2,5-[C4+C2] Ringtransformation of Pyrylium Salts with α-Sulfinylacetaldehydes

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Article

2,5-[C4+C2] Ringtransformation of Pyrylium Salts with α-Sulfinylacetaldehydes

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Abstract: A rapid synthesis of chiral sulfoxide-functionalized *meta*-terphenyl derivatives by a 2,5-[C4+C2] ring transformation reaction of pyrylium salts with *in-situ* generated enantiomerically pure α-sulfinylacetaldehydes is described. This synthetic method demonstrates for the first time the use of α-sulfinylacetaldehydes in a reaction sequence initiated by nucleophilic attack of pyrylium salts by α-sulfinylcarbanions to generate chiral aromatic systems. The method presented shows broad applicability starting with various methyl sulfoxides and a number of functionalized pyrylium salts, furnishing *meta*-terphenyls with complex substitution patterns from readily accessible starting compounds.

Keywords: α-sulfinylacetaldehyde; sulfoxide; pyrylium salt; ring transformation; *meta*-terphenyl

1. Introduction

Terphenyls are a class of organic compounds consisting of three interconnected phenyl rings. Depending on the arrangements of the aromatic rings, where substitutions can occur in the *ortho*-, *meta*- or *para*-position, different structural isomers and properties are obtained. The *meta*-terphenyl skeleton occurs in several natural compounds [1], such as trifucol [2], macranthol [3], and mulberrofuran R [4]. Due to their extensive conjugation, terphenyls exhibit distinct optical [5-8] and electronic properties [9] that make them valuable for the preparation of various materials, such as organic light-emitting diodes (OLEDs, Figure 1).

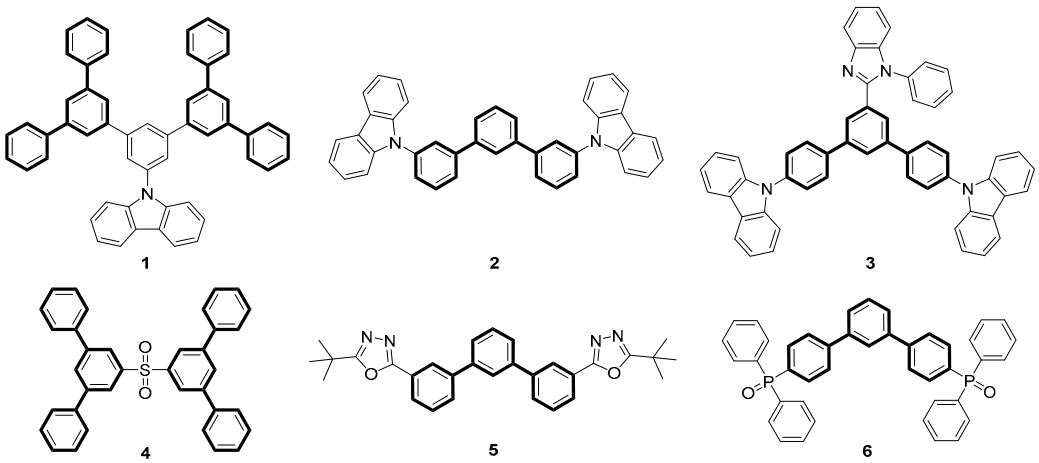

Figure 1. Examples of host **1-4** [10,11] and electron transport materials **5-6** [12] containing *meta*-terphenyl units.

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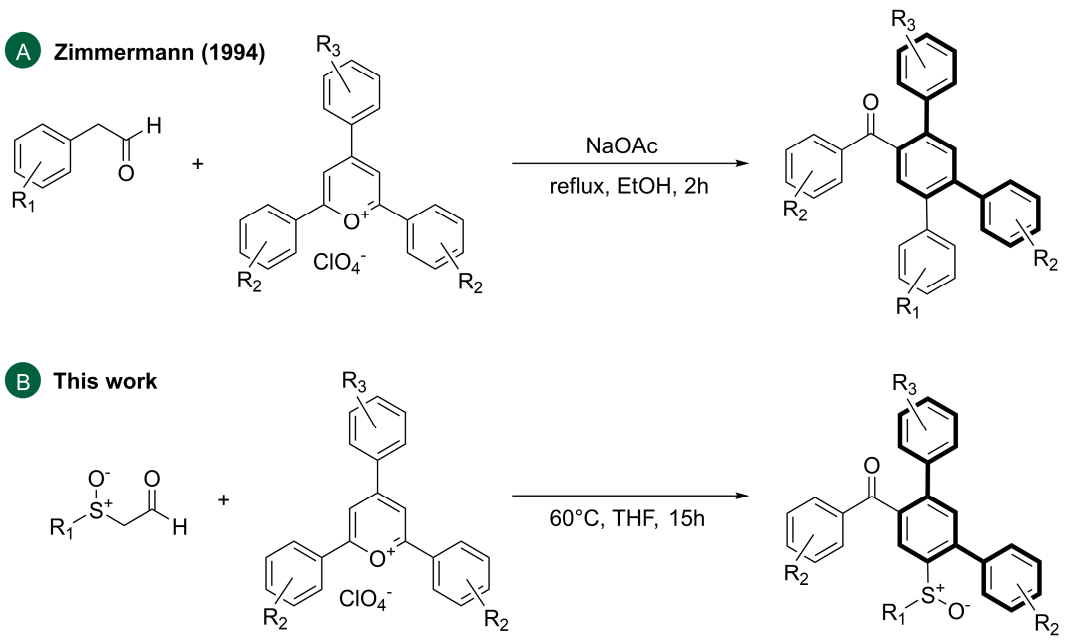
Here, the *meta*-terphenyl skeleton is mainly used in host materials. Especially carbazole substituted *meta*-terphenyl derivatives of type **1-3** show promising optoelectronic properties [11,13-15]. Besides these, SASABE *et al.* [10] synthesized a sulfone-bridged *meta*-terphenyl derivative **4** as a high performance host material for green and blue OLEDs. In addition, *meta*-terphenyl derivatives are used in electron transport materials. Examples include *m*-terphenyloxadiazole **5** synthesized by WU *et al.* [5] or *m*-terphenyldiphenylphosphine oxide **6** prepared by ZHANG *et al.* [12]. In general, two primary approaches to the preparation of terphenyl compounds can be distinguished: (i) coupling of dihalobenzene derivatives with aryl metal nucleophiles [16-19], or (ii) the use of open-chain precursor molecules to form the aromatic rings by concerted or sequential benzannulation reactions [19,20]. In 1994, ZIMMERMANN [21] reported a ring transformation reaction of triarylpyrylium salts with aryl acetaldehydes to give substituted carbocycles. He converted phenylacetaldehyde or 4-fluorophenylacetaldehyde with functionalized 2,4,6-triarylpyrylium salts in an ethanolic solution in the presence of sodium acetate as a weak base into the corresponding 2,4,5-triarylbenzophenones in high yields (Scheme 1).



Scheme 1. A Ring transformations of arylacetaldehydes with triarylpyrylium salts by ZIMMERMANN [21]. **B** Use of α-sulfinylacetaldehydes to perform an analogous ring transformation reaction for the preparation of sulfinyl functionalized *meta*-terphenyls.

Based on these results, we tried to use chiral, enantiomerically pure α-sulfinylacetaldehydes as nucleophiles to perform an analogous ring transformation with a series of 2,4,6-triarylpyrylium salts to obtain optically active sulfinylated *meta*-terphenyls.

2. Results and Discussion

The preparation of enantiomerically pure (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**) is carried out by the method developed by Andersen [22] and Solladie [23,24] starting from *p*-toluene sodium sulfinate. Subsequently, the synthesis of (*R*)-sulfinylacetaldehyde (**8a**) is achieved via deprotonation of (*R*)-**7a** with lithiumdiisopropylamide (LDA), followed by formyl transfer with *N*-formylpiperidine according to Pflieger *et al.* [25]. After isolation of the aldehyde **8a**, the ring transformation is performed with 2,4,6-triphenylpyrylium perchlorate (**9a**) [26] in ethanol in the presence of sodium acetate analogous to Zimmermann [21]. In this first attempt, the desired cyclization product **10a** is obtained in 20% yield. In addition to the desired product, the open chain 1,4-diketone **11** (Scheme 5) is isolated in 28% yield as a side product (Scheme 2).

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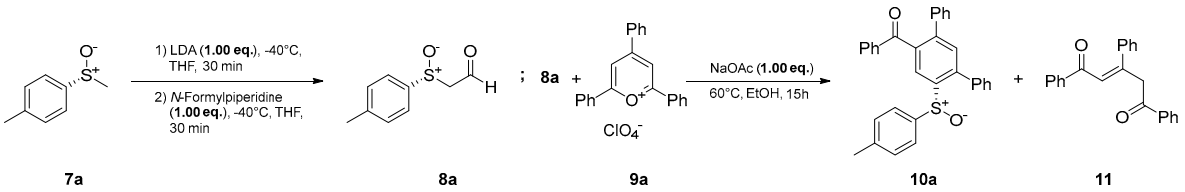
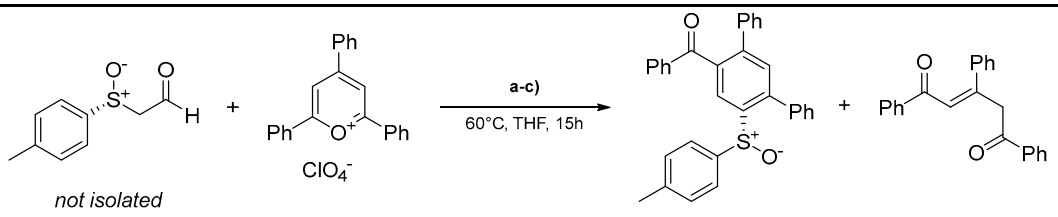


Scheme 2. Initial experiments employing isolated sulfinylacetaldehyde **8a**.

Due to the instability of **8a**, [27] we tried to avoid its isolation. After the reaction of the lithiated sulfoxide (*R*)-**7a** with the formylating reagent the -40°C cold THF solution is added directly to a room temperature suspension of pyrylium salt **9a** in THF and heated to 60°C overnight. This significantly increases the yield of **10a** to 32%. Nevertheless, the by-product **11** is isolated in approximately the same yield as before (Table 1, #1). By adding 4Å molecular sieves, its yield can be reduced from 26% to 10% (Table 1, #2). Surprisingly, increasing the equivalents of (*R*)-sulfinylacetaldehyde lowers the yield of the cyclization product dramatically, whereas the yield of the by-product remains unchanged (Table 1, #3). One reason for the low yield seems to be the high concentration of the sulfinylacetaldehyde, which is very unstable at elevated temperatures and may undergo self-condensation. By not isolating **8a**, it is no longer necessary to use sodium acetate as a base due to the formation of lithiumpiperidide in the course of the reaction. This leads to approximately the same product yield as entry 2, but the yield of the by-product decreases significantly (Table 1, #4). Carrying out the reaction with a 1:1.8 excess of the pyrylium salt increases the yield of **10a** even further to 49% (Table 1, #5).

Table 1. Optimization of reaction conditions.[a]



Entry	eq. 8a	eq. 9a	Base	Yield 10a / %	Yield 11 / %
1	1.0	1.0	NaOAc	32	26
2[b]	1.0	1.0	NaOAc	35	16
3	2.0	1.0	NaOAc	9	27
4	1.0	1.0	-	38	<10
5	**1.0**	**1.8**	**-**	**49**	**<10**

[a]a) 1.0 eq. LDA, -40°C, 30 min. b) 1.0 eq. *N*-formylpiperidine, -40°C, 40 min. c) 1.0 – 1.8 eq. **9a**, 0.0 – 1.0 eq. NaOAc (suspension in THF), 15h, 60°C [b] 4Å molecular sieves added.

The structure of the standard substrate **10a** was confirmed by single crystal X-ray analysis (Figure 2, CCDC deposition number 2302385).

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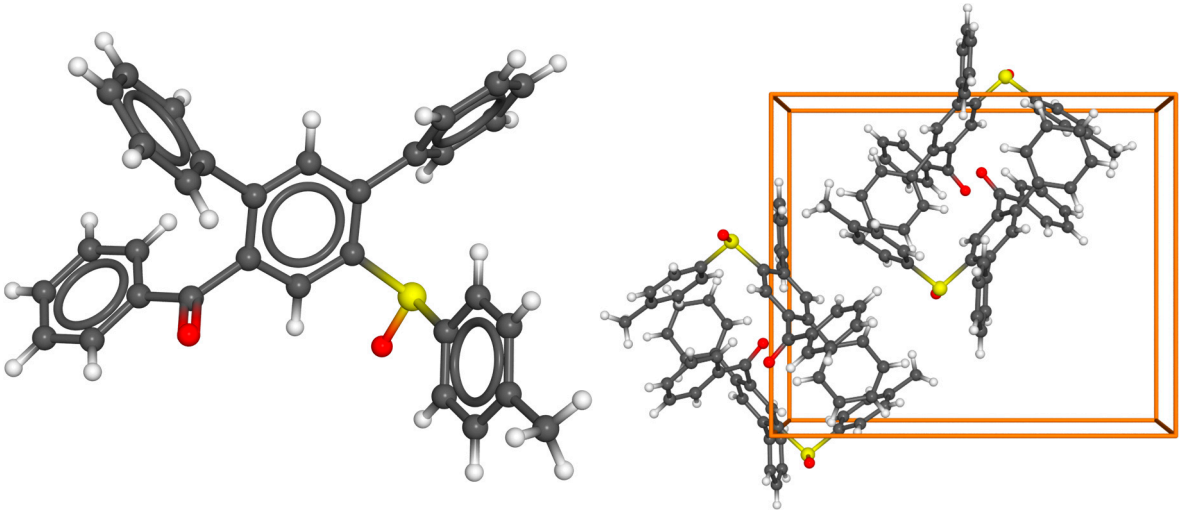
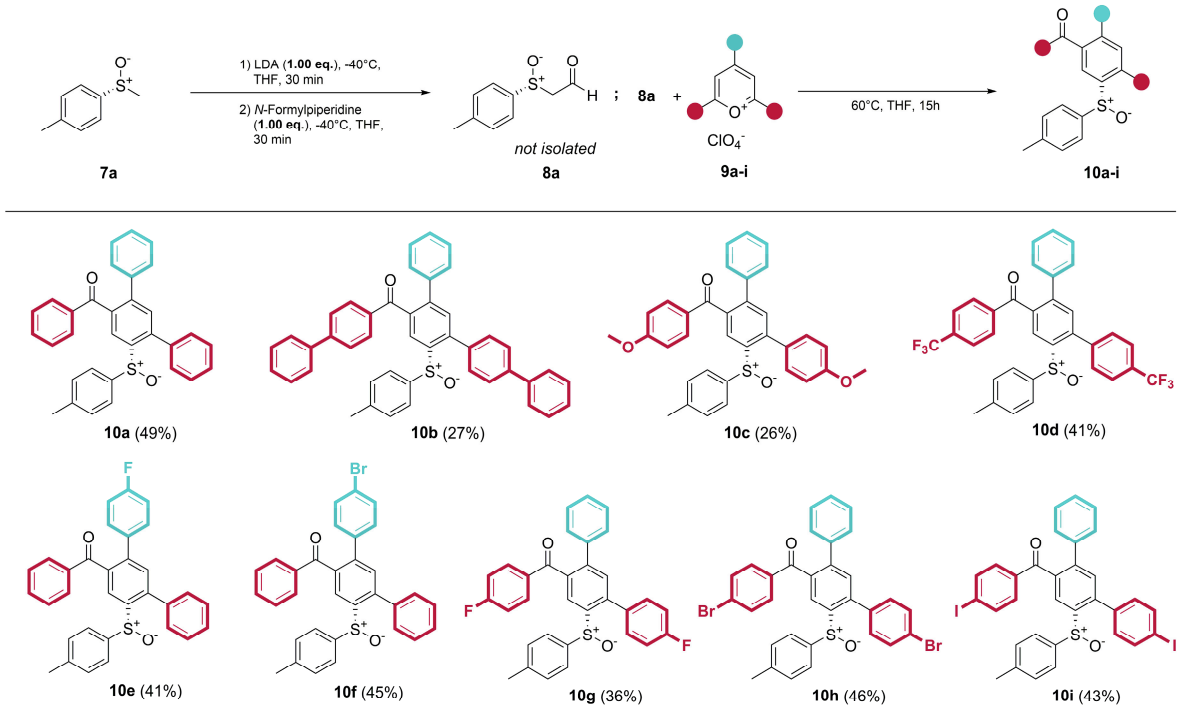


(**a**) (**b**)

Figure 2. (**a**) Molecular structure of **10a.** (**b**) Unit cell (Z = 4, space group *P* $2_12_12_1$) with anisotropic thermal ellipsoids (50% probability level). Hydrogen atoms were placed geometrically**.**

Employing the optimized reaction conditions, substrate variations were first investigated using a variety of functionalized pyrylium salts **9a-i** (Scheme 3). With the exception of **10b** and **10c** all products are obtained in 40 to 50% yield. The pyrylium salts reacting to **10b** and **10c** with electron donating substituents (**9b** -Ph, **9c** -OMe) are expected to show a decreased reactivity due to the reduced electrophilicity at the 2-position of the pyrylium salt. Indeed, both donor substituted products have been obtained with reduced yields.



Scheme 3. Substrate scope and isolated yields of ring transformation products **10a-i** with different pyrylium salts **9a-i.**

After varying the pyrylium salts, different racemic methyl sulfoxides **7b-h** were tested (Scheme 4). Here, almost all sulfoxides show comparable reactivity and the resulting terphenyls are obtained in similar yields as with the standard substrate (*R*)-**7a**. The method is well suitable for aromatic

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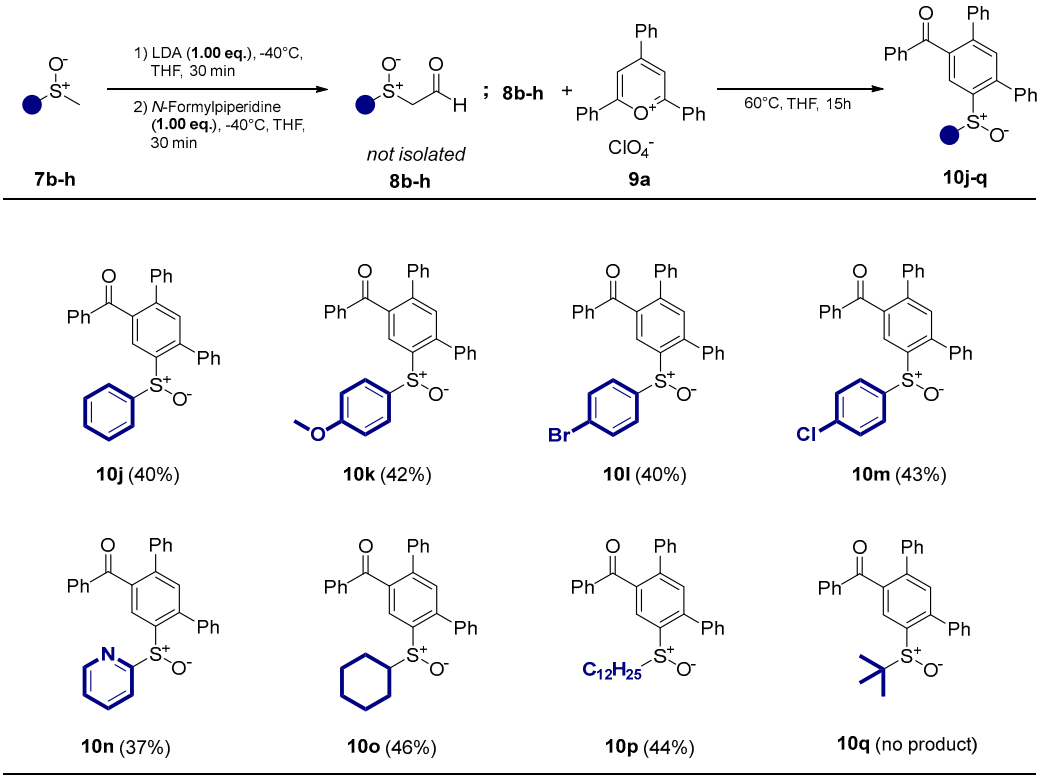
sulfoxides with electron donating substituents (**10k**) as well as with halogens (**10l-m**). Moreover, heteroaromatic sulfoxides (**10n**) and aliphatic sulfoxides with additional acidic protons in the α'-position show comparable reactivity to (*R*)-**7a** and are obtained with yields of 40% (**10o-p**). No product can be isolated with sterically demanding *tert*-butyl methyl sulfoxide (**10q**).



Scheme 4. Substrate scope and isolated yields of ring transformation products **10j-q** (racemic) with different methyl sulfoxides **7b-h**.

From the results obtained, we assume that the reaction mechanism described by Zimmermann [21] for phenylacetaldehyde may be transferred to our system (Scheme 5). Here, the carbanion of the α-sulfinylacetaldehydes **8** attacks the preferred 2-position [28] of the pyrylium salts **9**. The resulting *2H*-pyran **12** then reacts *via* electrocyclic ring opening to the ketoaldehyde **13** [29]. The intermediate **14** obtained by proton shift reacts with the acidic methylene group in the course of an aldol addition to give intermediate **15**. Condensation accompanied by rearomatization yields the ring transformation products **10**. In the presence of water, the pyrylium salts hydrolyze to the unstable cyclic hemiacetal **16**, which reacts by electrocyclic ring opening to form the open-chain 1,4-diketone **11** [30].

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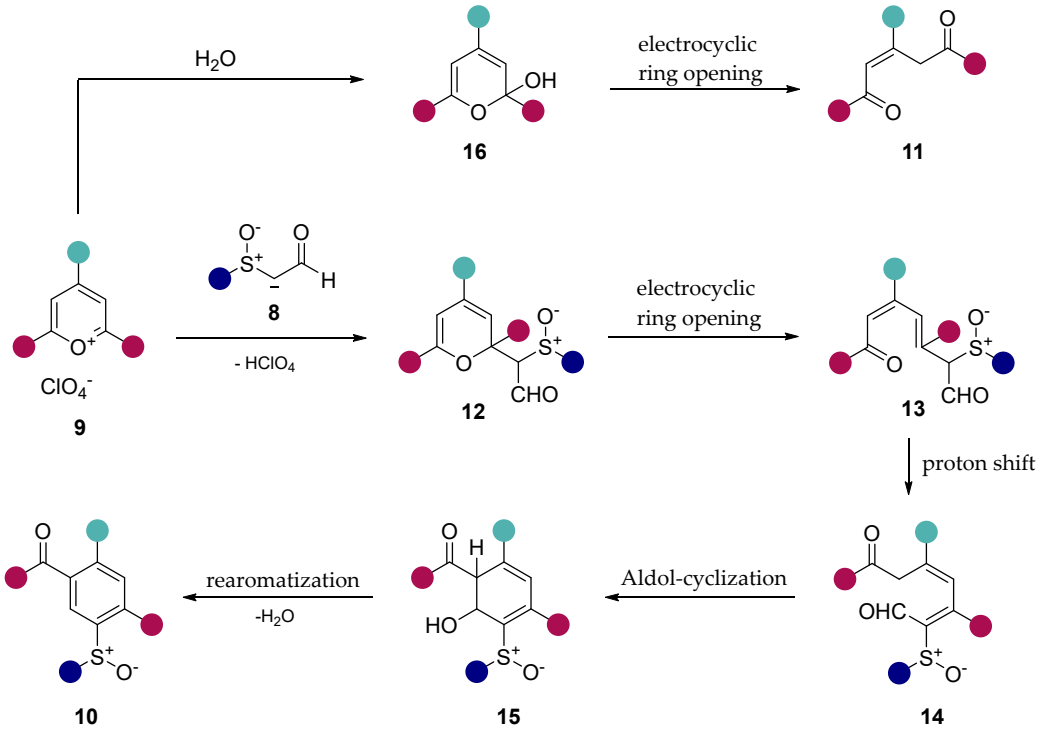

Scheme 5. Assumed reaction mechanism of the ring transformation reaction of α-sulfinylacetaldehydes with triarylpyrylium salts based on the work of ZIMMERMANN [21].

3. Conclusion

In summary, we have developed an efficient synthesis for the preparation of highly substituted *meta*-terphenyls bearing both a sulfoxide moiety and an acyl group at the central ring starting from readily available methyl sulfoxides **7a-h** and triarylpyrylium perchlorates **9a-i**. Starting from chiral, enantiomerically pure (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**), the optically active derivatives **10a-i** have been prepared. The method is broadly applicable to a variety of aromatic and alkyl methyl sulfoxides and differently functionalized pyrylium salts. All new compounds have been fully characterized by spectroscopic methods. A crystal structural analysis of **10a** rounds off the structural evidence.

4. Materials and Methods

4.1. General Methods

Melting points were determined on Stuart Smp10 melting point apparatus (Vernon Hills, IL, USA) and are uncorrected. Thin-layer chromatography (TLC) was performed using E. Merck silica gel SilG/UV254 by Macherey Nagel & Co., Düren (thickness of layer 0.2 mm) and visualized by UV fluorescence quenching. ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz at 300K. ^{13}C NMR spectra were recorded on the same instrument at 125 MHz. ^{19}F NMR spectra were recorded at 471 MHz. All chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) as internal standard (δ = 0.00 ppm). The spectra were referenced against the residual solvent signal as reported in the literature [31]. The fine structure of proton signals was specified as s (singlet), d (doublet), t (triplet). Quaternary carbons are designated with subscript q. IR spectra were recorded on a FTIR spectrometer Paragon 1000 (Perkin Elmer LAS GmbH). The specific optical rotations were determined on a Anton Paar MCP300 Polarimeter in 1 dm cuvettes. ESI-MS measurements were recorded on a Bruker Impact II. Elemental analyses were performed on Vario El from Elementar. The pyrylium salts **9a-i** were synthesized using established methods [26] by condensation of the corresponding benzaldehydes and acetophenones with phosphorus oxychloride and perchloric acid. The racemic methyl sulfoxides **7b-h** were synthesized from the corresponding thiols by methylation followed by oxidation with *m*CPBA following literature procedures [32]. All

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other reagents were obtained from commercial sources and used without further purification unless otherwise specified.

4.2. General procedure for the synthesis of the ring transformation products

The corresponding methyl sulfoxide **7a-h** (1.00 eq.) is placed in an oven-dried Schlenk tube under argon and dissolved in dry THF (1.00 ml/mmol). The solution is cooled to -40°C and lithium diisopropylamide (1.00 eq.; 2M solution in THF, ethylbenzene, *n*-heptane) is added and stirred for 30 min. *N*-formylpiperidine (1.00 eq.) is then added slowly and the mixture is stirred for an additional 40 minutes at -40°C. In a second Schlenk tube, the 2,4,6-triarylpyrylium salt **9a-i** is placed under argon and suspended with dry THF (2.00 ml/mmol). To this is quickly added the *in situ* synthesized α-sulfinylacetaldehyde and the mixture is heated to 60°C. After 15 hours, the mixture is cooled to room temperature and dichloromethane (10 ml/mmol) is added and transferred to a separatory funnel. The mixture is extracted with water and the aqueous phase is subsequently re-extracted twice with dichloromethane. The organic phases are combined and dried over magnesium sulfate. After removal of the solvent, the crude product is purified by column chromatography (for aromatic methyl sulfoxides 5% ethyl acetate to 20% ethyl acetate in *n*-pentane; for alkyl methyl sulfoxides 25% Et_2O in *n*-pentane).

(R)-Phenyl(6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)methanone (**10a**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield: 49% as an off-white solid. **mp** 186°C. R_f = 0.22 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1669, 1041, 697. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.30 (s, 1H), 7.77 – 7.71 (m, 2H), 7.52 – 7.40 (m, 4H), 7.39 – 7.26 (m, 7H), 7.25 – 7.16 (m, 3H), 7.07 – 7.02 (m, 2H), 7.00 – 6.94 (m, 2H), 2.30 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.2$_q$, 143.6$_q$, 143.0$_q$, 142.2$_q$, 141.7$_q$, 141.4$_q$, 138.9$_q$ (2C), 137.4$_q$, 137.0$_q$, 133.4, 132.4, 130.2, 129.7, 129.6, 129.0, 128.7, 128.7, 128.5, 128.5, 128.1, 125.7, 124.6, 21.5 ppm. **MS** (ESI) (*m*/*z*): 473.16 $[M+H]^+$, 495.14 $[M+Na]^+$, 511.11 $[M+K]^+$, 945.31 $[2M+H]^+$, 967.29 $[2M+Na]^+$, 983.26 $[2M+K]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{24}O_2S$ $[M+H]^+$ 473.15698; Found 473.15715. **Anal. Calc**. for $C_{32}H_{24}O_2S$: C 81.33; H 5.12. Found C 81.32; H 5.34. $[\alpha]_D^{20}$= +28.27° (c 0.53; acetone).

(R)-[1,1′-biphenyl]-4-yl(4′-(p-tolylsulfinyl)-[1,1′:3′,1′′:4′′,1′′′-quaterphenyl]-6′-yl)methanone (**10b**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 27% as an off-white solid. **mp** 116°C. R_f = 0.24 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1598, 754, 695. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.34 (s, 1H), 7.85 (d, *J* = 8.5 *Hz*, 2H), 7.73 – 7.64 (m, 4H), 7.63 – 7.57 (m, 4H), 7.55 – 7.50 (m, 2H), 7.50 – 7.44 (m, 3H), 7.42 (d, *J* = 8.1 *Hz*, 4H), 7.34 (d, *J* = 6.6 *Hz*, 2H), 7.28 – 7.20 (m, 3H), 7.06 (s, 4H), 2.32 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 196.7$_q$, 146.1$_q$, 143.7$_q$, 143.0$_q$, 141.9$_q$, 141.8$_q$, 141.6$_q$, 141.4$_q$, 140.3$_q$, 139.9$_q$, 139.0$_q$, 138.9$_q$, 136.4$_q$, 135.8$_q$, 132.5, 130.8, 130.1, 129.8, 129.1, 129.0, 129.0, 128.6, 128.4, 128.1, 127.9, 127.4, 127.4, 127.2, 127.2, 125.7, 124.7, 21.5 ppm. **MS** (ESI) (*m*/*z*): 625.21 $[M+H]^+$, 647.20 $[M+Na]^+$, 1249.43 $[2M+H]^+$, 1271.41 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{44}H_{32}O_2S$ $[M+H]^+$ 625.21958; Found 625.21987. **Anal. Calc**. for $C_{44}H_{32}O_2S$: C 84.58; H 5.16. Found C 84.28; H 5.27. $[\alpha]_D^{20}$= -30.94° (c 0.48; acetone).

(R)-(4-methoxy-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(4-methoxyphenyl)methanone (**10c**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 26% as a yellow solid. **mp** 188°C. R_f = 0.06 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1594, 1248, 1169, 1026. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.24 (s, 1H), 7.76 (d, *J* = 9.0 *Hz*, 2H), 7.37 (s, 1H), 7.32 (m, 2H), 7.30 – 7.21 (m, 5H), 7.09 (d, *J* = 8.3 *Hz*, 2H), 7.05 (d, *J* = 8.3 *Hz*, 2H), 6.99 (d, *J* = 8.8 *Hz*, 2H), 6.87 (d, *J* = 9.0 *Hz*, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 2.33 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 195.8$_q$, 163.8$_q$, 160.0$_q$, 143.4$_q$, 142.8$_q$, 141.7$_q$, 141.6$_q$, 141.5$_q$, 139.1$_q$, 139.0$_q$, 132.6, 132.5, 130.9, 130.1$_q$, 129.9$_q$, 129.7, 128.9, 128.5, 128.0, 125.6, 124.5, 114.1, 113.8, 55.6, 55.5, 21.5 ppm. **MS** (ESI) (*m*/*z*): 533.17 $[M+H]^+$, 555.16 $[M+Na]^+$, 1065.35 $[2M+H]^+$, 1087.33 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{34}H_{28}O_4S$ $[M+H]^+$ 533.17811; Found 533.17854. **Anal. Calc**. for $C_{34}H_{28}O_4S$: C 76.67; H 5.30. Found C 76.33; H 5.12. $[\alpha]_D^{20}$= +15.19° (c 0.25; acetone).

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(R)-(6′-(p-tolylsulfinyl)-4-(trifluoromethyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(4-(trifluoromethyl)phenyl)methanone (**10d**) Prepared from 300 mg (1.95 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 41% as an off-white solid. **mp** 91°C. R_f = 0.47 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1672, 1322, 1064. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.34 (s, 1H), 7.78 (d, *J* = 8.1 *Hz*, 2H), 7.69 (d, *J* = 8.0 *Hz*, 2H), 7.58 (d, *J* = 8.1 *Hz*, 2H), 7.42 (d, *J* = 8.0 *Hz*, 2H), 7.38 (s, 1H), 7.23 (m, 5H), 7.07 (d, *J* = 8.0 *Hz*, 2H), 6.99 (d, *J* = 8.0 *Hz*, 2H), 2.32 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 196.0$_q$, 143.9$_q$, 143.4$_q$, 142.3$_q$, 141.2$_q$, 140.9$_q$, 140.7$_q$, 139.6$_q$, 138.7$_q$, 138.3$_q$, 134.5$_q$ (d, $^2J_{CF}$ = 33 *Hz*), 132.3, 131.0$_q$ (d, $^2J_{CF}$ = 33 *Hz*), 130.2, 130.0 (2C), 129.0, 128.8, 128.5 , 125.9, 125.7 (q, $^3J_{CF}$ = 3.9 *Hz*), 125.5 (q, $^3J_{CF}$ = 3.9 *Hz*), 125.3, 124.0$_q$ ($^1J_{CF}$ = 271 *Hz*), 123.5$_q$ ($^1J_{CF}$ = 271 *Hz*), 21.5 ppm. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.6, -63.2 ppm. **MS** (ESI) (*m*/*z*): 609.13 $[M+H]^+$, 631.11 $[M+Na]^+$, 647.09 $[M+K]^+$, 1217.26 $[2M+H]^+$, 1239.24 $[2M+Na]^+$, 1255.21 $[2M+K]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{34}H_{22}F_6O_2S$ $[M+H]^+$ 609.13175; Found 609.13177. **Anal. Calc.** for $C_{34}H_{22}F_6O_2S$: C 67.10; H 3.64. Found C 67.17; H 3.66. $[\alpha]_D^{20}$ = +8.70° (c 0.53; Aceton).

(R)-(4′′-fluoro-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10e**) Prepared from 600 mg (3.98 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 41% as an off-white solid. **mp** 164°C. R_f = 0.20 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1667, 1039. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.29 (s, 1H), 7.77 – 7.69 (m, 2H), 7.56 – 7.48 (m, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.33 (s, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.04 (d, *J* = 8.0 *Hz*, 2H), 7.00 – 6.94 (m, 2H), 6.94 – 6.88 (m, 2H), 2.30 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.1$_q$, 162.6$_q$ (d, $^1J_{CF}$ = 248.0 *Hz*), 143.1$_q$, 142.5$_q$, 142.3$_q$, 141.8$_q$, 141.3$_q$, 138.8$_q$, 137.3$_q$, 136.9$_q$, 135.0$_q$ (d, $^4J_{CF}$ = 3.3 *Hz*), 133.6, 132.4, 130.7 ($^3J_{CF}$ = 8.2 *Hz*), 130.2, 129.8, 129.6, 128.8, 128.6, 128.5, 126.9, 125.7, 124.6, 115.6 (d, $^2J_{CF}$ = 21.6 Hz), 21.5 ppm. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -113.8 ppm. **MS** (ESI) (*m*/*z*): 491.15 $[M+H]^+$, 513.13 $[M+Na]^+$, 529.10 $[M+K]^+$, 981.29 $[2M+H]^+$, 1003.28 $[2M+Na]^+$, 1019.24 $[2M+K]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{23}FO_2S$ $[M+H]^+$ 491.14756; Found 491.14762. **Anal. Calc.** for $C_{32}H_{23}FO_2S$: C 78.34; H 4.73. Found C 78.46; H 4.96. $[\alpha]_D^{20}$ = +29.52° (c 0.49; acetone).

(R)-(4′′-bromo-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10f**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield: 46% as a white solid. **mp** 167°C. R_f = 0.21 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1660, 1046. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.29 (s, 1H), 7.77 – 7.72 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.34 (m, 7H), 7.32 (s, 1H), 7.31 – 7.27 (m, 2H), 7.19 – 7.11 (m, 2H), 7.04 (d, *J* = 8.0 *Hz*, 2H), 6.99 – 6.89 (m, 2H), 2.30 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 196.9$_q$, 143.4$_q$, 142.4$_q$, 142.3$_q$, 141.8$_q$, 141.2$_q$, 138.7$_q$, 137.9$_q$, 137.2$_q$, 136.9$_q$, 133.7, 132.3, 131.7, 130.5, 130.2, 129.8, 129.6, 128.8, 128.8, 128.6, 125.6, 124.6, 122.6$_q$, 21.5 ppm. **MS** (ESI) (*m*/*z*): 551.07 $[M+H]^+$, 573.05 $[M+Na]^+$, 1101.13 $[2M+H]^+$, 1123.11 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{23}BrO_2S$ $[M+H]^+$ 551.06749; Found 551.06752. **Anal. Calc**. for $C_{32}H_{23}BrO_2S$: C 69.69; H 4.20. Found C 69.21; H 3.99. $[\alpha]_D^{20}$ = +25.77° (c 0.50; acetone).

(R)-(4-fluoro-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(4-fluorophenyl)methanone (**10g**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 36% as an off-white solid. **mp** 190°C. R_f = 0.26 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1663, 1594, 1226. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.26 (s, 1H), 7.77 – 7.64 (m, 2H), 7.29 – 7.17 (m, 7H), 7.10 (t, *J* = 8.6 *Hz*, 2H), 7.06 (d, *J* = 8.0 *Hz*, 2H), 6.99 (t, *J* = 8.6 *Hz*, 4H), 2.30 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 195.6$_q$, 165.9$_q$ (d, $^1J_{CF}$ = 256.1 *Hz*), 163.12$_q$ (d, $^1J_{CF}$ = 248.9 *Hz*), 143.59$_q$, 143.20$_q$, 142.11$_q$, 141.33$_q$, 141.11$_q$, 138.83$_q$, 138.69$_q$, 133.5$_q$ (d, $^4J_{CF}$ = 5.46 *Hz*), 133.4$_q$ (d, $^4J_{CF}$ = 5.95 *Hz*), 132.7 (d, $^3J_{CF}$ = 9.5 *Hz*), 132.52, 131.4 (d, $^3J_{CF}$ = 8.1 *Hz*), 129.92, 128.96, 128.68, 128.33, 125.82, 124.77, 115.8 (d, $^2J_{CF}$ = 22.15 *Hz*), 115.7 (d, $^2J_{CF}$ = 21.91 *Hz*), 21.56 ppm. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -104.2, -112.5 ppm. **MS** (ESI) (*m*/*z*): 509.14 $[M+H]^+$, 531.12 $[M+Na]^+$, 1017.27 $[2M+H]^+$, 1039.25 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{22}F_2O_2S$ $[M+H]^+$ 509.13813; Found 509.13831. **Anal. Calc**. for $C_{32}H_{22}F_2O_2S$: C 75.57; H 4.36. Found C 75.66; H 4.38. $[\alpha]_D^{20}$ = +28.14° (c 0.50; acetone).

(R)-(4-bromo-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(4-bromophenyl)methanone (**10h**) Prepared from 600 mg (3.89 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 46% as an off-white solid. **mp**

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235°C. R_f = 0.41 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1667, 1039. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.26 (s, 1H), 7.60 – 7.51 (m, 4H), 7.47 (d, *J* = 8.5 *Hz*, 2H), 7.33 (s, 1H), 7.23 (s, 5H), 7.18 (d, *J* = 8.5 *Hz*, 2H), 7.10 (d, *J* = 8.3 *Hz*, 2H), 7.03 (d, *J* = 8.3 *Hz*, 2H), 2.33 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): 196.1$_q$, 143.7$_q$, 143.1$_q$, 142.2$_q$, 141.2$_q$, 141.0$_q$, 138.7$_q$, 138.5$_q$, 136.2$_q$, 135.7$_q$, 132.3, 131.9, 131.8, 131.5, 131.2, 129.9, 128.9, 128.8$_q$, 128.7, 128.4, 125.7, 124.9, 123.2$_q$, 21.5 ppm. **MS** (ESI) (*m*/*z*): 628.98 $[M+H]^+$, 650.96 $[M+Na]^+$, 666.93 $[M+K]^+$, 1256.95 $[2M+H]^+$, 1278.93 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{22}Br_2O_2S$ $[M+H]^+$ 628.97800; Found 628.97792. **Anal. Calc**. for $C_{32}H_{22}Br_2O_2S$: C 60.97; H 3.52. Found C 60.89; H 3.66. $[\alpha]_D^{20}$= -19.41° (c 0.50; acetone).

(R)-(4-iodo-6′-(p-tolylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(4-iodophenyl)methanone (**10i**) Prepared from 300 mg (1.95 mmol) (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-**7a**). Yield 43% as an off-white solid. **mp** 234°C. R_f = 0.36 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1659, 1038, 956. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.25 (s, 1H), 7.81 – 7.75 (m, 2H), 7.73 – 7.66 (m, 2H), 7.43 – 7.36 (m, 2H), 7.33 (s, 1H), 7.23 (m, 5H), 7.09 (d, *J* = 8.0 *Hz*, 2H), 7.07 – 7.00 (m, 4H), 2.33 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 196.2$_q$, 143.6$_q$, 142.9$_q$, 142.0$_q$, 141.2$_q$, 140.9$_q$, 138.5$_q$, 138.4$_q$, 137.8, 137.7, 136.7, 136.1, 132.1, 131.2, 131.1, 129.8, 128.8, 128.6, 128.3, 125.6, 124.8, 101.7$_q$, 94.7$_q$, 21.4 ppm. **MS** (ESI) (*m*/*z*): 724.95 $[M+H]^+$, 746.93 $[M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{22}I_2O_2S$ $[M+H]^+$ 724.95027; Found 724.95074. **Anal. Calc**. for $C_{32}H_{22}I_2O_2S$: C 53.06; H 3.06. Found C 53.04 ; H 2.99. $[\alpha]_D^{20}$= -32.45° (c 0.26; acetone).

Phenyl(6′-(phenylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)methanone (**10j**) Prepared from 309 mg (2.20 mmol) methylphenylsulfoxide. Yield 39% as an off-white solid. **mp** 140°C. R_f = 0.19 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1663, 1046. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.31 (s, 1H), 7.79 – 7.72 (m, 2H), 7.56 – 7.18 (m, 17H), 7.17 – 7.04 (m, 2H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.2$_q$, 144.5$_q$, 143.8$_q$, 142.7$_q$, 142.3$_q$, 139.0$_q$, 138.9$_q$, 137.4$_q$, 137.0$_q$, 133.4, 132.5, 131.2, 130.2, 129.6, 129.1, 129.0, 128.8, 128.8, 128.6, 128.5, 128.1, 125.6, 124.7 ppm. **MS** (ESI) (*m*/*z*): 459.14 $[M+H]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{31}H_{22}O_2S$ $[M+H]^+$ 459.1413; Found 459.1414.

(6′-((4-methoxyphenyl)sulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10k**) prepared from 355 mg (2.09 mmol) 4-methoxyphenylmethylsulfoxide. Yield 42% as an off-white solid. **mp** 94°C. R_f = 0.10 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1664, 1250, 1045, 698. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.35 (s, 1H), 7.77 (d, *J* = 8.3 *Hz*, 2H), 7.57 – 7.48 (m, 1H), 7.45 – 7.37 (m, 6H), 7.33 – 7.27 (m, 4H), 7.27 – 7.16 (m, 3H), 7.02 (d, *J* = 8.8 *Hz*, 2H), 6.75 (d, *J* = 8.9 *Hz*, 2H), 3.79 (s, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.2$_q$, 161.8$_q$, 143.4$_q$, 142.9$_q$, 142.0$_q$, 138.8$_q$, 138.7$_q$, 137.3$_q$, 136.9$_q$, 135.5$_q$, 133.3, 132.3, 130.1, 129.4, 128.9, 128.6, 128.5, 128.4, 128.4, 127.9, 127.7, 124.3, 114.4, 55.4 ppm. **MS** (ESI) (*m*/*z*): 489.15 $[M+H]^+$, 511.13 $[M+Na]^+$, 527.11 $[M+K]^+$, 977.30 $[2M+H]^+$, 999.28 $[2M+Na]^+$, 1015.25 $[2M+K]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{32}H_{24}O_3S$ $[M+H]^+$ 489.15189; Found 489.15195. **Anal. Calc**. for $C_{32}H_{24}O_3S$: C 78.66; H 4.95. Found C 78.53; H 5.01.

(6′-((4-bromophenyl)sulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10l**) prepared from 438 mg (2.00 mmol) 4-bromophenylmethylsulfoxid. Yield 43% as a white solid. **mp** 92°C. R_f = 0.34 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1664, 1048, 697. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.27 (s, 1H), 7.76 – 7.68 (m, 2H), 7.53 – 7.43 (m, 4H), 7.39 (s, 1H), 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 5H), 7.03 – 6.95 (m, 2H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.1$_q$, 144.0$_q$, 143.0$_q$, 142.4$_q$, 142.1$_q$, 139.1$_q$, 138.7$_q$, 137.5$_q$, 137.2$_q$, 136.9$_q$, 133.5, 132.6, 130.1, 129.6, 129.3, 129.0, 128.9, 128.6, 128.5, 128.2, 126.9, 124.5 ppm. **MS** (ESI) (*m*/*z*): 537.05 $[M+H]^+$, 559.03 $[M+Na]^+$, 575.00 $[M+K]^+$, 1073.09 $[2M+H]^+$, 1095.07 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{31}H_{21}BrO_2S$ $[M+H]^+$ 537.05184; Found 537.05130. **Anal. Calc**. for $C_{31}H_{21}BrO_2S$: C 75.52; H 4.29. Found C 75.48; H 4.32.

(6′-((4-chlorophenyl)sulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10m**) prepared from 350 mg (2.00 mmol) 4-chlorophenylmethylsulfoxid. Yield 40 % as a white solid. **mp** 122°C. R_f = 0.34 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1664, 1049, 697. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.26 (s, 1H), 7.72 (d, *J* = 8.0 *Hz*, 2H), 7.53 – 7.43 (m, 4H), 7.41 – 7.30 (m, 7H), 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 6.92 (d, *J* = 8.0 *Hz*, 2H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.1$_q$, 144.0$_q$, 143.7$_q$, 142.3$_q$,

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142.1$_q$, 139.1$_q$, 138.7$_q$, 137.2$_q$, 136.9$_q$, 133.5, 132.6, 132.3, 130.1, 129.6, 129.0, 128.9, 128.6, 128.5, 128.2, 127.0, 125.8$_q$, 124.5 ppm. **MS** (ESI) (*m*/*z*): 493.10 $[M+H]^+$, 515.08 [M+Na]+, 531.05 $[M+K]^+$, 985.19 $[2M+H]^+$, 1007.17 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{31}H_{21}ClO_2S$ $[M+H]^+$ 493.10236; Found 493.10232. **Anal. Calc**. for $C_{31}H_{21}ClO_2S$: C 69.28; H 3.94. Found C 69.42; H 3.80.

Phenyl(6′-(pyridin-2-ylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)methanone (**10n**) prepared from 300 mg (2.12 mmol) 2-pyridylmethylsulfoxid. Yield 36% as a white solid. **mp** 110°C. R_f = 0.04 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 1659, 1048, 689. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.44 (m, 1H), 7.80 (s, 1H), 7.78 – 7.69 (m, 2H), 7.65 – 7.58 (m, 2H), 7.56 – 7.52 (m, 2H), 7.42 (s, 1H), 7.41 – 7.32 (m, 4H), 7.24 – 7.14 (m, 5H), 7.14 – 7.06 (m, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 196.9$_q$, 165.5$_q$, 150.0, 144.4$_q$, 144.2$_q$, 142.1$_q$, 138.9$_q$ (2C), 138.1, 137.6$_q$, 136.9$_q$, 133.3, 132.5, 130.5, 130.1, 129.0, 128.7, 128.5, 128.4, 128.4, 128.2, 127.3, 124.7, 120.2 ppm. **MS** (ESI) (*m*/*z*): 460.13 $[M+H]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{30}H_{21}NO_2S$ $[M+H]^+$ 460.1366; Found 460.1368. **Anal. Calc**. for $C_{30}H_{21}NO_2S$: C 78.41 ; H 4.61; N 3.05. Found C 78.35 ; H 4.67; N 3.07.

(6′-(cyclohexylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10o**) prepared from 304 mg (2.08 mmol) cyclohexylmethylsulfoxid. Yield 46% as a white solid. **mp** 160°C. R_f = 0.22 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 2926, 1664, 1046, 697. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.11 (s, 1H), 7.77 – 7.69 (m, 2H), 7.52 – 7.42 (m, 7H), 7.38 – 7.32 (m, 4H), 7.28 – 7.20 (m, 3H), 2.27 (m, 1H), 1.84 – 1.73 (m, 1H), 1.70 – 1.61 (m, 1H), 1.60 – 1.50 (m, 2H), 1.48 – 1.16 (m, 3H), 1.16 – 0.99 (m, 3H), 0.92 – 0.81 (m, 1H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.3$_q$, 143.6$_q$, 142.1$_q$, 139.3$_q$, 138.9$_q$, 138.6$_q$, 137.6$_q$, 137.0$_q$, 133.4, 132.3, 130.1, 129.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.1, 126.0, 60.7, 27.3, 25.8, 25.3, 25.3, 22.8 ppm. **MS** (ESI) (*m*/*z*): 465.18 $[M+H]^+$, 487.17 $[M+Na]^+$, 503.14 $[M+K]^+$, 951.35 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{31}H_{28}O_2S$ 465.18828; Found 465.18810. **Anal. Calc**. for $C_{31}H_{28}O_2S$: C 80.14; H 6.07. Found C 80.22; H 6.02.

(6′-(dodecylsulfinyl)-[1,1′:3′,1′′-terphenyl]-4′-yl)(phenyl)methanone (**10p**) prepared from 465 mg (2.00 mmol) 1-dodecylmethylsulfoxid. Yield 44% as a yellow oil. R_f = 0.40 (20% ethyl acetate in *n*-pentane). **IR** (ATR) (cm^{-1}): 2922, 1666, 1047, 697. **^{1}H NMR** (500 MHz, Chloroform-*d*): δ 8.23 (s, 1H), 7.78 (d, *J* = 8.5 *Hz*, 2H), 7.58 – 7.45 (m, 6H), 7.45 – 7.33 (m, 4H), 7.28 (dd, *J* = 14.7, 7.7 *Hz*, 3H), 2.59 (dd, *J* = 14.0, 8.0 *Hz*, 1H), 2.56 – 2.39 (m, 1H), 1.72 – 1.58 (m, 1H), 1.54 – 1.41 (m, 1H), 1.39 – 1.07 (m, 18H), 0.93 (t, *J* = 7.0 *Hz*, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-*d*): δ 197.3$_q$, 143.6$_q$, 141.3$_q$, 141.3$_q$, 139.0$_q$, 138.9$_q$, 137.3$_q$, 137.0$_q$, 133.4, 132.3, 130.1, 129.1, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.1, 125.0, 54.9, 32.0, 29.7 (2C), 29.6, 29.4, 29.4, 29.0, 28.3, 22.8, 22.2, 14.2 ppm. **MS** (ESI) (*m*/*z*): 551.30 $[M+H]^+$, 573.28 $[M+Na]^+$, 1001.59 $[2M+H]^+$, 1123.57 $[2M+Na]^+$. **HRMS** (ESI) (*m*/*z*): Calcd for $C_{37}H_{43}O_2S$ $[M+H]^+$ 551.29783; Found 551.29773. **Anal. Calc**. for $C_{37}H_{43}O_2S$: C 80.68; H 7.69. Found C 80.38; H 7.75.

5. Patents

There have been no patent filings associated with this work.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. NMR spectra and crystallographic data.

Author Contributions: Conceptualization, D.B. and M.R.; synthetic work, D.B.; X-ray crystallography, K.H.; writing—original draft preparation, review, and editing, D.B. and M.R.; All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds **10a-p** are available from the authors.

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