Synthesis of 3-(*o*-stilbenyl)sydnone and 3-(*o*-stilbenyl)-4-substituted-sydnone derivatives and their antitumor evaluation

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Abstract

A series of novel stilbene-sydnone derivatives were synthesized by the following sequence of reactions: starting from methyl anthranilate *via* glycine- and nitrosoglycine derivatives the corresponding 3-(*o*-carbomethoxyphenyl)-4-H/Me/Ph-sydnones were prepared and transformed to 3-(*o*-formylphenyl)-4-H/Me/Ph-sydnones, starting materials for Wittig reaction with various phosphonium salts to stilbenylsydnone derivatives. Final products were evaluated for their cytotoxic properties on five cancer cell lines, whereby the *cis*-4-methyl-3-[2-[2-(4-methylphenyl)ethenyl]phenyl]sydnone **5** and *cis*-4-phenyl-3-[2-[2-(4-chlorophenyl)ethenyl]-phenyl]sydnone **10** showed the most pronounced activity.

Keywords: Stilbenes, sydnones, synthesis, antitumor evaluation

Introduction

Sydnones[1] are five-membered heterocycles. They belong to a class of dipolar compounds known as "mesoionic" and can be represented as hybrids of a number of mesomeric ionic forms (Figure 1). Since their first synthesis[2] diverse substituted sydnones have been synthesized and many of them have shown useful biological properties[3] (e.g., as antibacterial,[4] antineoplastic[5] and anti-inflammatory[6] agents). In an effort to prepare new sydnones of potential pharmacological activity, especially the combination of the sydnone moiety with some other pharmacophore, we turned our attention to the preparation of stilbene substituted sydnones. Stilbene-based compounds are widespread in nature and have become of particular interest to chemists and biologists because of their wide range of biological activities.[7] Stilbene itself does not occur in

nature, but hydroxylated stilbenes[8,9] have been found in many medicinal plants. We expected that the structures obtained by combining the stilbene and sydnone moieties might possess valuable biological activity (Figure 2).

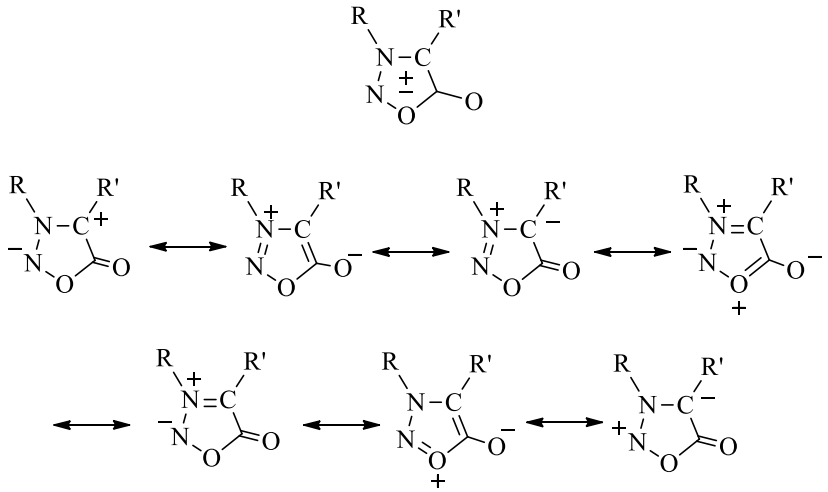


Figure 1

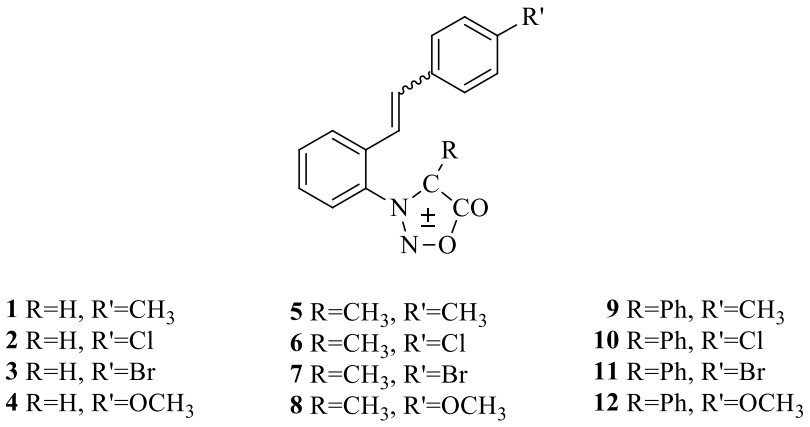


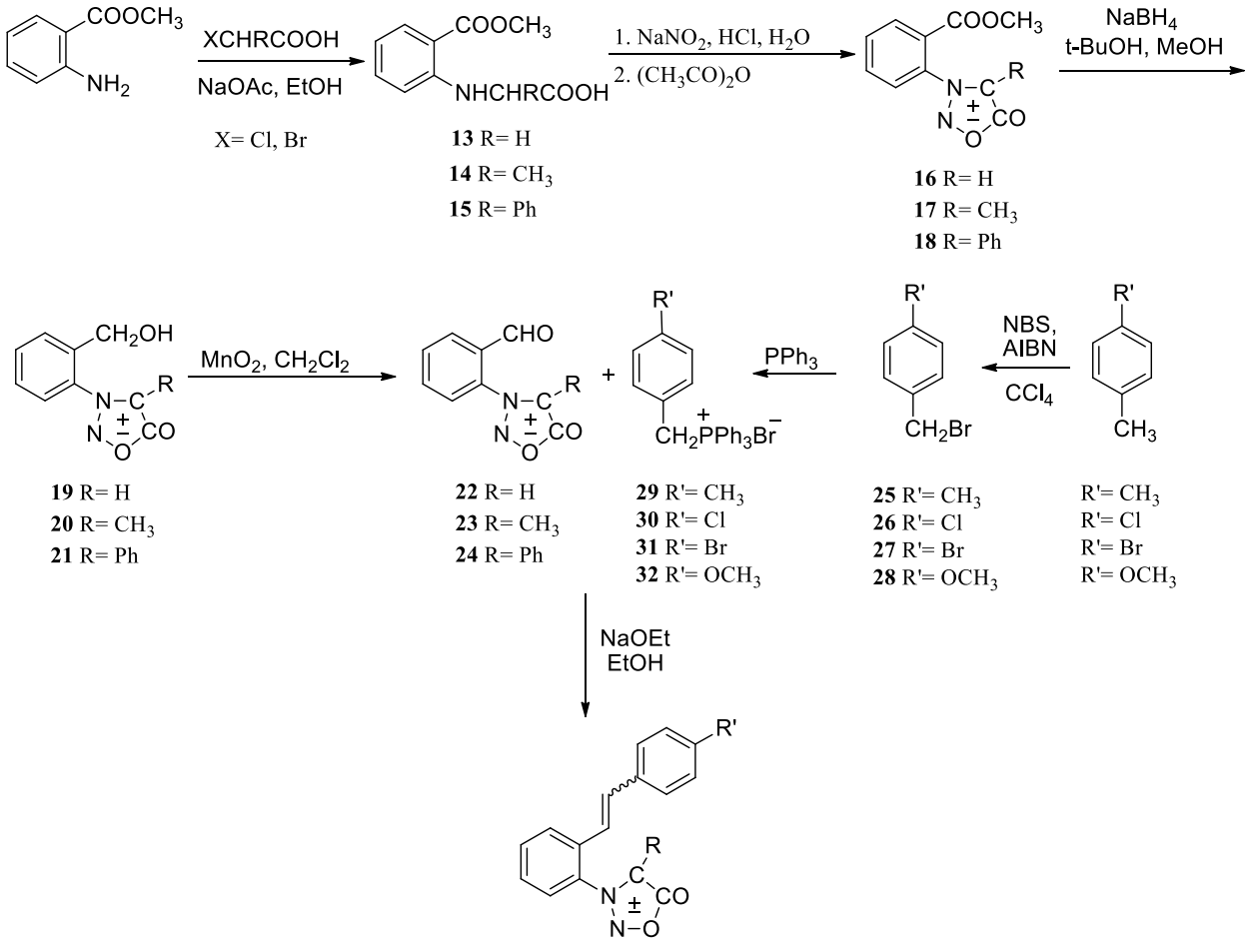
Figure 2

In the present paper we describe the synthesis of *cis*- and *trans*-3-(*o*-stilbenyl)sydnones **1-4** and *cis*- and *trans*-3-(*o*-stilbenyl)-4-substituted-sydnones **5-12**, a system in which are associated two pharmacophore groups, stilbene and sydnone, as potential new antitumor agents.

Results and Discussion

Chemistry

The *cis*/*trans*-stilbene-sydnones **1-12** were chosen in order to investigate the configurational influence of the stilbene moiety as well as the substituent effects (structure-activity relationship - SAR) on their biological behaviour. The first example of the stilbene moiety attached to sydnone ring was described by us previously and compounds **1**, **5** and **9** have been prepared from the corresponding stilbene derivatives by closing the sydnone ring at the end of the synthetic pathway.[10] Due to the needs in this work for a whole series of stilbene-sydnone derivatives in both *cis*- and *trans*-configurations, with different substituents in position 4′ of the stilbene moiety and position 4 of the sydnone moiety, it was necessary to elaborate a more efficient route than the one described previously. In this work a different synthetic approach to sydnones **1-12** is elaborated according to Scheme 1.



Scheme 1

The first step involves the reaction of methyl anthranilate with halogenoacetic acids to give *N*-(*o*-carbomethoxy)-aminoacids **13-15**. The resultant aminoacids were treated with sodium nitrite and the crude *N*-nitroso derivatives submitted to dehydration with acetic acid anhydride to give *N*-(*o*-carbomethoxyphenyl)sydnones **16**,[11] **17** and **18**. The sydnone derivatives were purified by column chromatography and isolated in 46% **16**, 59% **17** and 21% **18** yields. After reduction with $NaBH_4$ in methanol/*t*-butanol to hydroxymethyl derivatives **19-21**, followed by oxidation with MnO_2 and filtration through the column with silica gel, the formyl derivatives **22-24** were obtained in 61-68% yield. The resulting 3-(2-formylphenyl)sydnone **22**, 3-(2-formylphenyl)-4-methylsydnone **23** and 3-(2-formylphenyl)-4-phenylsydnone **24** were the starting compounds for the continuation of the synthesis to stilbene-sydnone derivatives **1-12**. The obtained formylphenylsydnone derivatives **22-24** were submitted to Wittig reaction with *p*-substituted-benzyltriphenylphosphonium salts **29-32**, which were prepared from the corresponding *p*-substituted-benzylbromides **25-28** and triphenylphosphine in toluene solution, by a standard procedure. The Wittig reactions were performed in ethanol with the addition of sodium ethoxide as a base. All sydnone derivatives were prepared as mixtures of *trans*- and *cis*-isomers, which were purified and separated by consecutive column chromatography.

All prepared compounds are identified and characterized by spectroscopic methods. Derivatives **14** and **15** have mass spectral molecular ions at *m*/*z* 224 and 286, respectively, and in their IR spectra exhibit two bands at 1694-1702 and 1667-1685 cm^{-1}, which correspond to acid and ester carbonyl groups. Also, their NMR spectra correspond to those expected for the proposed structures. The *N*-(*o*-carbomethoxyphenyl)sydnone derivatives **16**[11]**-18** have in their IR spectra two bands, which correspond to sydnone carbonyls and ester carbonyls, in the range 1772-1759 and 1732-1726 cm^{-1}. In their ^{13}C NMR spectra the signals of the two carbon atoms in the carbonyl groups are observed at 167-169 ppm and the sydnone ring carbon (C-4) appears at 107-109 ppm. The hydroxymethylphenyl derivatives **19-21** have not been analyzed spectroscopically but their oxidation products **22-24** have. The spectroscopic data for **22** correspond to those in the literature[12] and formylphenylsydnone derivatives **23** and **24** show singlets at ca 9.9 ppm in their ^1H NMR spectra, which correspond to aldehyde protons, and the characteristic signals of the sydnone carbon (C-4) appear in their ^{13}C NMR spectra at 108-110 ppm.

The stilbene-sydnone derivatives **1-12**, show, besides the characteristic signals for the carbonyl carbon and sydnone ring carbon, the corresponding signals for stilbene moieties in their ^{13}C NMR spectra. All carbonyl carbons and sydnone ring carbons of the *cis*- and *trans*-isomers appear in a very narrow region at 167-169 ppm and 97-109 ppm, respectively. The *cis*-**1-12** and *trans*-**1-12** isomers are easily recognizable in their ^1H NMR spectra by the coupling constants of the ethylenic protons which have values of ~ 12 Hz or ~ 16 Hz, respectively. In the cases of only 3-substituted sydnone derivatives **1-4** the characteristic singlets for the sydnone ring hydrogens at ~ 6.5 ppm for the *trans*-isomers and 6.4 ppm for *cis*-isomers unequivocally confirm the sydnone structures.

Biological evaluation

Stilbene-sydnones were screened for their antiproliferative activity in the Laboratory for Experimental Therapy at the Department for Molecular Medicine of Rudjer Bošković Institute. In vitro studies on 5 cell lines derived from 5 different tumor types: HeLa (cervical carcinoma), MCF-7 (breast carcinoma), SW 620 (colon carcinoma), MiaPaCa-2 (pancreatic carcinoma), and H 460 (lung carcinoma).

The tested compounds showed diverse, but overall very low, antiproliferative effects on the tested cell lines. Interestingly, although many *trans*-stilbenes, including resveratrol, pterostilbene, piceatannol etc. exhibit high levels of biological activities,[13] in our study *trans*-derivatives showed generally lower activity compared to *cis*-derivatives. Among the latter, the most interesting compounds are *cis*-**5** and *cis*-**10** which showed significantly more pronounced inhibitory effects towards all cell lines. Such activity can be correlated to the resveratrol activity in tumor cells.[14] Only *cis*-**2**, *cis*-**6** and c*is*-**7** did not show growth inhibition, while from tested *trans*-derivatives only *trans*-**3** and *trans*-**6** showed low inhibition of cell growth.

Conclusions

We have synthesized *cis*- and *trans*-stilbene-sydnones **1-12** using the strategy in which the properly substituted sydnone moiety was made first followed by building the stilbene moiety. This approach is especially convenient in the cases where both stilbene diastereomers are the target molecules.

Tested compounds showed diverse antiproliferative effects on tested cell lines that ranged from low to moderate, except *cis*-**5** and *cis*-**10,** which showed significantly stronger inhibitory effects towards all cell lines. In general *cis*-derivatives showed significantly better antiproliferative activity, compared to *trans*-derivatives, whereby only *trans*-**3** and *trans*-**6** showed low inhibition of cell growth.

Experimental Section

General. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 and 600 MHz. All NMR spectra were measured in $CDCl_3$ or DMSO using tetramethylsilane as reference. UV spectra were measured on a Varian Cary 50 UV/VIS Spectrophotometer. IR spectra were recorded on FTIR-ATR Vertex 70 Bruker or Perkin-Elmer M-297 spectrophotometer. Mass spectra were obtained on Extrel FT MS 2001 DD, Auto Spec Q (VG Analytical Manchester, GB), on Platform LCZ (Micromass, UK) and/or on a Varian Saturn 2200 equipped with Factor Four Capillary Column VF-5ms. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien). Elemental analyses were carried out on a Perkin-Elmer, Series II, CHNS Analyzer 2400 at Rudjer Bošković Institute. Silica gel

(Merck 0.063e0.2 mm) was used for chromatographic purifications. Thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F254 plates. Solvents were purified by distillation.

***N*-[2-(Methyloxycarbonyl)phenyl]glycine (13)**[15]

A mixture of methyl anthranilate (2.4 g, 15.9 mmol), chloroacetic acid (1.0 g, 10.6 mmol) and sodium acetate trihydrate (1.4 g, 10.6 mmol) in water (10 mL), was heated for 6 hours at reflux. The reaction mixture was cooled to 0°C (on ice bath), then an aqueous solution of NaOH (10%) was added until pH 8 was reached. After extraction with dichloromethane (3 x 30 mL) the water phase was acidified with hydrochloric acid to pH 3.5 resulting in a white solid precipitate. Filtration and desiccation afforded the title compound as a white solid (621 mg, 28%).

2-Methyl-2-[*N*-[2-(methyloxycarbonyl)phenyl]amino]acetic acid (14)

A mixture of methyl anthranilate (5.9 g, 39.0 mmol), 2-bromopropionic acid (4.0 g, 26.0 mmol) and anhydrous sodium acetate (2.1 g, 26.0 mmol) in absolute ethanol (30 mL) was refluxed for 18 hours. After cooling and evaporation water was added (40 mL) and the mixture was cooled to 0°C. An aqueous solution of NaOH (10%) was added dropwise until pH 8 was reached. After extraction with dichloromethane (3x30 mL) the water phase was acidified with hydrochloric acid to pH 3.5 resulting in precipitation of a white solid. Filtration and desiccation afforded the title compound **14** as a white solid (1.97 g, 34%).

14. White solid, yield 34%, mp 122-123°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 221 (29 179), 255 (9 806), 348 (6 379). IR (KBr) ν_{max}/cm^{-1}: ~3300-2500 (assoc. COOH), 3352 (NH), 1702 (CO), 1685 (CO). ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ/ppm: 8.19 (bs, 1H, NH), 7.89 (d, 1H, J = 8.0 Hz), 7.39 (t, 1H, J = 8.0 Hz), 6.73 (d, 1H, J = 8.0 Hz), 6.64 (t, 1H, J = 8.0 Hz), 4.30 (q, 1H, J = 7.2 Hz, CH), 3.85 (s, 3H), 1.54 (d, 3H, J = 7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $(CD_3)_2CO$,) δ/ppm: 175.1 (s), 166.3 (s), 150.7 (s), 135.5 (d), 132.4 (d), 116.1 (d), 112.6 (d), 111.4 (s), 51.9 (d), 51.4 (q), 19.0 (q). MS, *m/z*: 224 (M^++1, 100%).

2-Phenyl-2-*N*-[2-(methyoxycarbonyl)phenyl]aminoacetic acid (15)

Mixture of methyl anthranilate (2.3 g, 15.0 mmol), α-bromophenylacetic acid (2.15 g, 10.0 mmol) and anhydrous sodium acetate (820 mg, 10.0 mmol) in absolute ethanol (35 mL) was refluxed for 6 hours. After cooling and evaporation water was added (60 mL) and the mixture was cooled to 0°C. An Aqueous solution of NaOH (10%) was added dropwise until pH 8 was reached. After extraction with dichloromethane (3x30 mL) the water phase was acidified with hydrochloric acid to pH 3.5 resulting in precipitation of a white solid. Filtration and desiccation afforded the title compound **15** as a white solid (970 mg, 34%).

15. White solid, yield 34%, mp 148-149°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 222 (27 213), 256 (9 561), 348 (5 926). IR (KBr) ν_{max}/cm^{-1}: ~3300-2500 (assoc. COOH), 3354 (NH), 3029, 2955 (CH), 1694, 1667 (CO). ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ/ppm: 8.98 (d, 1H, J = 5.6 Hz, NH), 7.89 (d, 1H, J = 7.8 Hz), 7.58 (d, 2H, J = 8.4 Hz), 7.42-7.29 (m, 3H), 7.25 (t, 1H, J =

7.8 Hz), 6.60 (t, 1H, *J* = 7.8 Hz), 6.58 (d, 1H, *J* = 7.8 Hz), 5.30 (d, 1H, *J* = 5.6 Hz, CH), 3.88 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $(CD_3)_2CO$) *δ*/ppm: 172.9 (s), 169.8 (s), 150.3 (s), 139.8 (s), 135.8 (d), 132.8 (d), 130.2 (d), 129.6 (d), 128.7 (d), 116.8 (d), 114.0 (d), 112.3 (s), 60.8 (d), 52.5 (q). MS, *m/z*: 285.99 (M^+, 40%).

Synthesis of ester sydnone derivatives (16)[11] and (17)

To a suspension of the corresponding glycine **13** or **14** (9.2 mmol) in water (30 mL) cooled on an ice bath, was added hydrochloric acid (17%, 9.2 mmol) dropwise and the reaction mixture was stirred for 3 hours. Then a solution of sodium nitrite (952 mg, 13.8 mmol) in water (5 mL) was added dropwise during 2 hours with cooling on the ice bath. The reaction mixture was stirred for an additional one hour then dichloromethane was added and stirring was continued for an additional 30 minutes. After extraction, drying on anhydrous $MgSO_4$, filtration and evaporation, the nitroso-derivative was isolated. Without any further purification the nitroso-product was dissolved in quintuple the amount of acetic anhydride and the reaction mixture was put in a dark place for 7 days. Then the reaction mixture was poured onto cold water (100 mL) with cooling and vigorous stirring. Neutralization with sodium bicarbonate, extraction with dichloromethane (3×30 mL), drying, filtration and evaporation afford the crude sydnone derivative.

3-[2-(Methyloxycarbonyl)phenyl]sydnone (16).[11] From crude mixture isolated by column chromatography on silica-gel as adsorbent and dichloromethane as eluent. Pale yellow crystals, yield 46%, 940 mg, mp 102-104°C (lit.[11] 104-106 °C).

4-Methyl-3-[2-(methyloxycarbonyl)phenyl]sydnone (17). From crude mixture isolated by column chromatography on silica-gel as adsorbent and ethyl acetate/petroleum ether (17%) as eluent. Pale yellow crystals, yield 59%, 1.27 g, mp 102-103 °C (water); UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (23 122), 310 (7 150). IR (KBr) ν_{max}/cm^{-1}: 3077, 3048, 2958 (CH), 1772 (CO), 1732 (CO). ^1H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 8.23 (d, 1H, *J* = 9.2 Hz), 7.85-7.77 (m, 2H), 7.47 (d, 1H, *J* = 9.2 Hz), 3.83 (s, 3H, OCH_3), 1.99 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*/ppm: 168.5 (s), 163.5 (s), 133.8 (d), 132.7 (s), 132.5 (d), 132.3 (d), 127.5 (d), 127.3 (s), 107.2 (s), 53.1 (q), 7.4 (q). MS, *m/z*: 235 (M^++1, 100%); Elemental analysis, calcd for $C_{11}H_{10}N_2O_4$ (Mr = 234.21): C 56.41, H 4.30, N 11.96%; found C 56.57, H 4.25, N 12.11%.

4-Phenyl-3-[2-(methyloxycarbonyl)phenyl]sydnone (18)

To a suspension of **15** (2.2 g, 7.0 mmol) in water (50 mL) was added with cooling and stirring a solution of sodium nitrite (2.13 g, 30.8 mmol) in water (5 mL) dropwise and the reaction mixture was stirred for 3 hours. Then, HCl (17%) was added dropwise during 3 hours until pH 2 was reached. After an additional hour of stirring on the ice bath, dichloromethane was added (30 mL). Extraction, drying, filtration and evaporation afford the crude nitroso product which was dissolved in quintuple the amount of acetic anhydride and the reaction mixture was put in a dark place for 7 days. Then the reaction mixture was poured onto cold water (150 mL) with cooling and vigorous stirring. Neutralization with sodium bicarbonate, extraction with dichloromethane (3×30 mL), drying, filtration and evaporation afford the crude sydnone derivative which was

purified by column chromatography on silica-gel as adsorbent and petroleum ether/ether (15-40%) as eluent giving sydnone **18**.

18. Yellow crystals, yield 21%, 435 mg, mp 160°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (21 817), 338 (6 853). IR (KBr) ν_{max}/cm^{-1}: 2954, 2846 (CH), 1759 (CO), 1726 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.17 (d, 1H, J = 9.2 Hz), 7.80-7.74 (m, 2H), 7.49 (d, 1H, J = 9.2 Hz), 7.26 (bs, 5H), 3.75 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 167.0 (s, CO-syd), 163.8 (s, CO-est), 133.9 (d), 133.9 (s), 132.6 (d), 132.4 (d), 129.0 (2d), 129.0 (d), 127.9 (s), 127.7 (d), 126.9 (2d), 124.6 (s), 109.6 (s, C-syd), 53.3 (q, CH_3-est). MS, *m/z*: 297 (M^++1, 100%); Elemental analysis, calcd for $C_{16}H_{12}N_2O_4$ (Mr = 296.28): C 64.86, H 4.08, N 9.46%; found C 64.98, H 4.19, N 9.59%.

Synthesis of alcohol sydnone derivatives (19-21)

The reaction mixture of the corresponding sydnone **16-18** (1.9 mmol) and $NaBH_4$ (3.8 mmol) in *t*-BuOH (12 mL) was heated to reflux and MeOH (1mL) was added dropwise during 1 hour. After cooling to room temperature, water (15 mL) was added and the mixture was evaporated under reduced pressure to remove *t*-BuOH/MeOH as an azeotrope. The product was extracted from water with dichloromethane (3×25 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and evaporated to afford the crude product which was used in the next reaction without any further purification **19** (oily matter, yield 59%, 217 mg), **20** (oily matter, yield 58%, 395 mg), **21** (oily matter, yield 93%, 478 mg).

Synthesis of aldehyde sydnone derivatives (22),[12] (23) and (24)

The corresponding alcohol (**19-21**, 1.3 mmol) was dissolved in dichloromethane (15 mL), then MnO_2 (10 eq) was added and the reaction mixture was stirred at room temperature for three days with portionwise addition of additional amounts of MnO_2 (20 eq). The product was isolated by column chromatography with silica-gel as adsorbent and with dichloromethane/ether (0-3%) as eluent.

3-(2-Formylphenyl)sydnone (22). White solid, yield 68%, 170 mg, mp 93-94 °C (lit.[12] 93-94 °C).

3-(2-Formylphenyl)-4-methylsydnone (23). Oil, yield 61%, 163 mg; IR (neat) ν_{max}/cm^{-1}: 3072, 2934 (CH), 1717 (CO), 1687 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 9.86 (s, 1H, CHO), 8.18 (d, 1H, J = 9.1 Hz), 7.95-7.89 (m, 2H), 7.56 (d, 1H, J = 9.1 Hz), 2.03 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 186.7 (d, CHO), 171.3 (s, CO-syd), 135.2 (d), 133.3 (s), 133.0 (d), 131.9 (d), 130.7 (s), 127.2 (d), 107.7 (s, C-syd), 7.6 (q). MS, *m/z*: 205 (M^++1, 100%).

4-Phenyl-3-(2-formylphenyl)sydnone (24). Yellow crystals, yield 64%, 222 mg, mp 133°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 204 (20 042), 245 (8 464), 334 (8 926). IR (KBr) ν_{max}/cm^{-1}: 3065, 2953, 2858 (CH), 1739 (CO), 1704 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 9.86 (s, 1H, CHO), 8.13 (d, 1H, J = 9.1 Hz), 7.93-7.85 (m, 2H), 7.60 (d, 1H, J = 9.1 Hz), 7.27-7.23 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$,) δ/ppm: 186.5 (d, CHO), 166.7 (s, CO-syd), 135.5 (d),

134.5 (s), 133.1 (d), 132.0 (d), 130.8 (s), 129.2 (d), 129.1 (2d), 127.7 (d), 126.9 (2d), 124.1 (s), 110.3 (s, C-syd). MS, *m/z*: 266.99 (M^+, 100%).

General procedure for the synthesis of 4-methyl, 4-chloro, 4-bromo and 4-methoxybenzylbromides (25-28)

A mixture of *p*-xylene, *p*-chlorotoluene, *p*-bromotoluene or *p*-methylanisole (0.1 mol), CCl_4 (100 mL), *N*-bromosuccinimide (19.6 g, 0.11mol) and azoisobutyronitrile (0.6 g) was heated at reflux for 40 minutes. After succinimide filtration, washing with CCl_4 (40 mL) and solvent evaporation the crude product was isolated and used in the next reaction without any further purification.

General procedure for the synthesis of 4-methyl, 4-chloro, 4-bromo and 4-methoxybenzyltriphenylphosphonium bromides (29-32)

The corresponding 4-substituted benzylbromide **25-28** (0.1 mol,) was dissolved in toluene (40 mL) and a solution of triphenylphosphine (26.2 g, 0.1 mol) in toluene (50 mL) was added. The reaction mixture was stirred at room temperature overnight. Filtration, washing with petroleum ether (5 mL) and drying afford the corresponding *p*-substituted-benzyltriphenylphosphonium bromides **29** (85%), **30** (73%), **31** (60%) **32** (75%).

General procedure for the synthesis of stilbenylsydnones (1-12)

The previously prepared *p*-substituted benzyltriphenylphosphonium bromide **29**-**32** (1.6 mmol) was dissolved in absolute ethanol (10 mL) under argon and a solution of sodium ethoxide in ethanol, prepared by reaction of Na (36 mg, 1.6 mmol) in absolute ethanol (5 mL), was added dropwise. The reaction mixture was stirred for 15 minutes and a solution of the corresponding aldehyde **22-24** (1.0 mmol in 15 mL of ethanol) was added. The reaction mixture was stirred and heated at 40 °C for 1 hour. After solvent evaporation, water (20 mL) and benzene (15mL) were added to the residue. The water phase was washed with benzene (3x15 mL), the organic layers were collected, dried over anhydrous $MgSO_4$, filtrated and evaporated, affording crude product. The mixtures of the *trans*- and *cis*-stilbenylsydnones were separated by column chromatography on silica-gel as adsorbent and dichloromethane as eluent. Further column chromatography with dichloromethane and/or dichloromethane/ether (0-3%) afforded the pure *trans*- and pure *cis*-isomers.

3-[2-[2-(4-Methylphenyl)ethenyl]phenyl]sydnone (1). Yield 62%, 172 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/1.2. Dichloromethane/ether (0-3%) used as eluent. Spectroscopic data of *trans*- and *cis*-**1** correspond to data in the lit. [10].

3-[2-[2-(4-Chlorophenyl)ethenyl]phenyl]sydnone (2). Yield 77%, 230 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/1. Dichloromethane/ether (0-3%) used as eluent.

***trans*-2.** Pale yellow solid, mp 189-190°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (25 306), 223 (17 090), 302 (29 845). IR (diamond) ν_{max}/cm^{-1}: 3118 (CH-syd), 1745 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.88 (d, 1H, *J* = 7.9 Hz), 7.69-7.66 (m, 1H), 7.51-7.50 (m, 2H), 7.38 (d, 2H, *J* = 8.3 Hz, H-10/11), 7.34 (d, 2H, *J* = 8.3 Hz, H-10/11), 7.15 (d, 1H, *J* = 16.1 Hz,

H-7/8), 6.83 (d, 1H, *J* = 16.1 Hz, H-7/8), 6.55 (s, 1H, H-syd). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.7 (s, CO-syd), 134.9 (s), 134.31 (s), 133.5 (d), 133.0 (s), 132.6 (s), 132.4 (d), 129.2 (d), 128.8 (d), 128.3 (d), 127.3 (d), 125.6 (d), 120.5 (d), 98.0 (d, CH-syd). MS, *m/z*: 298.91 (M^+, 100%), 300.89 (M^+, 45%); Elemental analysis, calcd for $C_{16}H_{11}ClN_2O_2$ (Mr = 298.72): C 64.33, H 3.71, N 9.38%; found C 64.05, H 3.79, N 9.54%.

***cis*-2.** Pale yellow solid, mp 124-125°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (39 790), 264 (16 691), 290 (16 280). IR (diamond) ν_{max}/cm^{-1}: 3128 (CH-syd), 1720 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.56-7.49 (m, 3H), 7.42 (d, 1H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.6 Hz, H-10/11), 7.00 (d, 2H, *J* = 8.6 Hz, H-10/11), 6.73 (d, 1H, *J* = 12.0 Hz, H-7/8), 6.45 (d, 1H, *J* = 12.0 Hz, H-7/8), 6.46 (s, 1H, H-syd). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.8 (s, CO-syd), 134.1 (s), 133.9 (d), 133.3 (s), 132.9 (s, 2C), 132.3 (d), 131.6 (d), 130.2 (d), 129.2 (d), 128.9 (d), 125.4 (d), 123.6 (d), 97.3 (d, CH-syd). MS, *m/z*: 298.91 (M^+, 100%), 300.89 (M^+, 45%).

3-[2-[2-(4-Bromophenyl)ethenyl]phenyl]sydnone (3). Yield 72%, 247 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1.3/1. Dichloromethane/ether was (0-3%) used as eluent.

***trans*-3.** Yellow solid, mp 191-192°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (22 748), 226 (15 815), 302 (31 794). IR (diamond) ν_{max}/cm^{-1}: 3113 (CH-syd), 1732 (CO, syd). ^{1}H NMR (600 MHz, $CDCl_3$) *δ*/ppm: 7.88 (d, 1H, *J* = 8.0 Hz), 7.69-7.66 (m, 1H), 7.51-7.49 (m, 4H), 7.31 (d, 2H, *J* = 8.4 Hz, H-10/11), 7.13 (d, 1H, *J* = 16.2 Hz, H-7/8), 6.84 (d, 1H, *J* = 16.2 Hz, H-7/8), 6.55 (s, 1H, H-syd). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.9 (s, CO-syd), 134.9 (s), 133.7 (d), 133.1 (s), 132.7 (s), 132.6 (d), 132.3 (d), 129.0 (d), 128.7 (d), 127.4 (d), 125.8 (d), 123.3 (s), 120.8 (d), 98.2 (d, CH-syd). MS *m/z*: 344.81 (M^+, 100%), 342.81 (M^+, 100%). Elemental analysis, calcd for $C_{16}H_{11}BrN_2O_2$ (Mr = 343.11): C 56.00, H 3.23, N 8.16%; found C 56.24, H 3.12, N 8.25%.

***cis*-3.** Yellow solid, mp 151°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (60 792), 219 (44 234), 269 (27 861), 290 (27 357). IR (diamond) ν_{max}/cm^{-1}: 3130 (CH-syd), 1720 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.55-7.50 (m, 3H), 7.42 (d, 1H, *J* = 8.1 Hz), 7.35 (d, 2H, *J* = 8.4 Hz, H-10/11), 6.94 (d, 2H, *J* = 8.4 Hz, H-10/11), 6.70 (d, 1H, *J* = 12.0 Hz, H-7/8), 6.46 (d, 1H, *J* = 12.0 Hz, H-7/8), 6.44 (s, 1H, H-syd). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.9 (s, CO-syd), 134.3 (s), 134.0 (d), 133.3 (s), 132.9 (s), 132.3 (d), 131.9 (d), 131.6 (d), 130.4 (d), 129.2 (d), 125.4 (d), 123.7 (d), 122.4 (s), 97.3 (d, CH-syd). MS, *m/z*: 344.81 (M^+, 100%), 342.81 (M^+, 100%).

3-[2-[2-(4-Methoxyphenyl)ethenyl]phenyl]sydnone (4). Yield 73%, 215 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/1.2. Dichloromethane/ether was (4%) used as eluent.

***trans*-4.** Yellow solid, mp 112-113°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (21 723), 227 (13 623), 317 (24 230). IR (diamond) ν_{max}/cm^{-1}: 3111 (CH-syd), 1764 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) *δ*/ppm: 7.80 (d, 1H, *J* = 8.1 Hz), 7.66-7.63 (m, 1H), 7.48-7.46 (m, 2H), 7.40 (d, 2H, *J* = 8.8 Hz), 7.17 (d, 1H, *J* = 16.0 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 6.72 (d, 1H, *J* = 16.0 Hz), 6.57 (s, 1H, CH-syd), 3.86 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 169.0 (s, CO-syd), 160.6 (s), 134.6 (d), 133.8 (s), 132.5 (d), 132.5 (s), 128.8 (s), 128.7 (d), 128.2 (d), 127.2 (d), 125.7 (d), 117.7 (d), 114.6 (d), 98.3 (d, CH-syd), 55.63 (q, OCH_3). MS, *m/z*: 294.96

(M^+, 100%). Elemental analysis, calcd for $C_{17}H_{14}N_2O_3$ (Mr = 294.3): C 69.38, H 4.79, N 9.52%; found C 69.18, H 4.67, N 9.45%.

***cis*-4.** White solid, mp 111°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (35 218), 292 (15 657). IR (diamond) ν_{max}/cm^{-1}: 3120 (CH-syd), 1728 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.53-7.46 (m, 4H), 7.00 (d, 2H, J = 8.3 Hz), 6.73 (d, 2H, J = 8.3 Hz), 6.70 (d, 1H, J = 12.0 Hz, H-7/8), 6.42 (s, 1H, CH-syd), 6.31 (d, 1H, J = 12.0 Hz, H-7/8), 3.78 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 169.0 (s, CO-syd), 159.6 (s), 134.7 (d), 133.8 (s), 133.3 (s), 132.2 (d), 131.8 (d), 130.3 (d), 128.8 (d), 127.9 (s), 125.3 (d), 121.0 (d), 114.1 (d), 97.4 (d, CH-syd), 55.4 (q, OCH_3). MS, *m/z*: 294.96 (M^+, 100%).

4-Methyl-3-[2-[2-(4-methylphenyl)ethenyl]phenyl]sydnone (5). Yield 62%, 181 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1.3/1. Dichloromethane/ether was (0-3%) used as eluent.

***trans*-5.** White solid. Spectroscopic data correspond to data in ref. 10a.

***cis*-5.** White solid, mp 105-107°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 204 (30 095), 221 (18 600), 297 (13 093). IR (diamond) ν_{max}/cm^{-1}: 3021, 2921, 2857 (CH), 1733 (CO-syd); ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.52 (d, 1H, J = 9.0 Hz), 7.49-7.47 (m, 2H), 7.40 (d, 1H, J = 9.0 Hz), 7.03 (s, 4H, H-10 and H-11), 6.68 (d, 1H, J = 12.2 Hz, H-7/8), 6.16 (d, 1H, J = 12.2 Hz, H-7/8), 2.31 (s, 3H, CH_3), 1.96 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 168.9 (CO-syd), 138.4 (s), 135.1 (d), 134.7 (s), 132.6 (s), 132.3 (s), 131.9 (d), 131.5 (d), 129.4 (d), 128.9 (d), 128.9 (d), 126.4 (d), 121.6 (d), 106.7 (s, C-syd), 21.4 (q, CH_3), 7.6 (q, CH_3). MS, *m/z*: 292 (M^+, 100%), 248 (11), 207 (60). Elemental analysis, calcd for $C_{18}H_{16}N_2O_2$ (Mr = 292.12): C 73.95, H 5.52, N 9.58%; found C 73.70, H 5.44, N 9.70%.

3-[2-[2-(4-Chlorophenyl)ethenyl]phenyl]-4-methylsydnone (6). Yield 39%, 122 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1.2/1. Dichloromethane/ether was (0-3%) used as eluent.

***trans*-6.** Yellowish solid, mp 191-192°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (22 635), 228 (14 817), 305 (34 200). IR (diamond) ν_{max}/cm^{-1}: 3066 (CH), 1732 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.90 (d, 1H, J = 8.2 Hz), 7.68 (t, 1H, J = 8.2 Hz), 7.52 (t, 1H, J = 8.2 Hz), 7.39 (d, 1H, J = 8.2 Hz), 7.34 (s, 4H, H-10 and H-11), 7.14 (d, 1H, J = 16.2 Hz, H-7/8), 6.60 (d, 1H, J = 16.2 Hz, H-7/8), 1.96 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 168.7 (s, CO-syd), 135.0 (s), 134.4 (s), 133.6 (s), 133.5 (d), 132.6 (d), 131.4 (s), 129.3 (d), 129.0 (d), 128.4 (d), 127.1 (d), 126.6 (d), 120.4 (d), 107.1 (s, C-syd), 7.6 (q, CH_3). MS, *m/z*: 312.92 (M^+, 100%), 314.91 (M^+, 45%). Elemental analysis, calcd for $C_{17}H_{13}ClN_2O_2$ (Mr = 312.75): C 65.29, H 4.19, N 8.96%; found C 65.41, H 4.23, N 8.77%.

***cis*-6.** White solid, mp 148°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (22 244), 222 (22 088), 296 (15 468). IR (diamond) ν_{max}/cm^{-1}: 2925 (CH), 1730 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.51-7.50 (m, 2H), 7.46 (d, 1H, J = 8.8 Hz), 7.41 (d, 1H, J = 8.8 Hz), 7.20 (d, 2H, J = 8.4 Hz), 7.05 (d, 2H, J = 8.4 Hz), 6.67 (d, 1H, J = 12.2 Hz, H-7/8), 6.25 (d, 1H, J = 12.2 Hz, H-7/8), 1.97 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 168.7 (s, CO-syd), 134.3 (s),

134.1 (s), 134.0 (s), 133.9 (d), 132.4 (s), 132.1 (d), 131.3 (d), 130.2 (d), 129.2 (d), 129.0 (d), 126.5 (d), 123.2 (d), 106.4 (s, C-syd), 7.6 (q). MS, *m/z*: 312.92 (M^+, 100%), 314.91 (M^+, 45%).

3-[2-[2-(4-Bromophenyl)ethenyl]phenyl]-4-methylsydnone (7). Yield 64%, 229 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 0.8/1. Dichloromethane/ether was (0-3%) used as eluent.

***trans*-7.** Orange solid, mp 192-193°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (25 654), 228 (16 424), 306 (35 995). IR (diamond) ν_{max}/cm^{-1}: 2931, 2835 (CH), 1734 (CO-syd); ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.90 (d, 1H, *J* = 7.9 Hz), 7.69 (t, 1H, *J* = 7.9 Hz), 7.52 (t, 1H, *J* = 7.9 Hz), 7.49 (d, 2H, *J* = 8.4 Hz), 7.39 (d, 1H, *J* = 7.9 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 7.13 (d, 1H, *J* = 16.2 Hz, H-7/8), 6.62 (d, 1H, *J* = 16.2 Hz, H-7/8), 1.96 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.7 (s, CO-syd), 134.8 (s), 134.8 (s), 133.6 (d), 132.6 (d), 132.2 (d), 131.4 (s), 129.0 (d), 128.6 (d), 127.1 (d), 126.6 (d), 123.2 (s), 120.4 (d), 107.1 (s, C-syd), 7.6 (q). MS, *m/z*: 356.81 (M^+, 100%), 358.81 (M^+, 100%). Elemental analysis, calcd for $C_{17}H_{13}BrN_2O_2$ (Mr = 357.2): C 57.16, H 3.67, N 7.84%; found C 57.20, H 3.85, N 7.64%.

***cis*-7.** Pale brown solid, mp 139-140°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (32 832), 221 (20 037), 296 (14 567). IR (diamond) ν_{max}/cm^{-1}: 3062 (CH), 1732 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.52-7.40 (m, 4H), 7.35 (d, 2H, *J* = 8.5 Hz), 7.00 (d, 2H, *J* = 8.5 Hz), 6.65 (d, 1H, *J* = 12.2 Hz, H-7/8), 6.27 (d, 1H, *J* = 12.2 Hz, H-7/8), 1.97 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*/ppm: 168.7 (s, CO-syd), 134.3 (s), 133.9 (s), 133.9 (d), 132.3 (s), 132.1 (d), 131.9 (d), 131.3 (d), 130.5 (d), 129.2 (d), 126.5 (d), 123.2 (d), 122.4 (s), 106.5 (s, C-syd), 7.6 (q, CH_3). MS, *m/z*: 356.81 (M^+, 100%), 358.81 (M^+, 100%).

4-Methyl-3-[2-[2-(4-methoxyphenyl)ethenyl]phenyl]sydnone (8). Yield 54%, 167 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 0.8/1. Dichloromethane/ether (4%) was used as eluent.

***trans*-8.** Orange oil; IR (diamond) ν_{max}/cm^{-1}: 2930 (CH), 1724 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.89 (d, 1H, *J* = 7.9 Hz), 7.66 (t, 1H, *J* = 7.9 Hz), 7.46 (t, 1H, *J* = 7.9 Hz), 7.37-7.34 (m, 3H), 7.16 (d, 1H, *J* = 16.0 Hz, H-7/8), 6.89 (d, 2H, *J* = 8.7 Hz), 6.49 (d, 1H, *J* = 16.0 Hz, H-7/8), 3.83 (s, 3H, OCH_3), 1.96 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.8 (s, CO-syd), 160.6 (s), 134.4 (d), 134.3 (s), 132.4 (d), 131.1 (s), 128.7 (s), 128.6 (d), 128.3 (d), 126.7 (d), 126.5 (d), 117.4 (d), 114.5 (d), 107.1 (s, C-syd), 55.6 (q, OCH_3), 7.6 (q, CH_3). MS, *m/z*: 308.96 (M^+, 100%).

***cis*-8.** Yellowish oil; IR (diamond) ν_{max}/cm^{-1}: 2931 (CH), 1724 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.57-7.36 (m, 4H), 7.08 (d, 2H, *J* = 8.7 Hz), 6.75 (d, 2H, *J* = 8.7 Hz), 6.64 (d, 1H, *J* = 12.0 Hz, H-7/8), 6.11 (d, 1H, *J* = 12.0 Hz, H-7/8), 3.79 (s, OCH_3), 1.96 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 168.8 (s, CO-syd), 159.8 (s), 134.9 (s), 134.7 (d), 132.5 (s), 132.0 (d), 131.5 (d), 130.4 (d), 128.8 (d), 128.0 (s), 126.4 (d), 120.6 (d), 114.2 (d), 106.5 (s, C-syd), 55.4 (q, OCH_3), 7.6 (q). MS, *m/z*: 308.96 (M^+, 100%).

4-Phenyl-3-[2-[2-(4-methylphenyl)ethenyl]phenyl]sydnone (9). Yield 72%, 255 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/1.3. Dichloromethane was used as eluent.

***trans*-9.** White solid. Spectroscopic data correspond to data in ref. 10a.

***cis*-9.** White solid, mp 127-128°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (42 777), 226 (22 339), 313 (12 603). IR (diamond) ν_{max}/cm^{-1}: 3060, 3016, 2918 (CH), 1737 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.56 (d, 1H, *J* = 8.1 Hz), 7.51-7.23 (m, 8H), 6.93 (d, 2H, *J* = 8.0 Hz), 6.74 (d, 2H, *J* = 8.0 Hz), 6.56 (d, 1H, *J* = 12.2 Hz, H-7/8), 5.96 (d, 1H, *J* = 12.2 Hz, H-7/8), 2.28 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 167.0 (s, CO-syd), 137.9 (s), 135.2 (d), 134.4 (s), 133.2 (s), 132.3 (s), 131.7 (d), 131.4 (d), 129.0 (d), 128.8 (d), 128.7 (d), 128.6 (d), 128.6 (d), 126.7 (d), 126.6 (d), 124.7 (s), 121.3 (d), 109.1 (s, C-syd), 21.2 (q). MS, *m/z*: 355 (M^++1, 32%). Elemental analysis, calcd for $C_{23}H_{18}N_2O_2$ (Mr = 354.4): C 77.95, H 5.12, N 7.90%; found C 78.06, H 5.44, N 7.81%.

4-Phenyl-3-[2-[2-(4-chlorophenyl)ethenyl]phenyl]sydnone (10). Yield 72%, 270 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/0.6. Dichloromethane was used as eluent.

***trans*-10.** White solid, mp 163-164°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (22 244), 230 (11 774), 314 (17 619). IR (diamond) ν_{max}/cm^{-1}: 3065 (CH), 1732 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.85 (d, 1H, *J* = 7.7 Hz), 7.68 (t, 1H, *J* = 7.7 Hz), 7.50 (t, 1H, *J* = 7.7 Hz), 7.45 (d, 1H, *J* = 7.7 Hz), 7.30-7.18 (m, 9H), 6.97 (d, 1H, *J* = 16.3 Hz, H-7/8), 6.64 (d, 1H, *J* = 16.3 Hz, H-7/8). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 167.0 (s, CO-syd), 134.9 (s), 134.5 (s), 133.9 (s), 133.4 (d), 132.6 (d), 132.5 (s), 129.2 (d), 129.2 (d), 129.0 (d), 129.0 (d), 128.3 (d), 127.3 (d), 127.0 (d), 126.5 (d), 124.6 (s), 120.7 (d), 109.6 (s, C-syd). MS, *m/z*: 374.89 (M^+, 100%), 376.87 (M^+, 45%). Elemental analysis, calcd for $C_{22}H_{15}ClN_2O_2$ (Mr = 374.82): C 70.50, H 4.03, N 7.47%; found C 70.72, H 4.20, N 7.25%.

***cis*-10.** White solid, mp 147-148°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (37 730), 228 (21 445), 294 (12 400). IR (diamond) ν_{max}/cm^{-1}: 3072 (CH), 1732 (CO-syd); ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.59 (d, 1H, *J* = 7.8 Hz), 7.52 (t, 1H, *J* = 7.8 Hz), 7.46 (t, 1H, *J* = 7.8 Hz), 7.32-7.22 (m, 7H), 7.08 (d, 2H, *J* = 8.5 Hz), 6.72 (d, 2H, *J* = 8.5 Hz), 6.55 (d, 1H, *J* = 12.1 Hz, H-7/8), 6.03 (d, 1H, *J* = 12.1 Hz, H-7/8). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 166.9 (s, CO-syd), 133.9 (d), 133.8 (s), 133.8 (s), 133.6 (s), 133.2 (s), 131.9 (d), 131.3 (d), 129.9 (d), 129.0 (d), 128.8 (d), 128.8 (d), 128.5 (d), 126.8 (d, 2C), 124.7 (s), 122.9 (d), 109.2 (s, C-syd). MS, *m/z*: 374.89 (M^+, 100%), 376.87 (M^+, 45%).

3-[2-[2-(4-Bromphenyl)ethenyl]phenyl]-4-phenylsydnone (11). Yield 44%, 185 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/0.6. Dichloromethane was used as eluent.

***trans*-11.** White solid, mp 157-158°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (33 674), 231 (19 055), 315 (31 204). IR (diamond) ν_{max}/cm^{-1}: 3062 (CH), 1732 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.85 (d, 1H, *J* = 7.7 Hz), 7.68 (t, 1H, *J* = 7.7 Hz), 7.50 (t, 1H, *J* = 7.7 Hz), 7.47-7.43 (m, 3H), 7.28-7.14 (m, 7H), 6.95 (d, 1H, *J* = 16.2 Hz, H-7/8), 6.65 (d, 1H, *J* = 16.2 Hz, H-7/8). ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 167.0 (s, CO-syd), 135.0 (s), 134.0 (s), 133.6 (d), 132.6 (d), 132.6 (s), 132.2 (d), 129.2 (d), 129.0 (d), 128.9 (d), 128.6 (d), 127.4 (d), 127.0 (d), 126.6 (d), 124.7 (s), 123.7 (s), 120.9 (d), 109.5 (s, C-syd). MS, *m/z*: 418.80 (M^+, 100%), 420.80 (M^+, 100%). Elemental analysis, calcd for $C_{22}H_{15}BrN_2O_2$ (Mr = 419.27): C 63.02, H 3.61, N 6.68%; found C 63.00, H 3.73, N 6.87%.

***cis*-11.** White solid, mp 165-166°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (41 239), 228 (22 763), 280 (14 402). IR (diamond) ν_{max}/cm^{-1}: 3073 (CH), 1732 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.59 (d, 1H, *J* = 7.6 Hz), 7.52 (t, 1H, *J* = 7.6 Hz), 7.46 (t, 1H, *J* = 7.6 Hz), 7.32-7.22 (m, 9H), 6.65 (d, 2H, *J* = 8.5 Hz), 6.51 (d, 1H, *J* = 12.1 Hz), 6.05 (d, 1H, *J* = 12.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*/ppm: 167.1 (s), 134.3 (s), 134.1 (d), 134.0 (s), 133.4 (s), 132.1 (d), 131.7 (d), 131.6 (d), 131.5 (d), 130.4 (d), 129.2 (d), 129.0 (d), 129.0 (d), 127.0 (d), 124.8 (s), 123.2 (d), 109.4 (s, C-syd). MS, *m/z*: 418.80 (M^+, 100%), 420.80 (M^+, 100%).

4-Phenyl-3-[2-[2-(4-methoxyphenyl)ethenyl]phenyl]sydnone (12). Yield 71%, 263 mg. According to ^{1}H NMR spectrum *cis*/*trans* = 1/0.8. Dichloromethane was used as eluent.

***trans*-12.** Greenish solid, mp 122-123°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 203 (34 348), 236 (18 333), 324 (32 496). IR (diamond) ν_{max}/cm^{-1}: 3102 (CH), 1765 (CO-syd). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*/ppm: 7.85 (d, 1H, *J* = 7.9 Hz), 7.65 (t, 1H, *J* = 7.9 Hz), 7.47-7.39 (m, 2H), 7.30-7.19 (m, 7H), 7.00 (d, 1H, *J* = 16.2 Hz, H-7/8), 6.85 (d, 2H, *J* = 8.7 Hz), 6.53 (d, 1H, *J* = 16.2 Hz, H-7/8), 3.82 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*/ppm: 167.0 (s, CO-syd), 160.5 (s), 134.6 (s), 134.3 (d), 132.5 (d), 132.2 (s), 128.9 (d), 128.9 (d), 128.8 (s), 128.6 (d), 128.4 (d), 127.0 (d), 126.9 (d), 126.5 (d), 124.7 (s), 117.7 (d), 114.5 (d), 109.5 (s, C-syd), 55.6 (q, OCH_3). MS, *m/z*: 370.92 (M^+, 100%). Elemental analysis, calcd for $C_{23}H_{18}N_2O_3$ (Mr = 370.4): C 74.58, H 4.90, N 7.56%; found C 74.32, H 4.76, N 7.73%.

***cis*-12.** White solid, mp 124-125°C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 202 (41 307), 234 (22 003), 316 (15 554). IR (diamond) ν_{max}/cm^{-1}: 2958, 2832 (CH), 1730 (CO-syd). ^{1}H NMR (600 MHz, $CDCl_3$) *δ*/ppm: 7.55 (d, 1H, *J* = 7.6 Hz), 7.48 (t, 1H, *J* = 7.6 Hz), 7.45 (t, 1H, *J* = 7.6 Hz), 7.39 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.25-7.22 (m, 3H), 6.79 (d, 2H, *J* = 8.0 Hz), 6.64 (d, 2H, *J* = 8.0 Hz), 6.52 (d, 1H, *J* = 12.0 Hz, H-7/8), 5.9 (d, 1H, *J* = 12.0 Hz, H-7/8), 3.76 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*/ppm: 167.0 (s, CO-syd), 159.3 (s), 134.6 (d), 134.6 (s), 133.2 (s), 131.8 (d), 131.4 (d), 130.1 (d), 128.8 (d), 128.6 (d), 128.6 (d), 127.7 (s), 126.7 (d), 126.6 (d), 124.8 (s), 120.3 (d), 113.6 (d), 109.1 (s, C-syd), 55.2 (q, OCH_3). MS, *m/z*: 370.92 (M^+, 100%).

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