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Original Scientific Article

Photochemical Approach to New Polycyclic Substrates Suitable for Further Photocatalytic Functionalization†

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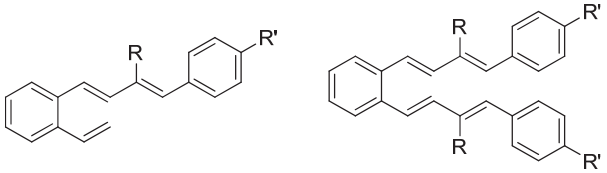
Abstract. New polycyclic compounds are synthesized by photocycloaddition reactions of methoxy, methyl or phenyl substituted butadiene derivatives **11**–**14**. Mono- and dimethoxy butadiene derivatives **11** and **12** undergo intramolecular [2+2] photocycloaddition giving benzobicyclo[3.2.1]octadiene structures (*endo*-**15**, *endo,trans*-**17**) as main products. As minor photoproducts tricyclic compounds *endo*-**16** and *endo,trans*-**18** are isolated, respectively, formed by [4+2] photoinduced cycloaddition of the starting molecules. The reaction of compounds **13** and **14** is more selective and only benzobicyclo[3.2.1]octadienes *endo,endo*-**19** and *endo,endo*-**20** are formed, respectively. New bicyclo[3.2.1]octadienes with isolated double bond can be suitable substrates for further efficient photocatalytic oxygenations in course of new functionalized polycycles, potentially new biologically active compounds.

Keywords: cycloaddition, photochemistry, butadienes, benzobicyclo[3.2.1.]octadiene, polycycles

INTRODUCTION

Photochemistry of mono- and dibutadienyl derivatives **1a**–**2d** (Figure 1) has been studied in detail.[1–3] Unsubstituted starting compounds **1a** and **2a**, upon irradiation at 350 nm, give as the main products of intramolecular cycloaddition benzobicyclo[3.2.1]octadiene structures *endo*-**3** and *endo,trans*-**4**, respectively.[1,2] The bicyclo[3.2.1]octane skeleton, saturated analogue of the bicyclo[3.2.1]octadiene, is found in numerous biologically important active natural products.[4–20] Moreover, benzobicyclo[3.2.1]octadiene skeleton is also an important fragment in biologically active compounds or it can be used as a suitable substrate for further transformations on the isolated double bond, easily derivatized to new compounds with various functionalities.[21–27]



1a: R = H, R' = H
b: R = CH_3, R' = H
c: R = Cl, R' = H
d: R =H, R' = Cl

2a: R = H, R' = H
b: R = CH_3, R' = H
c: R = Cl, R' = H
d: R =H, R' = Cl

Figure 1. Structures of the known butadiene derivatives.

As a part of our increasing interest in the photochemistry of conjugated butadiene systems and to explore the effect of substituents on the butadiene units on the photochemical reactions, studies are expanded to methyl- and chloro-butadiene derivatives **1b**–**d** and **2b**–**d**.[2,3] Methyl group effects sterically to photochemical reactions, causing diverse photoinduced behaviour and formation of completely different photoproducts.[2] Monosubstituted methyl derivative **1b** upon irradiation gives dihydronaphtalene derivative **5** (Figure 2), while disubstituted methyl derivative **2b** shows only geometric isomerization. Introduction of the chlorine atom to butadiene unit can lead the reaction course to various direction, under its steric and electronic effects. Upon irradiation, mono- and di-α-chloro derivatives **1c** and **2c** photocyclize to give six-membered ring products **6** and **7**.[3] In continuation of our studies on photochemical behaviour of butadiene derivatives we extended research to *p*-substituted chloro derivatives **1d** and **2d**.[3] The *p*-substitution increases molecular planarity, relative to α-substitution and shift conformer equilibrium, affecting the reaction pathways and yields. As the main products upon irradiation of *p*-chloro-butadiene derivatives **1d** and **2d** new benzobicyclo[3.2.1]octa-diene structures *endo*-**8** and

† Dedicated to Dr. Mirjana Eckert-Maksić on the occasion of her 70th birthday.
* Author to whom correspondence should be addressed. (E-mail: irena.skoric@fkit.hr)

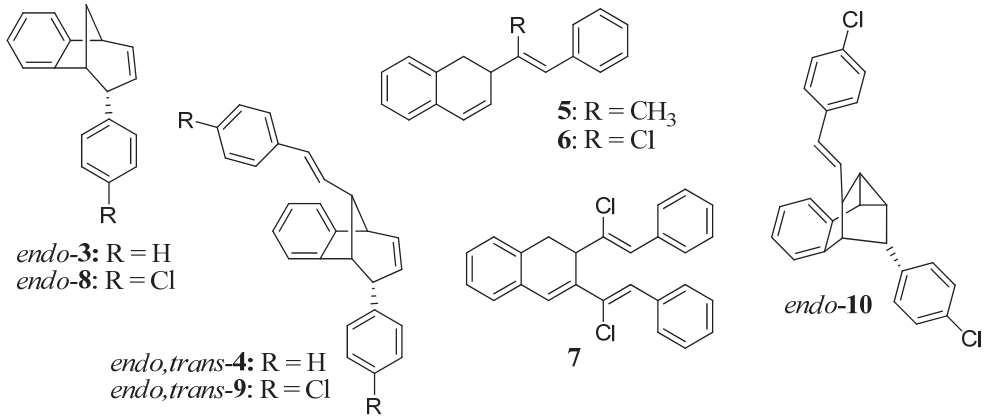


Figure 2. Structures of the isolated photoproducts.

endo,trans-**9** are formed in very good yields, with smaller amounts (10 %) of dihydronaphtalene derivative *endo*-**10** in case of **2d** (Figure 2).

Starting compounds **1a**–**2d** (Figure 1) possess very similar structures. Under steric and electronic effect of substituents, different products are formed. Therefore, understanding the influence and nature of substituents in the molecule is crucial for understanding the preffered reaction path and for prediction the behaviour of similar unresearched related compounds.

In the continuation of our research on photochemical behaviour of butadiene derivatives, we inserted one or two methoxy groups (as strong electron donating groups) to the *p*-position(s) of the aromatic ring(s) of the investigated compounds **11** and **12** (Figure 3). To explore the effect of methyl or phenyl group in the *β*-position of the *o*-vinyl group of **1a** (Figure 1) on photochemical behaviour, butadiene derivatives **13** and **14** (Figure 3) are prepared as related compounds to the molecule of **1a** (Figure 1), also in course of the investigation the effect of substitution.

EXPERIMENTAL

General Experimental Information

The ^{1}H spectra were recorded on a spectrometer at 600 MHz. The ^{13}C NMR spectra were registered at 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. UV spectra were measured on a UV/VIS Cary 50 spectrophotometer. IR spectra were recorded on a FTIR-ATR (film). Irradiation experiments were preformed in a Quartz vessel in toluene solution in a photochemical reactor equipped with 3500 Å lamps. All irradiation experiments were carried out in deaerated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using microscope equipped apparatus and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyzer) equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive (H+) or negative (H−) ion reflector mode. Silica gel (0.063−0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed silica gel 60 F_{254} plates. Solvents were purified by distillation.

Benzaldehyde and *p*-methoxy-cinnamaldehyde were obtained from a commercial source, *β*,*β*-*o*-xylyl(ditriphenylphosphonium) dibromide was prepared from *o*-xylyldibromide and triphenylphosphine in dimethylformamide.

The starting compounds 1-(*p*-methoxyphenyl)-4-(*o*-styryl)-1,3-butadiene **(11)**, 1-{*o*-[-4-(*p*-methoxyphe-nyl)-1,3-butadienyl]phenyl}-4-(*p*-methoxyphenyl)-1,3-butadiene **(12)** and (1*E*,3*E*)-1-{*o*-[(*E*)-1-propenyl]phenyl}-4-phenyl-1,3-butadiene (*trans,trans*-**13**) are described.[3] The data of the new compounds are given below.

*(1Z,3*E*)-1-[(Z)-2-Stilbenyl]-4-phenyl-1,3-butadiene (*cis,cis-***14***)*

Starting compound **14** was prepared by Wittig reaction from *o*-xylylbis(triphenylphosphonium bromide) and

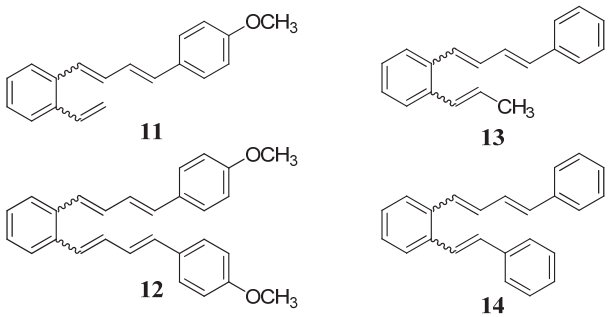


Figure 3. Structures of the starting butadiene derivatives **11**−**14**.

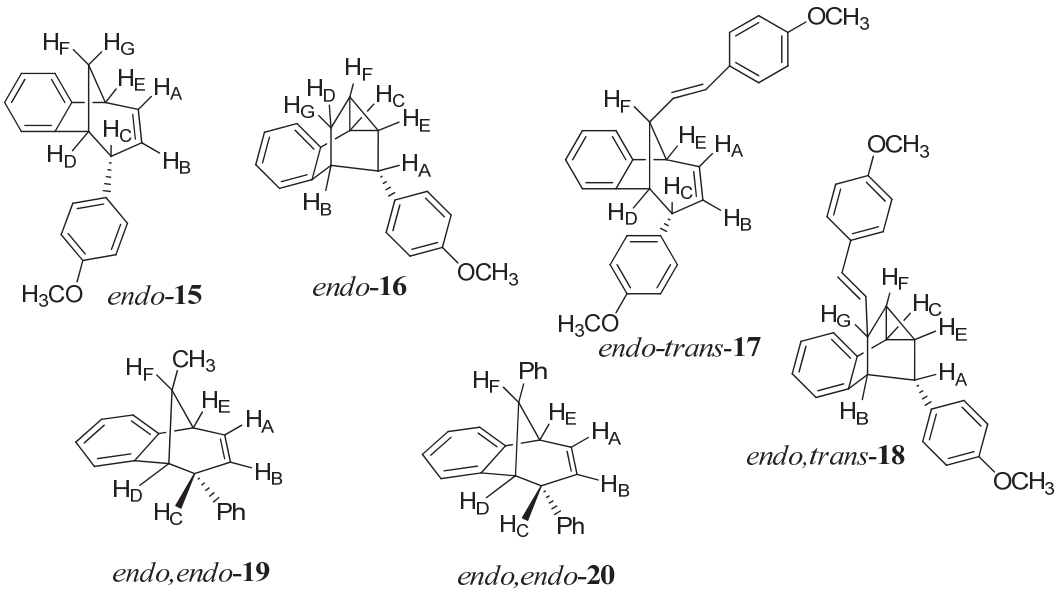


Chart 1.

cinnamaldehyde. To a stirred solution of the triphenylphosphonium salt (0.001 mol) and the cinnamaldehyde (0.011 mol) in absolute ethanol (200 mL), a solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for one hour at RT, when was 1.1 eq of benzaldehyde (0.011 mol) introduced and the next quantity of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was completed within 3−4 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and toluene. The toluene extracts were dried (anhydrous $MgSO_4$), concentrated and the crude reaction mixture was purified. The reaction mixture contained *cis,cis*-, *cis,trans*-, *trans,cis*- and *trans,trans*-isomers in the ratio 3:2:2:3. After repeated column chromatography on silica gel using petroleum ether as the eluent only the *cis,cis*-**14** was isolated and completely characterized.

cis,cis-**14**: yield 30 %; R_f 0.88 (petroleum ether/dichloromethane = 1:1); colourless oil; UV (96 % EtOH) λ_{max} / nm: 284 and 254 (log ε / dm^3 mol^{-1} cm^{-1}: 3.78 (sh) and 3.93); IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 3016, 2923, 1492, 1446, 1218, 958, 774, 692; ^{1}H NMR ($CDCl_3$; 300 MHz) δ/ppm: 7.41 (d, 1H, J = 7.6 Hz), 7.33 (d, 2H, J = 7.5 Hz), 7.24–7.29 (m, 4H), 7.20 (t, 1H, J = 7.6 Hz), 7.07–7.18 (m, 7H), 6.65 (d, 1H, J = 15.6 Hz), 6.63 (d, 1H, J = 12.2 Hz), 6.61 (d, 1H, J = 12.2 Hz), 6.56 (d, 1H, J = 11.3 Hz), 6.40 (t, 1H, J = 11.3); ^{13}C NMR ($CDCl_3$; 75 MHz) δ/ppm: 137.4 (s), 136.9 (2s), 136.3 (s), 134.4 (d), 130.9 (d), 130.8 (d), 130.0 (d), 129.4 (d), 129.4 (d), 129.2 (d), 129.0 (2d), 128.6 (2d), 128.1 (2d), 127.6 (d), 127.1 (2d), 127.0 (d), 126.6 (2d), 125.5 (d); HRMS (TOF ES$^+$) m/z for $C_{24}H_{20}$: M^+_{calcd} 308.1559; M^+_{found} 308.1559.

Irradiation Experiments

A mixture of isomers of **11**–**14** in toluene ($3.0\cdot10^{-3}$ M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 16 h (**11**), 96 h (**12**), 4 h (**13**) and 8 h (**14**). After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The photoproducts *endo*-**15**, *endo*-**16** (obtained from **11**), **17**, **18** (from **12**), *endo,endo*-**19** (from **13**) and *endo,endo*-**20** (from **14**) (Chart 1) were isolated from the enriched first chromatographic fractions followed by a mixture of several unidentified products (< 2 %). High-molecular-weight products remained on the column.

*(11*S*)-11-(4-methoxyphenyl)tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (*endo-***15***):*
Yield 55 %; R_f 0.27 (petroleum ether/dichloromethane = 8:2); colourless crystals; m.p. 45−47 °C; UV (96 % EtOH) λ_{max}/nm: 284, 276, 269 and 226 (log ε / dm^3 mol^{-1} cm^{-1}: 3.55, 3.67, 3.65 and 4.16); IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 2952, 1605 (C=C, ar), 1510 (C=C), 1249 (C_{ar}−O−CH_3), 1174, 1035, 771; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.11 (d, 1H, J = 7.3 Hz), 7.03 (dt, 1H, J = 7.3 Hz; 1.0 Hz), 6.82 (dt, 1H, J = 7.3 Hz; 1.0 Hz), 6.72 (d, 2H, J = 8.6 Hz), 6.64 (d, 2H, J = 8.6 Hz), 6.32−6.36 (m, 1H, H_A), 6.25 (d, 1H, J = 7.3 Hz), 5.28 (dt, 1H, H_B, J_{AB} = 9.6 Hz; J_{BC} = 2.6 Hz), 3.91−3.94 (m, 1H, H_C), 3.77 (s, 3H, -OCH_3), 3.35 (t, 1H, $J_{DC} = J_{DF}$ = 4.5 Hz, H_D), 3.27 (dd, 1H, J_{EA} = 6.3 Hz;

J_{EF} = 4.7 Hz, H_E), 2.49−2.53 (m, 1H, H_F), 2.37 (d, 1H, J_{GF} = 9.9 Hz, H_G); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 157.6 (s), 152.0 (s), 141.7 (s), 134.2 (s), 134.1 (d), 128.8 (2d), 126.3 (d), 125.8 (d), 125.5 (d), 124.5 (d), 119.6 (d), 112.6 (2d), 43.7 (t); HRMS (TOF ES$^+$) *m*/*z* for $C_{19}H_{18}O$: M^+_{calcd} 262.1352; M^+_{found} 262.1351.

*(10S)-10-(4-methoxyphenyl)tetracyclo[7.2.1.0^{2,11}.0^{3,8}]dodeca-3,5,7-triene (*endo-***16***)*

Yield 13 %; R_f 0.21 (petroleum ether/dichloromethane = 8:2); colourless crystals; m.p. 91−93 °C; UV (96 % EtOH) λ_{max}/nm: 285, 277, 270 and 227 (log ε / dm^3 mol^{-1} cm^{-1}: 4.10, 3.27, 3.19 and 4.18); ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.26 (d, 1H, *J* = 7.4 Hz), 7.06 (dt, 1H, *J* = 7.4 Hz; 0.8 Hz), 6.89 (dt, 1H, *J* = 7.4 Hz; 0.8 Hz), 6.79 (d, 2H, *J* = 8.6 Hz), 6.66 (d, 1H, *J* = 7.4 Hz), 6.55 (d, 2H, *J* = 8.6 Hz), 3.65 (s, 3H, -OCH_3), 3.37 (dd, 1H, J_{AB} = 4.6 Hz; J_{AE} = 2.8 Hz, H_A), 3.16 (t, 1H, J_{AB} = J_{BD} = 4.6 Hz, H_B), 2.33 (t, 1H, J_{CE} = J_{CF} = 7.2 Hz, H_C), 2.12 (ddd, 1H, J_{DG} = 11.7 Hz; J_{BD} = 4.6 Hz; J_{DF} = 2.8 Hz, H_D), 1.88 (dt, 1H, J_{CE} = J_{EF} = 7.2 Hz; J_{AE} = 2.8 Hz, H_E), 1.77 (dt, 1H, J_{CE} = J_{EF} = 7.2 Hz; J_{AE} = 2.8 Hz, H_F), 1.19 (d, 1H, J_{DG} = 11.7 Hz, H_G); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 157.0 (s), 136.3 (s), 135.2 (s), 132.3 (s), 128.0 (2d), 125.3 (d), 124.9 (d), 124.5 (d), 123.8 (d), 112.5 (2d), 29.5 (t).

*(11*S*)-11-(4-methoxyphenyl)-12-[(*E*)-2-(4-methoxyphenyl)ethenyl]tricyclo[6.3.1.0^{2,7}] dodeca-2,4,6,9-tetraene (*endo,trans-***17***)*

Yield 24 %; R_f 0.22 (petroleum ether/dichloromethane = 8:2); colourless oil; UV (96 % EtOH) λ_{max}/nm: 260 and 229 (log ε / dm^3 mol^{-1} cm^{-1}: 4.28 and 4.22); IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 3021, 1607 (C=C, ar), 1510 (C=C), 1247 (C_{ar}−O−CH_3), 1034, 833, 737; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.32 (d, 2H, *J* = 8.5 Hz), 7.14 (d, 1H, *J* = 7.3 Hz), 7.07 (dt, 1H, *J* = 7.3; 0.9 Hz), 6.95 (d, 2H, *J* = 8.5 Hz), 6.83−6.88 (m, 2H), 6.72 (d, 2H, *J* = 8.7 Hz), 6.65 (d, 2H, *J* = 8.7 Hz), 6.41 (ddd, 1H, *J* = 8.3; 3.2; 2.5 Hz), 6.25−6.29 (m, 2H), 5.32−5.33 (m, 1H), 3.97−4.00 (m, 2H, H_C), 3.85 (s, 3H, -OCH_3), 3.77 (s, 3H, -OCH_3), 3.75–3.79 (m, 1H, H_D), 3.24 (d, 1H, *J* = 4.7 Hz, H_E / H_F), 3.20 (d, 1H, *J* = 6.6 Hz, H_E / H_F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 158.0 (s), 157.7 (s), 150.5 (s), 150.2 (s), 140.0 (s), 139.7 (s), 134.1 (d), 132.7 (d), 129.5 (2d), 128.9 (2d), 128.2 (d), 126.8 (d), 126.7 (d), 126.7 (d), 126.5 (d), 125.9 (d), 125.9 (d), 124.9 (d), 124.8(d), 120.7 (d), 113.3 (q), 112.7 (q), 54.7 (d), 53.7 (d), 46.4 (d), 45.8 (d); HRMS (TOF ES$^+$) *m*/*z* for $C_{28}H_{26}O_2$: $[M+K]^+_{calcd}$ 433.1564; $[M+K]^+_{found}$ 433.1581.

*(10*S*)-10-(4-methoxyphenyl)-12-[(*E*)-2-(4-methoxyphenyl)ethenyl]tetracyclo [7.2.1.0^{2,11}.0^{3,8}]dodeca-3,5,7-triene (*endo,trans-***18***)*

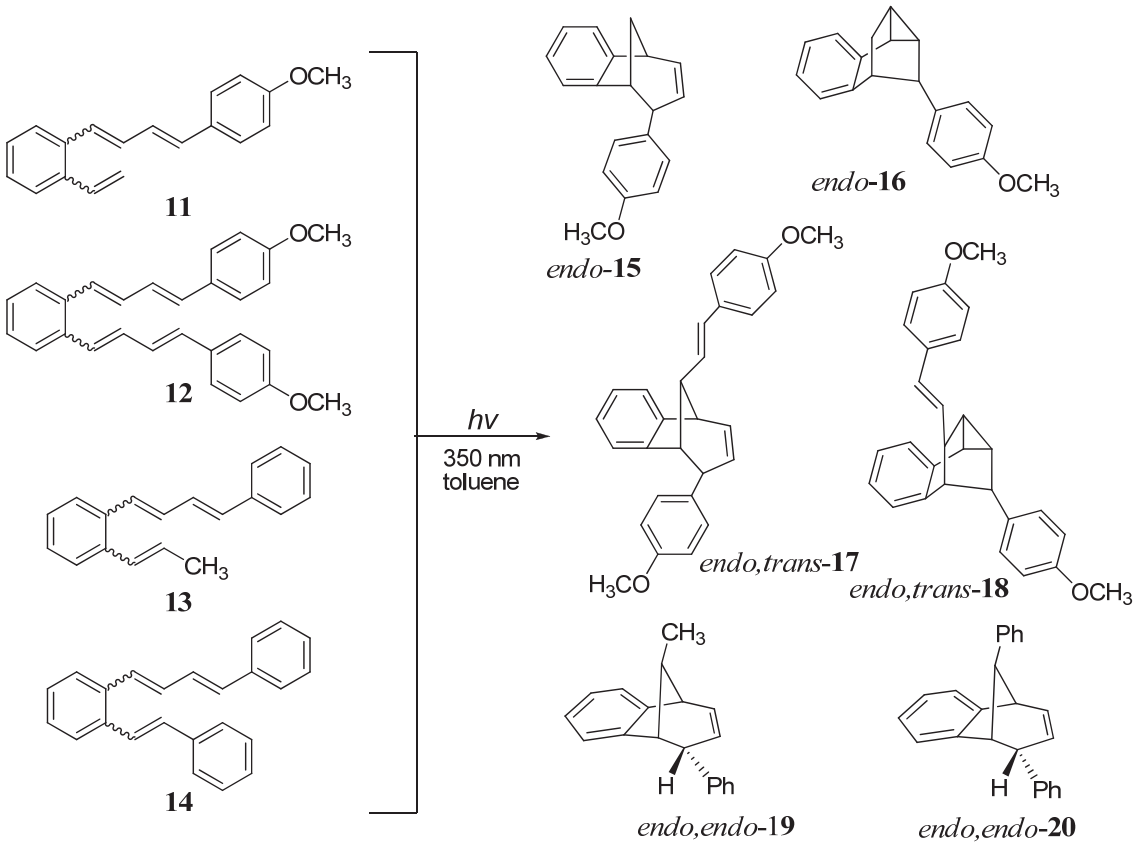
Yield 7 %; R_f 0.20 (petroleum ether/dichloromethane = 8:2); colourless oil; UV (96 % EtOH) λ_{max}/nm: 274, 264 and 230 (log ε / dm^3 mol^{-1} cm^{-1}: 4.24 (sh), 4.33 and 4.14); IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 2922, 1606 (C=C, ar), 1510 (C=C), 1247 (C_{ar}−O−CH_3), 1076, 1033, 964; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.28 (d, 1H, *J* = 7.6 Hz), 7.06 (dt, 1H, *J* = 7.6; 1.0 Hz), 7.00 (d, 2H, *J* = 8.7 Hz), 6.88 (dt, 1H, *J* = 7.6; 1.0 Hz), 6.80 (d, 2H, *J* = 8.7 Hz), 6.71 (d, 2H, *J* = 8.7 Hz), 6.61 (d, 1H, *J* = 7.6 Hz), 6.56 (d, 2H, *J* = 8.7 Hz), 6.32 (d, 1H, *J* = 15.7 Hz), 5.25 (dd, 1H, *J* = 15.7; 8.2 Hz), 3.73 (s, 3H, -OCH_3), 3.66 (s, 3H, -OCH_3), 3.51−3.54 (m, 1H, H_A), 3.20 (t, 1H, *J* = 4.6 Hz, H_B), 3.11–3.16 (m, 1H, H_G), 2.40 (t, 1H, *J* = 7.1 Hz, H_C), 1.95 (dt, 1H, *J* = 6.4; 1.8 Hz, H_E), 1.81 (dt, 1H, *J* = 6.4; 1.8 Hz, H_F); ^{13} C NMR ($CDCl_3$, 75 MHz) δ/ppm: 158.4 (s), 157.6 (s), 136.4 (s), 133.3 (s), 132.2 (s), 130.6 (d), 129.8 (d), 129.0 (d), 128.6 (2d), 127.1 (d), 126.8 (d), 126.0 (d), 125.2 (d), 124.5 (d), 113.7 (d), 113.7 (d), 112.9 (2d), 55.3 (d), 55.0 (d), 48.3 (d), 43.8 (d), 38.8 (d), 22.7 (d), 21.5 (d), 17.9 (d); HRMS (TOF ES$^+$) *m*/*z* for $C_{28}H_{26}O_2$: M^+_{calcd} 394.1927; M^+_{found} 394.1920.

*(11*S*)-12-methyl-11-phenyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (*endo,endo-***19***)*

Yield 77 %; R_f 0.88 (petroleum ether/dichloromethane = 1:1); colourless oil; UV (96 % EtOH) λ_{max}/nm: 324, 275, 268 and 259 (log ε / dm^3 mol^{-1} cm^{-1}: 2.94, 3.00, 3.02 and 2.96 (sh)); IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 3025, 1601, 1495, 1450, 1218, 1032, 755, 698; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.14–7.18 (m, 3H), 7.10 (d, 1H, *J* = 7.4 Hz), 7.03 (dt, 1H, *J* = 7.4; 0.8 Hz), 6.80 (dt, 1H, *J* = 7.4; 0.8, Hz), 6.70−6.74 (m, 2H), 6.36–6.42 (m, 1H, H_A), 6.16 (d, 1H, *J* = 7.4 Hz), 5.30–5.32 (m, 1H, H_B), 3.96–4.00 (m, 1H, H_C), 3.04 (d, 1H, *J* = 4.8 Hz, H_D), 2.96 (d, 1H, *J* = 6.6 Hz, H_E), 2.75 (dd, 1H, *J* = 6.6, 13.1 Hz, H_F), 0.93 (d, 3H, *J* = 6.6 Hz, -CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 150.5 (s), 141.9 (s), 139.8 (s), 135.1 (d), 127.9 (2d), 127.1 (2d), 126.9 (d), 125.8 (d), 125.7 (d), 125.6 (d), 124.6 (d), 120.9 (d), 55.0 (d), 49.1 (d), 47.1 (d), 46.7 (d), 17.8 (q); HRMS (TOF ES$^+$) *m*/*z* for $C_{19}H_{18}$: $[M-H]^-_{calcd}$ 245.1325; $[M-H]^-_{found}$ 245.1329.

*(11*S*)-11,12-diphenyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (*endo,endo-***20***)*

Yield 45 %; R_f 0.88 (petroleum ether/dichloromethane = 1:1); UV (96 % EtOH) λ_{max}/nm: 278 and 253 (log ε / dm^3 mol^{-1} cm^{-1}: 3.55 (sh) and 3.71; IR $\tilde{\nu}_{max.}$/cm^{-1} (evaporated from CH_2Cl_2): 3022, 2956, 1452, 1375, 1016, 746, 701; ^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm: 7.16–7.20 (m, 3H), 7.12 (d, 2H, *J* = 7.6 Hz), 7.08 (d, 2H, *J* = 7.6 Hz), 7.03 (d, 2H, *J* = 7.6 Hz), 7.00−7.03 (m, 1H), 6.80 (dt, 1H, *J* = 7.7; 0.9 Hz), 6.75–6.78 (m, 2H), 6.50–6.55 (m, 1H, H_A), 6.15 (d, 1H, *J* = 7.3 Hz), 5.42 (ddd, 1H, *J* = 9.7; 3.5; 1.7 Hz, H_B), 4.16–4.20 (m, 1H, H_C), 3.88 (s, 1H, H_F), 3.57 (d, 1H, *J* = 4.7 Hz, H_D), 3.48 (d, 1H, *J* = 6.7 Hz, H_E); ^{13}C NMR ($CDCl_3$, 150 MHz)



Scheme 1.

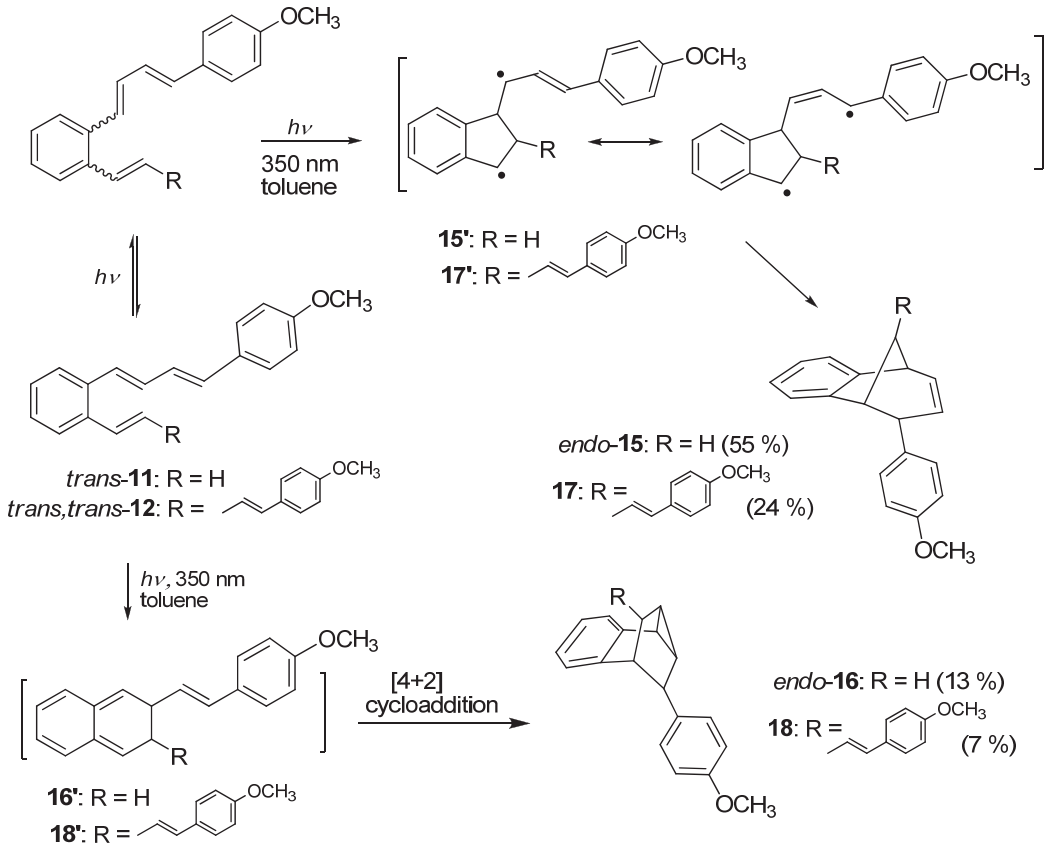
δ/ppm: 150.5 (s), 143.6 (s), 141.8 (s), 139.8 (s), 135.2 (d), 128.0 (2d), 127.6 (d), 127.3 (2d), 126.9 (d), 126.3 (d), 126.24 (d), 126.22 (d), 126.1 (2d), 125.9 (d), 125.5 (d), 124.9 (d), 120.4 (d), 58.8 (d), 54.2 (d), 47.6 (d), 46.6 (d). HRMS (TOF ES$^+$) *m*/*z* for $C_{24}H_{20}$: $[M-H]^-_{calcd}$ 307.1481; $[M-H]^-_{found}$ 307.1493.

RESULTS AND DISCUSSION

Starting compounds **11**–**14** are prepared by Wittig reaction according to the procedure described for butadienes in previous papers[1–3] from *o*-xylylbis(triphenylphosphonium bromide) and corresponding aldehydes. The products are obtained as mixture of two (in case of **11**), three (in case of **12**) or four (in case of **13** and **14**) isomers and subjected to irradiation. Irradiation experiments are performed in Rayonet reactor at 350 nm in toluene solutions under anaerobic conditions at low concentrations. Obtained photoproducts are isolated and completely characterized by spectroscopic methods.

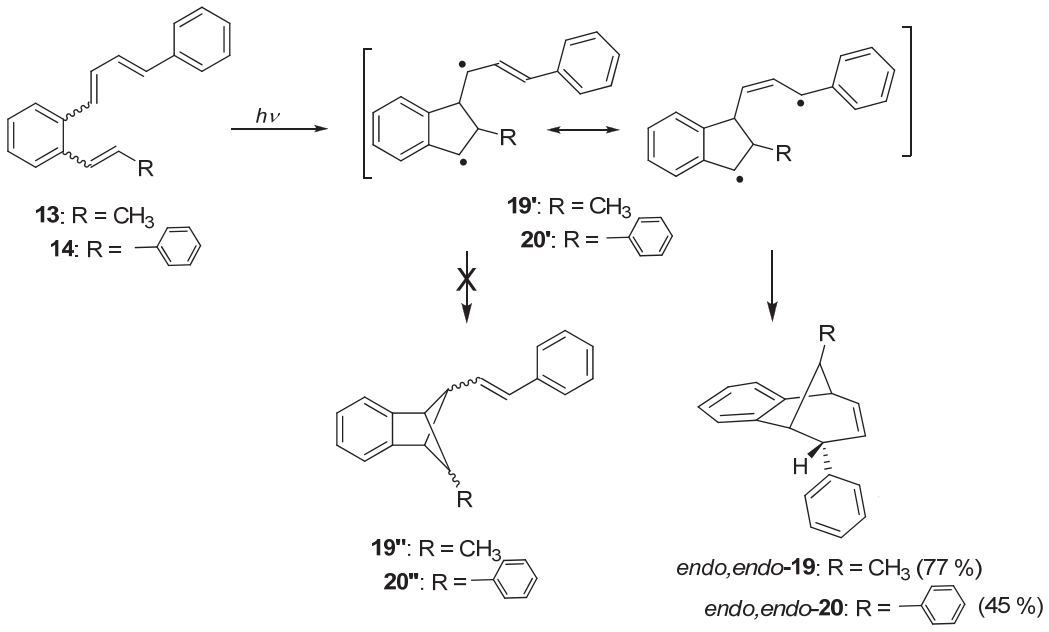
Mono- and di-methoxy derivatives **11** and **12** undergo photochemical reaction to form new polycyclic structures **15**–**18** (Scheme 1). On irradiation of monomethoxy derivative **11**, bicyclic derivative **15** was isolated as main product (55 %), with 13 % of tricyclic derivative **16**, while the high-molecular-weight products remained on the column (Scheme 1). The proposed mechanism of the formation of benzobicyclo[3.2.1] structure **15** involves intramolecular [2+2] cycloaddition *via* biradical intermediate **15'** followed by preffered 1,6 ring closure. Photoproduct **16** can be formed by 6π electrocyclization process followed by [4+2] cycloaddition of the intermediate **16'** (Scheme 2).

Inserting a second styryl substituent at the *β*-position of the vinyl group of **1a** (Figure 1), we prepared dimethoxy derivative **12** and obtained the system with extended conjugation, which can influence on the reaction course. Irradiation of compound **12** under the same conditions gave, after chromatograpfic separation on silica gel, very similar results (Scheme 2). Benzobicyclo[3.2.1]octadiene **17** and tricyclic derivative **18** were isolated. Their formation can be explained by the same mechanism as in the previous case of monomethoxy derivative **11**. The difference in photochemical behaviour between mono- and dimethoxy-derivative is the prolonged time of irradiation to the full conversion in case of **12**. This may be caused by insertion of the second styryl group, which might have influence on the additional stability of the starting molecule **12** in comparison to **11**.



Scheme 2.

Irradiation of starting compounds **13** and **14** gave different results. Under irradiation starting compounds **13** and **14** react giving new bicyclic cycloaddition products, interesting for further functionalization as it was shown for previously synthesized hetero-bicyclic photoproducts.[21–23] After chromatographic purification of crude reaction mixture, only bicyclo derivatives **19** and **20** were isolated, respectively (Scheme 3.) The mecha-



Scheme 3.

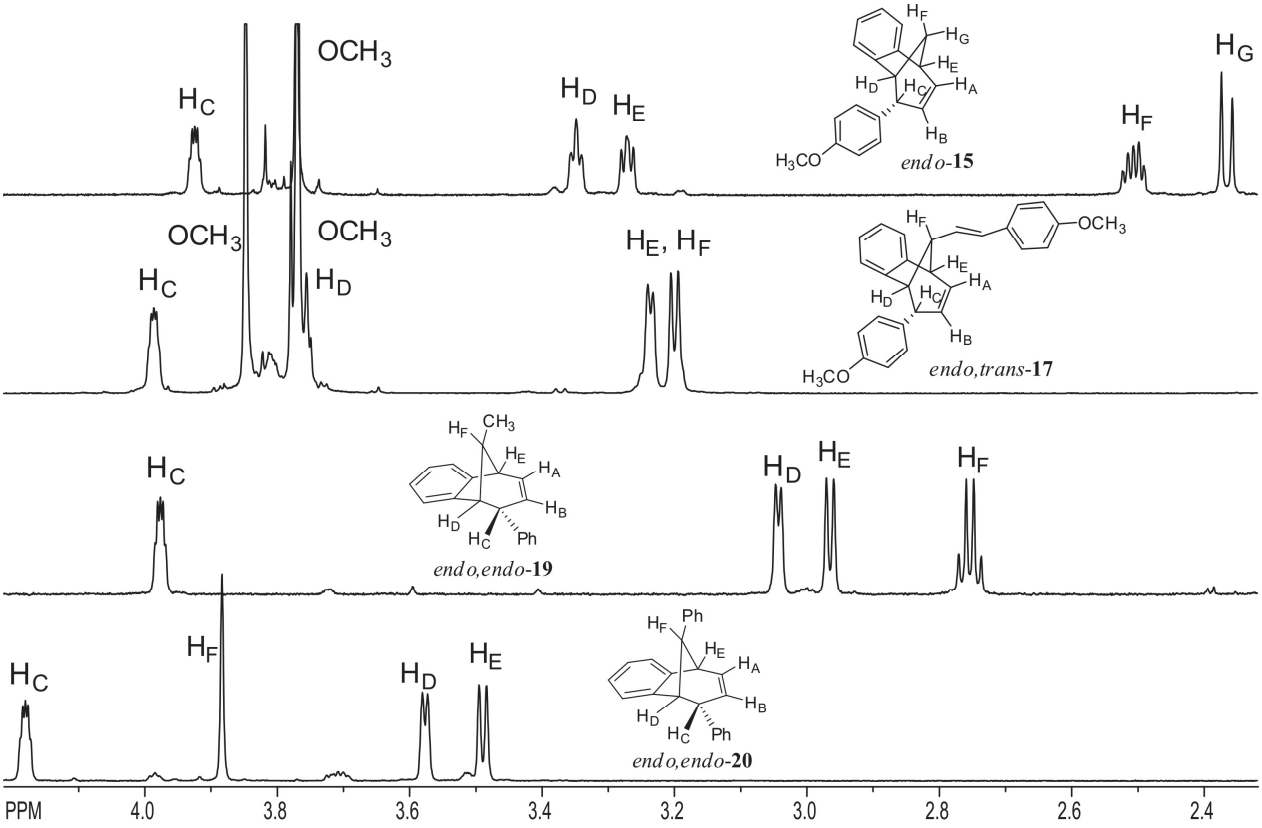


Figure 4. Part of ^{1}H NMR spectra of *endo*-**15**, *endo,trans*-**17**, *endo,endo*-**19** and *endo,endo*-**20** ($CDCl_3$, 600 MHz).

nism of their formation, as seen previously, involves intramolecular [2+2] cycloaddition and 1,6 ring closure of intermediate **19'** or **20'**. Benzobicyclo[2.1.1] hexene derivative **21** or **22**, which could be formed by 1,4-ring closure of **13** or **14**, was not detected.

The structures of new photoproducts have been elucidated from their spectral data, ^{1}H NMR being most informative. Figure 4 shows comparison of aliphatic region of isolated bicyclic derivatives *endo*-**15**, *endo,trans*-**17**, *endo,endo*-**19** and *endo,endo*-**20**. The recognizable pattern of ^{1}H NMR spectra of photoproducts in the region between 2.4 and 4.2 ppm indicates the same bicyclo[3.2.1]octadiene structure. Depending on substitution at the *β*-position of the vinyl group, the aliphatic protons are shifted to higher or lower field. Protons of compounds *endo,trans*-**17** and *endo,endo*-**19**, which possess the second phenyl group are deshielded and shifted to lower field in comparison to protons of *endo*-**15** and *endo,endo*-**20**. The accent is on H_F proton, which is shifted from 2.5 ppm (in *endo*-**15)** to 3.2 ppm (*endo,trans*-**17**) and from 2.8 ppm (*endo,endo*-**19**) to 3.9 ppm (*endo,endo*-**20**). Tricyclic derivatives *endo*-**16** and *endo,trans*-**18** has a completely different pattern in ^{1}H NMR spectrum (Figure 5) compared to bicyclic photoproducts. Patterns of aliphatic protons of both derivatives are very similar. The difference is disappearance of H_D proton in *endo,trans*-**18** due to the entry of the second styryl or benzyl group to the molecule. For the same reason proton H_G is strongly shifted to lower field from 1.2 ppm in *endo*-**16** to 3.1 ppm in *endo,trans*-**18**.

Methoxy group might have electronic and/or steric effects on the photochemical behaviour of the analyzed compound. But the results obtained under irradiation of mono-methoxy derivative **11** in comparison with previously reported unsubstituted **1a** and chloro-derivative **1d** are very similar. In all cases benzobicyclo[3.2.1]octadiene structures *endo*-**3**, *endo*-**8** and *endo*-**15** are isolated, respectively, as main product. Besides, methoxy derivative **11** gives tricyclic derivative *endo*-**16**. The yield on the isolated bicyclic derivative is the largest by use of the unsubstituted compound (90 %) where the steric and electronic effects are reduced. In case of chloro derivative the yield of the isolated product (77 %) is slightly higher compared to the methoxy compound *endo*-**15** (55 %), having potentially increased steric and electronic influence relative to a chlorine atom. Electronic effects may have influence on the reaction course, as in the case of methoxy derivative the reaction was less selective giving two photoproducts, in contrary to the previously described derivatives, where only the bicyclo derivative is isolated. In case of dibutadiene derivatives, unsubstituted compound **2a** under

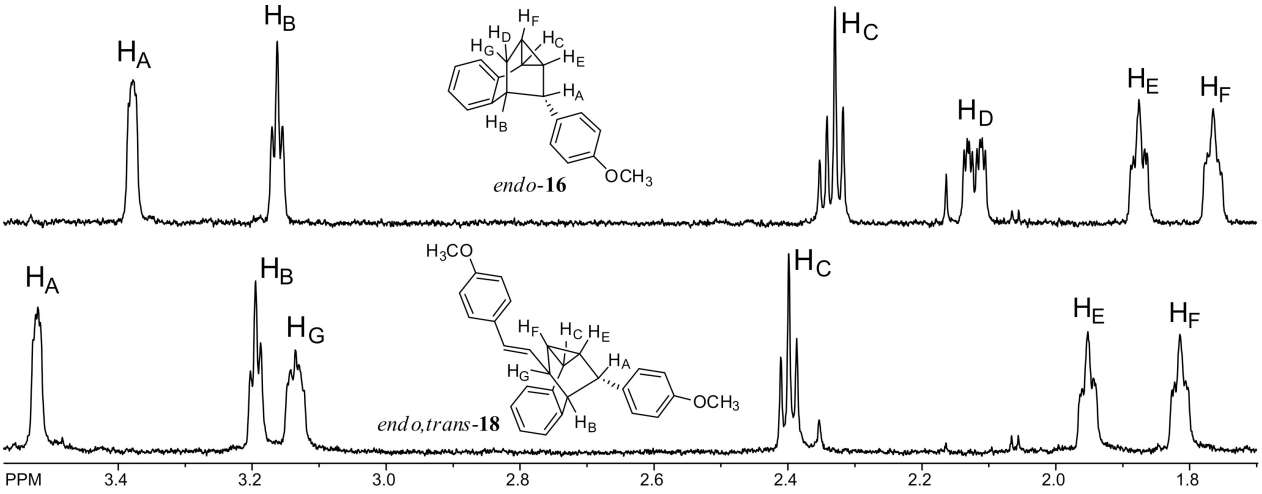


Figure 5. Part of ^{1}H NMR spectra of *endo*-**16** and *endo,trans*-**18** ($CDCl_3$, 600 MHz).

irradiation gives only benzobicyclo[3.2.1]octadiene structure (*endo,trans*-**4**). Chloro and methoxy derivatives, due to their different steric and electronic effect give the same type of products, benzobicyclo[3.2.1]octadiene structure (*endo,trans*-**9**, *endo,trans*-**17**) and tricyclic derivative (*endo*-**10**, *endo,trans*-**18**). On the other hand compounds **13** and **14** under irradiation behave as the unsubstituted derivative **1a** giving selectively only bicyclic structures *endo,endo*-**19** and *endo,endo*-**20**, respectively, but in lower yields.

In cases of all bicyclic photoproducts the ring closure predominantly gives *endo*-isomers. The stereoselectivity of the cycloaddition reaction and preferable ring closure to *endo*-isomer can be ascribed to the stabilization of the transition state in *endo*-orientation by the strong attractive intramolecular π-π interactions of the benzo-phenyl.[30–32]

CONCLUSION

Different substituted butadiene derivatives under irradiation show not so diverse mechanism of photochemical behavior but with different selectivity and yields. Considering the nature and the position of the substituents, new polycyclic structures are formed. Starting materials **13** and **14** under irradiation give stereospecific reaction to benzobicyclo[3.2.1]octadiene structure of *endo,endo*-**19** and *endo,endo*-**20**, respectively. On the other hand, methoxy derivatives **11** and **12** are less selective. Besides [2+2] cycloaddition to benzobicyclo[3.2.1]octadiene structures *endo*-**15** and *endo,trans*-**17**, they react in photoinduced [4+2] cycloaddition giving tricyclic derivatives (*endo*-**16** and *endo,trans*-**18**) as minor products. Understanding the effects of substituents is very important in the field of preparative photochemistry and predicting the mechanism and yields. The slightly change on the structure of starting materials affected the selectivity, stereoselectivity and the reaction course leading to bicyclic photoproducts in moderate to good yields (24−77 %). All new prepared and fully characterized bicyclic molecules are suitable substrates for further efficient photocatalytic oxygenation reactions in course of getting new functionalized polycycles, potentially biologically more active compounds with greater similarity to the structure of some naturally occurred terpenes.

Supplementary Materials. – Supporting informations to the paper are enclosed to the electronic version of the article. These data can be found on the website of *Croatica Chemica Acta* (http://public.carnet.hr/ccacaa).

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Synthesis of new polycyclic structures by photoirradiation of butadiene derivatives

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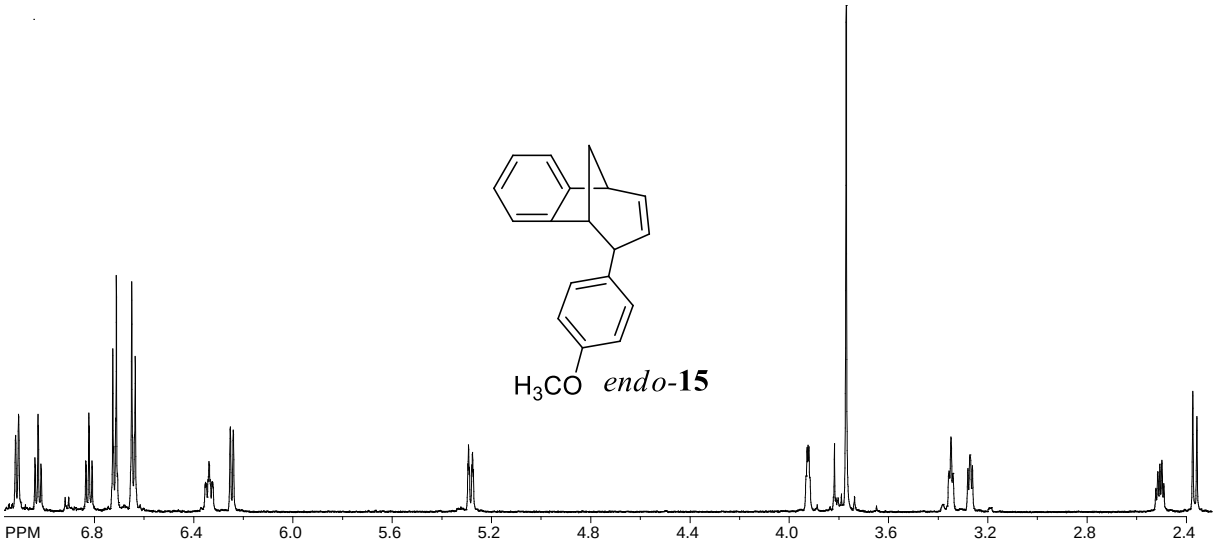
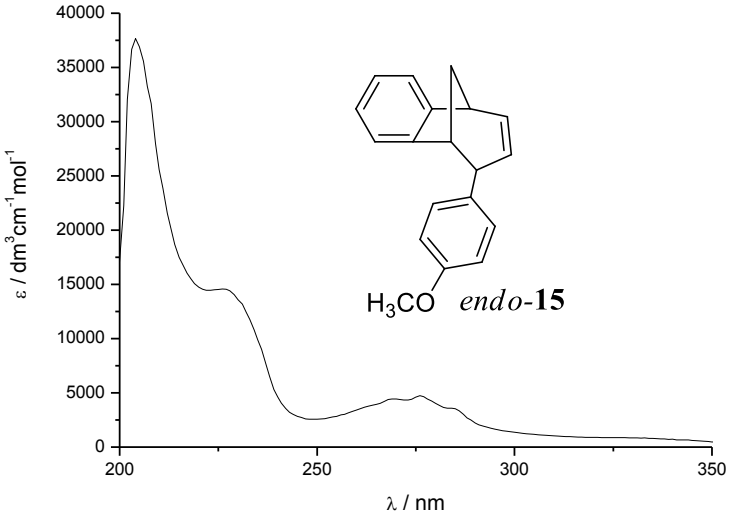
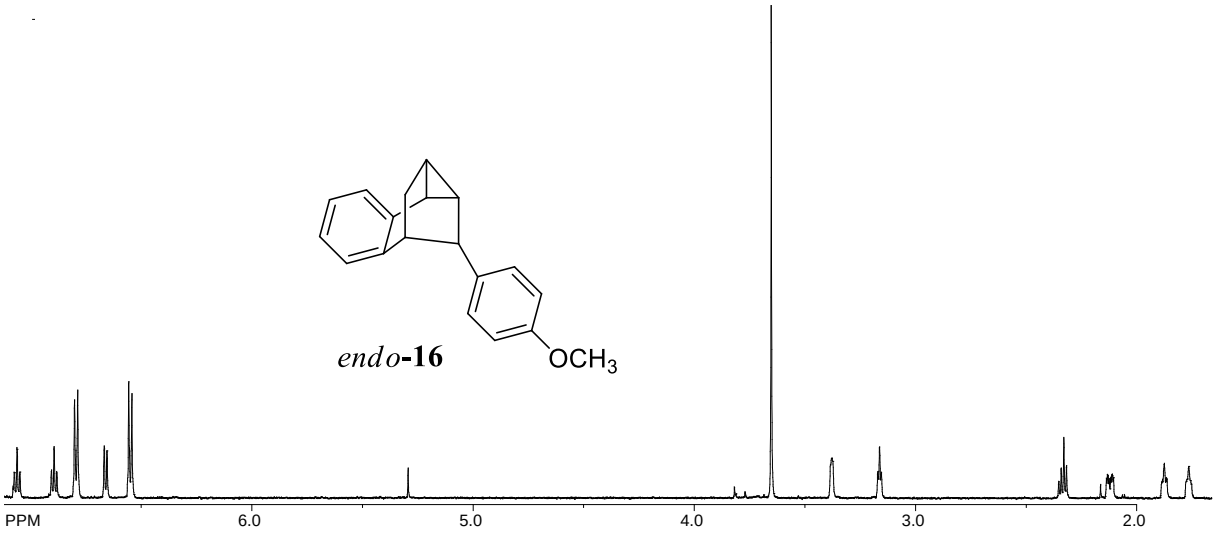


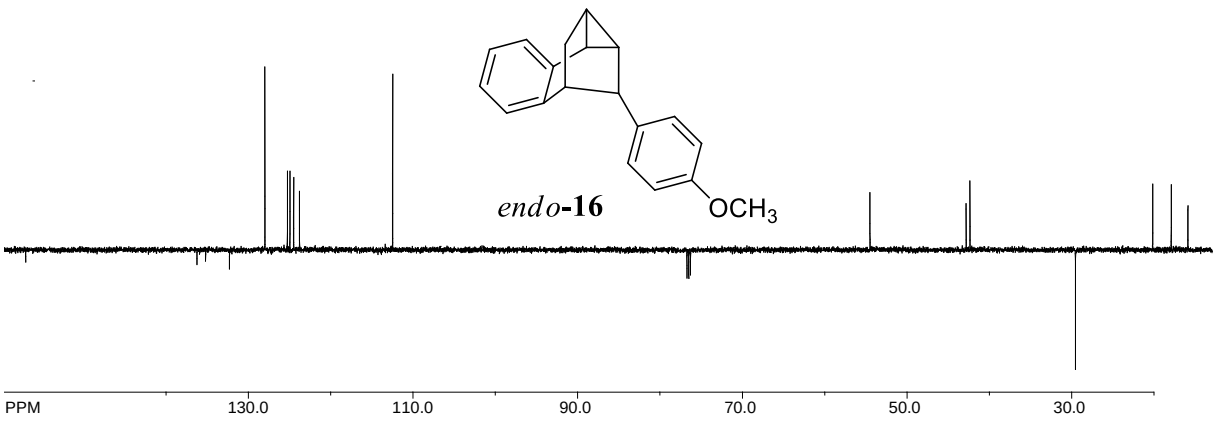
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo*-**15**



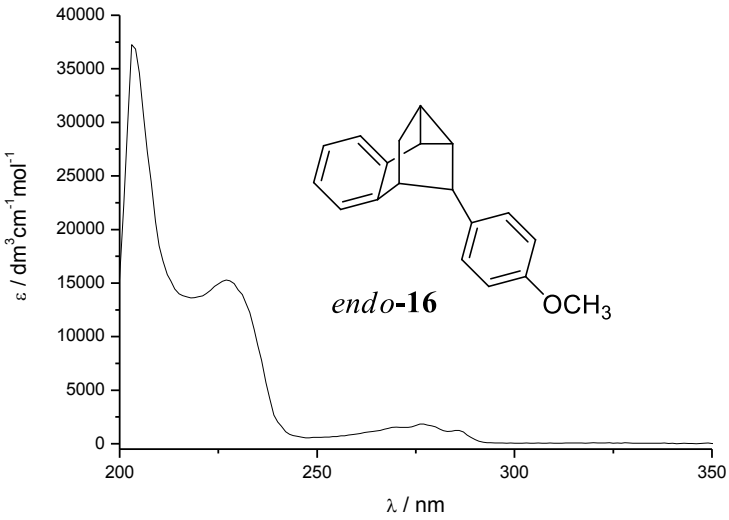
UV (96 % ethanol) spectrum for compound *endo*-**15**



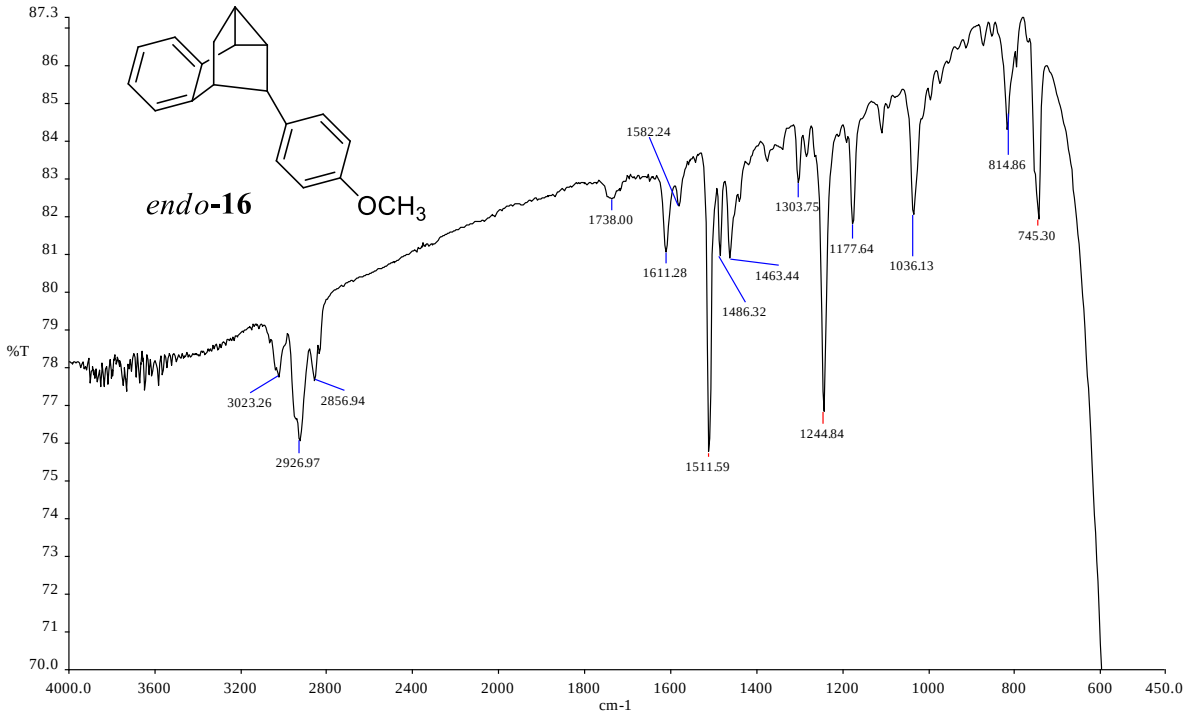
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo*-**16**



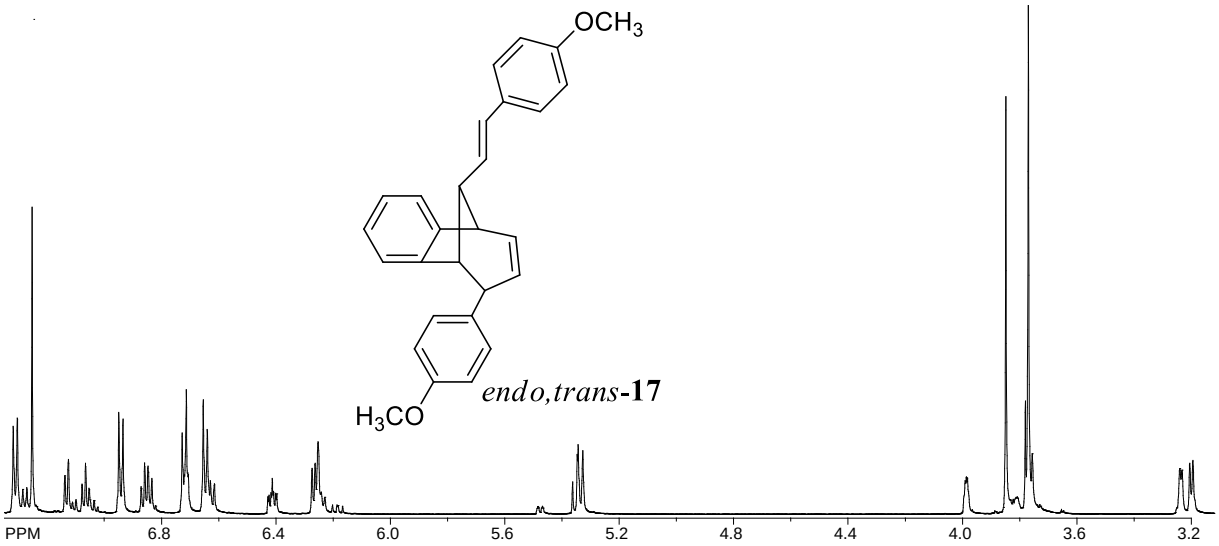
^{13}C NMR spectrum ($CDCl_3$, 150 MHz) for compound *endo*-**16**



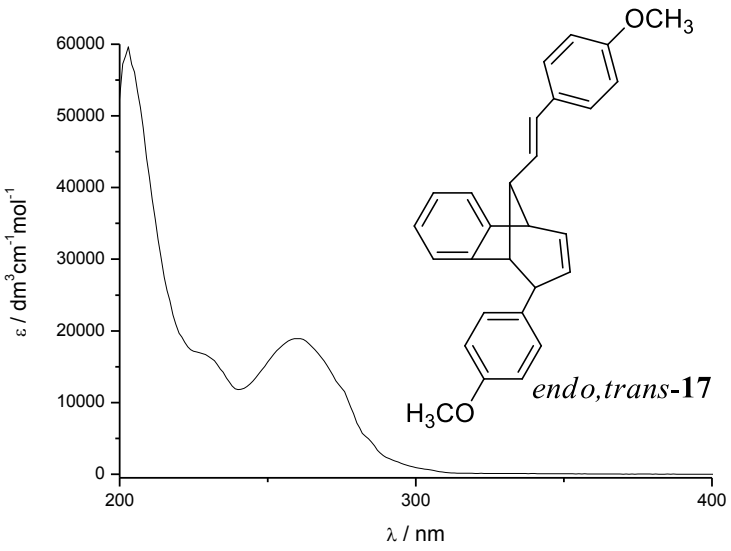
UV (96 % ethanol) spectrum for compound *endo*-**16**



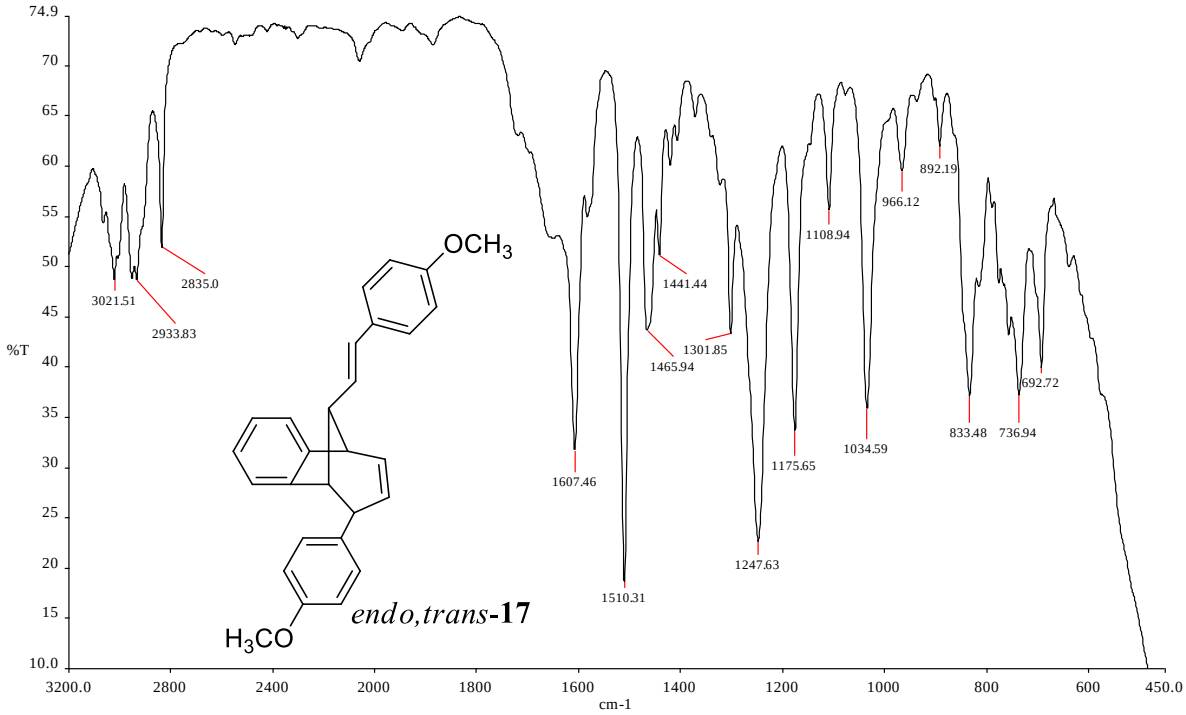
IR (evaporated film from CH_2Cl_2) spectrum for compound *endo*-**16**



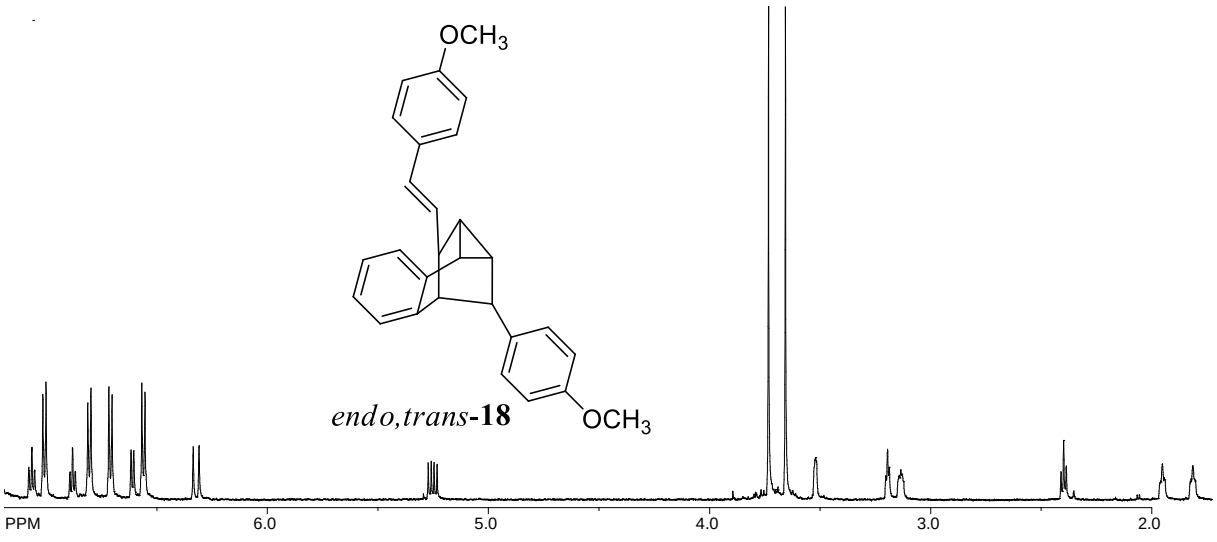
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo,trans*-**17**



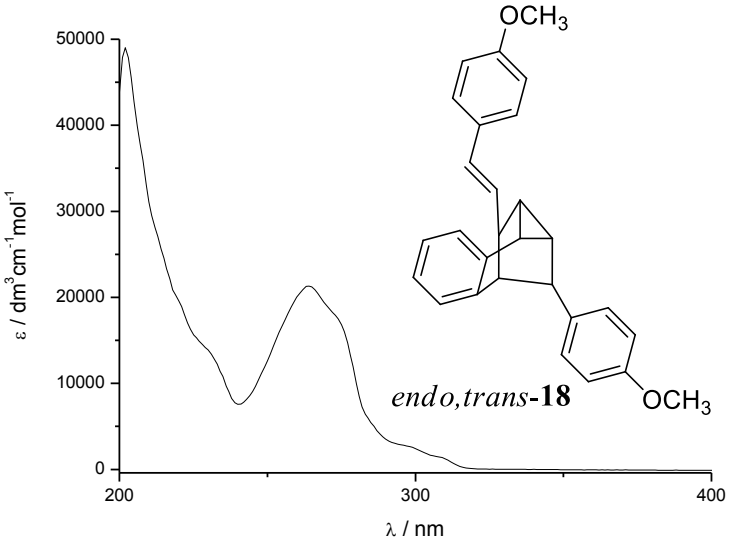
UV (96 % ethanol) spectrum for compound *endo,trans*-**17**



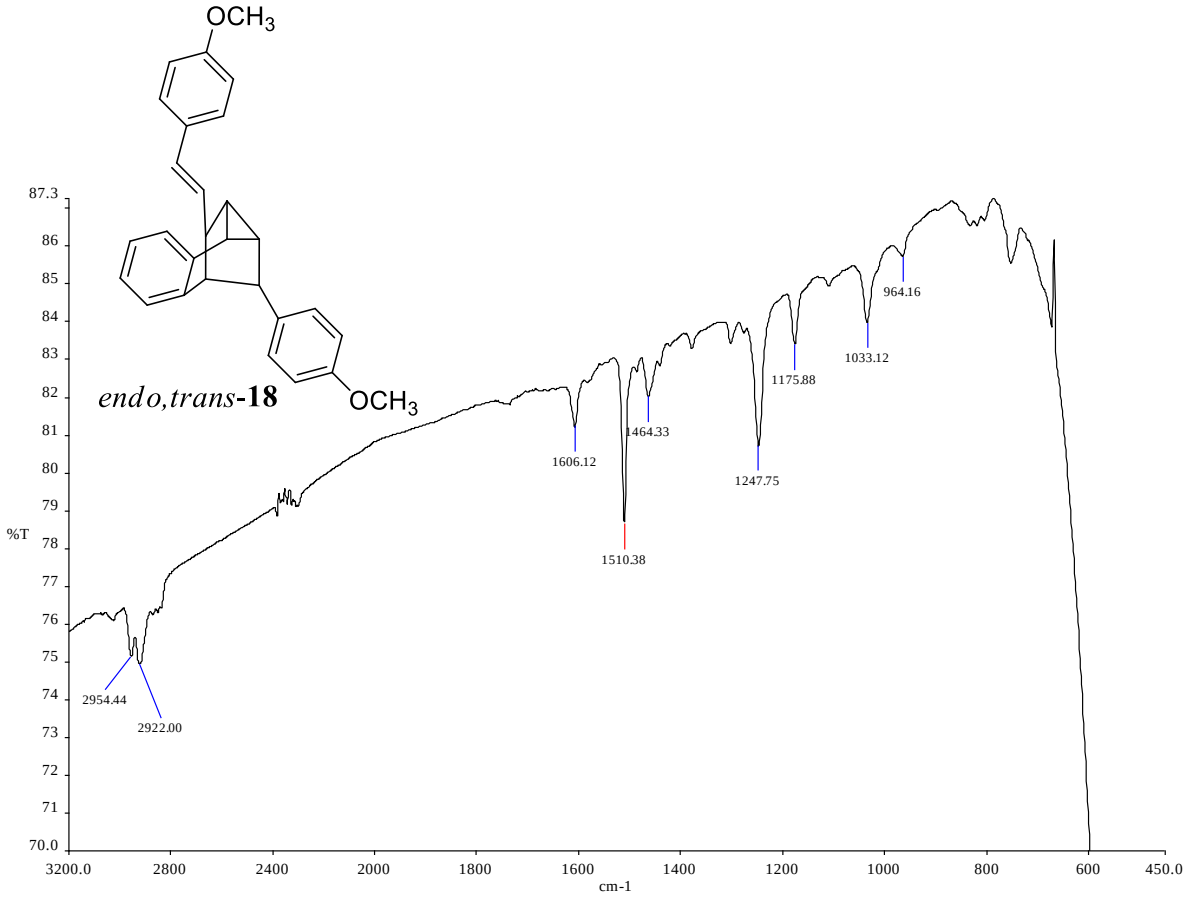
IR (evaporated film from CH_2Cl_2) spectrum for compound *endo,trans*-**17**



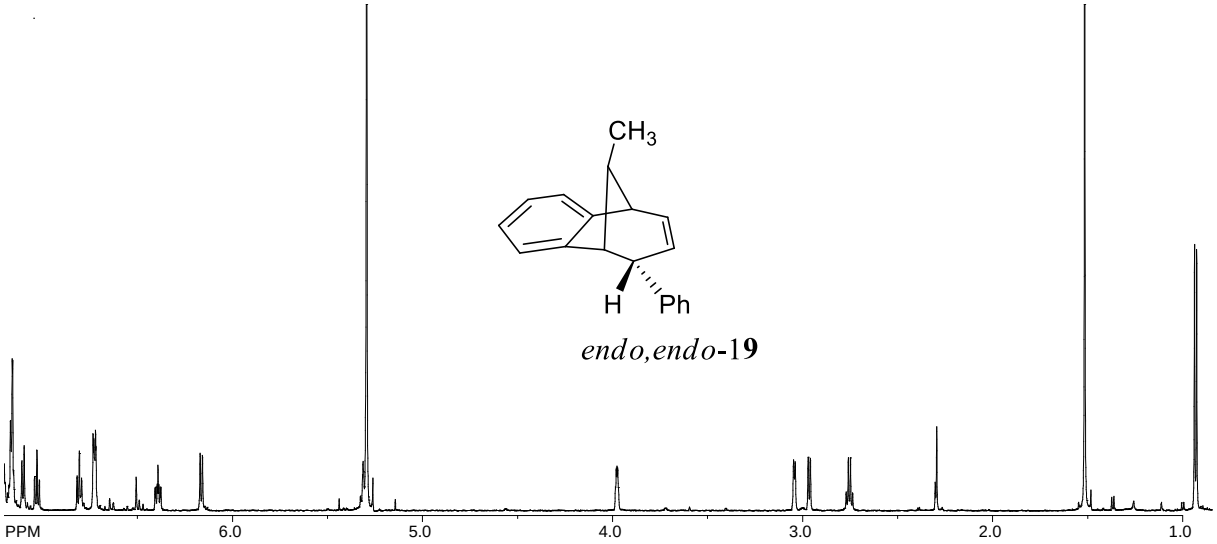
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo,trans*-**18**



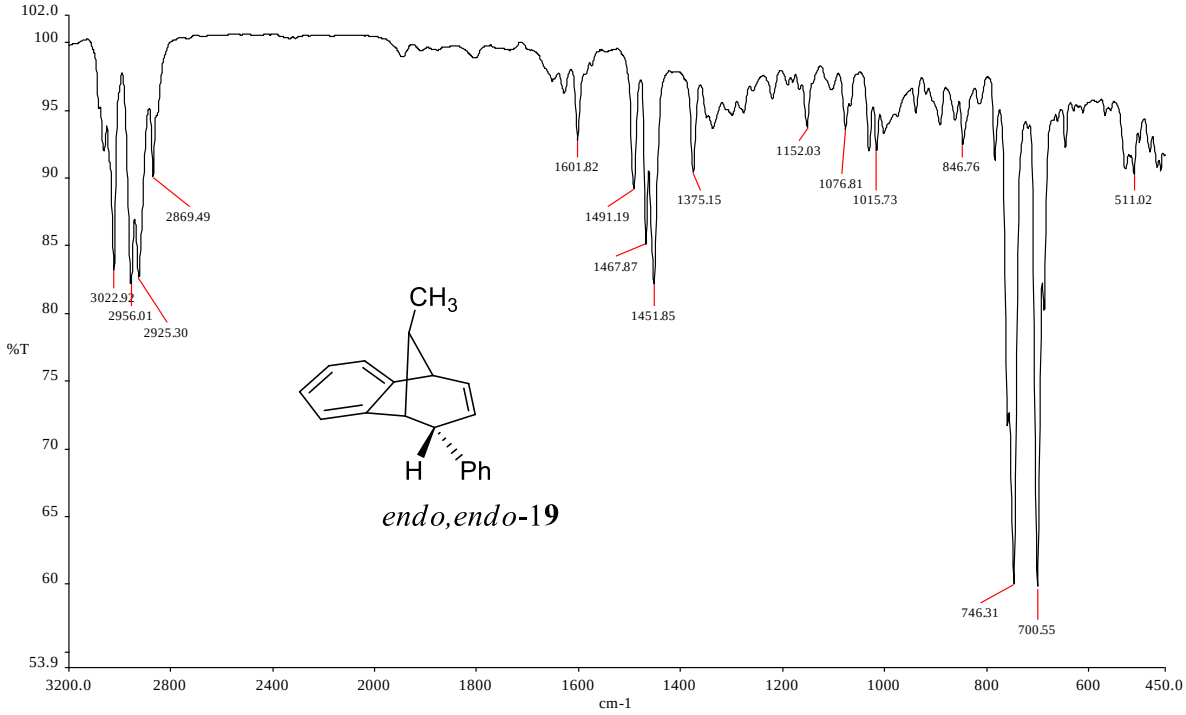
UV (96 % ethanol) spectrum for compound *endo,trans*-**18**



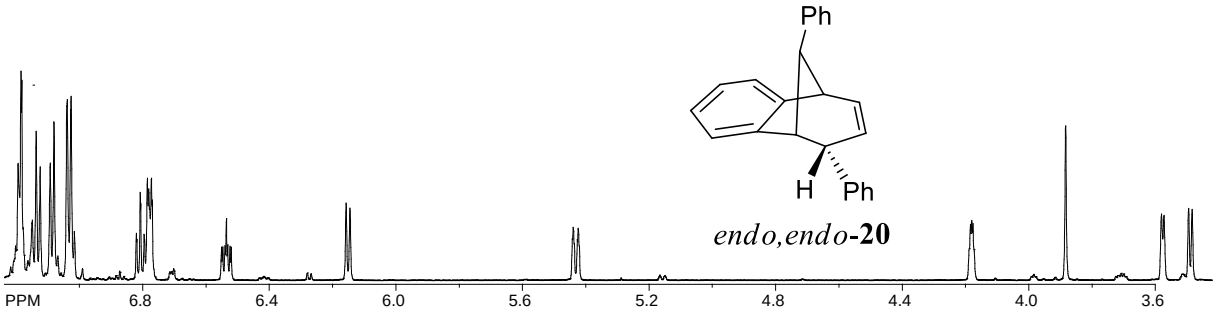
IR (evaporated film from CH_2Cl_2) spectrum for compound *endo,trans*-**18**



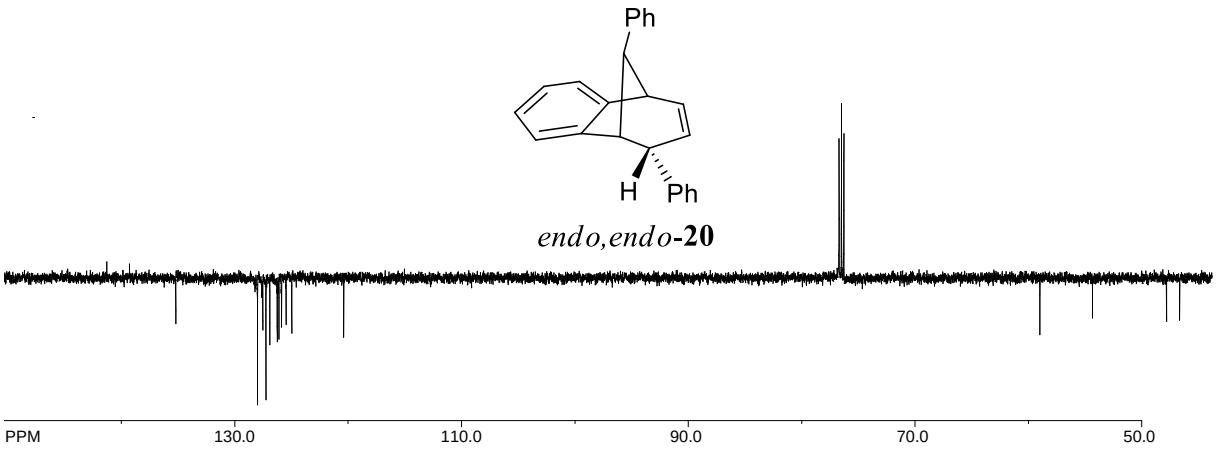
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo,endo*-**19**



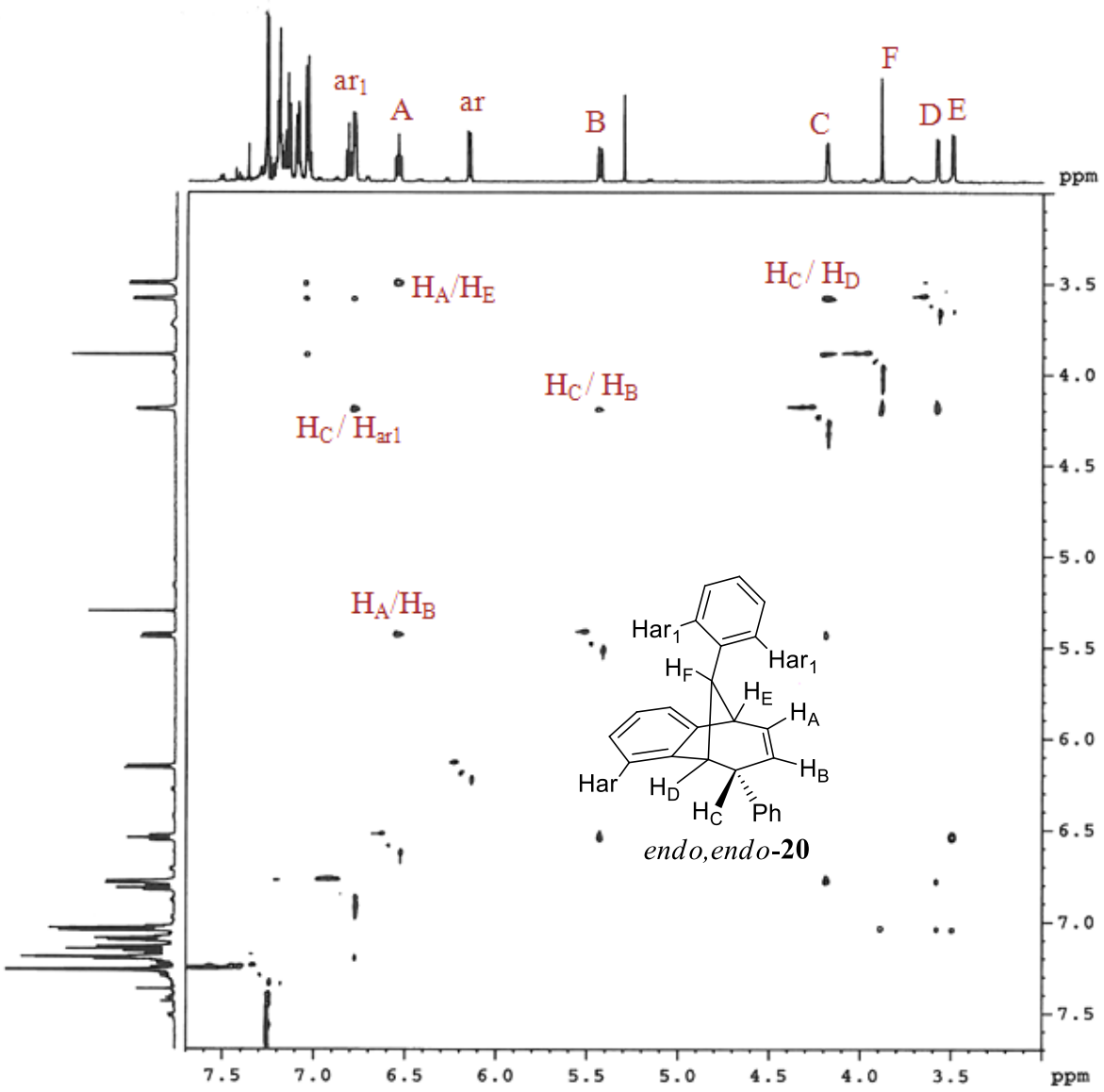
IR (evaporated film from CH_2Cl_2) spectrum for compound *endo,endo*-**19**



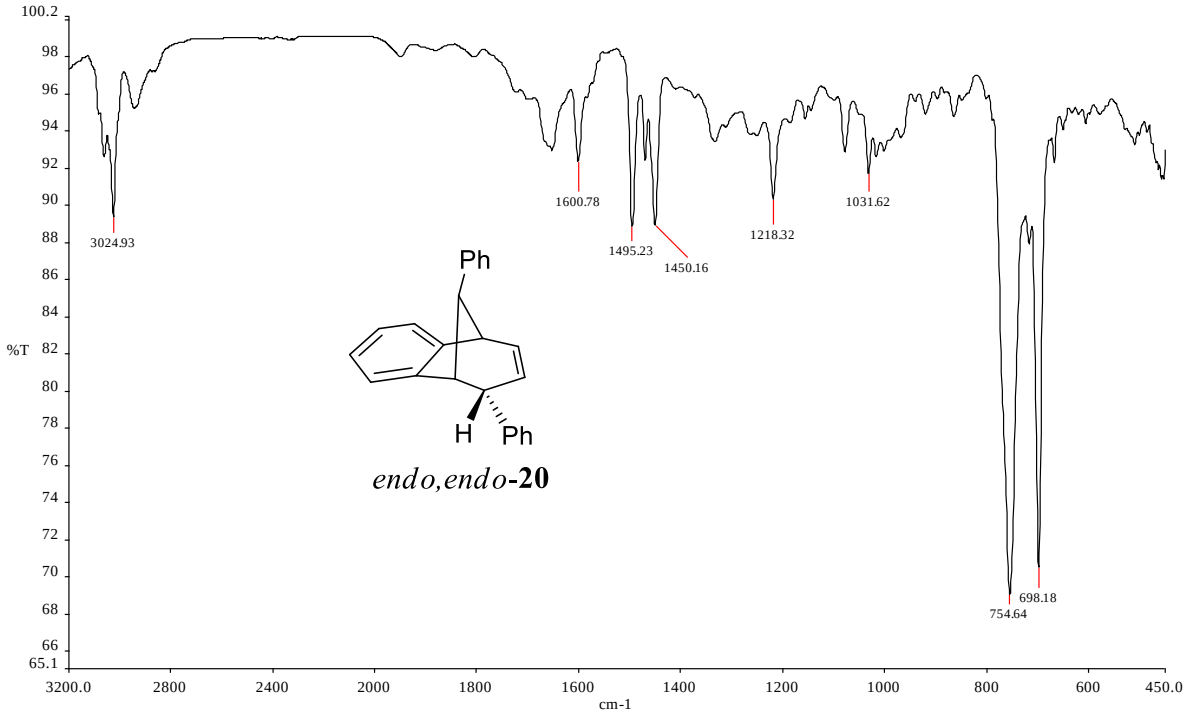
^{1}H NMR spectrum ($CDCl_3$, 600 MHz) for compound *endo,endo*-**20**



^{13}C NMR spectrum ($CDCl_3$, 150 MHz) for compound *endo,endo*-**20**



NOESY spectrum ($CDCl_3$) for compound *endo,endo*-**20**



IR (evaporated film from CH_2Cl_2) spectrum for compound *endo,endo*-**20**