

Preparation, Crystal Structures, and Spectroscopic and Chemical Properties of 2,4,6-Trifluorophenyl- or 4-(Methoxycarbonyl)-phenyl-Substituted (*E*)-1-(3-Guaiazulenyl)ethylene and (*2E,4E*)-1-(3-Guaiazulenyl)-1,3-butadiene Derivatives

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Wittig reactions in general provide a mixture of *E* and *Z* geometric isomers, while reactions of 2,4,6-trifluorobenzaldehyde [and (*E*)-3-(2,4,6-trifluorophenyl)propanal] with the Wittig reagent (3-guaiazulenyl)triphenylphosphonium bromide in ethanol containing NaOEt at 25 °C for 24 h under argon give only new *E* (and *2E,4E*)-forms selectively, i.e., (*E*)-1-(3-guaiazulenyl)-2-(2,4,6-trifluorophenyl)ethylene and (*2E,4E*)-1-(3-guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene. For comparative purposes, Wittig reactions of methyl 4-formylbenzoate, 4-(dimethylamino)benzaldehyde, methyl 4-[(*E*)-2-formylethenyl]benzoate, and (*E*)-3-[4-(dimethylamino)phenyl]propanal: namely, possessing an electron-withdrawing (–COOCH₃) {or an electron-donating [–N(CH₃)₂]} group at the C-4 position of the benzene ring, with (3-guaiazulenyl)triphenylphosphonium bromide in methanol (or ethanol) containing NaOMe (or NaOEt) at 25 °C for 24 h under argon afford a mixture of the corresponding geometric isomers respectively. Along with spectroscopic properties and crystal structures of the isolated products, the chemical behavior of those products toward 1,1,2,2-tetracyanoethylene (TCNE) in benzene at 25 °C for 24 h under argon is reported with a view to comparative study.

In previous papers,^{1–22} we reported facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of new conjugated π -electron systems possessing a 3-guaiazulenyl (=5-isopropyl-3,8-dimethylazulen-1-yl)^{1–16,18–22} [or an azulene-1-yl^{8,15} or a 3-(methoxycarbonyl)azulen-1-yl¹⁷] group. During the course of our basic and systematic investigations on azulenes, we found that **17**,⁸ **18**,⁸ **19**,¹⁸ and **20**¹⁸ (Chart 1) serve as strong two electron donors and one electron acceptors (or a two electron acceptor for **17**) respectively and further that the reactions of **17**–**20** with 2 equivalents of TCNE, which serves as a strong electron acceptor,^{11,12} in benzene at 25 °C for 24 h under argon give unique cycloaddition products **21**,¹² **22**,¹² **23**,¹⁸ and **24**¹⁸ (Chart 2), possessing interesting molecular structures selectively. Similar to our products **21**–**24**, in 2009 Shoji et al. reported that the reaction of 1,3,6-tri-*tert*-butylazulene with TCNE in ethyl acetate at room temperature for 15 h afforded 3,5,9-tri-*tert*-butyltricyclo[6.2.2.0^{2,6}]dodeca-2,4,6,9-tetraene-11,11,12,12-tetracarbonitrile,²³ quantitatively, whose proposed reaction mechanism was quoted from our literature.¹² Furthermore, in relation to the conjugated π -electron systems **17**–**20**, for example, preparation and anticancer activity of (*E*)-1-aryl-2-(3-guaiazulenyl)ethylenes (=1-[(*E*)-2-arylethenyl]-5-isopropyl-3,8-dimethylazulenes) and (*2E,4E*)-1-aryl-4-(3-guaiazulenyl)-1,3-butadienes (=1-[(*1E,3E*)-4-aryl-1,3-butadienyl]-5-isopropyl-3,8-dimethylazulenes) have been studied to

a considerable extent;²⁴ however, none have really been documented for the accurate crystal structures as well as the detailed spectroscopic and chemical properties of those compounds. Along with the above basic studies,^{1–24} we quite recently found that the Wittig reactions of 2,4,6-trifluorobenzaldehyde (**5**) [and (*E*)-3-(2,4,6-trifluorophenyl)propanal (**11**)] with (3-guaiazulenyl)triphenylphosphonium bromide (**4**) in ethanol containing NaOEt at 25 °C for 24 h under argon gave only new *E* (and *2E,4E*)-forms selectively, i.e., (*E*)-1-(3-guaiazulenyl)-2-(2,4,6-trifluorophenyl)ethylene (**7**; 63% isolated yield) (Chart 1) and (*2E,4E*)-1-(3-guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene (**13**; 54% isolated yield) (Chart 3). On the other hand, regiospecific photoisomerization of fluorinated (*2E,4E*)-1,4-diphenyl-1,3-butadienes²⁵ and crystal structures and emission properties of fluorinated diphenylpolyenes²⁶ have been documented; however, the fluorinated π -electron systems **7** and **13**, possessing a 3-guaiazulenyl group, have not yet been synthesized. Thus, our next challenge has been focused on the following clarification: namely, (i) the difference between the Wittig reactions of **5** (and **11**), methyl 4-formylbenzoate (**6**) {and methyl 4-[(*E*)-2-formylethenyl]benzoate (**12**)}, and 4-(dimethylamino)benzaldehyde [and (*E*)-3-[4-(dimethylamino)phenyl]propanal²⁷] with the reagent **4** in ethanol (or methanol) containing NaOEt (or NaOMe) at 25 °C for 24 h under argon; (ii) the difference between the spectroscopic properties and the crystal structures of new fluorinated

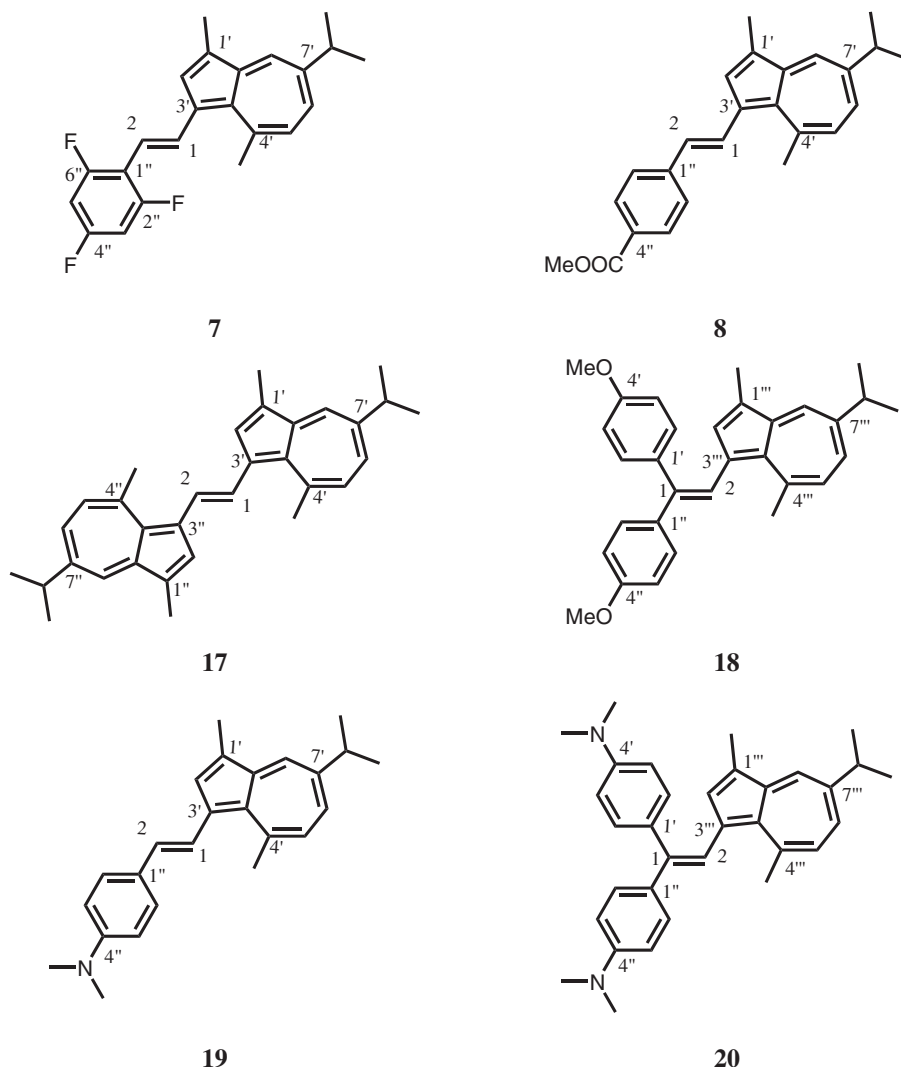


Chart 1.

π -electron systems **7** and **13** and those of (*E*)-1-(3-guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylene (**8**) (Chart 1), (*2E,4E*)-1-(3-guaiazulenyl)-4-[4-(methoxycarbonyl)phenyl]-1,3-butadiene (**14**) (Chart 3), (*E*)-1-(3-guaiazulenyl)-2-[4-(dimethylamino)phenyl]ethylene¹⁸ (**19**) (Chart 1), and (*2E,4E*)-1-(3-guaiazulenyl)-4-[4-(dimethylamino)phenyl]-1,3-butadiene²⁷ (**25**) (Chart 3): namely, possessing an electron-withdrawing ($-\text{COOCH}_3$) or an electron-donating [$-\text{N}(\text{CH}_3)_2$] group; and (iii) the difference between the chemical behavior of **7**, **8**, **13**, **14**, **19**, and **25** toward TCNE in benzene at 25 °C for 24 h under argon and further, a plausible reaction pathway for the formation of the resulting products **9**, **10**, **15**, **16**, **23**,¹⁸ and **26**²⁷ (Charts 2 and 3). We now wish to report detailed comparative studies of the above three points (i)–(iii).

Experimental

General. Melting points were taken on a Yanagimoto MP-S3 instrument. FAB- and EI-MS spectra were taken on a JEOL The Tandem Mstation JMS-700 TKM data system. UV–vis and IR spectra were taken on a Beckman DU640 spectrophotometer and a Shimadzu FTIR-4200 Grating spectrometer. NMR spectra were recorded with a JNM-ECA500 (500 MHz for ^1H

and 125 MHz for ^{13}C) and JNM-ECA700 (700 MHz for ^1H and 176 MHz for ^{13}C) cryospectrometer at 25 °C. ^1H NMR spectra were assigned using computer-assisted simulation (software: gNMR developed by Adept Scientific plc) on a DELL Dimension 9150 personal computer with a Pentium IV processor.

Preparation of (*E*)-1-(3-Guaiazulenyl)-2-(2,4,6-trifluorophenyl)ethylene (7**).** To a solution of 2,4,6-trifluorobenzaldehyde (**5**) (38 mg, 237 μmol) in ethanol (5 mL) was added a solution of (3-guaiazulenylmethyl)triphenylphosphonium bromide^{22,27} (**4**) (131, 237 μmol) in ethanol (5 mL) containing sodium ethoxide (32 mg, 470 μmol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture and the resulting product was then extracted with dichloromethane (10 mL $\times$ 3). The extract was washed with distilled water, dried (MgSO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–benzene (9:1, vol/vol) as an eluant. The crude product **7** was recrystallized from acetonitrile to provide pure **7** (53 mg, 150 μmol , 63% yield) as stable single crystals.

Compound **7**: Dark-green needles [R_f = 0.38 on silica gel TLC (solv. hexane:benzene = 9:1, vol/vol)]; mp 85 °C; UV–

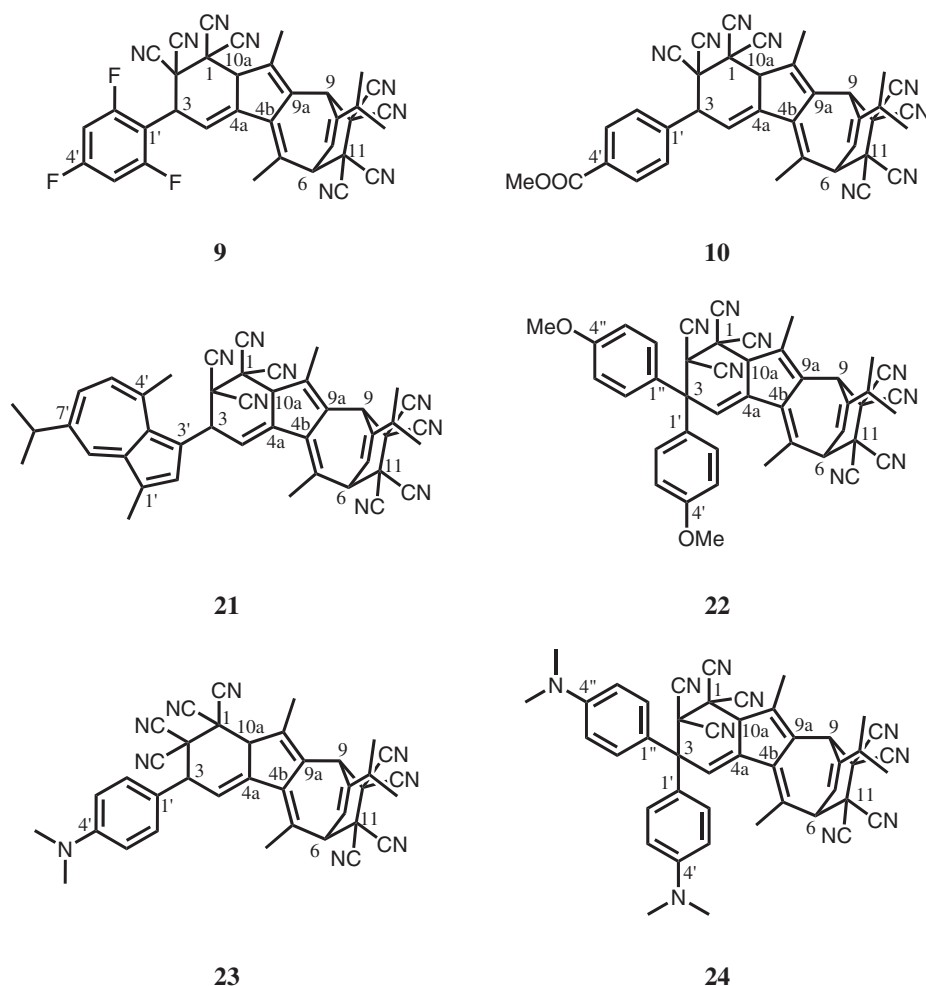


Chart 2.

vis $\lambda_{\max}/\text{nm}$ ($\log \epsilon$) in CH_2Cl_2 : 227 (4.20), 267 (4.31), 329 (4.41), 414 (4.41), and 635 (2.66); IR $\nu_{\max}/\text{cm}^{-1}$ (KBr): 2959–2866 (C–H), 2959, 826 (–CH=CH–), 1585, 1443 (C=C), and 1161, 1115, 1026 (C–F); exact EI-MS (70 eV), found: m/z 354.1575; calcd for $\text{C}_{23}\text{H}_{21}\text{F}_3$: M^+ , m/z 354.1595; 500 MHz ^1H NMR (acetonitrile- d_3), signals resulting from a 3-guaiazulenyl group: δ 1.31 (6H, d, $J = 6.9$ Hz, $(\text{CH}_3)_2\text{CH}-7'$), 2.57 (3H, br s, Me-1'), 2.95 (3H, s, Me-4'), 3.02 (1H, sept, $J = 6.9$ Hz, $(\text{CH}_3)_2\text{CH}-7'$), 6.92 (1H, d, $J = 10.6$ Hz, H-5'), 7.32 (1H, dd, $J = 10.6$, 2.3 Hz, H-6'), 7.94 (1H, br s, H-2'), and 8.06 (1H, d, $J = 2.3$ Hz, H-8'); signals resulting from a 2,4,6-trifluorophenyl group: δ 6.85 (2H, t, $J = 9.2$ Hz, H-3'',5''); and signals resulting from an (*E*)-ethylene unit: δ 6.80 (1H, d, $J = 16.4$ Hz, H-2) and 8.30 (1H, d, $J = 16.4$ Hz, H-1); 125 MHz ^{13}C NMR (acetonitrile- d_3): δ 174.2 (C-4''), 172.3 (C-2'',6''), 158.8 (C-4'), 154.7 (C-7'), 153.5 (C-8a'), 147.9 (C-6'), 147.5 (C-2'), 146.7 (C-8'), 145.7 (C-3a'), 144.6 (C-1), 140.8 (C-5'), 139.4 (C-1'), 138.3 (C-3'), 125.5 (C-1''), 123.2 (C-2), 113.2 (C-3'',5''), 50.0 ($(\text{CH}_3)_2\text{CH}-7'$), 40.3 (Me-4'), 36.2 ($(\text{CH}_3)_2\text{CH}-7'$), and 24.7 (Me-1').

X-ray Crystal Structure of (*E*)-1-(3-Guaiazulenyl)-2-(2,4,6-trifluorophenyl)ethylene (7). A total 4332 reflections with $2\theta_{\max} = 55.0^\circ$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated

Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$, rotating anode: 50 kV, 180 mA) at -75°C . The structure was solved by direct methods (SIR92)²⁸ and expanded using Fourier techniques (DIRDIF99).²⁹ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2 . All calculations were performed using the teXsan crystallographic software package.³⁰ Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-670806 for compound No. 7. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for 7: $\text{C}_{23}\text{H}_{21}\text{F}_3$ (FW: 354.41), dark-green prism (the crystal size, $0.20 \times 0.20 \times 0.20 \text{ mm}^3$), triclinic, $P\bar{1}$ (#2), $a = 10.336(3) \text{ \AA}$, $b = 16.863(5) \text{ \AA}$, $c = 5.336(2) \text{ \AA}$, $\alpha = 97.21(3)^\circ$, $\beta = 96.83(3)^\circ$, $\gamma = 101.09(2)^\circ$, $V = 895.6(5) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.314 \text{ g cm}^{-3}$, $\mu(\text{Mo } K\alpha) = 0.964 \text{ cm}^{-1}$, scan width: $(1.21 + 0.30 \tan \theta)^\circ$, scan mode: $\omega-2\theta$, scan rate: $4.0^\circ/\text{min}$, measured reflections: 4332, observed reflectons: 4107, No. of parameters: 257, $R1 = 0.0623$, $wR2 = 0.0942$, goodness of fit indicator: 1.000.

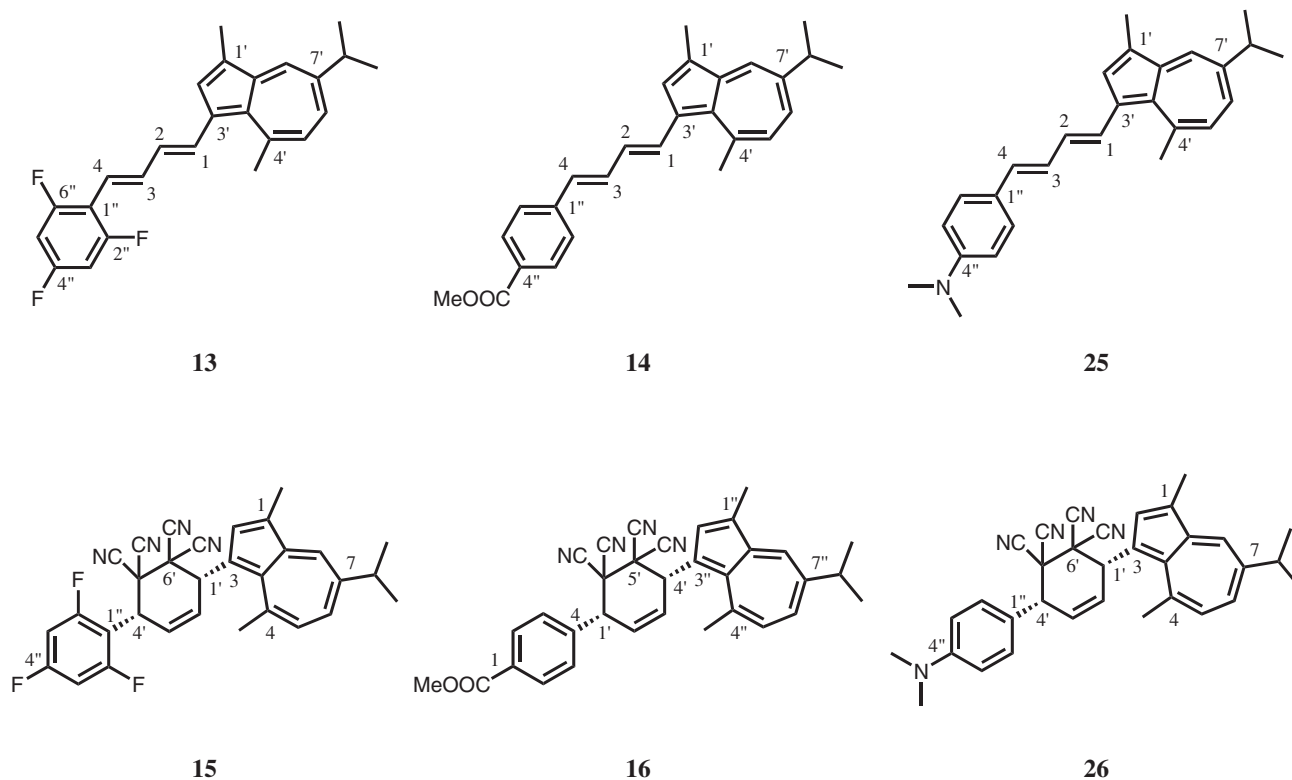


Chart 3.

Preparation of (*E*)-1-(3-Guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylene (8). To a solution of methyl 4-formylbenzoate (**6**) (57 mg, 347 μ mol) in methanol (5 mL) was added a solution of (3-guaiazulenylmethyl)triphenylphosphonium bromide^{22,27} (**4**) (180 mg, 325 μ mol) in methanol (5 mL) containing sodium methoxide (37 mg, 685 μ mol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture and then, the resulting product was extracted with dichloromethane (10 mL $\times$ 3). The extract was washed with distilled water, dried (MgSO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane-ethyl acetate (9:1, vol/vol) as an eluant. The crude product **8** was recrystallized from hexane to provide pure **8** (53 mg, 148 μ mol, 46% yield) as stable single crystals.

Compound 8: Dark-green needles [R_f = 0.23 on silica gel TLC (solvent: hexane:ethyl acetate = 9:1, vol/vol)]; mp 128 °C; UV-vis λ_{max} /nm (log ϵ) in CH_2Cl_2 : 235 (4.41), 280 (4.49), 335 (4.40), 436 (4.67), and 600 (2.90); IR ν_{max} /cm⁻¹ (KBr): 2959–2870 (C–H), 2959, 953 (–CH=CH–), 1717 (C=O), 1589 (C=C), and 1281, 1177 (C–O); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 358.1932; calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2$: M^+ , m/z 358.1933; 500 MHz ^1H NMR (acetonitrile- d_3), signals based on a 3-guaiazulenyl group: δ 1.32 (6H, d, J = 6.9 Hz, $(\text{CH}_3)_2\text{CH}$ -7'), 2.59 (3H, br s, Me-1'), 3.036 (1H, sept, J = 6.9 Hz, $(\text{CH}_3)_2\text{CH}$ -7'), 3.038 (3H, s, Me-4'), 6.96 (1H, d, J = 10.6 Hz, H-5'), 7.35 (1H, dd, J = 10.6, 2.0 Hz, H-6'), 7.98 (1H, br s, H-2'), and 8.07 (1H, d, J = 2.0 Hz, H-8'); signals arising from a 4-(methoxycarbonyl)phenyl group: δ 3.86 (3H, s, H_3COOC -4''), 7.62 (2H, dd, J = 8.3, 2.4 Hz, H-2'',6''), and 7.95 (2H, dd, J = 8.3, 2.4 Hz, H-3'',5''); and signals arising

from an (*E*)-ethylene unit: δ 7.03 (1H, d, J = 16.1 Hz, H-2) and 8.22 (1H, d, J = 16.1 Hz, H-1); 125 MHz ^{13}C NMR (acetonitrile- d_3): δ 167.5 (H_3COOC -4''), 147.3 (C-4'), 144.5 (C-1''), 143.1 (C-7'), 142.0 (C-8a'), 136.34 (C-2'), 136.27 (C-6'), 135.0 (C-8'), 134.2 (C-3a'), 130.7 (C-3'',5''), 129.4 (C-1), 129.1 (C-5'), 128.7 (C-4''), 127.7 (C-1'), 126.6 (C-2'',6''), 126.5 (C-3'), 125.6 (C-2), 52.5 (H_3COOC -4''), 38.3 ($(\text{CH}_3)_2\text{CH}$ -7'), 28.8 (Me-4'), 24.5 ($(\text{CH}_3)_2\text{CH}$ -7'), and 13.1 (Me-1').

X-ray Crystal Structure of (*E*)-1-(3-Guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylene (8). A total 4787 reflections with $2\theta_{\text{max}}$ = 55.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71069 Å, rotating anode: 50 kV, 180 mA) at –75 °C. The structure was solved by direct methods (SIR92)²⁸ and expanded using Fourier techniques (DIRDIF94).³¹ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2 . All calculations were performed using the teXsan crystallographic software package.³⁰ Deposition number CCDC-670966 for compound No. 8.

Crystallographic data for **8**: $\text{C}_{25}\text{H}_{26}\text{O}_2$ (FW: 358.48), dark-green plate (crystal size: 0.30 $\times$ 0.20 $\times$ 0.10 mm³), triclinic, $P\bar{1}$ (#2), a = 8.942(3) Å, b = 14.892(5) Å, c = 7.726(4) Å, α = 102.44(4)°, β = 94.16(5)°, γ = 77.57(3)°, V = 980.7(7) Å³, Z = 2, D_{calcd} = 1.214 g cm⁻³, $\mu(\text{Mo K}\alpha)$ = 0.751 cm⁻¹, scan width: (1.26 + 0.30 tan θ)°, scan mode: ω -2 θ , scan rate: 8.0°/min, measured reflections: 4787, observed reflections: 4499, No. of parameters: 349, $R1$ = 0.0602, $wR2$ = 0.2108, goodness of fit indicator: 0.987.

Reaction of (*E*)-1-(3-Guaiazulenyl)-2-(2,4,6-trifluoro-

phenyl)ethylene (7) with 1,1,2,2-Tetracyanoethylene (TCNE). To a solution of **7** (11 mg, 31 μ mol) in benzene (5 mL) was added a solution of TCNE (8 mg, 62 μ mol) in benzene (5 mL) under argon. The mixture was stirred at 25 °C for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The crude product thus obtained was recrystallized from benzene–dichloromethane (5:1, vol/vol) to provide pure 1,1,2,2,11,11,12,12-octacyano-3-(2,4,6-trifluorophenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (**9**) (5 mg, 8 μ mol, 26% yield) as stable crystals.

Compound 9: Colorless plates; mp >222 °C (decomp); UV λ_{max} /nm (log ϵ) in CH₂Cl₂: 291 (4.16); IR ν_{max} /cm^{−1} (KBr): 2966–2878 (C–H), 2253 (C $\equiv$ N), 1632 (C=C), and 1172, 1130 (C–F); exact EI-MS (70 eV), found: m/z 610.1871; calcd for C₃₅H₂₁N₈F₃: M⁺, m/z 610.1841; 700 MHz ¹H NMR (dichloromethane-*d*₂): δ 1.14 (6H, d, J = 6.6 Hz, (CH₃)₂CH-8), 2.27 (3H, s, Me-5), 2.40 (3H, s, Me-10), 2.62 (1H, sept, J = 6.6 Hz, (CH₃)₂CH-8), 3.82 (1H, d, J = 7.8 Hz, H-6), 4.13 (1H, s, H-10a), 4.33 (1H, d, J = 1.2 Hz, H-9), 4.96 (1H, s, H-3), 6.30 (1H, s, H-4), 6.38 (1H, dd, J = 7.8, 1.2 Hz, H-7), and 6.89 (1H, t, J = 8.6 Hz, H-3',5'); 176 MHz ¹³C NMR (benzene-*d*₆): δ 163.4 (C-4'), 160.6 (C-2',6'), 146.0 (C-8), 137.4 (C-9a), 136.1 (C-4b), 135.5 (C-4a), 130.4 (C-5), 122.8 (C-7), 122.1 (C-3), 111.9 (2CN-11), 111.6 (2CN-12), 111.0 (2CN-2), 109.9 (2CN-1), 107.2 (C-1), 101.5 (C-3',5'), 51.3 (C-10a), 50.4 (C-6), 45.6 (C-9), 45.5 (C-2), 45.3 (C-11), 44.8 (C-12), 39.4 (C-4), 34.3 ((CH₃)₂CH-8), 23.5 (Me-5), 19.9 ((CH₃)₂CH-8), and 13.3 (Me-10). The C-10 and C-1' carbon signals are included in other signals.

Reaction of (E)-1-(3-Guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylene (8) with 1,1,2,2-Tetracyanoethylene (TCNE). To a solution of **8** (15 mg, 42 μ mol) in benzene (5 mL) was added a solution of TCNE (10 mg, 78 μ mol) in benzene (5 mL) under argon. The mixture was stirred at 25 °C for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The crude product thus obtained was recrystallized from hexane–dichloromethane (5:1, vol/vol) to provide pure 1,1,2,2,11,11,12,12-octacyano-3-[4-(methoxycarbonyl)phenyl]-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (**10**) (13 mg, 21 μ mol, 50% yield) as stable crystals.

Compound 10: Colorless needles; mp >155 °C (decomp); UV λ_{max} /nm (log ϵ) in CH₂Cl₂: 233 (4.54) and 277 (4.22); IR ν_{max} /cm^{−1} (KBr): 2954–2878 (C–H), 2257 (C $\equiv$ N), 1717 (C=O), 1612, 1435 (C=C), and 1288, 1115 (C–O); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 614.2158; calcd for C₃₇H₂₆O₂N₈: M⁺, m/z 614.2179; 700 MHz ¹H NMR (dichloromethane-*d*₂): δ 1.14, 1.21 (3H each, d, J = 6.7 Hz, (CH₃)₂CH-8), 2.11 (3H, d, J = 1.8 Hz, Me-5), 2.26 (3H, d, J = 1.6 Hz, Me-10), 2.55 (1H, br sept, J = 6.7 Hz, (CH₃)₂CH-8), 3.75 (1H, dd, J = 7.8, 1.8 Hz, H-6), 3.94 (3H, s, H₃COOC-4'), 4.32 (1H, br s, H-10a), 4.760, 4.764 (0.5H each, d, J = 2.7 Hz, H-3), 6.28 (1H, br s, H-9), 6.33 (1H, ddd, J = 7.8, 1.6, 1.6 Hz, H-7), 7.057, 7.061 (0.5H each, d, J = 2.7 Hz, H-4), 7.57 (2H, dd, J = 8.3, 1.8 Hz, H-2',6'), and 8.21 (2H, dd, J = 8.3, 1.8 Hz, H-3',5').

Preparation of (E)-3-(2,4,6-Trifluorophenyl)propanal (11). To a solution of 2,4,6-trifluorobenzaldehyde (**5**)

(50 mg, 312 μ mol) in toluene (5 mL) was added a solution of (triphenylphosphoranylidene)acetaldehyde (106 mg, 348 μ mol) in toluene (5 mL). The mixture was refluxed for 2 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (5:1, vol/vol) as an eluant, providing pure **11** (48 mg, 258 μ mol, 83% yield).

Compound 11: White powder; exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 186.0279; calcd for C₉H₅OF₃: M⁺, m/z 186.0292.

Preparation of Methyl 4-[(E)-2-Formylethenyl]benzoate (12). To a solution of methyl 4-formylbenzoate (**6**) (52 mg, 317 μ mol) in toluene (5 mL) was added a solution of (triphenylphosphoranylidene)acetaldehyde (100 mg, 329 μ mol) in toluene (5 mL). The mixture was refluxed for 2 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (5:1, vol/vol) as an eluant, providing pure **12** (47 mg, 247 μ mol, 78% yield).

Compound 12: White powder; exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 190.0633; calcd for C₁₁H₁₀O₃: M⁺, m/z 190.0630.

Preparation of (2E,4E)-1-(3-Guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene (13). To a solution of (E)-3-(2,4,6-trifluorophenyl)propanal (**11**) (57 mg, 306 μ mol) in ethanol (5 mL) was added a solution of (3-guaiazulenylmethyl)triphenylphosphonium bromide^{22,27} (**4**) (170 mg, 307 μ mol) in ethanol (5 mL) containing sodium ethoxide (42 mg, 617 μ mol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture and then, the resulting product was extracted with dichloromethane (20 mL $\times$ 3). The extract was washed with distilled water, dried (MgSO₄), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (9:1, vol/vol) as an eluant. The crude product **13** was recrystallized from methanol–chloroform (5:1, vol/vol) (several times) to provide pure **13** (63 mg, 166 μ mol, 54% yield) as stable single crystals.

Compound 13: Dark-green needles [R_f = 0.50 on silica gel TLC (sol. hexane:ethyl acetate = 9:1, vol/vol)]; mp 115 °C; UV–vis λ_{max} /nm (log ϵ) in CH₂Cl₂: 237 (4.34), 281 (4.39), 326 (4.45), 339 (4.54), 439 (4.72), and 639 (2.85); IR ν_{max} /cm^{−1} (KBr): 2959–2870 (C–H), 2959, 980 (–CH=CH–), 1589, 1547 (C=C), and 1188, 1165, 1115 (C–F); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 380.1732; calcd for C₂₅H₂₃F₃: M⁺, m/z 380.1752; 500 MHz ¹H NMR (dichloromethane-*d*₂), signals from a 3-guaiazulenyl group: δ 1.33 (6H, d, J = 6.9 Hz, (CH₃)₂CH-7'), 2.59 (3H, br s, Me-1'), 2.989 (3H, s, Me-4'), 2.993 (1H, sept, J = 6.9 Hz, (CH₃)₂CH-7'), 6.86 (1H, J = 10.6 Hz, H-5'), 7.25 (1H, dd, J = 10.6, 2.3 Hz, H-6'), 7.88 (1H, br s, H-2'), and 7.98 (1H, d, J = 2.3 Hz, H-8'); signals from a 2,4,6-trifluorophenyl group: δ 6.71 (2H, t, J = 9.2 Hz, H-3'',5''); and signals from a (2E,4E)-1,3-butadiene unit: δ 6.52 (1H, d, J = 15.8 Hz, H-4), 6.83 (1H, d, J = 14.9, 10.9 Hz, H-2), 7.29 (1H, dd, J = 15.8, 10.9 Hz, H-3), and 7.65 (1H, d, J = 14.9 Hz, H-1); 125 MHz ¹³C NMR (dichloromethane-*d*₂): δ 161.3 (C-4''), 159.3 (C-2'',6''), 145.9 (C-4'), 141.5 (C-7'),

140.8 (C-8a'), 136.5 (C-3), 134.9 (C-2'), 134.8 (C-6'), 133.5 (C-8'), 132.5 (C-3a'), 131.6 (C-1), 127.6 (C-5'), 127.3 (C-2), 126.4 (C-1'), 125.5 (C-3'), 114.2 (C-4), 112.0 (C-1''), 100.1, 100.0 (C-3'',5''), 37.3 ((CH₃)₂CH-7'), 28.0 (Me-4'), 23.8 ((CH₃)₂CH-7'), and 12.4 (Me-1').

X-ray Crystal Structure of (2*E*,4*E*)-1-(3-Guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene (13). The X-ray measurement of a single crystal **13** was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K α radiation ($\lambda = 0.71075 \text{ \AA}$) at $-140 \pm 1^\circ \text{C}$. The structure was solved by direct methods (SIR92)²⁸ and expanded using Fourier techniques (DIRDIF99).²⁹ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2 . All calculations were performed using the CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Deposition number CCDC-744863 for compound No. **13**.

Crystallographic data for **13**: C₂₅H₂₃F₃ (FW: 380.45), dark-green needle (the crystal size: $0.53 \times 0.27 \times 0.19 \text{ mm}^3$), triclinic, $P\bar{1}$ (#2), $a = 7.4137(12) \text{ \AA}$, $b = 7.9708(14) \text{ \AA}$, $c = 17.117(3) \text{ \AA}$, $\alpha = 94.5313(14)^\circ$, $\beta = 95.550(3)^\circ$, $\gamma = 103.328(2)^\circ$, $V = 974.3(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.297 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.936 \text{ cm}^{-1}$, measured reflections: 9490, observed reflections: 3208, No. of parameters: 277, $R1 = 0.0453$, $wR2 = 0.1486$, goodness of fit indicator: 0.959.

Preparation of (2*E*,4*E*)-1-(3-Guaiazulenyl)-4-[4-(methoxycarbonyl)phenyl]-1,3-butadiene (14). To a solution of methyl 4-[(*E*)-2-formylethenyl]benzoate (**12**) (33 mg, 174 μmol) in methanol (5 mL) was added a solution of (3-guaiazulenylmethyl)triphenylphosphonium bromide^{22,27} (**4**) (97 mg, 175 μmol) in methanol (5 mL) containing sodium methoxide (20 mg, 370 μmol). The mixture was stirred at 25°C for 24 h under argon. After the reaction, distilled water was added to the mixture and the resulting product was then extracted with dichloromethane (20 mL $\times$ 3). The extract was washed with distilled water, dried (MgSO₄), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (9:1, vol/vol) as an eluant. The crude product **14** was recrystallized from methanol–chloroform (5:1, vol/vol) (several times) to provide pure **14** (9 mg, 24 μmol , 14% yield).

Compound **14**: Dark-green needles [$R_f = 0.26$ on silica gel TLC (solv. hexane:ethyl acetate = 9:1, vol/vol)]; mp 121°C ; UV–vis $\lambda_{\text{max}}/\text{nm}$ (log ϵ) in CH₂Cl₂: 228 (4.36), 249 (4.30), 275 (4.34), 294 (4.36), 347 (4.33), 459 (4.65), and 633 (2.83); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 2959–2870 (C–H), 2959, 980 (–CH=CH–), 1713 (C=O), 1574 (C=C), and 1277, 1173 (C–O); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 384.2070; calcd for C₂₇H₂₈O₂: M⁺, m/z 384.2089; 500 MHz ¹H NMR (dichloromethane-*d*₂), signals originating from a 3-guaiazulenyl group: δ 1.33 (6H, d, $J = 6.9 \text{ Hz}$, (CH₃)₂CH-7'), 2.59 (3H, br s, Me-1'), 3.00 (1H, sept, $J = 6.9 \text{ Hz}$, (CH₃)₂CH-7'), 3.01 (3H, s, Me-4'), 6.87 (1H, d, $J = 10.6 \text{ Hz}$, H-5'), 7.26 (1H, dd, $J = 10.6, 2.0 \text{ Hz}$, H-6'), 7.90 (1H, br s, H-2'), and 7.98 (1H, d, $J = 2.0 \text{ Hz}$, H-8'); signals arising from a 4-(methoxycarbonyl)phenyl group: δ 3.88 (3H, s, H₃COOC-4''), 7.50 (2H, dd, $J = 8.3, 1.9 \text{ Hz}$, H-2'',6''), 7.96 (2H, dd, $J = 8.3, 1.9 \text{ Hz}$, H-3'',5''); and signals from a (2*E*,4*E*)-1,3-butadiene unit: δ 6.62

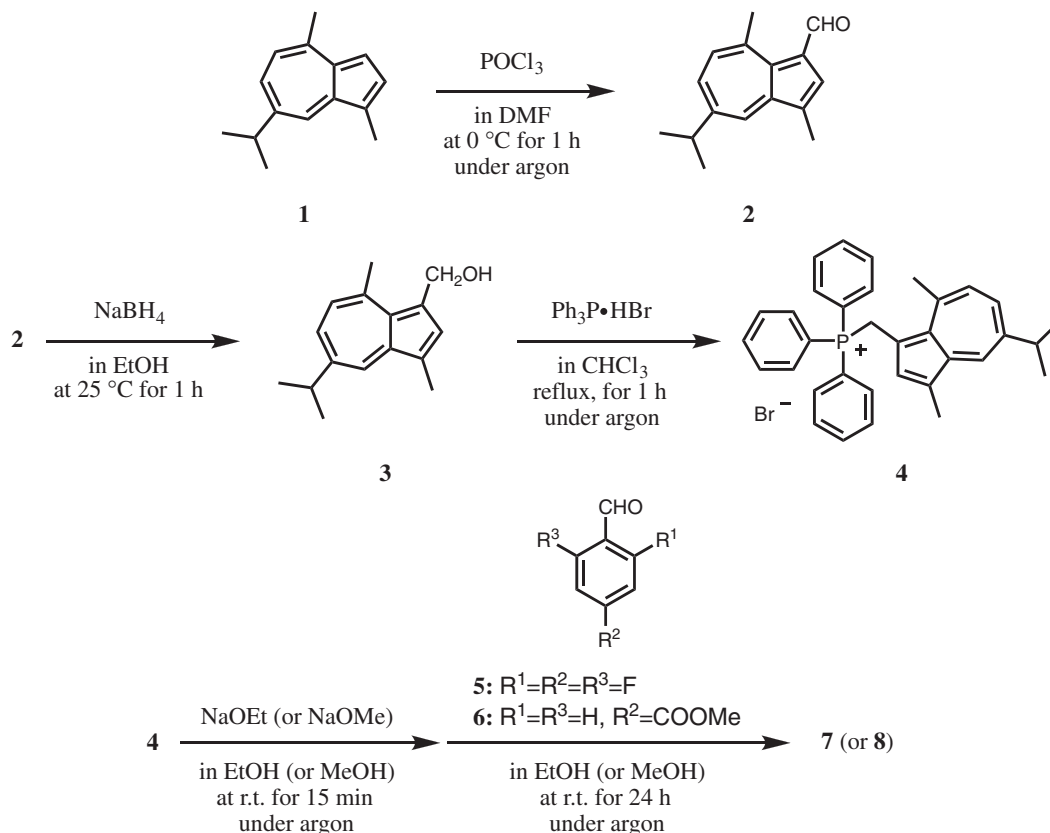
(1H, d, $J = 15.5 \text{ Hz}$, H-4), 6.88 (1H, dd, $J = 14.9, 10.9 \text{ Hz}$, H-2), 7.19 (1H, dd, $J = 15.5, 10.9 \text{ Hz}$, H-3), and 7.69 (1H, d, $J = 14.9 \text{ Hz}$, H-1); 125 MHz ¹³C NMR (dichloromethane-*d*₂): δ 166.4 (H₃COOC-4''), 145.9 (C-4'), 142.4 (C-1''), 141.6 (C-7'), 140.9 (C-8a'), 134.8 (C-6',2'), 133.5 (C-8'), 133.2 (C-3), 132.6 (C-3a'), 131.8 (C-1), 129.5 (C-3'',5''), 127.8 (C-4,5'), 127.7 (C-4''), 126.5 (C-1'), 126.2 (C-2), 125.6 (C-3'), 125.4 (C-2'',6''), 51.5 (H₃COOC-4''), 37.3 ((CH₃)₂CH-7'), 28.0 (Me-4'), 23.8 ((CH₃)₂CH-7'), and 12.4 (Me-1').

Reaction of (2*E*,4*E*)-1-(3-Guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene (13) with 1,1,2,2-Tetracyanoethylene (TCNE). To a solution of **13** (20 mg, 53 μmol) in benzene (5 mL) was added a solution of TCNE (15 mg, 117 μmol) in benzene (5 mL) under argon, turning the green solution of **13** into a blue solution gradually. The mixture was stirred at 25°C for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The crude product thus obtained was recrystallized from hexane–ethyl acetate (5:1, vol/vol) to provide pure 3-[5,5,6,6-tetracyano-*cis*-4-(2,4,6-trifluorophenyl)-2-cyclohexenyl]guaiazulene (**15**) (18 mg, 35 μmol , 66% yield) as a stable powder.

Compound **15**: Blue powder; mp $>129^\circ \text{C}$ (decomp); UV–vis $\lambda_{\text{max}}/\text{nm}$ (log ϵ) in benzene: 295 (4.59), 307 (4.47), 353 (3.82), 370 (3.88), 446 (2.59), 552 (2.65), 587 (2.73), 638 (2.64), and 712 (2.07); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3035–2963 (C–H), 2252 (C $\equiv$ N), 1632, 1601 (C=C), and 1173, 1126 (C–F); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 508.1903; calcd for C₃₁H₂₃N₄F₃: M⁺, m/z 508.1875; 700 MHz ¹H NMR (benzene-*d*₆), signals from a 3-guaiazulenyl group: δ 1.39 (6H, d, $J = 7.0 \text{ Hz}$, (CH₃)₂CH-7), 2.67 (3H, br s, Me-1), 3.140 (3H, s, Me-4), 3.144 (1H, sept, $J = 7.0 \text{ Hz}$, (CH₃)₂CH-7), 7.18 (1H, $J = 10.9 \text{ Hz}$, H-5), 7.54 (1H, dd, $J = 10.9, 2.2 \text{ Hz}$, H-6), 7.78 (1H, br s, H-2), and 8.32 (1H, d, $J = 2.2 \text{ Hz}$, H-8); signals from a 2,4,6-trifluorophenyl group: δ 6.93 (2H, t, $J = 9.0 \text{ Hz}$, H-3'',5''); and signals from a *cis*-1,4-disubstituted 5,5,6,6-tetracyano-2-cyclohexene unit: δ 5.04 (1H, m, H-4'), 5.86 (1H, m, H-1'), 6.04 (1H, m, H-3'), and 6.28 (1H, m, H-2'); 176 MHz ¹³C NMR (benzene-*d*₆): δ 164.6 (C-4''), 162.6 (C-2'',6''), 144.2 (C-4), 142.4 (C-7), 139.4 (C-8a), 137.3 (C-2), 135.5 (C-6), 134.8 (C-8), 133.8 (C-3a), 129.7 (C-5), 129.0 (C-2'), 125.5 (C-1), 123.8 (C-3'), 115.6 (C-3), 110.6, 110.3, 109.8, 109.6 (CN each), 105.6 (C-1''), 101.6 (C-3'',5''), 47.8 (C-6'), 45.0 (C-5'), 40.6 (C-1'), 38.0 (C-4'), 37.5 ((CH₃)₂CH-7), 27.6 (Me-4), 24.0 ((CH₃)₂CH-7), and 12.5 (Me-1).

Reaction of (2*E*,4*E*)-1-(3-Guaiazulenyl)-4-[4-(methoxycarbonyl)phenyl]-1,3-butadiene (14) with 1,1,2,2-Tetracyanoethylene (TCNE). To a solution of **14** (15 mg, 39 μmol) in benzene (5 mL) was added a solution of TCNE (10 mg, 78 μmol) in benzene (5 mL) under argon, turning the green solution of **14** into a blue solution gradually. The mixture was stirred at 25°C for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The crude product thus obtained was recrystallized from hexane–ethyl acetate (5:1, vol/vol) to provide pure methyl 4-[5,5,6,6-tetracyano-*cis*-4-(3-guaiazulenyl)-2-cyclohexenyl]benzoate (**16**) (14 mg, 27 μmol , 69% yield) as a stable powder.

Compound **16**: Blue powder; mp $>202^\circ \text{C}$ (decomp); UV–vis $\lambda_{\text{max}}/\text{nm}$ (log ϵ) in benzene: 295 (4.66), 307 (4.55), 353 (3.92), 370 (3.98), 470 (2.68), 589 (2.90), 638 (2.82), and 704



Scheme 1. The preparation of the Wittig reagent **4** and the reaction of **5** (or **6**) with **4** in ethanol (or methanol) in the presence of sodium ethoxide (or sodium methoxide) at 25 °C for 24 h under argon.

(2.45); IR $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 2959–2808 (C–H), 2245 (C $\equiv$ N), 1612 (C=O), and 1215, 1169 (C–O); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 512.2205; calcd for $\text{C}_{33}\text{H}_{28}\text{O}_2\text{N}_4$: M^+ , m/z 512.2212; 700 MHz ^1H NMR (benzene- d_6), signals from a 3-guaiazulenyl group: δ 1.137, 1.140 (3H each, $J = 7.0$ Hz each, $(\text{CH}_3)_2\text{CH}-7''$), 2.52 (3H, br s, Me-1''), 2.72 (1H, sept, $J = 7.0$ Hz, $(\text{CH}_3)_2\text{CH}-7''$), 3.01 (3H, s, Me-4''), 6.73 (1H, $J = 10.8$ Hz, H-5''), 7.11 (1H, dd, $J = 10.8, 2.2$ Hz, H-6''), 7.91 (1H, br s, H-2''), and 8.14 (1H, d, $J = 2.2$ Hz, H-8''); signals from a 4-substituted methyl benzoate: δ 3.51 (3H, s, $\text{H}_3\text{COOC}-1$), 7.09 (2H, dd, $J = 8.2, 1.8$ Hz, H-3,5), and 8.03 (2H, dd, $J = 8.2, 1.8$ Hz, H-2,6); and signals from a *cis*-1,4-disubstituted 5,5,6,6-tetracyano-2-cyclohexene unit: δ 4.29 (1H, m, H-1'), 5.19 (1H, m, H-2'), 5.80 (1H, m, H-3'), and 5.94 (1H, m, H-4'); 176 MHz ^{13}C NMR (benzene- d_6): δ 165.7 ($\text{H}_3\text{COOC}-1$), 144.8 (C-4'), 142.5 (C-7''), 140.3 (C-8a''), 138.0 (C-2''), 137.7 (C-4), 135.8 (C-6''), 135.2 (C-8''), 134.8 (C-3a''), 132.4 (C-1), 131.0 (C-3'), 130.7 (C-2,6), 130.5 (C-5''), 129.7 (C-3,5), 125.9 (C-1''), 124.9 (C-2'), 116.3 (C-3''), 111.6, 111.3, 111.0, 110.4 (CN each), 51.8 ($\text{H}_3\text{COOC}-1$), 47.7 (C-5'), 47.2 (C-1',6'), 41.3 (C-4'), 37.8 ($(\text{CH}_3)_2\text{CH}-7''$), 28.1 (Me-4''), 24.4 ($(\text{CH}_3)_2\text{CH}-7''$), and 13.0 (Me-1'').

Results and Discussion

Preparation and Spectroscopic Properties of 7 and 8. In 2008 we reported that the Wittig reaction of guaiazulene-3-carbaldehyde (=5-isopropyl-3,8-dimethylazulene-1-carbaldehyde) (**2**) with [4-(dimethylamino)benzyl]triphenylphosphonium bromide in ethanol containing NaOEt at 25 °C for 24 h under argon gave the E and Z isomers of 2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene, while only the E form **19** could be isolated as single crystals in 12% yield (Chart 1).¹⁸

Quite recently, we further found that the reversed Wittig reaction of 4-(dimethylamino)benzaldehyde with (3-guaiazulenyl)triphenylphosphonium bromide^{22,27} (**4**), which can be derived via the materials **1–3** (Scheme 1), under the same reaction conditions as the above afforded the same results. Similarly, the Wittig reaction of methyl 4-formylbenzoate (**6**) with **4** in methanol containing NaOMe at 25 °C for 24 h under argon gave a ca. 2:1 mixture of the corresponding E and Z isomers and similar to **19**, only the E form **8** could be isolated as single crystals in 46% yield (Scheme 1);³² however, the reaction of 2,4,6-trifluorobenzaldehyde (**5**) with **4** in ethanol containing NaOEt at 25 °C for 24 h under argon provided only the E form **7** as single crystals in 63% yield (Scheme 1). The great difference between the above Wittig reactions can be inferred that the reaction of 4-(dimethylamino)benzaldehyde (or **6**) with **4** yields a mixture of the corresponding geometric isomers, i.e., (*E*)- and (*Z*)-2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylenes {or (*E*)- and (*Z*)-1-(3-guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylenes}, via *trans*- and *cis*-oxaphosphetane intermediates, while the reaction of **5** with **4** provides only the E form **7**, whose structure is derived from the *trans*-oxaphosphetane **a**, forming an intramolecular CH $\cdots$ FC hydrogen bond at the two positions, illustrated in Chart 4. In relation to our studies, in 1994 Karatsu, Tokumaru et al.

Table 1. The ^1H NMR Spectral Data (δ) of **7** and **8** in Acetonitrile- d_3 , **13** and **14** in Dichloromethane- d_2 , **19** and **25** in Benzene- d_6

Compound	3-Guaiazulenyl group								Aryl group				Butadiene (or ethylene) part			
	Me-1'	H-2'	Me-4'	H-5'	H-6'	(CH ₃) ₂ CH-7'	(CH ₃) ₂ CH-7'	H-8'	H-2'',6''	(CH ₃) ₂ N-4''	H-3'',5''	H ₃ COOC-4''	H-1	H-2	H-3	H-4
7	2.57	7.94	2.95	6.92	7.32	3.02	1.31	8.06	—	—	6.85	—	8.30	6.80	—	—
8	2.59	7.98	3.038	6.96	7.35	3.036	1.32	8.07	7.62	—	7.95	3.86	8.22	7.03	—	—
13	2.59	7.88	2.989	6.86	7.25	2.993	1.33	7.98	—	—	6.71	—	7.65	6.83	7.29	6.52
14	2.59	7.90	3.01	6.87	7.26	3.00	1.33	7.98	7.50	—	7.96	3.88	7.69	6.88	7.19	6.62
19	2.56	8.01	2.88	6.56	7.00	2.73	1.20	7.97	7.57	2.56	6.67	—	8.10	7.15	—	—
25	2.523	7.98	2.81	6.55	6.97	2.71	1.19	7.93	7.47	2.519	6.61	—	7.67	7.07	7.15	6.77

Table 2. The ^{13}C NMR Spectral Data (δ) of **7** and **8** in Acetonitrile- d_3 , **13** and **14** in Dichloromethane- d_2 , **19** and **25** in Benzene- d_6

Compound	3-Guaiazulenyl group													
	C-1'	Me-1'	C-2'	C-3'	C-3a'	C-4'	Me-4'	C-5'	C-6'	C-7'	(CH ₃) ₂ CH-7'	(CH ₃) ₂ CH-7'	C-8'	C-8a'
7	139.4	24.7	147.5	138.3	145.7	158.8	40.3	140.8	147.9	154.7	50.0	36.2	146.7	153.5
8	127.7	13.1	136.34	126.5	134.2	147.3	28.8	129.1	136.27	143.1	38.3	24.5	135.0	142.0
13	126.4	12.4	134.9	125.5	132.5	145.9	28.0	127.6	134.8	141.5	37.3	23.8	133.5	140.8
14	126.5	12.4	134.8	125.6	132.6	145.9	28.0	127.8	134.8	141.6	37.3	23.8	133.5	140.9
19	126.1	13.1	136.7	128.4	132.7	146.2	28.4	126.9	134.6	140.1	37.9	24.5	133.4	141.2
25	126.5	13.1	136.4	126.5	132.8	146.4	28.4	127.3	134.7	140.6	37.9	24.4	133.4	141.6

Table 3. The ^{13}C NMR Spectral Data (δ) of **7** and **8** in Acetonitrile- d_3 , **13** and **14** in Dichloromethane- d_2 , **19** and **25** in Benzene- d_6

Compound	Aryl group								Butadiene (or ethylene) part			
	C-1''	C-2'',6''	C-3'',5''	C-4''	(CH ₃) ₂ N-4''	H ₃ COOC-4''	H ₃ COOC-4''	H ₃ COOC-4''	C-1	C-2	C-3	C-4
7	125.5	172.3	113.2	174.2	—	—	—	—	144.6	123.2	—	—
8	144.5	126.6	130.7	128.7	—	52.5	167.5	—	129.4	125.6	—	—
13	112.0	159.3	100.0, 100.1	161.3	—	—	—	—	131.6	127.3	136.5	114.2
14	142.4	125.4	129.5	127.7	—	51.5	166.4	—	131.8	126.2	133.2	127.8
19	128.4	127.4	113.2	149.9	40.2	—	—	—	123.0	128.0	—	—
25	127.4	127.7	113.0	150.1	40.1	—	—	—	128.7	129.2	127.5	131.2

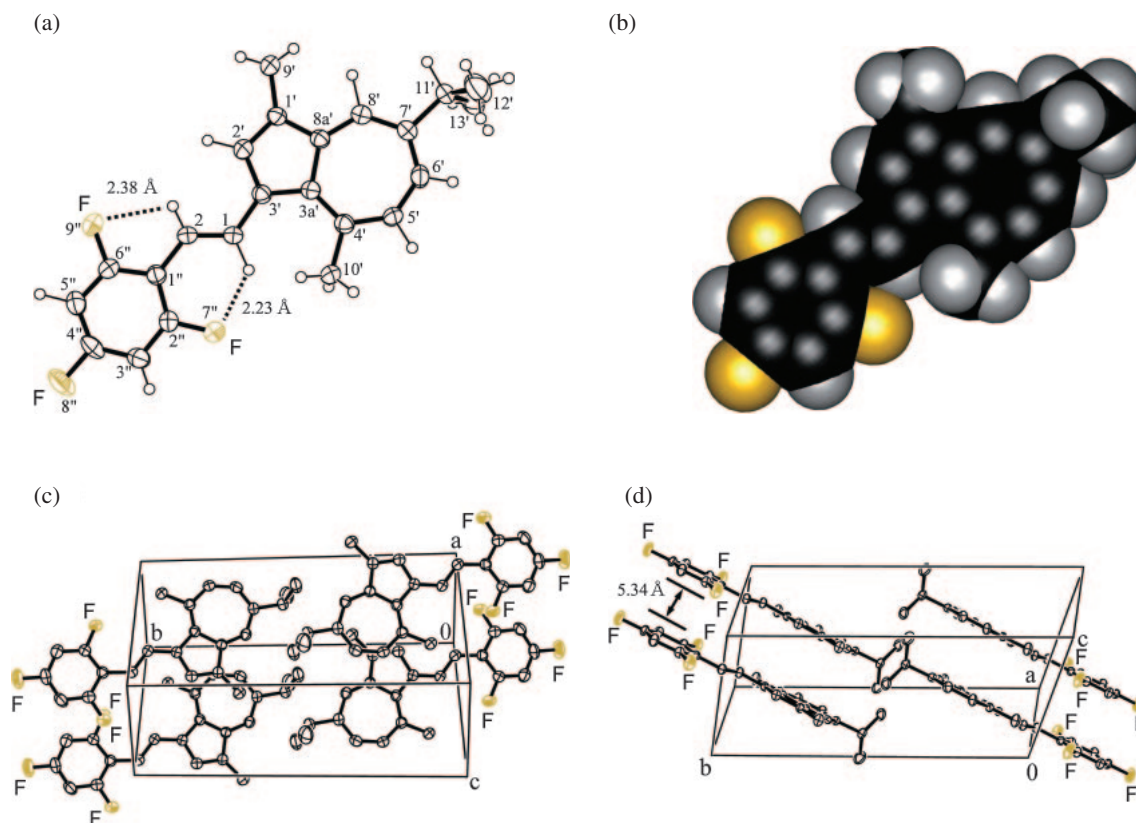


Figure 2. (a) The ORTEP drawing (30% probability thermal ellipsoids) of **7**. (b) The space filling molecular structure of **7**. The two different views [(c) and (d)] for the packing molecular structures of **7**. Hydrogen atoms are omitted for reasons of clarity.

comparison with those of **19** (Table 1). The ^{13}C NMR spectrum exhibited 22 carbon signals assigned using HMQC and HMBC (Tables 2 and 3). The C-3', C-4'', and C-2 carbon signals of **8** showed upfield shifts in comparison with those of **19**, while the ten carbon signals [C-1', C-3a', C-4', C-5', C-6', C-7', C-8', C-1'', C-3'', 5'', and C-1] of **8** showed downfield shifts in comparison with those of **19**. The other carbon signals of **8** coincided with those of **19**. An apparent difference between the UV-vis spectrum and the ^1H and ^{13}C NMR chemical shifts (δ) of **8** and those of **19** results from the influence of the 4-(methoxycarbonyl)phenyl substituent, which serves as an electron-withdrawing group, and the 4-(dimethylamino)phenyl substituent, which serves as an electron-donating group. The detailed spectroscopic analyses for **8** led to the molecular structure illustrated in Chart 1.

X-ray Crystal Structures of 7 and 8. The recrystallization (several times) of **7** from acetonitrile provided single crystals suitable for X-ray crystallographic analysis, while the recrystallization (several times) of **8** from hexane provided single crystals suitable for that purpose. The crystal structures of **7** and **8** were then determined by X-ray diffraction, producing accurate structural parameters. The ORTEP drawings of **7** and **8**, indicating the molecular structures illustrated in Chart 1, are shown in Figures 2a and 3a, 3b along with the selected bond lengths (Tables 4 and 5). As a result, it was found that from the dihedral angles between the least-squares planes, the planes of the 3-guaiazulenyl groups of **7** and **8** twisted by 6 and 46° from those of the benzene rings. Although the C–C bond alternation patterns observed for the azulene rings of **7**, **8**, and **19** were

slightly different (Table 4), owing to the influence of the 2,4,6-trifluorophenyl, 4-(methoxycarbonyl)phenyl, and 4-(dimethylamino)phenyl substituents, the average C–C bond length of the seven-membered ring for the 3-guaiazulenyl group of **7** (1.411 Å) coincided with those of **8** (1.407 Å) and **19** (1.407 Å). The C–C bond length of the five-membered ring for the 3-guaiazulenyl group of **7** appreciably varied between 1.368 and 1.509 Å; in particular, the C1'–C2' bond length (1.368 Å) was characteristically shorter than the average C–C bond length for the five-membered ring (1.430 Å), the results of which coincided with those of **19**. Similar to **7** and **19**, the C–C bond length of the five-membered ring for the 3-guaiazulenyl group of **8** appreciably varied between 1.367 and 1.491 Å; in particular, the C1'–C2' bond length (1.367 Å) was characteristically shorter than the average C–C bond length for the five-membered ring (1.425 Å). The C1–C2 bond lengths of **7** (1.331 Å) and **8** (1.342 Å) were longer than that of **19**¹⁸ (1.325 Å) (Table 5). The C1H...F7''C2'' and C2H...F9''C6'' distances of **7** (2.23 and 2.38 Å) and the space-filling molecular structure of **7** shown in Figure 2b were suggested to form an intramolecular CH...FC hydrogen bond between them. Along with the ORTEP drawings of **7** and **8**, the packing molecular structures of **7** and **8** are shown in Figures 2c, 2d and 3c, 3d. Figures 2c and 2d revealed that each average interplane distance between the overlapping molecules, whose directions were the same, was 5.34 Å for **7**, suggesting that each molecule forms a weak π -stacking structure in the single crystal; however, Figure 3d revealed that each average interplane distance between the overlapping molecules, which were

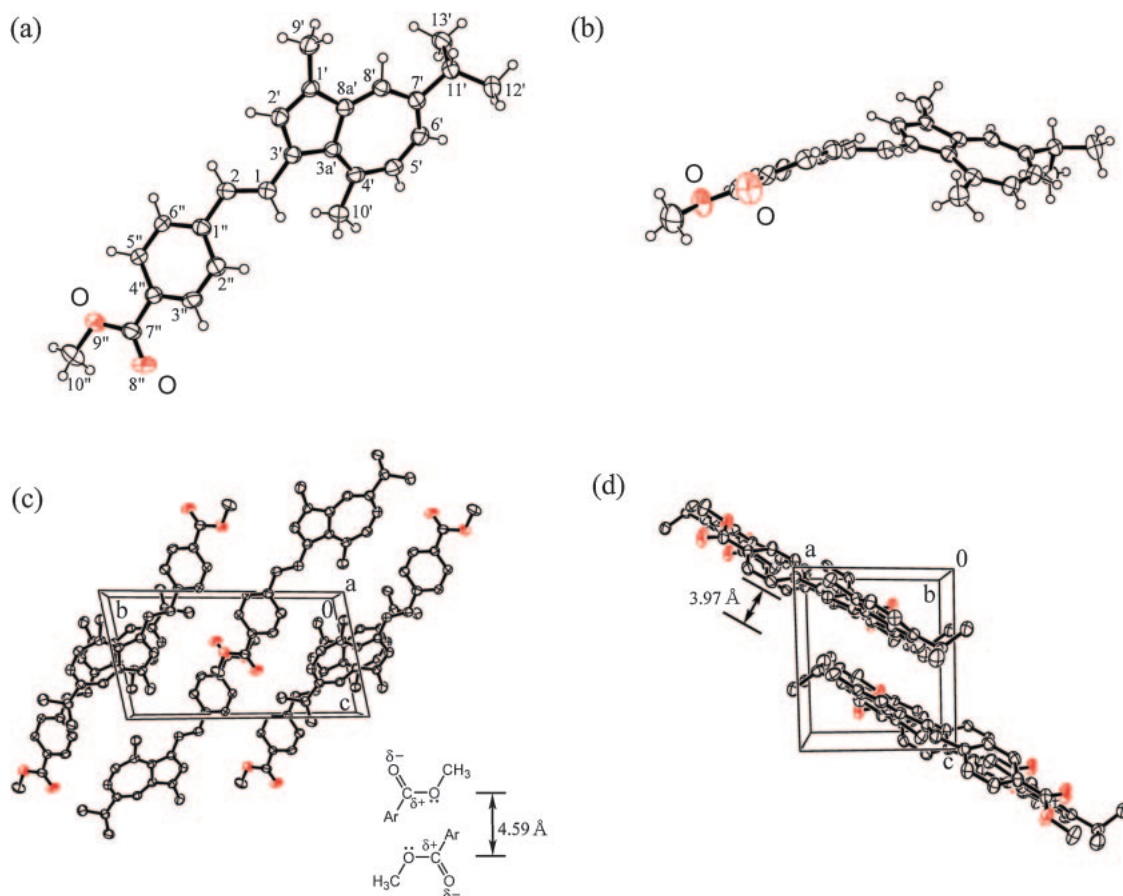


Figure 3. The two different [top (a) and side (b)] views of the ORTEP drawings (30% probability thermal ellipsoids) of **8**. The two different [top (c) and side (d)] views for the packing molecular structures of **8**. Hydrogen atoms are omitted for reasons of clarity.

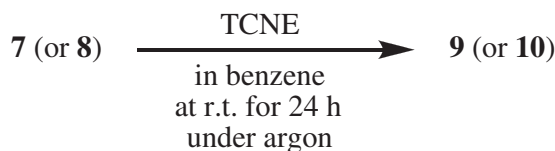
Table 4. The C–C Bond Lengths (Å) of **7**, **8**, **13**, **19**, and **25**

Atom	7	8	13	19	25
C1'–C2'	1.368(3)	1.367(3)	1.380(2)	1.373(4)	1.375(3)
C2'–C3'	1.419(4)	1.421(4)	1.425(2)	1.418(4)	1.419(2)
C3'–C3a'	1.430(4)	1.414(3)	1.417(2)	1.408(3)	1.421(3)
C3a'–C4'	1.390(4)	1.410(4)	1.410(2)	1.411(4)	1.402(2)
C4'–C5'	1.407(4)	1.397(3)	1.402(2)	1.380(4)	1.395(3)
C5'–C6'	1.402(3)	1.397(3)	1.397(2)	1.403(5)	1.402(3)
C6'–C7'	1.383(4)	1.378(4)	1.380(2)	1.370(5)	1.376(3)
C7'–C8'	1.399(4)	1.394(4)	1.404(2)	1.398(4)	1.403(3)
C8'–C8a'	1.385(3)	1.379(3)	1.390(2)	1.381(3)	1.379(3)
C8a'–C1'	1.423(4)	1.431(4)	1.416(2)	1.419(4)	1.423(2)
C1'–C9'	1.502(4)	1.498(4)	1.499(2)	1.495(5)	1.494(2)
C4'–C10'	1.523(3)	1.510(4)	1.505(2)	1.523(5)	1.521(3)
C7'–C11'	1.530(3)	1.528(3)	1.525(2)	1.520(4)	1.532(3)
C11'–C12'	1.514(4)	1.514(4)	1.528(2)	1.518(5)	1.505(4)
C11'–C13'	1.527(4)	1.514(3)	1.507(2)	1.529(6)	1.518(4)
C8a'–C3a'	1.509(3)	1.491(3)	1.502(2)	1.503(4)	1.505(2)

overlapped so that those dipole moments might be negated mutually, was 3.97 Å for **8**, suggesting that each molecule forms a π -stacking structure in the single crystal. Furthermore, Figure 3c showed that the distance between the intermolecular methoxycarbonyl groups was 4.59 Å, suggesting the formation of a weak $C^{\delta+} \cdots O^{\delta-}$ coordinate bond illustrated in that figure.

Table 5. The C–C, C–F, C–O, and C–N Bond Lengths (Å) of **7**, **8**, **13**, **19**, and **25**

Atom	7	8	13	19	25
C1–C2	1.331(4)	1.342(3)	1.348(2)	1.325(4)	1.342(3)
C2–C3	—	—	1.443(2)	—	1.436(3)
C3–C4	—	—	1.337(2)	—	1.349(3)
C1–C3'	1.457(3)	1.452(3)	1.454(2)	1.457(4)	1.447(3)
C4–C1''	—	—	1.460(2)	—	1.455(3)
C2–C1''	1.460(3)	1.469(3)	—	1.458(4)	—
C1''–C2''	1.396(4)	1.402(4)	1.395(2)	1.389(5)	1.393(3)
C2''–C3''	1.379(4)	1.385(3)	1.369(2)	1.372(4)	1.387(3)
C3''–C4''	1.373(5)	1.386(3)	1.362(2)	1.408(4)	1.398(3)
C4''–C5''	1.360(5)	1.385(4)	1.378(2)	1.382(6)	1.403(4)
C5''–C6''	1.377(4)	1.386(3)	1.378(2)	1.378(5)	1.387(3)
C6''–C1''	1.392(4)	1.394(3)	1.404(2)	1.391(4)	1.395(3)
C2''–F7''	1.357(4)	—	1.3565(18)	—	—
C4''–F8''	1.365(3)	—	1.357(2)	—	—
C6''–F9''	1.358(3)	—	1.3561(19)	—	—
C4''–C7''	—	1.482(3)	—	—	—
C7''–O8''	—	1.196(4)	—	—	—
C7''–O9''	—	1.338(3)	—	—	—
O9''–C10''	—	1.440(4)	—	—	—
C4''–N7''	—	—	—	1.377(4)	1.380(3)
N7''–C8''	—	—	—	1.461(6)	1.444(3)
N7''–C9''	—	—	—	1.427(5)	1.432(3)



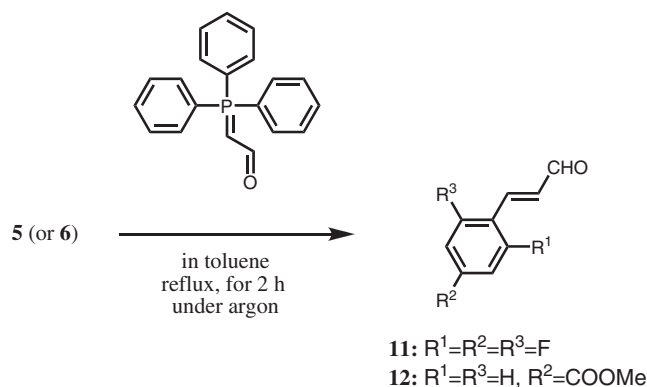
Scheme 2. The reaction of **7** (or **8**) with 2 equivalents of TCNE in benzene at 25 °C for 24 h under argon.

Reactions of 7 and 8 with TCNE. In 2008 we reported that the reaction of **19** with 2 equivalents of TCNE in benzene at 25 °C for 24 h under argon gave product **23** (Chart 2) in 41% isolated yield and further, a plausible reaction pathway for the formation of **23** was proposed.¹⁸ Along with the spectroscopic properties of **23**, the crystal structure of **23** could be determined. For comparative purposes, the reactions of **7** and **8** with 2 equivalents of TCNE were carried out under the same reaction conditions as for **19** (Scheme 2), affording new **23** analogs **9** and **10** (Chart 2), in 26 and 50% isolated yields, the molecular structures of which were established on the basis of similar spectroscopic analyses to those of **7** and **8**. A similar reaction pathway to **23**¹⁸ can be inferred for the formation of **9** and **10**.

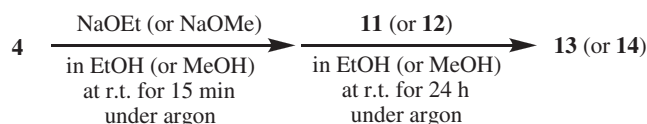
Compound **9** was obtained as colorless plates, while **10** was obtained as colorless needles. The characteristic UV–vis absorption bands of guaiazulene³⁴ (**1**) and **7** were not observed for **9** and the longest UV absorption wavelength appeared at λ_{max} 291 nm ($\log \varepsilon = 4.16$). Similar to **9**, the characteristic UV–vis absorption bands of **1**³⁴ and **8** were not observed for **10** and the longest UV absorption wavelength appeared at λ_{max} 277 nm ($\log \varepsilon = 4.22$). The IR spectra of **9** and **10** showed specific bands from the C–H, $\text{C}\equiv\text{N}$, C=C, and C–F bonds for **9** and specific bands from the C–H, $\text{C}\equiv\text{N}$, C=C, C=O, and C–O bonds for **10**. The molecular formula $\text{C}_{35}\text{H}_{21}\text{N}_8\text{F}_3$ of **9** was determined by exact EI-MS spectrum and the molecular formula $\text{C}_{37}\text{H}_{26}\text{O}_2\text{N}_8$ of **10** was determined by exact FAB-MS spectrum. The ¹H and ¹³C NMR spectra of **9** showed signals from a 3-(2,4,6-trifluorophenyl) group and a 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene unit and the ¹H NMR spectrum of **10** revealed signals from a 3-[4-(methoxycarbonyl)phenyl] group and an 8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydrobenz[*a*]azulene unit, the signals of which were carefully assigned using conventional methodology. Thus, the detailed spectroscopic analyses of **9** and **10** indicated similar structures to that of **23**, illustrated in Chart 2.

Preparation of 11 and 12. A facile preparation of the starting materials **11** and **12** of the target compounds **13** and **14** is as follows. The reactions of **5** and **6** with an equivalent of (triphenylphosphorane)diyl)acetaldehyde were carried out under the same reaction conditions (Scheme 3), affording the (*E*)-cinnamaldehydes **11** and **12** in 83 and 78% isolated yield.

Preparation and Spectroscopic Properties of 13 and 14. Quite recently, we reported that the Wittig reaction of (*E*)-3-[4-(dimethylamino)phenyl]propanal with the reagent **4** in ethanol containing NaOEt at 25 °C for 24 h under argon gives the 2*E*,4*E*- and 2*Z*,4*E*-isomers of 4-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)-1,3-butadiene, while only the 2*E*,4*E*-form **25** could be isolated as single crystals in 19% yield (Chart 3).²⁷



Scheme 3. The Wittig reaction of **5** (or **6**) with (triphenylphosphorane)diyl)acetaldehyde in toluene at reflux temperature for 2 h under argon, providing the corresponding cinnamaldehydes **11** and **12**.



Scheme 4. The Wittig reaction of **11** (or **12**) with **4** in ethanol (or methanol) in the presence of sodium ethoxide (or sodium methoxide) at 25 °C for 24 h under argon.

Similar to the above, the Wittig reaction of methyl 4-[(*E*)-2-formylethenyl]benzoate (**12**) with **4**^{22,27} in methanol containing NaOMe at 25 °C for 24 h under argon afforded a ca. 1:1 mixture of the corresponding 2*E*,4*E*- and 2*Z*,4*E*-isomers and similar to **25**, only the 2*E*,4*E*-form **14** could be isolated as single crystals in 14% yield (Scheme 4);³⁵ however, the reaction of (*E*)-3-(2,4,6-trifluorophenyl)propanal (**11**) with the Wittig reagent **4** in ethanol containing NaOEt at 25 °C for 24 h under argon provided only the 2*E*,4*E*-form **13** as single crystals in 54% yield (Scheme 4). Similar to **7**, **8**, and the previously reported **19**,¹⁸ the great difference between the above Wittig reactions can be inferred that the reaction of (*E*)-3-[4-(dimethylamino)phenyl]propanal (or **12**) with **4** yields a mixture of the corresponding geometric isomers, i.e., (2*E*,4*E*)- and (2*Z*,4*E*)-4-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)-1,3-butadienes {or (2*E*,4*E*)- and (2*Z*,4*E*)-1-(3-guaiazulenyl)-4-[4-(methoxycarbonyl)phenyl]-1,3-butadienes}, via *trans*- and *cis*-oxaphosphetane intermediates, while the reaction of **11** with **4** provides only the 2*E*,4*E*-form **13**, whose structure is derived from the *trans*-oxaphosphetane **b**, forming an intramolecular CF...HC...HC hydrogen bond at the two positions, illustrated in Chart 4. Similar to **7**, a rapid one-way isomerization from the yielded (2*Z*,4*E*)-1-(3-guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene to the 2*E*,4*E*-isomer **13** under the above reaction conditions cannot be excluded completely, the phenomenon of which is also currently under intensive investigation. The molecular structures of **13** and **14** were established on the basis of similar analyses to **7** and **8**.

The fluorinated compound **13** was obtained as dark-green needles. The spectroscopic properties of **13** compared with those of **25** are as follows. The UV–vis spectrum of **13** showed that the spectral pattern of **13** resembled that of **25**; the longest

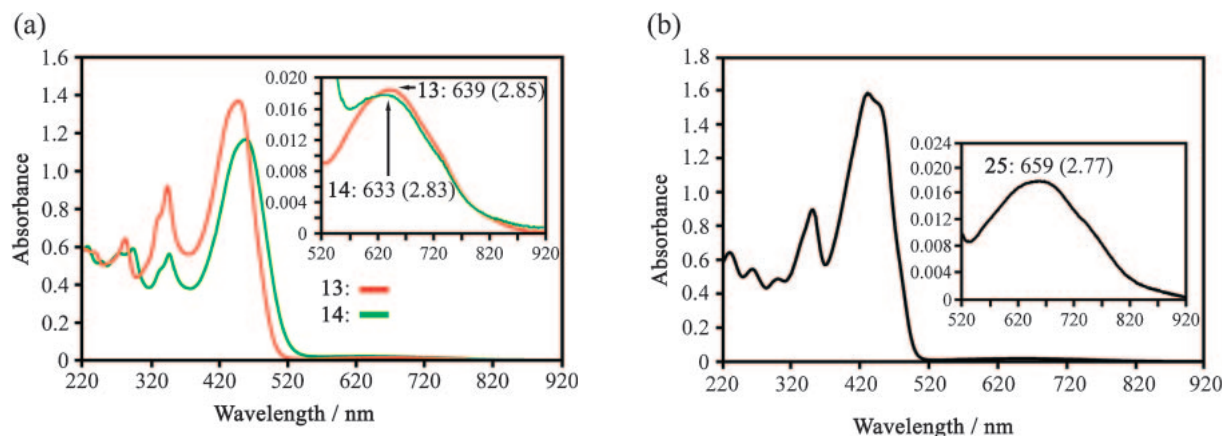


Figure 4. (a) The UV-vis spectra of **13** and **14** in CH_2Cl_2 . Concentrations, **13**: 0.10 g L^{-1} ($263 \mu\text{mol}$), **14**: 0.10 g L^{-1} ($260 \mu\text{mol}$). Length of the cell, 0.1 cm each. Each $\log \epsilon$ value is given in parenthesis. (b) The UV-vis spectrum of **25** in CH_2Cl_2 . Concentration, **25**: 0.11 g L^{-1} ($298 \mu\text{mol}$). Length of the cell, 0.1 cm. $\log \epsilon$ value is given in parenthesis.

absorption wavelength of **13** revealed a hypsochromic shift ($\Delta 20 \text{ nm}$) and a slight hyperchromic effect ($\Delta \log \epsilon = 0.08$) in comparison with that of **25** (Figure 4). The IR spectrum showed specific bands from the C–H, $-\text{HC}=\text{CH}-$, $\text{C}=\text{C}$, and C–F bonds, the wavenumbers (C–H, $-\text{HC}=\text{CH}-$, and $\text{C}=\text{C}$) of which revealed slight high and low frequency shifts in comparison with those of **25**. The molecular formula $\text{C}_{25}\text{H}_{23}\text{F}_3$ was determined by exact FAB-MS spectrum. The ^1H NMR spectrum showed signals arising from a 3-guaiazulenyl and 2,4,6-trifluorophenyl group and signals from a *2E,4E*-butadiene unit, the signals of which were carefully assigned using H–H COSY and computer-assisted simulation based on first-order analysis. Although the Me-1', H-8', and H-1 proton signals coincided with those of **25**,²⁷ the seven proton signals [Me-4', H-5', H-6', $(\text{CH}_3)_2\text{CH}-7'$, $(\text{CH}_3)_2\text{CH}-7'$, H-3'',5'', and H-3] of **13** showed downfield shifts and the H-2', H-2, and H-4 proton signals of **13** revealed upfield shifts in comparison with those of **25** (Table 1). The ^{13}C NMR spectrum exhibited 23 carbon signals assigned using HMQC and HMBC (Tables 2 and 3). Although the six carbon (C-2', C-3', C-1'', C-3'',5'', C-2, and C-4) and four carbon (C-2'',6'', C-4'', C-1, and C-3) signals of **13** showed up- and downfield shifts in comparison with those of **25**, the other carbon signals of **13** coincided with those of **25**. In particular, the C-3 and C-4 carbon signals of **13** were apparently down- and upfield shifts in comparison with those of **25**. Similar to the difference between **7** and **19**, an apparent difference between the UV-vis spectrum and the ^1H and ^{13}C NMR chemical shifts (δ) of **13** and those of **25** result from the influence of the 2,4,6-trifluorophenyl and 4-(dimethylamino)phenyl substituents. Besides the above, an apparent difference between the UV-vis spectrum and the ^1H and ^{13}C NMR chemical shifts (δ) of the (*2E,4E*)-1,3-butadiene **13** and those of the (*E*)-ethylene **7** was also observed (Figures 1, 4 and Tables 1–3). The detailed spectroscopic analyses for **13** led to the molecular structure illustrated in Chart 3.

Compound **14** was obtained as dark-green needles. The spectroscopic properties of **14** compared with those of **25** are as follows. The UV-vis spectrum of **14** showed that the spectral pattern of **14** resembled those of **13** and **25**; the longest absorption wavelength of **14** revealed a hypsochromic

shift ($\Delta 26 \text{ nm}$) and a slight hyperchromic effect ($\Delta \log \epsilon = 0.06$) in comparison with that of **25** (Figure 4). The IR spectrum showed specific bands arising from the C–H, $-\text{CH}=\text{CH}-$, $\text{C}=\text{C}$, $\text{C}=\text{O}$, and C–O bonds, the frequencies (C–H, $-\text{CH}=\text{CH}-$, and $\text{C}=\text{C}$) of which revealed slight high and low shifts in comparison with those of **13** and **25**. The molecular formula $\text{C}_{27}\text{H}_{28}\text{O}_2$ was determined by exact FAB-MS spectrum. The ^1H NMR spectrum showed signals from a 3-guaiazulenyl and 4-(methoxycarbonyl)phenyl group and signals from a *2E,4E*-butadiene unit, the signals of which were carefully assigned using H–H COSY and computer-assisted simulation based on first-order analysis. Although the six proton signals (Me-1', H-2', H-8', H-2'',6'', H-1, and H-3) of **14** coincided with those of **25**, the six proton signals [Me-4', H-5', H-6', $(\text{CH}_3)_2\text{CH}-7'$, $(\text{CH}_3)_2\text{CH}-7'$, and H-3'',5''] of **14** showed downfield shifts and the H-2 and H-4 proton signals of **14** showed upfield shifts in comparison with those of **25** (Table 1). The ^{13}C NMR spectrum exhibited 22 carbon signals assigned using HMQC and HMBC (Tables 2 and 3). Although the five carbon signals (C-7', C-1'', C-3'',5'', C-1, and C-3) of **14** showed downfield shifts in comparison with those of **25**, the five carbon signals (C-2', C-2'',6'', C-4'', C-2, and C-4) of **14** revealed upfield shifts in comparison with those of **25**. The other carbon signals of **14** coincided with those of **25**. Similar to the difference between **8** and **19**, an apparent difference between the UV-vis spectrum and the ^1H and ^{13}C NMR chemical shifts (δ) of **14** and those of **25** arise from the influence of the 4-(methoxycarbonyl)phenyl and 4-(dimethylamino)phenyl substituents. Besides the above, an apparent difference between the UV-vis spectrum and the ^1H and ^{13}C NMR chemical shifts (δ) of the (*2E,4E*)-1,3-butadiene **14** and those of the (*E*)-ethylene **8** was also observed (Figures 1, 4 and Tables 1–3). The detailed spectroscopic analyses of **14** led to the molecular structure illustrated in Chart 3.

X-ray Crystal Structure of 13. The crystal structure of **14** has not yet been elucidated because of difficulty in obtaining a single crystal suitable for X-ray crystallographic analysis, while the recrystallization of **13** from a mixed solvent of chloroform and methanol (1:5, vol/vol) provided single crystals suitable for that purpose. The crystal structure of **13**

was then determined by means of X-ray diffraction, producing accurate structural parameters. The ORTEP drawing of **13**, with a numbering scheme, indicating the molecular structure illustrated in Chart 3, is shown in Figure 5 along with selected bond lengths (Tables 4 and 5). As a result, it was found that from the dihedral angles between the least-squares planes, the plane of the 3-guaiazulenyl group of **13** twisted by 5° from that of the benzene ring. The average C–C bond length of the seven-membered ring for the 3-guaiazulenyl group of **13** ($1.412 \text{ \AA}$) coincided with those of **7** ($1.410 \text{ \AA}$) and **25** ($1.409 \text{ \AA}$). The C–C bond length of the five-membered ring for the 3-guaiazulenyl group of **13** appreciably varied between 1.380 and $1.502 \text{ \AA}$; in

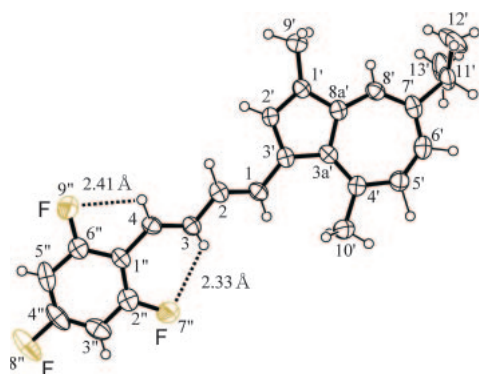


Figure 5. The ORTEP drawing (30% probability thermal ellipsoids) of **13**.

particular, the C1'–C2' bond length for the five-membered ring ($1.380 \text{ \AA}$) was characteristically shorter than the average C–C bond length for the five-membered ring ($1.428 \text{ \AA}$), whose results were similar to those of **7** and **25**. The C1–C2 and C2–C3 bond lengths of **13** were slightly longer than those of **25**, while the C3–C4 bond length of **13** was slightly shorter than that of **25**. The bond alternation pattern observed for the 3-guaiazulenyl and 2,4,6-trifluorophenyl groups of **13** coincided with that of **25**. Although the C4H...F9''C6'' and C3H...F7''C2'' distances of **13** (2.41 and $2.33 \text{ \AA}$) were slightly longer than the C2H...F9''C6'' and C1H...F7''C2'' distances of **7**, the results of which were suggested to form an intramolecular CH...FC hydrogen bond between them. Along with the ORTEP drawing of **13**, the packing molecular structures of **13**, illustrated using a space-filling molecular structure (Figures 6a and 6b) and a ball and stick molecular structure (Figures 6c and 6d), showed that each molecule formed a π -stacking structure and an intermolecular hydrogen bond between C12'H...F8''C4'' (and C13'H...F8''C4'') in the single crystal, and revealed that the average interplane and hydrogen bond distances between the overlapping molecules, which were overlapping so that those dipole moments might be negated mutually, were $3.35 \text{ \AA}$ (for the π -stacking structure) and $2.60 \text{ \AA}$ (for the hydrogen bond). Therefore, an apparent difference between the packing molecular structures of **7** and those of **13** could be observed.

Reactions of **13 and **14** with TCNE.** Quite recently, we reported that the reaction of **25** with 2 equivalents of TCNE in benzene at 25°C for 24 h under argon gave a Diels–Alder

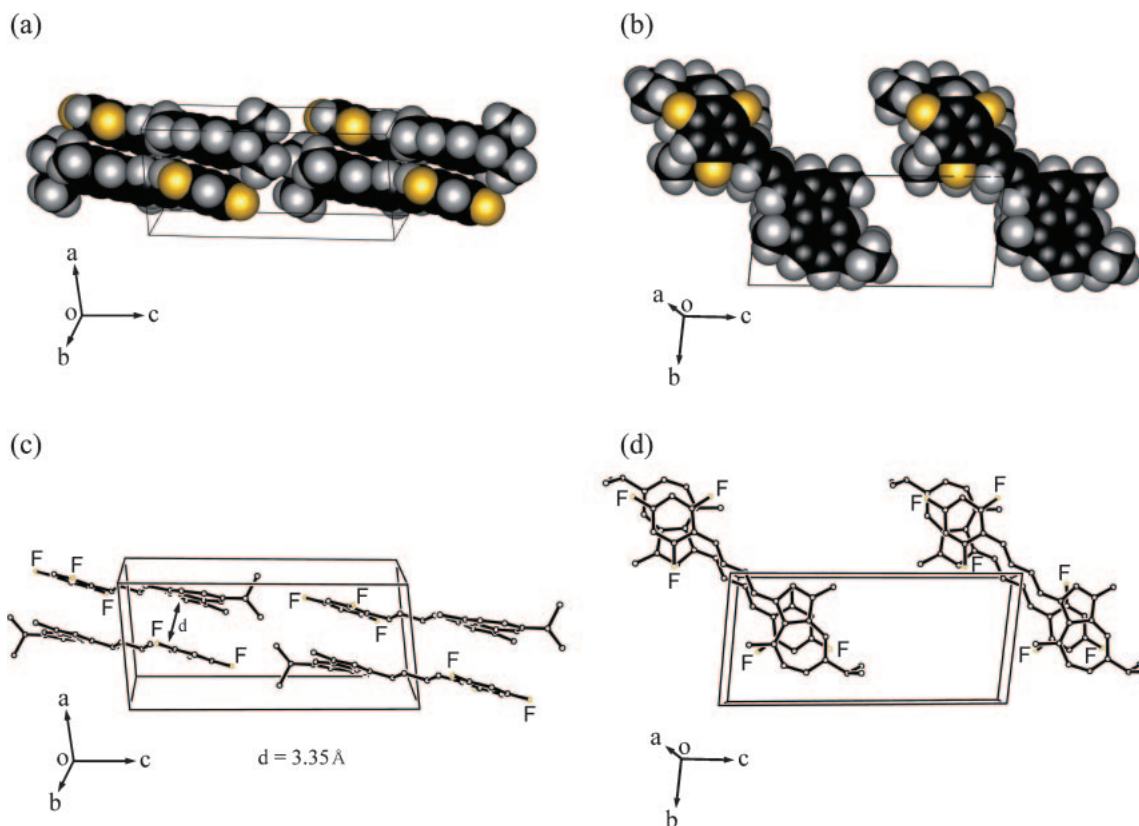
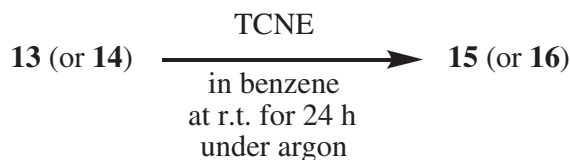


Figure 6. The two different [side (a) and top (b)] views for the packing molecules of the space-filling molecular structure **13**. The two different [side (c) and top (d)] views for the packing molecules of the ball and stick molecular structure **13**. Hydrogen atoms are omitted for reasons of clarity.



Scheme 5. The reaction of **13** (or **14**) with 2 equivalents of TCNE in benzene at 25 °C for 24 h under argon.

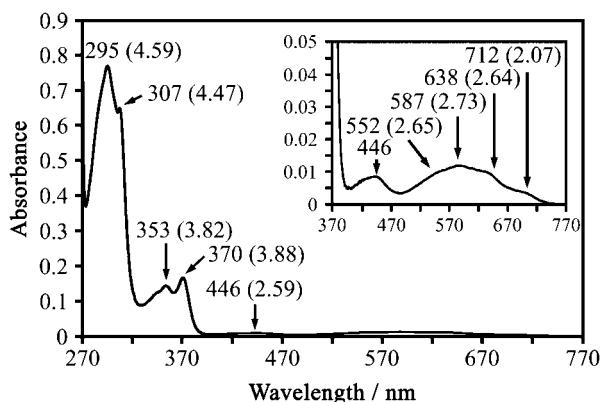


Figure 7. The UV-vis spectrum of **15** in benzene. Concentration, **15**: 0.10 g L⁻¹ (218 μmol). Length of the cell, 0.1 cm. Each log ϵ value is given in parenthesis.

adduct **26** (Chart 3) in 59% isolated yield.²⁷ Along with the spectroscopic properties of **26**, the crystal structure of **26** was determined. For comparative purposes, the reactions of **13** and **14** with 2 equivalents of TCNE were carried out under the same reaction conditions as for **25** (Scheme 5), affording new Diels-Alder adducts **15** and **16** in 66 and 69% isolated yields, the molecular structures of which were established on the basis of similar spectroscopic analyses to those of **13** and **14**. A similar reaction pathway (i.e., $[\pi 4 + \pi 2]$ cycloaddition reaction) to that of **26**²⁷ can be inferred for the formation of the resulting products **15** and **16**.

Compounds **15** and **16** were obtained as a blue powder. Similar to **26**, the characteristic UV-vis absorption bands of **13** were not observed for **15**, while those from guaiazulene³⁴ (**1**) with a band (446 nm, log ϵ = 2.59) were observed as shown in Figure 7 and the longest visible absorption wavelength appeared at λ_{max} 587 nm (log ϵ = 2.73). Similar to **15**, the characteristic UV-vis absorption bands of **14** were not observed for **16**, while those from **1**³⁴ with a band (470 nm, log ϵ = 2.68) were observed as shown in Figure 8 and the longest visible absorption wavelength appeared at λ_{max} 589 nm (log ϵ = 2.90). The IR spectra showed specific bands from the C-H, -C≡N, C=C, and C-F bonds for **15** and specific bands from the C-H, -C≡N, C=C, C=O, and C-O bonds for **16**. The molecular formulas C₃₁H₂₃N₄F₃ (for **15**) and C₃₃H₂₈O₂N₄ (for **16**) were determined by exact FAB-MS spectra. The ¹H NMR (including NOE) and ¹³C NMR spectra showed signals from a 2,4,6-trifluorophenyl and 3-guaiazulenyl group and a *cis*-1,4-disubstituted 5,5,6,6-tetracyano-2-cyclohexene unit for **15** and signals from a 4-(methoxycarbonyl)phenyl and 3-guaiazulenyl group and a *cis*-1,4-disubstituted 5,5,6,6-tetracyano-2-cyclohexene unit for **16**, the signals of which were carefully assigned

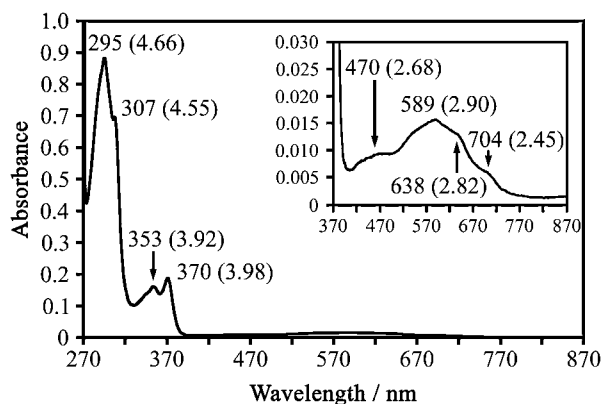


Figure 8. The UV-vis spectrum of **16** in benzene. Concentration, **16**: 0.10 g L⁻¹ (195 μmol). Length of the cell, 0.1 cm. Each log ϵ value is given in parenthesis.

using conventional methodology. Thus, the detailed spectroscopic analyses of **15** and **16** indicated similar structures to that of **26**, illustrated in Chart 3.

Conclusion

We have reported the following three interesting points for the title chemistry: namely, (i) the Wittig reactions in general provide a mixture of *E* and *Z* geometric isomers, while the reactions of 2,4,6-trifluorobenzaldehyde (**5**) [and (*E*)-3-(2,4,6-trifluorophenyl)propanal (**11**)] with the Wittig reagent (3-guaiazulenyl)triphenylphosphonium bromide (**4**) in ethanol containing NaOEt at 25 °C for 24 h under argon gave only *E* (and 2*E*,4*E*)-forms selectively, i.e., (*E*)-1-(3-guaiazulenyl)-2-(2,4,6-trifluorophenyl)ethylene (**7**) and (2*E*,4*E*)-1-(3-guaiazulenyl)-4-(2,4,6-trifluorophenyl)-1,3-butadiene (**13**); (ii) for comparative purposes, the Wittig reactions of methyl 4-formylbenzoate and methyl 4-[(*E*)-2-formylethenyl]benzoate, possessing an electron-withdrawing group (-COOCH₃), with reagent **4** in methanol containing NaOMe at 25 °C for 24 h under argon afforded a mixture of the corresponding geometric isomers, i.e., (*E*)- and (*Z*)-1-(3-guaiazulenyl)-2-[4-(methoxycarbonyl)phenyl]ethylenes and (2*E*,4*E*)- and (2*Z*,4*E*)-1-(3-guaiazulenyl)-4-[4-(methoxycarbonyl)phenyl]-1,3-butadienes, the results of which coincided with those of the reactions of 4-(dimethylamino)benzaldehyde and (*E*)-3-[4-(dimethylamino)phenyl]propanal, possessing an electron-donating group [-N(CH₃)₂], with **4**. A reaction mechanism for the formation of **7** (and **13**) via the *trans*-oxaphosphetane intermediates **a** (and **b**), forming an intramolecular CH...FC hydrogen bond at the two positions illustrated in Chart 4, was proposed; and (iii) along with the spectroscopic properties and the crystal structures of the isolated π -electron systems **7**, **8**, **13**, and **14** compared with those of the previously reported **19** and **25**, the chemical properties of **7**, **8**, **13**, and **14** toward 1,1,2,2-tetracyanoethylene (TCNE) compared with those of **19** and **25**, yielding the resulting cycloaddition products **9**, **10**, **15**, and **16**, were reported.

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- 35 The 2Z,4E-isomer of **14** was observed by silica gel TLC of the reaction mixture, while it could not be isolated using silica gel column chromatography and recrystallization. The 2Z,4E-isomer of **14**: Green paste [$R_f = 0.33$ on silica gel TLC (solv. hexane:ethyl acetate = 9:1, vol/vol) under the same conditions as for **14**]. The TLC analysis of a mixture of the 2E,4E- and 2Z,4E-isomers suggested a ca. 1:1 mixture.