Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 1314

www.rsc.org/greenchem

PAPER

Atom-economical synthesis of the functionalized spirocyclic oxindole-butenolide *via* three-component [2 + 2 + 1] cycloaddition strategy†

Jian Li,*[a] Yuejin Liu,[a] Chunju Li,[a] Haohua Jie[a] and Xueshun Jia*[a,b]

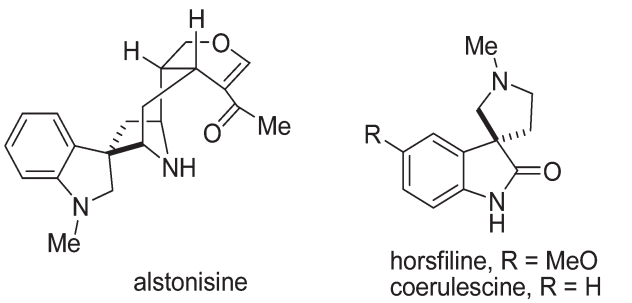
Received 5th January 2012, Accepted 10th February 2012
DOI: 10.1039/c2gc00015f

The intermolecular [2 + 2 + 1] multicomponent cycloadditions from readily available isocyanides, activated alkynes and isatins are disclosed. This reaction proceeds by way of a Michael addition–nucleophilic addition–intramolecular cyclization sequence, thus providing new access to spirocyclic oxindole-butenolide with exclusive stereoselectivity in an efficient and atom-economical manner. A broad range of isatins and isocyanides including sterically demanding ones are also found to be compatible with the present protocol, which offers an opportunity for the construction of a new compound library. This protocol also allows the insertion of carbon monoxide into organic molecules without the aid of transition metal catalyst after hydrolysis process. Moreover, the cycloaddition–hydrolysis process by step can be further developed into a practical and powerful one-pot strategy in good yields together with convenient experimental set-up, which adds to its attractiveness.

Introduction

Oxindoles are frequently found core structures in many natural products and compounds of pharmaceutical significance.[1] For instance, medicines containing this key structure have been used as the anti-Parkinson's drug ropinirole and the growth hormone secretagogues.[2] Among the family of these compounds, spirocyclic oxindoles are particularly important due to their unique structural characteristics and biological activities. Many natural products, such as alstonisine and horsfiline, have been interesting synthetic targets to synthetic chemists (Scheme 1).[3] As a result, much efforts have been devoted to their syntheses, thus providing considerable progress in this area.[4] Among these methods, those started from isatin seems to be the most straightforward approach to this end.[5] Recently, we have focused our attention on the syntheses of carbocycles and potentially bioactive heterocycles.[6] As a continuation, herein we wish to report an efficient and atom-economical synthesis of spirocyclic oxindole–butenolide derivatives by three-component [2 + 2 + 1] cycloaddition.

In the past few decades, isocyanides have proved themselves to be irreplaceable one-carbon building blocks in modern organic chemistry.[7] For example, an isocyanide-based multicomponent reaction has emerged as a powerful tool in the syntheses of heterocycles and pharmaceutical molecules.[8] From an organic



Scheme 1 Natural products possessing spiro-oxindole as core structure.

view of point, methods starting from isocyanides often have distinct advantages, including enhanced convergence, inherent atom economy, and the great variety of isocyanides readily available for use. In particular, the reactivity of isocyanide can be electronically and sterically controlled by simply changing the substituent on nitrogen. On the other hand, the isocyanide chemistry can serve as powerful carbonylation method, which enables insertion of carbon monoxide into organic molecules in an efficient manner. For instance, using isocyanide in Pauson–Khand reaction (PKR) in place of CO and other transition-metal-catalyzed insertions have also been investigated.[9,10] Considering the versatility of isocyanide chemistry, we are intended to develop new carbonylation strategy based on multicomponent reaction.

It is well known that conjugated alkynoates are among the most reactive Michael acceptors, nucleophiles including tertiary amines[11] and phosphines[12] have been used to trigger such species in many multibond-forming processes. Prior to this work, we have also shown that ethyl propiolate underwent a

[a]*Department of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444, P. R. China. E-mail: lijian@shu.edu.cn, xsjia@mail.shu.edu.cn; Fax: +86-21-66132408*
[b]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, P. R. China*

†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra for compound **4**, **5**, **6**. CCDC reference numbers 836563 (**4o**) and 836562 (**5a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2gc00015f

tandem conjugated addition process in the presence of *o*-phenylenediamine to deliver a novel strategy for the construction of functional 1,5-benzodiazepines.[6a] According to our assumption, isocyanide could also serve as a nucleophile to trigger the corresponding nucleophilic attack towards ethyl propiolate, thus offering an opportunity for the development of novel three-component [2 + 2 + 1] cycloaddition reactions. To our knowledge, multicomponent reaction involving isocyanide and alkyl propiolate has not been reported yet.

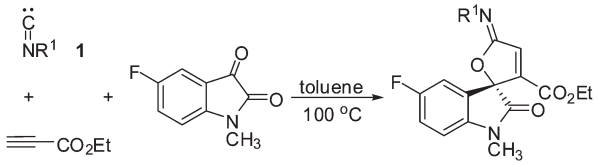
Results and discussion

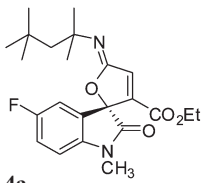
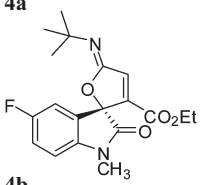
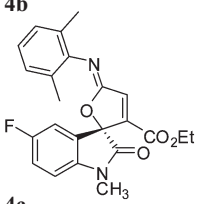
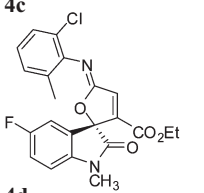
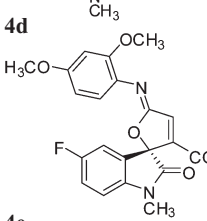
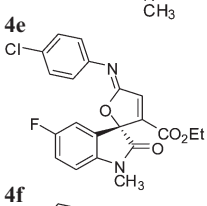
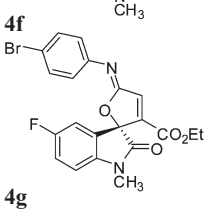
To probe the feasibility of the proposed transformation, 1,1,3,3-tetramethylbutyl isocyanide **1a**, ethyl propiolate **2a**, and isatin **3b** were used as starting materials. Upon treatment of **2a** with **1a** and **3b** at 100 °C for 18 hours, a 78% yield of adduct **4a** was observed (Table 1, entry 1). Following this encouraging result, we turned our attention to the scope and limitation of this process. A variety of isocyanides **1** were examined under the optimal conditions and the results were summarized in Table 1. As shown in Table 1, the present reactions proceeded smoothly in all cases and all compounds **4** were fully characterized by IR, ^{1}H NMR, ^{13}C NMR, and HRMS spectra.[13] Traditionally, aromatic isocyanide, especially sterically demanding aromatic isocyanides are considered to be less reactive. Despite the prolonged reaction time and somewhat lower yields, these isocyanides were found to be compatible with this cycloaddition protocol (Table 1, entries 3–7).

Having established the scope and limitations with structurally diverse isocyanides, we sought to briefly investigate the feasibility of substituted isatins **3**. During our screening efforts, various isatins **3** having electron-neutral (Table 2, entry 1), electron-deficient (Table 2, entries 2–5), and electron-rich substituents (Table 2, entries 6 and 7) on the aryl ring were used to test the substitution pattern. Gratifyingly, all isatins performed well with isocyanide **1a** and ethyl propiolate **2a** under the optimal conditions. Moreover, the structure of compound **4o** was unambiguously confirmed by single crystal X-ray analysis (Fig. 1).[14] During our investigation, the influence of different protecting group at the nitrogen of isatin **3** was also examined (Table 2, entries 8–10). In such cases, the benzyl group turned out to be another good choice. Furthermore, the protection of the nitrogen atom of isatin **3** was quite necessary, otherwise the reaction would become quite complex. With these encouraging results, other substituted conjugated alkynoate **2b** and **2c** were also tested under the optimal conditions. As shown in Table 2, the blending of selected starting materials essentially led to the formation of corresponding products **4** (Table 2, entries 11–13).

The mechanism of this three-component cycloaddition reaction has not been unequivocally established, but one reasonable possibility is proposed to account for the formation of spirocyclic oxindole-butenolide **4** (Scheme 2). The nucleophilic addition of isocyanide **1** towards conjugated alkynoate essentially leads to the formation of zwitterionic species **A**, which is subsequently captured by the reactive carbonyl group of isatin **3** to form **B**. This intermediate experiences further intramolecular cyclization to yield stable product **4**.

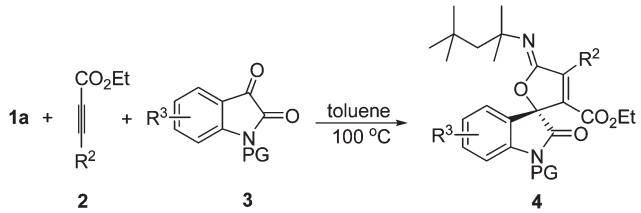
Table 1 Three-component [2 + 2 + 1] cycloaddition of isocyanide **1**, ethyl propiolate **2** and isatin **3b**[a]



Entry	Product **4**	Time (h)	Yield[b] (%)
1	 **4a**	18	78
2	 **4b**	18	89
3	 **4c**	48	39
4	 **4d**	36	72
5	 **4e**	72	41
6	 **4f**	48	44
7	 **4g**	24	65

[a] All reactions were carried out with 0.5 mmol of isocyanide **1**, 0.6 mmol ethyl propiolate **2**, 0.5 mmol isatin **3b** in 5 mL toluene and heated at 100 °C in air. [b] Yields of product after silica gel chromatography.

Table 2 Three-component [2 + 2 + 1] cycloaddition of isocyanide **1a**, ethyl propiolate **2** and substituted isatin **3**[a]



Entry	R^2	R^3	PG[b]	Yield[c] (%)
1	H	H	Me	**4h**: 91
2	H	5-Fluoro	Me	**4a**: 78
3	H	4,6-Dichloro	Me	**4i**: 88
4	H	6-Bromo	Me	**4j**: 93
5	H	5-Nitro	Me	**4k**: 90
6	H	5-Methoxy	Me	**4l**: 65
7[d]	H	5,7-Dimethyl	Me	**4m**: 92
8	H	H	Bn[e]	**4n**: 86
9	H	4-Chloro	Bn	**4o**: 85
10	H	7-Bromo	Bn	**4p**: 59
11[d]	Me	H	Ph	**4q**: 71
12	Me	5-Chloro	Me	**4r**: 63
13	Ph	H	Me	**4s**: 39

[a] Reaction conditions: 0.5 mmol of 1,1,3,3-tetramethylbutyl isocyanide **1a**, 0.6 mmol ethyl propiolate **2**, 0.5 mmol substituted isatin **3**, 5 mL toluene, 100 °C, 18 hours in air. [b] PG = protecting groups. [c] Yields of product after silica gel chromatography. [d] In such case, reaction was completed within 72 hours. [e] Bn = benzyl.

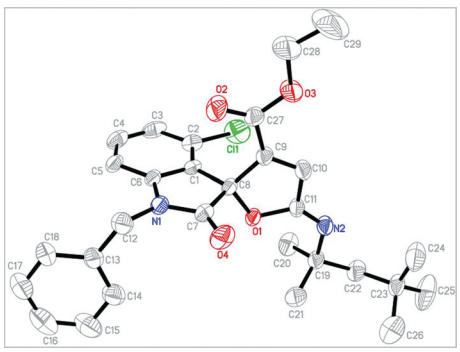
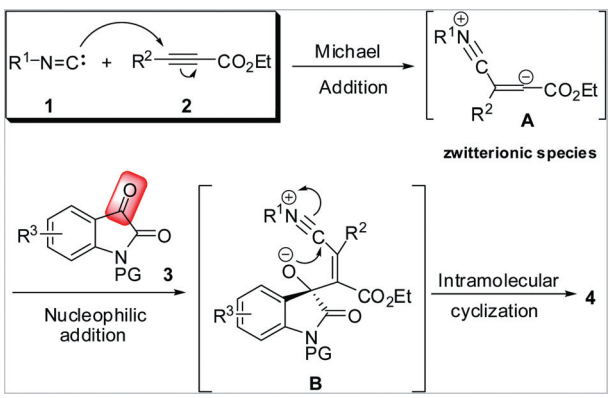
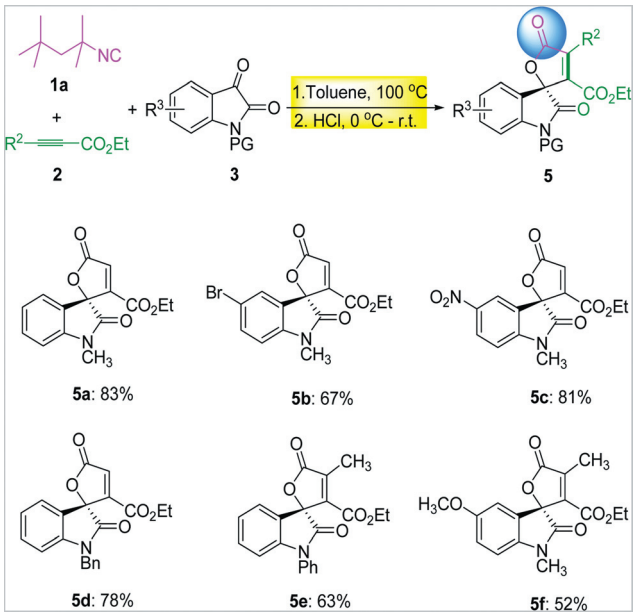


Fig. 1 Single-crystal X-ray structure of **4o**.



Scheme 2 Proposed mechanism for the formation of **4**.



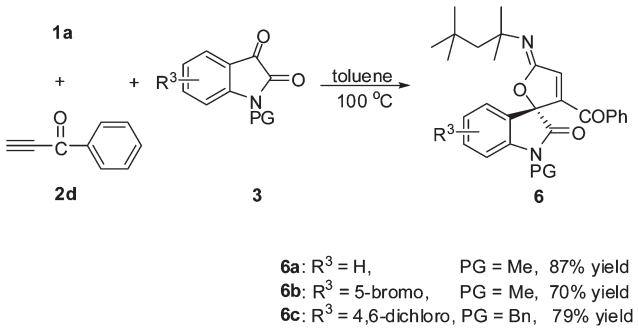
Scheme 3 One-pot syntheses of products **5**.

With this highly efficient cycloaddition protocol in hand, we attempted to hydrolyze the corresponding cycloaddition adducts **4**. Treatment of compounds **4** under standard hydrolysis conditions essentially gave products **5** in excellent yields. To our delight, the cycloaddition and hydrolysis reactions could be further developed into a one-pot strategy. As shown in Scheme 3, the reaction mixture was allowed to react at 0 °C with concentrated HCl in mixed solvent (EtOH and water) after the [2 + 2 + 1] cycloaddition was finished, then the mixture was elevated to room temperature until completion. By merging cycloaddition–hydrolysis sequences, this one-pot reaction achieved straightforward and efficient insertion of CO without the aid of any metal catalyst. During this process, the structure of **5a** also confirmed by X-ray analysis.[15] Traditionally, carbonylation chemistry serves as one of the most straightforward methodologies for introducing carbonyl functionalities into organic molecules.[16] The cycloaddition involving isocyanide followed by hydrolysis process enabled the introduction of carbon monoxide and quick access to spirocyclic oxindole–butenolide, which offers new opportunity for their applications in organic chemistry.

To further demonstrate the utility of the present annulation strategy, 1-phenylprop-2-yn-1-one **2d** was also examined (Scheme 4). Pleasingly, the above mentioned cycloaddition reaction proceeded smoothly with **2d** to give product **6** in good yields. In such runs, all reactions could be finished within 12 hours. In particular, these results also advanced the possibility of stereoselective synthesis of spirocycles with activated alkynone **2**.

Conclusions

In conclusion, we have described a novel three-component [2 + 2 + 1] cycloaddition reaction to generate functionalized spirocyclic oxindole-butenolides[17] from simple and readily



Scheme 4 Three-component reaction with 1-phenylprop-2-yn-1-one **2d**.

available starting materials in an efficient and atom-economical manner.[18] This method is quite flexible with respect to the variable two carbon units and the broad range of isocyanides as well as isatins. This protocol can also serve as a powerful carbonylation method without the aid of transition metal. As a result, the present strategy has potential to be applied in medicinal and synthetic chemistry.

Experimental section

General experimental procedures

The NMR spectra were recorded on Bruker AC – 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and TMS as an internal reference. ^{1}H NMR spectral data were reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). ^{13}C NMR spectral data were reported in terms of the chemical shift. When peak multiplicities are given, the following abbreviations are used: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublets; td = triplet of doublet, ddd = doublet of doublet of doublets. IR spectra were taken as KBr discs or liquid film with a Bruker vector 22 spectrometer. Low-resolution mass spectra were obtained on a Shimadzu LCMS-2010EV spectrometer in ESI mode and reported as *m*/*z*. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Chemical yields referred to pure isolated product. Purification of products was accomplished by column chromatography packed with silica gel. Solvents were reagent grade and purified by standard techniques: benzene, toluene, and dichloromethane were distilled afresh from CaH_2. Unless otherwise stated, all reagents were commercially purchased and used without further purification.

General procedure for the formation of 4

Isatin **3** (0.5 mmol) was added to a solution of isocyanide **1** (0.5 mmol) and alkynoate **2** (0.6 mmol) in 5 mL toluene. The stirred mixture was heated to 100 °C for several hours and the progress was monitored using TLC detection. After completion the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel [silica: 200–300; eluant: petroleum ether–ethyl acetate] to afford the desired product **4**.

General procedure for the formation of 5

In a 10 mL round-bottomed flask, isatin **3** (0.5 mmol) was added to a solution of isocyanide **1** (0.5 mmol) and alkynoate **2** (0.6 mmol) in 5 mL toluene. The stirred mixture was heated to 100 °C for several hours and the progress was monitored using TLC. After completion the reaction mixture was concentrated under vacuum. The mixture was then dissolved in a EtOH–H_2O (6 mL : 2 mL) solvent, which was then cooled to 0 °C. Hydrochloric acid (37%, 2 mmol) was subsequently added to this cooled solution. The reaction mixture was stirred at 0 °C for 1 hour and then allowed to react at room temperature until the complete conversion. The residue was poured into saturated $NaHCO_3$ (100 mL) and the product was extracted with EtOAc (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product **5**.

General procedure for the formation of 6

Isatin **3** (0.5 mmol) was added to a solution of isocyanide **1** (0.5 mmol) and 1-phenylprop-2-yn-1-one **2d** (0.6 mmol) in 5 mL toluene. The stirred mixture was heated to 100 °C for several hours and the progress was monitored using TLC detection. After completion the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **6**.

Characterization data for all compounds

(**4a**): White solid. m.p.: 79–81 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.09 (td, 1H, *J* = 9.0, 2.5 Hz), 7.05 (s, 1H), 6.84 (dd, 1H, *J* = 7.0, 2.5 Hz), 6.82 (dd, 1H, *J* = 8.5, 4.0 Hz), 4.06 (qd, 2H, *J* = 7.0, 4.0 Hz), 3.25 (s, 3H), 1.68 (q, 2H, *J* = 2.5 Hz), 1.33 (s, 6H), 1.11 (t, 3H, *J* = 7.0 Hz), 0.97 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.7, 160.5, 160.4, 158.4, 155.0, 143.7, 140.7, 136.0, 126.5, 126.4, 117.6, 112.4, 112.2, 109.6, 109.5, 88.2, 61.7, 59.0, 53.9, 32.0, 31.7, 30.5, 30.4, 29.7, 26.9, 13.8. IR (KBr) ν_{max} = 3433, 2953, 1739, 1689, 1497, 805 cm^{-1}. MS (ESI): *m*/*z*: 417 $[M + H]^+$. HRMS: Calcd for $C_{23}H_{30}FN_2O_4$ $[M + H]^+$ 417.2184, Found 417.2201.

(**4b**): Light yellow solid. m.p.: 142–143 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.09 (td, 1H, *J* = 8.5, 2.5 Hz), 7.04 (s, 1H), 6.84 (dd, 1H, *J* = 7.2, 2.5 Hz), 6.82 (dd, 1H, *J* = 9.0, 4.0 Hz), 4.05 (qd, 2H, *J* = 7.0, 3.5 Hz), 3.25 (s, 3H), 1.28 (s, 9H), 1.11 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.6, 160.5, 160.4, 158.5, 156.3, 143.8, 140.7, 140.6, 135.9, 126.3, 117.6, 117.4, 112.3, 112.1, 109.6, 109.5, 88.3, 88.2, 61.7, 55.2, 29.6, 26.9, 13.8. IR (KBr) ν_{max} = 3436, 2968, 1745, 1497, 1240, 1099 cm^{-1}. MS (ESI): *m*/*z*: 361 $[M + H]^+$. HRMS: Calcd for $C_{19}H_{22}FN_2O_4$ $[M + H]^+$ 361.1558, Found 361.1572.

(**4c**): Yellow solid. m.p.: 192–193 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.35 (s, 1H), 7.06 (td, 1H, *J* = 9.0, 2.5 Hz), 6.98 (d, 2H, *J* = 7.5 Hz), 6.89 (t, 1H, *J* = 7.5 Hz), 6.84 (dd, 1H,

J = 7.5, 2.5 Hz), 6.75 (dd, 1H, J = 9.0, 3.5 Hz), 4.13 (qd, 2H, J = 7.0, 4.0 Hz), 3.18 (s, 3H), 2.16 (s, 6H), 1.17 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.0, 160.4, 160.1, 158.4, 157.9, 146.4, 144.2, 141.0, 140.9, 133.2, 127.6, 125.5, 123.9, 118.0, 117.8, 112.5, 112.3, 109.7, 109.6, 88.2, 62.1, 31.0, 29.8, 27.0, 18.2, 13.9. IR (KBr) ν_{max} = 3429, 2923, 1741, 1692, 1497, 1014 cm^{-1}. MS (ESI): m/z: 409 $[M + H]^+$, 431 $[M + Na]^+$. HRMS: Calcd for $C_{23}H_{22}FN_2O_4$ $[M + H]^+$ 409.1558, Found 409.1557.

(**4d**): Light yellow solid. m.p.: 183–185 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.35 (s, 1H), 7.17 (d, 1H, J = 8.0 Hz), 7.08–7.03 (m, 2H), 6.92–6.87 (m, 2H), 6.73 (dd, 1H, J = 8.5, 4.0 Hz), 4.14 (qd, 2H, J = 7.0, 3.5 Hz), 3.17 (s, 3H), 2.21 (s, 3H), 1.17 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.6, 160.4, 159.9, 159.4, 158.4, 147.1, 142.7, 140.8, 132.9, 130.5, 128.5, 126.9, 125.1, 124.6, 118.1, 117.9, 112.8, 112.6, 109.7, 109.6, 88.6, 62.1, 29.8, 27.0, 18.5, 13.9. IR (KBr) ν_{max} = 2924, 1741, 1694, 1017 cm^{-1}. MS (ESI): m/z: 429 $[M + H]^+$, 451 $[M + Na]^+$. HRMS: Calcd for $C_{22}H_{19}ClFN_2O_4$ $[M + H]^+$ 429.1012, Found 429.1013.

(**4e**): Yellow solid. m.p.: 148–150 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.33 (s, 1H), 7.31 (s, 1H), 7.08 (td, 1H, J = 8.5, 2.5 Hz), 6.91 (dd, 1H, J = 8.5, 2.5 Hz), 6.80 (dd, 1H, J = 8.5, 4.0 Hz), 6.46 (d, 1H, J = 3.0 Hz), 6.36 (dd, 1H, J = 9.0, 2.5 Hz), 4.10 (qd, 2H, J = 7.5, 4.0 Hz), 3.84 (s, 3H), 3.75 (s, 3H), 3.24 (s, 3H), 1.14 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.2, 160.3, 160.2, 158.5, 158.3, 157.8, 153.9, 144.3, 140.7, 140.6, 135.0, 127.3, 125.8, 125.7, 124.4, 117.7, 117.5, 112.7, 112.5, 109.5, 109.4, 103.8, 99.0, 88.5, 61.8, 55.8, 55.4, 26.9, 13.8. IR (KBr) ν_{max} = 3434, 1736, 1498, 1271, 1021 cm^{-1}. MS (ESI): m/z: 441 $[M + H]^+$, 463 $[M + Na]^+$. HRMS: Calcd for $C_{23}H_{21}FN_2O_6Na$ $[M + Na]^+$ 463.1276, Found 463.1295.

(**4f**): Brown solid. m.p.: 66–68 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.24–7.19 (m, 5H), 7.12 (td, 1H, J = 9.0, 2.5 Hz), 6.91 (dd, 1H, J = 7.0, 2.5 Hz), 6.83 (dd, 1H, J = 8.5, 3.5 Hz), 4.11 (qd, 2H, J = 7.0, 3.5 Hz), 3.26 (s, 3H), 1.16 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.9, 160.4, 160.0, 158.7, 158.5, 145.7, 143.3, 134.6, 130.9, 128.9, 125.4, 118.2, 118.0, 112.8, 112.6, 109.9, 109.8, 89.0, 62.1, 27.1, 13.9. IR (KBr) ν_{max} = 3437, 1736, 1679, 1271, 1097, 1010 cm^{-1}. MS (ESI): m/z: 437 $[M + Na]^+$. HRMS: Calcd for $C_{21}H_{16}ClFN_2O_4Na$ $[M + Na]^+$ 437.0675, Found 437.0692.

(**4g**): Light yellow solid. m.p.: 138–140 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.39–7.37 (m, 2H), 7.23 (s, 1H), 7.15–7.09 (m, 3H), 6.91 (dd, 1H, J = 7.5, 2.5 Hz), 6.84 (dd, 1H, J = 8.5, 4.0 Hz), 4.14 (qd, 2H, J = 7.0, 2.5 Hz), 3.26 (s, 3H), 1.16 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.9, 160.0, 158.8, 145.8, 143.8, 140.7, 134.6, 131.9, 131.8, 125.7, 125.5, 118.8, 118.2, 118.0, 112.8, 112.6, 109.9, 109.8, 89.0, 62.1, 27.1, 13.9. IR (KBr) ν_{max} = 2925, 1736, 1271, 1007 cm^{-1}. MS (ESI): m/z: 481 $[M + Na]^+$. HRMS: Calcd for $C_{21}H_{16}BrFN_2O_4Na$ $[M + Na]^+$ 481.0170, Found 481.0192.

(**4h**): Light yellow solid. m.p.: 104–105 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.39 (td, 1H, J = 7.5, 1.5 Hz), 7.11–7.04 (m, 3H), 6.89 (d, 1H, J = 7.5 Hz), 4.04 (qd, 2H, J = 7.0, 3.5 Hz), 3.26 (s, 3H), 1.68 (q, 2H, J = 5.0 Hz), 1.34 (s, 3H), 1.33 (s, 3H), 1.08 (t, 3H, J = 7.5 Hz), 0.98 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.8, 160.5, 155.4, 144.6, 144.0, 135.8, 131.2, 124.9, 124.0, 123.2, 108.8, 88.3, 61.4, 58.8, 53.7, 31.9, 31.6, 30.4, 30.3, 26.7, 13.7. IR (KBr) ν_{max} = 3435, 2952, 1738, 1243 cm^{-1}. MS (ESI): m/z: 399 $[M + H]^+$. HRMS: Calcd for $C_{23}H_{31}N_2O_4$ $[M + H]^+$ 399.2278, Found 399.2278.

(**4i**): Light yellow solid. m.p.: 132–133 °C. IR (film) ν_{max} = 3432, 2952, 1749, 1607, 1011 cm^{-1}. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.06 (s, 1H), 6.99 (d, 1H, J = 1.5 Hz), 6.79 (d, 1H, J = 1.5 Hz), 4.09 (qd, 2H, J = 7.0, 3.5 Hz), 3.23 (s, 3H), 1.78 (d, 1H, J = 14.5 Hz), 1.56 (d, 1H, J = 14.5 Hz), 1.35 (s, 3H), 1.31 (s, 3H), 1.16 (t, 3H, J = 7.0 Hz), 0.98 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.5, 160.6, 154.8, 147.1, 141.9, 137.8, 137.1, 132.7, 123.8, 120.0, 108.2, 87.6, 61.7, 59.1, 54.4, 32.0, 31.7, 30.3, 30.0, 27.1, 13.9. MS (ESI): m/z: 467 $[M + H]^+$. HRMS: Calcd for $C_{22}H_{29}Cl_2N_2O_4$ $[M + H]^+$ 467.1499, Found 467.1514.

(**4j**): White solid. m.p.: 154–156 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.19 (dd, 1H, J = 7.5, 1.5 Hz), 7.04 (d, 1H, J = 1.5 Hz), 7.02 (s, 1H), 6.95 (d, 1H, J = 8.0 Hz), 4.06 (qd, 2H, J = 7.0, 3.5 Hz), 3.24 (s, 3H), 1.67 (s, 2H), 1.32 (s, 6H), 1.12 (t, 3H, J = 7.5 Hz), 0.96 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.2, 160.4, 154.1, 150.1, 143.8, 143.1, 136.2, 128.1, 126.0, 119.9, 108.6, 87.0, 61.9, 59.1, 54.0, 31.9, 31.6, 30.4, 30.3, 27.2, 13.8. IR (KBr) ν_{max} = 3433, 1744, 1608, 1002 cm^{-1}. MS (ESI): m/z: 477 $[M + H]^+$. HRMS: Calcd for $C_{23}H_{30}BrN_2O_4$ $[M + H]^+$ 477.1384, Found 477.1390.

(**4k**): Light yellow solid. m.p.: 143–145 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 8.38 (dd, 1H, J = 8.5, 2.5 Hz), 8.00 (d, 1H, J = 2.5 Hz), 7.08 (s, 1H), 7.00 (d, 1H, J = 8.5 Hz),4.10 (qd, 2H, J = 7.0, 3.5 Hz), 3.35 (s, 3H), 1.67 (q, 2H, J = 14.5 Hz), 1.35 (s, 3H), 1.34 (s, 3H), 1.17 (t, 3H, J = 7.5 Hz), 0.99 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.2, 160.4, 154.1, 150.1, 143.8, 143.1, 136.2, 128.1, 126.0, 119.9, 108.6, 87.0, 61.9, 59.1, 54.0, 31.9, 31.6, 30.4, 30.3, 27.2, 13.8. IR (KBr) ν_{max} = 3430, 2924, 1752, 1617 cm^{-1}. MS (ESI): m/z: 444 $[M + H]^+$, 466 $[M + Na]^+$. HRMS: Calcd for $C_{23}H_{30}N_3O_6$ $[M + H]^+$ 444.2129, Found 444.2141.

(**4l**): Light yellow solid. m.p.: 128–130 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.02 (s, 1H), 6.88 (dd, 1H, J = 8.5, 2.5 Hz), 6.78 (d, 1H, J = 8.5 Hz), 6.68 (d, 1H, J = 2.5 Hz), 4.04 (qd, 2H, J = 7.0, 3.5 Hz), 3.73 (s, 3H), 3.22 (s, 3H), 1.68 (q, 2H, J = 12.5 Hz), 1.33 (s, 3H), 1.32 (s, 3H), 1.09 (t, 3H, J = 7.0 Hz), 0.97 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.6, 160.5, 156.3, 155.5, 144.1, 137.9, 135.8, 126.0, 115.5, 111.1, 109.3, 88.6, 61.5, 58.8, 55.8, 53.7, 31.9, 31.7, 30.5, 30.4, 26.8, 13.8. IR (KBr) ν_{max} = 3445, 2952, 1732, 1030 cm^{-1}. MS (ESI): m/z: 451 $[M + Na]^+$. HRMS: Calcd for $C_{24}H_{32}N_2O_5Na$ $[M + Na]^+$ 451.2209, Found 451.2231.

(**4m**): Light yellow solid. m.p.: 91–93 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.01 (s, 1H), 6.91 (s, 1H), 6.72 (s, 1H), 4.06 (qd, 2H, J = 7.0, 3.5 Hz), 3.5 (s, 3H), 2.54 (s, 3H), 2.23 (s, 3H), 1.69 (q, 2H, J = 10.5 Hz), 1.34 (s, 3H), 1.33 (s, 3H), 1.13 (t, 3H, J = 7.0 Hz), 0.98 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.1, 160.7, 155.7, 144.4, 139.8, 135.6, 135.4, 132.7, 125.5, 122.7, 120.2, 88.3, 61.5, 58.8, 53.7, 32.0, 31.7, 30.5, 30.4, 30.2, 20.7, 18.9, 13.9. IR (KBr) ν_{max} = 3436, 2925, 1731, 1095 cm^{-1}. MS (ESI): m/z: 427 $[M + H]^+$, 449 $[M + Na]^+$. HRMS: Calcd for $C_{25}H_{35}N_2O_4$ $[M + H]^+$ 427.2591, Found 427.2596.

(**4n**): Light yellow solid. m.p.: 85–87 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.40 (d, 2H, J = 7.5 Hz), 7.33 (t, 2H, J = 7.5 Hz), 7.26 (q, 2H, J = 8.5 Hz), 7.11 (d, 1H, J = 6.5 Hz), 7.09 (s, 1H), 7.02 (t, 1H, J = 7.5 Hz), 6.76 (d, 1H, J = 8.0 Hz), 5.06 (d, 1H, J = 15.5 Hz), 4.83 (d, 1H, J = 16.0 Hz), 4.11 (qd, 1H, J = 11.0, 7.0 Hz), 3.95 (qd, 1H, J = 11.0, 7.0 Hz), 1.72 (q, 2H, J = 6.5 Hz), 1.37 (s, 3H), 1.36 (s, 3H), 1.01–0.99 (m, 12H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.2, 160.7, 155.5, 144.1, 143.9, 136.2, 135.3, 131.2, 128.9, 127.9, 127.5, 125.1, 124.2, 123.3, 110.0, 88.5, 61.6, 58.9, 53.7, 44.6, 32.0, 31.7, 30.6, 30.5, 13.8. IR (KBr) ν_{max} = 3437, 2952, 1726, 1614 cm^{-1}. MS (ESI): m/z: 475 $[M + H]^+$, 497 $[M + Na]^+$. HRMS: Calcd for $C_{29}H_{35}N_2O_4$ $[M + H]^+$ 475.2591, Found 475.2609.

(**4o**): Light yellow solid. m.p.: 103–104 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.38–7.32 (m, 4H), 7.28 (d, 1H, J = 7.5 Hz), 7.18 (t, 1H, J = 8.0 Hz), 7.13 (s, 1H), 6.93 (d, 1H, J = 8.0 Hz), 6.64 (d, 1H, J = 8.0 Hz), 5.03 (d, 1H, J = 16.0 Hz), 4.83 (d, 1H, J = 16.0 Hz), 4.15 (qd, 1H, J = 11.0, 7.0 Hz), 3.99 (qd, 1H, J = 11.0, 7.0 Hz), 1.86 (d, 1H, J = 14.5 Hz), 1.60 (d, 1H, J = 14.5 Hz), 1.40 (s, 3H), 1.36 (s, 3H), 1.05 (t, 3H, J = 7.0 Hz), 1.02 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 170.7, 160.6, 155.2, 145.5, 142.3, 137.2, 134.8, 132.2, 132.1, 127.9, 127.4, 124.2, 121.7, 108.2, 88.2, 61.5, 59.0, 54.2, 44.6, 31.9, 31.7, 30.5, 30.0, 13.8. IR (KBr) ν_{max} = 2924, 1739, 1606, 1220 cm^{-1}. MS (ESI): m/z: 509 $[M + H]^+$. HRMS: Calcd for $C_{29}H_{34}ClN_2O_4$ $[M + H]^+$ 509.2202, Found 509.2201.

(**4p**): Light yellow solid. m.p.: 120–121 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.43 (dd, 1H, J = 8.0, 1.0 Hz), 7.35–7.23 (m, 5H), 7.09 (s, 1H), 7.06 (dd, 1H, J = 7.5, 1.0 Hz), 6.91 (t, 1H, J = 8.0 Hz), 5.42 (q, 2H, J = 2.0 Hz), 4.15 (qd, 1H, J = 11.0, 7.0 Hz), 4.04 (qd, 1H, J = 11.0, 7.0 Hz), 1.75 (d, 1H, J = 14.5 Hz), 1.68 (d, 1H, J = 14.5 Hz), 1.36 (s, 3H), 1.35 (s, 3H), 1.11 (t, 3H, J = 7.0 Hz), 0.99 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 172.0, 160.5, 154.9, 143.6, 141.5, 137.0, 136.8, 136.3, 128.6, 128.2, 127.2, 126.5, 124.6, 123.3, 103.2, 87.4, 61.7, 59.0, 53.7, 45.3, 31.9, 31.7, 30.5, 30.4, 13.8. IR (KBr) ν_{max} = 2952, 1742, 1451, 1020 cm^{-1}. MS (ESI): m/z: 553 $[M + H]^+$. HRMS: Calcd for $C_{29}H_{34}BrN_2O_4$ $[M + H]^+$ 553.1697, Found 553.1723.

(**4q**): Light yellow solid. m.p.: 165–166 °C.[6d] ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.55–7.42 (m, 5H), 7.28 (t, 1H, J = 7.5 Hz), 7.12–7.05 (m, 2H), 6.88 (d, 1H, J = 8.0 Hz), 4.14 (qd, 1H, J = 11.0, 7.5 Hz), 4.03 (qd, 1H, J = 11.0, 7.5 Hz), 2.32 (s, 3H), 1.66 (q, 2H, J = 4.5 Hz), 1.35 (s, 3H), 1.33 (s, 3H), 1.06 (t, 3H, J = 7.0 Hz), 1.00 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.4, 162.0, 156.0, 147.2, 144.9, 135.5, 134.3, 130.7, 129.8, 128.3, 126.4, 125.9, 124.3, 123.5, 110.0, 86.8, 61.1, 58.3, 54.9, 32.1, 31.8, 30.2, 30.1, 14.0, 12.4. IR (KBr) ν_{max} = 3445, 2952, 1745, 1501, 1022 cm^{-1}.

(**4r**): Light yellow solid. m.p.: 137–139 °C.[6d] ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.34 (dd, 1H, J = 8.5, 2.0 Hz), 7.02 (d, 1H, J = 2.0 Hz), 6.80 (d, 1H, J = 8.0 Hz), 4.04 (qd, 2H, J = 11.0, 7.0 Hz), 3.25 (s, 3H), 2.30 (s, 3H), 1.56 (s, 2H), 1.32 (s, 3H), 1.30 (s, 3H), 1.07 (t, 3H, J = 7.0 Hz), 0.99 (s, 9H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.7, 161.8, 155.4, 147.5, 143.5, 134.8, 130.7, 128.5, 127.8, 124.4, 109.6, 86.3, 61.1, 58.3, 55.1, 32.1, 31.8, 30.1, 30.0, 26.9, 13.9, 12.4. IR (KBr) ν_{max} = 2956, 1743, 1612, 1487, 1328, 1230, 1054 cm^{-1}.

(**4s**): Viscous oil. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.58 (dd, 2H, J = 7.0, 1.5 Hz), 7.41–7.37 (m, 4H), 7.18 (d, 1H, J = 7. 0 Hz), 7.07 (t, 1H, J = 7.5 Hz), 6.90 (d, 1H, J = 7.5 Hz), 3.94 (qd, 1H, J = 11.0, 7.0 Hz), 3.85 (qd, 1H, J = 11.0, 7.0 Hz), 3.29 (s, 3H), 1.67 (t, 1H, J = 7.5 Hz), 1.60 (t, 1H, J = 7.5 Hz), 1.32 (s, 3H), 1.30 (s, 3H),0.94 (s, 9H), 0.86 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 171.9, 161.4, 154.5, 146.3, 144.9, 136.4, 131.1, 130.7, 130.6, 130.1, 129.9, 129.4, 128.7, 127.2, 125.9, 124.1, 123.2, 108.7, 86.7, 61.0, 58.7, 54.7, 32.0, 31.8, 31.6, 30.1, 30.0, 29.8, 26.8, 13.5. IR (film) ν_{max} = 3445, 2952, 1737, 1613, 1014 cm^{-1}. HRMS: Calcd for $C_{29}H_{35}N_2O_4$ $[M + H]^+$ 475.2597, Found 475.2580.

(**5a**): White solid. m.p.: 149–150 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.40 (td, 1H, J = 7.5, 1.5 Hz), 7.08–7.03 (m, 2H), 6.93 (s, 1H), 6.90 (d, 1H, J = 8.0 Hz), 4.07 (qd, 2H, J = 7.0, 3.5 Hz), 3.24 (s, 3H), 1.08 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.8, 168.9, 159.4, 153.9, 144.9, 132.0, 128.0, 124.3, 123.5, 122.2, 109.3, 85.5, 62.4, 27.0, 13.7. IR (KBr) ν_{max} = 3447, 1487, 1734, 1009 cm^{-1}. MS (ESI): m/z: 310 $[M + Na]^+$. HRMS: Calcd for $C_{15}H_{13}NO_5Na$ $[M + Na]^+$ 310.0686, Found 310.0696.

(**5b**): Light yellow solid. m.p.: 188–189 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.56 (dd, 1H, J = 8.0, 2.0 Hz), 7.22 (d, 1H, J = 2.0 Hz), 6.96 (s, 1H), 6.82 (d, 1H, J = 8.5 Hz), 4.15 (qd, 2H, J = 11.0, 7.0 Hz), 3.27 (s, 3H), 1.18 (t, 3H, J = 7.5 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.4, 168.5, 159.4, 153.5, 144.0, 134.8, 128.2, 127.6, 124.2, 116.0, 110.8, 84.9, 62.7, 27.2, 13.8. IR (KBr) ν_{max} = 3439, 2923, 1783, 1729, 1218 cm^{-1}. MS (ESI): m/z: 388 $[M + Na]^+$. HRMS: Calcd for $C_{15}H_{12}BrNO_5Na$ $[M + Na]^+$ 387.9797, Found 387.9815.

(**5c**): Light yellow solid. m.p.: 174–175 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 8.40 (d, 1H, J = 8.5 Hz), 8.00 (d, 1H, J = 2.0 Hz), 7.05 (d, 1H, J = 8.5 Hz), 7.01 (s, 1H), 4.16 (qd, 2H, J = 11.0, 7.0 Hz), 3.36 (s, 3H), 1.21 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.2, 169.0, 159.4, 152.9, 150.4, 143.9, 128.8, 128.4, 123.4, 120.4, 109.1, 84.0, 62.9, 27.6, 13.8. IR (KBr) ν_{max} = 3458, 1796, 1740, 1618, 1335 cm^{-1}. MS (ESI): m/z: 355 $[M + Na]^+$. HRMS: Calcd for $C_{15}H_{12}N_2O_7Na$ $[M + Na]^+$ 355.0537, Found 355.0553.

(**5d**): Light yellow solid. m.p.: 78–80 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.34–7.26 (m, 6H), 7.10 (dd, 1H, J = 7.5, 1.0 Hz), 7.05–0.99 (m, 2H), 6.79 (d, 1H, J = 8.0 Hz), 5.02 (d, 1H, J = 16.0 Hz), 4.87 (d, 1H, J = 16.0 Hz), 4.17 (qd, 1H, J = 11.0, 7.0 Hz), 4.02 (qd, 1H, J = 11.0, 7.0 Hz), 1.04 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 169.8, 169.1, 159.4, 153.9, 144.1, 134.7, 131.9, 128.9, 128.2, 128.0, 127.4, 124.4, 123.6, 122.3, 110.4, 85.5, 62.4, 44.7, 13.7. IR (film) ν_{max} = 2925, 1783, 1733, 1613 cm^{-1}. MS (ESI): m/z: 364 $[M + H]^+$, 386 $[M + Na]^+$. HRMS: Calcd for $C_{21}H_{17}NO_5Na$ $[M + Na]^+$ 386.0999, Found 386.1015.

(**5e**): Light yellow solid. m.p.: 145–146 °C.[6d] ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 7.55 (t, 2H, J = 8.5 Hz), 7.44 (t, 3H, J = 7.5 Hz), 7.35–7.07 (m, 3H), 6.88 (d, 1H, J = 8.0 Hz), 4.22 (qd, 1H, J = 11.0, 7.0 Hz), 4.11 (qd, 1H, J = 11.0, 7.0 Hz), 2.39 (s, 3H), 1.11 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 172.1, 169.1, 160.8, 145.3, 144.4, 139.7, 131.6, 129.9, 128.7, 126.4, 124.6, 123.8, 122.8, 110.5, 84.5, 62.0, 14.0, 11.5. IR (KBr) ν_{max} = 3439, 1779, 1738, 1614, 1024 cm^{-1}.

(**5f**): Viscous oil. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 6.92 (dd, 1H, J = 8.5, 2.5 Hz), 6.81 (d, 1H, J = 8.5 Hz), 6.65 (d, 1H, J = 2.5 Hz), 4.08 (qd, 2H, J = 11.0, 7.5 Hz), 3.70 (s, 3H), 3.25 (s, 3H), 2.37 (s, 3H), 1.09 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 172.1, 169.5, 160.7, 156.5, 144.2, 139.8, 138.4, 124.2, 116.2, 111.3, 109.6, 84.7, 61.8, 56.0, 27.1, 13.8, 11.5. IR (film) ν_{max} = 2927, 1716, 1498, 1234, 1021, 804 cm^{-1}. MS (ESI): m/z: 354 $[M + Na]^+$. HRMS: Calcd for $C_{17}H_{17}NO_6Na$ $[M + Na]^+$ 354.0954, Found 354.0971.

(**6a**): Brown solid. m.p.: 108–110 °C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 7.75 (d, 2H, J = 7.5 Hz), 7.57(t, 1H, J = 7.5 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.37 (t, 1H, J = 7.5 Hz), 7.15 (d, 1H, J = 7.0 Hz), 7.02 (t, 1H, J = 7.5 Hz), 6.91 (d, 1H, J = 7.5 Hz), 6.88 (s, 1H), 3.33 (s, 3H), 1.77 (s, 2 Hz), 1.38 (s, 3H), 1.37 (s, 3H), 1.00 (s, 9H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 188.6, 171.2, 156.3, 149.1, 145.0, 136.6, 136.1, 133.7, 131.3, 129.4, 129.0, 128.8, 128.5, 124.7, 123.8, 123.2, 109.1, 89.6, 59.1, 53.9, 32.0, 31.8, 30.5, 30.3, 29.8, 27.0. IR (KBr) ν_{max} = 3547, 2962, 1727, 1612, 1247, 1000 cm^{-1}. HRMS: Calcd for $C_{27}H_{31}N_2O_3$ $[M + H]^+$ 431.2335, Found 431.2323.

(**6b**): Light yellow solid. m.p.: 163–165 °C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 7.75 (t, 2H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.51–7.44 (m, 3H), 7.34 (d, 1H, J = 1.5 Hz), 6.91 (s, 1H), 6.80 (d, 1H, J = 8.0 Hz), 3.31 (s, 3H), 1.72 (q, 2H, J = 9.0 Hz), 1.37 (s, 6H), 1.00 (s, 9H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 188.5, 170.7, 155.7, 148.7, 144.1, 136.6, 136.5, 134.1, 133.9, 129.0, 128.9, 127.0, 126.8, 115.6, 110.6, 89.0, 59.3, 54.1, 32.0, 31.7, 30.5, 30.3, 29.8, 27.1. IR (KBr) ν_{max} = 3445, 2951, 1742, 1103 cm^{-1}. HRMS: Calcd for $C_{27}H_{30}BrN_2O_3$ $[M + H]^+$ 509.1440, Found 509.1437.

(**6c**): Yellow solid. m.p.: 143–145 °C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 7.83 (d, 2H, J = 8.0 Hz), 7.60 (t, 1H, J = 7.0 Hz), 7.49–7.31(m, 7H), 6.97 (s, 1H), 6.93 (d, 1H, J = 1.0 Hz), 6.63 (d, 1H, J = 1.0 Hz), 5.89 (d, 1H, J = 16.0 Hz), 4.92 (d, 1H, J = 16.0 Hz), 1.89 (d, 1H, J = 14.5 Hz), 1.64 (d, 1H, J = 14.5 Hz), 1.45 (s, 3H), 1.41(s, 3H), 1.03 (s, 9 Hz). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 188.8, 170.9, 155.7, 147.7, 146.6, 137.7, 137.4, 136.4, 134.4, 133.8, 132.6, 129.2, 129.1, 128.8, 128.1, 127.4, 127.3, 123.7, 119.9, 109.5, 88.8, 59.3, 54.3, 44.9, 32.0, 31.7, 30.6, 29.9, 29.8. IR (KBr) ν_{max} = 3459, 1749, 1607, 1338, 1217, 711 cm^{-1}. HRMS: Calcd for $C_{33}H_{33}Cl_2N_2O_3$ $[M + H]^+$ 575.1868, Found 575.1852.

Acknowledgements

We thank the National Natural Science Foundation of China (21002061, 21142012, 20902057), the State Key Laboratory of Applied Organic Chemistry, Lanzhou University and the Leading Academic Discipline Project of Shanghai Municipal Education Commission (no. J50101) for financial support. We also thank Dr Hongmei Deng and Min Shao of Laboratory for Microstructures, Shanghai University for the NMR and single crystal X-ray analyses.

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