Tetrahedron Letters 53 (2012) 6676–6681

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

A facile synthesis of novel ferrocene grafted spiro-indenoquinoxaline pyrrolizidines via one-pot multicomponent [3+2] cycloaddition of azomethine ylides

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ARTICLE INFO

Article history:
Received 5 July 2012
Revised 21 September 2012
Accepted 23 September 2012
Available online 2 October 2012

Keywords:
Ferrocene
1,2-Phenylenediammine
Azomethine ylide
Cycloaddition
Spiro-indenoquinoxaline
Pyrrolizidines

ABSTRACT

A facile one-pot synthesis of novel ferrocene grafted spiro-indenoquinoxaline pyrrolizidines via multi-component-[3+2]-cycloaddition of azomethine ylides is described. The methodology is very simple and applicable to a wide variety of ferrocene derived dipolarophiles. The structures of cycloadducts were confirmed by spectroscopic analysis. X-ray analysis of one of the analogs, adds conclusive support to the proposed structures.

Synthesis of novel pharmacological agents with minimum number of steps and less time is a major challenge for chemists.[1] In general; the conventional approach involves the use of multistep reaction sequences which are typically associated with low yields, high cost, and tedious isolation and purification of the resulting products. However, multicomponent reactions (MCRs) offer a valuable solution for such a situation[2,3] and they constitute a highly effective one pot procedure that has many advantages including atom economy and convenience in the construction of new bonds in a single step, paving way for the synthesis of complex heterocyclic compounds.[4]

Ferrocene derivatives remain at the forefront of attention offering advantage over other organometallics due to their synthetic versatility, thermal and photochemical stability, and biological activity. Hence, there has been a renewed interest in the synthesis of ferrocene based heterocycles with potential applications.

The intermolecular [3+2]-cycloaddition reactions of azomethine ylides with olefinic and acetylenic dipolarophiles represent an important approach for the formation of azaheterocycles such as pyrrolidines and pyrrolizidines prevalent in a variety of biologically active compounds.[5–7] Indenoquinoxaline derivatives are important classes of nitrogen containing heterocycles which constitute useful intermediates in the organic synthesis.[8] In the recent years, construction of spiro compounds by intermolecular [3+2]-cycloaddition reactions of azomethine ylides has been well developed and the reactions proceed with high regioselectivity.[9,10] Hence, with renewed interest in such complex ferrocene appended heterocycles and in continuation of our research in the area of 1,3-dipolar cycloaddition,[11–14] we herein report for the first time, a mild, expeditious, and a facile four-component, one-pot synthesis of novel ferrocene grafted monospiro-indenoquinoxaline pyrrolizidines through 1,3-dipolar cycloaddition of azomethine ylide generated from 1,2-phenylenediamine, ninhydrin, and L-proline with various unusual ferrocene derived dipolarophiles. Some of the properties of ferrocene derived dipolarophiles are mentioned in Table 1.

Initially, the four-component reaction of ninhydrin **2**, 1,2-phenylenediammine **3**, L-proline **4**, and ferrocene derived dipolarophile **1a** was investigated (Scheme 1).

The one-pot four-component reaction proceeded well in methanol as a solvent at reflux temperature to give ferrocene grafted spiro-indenoquinoxaline pyrrolizidine as the only product which was characterized on the basis of spectroscopic data. Thus, the IR spectrum of spiro[2.11′]indeno[1,2-*b*]quinoxaline-3-ferrocenoyl-4-(*p*-methoxylphenyl)-pyrrolizidine **5a** showed absorption at 1660 cm^{-1} indicating the presence of a carbonyl group. In ^1H NMR spectrum of the product **5a** the characteristic multiplets of pyrrolizidine ring appeared at δ 1.72–2.78. Additionally, the pyrrolizidine ring proton attached to the *p*-methoxylphenyl ring appeared as a triplet at δ 4.10 ($H^{1'}$, J = 10.5 Hz). The pyrrolizidine–NCH proton appeared as a doublet of triplet at δ 4.53

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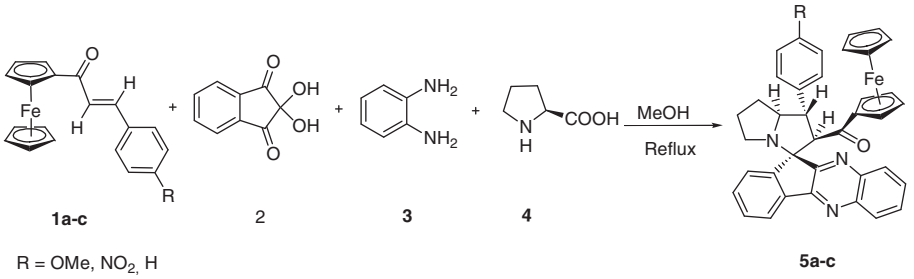
0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.09.104

Table 1
Physical properties and chemical yield of the ferrocene derived dipolarophile **1a–c**/**10a–b**/**12**/**14**/**16** and their [3+2]-cycloaddition product with 1,2-phenylenediammine **2**, ninhydrin **3**, and L-proline **4**

D	Color (solid)	Mp (°C)		Y (%)		IR KBr γ(C=O) (cm^{-1})	P	R	X	Color (solid)	Mp (°C)	Methanol/ reflux		Toluene/ reflux		IR KBr γ(C=O) (cm^{-1})
		A	B[26]	A	B[26]							T (h)	Y (%)	T (h)	Y (%)	
1a	Red	148–149	149	54	53	1646	**5a**	OMe	—	Pale Orange	118–120	3.6	78	6.5	40	1660
1b	Red	190–191	192	90	92	1658	**5b**	NO_2	—	Pale Orange	145–146	3.0	86	5.0	48	1668
1c	Red	142–143	141	62	63	1650	**5c**	H	—	Pale Orange	134–136	4.0	80	6.0	45	1664
10a	Red	153	152	90	92	1652	**11a**	—	O	Pale Yellow	152–154	5.4	82	—	—	1668
10b	Red	144–145	146	84	83	1642	**11b**	—	S	Pale Orange	138–139	4.0	80	—	—	1656
12	Red–brown	153	152–153	92	90	1658	**13**	—	—	Pale brown	145–146	4.2	90	—	—	1674
14	Red	212	211–213	62	57	1643	**15**	—	—	Pale Orange	196–198	5.5	83	—	—	1664
16	Blue	168–169	167–170	90	93	1712, 1718	**17**	—	—	Pale yellow	116–118	5.4	88	—	—	1728, 1734

D = dipolarophile; Y (%) = Yield in percentage; A = obtained; B = reported; mp = melting point; P = product; T (h) = time in hour.



Scheme 1. Synthesis of ferrocene grafted spiro-indenoquinoxaline-pyrrolizidine **5**.

($H^{7'a}$, J = 9.9, 6.3 Hz,) whereas the pyrrolizidine proton attached to the ferrocenoyl moiety is more deshielded and exhibited a doublet at δ 4.67 ($H^{2'}$, J = 11.1 Hz). The ferrocenyl protons exhibited triplet at δ 3.25 (J = 1.2 Hz), singlet at δ 3.44, doublet at δ 3.60 (J = 1.2 Hz), multiplet at δ 3.99–4.01, and triplet at δ 4.31 (J = 1.2 Hz). The methoxy group attached to the phenyl ring exhibited a singlet at δ 3.68. The aromatic protons appeared as a multiplet in the region δ 6.87–8.32.

The off resonance decoupled ^{13}C NMR spectra of **5a** exhibited characteristic peaks for the spiro carbon and carbonyl group attached to the ferrocene moiety at 76.55 and 197.81 ppm respectively and the signals for all other carbons are located at appropriate chemical shifts in agreement with the proposed structure. The formation of the product was confirmed by mass spectral and elemental analyses. The mass spectrum of **5a** showed a peak at m/z 493 (M^+).

The formation of the ferrocene grafted spiro-indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizidine scaffold probably involves a complex multistep sequence of events. The multicomponent reaction proceeds through cyclocondensation of ninhydrin **2** and phenylenediamine **3** to give indenoquinoxline-11-one **7**,[15] which further condensed with L-proline **4** to produce 1,3-dipole, azomethine ylide **9** by thermal decarboxylation of **8**[16] (Fig. 1).

The 1,3-dipole **9** subsequently undergoes cycloaddition reaction with chalcone **1**, to give the product **5**. In TS 1, R substituted phenyl ring gets sufficiently away from the indenoquinoxaline structure, therefore TS1 has lower steric hindrance compared to TS2 in which the R substituted phenyl ring is close to proline moiety. Consequently, the reaction proceeds via *exo*-transition state (TS1) (Figs. 2 and 3).

Stereochemical assignments of the cycloadduct **5a** were made on the basis of NOE studies and comparison with previously reported values in similar systems.[17] The possibility of the formation of other isomer, via TS2, was ruled out by ^1H NOESY studies. For example irradiation of $H^{1'}$ at δ = 4.10 (J = 10.5 Hz) caused no considerable enhancement of $H^{2'}$ and $H^{7'a}$ at δ 4.67 and 4.53 respectively, supporting the *trans*-arrangement of $H^{1'}$ with $H^{7'a}$ and $H^{2'}$. The formation of the regioisomer **6** was not observed due to the unfavorable transition states (TS3 and TS4) as depicted in Figs. 2 and 3.

These observations are also consistent and supportive with the X-ray crystal structure of a series of diverse ferrocene appended spiro-oxindolo-pyrrolizidines and dispiro-indenoquinoxaline-pyrrolidines reported recently by us.[18] Encouraged by the results obtained by using the dipolarophile **1a**, we extended the one-pot four-component reaction involving other ferrocene derived dipolarophiles (**1b–c**, **10a–b**, **12**, **14**, and **16**)[19a–c] with ninhydrin **2**, 1,2-phenylenediammine **3,** and L-proline **4** under optimized conditions in refluxing methanol to afford a series of novel ferrocene grafted mono-spiro-indenoquinoxaline-pyrrolizidines (**5b–c**, **11a–b**, **13**, **15**, and **17)** in good yields (78–90%) (Table 1). Their structures were confirmed through spectral analysis.

In order to improve the yield of the product, the one-pot four-component reaction was also carried out in toluene for the dipolarophiles **1a–c** and it was found that even under refluxing condition, there was no improvement in the isolated yield of the cycloadducts. This is attributed to the poor solubility of reactant in toluene specially the amino acid, L-proline **4** which is responsible for the formation of azomethine ylide with indenoquinoxaline-11-one **8**. Hence, methanol was invariably, chosen as a solvent for conducting the reaction with other dipolarophiles **10a–b**, **12**, **14**, and **16**.

Schemes 2–4 depict the reaction of 1-ferrocenyl-3-furyl-prop-2-ene-1-one **10a**/1-ferrocenyl-3-thienyl-prop-2-ene-1-one **10b**/1-ferrocenyl-3-pyridyl-prop-2-ene-1-one **12** and 1,3-diferrocenyl-prop-2-ene-1-one **14** with ninhydrin **2**, 1,2-phenylenediammine **3**, and L-proline **4** under optimized conditions in refluxing methanol leading to the formation of ferrocene substituted spiro-indenoquinoxaline-pyrrolizidines **11a**, **11b**, **13**, and **15** as evidenced by TLC and spectral analysis. All the newly synthesized cylcoadducts were obtained in good yields (Table 1).

To further expand the scope of this one-pot four-component 1,3-dipolar cycloaddition reaction, we successfully accomplished the synthesis of ferrocene grafted dispiro-indenoquinoxaline

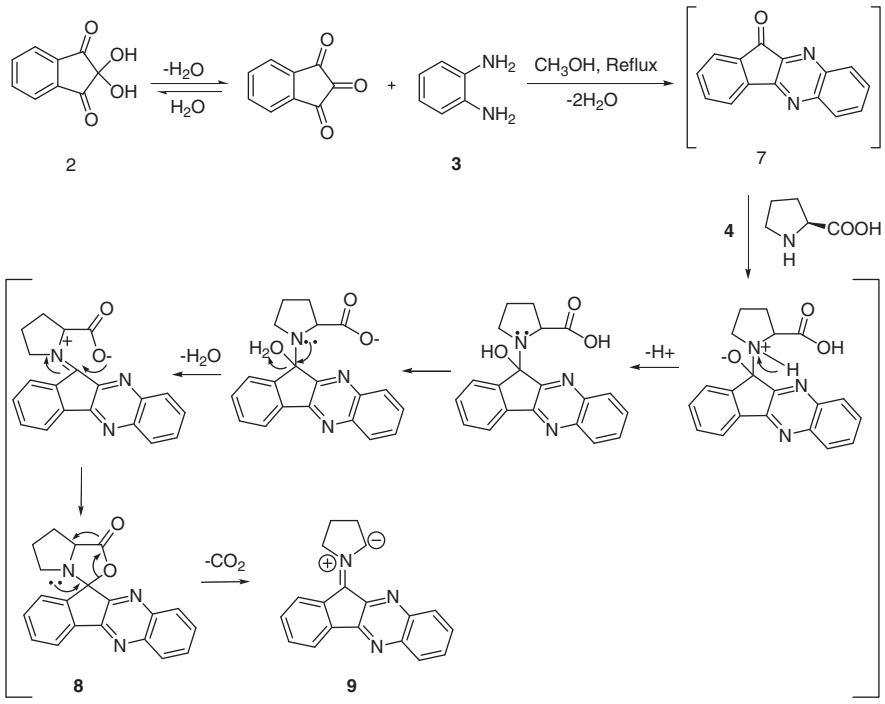


Figure 1. Mechanism for the formation of azomethine ylide **9** from ninhydrin **2**, 1,2-phenylenediammine **3**, and L-proline **4**.

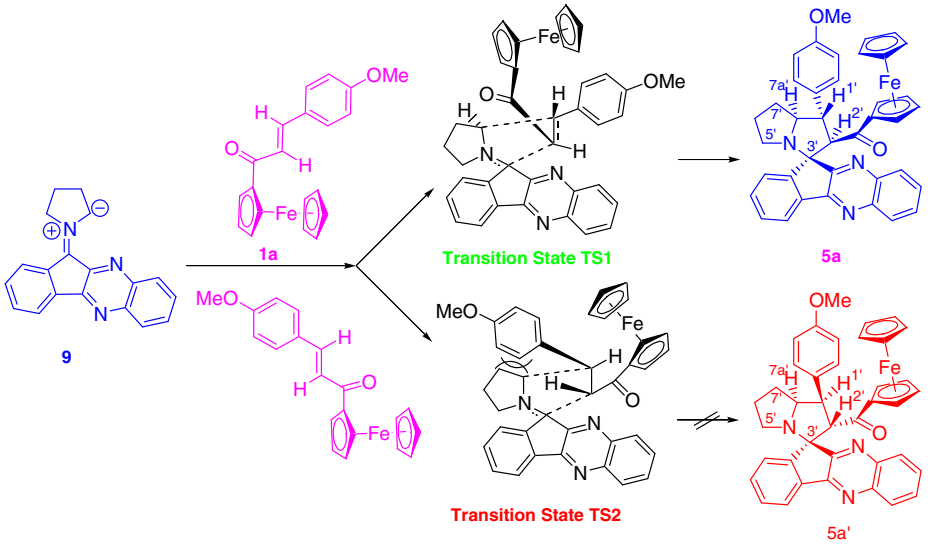


Figure 2. The proposed mechanism for one-pot four-component synthesis of ferrocene grafted spiro-indenoquinoxaline-pyrrolizidine **5**.

pyrrolizidine **17** by the reaction of 2-ferrocenylmethylidene-1,3-indanedione **16**,[19d] ninhydrin **2**, 1,2-phenylenediammine **3**, and L-proline **4** under optimized reaction condition (Scheme 5). The cycloadduct was obtained in good yield and was confirmed by spectral analysis.

The IR spectrum of **17** showed peaks at 1728 and 1734 cm^{-1} due to the indanedione ring carbonyls. In the ^1H NMR spectrum of **17**, the pyrrolizidine ring proton attached directly to the ferrocene moiety appeared as a doublet at δ 5.02 (J = 10.2 Hz) which clearly showed the regiochemistry of the cycloaddition reaction. If the other regioisomer **18** had formed, then the ^1H NMR spectrum would have shown a singlet for the pyrrolizidine ring proton attached directly to the ferrocene moiety and this is not observed. The stereochemistry of the cycloadducts **17** was deduced on the basis of ^1H NOESY. Irradiation of pyrrolizidine ring proton attached directly to the ferrocene moiety at δ 5.02 did not cause any enhancement of the signal for the pyrrolizidine–NCH proton which appeared as a multiplet at δ 4.62–4.66 supporting the mutual *trans*-arrangement of the pyrrolizidine ring proton attached to the ferrocene moiety and the pyrrolizidine–NCH proton.

The signals in the ^{13}C NMR spectrum of **17** at 74.14 and 75.67 ppm correspond to the two spiro carbons. The indanedione ring carbonyls resonated at 188.43 and 189.50 ppm, respectively. Moreover, the presence of a molecular ion peak at m/z 626 (M^+) in the mass spectrum of **17** confirmed the structure of the cycloadduct. The formation of indenoquinoxaline-11-one and regio- and stereochemical outcome of the cycloaddition reaction was unam-

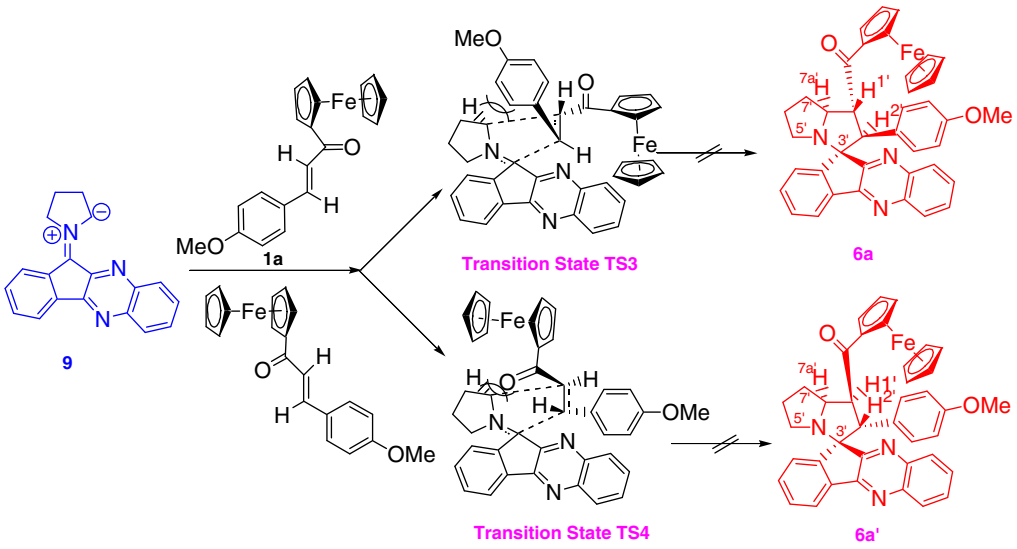
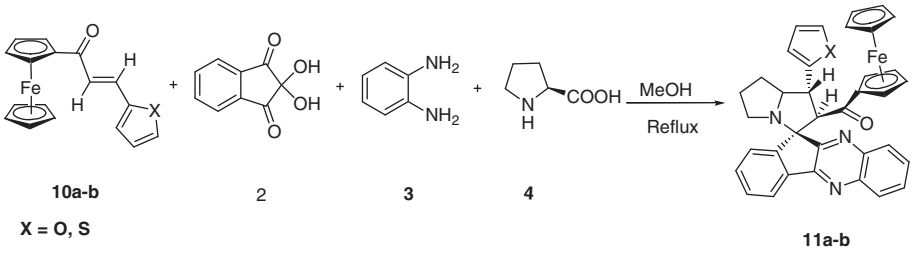
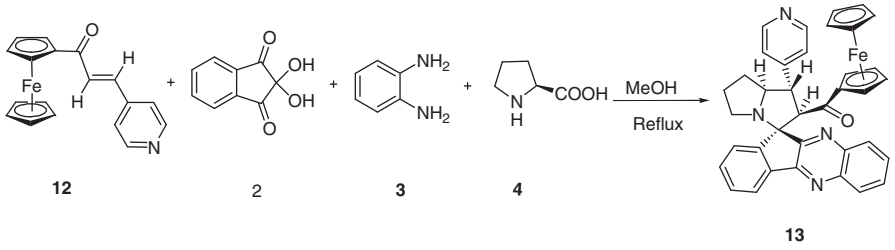


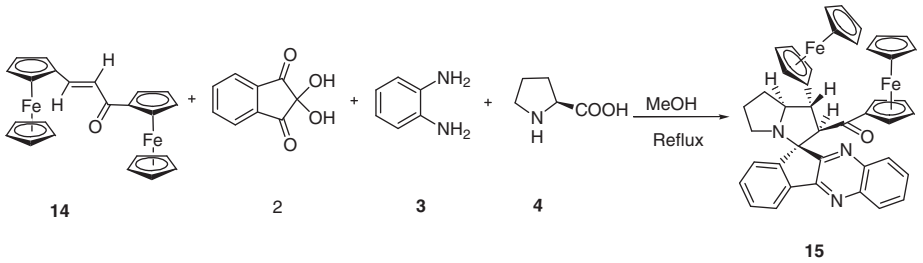
Figure 3. The proposed mechanism for the non-formation of regioisomer **6a** and **6a′** due to unfavourable transition states **TS3** and **TS4**.



Scheme 2. Synthesis of ferrocene grafted spiro-indenoquinoxaline furyl/thienyl pyrrolizidines **11**.



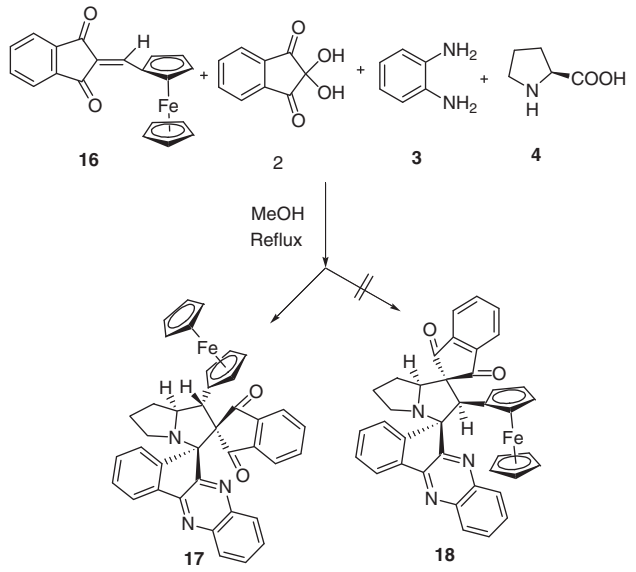
Scheme 3. Synthesis of ferrocene grafted spiro-indenoquinoxaline pyridyl pyrrolizidine **13**.



Scheme 4. Synthesis of ferrocene grafted spiro-indenoquinoxaline ferrocenyl pyrrolizidine 1**5**.

biguously ascertained by a single crystal X-ray analysis of one of the pyrrolizidine analogs in the spiro-indanedione-indenoquinoxaline series obtained by the reaction of 2-benzylidene-1,3-indanedione with ninhydrin **2**, 1,2-phenylenediammine **3**, and L-proline **4**.[20]

In conclusion, we have synthesized a series of hitherto unknown novel ferrocene grafted spiro-indenoquinoxaline pyrrolizidines via a facile one-pot four-component cycloaddition reaction.[21] The compounds synthesized carry a diverse substitution



Scheme 5. Synthesis of ferrocene grafted dispiro-indenoquinoxaline indane-1,3-dione pyrrolizidine **17**.

pattern by choice. This method offers several advantages including its simplicity with a one-pot four-component approach, mild reaction conditions, easy workup, affording the desired products from readily and cheaply available starting materials in a single step. This method is general and is applicable to a variety of unusual ferrocene derived dipolarophiles to synthesize such complex highly substituted pyrrolizidines containing ferrocene and spiro-indenoquinoxaline moiety of biological significance.

Acknowledgments

A.R.S. thanks CEFIPRA (*le Centre Indo - Français Pour la Recherche Avancée*) for the nomination under postdoctoral programme-2012. R.R. thanks DST and DST-FIST, New Delhi, for financial support.

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21. *General procedure for the synthesis of ferrocene based spiro-indenoquinoxaline pyrrolizidines*: A mixture of ninhydrin **2** (1 mmol) and 1,2-phenylenediamine **3** (1 mmol) was stirred for 10 min in 10 mL of methanol followed by the addition of L-proline **4** (1 mmol). To this mixture, a solution of dipolarophile **1a** (1 mmol) in 10 ml of methanol was added. The mixture was then refluxed until completion of the reaction as evidenced by TLC. The solvent was removed under reduced pressure and the crude product obtained was purified by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent. Alternatively, the reaction could also be carried out in toluene using a Dean-Stark apparatus. *Spiro-[2.11′]-indeno[1,2-b]quinoxaline-3-ferrocenoyl-4-(p-methoxylphenyl)- pyrrolizidine* ***5a***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72–1.98 (m, 2H), 2.00–2.22 (m, 2H), 2.43–2.46 (m, 1H), 2.72–2.78 (m, 1H), 3.25 (t, J = 1.2 Hz, 1H), 3.44 (s, 5H), 3.60 (d, J = 1.2.Hz 1H), 3.68 (s, 3H, –OMe), 3.99–4.01 (m, 1H), 4.10 (t, J = 10.5 Hz, 1H, $H^{1'}$), 4.30–4.31 (t, J = 1.2 Hz, 1H), 4.53 (dt, J = 9.9, 6.3 Hz, 1H, $H^{7'a}$), 4.67 (d, J = 11.1 Hz, 1H, $H^{2'}$), 6.87–6.90 (m, 2H), 7.30–7.42 (m, 2H), 7.56–7.72 (m, 5H), 7.89–7.92 (m, 1H), 7.99–8.02 (m, 1H), 8.30–8.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.76, 27.71, 45.68, 49.76, 52.92, 64.97, 65.97, 66.44, 66.77, 69.15, 69.72, 72.54, 74.16, 76.55, 111.82, 119.62, 126.15, 126.32, 122.63, 127.01, 127.04, 127.14, 127.42, 128.38, 130.58, 134.95, 139.68, 140.39, 141.56, 150.60, 156.58, 163.03, 197.81 ppm; EIMS m/z: 631(M^+); *CHN* analysis Calcd for $C_{39}H_{33}N_3O_2Fe$: C, 74.17; H, 5.27; N, 4.21%. Found: C, 74.36; H, 5.35; N, 4.29%. *Spiro-[2.11′]-indeno[1,2-b]quinoxaline-3-ferrocenoyl-4-furyl-pyrrolizidine* ***11a***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.80–2.20 (m, 4H), 2.48–2.52 (m, 1H), 2.68–2.72 (m, 1H), 3.40 (s, IH), 3.71 (s, 5H), 4.04 (s, 1H), 4.10 (s, 1H), 4.37 (t, J = 10.8 Hz, 1H, $H^{1'}$), 4.40 (s, 1H), 4.62–4.66 (m, 1H, $H^{7'a}$), 4.90 (d, J = 11.4 Hz, 1H, $H^{2'}$), 6.37–6.43 (m, 2H), 7.41–8.38 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.33, 29.68, 30.53, 46.06, 47.91, 63.96, 68.42, 69.47, 71.71, 72.37, 75.08, 78.84, 106.95, 110.65, 122.11, 128.43, 128.82, 129.56, 130.82, 137.34, 141.58, 142.10, 142.79, 143.71, 153.06, 153.77,164.91, 199.59 ppm; EIMS m/z: 591 (M^+); CHN analysis Calcd for $C_{36}H_{29}N_3O_2Fe$: C, 73.10; H, 4.94; N, 7.10%. Found: C, 72.93; H, 5.07; N, 7.22. *Spiro-[2.11′]-indeno[1,2-b]quinoxaline-3-ferrocenoyl-4-pyridyl-pyrrolizidine* **13**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.80–2.03 (m, 4H), 2.43–2.45 (m, 1H), 2.78–2.80 (m, 1H), 3.18 (s, IH), 3.45 (s, 5H), 3.63 (s, 1H), 4.03 (d, J = 2.1 Hz, 1H), 4.13 (t, J = 10.2 Hz, 1H, $H^{1'}$), 4.32 (d, J = 1.2 Hz, 1H), 4.52–4.58 (m, 1H, $H^{7'a}$), 4.68 (d, J = 10.8 Hz, 1H, $H^{2'}$), 7.32–7.51 (m, 2H), 7.66–7.72 (m, 2H), 7.90–8.04 (m, 4H), 8.28–8.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.93, 29.74, 47.99, 52.08, 60.36, 67.08, 68.97, 69.51, 71.80, 72.66, 74.67, 75.84, 122.17, 124.05, 128.34, 129.13, 129.70, 130.93, 137.46, 141.97, 142.83, 143.43, 146.15, 149.15, 150.09, 150.77, 153.03, 165.16, 200.34 ppm; EIMS m/z: 605 (M^+); CHN analysis Calcd for $C_{37}H_{30}N_4OFe$: C, 73.75; H, 5.02; N, 9.29%. Found: C, 73.88; H, 5.20; N, 9.45%. *Spiro-[2.11′]-indeno[1,2-b]quinoxaline-3-ferrocenoyl-4-ferrocenyl pyrrolizidine* ***15***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88–2.20 (m, 4H), 2.28–2.68 (m, 2H), 3.29 (s, 1H), 3.54 (s, 2H), 3.57 (s, 1H), 3.66 (s, 5H), 4.08 (t, J = 11 Hz, IH, $H^{1'}$), 4.21 (s, 2H), 4.25 (s, 2H), 4.27 (s, 5H), 4.52 (d, J = 11.0 Hz, 1H, $H^{7'a}$), 4.88 (d, J = 11.1 Hz, 1H, $H^{2'}$), 7.34–8.26 (m, 8H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.38, 28.68, 31.95, 44.27, 46.03, 64.89, 66.38, 67.67, 67.96, 68.40,

68.92, 69.92, 70.75, 74.44, 78.80, 120.96, 127.44, 127.96, 128.36, 128.73, 129.75, 136.31, 141.11, 141.77, 143.36, 152.25, 164.06, 200.21 ppm; EIMS *m*/*z*: 709 (M^+); CHN analysis Calcd for $C_{42}H_{35}N_3OFe_2$: C, 71.10; H, 4.97; N, 5.92%; Found: C, 70.95; H, 5.11; N, 6.08%. *Spiro-[2.11′]-indeno- [1,2-b]quinoxaline-spiro-[3.2′]indane-1′,3′-dione-4 ferrocenyl- pyrrolizidine* ***17***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10–2.20 (m, 2H), 2.32–2.42 (m, 2H), 2.58–2.68 (m, 2H), 3.42 (s, 1H), 4.08 (s, 5H), 4.62–4.66 (m, 1H), 5.02 (d, J = 10.2.Hz, 1H), 7.30–8.27 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.00, 28.65, 47.90, 59.34, 66.36, 67.74, 69.72, 74.25, 75.14, 75.67 123.17, 123.66, 128.61, 129.21, 130.12, 130.51, 131.44, 133.65, 135.73, 138.84, 140.45, 141.16, 141.57, 142.43, 148.39, 155.53, 170.07, 189.50, 188.43 ppm; EIMS *m*/*z*: 626 (M^+); CHN analysis Calcd for $C_{29}H_{24}N_2O_3Br_2Fe$: C, 74.79; H, 4.63; N, 6.71%. Found: C, 74.94; H, 4.48; N, 6.55%.