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Synthesis and rearrangement reactions of 1,4-dihydrospiro[1,4-methanonaphthalene-9,1′-cyclopropane] derivatives

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ABSTRACT

Reactions of benzyne with ester derivatives of spiro[2.4]hepta-4,6-dien-1-ylmethanol were performed. By rearrangement reaction of cyclopropyl methanol units of ((1s*,1′R*,2R*,4′S*)-1′,4′-dihydrospiro [cyclopropane-1,9'-[1,4]methanonaphthalen]-2-yl) methyl 3,5-dinitrobenzoate (**13**) and its isomer (**14**), corresponding allyl chlorides were obtained. Two rearrangement products were obtained from bromination of compound **13** with an equivalent amount of Br_2. A naphthalene derivative including allyl and CHO moiety was formed for reactions from compounds with epoxide of **13** and **14** with NaN_3 by sequential rearrangements. Formations of products are discussed.

1. Introduction

Among the molecular rearrangements in organic chemistry, Wagner-Meerwein rearrangement takes an important place [1]. This rearrangement can be seen in the form of single or sequential rearrangements, and they can lead to the formation of important structures. Transformation of cyclopropylmethanols and their derivatives into homoallylic derivatives is a useful reaction [2].

In compounds **1** and **2**, a cyclopropane ring is combined with benzonorbornadiene and benzobarrelene giving skeletal rearrangements [1b,3] in ionic medium. When R was CH_2OH in **1** and **2**, we observed that their reactions with $SOCl_2$ gave sequential rearrangements starting with cyclopropane rings [4]. Furthermore, we observed that the reaction of **2** (R = COOMe) with Br_2 gave products derived from skeletal rearrangements (Fig. 1) [5]. Starting from the compound **1** where R (COOMe) is *exo*-configuration, the same route was used in the synthesis of *exo*-9-ethyl-1,4-dihydro-1,4-methanonaphthalene [4b,6].

To form a substituted cyclohexene derivative, Diels–Alder reaction is realized stereospecifically between a conjugated diene and a dienophile. The Diels–Alder reactions are particularly used in synthetic organic chemistry, and their reaction product is called adduct [7]. Adducts **4** were synthesized from the reactions of compound **3** with different dienophiles, and their rearrangement reactions were investigated [8]. Recently, we reported that rearrangements of adduct **5** and adduct of compound **6** with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate rearranged without $SOCl_2$ (Fig. 1) [9]. These rearrangements are new and also include cleavages of carbon-nitrogen or carbon-carbon bonds in them [9].

Benzyne is used in the Diels-Alder reactions as dienophile [10]. It is used in the synthesis of cyclopropanetad benzonorbornadiene and benzobarrelene derivatives **1** and **2** as dienophile [1b,4]. Adducts of compound **3** and its derivatives with benzyne are important because interesting rearrangements may occur in them. Therefore, adducts of **3** and its ester derivatives with benzyne were synthesized, and investigated their rearrangements reactions.

2. Results and discussion

Spiro alcohol **3** and its ester derivatives **7**–**9** were synthesized by a known method [9a]. Benzyne is a good dienophile and is formed in the reaction medium as an intermediate product. The reaction medium is acidic because benzenediazonium 2-

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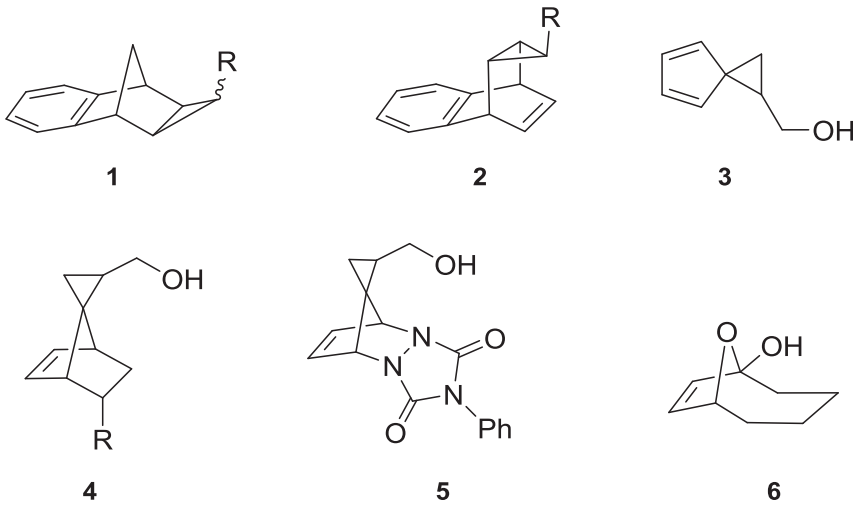


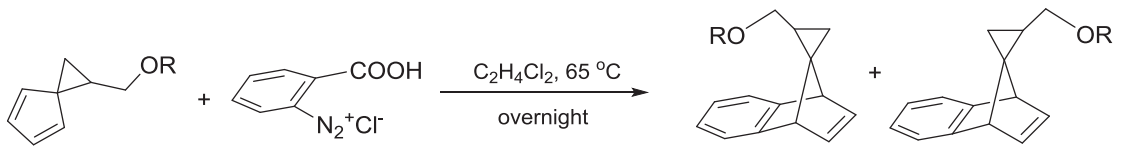
Fig. 1. Structures of compounds having tendency to rearrangement.

carboxylate hydrochloride salt (BDCHCl) was used as the source of the benzyne [10,11]. Spiro alcohol **3** was not used because it might be unstable in the related reaction condition.

The reaction of ester **7** whose R group is Ac with BDCHCl (**10**) was performed. The ^{1}H NMR spectrum of its reaction mixture was investigated and some peaks belonging to two isomeric adducts were determined. However, no adduct could be purified from this reaction mixture by chromatographic methods. The reaction of ester **8** with **10** was also performed in the same way. By carefully repeated column and thin layer chromatography, two products were isolated from their reaction (Scheme 1). Because approach of the benzyne to ester **8** is from two directions, these products should be isomeric adducts **11** and **12** as *exo*- and *endo*-products in the reaction of a diene such as **8**. The lack of isolation of the isomeric products formed in the reaction of **7** with benzyne should be due to their physical properties. The larger the group of isomeric adducts, the more their physical properties are different. The mass and volume of acetyl group is less than that of 4-nitrobenzoyl group. Probably, a molecule with R unit such as the 3,5-dinitrobenzoyl compared to the 4-nitrobenzoyl group will be more polar. Therefore, isomeric adducts may be isolated easily. Moreover, we observed similar properties in the reactions of **7**–**9** with phenyltriazolinedione (PTAD) [9a]. Therefore, two isomeric adducts **13** and **14** were obtained in pure from the reaction of ester **9** with **10** in the same condition. Their structures were determined from NMR spectra; especially NOE (Nuclear Overhauser Enhancement) measurements played an important role by determination of the correct structures. To be sure about the exact configurations of the isomeric adducts, X-ray analysis of the main product was performed. After determination of the correct structure of the isomer **13**, we assigned the isomeric structure to the compound **14** (Fig. 2). When the reactions of ester **9** with **10** and ester **8** with PTAD[9a] were considered, the structure of major isomer formed in the reaction of **8** with **10** may be that of compound **11** (Scheme 1).

X-ray diffraction analysis confirmed the structure of **13** (Fig. 2). The compound crystallizes in the triclinic space group P-1 with one isolated molecule in the asymmetric unit. C-C (cyclopropane) distances are in the range of 1.520(3)-1.484(3) Å. The structure contains three asymmetric carbon atoms and stereogenic centers are as follows: C5(S), C8(R), and C13(R).

Adducts **11**–**14** are benzonorbornadiene derivatives including a spirocyclopropane ring. The compounds **11**–**14** have now suitable functional groups that have great tendency for rearrangement [4,5]. To study the tendency for the skeletal rearrangement, the



7 R = Ac — **10** — * — *
8 R = 4-nitrobenzoyl — " — **11**, 55% — **12**, 20%
9 R = 3,5-dinitrobenzoyl — " — **13**, 78% — **14**, 16%

*they could not be isolated from the reaction mixture

Scheme 1. Cycloaddition reactions of benzyne with ester **7**–**9**.

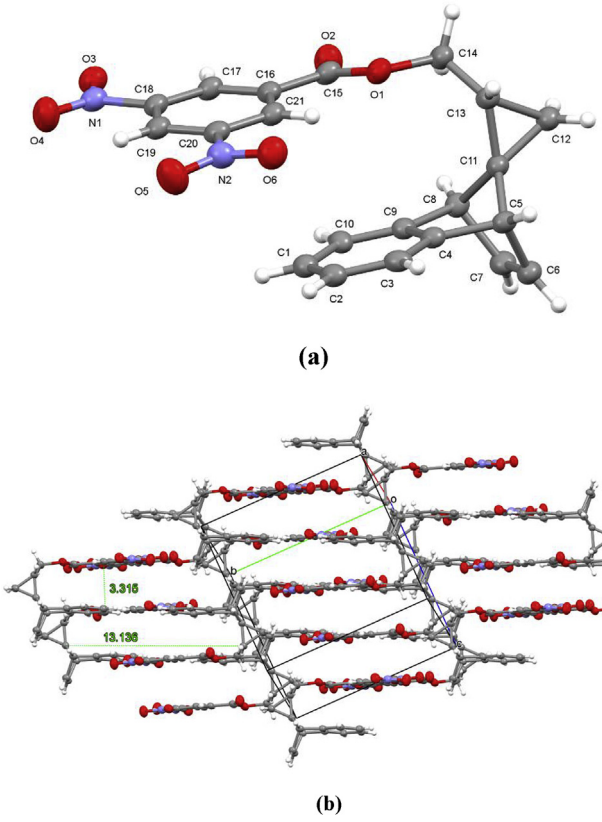


Fig. 2. a) Molecular structure of the compound **13**. Thermal ellipsoids are drawn at 40% probability level. **b**) Porous structure of the molecule viewed down along the diagonal axis.

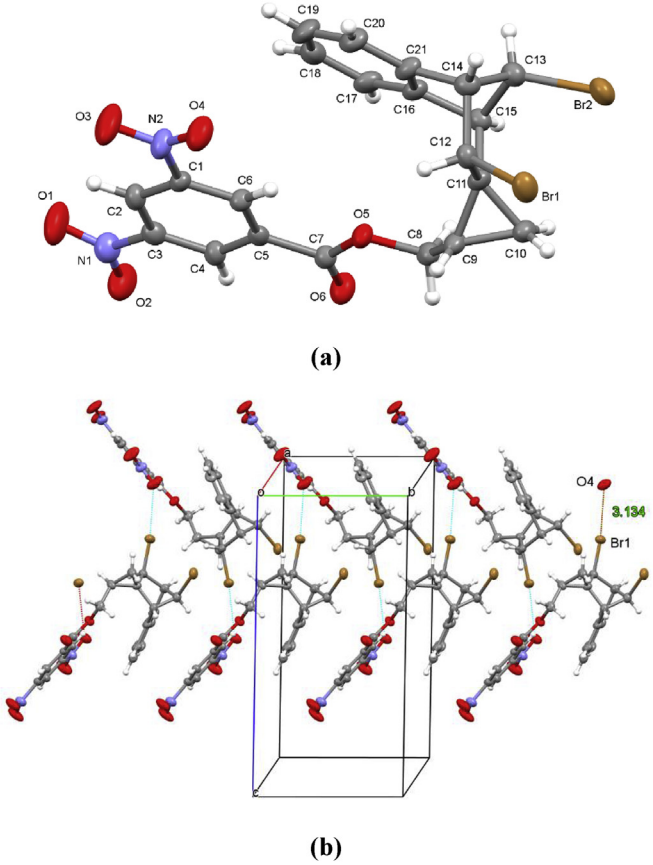


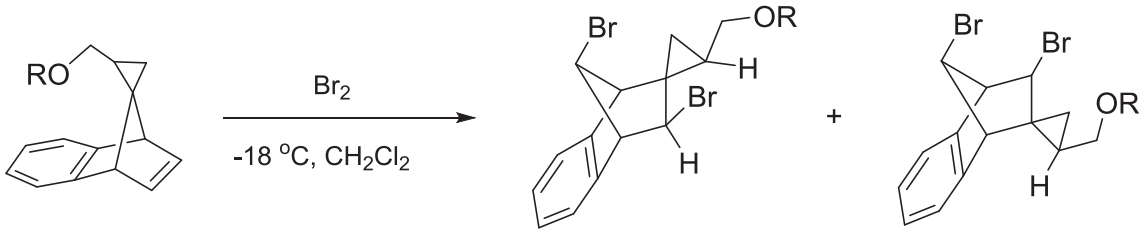
Fig. 3. a) Molecular structure of compound **15**. Thermal ellipsoids are drawn at 40% probability level. **b**) Halogen bonding interactions along the b-axis (Br1···O4 = 3.134 Å).

compound **13** was treated with bromine (1.0 equiv.) and two isomeric dibromides **15** and **16** were formed (Scheme 2). Based on the NMR spectra, it was determined that they are isomeric rearranged dibromides and spirocyclyopropane are rings present in these products. It is not easy to establish the exact configurations of the products. Therefore, the structure of the major product was determined as compound **15** by X-ray crystallographic analysis (Fig. 2). The other product should be **16**.

X-ray diffraction analysis also confirmed the structure of dibromide **15** (Fig. 3). The compound crystallizes in the monoclinic space group *P*21/*c* with one isolated molecule in the asymmetric unit. C12-Br1 and C13-Br2 bond distances are 1.682(2) and 1.680(3) Å respectively. C-C (cyclopropane) distances are in the range of 1.512(3)-1.488(3) Å and all have the single bond character. The non-covalent Br···O halogen interactions (sum of van der Waals radii = rO+ rBr = 3.35 Å.) are responsible for the rearrangement of molecules in crystals (Fig. 3b). However, Br2···O3 distance [3.422(3) Å] is greater than 3.35 Å. For this structure stereogenic centers are as follows; C9(S), C11(S), C12(S), C13(S), C14(R) and C15(R).

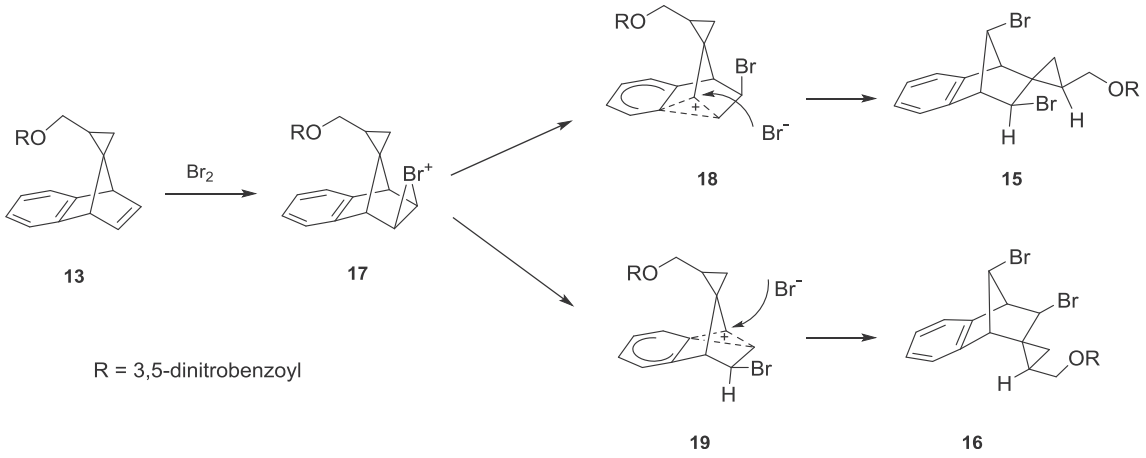
For the formation of the rearrangement products **15** and **16**, we propose the mechanism given in Scheme 3. Electrophiles attack the double bond of benzonorbornadiene and its derivatives from the *exo* position because of electron density [1,12]. Intermediate bromonium ion **17** occur by the attack of bromine on compound **13**. Two different aryl shifts may be because of the asymmetric structure of the intermediate **17**. The rearrangement products **15** and **16** occur *via* intermediates **18** and **19**, respectively.

Adducts such as **13** or **14** of benzyne include cyclopropylmethanol derivatives. Rearrangements may also occur in their cyclopropylmethanol moieties because cyclopropylmethanols



13 R = 3,5-Dinitrobenzoyl **15,** 53% **16,** 32%

Scheme 2. The reaction of compound **13** with bromine.



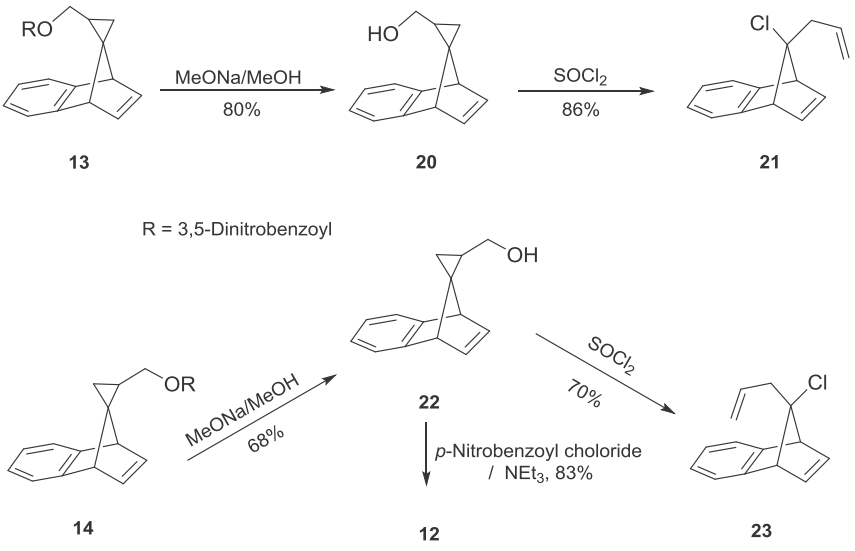
Scheme 3. Mechanism for formation of the rearrangement products **15** and **16**.

are rearranged with reagents such as $SOCl_2$ [5,7]. For this purpose compounds **13** and **14** were hydrolyzed in MeONa/MeOH and then their rearrangement reactions were performed with $SOCl_2$ (Scheme 4). From these reactions, cyclopropylmethanol derivatives **20** and **22** were obtained alone, and rearranged products **21** and **23** were also obtained, respectively. The configurations of the chlorides in **21** and **23** were elucidated on the basis of their NMR spectra including ^1H NMR NOE studies. Furthermore, synthesis of **12** from **22** supports the structures of **20**–**23**.

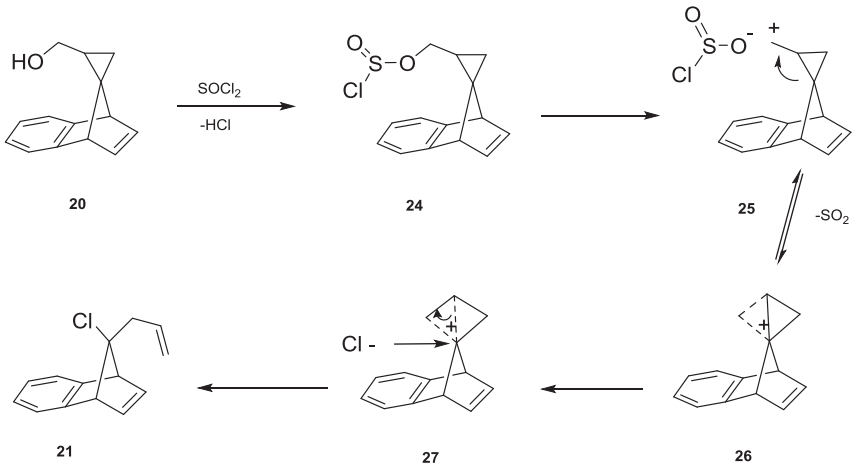
Formations of allyl chlorides **21** and **23** from the corresponding cyclopropylmethanols should be by the same mechanism. For example, the reaction mechanism in Scheme 5 is proposed for allyl chlorides **21**. Reaction of alcohol **20** with $SOCl_2$ forms ion pair **25** via **24** because formations of ion pairs are expressed in the reactions of alcohols with $SOCl_2$ [4,13]. The ion pair **25** is converted into non-classical carbocations **26** and **27**, respectively. Anion Cl^- transferred from $ClSO_2^-$ can attack the intermediate **27** to form chloride **21.**

To confirm the structures of adducts **11** and **12**, alcohol **22** was reacted with 4-nitrobenzoyl chloride and NEt_3. Adduct **12** was obtained from this reaction, and the structures of adducts **11** and **12** were also determined by chemical method (Scheme 5).

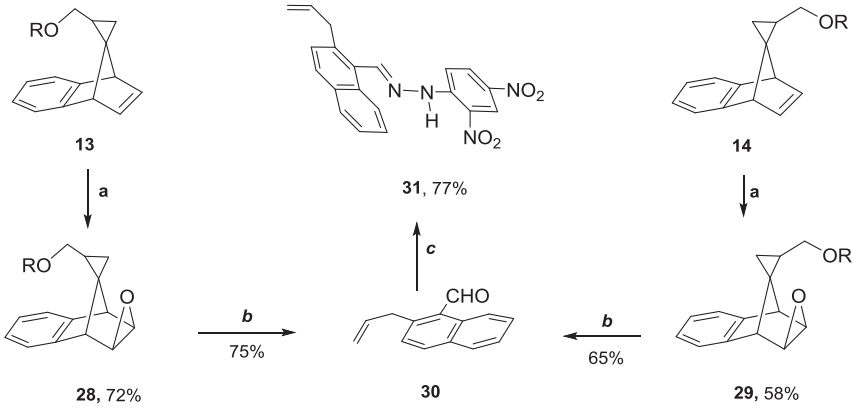
Reactions of benzonorbornadiene and its derivatives with some reagents gave rearrangement products including oxygen or nitrogen [1b,14]. For the synthesis of such products, a method is as follows: (i) epoxidation of compounds **13** and **14**; (ii) then the opening of epoxide rings in the corresponding products. For this purpose, the compounds **13** and **14** were reacted with *m*-CPBA (*m*-chloroperbenzoic acid) and the corresponding compounds **28** and **29** were obtained from these reactions as only *exo*-isomers



Scheme 4. Hydrolysis and rearrangement reactions of compounds **13** and **14**, respectively. Synthesis of **12** from **22**.



Scheme 5. Mechanism for formation of chloride **21**.



R = 3,5-Dinitrobenzoyl, ***a*** = *m*-CPBA, CH_2Cl_2;
b = NaN_3, NH_4Cl, MeOH, H_2O, 100 °C; ***c*** = 2,4-Dinitrophenylhydrazin / MeOH

Scheme 6. Synthesis and rearrangements of the compounds **28** and **29**.

(Scheme 6).

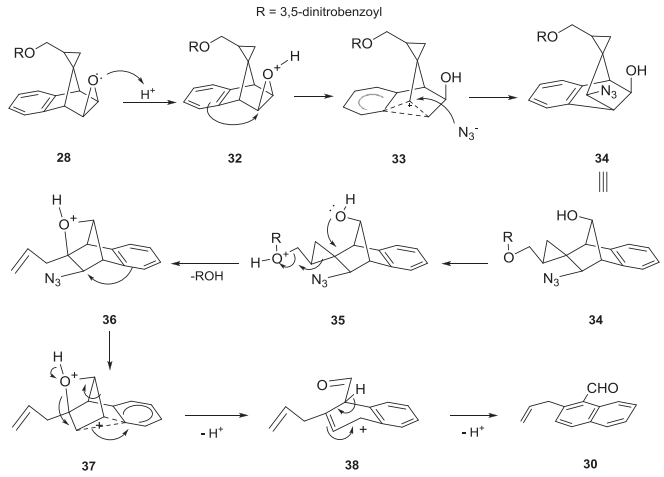
As NaN_3 is a reagent [15] used in the opening of epoxide rings, the compound **28** was reacted with NaN_3 in NH_4Cl/MeOH/H_2O at 100 °C and single product (**30**) was obtained in 75% yield. The same product (**30**) was also obtained from the reaction of compound **29** NaN_3 under the same conditions (Scheme 6). Two peaks present at 3.89 ppm (dt, $J = 6.0$, 1.4 Hz, 1H) in ^{1}H NMR and at 37.35 ppm in ^{13}C NMR spectra of compound **30**. These peaks should belong to its allylic CH_2, affecting to double bond hydrogens (at 6.14–4.99 ppm, 3H). In addition to, there was an aldehyde group resonating at 10.86 (s, 1H) and 193.5 ppm in the NMR spectra. The product obtained by sequential rearrangements should be naphthalene derivatives including aldehyde and allyl groups as substituents. Reactions of the compounds **28** and **29** were performed in the absence of NaN_3. It was determined that the naphthalene derivative **30** did not occur in the reaction. Therefore, NaN_3 must be found in these reactions.

Two substituent groups on the naphthalene derivative should be on a ring of this derivative. Because four doublet peaks are present in the ^{1}H NMR spectrum of compound **30** at 9.00, 7.98, 7.84, and 7.35 ppm, and their coupling constants (J) are 8.1-8.7Hz. Two of them belong to the naphthalene ring without substituent, but the other two belong to the substituted ring of naphthalene. These

coupling constants are high for *meta* coupling constants, and they should be for *ortho* coupling constants. On the other hand, these coupling constants should belong to vicinal hydrogens, and these peaks should belong to hydrogens of CH bonded to quaternary carbon atoms. The position of two substituents on the ring may be 1, 2 or 1, 4. However, 1, 2 position should be the favorite. To determine the exact structure of the product **30** which is a liquid, it was converted to crystallic hydrazone derivative **31** (Scheme 6). X-ray crystallographic analysis (Fig. 4) of the hydrazone derivative **31** explained the structures of naphthalene derivatives **30** and **31**.

The structure of the prepared compound **31** was confirmed by X-ray diffraction analysis (Fig. 4a). The compound crystallizes in the monoclinic space group *C*2/*c* with one isolated molecule in the asymmetric unit seen. C12-C13 and N1-C14 distances are 1.300(2) and 1.272(3) Å, respectively and all have a single bond character. The hexagonal stacking motif of the molecule with the unit cell is shown in Fig. 4b.

A plausible mechanism given in Scheme 7 may be proposed for the formation of the rearrangement product **30**. After the compound **28** is protonated like **32** in acidic media, it may be converted into intermediate **34** *via* intermediate **33** by rearrangement. Reactions of benzonorbornadiene or its epoxide derivatives with some reagents give similar products as rearrangement products [16]. As seen in Scheme 2, bromination of adduct **13** also formed

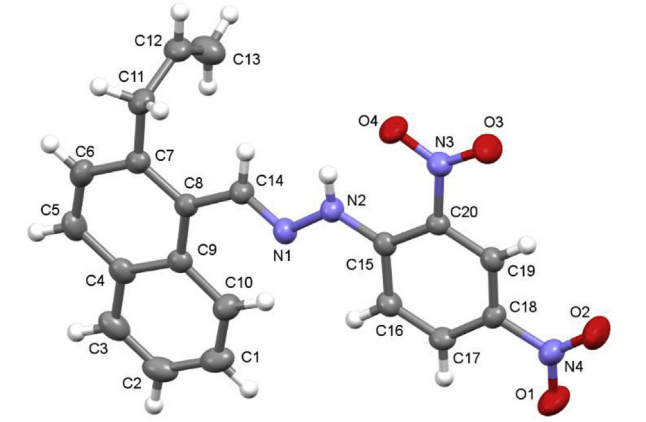


Scheme 7. Mechanism for formation of the naphthalene derivative **30**.

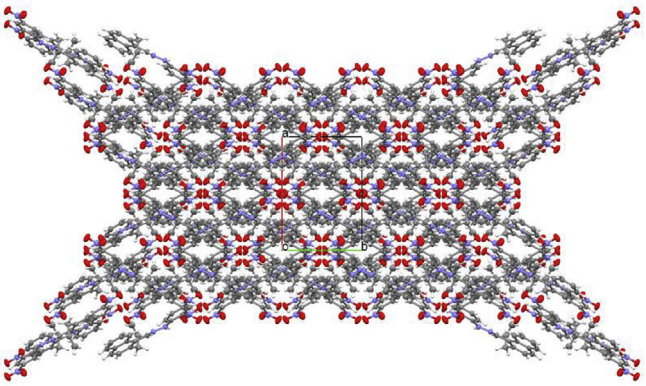
dibromides **15** and **16**, which are structures similar to **34**. After intermediate **34** having a cycloypropyl methanol derivative is also protonated like **35**, it is converted to intermediate **38** via intermediates **36** and **37** by sequential rearrangements. Aromatization of **38** also formed naphthalene derivative **30**.

3. Conclusion

Reactions of esters **7**–**9** with benzyne were performed with the same conditions (by reflux of a mixture of each ester, BDHCl and 1,2-dichloroethane). From adducts formed in the reactions, compounds **11**–**14** were isolated in the corresponding reaction mixtures. It was observed that the size of ester groups in adducts is effective in their isolations.



(a)



(b)

Fig. 4. a) Molecular structure of the hydrazone derivative **31**. Thermal ellipsoids are drawn at 40% probability level. **b**) Hexagonal stacking motif of the molecule viewed along the c-axis.

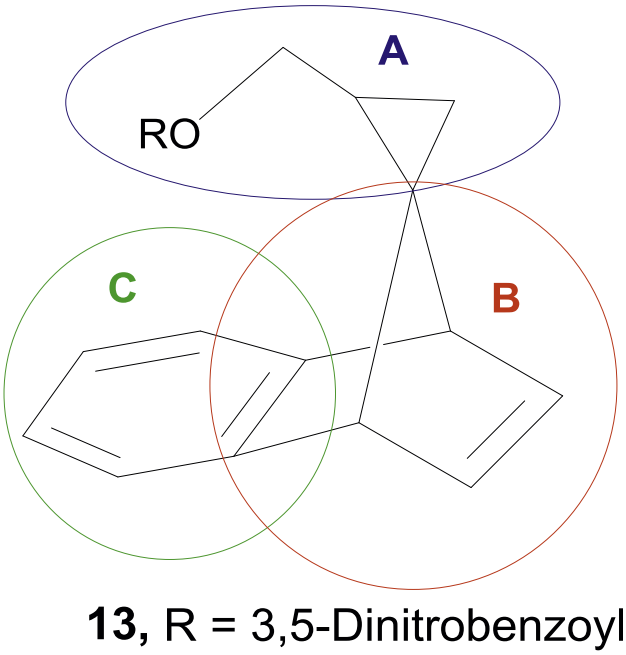


Fig. 5. Units of compound **13**.

As shown in Fig. 5, we can think of compounds such as **13** including three units as cyclopropyl methanol (A), norbornadiene or norbornene (B) and benzene (C) structures. The conversion of compounds **13** and **14** to chlorides **21** and **23** was realized by rearrangement occurring in unit A while the conversion of compound **13** to bromides **15** and **16** was realized by rearrangement occurring in unit B. It was determined that the benzene ring contributes to the rearrangement occurring in unit B. The conversion of both the compounds **28** and **29** to naphthalene derivative **30** was realized by sequential rearrangements occurring in units A and B with the contribution of benzene ring. Because the naphthalene derivative **30** was obtained from the sequential reactions of the adducts, this method may be applied for the synthesis of 1,2-substituted naphthalene derivatives.

4. Experimental section

4.1. General experimental procedures

Solvents were purified and dried by standard methods. Values as well as measurements of M.p. of all compounds, IR spectra, ^{1}H and ^{13}C NMR spectra, and chemical shift values were obtained, and elemental analyses, was performed as described previously [9]. PLC is preparative thin-layer chromatography: 1 mm of silica gel 60 PF (Merck, Darmstadt, Germany) on glass plates. HRMS were recorded by LC-MS-TOF electrospray ionization (1200/6210, Agilent).

4.1.1. Synthesis of compounds *3* and *7–9*

Spiro alcohol **3** and its ester derivatives **7–9** were synthesized by a known method [9a].

4.1.2. Cycloaddition reaction of nitrobenzoate 8 with benzyne: standard procedure for cycloaddition

In a round bottom flask (500 mL) was placed spiro nitrobenzoate **8** (5 g, 20 mmol, 1.0 equiv) and 1,2-dichloroethane (150 mL) was used as solvent. The compound **10** (5.25 g, 30 mmol, 1.5 equiv.) was added to the stirred solution, and then the reaction mixture was refluxed for 20 h. After the reaction mixture was cooled to room temperature (RT), the solvent of the mixture was removed under vacuum. CH_2Cl_2 (75 mL) and water (100 mL) were added to the reaction mixture. After it was extracted with CH_2Cl_2 (2 × 40 mL), the combined organic layer was washed with NaOH (0.5%, 4 × 100 mL, 0 °C) and water (1 × 50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under vacuum. According to TLC and the ^{1}H NMR spectrum of the residue, two products were observed. By carefully repeated column and thin layer chromatography, adducts **11** (3.80 g, 55%, white solid) and **12** (1.39 g, 20%, white solid) were isolated and crystallized from hexane/EtOAc (ethyl acetate).

4.1.3. *((1R*,1's*,2'R*,4S*)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1'-cyclopropan]-2'-yl) methyl 4-nitrobenzoate (**11**)*

Mp: 74–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.17 (d, J = 8.7 Hz, 2H, A part of AB system), 7.78 (d, J = 8.7 Hz, 2H, B part of AB system), 7.21 (d, J = 7.1 Hz, 1H), 7.03 (d, J = 7.1 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.86 (s, olefinic, 2H), 6.72 (t, J = 7.4 Hz, 1H), 4.45 (dd, J = 11.6, 6.1 Hz, methylene, 1H, A part of AB system), 3.91 (dd, J = 11.5, 9.5 Hz, 1H, methylene, B part of AB system), 3.60 (s, bridgehead, 1H), 3.37 (s, bridgehead, 1H), 1.38 (tt, J = 9.2, 5.8 Hz, cyclopropane, 1H), 0.98 (dd, J = 8.9, 6.1 Hz, cyclopropane, 1H), 0.67 (t, J = 5.7 Hz, cyclopropane, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.7 (CO), 151.0 (C), 150.8 (C), 150.7 (C), 142.7 (CH), 142.0 (CH), 135.6 (C), 130.9 (CH), 124.5 (CH), 124.3 (CH), 123.4 (CH), 121.6 (CH), 121.2 (CH), 69.4, 67.1, 56.2, 52.0, 20.3, 12.7; Rf: 0.34 EtOAc/Hexane (1/19); IR (CH_2Cl_2 cm^{-1}): 3072, 2991, 1721, 1608, 1526, 1453, 1347, 1274; HRMS (APCI-Tof) (m/z) calcd for $C_{21}H_{17}NO_4$: 347.1158; found: 347.1178.

4.1.4. *((1R*,1'r*,2'S*,4S*)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1'-cyclopropan]-2'-yl) methyl 4-nitrobenzoate (**12**)*

Mp: 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.30 (d, J = 8.9 Hz, A part of AB system, 2H), 8.23 (d, J = 8.9 Hz, B part of AB system, 2H), 7.25–7.14 (m, 1H), 7.00–6.91 (m, 1H), 6.83 (dd, J = 5.3, 3.1 Hz, 2H), 6.76 (dd, J = 5.3, 3.0 Hz, 2H), 4.45 (dd, J = 11.6, 7.2 Hz, 1H), 4.23 (dd, J = 11.6, 8.5 Hz, 1H), 3.61 (s, 1H), 3.36 (s, 1H), 1.60–1.48 (m, 1H), 0.83 (dd, J = 8.7, 6.3 Hz, 1H), 0.56 (t, J = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.7 (CO), 150.6 (C), 150.5 (C), 150.4 (C), 142.2 (CH), 142.1 (CH), 135.8 (C), 130.75 (CH), 124.4 (CH), 124.4 (CH), 123.6 (CH), 121.4 (CH), 121.4 (CH), 69.4, 67.6, 56.0, 52.0, 19.7, 14.0; Rf: 0.33 EtOAc/Hexane (1/19); IR (CH_2Cl_2 cm^{-1}): 3071, 3018, 1722, 1643, 1527, 1452, 1347, 1274; HRMS (APCI-Tof) (m/z) calcd for $C_{21}H_{17}NO_4$: 347.1158; found: 347.1174.

4.2. Synthesis of 12 via reaction of the alcohol 22 with p-nitrobenzoyl chloride

A mixture of alcohol **22** (200 mg, 1.01 mmol, 1.0 equiv.), triethylamine (153 mg, 1.51 mmol, 1.5 equiv.) and p-nitrobenzoyl chloride (187 mg, 1.01 mmol, 1.0 equiv.) was stirred overnight at RT. The mixture was cooled to 0 °C and poured into a cold solution (1.0%, 250 mL) of HCl. Then it was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with water (1 × 50 mL), and then dried over Na_2SO_4. The solvent was evaporated, and ester **12** (270 mg, 77% yield) was obtained.

4.3. Cycloaddition reaction of dinitrobenzoate 9 with benzyne

This reaction was performed according to the standard procedure. In the reaction, dinitrobenzoate **9** (6 g, 19 mmol, 1 equiv.) and **10** (5.25 g, 28.50 mmol, 1.5 equiv.) were used. The residue was submitted to silica gel (100 g) column chromatography with EtOAc/hexane (3/97) elution. Compound **13** (2.05 g, 78%, light yellow solid) and compound **14** (0.40 g, 16%, white solid) were isolated as pure and crystallized from hexane/EtOAc.

4.3.1. *((1R*,1's*,2'R*,4S*)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1'-cyclopropan]-2'-yl) methyl 3,5-dinitrobenzoate (**13**)*

Mp: 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 9.17 (t, J = 2.2 Hz, aromatic, 1H), 8.76 (d, J = 2.2 Hz, aromatic, 1H), 7.18 (d, J = 7.1 Hz, aromatic, 1H), 6.96 (d, J = 7.0 Hz, aromatic, 1H), 6.86–6.84 (m, olefinic, 2H), 6.72 (t, J = 7.4 Hz, aromatic, 1H), 6.42 (t, J = 7.9 Hz, aromatic, 1H), 4.46 (dd, A part of AB system, J = 11.5, 5.91 Hz, CH_2O, 1H), 4.08 (dd, B part of AB system, J = 11.5, 9.88 Hz, CH_2O, 1H), 3.59 (s, bridgehead, 1H), 3.38 (s, bridgehead, 1H), 1.54–1.48 (m,

cyclopropane, CH, 1H), 1.02 (dd, $J = 9.0$, 6.18 Hz, cyclopropane, CH_2, 1H), 0.70 (t, $J = 5.8$ Hz, cyclopropane, CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.3 (CO), 150.7 (CH), 148.4 (C), 142.4 (CH), 141.7 (CH), 133.8 (C), 129.5 (C and CH), 124.2 (CH), 123.8 (CH), 122.1 (CH), 121.5 (CH), 120.5 (CH), 69.4, 68.1, 55.8, 51.8, 20.0, 12.7; Rf: 0.38 EtOAc/Hexane (1/9). IR (CH_2Cl_2 cm^{-1}): 3441, 3100, 2989, 2893, 1728, 1629, 1544, 1455, 1344, 1314, 1279, 1169, 1075; HRMS (APCI-Tof) (m/z +H) calcd for $C_{21}H_{16}N_2O_6$: 393.1086; found: 393.1050.

4.3.2. *((1R*,1′r*,2′S*,4S*)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1′-cyclopropan]-2′-yl)methyl 3,5-dinitrobenzoate (**14**)*

Mp: 132–134 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.24–9.21 (m, aromatic, 1H), 9.21–9.18 (m, aromatic, 2H), 7.26–7.20 (m, aromatic, 2H), 6.99–6.94 (m, aromatic, 2H), 6.87 (dd, A part of AB system, $J = 5.5$, 3.08 Hz, olefinic, 1H), 6.80 (dd, B part of AB system, $J = 5.5$, 3.0 Hz, olefinic, 1H), 4.60 (dd, A part of AB system, $J = 11.6$, 7.09 Hz, CH_2O, 1H), 4.27 (dd, B part of AB system, $J = 11.6$, 8.79 Hz, CH_2O, 1H), 3.64 (bs, bridgehead, 1H), 3.40 (bs, bridgehead, 1H), 1.64–1.56 (m, cyclopropane CH, 1H), 0.88 (dd, $J = 8.7$, 6.30 Hz, cyclopropane CH_2, 1H), 0.60 (t, $J = 5.8$ Hz, cyclopropane CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.7 (CO), 150.7 (C), 150.4 (C), 148.9 (C), 142.6 (CH), 142.4 (CH), 134.4 (C), 129.7 (CH), 124.6 (CH), 124.6 (CH), 122.5 (C), 121.7 (CH), 121.6 (CH), 69.4 (C), 68.7 (CH_2O), 56.2 (CH), 52.2 (CH), 19.9 14.3; Rf: 0.34 EtOAc/Hexane (1/9); IR (CH_2Cl_2 cm^{-1}): 3422, 3119, 3098, 3014, 2985, 2955, 2892, 1721, 1630, 1541, 1453, 1342, 1286, 1171, 1073, 1036; HRMS (APCI-Tof) (m/z +H) calcd for $C_{21}H_{16}N_2O_6$: 393.1086; found: 393.1065.

4.3.3. *Reaction of 13 with bromine: formation of rearranged dibromides **15** and **16***

A magnetically stirred solution of the compound **13** (1.0 g, 2.5 mmol, 1 equiv.) in CH_2Cl_2 (25 mL) was cooled in ice-salt bath and then Br_2 (500 mg, 2.78 mmol 1.11 equiv.) was added slowly and carefully. Red-brown color of Br_2 disappeared in the solution and the solution was allowed to stir for 2 h without cooling. After reaction solvent was removed under vacuum. The residue was submitted to silica gel (80 g) column chromatography with EtOAc/hexane (1/19) elution. Compound **16** (0.45 g, 32%, white solid) and compound **15** (0.75 g, 53%, white solid) were isolated, respectively.

4.3.4. *((1R*,1′S*,2′S*,3S*,4R*,9S*)-3,9-dibromo-3,4-dihydro-1H-spiro[1,4-methano naphthalene-2,1′-cyclopropan]-2′-yl)methyl 3,5-dinitrobenzoate (**15**)*

Mp: 218–219 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.23–9.21 (m, aromatic, 1H), 9.00 (s, aromatic, 2H), 7.32 (d, $J = 7.3$ Hz, A part of AB system, aromatic, 1H), 7.17–7.12 (m, aromatic, 2H), 7.01 (t, $J = 7.5$ Hz, B part of AB system, aromatic, 1H), 4.55 (dd, $J = 11.6$, 7.26 Hz, A part of AB system, CH_2O, 1H), 4.41 (dd, $J = 11.6$, 6.96 Hz, B part of AB system, CH_2O, 1H), 4.27 (bs, 1H), 4.07 (bs, 1H), 3.92 (bs, 1H), 3.21 (bs, 1H), 1.83 (dd, $J = 8.5$, 5.51 Hz, cyclopropane, 1H), 1.43–1.33 (m, cyclopropane, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.8 (CO), 148.8 (C), 143.8 (C), 143.0 (C), 133.9 (C), 129.7 (CH), 128.0 (CH), 127.9 (CH), 122.7 (CH), 122.2 (CH), 121.9 (CH), 67.7, (CH_2O), 57.8, 56.6, 56.0, 55.2, 34.2 (C), 22.1 (CH_2), 18.5 (CH); Rf: 0.13 EtOAc/Hexane (1/19); IR (CH_2Cl_2 cm^{-1}): 3054, 2980, 1728, 1628, 1544, 1460, 1344, 1265, 1164. HRMS (APCI-Tof) (m/z +H) calcd for $C_{21}H_{16}Br^{81}Br^{81}N_2O_6$: 554.9453; found: 554.9492.

4.3.5. *2-((1S*,1′R*,2′S*,4S*,9R*)-3,9-dibromo-3,4-dihydro-1H-spiro[1,4-methanonaphthalene-2,1′-cyclopropan]-2′-yl)ethyl-3,5-dinitrobenzoate (**16**)*

It was crystallized from CH_2Cl_2/Hexane. Mp: 151–153 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.18–9.16 (m, aromatic, 1H), 8.61–8.46 (m, aromatic, 2H), 7.19–7.16 (m, aromatic, 1H), 7.04–7.02 (m, aromatic, 1H), 6.78–6.66 (m, aromatic, 2H), 4.91 (dd, $J = 11.90$, 4.71 Hz, A part of AB system, CH_2O, 1H), 4.22 (bs, 1H), 4.09 (bs, 1H), 3.97 (bs, 1H), 3.70 (dd, $J = 11.9$, 10.36 Hz, B part of AB system, CH_2O, 1H), 2.81 (bs, 1H), 1.75–1.52 (m, cyclopropane, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.1 (CO), 148.6 (C), 144.8 (C), 142.6 (C), 133.4 (C), 129.4 (CH), 127.7 (CH), 122.5 (CH), 121.8 (CH), 121.4 (CH), 68.2, 58.6, 58.1, 55.5, 52.3, 34.9, 22.9, 19.7; Rf: 0.17 EtOAc/Hexane (1/19); IR (CH_2Cl_2 cm^{-1}): 3551, 3368, 3064, 2987, 2924, 2868, 1453, 1289, 1265, 1158, 1054, 1024; HRMS (APCI-Tof) (m/z +H) calcd for $C_{21}H_{16}^{79}Br^{81}BrN_2O_6$: 552.9433; found: 552.9496.

4.3.6. *Standard procedure for hydrolysis reactions*

Metallic sodium (46 mg, 2.0 mmol) as small pieces were added slowly and carefully to the stirred MeOH (50 mL) in a round flask (100 mL) at RT. After all metallic sodium reacted with methanol and was exhausted; the solution was additionally stirred for 3 h. Ester **13** (1.0 g, 2.5 mmol) was added and the reaction mixture was stirred at RT for 20 h. The solvent of the mixture was removed under vacuum. Water (100 mL) and EtOAc (40 mL) were added, respectively. The organic phase was separated and the aqueous phase was extracted with EtOAc (40 mL). Combined organic phases were washed with water (30 mL) and dried over Na_2SO_4. After the solvent was evaporated under vacuum, the compound **20** (0.40 g, 80%, yellow solid) was obtained.

4.3.7. *((1R,1's,2′R,4S)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1′-cyclopropan]-2′-yl)methanol (**20**)*

Mp: 92–93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 7.25 (d, $J = 6.7$ Hz, aromatic, 2H), 7.02–6.94 (m, aromatic, 2H), 6.89–6.84 (m, olefinic, 2H), 3.63–3.57 (m, CH_2O, and bridgehead, 2H), 3.37 (bs, bridgehead, 1H), 3.22 (dd, $J = 11.4$, 8.95 Hz, B part of AB system, CH_2O, 1H), 1.22–1.12 (m, cyclopropane CH, 1H), 0.89 (dd, $J = 8.8$, 5.98 Hz, cyclopropane, CH_2, 1H), 0.79 (bs, OH, 1H), 0.57 (t, $J = 5.7$ Hz, cyclopropane CH_2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 151.7 (C), 150.9 (C), 142.2 (CH), 141.7 (CH), 125.0 (CH), 124.8 (CH), 121.9 (CH), 120.9 (CH), 70.9 (C), 64.8, 56.3, 51.9, 24.0, 13.0; Rf: 0.79 EtOAc/Hexane (3/7); IR (CH_2Cl_2 cm^{-1}): 3551, 3368, 3064, 2987, 2924, 2868, 1453, 1289, 1265, 1158, 1054, 1024; HRMS (APCI-Tof) (m/z) calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1000.

4.3.8. *((1R,1′r,2′S,4S)-1,4-dihydrospiro[1,4-methanonaphthalene-9,1′-cyclopropan]-2′-yl) methanol (**22**)*

This reaction was performed according to the standard procedure for hydrolysis reactions. In the reaction, Na (0.36 g, 1.56 mmol, 1.25 equiv.) and compound **14** (0.5 g, 1.25 mmol, 1 equiv.) were used. Compound **22** was obtained as brown solid (0.17 g, %68). Mp: 94–95 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 7.30–7.19 (m, aromatic, 2H), 7.02–6.88 (m, aromatic, 2H, and olefinic, 2H), 3.77 (dd, $J = 11.2$, 6.10 Hz, A part of AB system,

CH_2O,1H), 3.57 (bs, bridgehead, 1H), 3.49 (s, 1H), 3.38–3.29 (m, bridgehead and CH_2O, 2H), 1.40–1.30 (m, cyclopropane, 1H), 0.74 (dd, $J = 8.7$, 6.14 Hz, cyclopropane, 1H), 0.43 (t, $J = 5.7$ Hz, cyclopropane, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 150.6 (C), 150.5 (C), 144.6 (CH), 142.1 (CH), 124.6 (CH), 124.5 (CH), 121.8 (CH), 121.6 (CH), 70.4 (C), 64.7, 53.4, 51.8, 23.6, 13.7; Rf: 0.79 EtOAc/Hexane (3/7); IR (CH_2Cl_2 cm^{-1}): 3398, 3077, 2989, 2880, 1734, 1630, 1544, 1462, 1437, 1345, 1286, 1194, 1162, 1077, 1055, 1024; HRMS (APCI-Tof) (m/z + H) calcd for $C_{14}H_{15}O$: 199.1122; found: 199.1104.

4.3.9. (1R,4S*,9r*)-9-allyl-9-chloro-1,4-dihydro-1,4-methanonaphthalene (21): standard procedure for reaction with $SOCl_2$*

To a stirred solution of alcohol **20** (620 mg, 3.37 mmol) in CH_2Cl_2 (25 mL), $SOCl_2$ (60 mg, 0.5 mmol 1 equiv.) was immediately added at RT. Gas evolution was observed during the reaction. After stirring for 2 h, the solvent was removed under vacuum, and compound **21** was obtained as a yellow solid (95 mg, 86%). Mp: 82–83 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 7.25–7.23 (AA′ part of AA'BB′ system, aromatic, 2H), 7.04–7.01 (BB′ part of AA'BB′ system, aromatic, 2H), 6.78–6.75 (m, olefinic, 2H), 6.04–5.93 (m, olefinic, 1H), 5.20–5.09 (m, olefinic, 2H), 3.92 (t, $J = 2.1$ Hz, bridge, 2H), 2.98 (d, $J = 7.0$ Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 149.2 (C), 141.3 (CH), 134.1 (C), 125.2 (CH), 122.9 (CH), 118.2 (CH), 103.7 (C), 60.1, 41.0; Rf: 0.53 EtOAc/Hexane (1/9); IR (CH_2Cl_2 cm^{-1}): 3457, 3385, 3100, 3008, 3955, 1735, 1696, 1631, 1595, 1543, 1457, 1436, 1413, 1345, 1330, 1286, 1262, 1194, 1162, 1130, 1076; HRMS (APCI-Tof) (m/z + H) calcd for $C_{14}H_{14}^{35}Cl$: 217.0784; found: 217.0767.

4.3.10. (1R,4S*,9s*)-9-allyl-9-chloro-1,4-dihydro-1,4-methanonaphthalene (**23**)*

This reaction was performed according to the standard procedure described for the reaction with $SOCl_2$. In the reaction, alcohol **22** (100 mg, 0.50 mmol, 1 equiv.) and $SOCl_2$ (0.06 g, 0.5 mmol, 1 equiv.) were used. Compound **23** was obtained as brown solid (83 mg, 70%). Mp:140–141 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 7.22–7.18 (AA′ part of AA'BB′ system, aromatic, 2H), 7.04–7.00 (BB′ part of AA'BB′ system, aromatic, 2H), 6.80–6.77 (m, olefinic, 2H), 5.94–5.82 (m, olefinic, 1H), 5.05 (bd, $J = 10.2$ Hz, olefinic, 1H), 4.80 (bd, $J = 17.1$ Hz, olefinic, H), 3.94–3.90 (m, bridgehead, 2H), 2.27 (d, $J = 7.0$ Hz, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 147.5 (C), 141.48 (CH), 133.3 (CH), 125.8 (CH), 122.8 (CH), 118.3 (CH), 101.6 (C), 60.28, 41.58; Rf: 0.28 EtOAc/Hexane (1/9); IR (CH_2Cl_2 cm^{-1}): 3450, 3100, 3008, 2956, 1736, 1631, 1599, 1545, 1462, 1436, 1345, 1330, 1286, 1225, 1197, 1162, 1124, 1076; HRMS (APCI-Tof) (m/z + H) calcd for $C_{14}H_{14}{}^{35}Cl$: 217.0784; found: 217.0792.

4.3.11. ((1s,1a'R*,2R*,2′R*,7′S*,7a'S*)-1a',2′,7′,7a' tetrahydrospiro [cyclopropane-1,8'-[2,7] methanonaphtho[2,3-b]oxiren]-2-yl) methyl 3,5-dinitrobenzoate (**28**): standard procedure for epoxidation*

To a solution of compound **13** (1.0 g, 25 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) was *m*-CPBA (48 mg, 28 mmol, 1.1 equiv.) and $NaHCO_3$ (100 mg) was added, and the mixture was stirred at RT for 4 h. After the reaction was completed and CH_2Cl_2 (20 mL) was added, organic phase was separated and aqueous phase extracted with CH_2Cl_2 (2 × 20 mL). and the mixture was washed with a cold solution of NaOH (1.0%, 3 × 20 mL) and extracted by CH_2Cl_2. Combined organic phases were washed with a cold solution of NaOH (1.0%, 2 × 20 mL) and water (20 mL), and then it was dried over Na_2SO_4. Solvent was removed under vacuum and compound **28** was obtained as a yellow solid (75 mg, 72%). Mp: 86–87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.17 (t, $J = 2.1$ Hz, aromatic, 1H), 8.71 (d, $J = 2.1$ Hz, aromatic, 2H), 7.21 (d, $J = 7.2$ Hz, aromatic, 1H), 6.99 (d, $J = 7.2$ Hz, aromatic, 1H), 6.86 (t, $J = 7.5$ Hz, aromatic, 1H), 6.56 (t, $J = 7.5$ Hz, aromatic, 1H), 4.48 (dd, $J = 11.7$, 4.91 Hz, A part of AB system, OCH_2, 1H), 4.02–3.96 (m, OCH_2, 1H), 3.50 (m, epoxide, 2H), 3.21 (s, bridgehead, 1H), 3.00 (s, bridgehead, 1H), 1.57 (bs, cyclopropane, CH, 1H), 1.21–1.15 (m, cyclopropane, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 162.4 (CO), 148.6 (C), 147.8 (C), 147.7 (C), 133.9 (C), 129.6 (CH), 125.9 (CH), 125.5 (CH), 122.9 (CH), 122.4 (CH), 68.7, 57.9, 57.9, 52.2, 48.2, 43.7 (C), 15.2, 11.7; Rf: 0.37 EtOAc/Hexane (1/9); IR: (CH_2Cl_2, cm^{-1}) 3449, 3101, 2959, 2090, 1728, 1629, 1599, 1544, 1462, 1345, 1279, 1165; HRMS (APCI-Tof) (m/z + H) calcd for $C_{21}H_{16}N_2O_7$: 409.1035; found: 409.1004.

*4.3.12. ((1r,1a'R,2S,2′R,7′S,7a'S)-1a',2′,7′,7a'-tetrahydrospiro [cyclopropane-1,8'-[2,7] methanonaphtho[2,3-b]oxiren]-2-yl) methyl 3,5-dinitrobenzoate (**29**)*

This reaction was performed according to the standard procedure described for epoxidation. In the reaction, compound **14** (1.0 g, 25 mmol 1 equiv.), $NaHCO_3$ (100 mg) and *m*-CPBA (0.48 g, 28 mmol, 1.1 equiv.) were used. Compound **29** was obtained as a yellow solid (60 mg, 58%). Mp:114–116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.22 (d, $J = 2.2$ Hz, aromatic, 2H), 9.19 (t, $J = 4.3$ Hz, aromatic, 1H), 7.28–7.25 (m, aromatic, 1H), 7.73–7.21 (m, aromatic, 1H), 7.11–7.07 (m, aromatic, 2H), 4.55 (dd, $J = 11.7$ Hz, 3.84 Hz, A part of AB system, OCH_2, 1H), 4.44 (dd, $J = 11.7$ Hz, 3.77 Hz, B part of AB system, OCH_2, 1H), 3.44–3.41 (m, epoxide, 2H), 3.32 (bs, bridgehead, 1H), 2.97 (bs, bridgehead, 1H), 1.65–1.62 (m, cyclopropane, CH, 1H), 0.57 (dd, $J = 8.8$ Hz, 2.92 Hz, cyclopropane, 1H), 0.30 (t, $J = 5.7$ Hz, cyclopropane, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 163.0 (CO), 148.8 (C), 147.2 (2 C), 134.7 (CH), 129.8 (CH), 126.1 (CH), 126.1 (CH), 122.9 (CH), 122.8 (CH), 122.4 (CH), 68.5, 57.9, 57.8, 52.2, 48.8, 42.9 (C), 21.4, 6.7; Rf: 0.33 EtOAc/Hexane (1/9); IR: (CH_2Cl_2, cm^{-1}) 3101, 2925, 2854, 1730, 1630, 1546, 1461, 1346, 1279, 1169; HRMS (APCI-Tof) (m/z + H) calcd for $C_{21}H_{16}N_2O_7$: 409.1035; found: 409.1059.

*4.3.13. 4-Allyl-1-naphthaldehyde (30): via reaction of the compound **28** with NaN_3*

To a stirred mixture of the compound **28** (1.0 g, 25 mmol, 1 equiv.), MeOH (20 mL) and water (10 mL), NaN_3 (0.2 g, 2.9 mmol, 1.2 equiv.) and NH_4Cl (0.12 g 2.45 mmol 1.0 equiv.) were added and the reaction mixture was refluxed for 20 h. The solvent (MeOH) was removed under vacuum. Water (75 mL) was added and the mixture extracted with EtOAc (3 × 20 mL). After combined organic phases were dried over Na_2SO_4, the solvent was removed under vacuum and compound **30** was obtained as yellow liquid (40 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 10.86 (s, aldehyde, 1H), 9.00 (d, $J = 8.7$ Hz, aromatic, 1H), 7.98 (d, A part of AB system, $J = 8.4$ Hz, aromatic, 1H), 7.84 (d, $J = 8.1$ Hz, aromatic, 1H), 7.65–7.59 (m, aromatic, 1H), 7.55–7.49 (m, aromatic, 1H), 7.35 (d, B part of AB system,

$J = 8.4$ Hz, aromatic, H), 6.14–6.03 (m, vinyl, 1H), 5.13 (d, $J = 10.1$ Hz, olefinic, 1H), 4.99 (d, $J = 17.1$ Hz, olefinic, 1H), 3.89 (dt, $J = 6.0$ Hz, 1.42 Hz, allyl, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 193.5 (CO), 144.1 (C), 137.1 (CH), 134.8 (C), 132.9 (C), 131.5 (C), 129.2 (CH), 129.0 (CH), 128.7 (C), 128.6 (CH), 126.4 (CH), 125.0 (CH), 117.0 (CH), 37.4 (CH_2); Rf: 0.62 EtOAc/Hexane (1/9); IR: (CH_2Cl_2, cm^{-1}) 3092, 2923, 2851, 1730, 1625, 1543, 1460, 1344, 1267, 1159, 1074, 729; HRMS (APCI-Tof) (m/z + H) calcd for $C_{14}H_{12}O$: 197.0966; found: 197.0965.

4.3.14. *Via reaction of the compound **29** with NaN_3*

This reaction was performed according to the above procedure. In the reaction, compound **29** (1.0 g, 2.45 mmol 1.0 equiv.), NaN_3 (0.2 g, 2.90 mmol, 1.2 equiv.) and NH_4Cl (0.12 g 2.40 mmol 1.0 equiv.) were used and compound **30** was obtained (0.36 g, 65%).

4.3.15. *(E)-1-((4-allylnaphthalen-1-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine (**31**)*

A mixture of the compound **30** (300 mg, 1.53 mmol, 1.0 equiv.), ethyl alcohol (15 mL) and 2,4-dinitrophenylhydrazine (305 mg, 1.53 mmol, 1 equiv.) was refluxed for 24 h. After the solvent was removed under vacuum, water (15 mL) was added and then it was extracted with EtOAc (2 × 25 mL). Combined organic phases were dried over Na_2SO_4 and the solvent was removed under vacuum. Hydrazone **31** (430 mg, 75%) was obtained from crystallization of residue in ethyl alcohol as a red crystal. Mp: 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 11.45 (s, NH, 1H) 9.17 (d, $J = 2.5$ Hz, 1H), 8.77 (bs, 1H), 8.57 (d, A part of AB system, $J = 8.6$ Hz, 1H), 8.36 (dd, A part of AB system, $J = 9.6$, 2.5 Hz, 1H), 8.03 (d, B part of AB system, $J = 9.6$ Hz, 1H), 7.91–7.86 (m, 1H), 7.66–7.57 (m, 1H), 7.57–7.48 (m, 1H), 7.41 (d, B part of AB system, $J = 8.6$ Hz, 1H), 7.26 (s, 1H), 6.14–6.02 (m, olefinic, 1H), 5.15 (bd, $J = 10.1$ Hz, olefinic, 1H), 5.01 (bd, $J = 17.1$ Hz, olefinic, 1H)), 3.79 (bd, $J = 5.9$ Hz, methylenic, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 146.9 (CH), 145.1 (C), 138.9 (C), 136.9 (C), 133.0 (C), 131.6 (C), 131.3 (CH), 130.5 (2 CH), 128.98 (CH), 128.97 (CH), 127.8 (CH), 126.8 (C), 126.2 (CH), 124.8 (CH), 123.7 (2 CH), 117.0 (CH_2), 116.9 (C), 38.8 (CH_2); Rf: 0.70 EtOAc/Hexane (1/9). IR: (CH_2Cl_2, cm^{-1}) 3449, 3101, 2959, 2090, 1728, 1629, 1599, 1544, 1462, 1345, 1279, 1165; HRMS (APCI-Tof) (m/z) calcd for $C_{20}H_{16}N_4O_4$: 376.1172; found: 376.1152.

5. Crystallographic data

For the crystal structure determination, single-crystal compounds **13**, **15** and **31** were used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and oscillation scans technique with $\Delta w = 5^\circ$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc.,2005) software [17]. The structures were solved by direct methods using SHELXS-97,[18] which allowed for the location of most of the heaviest atoms, with the remaining non-hydrogen atoms being located from different Fourier maps calculated from successive full-matrix least squares refinement cycles on F2 using SHELXL-97 [18]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogens attached to carbons were located at their geometric positions using appropriate HFIX instructions in SHELXL. The final difference Fourier maps showed no peaks of chemical significance.

Crystallographic data for all the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-1533107 (**13**), 1531967 (**15**) and 1556630 (**31**). Copies of these data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; FAX: (+44) 1223 336033, or online via www.ccdc.cam.ac.uk/data request/cif, or by emailing data_request@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.07.060.

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