# A New Synthesis of Methyl 7*H*-Dibenz[*b*,*g*]oxocin-6-carboxylates from Morita–Baylis–Hillman Adducts of 2-Phenoxybenzaldehydes

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**Abstract:** A new synthetic method for methyl 7*H*-dibenz[*b*,*g*]oxocin-6-carboxylates by Friedel–Crafts reaction of readily available bromides of Morita–Baylis–Hillman adducts with aluminum chloride has been developed.

**Key words:** Morita–Baylis–Hillman reaction, Friedel–Crafts reaction, methyl 7*H*-dibenz[*b*,*g*]oxocin-6-carboxylates, aluminum chloride, 2-phenoxybenzaldehydes

Medium-sized oxacycles, oxocines, are important structural unit present in numerous biologically active molecules.[1] Especially those annulated with aromatic rings such as benzoxocines and dibenzoxocines, are of current interest due to their presence in a large number of bioactive natural products. Benzoxocin derivatives are found in allelopathic sesquiterpenes such as helianane,[2] heliannuols A,[3] H, and K.[4] Dibenzoxocin core structure occurs in protosappanins A,[5] B,[6] C[7] and protosappanins E-1 and E-2,[8] which are isolated from sappan lignum, the dried heartwood of *Caesalpinia sappan* L.

The several synthetic pathways towards benzoxocines include combination of directed ortho-metalation and ring-closing metathesis of allyl 2-allylphenyl ethers,[9] combination of [3+3] cyclization of 1,3-bis(silyl enol ethers) and olefin-metathesis strategy,[10] thiophenol-mediated intramolecular radical cyclization of 2-allylphenyl propargyl ethers,[11] and palladium-catalyzed intramolecular Heck reaction of 2-bromobenzyl 2-vinyl ethers.[12] However, only a few synthetic procedures exist for the preparation of dibenzoxocin derivatives. Dibenz[*b*,*g*]oxocines were prepared from dibenz[*b*,*f*]oxepinmethanol by solvolytic ring expansion and dehydration of oxocinol via the mesylate,[13] and from dimethyl (diphenyl ether)-2,2′-diacetate by use of the Dieckmann reaction under high dilution conditions.[14] This heterocyclic system has been studied for its aromaticity.[15]

Recently, we[16] and others[17] have reported the use of Morita–Baylis–Hillman (MBH) adducts[18] for the syntheses of a variety of heterocyclic compounds via the Friedel–Crafts reaction as the key step. We disclose here a facile synthesis of 7*H*-dibenz[*b*,*g*]oxocin derivatives from the MBH adducts of several 2-phenoxybenzaldehydes with methyl acrylate.

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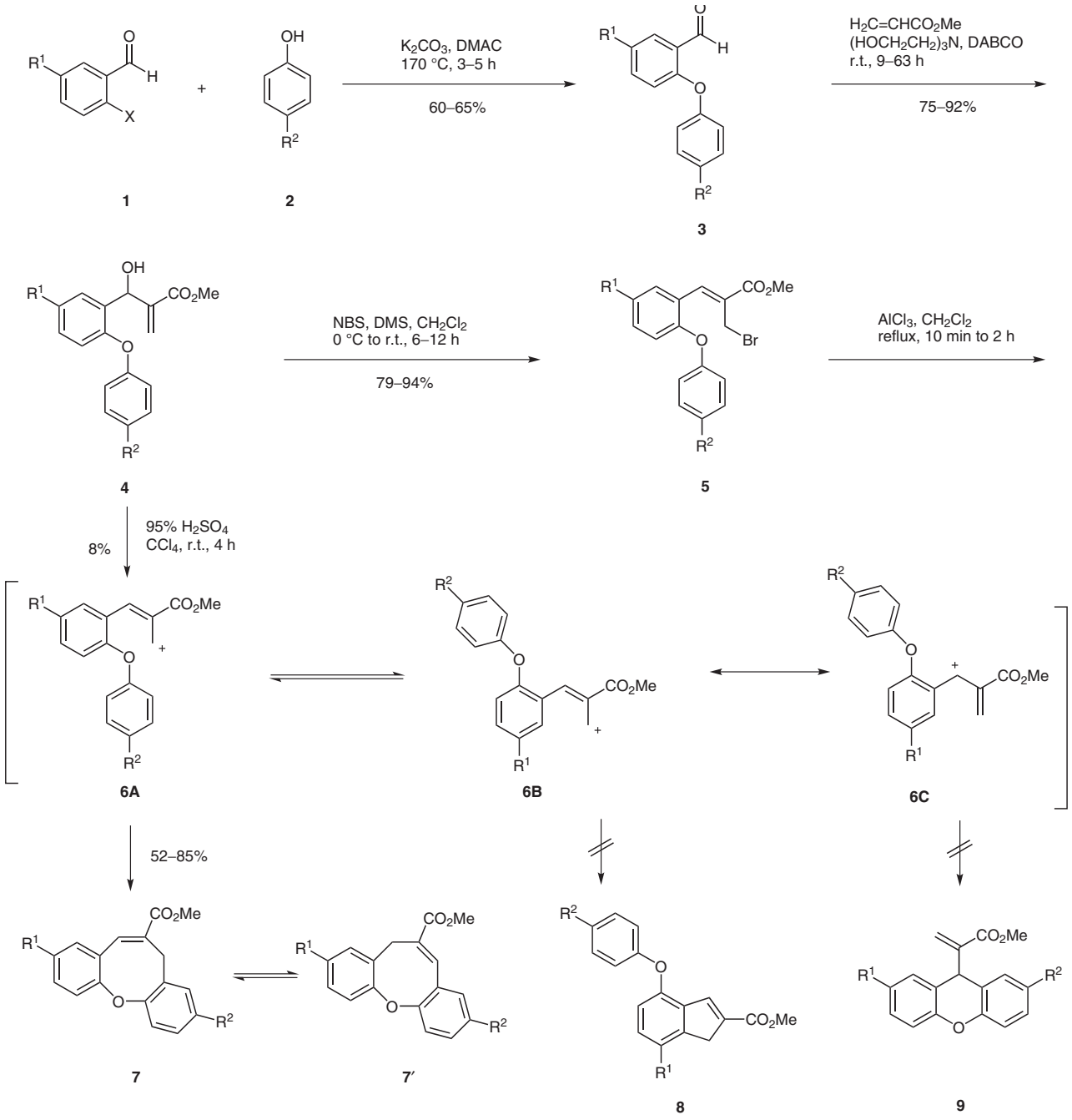
The required key starting material, 2-phenoxybenzaldehydes **3a**–**h** were prepared by the reaction of 2-halobenzaldehydes **1a**–**d** with phenols **2a**–**c** in the presence of anhydrous potassium carbonate in *N*,*N*-dimethylacetamide (DMAC) or hexamethylphosphoramide (HMPA) at 170 °C in 60–65% yields following the earlier reported procedure.[19] The MBH reaction of **3a**–**h** with methyl acrylate in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) and triethanolamine without solvent at room temperature gave the MBH adducts **4a**–**h** in 75–92% yields. The Friedel–Crafts cyclization of MBH adduct **4a** was examined first in carbon tetrachloride at room temperature for four hours using concentrated sulfuric acid leading to a very disappointing yield (8%) of methyl 7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (**7a**).[20] Thus, our attention was turned to explore the Friedel–Crafts cyclization of the MBH allyl bromides **5a**–**h**. The adducts **4a**–**h** were treated with *N*-bromosuccinimide/dimethyl sulfide (NBS/DMS)[21] in dichloromethane to smoothly produce the MBH allyl bromides **5a**–**h** in 79–94% yields. In the $^1$H NMR spectra, the characteristic chemical shift of the methylene and the methine protons of **5a**–**h** were found at $\delta$ = 4.36–4.41 and 7.88–8.06 as singlet, respectively. In all cases, the stereoselectivity was found to be 100% *Z*-selectivity as determined by $^1$H NMR analysis in comparison with literature values.[22] On Friedel–Crafts cyclization of **5a**–**h** with aluminum chloride in dichloromethane at reflux temperature for 10 minutes to two hours, methyl 7*H*-dibenz[*b*,*g*]oxocin-6-carboxylates **7a**–**h** were produced in 52–85% yields (Scheme 1 and Table 1), presumably

**Table 1** Preparation of MBH Adducts **4**, Allyl Bromides **5**, and 7*H*-Dibenz[*b*,*g*]oxocines **7**

| Entry | Product | Time (h) | Yield (%) | Product | Time (h) | Yield (%) | Product | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **4a** | 24 | 90 | **5a** | 7 | 82 | **7a** | 1 | 52 |
| 2 | **4b** | 48 | 92 | **5b** | 6 | 79 | **7b** | 10 min | 64 |
| 3 | **4c** | 63 | 75 | **5c** | 9 | 81 | **7c** | 25 min | 85 |
| 4 | **4d** | 48 | 78 | **5d** | 10 | 94 | **7d** | 1 | 59 |
| 5 | **4e** | 46 | 81 | **5e** | 12 | 88 | **7e** | 1 | 54 |
| 6 | **4f** | 48 | 83 | **5f** | 8 | 92 | **7f** | 1 | 78 |
| 7 | **4g** | 48 | 83 | **5g** | 8 | 84 | **7g** | 1 | 64 |
| 8 | **4h** | 9 | 82 | **5h** | 8 | 85 | **7h** | 2 | 52 |




| 1 | $R^1$ | X | 2 | $R^2$ | 3,4,5,7 | $R^1$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| **a** | H | F | **a** | H | **a** | H | H |
| **b** | MeO | F | **b** | Me | **b** | H | Me |
| **c** | Cl | Cl | **c** | Cl | **c** | H | Cl |
| **d** | F | F | | | **d** | MeO | H |
| | | | | | **e** | MeO | Me |
| | | | | | **f** | MeO | Cl |
| | | | | | **g** | Cl | H |
| | | | | | **h** | F | H |

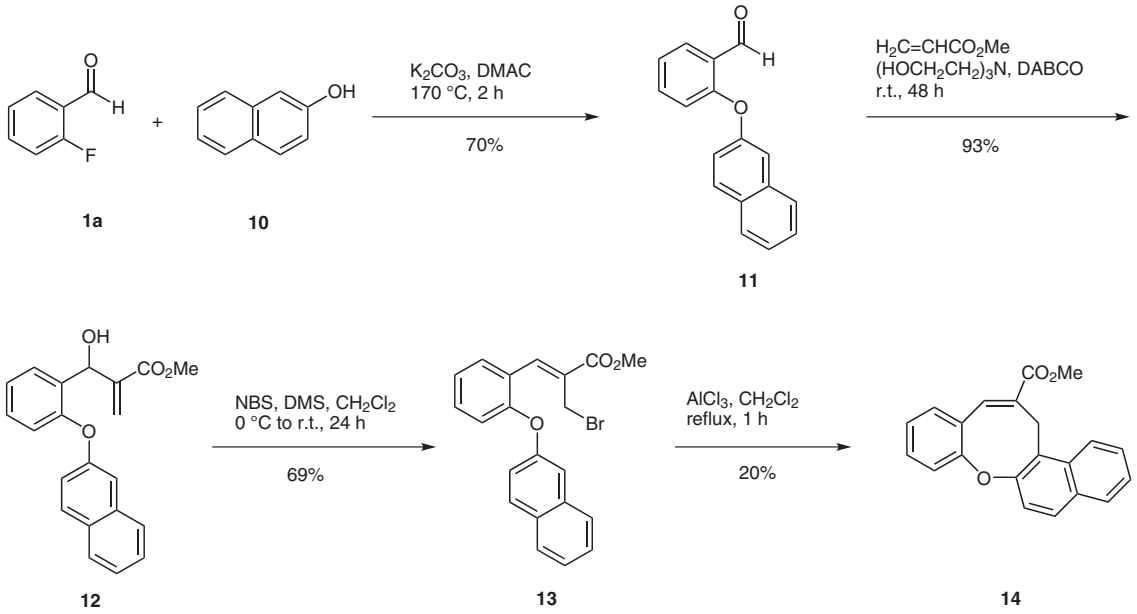
**Scheme 1**

through the resonance stabilized allylic carbocation **6A**. No indenes **8** or dibenzopyrans **9**, which are possible from the other resonance structures **6B** or **6C**, were formed.

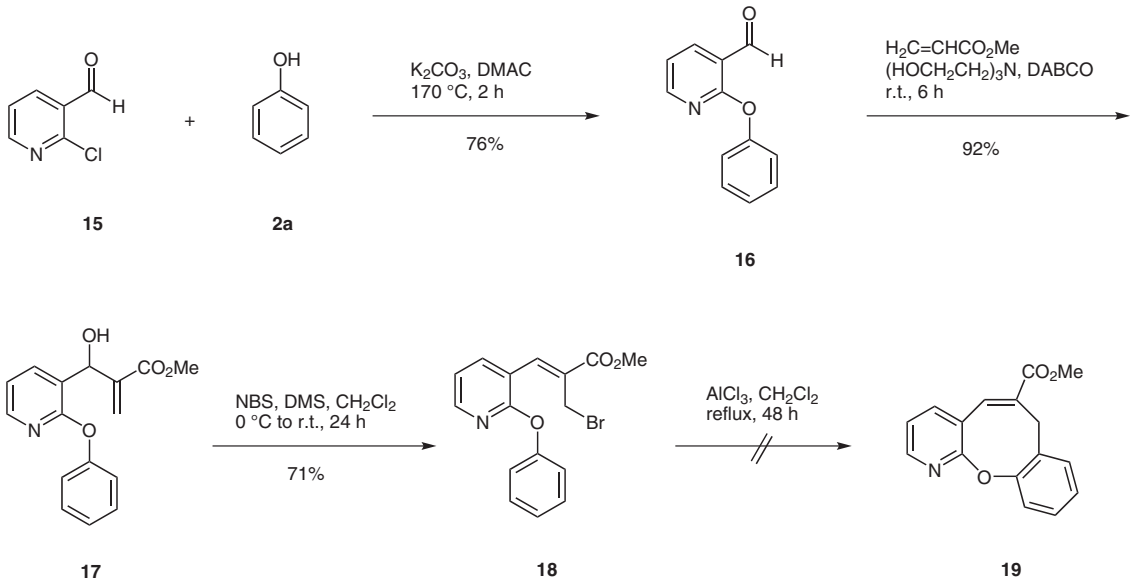
The structures of **7a–h** were elucidated by $^1$H and $^{13}$C NMR and mass spectral analyses. In the $^1$H NMR spectra, the characteristic chemical shift of the methylene proton at C7 was found at δ = 3.50–3.56 and the methine protons

at C5 were observed at δ = 7.77–7.86 as singlet, respectively. In the $^{13}C$ NMR spectra, the chemical shifts of the C5 and C7 were found at δ = 136.3–138.1 and 31.2–31.6, respectively. From the number of carbon signals the possible indene structure **8** could be ruled out easily. The structure **7** was confirmed further by NOE experiment of compound **7d**. Irradiation of the methine proton (δ = 7.83) showed NOE increment of one aromatic proton at C4 (δ = 6.76) and irradiation of the methylene protons (δ = 3.54) showed no NOE increment of the same aromatic proton (δ = 6.76). Instead, NOE increment of other aromatic protons (δ = 7.19–7.24) was observed. From the NOE experiment we can exclude the possible regioisomeric structure **7′**. The EI-MS spectra of **7a**–**h** showed very intensive molecular ion peaks.

We also examined whether MBH allyl bromides of 2-(naphthalen-2-yloxy)benzaldehyde (**11**) and 2-phenoxy-3-pyridinecarboxaldehyde (**16**) might participate in Friedel–Crafts reaction to afford the corresponding oxocin derivatives **14** and **19** (Scheme 2 and Scheme 3). Thus, a solution of 2-fluorobenzaldehyde (**1a**) and 2-naphthol (**10**) in DMAC was heated at 170 °C for two hours in the presence of anhydrous potassium carbonate to produce the aldehyde **11** in 70% yield.[23] Similarly, the use of 2-chloro-3-pyridinecarboxaldehyde (**15**) and phenol (**2a**) afforded **16** in 76% yield.[24] The MBH adducts **12** (93%) and **17** (92%), and the MBH allyl bromides **13** (69%) and **18** (71%) were obtained according to the aforementioned reaction procedures. In the $^{1}H$ NMR spectra, the chemical shift of the methylene protons of **13** and **18**




**Scheme 2**




**Scheme 3**

were observed at δ = 4.42 and 4.38, and the methine protons were found at δ = 8.07 and 8.04 as each singlet, respectively. On Friedel–Crafts cyclization of **13** with aluminum chloride in dichloromethane at reflux temperature for one hour, methyl 14*H*-benz[*b*]naphth[1,2-*g*]oxocin-13-carboxylate (**14**) was produced in low yield (20%).[25] But the treatment of **18** with aluminum chloride under the same reaction condition was unsuccessful. The use of some other well-known Friedel–Crafts Lewis acid catalysts [$FeCl_3$, $SnCl_4$, and $Sc(OTf)_3$], the increase of the amount of Lewis catalysts, and the elevation of temperature using other solvent systems such as dichloroethane, nitrobenzene, and carbon disulfide were also ineffective.[25]

With the intent to introduce more diversity in the products employing this strategy, we carried out Morita–Baylis–Hillman reaction of **3a** with methyl vinyl ketone and cyclohex-2-enone. Unfortunately the corresponding MBH adducts were not produced under the typical reaction conditions such as DABCO, DMAP, DBU or $TiCl_4$ in tetrahydrofuran, 1,4-dioxane, and dimethylformamide solvent systems.

In conclusion, we have successfully elaborated a new synthetic method for methyl 7*H*-dibenz[*b*,*g*]oxocin-6-carboxylates by Friedel–Crafts reaction of readily available bromides of Morita–Baylis–Hillman adducts with aluminum chloride.

Silica gel 60 (70–230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical TLC was carried out on Merck silica gel 60 $F_{254}$ TLC plates. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were obtained using a Thermo Electron Corporation Flash EA 1112 instrument. Low-resolution mass spectra were recorded on a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian 300 spectrometer using $CDCl_3$. All chemical shifts are reported in ppm relative to TMS. The coupling constants (*J*) are expressed in Hz.

The known 2-phenoxybenzaldehyde (**3a**), 2-(*p*-tolyloxy)benzaldehyde (**3b**), 2-(4-chlorophenoxy)benzaldehyde (**3c**), and 5-methoxy-2-phenoxybenzaldehyde (**3d**) were prepared according to the literature procedures.[19] Petroleum ether (PE) used refers to the fraction boiling in the range 30–60 °C.

**2-Aryloxybenzaldehydes 3; General Procedure**

A mixture of 2-halobenzaldehyde **1** (10 mmol), phenol **2** (11 mmol), and $K_2CO_3$ (2.08 g, 15 mmol) in anhyd DMAC (20 mL) was stirred at 170 °C for 3–5 h. After cooling to r.t., $H_2O$ (30 mL) was added and the mixture was extracted with $Et_2O$ (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to afford **3** as an oil.

In the case of **3g**, HMPA was used as a solvent.

**5-Methoxy-2-(*p*-tolyloxy)benzaldehyde (3e)**

Reaction time: 5 h; yield: 65%; yellow oil.

IR ($CH_2Cl_2$): 1690, 1611, 1507, 1487, 1219 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.34 (s, 3 H, $CH_3$), 3.84 (s, 3 H, $OCH_3$), 6.88–6.91 (m, 3 $H_{arom}$), 7.09–7.16 (m, 3 $H_{arom}$), 7.39 (d, *J* = 3.3 Hz, 1 $H_{arom}$), 10.41 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 20.6, 55.8, 109.5, 118.2, 121.0, 123.8, 127.6, 130.4, 133.2, 154.0, 155.4, 155.6, 189.3.

EIMS: *m*/*z* (%) = 242 (72, [$M^+$]), 241 (17), 227 (36), 225 (24), 151 (21), 150 (100), 122 (13), 107 (11).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.05; H, 5.64.

**2-(4-Chlorophenoxy)-5-methoxybenzaldehyde (3f)**

Reaction time: 5 h; yield: 62%; yellow oil.

IR ($CH_2Cl_2$): 1691, 1608, 1589, 1494, 1278, 1209 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.86 (s, 3 H, $OCH_3$), 6.90–6.95 (m, 3 $H_{arom}$), 7.12–7.16 (m, 1 $H_{arom}$), 7.28–7.33 (m, 2 $H_{arom}$), 7.40 (d, *J* = 3.0 Hz, 1 $H_{arom}$), 10.35 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 55.8, 110.0, 119.2, 121.5, 123.8, 128.0, 128.6, 129.9, 152.9, 156.2, 156.5, 188.9.

EIMS: *m*/*z* (%) = 264 (9), 262 (27, [$M^+$]), 151 (14), 150 (100), 122 (11), 107 (10).

Anal. Calcd for $C_{14}H_{11}ClO_3$: C, 64.01; H, 4.22. Found: C, 63.84; H, 4.38.

**5-Chloro-2-phenoxybenzaldehyde (3g)**

Reaction time: 3 h; yield: 60%; reddish oil.

IR ($CH_2Cl_2$): 1688, 1606, 1482, 1393, 1219 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 6.84–6.87 (m, 1 $H_{arom}$), 7.05–7.09 (m, 2 $H_{arom}$), 7.18–7.24 (m, 1 $H_{arom}$), 7.38–7.47 (m, 3 $H_{arom}$), 7.89–7.90 (m, 1 $H_{arom}$), 10.46 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 119.4, 119.8, 124.7, 127.6, 128.0, 128.9, 130.2, 135.4, 155.9, 158.5, 188.1.

EIMS: *m*/*z* (%) = 234 (10), 233 (38), 232 (32, [$M^+$]), 231 (100), 215 (13), 168 (17), 155 (12), 154 (18), 139 (16), 126 (12).

Anal. Calcd for $C_{13}H_9ClO_2$: C, 67.11; H, 3.90. Found: C, 67.33; H, 4.13.

**5-Fluoro-2-phenoxybenzaldehyde (3h)**

Reaction time: 3 h; yield: 70%; yellow oil.

IR ($CH_2Cl_2$): 1691, 1613, 1590, 1480, 1426, 1394, 1262, 1247 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 6.93 (dd, *J* = 9.1, 4.1 Hz, 1 $H_{arom}$), 7.02–7.05 (m, 2 $H_{arom}$), 7.15–7.26 (m, 2 $H_{arom}$), 7.36–7.41 (m, 2 $H_{arom}$), 7.59 (dd, *J* = 8.0, 3.0 Hz, 1 $H_{arom}$), 10.42 (d, *J* = 3.0 Hz, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 113.9 (d, *J* = 23.7 Hz), 118.7, 120.8 (d, *J* = 7.4 Hz), 122.7 (d, *J* = 24.2 Hz), 124.2, 128.0 (d, *J* = 6.3 Hz), 130.1, 155.7 (d, *J* = 2.3 Hz), 156.8, 158.4 (d, *J* = 244.9 Hz), 188.1 (d, *J* = 1.4 Hz).

EIMS: *m*/*z* (%) = 216 (28, [$M^+$]), 215 (100), 199 (11), 159 (12).

Anal. Calcd for $C_{13}H_9FO_2$: C, 72.22; H, 4.20. Found: C, 70.08; H, 3.99.

**Morita–Baylis–Hillman Adducts 4; General Procedure**

A mixture of 2-phenoxybenzaldehyde **3** (5 mmol), methyl acrylate (1.35 mL, 15 mmol), DABCO (0.56 g, 5 mmol), and triethanolamine (0.56 g, 4 mmol) was stirred at r.t. for 9–63 h. The reaction mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to afford **4** as an oil.

**Methyl 3-Hydroxy-2-methylene-3-[(2-phenoxy)phenyl]propanoate (4a)**
Reaction time: 24 h; yield: 90%; yellow oil.

IR ($CH_2Cl_2$): 3438, 1721, 1630, 1583, 1485 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.38 (d, *J* = 5.8 Hz, 1 H, OH), 3.72 (s, 3 H, $OCH_3$), 5.78 (s, 1 H, CH), 5.94 (d, *J* = 5.8 Hz, 1 H, CH), 6.32 (s, 1 H, CH), 6.82–6.85 (m, 1 $H_{arom}$), 6.95–6.98 (m, 2 $H_{arom}$), 7.07–7.35 (m, 5 $H_{arom}$), 7.50–7.54 (m, 1 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 51.9, 68.0, 118.4, 118.6, 123.3, 123.6, 126.3, 128.0, 129.0, 129.7, 131.9, 141.0, 154.2, 156.9, 166.9.

EIMS: *m*/*z* (%) 284 (1, [$M^+$]), 283 (3), 267 (15), 252 (15), 223 (58), 205 (23), 197 (56), 191 (48), 181 (100), 121 (37).

Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.56; H, 5.40.

**Methyl 3-Hydroxy-2-methylene-3-[2-(*p*-tolyloxy)phenyl]propanoate (4b)**
Reaction time: 48 h; yield: 92%; yellow oil.

IR ($CH_2Cl_2$): 3444, 1722, 1630, 1506, 1485 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.33 (s, 3 H, $CH_3$), 3.39 (d, *J* = 6.1 Hz, 1 H, OH), 3.73 (s, 1 H, $OCH_3$), 5.79 (s, 1 H, CH), 5.95 (d, *J* = 5.5 Hz, 1 H, CH), 6.33 (s, 1 H, CH), 6.78–6.89 (m, 3 $H_{arom}$), 7.06–7.24 (m, 4 $H_{arom}$), 7.48–7.52 (m, 1 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 20.7, 51.9, 68.2, 117.8, 118.9, 123.2, 126.3, 128.0, 128.9, 130.2, 131.5, 133.0, 141.1, 154.4, 154.8, 167.0.

EIMS: *m*/*z* (%) = 298 (1, [$M^+$]), 297 (2), 281 (8), 266 (13), 238 (15), 221 (19), 211 (40), 195 (100), 177 (13), 121 (66)

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.36; H, 6.27.

**Methyl 3-[2-(4-Chlorophenoxy)phenyl]-3-hydroxy-2-methylenepropanoate (4c)**
Reaction time: 63 h; yield: 75%; yellow oil.

IR ($CH_2Cl_2$): 3415, 1719, 1630, 1582, 1483 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.27 (d, *J* = 5.8 Hz, 1 H, OH), 3.73 (s, 3 H, $OCH_3$), 5.76 (s, 1 H, CH), 5.91 (d, *J* = 5.8 Hz, 1 H, CH), 6.32 (s, 1 H, CH), 6.74–6.92 (m, 3 $H_{arom}$), 7.16–7.29 (m, 4 $H_{arom}$), 7.52–7.55 (m, 1 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 52.0, 67.9, 118.6, 119.8, 124.1, 126.5, 128.1, 129.2, 129.4, 129.7, 132.0, 140.9, 153.9, 155.6, 166.9.

EIMS: *m*/*z* (%) = 318 (2, [$M^+$]), 317 (6), 301 (5), 286 (17), 257 (35), 215 (100), 205 (42), 191 (59), 121 (78).

Anal. Calcd for $C_{17}H_{15}ClO_4$: C, 64.06; H, 4.74. Found: C, 63.85; H, 4.59.

**Methyl 3-Hydroxy-3-[(5-methoxy-2-phenoxy)phenyl]-2-methylenepropanoate (4d)**
Reaction time: 48 h; yield: 78%; yellow oil.

IR ($CH_2Cl_2$): 3437, 1721, 1631, 1589, 1486 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.31 (d, *J* = 5.8 Hz, 1 H, OH), 3.72 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 5.75 (s, 1 H, CH), 5.84 (d, *J* = 5.5 Hz, 1 H, CH), 6.31 (s, 1 H, CH), 6.79–6.98 (m, 4 $H_{arom}$), 7.01–7.08 (m, 2 $H_{arom}$), 7.26–7.32 (m, 2 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 52.0, 55.6, 67.9, 112.8, 114.5, 117.3, 120.9, 122.6, 126.6, 129.6, 133.6, 140.8, 147.0, 156.1, 158.0, 166.9.

EIMS: *m*/*z* (%) = 314 (24, [$M^+$]), 282 (22), 253 (18), 227 (18), 221 (100), 211 (45), 189 (16), 151 (30).

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.48; H, 5.62.

**Methyl 3-Hydroxy-3-[5-methoxy-2-(*p*-tolyloxy)phenyl]-2-methylenepropanoate (4e)**
Reaction time: 46 h; yield: 81%; yellow oil.

IR ($CH_2Cl_2$): 3437, 1721, 1612, 1490 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.31 (s, 3 H, $CH_3$), 3.32 (d, *J* = 5.8 Hz, 1 H, OH), 3.73 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$), 5.75 (s, 1 H, CH), 5.85 (d, *J* = 5.5 Hz, 1 H, CH), 6.31 (s, 1 H, CH), 6.76–6.83 (m, 4 $H_{arom}$), 7.05–7.10 (m, 3 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 20.6, 52.0, 55.6, 68.0, 112.7, 114.5, 117.5, 120.4, 126.5, 130.1, 132.1, 133.3, 140.8, 147.6, 155.7, 155.8, 166.9.

EIMS: *m*/*z* (%) 328 (32, [$M^+$]), 296 (17), 267 (14), 225 (46), 221 (100), 151 (41).

Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.28; H, 6.05.

**Methyl 3-[2-(4-Chlorophenoxy)-5-methoxyphenyl]-3-hydroxy-2-methylenepropanoate (4f)**
Reaction time: 48 h; yield: 83%; yellow oil.

IR ($CH_2Cl_2$): 3461, 1720, 1634, 1483 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.23 (d, *J* = 5.5 Hz, 1 H, OH), 3.73 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 5.73 (s, 1 H, CH), 5.80 (d, *J* = 5.5 Hz, 1 H, CH), 6.30 (s, 1 H, CH), 6.79–6.86 (m, 4 $H_{arom}$), 7.07–7.08 (m, 1 $H_{arom}$), 7.21–7.25 (m, 2 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 52.0, 55.6, 67.8, 112.9, 114.7, 118.5, 121.0, 126.7, 127.5, 129.6, 133.8, 140.8, 146.6, 156.4, 156.7, 166.9.

EIMS: *m*/*z* (%) = 350 (10), 348 (29, [$M^+$]), 318 (8), 316 (21), 289 (7), 287 (14), 247 (13), 245 (35), 221 (100), 189 (34), 151 (39).

Anal. Calcd for $C_{18}H_{17}ClO_5$: C, 61.99; H, 4.91. Found: C, 60.77; H, 4.83.

**Methyl 3-[(5-Chloro-2-phenoxy)phenyl]-3-hydroxy-2-methylenepropanoate (4g)**
Reaction time: 48 h; yield: 83%; reddish oil.

IR ($CH_2Cl_2$): 3438, 1720, 1630, 1588, 1476 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.35 (d, *J* = 5.8 Hz, 1 H, OH), 3.75 (s, 3 H, $OCH_3$), 5.77 (s, 1 H, CH), 5.90 (d, *J* = 5.5 Hz, 1 H, CH), 6.34 (s, 1 H, CH), 6.75–6.77 (m, 1 $H_{arom}$), 6.93–6.96 (m, 2 $H_{arom}$), 7.09–7.21 (m, 2 $H_{arom}$), 7.31–7.37 (m, 2 $H_{arom}$), 7.52–7.53 (m, 1 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 52.1, 67.7, 118.7, 119.5, 123.7, 126.8, 128.0, 128.7, 128.9, 129.9, 133.6, 140.5, 152.8, 156.5, 166.8.

EIMS: *m*/*z* (%) = 318 (1, [$M^+$]), 317 (3), 286 (15), 285 (10), 259 (14), 258 (12), 257 (31), 227 (32), 226 (13), 225 (100), 223 (57), 217 (31), 215 (92), 205 (27), 157 (21), 155 (61).

Anal. Calcd for $C_{17}H_{15}ClO_4$: C, 64.06; H, 4.74. Found: C, 64.18; H, 4.51.

**Methyl 3-[(5-Fluoro-2-phenoxy)phenyl]-3-hydroxy-2-methylenepropanoate (4h)**
Reaction time: 9 h; yield: 82%; yellow oil.

IR ($CH_2Cl_2$): 3449, 1720, 1631, 1589, 1484 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.36 (d, *J* = 5.8 Hz, 1 H, OH), 3.74 (s, 3 H, $OCH_3$), 5.75 (s, 1 H, CH), 5.86 (d, *J* = 5.8 Hz, 1 H, CH), 6.32 (s, 1 H, CH), 6.80–6.85 (m, 1 $H_{arom}$), 6.89–6.97 (m, 3 $H_{arom}$), 7.06–7.11 (m, 1 $H_{arom}$), 7.25–7.35 (m, 3 $H_{arom}$).

$^{13}C$ NMR ($CDCl_3$): δ = 52.0, 67.7, 114.8 (d, *J* = 24.5 Hz), 115.6 (d, *J* = 23.7 Hz), 118.0, 120.3 (d, *J* = 8.3 Hz), 123.3, 126.8, 129.8, 134.3 (d, *J* = 7.1 Hz), 140.5, 149.7 (d, *J* = 2.6 Hz), 157.3, 158.9 (d, *J* = 242.7 Hz), 166.8.

EIMS: *m*/*z* (%) = 302 (2, [$M^+$]), 301 (2), 285 (13), 270 (17), 241 (56), 226 (21), 215 (40), 209 (64), 199 (100), 139 (37).

Anal. Calcd for $C_{17}H_{15}FO_4$: C, 67.54; H, 5.00. Found: C, 67.29; H, 4.84.

**Morita–Baylis–Hillman Allyl Bromides 5; General Procedure**

To a mixture of NBS (0.98 g, 5.5 mmol) and DMS (0.56 mL, 7.5 mmol) in $CH_2Cl_2$ (10 mL) was added the MBH adduct **4** (5 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 6–12 h. The mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (3:1) to afford **5** as a solid.

**(*Z*)-Methyl 2-Bromomethyl-3-[(2-phenoxy)phenyl]propenoate (5a)**

Reaction time: 7 h; yield: 82%; white solid; mp 76–77 °C ($Et_2O$–PE).

IR (KBr): 1717, 1626, 1480, 1268 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.85 (s, 3 H, $OCH_3$), 4.40 (s, 2 H, $CH_2$), 6.86–6.88 (m, 1 $H_{arom}$), 6.97–7.02 (m, 2 $H_{arom}$), 7.11–7.24 (m, 2 $H_{arom}$), 7.31–7.39 (m, 3 $H_{arom}$), 7.78–7.81 (m, 1 $H_{arom}$), 8.04 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 27.1, 52.4, 118.0, 119.3, 123.3, 123.9, 125.6, 129.3, 129.8, 129.9, 131.1, 138.1, 156.1, 156.5, 166.5.

EIMS: *m*/*z* (%) = 267 (3), 207 (11), 182 (15), 181 (100).

Anal. Calcd for $C_{17}H_{15}BrO_3$: C, 58.81; H, 4.35. Found: C, 58.70; H, 4.26.

**(*Z*)-Methyl 2-Bromomethyl-3-[2-(*p*-tolyloxy)phenyl]propenoate (5b)**

Reaction time: 6 h; yield: 79%; white solid; mp 78–79 °C ($Et_2O$–PE).

IR (KBr): 1717, 1625, 1505, 1480, 1238 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.34 (s, 3 H, $CH_3$), 3.85 (s, 3 H, $OCH_3$), 4.41 (s, 2 H, $CH_2$), 6.82–6.91 (m, 3 $H_{arom}$), 7.14–7.20 (m, 3 $H_{arom}$), 7.29–7.34 (m, 1 $H_{arom}$), 7.77–7.80 (m, 1 $H_{arom}$), 8.06 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 20.7, 27.2, 52.4, 117.4, 119.4, 122.9, 125.3, 129.2, 129.7, 130.4, 131.0, 133.6, 138.3, 154.0, 156.6, 166.5.

EIMS: *m*/*z* (%) = 281 (4), 221 (6), 196 (16), 195 (100).

Anal. Calcd for $C_{18}H_{17}BrO_3$: C, 59.85; H, 4.74. Found: C, 59.73; H, 4.62.

**(*Z*)-Methyl 2-Bromomethyl-3-[2-(4-chlorophenoxy)phenyl]propenoate (5c)**

Reaction time: 9 h; yield: 81%; white solid; mp 80–81 °C ($Et_2O$–PE).

IR (KBr): 1717, 1626, 1481, 1238 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.86 (s, 3 H, $OCH_3$), 4.38 (s, 2 H, $CH_2$), 6.87–6.94 (m, 3 $H_{arom}$), 7.21–7.39 (m, 4 $H_{arom}$), 7.78–7.81 (m, 1 $H_{arom}$), 7.98 (s, 1 H, CH)

$^{13}C$ NMR ($CDCl_3$): δ = 26.8, 52.5, 118.1, 120.3, 123.8, 125.8, 128.9, 129.6, 129.9 (2 peaks), 131.2, 137.7, 155.1, 155.6, 166.4.

EIMS: *m*/*z* (%) = 303 (3), 301 (7), 241 (10), 217 (35), 216 (15), 215 (100), 206 (10).

Anal. Calcd for $C_{17}H_{14}BrClO_3$: C, 53.50; H, 3.70. Found: C, 53.35; H, 3.54.

**(*Z*)-Methyl 2-Bromomethyl-3-[(5-methoxy-2-phenoxy)phenyl]propenoate (5d)**

Reaction time: 10 h; yield: 94%; yellow solid; mp 103–104 °C ($Et_2O$–PE).

IR (KBr): 1718, 1626, 1484, 1214 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.83 (s, 3 H, $CH_3$), 3.88 (s, 3 H, $OCH_3$), 4.41 (s, 2 H, $CH_2$), 6.89–6.95 (m, 4 $H_{arom}$), 7.05–7.10 (m, 1 $H_{arom}$), 7.27–7.33 (m, 2 $H_{arom}$), 7.38–7.39 (m, 1 $H_{arom}$), 7.94 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 27.2, 52.5, 55.9, 113.3, 117.7, 117.8, 120.8, 123.0, 127.0, 129.6, 129.8, 138.2, 149.0, 155.6, 157.7, 166.3.

EIMS: *m*/*z* (%) = 285 (9), 283 (8), 212 (16), 211 (100), 205 (5).

Anal. Calcd for $C_{18}H_{17}BrO_4$: C, 57.31; H, 4.54. Found: C, 57.08; H, 4.32.

**(*Z*)-Methyl 2-Bromomethyl-3-[5-methoxy-2-(*p*-tolyloxy)phenyl]propenoate (5e)**

Reaction time: 12 h; yield: 88%; yellow solid; mp 84–85 °C ($Et_2O$–PE).

IR (KBr): 1718, 1626, 1488, 1216 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.32 (s, 3 H, $CH_3$), 3.83 (s, 3 H, $OCH_3$), 3.87 (s, 3 H, $OCH_3$), 4.41 (s, 2 H, $CH_2$), 6.79–6.93 (m, 4 $H_{arom}$), 7.10 (d, *J* = 8.3 Hz, 2 $H_{arom}$), 7.38 (d, *J* = 3.0 Hz, 1 $H_{arom}$), 7.97 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 20.6, 27.3, 52.4, 55.9, 113.3, 117.7, 118.0, 120.2, 126.6, 129.4, 130.2, 132.7, 138.4, 149.6, 155.3, 155.4, 166.4.

EIMS: *m*/*z* (%) = 311 (5), 285 (5), 283 (5), 251 (5), 226 (17), 225 (100).

Anal. Calcd for $C_{19}H_{19}BrO_4$: C, 58.33; H, 4.89. Found: C, 58.49; H, 5.13.

**(*Z*)-Methyl 2-Bromomethyl-3-[2-(4-chlorophenoxy)-5-methoxyphenyl]propenoate (5f)**

Reaction time: 8 h; yield: 92%; yellow solid; mp 91–92 °C ($Et_2O$–PE).

IR (KBr): 1718, 1624, 1482, 1223 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.84 (s, 3 H, $OCH_3$), 3.88 (s, 3 H, $OCH_3$), 4.39 (s, 2 H, $CH_2$), 6.81–6.97 (m, 4 $H_{arom}$), 7.23–7.28 (m, 2 $H_{arom}$), 7.37–7.38 (m, 1 $H_{arom}$), 7.88 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 26.9, 52.5, 55.9, 113.5, 117.7, 118.9, 120.9, 127.1, 128.0, 129.7, 129.9, 137.8, 148.5, 156.0, 156.4, 166.2.

EIMS: *m*/*z* (%) = 285 (21), 283 (22), 247 (33), 246 (16), 245 (100), 205 (12), 204 (16).

Anal. Calcd for $C_{18}H_{16}BrClO_4$: C, 52.52; H, 3.92. Found: C, 52.44; H, 3.76.

**(*Z*)-Methyl 2-Bromomethyl-3-[(5-chloro-2-phenoxy)phenyl]propenoate (5g)**

Reaction time: 8 h; yield: 84%; yellow solid; mp 89–90 °C ($Et_2O$–PE).

IR (KBr): 1719, 1627, 1588, 1471, 1241 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 3.85 (s, 3 H, $OCH_3$), 4.36 (s, 2 H, $CH_2$), 6.80–6.83 (m, 1 $H_{arom}$), 6.96–7.00 (m, 2 $H_{arom}$), 7.13–7.19 (m, 1 $H_{arom}$), 7.27–7.40 (m, 3 $H_{arom}$), 7.76–7.77 (m, 1 $H_{arom}$), 7.93 (s, 1 H, CH).

$^{13}C$ NMR ($CDCl_3$): δ = 26.2, 52.6, 119.1, 119.3, 124.3, 126.9, 128.3, 129.3, 130.0, 130.5, 130.8, 136.6, 154.7, 156.1, 166.1.

EIMS: *m*/*z* (%) = 301 (4), 217 (33), 216 (15), 215 (100).

Anal. Calcd for $C_{17}H_{14}BrClO_3$: C, 53.50; H, 3.70. Found: C, 53.34; H, 3.68.

**(*Z*)-Methyl 2-Bromomethyl-3-[(5-fluoro-2-phenoxy)phenyl]propenoate (5h)**

Reaction time: 8 h; yield: 85%; yellow solid; mp 79–80 °C ($Et_2O$–PE).

IR (KBr): 1719, 1626, 1589, 1479, 1211 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.84 (s, 3 H, $OCH_3$), 4.36 (s, 2 H, $CH_2$), 6.86–6.96 (m, 3 $H_{arom}$), 7.02–7.15 (m, 2 $H_{arom}$), 7.30–7.37 (m, 2 $H_{arom}$), 7.51–7.55 (m, 1 $H_{arom}$), 7.91 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 26.1, 52.5, 116.1 (d, *J* = 24.5 Hz), 117.7 (d, *J* = 23.4 Hz), 118.6, 120.0 (d, *J* = 8.3 Hz), 123.8, 127.1, 127.2, 129.9, 130.5, 136.7, 151.8, 158.4 (d, *J* = 221.9 Hz), 166.1.

EIMS: *m*/*z* (%) = 285 (4), 225 (10), 200 (18), 199 (100).

Anal. Calcd for $C_{17}H_{14}BrFO_3$: C, 55.91; H, 3.86. Found: C, 55.85; H, 3.72.

**Methyl 7*H*-Dibenz[*b*,*g*]oxocin-6-carboxylates 7; General Procedure**

To a stirred suspension of $AlCl_3$ (0.54 g, 4 mmol) in $CH_2Cl_2$ (20 mL) was added allyl bromide **5** (2 mmol) at r.t. The reaction mixture was heated at reflux temperature for 10 min to 2 h. The mixture was quenched with $H_2O$ (20 mL), and then extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (3:1) to give **7** as a solid.

**Methyl 7*H*-Dibenz[*b*,*g*]oxocin-6-carboxylate (7a)**

Reaction time: 1 h; yield: 52%; white solid; mp 89–90 °C ($Et_2O$–PE).

IR (KBr): 1713, 1632, 1480, 1251 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.56 (s, 2 H, $CH_2$), 3.79 (s, 3 H, $OCH_3$), 7.05–7.12 (m, 1 $H_{arom}$), 7.17–7.28 (m, 6 $H_{arom}$), 7.33–7.39 (m, 1 $H_{arom}$), 7.86 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.4, 52.2, 121.3, 123.1, 124.5, 125.0, 127.6, 128.1, 128.9, 130.6, 131.2, 131.3, 131.4, 137.8, 153.4, 156.5, 167.3.

EIMS: *m*/*z* (%) = 266 (61, [$M^+$]), 234 (74), 205 (100), 181 (65), 178 (56), 176 (20), 152 (19).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.46; H, 5.24.

**Methyl 9-Methyl-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7b)**

Reaction time: 10 min; yield: 64%; white solid; mp 96–97 °C ($Et_2O$–PE).

IR (KBr): 1714, 1632, 1481, 1205 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, $CH_3$), 3.52 (s, 2 H, $CH_2$), 3.80 (s, 3 H, $OCH_3$), 7.01–7.04 (m, 2 $H_{arom}$), 7.11–7.27 (m, 4 $H_{arom}$), 7.32–7.38 (m, 1 $H_{arom}$), 7.84 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 20.6, 31.3, 52.2, 121.0, 123.0, 124.8, 127.4, 128.5, 129.1, 130.6, 131.2, 131.4, 131.8, 134.0, 137.8, 153.8, 154.5, 167.4.

EIMS: *m*/*z* (%) = 280 (97, [$M^+$]), 265 (27), 249 (24), 248 (69), 221 (100), 205 (78), 195 (85), 189 (29), 178 (58).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.01; H, 5.68.

**Methyl 9-Chloro-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7c)**

Reaction time: 25 min; yield: 85%; white solid; mp 96–97 °C ($Et_2O$–PE).

IR (KBr): 1712, 1633, 1474, 1251 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.51 (s, 2 H, $CH_2$), 3.81 (s, 3 H, $OCH_3$), 7.14–7.28 (m, 6 $H_{arom}$), 7.34–7.40 (m, 1 $H_{arom}$), 7.86 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.2, 52.3, 122.6, 122.9, 125.2, 127.9, 129.1, 129.2, 129.3, 130.8 (2 peaks), 131.0, 131.1, 138.1, 153.2, 155.1, 167.1.

EIMS: *m*/*z* (%) = 302 (6), 300 (19, [$M^+$]), 283 (12), 282 (15), 281 (50), 268 (25), 241 (20), 207 (100), 205 (42).

Anal. Calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36. Found: C, 67.69; H, 4.22.

**Methyl 3-Methoxy-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7d)**

Reaction time: 1 h; yield: 59%; white solid; mp 124–125 °C ($Et_2O$–PE).

IR (KBr): 1712, 1634, 1481, 1243 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.54 (s, 2 H, $CH_2$), 3.79 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$), 6.76 (d, *J* = 3.0 Hz, 1 $H_{arom}$), 6.87 (dd, *J* = 8.8, 3.0 Hz, 1 $H_{arom}$), 7.03–7.09 (m, 1 $H_{arom}$), 7.14 (d, *J* = 8.8 Hz, 1 $H_{arom}$), 7.19–7.24 (m, 3 $H_{arom}$), 7.83 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.6, 52.1, 55.6, 112.8, 115.8, 121.2, 123.8, 124.3, 127.1, 128.1, 131.4, 131.6, 132.1, 137.7, 146.9, 156.3, 156.7, 167.2.

EIMS: *m*/*z* (%) = 296 (77, [$M^+$]), 264 (38), 237 (100), 235 (45), 221 (38), 194 (42), 165 (46).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.84; H, 5.38.

**Methyl 3-Methoxy-9-methyl-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7e)**

Reaction time: 1 h; yield: 54%; white solid; mp 107–108 °C ($Et_2O$–PE).

IR (KBr): 1713, 1633, 1484, 1244, 1215 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.29 (s, 3 H, $CH_3$), 3.51 (s, 2 H, $CH_2$), 3.79 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$), 6.75 (d, *J* = 3.0 Hz, 1 $H_{arom}$), 6.86 (dd, *J* = 8.8, 3.0 Hz, 1 $H_{arom}$), 7.03–7.11 (m, 3 $H_{arom}$), 7.13 (d, *J* = 8.8 Hz, 1 $H_{arom}$), 7.81 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 20.6, 31.5, 52.1, 55.6, 112.9, 115.8, 120.9, 123.7, 126.9, 128.5, 131.5, 132.0 (2 peaks), 133.8, 137.7, 147.2, 154.6, 156.2, 167.3.

EIMS: *m*/*z* (%) = 310 (100, [$M^+$]), 295 (11), 278 (45), 263 (39), 251 (81), 235 (67).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.47; H, 5.98.

**Methyl 9-Chloro-3-methoxy-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7f)**

Reaction time: 1 h; yield: 78%; white solid; mp 108–109 °C ($Et_2O$–PE).

IR (KBr): 1713, 1634, 1475, 1243 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.50 (s, 2 H, $CH_2$), 3.80 (s, 3 H, $OCH_3$), 6.76 (d, *J* = 3.0 Hz, 1 $H_{arom}$), 6.88 (dd, *J* = 8.8, 3.0 Hz, 1 $H_{arom}$), 7.11 (d, *J* = 8.8 Hz, 1 $H_{arom}$), 7.12–7.22 (m, 3 $H_{arom}$), 7.83 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.3, 52.2, 55.6, 112.9, 116.0, 122.4, 123.6, 127.9, 128.8, 129.0, 130.9, 131.1, 131.9, 138.0, 146.6, 155.3, 156.5, 166.9.

EIMS: *m*/*z* (%) = 332 (34), 330 (88, [$M^+$]), 300 (21), 298 (83), 283 (48), 271 (100), 270 (54), 255 (77).

Anal. Calcd for $C_{18}H_{15}ClO_4$: C, 65.36; H, 4.57. Found: C, 65.52; H, 4.72.

**Methyl 3-Chloro-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7g)**

Reaction time: 2 h; yield: 64%; white solid; mp 100–102 °C ($Et_2O$–PE).

IR (KBr): 1715, 1633, 1473, 1250 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.54 (s, 2 H, $CH_2$), 3.79 (s, 3 H, $OCH_3$), 7.06–7.33 (m, 7 $H_{arom}$), 7.77 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.4, 52.3, 121.3, 124.4, 124.7, 127.1, 128.2, 128.4, 130.4, 131.6, 132.3, 132.9, 134.2, 136.3, 151.8, 156.3, 166.9.

EIMS: *m*/*z* (%) 302 (17), 300 (41, [M$^+$]), 270 (16), 268 (46), 205 (100), 176 (51).

Anal. Calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36. Found: C, 67.64; H, 4.12.

**Methyl 3-Fluoro-7*H*-dibenz[*b*,*g*]oxocin-6-carboxylate (7h)**
Reaction time: 2 h; yield: 52%; white solid; mp 99–100 °C ($Et_2O$–PE).

IR (KBr): 1715, 1634, 1480, 1237 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.54 (s, 2 H, $CH_2$), 3.79 (s, 3 H, $OCH_3$), 6.94–7.11 (m, 3 $H_{arom}$), 7.17–7.26 (m, 4 $H_{arom}$), 7.79 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 31.5, 52.2, 114.8 (d, *J* = 23.7 Hz), 117.0 (d, *J* = 23.4 Hz), 121.3, 124.3 (d, *J* = 8.8 Hz), 124.6, 126.9, 128.2, 131.6, 132.1, 132.9 (d, *J* = 8.6 Hz), 136.5 (d, *J* = 1.7 Hz), 149.2 (d, *J* = 2.6 Hz), 156.4, 159.1 (d, *J* = 244.9 Hz), 166.9.

EIMS: *m*/*z* (%) = 284 (74, [M$^+$]), 253 (85), 225 (100), 223 (87).

Anal. Calcd for $C_{17}H_{13}FO_3$: C, 71.82; H, 4.61. Found: C, 71.61; H, 4.45.

**2-(Naphthalen-2-yloxy)benzaldehyde (11)[23a]**
A mixture of 2-fluorobenzaldehyde (**1a**; 1.24 g, 10 mmol), 2-naphthol (**10**; 1.59 g, 11 mmol), and $K_2CO_3$ (2.07 g, 15 mmol) in anhyd DMAC (20 mL) was stirred at 170 °C for 2 h. After cooling to r.t., $H_2O$ (30 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to afford **11** (1.74 g, 70%) as a yellow oil.

IR ($CH_2Cl_2$): 1691, 1599, 1509, 1455, 1246, 1225 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 6.95 (d, *J* = 8.5 Hz, 1 $H_{arom}$), 7.20–7.32 (m, 2 $H_{arom}$), 7.37–7.38 (m, 1 $H_{arom}$), 7.43–7.56 (m, 3 $H_{arom}$), 7.72–7.75 (m, 1 $H_{arom}$), 7.84–7.91 (m, 2 $H_{arom}$), 7.98 (dd, *J* = 7.6, 1.8 Hz), 10.56 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 115.1, 118.8, 119.8, 123.5, 125.3, 126.8, 127.0, 127.2, 127.8, 128.5, 130.3, 130.5, 134.2, 135.8, 154.2, 159.9, 189.4.

EIMS: *m*/*z* (%) = 248 (43, [M$^+$]), 247 (100), 231 (13), 191 (19), 189 (17), 128 (20).

**Methyl 3-Hydroxy-2-methylene-3-[2-(naphthalen-2-yloxy)phenyl]propanoate (12)**
A mixture of **11** (1.24 g, 5 mmol), methyl acrylate (1.35 mL, 15 mmol), DABCO (0.56 g, 5 mmol), and triethanolamine (0.56 g, 4 mmol) was stirred at r.t. for 48 h. The reaction mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to afford **12** (1.55 g, 93%) as a colorless oil.

IR ($CH_2Cl_2$): 3438, 1721, 1630, 1584, 1486 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.36 (d, *J* = 5.6 Hz, 1 H, OH), 3.71 (s, 3 H, $OCH_3$), 5.81 (s, 1 H, CH), 5.98 (d, *J* = 5.6 Hz, 1 H, CH), 6.33 (s, 1 H, CH), 6.90 (dd, *J* = 7.9, 1.5 Hz, $H_{arom}$), 7.15–7.29 (m, 4 $H_{arom}$), 7.37–7.48 (m, 2 $H_{arom}$), 7.56–7.59 (m, 1 $H_{arom}$), 7.68 (d, *J* = 7.9 Hz, 1 $H_{arom}$), 7.80–7.84 (m, 2 $H_{arom}$).

$^{13}$C NMR ($CDCl_3$): δ = 52.0, 68.1, 113.8, 118.9, 119.6, 123.9, 124.7, 126.4, 126.6, 127.1, 127.7, 128.1, 129.1, 129.9, 130.1, 132.1, 134.2, 141.0, 154.1, 154.8, 166.9.

EIMS: *m*/*z* (%) = 334 (1, [M$^+$]), 316 (15), 302 (53), 284 (72), 276 (33), 233 (35), 231 (100), 191 (54), 181 (48).

Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 74.16; H, 5.65.

**(*Z*)-Methyl 2-Bromomethyl-3-[2-(naphthalen-2-yloxy)phenyl]propenoate (13)**
To a mixture of NBS (0.98 g, 5.5 mmol) and DMS (0.56 mL, 7.5 mmol) in $CH_2Cl_2$ (10 mL) was added the MBH adduct **12** (1.67 g, 5 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 24 h. The mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (3:1) to afford **13** (1.37 g, 69%) as a white solid, which was recrystallized from $Et_2O$–PE; mp 87–89 °C.

IR (KBr): 1716, 1629, 1481, 1247 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, $OCH_3$), 4.42 (s, 2 H, $CH_2$), 6.93–6.97 (m, 1 $H_{arom}$), 7.22–7.50 (m, 6 $H_{arom}$), 7.69–7.72 (m, 1 $H_{arom}$), 7.82–7.87 (m, 3 $H_{arom}$), 8.07 (s, 1 H, CH).

$^{13}$C NMR ($CDCl_3$): δ = 27.0, 52.4, 114.7, 118.4, 119.9, 123.6, 125.0, 125.8, 126.7, 127.2, 127.8, 129.5, 129.9, 130.1, 130.4. 131.2, 134.2, 138.0, 154.3, 156.0, 166.4

EIMS: *m*/*z* (%) = 316 (14), 255 (13), 233 (55), 231 (100), 202 (28).

Anal. Calcd for $C_{21}H_{17}BrO_3$: C, 63.49; H, 4.31. Found: C, 63.28; H, 4.19.

**Methyl 14*H*-Benz[*b*]naphth[1,2-*g*]oxocin-13-carboxylate (14)**
To a stirred suspension of $AlCl_3$ (0.54 g, 4 mmol) in $CH_2Cl_2$ (20 mL) was added allyl bromide **13** (0.79 g, 2 mmol) at r.t. The reaction mixture was heated at reflux temperature for 1 h. The mixture was quenched with $H_2O$ (20 mL), and then extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (3:1) as eluent to give **14** (0.13 g, 20%) as a white solid, which was recrystallized from $Et_2O$–PE; mp 122–124 °C.

IR (KBr): 1704, 1620, 1593, 1436, 1250 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, $OCH_3$), 4.45 (s, 2 H, $CH_2$), 7.11–7.21 (m, 1 $H_{arom}$), 7.22–7.28 (m, 1 $H_{arom}$), 7.33–7.39 (m, 3 $H_{arom}$), 7.40–7.45 (m, 1 $H_{arom}$), 7.52–7.58 (m, 1 $H_{arom}$), 7.60 (s, 1 H, CH), 7.66–7.86 (m, 2 $H_{arom}$), 8.34 (d, *J* = 8.8 Hz, 1 $H_{arom}$).

$^{13}$C NMR ($CDCl_3$): δ = 23.9, 52.4, 121.1, 123.3, 124.0, 124.9, 125.1, 126.3, 126.6, 128.3, 128.4, 129.2, 131.5, 131.6, 132.0, 132.1, 134.4, 138.9, 154.0, 157.3, 168.3.

EIMS: *m*/*z* (%) = 316 (96, [M$^+$]), 286 (35), 284 (67), 258 (100), 257 (77), 255 (81), 231 (99), 228 (63), 226 (52), 207 (21), 202 (26).

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.57; H, 4.99.

**2-Phenoxy-3-pyridinecarboxaldehyde (16)**
A mixture of 2-chloro-3-pyridinecarboxaldehyde (**15**; 1.41 g, 10 mmol), phenol (**2a**; 1.41 g, 15 mmol), and $K_2CO_3$ (2.08 g, 15 mmol) in anhyd DMAC (20 mL) was stirred at 170 °C for 2 h. After cooling to r.t., $H_2O$ (30 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to give **16** (1.51 g, 76%) as a white solid, which was recrystallized from $Et_2O$–PE; mp 86–88 °C (Lit.[24] mp 88–90 °C).

IR (KBr): 1689, 1583, 1428, 1389, 1249 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 7.10–7.14 (m, 1 $H_{arom}$), 7.18–7.30 (m, 3 $H_{arom}$), 7.41–7.49 (m, 2 $H_{arom}$), 8.23–8.26 (m, 1 $H_{arom}$), 8.33–8.36 (m, 1 $H_{arom}$), 10.56 (s, 1 H, CH)

$^{13}$C NMR ($CDCl_3$): δ = 118.9, 119.5, 121.6, 125.4, 129.7, 138.1, 153.0, 153.1, 164.0, 188.8.

EIMS: *m*/*z* (%) = 200 (12), 199 (3, [$M^+$]), 198 (7), 172 (29), 171 (100), 170 (33), 115 (21).

**Methyl 3-Hydroxy-2-methylene-3-[(2-phenoxy)pyridin-3-yl]propanoate (17)**

A mixture of **16** (1.00 g, 5 mmol), methyl acrylate (1.35 mL, 15 mmol), DABCO (0.56 g, 5 mmol), and triethanolamine (0.56 g, 4 mmol) was stirred at r.t. for 6 h. The reaction mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (5:1) to afford **17** (1.32 g, 92%) as a yellow oil.

IR ($CH_2Cl_2$): 3427, 1720, 1631, 1582, 1491, 1426 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.66 (s, 1 H, OH), 3.77 (s, 3 H, $OCH_3$), 5.84 (s, 1 H, CH), 5.92 (s, 1 H, CH), 6.38 (s, 1 H, CH), 7.02 (m, 3 $H_{arom}$), 7.17–7.23 (m, 1 $H_{arom}$), 7.36–7.43 (m, 2 $H_{arom}$), 7.87–7.90 (m, 1 $H_{arom}$), 8.07–8.10 (m, 1 $H_{arom}$).

$^{13}$C NMR ($CDCl_3$): δ = 52.1, 68.3, 118.8, 121.3, 124.6, 124.8, 126.8, 129.6, 137.2, 140.2, 146.6, 153.7, 160.3, 166.9.

EIMS: *m*/*z* (%) = 285 (3, [$M^+$]), 284 (7), 268 (22), 253 (16), 226 (100), 200 (26), 198 (49), 170 (19).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.22; H, 5.18; N, 4.79.

**(*Z*)-Methyl 2-Bromomethyl-3-[(2-phenoxy)pyridin-3-yl]propenoate (18)**

To a mixture of NBS (0.98 g, 5.5 mmol) and DMS (0.56 mL, 7.5 mmol) in $CH_2Cl_2$ (10 mL) was added the MBH adduct **17** (1.43 g, 5 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 24 h. The mixture was diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane–EtOAc (3:1) to afford **18** (1.24 g, 71%) as a white solid, which was recrystallized from $Et_2O$–PE; mp 119–120 °C.

IR (KBr): 1717, 1626, 1573, 1491, 1415, 1266 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, $OCH_3$), 4.38 (s, 2 H, $CH_2$), 7.10–7.15 (m, 3 $H_{arom}$), 7.21–7.26 (m, 1 $H_{arom}$), 7.39–7.46 (m, 2 $H_{arom}$), 8.04 (s, 1 H, CH), 8.11–8.19 (m, 2 $H_{arom}$).

$^{13}$C NMR ($CDCl_3$): δ = 26.4, 52.6, 118.4, 118.5, 121.6, 125.1, 129.6, 130.6, 136.5, 138.7, 148.5, 153.4, 161.3, 166.1.

EIMS: *m*/*z* (%) = 327 (5), 302 (5), 271 (17), 268 (27), 254 (38), 248 (21), 246 (72), 244 (100), 219 (76).

Anal. Calcd for $C_{16}H_{14}BrNO_3$: C, 55.19; H, 4.05; N, 4.02. Found: C, 54.90; H, 3.87; N, 3.85.

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