First TDAE Reactivity Using Benzonitrile Derivatives as Substrates and Its Application to the Synthesis of 3-Substituted Isochroman-1-ones

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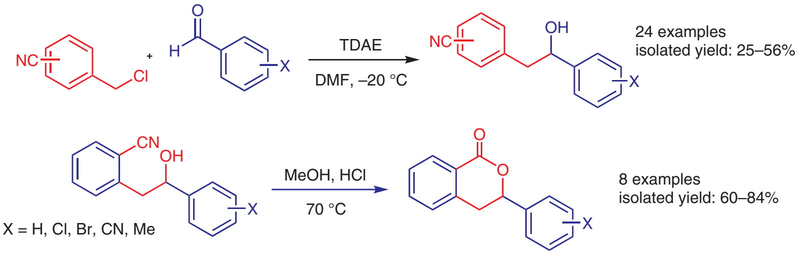
In memory of Professor Jacques Barbe



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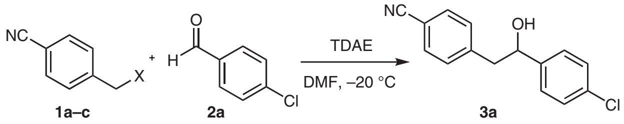
Abstract The first TDAE-initiated reaction between benzonitrile derivatives as substrates and substituted benzaldehydes to form substituted hydroxyethylbenzonitrile derivatives is reported. The 2-hydroxyethyl benzonitrile derivatives thus formed were good candidates for one-pot lactonization in a mixture of hydrochloric acid and methanol at 70 °C over five hours. These reactions furnished the corresponding 3-substituted isochroman-1-one derivatives in good yields.

Key words TDAE, benzonitrile, benzaldehydes, one-pot lactonization, isochroman-1-one

The nitrile derivatives are highly valuable in synthesis offering easy access to various functional groups such as aldehydes, ketones, amines, and acids. Moreover, benzonitrile groups are present in numerous industrial products such as dyes, herbicides, agrochemicals, pharmaceuticals, and natural products.[1] Since 2003, we have developed a program directed toward the use of organic reducing agents such as TDAE (*t*etrakis *d*imethyl*a*mino *e*thylene) in the reactions of bioreductive alkylating agents to form anionic species, which react with various electrophiles.[2] This program was initiated with nitrobenzyl derivatives and extended to heterocyclic series in 2005[3] and in quinonic series in 2008.[4] In continuation of our research program, we report here the first TDAE-initiated reaction between benzonitrile derivatives as substrates and substituted benzaldehydes, and its application to the synthesis of 3-substituted isochroman-1-ones.

Using benzonitrile substrate in TDAE warranted a preliminary study to determine the optimal reaction conditions. By analogy with TDAE reactivity in *p*-nitrobenzyl chloride series, we started our study from the commercially available 4-chloromethylbenzonitrile (**1a**) and 4-chlorobenzaldehyde (**2a**). No reaction was observed between **1a** and **2a** in the presence of TDAE under classical TDAE conditions[2b] (Table 1, entry 1). The addition of NaI (entries 2 and 3) led to the desired product **3a** in 44% yield. We therefore employed the commercially available 4-bromomethylbenzonitrile (**1b**) and the synthesized (NaI in acetone)[5] 4-iodomethylbenzonitrile (**1c**). Exchanging the halogen atom on the benzonitrile substrate for bromine **1b** or iodine **1c** furnished the desired product **3a** in 34% and 50% yield, respectively.

Table 1 Preliminary Study[a]

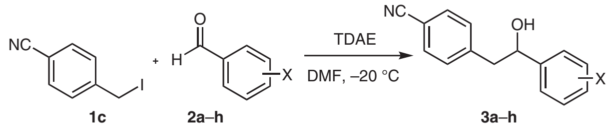


Substrate	X	NaI (equiv)	Yield (%)[b] of **3a**
1a	Cl	0	0
1a	Cl	1	44
1a	Cl	2	44
1b	Br	0	34
1c	I	0	50

[a] All reactions were performed using 3 equiv of benzaldehyde (**2a**), 1 equiv of the respective benzonitrile **1a–c**, and 1 equiv of TDAE in anhyd DMF.
[b] All yields refer to chromatographically isolated pure products and are relative to the respective benzonitrile **1a–c**.

These results led us to generalize this reactivity using 4-iodomethylbenzonitrile derivatives as TDAE-substrates. On treatment under inert atmosphere with 3 equivalents of benzaldehydes **2a–h** in the presence of TDAE at –20 °C for 1 hour, followed by 2 hours at room temperature, the 4-iodomethylbenzonitrile (**1c**) furnished the corresponding alcohols **3a**–**h** (Table 2) in 37–56% yields. The formation of these alcohol derivatives may be explained by the formation of a benzylic anion using TDAE and its nucleophilic addition to benzaldehydes. We note that no dimers of 4-iodomethylbenzonitrile were observed.

Table 2 Reaction of Benzonitrile **1c** with Aldehydes **2a**–**h** in the Presence of TDAE[a]



X	Product	Yield (%)[b]
4-Cl	**3a**	50
H	**3b**	43
2-Cl	**3c**	52
4-CN	**3d**	45
4-Me	**3e**	37
3-Br	**3f**	56
4-Br	**3g**	44
2-Br	**3h**	40

[a] All reactions were performed using 3 equiv of the respective benzaldehyde **2a**–**h**, 1 equiv of benzonitrile **1c**, and 1 equiv of TDAE in anhyd DMF.
[b] All yields refer to chromatographically isolated pure products and are relative to benzonitrile **1c**.

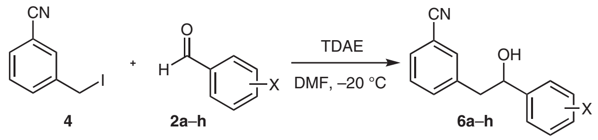
Carrying on from this first reaction, we extended our study to the two other isomers of iodomethylbenzonitriles, that is, 2- and 3-iodomethylbenzonitriles (**4** and **5**). These new starting materials were synthesized according to previously described procedures (NaI in acetone)[5] from the corresponding chloro- or bromomethylbenzonitriles. The reactions were conducted under the same conditions and furnished the corresponding alcohols **6a**–**h** (Table 3) and **7a**–**h** (Table 4).

The chemical promise of benzonitriles substituted by an ethyl alcohol group in the *ortho*-position led us to investigate the possible lactonization of these alcohols **7a**–**h**. The reaction of 2-substituted benzonitriles **7a**–**h** in a mixture of hydrochloric acid and methanol at 70 °C for 5 hours furnished the corresponding 3-substituted isochroman-1-ones **8** (Table 5).[6]

However, the reaction from alcohol **7d** (X = CN) led to the cyclized compound **8d**, with the nitrile group transformed into a methyl ester group (X = CO_2Me) due to the hydrolysis of nitrile followed by solvent esterification. Concerning, the reaction from alcohol **7e** (X = Me), no cyclized product **8e** was observed, but an ethylenic derivative, (*E*)-2-(4-methylstyryl)benzonitrile (**9**), was formed in 68% yield resulting from dehydration of compound **7e** due to acidic conditions. In this compound, the hydrogen atoms of the hydroxyethyl group seem more sensitive to the acid conditions due to the presence of an electron-donating group (Me) on the benzene.

In conclusion, we have reported the first TDAE-initiated reaction between benzonitrile derivatives as substrates and substituted benzaldehydes to form substituted hydroxyethylbenzonitrile derivatives in moderate to good yields. The 2-hydroxyethylbenzonitrile derivatives thus formed

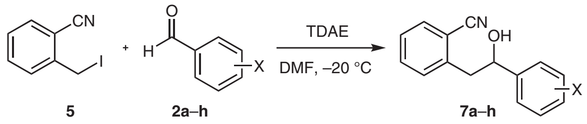
Table 3 Reaction of Benzonitrile **4** with Aldehydes **2a**–**h** in the Presence of TDAE[a]



X	Product	Yield (%)[b]
4-Cl	**6a**	34
H	**6b**	25
2-Cl	**6c**	34
4-CN	**6d**	36
4-Me	**6e**	32
3-Br	**6f**	37
4-Br	**6g**	31
2-Br	**6h**	30

[a] All reactions were performed using 3 equiv of the respective benzaldehyde **2a**–**h**, 1 equiv of benzonitrile **4**, and 1 equiv of TDAE in anhyd DMF.
[b] All yields refer to chromatographically isolated pure products and are relative to benzonitrile **4**.

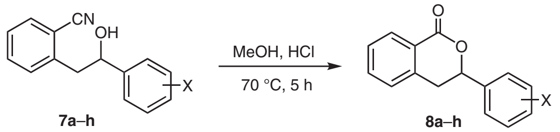
Table 4 Reaction of Benzonitrile **5** with Aldehydes **2a**–**h** in the Presence of TDAE[a]



X	Product	Yield (%)[b]
4-Cl	**7a**	37
H	**7b**	48
2-Cl	**7c**	38
4-CN	**7d**	32
4-Me	**7e**	30
3-Br	**7f**	42
4-Br	**7g**	38
2-Br	**7h**	46

[a] All reactions were performed using 3 equiv of the respective benzaldehyde **2a**–**h**, 1 equiv of benzonitrile **5**, and 1 equiv of TDAE in anhyd DMF.
[b] All yields refer to chromatographically isolated pure products and are relative to benzonitrile **5**.

Table 5 One-Pot Hydrolysis/Lactonization Reaction of Benzonitriles **7a–h**[a]



X	Product	Yield (%)[b]
4-Cl	**8a**	68
H	**8b**	60
2-Cl	**8c**	81
4-CN	**8d**	70[c]
4-Me	**9**[d]	68
3-Br	**8f**	78
4-Br	**8g**	83
2-Br	**8h**	84

[a] All reactions were performed in a mixture of HCl and MeOH at 70 °C for 5 h.
[b] All yields refer to chromatographically isolated pure products and are relative to benzonitriles **7a–h**.
[c] The nitrile substituent in the alcohol **7d** (X = CN) was converted into a methyl ester group (X = CO_2Me) in the cyclized compound **8d**.
[d] No cyclized product **8e** was observed, but an ethylenic derivative **9** (see also experimental).

were good candidates for one-pot hydrolysis-lactonization reactions in a mixture of hydrochloric acid and methanol at 70 °C over 5 hours. These reactions furnished the corresponding 3-substituted isochroman-1-one derivatives in good yields.

TDAE is commercially available. Melting points were determined on Büchi B-540 and are uncorrected. Elemental analyses and HRMS were carried out at the Spectropole, Faculté des Sciences et Techniques de Saint-Jérôme, Marseille. ^{1}H NMR spectra (250 MHz, reference $CDCl_3$ δ = 7.26, DMSO-d_6 δ = 2.50) and ^{13}C NMR spectra (62.5 MHz, reference $CDCl_3$ δ = 77.0, DMSO-d_6 δ = 39.7) were recorded on a Bruker ARX 200 spectrometer in $CDCl_3$ and DMSO-d_6 solvents at the Faculté de Pharmacie de Marseille. Solvents were dried by conventional methods. The following adsorbent was used for column chromatography: silica gel 60 (Merck, particle size 0.063–0.200 mm, 70–230 mesh ASTM). TLC was performed on 5 cm × 10 cm aluminum plates coated with silica gel 60F-254 (Merck) in an appropriate eluent. HRMS were recorded on QStar Elite (Applied Biosystems SCIEX) spectrometer using PEG as the matrix.

Reaction of Iodomethylbenzonitriles 1c, 4, and 5 with Benzaldehydes 2a–h; General Procedure

To a two-necked round-bottomed flask equipped with a drying tube (silica gel) and a N_2 inlet was added an anhyd DMF solution of iodomethyl derivative **1c**, **4**, or **5** (300 mg, 1.23 mmol, 15 mL, 1 equiv) and the respective benzaldehyde **2a–h** (3 equiv). The solution was cooled to –20 °C, maintained at this temperature for 30 min, and then the TDAE (0.29 mL, 1.23 mmol, 1 equiv) was added dropwise via a syringe. The solution was vigorously stirred at –20 °C for 1 h and then maintained at r.t. for 2 h. The solution was filtered (to remove the octamethyloxamidinium diiodide) and hydrolyzed with H_2O (70 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers washed with H_2O (2 × 40 mL), and dried ($MgSO_4$). Evaporation of the solvent furnished an orange viscous liquid as crude product. Purification by silica gel chromatography (CH_2Cl_2) gave the corresponding alcohol **3a–h**, **6a–h**, **7a–h**.

4-[2-(4-Chlorophenyl)-2-hydroxyethyl]benzonitrile (3a)

Yield: 150 mg (50%); white solid; mp 124 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (br, 1 H, OH), 3.02 (dd, *J* = 13.6, 5.6 Hz, 1 H, CH_2), 3.08 (dd, *J* = 13.6, 7.4 Hz, 1 H, CH_2), 4.90 (dd, *J* = 7.4, 5.6 Hz, 1 H, CH), 7.22 (d, *J* = 8.6 Hz, 2 H, ArH), 7.26 (d, *J* = 8.3 Hz, 2 H, ArH), 1.33 (d, *J* = 8.6 Hz, 2 H, ArH), 7.58 (d, *J* = 8.3 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.7, 74.2, 110.5, 118.9, 127.2 (2 C), 128.7 (2 C), 130.4 (2 C), 132.1 (2 C), 133.6, 141.7, 143.3.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{12}ClNONa$: 280.0500; found: 280.0499.

4-(2-Hydroxy-2-phenylethyl)benzonitrile (3b)

Yield: 120 mg (43%); beige solid; mp 79 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00 (br, 1 H, OH), 3.04 (dd, *J* = 13.6, 5.5 Hz, 1 H, CH_2), 3.11 (dd, *J* = 13.6, 7.6 Hz, 1 H, CH_2), 4.91 (dd, *J* = 7.4, 5.5 Hz, 1 H, CH), 7.25 (d, *J* = 8.6 Hz, 2 H, ArH), 7.29–7.37 (m, 5 H, ArH), 7.55 (d, *J* = 8.3 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.7, 74.9, 110.2, 118.9, 125.8 (2 C), 128.0, 128.5 (2 C), 130.3 (2 C), 132.0 (2 C), 143.2, 143.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{13}NONa$: 246.0889; found: 246.0889.

4-[2-(2-Chlorophenyl)-2-hydroxyethyl]benzonitrile (3c)

Yield: 165 mg (52%); white solid; mp 120 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.96 (br, 1 H, OH), 2.92 (dd, *J* = 13.7, 8.5 Hz, 1 H, CH_2), 3.18 (dd, *J* = 13.7, 3.5 Hz, 1 H, CH_2), 5.34 (dd, *J* = 8.5, 3.5 Hz, 1 H, CH), 7.23 (dd, *J* = 7.4, 1.9 Hz, 1 H, ArH), 7.28–7.32 (m, 3 H, ArH), 7.34 (d, *J* = 8.4 Hz, 2 H, ArH), 7.54 (dd, *J* = 7.6, 1.9 Hz, 1 H, ArH), 7.59 (d, *J* = 8.4 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 43.9, 71.3, 110.4, 119.0, 126.9, 127.2, 128.8, 129.4, 130.4 (2 C), 131.4, 132.0 (2 C), 140.8, 143.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{13}ClNONa$: 280.0500; found: 280.0500.

4,4′-(1-Hydroxyethane-1,2-diyl)dibenzonitrile (3d)

Yield: 136 mg (45%); white solid; mp 188 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.17 (br, 1 H, OH), 3.06 (d, *J* = 6.5 Hz, 2 H, CH_2), 5.01 (t, *J* = 6.5 Hz, 1 H, CH), 7.27 (d, *J* = 8.2 Hz, 2 H, ArH), 7.43 (d, *J* = 8.2 Hz, 2 H, ArH), 7.59 (d, *J* = 8.4 Hz, 2 H, ArH), 7.63 (d, *J* = 8.4 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.6, 74.0, 110.8, 111.7, 118.6, 118.7, 126.5 (2 C), 130.4 (2 C), 132.2 (2 C), 132.3 (2 C), 142.7, 148.4.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{16}H_{12}N_2O$: 266.1288; found: 266.1286.

4-[2-Hydroxy-2-(*p*-tolyl)ethyl]benzonitrile (3e)

Yield: 106 mg (37%); white solid; mp 93 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26 (s, 1 H, OH), 2.36 (br, 3 H, CH_3), 3.03 (dd, J = 13.6, 5.5 Hz, 1 H, CH_2), 3.18 (dd, J = 13.6, 7.6 Hz, 1 H, CH_2), 4.86 (dd, J = 7.6, 5.5 Hz, 1 H, CH), 7.15 (d, J = 8.5 Hz, 2 H, ArH), 7.19 (d, J = 8.5 Hz, 2 H, ArH), 7.25 (d, J = 8.4 Hz, 2 H, ArH), 7.55 (d, J = 8.4 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.1, 45.6, 74.7, 110.1, 119.0, 125.7 (2 C), 129.1 (2 C), 130.3 (2 C), 131.9 (2 C), 137.6, 140.2, 143.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}NONa$: 260.1046; found: 260.1048.

4-[2-(3-Bromophenyl)-2-hydroxyethyl]benzonitrile (3f)

Yield: 206 mg (56%); white solid; mp 86 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.47 (br, 1 H, OH), 3.03 (d, J = 6.9 Hz, 2 H, CH_2), 4.85 (dd, J = 6.6, 6.3 Hz, 1 H, CH), 7.18–7.20 (m, 2 H, ArH), 7.26 (d, J = 8.2 Hz, 2 H, ArH), 7.37–7.43 (m, 1 H, ArH), 7.46–7.48 (m, 1 H, ArH), 7.53 (d, J = 8.2 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.6, 73.9, 110.2, 118.8, 122.5, 124.4, 128.8, 130.0, 130.3 (2 C), 130.8, 132.0 (2 C), 143.3, 145.6.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0438.

4-[2-(4-Bromophenyl)-2-hydroxyethyl]benzonitrile (3g)

Yield: 163 mg (44%); white solid; mp 131 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.18 (br, 1 H, OH), 3.00 (dd, J = 13.6, 5.6 Hz, 1 H, CH_2), 3.07 (dd, J = 13.6, 7.3 Hz, 1 H, CH_2), 4.88 (dd, J = 7.3, 5.6 Hz, 1 H, CH), 7.15 (d, J = 8.4 Hz, 2 H, ArH), 7.25 (d, J = 8.2 Hz, 2 H, ArH), 7.45 (d, J = 8.4 Hz, 2 H, ArH), 7.53 (d, J = 8.2 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.6, 74.1, 110.3, 118.8, 121.6, 127.5 (2 C), 130.3 (2 C), 131.5 (2 C), 132.0 (2 C) 142.2, 143.3.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0444.

4-[2-(2-Bromophenyl)-2-hydroxyethyl]benzonitrile (3h)

Yield: 148 mg (40%); white solid; mp 110 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (br, 1 H, OH), 2.87 (dd, J = 13.8, 8.8 Hz, 1 H, CH_2), 3.18 (dd, J = 13.8, 3.3 Hz, 1 H, CH_2), 5.26 (dd, J = 8.8, 3.3 Hz, 1 H, CH), 7.16 (dt, J = 7.6, 1.7 Hz, 1 H, ArH), 7.31–7.37 (m, 1 H, ArH), 7.38 (d, J = 8.2 Hz, 2 H, ArH), 7.53–7.58 (m, 2 H, ArH), 7.57 (d, J = 8.2 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 43.9, 73.4, 110.2, 118.9, 121.5, 127.2, 127.8, 129.1, 130.3 (2 C), 132.0 (2 C), 132.6, 142.3, 144.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0443.

3-[2-(4-Chlorophenyl)-2-hydroxyethyl]benzonitrile (6a)

Yield: 105 mg (34%); white solid; mp 65 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26 (br, 1 H, OH), 2.97 (dd, J = 13.9, 5.7 Hz, 1 H, CH_2), 3.03 (dd, J = 13.9, 7.4 Hz, 1 H, CH_2), 4.87 (dd, J = 7.4, 5.7 Hz, 1 H, CH), 7.23 (d, J = 8.7 Hz, 2 H, ArH), 7.31 (d, J = 8.7 Hz, 2 H, ArH), 7.36–7.38 (m, 2 H, ArH), 7.47–7.52 (m, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.0, 74.1, 112.1, 118.8, 127.1 (2 C), 128.6 (2 C), 129.0, 130.2, 133.0, 133.4, 134.1, 139.2, 141.7.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{15}H_{12}ClNO$: 275.0946; found: 275.0952.

3-(2-Hydroxy-2-phenylethyl)benzonitrile (6b)

Yield: 68 mg (25%); colorless oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.07 (br, 1 H, OH), 2.92 (dd, J = 13.8, 5.6 Hz, 1 H, CH_2), 2.98 (dd, J = 13.8, 4.3 Hz, 1 H, CH_2), 4.80 (dd, J = 5.6, 4.3 Hz, 1 H, CH), 7.18–7.29 (m, 7 H, ArH), 7.36–7.44 (m, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.1, 74.9, 112.2, 118.9, 125.8 (2 C), 128.0, 128.5 (2 C), 129.0, 130.2, 133.1, 134.2, 139.6, 143.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}NONa$: 246.0889; found: 246.0893.

3-[2-(2-Chlorophenyl)-2-hydroxyethyl]benzonitrile (6c)

Yield: 105 mg (34%); white solid; mp 103 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (br, 1 H, OH), 2.89 (dd, J = 13.9, 8.7 Hz, 1 H, CH_2), 3.15 (dd, J = 13.9, 3.3 Hz, 1 H, CH_2), 5.33 (dd, J = 8.7, 3.3 Hz, 1 H, CH), 7.21–7.29 (m, 1 H, ArH), 7.31–7.39 (m, 2 H, ArH), 7.43 (d, J = 8.2 Hz, 1 H, ArH), 7.48–7.56 (m, 4 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 43.3, 71.3, 112.3, 118.9, 126.9, 127.2, 128.8, 129.0, 129.4, 130.3, 131.5, 133.1, 134.2, 139.7, 140.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}ClNONa$: 280.0500; found: 280.0498.

3-[2-(4-Cyanophenyl)-2-hydroxyethyl]benzonitrile (6d)

Yield: 110 mg (36%); white solid; mp 133 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (br, 1 H, OH), 2.98 (d, J = 6.6 Hz, 2 H, CH_2), 4.95 (t, J = 6.6 Hz, 1 H, CH), 7.34–7.4 (m, 2 H, ArH), 7.43 (d, J = 8.5 Hz, 2 H, ArH), 7.51–7.57 (m, 2 H, ArH), 7.65 (d, J = 8.5 Hz, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.0, 74.0, 111.6, 112.4, 118.6, 118.7, 126.5 (2 C), 129.2, 130.6, 132.3 (2 C), 133.1, 134.1, 138.7, 148.5.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{12}N_2O$: 266.1288; found: 266.1289.

3-[2-Hydroxy-2-(*p*-tolyl)ethyl]benzonitrile (6e)

Yield: 93 mg (32%); white solid; mp 53 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.06 (s, 1 H, OH), 2.36 (s, 3 H, CH_3), 2.99 (dd, J = 13.7, 5.5 Hz, 1 H, CH_2), 3.07 (dd, J = 13.7, 7.7 Hz, 1 H, CH_2), 4.85 (dd, J = 7.7, 5.5 Hz, 1 H, CH), 7.15 (d, J = 8.7 Hz, 2 H, ArH), 7.20 (d, J = 8.7 Hz, 2 H, ArH), 7.36–7.42 (m, 2 H, ArH), 7.46–7.53 (m, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.1, 45.0, 74.7, 112.1, 118.9, 125.7 (2 C), 128.9, 129.2 (2 C), 130.1, 133.0, 134.1, 137.7, 139.7, 140.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}NONa$: 260.1046; found: 260.1047.

3-[2-(3-Bromophenyl)-2-hydroxyethyl]benzonitrile (6f)

Yield: 137 mg (37%); white solid; mp 77 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08 (br, 1 H, OH), 3.01 (d, J = 6.5 Hz, 2 H, CH_2), 4.87 (t, J = 6.5 Hz, 1 H, CH_2), 7.22–7.24 (m, 2 H, ArH), 7.38–7.45 (m, 3 H, ArH), 7.47–7.49 (m, 2 H, ArH), 7.51–7.55 (m, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.1, 74.1, 112.3, 118.8, 122.6, 124.4, 128.9, 129.1, 130.1, 130.4, 130.9, 133.0, 134.1, 139.1, 145.6.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0443.

3-[2-(4-Bromophenyl)-2-hydroxyethyl]benzonitrile (6g)

Yield: 111 mg (31%); white solid; mp 68 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (br, 1 H, OH), 2.95 (dd, *J* = 13.7, 5.8 Hz, 1 H, CH_2), 3.02 (dd, *J* = 13.7, 7.2 Hz, 1 H, CH_2), 4.86 (dd, *J* = 7.2, 5.8 Hz, 1 H, CH), 7.57 (d, *J* = 8.5 Hz, 2 H, ArH), 7.57 (d, *J* = 8.5 Hz, 2 H, ArH), 7.53–7.58 (m, 2 H, ArH), 7.53–7.58 (m, 2 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 45.0, 74.1, 112.1, 118.8, 127.1 (2 C), 128.6 (2 C), 129.0, 130.3, 133.0, 133.5, 134.2, 139.2, 141.7.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0444.

3-[2-(2-Bromophenyl)-2-hydroxyethyl]benzonitrile (6h)

Yield: 110 mg (30%); white solid; mp 102 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (br, 1 H, OH), 2.84 (dd, *J* = 13.9, 8.7 Hz, 1 H, CH_2), 3.15 (dd, *J* = 13.9, 3.3 Hz, 1 H, CH_2), 5.25 (dd, *J* = 8.7, 3.3 Hz, 1 H, CH), 7.16 (dt, *J* = 7.6, 1.7 Hz, 1 H, ArH), 7.35 (dt *J* = 7.7, 0.7 Hz, 1 H, ArH), 7.42 (dd *J* = 7.2, 0.7 Hz, 1 H, ArH), 7.49–7.56 (m, 5 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 43.3, 73.4, 112.1, 118.9, 121.5, 127.2, 127.8, 129.0, 129.1, 130.2, 132.6, 133.1, 134.2, 139.7, 142.3.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0437.

2-[2-(4-Chlorophenyl)-2-hydroxyethyl]benzonitrile (7a)

Yield: 116 mg (37%); white solid; mp 87 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.13 (br, 1 H, OH), 3.15 (dd, *J* = 13.7, 8.1 Hz, 1 H, CH_2), 3.24 (dd, *J* = 13.7, 5.0 Hz, 1 H, CH_2), 5.00 (dd, *J* = 8.1, 5.0 Hz, 1 H, CH), 7.27–7.31 (m, 5 H, ArH), 7.34 (dt, *J* = 7.6, 1.1 Hz, 1 H, ArH), 7.51 (dt *J* = 7.6, 1.4 Hz, 1 H, ArH), 7.63 (d *J* = 7.6 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 44.4, 73.7, 112.9, 118.1, 127.1 (2 C), 127.2, 128.6 (2 C), 131.0, 132.6, 132.8, 133.5, 141.7, 141.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{12}ClNONa$: 280.0500; found: 280.0500.

2-(2-Hydroxy-2-phenylethyl)benzonitrile (7b)

Yield: 130 mg (48%); white solid; mp 75 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04 (br, 1 H, OH), 3.08 (dd, *J* = 13.7, 8.2 Hz, 1 H, CH_2), 3.15 (dd, *J* = 13.7, 5.5 Hz, 1 H, CH_2), 4.90 (dd, *J* = 8.2, 5.5 Hz, 1 H, CH), 7.16–7.27 (m, 7 H, ArH), 7.40 (dt, *J* = 7.4, 1.4 Hz, 1 H, ArH), 7.52 (dd, *J* = 7.4, 1.4 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 44.3, 74.3, 112.9, 118.1, 125.7 (2 C), 127.0, 127.8, 128.5 (2 C), 131.0, 132.5, 132.7, 142.2, 143.2.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{13}NO$: 241.1335; found: 241.1341.

2-[2-(2-Chlorophenyl)-2-hydroxyethyl]benzonitrile (7c)

Yield: 120 mg (38%); white solid; mp 84 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.14 (br, 1 H, OH), 3.10 (dd, *J* = 13.9, 8.0 Hz, 1 H, CH_2), 3.22 (dd, *J* = 13.9, 4.3 Hz, 1 H, CH_2), 5.34 (dd, *J* = 8.0, 4.3 Hz, 1 H, CH), 7.10–7.26 (m, 5 H, ArH), 7.38–7.57 (m, 3 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 42.0, 70.8, 113.5, 118.1, 127.0, 127.1, 127.2, 128.8, 129.3, 130.8, 131.7, 132.4, 132.7, 140.4, 141.6.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}ClNO$: 275.0946; found: 275.0943.

2-[2-(4-Cyanophenyl)-2-hydroxyethyl]benzonitrile (7d)

Yield: 96 mg (32%); white solid; mp 118 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (br, 1 H, OH), 3.13 (dd, *J* = 13.7, 8.4 Hz, 1 H, CH_2), 3.25 (dd, *J* = 13.7, 4.6 Hz, 1 H, CH_2), 5.10 (dd, *J* = 8.8, 4.6 Hz, 1 H, CH), 7.30 (dd, *J* = 7.6, 1.0 Hz, 1 H, ArH), 7.37 (dd, *J* = 7.6, 1.3 Hz, 1 H, ArH), 7.49 (d, *J* = 8.5 Hz, 2 H, ArH), 7.53 (dt, *J* = 7.7, 1.4 Hz, 1 H, ArH), 7.62 (d, *J* = 8.5 Hz, 2 H, ArH), 7.64 (dt, *J* = 7.3, 1.1 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 44.4, 73.5, 111.4, 112.9, 118.0, 118.7, 126.4 (2 C), 127.4, 131.1, 132.3 (2 C), 132.7, 132.8, 141.2, 148.4.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{12}N_2ONa$: 271.0842; found: 271.0844.

2-[2-Hydroxy-2-(*p*-tolyl)ethyl]benzonitrile (7e)

Yield: 85 mg (30%); beige solid; mp 89 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.14 (br, 1 H, OH), 2.35 (s, 3 H, CH_3), 3.17 (dd, *J* = 13.7, 7.9 Hz, 1 H, CH_2), 3.25 (dd, *J* = 13.7, 2.2 Hz, 1 H, CH_2), 4.96 (dd, *J* = 7.9, 2.2 Hz, 1 H, CH), 7.17 (d, *J* = 7.9 Hz, 2 H, ArH), 7.28 (d, *J* = 7.9 Hz, 2 H, ArH), 7.30–7.36 (m, 2 H, ArH), 7.51 (dt, *J* = 7.7, 1.4 Hz, 1 H, ArH), 7.63 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.0, 44.3, 74.2, 112.9, 118.1, 125.6 (2 C), 126.9, 129.1 (2 C), 130.9, 132.4, 132.6, 137.5, 140.3, 142.3.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{16}H_{15}NO$: 255.1492; found: 255.1493.

2-[2-(3-Bromophenyl)-2-hydroxyethyl]benzonitrile (7f)

Yield: 155 mg (42%); colorless oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.13 (br, 1 H, OH), 3.14 (dd, *J* = 13.9, 8.5 Hz, 1 H, CH_2), 3.255 (dd, *J* = 13.9, 4.6 Hz, 1 H, CH_2), 4.98 (dd, *J* = 8.5, 4.6 Hz, 1 H, CH), 7.18–7.32 (m, 3 H, ArH), 7.36 (dd, *J* = 7.6, 1.3 Hz, 1 H, ArH), 7.44 (dt, *J* = 7.7, 1.9 Hz, 1 H, ArH), 7.49–7.55 (m, 2 H, ArH), 5.65 (dd, *J* = 7.7, 1.3 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 44.4, 73.6, 112.9, 118.1, 122.6, 124.4, 127.2, 128.8, 130.1, 130.9, 131.1, 132.6, 132.8, 141.7, 145.5.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0441.

2-[2-(4-Bromophenyl)-2-hydroxyethyl]benzonitrile (7g)

Yield: 140 mg (38%); white solid; mp 72 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.12 (br, 1 H, OH), 3.14 (dd, *J* = 13.9, 8.2 Hz, 1 H, CH_2), 3.255 (dd, *J* = 13.9, 5.0 Hz, 1 H, CH_2), 4.98 (dd, *J* = 8.2, 5.0 Hz, 1 H, CH), 7.25 (d, *J* = 8.4 Hz, 2 H, ArH), 7.34 (dt, *J* = 7.6, 1.1 Hz, 2 H, ArH), 7.46 (d, *J* = 8.4 Hz, 2 H, ArH), 7.51 (dt, *J* = 7.6, 1.4 Hz, 1 H, ArH), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 44.3, 73.6, 112.8, 118.0, 121.5, 127.1, 127.4 (2 C), 131.0, 131.5 (2 C), 132.6, 132.7, 141.7, 142.2.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0443.

2-[2-(2-Bromophenyl)-2-hydroxyethyl]benzonitrile (7h)

Yield: 170 mg (46%); white solid; mp 100 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.45 (br, 1 H, OH), 3.12 (dd, *J* = 14.0, 8.2 Hz, 1 H, CH_2), 3.22 (dd, *J* = 14.0, 4.4 Hz, 1 H, CH_2), 5.32 (dd, *J* = 8.2, 44 Hz, 1 H, CH), 7.09 (dt, *J* = 7.6, 1.7 Hz, 1 H, ArH), 7.24–7.32 (m, 3 H, ArH), 7.42–7.48 (m, 3 H, ArH), 7.52 (dt, *J* = 8.0, 1.6 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 41.9, 72.8, 113.8, 118.1, 121.7, 126.9, 127.5, 126.7, 129.1, 130.7, 132.4, 132.5, 132.6, 141.5, 141.9.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{12}BrNO$: 319.0441; found: 319.0442.

Lactonization of 2-Hydroxyethylbenzonitriles 7a–h; General Procedure

The respective 2-hydroxyethyl benzonitrile **7a–h** (100 mg) was dissolved in a mixture of 1:1 solution of MeOH (40 mL) and HCl (37%, 40 mL). The mixture was heated at 70 °C for 5 h. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers washed with H_2O (2 × 40 mL), dried ($MgSO_4$), and evaporated. Purification of the residue by silica gel chromatography (CH_2Cl_2/PE 1:1) gave the corresponding isochroman-1-one derivative **8a–h**.

3-(4-Chlorophenyl)isochroman-1-one (8a)

Yield: 67 mg (68%); white solid; mp 72 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.12 (dd, *J* = 16.4, 3.3 Hz, 1 H, CH_2), 3.31 (dd, *J* = 16.4, 11.8 Hz, 1 H, CH_2), 5.55 (dd, *J* = 12.0, 3.3 Hz, 1 H, CH), 7.29 (d, *J* = 7.6 Hz, 1 H, ArH), 7.37–7.48 (m, 5 H, ArH), 7.59 (td, *J* = 7.4, 1.4 Hz, 1 H, ArH), 8.15 (dd, *J* = 7.7, 1.4 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 35.5, 79.1, 124.9, 127.3, 127.5 (2 C), 128.0, 128.9 (2 C), 130.4, 134.0, 134.4, 137.0, 138.6, 165.0.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}ClO_2$: 259.0520; found: 259.0518.

3-Phenylisochroman-1-one (8b)

Yield: 60 mg (60%); white solid; mp 74 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.03 (dd, *J* = 16.4, 3.3 Hz, 1 H, CH_2), 3.24 (dd, *J* = 16.4, 11.8 Hz, 1 H, CH_2), 5.45 (dd, *J* = 12.0, 3.3 Hz, 1 H, CH), 7.27–7.52 (m, 7 H, ArH), 7.48 (td, *J* = 7.6, 1.4 Hz, 1 H, ArH), 8.06 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 35.5, 79.9, 125.5, 126.1 (2 C), 126.5, 127.3, 127.8, 128.4, 128.5, 128.6 (2 C), 130.0, 133.9, 138.5, 138.9, 165.3.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}O_2Na$: 247.0730; found: 247.073.

3-(2-Chlorophenyl)isochroman-1-one (8c)

Yield: 81 mg (81%); white solid; mp 104 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.14 (dd, *J* = 16.4, 11.7 Hz, 1 H, CH_2), 3.27 (dd, *J* = 16.4, 3.5 Hz, 1 H, CH_2), 5.95 (dd, *J* = 11.7, 3.5 Hz, 1 H, CH), 7.28–7.48 (m, 6 H, ArH), 7.59 (td, *J* = 7.4, 1.4 Hz, 1 H, ArH), 7.59 (td, *J* = 7.7, 1.9 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 34.3, 76.8, 124.9, 127.4 (2 C), 127.5, 127.9, 129.5, 129.6, 130.4, 131.4, 134.0, 136.3, 138.8, 165.2.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}ClO_2$: 259.0520; found: 259.0518.

Methyl 4-(1-Oxoisochroman-3-yl)benzoate (8d)

Yield: 78 mg (70%); white solid; mp 151 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.15 (dd, *J* = 16.4, 3.5 Hz, 1 H, CH_2), 3.31 (dd, *J* = 16.4, 11.5 Hz, 1 H, CH_2), 3.93 (s, 3 H, CH_3), 5.62 (dd, *J* = 11.5, 3.5 Hz, 1 H, CH), 7.30 (d, *J* = 7.4 Hz, 1 H, ArH), 7.45 (t *J* = 7.4 Hz, 1 H, ArH), 7.57 (d, *J* = 8.2 Hz, 2 H, ArH), 7.59 (td, *J* = 6.0, 1.4 Hz, 1 H, ArH), 8.09 (d, *J* = 8.2 Hz, 2 H, ArH), 8.15 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 35.5, 52.2, 79.2, 124.9, 125.9 (2 C), 127.3, 128.0, 130.0 (2 C), 130.3, 130.5, 134.1, 138.5, 143.4, 164.9, 166.6.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{14}O_4Na$: 305.0784; found: 305.0783.

3-(3-Bromophenyl)isochroman-1-one (8f)

Yield: 78 mg (78%); white solid; mp 113 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.11 (dd, *J* = 16.4, 3.5 Hz, 1 H, CH_2), 3.27 (dd, *J* = 16.4, 11.8 Hz, 1 H, CH_2), 5.50 (dd, *J* = 11.8, 3.5 Hz, 1 H, CH), 7.28 (d, *J* = 7.6 Hz, 1 H, ArH), 7.38–7.47 (m, 3 H, ArH), 7.50 (dd, *J* = 1.4, 1.3 Hz, 1 H, ArH), 7.57 (td, *J* = 7.6, 1.4 Hz, 1 H, ArH), 7.64 (dd, *J* = 1.7, 1.4 Hz, 1 H, ArH), 8.12 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 35.5, 78.9, 122.7, 124.6, 124.8, 127.3, 127.9, 129.1, 130.2, 130.4, 131.6, 134.0, 138.4, 140.7, 164.9.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}BrO_2$: 303.0015; found: 303.0013.

3-(4-Bromophenyl)isochroman-1-one (8g)

Yield: 83 mg (83%); white solid; mp 80 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 3.13 (dd, *J* = 16.4, 3.5 Hz, 1 H, CH_2), 3.30 (dd, *J* = 16.4, 11.8 Hz, 1 H, CH_2), 5.53 (dd, *J* = 11.8, 3.5 Hz, 1 H, CH), 7.27–7.31 (m, 2 H, ArH), 7.36 (d, *J* = 8.4 Hz, 2 H, ArH), 7.45 (td, *J* = 7.6, 1.6 Hz, 1 H, ArH), 7.56 (d, *J* = 8.5 Hz, 2 H, ArH), 7.59 (td, *J* = 7.6, 1.6 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 35.5, 79.2, 122.6, 124.9, 127.3, 127.7 (2 C), 128.0, 130.5, 131.8 (2 C), 134.0, 137.6, 138.5, 165.0.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{11}BrO_2Na$: 324.9835; found: 324.9833.

3-(2-Bromophenyl)isochroman-1-one (8h)

Yield: 84 mg (84%); white solid; mp 111 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 2.8 (dd, *J* = 16.4, 12.0 Hz, 1 H, CH_2), 3.00 (dd, *J* = 16.4, 3.2 Hz, 1 H, CH_2), 5.58 (dd, *J* = 12.0, 3.2 Hz, 1 H, CH), 7.22 (dd, *J* = 7.7, 1.7 Hz, 1 H, ArH), 7.30 (d, *J* = 7.4 Hz, 1 H, ArH), 7.38–7.47 (m, 2 H, ArH), 7.56–7.62 (m, 2 H, ArH), 8.73 (dd, *J* = 7.7, 1.6 Hz, 1 H, ArH), 8.16 (dd, *J* = 7.7, 1.3 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 34.4, 78.9, 121.1, 124.8, 127.3, 127.6, 127.8, 127.9, 129.8, 130.3, 132.7, 134.0, 137.8, 138.6, 165.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{11}BrO_2$: 303.0015; found: 303.0016.

(*E*)-2-(4-Methylstyryl)benzonitrile (9)

Yield: 62 mg (68%); beige solid; mp 55 °C.

^1H NMR (250 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 7.21 (d, *J* = 8.0 Hz, 2 H, ArH), 7.24 (d, *J* = 16.2 Hz, 1 H, ArH), 7.31 (td, *J* = 7.6, 1.0 Hz, 1 H, ArH), 7.40 (d, *J* = 16.2 Hz, 1 H, ArH), 7.47 (d, *J* = 8.0 Hz, 2 H, ArH), 7.55 (td, *J* = 8.0, 1.0 Hz, 1 H, ArH), 7.62 (dd, *J* = 7.8, 1.0 Hz, 1 H, ArH), 7.78 (d, *J* = 8.0 Hz, 1 H, ArH).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.3, 111.1, 118.20, 123.0, 125.1, 127.1 (2 C), 127.3, 129.6 (2 C), 132.7, 133.1, 133.4, 138.9, 140.8.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{13}N$: 242.2703; found: 242.2701.

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