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PAPER

One-pot synthesis of substituted benzene *via* intermolecular [2+2+2] cycloaddition catalyzed by air-stable Ru(II)-complex†

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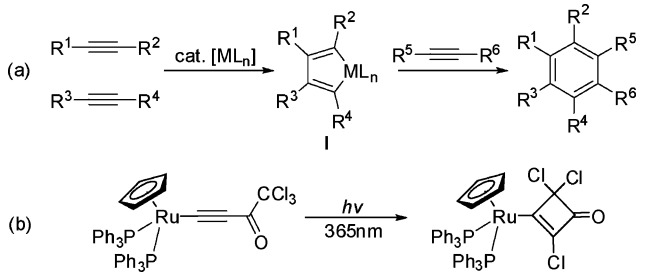
Intermolecular [2+2+2] cycloaddition reaction employing an air-stable ruthenium perchloro-cyclobutenonyl complex as a catalyst is reported. A series of internal alkynes were incorporated with dimethyl acetylene-dicarboxylate in a ratio of 1 : 2 to give various substituted benzenes in high yield and high chemoselectivity.

Introduction

[2+2+2] cycloaddition reaction of alkynes, diynes and oligoynes has become a vital and efficient atom-economical approach for the construction of poly-substituted carbo- and heterocycles.[1] However, chemoselectivity remains a challenge for cross intermolecular [2+2+2] cycloaddition of two or three different alkynes, especially the restriction for the use of substrates. Generally, terminal aliphatic alkynes or internal alkynes with activated functional groups are chosen for attaining better chemoselectivity.[1a] Several diynes and triynes have also been applied in the [2+2+2] cycloaddition,[2] generating extra rings on the final products.[1a] In both half[2c,3] and complete[2a,4] intermolecular [2+2+2] cycloaddition reactions, diarylacetylene was considered as an inefficient monoyne to react with the metallacycle intermediate **I** (see Scheme 1(a)). Low yield and poor selectivity have been reported occasionally even in the presence of excess diarylacetylene[4a,4b,5] Only few reports describe the [2+2+2] cycloaddition of multialkynes, linked by aromatic-fragments to give polycyclic products.



Scheme 1 (a) Complete intermolecular [2+2+2] cycloaddition; (b) complex **1** prepared from photoisomerization.

Many polycyclics, such as phenyl-, naphthyl- or thienyl-substituted benzenes, have attracted a great deal of attention due to their versatile applications in material science[6] and polymer chemistry.[6i,7] Their configurational effect have also been intensively investigated.[8] Moreover, these polycyclics are also employed as precursors to synthesize triphenylenes that are widely utilized in liquid crystal.[9]

It is also noteworthy that synthesis of the 1,2-diarylbenzene was commonly carried out under inert atmosphere by using functionalized substrates,[10] since air-tolerant [2+2+2] cycloaddition reaction was rare.[11] Therefore, searching for catalysts for cycloaddition to be used in air is of great interest.[12] Herein, we report facile one-pot, cross intermolecular [2+2+2] cycloaddition of 2 equiv. of DMAD (**2**, dimethyl acetylene-dicarboxylate) with 1 equiv. of various biaryl alkynes catalyzed by CpRu(PPh$_3$)$_2$(C$_4$Cl$_3$O) (**1**) (see Table 1) under mild conditions in air. The reaction gave desired products with high yield and with high chemoselectivity.

Results and discussion

The half sandwiched Ru(II) complex **1** bearing a cyclobutenonyl was synthesized *via* a solid state photo-induced isomerization of a ruthenium trichloroacetyl acetylide complex Cp(PPh$_3$)$_2$RuC≡CC(=O)CCl$_3$ (Scheme 1(b)).[13] Complex **1** is stable in common organic solvents under aerated as well as moisturized conditions. To investigate the 2 : 1 cross trimerization of **2** with various internal alkynes catalyzed by **1**, 3-hexyne (**3a**) was first examined. The reaction was conducted in C$_6$H$_6$ at 70 °C in air with a ratio of **2** : **3a** = 1 : 1. The cross product **4a** was isolated in 91% yield with high chemoselectivity in 2 h. Cyclotrimerization of **2** to yield hexamethyl mellitate **13** was known to be much faster than the 2 : 1 cross trimerization. This decreased the yield of the desired product, especially in the case of internal or diaryl alkynes as the third monoyne.[4a,4b,5,14] By changing the ratio of **2** : **3a** to 1 : 2.5, the homocyclo-trimerization of **2** was almost completely suppressed resulting in a 92% yield of **4a**. Aryl compound **4b** was synthesized under similar conditions from **3b** in 89% yield. Excess alkyne was readily recovered by flash column chromatography and recycled. The reaction of **2** with diphenyl acetylene **3c**, affording **4c**, displays effective suppression of **13**, as the portion of **3c** was increased at 70 °C. Notably, at 25 °C, **13** was obtained only in 2% yield. Use

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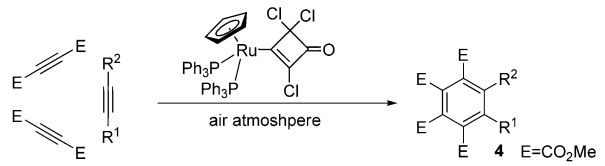
Table 1 Cross [2+2+2] cycloaddition by complex **1**[a]



3a: R^1=R^2=Et **3d**: R^1=R^2=2-thienyl **3g**: R^1=R^2=1-naphthy
3b: Me, *p*-$C_6H_4NO_2$ **3e**: R^1=R^2=3-thienyl **3h**: Ph, P(O)Ph_2
3c: R^1=R^2=Ph **3f**: Ph, 1-naphthyl **3i**: R^1=R^2=*p*-C_6H_4(CHO)

Entry	Alkyne and Condition	Ratio[b](**2**:**3**)	Time (h)	Product	Yield[c] (%)
1	**3a**, C_6H_6, 70 °C	1 : 1	2	**4a**	91(4)
2	**3a**, C_6H_6, 70 °C	1 : 2.5	2	**4a**	92
3	**3b**, C_6H_6, 70 °C	1 : 2.5	2.5	**4b**	89
4	**3c**, C_6H_6, 70 °C	1 : 0.5	3	**4c**	62(25)
5	**3c**, C_6H_6, 70 °C	1 : 2	3	**4c**	81(12)
6	**3c**, C_6H_6, 70 °C	1 : 4	3	**4c**	92(5)
7	**3c**, C_6H_6, 25 °C	1 : 4	144	**4c**	96(2)
8	**3c**, THF, 70 °C	1 : 4	22	**4c**	92(2.5)
9	**3c**, THF, reflux	1 : 4	5.5	**4c**	83(2.5)
10	**3d**, C_6H_6, 70 °C	1 : 4	3	**4d**	92
11	**3e**, C_6H_6, 70 °C	1 : 4	3	**4e**	91
12	**3f**, C_6H_6, 70 °C	1 : 6	4	**4f**	88(2.5)
13	**3g**, C_6H_6, 70 °C	1 : 7.5	4	**4gs**, **4ga** (0.8 : 1)[d]	88(6)
14	**3g**, C_6H_6, 25 °C	1 : 5	84	**4gs**, **4ga** (0.5 : 1)	90(7)
15	**3g**, C_6H_6, 8 °C	1 : 1.3	744	**4gs**, **4ga** (0.44 : 1)	87(8)
16	**3h**, C_6H_6, 70 °C	1 : 7.5	4	**4h**	71
17	**3i**, THF, 70 °C	1 : 5	22	**4i**	90

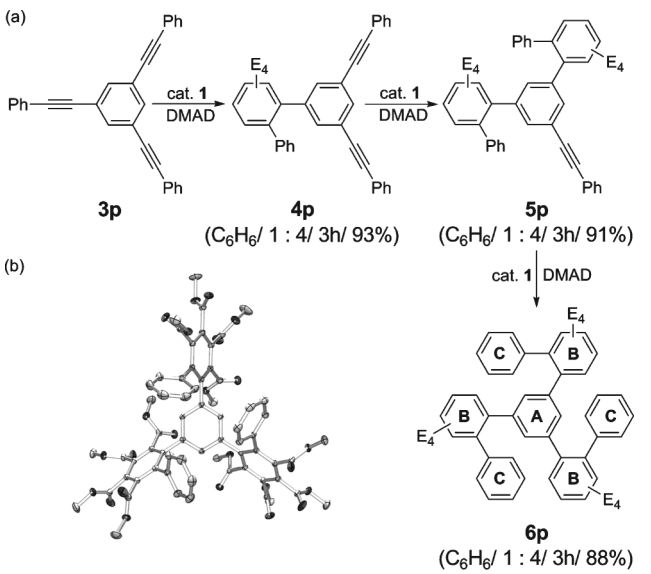
[a] A mixture of **1** (0.006 mmol), **2** (0.116 mmol) and alkyne in the selected solvent was stirred at the specified temperature. [b] Excess alkynes could be readily recovered unchanged by flash column and recycled. [c] Isolated yields based on **2** (yield of **13** in parentheses). [d] Compounds **4gs** and **4ga** are *syn*- and *anti*-form, respectively.

of THF instead of C_6H_6, could also decrease the yield of **13**.[15] As shown in Table 1, elevating the reaction temperature would speed up the reaction. Furthermore, when the two dithienylacetylenes **3d** and **3e** were employed, *o*-dithienylbenzenes **4d** and **4e**, respectively, were obtained in >90% yield without giving **13**. In the reaction of dinaphthylacetylene, the steric hindrance was known to restrict the access of alkyne to the metallacycle intermediate **I** (Scheme 1(a)), resulting in much lower yield of *o*-dinaphthylbenzene.[2c,8a] Our reaction of naphthylphenylacetylene **3f** generated **4f** in 88% yield. For the bulkier dinaphthylacetylene **3g** giving **4g**, a higher ratio of **3g** was required to suppress the formation of **13**. Alternatively, lower temperature could be employed to effectively reduce the use of **3g**. The catalytic activity of **1** remained effective at 8 °C though the reaction took longer, while it ceased at ~0 °C.

Product **4g** comprises *syn* and *anti* isomers,[8f] for which the selectivity is found to be temperature dependent. The *syn*/*anti* ratio varied from 0.44 : 1 to 0.80 : 1 as the temperature was raised from 8 °C to 70 °C. Such an increase of *syn*-form at higher temperature might be due to higher thermal energy, thus overcoming the steric repulsion for the *syn*-conformation. Separation of *anti* and *syn* isomers was readily accomplished by sequential recrystallizations. Structures of both isomers have been confirmed by single crystal X-ray diffraction analysis (See ESI†). Also, alkynylphosphine oxide **3h** was used to give **4h** in 71% yield. Reasonable formyl group tolerance was observed in the reaction of di(4-formylphenyl)acetylene **3i**, giving **4i** in 90% yield.

Table 2 lists results of the cycloaddition reaction of five diyne substrates **3j–3n** with **2**. For **3j–3l**, the consecutive cycloadditions were carried out separately to give the aryl alkynes **4j–4l**. This reaction exhibits complete selectivity in the presence of excess diynes to afford compounds **4** with four aromatic rings. After running flash column to isolate the intermediates, then **5j–5l** were synthesized, respectively, by an additional step. **5j–5l** appear as white solids and could be purified by decanting the mixture solution due to their poor solubility. For **3m** and **3n** possessing cumulative triple bonds, the cycloaddition was achieved only for the first triple bond, giving **4m** and **4n**, respectively. The steric hindrance prohibits the second cycloaddition reaction.

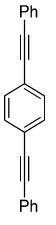
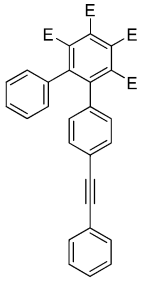
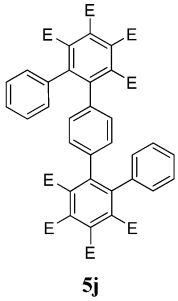
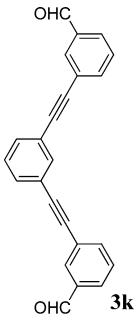
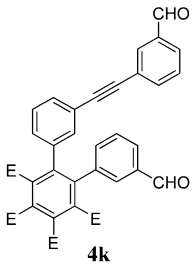
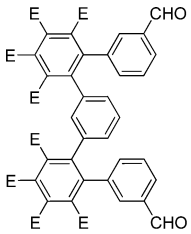
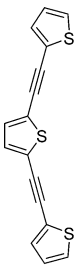
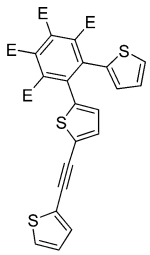
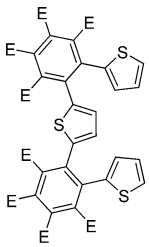
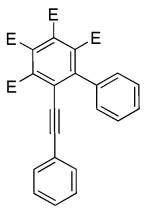
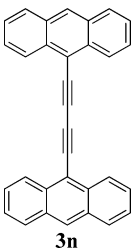
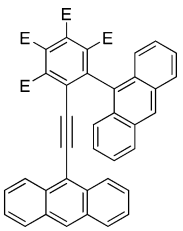
The three-step cycloadditions of the triyne compound **3p** with **2** were all carried out in the presence of excess **3p** (Scheme 2(a)). All three triple bonds in **3p** were transformed to aryl fragments with excellent selectivity. Trimerization of **2** was not observed during the synthesis of **4p** and **5p**, possibly due to their multiple triple bonds, which increases the probabilities of alkynes to approach the metallacycle intermediate **I**. Ultimately, cycloaddition of **5p** with **2** gave the pinwheel-like compound **6p** in good yield and selectivity. (See Scheme 2) Poor solubility of **6p** in benzene also simplified the purification process. The structure of **6p** determined by an X-ray diffraction analysis exhibits C_3-symmetry with the threefold axis passing through the central ring, A. The average dihedral angle between A and the ester-substituted ring, B, is *ca.* 60°; and that between B and the adjacent terminal ring, C, is *ca.* 70°. In the 3D framework of **6p**, as shown in Scheme 2(b), a tetrahedral cavity is formed by three C rings and one A ring.



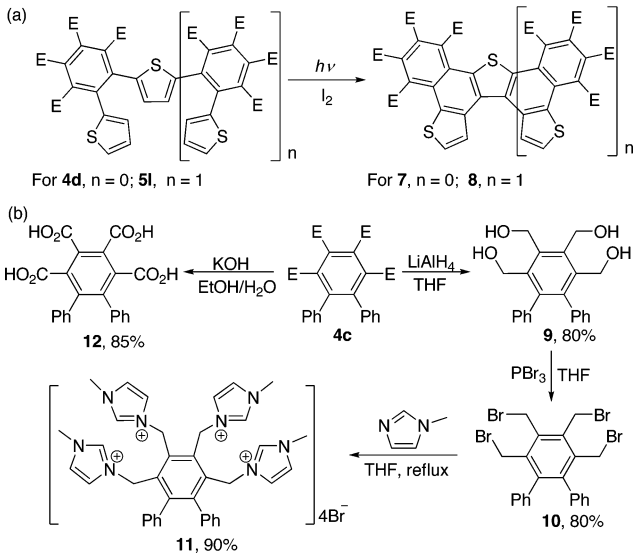
Scheme 2 (a) Synthesis of the pinwheel molecule **6p** by a three-step trimerization. Reaction conditions are shown in the parentheses (solvent/ratio (**2** : **3p**, **4p** or **5p**)/reaction time/yield); (b) X-ray crystal structure of **6p** (the gray and black balls represent C and O atoms, respectively).

Several functionalization reactions aiming at expanding the scope of various polycyclics were also accomplished. As shown in Scheme 3(a), photocyclizations of **4d** and **5l** were then carried out in the presence of I_2 to afford the aromatic compounds **7** and **8**, respectively. The structure of **7** was also determined by an X-ray diffraction study (see ESI†). Yellow solid compound **8**

Table 2 Sequential cross [2+2+2] cycloaddition of diyne by complex **1** at 70 °C. Reaction conditions are shown in the parentheses (solvent/ratio (**2** : **3** or **4**)/reaction time/yield)[a]

Diyne	**4**	**5**
 **3j**	 **4j** (C_6H_6/ 1 : 4/ 3h/ 90%)	 **5j** (C_6H_6/ 1 : 5/ 3h/ 88%)
 **3k**	 **4k** (C_6H_6/ 1 : 3/ 4h/ 80%)	 **5k** (C_6H_6/ 1 : 3/ 4h/ 77%)
 **3l**	 **4l** (C_6H_6/ 1 : 4/ 4h/ 91%)	 **5l** (C_6H_6/ 1 : 4/ 5h/ 87%)
 **3m**	 **4m** (C_6H_6/ 1 : 3/ 4h/ 92%)	—
 **3n**	 **4n** (THF/ 1 : 5/ 20h/ 83%)	—

[a] Isolated yields based on DMAD used.



Scheme 3 (a) Photocyclization reaction of **4d** and **5l**; (b) functionalization reactions of **4c**.

exhibits intense fluorescence (Φ_p ~ 0.35) maximized at 455 nm in *e.g.* CH_3CN. Besides, the reaction of **4c** with $LiAlH_4$ in THF gave the tetrahydroxymethyl compound **9**, and further bromination by PBr_3 afforded the tetra(bromomethyl)terphenyl **10**. Treatment of this tetrabenzyl bromide with 1-methylimidazole in THF under reflux, afforded the imidazolium bromide **11** in high yield. Also, hydrolysis of **4c** in the presence of KOH gave the tetracarboxylic acid **12** in good yield. These straightforward reactions pave the way to a rather broad variety of new polycyclics.

Conclusion

In summary, the air-stable complex [Ru]-C_4Cl_3O (**1**) efficiently catalyzes the 2 : 1 intermolecular [2+2+2] cyclo-additions of DMAD and various internal alkynes to give aromatic compounds with dual substituents at the *ortho* position. This catalytic reaction could be carried out in solvents of reagent grade and exhibits high yield in air. Temperature control could decrease the amount of excess alkyne required and achieve high chemoselectivity. Cycloaddition reactions of multialkynes are also achieved by **1**, affording assorted polycyclic aromatic compounds. These facile, one-pot reactions thus pave an avenue *en route* to synthesize a broad spectrum of polycyclics *via* an atom-economical approach.

Experimental section

General procedures

The [2+2+2] cycloaddition reactions were performed in air. All reagents were obtained from commercial suppliers. DMAD (dimethyl acetylenedicarboxylate) was purified by dissolving in C_6H_6, washed with $NaHCO_3$, H_2O, dried over Na_2SO_4, filtered, evaporated and distilled under vacuum. The C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded using a Thermo Finnigan LCQ Advantage (ESI) and Finnigan TSQ 700 spectrometers (EI). NMR spectra were recorded on a Bruker AVANCE 400 instrument at 400 MHz (^1H), 162.0 MHz (^{31}P), or 100.6 MHz (^{13}C) using $SiMe_4$ or 85%

H_3PO_4 as a standard or an Avance 500 FT-NMR spectrometers. Alkynes **3b**,[16] **3d**,[17] **3e**,[17] **3f**,[18] **3g**,[17] **3h**,[19] **3i**,[17] **3j**,[18] **3k**,[20] **3l**,[21] **3m**,[17] **3n**[22] and **3p**[23] were prepared according to the literatures.

General procedure for 2 : 1 cross intermolecular [2+2+2] cycloaddition

A typical procedure is described for **4c**. To a mixture of **1** (5 mg, 0.006 mmol), DMAD (16.5 mg, 0.116 mmol), and diphenylacetylene (82.7 mg, 0.464 mmol) in C_6H_6 (3 mL) was heated to 70 °C for 3 h. Progress of the reaction was monitored by TLC, until complete consumption of DMAD. After all DMAD was consumed, C_6H_6 was removed by a rotary evaporator and the residue was passed through silica gel flash column chromatography eluted with EA and hexanes (1 : 5). Generally, the excess alkynes would be eluted first, following by the cycloaddition products. The excess alkynes could be recovered unchanged and recycled.

4a. ^{1}H NMR (δ, $CDCl_3$): δ = 3.86 (s, 6H, OCH_3), 3.81 (s, 6H, OCH_3), 2.70 (q, J = 7.5 Hz, 4H; CH_2), 1.17 (t, J = 7.5 Hz, 6H, CH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 168.0, 166.7, 143.5, 135.0, 129.1, 53.0, 52.7, 23.6, 15.4; EI-MS (20 eV) m/z: 336.13. Anal. Calcd for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 59.04; H, 6.11.

4b. ^{1}H NMR (δ, $CDCl_3$): δ = 8.27 (d, J = 8.5 Hz, 2H, Ph), 7.34 (d, J = 8.5 Hz, 2H, Ph), 3.90 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 2.07 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.3, 166.5, 166.2, 166.0, 147.8, 146.6, 143.8, 140.9, 137.5, 135.3, 134.7, 133.1, 131.1, 130.1, 53.2, 53.2, 53.0, 52.6, 17.9; EI-MS (20 eV) m/z: 445.1. Anal. Calcd for $C_{21}H_{19}O_{10}$: C, 56.63; H, 4.30. Found: C, 56.27; H, 4.21.

4c. ^{1}H NMR (δ, $CDCl_3$): δ = 7.12 (m, 6H, Ph), 6.94 (m, 4H, Ph), 3.88 (s, 6H, OCH_3), 3.45 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.3, 166.3, 142.5, 136.6, 135.5, 132.1, 132.0, 131.9, 130.0, 128.0, 127.8, 53.1, 52.4; EI-MS (20 eV) m/z: 462.13. Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53; H, 4.80. Found: C, 67.55; H, 4.82.

4d. ^{1}H NMR (δ, $CDCl_3$): δ = 7.27 (m, 2H), 6.88 (m, 2H), 6.83 (m, 2H), 3.86 (s, 6H, OCH_3), 3.57 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, 25 °C): δ = 166.9, 165.9, 136.6, 130.6, 129.4, 128.2, 126.4, 124.8, 124.0, 53.3, 52.7; EI-MS (20 eV) m/z: 474.0. Anal. Calcd for $C_{22}H_{18}O_8S_2$: C, 55.69; H, 3.82. Found: C, 55.60; H, 3.88.

4e. ^{1}H NMR (δ, $CDCl_3$): δ = 7.10 (dd, J = 3.0, 5.0 Hz, 2H), 6.98 (dd, J = 1.3, 3.0 Hz, 2H), 6.60 (dd, J = 1.3, 5.0 Hz, 2H), 3.85 (s, 6H, OCH_3), 3.54 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.4, 166.1, 137.9, 136.4, 135.7, 129.9, 128.4, 125.1, 124.7, 53.1, 52.6; EI-MS (20 eV) m/z: 474.0. Anal. Calcd for $C_{22}H_{18}O_8S_2$: C, 55.69; H, 3.82. Found: C, 55.79; H, 3.90.

4f. ^{1}H NMR (δ, $CDCl_3$): δ = 7.66 (m, 2H, Ph), 7.36–7.25 (m, 4H, Ph), 7.09 (m, 1H, Ph), 6.96–6.92 (m, 3H, Ph), 6.80 (m, 2H, Ph), 3.90 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.15 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.4, 166.8, 166.4, 166.3, 143.6, 141.3, 136.5, 136.2, 135.6, 134.0, 132.8, 131.7, 131.5, 130.6, 130.1, 129.1, 128.4, 128.2, 128.1, 127.9, 127.5, 127.3, 127.1, 126.0, 125.9, 125.8, 124.4, 53.2, 53.2, 52.5, 52.2; EI-MS (20 eV) m/z: 512.2. Anal. Calcd for $C_{30}H_{24}O_8$: C, 70.31; H, 4.72. Found: C, 70.52; H, 4.88.

4gs (*syn*-form). ^{1}H NMR (δ, $CDCl_3$): δ = 7.49–7.46 (m, 6H, Ph), 7.17–7.13 (m, 4H, Ph), 7.09–7.03 (m, 4H, Ph), 3.90 (s, 6H, OCH_3), 3.14 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 166.9, 166.5, 142.5, 136.5, 133.8, 132.7, 130.9, 130.8, 128.6, 128.2, 127.6, 126.1, 125.5, 125.4, 124.0, 53.2, 52.2; EI-MS (20 eV) m/z: 562.16. Anal. Calcd for $C_{34}H_{26}O_8$: C, 72.59; H, 4.66. Found: C, 72.60; H, 4.67.

4ga (*anti*-form). ^{1}H NMR (δ, $CDCl_3$): δ = 7.62–7.60 (m, 2H, Ph), 7.49–7.43 (m, 4H, Ph), 7.40–7.34 (m, 4H, Ph), 6.93–6.86 (m, 4H, Ph), 3.90 (s, 6H, OCH_3), 3.15 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 166.8, 166.4, 142.5, 136.3, 133.6, 132.6, 131.6, 130.7, 128.3, 127.8, 126.8, 126.0, 125.9, 125.6, 124.1, 53.2, 52.2; EI-MS (20 eV) m/z: 562.16. Anal. Calcd for $C_{34}H_{26}O_8$: C, 72.59; H, 4.66. Found: C, 72.60; H, 4.67.

***4h*.** ^{1}H NMR (δ, $CDCl_3$): δ = 7.28–6.84 (m, 15H, Ph), 3.56 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.08 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 166.6, 166.6, 166.4, 165.1, 140.0, 139.9, 137.5, 137.5, 135.3, 134.6, 134.4, 134.4, 134.4, 133.0, 133.0, 132.9, 132.9, 132.5, 132.4, 132.2, 131.6, 131.6, 129.6, 129.1, 128.0, 53.3, 53.2, 52.8, 52.7; EI-MS (20 eV) m/z: 586.14. Anal. Calcd for $C_{32}H_{27}O_9P$: C, 65.53; H, 4.64. Found: C, 65.99; H, 4.82.

4i. ^{1}H NMR (δ, $CDCl_3$): δ = 9.88 (s, 2H, CHO), 7.64 (d, J = 8.0 Hz, 4H, Ph), 7.10 (d, J = 8.0 Hz, 4H, Ph), 3.88 (s, 6H, OCH_3), 3.46 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 191.5, 166.5, 165.8, 142.4, 140.9, 135.4, 135.3, 131.0, 130.0, 129.1, 53.3, 52.7; EI-MS (20 eV) m/z: 518.12. Anal. Calcd for $C_{28}H_{22}O_{10}$: C, 64.86; H, 4.28. Found: C, 65.34; H, 4.52.

4j. ^{1}H NMR (δ, $CDCl_3$): δ = 7.43 (m, 2H, Ph), 7.19 (m, 2H, Ph), 6.99–6.97 (m, 3H, Ph), 6.87–6.85 (m, 3H, Ph), 6.80–6.79 (m, 2H, Ph), 6.71 (m, 2H, Ph), 3.53 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.18 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.2, 167.2, 166.2, 166.2, 142.4, 141.8, 136.7, 136.4, 135.7, 135.4, 134.2, 131.6, 130.9, 130.3, 130.2, 129.4, 129.3, 128.3, 128.4, 127.8, 122.9, 122.6, 90.2, 88.9, 53.2, 53.2, 52.6, 52.5; EI-MS (20 eV) m/z: 562.16. Anal. Calcd for $C_{34}H_{26}O_8$: C, 72.59; H, 4.66. Found: C, 72.68; H, 4.77.

5j. ^{1}H NMR (δ, $CDCl_3$): δ = 7.19–7.06 (m, 6H, Ph), 6.91 (d, J = 7.6 Hz, 2H, Ph), 6.80 (d, J = 7.6 Hz, 2H, Ph), 6.76 (d, J = 15.4 Hz, 4H, Ph), 3.85 (bs, 12H, OCH_3), 3.54 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.19 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.1, 167.0, 166.7, 166.2, 166.2, 166.1, 166.1, 142.4, 142.4, 141.6, 141.4, 136.5, 136.3, 136.2, 136.1, 135.7, 135.6, 130.2, 130.2, 129.9, 129.7, 129.4, 129.2, 128.9, 127.9, 127.8, 127.6, 127.6, 53.4, 53.1, 52.6, 52.4, 52.4; EI-MS (20 eV) m/z: 846.22. Anal. Calcd for $C_{46}H_{38}O_{16}$: C, 65.25; H, 4.52. Found: C, 65.17; H, 4.55.

4k[24]**.** ^{1}H NMR (δ, $CDCl_3$): δ = 10.01–9.85 (2H, CHO), 8.01–7.11(12H, Ph), 3.90–3.45 (12H, OMe); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 191.4(CHO), 166.7–165.9 (CO_2Me), 141.5–128.0 (Ph), 53.4–52.5 (OMe); EI-MS (20 eV) m/z: 618.59. Anal. Calcd for $C_{36}H_{26}O_{10}$: C, 65.25; H, 4.52. Found: C, 65.17; H, 4.55.

5k[24]**.** ^{1}H NMR (δ, C_6D_6): δ = 9.70–9.49 (2H, CHO), 7.63–6.32 (12H, Ph), 3.62–3.06 (12H, OMe); ESI MS for [M+Na] m/z: 925.5. Anal. Calcd for $C_{48}H_{38}O_{18}$: C, 63.86; H, 4.24. Found: C, 63.99; H, 4.33.

4l. ^{1}H NMR (δ, $CDCl_3$): δ = 7.31 (dd, J = 1.1, 5.1 Hz, 1H), 7.27 (dd, J = 1.1, 5.1 Hz, 1H), 7.21 (dd, J = 1.1, 3.6 Hz, 1H), 7.03

(d, J = 3.7 Hz, 1H), 6.96 (dd, J = 3.6, 5.1 Hz, 1H), 6.91 (dd, J = 3.6, 5.1 Hz, 1H), 6.85 (dd, J = 1.1, 3.6 Hz, 1H), 6.71 (d, J = 3.7 Hz, 1H), 3.85 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.7, 166.7, 165.7, 138.4, 136.7, 136.6, 136.5, 136.0, 135.5, 132.3, 131.4, 130.8, 129.5, 129.3, 128.7, 128.5, 127.9, 127.2, 126.6, 125.8, 122.4, 87.8, 85.5, 52.8, 52.7, 52.6; EI-MS (20 eV) m/z: 580.03. Anal. Calcd for $C_{28}H_{20}O_8S_3$: C, 57.92; H, 3.47. Found: C, 57.99; H, 3.52

5l. ^1H NMR (δ, $CDCl_3$): δ = 7.30 (d, J = 4.8 Hz, 2H), 6.91 (dd, J = 3.7, 4.8 Hz, 2H), 6.75 (m, 2H), 6.58 (s, 2H), 3.85 (s, 12H, OCH_3), 3.65 (s, 6H, OCH_3), 3.56 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 166.7, 166.5, 165.7, 138.9, 136.7, 136.5, 136.5, 136.0, 135.5, 130.7, 130.5, 129.4, 128.9, 128.0, 126.6, 53.2, 52.9, 52.7; EI-MS (20 eV) m/z: 864.09. Anal. Calcd for $C_{40}H_{32}O_{16}S_3$: C, 55.55; H, 3.73. Found: C, 55.60; H, 3.78.

4m. ^1H NMR (δ, $CDCl_3$): δ = 7.42–7.35 (m, 5H, Ph), 7.22 (m, 3H, Ph), 7.08 (m, 2H, Ph), 3.97 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 166.6, 166.5, 165.9, 165.6, 145.3, 136.9, 136.6, 135.1, 131.6, 130.0, 129.8, 129.2, 129.1, 128.5, 128.2, 127.8, 124.8, 121.8, 100.6, 84.5, 53.1, 53.1, 52.9, 52.4; EI-MS (20 eV) m/z: 486.13. Anal. Calcd for $C_{28}H_{22}O_8$: C, 69.13; H, 4.56. Found: C, 70.17; H, 4.66.

4n. ^1H NMR (δ, acetone-d_6): δ = 8.87 (s, 1H, Ph), 8.40 (s, 1H, Ph), 8.20 (m, 2H, Ph), 7.87 (m, 2H, Ph), 7.57 (m, 2H, Ph), 7.53–7.44 (m, 4H, Ph), 7.38 (m, 2H, Ph), 7.36 (m, 2H, Ph), 7.00 (m, 2H, Ph), 4.05 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.02 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 167.0, 166.0, 166.0, 142.8, 137.2, 137.2, 132.8, 131.2, 130.5, 130.3, 130.3, 130.0, 129.0, 128.4, 128.3, 128.3, 127.3, 126.6, 126.6, 126.0, 125.9, 125.5, 115.2, 97.3, 94.8, 53.5, 53.4, 53.2; EI-MS (20 eV) m/z: 686.19.

4p. ^1H NMR (δ, $CDCl_3$): δ = 7.48–7.45 (m, 5H, Ph), 7,32–7.30 (m, 6H, Ph), 7.19–7.17 (m, 3H, Ph), 7.06 (bs, 2H, Ph), 7.70–6.98 (m, 2H, Ph), 3.88 (s, 6H, OCH_3), 3.56 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 166.9, 166.8, 166.0, 142.5, 140.6, 137.2, 135.9, 135.6, 135.2, 133.6, 131.8, 131.5, 130.4, 130.2, 129.2, 128.5, 128.3, 127.9, 127.8, 123.2, 122.6, 90.3, 87.7, 53.1, 52.6, 52.4; EI-MS (20 eV) m/z: 662.19. Anal. Calcd for $C_{42}H_{30}O_8$: C, 76.12; H, 4.56. Found: C, 76.20; H, 4.59.

5p. ^1H NMR (δ, $CDCl_3$): δ = 7.37–7.21 (m, 8H, Ph), 7.09 (t, J = 7.4 Hz, 2H, Ph), 6.95 (d, J = 7.3 Hz, 2H, Ph), 6.87 (d, J = 1.5 Hz, 2H, Ph), 6.56 (t, J = 1.5 Hz, 2H, Ph), 6.37 (d, J = 2.7 Hz, 2H, Ph), 3.85 (s, 12H, OCH_3), 3.61 (s, 6H, OCH_3), 3.42 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 167.1, 166.6, 166.2, 142.3, 140.3, 136.8, 136.1, 135.8, 135.5, 131.9, 131.6, 130.5, 130.3, 130.0, 129.5, 129.2, 128.5, 128.3, 128.2, 127.8, 122.7, 122.7, 90.1, 87.8, 53.2, 53.1, 52.9, 52.4; EI-MS (20 eV) m/z: 946.25. Anal. Calcd for $C_{54}H_{42}O_{16}$: C, 68.49; H, 4.47. Found: C, 68.51; H, 4.59.

6p. ^1H NMR (δ, $CDCl_3$): δ = 7.29 (3H, Ph), 7.20 (6H, Ph), 6.49 (s, 3H, Ph), 6.34 (6H, Ph), 3.83 (s, 18H, OCH_3), 3.66 (s, 9H, OCH_3), 3.37 (s, 9H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 167.0, 166.2, 166.1, 166.1, 142.0, 139.6, 136.3, 136.2, 136.1, 135.9, 130.7, 130.1, 130.1, 129.4, 128.2, 127.4, 53.2, 52.4; EI-MS (20 eV) m/z: 1230.3. Anal. Calcd for $C_{66}H_{54}O_{24}$: C, 64.39; H, 4.42. Found: C, 64.55; H, 4.45.

General procedure for photocyclization of 4d and 5l

To a mixture of **4d** (100 mg, 0.21 mmol) (or **5l**, 100 mg, 0.12 mmol) and I_2 (10 mol%) in C_6H_6 (15 ml) was exposed to light from six 8 W mercury lamps (365 nm) for 24 h (80 h for **5l**) under air atmosphere. Solvent was removed and the product was recrystallized from CH_2Cl_2 and hexanes to yield a yellow solid as final product.

7. (73 mg, 73%): ^1H NMR (δ, $CDCl_3$): δ = 7.88–7.73 (m, 4H), 4.11 (s, 6H, OCH_3), 3.90 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, C_6D_6): δ = 168.5, 166.5, 136.8, 132.3, 132.2, 129.3, 127.2, 125.3, 122.3, 53.6, 53.5; EI-MS (20 eV) m/z: 472.03. Anal. Calcd for $C_{22}H_{16}O_8S_2$: C, 55.92; H, 3.41. Found: C, 55.99; H, 3.57.

8. (71 mg, 71%): ^1H NMR (δ, $CDCl_3$): δ = 8.04 (d, J = 5.5 Hz, 2H), 7.70 (d, J = 5.5 Hz, 2H), 4.18 (s, 6H, OCH_3), 4.04 (s, 6H, OCH_3), 3.86 (s, 12H, OCH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 168.6, 168.1, 166.4, 166.3, 135.6, 134.5, 133.9, 132.7, 131.6, 131.0, 128.9, 128.6, 127.7, 126.9, 124.7, 124.4, 54.3, 53.7, 53.4; EI-MS (20 eV) m/z: 860.05. Anal. Calcd for $C_{40}H_{28}O_{16}S_3$: C, 55.81; H, 3.28. Found: C, 55.80; H, 3.29.

9. To a suspension of $LiAlH_4$ (0.16 g, 4.2 mmol) in anhydrous THF (10 mL), a solution of tetraester **4c** (0.25 g, 0.54 mmol) in THF (10 ml) was added at 0 °C under N_2. The mixture was stirred for 8 h at RT, followed by hydrolysis using 2.0 N H_2SO_4. After removing THF on a rotary evaporator, the residue was extracted with CH_2Cl_2. The extract was washed by brine and dried over $MgSO_4$, and the solvent was removed to give the product as a white solid. (0.15 g, 80%). ^1H NMR (δ, CD_3OD): δ = 7.10–6.98 (m, 10H, Ph), 5.05 (s, 4H, CH_2), 4.50 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR (δ, CD_3OD): δ = 144.0, 141.3, 140.7, 138.9, 131.5, 128.2, 127.3, 60.5, 59.2; EI-MS (20 eV) m/z: 350.15 Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C,75.01; H, 6.34.

10. Phosphorus tribromide (80 µl, 0.86 mmol) was added dropwise to a solution of **9** (50 mg, 0.14 mmol) in anhydrous THF (10 mL) at 0 °C. After stirring for 2 h at RT, the mixture was treated with water and then removed THF by on a rotary evaporator. The residue was extracted with CH_2Cl_2. The extract was washed by brine and dried over $MgSO_4$, and the solvent was removed. After chromatography on silica gel (CH_2Cl_2 : hexanes = 1 : 10), **10** was afforded as yellow solid (77 mg, 90%). ^1H NMR (δ, $CDCl_3$, 25 °C): δ = 7.16–7.05 (m, 10H; Ph), 4.95 (s, 4H; CH_2), 4.37 (bs, 4H; CH_2); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): δ = 144.6, 137.6, 136.7, 136.4, 129.5, 127.6, 127.2, 28.3, 25.5; EI-MS (20 eV) m/z: 597.81 Anal. Calcd for $C_{22}H_{18}Br_4$: C, 43.89; H, 3.01. Found: C, 43.55; H, 2.96.

11[25]. A mixture of **10** (40 mg, 0.066 mmol) and 1-methylimidazole (23 µL, 0.29 mmol) in anhydrous THF was stirred and heated under reflux for 22 h. The precipitate was filtered, washed by anhydrous THF (3 × 10 mL), and dried under vacuum to afford **11** as a white solid. (56 mg, 90%). ^1H NMR (δ, DMSO): δ = 9,.33 (s, 2H; NCHN), 9.27 (s, 2H; NCHN), 7.77, 7.73, 7.55 and 7.47 (s, 4 × 2H, NCHCHN), 7.16 (m, 4H, Ph), 7.06 (m, 6H, Ph), 5.80 (s, 4H, NCH_2), 5.30 (s, 4H, NCH_2), 3.91 (s, 6H, CH_3), 3.81 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR (δ, DMSO): δ = 146.9, 137.3, 136.5, 136.5, 134.0, 133.3, 128.8, 127.7, 127.5, 127.1, 123.3, 123.1, 122.4, 47.9, 47.2, 35.9, 35.6.

12. To an aqueous solution of $KOH_{(aq)}$ (20 mg (0.36 mmol) in water (10 mL)), a solution of tetraester **4c** (10 mg, 0.022 mmol) in ethanol (20 mL) was added at RT. The mixture was stirred and heated under reflux for 7 h. After evaporation of ethanol, the acid was precipitated by addition of 2 N H_2SO_4 until maximal precipitation has been obtained. (pH *ca.* 6). The solid was filtered, washed by water (3 × 5 mL), and dried under vacuum to afford **12** as white solid. (7.5 mg, 85%). ^{1}H NMR (δ, DMSO): δ = 7.15–7.14 (m, 6H, Ph), 6.98–6.95 (m, 4H, CH_2); $^{13}C\{^1H\}$ NMR (δ, DMSO): δ = 167.4, 167.2, 140.8, 136.7, 135.0, 131.6, 129.4, 127.4.

Single-crystal X-ray diffraction analysis of 4gs, 4ga, 6p and 7. Single crystals of **4ga** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.20 × 0.10 × 0.15 mm^3 was glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube Mo KR radiation (T = 295 K). Exposure time was 5 s per frame. SADABS[26] (Siemens area detector absorption) absorption corrections were applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[27] program. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens.

Notes and references

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