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PAPER

Synthetic and mechanistic studies of metal-free transfer hydrogenations applying polarized olefins as hydrogen acceptors and amine borane adducts as hydrogen donors†‡

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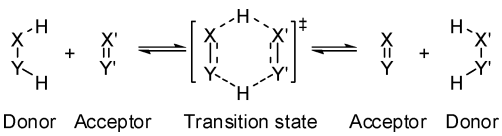
Metal-free transfer hydrogenation of polarized olefins (RR′C═CEE′: R, R′ = H or organyl, E, E′ = CN or CO_2Me) using amine borane adducts RR′NH–BH_3 (R = R′ = H, **AB**; R = Me, R′ = H, **MAB**; R = ^{t}Bu, R′ = H, **tBAB**; R = R′ = Me, **DMAB**) as hydrogen donors, were studied by means of *in situ* NMR spectroscopy. Deuterium kinetic isotope effects and the traced hydroboration intermediate revealed that the double H transfer process occurred regio-specifically in two steps with hydride before proton transfer characteristics. Studies on substituent effects and Hammett correlation indicated that the rate determining step of the H_N transfer is in agreement with a concerted transition state. The very reactive intermediate [NH_2═BH_2] generated from **AB** was trapped by addition of cyclohexene into the reaction mixture forming Cy_2BNH_2. The final product borazine $(BHNH)_3$ is assumed to be formed by dehydrocoupling of [NH_2═BH_2] or its solvent stabilized derivative [NH_2═BH_2]–(solvent), rather than by dehydrogenation of cyclotriborazane $(BH_2NH_2)_3$ which is the trimerization product of [NH_2═BH_2].

Introduction

Transfer hydrogenations are hydrogenation reactions that involve a double H transfer from hydrogen donors to hydrogen acceptors containing unsaturated bonds, such as C═C, C═O and C═N bonds,[1] which can principally be carried out in a metal-free fashion (Scheme 1), but can also be catalyzed by transition metal complexes. The metal mediated reactions play an important role in modern organic synthesis and industrial processes.[2] Given suitable hydrogen donor and acceptor molecules, transfer hydrogenations offer in the metal-free form an eco-friendly alternative to present hydrogenation methods.[3] They are expected to be operable on a metal-free base especially when polar hydrogen donors and acceptors are applied.[1]



Scheme 1 Metal-free double H transfer as a concerted elementary process. X, Y, X′ and Y′: main group element fragments.

A great deal of hydrogen-rich molecules have been applied as hydrogen donors in hydrogen transfer reactions, such as hydrazine, dihydronaphthalene, dihydroanthracene, formic acid,[4] alcohols, esters,[2] and also ammonia borane (**AB**) and related amine boranes.[5] In recent years, amine borane adducts have attracted additional attention for their very high volumetric and gravimetric hydrogen storage density as potentially safe and stable hydrogen storage materials.[6] Intensive studies were carried out on the dehydrogenation and the hydrogenation (regeneration) of these compounds, which remains as a practically unsolved problem.[7] Therefore, we became also interested in the use of such compounds as *in situ* hydrogen sources for the transfer hydrogenation of unsaturated compounds exploring new reaction pathways in the hope to create more reversible dehydrogenation processes of **AB**.

The catalytic reaction of **AB** in the presence of cyclohexene was reported to result in a hydroboration reaction with formation of Cy_2BNH_2 when using rhodium[8] or platinum[9] catalysts. On the other hand, olefins including cyclohexene were seen to be transfer hydrogenated by **AB** or dimethylamine borane (**DMAB**) using Rh colloid or nitrosyl Re(I) complexes.[5] Since the reaction course was found to be quite sensitive to the type of the catalyst, it might change completely if the substrate, solvent or other conditions are adjusted. Considering the strongly polarized hydridic H_B and protic H_N atoms in the amine borane molecules, the pathway might be switched from stepwise transfers to concerted double-H transfers as depicted in Scheme 1.

We have previously reported that aromatic imines, bearing a polarized C═N double bond, can be directly hydrogenated by **AB** *via* a 'polarity matched' concerted double-H transfer process.[10]

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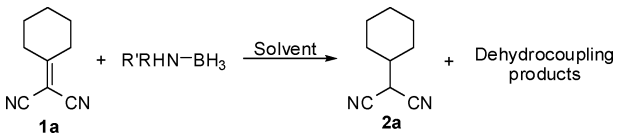
Table 1 Reactions of 2-cyclohexylidenemalononitrile (**1a**) with various amine borane adducts in different solvents[a]



Entry	R, R′	Solvent	Temp.	Time[b]	Dehydrocoupling compounds[c]
1	R = R′ = H	THF-D_8	r.t./0 °C	< 10 min/1 h	30.71 (d, J = 133 Hz), $(BHNH)_3$
2	R = R′ = H	CD_3CN	r.t.	1 h	$(BHNH)_3$
3[d]	R = R′ = H	Tol-D_8	r.t.	16 h	$(BHNH)_3$
4[d]	R = R′ = H	C_6D_6	r.t.	20 h	$(BHNH)_3$
5[d]	R = R′ = H	CD_2Cl_2	r.t.	2 d	$(BHNH)_3$
6[d]	R = R′ = H	$CDCl_3$	r.t.	5 d	$(BHNH)_3$
7[e]	R = R′ = H	C_2D_6SO	r.t.	> 5 d	$(BHNH)_3$
8	R = R′ = H	no solvent	r.t.	< 10 min	$(BHNH)_3$
9	R = R′ = H	CD_3OD	r.t.	< 10 min	12.26 (s), $B(OCD_3)_3$
10	R = H, R′ = Me	CD_3CN	r.t.	15 h	33.42 (d, J = 154 Hz), $(BHNMe)_3$
11	R = H, R′ = ^{t}Bu	CD_3CN	r.t./60 °C	3 d/5 h	28.78 (d, J = 124 Hz), $(BHN^tBu)_3$
12[f]	R = R′ = Me	CD_3CN	r.t./60 °C	5 d/20 h	8.23 (t, J = 112 Hz), $(BH_2NMe_2)_2$ + 31.15 (d, J = 131 Hz), $BH(NMe_2)_2$

[a] The reactions were carried out in a NMR tube and monitored by *in situ* ^{1}H and ^{11}B NMR spectroscopy (1 : 1 molar ratio of **1a** to **AB** or 1 : 2 molar ratio of **1a** to other amine boranes). [b] Required reaction times for full conversion of **1a** to **2a**. [c] The structure of the dehydrocoupling products of the amine boranes were determined by comparison of the resonances (in ppm) in the ^{11}B NMR spectrum to literature values; a small amount of unidentified insoluble white solid was also observed. [d] The solubility of **AB** in toluene, benzene, dichloromethane or chloroform is very low. [e] Less than 10% of the olefin was hydrogenated after 5 days at room temperature. [f] The ratio of the two dehydrocoupling compounds is 9 : 1 by integrations in the ^{11}B NMR spectra.

Ketones and aldehydes can also be transfer hydrogenated by **AB**, but a protic solvent such as methanol was required, since otherwise in an aprotic solvent, like THF, hydroboration would take place.[11] Furthermore, a step-by-step H_B before H_N transfer from **AB** to polarized olefins was found to proceed under mild conditions in THF or acetonitrile.[12] In this paper, we report a detailed study of the metal-free transfer hydrogenation and its mechanism of polar olefins with amine borane adducts.

Results and discussion

1. Solvent dependence and scope of amine borane adducts

2-Cyclohexylidenemalononitrile (**1a**) was selected as the model olefin and **AB** as a model amine borane adduct to test the general propensity of such compounds for hydrogen transfer reactions in a variety of solvents (Table 1). The reaction in THF was completed within 10 min at room temperature (Table 1, entry 1). When the conditions were adjusted by changing the solvent to higher polarity, like acetonitrile or by decreasing the temperature to 10 °C, 1 h was required to bring the hydrogen transfer to completion (entries 1–2). Other aprotic solvents were also tried. In toluene, benzene, dichloromethane (DCM), chloroform and DMSO the reactions were slow, partially due to also poor solubility of **AB** in these solvents (reasonable solubility in DMSO). The reaction rates in less polar solvents, toluene, benzene and DCM (entries 3–5), were higher than in the more polar solvents, like chloroform and DMSO (entries 6–7). Such a preference for apolar solvent supports the idea of a non-polar transition state.[13] In all these reactions, borazine ($(BHNH)_3$, **BZ**) was the main dehydrocoupling product of **AB**.

Compound **1a** is a liquid at room temperature and was found to dissolve **AB** and to induce solvent-free transfer hydrogenation forming **2a** and **BZ** at room temperature nearly instantaneously (Table 1, entry 7).

When the protic solvent methanol was applied as the reaction media, transfer hydrogenation of **1a** occurred also very fast. However, a completely different reaction took place in this case, only trimethyl borate was observed as the alcoholysis product of **AB** (Table 1, entry 8). The reaction proceeded along a hydroboration process, related to the reactions of **AB** with carbonyl compounds in methanol.[11]

Amine borane adducts other than **AB**, such as *N*-methyl amine borane (**MAB**), *N*-*tert*-butyl amine borane (**tBAB**) and *N*,*N*-dimethyl amine borane (**DMAB**), were then employed to react with **1a** in acetonitrile at room temperature. Transfer hydrogenation reactions similar to those with **AB** took place, but at much lower rates. Among these substituted amine boranes, **MAB** displayed superior reactivity towards **1a** with formation of the borazine analog $(BHNMe)_3$ as the dehydrocoupling product (Table 1, entry 9). The more sterically hindered mono-substituted amine borane adduct **tBAB** required a much longer time to complete the hydrogen transfer (entry 10), while the di-substituted **DMAB** turned out to react slowest, with the four-membered ring $(BH_2NMe_2)_2$ as the main dehydrocoupling product together with about 10% of $BH(NMe_2)_2$[14] (entry 11). Naturally, an increase of the temperature to 60 °C accelerated the reaction rates significantly (entries 10 and 11).

2. Range of the applied polar olefins

Based on the suitability of polar solvents in the transfer hydrogenations, acetonitrile was selected as the preferred solvent to test

the substrate dependence of the double H transfer reaction with **AB** as the model amine borane adduct (THF was the best solvent for the reaction, but it was too fast for study of the reaction course at room temperature). A series of activated olefins was employed to test the range of the substituent tolerance.

Most of the olefins with geminal electron-withdrawing (EWD) groups on one side of the CC double bond and H, alkyl or aromatic substituents on the other side could be successfully transfer hydrogenated by **AB** (Table 2, entries 1–7). In cases where there were two strongly polarized vinyl groups attached to a methylene group, deprotonation of the alkylic H took place yielding a stable anion (**2h**, entry 8). Otherwise, transfer hydrogenation of diolefinic substrates tended to occur primarily at the more strongly polarized double bond (**2i** and **2j**, entries 9–10). A completely different type of reaction takes place when the olefin is stabilized by a π push-pull interaction, such as in **1k**, or depolarized by two geminal strong EWD groups on the other side of the double bond as in **1l**, a complex mixture of compounds other than those originating from hydrogenation or hydroboration resulted (entries 11–12). Olefins with only one EWD group on the double bond were found to be much more reluctant to undergo transfer hydrogenation, even when heated to 60 °C for a prolonged reaction time (entries 13–14). The dehydrogenated Hantzsch ester could not at all be directly hydrogenated by **AB** (**1o**, entry 15).

3. Regio-specificity of the H transfers and deuterium kinetic isotope effects[12]

The regio-specificity and deuterium kinetic isotope effect (DKIE) were exemplarily investigated *via* the reactions of **1a** with **AB** using the selectively deuterated **AB** derivatives (NH_3BD_3 (**AB(D)**), ND_3BH_3 (**A(D)B**) and ND_3BD_3 (**A(D)B(D)**).

Tracing the regioselectivity of the deuterium addition, it was found that the protic H_N/D_N and the hydridic H_B/D_B end up at the C_{CN} atom of the double bond and the cyclohexylidene C atom, respectively. According to the kinetic conversion chart obtained by *in situ* ^{11}B NMR analyses for the reactions under pseudo-first order conditions (Fig. 1), the DKIE values were calculated from the simulated rate constants (k). Nearly no DKIE could be observed for deuterium labeling on the boron atoms (Fig. 1, $k_{AB}/k_{AB(D)} = 1$, $k_{A(D)B}/k_{A(D)B(D)} = 1.04$) and normal DKIEs were obtained with deuterium on the nitrogen atoms (Fig. 1, $k_{AB}/k_{A(D)B} = 1.55$, $k_{AB(D)}/k_{A(D)B(D)} = 1.62$). Assuming that the H_B transfer constitutes the rate determining step (RDS), this was expected to render DKIE values ≠ 1. A DKIE of 1 is expected to indicate that the double H transfer is stepwise and the H_B transfer would be fast occurring before or after the rate determining step.[15]

4. *p*-Aryl substituent effects of the polar olefins and Hammett correlations

Electronic substituent effects are usually studied by the effect of *para*-substituted phenyl groups at the crucial C atoms of the substrate.[16] Since the reaction of **AB** with the phenyl substituted olefin **1c** in CD_3CN was too fast to be measured at ambient conditions and the reaction with **1e** was too slow, **1d** was chosen for a model study of substituent effects (Table 2, entries 3–5). Several *para*-substituted derivatives of **1d** were used to react with **AB** at room temperature in CD_3CN in a 1 : 1 molar ratio (Scheme 2).

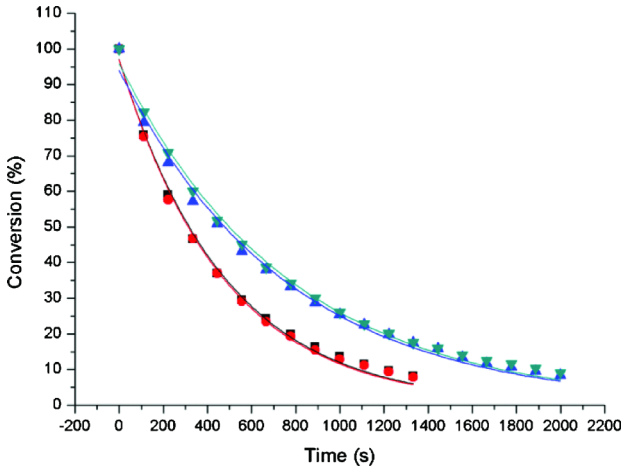
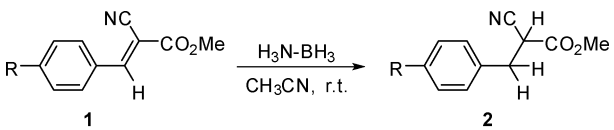


Fig. 1 Kinetic conversion chart of the reactions of 0.5 mmol **1a** with 0.1 mmol **AB**, **AB(D)**, **A(D)B** or **A(D)B(D)** pursued by *in situ* ^{11}B NMR spectroscopy in acetonitrile at room temperature with 2 min intervals. Concentrations were taken from the intensities of **AB** of the ^{11}B NMR spectra and filled to the first order reactions. The ■ stands for reactions with **AB**, ● for **AB(D)**, ▲ for **A(D)B** and ▼ for **A(D)B(D)**. Simulated deuterium kinetic isotope effects: $k_{AB}/k_{AB(D)} = 1.00$, $k_{A(D)B}/k_{A(D)B(D)} = 1.04$, $k_{AB}/k_{A(D)B} = 1.55$, $k_{AB(D)}/k_{A(D)B(D)} = 1.62$.



1 **2**

Substrate		Time	Yield
R = OMe	**1p**	3 h	99%
R = H	**1d**	0.5 h	99%
R = Cl	**1q**	20 min	99%
R = NO_2	**1r**	8 min	99%
R = CN	**1s**	5 min	99%

Substituent constants	
-OMe:	-0.268
-H:	0
-Cl:	0.227
-NO_2:	0.778
-CN:	1.00

Scheme 2 Transfer hydrogenation of **AB** with **1d** derivatives with different substituents in the *para*-positions (1 : 1 molar ratio) carried out in acetonitrile at room temperature. The trend in reaction times is comparable with the sequence of the substituent constants.

A sequence of reaction rates **1s** > **1r** > **1q** > **1d** > **1p** was derived (Scheme 2), closely correlating with the sequence of the substituents constants[17] –CN > –NO_2 > –Cl > –H > –OMe. Nevertheless, the solubility of the -NO_2 and -CN substituted olefins were not good in acetonitrile, but did not show much influence on the reaction rates.

$$\log (k/k_0) = \log k - \log k_0 = \rho^*\sigma \quad (1)$$

$$\log k = \rho^*\sigma + \log k_0 \quad (2)$$

Where k and k_0 are the rate constants of the reactions with substituted and unsubstituted substrates, respectively; σ is the substituent constant and ρ is the reaction constant.

Based on the Hammett eqn 1,[17] the reaction constant ρ was obtained as the slope of the σ *vs.* $\log k$ plot (eqn (2)). The Hammett correlation was plotted with **1d**, **1p**, **1q**, **1r** and **1s** (Fig. 2) and a $\rho = 1.02$ was obtained. The positive ρ value indicated increased electron density in the aromatic ring[18] suggesting that negative

Table 2 Transfer hydrogenation of various polarized olefins with **AB** (1 : 1 molar ratio) in CD_3CN

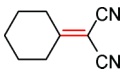
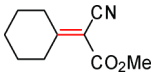
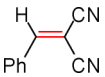
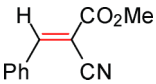
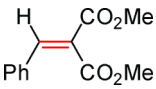
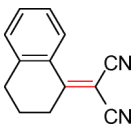
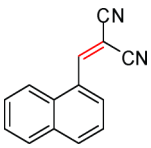
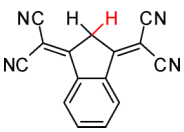
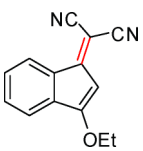
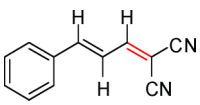
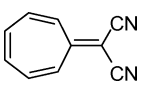
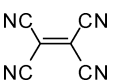
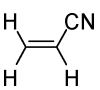
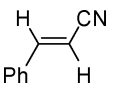
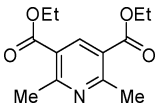
Entry	Substrates	Abbreviations	Temp.	Time	Yield (%)[a]
1		**1a/2a**	r.t.	1 h	99 (86)
2		**1b/2b**	r.t.	2 h	99
3		**1c/2c**	r.t.	10 min	99
4		**1d/2d**	r.t.	30 min	99
5		**1e/2e**	r.t.	3 d	98
6		**1f/2f**	r.t.	10 h	99
7		**1g/2g**	r.t.	30 min	99
8		**1h/2h**	r.t.	1 d	0[b]
9[c]		**1i/2i**	60 °C	1 d	86
10[c]		**1j/2j**	r.t. 60 °C	2 d 1.5 h	85 82
11[d]		**1k**	r.t. 60 °C	5 d 1 d	Complex mixture
12[d]		**1l**	r.t.	10 min	Complex mixture
13		**1m**	r.t. 60 °C	2 d 2 d	Trace 50
14		**1n**	r.t. 60 °C	5 d 5 d	n.r. Trace

Table 2 (*Contd.*)

Entry	Substrates	Abbreviations	Temp.	Time	Yield (%)[a]
15		**1o**	60 °C	5 d	n.r.

[a] The reactions were monitored by *in situ* ^{1}H NMR spectroscopy and the yields of the hydrogenated products were determined by integrations of the GC peaks within the GC-MS analyses (in brackets is the isolated yield). [b] Deprotonation of **1h** took place exclusively, yielding the anionic product dicyano(1-(dicyanomethylene)-1*H*-inden-3-yl)methanide **2h** with 99% yield. [c] Hydrogenation reactions occurred mainly with the double bond substituted by two –CN groups, the percentages adding up to 100% were attributed to products with both double bonds hydrogenated. [d] Neither transfer hydrogenation nor hydroboration was observed, the resulting mixture displayed a very broad complex peak ranging from 1.5 to 6.5 ppm in the ^{1}H NMR spectra.

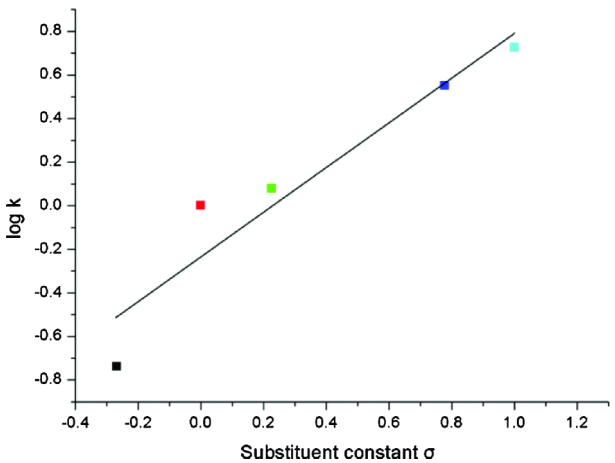
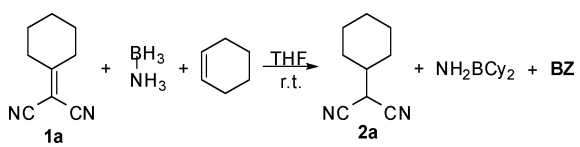


Fig. 2 Hammett correlation for the substituent effect in the transfer hydrogenation of polarized olefins with **AB**. The rate constants k were obtained from kinetic pursuits of the ^{11}B NMR spectra of the reactions of 0.1 mmol **AB** with 0.5 mmol of the *p*-substituted **1d** derivatives in acetonitrile. The values of the substituent constant σ were taken from literature. ■ Represents the –OMe, ■ –H, ■ –Cl, ■ -NO_2 and ■ –CN group, respectively. The slope of the kinetic curve was $\rho = 1.02$.

charge is generated in the transition state of the RDS. Since the transfer of the protic H_N is participating in the RDS of these reactions and the attack of a H^+ ion would generate positive charge, it seemed reasonable to assume that the reaction passes over a concerted transition state.

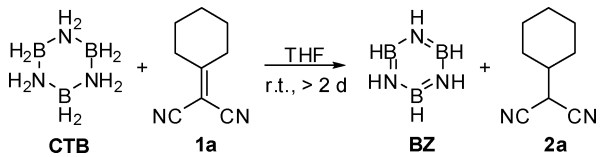
5. The dehydrocoupling pathway of AB

In an attempt to trap boron based intermediates, cyclohexene (2 eq. to the amount of **AB**) was added into the reaction mixture of **1a** with **AB** in THF. Cy_2BNH_2 was observed at a much faster rate than the direct reaction of cyclohexene with **AB** (Scheme 3). As reported in the literature, such an observation indicated the intermediacy of $[NH_2{=}BH_2]$ along the reaction path.[7a,8,9]



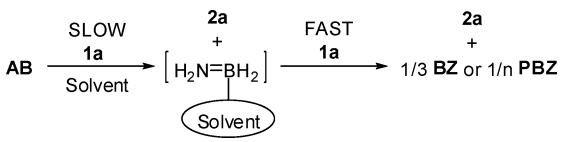
Scheme 3 Transfer hydrogenation of **1a** with **AB** in the presence of excess cyclohexene in THF at room temperature.

To determine whether the final dehydrocoupling product **BZ** was formed *via* dehydrogenation of cyclotriborazane (**CTB**), a reaction of **1a** with **CTB** (1 : 2 molar ratio) was carried out in THF. After 2 days at room temperature **1a** was still not completely hydrogenated (Scheme 4).



Scheme 4 Hydrogenation of **1a** with **CTB** in a 1 : 2 molar ratio in THF at room temperature.

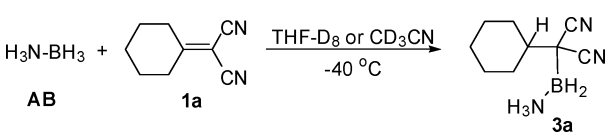
This reaction proceeded much slower than the reaction of **1a** with **AB** which was finished within 10 min in THF at room temperature (Table 1, entry 1). Since the formation of **BZ** *via* the dehydrogenation of **CTB** was so slow, we anticipated the existence of another pathway leading to **BZ** or polyborazylene (**PBZ**), for instance the direct dehydrocoupling of $[NH_2{=}BH_2]$ or probably a solvent-stabilized $[NH_2{=}BH_2]$–(solvent) pathway (Scheme 5).



Scheme 5 Possible formation pathway of **BZ** (**PBZ**) from direct dehydrocoupling of a solvent-stabilized $[NH_2{=}BH_2]$–(solvent).

6. Reactivity of the hydroboration intermediate

According to ^{13}C and ^{11}B NMR spectra,[12] the intermediate **3a** is formed *via* hydroboration of **1a** by **AB** (Scheme 6). A triplet appeared for **3a** at around –14 ppm at temperatures below –40 °C in THF or acetonitrile.



Scheme 6 Trapping of the hydroboration intermediate (**3a**) by *in situ* NMR spectroscopy of the reaction of **1a** with **AB** at low temperature.

In another reaction batch using **1a** in excess, **AB** was completely transformed into **3a** (together with some **BZ**) at –40 °C in THF-D_8 requiring 7 days. The subsequent reaction step of **3a** was then pursued at room temperature by *in situ* ^{11}B NMR spectroscopy. It was found that **3a** was rapidly converted to **BZ** and **PBZ**, with **CTB** to be initially detected in tiny amounts as a shoulder to the signal of **3a**. **CTB** finally remained as the only –BH_2– containing species remaining until the end of the reaction (Fig. 3).

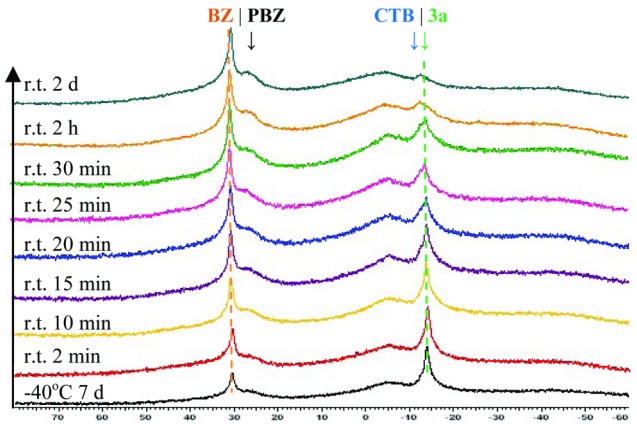
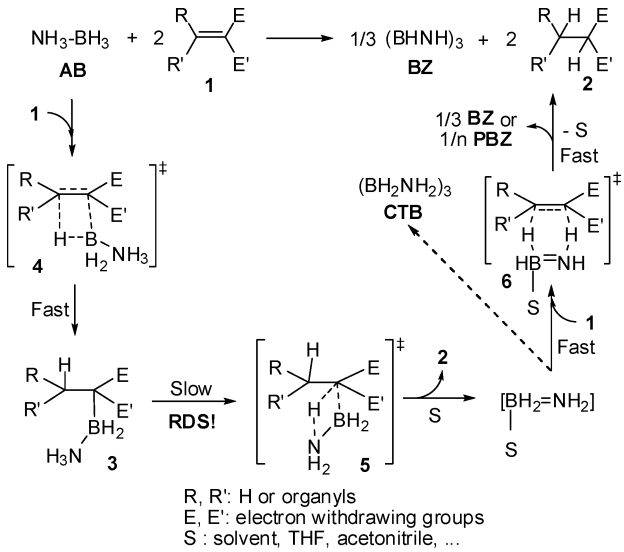


Fig. 3 *In situ* ^{11}B NMR spectra in THF-D_8 showing the decomposition of **3a** at room temperature. Initially **3a** was formed by keeping a NMR sample of **1a** with **AB** (3 : 1 molar ratio) at –40 °C over a week; by that time **AB** was completely consumed with concomitant formation of a small amount of **BZ**.

This further substantiated that **CTB** reacts very slowly with **1a**. Nevertheless, if the reaction was carried out at low temperature with a 1 : 2 molar ratio of **1a** to **AB** until **3a** had completely been formed (no free olefin detectable in the mixture) and then was warmed up to room temperature, **CTB** was the only dehydrocoupling product of **AB** to be detected. Since in the room temperature reactions of **1a** with **AB** only –BH– species from **BZ** and **PBZ** were observed, they are expected to originate from direct dehydrocoupling of [NH_2=BH_2] after elimination from **3a** rather than from dehydrogenation of **CTB**.

7. Mechanism of the double H transfer reaction

Based on the acquired mechanistic facts, a two-step hydrogen transfer mechanism is proposed for the reactions of polar olefins with **AB** (Scheme 7). The first step is the H_B transfer forming a hydroboration intermediate **3**, presumably *via* the concerted transition state **4**. Subsequently H_N transfer occurred as the RDS, which might be transferred in an intra-molecular mode as shown in **5** of Scheme 7, releasing the reactive aminoborane species [NH_2=BH_2] presumably in a solvent stabilized form [NH_2=BH_2]–(solvent). [NH_2=BH_2] or [NH_2=BH_2]–(solvent) is then dehydrogenated subsequently in a fast reaction by another equivalent of **1** generating **BZ** and **PBZ** as the final dehydrocoupling products, presumably *via* simultaneous double H transfer as shown in **6** (Scheme 7). The cyclic trimer **CTB** can be formed by direct cyclization of [NH_2=BH_2], but only in a side reaction in small amount or when the dehydrogenation of [NH_2=BH_2] is slowed by applying low temperature and/or low concentrations of the olefin. Such a mechanistic scheme is anticipated to be applicable to other amine boranes.



Scheme 7 Mechanistic scheme for the transfer hydrogenation of polarized olefins with ammonia borane.

Conclusions

In conclusion, the transfer hydrogenation of a series of activated olefins, equipped with geminal electron-withdrawing groups on one side of the double bond and H or organyl on the other side, with amine borane adducts as hydrogen donors could be accomplished metal-free under mild conditions. The reaction constant obtained from Hammett correlations indicated that negative charge is accumulated in the transition state. Together with deuterium kinetic isotope studies and explorations on the hydroboration intermediate, the actual reaction course could be established: primary hydridic H_B transfer occurs rapidly from the borane part to the olefin before the RDS, then the transfer of the protic H_N occurs as the RDS, presumably *via* a concerted cyclic transition state. The routes to the dehydrocoupling products of ammonia borane were rationalized on the basis that the main product borazine was probably formed directly from dehydrocoupling of [NH_2=BH_2] or of its solvent stabilized adduct [NH_2=BH_2]–(solvent), rather than by dehydrogenation of cyclotriborazane formed by trimerization of [NH_2=BH_2].

Experimental

All of the hydrogen-transfer reactions were carried out at least twice with reported reproducible results.

All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a dry-box (Model MB-150B-G). Reagent grade benzene, toluene, hexane, diethyl ether, and THF were dried and distilled from sodium benzophenone ketyl prior to use. Acetonitrile was distilled from CaH_2, and chloroform was dried by P_2O_5. All the amine borane adducts and olefins **1l–1o** are commercially available and purified prior to use. Olefins **1a–1e** were synthesized as described in our previous communication.[12] NMR spectra were measured on a Varian Mercury spectrometer at 200 MHz for ^{1}H, Varian Gemini-2000 spectrometer at 300.1 MHz for ^{1}H, 96.3 MHz for ^{11}B{^{1}H} and 75.5 MHz for ^{13}C{^{1}H} and on a Bruker-DRX-500 spectrometer at 500.2 MHz for ^{1}H, 107 MHz for ^{11}B{^{1}H} and 125.8 MHz for

$^{13}C\{^{1}H\}$. Chemical shifts for ^{1}H and ^{13}C are given in parts per million relative to TMS and those for ^{11}B relative to $Et_2O{\cdot}BF_3$. GC-MS was measured on a Varian 450 GC (Saturn 2000 GC-MS/MS).

Olefins **1f**, **1g**, **1j** and **1p–1t** were prepared *via* the following method with nearly 100% yield: To a stirred solution of 0.01 mol of aldehyde in 0.01 mol of malononitrile (or methylcyanoacetate) was added 3 g of alumina Merck 90. The reaction was exothermic. After the reaction was cooled down, the product was extracted with dichloromethane (2 × 20 ml).[19] The solvent was then removed, leaving a product with appropriate purity.

2-(3,4-Dihydronaphthalen-1(2H)-ylidene)malononitrile (**1f**),[20] white solid: δ_H (ppm; 300 MHz; CD_3CN) 1.89–2.14 (m, 2H, -CH_2-), 2.85 (t, J = 6 Hz, 2H, -CH_2-), 2.98 (t, J = 6 Hz, 2H, -CH_2-), 7.33–7.38 (m, 2H), 7.50–7.55 (m, 1H), 8.12 (d, J = 8 Hz, 1H); δ_C (ppm; 75.4 MHz; CD_3CN) 22.64, 30.12, 33.68, 80.45 (=$\underline{C}$–$(CN)_2$), 114.57 (=C–($\underline{C}N)_2$), 115.35 (=C–($\underline{C}N)_2$), 127.36, 128.63, 130.38, 131.10, 134.53, 143.80, 174.39 ($\underline{C}$=C–$(CN)_2$).

2-(Naphthalen-1-ylmethylene)malononitrile (**1g**),[21] yellow solid: δ_H (ppm; 300 MHz; CD_3CN) 7.60–7.73 (m, 3H), 7.98–8.19 (m, 4H), 8.90 (s, 1H); δ_C (ppm; 75.4 MHz; CD_3CN) 86.58 (=$\underline{C}$–$(CN)_2$), 113.96 (=C–($\underline{C}N)_2$), 114.85 (=C–($\underline{C}N)_2$), 124.24, 126.34, 128.23, 129.13, 129.16, 129.33, 130.04, 131.93, 134.45, 135.22, 160.36 ($\underline{C}$=C–$(CN)_2$).

(E)-2-(3-Phenylallylidene)malononitrile (**1j**),[21] Yellow solid: δ_H (ppm; 300 MHz; CD_3CN) 7.18–7.23 (m, 1H), 7.25–7.31 (m, 1H), 7.39–7.49 (m, 3H), 7.65–7.70 (m, 2H), 7.81–7.87 (m, 1H); δ_C (ppm; 75.4 MHz; CD_3CN) 83.06 (=$\underline{C}$–$(CN)_2$), 112.94 (=C–($\underline{C}N)_2$), 114.93 (=C–($\underline{C}N)_2$), 123.46, 130.04, 130.19, 132.75, 135.35, 151.53, 162.18 ($\underline{C}$=C–$(CN)_2$).

(E)-Methyl 2-cyano-3-(4-methoxyphenyl)acrylate (**1p**),[22] white solid: δ_H (ppm; 300 MHz; C_6D_6) 3.84 (s, 3H, -Me), 3.87 (s, 3H, -Me), 7.06 (d, J = 9 Hz, 2H), 8.00 (d, J = 9 Hz, 2H), 8.19 (s, 1H, -C$\underline{H}$=C(CN)(CO_2Me)); δ_C (ppm; 75.4 MHz; C_6D_6) 53.77 (-Me), 56.49 (-Me), 100.06 (=$\underline{C}$(CN)(CO_2Me)), 115.78, 117.21 (-$\underline{C}$N), 125.28, 134.49, 155.33 (-$\underline{C}$H=C(CN)(CO_2Me)), 164.32, 164.88 (-$\underline{C}O_2$Me).

(E)-Methyl 3-(4-chlorophenyl)-2-cyanoacrylate (**1q**),[23] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.87 (s, 3H, -Me), 7.54 (d, J = 8 Hz, 2H), 7.96 (d, J = 8 Hz, 2H), 8.25 (s, 1H, -C$\underline{H}$=C(CN)(CO_2Me)); δ_C (ppm; 75.4 MHz; CD_3CN) 54.11 (-Me), 104.54 (=$\underline{C}$(CN)(CO_2Me)), 116.31 (-$\underline{C}$N), 130.46, 131.34, 133.26, 139.66, 154.40 (-$\underline{C}$H=C(CN)(CO_2Me)), 163.52 (-$\underline{C}O_2$Me).

(E)-Methyl 2-cyano-3-(4-nitrophenyl)acrylate (**1r**),[24] milk-yellow solid: δ_H (ppm; 300 MHz; $CDCl_3$) 3.99 (s, 3H, -Me), 8.12–8.15 (m, 2H), 8.32–8.37 (m, 3H); δ_C (ppm; 75.4 MHz; $CDCl_3$) 53.85 (-Me), 106.87 (=$\underline{C}$(CN)(CO_2Me)), 114.44 (-$\underline{C}$N), 124.29, 131.51, 136.75, 149.72, 151.95 (-$\underline{C}$H=C(CN)(CO_2Me)), 161.86 (-$\underline{C}O_2$Me).

(E)-Methyl-2-cyano-3-(4-cyanophenyl)acrylate (**1s**),[24] white solid: δ_H (ppm; 300 MHz; $CDCl_3$) 3.98 (s, 3H, -Me), 7.78–7.81 (m, 2H), 8.05–8.08 (m, 2H), 8.26 (s, 1H); δ_C (ppm; 75.4 MHz; $CDCl_3$) 53.80 (-Me), 106.26 (=$\underline{C}$(CN)(CO_2Me)), 114.54, 116.05 (-$\underline{C}$N), 117.64 (-$\underline{C}$N), 131.00, 132.82, 135.09, 152.47 (-$\underline{C}$H=C(CN)(CO_2Me)), 161.97 (-$\underline{C}O_2$Me).

Olefin 2,2′-(1*H*-indene-1,3(2H)-diylidene)dimalononitrile (**1h**) was prepared *via* the following method:[25] A solution of indane-1,3-dione (0.48 g, 3.2 mmol), malononitrile (0.54 g, 8.2 mmol) and ammonium acetate (0.25 g, 3.2 mmol) dissolved in absolute ethanol (6 mL) was heated at reflux for 30 min. After cooling to room temperature, water (5 mL) was added and the solution acidified with concentrated hydrochloric acid. The brown precipitate was filtered off and washed with water. Recrystallisation from glacial acetic acid afforded compound **1h** (0.35 g, 45%) as a brown yellow crystal. 2,2′-(1*H*-Indene-1,3(2H)-diylidene)dimalononitrile:[25] δ_H (ppm; 300 MHz; CD_3CN) 4.31 (s, 2H, -C$\underline{H}_2$-), 7.93–9.96 (m, 2H), 8.53–8.56 (m, 2H); δ_C (ppm; 75.4 MHz; CD_3CN) 42.94 (-$\underline{C}H_2$-), 79.10 (=$\underline{C}$$(CN)_2$), 113.07 (-$\underline{C}$N), 113.29 (-$\underline{C}$N), 127.33, 137.03, 141.70, 167.92 (-$\underline{C}$H=C$(CN)_2$).

Olefin 2-(3-ethoxy-1*H*-inden-1-ylidene)malononitrile (**1i**) was prepared *via* the following method:[25] A solution of indane-l,3-dione (0.4 g, 2.74 mmol), malononitrile (0.45 g, 6.8 mmol) and ammonium acetate (60 mg, 0.78 mmol) dissolved in absolute ethanol (20 mL) was heated at reflux for 24 h. The solvent was removed in vacuo, leaving a purple solid from which a red product was extracted with boiling light petroleum (b.p. 40–60 °C). Recrystallisation of the red product in light petroleum afforded compound **1i** (10 mg, 10%) as a bright red powder. 2-(3-Ethoxy-1*H*-inden-1-ylidene)malononitrile (**1i**):[25] δ_H (ppm; 300 MHz; CD_3CN) 1.45 (t, J = 7 Hz, 3H, -Me), 4.34 (q, J = 7 Hz, 2H, -OC$\underline{H}_2$-), 5.75 (s, 1H), 7.28–7.31 (m, 1H), 7.37–7.46 (m, 2H), 7.98–8.00 (m, 1H); δ_C (ppm; 75.4 MHz; CD_3CN) 14.48 (-Me), 69.93 (-O$\underline{C}H_2$-), 70.08 (=$\underline{C}$$(CN)_2$), 97.75 (-$\underline{C}$H=C-OEt), 114.77 (-$\underline{C}$N), 121.00, 124.89, 131.32, 133.37, 138.65, 166.84 (-CH=$\underline{C}$-OEt), 173.46 (-$\underline{C}$H=C$(CN)_2$).

Olefin cyclohepta-2,4,6-trienylidene malononitrile (**1k**) was prepared *via* the following method:[26] An oven-dried 50 mL three-necked round-bottomed flask, equipped with a nitrogen gas inlet, magnetic stirring bar, dropping funnel, thermometer, and condenser, under an inert nitrogen atmosphere, was placed in an ice bath and charged, while stirring, with 10 mL of pyridine and 0.9 g (5 mmol) of cycloheptatrienylium tetrafluoroborate at 0 °C. Bromomalononitrile (0.73 g, 5 mmol) is added drop by drop within a 10 min period, and the mixture is vigorously stirred at that temperature for 1 h. The ice bath is replaced by a water bath, the temperature is gradually raised to 40 °C, and the stirring mixture is kept at that temperature for 5 h. The solution was acidified with 1 M HCl solution and the organic phase was extracted with chloroform. The final product **1k** was obtained as red powder by column chromatography eluted with hexane : Ethyl ester = 1 : 5 (yield: 60%). Cyclohepta-2,4,6-trienylidene malono-nitrile (**1k**): δ_H (ppm; 300 MHz; THF-D_8) 6.96–7.11 (m, 4H), 7.32–7.37 (d*m, 2 H, J = 12 Hz); δ_C (ppm; 300 MHz; THF-D_8) 115.10 (-$\underline{C}$N), 135.76, 138.47, 140.15, 164.47 (-$\underline{C}$H=C$(CN)_2$).

General procedure for the transfer hydrogenation reactions

In a glove-box, a 0.5 mm Young NMR tube was charged with olefin (0.1 mmol), amine-borane adducts (0.1 mmol) and dry THF-D_8 or acetonitrile-D_3 (0.6 mL). The tube was sealed with a screw cap and then stored at room temperature or the required temperature after shaking. The reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy every several minutes (depends on the reaction rate). The typical resonance of the starting materials decreased, and a new signal of the saturated products gradually appeared. The disappearance of the starting olefin indicates that the transformation has completed, ^{13}C and ^{11}B NMR spectra were

then recorded. Finally the reaction mixture was diluted for GC-MS analysis. Samples for low-temperature NMR spectroscopy were prepared at room temperature using chilled solvents, and immediately put into a freezer until required for NMR measurement. Samples for kinetic study were prepared with pseudo-first order conditions with the 0.1 mmol **AB** and the olefin in great excess (0.5 mmol).

The reaction of **1a** with **AB** was also carried out in large scale using a Young Schlenk tube: In a glove-box, a 50 mL Young Schlenk tube was charged firstly with a magnetic stirring bar and 30 mg **AB** (1 mmol), then 10 ml dry THF and finally 0.144 mL **1a** (1 mmol). Then the tube was sealed with a screw cap and stirred for 10 min. As inspected by GC-MS, the olefin was completely hydrogenated. After that, all the volatile species (THF, **BZ**) were removed from the tube by applying high vacuum, the remaining residue was further purified by distillation. Finally **2a** was obtained as a colorless liquid in 86% yield (127 mg).

All the hydrogenated products were described earlier. The obtained NMR data match literature values.

2-Cyclohexylmalononitrile (**2a**),[27] colorless liquid, δ_H (ppm; 300 MHz; THF-D_8) 1.15–1.44 (m, 5 H, -C*H*-), 1.69–2.06 (m, 6 H, -C*H*-), 4.25 (d, J = 5 Hz, 1 H, -C*H*-); δ_C (ppm; 300 MHz; THF-D_8) 26.34, 26.41, 29.57, 30.76, 40.06, 113.64 (-*C*N); GC retention time: 5.145 min; MS (m/z) = 149.

Methyl 2-cyano-2-cyclohexylacetate (**2b**),[28] colorless liquid: δ_H (ppm; 300 MHz; CD_3CN) 1.08–1.35 (m, 5 H, -C*H*-), 1.63–1.82 (m, 5 H, -CH-), 1.94–2.07 (m, 1 H, -C*H*-), 3.64 (d, J = 5 Hz, 1 H, -C*H*-), 3.74 (s, 3 H, -Me); δ_C (ppm; 75.4 MHz; CD_3CN) 26.27, 26.34, 26.51, 30.00, 31.62, 39.43, 45.11, 53.83, 117.10 (-*C*N), 167.60 (-*C*=O); MS (m/z) = 181.

2-benzylmalononitrile (**2c**),[20,27–29] slightly yellow solid: δ_H (ppm; 300 MHz; THF-D_8) 3.31 (d, J = 7 Hz, 2 H, -CH_2-), 4.59 (t, J = 7 Hz, 1 H, -C*H*$(CN)_2$), 7.32–7.38 (m, 5 H, -C*H*=); δ_C (ppm; 75.4 MHz; THF-D_8) 25.25, 36.91, 114.19 (-*C*N), 128.90, 129.61, 130.19, 135.65; GC retention time: 5.807 min; MS (m/z) = 156.

Methyl 2-cyano-3-phenylpropanoate (**2d**),[20,28,30] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.10–3.32 (m, 2 H, -CH_2-), 3.74 (s, 3 H, -Me), 4.01–4.13 (m, 1 H, -C*H*-), 7.25–7.41 (m, 5 H, -C*H*=); δ_C (ppm; 75.4 MHz; CD_3CN) 35.47, 39.80, 53.53, 117.07 (-*C*N), 127.96, 129.11, 129.59, 136.55, 166.89 (-*C*=O); GC retention time: 7.770 min; MS (m/z) = 189.

Dimethyl 2-benzylmalonate (**2e**),[20,31] colorless liquid: δ_H (ppm; 300 MHz; CD_3CN) 3.13–3.17 (d, J = 8 Hz, 2 H, -CH_2-), 3.63 (s, 6 H, -Me), 3.71 (t, J = 8 Hz, 1 H, -C*H*-), 7.09–7.36 (m, 5 H, -C*H*=); δ_C (ppm; 75.4 MHz; CD_3CN) 35.30, 53.04, 54.35, 127.70, 129.46, 129.76, 139.03, 170.12 (-*C*=O); GC retention time: 8.059 min; MS (m/z) = 223.

2-(1,2,3,4-Tetrahydronaphthalen-1-yl)malononitrile (**2f**),[20,32] white solid: δ_H (ppm; 300 MHz; CD_3CN) 1.67–1.81 (m, 1 H), 1.85–2.07 (m, 2H), 2.20–2.30 (m, 1H), 2.72–2.89 (m, 2H), 3.56–3.62 (m, 1H, -C*H*-), 4.63 (d, J = 5.5 Hz, 1H, -C*H*$(CN)_2$), 7.16–7.30 (m, 4 H,=C*H*-); δ_C (ppm; 75.4 MHz; CD_3CN) 20.99, 27.74, 29.78, 30.44, 39.44, 114.10 (-*C*N), 114.30 (-*C*N), 127.21, 128.66, 128.74, 130.71, 133.73, 139.52; GC retention time: 9.461 min MS (m/z) = 196.

2-(Naphthalen-1-ylmethyl)malononitrile (**2g**),[33] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.81–3.84 (m, 2H, -CH_2-), 4.48–4.54 (m, 1H, -C*H*$(CN)_2$), 7.49–7.63 (m, 4H), 7.90–7.97 (m, 2H), 8.11–8.14 (m, 1H); δ_C (ppm; 75.4 MHz; CD_3CN) 24.60, 32.70, 113.91 (-*C*N), 123.68, 125.93, 126.69, 127.16, 128.81, 129.38, 129.46, 130.82, 131.74, 134.36; MS (m/z) = 206.

Dicyano(1-(dicyanomethylene)-1*H*-inden-3-yl)methanide (**2h**),[34] purple solid: δ_H (ppm; 300 MHz; CD_3CN) 5.73 (s, 1 H, -C*H*=C(C$(CN)_2^-$)), 7.32–7.36 (m, 2H), 7.92–7.96 (m, 2H); δ_C (ppm; 75.4 MHz; CD_3CN) 104.19 (-*C*H=C(C$(CN)_2^-$)), 119.11 (-*C*N), 119.27 (-*C*N), 122.68, 124.93, 126.38, 130.65, 139.46, 159.75 (-*C*=C$(CN)_2$); GC retention time: 13.582 min; (–)MS (m/z) = 241.

2-(3-Ethoxy-1*H*-inden-1-yl)malononitrile (**2i**), purple solid: δ_H (ppm; 300 MHz; CD_3CN) 1.67–1.81 (m, 1 H), 1.85–2.07 (m, 2H), 2.20–2.30 (m, 1H), 2.72–2.89 (m, 2H), 3.56–3.62 (m, 1H, -C*H*-), 4.63 (d, J = 5.5 Hz, 1H, -C*H*$(CN)_2$), 7.16–7.30 (m, 4 H,=C*H*-); δ_C (ppm; 75.4 MHz; CD_3CN) 14.69, 27.58, 45.67, 66.81, 98.24, 119.66 (-*C*N), 124.39, 126.48, 128.10, 128.85, 129.66, 161.35; GC retention time: 9.849 min; MS (m/z) = 224.

2-Cinnamylmalononitrile (**2j**),[27,29] white solid: δ_H (ppm; 300 MHz; CD_3CN) 2.92–2.97 (m, 2H, -CH_2-), 4.28–4.32 (m, 1H, -C*H*$(CN)_2$), 6.24–6.35 (m, 1H, =C*H*-), 6.73–6.78 (m, 1H, =C*H*-), 7.26–7.51 (m, 5H); δ_C (ppm; 75.4 MHz; CD_3CN) 24.41, 34.41, 114.45 (-*C*N), 122.62, 127.39, 129.12, 129.31, 129.68, 136.65; GC retention time: 8.973 min;MS (m/z) = 182.

Methyl 2-cyano-3-(4-methoxyphenyl)propanoate (**2p**),[20,27,30] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.14–3.28 (m, 2H, -CH_2-), 3.74 (s, 3H, -CH_3), 4.01–4.08 (m, 1H, -C*H*$(CN)_2$), 7.31–7.37 (m, 5H); δ_C (ppm; 75.4 MHz; CD_3CN) 35.99, 40.32, 54.07, 117.62 (-*C*N), 128.53, 129.67, 130.15, 137.11, 167.47 (-*C*O_2Me); GC retention time: 9.387 min; MS (m/z) = 219.

Methyl 3-(4-chlorophenyl)-2-cyanopropanoate (**2q**),[29,30] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.17–3.33 (m, 2H, -CH_2-), 3.79 (s, 3H, -CH_3), 4.06–4.11 (m, 1H, -C*H*$(CN)_2$), 7.29–7.44 (m, 4H); δ_C (ppm; 75.4 MHz; CD_3CN) 34.67, 39.56, 53.60, 116.90 (-CN), 129.08, 131.35, 133.35, 135.43, 166.69 (-*C*O_2Me); GC retention time: 9.092 min; MS (m/z) = 223.

Methyl 2-cyano-3-(4-nitrophenyl)propanoate (**2r**),[20,29,35] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.31–3.47 (m, 2H, -CH_2-), 3.80 (s, 3H, -CH_3), 4.16–4.21 (m, 1H, -C*H*$(CN)_2$), 7.56–7.59 (d, J = 10 Hz, 2H), 8.22–8.25 (d, J = 10 Hz, 2H); δ_C (ppm; 75.4 MHz; CD_3CN) 34.82, 39.00, 53.73, 116.69 (-*C*N), 124.11, 130.85, 144.20, 166.45 (-*C*O_2Me); GC retention time: 10.799 min; MS (m/z) = 235.

Methyl 2-cyano-3-(4-cyanophenyl)propanoate (**2s**),[36] white solid: δ_H (ppm; 300 MHz; CD_3CN) 3.25–3.43 (m, 2H), 3.79 (s, 3H, -CH_3), 4.11–4.17 (m, 1H, -C*H*$(CN)_2$), 7.49–7.53 (m, 2H), 7.74–7.78 (m, 2H); δ_C (ppm; 75.4 MHz; CD_3CN) 35.15, 39.05, 53.70, 111.61, 116.71 (-*C*N), 118.96, 130.61, 132.92, 142.14, 166.48 (-*C*O_2Me); GC retention time: 9.989 min; MS (m/z) = 214.

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