Received: 28 February 2011,

Revised: 10 May 2011,

(wileyonlinelibrary.com) DOI 10.1002/poc.1898

Published online in Wiley Online Library: 18 July 2011

# Generation and reactivities of triplet diphenylcarbenes protected by bulky groups as *para* substituents

Katsuyuki Hirai<sup>a</sup>\*, Keiji Hatanaka<sup>b</sup>, Tsuyoshi Yamaguchi<sup>b</sup>, Akiko Miyajima<sup>b</sup>, Toshikazu Kitagawa<sup>b</sup>\* and Hideo Tomioka<sup>c,d</sup>

Accepted: 16 May 2011,

Bis(2,6-dimethylphenyl)diazomethane (1b-N<sub>2</sub>) having 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-di(phenylethynyl)-9anthrylethynyl groups at the 4,4'-positions was synthesized. Triplet diphenylcarbene <sup>3</sup>1b was generated by photolysis of the precursor and was characterized by electron spin resonance and UV-Vis spectroscopies at low temperature, and laser flash photolysis techniques at room temperature. Irradiation of 1b-N2 in a 2-methyltetrahydrofuran matrix at 77 K gave electron spin resonance signals ascribable to triplet carbene <sup>3</sup>1b. UV-Vis spectra of <sup>3</sup>1b were obtained by irradiating 1b-N<sub>2</sub> under identical conditions. The laser flash photolysis of 1b-N<sub>2</sub> in a degassed benzene solution gave transient absorption bands ascribable to <sup>3</sup>1b, which decayed in a first-order fashion with a rate constant of 0.46 s<sup>-1</sup>. The carbene was shown to be less reactive than the triplet bis(2,6-dimethylphenyl)carbene (<sup>3</sup>1a) having 9-anthrylethynyl groups at the 4,4'-positions, which decayed in a second-order fashion with a rate constant  $(2 k/\epsilon l)$  of  $0.69 s^{-1}$ . Triplet carbene <sup>3</sup>1b was trapped by oxygen to generate ketone oxide 1b-O with a rate constant of  $1.9 \times 10^7 M^{-1} s^{-1}$  and also by 1,4-cyclohexadiene with a rate constant of  $1.2 M^{-1} s^{-1}$ . Similar studies with diphenyldiazomethanes (1c-N2 and 1d-N2) having bulky substituents, 10-(4-tert-butyl-2,6-dimethylphenyl)-2,7-bis[3,5-di(phenylethynyl)phenylethynyl]-9-anthrylethynyl and 10-(4-tert-butyl-2,6-dimethylphenyl)-2,7-bis(9triptycylethynyl)-9-anthrylethynyl groups at the 4,4'-positions respectively indicated that the corresponding triplet carbenes <sup>3</sup>1c and <sup>3</sup>1 d were more persistent than <sup>3</sup>1b. Steady-state irradiation of 1a-N<sub>2</sub>, 1c-N<sub>2</sub>, and 1 d-N<sub>2</sub> in degassed benzene afforded tetraarylethenes 2a, 2c, and 2d in 83, 50, and 51% yield, respectively. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: diazo compound; kinetics; steric protection; triplet carbene

### INTRODUCTION

Triplet carbenes are highly reactive organic radicals that are also notoriously difficult to stabilize.<sup>[1–7]</sup> To isolate the triplet carbene with its electronic integrity (one centered diradical) intact, steric protection is the ideal method. According to this concept, attempts to stabilize triplet diphenylcarbenes by introducing various substituents at the *ortho* positions have been made.<sup>[8–11]</sup> For example, triplet bis(2-bromo-4-phenyl-6-trifluoromethylphenyl) carbene was shown to have a half-life of 40 min in solution at room temperature,<sup>[12]</sup> about 10 orders of magnitude greater than the 'parent' diphenylcarbene. The strategy, however, encounters a limitation when bulky substituents are employed as protecting groups. Persistent triplet diphenylcarbenes are generated by photolysis of the nitrogen precursors, diphenyldiazomethanes, which are almost always synthesized from the corresponding benzhydrols via the carbamate pathway.[12-20] However, synthesis of a carbamate derivative having substituents bulkier than a trifluoromethyl group at the ortho position was not successful. That is, generation of a diphenylcarbene having the bulkier substituents is difficult synthetically.

Is it possible to introduce a substituent at the *para* position that is sufficiently bulky to extend around the carbene carbon? To confirm the possibility of steric protection of carbene by *para* substituent, triplet 2,6-dimethylphenylcarbene having 2,7-bis

[3,5-di(phenylethynyl)phenylethynyl]-9-anthrylethynyl group at the *para* position was optimized by DFT calculations.<sup>[21,22]</sup> The optimized geometry at B3LYP/3-21G\* level of theory indicated that the two terminal benzene rings are located at both sides of the carbene carbon and that even a hydrogen on the phenyl group that is closest to the carbene carbon is 603 pm away from the carbon (Fig. 1). Therefore, the *para* substituent may block the

\* Correspondence to: K. Hirai, Instrumental Analysis Facilities, Social Cooperation Research Center, Mie University, Tsu, Mie 514–8507, Japan. E-mail: hirai@chem.mie-u.ac.jp

a K. Hirai

Instrumental Analysis Facilities, Social Cooperation Research Center, Mie University, Tsu, Mie 514–8507, Japan

b K. Hatanaka, T. Yamaguchi, A. Miyajima, T. Kitagawa Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514–8507, Japan

c H. Tomioka

#### d H. Tomioka

Nagoya Industrial Science Research Institute, Department of Research, Nagoya, Aichi 464–0819, Japan

Department of Applied Chemistry, Aichi Institute of Technology, Toyota, Aichi 470–0392, Japan



**Figure 1.** Optimized structure of triplet 4-{2,7-bis[3,5-di(phenylethynyl) phenylethynyl]-9-anthrylethynyl}-2,6-dimethylphenylcarbene at B3LYP/ 3-21G\* level of theory

carbene center from external reagents without intramolecular reaction with carbene.

In benzene, most sterically hindered diphenylcarbenes decay by dimerization at the carbene center to give either tetraphenylethenes<sup>[13,14,23]</sup> or phenanthrenes, which are formed by photocyclization of the ethenes followed by dehalogenation.<sup>[17,18,20]</sup> If dimerization can be prevented by the *para* substituent, the carbene might become more persistent.

We found that a diphenyldiazomethane derivative, synthesized as a precursor to a persistent triplet carbene, itself is also stable and hence can be further modified at the *para* position with the diazo group intact. For instance, (2,4,6-tribromophenyl) (2,6-dibromo-4-*tert*-butylphenyl)diazomethane survives under Sonogashira coupling reaction conditions and undergoes substitution with trimethylsilylacetylene at the *para* positions, leading to (2,6-dibromo-4-trimethylsilylethynylphenyl)(2,6-dibromo-4-*tert*-butylphenyl)diazomethane.<sup>[24]</sup> That is, it may be relatively easy to introduce bulky substituents at the *para* positions of sterically hindered diphenyldiazomethanes.

To test the validity of this idea, we attempted to protect diphenylcarbene using the *para* substituents. We employed the following approach to introduce bulky substituents to diphenyldiazomethane. First, an anthracene ring was selected as a base where steric protectors are put on. To prevent unfavorable reactions on the anthracene base because of a leak of the unpaired electrons of the carbene, 4-*tert*-butyl-2,6dimethylphenyl group was introduced at the 10-position of the base. Protecting groups were introduced at the 2,7-positions of the base using coupling reaction. Second, to the base having the protectors in place, an ethynyl linker was introduced at the 9-position. Finally, the resulting bases were introduced at the *para* positions of diphenyldiazomethane.

Structures projected into both sides from the center of an airport building are called a 'wing'. Because the substituents at 2,7-positions of the anthracene in Fig. 1 are similar in appearance to the wing, we also refer to protecting groups at these positions as 'wings'. As 'wing,' phenylethynyl (PE), 3,5-bis(phenylethynyl)phenylethynyl (BPEPE), and triptycylethynyl (TrpE) groups were chosen for the synthetic ease. We wish to report here that triplet diphenylcarbenes <sup>3</sup>**1b**, <sup>3</sup>**1c**, and <sup>3</sup>**1d** with 'wings,' generated from the precursor diazo compounds, were more persistent than the triplet diphenylcarbene without 'wings,' <sup>3</sup>**1a** (Scheme 1).

### **RESULTS AND DISCUSSION**

#### Preparation of para substituents

The *para* substituents having steric protectors were prepared according to the reaction procedures outlined in Schemes 2 and 3. Thus, treatment of 3,5-diiodo-1-trimethylsilylethynylbenzene (**3**)<sup>[25]</sup> with phenylacetylene in the presence of  $(Ph_3P)_2PdCl_2$  and Cul in NEt<sub>3</sub> at 40 °C for one day, followed by gel permeation chromatography (GPC) gave 3,5-bis(phenylethynyl)-1-trimethylsilylethynylbenzene (**4**) in 93% yield. The deprotection of the trimethylsilyl group in **4** proceeded smoothly by treating it with K<sub>2</sub>CO<sub>3</sub> in MeOH-tetrahydrofuran (THF) at room temperature. 10-(4-*tert*-Butyl-2,6-dimethylphenyl)-2,7-bis[3,5-bis(phenylethynyl)-



Scheme 1. Generation of bis[4-(9-anthrylenthnyl)-2,6-dimethylphenyl]carbenes 1



Scheme 2. Preparation of 3,5-bis(phenylethynyl)phenylacetylene 5

phenylethynyl]-9-bromoanthracene (**10**) was synthesized by Sonogashira cross coupling reaction of tribromide  ${\bf 6}^{[26]}$  and 3 equiv

of the phenylacetylene **5** in 68% yield. Sonogashira coupling of **10** with an excess of trimethylsilylacetylene followed by deprotection of the trimethylsilyl group afforded the ethynyl derivative **12** in moderate yield. Ethynylanthracenes **9** and **16** were synthesized in a similar manner from **6**, and the corresponding acetylenes in 20 and 29% total yields, respectively (Scheme 3).

### Coupling of diazomethane with para substituents

Sonogashira coupling of bis(4-iodo-2,6-dimethylphenyl)diazomethane (**17**)<sup>[27]</sup> with 2.8 equiv of ethynylanthracene **12** resulted in the formation of a desired diazo compound **1c**-N<sub>2</sub> as red crystals in 85% yield under mild conditions (Scheme 4). Diazomethanes **1a**, **b**, and **d** were obtained by similar procedures in 40–75% yields. All of the diazomethanes were purified by repeated chromatography on a gel permeation column. The characterization of diazo compounds **1a-d** was mainly based on <sup>1</sup>H-



(i) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, Et<sub>3</sub>N, rt. (ii) K<sub>2</sub>CO<sub>3</sub>, MeOH-THF, rt. (iii) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, Et<sub>3</sub>N-THF, 40 °C. (iv) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, <sup>*i*</sup><sub>Pr<sub>2</sub>NH-benzene, rt. (v) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, Et<sub>3</sub>N-benzene, rt.</sub>

Scheme 3. Preparation of para substituents 9, 12, and 16



(i) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, Et<sub>3</sub>N, 40 °C. (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, <sup>*i*</sup>Pr<sub>2</sub>NHbenzene, 40 °C. (iii) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, Cul, <sup>*i*</sup>Pr<sub>2</sub>NH-benzene, 40 °C.

Scheme 4. Preparation of diazo compounds 1-N<sub>2</sub>

NMR and infrared (IR) spectroscopy. For example, the <sup>1</sup>H NMR spectrum of **1c** showed three singlet peaks at 1.47, 1.79 and 2.29 ppm, which were assigned to *tert*-butyl, inner and outer methyl groups, respectively, and five aromatic singlet peaks in the ratio of 1:2:1:1:1 at 7.32, 7.29, 7.48, 7.61, and 8.93 ppm, in agreement with the calculated values. In the IR spectrum a strong and sharp band assigned to a diazo group was observed at 2046 cm<sup>-1</sup>.

#### **Spectroscopic studies**

#### Electron spin resonance studies in rigid matrix at low temperature

Irradiation ( $\lambda$  > 300 nm) of diazomethane **1b**-N<sub>2</sub> having PE groups in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to electron spin resonance (ESR) signals with a fine structure pattern typical of an unoriented triplet species (Fig. 2(a)). <sup>[28,29]</sup> The signals were analyzed in terms of zero-field splitting (zfs) parameters to be D = 0.273 cm<sup>-1</sup> and E = 0.0075 cm<sup>-1</sup> (E/D = 0.0269),



**Figure 2.** (a) ESR spectrum obtained by irradiation of diazo compound 1b-N<sub>2</sub> in 2-methyltetrahydrofuran at 77 K. The same sample measured at 77 K after thawing to 90 K (b), 150 K (c), and 190 K (d)

unequivocally showing the formation of triplet carbene <sup>3</sup>1b (Table 1). The ESR signals were stable at this temperature. The thermal stability of the triplet carbenes could be estimated by thawing the matrix containing triplet carbenes gradually and recooling to 77 K to measure the signals. This procedure can compensate for a weakening of signals because of the Currie law.<sup>[30-32]</sup> When the sample was warmed up to 90 K, a new set of triplet signals with zfs parameters of  $D = 0.221 \text{ cm}^{-1}$  and  $E = 0.0010 \text{ cm}^{-1}$  (E/D = 0.0046) appeared at the expense of the original signals (Fig. 2(b), Table 1). ESR signals of sterically hindered diarylcarbenes often become sharper when the measurements are made after the sample is warmed and recooled. This is partly because as the temperature is raised, the matrix softens and allows the carbene to assume the most stable geometry rather than several slightly distorted orientations dictated by the trapping of the precursor in the frozen matrix.<sup>[33–38]</sup> The signal intensity decreased gradually as the sample was warmed up to 150 K (Fig. 2(c)) and the signal disappeared at 190 K irreversibly (Fig. 2(d)).

Similar irradiation of the other diazomethanes  $1a-N_2$ ,  $1c-N_2$ , and  $1 d-N_2$  in 2-MTHF glass at 77 K also gave rise to ESR spectra characteristic of randomly oriented triplet carbenes (i.e.,  ${}^{3}1a$ ,  ${}^{3}1c$ , and  ${}^{3}1d$ ) (Figs. S1–S3 and Table 1).<sup>[28,29]</sup> When the matrices were warmed up, signals of 1a, 1c, and 1 d started to decrease at 140, 170, and 160 K, respectively.

The *D* and *E* values of the carbenes **1a-d** are significantly smaller than those of triplet bis(2,6-dimethylphenyl)carbene  $(D = 0.377 \text{ cm}^{-1} \text{ and } E = 0.0101 \text{ cm}^{-1})$ ,<sup>[39]</sup> indicating that the two unpaired electrons of the triplet carbenes **1a-d** are delocalized to the anthracene rings. The zfs parameters of **1a-d** are almost constant regardless of not only the presence or absence of the 'wings' but also the types of the 'wings,' suggesting that the unpaired electrons are delocalized only to the anthracene rings. However, the temperature  $(T_d)$  at which the ESR signals because <sup>3</sup>1 started to disappear became higher in the other 1a < 1b < 1**d** < 1c. The different tendencies observed for zfs and  $T_{\rm d}$  can be explained in terms of the steric effect of the 'wings'. We have reported that the triplet diphenvlcarbenes decay in 2-MTHF at low temperature by abstracting a hydrogen from the solvent to form the corresponding diphenylmethyl radicals.[12,19,20] Thus, large 'wings' would retard the approach of 2-MTHF to the carbene center, resulting in the high  $T_{ds}$ .

#### UV-Vis studies in rigid matrices at low temperature

Photolysis ( $\lambda > 300 \text{ nm}$ ) of **1b**-N<sub>2</sub> in a 2-MTHF matrix at 77 K resulted in the appearance of new bands at the expense of the original absorption because of the diazo compound (Fig. 3 (Ab)). The new bands consisted of two identifiable features, strong and sharp maxima at 340 and 353 nm and a broad band from 530 to 590 nm. These features, that is, strong absorption bands in the UV region and a broad band in the visible region, are usually present in the spectra of triplet diphenylcarbenes.<sup>[28,29]</sup> The glassy solution exhibited no change for hours when kept at 77 K, but disappeared irreversibly when it was allowed to warm to room temperature and was then cooled to 77 K. On the basis of these observations, coupled with the ESR data, the absorption spectrum can be safely assigned to triplet carbene <sup>3</sup>**1b**.

The thermal stability is then estimated by raising the sample temperature in 10 K increments to the desired temperature, allowing it to stand for 15 min, and measuring the absorption

| Table 1. ESR and UV-Vis spectroscopic data of carbenes 1  |                        |                        |                                      |        |                           |                        |                              |                           |  |  |
|---|------------------------|------------------------|--------------------------------------|--------|---------------------------|------------------------|------------------------------|---------------------------|--|--|
| Carbenes  | Temp. <sup>a</sup> (K) | D  (cm <sup>-1</sup> ) | ESR   <i>E</i>   (cm <sup>-1</sup> ) | E / D  | <i>Т</i> <sub>d</sub> (К) | Temp. <sup>a</sup> (K) | UV–Vis $\lambda_{\max}$ (nm) | <i>Т</i> <sub>d</sub> (К) |  |  |
| 1a  | 77                     | 0.224                  | 0.0030                               | 0.0134 | 140                       | 77                     | 342, 437, 480, 516           | 140                       |  |  |
|   | 90→77 <sup>b</sup>     | 0.224                  | 0.0018                               | 0.0080 |                           | 100                    | 341, 437, 484, 517           |                           |  |  |
| 1b  | 77                     | 0.273                  | 0.0075                               | 0.0269 | 150                       | 77                     | 340, 353, 413, 562           | 140                       |  |  |
|   | 90→77 <sup>b</sup>     | 0.221                  | 0.0010                               | 0.0046 |                           | 90                     | 344, 352, 392, 421, 531, 572 |                           |  |  |
| 1c  | 77                     | 0.234                  | 0.0013                               | 0.0054 | 170                       | 77                     | 345, 360, 395, 421, 568      | 170                       |  |  |
|   | 90→77 <sup>b</sup>     | 0.234                  | 0.0017                               | 0.0074 |                           | 100                    | 348, 360, 426, 535, 576      |                           |  |  |
| 1d  | 77                     | 0.280                  | 0.0084                               | 0.0300 | 160                       | 77                     | 313, 328, 341, 385, 512, 549 | 160                       |  |  |
|   | 90→77 <sup>b</sup>     | 0.223                  | 0.0015                               | 0.0067 |                           | 100                    | 312, 331, 344, 391, 521, 559 |                           |  |  |
| <sup>a</sup> Temperature at which the spectrum was measured.<br><sup>b</sup> Measured at 77 K after warming up to 90 K. |                        |                        |                                      |        |                           |                        |                              |                           |  |  |

bands. When the matrix was warmed gradually to 90 K, the broad absorption band at 562 nm changed rather dramatically to a sharp and strong band with its maximum shifting to a longer wavelength at 572 nm, while the strong band at 353 nm shifted very little (Fig. 3(Ac), Table 1). Similar changes in the UV–Vis spectra upon thawing the matrix were also observed for sterically hindered diarylcarbenes and are generally interpreted in terms of geometrical changes of the carbenes.<sup>[28,29,33–38]</sup> The bands started to decay at 140 K and disappeared irreversibly at 230 K (Fig. 3(B)). The decay-initiating temperature was almost consistent with that observed in the ESR study.

Similar spectra were obtained in the photolysis of other diazo precursors  $1-N_2$  in 2-MTHF at 77 K (Figs. S4–S6). The absorption maxima observed for <sup>3</sup>1 and the temperature ( $T_d$ ) at which the



**Figure 3.** UV–Vis spectra obtained by irradiation of diazo compound **1b**-N<sub>2</sub>. (A) (a) Spectrum of **1b**-N<sub>2</sub> in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ( $\lambda > 300$  nm). (c) The same sample after thawing to 90 K. (B) UV–Vis spectral changes measured at 90, 140, 230, and 260 K, respectively

absorption maxima because of <sup>3</sup>1 started to disappear are summarized in Table 1. The  $T_{ds}$  are almost the same as those determined by ESR and the general trends are similar. Thus, a rather high  $T_d$  is noted for 1c (170 K) and 1d (160 K) compared with the other carbenes (1a and 1b) (Table 1), which is attributed to effective steric protection by the BPEPE and TrpE groups at the *para* positions.

#### Laser flash photolysis studies in solution at room temperature

For quantitative evaluation of the stabilities of the present carbenes, the lifetimes were estimated in a degassed benzene at room temperature, in which we have measured the lifetime of a series of other sterically congested diarylcarbenes.<sup>[8–10]</sup> Laser flash photolysis (LFP) of **1b**-N<sub>2</sub> ( $5.0 \times 10^{-5}$  M) in degassed benzene at room temperature with a 10 ns, 100 mJ, 308 nm pulse from a XeCl laser produced a transient species showing a maximum at 560 nm, which appeared coincidentally with the pulse (Fig. 4). The maximum of the band was shifted to a shorter wavelength than that observed in the photolysis of **1b**-N<sub>2</sub> in 2-MTHF at 77 K. However, the transient band was markedly quenched by oxygen to give the corresponding diaryl ketone oxide (*vide infra*), and hence we assigned the band to <sup>3</sup>**1b**. The absorption bands decayed very slowly, and did not disappear completely even



**Figure 4.** Transient absorption spectrum obtained in the LFP of diazo compound 1b-N<sub>2</sub> in degassed benzene at room temperature with a 308 nm excimer laser recorded after 10  $\mu$ s. The inset shows the time course of the absorption at 550 nm

after 5 s under the employed conditions. The decay was found to be a first-order process ( $k = 0.46 \text{ s}^{-1}$ ) with a lifetime ( $\tau$ ) of 2.2 s (Table 2).

Photolysis of the other diazomethanes 1a-N<sub>2</sub>, 1c-N<sub>2</sub>, and 1 d-N<sub>2</sub> was carried out under similar conditions. LFP of **1a**-N<sub>2</sub> produced a transient band at 510 nm, which was assigned to <sup>3</sup>1a (Fig. S7). The spectrum of <sup>3</sup>1a decayed with a second-order kinetics  $(2 k/\epsilon l = 0.69 s^{-1})$  and the approximate half-life  $(t_{1/2})$  was estimated to be 0.41 s. Because the lifetimes of <sup>3</sup>1c and <sup>3</sup>1d were too long to monitor by the LFP technique, a conventional UV-Vis spectroscopic method was more conveniently employed in these cases. Laser photolysis of these diazomethanes also produced transient bands at 550 and 552 nm, respectively, which were assigned to <sup>3</sup>1c and <sup>3</sup>1d, respectively (Figs. S8 and S9). The absorption band of <sup>3</sup>1c decayed slightly more slowly than that of <sup>3</sup>1b. The decay was also found to be a first-order process  $(k=0.40 \text{ s}^{-1}, \tau=2.5 \text{ s})$ . The lifetimes of <sup>3</sup>**1b** and <sup>3</sup>**1c** were five times longer than the half-life of <sup>3</sup>1a. Triplet carbene <sup>3</sup>1d having triptycyl groups also decayed in a first-order fashion. The decay  $(k=0.10 \text{ s}^{-1}, \tau = 10 \text{ s})$  was the slowest among the four carbenes studied (Table 2). The parent **1a** decayed in a second-order fashion, while the carbenes having the 'wings' (i.e., 1b, 1c, and 1d) exhibited in first-order kinetics, which suggests that the PhE, BPEPE, and TrpE groups on the para substituents prevented the dimerization of the carbenes under the LFP conditions.

The rate constants of the decays cannot be compared directly because of the differing reaction order of the decays of <sup>3</sup>1a and the others. The rate constant of the reactions of triplet carbenes with a typical triplet guencher can be employed as a more guantitative scale of reactivity. In general, carbenes with triplet ground states are readily trapped with oxygen or a good hydrogen donor such as 1.4-cyclohexadiene (CHD).<sup>[40]</sup> Therefore, the rate constants for the trapping by  $O_2$  ( $k_{O2}$ ) and CHD ( $k_{CHD}$ ) serve as more quantitative scales for the estimation of the reactivities of triplet carbenes. The LFP of **1b**-N<sub>2</sub> in O<sub>2</sub> saturated benzene resulted in a dramatic decrease in the lifetime of <sup>3</sup>1b and a concurrent appearance of a new broad absorption band at approximately 470 nm. The spent solution was found to contain the corresponding benzophenone. It is well-documented<sup>[41-48]</sup> that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which show a broad absorption band from 360 to 480 nm (Scheme 5). Thus, our observations can be interpreted as indicating that the transient absorption guenched by oxygen is due to <sup>3</sup>1b. The rate of increase in the band at 470 nm is practically the same as the rate of decrease of the peak because of <sup>3</sup>1b, showing that <sup>3</sup>1b is quenched with oxygen to form ketone oxide **1b**-O<sub>2</sub>. The rate constant  $(k_{O2})$  for the quenching of <sup>3</sup>**1b** by oxygen is determined to be  $1.9 \times 10^7 \,\mathrm{M^{-1} \, s^{-1}}$  from a plot of the observed pseudo-first-order growth rate of **1b**-O<sub>2</sub> as a function of  $[O_2]$  (Fig. 5, Table 2). This is one order of magnitude smaller than that observed with triplet bis(2,6-dimethylphenyl)carbene  $(k_{O2} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ .<sup>[39]</sup> The rate constants  $k_{O2}$  of the other carbenes (**1a**, **b**, and **d**) were measured and are listed in Table 2, which indicate that there is not much difference in the  $k_{O2}$ .

When a degassed benzene solution of 1b-N<sub>2</sub> containing 1,4-cyclohexadiene (CHD) was excited, the decay of <sup>3</sup>1b was accelerated compared with that in the absence of the diene. It is now well documented that triplet diarylcarbenes, generated in good hydrogen donor solvents, undergo a hydrogen abstraction leading to the corresponding radical species (1-H) (Scheme 5).<sup>[40,49-58]</sup> The excellent hydrogen donor properties of CHD have been well recognized.<sup>[59]</sup> In the photolysis of diazomethane 1b-N<sub>2</sub>, because the absorption band of the radical **1b**-H overlapped the tail band of the carbene <sup>3</sup>**1b**, the growth curve of the radical could not be observed precisely. However, a plot of the observed pseudo-first-order rate constants of the decay of <sup>3</sup>1b monitored at 550 nm against the diene concentrations [CHD] is linear (Fig. 6), and the slope of this plot yields the absolute rate constant for the reaction of <sup>3</sup>1b with the diene,  $k_{CHD} = 1.2 \text{ M}^{-1} \text{ s}^{-1}$ , which is approximately 1/80 of that observed with triplet bis(2,6-dimethylphenyl)carbene ( $k_{CHD} = 94 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>[39]</sup> The decay rates of the other carbenes 1a, 1c, and 1d were also accelerated in the presence of the diene (Table 2), indicating that these carbenes were also guenched by the diene. The data indicate that the rate constants of the bimolecular reactions of  ${}^{3}$ **1b**,  ${}^{3}$ **1c**, and  ${}^{3}$ **1d** with the diene (1.2, 1.5, and 7.3 M<sup>-1</sup> s<sup>-1</sup>, respectively) are approximately one order smaller than  $k_{CHD}$  of  $^{3}$ **1a** (48 M<sup>-1</sup> s<sup>-1</sup>).

Although carbenes **1a–d** showed similar bimolecular reaction rate constants ( $k_{O2}$ ) with oxygen, the rate constants with CHD ( $k_{CHD}$ ) varied on the order of **1a** = **1b** < **1d** < < **1c**. The difference in the trend of  $k_{O2}$  and  $k_{CHD}$  is explained in terms of the reactivities and sizes of oxygen and the diene. Because oxygen is much more reactive than the diene toward triplet carbenes, differences among the rate constants  $k_{O2}$  are negligibly small compared with  $k_{CHD}$ . In addition, an oxygen molecule is too small to be blocked by the 'wings'. However, because 1,4-cyclohexadiene is evidently a larger molecule than oxygen, the 'wings' can protect the carbenic carbon from the diene. On the basis of the observed values of  $k_{CHD}$ , the TrpE group is a less efficient protecting group than the PE and BPEPE groups. This may be explained in terms of poor electronic stabilization of the carbenes by the TrpE groups.

### **Product analysis studies**

Most of the sterically congested triplet diphenylcarbenes decay mainly by undergoing dimerization at the carbene center to give

| Table 2. Kinetic data of carbenes 1 |                      |                   |                          |   |  |  |  |  |  |
|-------------------------------------|----------------------|-------------------|--------------------------|---|--|--|--|--|--|
| Carbenes                            | k (s <sup>-1</sup> ) | τ (s)             | $k_{O2} (M^{-1} s^{-1})$ | $k_{\rm CHD} \ ({\rm M}^{-1} \ {\rm s}^{-1})$ |  |  |  |  |  |
| 1a                                  | 0.69 <sup>a</sup>    | 0.41 <sup>b</sup> | $2.4 \times 10^{7}$      | 48  |  |  |  |  |  |
| 1b                                  | 0.46                 | 2.2               | $1.9 \times 10^{7}$      | 1.2   |  |  |  |  |  |
| 1c                                  | 0.40                 | 2.5               | $2.0 \times 10^{7}$      | 1.5   |  |  |  |  |  |
| 1d                                  | 0.10                 | 10                | $1.4 \times 10^{7}$      | 7.3   |  |  |  |  |  |
| a7k/sl                              |                      |                   |                          |   |  |  |  |  |  |
| <sup>b</sup> t <sub>1/2.</sub>      |                      |                   |                          |   |  |  |  |  |  |



Scheme 5. Photolysis of diazo compounds  $1-N_2$  in the presence of carbene quenchers



0.8

0.6

0.4

k<sub>obs</sub> / s<sup>-1</sup>

**Figure 6.** A plot of the decay rate constants of <sup>3</sup>**1b** monitored at 550 nm as a function of the concentration of 1,4-cyclohexadiene

tetraarylethenes as the main product, when generated in degassed benzene at room temperature in the absence of appropriate carbene quenchers (Scheme 6).<sup>[13,14,23]</sup> To determine the decay pathway of the present carbenes, we carried out product analysis of the photolysis of **1a**-N<sub>2</sub>, **1c**-N<sub>2</sub>, and **1d**-N<sub>2</sub> in degassed benzene at room temperature.<sup>[60]</sup>

Photolysis (>300 nm) of 1d-N<sub>2</sub> (5.0 mg) in degassed benzened<sub>6</sub> (0.5 mL) in a sealed NMR tube at 25 °C was monitored by <sup>1</sup>H-NMR spectroscopy. The irradiation for 6 min gave new peaks at 9.71, 5.09, 1.93, 1.65, 1.51, and 1.46 ppm along with weak complex peaks at the expense of the signals of 1d-N<sub>2</sub>. The <sup>1</sup>H-NMR spectrum of a fraction obtained by recycled GPC of the photoproducts showed the dimerization product, tetraarylethene 2d (yellow crystals in 51% yield) (Scheme 6). In the photolysis, it is reasonable that ethene 2d was formed as a result of dimerization at the carbene center. Similar irradiations of 1a-N<sub>2</sub> and 1c-N<sub>2</sub> also afforded the corresponding ethenes 2a and 2c in 83 and 50% yields, respectively. It is rather surprising that even heavily congested carbenes 1c and 1d gave a considerable amount of dimers.

This result seems inconsistent with the fact that in the LFP experiments **1c** and **1d** decayed with first-order kinetics in

degassed benzene. The dimerization of carbenes with huge 'wings' should be very slow compared with **1a**. Furthermore, the concentration of **1** ( $\sim 10^{-5}$  M) in the LFP measurements is three orders of magnitude lower than in the product study ( $\sim 10^{-2}$  M). Although highly pure special grade benzene was used in the LFP study, the observed first-order-decays in the LFP could be because of the quenching of carbenes **1c** and **1d** with a residual amount of impurities in the solvent. Alternatively, in the LFP conditions, the carbenes may decay by an intramolecular C–H insertion to the *ortho* methyl groups.

To check the reaction mode of 1, we also carried out an analysis of the photoproducts from 1d-N<sub>2</sub>, which generates the longest-lived carbene 1d, in the presence of the carbene guenchers, oxygen and 1,4-cyclohexadiene. Photolysis (>300 nm) of 1d-N<sub>2</sub> in an oxygen-saturated benzene solution afforded diaryl ketone 1d-O in 89% yield (Scheme 5). Formation of the ketone suggests that the intermediate observed in the oxygen-saturated solution in the LFP experiments is a ketone oxide  $1-O_2$ . On the other hand, irradiation (>300 nm) of 1d-N<sub>2</sub> in degassed benzene containing 1,4-cyclohexadiene afforded diarylmethane 1d-H<sub>2</sub> in 75% yield, as a result of the double-hydrogen abstraction reaction of triplet <sup>3</sup>1d from the diene (Scheme 5). A diphenyl ketone and a diphenylmethane are well-known products frequently obtained by reactions of triplet diphenylcarbene with O2 and 1,4-cyclohexadiene, respectively.



**Figure 5.** A plot of the growth rate constants of the diaryl ketone oxide **1b**-O<sub>2</sub> monitored at 470 nm as a function of the concentration of oxygen



Scheme 6. Photolysis of diazo compounds  $1\text{-}N_2$  in degassed benzene at 25  $^\circ\text{C}$ 

### CONCLUSION

In the present study, diphenyldiazomethanes  $1-N_2$  having either the PE, BPEPE, or TrpE groups on the *para* substituents were synthesized, and triplet carbenes generated by their photolysis were characterized by ESR and UV-Vis spectroscopies at low temperatures. Triplet carbenes <sup>3</sup>1b, <sup>3</sup>1c, and <sup>3</sup>1d decayed in degassed benzene at room temperature in a first-order fashion with rate constants of 0.46, 0.49, and 0.10 s<sup>-1</sup>, respectively, which were smaller than that of the parent <sup>3</sup>1a. The rate constants of the reaction of <sup>3</sup>1b, <sup>3</sup>1c, and <sup>3</sup>1d with oxygen were similar to <sup>3</sup>1a having no 'wings'. On the other hand, the rate constants with 1,4-cyclohexadiene were greatly changed depending on the type of the 'wings'. The major photoproducts from  $1c-N_2$  and 1d-N<sub>2</sub> in degassed benzene were tetraarylethenes 2c and 2d, respectively, in contrast to the kinetics of decay derived from LFP experiments. The results of the present study demonstrated that the introduction of large 'wings' on the para substituents is a promising new strategy for the kinetic stabilization of diphenylcarbene.

### **EXPERIMENTAL SECTION**

### **General information**

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were determined with a FT NMR spectrometer (JNM-AL300, JEOL) in CDCl<sub>3</sub> with Me<sub>4</sub>Si as an internal reference. IR spectra were measured either with films on a NaCl plate (oils and semisolids) with KBr pellets (solids). IR spectra were recorded on an IR spectrometer (FT/IR400, JASCO) and UV-Vis spectra were recorded on a UV-Vis spectrometer (V-560, JASCO or MultiSpec-1500, Shimadzu). The mass spectra were recorded on an EI mass spectrometer (JMS-600H, JEOL) or a MALDI-TOF mass spectrometer (Voyager DE-Pro, Applied Biosystems). Thin layer chromatography (TLC) was performed using Merck silica gel 60 F<sub>254</sub> or Merck aluminum oxide 60 PF<sub>254</sub> on a glass plate (Type E) for diazo compounds. Column chromatography was performed using silica gel (63-210 µm) or neutral alumina (Act. I, inactivated with 5% water) for diazo compounds. Recycle GPC was undertaken with a HPLC pump (PU-2086, JASCO) with a UV-Vis detector (UV-2070, JASCO) using a GPC column (H-2001, 20mm× 50 cm, Shodex).

### Preparation of 3,5-bis(phenylethynyl)-1-trimethylsilylethynylbenzene (4)

To a mixture of 3,5-diiodo-1-trimethylsilylethynylbenzene (3)<sup>[25]</sup> (231 mg, 0.54 mmol), bis(triphenylphosphine)palladium(II) dichloride (8.1 mg, 11 µmol), and copper(I) iodide (4.0 mg, 21 µmol) in anhydrous triethylamine (6 mL) was added phenylacetylene (155 µL, 1.63 mmol) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen and the mixture was stirred for 3 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) at 0°C and then purified by preparative TLC (silica gel, hexane) to give 3,5-bis(phenylethynyl)-1-rimethylsilylethynylbenzene (4) as a yellow viscous oil (190 mg, 93%): IR (NaCl, neat, cm<sup>-1</sup>) 2214 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR  $(300 \text{ MHz}, \text{ CDCl}_3, \text{ ppm}) \delta$  7.62 (t, J = 1.6 Hz, 1 H), 7.58 (d, J = 1.6 Hz, 2H), 7.53–7.50 (m, 4H), 7.36–7.34 (m, 6H), 0.26 (s, 9H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 134.5, 134.4, 131.8, 128.7, 128.5, 124.1, 124.0, 122.9, 103.4, 95.8, 90.6, 87.9, 0.0; EI-MS (m/z) 374 (M<sup>+</sup>, 57), 359 (100), 309 (15), 180 (18); HRMS calcd for  $\rm C_{27}H_{22}Si$  374.1491, found m/z 374.1464.

### Preparation of 1-ethynyl-3,5-bis(phenylethynyl)benzene (5)

A mixture of **4** (190 mg, 0.51 mmol), K<sub>2</sub>CO<sub>3</sub> (245 mg, 1.78 mmol), MeOH (6 mL), and THF (6 mL) was stirred at room temperature for 30 min. After workup of the reaction mixture, the crude product was purified by GPC (5 cycles, chloroform, monitored at 260 nm) to afford 1-ethynyl-3,5-bis(phenylethynyl)benzene (**5**) as yellow crystals (145 mg, 95%): mp 96.1–96.7 °C; IR (KBr, cm<sup>-1</sup>) 3303 (s,  $v_{C=\underline{C-H}}$ ), 2211 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.67 (t, J=1.6 Hz, 1H), 7.60 (d, J=1.5 Hz, 2H), 7.54–7.51 (m, 4H), 7.38–7.36 (m, 6H), 3.11 (s, 1H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  134.6, 134.5, 131.7, 128.7, 128.4, 124.1, 122.8, 122.7, 90.6, 87.6, 82.0, 78.3; El-MS (m/z) 302 (M<sup>+</sup>, 100), 300 (22); HRMS calcd for C<sub>24</sub>H<sub>14</sub> 302.1096, found m/z 302.1134.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis (phenylethynyl)-9-bromoanthracene (7)

To a mixture of 10-(4-tert-butyl-2,6-dimethylphenyl)-2,7,9-tribromoanthracene ( $\mathbf{6}$ )<sup>[26]</sup> (30 mg, 52 µmol), bis(triphenylphosphine) palladium(II) dichloride (0.5 mg, 0.7 µmol), and copper(I) iodide (0.4 mg, 2.0 µmol) in anhydrous triethylamine (0.5 mL) was added phenylacetylene (23 µL, 210 µmol) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was stirred at 35 °C for 13 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform at 0°C) and then purified by preparative TLC (silica gel, hexane) to aive 10-(4-tert-butyl-2,6-dimethylphenyl)-2,7-bis(phenylethynyl)-9-bromoanthracene (7) as yellow crystals (11 mg, 35%): mp 278.9–281.9 °C; IR (KBr, cm<sup>-1</sup>) 2210 (w, v<sub>C=C</sub>); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 8.87 (s, 2H), 7.62–7.61 (m, 4H), 7.43–7.42 (m, 6H), 7.40-7.37 (m, 4H), 7.25 (s, 2H), 1.74 (s, 6H), 1.45 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.0, 136.9, 136.8, 136.1, 133.3, 131.8, 130.6, 130.1, 128.6, 128.5, 128.4, 126.8, 124.7, 123.1, 122.3, 121.8, 91.4, 89.8, 34.5, 31.5, 20.4; EI-MS (m/z) 618 (M + 2, 99), 616 (M<sup>+</sup>, 100), 522 (23), 368 (22), 236 (27); HRMS calcd for C<sub>42</sub>H<sub>33</sub>Br 616.1765, found *m/z* 616.1667.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis (phenylethynyl)-9-trimethylsilylethynylanthracene (8)

To a mixture of 9-bromoanthracene 7 (10.6 mg, 17 µmol), bis (triphenylphosphine)palladium(II) dichloride (0.5 mg, 0.7 µmol), and copper(I) iodide (0.2 mg, 1.0 µmol) in anhydrous triethylamine (0.5 mL) was added trimethylsilylacetylene (24 µL, 170 µmol) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was stirred at 50 °C for 16 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide, chloroform) and then purified by GPC (14 cycles, chloroform, monitored at 300 nm) to give 10-(4-tert-butyl-2,6-dimethylphenyl)-2,7-bis(phenylethynyl)-9trimethylsilylethynylanthracene (8) as yellow crystals (8.5 mg, 79%): mp 262.5–264.6 °C; IR (KBr, cm<sup>-1</sup>) 2208 (w, v<sub>C=C</sub>), 2140 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.82 (s, 2H), 7.62– 7.60 (m, 4H), 7.42-7.37 (m, 10H), 7.25 (s, 2H), 1.73 (s, 6H), 1.44 (s, 9H), 0.50 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 150.9, 137.8, 136.8, 133.4, 132.7, 131.8, 131.0, 129.0, 128.5, 128.4, 126.7, 124.6, 123.2, 121.6, 116.7, 108.0, 101.3, 91.1, 90.2, 34.5, 31.5, 20.3, 0.3; EI-MS (*m/z*) 634 (M<sup>+</sup>, 100), 618 (5.6), 309 (5.4), 288 (8.6); HRMS calcd for C<sub>47</sub>H<sub>42</sub>Si 634.3056, found *m/z* 634.3107.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-9-ethynyl-2,7-bis(phenylethynyl)anthracene (9)

A mixture of **8** (7.0 mg, 11 μmol), K<sub>2</sub>CO<sub>3</sub> (5.2 mg, 38 μmol), MeOH (0.5 mL), and THF (0.5 mL) was stirred at room temperature for 25 min. After evaporation of the solvent, the residue was extracted with chloroform. The organic layer was washed with brine and dried over anhydrous Na2SO4, and the solvent was removed under reduced pressure. The crude product was purified by GPC (6 cycles, chloroform, monitored at 300 nm) to afford 10-(4*tert*-butyl-2,6-dimethylphenyl)-9-ethynyl-2,7-bis(phenylethynyl) anthracene (9) as yellow crystals (4.4 mg, 71%): mp 286.3–289.1 °C; IR (NaCl, neat cm<sup>-1</sup>) 3301 (s,  $v_{C=C-H}$ ), 2207 (w,  $v_{C=C}$ ), 2139 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 8.85 (s, 2H), 7.62–7.61 (m, 4H), 7.44-7.37 (m, 10H), 7.24 (s, 2H), 4.14 (s, 1H), 1.74 (s, 6H), 1.45 (s, 9H);  $^{13}$  C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  151.0, 138.2, 136.8, 133.3, 133.0, 131.8, 131.0, 129.0, 128.6, 128.5, 128.4, 126.8, 124.6, 123.1, 121.8, 115.6, 91.2, 90.0, 89.6, 80.0, 34.5, 31.5, 20.3; EI-MS (*m/z*) 562 (M<sup>+</sup>, 48), 561 (100), 368 (10), 273 (11), 83 (11); HRMS calcd for C<sub>44</sub>H<sub>34</sub> 562.2660, found *m/z* 562.2678.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis [3,5-bis(phenylethynyl)phenylethynyl]-9-bromoanthracene (10)

To a mixture of tribromoanthracene 6 (92 mg, 0.16 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 14 µmol), and copper(I) iodide (5.0 mg, 26 µmol) in anhydrous triethylamine (10 mL) was added a solution of 5 (145 mg, 0.48 mmol) in anhydrous tetrahydrofuran (7 mL) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was stirred at 40 °C for 13 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) and then purified by preparative GPC (6 cycles, chloroform, monitored at 300 nm) to give bromoanthracene **10** as yellow crystals (110 mg, 68%): mp 157.9–160.7 °C; IR (KBr, cm<sup>-1</sup>) 2252 (m,  $v_{C=C}$ ), 2211 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.83 (s, 2H), 7.74 (d, J = 1.7 Hz, 4H), 7.69 (t, J = 1.7 Hz, 2H), 7.56-7.53 (m, 8H), 7.48-7.42 (m, 4H), 7.39–7.36 (m, 12H), 7.27 (s, 2H), 1.76 (s, 6H), 1.46 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.1, 137.0, 136.8, 134.3, 134.2, 133.2, 132.2, 131.7, 130.6, 130.3, 128.6, 128.5, 128.4, 127.0, 124.7, 124.2, 123.8, 122.8, 122.1, 121.9, 90.9, 90.7, 89.9, 87.8, 34.5, 31.5, 20.4; MALDI-TOF-MS calcd for C74H49Br 1016.30, found m/z 1016.41.

# Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis [3,5-bis(phenylethynyl)phenylethynyl]-9-trimethylsilylethy-nylanthracene (11)

To a mixture of the 9-bromoanthracene **10** (58 mg, 57  $\mu$ mol), bis (triphenylphosphine)palladium(II) dichloride (7.0 mg, 6.0  $\mu$ mol), copper(I) iodide (1.0 mg, 5.0  $\mu$ mol), anhydrous diisopropylamine (3 mL), and anhydrous benzene (3 mL) was added trimethylsilylacetylene (10  $\mu$ L, 0.14 mmo I) at room temperature under an argon atmosphere, and the mixture was refluxed for 15 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide, chloroform) and then purified by GPC (7 cycles, chloroform, monitored at 300 nm) to give

trimethylsilylethylylanthracene **11** as yellow crystals (50 mg, 61%): mp 164.4–165.0 °C; IR (KBr, cm<sup>-1</sup>) 2212 (w,  $v_{C=C}$ ), 2142 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.83 (s, 2H), 7.73 (d, J = 1.5 Hz, 4H), 7.69 (t, J = 1.5 Hz, 2H), 7.57–7.54 (m, 8H), 7.44-7.43 (m, 4H), 7.39–7.36 (m, 12H), 7.26 (s, 2H), 1.74 (s, 6H), 1.45 (s, 9H), 0.53 (s, 9H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  150.7, 137.6, 133.9, 133.8, 133.0, 132.3, 131.4, 131.0, 128.8, 128.3, 128.1, 126.5, 124.4, 123.8, 123.7, 122.5, 120.9, 116.7, 108.0, 100.8, 90.9, 90.3, 89.3, 87.5, 34.2, 3und *m/z* 1034.57.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis [3,5-bis(phenylethynyl)phenylethynyl]-9-ethynylanthracene (12)

A mixture of **11** (22 mg, 21 µmol), K<sub>2</sub>CO<sub>3</sub> (7.3 mg, 53 µmol), MeOH (2 mL), and THF (2 mL) was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was extracted with chloroform. The organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified by GPC (5 cycles, chloroform, monitored at 300 nm) to afford ethynylanthracene 12 as yellow crystals (16 mg, 79%): mp 159.8-161.6 °C; IR (KBr, cm<sup>-1</sup>) 3303 (w, v<sub>C=C-H</sub>), 2252 (m, v<sub>C=C</sub>), 2213 (w, v<sub>C=C</sub>); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.87 (s, 2H), 7.74 (d, J=1.5 Hz, 4H), 7.68 (t, J = 1.5 Hz, 2H), 7.56–7.53 (m, 8H), 7.47 (d, J = 9.0 Hz, 2H), 7.43 (dd, J=9.0, 1.3 Hz, 2H), 7.39-7.36 (m, 8H), 7.35 (s, 4H), 7.27 (s, 2H), 4.16 (s, 1H), 1.76 (s, 6H), 1.45 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.1, 138.3, 136.8, 134.3, 134.2, 133.2, 133.0, 131.7, 131.1, 129.1, 128.6, 128.4, 128.3, 126.9, 124.7, 124.1, 123.9, 122.8, 121.4, 115.9, 91.2, 90.6, 89.9, 89.7, 87.8, 79.9, 34.5, 31.5, 20.3; MALDI-TOF-MS calcd for C76H50 962.39, found m/z 962.52.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis (9-triptycylethynyl)-9-bromoanthracene (14)

To a mixture of tribromoanthracene 6 (131 mg, 0.23 mmol), 9-ethynyltriptycene (13)<sup>[61]</sup> (152 mg, 0.60 mmol), bis(triphenylphosphine)palladium(II) dichloride (16 mg, 23 µmol), and copper (I) iodide (4.3 mg, 23 µmol) were added anhydrous triethylamine (13 mL) and anhydrous benzene (13 mL) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was refluxed for 16 h. After evaporation of the solvent, the residue was passed through a short column (silica gel, chloroform) and then purified by preparative GPC (6 cycles, chloroform, monitored at 300 nm) to give bromoanthracene 14 as yellow crystals (152 mg, 71%): mp 307.3-309.4 °C; IR (KBr, cm<sup>-1</sup>) 2232 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 9.14 (s, 2H), 7.91–7.88 (m, 6H), 7.75(dd, J=1.5, 9.0 Hz, 2H), 7.62 (d, J=9.0 Hz, 2H), 7.43 (dd, J=6.8, 1.3 Hz, 6H), 7.32 (s, 2H), 7.14-7.04 (m, 12H), 5.48 (s, 2H), 1.85 (s, 6H), 1.48 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.2, 144.4, 144.3, 137.3, 136.9, 133.2, 132.3, 130.8, 130.5, 129.2, 127.2, 125.8, 125.3, 124.8, 123.5, 122.6, 122.1, 93.1, 86.1, 53.7, 53.3, 34.6, 31.5, 29.7, 20.4; MALDI-TOF-MS calcd for  $C_{70}H_{49}Br$  968.30, found m/z 968.33.

# Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis (9-triptycylethynyl)-9-trimethylsilylethynylanthracene (15)

To a mixture of 9-bromoanthracene **14** (78 mg, 84  $\mu$ mol), bis (triphenylphosphine)palladium(II) dichloride (12 mg, 17  $\mu$ mol),

copper(I) iodide (3.2 mg, 17 µmol), anhydrous triethylamine (15 mL), and anhydrous benzene (15 mL) was added trimethylsilylacetylene (60 µL, 424 µmol) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was refluxed for 19 h. After evaporation of the solvent, the residue was passed through a short column (silica gel, chloroform) and then purified by GPC (17 cycles, chloroform, monitored at 300 nm) to give trimethylsilylethylylanthracene 15 as yellow crystals (45 mg, 52%): mp 318.3–322.0 °C; IR (KBr, cm<sup>-1</sup>) 2142 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 9.16 (s, 2H), 7.92-7.89 (m, 6H), 7.74 (dd, J=9.0, 1.4 Hz, 2H), 7.60 (d, J=9.0 Hz, 2H), 7.44-7.42 (m, 6H), 7.32 (s, 2H), 7.13-7.03 (m, 12H), 5.47 (s, 2H), 1.83 (s, 6H), 1.48 (s, 9H), 0.51 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.1, 144.4, 144.4, 138.1, 136.8, 133.3, 132.8, 131.8, 129.3, 128.9, 127.1, 125.8, 125.2, 124.7, 123.5, 122.6, 122.4, 116.9, 108.3, 101.2, 93.3, 85.6, 53.7, 53.3, 34.6, 31.5, 20.3, 0.22; MALDI-TOF-MS calcd for C<sub>75</sub>H<sub>58</sub>Si 986.43, found m/z 986.45.

### Preparation of 10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis (9-triptycylethynyl)-9-ethynylanthracene (16)

A mixture of **15** (84 mg, 81 µmol), K<sub>2</sub>CO<sub>3</sub> (39 mg, 282 µmol), MeOH (30 mL), and THF (40 mL) was stirred at room temperature for 4 h. After evaporation of the solvent, the residue was extracted with chloroform. The organic laver was washed with water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified by GPC (3 cycles, chloroform, monitored at 300 nm) to afford ethynylanthracene 16 as yellow crystals (16 mg, 79%): mp 142.2–144.5 °C; IR (KBr, cm<sup>-1</sup>) 3300 (w,  $v_{C=C-H}$ ), 2239 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 9.17 (s, 2H), 7.91-7.89 (m, 6H), 7.76 (dd, J=9.0, 1.7 Hz, 2H), 7.63 (d, J=8.5 Hz, 2H), 7.43-7.41 (m, 6H), 7.33 (s, 2H), 7.13-7.03 (m, 12H), 5.47 (s, 2H), 4.25 (s, 1H), 1.85 (s, 6H), 1.48 (s, 9H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.1, 144.4, 144.3, 138.5, 136.8, 133.2, 133.1, 131.1, 129.3, 128.2, 127.2, 125.8, 125.2, 124.7, 123.5, 122.6, 121.6, 115.9, 93.2, 90.1, 85.9, 79.9, 53.7, 53.2, 34.6, 31.5, 20.4; MALDI-TOF-MS calcd for C76H50 914.39, found m/z 914.42.

# Preparation of bis[4-(9-anthrylethynyl)-2,6-dimethylphenyl] diazomethane (1a- $N_2$ )

To a mixture of bis(4-iodo-2,6-dimethylphenyl)diazomethane **17**<sup>[27]</sup> (25 mg, 50 µmol), 9-ethynylanthracene<sup>[62]</sup> (31 mg, 153 µmol), bis (triphenylphosphine)palladium(II) dichloride (4.0 mg, 5.7 µmol), and copper(I) iodide (2.0 mg, 11 µmol) was added anhydrous triethylamine (1 mL) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was stirred at 40 °C for 15 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) at 0°C and then purified by GPC (12 cycles, chloroform, monitored at 300 nm) to give diazomethane **1a**-N<sub>2</sub> as red crystals (17 mg, 52%): mp 120.3–123.8 °C (dec.); IR (KBr, cm<sup>-1</sup>) 2194 (w,  $v_{C=C}$ ); 2041 (s, v<sub>C=N2</sub>); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 8.66 (d, J=8.6 Hz, 4H), 8.43 (s, 2H), 8.02 (d, J=8.6 Hz, 4H), 7.64-7.58 (m, 4H), 7.54–7.49 (m, 8H), 2.23 (s, 12H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 137.4, 132.6, 132.1, 131.2, 129.7, 128.7, 127.7, 126.8, 126.6, 125.7.

### Preparation of bis{4-[10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis(phenylethynyl)-9-anthrylethynyl]-2,6-dimethylphenyl}diazomethane (1b-N<sub>2</sub>)

To a mixture of diazomethane **17** (6.5 mg, 13 µmol), 10-(4-tertbutyl-2,6-dimethylphenyl)-9-ethynyl-2,7-bis(phenylethynyl)anthracene (9) (14 mg, 25 µmol), bis(triphenylphosphine)palladium (II) dichloride (0.8 mg, 1.2 µmol), and copper(I) iodide (0.4 mg, 2.4 µmol) was added anhydrous triethylamine (1 mL) at room temperature under an atmosphere of a 1:1 mixture of nitrogen and hydrogen, and the mixture was stirred at 40 °C for 11 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) at 0 °C and then purified by GPC (9 cycles, chloroform, monitored at 300 nm) to give diazomethane 1b-N<sub>2</sub> as a red semisolid (7.2 mg, 40%): IR (NaCl, neat, cm<sup>-1</sup>) 2204 ( $v_{C=C}$ ), 2041 (s, v<sub>C=N2</sub>); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 8.91 (s, 4H), 7.63-7.61 (m, 12H), 7.45 (m, 4H), 7.38-7.34 (m, 16H), 7.25 (s, 4H), 2.30 (s, 12H), 1.77 (s, 12H), 1.46 (s, 18H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 150.9, 137.6, 137.5, 136.8, 133.4, 132.5, 132.3, 131.7, 130.8, 130.0, 129.1, 128.6, 128.5, 128.4, 126.8, 124.6, 123.2, 122.2, 121.5, 117.0, 101.9, 91.2, 90.2, 86.5, 59.5, 34.5, 31.5, 20.9, 20.4.

### Preparation of bis[4-(10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis(3,5-bis(phenylethynyl)phenylethynyl)-9-anthrylethynyl)-2,6-dimethylphenyl]diazomethane (1c-N<sub>2</sub>)

To a mixture of diazomethane 17 (3.0 mg, 6.0 µmol), anthracene 12 (16.3 mg, 17.0 µmol), tetrakis(triphenylphosphine)palladium (II) (2.0 mg, 2.0 µmol), and copper(I) iodide (1.0 mg, 5.0 µmol) were added anhydrous diisopropylamine (1 mL) and anhydrous benzene (1 mL) at room temperature under an argon atmosphere, and the mixture was stirred at 40 °C for 20 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) at 0 °C and then purified by GPC (13 cycles, chloroform, monitored at 300 nm) to give diazomethane 1c-N<sub>2</sub> as red crystals (11 mg, 85%): mp 126.5–130.2 °C (dec.); IR (KBr, cm<sup>-1</sup>) 2212 (w,  $v_{C=C}$ ), 2046 (s,  $v_{C=N2}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.93 (s, 4H), 7.72 (d, J = 1.7 Hz, 8H), 7.64 (d, J = 1.6 Hz, 4H), 7.61 (s, 4H), 7.53-7.43 (m, 24H), 7.35-7.32 (m, 24H), 7.29 (s, 4H), 2.29 (s, 12H), 1.79 (s, 12H), 1.47 (s, 18H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.0, 137.7, 137.6, 136.9, 134.2, 134.1, 133.4, 132.4, 132.3, 131.7, 131.3, 130.1, 129.3, 128.7, 128.4, 128.3, 127.0, 124.7, 124.2, 123.9, 122.8, 122.2, 121.1, 117.3, 91.4, 90.7, 89.8, 89.7, 87.8, 86.3, 59.6, 34.6, 31.6, 20.9, 20.4.

### Preparation of bis[4-(10-(4-*tert*-butyl-2,6-dimethylphenyl)-2,7-bis(9-triptycylethynyl)-9-anthrylethynyl)-2,6-dimethylphenyl]diazomethane (1d-N<sub>2</sub>)

To a mixture of **17** (13 mg, 25 µmol), anthracene **16** (69 mg, 75 µmol), bis(triphenylphosphine)palladium(II) dichloride (5.3 mg, 7.5 µmol), and copper(I) iodide (2.9 mg, 15 µmol) was added anhydrous diisopropylamine (9 mL) and anhydrous benzene (9 mL) at room temperature under an argon atmosphere, and the mixture was stirred at 40 °C for 22 h. After evaporation of the solvent, the residue was passed through a short column (aluminum oxide deactivated with 5% water, chloroform) at 0 °C and then purified by GPC (7 cycles, chloroform, monitored at 320 nm) to give diazomethane **1d**-N<sub>2</sub> as orange crystals (39 mg, 75%): mp 121.3–123.6 °C (dec.); IR (KBr, cm<sup>-1</sup>) 2187 (w,  $v_{C=C}$ ), 2042 (s,  $v_{C=N2}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  9.24–9.23 (m,

4H), 7.92–7.89 (m, 12H), 7.76 (dd, J=9.0, 1.7 Hz, 4H), 7.63 (d, J=9.0 Hz, 4H), 7.59 (s, 4H), 7.39–7.36 (m, 12H), 7.33 (s, 4H), 7.08–6.98 (m, 24H), 5.43 (s, 4H), 2.13 (s, 12H), 1.87 (s, 12H), 1.49 (s, 18H); <sup>13</sup> C-NMR (75.5 MHz, CDCI<sub>3</sub>, ppm)  $\delta$  151.1, 144.5, 144.4, 137.9, 137.6, 136.9, 133.4, 132.5, 132.2, 131.6, 130.1, 129.5, 129.0, 127.2, 125.8, 125.2, 124.7, 123.5, 122.5, 122.2, 121.3, 117.3, 102.5, 93.4, 86.6, 85.9, 59.5, 53.8, 53.3, 34.6, 31.6, 20.9, 20.4.

### **Product analysis**

Photolysis ( $\lambda$  > 300 nm) of **1a**-N<sub>2</sub>, **1c**-N<sub>2</sub>, and **1d**-N<sub>2</sub> (5.0 mg) in degassed benzene-*d*<sub>6</sub> (0.5 mL) at 25 °C gave tetraarylethenes **2a**, **2c**, and **2 d**, respectively.

**2a**: yellow crystals (4.1 mg, 83%); mp 389.0–390.0 °C; IR (KBr, cm<sup>-1</sup>) 2357 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.66 (d, J=8.3 Hz, 8H), 8.42 (s, 4H), 8.01 (d, J=7.7 Hz, 8H), 7.61–7.56 (m, 8H), 7.52–7.47 (m, 8H), 7.37–7.33 (m, 8H), 2.21 (s, 12H), 1.99 (s, 12H); MALDI-TOF-MS calcd for C<sub>98</sub>H<sub>68</sub> 1244.53, found *m/z* 1244.52.

**2c**: yellow crystals (2.4 mg, 50%); mp 328.0–331.0 °C; IR (KBr, cm<sup>-1</sup>) 2357 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm)  $\delta$  9.38 (s, 8H), 7.65 (d, J=9.0 Hz, 16H), 1.98 (s, 12H), 1.87 (s, 12H), 1.74 (s, 12H), 1.44 (s, 36H); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.77 (s, 8H), 7.53 (d, J=1.5 Hz, 16H), 7.40 (s, 4H), 7.36 (s, 4H), 2.14 (s, 12H), 1.91 (s, 12H), 1.83 (s, 24H), 1.47 (s, 36H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  136.9, 134.0, 131.7, 128.5, 128.4, 126.5, 124.7, 123.9, 122.8, 120.9, 91.4, 90.5, 89.7, 88.0, 34.6, 31.6, 26.6, 30.0, 20.5; MALDI-TOF-MS calcd for C<sub>338</sub>H<sub>228</sub> 4285.78, found *m/z* 4285.40.

**2d**: yellow crystals (2.5 mg, 51%); mp 234.8–240.1 °C; IR (KBr, cm<sup>-1</sup>) 1605 (w,  $v_{C=C}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  9.18 (s, 8H), 7.83–7.80 (m, 24H), 7.76 (dd, *J*=9.0, 1.5 Hz, 8H), 7.57 (d, *J*=9.0 Hz, 8H), 7.36 (s, 4H), 7.32 (s, 4H), 7.29–7.23 (m, 48H), 6.96–6.89 (m, 48H), 5.31 (s, 8H), 1.92 (s, 12H), 1.82 (s, 24H), 1.71 (s, 12H), 1.46 (s, 36H); <sup>13</sup> C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  149.3, 130.9, 126.5, 126.3, 125.9, 125.5, 124.9, 121.3, 121.1, 120.7, 120.6, 118.9, 118.6, 117.1, 115.9, 115.5, 115.1, 114.1, 113.9, 113.6, 113.4, 112.3, 93.5, 90.1, 84.0, 82.6, 58.3, 58.0, 43.0, 40.6, 33.3, 31.7, 15.4; MALDI-TOF-MS calcd for C<sub>322</sub>H<sub>228</sub> 4093.84, found *m/z* 4093.81.

Photolysis ( $\lambda$  > 300 nm) of **1d**-N<sub>2</sub> (5.0 mg, 2.4 µmol) in oxygensaturated benzene (1.0 mL) at 25 °C gave the ketone **1d**-O: yellow crystals (4.4 mg, 89%); IR (KBr, cm<sup>-1</sup>) 1662 ( $v_{C=O}$ ); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  9.22 (s, 4H), 7.90 (m, 12H), 7.77 (dd, J=8.9, 1.6 Hz, 4H), 7.64 (d, J=9.0 Hz, 4H), 7.56 (s, 4H), 7.39–7.36 (m, 12H), 7.33 (s, 4H), 7.07–6.98 (m, 24H), 5.43 (s, 4H), 2.19 (s, 12H), 1.87 (s, 12H), 1.49 (s, 18H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  200.3, 151.1, 144.4, 144.3, 140.0, 137.2, 136.8, 133.3, 132.6, 132.2, 131.6, 131.5, 129.4, 129.1, 127.3, 125.8, 125.2, 124.8, 123.5, 122.5, 122.2, 121.5, 116.7, 101.9, 93.3, 87.5, 86.0, 53.7, 53.3, 34.6, 31.5, 20.9, 20.4; MALDI-TOF-MS calcd for C<sub>161</sub>H<sub>114</sub>O 2062.89, found *m/z* 2062.93.

Photolysis (λ > 300 nm) of **1d**-N<sub>2</sub> (5.0 mg, 2.4 μmol) in degassed benzene (0.8 mL) in the presence of 1,4-cyclohexadiene (0.2 mL, 2.1 mmol) gave the double-hydrogen abstraction product **1d**-H<sub>2</sub>: yellow crystals (3.4 mg, 75%); mp 153.0–156.0 °C; IR (KBr, cm<sup>-1</sup>) 2355 (w,  $v_{C=C}$ );<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 9.25 (s, 4H), 7.91–7.88 (m, 12H), 7.76 (dd, *J* = 1.4, 8.7 Hz, 4H), 7.62 (d, *J* = 9.0 Hz, 4H), 7.50 (s, 4H), 7.37 (dd, *J* = 6.7, 1.6 Hz, 12H), 7.33 (s, 4H), 7.07–6.98 (m, 24H), 5.43 (s, 4H), 4.13 (s, 2H), 2.15 (s, 12H), 1.87 (s, 12H), 1.56 (s, 18H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>, ppm) δ 151.0, 144.41, 144.36, 137.5, 137.4, 136.9, 133.4, 132.4, 131.8, 131.7, 129.4, 129.0, 127.2, 127.1, 125.7, 125.2, 124.7, 123.5, 122.5, 121.2, 120.6, 114.8, 99.8, 93.4, 85.7, 85.5, 53.7, 53.3, 34.6, 31.5, 21.0, 20.4; MALDI-TOF-MS calcd for C<sub>161</sub>H<sub>116</sub> 2048.91, found *m/z* 2048.93.

### Electron spin resonance measurements

The diazo compound was dissolved in 2-methyltetrahydrofuran  $(1.5 \times 10^{-2} \text{ M})$ , and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission ESR cavity at 77 K and irradiated with a 500 W Xe lamp (Wacom) through a filter ( $\lambda > 300 \text{ nm}$ ). ESR spectra were measured on an ESR spectrometer (JES TE 200, X-band microwave unit, 100 kHz field modulation, JEOL). The signal positions were read by the use of a gaussmeter. The temperature was controlled by a 9650 microprocessor-based digital temperature indicator/controller, which provided the measurements accuracy within ± 0.1 K and the control ability within ± 0.2 K. Errors in the measurements of component amplitudes did not exceed 5%; the accuracy of the resonance fields determination was within ± 0.5 mT.

### Low-temperature UV-Vis spectra

UV–Vis spectra at 77 K were obtained by using a variabletemperature liquid-nitrogen cryostat (DN 1704, Oxford Inst.) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF ( $1.5 \times 10^{-3}$  M), placed in a long-necked quartz cuvette of 1-mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near  $10^{-5}$  Torr. The cuvette was flame-sealed under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Wacom 500 W Xe lamp through a filter ( $\lambda > 300$  nm), and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with a intelligent temperature controller (ITC 4, Oxford Inst.).

### Laser flash photolysis

All flash photolysis measurements were made on a flash spectrometer (TSP-601, Unisoku). The excitation source for the laser flash photolysis was a XeCl excimer laser (LEXTRA50, Lambda Physik). A 150 W xenon short arc lamp (L2195, Hamamatsu) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a photomultiplier tube (R2949, Hamamatsu) through a linear image sensor (S3701-512Q, 512 photodiodes used, Hamamatsu). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through a digital synchroscope (DS-8631, Iwatsu), which was interfaced to a computer (PC-9821 RA266, NEC).

A sample was placed in a long-necked Pyrex tube that had a sidearm connected to a quartz fluorescence cuvette and was degassed using a minimum of five freeze-degas-thaw cycles at a pressure near  $10^{-5}$  Torr immediately prior to being flashed. The sample system was sealed, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light.

### Acknowledgement

We are grateful to the Ministry of Education, Culture, Sports, Science and Technology of Japan for support of this work through a Grant-in-Aid for Scientific Research (No. 21550044 and 21106013).

### REFFERENCES

- [1] M. Regitz, Angew. Chem. Int. Ed. Engl. **1991**, 30, 674–676.
- [2] R. Dagani, Chem. Eng. News 1991, Jan 28, 19; 1994, May 2, 20.
- [3] C. Heinemann, T. Müller, Y. Apeloig, H. Schwartz, J. Am. Chem. Soc. 1996, 118, 2023–2038.
- [4] C. Boehme, G. Frenking, J. Am. Chem. Soc. 1996, 118, 2039-2046.
- [5] C. Wentrup, Science 2001, 292, 1846–1847.
- [6] H. D. Roth, Nature 2001, 412, 598-601.
- [7] W. Kirmse, Angew. Chem. Int. Ed. 2003, 42, 2117-2119.
- [8] H. Tomioka, Acc. Chem. Res. **1997**, 30, 315–321.
- [9] H. Tomioka, in: Advances in Carbene Chemistry (Ed: U. Brinker), Vol. 2, JAI Press, Greenwich CT, 1998, 175–214.
- [10] H. Tomioka, in: Carbene Chemistry (Ed: G. Bertrand), Fontis Media S. A., Lausanne, 2002, 103–152.
- [11] K. Hirai, T. Itoh, H. Tomioka, Chem. Rev. 2009, 109, 3275-3332.
- [12] T. Itoh, Y. Nakata, K. Hirai, H. Tomioka, J. Am. Chem. Soc. 2006, 128,
- 957–967. [13] H. E. Zimmerman, D. H. Paskovich, J. Am. Chem. Soc. **1964**, 86, 2149–2160.
- [14] H. Tomioka, K. Hirai, T. Nakayama, J. Am. Chem. Soc. 1993, 115, 1285–1289.
- [15] H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, K. Itoh, J. Am. Chem. Soc. **1995**, 117, 6376–6377.
- [16] H. Tomioka, M. Hattori, K. Hirai, J. Am. Chem. Soc. 1996, 118, 8723–8724.
- [17] H. Tomioka, T. Watanabe, M. Hattori, N. Nomura, K. Hirai, J. Am. Chem. Soc. 2002, 124, 474–482.
- [18] K. Hirai, T. likubo, H. Tomioka, Chem. Lett. 2002, 31, 1226–1227.
- [19] K. Hirai, H. Tomioka, J. Am. Chem. Soc. 1999, 121, 10213-10214.
- [20] K. Hirai, K. Bessho, T. Kitagawa, H. Tomioka, J. Phys. Org. Chem. 2010, 23, 347–356.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian-03. Gaussian, Inc., Wallingford CT, 2003.
- [22] Triplet diphenylcarbene having bulky substituents at 4,4'-positions could not be optimized because of a large number of the atoms in the carbene.
- [23] H. Tomioka, H. Okada, T. Watanabe, K. Banno, K. Komatsu, K. Hirai, J. Am. Chem. Soc. **1997**, 119, 1582–1593.
- [24] H. Tomioka, M. Hattori, K. Hirai, K. Sato, D. Shiomi, T. Takui, K. Itoh, J. Am. Chem. Soc. **1998**, 120, 1106–1107.

- [25] O. Mongin, C. Papamicaeel, N. Hoyler, A. Gossauer, J. Org. Chem. 1998, 63, 5568–5580.
- [26] T. Itoh, M. Matsuno, E. Kamiya, K. Hirai, H. Tomioka, J. Am. Chem. Soc. 2005, 127, 7078–7093.
- [27] K. Hirai, E. Kamiya, T. Itoh, H. Tomioka, Org. Lett. 2006, 8, 1847–1850.
- [28] W. Sander, G. Bucher, S. Wierlacher, Chem. Rev. 1993, 93, 1583–1621.
- [29] A. M. Trozzolo, E. Wasserman, in Carbenes (Eds: M. Jones, R. A. Moss, Jr.), Vol. 2, Wiley, New York, **1975**, 185–206.
- [30] M. S. Platz, in Diradicals (Ed: W. T. Borden), Wiley, New York, 1982, 195–258.
- [31] E. Wasserman, R. S. Hutton, Acc. Chem. Res. 1977, 10, 27-32.
- [32] R. Breslow, H. W. Chang, E. Wasserman, J. Am. Chem. Soc. 1967, 89, 1112–1119.
- [33] H. Tukada, T. Sugawara, S. Murata, H. Iwamura, *Tetrahedron Lett.* 1986, 27, 235–238.
- [34] A. S. Nazran, F. J. Gabe, Y. LePage, D. J. Northcott, J. M. Park, D. Griller, J. Am. Chem. Soc. 1983, 105, 2912–2913.
- [35] A. S. Nazran, D. Griller, J. Chem. Soc. Chem. Commun. 1983, 850–851.
- [36] B. C. Gilbert, D. Griller, A. S. Nazran, J. Org. Chem. 1985, 50, 4738–4742.
- [37] A. S. Nazran, F. L. Lee, Y. LePage, D. J. Northcott, J. M. Park, D. Griller, J. Phys. Chem. 1984, 88, 5251–5254.
- [38] H. Tomioka, in Advances in Strained and Interesting Organic Molecules (Ed: B. Halton), Vol. 8, JAI Press, Greenwich CT, 2000, 83–112.
- [39] Y. Hu, Y. Ishikawa, K. Hirai, H. Tomioka, Bull. Chem. Soc. Jpn. 2001, 74, 2207–2218.
- [40] H. Tomioka, in Reactive Intermediate Chemistry (Eds: R. A. Moss, M. S. Platz, M. Jones, Jr.), Wiley, New York, 2004, 375–461.
- [41] W. Sander, Angew. Chem. Int. Ed. Engl. 1990, 29, 344-354.
- [42] W. Bunnelle, Chem. Rev. 1991, 91, 335-362.
- [43] T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando, M. T. H. Liu, Chem. Lett. **1983**, *12*, 1261–1262.
- [44] M. L. Casal, S. E. Sugamori, J. C. Scaiano, J. Am. Chem. Soc. 1984, 106, 7623–7624.
- [45] H. L. Casal, M. Tanner, N. H. Werstiuk, J. C. Scaiano, J. Am. Chem. Soc. 1985, 107, 4616–4620.
- [46] R. L. Barcus, L. M. Hadel, L. J. Johnston, M. L. Platz, T. G. Savino, J. C. Scaiano, J. Am. Chem. Soc. **1986**, 108, 3928–3937.
- [47] Y. Fujiwara, Y. Tanimoto, M. Itoh, K. Hirai, H. Tomioka, J. Am. Chem. Soc. 1987, 109, 1942–1946.
- [48] J. C. Scaiano, W. G. McGrimpsey, H. L. Casal, J. Org. Chem. 1989, 54, 1612–1616.
- [49] M. S. Platz, Ed. Kinetics and Spectroscopy of Carbenes and Biradicals. Plenum, New York, 1990.
- [50] J. E. Jackson, M. S. Platz, in Advances in Carbene Chemistry (Ed: U. Brinker), Vol. 1, JAI Press, Greenwich CT, **1994**, 87–160.
- [51] I. Moritani, S. Murahashi, H. Ashitake, K. Kimura, H. Tsubomura, J. Am. Chem. Soc. **1968**, 90, 5918–5919.
- [52] G. L. Closs, B. E. Rabinow, J. Am. Chem. Soc. 1976, 98, 8190-8198.
- [53] P. G. Grasse, B.-E. Brauer, J. J. Zupancic, K. J. Kaufmann, G. B. Schuster, J. Am. Chem. Soc. **1983**, 105, 6833–6845.
- [54] T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando, M. T. H. Liu, *Chem. Lett.* **1983**, *12*, 1257–1260.
- [55] S. C. Lapin, B. E. Brauer, G. B. Schuster, J. Am. Chem. Soc. 1984, 106, 2092–2100.
- [56] L. M. Hadel, M. S. Platz, J. C. Scaiano, J. Am. Chem. Soc. 1984, 106, 283–287.
- [57] G. W. Griffin, K. A. Horn, J. Am. Chem. Soc. 1987, 109, 4919–4926.
- [58] S. H. Doss, A. A. Abdel-Wahab, E. M. Fruhof, H. Dürr, I. R. Gould, N. J. Turro, J. Org. Chem. 1987, 52, 434–438.
- [59] M. V. Encinas, J. C. Scaiano, J. Am. Chem. Soc. **1981**, 103, 6393–6397.
- [60] Product analysis of the photolysis of  $\mathbf{1b}$ -N<sub>2</sub> could not be performed because only a small amount of the diazomethane was obtained.
- [61] S. Toyota, T. Yamamori, M. Asakura, M. Oki, Bull. Chem. Soc. J. 2000, 73, 205–213.
- [62] M. E. Wright, D. A. Schorzman, Macromolecules 2001, 34, 4768–4773.