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# 1,3-Dipolar cycloaddition reaction of bipyridinium ylides with the propynamido-β-cyclodextrin. A regiospecific synthesis of a new class of fluorescent β-cyclodextrins

François Delattre,[a] Patrice Woisel,[a,*] Gheorghe Surpateanu,[a] Marc Bria,[b] Francine Cazier[a] and Patrick Decock[a]

[a]*Laboratoire de Synthèse Organique et Environnement, EA: 2599, MREID 145, Avenue Maurice Schumann, 59140 Dunkerque, France*
[b]*Service Commun de RMN, Université des Sciences et Technologies de Lille, rue Paul Langevin, 59655 Villeneuve d'Ascq cedex, France*

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**Abstract**—The 1,3-dipolar cycloaddition reaction of bipyridinium ylides with the electron deficient propynamido-β-cyclodextrin was studied. This reaction resulted in the regiospecific formation of a new class of fluorescent β-cyclodextrins. The new fluorophore systems were characterized spectroscopically by their absorption and emission maxima and their quantum yields.

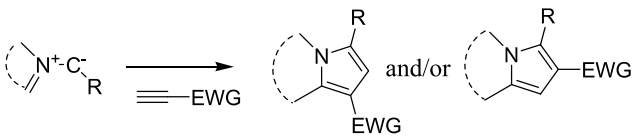

## 1. Introduction

The 1,3-dipolar [3+2] cycloaddition constitutes undoubtedly the most efficient, versatile and widely used method for the synthesis of nitrogen pentaatomic heterocycles.[1] In particular, cycloimmonium ylides undergo [3+2] dipolar cycloaddition reactions with various activated carbon–carbon multiple bonds and have proved to be the most attractive precursors for the preparation of indolizines derivatives (Scheme 1).[2] Indolizine ring systems are a common structural motif found in natural products which have received particular attention due to their wide range of biological and medicinal activity.[3] In addition to exhibiting a spectrum of pharmacological effects, synthetic indolizine derivatives and more specially those including a pyridine subunit, have also been recently studied extensively for their fluorescent properties and some of them already have practical applications as markers.[4]

During the last few years, the design and the construction of supramolecular based materials exhibiting fluorescent properties have and continue to pose a great challenge to synthetic chemists and materials scientists.[5] A survey of the literature shows that the most commonly employed supramolecular architecture is one in which a fluorophore and a receptor are covalently linked.[6] In particular, in recent years fluorescent cyclodextrins have generated considerable interest from the synthetic community as witnessed by recent articles dealing with their synthesis and emphasizing their sensory,[7] biochemical[8] and photoelectronic[9] properties. Consequently, the design and the synthesis of new fluorescent appended β-cyclodextrins are still the object of considerable attention.

As a part of our ongoing research program in the reactivity of cycloimmonium ylides[10] and with a view to synthesizing a new class of fluorescent β-cyclodextrins, we herein report the synthesis of pyridinoindolizine-βCD conjugates **9a–f** via 1,3-dipolar cycloaddition of the 6-propynamido-β-cyclodextrin **4** with various bipyridinium ylides **7a–f** (Scheme 2).

To the best of our knowledge, there is no report dealing with the 1,3-dipolar [3+2] cycloaddition reactions between cycloimmonium ylide and β-CD bearing an activated triple bond. The emission and fluorescence maxima as well the quantum yield of each new synthesized compounds **9a–f** are also reported.




**Scheme 1.**

*Keywords*: Cycloaddition; Ylides; β-Cyclodextrin; Fluorescence.
* Corresponding author. Tel.: +33-328658246; fax: +33-328658254; e-mail address: woisel@univ-littoral.fr

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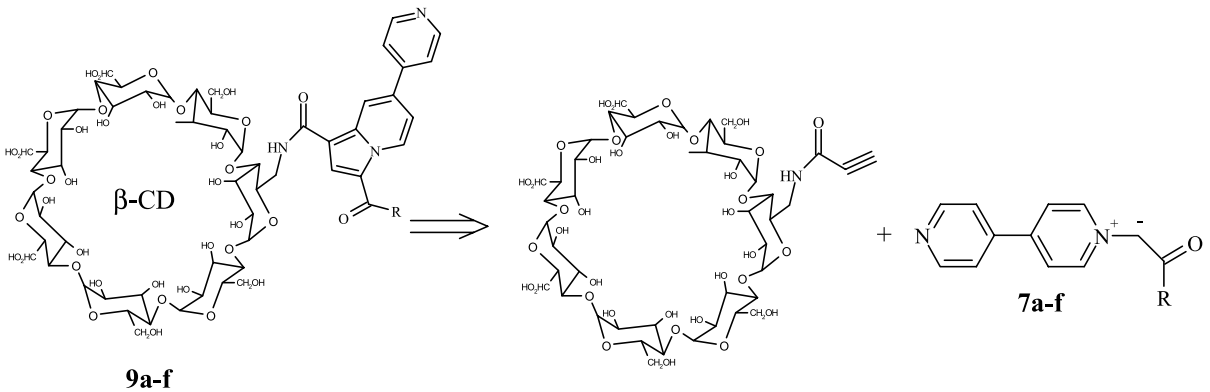



**9a** : R = $OC_2H_5$
**9b** : R= Ph
**9c** : R = 4-$CH_3$-$C_6H_4$
**9d** : R = 4-MeO-$C_6H_4$
**9e**: R = 4-Cl -$C_6H_4$
**9f**: R= 4-$NO_2$-$C_6H_4$

**Scheme 2.**

## 2. Results and discussion

### 2.1. Synthesis

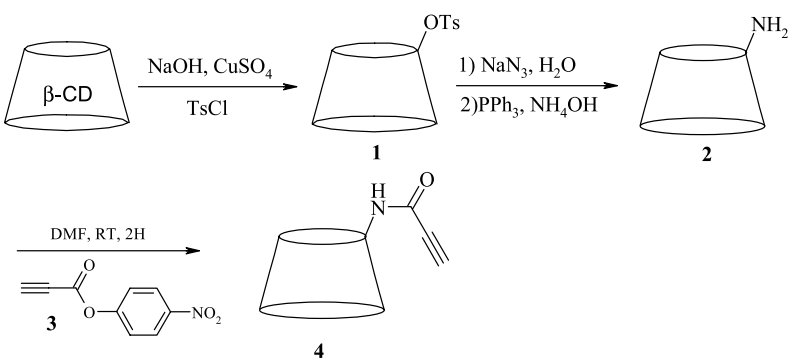
The starting material mono-6-deoxy-6-(*p*-tolylsulfonyl)-β-cyclodextrin **1** was synthesized as reported previously (Scheme 3).[11] The 6-amino-6-desoxy-β-cyclodextrin **2** was prepared in two step according to the method of Hamasaki.[12]

An early report for the preparation of the propynamido-β-cyclodextrin **4**[13] involved the reaction of **2** with the propyonic chloride under basic (NaOH) aqueous conditions (yield=71%). In the present work, the propynamido-β-cyclodextrin **4** was readily prepared in 80% yield by the condensation of **2** with the 4-nitrophenyl propynoate **3**,[14] which is easier to prepare and handle than propionic chloride, in DMF at room temperature. The crude product could be used for the subsequent preparation of the pyridinoindolizine core without further purification.

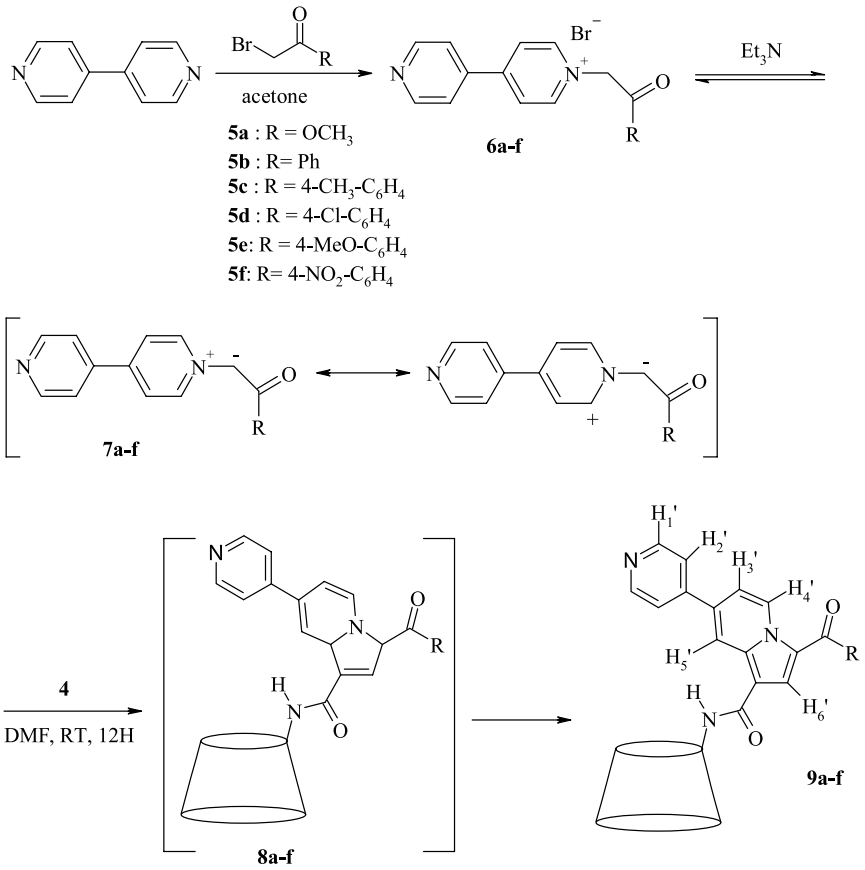
The 'salt method'[15] has been applied in order to obtain the bipyridinium ylides (Scheme 4). Thus, the commercially available 1,4-bipyridine quaternized with ω-brominated derivatives in boiling dry acetone furnished, after recrystallization (ethanol), the corresponding salts **6a**–**f**, in good yield.[16] Next, these salts, in the presence of the mild base triethylamine, form in situ, at room temperature in DMF, the red monosubstituted carbanions ylides **7a**–**f**. The ylides were then reacted with **4** to generate the primary cycloadducts **8a**–**f** which subsequently eliminate hydrogen to give the crude indolizine-βCD derivatives **9a**–**f**. It should be noted that this reaction must be carried out without light in order to prevent cleavage of the $C^-$–$N^+$bond. After 2 h, fluorescent β-CD were precipitated by addition of acetone (in all cases, the $^1H$ NMR spectra of the crude products reveal the presence of only one fluorescence derivative) and then successively purified by ion exchange chromatography on a CM-25 column and by gel filtration using Sephadex G-15.

### 2.2. Characterization

Evidence for the structures of new compounds was obtained from their elemental analysis and their spectroscopic data (MS, IR, $^1H$ and $^{13}C$ spectrometries). Complete spectral characterization of new compounds is provided in the experimental section. In all cases, the mass spectra




**Scheme 3.**




**Scheme 4.**

(ESMS+, $H_2O/CH_3OH$: 1:1, cone voltage: 110 V) showed a peak at $m/z$ +23 due to the $[M+Na]^+$ ion. $^1H$ NMR spectra of **9a–f** exhibited broad resonance signals in the regions expected for the glycon moiety. The $^{13}C$ data clearly indicated the presence of two C=O bonds ($\delta_{CONH}$ 160–165 ppm, $\delta_{COAr}$ 178–186 ppm and $\delta_{COOEt}$ 164.4) which were confirmed by the presence of two overlapping absorption bands (1592–1676 $cm^{-1}$) in the IR spectrum. These data are in good agreement with typical literature values.[2b,c] DEPT, $^1H$–$^1H$ COSY and $^1H$–$^{13}C$ experiments allowed the assignment of all the proton and carbon resonances of the glycon moiety. The relative position of the amido fragment of the pyridinoisoindole backbone was established through TOCSY[17] and NOESY experiments. Correlations between $H_5'/H_3'$ and $H_5'/H_4'$ were observed, while no correlations were detected between $H_5'$ and $H_6'$ on TOCSY spectra. NOESY spectra confirmed the position of $H_6'$ since in all cases no correlation was observed between $H_5'$ and $H_6'$.

Table 1 summarizes data collected to assess the optical properties of compounds **9a–f**. All new modified β-cyclodextrins **9**, except **9f**, fluoresce. Compound **9g** does not exhibit recordable fluorescence probably due to a well known quenching effect of the $NO_2$ group linked to the phenylic ring. While **9b–c** (R=aromatic) result in only a weak fluorescence ($\phi_f$<0.019), the fluorescence of compound **9a** (R=COOEt) displays a markedly improved quantum yield ($\phi_f$=0.51). This particularity observed for **9a** in respect to the other similar compounds **9b–e** could be only explained by a deep modification of its polarity (perhaps due to the partial inclusion of the fluorophore arm in the apolar β-CD cavity).

## 3. Conclusion

In conclusion, the present work provides the first insight into the [3+2] cycloaddition reactions between cycloimmonium ylides and β-cyclodextrin bearing a dipolarophile moiety. This procedure, starting from 4,4′-bipyridinium salts, has allowed the synthesis of six new fluorescent β-cyclodextrins. The fluorescent properties of each compound has also been proved. It is likely that this new class of fluorescent β-cyclodextrin will find application as chemical sensors, furthermore, we are also trying to extend this reaction in order to synthesize new fluorescent β-cyclodextrins dimers. In addition, in order to explain the regiospecificity observed, further theoretical investigation of the reaction pathway is currently underway.

## 4. Experimental

### 4.1. General

$^1H$ and $^{13}C$ NMR spectra were recorded with a Brüker AMX 400 spectrometer with tetramethylsilane as internal standard. Chemical shift values $\delta$ are reported in ppm and coupling constants ($J$) are in Hz. Mass spectra were measured using a Platform II Micromass Apparatus. FT-IR spectra were recorded using a Perkin–Elmer 2000

**Table 1**. Yields and optical properties of compounds **9a–f**

| Compound | Yield (%) | $\lambda_{max.abs}$ (nm) | $\lambda_{max.emis}$ (nm) | Stokes shift ($cm^{-1}$) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $\phi_f$ |
|---|---|---|---|---|---|---|
| **9a** | 35 | 257[a] | 442 | 4476 | 19,578[a] | 0.51[b] |
| | | 269[c] | 446 | 4901 | 17,459[c] | |
| **9b** | 27 | 274[c] | 454 | 3337 | 45,418[c] | 0.013[d] |
| **9c** | 21 | 273[c] | 450 | 3777 | 18,370[c] | 0.019[d] |
| **9d** | 18 | 275[c] | 456 | 3759 | 14,108[c] | 0.017[d] |
| **9e** | 28 | 276[c] | 468 | 4150 | 18,958[c] | 0.013[d] |
| **9f** | 21 | 269[c] | —[e] | —[e] | 21,350[c] | —[e] |

[a] In ethanol.
[b] Anthracene as reference ($\phi_f$=0.27).[15]
[c] In water, PH=7.2, 25 °C.
[d] Tryptophan as reference ($\phi_f$=0.14).[16]
[e] Too low to be measured accurately.

instrument. Absorbance and fluorescence spectra were recorded on a Perkin–Elmer LS50B, respectively. Melting points were obtained with a Reichert Thermopan apparatus and are uncorrected. All reagents were used as purchased unless otherwise stated. Cyclodextrin derivatives were dried under vacuum at 120 °C for 12 h. $6^A$-Amino-$6^A$-desoxy-β-cyclodextrin **2**,[9,10] 4-nitrophenyl-propynoate **3**[12] and 4-(4′-pyridyl)pyridinium salts **6a–f**16 were prepared as reported previously.

**4.1.1. $6^A$-Deoxy-$6^A$-propynamido-β-cyclodextrin 4.** The 4-nitrophenylpropynoate **3** (0.007 g, 0.35 mmol) was added at room temperature under argon to a solution of $6^A$-amino-$6^A$-desoxy-β-cyclodextrin **2** (0.4 g, 0.35 mmol) in dry DMF (10 mL). The mixture was stirred for 2 h before it was poured into acetone (80 mL) dropwise. The resultant precipitate was collected and washed with acetone (20 mL) and diethyl ether (20 mL). $^1H$ and $^{13}C$ NMR spectra of this compound were consistent with literature data.[11]

**4.1.2. General procedure for reactions of the $6^A$-deoxy-$6^A$-propynamido-β-cyclodextrin 4 with 4-(4′-pyridyl)-pyridinium salts 6a–f.** A solution of freshly distilled $Et_3N$ (0.012 mmol) in DMF (0.5 mL) was added to a stirred solution of **6a–f** (0.085 mmol) and **4** (0.1 g, 0.085 mmol) in DMF (1 mL) at room temperature at O °C under Ar. The mixture was allowed to warm to room temperature, in the absence of light, over 12 h. The reaction was poured in acetone (50 mL) and the resultant precipitate was passed through a CM-25 column by eluting with water. The fractions containing the fluorescent β-cyclodextrin were combined, concentrated in vacuo. Finally, the mixture was applied to gel filtration using Sephadex G-15 to give **9a–f** as fine yellow powder.

**4.1.3. *N*-($6^A$-Deoxy-β-cyclodextrin-$6^A$-yl)-1-(aminocarbonyl)-3-(ethoxycarbonyl)-7-pyridin-4-ylindolizine 9a.** $^1H$ NMR (DMSO-$d_6$, δ, *J*, Hz): 1.38 (3H, t, $-CH_3$), 3.18–3.98 (42H, m, *H*-2, *H*-4, *H*-3, *H*-5, *H*-$6^{A,B}$), 4.38–4.62 (8H, m, $-CH_2-$, $-OH_6$), 4.81–5.05 (7H, m, *H*-1), 5.59–6.92 (14H, m, $-OH_2$, $-OH_3$), 7.61 (1H, dd, *J*=2.0, 7.7 Hz, $H_3'$), 7.80 (2H, d, *J*=5.9 Hz, $H_2'$), 8.12 (1H, m, N*H*), 8.27 (1H, s, $H_6'$), 8.71 (2H, d, *J*=6.0 Hz, $H_1'$), 8.87 (1H, s, $H_5'$), 9.48 (1H, d, *J*=7.8 Hz, $H_4'$); $^{13}C$ NMR (DMSO-$d_6$, δ): 15.27 ($-CH_3$), 60.44, 60.77, 60.99 ($C_6$), 60.79 ($-CH_2$), 70.72, 73.07, 73.27, 73.90 ($C_2$, $C_3$, $C_5$), 81.96, 82.28, 82.51, 84.70 ($C_4$), 102.78, 103.04 ($C_1$), 113.59 ($C_3'$), 117.97 ($C_5'$), 121.61 ($C_2'$), 122.59 ($C_6'$), 128.34 ($C_4'$), 151.42 ($C_1'$), 161.35 (NH–*C*O), 164.38 (*C*O–OEt); IR (KBr, $cm^{-1}$): 3398 (OH free, NH), 2918 (C–H strech), 1676 (CO); *m*/*z* (%): 1449 (M+Na, 100), 1427 (M+1, 25). Anal. calcd for $C_{59}H_{83}N_3O_{37}\cdot 6H_2O$: C, 46.18; H, 6.24; N, 2.74. Found: C, 46.31; H, 6.54; N, 2.95.

**4.1.4. *N*-($6^A$-Deoxy-β-cyclodextrin-$6^A$-yl)-1-(aminocarbonyl)-3-benzoyl-7-pyridin-4-ylindolizine 9b.** $^1H$ NMR (DMSO-$d_6$, δ, *J*, Hz): 3.25–3.90 (42H, m, *H*-2, *H*-4, *H*-3, *H*-5, *H*-$6^{A,B}$), 4.28–4.58 (6H, m, $-OH_6$), 4.84–5.01 (7H, m, *H*-1), 5.63–6.08 (14H, m, $-OH_2$, $-OH_3$), 7.52–7.76 (4H, m, $H_3'$, *H meta*/*CO*, *H para*/*CO*), 7.92 (2H, d, *J*=8.3 Hz, *H ortho*/*CO*), 7.94 (2H, d, *J*=5.9 Hz, $H_2'$), 8.21 (1H, s, $H_6'$), 8.39 (1H, m, N*H*), 8.73 (2H, d, *J*=5.9 Hz, $H_1'$), 9.02 (1H, s, $H_5'$), 9.92 (1H, d, *J*=7.3 Hz, $H_4'$); $^{13}C$ NMR (DMSO-$d_6$, δ): 60.82, 60.84 ($C_6$), 70.97, 72.77, 73.17, 73.99 ($C_2$, $C_3$, $C_5$), 81.95, 82.27, 82.50, 82.73, 85.13 ($C_4$), 102.72, 103.11 ($C_1$), 113.82 ($C_3'$), 117.35 ($C_5'$), 121.24 ($C_2'$), 126.43 ($C_6'$), 128.66 ($C_4'$), 128.80 ($C_8'$), 129.31 ($C_7'$), 131.83 ($C_9'$), 150.84 ($C_1'$), 164.24 (NH–*C*O), 185.41 (*C*O-φ); IR (KBr, $cm^{-1}$) 3399 (OH free, NH), 2919 (C–H strech), 1602 (CO); *m*/*z* (%): 1481 (M+Na,100), 1459 (M+1, 22). Anal. calcd for $C_{63}H_{83}N_3O_{36}\cdot 5H_2O$: C,48.87; H, 6.05; N, 2.71. Found: C, 49.21; H, 6.23; N, 3.02.

**4.1.5. *N*-($6^A$-Deoxy-β-cyclodextrin-$6^A$-yl)-1-(aminocarbonyl)-3-(4-methylbenzoyl)-7-pyridin-4-ylindolizine 9c.** $^1H$ NMR (DMSO-$d_6$, δ, *J*, Hz): 2.44 (3H, s, $-CH_3$), 3.13–3.84 (42H, m, *H*-2, *H*-3, *H*-4, *H*-5, *H*-$6^{A,B}$), 4.38–4.58 (6H, m, $-OH_6$), 4.78–4.97 (7H, m, *H*-1), 5.58–6.01 (14H, m, $-OH_2$, $OH_3$), 7.14 (2H, d, *J*=8.8 Hz, *H meta*/*CO*), 7.76 (1H, dd, *J*=1.9, 7.4 Hz, $H_3'$), 7.85 (2H, d, *J*=5.8 Hz, $H_2'$), 7.89 (2H, d, *J*=8.8 Hz, *H ortho*/CO), 8.15 (1H, s, $H_6'$), 8.34 (1H, m, N*H*), 8.73 (2H, d, *J*=5.7 Hz, $H_1'$), 8.95 (1H, s, $H_5'$), 9.84 (1H, d, *J*=7.4 Hz, $H_4'$); $^{13}C$ NMR (DMSO-$d_6$, δ): 21.90 ($-CH_3$), 60.57, 60.86 ($C_6$), 71.23, 73.19, 73.32, 73.92, 74.03 ($C_2$, $C_3$, $C_5$), 82.10, 82.47, 82.54, 85.05 ($C_4$), 102.71, 102.86, 103.10 ($C_1$), 114.60 ($C_3'$), 117.85 ($C_5'$), 121.65 ($C_2'$), 126.68 ($C_6'$), 129.32 ($C_4'$), 130.07 ($C_7'$), 151.48 ($C_1'$), 164.30 (NH–*C*O), 185.23 (*C*O-φ); IR (KBr, $cm^{-1}$): 3402 (OH free, NH), 2918 (C–H strech), 1624 (CO); *m*/*z* (%): 1495 (M+Na, 100); 1473 (M+1, 20). Anal. calcd for $C_{64}H_{85}N_3O_{36}\cdot 5H_2O$: C, 49.20; H, 6.13; N, 2.69. Found: C, 49.46; H, 6.20; N, 2.72.

**4.1.6. *N*-($6^A$-Deoxy-β-cyclodextrin-$6^A$-yl)-1-(aminocarbonyl)-3-(4-methoxybenzoyl)-7-pyridin-4-ylindolizine 9d.** $^1H$ NMR (DMSO-$d_6$, δ, *J*, Hz): 3.03–3.88 (42H, m, *H*-2,

*H*-3, *H*-4, *H*-5, *H*-6$^{A,B}$), 3.95 (3H, s, –OC*H*$_3$), 4.33–4.59 (6H, m, –O*H*$_6$), 4.78–4.97 (7H, m, *H*-1), 5.54–6.07 (14H, m, –O*H*$_2$, *OH*$_3$), 7.14 (2H, d, *J*=8.7 Hz, *H meta*/*CO*), 7.73 (1H, d, *J*=7.4 Hz, *H*$_3'$), 7.89 (2H,d, *J*=8.66 Hz, *H ortho*/*CO*), 8.21 (1H, s, *H*$_6'$), 8.23 (2H, d, *J*=6.1 Hz, *H*$_2'$), 8.40 (m, 1H, N*H*), 8.88 (2H, d, *J*=6.1 Hz, *H*$_1'$), 9.03 (1H, s, *H*$_5'$), 9.82 (1H, d, *J*=7.38 Hz, *H*$_4'$); $^{13}$C NMR (DMSO-*d*$_6$, 100 MHz) $\delta$ ppm: 56.39 (–O*C*H$_3$), 60.54, 60.75, 60.93 (*C*$_6$), 71.05, 72.23–74.34 (*C*$_2$, *C*$_3$, *C*$_5$), 82.02–82.70, 84.96 (*C*$_4$), 102.62, 102.79, 103.05 (*C*$_1$), 113.76 (*C*$_3'$), 114.77 (*C*$_8'$), 119.36 (*C*$_5$), 123.45 (*C*$_2'$), 126.22 (*C*$_6'$), 129.32 (*C*$_4'$), 132.30 (*C*$_7'$), 146.52 (*C*$_1'$), 163.19 (NH–*C*O), 184.52 (*C*O-φ); IR(KBr, cm$^{-1}$) 3399 (OH free, NH), 2916 (C–H strech), 1618 (CO); *m*/*z* (%): 1511 (M+Na, 100), 1489 (M+H, 20). Anal. calcd for $C_{64}H_{85}N_3O_{37}\cdot 6H_2O$: C, 48.15; H, 6.12; N, 2.63. Found: C, 48.41; H, 6.25; N, 2.72.

**4.1.7. *N*-(6$^{A}$-Deoxy-β-cyclodextrin-6$^{A}$-yl)-1-(aminocarbonyl)-3-(4-chlorobenzoyl)-7-pyridin-4-ylindolizine 9e.** $^1$H NMR (DMSO-*d*$_6$, δ, *J*, Hz): 3.23–3.90 (42H, m, *H*-2, *H*-4 *H*-3, *H*-5, *H*-6$^{A,B}$), 4.20–4.57 (6H, m, –O*H*$_6$), 4.76–4.94 (7H, m, *H*-1), 5.51–5.99 (14H, m, –O*H*$_2$, *OH*$_3$), 7.64 (2H, d, *J*=8.5 Hz, *H meta*/*CO*), 7.70 (1H, dd, *J*=7.4 Hz, *H*$_3'$), 7.81 (2H, d, *J*=8.5 Hz, *H ortho*/CO), 7.83 (2H, d, *J*=6.1 Hz, *H*$_2'$), 8.15 (1H, s, *H*$_6'$), 8.26 (1H, m, N*H*), 8.7 (2H, d, *J*=6.1 Hz, *H*$_1'$), 8.94 (1H, s, *H*$_5'$), 9.87 (1H, d, *J*=7.5 Hz, *H*$_4'$); $^{13}$C NMR (DMSO-*d*$_6$, δ): 60.42, 60.53, 60.82 (*C*$_6$), 71.11, 72.76–74.04 (*C*$_2$, *C*$_3$, *C*$_5$), 81.92, 82.05, 82.10, 82.48, 82.61, 82.87, 85.07 (*C*$_4$), 102.71, 102.86, 103.12 (*C*$_1$), 114.43 (*C*$_3'$), 117.86 (*C*$_5'$), 121.69 (*C*$_2'$), 127.06 (*C*$_6'$), 129.41 (*C*$_4'$), 129.46 (*C*$_8'$), 131.75 (*C*$_7'$), 151.49 (*C*$_1'$), 164.22 (NH–*C*O), 184.21 (*C*O-φ); IR (KBr, cm$^{-1}$): 3397 (OH free, NH), 2918 (C–H strech), 1601 (CO); *m*/*z* (%): 1516 (M+Na, 32), 1514 (M+Na−2). Anal. calcd for $C_{63}H_{82}ClN_3O_{36}\cdot 5H_2O$: C, 47.81; H, 5.86; N, 2.65. Found: C, 48.02; H, 5.99; N, 2.84.

**4.1.8. *N*-(6$^{A}$-Deoxy-β-cyclodextrin-6$^{A}$-yl)-1-(aminocarbonyl)-3-(4-nitrobenzoyl)-7-pyridin-4-ylindolizine 9f.** $^1$H NMR (DMSO-*d*$_6$, δ, *J*, Hz): 3.21–4.04 (42H, m, *H*-2, *H*-3, *H*-4, *H*-5, *H*-6$^{A,B}$), 4.42–4.71 (6H, m, –O*H*$_6$), 4.80–5.06 (7H, m, *H*-1), 5.72–6.01 (14H, m, –*OH*$_2$, –*OH*$_3$), 7.83 (1H, d, *J*=7.5 Hz, *H*$_3'$), 7.92 (2H, d, *J*=5.8 Hz, *H*$_2'$), 8.14 (2H, d, *J*=8.5 Hz, *H meta*/*CO*), 8.22 (1H, s, *H*$_6'$), 8.47 (2H, d, *J*=8.5 Hz, *H ortho*/*CO*), 8.40 (1H, m, N*H*), 8.80 (2H, d, *J*=5.8 Hz, *H*$_1'$), 9.02 (1H, s, *H*$_5'$), 9.98 (1H, d, *J*=7.5 Hz, *H*$_4'$); $^{13}$C NMR (DMSO-*d*$_6$, δ): 59.88, 60.42 (*C*$_6$), 73.02, 73.56, 74.34 (*C*$_2$, *C*$_3$, *C*$_5$), 80.53, 80.98, 81.37, 82.42 (*C*$_4$), 102.09, 102.38, 103.01 (*C*$_1$), 115.39 (*C*$_3'$), 119.02 (*C*$_5'$), 123.73 (*C*$_2'$), 124.51 (*C*$_6'$), 129.17 (*C*$_8'$), 130.82 (*C*$_4'$), 131.33 (*C*$_7'$), 151.53 (*C*$_1'$), 160.48 (NH–*C*O), 178.57 (*C*O-φ); IR (KBr, cm$^{-1}$): 3402 (OH free, NH), 2915 (C–H strech), 1649 (CO); *m*/*z* (%): 1526 (M+Na, 100), 1504 (M+1, 30). Anal. calcd for $C_{63}H_{82}N_4O_{38}\cdot 5H_2O$: C, 47.49; H, 5.82; N, 3.52. Found: C, 47.76; H, 5.96; N, 3.61.

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