Exploration of the Materials Science- and the Physiology-Oriented Chemistry of the sp-Carbon Rich Hydrocarbons, Allenes, Cumulenes and Acetylenes

アレン，クムレン，アセチレンの sp 炭素を活用した新規機能性材料及び生理活性物質の創出

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1. Introduction
1. Introduction

sp-Carbon atoms of unsaturated organic compounds, especially allene / cumulene and acetylene, are unique and these synthesis and reactivity have been reported in several reviews. Consecutive C=C bonds of allene or cumulene and C≡C bond of acetylene are contained in many organic functional materials and physiologically active substances (Fig. 1). For example, radialene and ketene dimer are expected to be used as organic electronics materials and dyes. Cumulene also draws attention as a material for synthesis of novel organometallic compound and functional polymer. On the other hand, 1,2,4-heptatriene-6-yn and 1,5-hexadiyne-3-ene are generally known as potent antitumor agents. Recently, various functional ene-yne-allene and enediyne precursors have been developed. In addition, several literatures reported metal catalyzed syntheses of physiologically active hetero rings from aminoallene. Despite the fact that the chemistry of these compounds has been studied fairly extensively, the rich chemistry of these unsaturated molecules is yet to be revealed. In the present study, I focused on the two aspects of charge-transfer reactions of allene / [3]cumulene with electron acceptor and development of physiologically active substances possessing allene or acetylene moiety.

Fig. 1 Organic functional materials and physiologically active substances associated with allene / cumulene and acetylene.
Allenes (propadienes) are the simplest cumulated diene and the central carbon is sp-hybridized. The synthesis and chemistry of allene have attracted attention because of the unique strained structure possessing axial chirality and interesting reactivity. Several literatures showed that allene derivatives are useful for syntheses of physiologically active substances, dye molecules and polymer molecules.\textsuperscript{14} In addition, cumulenes are the homologous series of hydrocarbons that contain three or more sequential double bonds sharing the sp-hybridized carbon atoms. The consecutive sp-hybridized carbon atoms of cumulene are very unique and may lead to a wide variety of reactions; particularly, the chemistry of [3]cumulenes (butatrienes) has been investigated.\textsuperscript{15} For example, a [3]cumulene possessing an electron withdrawing group such as Cl as a terminal group thermally dimerizes to a [4]radialene.\textsuperscript{16} Early studies showed that tetraphenyl[3]cumulene photodimerizes to a head-to-tail dimer at the terminal C=C bond of two molecules of the [3]cumulene.\textsuperscript{17} Recently, nickel-catalyzed cycloaddition of tetramethyl[3]cumulene yielded not only octamethyl[4]radialene but also dodecamethyl[6]radialene. On the other hand, tetraphenyl[3]cumulene, which is more stable than tetramethyl[3]cumulene, was unreactive even in the presence of a nickel(0) catalyst.\textsuperscript{18}

Firstly, I have investigated the charge-transfer reactions of tetraarylallene (1) / tetraarylcumulene (2) with tetracyanoethene (TCNE) (Fig. 2). The ethene, TCNE, was discovered in 1957 as the simplest of the symmetrical percyanoalkene.\textsuperscript{19} Not only was it found to be extremely reactive and to undergo a series of addition and substitution reactions, but also the forerunner of the cyano-based acceptor molecules known to date. It is well established that the π-orbitals of the alkene group in TCNE possess low-lying energies and thus TCNE may lead to a wide variety of reactions.\textsuperscript{20}

Secondly, I focused on DNA cleaving molecules possessing allene and acetylene. Natural ene-yne-allene and enediyne precursors such as calicheamicin\textsuperscript{7}, dynemicin\textsuperscript{8} and neocarzinostatin\textsuperscript{9} are known to be DNA cleaving molecules derived from bacteria. These precursors can undergo either Myers-Saito\textsuperscript{10} or Masamune-Bergman\textsuperscript{11} cyclization, with the produced diradical being able to abstract hydrogen from the phosphate backbone of DNA (Scheme 1).\textsuperscript{20} However, these precursors are toxic to not only tumor cells but also normal cells; therefore, they are not effective antitumor agents.\textsuperscript{21} Alternatively, ene-yne-allene and enediyne precursors with various functionalities have been designed and reported in several reviews.\textsuperscript{12} Early studies showed that an enediyne constrained in a 10-membered ring could easily undergo Bergman cyclization at room temperature. Following this, a water-soluble 10-membered ring enediyne possessing hydroxyl groups was prepared and found to undergo a Bergman cycloaromatization at 37 °C. It was also found to cleave double-stranded DNA.\textsuperscript{12(a)} A bicyclic enediyne was also synthesized. Although it was stable at room temperature, cyclization only occurred at elevated temperatures.\textsuperscript{12(b)} In addition, ene-yne-allenes and
enediynes possessing phototriggering functionalities have attracted attention. Recently, Suzuki and co-workers developed novel enediyne model compounds with photochemically removable protecting groups such as o-nitrobenzyl ester and ether. In this study, I report the synthesis of ene-yne-allene (3, 4) and enediyne precursors (5) (Fig. 2) possessing phototriggering functionality via a Norrish Type II reaction. In addition, I have extended the photochemistry of 3–5 and explored its use as novel DNA cleaving molecules.

![Chemical structures](image)

**Fig. 2** Major compounds in this study.

![Scheme 1](image)

**Scheme 1** Myers-Saito and Masamune-Bergman reactions.
2. Reactions of tetraaryallenes with tetracyanoethene (TCNE)
2. Reactions of tetraaryllenes with tetracyanoethene (TCNE)

Allene (propadiene) is the simplest cumulated diene and the central carbon is sp-hybridized. Recently, the chemistry of allene has attracted attention because of the usability for syntheses of hetero rings, dye molecules and polymer molecules. In this study, I have investigated the charge-transfer reactions of tetraaryllallenes with tetracyanoethene (TCNE), a strong electron-accepting molecule.

2.1 Syntheses

The synthesis of tetraaryllallene 1 was undertaken as shown in Scheme 2. Ethyl acetate was reacted with Grignard reagent 6 to give alcohol 7, which was treated with conc. HCl in MeOH to afford diarylethene 8. After the reduction of diaryl ketone 9 with NaBH₄, the condensation of alcohol 10 and ethene 8 with conc. HCl in AcOH afforded compound 11. The bromination of 11 followed by E2 elimination of compound 12 with KOH in EtOH gave tetraaryllallenes 1a–d (Fig. 3).

X-ray data of 1a:
empirical formula: C_{27}H_{30}, formula weight: 344.45,
crystal habit: needle, crystal system: monoclinic, space group: P2₁/c,
unit cell dimensions: a = 12.0653(2) Å, b = 8.22826(15) Å, c = 19.0740(4) Å,
β = 101.4288(7)°, V = 1856.06(6) Å³, Z = 4,
no. of observations = 3399, no. of variables = 244, reflection/parameter ratio = 13.93, 
R = 0.0423 (R = 0.0505, wR (all reflections) = 0.1052, 
GoF = 1.090.

Fig. 3 Crystal structure of tetraaryllallene 1a.
2.2 Reactions and the mechanism

![Scheme 3 The reaction of tetraarylallene 1 with TCNE.](image)

**Table 1 Yields of 13–15 formed by the reaction of tetraarylallene 1 with TCNE.**

<table>
<thead>
<tr>
<th>Allenes</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>13 (13')</th>
<th>14</th>
<th>15</th>
<th>1 (Starting material)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>3 h</td>
<td>trace&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>4 days</td>
<td>4</td>
<td>19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>8 days</td>
<td>17</td>
<td>22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a</td>
<td>CH₂Cl₂</td>
<td>40 °C</td>
<td>2 days</td>
<td>22</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a</td>
<td>CH₂Cl₂</td>
<td>40 °C</td>
<td>4 days</td>
<td>16</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a</td>
<td>THF</td>
<td>rt</td>
<td>2 days</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29–100&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1b</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>3 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87</td>
</tr>
<tr>
<td>1c</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>3 h</td>
<td>37 (45)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>trace&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1d</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>3 h</td>
<td>93</td>
<td>trace&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Because the yields were very small, it was difficult to measure <sup>1</sup>H-NMR spectra of these compounds. To confirm the production of these compounds, we measured exact masses on ESI-TOF-MS.

<sup>b</sup>The yields of 15a and starting material by the reaction in THF were estimated by the integrations of <sup>1</sup>H-NMR spectra of the reaction mixture. The yield of 15a was assumed to depend on the scale of the reaction mixture (see 7. Experimental).

<sup>c</sup>The yields of 13c and 13c' were estimated by the integrations of 2D-NMR spectra (H-H COSY, HMQC and HMBC) of the mixture of 13c and 13c'.

When tetraarylallene 1 was stirred with TCNE in CH₂Cl₂ at room temperature for 3 h, the solution color changed from colorless or yellow to dark purple to afford products 13 and 14 (Scheme 3, Table 1). The addition of TCNE to unsymmetrical allene 1c or 1d seems to form four-membered ring compound 13c, 13c’ and 13d by [2+2] cycloadition of the C=C bond of allene with TCNE. Because the dipole moment of allene 1d (5.124 D) is larger than that of 1c (2.104 D), based on molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)) (2,3, Table 2 and Fig. 10), allene 1d reacted with TCNE at the electron-rich C=C bond, affording products 13d, 14d, and 15a.
bond close to the methoxyphenyl groups and afforded only 13d. On the other hand, the reaction of symmetric 1a with TCNE for 3 h proceeded poorly and gave small amount of products 13a (Fig. 4) and 14a as colorless and blight red-violet color crystals, respectively. X-ray analysis shows that 14a was a novel tetracyclic compound containing two nitrogens (Fig 5) similar to a imidazo[1,5-a]pyridine. Several literatures show that imidazo[1,5-a]pyridine derivatives exhibit physiological activity and possess emission property (Fig. 6). In addition, nitrogen-containing tetra- or multi-cyclic compound such as azaazulene derivatives and azafullerene are also expected to use as dyes, electronic materials or antitumor agents. To produce 14a in good yield, I investigated terms of reaction time, temperature and solvent. In the case of the reaction at room temperature for 8 days, the yield of 14a increased from 4% (at room temperature for 3 h) to 22%. The reaction at 40 °C for 4 days also formed 14a in 25% yield. However, more than one by-product was obtained and these structures have yet to be revealed. The reaction in polar solvent such as THF at room temperature afforded a different product 15a. Compound 15a was determined to be a structural isomer of 1a by X-ray analysis (Fig. 7). Schemes 4 and 5 show the putative mechanisms for the formation of 14 and 15, respectively. Because 14 could not be formed in polar solvent such as THF, the reaction of 1 with TCNE was expected to occur through a radical mechanism. C=C Bond of allene 1 was assumed to react with cyano nitrogen of TCNE to give a diradical species [A], and then [A] reacted with another molecule of TCNE and converted to a new diradical species [B] as shown from Scheme 4. Dicyanocarbene was considered to be eliminated from [B], subsequently dimerized to TCNE. As a result of intramolecular nucleophilic attack in [C] and simultaneous loss of cyanide ion, a heterocyclic intermediate [D] was expected to be formed. The cationic intermediate [D] might suffer simple electrophilic substitution to give the tetracyclic compound 14. However, it is not clear from the current results whether the intermediates [A]–[D] were formed. The possibility of the formation of 14 through an ionic mechanism might also not be excluded. On the other hand, allene 1a could not react with TCNE in THF. In addition, 15a could not be yielded by the reaction of allene 1a in the absence of TCNE. Several literatures reported that heating or use of stronger acid or frustrated Lewis pairs (FLPs) yielded indene 15. The allene 1 was expected to be bonded at the central carbon atom with TCNE possessing a property as Lewis acid catalyst and form an ionic intermediate. The intermediate was assumed to cyclize and convert to bicyclic indene 15 as shown in Scheme 5.

X-ray data of 13a:
empirical formula: C_{13}H_{20}N_{4}, formula weight: 472.55,
crystal habit: needle, crystal system: triclinic, space group: P-1,
unit cell dimensions: a = 8.33641(15) Å, b = 11.3319(2) Å, c = 13.3288(2) Å, 
α = 93.3592(7)°, β = 98.8253(7)°, γ = 95.3809(7)°, V = 1235.33(4) Å³, Z = 2,
no. of observations = 4424, no. of variables = 334, reflection/parameter ratio = 13.25,
R = 0.0400 (3σ(1)), R (all reflections) = 0.0432, wR (all reflections) = 0.1064,
GoF = 1.096.

**Fig. 4** Crystal structure of compound 13a.
X-ray data of 14a:
empirical formula: C_{35}H_{19}N_{5}, formula weight: 509.55;
crystal habit: needle, crystal system: triclinic, space group: P-1,
unit cell dimensions: a = 8.6983(2) Å, b = 10.3312(3) Å, c = 14.5749(4) Å,
α = 101.8108(16)°, β = 93.5453(16)°, γ = 101.5506(16)°, V = 1248.82(6) Å³, Z = 2,
no. of observations = 4473, no. of variables = 361, reflection/parameter ratio = 12.39,
R = 0.0859 (R > 2σ(I)), R (all reflections) = 0.0859, wR (all reflections) = 0.2688,
GoF = 1.110.

Fig. 5 Crystal structure of compound 14a.

[Diagram of 14a]

Fig. 6 The structures of imidazo[1,5-α]pyridine, azaazulene and azafullerene.

X-ray data of 15a:
empirical formula: C_{27}H_{20}, formula weight: 344.45,
crystal habit: block, crystal system: triclinic, space group: P-1,
unit cell dimensions: a = 11.0303(2) Å, b = 14.3844(3) Å, c = 14.5364(3) Å,
α = 99.9878(12)°, β = 110.8720(12)°, γ = 111.4450(9)°, V = 1879.59(7) Å³, Z = 4,
no. of observations = 6754, no. of variables = 487, reflection/parameter ratio = 13.87,
R = 0.0448 (R > 2σ(I)), R (all reflections) = 0.0663, wR (all reflections) = 0.1199,
GoF = 1.052.

Fig. 7 Crystal structure of compound 15a.

[Diagram of 15a]

Scheme 4 Putative mechanism for the formation of 13a and 14a by the reaction of allene 1a with TCNE.
2.3 UV-vis spectra, MO calculations and cyclic voltammetry

While the solution of tetraarylallene 1 in CH$_2$Cl$_2$ was colorless or pale yellow, that of tetracyclic product 14 was blight red-violet color. In Figs. 8 and 9, I measured the UV-vis absorption spectra of 1a, 1d, 13a, 13d, 14a and 14d. In comparison to 1a, which features the longest-wavelength absorption maximum at $\lambda_{\text{max}} = 266$ nm ($\varepsilon = 33,800$ M$^{-1}$cm$^{-1}$), 14a shows the absorption at the remarkably longer wavelength. In the CH$_2$Cl$_2$ solution of 14a, the maxima at $\lambda_{\text{max}} = 584$ nm ($\varepsilon = 10,000$ M$^{-1}$cm$^{-1}$), $\lambda_{\text{max}} = 542$ nm ($\varepsilon = 11,400$ M$^{-1}$cm$^{-1}$) and $\lambda_{\text{max}} = 504$ nm ($\varepsilon = 6,800$ M$^{-1}$cm$^{-1}$) were observed. The expanded conjugation, the nitrogen-containing hetero ring and three cyano groups were expected to lead the long-wavelength absorption of 14a. The absorption spectra of 1d, 13d and 14d showed the same trend as that of 1a, 13a and 14a, respectively. Table 2 and Figs. 10–12 show the MO calculations of 1a–d, 13a–d, 14a and strong electron acceptors (TCNE, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and dimethyl acetylenedicarboxylate (DMAD)) by density functional theory (DFT) (B3LYP/6-31G(d)). Although LUMO level of 13d (−0.070 eV) and 14a (−0.112 eV) are higher than that of TCNE (−0.182 eV) and TCNQ (−0.217 eV), these are lower than that of DMAD (−0.055 eV). In addition, I carried out cyclic voltammetry (CV) of allene 1, products 13, 14, reference compounds TCNE and TCNQ in CH$_3$CN (0.3 M tetrabutylammonium perchlorate) (Table 3). The reversible reductions were recorded at −0.04 V in the case of 13d. However, in the case of 14a, the only irreversible reduction was recorded at −1.48 V. The result of 13d was comparable level with TCNE (−0.04 V) and TCNQ (−0.05 V), and shows that compound 13d is assumed to produce a stable anion radical.

![Fig. 8 UV-vis absorption spectra of 1a, 13a and 14a in CH$_2$Cl$_2$ at room temperature.](image)

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*Scheme 5* Putative mechanism for the formation of 15a with Lewis acid.$^{25}$
Fig. 9 UV-vis absorption spectra of 1d, 13d and 14d in CH₂Cl₂ at room temperature.

Table 2 Molecular orbital (MO) calculations of 1a–d, 13a–d, 13c’, 14a and electron acceptors (TCNE, TCNQ and DMAD) by density functional theory (DFT) (B3LYP/6-31G(d)).

<table>
<thead>
<tr>
<th>Compds</th>
<th>Total Energy (a. u.)</th>
<th>Dipole Moment (D)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>−1040.9</td>
<td>0.171</td>
<td>−0.209</td>
<td>−0.039</td>
</tr>
<tr>
<td>1b</td>
<td>−1499.0</td>
<td>0.759</td>
<td>−0.186</td>
<td>−0.025</td>
</tr>
<tr>
<td>1c</td>
<td>−1348.6</td>
<td>2.104</td>
<td>−0.191</td>
<td>−0.029</td>
</tr>
<tr>
<td>1d</td>
<td>−2189.1</td>
<td>5.124</td>
<td>−0.201</td>
<td>−0.044</td>
</tr>
<tr>
<td>13a</td>
<td>−1488.4</td>
<td>8.641</td>
<td>−0.247</td>
<td>−0.063</td>
</tr>
<tr>
<td>13b</td>
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<td>10.291</td>
<td>−0.218</td>
<td>−0.055</td>
</tr>
<tr>
<td>13c</td>
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<td>9.749</td>
<td>−0.228</td>
<td>−0.056</td>
</tr>
<tr>
<td>13c’</td>
<td>−1796.1</td>
<td>10.171</td>
<td>−0.220</td>
<td>−0.058</td>
</tr>
<tr>
<td>13d</td>
<td>−2636.6</td>
<td>8.842</td>
<td>−0.235</td>
<td>−0.070</td>
</tr>
<tr>
<td>14a</td>
<td>−1618.9</td>
<td>13.478</td>
<td>−0.219</td>
<td>−0.112</td>
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<tr>
<td>TCNE</td>
<td>−447.52</td>
<td>0</td>
<td>−0.335</td>
<td>−0.182</td>
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<tr>
<td>TCNQ</td>
<td>−750.36</td>
<td>0.653</td>
<td>−0.324</td>
<td>−0.217</td>
</tr>
<tr>
<td>DMAD</td>
<td>−533.08</td>
<td>2.481</td>
<td>−0.289</td>
<td>−0.055</td>
</tr>
</tbody>
</table>
Fig. 10 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of allene 1 by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).
Fig. 11 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of compound 13 by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).
**Fig. 12** The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of compound 14a by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).

**Table 3** Cyclic voltammetry (CV; scan rate $\nu = 20$–50 V/min) data of 1a, 1b, 1d, 13a, 13c, 13d, 14a and reference compounds TCNE and TCNQ in CH$_3$CN (+0.3 M tetrabutylammonium perchlorate).$^a$

<table>
<thead>
<tr>
<th>Compds</th>
<th>$E^\circ$ (V)$^b$</th>
<th>$\Delta E_p$ (mV)$^c$</th>
<th>$E_p$ (V)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-</td>
<td>-</td>
<td>+1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.36</td>
</tr>
<tr>
<td>1b</td>
<td>-</td>
<td>-</td>
<td>+1.94</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td>13c</td>
<td>-</td>
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</tr>
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<td>13d</td>
<td>+0.63</td>
<td>100</td>
<td>-</td>
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<td>-0.04</td>
<td>100</td>
<td>-</td>
</tr>
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<td>-</td>
<td>-1.46</td>
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<td>14a</td>
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<td>-</td>
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</tr>
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<td></td>
<td>-</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

$^a$All potentials are given vs. the Ag$^+$/Ag couple used as the internal standard.

$^b E^\circ = (E_{pc} + E_{pa}) / 2$, where $E_{pc}$ and $E_{pa}$ correspond to the cathodic and anodic peak potentials, respectively.

$^c \Delta E_p = E_{pa} - E_{pc}$.

$^d E_p$ = Irreversible peak potential.

Cumulenes are the homologous series of hydrocarbons that contain multiple, sequential double bonds sharing the sp-hybridized carbon atoms. Many synthetic methods and reactions of cumulenes have been investigated, and some of these are reported in several reviews. In the present study, I have investigated the charge-transfer reactions of tetraaryl[3]cumulenes (butatrienes) with TCNE for the rich chemistry of these unsaturated molecules.

3.1 Syntheses

The synthesis of tetraaryl[3]cumulene 2 was undertaken as shown in Scheme 6. Compound 11 was synthesized by the method similar to tetraarylallene 1 (Scheme 2). The reaction of 11 with benzyltriethylammonium chloride (BTEAC) as a phase transfer catalysis in 50w/v% NaOH aq. and CHCl₃ afforded dichlorocyclopropane 16. Cyclopropane 16 was reacted with strong base t-BuOK to give [3]cumulene 2 (Fig. 13) through dehydrochlorination.

X-ray data of 2b:
empirical formula: C₉₂H₅₆O₂, formula weight: 444.54,
crystal habit: needle, crystal system: orthorhombic, space group: Pbcn,
unit cell dimensions: a = 7.52750(10) Å, b = 27.5908(6) Å, c = 26.1680(6) Å,
V = 5434.83(19) Å³, Z = 8, no. of observations = 91704,
no. of variables = 4973, reflection/parameter ratio = 15.99,
R = 0.0631 (I>2σ(I)), R (all reflections) = 0.0840, wR (all reflections) = 0.1934,
GoF = 1.099,
Selected bond length: C1–C2 = 1.346 (3) Å, C2–C3 = 1.248 (3) Å,
C3–C4 = 1.334 (3) Å.

Fig. 13 Crystal structure of tetraaryl[3]cumulene 2b (CCDC 937964).
3.2 Reactions and the mechanism

Scheme 5 Formation of head-to-tail unsymmetrically substituted diarylallene dimer 17 by the reaction of tetraaryl[3]cumulene 2 with TCNE.

Table 4 Yields of products 17 and 18 formed by the reaction of 2 with TCNE at room temperature.

<table>
<thead>
<tr>
<th>Cumulenes</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>CH₂Cl₂</td>
<td>4</td>
<td>69</td>
</tr>
<tr>
<td>2a</td>
<td>MeOH</td>
<td>5</td>
<td>No reaction</td>
</tr>
<tr>
<td>2b</td>
<td>CH₂Cl₂</td>
<td>3</td>
<td>65 (11)</td>
</tr>
<tr>
<td>2c</td>
<td>CH₂Cl₂</td>
<td>3</td>
<td>80 (4)</td>
</tr>
</tbody>
</table>

*The yields of 17b' and 17c' were estimated by comparing the integrations of the methyl signals of the methoxyphenyl group against those of 17b and 17c by the 1H-NMR spectra in CDCl₃ (see Figs. 17 and 18).*

When tetraaryl[3]cumulene 2 was stirred with TCNE in CH₂Cl₂ at room temperature for 3–4 h, the solution color changed from yellow to deep red and the nature of the main product 17 (Scheme 5) was determined by X-ray analysis. Fig. 14 shows that 17 was a novel four-membered ring compound, a head-to-tail unsymmetrically substituted diarylallene dimer. I wish to name the products 17 ‘bisalkyldienecyclobutane’, as ‘diarylallene dimer’ in order to represent their unique structures. It reminds us of the name ‘ketene dimer’. The crystal packing of 17 shows several interesting short intermolecular interactions. For example, a favorable antiparallel dipolar alignment of two cyano groups was observed in the crystal structure of 17a (Fig. 15, C⋯N = 3.140 Å).²

Although the reaction of symmetric 2a with TCNE formed pure compound 17a in 69% yield, the products from the reaction of unsymmetrical 2b and 2c with TCNE were presumed to give not only main products 17b and 17c but also isomers 17b' and 17c', respectively (Table 4). In Figs. 17 and 18, 1H NMR showed that the isomers 17b' and 17c' were formed in 1/6 and 1/20 of the yields of the
main products 17b and 17c, respectively. Unsymmetrical [3]cumulene 2c also formed head-to-tail dimer 18c as a minor product, which was confirmed by X-ray analysis (Fig. 16). A solution of 2c in the absence of TCNE also formed the same amount of 18c. Because the dipole moment of 2c (6.290 D) is larger than those of [3]cumulenes 2a (0.002 D) and 2b (2.659 D), based on MO calculations by density functional theory (DFT) (B3LYP/6-31G(d)) (3.3, Table 5, p. 28), cumulene 2c can more easily dimerize at each of the electron-rich lateral C=C bonds close to the methoxyphenyl groups. Actually, the reaction of 2c in toluene at 90 °C for 3 h afforded 18c in 20% yield. The photoreaction (≧280 nm, high-pressure mercury lamp) of 2c in CDCl₃ for 3 h also yielded dimer 18c in 60% yield.¹⁷

X-ray data of 17a:
empirical formula: C₃₆H₂₅N₄O₄, formula weight: 604.66,
crystal habit: block, crystal system: orthorhombic, space group: Pbcn,
unit cell dimensions: a = 23.3123(4) Å, b = 14.7753(2) Å, c = 18.2560(3) Å,
V = 6288.2(2) Angstrom³, Z = 8,
no. of observations = 5755, no. of variables = 419, reflection/parameter ratio = 13.74,
R = 0.0375 (I>2σ(I)), R (all reflections) = 0.0481, wR (all reflections) = 0.0994,
GoF = 1.072.

X-ray data of 17b:
empirical formula: C₃₆H₂₅N₄O₂, formula weight: 572.66,
crystal habit: block, crystal system: triclinic, space group: P-1,
unit cell dimensions: a = 11.1289(4) Å, b = 12.3596(4) Å, c = 12.6371(4) Å,
a = 102.539(2)°, β = 96.811(2)°, γ = 113.934(2)°, V = 6288.2(2) Angstrom³, Z = 2,
no. of observations = 5408, no. of variables = 401, reflection/parameter ratio = 13.49,
R = 0.0440 (I>2σ(I)), R (all reflections) = 0.0549, wR (all reflections) = 0.1348,
GoF = 1.096.

X-ray data of 17c:
empirical formula: C₃₆H₂₅N₄O₂Cl₂, formula weight: 613.48,
crystal habit: needle, crystal system: triclinic, space group: P-1,
unit cell dimensions: a = 13.0039(3) Å, b = 14.3980(3) Å, c = 18.6793(4) Å,
a = 99.561(7)°, β = 91.793(7)°, γ = 103.561(7)°, V = 3356.3(1) Angstrom³, Z = 4,
no. of observations = 12006, no. of variables = 815, reflection/parameter ratio = 14.73,
R = 0.0784 (I>2σ(I)), R (all reflections) = 0.1428, wR (all reflections) = 0.1922, GoF = 1.021.
Fig. 15 Crystal structure of allene dimer 17a. (a) ORTEP plot along a line-a. (b) ORTEP plot along a line-c. (c) Arrangement of neighboring molecules in the crystal packing.

X-ray data of 18c:
empirical formula: C₆₀H₄₄O₄Cl₄, formula weight: 970.75,
crystal habit: needle, crystal system: monoclinic, space group: P₂₁/n,
unit cell dimensions: a = 15.9572(3) Å, b = 8.7817(2) Å, c = 16.7713(3) Å,
β = 91.2657(12)°, V = 2349.61(8) Å³, Z = 2,
no. of observations = 4305, no. of variables = 309, reflection/parameter ratio = 13.93,
R = 0.0449 (I>2σ(I)), R (all reflections) = 0.0601, wR (all reflections) = 0.1328,
GoF = 1.075.

Fig. 16 Crystal structure of head-to-tail dimer 18c (CCDC 937947).
Fig. 17 ¹H-NMR spectra of crude product by the reaction of [3]cumulene 2b with TCNE. Three singlets (2.42, 3.88 and 3.89 ppm) derived from the methyl signals of the methylphenyl and methoxyphenyl groups are confirmed. In addition, two singlets (2.43, 3.87 ppm) are also appeared close to signals of 17b (b) and the integrations of these two signals are equivalent each other. As compared with the methyl signals of the methoxyphenyl groups of 17a (a) and analogous compound I²⁶ (c), these signals are presumed to be due to 17b', which is the regioisomer of 17b. From integration of ¹H-NMR spectra, the isomer 17b' was obtained in 1/6 of the yield of 17b.
Fig. 18 ¹H-NMR spectra of crude product by the reaction of [3]cumulene 2c with TCNE. Not only the methyl signals of the methoxyphenyl group of 17c (3.90 ppm) but also two singlets (3.86 and 3.87 ppm) were observed. One singlet at 3.87 ppm is confirmed to be derived from 2c (see 7. Experimental). Along with the case of 17b', the other singlet 3.86 ppm is assumed to be due to 17c' which is the regioisomer of 17c. From integration of ¹H-NMR spectra, the isomer 17c' was obtained in 1/20 of the yield of 17c. In addition, the methyl signals of the methoxyphenyl group of 18c could be confirmed (see 7. Experimental).

To investigate the reaction mechanism of tetraaryl[3]cumulenes 2 with TCNE, I measured time-dependent ¹H-NMR spectra of the reaction mixture in CDCl₃. In Fig. 19, the signals of 2a disappeared within 4 min, and two doublets (6.34, 6.69 ppm) appeared further upfield of the chemical shift region commonly associated with the signals of aromatic protons. After 60 min, these upfield aromatic signals had almost disappeared, and aromatic proton signals of 17a appeared. The addition of TCNE to 2a seems to give intermediate 19a, a head-to-head symmetrically substituted diarylallene dimer through [2+2] cycloaddition at the central C=C bond; the two more upfield signals are attributed to the effect of π-π stacking of the aromatic rings in 19a (Scheme 6). According to the DFT MO calculation of 19a, the distance between the two aryl groups is 3.9 Å (B3LYP/6-31G(d)); thus, they are expected to interact with each other. Fig. 22 (a) shows the relative
ratio of 2a, 17a and 19a estimated by integration of the methyl signals of the methoxyphenyl group observed in the 1H-NMR spectra. Due to complexity and overlapping of each signal, these values were determined by measuring the weight of paper pieces cut out from the digitally enlarged NMR signals. [3]Cumulene 2a disappeared quickly, while the allene dimer 19a signals increased simultaneously. Subsequently, the amount of 17a increased as the amount of 19a decreased. The results demonstrated that 19a was converted to an intermediate and then rearranged to product 17a, which is more stable than 19a.

Fig. 19 Time dependent 1H-NMR spectra (in CDCl₃) of the reaction of tetraaryl[3]cumulene 2a with TCNE at room temperature.
**Fig. 20** Time dependent $^1$H-NMR spectra (in CDCl$_3$) of the reaction of tetraaryl[3]cumulene 2b with TCNE at room temperature.
Fig. 21 Time dependent $^1$H-NMR spectra (in CDCl$_3$) of the reaction of tetraaryl[3]cumulene 2c with TCNE at room temperature.
Scheme 6 Putative reaction mechanism of tetraaryl[3]cumulenes 2a-c with TCNE. 1H-NMR assignments of 19a and 19c are shown in the references and notes. 27,28

The reactions of [3]cumulene 2b and 2c with TCNE are likely to follow the same mechanism as that of 2a. In the case of 2c, four doublets (6.42, 6.70, 6.74 and 6.83 ppm) resulting from the π-π stacking aromatic rings appeared at 4–120 min. However, two distorted singlets (4.74, 4.82 ppm) and two doublets (5.83, 6.12 ppm) also appeared at 4–30 min (Fig. 21). These signals suggested that [4+2] cyclic compound 20c temporarily existed in equilibrium with 2c (Scheme 6). The anomalous signals that appeared in the region of the methine and olefinic protons were simulated by GIAO MO calculations (4.41, 5.31, 5.80 and 6.15 ppm, HF/6-31G(d)//B3LYP/6-31G(d)). The data supported the assignment of the corresponding signals in Fig. 21 to compound 20c. In Fig. 22 (b), the relative ratio of 19c and 20c rapidly increased with simultaneous disappearance of 2c. However, it is not clear whether 20c intervened in the formation of 17c from the current results. In addition, 1H-NMR spectra of the reaction of 2b with TCNE showed the same trend as the reaction of 2c, but the signals resulting from [4+2] cycloaddition appeared for only 12 min (Fig. 20).
Fig. 22 Time course of the reactions of 2a (a) or 2c (b) with TCNE in CDCl₃ at room temperature. Values are estimated by comparing the integrations of the methyl signals of the methoxyphenyl group against the methyl signal of tetramethylsilane (TMS) as an internal standard observed by the ¹H-NMR spectra (400 MHz).
3.3 UV-vis spectra, MO calculations and cyclic voltammetry

**Fig. 23** Time dependent UV-vis absorption spectra of the reaction of tetraaryl[3]cumulene $2c$ with TCNE in CH$_2$Cl$_2$ at room temperature. The lower drawing (b) is the enlarged drawing of (a).

I measured the time dependent UV-vis absorption spectra of the reaction of [3]cumulene $2c$ with TCNE in CH$_2$Cl$_2$ at room temperature (Fig. 23). The longest-wavelength absorption maximum at $\lambda_{\text{max}} = 446$ nm ($\varepsilon = 45,500$ M$^{-1}$cm$^{-1}$) derived from $2c$ was confirmed at 0 min. However, the absorption was quickly disappeared and converted to the other absorption maximum at $\lambda_{\text{max}} = 412$ nm ($\varepsilon = 21,500$ M$^{-1}$cm$^{-1}$) for 30 min, which was assumed to be derived from intermediate $19c$ (Scheme 6, Fig. 22 (b)). After 240 min, two maxima at $\lambda_{\text{max}} = 408$ nm ($\varepsilon = 26,100$ M$^{-1}$cm$^{-1}$) and $\lambda_{\text{max}}$...
= 484 nm (ε = 20,000 M⁻¹ cm⁻¹) were observed. In the results, it is not sure if the charge-transfer (CT) band of 2c with TCNE was formed.

Table 5 and Fig. 24 show that the MO calculations of diaryllallene dimers 17a–c and strong electron acceptors (TCNE, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and dimethyl acetylenedicarboxylate (DMAD)) by density functional theory (DFT) (B3LYP/6-31G(d)). Although LUMO level of 17a–c are less than that of TCNE and TCNQ, these are better than that of DMAD. Actually, I measured the cyclic voltammetry of the products (Table 6). While [3]cumulenes 2a–c showed irreversible reduction waves at −1.33, −1.33 and −1.44 V, the reversible reductions were recorded at −0.07, −0.08 and −0.05 V in the case of 17a–c, respectively. The results of 17a–c are comparable level with TCNE and TCNQ, and show that the allene dimer 17 is assumed to produce a stable anion radical. Because cyclic compound 17 possesses the reactive cyclobutane ring and the four cyano groups, 17 and the resulting products may be novel electron-accepting compounds. I tried to form the crystal of the CT complex of 17 with tetraphiafulvalene (TTF), a strong electron-donor, at room temperature. However, the crystal could not form in various solvents and concentrations. Further study including the investigation of the properties and reactivity of 17 is in progress.

Table 5 Molecular orbital (MO) calculations of 17a–c and electron acceptors (TCNE, TCNQ and DMAD) by density functional theory (DFT) (B3LYP/6-31G(d)).

<table>
<thead>
<tr>
<th>Compds</th>
<th>Total E (a. u.)</th>
<th>Dipole Moment (D)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17a</td>
<td>−1984.2</td>
<td>4.161</td>
<td>−0.215</td>
<td>−0.105</td>
</tr>
<tr>
<td>17b</td>
<td>−1833.8</td>
<td>3.846</td>
<td>−0.219</td>
<td>−0.107</td>
</tr>
<tr>
<td>17c</td>
<td>−2674.4</td>
<td>7.947</td>
<td>−0.229</td>
<td>−0.116</td>
</tr>
<tr>
<td>TCNE</td>
<td>−447.52</td>
<td>0</td>
<td>−0.335</td>
<td>−0.182</td>
</tr>
<tr>
<td>TCNQ</td>
<td>−750.36</td>
<td>0.653</td>
<td>−0.324</td>
<td>−0.217</td>
</tr>
<tr>
<td>DMAD</td>
<td>−533.08</td>
<td>2.481</td>
<td>−0.289</td>
<td>−0.055</td>
</tr>
</tbody>
</table>
Fig. 24 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of allene dimer 17 by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).
Table 6  Cyclic voltammetry (CV; scan rate \( v = 20\text{–}50 \text{ V/min} \)) data of 2a–c, 17a–c, 18c and reference compounds TCNE and TCNQ in CH$_3$CN (+0.3 M tetrabutylammonium perchlorate).$^a$

<table>
<thead>
<tr>
<th>Compds</th>
<th>$E^0$ (V)$^b$</th>
<th>$\Delta E_p$ (mV)$^c$</th>
<th>$E_p$ (V)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td></td>
<td>-1.33</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td>-1.33</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td></td>
<td>-1.44</td>
<td></td>
</tr>
<tr>
<td>17a</td>
<td></td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.07</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.93</td>
<td></td>
</tr>
<tr>
<td>17b</td>
<td></td>
<td>+0.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.08</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.87</td>
<td></td>
</tr>
<tr>
<td>17c</td>
<td></td>
<td>+0.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.81</td>
<td></td>
</tr>
<tr>
<td>18c</td>
<td></td>
<td>-1.39</td>
<td></td>
</tr>
<tr>
<td>TCNE</td>
<td></td>
<td>+1.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.04</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1.58</td>
<td></td>
</tr>
<tr>
<td>TCNQ</td>
<td>-0.05</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.61</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1.38</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All potentials are given vs. the Ag$^+$/Ag couple used as the internal standard.

$^b$ $E^0 = (E_{pc} + E_{pa})/2$, where $E_{pc}$ and $E_{pa}$ correspond to the cathodic and anodic peak potentials, respectively.

$^c$ $\Delta E_p = E_{pa} - E_{pc}$.

$^d$ $E_p$ = Irreversible peak potential.
3.4 Reaction of diarylallene dimer in a polar solvent

Although compounds 17a–c are stable in CH$_2$Cl$_2$ and other nonpolar solvents, they converted to other cyclic compounds 21a–c in polar solvents (Scheme 7). When the solutions of 17a–c in MeOH or CH$_3$CN were stirred at room temperature for 3–24 h, the color of the solutions changed from deep red to dark yellow. Compounds 21a and 21c were obtained in MeOH after recrystallization in 67% and 35% yield, respectively. The reaction of 17b in MeOH was also found to yield 21b, but the product could not be completely purified by recrystallization or preparative thin-layer chromatography. The four-membered ring of 17 was assumed to open in polar solvents and give an ionic intermediate, which rearranged to a more stable six-membered ring. When products obtained by stirring 2b or 2c in MeOH were analysed by a Waters UPLC-MS (Ultra Performance Liquid Chromatography–LCT Premier), a shoulder ion peak right next to the main ion peak appeared. The results implied that 21b and 21c were formed not regiospecifically but highly regioselectively (Figs. 25 and 26). However, the regioisomers of 21b and 21c could not be isolated. In the case of 17b, byproduct 23b, which is a tricyclic compound, was also obtained. In addition, I produced crystals of the products by vapor diffusion method and obtained not only 21a–c as pale yellow needles (Fig. 27) but also a small amount of each of 23a–c as red needles (Fig. 28). It is presumed that the ionic intermediates rearranged to 22a–c and the latter subsequently hydrolysed to 23a–c.
Column: 1.7 μm ACQUITY UPLC BEH C₁₈, 50 × 2.1 mm
Injection volume: 3 ppm × 7 μl
Column temperature: 40 °C

<table>
<thead>
<tr>
<th>Time</th>
<th>Flow [ml/min]</th>
<th>0.1% Formic acid H₂O [%]</th>
<th>0.1% Formic acid CH₃CN [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
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<tr>
<td>10 min</td>
<td>0.1</td>
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<tr>
<td>10.1 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>11 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

Gradient separations

Fig. 25 UPLC-MS analysis of 21b.

Calc. Mass 573.2291
Formula C₃₈H₂₉N₄O₂

Ar¹ = p-MeOC₆H₄ Ar² = p-MeC₆H₄
Column : 1.7 μm ACQUITY UPLC BEH C₁₈, 50 × 2.1 mm  
Injection volume: 3 ppm × 7 μl  
Column temperature: 40 °C  
Gradient separations

<table>
<thead>
<tr>
<th>Time</th>
<th>Flow [ml/min]</th>
<th>0.1% Formic acid H₂O [%]</th>
<th>0.1% Formic acid CH₃CN [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>10 min</td>
<td>0.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>10.1 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>11 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 26 UPLC-MS analysis of 21b.
X-ray data of **21a**:
- empirical formula: C$_{38}$H$_{28}$N$_{4}$O$_{4}$, formula weight: 604.66,
- crystal habit: needle, crystal system: orthorhombic, space group: $Pbca$,
- unit cell dimensions: $a = 20.9635(3)$ Å, $b = 13.2472(2)$ Å, $c = 22.6274(4)$ Å,
- $V = 6283.8(2) \text{ Å}^3$, $Z = 8$,
- no. of observations = 5732, no. of variables = 419,
- reflection/parameter ratio = 13.72,
- $R = 0.1072$ ($I > 2\sigma(I)$), $R$(all reflections) = 0.1894,
- $wR$(all reflections) = 0.2968, GoF = 1.064.

Fig. 27 Crystal structure of compound **21a** (CCDC 942250).

X-ray data of **23a**:
- empirical formula: C$_{38}$H$_{27}$N$_{3}$O$_{5}$, formula weight: 605.63,
- crystal habit: block, crystal system: monoclinic, space group: $P2_1/c$,
- unit cell dimensions: $a = 10.0721(2)$ Å, $b = 13.6832(3)$ Å, $c = 23.3065(4)$ Å,
- $\beta = 95.6174(9)^\circ$, $V = 3196.64(11) \text{ Å}^3$, $Z = 4$,
- no. of observations = 36081, no. of variables = 5845,
- reflection/parameter ratio = 13.95,
- $R = 0.0426$ ($I > 2\sigma(I)$), $R$(all reflections) = 0.0701, $wR$(all reflections) = 0.1368, GoF = 1.118.

X-ray data of **23b**:
- empirical formula: C$_{38}$H$_{27}$N$_{3}$O$_{5}$, formula weight: 573.63,
- crystal habit: block, crystal system: monoclinic, space group: $C2/c$,
- unit cell dimensions: $a = 28.1011(5)$ Å, $b = 10.9295(2)$ Å, $c = 23.4906(4)$ Å,
- $\beta = 97.8432(10)^\circ$, $V = 7147.2(2) \text{ Å}^3$, $Z = 8$,
- no. of observations = 40630, no. of variables = 6463,
- reflection/parameter ratio = 16.11,
- $R = 0.0644$ ($I > 2\sigma(I)$), $R$(all reflections) = 0.1127, $wR$(all reflections) = 0.1923, GoF = 0.998.

X-ray data of **23c**:
- empirical formula: C$_{36}$H$_{21}$N$_{3}$O$_{3}$Cl$_{2}$, formula weight: 614.46,
- crystal habit: needle, crystal system: monoclinic, space group: $C2/c$,
- unit cell dimensions: $a = 28.4477(18)$ Å, $b = 10.8997(6)$ Å, $c = 23.5205(14)$ Å,
- $\beta = 98.339(3)^\circ$, $V = 7215.97(7) \text{ Å}^3$, $Z = 8$,
- no. of observations = 38808, no. of variables = 6596,
- reflection/parameter ratio = 16.53,
- $R = 0.0839$ ($I > 2\sigma(I)$), $R$(all reflections) = 0.1457, $wR$(all reflections) = 0.2747, GoF = 0.985.

Fig. 28 Crystal structures of compounds **23a–c** (CCDC 958311, 958310, 937949).
4. Development of ene-yne-allene precursor
4. Development of ene-yne-allene precursor

Ene-yne-allene and enediyne precursors such as calicheamicin\(^7\), dynemicin\(^8\) and neocarzinostatin\(^9\) (Fig. 29), undergo either Myers-Saito\(^10\) or Masamune-Bergman\(^11\) cyclization and the following diradical could abstract hydrogen from the phosphate backbone of DNA (Scheme 1). For example, neocarzinostatin chromophore is known to lead the DNA cleavage at the 5'-aldehyde of the adenine and thymine residues selectively. The diradical species derived from neocarzinostatin abstract hydrogen atom from C5' and oxygen atom transfer from molecular oxygen to the resulting DNA radical. The aldehyde residues are eventually formed according to the pathway shown in Scheme 8.\(^29\)

Ene-yne-allene and enediyne precursors possessing various functionalities have been designed, and some of these are reported in several reviews.\(^12\) Recently, these precursors possessing phototriggering functionalities have attracted attention.\(^22\) In the present study, I reported the development of a novel ene-yne-allene precursor 3 possessing phototriggering functionality via a Norrish Type II reaction\(^30\). Norrish Type II reaction is the photochemical intramolecular abstraction of a \(\gamma\)-hydrogen by the \(n\pi^*\) excited carbonyl compound to produce a 1,4-diradical as primary photoproduct. In the case of precursor 3, the diradical intermediate is expected to be cleaved at \(\beta\)-position to afford acetophenone 24 and ene-yne-allene 25 (Scheme 9).

Fig. 29 Structure of the ene-yne-allene and enediyne antibiotics, calicheamicin \(\gamma_1\), dynemicin A and neocarzinostatin chromophore.
Scheme 8 DNA strand cleavage initiated by C5' hydrogen atom abstraction. Less than 20% of the strand breaks by neocarzinostatin chromophore result from pathways initiated by hydrogen atom abstraction from C4' and C1'.

Scheme 9 Putative reaction mechanism of ene-yne-allene precursor 3 under UV irradiation.

4.1 Syntheses

Scheme 10 shows the synthetic procedure of ene-yne-allene precursor 3. The Friedel-Crafts reaction of 4-bromobutyryl chloride followed by the reaction with triphenylphosphine in CH₃CN afforded the phosphonium salt 26. On the other hand, the Sonogashira-Hagihara cross coupling of 2-bromobenzaldehyde and trimethylsilylacetylene gave compound 27. In addition, the Wittig reaction of 26 and 27 with t-BuOK followed by deprotection gave ene-yne-allene precursor 3 (E : Z = 1 : 0.85) as yellow oil.
Scheme 10 Synthesis of ene-yne-allene precursor 3.

4.2 Photoreaction of ene-yne-allene precursor

Scheme 11 Photoreaction of ene-yne-allene precursor 3.

Fig. 30 $^1$H-NMR spectra of the photoreaction product of ene-yne-allene precursor 3 in CDCl$_3$ for 0 h or 16 h at room temperature.
When ene-yne-allene precursor 3 was reacted in CDCl₃ under UV irradiation (≥280 nm, high-pressure mercury lamp) at room temperature, acetophenone 24 and ene-yne-allene 25 could not be obtained and Norrish Type II reaction was not assumed to proceed (Scheme 11). Fig. 30 shows ¹H-NMR spectra of the photoreaction product of precursor 3. After 16 h, because the ratio of (Z)-3 to (E)-3 increased (E : Z = 1 : 0.85 → 1 : 1.70), (E)-3 was expected to be photoisomerized to (Z)-3. However, the signals of 3 were totally decreased and anomalous two double doublets (5.94 ppm (dd, J = 10.7 Hz, 1.8 Hz), 6.44 ppm (dd, J = 17.0 Hz, 1.8 Hz)) appeared. To isolate the main product, I underwent HPLC analysis of the crude mixture (Fig. 31). However, sole separation of the main product from the crude mixture was very difficult due to the complexity and overlapping of each peak. It was assumed to be not easy for the nπ* excited carbonyl oxygen to abstract the γ-hydrogen. Further study including the design of a novel ene-yne-allene precursor 4 expected to abstract hydrogen of methyl group is in progress (Scheme 12).

<table>
<thead>
<tr>
<th>Time</th>
<th>Flow [ml/min]</th>
<th>0.1% Formic acid H₂O [%]</th>
<th>0.1% Formic acid CH₃CN [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>1.0</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>7 min</td>
<td>1.0</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9 min</td>
<td>1.0</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>24 min</td>
<td>1.0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>29 min</td>
<td>1.0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>30 min</td>
<td>1.0</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. 31 HPLC analysis of the photoreaction product of ene-yne-allene precursor 3.
Scheme 12 Design of a novel ene-yne-allene precursor 4.
5. Development of enediyne precursor
5. Development of enediyne precursor

I developed a novel enediyne precursor 5 possessing photo-triggering functionality via a Norrish Type II reaction. Precursor 5 is expected to change to acetophenone 29 and (E/Z)-enediyne 30 via a Norrish Type II reaction following hydrogen abstraction from a hydrogen source such as 1,4-cyclohexane (CHD) (Scheme 13). Actually, Nuss and Murphy showed that irradiation of 5a in benzene afforded a quantitative yield of acetophenone and a modest yield of enediyne.\textsuperscript{31} In addition, I have extended the photochemistry of 5 and explored its use as a novel DNA cleaving molecule.

\textbf{Scheme 13} Putative reaction mechanism of enediyne precursor 5 under UV irradiation.

5.1 Syntheses

\textbf{Scheme 14} Synthesis of enediyne precursor 5.
Scheme 14 shows the synthetic procedure of enediyne precursor 5. 1,5-Hexadiyne was reacted with n-BuLi and tetramethylethylenediamine (TMEDA) to afford trianion as intermediate, which was treated with ethylene oxide affording alcohol 31. After the PCC oxidation of 31, the Grignard reaction of aldehyde 32 and bromobenzene followed by the Jones oxidation of alcohol 33 gave enediyne precursor 5a. On the other hand, 5b was synthesized from 4-iodobenzoic acid. After the protection of carboxylic acid by EtOH with H2SO4, the reaction of ethyl 4-iodobenzoate and 32 with i-PrMgCl·LiCl afforded alcohol 34. The Jones oxidation of 34 and deprotection gave 5b, which is slightly soluble in water (0.2 mg/mL).

5.2 Photoreaction of enediyne precursor

Fig. 32 Time course of the reactions of 5a in acetonitrile-d3 (a) and cyclohexane-d12 (b) under UV irradiation (λ ≥ 280 nm) at room temperature. Yields are estimated by comparing the integration of the respective 1H-NMR signals against the methyl signal of tetramethylsilane (TMS) as an internal standard (400 MHz).

First, I measured the time-dependent 1H-NMR spectra of the reaction of 5 under UV irradiation (λ ≥ 280 nm, high-pressure mercury lamp) at room temperature in acetonitrile-d3 or cyclohexane-d12. Fig. 32 shows that the yields of 5a, acetophenone 29a and enediyne (E/Z)-30 estimated by the integration of the respective signals against the methyl signal of tetramethylsilane (TMS) as an internal standard. While precursor 5a decreased quickly, acetophenone 29a increased simultaneously. (E/Z)-30 showed a slight decrease after increasing gradually within 2–6 h. Because 29a and 30 were formed, the Norrish Type II reaction of 5a was expected to proceed by photoirradiation. Especially, the reaction in cyclohexane-d12 (Fig. 32 (b)) formed more 29a and 30 than that in acetonitrile-d3 (Fig. 32 (a)). It was assumed that this is because of the nπ* excitation of the carbonyl group tends to effectively proceed in nonpolar solvents over polar solvents. Because not only sterically stable (E)-30 but also (Z)-30 was formed, (E)-30 was assumed to be

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photoisomerized to (Z)-30 in the presence of 29a as a photosensitizer. After photoreaction for 24 h, an insoluble precipitate was formed in the case of cyclohexane-d_{12}, showing that part of enediyne 30 was presumably polymerized.

Second, I measured the time-dependent $^1$H-NMR spectra of the photoreaction of 5 with 1,4-cyclohexadiene (CHD) as a hydrogen source (Fig. 33). Table 7 shows the yields of CHD, precursor 5, acetophenone 29, (E/Z)-enediyne 30 and benzene from the photoreaction of 5 at room temperature. In the reaction of 5a with CHD in cyclohexane-d_{12} for 24 h, the yield of benzene increased to 38 μmol, while 30 μmol of CHD was consumed. This shows that benzene was expected to be derived from not only CHD but also a Bergman cyclization of (Z)-30. If a Bergman cyclization of (Z)-30 occurred, 29a was assumed to act as a photosensitizer in the cyclization. In addition, the reaction of 5b with CHD also gave 30 and benzene. The Norrish Type II reaction of 5b and subsequent Bergman cyclization were also assumed to proceed by photoirradiation. However, the reaction using pristine acetophenone instead of 5 could also effectively abstract hydrogens from CHD (Table 7, Entries 1 and 5) to give 1-phenylethanol. The $\pi\pi^*$ excited acetophenone was expected to directly abstract two hydrogens from CHD and convert itself to 1-phenylethanol. In summary, although photoexcited 5 is capable of intermolecularly abstracting hydrogen of CHD, the $^3\pi\pi^*$ state of 5 seems to more favorably abstract an intramolecular $\gamma$-hydrogen to give 30 as well as 29. There is also the possibility of hydrogen abstraction by one of the putative Norrish Type II reaction products such as acetophenone 29.
Table 7 Photoreactions of enediyne precursor 5 or pristine acetophenone at room temperature for 6 h/24 h in three deuterated solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compds</th>
<th>Solvent</th>
<th>Consumption of CHD</th>
<th>Consumption of 5 or pristine acetophenone</th>
<th>29</th>
<th>(E)-30</th>
<th>(Z)-30</th>
<th>Benzene</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetophenone</td>
<td>Acetonitrile-(d_3)</td>
<td>51/78</td>
<td>17/20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13/18</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5a</td>
<td>Acetonitrile-(d_3)</td>
<td>-</td>
<td>13/17</td>
<td>6.2/11.0</td>
<td>2.2/1.7</td>
<td>3.9/4.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5a</td>
<td>Acetonitrile-(d_3)</td>
<td>58/85</td>
<td>18/20</td>
<td>3.3/1.1</td>
<td>1.0/0.7</td>
<td>2.5/2.0</td>
<td>16/35</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5b(^c)</td>
<td>Acetonitrile-(d_3)</td>
<td>48/52</td>
<td>10/10</td>
<td>0.1/0</td>
<td>0.2/0</td>
<td>0.5/0.1</td>
<td>5/7</td>
<td>1/2(^c)</td>
</tr>
<tr>
<td>5</td>
<td>Acetophenone</td>
<td>Cyclohexane-(d_{12})</td>
<td>21/25</td>
<td>19/20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15/23</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5a</td>
<td>Cyclohexane-(d_{12})</td>
<td>-</td>
<td>17/19</td>
<td>12.9/14.1</td>
<td>3.8/1.9</td>
<td>4.7/3.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5a</td>
<td>Cyclohexane-(d_{12})</td>
<td>28/30</td>
<td>18/20</td>
<td>6.7/0.1</td>
<td>1.5/0.9</td>
<td>4.0/1.8</td>
<td>18/38</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5b(^c)</td>
<td>Chloroform-(d)</td>
<td>29/41</td>
<td>10/10</td>
<td>N.D.(^d)</td>
<td>0.4/0.1</td>
<td>0.8/0.2</td>
<td>6/8</td>
<td>1/2(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Yields (\(\mu\)mol) of 1,4-cyclohexadiene (CHD), enediyne precursor 5 or pristine acetophenone, acetophenone 29 formed via a Norrish Type II reaction, (E/Z)-Enediyne 30, and benzene generated by the photoreaction of 5 or pristine acetophenone at room temperature for 6 h or 24 h in acetonitrile-\(d_3\), cyclohexane-\(d_{12}\) or chloroform-\(d\). Yields are estimated by comparing the integration of the respective compounds against the methyl signal of tetramethylsilane (TMS) as an internal standard observed in the \(^1\)H-NMR spectra.

\(^b\) Pristine acetophenone or 5a (20 \(\mu\)mol) was reacted with or without CHD (10 eq) in each solvent (0.5 ml) in a sealed NMR tube.

\(^c\) 5b is less soluble in acetonitrile and chloroform; therefore 5b (10 \(\mu\)mol) was dissolved with CHD (10 eq) in each solvent (0.5 ml). Diyne 5b could not be dissolved in cyclohexane.

\(^d\) In the case of 5b in chloroform-\(d\), the 29b peak could not be detected due to overlap with 5b and CHD.
5.3 DNA cleaving assays of enediyne precursor

I performed DNA cleaving assays of synthetic enediyne precursor 5, pristine acetophenone or Xho I restriction enzyme (Scheme 15). Xho I (cleaving site = 1) recognizes base sequence (C^TCGAG site) and cleaves φX174RFI plasmid DNA at 37 °C. φX174RFI plasmid DNA was incubated with each compound in 25% acetonitrile in TE (10 mM Tris HCl, 1 mM ethylenediaminetetraacetic acid (EDTA), pH 8.0) or only TE under UV irradiation (≧280 nm, high-pressure mercury lamp) at room temperature. Products were separated by electrophoresis on agarose gel and stained with ethidium bromide. Fig. 35 shows that Xho I can easily cleave DNA (supercoiled Form I) to afford the nicked open circular Form II and linear Form III (Fig. 34).22,37 Precursor 5a can also cleave DNA to afford the Form II (Fig. 36 (b)). The cleaving ability of 5a was apparent through comparison with the control. However, the ability of 5a was comparable to that of acetophenone (Fig. 36 (d)). In the case of 5b, Form II as well as linear Form III were partially formed (Fig. 36 (c)). Because 5b is slightly soluble in water, I investigated the cleaving ability of 5b without acetonitrile. This revealed that 5b can cleave DNA to give Form II and a small quantity of Form III in TE. Nucleic acids are generally only soluble in water,38 thus 5b can effectively cleave DNA in TE (without organic solvent).

![Putative cleaving mechanism of a plasmid DNA.](image)
Scheme 15 Cleavage of φX174RFI plasmid DNA by Xho I restriction enzyme (cleaving site = 1) at 37 °C and photocleavage of plasmid DNA by enediyne precursor 5 or acetophenone at room temperature.

Fig. 35 Cleavage of supercoiled φX174RFI plasmid DNA ((0.1 μg, TAKARA BIO INC.) by Xho I (restriction enzyme, cleavage site = 1, TAKARA BIO INC.). φX174RFI DNA solution was incubated with Xho I in TE (10 mM Tris HCl, 1 mM EDTA, pH 8.0) containing 10× concentrated high salt concentration (10×H) buffer at 37 °C for 0–1 h. After heat shock for 10 min, products were loaded on 0.9% agarose gel. After electrophoresis (120 V) for 30 min, the gel was stained with ethidium bromide and destained in water.

a Ladder (Trackit 1 kb Plus DNA Ladder 0.1 μg/μL, 3 or 5 μL, Invitrogen)
b Mass ladder (High DNA Mass Ladder, 4 μL, Invitrogen)
Fig. 36 Photocleavage of supercoiled φX174RFI plasmid DNA by enediyne precursor 5 or pristine acetophenone. φX174RFI DNA solution was incubated with 5a, 5b or acetophenone (1.25 mM) in 25% acetonitrile or TE (10 mM Tris HCl, 1 mM EDTA, pH 8.0) at room temperature for 0–8 h under UV irradiation (≥280 nm). Products were loaded on 0.9% agarose gel. After electrophoresis (120 V) for 30 min, the gel was stained with ethidium bromide and destained in water (none in TE (a), none in 25% acetonitrile or 5a in 25% acetonitrile (b), 5b in 25% acetonitrile or TE (c) and acetophenone in 25% acetonitrile or TE (d)).
6. Conclusion
6. Conclusion

In the current study, I focused on the chemistry of sp-carbon atoms of unsaturated compounds such as allene, cumulene and acetylene. Especially, I interested in the organic functional materials and physiologically active substances with the use of consecutive C=C bonds and C≡C bonds.

Firstly, I have investigated the charge-transfer reactions of tetraaryllallene 1 and tetraaryl[3]cumulene 2 with tetracyanoethene (TCNE) in anticipation of generation of novel functional materials (Fig. 37). The reaction of allene 1 with TCNE at room temperature yielded the main four-membered ring compound 13 and the minor product 14. Cyclobutane 13 was probably formed by [2+2] cycloaddition of the C=C bond of 1 with TCNE. On the other hand, 14 was determined by X-ray analysis to be a novel tetracyclic compound containing two nitrogens similar to imidazo[1,5-a]pyridine derivative. Several literatures show that imidazo[1,5-a]pyridine derivatives possess emission property and exhibit physiological activity. Actually, the solution of 14 displayed bright red-violet color and possessed long-wavelength absorption. In the case of the reaction of [3]cumulene 2 with TCNE at room temperature, a novel four-membered ring compound 17 (a head-to-tail unsymmetrically substituted diaryllallene dimer) was formed by [2+2]
cycloaddition of the central C=C bond of the [3]cumulene with TCNE in good yield; during this reaction, head-to-head symmetrically substituted diarylallene dimer intermediate 19 (not shown in Fig. 37) was formed. Unsymmetrical [3]cumulene also formed a small amount of another head-to-tail dimer 18. Although allene dimer 17 was stable in nonpolar solvents, the four-membered ring of 17 cleaved to give the further-rearranged bicyclic and tricyclic compounds 21 and 23 in MeOH or CH$_3$CN. The MO calculations and cyclic voltammetry of products showed that the allene dimer 17 is assumed to produce a stable anion radical and may be a novel electron-accepting compound.

Scheme 16 The putative reactions of ene-yne-allene precursor 3 and enediyne precursor 5 under UV irradiation at room temperature.

Secondly, I reported the development of novel DNA cleaving molecules possessing allene and acetylene. Ene-yne-allene and enediyne precursors are known to undergo either Myers-saito or Masamune-Bergman cyclization, with the produced diradical being able to abstract hydrogen from the phosphate backbone of DNA. I developed novel ene-yne-allene precursor 3 and enediyne precursor 5 possessing phototriggering functionality via a Norrish Type II reaction (Scheme 16).
The reaction of 3 under UV irradiation (≥ 280 nm) at room temperature could not yield acetophenone 24 and ene-yne-allene 25; therefore Norrish Type II reaction was assumed to not proceed. It was probably not easy for the nπ* excited carbonyl oxygen to abstract the γ-hydrogen. On the other hand, enediyne precursor 5 afforded acetophenone 29 and (E/Z)-enediyne 30 under UV irradiation at room temperature through a Norrish Type II reaction, followed by hydrogen abstraction from 1,4-cyclohexadiene (CHD) to give benzene. Enediyne (Z)-30 derived from 5 was assumed to undergo a Bergman cyclization and abstract hydrogen, but it was not clear from the current results whether (Z)-30 formed the diradical intermediate. Because acetophenone itself abstracted hydrogen from CHD, the carbonyl oxygen of 5 was also expected to directly abstract hydrogen. In addition, 5 was able to cleave supercoiled DNA (Form I) to afford the nicked open circular Form II. As well, 5b, which possessed a carboxylic acid, was slightly soluble in water and effectively cleaved DNA to give Form II and linear Form III in TE without organic solvent.

In summary, I explored the chemistry and utility of sp-carbon atoms of allene / cumulene and acetylene. To contribute to growth of the rich chemistry of these compounds, further study including the investigation of the properties and reactivity of other higher cumulenes and the development of novel precursors such as 9- or 10-membered ring ene-yne-allene and enediyne with phototriggering functionalities are in progress.
7. Experimental
7. Experimental

General

All melting points were measured on a Yanaco MP-J13 micro melting-point apparatus and are uncorrected. The \(^1\)H and \(^{13}\)C NMR spectra were recorded in CDCl\(_3\) on JEOL ECX-400 and ECA-400 spectrometers at 400 and 100 MHz, respectively. Chemical shift values, reported in parts per million (ppm), were referenced to TMS. Abbreviations are as follows: s, singlet; d, doublet; m, multiplet. Elemental analyses were performed with a Yanaco MT-5 CHN-Corder. Exact masses were determined on a Waters LCT Premier (ESI-TOF-MS) spectrometer and Bruker Daltonics autoflex speed-TOF (NALDI (Nano-Assisted Laser Desorption/Ionization) -TOF-MS). UV-vis spectra were measured with a Hitachi UV-2000 spectrophotometer. Single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II diffractometer equipped with a curved imaging plate detector and a monochromatized Cu-\(K\alpha\) radiation source. HPLC analysis was performed on a Shimadzu HPLC system with a UV detector. Reactions were performed in air unless otherwise noted. Thin-layer chromatography was carried out with Kieselgel 60 F\(_{254}\) (Merck). Materials were purchased from Kanto Chemicals, Co., Inc.; Wako Pure Chemicals, Tokyo Chemical Industry Co., LTD.; Nacalai Tesquet, Inc.; and Junsei Chemical Co., LTD.

Electrochemistry

Cyclic voltammetry (CV) curves were recorded in CH\(_3\)CN / nBu\(_4\)NClO\(_4\) (0.3 M \(n\)-tetrabutylammonium perchlorate) solution with a three-electrode system consisting of Ag / Ag\(^+\) as a reference electrode (BAS, RE-7), glassy carbon wire as a working electrode, and Pt wire as a counter electrode by using a Hokuto Denko HAB-151 potentiostat equipped with a function generator (scan rate: 20–50 V/min).

\[
\begin{align*}
\text{BrMg–Ar}^1 & \rightarrow_6 \text{Ar}^1\text{OH} & \text{HCl} & \rightarrow_4 \text{Ar}^1\text{MeOH} \\
\text{Ar}^1\text{OH} & \rightarrow_7 \text{Ar}^1\text{MeOH} & 40^\circ\text{C}, 0.5–3 \text{ h} & \rightarrow_8 \text{Ar}^1
\end{align*}
\]

a: Ar\(^1\) = C\(_6\)H\(_5\)  b: Ar\(^1\) = MeOC\(_6\)H\(_4\)  c: Ar\(^1\) = MeC\(_6\)H\(_4\)

1,1-Diphenylethene (8a)

A three necked flask connected with a firestone valve, dropping funnel and reflux condenser was prepared. Magnesium (1.2 g, 48 mmol, 2.2 eq) was put in the flask and nitrogen gas was purged in the system. Firstly, dry THF (50 ml) and a piece of iodine were added, and then bromobenzene (5.0 ml, 48 mmol, 2.2 eq) was run very slowly into the flask through the dropping funnel. After stirring for 0.5 h, colour of the solution was converted to dark brown. After the flask was cooled, dry ethyl
acetate (2.2 ml, 22 mmol) was added over a period of 15 min and the mixture was stirred for 0.5 h. When the reaction flask was cooled, a saturated NH₄Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO₄, filtered, evaporated under reduced pressure and brown oil 7a was separated. Secondly, the brown oil was dissolved in MeOH (40 ml) and heated up to 40 °C. Conc. HCl (1.5 ml) was added and stirred for 3 h. The reaction mixture was extracted with ether and combined organic extract was washed with brine, dried over MgSO₄ and evaporated under reduced pressure to give 8a (3.8 g, 21 mmol, 97% yield) as pale yellow oil.

1H NMR δ: 5.45 (s, 2H), 7.27–7.36 (m, 10H).

13C NMR δ: 114.3, 126.7, 128.1, 128.2, 141.5, 150.0.

1,1-Bis(p-methoxyphenyl)ethane (8b)
A three-necked flask connected with a firestone valve, dropping funnel and reflux condenser was equipped. Magnesium (0.92 g, 44 mmol, 2.2 eq) was put in the flask and nitrogen gas was purged in system. Firstly, dry THF (50 ml) and a piece of iodine were added, and then p-bromoanisole (5.5 ml, 44 mmol, 2.2 eq) was run very slowly into the flask through the dropping funnel. After stirring for 1 h, color of the solution was converted to pale gray. After the flask was cooled, dry ethyl acetate (2 ml, 20 mmol) was added over a period of 15 min. When the reaction flask was cooled again, a saturated NH₄Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO₄ and evaporated under reduced pressure and brown oil 7b was separated. Secondly, the brown oil was dissolved in MeOH (40 ml) and heated up to 40 °C. Conc. HCl (1 ml) was added and stirred for 0.5 h. After filtering of the reaction mixture and washing with H₂O and MeOH, pale yellow crystals 8b (4.4 g, 18 mmol, 92% yield) were separated, mp 140–142 °C.

1H NMR δ: 3.83 (s, 6H), 5.29 (s, 2H), 6.86 (d, 4H, J = 8.8 Hz), 7.28 (d, 4H, J = 8.8 Hz).

1,1-Bis(p-methylphenyl)ethane (8c)
A three-necked flask connected with a firestone valve, dropping funnel and reflux condenser was equipped. Magnesium (1.3 g, 54 mmol, 2.0 eq) was put in the flask and nitrogen gas was purged in the system. Firstly, dry THF (50 ml) and a piece of iodine were added, and then p-bromotoluene (13 ml, 54 mmol, 2.0 eq) was run very slowly in to the flask through the dropping funnel. After stirring for 1 h, color of the solution was converted to pale gray. After the flask was cooled, dry ethyl acetate (2.6 ml, 27 mmol) was added over a period of 20 min. When the reaction flask was cooled again, a saturated NH₄Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO₄, filtered, evaporated under reduced pressure and yellow oil 7c was separated. Secondly, the yellow oil was dissolved in MeOH (50 ml) and heated up to 40 °C. Conc. HCl (2 ml)
was added and stirred for 0.5 h. The reaction mixture was extracted with EtOAc and the combined organic extract was washed with brine, dried over MgSO₄, filtered, evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (hexane) to give 8c (3.9 g, 19 mmol, 69% yield) as colorless oil.

\[ ^1H \text{ NMR} \delta: 2.36 (s, 6H), 5.37 (s, 2H), 7.13 (d, 4H, \text{J} = 8.2 \text{ Hz}), 7.23 (d, 4H, \text{J} = 8.2 \text{ Hz}). \]

\[ ^{13}C \text{ NMR} \delta: 21.1, 113.0, 128.2, 128.8, 137.4, 138.8, 149.7. \]

**Diphenylmethanol (10a)**

A two- or three-necked flask connected with a reflux condenser was prepared and, benzophenone 9a (4.0 g, 22 mmol) and EtOH (40 ml) were added to the flask. After heating up to 80 °C, sodium borohydride (0.83 g, 22 mmol, 1.0 eq) was slowly dissolved and the reaction mixture was stirred for 1 h. When the reaction flask was cooled, a saturated NH₄Cl solution was added, and then the colorless crystals 10a (4.2 g, 22 mmol, 100% yield) were separated, mp 59–60 °C.

\[ ^1H \text{ NMR} \delta: 2.29 (d, 1H, \text{J} = 3.4 \text{ Hz}), 5.84 (d, 1H, \text{J} = 3.4 \text{ Hz}), 7.24–7.28 (m, 2H), 7.32–7.39 (m, 8H). \]

\[ ^{13}C \text{ NMR} \delta: 76.2, 126.5, 127.6, 128.5, 143.8. \]

**Bis(p-methoxyphenyl)methanol (10b)**

A two- or three-necked flask connected with a reflux condenser was prepared, and \( p \)-methoxybenzophenone 9b (10 g, 42 mmol) and EtOH (100 ml) were added to the flask. After heating up to 80 °C, sodium borohydride (1.6 g, 42 mmol, 1.0 eq) was slowly dissolved and the reaction mixture was stirred for 4 h. When the reaction flask was cooled, a saturated NH₄Cl solution was added. Evaporation of the solvent and recrystallization from MeOH yielded white solid 10b (9.1 g, 37 mmol, 88% yield), mp 57–58 °C.

\[ ^1H \text{ NMR} \delta: 2.11 (d, 1H, \text{J} = 3.4 \text{ Hz}), 3.78 (s, 6H), 5.78 (d, 1H, \text{J} = 3.4 \text{ Hz}), 6.87 (d, 4H, \text{J} = 8.7 \text{ Hz}), 7.28 (d, 4H, \text{J} = 8.7 \text{ Hz}). \]

**Bis(p-methylphenyl)methanol (10c)**

Compound 10c (8.2 g, 39 mmol, 92% yield) was prepared by the same procedure as 10b, mp 58–59 °C.
\(^1\)H NMR \(\delta\): 2.14 (d, 1H, \(J = 3.6\) Hz), 2.32 (s, 6H), 5.78 (d, 1H, \(J = 3.6\) Hz), 7.12 (d, 4H, \(J = 8.2\) Hz), 7.25 (d, 4H, \(J = 8.2\) Hz).

**Bis(p-chlorophenyl)methanol (10d)**

Compound 10d (10 g, 40 mmol, 99% yield) was prepared by the same procedure as 10b, mp 88–90 °C.

\(^1\)H NMR \(\delta\): 2.23 (d, 1H, \(J = 3.5\) Hz), 5.79 (d, 1H, \(J = 3.5\) Hz), 7.23–7.33 (m, 8H).

1,1,3,3-Tetraphenylpropene (11a)

A glacial AcOH solution (20 ml) of 8a (2.7 g, 14 mmol) and 10a (2.6 g, 14 mmol) was heated to 110 °C. Conc. HCl (1.5 ml) was added to the reaction mixture and stirred for 1 h. The mixture was allowed to cool to room temperature and then neutralized with aq. NaOH solution. After the organic layer was extracted with CH\(_2\)Cl\(_2\), the combined extract was dried over MgSO\(_4\), evaporated under reduced pressure. After recrystallization with CH\(_2\)Cl\(_2\)-hexane, 11a (2.7 g, 7.9 mmol, 56% yield) was separated as colorless crystals, mp 120–122 °C.

\(^1\)H NMR \(\delta\): 4.82 (d, 1H, \(J = 10.4\) Hz), 6.54 (d, 1H, \(J = 10.4\) Hz), 7.15–7.39 (m, 20H).

\(^13\)C NMR \(\delta\): 50.5, 101.4, 126.2, 127.2, 127.5, 128.1, 128.3, 128.4, 128.5, 129.8, 131.0, 139.6, 141.6, 144.5.

1,1,3,3-Tetrakis(p-methoxyphenyl)-1-propene (11b)

A glacial AcOH solution (25 ml) of 8b (3.7 g, 15 mmol) and 10b (3.7 g, 15 mmol) was heated to 110 °C. Conc. HCl (1.5 ml) was added to the reaction mixture and stirred for 1 h. The mixture was allowed to cool to room temperature and then neutralized with aq. NaOH solution. After the organic layer was extracted with CH\(_2\)Cl\(_2\), the combined extract was dried over MgSO\(_4\), evaporated under reduced pressure to afford yellow oil 11b (6.6 g, 14 mmol, 92% yield).

\(^1\)H NMR \(\delta\): 3.78 (s, 9H), 3.83 (s, 3H), 4.72 (d, 1H, \(J = 10.5\) Hz), 6.33 (d, 1H, \(J = 10.5\) Hz), 6.79 (d, 2H, \(J = 8.7\) Hz), 6.82 (d, 4H, \(J = 8.7\) Hz), 6.88 (d, 2H, \(J = 8.7\) Hz), 7.06 (d, 4H, \(J = 8.7\) Hz), 7.08 (d, 2H, \(J = 8.7\) Hz), 7.17 (d, 2H, \(J = 8.7\) Hz).
1,1-Bis(p-methoxyphenyl)-3,3-bis(p-methylphenyl)-1-propene (11c)

A glacial AcOH solution (20 ml) of 8b (3.0 g, 13 mmol) and 10c (2.7 g, 13 mmol) was heated to 110 °C. Conc. HCl (1.2 ml) was added to the reaction mixture and stirred for 1 h. The mixture was allowed to cool to room temperature and then neutralized with aq. NaOH solution. The organic layer was extracted with CH₂Cl₂, dried over MgSO₄ and evaporated under reduced pressure to give 11c (5.4 g, 13 mmol, 100% yield) as pale yellow oil.

¹H NMR δ: 2.31 (s, 6H), 3.78 (s, 3H), 3.83 (s, 3H), 4.75 (d, 1H, J = 10.5 Hz), 6.37 (d, 1H, J = 10.5 Hz), 6.79 (d, 2H, J = 8.8 Hz), 6.88 (d, 2H, J = 8.8 Hz), 7.03–7.10 (m, 10H), 7.17 (d, 2H, J = 8.8 Hz).

3,3-Bis(p-methoxyphenyl)-1,1-bis(p-methylphenyl)-1-propene (11c’)

A glacial AcOH solution (25 ml) of 8c (3.0 g, 15 mmol) and 10b (3.5 g, 15 mmol) was heated to 110 °C. Conc. HCl (2 ml) was added to the reaction mixture and stirred for 1 h. The mixture was allowed to cool to room temperature and then neutralized with aq. NaOH solution. The organic layer was extracted with CH₂Cl₂, dried over MgSO₄ and evaporated under reduced pressure to give 11c’ (6.3 g, 15 mmol, 100% yield) as pale yellow oil.

¹H NMR δ: 2.39 (s, 3H), 2.45 (s, 3H), 3.83 (s, 6H), 4.85 (d, 1H, J = 10.6 Hz), 6.52 (d, 1H, J = 10.6 Hz), 6.91 (d, 4H, J = 8.6 Hz), 7.14 (d, 2H, J = 8.6 Hz), 7.17 (d, 6H, J = 8.6 Hz), 7.23–7.26 (m, 4H).

¹³C NMR δ: 20.9, 21.1, 48.8, 55.0, 113.7, 127.3, 128.7, 128.8, 129.1, 129.6, 130.5, 136.6, 136.7, 136.8, 137.1, 139.7, 140.6, 157.8.

3,3-Bis(p-chlorophenyl)-1,1-bis(p-methoxyphenyl)-1-propene (11d)

A glacial AcOH solution (25 ml) of 8b (2.4 g, 10 mmol) and 10d (2.5 g, 10 mmol) was heated to 110 °C. Conc. HCl (1.5 ml) was added to the reaction mixture and stirred for 1 h. The mixture was allowed to cool to room temperature and then neutralized with aq. NaOH solution. The organic layer was extracted with CH₂Cl₂, dried over MgSO₄ and evaporated under reduced pressure to give 11d (4.5 g, 9.5 mmol, 95% yield) as pale yellow oil.

¹H NMR δ: 3.79 (s, 3H), 3.84 (s, 3H), 4.75 (d, 1H, J = 10.4 Hz), 6.25 (d, 1H, J = 10.4 Hz), 6.80 (d, 2H, J = 8.7 Hz), 6.89 (d, 2H, J = 8.7 Hz), 7.03 (d, 2H, J = 8.7 Hz), 7.06 (d, 4H, J = 8.4 Hz), 7.16 (d, 2H, J = 8.7 Hz), 7.26 (d, 2H, J = 8.4 Hz).
In an inert atmosphere, to a solution of propene 11a (1.3 g, 3.8 mmol) in chloroform (20 ml) was slowly added a solution of bromine (0.23 ml, 4.5 mmol, 1.2 eq) in chloroform (10 ml) at room temperature and stirred for 1 h. The resulting solution was dehalogenated by saturated sodium thiosulfate solution, extracted with chloroform and washed with H$_2$O and brine. After evaporation, 12a (1.8 g, 4.2 mmol, 112% yield) was obtained as yellow oil containing a lot of allene 1a.

1H NMR δ: 5.49 (s, 1H), 7.20–7.35 (m, 20H).

13C NMR δ: 55.3, 100.7, 126.8, 127.3, 127.7, 128.1, 128.2, 128.3, 128.6, 128.9, 129.0, 129.4, 141.1, 141.5, 142.8, 144.3.

2-Bromo-1,1,3,3-tetraphenylpropene (12a)

In an inert atmosphere, to a solution of propene 11b (2.5 g, 5.3 mmol) in chloroform (20 ml) was slowly added a solution of bromine (0.33 ml, 6.4 mmol, 1.2 eq) in chloroform (10 ml) at room temperature and stirred for 1 h. The resulting solution was dehalogenated by saturated sodium thiosulfate solution, extracted with chloroform and washed with H$_2$O and brine. After evaporation, the crude material was purified by silica gel column chromatography (EtOAc : hexane = 0.6 : 3.5 → 1 : 3) to give not 12b but allene 1b (1.7 g, 5.3 mmol, 32% yield) as colorless crystals.

1H NMR δ: 2.31 (s, 3H), 2.32 (s, 3H), 3.81 (s, 6H), 5.39 (s, 1H), 6.86 (d, 4H, $J = 9.2$ Hz), 7.12–7.18 (m, 8H), 7.42 (d, 4H, $J = 8.3$ Hz).

13C NMR δ: 21.0, 21.3, 55.2, 113.5, 125.6, 128.2, 128.7, 129.0, 130.4, 134.0, 136.9, 137.5, 138.5, 139.8, 140.2, 143.5, 158.3.

2-Bromo-1,1,3,3-tetraphenylpropene (12a)

In an inert atmosphere, to a solution of propene 11c' (1.5 g, 3.5 mmol) in chloroform (10 ml) was slowly added a solution of bromine (0.18 ml, 3.5 mmol, 1.2 eq) in chloroform (5 ml) at room temperature and stirred for 1 h. The resulting solution was dehalogenated by saturated sodium thiosulfate solution, extracted with chloroform and washed with H$_2$O and brine. After evaporation, the crude material was purified by silica gel column chromatography (EtOAc : hexane = 0.3 : 3.7) to give 12c (0.37 g, 0.72 mmol, 21% yield) as pale yellow oil.

1H NMR δ: 2.31 (s, 3H), 2.32 (s, 3H), 3.81 (s, 6H), 5.39 (s, 1H), 6.86 (d, 4H, $J = 9.2$ Hz), 7.12–7.18 (m, 8H), 7.42 (d, 4H, $J = 8.3$ Hz).

13C NMR δ: 21.0, 21.3, 55.2, 113.5, 125.6, 128.2, 128.7, 129.0, 130.4, 134.0, 136.9, 137.5, 138.5, 139.8, 140.2, 143.5, 158.3.
2-Bromo-1,1-bis(p-methoxyphenyl)-3,3-bis(p-chlorophenyl)propene (12d)

Pale yellow oil 12d (1.71 g, 3.09 mmol, 98% yield) was prepared by the same procedure as 12c.

\[ \text{1H NMR} \delta: 3.78 \ (s, 3H), 3.79 \ (s, 3H), 6.81 \ (d, 2H, J = 8.6 \text{ Hz}), 6.83 \ (d, 2H, J = 8.6 \text{ Hz}), 7.05 \ (d, 2H, J = 8.6 \text{ Hz}), 7.16 \ (d, 4H, J = 8.6 \text{ Hz}), 7.18 \ (d, 2H, J = 8.6 \text{ Hz}), 7.30 \ (d, 4H, J = 8.6 \text{ Hz}) \]

\[ \text{13C NMR} \delta: 54.5, 55.1, 55.2, 113.4, 114.0, 126.4, 128.4, 129.5, 130.6, 130.7, 132.8, 133.4, 135.0, 139.9, 144.2, 158.8, 159.1 \]

1,1,3,3-Tetraphenylallene (1a)

To a solution of bromopropene 12a (1.7 g, 4.0 mmol) in EtOH (5 ml) was added 20w/v% KOH solution in EtOH (10 ml) and stirred at reflux for 1 h. The resulting solution was poured into H\_2O, and then colorless crystals 1a (1.1 g, 3.3 mmol, 81% yield) were separated, mp 162–164 °C.

\[ \text{1H NMR} \delta: 7.29–7.31 \ (m, 12H), 7.42–7.44 \ (m, 8H) \]

\[ \text{13C NMR} \delta: 112.6, 127.5, 128.4, 128.5, 136.3, 208.5 \]

Elemental analysis: calcd for C\_2\_7H\_30: C, 94.19; H, 5.85. Found: C, 94.19; H, 5.84.

X-ray data: empirical formula: C\_2\_7H\_30, formula weight: 344.45, crystal habit: needle, crystal system: monoclinic, space group: P2\_1/c, unit cell dimensions: a = 12.0653(2) Å, b = 8.22826(15) Å, c = 19.0740(4) Å, \( \beta = 101.4288(7) \) °, \( V = 1856.06 \) (6) Å\_3, Z = 4, no. observations = 3399, no. variables = 244, reflection/parameter ratio = 13.93, \( R = 0.0423 \) (I/2\( \sigma(I) \)), \( R \) (all reflections) = 0.0505, wR (all reflections) = 0.1052, GoF = 1.090.

1,1-Bis(p-methoxyphenyl)-3,3-bis(p-methoxyphenyl)allene (1b)

See the synthetic procedure of 12b, mp 118–121 °C (decomp).

\[ \text{1H NMR} \delta: 3.89 \ (s, 12H), 6.95 \ (d, 8H, J = 8.6 \text{ Hz}), 7.79 \ (d, 8H, J = 8.6 \text{ Hz}) \]

\[ \text{13C NMR} \delta: 55.5, 113.4, 130.8, 132.2, 162.8, 194.5 \]

Elemental analysis: calcd for C\_3\_1H\_38O\_4: C, 80.15; H, 6.08. Found: C, 80.40; H, 6.04.

1,1-Bis(p-methoxyphenyl)-3,3-bis(p-methylphenyl)allene (1c)

To a solution of bromopropene 12c (0.36 g, 0.70 mmol) in EtOH (1 ml) was added 20w/v% KOH solution in EtOH (3 ml) and stirred at reflux for 1 h. The resulting solution was poured into H\_2O and
the mixture was extracted with CH₂Cl₂. After washing with brine, evaporation and recrystallization (chloroform–MeOH), allene 1c was obtained as white solid (0.070 g, 0.16 mmol, 23% yield), mp 130–132 °C.

¹H NMR δ: 2.36 (s, 6H), 3.81 (s, 6H), 6.87 (d, 4H, J = 8.6 Hz), 7.14 (d, 4H, J = 8.2 Hz), 7.29 (d, 4H, J = 8.2 Hz), 7.33 (d, 4H, J = 8.6 Hz).

¹³C NMR δ: 21.2, 55.3, 113.9, 128.3, 129.1, 129.5, 133.9, 137.0, 159.0, 207.8.

Elemental analysis: calcd for C₃₁H₂₈O₂: C, 86.08; H, 6.52. Found: C, 86.10; H, 6.48.

1,1-Bis(p-methoxyphenyl)-3,3-bis(p-chlorophenyl)allene (1d)
To a solution of bromopropene 12d (1.6 g, 2.9 mmol) in EtOH (5 ml) was added 20w/v% KOH solution in EtOH (10 ml) and stirred at reflux for 1 h. The resulting solution was poured into H₂O and the mixture was extracted with CH₂Cl₂. After washing with brine and evaporation, allene 1d was obtained as pale orange solid (1.3 g, 2.7 mmol, 94% yield), mp 104–106 °C.

¹H NMR δ: 3.81 (s, 6H), 6.89 (d, 4H, J = 8.8 Hz), 7.28 (d, 4H, J = 8.8 Hz), 7.29 (s, 8H).

¹³C NMR δ: 55.3, 110.4, 112.6, 114.0, 128.1, 128.8, 129.5, 133.3, 134.9, 159.3, 208.1.

Elemental analysis: calcd for C₂₉H₂₂Cl₂O₂: C, 73.58; H, 4.68. Found: C, 73.78; H, 4.51.

4,4-Diphenyl-3-(diphenylmethylene)-1,1,2,2-tetracyanocyclobutane (13a)
Allene 1a (0.17 g, 0.50 mmol) and TCNE (0.065 g, 0.50 mmol, 1.0 eq) were mixed in CH₂Cl₂ (5 ml) at room temperature for 8 days. After evaporation of the solvent, the crude material was purified by silica gel column chromatography (EtOAc : hexane = 0.8 : 3.2 → 1.5 : 2.5) to give the starting material (colorless crystals, 0.055 g, 0.16 mmol, 32% yield), 13a (pale green solid, 0.039 g, 0.083 mmol, 17%, mp 174–179 °C (decomp) and 14a (red-violet crystals, 0.057 g, 0.11 mmol, 22% yield).

¹H NMR δ: 6.70 (d, 2H, J = 7.3 Hz), 6.82 (t, 2H, J = 7.3 Hz), 6.98 (t, 1H, J = 7.3 Hz), 7.40–7.56 (m, 15H).

¹³C NMR δ: 109.7, 110.0, 127.9, 128.8, 128.9, 129.1, 129.4, 129.6, 130.0, 130.3, 134.0, 134.2, 134.3. (Due to the low concentration of 13a in CDCl₃, the rest of signals could not be detected.)
TOF-ESI-MS $m/z$: caled for: C$_{13}$H$_{21}$Na$_4^+$ 473.1766. Found: 473.1775 ([M+H]$^+$).

X-ray data: empirical formula: C$_{33}$H$_{30}$Na$_4$, formula weight: 472.55, crystal habit: block, crystal system: triclinic, space group: $P1$, unit cell dimensions: $a = 8.33641(15)$ Å, $b = 11.3319(2)$ Å, $c = 13.3288(2)$ Å, $\alpha = 93.3592(7)$ °, $\beta = 98.8258(7)$ °, $\gamma = 95.3809(7)$ °, $V = 1235.33(4)$ Å$^3$, $Z = 2$, no. observations = 4424, no. variables = 334, reflection/parameter ratio = 13.25, $R = 0.0400$ ($>2\sigma(I)$), $R$(all reflections) = 0.0432, $wR$(all reflections) = 0.1064, GoF = 1.096.

4,4-Bis(p-methoxyphenyl)-3-(di-p-methylphenylmethylene)-1,1,2,2-tetracyanocyclobutane (13c) and 4,4-bis(p-methylphenyl)-3-(di-p-methoxyphenylmethylene)-1,1,2,2-tetracyano cyclobutane (13c')

Allene 1c (0.060 g, 0.14 mmol) and TCNE (0.018 g, 0.14 mmol, 1.0 eq) were mixed in CH$_2$Cl$_2$ (5 ml) at room temperature for 5 h. After evaporation of the solvent, the crude material was purified by silica gel column chromatography (EtOAc : hexane = 1.2 : 2.8) to give the mixture of 13c and 13c' (0.073 g, 0.13 mmol, 93% yield, 13c : 13c' = 1 : 1.2, mp 122–125 °C) as pale brown solid and 14c or 1 and 14c' (trace) as dark purple solid.

$^1$H NMR (13c) δ: 2.14 (s, 3H), 2.47 (s, 3H), 3.84 (s, 6H), 6.67–6.71 (m, 4H), 6.97 (d, 4H, $J = 8.7$ Hz), 7.37–7.39 (m, 4H), 7.53 (d, 4H, $J = 8.7$ Hz).

$^1$C NMR (13c) δ: 21.1, 21.5, 55.4, 110.0, 110.1, 114.2, 125.8, 129.3, 129.5, 129.6, 129.8, 131.3, 139.8, 139.9, 160.6.

$^1$H NMR (13c') δ: 2.40 (s, 6H), 3.64 (s, 3H), 3.91 (s, 3H), 6.41 (d, 2H, $J = 9.2$ Hz), 6.74 (d, 2H, $J = 9.2$ Hz), 7.12 (d, 2H, $J = 8.7$ Hz), 7.28 (d, 4H, $J = 8.3$ Hz), 7.41 (d, 2H, $J = 8.7$ Hz), 7.53 (d, 4H, $J = 8.3$ Hz).

$^1$C NMR (13c') δ: 21.2, 55.2, 55.3, 110.2, 110.3, 113.2, 114.9, 126.1, 127.0, 129.6, 129.7, 131.2, 131.6, 140.3, 150.9, 160.4, 160.5.

TOF-ESI-MS $m/z$: caled for: C$_{37}$H$_{32}$N$_{28}$O$_{12}$Cl$_2^+$ 561.2291. Found: 561.2295 ([M+H]$^+$).

4,4-Bis(p-methylphenyl)-3-(di-p-chlorophenylmethylene)-1,1,2,2-tetracyanocyclobutane (13d)

Allene 1d (0.50 g, 1.1 mmol) and TCNE (0.14 g, 1.1 mmol, 1.0 eq) were mixed in CH$_2$Cl$_2$ (10 ml) at room temperature for 3 h. After evaporation of the solvent, the crude material was purified by silica gel column chromatography (EtOAc : hexane = 0.8 : 3.2 → 1.5 : 2.5) to give 13d (0.52 g, 0.87 mmol, 82% yield, mp 139–142 °C (decomp)) as pale pink solid and 14d (trace) as dark purple solid.

$^1$H NMR δ: 3.86 (s, 6H), 6.69 (d, 2H, $J = 8.7$ Hz), 6.91 (d, 2H, $J = 8.7$ Hz), 6.99 (d, 4H, $J = 9.2$ Hz), 7.45 (d, 2H, $J = 8.7$ Hz), 7.49 (d, 4H, $J = 9.2$ Hz), 7.61 (d, 2H, $J = 8.7$ Hz).

$^1$C NMR δ: 41.3, 49.7, 55.4, 109.6, 110.0, 114.3, 125.3, 126.6, 128.3, 130.1, 130.3, 130.6, 131.2, 132.0, 132.3, 136.4, 136.4, 149.3, 160.8.

TOF-ESI-MS $m/z$: caled for: C$_{35}$H$_{39}$Cl$_2$Na$_4$O$_{12}$ 601.1198. Found: 601.1172 ([M+H]$^+$).
1,2,3-Tricyano-5,5,6-triphenyl-5H-4,10c-diazaacephenanthrylene (14a)
See the synthetic procedure of 13a, mp > 300 °C.

$^1$H NMR $\delta$: 6.54 (dd, 2H, $J = 8.2, J = 1.4$ Hz), 6.83 (dd, 4H, $J = 6.8$ Hz, $J = 1.8$ Hz), 7.02 (t, 2H, $J = 8.2$ Hz), 7.09–7.24 (m, 8H), 7.70–7.77 (m, 2H), 9.57–9.59 (m, 1H).

$^{13}$C NMR $\delta$: 81.1, 86.0, 112.2, 112.4, 116.7, 123.0, 127.0, 127.3, 128.0, 128.1, 128.4, 128.7, 130.0, 130.3, 130.8, 137.8, 140.2, 143.3, 147.7.

TOF-ESI-MS m/z: calcld for: C$_{35}$H$_{28}$N$_5$S$^+$ 510.1719. Found: 510.1705 ([M+H]$^+$).

X-ray data: empirical formula: C$_{35}$H$_{28}$NS$_5$, formula weight: 509.55, crystal habit: needle, crystal system: triclinic, space group: P-1, unit cell dimensions: $a = 8.6983(2)$ Å, $b = 10.3312(3)$ Å, $c = 14.5749(4)$ Å, $\alpha = 101.8108(16)$ °, $\beta = 93.5453(16)$ °, $\gamma = 101.5506(16)$ °, $V = 1248.82(6)$ Å$^3$, $Z = 2$, no. observations = 4473, no. variables = 361, reflection/parameter ratio = 12.39, $R$ = 0.0859 ($I/2\sigma(I)$), $R$ (all reflections) = 0.0859, $wR$ (all reflections) = 0.2688, GoF = 1.110.

5,5-Bis(p-methylphenyl)-9-methoxy-6-p-methoxyphenyl-1,2,3-tricyano-5H-4,10c-diazaacephenanthrylene (14c or / and 5,5-Bis(p-methoxyphenyl)-9-methyl-6-p-methylphenyl -1,2,3-tricyano-5H-4,10c-diazaacephenanthrylene (14c$^+$)
See the synthetic procedure of 13c. Because the yields were very small, it is not clear whether 14c, 14c$^+$ or both were yielded.

TOF-ESI-MS m/z: calcld for: C$_{39}$H$_{28}$N$_5$O$_2$S$^+$ 597.2165. Found: 597.2171 ([M+H]$^+$).

5,5-Bis(p-chlorophenyl)-9-methoxy-6-p-methoxyphenyl-1,2,3-tricyano-5H-4,10c-diazaacephenanthrylene (14d)
See the synthetic procedure of 13d. Because the yields were very small, it is not clear whether 14d, regiosomer of 14d or both were yielded.

TOF-ESI-MS m/z: calcld for: C$_{39}$H$_{26}$N$_5$O$_2$Cl$_2$S$^+$ 638.1151. Found: 638.1160 ([M+H]$^+$).

1,1,3-Triphenylindene (15a)
Allene 1a (0.029 g, 0.084 mmol) and TCNE (0.011 g, 0.084 mmol, 1.0 eq) were mixed in THF (3 ml) at room temperature for 2 days. After evaporation of the solvent, colorless crystals 15a (100% yield) containing TCNE was obtained. On the other hand, the reaction of 1a (0.039 g, 0.11 mmol) and TCNE (0.015 g, 0.11 mmol, 1.0 eq) in THF (6 ml) afford 15a (29% yield) containing 1a (71% yield) and TCNE. The yields of 15a and starting material 1a were estimated by the integrations of $^1$H NMR spectra of the reaction mixture. The crude material was tried to purify by silica gel column chromatography (EtOAc : hexane = 0.8 : 3.2), but 15a completely changed to 1a and could not be isolated.

$^1$H NMR $\delta$: 6.83 (s, 1H), 7.22–7.33 (m, 12H), 7.37–7.42 (m, 2H), 7.43–7.47 (m, 2H), 7.57 (d, 1H, $J =$ 7.8 Hz), 7.63–7.66 (m, 2H).
$^{13}$C NMR $\delta$: 65.6, 121.4, 125.7, 125.9, 126.7, 127.0, 127.8, 127.9, 128.0, 128.3, 128.6, 135.3, 141.6, 142.4, 142.5, 143.7, 151.1.

X-ray data: empirical formula: C$_{27}$H$_{20}$, formula weight: 344.45, crystal habit: block, crystal system: triclinic, space group: P-1, unit cell dimensions: $a = 11.0303(2)$ Å, $b = 14.3844(3)$ Å, $c = 14.5364(3)$ Å, $\alpha = 99.9878$ (12) $^\circ$, $\beta = 110.8720$ (12) $^\circ$, $\gamma = 111.4450$ (9) $^\circ$, $V = 1879.59$ (7) Å$^3$, $Z = 4$, no. observations = 6754, no. variables = 487, reflection/parameter ratio = 13.87, $R = 0.0448 \ (I>2\sigma(I))$, $R$ (all reflections) = 0.0663, $wR$ (all reflections) = 0.1199, $GoF = 1.052$.

1,1-Dichloro-2,2,4,4-tetrakis($p$-methoxyphenyl)methylcyclopropane (16a)

A chloroform (150 ml) solution of 11b (4.7 g, 10 mmol), aq. 50w/v% NaOH solution (100 ml) and benzyltriethylammonium chloride (BTEAC, 0.23 g, 1.0 mmol, 0.10 eq) were added to a round-bottomed flask and stirred vigorously for 3 days at room temperature. After the organic extract was separated by chloroform and washed well with brine, the combined extract was dried over MgSO$_4$, evaporated under reduced pressure and colourless crystals 16a (1.4 g, 2.6 mmol, 26% yield) were obtained, mp 146–148 $^\circ$C.

$^1$H NMR $\delta$: 3.20 (d, 1H, $J=11.4$ Hz), 3.62 (d, 1H, $J=11.4$ Hz), 3.73 (s, 3H), 3.75 (s, 3H), 3.76 (s, 3H), 3.84 (s, 3H), 6.74 (d, 2H, $J=8.8$ Hz), 6.78 (d, 2H, $J=8.8$ Hz), 6.82 (d, 2H, $J=8.8$ Hz), 6.94 (d, 2H, $J=8.5$ Hz), 7.14 (d, 2H, $J=8.8$ Hz), 7.24 (d, 2H, $J=8.8$ Hz), 7.28 (d, 2H, $J=8.8$ Hz), 7.33 (d, 2H, $J=8.5$ Hz).

1,1-Dichloro-2,2-bis($p$-methoxyphenyl)-3-[bis($p$-methylphenyl)methyl]cyclopropane (16b)

Compound 16b (2.7 g, 5.3 mmol, 53% yield) was prepared by the same procedure as 16a.

$^1$H NMR $\delta$: 2.26 (s, 3H), 2.36 (s, 3H), 2.36 (d, 1H, $J=11.5$ Hz), 3.64 (d, 1H, $J=11.5$ Hz), 3.72 (s, 3H), 3.75 (s, 3H), 6.74 (d, 2H, $J=8.8$ Hz), 6.78 (d, 2H, $J=8.8$ Hz), 7.07 (d, 2H, $J=8.1$ Hz), 7.14 (d, 2H, $J=8.8$ Hz), 7.20 (d, 2H, $J=7.8$ Hz), 7.24 (d, 2H, $J=8.8$ Hz), 7.27 (d, 2H, $J=7.8$ Hz), 7.32 (d, 2H, $J=8.1$ Hz).
1,1-Dichloro-2,2-bis(p-methoxyphenyl)-4,4-bis(p-chlorophenyl)methylcyclopropane (16c)

Compound 16c (2.9 g, 5.2 mmol, 51% yield) was prepared by the same procedure as 16a, mp 180–182 °C.

$^1$H NMR $\delta$: 3.16 (d, 1H, $J = 11.3$ Hz), 3.66 (d, 1H, $J = 11.3$ Hz), 3.73 (s, 3H), 3.76 (s, 3H), 6.75 (d, 2H, $J = 9.1$ Hz), 6.79 (d, 2H, $J = 9.1$ Hz), 7.10 (d, 2H, $J = 9.1$ Hz), 7.19 (d, 2H, $J = 9.1$ Hz), 7.25 (d, 2H, $J = 8.6$ Hz), 7.29 (d, 2H, $J = 8.6$ Hz), 7.35 (d, 2H, $J = 8.6$ Hz), 7.41 (d, 2H, $J = 8.6$ Hz).

Elemental analysis: calcd. for C$_{30}$H$_{24}$Cl$_4$O$_2$: C, 64.54; H, 4.33. Found: C, 64.55; H, 4.28.

1,1,4,4-Tetrakis(p-methoxyphenyl)butatriene (2a)

In an inert atmosphere, 16a (0.38 g, 0.78 mmol) and potassium t-butoxide (0.26 g, 2.3 mmol, 3.0 eq) were suspended in ether (5 ml), followed by the addition of DMSO (5 ml). The reaction mixture was stirred at room temperature for 3 h and then poured into water. Yellow powder 1a (0.23 g, 0.56 mmol, 72% yield) was separated by centrifugation, mp 256–257 °C.

$^1$H NMR $\delta$: 3.86 (s, 12H), 6.91 (d, 8H, $J = 9.0$ Hz), 7.49 (d, 8H, $J = 9.0$ Hz).

$^{13}$C NMR $\delta$: 55.4, 113.8, 119.4, 130.5, 131.9, 148.5, 159.3.

Elemental analysis: calcd for C$_{32}$H$_{28}$O$_4$: C, 80.65; H, 5.92. Found: C, 80.50; H, 6.04.

1,1-Bis(p-methoxyphenyl)-4,4-bis(p-methylphenyl)butatriene (2b)

In an inert atmosphere, 16b (0.38 g, 0.73 mmol) and potassium t-butoxide (0.25 g, 2.2 mmol, 3.0 eq) were suspended in ether (5 ml), followed by the addition of DMSO (5 ml). The reaction mixture was stirred at room temperature for 3 h and then poured into water. Yellow powder 2b (0.24 g, 0.54 mmol, 74% yield) was separated by centrifugation, mp 249–250 °C.

$^1$H NMR $\delta$: 2.40 (s, 6H), 3.86 (s, 6H), 6.92 (d, 4H, $J = 8.8$ Hz), 7.18 (d, 4H, $J = 8.3$ Hz), 7.46 (d, 4H, $J = 8.3$ Hz), 7.51 (d, 4H, $J = 8.8$ Hz).

$^{13}$C NMR $\delta$: 21.3, 55.4, 113.8, 120.1, 120.9, 129.1, 129.2, 130.7, 131.8, 136.3, 137.5, 148.8, 150.0, 159.4.

Elemental analysis: calcd for C$_{32}$H$_{30}$O$_4$•nH$_2$O (n = 2/3): C, 84.17; H, 6.48. Found: C, 84.03; H, 6.42.
X-ray data: empirical formula: C\textsubscript{32}H\textsubscript{28}O\textsubscript{2}, formula weight: 444.54, crystal habit: needle, crystal system: orthorhombic, space group: \textit{pbcn}, unit cell dimensions: \(a = 7.52750(10) \text{ Å}, b = 27.5908(6) \text{ Å}, c = 26.1680(6) \text{ Å}, \alpha = \beta = \gamma = 90^\circ, V = 5434.83(19) \text{ Å}^3\), \(Z = 8\), no. observations = 91704, no. variables = 4973, reflection/parameter ratio = 15.99, \(R = 0.0631\) \((I>2\sigma(I))\), \(R\) (all reflections) = 0.0840, \(wR\) (all reflections) = 0.1934, GoF = 1.099.

1,1-Bis(p-chlorophenyl)-4,4-bis(p-methylphenyl)butatriene (2c)

In an inert atmosphere, 16c (0.21 g, 0.37 mmol) and potassium \(t\)-butoxide (0.12 g, 1.1 mmol, 3.0 eq) were suspended in ether (5 ml), followed by the addition of DMSO (5 ml). The reaction mixture was stirred at room temperature for 4 h and then poured into water. Yellow powder 2c (0.10 g, 0.22 mmol, 59% yield) was separated by centrifugation, mp 289–292 °C.

\(^1\)H NMR \(\delta\): 3.87 (s, 6H), 6.93 (d, 4H, \(J = 8.6\) Hz), 7.34 (d, 4H, \(J = 8.6\) Hz), 7.44 (d, 4H, \(J = 8.6\) Hz), 7.48 (d, 4H, \(J = 8.6\) Hz).

\(^{13}\)C NMR \(\delta\): 55.4, 114.0, 128.7, 130.2, 130.8, 133.4, 137.3, 160.0.

Elemental analysis: calcd for C\textsubscript{30}H\textsubscript{22}Cl\textsubscript{2}O\textsubscript{2}: C, 74.23; H, 4.57. Found: C, 74.19; H, 4.60.

\[\begin{array}{c}
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2 \\
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2
\end{array}\]

\text{r.t., 4 h}

CH\textsubscript{2}Cl\textsubscript{2}

\[\begin{array}{c}
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2 \\
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2
\end{array}\]

1,1-Dicyano-3-dicyanomethylene-4-bis(p-methoxyphenyl)-2-[bis(p-methoxyphenyl)-methylene]cyclobutane (17a)

\[\begin{array}{c}
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2 \\
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2
\end{array}\]

\[\begin{array}{c}
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2 \\
\text{Ar}^1 \text{C}=\text{C} \text{C}=\text{C} \text{Ar}^2
\end{array}\]

[3]Cumulene 2a (0.10 g, 0.21 mmol) and TCNE (0.032 g, 0.25 mmol, 1.2 eq) were mixed in CH\textsubscript{2}Cl\textsubscript{2} (10 ml) at room temperature for 4 h. After evaporation of the solvent, recrystallization from CH\textsubscript{2}Cl\textsubscript{2}–hexane afforded red crystals 17a (0.088 g, 0.14 mmol, 69% yield), mp 179–181 °C.

\(^1\)H NMR \(\delta\): 3.87 (s, 6H), 3.88 (s, 3H), 3.89 (s, 3H), 7.00 (d, 2H, \(J = 9.1\) Hz), 7.03 (d, 4H, \(J = 9.1\) Hz), 7.04 (d, 2H, \(J = 9.1\) Hz), 7.28 (d, 2H, \(J = 9.1\) Hz), 7.41 (d, 2H, \(J = 9.1\) Hz), 7.44 (d, 4H, \(J = 9.1\) Hz), 7.47 (d, 2H, \(J = 9.1\) Hz).

\(^{13}\)C NMR \(\delta\): 55.4, 55.6, 70.9, 111.0, 111.6, 113.3, 114.2, 114.8, 115.5, 125.9, 131.1, 132.5, 133.9, 160.5, 163.1, 163.8, 174.7.
Elemental analysis: calcd for C₃₈H₂₈N₄O₄: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.18; H, 4.83; N, 9.51.

TOF-ESI-MS m/z: calcd for C₃₈H₂₈N₄O₄⁺ 605.2189. Found: 605.2192 ([M+H⁺]).

X-ray data: empirical formula: C₃₈H₂₈N₄O₄, formula weight: 604.66, crystal habit: block, crystal system: orthorhombic, space group: pben, unit cell dimensions: \(a = 23.3123(4) \, \text{Å}, b = 14.7753(2) \, \text{Å}, c = 18.2560(3) \, \text{Å}\), \(\alpha = \beta = \gamma = 90°\), \(V = 6288.2(2) \, \text{Å}^3\), \(Z = 8\), no. observations = 5755, no. variables = 419, reflection/parameter ratio = 13.74, \(R = 0.0375 (I>2\sigma(I))\), \(R\) (all reflections) = 0.0481, \(wR\) (all reflections) = 0.0994, GoF = 1.072.

1,1-Dicyano-3-dicyanomethylene-4-bis(p-methoxyphenyl)-2-[bis(p-methylphenyl)methylene]-cyclobutane (17b)

[3]Cumulene 2b (0.14 g, 0.28 mmol) and TCNE (0.043 g, 0.34 mmol, 1.2 eq) were mixed under the same reaction conditions as the reaction of 2a and TCNE. Recrystallization from CH₂Cl₂–hexane gave red crystals 17b (0.12 g, 0.21 mmol, 76% yield), mp 165 °C (decomp).

\(^1\)H NMR: \(\delta: 2.42 (s, 6H), 3.89 (s, 6H), 7.00 (d, 2H, \text{J} = 8.4 \, \text{Hz}), 7.04 (d, 2H, \text{J} = 8.6 \, \text{Hz}), 7.28 (d, 2H, \text{J} = 8.9 \, \text{Hz}), 7.33 (d, 4H, \text{J} = 8.6 \, \text{Hz}), 7.40 (d, 4H, \text{J} = 8.6 \, \text{Hz}), 7.41 (d, 2H, \text{J} = 8.4 \, \text{Hz}).\)

\(^{13}\)C NMR: \(\delta: 21.2, 55.6, 71.0, 113.2, 114.2, 114.8, 115.5, 129.5, 129.6, 130.9, 132.5, 133.9, 140.1, 163.1, 163.8.\)

TOF-ESI-MS m/z: calcd for: C₃₈H₂₇N₄O₄− 571.2134. Found: 571.2136 ([M−H]−).

X-ray data: empirical formula: C₃₈H₂₈N₄O₂, formula weight: 572.66, crystal habit: block, crystal system: triclinic, space group: P-1, unit cell dimensions: \(a = 11.1289(4) \, \text{Å}, b = 12.3596(4) \, \text{Å}, c = 12.6371(4) \, \text{Å}\), \(\alpha = 102.539(2)°, \text{J} = 96.811(2)°, \gamma = 113.934(2)°, \text{J} = 6288.2(2) \, \text{Å}^3, Z = 2\), no. observations = 5408, no. variables = 401, reflection/parameter ratio = 13.49, \(R = 0.0440 (I>2\sigma(I))\), \(R\) (all reflections) = 0.0549, \(wR\) (all reflections) = 0.1348, GoF = 1.096.

1,1-Dicyano-3-dicyanomethylene-4-bis(p-methoxyphenyl)-2-[bis(p-chlorophenyl)methylene]-cyclobutane (17c)

[3]Cumulene 2c (0.10 g, 0.22 mmol) and TCNE (0.033 g, 0.24 mmol, 1.2 eq) were mixed under the same reaction conditions as the reaction of 2a and TCNE. Recrystallization from CH₂Cl₂–hexane gave red crystals 17c (0.11 g, 0.18 mmol, 84% yield), mp 160 °C (decomp).

\(^1\)H NMR: \(\delta: 3.90 (s, 6H), 7.02 (d, 2H, \text{J} = 8.6 \, \text{Hz}), 7.06 (d, 2H, \text{J} = 9.1 \, \text{Hz}), 7.25 (d, 2H, \text{J} = 9.1 \, \text{Hz}), 7.42 (d, 2H, \text{J} = 8.6 \, \text{Hz}), 7.44 (d, 4H, \text{J} = 8.6 \, \text{Hz}), 7.54 (d, 4H, \text{J} = 8.6 \, \text{Hz}).\)

\(^{13}\)C NMR: \(\delta: 55.6, 55.7, 69.8, 112.8, 114.9, 115.7, 119.0, 129.4, 130.5, 131.9, 132.7, 134.1, 136.6, 163.4, 164.2, 172.6.\)

TOF-ESI-MS m/z: calcd for: C₃₆H₂₁N₄O₂Cl₂⁻ 611.1042. Found: 611.1021 ([M-H]⁻).
X-ray data: empirical formula: C_{36}H_{22}N_{4}O_{2}Cl_{2}, formula weight: 613.48, crystal habit: needle, crystal system: triclinic, space group: P-1, unit cell dimensions: \( a = 13.0039(3) \text{ Å}, b = 14.3980(3) \text{ Å}, c = 18.6793(4) \text{ Å}, \alpha = 99.561(7)^\circ, \beta = 91.793(7)^\circ, \gamma = 103.561(7)^\circ \), \( V = 3356.3(1) \text{ Å}^3 \), \( Z = 4 \), no. observations = 12006, no. variables = 815, reflection/parameter ratio = 14.73, \( R = 0.0784 \) \((I>2\sigma(I))\), \( R \) (all reflections) = 0.1428, \( wR \) (all reflections) = 0.1922, \( \text{GoF} = 1.021 \).

1,3-Bis(dichlorophenylvinylidene)-2,2,4,4-tetramethoxyphenylcyclobutane (18c)

\(^1\text{H} \) NMR spectra showed that the reaction of 2c and TCNE in CH\(_2\)Cl\(_2\) at room temperature gave not only main product 17c but also a small amount of minor product, head-to-tail dimer 18c. Although 18c could not be isolated from a solution of 17c in CH\(_2\)Cl\(_2\), stirring 2c (0.043 g, 0.088 mmol) in toluene at 90 °C for 3 h followed by recrystallization from CH\(_2\)Cl\(_2\)-hexane gave yellow crystals 18c (0.017 g, 0.018 mmol, 20% yield), mp 300 °C (decomp).

\(^1\text{H} \) NMR \( \delta \): 3.77 (s, 12H), 6.65 (d, 8H, \( J = 9.1 \text{ Hz} \)), 6.91 (d, 8H, \( J = 8.6 \text{ Hz} \)), 7.00 (d, 8H, \( J = 9.1 \text{ Hz} \)), 7.20 (d, 8H, \( J = 8.6 \text{ Hz} \)).

\(^{13}\text{C} \) NMR \( \delta \): 55.4, 113.5, 115.8, 128.7, 128.9, 129.8, 133.8, 134.7, 136.8, 158.5, 200.3.

Elemental analysis: calcd for C\(_{60}\)H\(_{44}\)O\(_4\)Cl\(_4\)·nH\(_2\)O (n = 1/2): C, 73.55; H, 4.63. Found: C, 73.63; H, 4.75.

X-ray data: empirical formula: C\(_{60}\)H\(_{44}\)O\(_4\)Cl\(_4\), formula weight: 970.75, crystal habit: needle, crystal system: monoclinic, space group: \( P2_1/n \), unit cell dimensions: \( a = 15.9572(3) \text{ Å}, b = 8.7817(2) \text{ Å}, c = 16.7713(3) \text{ Å}, \alpha = \gamma = 90^\circ, \beta = 91.2657(12)^\circ, V = 2349.61(8) \text{ Å}^3 \), \( Z = 2 \), no. observations = 4305, no. variables = 309, reflection/parameter ratio = 13.93, \( R = 0.0449 \) \((I>2\sigma(I))\), \( R \) (all reflections) = 0.0601, \( wR \) (all reflections) = 0.1328, \( \text{GoF} = 1.075 \).

\[ \text{OMe} \quad \text{MeOH or CH}_2\text{CN} \quad \text{rt, 3—24 h} \]

4-(\(\rho\)-Methoxyphenyl)-2-\(\rho\)-(Methoxyphenyl)methylene-1,1-dicyano-3-dicyanomethyl-7-methoxy-1,2-dihydropyrene (21a)

Compound 17a (0.017 g, 0.029 mmol) was stirred in MeOH at room temperature for 4 h. The mixture was evaporated under reduced pressure and the residue was recrystallized from CH\(_2\)Cl\(_2\)—
hexane to give 21a (0.011 g, 0.019 mmol, 67% yield) as pale yellow crystals, mp 164–166 °C.

1H NMR (at 51 °C) δ: 3.84 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.89 (s, 3H, OMe), 4.64 (s, 1H, CH(CN)₂), 6.83 (s, 1H, ring C), 6.84 (d, 1H, J = 2.3 Hz, ring C), 6.92 (d, 2H, J = 9.1 Hz, PhOMe), 6.98–7.03 (m, 6H, PhOMe), 7.13 (d, 2H, J = 9.1 Hz, PhOMe), 7.19 (d, 2H, J = 8.6 Hz, PhOMe), 7.39 (d, 1H, J = 2.3 Hz, ring C).

13C NMR (at 51 °C) δ: 27.6, 55.4, 55.5, 55.6, 55.8, 110.9, 112.9, 115.0, 115.4, 115.7, 118.0, 118.4, 126.6, 130.6, 130.7, 131.2, 132.6, 133.2, 134.1, 146.0, 152.6, 160.8, 161.8, 162.1, 163.3.

Elemental analysis: calcd for C₃₈H₂₈N₄O₄: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.69; H, 4.57; N, 9.02.

X-ray data: empirical formula: C₃₈H₂₈N₄O₄, formula weight: 604.66, crystal habit: needle, crystal system: orthorhombic, space group: Pbc a, unit cell dimensions: a = 20.9635(3) Å, b = 13.2472(2) Å, c = 22.6274(4) Å, α = β = γ = 90°, V = 6283.8(2) Å³, Z = 8, no. observations = 5732, no. variables = 419, reflection/parameter ratio = 13.72, R = 0.1072 (I>2σ(I)), R (all reflections) = 0.1894, wR (all reflections) = 0.2968, GoF = 1.050.

4-(p-Methylphenyl)-2-bis(p-methoxyphenyl)methylene-1,1-dicyano-3-dicyanomethyl-7-methyl-1,2-dihydronaphthalene (21b)

Compound 17b (0.040 g, 0.070 mmol) was stirred in MeOH at room temperature for 24 h. After usual workup, 21b was obtained as yellow powder, mp 127–132 °C (decomp). No further purification was done by recrystallization or by preparative layer chromatography.

1H NMR (at 51 °C) δ: 2.40 (s, 3H, Me), 2.42 (s, 3H, Me), 3.84 (s, 3H, OMe), 3.89 (s, 3H, OMe), 4.64 (s, 1H, CH(CN)₂), 6.84 (s, 1H, ring C), 6.85 (d, 1H, J = 2.3 Hz, ring C), 6.92 (d, 2H, J = 9.1 Hz, PhMe), 6.98–7.03 (m, 6H, PhOMe), 7.12 (d, 2H, J = 9.1 Hz, PhMe), 7.19 (d, 2H, J = 8.6 Hz, PhOMe), 7.38 (d, 1H, J = 2.3 Hz, ring C).

13C NMR (at 51 °C) δ: 21.4, 21.6, 27.5, 55.4, 55.5, 110.8, 112.9, 115.0, 115.5, 115.8, 126.8, 129.6, 130.5, 132.6, 133.2, 134.2, 140.1, 141.3, 146.3, 162.2, 163.4.


4-(p-Chlorophenyl)-2-bis(p-methoxyphenyl)methylene-1,1-dicyano-3-dicyanomethyl-7-chloro-1,2-dihydronaphthalene (21c)

Compound 17c (0.030 g, 0.049 mmol) was stirred in MeOH at room temperature for 4 h. After usual workup, 21c (0.011 g, 0.017 mmol, 35% yield) was obtained as yellow powder, mp 146–147 °C (decomp).

1H NMR (at 51 °C) δ: 3.85 (s, 3H, OMe), 3.86 (s, 3H, OMe), 4.65 (s, 1H, CH(CN)₂), 6.86 (s, 1H, ring C), 6.87 (d, 1H, J = 2.3 Hz, ring C), 7.03 (d, 2H, J = 9.1 Hz, PhCl), 7.14–7.18 (m, 6H, PhOMe), 7.38 (d, 1H, J = 2.3 Hz, ring C), 7.40 (d, 2H, J = 8.6 Hz, PhOMe), 7.46 (d, 2H, J = 9.1 Hz, PhCl).

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6-Methoxy-2-oxo-4,4,9-tris(\(p\)-methoxyphenyl)-1H-cyclopenta[\(b\)]naphthalene-1,1,3(2\(H,4\)\(H\))-tricarbonitrile (23a)

Recrystallization of 21a by a vapor diffusion method with MeOH–cyclohexane mainly yielded yellow crystals together with a few red crystals 23a, mp 235–239 °C.

NALDI-TOF-MS \(m/z\): calcd for: \(C_{36}H_{28}N_{8}O_5^+\) 606.20. Found: 606.19 ([M+H\(^+\)]). Calcd for: \(C_{36}H_{28}N_{8}O_5Na^+\) 628.19. Found: 628.17 ([M+Na\(^+\)]).

TOF-ESI-MS \(m/z\): calcd for: \(C_{36}H_{28}N_{8}O_5Na^+\) 606.20. Found: 606.2017 ([M+H\(^+\)]).

X-ray data: empirical formula: \(C_{36}H_{28}N_{8}O_5\), formula weight: 605.63, crystal habit: block, crystal system: monoclinic, space group: \(P2_1/c\), unit cell dimensions: \(a = 10.0721(2) \ \AA, b = 13.6832(3) \ \AA, c = 23.3065(4) \ \AA, \ \alpha = \gamma = 90^\circ, \beta = 95.6174(9)^\circ, V = 3196.64(11) \ \AA^3, Z = 4, \ \text{no. observations} = 36081, \ \text{no. variables} = 5845, \ \text{reflection/parameter ratio} = 13.95, \ \text{R} = 0.0426 (I>2\sigma(I)), \ R (all \ reflections) = 0.0701, wR (all \ reflections) = 0.1368, \ GoF = 1.118.

4,4-Bis(\(p\)-methylphenyl)-6-methoxy-2-oxo-9-(\(p\)-methoxyphenyl)-1H-cyclopenta-[\(b\)]naphthalene-1,1,3(2\(H,4\)\(H\))-tricarbonitrile (23b)

Compound 2b (0.10 g, 0.17 mmol) was stirred in MeOH at room temperature for 24 h. The mixture was separated by preparative layer chromatography, but 23b could not be further purified. Single crystals of the product were, therefore, produced by a vapor diffusion method with \(CH_3Cl_2\)-hexane, which afforded pure red single crystals. In addition, recrystallization of 21b by a vapor diffusion method with \(CH_3Cl_2\)-hexane mainly produced yellow crystals together with a few red crystals 23b, mp 244–246 °C.

\(^1\)H NMR \(\delta\): 2.38 (s, 6H, \(2xMe\)), 3.71 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.58 (d, 1H, \(J = 1.8 \ \text{Hz, ring D}\)), 6.81 (dd, 1H, \(J = 1.8 \ \text{and 8.8 Hz, ring D}\)), 7.07 (d, 4H, \(J = 8.2 \ \text{Hz, PhMe}\)), 7.11 (d, 2H, \(J = 8.2 \ \text{Hz, PhOMe}\)), 7.20 (d, 4H, \(J = 8.2 \ \text{Hz, PhMe}\)), 7.30 (d, 1H, \(J = 8.8 \ \text{Hz, ring D}\)), 7.33 (d, 2H, \(J = 8.2 \ \text{Hz, PhOMe}\)).

NALDI-TOF-MS \(m/z\): calcd for: \(C_{36}H_{37}N_{8}O_5Na^+\) 596.20. Found: 596.24 ([M+Na\(^+\)].

TOF-ESI-MS \(m/z\): calcd for: \(C_{36}H_{37}N_{8}O_5Na^+\) 574.2131. Found: 574.2159 ([M+H\(^+\)].

X-ray data: empirical formula: \(C_{36}H_{37}N_{8}O_5\), formula weight: 573.63, crystal habit: block, crystal system: monoclinic, space group: \(C2/c\), unit cell dimensions: \(a = 28.1011(5) \ \AA, b = 10.9295(2) \ \AA, c = 23.4906(4) \ \AA, \ \alpha = \gamma = 90^\circ, \beta = 97.8432(10)^\circ, V = 7147.2(2) \ \AA^3, Z = 8, \ \text{no. observations} = 40636, \ \text{no. variables} = 6463, \ \text{reflection/parameter ratio} = 16.11, \ R = 0.0644 (I>2\sigma(I)), \ R (all \ reflections) = 0.1127, wR (all \ reflections) = 0.1923, \ GoF = 0.998.
4,4-Bis(p-chlorophenyl)-6-methoxy-2-oxo-9-(p-methoxyphenyl)-1H-cyclopenta[b]naphthalene-1,1,3(2H,4H)-tricarbonitrile (23c)

Recrystallization of 21c by a vapor diffusion method with toluene–hexane mainly produced yellow crystals together with a few red crystals 23c, mp > 300 °C.

NALDI-TOF-MS \( m/z \): calcd for: \( \text{C}_{36}\text{H}_{21}\text{N}_{3}\text{O}_{3}\text{Cl}_{2}\text{Na}^+ \) 636.09. Found: 636.11 \( ([\text{M}+\text{Na}]^+) \).

TOF-ESI-MS \( m/z \): calcd for: \( \text{C}_{36}\text{H}_{22}\text{N}_{3}\text{O}_{3}\text{Cl}_{2}^+ \) 614.1038. Found: 614.1024 \( ([\text{M}+\text{H}]^+) \).

X-ray data: empirical formula: \( \text{C}_{36}\text{H}_{21}\text{N}_{3}\text{O}_{3}\text{Cl}_{2} \), formula weight: 614.46, crystal habit: needle, crystal system: monoclinic, space group: \( \text{C}2/c \), unit cell dimensions: \( a = 28.4477(18) \text{ Å}, b = 10.8997(6) \text{ Å}, c = 23.5205(14) \text{ Å}, \alpha = \gamma = 90^\circ, \beta = 98.339(3)^\circ, V = 7215.9(7) \text{ Å}^3, Z = 8, \) no. observations = 38808, no. variables = 6596, reflection/parameter ratio = 16.53, \( R = 0.0839 \) \( (I>2\sigma(I)) \), \( R \) (all reflections) = 0.1457, \( wR \) (all reflections) = 0.2747, \( \text{GoF} = 0.985 \).

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{AlCl}_3, \text{Benzene}} \text{O} & \text{Cl} \\
0^\circ \text{C} & \quad 1 \text{ h} \\
\end{align*}
\]

4-Chloro-1-phenylbutan-1-one

In an inert atmosphere, 4-bromobutyryl chloride (5.0 g, 43 mmol) was added dropwise to the solution of aluminum chloride (5.7 g, 43 mmol, 1.0 eq) in benzene (15 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 30 min at room temperature, and then poured on iced water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic extract was dried over MgSO\(_4\). The residue was evaporated under reduced pressure to give yellow oil (9.3 g, 41 mmol, 96% yield).

\(^1\text{H NMR} \delta: 2.31 \text{ (q, 2H, } J = 6.8 \text{ and } 6.4 \text{ Hz)}, 3.19 \text{ (t, 2H, } J = 6.8 \text{ Hz}), 3.55 \text{ (t, 2H, } J = 6.4 \text{ Hz)}, 7.45–7.49 \text{ (m, 2H)}, 7.56–7.59 \text{ (t, 1H, } J = 6.8 \text{ and } 1.4 \text{ Hz}), 7.98 \text{ (dd, 2H, } J = 8.5 \text{ and } 1.4 \text{ Hz}).

\(^{13}\text{C NMR} \delta: 26.8, 33.6, 36.5, 128.0, 128.6, 133.2, 136.6, 198.8.\)
(4-Oxo-4-phenylbutyl)triphenylphosphonium bromide (26)
A mixture of 4-chloro-1-phenylbutan-1-one (3.5 g, 15 mmol) and triphenylphosphine (PPh₃) (4.0 g, 15 mmol, 1.0 eq) in CH₃CN (25 ml) was refluxed for 24 h in an inert atmosphere. The resulting mixture was cooled to room temperature and evaporated under reduced pressure. The crude material was tried to be recrystallized from CH₃CN–ether, and then not crystal but green oil 26 (4.9 g, 10 mmol, 65% yield) containing PPh₃ was yielded.

$^1$H NMR δ: 2.08 (m, 2H), 3.62 (t, 3H, $J = 5.5$ Hz), 3.92 (t, 2H, $J = 13.3$ Hz), 7.44 (t, 2H, $J = 7.3$ Hz), 7.54 (t, 1H, $J = 7.3$ Hz), 7.38–7.73 (m, 6H), 7.78–7.81 (m, 3H), 7.86–7.91 (m, 6H), 8.02 (d, 2H, $J = 7.3$ Hz).

$^{13}$C NMR δ: 15.3, 20.4, 36.5, 116.5, 126.3, 126.6, 128.5, 128.7, 131.9, 133.1, 134.4, 197.7.

2-Trimethylsilylethynylbenzaldehyde (27)
To a solution of Pd(PPh₃)₄ (0.28 g, 0.24 mmol, 0.030 eq) and CuI (0.16 g, 0.82 mmol, 0.10 eq) in triethylamine (TEA) (12 ml), was added 2-bromobenzaldehyde (1.5 g, 0.95 ml, 8.2 mmol) and stirred for 15 min at room temperature in an inert atmosphere. To the resulting mixture was added trimethylsilylacetylene (1.3 ml, 9.0 mmol, 1.1 eq) and stirred for 12 h at room temperature. After filtering through celite, the reaction mixture was extracted with CH₂Cl₂. The organic extract was washed well with saturated NH₄Cl solution and H₂O. The residue was dried over MgSO₄, filtered, evaporated under reduced pressure and purified by silica gel column chromatography (EtOAc : hexane = 0.3 : 3.7) to afford pale orange oil 27 (1.5 g, 7.7 mmol, 94% yield).

$^1$H NMR δ: 0.28 (s, 9H), 7.42–7.56 (m, 1H), 7.52–7.58 (m, 2H), 7.91 (d, 1H, $J = 8.2$ Hz).

$^{13}$C NMR δ: 0.3, 100.3, 102.7, 127.1, 129.1, 133.7, 133.9, 136.4, 192.1.
In an inert atmosphere, a solution of 27 (0.40 g, 2.0 mmol) and 26 (1.4 g, 2.9 mmol, 1.5 eq) in dry THF (10 ml) was stirred for 20 min at 0 °C. To the resulting solution was added slowly potassium t-butoxide (0.53 g, 4.7 mmol, 2.4 eq) in dry THF (20 ml) and stirred for 17 h at room temperature. The mixture was cooled again to 0 °C, quenched with H2O, neutralized with conc. HCl and extracted with ether. The combined organic extract was evaporated under reduced pressure and purified by silica gel column chromatography (EtOAc : hexane = 0.3 : 3.7) to afford yellow oil (0.30 g, 0.89 mmol, 45% yield).

(E): 1H NMR δ: 0.27 (s, 9H), 2.65–2.73 (m, 2H), 3.20 (t, 2H, J = 7.2 Hz), 6.37–6.44 (m, 1H), 6.96 (d, 1H, J = 16.3 Hz).
(Z): 1H NMR δ: 0.25 (s, 9H), 2.65–2.73 (m, 2H), 3.11 (t, 2H, J = 7.2 Hz), 5.78–5.85 (m, 1H), 6.72 (d, 1H, J = 11.5 Hz). (Due to the complexity and overlapping of each signal, the rest of the signals (protons attributed to phenyl group) could not be identified.)

To a solution of (E/Z)-1-phenyl-5-(2-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-one (0.50 g, 1.5 mmol) in CH2Cl2 (5 ml) and anhydrous MeOH (5 ml) was added K2CO3 (0.63 g, 4.5 mmol, 3.0 eq) and stirred at room temperature for 18 h in an inert atmosphere. The resulting solution was quenched with saturated NH4Cl solution and extracted with CH2Cl2. The combined organic extract was washed with brine, dried over MgSO4, filtered and evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (EtOAc : hexane = 0.2 : 3.8) to afford ene-yne-allene precursor 3 (0.30 g, 1.2 mmol, 77% yield, E : Z = 1 : 0.85) as yellow oil.

(E)-3: 1H NMR δ: 2.68–2.74 (m, 2H), 3.20 (t, 2H, J = 7.2 Hz), 3.28 (s, 1H), 6.36–6.42 (m, 1H), 6.97 (d, 1H, J = 15.8 Hz), 7.20 (dt, 1H, J = 7.6, 1.2 Hz), 7.32 (dt, 1H, J = 7.6, 1.2 Hz), 7.43–7.59 (m, 5H), 7.99 (d, 2H, J = 7.2 Hz).
(Z)-3: \(^1^H\) NMR \(\delta\): 2.68–2.74 (m, 2H), 3.11 (t, 2H, \(J = 7.2\) Hz), 3.28 (s, 1H), 5.82–5.87 (m, 1H), 6.74 (d, 1H, \(J = 15.8\) Hz), 7.16 (dt, 1H, \(J = 7.6, 1.2\) Hz), 7.28 (dt, 1H, \(J = 7.6, 1.2\) Hz), 7.43–7.59 (m, 5H), 7.94 (d, 2H, \(J = 7.2\) Hz).

(E+Z)-3: \(^1^C\) NMR \(\delta\): 23.3, 27.7, 38.2, 38.5, 81.4, 81.6, 82.1, 82.4, 120.2, 121.5, 124.6, 126.7, 128.0, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 131.4, 132.1, 132.9, 133.1, 136.8, 136.9, 139.5, 139.7.

TOF-ESI-MS \(m/z\): calcd for: C\(_{19}\)H\(_{17}\)O\(^+\) 261.1279. Found: 261.1286 ([M + H]\(^+\)).

UV-vis: (\(\lambda_{\text{max}}\) nm, acetonitrile): 195 (\(\varepsilon\) 78,200), 220 (\(\varepsilon\) 41,400), 260 (\(\varepsilon\) 8,000), 335 (\(\varepsilon\) 1,300).

UV-vis: (\(\lambda_{\text{max}}\) nm, cyclohexane): 195 (\(\varepsilon\) 86,900), 220 (\(\varepsilon\) 44,000), 260 (\(\varepsilon\) 8,800) 335 (\(\varepsilon\) 1,800).

**3-Ethynyl-5-hexyn-1-ol (31)**

In an inert atmosphere, a solution of \(n\)-BuLi (35 ml, 56 mmol, 3.5 eq) and \(N,N,N',N'\)-Tetramethylethylenediamine (TMEDA) (2.4 ml, 16 mmol, 1.0 eq) in THF (20 ml) was cooled to \(-40\) °C, and 1,5-hexadiyne (3.1 ml, 16 mmol) was slowly added to the solution over a period of 5 min. After stirring at \(-10\) °C for 2 h, the solution was cooled again to \(-40\) °C and ethylene oxide (1.0 M in THF, 25 ml, 25 mmol, 1.5 eq) was added. After stirring at room temperature for 2 h, the reaction was quenched with saturated NH\(_4\)Cl solution and extracted with ether. The combined organic extract was washed with brine, dried over MgSO\(_4\), filtered and evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (EtOAc : hexane = 1 : 3) to give 31 (1.3 g, 11 mmol, 66% yield) as pale yellow oil.

\(^1^H\) NMR \(\delta\): 1.74–1.82 (m, 2H), 1.91–1.96 (m, 1H), 2.08 (t, 1H, \(J = 2.7\) Hz), 2.19 (d, 1H, \(J = 2.7\) Hz), 2.47 (dt, 2H, \(J = 5.9\) Hz, 2.7 Hz), 2.76–2.82 (m, 1H), 3.85 (t, 2H, \(J = 5.4\) Hz).

\(^1^C\) NMR \(\delta\): 24.6, 27.6, 36.3, 60.4, 70.3, 70.6, 81.2, 85.3.
3-(Formylmethyl)-1,5-hexadiyne (32)
To a solution of 31 (0.53 g, 4.3 mmol) in CH$_2$Cl$_2$ (12 ml) was added pyridinium chlorochromate (PCC) (1.4 g, 6.5 mmol, 1.5 eq) and stirred at room temperature for 4 h. After filtering through celite, the reaction mixture was extracted with ether. The combined organic extract was washed with H$_2$O and brine, dried over MgSO$_4$, filtered and evaporated under reduced pressure to give 32 (0.36 g, 3.0 mmol, 70% yield) as brown oil.

$^1$H NMR $\delta$: 2.11 (t, 1H, $J = 2.3$ Hz), 2.20 (d, 1H, $J = 2.3$ Hz), 2.44–2.54 (m, 2H), 2.71–2.87 (m, 2H), 3.10–3.14 (m, 1H), 9.82 (s, 1H).

$^{13}$C NMR $\delta$: 24.1, 24.8, 46.8, 70.9, 71.2, 80.2, 83.9, 199.7.

3-Ethynyl-1-phenyl-5-hexyn-1-ol (33)
A three-necked flask connected with a firestone valve, dropping funnel and reflux condenser was equipped. Magnesium (0.10 g, 4.2 mmol, 2.0 eq) was put in the flask and nitrogen gas was purged in the system. Firstly, dry THF (3 ml) and a piece of iodine was added, and then bromobenzene (0.44 ml, 4.2 mmol, 2.0 eq) was run very slowly in to the flask through the dropping funnel. After stirring for 0.5 h at room temperature, color of the solution was converted to pale yellow. The solution of 32 (0.25 g, 2.1 mmol) in dry THF (2 ml) was added over a period of 10 min and stirred for 1 h. Then the reaction was quenched with saturated NH$_4$Cl solution. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (EtOAc : hexane = 1.2 : 2.8) to afford 33 (0.38 g, 1.9 mmol, 90% yield) as yellow oil.
3-(Benzoylmethyl)-1,5-hexadiyne (5a)
To a solution of chromium (VI) oxide (0.37 g, 3.7 mmol, 3.0 eq) in H₂O (1.5 ml) was added conc. H₂SO₄ (0.13 ml, 2.5 mmol, 2.0 eq) in H₂O (1.5 ml) at 0 °C (Jones reagent). To a solution of 33 (0.25 g, 1.2 mmol) in acetone (5 ml) was added Jones reagent and stirred at room temperature for 1.5 h. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure to give brown oil. The crude material was purified by silica gel column chromatography (EtOAc : hexane = 1 : 3) to afford enediyne precursor 5a (0.31 g, 1.6 mmol, 84% yield) as colourless solid, mp 54–56 °C.

\( ^1 \text{H} \text{NMR} \delta: 2.10 (t, 1H, J = 2.8 Hz), 2.15 (d, 1H, J = 2.3 Hz), 2.58–2.15 (m, 2H), 3.30–3.42 (m, 3H), 7.48 (t, 2H, J = 7.3 Hz), 7.59 (t, 1H, J = 7.3 Hz), 7.99 (d, 2H, J = 7.3 Hz). \)

\( ^{13} \text{C} \text{NMR} \delta: 24.0, 25.9, 70.0, 70.9, 80.8, 85.2, 128.1, 128.7, 133.4, 136.6, 197.1. \)

Elemental analysis: calcd for C₁₄H₁₂O; C, 85.68; H, 6.16. Found: C, 85.44; H, 6.23.

TOF-ESI-MS m/z: calcd for C₁₄H₁₃O⁺ 197.0966. Found: 197.0970 ([M + H⁺]).

UV-vis: (λ_max nm, acetonitrile): 240 (ε 12,800), 275 (ε 1,300).

UV-vis: (λ_max nm, cyclohexane): 240 (ε 14,200), 280 (ε 1,200).

Ethyl 4-iodobenzoate
To a solution of 4-iodobenzoic acid (2.0 g, 8.1 mmol) in EtOH (60 ml) was added conc. H₂SO₄ (2 ml) and refluxed for 22 h. After cooling to room temperature, a solution of NaHCO₃ (6.0 g) in H₂O (80 ml) was added and extracted with ether. The organic extract was washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure to give colorless oil (2.2 g, 7.8 mmol, 97% yield).

\( ^1 \text{H} \text{NMR} \delta: 1.39 (t, 3H, J = 7.3 Hz), 4.37 (q, 2H, J = 7.3 Hz), 7.74 (d, 2H, J = 8.7 Hz), 7.80 (d, 2H, J = 8.7 Hz). \)

\( ^{13} \text{C} \text{NMR} \delta: 14.3, 61.2, 100.5, 129.9, 131.0, 137.6, 166.1. \)
Ethyl 4-(3-ethynyl-1-hydroxyhex-5-yn-1-yl)benzoate (34)

To a solution of ethyl 4-iodobenzoate (0.77 g, 2.8 mmol) in dry THF (2 ml) was added isopropylmagnesium chloride lithium chloride complex solution (1.4 M in THF, 3.0 ml, 4.2 mmol, 1.5 eq) dropwise in an inert atmosphere at −40 °C. After stirring for 1 h, the solution of 32 (0.4 g, 3.3 mmol, 1.2 eq) in dry THF (2 ml) was added dropwise and stirred for 2.5 h. The reaction was quenched with saturated NH₄Cl solution and the mixture was extracted with EtOAc. The combined organic extract was washed with brine, and then dried over MgSO₄. This was evaporated under reduced pressure and pale yellow oil 34 (0.39 g, 1.5 mmol, 53% yield) was obtained.

$^1$H NMR δ: 1.40 (t, 3H, $J = 7.3$ Hz), 1.96–2.50 (m, 7H), 4.37 (q, 2H, $J = 7.3$ Hz), 4.98–5.10 (m, 1H), 7.46 (d, 2H, $J = 8.2$ Hz), 8.03 (d, 2H, $J = 8.2$ Hz).

$^{13}$C NMR δ: 10.4, 20.7, 24.0, 38.7, 57.1, 66.8, 67.5, 68.6, 76.9, 77.1, 81.3, 81.4, 121.6, 122.0, 126.0, 144.8, 162.5.

Ethyl 4-(3-ethynylhex-5-ynoyl)benzoate

To a solution of chromium (VI) oxide (0.21 g, 2.2 mmol, 3.0 eq) in H₂O (1 ml) was added conc. H₂SO₄ (80 μl, 1.4 mmol, 2.0 eq) in H₂O (1 ml) at 0 °C (Jones reagent). To a solution of 34 (0.11 g, 0.42 mmol) in acetone (2.5 ml) was added Jones reagent and stirred at room temperature for 2 h. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (EtOAc : hexane = 1 : 3) to afford pale yellow oil (0.094 g, 0.35 mmol, 83% yield).

$^1$H NMR δ: 1.43 (t, 3H, $J = 7.3$ Hz), 2.10 (t, 1H, $J = 2.3$ Hz), 2.15 (d, 1H, $J = 2.3$ Hz), 2.58–2.60 (m, 2H), 3.30–3.49 (m, 3H), 4.42 (q, 2H, $J = 7.3$ Hz), 8.03 (d, 2H, $J = 8.2$ Hz), 8.14 (d, 2H, $J = 8.2$ Hz).

$^{13}$C NMR δ: 14.3, 24.0, 25.9, 42.4, 61.5, 70.3, 71.1, 80.6, 84.9, 128.0, 129.8, 134.5, 139.7, 165.7, 196.7.
4-(3-Ethynylhex-5-ynoyl)benzoic acid (5b)

To a solution of ethyl 4-(3-ethynylhex-5-ynoyl)benzoate (0.092 g, 0.34 mmol) in EtOH (2 ml) was added 2N NaOH solution (2 ml) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with conc. HCl (pH 3–4) and extracted with EtOAc. The combined organic extract was washed with brine, and then dried over MgSO₄. This was evaporated under reduced pressure and white solid 5b (0.077 g, 0.32 mmol, 95% yield) was obtained, mp 164–166 °C.

1H NMR δ: 2.11 (t, 1H, J = 2.3 Hz), 2.16 (d, 1H, J = 2.3 Hz), 2.60–2.61 (m, 2H), 3.33–3.45 (m, 3H), 8.08 (d, 2H, J = 8.3 Hz), 8.22 (d, 2H, J = 8.3 Hz).

13C NMR δ: 24.0, 25.9, 42.5, 70.3, 71.1, 80.6, 84.8, 128.1, 130.5, 133.1, 140.4, 170.1, 196.7.

Elemental analysis: calcd for C₁₅H₁₂O₃・nEtOH (n = 0.32); C, 73.65; H, 5.51. Found: C, 73.64; H, 5.50.


UV-vis (λ_max nm, acetonitrile): 250 (ε 41,800), 290 (ε 4,200).

UV-vis (λ_max nm, cyclohexane): 250 (ε 37,000), 300 (ε 900).

Cleavage of supercoiled φX174RFI plasmid DNA by Xho I, enediyne precursor 5 and acetophene

φX174RFI plasmid DNA solution (TAKARA BIO INC., Japan) (Table 8, (1)) was incubated with each compound solution (Table 10, (3)–(9)) in 25% acetonitrile in TE (10 mM Tris HCl, 1 mM ethylenediaminetetraacetic acid (EDTA), pH 8.0) or only TE under UV irradiation (≧280 nm, high-pressure mercury lamp) in 96 well micro plate at room temperature for 0–8 h (Table 12). On the other hand, DNA solution with Xho I (restriction enzyme, cleaving site = 136, TAKARA BIO INC.) (Table 9, (2)) was incubated at 37 °C for 0–1 h (Table 11) followed by heat shock for 10 min. Total amounts of each product, ladder (Trackit 1 kb Plus DNA Ladder 0.1 μg/μL, 3 or 5 μl, Invitrogen) and mass ladder (High DNA Mass Ladder, 4 μl, Invitrogen) were loaded on 0.9% agarose gel. After electrophoresis (120 V) for 30 min, the gel was stained with ethidium bromide and destained in water (5,3, Figs. 35 and 36).
Table 8 DNA solution.

<table>
<thead>
<tr>
<th>No.</th>
<th>φX174RFI plasmid DNA (μl)</th>
<th>TEa (μl)</th>
<th>Dyeb (μl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>4.0</td>
<td>96.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

a TE = Mixture of 10 mmol/L Tris-HCl (pH 8.0) and 1 mmol/L EDTA (pH 8.0)
b Dye = 6 × Loading Dye (Bromophenol Blue (BPB), Orange G (OrG))

Table 9 DNA solution with Xho I.

<table>
<thead>
<tr>
<th>No.</th>
<th>φX174RFI plasmid DNA (μl)</th>
<th>10×H buffera (μl)</th>
<th>Xho I (μl)</th>
<th>mQ (μl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>6.0</td>
<td>1.5</td>
<td>0.5</td>
<td>7.0</td>
</tr>
</tbody>
</table>

a 10× Concentrated high salt concentration buffer (TAKARA BIO INC., Japan) (500 mM Tris-HCl (pH 7.5), 100 mM MgCl2, 10 mM dithiothreitol (DTT) and 1000 mM NaCl)

Table 10 Solutions of enediyne precursor 5 (5.00 mM) or acetophenone (5.00 mM).

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)</td>
<td>-</td>
<td>TE</td>
</tr>
<tr>
<td>(4)</td>
<td>-</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>(5)</td>
<td>5a</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>(6)</td>
<td>5b</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>(7)</td>
<td>5b</td>
<td>TE</td>
</tr>
<tr>
<td>(8)</td>
<td>Acetophenone</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>(9)</td>
<td>Acetophenone</td>
<td>TE</td>
</tr>
</tbody>
</table>

Table 11 Cleavage conditions of supercoiled φX174RFI plasmid DNA by Xho I (restriction enzyme, cleavage site = 1) at 37 °C for 0–60 min (see 5.3, Fig. 35).

<table>
<thead>
<tr>
<th>Run</th>
<th>DNA solution</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(1) 6.0 μl</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>(2) 15 μl</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>(2) 15 μl</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>(2) 15 μl</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>(2) 15 μl</td>
<td>60</td>
</tr>
</tbody>
</table>
Table 12 Cleavage conditions of supercoiled φX174RFI plasmid DNA by precursor 5 or acetophenone at room temperature under UV irradiation (≥280 nm) for 0–8 h (see 5.3, Fig. 36).

<table>
<thead>
<tr>
<th>Run</th>
<th>DNA solution</th>
<th>Compound solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TE</th>
<th>UV-irradiation (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)-0</td>
<td>(1) 6.0 μl</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>(a)-1</td>
<td>(1) 6.0 μl</td>
<td>(3) 6.0 μl</td>
<td>12.0 μl</td>
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</tr>
<tr>
<td>(a)-2</td>
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<td>(3) 6.0 μl</td>
<td>12.0 μl</td>
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</tr>
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<td>(a)-3</td>
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<td>(3) 6.0 μl</td>
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</tr>
<tr>
<td>(a)-4</td>
<td>(1) 6.0 μl</td>
<td>(3) 6.0 μl</td>
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<td>8</td>
</tr>
<tr>
<td>(b)-0</td>
<td>(1) 6.0 μl</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>(b)-1</td>
<td>(1) 6.0 μl</td>
<td>(4) 6.0 μl</td>
<td>12.0 μl</td>
<td>1</td>
</tr>
<tr>
<td>(b)-2</td>
<td>(1) 6.0 μl</td>
<td>(4) 6.0 μl</td>
<td>12.0 μl</td>
<td>2</td>
</tr>
<tr>
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<td>(1) 6.0 μl</td>
<td>(4) 6.0 μl</td>
<td>12.0 μl</td>
<td>4</td>
</tr>
<tr>
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<td>(4) 6.0 μl</td>
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<td>(b)-8</td>
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<tr>
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<td>-</td>
<td>-</td>
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<td>(7) 6.0 μl</td>
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<td>4</td>
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<tr>
<td>(c)-8</td>
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<td>(7) 6.0 μl</td>
<td>12.0 μl</td>
<td>8</td>
</tr>
<tr>
<td>(d)-0</td>
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<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
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<td>(8) 6.0 μl</td>
<td>12.0 μl</td>
<td>1</td>
</tr>
<tr>
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<td>(8) 6.0 μl</td>
<td>12.0 μl</td>
<td>2</td>
</tr>
<tr>
<td>(d)-3</td>
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<td>(8) 6.0 μl</td>
<td>12.0 μl</td>
<td>4</td>
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<tr>
<td>(d)-4</td>
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<td>12.0 μl</td>
<td>8</td>
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<td>(d)-6</td>
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<td>(d)-7</td>
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<td>4</td>
</tr>
<tr>
<td>(d)-8</td>
<td>(1) 6.0 μl</td>
<td>(9) 6.0 μl</td>
<td>12.0 μl</td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>a</sup>The final concentration of compound solutions (5 or acetophenone) was 1.25 mM.
References and notes


27. (a) H NMR (19a): 3.70 (s, 6H, 2 × OMe), 3.89 (s, 6H, 2 × OMe), 6.34 (d, 4H, J = 8.6 Hz, ring A), 6.69 (d, 4H, J = 8.6 Hz, ring A), 7.03 (d, 4H, J = 8.6 Hz, ring B), 7.33 (d, 4H, J = 8.6 Hz, ring B). See Fig. 19.
28. ^1^H NMR (19c) δ: 3.75 (s, 3H, OMe), 3.89 (s, 3H, OMe), 6.42 (d, 2H, J = 9.2 Hz, PhOMe, ring A), 6.70 (d, 2H, J = 8.7 Hz, PhCl, ring A), 6.74 (d, 2H, J = 9.2 Hz, PhOMe, ring A), 6.83 (d, J = 8.7 Hz, PhCl, ring A). Due to the complexity and overlapping of each signal, the rest of the signals could not be identified. See Fig. 21.


32. ^1^H NMR (acetophenone 29a, acetonitrile-d$_3$) δ: 2.57 (s, 3H), 7.48–7.52 (m, 2H), 7.59–7.63 (m, 1H), 7.95–7.98 (m, 2H). ^1^H NMR (acetophenone 29a, cyclohexane-d$_{12}$) δ: 2.43 (s, 3H), 7.29–7.34 (m, 2H), 7.37–7.41 (m, 1H), 7.86–7.89 (m, 2H).

33. ^1^H NMR (Z-enediyne 30a, acetonitrile-d$_3$) δ: 2.92 (s, 2H) 5.92 (s, 2H). ^1^H NMR (E-enediyne 30a, acetonitrile-d$_3$) δ: 3.08 (s, 2H), 5.71 (s, 2H). ^1^H NMR (E-enediyne 30a, cyclohexane-d$_{12}$) δ: 3.69 (s, 2H), 5.99 (s, 2H).


35. ^1^H NMR (1-phenylethanol, acetonitrile-d$_3$) δ: 1.38 (d, 3H, J = 6.3 Hz), 4.80 (m, 1H). ^1^H NMR (1-phenylethanol, cyclohexane-d$_{12}$) δ: 1.36 (d, 3H, J = 6.8 Hz), 4.74 (q, 1H, J = 6.8 Hz). Due to the complexity and overlapping of each signal, the rest of the signals could not be identified.


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