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Synthesis of new [2]rotaxane including a macrocyclic receptor and a photochromic unit

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Abstract

The novel photochromic [2]rotaxane based on chromene molecule introduced into a crown-containing macrocyclic receptor was synthesized. The photochemical properties of rotaxane could be modified by the complexation of the crown ether moiety.

Keywords: [2]Rotaxane; Chromene; Naphthopyran; Crown ether

The design and the synthesis of organic molecular materials in which structure and macroscopic properties can be controlled by external triggers, are of major importance in emerging optoelectronic and nanotechnologies.[1] In this context, the photochromic crown compounds which combine properties of ion-selective binding and photo-induced switching are of particular interest.[2] Furthermore, a number of crown-containing [2]rotaxanes with salt-binding properties were developed.[3] The incorporation of a photochromic unit into such molecule can allow control of its dynamics by color changing because of metal cations and anions binding. In the present work, we report a convenient synthetic approach to introduce chromene molecules into crown-containing macrocyclic receptor with a formation of [2]rotaxane possessing photochromic metal-ion sensitive properties.

The aim of the present study is a rotaxane including chromene and crown units: the motions of such system have good perspectives to be controlled by metallocomplexation between crown ether and the merocyanine form of a chromene under the light irradiation (Fig. 1). The

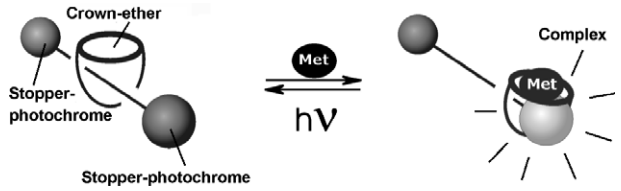

Fig. 1. New rotaxane which can be controlled by metallocomplexation.

new targeted [2]rotaxane system consists of a binaphthopyran light-sensitive axle **1** and the macrocyclic receptor **2**[3] (Scheme 1), the last one was synthesized by Smith and co-workers. The constituents of both units are rather convenient starting materials for the synthesis. 18-Dibenzo-crown-6 ether is a reasonable price compound; hydroxynaphthopyrans can be easily obtained[4] through the condensation of commercially available 1,1-diphenyl-propyn-1-ol with hydroxynaphthalene.

Computer modeling was used to predict the conformation of the receptor-wheels and the chromene-axles. It demonstrated that the dimensions of the stoppers efficiently prevent the axles to escape from the wheels and at the same time they are suitable to allow a complexation. Modeling study was realized with Ampac 8.15 using semi-empirical AM1 force field[5] (Fig. 2).

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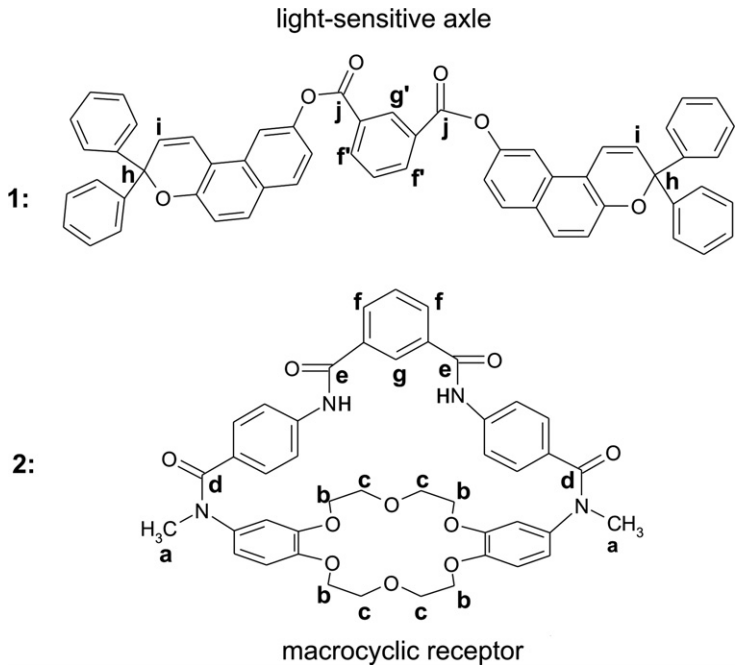


Scheme 1. Structures of the light-sensitive axle **1** and the macrocyclic receptor **2**.

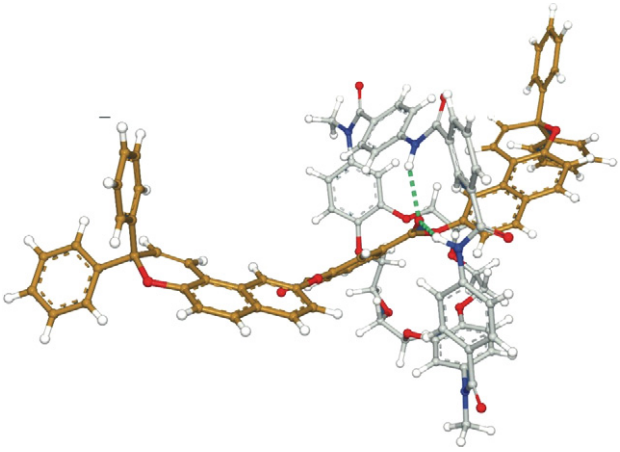
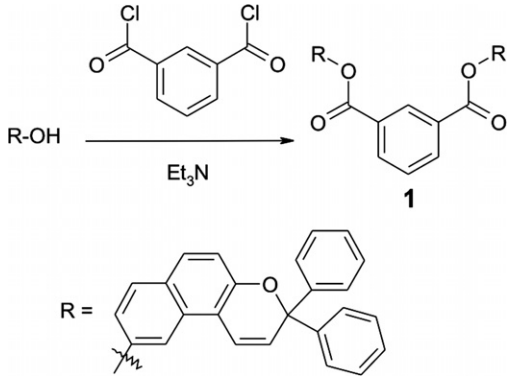


Fig. 2. Modeled conformation of rotaxane **3**.



Scheme 2. Synthesis of binaphthopyran unit **1**.

At the beginning of our study, the synthesis of free chromene-axle was accomplished to confirm its photochemical properties. Binaphthopyran unit **1** was obtained[6] by the condensation of 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]-pyran with isophthaloyl dichloride (Scheme 2) in 98% yield.

The novel compound showed absorbance in the UV spectra region but it was transparent in the visible spectra region (Fig. 3). After the irradiation of UV light[7] during

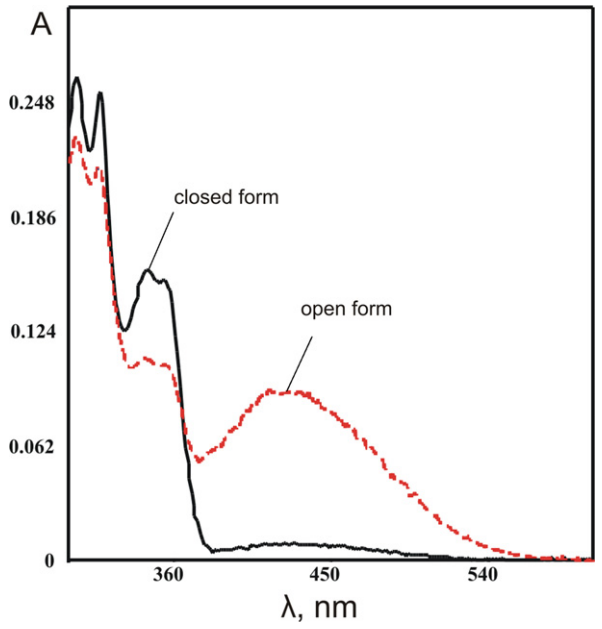
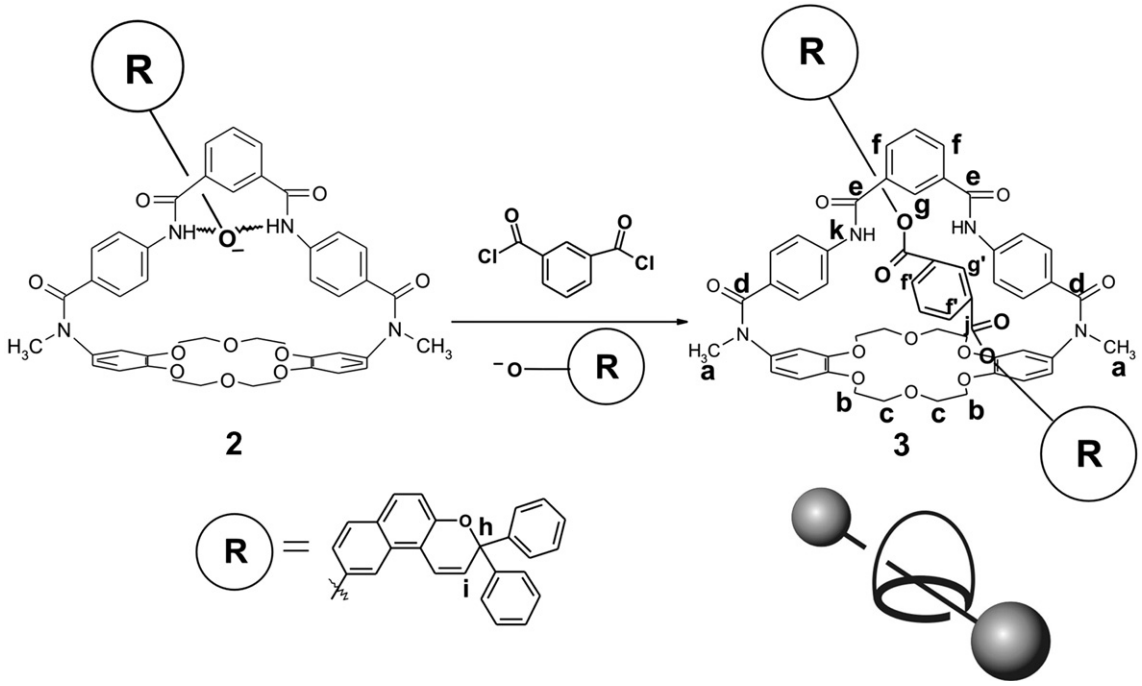


Fig. 3. Absorption spectra of **1** (acetonitrile solutions, $C = 0.84 \times 10^{-5}$ M) under dark condition (closed form) and after UV-irradiation during 1 min (open form.)



Scheme 3. Formation of rotaxane **3**.

10 s, the absorbance of closed form of chromene decreased, while a new absorption peak was found in 400 nm region indicating that the pyran moiety isomerizes to its merocyanine form. Binaphthopyran acetonitrile solution changed rapidly from transparent to orange saturated color.

Wheel constituent **2** for [2]rotaxane was synthesized according to the procedure described by Smith and coworkers.[3] For [2]rotaxane synthesis, we used the anion-templated methodology recently introduced by Vögtle.[8] Macrocycle **2** (1 M equiv) was treated with 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran (2 M equiv) and tenfold excess of K_2CO_3 at 0 °C in THF–DMF mixture (5:1) for 15–30 min. The bulky complex anion was formed due to the hydrogen bonding between the NH-groups of isophthalamide part of macrocycle and O^- of naphtholate anion (Scheme 3).

This molecular recognition was the driving force for the formation of [2]rotaxane **3**. Upon single addition of isophthaloyl dichloride (1 M equiv), the bulky anion was alkylated through the cavity of the macrocycle. Formed chloromethyl ether then reacted in situ with a second potassium naphtholate anion producing the target [2]rotaxane **3**. Formation of the rotaxane competed with the formation of the free axles. Targeted rotaxane **3** was obtained[9] in 19% yield by thin-layer chromatography. The independent spot of compound revealed photochromic properties and was different from the spots of starting reagents and free axels.

The formation of the rotaxane was confirmed by a comparative analysis of NMR spectra of compounds **1**, **2** and **3**. The signals of **a**, **b**, **c**, and **h**-carbons can be observed in compound **3** in 20–90 ppm ^{13}C NMR spectra region (Fig. 4).

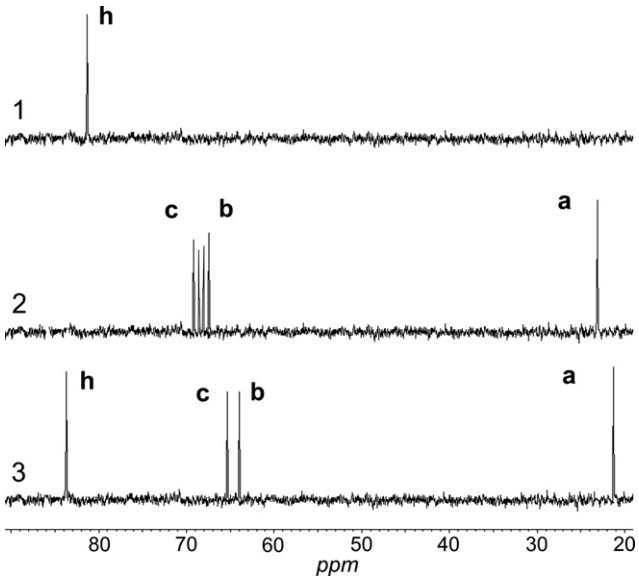


Fig. 4. Partial ^{13}C NMR (acetone-d_6, 250 MHz, 273 K) spectra of **1**, **2**, and **3**. Peak labels are defined in Scheme 1.

The presence of all characteristic signals of both wheel and axle ester carbons **d**, **e**, and **j** was observed in 160–190 ppm region of ^{13}C NMR spectra of targeted rotaxane **3** (Fig. 5). The ^1H and ^{13}C chemical shifts of key points of rotaxane are collected in Table 1.

We further studied the binding properties of the rotaxane. The addition of tenfold excess of Na^+ to a solution of **3** in acetonitrile induced changes in photochemical behavior. The increase in absorbance, the broadening of the spectra signal, and the slight shift of λ_{max} of the open form were seen (Fig. 6). At the same time, the absorbance

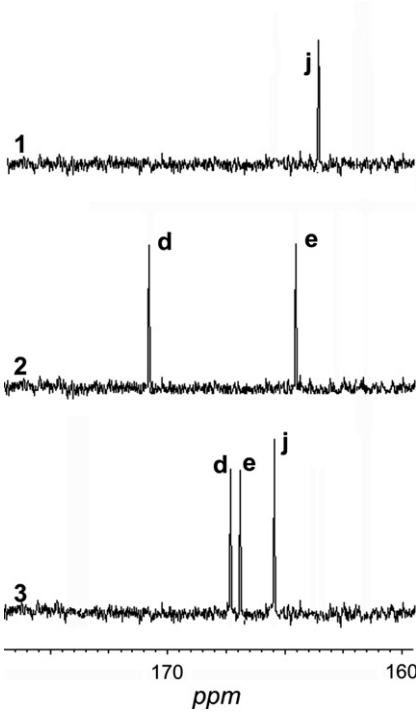


Fig. 5. Partial ^{13}C NMR (acetone-d_6, 250 MHz, 273 K) spectra of **1**, **2** and **3**. Peak labels are defined in Schemes 1 and 3.

Table 1
^{1}H, ^{13}C assignments for rotaxane **3** in C_3D_6O

Position	δ_H (ppm)	δ_C (ppm)
a	1.84	20.1
b	3.50–3.49	63.9
c	3.93–3.91	65.1
d	—	167.4
e	—	166.9
f	8.23	131.7
f′	8.32	131.2
g,g′	8.72	125.9,129.0
h	—	83.5
i	6.23	130.9
j	—	165.3
k	7.92	—

of closed form of chromene in **3**–Na^+ system is decreased. These results suggest that the optical properties of compound **3** could be modified by the complexation of the crown ether moiety.

In summary, the novel photochromic [2]rotaxane based on chromene molecule introduced into macrocyclic receptor was efficiently synthesized. The binding of Na^+ showed that the optical properties of rotaxane could be modified by the complexation of the crown ether moiety. Further experiments are in progress to gain more details about the ion-selective binding properties of this molecule. New [2]rotaxane could be a good basis for the creation of artificial molecular machines with salt-dependent properties.

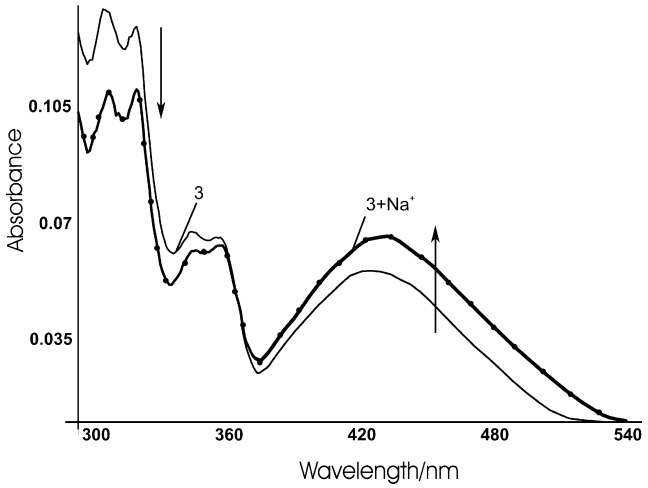


Fig. 6. Absorption-spectral changes of open forms of **3** (acetonitrile solutions, $C = 0.84 \times 10^{-5}$ M) and **3**–Na^+ system after UV-irradiation during 2 min.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.110.

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6. *Bis-(3,3-biphenyl-3H*-benzo[*f*]chromene-9-yl) isophthalic acid ether (binaphtopyrane unit 1): A sample of 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran (30.1 mg, 0.086 mmol) was dissolved in 6 mL of anhydrous THF–DMF mixture (5:1). The solution was cooled to 0 °C, then isophthaloyl dichloride (8.7 mg, 0.043 mmol) and triethylamine (0.012 mL, 0.086 mmol) were added. The mixture was stirred at room temperature for 12 h, at which time the starting material was consumed according to TLC analysis. The reaction was extracted with EtOAc (3×15 mL), washed with H_2O (2×20 mL), brine (2×20 mL), dried over Mg_2SO_4, and purified by column chromatography with dichloromethane–methanol (100:0→90:10) to give 98% of binaphtopyrane **1** (34.9 mg, 0.042 mmol). ^{1}H NMR (acetone, ppm): δ 9.12 (s, 1H, H-2, COC_6H_3CO), 8.50 (dd, $J = 7.74$, 1.74, 2H, H-4, H-6, COC_6H_3CO), 7.86–7.82 (m, 7H, 4H-4, C_6H_5, H-5, COC_6H_3CO, 2H-7), 7.50–7.47 (m, 8H, 4H-5, 4H-3, C_6H_5), 7.40–7.20 (m, 18H, 4H-6, 4H-2, C_6H_5, 2H-1, 2H-5, 2H-6, 2H-8, 2H-10), 6.26 (d, $J = 9.95$, 2H, H-2). ^{13}C NMR (acetone, ppm): δ 163.4 (2C, CO), 150.2 (2C, C-4a), 148.4 (2C, C-9), 143.6 (4C, C-1, C_6H_5), 134.0 (2C, C-10a), 130.8 (1C, C-2, COC_6H_3CO), 129.5 (2C, C-6), 129.3 (2C, C-4, C-6, COC_6H_3CO), 129.1 (2C, C-7), 128.7 (2C, C-3, C-1, COC_6H_3CO), 128.1 (1C, C-5, COC_6H_3CO), 127.1 (8C, 4C-3, 4C-5, C_6H_5), 126.9 (2C, C-2), 126.6 (4C, 4C-4, C_6H_5), 126.5 (2C, C-6a), 125.9 (8C, 4C-2, 4C-6, C_6H_5), 118.3 (2C, C-8), 117.6 (2C, C-1), 117.3 (2C, C-5), 113.1 (2C, C-10b), 111.9 (2C, C-10), 81.7 (2C, C-3). TOF MS ES+: 832 $[M+H]^+$.
7. Photochemical measures were performed in acetonitrile solutions ($C = 0.84 \times 10^{-5}$ M) of spectrometric grade at 20°. The analysis cell was placed in a sample chamber in *Cary 50 Scan* spectrophotometer. Solutions were stirred continuously during the experiments. An *Oriel-150-W-high-pressure* Xe lamp was used for irradiation, 520 mW/cm^2.
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9. *Rotaxane* **3**: K_2CO_3 (14.1 mg, 0.116 mmol) was added to a solution of macrobicycle **2** (22.7 mg, 0.029 mmol) and 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran (20.3 mg, 0.058 mmol) in 18 mL of anhydrous THF–DMF mixture (5:1). The solution was cooled to 0 °C, then solid isophthaloyl dichloride (5.9 mg, 0.029 mmol) was added and the reaction was stirred for 4 days at room temperature. After the removal of the solvent, the residue was purified on silica column by dichloromethane–methanol (100:0→90:10) to remove the binaphtopyrane unit **1** and unreacted hydroxychromene to obtain 19% of rotaxane **3** (8.9 mg, 0.006 mmol). ^{1}H NMR (acetone, ppm; A-Axle, M-Macrocycle constituents): δ 8.72 (s, 2H, H-2, COC_6H_3CO, A); H-3, COC_6H_3CO, M, 8.32 (d, $J = 7.74$, 2H, H-4, H-6, COC_6H_3CO, A), 8.23 (d, $J = 7.74$, 2H, H-5, H-1, COC_6H_3CO, M), 7.92 (s, 2H, 2NH, M), 7.81–7.64 (m, 10H, 4H-4, C_6H_5, H-5, COC_6H_3CO, 2H-1, 2H-7, A; H-6, COC_6H_3CO, M), 7.44–7.13 (m, 38H, 4H-6, 4H-2, 4H-5, 4H-3, C_6H_5, 2H-5, 2H-6, 2H-8, 2H-10, A; H-3, H-13, C_6H_3, H-4, H-12, H-1, H-15, C_6H_3, 2H-2, 2H-6, 2H-3, 2H-5, C_6H_4, M), 6.23 (d, $J = 9.95$, 2H, 2H, H-2, A), 3.93-3.91 (m, 8H, $2CH_2$-18, 9, 20, 7, M), 3.50-3.49 (m, 8H, $2CH_2$-17, 10, 21, 6, M), 1.84 (s, 6H, $2CH_3$, M). ^{13}C NMR, (acetone, ppm; A-Axle, M-Macrocycle constituents): δ 167.4 (2C, 2*C*ONCH$_3$, M), 166.9 (2C, 2*C*ONH, M), 165.3 (2C, *C*O, A), 152.3 (2C, C-4a, A), 151.1 (2C, C-9, A), 149.4 (2C, C-22a, C-15a, M), 146.1 (4C, 4C-1, C_6H_5, A), 135.7 (2C, C-4a, C-11a, C_6H_3, M), 135.6 (2C, 2C-4, C_6H_4, M), 135.2 (2C, C-2, C-14 C_6H_3, M), 132.5 (2C, C-10a, A), 132.3 (2C, C-2, C-4, COC_6H_3CO, M), 131.9 (2C, 2C-1, C_6H_4, M), 131.7 (2C, C-5, C-1, COC_6H_3CO, M), 131.4 (2C, C-6, A), 131.2 (2C, C-4, C-6, COC_6H_3CO, A), 130.9 (2C, C-2, A), 130.4 (2C, C-7, A), 129.6 (4C, 2C-2, 2C-6, C_6H_4, M), 129.4 (1C, C-6, COC_6H_3CO, M), 129.2 (8C, 4C-3, 4C-5, C_6H_5, A), 129.0 (1C, C-2, COC_6H_3CO, A), 128.7 (2C, C-3, C-1, COC_6H_3CO, A), 128.6 (4C, 4C-4, C_6H_5, A), 127.9 (1C, C-5, COC_6H_3CO, A), 127.8 (8C, 4C-2, 4C-6, C_6H_5, A), 126.7 (2C, C-6a, A), 125.9 (1C, C-3, COC_6H_3CO, M), 120.4 (2C, C-4, C-12, C_6H_3, M), 119.6 (2C, C-8, A), 119.3 (2C, C-1, A), 116.4 (2C, C-5, A), 115.5 (2C, C-10b, A), 114.8 (2C, C-10, A), 114.7 (2C, C-3, C-13, C_6H_3, M), 114.4 (4C, 2C-3, 2C-5, C_6H_4, M), 102.1 (2C, C-1, C-15, C_6H_3, M), 83.5 (2C, C-3, A), 65.1 (4C, C-18, C-9, C-20, C-7, CH_2, M), 63.9 (4C, C-21, C-6, C-17, C-10, CH_2, M), 20.1 (2C, 2*C*H$_3$, M). TOF MS ES+: 1278 $[M+H]^+$; 769 $[M+H]^+$, 786 $[M+NH_4]^+$ (ring—H_2O).