ORIGINAL RESEARCH

Variations of bistricyclic aromatic enes: mono-bridged tetraarylethene naphthologs

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Abstract The syntheses, molecular and crystal structures, NMR spectroscopic study, and DFT computational study of naphthologs of mono-bridged (X = -, O, S, Se, and Te) tetraarylethene (BAE-1s) **11–25** with α, α -, β, β -, and α,β -dinaphthalenyl substituents have been reported. The BAE-1s have been prepared by Barton-Kellog twofold extrusion from the respective chalcogenothiones and diazomethylenebisnaphthylenes. Complete assignments of ¹Hand ¹³C-NMR spectra of 11–25 have been made through 2-dimensional correlation spectroscopy (DQF-COSY, HSQC, HMBC, and NOESY). The corresponding intermediates, thiiranes 33-47, have been also isolated (except 38), and their molecular and crystal structures have been determined. The molecular structures of BAE-1s 12-15, 20, and 22-25 adopted folded-twisted conformations with considerably folded ($\varphi = 30^{\circ}-57^{\circ}$) tricyclic moieties. The α,α - and α,β -dinaphthalenyl derivatives are more overcrowded than β , β -dinaphthalenyl derivatives. The relief of the steric strain due to the overcrowding around $C^9 = C^{9'}$ caused by the presence of naphthalenyl substituents was achieved by their twisting around the single bonds that connect the α -naphthalenyl and β -naphthalenyl moieties to $C^{9'}$. The ¹H-NMR spectra have shown shielding of H², H⁷ of 11-25 and the pronounced deshielding of H^{8'}, H^{8"} of α,α -dinaphthalenyl-substituted BAE-1s 13–15 in contrast to β , β -dinaphthalenyl-substituted BAE-1s **16–20**. The

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upfield shifts of H², H⁷ suggested conformations in which these hydrogens are located above the planes of the opposing naphthalene rings. DFT calculations of 11-20 have been performed at B3LYP/6-31G(d) and B3LYP/ SDD. The results have shown that the global minima of BAE-1s without a chalcogen bridge 11 and 16 are twisted (-sc, -sc)- C_2 -t conformations. The global minima of BAE-1s with a chalcogen bridge are folded-twisted $(-sc, -ac)-C_1$ ft conformations for α, α -dinaphthalenyl-substituted BAE-1s 12–15 and either *anti*- or $syn-(-sc,ac)-C_1$ -ft conformations for β , β -dinaphthalenyl-substituted BAE-1s 17–20. The pronounced differences between the α,α -dinaphthalenyl and the β , β -dinaphthalenyl derivatives are noted. Dispersion-corrected **B3LYP** calculations stabilize significantly the α, α -dinaphthalenyl derivatives versus the β,β-dinaphthalenyl derivatives. The geometrical parameters of BAEs-1 11-15 and 20, derived from their molecular X-ray structures and from their B3LYP-optimized geometries are in a good agreement.

Keywords Naphthalene \cdot Te \cdot Se \cdot Overcrowding \cdot Conformations \cdot AIE luminogen \cdot DFT \cdot NMR \cdot Empirical dispersion correction

Introduction

Bistricyclic aromatic enes (BAEs) [1–4] (Fig. 1) have fascinated chemists since the parent BAE bifluorenylidene (1) was synthesized in 1875 [5]; dixanthylene (2) was synthesized in 1895 [6]; and thermochromism, piezochromism, and photochromism were revealed in bianthrone (3) [7, 8] and dixanthylene (2) [9]. BAEs are defined by the general structure shown in Fig. 1 and consist of two tricyclic moieties that are connected at the central positions

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Fig. 1 Bistricyclic aromatic enes

 C^9 and $C^{9'}$ by a double bond. BAEs are classified as *homomerous* BAEs (Fig. 1, X = Y) and heteromerous BAEs (Fig. 1, $X \neq Y$). They may be viewed as doubly bridged tetraarylethenes and as tetrabenzofulvalenes. The BAEs are attractive substrates for the study of the ground-state properties and dynamic stereochemistry of overcrowded polycyclic aromatic enes (PAEs) and for their thermochromic, photochromic, electrochromic, and piezochromic behavior [2]. The homomerous BAEs dithioxanthylene (4) [10], diselenoxanthylene (5) [11], and ditelluroxanthylene (6) [12] are not thermochromic. Heteromerous derivatives of 2 and 4 and related overcrowded enes serve as candidates for chiroptical molecular switches and molecular motors [13].

The BAEs, including **1–6**, are overcrowded in their *fjord* regions on both sides of the central double bond ($C^9 = C^{9'}$) (Fig. 1) [1, 4]. The intramolecular overcrowding in BAEs [14, 15] imposes out-of-plane deformation to alleviate prohibitively close contacts of non-bonded atoms in the fjord regions ($C^1 \cdots C^{1'}$, $C^8 \cdots C^{8'}$, $C^1 \cdots H^{1'}$, $C^8 \cdots H^{8'}$, $H^1 \cdots H^{1'}$, $H^8 \cdots H^{8'}$). The unique molecular architecture of BAEs gives rise to three basic conformations: *anti*-folded, *syn*-folded, and twisted [2]. Each conformation represents a compromise between π -delocalization and steric strain. The bridges X and Y play an important role in the relative stability of the three conformations, leading in favorable cases to thermochromism [16–19]. The stereochemistry of BAEs has very recently been reviewed and analyzed [4].



Fig. 2 BAE-1s naphthologs



The degree of the overcrowding in BAEs may be reduced by removing the bridges X and/or Y [20]. The following two variations leading to open BAEs exist: (i) removal of one bridge (X or Y) of the BAE to give BAE-1, i.e., mono-bridged tetraarylethene e.g., 9-diphenvlmethylen-9H-fluorene (7) [21] and-9-diphenylmethylen-9*H*-xanthene (8) [22]; and (ii) removal of the two bridges of BAE to give BAE-2, i.e., tetraarylethene, e.g., tetraphenylethene (9) [23] and tetrakis (2-naphthalenvl)ethene (10) [24, 25]. Removal of the ring constraint (and of π -delocalization when the central ring had aromatic character) facilitates rotations of the aryl groups about the formal single C-C bonds between the ene carbon atoms (C^9 and/or $C^{9'}$) and the aryl group bonded to C^9 and/or $C^{9'}$. This conformational flexibility in BAE-1 and BAE-2 reduces overcrowding in the nonplanar ground state, while rotation is hindered by steric overlap.



BAE-2 tetraphenylethene (9) is one of the popular aggregation-induced emission (AIE) luminogens. [23, 26]. The twisted, propeller-shaped 9 was described as an ethene stator completely surrounded by phenyl rotors [23]. Very recently, it was discovered that locking the phenyl rings in **9** with "O" bridges to give diphenylmethylenexanthene (**8**) and dixanthylene (2) increases gradually the emission efficiency of luminogen solutions, thus supporting the restriction of intermolecular rotation (RIR) mechanism of the AIE phenomenon [22, 26]. By contrast, introducing naphthalenyl substituents at the ω positions of the 9-methylene-tricyclic aromatic enes in place of the respective benzene rings to give e.g., 10 may enhance the overcrowding [24, 25]. Recent studies of highly overcrowded naphthologs of BAE bis-dibenzo[a,i]fluorenylidene [27] and bis-benzo[a]fluorenylidene [28] have been reported.

We report here the synthesis, molecular and crystal structures, and NMR spectroscopic study of naphthologs of mono-bridged tetraarylethene (BAE-1s). The following BAE-1s with 1-naphthalenyl and 2-naphthalenyl substituents at the ω position of the 9-methylene-fluorenylidene and chalcogenoxanthene were targeted: (Fig. 2): 9-(di-1naphthalenylmethylene)-9H-fluorene (11), 9-(di-1-naphthalenylmethylene)-9H-xanthene (12), 9-(di-1-naphthalenylmethylene)-9H-thioxanthene (13), 9-(di-1-naphthalenyl methylene)-9H-selenoxanthene (14), 9-(di-1-naphthalenylmethylene)-9H-telluroxanthene (15), 9-(di-2-naphthalenvlmethylene)-9H-fluorene (16), 9-(di-2-naphthalenylme thylene)-9*H*-xanthene (17), 9-(di-2-naphthalenylmethylene)-9*H*-thioxanthene (18), 9-(di-2-naphthalenylmethylene)-9H-selenoxanthene (19), 9-(di-2-naphthalenylmethyl ene)-9*H*-telluroxanthene (20), 9-(di-1,2'-naphthalenylmethylene)-9*H*-fluorene (21), 9-(di-1,2'-naphthalenylmethylene)-9*H*-xanthene (22), 9-(di-1,2'-naphthalenylmethyle ne)-)-9H-thioxanthene (23), 9-(di-1,2'-naphthalenylmethyl

ene)-9*H*-selenoxanthene (24), and 9-(di-1,2'-naphthale-nylmethylene)-9*H*-telluroxanthene (25).

The aim of the study was to compare the effects of the bridges X = -, O, S, Se, Te, and of the substitution site of the naphthalene rings (1-naphthalenyl versus 2-naphthalenyl) on the conformations of these BAE-1 naphthologs. The emphasis in the present study is on BAE-1s of the dinaphthalenylmethylene chalcogenoxanthene series. The BAE-1s naphthologs **11** and **12** have previously been described [20].

Experimental section

Melting points are uncorrected. All NMR spectra were recorded with a Bruker DRX 500 spectrometer; ¹H NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500.2 MHz using CDCl₃ as solvent and as internal standard (δ (CHCl₃) = 7.26 ppm). ¹³C NMR spectra were recorded at 125.78 MHz using CDCl₃ as solvent and as internal standard (δ (CDCl₃) = 77.00 ppm). Complete assignments were made through 2-dimensional correlation spectroscopy (DQF-COSY, HSQC, HMBC, and NOESY). Petroleum ether (PE, b.p. 40°–60°) was used. Benzene and toluene were dried on sodium.

Single-crystal X-ray diffraction was carried out on a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite monochromator and using MoK_{α} radiation ($\lambda = 0.71073$ Å). Single crystals were attached to glass fibers, with either epoxy glue or mineral oil. Data were collected at 173 K. Low temperature was maintained with a Bruker KRYOFLEX nitrogen cryostat. The diffractometer was controlled by a Pentium-based PC running the SMART software package [29]. Immediately after collection, the raw data frames were transferred to a second PC computer for integration and reduction by the SAINT program package [30]. The structures were solved and refined anisotropically by full matrix least squares on F2 values by the SHELXTL software package [31].

The quantum mechanical calculations of the BAE-1s under study were performed with the Gaussian03 [32] and Gaussian09 [33] packages. Becke's three-parameter hybrid density functional B3LYP [34], with the non-local correlation functional of Lee et al. [35], was used. The Pople-style split-valence 6-31G(d) basis set and double-zeta SDD basis set were employed for geometry optimizations. All structures were fully optimized, using symmetry constrains as indicated. Vibrational frequencies were calculated at B3LYP/6-31G(d) and B3LYP/SDD to verify the nature of the stationary points. Non-scaled thermal corrections to enthalpy and to free energy calculated at the same levels

were applied. The dispersion-corrected DFT calculations were performed in the form of the most recently developed D3 method, as implemented in Gaussian 09 [36–38].

BAE-1s 11-25 were synthesized by Barton's doubleextrusion diazo-thione coupling method (aka Barton-Kellog olefination) [39-41]. The syntheses of the BAE-1s 9-(di-1-naphthalenylmethylene)-9*H*-fluorene (11)and 9-(di-1-naphthalenylmethylene)-9*H*-xanthene (12) were described [20]. The starting compounds for the syntheses of 11–15 were 1,1'-(diazomethylene)bisnaphthylene (26) and 9H-chalcogenoxanthene-9-thiones (27) [42]. The starting compounds for the synthesis of 16 were 2,2'-dinaphthalenyl thioketone (28) [20] and 9-diazo-9H-fluorene (29) [42]. The staring compounds for the syntheses of 17–20 were 2.2'-(diazomethylene)bisnaphthylene (30) and thiones **27** [42]. The starting compounds for the syntheses of 21–25 were 1,2'-(diazomethylene)bisnaphthylene (32) and thiones 27 [42]. Thiiranes 33-37, 39-42, and 43-47 were the intermediate compounds in syntheses of 11-15, 16-20 and 21-25, respectively.

3',3'-Di-(1-naphthalenyl)-spiro[9*H*-thioxanthene-9,2'-thiiran] (**35**)

To a stirred solution of 1,1'-(diazomethylene)bisnaphthylene (**26**) [42] (0.31 g, 1.36 mmol), protected by CaCl₂ tube, 9*H*-thioxanthene-9-thione (**27**, X = S) [42] (0.4 g, 1.36 mmol) in benzene (10 mL) was added. The reaction mixture was stirred with reflux for 2 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A light yellow powder of **35** was obtained, 0.23 g, yield 34 %. mp 218 °C. Yellow single crystals of **35** were obtained from CH₂Cl₂. ¹H, ¹³C, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.739 (td, ³J = 8.0 Hz, ${}^{3}J = 7.0 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{7}), 6.776$ (td. ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H⁶), 6.952 (t, ${}^{3}J = 8.0$ Hz, 1H, $H^{3''}$), 7.002 (dd, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H^{5}), 7.029 (td, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H²), 7.159 (d, ${}^{3}J = 7.0$ Hz 1H, H^{2"}), 7.195 (td, ${}^{4}J = 1.5$ Hz,1H, $^{3}J = 7.5$ Hz, H^{6'}), 7.267 (td, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H^{7'}), 7.331 (td, ${}^{3}J = 8.0 \text{ Hz}, {}^{3}J = 7.5 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{3}$), 7.339 (td, ${}^{3}J = 8.5$ Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz 1H, $H^{6''}$), 7.423 (t, ${}^{3}J = 8.0 \text{ Hz}$, ${}^{3}J = 7.5 \text{ Hz}$, 1H, $H^{3'}$), 7.468–7.527 (m, 5H, H⁸, H^{4'}, H^{4''}, H^{5'}, H^{7''}), 7.590 (dd, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{1}), 7.653$ (dd. ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H⁴), 7.679 (d, ${}^{3}J = 7.5$ Hz, 1H, $H^{5''}$), 8.607 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, $H^{2'}$), 8.668 (d, ${}^{3}J = 8.5$ Hz, 1H, H ${}^{8''}$), 8.884 (d, ${}^{3}J = 9.0$ Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ(ppm): 62.84 (C⁹), 67.27 (C^{9'}), 123.02 (C^{3"}), 124.05 (C^{3'}), 124.17 (C^{7'}), 124.87 (C^{6'}), 124.89 (C^{6"}), 124.96 (C⁷), 125.06 (C^{8"}), 125.73 (C⁵), 125.80 (C^{7"}), 126.15 (C⁴), 126.38 (C²), 126.49 (C^{8'}), 126.80 (C⁶), 127.73 (C³), 127.78 (C^{5'}), 128.34 (C^{2"}), 128.39 (C^{4"}), 128.60 (C^{4'}), 129.17 (C^{5"}), 130.22 (C⁸), 130.82 (C^{8a'}), 131.75 (C^{8a}), 132.02 (C^{2'}), 132.13 (C¹), 132.71 (C^{4a'}), 132.78 (C^{8a''}), 133.82 (C^{1"}), 133.92 (C^{1'}), 133.99 (C^{4a''}), 134.19 (C^{10a}), 134.21 (C^{9a}), 135.53 (C^{4a}).

9-(Di-1-naphthalenylmethylene)-9H-thioxanthene (13)

To a stirred solution of thiirane **35** (0.06 g, 0.12 mmol) in toluene (6 mL), protected by CaCl₂ tube, PPh₃ (0.07 g, 0.25 mmol) was added. After refluxing for 3 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder of **13** was obtained, 0.04 g, yield 71 %, mp 244 °C. Yellow single crystals of **13** were obtained from benzene. ¹H, ¹³C, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.634 (t, ³J = 8.5 Hz, ³J = 7.5 Hz, 1H, H⁷), 6.770 (t, ³J = 7.5 Hz, ³J = 7.0 Hz, 1H, H⁶), 6.860 (t, ³J = 7.5 Hz, ³J = 7.0 Hz, 1H, H³), 7.008 (t, ³J = 8.0 Hz, ³J = 7.0 Hz, 1H, H⁶), 7.024 (d, ³J = 8.0 Hz, ³J = 7.5 Hz, 1H, H⁸), 7.150-7.157 (m, 1H, H^{3'}), 7.282-7.313 (m, 4H, H¹, H⁴, H^{3''}, H^{6''}), 7.350 (t, ³J = 8.0 Hz, 1H, H^{7''}), 7.474 (td, ³J = 7.5 Hz, 1H, H⁵), 7.588 (d, ³J = 8.0 Hz, 1H, H^{4''}), 7.625-7.692 (m, 4H, H^{2'}, H^{4'}, H^{6''}, H^{5''}), 7.895 (t, ³J = 7.5 Hz, ³J = 7.0 Hz, 1H, H^{7''}), 7.934 (d, ³J = 8.0 Hz, 1H, H^{5'}), 7.994 (d, ³J = 7.0 Hz, 1H, H^{2''}), 8.427 (d, ³J = 8.5 Hz, 1H, H^{8''}), 9.007 (d, ³J = 8.0 Hz, 1H, H^{8''}).

¹³C NMR (CDCl₃) δ(ppm): 124.76 (C^{3″}), 125.13 (C²), 125.27 (C^{6″}), 125.51 (C^{8″}), 125.62 (C^{7″}), 125.68 (C^{6′}, C⁷), 125.89 (C^{3′}), 126.20 (C⁴), 126.29 (C⁵), 126.50 (C⁶), 126.55 (C³), 126.68 (C^{7′}), 126.77 (C^{2″}), 126.99 (C⁸), 127.06 (C^{2′}, C^{4′}, C^{8′}), 127.15 (C^{4″}), 127.97 (C^{5″}), 128.56 (C^{8a″}), 128.90 (C^{5′}), 129.36 (C¹), 133.33 (C^{4a″}), 133.36 (C^{10a}), 133.40 (C^{4a′}), 133.42 (C^{4a}), 133.74 (C^{8a′}), 135.36 (C^{9′}), 135.48 (C^{8a}), 136.74 (C^{9a}), 138.74 (C⁹), 139.62 (C^{1″}), 140.05 (C^{1′}).

3',3'-Di-(1-naphthalenyl)-spiro[9*H*-selenoxanthene-9,2'-thiiran] (**36**)

To a stirred solution of 1,1'-(diazomethylene)bisnaphthylene (**26**) [42] (0.5 g, 1.36 mmol) in benzene (15 mL), protected by CaCl₂ tube, 9*H*-selenoxanthene-9-thione (**27**, X = Se) [42] (0.46 g, 1.70 mmol) was added. The reaction mixture was stirred with reflux for 4 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Purification of the crude product took place by column chromatography on silica gel using PE-Et₂O 99:1 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **36** was isolated and obtained as colorless powder, 0.104 g, yield 11 %, mp 212 °C. Colorless single crystals of **36** were obtained from CH₂Cl₂. ¹H, ¹³C, ⁷⁷Se, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.756 (t, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, 1H, H³), 6.872 (t, ³*J* = 7.5 Hz, 1H, H²), 6.989 (t, ³*J* = 8.0 Hz, 1H, H^{3"}), 7.091 (t, ³*J* = 7.5 Hz, 1H, H⁷), 7.114 (d, ³*J* = 7.5 Hz, 1H, H⁴), 7.183–7.234 (m, 2H, H^{6'}, H^{7'}), 7.279–7.332 (m, 3H, H^{2"}, H⁶,H^{6"}) 7.382 (t, ³*J* = 8.5 Hz, ³*J* = 7.5 Hz, 1H, H^{3'}), 7.430 (t, ³*J* = 7.5 Hz, 1H, H^{7"}), 7.488-7.517 (m, 2H, H^{4'}, H^{5'}), 7.533 (d, ³*J* = 8.5 Hz, 1H, H^{4"}), 7.661–7.701 (m, 3H, H¹, H^{5"}, H⁸), 7.785 (d, ³*J* = 7.0 Hz, 1H, H⁵), 8.504 (d, ³*J* = 8.5 Hz, 1H, H^{8"}), 8.576 (d, ³*J* = 7.5 Hz, 1H, H^{2'}), 8.985 (d, ³*J* = 8.0 Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ (ppm): 66.81 (C⁹), 67.57 (C^{9'}), 123.08 (C^{3''}), 124.96 (C^{3'}), 124.00 (C^{7'}), 124.880 (C^{6'}), 124.86 (C^{6''}), 125.09 (C^{8''}), 125.48 (C²), 125.82 (C^{7''}), 126.84 (C³), 126.88 (C⁷), 127.42 (C^{8'}), 127.72 (C^{5'}), 127.76 (C⁶), 127.88 (C^{2''}), 128.38 (C^{4''}), 128.71 (C^{4'}), 128.73 (C⁴), 128.86 (C⁵), 129.10 (C^{5''}), 131.22 (C^{8a'}), 131.29 (C¹), 131.56 (C^{4a}), 131.86 (C^{2'}), 132.77 (C^{8a''}), 133.01 (C⁸), 133.04 (C^{4a''}), 133.39 (C^{9a}), 133.44 (C^{10a}), 133.57 (C^{1'}), 133.91 (C^{4a''}), 134.81 (C^{1''}), 136.12 (C^{8a}).

⁷⁷Se NMR (CDCl₃) δ (ppm): 352.35.

9-(Di-1-naphthalenylmethylene)-9*H*-selenoxanthene (14)

To a stirred solution of thiirane **36** (0.10 g, 0.18 mmol) in toluene (20 mL), protected by CaCl₂ tube, PPh₃ (0.09 g, 0.36 mmol) was added. After refluxing for 3 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using only PE as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **14** was isolated and obtained as yellow powder, 0.05 g, yield 55 %, mp 233 °C. Yellow single crystals of **14** were obtained from CH₂Cl₂. ¹H, ¹³C, ⁷⁷Se, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.645 (td, ³J = 8.5 Hz, $^{3}J = 7.0$ Hz, $^{4}J = 1.5$ Hz, 1H, H²), 6.721 (td, ${}^{4}J = 1.5$ Hz, $^{3}J = 7.5$ Hz, 1H, H^{7}), 6.818 (td, $^{3}J = 8.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H⁶), 6.952 (td, ${}^{4}J = 1.5$ Hz, $^{3}J = 8.0$ Hz, 1H, H^{3}), 7.137 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H ${}^{3'}$), 7.145 (d, ${}^{3}J = 8.0$ Hz, 1H, H¹), 7.198 (dd, ${}^{3}J = 7.0$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^{2'}) 7.288–7.319 (m, 2H, $H^{3''}$, $H^{6''}$), 7.356 (dd, ${}^{3}J = 7.5$ Hz,

1H, H⁸), $^{3}J = 7.5$ Hz, $^{4}J = 1.5$ Hz. 7.370 (td. ${}^{4}J = 1.0$ Hz, 1H, H^{7"}), 7.417 (dd, $^{3}J = 7.5$ Hz, ${}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{5}), 7.575 \text{ (d, }{}^{3}J = 8.0 \text{ Hz}, 1\text{H}, \text{H}^{4''}),$ 7.592 (d, ${}^{3}J = 7.0$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H⁴), 7.615-7.639 (m, 3H, $H^{6'}$, $H^{4'}$, $H^{5''}$), 7.889 (td, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^{7'}), 7.902 (d, ${}^{3}J = 7.5$ Hz, 1H, H^{5'}), 8.051 (d, ${}^{3}J = 7.0$ Hz, 1H, H^{2"}), 8.589 (d, ${}^{3}J = 8.5$ Hz, 1H, $H^{8''}$), 9.017 (d, ${}^{3}J = 8.5$ Hz, 1H, $H^{8'}$).

¹³C NMR (CDCl₃) δ(ppm): 124.41 (C^{3"}), 124.87 (C^{2'}), 125.28 (C^{6"}), 125.42 (C^{7"}), 125.53 (C⁷), 125.61 (C^{6'}), 125.81 (C^{3'}), 126.04 (C²), 126.05 (C^{8"}), 126.49 (C^{7'}), 126.57 (C³), 126.64 (C⁶), 126.69 (C^{2"}), 127.04 (C^{4'}), 127.11 (C^{4"}), 127.19 (C^{8'}), 127.51 (C¹), 127.94 (C^{5"}), 128.76 (C^{8a"}), 128.85 (C⁵), 128.88 (C^{5'}), 128.90 (C⁴), 130.00 (C⁸), 130.46 (C^{4a}), 130.59 (C^{10a}), 133.14 (C^{8a'}), 133.27 (C^{4a'}), 133.40 (C^{1"}), 136.15 (C^{9'}), 136.94 (C^{9a}), 137.87 (C^{8a}), 139.27 (C^{4a"}), 139.92 (C^{1'}), 141.87 (C⁹). ⁷⁷Se NMR (CDCl₃) δ(ppm): 359.43, 360.46.

3',3'-Di-(1-naphthalenyl)-spiro[9*H*-telluroxanthene-9,2'-thiiran] (**37**)

To a stirred solution of 1,1'-(diazomethylene)bisnaphthylene (**26**) [42] (0.3 g, 1.03 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9*H*-teloroxanthene-9-thione (**27**, X = Te) [42] (0.33 g, 1.03 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 3 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder was obtained, 0.10 g, yield 16 %, mp 273 °C. Yellow single crystals of **37** were obtained from benzene. ¹H, ¹³C, ¹²⁵Te, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.741 (t, ³*J* = 7.0 Hz, 1H, H³), 7.017 (t, ³*J* = 7.5 Hz, 1H, H^{3''}), 7.032 (t, ³*J* = 7.5 Hz, ³*J* = 6.5 Hz, 1H, H²), 7.078 (t, ³*J* = 8.0 Hz, ³*J* = 7.0 Hz, 1H, H^{7'}), 7.142 (t, ³*J* = 8.5 Hz, ³*J* = 7.5 Hz, 1H, H⁷), 7.178 (t, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, 1H, H^{6'}), 7.206 (t, ³*J* = 7.0 Hz, 1H, H⁶) 7.253–7.303 (m, 4H, H⁴, H^{3'}, H^{6''}, H^{7''}), 7.384 (d, ³*J* = 7.5 Hz, 1H, H^{2''}), 7.474–7.512 (m, 2H, H^{4''}, H^{5''}), 7.560 (d, ³*J* = 8.0 Hz, 1H, H^{4''}), 7.648 (d, ³*J* = 8.0 Hz, 1H, H^{5''}), 7.745 (d, ³*J* = 7.5 Hz, 1H, H⁸), 7.924 (d, ³*J* = 7.5 Hz, 1H, H¹), 7.938 (d, ³*J* = 6.5 Hz, 1H, H⁵), 8.217 (d, ³*J* = 8.0 Hz, 1H, H^{8''}), 8.402 (d, ³*J* = 7.5 Hz, 1H, H^{2''}), 8.882 (d, ³*J* = 8.5 Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ(ppm): 66.99 (C^{9'}), 73.68 (C⁹), 118.24 (C^{4a}), 121.23 (C^{10a}), 123.28 (C^{3"}), 123.77 (C^{7'}), 123.92 (C^{3'}), 124.68 (C^{6'}), 124.91 (C^{6"}), 125.07 (C^{8"}), 125.85 (C^{7"}), 126.34 (C²), 126.69 (C³), 126.90 (C^{2"}), 127.59 (C⁶), 127.63 (C⁷), 127.79 (C^{5'}), 128.30 (C^{4"}), 128.75 (C^{8'}), 128.81 (C^{4'}), 129.02 (C^{5"}), 131.34 (C^{2'}), 131.71 (C^{8a'}), 132.51 (C¹), 132.78 (C^{8a"}), 133.02 (C^{1'}), 133.48 ($C^{4a'}$), 133.76 (C^{8}), 133.87 ($C^{4a''}$), 134.87 (C^{5}), 135.47 (C^{4}), 136.82 ($C^{1''}$), 137.43 (C^{9a}), 139.96 (C^{8a}). ¹²⁵Te NMR (CDCl₃) δ (ppm): 547.16.

9-(Di-1-naphthalenylmethylene)-9*H*-telluroxanthene (15)

To a stirred solution of thiirane **37** (0.05 g, 0.08 mmol) in toluene (15 mL), protected by CaCl₂ tube, PPh₃ (0.04 g, 0.17 mmol) was added. After refluxing for 3 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using only PE as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired **15** product was isolated and obtained as yellow powder, 0.03 g, yield 32 %, mp 242 °C. Yellow single crystals of **15** were obtained from toluene. ¹H, ¹³C, ¹²⁵Te, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.648 (td, ³J = 7.5 Hz, ${}^{4}J = 1.0$ Hz, $^{3}J = 7.5$ Hz, 1H, H^{7}), 6.741 (td, ${}^{4}J = 1.5$ Hz, $^{3}J = 7.5$ Hz, 1H, H^{3}), 6.784 (td, H²), $^{3}J = 7.5$ Hz, $^{4}J = 1.5$ Hz, 1H, 6.858 (td, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H⁶), 7.132 (t, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.5 \text{ Hz}, 1\text{H}, \mathrm{H}^{3'}, 7.282 \text{ (dd,}$ $^{3}J = 8.0$ Hz, ${}^{3}J = 1.0$ Hz, 1H, H⁸), 7.295–7.334 (m, 3H, H^{2'}, H^{3''}, H^{6''}) 7.391 (td, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, $H^{7''}$), 7.478 (dd, ${}^{3}J = 7.5 \text{ Hz}$, ${}^{4}J = 1.5 \text{ Hz}$, 1H, H¹), 7.563 $(dd, {}^{3}J = 8.5 \text{ Hz}, 1\text{H}, \text{H}^{4}), 7.572-7.602 \text{ (m, 3H, H}^{4'}, \text{H}^{4''},$ $H^{6'}$), 7.610 (d, ${}^{3}J = 8.0 \text{ Hz}$, 1H, $H^{5''}$), 7.744 (td, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H⁵), 7.852 (d, ${}^{3}J = 7.5$ Hz, 1H, $H^{5'}$), 7.868 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{7'}$), 8.150 (d, ${}^{3}J = 7.0 \text{ Hz}, 1\text{H}, \text{H}^{2''}$), 8.802 (d, ${}^{3}J = 8.5$ Hz, 1H, H ${}^{8''}$), 9.023 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ(ppm): 116.23 (C^{10a}), 116.62 (C^{4a}), 124.49 (C^{3"}), 125.12 (C^{7"}), 125.31 (C^{6"}), 125.49 (C^{6'}), 125.52 (C^{2'}), 125.69 (C^{3'}), 126.15 (C^{7'}), 126.27 (C^{2'}), 126.48 (C³), 126.62 (C⁶), 126.73 (C⁷), 126.93 (C^{2"}), 127.06 (C^{4'}, C^{4"}, C^{8"}), 127.32 (C^{8'}), 127.93 (C^{5"}), 127.97 (C⁸), 128.83 (C^{5'}), 129.13 (C^{8a"}), 130.49 (C¹), 132.69 (C^{8a'}), 133.23 (C^{4a"}), 133.44 (C^{4a'}), 134.76 (C⁴), 134.87 (C⁵), 137.28 (C^{9'}), 138.62 (C^{1"}), 139.72 (C^{1'}), 140.91 (C^{8a}, C^{9a}), 147.12 (C⁹).

¹²⁵Te NMR (CDCl₃) δ(ppm): 551.38, 550.26.

9-(Di-2-naphthalenylmethylene)-9H-fluorene (16)

To a stirred solution of 2,2'-dinaphthalenyl thioketone (**28**) [20] (0.22 g, 0.72 mmol) in benzene (15 mL), protected by CaCl₂ tube, 9-diazo-9*H*-fluorene (**29**) (0.14 g, 0.72 mmol) dissolved in benzene (10 mL) was added. The reaction

mixture was stirred with reflux for 3 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder of **16** was obtained, 0.12 g, yield 16 %. mp 182 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.739 (t, ³*J* = 7.0 Hz, 2H, H³, H⁶), 6.869 (td, ³*J* = 8.0 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H², H⁷), 7.256 (td, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.0 Hz, 2H, H¹, H⁸), 7.503-7.572 (m, 6H, H^{3'}, H^{3''}, H^{6''}, H^{6''}, H^{7''}, H^{7''}), 7.744 (d, ³*J* = 7.5 Hz, 2H, H⁴, H⁵), 7.809 (d, ³*J* = 7.5 Hz, 2H, H^{8'}, H^{8''}), 7.893-7.923 (m, 4H, H^{4'}, H^{4''}, H^{5''}, H^{5''}), 7.927 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ(ppm): 119.28 (C⁴, C⁵), 124.95 (C³, C⁶), 127 (C^{3′}, C^{3″}, C^{7′}, C^{7″}), 126.49 (C², C⁷), 126.57 (C^{6′}, C^{6″}), 127.71 (C¹, C⁸), 127.80 (C^{4′}, C^{4″}), 128.39 (C^{5′}, C^{5″}), 128.47 (C^{8′}, C^{8″}), 129.56 (C^{1′}, C^{1″}), 133.12 (C^{4a′}, C^{4a″}), 133.46 (C^{9′}), 133.51 (C^{8a′}, C^{8a″}), 138.81 (C^{8a}, C^{9a}), 140.43 (C⁹), 140.54 (C^{4a}, C^{4b}), 145.18 (C^{2′}, C^{2″}).

3',3'-Di-(2-naphthalenyl)-spiro[9*H*-xanthene-9,2'-thiiran] (**39**)

To a stirred solution of 2,2'-(diazomethylene)bisnaphthylene (**30**) [42] (0.3 g, 1.02 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9*H*-xanthene-9-thione (**27**, X = O) [42] (0.22 g, 1.02 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 13 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A colorless powder was of **39** obtained, 0.06 g, yield 12 %, mp 242 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.566 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.0 Hz, 2H, H², H⁷), 7.003 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H¹, H⁸), 7.113 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.5 Hz,2H, H³, H⁶), 7.232 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 2H, H⁴, H⁵), 7.261 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{3''}, H^{3'''}), 7.335 (td, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.0 Hz, 2H, H^{6''}, H^{6''}), 7.335 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.0 Hz, 2H, H^{7'}, H^{7''}), 7.424 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.607 (d, ³*J* = 8.0 Hz, 2H, H^{5''}, H^{5''}), 7.657 (d, ³*J* = 8.0 Hz, 2H, H^{8''}, H^{8'''}), 7.785 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ(ppm): 55.16 (C⁹), 69.42 (C^{9'}), 115.60 (C⁴, C⁵), 121.81 (C^{3'}, C^{3"})122.76 (C², C⁷), 125.84 (C^{6'}, C^{6"}), 125.90 (C^{7'}, C^{7"}), 127.04 (C^{3'}, C^{3"}), 127.20 (C^{4'}, C^{4"}), 127.35 (C^{5'}, C^{5"}), 127.83 (C^{8'}, C^{8"}), 128.61 (C^{8a}, C^{9a}). 128.64 (C^{1'}, C^{1"}), 129.07 (C¹, C¹), 132.02 (C^{4a'}, C^{4a"}), 132.77 (C^{8a'}, C^{8a"}), 138.56 (C^{2'}, C^{2"}), 154.62 (C^{4a}, C^{10a}).

9-(Di-2-naphthalenylmethylene)-9H-xanthene (17)

To a stirred solution of thiirane **39** (0.05 g, 0.10 mmol) in toluene (20 mL), protected by $CaCl_2$ tube, PPh₃ (0.04 g, 0.15 mmol) was added. After refluxing for 2 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder of **17** was obtained, 0.03 g, yield 58 %, mp 222 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.599 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz 2H, H², H⁷), 7.002 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 2H, H¹, H⁸), 7.112 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.186 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 2H, H⁴, H⁵), 7.400–7.438 (m, 6H, H^{3'}, H^{3''}, H^{6'}, H^{6''}, H^{7'}, H^{7''}), 7.726 (d, ³*J* = 8.5 Hz, 2H, H⁴, H^{4'}), 7.735–7.782 (m, 4H, H^{5'}, H^{5''}, H^{8'}, H^{8''}), 7.828 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ(ppm): 166.35 (C⁴, C⁵), 122.49 (C², C⁷), 124.56 (C^{8a}, C^{9a}), 125.87 (C^{7'}, C^{7''}), 126.00 (C^{6'}, C^{6''}), 126.06 (C⁹), 127.65 (C⁵, C^{5'}), 128.01 (C^{3'}, C^{3''}), 128.04 (C^{8'}, C^{8''}), 128.10 (C³, C⁶), 128.12 (C^{4'}, C^{4''}), 128.65 (C^{1'}, C^{1''}), 129.05 (C¹, C⁸), 132.24 (C^{4a'}, C^{4a''}), 133.52 (C^{8a'}, C^{8a''}), 138.14 (C^{9'}), 140.73 (C^{2'}, C^{2'''}), 153.61 (C^{4a}, C^{10a}).

3',3'-Di-(2-naphthalenyl)-spiro[9*H*-thioxanthene-9,2'-thiiran] (**40**)

To a stirred solution of 2,2'-(diazomethylene)bisnaphthylene (**30**) [42] (0.15 g, 0.50 mmol) in benzene (15 mL), protected by CaCl₂ tube 9*H*-thioxanthene-9-thione (**27**, X = S) [42] (0.11 g, 0.50 mmol) dissolved in benzene (15 mL) was added. The reaction mixture was stirred with reflux for 5 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Purification of the crude product took place by column chromatography on silica gel using PE–Et₂O 99:1 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **40** was isolated and obtained as yellow powder, 0.07 g, yield 28 %, mp 159 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.867 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H², H⁷), 7.031 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.307 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{6'}, H^{6''}), 7.345 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{7'}, H^{7''}), 7.412 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.475 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 2H, H⁴, H⁵), 7.502 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H¹, H⁸), 7.542 (dd, ³*J* = 8.5 Hz, 2H, H^{5'}, H^{5''}), 7.650 (d, ³*J* = 8.0 Hz, 2H, H^{8''}, H^{8'''}), 7.883 (s, 2H, H^{1'}, H^{1'''}).

¹³C NMR (CDCl₃) δ(ppm): 64.35 (C⁹), 71.67 (C^{9'}), 125.75 (C^{7'}, C^{7''}), 125.76 (C^{6'}, C^{6''}), 126.18 (C⁴, C⁵), 126.48 (C^2 , C^7), 127.02 ($C^{4'}$, $C^{4''}$), 127.25 (C^5' , $C^{5''}$), 127.35 (C^3 , C^6), 127.36 ($C^{3'}$, $C^{3''}$), 127.97 ($C^{8'}$, $C^{8''}$), 128.40 ($C^{1'}$, $C^{1''}$), 129.93 (C^1 , C^8), 132.13 ($C^{4a'}$, $C^{4a''}$), 132.67 ($C^{8a'}$, $C^{8a''}$), 134.99 (C^{8a} , C^{9a}), 135.42 (C^{4a} , C^{10a}), 137.83 ($C^{2'}$, $C^{2''}$).

9-(Di-2-naphthalenylmethylene)-9H-thioxanthene (18)

To a stirred solution of thiirane **40** (0.06 g, 0.12 mmol) in toluene (20 mL), protected by CaCl₂ tube, PPh₃ (0.06 g, 0.24 mmol) was added. After refluxing for 4 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder of **18** was obtained, 0.052 g, yield 94 %, mp 230 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.788 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 2H, H², H⁷), 7.025 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.177 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 2H, H¹, H⁸), 7.352 (dd, ³*J* = 9.0 Hz, ⁴*J* = 1.5 Hz, 2H, H^{3'}, H^{3''}), 7.383–7.428 (m, 4H, H^{6'}, H^{6''} H^{7'}, H^{7''}), 7.487 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 2H, H⁴, H⁵), 7.642 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.715–7.740 (m, 4H, H^{5'}, H^{5''} H^{8'}, H^{8''}), 7.822 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ(ppm): 125.81 (C², C⁷, C^{6'}, C^{6''}), 125.93 (C^{7'}, C^{7''}), 126.35 (C³, C⁶), 126.53 (C⁴, C⁵), 127.56 (C^{5'}, C^{5''}), 127.58 (C^{4'}, C^{4''}), 128.01 (C^{8'}, C^{8''}), 128.11 (C^{3'}, C^{3''}), 128.65 (C^{1'}, C^{1''}), 129.77 (C¹, C⁸), 132.13 (C^{4a'}, C^{4a''}), 133.18 (C^{8a'}, C^{8a''}), 134.55 (C^{4a}, C^{10a}), 136.02 (C⁹), 136.77 (C^{8a}, C^{9a}), 139.33 (C^{2'}, C^{2''}), 142.05 (C^{9'}).

3',3'-Di-(2-naphthalenyl)-spiro[9*H*-selenoxanthene-9,2'-thiiran] (**41**)

To a stirred solution of 2,2'-(diazomethylene)bisnaphthylene (**30**) [42] (0.10 g, 0.34 mmol) in benzene (15 mL), protected by CaCl₂ tube, 9*H*-selenoxanthene-9-thione (**27**, X = Se) [42] (0.10 g, 0.34 mmol) dissolved in benzene (15 mL) was added. The reaction mixture was stirred with reflux for 3 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder was of **41** obtained, 0.13 g, yield 73 %, mp 190 °C. Yellow single crystals of **41** were obtained from benzene. ¹H, ¹³C, ⁷⁷Se, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.927 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 2H, H², H⁷), 6.987 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.309 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 2H, H^{6'}, H^{6''}), 7.345 (td, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{7'}, H^{7''}), 7.427 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.563 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 2H, H⁴, H⁵), 7.583 (td, ${}^{3}J = 9.0$ Hz, H^{5'}, H^{5"}), 7.612–7.651 (m, 6H, H¹, H⁸, H^{3'}, H^{3"}, H^{8'}, H^{8"}), 7.937 (s, 2H, H^{1'}, H^{1"}).

¹³C NMR (CDCl₃) δ (ppm): 67.63 (C⁹), 71.47 (C^{9'}), 125.72 (C^{7'}, C^{7"}), 125.76 (C^{6'}, C^{6"}), 126.79 (C², C⁷), 126.91 (C^{4'}, C^{4"}), 127.23 (C^{5'}, C^{5"}), 127.34 (C³, C⁶), 128.02 (C^{8'}, C^{8"}), 128.34 (C^{3'}, C^{3"}), 128.47 (C^{1'}, C^{1"}), 128.83 (C⁴, C⁵), 131.03 (C¹, C⁸), 132.11 (C^{4a'}, C^{4a"}), 132.61 (C^{8a'}, C^{8a"}), 132.82 (C^{4a}, C^{10a}), 136.12 (C^{8a}, C^{9a}), 137.73 (C^{2'}, C^{2"}).

⁷⁷Se NMR (CDCl₃) δ(ppm): 351.84.

9-(Di-2-naphthalenylmethylene)-9*H*-selenoxanthene (19)

To a stirred solution of thiirane **41** (0.12 g, 0.23 mmol) in toluene (25 mL), protected by CaCl₂ tube, PPh₃ (0.1 g, 0.53 mmol) was added. After refluxing for 4 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A colorless powder of **19** was obtained, 0.04 g, yield 34 %, mp 318 °C. ¹H, 13 C, ⁷⁷Se, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.824 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H², H⁷), 6.977 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.212 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 2H, H¹, H⁸), 7.394 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{3'}, H^{3''}), 7.372–7.420 (m, 4H, H^{6'}, H^{6''}), H^{7'}, H^{7''}), 7.623 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 4H, H⁴, H⁵), H^{4'}, H^{4''}), 7.703-7.737 (m, 4H, H^{5'}, H^{5'''} H^{8''}, H^{8'''}), 7.819 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ (ppm): 125.78 (C^{6'}, C^{6''}), 125.90 (C^{7'}, C^{7''}), 126.28 (C², C⁷), 126.37 (C³, C⁶), 127.48 (C^{4'}, C^{4''}), 127.54 (C^{5'}, C^{5''}), 128.01 (C^{8'}, C^{8''}), 128.05 (C^{3'}, C^{3''}), 128.57 (C^{1'}, C^{1''}), 129.15 (C⁴, C⁵), 130.12 (C¹, C⁸), 131.17 (C^{4a}, C^{10a}), 132.10 (C^{4a'}, C^{4a''}), 133.12 (C^{8a'}, C^{8a''}), 138.33 (C^{8a}, C^{9a}), 139.10 (C^{2'}, C^{2''}), 139.42 (C⁹), 142.26 (C^{9'}).

⁷⁷Se NMR (CDCl₃) δ(ppm): 362.07.

3',3'-Di-(2-naphthalenyl)-spiro[9*H*-telluroxanthene-9,2'-thiiran] (**42**)

To a stirred solution of 2,2'-(diazomethylene)bisnaphthylene (**30**) [42] (0.10 g, 0.34 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9*H*-telluroxanthene-9-thione (**27**, X = Te) [42] (0.10 g, 0.34 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 3 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A colorless powder of **42** was obtained, 0.23 g, yield 62 %, mp 225 °C. $^1\text{H},\,^{13}\text{C},\,^{125}\text{Te},$ and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.905 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.006 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H², H⁷), 7.317 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H^{6'}, H^{6''}), 7.344 (td, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H^{7'} H^{7''}), 7.436 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.590–7.614 (m, 4H, H^{5'}, H^{5''}, H^{8'}, H^{8''}), 7.660–7.684 (m, 4H, H⁴, H⁵, H^{3''}, H^{3''}), 7.786 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 2H, H¹, H⁸), 7.941 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ (ppm): 70.61 (C⁹), 73.16 (C⁹), 119.53 (C^{4a}, C^{10a}), 125.68 (C^{7'}, C^{7"}), 125.79 (C^{6'}, C^{6"}), 126.65 (C^{4'}, C^{4"}), 127.19 (C^{5'}, C^{5"}), 127.36 (C², C⁷, C³, C⁶), 128.09 (C¹, C⁸), 128.58 (C^{3'}, C^{3"}), 128.75 (C^{1'}, C^{1"}), 132.06 (C^{4a'}, C^{4a"}), 132.40 (C¹, C⁸), 132.45 (C^{8a'}, C^{8a"}), 134.93 (C⁴, C⁵), 137.56 (C^{2'}, C^{2"}), 139.33 (C^{8a}, C^{9a}).

¹²⁵Te NMR (CDCl₃) δ(ppm): 548.68.

9-(Di-2-naphthalenylmethylene)-9*H*-telluroxanthene (**20**)

To a stirred solution of thiirane **42** (0.12 g, 0.20 mmol) in toluene (25 mL), protected by CaCl₂ tube, PPh₃ (0.11 g, 0.40 mmol) was added. After refluxing for 4 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using PE-Et₂O 99:1 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **20** was isolated and obtained as yellow powder, 0.07 g, yield 64 %, mp 209 °C. Yellow single crystals of **20** were obtained from CDCl₃. ¹H, ¹³C, ¹²⁵Te NMR, and 2D spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.863 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H², H⁷), 6.895 (td, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H⁶), 7.283 (dd, ³*J* = 6.5 Hz, ⁴*J* = 1.5 Hz, 2H, H¹, H⁸), 7.359–7.418 (m, 6H, H^{3'}, H^{3''}) H^{6'}, H^{6''} H^{7''}, H^{7'''}), 7.606 (d, ³*J* = 8.5 Hz, 2H, H^{4'}, H^{4''}), 7.698 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.5 Hz, 2H, H^{5''}, H^{5'''}), 7.727 (dd, ³*J* = 7.0 Hz, ⁴*J* = 2.0 Hz, 2H, H^{8'}, H^{8''}), 7.794 (dd, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H⁴, H⁵), 7.825 (s, 2H, H^{1'}, H^{1''}).

¹³C NMR (CDCl₃) δ(ppm): 117.88 (C^{4a}, C^{10a}), 125.72 (C^{6'}, C^{6''}), 125.84 (C^{7'}, C^{7''}), 126.32 (C³, C⁶), 127.11 (C², C⁷), 127.36 (C^{4'}, C^{4''}), 127.51 (C^{5'}, C^{5''}), 127.91 (C^{3'}, C^{3''}), 128.00 (C^{8'}, C^{8''}), 128.43 (C^{1'}, C^{1''}), 130.35 (C¹, C⁸), 132.05 (C^{4a'}, C^{4a''}), 133.05 (C^{8a'}, C^{8a''}), 134.99 (C⁴, C⁵), 138.86 (C^{2'}, C^{2''}), 142.12 (C⁹), 142.13 (C^{9a}, C^{8a}), 145.15 (C⁹).

¹²⁵Te NMR (CDCl₃) δ(ppm): 549.63.

3',3'-Di-(1,2'-naphthalenyl)-spiro[9*H*-fluorene-9,2'thiirane] (**43**)

To a stirred solution of 1-naphthalenyl-2'-naphthalenyl thioketone (**31**) [42] (0.5 g, 1.67 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9-diazo-9*H*-fluorene (**29**) (0.3 g, 1.67 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 2 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A yellow powder of **43** was obtained, 0.35 g, yield 45 %, mp 194 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C and -30 °C.

At 25 °C:

¹H NMR (CDCl₃) δ (ppm): 6.109 (d, ³*J* = 8.0 Hz, 1H, H⁸), 6.453 (d, ³*J* = 7.5 Hz, 1H, H¹), 6.514 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H⁷), 6.919 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H²), 6.988 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{7'}), 7.130 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{3''}), 7.177 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{6'}), 7.278 (d, ³*J* = 8.5 Hz, 1H, H⁸), 7.536 (td, ³*J* = 7.5 Hz, ³*J* = 1.0 Hz, 1H, H^{3'}), 7.655 (d, ³*J* = 8.0 Hz, 1H, H^{5'}), 7.718–7.734 (m, 2H, H⁵, H^{4'}), 7.874 (d, ³*J* = 7.5 Hz, 1H, H⁴), 8.085 (s, 1H, H^{1''}), 8.327 (d, ³*J* = 7.5 Hz, 1H, H^{2'}).

¹³C NMR (CDCl₃) δ(ppm): 59.46 (C⁹), 65.46 (C^{9'}), 119.49 (C⁵), 120.01 (C⁴), 124.49 (C⁸), 125.09 (C^{7'}), 125.12 (C^{6'}), 125.57 (C^{3'}), 125.70 (C^{8'}), 126.36 (C⁷), 126.42 (C²), 126.70 (C¹), 127.94 (C⁶), 128.26 (C^{5'}), 128.40 (C³), 128.66 (C^{4'}, C^{1''}), 129.52 (C^{8a'}), 130.27 (C^{2'}), 133.35 (C^{4a'}), 139.79 (C^{1'}), 140.25 (C^{4b'}), 141.58 (C^{4a}), 142.22 (C^{9a}), 144.02 (C^{8a}).

At −30 °C:

¹H NMR (CDCl₃) δ(ppm): 6.157 (d, ${}^{3}J = 7.5$ Hz, 1H, H⁸), 6.259 (d, ${}^{3}J = 7.5$ Hz, 1H, H¹), 6.743 (t, ${}^{3}J = 7.5$ Hz, 1H, H⁷), 6.935 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 2.0$ Hz, 1H, H²), 7.004 (t, ${}^{3}J = 7.5$ Hz, 1H, H²), 7.130 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{3"}), 7.139 (t, ${}^{3}J = 7.5$ Hz, 1H, H^{3"}), 7.273 (t, ${}^{3}J = 7.5$ Hz, ${}^{3}J = 7.5$ Hz, 1H, H⁶), 7.349 (t, ${}^{3}J = 7.5$ Hz, 1H, H³), 7.459–7.511 (m, 3H, H^{6'}, H^{4"} H^{6"}), 7.564 (t, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.0$ Hz, 1H, H^{7"}), 7.656–7.693 (m, 2H, H^{7'}, H^{5"}), 7.709–7.783 (m, 2H, H⁵, H^{4'}), 7.808 (d, ${}^{3}J = 7.5$ Hz, 1H, H⁴), 7.851 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{5'}), 8.069 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{8"}), 8.799 (s, 1H, H^{1"}), 8.838 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ (ppm): 56.73 (C⁹), 60.85 (C^{9'}), 119.63 (C⁵), 119.72 (C⁴), 124.42 (C^{8'}), 124.99 (C⁸), 125.58 (C^{6'}), 125.90 (C²), 126.22 (C^{7''}), 126.27 (C^{6''}), 126.38 (C⁷,C^{7'}), 127.40 (C^{4''}), 127.48 (C^{5''}), 127.55 (C¹,C^{3''}), 127.94 (C^{3'}), 127.98 (C³), 128.09 (C⁶), 128.32 (C^{8''}), 128.95 (C^{4''}), 129.17 (C^{5'}), 129.20 (C^{1''}), 129.39 (C^{2'}), 131.10 (C^{8a'}), 132.07 (C^{4a''}), 132.56 (C^{8a''}), 133.95 (C^{4a'}), 134.98 ($C^{4'}$), 134.98 ($C^{1'}$) 138.37 ($C^{2''}$), 140.56 (C^{4a}), 141.10 (C^{4b}), 143.30 (C^{9a}), 143.68 (C^{8a}).

9-(Di-1,2'-naphthalenylmethylene)-9H-fluorene (21)

To a stirred solution of thiirane **43** (0.35 g, 0.75 mmol) in toluene (40 mL), protected by $CaCl_2$ tube, PPh₃ (0.40 g, 1.5 mmol) was added. After refluxing for 2 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using only PE as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **21** was isolated and obtained as yellow powder, 0.13 g, yield 93 %, mp 206 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.167 (d, ³J = 8.0 Hz, 1H, H⁸), 6.776 (t, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.5$ Hz, 1H, H⁷), 6.971 (td, ${}^{3}J = 8.0 \text{ Hz}, {}^{3}J = 6.5 \text{ Hz}, 1\text{H}, \text{H}^{2}$), 7.022 (d, (td, ${}^{3}J = 7.5$ Hz. 1H, H¹), 7.216 $^{3}J = 7.5$ Hz, $^{3}J = 8.0$ Hz, $^{3}J = 1.0$ Hz. H^{6}). 1H. 7.326 (td, $^{3}J = 7.5$ Hz, H³), $^{3}J = 8.0$ Hz, 1H, 7.389 (td, ${}^{3}J = 7.5$ Hz, 1H, H^{7'}), 7.480–7.517 (m, 2H, H^{6'}, H^{7"}), 7.543 (td, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H $^{6''}$), 7.601 (td, ${}^{3}J = 7.0$ Hz, ${}^{3}J = 6.5$ Hz, 1H, H ${}^{3'}$), 7.654 (d, ${}^{3}J = 7.5$ Hz, 1H, $H^{2'}$), 7.741 (d, ${}^{3}J = 7.5$ Hz, 1H, H^{5}), 7.788 (2d, ${}^{3}J = 7.5$ Hz, 2H, H⁴, H^{3"}), 7.904 (3d, ${}^{3}J = 8.0$ Hz, 3H, $H^{4''}$, $H^{5''} \cdot H^{8''}$), 7.959 (d, ${}^{3}J = 8.5$ Hz, 1H, $H^{5'}$), 7.987 (d, ${}^{3}J = 8.0 \text{ Hz}, 1 \text{H}, \text{H}^{4'}), 8.122 \text{ (s, 1H, H}^{1''}), 8.180 \text{ (d,}$ ${}^{3}J = 8.0$ Hz, 1H, H $^{8'}$).

¹³C NMR (CDCl₃) δ (ppm): 119.13 (C⁵), 119.35 (C⁴), 124.99 (C⁸), 125.19 (C¹), 125.79 (C^{8'}), 125.99 (C^{3'}), 126.13 (C^{6'}), 126.23 (C^{6''}, C^{7''}), 126.53 (C²), 126.64 (C^{7'}), 126.73 (C⁷), 127.12 (C^{2'}), 127.66 (C⁶), 127.71 (C^{5''}, C^{8''}), 127.97 (C³), 128.36 (C^{5'}, C^{1''}, C^{4''}), 128.39 (C^{3''}), 128.49 (C^{4'}), 131.15 (C^{8a'}), 132.96 (C^{4a''}), 133.43 (C^{8a''}), 134.03 (C^{4a'}), 136.15 (C⁹), 138.11 (C^{9a}), 138.51 (C^{8a}), 139.95 (C^{2''}), 140.37 (C^{4b}), 140.60 (C^{1'}), 140.84 (C^{4a}), 142.68 (C^{9'}).

3',3'-Di-(1,2'-naphthalenyl)-spiro[9*H*-xanthene-9,2'thiiran] (**44**)

To a stirred solution of 1,2'-(diazomethylene)bisnaphthylene (**32**) [42] (2.5 g, 8.5 mmol) in benzene (30 mL), protected by CaCl₂ tube, 9*H*-xanthene-9-thione (**27**, X = O) [42] (1.8 g, 8.5 mmol) dissolved in benzene (30 mL) was added. The reaction mixture was stirred with reflux for 5 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off. A colorless powder was of **44** obtained, 2.89 g, yield 73 %, mp 259–260 °C. Colorless single crystals of **44** were obtained from acetonitrile. 1 H, 13 C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.497 (td, ³*J* = 8.0 Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H²), 6.718 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H⁷), 6.858 (td, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{3}$), 6.927 (dd, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{8}$), 6.994 (t, $^{3}J = 8.0$ Hz, $^{3}J = 7.5$ Hz, 1H, $H^{3'}$), 7.072 (dd. $^{3}J = 7.5$ Hz, $^{4}J = 1.5$ Hz, 1H. H¹), 7.126 (dd, ${}^{4}J = 1.0$ Hz, H⁴), $^{3}J = 8.0$ Hz, 1H, 7.264 (td, ${}^{4}J = 1.5$ Hz, $^{3}J = 8.5$ Hz. 1H. H^{6}). 7.308 (dd. ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H⁵), 7.311–7.344 (m, 4H, $H^{4'}$, $H^{3''}$, $H^{4''}$, $H^{6''}$) 7.386 (td, ${}^{3}J = 8.5 \text{ Hz}$, ${}^{4}J = 1.5 \text{ Hz}$, 1H, $H^{7''}$), 7.428 (td, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, $H^{6'}$), 7.479 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{2'}), 7.567 (t, ${}^{3}J = 7.5$ Hz, 1H, $H^{7'}$), 7.596 (d, ${}^{3}J = 8.0 \text{ Hz}$, 1H, $H^{5''}$), 7.742 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{5'}), 7.788 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{8"}), 8.213 (s, 1H, $H^{1''}$), 8.718 (d, ${}^{3}J = 8.5$ Hz, 1H, $H^{8'}$).

¹³C NMR (CDCl₃) δ(ppm): 53.74 (C⁹), 64.26 (C^{9'}), 115.52 (C⁴), 115.88 (C⁵), 121.47 (C^{9a}), 122.41 (C²), 122.96 (C⁷), 123.03 (C^{8a}), 123.68 (C^{3'}), 124.55 (C^{8'}), 124.82 (C^{2'}), 125.38 (C^{6'}), 125.86 (C^{6''}, C^{7''}), 125.99 (C^{4'}), 126.96 (C^{4''}), 127.25 (C^{3''}), 127.30 (C^{5''}), 127.93 (C^{8''}), 128.15 (C^{7'}), 128.20 (C^{2''}), 128.36 (C³), 128.80 (C⁶), 129.01 (C¹), 129.18 (C^{5'}), 129.56 (C^{1''}), 129.93 (C⁸), 132.00 (C^{4a''}), 132.34 (C^{8a'}), 132.62 (C^{8a''}), 134.11 (C^{4a'}), 135.24 (C^{1'}), 154.67 (C^{4a}), 155.21 (C^{10a}).

9-(Di-1,2'-naphthalenylmethylene)-9*H*-xanthene (22)

To a stirred solution of thiirane **44** (2 g, 3.4 mmol) in toluene (30 mL), protected by CaCl₂ tube, PPh₃ (1.7 g, 6.5 mmol) was added. After refluxing for 2 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using PE-CH₂Cl₂ 98:2 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **22** was isolated and obtained as yellow powder, 1.5 g, yield 78 %, mp 178 °C. Yellow single crystals of **22** were obtained from CHCl₃. ¹H, ¹³C, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.454 (td, ³J = 8.0 Hz, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H²), 6.666 $(dd, {}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{1}), 6.717 \text{ (td,})$ ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H⁷), 7.024 (td, ${}^{3}J = 8.0 \text{ Hz}, {}^{3}J = 7.5 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz},$ $^{3}J = 8.0$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^3), 7.150 (ddd, $^{3}J = 8.0$ Hz, ${}^{5}J = 0.5$ Hz, H⁴), 1H, 7.179 (td, H⁶), (dd, $^{3}J = 8.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, 7.193 ${}^{4}J = 1.5$ Hz, ${}^{3}J = 8.5$ Hz, 1H, H⁸), 7.450 (dd, H⁵), $^{3}J = 8.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, 7.354 (td, $^{3}J = 7.0$ Hz, ${}^{4}J = 1.5$ Hz, $H^{7''}$), 1H, 7.381 (td, ${}^{3}J = 8.5$ Hz, ${}^{3}J = 7.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H^{6"}), 7.424 (dd, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 2.0$ Hz, 1H, H^{3"}), 7.457-7.479 (m, 2H,, H^{6'}, H^{7'}), 7.511 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^{3"}), 7.569 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^{3"}), 7.598 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{4"}), 7.612 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{8"}), 7.703 (dd, ${}^{3}J = 8.5$ Hz, 4J = 2.0, 1H, H^{5"}), 7.796 (s, 1H, H^{1"}), 7.824 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{4"}), 7.866 (dd, ${}^{3}J = 7.5$ Hz, ${}^{3}J = 1.5$ Hz, 1H, H^{5"}), 8.268 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, ${}^{5}J = 0.5$ Hz, 1H, H^{8"}).

¹³C NMR (CDCl₃) δ(ppm): 116.21 (C⁴), 116.44 (C⁵), 122.44 (C²), 122.52 (C⁷), 124.55 (C^{9a}), 124.63 (C^{8a}), 125.76 (C^{8'}), 125.80 (C^{6''},C^{7''}), 125.82 (C^{3'}), 125.95 (C^{6'}), 126.61 (C^{7'}), 126.77 (C¹), 127.26 (C^{2'}), 127.45 (C^{5''}), 127.54 (C^{4''}), 127.57 (C^{4'}), 127.96 (C⁶), 128.04 (C^{3''},C^{8''}), 128.36 (C³), 128.50 (C^{5'}), 128.62 (C^{1''}), 130.44 (C⁸), 131.95 (C^{8a'}), 132.21 (C^{4a''}), 133.51 (C^{8a''}), 133.94 (C^{4a'}), 135.57 (C⁹), 140.49 (C^{1'}), 140.59 (C^{2''}), 152.99 (C^{4a}), 153.95 (C^{10a}).

3',3'-Di-(1,2'-naphthalenyl)-spiro[9*H*-thioxanthene-9,2'-thiiran] (**45**)

To a stirred solution of 1,2'-(diazomethylene)bisnaphthylene (**32**) [42] (0.25 g, 0.84 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9*H*-thioxanthene-9-thione (**27**, X = S) [42] (0.2 g, 0.84 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 2 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off, 0.28 g of **45**, yield 66 %, mp 216 °C. ¹H, ¹³C, and 2D NMR spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.875 (td, ³J = 8.5 Hz, ${}^{4}J = 1.5$ Hz, $^{3}J = 7.5$ Hz, 1H, H^7), 6.882 (td, ${}^{4}J = 2.0$ Hz, H⁶), ${}^{3}J = 8.0$ Hz, 1H, 7.003 (td, $^{3}J = 8.0$ Hz, ${}^{4}J = 1.0$ Hz, 2H, H²), 7.026 (td, $^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, 7.239 (td, $H^{3'}$), ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H³), 7.284 (d, ${}^{3}J = 8.5$ Hz, 1H, H^5), 7.306–7.327 (m, 2H, $H^{2'}$, $H^{6''}$), 7.329 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{4"}), 7.380 (2td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 2H, H^{6'}, H^{7"}), 7.354 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5 \text{ Hz}, 1 \text{H}, \text{H}^{1}, 7.506 \text{ (td, } {}^{3}J = 8.5 \text{ Hz},$ ${}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{7'}), 7.548 \text{ (d, } {}^{3}J = 8.0 \text{ Hz}, 1\text{H}, \text{H}^{5''}),$ 7.555 (d, ${}^{3}J = 8.5$ Hz, 1H, H ${}^{3''}$), 7.576 (d, ${}^{3}J = 8.0$ Hz, 1H, $H^{4'}$), 7.620 (dd, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.0$ Hz, 1H, H^{4}), 7.638 (dd, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H⁸), 7.721 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{5'}), 7.780 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{8"}), 8.190 (s, 1H, $H^{1''}$), 8.462 (d, ${}^{3}J = 8.5$ Hz, 1H, $H^{8'}$).

¹³C NMR (CDCl₃) δ(ppm): 62.72 (C⁹), 65.61 (C^{9'}), 123.73 (C^{3'}), 124.24 (C^{8'}), 125.17 (C^{6'}), 125.58 (C^{7"}), 125.59 (C^{6"}), 125.76 (C⁷), 126.00 (C^{7'}), 126.22 (C⁵),

126.32 (C⁴), 126.64 (C^{4″}), 126.78 (C²), 126.85 (C^{3″}), 126.87 (C^{2′}), 127.00 (C⁶), 127.09 (C^{2″}, C^{5″}), 127.43 (C³), 127.89 (C^{8″}), 128.24 (C^{4′}), 128.51 (C^{1″}), 129.02 (C^{5′}), 130.03 (C⁸), 130.55 (C¹), 131.70 (C^{4a″}), 131.87 (C^{8a′}), 132.04 (C^{8a″}), 133.66 (C^{4a′}), 133.56 (C^{8a}), 134.55 (C^{1′}), 134.64 (C^{10a}), 135.79 (C^{9a}), 136.50 (C^{4a}).

9-(Di-1,2'-naphthalenylmethylene)-9*H*-thioxanthene (23)

To a stirred solution of thiirane **45** (0.18 g, 0.36 mmol) in toluene (30 mL), protected by CaCl₂ tube, PPh₃ (1.9 g, 0.73 mmol) was added. After refluxing for 4 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification of the crude product took place by column chromatography on silica gel using PE-Et₂O 98:2 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **23** was isolated and obtained as yellow powder, 0.06 gr, yield 36 %, mp 202 °C. Yellow single crystals of **23** were obtained from C₆H₆. ¹H, ¹³C, NMR, and 2D spectra were recorded at -25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.732 (t, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 1H, H²), 6.875 (t, ³*J* = 7.0 Hz, 1H, H⁷), 6.904 (d, ³*J* = 8.5 Hz, ³*J* = 7.5 Hz, 1H, H³), 7.141 (t, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 1H, H⁶), 7.179 (d, ³*J* = 7.5 Hz, 1H, H⁸), 7.224–7.255 (m, 2H, H^{6'}, H^{7'}), 7.294 (d, ³*J* = 7.5 Hz, 1H, H¹), 7343–7.392 (m, 4H, H⁴, H^{3''}, H^{6''}, H^{7''}), 7.560 (d, ³*J* = 7.0 Hz, 1H, H^{4''}), 7.593 (d, ³*J* = 7.5 Hz, 1H, H⁵), 7.664-7.708 (m, 4H, H^{3'}, H^{5''}, H^{8''}), 7.774 (d, ³*J* = 8.0 Hz, 1H, H^{4'}), 7.876 (s, 1H, H^{1''}), 7.967 (dd, ³*J* = 7.5 Hz, ⁴*J* = 2.0 Hz, 1H, H^{8'}), 8.194 (d, ³*J* = 7.0 Hz, 1H, H^{2'}).

¹³C NMR (CDCl₃) δ(ppm): 124.45 (C^{3′}), 125.01 (C^{8′}), 125.22 (C²), 125.54 (C^{6′}, C^{7′}), 125.80 (C^{7″}), 125.93 (C^{6″}), 126.02 (C⁷), 126.19 (C³), 126.34 (C⁴), 126.59 (C⁵, C⁶), 126.95 (C^{4″}), 127.29 (C^{5″}), 127.41 (C^{4′}), 127.90 (C^{5′}, C^{8″}), 128.18 (C¹), 128.25 (C^{2′}), 128.38 (C^{3″}), 128.99 (C^{1″}), 129.48 (C^{8a′}), 130.23 (C⁸), 131.73 (C^{4a″}), 132.64 (C^{8a″}), 133.65 (C^{4a}, C^{4a′}), 134.57 (C^{10a}), 135.98 (C^{9a}), 136.69 (C⁹), 137.01 (C^{8a}), 138.06 (C^{1′}), 138.09 (C^{2″}), 138.36 (C^{9′}).

3',3'-Di-(1,2'-naphthalenyl)-spiro[9*H*-selenoxanthene-9,2'-thiiran] (**46**)

To a stirred solution of 1,2'-(diazomethylene)bisnaphthylene (**32**) [42] (0.3 g, 1.0 mmol) in benzene (25 mL), protected by CaCl₂ tube, 9*H*-selenoxanthene-9-thione (**27**, X = Se) [42] (0.28 g, 1.0 mmol) dissolved in benzene (25 mL) was added. The reaction mixture was stirred with reflux for 3 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Trituration of the crude product in hot ethanol gave precipitate which was filtered off, 0.4 g of **46**, yield 72 %, mp 196 °C. ¹H, ¹³C, ⁷⁷Se, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.812 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H⁶), 6.954 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 1H, H⁷), 7.031 (2td, ³*J* = 8.5 Hz, ³*J* = 6.5 Hz, ⁴*J* = 1.0 Hz, 2H, H², H^{3'}), 7.190 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H³), 7.282 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{6''}), 7.306–7.360 (m, 4H, H⁵, H^{6'} H^{4''}, H^{7''}), 7.430 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{7'}), 7.491 (d, ³*J* = 7.5 Hz, 1H, H^{2'}), 7.510 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 1H, H¹), 7.536 (d, ³*J* = 8.5 Hz, 1H, H^{5''}), 7.573 (d, ³*J* = 8.5 Hz, 1H, H^{4'}), 7.644 (dd, ³*J* = 9.0 Hz, ⁴*J* = 1.5 Hz, 1H, H^{3''}), 7.695 (d, ³*J* = 8.0 Hz, 1H, H^{8''}), 7.703 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.0 Hz, 1H, H^{5'}), 7.723 (dd, ³*J* = 7.5 Hz, 1H, H⁸), 8.106 (s, 1H, H^{1''}), 8.372 (d, ³*J* = 8.5 Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ(ppm): 65.52 (C^{9'}), 66.30 (C⁹), 123.71 (C^{3'}), 124.72 (C^{8'}), 125.13 (C^{6'}), 125.56 (C^{7"}), 125.62 (C^{6"}), 125.96 (C^{7'}), 125.03 (C⁷), 126.47 (C^{4"}), 126.94 (C^{2'}), 127.12 (C⁶), 127.14 (C^{3"}, C^{5"}), 127.19 (C²), 127.48 (C³), 127.97 (C^{8"}), 128.29 (C^{4'}), 128.68 (C^{1"}), 128.95 (C⁴), 129.03 (C⁵, C^{5'}), 131.48 (C⁸), 131.63 (C¹), 132.05 (C^{4a"}), 132.29 (C^{8a"}), 132.31 (C^{10a}), 132.43 (C^{8a'}), 134.04 (C^{4a'}), 134.65 (C^{4a}), 135.23 (C^{1'}), 135.32 (C^{8a}), 135.82 (C^{2"}), 137.42 (C^{9a}).

⁷⁷Se NMR (CDCl₃) δ(ppm): 356.22.

9-(Di-1,2'-naphthalenylmethylene)-9*H*-selenoxanthene (**24**)

To a stirred solution of thiirane **46** (0.2 g, 0.40 mmol) in toluene (30 mL), protected by CaCl₂ tube, PPh₃ (1.4 g, 0.60 mmol) was added. After refluxing for 2 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Trituration of the crude product in hot ethanol, methanol, and acetonitrile gave a precipitate, which was filter off. A yellow powder of **24** was obtained. Further Purification was achieved by column chromatography on silica gel using PE-Et₂O 99:1 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **24** was isolated and obtained as yellow powder, mp 214 °C. Yellow single crystals of **24** were obtained from mixture of CH₂Cl₂ and methanol 1:5. ¹H, ¹³C, ⁷⁷Se, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (pm): 6.728 (t, ³*J* = 7.5 Hz, 1H, H²), 6.803 (t, ³*J* = 7.0 Hz, ⁴*J* = 6.5 Hz, 1H, H³), 6.871 (t, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 1H, H⁷), 7.057 (t, ³*J* = 7.5 Hz, 1H, H⁶), 7.190 (d, ³*J* = 8.0 Hz, 1H, H⁸), 7.223 (t, ³*J* = 8.0 Hz, 1H, H^{7'}), 7.291 (d, ³*J* = 7.0 Hz, 1H, H⁸), 7.330–7.348 (m, 2H, H^{6'}, H^{6''}), 7.374 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{3''}), 7.439 (d, ³*J* = 7.5 Hz, 1H, H^{4''}), 7.511 (d, ³*J* = 8.5 Hz, 1H, H^{4''}), 7.621–7.644 (m, 5H, H^{3'}),

 $H^{5'}, H^{5''}, H^{7''}, H^{8''}$), 7.689 (d, ${}^{3}J = 8.0$ Hz, 1H, H⁵), 7.721 (d, ${}^{3}J = 8.0$ Hz, 1H, H^{4'}), 7.811 (s, 1H, H^{1''}), 8.071 (dd, ${}^{3}J = 9.5$ Hz, ${}^{4}J = 5.5$ Hz, 1H, H^{8''}), 8.115 (d, ${}^{3}J = 8.5$ Hz, 1H, H^{2'}).

¹³C NMR (CDCl₃) δ(ppm): 124.28 (C^{3'}), 125.59 (C², C^{7'}), 125.66 (C^{8'}), 125.74 (C^{6'}), 125.96 (C^{6''}), 126.23 (C³), 126.57 (C⁷), 126.64 (C^{6'}), 127.02 (C^{4''}), 127.37 (C^{5''}), 127.51 (C^{4'}), 127.90 (C^{5'}, C^{8''}), 127.09 (C^{7''}), 128.09 (C^{2'}), 128.23 (C^{3''}), 129.04 (C⁴), 129.13 (C¹), 129.15 (C^{1''}), 129.26 (C⁵), 130.12 (C^{8a'}), 130.68 (C⁸), 131.04 (C^{4a}), 132.11 (C^{4a''}), 132.20 (C^{10a}), 132.99 (C^{2''}), 133.72 (C^{4a'}), 137.63 (C^{9a}), 138.21 (C^{1'}, C^{8a''}), 139.10 (C^{9'}, C^{8a}), 140.40 (C⁹).

⁷⁷Se NMR (CDCl₃) δ(ppm): 361.85, 362.66.

3',3'-Di-(1,2'-naphthalenyl)-spiro[9*H*-telluroxanthene-9,2'-thiiran] (**47**)

To a stirred solution of 1,2'-(diazomethylene)bisnaphthylene (**32**) [42] (0.13 g, 0.4 mmol) in benzene (20 mL), protected by CaCl₂ tube, 9*H*-telluroxanthene-9-thione (**27**, X = Te) [42] (0.14 g, 0.4 mmol) dissolved in benzene (20 mL) was added. The reaction mixture was stirred with reflux for 4 h. After cooling to rt, the reaction mixture was evaporated under reduced vacuum. Purification was achieved by column chromatography on silica gel using PE-Et₂O 99:1 as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **47** was isolated and obtained as colorless powder, 0.4 g, yield 31 %, mp 208 °C. Colorless single crystals of **47** were obtained from CH₂Cl₂. ¹H, ¹³C, ¹²⁵Te, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.732 (td, ³J = 7.5 Hz, ${}^{4}J = 1.5 \text{ Hz}, 1 \text{H}, \text{H}^{6}, 7.044 \text{ (td, } {}^{3}J = 8.0 \text{ Hz},$ ${}^{3}J = 7.5$ Hz, ${}^{5}J = 0.5$ Hz, 1H, H ${}^{3'}$), 7.064–7.102 (m, 2H, H^{2} , H^{7}), 7.125 (td, ${}^{3}J = 7.5 \text{ Hz}$, ${}^{4}J = 1.5 \text{ Hz}$, 1H, H^{3}), 7.277 (td, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{4}J = 1.0$ Hz, 1H, $H^{6''}$), 7.301 (td, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.0$ Hz, ${}^{5}J = 0.5$ Hz, 1H, H^{7"}), 7.315–7.348 (m, 3H, H^{6'}, H^{7'}, H^{4"}), 7.369 (dd, ${}^{4}J = 1.0$ Hz, 1H, H⁵), $^{3}J = 7.5$ Hz, 7.540 (dd. ${}^{4}J = 1.0$ Hz, H^{5"}), $^{3}J = 8.5$ Hz, 1H, 7.571 (dd,

 ${}^{3}J = 8.5 \text{ Hz}, {}^{3}J = 7.5 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{2'}),$ 7.593–7.637 (m, 4H, H¹, H^{4'}, H^{3''}, H^{8''}), 7.705 (dd, ${}^{3}J = 7.5 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{5'}),$ 7.883 (dd, ${}^{3}J = 7.0 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{4}),$ 7.993 (s, 1H, H^{1''}), 8.036 (dd, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.0 \text{ Hz}, 1\text{H}, \text{H}^{8}),$ 8.173 (dd, ${}^{3}J = 7.0 \text{ Hz}, {}^{4}J = 1.5 \text{ Hz}, 1\text{H}, \text{H}^{8'}).$

¹³C NMR (CDCl₃) δ(ppm): 64.58 (C^{9'}), 71.92 (C⁹), 118.65 (C^{10a}), 122.14 (C^{4a}), 123.59 (C^{3'}), 125.03 (C^{8'}), 125.08 (C^{6'}), 125.45 (C^{7''}), 125.58 (C^{6''}), 126.03 (C^{7'}), 126.05 (C⁵, C^{4''}), 126.59 (C⁷), 126.95 (C⁶), 127.99 (C^{2'}), 127.12 (C^{5''}), 127.32 (C^{3''}), 127.41 (C³), 127.86 (C²), 127.99 (C^{8''}), 128.33 (C^{4'}), 128.80 (C^{1''}), 128.99 (C^{5'}), 132.05 (C^{4a''}), 132.12 (C^{8a''}), 132.63 (C¹), 132.65 (C^{8a'}), 132.94 (C⁸), 134.12 (C^{1'}), 134.87 (C⁴), 135.42 (C⁵), 135.55 (C^{2''}), 135.82 (C^{4a'}), 138.49 (C^{8a}), 140.74 (C^{9a}). ¹²⁵Te NMR (CDCl₃) δ(ppm): 559.53.

9-(Di-1,2'-naphthalenylmethylene)-9*H*-telluroxanthene (**25**)

To a stirred solution of thiirane **47** (0.08 g, 0.1 mmol) in toluene (20 mL), protected by CaCl₂ tube, PPh₃ (0.07 g, 0.1 mmol) was added. After refluxing for 2 h, the mixture was cooled to the rt and the solvent removed under reduced pressure. Purification was achieved by column chromatography on silica gel using only PE as eluent. The crude product was dissolved in chloroform and evaporated on silica gel. The desired product **25** was isolated and obtained as yellow powder, 0.05 g, yield 66 %. mp 189 °C. Yellow single crystals of **25** were obtained from mixture of CH₂Cl₂ and methanol 1:5. ¹H, ¹³C, ¹²⁵Te, and 2D NMR spectra were recorded at 25 °C.

¹H NMR (CDCl₃) δ (ppm): 6.727 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H⁶), 6.801 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H⁷), 6.902 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H²), 6.988 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 1H, H³), 7.223–7.255 (m, 3H, H¹, H^{6''}, H^{7''}), 7.329–7.348 (m, 2H, H^{6''}, H^{7''}), 7.391 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.0 Hz, 1H, H^{3''}), 7.411 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 1H, H⁸), 7.449 (d, ³*J* = 8.5 Hz, 1H, H^{4''}), 7.594 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H⁵), 7.615-7.639 (m, 4H, H^{3''}, H^{5''}, H^{5'''}, H^{8'''}), 7.718 (dd, ³*J* = 8.5 Hz, 1H, H^{4''}), 7.813 (s, 1H, H^{4''}), 7.878 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H^{4''}), 8.108

Scheme 1 Syntheses of BAE-1s 11–15





Scheme 2 Syntheses of diazo compound 26 and of chalcogenox-anthene-9-thiones 27

(dd, ${}^{3}J = 7.0$ Hz, ${}^{4}J = 1.5$ Hz, 1H, H^{2'}), 8.232 (ddd, ${}^{3}J = 8.5$ Hz, ${}^{4}J = 1.5$ Hz, ${}^{5}J = 0.5$ Hz, 1H, H^{8'}).

¹³C NMR (CDCl₃) δ(ppm): 116.97 (C^{10a}), 118.39 (C^{4a}), 124.18 (C^{3'}), 125.62 (C^{6'}), 125.65 (C^{7'}), 125.72 (C^{7"}), 125.86 (C^{6"}), 126.19 (C⁶), 126.30 (C⁷), 126.33 (C^{8'}), 126.62 (C³), 126.92 (C^{4"}), 127.36 (C^{5"}), 127.47 (C²), 127.48 (C^{4'}), 127.87 (C^{5'}), 128.12 (C^{8"}), 128.23 (C^{2'}), 128.35 (C^{3"}), 129.24 (C^{1"}), 129.79 (C⁸), 130.43 (C^{8a'}), 130.94 (C¹), 132.08 (C^{4a"}), 132.90 (C^{8a"}), 133.64 (C^{4a'}), 135.05 (C⁵), 135.07 (C⁴), 137.89 (C^{2"}), 137.91 (C^{1'}), 139.43 (C^{9'}), 140.84 (C^{8a}), 143.18 (C^{9a}), 145.63 (C⁹). ¹²⁵Te NMR (CDCl₃) δ(ppm): 549.47, 552.37.

Results and discussion

Synthesis

BAE-1s **11–15**, **16–20**, and **21–25** were synthesized by Barton's double-extrusion diazo-thione coupling method (aka Barton–Kellog olefination) [41].

Scheme 3 Syntheses of BAE-1s 17–20

BAE-1s 11–15 with two α -naphthalenyl substituents

The syntheses of BAE-1s **11–15** are shown in Scheme 1. The couplings of 1,1'-(diazomethylene)bisnaphthylene (**26**) and 9*H*-chalcogenoxanthene-9-thiones (**27**, X = –, O, S, Se, Te) in boiling benzene gave thiiranes **33–37**. Their ¹³C-NMR spectra showed the characteristic thiirane carbon chemical shifts at 53.60–73.68 ppm. Treatment of the thiiranes **33–37** with triphenylphosphine in boiling toluene gave the respective BAE-1s **11–15** in 32–93 % yields. The syntheses of diazo **26** and of thioketones **27** are described in Scheme 2.

BAE-1s 16–20 with two β -naphthalenyl substituents

The syntheses of BAE-1s with 2-naphthalenyl substituents **17–20** are shown in Scheme 3. The couplings of 2,2'-(diazomethylene)bisnaphthylene (**30**) and 9*H*-chalcogenoxanthene-9-thiones (**27**, X = O, S, Se, Te) in boiling benzene gave thiiranes **39–42** Their ¹³C-NMR spectra showed the characteristic thiirane carbon chemical shifts at 55.2–73.2 ppm. Treatment of the thiiranes **39–42** with triphenylphosphine in boiling toluene gave the respective BAE-1s **17–20** in 16–94 % yields. The coupling of thioketone **28** and 9-diazo-9*H*-fluorene (**29**) gave directly **16** (Scheme 4); thiirane **38** was not isolated. The syntheses of diazo **30** and thione **28** are described in Scheme **5**.

BAE-1s **21–25** with α -naphthalenyl and β -naphthalenyl substituents

The syntheses of BAE-1s with α -naphthalenyl and β -naphthalenyl substituents **21–25** are shown in Scheme 6. The coupling of thioketones **31** and diazofluorene (**29**) gave thiirane **43**. The couplings of 1,2'-(diazomethylene)bisnaphthylene (**32**) and chalcogenoxanthene thiones (**27**, X = O, S, Se, Te) in boiling benzene gave thiiranes **44–47**. Their ¹³C-NMR spectra showed the characteristic thiirane carbon chemical shifts at 53.7–71.9 ppm. Treatment of the thiiranes **43–47** with triphenylphosphine in boiling toluene gave the respective BAE-1s **21–25** in





Scheme 4 Syntheses of BAE-1 16



Scheme 5 Syntheses of thione 28 and of diazo compound 30

36–93 % yields. The syntheses of diazo **32** and thione **31** are described in Scheme 7.

Molecular and crystal structures

The crystal and the molecular structures of 9-diphenylmethylen-9*H*-fluorene (7) and 9-diphenylen-9*H*-xanthene (8) have been reported [21, 22].

The crystallographic data for the BAE-1s naphthologs **13–15**, **20**, **22–25**, and for **7**, **8** are given in Table 1 [43]. The crystal structures of BAEs **11** and **12** have previously been reported [20]. The ORTEP diagrams of **13–15**, **20**, and **22–25** as determined by X-ray crystallography are presented in Figs. 3, 4, 5, 6, 7, 8, 9, and 10 (the ellipsoids at the 50 % probability level). BAE-1s **13**, **23**, and **24** crystallize in the orthorhombic space group *Pbca*. BAE-1s **14**

and **22** crystallize in the triclinic space group *P*-1. BAE-1s **15**, **20**, and **25** crystallize in the monoclinic space group $P2_1/c$.

The crystallographic data for the thiiranes **33**, **35–37**, **41**, **44**, and **47** are given in Table 2 [43]. The crystal structure of thiirane **33** has previously been reported [20]. The ORTEP diagrams of **35–37**, **41**, **44**, and **47** as determined by X-ray crystallography are presented in Figs. 11, 12, 13, 14, 15, and 16 (the ellipsoids at the 50 % probability level). Thiiranes **35** and **36** crystallize in the orthorhombic space group $P2_12_12_1$. Thiiranes **37**, **41**, **44**, and **47** crystallize in the orthorhombic space group $P2_12_12_1$. Thiiranes **37**, **41**, **44**, and **47** crystallize in the orthorhombic space group $P2_12_1c_1$. Thiiranes **37**, **41**, **44**, and **47** crystallize in the orthorhombic space group $P2_1c_2$, and in monoclinic space group $P2_1/c$, respectively.

Table 3 gives selected geometrical parameters derived from the crystal structures of BAE-1s **11–15**, **20**, **22–25**, and of homomerous BAEs 1 [44], 2 [22], 6 [11], and 7 [11].

Table 4 gives selected geometrical parameters derived from the crystal structures of the thiiranes 33, 35–37, 41, 44, and 47.

Structural parameters of the BAE-1s 11–15, 20, and 22–25 and the thiiranes 35–37, 41, 44, and 47 are defined as follows:

- ω : pure ethylenic twist around $C^9 = C^{9'}$ is the average value of the torsion angles $C^{9a}-C^9 = C^{9'}-C^{1'}$ and $C^{8a}-C^9 = C^{9'}-C^{1''}$ for **11–15** and **33**, **35–37**, $C^{9a}-C^9 = C^{9'}-C^{2''}$ and $C^{8a}-C^9 = C^{9'}-C^{2''}$ for **20** and **41**, $C^{9a}-C^9 = C^{9'}-C^{1''}$ and $C^{8a}-C^9 = C^{9'}-C^{2''}$ for **22–25**, **44**, and **47**.
- φ: folding angle of the tricyclic moiety is the dihedral angle between the benzene rings of each tricyclic moiety for BAE-1s 11–15, 20, and 22–25 and thiiranes 33, 35–37, 41, 44, and 47.
- τ: naphthalenyl twists are the values of the torsion angles C⁹-C^{9'}-C^{1'}-C^{8a'} and C⁹-C^{9'}-C^{1''}-C^{8a''} for 11-15 and 33, 35-37 and C⁹-C^{9'}-C^{2'}-C^{1'} and C⁹-C^{9'}-C^{2''}-C^{1''} for 20 and 41, C⁹-C^{9'}-C^{1''}-C^{8a'} and C⁹-C^{9'}-C^{2''}-C^{1''} for 22-25, 44, and 47.
- θ : the dihedral angle between the naphthalenyl substituents.
- χ : pyramidalization angles $\chi(C^9)$ and $\chi(C^{9'})$ are the improper torsion angles $C^{9a}-C^9 = C^{9'}-C^{8a}$ and $C^{1'}-C^{9'} = C^9-C^{1''}$, respectively, minus 180° for **11–15** and **33**, **35–37** and $C^{9a}-C^9 = C^{9'}-C^{8a}$ and $C^{2'}-C^{9'} = C^9-C^{2''}$, respectively, minus 180° for **20** and **41**, $C^{9a}-C^9 = C^{9'}-C^{8a}$ and $C^{1'}-C^{9'} = C^9-C^{2''}$, respectively, minus 180° for **20** and **41**, $C^{9a}-C^9 = C^{9'}-C^{8a}$ and $C^{1'}-C^{9'} = C^9-C^{2''}$, respectively, minus 180° for **22–25**, **44**, and **47**.

The following points concerning the molecular structures of BAE-1s and their respective thiiranes are noted:

 BAE-1s 12–15, 20, and 22–25 with chalcogen bridges adopt folded-twisted conformations: the dihedral angles

Scheme 6 Syntheses of BAE-1s 21–25





Scheme 7 Synthess of thione 31 and of diazo compound 32

 φ are 35.5° (12), 45.1° (13), 48.1° (14), 56.7° (15), 54.1° (20), 28.0° (22), 44.3° (23), 47.7° (24), and 50.8° (25). The twist angles ω are in the range 0.3°–7.4°. In contrast, in 11, the fluorene moiety is almost planar; the dihedral angle is 2.4°. The folding angle φ is strongly dependent on the bridges X: $\varphi(\text{Te}) > \varphi(\text{Se}) > \varphi(\text{S}) > \varphi(\text{O})$. The tricyclic moieties in BAE-1s with α -naphthalenyl and β -naphthalenyl substituents **22–25** and in BAE-1s with two β -naphthalenyl substituents **20** are less folded. In **15**, **20**, and **25** (X = Te), the highest φ is in the BAE-1 with two α -naphthalenyl substituents **15**. The twist of the central double bond is small, and ω values are ranged from 0.3° (**20**) to 7.4° (**22**).

The severe overcrowding in the hypothetical planar conformations of 11-15, 20, and 22-25 is overcome by the deviations from planarity of the α -naphthalenyl and β -naphthalenyl substituents and the tricyclic moieties. These deviations from planarity are manifested in the twisting around the single bonds that connect the α naphthalenyl and β -naphthalenyl moieties to C^{9'} and in the folding of the tricyclic moieties. The respective naphthalenyl twist angles τ'/τ'' are 68.5°/86.2° in 11, $67.7^{\circ}/97.1^{\circ}$ in **12**, $-97.2^{\circ}/-69.24^{\circ}$ in **13**, $-103.1^{\circ}/$ -68.1° in **14**, $-97.9^{\circ}/-70.1^{\circ}$ in **15**, $-129.9^{\circ}/-109.3^{\circ}$ in 20, -80.5°/-125.7° in 22, -83.3°/-133.9° in 23, $-81.2^{\circ}/-135.0^{\circ}$ in **24**, and $-84.9^{\circ}/-136.9^{\circ}$ in **25**. The dihedral angles θ are 72.3°–77.5° between the α -naphthalenyl moieties (11–15), 64.9° (20) between the β -naphthalenyl moieties, and 74.8°–76.3° between the α -naphthalenyl and β -naphthalenyl moieties (22– 25). Thus, the two naphthalene moieties in 11–15, 20, and 22-25 are highly twisted with similar degrees of twist. The α -naphthalenyl rings in 11–15 and 22–25 are almost orthogonal to the central $C^9 = C^{9'}$ bond.

Table 1 Cr.	ystalographic data i	for BAE-1s 13–15,	, 20, 22–25, 7 and 8	~						
	13	14	15	20	22	23	24	25	7	8
Empirical formula	$C_{34}H_{22}S$	$C_{34}H_{22}Se$	$C_{34}H_{22}Te$	$\mathrm{C}_{34}\mathrm{H}_{22}\mathrm{Te}$	C ₃₅ H ₂₃ Cl ₃ O	C_{74} $H_{50}S2$	$C_{34}H_{22}Se$	$C_{34}H_{22}Te$	$C_{26}H_{28}$	C ₂₆ H ₁₈ O
Formula weight	462.58	509.48	558.12	558.12	565.88	1003.26	509.48	558.12	330.42	346.40
Temp. (K)	173 (1)	295 (1)	173 (1)	173 (1)	173 (1)	173 (1)	173 (1)	295 (1)	293	150 (2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	<i>P</i> -1	$P2_1/c$	$P2_1/c$	<i>P</i> -1	Pbca	Pbca	$P2_1/c$	$P2_1/n$	$P2_1/c$
<i>a</i> (Å)	14.2983 (7)	10.065 (2)	9.4493 (6)	11.315 (2)	10.234 (2)	8.2632 (9)	8.3387 (6)	17.424 (1)	9.682 (5)	11.975 (2)
b (Å)	14.3142 (8)	11.338 (2)	29.114 (2)	18.721 (3)	12.505 (2)	16.662 (2)	16.528 (1)	8.6105 (6)	9.310 (5)	9.480 (1)
<i>c</i> (Å)	22.936 (1)	11.606 (2)	8.8074 (5)	12.672 (2)	13.031 (2)	38.750 (4)	35.145 (3)	16.778 (1)	20.44 (1)	19.864 (2)
α (°)	90	96.059 (3)	06	99.700 (4)	116.663 (2)	90	90	06	06	06
β (°)	90	108.318 (3)	95.321 (1)	113.450 (2)	100.015 (3)	90	90	90.403 (1)	102.48 (3)	125.669 (5)
γ (°)	90	97.186 (3)	06	90.227 (3)	102.996 (3)	90	90	06	06	06
V (Å ³)	4694.3 (4)	1232.7 (3)	2412.5 (2)	2462.6 (6)	1378.0 (4)	5335 (1)	4843.8 (6)	2517.0 (3)	1799.19	1831.9 (4)
Z	8	2	4	4	2	4	8	4	4	4
$\rho_{\rm calc}~({ m g/cm}^3)$	1.309	1.373	1.537	1.505	1.364	1.249	1.397	1.473	1.220	1.256
μ (mm ⁻¹)	0.160	1.544	1.254	1.229	0.360	0.146	1.571	1.202	0.06	0.075
F(000)	1,936	520	1,112	1,112	584	2,104	2,080	1,112		728
Crystal size	$0.39 \times 0.12 \times 0.10$	$0.22 \times 0.15 \times 0.10$	$0.17\times0.13\times0.10$	$0.40 \times 0.15 \times 0.08$	$0.26 \times 0.18 \times 0.10$	$0.20 \times 0.20 \times 0.08$	$0.35 \times 0.16 \times 0.09$	$0.42 \times 0.38 \times 0.32$		0.57×0.43
(IIIII)										$\times 0.40$
θ range (°)	1.78-27.00	2.16-27.97	2.16-27.00	2.24-27.00	2.15-27.00	2.44-27.00	2.32-28.01	2.34-28.06	3-50	2.52-27.56
Reflections collected	49,315	13,865	26,728	26,978	14,566	56,096	51,377	27,992	3,592	10,566
Independent reflections $[R_{int}=]$	5,130 [0.0879]	5,652 [0.0524]	5,267 [0.0463]	5,365 [0.0533]	5,894 [0.0491]	5,824 [0.2458]	5,762 [0.0519]	6,014 [0.0191]	1,679	2,295 [0.0354]
Absorption correction	None	Multi-scan	None	Multi-scan	None	None	Multi-scan	Multi-scan		Multi-scan
Data/ restraints/ parameters	5,130/0/316	5,652/0/316	5,267/0/316	5,365/0/316	5,894/0/352	5,824/0/343	5,762/0/316	6,014/0/316		4,208/0/3244
Goodness- of-fit on F^2	1.463	0.954	1.345	1.082	1.094	1.250	1.107	1.065	1.2469	1.045
Final R indices $[I > 2\sigma_{I}]$	$R_1 = 0.1393,$ $wR_2 = 0.2566$	$R_1 = 0.0548,$ $wR_2 = 0.1097$	$R_1 = 0.0724,$ $wR_2 = 0.1448$	$R_1 = 0.0808,$ $wR_2 = 0.1893$	$R_1 = 0.0823,$ $wR_2 = 0.1675$	$R_1 = 0.1559,$ $wR_2 = 0.2219$	$R_1 = 0.0583,$ $wR_2 = 0.1292$	$R_1 = 0.0482,$ $wR_2 = 0.1320$	R = 0.038, wR = 0.036	$R_1 = 0.0456,$ $wR_2 = 0.0994$
<i>R</i> ₁ indices (all data)	0.1486	0.1332	0.0806	0.0964	0.1194	0.2256	0.0739	0.0570	I	0.0469
<i>wR</i> ² indices (all data)	0.2611	0.1324	0.1485	0.1993	0.1834	0.2484	0.1366	0.1391	I	0.1092

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Fig. 5 ORTEP drawing of BAE-1 15

Fig. 3 ORTEP drawing of BAE-1 13



Fig. 4 ORTEP drawing of BAE-1 14

- The central C⁹ = C^{9'} bond lengths are 135.1 (11), 134.7 (12), 134.0 (13), 133.2 (14), and 134.2 (15) 132.9 (20), 135.7 (22), 134.7 (23), 134.3 (24), and 134.4 pm (25).
- Significant pyramidalization angles χ are noted at C⁹ and C^{9'} of BAE-1s 12–15, 20, and 22–25 with



Fig. 6 ORTEP drawing of BAE-1 20

chalcogen bridges: $|\chi(C^9)| = 3.1-6.6^\circ$, $|\chi(C^{9'})| = 5.9^\circ - 10.3^\circ$, but not in **11** $(\chi(C^9) = -0.7^\circ$, $\chi(C^{9'}) = 1.1^\circ$). *Anti*-pyramidalization is dominant; *syn*-pyramidalization in **22** is an exceptions.

The overcrowding in the fjord regions of BAE-1s is estimated by the non-bonding contact distances vis-a-vis the sum of the van der Waals radii (171 pm (C), 115 pm (H)). [45]. Pronounced short C···C, C···H and H···H contact distances were indicated in BAE-1s with α-naphthalenyl moieties: 11 (C⁸···C^{1″} = 306.9 pm), (H¹···C^{1″} = 248.9 pm), 12 (C¹···C^{1″} = 302.9 pm),



Fig. 7 ORTEP drawing of BAE-1 22



Fig. 9 ORTEP drawing of BAE-1 24



Fig. 8 ORTEP drawing of BAE-1 23

(H¹...C^{1'} = 262.0 pm), **13** (C⁸...C^{1"} = 305.2 pm), (H⁸...C^{1'} = 288.4 pm), and **14** (C⁸...C^{1"} = 305.2 pm), (H⁸...C^{1'} = 277.7 pm). The molecular structure of **15** is less overcrowded: C¹...C^{1'} = 330.2 pm, H¹...C^{1"} = 300.2 pm. BAE-1 **20** with two β -naphthalenyl moieties is free of overcrowding. BAE-1s **22–25** with one α naphthalenyl and one β -naphthalenyl moieties are slightly more overcrowded than **11–15** with short



Fig. 10 ORTEP drawing of BAE-1 25

non-bonding contact distances in **22** $(C^1 \cdots C^{1''} = 295.8 \text{ pm}, H^1 \cdots C^{1'} = 244.5 \text{ pm}),$ **23** $<math>(C^1 \cdots C^{1''} = 307.8 \text{ pm}, H^1 \cdots C^{1'} = 278.9 \text{ pm}),$ **24** $<math>(C^1 \cdots C^{1''} = 307.3 \text{ pm}, H^1 \cdots C^{1'} = 279.9 \text{ pm}), \text{ and$ **25** $} <math>(C^1 \cdots C^{1'} = 309.8 \text{ pm}), (H^1 \cdots C^{2''} = 286.5 \text{ pm}) \text{ in$ **25** $}. \text{ The non-bonding C \cdots C, C \cdots H and H \cdots H distances are increased with the increase of the radius of the chalcogen atom, decreasing the overcrowding.$

Table 2 Crystallograph	ic data for thiiranes 33,	35–37, 41, 44 and 47					
	33	35	36	37	41	44	47
Empirical formula	$C_{34}H_{22}S$	$C_{35}H_{24}Cl_2S_2$	C ₃₅ H ₂₄ Cl ₂ SSe	$C_{40}H_{28}STe$	$C_{74}H_{50}S_2Se_2$	$C_{34}H_{22}OS$	$C_{34}H_{22}STe$
Formula weight	462.58	579.56	626.46	668.28	1161.18	478.58	590.18
Temp. (K)	173 (1)	173 (1)	173 (1)	173 (1)	173 (1)	173 (1)	295 (1)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	Pbca	<i>P</i> -1	C2/c	$P2_1/c$
a (Å)	7.706 (3)	8.7420 (6)	8.7884 (6)	18.088 (1)	9.126 (2)	34.460 (5)	15.0068 (9)
b (Å)	10.139 (4)	15.677 (1)	15.752 (1)	13.547 (1)	15.040 (3)	8.202 (1)	10.4290 (6)
<i>c</i> (Å)	15.779 (6)	19.914 (1)	19.847 (1)	23.969 (2)	20.347 (4)	17.972 (2)	32.207 (2)
α (₀)	103.235 (6)	06	90	06	99.700 (4)	90	06
β (°)	102.096 (6)	06	90	06	93.468 (4)	108.027 (2)	94.853 (1)
γ (°)	90.506 (6)	06	90	06	90.227 (3)	90	06
$V(\text{\AA}^3)$	1171.4 (8)	2729.3 (3)	2747.5 (3)	5873.1 (7)	2747.5 (9)	4830 (1)	5022.6 (5)
Z	2	4	4	8	2	8	8
$\rho_{\rm calc}~({\rm g/cm}^3)$	1.311	1.410	1.514	1.512	1.404	1.316	1.561
μ , mm ⁻¹	0.160	0.416	1.662	1.113	1.468	0.161	1.290
F(000)	484	1,200	1,272	2,688	1,188	2,000	2,352
Crystal size (mm)	$0.22 \times 0.20 \times 0.07$	$0.32 \times 0.09 \times 0.08$	$0.44 \times 0.24 \times 0.24$	$0.26 \times 0.19 \times 0.06$	$0.22\times0.08\times0.05$	$0.30\times0.12\times0.07$	$0.50 \times 0.23 \times 0.16$
θ range for data collection, deg	2.07–28.34	2.05-27.00	2.43–28.00	2.06–25.99	1.37-27.00	2.32-27.00	1.78–27.00
Reflections collected	13,674	30,151	31,554	57,652	30,019	25,500	54,260
Independent reflections $[R_{int}=]$	5,486 [$R_{\rm int} = 0.0408$]	5,948 [$R_{ m int} = 0.0784$]	6,548 [$R_{\rm int} = 0.0225$]	5,769 [$R_{\rm int} = 0.0969$]	11,862 [$R_{\rm int} = 0.1379$]	5,259 [$R_{\rm int} = 0.0882$]	10,937 [$R_{\rm int} = 0.0241$]
Absorption correction	Integration	None	Multi-scan	Multi-scan	None	None	Multi-scan
Data/restraints/ parameters	5486/0/316	5948/0/353	6548/0/352	5769/0/379	11862/0/703	5259/0/325	10937/0/649
Goodness-of-fit on F^2	1.038	1.136	1.052	1.458	1.056	1.154	1.182
Final <i>R</i> indices $[I > 2\sigma_I]$	$R_1 = 0.0588,$ $wR_2 = 0.1199$	$R_1 = 0.0801,$ $wR_2 = 0.1685$	$R_1 = 0.0255,$ $wR_2 = 0.0631$	$R_1 = 0.0974,$ $wR_2 = 0.1648$	$R_1 = 0.1215,$ $wR_2 = 0.2269$	$R_1 = 0.0880,$ $wR_2 = 0.1641$	$R_1 = 0.0510,$ $wR_2 = 0.1190$
R_1 indices (all data)	$R_1 = 0.0824,$ $wR_2 = 0.129$	$R_1 = 0.0940,$ $wR_2 = 0.1760$	$R_1 = 0.0267,$ $wR_2 = 0.0637$	$R_1 = 0.1081,$ $wR_2 = 0.1688$	$R_1 = 0.2313,$ $wR_2 = 0.2632$	$R_1 = 0.1229,$ $wR_2 = 0.1778$	$R_1 = 0.0577,$ $wR_2 = 0.1221$



Fig. 11 ORTEP drawing of thiirane 35



Fig. 12 ORTEP drawing of thiirane 36

The comparison between the α-naphthalenyl-, β-naphthalenyl-, and α,β-naphthalenyltellurium-bridged BAE-1s 15, 20, and 25 is revealing that The naphthalenyl twist angles τ is significantly closer to orthogonal in 15 (70°/-98°), as compared with 25 (-85°/-135°) and 20 (109°/-130°). It indicates a higher degree of



Fig. 13 ORTEP drawing of thiirane 37



Fig. 14 ORTEP drawing of thiirane 41

- overcrowding in the α -naphthalenyl derivative 15. The non-bonding distances in the fjord regions are considerably shorter in 15 and 25 than in 20 (e.g., $C^1 \cdots C1' = 310 \text{ pm}$ (25) and 330 pm (15) versus 382 pm (20). However, the folding angles φ in the telluroxanthene moieties are similar: 56.7° (15), 50.8° (25), and 54.1° (20). Thus, the relief of overcrowding due to the presence of α -naphthalenyl substituents in BAE-1s 15 and 25 is achieved by twisting the α -naphthalenyl substituents (as reflected by the τ values) rather than by folding of the bistricyclic moieties (reflected by the φ values).
- The unit cell of thiirane **41** contains two molecules of two conformations **41a** and **41b**. These conformations differ in the folding angles of their tricyclic moieties



Fig. 15 ORTEP drawing of thiirane 44

 $\varphi = 51.5^{\circ}$ and 41.0° , respectively, and in the naphthalenyl twist angles τ : $90.0^{\circ}/51.8^{\circ}$ in **41a** versus $-95.7^{\circ}/-41.1^{\circ}$ in **41b**. One of the β -naphthalenyl moieties in **41a** and **41b** is orthogonal to the central $C^9 = C^{9'}$ bond. Thiirane **47** also have two crystallographic conformations **47a** and **47b**. The unit cell of **47** contains 8 molecules. Both conformations have similar structures; the folding angles of the tricyclic moieties φ are 54.7° and 58.3°, respectively. The naphthalenyl twist angles τ'/τ'' are $-140.4^{\circ}/71.8^{\circ}$ in **47a**, $138.2^{\circ}/-69.2^{\circ}$ in **47b**.

Thiiranes 35–37, 41, 44, and 47 with chalcogen bridges adopt folded conformations; the dihedral angles φ are 47.4° (35), 51.1° (36), 64.4° (36), 56.7° (41a), 54.1° (41b), 25.7° (44), 54.7° (47a), and 58.3° (47b). In 33, the fluorene moiety is almost planar, and the dihedral angle is φ = 5.5°. The folding angle φ is strongly

dependent on the bridges X: $\varphi(\text{Te}) > \varphi(\text{Se}) > \varphi$ (S) > $\varphi(\text{O})$. The deviations from planarity in the thiiranes are also manifested in the twisting around the single bond that connects the α -naphthalenyl moieties and β -naphthalenyl moieties to C^{9'}. The respective naphthalenyl twist angles τ'/τ'' are 72.2°/133.2° in **33**, 85.2°/136.6° in **35**, 85.9°/135.2° in **36**, -136.3°/-108.6° in **37**, 90.0°/51.8° in **41a**, -95.7°/-41.1° in **41b**, 128.1°/-88.9° in **44**, -140.4°/71.8° in **47a**, and 138.2°/-69.2° in **47b**. The range of the dihedral angles θ is similar to that in the respective BAE-1s: 72.5-88.1° between the α -naphthalenyl moieties (**33**, **35**-**37**), 76.2-78.4° (**41**) between the β -naphthalenyl moieties, and 68.9°-83.9° between the α -naphthalenyl and β -naphthalenyl moieties (**22**-**25**)

• Thiiranes **33**, **35**, **36**, and **44** are overcrowded with some short non-bonding contact distances: $(C^{1-} \cdots C^{1'} = 315.7 \text{ pm})$, $(C^8 \cdots C^{1''} 323.4 \text{ pm})$, in **33**, $(C^{1-} \cdots C^{1'} = 336.8 \text{ pm})$, $(H^{2'} \cdots H^{8'} = 217.1 \text{ pm})$ in **35**, $(C^1 \cdots C^{1'} = 341.5 \text{ pm})$, $(H^{2'} \cdots H^{8'} = 218.5 \text{ pm})$ in **36**, and $(H^{2'} \cdots H^{3''} = 243.8 \text{ pm})$ in **44**. Thiiranes **37**, **41**, and **47** are free of overcrowding.

NMR spectroscopy

Tables 5, 6, and 7 give the ¹H-NMR chemical shifts (δ (¹H), ppm) of the BAE-1s **11–15**, **16–20**, and **21–25**, respectively. Table 5 included also homomerous BAEs **1**, **2**, and **4–6**. Tables S1, S2, and S3 in the Supporting Information give the ¹³C-NMR chemical shifts (δ (¹³C), ppm) of the BAE-1s **11–15**, **16–20**, and **21–25**, respectively. Table S1 included also homomerous BAEs **1**, **2**, and **4–6**. Tables 8, 9, and 10 give the ¹H-NMR chemical shifts (δ (¹H), ppm) of the thiiranes **33–37**, **39–42**, and **43–47**, respectively. Tables S4, S5, and S6 in the Supporting Information give the ¹³C-NMR chemical shifts (δ (¹³C), ppm) of the thiiranes **33–37**, **38–42**, and **43–47**, respectively. Tables **11** gives the ⁷⁷Se-



Fig. 16 ORTEP drawing of thiirane 47

X-ray	ω (°)	φ (°)	τ(°)	θ (°)	$\chi(C^9),\chi(C^{9'}),^\circ$	C ⁹ =C ^{9'} , pm	$C^{1} \cdots C^{1'/2'}$ $C^{8} \cdots C^{1''/2''}$ (pm)	$\begin{array}{l} H^{1} \cdots C^{1'/2'} \\ H^{8} \cdots C^{1'/2''} \ (pm) \end{array}$	$\begin{array}{c} H^1 \cdots C^{8a'} \\ H^8 \cdots C^{8a''} \ (pm) \end{array}$
11, X = -	4.6	2.4	68.5, 86.2	72.3	-0.7, 1.1	135.1	315, 307	256, 249	262, 278
12, X = O	2.8	35.5	67.7, 97.1	75.1	-6.6, 8.7	134.7	303, 313	262, 271	313, 263
13, X = S	3.3	45.1	-97.2, -69.2	77.5	5.5, -6.8	134.0	321, 305	288, 275	228, 338
14, X = Se	0.7	48.1	-103.1, -68.1	77.5	3.1, -8.6	133.2	318, 305	290, 278	299, 349
15 , X = Te	2.5	56.7	-97.9, -70.1	77.3	4.3, -8.8	134.2	330, 332	313, 300	303, 376
20 , X = Te	0.3	54.1	-129.9, 109.3	64.9	3.6, -10.3	132.9	382,360	328, 308	313,320 $H^{2'}\cdots H^{3''}$ $C^{2'}\cdots C^{3''}$
22 , X = O	7.4	28.0	-80.5, -125.7	74.9	3.2, 5.9	135.7	296,304	245, 256	510, 453
23 , X = S	4.3	44.3	-83.3, -133.9	74.8	-6.4, 6.3	134.7	308, 313	279, 287	519, 465
24, X = Se	6.1	47.7	-81.2, -135.0	75.6	5.5, -8.9	134.3	307, 318	280, 296	519, 466
25 , X = Te	5.3	50.8	-84.9, -136.9	76.3	3.1, -7.5	134.4	310, 318	287, 301	522, 472
7	1.8	3.7	80.3, 74.0	74.3	3.3, -0.7	134.8	328, 333	264, 266	-
8	6.1	32.0	56.7, 81.1	80.3	-6.5, 7.5	135.9	315, 327	247, 298	-
Homomerous BAEs						$C^{11} = C^{11'}$	$C^1 \cdots C^{1'}$		
1, X,Y = -	33.0	5.2, 4.2			5.9, 3.9	136.7	318		
2, X, Y = O	0.0	41.0			3.3, -3.3	135.7	301		
5 , $X,Y = Se$	1.6	52.5, 54.6			0.6, 1.0	133.9	326		
6 , X,Y = Te	0.0	53.1			0.9, -0.9	135.0	325		

Table 3Selected geometrical parameters of the X-ray molecular structures of BAE-1s 11–15, 20, 22–25, 7, and 8 and the homomerous BAEs 1,2, 5, and 6

Table 4 Selected geometrical parameters of the X-ray molecular structures of thiiranes 33, 35–37, 41, 44, and 47

	ω (°)	φ (°)	τ (°)	θ (°)	χ(C ⁹)/χ(C ^{9'}), (°)	$C^9 = C^{9'}$ (pm)	$C^{1} \cdots C^{1'}, C^{8} \cdots C^{1''/2''}$ (pm)	$H^{1}\cdots C^{1'}, H^{8}\cdots C^{1''/2''}$ (pm)	$\begin{array}{c} H^{2'}\cdots H^{8''},\\ H^{2''}\cdots H^{8'} (pm)\end{array}$
33 , X = -	1.0	5.5	72.2, 133.2	88.1	-41.0, 36.9	152.6	316, 323	274, 286	235, 210
35 , X = S	2.1	47.4	85.2, 136.6	72.5	35.8, -27.8	154.5	337, 362	342, 361	230, 217
36 , X = Se	1.9	51.1	85.9, 135.2	78.4	34.0, -27.3	155.3	342, 366	347, 366	232, 219
37 , X = Te	1.7	64.4	-136.3, -108.6	83.8	32.6, -22.4	154.6	374, 360	376, 370	244, 279
41a , X = Se	4.3	51.5	90.0, 51.8	76.2	37.7, -27.9	154.1	370, 363	406, 354	_
41b , X = Se	3.1	41.0	-95.7, -41.1	78.4	32.7, -37.6	153.8	361, 346	351, 385	-
44 , X = O	1.3	25.7	128.1, -88.9	68.9	40.2, -36.8	155.2	320, 329	312, 320	-
47a , X = Te	1.5	54.7	-140.4, 71.8	80.4	36.5, 33.7	155.7	390, 352	401, 377	_
47b , X = Te	7.3	58.3	138.2, -69.3	83.9	32.2, 35.7	155.1	390, 352	401, 377	-

NMR chemical shifts (δ (⁷⁷Se), ppm) of Se derivatives 14, 19, 24, 36, 41, 46, and 5 and the ¹²⁵Te-NMR chemical shifts (δ (¹²⁵Te), ppm) of Te derivatives 15, 20, 25, 37, 42, 47, and 6. Table 12 gives selected ¹³C-NMR chemical shifts of BAE-1s 11–15, 16–20, 21–25, 1, 2, and 4–6. Table 13 gives selected ¹³C-NMR chemical shifts of thiiranes 33–37, 39–42, and 43–47. The ¹H-, ¹³C-, and 2D-NMR spectra (DQF-COSY, HSQC, HMBC, and NOESY) of BAE-1s **13–15** and **23** and of thiiranes **35–37**, **38**, and **40** were recorded at low temperatures (–25 to –30 °C). The ¹H-, ¹³C-, and 2D-NMR spectra for the other derivatives BAE-1s and thiiranes were recorded at room temperature (24 °C).

The following salient points in the NMR spectra of the BAE-1s are noteworthy:

- The pronounced shielding of H² and H⁷ of the bis (1-naphthalenyl)-BAE-1s 12 (X = O) and 15 (X = Te): δ = 6.440 ppm and δ = 6.484 ppm, as compared with the corresponding homomerous BAEs 2 and 6: δ = 6.877 ppm and δ = 6.879 ppm, respectively. Note also the shielding of H² in 22 (X = O) (δ = 6.454 ppm). These shieldings are attributed to the exposure of these hydrogens to the diamagnetic ring current of the opposing almost orthogonal naphthalenyl rings [46].
- The pronounced deshielding and non-equivalence of $H^{8'}$ and $H^{8''}$ of **13–15**, (X = S, Se, Te): ca. $\delta = 9.00$ ppm ($H^{8'}$) and $\delta = 8.43-8.80$ ppm ($H^{8''}$), at low temperature (-30 °C). These effects are absent in the bis(2-naphthalenyl) BAEs **18–20**: $\delta(H^{8'}, H^{8''}) = 7.72-7.74$ ppm
- The shielding of C^{4a} and C^{10a} in the Te-bridged **15**, **20**, and **25**, $\delta = 116-118$ ppm and the deshielding of of the O-bridged **12**, **17**, and **22**, $\delta = 153-154$ ppm, irrespective of the substitution pattern of the naphthalenyl groups. These effects are probably governed by the direct bonding of the chalcogen atom to C^{4a}/C^{10a} . In the chalcogen series, tellurium causes the lowest chemical shift [47].
- The pronounce deshielding of C⁹ in the Te-bridged 15, 20, 25, δ = 145–147 ppm, which appears at slightly lower field than in homomerous Te-bridged BAE 6, ca. δ = 144 ppm. This effect may be due to the through-space interactions of the tellurium atoms with the sp² carbon atoms C⁹ (e.g., Te···C⁹) [11]: Te···C⁹ = 322.2 pm (15), 318.6 pm (20), and 322.7 pm (25).
- The pronounced variation in the $\Delta\delta(C^9/C^{9'}) = \delta(C^9)$ $-\delta(C^{9'})$ difference, which increases, e.g., in the series **22** (X = O, $\Delta \delta = -12.1$ ppm) <**23** (X = S, $\Delta \delta =$ -1.7 ppm) <24 (X = Se, $\Delta\delta = 1.3 \text{ ppm}$) <25 $(X = Te, \Delta \delta = 6.2 \text{ ppm})$. The analogous trends are noted in the series 12–15 ($\Delta\delta$ increases from 2.3 to 9.8 ppm) and 17–20 ($\Delta\delta$ increases from -12.1 to 3.0 ppm). These variations are not fully accounted for by shortening the non-bonding distances $X \cdots C^9$. Based on the values of the van der Waals radii provided by Bondi [48] (rC = 170, rO = 152, rS = 180, rSe =190 and rTe = 206 pm), the penetration between the chalcogen atom and C⁹ increases only marginally, from 13.0 to 14.3 % for the series 12-15, and from 12.4 to 14.2 % in the series 22–25. The variation in the $\Delta\delta(C^9/$ $C^{9'}$) = $\delta(C^{9})$ - $\delta(C^{9'})$ difference is exhibited also in the series of thiiranes, e.g., in the series 44 (X = O, $\Delta \delta$ = -10.5 ppm <45 (X = S, $\Delta \delta = -2.9 \text{ ppm}$) <46 (X = Se, $\Delta \delta = 0.8$ ppm) <47 (X = Te, $\Delta \delta = 7.3$ ppm).

• The δ^{125} Te/ δ^{77} Se parameter [49] in BAE-1s 15/14, 20/ 19, and 25/24 pairs is hardly sensitive to the substitution pattern of the naphthalenyl groups.. These ratios are somewhat higher, 1.52–1.53, than the corresponding ratio in the homomerous BAEs 5 and 6, 1.49. In the thiiranes 37/36, 42/41, and 47/46 pairs, the corresponding ratio is significantly higher, 1.55–1.57. These differences may be ascribed to a conformational effect [49].

DFT study

The characteristic geometrical parameters of various calculated conformations of BAE-1 naphthologs **11–15** and **16–20** are analogous to those of BAEs [1, 2] (vide supra, Crystal and the Molecular Structure section):

- the pure ethylenic twist angle ω around the central double bond (defined as the average of the torsion angles $C^{9a}-C^9-C^{9'}-C^{1'}$ and $C^{8a}-C^9-C^{9'}-C^{1'}$ for 11–15 and of $C^{9a}-C^9-C^{9'}-C^{2'}$ and $C^{8a}-C^9-C^{9'}-C^{2'}$ for 16–20)
- the folding angle φ of the tricyclic moiety is the dihedral angle between the benzene rings of each tricyclic moiety for 11-20
- the dihedral angle θ between the least-square planes of the naphthalenyl substituents.
- the pyramidalization angles χ at C⁹/C^{9'} (defined as the improper torsion angles C^{9a}-C⁹-C^{9'}-C^{8a}/C^{1'}-C^{9'}-C⁹-C^{1'} for 11-15 and C^{9a}-C⁹-C^{9'}-C^{8a}/C^{2'}-C^{9'}-C⁹-C^{2''} for 16-20 MOD 360 minus 180°)
- the naphthalenyl torsion angles $\tau'(C^9-C^{9'}-C^{1'}-C^{8a'})/\tau''(C^9-C^{9'}-C^{1''}-C^{8a''})$ for **11–15** and $\tau'(C^9-C^{9'}-C^{2'}-C^{1'})/\tau''(C^9-C^{9'}-C^{2''}-C^{1''})$ for **16–20**)
- torsion angles $v'(C^{4a}-C^{9a}-C^{1'}-C^{8a'})/v''(C^{4b}-C^{8a}-C^{1''}-C^{8a''})$ for 11–15 and $v'(C^{4a}-C^{9a}-C^{2'}-C^{1'})/v''(C^{4b}-C^{8a}-C^{2''}-C^{1''})$ for 16–20.

The BAE-1 naphthologs adopt twisted (**t**, large twist angle ω , zero or small folding angle φ) and folded-twisted (**ft**, folding angle φ is larger than twist angle ω) conformations [20]. The naphthalenyl moieties may adopt synclinal ($\pm sc$, for τ'/τ'' angles in the range from $\pm 30^{\circ}$ to $\pm 90^{\circ}$) and anticlinal ($\pm ac$, for τ'/τ'' angles in the range from $\pm 90^{\circ}$ to $\pm 150^{\circ}$) orientations. The relative energies of the conformers of the BAE-1s naphthologs under study together with the selected geometrical parameters are presented in Table 14 (B3LYP/6-31G(*d*)) and Table 15 (B3LYP/SDD). The values of the geometrical parameters provided below are derived from both B3LYP/6-31G(*d*) and B3LYP/SDD calculations, unless specified otherwise. Figs. 17 and 18 depict the B3LYP/SDD optimized geometries of **15** and **20**, respectively. **Table 5** ¹H-NMR chemical shifts (δ , ppm, at room temperature) and multiplicities of BAE-1s **11–15** and of homomerous BAEs **1**, **2**, and **4–6**

BAE-1s	11, X = -	12 , X = O	13 , $X = S^a$	$14, X = Se^a$	15 , $X = Te^{a}$
H ¹	6.123 d	6.830 dd	7.282–7.313 m	7.145 d	7.478 dd
H^2	6.707 td	6.440 td	6.670 t	6.645 td	6.484 td
H ³	7.171 td	7.011 td	6.860 t	6.952 td	6.741 td
H^4	7.668 td	7.128 dd	7.282–7.313 m	7.592 dd	7.563 d
H^5	7.668 d	7.128 dd	7.474 d	7.417 dd	7.744 dd
H^6	7.171 td	7.011 td	7.008 t	6.818 td	6.858 td
H^7	6.707 td	6.440 td	6.634 t	6.721 td	6.648 td
H^8	6.123 d	6.830 dd	7.024 d	7.356 dd	7.282 dd
$H^{1'}$	-	-	-	-	-
$H^{2'}$	7.540 dd	7.471 dd	7.625–7.692 m	7.198 dd	7.295–7.334 m
$H^{3'}$	7.441 td	7.262 td	7.150–7.157 m	7.137 td	7.132 t
$\mathrm{H}^{4'}$	7.867 d	7.688 d	7.625–7.692 m	7.615–7.639 m	7.295–7.334 m
H ^{5'}	7.914 dd	7.816 d	7.934 d	7.902 d	7.852 d
H ^{6′}	7.495 td	7.456 td	7.625–7.692 m	7.615–7.639 m	7.295–7.334 m
$\mathrm{H}^{7'}$	7.419 td	7.521 td	7.895 t	7.889 td	7.868 td
H ^{8′}	8.363 d	8.473 d	9.007	9.017 d	9.023 d
$H^{1''}$	-	_	-	_	_
$H^{2''}$	7.540 dd	7.471 dd	7.994 t	8.051 d	8.150 d
H ^{3"}	7.441 td	7.262 td	7.282–7.313 m	7.288–7.319 m	7.295–7.334 m
$\mathrm{H}^{4''}$	7.867 d	7.688 d	7.588 d	7.575 d	7.295–7.334 m
H ^{5″}	7.914 dd	7.816 d	7.625–7.692 m	7.615–7.639 m	7.610 d
H ^{6″}	7.495 td	7.456 td	7.282–7.313 m	7.288–7.319 m	7.295–7.334 m
H ^{7″}	7.419 td	7.521 td	7.350 t	7.370 td	7.391 td
H ^{8″}	8.363 d	8.473 d	8.427 d	8.589 d	8.802 d
Homomerous BAEs	1	2	4	5	6
H^1 , H^8	8.386 d	7.146 dd	6.818 ddd	6.787 ddd	6.796 ddd
$\mathrm{H}^2,\mathrm{H}^7$	7.211 t	6.877	6.911 td	6.904 td	6.879 td
H ³ , H ⁶	7.332 t	7.226	7.120 td	7.072 td	6.963 td
H^4 , H^5	7.709 d	7.270	7.537 ddd	7.656 ddd	7.801 ddd

$^{\rm a}$ At –25 $^{\circ}{\rm C}$

Table 6 ¹ H-NMR chemical
shifts (δ , ppm, at room
temperature) of BAE-1s 16-20

	16, X = -	17 , X = O	18 , X = S	19 , X = Se	20 , X = Te
H^1 , H^8	7.256 d	7.002 dd	7.177 dd	7.212 dd	7.283 dd
$\mathrm{H}^2,\mathrm{H}^7$	6.869 td	6.599 td	6.788 td	6.824 td	6.863 td
H ³ , H ⁶	6.739 t	7.112 td	7.025 td	6.977 td	6.895 td
H^4 , H^5	7.744 d	7.186 dd	7.487 dd	7.623 dd	7.794 dd
$H^{1'}, H^{1''}$	7.927 s	7.728 s	7.822 s	7.819 s	7.825 s
$H^{2'}, H^{2''}$	_	_	_	-	_
$H^{3'}, H^{3''}$	7.503–7.572 m	7.400–7.445 m	7.352 dd	7.349 dd	7.359–7.418 m
$H^{4'}, H^{4''}$	7.893–7.923 m	7.726 dd	7.642 d	7.623 dd	7.606 d
$H^{5'}, H^{5''}$	7.983–7.923 m	7.735–7.782 m	7.715–7.74 m	7.720 dd	7.698 dd
$H^{6'}, H^{6''}$	7.503–7.572 m	7.400–7.445 m	7.383–7.428 m	7.385–7.410 m	7.359–7.418 m
$H^{7'}, H^{7''}$	7.503–7.572 m	7.400–7.445 m	7.383–7.428 m	7.385–7.410 m	7.359–7.418 m
$H^{8'}, H^{8''}$	7.809 d	7.735–7.782 m	7.715–7.740 m	7.720 dd	7.727 dd

Table 7 ¹H-NMR chemical shifts (δ, ppm, at room temperature) of BAE-1s **21–25**

	21 , X = -	22 , X = O	23 , $X = S^a$	24, X = Se	25 , X = Te
H^1	7.022 d	6.666 dd	7.293 d	7.291 d	7.223–7.255 m
H^2	6.971 t	6.454 td	6.732 t	6.728 t	6.902 td
H^3	7.326 td	7.024 td	6.904 t	6.803 t	6.988 td
H^4	7.788 d	7.150 dd	7.342–7.392 m	7.439 d	7.878 dd
H^5	7.741 d	7.450 dd	7.293 d	7.689 d	7.594 dd
H^6	7.216 td	7.164–7.203 m	7.141 t	7.057 t	6.727 td
H^7	6.776 t	6.717 td	6.875 t	6.871 t	6.801 td
H^8	6.167 d	7.164–7.203 m	7.179 d	7.190 d	7.411 dd
$H^{1'}$	_	_	_	_	_
$H^{2'}$	7.654 d	7.569 dd	8.194 d	8.115 d	8.108 dd
$H^{3'}$	7.601 t	7.511 td	7.664–7.708 m	7.621–7.644 m	7.615–7.639 m
$\mathrm{H}^{4'}$	7.9967 d	7.824 d	7.774 d	7.721 d	7.718 dd
H ^{5′}	7.959 d	7.866 dd	7.664–7.708 m	7.621–7.644 m	7.615–7.639 m
H ^{6′}	7.480–7.517 m	7.457–7.479 m	7.224–7.255 m	7.330–7.348 m	7.223–7.255 m
$H^{7'}$	7.389 t	7.457–7.479 m	7.224–7.255 m	7.223 t	7.223–7.255 m
$H^{8'}$	8.180 d	8.268 dd	7.967 dd	8.071 ddd	8.232 ddd
$H^{1''}$	8.022 s	7.796 s	7.876 s	7.811s	7.813 s
$H^{2''}$	_	_	_	_	_
H ^{3″}	7.788 d	7.424 dd	7.342–7.392 m	7.374 dd	7.391 dd
$H^{4''}$	7.904 d	7.598 d	7.560 d	7.511 d	7.449 d
$H^{5''}$	7.904 d	7.703 dd	7.664–7.708 m	7.621–7.644 m	7.615–7.639 m
$H^{6''}$	7.543 td	7.340–7.395 m	7.342–7.392 m	7.330–7.348 m	7.329–7.348 m
$\mathrm{H}^{7''}$	7.480–7.517 m	7.340–7.395 m	7.342–7.392 m	7.621–7.644 m	7.329–7.348 m
$H^{8''}$	7.904 d	7.612 d	7.664–7.708 m	7.621–7.644 m	7.615–7.639 m

^a At −30 °C

Conformers of BAE-1 naphthologs 11 and 16

- Bis(α -naphthalenyl) derivative **11** adopts a twisted (-sc, -sc)- C_2 -t conformation as its global minimum. It is characterized by a moderate twist angle ω (9°–10°), a negligible folding angle φ (ca. 1°) of the tricyclic moiety and zero pyramidalization angles χ due to the absence of the X bridge. The geometry of (-sc, -sc)- C_2 t corresponds well to the X-ray geometry of 11 (vide supra). The local minima are twisted $(sc,-ac)-C_1$ t ($\Delta\Delta G_{298} = 3.0$ (6-31G(*d*)) and 2.8 (SDD) kJ/mol) and $(-ac, -ac)-C_2$ -t ($\Delta G_{298} = 11.1$ (6-31G*) and 10.0 (SDD) kJ/mol) conformations. They are characterized by larger twist angles ω (16°–20°) and, in the case of $(sc, -ac)-C_1$ -ft, a large pyramidalization angle $\chi(C^{9'}) = -7^{\circ}.$
- Bis(β -naphthalenyl) derivative **16** adopts a twisted (*sc*,*ac*)-*C*₁-**t** conformation as its global minimum. Its tricyclic moiety is characterized by a large twist angle ω (19°–21°), a negligible folding angle φ (2°), and zero pyramidalization angles χ . The local minima are twisted (-*sc*,-*sc*)-*C*₂-**t** ($\Delta G_{298} = 1.2$ (6-31G(*d*)) and 1.6 (SDD) kJ/mol) and (-*ac*,-*ac*)-*C*₂-**t** ($\Delta G_{298} = 2.7$ (6-31G(*d*)) and 2.0 (SDD) kJ/mol).

Conformers of BAE-1 naphthologs 12-15 and 17-20

BAE-1s **12–15** and **17–20** with a chalcogen bridge X share a common conformational pattern. These BAE-1s adopt three folded-twisted conformations, which may be differentiated by their ω , τ'/τ'' , and ν'/ν'' angles. Note that the fold angles φ are not conformation specific; their values reflect the nature of the chalcogen atom rather than the conformational type. Pyramidalization angles χ are characteristic only for the *syn*-(*-sc*,*ac*)-*C*₁-**ft** conformation.

- Conformation (-sc,-ac)-C₁-ft is characterized by small (2-6° for 12-15 and 6-17° for 17-20) twist angles ω, one positive (v' < 90°) and one negative (lv"| > 90°) torsion angles v'/v", and two negative naphthalenyl torsion angles τ' = -66 to -71° (-sc) and τ" = -91 to -97° (-ac) for 12-15 and τ' = -48 to -54° (-sc) and τ'' = -76 to -98° (-ac) for 17-20 (for consistency, the values of τ'' = -76 to -89° are still denoted as *anticlinal*). This conformer is a global minimum for 12-15 and either global minimum or the lowest local minimum (depending on the basis set used) for 17-20.
- Anti-folded-twisted conformation anti-(-sc,ac)-C₁-ft features the anti-folded tricyclic moiety relative to

Table 8 ¹H-NMR chemical shifts (δ , ppm, at -25 °C) of thiiranes **33**-**37**

	33 , $X = -^{a}$	34 , X = 0	35 , X = S	36 , X = Se	37 , X = Te
H^1	6.517 d	7.081 dd	7.590 dd	7.661–7.701 m	7.924 d
H^2	7.019 td	6.814 td	7.029 td	6.872 t	7.032 t
H^3	7.426 td	7.373 td	7.331 td	6.756 t	6.741 t
H^4	7.881 dd	7.413 d	7.653 dd	7.114 d	7.253–7.303 m
H^{5}	7.721 dd	6.881 dd	7.002 dd	7.785 d	7.938 d
H^{6}	7.101 td	6.826 td	6.776 td	7.279–7.332 m	7.206 t
H^{7}	6.498 td	6.394 td	6.739 td	7.091 t	7.142 t
H^8	6.150 d	6.953 d	7.486–7.527 m	7.661–7.701 m	7.745 d
$\mathrm{H}^{1'}$	_	_	_	_	-
$\mathrm{H}^{2'}$	8.733 dd	8.599 dd	8.607 dd	8.576 d	8.402 d
$\mathrm{H}^{3'}$	7.566 t	7.473 t	7.423 t	7.382 t	7.253–7.303 m
$\mathrm{H}^{4'}$	7.678–7.698 m	7.599 d	7.486–7.527 m	7.488–7.517 m	7.474–7.512 m
$\mathrm{H}^{5'}$	7.613 d	7.509 d	7.486–7.527 m	7.488–7.517 m	7.474–7.512 m
$\mathrm{H}^{6'}$	7.127 td	7.165 td	7.195 td	7.183–7.234 m	7.178 t
$\mathrm{H}^{7'}$	6.961 td	7.255 td	7.267 td	7.183–7.234 m	7.078
$\mathrm{H}^{8'}$	7.443 d	8.129 d	8.884 d	8.985 d	8.882 d
$H^{1^{\prime\prime}}$	_	_	_	_	-
$\mathrm{H}^{2^{\prime\prime}}$	7.398 dd	6.956 d	7.159 d	7.279–7.332 m	7.384 d
$\mathrm{H}^{3^{\prime\prime}}$	7.057 t	6.909 t	6.952 t	6.989 t	7.017 t
$\mathrm{H}^{4^{\prime\prime}}$	7.649 d	7.522 d	7.486–7.527 m	7.533 d	7.560 d
$\mathrm{H}^{5^{\prime\prime}}$	7.799 d	7.729 d	7.679 d	7.661–7.701 m	7.648 dd
$\mathrm{H}^{6^{\prime\prime}}$	7.467 td	7.420 td	7.339 td	7.279–7.332 m	7.253–7.303 m
$\mathrm{H}^{7^{\prime\prime}}$	7.678–7.698 m	7.635 td	7.486–7.527 m	7.430 t	7.253–7.303 m
$\mathrm{H}^{8^{\prime\prime}}$	9.133 d	8.798 dd	8.668 d	8.504 d	8.217 d

^a At room temperature

Table 9 ¹H-NMR chemical shifts (δ, ppm, at room temperature) of thiiranes 39–42

	39 , X = O	40 , X = S	41 , X = Se	42 , X = Te
H ¹ , H ⁸	7.003 dd	7.502 dd	7.612–7.651 m	7.786 dd
H ² , H ⁷	6.566 td	6.867 td	6.927 td	7.006 td
H ³ , H ⁶	7.113 td	7.031 td	6.987 td	6.905 td
H ⁴ , H ⁵	7.232 dd	7.475 dd	7.563 dd	7.668 dd
$H^{1'}, H^{1''}$	7.785 s	7.883 s	7.937 s	7.941 s
$H^{2'}, H^{2''}$	_	_	_	_
H ^{3'} , H ^{3"}	7.261 dd	7.542 dd	7.612–7.651 m	7.673 dd
$H^{4'}, H^{4''}$	7.424 d	7.412 d	7.427 d	7.436 d
H ^{5'} , H ^{5"}	7.607 d	7.577 d	7.583 d	7.590–7.614 m
$H^{6'}, H^{6''}$	7.335 td	7.307 td	7.309 td	7.317 td
H ^{7′} , H ^{7″}	7.372 td	7.345 d	7.345 td	7.344 td
H ^{8'} , H ^{8''}	7.657 d	7.650 d	7.612–7.651 m	7.590–7.614 m

the naphthalenyl moieties. This is possible due to the M,P helicity of (-sc,ac)- C_1 -**ft**, contrary to the M,M helicity of the global minima (-sc,-ac)- C_1 -**ft**. It is characterized by small to medium $(4^\circ-16^\circ \text{ for } 12-15, 17-20)$ twist angles ω , torsion angles v'/v'' of the opposite signs (v',|v''| < 90)), and naphthalenyl torsion angles of the opposite signs $\tau' = -56^\circ$ to -62° (-sc) and $\tau'' = 92-107^\circ$ (ac) for 12-15 and

 $\tau' = -49^{\circ}$ to -53° (*-sc*) and $\tau'' = 86^{\circ}-103^{\circ}$ (*ac*) for **17–20**. This conformer is usually a local minimum (except for **17**).

Syn-folded-twisted conformation syn-(-sc,ac)-C₁-ft features the syn-folded tricyclic moiety relative to the naphthalenyl moieties. It is characterized by medium (12°-20° for 12–15 and 6°-18° 17–20) twist angles ω, torsion angles v'/v" of the opposite signs (v', /v"|>90), and

Table 10 ¹H-NMR chemical shifts (δ, ppm, at room temperature) of thiiranes **43–47**

	43 , $X = -^{a}$	44 , X = 0	45 , $X = S^{a}$	46 , X = Se	47 , X = Te
H^1	6.259 d	7.072 dd	7.354 dd	7.510 dd	7.590–7.637 m
H^2	6.935 td	6.497 td	7.003 td	7.031 td	7.079 td
H^3	7.349 t	6.858 td	7.239 td	7.190 td	7.126 td
H^4	7.808 d	7.1268 dd	7.620 dd	7.723 dd	7.883 ddd
H^{5}	7.709–7.783 m	7.308 dd	7.280 d	7.306–7.360 m	7.639 dd
H^{6}	7.273 t	7.264 td	6.882 td	6.812 td	6.632 td
H^{7}	6.743 t	6.718 td	6.857 td	6.954 td	7.091 td
H^8	6.157 d	6.927 dd	7.638 dd	7.819 dd	8.036 dd
$H^{1^{\prime}}$	_	_	-	_	_
$H^{2'}$	7.004 t	7.479 d	7.306–7.329 m	7.491 d	7.571 dd
$\mathrm{H}^{3'}$	7.139 t	6.949 t	7.026 td	7.031 td	7.044 td
$\mathrm{H}^{4'}$	7.709–7.783 m	7.311–7.330 m	7.576 d	7.573 d	7.590–7.637 m
$\mathrm{H}^{5'}$	7.851 d	7.742 d	7.712 d	7.703 dd	7.705 dd
$\mathrm{H}^{6'}$	7.459–7.511 m	7.428 td	7.380 td	7.306–7.360 m	7.310–7.348 m
$\mathrm{H}^{7'}$	7.656–7.693 m	7.567 t	7.506 td	7.430 td	7.310–7.348 m
$\mathrm{H}^{\mathrm{8'}}$	8.838 d	8.718 d	8.462 d	8.372 d	8.173 ddd
$H^{1^{\prime\prime}}$	8.799 s	8.213 s	8.190 s	8.106 s	7.993 s
$\mathrm{H}^{2^{\prime\prime}}$	_	_	-	_	_
$H^{3^{\prime\prime}}$	7.130 d	7.311–7.330 m	7.555 d	7.644 dd	7.590–7.637 m
$\mathrm{H}^{4^{\prime\prime}}$	7.459–7.511 m	7.311–7.330 m	7.329 d	7.306–7.360 m	7.310–7.348 m
$\mathrm{H}^{5^{\prime\prime}}$	7.656–7.693 m	7.596 d	7.548 d	7.536 d	7.540 dd
$\mathrm{H}^{6''}$	7.459–7.511 m	7.311–7.330 m	7.306–7.329 m	7.282 td	7.277 td
$\mathrm{H}^{7''}$	7.564 t	7.386 td	7.380 td	7.306–7.360 m	7.301 td
$\mathrm{H}^{8^{\prime\prime}}$	8.069 d	7.788 d	7.780 d	7.695 d	7.590–7.637 m

^a −30 °C

Table 11 ⁷⁷Se- and ¹²⁵Te-NMR chemical shifts (δ , ppm, at room temperature) of BAE-1s **14**, **15**, **19**, **20**, **24** and **25**, of thiiranes **36**, **37**, **41**, **42**, **46** and **47** and of homomerous BAEs **5** and **6**

	$\delta(^{77}\text{Se})$		δ(¹²⁵ Te)	δ^{125} Te/ δ^{77} Se
14 ^a	359.43, 360.46	15 ^a	551.38, 550.26	1.53, 1.53
19	362.07	20	549.63	1.52
24	361.85, 362.66	25	549.47, 552.37	1.52, 1.52
36 ^a	352.35	37 ^a	547.16	1.55
41	351.84	42	548.68	1.56
46	356.22	47	559.53	1.57
5	366.31	6	547.12	1.49

^a At −25 °C

naphthalenyl torsion angles of the opposite signs $\tau' = -70 \text{ to} -82^{\circ}(-sc) \text{ and } \tau'' = 125-128^{\circ}(ac) \text{ for 12-15} \text{ and } \tau' = -77 \text{ to} -96^{\circ}(-sc) \text{ and } \tau'' = 137-142^{\circ}(ac) \text{ for 17-20}$. Additional characteristic feature of *syn*-(*-sc,ac*)-*C*₁-**ft** of **12-15** is large pyramidalization angles $\chi(C^{9'}) = -13^{\circ}$ to -15° . This conformer could be either a global or a local minimum, except for **19** (X = Se), where the *syn*-(*-sc,ac*)-*C*₁-**ft** conformation is a transition state.

The global minima of the bis(α -naphthalenyl) derivatives **12–15** are the (*-sc,-ac*)-*C*₁-**ft** conformers. The *anti*- (-sc,ac)- C_1 -ft and the syn-(-sc,ac)- C_1 -ft conformers of 12-15 are less stable than the corresponding global minima by 2-6 kJ/mol and by 7-13 kJ/mol, respectively. In each of the bis(β -naphthalenyl) series 17–20, the three conformers possess similar relative energies (see Tables 14, 15), which are dependent of the basis set used. At B3LYP/6-31G(d), the global minima are $(-sc, -ac)-C_1$ -ft for 17 and 18, and anti-(-sc,sc)- C_s -ft for 19. At B3LYP/SDD, the global minima are anti-(-sc.ac)- C_1 -ft for 17 and syn-(-sc.ac)- C_1 ft for 18-20. The geometries of these conformers are dependent on the chalcogen bridge X. In the series O, S, Se, and Te, the twist angles ω decrease with the increase in the van der Waals radius of the chalcogen. The exception is the 2,2'-dinaphthalenyl derivatives calculated at B3LYP/6-31G(d). By contrast, the folding angles φ increase considerably from $22^{\circ}-31^{\circ}$ for X = O to $46^{\circ}-53^{\circ}$ for X = Te.

Table 16 provides a comparison between selected geometrical parameters of BAE-1s **11–15** and **20**, derived from their molecular X-ray structures and from the B3LYP optimized geometries. There is a good agreement between the experimental and the calculated values of ethylenic twist angle ω , folding angle φ , naphthalenyl dihedral angle θ , and pyramidalization angles χ at C⁹/C^{9'}. The differences

	δC^9	$\delta C^{9'}$	$\Delta C^9 - \delta C^{9'}$	δC^{4a}	δC^{10a}
11	137.69	137.41	0.28	140.72	140.72
16	140.43	133.47	6.96	140.54	140.54
21	136.15	142.68	-6.53	140.84	140.37
1	141.01			141.31	
12	131.79	129.53	2.26	153.06	153.06
17	126.06	138.14	-12.08	153.61	153.61
22	127.43	139.57	-12.14	152.99	153.95
2	121.44			155.48	
13	138.74	135.36	3.38	133.42	133.36
18	136.02	142.05	-6.03	134.55	134.55
23	136.69	138.36	-1.67	133.37	134.57
4	133.56			135.65	
14	141.87	136.15	5.72	130.46	130.59
19	139.42	142.26	-2.84	131.17	131.17
24	140.40	139.10	1.3	131.04	132.20
5	137.44			132.42	
15	147.12	137.28	9.84	116.46	116.23
20	145.15	142.12	3.03	117.88	117.88
25	145.63	139.43	6.2	118.39	116.97
6	143.69			118.01	
	11 16 21 1 12 17 22 2 13 18 23 4 14 19 24 5 15 20 25 6	δC ⁹ 11 137.69 16 140.43 21 136.15 1 141.01 12 131.79 17 126.06 22 127.43 2 121.44 13 138.74 18 136.02 23 136.69 4 133.56 14 141.87 19 139.42 24 140.40 5 137.44 15 147.12 20 145.15 25 145.63 6 143.69	δC ⁹ δC ⁹ 11 137.69 137.41 16 140.43 133.47 21 136.15 142.68 1 141.01 129.53 17 126.06 138.14 22 127.43 139.57 2 121.44 13 13 138.74 135.36 18 136.02 142.05 23 136.69 138.36 4 133.56 14 14 141.87 136.15 19 139.42 142.26 24 140.40 139.10 5 137.44 137.28 20 145.15 142.12 25 145.63 139.43 6 143.69 143.69	δC^9 $\delta C^{9'}$ $\Delta C^{9-\delta} C^{9'}$ 11137.69137.410.2816140.43133.476.9621136.15142.68-6.531141.011212131.79129.532.2617126.06138.14-12.0822127.43139.57-12.142121.441313138.74135.363.3818136.02142.05-6.0323136.69138.36-1.674133.561414141.87136.155.7219139.42142.26-2.8424140.40139.101.35137.4415147.123.0325145.63139.436.26143.69145.15142.12	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 12 Selected ¹³C-NMR chemical shifts (δ , ppm) of BAE-1s **11–15**, **16–20**, **21–25**, **1–2** and **4–6**

between the experimental and the calculated naphthalenyl torsion angles τ'/τ'' stem probably from the solid-state interactions in the molecular structures of these BAE-1s.

The effect of empirical dispersion correction on calculations of naphthologs **11–20**

B3LYP has shown a good accuracy and transferability for thousands of real-world systems during the past 15 years and has become the most popular density functional for application studies in chemical literature [50]. Its general performance has been extensively evaluated [51]. Recently, the B3LYP hybrid functional was successfully employed to treat dinaphthyl ketones, dinaphthyl thioketones and dinaphthyl diazomethanes [42], and overcrowded BAEs [18, 52, 53]. However, B3LYP often fails to accurately represent London dispersion interactions, often underestimating interaction energies of dispersion and dipole-dipole bound complexes [50]. One of the ways to improve upon B3LYP for non-covalent interactions is using the semiclassical correction, treating the (quantum mechanically) difficult dispersion interactions semiclassically and combining the resulting potential with a quantum chemical approach [36]. It can be achieved in the form of the popular pairwise correction implemented by Grimme and co-workers (DFT-D), which has now been tested thoroughly and applied successfully on thousands of

Table 13 Selected ¹³C-NMR chemical shifts (δ , ppm) of thiiranes 33–37, 39–42 and 43–47

		δC^9	$\delta C^{9'}$	$\delta C^9 \delta C^{9'}$	δC^{4a}	δC^{10a}
X = -	33	57.65	59.91	-2.26	141.38	140.62
	43	56.73	60.85	-4.12	140.56	141.10
$\mathbf{X} = \mathbf{O}$	34	53.60	63.58	-9.98	154.64	154.32
	39	55.16	69.42	-14.26	154.62	154.62
	44	53.74	64.26	-10.52	154.67	155.21
$\mathbf{X} = \mathbf{S}$	35	62.84	67.27	-4.43	135.53	134.19
	40	64.35	71.67	-7.32	134.42	134.42
	45	62.72	65.61	-2.89	136.50	134.64
X = Se	36	66.81	67.57	-0.76	131.56	133.57
	41	67.63	71.74	-4.11	132.82	132.82
	46	66.30	65.52	0.78	134.65	132.31
X = Te	37	73.68	66.99	6.69	118.24	121.23
	42	73.16	70.61	2.55	119.53	119.53
	47	71.92	64.58	7.34	122.14	118.56

different systems, including intermolecular as well as intramolecular cases [37, 38].

The results of the dispersion-corrected B3LYP calculations have been performed on naphthologs 11-20. Intramolecular dispersion interactions in 11-20 are due to the non-bonding C…C, C…H, and H…H interactions between the naphthalenyl moieties, and between the central bistricyclic unit and the naphthalenyl moieties. The data presented in Table 14 and Table 15 indicate that the shortest H···H non-bonding distances in the α,α -dinaphthalenyl derivatives 11-15 (210-255 pm) are considerably shorter than the respective distances in the β , β -dinaphthalenyl derivatives 16-20 (227-365 pm). The H…C and C…C non-bonding distances in 11-15 are very close to those in 16-20. Therefore, the inclusion of the dispersion interactions was expected to stabilize the α . α -dinaphthalenyl derivatives relative to the β , β -dinaphthalenyl derivatives.

Table 17 gives the B3LYP/6-31G(*d*) and B3LYP/SDD dispersion-corrected (D3) free relative energies of the optimized conformers of naphthologs **11–20**. The conformers of the α, α -dinaphthalenyl derivatives **11–15** are stabilized considerably relative to the respective conformers of the β,β -dinaphthalenyl derivatives **16–20**. The empirical dispersion correction reduces the relative free energies differences between the global minima conformers, i.e., **11** versus **16**, **12** versus **17**, **13** versus **18**, **14** versus **19**, and **15** versus **20**, from 17–22 (6-31G(*d*)) and 18–25 (SDD) kJ/mol to 0.5–2 (6-31G(*d*)) and 0.9–4 (SDD) kJ/mol. In rare cases, the α, α -dinaphthalenyl conformers may become more stabilized than the respective β,β -dinaphthalenyl conformers, as a result of the dispersion correction. The global minimum (–*sc*,–*ac*)-*C*₁-**ft-14** is lower in energy

Table 14 Ré	elative B3LYP/6-31C	j(d) free ene	rgies and se	lected cal	culated g	eometric	al parame	sters for	BAE-1s	11–14 a	nd 16–19				
	Conformation	ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)	v' (°)	v" (°)	(°) w	ť' (°)	τ" (°)	(_o) <i>θ</i>	(°) q	χ(C ⁹) (°)	χ(C ^{9′}) (°)	$H\cdots C^{a}$ (pm)	C…C ^b (pm)	HH ^c (pm)
11 , X = –	$(-sc,-sc)-C_2-t$	18.73	0.00	105	105	10	-72	-72	81	1	0	0	253	315	275
11 , X = –	$(-ac, -ac)-C_2-t$	29.85	11.12	145	145	20	-124	-124	88	2	0	0	255	315	251
11, X = –	$(sc, -ac)-C_1-t$	21.69	2.96	147	-107	16	61	-121	90	2	1	L—	254,257	314,319	252,299
16 , X = –	$(-sc,-sc)-C_2-t$	1.20	1.20	76	97	19	55	55	80	2	0	0	259	319	351
16 , X = –	$(-ac, -ac)-C_2-t$	2.66	2.66	138	138	20	-133	-133	78	2	0	0	259	318	368
16 , X = –	$(sc, -ac)-C_1-t$	0.0	0.0	139	-97	20	54	-134	76	2	1	0	259	319	356,367
12, X = 0	$(-sc,-ac)-C_1-ft$	18.99	0.0	31	-163	9	-67	-91	79	30	9-	9	260,259	305,309	239,262
12, X = 0	$anti-(-sc,ac)-C_1-\mathbf{ft}$	23.63	4.64	32	-47	15	-58	105	82	30	9-	-3	261,251	305,309	233,259
12, X = 0	syn -($-sc$, ac)- C_1 - ft	27.70	8.71	142	-168	18	-74	126	89	26	7	-13	264,257	302,314	231,259
17, X = 0	$(-sc,-ac)-C_1-ft$	0.0	0.0	34	-167	-10	-54	-90	81	31	-5	7	264,255	307,308	264,342
17 , $X = 0$	$anti-(-sc,ac)-C_1$ -ft	1.33	1.33	35	-38	-10	-53	94	80	31	-5	9	264,253	307,306	259,350
17 , $X = 0$	syn -($-sc$, ac)- C_1 -ft	0.38	0.38	-170	160	-13	-85	138	86	30	5	-5	264,254	307,309	255,365
13 , X = S	$(-sc,-ac)-C_1-ft$	21.66	0.00	22	-149	4	-69	-95	LL	4	-4	7	279,281	311,315	230,258
13 , X = S	anti-($-sc$, ac)- C_1 -ft	27.15	5.48	28	-28	6	-60	76	76	45	-3	-2	280,273	312,313	218,238
13 , X = S	syn -($-sc$, ac)- C_1 -ft	32.15	10.49	135	-149	14	-80	125	83	4	7	-14	291,294	324,314	218,282
18 , X = S	$(-sc,-ac)-C_1-ft$	0.0	0.0	31	151	9-	-51	-94	77	46	-4	7	286,278	317,313	247,361
18 , X = S	$anti-(-sc,ac)-C_1-\mathbf{ft}$	1.15	1.15	31	-24	9-	-52	86	74	46	-3	9	284,275	316,310	242,357
18 , X = S	syn -($-sc$, ac)- C_1 -ft	0.48	0.48	155	-152	L	-94	137	78	46	3	9-	277,285	312,316	255,365
14 , X = Se	$(-sc, -ac)-C_1$ -ft	16.79	0.00	20	-145	4-	-69	94	76	50	-4	7	291,293	318,319	225,259
14 , X = Se	anti-($-sc,sc$)- C_s -ft	17.31	0.53	25	-25	0	-75	75	75	52	-4	1	292	319	210,220
14 , X = Se	syn -($-sc$, ac)- C_1 -ft	30.01	13.22	134	-145	-13	-79	128	83	51	6	-15	331,326	310,315	220,288
19 , X = Se	$(-sc, -ac)-C_1$ -ft	0.23	0.23	24	-150	-11	-50	-85	83	52	9-	7	310,297	327,323	284,346
19 , X = Se	anti-($-sc,sc$)- C_s -ft	0.0	0.0	24	-24	0	-62	62	66	54	-8	12	312	327	227,339
19 , X = Se	syn -($-sc$, ac)- C_1 -ft	5.55	5.55	149	-151	10	-89	138	81	52	-5	7	292,305	320,325	276,358
^a H ¹ C ¹ /H ⁸	C ^{1"} for 11–14 , H ¹ C ^{1"} for 11–14 C ¹	$C^{2'}/H^8 \dots C^{2''}$	for 16–19 for 16–19												

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^c $H^{2'} \cdots H^{8'}/H^{8'} \cdots H^{2''}$ for (-sc, -ac)- C_1 of **11–14**, $H^{2'} \cdots H^{2''}/H^{8''} \cdots H^{8''}$ for anti-(-sc, ac)- C_1 and anti-(-sc, ac)- C_1 of **11–14**, $H^{1'} \cdots H^{3'}/H^{3'} \cdots H^{1''}$ for (-sc, -ac)- C_1 of **16–19**, $H^{1'} \cdots H^{3''}/H^{3'} \cdots H^{2''}/H^{3''}$ for anti-(-sc, ac)- C_1 and anti-(-sc, ac)- C_1 of **16–19**.

Table 15 R	telative B3LYP/SDD	free energies and	selected calculated	l geome	trical pa	arametei	s for B∕	vE-1s 11	20						
	Conformation	ΔG_{298} (kJ/mol)	$\Delta \Delta G_{298}$ (kJ/mol)	v' (°)	v" (°)	(°) w	τ' (°)	τ'' (°)	(_) θ	ϕ (°)	$\chi({\rm C}^9)~(^\circ)$	$\chi({\rm C}^{9'})~(^{\circ})$	$H{\cdots}C^a \;(pm)$	$C{\cdots}C^{b}~(pm)$	$H{\cdots}H^c \ (pm)$
11 , X = –	$(-sc,-sc)-C_2-t$	18.97	0.00	106	106	6-	-72	-72	81	1	0	0	253	316	277
11, X = -	$(-ac, -ac)-C_2-t$	28.98	10.01	146	146	20	-125	-125	87	5	0	0	257	317	258
11, X = -	$(sc,-ac)-C_1-t$	21.77	2.79	147	-107	17	09	-122	90	5	1	L	255,258	315,320	255,305
16 , X = -	$(-sc,-sc)-C_2-t$	1.62	1.62	-95	-95	21	51	51	LL	5	0	0	261	321	364
16 , X = -	$(-ac, -ac)-C_2-t$	2.01	2.01	140	140	22	-135	-135	73	7	0	0	207	321	378
16 , X = -	$(sc, -ac)-C_1-t$	0.0	0.0	139	-95	21	52	-136	76	7	0	0	261	321	365,374
12, X = 0	$(-sc,-ac)-C_1-ft$	18.07	0.00	30	-162	9	-66	-91	80	29	-5	7	257,256	304,308	244,265
12, X = 0	anti-($-sc$, ac)- C_1 -ft	21.76	3.69	31	-49	16	-56	107	84	28	-5	-2	258,246	304,308	236,267
12, X = 0	syn -($-sc$, ac)- C_1 -ft	24.65	6.58	141	-174	20	-70	128	88	22	5	-11	258,248	300,312	248,304
17, X = 0	$(-sc,-ac)-C_1-ft$	0.35	0.35	30	-174	17	-48	-76	89	27	-5	4	250,262	310,306	299,358
17, X = 0	$anti-(-sc,ac)-C_1-\mathbf{ft}$	0.0	0.0	32	-42	15	-50	103	87	28	-4	5	248,268	307,304	283,361
17, X = 0	syn -($-sc$, ac)- C_1 -ft	0.53	0.53	156	-175	18	LL-	142	87	27	4	-4	249,262	310,305	305,372
13 , X = S	$(-sc,-ac)-C_1-ft$	20.46	0.00	22	-148	4	-67	-95	76	46	-3	8	280,282	313,316	229,257
13 , X = S	anti-($-sc$, ac)- C_1 -ft	25.45	4.99	27	-27	6	-59	96	76	47	-2		281,275	314,314	218,240
13 , X = S	syn -($-sc$, ac)- C_1 -ft	30.63	10.17	134	-149	14	-79	127	85	45	9	-14	290,295	315,325	223,291
18 , X = S	$(-sc,-ac)-C_1$ -ft	0.32	0.32	31	-150	L	-48	-95	LL	48	-2	7	279,288	313,319	253,360
18 , X = S	anti-($-sc$, ac)- C_1 -ft	0.62	0.62	31	-24	9	-49	85	74	47	-2	7	275,287	311,318	243,366
18 , X = S	syn -($-sc$, ac)- C_1 -ft	0.0	0.0	155	-151	L	-95	140	78	48	2	L	277,288	313,318	257,370
14 , X = Se	$(-sc,-ac)-C_1-\mathbf{ft}$	24.44	0.00	20	-145	ю	-68	-96	76	47	-2	-8	283,286	313,317	225,252
14, X = Se	anti-($-sc$, ac)- C_1 -ft	29.26	4.82	26	-23	Ζ	-60	95	76	49	-1		282,278	314,314	216,235
14, X = Se	syn -($-sc$, ac)- C_1 -ft	34.20	9.76	132	-146	13	-80	126	83	47	5	-15	297,300	327,317	218,286
19 , X = Se	$(-sc,-ac)-C_1-\mathbf{ft}$	1.80	1.80	29	-147	9	-48	-95	LL	50	-2	7	292,284	320,315	252,359
19 , $X = Se$	$anti-(-sc,ac)-C_1-\mathbf{ft}$	3.85	3.85	29	-21	9	-50	85	74	50	-1	7	289,280	318,313	242,364
19 , X = Se	syn -(- sc , ac)- C_1 -ft	0.0	0.0	153	-148	٢	-96	140	78	50	1	L	281,291	314,319	255,370
15, X = Te	$(-sc,-ac)-C_1$ -ft	25.46	0.00	17	-141	7	-71	L6-	75	51	0	7	286,291	314,318	219,245
15, X = Te	$anti-(-sc,ac)-C_1-\mathbf{ft}$	29.31	3.85	26	-18	4	-62	92	73	53	1	-1	285,285	316,315	212,227
15 , $X = Te$	syn -($-sc$, ac)- C_1 -ft	33.96	8.50	131	-141	12	-82	126	83	51	4	-15	305,306	329,320	214,284
20 , $X = Te$	$(-sc,-ac)-C_1$ -ft	0.08	0.08	28	-144	9	-48	-98	75	53	0	7	299,290	323,316	246,364
20 , X = Te	$anti-(-sc,ac)-C_1-\mathbf{ft}$	0.94	0.94	28	-16	4	-50	84	73	53	0	7	295,289	321,315	240,363
20 , X = Te	syn -(- sc , ac)- C_1 - ft	0.0	0.0	152	-143	9	-95	140	LL	53	0	9-	290,297	316,322	257,372
^a H ¹ C ^{1/} /H ⁶	8 C ^{1"} for 11–15 , H ¹ .	$\cdots C^{2'}/H^8 \cdots C^{2''}$ for]	16-20												
$^{b} C^{1} \cdots C^{1'}/C^{t}$	8 C ^{1"} for 11–15 , C ¹ .	$\dots C^{2'}/C^8 \dots C^{2''}$ for 1	6-20												
° H ^{2′} H ^{8″} /F <i>C</i> ₁ and <i>anti</i> -($H^{8'} \cdots H^{2''}$ for (-sc,-ac)- (-sc,ac)-C ₁ of 16-20	-C ₁ of 11–15 , H ^{2′}	$\mathrm{H}^{2''}/\mathrm{H}^{8'}\cdots\mathrm{H}^{8''}$ for an	ti-(-sc,a	c)-C ₁ and	d <i>anti-</i> (sc,ac)-C ₁	of 11-1:	5, H ^{1′} …]	H ^{3″} /H ^{3′}	·H ^{1"} for (–s	$c,-ac$)- C_1 of	16–20, H ^{1′} …H	1″/H ^{3′} H ^{3″} for	anti-(-sc,ac)-



 $(-sc,-ac)-C_1-ft$

anti-(-sc,ac)-C1-ft

 $syn-(-sc,ac)-C_1-ft$





 $(-sc,-ac)-C_1-\mathbf{ft}$

anti-(-sc,ac)-C₁-**ft**

syn-(-sc,ac)-C₁-ft

Fig. 18 The B3LYP/SDD optimized geometries of the conformers of 20

		v' (°)	v" (°)	ω (°)	τ' (°)	τ″ (°)	θ (°)	φ (°)	χ(C ⁹) (°)	χ(C ^{9'}) (°)	$\begin{array}{c} H^1 \cdots C^{1'} \\ H^8 \cdots C^{1''} \\ (pm) \end{array}$	$\begin{array}{c} C^{1} \cdots C^{1'} \\ C^{8} \cdots C^{1''} \\ (pm) \end{array}$
11, X = -	B3LYP/6-31G(d)	105	105	10	-72	-72	81	1	0	0	253	315
	B3LYP/SDD	106	106	-9	-72	-72	81	1	0	0	253	316
	X-ray	-111	-114	5	69	86	72	2	-1	1	256,249	307,315
12, X = O	B3LYP/6-31G(<i>d</i>)	31	-163	6	-67	-91	79	30	-6	6	260,259	305,309
	B3LYP/SDD	30	-162	6	-66	-91	80	29	-5	7	257,256	304,308
	X-ray	-37	154	3	68	97	75	36	-7	9	262,271	303,313
13, X = S	B3LYP/6-31G(d)	22	-149	4	-69	-95	76	44	-4	7	279,281	311,315
	B3LYP/SDD	22	-148	4	-67	-95	76	46	-3	8	280,282	313,316
	X-ray	28	-146	3	-69	-97	78	45	6	-7	275,288	305,321
14, X = Se	B3LYP/6-31G(d)	20	-145	-4	-69	-94	77	50	-4	7	291,293	318,319
	B3LYP/SDD	20	-145	3	-68	-96	76	47	-2	-8	283,286	313,317
	X-ray	23	-146	1	-68	-103	78	48	3	-9	278,290	305,318
15, X = Te	B3LYP/SDD	17	-141	2	-71	-97	75	51	0	7	286,291	314,318
	X-ray	22	-138	3	-70	-98	77	57	4	-9	300,313	330,332
20 , X = Te	B3LYP/SDD	152	-143	6	-95	140	77	53	0	-6	290,297	316,322
	X-ray	140	-148	0	109	-130	65	54	4	-10	308,328	360,382

Table 16 Experimental and DFT calculated selected geometrical parameters of BAE-1s 11-15 and 20

than syn-(-sc,sc)- C_1 -**ft**-**19** by 8.9 kJ/mol (6-31G(d)), and (-sc,-ac)- C_1 -**ft**-**12** is lower in energy than (-sc,-ac)- C_1 -**ft**-**17** by 0.4 kJ/mol (SDD).

The relative stabilities of the conformers in the series of α, α -dinaphthalenyl derivatives usually do not change after applying the dispersion correction, with the exception of **11**

Table 17	Relative	dispersion-con	rrected H	B3LYP/6-3	31G(d) a	and B3L	YP/SDD	free	energies	and	selected	calculated	geometrical	parameters	for
BAE-1s 1	1–20														

	Conformation	B3LYP/6-31G(a	1)	B3LYP/SDD	
		ΔG_{298} (kJ/mol)	$\frac{\Delta\Delta G_{298}}{\text{(kJ/mol)}}$	ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)
11, X = -	$(-sc,-sc)$ - C_2 -t	2.47	0.00	5.58	2.91
11, X = -	(<i>-ac</i> , <i>-ac</i>)- <i>C</i> ₂ - t	15.85	13.38	2.67	0.00
11, X = -	$(sc,-ac)$ - C_1 -t	5.49	3.02	15.05	12.37
16, X = -	$(-sc,-sc)$ - C_2 - t	0.38	0.38	0.00	0.00
16, X = -	$(-ac,-ac)-C_2-\mathbf{t}$	2.40	2.40	1.38	1.38
16, X = -	$(sc,-ac)$ - C_1 - t	0.00	0.00	1.93	1.93
12, X = O	$(-sc,-ac)$ - C_1 -ft	0.53	0.00	0.00	0.00
12, X = O	anti-(-sc,ac)- C_1 -ft	3.60	3.07	2.66	2.66
12, X = O	syn -(- sc , ac)- C_1 -ft	10.68	10.15	8.30	8.30
17 , X = O	$(-sc,-ac)$ - C_1 -ft	0.00	0.00	0.44	0.00
17 , X = O	anti-($-sc,ac$)- C_1 - ft	2.41	2.41	0.96	0.52
17 , X = O	syn -(- sc , ac)- C_1 -ft	0.26	0.26	0.55	0.11
13 , X = S	$(-sc,-ac)$ - C_1 -ft	1.46	0.00	0.87	0.00
13 , X = S	anti-($-sc,ac$)- C_1 - ft	2.94	1.48	2.57	1.71
13 , X = S	syn -(- sc , ac)- C_1 -ft	15.00	13.55	13.90	13.03
18 , X = S	$(-sc,-ac)$ - C_1 -ft	0.04	0.04	0.00	0.00
18 , X = S	anti-($-sc,ac$)- C_1 - ft	0.74	0.74	0.96	0.96
18 , X = S	syn -(- sc , ac)- C_1 -ft	0.00	0.00	0.04	0.04
14, X = Se	$(-sc,-ac)$ - C_1 -ft	5.68	5.68	2.72	0.00
14, X = Se	anti-($-sc,sc$)- C_s -ft	0.00	0.00	3.07	0.35
14, X = Se	syn -(- sc , ac)- C_1 -ft	22.67	22.67	15.00	12.28
19 , X = Se	$(-sc,-ac)$ - C_1 -ft	9.13	0.28	0.00	0.00
19 , X = Se	anti-($-sc,ac$)- C_s -ft	9.68	0.83	0.67	0.67
19 , X = Se	syn -(- sc , sc)- C_1 -ft	8.85	0.00	1.18	1.18
14 , X = Te	$(-sc,-ac)-C_1$ -ft	-	_	4.35	0.00
14 , X = Te	anti-($-sc,ac$)- C_1 -ft	-	_	4.71	0.36
14 , X = Te	anti-(-sc,sc)-C _s -ft	_	-	16.60	12.25
14 , X = Te	syn -(- sc , ac)- C_1 -ft	_	-	0.00	0.00
19 , X = Te	$(-sc,-ac)-C_1$ -ft	_	-	0.30	0.30
19 , X = Te	anti-($-sc$, ac)- C_1 - ft	-	-	0.09	0.09

(at SDD) and **14** (at 6-31G(*d*)). The relative stabilities of the conformers in the series of β , β -dinaphthalenyl derivatives change, dues to the low absolute differences in the energies of the conformers.

Conclusions

The present study describes the syntheses and conformations of thirteen new mono-bridged tetraarylethenes (BAE-1s) with α, α -, β, β -, and α, β -dinaphthalenyl substituents, most of them with chalcogen bridges. Crystal structures of eight BAE-1s of this series indicate folded-twisted conformations of the chalcogen-bridged derivatives, with folding angles dependent on the chalcogen bridges. Their NMR spectra indicate considerable shielding of hydrogens in the tricyclic moieties, attributed to their exposure to the diamagnetic ring current of the opposing almost orthogonal naphthalenyl rings. The pronounced deshielding and the non-equivalence of the *peri* hydrogens in the α -naphthalenyl rings are noted. The pronounced deshielding of C⁹ in the Te-bridged BAE-1s is ascribed to through-space Te···C⁹ interactions. DFT calculations show folded-twisted global minimum conformations of the chalcogen derivatives **12–15** and **17–20** and twisted conformations of the fluorenylidene derivatives **11** and **16**. The naphthalenyl substituents are highly twisted. The enhanced overcrowding of the α,α -dinaphthalenyl derivatives as compared to the β,β -dinaphthalenyl derivatives is noted. Finally, the library of BAE-1 naphthologs reported here may serve as a source of potential AIE luminogens.

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