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Imidazole-Mediated Cascade [2 + 2 + 2] Annulation Reactions: A Highly Diastereoselective Synthetic Protocol for the Construction of Multiply Substituted Cyclohexanes

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A novel imidazole-mediated [2 + 2 + 2] annulation process that enables the diastereoselective synthesis of multiply substituted cyclohexanes **3** in a one-pot, three-component manner from two units of (arylmethylidene)malononitriles **1** and one unit of nitroalkenes **2** is described. These cyclohexane derivatives were obtained in moderate to good yields under mild conditions.

Introduction

The development of efficient methods to allow rapid transformation of readily accessible starting materials into complex cyclic molecules is an ongoing challenge in preparative chemistry.[1] Advances in these methodologies have mainly focused on metal-catalyzed procedures, with palladium, rhodium, ruthenium, nickel, and gold being the most prevalent.[2] A recent new direction in this field is the development of cascade or tandem reactions based on organocatalysis.[3] This approach also allows the rapid construction of structurally complex molecules from simple starting materials in only one operation, thereby minimizing cost, waste, and manual effort.

In particular, chiral secondary amines have been used successfully in cascade reactions as a result of their two modes of activating carbonyl compounds (enamine and iminium activation).[4] A great number of examples have been reported, including a secondary-amine-catalyzed triple-cascade/Diels–Alder sequence,[5] tandem Michael/Morita–Baylis–Hillman reactions,[6] tandem Michael/aldol reactions,[7] and tandem Michael/Henry reactions.[8]

In addition to the above enamine and iminium activation modes, nucleophilic phosphane catalysis has emerged recently as an efficient means of generation of carbo- and heterocycles. In particular, Lu's [3 + 2] cycloaddition to form cyclopentenes from allenoates and alkenes under phosphane catalysis conditions has been applied in the synthesis of several natural products.[9] Very recently, Kwon reported phosphane-catalyzed [4 + 2] annulations for the synthesis of tetrahydropyridines and cyclohexenes.[10] Although many catalytic systems for a variety of important transformations have been developed, catalytic cascade chemistry has not yet achieved its full potential. The development of novel reactions, useful reagents, and efficient catalysts to enable the formation of carbon–carbon bonds, particularly in the construction of ring systems, is highly desirable.

The construction of highly functionalized cyclohexane frameworks plays an important role in many natural product syntheses,[11] providing a highly attractive research field in the form of the development of mild, efficient, and modular methods for the synthesis of these densely substituted systems. (Arylmethylidene)malononitriles[12] and nitroalkenes[13] have proven to be extremely useful reagents in organic synthesis. Their reactivities and synthetic diversity provide an important platform for the development of novel cascade strategies. Here we wish to disclose a facile synthetic protocol for multiply substituted cyclohexane compounds through the use of imidazole-mediated[14] [2 + 2 + 2] annulations with two units of (arylmethylidene)malononitriles **1** and one unit of a nitroalkene **2** under mild conditions. This new chemistry can provide a straightforward, diastereoselective, and potentially powerful method for the modular construction of highly substituted cyclohexanes.

Results and Discussion

We initially examined the reaction between benzylidenemalononitrile (**1a**) and nitroalkene **2a** (ratio of **1a**/**2a** = 1:1) in the presence of several amine and phosphane promoters

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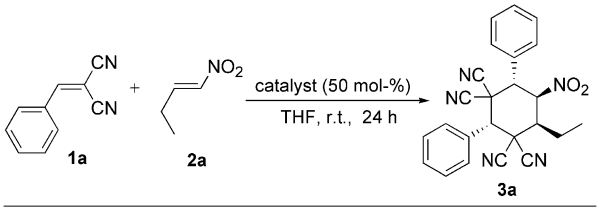
(50 mol-%) in tetrahydrofuran (THF) at room temperature (20 °C), and the results of these experiments are summarized in Table 1. As can be seen, in the presence of PPh_3 and PPh_2OMe as the promoters, no reactions had occurred after 24 h (Table 1, Entries 1 and 3), whereas use of other nucleophilic phosphanes as the promoters afforded complex product mixtures (Table 1, Entries 2 and 4–5). Moreover, use of tertiary amines – such as 1,4-diazabicyclo[2.2.2]-octane (DABCO), 4-(dimethylamino)pyridine (DMAP), Et_3N, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), piperidine, and pyrrolidine – as the promoters resulted in complex product mixtures (Table 1, Entries 6–9, 11, and 12). With pyridine as the promoter, no reaction occurred (Table 1, Entry 10). To our delight, however, the reaction proceeded smoothly to give the annulation product **3a** in 35% yield in 24 h when *N*-methylimidazole was used as the promoter (Table 1, Entry 15), although traces of **3a** were also formed in the presence of 1,2,4-triazole and pyrazole (Table 1, Entries 13 and 14). The yield of **3a** was improved to 60% when imidazole was used as the promoter instead of *N*-methylimidazole (Table 1, Entry 16). It should be noted that **3a** was formed diastereospecifically, as no other diastereoisomers could be detected in the ^1H NMR spectroscopic data for the crude reaction mixtures (see the Supporting Information). Because the structure of product **3a** contains two units of the benzylidenemalononitrile (**1a**) component and one unit of the nitroalkene component **2a**, it was found that the yield of **3a** could be slightly improved to 66% when the reaction was carried out with 2 equiv. of **1a** and 1 equiv. of **2a** under otherwise identical conditions (Table 1, Entry 17).

Encouraged by the above results, we examined the reaction in further detail under a variety of sets of conditions in an attempt to improve the yield of **3a**. A survey of solvents revealed that THF was the best solvent for this reaction (Table 2, Entries 1–8). Interestingly, in all these solvents, **3a** was produced as a single diastereoisomer. In addition, it was observed that prolonging the reaction time did not give any improvement in the yield of **3a** in THF (Table 1, Entry 9). Moreover, it was also found that increasing the employed amounts of imidazole to 100 mol-% did not improve the yield of **3a**, whereas decreasing the employed amounts of imidazole to 20 mol-% resulted in the formation of **3a** in lower yield under otherwise identical conditions (Table 2, Entries 10 and 11). When the reaction was conducted at a higher temperature (45 °C), no improvement in the yield of **3a** was observed, **3a** being obtained in 21% yield in THF (Table 2, Entry 12). Further optimization of the reaction conditions revealed that when the reaction was carried out with **1a** (3.0 equiv.) and **2a** (1.0 equiv.) in the presence of imidazole (50 mol-%) in THF at room temperature over 24 h, **3a** was obtained in 58% yield (Table 2, Entry 13). Therefore, the best conditions found to carry out the reac-

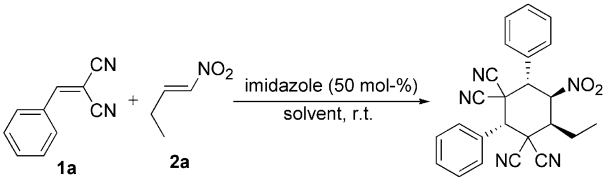
Table 1. Survey of several amine and phosphane promoters for the [2 + 2 + 2] annulation of benzylidenemalononitrile (**1a**) and nitroalkene **2a**.[a]



Entry	Ratio	Catalyst	Yield (%)[b]
1[c]	1:1	PPh_3	n.r.[d]
2[c]	1:1	PBu_3	complex
3[c]	1:1	PPh_2OMe	n.r.[d]
4[c]	1:1	PPh_2Me	complex
5[c]	1:1	$PPhMe_2$	complex
6	1:1	DABCO	complex
7	1:1	DMAP	complex
8	1:1	Et_3N	complex
9	1:1	DBU	complex
10	1:1	pyridine	n.r.[d]
11	1:1	piperidine	complex
12	1:1	pyrrolidine	complex
13	1:1	1,2,4-triazole	trace
14	1:1	pyrazole	trace
15	1:1	*N*-methylimidazole	35
16	1:1	imidazole	60
17	*2:1*	*imidazole*	*66*

[a] The reaction was carried out with **1a** (0.3 mmol), **2a** (0.3 mmol), and catalyst (0.15 mmol) in THF under ambient atmosphere. [b] Isolated yields. [c] The reaction was carried out under argon. [d] No reaction.

Table 2. Solvent effects and other conditions in the imidazole-mediated [2 + 2 + 2] annulation of benzylidenemalononitrile (**1a**) and nitroalkene **2a**.[a]



Entry	Ratio (**1a**/**2a**)	Solvent	Time (h)	Yield (%)[b]
1	*2:1*	*THF*	*24*	*66*
2	2:1	1,4-dioxane	24	49
3	2:1	DCM	24	57
4	2:1	MeOH	24	43
5	2:1	toluene	24	52
6	2:1	CH_3CN	24	61
7	2:1	DMF	24	51
8	2:1	Et_2O	24	62
9	2:1	THF	48	62
10[c]	2:1	THF	24	65
11[d]	2:1	THF	24	41
12[e]	2:1	THF	24	27
13	3:1	THF	24	58

[a] The reaction was carried out with **1a** (0.30 mmol), **2a** (0.15 mmol), and imidazole (0.075 mmol) in THF under ambient atmosphere. [b] Isolated yield. [c] Imidazole (100 mol-%) was used. [d] Imidazole (20 mol-%) was used. [e] The reaction was carried out at 45 °C.

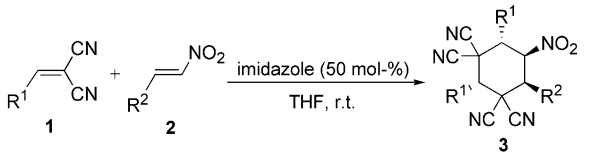
tion involved the use of **1a** (2.0 equiv.) with **2a** (1.0 equiv.) in THF in the presence of imidazole (50 mol-%) as the promoter at room temperature over 24 h.

With these optimized reaction conditions to hand, we next turned our interest to the reaction generality. A variety of (arylmethylidene)malononitriles **1** was examined under these optimal conditions, and the results of these experiments are shown in Entries 1–7 of Table 3. As summarized, the reactions proceeded smoothly to produce cyclohexanes **3** in moderate to good yields, in each case as single diastereoisomer regardless of whether an electron-withdrawing or an electron-donating group was present on the benzene ring of **1**. Only in the case of (arylmethylidene)malononitrile **1g**, with a strongly electron-donating methoxy group on the benzene ring, was a prolonged reaction time required to give the corresponding cyclohexane **3g** in 48% yield (Table 3, Entry 6). Notably, a similar result was obtained with the heterocyclic methylidenemalononitrile **1h**, which afforded the corresponding cyclohexane **3h** in 44% yield (Table 3, Entry 7).

Moreover, a variety of nitroalkenes **2** were also examined under the optimized reaction conditions, and the results of these experiments are summarized in Entries 8–12 of Table 3. As can be seen, variation in the alkyl chain length of the R^2 group in **2** did not affect the yields of the corresponding products **3** in any instance, with the cyclohexanes **3i**–**3m** being obtained in moderate to good yields (Table 3, Entries 8–12). Use of an aromatic nitroalkene such as (*E*)-(2-nitrovinyl)benzene (**2e**) as the substrate afforded the desired product **3n** in 13% yield along with some other unidentified byproducts under the optimized reaction conditions, accompanied by the recovery of 25% of the starting materials (Table 3, Entry 13). Furthermore, use of the alkyl-substituted methylidenemalononitrile **1i** as the substrate provided complex product mixtures within a very short time (Table 3, Entry 14).

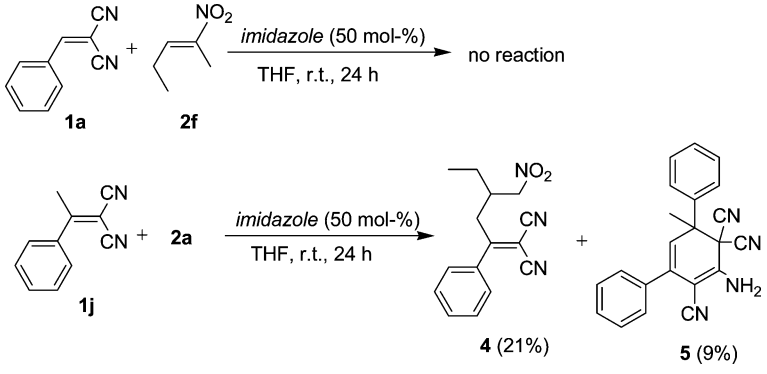
The scope and limitations of this reaction with regard to the introduction of further substituents into the employed (arylmethylidene)malononitriles **1** or the nitroalkenes **2** still remained obscure, so (*E*)-2-nitropent-2-ene (**2f**) was synthesized and utilized as the substrate to examine its reaction with **1a**. However, no reaction occurred upon treatment of **1a** with **2f** in the presence of imidazole in THF (Scheme 1). Moreover, when 2-(1-phenylethylidene)malononitrile (**1j**) was used as the substrate to react with (*E*)-1-nitrobut-1-ene (**2a**) in the presence of imidazole in THF at room temperature, it was found that the corresponding vinylogous Michael addition product **4**[15] and the dimerization product of **1j**, which has been identified as compound **5**,[16] were formed in 21% and 9% yields, respectively, along with the recovery of the starting materials in 30% yield, suggesting that the introduction of a substituent in **1** could change the reaction pathway (Scheme 1).

Table 3. Survey of (arylmethylidene)malononitriles **1** for the [2 + 2 + 2] annulations with the nitroalkenes **2**.[a]



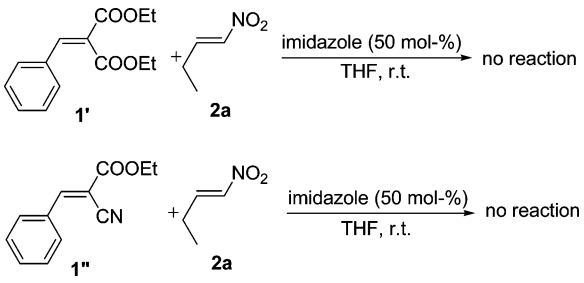
Entry	R^1	R^2	Time (h)	Product, yield (%)[b]
1	4-BrC_6H_4 (**1b**)	Et (**2a**)	24	**3b**, 68
2	3-BrC_6H_4 (**1c**)	Et (**2a**)	24	**3c**, 64
3	4-ClC_6H_4 (**1d**)	Et (**2a**)	24	**3d**, 61
4	3-MeC_6H_4 (**1e**)	Et (**2a**)	24	**3e**, 62
5	4-MeC_6H_4 (**1f**)	Et (**2a**)	24	**3f**, 57
6	4-$MeOC_6H_4$ (**1g**)	Et (**2a**)	48	**3g**, 48
7	3-pyridyl (**1h**)	Et (**2a**)	24	**3h**, 44
8	C_6H_5 (**1a**)	*n*Pr (**2b**)	36	**3i**, 69
9	3-BrC_6H_4 (**1c**)	*n*Pr (**2b**)	36	**3j**, 66
10	C_6H_5 (**1a**)	*n*Bu (**2c**)	36	**3k**, 76
11	4-MeC_6H_4 (**1f**)	*n*Bu (**2c**)	36	**3l**, 52
12[c]	C_6H_5 (**1a**)	Me (**2d**)	24	**3m**, 57
13[d]	C_6H_5 (**1a**)	C_6H_5 (**2e**)	24	**3n**,13
14[e]	Et (**1i**)	Et (**2a**)	1/6	–

[a] The reaction was carried out with **1** (0.30 mmol), **2** (0.15 mmol), and imidazole (0.075 mmol) in THF under ambient atmosphere. [b] Isolated yield. [c] 1-Nitropropene was used as a solution in diethyl ether in a large excess. [d] The reaction was incomplete, and the product was accompanied by some other unidentified byproducts, together with the recovery of 25% of the starting materials. [e] Complex product mixtures were obtained.



Scheme 1. Lack of reaction between benzylidenemalononitrile (**1a**) and (*E*)-2-nitropent-2-ene (**2b**), together with the reaction between (1-phenylethylidene)malononitrile (**1j**) and (*E*)-1-nitrobut-1-ene (**2a**).

It should be also noted that the reactions between diethyl 2-benzylidenemalonate (**1′**) or ethyl (*E*)-2-cyano-3-phenylacrylate (**1′′**) and nitroalkene **2a** did not take place under the optimized reaction conditions, indicating that the strongly electron-withdrawing dicyano groups in the substrate **1** are essential for this imidazole-mediated reaction (Scheme 2).[17]



Scheme 2. The absence of reactions between diethyl benzylidenemalonate (**1′**) or ethyl (*E*)-2-cyano-3-phenylacrylate (**1′′**) and nitroalkene **2a**.

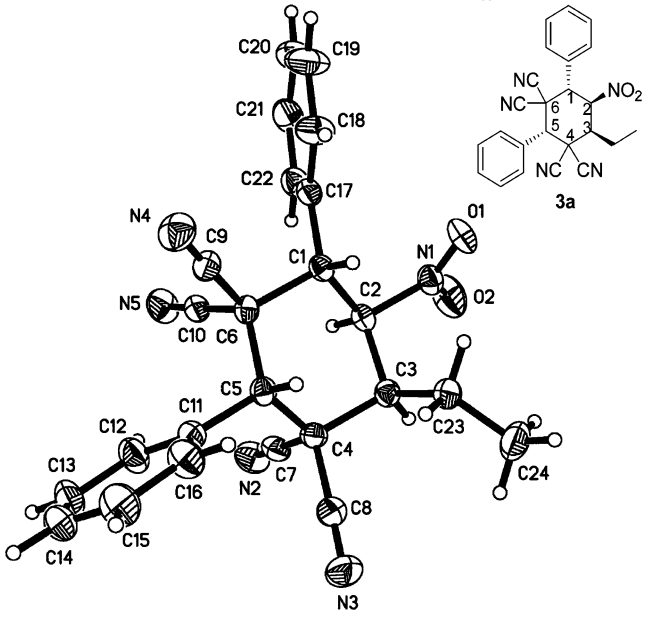
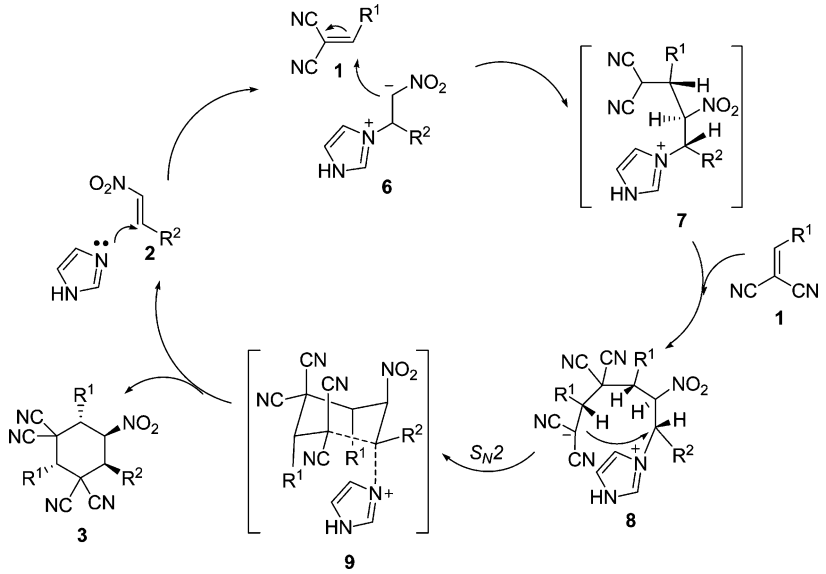


Figure 1. X-ray crystal structure of **3a**.

The structures of these isolated cyclohexane products **3a**–**3n** were determined from their IR, ^{1}H NMR, ^{13}C NMR, and HMRS spectroscopic data, as well as from microanalyses (see the Supporting Information). The diastereochemical outcome in compounds **3** was assigned by single-crystal X-ray diffraction on **3a**. This showed the ethyl group adjacent to C-3 in a *cis* configuration with respect to the nitro group adjacent to C-2, whereas the phenyl groups adjacent to C-1 and C-5 are in a *trans* configuration with respect to the nitro group adjacent to C-2. The ORTEP drawing is shown in Figure 1.[18]

The mechanism of this novel imidazole-mediated cyclization reaction has not been unequivocally established, but one straightforward and still reasonable mechanism for this transformation is outlined in Scheme 3. The zwitterionic intermediate **6** initially formed by nucleophilic attack of imidazole onto nitroalkene **2** is trapped by the (arylmethylidene)malononitrile **1**, leading to the formation of intermediate **7** in an *anti*,*anti* configuration, presumably due to the steric effect. The intermediate **7** can be further trapped by another (arylmethylidene)malononitrile **1** to produce intermediate **8**, which undergoes an intramolecular S_N2 cyclization through the sterically favored chair configuration of intermediate **9** to yield cyclohexane **3** and regenerates the imidazole at the same time. The high electrophilicity of (arylmethylidene)malononitrile **1** plays a key role in this reaction.



Scheme 3. A plausible reaction mechanism.

Conclusions

We have developed a quite simple, one-pot, three-component synthesis of multiply substituted cyclohexanes in a novel, imidazole-mediated [2 + 2 + 2] annulation process. Moderate to good yields and high stereoselectivities, the use of simple and cheap starting materials and catalyst, as well as mild reaction conditions are the main advantages of this method. In addition, the presented synthesis tolerates carbonitrile, aryl, and nitro functional groups. Further effort will focus on expanding the versatility of this new [2 + 2 + 2] annulation as well as on performing the annulations in an enantioselective manner.

Experimental Section

General Remarks: Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. MS and HRMS data were recorded by EI methods. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out with silica gel at increased pressure.

Typical Reaction Procedure for the Imidazole-Mediated [2 + 2 + 2] Annulation: The nitroalkene **2** (0.15 mmol) was added under ambient atmosphere to a mixture of the (arylmethylidene)malononitrile **1** (0.30 mmol) and imidazole (0.075 mmol) in solvent, and the reaction mixture was stirred at room temperature for the required time as indicated in the tables. After the reaction, the solution was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: EtOAc/petroleum ether, 1:4) to afford the pure product **3**.

4-Ethyl-5-nitro-2,6-diphenylcyclohexane-1,1,3,3-tetracarbonitrile (3a): M.p. 214–216 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.15 (t, J = 7.5 Hz, 3 H, CH_3), 1.94–2.18 (m, 2 H, CH_2), 3.30 (q, J = 4.5 Hz, 1 H, CH), 3.56 (s, 1 H, CH), 4.00 (d, J = 12.0 Hz, 1 H, CH), 5.80 (dd, J_1 = 4.5, J_2 = 12.0 Hz, 1 H, CH), 7.48–7.63 (m, 8 H, Ar), 7.82–7.85 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.9, 20.4, 42.0, 45.1, 47.6, 48.0, 48.2, 81.4, 109.8, 111.2, 111.6, 112.2, 129.2, 129.3, 129.7, 130.2, 130.3, 130.7, 131.7 ppm. MS (EI): m/z = 409 $[M]^+$ (19.1), 209 $[M - 1]^+$ (42.2), 208 $[M - 18]^+$ (61.7), 167 $[M - 35]^+$ (43.3), 154 $[M - 53]^+$ (54.9), 145 $[M - 71]^+$ (57.7), 127 $[M - 74]^+$ (41.5), 155 $[M - 81]^+$ (20.9), 145 $[M - 91]^+$ (10.1). IR (CH_2Cl_2): $\tilde{\nu}$ = 3066, 3037, 2982, 2942, 2883, 2244, 1562, 1497, 1458, 1366, 1299, 1004, 737, 701 cm^{-1}. $C_{24}H_{19}N_5O_2$ (409.15): calcd. C 70.40, H 4.68, N 17.10; found C 70.24, H 4.76, N 17.16.

2,4-Bis(4-bromophenyl)-6-ethyl-5-nitrocyclohexane-1,1,3,3-tetracarbonitrile (3b): M.p. 204–206 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.15 (t, J = 7.2 Hz, 3 H, CH_3), 1.93–2.12 (m, 2 H, CH_2), 3.31 (q, J = 4.5 Hz, 1 H, CH), 3.51 (s, 1 H, CH), 3.96 (d, J = 11.7 Hz, 1 H, CH), 5.72 (dd, J_1 = 4.5, J_2 = 11.7 Hz, 1 H, CH), 7.39 (d, J = 8.7 Hz, 2 H, Ar), 7.64 (d, J = 8.7 Hz, 2 H, Ar), 7.68–7.75 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.9, 20.3, 41.7, 44.6, 47.1, 47.5, 48.1, 81.1, 109.5, 111.0, 111.4, 111.9, 125.4, 126.4, 128.0, 129.1, 130.7, 133.1, 133.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3067, 2979, 2942, 1660, 1592, 1566, 1493, 1417, 1365, 1079, 1011, 830, 740 cm^{-1}. MS (EI): m/z = 569 $[M + 4]^+$ (3.8), 567 $[M + 2]^+$ (6.0), 565 $[M]^+$ (3.1), 234 (51.9), 232 (59.9), 153 (93.4), 142 (35.9), 126 (38.7), 86 (73.1), 84 (100.0), 51 (48.5). HRMS (EI): calcd. for $C_{24}H_{17}Br_2N_5O_2$ $[M]^+$ 564.9749; found 564.9735.

2,4-Bis(3-bromophenyl)-6-ethyl-5-nitrocyclohexane-1,1,3,3-tetracarbonitrile (3c): M.p. 211–213 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.14 (t, J = 7.2 Hz, 3 H, CH_3), 1.92–2.11 (m, 2 H, CH_2), 3.33 (q, J = 4.2 Hz, 1 H, CH), 3.51 (s, 1 H, CH), 3.95 (d, J = 12.0 Hz, 1 H, CH), 5.73 (dd, J_1 = 4.2, J_2 = 12.0 Hz, 1 H, CH), 7.37 (t, J = 8.1 Hz, 1 H, Ar), 7.48 (t, J = 8.1 Hz, 2 H, Ar), 7.63–7.67 (m, 2 H, Ar), 7.76 (d, J = 9.6 Hz, 1 H, Ar), 7.87–7.92 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.8, 20.3, 41.7, 44.5, 46.9, 47.3, 48.0, 81.0, 109.3, 110.9, 111.1, 111.8, 123.7, 124.1, 127.1, 131.1, 131.2, 131.8, 132.2, 132.8, 134.0, 135.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3052, 2978, 2940, 1664, 1567, 1479, 1367, 1265, 1079, 738 cm^{-1}. MS (EI): m/z = 569 $[M + 4]^+$ (1.8), 567 $[M + 2]^+$ (3.4), 565 $[M]^+$ (1.8), 234 (43.6), 232 (45.7), 153 (100.0), 142 (44.1), 141 (19.8), 76 (18.2), 75 (19.7). HRMS (EI): calcd. for $C_{24}H_{17}Br_2N_5O_2$ $[M]^+$ 564.9749; found 564.9762.

2,4-Bis(4-chlorophenyl)-6-ethyl-5-nitrocyclohexane-1,1,3,3-tetracarbonitrile (3d): M.p. 211–213 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.14 (t, J = 7.5 Hz, 3 H, CH_3), 1.92–2.14 (m, 2 H, CH_2), 3.32 (q, J = 4.2 Hz, 1 H, CH), 3.55 (s, 1 H, CH), 3.98 (d, J = 12.0 Hz, 1 H, CH), 5.74 (dd, J_1 = 4.2, J_2 = 12.0 Hz, 1 H, CH), 7.44–7.50 (m, 4 H, Ar), 7.57 (d, J = 8.7 Hz, 2 H, Ar), 7.78 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.8, 20.3, 41.7, 44.8, 46.9, 47.3, 48.0, 81.1, 109.5, 111.0, 111.4, 111.9, 127.5, 128.6, 130.1, 130.5, 130.6, 137.1, 138.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3059, 2979, 1900, 1704, 1597, 1567, 1496, 1099, 1015, 834 cm^{-1}. MS (EI): m/z = 477 $[M]^+$ (4.2), 188 (64.6), 161 (22.3), 153 (70.7), 149 (32.4), 86 (68.0), 84 (100.0), 75 (22.5), 51 (40.7). HRMS (EI): calcd. for $C_{24}H_{17}C_{l2}N_5O_2$ $[M]^+$ 477.0759; found 477.0776.

4-Ethyl-5-nitro-2,6-bis(*m*-tolyl)cyclohexane-1,1,3,3-tetracarbonitrile (3e): M.p. 209–211 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.13 (t, J = 7.2 Hz, 3 H, CH_3), 1.92–2.18 (m, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.28 (q, J = 4.5 Hz, 1 H, CH), 3.50 (s, 1 H, CH), 3.94 (d, J = 12.0 Hz, 1 H, CH), 5.78 (dd, J_1 = 4.5, J_2 = 12.0 Hz, 1 H, CH), 7.25–7.40 (m, 5 H, Ar), 7.44 (t, J = 7.8 Hz, 1 H, Ar), 7.57 (s, 1 H, Ar), 7.67 (d, J = 7.2 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.8, 20.3, 21.4, 21.5, 42.0, 45.0, 47.5, 48.0, 48.2, 81.5, 109.9, 111.3, 111.7, 112.3, 126.0, 129.3, 129.5, 130.0, 130.2, 131.4, 132.5, 139.6, 140.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3037, 2978, 2926, 2874, 1708, 1608, 1566, 1493, 1464, 1367, 738, 702 cm^{-1}. MS (EI): m/z = 437 $[M]^+$ (55.7), 168 (100.0), 167 (55.5), 159 (50.5), 141 (67.9), 140 (65.1), 129 (51.7), 105 (66.1). $C_{26}H_{23}N_5O_2$ (437.19): calcd. C 71.38, H 5.30, N 16.01; found C 71.39, H 5.51, N 16.00.

4-Ethyl-5-nitro-2,6-bis(*p*-tolyl)cyclohexane-1,1,3,3-tetracarbonitrile (3f): M.p. 176–178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.13 (t, J = 7.5 Hz, 3 H, CH_3), 1.93–2.19 (m, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 3.29 (q, J = 4.5 Hz, 1 H, CH), 3.53 (s, 1 H, CH), 3.97 (d, J = 12.0 Hz, 1 H, CH), 5.78 (dd, J_1 = 4.5, J_2 = 12.0 Hz, 1 H, CH), 7.28 (d, J = 9.0 Hz, 2 H, Ar), 7.36 (d, J = 7.8 Hz, 2 H), 7.41 (d, J = 7.8 Hz, 2 H), 7.71 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.9, 20.3, 21.2, 21.3, 42.1, 45.4, 47.2, 47.7, 48.2, 81.5, 110.0, 111.4, 111.8, 112.3, 126.4, 127.3, 129.0, 130.3, 130.8, 140.8, 142.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3034, 2977, 2926, 2885, 1915, 1719, 1566, 1517, 823 cm^{-1}. MS (EI): m/z = 437 $[M]^+$ (15.6), 168 (100.0), 167 (34.9), 142 (37.0), 141 (59.5), 140 (46.9), 129 (39.0), 115 (37.4), 105 (35.5). HRMS (EI): calcd. for $C_{26}H_{23}N_5O_2$ $[M]^+$ 437.1852; found 437.1841.

4-Ethyl-2,6-bis(4-methoxyphenyl)-5-nitrocyclohexane-1,1,3,3-tetracarbonitrile (3g): M.p. 144–146 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.13 (t, J = 7.8 Hz, 3 H, CH_3), 1.91–2.18 (m, 2 H, CH_2),

3.25 (q, J = 4.2 Hz, 1 H, CH), 3.51 (s, 1 H, CH), 3.82 (s, 3 H, OCH_3), 3.86 (s, 3 H, CH_3), 3.94 (d, J = 12.0 Hz, 1 H, CH), 5.72 (dd, J_1 = 4.2, J_2 = 12.0 Hz, 1 H, CH), 6.98 (d, J = 8.4 Hz, 2 H, Ar), 7.05 (d, J = 9.0 Hz, 2 H, Ar), 7.43 (d, J = 8.4 Hz, 2 H, Ar), 7.75 (d, J = 9.0 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.9, 20.3, 42.3, 45.8, 47.0, 47.4, 48.2, 55.3, 55.4, 81.6, 110.1, 111.4, 111.9, 112.3, 115.0, 115.4, 121.1, 122.0, 130.6, 161.1, 161.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2962, 2939, 2842, 1708, 1612, 1565, 1517, 1464, 1288, 1262, 1186, 1031, 836 cm^{-1}. MS (EI): m/z = 469 $[M]^+$ (6.8), 239 (18.4), 185 (15.6), 184 (100.0), 179 (31.4), 174 (14.8), 149 (34.3), 141 (28.7), 114 (38.71). HRMS (EI): calcd. for $C_{26}H_{23}N_5O_4$ $[M]^+$ 469.1750; found 469.1760.

4-Ethyl-5-nitro-2-(pyridin-3-yl)-6-(pyridin-4-yl)cyclohexane-1,1,3,3-tetracarbonitrile (3h): M.p. 170–172 °C. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz, TMS]: δ = 0.97 (t, J = 7.5 Hz, 3 H, CH_3), 1.86–2.08 (m, 2 H, CH_2), 4.03 (q, J = 4.2 Hz, 1 H, CH), 4.75 (s, 1 H, CH), 4.78 (d, J = 12.0 Hz, 1 H, CH), 6.41 (dd, J_1 = 4.2, J_2 = 12.0 Hz, 1 H, CH), 7.54 (dd, J_1 = 4.8, J_2 = 7.8 Hz, 1 H, Ar), 7.75 (dd, J_1 = 4.8, J_2 = 8.1 Hz, 1 H, Ar), 8.41 (d, J = 9.0 Hz, 1 H, Ar), 8.36–8.43 (m, 1 H, Ar), 8.66 (d, J = 4.5 Hz, 1 H, Ar), 8.84 (d, J = 4.8 Hz, 1 H, Ar), 9.01 (d, J = 2.4 Hz, 1 H, Ar), 8.92–9.02 (m, 1 H, Ar) ppm. ^{13}C NMR [$(CD_3)_2SO$, 75 MHz]: δ = 14.5, 20.4, 41.5, 42.1, 42.6, 45.0, 45.6, 81.1, 111.0, 112.2, 112.6, 112.7, 124.4, 125.2, 127.7, 129.3, 136.3, 151.2, 152.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2904, 1712, 1560, 1548, 1431, 1025, 713 cm^{-1}. MS (EI): m/z = 411 $[M]^+$ (3.5), 155 (100.0), 128 (48.3), 104 (57.5), 101 (34.4), 79 (23.0), 77 (15.7), 75 (22.0), 51 (16.6). HRMS (EI): calcd. for $C_{22}H_{17}N_7O_2$ $[M]^+$ 411.1444; found 411.1438.

5-Nitro-2,4-diphenyl-6-propylcyclohexane-1,1,3,3-tetracarbonitrile (3i): M.p. 213–215 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.98 (t, J = 6.9 Hz, 3 H, CH_3), 1.28–1.43 (m, 1 H, CH_2), 1.50–1.64 (m, 1 H, CH_2), 1.80–1.92 (m, 1 H, CH_2), 1.97–2.09 (m, 1 H, CH_2), 3.34 (q, J = 4.2 Hz, 1 H, CH), 3.56 (s, 1 H, CH), 4.00 (d, J = 12.3 Hz, 1 H, CH), 5.81 (dd, J_1 = 4.2, J_2 = 12.3 Hz, 1 H, CH), 7.47–7.62 (m, 8 H, Ar), 7.83–7.86 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.4, 23.5, 28.7, 42.1, 45.1, 46.2, 47.5, 48.0, 81.5, 109.8, 111.3, 111.6, 112.2, 129.2, 129.4, 129.7, 130.2, 130.7, 131.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3067, 2966, 2935, 2877, 1712, 1566, 1458, 700 cm^{-1}. MS (EI): m/z = 423 $[M]^+$ (16.1), 222 (40.5), 155 (43.7), 154 (100.0), 128 (42.1), 127 (69.1), 115 (68.5), 103 (59.1), 91 (94.3). HRMS (EI): calcd. for $C_{25}H_{21}N_5O_2$ $[M]^+$ 423.1695; found 423.1691.

2,4-Bis(3-bromophenyl)-5-nitro-6-propylcyclohexane-1,1,3,3-tetracarbonitrile (3j): M.p. 185–187 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.98 (t, J = 7.2 Hz, 3 H, CH_3), 1.32–1.42 (m, 1 H, CH_2), 1.53–1.65 (m, 1 H, CH_2), 1.80–2.01 (m, 2 H, CH_2), 3.36 (q, J = 4.2 Hz, 1 H, CH), 3.50 (s, 1 H, CH), 3.94 (d, J = 12.6 Hz, 1 H, CH), 5.73 (dd, J_1 = 4.2, J_2 = 12.6 Hz, 1 H, CH), 7.37 (t, J = 8.1 Hz, 1 H, Ar), 7.46–7.51 (m, 2 H, Ar), 7.63–7.67 (m, 2 H, Ar), 7.76 (d, J = 7.5 Hz, 1 H, Ar), 7.88–7.93 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.4, 23.5, 28.6, 41.8, 44.5, 46.1, 47.0, 47.3, 81.1, 109.3, 110.9, 111.1, 111.8, 123.7, 124.1, 127.1, 131.1, 131.2, 131.8, 132.1, 132.8, 134.1, 135.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3067, 2966, 2876, 1709, 1567, 1479, 1079, 736 cm^{-1}. MS (EI): m/z = 582 $[M + 4]^+$ (2.8), 581 $[M + 2]^+$ (4.9), 579 $[M]^+$ (2.2), 234 (45.3), 232 (46.7), 156 (22.1), 153 (100.0), 126 (36.1), 115 (20.5), 76 (20.5), 75 (20.5). $C_{25}H_{19}Br_2N_5O_2$ (578.99): calcd. C 51.66, H 3.29, N 12.05; found C 51.36, H 3.44, N 11.78.

4-Butyl-5-nitro-2,6-diphenylcyclohexane-1,1,3,3-tetracarbonitrile (3k): M.p. 180–182 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.92 (t, J = 6.6 Hz, 3 H, CH_3), 1.12–1.58 (m, 4 H, CH_2), 1.83–2.09 (m, 2 H, CH_2), 3.34 (q, J = 4.5 Hz, 1 H, CH), 3.56 (s, 1 H, CH), 4.00 (d, J = 11.7 Hz, 1 H, CH), 5.81 (dd, J_1 = 4.5, J_2 = 11.7 Hz, 1 H, CH), 7.47–7.63 (m, 8 H, Ar), 7.83–7.86 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.5, 22.1, 26.5, 32.3, 42.1, 45.1, 46.4, 47.5, 48.0, 81.5, 109.8, 111.2, 111.6, 112.2, 129.2, 129.3, 129.7, 130.2, 130.6, 131.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3067, 3038, 2962, 2934, 2875, 1718, 1565, 1500, 737 cm^{-1}. MS (EI): m/z = 437 $[M]^+$ (14.9), 236 (33.7), 155 (32.9), 154 (100.0), 128 (32.5), 127 (62.9), 115 (36.7), 103 (48.5), 91 (65.5). $C_{26}H_{23}N_5O_2$ (437.19): calcd. C 71.38, H 5.30, N 16.01; found C 71.54, H 5.31, N 15.83.

4-Butyl-5-nitro-2,6-bis(*p*-tolyl)cyclohexane-1,1,3,3-tetracarbonitrile (3l): M.p. 125–127 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.92 (t, J = 6.9 Hz, 3 H, CH_3), 1.22–1.41 (m, 3 H, CH_2), 1.45–1.59 (m, 1 H, CH_2), 1.81–1.91 (m, 1 H, CH_2), 1.98–2.08 (m, 1 H, CH_2), 2.37 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 3.30 (q, J = 4.2 Hz, 1 H, CH), 3.50 (s, 1 H, CH), 3.94 (d, J = 12.6 Hz, 1 H, CH), 5.77 (dd, J_1 = 4.2, J_2 = 12.6 Hz, 1 H, CH), 7.27 (d, J = 9.0 Hz, 2 H, Ar), 7.35 (d, J = 8.1 Hz, 2 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.71 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.5, 21.2, 21.3, 22.1, 26.5, 32.4, 42.2, 45.4, 46.5, 47.3, 47.8, 81.6, 109.9, 111.4, 111.8, 112.3, 126.4, 127.2, 129.1, 130.3, 130.8, 140.9, 142.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3022, 2960, 2874, 1732, 1608, 1567, 1517, 1365 cm^{-1}. MS (EI): m/z = 465 $[M]^+$ (16.5), 168 (100.0), 167 (41.6), 163 (39.5), 141 (49.7), 140 (45.8), 129 (40.5), 115 (35.3), 105 (61.5). HRMS (EI): calcd. for $C_{28}H_{27}N_5O_2$ $[M]^+$ 465.2165; found 465.2167.

4-Methyl-5-nitro-2,6-diphenylcyclohexane-1,1,3,3-tetracarbonitrile (3m): M.p. 236–238 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.61 (d, J = 7.2 Hz, 3 H, CH_3), 3.61 (s, 1 H, CH), 3.65 (q, J = 4.5 Hz, 1 H, CH), 4.06 (d, J = 12.9 Hz, 1 H, CH), 5.87 (dd, J_1 = 4.5, J_2 = 12.9 Hz, 1 H, CH), 7.48–7.62 (m, 8 H, Ar), 7.84–7.87 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 11.1, 41.1, 41.9, 45.4, 46.4, 47.1, 82.0, 109.7, 111.1, 111.6, 112.2, 129.2, 129.3, 129.7, 130.1, 130.2, 130.7, 131.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3204, 2963, 1736, 1560, 1458, 1361, 1296, 1004, 734, 699 cm^{-1}. MS (EI): m/z = 395 $[M]^+$ (100.0), 349 (43.4), 195 (80.0), 194(56.6), 168 (42.6), 154 (67.8), 129 (49.4), 127 (41.4), 91 (50.0). HRMS (EI): calcd. for $C_{23}H_{17}N_5O_2$ $[M]^+$ 395.1382; found 395.1369.

5-Nitro-2,4,6-triphenylcyclohexane-1,1,3,3-tetracarbonitrile (3n): M.p. 132–134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 4.13 (s, 1 H, CH), 4.49 (d, J = 12.9 Hz, 1 H, CH), 4.74 (d, J = 5.7 Hz, 1 H, CH), 6.09 (dd, J_1 = 5.7, J_2 = 12.9 Hz, 1 H, CH), 7.47–7.60 (m, 13 H, Ar), 7.87–7.89 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 42.2, 45.1, 47.7, 48.5, 52.4, 81.9, 109.9, 110.5, 111.9, 112.4, 128.4, 129.2, 129.4, 129.5, 129.7. 129.8, 130.1, 130.3, 130.7, 131.4, 131.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3065, 2922, 2852, 2357, 2320, 1568, 1499, 1456, 1361, 737, 699 cm^{-1}. MS (EI): m/z = 457 $[M]^+$ (12.5), 410 (10.5), 256 (99.7), 191 (100.0), 155 (87.5), 127 (55.6), 115 (74.7), 91 (62.3). HRMS (EI): calcd. for $C_{28}H_{19}N_5O_2$ $[M]^+$ 457.1539; found 457.1541.

2-[3-(Nitromethyl)-1-phenylpentylidene]malononitrile (4): ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.25–1.60 (m, 1 H, CH), 2.03–2.27 (m, 2 H, CH_2), 3.11 (d, J = 6.9 Hz, 2 H, CH_2), 4.24 (dd, J_1 = 12.9, J_2 = 8.1 Hz, 1 H, CH_2), 4.35 (dd, J_1 = 12.9, J_2 = 5.4 Hz, 1 H, CH_2), 7.45–7.49 (m, 2 H, Ar), 7.52–7.63 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.4, 23.9, 37.8, 39.1, 77.8, 86.7, 112.2, 112.3, 127.5, 129.6, 132.6, 133.6, 178.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2967, 2926, 2360, 2324, 2228, 1550, 1381, 705 cm^{-1}. MS (EI): m/z = 269 $[M]^+$ (0.8), 239 (5.9), 223 (15.1), 193 (37.4), 183 (100.0), 179 (49.5), 155 (37.7), 91 (17.6). HRMS (EI): calcd. for $C_{15}H_{15}N_3O_2$ $[M]^+$ 269.1164; found 269.1166.

2-Amino-6-methyl-4,6-diphenylcyclohexa-2,4-diene-1,1,3-tricarbonitrile (5): A known compound.[16] ^{1}H NMR ($CDCl_3$, 300 MHz,

TMS): δ = 1.91 (s, 3 H, CH_3), 5.61 (s, 2 H, NH_2), 5.81 (s, 1 H, CH=), 7.40–7.45 (m, 8 H, Ar), 7.61–7.65 (m, 2 H, Ar) ppm.

Supporting Information (see footnote on the first page of this article): NMR spectra of the products.

Acknowledgments

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[18] CCDC-686804 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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