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Synthesis, Structures, and Solid State Self-Assemblies of Formyl and Acetyl Substituted Triptycenes and Their Derivatives

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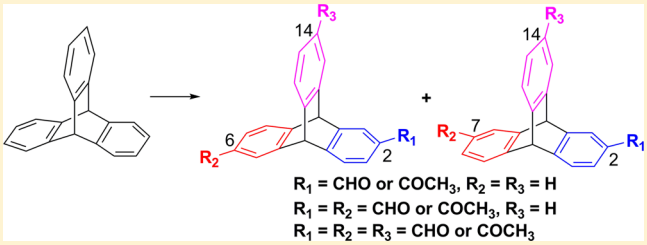
Supporting Information

ABSTRACT: Starting from triptycene, 2-, (2,6- or 2,7-)di-, and (2,6,14- or 2,7,14-)triformyl or acetyl substituted triptycenes were selectively synthesized. The derivatization of the formyl or acetyl substituted triptycenes was then investigated. Consequently, it was found that the formyl-substituted triptycenes could be transformed into cyano substituted triptycene derivatives by the aldoxime formation and dehydration. Acetoxyl- and acetamino-substituted triptycenes were synthesized by Baeyer–Villiger oxidation of acetyl-substituted triptycenes and Beckmann rearrangement of acetyl-oxime triptycenes, respectively. Deacetylation of triacetaminotriptycene provided an alternative way to the synthesis of triaminotriptycene. In addition, 2-ethynyltriptycene could be conveniently synthesized by Corey–Fuchs reaction of 2-formyltriptycene, and 1,3,5-tritriptycenebenzene was obtained in high yield by the dehydration cyclotrimerization of 2-acetyltriptycene. The different functionalized triptycene derivatives and their regioisomers were well characterized by the FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra, and single crystal X-ray analyses. Moreover, it was also found that 2,6,14-triacetaminotriptycene with the three amide groups paralleled to their connected aromatic rings could self-assemble into a 2D layer with porous structure, and further 3D microporous architecture by the hydrogen-bond network in the solid state.



INTRODUCTION

In the past decade, triptycene derivatives with unique three-dimensional rigid structures have attracted increasing interest for their more and more applications in supramolecular chemistry,[1] synthetic molecular machines,[2] materials science,[3] and other research areas.[4] Undoubtedly, the triptycene derivatives with different functional groups are always the basis of the practical applications, and they can be usually synthesized by the direct addition of benzyne or aryne to substituted anthracenes.[5] However, this method does not work to the synthesis of some triptycene derivatives for the difficultly available aryne precursors and the anthracene derivatives. Instead, the selective reactions and the further derivatization of simple triptycene become an efficient and alternative route to the synthesis of triptycene derivatives with specific functional groups. For example, it was found that the selective nitration of triptycene provided 2,6,14-trinitrotriptycene and 2,7,14-trinitrotriptycene, which could be easily transformed to other 2,6,14- and 2,7,14-trisubstituted triptycene derivatives containing amino, hydroxyl, bromo, and iodo groups, respectively.[6] These trisubstituted triptycenes have been utilized as useful building blocks for the construction of nanosized molecular cages[7] and polymeric materials.[8]

It was known that acyl groups, especially formyl and acetyl groups, are a kind of important functional groups, and they can be transformed into various other useful organic functional groups. Although the selective introduction of the formyl and acetyl groups to triptycene skeleton is very important and attractive, few reports are known about them.[9] Especially, except the synthesis of 2-acetyltriptycene reported by Paget and co-workers,[9a] no pure regioisomers of (2,6- or 2,7-)di-, (2,6,14- or 2,7,14-)triformyl and acetyl substituted triptycene derivatives were synthesized and well characterized so far. Moreover, reports on the derivatization of formyl and acetyl substituted triptycenes are very limited as well. These results subsequently prevented the practical applications of these triptycene derivatives. In this paper, we report the selective synthesis of mono-(2-), (2,6- or 2,7-)di-, and (2,6,14- or 2,7,14-)triformyl or acetyl substituted triptycenes, and their functional transformation into other triptycene derivatives containing cyano, ethynyl, acetamino and acetoxy groups, respectively. The regioisomers and structures of the triptycene derivatives with different functional groups were well identified by the FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra and X-ray single crystal structures. These substituted triptycene derivatives could find potential applications in supramolecular chemistry and materials science. Moreover, the solid state self-assemblies of the triptycene derivatives were also described, and it was found that 2,6,14-triacetaminotriptycene with the three amide groups

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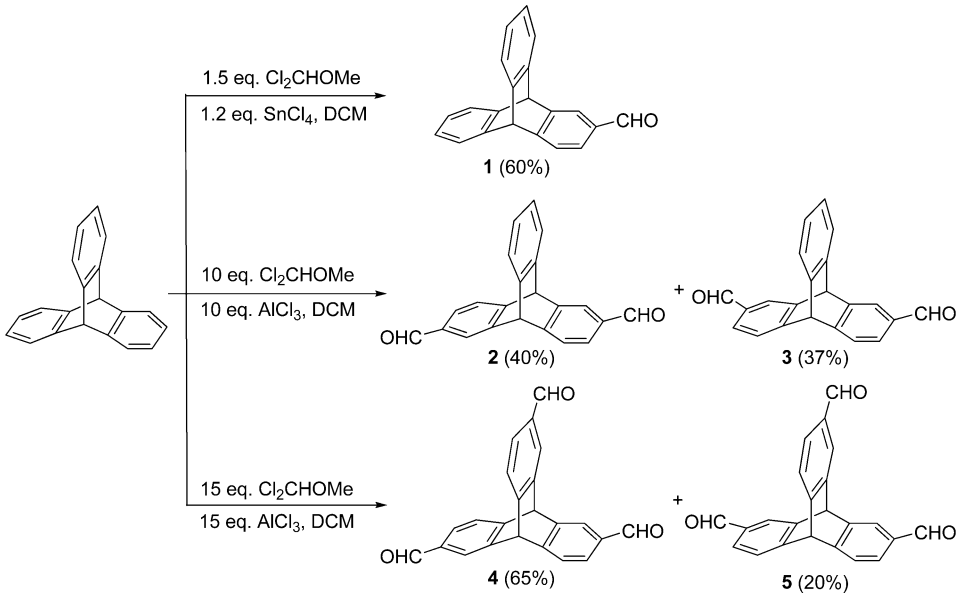
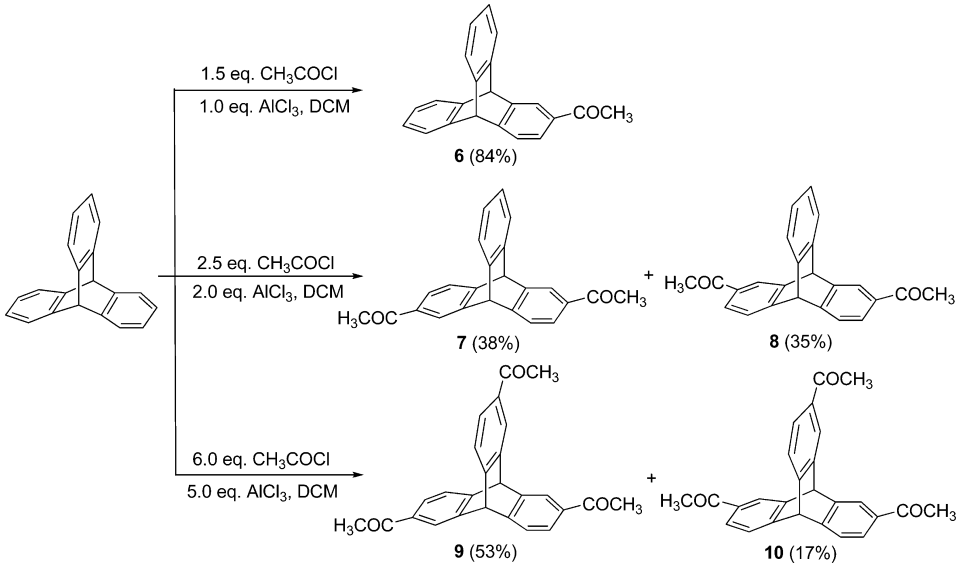
Scheme 1. Selective Synthesis of Formyl Substituted Triptycenes



Scheme 2. Selective Synthesis of Acetyl Substituted Triptycenes



paralleled to their connected aromatic rings could self-assemble into a 2D layer with porous structure, and further 3D microporous architecture by the hydrogen-bond network.

RESULTS AND DISCUSSION

Synthesis of Formyl and Acetyl Substituted Triptycenes. First, we tried the selective synthesis of 2-formyltriptycene **1** by aluminum chloride catalyzed Friedel–Crafts acylation of triptycene, and found that the reaction could not stop at the mono formylated stage. But we found that when triptycene was treated with 1.5 equiv of 1,1-dichlorodimethyl ether and 1.2 equiv of stannic chloride in dichloromethane at 0 °C for 1 h, 2-formyltriptycene **1** could be selectively obtained in 60% yield (Scheme 1). It was noteworthy that no further formylation occurred even if 2.2 equiv of stannic chloride and refluxed conditions were used. Thus, aluminum chloride instead of stannic chloride was then utilized for the synthesis of diformyltriptycenes **2** and **3**, and triformyltriptycenes **4** and **5** (Scheme 1). The results showed that by the reaction of triptycene and 10 equiv of 1,1-dichlorodimethyl ether in dichloromethane at −15 °C overnight in the presence of 10 equiv of aluminum chloride, 2,6-diformyltriptycene **2** and 2,7-diformyltriptycene **3** could be obtained in 40 and 37% yield, respectively, which was different from the literature method[9c] with bubbling hydrogen chloride into the system. By further increasing both 1,1-dichlorodimethyl ether and aluminum chloride up to 15 equiv, 2,6,14-triformyltriptycene **4** and 2,7,14-triformyltriptycene **5** were obtained in 65 and 20% yield, respectively. Under the similar reaction conditions, selective acetylation of triptycene could also be realized by using the different amount of acetylation reagent and aluminum chloride (Scheme 2). Thus, treatment of triptycene with 1.5 equiv of acetyl chloride and 1.0 equiv of aluminum chloride in dichloromethane for 1h led to the isolation of 2-acetyltriptycene **6** in 84% yield. When triptycene was reacted with 2.5 equiv of acetyl chloride and 2.0 equiv of aluminum chloride in

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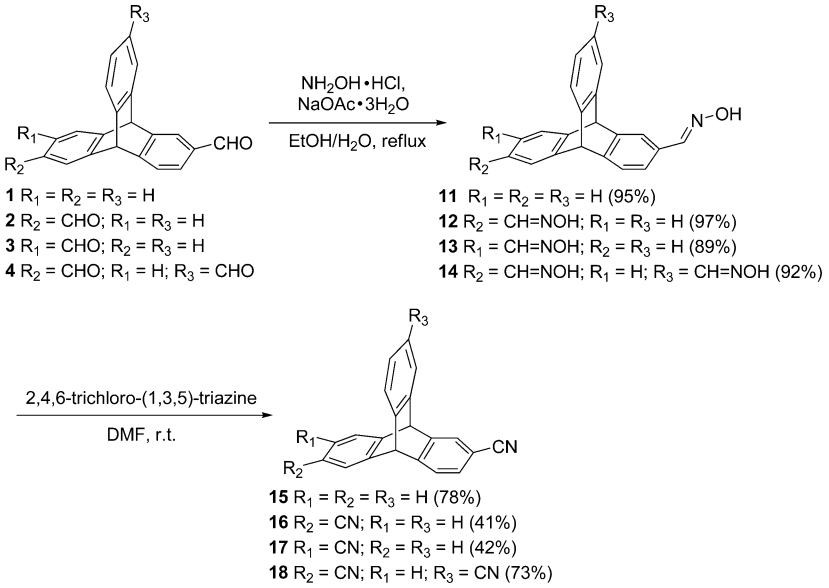
Scheme 3. Synthesis of Cyano-Substituted Triptycene Derivatives

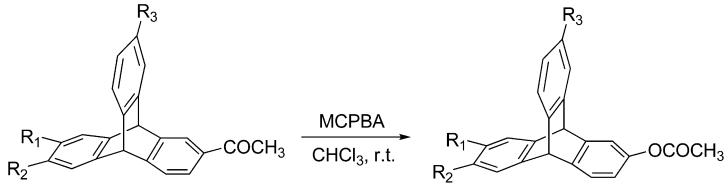


1 $R_1 = R_2 = R_3 = H$
2 $R_2 = CHO$; $R_1 = R_3 = H$
3 $R_1 = CHO$; $R_2 = R_3 = H$
4 $R_2 = CHO$; $R_1 = H$; $R_3 = CHO$

11 $R_1 = R_2 = R_3 = H$ (95%)
12 $R_2 = CH{=}NOH$; $R_1 = R_3 = H$ (97%)
13 $R_1 = CH{=}NOH$; $R_2 = R_3 = H$ (89%)
14 $R_2 = CH{=}NOH$; $R_1 = H$; $R_3 = CH{=}NOH$ (92%)

15 $R_1 = R_2 = R_3 = H$ (78%)
16 $R_2 = CN$; $R_1 = R_3 = H$ (41%)
17 $R_1 = CN$; $R_2 = R_3 = H$ (42%)
18 $R_2 = CN$; $R_1 = H$; $R_3 = CN$ (73%)

Scheme 4. Baeyer–Villiger Oxidation of Acetyl-Substituted Triptycenes



6 $R_1 = R_2 = R_3 = H$
7 $R_2 = COCH_3$; $R_1 = R_3 = H$
8 $R_1 = COCH_3$; $R_2 = R_3 = H$
9 $R_2 = COCH_3$; $R_1 = H$; $R_3 = COCH_3$
10 $R_1 = COCH_3$; $R_2 = H$; $R_3 = COCH_3$

19 $R_1 = R_2 = R_3 = H$ (84%)
20 $R_2 = OCOCH_3$; $R_1 = R_3 = H$ (86%)
21 $R_1 = OCOCH_3$; $R_2 = R_3 = H$ (81%)
22 $R_2 = OCOCH_3$; $R_1 = H$; $R_3 = OCOCH_3$ (94%)
23 $R_1 = OCOCH_3$; $R_2 = H$; $R_3 = OCOCH_3$ (93%)

dichloromethane for two days, 2,6-diacetyltriptycene **7** and 2,7-diacetyltriptycene **8** were isolated in 38 and 35% yield, respectively. By the reaction of triptycene with 6.0 equiv of acetyl chloride and 5.0 equiv of aluminum chloride in dichloromethane at 0 °C, 2,6,14-triacetyltriptycene **9** and 2,7,14-triacetyltriptycene **10** were obtained in 53 and 17% yield, respectively. It was found that the cis-substituted products with two or three substituents in same direction had larger polarity, and showed little deep color. In addition, two pairs of disubstituted products **2**, **3** and **7**, **8** were yielded in roughly 1:1 ratio, respectively, and the ratio of trans- and cis-trisubstituted triptycenes **4**, **5** or **9**, **10** is about 3:1, which are all consistent with the statistics.

Functional Transformation of Formyl and Acetyl Substituted Triptycenes. It was known that formyl and acetyl are versatile groups, and they can be easily transformed to other useful functional groups. Thus, various functionalized triptycene derivatives could be synthesized by the proper functional transformation of formyl and acetyl substituted triptycenes. First, we investigated the transformation of the formyltriptycenes to cyano substituted triptycene derivatives by aldoxime formation and dehydration.[10] As shown in Scheme 3, when triptycene **1** was treated by 1.2 equiv of hydroxylamine hydrochloride and 1.5 equiv of sodium acetate trihydrate in a refluxed solution of ethanol and water (v/v =1:1) for 12 h, the oxime substituted triptycene **11** could be quantitatively obtained. Then, treatment of **11** with 1.1 equiv of 2,4,6-trichloro-1,3,5-triazine in DMF gave the corresponding nitrile **15** in 78% yield. Under the similar conditions, treatment of **2**–**4** with hydroxylamine hydrochloride (1.2 mmol per formyl group) and sodium acetate trihydrate (1.5 mmol per formyl group) gave the oximes **12**–**14**, respectively, which were then dehydrated by 2,4,6-trichloro-1,3,5-triazine (1.1 mmol per formyl oxime group) in DMF to produce the dinitriles **16**–**17** and trinitrile **18** in 41–73% yield.

By Baeyer–Villiger oxidation, the acetyl group can be transformed to acetoxy group. Thus, when acetyl substituted triptycene **6** was treated by 2 equiv of *m*-chloroperbenzoic acid in $CHCl_3$ at ambient temperature, the triptycene derivatives **19** could be obtained in 84% yield. Similarly, treatment of **7**–**10** with *m*-chloroperbenzoic acid (2 mmol per acetyl group) in $CHCl_3$ gave **20**–**23** in 81–94% yield (Scheme 4). The acetyl group(s) in **19**–**23** could be easily removed by conventional hydrolysis method, and it could also afford an efficient method for the synthesis of hydroxyl substituted triptycenes, which were previously obtained by a multistep synthesis.[11]

Similar to the above-mentioned method, acetyl substituted triptycenes **6**–**10** could be transformed to acetyl oxime products **24**–**28** in 72–98% yield by treatment of **6**–**10** with hydroxylamine hydrochloride and sodium acetate trihydrate in 1:1 (v/v) ethanol/water. Then, Beckmann rearrangement of **24**–**28** in acetonitrile in the presence of a catalytic amount of mercury(II) chloride[13] yielded acetamino substituted products **29**–**33** in 76–90% yields (Scheme 5), which provided a short

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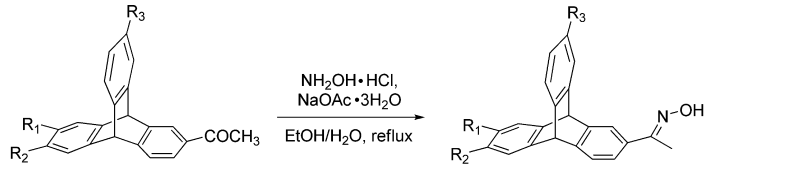
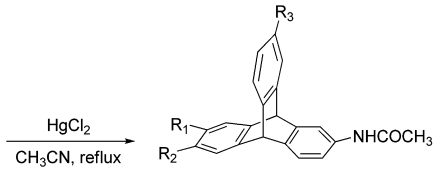
Scheme 5. Beckmann Rearrangement of Acetyl-Oxime Triptycenes



6 $R_1 = R_2 = R_3 = H$
7 $R_2 = COCH_3$; $R_1 = R_3 = H$
8 $R_1 = COCH_3$; $R_2 = R_3 = H$
9 $R_2 = COCH_3$; $R_1 = H$; $R_3 = COCH_3$
10 $R_1 = COCH_3$; $R_2 = H$; $R_3 = COCH_3$

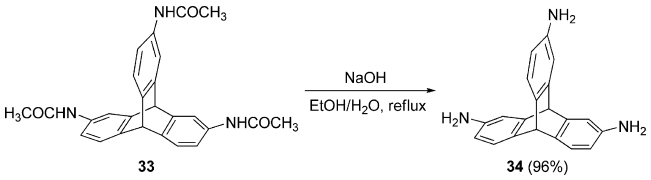
24 $R_1 = R_2 = R_3 = H$ (79%)
25 $R_2 = CN(OH)CH_3$; $R_1 = R_3 = H$ (80%)
26 $R_1 = CN(OH)CH_3$; $R_2 = R_3 = H$ (98%)
27 $R_2 = CN(OH)CH_3$; $R_1 = H$; $R_3 = CN(OH)CH_3$ (87%)
28 $R_1 = CN(OH)CH_3$; $R_2 = H$; $R_3 = CN(OH)CH_3$ (72%)



29 $R_1 = R_2 = R_3 = H$ (86%)
30 $R_2 = NHCOCH_3$; $R_1 = R_3 = H$ (88%)
31 $R_1 = NHCOCH_3$; $R_2 = R_3 = H$ (76%)
32 $R_2 = NHCOCH_3$; $R_1 = H$; $R_3 = NHCOCH_3$ (78%)
33 $R_1 = NHCOCH_3$; $R_2 = H$; $R_3 = NHCOCH_3$ (90%)

route to acetamino substituted triptycenes. The 2,7-diacetamino triptycene **31** was previously synthesized by three steps in 53% total yield starting from 2,7-diacetaminoanthracene.[12] The current method is obviously better than the previous reported one. Moreover, treatment of **33** with sodium hydroxide in ethanol/water solution gave the 2,7,14-triaminotriptycene **34** in 96% yield (Scheme 6), which also provided an alternative way to the synthesis of 2,7,14-triaminotriptycene **34**.[6]

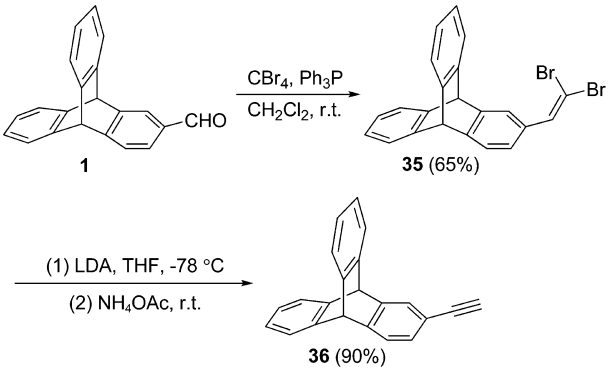
Scheme 6. Deacetylation of Triacetaminotriptycene 33



33 **34** (96%)

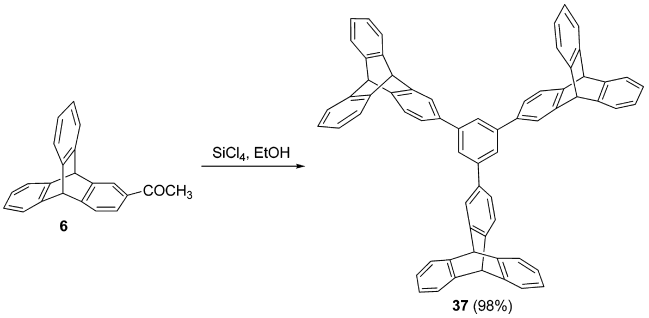
As shown in Scheme 7, starting from 2-formyltriptycene **1**, 2-ethynyltriptycene **36** could be conveniently synthesized in two steps in 59% total yield by Corey–Fuchs reaction.[14] Moreover, it was also found that simply dehydration cyclotrimerization[15] of three molecules of 2-acetyltriptycene **6** produced 1,3,5-tritriptycenebenzene **37** in 98% yield (Scheme 8). Compound **37** is a concave molecule similar to benzocyclotrimers[16] but has a large cavity.

Scheme 7. Corey–Fuchs Reaction of 2-Formyltriptycene



1 **35** (65%) **36** (90%)

Scheme 8. Dehydration Cyclotrimerization of 2-Acetyltriptycene



6 **37** (98%)

Structures of Triptycene Derivatives in Solution. The structures of monosubstituted triptycene derivatives could be easily evidenced by their ^{1}H NMR, ^{13}C NMR, and MS spectral data. It was found that not only formylation but also acetylation occurred at the 2-position of triptycene to give 2-substituted triptycene derivatives. For the diformyl or acetyl substituted triptycenes, there are two possible regioisomers: 2,6- and 2,7-disubstituted triptycenes, and they could be differentiated by their ^{1}H NMR and ^{13}C NMR spectra as well. First of all, ^{1}H NMR spectrum of the 2,6-disubstituted triptycene showed one signal (5.61 ppm in **2** and 5.57 ppm in **7**) for the bridgehead protons of triptycene due to its C_2 symmetric structure, while for the 2,7-disubstituted triptycene, two signals for the bridgehead protons (5.60, 5.62 ppm in **3** and 5.56, 5.58 ppm in **8**) were observed. The regioisomers could be also differentiated by their ^{13}C NMR spectra. As shown in Figure 1, 2,6-diformyltriptycene showed nine aromatic carbon signals and one signal at 54.0 ppm for the bridgehead carbons; meanwhile, for 2,7-diformyltriptycene, 12 aromatic carbon signals and two bridgehead carbon signals (53.6 and 54.4 ppm) were observed for it has a symmetric plane. For the two regioisomers of diacetyl substituted triptycenes, similar NMR

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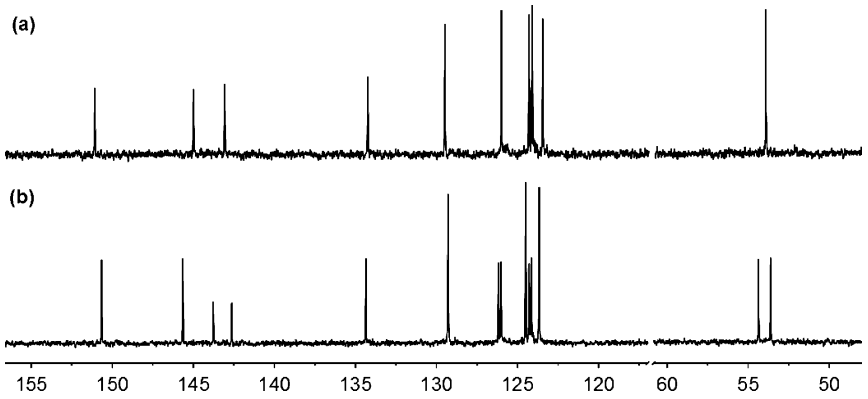

Figure 1. Partial ^{13}C NMR spectra (75 MHz, $CDCl_3$, 298 K) of (a) 2,6-diformyltriptycene (**2**), and (b) 2,7-diformyltriptycene (**3**).

spectral phenomena were also found (Figures S72 and S73, Supporting Information).

Similar to the disubstituted triptycenes, triformyl- or triacetyl substituted triptycenes also have two regioisomers: 2,6,14- and 2,7,14-trisubstituted triptycenes. The ^1H NMR spectra of the two regioisomers are nearly identical, mainly because of the collaborative electron pull function of three formyl or acetyl groups. However, their ^{13}C NMR spectra are obviously different. Consequently, 12 aromatic carbon signals and two bridgehead carbon signals were found for the 2,6,14-trisubstituted triptycene with a symmetric plane, while the 2,7,14-trisubstituted triptycene isomer showed only six aromatic carbon signals and two bridgehead carbon signals with a C_3 axis. Other functional group substituted triptycene derivatives showed similar spectral features to those ones of formyl- or acetyl substituted triptycenes but only different chemical shifts due to the electron withdrawing abilities of the substituted groups.

Solid Structures and Self-Assemblies of Triptycene Derivatives. To further confirm the structures of the substituted triptycene isomers and their derivatives, we obtained single crystals of disubstituted triptycene derivatives **8**, **16**, and **21** suitable for X-ray analysis by slow evaporation of *n*-hexane into a dichloromethane solution of **8**, **16**, and **21**, respectively. By slow evaporation of *n*-hexane into an acetone or a THF solution of **33**, we also obtained the single crystals of 2,6,14-triacetaminotriptycene **33**. The crystal structures of the triptycene derivatives (Figures 2−4) provided direct evidence for the substituted triptycene isomers, and the results are consistent with those ones in solution. Moreover, we also investigated the self-assemblies of the triptycene derivatives in the solid state. For 2,7-diacetyltriptycene **8**, the two acetyl groups are almost parallel with their connected aromatic rings (Figure 2a,b). Then, by a pair of C−H···O hydrogen bonding interactions between the adjacent molecules with the distances of 2.57−2.69 Å, molecule **8** could pack into a herringbone-like structure viewed along *c*-axis (Figure S77, Supporting Information). In the case of **21**, the two acetoxyl groups were just like a crab pincers (Figure 2c), and the two carbonyl oxygen atoms are positioned at same direction with the O−O distance of 5.74 Å, which is different from that of **8**. In addition, it was found that one of the methyl groups in **21** is situated in the crab pincers of another molecule with the C−H···O distance of 3.14 Å, and the molecule **21** could stack into a microporous-like architecture viewed along *c*-axis (Figure S78, Supporting Information).

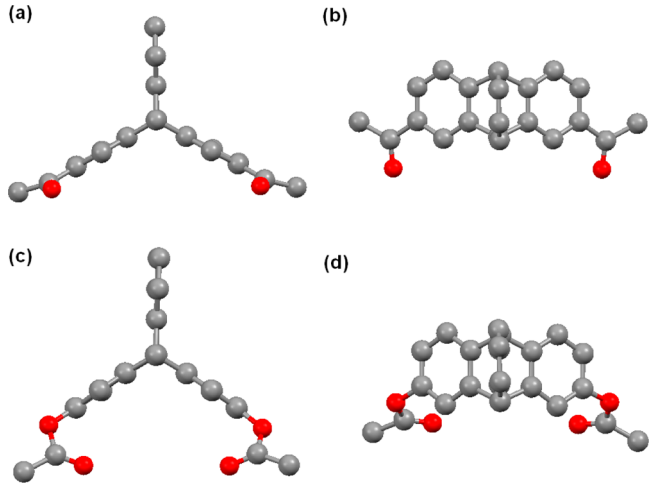

Figure 2. (a) Top view and (b) side view of crystal structure of **8**. (c) Top view and (d) side view of crystal structure of **21**. Hydrogen atoms are omitted for clarity.

Similar to **8**, the two nitrile groups in **16** are almost parallel with their connected aromatic rings as well (Figures 3a,b). By two pairs of C−H···π interactions between one triptycene and its adjacent four molecules (Figure S79, Supporting Information), triptycene derivative **16** self-assembled into a 2D layer structure, which could further pack into a 3D microporous architecture viewed along *c*-axis (Figure 3c).

The self-assemblies of 2,6,14-triacetaminotriptycene **33** in the solid state was also studied. It was found that three amide groups in **33** are all parallel with their connected aromatic rings, but pointed to two different directions (Figure 4a,b). Such structural features of **33** would benefit its further self-assembly. Thus, six molecules of **33** could self-assemble into a macrocycle by two pairs of NH···O and CH···O hydrogen bonding interactions between the adjacent molecules, which then formed a 2D layer with porous structure by the hydrogen-bond network (Figures 4c and S80, Supporting Information). The layers could further alternately stack to form a 3D microporous architecture (Figure 4d) by multiple N−H···O, C−H···O and C−H···π interactions between the adjacent molecules of different layers. Although two kinds of single crystals of **33** were grown from different solvent systems, they showed same space group and nearly same cell parameters, which suggested that the role of solvents in the formation of the crystal structure and the further self-assembly might be probably less important. Actually, the same self-assembled

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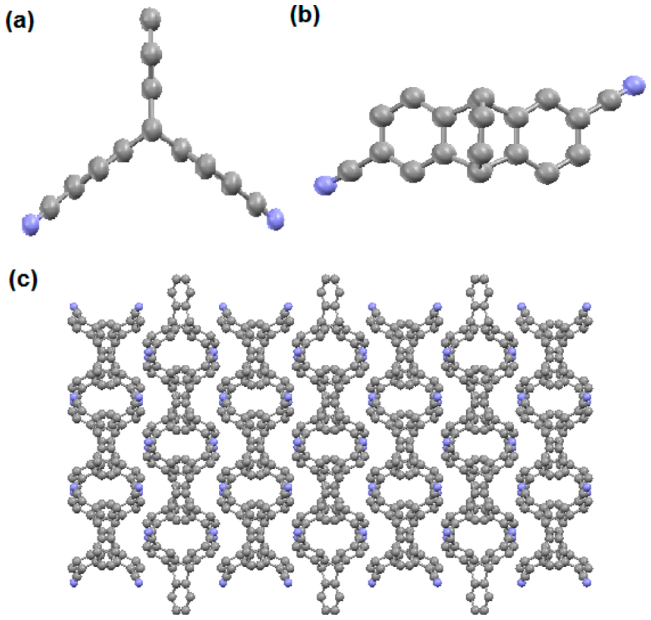

Figure 3. (a) Top view and (b) side view of crystal structure of **16**. (c) Packing of **16** viewed along *c*-axis. Hydrogen atoms are omitted for clarity.

structures were formed in the two cases, except the different disordered THF and acetone molecules as guest species were encapsulated in the channel, respectively (Figure S80, Supporting Information). In the former, THF molecules are situated in the channel by the N−H···O hydrogen bonding ($d_{C\cdots N}$ = 2.86 Å) between the amide proton of the triptycene and the oxygen atom of the guest THF, while in the latter acetone molecules show the similar N−H···O hydrogen bonding interactions ($d_{C\cdots N}$ = 2.87 Å) between the amide proton of the triptycene and the oxygen atom of the guest acetone (Figure S80, Supporting Information).

CONCLUSION

In conclusion, a series of mono-(2-), (2,6- or 2,7-)di-, and (2,6,14- or 2,7,14-)tri- formyl or acetyl substituted triptycenes have been selectively synthesized, and their functional transformations into other triptycene derivatives containing cyano, ethynyl, acetamino and acetoxy groups, respectively, have been reported. The different functionalized triptycene derivatives were well characterized by the FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra, and X-ray crystal analyses. Moreover, it was also found that 2,6,14-triacetaminotriptycene with the three amide groups paralleled to their connected aromatic rings could self-assemble into a 2D layer with porous structure, and further 3D microporous architecture by the hydrogen-bond network in the solid state, and the guest molecules of THF and acetone could be encapsulated inside the channels, respectively. The substituted triptycene derivatives presented here could be utilized as useful building blocks for constructing novel functional molecules with potential applications in supramolecular chemistry and materials science, which are underway in our laboratory.

EXPERIMENTAL SECTION

2-Formyltriptycene (1). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added stannic chloride (140 μL, 1.2 mmol), and the mixture was cooled to 0 °C under an argon

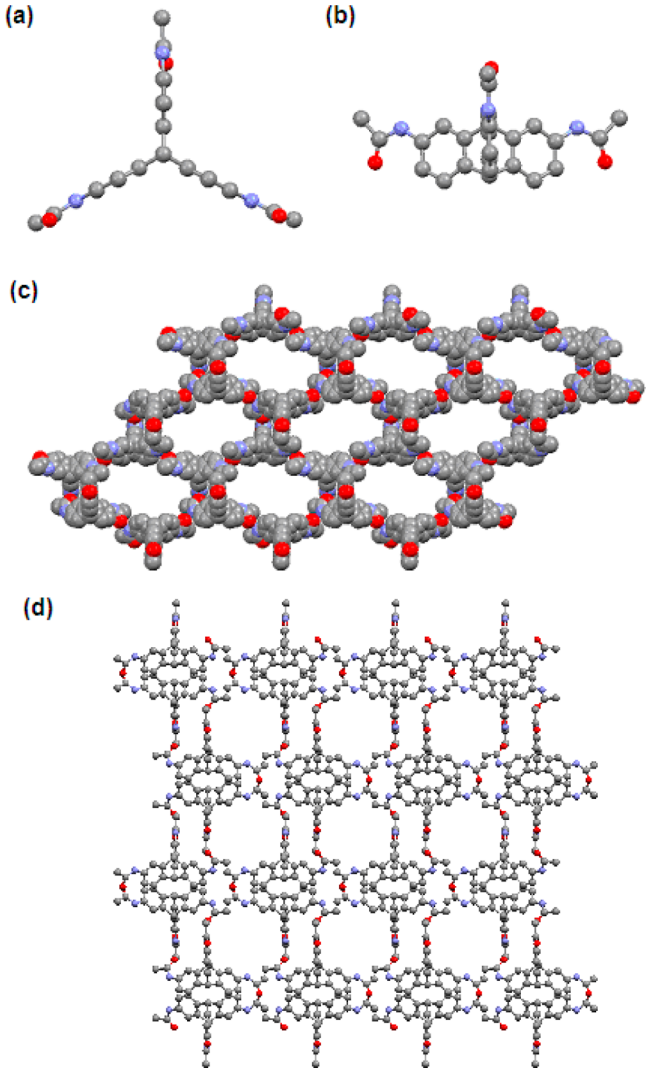

Figure 4. (a) Top view and (b) side view of crystal structure of **33**. (c) A 2D layer with porous structure, and (d) a 3D microporous architecture viewed along *c*-axis. Hydrogen atoms and solvents are omitted for clarity.

atmosphere. Then, 1,1′-dichlorodimethyl ether (136 μL, 1.5 mmol) was added by a syringe, and the mixture was stirred at 0 °C for 1h. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: petroleum ether/CH_2Cl_2 = 1:1, R_f = 0.3) to give the product (164 mg, 58% yield) as a pale yellow solid: mp 200−202 °C (lit. 185−187 °C[9d]); IR ν 1690 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.86 (s, 1H), 7.49 (s, 2H), 7.42−7.38 (m, 4H), 7.03−6.99 (m, 4H), 5.51 (s, 1H), 5.50 (s, 1H).

2,6-Diformyltriptycene (2) and 2,7-Diformyltriptycene (3). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added aluminum chloride (1.33 g, 10 mmol), and the mixture was cooled to −15 °C under an argon atmosphere. Then, 1,1′-dichlorodimethyl ether (904 μL, 10 mmol) was added by a syringe, and the mixture was stirred at −15 °C overnight. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and

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then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: CH_2Cl_2/CH_3CO_2Et = 100:1) to give 2,6-diformyltriptycene (124 mg, 40% yield) as a pale yellow solid and 2,7-diformyltriptycene (114 mg, 37% yield) as a pale yellow solid.

2,6-Diformyltriptycene (2). R_f = 0.55 (CH_2Cl_2/CH_3CO_2Et = 100:1): mp 247−250 °C; IR 1681 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 2H), 7.90 (s, 2H), 7.54 (s, 4H), 7.45−7.43 (m, 2H), 7.06−7.04 (m, 2H), 5.61 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 151.2, 145.1, 143.2, 134.3, 129.6, 126.1, 124.4, 124.2, 123.6, 54.0; EI-TOF MS m/z 310 (M^+). Anal. Calcd for $C_{22}H_{14}O_2{\cdot}H_2O$: C, 80.47; H, 4.91. Found: C, 80.58; H, 4.78.

2,7-Diformyltriptycene (3). R_f = 0.43 (CH_2Cl_2/CH_3CO_2Et = 100:1): mp 208−210 °C; IR ν 1689 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 2H), 7.90 (s, 2H), 7.55 (s, 4H), 7.46−7.43 (m, 2H), 7.07−7.04 (m, 2H), 5.62 (s, 1H), 5.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 150.6, 145.6, 143.7, 142.6, 134.3, 129.3, 126.2, 126.0, 124.5, 124.3, 124.1, 123.7, 54.4, 53.6; EI-TOF MS m/z 310 (M^+); EI-TOF MS m/z 310 (M^+). Anal. Calcd for $C_{22}H_{14}O_2{\cdot}0.9H_2O$: C, 80.92; H, 4.88. Found: C, 80.66; H, 4.84.

2,6,14-Triformyltriptycene (4) and 2,7,14-Triformyltriptycene (5). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added aluminum chloride (2 g, 15 mmol), and the mixture was cooled to −15 °C under an argon atmosphere. Then, 1,1′-dichlorodimethyl ether (1.36 mL, 15 mmol) was added by a syringe, and the mixture was stirred at −15 °C for 48 h. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: CH_2Cl_2/CH_3CO_2Et = 60:1) to give 2,6,14-triformyltriptycene (220 mg, 65% yield) as a pale yellow solid and 2,7,14-triformyltriptycene (68 mg, 20%) as a pale yellow solid.

2,6,14-Triformyltriptycene (4). R_f = 0.33 (CH_2Cl_2/CH_3CO_2Et = 60:1): mp 139−141 °C; IR ν 1689 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 3H), 7.96 (s, 3H), 7.61 (s, 6H), 5.74 (s, 1H), 5.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 150.3, 149.7, 144.4, 143.9, 134.65, 134.61, 130.0, 129.7, 127.75, 127.67, 123.9, 123.8, 54.1, 53.7; EI-TOF MS m/z 338 (M^+). Anal. Calcd for $C_{23}H_{14}O_3{\cdot}0.55CH_2Cl_2$: C, 73.46; H, 3.95. Found: C, 73.54; H, 4.18.

2,7,14-Triformyltriptycene (5). R_f = 0.23 (CH_2Cl_2/CH_3CO_2Et = 60:1): mp 232−234 °C; IR ν 1688 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 3H), 7.95 (s, 3H), 7.61 (s, 6H), 5.74 (s, 1H), 5.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 149.2, 144.9, 134.7, 129.4, 124.8, 124.0, 54.4, 53.4; EI-TOF MS m/z 338 (M^+); HRMS calcd for $C_{23}H_{14}O_3$: $[M]^+$ 338.0943, found 338.0948.

2-Acetyltriptycene (6). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added aluminum chloride (133 mg, 1 mmol), and the mixture was cooled to 0 °C under an argon atmosphere. Then acetyl chloride (106 μL, 1.5 mmol) was added by a syringe. The mixture was stirred at 0 °C for 1h. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then was quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: petroleum ether/CH_2Cl_2 = 1:1) to give 2-acetyltriptycene (249 mg, 84% yield) as a pale yellow solid.

2-Acetyltriptycene (6). R_f = 0.2 (petroleum ether/CH_2Cl_2 = 1:1): mp 204−206 °C (lit. 200−201 °C[9a]); IR ν 1677 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 1.5 Hz, 1H), 7.57 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.35−7.31 (m, 4H), 6.96−6.93 (m, 4H), 5.43 (s, 1H), 5.42 (s, 1H), 2.46 (s, 3H).

2,6-Diacetyltriptycene (7) and 2,7-Diacetyltriptycene (8). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added aluminum chloride (267 mg, 2 mmol), and the mixture was cooled to 0 °C under an argon atmosphere. Then acetyl chloride (176 μL, 2.5 mmol) was added by a syringe. The mixture was stirred at 0 °C for 48 h. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then was quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: CH_2Cl_2/CH_3CO_2Et = 60:1) to give 2,6-diacetyltriptycene (128 mg, 38% yield) as a pale yellow solid and 2,7-diacetyltriptycene (118 mg, 35% yield) as a pale yellow solid.

2,6-Diacetyltriptycene (7). R_f = 0.5 (CH_2Cl_2/CH_3CO_2Et = 80:1): mp 167−168 °C; IR ν 1671 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 1.4 Hz, 2H), 7.64 (dd, J = 7.7, 1.6 Hz, 2H), 7.47 (d, J = 7.7 Hz, 2H), 7.44−7.40 (m, 2H), 7.06−7.00 (m, 2H), 5.57 (s, 2H), 2.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 149.9, 144.9, 143.6, 134.8, 126.8, 125.9, 124.1, 123.8, 123.3, 54.0, 26.7; EI-TOF MS m/z 338 (M^+). Anal. Calcd for $C_{24}H_{18}O_2{\cdot}0.1H_2O$: C, 84.73; H, 5.39. Found: C, 84.87; H, 5.41.

2,7-Diacetyltriptycene (8). R_f = 0.45 (CH_2Cl_2/CH_3CO_2Et = 80:1): mp 184−186 °C; IR ν 1677 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 1.2 Hz, 2H), 7.66 (dd, J = 7.7, 1.6 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.44−7.40 (m, 2H), 7.05−7.02 (m, 2H), 5.58 (s, 1H), 5.56 (s, 1H), 2.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 149.4, 145.3, 144.1, 143.1, 134.8, 126.7, 125.9, 125.8, 124.1, 124.0, 123.9, 123.3, 54.1, 53.9, 26.7; EI-TOF MS m/z 338 (M^+). Anal. Calcd for $C_{24}H_{18}O_2{\cdot}0.04CH_2Cl_2$: C, 84.48; H, 5.33. Found: C, 84.84; H, 5.44.

2,6,14-Triacetyltriptycene (9) and 2,7,14-Triacetyltriptycene (10). To a solution of triptycene (254 mg, 1 mmol) in CH_2Cl_2 (25 mL) was added aluminum chloride (666 mg, 5 mmol), and the mixture was cooled to 0 °C under an argon atmosphere. Then acetyl chloride (424 μL, 6 mmol) was added by a syringe. The mixture was stirred at 0 °C for 72 h. The reaction was monitored by TLC. After completion, the reaction mixture was gradually warmed to room temperature and then was quenched with ice−water, acidified by dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give an oil-like crude product, which was separated by flash column chromatography on silica gel (eluant: CH_2Cl_2:CH_3CO_2Et = 20:1) to give 2,6,14-triacetyltriptycene (202 mg, 53% yield) as a pale yellow solid and 2,7,14-triacetyltriptycene (65 mg, 17%) as a pale yellow solid.

2,6,14-Triacetyltriptycene (9). R_f = 0.33 (CH_2Cl_2/CH_3CO_2Et = 20:1): mp 133−136 °C; IR ν 1682 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 3H), 7.68 (d, J = 7.7 Hz, 3H), 7.51 (d, J = 7.7 Hz, 3H), 5.66 (s, 1H), 5.65 (s, 1H), 2.54 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.35, 197.31, 149.2, 148.7, 144.3, 143.8, 135.1, 135.0, 127.1, 127.0, 124.1, 124.0, 123.5, 53.94, 53.88, 26.6; EI-TOF MS m/z 380 (M^+). Anal. Calcd for $C_{26}H_{20}O_3{\cdot}0.25CH_2Cl_2$: C, 78.49; H, 5.14. Found: C, 78.66; H, 5.57.

2,7,14-Triacetyltriptycene (10). R_f = 0.21 (CH_2Cl_2/CH_3CO_2Et = 20:1): mp 241−243 °C; IR ν 1682 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 3H), 7.55 (d, J = 7.4 Hz, 3H), 7.39 (d, J = 7.6 Hz, 3H), 5.57 (s, 1H), 5.56 (s, 1H), 2.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 148.3, 144.8, 135.1, 126.8, 124.1, 123.5, 54.0, 53.8, 26.7; EI-TOF MS m/z 380 (M^+). Anal. Calcd for $C_{26}H_{20}O_3{\cdot}H_2O$: C, 78.37; H, 5.57. Found: C, 78.48; H, 5.74.

General Method for the Synthesis of Formyl Oxime Substituted Triptycenes. A mixture of formyl-substituted triptycene (1 mmol), hydroxylamine hydrochloride (1.2 mmol per formyl group), sodium acetate trihydrate (1.5 mmol per formyl group), and ethanol/water (10 mL/10 mL) was stirred and reflux for 12 h. After that, the mixture was extracted with ether and then washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give a white solid, which is sufficient pure for characterization.

Compound 11. R_f = 0.35 (CH_2Cl_2). Yield: 95%: mp 116−118 °C; IR ν 1682 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.66 (s, 1H), 7.40−7.36 (m, 5H), 7.15−7.12 (m, 1H), 7.02−6.98 (m, 4H), 5.43 (s, 1H), 5.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 147.4, 146.0, 144.8, 144.6, 129.0, 125.39, 125.38, 125.1, 123.85,

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123.74, 123.70, 121.5, 54.0; EI-TOF MS m/z 297 (M^+). Anal. Calcd for $C_{21}H_{15}NO{\cdot}0.25CH_2Cl_2$: C, 80.11; H, 4.90; N, 4.40. Found: C, 80.25; H, 4.98; N, 4.41.

Compound 12. R_f = 0.32 (CH_2Cl_2/CH_3CO_2Et = 10:1). Yield: 97%: mp 170−172 °C; IR ν 1696 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.66 (s, 2H), 7.38−7.36 (m, 4H), 7.33 (s, 1H), 7.14−7.11 (m, 2H), 7.01−6.99 (m, 2H), 5.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 146.9, 145.4, 144.1, 129.2, 125.6, 125.4, 124.0, 123.9, 121.5, 53.8; EI-TOF MS m/z 340 (M^+); HRMS calcd for $C_{22}H_{16}N_2O_2$, $[M]^+$ 340.1212, found 340.1217.

Compound 13. R_f = 0.25 (CH_2Cl_2/CH_3CO_2Et = 10:1). Yield: 89%: mp 166−168 °C; IR ν 1682 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (s, 2H), 8.06 (s, 2H), 7.66 (s, 2H), 7.39−7.35 (m, 4H), 7.17−7.14 (m, 2H), 7.02−6.99 (m, 2H), 5.46 (s, 1H), 5.44 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 146.7, 145.5, 144.3, 143.9, 129.3, 125.65, 125.61, 125.3, 124.0, 123.9, 123.8, 121.6, 53.82, 53.77; EI-TOF MS m/z 340 (M^+); HRMS calcd for $C_{22}H_{16}N_2O_2$, $[M]^+$ 340.1212, found 340.1217.

Compound 14. R_f = 0.48 (CH_2Cl_2/CH_3CO_2Et = 2:1). Yield: 92%: mp 202−204 °C; IR ν 1682 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 3H), 8.08 (s, 3H), 7.78 (s, 3H), 7.50−7.46 (m, 3H), 7.25−7.23 (m, 3H), 5.73 (s, 1H), 5.72 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 149.3, 147.2, 147.1, 146.3, 146.2, 131.6, 125.6, 124.9, 122.23, 122.19, 54.1, 54.0; EI-TOF MS m/z 383 (M^+); HRMS calcd for $C_{23}H_{17}N_3O_3$, $[M]^+$ 383.1270, found 383.1275.

General Method for the Dehydration of Formyl Oxime Substituted Triptycenes. After a solution of 2,4,6-trichloro-[1,3,5]triazine (1.1 mmol per formyl oxime group) in DMF (25 mL) was stirred for 10 min, formyl oxime compound (1 mmol) in DMF (15 mL) was added. The mixture was stirred at room temperature for 10 h and then poured into water and extracted with dichloromethane. The organic phase was washed with a saturated solution of Na_2CO_3 (15 mL), followed by dilute hydrochloric acid and brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated to give an oil-like crude product. Chromatography of the residue over silica gel gave the product.

Compound 15. R_f = 0.4 (petroleum ether/CH_2Cl_2 = 1:1). Yield: 78%: mp 285−287 °C; IR ν 2218 cm^{-1} (C≡N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 1.0 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.41−7.38 (m, 4H), 7.32 (dd, J = 7.6, 1.5 Hz, 1H), 7.06−7.00 (m, 4H), 5.48 (s, 1H), 5.47 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 146.6, 144.0, 143.8, 130.0, 126.7, 125.8, 125.7, 124.3, 124.01, 123.98, 119.1, 108.7, 54.1, 53.5; EI-TOF MS m/z 279 (M^+). Anal. Calcd for $C_{21}H_{13}N{\cdot}0.2H_2O$: C, 89.14; H, 4.77; N, 4.95. Found: C, 89.23; H, 4.71; N, 4.98.

Compound 16. R_f = 0.51 (petroleum ether/CH_2Cl_2═1:4). Yield: 41%: mp >300 °C; IR ν 2227 cm^{-1} (C≡N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.46−7.43 (m, 2H), 7.35 (dd, J = 7.6, 1.2 Hz, 2H), 7.10−7.07 (m, 2H), 5.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 145.2, 142.6, 130.5, 127.1, 126.3, 124.6, 124.4, 118.7, 109.4, 53.4; EI-TOF MS m/z 304 (M^+); HRMS calcd for $C_{22}H_{12}N_2$, $[M]^+$ 304.1000, found 304.0997.

Compound 17. R_f = 0.36 (petroleum ether/CH_2Cl_2 = 1:4). Yield: 42%: mp 141−143 °C; IR ν 2226 cm^{-1} (C≡N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.46−7.42 (m, 2H), 7.36 (dd, J = 7.6, 1.5 Hz, 2H), 7.10−7.07 (m, 2H), 5.56 (s, 1H), 5.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 145.3, 142.8, 142.4, 130.5, 127.1, 126.4, 126.3, 124.7, 124.4, 124.3, 109.5, 54.0, 52.9; EI-TOF MS m/z 304 (M^+); HRMS calcd for $C_{22}H_{12}N_2$, $[M]^+$ 304.1000, found 304.0995.

Compound 18. R_f = 0.38 (CH_2Cl_2). Yield: 73%: mp 190−192 °C; IR ν 2229 cm^{-1} (C≡N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 3H), 7.57−7.54 (m, 3H), 7.44−7.41 (m, 3H), 5.65 (s, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 149.7, 149.6, 145.8, 145.7, 131.7, 131.6, 128.5, 126.4, 119.2, 110.52, 110.49, 53.5, 53.0; EI-TOF MS m/z 329 (M^+); HRMS calcd for $C_{23}H_{11}N_3$, $[M]^+$ 329.0953, found 329.0949.

General Method for the Baeyer−Villiger Oxidation of Acetyl Substituted Triptycenes. To a solution of acetyl substituted triptycene (1 mmol) in $CHCl_3$ (20 mL) was added m-chloroperbenzoic acid (84%, 2 mmol per acetyl group), and the mixture was stirred for 10 h at ambient temperature. The reaction was monitored by TLC, and a further equivalent of MCPBA was added until full consumption of the starting material. The solution was washed with saturated aqueous Na_2CO_3 and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Chromatography of the residue over silica gel gave the product.

Compound 19. R_f = 0.15 (petroleum ether/CH_2Cl_2 = 2:1). Yield: 84%: mp 185−187 °C; IR ν 1751 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38−7.31 (m, 5H), 7.12 (d, J = 2.1 Hz, 1H), 7.00−6.94 (m, 4H), 6.68 (dd, J = 7.9, 2.2 Hz, 1H), 5.40 (s, 1H), 5.37 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 147.9, 146.8, 145.2, 144.9, 142.9, 125.4, 125.3, 124.2, 123.8, 123.7, 117.8, 117.5, 54.1, 53.6, 21.1; EI-TOF MS m/z 312 (M^+). Anal. Calcd for $C_{22}H_{16}O_2{\cdot}0.05CH_2Cl_2$: C, 83.65; H, 5.13. Found: C, 83.63; H, 5.36.

Compound 20. R_f = 0.16 (petroleum ether/CH_2Cl_2 = 1:2). Yield: 86%: mp 105−107 °C; IR ν 1755 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.30 (m, 4H), 7.12 (s, 2H), 6.99−6.96 (m, 2H), 6.70−6.67 (m, 2H), 5.36 (s, 2H), 2.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 148.0, 146.7, 144.7, 142.4, 125.4, 124.3, 123.8, 117.8, 117.5, 53.5, 21.1; EI-TOF MS m/z 370 (M^+); HRMS calcd for $C_{24}H_{18}O_4$, $[M]^+$ 370.1205, found 370. 1209.

Compound 21. R_f = 0.13 (petroleum ether/CH_2Cl_2 = 1:2). Yield: 81%: mp 103−105 °C; IR ν 1755 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.31 (m, 4H), 7.12 (s, 2H), 6.99−6.97 (m, 2H), 6.71−6.68 (m, 2H), 5.39 (s, 1H), 5.34 (s, 1H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 147.9, 146.3, 144.9, 144.3, 142.7, 125.5, 125.4, 124.2, 123.9, 123.6, 117.9, 117.6, 53.9, 53.1, 21.1; EI-TOF MS m/z 370 (M^+); HRMS calcd for $C_{24}H_{18}O_4$, $[M]^+$ 370. 1205, found 370. 1210.

Compound 22. R_f = 0.19 (CH_2Cl_2). Yield: 94%: mp 123−125 °C; IR ν 1755 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 7.9 Hz, 3H), 7.11 (d, J = 1.9 Hz, 3H), 6.70 (dd, J = 7.9, 2.1 Hz, 3H), 5.36 (s, 1H), 5.34 (s, 1H), 2.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 148.1, 148.0, 146.5, 146.2, 142.2, 141.9, 124.5, 124.3, 118.0, 117.9, 117.6, 117.5, 53.3, 52.9, 21.1; EI-TOF MS m/z 428 (M^+). Anal. Calcd for $C_{26}H_{20}O_6$: C, 72.89; H, 4.71. Found: 72.82; H, 4.96.

Compound 23. R_f = 0.54 (CH_2Cl_2/CH_3CO_2Et = 30:1). Yield: 93%: mp 124−126 °C; IR ν 1755 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 3H), 7.11 (d, J = 2.2 Hz, 3H), 6.71 (dd, J = 7.9, 2.2 Hz, 3H), 5.39 (s, 1H), 5.30 (s, 1H), 2.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 147.9, 145.8, 142.5, 124.2, 118.1, 117.7, 53.7, 52.5, 21.1; EI-TOF MS m/z 428 (M^+); HRMS calcd for $C_{26}H_{20}O_6$, $[M]^+$ 428.1260, found 428.1264.

General Method for the Synthesis of Acetyl Oxime Substituted Triptycenes. A mixture of acetyl substituted triptycene (1 mmol), hydroxylamine hydrochloride (1.2 mmol per acetyl group), sodium acetate trihydrate (1.5 mmol per acetyl group), and ethanol/water (25 mL/25 mL) was stirred and reflux for 12 h. After that, the mixture was extracted with ether and then washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtrated, and then concentrated to give a residue. Chromatography of the residue over silica gel yielded the product.

Compound 24. R_f = 0.26 (CH_2Cl_2). Yield: 79%: mp 108−110 °C; IR ν 1722 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.39−7.34 (m, 5H), 7.22−7.18 (m, 1H), 6.99−6.95 (m, 4H), 5.43 (s, 1H), 5.41 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 146.6, 145.7, 145.0, 144.9, 133.6, 125.4, 123.8, 123.7, 123.6, 123.4, 121.4, 54.2, 53.9, 12.5; EI-TOF MS m/z 311 (M^+); HRMS calcd for $C_{22}H_{17}NO$, $[M]^+$ 311.1310, found 311.1315.

Compound 25. R_f = 0.36 (CH_2Cl_2/CH_3CO_2Et = 5:1). Yield: 80%: mp 246−247 °C; IR ν 1705 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 1.2 Hz, 2H), 7.39−7.36 (m, 4H), 7.21 (dd, J = 7.7, 1.6 Hz, 2H), 7.01−6.99 (m, 2H), 5.44 (s, 2H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, acetone-d_6) δ 154.3, 146.9, 146.4, 146.1, 135.4, 126.0, 124.5, 124.3, 123.7, 121.9, 54.3, 11.6; EI-TOF MS m/z 368 (M^+); HRMS calcd for $C_{24}H_{20}N_2O_2$, $[M]^+$ 368.1525, found 368.1529.

Compound 26. R_f = 0.3 (CH_2Cl_2/CH_3CO_2Et = 5:1). Yield: 98%: mp 166−168 °C; IR ν 1740 cm^{-1} (C═N); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.36−7.33 (m, 4H), 7.23−7.21 (m, 2H), 6.96 (s, 2H), 5.47 (s, 1H), 5.42 (s, 1H), 2.20 (s, 6H); ^{13}C NMR (75 MHz,

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$CDCl_3$) δ 156.0, 146.1, 145.4, 144.7, 144.4, 133.8, 125.5, 124.5, 123.9, 123.7, 123.5, 121.5, 54.1, 53.6, 12.6; EI-TOF MS m/z 368 (M^+); HRMS calcd for $C_{24}H_{20}N_2O_2$, $[M]^+$ 368.1525, found 368.1529.

Compound 27. R_f = 0.22 (CH_2Cl_2/CH_3CO_2Et = 3:1). Yield: 87%: mp 210−212 °C; IR ν 1627 cm^{-1} (C═N); ^1H NMR (300 MHz, DMSO-d_6) δ 11.08 (s, 3H), 7.75 (s, 3H), 7.45 (d, J = 7.7 Hz, 3H), 7.29 (d, J = 7.7 Hz, 3H), 5.46 (s, 1H), 5.43 (s, 1H), 2.21 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 152.7, 145.3, 145.2, 145.11, 145.06, 144.98, 144.86, 134.1, 123.5, 122.6, 120.9, 52.3, 51.0, 11.6; EI-TOF MS m/z 425 (M^+); HRMS calcd for $C_{26}H_{23}N_3O_3$, $[M]^+$ 425.1739, found 425.1744.

Compound 28. R_f = 0.14 (CH_2Cl_2/CH_3CO_2Et = 3:1). Yield: 72%: mp 205−207 °C; IR ν 1631 cm^{-1} (C═N); ^1H NMR (300 MHz, DMSO-d_6) δ 10.18 (s, 3H), 7.85 (d, J = 1.4 Hz, 3H), 7.46 (d, J = 7.7 Hz, 3H), 7.33 (dd, J = 7.7, 1.7 Hz, 3H), 5.74 (s, 1H), 5.70 (s, 1H), 2.18 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.3, 146.4, 146.3, 135.5, 124.2, 123.8, 122.0, 54.7, 53.7, 11.6; EI-TOF MS m/z 425 (M^+); HRMS calcd for $C_{26}H_{23}N_3O_3$, $[M]^+$ 425.1739, found 425.1745.

General Method for the Beckmann Rearrangement of Acetyl Oxime Substituted Triptycenes. To a solution of acetyl oxime substituted triptycenes (1 mmol) in 25 mL of acetonitrile under an argon atmosphere was added mercury-(II) chloride (0.01 mmol). After being stirred at 80 °C for 8 h, the reaction mixture was allowed to cool, poured into water, and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Chromatography of the residue over silica gel gave the product.

Compound 29. R_f = 0.42 (CH_2Cl_2). Yield: 86%: mp 128−130 °C; IR ν 1659 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 1.5 Hz, 1H), 7.36−7.33 (m, 4H), 7.25 (d, J = 8.9 Hz, 2H), 6.98−6.95 (m, 4H), 6.90 (dd, J = 7.9, 1.9 Hz, 1H), 5.37 (s, 1H), 5.36 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 146.3, 145.2, 144.9, 141.5, 135.0, 125.23, 125.16, 123.7, 123.5, 116.25, 116.19, 54.1, 53.5, 24.5; EI-TOF MS m/z 311 (M^+). Anal. Calcd for $C_{22}H_{17}NO{\cdot}0.9CH_2Cl_2$: C, 70.92; H, 4.89; N, 3.61. Found: C, 70.68; H, 4.97; N, 3.55.

Compound 30. R_f = 0.33 (CH_2Cl_2/CH_3CO_2Et = 1:2). Yield: 88%: mp 285−286 °C; IR ν 1659 cm^{-1} (C═O); ^1H NMR (300 MHz, DMSO-d_6) δ 9.81 (s, 2H), 7.76 (d, J = 1.6 Hz, 2H), 7.43−7.40 (m, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.06 (dd, J = 7.9, 1.9 Hz, 2H), 7.00−6.96 (m, 2H), 5.51 (s, 2H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.0, 145.9, 145.4, 139.8, 136.3, 124.8, 123.5, 123.4, 115.1, 115.0, 52.1, 23.9; EI-TOF MS m/z 368 (M^+). Anal. Calcd for $C_{24}H_{20}N_2O_2{\cdot}1.8H_2O$: C, 71.91; H, 5.93; N, 6.99. Found: C, 71.96; H, 5.75; N, 6.88.

Compound 31. R_f = 0.26 (CH_2Cl_2/CH_3CO_2Et = 1:2). Yield: 76%: mp 198−200 °C (lit. 189−190 °C[12]); IR ν 1667 cm^{-1} (C═O); ^1H NMR (300 MHz, DMSO-d_6) δ 9.82 (s, 2H), 7.77 (d, J = 1.6 Hz, 2H), 7.46−7.37 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.07 (dd, J = 7.9, 1.9 Hz, 2H), 7.00−6.96 (m, 2H), 5.56 (s, 1H), 5.48 (s, 1H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.0, 145.6, 145.1, 140.1, 136.2, 124.9, 124.7, 123.6, 123.3, 123.2, 115.3, 52.8, 51.4, 23.9.

Compound 32. R_f = 0.44 (CH_3CO_2Et/acetone=1:1). Yield: 78%: mp 250−252 °C; IR ν 1667 cm^{-1} (C═O); ^1H NMR (300 MHz, DMSO-d_6) δ 9.81 (s, 3H), 7.73 (s, 3H), 7.34−7.29 (m, 3H), 7.08−7.03 (m, 3H), 5.48 (s, 1H), 5.44 (s, 1H), 1.99 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.0, 146.1, 145.8, 140.0, 139.8, 136.3, 136.2, 123.5, 123.3, 115.1, 115.0, 52.2, 51.6, 23.9; EI-TOF MS m/z 425 (M^+). Anal. Calcd for $C_{26}H_{23}N_3O_3{\cdot}2.4H_2O$: C, 66.37; H, 6.00; N, 8.93. Found: C, 66.62; H, 5.98; N, 8.96.

Compound 33. R_f = 0.35 (CH_3CO_2Et/acetone=1:1). Yield: 90%: mp 236−238 °C; IR ν 1667 cm^{-1} (C═O); ^1H NMR (300 MHz, DMSO-d_6) δ 9.81 (s, 3H), 7.74 (d, J = 1.5 Hz, 3H), 7.27 (d, J = 8.0 Hz, 3H), 7.07 (dd, J = 7.9, 1.9 Hz, 3H), 5.54 (s, 1H), 5.41 (s, 1H), 1.98 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.0, 145.6, 140.3, 136.1, 123.1, 115.4, 115.2, 52.8, 50.9, 23.9; EI-TOF MS m/z 425 (M^+). Anal. Calcd for $C_{26}H_{23}N_3O_3{\cdot}0.4H_2O$: C, 72.17; H, 5.54; N, 9.71. Found: C, 72.26; H, 5.47; N, 9.75.

Compound 34. A mixture of compound **33** (1 mmol), sodium hydroxide (3.2 mmol), and ethanol/water (10 mL/10 mL) was stirred and reflux for 12 h. The reaction mixture was allowed to cool and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Chromatography of the residue over silica gel (CH_2Cl_2/CH_3CO_2Et = 1:2, R_f = 0.17) gave the product in 96% yield: mp 151−152 °C (lit. 152−154 °C[6]); ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, J = 7.7 Hz, 3H), 6.69 (d, J = 2.1 Hz, 3H), 6.22 (dd, J = 7.7, 2.2 Hz, 3H), 5.05 (s, 1H), 4.96 (s, 1H), 3.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 143.4, 137.3, 123.3, 111.8, 110.9, 54.4, 51.4, 23.9.

Compound 35. To a solution of CBr_4 (352 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) was added Ph_3P (550 mg, 2.1 mmol) at 0 °C. The resultant yellow solution was stirred at room temperature for 15 min. The aldehyde **1** (100 mg, 0.35 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Chromatography of the residue (silica gel, petroleum ether/CH_2Cl_2 = 4:1, R_f = 0.46) gave 100 mg (65%) of **35** as a white solid: mp 63−65 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.38−7.32 (m, 6H), 7.18−7.13 (m, 1H), 7.00−6.94 (m, 4H), 5.41 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 145.6, 145.3, 145.0, 144.8, 136.8, 132.2, 125.8, 125.4, 125.2, 123.77, 123.67, 123.63, 123.5, 88.7, 54.2, 54.1, 54.0; EI-TOF MS m/z 436 (M^+); HRMS calcd for $C_{22}H_{14}Br_2$, $[M]^+$ 435. 9462, found 435. 9469.

Compound 36. To a solution of i-Pr_2NH (0.5 mL, 3.5 mmol) in THF (10 mL) cooled to −78 °C was added n-BuLi (2.8 mL, 2.5 M in hexanes, 7 mmol). The resultant mixture was warmed to room temperature and stirred for 30 min. Then, 2.5 mL of the above prepared solution was added dropwise by a syringe to a solution of compound **35** (60 mg, 0.14 mmol) in THF (2.5 mL) at −78 °C. The reaction mixture was stirred for 15 min and then 15 min at room temperature. Then the reaction was quenched with saturated NH_4OAc, extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Chromatography of the residue (silica gel, petroleum ether/CH_2Cl_2 = 6:1, R_f = 0.25) gave 35 mg (90%) of **36** as a white solid: mp 78−80 °C; IR ν 2103 cm^{-1} (C≡C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38−7.35 (m, 4H), 7.31 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 7.00−6.98 (m, 4H), 5.41 (s, 1H), 5.39 (s, 1H), 2.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 145.5, 144.73, 144.68, 129.4, 127.2, 125.39, 125.37, 123.74, 123.71, 123.6, 118.8, 83.9, 76.1, 53.9, 53.8; EI-TOF MS m/z 278 (M^+). Anal. Calcd for $C_{22}H_{14}{\cdot}0.02CH_2Cl_2$: C, 94.44; H, 5.05. Found: C, 94.36; H, 5.34.

Compound 37. To a solution of compound **6** (218 mg, 0.74 mmol) in anhydrous ethanol (15 mL) under argon was added dropwise $SiCl_4$ (0.421 mL, 3.68 mmol) at 0 °C. After the addition was completed, the reaction mixture was heated to reflux overnight. After cooling to room temperature, the mixture was poured into ice−water. The suspension was filtrated and washed with water and then dried to afford 201 mg (98%) of compound **37** as a white solid (petroleum ether/CH_2Cl_2 = 2:1, R_f = 0.25): mp >300 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.89 (s, 3H), 7.69 (s, 3H), 7.54−7.42 (m, 18H), 7.04-6.99 (m, 12H), 5.70 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 146.4, 145.6, 145.1, 142.5, 138.7, 125.69, 125.63, 125.3, 124.5, 124.2, 124.0, 123.2, 54.5, 54.0. MALDI-TOF MS m/z 835.4 (M^+). Anal. Calcd for $C_{66}H_{42}{\cdot}0.3CH_2Cl_2$: C, 92.54; H, 4.99. Found: C, 92.63; H, 5.13.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra for new compounds; NMR spectral comparison of di- or trisubstituted triptycene derivatives; X-ray crystallographic data and the refinement parameters for compounds **8**, **16**, **21**, and **33** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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