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[1] and acetylene, are unique and these synthesis and reactivity have been reported in several reviews.[2] 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[3] and dyes.[4] Cumulene also draws attention as a material for synthesis of novel organometallic compound[5] and functional polymer.[6] On the other hand, 1,2,4-heptatriene-6-yne and 1,5-hexadiyne-3-ene are generally known as potent antitumor agents.[7–11] Recently, various functional ene-yne-allene and enediyne precursors have been developed.[12] In addition, several literatures reported metal catalyzed syntheses of physiologically active hetero rings from aminoallene.[13] 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.

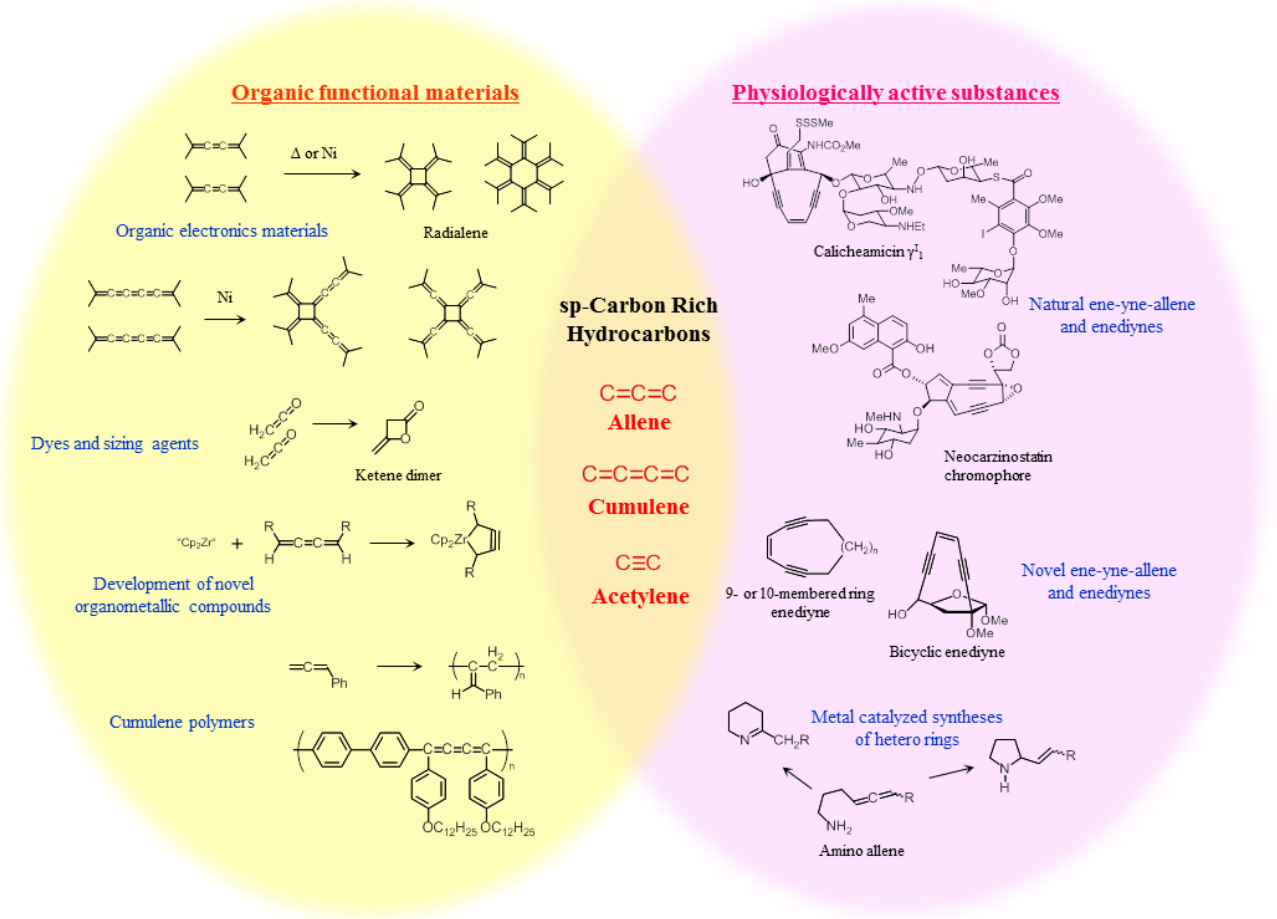


Fig. 1 Organic functional materials and physiologically active substances associated with allene / cumulene and acetylene.

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.[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.[15] For example, a [3]cumulene possessing an electron withdrawing group such as Cl as a terminal group thermally dimerizes to a [4]radialene.[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.[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.[18]

Firstly, I have investigated the charge-transfer reactions of tetraarylallene (**1**) / tetraaryl[3]cumulene (**2**) with tetracyanoethene (TCNE) (Fig. 2). The ethene, TCNE, was discovered in 1957 as the simplest of the symmetrical percyanoalkene.[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.[20]

Secondly, I focused on DNA cleaving molecules possessing allene and acetylene. Natural ene-yne-allene and enediyne precursors such as calicheamicin[7], dynemicin[8] and neocarzinostatin[9] are known to be DNA cleaving molecules derived from bacteria. These precursors can undergo either Myers-Saito[10] or Masamune-Bergman[11] cyclization, with the produced diradical being able to abstract hydrogen from the phosphate backbone of DNA (Scheme 1).[29] However, these precursors are toxic to not only tumor cells but also normal cells; therefore, they are not effective antitumor agents.[21] Alternatively, ene-yne-allene and enediyne precursors with various functionalities have been designed and reported in several reviews.[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.[12(a)] A bicyclic enediyne was also synthesized. Although it was stable at room temperature, cyclization only occurred at elevated temperatures.[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.[22] 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.

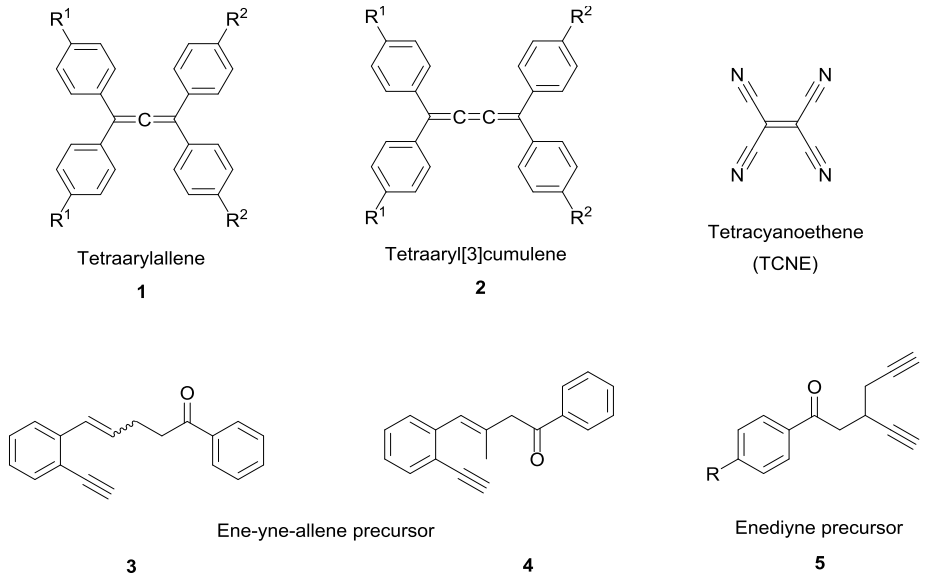
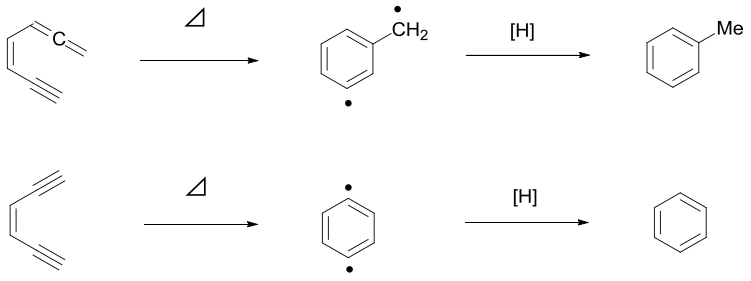


Fig. 2 Major compounds in this study.



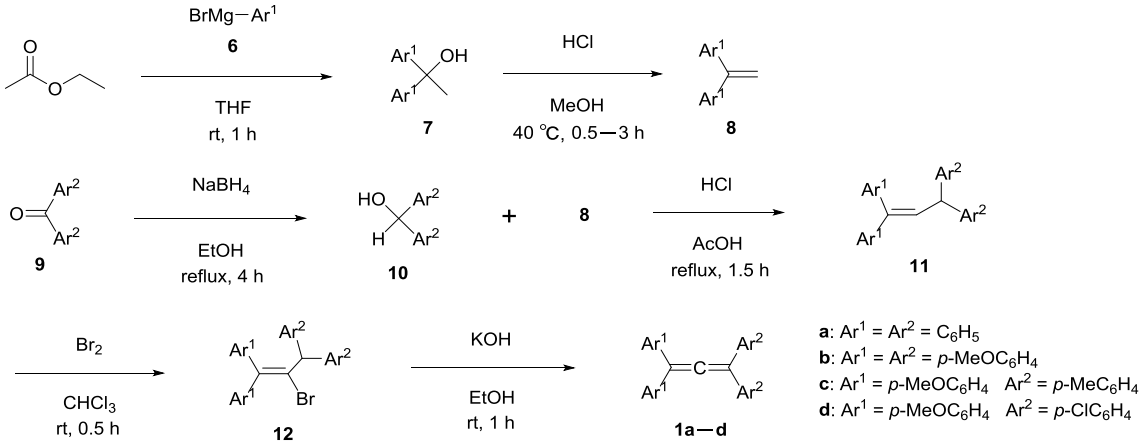
Scheme 1 Myers-Saito and Masamune-Bergman reactions.

2. Reactions of tetraaryallenes with tetracyanoethene (TCNE)

2. Reactions of tetraaryallenes with tetracyanoethene (TCNE)

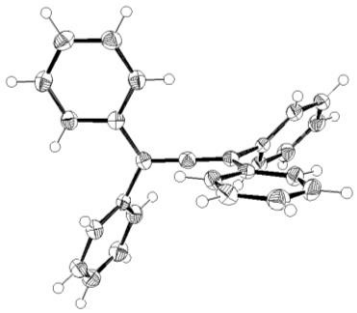
Allene (propadiene) is the simplest cumulated diene and the central carbon is sp-hybridized. Recently, the chemistry of allene has attracted attention because of the usability for syntheses of hetero rings, dye molecules and polymer molecules.[14] In this study, I have investigated the charge-transfer reactions of tetraarylallenes with tetracyanoethene (TCNE), a strong electron-accepting molecule.

2.1 Syntheses



Scheme 2 The synthesis of tetraarylallene **1**.

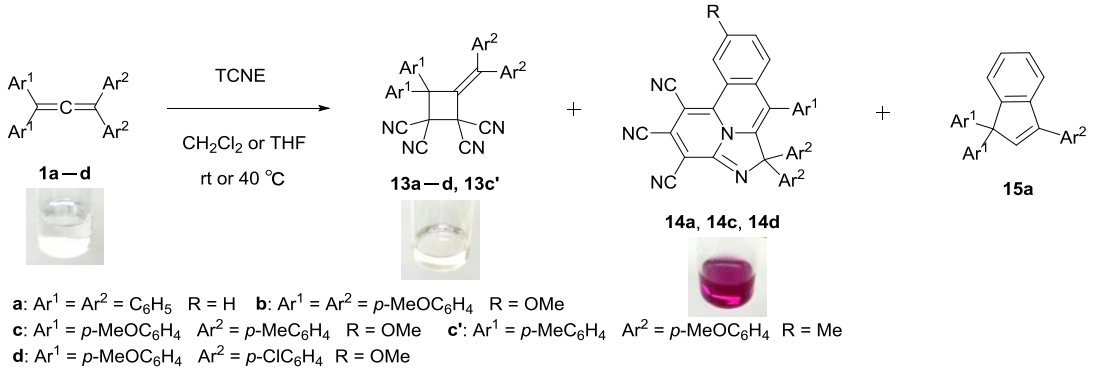
The synthesis of tetraarylallene **1** was undertaken as shown in Scheme 2. Ethyl acetate was reacted with Grignard reagent **6** to give alcohol **7**, which was treated with conc. HCl in MeOH to afford diarylethene **8**. After the reduction of diaryl ketone **9** with $NaBH_4$, the condensation of 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 tetraarylallenes **1a**–**d** (Fig. 3).



X-ray data of **1a**:
empirical formula: $C_{27}H_{20}$, 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,
β = 101.4288(7)°, V = 1856.06(6) Å^3, Z = 4,
no. of observations = 3399, no. of variables = 244, reflection/parameter ratio = 13.93,
R = 0.0423 (I>2σ(I)), R (all reflections) = 0.0505, wR (all reflections) = 0.1052,
GoF = 1.090.

Fig. 3 Crystal structure of tetraarylallene **1a**.

2.2 Reactions and the mechanism



Scheme 3 The reaction of tetraarylallene **1** with TCNE.

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

Allenes	Solvent	Temperature	Time	Yields (%)			
				13 (13')	**14**	**15**	**1 (Starting material)**
1a	CH_2Cl_2	rt	3 h	trace[a]	4	-	87
1a	CH_2Cl_2	rt	4 days	trace[a]	19	-	80
1a	CH_2Cl_2	rt	8 days	17	22	-	32
1a	CH_2Cl_2	40 °C	2 days	22	7	-	44
1a	CH_2Cl_2	40 °C	4 days	16	25	-	33
1a	THF	rt	2 days	-	-	29–100[b]	0–71[b]
1b	CH_2Cl_2	rt	3 h	-	-	-	87
1c	CH_2Cl_2	rt	3 h	37 (45)[c]	trace[a]	-	-
1d	CH_2Cl_2	rt	3 h	93	trace[a]	-	-

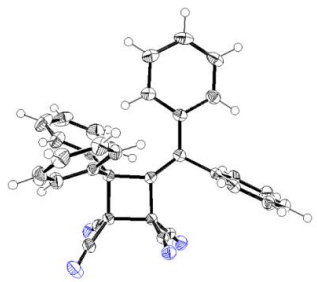
[a] Because the yields were very small, it was difficult to measure ^{1}H-NMR spectra of these compounds. To confirm the production of these compounds, we measured exact masses on ESI-TOF-MS.

[b] The yields of **15a** and starting material by the reaction in THF were estimated by the integrations of ^{1}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).

[c] 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'**.

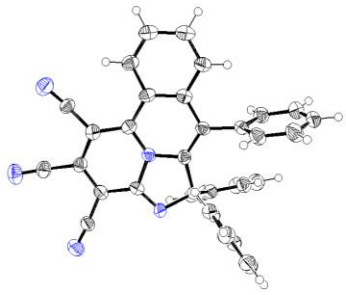
When tetraarylallene **1** was stirred with TCNE in CH_2Cl_2 at room temperature for 3 h, the solution color changed from colorless or yellow to dark purple to afford products **13** and **14** (Scheme 3, Table 1). The addition of TCNE to unsymmetrical allene **1c** or **1d** seems to form four-membered ring compound **13c, 13c'** and **13d** by [2+2] cycloaddition 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 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).[23] 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.[24] 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**.[25] 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: $C_{33}H_{20}N_4$, 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) Å^3, Z = 2,
no. of observations = 4424, no. of variables = 334, reflection/parameter ratio = 13.25,
R = 0.0400 (I>2σ(I)), 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) Å^3, Z = 2,
no. of observations = 4473, no. of variables = 361, reflection/parameter ratio = 12.39,
R = 0.0859 (I>2σ(I)), R (all reflections) = 0.0859, wR (all reflections) = 0.2688,
GoF = 1.110.

Fig. 5 Crystal structure of compound **14a**.

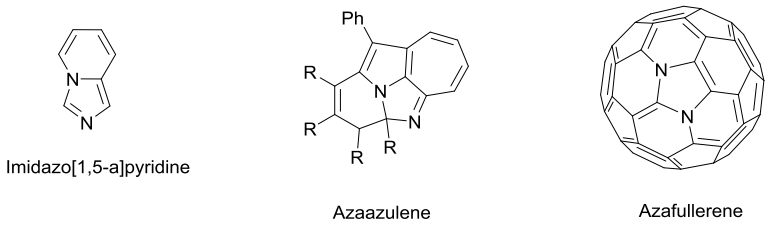
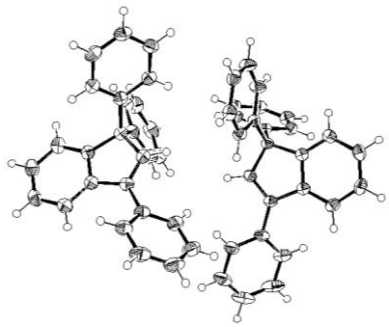
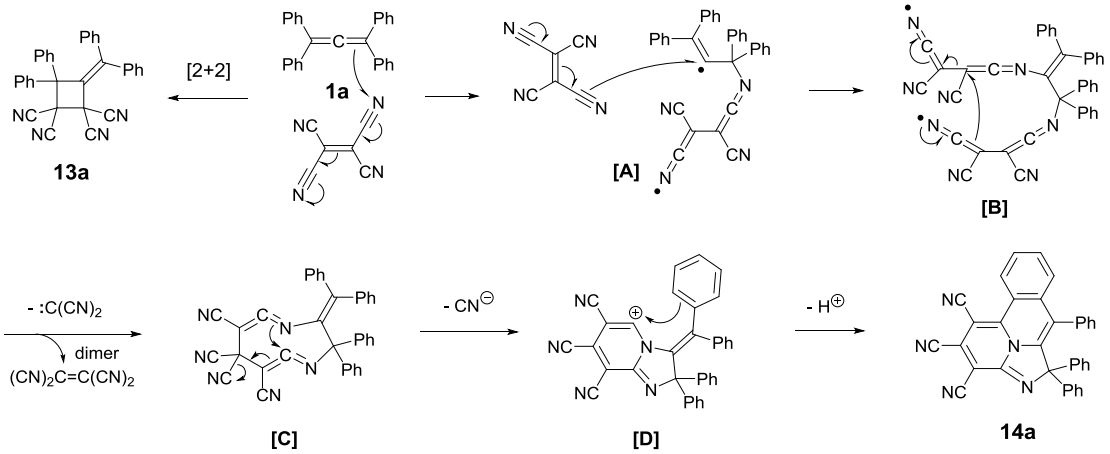


Fig. 6 The structures of imidazo[1,5-*a*]pyridine, azaazulene and azafullerene.

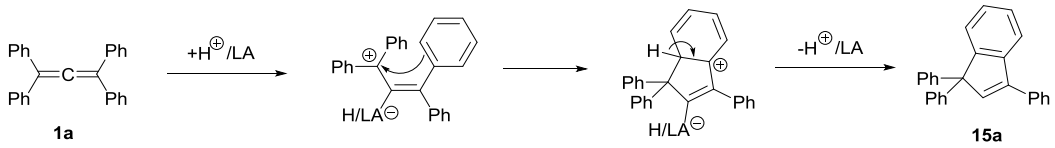


X-ray data of **15a**:
empirical formula: $C_{27}H_{20}$, formula weight: 344.45,
crystal habit: block, crystal system: triclinic, space group: *P*-1,
unit cell dimensions: a = 11.0303(2) Å, b = 14.3844(3) Å, c = 14.5364(3) Å,
α = 99.9878(12)°, β = 110.8720(12)°, γ = 111.4450(9)°, V = 1879.59(7) Å^3,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

Fig. 7 Crystal structure of compound **15a**.



Scheme 4 Putative mechanism for the formation of **13a** and **14a** by the reaction of allene **1a** with TCNE.



Scheme 5 Putative mechanism for the formation of **15a** with Lewis acid.[25]

2.3 UV-vis spectra, MO calculations and cyclic voltammetry

While the solution of tetraarylallene **1** in CH_2Cl_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 λ_{max} = 266 nm (ε = 33,800 $M^{-1}cm^{-1}$), **14a** shows the absorption at the remarkably longer wavelength. In the CH_2Cl_2 solution of **14a**, the maxima at λ_{max} = 584 nm (ε = 10,000 $M^{-1}cm^{-1}$), λ_{max} = 542 nm (ε = 11,400 $M^{-1}cm^{-1}$) and λ_{max} = 504 nm (ε = 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_3CN (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.

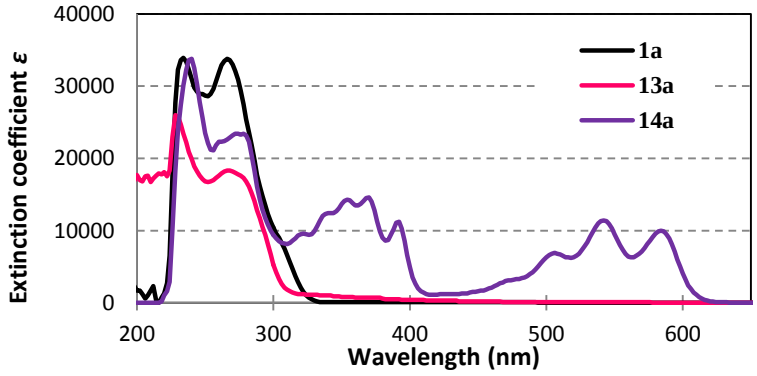


Fig. 8 UV-vis absorption spectra of **1a**, **13a** and **14a** in CH_2Cl_2 at room temperature.

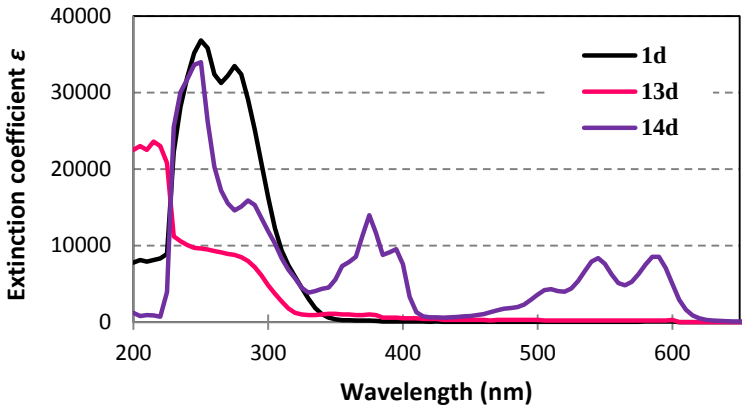
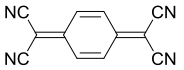


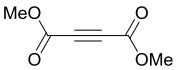
Fig. 9 UV-vis absorption spectra of **1d**, **13d** and **14d** in CH_2Cl_2 at room temperature.

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)).

Compds	Total Energy (a. u.)	Dipole Moment (D)	HOMO (eV)	LUMO (eV)
1a	−1040.9	0.171	−0.209	−0.039
1b	−1499.0	0.759	−0.186	−0.025
1c	−1348.6	2.104	−0.191	−0.029
1d	−2189.1	5.124	−0.201	−0.044
13a	−1488.4	8.641	−0.247	−0.063
13b	−1946.5	10.291	−0.218	−0.055
13c	−1796.1	9.749	−0.228	−0.056
13c'	−1796.1	10.171	−0.220	−0.058
13d	−2636.6	8.842	−0.235	−0.070
14a	−1618.9	13.478	−0.219	−0.112
TCNE	−447.52	0	−0.335	−0.182
TCNQ	−750.36	0.653	−0.324	−0.217
DMAD	−533.08	2.481	−0.289	−0.055



7,7,8,8-Tetracyanoquinodimethane (TCNQ)



Dimethyl acetylenedicarboxylate (DMAD)

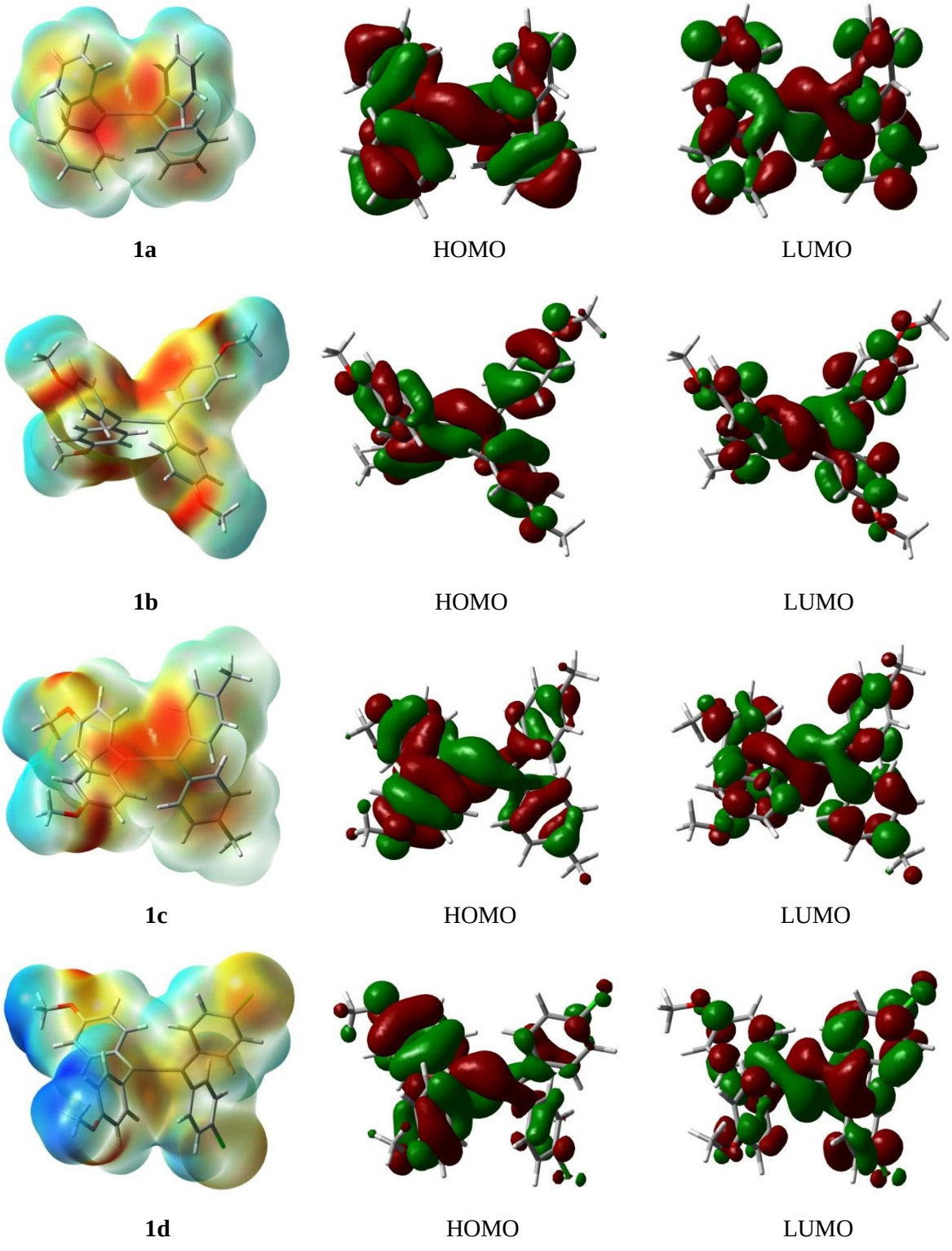


Fig. 10 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of allene **1** by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).

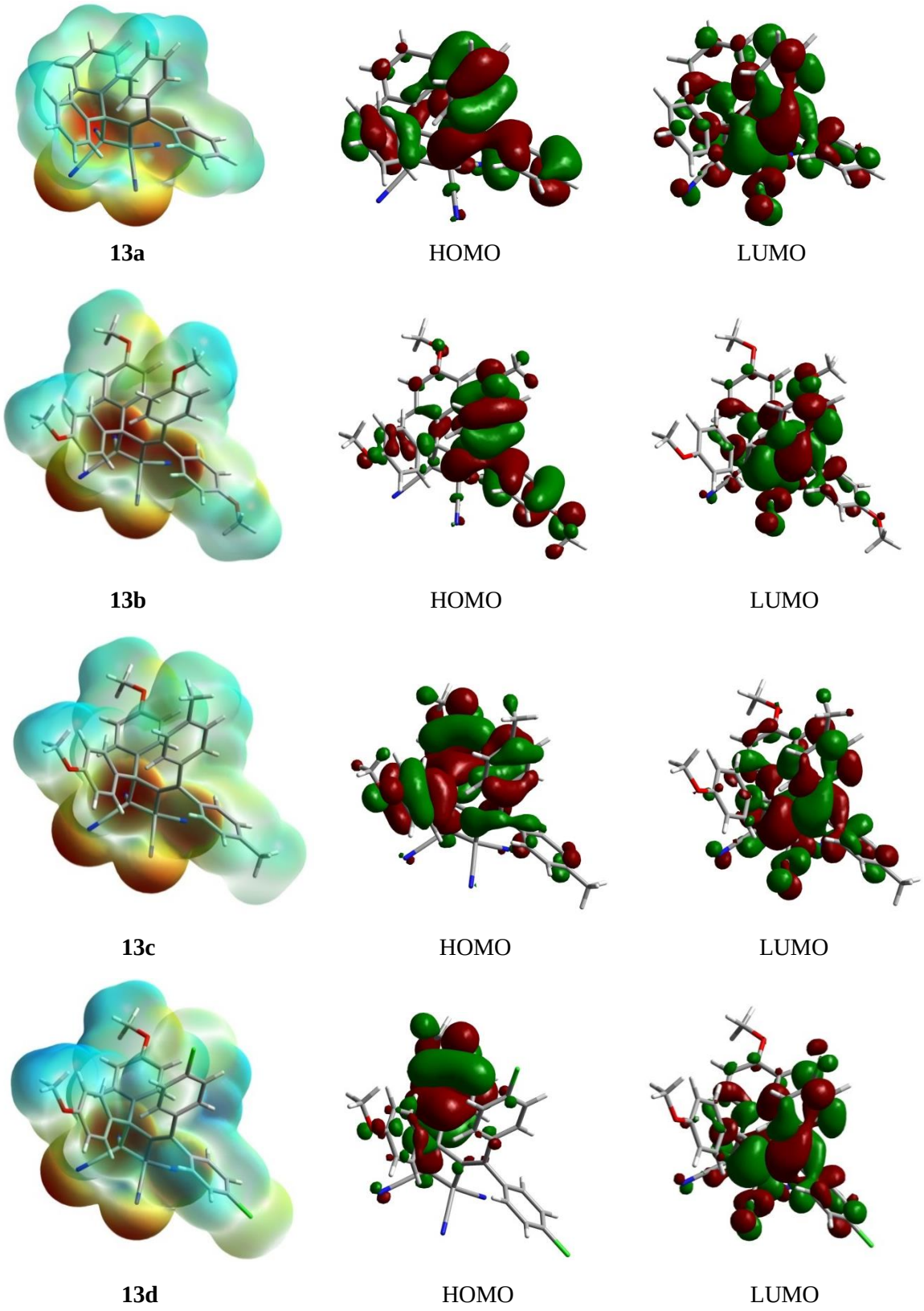
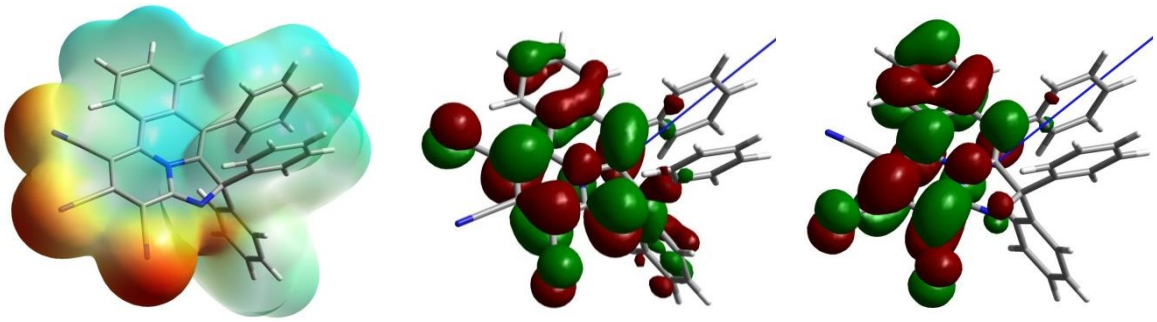


Fig. 11 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of compound **13** by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).



14a HOMO LUMO

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 v = 20–50 V/min) data of **1a**, **1b**, **1d**, **13a**, **13c**, **13d**, **14a** and reference compounds TCNE and TCNQ in CH_3CN (+0.3 M tetrabutylammonium perchlorate).[a]

Compds	E^o (V)[b]	ΔE_p (mV)[c]	E_p (V)[d]
1a	-	-	+1.32
	-	-	−1.36
1b	-	-	+1.94
	-	-	−1.60
1d	-	-	+1.09
	-	-	−1.39
13a	-	-	−1.52
13c	-	-	−1.54
13d	+0.63	100	-
	−0.04	100	-
	-	-	−1.46
14a	-	-	−1.48
TCNE	-	-	+1.07
	−0.04	60	-
	-	-	−1.58
TCNQ	−0.05	100	-
	−0.61	110	-
	-	-	−1.38

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

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

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

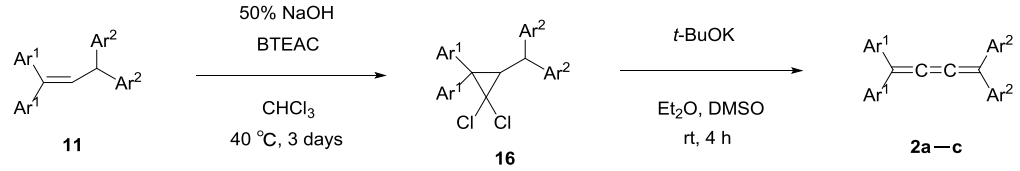
[d] E_p = Irreversible peak potential.

3. Reactions of tetraaryl [3]cumulenes with TCNE

3. Reactions of tetraaryl[3]cumulenes with TCNE

Cumulenes[1] 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.[2] 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

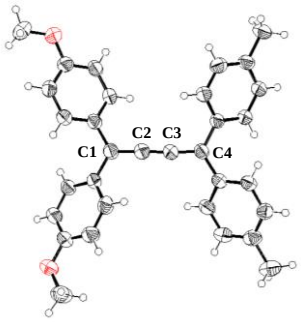


BTEAC = Benzyltriethylammonium chloride

a: $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$ **b**: $Ar^1 = p\text{-}MeOC_6H_4$ $Ar^2 = p\text{-}MeC_6H_4$ **c**: $Ar^1 = p\text{-}MeOC_6H_4$ $Ar^2 = p\text{-}ClC_6H_4$

Scheme 6 Synthesis of tetraaryl[3]cumulene **2**.

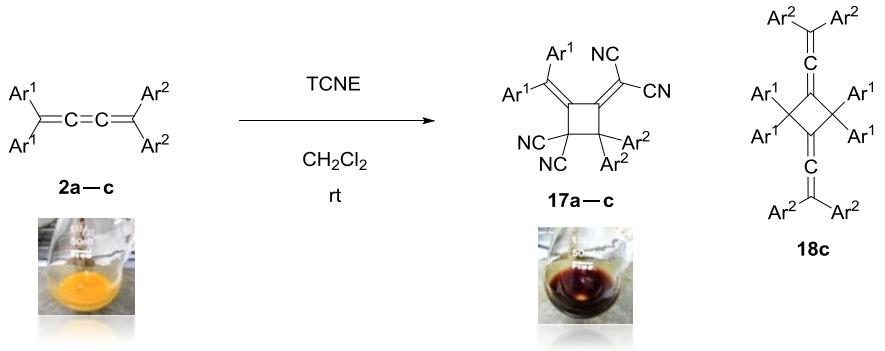
The synthesis of tetraaryl[3]cumulene **2** was undertaken as shown in Scheme 6. Compound **11** was synthesized by the method similar to tetraarylallene **1** (Scheme 2). The reaction of **11** with benzyltriethylammonium chloride (BTEAC) as a phase transfer catalysis in 50w/v% NaOH aq. and $CHCl_3$ 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: $C_{32}H_{28}O_2$, formula weight: 444.54,
crystal habit: needle, crystal system: orthorhombic, space group: *Pbca*,
unit cell dimensions: a = 7.52750(10) Å, b = 27.5908(6) Å, c = 26.1680(6) Å,
V = 5434.83(19) Å^3, 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



a: $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$ **b**: $Ar^1 = p\text{-}MeOC_6H_4$ $Ar^2 = p\text{-}MeC_6H_4$ **c**: $Ar^1 = p\text{-}MeOC_6H_4$ $Ar^2 = p\text{-}ClC_6H_4$

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.

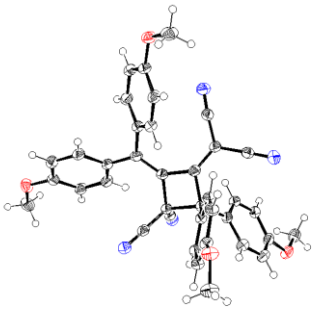
Cumulenes	Solvent	Time	Yields (%)	
		(h)	**17** (**17'**)[a]	**18**
2a	CH_2Cl_2	4	69	-
2a	MeOH	5	No reaction	
2b	CH_2Cl_2	3	65 (11)	-
2c	CH_2Cl_2	3	80 (4)	trace

[a] 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 ^{1}H-NMR spectra in $CDCl_3$ (see Figs. 17 and 18).

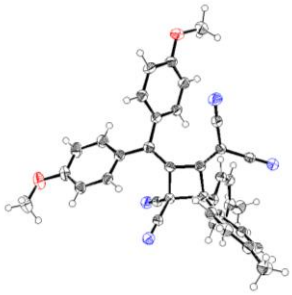
When tetraaryl[3]cumulene **2** was stirred with TCNE in CH_2Cl_2 at room temperature for 3–4 h, the solution color changed from yellow to deep red and the nature of the main product **17** (Scheme 5) was determined by X-ray analysis. Fig. 14 shows that **17** was a novel four-membered ring compound, a head-to-tail unsymmetrically substituted diarylallene dimer. I wish to name the products **17** 'bisalkylidenecyclobutane', 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(d)]

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, ^{1}H NMR showed that the isomers **17b'** and **17c'** were formed in 1/6 and 1/20 of the yields of the

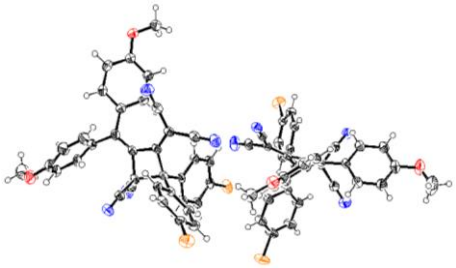
main products **17b** and **17c**, respectively. Unsymmetrical [3]cumulene **2c** also formed head-to-tail dimer **18c** as a minor product, which was confirmed by X-ray analysis (Fig. 16). A solution of **2c** in the absence of TCNE also formed the same amount of **18c**. Because the dipole moment of **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 $CDCl_3$ for 3 h also yielded dimer **18c** in 60% yield.[17]



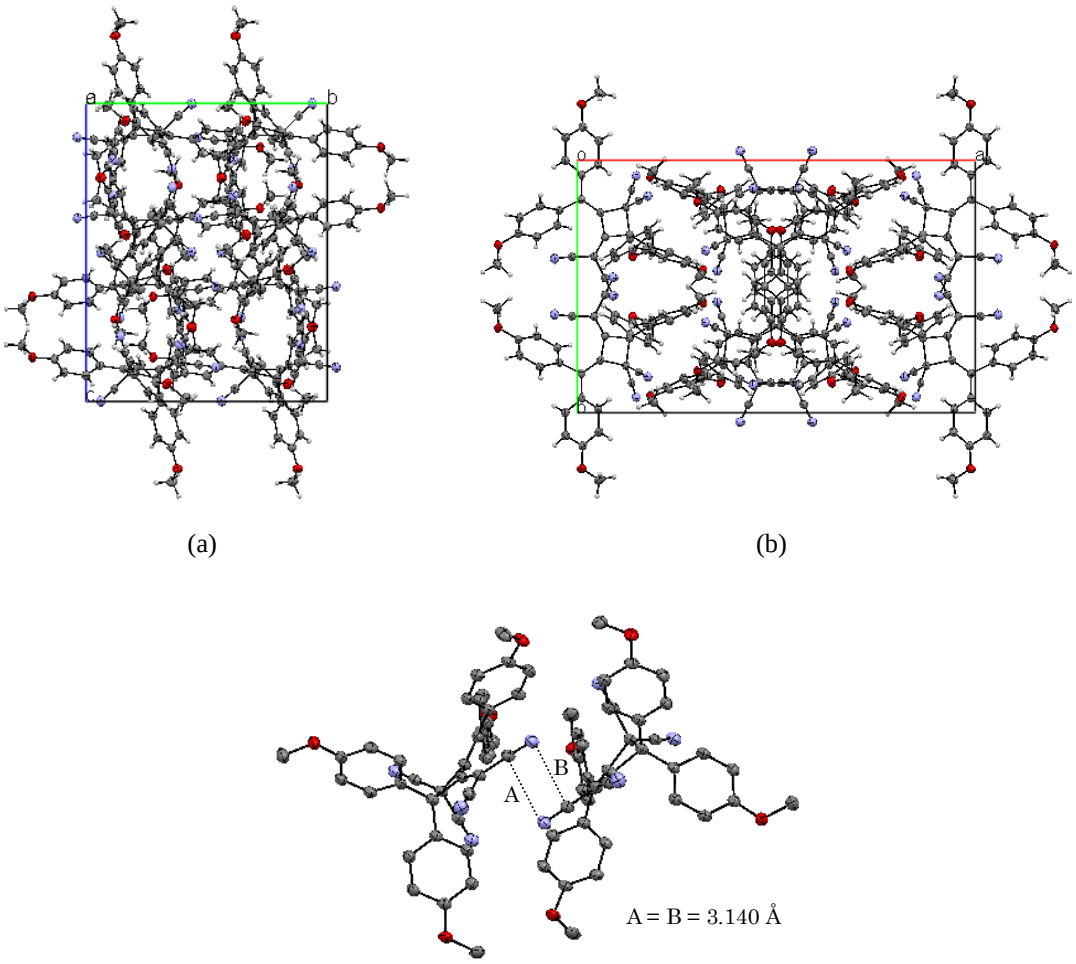
X-ray data of **17a**:
empirical formula: $C_{38}H_{28}N_4O_4$, formula weight: 604.66,
crystal habit: block, crystal system: orthorhombic, space group: *Pbcn*,
unit cell dimensions: a = 23.3123(4) Å, b = 14.7753(2) Å, c = 18.2560(3) Å,
V = 6288.2(2) Å^3, Z = 8,
no. of observations = 5755, no. of variables = 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: $C_{38}H_{28}N_4O_2$, 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,
α = 102.539(2)°, β = 96.811(2)°, γ = 113.934(2)°, V = 6288.2(2) Å^3, 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.



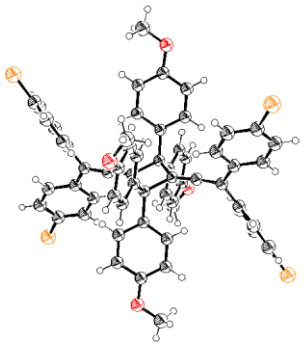
X-ray data of **17c**:
empirical formula: $C_{36}H_{22}N_4O_2Cl_2$, formula weight: 613.48,
crystal habit: needle, crystal system: triclinic, space group: *P*-1,
unit cell dimensions: a = 13.0039(3) Å, b = 14.3980(3) Å, c = 18.6793(4) Å,
α = 99.561(7)°, β = 91.793(7)°, γ = 103.561(7)°, V = 3356.3(1) Å^3, 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.



(a) (b)

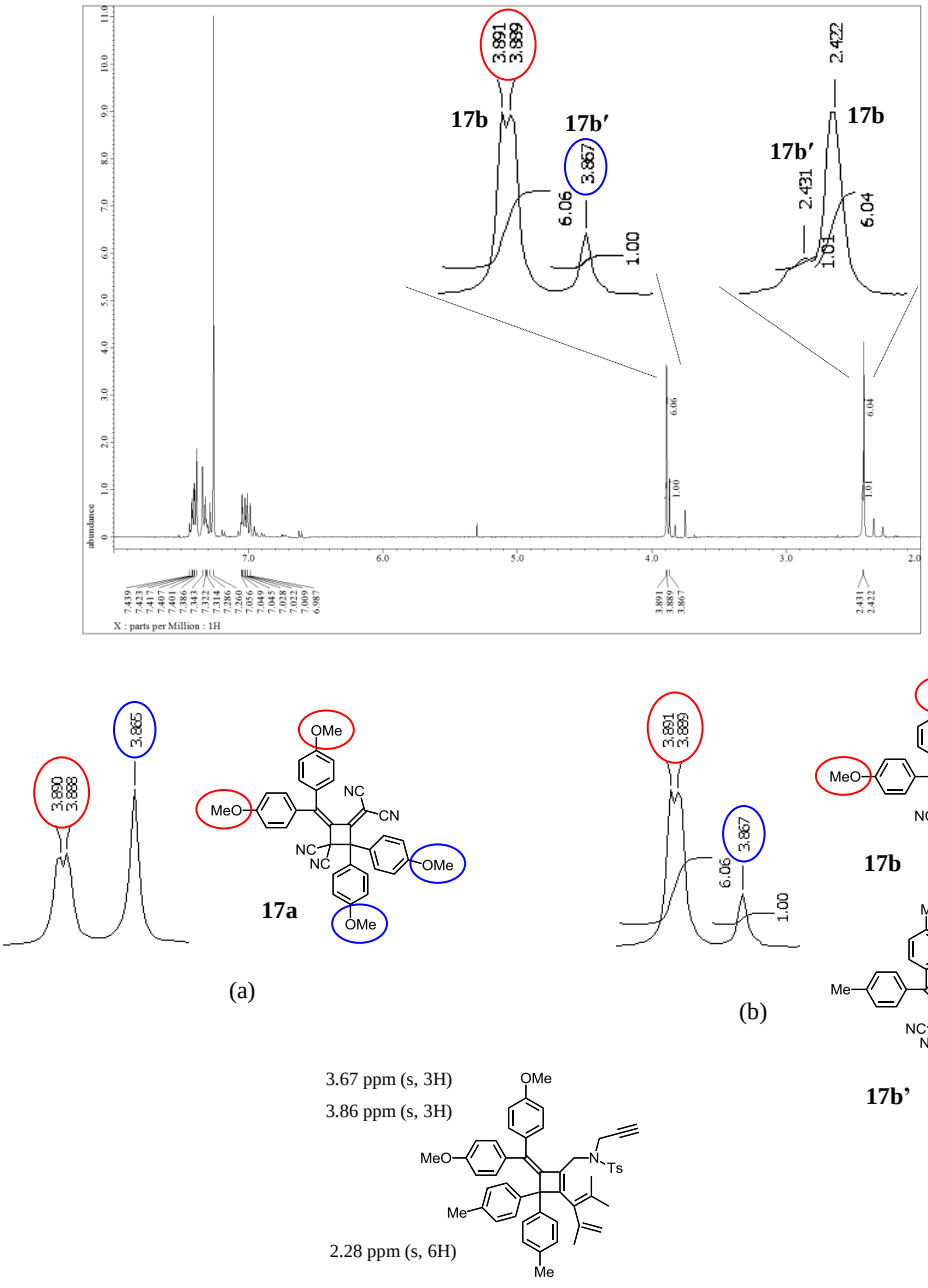
(c)

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 neghboring molecules in the crystal packing.



X-ray data of **18c**:
empirical formula: $C_{60}H_{44}O_4Cl_4$, formula weight: 970.75,
crystal habit: needle, crystal system: monoclinic, space group: $P2_1/n$,
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) Å^3, 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).



Analogous compound I[26]

Fig. 17 [1]H-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 **I**[26] (c), these signals are presumed to be due to **17b'**, which is the regioisomer of **17b**. From integration of [1]H-NMR spectra, the isomer **17b'** was obtained in 1/6 of the yield of **17b**.

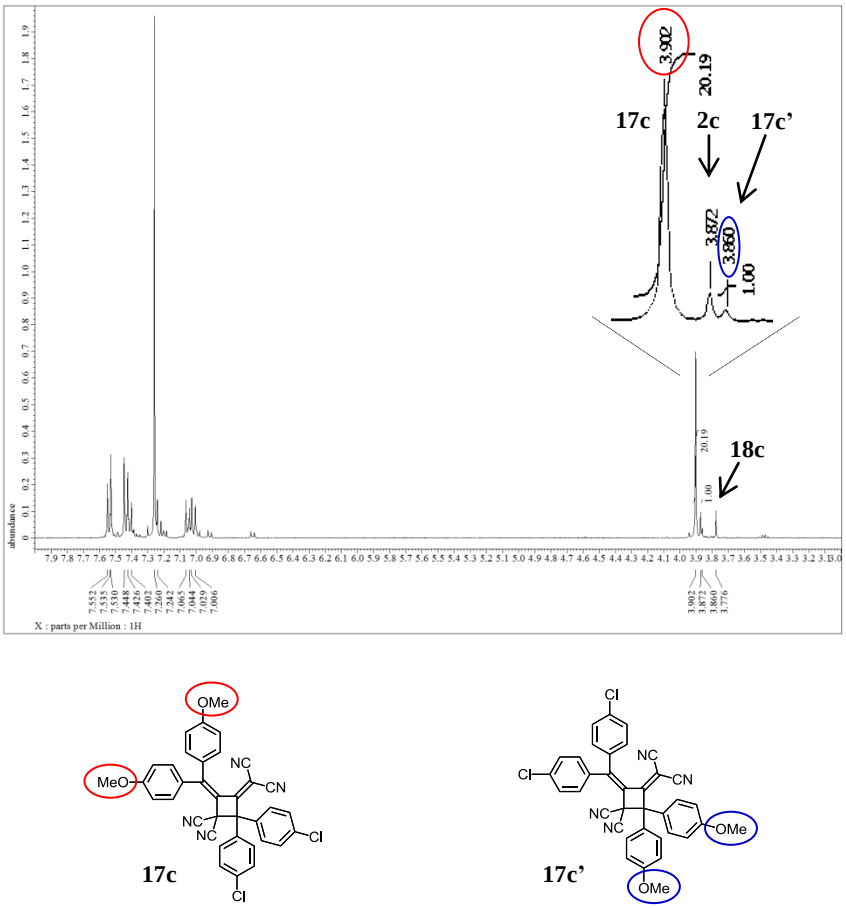


Fig. 18 ^{1}H-NMR spectra of crude product by the reaction of [3]cumulene **2c** with TCNE. Not only the methyl signals of the methoxyphenyl group of **17c** (3.90 ppm) but also two singlets (3.86 and 3.87 ppm) were observed. One singlet at 3.87 ppm is confirmed to be derived from **2c** (see **7.** 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 ^{1}H-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 ^{1}H-NMR spectra of the reaction mixture in $CDCl_3$. 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 ^{1}H-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**.

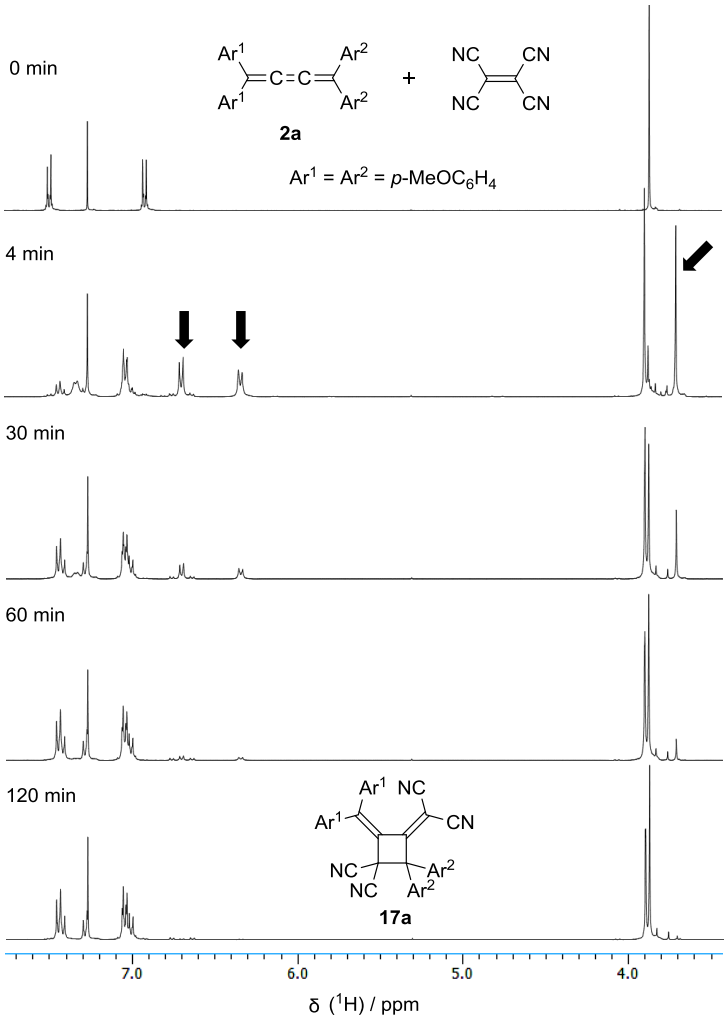


Fig. 19 Time dependent ^{1}H-NMR spectra (in $CDCl_3$) of the reaction of tetraaryl[3]cumulene **2a** with TCNE at room temperature.

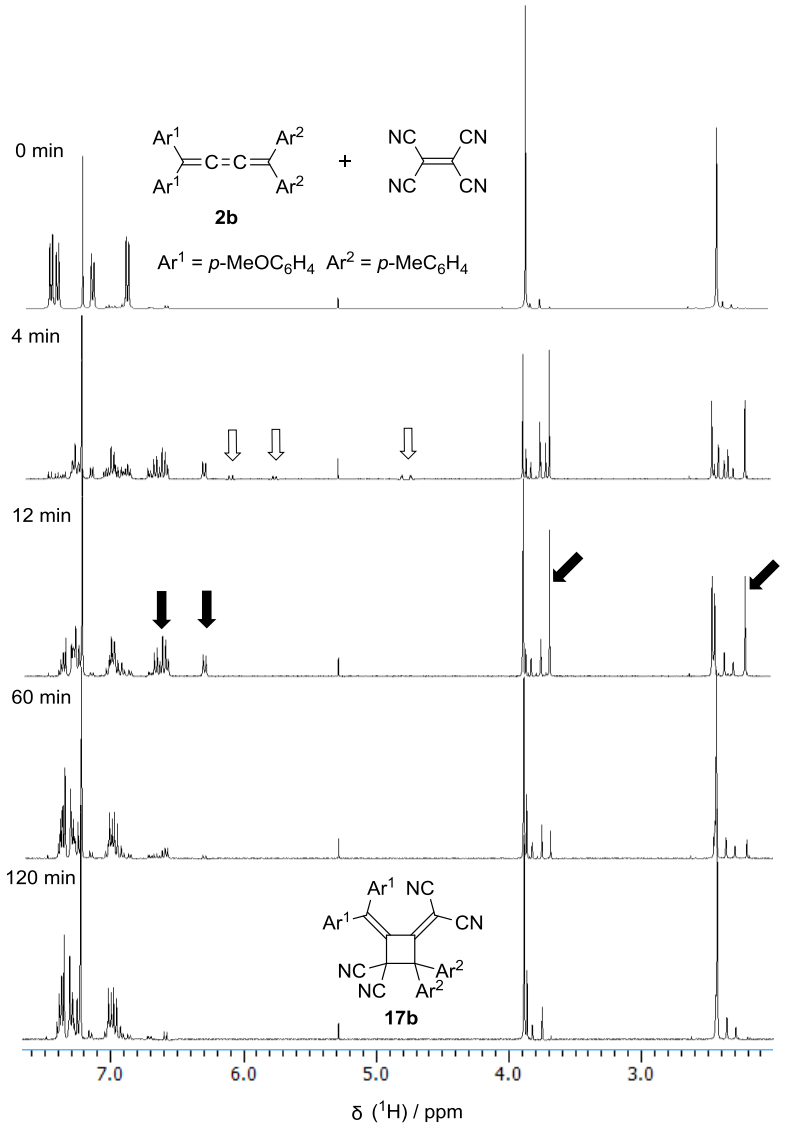


Fig. 20 Time dependent ^{1}H-NMR spectra (in $CDCl_3$) of the reaction of tetraaryl[3]cumulene **2b** with TCNE at room temperature.

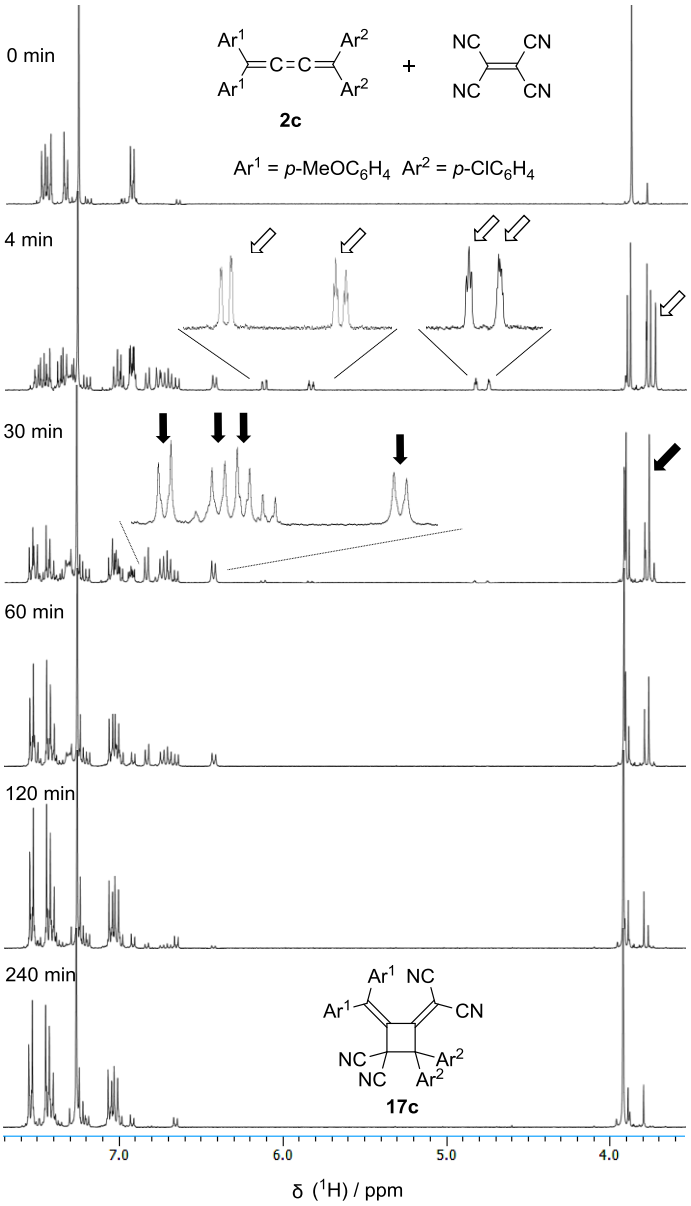
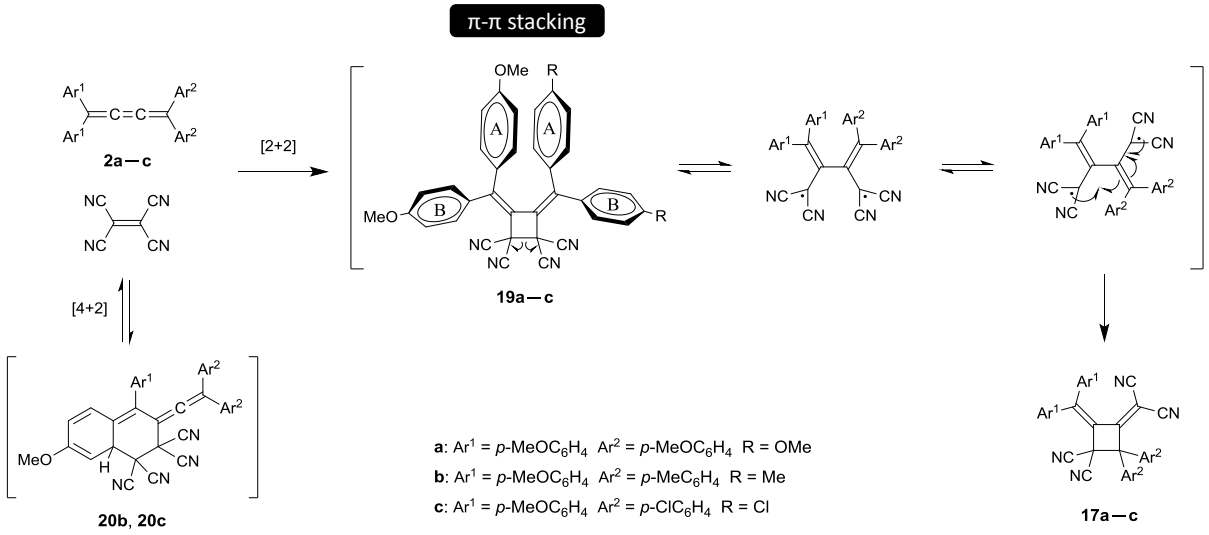
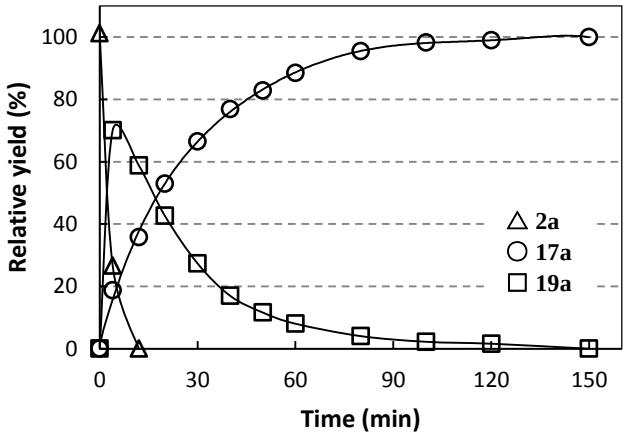


Fig. 21 Time dependent ^{1}H-NMR spectra (in $CDCl_3$) of the reaction of tetraaryl[3]cumulene **2c** with TCNE at room temperature.

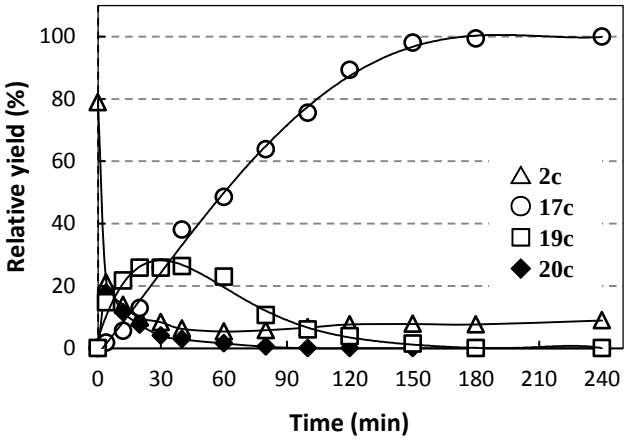


Scheme 6 Putative reaction mechanism of tetraaryl[3]cumulenes **2a**–**c** with TCNE. ^{1}H-NMR assignments of **19a** and **19c** are shown in the references and notes.[27, 28]

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, ^{1}H-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).



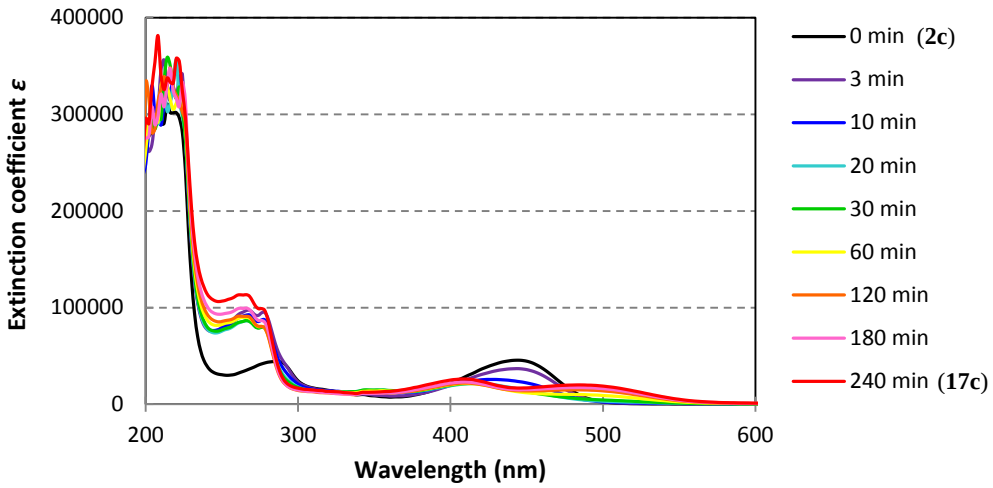
(a)



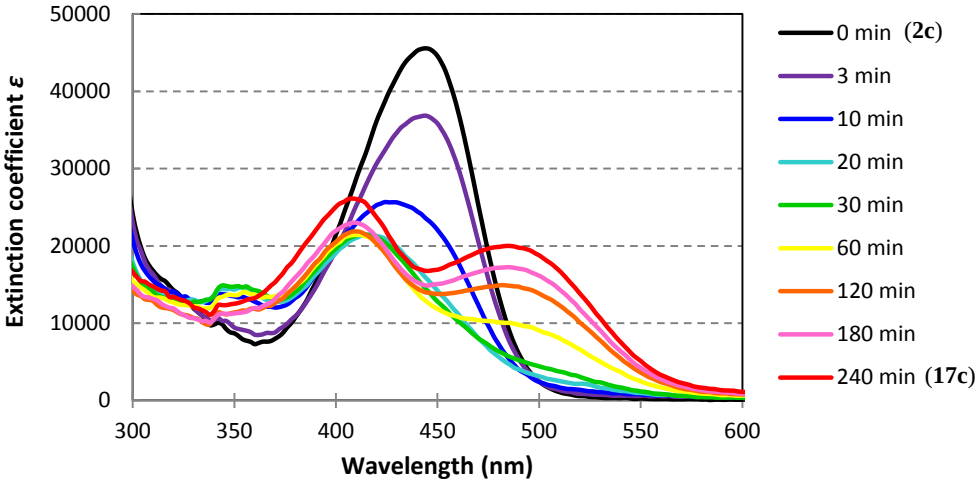
(b)

Fig. 22 Time course of the reactions of **2a** (a) or **2c** (b) with TCNE in $CDCl_3$ 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 ^{1}H-NMR spectra (400 MHz).

3.3 UV-vis spectra, MO calculations and cyclic voltammetry



(a)



(b)

Fig. 23 Time dependent UV-vis absorption spectra of the reaction of tetraaryl[3]cumulene **2c** with TCNE in CH_2Cl_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_2Cl_2 at room temperature (Fig. 23). The longest-wavelength absorption maximum at λ_{max} = 446 nm (ε = 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 λ_{max} = 412 nm (ε = 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 λ_{max} = 408 nm (ε = 26,100 $M^{-1}cm^{-1}$) and λ_{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 diarylallene 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 tetrathiafulvalene (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)).

Compds	Total E (a. u.)	Dipole Moment (D)	HOMO (eV)	LUMO (eV)
17a	−1984.2	4.161	−0.215	−0.105
17b	−1833.8	3.846	−0.219	−0.107
17c	−2674.4	7.947	−0.229	−0.116
TCNE	−447.52	0	−0.335	−0.182
TCNQ	−750.36	0.653	−0.324	−0.217
DMAD	−533.08	2.481	−0.289	−0.055

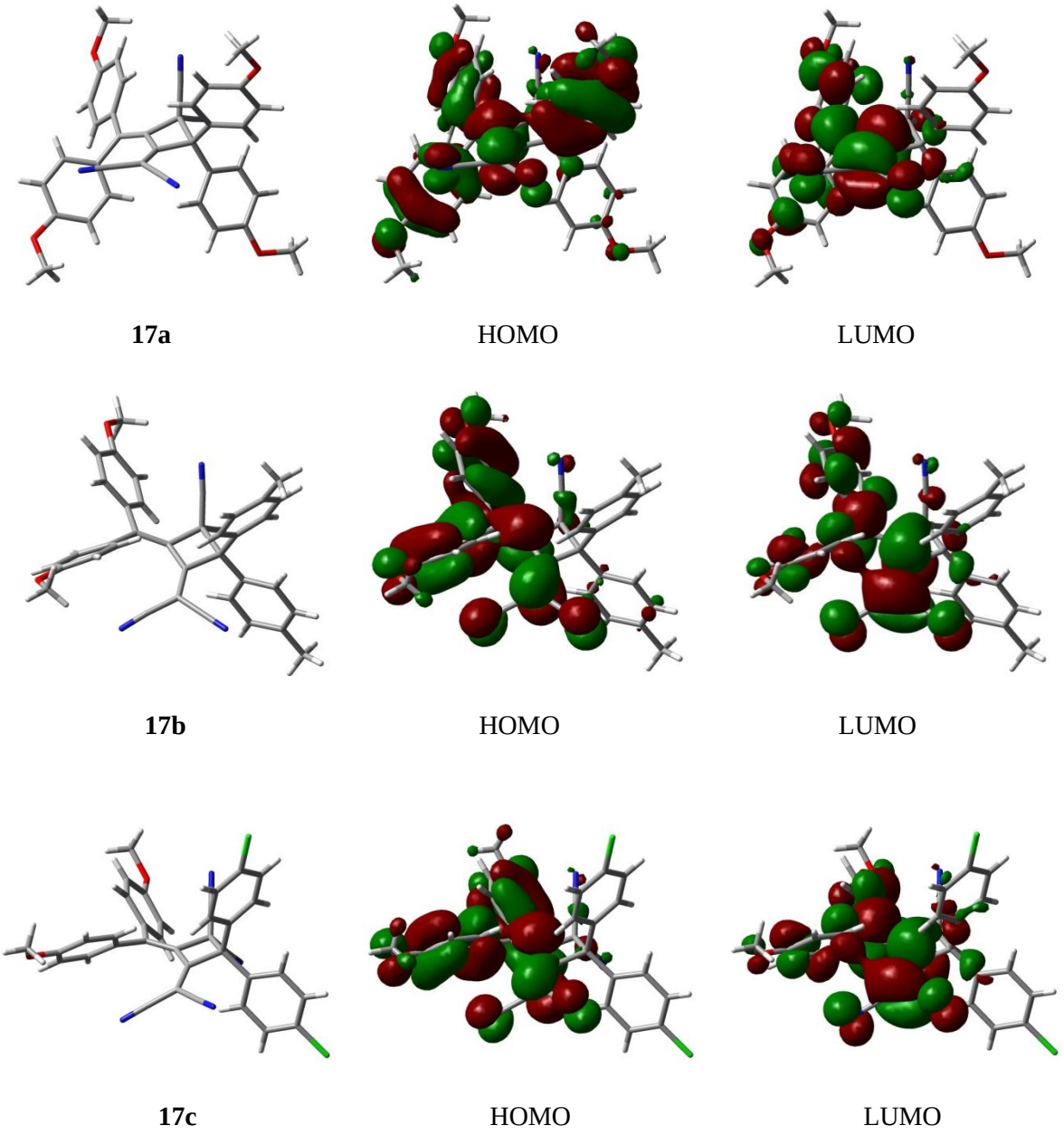


Fig. 24 The display of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (solid) of allene dimer **17** by molecular orbital (MO) calculations by density functional theory (DFT) (B3LYP/6-31G(d)).

Table 6 Cyclic voltammetry (CV; scan rate v = 20–50 V/min) data of **2a**−**c**, **17a**−**c**, **18c** and reference compounds TCNE and TCNQ in CH_3CN (+0.3 M tetrabutylammonium perchlorate).[a]

Compds	E^o **(V)**[b]	ΔE_p **(mV)**[c]	E_p **(V)**[d]
2a	-	-	−1.33
2b	-	-	−1.33
2c	-	-	−1.44
17a	-	-	+0.53
	−0.07	100	-
	-	-	−0.93
17b	-	-	+0.78
	−0.08	120	-
	-	-	−0.87
17c	-	-	+0.59
	−0.05	60	-
	-	-	−0.81
18c	-	-	−1.39
TCNE	-	-	+1.07
	−0.04	60	-
	-	-	−1.58
TCNQ	−0.05	100	-
	−0.61	110	-
	-	-	−1.38

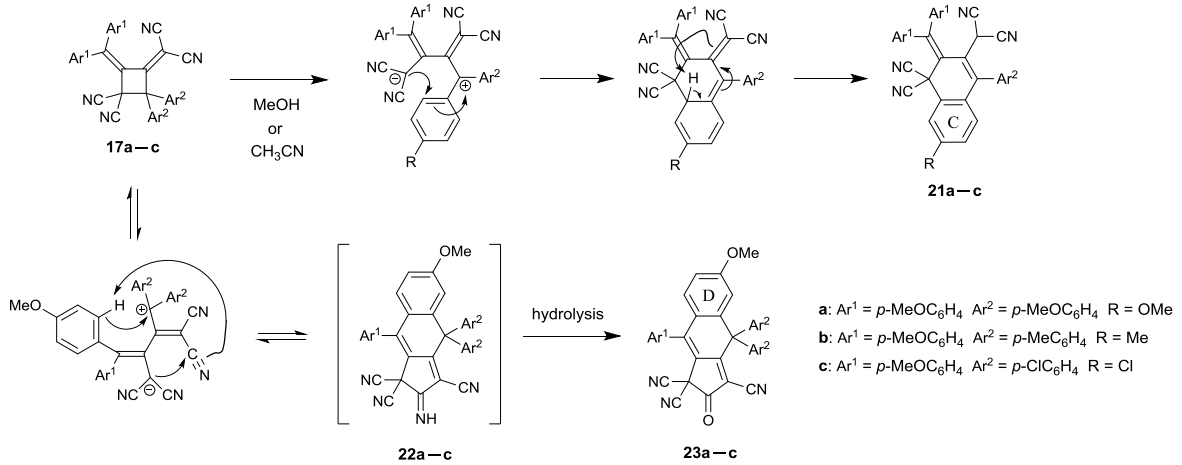
[a] All potentials are given *vs*. the Ag^+ / Ag couple used as the internal standard.

[b] $E^o = (E_{pc} + E_{pa}) / 2$, 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

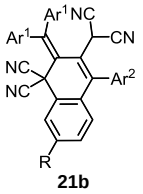


Scheme 7 Putative reaction mechanism of diarylallene dimer **17a**−**c** in MeOH or CH_3CN.

Although compounds **17a**−**c** are stable in CH_2Cl_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_3CN 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 C_{18}, 50×2.1 mm
Injection volume: 3 ppm×7 μl
Column temperature: 40 °C
Gradient separations

Time	Flow [ml/min]	0.1% Formic acid H_2O [%]	0.1% Formic acid CH_3CN [%]
0 min	0.1	40	60
10 min	0.1	0	100
10.1 min	0.1	40	60
11 min	0.1	40	60



21b

Ar^1 = *p*-$MeOC_6H_4$ Ar^2 = *p*-MeC_6H_4

Calc. Mass	573.2291
Formula	$C_{38}H_{29}N_4O_2^+$

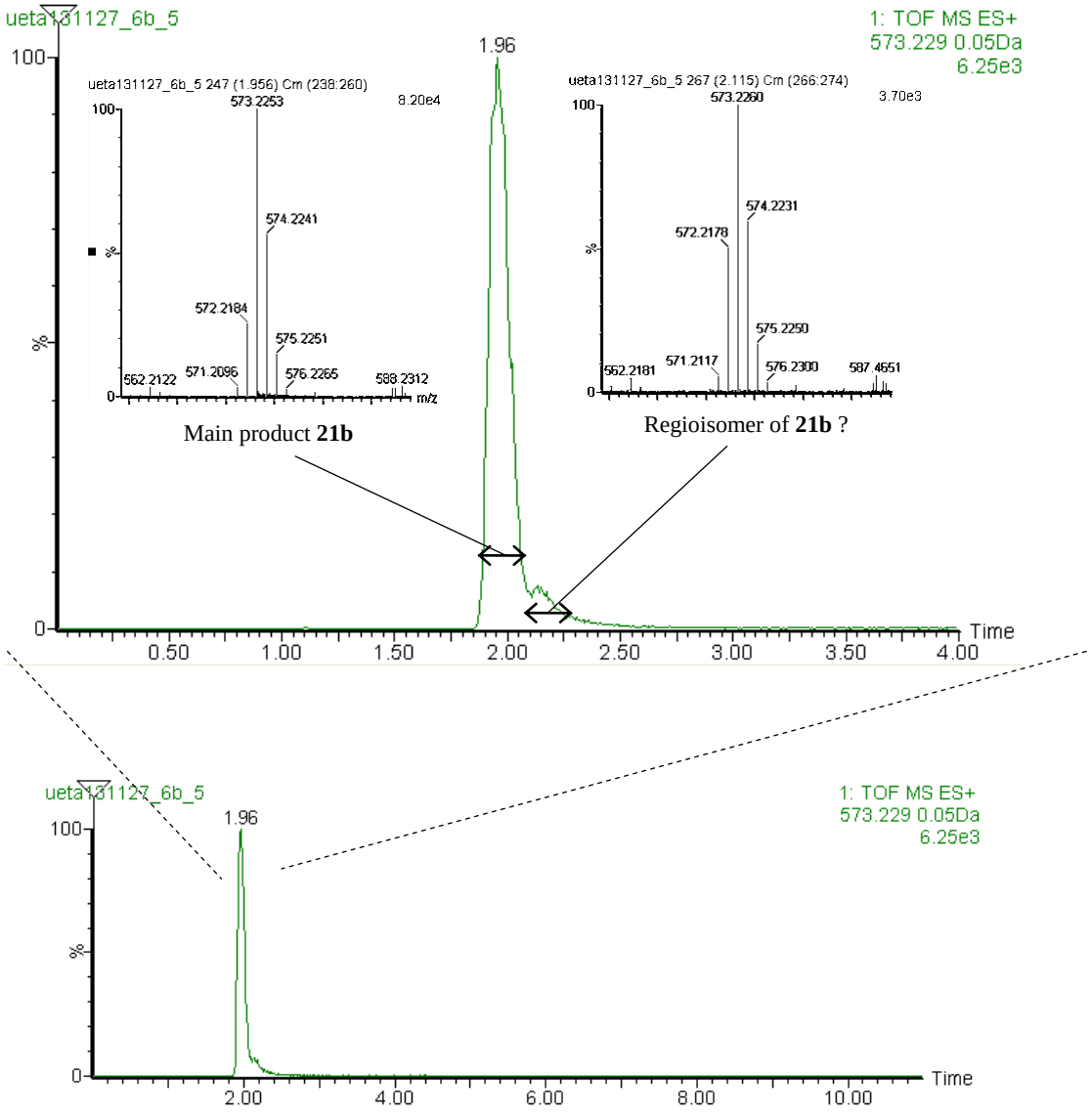
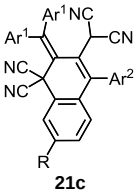


Fig. 25 UPLC-MS analysis of **21b**.

Column : 1.7 μm ACQUITY UPLC BEH C_{18}, 50×2.1 mm
Injection volume: 3 ppm×7 μl
Column temperature: 40 °C
Gradient separations

Time	Flow [ml/min]	0.1% Formic acid H_2O [%]	0.1% Formic acid CH_3CN [%]
0 min	0.1	40	60
10 min	0.1	0	100
10.1 min	0.1	40	60
11 min	0.1	40	60



21c

Ar^1 = *p*-$MeOC_6H_4$ Ar^2 = *p*-ClC_6H_4

Calc. Mass	611.1042
Formula	$C_{36}H_{21}N_4O_2Cl_2^-$

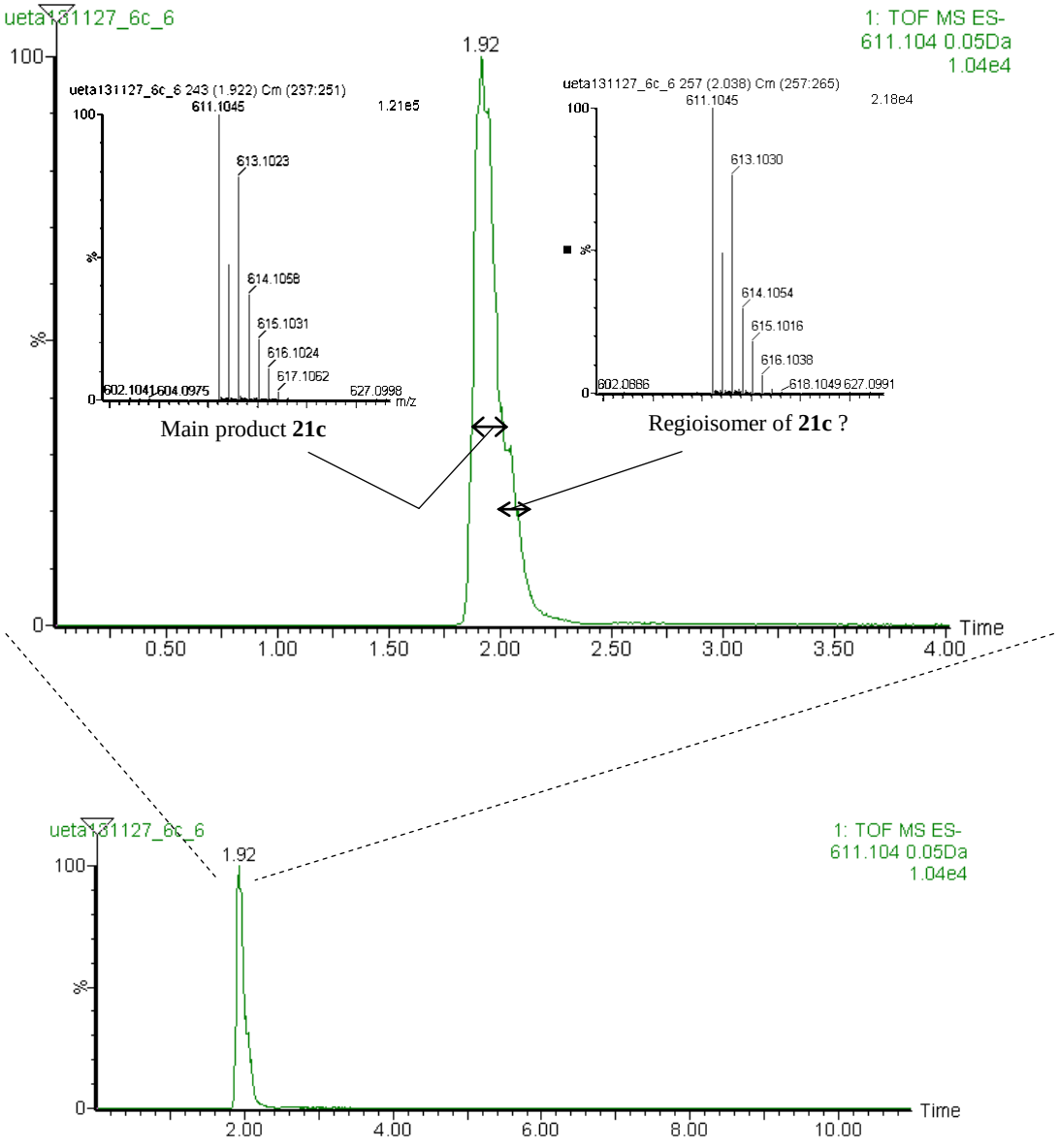
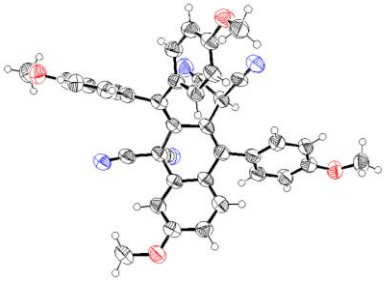
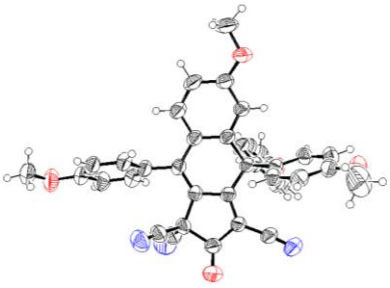


Fig. 26 UPLC-MS analysis of **21b**.

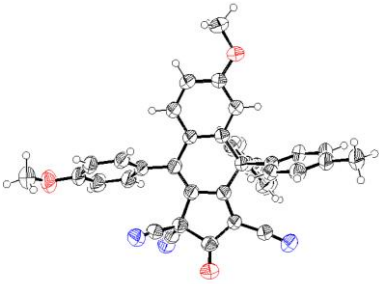


X-ray data of **21a**:
empirical formula:$C_{38}H_{28}N_4O_4$, formula weight: 604.66,
crystal habit: needle,crystal system: orthorhombic, space group: *Pbca*,
unit celldimensions: a = 20.9635(3) Å, b = 13.2472(2) Å, c = 22.6274(4)Å,
V = 6283.8(2) Å^3, Z = 8,
no. of observations =5732, no. of variables = 419,
reflection/parameter ratio = 13.72,
R = 0.1072 (I>2σ(I)), R (all reflections) = 0.1894,
wR (all reflections) = 0.2968, GoF =1.064.

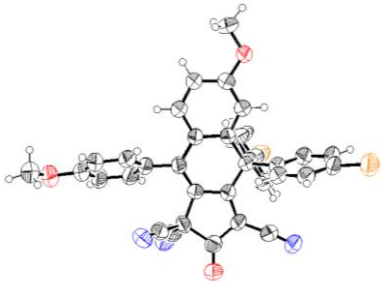
Fig. 27 Crystal structure of compound **21a** (CCDC 942250).



X-ray data of **23a**:
empirical formula: $C_{38}H_{27}N_3O_5$, formulaweight: 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,
β = 95.6174(9)°, V =3196.64(11) Å^3, Z = 4,
no. of observations = 36081, no. of variables= 5845,
reflection/parameter ratio = 13.95,
R = 0.0426 (I>2σ(I)), R (all reflections)= 0.0701, wR (all reflections) = 0.1368,
GoF = 1.118.



X-ray data of **23b**:
empirical formula: $C_{38}H_{27}N_3O_3$, formulaweight: 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,
β = 97.8432(10)°, V =7147.2(2) Å^3, Z = 8,
no. of observations = 40630, no. of variables= 6463,
reflection/parameter ratio = 16.11,
R = 0.0644 (I>2σ(I)), R (all reflections)= 0.1127, wR (all reflections) = 0.1923,
GoF = 0.998.



X-ray data of **23c**:
empirical formula: $C_{36}H_{21}N_3O_3Cl_2$, formulaweight: 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,
β = 98.339(3)°, V =7215.9(7) Å^3, Z = 8,
no. of observations = 38808, no. of variables= 6596,
reflection/parameter ratio = 16.53,
R = 0.0839 (I>2σ(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 γ-hydrogen by the nπ* 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 β-position to afford acetophenone **24** and ene-yne-allene **25** (Scheme 9).

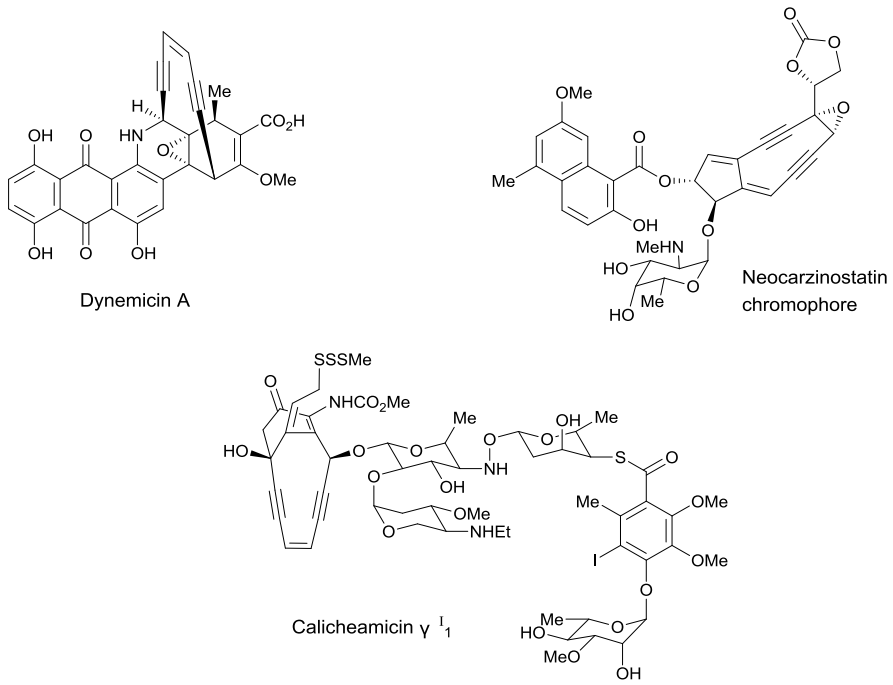
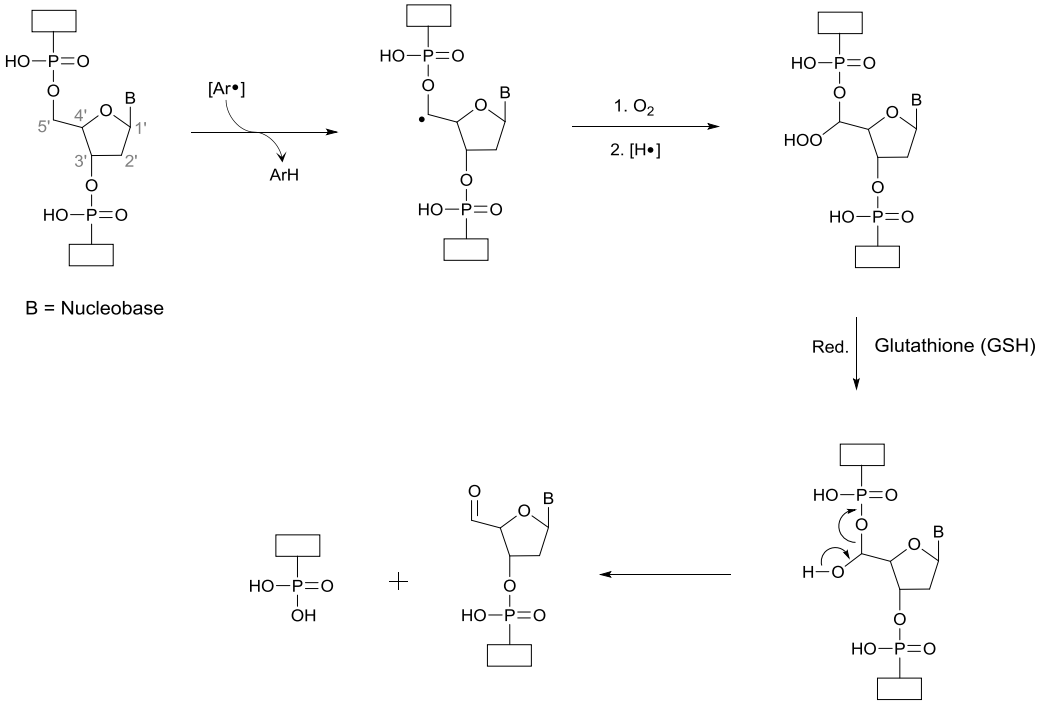
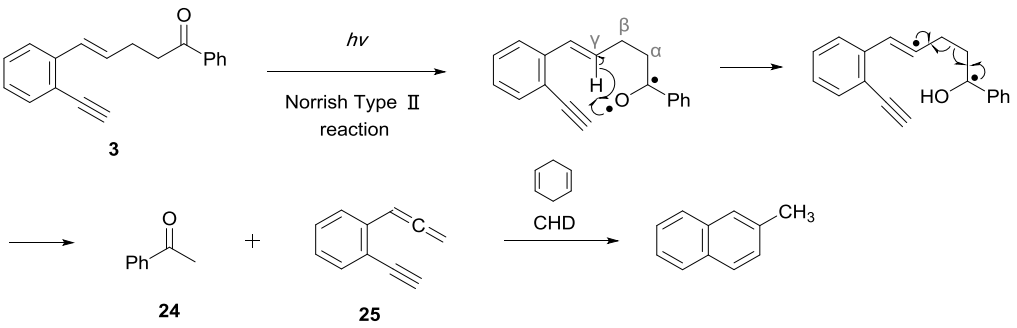


Fig. 29 Structure of the ene-yne-allene and enediyne antibiotics, calicheamicin γ^{I}_{1}, dynemicin A and neocarzinostatin chromophore.



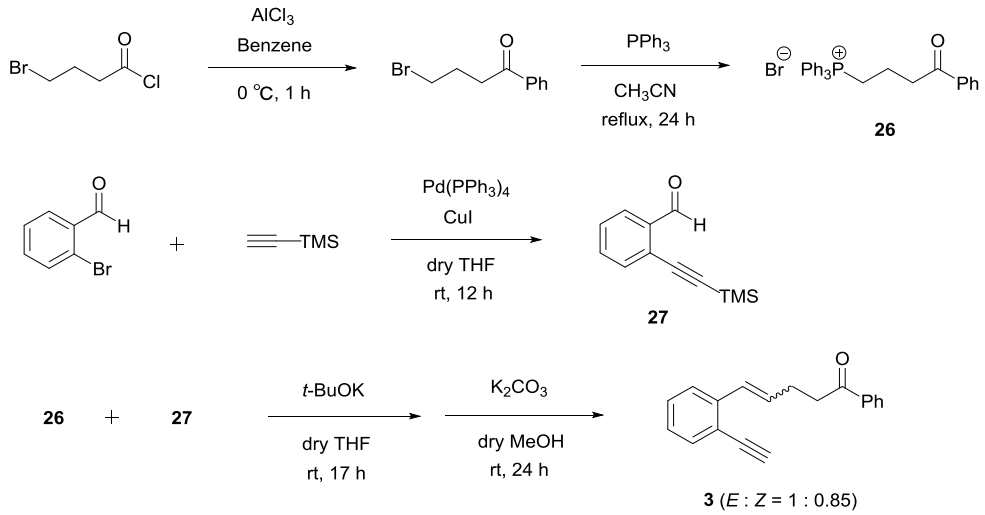
Scheme 8 DNA strand cleavage initiated by C5' hydrogen atom abstraction. Less than 20% of the strand breaks by neocarzinostatin chromophore result from pathways initiated by hydrogen atom abstraction from C4' and C1'.[29]



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

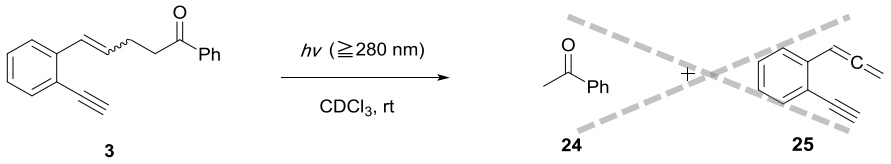
4.1 Syntheses

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 CH_3CN 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**.

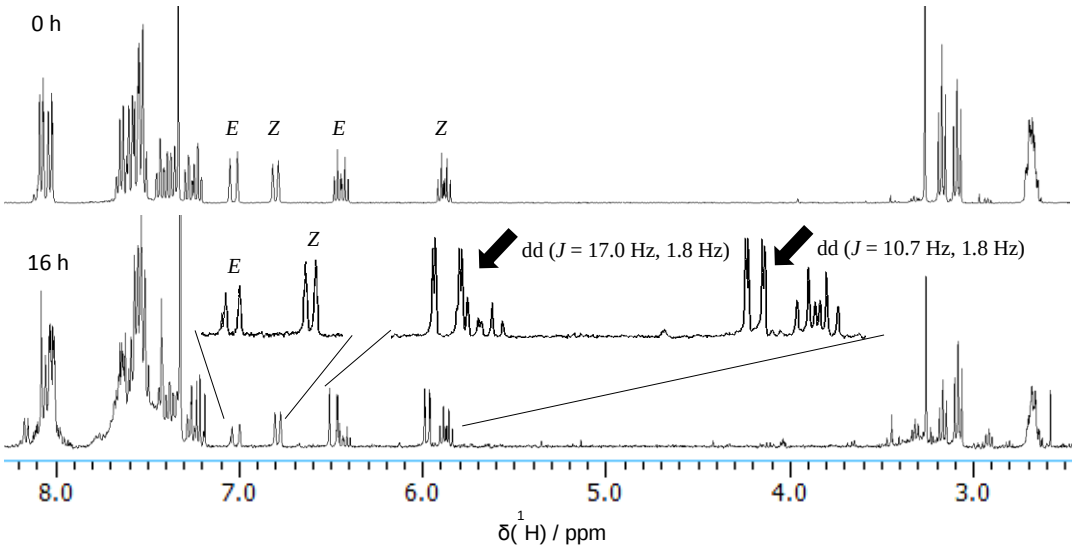


Fig. 30 ^{1}H-NMR spectra of the photoreaction product of ene-yne-allene precursor **3** in $CDCl_3$ for 0 h or 16 h at room temperature.

When ene-yne-allene precursor **3** was reacted in $CDCl_3$ 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 ^{1}H-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).

Column: Gemini-NX 5 μm C_{18} 110 Å, 150×4.6 mm (Phenomenex)
Injection volume: 50 ppm×80 μl
Column temperature: 40 °C
Gradient separations

Time	Flow [ml/min]	0.1% Formic acid H_2O [%]	0.1% Formic acid CH_3CN [%]
0 min	1.0	50	50
7 min	1.0	50	50
9 min	1.0	20	80
24 min	1.0	0	100
29 min	1.0	0	100
30 min	1.0	50	50

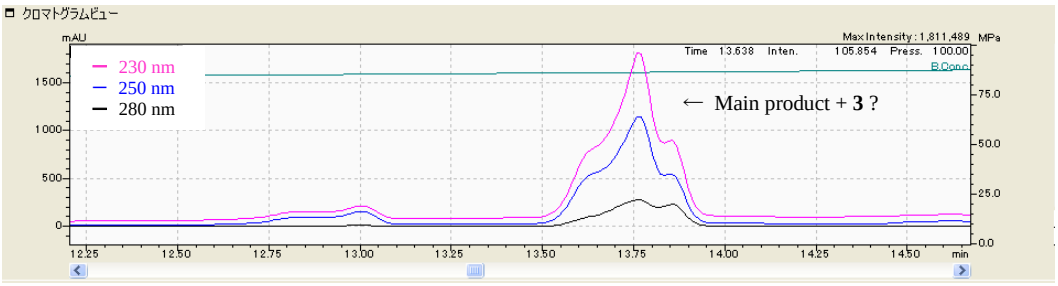
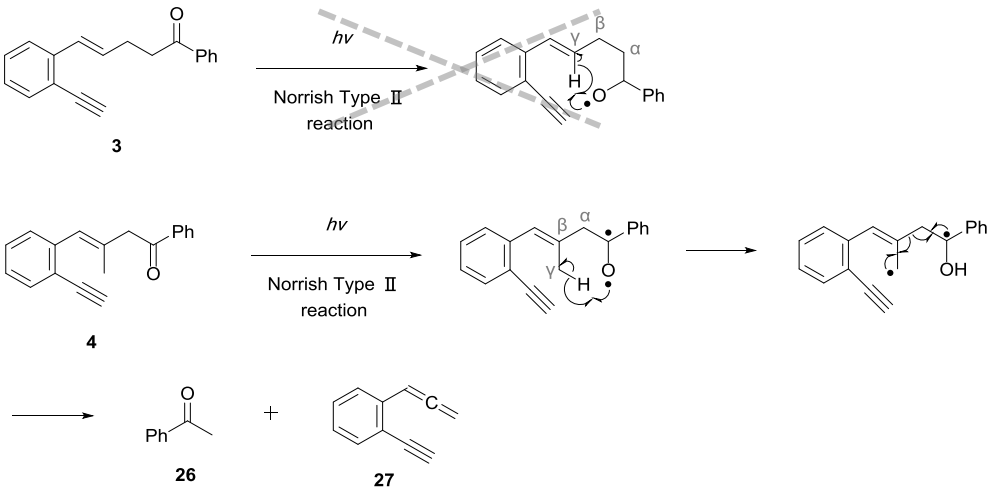


Fig. 31 HPLC analysis of the photoreaction product of ene-yne-allene precursor **3**.

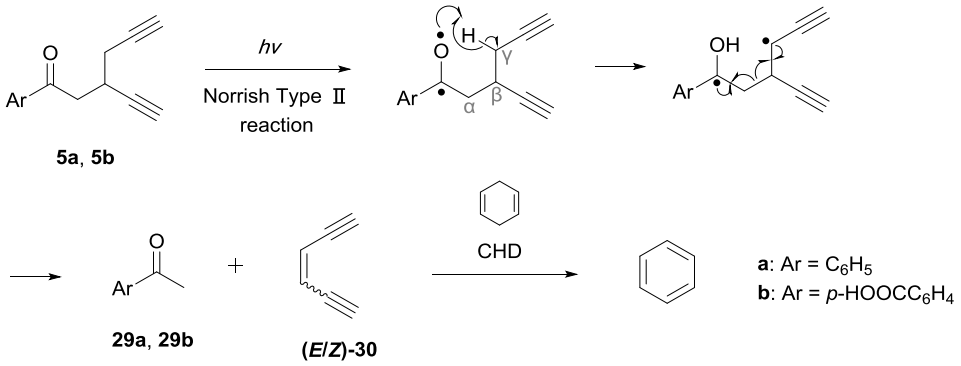


Scheme 12 Design of a novel ene-yne-allene precursor **4**.

5. Development of enediyne precursor

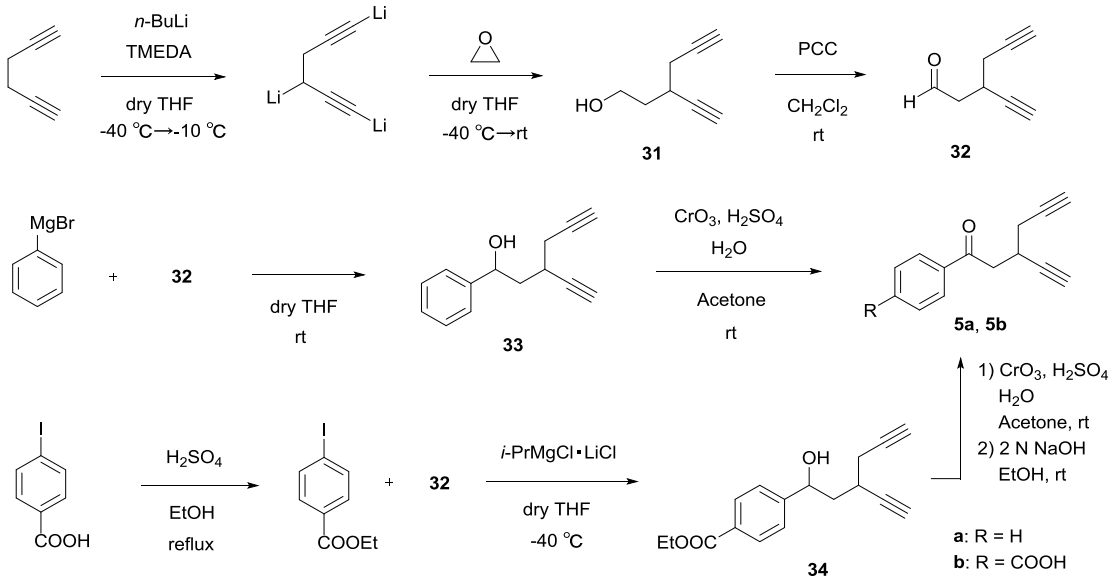
5. Development of enediyne precursor

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.[31] In addition, I have extended the photochemistry of **5** and explored its use as a novel DNA cleaving molecule.



Scheme 13 Putative reaction mechanism of enediyne precursor **5** under UV irradiation.

5.1 Syntheses



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 H_2SO_4, 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

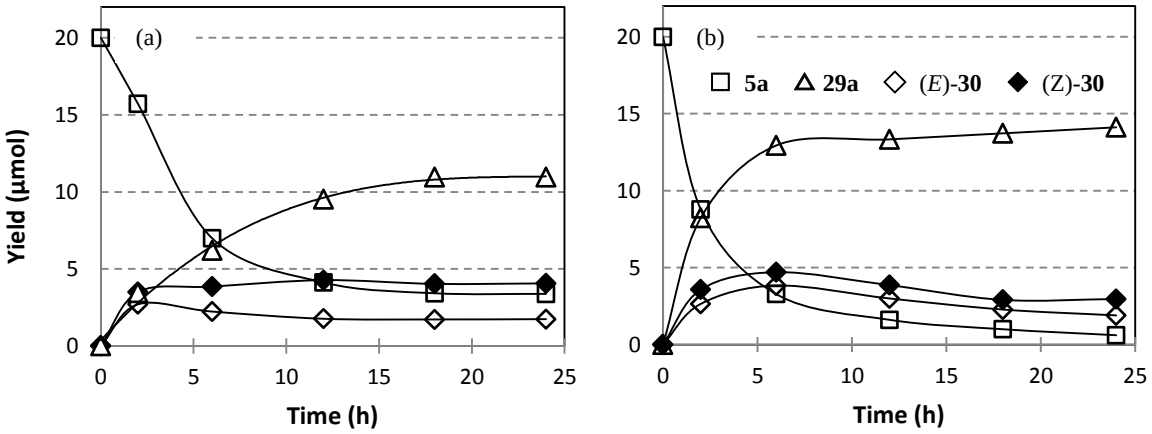


Fig. 32 Time course of the reactions of **5a** in acetonitrile-d_3 (a) and cyclohexane-d_{12} (b) under UV irradiation (≧280 nm) at room temperature. Yields are estimated by comparing the integration of the respective ^{1}H-NMR signals against the methyl signal of tetramethylsilane (TMS) as an internal standard (400 MHz).

First, I measured the time-dependent ^{1}H-NMR spectra of the reaction of **5** under UV irradiation (≧280 nm, high-pressure mercury lamp) at room temperature in acetonitrile-d_3 or cyclohexane-d_{12}. Fig. 32 shows that the yields of **5a**, acetophenone **29a**[32] and enediyne (*E*/*Z*)-**30**[33] 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-d_{12} (Fig. 32 (b)) formed more **29a** and **30** than that in acetonitrile-d_3 (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

photoisomerized to (*Z*)-**30** in the presence of **29a** as a photosensitizer.[34] 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.

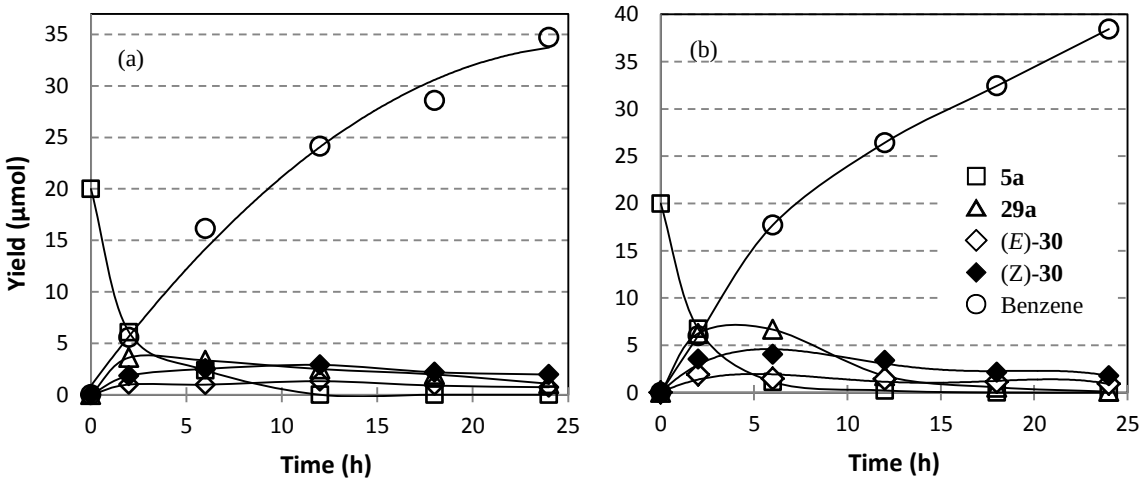


Fig. 33 Time course of the reactions of **5a** with 1,4-cyclohexadiene (CHD, 10 eq) in acetonitrile-d_3 (a) and cyclohexane-d_{12} (b) under UV irradiation (≧280 nm) at room temperature. Yields are estimated by comparing the integration of the respective ^{1}H-NMR signals against the methyl signal of tetramethylsilane (TMS) as an internal standard (400 MHz).

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.[35] The nπ* 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}nπ* state of **5** seems to more favorably abstract an intramolecular γ-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.[a]

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

[a] Yields (μmol) 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 prostine 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 μmol) 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 μmol) 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.[36] 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).

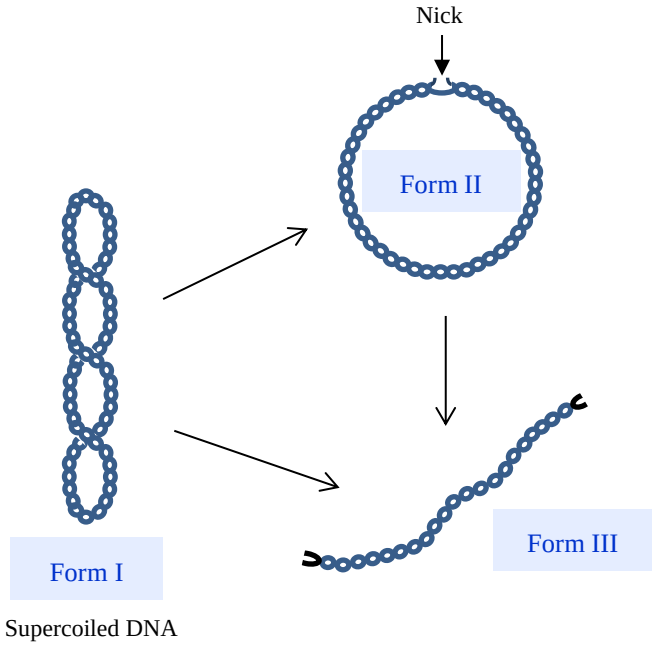
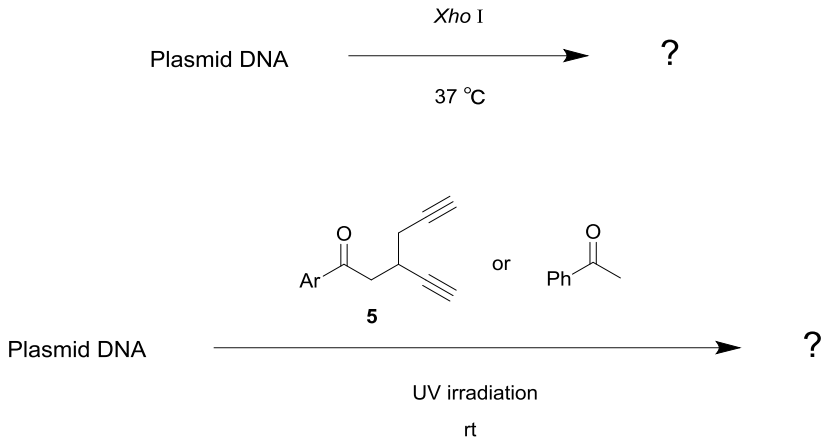


Fig. 34 Putative cleaving mechanism of a plasmid DNA.



Scheme 15 Cleavage of *φ*X174RFI 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.

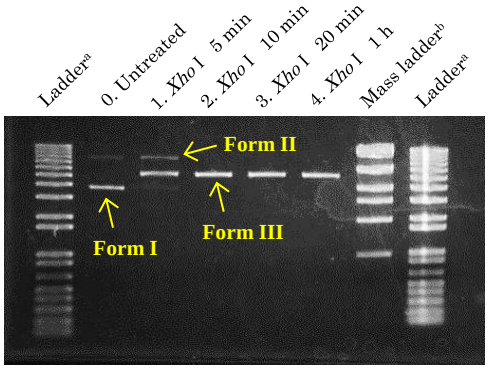
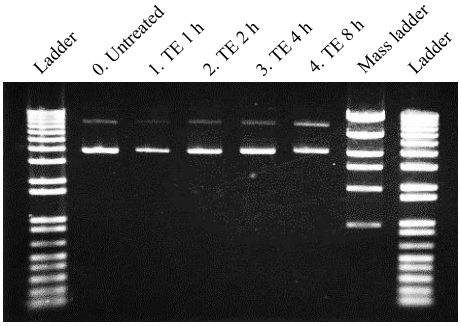


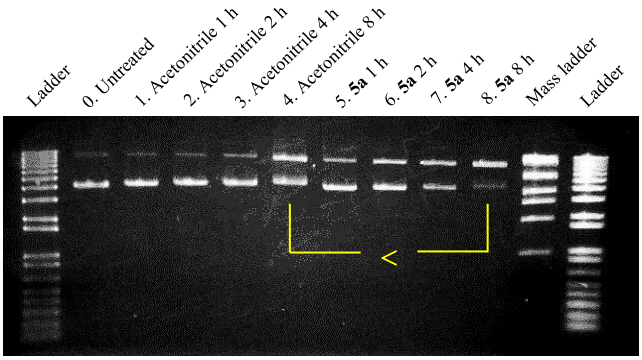
Fig. 35 Cleavage of supercoiled *φ*X174RFI plasmid DNA ((0.1 μg, TAKARA BIO INC.) by *Xho* I (restriction enzyme, cleavage site = 1, TAKARA BIO INC.). *φ*X174RFI DNA solution was incubated with *Xho* I in TE (10 mM Tris HCl, 1 mM EDTA, pH 8.0) containing 10×concentrated high salt concentration (10×H) 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)

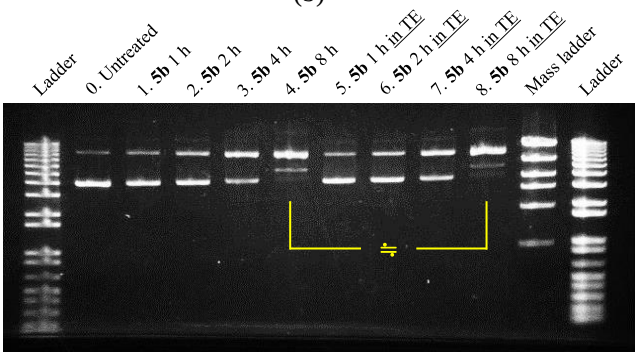
[b] Mass ladder (High DNA Mass Ladder, 4 μl, Invitrogen)



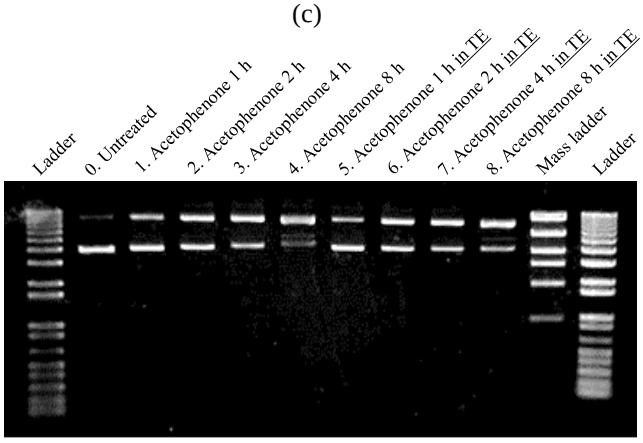
(a)



(b)



(c)



(d)

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 sataind 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

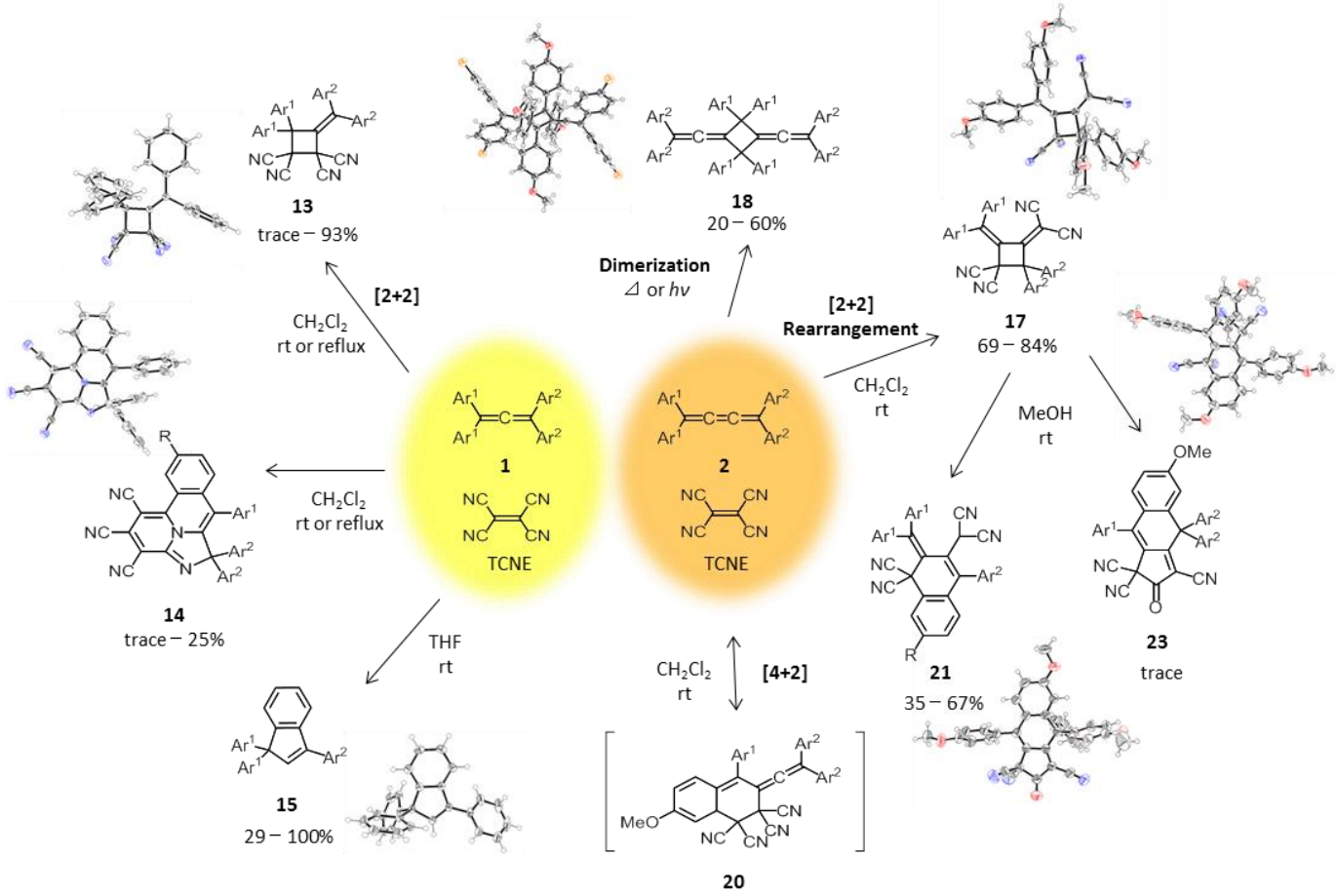
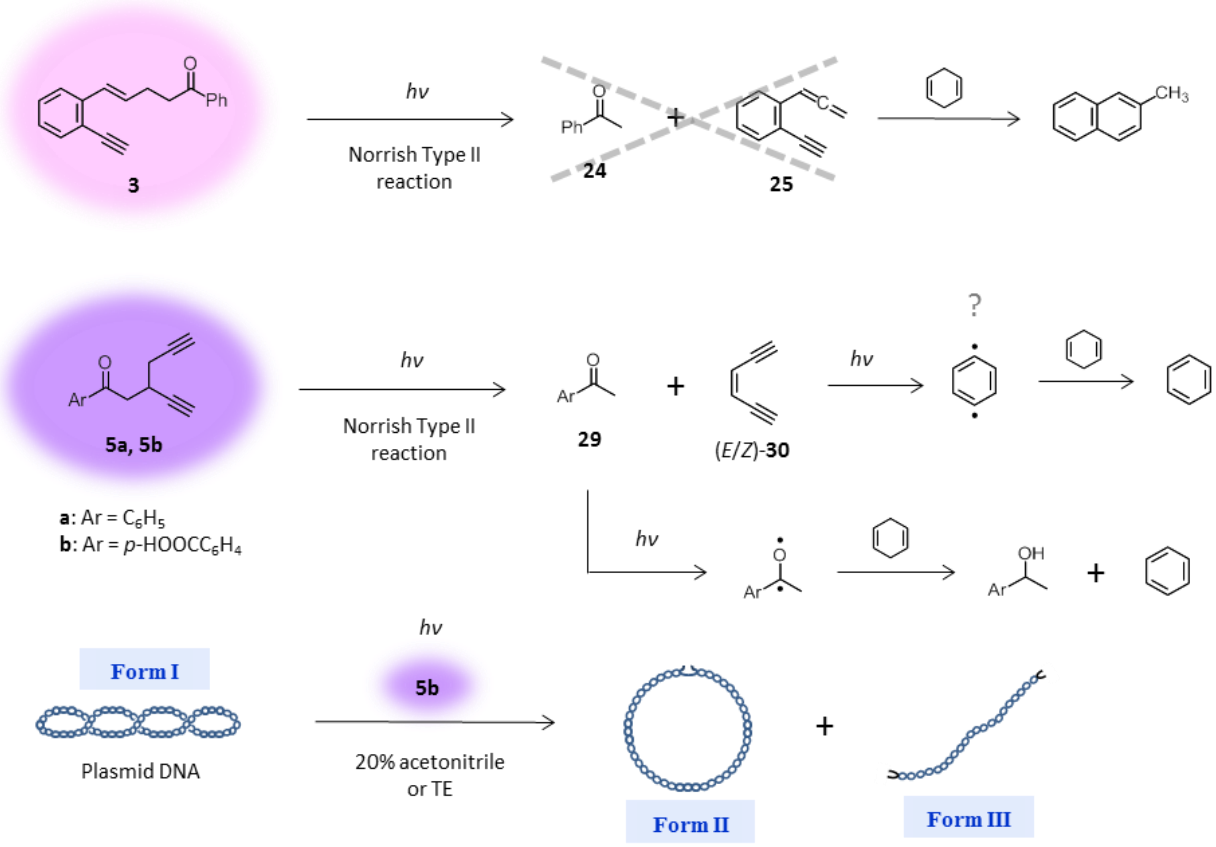


Fig. 37 The reactions of tetraarylallene **1** and tetraaryl[3]cumulene **2** with TCNE.

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 tetraarylallene **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 diarylallene 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_3CN. 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

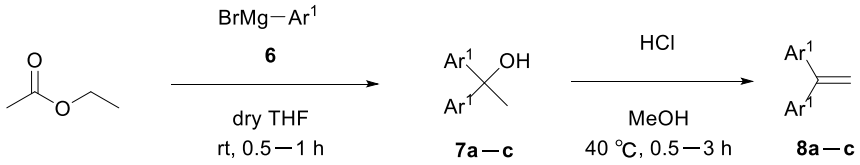
7. Experimental

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-TK (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-*Kα* 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_3CN / 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).



a: $Ar^1 = C_6H_5$ **b**: $Ar^1 = MeOC_6H_4$ **c**: $Ar^1 = MeC_6H_4$

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 NH_4Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over $MgSO_4$, 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 $MgSO_4$ and evaporated under reduced pressure to give **8a** (3.8 g, 21 mmol, 97% yield) as pale yellow oil.

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

^{13}C 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 NH_4Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over $MgSO_4$, filtered, 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 H_2O and MeOH, pale yellow crystals **8b** (4.4 g, 18 mmol, 92% yield) were separated, mp 140–142 °C.

^{1}H 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)

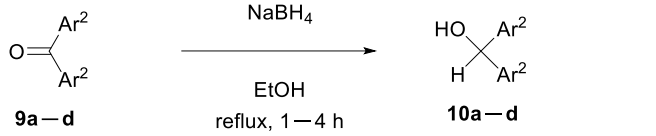
A three-necked flask connected with a firestone valve, dropping funnel and reflux condenser was equipped. Magnesium (1.3 g, 54 mmol, 2.0 eq) was put in the flask and nitrogen gas was purged in the system. Firstly, dry THF (50 ml) and a piece of iodine were added, and then *p*-bromotoluene (13 ml, 54 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 NH_4Cl solution was added. The reaction mixture was extracted with ether and the combined organic extract was washed with brine, dried over $MgSO_4$, 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 $MgSO_4$, 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.

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

^{13}C NMR δ: 21.1, 113.0, 128.2, 128.8, 137.4, 138.8, 149.7.



9a—d **10a—d**

a: $Ar^2 = C_6H_5$ **b**: $Ar^2 = MeOC_6H_4$ **c**: $Ar^2 = MeC_6H_4$ **d**: $Ar^2 = ClC_6H_4$

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 NH_4Cl solution was added, and then the colorless crystals **10a** (4.2 g, 22 mmol, 100% yield) were separated, mp 59–60 °C.

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

^{13}C NMR δ: 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 NH_4Cl solution was added. Evaporation of the solvent and recrystarization from MeOH yielded white solid **10b** (9.1 g, 37 mmol, 88% yield), mp 57–58 °C.

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

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

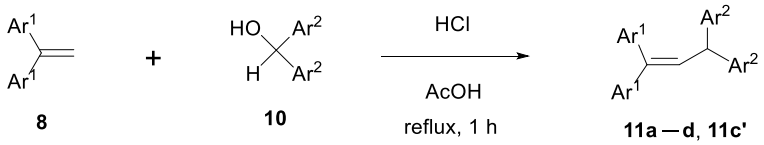
Compound **10c** (8.2 g, 39 mmol, 92% yield) was prepared by the same procedure as **10b**, mp 58–59 °C.

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



11a: $Ar^1 = Ar^2 = C_6H_5$ **11b**: $Ar^1 = Ar^2 = MeOC_6H_4$ **11c**: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$
11c': $Ar^1 = MeC_6H_4$ $Ar^2 = MeOC_6H_4$ **11d**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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_2Cl_2, the combined extract was dried over $MgSO_4$, evaporated under reduced pressure. After recrystallization with CH_2Cl_2–hexane, **11a** (2.7 g, 7.9 mmol, 56% yield) was separated as colorless crystals, mp 120–122 °C.

^{1}H NMR δ: 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 δ: 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_2Cl_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 δ: 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 CH_2Cl_2, dried over $MgSO_4$ and evaporated under reduced pressure to give **11c** (5.4 g, 13 mmol, 100% yield) as pale yellow oil.

^{1}H 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 CH_2Cl_2, dried over $MgSO_4$ and evaporated under reduced pressure to give **11c'** (6.3 g, 15 mmol, 100% yield) as pale yellow oil.

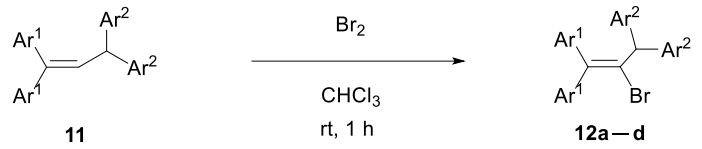
^{1}H NMR δ: 2.39 (s, 3H), 2.45 (s, 3H), 3.83 (s, 6H), 4.85 (d, 1H, J = 10.6 Hz), 6.52 (d, 1H, J = 10.6 Hz), 6.91 (d, 4H, J = 8.6 Hz), 7.14 (d, 2H, J = 8.6 Hz), 7.17 (d, 6H, J = 8.6 Hz), 7.23–7.26 (m, 4H).

^{13}C 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 CH_2Cl_2, dried over $MgSO_4$ and evaporated under reduced pressure to give **11d** (4.5 g, 9.5 mmol, 95% yield) as pale yellow oil.

^{1}H 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).



12a: $Ar^1 = Ar^2 = C_6H_5$ **12b**: $Ar^1 = Ar^2 = MeOC_6H_4$
12c: $Ar^1 = MeC_6H_4$ $Ar^2 = MeOC_6H_4$ **12d**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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

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_2O and brine. After evaporation, **12a** (1.8 g, 4.2 mmol, 112% yield) was obtained as yellow oil containing a lot of allene **1a**.

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

^{13}C 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-bis(*p*-methoxyphenyl)-3,3-bis(*p*-methoxyphenyl)peopene (12b)

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_2O 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.

2-Bromo-1,1-bis(*p*-methylphenyl)-3,3-bis(*p*-methoxyhenyl)peopene (12c)

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_2O 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.

^{1}H 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).

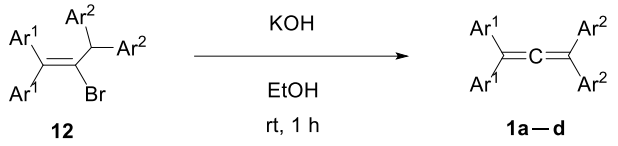
^{13}C NMR δ: 21.0, 21.3, 55.2, 113.5, 125.6, 128.2, 128.7, 129.0, 130.4, 134.0, 136.9, 137.5, 138.5, 139.8, 140.2, 143.5, 158.3.

2-Bromo-1,1-bis(*p*-methoxyphenyl)-3,3-bis(*p*-chlorophenyl)peopene (12d)

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

^{1}H NMR δ: 3.78 (s, 3H), 3.79 (s, 3H), 6.81 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 7.05 (d, 2H, J = 8.6 Hz), 7.16 (d, 4H, J = 8.6 Hz), 7.18 (d, 2H, J = 8.6 Hz), 7.30 (d, 4H, J = 8.6 Hz).

^{13}C NMR δ: 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.



1a: $Ar^1 = Ar^2 = C_6H_5$ **1b**: $Ar^1 = Ar^2 = MeOC_6H_4$
1c: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$ **1d**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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.

^{1}H NMR δ: 7.29–7.31 (m, 12H), 7.42–7.44 (m, 8H).

^{13}C NMR δ: 112.6, 127.5, 128.4, 128.5, 136.3, 208.5.

Elemental analysis: calcd for $C_{27}H_{20}$: C, 94.19; H, 5.85. Found: C, 94.19; H, 5.84.

X-ray data: empirical formula: $C_{27}H_{20}$, 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, β = 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>2σ(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).

^{1}H NMR δ: 3.89 (s, 12H), 6.95 (d, 8H, J = 8.6 Hz), 7.79 (d, 8H, J = 8.6 Hz).

^{13}C NMR δ: 55.5, 113.4, 130.8, 132.2, 162.8, 194.5.

Elemental analysis: calcd for $C_{31}H_{28}O_4$: 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 CH_2Cl_2. 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.

^{1}H 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).

^{13}C 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 $C_{31}H_{28}O_2$: C, 86.08; H, 6.52. Found: C, 86.10; H, 6.48.

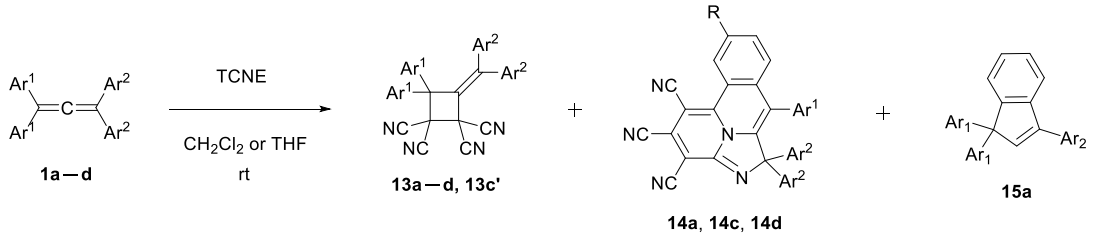
1,1-Bis(*p*-methoxyphenyl)-3,3-bis(*p*-chlorophenyl)allene (1d)

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 H_2O and the mixture was extracted with CH_2Cl_2. 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.

^{1}H 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).

^{13}C 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 $C_{29}H_{22}Cl_2O_2$: C, 73.58; H 4.68. Found: C, 73.78; H, 4.51.



a: $Ar^1 = Ar^2 = C_6H_5$ R = H **b**: $Ar^1 = Ar^2 = p$-$MeOC_6H_4$ R = OMe
c: $Ar^1 = p$-$MeOC_6H_4$ $Ar^2 = p$-MeC_6H_4 R = OMe **c'**: $Ar^1 = p$-MeC_6H_4 $Ar^2 = p$-$MeOC_6H_4$ R = Me
d: $Ar^1 = p$-$MeOC_6H_4$ $Ar^2 = p$-ClC_6H_4 R = OMe

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 CH_2Cl_2 (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).

^{1}H 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).

^{13}C 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 $CDCl_3$, the rest of signals could not be detected.)

TOF-ESI-MS *m*/*z*: calcd for: $C_{33}H_{21}N_4^+$ 473.1766. Found: 473.1775 ([M+H]$^+$).

X-ray data: empirical formula: $C_{33}H_{20}N_4$, formula weight: 472.55, crystal habit: block, 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* = 98.8258 (7) °, *γ* = 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 (*I*>2σ(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_2Cl_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 / 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), 7.55 (d, 4H, *J* = 8.7 Hz).

^{13}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).

^{13}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*: calcd for: $C_{37}H_{29}N_4O_2^+$ 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_2Cl_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).

^{13}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*: calcd for: $C_{35}H_{23}N_4O_2Cl_2^+$ 601.1198. Found: 601.1172 ([M+H]$^+$).

1,2,3-Tricyano-5,5,6-triphenyl-5*H*-4,10c-diazaacephenanthrylene (14a)

See the synthetic procedure of **13a**, mp ＞300 °C.

^{1}H NMR δ: 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 δ: 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, 135.2, 137.8, 140.2, 143.3, 147.7.

TOF-ESI-MS m/z: calcd for: $C_{35}H_{20}N_5^+$ 510.1719. Found: 510.1705 ([M+H]$^+$).

X-ray data: 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) Å^3, Z = 2, no. observations = 4473, no. variables = 361, reflection/parameter ratio = 12.39, R = 0.0859 (I>2σ(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-5*H*-4,10c -diazaacephenanthrylene (14c) or / and 5,5-Bis(*p*-methoxyphenyl)-9-methyl-6-*p*-methylphenyl -1,2,3-tricyano-5*H*-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: calcd for: $C_{39}H_{28}N_5O_2^+$ 597.2165. Found: 597.2171 ([M+H]$^+$).

5,5-Bis(*p*-chlorophenyl)-9-methoxy-6-*p*-methoxyphenyl-1,2,3-tricyano-5*H*-4,10c -diazaacephenanthrylene (14d)

See the synthetic procedure of **13d**. Because the yields were very small, it is not clear whether **14d**, regioisomer of **14d** or both were yielded.

TOF-ESI-MS m/z: calcd for: $C_{37}H_{22}N_5O_2Cl_2^+$ 638.1151. Found: 638.1160 ([M+H]$^+$).

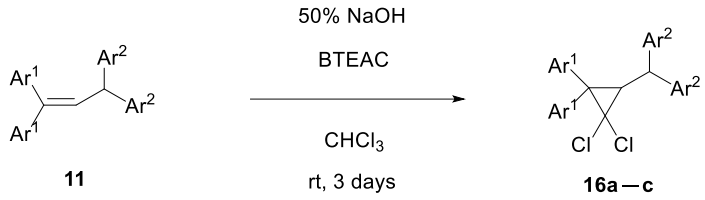
1,1,3-Triphenylindene (15a)

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 δ: 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 δ: 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, α = 99.9878 (12) °, β = 110.8720 (12) °, γ = 111.4450 (9) °, V = 1879.59 (7) Å^3, Z = 4, no. observations = 6754, no. variables = 487, reflection/parameter ratio = 13.87, R = 0.0448 (I>2σ(I)), R (all reflections) = 0.0663, wR (all reflections) = 0.1199, GoF = 1.052.



BTEAC = Benzyltriethylammonium chloride

16a: $Ar^1 = Ar^2 = MeOC_6H_4$ **16b**: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$ **16c**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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 °C.

^{1}H NMR δ: 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 = 8.8Hz), 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*-methothyphenyl)-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**.

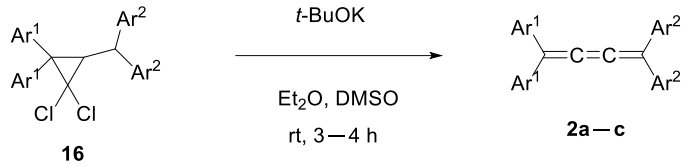
^{1}H NMR δ: 2.26 (s, 3H), 2.36 (s, 3H), 3.26 (d, 1H, J = 11.5 Hz), 3.64 (d, 1H, J = 11.5 Hz), 3.72 (s, 3H), 3.75 (s, 3H), 6.74 (d, 2H, J = 8.8 Hz), 6.78 (d, 2H, J = 8.8 Hz), 7.07 (d, 2H, J = 8.1 Hz), 7.14 (d, 2H, J = 8.8 Hz), 7.20 (d, 2H, J = 7.8 Hz), 7.24 (d, 2H, J = 8.8 Hz), 7.27 (d, 2H, J = 7.8 Hz), 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 δ: 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 $C_{30}H_{24}Cl_4O_2$: C, 64.54; H, 4.33. Found: C, 64.55; H, 4.28.



2a: $Ar^1 = Ar^2 = MeOC_6H_4$ **2b**: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$ **2c**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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 δ: 3.86 (s, 12H), 6.91 (d, 8H, J = 9.0 Hz), 7.49 (d, 8H, J = 9.0 Hz).

^{13}C NMR δ: 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 δ: 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 δ: 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 $C_{32}H_{28}O_2 \bullet nH_2O$ (n = 2/3): C, 84.17; H, 6.48. Found: C, 84.03; H, 6.42.

X-ray data: empirical formula: $C_{32}H_{28}O_2$, formula weight: 444.54, crystal habit: needle, crystal system: orthorhombic, space group: *pbca*, unit cell dimensions: a = 7.52750(10) Å, b = 27.5908(6) Å, c = 26.1680(6) Å, $\alpha = \beta = \gamma = 90°$, V = 5434.83(19) Å^3, Z = 8, no. observations = 91704, no. 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.

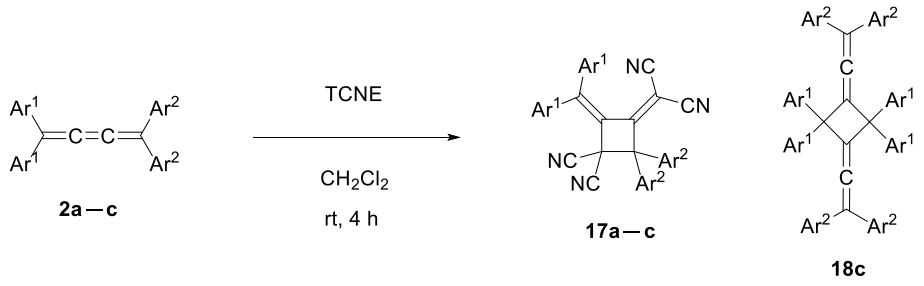
1,1-Bis(*p*-chlorophenyl)-4,4-bis(*p*-methylphenyl)butatriene (2c)

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 δ: 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 δ: 55.4, 114.0, 128.7, 130.2, 130.8, 133.4, 137.3, 160.0.

Elemental analysis: calcd for $C_{30}H_{22}Cl_2O_2$: C, 74.23; H, 4.57. Found: C, 74.19; H, 4.60.



a: $Ar^1 = Ar^2 = MeOC_6H_4$ **b**: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$ **c**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$

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

[3]Cumulene **2a** (0.10 g, 0.21 mmol) and TCNE (0.032 g, 0.25 mmol, 1.2 eq) were mixed in CH_2Cl_2 (10 ml) at room temperature for 4 h. After evaporation of the solvent, recrystallization from CH_2Cl_2–hexane afforded red crystals **17a** (0.088 g, 0.14 mmol, 69% yield), mp 179–181 °C.

^{1}H NMR δ: 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).

^{13}C NMR δ: 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 $C_{38}H_{28}N_4O_4$: 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: $C_{38}H_{29}N_4O_4^+$ 605.2189. Found: 605.2192 ($[M+H]^+$).

X-ray data: empirical formula: $C_{38}H_{28}N_4O_4$, 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, $\alpha = \beta = \gamma = 90°$, V = 6288.2(2) 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 CH_2Cl_2–hexane gave red crystals **17b** (0.12 g, 0.21 mmol, 76% yield), mp 165 °C (decomp).

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

^{13}C NMR δ: 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: $C_{38}H_{27}N_4O_2^-$ 571.2134. Found: 571.2136 ($[M-H]^-$).

X-ray data: empirical formula: $C_{38}H_{28}N_4O_2$, 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, α = 102.539(2)°, β = 96.811(2)°, γ = 113.934(2)°, V = 6288.2(2) 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 CH_2Cl_2–hexane gave red crystals **17c** (0.11 g, 0.18 mmol, 84% yield), mp 160 °C (decomp).

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

^{13}C NMR δ: 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: $C_{36}H_{21}N_4O_2Cl_2^-$ 611.1042. Found: 611.1021 ($[M-H]^-$).

X-ray data: empirical formula: $C_{36}H_{22}N_4O_2Cl_2$, 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, α = 99.561(7)°, β = 91.793(7)°, γ = 103.561(7)°, *V* = 3356.3(1) Å^3, *Z* = 4, no. observations = 12006, no. 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.

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

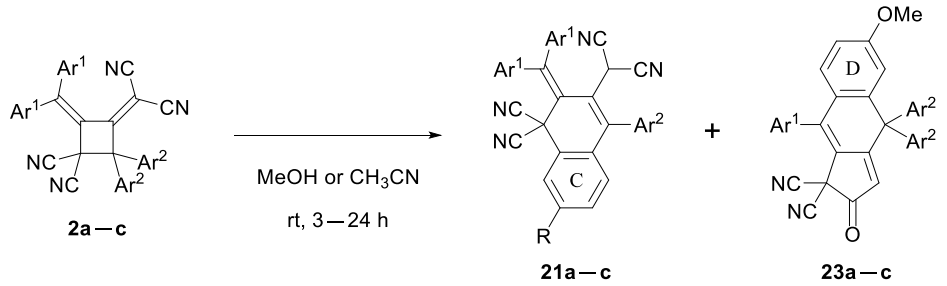
^{1}H NMR spectra showed that the reaction of **2c** and TCNE in CH_2Cl_2 at room temperature gave not only main product **17c** but also a small amount of minor product, head-to-tail dimer **18c**. Although **18c** could not be isolated from a solution of **17c** in CH_2Cl_2, stirring **2c** (0.043 g, 0.088 mmol) in toluene at 90 °C for 3 h followed by recrystallization from CH_2Cl_2–hexane gave yellow crystals **18c** (0.017 g, 0.018 mmol, 20% yield), mp 300 °C (decomp).

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

^{13}C NMR δ: 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 $C_{60}H_{44}O_4Cl_4$•nH_2O (n = 1/2): C, 73.55; H, 4.63. Found: C, 73.63; H, 4.75.

X-ray data: empirical formula: $C_{60}H_{44}O_4Cl_4$, formula weight: 970.75, crystal habit: needle, crystal system: monoclinic, space group: $P2_1/n$, unit cell dimensions: *a* = 15.9572(3) Å, *b* = 8.7817(2) Å, *c* = 16.7713(3) Å, $\alpha = \gamma$ = 90°, β = 91.2657(12)°, *V* = 2349.61(8) Å^3, *Z* = 2, no. observations = 4305, no. 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.



a: $Ar^1 = Ar^2 = MeOC_6H_4$ R = OMe **b**: $Ar^1 = MeOC_6H_4$ $Ar^2 = MeC_6H_4$ R = Me **c**: $Ar^1 = MeOC_6H_4$ $Ar^2 = ClC_6H_4$ R = Cl

4-(*p*-Methoxyphenyl)-2-bis(*p*-methoxyphenyl)methylene-1,1-dicyano-3-dicyanomethyl-7-methoxy-1,2-dihydronaphthalene (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_2Cl_2–

hexane to give **21a** (0.011 g, 0.019 mmol, 67% yield) as pale yellow crystals, mp 164–166 °C.
^{1}H NMR (at 51 °C) δ: 3.84 (s, 3H, O*Me*), 3.85 (s, 3H, O*Me*), 3.86 (s, 3H, O*Me*), 3.89 (s, 3H, O*Me*), 4.64 (s, 1H, C*H*(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, *Ph*OMe), 6.98–7.03 (m, 6H, *Ph*OMe), 7.13 (d, 2H, *J* = 9.1 Hz, *Ph*OMe), 7.19 (d, 2H, *J* = 8.6 Hz, *Ph*OMe), 7.39 (d, 1H, *J* = 2.3 Hz, ring C).
^{13}C 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 $C_{38}H_{28}N_4O_4$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.69; H, 4.57; N, 9.02.
X-ray data: empirical formula: $C_{38}H_{28}N_4O_4$, 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, $\alpha = \beta = \gamma = 90°$, *V* = 6283.8(2) Å^3, *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.
^{1}H NMR (at 51 °C) δ: 2.40 (s, 3H, *Me*), 2.42 (s, 3H, *Me*), 3.84 (s, 3H, O*Me*), 3.89 (s, 3H, O*Me*), 4.64 (s, 1H, C*H*(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, *Ph*Me), 6.98–7.03 (m, 6H, *Ph*OMe), 7.12 (d, 2H, *J* = 9.1 Hz, *Ph*Me), 7.19 (d, 2H, *J* = 8.6 Hz, *Ph*OMe), 7.38 (d, 1H, *J* = 2.3 Hz, ring C).
^{13}C 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.
TOF-ESI-MS *m*/*z*: calcd for: $C_{38}H_{29}N_4O_2^+$ 573.2291. Found: 573.2285 ([M+H]$^+$).

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).
^{1}H NMR (at 51 °C) δ: 3.85 (s, 3H, O*Me*), 3.86 (s, 3H, O*Me*), 4.65 (s, 1H, C*H*(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, *Ph*Cl), 7.14–7.18 (m, 6H, *Ph*OMe), 7.38 (d, 1H, *J* = 2.3 Hz, ring C), 7.40 (d, 2H, *J* = 8.6 Hz, *Ph*OMe), 7.46 (d, 2H, *J* = 9.1 Hz, *Ph*Cl).

^{13}C NMR (at 51 °C) δ: 30.8, 55.5, 55.9, 110.9, 113.1, 115.1, 115.8, 116.4, 122.2, 126.1, 129.3, 130.3, 130.9, 131.4, 132.5, 133.4, 137.4, 137.7, 138.6, 138.7, 148.1, 150.3, 161.18, 162.2.
TOF-ESI-MS *m*/*z*: calcd for: $C_{36}H_{21}N_4O_2Cl_2^-$ 611.1042. Found: 611.1014 ([M-H]$^-$).

6-Methoxy-2-oxo-4,4,9-tris(*p*-methoxyphenyl)-1*H*-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: $C_{38}H_{28}N_3O_5^+$ 606.20. Found: 606.19 ([M+H]$^+$). Calcd for: $C_{38}H_{27}N_3O_5Na^+$ 628.19. Found: 628.17 ([M+Na]$^+$).
TOF-ESI-MS *m*/*z*: calcd for: $C_{38}H_{28}N_3O_5^+$ 606.2029. Found: 606.2017 ([M+H]$^+$).
X-ray data: empirical formula: $C_{38}H_{27}N_3O_5$, 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, $\alpha = \gamma$ = 90°, β = 95.6174(9)°, V = 3196.64(11) Å^3, Z = 4, no. observations = 36081, no. variables = 5845, reflection/parameter ratio = 13.95, R = 0.0426 (I>2σ(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)-1*H*-cyclopenta-[*b*]naphthalene-1,1,3(2*H*,4*H*)-tricarbonitrile (23b)

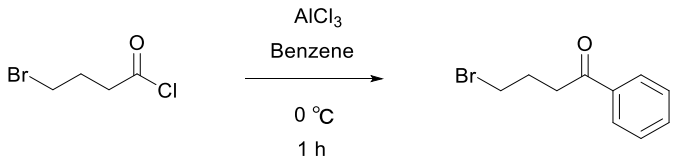
Compound **2b** (0.10 g, 0.17 mmol) was stirred in MeOH at room temperature for 24 h. The mixture was separated by preparative layer chromatography, but **23b** could not be further purified. Single crystals of the product were, therefore, produced by a vapor diffusion method with CH_2Cl_2–hexane, which afforded pure red single crystals. In addition, recrystallization of **21b** by a vapor diffusion method with CH_2Cl_2–hexane mainly produced yellow crystals together with a few red crystals **23b**, mp 244–246 °C.
^{1}H NMR δ: 2.38 (s, 6H, 2×*Me*), 3.71 (s, 3H, O*Me*), 3.92 (s, 3H, O*Me*), 6.58 (d, 1H, J = 1.8 Hz, ring D), 6.81 (dd, 1H, J = 1.8 and 8.8 Hz, ring D), 7.07 (d, 4H, J = 8.2 Hz, *Ph*Me), 7.11 (d, 2H, J = 8.2 Hz, *Ph*OMe), 7.20 (d, 4H, J = 8.2 Hz, *Ph*Me), 7.30 (d, 1H, J = 8.8 Hz, ring D), 7.33 (d, 2H, J = 8.2 Hz, *Ph*OMe).
NALDI-TOF-MS *m*/*z*: calcd for: $C_{38}H_{27}N_3O_3Na^+$ 596.20. Found: 596.24 ([M+Na]$^+$).
TOF-ESI-MS *m*/*z*: calcd for: $C_{38}H_{28}N_3O_3^+$ 574.2131. Found: 574.2159 ([M+H]$^+$).
X-ray data: empirical formula: $C_{38}H_{27}N_3O_3$, 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, $\alpha = \gamma$ = 90°, β = 97.8432(10)°, V = 7147.2(2) Å^3, Z = 8, no. observations = 40636, no. variables = 6463, reflection/parameter ratio = 16.11, R = 0.0644 (I>2σ(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)-1*H*-cyclopenta[*b*]naphthalene-1,1,3(2*H*,4*H*)-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: $C_{36}H_{21}N_3O_3Cl_2Na^+$ 636.09. Found: 636.11 ($[M+Na]^+$). TOF-ESI-MS *m*/*z*: calcd for: $C_{36}H_{22}N_3O_3Cl_2^+$ 614.1038. Found: 614.1024 ($[M+H]^+$).

X-ray data: empirical formula: $C_{36}H_{21}N_3O_3Cl_2$, formula weight: 614.46, crystal habit: needle, crystal system: monoclinic, space group: *C*2/*c*, unit cell dimensions: *a* = 28.4477(18) Å, *b* = 10.8997(6) Å, *c* = 23.5205(14) Å, $\alpha = \gamma = 90°$, $\beta = 98.339(3)°$, *V* = 7215.9(7) $Å^3$, *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, GoF = 0.985.

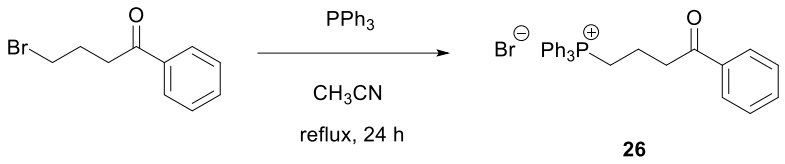


4-Chloro-1-phenylbutan-1-one

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

^{13}C NMR δ: 26.8, 33.6 36.5, 128.0, 128.6, 133.2, 136.6, 198.8.



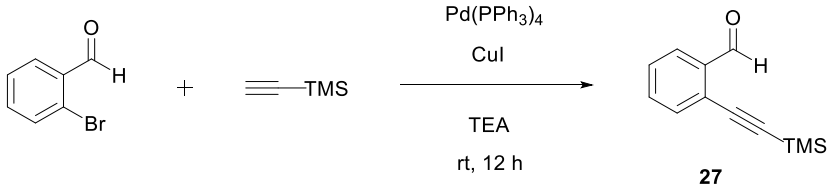
26

(4-Oxo-4-phenylbutyl)triphenylphosphonium bromide (26)

A mixture of 4-chloro-1-phenylbutan-1-one (3.5 g, 15 mmol) and triphenyl phosphine (PPh_3) (4.0 g, 15 mmol, 1.0 eq) in CH_3CN (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 CH_3CN–ether, and then not crystal but green oil **26** (4.9 g, 10 mmol, 65% yield) containing PPh_3 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.



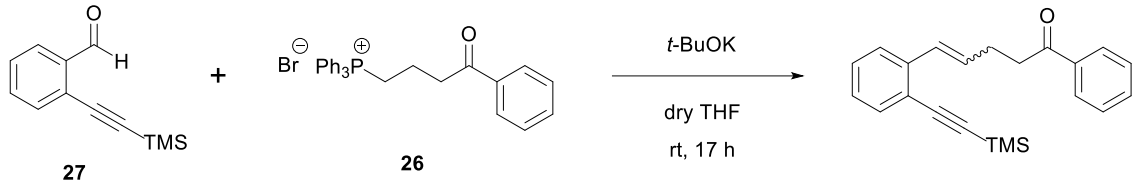
27

2-Trimethylsilanylethynylbenzaldehyde (27)

To a solution of $Pd(PPh_3)_4$ (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 CH_2Cl_2. The organic extract was washed well with saturated NH_4Cl solution and H_2O. The residue was dried over $MgSO_4$, 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.

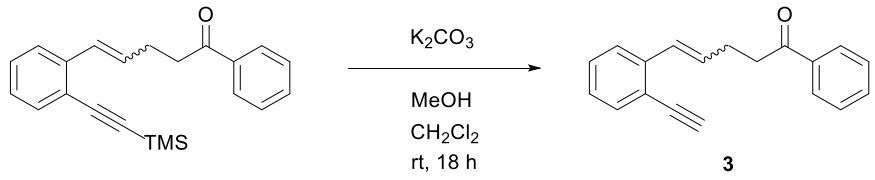


(*E*/*Z*)-1-Phenyl-5-(2-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-one

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 H_2O, 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*): ^{1}H 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*): ^{1}H 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.)



(*E*/*Z*)-5-(2-Ethynylphenyl)-1-phenylpent-4-en-1-one (3)

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 CH_2Cl_2 (5 ml) and anhydrous MeOH (5 ml) was added K_2CO_3 (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 NH_4Cl solution and extracted with CH_2Cl_2. 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 = 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**: ^{1}H 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).

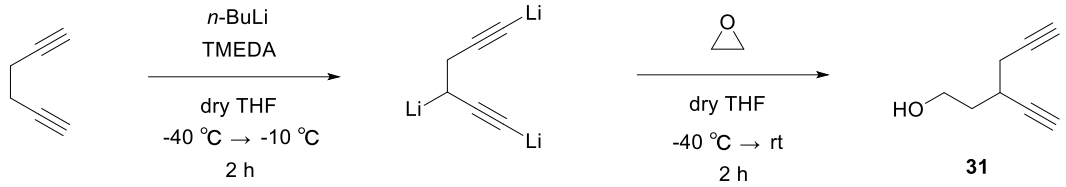
(*Z*)-**3**: ^{1}H NMR δ: 2.68–2.74 (m, 2H), 3.11 (t, 2H, J = 7.2 Hz), 3.28 (s, 1H), 5.82–5.87 (m, 1H), 6.74 (d, 1H, J = 15.8 Hz), 7.16 (dt, 1H, J = 7.6, 1.2 Hz), 7.28 (dt, 1H, J = 7.6, 1.2 Hz), 7.43–7.59 (m, 5H), 7.94 (d, 2H, J = 7.2 Hz).

(*E*+*Z*)-**3**: ^{13}C NMR δ: 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: (λ_{max} nm, acetonitrile): 195 (ε 78,200), 220 (ε 41,400), 260 (ε 8,000), 335 (ε 1,300).

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

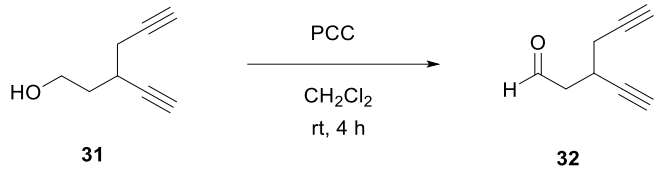


3-Ethynyl-5-hexyn-1-ol (31)

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_4Cl 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 δ: 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).

^{13}C NMR δ: 24.6, 27.6, 36.3, 60.4, 70.3, 70.6, 81.2, 85.3.



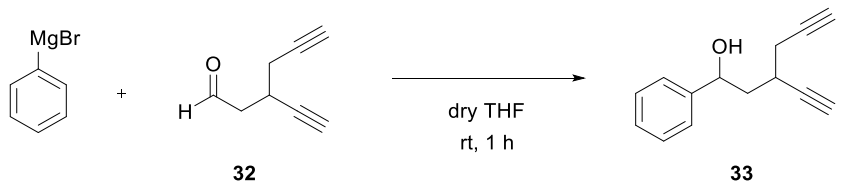
31 **32**

3-(Formylmethyl)-1,5-hexadiyne (32)

To a solution of **31** (0.53 g, 4.3 mmol) in CH_2Cl_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_2O 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 δ: 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).

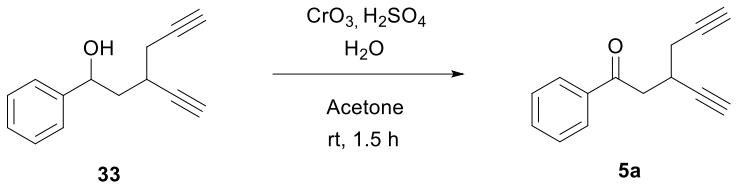
^{13}C NMR δ: 24.1, 24.8, 46.8, 70.9, 71.2, 80.2, 83.9, 199.7.



32 **33**

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_4Cl 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.



33 **5a**

3-(Benzoylmethyl)-1,5-hexadiyne (5a)

To a solution of chromium (VI) oxide (0.37 g, 3.7 mmol, 3.0 eq) in H_2O (1.5 ml) was added conc. H_2SO_4 (0.13 ml, 2.5 mmol, 2.0 eq) in H_2O (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 $MgSO_4$, 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}H NMR δ: 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).

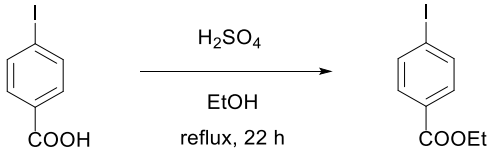
^{13}C NMR δ: 24.0, 25.9, 70.0, 70.9, 80.8, 85.2, 128.1, 128.7, 133.4, 136.6, 197.1.

Elemental analysis: calcd for $C_{14}H_{12}O$; C, 85.68; H, 6.16. Found: C, 85.44; H, 6.23.

TOF-ESI-MS m/z: calcd for $C_{14}H_{13}O^+$ 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).

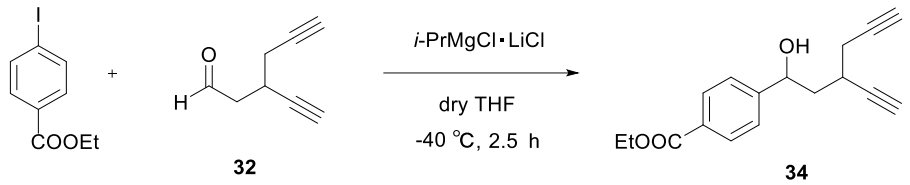


Ethyl 4-iodobenzoate

To a solution of 4-iodobenzoic acid (2.0 g, 8.1 mmol) in EtOH (60 ml) was added conc. H_2SO_4 (2 ml) and refluxed for 22 h. After cooling to room temperature, a solution of $NaHCO_3$ (6.0 g) in H_2O (80 ml) was added and extracted with ether. The organic extract was washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to give colorless oil (2.2 g, 7.8 mmol, 97% yield).

^{1}H NMR δ: 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}C NMR δ: 14.3, 61.2, 100.5, 129.9, 131.0, 137.6, 166.1.

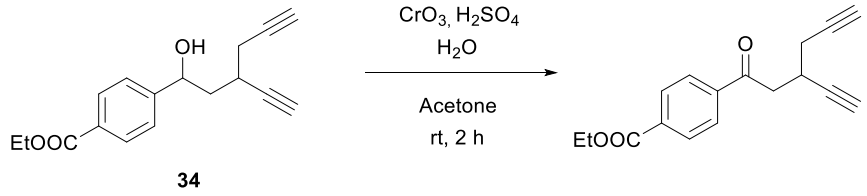


Ethyl 4-(3-ethynyl-1-hydroxyhex-5-yn-1-yl)benzoate (34)

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 NH_4Cl solution and the mixture was extracted with EtOAc. The combined organic extract was washed with brine, and then dried over $MgSO_4$. 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.

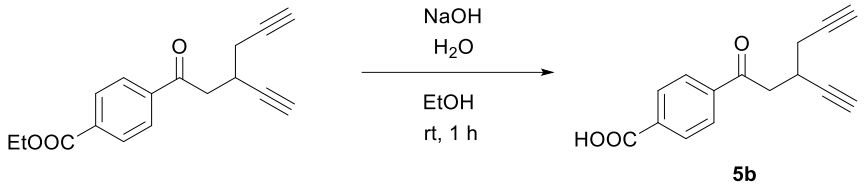


Ethyl 4-(3-ethynylhex-5-ynoyl)benzoate

To a solution of chromium (VI) oxide (0.21 g, 2.2 mmol, 3.0 eq) in H_2O (1 ml) was added conc. H_2SO_4 (80 μl, 1.4 mmol, 2.0 eq) in H_2O (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 $MgSO_4$, 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.



5b

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 $MgSO_4$. This was evaporated under reduced pressure and white solid **5b** (0.077 g, 0.32 mmol, 95% yield) was obtained, mp 164–166 °C.

^{1}H 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).

^{13}C 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 $C_{15}H_{12}O_3 \cdot n$EtOH (n = 0.32); C,73.65; H, 5.51. Found: C, 73.64; H, 5.50.

TOF-ESI-MS m/z: calcd for $C_{15}H_{13}O_3^+$ 241.0865. Found: 241.0866 ($[M + H]^+$).

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 acetopheone

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 = 1[36], 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.

No.	*φ*X174RFI plasmid DNA (μl)	TE[a] (μl)	Dye[b] (μl)
(1)	4.0	96.0	20.0

[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.

No.	*φ*X174RFI plasmid DNA (μl)	10×H buffer[a] (μl)	*Xho* I (μl)	mQ (μl)
(2)	6.0	1.5	0.5	7.0

[a] 10×Concentrated high salt concentration buffer (TAKARA BIO INC., Japan) (500 mM Tris-HCl (pH 7.5), 100 mM $MgCl_2$, 10 mM dithiothreitol (DTT) and 1000 mM NaCl)

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

No.	Comounds	Solvent
(3)	-	TE
(4)	-	Acetonitrile
(5)	**5a**	Acetonitrile
(6)	**5b**	Acetonitrile
(7)	**5b**	TE
(8)	Acetophenone	Acetonitrile
(9)	Acetophenone	TE

Table 11 Cleavage conditions of supercoiled *φ*X174RFI plasmid DNA by *Xho* I (restriction enzyme, cleavage site = 1) at 37 °C for 0–60 min (see **5.3**, Fig. 35).

Run	DNA solution	Time (min)
0	(1) 6.0 μl	0
1	(2) 15 μl	5
2	(2) 15 μl	10
3	(2) 15 μl	20
4	(2) 15 μl	60

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).

Run	DNA solution	Compound solution[a]	TE	UV-irradiation (h)
(a)-0	(1) 6.0 μl	-	-	0
(a)-1	(1) 6.0 μl	(3) 6.0 μl	12.0 μl	1
(a)-2	(1) 6.0 μl	(3) 6.0 μl	12.0 μl	2
(a)-3	(1) 6.0 μl	(3) 6.0 μl	12.0 μl	4
(a)-4	(1) 6.0 μl	(3) 6.0 μl	12.0 μl	8
(b)-0	(1) 6.0 μl	-	-	0
(b)-1	(1) 6.0 μl	(4) 6.0 μl	12.0 μl	1
(b)-2	(1) 6.0 μl	(4) 6.0 μl	12.0 μl	2
(b)-3	(1) 6.0 μl	(4) 6.0 μl	12.0 μl	4
(b)-4	(1) 6.0 μl	(4) 6.0 μl	12.0 μl	8
(b)-5	(1) 6.0 μl	(5) 6.0 μl	12.0 μl	1
(b)-6	(1) 6.0 μl	(5) 6.0 μl	12.0 μl	2
(b)-7	(1) 6.0 μl	(5) 6.0 μl	12.0 μl	4
(b)-8	(1) 6.0 μl	(5) 6.0 μl	12.0 μl	8
(c)-0	(1) 6.0 μl	-	-	0
(c)-1	(1) 6.0 μl	(6) 6.0 μl	12.0 μl	1
(c)-2	(1) 6.0 μl	(6) 6.0 μl	12.0 μl	2
(c)-3	(1) 6.0 μl	(6) 6.0 μl	12.0 μl	4
(c)-4	(1) 6.0 μl	(6) 6.0 μl	12.0 μl	8
(c)-5	(1) 6.0 μl	(7) 6.0 μl	12.0 μl	1
(c)-6	(1) 6.0 μl	(7) 6.0 μl	12.0 μl	2
(c)-7	(1) 6.0 μl	(7) 6.0 μl	12.0 μl	4
(c)-8	(1) 6.0 μl	(7) 6.0 μl	12.0 μl	8
(d)-0	(1) 6.0 μl	-	-	0
(d)-1	(1) 6.0 μl	(8) 6.0 μl	12.0 μl	1
(d)-2	(1) 6.0 μl	(8) 6.0 μl	12.0 μl	2
(d)-3	(1) 6.0 μl	(8) 6.0 μl	12.0 μl	4
(d)-4	(1) 6.0 μl	(8) 6.0 μl	12.0 μl	8
(d)-5	(1) 6.0 μl	(9) 6.0 μl	12.0 μl	1
(d)-6	(1) 6.0 μl	(9) 6.0 μl	12.0 μl	2
(d)-7	(1) 6.0 μl	(9) 6.0 μl	12.0 μl	4
(d)-8	(1) 6.0 μl	(9) 6.0 μl	12.0 μl	8

[a] The final concentration of compound solutions (**5** or acetophenone) was 1.25 mM.

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27. ^{1}H NMR (**19a**) δ: 3.70 (s, 6H, 2 × O*Me*), 3.89 (s, 6H, 2 × O*Me*), 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, O*Me*), 3.89 (s, 3H, O*Me*), 6.42 (d, 2H, J = 9.2 Hz, *Ph*OMe, ring A), 6.70 (d, 2H, J = 8.7 Hz, *Ph*Cl, ring A), 6.74 (d, 2H, J = 9.2 Hz, *Ph*OMe, ring A), 6.83 (d, J = 8.7 Hz, *Ph*Cl, ring A). Due to the complexity and overlapping of each signal, the rest of the signals could not be identified. See Fig. 21.

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33. ^{1}H NMR ((*E*)-enediyne **30a**, acetonitrile-d_3) δ: 2.92 (s, 2H) 5.92 (s, 2H). ^{1}H NMR ((*Z*)-enediyne **30a**, acetonitrile-d_3) δ: 3.08 (s, 2H), 5.71 (s, 2H). ^{1}H NMR ((*E*)-enediyne **30a**, cyclohexane-d_{12}) δ: 3.53 (s, 2H) 6.11 (s, 2H). ^{1}H NMR ((*Z*)-enediyne **30a**, cyclohexane-d_{12}) δ: 3.69 (s, 2H), 5.99 (s, 2H).

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