



Solventless DBU-promoted Mannich-type reactions of α -amido *p*-tolylsulfones with diethyl fluoromalonates and diethyl malonates

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ARTICLE INFO

Article history:

Received 16 April 2010

Received in revised form 18 May 2010

Accepted 18 May 2010

Available online 25 May 2010

Keywords:

α -Amido *p*-tolylsulfones

α -Fluoro β -amino esters

N-protected imines

Mannich reaction

ABSTRACT

Mannich-type reactions of α -amido *p*-tolylsulfones with diethyl fluoromalonates and diethyl malonates, respectively in presence of catalytic amount of DBU have been developed. A variety of α -amido *p*-tolylsulfones prepared from aromatic and aliphatic aldehydes reacts with diethyl fluoromalonates and diethyl malonates, respectively under mild reaction conditions to afford α -fluoro β -amino esters and β -amino esters in moderate to good yield.

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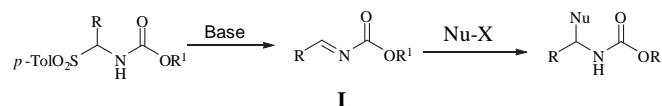
1. Introduction

Fluorine containing organic molecules is of great influence on drug and pharmaceutical industry. Fluorinated compound imparts desirable characteristic to drug by modulating both pharmacokinetic and pharmacodynamic properties of the drug. Therefore incorporation of fluorine into drug increases the metabolic stability, lipophilicity and bioavailability.¹ Thus the preparation of fluorinated compounds has attracted great attention in medicinal chemistry. The catalytic method for the construction of fluorinated molecules is a formidable synthetic challenge and various productive progress has been made in recent years.²

The incorporation of fluorine can be achieved both by nucleophilic and electrophilic fluorinations. Nucleophilic fluoroalkylations have become one of the most important and fast growing field in the fluorine chemistry. Most of the methods involve the transfer of fluorinated carbanion to electrophile. Shibata et al. have described various asymmetric fluorination methods of ketones and α -amido sulfones by cinchona alkaloid.³ Fluoroalkylations of α,β -enones, arynes and activated alkynes with fluorinated sulfones have been reported by Hu et al.⁴ Organocatalyzed asymmetric fluoroalkylations of α,β -unsaturated aldehydes have been described with fluoromalontae by Rios et al.⁵ Similarly, Wang et al. reported the asymmetric Michael reactions of α -fluoro ketoesters with nitroolefines by using cinchona alkaloid

as a catalyst.⁶ Electrophilic fluorinations are another popular option for effective fluorinations. Kim et al. have utilized the phase transfer catalyst for the enantioselective addition of fluorine to β -keto esters.⁷ Asymmetric α -fluorinations of aldehydes have been reported by three independent workers.⁸

α -Amido *p*-tolylsulfones are considered as a precursor of *N*-protected imines **I**. Under the basic conditions, α -amido *p*-tolylsulfones are readily converted to the *N*-protected imines that can further react with various nucleophiles (Scheme 1).^{9a–c} α -Amido *p*-tolylsulfones can be easily prepared by three-component coupling of corresponding aldehyde, sodium *p*-toluenesulfinate and carbamate in presence of formic acid.^{9d}



Scheme 1. Nucleophilic substitution of α -amido *p*-tolylsulfones through *N*-protected imines.

The reactions of α -amido *p*-tolylsulfones have been employed for the synthesis of *N*-homoallylic amines,^{10a} enecarbamates,^{10b} α -amino phosphonates,^{10c} β -amino carbonyl compounds^{10d} and α -amino nitriles.^{10e,f} Ballini et al. have reported that the Montmorillonite K-10 could be an efficient catalyst for the Friedel–Crafts reactions of α -amido *p*-tolylsulfones with indoles.^{10g} Kim et al. demonstrate the Friedel–Crafts alkylation of α -amido *p*-tolylsulfones with arenes and heteroarenes.^{10h–j} Gianelli et al. have

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utilized the amino catalyst for the *anti*-Mannich reaction of aldehydes with α -amido *p*-tolylsulfones.^{10k} Das et al. have explored α -amido *p*-tolylsulfones as a new substrate for aza-Morita-Baylis–Hillman reaction through DABCO as efficient catalyst.^{10l}

Mannich reactions are fundamental method for the carbon–carbon bond formation adjacent to nitrogen atom.¹¹ The key element in the Mannich reactions is an iminium intermediate, which is susceptible to nucleophilic attack by various nucleophiles such as enolized ketones. Due to the synthetic utility of the products, tremendous efforts have been made for Mannich reactions.¹² The use of carbamate-protected alkyl or aryl imines in Mannich reactions raises problem due to their instability.^{13,14c} This problem can be overcome by the use of gradual and in situ generated carbamate protected imines from stable α -amido *p*-tolylsulfones. Recently Schaus et al.,^{14a} Deng et al.^{14b} Ricci et al.^{14c} and Ananthanawat et al.^{14d} have demonstrated Mannich reaction of α -amido sulfones with enolizable carbonyl nucleophiles such as 1,3-diketones, diethyl malonate and β -keto esters. On the basis of their reports the fluorine containing enolizable carbonyl compounds like diethyl fluoromalonate may react with in situ generated *N*-carbamate imines from α -amido sulfones. The development of Mannich reactions of fluoromalonates with α -amido *p*-tolylsulfones yet to be reported.

DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) is well-known as sterically hindered, non-nucleophilic, strong amine base.^{15a,15b} Recently DBU has been widely used as the catalyst for various organic transformations such as cyanoacylation of ketones,^{15c} amidation of cyanoacetates,^{15d} benzylation of nitrogen oxygen or sulfur atoms,^{15e} synthesis of 2*H*-1-chromenes,^{15f} β -hydroxy α -diazo carbonyl compounds^{15g} and synthesis of tetramic acid.^{15h}

2. Results and discussions

In continuation of new synthetic application of α -amido *p*-tolylsulfones,^{10g–j} the DBU-catalyzed Mannich reactions of diethyl fluoromalonates and α -amido *p*-tolylsulfones are herein described. The optimization of reaction conditions has been performed between α -amido *p*-tolylsulfone **1** and diethyl fluoromalonate **2** in presence of various amino bases as shown in Table 1. The organic bases such as DABCO (1,4-diazabicyclo[2.2.2]octane), Guanidino-benzimidazole and ^tBuTMG (2-^tBu-1,1,3,3-tetramethylguanidine) are unable to give the product even after 4 h reaction time (Table 1, entries 2–4). TMG (1,1,3,3-tetramethylguanidine) and DBU (50 mol

Table 1
Mannich-type reactions of α -amido *p*-tolylsulfones **1** with diethyl fluoromalonates **2** in presence of various bases and solvents^a

Entry	Base (mol %)	2 (equiv)	Solvent	Time (h)	Yield ^b (%)
1	TMG (50)	1.0	CH ₂ Cl ₂	4.0	28
2	DABCO (50)	1.0	CH ₂ Cl ₂	4.0	NR
3	Guanidinobenzimidazole (50)	1.0	CH ₂ Cl ₂	4.0	NR
4	^t BuTMG (50)	1.0	CH ₂ Cl ₂	4.0	NR
5	DBU (50)	1.0	CH ₂ Cl ₂	4.0	46
6	DBU (50)	1.0	THF	4.0	Trace
7	DBU (50)	1.0	CH ₃ CN	4.0	NR
8	DBU (50)	1.0	DMF	4.0	NR
9	DBU (50)	2.0	CH ₂ Cl ₂	3.0	68
10	DBU (30)	2.0	CH ₂ Cl ₂	3.0	67
11	DBU (10)	2.0	CH ₂ Cl ₂	3.0	68
12	DBU (10)	2.0	Neat	2.0	70
13	DBU (10)	3.0	Neat	2.0	75

^a Reagent and conditions: **1** (0.5 mmol), **2** (x mmol) at rt.

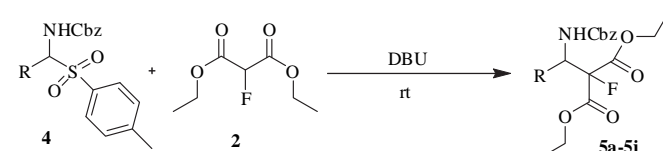
^b Isolated yield.

%) successively offer the 28 % and 46 % yield of product in CH₂Cl₂ (entries 1 and 5). Further survey of reaction parameters such as catalyst loading, reaction time and reagent ratio were performed. DBU (10 mol %) and 3.0 equiv of **2** under solvent-free condition have been found to be the choice of reaction conditions (entry 13).

The reactions of aromatic, aliphatic and heteroaromatic α -amido *p*-tolylsulfones have been investigated to produce the fluorinated β -amino esters (Table 2). The aromatic α -amido *p*-tolylsulfones bearing electron-donating and electron-withdrawing substituents show the clean reaction under the reaction conditions (entries 1–7). Electron-donating *p*-Me and *p*-MeO substituents in **4** shows 80 and 78% yield of the products, respectively (entries 2 and 4). Relative to *p*-Me, *o*-Me gives the lower yield (67%) due to the steric hindrance (entry 3).

Table 2

Mannich-type reactions of various α -amido *p*-tolylsulfones with diethyl fluoromalonate **2**^a



Entry	R in 4	Time (h)	5a–i	Yield ^b (%)
1		2	5a	74
2		2	5b	80
3		2	5c	67
4		2	5d	78
5		2	5e	65
6		4	5f	58
7		4	5g	61
8		2	5h	78
9		2	5i	55

^a Reagent and condition: **4** (0.5 mmol), **2** (3.0 mmol) and 10 mol % of DBU at rt without using solvent.

^b Isolated yield.

α -Amido *p*-tolylsulfone having bromine atom offers the product in lower yield because of electron-withdrawing power (entry 5). This trend becomes even augmented with *p*-CN and *p*-NO₂ (entries 6 and 7). α -Amido *p*-tolylsulfone derived from 2-pyridinecarboxylaldehyde also reacts with diethyl fluoromalonate **2** to yield the product in 78 % yield (entry 8). In addition to aromatic and

heteroaromatic α -amido *p*-tolylsulfones, this catalytic protocol is also applicable for Mannich reactions of aliphatic α -amido *p*-tolylsulfones. α -Amido *p*-tolylsulfone bearing aliphatic chain have shown the somewhat moderate yield (55%) of the adduct (entry 9).

The Mannich-type reactions between α -amido *p*-tolylsulfones and diethyl malonate under the same reaction conditions are also performed (Table 3). α -Amido *p*-tolylsulfone containing no substituent at the benzene ring gives 90% yield of product (entry 1). α -Amido *p*-tolylsulfones containing electron-donating MeO- and Me- groups in the benzene ring are successfully converted into the Mannich adducts with quite high yield (73–90%) (entries 2–5).

Table 3
Mannich-type reactions of various α -amido *p*-tolylsulfones with diethylmalonate^a

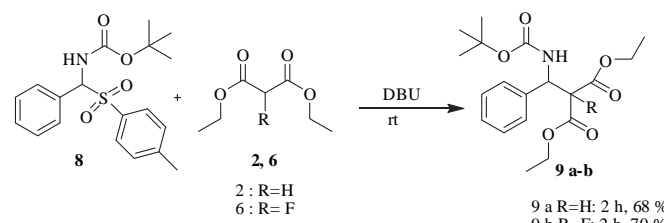
Entry	R in 4	Time (h)	7	Yield ^b (%)
1		2	7a	90
2		2	7b	78
3		2	7c	73
4		2	7d	88
5		2	7e	90
6		2	7f	80
7		2	7g	70
8		5	7h	62
9		2	7i	81
10		2	7j	55
11		2	7k	62

^a Reagent and condition: **4** (0.5 mmol), **6** (3.0 mmol) and 10 mol % of DBU at rt without using solvent.

^b Isolated yield.

p-Bromo and *p*-chloro substituted benzene ring present in **4** (entries 6 and 7) shows 80 and 70% yield, respectively. α -Amido *p*-tolylsulfone with aromatic ring substituted with deactivating

p-NO₂ group require quite longer reaction time with lower yield (entry 8). α -Amido *p*-tolylsulfone derived from acid-sensitive heterocyclic 2-pyridinecarboxylaldehyde undergoes smoothly for the formation of the Mannich product (81%) (entry 9). Aliphatic analogues of α -amido *p*-tolylsulfones are moderately reactive towards the Mannich reactions with quite lower yield (entries 10 and 11). The electron-withdrawing power of fluorine of diethyl fluoromalonates dominates over the statistical factor for diethyl malonates to give the higher yield for the former (compare entry 1 of Table 2, and entry 1 of Table 3, etc.). The reaction conditions are also proved to be equally effective in Mannich-type reactions of *N*-Boc amido *p*-tolylsulfones with diethyl fluoromalonate and diethyl malonate, respectively (Scheme 2). The *N*-Boc amido *p*-tolylsulfones show the similar yield of Mannich adducts relative to *N*-Cbz amido *p*-tolylsulfone under identical reaction conditions.

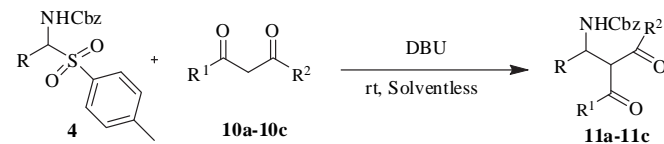


Scheme 2. The Mannich-type reactions of **2** and **6** with *N*-Boc amido *p*-tolylsulfones.

Although several other catalytic methods of carbon–carbon bond formation at the α -position of amine have been reported, present protocol is simple and efficient in terms of reaction condition such as lower temperature and strong Lewis acid.^{13a,16}

DBU-catalyzed Mannich-type reactions of α -amido *p*-tolylsulfones are also applicable with 1,3-diketone, β -keto ester and cyclic diketone (Table 4). Acetylacetone shows quite high reactivity towards α -amido *p*-tolylsulfone in presence of 10 mol % of DBU (50 min and 94%) (entry 1). Ethylacetoacetate gives the 81% yield of Mannich products within 2 h. But cyclic 1,3-dicarbonyl compound produces somewhat lower yield relative long chain 1,3-dicarbonyl substrate under the same reaction conditions (79%, 3 h).

Table 4
Mannich-type reactions of α -amido *p*-tolylsulfones **4** with 1,3-diketone, β -keto ester and cyclic diketone^a



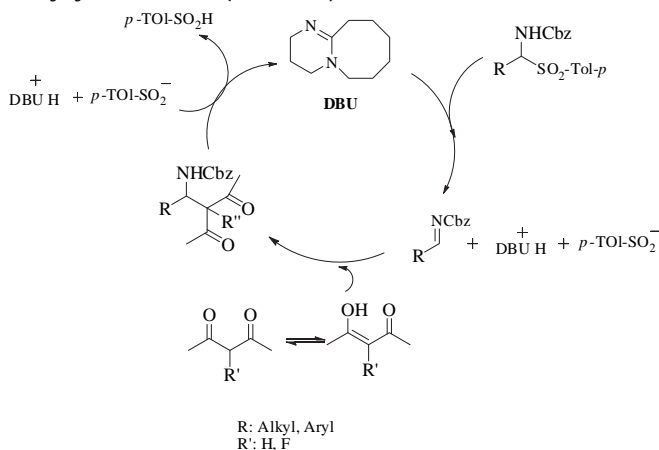
Entry	10a–c	11a–c	Time (h)	Yield ^b (%)
1		11a	50 min	94
2		11b	2	81
3		11c	3	79 ^c

^a Reagent and condition: **1** (0.5 mmol), **8** (2.0 mmol) and 10 mol % of DBU at rt without using solvent.

^b Isolated yield.

^c CH₂Cl₂ was used at rt.

Plausible mechanism and role of DBU are shown in Scheme 3. The reaction includes the formation of *N*-acylimine by the elimination of benzenesulfinate. The intermediate *N*-acylimine undergoes the nucleophilic addition with enolate of dicarbonyl compound or diethyl malonate to give the corresponding addition product. Finally benzenesulfinate abstracts the proton from DBU+H to release DBU and benzenesulfonic acid. This mechanism consists of DBU (5 mol %) catalyzed intramolecular cyclization reaction of *o*-alkynylbenzoic acid (0.3 mmol).¹⁷



Scheme 3. Plausible mechanism for Mannich-type reaction of α -amido *p*-tolylsulfones.

DBU-catalyzed Mannich-type reactions of diethyl fluoromalonates and diethyl malonates with in situ generated carbamate protected imines from α -amido *p*-tolylsulfones are developed. The present process is efficiently catalyzed by readily available base under solvent-free conditions. This strategy is extended to diethyl malonate, 1,3-dicarbonyl compound and β -keto ester too.

3. Experimental section

3.1. General

In all cases the ^1H NMR (400 MHz) spectra were recorded with Varian Gemini 4000 spectrometer. Chemical shifts are reported in parts per million in CDCl_3 with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on a Varian Gemini 2000 spectrometer (50 MHz).

3.2. Experimental procedure for the Mannich-type reaction of α -amido *p*-tolylsulfones with diethyl fluoromalonates and diethyl malonates

To a mixture of α -amido *p*-tolylsulfone (0.5 mmol) and diethyl malonate or diethyl fluoromalonate (3.0 mmol), DBU (10 mol %) was added and stirred at rt. The progress of the reaction mixture was monitored by TLC. After completion of reaction the crude product was subject to column chromatography to obtain the pure product.

^1H , ^{13}C NMR data HRMS and IR values for all products are given below.

3.2.1. Compound 5a. IR (KBr): 3414, 3330, 2841, 1728, 1690, 1590, 1218, 1131, 1008, 745, 657 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.37–7.31 (m, 10H), 5.77–5.75 (m, 1H), 4.22 (q, $J=2.8$ Hz, 2H), 4.09 (q, $J=2.8$ Hz, 2H), 1.23 (t, $J=7.2$ Hz, 3H), 1.09 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 175.8, 164.5, 164.0, 163.3, 155.0, 135.9, 135.3,

128.6, 128.5, 128.4, 128.1, 122.3, 67.2, 63.1, 62.8, 57.7, 57.3, 13.7, 13.6. HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{FNO}_6$: 418.1666, found: 418.1667.

3.2.2. Compound 5b. IR (KBr): 3426, 3320, 2817, 1742, 1685, 1581, 1278, 1128, 1011, 780, 627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.30–7.24 (m, 7H), 7.12 (d, $J=7.6$ Hz, 2H), 5.79–5.70 (m, 2H), 5.11 (d, $J=12.0$ Hz, 1H), 5.00 (d, $J=12.4$ Hz, 1H), 4.23 (q, $J=3.0$ Hz, 2H), 4.10 (q, $J=3.0$ Hz, 2H), 2.31 (s, 3H), 1.23 (t, $J=7.0$ Hz, 3H), 1.09 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 164.53, 164.00, 163.83, 163.33, 155.0, 138.3, 136.0, 132.6, 129.0, 128.3, 128.0, 127.2, 122.1, 67.0, 63.0, 62.6, 57.4, 57.0, 21.0, 13.6, 13.5. HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{FNO}_6$: 432.1822, found: 432.1824.

3.2.3. Compound 5c. IR (KBr): 3436, 3318, 1752, 1680, 1571, 1248, 1131, 1008, 770, 650 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.39–7.14 (m, 9H), 6.08–6.01 (m, 1H), 5.59 (d, $J=10$ Hz, 1H), 5.10 (d, $J=12$ Hz, 1H), 4.98 (d, $J=12.0$ Hz, 1H), 4.26 (q, $J=3.0$ Hz, 2H), 4.04 (q, $J=3.0$ Hz, 2H), 2.54 (s, 3H), 1.28 (t, $J=7.0$ Hz, 3H), 1.02 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ : 176.0, 155.5, 137.1, 136.0, 130.7, 128.5, 128.4, 128.1, 128.0, 126.5, 122.4, 67.1, 36.2, 62.7, 19.8, 13.8, 13.4. HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{FNO}_6$: 432.1822, found: 432.1823.

3.2.4. Compound 5d. IR (KBr): 3426, 3289, 2847, 1765, 1690, 1577, 1238, 1191, 1042, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.30–7.25 (m, 7H), 6.83 (d, $J=8.8$ Hz, 2H), 5.70 (s, 2H), 5.10 (d, $J=12.0$ Hz, 1H), 5.00 (d, $J=12.0$ Hz, 1H), 4.22 (q, $J=3.3$ Hz, 2H), 4.10 (q, $J=3.0$ Hz, 2H), 3.77 (s, 3H), 1.23 (t, $J=7.0$ Hz, 3H), 1.11 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.5, 160.3, 130.1, 129.0, 128.7, 128.1, 122.6, 14.5, 67.7, 63.7, 63.4, 55.8, 14.3.

3.2.5. Compound 5e. IR (KBr): 3436, 3318, 2845, 1752, 1680, 1571, 1248, 1131, 1008, 770, 664 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.42 (d, $J=8.4$ Hz, 2H), 7.38–7.25 (m, 7H), 5.81 (d, $J=10.0$ Hz, 1H), 5.73–5.66 (m, 1H), 5.10 (d, $J=12.0$ Hz, 1H), 5.00 (d, $J=12.0$ Hz, 1H), 4.22 (q, $J=3.0$ Hz, 2H), 4.10 (d, $J=3.0$ Hz, 2H), 1.21 (t, $J=7.2$ Hz, 3H), 1.11 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.0, 164.4, 164.0, 163.7, 163.2, 155.0, 143.7, 136.0, 134.4, 131.7, 130.0, 128.5, 128.2, 128.1, 123.0, 67.3, 63.3, 63.0, 57.2, 56.8, 13.8, 13.7. HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{BrFNO}_6$: 496.0771, found: 496.0772.

3.2.6. Compound 5f. IR (KBr): 3328, 3358, 2913, 1690, 1645, 1571, 1278, 1124, 1155, 1018, 780 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (d, $J=7.6$ Hz, 2H), 7.45 (d, $J=8.0$ Hz, 2H), 7.26–7.22 (m, 5H), 5.95 (d, $J=9.6$ Hz, 1H), 5.77–5.68 (m, 1H), 5.06 (d, $J=12.4$ Hz, 1H), 4.95 (d, $J=12.0$ Hz, 1H), 4.20 (q, $J=3.2$ Hz, 2H), 4.10 (q, $J=3.0$ Hz, 2H), 1.18 (t, $J=7.0$ Hz, 3H), 1.10 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 164.7, 164.2, 164.1, 155.6, 141.1, 136.2, 132.8, 129.7, 129.0, 128.9, 128.7, 122.8, 118.5, 113.1, 68.0, 64.0, 63.8, 57.8, 57.4, 14.3, 14.2. GC–MS: m/z : 443 $[\text{M}^+]$, 221, 107, 106, 91.

3.2.7. Compound 5g. IR (KBr): 3346, 3318, 2895, 1782, 1647, 1544, 1248, 1138, 1157, 770, 685 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (d, $J=7.6$ Hz, 2H), 7.53 (d, $J=7.6$ Hz, 2H), 7.25–7.20 (m, 5H), 5.88–5.71 (m, 2H), 4.25–4.19 (m, 2H), 4.10–4.07 (m, 2H), 1.19–1.07 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 204.2, 203.6, 157.5, 129.4, 128.4, 128.0, 122.4, 120.6, 110.9, 74.5, 55.2, 41.5, 30.4, 28.3, 26.7, 11.5; HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{FN}_2\text{O}_8$: 463.1517, found: 463.1522.

3.2.8. Compound 5h. IR (KBr): 3385, 3018, 2877, 1738, 1675, 1578, 1228, 1176, 1048, 784, 650 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H), 7.54 (t, $J=7.6$ Hz, 2H), 7.28–7.23 (m, 5H), 7.13 (d, $J=7.5$ Hz, 1H), 6.19 (d, $J=9.2$ Hz, 1H), 5.79–5.82 (m, 1H), 5.00 (s, 12H), 4.26–4.23 (m, 2H), 4.18–4.13 (m, 2H), 1.24–1.12 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.0, 157.0, 149.0, 143.7, 136.7, 136.2, 128.5,

128.5, 128.2, 128.1, 123.3, 67.2, 66.8, 63.2, 57.7, 13.8, 13.9. GC–MS: m/z : 418 $[M^+]$, 241, 197, 107, 91.

3.2.9. **Compound 5i**. IR (KBr): 3245, 3342, 2755, 1760, 1635, 1590, 1247, 1210, 1008, 847, 760, 645 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.34–7.25 (m, 5H), 5.00–4.99 (m, 2H), 4.64–4.53 (m, 1H), 4.30–4.15 (m, 2H), 4.16–4.13 (m, 2H), 1.05–1.18 (m, 14H), 0.84 (t, $J=13.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.8, 164.6, 155.6, 136.1, 128.3, 127.9, 127.9, 122.5, 66.7, 62.7, 54.2, 53.8, 31.4, 29.7, 28.6, 25.3, 22.3, 13.9, 13.6. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{22}\text{H}_{33}\text{FNO}_6$: 426.2292, found: 426.2290.

3.2.10. **Compound 7a**. IR (KBr): 3436, 3318, 1752, 1680, 1571, 1248, 1131, 1008, 780 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.33–7.25 (m, 10H), 6.50 (d, $J=8.4$ Hz, 1H), 5.55 (d, $J=4.4$ Hz, 1H), 3.7 (d, $J=4.4$ Hz, 1H), 4.20–4.09 (m, 4H), 1.21–1.09 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.9, 167.9, 155.6, 139.1, 136.3, 128.5, 128.4, 128.0, 127.7, 126.2, 66.8, 62.0, 61.6, 56.7, 53.8, 13.8. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_6$: 400.1760, found: 400.1758.

3.2.11. **Compound 7b**. IR (KBr): 3325, 3250, 2730, 1740, 1645, 1584, 1247, 1110, 1048, 783 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.31–7.29 (m, 5H), 7.23 (d, $J=8.6$ Hz, 2H), 7.15 (d, $J=8.6$ Hz, 2H), 6.47 (d, $J=7.6$ Hz, 1H), 5.51 (s, 1H), 5.11–5.03 (m, 2H), 4.20–3.88 (m, 4H), 2.30 (s, 3H), 1.17–1.09 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.0, 167.0, 155.7, 137.3, 136.4, 136.2, 129.2, 128.4, 128.0, 126.2, 66.8, 61.9, 61.6, 56.8, 53.7, 21.0, 14.0, 13.8. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{23}\text{H}_{28}\text{O}_6\text{N}$: 414.1917, found: 414.1924.

3.2.12. **Compound 7c**. IR (KBr): 3315, 3302, 2865, 1789, 1675, 1510, 1267, 1145, 1035, 827 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.30–7.23 (m, 6H), 7.15 (d, $J=8.4$ Hz, 3H), 6.50 (d, $J=8.4$ Hz, 1H), 5.72 (q, $J=4.2$ Hz, 1H), 5.03 (q, $J=13.2$ Hz, 2H), 4.18–4.02 (m, 4H), 3.75 (d, $J=4.8$ Hz, 1H), 2.46 (s, 3H), 1.20–1.08 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.0, 167.0, 155.4, 137.4, 136.3, 135.0, 130.6, 128.3, 128.0, 127.6, 126.1, 125.6, 66.7, 62.0, 61.6, 55.2, 50.8, 19.0, 13.8, 13.7. GC–MS: m/z : 414 $[M^+]$, 254, 210, 117, 90.

3.2.13. **Compound 7d**. IR (KBr): 3245, 3342, 2755, 1760, 1635, 1590, 1247, 1210, 1008, 847 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.35–7.20 (m, 7H), 6.84 (d, $J=8.4$ Hz, 2H), 6.46 (d, $J=9.2$ Hz, 1H), 5.53–5.46 (m, 1H), 5.08–5.05 (m, 2H), 4.16–4.09 (m, 4H), 3.79 (s, 3H), 1.22–1.10 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.9, 166.8, 158.8, 155.5, 136.3, 128.3, 127.9, 127.3, 113.8, 66.7, 61.8, 61.5, 56.7, 55.1, 53.3, 13.8. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{23}\text{H}_{28}\text{O}_7\text{N}$: 429.1788, found: 429.1783.

3.2.14. **Compound 7e**. IR (KBr): 3376, 3348, 1652, 1680, 1570, 1274, 1131, 1011, 860 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.36–7.26 (m, 5H), 6.49 (d, $J=7.2$ Hz, 2H), 5.48–5.42 (m, 1H), 5.09 (s, 2H), 4.20–4.05 (m, 4H), 3.81 (s, 9H), 1.25 (t, $J=3.0$ Hz, 3H), 1.10 (t, $J=3.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.3, 128.4, 128.1, 103.2, 67.0, 62.1, 61.7, 60.8, 56.07, 15.3, 14.0. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{25}\text{H}_{32}\text{O}_9\text{N}$: 489.1999, found: 489.2003.

3.2.15. **Compound 7f**. IR (KBr): 3350, 3328, 1614, 1660, 1548, 1525, 1234, 1107, 1028, 850, 670 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.46–7.33 (m, 7H), 7.44 (d, $J=8.4$ Hz, 2H), 7.39–7.33 (m, 4H), 7.19 (d, $J=8.4$ Hz, 2H), 6.50 (d, $J=8.0$ Hz, 1H), 5.47 (d, $J=3.2$ Hz, 1H), 5.12–5.04 (m, 2H), 4.1–4.08 (m, 4H), 3.82 (d, $J=3.6$ Hz, 1H), 1.21–1.12 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.0, 156.2, 131.7, 128.5, 128.0, 124.0, 67.0, 62.2, 62.0, 55.3, 13.0, 13.8; EIMS (m/z): $[M+H]^+$: 389.2.

3.2.16. **Compound 7g**. IR (KBr): 3361, 3288, 1672, 1660, 1515, 1520, 1274, 1131, 1011, 855 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.41–7.24 (m, 9H), 6.62 (d, $J=8.8$ Hz, 1H), 5.60–5.56 (m, 1H), 5.16–5.09 (m, 2H), 4.25–4.13 (m, 4H), 3.94 (s, 1H), 1.27–1.18 (m, 6H); ^{13}C NMR

(100 MHz, CDCl_3) δ : 168.0, 166.6, 155.5, 137.6, 136.1, 133.4, 128.6, 128.3, 128.0, 127.6, 6.8, 62.1, 61.7, 56.3, 53.3, 13.8, 13.7. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{ClO}_6\text{N}$: 434.1370, found: 434.1370.

3.2.17. **Compound 7h**. IR (KBr): 3353, 3325, 1642, 1630, 1470, 1254, 1131, 1011, 860, 725 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.15 (d, $J=7.6$ Hz, 2H), 7.50 (d, $J=7.6$ Hz, 2H), 7.33–7.25 (m, 5H), 6.55 (d, $J=8.0$ Hz, 1H), 5.60 (d, $J=3.2$ Hz, 1H), 5.10–5.05 (m, 2H), 4.21–4.10 (m, 4H), 3.89 (d, $J=3.2$ Hz, 1H), 1.2–1.09 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.0, 155.2, 148.6, 141.5, 131.7, 128.8, 128.2, 124.0, 67.0, 62.2, 62.0, 55.3, 13.0. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{O}_8\text{N}_2$: 445.1611, found: 445.1613.

3.2.18. **Compound 7i**. IR (KBr): 3376, 3348, 3052, 1752, 1680, 1470, 1274, 1162, 1001, 860, 758 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.42 (d, $J=4.8$ Hz, 1H), 7.60 (t, $J=7.6$ Hz, 1H), 7.31–7.22 (m, 6H), 7.13–7.10 (m, 1H), 6.35 (d, $J=8.0$ Hz, 1H), 5.61–5.59 (m, 1H), 5.13–5.06 (m, 2H), 4.41 (d, $J=5.2$ Hz, 1H), 4.19–4.10 (m, 4H), 1.24–1.14 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.8, 168.5, 158.1, 148.7, 136.7, 128.4, 127.9, 122.4, 121.5, 66.8, 61.7, 54.8, 13.8. GC–MS: m/z : 419 $[M^+]$, 307, 197, 107, 91.

3.2.19. **Compound 7j**. IR (KBr): 3346, 3323, 2928, 1627, 1605, 1570, 1230, 1131, 1021, 860, 746 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.31–7.24 (m, 5H), 5.79 (d, $J=40.4$ Hz, 1H), 5.03 (q, $J=10.4$ Hz, 2H), 4.22–4.15 (m, 2H), 4.09–4.04 (m, 2H), 3.67 (d, $J=4.0$ Hz, 1H), 1.82–1.59 (m, 8H), 1.40–1.38 (m, 2H), 1.26–1.25 (m, 1H), 1.24–1.10 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.1, 168.6, 156.1, 136.6, 128.3, 127.8, 66.4, 61.5, 55.6, 52.4, 41.2, 30.0, 29.4, 25.9, 25.8, 25.6, 13.8, 13.6. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{22}\text{H}_{32}\text{O}_6\text{N}$: 406.2230, found: 406.2232.

3.2.20. **Compound 7k**. IR (KBr): 3246, 3215, 2845, 1640, 1675, 1570, 1212, 1145, 1047, 840, 730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.33–7.28 (m, 5H), 5.65 (d, $J=1.0$ Hz, 1H), 5.06 (s, 2H), 4.30–4.11 (m, 4H), 3.55 (d, $J=4.4$ Hz, 1H), 1.57–1.49 (m, 2H), 1.29–1.19 (m, 14H), 0.86 (t, $J=6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.8, 168.3, 167.7, 155.8, 136.5, 128.3, 127.8, 66.5, 61.7, 61.4, 54.8, 50.7, 33.6, 31.5, 28.8, 26.1, 22.4, 13.9, 13.8. EIMS: m/z : 408 $[M^+]$, 322, 278, 106, 90.

3.2.21. **Compound 9a**. IR (KBr): 3323, 3304, 2945, 1615, 1600, 1540, 1230, 1145, 1042, 870, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.29–7.25 (m, 5H), 6.11–6.21 (m, 1H), 5.59–5.62 (m, 1H), 4.30–4.10 (m, 4H), 3.94 (s, 1H), 1.41 (s, 9H), 1.38 (t, $J=6.4$ Hz, 3H), 1.14 (t, $J=6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.9, 154.5, 135.6, 128.4, 127.4, 126.1, 79.5, 61.8, 61.00, 56.8, 62.7, 56.8, 28.1, 13.9, 13.7. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{19}\text{H}_{28}\text{O}_6\text{N}$: 366.1917, found: 366.1911.

3.2.22. **Compound 9b**. IR (KBr): 3391, 3062, 2950, 2913, 1680, 1570, 1230, 1131, 1021, 860, 746 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.34–7.25 (m, 5H), 5.65–5.62 (m, 1H), 5.42–5.46 (m, 1H), 4.33–4.25 (m, 4H), 4.14–4.08 (m, 4H), 3.84–3.82 (m, 1H), 1.37–1.30 (m, 12H), 1.12 (t, $J=6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 175.8, 154.2, 135.6, 128.4, 128.2, 80.2, 63.0, 62.7, 57.2, 56.8, 28.0, 13.8, 13.6. HRMS-FAB: $[MH]^+$ calcd for $\text{C}_{19}\text{H}_{27}\text{FO}_6\text{N}$: 384.1822, found: 384.1821.

3.2.23. **Compound 11a**. IR (KBr): 3325, 3012, 2940, 2910, 1630, 1545, 1230, 1021, 860; ^1H NMR (400 MHz, CDCl_3) δ : 7.25–7.19 (m, 10H), 6.0 (s, 1H), 5.18 (s, 1H), 5.01 (d, $J=8.8$ Hz, 2H), 4.15 (d, $J=5.6$ Hz, 1H), 2.11–2.00 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 202.2, 202.1, 155.7, 139.5, 136.0, 128.7, 128.5, 128.3, 128.0, 127.8, 127.7, 126.3, 71.4, 66.9, 54.2, 30.2, 29.9.

3.2.24. **Compound 11b**. IR (KBr): 3338, 3310, 2854, 2951, 1627, 1552, 1260, 1021, 827; ^1H NMR (400 MHz, CDCl_3) δ : 7.28–7.21 (m, 10H), 6.54–6.39 (m, 1H), 5.60–5.50 (m, 1H), 5.05–5.00 (m, 2H),

4.09–3.99 (m, 3H), 2.12 (s, 3H), 1.03 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 202.9, 202.7, 168.3, 166.8, 155.6, 155.5, 139.2, 139.1, 136.1, 128.5, 128.2, 128.0, 127.8, 127.5, 126.4, 126.0, 66.7, 64.0, 61.6, 54.2, 30.3, 13.6; HRMS-FAB (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{N}$: 370.1654, found: 370.1655.

3.2.25. **Compound 11c**. IR (KBr): 3335, 3022, 2870, 2932, 1665, 1545, 1228, 1021, 852; ^1H NMR (400 MHz, CDCl_3) δ : 7.35–7.23 (m, 10H), 6.20 (d, $J=9.6$ Hz, 2H), 5.10 (d, $J=12.8$ Hz, 2H), 2.30–2.16 (m, 4H), 1.05 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 192.9, 167.7, 157.2, 157.9, 136.6, 134.1, 133.4, 129.0, 128.6, 128.5, 113.9, 113.8, 61.4, 59.8, 55.1, 55.0, 49.3, 13.7; HRMS-FAB: $[\text{MH}]^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}$: 380.1862, found: 380.1863.

Acknowledgements

The authors thank the Center for Biological Modulators of the KRICT for the financial support. Thanks are also due to BK 21 administrated by Korea Research Council.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.05.075.

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