Synthesis of 2-Substituted 3-Alkylidene-2,3-dihydro-1*H*-isoindol-1-imines through Cyclization of [1-(2-Cyanophenyl)alkylidene]aminide Intermediates Generated from the Reaction of 2-(1-Azidoalkyl)benzonitriles with NaH

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A convenient sequence for the preparation of 3-alkylidene-2,3-dihydro-1*H*-isoindol-1-imine derivatives **6** has been developed. Thus, 2-(1-azidoalkyl)benzonitriles **2**, readily accessible from 2-alkylbenzonitriles, are allowed to react with NaH in DMF at 0° to room temperature to generate [1-(2-cyanophenyl)alkylidene]aminide intermediates **3**, of which cyclization and the subsequent rearrangement, followed by alkylation with alkyl halides, affords 2-substituted 1-alkylidene-2,3-dihydro-1*H*-isoindol-2-imines **6** in generally moderate yields.

Introduction. – Due to their biological significance [1], 2,3-dihydro-1*H*-isoindol-1-imine derivatives have become of increasingly important, and several members of this class of heterocycles have been recently synthesized [2]. On the other hand, in our preceding study we have developed a novel method for the preparation of quinazolines by cyclization of [1-(2-isocyanophenyl)alkylidene]amines, generated by the treatment of 2-(1-azidoalkyl)phenyl isocyanides with NaH [3]. As an extension of this synthesis, we became interested in investigating a similar generation of [1-(2-cyanophenyl)alkylidene]aminides **3** from 2-(1-azidoalkyl)benzonitriles **2**. We have found that the reaction permits the construction of the 3-alkylidene-2,3-dihydro-1*H*-isoindol-1-imine system. Herein, we report that 2-substituted 3-alkylidene-2,3-dihydro-1*H*-isoindol-1-imines **6** can be conveniently synthesized by reacting **2**, easily accessible from 2-alkylbenzonitriles by a two-step sequence, with NaH, followed by treatment with alkyl halides.

Results and Discussion. – The preparation of **6** was accomplished as outlined in *Scheme 1*. 2-(1-Bromoalkyl)benzonitriles **1** were prepared by bromination of the benzylic C-atom of 2-alkylbenzonitriles with *N*-bromosuccinimide (NBS) using azobisisobutyronitrile (AIBN) as a catalyst in refluxing CCl_4 [4] and were allowed to react with NaN_3 in DMF at room temperature to afford 2-(1-azidoalkyl)benzonitriles **2** in excellent yields. When the nitriles **2** were treated with NaH at 0°, and the temperature was raised to room temperature, evolution of probably H_2 and N_2, was observed. After 30 min, alkyl halides were added, and the stirring was continued overnight. The aqueous workup and the subsequent purification by column chromatography on SiO_2 afforded **6** in generally moderate yields, as compiled in the *Table* . The conversion of 2-(1-azidopropyl)benzonitrile (**1b**) to 3-ethylidene derivatives **6h**–**6j**

Scheme 1

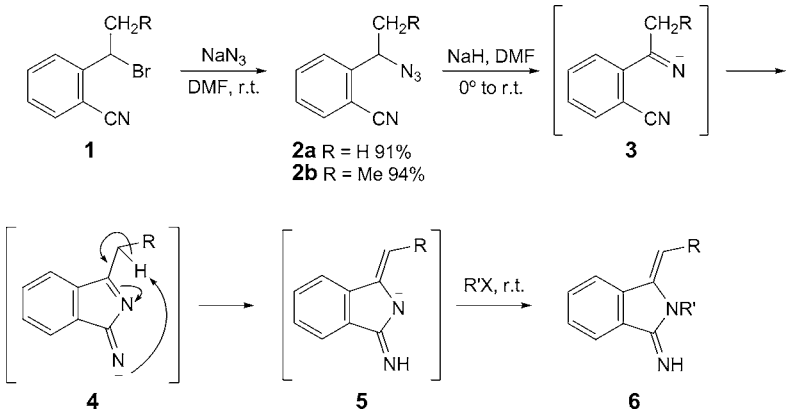


Table. *Preparation of 2-Substituted 3-Alkylidene-1*H*-isoindol-1-imines* **6**

Entry	**2**	R′X	**6**	Yield[a]) [%]
1	**2a** (R = H)	BnBr	**6a**	64
2	**2a**	4-Cl–$C_6H_4CH_2Cl$	**6b**	66
3	**2a**	4-NO_2–$C_6H_4CH_2Br$	**6c**	53
4	**2a**	BuBr	**6d**	43
5	**2a**	$BnOCH_2Cl$	**6e**	60
6	**2a**	^{t}BuOCOCH_2Br	**6f**	62
7	**2a**	4-NO_2–C_6H_4F	**6g**	26
8	**2b** (R = Me)	BnBr	**6h**	37
9	**2b**	$BnOCH_2Cl$	**6i**	43
10	**2b**	^{t}BuOCOCH_2Br	**6j**	38

[a]) Yields of isolated products.

was shown to occur less efficiently under the conditions mentioned. The yields of these products were lower than those of 3-methylidene derivatives (see *Entries 8–10*).

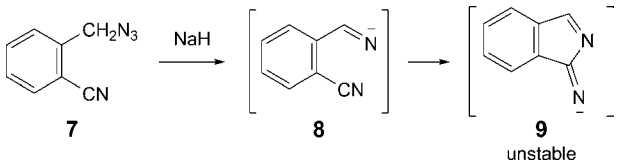
The structures of **6** were determined on the basis of NMR spectroscopy coupled with IR, MS, and elemental analyses (see *Exper. Part*). For example, the structure of **6h**, including the (*Z*)-configuration of the 3-ethylidene moiety, was confirmed by its NOESY spectrum, in which strong interactions between the ethylidene Me group (δ(H) 1.86) and the benzyl CH_2 group (δ(H) 5.32), as well as between the vinyl H-atom (δ(H) 5.44) and the H–C(4) (δ(H) 7.58), were observed.

The pathway leading to the formation of **6** may be explained as follows (*Scheme 1*). The [1-(2-cyanophenyl)alkylidene]aminide intermediate **3** results from denitrogenation from the benzylic anion intermediate. An intramolecular cyclization of **3** gives the (3-alkyl-1*H*-isoindol-1-ylidene)aminide intermediate **4**. Then, migration of one of the α-H-atoms of alkyl group at C(3) to the imino N-atom gives rise to the 3-alkylidene-1-imino-2,3-dihydro-1*H*-isoindol-2-ide intermediate **5**. Trapping of this intermediate with alkyl halides at the 2-position takes place selectively to result in the formation of **6**.

Trapping of a 2,3-dihydro-1-imino-3-methylidene-1*H*-isoindol-2-ide intermediate **5** (R = H) with 1-fluoro-4-nitrobenzene could also be accomplished to afford 2,3-dihydro-3-methylidene-2-(4-nitrophenyl)-1*H*-isoindol-1-imine (**6g**), albeit in considerably lower yield (*Entry 7*). All attempts to obtain 2,3-dihydro-3-methylidene-1*H*-isoindol-1-imine from **2a** in a pure form, however, were unsuccessful, due to its instability during chromatographic separation.

It should be noted that the reaction of 2-(azidomethyl)benzonitrile (**7**) [5] with NaH, followed by BnBr under the same conditions for the formation of **6**, resulted in the formation of a considerably intractable mixture of products, presumably due to the instability of (1*H*-isoindol-1-ylidene)iminide intermediate, **9**, formed by cyclization of (2-cyanophenyl)methylidenaminide (**8**; *Scheme 2*).

Scheme 2



In summary, we have shown that the reaction sequence starting with the treatment of 2-(1-azidoalkyl)benzonitriles with NaH provides a convenient route to 3-alkylidene-2,3-dihydro-1*H*-isoindol-1-imines. Since the starting materials are readily available, and the operations are very simple, the present method may find some applications in organic synthesis. Further study on heterocycle synthesis initiated by denitrogenation from *o*-functionalized benzyl azides is under way in our laboratory.

Experimental Part

General. All org. solvents used in this study were dried over appropriate drying agents and distilled prior to use. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel C-200E*. M.p.: *Laboratory Devices MEL-TEMP II* melting-point apparatus; uncorrected. IR Spectra: *PerkinElmer Spectrum 65* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *JEOL ECP500* FT NMR spectrometer (for ^1H and ^{13}C) or *JEOL LA400* FT NMR spectrometer (at 500 or 400, and 125 MHz, resp.), in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard; *J* in Hz. HR-MS (DART, pos.): *Thermo Scientific Exactive* spectrometer; in *m*/*z*.

BuLi was supplied by *Asia Lithium Corporation*. All other chemicals used were commercially available.

2-Ethylbenzonitrile [4]: *Representative Procedure.* A deep red soln. of 2-(lithiomethyl)benzonitriles, generated by the treatment of 2-methylbenzonitrile (1.2 g, 10 mmol) with LDA (LiN^iPr_2; 20 mmol) in diglyme (12.5 ml) as describe in [6], was treated with MeI (2.8 g, 20 mmol) under stirring. The deep red color turned immediately to light red. Sat. aq. NH_4Cl (50 ml) was added, and the mixture was warmed to r.t. and extracted with AcOEt (3 × 30 ml). The combined extracts were washed with H_2O (5 × 30 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by CC to give the title compound (0.89 g, 68%). Colorless liquid. R_f (AcOEt/hexane 1:10) 0.53. IR (neat) 2226, 1601. ^1H-NMR (500 MHz): 1.30 (*t*, *J* = 7.6, 3 H); 2.88 (*q*, *J* = 7.6, 2 H); 7.28 (*t*, *J* = 7.6, 1 H); 7.34 (*d*, *J* = 7.6, 1 H); 7.52 (*td*, *J* = 7.6, 1.5, 1 H); 7.61 (*dd*, *J* = 7.6, 1.5, 1 H).

2-Propylbenzonitrile [7]. Yield: 87%. Pale-yellow liquid. R_f (AcOEt/hexane 1:10) 0.49. IR (neat): 2224. ^{1}H-NMR (500 MHz): 0.99 (*t*, *J* = 7.6, 3 H); 1.68–1.75 (*m*, 2 H); 2.82 (*t*, *J* = 7.6, 2 H); 7.28 (*t*, *J* = 7.6, 1 H); 7.31 (*d*, *J* = 7.6, 1 H); 7.50 (*t*, *J* = 7.6, 1 H); 7.61 (*d*, *J* = 7.6, 1 H).

2-(1-Bromoalkyl)benzonitriles **1** were prepared by the bromination of respective 2-alkylbenzonitriles with NBS as described in [4] for the preparation of **1a**.

2-(1-Bromoethyl)benzonitrile (**1a**). Yield: 92%. Pale-yellow liquid. R_f (AcOEt/hexane 1:10) 0.27. IR (neat): 2227. ^{1}H-NMR (400 MHz): 2.08 (*d*, *J* = 6.8, 3 H); 5.54 (*q*, *J* = 6.8, 1 H); 7.40 (*ddd*, *J* = 7.8, 7.3, 1.0, 1 H); 7.62–7.66 (*m*, 2 H); 7.74 (*dd*, *J* = 7.3, 1.5, 1 H). Anal. calc. for C_9H_8BrN (210.07): C 51.46, H 3.84, N 6.67; found: C 51.20, H 3.87, N 6.61.

2-(1-Bromopropyl)benzonitrile (**1b**). Yield: 94%. Colorless liquid. R_f (AcOEt/hexane 1:10) 0.29. IR (neat): 2226. ^{1}H-NMR (500 MHz): 1.05 (*t*, *J* = 7.6, 3 H); 2.15–2.23 (*m*, 1 H); 2.29–2.38 (*m*, 1 H); 5.25 (*t*, *J* = 7.6, 1 H); 7.39 (*td*, *J* = 7.6, 1.5, 1 H); 7.61–7.64 (*m*, 2 H); 7.69 (*dd*, *J* = 8.4, 1.5, 1 H). Anal. calc. for $C_{10}H_{10}BrN$ (224.10): C 53.60, H 4.50, N 6.25; found: C 53.49, H 4.77, N 6.07.

2-(1-Azidoethyl)benzonitrile (**2a**): *Representative Procedure.* The mixture of **1a** (1.3 g, 6.3 mmol) and NaN_3 (0.45 g, 6.9 mmol) in DMF (19 ml) was stirred at r.t. for 14 h. H_2O (30 ml) was added, and the mixture was extracted with AcOEt (3 × 20 ml). The combined extracts were washed with H_2O (5 × 30 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by CC to give **2a** (0.98 g, 91%). Pale-yellow liquid. R_f (CH_2Cl_2/hexane 1:10) 0.47. IR (neat): 2226, 2102. ^{1}H-NMR (500 MHz): 1.59 (*d*, *J* = 6.9, 3 H); 5.09 (*q*, *J* = 6.9, 1 H); 7.42 (*td*, *J* = 7.6, 1.5, 1 H); 7.58 (*d*, *J* = 7.6, 1 H); 7.63–7.69 (*m*, 2 H). Anal. calc. for $C_9H_8N_4$ (172.19): C 62.78, H 4.68, N 32.54; found: C 62.71, H 4.72, N 32.50.

2-(1-Azidopropyl)benzonitrile (**2b**). Yield: 94%. Pale-yellow liquid. R_f (AcOEt/hexane 1:5) 0.62. IR (neat): 2226, 2100. ^{1}H-NMR (500 MHz): 0.99 (*t*, *J* = 7.6, 3 H); 1.84–1.94 (*m*, 2 H); 4.87 (*t*, *J* = 7.6, 1 H); 7.43 (*t*, *J* = 7.6, 1 H); 7.54 (*d*, *J* = 7.6, 1 H); 7.65 (*t*, *J* = 7.6, 1 H); 7.68 (*d*, *J* = 7.6, 1 H). Anal. calc. for $C_{10}H_{10}N_4$ (186.21): C 64.50, H 5.41, N 30.09; found: C 64.46, H 5.51, N 30.06.

*2-Benzyl-2,3-dihydro-3-methylidene-1*H-*isoindol-1-imine* (**6a**): *Representative Procedure.* To a stirred soln. of **2a** (0.20 g, 1.2 mmol) in DMF (4 ml) at 0° was added NaH (60% mineral oil; 46 mg, 1.2 mmol) in several portions. The mixture was warmed to r.t., and stirring was continued for 30 min, before BnBr (0.20 g, 1.2 mmol) was added dropwise. After stirring overnight at the same temp., sat. aq. NH_4Cl (20 ml) was added, and the mixture was extracted with AcOEt (3 × 10 ml). The combined extracts were washed with H_2O (2 × 15 ml) and brine (15 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by CC (AcOEt/hexane 1:2) to give **6a** (0.15 g, 53%). Beige solid. M.p. 130–132° (hexane/CH_2Cl_2). IR (KBr) 3260, 1633, 1616. ^{1}H-NMR (500 MHz): 4.51 (*d*, *J* = 2.3, 1 H); 4.90 (*d*, *J* = 2.3, 1 H); 5.07 (*s*, 2 H); 5.53 (*br*, 1 H); 7.21–7.32 (*m*, 5 H); 7.50 (*t*, *J* = 7.6, 6.9, 1 H); 7.54 (*t*, *J* = 7.6, 1 H); 7.66 (*d*, *J* = 7.6, 1 H); 7.71 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 43.5; 84.5; 120.1; 121.2; 126.8; 127.1; 128.6; 129.0; 130.0; 130.8; 135.6; 137.2; 143.9; 162.2. HR-MS: 235.1212 ($[M+H]^+$, $C_{16}H_{15}N_2^+$; calc. 235.1235). Anal. calc. for $C_{16}H_{14}N_2$ (234.30): C 82.02, H 6.02, N 11.96; found: C 81.97, H 6.05, N 11.94.

*2-(4-Chlorobenzyl)-2,3-dihydro-3-methylidene-1*H-*isoindol-1-imine* (**6b**). Beige solid. M.p. 90–92° (hexane/Et_2O). IR (KBr): 3307, 1639, 1626. ^{1}H-NMR (400 MHz): 4.47 (*d*, *J* = 2.4, 1 H); 4.90 (*d*, *J* = 2.4, 1 H); 5.04 (*s*, 2 H); 5.55 (br., 1 H); 7.20 (*d*, *J* = 8.8, 2 H); 7.27 (*d*, *J* = 8.8, 2 H); 7.50 (*dd*, *J* = 7.8, 7.3, 1 H); 7.55 (*td*, *J* = 7.3, 1.5, 1 H); 7.66 (*d*, *J* = 7.8, 1 H); 7.74 (*d*, *J* = 7.3, 1 H). ^{13}C-NMR: 43.00; 84.5; 120.2; 121.2; 128.2; 128.7; 129.1; 129.6; 131.0; 132.8; 135.5; 135.8; 143.7; 162.2. HR-MS: 269.0832 ($[M+H]^+$, $C_{16}H_{14}ClN_2^+$; calc. 269.0840). Anal. calc. for $C_{16}H_{13}ClN_2$ (268.08): C 71.51, H 4.88, N 10.42; found: C 71.35, H 4.90, N 10.35.

*2,3-Dihydro-3-methylidene-2-(4-nitrobenzyl)-1*H-*isoindol-1-amine* (**6c**). White needles. M.p. 110–112° (hexane/CH_2Cl_2). IR (KBr): 3310, 1641, 1625, 1518, 1344. ^{1}H-NMR (500 MHz): 4.43 (*d*, *J* = 2.3, 1 H); 4.93 (*d*, *J* = 2.3, 1 H); 5.17 (*s*, 2 H); 5.52 (br., 1 H); 7.42 (*d*, *J* = 8.4, 2 H); 7.53 (*t*, *J* = 7.6, 1 H); 7.58 (*t*, *J* = 7.6, 1 H); 7.69 (*d*, *J* = 7.6, 1 H); 7.70 (*d*, *J* = 7.6, 1 H); 8.16 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR: 43.1; 84.5; 120.4; 121.2; 123.9; 127.6; 129.3; 131.2; 135.3; 137.6; 141.2; 143.6; 149.8; 158.8. HR-MS: 280.1073 ($[M+H]^+$, $C_{16}H_{14}N_3O_2^+$; calc. 280.1086). Anal. calc. for $C_{16}H_{13}N_3O_2$ (279.10): C 68.81, H 4.69, N 15.05; found: C 68.75, H 4.90, N 14.80.

*2-Butyl-2,3-dihydro-3-methylidene-1*H-*isoindol-1-imine* (**6d**). Brown oil. R_f (AcOEt/hexane 1:3) 0.40. IR (neat): 3250, 1636, 1617. ^{1}H-NMR (500 MHz): 0.97 (*t*, *J* = 7.6, 3 H); 1.25–1.50 (*m*, 2 H); 1.66–

1.74 (*m*, 2 H); 3.80 (*t*, *J* = 7.6, 2 H); 4.57 (*d*, *J* = 2.3, 1 H); 4.93 (*d*, *J* = 2.3, 1 H); 5.47 (br., 1 H); 7.46 (*td*, *J* = 7.6, 1.5, 1 H); 7.51 (*td*, *J* = 7.6, 1.5, 1 H); 7.65 (*d*, *J* = 7.6, 1 H); 7.67 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 13.9; 20.3; 29.7; 39.8; 83.2; 119.9; 120.3; 128.8; 129.0; 130.5; 135.5; 143.9; 164.1. HR-MS: 201.1383 ($[M+H]^+$, $C_{13}H_{17}N_2^+$; calc. 201.1392). Anal. calc. for $C_{13}H_{16}N_2$ (200.28): C 77.96, H 8.05, N 13.99; found: C 77.93, H 8.25, N 13.87.

*2,3-Dihydro-3-methylidene-2-[(phenylmethoxy)methyl]-1*H-*isoindol-1-imine* (**6e**). Beige solid. M.p. 51–53° (hexane/Et_2O). IR (KBr): 3301, 1645, 1628. ^{1}H-NMR (500 MHz): 4.62 (*s*, 2 H); 4.87 (*d*, *J* = 2.3, 1 H); 5.03 (*d*, *J* = 2.3, 1 H); 5.43 (*s*, 2 H); 6.18 (br., 1 H); 7.26 (*tt*, *J* = 7.6, 1.5, 1 H); 7.32 (*td*, *J* = 7.6, 1.5, 2 H); 7.35 (*dd*, *J* = 7.6, 1.5, 2 H); 7.49 (*t*, *J* = 7.6, 1 H); 7.55 (*td*, *J* = 7.6, 1.5, 1 H); 7.69 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR: 69.7; 70.2; 85.5; 120.3; 121.3; 127.6; 127.8; 128.3; 128.4; 129.1; 131.2; 135.4; 137.8; 143.4; 162.5. HR-MS: 265.1332 ($[M+H]^+$, $C_{17}H_{17}N_2O^+$; calc. 265.1341). Anal. calc. for $C_{17}H_{16}N_2O$ (264.32): C 77.25, H 6.10, N 10.60; found: C 77.33, H 6.25, N 10.03.

tert-*Butyl (1,3-Dihydro-1-imino-3-methylidene-2*H-*isoindol-2-yl)acetate* (**6f**). Beige solid. M.p. 85–87° (hexane/Et_2O). IR (KBr): 3304, 1741, 1625. ^{1}H-NMR (400 MHz): 1.47 (*s*, 9 H); 4.45 (*d*, *J* = 2.9, 1 H); 4.52 (*s*, 2 H); 4.95 (*d*, *J* = 2.9, 1 H); 5.49 (br., 1 H); 7.47 (*td*, *J* = 7.3, 1.0, 1 H); 7.53 (*td*, *J* = 7.3, 1.0, 1 H); 7.64 (*d*, *J* = 7.3, 1 H); 7.67 (*d*, *J* = 7.3, 1 H). ^{13}C-NMR: 28.0; 42.3; 82.1; 83.4; 120.3; 121.1; 129.0 (two overlapped Cs); 130.9; 135.4; 144.0; 162.1; 167.6. HR-MS: 259.1432 ($[M+H]^+$, $C_{15}H_{19}N_2O_2^+$; calc. 259.1447). Anal. calc. for $C_{15}H_{18}N_2O_2$ (258.32): C 69.74, H 7.02, N 10.84; found: C 69.51, H 7.09, N 10.87.

*2,3-Dihydro-3-methylidene-2-(4-nitrophenyl)-1*H-*isoindol-1-imine* (**6g**). Brown oil. R_f (AcOEt/hexane 1:2) 0.50. IR (neat): 3296, 1630, 1520, 1347. ^{1}H-NMR (400 MHz): 4.59 (*d*, *J* = 2.3, 1 H); 5.07 (*d*, *J* = 2.3, 1 H); 5.85 (br., 1 H); 7.58 (*t*, *J* = 7.6, 1 H); 7.64 (*d*, *J* = 8.4, 2 H); 7.76 (*d*, *J* = 7.6, 1 H); 7.84 (*d*, *J* = 7.6, 1 H); 8.08 (*t*, *J* = 7.6, 1 H); 8.41 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR: 86.3; 115.6; 120.5; 122.0; 125.1; 126.1; 129.4; 129.9; 131.8; 141.5; 146.4; 155.0; 158.4. HR-MS: 266.0926 ($[M+H]^+$, $C_{15}H_{12}N_3O_2^+$; calc. 266.0930). Anal. calc. for $C_{15}H_{11}N_3O_2$ (265.27): C 67.92, H 4.18, N 15.84; found: C 67.84, H 4.39, N 15.68.

*(3Z)-2-Benzyl-3-ethylidene-2,3-dihydro-1*H-*isoindol-1-imine* (**6h**). Beige solid. M.p. 69–70° (hexane/Et_2O). IR (KBr): 3304, 1634. ^{1}H-NMR (500 MHz): 1.86 (*d*, *J* = 7.6, 3 H); 5.32 (*s*, 2 H); 5.44 (*q*, *J* = 7.6, 1 H); 6.57 (br., 1 H); 7.18 (*d*, *J* = 7.6, 2 H); 7.21 (*t*, *J* = 7.6, 1 H); 7.30 (*t*, *J* = 7.6, 2 H); 7.42 (*dd*, *J* = 7.6, 6.9, 1 H); 7.50 (*dd*, *J* = 7.6, 6.9, 1 H); 7.58 (*d*, *J* = 7.6, 1 H); 7.67 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 11.8; 45.5; 97.5; 119.1; 121.1; 125.7; 126.8; 127.8; 128.6; 130.6; 137.0; 137.3; 138.4; 142.6; 163.5. HR-MS: 249.1386 ($[M+H]^+$, $C_{17}H_{17}N_2^+$; calc. 249.1392). Anal. calc. for $C_{17}H_{16}N_2$ (248.32): C 82.22, H 6.49, N 11.28; found: C 82.19, H 6.63, N 11.13.

*(3Z)-3-Ethylidene-2,3-dihydro-2-[(phenylmethoxy)methyl]-1*H-*isoindol-1-imine* (**6i**). Beige solid. M.p. 61–63° (hexane/CH_2Cl_2). IR (KBr): 3260, 1621. ^{1}H-NMR (500 MHz): 2.18 (*d*, *J* = 7.6, 3 H); 4.68 (*s*, 2 H); 5.57 (*s*, 2 H); 5.59 (*q*, *J* = 7.6, 1 H); 6.08 (br., 1 H); 7.24 (*t*, *J* = 7.6, 1 H); 7.30 (*t*, *J* = 7.6, 2 H); 7.35 (*d*, *J* = 7.6, 2 H); 7.40 (*t*, *J* = 7.6, 1 H); 7.49 (*t*, *J* = 7.6, 1 H); 7.57 (*d*, *J* = 7.6, 1 H); 7.62 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 11.8; 70.1; 70.9; 99.3; 119.2; 121.2; 127.4; 127.6; 127.9; 128.0; 128.2; 131.0; 136.5; 137.0; 138.2; 164.1. HR-MS: 279.1487 ($[M+H]^+$, $C_{18}H_{19}N_2O^+$; calc. 279.1497). Anal. calc. for $C_{18}H_{18}N_2O$ (278.35): C 77.67, H 6.52, N 10.06; found: C 77.52, H 6.77, N 10.00.

tert-*Butyl [(1Z)-1-Ethylidene-1,3-dihydro-3-imino-2*H-*isoindol-2-yl]acetate* (**6j**). Colorless needles. M.p. 81–83° (hexane/Et_2O). IR (KBr): 3298, 1744, 1630. ^{1}H-NMR (500 MHz): 1.48 (*s*, 9 H); 2.00 (*d*, *J* = 7.6, 3 H); 4.80 (*s*, 2 H); 5.47 (*q*, *J* = 7.6, 1 H); 6.49 (br., 1 H); 7.38 (*t*, *J* = 7.6, 1 H); 7.46 (*t*, *J* = 7.6, 1 H); 7.55 (*d*, *J* = 7.6, 1 H); 7.59 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR: 11.5; 28.0; 44.7; 81.8; 96.8; 119.2; 120.9; 127.7; 128.0; 130.6; 136.9; 137.0; 163.5; 168.6. HR-MS: 273.1592 ($[M+H]^+$, $C_{16}H_{21}N_2O_2^+$; calc. 273.1598). Anal. calc. for $C_{16}H_{20}N_2O_2$ (272.34): C 70.56, H 7.40, N 10.29; found: C 70.80, H 7.29, N 10.21.

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