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Amberlite IRA900F as a Solid Fluoride Source for a Variety of Organic Transformations under Solvent-Free Conditions

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We have reported that Amberlite IRA900F (Amb-F) is an efficient metal-free catalyst for the activation of Si–N and Si–O bonds and a mild base in a variety of organic transformations under solvent-free conditions, such as the addition of $TMSN_3$ to (*E*)-2-aryl-1-cyano-1-nitroethenes, nitriles, α,β-unsaturated acids and their esters, and the addition of dimethylsilyl ketene acetal and ethyl nitroacetate to β-nitrostyrenes.

Introduction

Solvent-free organic transformations have been attracting growing attention as effective tools for increasing the chemical efficiency and reducing the environmental cost of organic synthesis.[1] As clearly pointed out by Raston et al.,[1c] there are several advantages in performing reactions in the absence of an organic medium, including the possibility of using simpler equipment and reducing the costly procedures for collecting, purifying, and recycling the generally toxic organic reaction media. In addition, the isolation of the reaction products from a solvent-free reaction mixture is often easier and when the product is solid, a simple recrystallization step is generally sufficient.

Fluoride ions have been widely used as valuable catalysts in organic synthesis.[2] KF/alumina,[3] CsF/alumina,[4] KF/18-crown-6,[5] or layered double hydroxide fluoride[6] have been used as solid catalysts to overcome solubility problems of KF in organic solvents.

In the last few years, we have been contributing in this field and we have demonstrated that solvent-free conditions (SolFC) have beneficial effects on some organic transformations,[7] such as Michael additions,[7a,7j] oxirane ring-opening reactions,[7e,7f] Diels–Alder reactions,[7g–7i] and [3+2][7c,7d] and 1,3-dipolar[7b] cycloadditions allowing the chemically and environmentally efficient preparation of target molecules such as 1*H*-1,2,3-triazoles, 1*H*-tetrazoles, biphenyl-2-ylcarbonitriles, and benzo[*e*]1,4-oxathiepin-5-ones among others.

In particular, we reported that under SolFC, tetrabutylammonium salts efficiently activate the Si–N bond of trimethylsilyl azide ($TMSN_3$).[7b–7d,7j] In a recent paper we have also shown that Amberlite IRA900F (Amb-F),[7j] a commercially available solid source of fluoride ions,[8] promptly reacts with $TMSN_3$ to form the corresponding Amb-N_3, which is an excellent catalyst for the azidation of α,β-unsaturated ketones under SolFC.[7j] By following our procedure, β-azido ketones were isolated in high yields, and the catalyst was recovered and recycled; the best efficiency was achieved in the absence of any reaction medium. We decided to further investigate the catalytic efficiency of polymer-supported ammonium fluoride (Amb-F) as a metal-free alternative for the activation of the Si–N and Si–O bonds and as a mild base under SolFC.

In this paper we present the results obtained in some representative organic processes catalyzed by Amb-F under SolFC, such as the (a) [3+2] cycloaddition of nitroalkenes **1** with $TMSN_3$ (**2**) and its multicomponent one-pot version, (b) azidation of aryl nitriles **4**, (c) Michael addition of $TMSN_3$ (**2**) to α,β-unsaturated carboxylic acids and esters **6**, and (d) Michael addition of ketene silyl acetal (KSA) (**9**) and ethyl nitroacetate (**11**) with nitro olefins **8**. The results are illustrated in Tables 1–4 and Schemes 1 and 2.

Results and Discussion

Amb-F effectively catalyzed the [3+2] cycloaddition of (*E*)-2-phenyl-1-cyano-1-nitroethene (**1a**) with $TMSN_3$ (**2**), still maintaining a comparable efficiency with the nonsupported tetrabutylammonium fluoride (TBAF) catalyst[7c] (Table 1, Entry 1 vs. 5). When the reaction of **1a** was performed in 2 mL/mmol of tetrahydrofuran (THF) or 1,2-dichloroethane (DCE) (chosen as adequate organic solvents for the complete swelling of Amb-F), isolation yield of triazole **3a** was lower (Table 1, Entries 3 and 4), proving the higher efficiency of Amb-F in SolFC. Good results were obtained also in the case of deactivated substrates **1b**–**d**.

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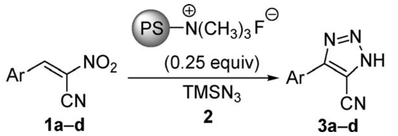
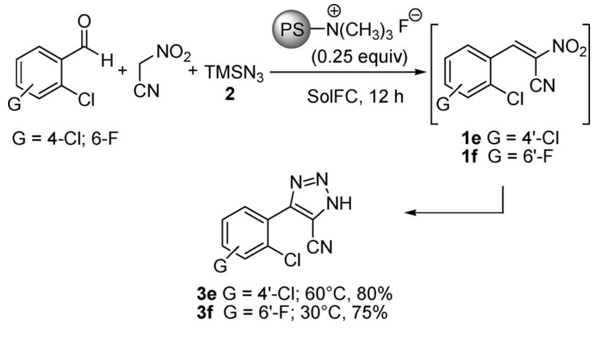
Table 1. Amb-F-catalyzed [3+2] cycloaddition of (*E*)-2-aryl-1-cyano-1-nitroethenes (**1a–d**) with $TMSN_3$ (**2**).



Entry	Ar	*T* [°C]	*t* [h]	Yield [%][a]
1	C_6H_5 (**1a**)	30	3	95
2	C_6H_5 (**1a**)	30	9	93[b]
3	C_6H_5 (**1a**)	30	3	82[c]
4	C_6H_5 (**1a**)	30	3	83[d]
5	C_6H_5 (**1a**)	30	3	60[e]
6	(2-OMe)C_6H_4 (**1b**)	60	12	92
7	(2,4-OMe)C_6H_3 (**1c**)	60	15	90
8	(2,4,6-Me)C_6H_2 (**1d**)	60	14	90
9	C_6H_5 (**1a**)	30	3	94[f]
10	C_6H_5 (**1a**)	30	3	95[f]

[a] Yield of the isolated pure product obtained by using 3.0 equiv. of $TMSN_3$ (**2**). [b] By using 0.10 equiv. of Amb-F. [c] Reaction performed in 2 mL/mmol of THF. [d] Reaction performed in 2 mL/mmol of DCE. [e] By using 0.10 equiv. of TBAF.[7c] [f] By using the recovered catalyst.

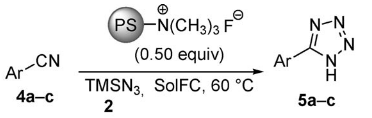
The preparation of triazoles **3e**,**f** was performed by following a multicomponent one-pot protocol (Scheme 1) by mixing 2,4-dichlorobenzaldehyde or 2-chloro-6-fluorobenzaldehyde, nitroacetonitrile and $TMSN_3$ (**2**) in the presence of Amb-F under solvent-free conditions. This protocol offered obvious advantages, especially in the case of nitroethenes containing electron-withdrawing group such as **1e** and **1f**. In fact, these acceptors, which come from the reaction of the corresponding aldehydes with nitroacetonitrile, are isolated in generally poor yields due to their high tendency to undergo the retro-Knoevenagel process under the reaction conditions, making this approach unsuitable for the preparation of **3e** and **3f** (see Scheme 1).



Scheme 1. Amb-F-catalyzed multicomponent one-pot synthesis of 1*H*-1,2,3-triazoles **3e**,**f**.

By employing a multicomponent one-pot procedure, 1*H*-1,2,3-triazoles **3e**,**f** were successfully synthesized starting from the corresponding aldehydes in good yields. Products **3a–f** were obtained in satisfactory purity by filtering the catalyst from the reaction mixture with a minimal amount organic solvent (see Experimental Section).

Amb-F was also effective in the preparation of representative 1*H*-1,2,3,4-tetrazoles **5a–c** (Scheme 2). The efficiency of Amb-F and TBAF in the 1,3-dipolar cycloaddition under SolFC was also in this case comparable,[7b] whereas the use of THF or DCE as reaction medium resulted in the isolation of tetrazole **5b** in lower yield (Scheme 2). The results are satisfactory considering that we performed the azidation of **4a–c** at 60 °C, which is a low reaction temperature for this transformation.[7b]



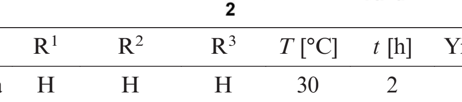
Entry		Ar	*t* [h]	Yield [%][a]
1	**4a**	(4-Ac)C_6H_4	48	76
2	**4b**	3-pyridyl	3	78
3	**4b**	3-pyridyl	3	54[b]
4	**4b**	3-pyridyl	3	56[c]
5	**4c**	2-furyl	2	75
6	**4c**	2-furyl	2	76[d]
7	**4c**	2-furyl	2	74[d]

[a] Isolated yield of pure product **5** by using 3.0 equiv. of $TMSN_3$ (**2**). [b] Reaction performed in 2 mL/mmol of THF. [c] Reaction performed in 2 mL/mmol of DCE. [d] By using recovered catalyst.

Scheme 2. Amb-F-catalyzed 1,3-dipolar cycloaddition of nitriles **4a–c** with $TMSN_3$ (**2**).

β-Azidation of α,β-unsaturated carboxylic acids and esters is an interesting process for direct access to the β-amino acid moiety. We found that Amb-F promotes this transformation in some representative examples (Table 2). The protocol worked well in the case of carboxylic acids **6a** and **6c** (Table 2, Entries 1 and 3), although, as expected, the reaction was significantly less efficient in the case of the less electrophilic ester derivatives **6b** and **6d** (Table 2, Entries 2 and 4). In fact, the reaction of **6a** with $TMSN_3$ (**2**) was complete in only 2 h and gave β-azido acid **7a**, and its ethyl ester **6b** required 20 h to convert into **7b** (Table 2, Entry 1 vs. 2). Accordingly, to convert poorly reactive *trans*-3-hexenoic acid (**6c**) into the corresponding β-azido carboxylic

Table 2. Comparison of the efficiency of Amb-F in the β-azidation of α,β-unsaturated acids and esters **6a–d**.



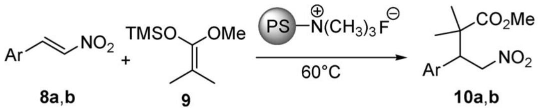
Entry		R^1	R^2	R^3	*T* [°C]	*t* [h]	Yield [%][a]
1	**6a**	H	H	H	30	2	73
2	**6b**	H	H	Et	30	20	70
3	**6c**	H	n-C_3H_7	H	60	18	86
4	**6c**	H	n-C_3H_7	H	60	18	55[b]
5	**6c**	H	n-C_3H_7	H	60	18	58[c]
6	**6d**	H	n-C_3H_7	Et	60	18	–[d]
7	**6c**	H	n-C_3H_7	H	60	18	85[e]
8	**6c**	H	n-C_3H_7	H	60	18	84[e]

[a] Yield of isolated products **7** by using 2.0 equiv. of $TMSN_3$ (**2**). [b] Reaction performed in 2 mL/mmol of THF. [c] Reaction performed in 2 mL/mmol of DCE. [d] Product **7d** was not detected by GLC analyses. [e] By using the recovered catalyst.

acid **7c** 18 h at 60 °C were required and its ethyl ester derivative **6d** gave no reaction at all (Table 2, Entry 3 vs. 6). When the reaction of **6c** was performed in THF or DCE the corresponding β-azido carboxylic acid was isolated in lower yields (Table 2, Entries 4 and 5).

The use of Amb-F was also extended to the addition of ketene silyl acetal (KSA) **9** to β-nitrostyrenes **8a**,**b**. Amb-F proved to be also effective towards Si–O bond activation and γ-nitro esters **10a**,**b**, resulting from the addition of **9** to **8a**,**b**, were obtained in satisfactory yields (Table 3, Entries 1 and 3). This transformation is very attractive because it allows the synthesis of γ-nitro esters **10**, which are direct precursors of γ-amino acids and γ-lactams. The role of the organic reaction medium was also evaluated and it is evident that there is a positive influence of SolFC on the efficiency of this transformation (Table 3, Entry 1 vs. 2). (*E*)-2-(4′-Methyl)-phenyl-1-nitroethene (**8b**) gave the corresponding γ-nitro ester **10b** with satisfactory yield (70%), considering that some decomposition occurred due to the long reaction time (60 h; Table 3, Entry 3).

Table 3. Amb-F-catalyzed Michael addition of dimethylsilyl ketene acetal (**9**) to β-nitrostyrenes **8a**,**b**.



Entry	Amb-F [%]	Medium	Ar	*t* [h]	Yield [%][a]
1	5	SolFC	C_6H_5 (**8a**)	36	88
2	5	DCE	C_6H_5 (**8a**)	36	48
3	10	SolFC	(4′-Me)C_6H_5 (**8b**)	60	70
4	5	SolFC	C_6H_5 (**8a**)	36	61[b]
5	5	SolFC	C_6H_5 (**8a**)	36	87[c]

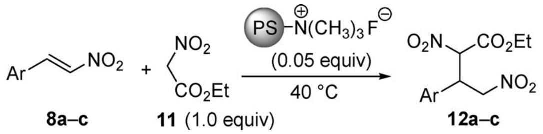
[a] Yield of isolated pure products **10** obtained by using 3.0 equiv. of KSA (**9**). [b] By using the recovered catalyst. [c] By using the regenerated catalyst.

The fluoride ion is attractive for its very useful chemical interaction with silicon, but fluoride ion can also be used as a mild Brönsted base (pK_a of HF is 3.7 in water and 15 in DMSO).[9] In fact, we also employed Amb-F as a solid mild base for promoting some representative Michael additions of ethyl nitroacetate (**11**) to β-nitrostyrenes **8a**–**c** (Table 4). The additions of **11** to **8a**–**c** at 40 °C proceed smoothly under SolFC, by using 5 mol-% of Amb-F and equimolar amounts of reagents giving after 3–10 h products **12a**–**c** in high yields and purity, making unnecessary further purification. As expected, products **12a**–**c** were in a 1:1 diastereoisomeric mixture.

γ-Nitro esters **10a**,**b** and α,γ-dinitro esters **12a**–**c** are new compounds, and they were fully characterized (see below for spectroscopic data).

In all the cases we also paid attention to the recovery and reuse of the solid catalyst. In the cases of the addition of $TMSN_3$ (**2**), as we already proved,[7c] at the end of the reaction the recovered catalyst was Amb-N_3 formed after the substitution of the fluoride ion by the azido one and formation of the volatile trimethylsilyl fluoride (b.p. 16 °C).

Table 4. Amb-F-catalyzed Michael addition of ethyl nitroacetate (**11**) to β-nitrostyrenes **8a**–**c**.



Entry	Medium	Ar	*t* [h]	Yield [%][a]
1	SolFC	C_6H_5 (**8a**)	10	93
2	DCE	C_6H_5 (**8a**)	10	68
3	SolFC	(4′-Me)C_6H_4 (**8b**)	4	96
4	SolFC	(2-Cl)C_6H_4 (**8c**)	3	94
5	SolFC	C_6H_5 (**8a**)	10	92[b]
6	SolFC	C_6H_5 (**8a**)	10	91[b]

[a] Yield of isolated pure products **12**. [b] By using the recovered catalyst.

In these transformations, the recovered catalyst showed no decrease in its efficiency (Table 1, Entries 9 and 10; Scheme 2, Entries 6 and 7; Table 2, Entries 7 and 8).

In the case of the activation of dimethylsilyl ketene acetal (**9**), the recovered catalyst showed a decreased efficiency (ca. 70% of the catalyst used in the first run, Table 3, Entry 4), and in fact, the fluoride content of the recovered catalyst was ca. 70% of the initial one. This loss may presumably be ascribed to the formation of trimethylsilyl fluoride. In contrast, the catalyst was successfully regenerated by washing it with a NaF aqueous solution. Dried regenerated Amb-F showed the original catalytic efficiency (Table 3, Entry 5)

Finally, when Amb-F was used as a mild base for the Michael addition of nitroacetate (**11**) with β-nitrostyrenes (**8a**–**c**), the recovered catalyst was still active showing no decrease of its efficiency after three runs (Table 4, Entries 5 and 6).

Conclusions

We showed that Amberlite IRA900F is a chemically efficient solid source of fluoride ions. It can be profitably used in a series of chemical transformations where it can act as an activator of Si–N and Si–O bonds or as a mild base. Its efficiency is comparable to that of its nonsupported counterpart, tetrabutylammonium fluoride[7b,7c] (e.g. Table 1 and Scheme 2), and it is also effective in other SolFC processes that have never been investigated before (Tables 2–4).

Experimental Section

All chemicals were purchased and used without any further purification. All ^1H and ^{13}C NMR spectra were recorded at 200 or 400 MHz and at 50.3 or 100.6 MHz, respectively, generally by using $CDCl_3$ as deuterated solvent and TMS as internal standard. TLC analyses were performed on silica gel on aluminum plates and UV and/or $KMnO_4$ were used as revealing agents. Column chromatography was performed by using silica gel (230–400 mesh) and eluting as reported in the following characterization charts. All the products are known compounds except for **10a**,**b** and **12a**–**c**, which are new compounds and characterization data (^{1}H and ^{13}C NMR spectroscopic data, elemental analysis) are reported below.

Procedure for the Amb-F-catalyzed [3+2] Cycloaddition of Nitroethenes (1a–d) with TMSN$_3$ (2): In a screw-capped vial equipped with a magnetic stirrer was consecutively added (*E*)-2-aryl-1-cyano-1-nitroethenes **1a**–**d** (1.0 mmol), TMSN$_3$ (0.34 g, 3.0 mmol), and Amb-F (0.10 g, 0.25 mmol, 2.6 mmol/g), and the resulting mixture was stirred at the temperature and for the time reported in Table 1. At the end of the reaction, ethyl acetate was added, the catalyst was recovered by filtration, and the organic layer was evaporated under high vacuum to give pure products **3a**–**d** (90–95% yield; see Table 1).

Amb-F-Catalyzed Multicomponent Synthesis of 1*H*-1,2,3-Triazoles 3e and 3f: In a screw-capped vial equipped with a magnetic stirrer was added 2,4-dichlorobenzaldehyde (0.174 g, 1.0 mmol), nitroacetonitrile[10] (0.13 g, 1.5 mmol), TMSN$_3$ (0.35 g, 3.0 mmol), and Amb-F (0.10 g, 0.25 mmol, 2.6 mmol/g), and the reaction mixture was stirred for 12 h at 60 °C. At the end of the reaction, ethyl acetate was added, the catalyst was recovered by filtration, and the organic layer was concentrated under vacuum and then purified by silica gel flash chromatography (petroleum ether/EtOAc, 8:2) to give pure **3e** in 80% yield (0.190 g). A similar protocol furnished pure product **3f** in 75% yield (0.167 g; see Scheme 1).

Procedure for the Amb-F-Catalyzed 1,3-Dipolar Cycloaddition of Nitriles 4a–c with TMSN$_3$ (2): In a screw-capped vial equipped with a magnetic stirrer was consecutively added aryl nitriles **4a**–**c** (1.0 mmol), TMSN$_3$ (0.34 g, 3.0 mmol), and Amb-F (0.20 g, 0.50 mmol, 2.6 mmol/g), and the resulting mixture was stirred at 60 °C for the time reported in Scheme 2. At the end of the reaction, ethyl acetate was added, the catalyst was filtered off, and the organic solvent was removed under vacuum to give pure products **5a**–**c** (75–78% yield; see Scheme 2).

Amb-F-Catalyzed β-Azidation of α,β-Unsaturated Acids and Esters 6a–d: In a screw-capped vial equipped with a magnetic stirrer was consecutively added α,β-unsaturated acids or esters **6a**–**d** (1.0 mmol), TMSN$_3$ (0.23 g, 2.0 mmol), and Amb-F (0.10 g, 0.25 mmol, 2.6 mmol/g), and the mixture was allowed to react under the conditions reported in Table 2. At the end of the reaction, ethyl acetate was added, the catalyst was recovered by filtration, and the organic solvent was evaporated under vacuum to give products **7a**–**d** in 95% purity (70–86% yield; see Table 2).

Amb-F-Catalyzed Michael Additions of Dimethylsilyl Ketene Acetal (9) to β-Nitrostyrenes 8a,b in SolFC: In a screw-capped vial equipped with a magnetic stirrer was consecutively added β-nitrostyrene **8a** or **8b** (1.0 mmol), dimethylsilyl ketene acetal (**9**) (0.52 g, 3.0 mmol), and Amb-F (5–10 mol-%, 2.6 mmol/g), and the mixture was allowed to react under the conditions reported in Table 3. At the end of the reaction, ethyl acetate was added, the catalyst was filtered off, and the organic solvent was removed under vacuum. Crude products **10a**,**b** were purified by silica gel flash chromatography (petroleum ether/EtOAc, 9:1) to give pure **10a** (88% yield, 0.22 g) and **10b** (70% yield, 0.18 g). Physical data for **10a**: Oil. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.16 (s, 3 H, CH$_3$), 1.20 (s, 3 H, CH$_3$), 3.58 (s, 3 H, OCH$_3$), 3.77 (dd, J = 4.3, 11.0 Hz, 1 H, CH), 4.76 (dd, J = 4.3, 13.1 Hz, 1 H, C*H*H), 4.96 (dd, J = 11.0, 13.1 Hz, 1 H, C*H*H), 7.12–7.31 (m, 5 H, Ar) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 22.1, 24.9, 45.3, 51.2, 52.0, 76.9, 127.9, 128.3, 128.8, 135.9, 176.2 ppm. $C_{13}H_{17}NO_4$ (251): calcd. C 62.14, H 6.82, N 5.57; found C 62.15, H 6.80, N 5.44. Physical data for **10b**: Oil. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.16 (s, 3 H, CH$_3$), 1.92 (s, 3 H, CH$_3$), 2.30 (s, 3 H, Ar-CH$_3$), 3.69 (s, 3 H, OCH$_3$), 3.73 (dd, J = 4.3, 11.0 Hz, 1 H, CH), 4.75 (dd, J = 4.3, 13.0 Hz, 1 H, C*H*H), 4.93 (dd, J = 11.0, 13.0 Hz, 1 H C*H*H), 7.02–7.25 (m, 4 H) ppm. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 20.8, 22.1, 24.8, 45.3, 50.8, 52.0, 76.8, 128.6, 129.0, 132.7, 137.5, 176.3 ppm. $C_{14}H_{19}NO_4$ (265): calcd. C 63.38, H 7.22, N 5.28; found C 63.35, H 7.30, N 5.24.

Amb-F-Catalyzed Michael Additions of Ethyl Nitroacetate (11) to β-Nitrostyrenes 8a–c in SolFC: In a screw-capped vial equipped with a magnetic stirrer was consecutively added β-nitrostyrene **8a**, **8b**, or **8c** (1.0 mmol), ethyl nitroacetate (0.13 g, 1.0 mmol), and Amb-F (0.02 g, 0.05 mmol, 2.6 mmol/g), and the resulting mixture was stirred at 40 °C for the time reported in Table 4. At the end of the reaction, ethyl acetate was added, the catalyst was recovered by filtration, and the organic layer was evaporated under high vacuum to give pure products **12a** (93% yield, 0.26 g), **12b** (96% yield, 0.28 g) or **12c** (94% yield, 0.30 g). Physical data for **12a**: characterized as a 1:1 diastereoisomeric mixture. Oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.10 (t, J = 7.0 Hz, 3 H, CH$_2$-C*H*$_3$), 1.30 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 4.13 (q, J = 7.1 Hz, 4 H, 2 × CH$_2$), 4.27–4.30 (m, 2 H, 2 × Ar-CH), 4.50–4.55 (m, 2 H, 2 × C*H*H-NO$_2$), 4.88–5.00 (m, 2 H, 2 × C*H*H-NO$_2$), 5.50 (d, J = 8.0 Hz, 1 H, C*H*H), 5.58 (d, J = 9.4 Hz, 1 H, C*H*H), 7.20–7.48 (m, 10 H, Ar) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 13.5, 13.6, 43.8, 43.9, 63.6, 63.8, 75.7, 75.8, 88.8, 89.1, 127.8, 128.0, 129.2, 129.2, 129.3, 129.4, 132.7, 133.2, 162.2, 162.7 ppm. Physical data for **12b**: characterized as a 1:1 diastereoisomeric mixture. Oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.13 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 1.31 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 2.31 (s, 3 H, CH$_3$), 2.32 (s, 3 H, CH$_3$), 4.15 (q, J = 7.1 Hz, 2 H, C*H*$_2$-CH$_3$), 4.31 (q, J = 7.1 Hz, 2 H, C*H*$_2$-CH$_3$), 4.45–4.50 (m, 2 H, Ar-CH), 4.85–4.98 (m, 4 H, CH$_2$-NO$_2$), 5.48 (d, J = 8.0 Hz, 1 H, CH), 5.55 (d, J = 9.5 Hz, 1 H, CH), 7.10–7.18 (m, 8 H, Ar) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 13.3, 13.6, 21.0, 43.5, 43.6, 63.5, 63.8, 75.8, 75.9, 88.9, 89.3, 127.6, 127.9, 129.6, 130.0, 139.1, 139.2, 162.2, 162.8 ppm. Physical data for **12c**: characterized as a 1:1 diastereoisomeric mixture. Oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.20 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 1.29 (t, J = 7.1 Hz, 3 H, CH$_2$-C*H*$_3$), 4.22–4.32 (m, 4 H, C*H*$_2$-CH$_3$), 4.95–5.17 (m, 6 H, Ar-CH, CH$_2$-NO$_2$), 5.71 (d, J = 6.9 Hz, 1 H, CH), 5.83 (d, J = 8.8 Hz, 1 H, CH), 7.20–7.60 (m, 8 H, Ar) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 13.5, 13.6, 40.3, 40.8, 63.8, 73.9, 74.0, 86.8, 87.9, 127.7, 127.8, 130.4, 130.4, 130.5, 130.7, 130.8, 134.0, 162.2, 162.7 ppm.

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