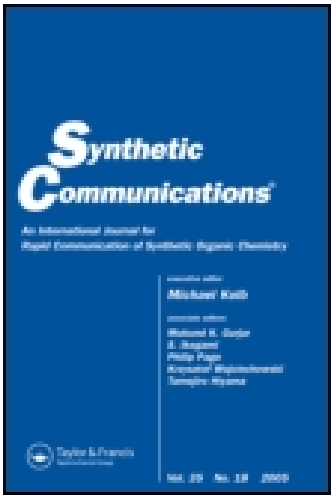

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Chemoselective Removal of Acyloxy in 1-(Benzotriazole-1-yl)alkyl Esters and Its Application in the Preparation of β-(Benzotriazole-1-yl)alcohols

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Chemoselective Removal of Acyloxy in 1-(Benzotriazole-1-yl)alkyl Esters and Its Application in the Preparation of β-(Benzotriazole-1-yl)alcohols

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Abstract: Mediated by samarium diiodide, 1-(benzotriazole-1-yl)alkyl esters **1** underwent cross-coupling with aldehydes or ketones to afford β-(benzotriazole-1-yl)-alcohols **2** exclusively with the selective removal of acyloxy over benzotriazolyl.

Keywords: 1-(Benzotriazole-1-yl)alkyl esters, carbonyl compounds, chemoselective reduction, cross-coupling, samarium diiodide

Bifunctional derivatives in which two leaving groups with different reactivity attach to the same carbon (containing X-C-Y structure, where X, Y is the leaving group) constitute a class of useful substrates for the construction of multifunctional groups based on selective elimination of one of the leaving groups. The breaking of either the C-X or C-Y bond can usually be distinguished by a reducing agent. For example, the reductive cleavage of the C-halogen bond occurred preferably over the C-P bond when α-haloalkylphosphonates were treated with Bu_3SnH.[1] The Br-C-OAc structure underwent a reductive cleavage of the C-Br bond and underwent cross-coupling with ketones by treatment with SmI_2-HMPA.[2] Reductive lithiation of α-aminosulfides R_2N-C-SPh could afford nonstabilized α-aminocarbanions with the sulfenyl group

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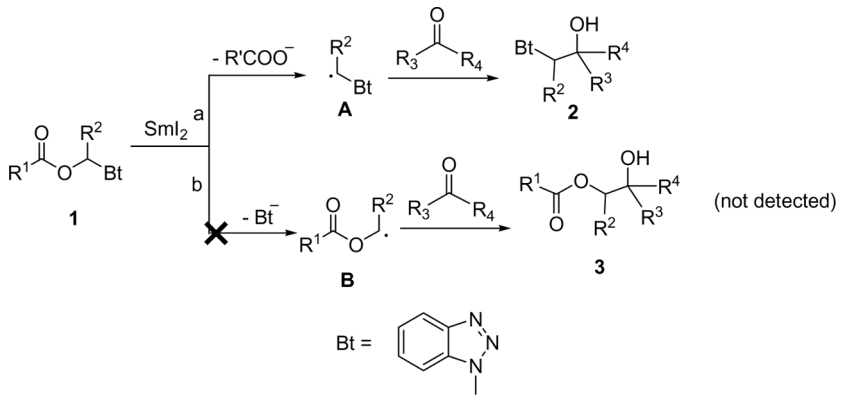
being cleaved first.[3a] The selective removal of the sulfenyl has also been observed in the reduction of O,S-acetals[3b] (RO-C-SPh) by SmI_2 in benzene–HMPA solution with *t*-BuOH as an additive.

Compounds with a benzotriazolyl group (Bt) attached to an α-heteroatom carbon no doubt constitute a fairly considerable part of such building blocks (Bt-C-X, X = halogen, NR_2, alkoxy [OR], sulfenyl [SR], etc.).[4] Likewise, the C-Bt bond could be selectively cleaved and used for different synthetic purposes. SmI_2 causes the C-Bt bond cleavage in *N*-[(*N*,*N*-dialkylamino)-alkyl]-benzotriazoles (Bt-C-NR_2) to form a variety of compounds such as tertiary vicinal diamines,[5a] *N*-cycloalkylamines,[5b] and 1,2-amino alcohols.[5c] We previously reported the cleavage of C-Bt bonds in *N*-(α-benzotriazol-1-ylalkyl)amides (Bt-C-NHCOR) and *N*-(α-benzotriazol-1-ylalkyl)sulfonamides (Bt-C-NHTs) to synthesize vicinal diamides, vicinal disulfamides, and α-hydroxyalkylated sulfonamides.[6]

Herein we report the chemoselective reduction of Bt-C-OCOR compounds [1-(benzotriazole-1-yl)alkyl esters **1**] and their cross-coupling with carbonyl compounds. It should be noted that compounds **1** contain two good leaving groups, namely the acyloxy and benzotriazolyl groups. The selective elimination of either of the leaving groups from the bifunctional derivatives followed by a cross-coupling with carbonyl compounds can provide a useful protocol for the construction of β-heteroatom-substituted alcohols via hydroxyalkylation.[7]

Thus, a mixture of **1** and a carbonyl compound (aldehyde or ketone) was added simultaneously to a SmI_2-THF solution at room temperature with an expectation to produce two kinds of coupling products corresponding to the two cleavage pathways (Scheme 1). Path A involves the



Scheme 1. Two possible pathways for the reductive coupling of **1** with carbonyl compounds.

reductive cleavage of the acyloxy by SmI_2, and the resulting radical **A** then attacks the carbonyl or ketyl[8] to give product **2**, whereas in path B the benzotriazolyl was cleaved to produce radical **B**, which coupled with carbonyl or ketyl to afford compound **3**.

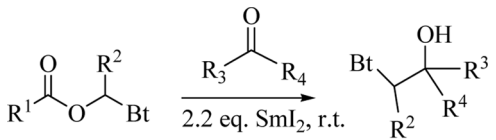
Surprisingly, though the benzotriazolyl moiety in the Bt-C-OCOR compounds could be selectively substituted by an alkyl, alkenyl, or aryl group in organozinc reagents to afford carboxylic esters,[9] exclusive removal of the acyloxy was observed (only path A was followed) under the reductive conditions here. Correspondingly, the corresponding cross-coupling products β-(benzotriazole-1-yl)alcohols **2** were obtained in good to excellent yields. The results are listed in Table 1. The type of product **3** was not detected in all the cases of the reductive coupling reaction, indicating path B was not followed at all.

As can be summarized from Table 1, both aliphatic aldehydes and ketones underwent the reductive coupling smoothly. Diphenylmethanone also gave satisfactory yields (Table 1, entries 6 and 12). Aromatic aldehyde such as benzaldehyde mainly afforded pinacols as in the other cross-coupling reaction.[7a] Generally, the yields of the cross-coupling products resulting from ketones were higher than those from aldehydes. The lower efficiency of the coupling involving aldehydes may result from the side reactions such as simple reduction and pinacol coupling, to which the aldehydes were prone.[11]

Under the reaction conditions, the removal of the acyloxy over the benzotriazolyl group was always observed, no matter if R^1 was an alkyl or aryl. Theoretically, an electron-withdrawing group (such as chloro) present in R^1 could facilitate the leaving tendency of the corresponding acyloxy (Table 1, entries 12 and 13); however, the electron-donating group (methoxy) at the aryl in the acyloxy moiety does not diminish the leaving ability to a remarkable extent (Table 1, entries 7–11).

R^2 can be an alkyl or aryl and therefore broaden the scope for the synthesis of compounds **2**. Although β-(benzotriazole-1-yl)alcohols with the structure $Bt{-}CH_2{-}C(OH)R^1R^2$ could be smoothly prepared,[7i,j] their homologues with a substituent at the methylene carbon could not be obtained because of the limited substrates ($Bt{-}CH_2{-}X$). The Katritzky group reported the preparation of such compounds from *N*-allyl- or *N*-benzyl benzotriazoles by treatment with n-butyllithium at $-78\,^{\circ}C$ followed by the nucleophilic attack on aldehydes and ketones.[12] However, the compounds with common substituents other than benzyl and allyl remained unexplored, to which difficult lithiation may be ascribed. Therefore, the cross-coupling between easily available 1-(benzotriazole-1-yl)alkyl esters **1** and carbonyl compounds mediated by SmI_2 provides a general and highly efficient method for the preparation of a variety of β-(benzotriazole-1-yl) alcohols though the diastereoselectivities are not satisfactory at this stage.

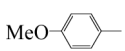
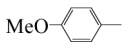
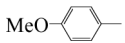
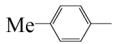
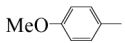
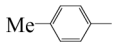
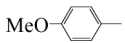
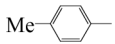
Table 1. Samarium diiodide–promoted reductive coupling between 1-(benzotriazole-1-yl)alkyl esters **1** and carbonyl compounds to prepare β-(benzotriazole-1-yl)alcohols **2**



Entry	R^1	R^2	Substrates **1**	R^3	R^4	Products **2**[b]	Time (h)	Yields (%)[c]	D.r.[d]
1	n-C_3H_7-	C_2H_5-	**1a**[a]	CH_3-	CH_3-	**2a**	0.5	82	—
2	n-C_3H_7-	C_2H_5-	**1a**	C_2H_5-	C_2H_5-	**2b**	0.5	92	—
3	C_2H_5-		**1b**	n-C_3H_7-	H	**2c**	0.5	80	70:30
4		C_2H_5-	**1c**	CH_3-	CH_3-	**2a**	1	86	—
5		C_2H_5-	**1c**	CH_3	C_2H_5-	**2d**	1	83	53:47
6		C_2H_5-	**1c**	Ph-	Ph-	**2e**	1	75	—

(*Continued*)

Table 1. Continued

Entry	R^1	R^2	Substrates **1**	R^3	R^4	Products **2**[b]	Time (h)	Yields (%)[c]	D.r.[d]
7			**1d**	CH_3-	CH_3-	**2f**	1	85	—
8			**1d**	CH_3-	H	**2g**	1	64	52:48
9			**1e**	CH_3-	H	**2h**	1	76	53:47
10			**1e**	CH_3-	CH_3-	**2i**	1	87	—
11			**1e**	C_2H_5-	C_2H_5-	**2j**	1	79	—
12		i-C_3H_7	**1f**	Ph-	Ph-	**2k**	1	78	—
13		i-C_3H_7	**1f**	CH_3-	CH_3-	**2l**	1	83	—
14		C_2H_5-	**1g**	CH_3-	C_2H_5-	**2d**	1	86	53:47

[a]Novel compounds prepared according to Ref.[10].
[b]The products were characterized by ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis.
[c]Isolated yields.
[d]D.r. = diastereoselective ratio. Determined by ^{1}H NMR.

In summary, mediated by SmI_2 in THF at room temperature, the reductive elimination of acyloxy over benzotriazolyl in a variety of 1-(benzotriazole-1-yl)alkyl esters occurred preferentially in the cross-coupling reaction with carbonyl compounds. Good yields of a variety of β-(benzotriazole-1-yl)alcohols can be prepared this way.

It was reported that different additives could alter the reductive removal sequence of sulfenyl and alkoxy in monothioacetals[3b] with SmI_2 as the reducing agent. With the potential good leaving ability of benzotriazolyl,[13] the possibility of reversing the reductive removal sequence of acyloxy and benzotriazoyl in 1-(benzotriazole-1-yl)alkyl esters is worth exploring further.

EXPERIMENTAL

Tetrahydrofuran was distilled from sodium benzophenone immediately prior to use. Melting points are uncorrected. ^{1}H NMR (400-MHz) spectra were recorded on a Bruker AV400 NMR instrument as $CDCl_3$ solutions using TMS as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants *J* are given in hertz. IR spectra were recorded in film or using KBr disks with a Nicolet Nexus 670 FT-IR spectrometer. Mass spectra were recorded on an HP 5989B MS spectrometer (70 eV). Elemental analyses were performed on a Vario-ELIII instrument.

General Procedure for the Reductive Tandem Deacyloxy and Cross-Coupling Reaction

1-(Benzotriazole-1-yl)alkyl esters **1** (1 mmol) dissolved in dry THF (10 mL) were added at room temperature to 2.2 mmol of SmI_2 dissolved in THF (20 mL) under nitrogen. The resulting solution turned yellow in 0.5–1 h. Dilute hydrochloric acid (0.5 M, 5 mL) was added, and the resulting mixture was extracted with diethyl ether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a residue, which was purified by column chromatography on silica gel with ethyl acetate and cyclohexane (1:6) as eluent to afford the β-(benzotriazole-1-yl) alcohols **2**.

DATA

Compound **1a**: colorless oil. ν_{max}(film)/cm^{-1}: 2971, 2939, 2819, 1748 (C=O), 1614 (N=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (1H, d, *J*

8.4 Hz), 7.79 (1H, d, *J* 8.4 Hz), 7.54 (1H, t, *J* 7.6 Hz), 7.40 (1H, t, *J* 7.6 Hz), 7.22 (1H, t, *J* 7.2 Hz, C*H*), 2.50–2.58 (2H, m, CH_2), 2.28–2.38 (2H, m, CH_2), 1.59–1.64 (2H, m, CH_2), 0.97 (3H, t, *J* 7.2 Hz, CH_3), 0.88 (3H, t, *J* 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3 (*C*=O), 145.9, 132.5, 127.9, 124.3, 120.0, 110.3, 80.5, 35.7, 26.5, 18.1, 13.4, 9.2. Anal. calcd. for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 62.98; H, 6.95; N, 16.93%.

Compound **2a**: colorless oil. ν_{max}(film)/cm^{-1}: 3390 (OH), 2975, 2834, 1614 (N=N), 1453, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* 8.0 Hz, 1H), 7.57 (d, *J* 8.0 Hz, 1H), 7.36 (t, *J* 8.0 Hz, 1H), 7.24 (t, *J* 7.6 Hz, 1H), 4.43 (dd, *J* 2.8, 12 Hz, 1H), 3.52 (br, s, 1H), 2.38–2.43 (m, 1H), 2.07–2.13 (m, 1H), 1.26 (s, 3H), 1.06 (s, 3H), 0.53 (t, *J* 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 134.8, 127.3, 124.0, 119.6, 110.5, 71.3, 70.6, 29.2, 27.5, 22.1, 11.0. *m*/*z* (%): 221 ($M^+ + 2$, 1.3), 161 (100), 132 (81.6), 104 (71.9), 77 (49.8), 59 (82.5). Anal. calcd. for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.81; N, 19.16. Found: C, 65.87; H, 7.80; N, 19.27%.

Compound **2b**: colorless oil. ν_{max}(film)/cm^{-1}: 3396 (OH), 3062, 2971, 2881, 1615 (N=N), 1453, 747. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* 8.4 Hz, 1H), 7.63 (d, *J* 8.4 Hz, 1H), 7.32 (t, *J* 8.0 Hz, 1H), 7.20 (t, *J* 7.6 Hz, 1H), 4.59 (dd, *J* 3.2, 12 Hz, 1H), 3.41 (br, s, 1H), 2.34–2.37 (m, 1H), 1.97–2.02 (m, 1H), 1.60–1.71 (m, 2H), 1.04–1.08 (m, 1H), 0.95–0.98 (m, 1H), 0.83 (t, *J* 7.2 Hz, 3H), 0.66 (t, *J* 7.6 Hz, 3H), 0.44 (t, *J* 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 134.4, 127.3, 123.9, 119.6, 111.0, 77.0, 67.6, 28.2, 27.3, 21.4, 10.8, 7.9, 7.5. *m*/*z* (%): 248 ($M^+ + 1$, 2.5), 161 (100), 146 (75.0), 132 (50.3), 104 (31.7), 87 (28.3), 77 (27.9). Anal. calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56; N, 16.99. Found: C, 67.85; H, 8.58; N, 17.05%.

Compound **2c**: colorless oil. ν_{max}(film)/cm^{-1}: 3361 (OH), 2932, 2857, 1620 (N=N), 1453, 744. Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* 8.0 Hz, 1H), 7.24–7.40 (m, 8H) 5.57 (d, *J* 8.0 Hz, 1H), 4.96–4.96 (m, 1H), 3.97 (br, s, 1H), 1.39–1.53 (m, 2H), 1.22–1.26 (m, 2H), 0.87 (t, *J* 7.2 Hz, 3H). Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* 8.0 Hz, 1H), 7.24–7.40 (m, 8H), 5.57 (d, *J* 8.0 Hz, 1H), 4.96–4.96 (m, 1H), 3.97 (br, s, 1H), 1.86–1.87 (m, 1H), 1.65–1.70 (m, 1H), 1.39–1.53 (m, 2H), 1.22–1.26 (m, 3H). *m*/*z* (%): 281 (M^+, 2.3), 208 (29.9), 180 (100), 91 (13.1), 77 (15.4). Anal. calcd. for $C_{17}H_{19}N_3O$: C, 72.57; H, 6.81; N, 14.94. Found: C, 72.66; H, 6.83; N, 14.89%.

Compound **2d**: colorless oil. ν_{max}(film)/cm^{-1}: 3405 (OH), 2953, 2863, 1615 (N=N), 1445, 742. Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.12 (m, 1H), 7.59–7.62 (m, 1H), 7.47–7.53 (m, 1H), 7.40 (t, *J* 8.0 Hz, 1H), 4.50–4.56 (m, 1H), 2.49–2.53 (m, 1H), 2.16–2.19 (m, 1H), 1.70–1.75 (m, 1H), 1.25 (q, *J* 7.2 Hz, 1H), 1.01 (t, *J* 7.2 Hz, 3H), 0.96 (s, 3H), 0.65 (t, *J* 7.2 Hz, 3H). Minor: ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.10–8.12 (m, 1H), 7.59–7.62 (m, 1H), 7.47–7.53 (m, 1H), 7.40 (t, *J* 8.0 Hz, 1H), 4.50–4.56 (m, 1H), 2.49–2.53 (m, 1H), 2.16–2.19 (m, 1H), 1.70–1.75 (m, 1H), 1.36 (s, 3H), 1.25 (q, *J* 7.2 Hz, 1H), 0.87 (s, 3H), 0.65 (t, *J* 7.2 Hz, 3H). *m/z* (%): 233 (M^+, 1.3), 218 (1.8), 161 (100), 146 (73.5), 132 (69.2), 104 (49.8), 77 (34.7), 73 (53.8). Anal. calcd. for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.81; H, 8.19; N, 18.05%.

Compound **2e**: colorless oil. ν_{max}(film)/cm^{-1}: 3402, 2963, 2875, 1623 (N=N), 1448, 745. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–8.14 (m, 3H), 7.74–7.77 (m, 3H), 7.55–7.65 (m, 2H), 7.42–7.51 (m, 6H), 5.77 (dd, *J* 6.4, 8.8 Hz, 1H), 2.81–2.89 (m, 1H), 2.53–2.61 (m, 1H), 0.93 (t, *J* 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 143.6, 137.5, 137.2, 133.5, 132.7, 130.7, 130.1, 128.45, 128.40, 127.5, 126.8, 124.4, 120.1, 109.7, 65.1, 28.1, 11.3. *m/z* (%): 343 (M^+, 1.0), 183 (71.8), 161 (100), 146 (63.7), 132 (45.3), 104 (43.6), 77 (38.1). Anal. calcd. for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 76.86; H, 6.15; N, 12.30%.

Compound **2f**: white solid, mp 147–149 °C. ν_{max}(film)/cm^{-1}: 3457 (OH), 2975, 1614 (N=N), 1452, 741. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* 8.0 Hz, 1H), 7.51 (d, *J* 8.0 Hz, 2H), 7.36–7.44 (m, 2H), 7.30–7.36 (m, 4H), 5.54 (s, 1H), 4.22 (s, 1H, O*H*), 1.36 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 135.8, 133.8, 128.9, 128.5, 128.4, 127.8, 124.4, 120.1, 109.6, 73.5, 71.4, 28.7, 27.3. *m/z* (%): 252 ($M^+ - 15$, 1.2), 209 (35.7), 180 (100), 104 (20.8), 77 (14.3), 59 (22.8). Anal. calcd. for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72. Found: C, 72.01; H, 6.38; N, 15.67%.

Compound **2g**: colorless oil. ν_{max}(film)/cm^{-1}: 3450 (OH), 2971, 1621 (N=N), 1442, 748. Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* 8.4 Hz, 1H), 7.28–7.41 (m, 8H), 5.49–5.52 (m, 1H), 5.09–5.16 (m, 1H), 1.26 (d, *J* 6.0 Hz, 3H). Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* 8.4 Hz, 1H), 7.28–7.41 (m, 8H), 5.49–5.52 (m, 1H), 5.09–5.16 (m, 1H), 1.26 (d, *J* 6.0 Hz, 3H). *m/z* (%): 253 (M^+, 0.9), 209 (35.8), 180 (100), 152 (24.1), 104 (21.9), 91 (6.7), 77 (16.4). Anal. calcd. for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.22; H, 5.99; N, 16.55%.

Compound **2h**: colorless oil. ν_{max}(film)/cm^{-1}: 3461 (OH), 2953, 1619 (N=N), 1450, 743. Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* 8.0 Hz, 1H), 7.14–7.34 (m, 5H), 7.10–7.12 (m, 2H), 5.45–5.48 (m, 1H), 5.07–5.13 (m, 1H), 3.50 (s, 1H, O*H*), 2.29 (s, 3H), 1.23 (d, *J* 6.4 Hz, 3H). Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* 8.0 Hz, 1H), 7.14–7.34 (m, 5H), 7.10–7.12 (m, 2H), 5.45–5.48 (m, 1H), 5.07–5.13 (m, 1H), 3.90 (s, 1H, O*H*), 2.29 (s, 3H), 1.23 (d, *J* 6.4 Hz, 3H). *m/z* (%): 269 ($M^+ + 2$, 1.5), 223 (100), 194 (77.3), 180 (65.8), 118 (26.1), 104

(19.5), 77 (14.6). Anal. calcd. for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72. Found: C, 71.84; H, 6.38; N, 15.75%.

Compound **2i**: colorless oil. ν_{max}(film)/cm^{-1}: 3441 (OH), 2979, 2930, 1627 (N=N), 1452, 744. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* 8.4 Hz, 1H), 7.32–7.47 (m, 5H), 7.10 (d, *J* 8.0 Hz, 2H), 5.57 (s, 1H), 4.30 (s, 1H, O*H*), 2.27 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). *m*/*z* (%): 281 (M^+, 2.5), 223 (100), 194 (74.1), 180 (69.0), 118 (24.8), 104 (21.6), 77 (17.2). Anal. calcd. for $C_{17}H_{19}N_3O$: C, 72.57; H, 6.81; N, 14.94. Found: C, 72.53; H, 6.84; N, 14.88%.

Compound **2j**: colorless oil. ν_{max}(film)/cm^{-1}: 3492 (OH), 2969, 2941, 1613 (N=N), 1452, 745. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* 8.0 Hz, 1H), 7.58 (d, *J* 8.0 Hz, 1H), 7.51 (d, *J* 8.0 Hz, 1H), 7.30–7.45 (m, 2H), 7.09–7.17 (m, 3H), 5.68 (s, 1H), 4.30 (s, 1H, O*H*), 2.25 (s, 3H), 1.42–1.58 (m, 4H), 0.93–0.97 (m, 3H), 0.82 (t, *J* 7.2 Hz, 3H). *m*/*z* (%): 309 (M^+, 2.1), 252 (4.2), 223 (100), 194 (68.3), 180 (53.1), 118 (28.4), 104 (21.6), 87 (11.4), 77 (9.6). Anal. calcd. for $C_{19}H_{23}N_3O$: C, 73.76; H, 7.49; N, 13.58. Found: C, 73.70; H, 7.45; N, 13.61%.

Compound **2k**: colorless oil. ν_{max}(film)/cm^{-1}: 3408 (OH), 2965, 2929, 1659 (N=N), 1450, 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* 8.4 Hz, 1H), 7.75 (t, *J* 8.4 Hz, 4H), 7.65 (d, *J* 8.4 Hz, 2H), 7.54–7.57 (m, 2H), 7.43–7.48 (m, 4H), 7.36 (t, *J* 7.6 Hz, 1H), 5.33 (d, *J* 10.4 Hz, 1H), 3.25–3.31 (m, 1H), 1.02 (d, *J* 6.8 Hz, 3H), 0.95 (d, *J* 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 142.7, 137.6, 137.2, 133.3, 132.6, 130.5, 130.0, 128.3, 127.8, 127.4, 124.0, 120.1, 109.3, 70.4, 32.9, 20.4, 20.3. *m*/*z* (%): 357 (M^+, 0.7), 183 (47.6), 161 (100), 146 (61.3), 132 (57.1), 104 (49.6), 77 (36.5). Anal. calcd. for $C_{23}H_{23}N_3O$: C, 77.28; H, 6.49; N, 11.76. Found: C, 77.35; H, 6.46; N, 11.79%.

Compound **2l**: colorless oil. ν_{max}(film)/cm^{-1}: 3404 (OH), 2956, 2864, 1619 (N=N), 1451, 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* 8.4 Hz, 1H), 7.50–7.56 (m, 2H), 7.41 (t, *J* 8.4 Hz, 1H), 4.41 (d, *J* 4.8 Hz, 1H), 2.76–2.84 (m, 1H), 1.03 (s, 3H), 0.97–0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 135.3, 127.8, 124.2, 120.0, 109.8, 74.1, 71.8, 29.8, 28.7, 27.6, 23.0, 18.9. *m*/*z* (%): 234 ($M^+ + 1$, 1.7), 161 (100), 146 (70.2), 132 (56.1), 104 (45.7), 77 (41.9). Anal. calcd. for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.87; H, 8.25; N, 18.05%.

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