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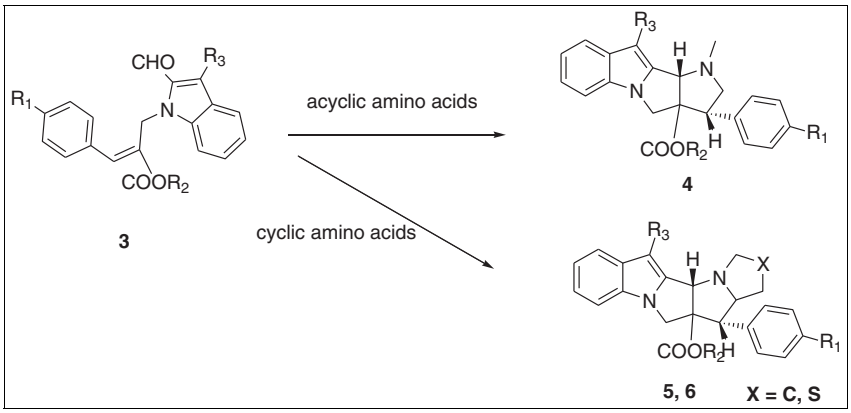

A straightforward and general approach for the stereoselective synthesis of fused pyrrolo[1,2-*a*] indoles frameworks from >intramolecular 1,3-dipolar cycloaddition using *N*-alkylated Baylis–Hillman derivatives is presented. It was found that the cycloaddition proceeded efficiently under microwave irradiation in solvent-free condition to afford highly stereoselective cycloadducts in good yield.

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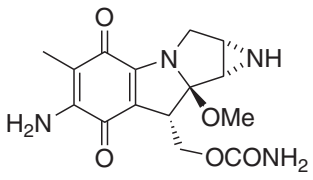
INTRODUCTION

The indole ring is one of the most widely distributed heterocycles in nature. Many of natural and synthetic biologically active compounds and a vast number of pharmaceuticals containing the indole skeleton are being used for therapeutic purposes [1]. *N*-fused [1,2-*a*]-annealed indole is present in a number of biologically active indole derivatives such as mitomycin and vincamine. The development of methods for the construction of [1,2-*a*]-annealed indole nuclei has been the subject of a number of reports [2]. In particular, mitomycin-C is used in clinical cancer chemotherapy [3]. Following the discovery and total synthesis of mitomycin-C, a number of compounds have been synthesized by molecular modifications at the pyrrolo[1,2-*a*] indole without significant loss of biological activity [4]. Therefore, large efforts have been directed towards the synthesis of functionalized pyrrolo[1,2-*a*] indole derivatives as mitomycin analogues, and as a result, numerous heterocycle-annulated pyrrolo[1,2-*a*] indole derivatives have been reported [5].



Biologically active *N*-fused indole. Therefore, *N*-fused indole derivatives are promising candidates in the synthesis of new class of compounds, which has not yet been fully developed. However, synthetic approach towards tricyclic indole derivative and alkyl chain elongation on an existing indole platform has been reported by many research groups [6–8]. These strategies still pose several problems, and most primarily, a multistep synthesis of the substrates is required regardless of the synthetic strategy selected.

The use of intramolecular 1,3-dipolar cycloadditions of azomethine ylides acts as a powerful tool in the synthesis of complex cyclic system from relatively simple precursors. In recent years, the azomethine ylide has gained a vital place in the field of heterocyclic chemistry as it serves as an important building block for the construction of natural products and pharmacologically important compounds with regio- and stereocontrol [9].

The synthetic application of Morita–Baylis–Hillman (MBH) derivatives is well documented in literature. In fact, the B–H adducts and their derivatives are useful intermediates for the synthesis of various cyclic and tricyclic compounds containing heteroatoms [10].

In addition, there has been considerable interest in the microwave (MW) irradiation protocol for rapid synthesis of a variety of organic compounds due to the selective

absorption of MW energy by polar molecules [11]. MW reactions are comparatively cleaner, faster, and high-yielding than conventional ones. This methodology can be regarded as environment-friendly, mainly because solvent-free reactions using solid supports are essentially suited to MW condition.

RESULTS AND DISCUSSION

The scope of cycloaddition chemistry in the synthesis of polycyclic molecule prompted us to report an expedient synthesis of *N*-fused indoles by intramolecular [3 + 2]-cycloaddition involving MBH derivatives under MW irradiation in solvent-free condition, which is shown in the retrosynthetic strategy (Scheme 1).

Accordingly, the synthesis of pyrrolo[1,2-*a*] indole derivatives were prepared by exploiting Baylis–Hillman bromides with substituted indole carbaldehydes (Scheme 2). We envisaged that the *N*-alkylated indole carbaldehyde derivatives prepared from MBH bromides would be a suitable precursors for the synthesis of pyrrolo[1,2-*a*] indole via a key intramolecular [3 + 2]-cycloaddition reaction using various cyclic and acyclic secondary amino acids. The synthesis herein is the first to be reported using MBH derivatives under solvent-free MW irradiation.

Our objective in the synthesis of new polycyclic indole derivative can be well demonstrated by first considering ethyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate **(1a)**, a bromo derivative that was synthesized by the application of MBH reaction as described in the literature procedure [12]. The bromo derivative was treated with substituted indole-2-carbaldehyde in the presence of K_2CO_3/acetone and K_2CO_3/DMF. We found that DMF is solvent gave a good yield of the *N*-alkylated MBH derivatives as shown in Table 1.

The synthesized compounds were characterized by ^1H, ^{13}C NMR, IR, and mass spectra. In a prototype experiment, the

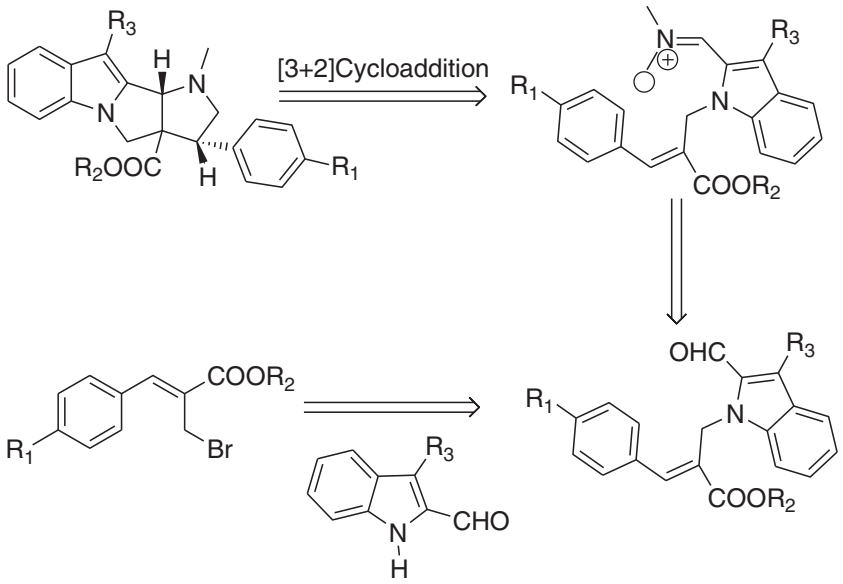
Table 1

Preparation of *N*-alklylated MBH derivatives.[a]

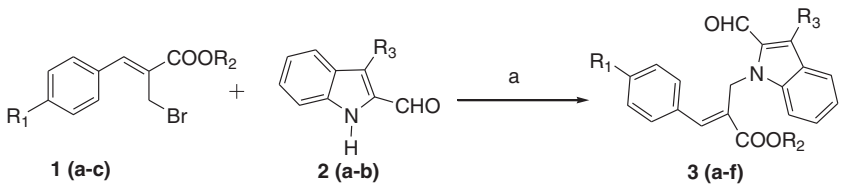
Entry	R_1	R_2	R_3	Time (h)	Yield[b] (%)
3a	H	C_2H_5	H	6	69
3b	H	C_2H_5	Me	6	70
3c	Cl	C_2H_5	H	6	73
3d	Cl	C_2H_5	Me	7	77
3e	OMe	C_2H_5	H	6	71
3f	OMe	C_2H_5	Me	6	80

MBH, Morita–Baylis–Hillman.
[a]K_2CO_3/acetone, reflux,3 h, 68–80%, or K_2CO_3/DMF, RT, 6–12 h, 83–94%.
[b]Isolated yield.

Scheme 1. Retrosynthetic strategy for the synthesis of pyrrolo[1,2-*a*] indole.



Scheme 2. Synthesis of *N*-alklylated Morita–Baylis–Hillman derivatives; (a) K_2CO_3/acetone, reflux, 3 h, 68–80% or K_2CO_3/DMF, RT, 6–12 h, 83–94%.



reaction of the *N*-alkylated MBH derivatives was treated with sarcosine (Scheme 3) in refluxing acetonitrile for 24 h without any progress in the reaction, the starting material was recovered, and changing the solvent to toluene gave a yield of 65% in 8 h.

In the intramolecular [3 + 2]-cycloaddition of the MBH derivatives, a large number of variables including solvents, reaction time, and temperature were tested. During this process, we found out that xylene, methanol, dioxane, and toluene/MW gave less yield with more reaction time. However, using neat condition under MW irradiation, we were surprised to see a substantial increase in the yield of the cycloadducts with a decrease in reaction time to obtain a novel fused pyrrolo[1,2-*a*] indoles with high regioselectivity and stereoselectivity. The results are tabulated in Table 2.

Encouraged by the preliminary study, we extended the study to [3 + 2]-cycloaddition reaction of Baylis–Hillman derivatives **3(a–f)** with azomethine ylide derived from sarcosine under optimized reaction conditions to afford pyrrolo[1,2-*a*] indole derivatives **4(a–f)** in excellent yield. All the compounds were thoroughly characterized by spectroscopic methods (IR, ^{1}H, ^{13}C NMR, and LC/MS). It is important to mention that the reaction is highly stereoselective as evidenced by NMR spectra, and results are tabulated in Table 3.

The ^{1}H NMR spectrum of compound **4e** showed a singlet for the Ha proton at δ 4.93 and a triplet for the H_b proton at δ 3.81. The CH_2 proton adjacent to indole nitrogen appeared as separate doublets at δ 4.11 and δ 4.14, and the N–CH_3 as singlet at δ 2.67.

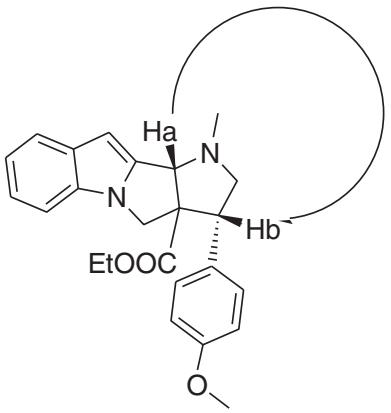


Table 2

Optimization of reaction conditions for the synthesis of **4a**.

Reaction condition	Time (h)	Yield[a] (%)
Acetonitrile/reflux	24	No reaction
Methanol/reflux	12	5
Dioxane/reflux	12	14
Xylene/reflux	10	20
Toluene/reflux	8	65
Toluene/MW	0.5	40
Neat/MW	0.15	94

MW, microwave.
[a]Isolated yield.

Table 3

Cycloaddition of MBH derivatives.[a]

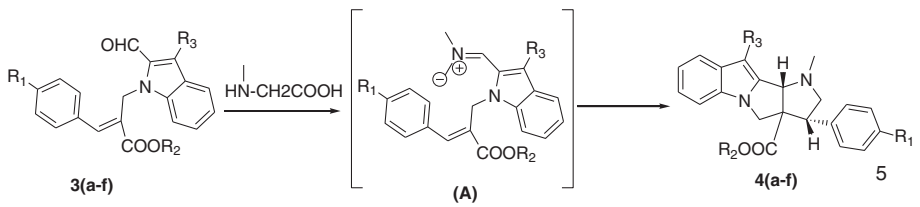
Entry R_1	R_2	R_3	Time(min)	Yield[b] (%)
4a H	C_2H_5	H	10	94
4b H	C_2H_5	Me	7	92
4c Cl	C_2H_5	H	8	90
4d Cl	C_2H_5	Me	5	89
4e OMe	C_2H_5	H	6	90
4f OMe	C_2H_5	Me	8	88

MBH, Morita–Baylis–Hillman.
[a]**3(a–f)** (1 mmol), sarcosine (1 mmol), neat-MW irradiation.
[b]Isolated yield.

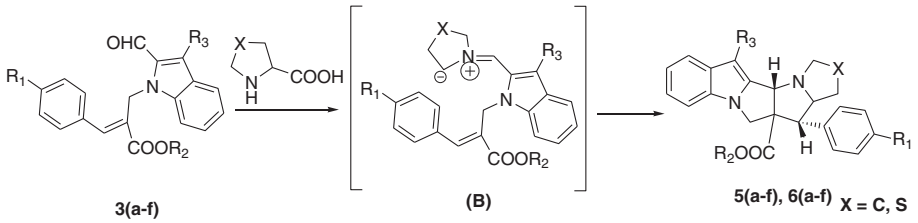
NOE correlations for compound 4e. The stereochemistry of the product was assigned as cis using NOE studies by irradiating the benzylic and ring junction proton; 8% of NOE was observed. The ester group was reduced using $LIBH_4$/methanol to alcohol, and further NOE studies between H_a and –CH_2OH was found to be cis to each other, thus confirming the structure. Similarly, other Baylis–Hillman derivatives **3(a–f)** having different substituents at the heterocyclic nitrogen and an activated alkenes underwent [3 + 2]-cycloaddition smoothly with dipole **A** and afforded the corresponding **4(a–f)** in excellent yields.

Following excellent preliminary results with acyclic amino acids, we decided to examine the reaction of Baylis–Hillman derivatives with cyclic amino acids (Scheme 4). As a result, these reactions under optimized reaction conditions furnished novel pyrrolo[1,2-*a*] indolo pyrrolizidines **5(a–f)** and pyrrolo [1,2-*a*] indolo thiopyrrolizidines derivatives **6(a–f)** with good yields in less reaction time.

Scheme 3. Synthetic route to compounds **4(a–f)**. Reaction conditions: neat-microwave irradiation, 5–12 min.



Scheme 4. Synthesis of **5(a–f)** and **6(a–f)**. Reaction conditions: neat-microwave irradiation, 6–12 min.



The structure was confirmed by ^{1}H NMR. The ^{1}H NMR spectrum of **5a** exhibited a doublet at δ 4.05 (J = 11.2 Hz) for benzylic proton and singlet at δ 4.91for ring junction proton. Finally, the structure was confirmed by NOE studies and LCMS, which showed a peak at *m*/*z* 387 (M + 1). The results are collected in Table 4.

In conclusion, our studies have demonstrated a straightforward stereoselective synthesis of fused pyrrolo[1,2-*a*] indoles from intramolecular 1,3-dipolar cycloaddition using *N*-alkylated MBH derivatives under neat-MW irradiation, in very good yield and less reaction time. The geometry of this polycyclic framework as well as its possible modification was considered a very important feature from a medicinal chemistry point of view. We are continuing to explore the scope and mechanistic details of these intramolecular 1,3-dipolar cycloaddition reactions in the anticancer field, and we will report additional findings at a later date. Further utilization of intramolecular 1,3-dipolar cycloaddition sequence for the stereocontrolled synthesis of complex cyclic system is currently under investigation.

EXPERIMENTAL

General. Microwave irradiations were carried out in MW vials* 0.2–0.5 mL of Biotage Initiator + at 120°C, 300 W. Reactions were monitored by TLC using 0.25-mm-thick Merck plates (white house station, NJ, USA), silica gel 60 F254. Products were purified by flash column chromatography on silica gel Merck (40–63 μm, 60.08 g/mol). NMR spectra were recorded with a Bruker (CA 93012, USA) DRX 400-MHz spectrometer in CDCl3. ^{13}C spectra were recorded with 100 MHz. The chemical shifts (δ) are given in parts per million (ppm) relative to TMS for ^{1}H and ^{13}C nuclei. Conventional abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, and br = broad. Coupling constants (*J*) are given in Hertz (Hz). Mass spectra were obtained on a GC/MS Saturn 2000 (Agilent Technologies, CA 95051, USA) spectrometer. LC/MS were performed on 6410A Series ESI. IR spectra were recorded with a PerkinElmer (Massachusetts 02451), USA 16 PC FT-IR spectrometer.

Table 4

Cycloadditions of MBH derivatives.[a]

Entry	R_1	R_2	R_3	X	Time (min)	Yield[b] (%)
5a	H	C_2H_5	H	CH_2	5	88
6a	H	C_2H_5	H	S	7	86
5b	Cl	C_2H_5	H	CH_2	10	91
6b	Cl	C_2H_5	H	S	8	93
5c	OMe	C_2H_5	H	CH_2	5	87
6c	OMe	C_2H_5	H	S	5	94
5d	H	C_2H_5	CH_3	CH_2	8	92
6d	H	C_2H_5	CH_3	S	4	90
5e	Cl	C_2H_5	CH_3	CH_2	7	89
6e	Cl	C_2H_5	CH_3	S	6	87
5f	OMe	C_2H_5	CH_3	CH_2	10	88
6f	OMe	C_2H_5	CH_3	S	8	93

MBH, Morita–Baylis–Hillman.
[a]**3(a–f)**, (1 mmol), proline(1 mmol), and thio proline(1 mmol), neat-MW irradiation.
[b]Isolated yield.

General procedure for synthesis of *N*-allyl derivatives of indole 3(a–f). To a solution of indole-2-carboxaldehyde/3-methyl-1*H*-indole-2-carboxaldehyde (20 mmol) and K_2CO_3 (30 mmol), in a 25 mL of DMF, a Baylis–Hillman derivative **1(a–c)** (22 mmol) was added. The reaction mixture was stirred for 6–12 h at RT. LC/MS indicated the depletion of SM **1(a–c)**, most of the DMF was removed by distillation, and 25 mL of water was added. The aqueous layer was then extracted with ethyl acetate (3 × 25 mL), the combined organic layer was washed with brine and dried over Na_2SO_4, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using hexane–ethyl acetate mixture (8:2) and isolated as a pale yellow solid.

General procedure for the synthesis of cycloadducts 4(a–f), 5(a–f), (6a–f).

Method A. A solution of *N*-allyl derivatives of indole **3(a–f)**, (1 mmol), cyclic, and acyclic amino acids (1 mmol) in anhydrous toluene was refluxed for 10–14 h. The completion of the reaction was evidenced by LC/MS. The solvent was removed under vacuo. The crude product was purified by Biotage on SNAP 10 g (230 × 400) silica gel using hexane–ethyl acetate mixture (6:4).

Method B. A solution of *N*-allyl derivatives of indole **3(a–f)** (1 mmol), cyclic, and acyclic amino acids (1 mmol) was irradiated by MW irradiations in MW vials* 0.2–0.5 mL of Biotage Initiator + at 120°C, 300 W, 2-bar reaction pressure for 10 min and until the depletion of starting material. The completion of the reaction was evidenced by LC/MS. At ambient temperature brown solid obtained was recrystalized by diethyl ether.

Ethyl 2-[(2-formyl-1H-indol-1-yl)methyl]-3-phenylprop-2-enoate (3a). This compound was prepared according to the general procedure as pale yellow solid. mp 65.3-68.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.08 (t, J = 7.1 Hz, 3H), 4.03 (q, J = 7.1 Hz, 2H), 5.90 (s, 2H), 6.92 (d, J = 8.4 Hz, 1H), 7.12 (q, J = 7.6 Hz, 1H), 7.20–7.24 (m, 1H), 7.38–7.46 (m, 6H), 7.65 (d, J = 8.0 Hz, 1H), 7.92 (s, 1H), 9.87 (s, 1H); ^{13}C NMR (100 MHz): δ (ppm): 13.9, 41.0, 60.8, 60.8, 111.3, 112.2, 117.7, 120.7, 121.2, 123.3, 126.5, 127.2, 128.5, 128.9, 129.0, 129.1, 134.5, 136.0, 140.1, 141.6, 166.4, 182.7; IR (neat), (cm^{-1}) 1703.5, 1663.4; MS (ESI) *m*/*z* 334 (M + 1); *Anal.* Calcd for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20%. Found: C, 75.32; H, 5.71; N, 4.15%.

Ethyl 2-[(2-formyl-3-methyl-1H-indol-1-yl)methyl]-3-phenylprop-2-enoate (3b). This compound was prepared according to the general procedure as a pale yellow solid. mp 108.8–110.9°C: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.09 (t, J = 7.1 Hz, 3H), 2.57 (s, 3H), 4.03 (q, J = 7.1 Hz, 2H), 5.86 (s, 2H), 6.89 (d, J = 8. Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.21–7.25 (m, 1H), 7.32–7.38 (m, 2H), 7.38–7.43 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 10.12 (s, 1H); ^{13}C NMR (100 MHz): δ (ppm): 8.5, 13.9, 41.0, 60.8, 111.2, 120.0, 121.0, 126.5, 127.0, 127.1, 128.0, 128.4, 128.7, 129.0, 129.6, 131.3, 134.6, 139.0, 141.3, 166.6, 181.6: IR (neat), (cm_{-1}) 1760.5, 1563.4 cm^{-1}; MS (ESI) m/z 348 (M + 1); *Anal*. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03%. Found: C, 75.75; H, 5.99; N, 3.81%.

Ethyl 3-(4-chlorophenyl)-2-[(2-formyl-1H-indol-1-yl)methyl] prop-2-enoate (3c). This compound was prepared according to the general procedure as a pale yellow solid. mp 88.2–91.6°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.08 (t, J = 7.1 Hz, 3H), 4.03 (q, J = 7.1 Hz, 2H), 5.84 (s, 2H), 6.93 (d, J = 8.5 Hz, 1H), 7.10 (t, J = 7.8 Hz, 2H), 7.16 (s, 1H), 7.26 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 9.84 (s, 1H): ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 13.9, 40.0, 59.9, 111.3, 117.7, 120.7, 122.2, 124.1, 126.3, 126.5, 127.0, 128.5, 128.9, 128.0, 129.0, 134.5, 137.4, 139.1, 140.6, 166.4, 186.7; IR (neat), (cm^{-1}): 1589, 1639, 3436; MS (ESI) m/z 368 (M + 1); *Anal*. Calcd for $C_{21}H_{18}ClNO_3$: C, 68.57; H, 4.93; N, 3.81%. Found: C, 68.38; H, 4.72; N, 3.75%.

Ethyl 3-(4-chlorophenyl)-2-[(2-formyl-3-methyl-1H-indol-1-yl) methyl]prop-2-enoate (3d). This compound was prepared according to the general procedure as a pale yellow solid. mp 128.8–130.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.11 (t, J = 7.2 Hz, 3H), 2.59 (s, 3H), 4.05 (q, J = 7.2 Hz, 2H), 5.86 (s, 2H), 6.99 (d, J = 8.2 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 7.37–7.39 (m, 5H), 7.42 (d, J = 6.4 Hz, 1H), 7.91 (s, 1H), 10.12 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 9.8, 13.2, 41.0, 62.8, 111.1, 120.7, 121.0, 126.5, 127.0, 127.5, 127.9, 128.0, 128.1, 129.2, 129.6, 130.3, 133.8, 138.0, 140.3, 165.6, 183.6 ppm. IR (neat), (cm^{-1}): 1619, 1709, 3316; MS (ESI) m/z 382 (M + 1); *Anal*. Calcd for $C_{22}H_{20}ClNO_3$: C, 69.20; H, 5.28; N, 3.67%. Found: C, 69.08; H, 5.21; N, 3.56%.

Ethyl 2-[(2-formyl-1H-indol-1-yl)methyl]-3-(4-methoxyphenyl) prop-2-enoate (3e). This compound was prepared according to the general procedure as an off-white solid. mp 105.8–107.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.27 (t, J = 7.1 Hz, 3H), 3.87 (s, 3H), 3.99 (q, J = 7.1 Hz, 2H), 5.92 (s, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 7.19–7.23 (m, 2H), 7.27–7.41 (m, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 9.90 (s, 1H): ^{13}C NMR (100 MHz): δ (ppm): 12.6, 14.1, 39.6, 55.2, 58.9, 110.3, 114.6, 120.3, 120.8, 121.6, 122.8, 123.4, 124.6, 125.1, 127.8, 131.0, 132.7, 133.1, 134.5, 136.9, 159.4, 165.1, 182.7 ppm. IR (neat), (cm_{-1}) 1726.5, 1260.4; MS (ESI) m/z 364 (M + 1); *Anal*. Calcd for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85%. Found: C, 72.65; H, 5.79; N, 3.78%.

Ethyl 2-[(2-formyl-3-methyl-1H-indol-1-yl)methyl]-3-(4-methoxyphenyl)prop-2-enoate (3f). This compound was prepared according to the general procedure as a dirty brown solid. mp 112.8-114.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):1.28 (t, J = 7.1 Hz, 3H), 2.57 (s, 3H), 3.72 (s, 3 H),4.12 (q, J = 7.1 Hz, 2H), 5.91 (s, 2H), 6.91 (d, J = 8.4 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.21–7.25 (m, 1H), 7.32–7.38 (m, 2H), 7.38–7.43 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 9.71 (s, 1H): ^{13}C NMR (100 MHz): δ (ppm): 12.9, 14.2, 40.8, 54.1, 59.9, 110.4, 114.7, 121.6, 124.1, 125.6, 127.8, 128.1, 131.0, 132.7, 133.1, 134.5, 136.9, 139.3, 140.6, 159.4, 165.1, 183.4 ppm. IR (neat), (cm^{-1}) 1713.5, 1263.4; MS (ESI) m/z 378 (M + 1); *Anal*. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71%. Found: C, 72.96; H, 6.02; N, 3.66%.

Ethyl 1-methyl-3-phenyl-1,2,3,10b-tetrahydropyrrolo[2′,3′:3,4] pyrrolo[1,2-a]indole-3a(4H)-carboxylate (4a). This compound was prepared according to the general procedure, method B as colorless semi-solid. ^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm): 1.34 (t, J = 7.1 Hz, 3H), 2.69 (s, 3H), 2.92 (t, J = 9.5 Hz, 1H), 3.23 (q, J = 6.8 Hz, 1H), 3.79 (d, J = 11.2 Hz, 1H), 4.16 (d, J = 11.0 Hz, 1H), 4.21 (d, J = 6.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.93 (s, 1H), 6.35 (s, 1H), 7.08–7.14 (m, 5H), 7.27–7.31 (m, 3H), 7.63 (d, J = 1.5 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.2, 38.6, 47.8, 50.5, 58.8, 61.9, 67.3, 71.1, 95.4, 109.7, 119.6, 120.9, 121.0, 127.3, 128.6, 132.5, 132.8, 138.3, 139.6, 174.3 ppm. IR (neat), (cm^{-1}) 1728.0, 1455.3, 1372.2; MS (ESI) m/z 361 (M + 1); *Anal*. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77%. Found: C, 76.34; H, 6.41; N, 7.55%.

Ethyl 1,10-dimethyl-3-phenyl-1,2,3,10b-tetrahydropyrrolo [2′,3′:3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (4b). This compound was prepared according to the general procedure method B as a semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.34 (t, J = 7.1 Hz, 3H), 2.69 (s, 3H), 2.92 (t, J = 9.5 Hz, 1H), 3.23 (q, J = 6.8 Hz, 1H), 3.79 (d, J = 11.2 Hz, 1H), 4.16 (d, J = 11.0 Hz, 1H), 4.21 (d, J = 6.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.93 (s, 1H), 6.35 (s, 1H), 7.08–7.14 (m, 5H), 7.27–7.31 (m, 3H), 7.63 (d, J = 1.5 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 11.1, 14.0, 38.4, 43.7, 44.5, 47.2, 50.1, 57.6, 61.3, 66.9, 71.0, 95.2, 108.7, 119.6, 120.5, 121.2, 127.1, 128.2, 128.3, 131.6, 132.8, 138.1, 139.3, 176.4: IR (neat), (cm^{-1}) 1720.0, 1442.3, 1362.2: MS (ESI) m/z 375 (M + 1); *Anal*. Calcd for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48%. Found: C, 76.78; H, 6.90; N, 7.32%.

***Ethyl 3-(4-chlorophenyl)-1-methyl-1,2,3,10b-tetrahydropyrrolo [2′,3′:3,4]pyrrolo[1,2-a]*indole-3a(4*H*)-carboxylate (4c).** This compound was prepared according to the general procedure method B as a viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):1.33 (t, J = 7.1 Hz, 3H), 2.67 (s, 3H), 2.86 (t, J = 9.2 Hz, 1H), 3.20 (q, J = 6. Hz, 1H), 3.75 (d, J = 11.1 Hz, 1H), 4.14 (d, J = 11.0 Hz, 1H), 4.29 (d, J = 6.9 Hz, 1H), 4.32(q, J = 7.1 Hz, 2H), 4.90 (s, 1H), 6.35 (s, 1H), 7.06–7.16 (m, 5H), 7.26–7.28 (m, 2H), 7.62 (d, J = 7.60 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):14.2, 38.6, 47.9, 49.8, 59.0, 62.0, 67.1, 71.0, 95.6, 109.7, 119.7, 120.9, 121.2, 128.8, 130.0, 132.4, 132.8, 133.2, 136.9, 139.5, 174.1: IR (neat), (cm^{-1}) 1726.3, 1492.1, 1454.3; MS (ESI) m/z 395 (M + 1); *Anal*. Calcd for HRMS calcd for $C_{23}H_{23}ClN_2O_2$: C, 69.95; H, 5.87; N, 7.09%. Found: C, 69.81; H, 5.64; N, 7.01%.

Ethyl 3-(4-chlorophenyl)-1,10-dimethyl-1,2,3,10b-tetrahydropyrrolo [2′,3′:3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (4d). This compound was prepared according to the general procedure method B as a viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):1.32 (t, J = 7.1 Hz, 3H), 2.67 (s, 3H), 2.69 (s, 3H), 2.86 (t, J = 9.2 Hz, 1H), 3.20 (q, J = 6.8 Hz, 1H), 3.75 (d, J = 11.1 Hz, 1H), 4.14 (d, J = 11.0 Hz, 1H), 4.29 (d, J = 6.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.90 (s, 1H), 7.06–7.16 (m, 5H), 7.24–7.29 (m, 2H), 7.62 (d, J = 7.60 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.5, 14.2, 38.4, 44.7, 47.8, 48.9, 59.1, 61.0, 66.8, 71.2, 95.6, 110.8, 118.6, 120.4, 121.3, 129.0, 130.1, 131.8, 132.5, 133.1, 137.3, 140.1, 176.2: IR (neat), (cm^{-1}) 1720.2, 1472.1, 1454.1: MS (ESI) m/z 409 (M + 1); *Anal*. Calcd for $C_{24}H_{25}ClN_2O_2$: C, 70.49; H, 6.16; N, 6.85%. Found: C, 70.38; H, 6.02; N, 6.72%.

Ethyl 3-(4-methoxyphenyl)-1-methyl-1,2,3,10b-tetrahydropyrrolo [2′,3′:3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (4e). This compound was prepared according to the general procedure method B as a dark-brown semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):1.34 (t, *J* = 7.1 Hz, 3H), 2.67 (s, 3H), 2.85 (t, *J* = 9.6 Hz, 1H), 3.20 (dd, *J* = 6.84, 9.52 Hz, H), 3.81 (t, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 4.11 (d, *J* = 5.60 Hz, 1H), 4.14 (d, *J* = 8.2 Hz, 1H),4.31 (q, *J* = 7.1 Hz, 2H), 4.93 (s, 1H), 6.35 (s, 1H), 6.83 (d, *J* = 1.8 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 7.09–7.13 (m, 3H), 7.60–7.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.2, 38.6, 47.8, 50.0, 55.2, 58.9, 61.8, 67.3, 70.9, 95.4, 109.7, 113.9, 119.6, 120.8, 121.0, 129.6, 130.1, 132.5, 132.8, 139.7, 158.8, 174.3: IR (neat), (cm^{-1}) 1726.5, 1513.0, 1454.7; MS (ESI) *m/z* 391 (M + 1); *Anal*. Calcd for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17%. Found: C, 73.73; H, 6.66; N, 7.03%.

Ethyl 3-(4-methoxyphenyl)-1,10-dimethyl-1,2,3,10b-tetrahydropyrrolo [2′,3′:3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (4f). This compound was prepared according to the general procedure method B as a viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.34 (t, *J* = 7.1 Hz, 3H), 2.67 (s, 3H), 2.85 (t, *J* = 9.6 Hz, 1H), 3.20 (q, *J* = 6.8 Hz, 1H), 3.81 (t, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 4.11 (d, *J* = 5.60 Hz, 1H), 4.14 (d, *J* = 8.2 Hz, 1H),4.31 (q, *J* = 7.1 Hz, 2H), 4.93 (s, 1H), 6.35 (s, 1H), 6.83 (d, *J* = 1.8 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 7.09–7.13 (m, 3H), 7.60–7.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.2, 38.6, 47.8, 50.0, 55.2, 58.9, 61.8, 67.3, 70.9, 95.4, 109.7, 113.9, 119.6, 120.8, 121.0, 129.6, 130.1, 132.5, 132.8, 139.7, 158.8, 174.3: IR (neat),(cm^{-1}) 1722.5, 1509.0, 1464.7; MS (ESI) *m/z* 405 (M + 1); *Anal*. Calcd for $C_{25}H_{28}N_2O_3$: C, 74.23; H, 6.98; N, 6.93%. Found: C, 74.05; H, 6.92; N, 6.88%.

Ethyl 4-phenyl-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino[3′,2′:3,4] pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5a). This compound was prepared according to the general procedure method B as a pale yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.27 (t, *J* = 7.1 Hz, 3H), 1.43 (m, 2H), 1.72 (m, 3H), 2.85 (t, *J* = 8.0 Hz, 1H), 3.20 (m, 1H), 4.0 (m, 2H), 4.05 (d, *J* = 11.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.91 (s, 1H), 6.39 (s, 1H), 7.09–7.15 (m, 4H), 7.25–7.34 (m, 4H), 7.61 (d, *J* = 7.60 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.7, 26.0, 26.4, 48.3, 48.4, 51.1, 62.1, 68.6, 70.4, 72.1, 95.1, 109.9, 119.6, 121.0, 121.1, 126.9, 128.6, 128.9, 132.4, 132.9, 137.9, 141.3, 174.5: IR (neat), (cm^{-1}) 1726.5, 1455.8, 1374.4: MS (ESI) *m/z* 387 (M + 1); *Anal*. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25%. Found: C, 77.61; H, 6.60; N, 7.13%.

Ethyl 4-(4-chlorophenyl)-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino [3′,2′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5b). This compound was prepared according to the general procedure method B as a semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.31 (t, *J* = 7.1 Hz, 3H), 1.69 (m, 2H), 2.03–2.07 (m, 3H), 2.85 (t, *J* = 8.0 Hz, 1H), 3.12 (q, *J* = 8.6 Hz, 1H), 3.42 (m, 1H), 3.86 (d, *J* = 8.6 Hz, 2H), 3.91 (d, *J* = 11.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz,, 2H), 5.08 (s, 1H), 6.38 (s, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 7.07–7.11 (m, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.27–7.31 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.2, 24.4, 28.6, 47.2, 53.6, 55.7, 62.0, 68.8, 70.4, 72.5, 93.6, 109.6, 119.6, 120.9, 121.1, 128.9, 128.6, 128.9, 129.9, 132.2, 133.3, 133.4, 135.7, 143.8, 174.7 ppm. IR (neat), (cm^{-1}) 1723.1, 1492.7, 1454.8; MS (ESI) *m/z* 421 (M + 1); *Anal*. Calcd for $C_{25}H_{25}ClN_2O_2$: C, 71.33; H, 5.99; N, 6.66%. Found: C, 71.21; H, 5.90; N, 6.62%.

Ethyl 4-(4-methoxyphenyl)-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino [3′,2′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5c). This compound was prepared according to the general procedure method B as a dark red semi-solid. ^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm): 1.31 (t, *J* = 7.1 Hz, 3H), 1.73 (m, 2H), 2.02–2.13 (m, 3H), 2.85 (t, *J* = 8.0 Hz, 1H), 3.18 (q, *J* = 8.6 Hz, 1H), 3.32–3.42 (m, 1H), 3.82 (s, 3H), 3.85 (d, *J* = 8 Hz, 1H), 3.91 (d, *J* = 11.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz,, 2H), 5.06 (s, 1H), 6.37 (s, 1H), 6.86 (d, *J* = 8.6 Hz,2H), 7.04 (d, *J* = 8.6 Hz, 2H), 7.09–7.14 (m, 3H), 7.59 (d, *J* = 7.2 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.2, 24.5, 28.6, 47.1, 53.7, 55.2, 55.8, 61.9, 68.7, 70.6, 72.3, 93.4, 109.7, 114.1, 119.4, 120.7, 121.1, 128.9, 129.6, 131.5, 132.3, 133.4, 144.1, 158.3, 174.9: IR (neat), (cm^{-1}) 1722.2, 1610.0, 1510.9, 1452.7; MS (ESI) *m/z* 417 (M + 1); *Anal*. Calcd for $C_{26}H_{28}N_2O_3$: C, 74.97; H, 6.78; N, 6.73%. Found: C, 74.88; H, 6.69; N, 6.70%.

Ethyl 11-methyl-4-phenyl-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino [3′,2′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5d). This compound was prepared according to the general procedure method B as a pale yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.28 (t, *J* = 7.1 Hz, 3H), 1.67 (m, 1H), 1.75–1.77 (m, 2H), 2.38 (s, 3H), 2.71 (t, *J* = 8.0 Hz, 1H), 3.03–3.04 (m, 1H), 3.98 (d, *J* = 8 Hz, 2H), 4.01 (d, *J* = 11.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.38 (d, *J* = 7.0 Hz,, 1H), 4.59 (d, *J* = 11.1 Hz 1H), 4.79 (s, 1H), 7.07–7.11 (m, 3H), 7.11–7.26 (m, 5H), 7.59 (d, *J* = 7.6 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 9.3, 14.0, 25.8, 26.7, 47.9, 48.8, 51.1, 61.9, 67.4, 71.4, 72.8, 103.7, 109.6, 118.6, 119.0, 121.0, 126.7, 128.4, 128.9, 132.5, 132.7, 138.0, 138.2, 174.6: IR (neat, cm^{-1}) 1723.4, 1455.6, 1377.5; MS (ESI) *m/z* 401 (M + 1); *Anal*. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99%. Found: C, 77.87; H, 6.92; N, 6.93%.

Ethyl 4-(4-chlorophenyl)-11-methyl-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino[3′,2′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5e). This compound was prepared according to the general procedure method B as a dark red semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.32 (t, *J* = 7.1 Hz, 3H), 1.69 (m, 2H), 2.03–2.07 (m, 3H), 2.69 (s, 3H), 2.85(t, *J* = 8.2 Hz, 1H), 3.14 (q, *J* = 8.6 Hz, 1H), 3.32–3.42 (m, 1H), 3.82 (s, 3H), 3.85 (d, *J* = 8 Hz, 1H), 3.99 (d, *J* = 11.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz,, 2H), 5.06 (s, 1H), 6.86 (d, *J* = 8.6 Hz,2H), 7.02 (d, *J* = 8.6 Hz,2H), 7.09–7.14 (m, 3H), 7.58 (d, *J* = 7.2 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.2, 13.9, 23.2, 28.6, 47.1, 52.6, 55.7, 55.8, 62.0, 67.8, 70.3, 71.2, 93.6, 109.0, 119.1, 119.9, 120.7, 121.1, 128.4, 129.6, 132.1, 133.3, 134.6, 144.1, 158.3, 172.7: IR (neat), (cm^{-1}) 1713.1, 1482.7, 1458.8; MS (ESI) *m/z* 435 (M + 1); *Anal*. Calcd for $C_{26}H_{27}ClN_2O_2$: C, 71.80; H, 6.26; N, 6.44%. Found: C, 71.69; H, 6.11; N, 6.38%.

Ethyl 4-(4-methoxyphenyl)-11-methyl-2,3,3a,4-tetrahydro-1H,5H-pyrrolizino[3′,2′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (5f). This compound was prepared according to the general procedure method B as a semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.26 (t, *J* = 7.1 Hz, 3H), 1.73(m, 2H), 2.01–2.11 (m, 3H), 2.69 (s, 3H), 2.85 (t, *J* = 8.2 Hz, 1H), 3.18(q, *J* = 8.6 Hz, 1H), 3.31–3.39 (m, 1H), 3.82 (s, 3H), 3.86 (d, *J* = 8.2 Hz, 1H), 3.90 (d, *J* = 11 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.95 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H),7.15–7.21 (m, 3H), 7.61 (d, *J* = 7.1 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 10.9, 14.1, 37.1, 48.1, 53.9, 55.3, 58.2, 62.1, 68.5, 69.9, 109.7, 114.2, 119.5, 121.2, 121.3, 129.4, 132.5, 128.9, 132.7, 159.0, 173.6: IR (neat), (cm^{-1}) 1710.2, 1621.0, 1510.9, 1472.7; MS (ESI) *m/z* 431 (M + 1); *Anal*. Calcd for $C_{27}H_{30}N_2O_3$: C, 75.32; H, 7.02; N, 6.51%. Found: C, 75.11; H, 6.80; N, 6.47%.

Ethyl 4-phenyl-3a,4-dihydro-3H,5H-[1,3]thiazolo[3″,4″:1′,5′] pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (6a). This compound was prepared according to the general procedure method B as a pale viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.26 (t, *J* = 7.1 Hz, 3H), 3.04 (dd, *J* = 6.2,

10.7 Hz, 1H), 3.25 (d, *J* = 6.8 Hz, 1H), 3.94 (d, *J* = 10.0 Hz, 1H), 4.07 (q, *J* = 4.4 Hz, 2H), 4.18 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 4.82 (s, 1H), 6.38 (s, 1H), 7.05–7.11 (m, 3H), 7.26–7.38 (m, 5H), 7.58 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.0, 37.2, 48.1, 54.4, 58.2, 62.1, 68.6, 69.8, 75.8, 93.8, 109.7, 119.5, 121.2, 121.3, 127.7, 128.4, 128.9, 132.5, 132.7, 173.6 ppm. IR (neat), (cm^{-1}) 1722.2, 1478.6, 1453.5; MS (ESI) *m/z* 405 (M + 1); *Anal*. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.26; H, 5.98; N, 6.93%. Found: C, 71.19; H, 5.78; N, 6.89%.

Ethyl 4-(4-chlorophenyl)-3a,4-dihydro-3H,5H-[1,3]thiazolo [3″,4″:1′,5′]pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (6b). This compound was prepared according to the general procedure method B as a pale viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.26 (t, *J* = 7.1 Hz, 3H), 3.04 (dd, *J* = 6.2, 10.7 Hz, 1H), 3.20 (d, *J* = 6.6 Hz, 1H), 3.95 (d, *J* = 10.2 Hz, 1H), 4.05 (q, *J* = 4.2 Hz, 2H), 4.18 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.33 (d, *J* = 10.4 Hz, 1H), 4.45 (d, *J* = 9.8 Hz, 1H), 4.82 (s, 1H), 6.38 (s, 1H), 7.05(d, *J* = 8.6 Hz, 2H), 7.07–7.11 (m, 1H), 7.12(d, *J* = 8.6 Hz, 2H), 7.25–7.30 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.1, 33.6, 51.0, 53.3, 54.4, 56.8, 61.9, 65.7, 69.8, 75.8, 93.8, 109.7, 119.5, 121.2, 121.3, 127.7, 128.0, 128.9, 131.5, 132.7, 139.1, 175.6 ppm. IR (neat), (cm^{-1}) 1726.1, 1472.7, 1452.8: MS (ESI) *m/z* 439 (M + 1); *Anal*. Calcd for $C_{24}H_{23}ClN_2O_2S$: C, 65.67; H, 5.28; N, 6.38%. Found: C, 65.52; H, 5.11; N, 6.28%.

Ethyl 4-(4-methoxyphenyl)-3a,4-dihydro-3H,5H-[1,3]thiazolo [3″,4″:1′,5′]pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (6c). This compound was prepared according to the general procedure method B as a semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.21 (t, *J* = 7.1 Hz, 3H), 3.02 (dd, *J* = 6.2, 10.7 Hz, 1H), 3.23 (d, *J* = 6.8 Hz, 1H), 3.82 (s, 3H),3.90 (d, *J* = 11 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 2H), 4.18 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.32 (d, *J* = 9.9 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 4.81 (s, 1H), 6.38 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H),7.04–7.09 (m, 3H), 7.26 (d, 8.7 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.1, 37.1, 48.1, 53.9, 55.3, 58.2, 62.1, 68.5, 69.9, 109.7, 114.2, 119.5, 121.2, 121.3, 129.4, 132.5, 128.9, 132.7, 159.0, 173.6: IR (neat), (cm^{-1}) 1722.2, 1610.0, 1510.9, 1452.7: MS (ESI) *m/z* 435 (M + 1); *Anal*. Calcd for $C_{25}H_{26}N_2O_3S$: C, 69.10; H, 6.03; N, 6.45%. Found: C, 69.03; H, 5.99; N, 6.41%.

Ethyl 11-methyl-4-phenyl-3a,4-dihydro-3H,5H-[1,3]thiazolo [3″,4″:1′,5′]pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a(11bH)-carboxylate (6d). This compound was prepared according to the general procedure method B as a pale viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.26 (t, *J* = 7.1 Hz, 3H), 2.67(s, 3H), 3.04 (dd, *J* = 6.2, 10.7 Hz, 1H), 3.25 (d, *J* = 6.8 Hz, 1H), 3.94 (d, *J* = 10.0 Hz, 1H), 4.07 (q, *J* = 4.4 Hz, 2H), 4.18 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 4.82 (s, 1H), 7.02–7.08 (m, 3H), 7.22–7.34 (m, 5H), 7.58 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.9, 14.0, 35.2, 48.1, 56.4, 59.1, 62.1, 65.7, 69.8, 75.8, 93.8, 109.7, 119.5, 121.2, 125.3, 127.9, 128.6, 128.9, 132.5, 132.7, 141.0, 174.6: IR (neat), (cm^{-1}) 1722.2, 1478.6, 1453.5: MS (ESI) *m/z* 419 (M + 1); *Anal*. Calcd for $C_{25}H_{26}N_2O_2S$: C, 71.74; H, 6.26; N, 6.69%. Found: C, 71.42; H, 6.04; N, 6.52%.

Ethyl 4-(4-chlorophenyl)-11-methyl-3a,4-dihydro-3H,5H-[1,3] thiazolo[3″,4″:1′,5′]pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a (11bH)-carboxylate (6e). This compound was prepared according to the general procedure method B as a pale viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):1.31 (t, *J* = 7.1 Hz, 3H), 2.67(s, 3H), 3.02 (dd, *J* = 6.2, 10.7 Hz, 1H), 3.20 (d, *J* = 6.6 Hz, 1H), 3.94 (d, *J* = 10.2 Hz, 1H), 4.06 (q, *J* = 4.2 Hz, 2H), 4.18 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.31 (d, *J* = 10.4 Hz, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 4.82 (s, 1H), 7.05(d, *J* = 8.6 Hz, 2H), 7.07–7.11 (m, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.25–7.30 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.1, 14.0, 33.6, 51.0, 53.3, 54.2, 56.8, 61.9, 65.7, 69.8, 75.8, 93.8, 109.7, 119.5, 121.2, 121.3, 127.7, 128.0, 128.9, 131.5, 132.7, 139.1, 173.9; IR (neat), (cm^{-1}) 1720.1, 1482.7, 1462.8; MS (ESI) *m/z* 453 (M + 1); *Anal*. Calcd for $C_{25}H_{25}ClN_2O_2S$: C, 66.28; H, 5.56; N, 6.18%. Found: C, 66.13; H, 5.42; N, 6.11%.

Ethyl 4-(4-methoxyphenyl)-11-methyl-3a,4-dihydro-3H,5H-[1,3]thiazolo[3″,4″:1′,5′]pyrrolo[2′,3′:3,4]pyrrolo[1,2-a]indole-4a (11bH)-carboxylate (6f). This compound was prepared according to the general procedure method B as a semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.21 (t, *J* = 7.1 Hz, 3H), 2.69 (s, 3H) 3.02 (dd, *J* = 6.2, 10.7 Hz, 1H), 3.23 (d, *J* = 6.3 Hz, 1H), 3.82 (s, 3H), 3.90 (d, *J* = 11 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 2H) 4.02 (m, 2H), 4.18(d, *J* = 9.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.81 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.04–7.09 (m, 3H), 7.26 (d, 8.6 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 1H): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 10.2, 14.0, 37.2, 48.1, 52.9, 55.3, 58.2, 62.7, 68.5, 69.9, 109.7, 113.5, 120.4, 121.2, 121.3, 128.7, 130.3, 132.5, 132.7, 157.9, 174.2: IR (neat), (cm^{-1}) 1620.0, 1519.9, 1432.7: MS (ESI) *m/z* 449 (M + 1); *Anal*. Calcd for $C_{26}H_{28}N_2O_3S$: C, 69.62; H, 6.29; N, 6.24%. Found: C, 69.43; H, 6.21; N, 6.13%.

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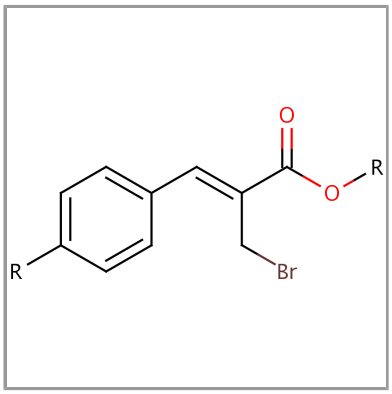

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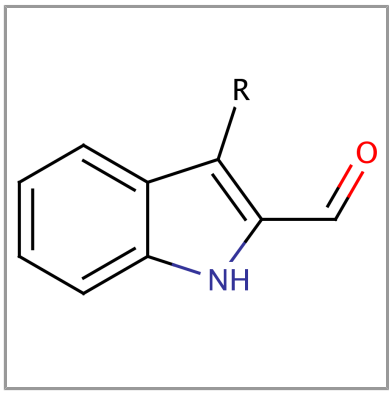

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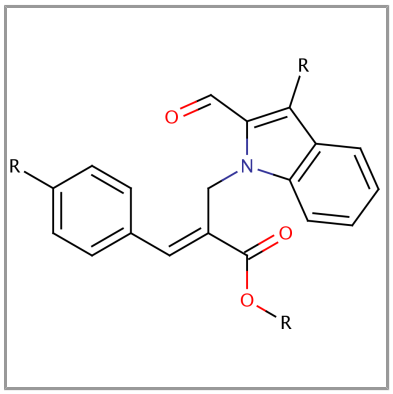

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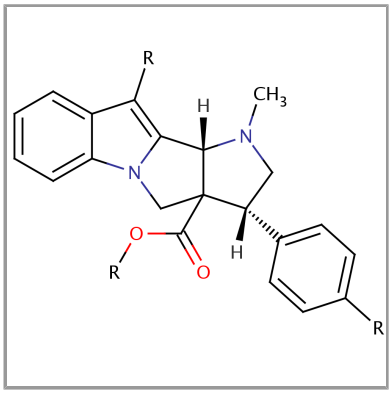

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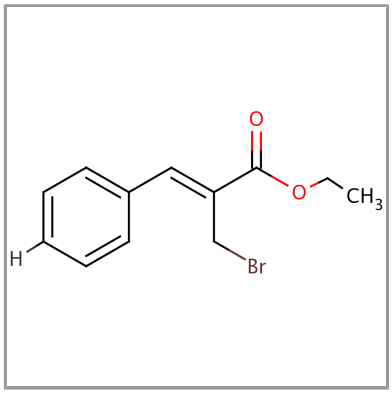

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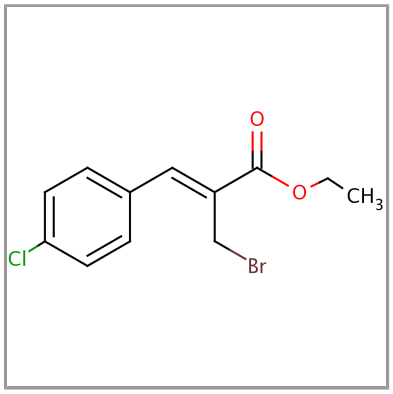

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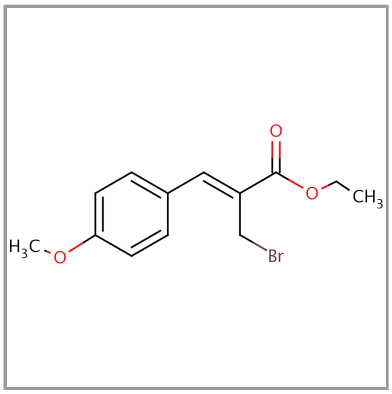

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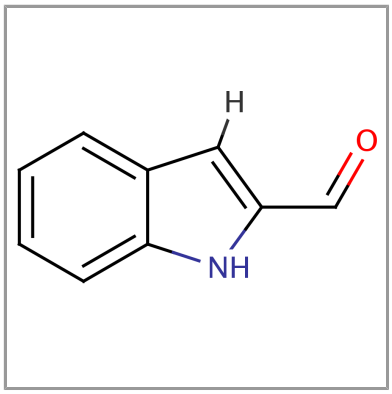

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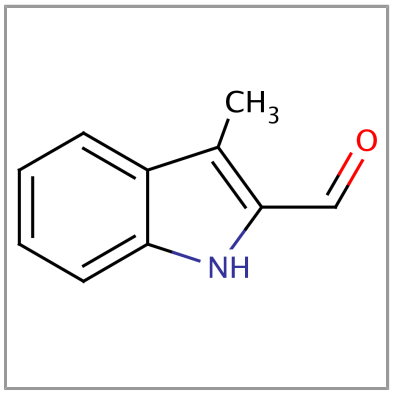

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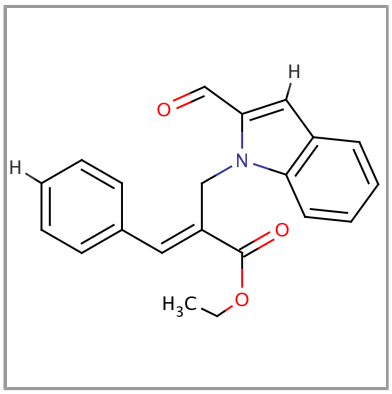

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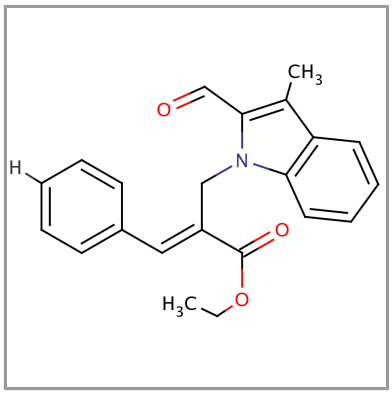

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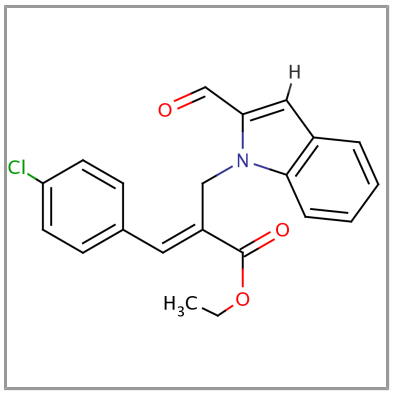

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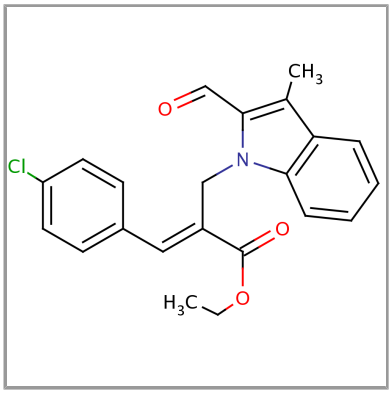

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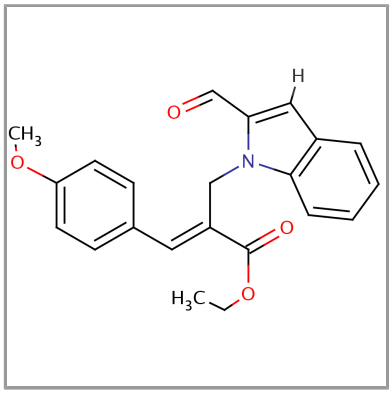

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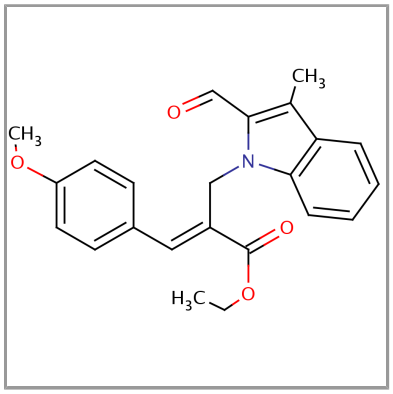

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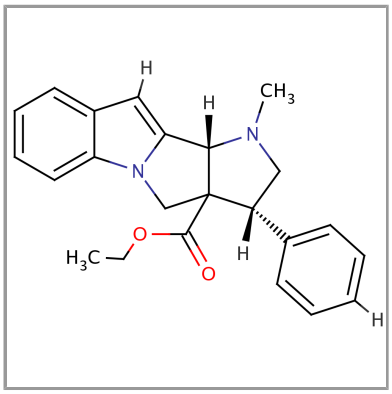

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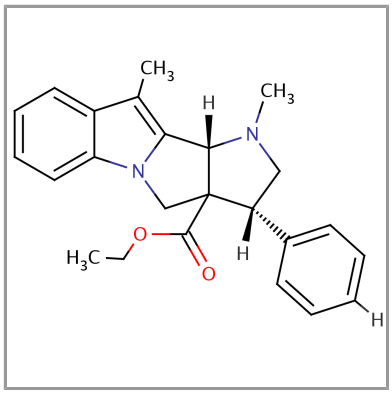

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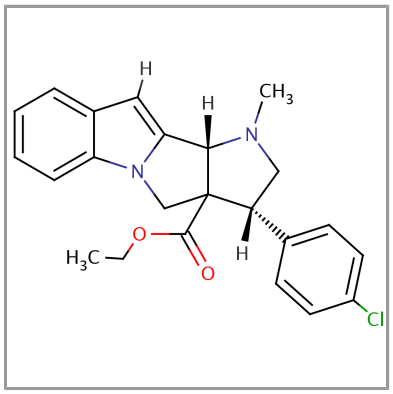

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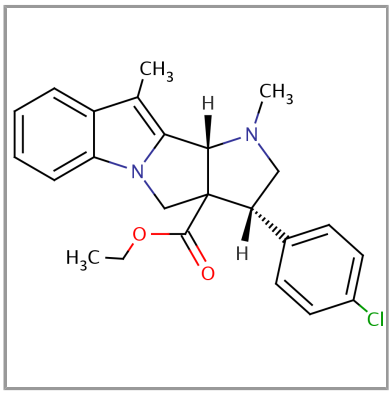

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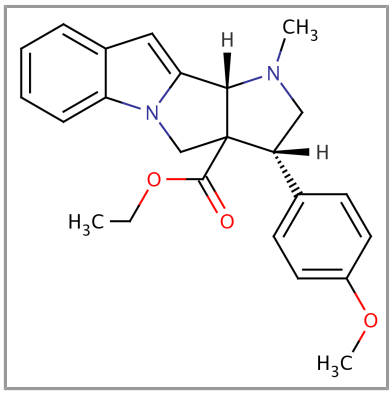

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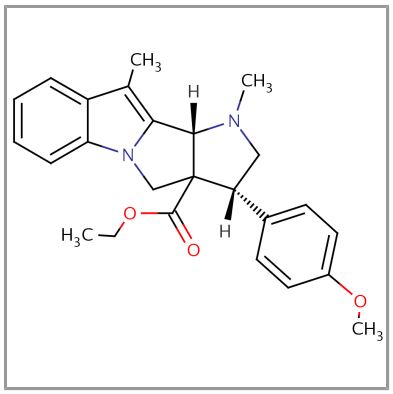

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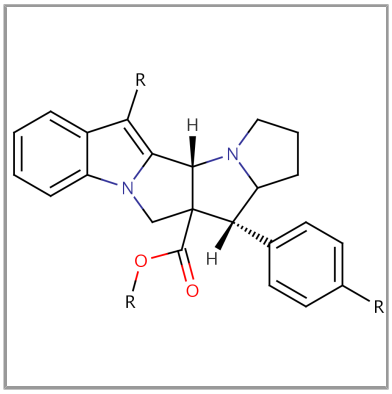

Compound Details Structure Search

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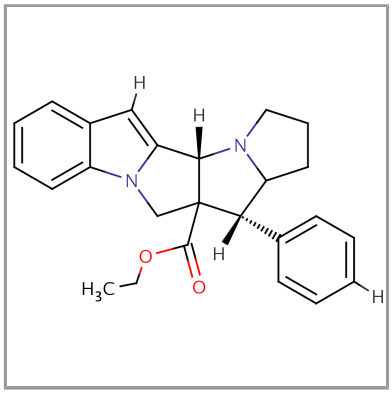

Compound Details Structure Search

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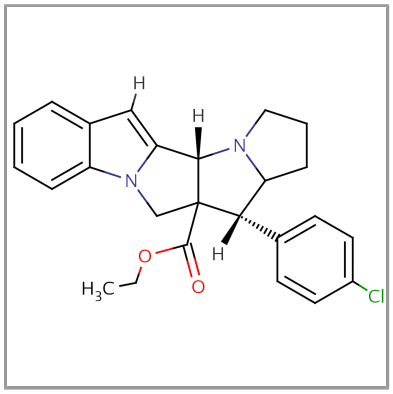

Compound Details Structure Search

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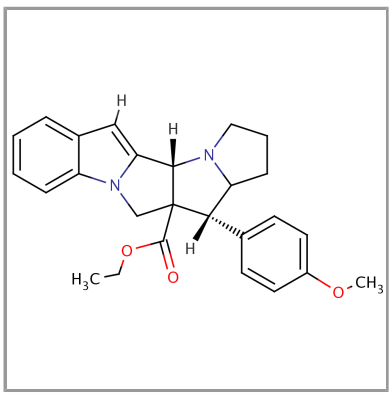

Compound Details Structure Search

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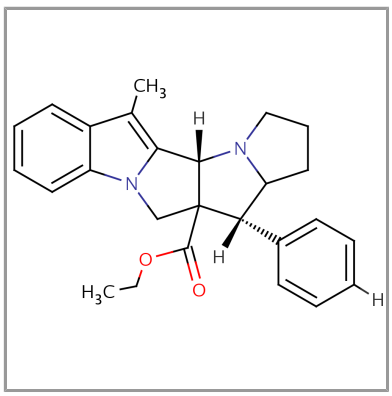

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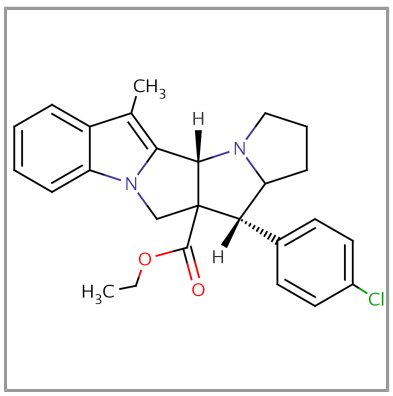

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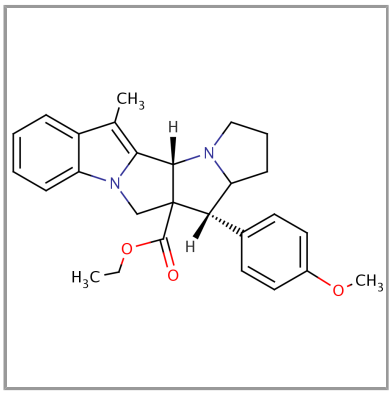
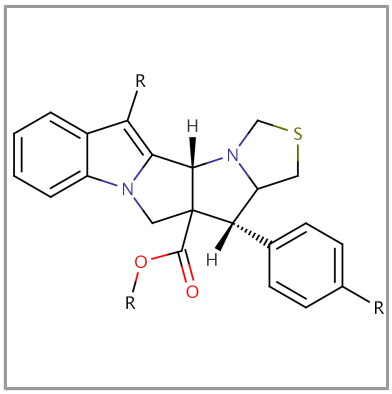


Compound Details Structure Search

6



Compound Details Structure Search

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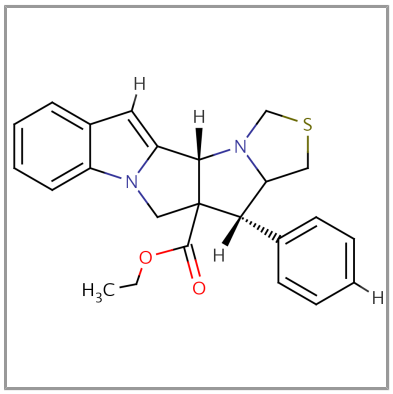

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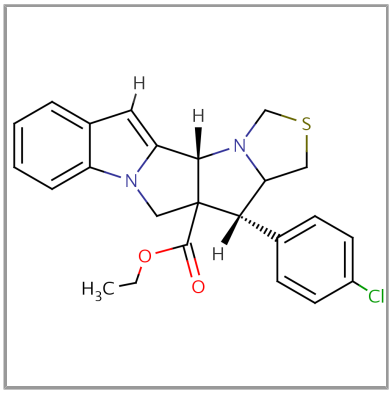

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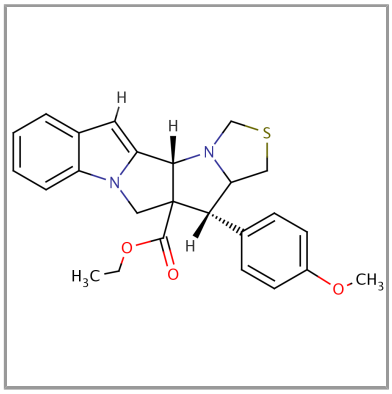

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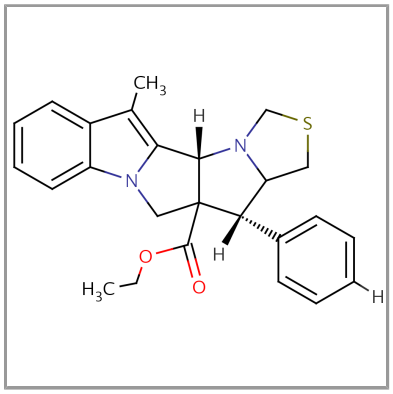

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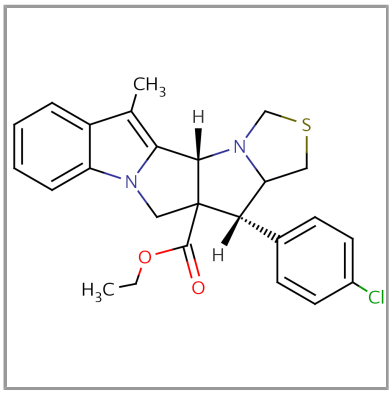

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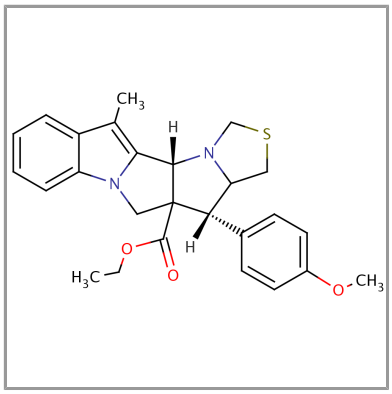

Compound Details Structure Search