Tetrahedron 65 (2009) 4703–4708

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Morita–Baylis–Hillman route to 4*H*-pyrrolo[1,2-*a*][1]benzazepine derivatives

Sun Pil Park, Young Seok Song, Kee-Jung Lee *

Organic Synthesis Laboratory, Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

ARTICLE INFO

Article history:
Received 19 February 2009
Received in revised form 8 April 2009
Accepted 8 April 2009
Available online 16 April 2009

Keywords:
Morita–Baylis–Hillman
4*H*-Pyrrolo[1,2-*a*][1]benzazepines
2-(1*H*-Pyrrol-1-yl)benzaldehydes
Friedel–Crafts reaction
Sulfuric acid

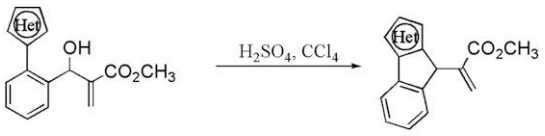
ABSTRACT

A simple method for synthesizing substituted 4*H*-pyrrolo[1,2-*a*][1]benzazepines using acid-assisted cyclization of the Morita–Baylis–Hillman adducts of 2-(1*H*-pyrrol-1-yl)benzaldehydes with methyl acrylate or methyl vinyl ketone as a key step has been developed.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Pyrrolo[1,2-*a*][1]benzazepine derivatives have attracted the attention of synthetic chemists due to their potential biological activity.[1] There are only a few known synthetic approaches to pyrrolo[1,2-*a*][1]benzazepine ring systems. The Wadsworth–Emmons olefination between 2-(1*H*-pyrrol-1-yl)benzaldehyde and methyl α-(diethylphosphonyl)phenylacetate led to the methyl 2-(1*H*-pyrrol-1-yl)-α-phenylcinnamate, which, after transformation into the corresponding acid chloride, was cyclized to the 5-phenyl-4*H*-pyrrolo[1,2-*a*][1]benzazepine-4-one.[2] The 1-benzazepine-2-one was *N*-alkylated with ethyl 2-bromopropionate, the ethyl ester was hydrolyzed, and the resulting α-amino acids were treated with acetic anhydride to the mesoionic oxazolone, which underwent 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate to give dimethyl 1-methyl-5,6-dihydro-4*H*-pyrrolo[1,2-*a*][1]benzazepine-2,3-dicaboxylate.[1b] Transition metal catalyzed cycloisomerization reaction of 2-allenyl-1-(1*H*-pyrrol-1-yl)benzene produced pyrrolobenzazepine.[3] In our program aimed at expanding the repertoire of synthetic applications of the Morita–Baylis–Hillman chemistry[4] for the preparation of heterocyclic systems we have reported the synthesis of 2-(9-fluorenyl)acrylic acid methyl esters,[5] 4*H*-indeno[1,2-*b*]thiophenes, 8*H*-indeno[2,1-*b*]thiophenes, and 8*H*-indeno[2,1-*b*]furans having acrylic acid unit,[6] from the Morita–Baylis–Hillman adducts of 2-biphenylcarboxaldehyde, 2-(thiophen-2-yl)benzaldehyde, 2-(thiophen-3-yl)benzaldehyde, and 2-(furan-3-yl)benzaldehyde by Friedel–Crafts reaction with sulfuric acid, respectively, as shown in Scheme 1.



Het = 2-thienyl, 3-thienyl, and 3-furyl

Scheme 1.

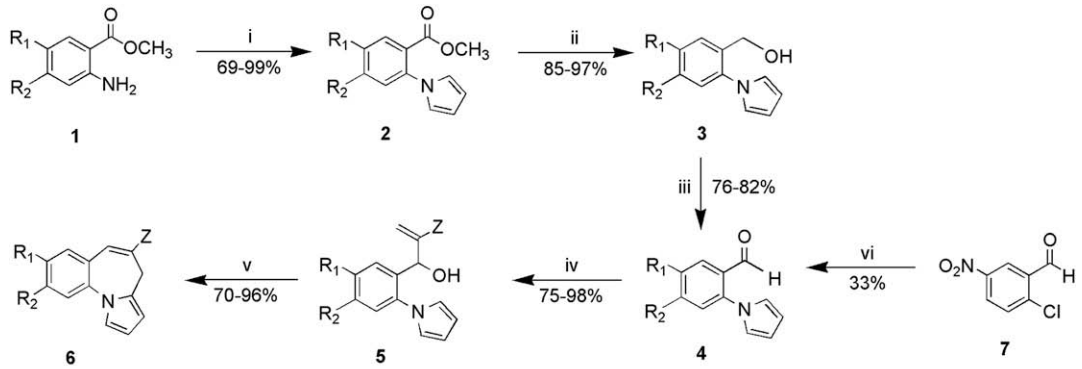
Herein, we describe the synthesis of 4*H*-pyrrolo[1,2-*a*][1]benzazepine derivatives from the Morita–Baylis–Hillman adducts of 2-(1*H*-pyrrol-1-yl)benzaldehydes with methyl acrylate and methyl vinyl ketone.

2. Results and discussion

Our synthesis commenced by generation of key starting material 2-(1*H*-pyrrol-1-yl)benzaldehydes **4a–e** from methyl anthranilates **1a–e** following the earlier reported procedure[7] (Scheme 2). The condensation of 2,5-dimethoxytetrahydrofuran with methyl anthranilate **1a–e** proceeded in good yields and afforded methyl-2-(1*H*-pyrrol-1-yl)phenylbenzoates **2a–e**.[8] Reduction of **2a–e** with lithium aluminium hydride in tetrahydrofuran and acidification provided the 2-(1*H*-pyrrol-1-yl)phenylmethanols **3a–e**. Oxidation of the latter with pyridinium chlorochromate (PCC) in dichloromethane gave 2-(1*H*-pyrrol-1-yl)benzaldehydes **4a–e**. The nitro-substituted benzaldehyde **4f** was synthesized through palladium-catalyzed

* Corresponding author. Tel.: +822 2220 0528; fax: +822 2298 4101.
E-mail address: leekj@hanyang.ac.kr (K.-J. Lee).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.04.026



1, 2, 3, 4	R_1	R_2	5, 6	R_1	R_2	Z
a	H	H	**a**	H	H	CO_2CH_3
b	Br	H	**b**	Br	H	CO_2CH_3
c	H	Cl	**c**	H	Cl	CO_2CH_3
d	F	H	**d**	F	H	CO_2CH_3
e	CH_3O	H	**e**	CH_3O	H	CO_2CH_3
f	NO_2	H	**f**	NO_2	H	CO_2CH_3
			g	H	H	$COCH_3$
			h	Br	H	$COCH_3$
			i	H	Cl	$COCH_3$
			j	F	H	$COCH_3$
			k	CH_3O	H	$COCH_3$
			l	NO_2	H	$COCH_3$

Scheme 2. Reagents and conditions: (i) 2,5-dimethoxytetrahydrofuran, AcOH, reflux, 1–4 h; (ii) LAH, THF, rt, 30–60 min; (iii) PCC, Celite, CH_2Cl_2, rt 40–60 min; (iv) method A: methyl acrylate, DABCO, $N(CH_2CH_2OH)_3$, rt, 7 h to 3 days. method B: methyl vinyl ketone, DMAP, DMF, rt, 1–20 days; (v) 95% H_2SO_4, CCL_4, rt, 10 min; (vi) pyrrole, xanthos, $Pd(OAc)_2$, K_2CO_3, *o*-xylene, 120 °C, 13 h.

amination of 2-chloro-5-nitrobenzldehyde (**7**) with pyrrole in the presence of xantphos following recently published procedure.[9]

The Morita–Baylis–Hillman reaction of **4a–f** with methyl acrylate, 1,4-diazabicyclo[2,2,2]octane (DABCO), and triethanolamine without solvent the Morita–Baylis–Hillman adducts **5a–f** were produced in 75–98% yields. On Friedel–Crafts cyclization of **5a–f** with 95% sulfuric acid in tetrachloromethane at room temperature for 10 min, methyl 4*H*-pyrrolo[1,2-*a*][1]benzazepine-5-carboxylates **6a–f** were obtained in 70–96% yields (Scheme 2, Table 1). The possible five-membered ring closure product 9*H*-pyrrolo[1,2-*a*]indole derivatives were not produced at all. Brönsted-acid-catalyzed allylation of electron-rich arenes including 2-methylfuran and pyrrole with substituted allylic and secondary benzylic alcohols gives the corresponding branched allylated products with a high regioselectivity.[10] The different ring closure mode between pyrrole- and furan/thiophene-substituted Morita–Baylis–Hillman adducts is uncertain. With the intent to introduce more diversity in the products employing this strategy, it was decided to carry the Morita–Baylis–Hillman reaction of **4a–f** with methyl vinyl ketone. Consequently, the reaction of **4a–f** with methyl vinyl ketone, *N*,*N*-dimethylaminopyridine (DMAP) in *N*,*N*-dimethylformamide yielded the adducts **5g–l**, which were unstable and could not be isolated as a pure form. As a result the crude Morita–Baylis–Hillman adducts **5g–l** were subjected to treatment with 95% sulfuric acid similarly led to the formation of the corresponding benzazepines **6g–l** in 33–57% two-step yields. It works well with hydrogen, electron-withdrawing or electron-donating substituents on the phenyl ring of the Morita–Baylis–Hillman adducts.

Table 1
Preparation of Morita–Baylis–Hillman adducts **5** and 4*H*-pyrrolo[1,2-*a*][1]benzazepines **6**

Entry	4	Method[a]	5 (Yield %)[b]	6 (Yield %)[c]
1	**4a**	A	**5a** (82)	**6a** (79)
2	**4b**	A	**5b** (82)	**6b** (79)
3	**4c**	A	**5c** (88)	**6c** (70)
4	**4d**	A	**5d** (90)	**6d** (91)
5	**4e**	A	**5e** (75)	**6e** (76)
6	**4f**	A	**5f** (98)	**6f** (96)
7	**4a**	B	**5g**	**6g** (35)
8	**4b**	B	**5h**	**6h** (47)
9	**4c**	B	**5i**	**6i** (41)
10	**4d**	B	**5j**	**6j** (39)
11	**4e**	B	**5k**	**6k** (57)
12	**4f**	B	**5l**	**6l** (40)

[a] Method A: DABCO/methyl acrylate; method B: DMAP/methyl vinyl ketone.
[b] Isolated yields of **5g–l** were not determined due to the instability.
[c] Two step yields of **6g–l** based on **4a–f**.

3. Conclusions

In summary, we have achieved for the expedient synthesis of 4*H*-pyrrolo[1,2-*a*][1]benzazepine derivatives from the Morita–Baylis–Hillman adducts of 2-(1*H*-pyrrol-1-yl)benzaldehydes under the acidic condition. This method may be of value in organic synthesis because of the ease of operation.

4. Experimental

4.1. Synthesis general

The melting points were measured on an Electrothermal melting point apparatus and are uncorrected. TLC analyses were carried out on Merck silica gel $60F_{254}$ and spots were visualized under UV light. Chromatography on silica gel was carried out on Merck silica (70–230 mesh ASTM). IR spectra were determined on a Nicolet Magna 550 FTIR spectrometer using KBr discs. ^1H NMR spectra were recorded on a Varian 300 spectrometer in $CDCl_3$ at 300 MHz. All chemical shifts are given in parts per million (ppm) using δ_H Me_4Si=0 ppm as reference and *J* values are given in hertz. ^{13}C NMR spectra were run in the same instrument at 75.4 MHz using the solvent peak as internal reference. Low resolution mass spectra were recorded on a ThermoQuest Polaris Q mass spectrometer

operating at 70 eV. Elemental analyses were carried out on a Thermo Electron Corporation Flash EA 1112 instrument. All reagents were used as received. 2,5-Dimethoxytetrahydrofuran, methyl 2-aminobenzoate (**1a**), methyl 2-amino-5-bromobenzoate (**1b**), methyl 2-aminio-4-chlorobenzoate (**1c**), methyl 2-amino-5-fluorobenzoate (**1d**), and 2-chloro-5-nitrobenzaldehyde (**7**) are commercially available (Aldrich). The known methyl 2-amino-5-methoxybenzoate (**1e**),[11] methyl 2-(1*H*-pyrrol-1-yl)benzoate (**2a**),[2] methyl 4-chloro-2-(1*H*-pyrrol-1-yl)benzoate(**2c**),[7d] 2-(1*H*-pyrrol-1-yl)phenylmethanol (**3a**),[2] 4-chloro-2-(1*H*-pyrrol-1-yl)phenylmethanol (**3c**),[7d] 2-(1*H*-pyrrol-1-yl)benzaldehyde (**4a**),[2] and 4-chloro-2-(1*H*-pyrrol-1-yl)benzaldehyde (**4c**)[7d] were prepared according to the reported procedures.

4.2. General procedure for the synthesis of methyl 2-(1*H*-pyrrol-1-yl)benzoates 2

2,5-Dimethoxytetrahydrofuran (4.76 g, 36 mmol) was added to a well stirred solution of methyl 2-aminobenzoate **1** (30 mmol) in 15 mL of glacial acetic acid. The clear solution was heated at reflux for 1–4 h, and then the acetic acid was removed by evaporation at reduced pressure. The mixture was poured over saturated aq $NaHCO_3$ solution and extracted with ethyl acetate (3×20 mL). After drying over anhydrous $MgSO_4$ and evaporation of the solvent under reduced pressure, the crude compound was subjected to column chromatography with silica gel by elution with hexane and ethyl acetate (15:1). The fractions containing the pure compound were combined and evaporated under reduced pressure to afford **2**.

*4.2.1. Methyl 5-bromo-2-(1H-pyrrol-1-yl)benzoate (**2b**)*

Reaction time: 4 h; yield: 95%; white solid: mp 43–45 °C (hexane–EtOAc); IR (KBr) 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (s, 3H, CH_3), 6.32 (t, J=2.1 Hz, 2H, pyrrole), 6.77 (t, J=2.1 Hz, 2H, pyrrole), 7.26 (d, J=8.5 Hz, 1H, aromatic), 7.67 (dd, J=8.5 and 2.4 Hz, 1H, aromatic), 7.93 (d, J=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.6, 110.0, 120.4, 121.8, 128.2, 129.2, 133.3, 135.1, 139.3, 166.0; EIMS: m/z (%) 281 (78), 279 (83) [M^+], 249 (34), 247 (25), 223 (96), 221 (100), 142 (36), 140 (22), 115 (52). Anal. Calcd for $C_{12}H_{10}BrNO_2$: C, 51.45; H, 3.60; N, 5.00. Found: C, 51.60; H, 3.73; N, 4.86.

*4.2.2. Methyl 5-fluoro-2-(1H-pyrrol-1-yl)benzoate (**2d**)*

Reaction time: 1 h; yield: 99%; yellow oil; IR (neat) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (s, 3H, CH_3), 6.30 (t, J=2.1 Hz, 2H, pyrrole), 6.76 (t, J=2.1 Hz, 2H, pyrrole), 7.22–7.28 (m, 1H, aromatic), 7.36 (dd, J=8.9 and 4.9 Hz, 1H, aromatic), 7.51 (dd, J=8.5 and 3.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.6, 109.6, 117.3 (d, J_{CF}=25.6 Hz), 119.1 (d, J_{CF}=21.9 Hz), 122.2, 128.8 (d, J_{CF}=8.5 Hz), 136.6, 160.9 (d, J_{CF}=249.0 Hz), 165.9; EIMS: m/z (%) 219 (74) [M^+], 161 (100), 134 (32), 133 (60). Anal. Calcd for $C_{12}H_{10}FNO_2$: C, 65.75; H, 4.60; N, 6.39. Found: C, 65.58; H, 4.49; N, 6.27.

*4.2.3. Methyl 5-methoxy-2-(1H-pyrrol-1-yl)benzoate (**2e**)*

Reaction time: 4 h; yield: 69%; yellow oil; IR (neat) 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.69 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.28 (t, J=2.1 Hz, 2H, pyrrole), 6.75 (t, J=2.1 Hz, 2H, pyrrole), 7.06 (dd, J=8.5 and 2.7 Hz, 1H, aromatic), 7.29 (d, J=8.5 Hz, 1H, aromatic), 7.31 (d, J=2.7 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.4, 55.7, 109.1, 114.7, 118.1, 122.3, 128.3, 128.9, 133.5, 158.3, 167.0; EIMS: m/z (%) 231 (100) [M^+], 199 (62), 184 (83), 158 (46). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.02. Found: C, 67.34; H, 5.73; N, 5.81.

4.3. General procedure for the synthesis of 2-(1*H*-pyrrol-1-yl)phenylmethanol 3

To an ice-cooled stirred solution of methyl 2-(1*H*-pyrrol-1-yl)benzoate **2** (7.26 mmol) in dry THF (30 mL) was added dropwise 1 M THF solution of LAH (14 mL, 14 mmol). After 0.5–1 h, the unreacted LAH was cautiously quenched with ethyl acetate and a few drops of 15% sulfuric acid. The mixture was then extracted with ethyl acetate and the organic layer was evaporated to dryness to give crude product, which was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (6:1 to 3:1) to produce the pure product **3**.

*4.3.1. 5-Bromo-2-(1H-pyrrol-1-yl)phenylmethanol (**3b**)*

Reaction time: 30 min; yield: 85%; white solid: mp 90–92 °C (hexane–EtOAc); IR (neat) 3322 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (t, J=5.8 Hz, 1H, OH), 4.54 (d, J=5.8 Hz, 2H, CH_2), 6.33 (t, J=2.1 Hz, 2H, pyrrole), 6.81 (t, J=2.1 Hz, 2H, pyrrole), 7.17 (d, J=8.2 Hz, 1H, aromatic), 7.49 (dd, J=8.2 and 2.4 Hz, 1H, aromatic), 7.74 (d, J=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.7, 109.7, 121.5, 122.2, 128.1, 131.4, 131.9, 138.1, 138.5; EIMS: m/z (%) 253 (31), 251 (31) [M^+], 235 (19), 233 (22), 154 (100), 143 (34), 115 (26). Anal. Calcd for $C_{11}H_{10}BrNO$: C, 52.41; H, 4.00; N, 5.56. Found: C, 52.51; H, 4.06; N, 5.68.

*4.3.2. 5-Fluoro-2-(1H-pyrrol-1-yl)phenylmethanol (**3d**)*

Reaction time: 30 min; yield: 95%; white solid: mp 36–38 °C (hexane–EtOAc); IR (neat) 3402 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (s, 1H, OH), 4.51 (s, 2H, CH_2), 6.32 (t, J=2.1 Hz, 2H, pyrrole), 6.77 (t, J=2.1 Hz, 2H, pyrrole), 7.00–7.07 (m, 1H, aromatic), 7.25–7.32 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.7, 109.4, 114.9 (d, J_{CF}=21.9 Hz), 115.3 (d, J_{CF}=23.1 Hz), 122.4, 128.3 (d, J_{CF}=8.5 Hz), 135.3, 138.9, 162.0 (d, J_{CF}=246.6 Hz); EIMS: m/z (%) 191 (83) [M^+], 173 (100), 162 (32), 148 (18). Anal. Calcd for $C_{11}H_{10}FNO$: C, 69.10; H, 5.27; N, 7.33. Found: C, 69.22; H, 5.14; N, 7.17.

*4.3.3. 5-Methoxy-2-(1H-pyrrol-1-yl)phenylmethanol (**3e**)*

Reaction time: 1 h; yield: 97%; white solid: mp 90–93 °C (hexane–EtOAc); IR (neat) 3212 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (s, 1H, OH), 3.85 (s, 3H, OCH_3), 4.47 (s, 2H, CH_2), 6.30 (t, J=2.1 Hz, 2H, pyrrole), 6.77 (t, J=2.1 Hz, 2H, pyrrole), 6.86 (dd, J=8.5 and 2.7 Hz, 1H, aromatic), 7.06 (d, J=2.7 Hz, 1H, aromatic), 7.21 (d, J=8.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 55.5, 61.3, 109.0, 113.5, 113.6, 122.6, 127.9, 132.6, 137.9, 159.1; EIMS: m/z (%) 203 (100) [M^+], 185 (32), 160 (31), 115 (20). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.69; H, 6.52; N, 6.97.

4.4. General procedure for the synthesis of 2-(1*H*-pyrrol-1-yl)benzaldehydes 4

To a stirred solution of 2-(1*H*-pyrrol-1-yl)phenylmethanol **3** (10 mmol) in CH_2Cl_2 (60 mL) containing Celite (20 g) was added PCC (6.25 g, 29 mmol) portionwise. After 40–60 min, the mixture was filtered by suction. The filtrate was washed with 5% hydrochloric acid and then brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (10:1 to 6:1) to produce the aldehyde **4**.

*4.4.1. 5-Bromo-2-(1H-pyrrol-1-yl)benzaldehyde (**4b**)*

Reaction time: 1 h; yield: 79%; yellow oil; IR (neat) 1686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.41 (t, J=2.1 Hz, 2H, pyrrole), 6.90 (t, J=2.1 Hz, 2H, pyrrole), 7.33 (d, J=8.5 Hz, 1H, aromatic), 7.79 (dd, J=8.5 and 2.4 Hz, 1H, aromatic), 8.11 (d, J=2.4 Hz, 1H, aromatic), 9.75 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 111.1, 121.6, 123.6, 128.1, 131.1, 131.9, 137.4, 142.6, 188.5; EIMS: m/z (%) 251 (19), 249 (19) [M^+], 223 (62), 221 (64), 142 (36), 115 (100). Anal. Calcd for $C_{11}H_8BrNO$: C, 52.83; H, 3.22; N, 5.60. Found: C, 52.78; H, 3.07; N, 5.36.

*4.4.2. 5-Fluoro-2-(1H-pyrrol-1-yl)benzaldehyde (**4d**)*

Reaction time: 1 h; yield: 76%; yellow oil; IR (neat) 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.39 (t, J=2.1 Hz, 2H, pyrrole), 6.90 (t, J=2.1 Hz,

2H, pyrrole), 7.33–7.47 (m, 2H, aromatic), 7.64–7.68 (m, 1H, aromatic), 9.69 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 110.7, 114.2 (d, J_{CF}=23.2 Hz), 121.7 (d, J_{CF}=23.2 Hz), 123.9, 128.7 (d, J_{CF}=8.5 Hz), 132.5, 140.1, 161.6 (d, J_{CF}=250.3 Hz), 188.8; EIMS: *m*/*z* (%) 189 (71) [M^+], 161 (100), 134 (39), 133 (82). Anal. Calcd for $C_{11}H_8FNO$: C, 69.83; H, 4.26; N, 7.40. Found: C, 70.01; H, 4.17; N, 7.25.

4.4.3. 5-Methoxy-2-(1H-pyrrol-1-yl)benzaldehyde (**4e**)

Reaction time: 40 min; yield: 82%; yellow oil; IR (neat) 1686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 3H, OCH_3), 6.37 (t, *J*=2.1 Hz, 2H, pyrrole), 6.88 (t, *J*=2.1 Hz, 2H, pyrrole), 7.20 (dd, *J*=8.5 and 3.0 Hz, 1H, aromatic), 7.36 (d, *J*=8.5 Hz, 1H, aromatic), 7.45 (d, *J*=3.0 Hz, 1H, aromatic), 9.68 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 55.8, 110.0, 110.1, 122.0, 124.0, 128.2, 131.9, 137.5, 158.9, 189.9; EIMS: *m*/*z* (%) 201 (41) [M^+], 173 (65), 158 (100), 130 (72). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.44; H, 5.55; N, 7.15.

4.4.4. 5-Nitro-2-(1H-pyrrol-1-yl)benzaldehyde (**4f**)

Aldehyde **4f** was prepared from 2-chloro-5-nitrobenzaldehyde (**7**) with pyrrole according to the reported procedure.[9] In a Schlenck tube, 2-chloro-5-nitrobenzaldehyde (**7**, 401 mg, 2.17 mmol), pyrrole (133 mg, 1.97 mmol), palladium acetate (4.4 mg, 0.02 mmol), xantphos (34 mg, 0.059 mmol), and potassium carbonate (817 mg, 5.91 mmol) were mixed in 5 mL of *o*-xylene. The mixture was degassed and the tube refilled with argon. After heating at 120 °C for 13 h, the mixture was cooled to room temperature, washed with water, and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (10:1) providing 155 mg (33%) of **4f** as a yellow solid: mp 57–59 °C (hexane–EtOAc); IR (neat) 1694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.50 (t, *J*=2.1 Hz, 2H, pyrrole), 6.99 (t, *J*=2.1 Hz, 2H, pyrrole), 7.64 (d, *J*=8.5 Hz, 1H, aromatic), 8.52 (dd, *J*=8.5 and 2.4 Hz, 1H, aromatic), 8.84 (d, *J*=2.4 Hz, 1H, aromatic), 9.98 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 112.5, 123.4, 124.4, 126.9, 128.8, 130.2, 146.2, 147.7, 187.7; EIMS: *m*/*z* (%) 216 (37) [M^+], 188 (100), 158 (40), 115 (76). Anal. Calcd for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73; N, 12.96. Found: 61.01; H, 3.85; N, 12.89.

4.5. General procedure for the synthesis of the Morita–Baylis–Hillman adducts 5

Method A. A mixture of 2-(1*H*-pyrrol-1-yl)benzaldehyde **4a**–**f** (10 mmol), methyl acrylate (2.58 g, 30 mmol), DABCO (1.12 g, 10 mmol), and triethanolamine (1.19 g, 8 mmol) without solvent was stirred at room temperature for 7 h to 3 days. The reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (3×40 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (6:1 to 3:1) to produce **5a**–**f** as an oil.

Method B. A mixture of 2-(1*H*-pyrrol-1-yl)benzaldehyde **4a**–**f** (10 mmol), methyl vinyl ketone (1.40 g, 20 mmol), and DMAP (0.11 g, 1 mmol) in 15 mL of DMF was stirred at room temperature for 1–20 days. The reaction mixture was diluted with water (20 mL) and extracted with ethyl ether (3×40 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and solvent was evaporated in vacuo to afford the crude Morita–Baylis–Hillman adduct **5g**–**l**, which was subjected to next step without purification.

4.5.1. Methyl 2-[1-hydroxy-1-{2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5a**)

Reaction time: 3 days; yield: 82%; yellow oil; IR (neat) 3436, 1722, 1630, 1501 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.02 (d, *J*=5.5 Hz, 1H, OH), 3.67 (s, 3H, OCH_3), 5.57 (d, *J*=5.5 Hz, 1H, CH), 5.64 (s, 1H, CH), 6.29 (t, *J*=2.1 Hz, 2H, pyrrole), 6.30 (s, 1H, CH), 6.82 (t, *J*=2.1 Hz, 2H, pyrrole), 7.25–7.55 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$) δ 51.9, 67.7, 109.1, 122.6, 126.4, 127.2, 127.6, 128.1, 128.6, 136.8, 139.7, 141.4, 166.4; EIMS: *m*/*z* (%) 239 (14), 238 (16), 224 (17), 198 (100), 180 (40), 168 (24), 154 (27), 115 (15). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.87; H, 5.65; N, 5.20.

4.5.2. Methyl 2-[1-hydroxy-1-{5-bromo-2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5b**)

Reaction time: 2 days; yield: 82%; yellow oil; IR (neat) 3443, 1720, 1631, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.97 (d, *J*=5.5 Hz, 1H, OH), 3.71 (s, 3H, OCH_3), 5.54 (d, *J*=5.5 Hz, 1H, CH), 5.65 (s, 1H, CH), 6.30 (t, *J*=2.1 Hz, 2H, pyrrole), 6.33 (s, 1H, CH), 6.78 (t, *J*=2.1 Hz, 2H, pyrrole), 7.15 (d, *J*=8.5 Hz, 1H, aromatic), 7.49 (dd, *J*=8.5 and 2.4 Hz, 1H, aromatic), 7.68 (d, *J*=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.1, 67.6, 109.6, 121.9, 122.5, 126.9, 128.9, 130.8, 131.8, 138.7, 139.0, 140.8, 166.3; EIMS: *m*/*z* (%) 258 (25), 197 (63), 179 (65), 169 (79), 167 (100), 154 (44), 141 (34), 115 (56). Anal. Calcd for $C_{15}H_{14}BrNO_3$: C, 53.59; H, 4.20; N, 4.17. Found: C, 53.31; H, 4.03; N, 4.31.

4.5.3. Methyl 2-[1-hydroxy-1-{4-chloro-2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5c**)

Reaction time: 3 days; yield: 88%; yellow oil; IR (neat) 3418, 1720, 1596, 1497 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.96 (d, *J*=5.2 Hz, 1H, OH), 3.70 (s, 3H, OCH_3), 5.55 (d, *J*=5.2 Hz, 1H, CH), 5.62 (s, 1H, CH), 6.30 (m, 3H, CH and pyrrole), 6.81 (dd, *J*=8.5 and 2.1 Hz, 1H, aromatic), 7.28 (d, *J*=2.1 Hz, 1H, aromatic), 7.38 (t, *J*=2.1 Hz, 2H, pyrrole), 7.49 (d, *J*=8.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.0, 67.6, 109.7, 122.4, 126.6, 127.3, 128.2, 129.0, 134.0, 135.4, 140.7, 141.0, 166.4; EIMS: *m*/*z* (%) 273 (19), 234 (31), 232 (100), 216 (28), 214 (46), 188 (25), 167 (33). Anal. Calcd for $C_{15}H_{14}ClNO_3$: C, 61.76; H, 4.84; N, 4.80. Found: C, 61.49; H, 4.73; N, 4.54.

4.5.4. Methyl 2-[1-hydroxy-1-{5-fluoro-2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5d**)

Reaction time: 3 days; yield: 90%; yellow oil; IR (neat) 3437, 1721, 1629, 1505 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.07 (d, *J*=5.0 Hz, 1H, OH), 3.71 (s, 3H, OCH_3), 5.50 (d, *J*=5.0 Hz, 1H, CH), 5.61 (s, 1H, CH), 6.29 (t, *J*=2.1 Hz, 2H, pyrrole), 6.31 (s, 1H, CH), 6.77 (t, *J*=2.1 Hz, 2H, pyrrole), 7.02–7.09 (m, 1H, aromatic), 7.25–7.28 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.1, 67.8, 109.3, 114.5 (d, J_{CF}=23.2 Hz), 115.5 (d, J_{CF}=23.2 Hz), 122.7, 126.9, 129.1 (d, J_{CF}=8.5 Hz), 135.6, 139.6 (d, J_{CF}=7.3 Hz), 140.7, 162.0 (d, J_{CF}=247.8 Hz), 166.3; EIMS: *m*/*z* (%) 257 (6), 216 (100), 198 (39), 186 (27), 172 (29). Anal. Calcd for $C_{15}H_{14}FNO_3$: C, 65.45; H, 5.13; N, 5.09. Found: C, 65.22; H, 4.88; N, 4.81.

4.5.5. Methyl 2-[1-hydroxy-1-{5-methoxy-2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5e**)

Reaction time: 3 days; yield: 75%; yellow oil; IR (neat) 3465, 1721, 1610, 1508 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.98 (d, *J*=5.2 Hz, 1H, OH), 3.70 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.48 (d, *J*=5.2 Hz, 1H, CH), 5.62 (s, 1H, CH), 6.27 (t, *J*=2.1 Hz, 2H, pyrrole), 6.29 (s, 1H, CH), 6.75 (t, *J*=2.1 Hz, 2H, pyrrole), 6.88 (dd, *J*=8.5 and 3.1 Hz, 1H, aromatic), 7.05 (d, *J*=2.7 Hz, 1H, aromatic), 7.23 (d, *J*=8.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.0, 55.5, 67.9, 108.8, 112.4, 113.9, 122.8, 126.6, 128.5, 132.7, 138.4, 141.2, 159.2, 166.5; EIMS: *m*/*z* (%) 228 (100), 210 (28), 198 (21), 167 (13). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.72; H, 5.70; N, 4.63.

4.5.6. Methyl 2-[1-hydroxy-1-{5-nitro-2-(1H-pyrrol-1-yl)phenyl}methyl]propenoate (**5f**)

Reaction time: 7 h; yield: 98%; yellow oil; IR (neat) 3440, 1715, 1615, 1588, 1529, 1497 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.14 (d, *J*=5.2 Hz, 1H, OH), 3.71 (s, 3H, OCH_3), 5.72 (s, 1H, CH), 5.75 (d, *J*=5.2 Hz, 1H, CH), 6.37 (t, *J*=2.1 Hz, 2H, pyrrole), 6.39 (s, 1H, CH), 6.89 (t, *J*=2.1 Hz, 2H, pyrrole), 7.45 (d, *J*=8.5 Hz, 1H, aromatic), 8.24 (dd, *J*=8.5 and 2.4 Hz, 1H, aromatic), 8.45 (d, *J*=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$)

δ 52.2, 67.6, 110.7, 122.3, 123.8, 123.9, 127.3, 127.8, 138.1, 140.4, 144.8, 146.9, 166.1; EIMS: *m*/*z* (%) 243 (86), 225 (33), 197 (100), 179 (20), 167 (31). Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27. Found: C, 59.78; H, 4.39; N, 8.98.

4.6. General procedure for the synthesis of 4*H*-pyrrolo-[1,2-*a*][1]benzazepines 6

Method A. To a stirred solution of the Morita–Baylis–Hillman adduct **5a**–**f** (2 mmol) in 5 mL of CCl_4 was added dropwise 95% H_2SO_4 (1.18 g, 12 mmol) at room temperature. After 10 min, the mixture was quenched with water (5 mL) and dichloromethane (10 mL), and then extracted with dichloromethane (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (10:1 to 4:1) to give **6a**–**f** as a yellow solid.

Method B. To a stirred solution of the crude Morita–Baylis–Hillman adduct **5g**–**l**, which was obtained from aldehyde **4a**–**f** (10 mmol) and methyl vinyl ketone (20 mmol) in 20 mL of CCl_4, was added dropwise 95% H_2SO_4 (5.88 g, 60 mmol) at room temperature. After 10 min, the mixture was quenched with water (10 mL) and dichloromethane (20 mL). The work-up procedure was the same as above to give **6g**–**l** as a yellow solid.

4.6.1. Methyl 4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6a*)

Yield: 79%; yellow solid: mp 67–68 °C (hexane–EOAc); IR (KBr) 1709, 1634, 1491 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.61 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.00 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.31 (dd, *J*=3.4 and 3.4 Hz, 1H, pyrrole), 6.97 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 7.26–7.53 (m, 4H, aromatic), 7.63 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.3, 105.7, 110.9, 120.3, 123.3, 125.1, 128.0, 130.0, 131.7, 132.8, 135.7, 137.3, 139.5, 166.4; EIMS: *m*/*z* (%) 239 (65) [M^+], 238 (95), 224 (91), 180 (100), 178 (43), 152 (27). Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.12; H, 5.25; N, 5.63.

4.6.2. Methyl 8-bromo-4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6b*)

Yield: 79%; yellow solid: mp 92–94 °C (hexane–EtOAc); IR (KBr) 1711, 1634, 1488 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.01 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.32 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 6.93 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.36–7.39 (m, 1H, aromatic), 7.51–7.54 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.4, 106.1, 111.4, 118.3, 120.2, 125.0, 129.7, 132.8, 134.0, 134.1, 135.5, 135.7, 138.5, 166.1; EIMS: *m*/*z* (%) 319 (52), 318 (77), 317 (52) [M^+], 316 (72), 304 (78), 302 (84), 260 (48), 258 (52), 179 (100). Anal. Calcd for $C_{15}H_{12}BrNO_2$: C, 56.62; H, 3.80; N, 4.40. Found: C, 56.79; H, 3.58; N: 4.21.

4.6.3. Methyl 9-chloro-4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6c*)

Yield: 70%; yellow solid: mp 96–98 °C (hexane–EtOAc); IR (KBr) 1712, 1634, 1487 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.00 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.33 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 6.95 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.26 (dd, *J*=8.2 and 1.8 Hz, 1H, aromatic), 7.33 (d, *J*=8.2 Hz, 1H, aromatic), 7.51 (d, *J*=1.8 Hz, 1H, aromatic), 7.57 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.4, 106.2, 111.4, 118.3, 120.3, 125.0, 129.7, 132.8, 134.0, 134.1, 135.5, 135.8, 138.5, 166.1; EIMS: *m*/*z* (%) 275 (17), 274 (30), 273 (55) [M^+], 272 (69), 260 (28), 258 (92), 216 (34), 214 (100), 178 (63), 151 (19). Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.70; H, 4.22; N, 4.89.

4.6.4. Methyl 8-fluoro-4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6d*)

Yield: 91%; yellow solid: mp 70–72 °C (hexane–EtOAc); IR (KBr) 1712, 1637, 1498 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.00 (dd, *J*=3.1 and 1.5 Hz, 1H, pyrrole), 6.30 (dd, *J*=3.1 and 3.1 Hz, 1H, pyrrole), 6.92 (dd, *J*=3.1 and 1.5 Hz, 1H, pyrrole), 7.07–7.17 (m, 2H, aromatic), 7.45–7.49 (m, 1H, aromatic), 7.53 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.4, 105.7, 111.0, 117.0 (d, J_{CF}=18.3 Hz), 117.3 (d, J_{CF}=18.3 Hz), 120.4, 125.1 (d, J_{CF}=8.5 Hz), 129.6 (d, J_{CF}=7.3 Hz), 134.1, 135.5, 135.9 (two), 159.6 (d, J_{CF}=245.4 Hz), 166.1; EIMS: *m*/*z* (%) 257 (49) [M^+], 256 (72), 242 (79), 198 (100), 196 (36). Anal. Calcd for $C_{15}H_{12}FNO_2$: C, 70.03; H, 4.70; N, 5.44. Found: C.69.85; H, 4.92; N, 5.23.

4.6.5. Methyl 8-methoxy-4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6e*)

Yield: 76%; yellow solid: mp 80–82 °C (hexane–EtOAc); IR (KBr) 1708, 1634, 1502 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.59 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.98 (d, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.28 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 6.89 (d, *J*=3.1 Hz, 1H, aromatic), 6.92 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.00 (dd, *J*=8.9 and 3.1 Hz, 1H, aromatic), 7.44 (d, *J*=8.9 Hz, 1H, aromatic), 7.58 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.3, 55.6, 105.1, 110.4, 115.1, 116.5, 120.1, 124.6, 129.0, 133.2 (two), 135.3, 137.1, 156.7, 166.4; EIMS: *m*/*z* (%) 269 (62) [M^+], 268 (97), 254 (100), 225 (50), 210 (52), 167 (52). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.15; H, 5.49; N, 5.02.

4.6.6. Methyl 8-nitro-4H-pyrrolo[1,2-a][1]benzazepine-5-carboxylate (*6f*)

Yield: 96%; yellow solid: mp 158–160 °C (hexane–EtOAc); IR (KBr) 1712, 1641, 1578, 1521, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3), 6.07 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.39 (dd, *J*=3.4 and 3.4 Hz, 1H, pyrrole), 7.01 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 7.63 (d, *J*=8.5 Hz, 1H, aromatic), 7.64 (s, 1H, CH), 8.27 (dd, *J*=8.5 and 2.4 Hz, 1H, aromatic), 8.31 (d, *J*=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 24.7, 52.6, 107.6, 112.8, 120.7, 124.1, 124.7, 127.4, 128.3, 135.0, 135.3, 135.8, 144.0, 144.3, 165.8; EIMS: *m*/*z* (%) 284 (73) [M^+], 283 (65), 269 (100), 237 (66), 225 (51), 223 (48), 179 (47), 178 (52). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.22; H, 4.07; N, 9.57.

4.6.7. 5-Acetyl-4H-pyrrolo[1,2-a][1]benzazepine (*6g*)

Two steps yield: 35%; yellow solid: mp 63–65 °C (hexane–EtOAc); IR (KBr) 1665, 1625, 1492 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 5.99 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.31 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 6.98 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.28–7.55 (m, 4H, aromatic), 7.47 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.3, 105.7, 111.0, 120.1, 123.4, 125.1, 127.9, 130.3, 131.6, 135.7, 137.7, 139.6, 141.7, 196.4; EIMS: *m*/*z* (%) 223 (37) [M^+], 222 (42), 180 (100), 152 (14). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.52; H, 5.60; N, 6.05.

4.6.8. 5-Acetyl-8-bromo-4H-pyrrolo[1,2-a][1]benzazepine (*6h*)

Two steps yield: 47%; yellow solid: mp 156–158 °C (hexane–EtOAc); IR (KBr) 1666, 1628, 1488 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 5.99 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.31 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 6.93 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.36 (s, 1H, CH), 7.39 (d, *J*=8.2 Hz, 1H, aromatic), 7.56 (d, *J*=8.2 Hz, 1H, aromatic), 7.64 (s, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.3, 106.2, 111.5, 118.3, 120.0, 125.0, 129.7, 133.0, 134.0, 135.5, 136.0, 138.6, 142.7, 196.1; EIMS: *m*/*z* (%) 303 (38), 302 (47), 301 (40) [M^+], 300 (45), 260 (97), 258 (100), 179 (88), 178 (43). Anal. Calcd for $C_{15}H_{12}BrNO$: C, 59.62; H, 4.00; N, 4.64. Found: C, 59.79; H, 3.81; N, 4.58.

4.6.9. 5-Acetyl-9-chloro-4H-pyrrolo[1,2-a][1]benzazepine (*6i*)

Two steps yield: 41%; yellow solid: mp 99–101 °C (hexane–EtOAc); IR (KBr) 1665, 1629, 1594, 1489 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 5.99 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.32 (dd, *J*=3.4 and 3.4 Hz, 1H, pyrrole), 6.95 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 7.29–7.37 (m, 2H, aromatic), 7.40 (s, 1H, CH),

7.53 (s, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.3, 106.3, 111.6, 120.1, 123.4, 125.3, 126.4, 132.8, 135.6, 135.8, 136.6, 140.4, 141.8, 196.1; EIMS: *m*/*z* (%) 259 (6), 258 (11), 257 (22) [M^+], 256 (22), 216 (33), 214 (100), 179 (35), 178 (35). Anal. Calcd for $C_{15}H_{12}ClNO$: C, 67.91; H, 4.69; N, 5.43. Found: C, 70.22; H, 4.48; N, 5.23.

*4.6.10. 5-Acetyl-8-fluoro-4H-pyrrolo[1,2-a][1]benzazepine (**6j**)*

Two steps yield: 39%; yellow solid: mp 100–103 °C (hexane–EtOAc); IR (KBr) 1667, 1630, 1582, 1498 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 6.00 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 6.31 (dd, *J*=3.1 and 3.1 Hz, 1H, pyrrole), 6.93 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.10–7.20 (m, 2H, aromatic), 7.37 (s, 1H, CH), 7.49 (dd, *J*=8.9 and 4.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.3, 105.8, 111.1, 117.2 (d, J_{CF}=22.0 Hz), 117.3 (d, J_{CF}=22.0 Hz), 120.1, 125.2 (d, J_{CF}=8.5 Hz), 129.6 (d, J_{CF}=7.3 Hz), 135.5, 135.9, 136.2, 142.7, 159.6 (d, J_{CF}=246.6 Hz), 196; EIMS: *m*/*z* (%) 241 (28) [M^+], 240 (32), 198 (100), 178 (10). Anal. Calcd for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.48; H, 4.79; N, 5.70.

*4.6.11. 5-Acetyl-8-methoxy-4H-pyrrolo[1,2-a][1]benzazepine (**6k**)*

Two steps yield: 57%; yellow solid: mp 62–64 °C (hexane–EtOAc); IR (KBr) 1664, 1628, 1608, 1502 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 5.96 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 6.28 (dd, *J*=3.1 and 3.1 Hz, 1H, pyrrole), 6.90 (d, *J*=2.7 Hz, 1H, aromatic), 6.93 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.02 (dd, *J*=8.9 and 2.7 Hz, 1H, aromatic), 7.41 (s, 1H, CH), 7.45 (d, *J*=8.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.4, 55.6, 105.2, 110.4, 115.1, 116.7, 119.9, 124.7, 128.9, 133.3, 135.3, 137.5, 141.9, 156.7, 196.4; EIMS: *m*/*z* (%) 253 (44) [M^+], 252 (52), 210 (100), 167 (36). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.58; H, 5.73; N, 5.38.

*4.6.12. 5-Acetyl-8-nitro-4H-pyrrolo[1,2-a][1]benzazepine (**6l**)*

Two steps yield: 40%; yellow solid: mp 193–195 °C (hexane–EtOAc); IR (KBr) 1660, 1633, 1610, 1572, 1523, 1491 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3H, CH_3), 3.62 (s, 2H, CH_2), 6.06 (dd, *J*=3.4 and 1.8 Hz, 1H, pyrrole), 6.39 (dd, *J*=3.4 and 3.1 Hz, 1H, pyrrole), 7.01 (dd, *J*=3.1 and 1.8 Hz, 1H, pyrrole), 7.49 (s, 1H, CH), 7.66 (d, *J*=8.9 Hz, 1H, aromatic), 8.30 (dd, *J*=8.9 and 2.4 Hz, 1H, aromatic), 8.36 (d, *J*=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.7, 25.4, 107.7, 112.9, 120.5, 124.2, 124.9, 127.3, 128.3, 135.5, 135.9, 143.3, 144.1, 144.3, 195.9; EIMS: *m*/*z* (%) 268 (39) [M^+], 267 (26), 225 (100), 221 (47), 179 (66), 178 (34). Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 66.88; H, 4.34; N, 10.16.

Acknowledgements

This work was supported in part by Brain Korea 21 program, Republic of Korea.

References and notes

1. (a) Anderson, W. K.; Heider, A. R.; Raju, N.; Yucht, J. A. *J. Med. Chem.* **1988**, *31*, 2097–2102; (b) Fattorusso, C.; Gemma, S.; Butini, S.; Huleatt, P.; Catalanotti, B.; Persico, M.; Angelis, M. D.; Fiorini, I.; Nacci, V.; Ramunno, A.; Rodriquez, M.; Greco, G.; Novellino, E.; Bergamini, A.; Marini, S.; Coletta, M.; Maga, G.; Spadari, S.; Campiani, G. *J. Med. Chem.* **2005**, *48*, 7153–7165.
2. Garofalo, A.; Ragno, G.; Campiani, G.; Brizzi, A.; Nacci, V. *Tetrahedron* **2000**, *56*, 9351–9355.
3. Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556–4573.
4. For reviews of the Morita–Baylis–Hillman reaction, see: (a) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653–4670; (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001–8062; (c) Ciganek, E. *Org. React.* **1997**, *51*, 201–350; (d) Langer, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049–3052; (e) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–891; (f) Kataoka, T.; Kinoshita, H. *Eur. J. Org. Chem.* **2005**, 45–58; (g) Basavaiah, D.; Rao, K. V.; Reddy, R. J. *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; (h) Singh, V.; Batra, S. *Tetrahedron* **2008**, *64*, 4511–4574; (i) Declerck, V.; Martinez, J.; Lamaty, F. *Chem. Rev.* **2009**, *109*, 1–48.
5. Lim, H. N.; Ji, S.-H.; Lee, K.-J. *Synthesis* **2007**, 2454–2460.
6. Jeon, K. J.; Lee, K.-J. *J. Heterocycl. Chem.* **2008**, *45*, 615–619.
7. (a) Kobayashi, K.; Nakahashi, R.; Takanohashi, A.; Kitamura, T.; Morikawa, O.; Konishi, H. *Chem. Lett.* **2002**, 624–625; (b) Kobayashi, K.; Takanohashi, A.; Hashimoto, K.; Morikawa, O.; Konishi, H. *Tetrahedron* **2006**, *62*, 3158–3161; (c) Kobayashi, K.; Takanohashi, A.; Hashimoto, K.; Morikawa, O.; Konishi, H. *Tetrahedron* **2006**, *62*, 10379–10382; (d) Kobayashi, K.; Himei, Y.; Fukamachi, S.; Tanmatsu, M.; Morikawa, O.; Konishi, H. *Tetrahedron* **2007**, *63*, 4356–4359.
8. Josey, A. D.; Jenner, E. L. *J. Org. Chem.* **1962**, *27*, 2466–2470.
9. Wu, Y.; Lawson, P. V.; Henary, M. M.; Schmidt, K.; Brédas, J.-U.; Fahrni, C. J. *J. Phys. Chem. A* **2007**, *111*, 4584–4595.
10. Bras, J. L.; Muzart, J. *Tetrahedron* **2007**, *63*, 7942–7948.
11. Theeraladanon, C.; Arisawa, M.; Nishida, A.; Nakagawa, M. *Tetrahedron* **2004**, *60*, 3017–3035.