D_5NNa^+$: 171.0941).

(*Z*)-3-(Pyridin-3-yl)but-2-enenitrile (30) Prepared according to General Procedure **B**, ***E*-30** (14 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **30** in 12 h yielding a pale yellow oil (12 mg, 82%; *Z*:*E* 91:9) after filtration over a SiO_2-plug. R_f = 0.04 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.75 – 8.73 (m, 1H; H6), 8.64 (dd, *J* = 4.8, 1.7 Hz, 1H; H7), 7.92 – 7.85 (m, 1H; H9), 7.36 (m, 1H; H8), 5.49 (qd, *J* = 1.5, 0.4 Hz, 1H; H2), 2.30 (dd, *J* = 1.6, 0.4 Hz, 3H; H4) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.7 (C3), 150.9 (C7), 148.0 (C6), 134.7 (C9), 133.8 (C5), 123.5 (C8), 116.9 (C1), 97.6 (C2), 24.5 (C4) ppm; IR (ATR): ῡ = 3039(w), 2924(w), 2853(w), 2216(m), 1733(m), 1690(w), 1614(m), 1587(m), 1566(w), 1477(w), 1438(m), 1411(m), 1379(m), 1359(w), 1335(w), 1243(m), 1190(w), 1130(w), 1094(w), 1046(m), 1021(s), 958(w), 919(w), 819(s), 757(w), 733(m), 711(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 167.0585 ($[M+Na]^+$, calcd. for $C_9H_8N_2Na$: 167.0580); analytical data in agreement with literature.[68]

(*E*)-3-(Naphthalen-2-yl)but-2-enenitrile (31)[41] Prepared according to General Procedure **B**, ***E*-31** (19 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **31** in 12 h yielding a white solid (19 mg, quant.; *Z*:*E* 91:9) after filtration over a SiO_2-plug. R_f = 0.35 (Et_2O/*n*-pentane 1:9); M.p.: 71.2 – 71.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 – 7.87 (m, 2H; H10/8), 7.77 – 7.73 (m, 1H; H13), 7.57 – 7.49 (m, 3H; H12/11/7), 7.35 (dd, *J* = 7.0, 1.2 Hz, 1H; H6), 5.72 (q, *J* = 1.5 Hz, 1H; H2), 2.37 (d, *J* = 1.6 Hz, 3H; H4) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.9 (C3), 137.1 (C5), 133.9 (C9), 129.6 (C14), 129.3 (C8), 128.9 (C10), 126.8 (C12), 126.4 (C11), 125.5 (C7),

124.7 (C6), 124.5 (C13), 116.6 (C1), 99.8 (C2), 26.4 (C4) ppm; IR (ATR): ῡ = 3056(w), 2975(w), 2944(w), 2218(m), 1961(w), 1827(w), 1722(w), 1624(m), 1591(m), 1578(w), 1506(m), 1426(m), 1400(w), 1371(m), 1346(w), 1259(w), 1230(w), 1208(w), 1180(w), 1144(w), 1129(w), 1059(w), 1046(w), 1031(w), 1020(w), 997(w), 955(w), 917(w), 870(m), 841(w), 816(m), 804(s), 783(s), 745(m), 686(w), 661(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 216.0793 ($[M+Na]^+$, calcd. for $C_{14}H_{11}NNa$: 216.0784).

(*E*)-4,4,4-Trifluoro-3-phenylbut-2-enenitrile (32) Prepared according to General Procedure **B**, ***E*-32** (19 mg, 0.1 mmol, *Z*:*E* >20:1) was converted to **32** in 12 h yielding a clear oil (17 mg, 88%; *Z*:*E* 7:93) after filtration over a SiO_2-plug. R_f = 0.64 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.56 – 7.52 (m, 3H; H6/8), 7.52 – 7.48 (m, 2H; H7), 6.17 (q, *J* = 1.6 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.3 (q, J_{CF} = 31.6 Hz; C3), 131.4 (C8), 129.5 (C5), 129.2 (2C; C7), 128.5 (2C; C6), 122.0 (q, J_{CF} = 275.6 Hz; C4), 114.5 (C1), 103.9 (q, J_{CF} = 6.8 Hz; C2) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -66.14 (d, 3F, *J* = 1.6 Hz) ppm; IR (ATR): ῡ = 3071(w), 2232(w), 1719(w), 1635(w), 1577(w), 1500(w), 1446(w), 1374(w), 1277(s), 1172(s), 1132(s), 1083(m), 1030(m), 1005(m), 937(m), 915(m), 857(m), 774(s), 747(w), 708(s), 695(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.0346 ($[M+Na]^+$, calcd. for $C_{10}H_6F_3NNa$: 220.0345); analytical data in agreement with literature.[69]

(*Z*)-2-(2,3-Dihydro-1*H*-inden-1-ylidene)acetonitrile (33) Prepared according to General Procedure **B**, ***E*-33** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **33** in 12 h yielding a white solid (16 mg, 91%; *Z*:*E* 46:54) after filtration over a SiO_2-plug. R_f = 0.35 (Et_2O/*n*-pentane 1:9); M.p.: 31.8 – 33.1 °C; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.34 (m, 1H; H10), 7.41 (td, *J* = 7.4, 1.1 Hz, 1H; H8), 7.38 – 7.31 (m, 2H; H7/9), 5.33 (t, *J* = 2.2 Hz, 1H; H2), 3.07 – 3.03 (m, 2H; H5), 2.97 – 2.93 (m, 2H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.5 (C3), 150.3 (C6), 137.5 (C11), 131.8 (C8), 127.3 (C9), 125.7 (C7), 125.0 (C10), 117.9 (C1), 85.7 (C2), 33.3 (C4), 29.8 (C5) ppm; IR (ATR): ῡ = 3070(w), 3047(w), 2953(w), 2927(w), 2868(w), 2842(w), 2202(s), 1968(w), 1927(w), 1731(w), 1618(m), 1599(m), 1537(w), 1464(m), 1438(s), 1421(m), 1361(m), 1199(w), 1179(w), 1157(m), 1097(w), 1068(w), 1026(w), 1015(w), 984(w), 953(w), 812(m), 774(s), 756(s), 738(m), 696(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 178.0647 ($[M+Na]^+$, calcd. for $C_{11}H_9NNa$: 178.0627).

(*Z*)-2-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)acetonitrile (34) Prepared according to General Procedure **B**, ***E*-34** (18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **34** in 12 h yielding a clear oil (18 mg, quant.; *Z*:*E* 67:33) after filtration over a SiO_2-plug. R_f = 0.46 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, CD_2Cl_2): δ = 8.28 – 8.23 (m, 1H; H11), 7.35 (td, *J* = 7.4, 1.3 Hz, 1H; H9), 7.27 (m, 1H; H10), 7.22 (ddq, *J* = 7.6, 1.5, 0.7 Hz, 1H; H8), 5.30 (t, *J* = 1.4 Hz, 1H; H2), 2.90 (t, *J* = 6.4 Hz, 2H; H6), 2.60 (m, 2H; H4), 1.95 (p, *J* = 6.4 Hz, 2H; H5) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 159.8 (C3), 140.4 (C7), 132.5 (C12), 131.1 (C9), 129.8 (C8), 127.5 (C11), 126.5 (C10), 119.0 (C1), 91.1 (C2), 35.2 (C4), 30.3 (C6), 24.1 (C5) ppm; IR (ATR): ῡ = 3038(w), 2934(m), 2867(w), 2208(s), 1612(m), 1594(m), 1567(w), 1485(m), 1455(m), 1442(m), 1430(m),

1372(w), 1326(w), 1295(w), 1275(w), 1209(w), 1198(w), 1164(w), 1148(w), 1118(w), 1036(w), 950(w), 918(w), 878(w), 857(w), 793(s), 766(s), 727(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 192.0786 ($[M+Na]^+$, calcd. for $C_{12}H_{11}NNa$: 192.0784); analytical data in agreement with literature.[70]

(*Z*)-2-(6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-ylidene)acetonitrile (35)[71] Prepared according to General Procedure **B**, ***E*-35** (17 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **35** in 12 h yielding a clear oil (17 mg, quant.; *Z*:*E* 97:3) after filtration over a SiO_2-plug. R_f = 0.34 (EtOAc/cyclohexane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 7.1, 1.9 Hz, 1H; H12), 7.29 – 7.23 (m, 2H; H10/11), 7.18 – 7.15 (m, 1H; H9), 5.45 (t, *J* = 1.0 Hz, 1H; H2), 2.78 – 2.74 (m, 2H; H7), 2.51 – 2.46 (m, 2H; H4), 1.93 – 1.85 (m, 2H; H5), 1.81 – 1.73 (m, 2H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.5 (C3), 139.9 (C8), 139.0 (C13), 129.8 (C9), 129.4 (C10), 128.2 (C12), 126.6 (C11), 117.3 (C1), 96.4 (C2), 37.5 (C4), 35.8 (C7), 31.2 (C5), 27.2 (C6) ppm; IR (ATR): ϑ̃ = 3074(w), 3039(w), 2924(s), 2848(m), 2323(w), 2215(s), 2163(w), 2029(w), 1981(w), 1947(w), 1831(w), 1733(w), 1614(s), 1599(m), 1486(m), 1446(s), 1367(m), 1346(m), 1301(w), 1255(w), 1218(w), 1176(w), 1143(w), 1101(m), 1087(w), 1066(w), 1037(m), 991(m), 975(w), 959(w), 931(w), 902(m), 882(m), 856(w), 836(m), 819(s), 809(s), 768(s), 747(s), 704(m), 672(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 206.0928 ($[M+Na]^+$, calcd. for $C_{13}H_{13}NNa$: 206.0940).

(*Z*)-2-(7,8,9,10-Tetrahydrobenzo[8]annulen-5(6*H*)-ylidene)acetonitrile (36) Prepared according to General Procedure **B**, ***E*-36** (20 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **36** in 12 h yielding a clear oil (19 mg, 97%; *Z*:*E* 99:1) after filtration over a SiO_2-plug. R_f = 0.52 (EtOAc/cyclohexane 1:9); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.29 (td, *J* = 7.5, 1.5 Hz, 1H; H11), 7.24 (td, *J* = 7.5, 1.4 Hz, 1H; H12), 7.20 (dd, *J* = 7.4, 1.3 Hz, 1H; H10), 7.00 (dd, *J* = 7.5, 1.5 Hz, 1H; H13), 5.53 (t, *J* = 1.3 Hz, 1H; H2), 2.72 – 2.66 (m, 2H; H8), 2.55 – 2.46 (m, 2H; H4), 1.72 – 1.65 (m, 2H; H7), 1.56 (m, 2H; H5), 1.49 – 1.41 (m, 2H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.6 (C3), 139.0 (C9), 138.4 (C14), 129.5 (C10), 128.9 (C11), 126.5 (C12), 125.9 (C13), 116.5 (C1), 98.4 (C2), 42.1 (C4), 32.3 (C8), 31.5 (C7), 26.5 (C6), 26.2 (C5) ppm; IR (ATR): ϑ̃ = 3065(w), 3017(w), 2929(m), 2853(m), 2219(m), 2027(w), 1698(w), 1618(m), 1598(w), 1486(m), 1446(m), 1359(w), 1339(w), 1300(w), 1275(w), 1241(w), 1193(w), 1145(w), 1114(w), 1090(w), 1041(w), 1006(w), 972(w), 948(w), 933(w), 904(w), 862(w), 831(m), 812(m), 785(m), 755(s), 702(m), 676(m), 655(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 220.1103 ($[M+Na]^+$, calcd. for $C_{14}H_{15}NNa$: 220.1097).

(*Z*)-3-(2-Fluorophenyl)acrylonitrile (37)[72] Prepared according to General Procedure **B**, ***E*-37** (14 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **37** in 12 h yielding a clear oil (14 mg, quant.; *Z*:*E* 56:44) after filtration over a SiO_2-plug. R_f = 0.52 (Et_2O/*n*-pentane 1:9); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (dt, *J* = 7.7, 1.7 Hz, 1H; H9), 7.32 (m, 1H; H7), 7.27 (d, *J* = 12.2 Hz, 1H; H3), 7.09 (td, *J* = 7.7, 1.1 Hz, 1H; H8), 6.97 (ddd, *J* = 10.4, 8.3, 1.2 Hz, 1H; H6), 5.40 (d, *J* = 12.2 Hz, 1H; H2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.6 (d, J_{CF} = 253.4 Hz; C5), 140.5 (d,

J_{CF} = 7.0 Hz; C3), 132.9 (d, J_{CF} = 8.8 Hz; C7), 128.4 (C9), 124.7 (t, J_{CF} = 2.7 Hz; C8), 121.8 (d, J_{CF} = 11.2 Hz; C4), 117.0 (C1), 115.9 (d, J_{CF} = 20.9 Hz; C6), 97.2 (d, J_{CF} = 2.4 Hz; C2) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.33 (ddd, J = 10.4, 7.5, 5.3 Hz) ppm; IR (ATR): ῡ = 3072(w), 2986(w), 2217(w), 1734(m), 1620(m), 1609(m), 1574(w), 1484(s), 1457(s), 1373(m), 1311(w), 1245(s), 1207(m), 1154(w), 1099(m), 1046(m), 946(w), 914(w), 831(m), 766(s), 734(m), 713(m), 680(w), 656(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 170.0373 ([M+Na]$^+$, calcd. for C_9H_6FNNa: 170.0382).

(*Z*)-3-(2-Chlorophenyl)acrylonitrile (38) Prepared according to General Procedure **B**, ***E*-38** (16 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **38** in 12 h yielding a clear oil (16 mg, quant.; *Z*:*E* 68:32) after filtration over a SiO_2-plug. R_f = 0.5 (EtOAc/cyclohexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12 – 8.05 (m, 1H; H9), 7.56 (dd, J = 12.1, 0.5 Hz, 1H; H3), 7.47 – 7.43 (m, 1H; H6), 7.40 – 7.35 (m, 2H; H7/8), 5.60 (dd, J = 12.1, 0.4 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.5 (C3), 134.5 (C5), 131.9 (C7), 131.9 (C4), 130.1 (C6), 129.2 (C9), 127.4 (C8), 116.7 (C1), 98.3 (C2) ppm; IR (ATR): ῡ = 3065(w), 2218(m), 1926(w), 1708(w), 1613(m), 1592(m), 1469(m), 1439(s), 1304(w), 1223(w), 1184(w), 1162(w), 1129(w), 1052(s), 1039(s), 950(w), 868(w), 808(m), 772(s), 743(s), 702(w), 672(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 186.0087 ([M+Na]$^+$, calcd. for C_9H_6ClNNa: 186.0086); analytical data in agreement with literature.[73]

(*Z*)-3-(2-Bromophenyl)acrylonitrile (39) Prepared according to General Procedure **B**, ***E*-39** (21 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **39** in 12 h yielding a pale yellow solid (21 mg, quant.; *Z*:*E* 72:28) after filtration over a SiO_2-plug. R_f = 0.48 (Et_2O/*n*-pentane 1:9); M.p.: 38.8 – 39.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (ddt, J = 7.7, 1.6, 0.5 Hz, 1H; H9), 7.65 (ddd, J = 8.0, 1.3, 0.4 Hz, 1H; H6), 7.50 (dt, J = 12.1, 0.6 Hz, 1H; H3), 7.42 (dddd, J = 7.9, 7.4, 1.3, 0.6 Hz, 1H; H8), 7.29 (dddd, J = 7.8, 7.4, 1.6, 0.4 Hz, 1H; H7), 5.59 (d, J = 12.0 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.1 (C3), 133.6 (C4), 133.3 (C6), 132.0 (C7), 129.5 (C9), 128.0 (C8), 124.7 (C5), 116.6 (C1), 98.5 (C2) ppm; IR (ATR): ῡ = 3082(w), 3063(m), 2966(w), 2224(m), 1970(w), 1931(w), 1853(w), 1816(w), 1709(w), 1615(m), 1588(m), 1563(w), 1463(m), 1436(s), 1422(m), 1388(w), 1351(w), 1283(m), 1215(m), 1188(m), 1120(w), 1044(m), 1023(s), 961(w), 949(m), 916(w), 864(w), 804(w), 762(m), 733(s), 691(m), 653(m) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 229.9584 ([M+Na]$^+$, calcd. for C_9H_6BrNNa: 229.9581); analytical data in agreement with literature.[55]

(*Z*)-3-(2-Iodophenyl)acrylonitrile (40)[74] Prepared according to General Procedure **B**, ***E*-40** (25 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **40** in 12 h yielding a yellow solid (25 mg, quant.; *Z*:*E* 74:26) after filtration over a SiO_2-plug. R_f = 0.44 (Et_2O/*n*-pentane 1:9); M.p.: 38.2 – 38.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (m, 2H; H9/6), 7.45 (dddd, J = 7.9, 7.4, 1.3, 0.6 Hz, 1H; H8), 7.38 – 7.32 (m, 1H; H3), 7.11 (td, J = 7.7, 1.6 Hz, 1H; H7), 5.56 (d, J = 11.9 Hz, 1H; H2) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 152.6 (C3), 139.8 (C6), 136.9 (C4), 131.9 (C7), 129.1 (C9), 128.8 (C8), 116.4 (C1), 100.1 (C5), 98.5 (C2) ppm; IR

(ATR): ῡ = 3080(w), 3063(w), 3035(w), 3017(w), 2964(w), 2219(m), 1964(w), 1925(w), 1852(w), 1815(w), 1732(w), 1705(w), 1659(w), 1610(m), 1581(m), 1557(w), 1514(w), 1465(m), 1431(s), 1413(m), 1389(w), 1345(w), 1291(w), 1218(w), 1183(m), 1115(w), 1045(w), 1012(s), 986(m), 963(w), 951(m), 943(m), 903(w), 873(w), 800(m), 767(s), 742(s), 728(s), 695(s) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 277.9449 ($[M+Na]^+$, calcd. for C_9H_6INNa: 277.9443).

(*Z*)-3-(2-Fluorophenyl)but-2-enenitrile (41) Prepared according to General Procedure **B**, ***E*-41** (16 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **41** in 12 h yielding a clear oil (15 mg, 94%; *Z*:*E* 99:1) after filtration over a SiO_2-plug. R_f = 0.67 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.40 – 7.36 (m, 1H; H8), 7.35 (m, 1H; H10), 7.19 (td, *J* = 7.5, 1.1 Hz, 1H; H9), 7.13 (ddd, *J* = 10.5, 8.2, 1.1 Hz, 1H; H7), 5.50 (q, *J* = 1.6 Hz, 1H; H2), 2.27 (dd, *J* = 1.6, 1.0 Hz, 3H; H4) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.1 (d, J_{CF} = 249.4 Hz; C6), 157.7 (C3), 131.4 (d, J_{CF} = 8.3 Hz; C8), 129.5 (d, J_{CF} = 3.2 Hz; C10), 126.4 (d, J_{CF} = 14.7 Hz; C5), 124.6 (d, J_{CF} = 3.5 Hz; C9), 116.7 (C1), 116.4 (d, J_{CF} = 21.8 Hz; C7), 99.4 (C2), 24.7 (d, J_{CF} = 3.4 Hz; C4) ppm; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -110.56 – -120.05 (m) ppm; IR (ATR): ῡ = 3049(w), 2984(w), 2221(m), 1624(m), 1610(m), 1573(w), 1488(s), 1448(m), 1434(m), 1378(w), 1354(w), 1268(w), 1229(s), 1200(m), 1157(w), 1112(w), 1079(w), 1027(w), 946(w), 913(w), 830(s), 812(m), 760(s), 737(m), 706(w) cm^{-1}; HR-ESI-MS (MicroTOF): m/z: 184.0539 ($[M+Na]^+$, calcd. for $C_{10}H_8FNNa$: 184.0538); analytical data in agreement with literature.[44]

Ethyl (*Z*)-3-phenylhept-2-enoate (42)[75] Prepared according to General Procedure **B**, ***E*-42** (23 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **42** in 12 h yielding a clear oil (18 mg, 78%.; *Z*:*E* 99:1) after filtration over a SiO_2-plug. R_f = 0.58 (Et_2O/*n*-pentane 1:9); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.31 (m, 3H; H12/13), 7.17 – 7.12 (m, 2H; H11), 5.86 (d, *J* = 2.4 Hz, 1H; H4), 3.97 (q, *J* = 7.2 Hz, 2H; H2), 2.43 (t, *J* = 7.1 Hz, 2H; H6), 1.41 – 1.27 (m, 4H; H7/8), 1.05 (t, *J* = 7.0 Hz, 3H; H1), 0.87 (t, *J* = 6.7 Hz, 3H; H9) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.2 (C3), 159.9 (C5), 140.5 (C10), 127.9 (2C; C12), 127.6 (C13), 127.2 (2C; C11), 117.3 (C4), 59.9 (C2), 40.3 (C6), 29.6 (C7), 22.3 (C8), 14.1 (C1), 14.0 (C9) ppm; IR (ATR): ῡ = 3055(w), 2958(m), 2932(m), 2872(w), 1725(s), 1707(s), 1661(w), 1637(m), 1575(w), 1494(w), 1465(w), 1378(m), 1276(m), 1222(s), 1158(s), 1112(m), 1096(m), 1061(m), 1040(m), 961(w), 868(w), 775(w), 728(w), 698(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 255.1364 ($[M+Na]^+$, calcd. for $C_{15}H_{20}O_2Na^+$: 255.1361).

(*Z*)-3-Phenylacrylamide (43) Prepared according to General Procedure **B**, ***E*-43** (15 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **43** in 24 h yielding a white solid (14 mg, 98%.; *Z*:*E* 68:32) after filtration over a SiO_2-plug. R_f = 0.05 (Et_2O/*n*-pentane 1:9); M.p.: 132.3 – 134.4 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 2H; H5), 7.39 – 7.29 (m, 3H; H6/7), 6.84 (d, *J* = 12.6 Hz, 1H; H3), 5.98 (d, *J* = 12.6 Hz, 1H; H2), 5.77 (s, 1H; N-H), 5.49 (s, 1H; NH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1 (C1), 137.7 (C3), 135.0 (C4), 129.0 (2C; C5), 128.9 (C7), 128.7 (2C; C6), 124.0 (C2) ppm; IR (ATR): ῡ = 3319(m), 3146(m), 3085(m), 3023(w), 1949(w), 1837(w), 1663(s), 1614(s), 1575(m), 1494(s), 1456(m), 1433(s), 1345(s), 1320(m),

1240(w), 1189(w), 1156(w), 1134(m), 1078(w), 1031(w), 1002(w), 987(w), 976(w), 925(m), 800(s), 762(s), 752(s), 711(m), 688(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 170.0577 ([*M*+Na]$^+$, calcd. for $C_9H_9NONa^+$: 170.0576); analytical data in agreement with literature.[76]

(*Z*)-3-Phenylbut-2-enamide (44) Prepared according to General Procedure **B**, ***E*-44** (16 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **44** in 24 h yielding a white solid (16 mg, quant.; *Z*:*E* 93:7) after filtration over a SiO_2-plug. R_f = 0.06 (Et_2O/*n*-pentane 1:9); M.p.: 88.2 – 89.3 °C; ^{1}H NMR (600 MHz, CD_3OD): δ = 7.39 – 7.34 (m, 2H; H6), 7.31 (tt, *J* = 8.0, 1.5 Hz, 3H; H7/8), 5.99 (q, *J* = 1.5 Hz, 1H; H2), 2.18 – 2.17 (m, 3H; H4) ppm; ^{13}C NMR (151 MHz, CD_3OD): δ = 172.0 (C1), 150.7 (C3), 141.9 (C5), 129.2 (2C; C6), 128.9 (C8), 128.3 (2C; C7), 121.7 (C2), 26.6 (C4) ppm; IR (ATR): ῡ = 3326(w), 3080(w), 3057(w), 3046(w), 3023(w), 2999(w), 2957(w), 2906(w), 2556(m), 2464(w), 2391(m), 2341(w), 1988(w), 1962(w), 1938(w), 1885(w), 1764(w), 1666(m), 1640(m), 1609(s), 1597(s), 1572(s), 1492(m), 1442(m), 1402(m), 1346(s), 1312(m), 1289(m), 1266(m), 1217(w), 1144(m), 1079(w), 1035(w), 1025(w), 1011(w), 995(w), 964(w), 916(m), 879(m), 853(m), 841(m), 769(s), 750(m), 722(m), 698(s), 670(m) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 184.0737 ([*M*+Na]$^+$, calcd. for $C_{10}H_{11}NONa^+$: 184.0738).

(*Z*)-3-Phenylpent-2-enamide (45) Prepared according to General Procedure **B**, ***E*-45 (**18 mg, 0.1 mmol, *E*:*Z* >20:1) was converted to **45** in 24 h yielding a white solid (18 mg, quant.; *Z*:*E* 98:2) after filtration over a SiO_2-plug. R_f = 0.11 (EtOAc/cyclohexane 1:1); M.p.: 96.0 – 100.0 °C; ^{1}H NMR (600 MHz, CD_3OD): δ = 7.39 – 7.35 (m, 2H; H8), 7.34 – 7.30 (m, 1H; H9), 7.27 –7.24 (m, 2H; H7), 5.96 (t, *J* = 1.4 Hz, 1H; H2), 2.50 (qd, *J* = 7.4, 1.4 Hz, 2H; H4),1.05 (t, *J* = 7.4 Hz, 3H; H5) ppm; ^{13}C NMR (151 MHz, CD_3OD): δ = 172.2 (C1),156.5 (C3), 141.2 (C6), 129.2 (2C; C8), 128.8 (C9), 128.6 (2C; C7), 120.4 (C2), 33.7 (C4),12.6 (C5) ppm; IR (ATR): ῡ = 3476(m), 3293(m), 3057(w), 2932(w), 2885(w), 1661(s), 1634(s), 1606(s), 1597(s), 1491(m), 1423(m), 1330(m), 1307(m), 1208(m), 1052(m), 906(w), 887(s), 766(s), 738(m), 699(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 198.0891 ([*M*+Na]$^+$, calcd. for $C_{11}H_{13}NONa^+$: 198.0889).

(*Z*)-3-Phenylhex-2-enamide (46) Prepared according to General Procedure **B**, ***E*-46 (**38 mg, 0.2 mmol, *E*:*Z* >20:1) was converted to **46** in 12 h yielding a white solid (38 mg, quant.; *Z*:*E* 97:3) after filtration over a SiO_2-plug. R_f = 0.1 (Et_2O/*n*-pentane 1:9); M.p.: 100.2 - 101°C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.38 (m, 2H; H9), 7.37 – 7.33 (m, 1H; H10), 7.25 – 7.22 (m, 2H; H8), 5.89 (s, 1H; H2), 2.44 – 2.35 (m, 2H; H4), 1.41 (sext, *J* = 7.4 Hz, 2H; H5), 0.91 (t, *J* = 7.3 Hz, 3H; H6) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.7 (C1), 153.4 (C3), 139.5 (C7), 129.0 (2C; C9), 128.5 (C10), 127.5 (2C; C8), 121.9 (C2), 42.5 (C4), 20.6 (C5), 13.7 (C6) ppm; IR (ATR): ῡ = 3390(m), 3336(m), 3190(m), 3067(w), 2958(m), 2942(w), 2930(w), 2871(w), 2861(w), 1897(w), 1665(s), 1620(s), 1601(s), 1493(w), 1457(m), 1441(m), 1408(m), 1376(w), 1337(m), 1327(m), 1315(s), 1220(w), 1208(m), 1121(w), 1086(w), 1066(w), 1033(w), 1007(w), 979(w), 967(w), 946(w), 919(w), 890(m), 851(m), 795(m), 766(s), 745(m), 704(s), 666(m) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 212.1058 ([*M*+Na]$^+$, calcd. for $C_{12}H_{15}NONa^+$: 212.1051).

(*Z*)-3-Phenylhept-2-enamide (47) Prepared according to General Procedure **B**, ***E*-47 (**10 mg, 0.05 mmol, *E*:*Z* >20:1) was converted to **47** in 12 h yielding a white solid (10 mg, quant.; *Z*:*E* 97:3) after filtration over a SiO_2-plug. R_f = 0.2 (EtOAc/*n*-pentane 1:5); M.p.: 63.4 – 64.3°C ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.38 (m, 2H; H10), 7.37 – 7.33 (m, 1H; H11), 7.24 – 7.21 (m, 2H; H9), 5.89 – 5.87 (m, 1H; H2), 5.18 (s, 1H; HNH), 4.91 (bs, 1H; NH), 2.45 – 2.39 (m, 2H; H4), 1.40 – 1.29 (m, 4H; H5/6), 0.87 (t, *J* = 7.1 Hz, 3H; H7) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.8 (C1), 153.7 (C3), 139.6 (C8), 129.0 (2C; C10), 128.4 (C11), 127.5 (2C; C9), 121.7 (C2), 40.2 (C4), 29.5 (C5), 22.3 (C6), 14.0 (C7) ppm; IR (ATR): ῡ = 3450(w), 3283(w), 3170(w), 3053(w), 2960(w), 2930(w), 2871(w), 2858(w), 1730(w), 1674(m), 1661(s), 1635(m), 1608(s), 1491(w), 1466(w), 1455(w), 1439(w), 1410(m), 1380(w), 1318(m), 1204(w), 1172(w), 1102(w), 1074(m), 1053(w), 1023(w), 968(w), 951(w), 904(w), 886(w), 874(w), 858(w), 817(w), 776(s), 744(w), 729(w), 698(s) cm^{-1}; HR-ESI-MS (MicroTOF): *m*/*z*: 226.1214 ([*M*+Na]$^+$, calcd. for $C_{13}H_{17}NONa^+$: 226.1202).

ASSOCIATED CONTENT

Supporting Information

NMR spectra, absorption spectra, experimental procedures and mechanistic studies. Supporting information is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*j_mett03@uni-muenster.de
*j.neugebauer@uni-muenster.de
*ryan.gilmour@uni-muenster.de

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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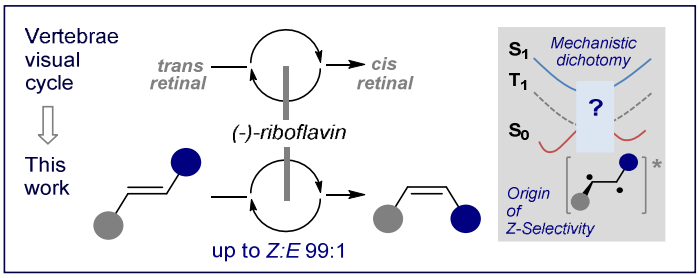
Vertebrae visual cycle
trans retinal
cis retinal
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This work
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Mechanistic dichotomy
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Origin of Z-Selectivity
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