Supporting Information for

Acrolein Triftosylhydrazone: A Versatile Vinylcarbene Reagent

Ying Gan,^a Jin Zhang,^a Karunanidhi Murali,^a Yongquan Ning,^{*a} Yong Wu,^a Jacek Mlynarski,^b Zhaohong Liu^{*a}

^aDepartment of Chemistry, Northeast Normal University, Changchun 130024, China.

^bInstitute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

*Corresponding author, Email: <u>ningyq508@nenu.edu.cn</u>; <u>liuzh944@nenu.edu.cn</u>

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I. General Information

The products were purified by column chromatography over silica gel (200-300 mesh). NMR spectra were recorded on a Brüker Advance 600 (¹H: 600 MHz, ¹³C: 150 MHz, ¹⁹F: 564 MHz) and Brüker Advance 500 (¹H: 500 MHz, ¹³C: 125 MHz, ¹⁹F: 470 MHz) at ambient temperature. ¹H and ¹³C NMR spectra were reported as chemical shifts in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent (CHCl₃ at 7.26 ppm ¹H NMR, 77.00 ppm ¹³C NMR) or tetramethylsilane as reference. ¹⁹F NMR spectra were reported as chemical shifts in parts per million (ppm) using CFCl₃ (0 ppm) in CDCl₃ as reference. Coupling constants were reported in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

Allyl sulfides/propargyl sulfides and other reagents were purchased from Adamas-Beta, Energy Chemical Company, ALDRICH, and J&K Scientific Ltd, and were used as received from the commercial suppliers without further purification unless mentioned otherwise. Dry CHCl₃ was dried and degassed at reflux over CaH in a 250 mL round bottom flask for 3 hours under an argon atmosphere, distilled, then stored under an argon atmosphere and was used directly.

II. General Procedures for the Synthesis of Substrates

2.1 General procedure for the synthesis of acrolein sulfonylhydrazones



General procedure (A) for the synthesis of acrolein sulfonylhydrazones: Acrolein (21.0 mmol, 1.05 equiv.) was added dropwise to a vigorously stirred solution of *N*-sulfonyl hydrazide (20 mmol) in anhydrous EtOH (30 mL) under ambient conditions. The resulting mixture was stirred at room temperature for 4–5 hours until the reaction was complete (as monitored by TLC). The reaction mixture was then filtered, and the obtained solid was washed with a cooled mixture of petroleum ether and diethyl ether and dried under reduced pressure to afford the desired acrolein sulfonylhydrazone as a white solid.

2.2 Preparation of allyl and propargyl sulfides

$$R-SH + \swarrow Br \xrightarrow{K_2CO_3 (2.0 \text{ equiv.})} R^{-S} \xrightarrow{S} R^{-S}$$

To a stirred solution of mercaptan (3.0 mmol) and allyl bromide (3.6 mmol, 1.2 equiv.) in ethanol (10 mL) were added K_2CO_3 (6.0 mmol, 1.2 equiv.) and the mixture was stirred overnight at room temperature, diluted with water (10 mL) and extracted with DCM (20 mL×3). The combined organic layer was dried with anhydrous Na₂SO₄, filtered, and condensed under pressure. The residue was purified by flash column chromatography on silica gel to obtain the desired allyl sulfides.

Ar-SH + Br
$$\xrightarrow{K_2CO_3 (2.5 \text{ equiv.})}$$
 Ar S \xrightarrow{Ar} S \xrightarrow{Ar} S \xrightarrow{Ar} S

To a stirred solution of thiophenol (3.0 mmol) and 3-bromopropyne (6.0 mmol, 2.0 equiv.) in N,N-dimethylformamide (DMF, 3.0 mL), K₂CO₃ (7.5 mmol, 2.5 equiv.) was added. The resulting mixture was heated to 50 °C and stirred overnight. The reaction was carefully quenched with 1 M HCl (6.0 mL). The aqueous layer was extracted with DCM (10 mL × 3). The combined organic layers were washed with water (20 mL × 3), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired propargyl sulfides.

+ TMSN₃
$$\xrightarrow{H_2O(2.0 \text{ equiv.})}{DMSO, 80 °C}$$
 $\xrightarrow{N_3}$

Prepared according to literature procedure:¹ To a solution of 4-ethynyltoluene (127 μ L, 116.2 mg, 1.0 mmol), TMSN₃ (0.132 mL, 2.0 mmol), and H₂O (0.036 mL, 2.0 mmol) in DMSO (4 mL) at 80 °C, Ag₂CO₃ (276.0 mg, 0.1 mmol) was added. The mixture was stirred for 1 h until the substrate was fully consumed as indicated by TLC. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (3 × 15 mL), and washed with brine (3 × 40 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel; petroleum ether) and concentrated in vacuo to afford the product in 70% yield as a yellow oil.

III. Optimization of Reaction Conditions.

Table S1. Optimization of the Doyle-Kirms reaction of allyl sulfides with AHZ-Tfs

| | | HSO ₂ Ar | Cat. (1.0-10.0 mol%) Base (4.0 equiv.) | Ş | .Ph |
|-------|------------|---|---|-------------------|------------------------|
| | | Ph ⁻ | Solvent, 40 °C, N ₂ | | |
| | AHZ (1) 2a | | | 3 | |
| Entry | AHZ | Catalyst | Base | Solvent | Yield (%) ^a |
| 1 | la | XX | NaH | DCE | n.d. |
| 2 | la | FeTPPCl (3.0 mol%) | NaH | DCE | 8 |
| 3 | 1a | Tp ^{Br3} Ag(thf) (10.0 mol%) | NaH | DCE | 46 |
| 4 | 1a | Ru(PPh ₃) ₂ Cl | NaH | DCE | 25 |
| 5 | la | Tp ^{(CF3)2} Ag(thf) (10.0 mol%) | NaH | DCE | 73 |
| 6 | la | Tp ^{Br3} Cu(MeCN) (10.0 mol%) |) NaH | DCE | 94 |
| 7 | 1 a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 98 |
| 8 | 1a | Rh ₂ (esp) ₂ (0.5 mol%) | NaH | DCE | 94 |
| 9 | 1a | Rh ₂ (Oct) ₄ (1.0 mol%) | NaH | DCE | 95 |
| 10 | 1a | Rh ₂ (Oct) ₄ (0.5 mol%) | NaH | DCE | 92 |
| 11 | 1a | Rh ₂ (OAc) ₄ (0.5 mol%) | NaH | DCE | 85 |
| 12 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | K ₂ CO ₃ | DCE | 68 |
| 13 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | DIPEA | DCE | 73 |
| 14 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | PhCF ₃ | 77 |
| 15 | la | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | THF | 30 |
| 16 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | CHCl ₃ | 18 |
| 17 | 1b | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 80 |
| 18 | 1c | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 42 |
| 19 | 1d | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | trace |



Reaction conditions: AHZ (0.6 mmol), allyl phenyl sulfide **2a** (0.3 mmol), Cat (0.5-10 mol%), Base (4.0 equiv.) in solvent (5.0 mL) at 40 °C for 12 h. ^{*a*} Isolated yield.

| Table S2. | Optimization | of cycloprop | panation of | AHZ-Tfs |
|-----------|--------------|--------------|-------------|---------|
|-----------|--------------|--------------|-------------|---------|

| | | NHSO ₂ Ar Ph Ba + Cat. | ise (1.2 mmol (1.0-10.0 mo | | ۰Ph |
|-------|---------------------|---|--------------------------------|-------------------|--------------------------------------|
| | | H Ph solver | nt, 40 °C, N ₂ , 2 | 24 h | Ph |
| | 1a 0.6 mi | 43a mol 0.2 mmol | | 44 | |
| Entry | 1 | Catalyst | Base | Solvent | Yield (%) ^{<i>a</i>} |
| 1 | 1a | FeTPPC1 (3.0 mol%) | NaH | DCE | 30 |
| 2 | 1a | Tp ^{Br3} Ag(thf) (10.0 mol%) | NaH | DCE | 28 |
| 3 | 1a | Tp ^{(CF3)2} Ag(thf) (10.0 mol%) | NaH | DCE | 35 |
| 4 | 1a | Tp ^{Br3} Cu(NCMe) (10.0 mol%) | NaH | DCE | 22 |
| 5 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 88 |
| 6 | 1a | Rh ₂ (Oct) ₄ (0.5 mol%) | NaH | DCE | 46 |
| 7 | 1a | Rh ₂ (OAc) ₄ (0.5 mol%) | NaH | DCE | 35 |
| 8 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | K ₂ CO ₃ | DCE | 69 |
| 9 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | DIPEA | DCE | 78 |
| 10 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | PhCF ₃ | 82 |
| 11 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | 1,4-dioxane | 40 |
| 12 | 1a | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | CHCl ₃ | 54 |
| 13 | 1b | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 76 |
| 14 | 1c | Rh ₂ (esp) ₂ (1.0 mol%) | NaH | DCE | 62 |

Reaction conditions: AHZ (0.6 mmol), 1,1-diphenylethylene **43a** (0.2 mmol), cat. (1.0-10.0 mol%), base (1.2 mmol) in DCE (5.0 mL) at 40 °C for 24 h. ^{*a*} Isolated yield.

| NNHTfs | Cat. (1.0-10.0 mol%) Base (2.0 equiv.) | | ų | | |
|--|--|---|---|--|--|
| H + Ph ₃ SI-H | Solvent, <i>T</i> , | Solvent, <i>T</i> , N ₂ , 24 h | | SiPh ₃ | |
| 1a 61a (0.3 mol) (3.0 equiv.) | | | 62 | | |
| Cat. (mol%) | Base | Solvent | <i>T</i> (°C) | Yield (%) ^{<i>a</i>} | |
| $Rh_2(esp)_2(1.0 \text{ mol}\%)$ | NaH | DCM | 80 | 10% | |
| FeTPPCl (3.0 mol%) | NaH | DCM | 80 | trace | |
| Tp ^{Br3} Ag(thf) (10 mol%) | NaH | DCM | 80 | 19% | |
| Tp ^{(CF3)2} Ag(thf) (10 mol%) | NaH | DCM | 80 | 13% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | DCM | 80 | 58% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | K ₂ CO ₃ | DCM | 80 | 35% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | DIPEA | DCM | 80 | 10% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | DCE | 80 | 54% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | PhCF ₃ | 80 | 30% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | DCM | 40 | 39% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | DCM | 60 | 40% | |
| Tp ^{Br3} Cu(NCMe) (10 mol%) | NaH | DCM | 100 | 52% | |
| | NNHTfs Ph3Si—H 1a 61a (0.3 mol) 61a (3.0 equiv.) 610 (10 mol%) 610 (10 pBr3Cu(NCMe) (10 mol%) 61 (10 pBr3Cu(NCMe) (10 mol%) <td< td=""><td>$\begin{array}{c} \begin{array}{c} \begin{array}{c} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$</td><td>NNHTfs Ph₃Si—H Cat. (1.0-10.0 mol%) Base (2.0 equiv.) 1a 61a (0.3 mol) (3.0 equiv.) Cat. (mol%) Base Solvent Rh₂(esp)₂ (1.0 mol%) NaH DCM FeTPPC1 (3.0 mol%) NaH DCM Tp^{Br3}Ag(thf) (10 mol%) NaH DCM Tp^{Br3}Ag(thf) (10 mol%) NaH DCM Tp^{Br3}Cu(NCMe) (10 mol%) NaH DCE Tp^{Br3}Cu(NCMe) (10 mol%) NaH DCE Tp^{Br3}Cu(NCMe) (10 mol%) NaH DCM Tp^{Br3}Cu(NCMe) (10 m</td><td>$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c}$</td></td<> | $ \begin{array}{c} \begin{array}{c} \begin{array}{c} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$ | NNHTfs Ph ₃ Si—H Cat. (1.0-10.0 mol%) Base (2.0 equiv.) 1a 61a (0.3 mol) (3.0 equiv.) Cat. (mol%) Base Solvent Rh ₂ (esp) ₂ (1.0 mol%) NaH DCM FeTPPC1 (3.0 mol%) NaH DCM Tp ^{Br3} Ag(thf) (10 mol%) NaH DCM Tp ^{Br3} Ag(thf) (10 mol%) NaH DCM Tp ^{Br3} Cu(NCMe) (10 mol%) NaH DCE Tp ^{Br3} Cu(NCMe) (10 mol%) NaH DCE Tp ^{Br3} Cu(NCMe) (10 mol%) NaH DCM Tp ^{Br3} Cu(NCMe) (10 m | $ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c}$ | |

Table S3. Optimization of Si-H insertion

Reaction conditions: AHZ (0.3 mmol), Ph₃SiH **61a** (0.6 mmol), Cat. (1.0-10.0 mol%), Base (0.60 mmol) in DCM (5.0 mL) at the specified temperature for 24 h. ^{*a*} Isolated yield.

IV. Proposed Reaction Mechanism

Based on our understanding of the carbene tansformation of triftosylhydrazone and previous studies on Doyle–Kirmse Reaction,³⁻⁵ a plausible mechanism for the rhodium-catalysed D-K reaction of acrolein triftosylhydrazone is proposed in Scheme S1.



Scheme S1. Possible Reaction Mechanism for Rhodium-Catalysed Doyle-Kirmse reaction

V. Experimental Procedures



General procedure (B) for the D-K reaction of allyl sulfides: In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with AHZ-Tfs (167.0 mg, 0.6 mmol), NaH (48.0 mg, 1.2 mmol, 60 wt% dispersion in mineral oil), $Rh_2(esp)_2$ (1.0 mol%), and allyl sulfides (0.3 mmol) in DCE (5.0 mL). The tube was sealed with a screw cap equipped with a septum and then removed from the glovebox. The reaction mixture was stirred at 40 °C for 12 h or 24 h. After completion of the reaction, the crude product was filtered through a short pad of silica gel with ethyl acetate as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel using *n*-hexane as the eluent, affording the final product.



General procedure (C) for the Doyle-Kirmse reaction: In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with AHZ-

Tfs (167.0 mg, 0.6 mmol), NaH (48.0 mg, 1.2 mmol, 60 wt% dispersion in mineral oil), $Rh_2(esp)_2$ (1.0 mol%), and propargyl sulfides (0.3 mmol) in DCE (5.0 mL). The tube was sealed with a screw cap equipped with a septum and then removed from the glovebox. The reaction mixture was stirred at 40 °C for 24 h. After completion of the reaction, the crude product was filtered through a short pad of silica gel with ethyl acetate as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel using *n*-hexane as the eluent, affording the final product.



Gram-Scale Experiment: In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a magnetic stir bar was charged with AHZ-Tfs (3.34 g, 12 mmol), NaH (960.0 mg, 24 mmol, 60 wt% dispersion in mineral oil), $Rh_2(esp)_2$ (1.0 mol%), and allyl(phenyl)sulfane (0.90 g, 6 mmol) in DCE (100 mL). The tube was sealed with a screw cap equipped with a septum and then removed from the glovebox. The reaction mixture was stirred at 40 °C for 36 h. After completion of the reaction, the crude product was filtered through a short pad of silica gel with ethyl acetate as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel using *n*-hexane as the eluent, affording product **3** (1.04 g, 91%).



Synthetic procedure (D) for the oxidation of 3: ² A screw-capped reaction vial was charged with compound 3 (95.0 mg, 0.5 mmol) and m-CPBA (1.25 mmol) under air. Subsequently, DCM (5.0 mL) was added to the reaction mixture, which was then stirred at 0 °C for 4 h. The reaction was quenched with sodium subsulfite solution. The organic layer was separated, dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography to afford sulfone **40** (99.9 mg, 90%).



Synthetic procedure (E): In an oven-dried screw-cap reaction tube equipped with a Tefloncoated magnetic stir bar, copper (I) thiophene-2-carboxylate salt (CuTC, 11.5 mg, 0.06 mmol), phenylacetylene (20.4 mg, 0.2 mmol), and dried toluene (3.0 mL) were sequentially added at room temperature. Subsequently, compound **25** (0.2 mmol) was introduced into the reaction mixture. The resulting solution was stirred at room temperature for approximately 2 h. Upon completion of the reaction (monitored by TLC), the mixture was quenched with saturated aqueous NH₄Cl solution (5 mL) and extracted with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified via flash column chromatography on silica gel to afford the desired product **42** as a yellow oil.



General procedure (F) for cyclopropanation reaction: In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a magnetic stir bar was sequentially charged with AHZ-Tfs (167.0 mg, 0.6 mmol), NaH (48.0 mg, 1.2 mmol, 60 wt% dispersion in mineral oil), $Rh_2(esp)_2$ (1.0 mol%), and a solution of alkenes (0.3 mmol in 5.0 mL DCE). The tube was sealed and subsequently removed from the glovebox. The reaction mixture was stirred at 40 °C for 24 h under a nitrogen atmosphere. After completion of the reaction, the crude product was filtered through a short pad of silica gel with ethyl acetate as an eluent. The filtrate was concentrated under reduced pressure, yielding a crude residue. Purification was achieved via silica gel flash column chromatography using *n*-hexane as the eluent, affording the final product.



General procedure (G) for Si–H insertion: In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a magnetic stir bar was sequentially charged with AHZ-Tfs (55.7 mg, 0.2 mmol), NaH (16.0 mg, 0.4 mmol, 60 wt% dispersion in mineral oil), silane (0.6 mmol), Tp^{Br3}Cu(NCMe) (0.02 mmol, 10 mol%), and dry DCM (5.0 mL). The resulting mixture was stirred at 80 °C for 24 h under an inert atmosphere. Upon completion of the reaction, the mixture was allowed to cool to room temperature, filtered through a short pad of silica gel with ethyl acetate as an eluent. The filtrate was concentrated under reduced pressure, yielding a crude residue. Purification was achieved via silica gel flash column chromatography using *n*-hexane as the eluent, affording the final product.

VI. Characterization Data for New Compounds



AHZ-Tfs, 1a

Acrolein triftosylhydrazone (AHZ-Tfs, 1a): According to General Procedure A, compound 1a was obtained as a white solid, m.p. 110-112 °C; ¹H NMR (500 MHz, DMSO) δ 11.99 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.90 (t, *J* = 7.0 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 9.5 Hz, 1H), 6.29 (dt, *J* = 17.5, 10.0 Hz, 1H), 5.65 (d, *J* = 17.5 Hz, 1H), 5.60 (d. *J* = 10.5 Hz, 1H). ¹³C NMR (125 MHz, DMSO) δ 149.5, 138.5, 133.9, 133.8, 133.7, 131.5, 128.9 (q, *J* = 6.0 Hz), 126.8 (q, *J* = 32.5 Hz), 126.0, 123.2 (q, *J* = 272.5 Hz); ¹⁹F NMR (470 MHz, DMSO) δ (-56.33)-(-56.37) (m, 3F); HRMS (ESI) m/z calcd for C₁₀H₁₀F₃N₂O₂S [M+H]⁺ 279.0410, found 279.0402.



AHZ-Ns, 1b

Acrolein nosylhydrazone (AHZ-Ns, 1b): According to General Procedure A, compound 1b was obtained as a white solid. ¹H NMR (500 MHz, DMSO) δ 8.32 (s, 1H), 8.30–8.23 (m, 1H), 7.87 (m, 1H), 7.83–7.76 (m, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 6.48–6.36 (m, 1H), 5.65 (m, 2H). ¹³C NMR (125 MHz, DMSO) δ 151.7, 134.3, 133.0, 132.9, 132.7, 131.6, 126.6, 125.3. HRMS (ESI) m/z calcd for C₉H₁₀N₃O₄S [M+H]⁺ 256.0932, found 256.0937.



AHZ-Ts, 1c

Acrolein tosylhydrazone (AHZ-Ts, 1c): According to General Procedure A, compound 1a was obtained as a white solid. ¹H NMR (500 MHz, DMSO) δ 11.34 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 9.5 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 6.28 (dd, J = 9.5, 7.5 Hz, 1H), 5.65–5.54 (m, 2H), 2.37 (s, 3H). ¹³C NMR (150 MHz, DMSO) δ 149.6, 144.3, 135.1, 133.1, 129.7, 127.8, 125.3, 21.6. (ESI) m/z calcd for C₁₀H₁₃N₂O₂S [M+H]⁺ 255.0698, found 255.0700.



Hexa-1,5-dien-3-yl(phenyl)sulfane (3): According to General Procedure B, compound 3 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 55.9 mg, 98% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, J = 7.8 Hz, 2H), 7.30-7.26 (m, 2H), 7.25-7.21 (m, 1H), 5.88-5.80 (m, 1H), 5.74-5.68 (m, 1H), 5.11-5.08 (m, 2H), 4.97 (d, J = 10.2 Hz, 1H), 4.90(d, J = 16.8 Hz, 1H), 3.67-3.62 (m, 1H), 2.52-2.39 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 138.1, 135.0, 134.4, 132.8, 128.7, 127.2, 117.2, 116.0, 51.7, 38.6; HRMS (ESI) m/z calcd for C₁₂H₁₅S [M+H]⁺ 191.0889, found 191.0872.



(4-(*Tert*-butyl)phenyl)(hexa-1,5-dien-3-yl)sulfane (4): According to General Procedure B, compound 4 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 72.4 mg, 98% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.28 (m, 4H), 5.87-5.79 (m, 1H), 5.75-5.68 (m, 1H), 5.10-5.06 (m, 2H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.92 (d, *J* = 17.0 Hz, 1H), 3.62-3.58 (m, 1H), 2.51-2.34 (m, 2H), 1.30 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 150.5, 138.3, 135.2, 132.8, 130.7, 125.7, 117.1, 115.9, 51.7, 38.6, 34.5, 31.2; HRMS (ESI) m/z calcd for C₁₅H₂₃S⁻[M+H]⁻ 247.1495, found 247.1495.



Hexa-1,5-dien-3-yl(*p*-tolyl)sulfane (5): According to General Procedure B, compound 5 as obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 55.8 mg, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0Hz, 2H), 5.88-5.80 (m, 1H), 5.75-5.66 (m, 1H), 5.12-5.06 (m, 2H), 4.97 (d, *J*=10.0 Hz, 1H), 4.88 (d, *J* = 17.0 Hz, 1H), 3.60-3.55 (m, 1H), 2.47-2.36 (m, 2H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.2, 137.4, 135.1,133.5, 130.5, 129.5, 117.0, 115.8, 52.1, 38.5, 21.1; HRMS (ESI) m/z calcd for C₁₃H₁₅S⁻[M-H]⁻ 203.0900, found 203.0919.



(4-Fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (6): According to General Procedure B, compound 6 as obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 59.4 mg, 95%)

yield).¹H NMR (600 MHz, CDCl₃) δ 7.32-7.29 (m, 2H), 7.26-7.23 (m, 2H), 5.85-5.78 (m, 1H), 5.70-5.64 (m, 1H), 5.11-5.08 (m, 2H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.80 (d, *J* = 17.4 Hz, 1H), 3.61-3.57 (m, 1H), 2.47-2.37 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 162.5 (d, *J* = 249.0 Hz), 138.0, 135.9 (d, *J* = 9.0 Hz), 134.9, 129.2, 117.3, 116.1, 115.7 (d, *J* = 21.5 Hz), 52.8, 38.4; ¹⁹F NMR (564 MHz, CDC1:) δ (-113.85)-(-113.99) (m); HRMS (ESI) m/z calcd for C₁₂H₁₄FS⁻ [M+H]⁻209.0795, found 209.0773.



(4-Chlorophenyl)(hexa-1,5-dien-3-yl)sulfane (7): According to General Procedure B, compound 7 was obtained as a yellow oil by silica gel flash (*n*-hexane as eluent, 59.3 mg, 88% yield).¹H NMR (600 MHz, CDCl₃) δ 7.32-7.29 (m, 2H), 7.26-7.23 (m, 2H), 5.85-5.78 (m, 1H), 5.70-5.64 (m, 1H), 5.11-5.08 (m, 2H), 4.98 (d, *J* = 9.6 Hz, 1H), 4.87 (d, *J* = 17.4 Hz, 1H), 3.61-3.57 (m, 1H), 2.47-2.37 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.8, 134.7, 134.3, 133.4, 132.9, 128.8, 117.4, 116.2, 52.1, 38.4; HRMS (ESI) m/z calcd for C₁₂H₁₂ClS⁻ [M-H]⁻ 223.0354, found 223.0344.



(4-Bromophenyl)(hexa-1,5-dien-3-yl)sulfane (8): According to General Procedure B, compound 8 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 80.0 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 5.86-5.77 (m, 1H), 5.73-5.62 (m, 1H), 5.12-5.07 (m, 2H), 4.99 (d, J = 10.0 Hz, 1H), 4.89 (d, J = 17.0 Hz, 1H), 3.63-3.57 (m, 1H), 2.48-2.36 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.8, 134.7, 134.4, 133.6, 131.8, 121.4, 117.4, 116.3, 51.9, 38.5; HRMS (ESI) m/z calcd for C₁₂H₁₂BrS⁻ [M-H]⁻ 266.9849, found 266.9829.



Hexa-1,5-dien-3-yl(4-nitrophenyl)sulfane (9): According to General Procedure B, compound 9 was obtained as a brown oil by silica gel flash (*n*-hexane as eluent, 67.1 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 5.86-5.69 (m, 2H), 5.16-5.10 (m, 4H), 3.88 (q, J = 7.5 Hz, 1H), 2.51-2.48 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 145.7, 145.6, 137.1, 133.9, 129.1, 123.7, 118.1, 117.3, 50.1, 38.6; HRMS (ESI) m/z calcd for C₁₂H₁₂NO₂S⁻ [M-H]⁻ 234.0594, found 234.0576.



Hexa-1,5-dien-3-yl(4-(trifluoromethyl)phenyl)sulfane (10): According to General Procedure B, compound 10 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 72.8 mg, 94% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 5.87-5.78 (m, 1H), 5.75-5.67 (m, 1H), 5.15-5.11 (m, 2H), 5.06-5.01 (m, 2H), 3.77 (q, J = 7.5 Hz, 1H), 2.52-2.44 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 140.3, 137.5, 134.4, 130.9, 128.5 (q, J = 32.0 Hz), 125.5 (q, J = 3.5 Hz), 117.7, 116.7, 50.8, 38.6; ¹⁹F NMR (564 MHz, CDCl₃) δ -62.53 (s); HRMS (ESI) m/z calcd for C₁₃H₁₂F₃S⁻ [M-H]⁻ 257.0617, found 257.0599.



(3-Fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (11): According to General Procedure B, compound 11 was obtained as a yellow oil by silica gel flash (*n*-hexane as eluent, 56.9 mg, 91% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.26-7.21 (m, 1H), 7.15-7.13 (m, 1H), 7.11-7.07 (m, 1H), 6.94-6.88 (m, 1H), 5.86-5.80 (m, 1H), 5.74-5.68 (m, 1H), 5.14-5.07 (m, 2H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.96 (d, *J* = 16.8 Hz, 1H), 3.71-3.66 (m, 1H), 2.52-2.38 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 162.5 (d, *J* = 246.0 Hz), 137.8, 137.0 (d, *J* = 7.5 Hz), 134.6, 129.9 (d, *J* = 7.5 Hz), 127.7 (d, *J* = 4.5 Hz), 118.8 (d, *J* = 22.5 Hz), 117.5, 116.4, 113.9 (d, *J* = 21.0 Hz), 51.5, 38.5; ¹⁹F NMR (564 MHz, CDCl₃) δ (-112.64)-(-112.68) (m); HRMS (ESI) m/z calcd for C₁₂H₁₄FS⁺ [M+H]⁺ 209.0795, found 209.0774.



(3-Chlorophenyl)(hexa-1,5-dien-3-yl)sulfane (12): According to General Procedure B, compound 12 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 64.1 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (s, 1H), 7.26-7.23 (m, 1H), 7.20-7.19 (m, 2H), 5.87-5.78 (m, 1H), 5.75-5.65 (m, 1H), 5.14-5.07 (m, 2H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.94 (d, *J* = 17.0 Hz, 1H), 3.70-3.64 (m, 1H), 2.51-2.38 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.7, 136.7, 134.6, 134.2, 131.9, 130.4, 129.7, 127.1, 117.5, 116.4, 51.6, 38.5; HRMS (ESI) m/z calcd for C₁₂H₁₂ClS⁻ [M-H]⁻ 223.0354, found 223.0334.



13

Hexa-1,5-dien-3-yl(*m*-tolyl)sulfane (13): According to General Procedure B, compound 13 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 53.9 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.21-7.15 (m, 3H), 7.03 (d, *J* = 7.0 Hz, 1H), 5.89-5.80 (m, 1H), 5.76-5.66 (m, 1H), 5.15-5.05 (m, 2H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.92 (d, *J* = 17.0 Hz, 1H),

3.67-3.62 (m, 1H), 2.50-2.34 (m, 2H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 138.4, 138.1, 135.1, 134.1, 133.3, 129.7, 128.5, 128.0, 117.1, 115.9, 51.5, 38.6, 21.3; HRMS (ESI) m/z calcd for C₁₃H₁₇S⁺ [M+H]⁺ 205.1046, found 205.1027.



(2-Bromophenyl)(hexa-1,5-dien-3-yl)sulfane (14) : According to General Procedure B, compound 14 was obtained as a yellow oil by silica gel flash (*n*-hexane as eluent, 80.0 mg, 99% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.58-7.57 (m, 1H), 7.40-7.39 (m, 1H), 7.25-7.22 (m, 1H), 7.08-7.06 (m, 1H), 5.90-5.84 (m, 1H), 5.76-5.70 (m, 1H), 5.15-5.08 (m, 2H), 5.02-4.96 (m, 2H), 3.85-3.81 (m, 1H), 2.55-2.42 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.5, 136.0, 134.6, 133.1, 133.0, 128.0, 127.4, 126.9, 117.4, 116.6, 50.7, 38.5; HRMS (ESI) m/z calcd for C₁₂H₁₂BrS⁻ [M-H]⁻ 268.9994, found 268.9969.



(2-Chlorophenyl)(hexa-1,5-dien-3-yl)sulfane (15): According to General Procedure B, compound 15 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 59.3 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.37 (m, 2H), 7.20-7.14 (m, 2H), 5.89-5.80 (m, 1H), 5.74-5.67 (m, 1H), 5.15-5.07 (m, 2H), 4.99-4.93 (m, 2H), 3.85-3.78 (m, 1H), 2.56-2.40 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 136.4, 134.6, 133.9, 133.6, 129.8, 128.1, 126.8, 117.5, 116.5, 50.4, 38.6; HRMS (ESI) m/z calcd for C₁₂H₁₄ClS⁺ [M+H]⁺ 225.0499, found 225.0477.



Methyl 2-(hexa-1,5-dien-3-ylthio)benzoate (16): According to **General Procedure B**, compound 16 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 67.1 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 3.5 Hz, 2H), 7.20-7.14 (m, 1H), 5.91-5.78 (m, 1H), 5.78-5.68 (m, 1H), 5.16-5.04 (m, 4H), 3.90 (s, 3H), 3.85-3.78 (m, 1H), 2.56-2.51 (m, 1H), 2.50-2.42 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 167.2, 139.0, 137.8, 134.8, 131.7, 130.7, 129.3, 127.4, 124.8, 117.4, 116.8, 52.1, 49.3, 38.6.



Methyl 2-(hexa-1,5-dien-3-ylthio)benzoate (17): According to **General Procedure B**, compound 17 was obtained as a yellow oil by silica gel flash (*n*-hexane as eluent, 64.9 mg, 99% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.20 (s, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 5.89-5.82 (m, 1H), 5.74-5.68 (m, 1H), 5.13-5.08 (m, 2H), 4.97 (dd, J = 10.2, 0.6 Hz, 1H), 4.90 (d, J = 17.4 Hz, 1H), 3.64-3.60 (m, 1H), 2.51-2.45 (m, 1H), 2.43-2.41 (m, 1H), 2.37 (s, 3H), 2.29 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 138.1, 137.0, 135.6, 135.1, 133.7, 133.4, 130.0, 128.0, 117.1, 115.8, 51.2, 38.8, 20.8, 20.4; HRMS (ESI) m/z calcd for C₁₄H₁₇S⁻ [M-H]⁻ 217.1057, found 217.1033.



(2,3-Dichlorophenyl)(hexa-1,5-dien-3-yl)sulfane (18) : According to General Procedure B, compound 18 was obtained as a yellow oil by silica gel flash (*n*-hexane as eluent, 76.2 mg, 98%

yield). ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 1.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.83-5.76 (m, 1H), 5.69-5.62 (m, 1H), 5.13-5.08 (m, 2H), 5.02 (d, *J* = 10.2 Hz, 1H), 4.91 (d, *J* = 16.8 Hz, 1H), 3.64-3.59 (m, 1H), 2.49-2.37 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.5, 134.9, 134.4, 133.9, 132.5, 131.7, 131.3, 130.3, 117.6, 116.7, 52.0, 38.4; HRMS (ESI) m/z calcd for C₁₂H₁₁Cl₂S⁻ [M-H]⁻ 256.9964, found 256.9944.



Hexa-1,5-dien-3-yl(naphthalen-2-yl)sulfane (19): According to General Procedure B, compound 19 was obtained as a brown oil by silica gel flash (*n*-hexane as eluent, 70.7 mg, 98% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 0.6 Hz, 1H), 7.80-7.73 (m, 3H), 7.52-7.42 (m, 3H), 5.90-5.83 (m, 1H), 5.78-5.72 (m, 1H), 5.15-5.10 (m, 2H), 5.01-4.93 (m, 2H), 3.81-3.77 (m, 1H), 2.56-2.44 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 138.0, 135.0, 133.6, 132.3, 131.9, 131.5, 130.1, 128.1, 127.7, 127.4, 126.4, 126.1, 117.3, 116.2, 51.6, 38.6; HRMS (ESI) m/z calcd for C₁₆H₁₅S⁻ [M-H]⁻ 239.0900, found 239.0881.



2-(Hexa-1,5-dien-3-ylthio)thiophene (20): According to **General Procedure B**, compound **20** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 56.5 mg, 96% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.36 (dd, J = 5.4, 1.2 Hz, 1H), 7.11 (dd, J = 2.4, 1.2 Hz, 1H), 6.98 (dd, J = 4.8, 3.0 Hz, 1H), 5.85-5.78 (m, 1H), 5.73-5.67 (m, 1H), 5.14-5.06 (m, 2H), 5.00 (dd, J = 10.2, 0.6 Hz, 1H), 4.90-4.83 (m, 1H), 3.49-3.43 (m, 1H), 2.50-2.34 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 137.7, 135.6, 134.9, 132.1, 130.2, 127.4, 117.3, 116.5, 54.5, 38.0; HRMS (ESI) m/z calcd for C₁₀H₁₁S₂⁻ [M-H]⁻ 195.0308, found 195.0287.



Allyl(hexa-1,5-dien-3-yl)sulfane (21): According to General Procedure B, compound 21 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 32.9 mg, 71% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.84-5.73 (m, 2H), 5.63-5.55 (m, 1H), 5.10-5.05 (m, 5H), 4.98 (d, J = 17.0 Hz, 1H), 3.23-3.16 (m, 1H), 3.09 (d, J = 7.0 Hz, 2H), 2.41-2.30 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 138.6, 135.1, 134.6, 116.94, 116.91, 115.7, 47.1, 38.5, 33.4; HRMS (ESI) m/z calcd for C₉H₁₃S⁻ [M-H]⁻ 153.0744, found 153.0722.



Benzyl(hexa-1,5-dien-3-yl)sulfane (22): According to General Procedure B, compound 22 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 53.9 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.25 (m, 4H), 7.23-7.19 (m, 1H), 5.79-5.70 (m, 1H), 5.70-5.60 (m, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.05-4.96 (m, 3H), 3.69-3.58 (m, 2H), 3.15-3.07 (m, 1H), 2.39-2.27 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 138.6, 138.4, 135.0, 129.0, 128.4, 126.9, 116.9, 115.8, 47.7, 38.5, 34.9; HRMS (ESI) m/z calcd for C₁₃H₁₅S⁻ [M-H]⁻ 203.0900, found 203.0879.



(5-Methylhexa-1,5-dien-3-yl)(p-tolyl)sulfane (23): According to General Procedure B, compound 23 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 33.4 mg, 51% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.70-5.59 (m, 1H), 4.92 (dd, J = 10.0, 0.5 Hz, 1H), 4.84-4.74 (m, 3H), 3.71-3.66 (m, 1H), 2.42 (dd, J = 14.0, 6.5 Hz, 1H), 2.34-2.29 (m, 4H), 1.73 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ

142.3, 138.4, 137.4, 133.6, 130.6, 129.4, 115.6, 113.0, 50.7, 42.7, 22.2, 21.1; HRMS (ESI) m/z calcd for C₁₄H₁₇S⁻ [M-H]⁻ 217.1057, found 217.1035.



(5-Bromohexa-1,5-dien-3-yl)(p-tolyl)sulfane (24): According to General Procedure B, compound 24 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 53.5 mg, 63% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.70-5.62 (m, 2H), 5.49 (d, J = 1.0 Hz, 1H), 5.01 (d, J = 10.0 Hz, 1H), 4.95 (d, J = 17.0 Hz, 1H), 3.89-3.85 (m, 1H), 2.76 (dd, J = 14.5, 6.5 Hz, 1H), 2.66 (dd, J = 14.5, 8.5 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.8, 136.9, 133.8, 130.6, 129.8, 129.6, 119.2, 116.7, 50.1, 45.8, 21.1; HRMS (ESI) m/z calcd for C₁₃H₁₄BrS⁻ [M-H]⁻ 281.0005, found 281.0014.



(5-Azidohexa-1,5-dien-3-yl)(phenyl)sulfane (25): According to General Procedure B, compound 25 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 37.5 mg, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.0 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 5.72-5.62 (m, 1H), 5.00 (d, J = 10.0 Hz, 1H), 4.93 (d, J = 17.0 Hz, 1H), 4.80-4.73 (m, 2H), 3.82-3.76 (m, 1H), 2.44 (dd, J = 14.5, 6.5 Hz, 1H), 2.34 (dd, J = 14.5, 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 142.7, 136.2, 132.9, 132.0, 130.2, 127.7, 126.4, 115.5, 48.3, 38.0; HRMS (ESI) m/z calcd for C₁₂H₁₂N₃S⁻ [M-H]⁻ 230.0757, found 230.0736.



(1-(Cyclohex-3-en-1-yl)but-3-en-2-yl)(p-tolyl)sulfane (26): According to General Procedure B, compound 26 was obtained as a colorless oil by silica gel flash (n-hexane as eluent, 65.1 mg, 84% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, J = 8.0 Hz, minor, 2H), 7.28 (d, J = 8.0 Hz, major, 2H), 7.10 (d, J = 8.0 Hz, minor, 2H), 7.08 (d, J = 8.0 Hz, major, 2H), 5.87-5.73 (m, major, 3H), 5.72-5.63 (m, minor, 3H), 4.95 (dd, J = 10.5, 1.5 Hz, major, 1H), 4.94 (dd, J = 10.5, 1.5 Hz, minor, 1H), 4.85-4.80 (m, minor, 1H), 4.82-4.76 (m, major, 1H), 3.49-3.44 (m, major, 1H), 3.44-3.41 (m, minor, 1H), 2.48-2.40 (m, major, 1H), 2.41-2.37 (m, minor, 1H), 2.33 (s, minor, 3H), 2.31 (s, minor, 3H), 2.06-2.00 (m, minor, 2H), 2.00-1.96 (m, major, 2H), 1.92-1.86 (m, major, 1H), 1.86-1.82 (m, minor, 1H), 1.81-1.76 (m, major, 1H), 1.76-1.71 (m, minor, 1H), 1.56-1.50 (m, major, 2H), 1.50-1.43 (m, minor, 2H); ¹³C NMR (125 MHz, CDCl₃) (major) δ 136.9, 133.5, 133.2, 132.2, 129.6, 129.4, 129.0, 128.2, 116.5, 58.8, 39.1, 27.4, 25.2, 21.7, 21.1; (minor) & 137.2, 137.1, 133.2, 131.1, 130.2, 128.9, 128.8, 127.1, 115.8, 58.9, 39.0, 26.7, 25.2, 24.9, 21.6, 19.5; HRMS (ESI) m/z calcd for C₁₆H₂₁S⁺ [M+H]⁺ 245.1359, found 245.1331.



Phenyl(4-phenylhexa-1,5-dien-3-yl)sulfane (27): According to General Procedure B, compound 27 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 74.9 mg, 89% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.21 (m, major, 7H, minor, 7H), 7.11-7.04 (m, major, 2H, minor, 2H), 6.29-6.07 (m, major, 1H, minor, 1H), 5.77-5.52 (m, major, 1H, minor, 1H), 5.23-5.04 (m, major, 2H, minor, 2H), 4.96 (d, *J* = 10.0 Hz, minor, 1H), 4.87-4.72 (m, major, 1H, minor, 1H), 4.61 (d, *J* = 17.0 Hz, major, 1H), 3.86-3.82 (m, major, 1H, minor, 1H), 2.32 (s, major, 3H, minor, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.64, 141.58, 139.0, 138.3, 137.4, 136.9, 136.6, 133.7, 133.6, 130.94, 130.89, 129.5, 128.44, 128.37, 128.3, 128.0, 126.83, 126.75, 117.0, 116.84, 116.77, 116.4, 58.3, 58.2, 54.2, 53.9, 21.2; HRMS (ESI) m/z calcd for C₁₉H₁₉S⁻ [M-H]⁻ 279.1213, found 279.1191.



(4,4-Dimethylhexa-1,5-dien-3-yl)(phenyl)sulfane (28): According to General Procedure B, compound 28 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 47.4 mg, 68% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.97 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.78-5.70 (m, 1H), 5.12-4.99 (m, 2H), 4.87 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.63 (dd, *J* = 17.0, 1.0 Hz, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.30 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 145.3, 137.0, 136.1, 133.5, 131.8, 129.4, 115.9, 112.4, 65.4, 40.0, 25.9, 24.8, 21.1; HRMS (ESI) m/z calcd for C₁₅H₂₁S⁺ [M+H]⁺ 233.1359, found 233.1378.



Hexa-1,4,5-trien-3-yl(phenyl)sulfane (30): According to General Procedure C, compound 30 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 30.5 mg, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 6.5 Hz, 2H), 7.32-7.25 (m, 3H), 5.93-5.86 (m, 1H), 5.30-5.25 (m, 1H), 5.13-5.00 (m, 2H), 4.82-4.71 (m, 2H), 4.26-4.19 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 208.6, 136.4, 134.2, 133.5, 128.6, 127.5, 116.3, 90.7, 77.1, 51.1; HRMS (ESI) m/z calcd for C₁₂H₁₃S⁺ [M+H]⁺ 189.0733, found 189.0716.



Hexa-1,4,5-trien-3-yl(p-tolyl)sulfane (31): According to General Procedure C, compound 31 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 43.1 mg, 71% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.89-5.82 (m, 1H), 5.27 (dt, *J* = 7.5, 6.5 Hz, 1H), 5.07-5.00 (m, 2H), 4.81-4.77 (m, 1H), 4.74-4.70 (m, 1H), 4.18-4.14 (m, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 208.6, 137.8, 136.5, 134.0, 130.3, 129.4, 116.2, 90.7, 77.1, 51.4, 21.2; HRMS (ESI) m/z calcd for C₁₃H₁₅S⁺ [M+H]⁺ 203.0869, found 203.0869.



(4-(*Tert*-butyl)phenyl)(hexa-1,4,5-trien-3-yl)sulfane (32): According to General Procedure C, compound 32 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 30.1 mg, 41% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.91-5.84 (m, 1H), 5.29-5.24 (m, 1H), 5.13-5.03 (m, 2H), 4.78-4.61 (m, 2H), 4.20-4.15 (m, 1H), 1.31 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 208.6, 151.0, 136.5, 133.5, 130.5, 125.7, 116.2, 90.8, 76.9, 51.2, 34.6, 31.3. HRMS (ESI) m/z calcd for C₁₆H₂₁S [M+H]⁺ 245.1359, found 245.1368.



Hexa-1,4,5-trien-3-yl(4-(trifluoromethyl)phenyl)sulfane (33): According to General Procedure C, compound 33 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 35.4 mg, 46% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 5.89-5.79 (m, 1H), 5.17-5.11 (m, 2H), 3.88 (q, *J* = 7.5 Hz, 1H), 2.66-2.57 (m, 2H), 2.12 (t, *J* = 2.5 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 139.3, 136.2, 131.5, 129.0 (q, *J* = 33.2 Hz), 125.6 (q, *J* = 3.5 Hz), 124.0 (q, *J* = 270.0 Hz), 117.6, 80.3, 71.1, 49.6, 24.5; ¹⁹F NMR (564 MHz, CDCl₃) δ -62.60 (s); HRMS (ESI) m/z calcd for C₁₃H₁₀F₃S [M-H]⁻ 255.0461, found 255.0441.



Hexa-1,4,5-trien-3-yl(naphthalen-2-yl)sulfane (34): According to General Procedure C, compound 34 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 32.2 mg, 45% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.90 (s, 1H), 7.81-7.74 (m, 3H), 7.50-7.45 (m, 3H), 5.94-5.87 (m, 1H), 5.35-5.30 (m, 1H), 5.13-5.05 (m, 2H), 4.79-4.75 (m, 1H), 4.70-4.66 (m, 1H), 4.39-4.33 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 208.7, 136.3, 133.6, 132.5, 132.1, 131.7, 130.4, 128.1, 127.7, 127.5, 126.4, 126.2, 116.5, 90.7, 77.3, 50.9; HRMS (ESI) m/z calcd for C₁₆H₁₇S⁺ [M+H]⁺ 239.0889, found 239.0867.



Benzyl(hexa-1,4,5-trien-3-yl)sulfane (35): According to General Procedure C, compound 35 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 53.4 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.31 (m, 4H), 7.24 (m, 1H), 5.88–5.75 (m, 1H), 5.23 (m, 1H), 5.14 (m, 2H), 4.87 (m, 2H), 3.76 (m, 1H), 3.70 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 137.2, 133.7, 132.9, 129.8, 129.3, 128.9, 123.9, 118.4, 69.3, 31.6. HRMS (ESI) m/z calcd for C₁₃H₁₅S⁺ [M+H]⁺ 203.0894, found 203.0899.



(4-Methylhexa-1,4,5-trien-3-yl)(p-tolyl)sulfane (36): According to General Procedure C, compound 36 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 48.7 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H),

5.88-5.78 (m, 1H), 5.05-4.95 (m, 2H), 4.66-4.56 (m, 2H), 3.98 (d, J = 8.5 Hz, 1H), 2.33 (s, 3H), 1.82 (t, J = 3.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 207.1, 137.6, 136.3, 133.8, 130.8, 129.4, 115.9, 98.1, 75.9, 56.2, 21.2, 16.4; HRMS (ESI) m/z calcd for C₁₄H₁₅S⁻ [M-H]⁻ 215.0900, found 215.0888.



(4-Phenylhexa-1,4,5-trien-3-yl)(p-tolyl)sulfane (37): According to General Procedure C, compound 37 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 73.5 mg, 88% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, J = 7.2 Hz, 2H), 7.38-7.31 (m, 4H), 7.30-7.22 (m, 1H), 7.11 (d, J = 7.8 Hz, 2H), 6.01-5.95 (m, 1H), 5.15 (dd, J = 12.0, 1.8 Hz, 1H), 5.08 (dd, J = 12.0, 1.8 Hz, 1H), 5.03-4.96 (m, 2H), 4.47-4.43 (m, 1H), 2.34 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 209.2, 137.9, 136.8, 134.9, 134.1, 130.7, 129.4, 128.4, 127.1, 126.6, 115.4, 105.5, 80.5, 52.1, 21.2; HRMS (ESI) m/z calcd for C₁₉H₁₇S⁻ [M-H]⁻ 277.1057, found 277.1031.



Trimethyl(4-(p-tolylthio)hexa-1,2,5-trien-3-yl)silane (38): According to **General Procedure C**, compound 38 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 45.3 mg, 55% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.90-5.82 (m, 1H), 4.89 (d, J = 10.0 Hz, 1H), 4.74 (d, J = 17.0 Hz, 1H), 4.57-4.51 (m, 2H), 3.92-3.87 (m, 1H), 2.33 (s, 3H), 0.19 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 209.9, 138.1, 137.6, 133.8, 131.5, 129.4, 114.4, 95.6, 72.0, 52.3, 21.2, -1.1; HRMS (ESI) m/z calcd for C₁₆H₂₁SSi⁻ [M-H]⁻ 273.1139, found 273.1122.



(4-Cyclopropylhexa-1,4,5-trien-3-yl)(p-tolyl)sulfane (39): According to General Procedure C, compound 39 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 34.9 mg, 48% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.94-5.86 (m, 1H), 5.01-4.93 (m, 2H), 4.78-4.71 (m, 2H), 4.13 (d, J = 9.0 Hz, 1H), 2.33 (s, 3H), 1.43-1.36 (m, 1H), 0.78-0.67 (m, 2H), 0.47-0.39 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 205.2, 137.5, 136.7, 133.7, 131.0, 129.4, 115.5, 106.8, 79.1, 55.8, 21.1, 10.3, 7.2, 6.9; HRMS (ESI) m/z calcd for C₁₆H₁₇S⁻ [M-H]⁻ 241.1057, found 241.1036.



(Hexa-1,5-dien-3-ylsulfonyl)benzene (40): According to General Procedure D, compound 40 was obtained as a white soild by silica gel flash (*n*-hexane as eluent, 99.9 mg, 90% yield). m.p.: 47-49 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 5.72-5.58 (m, 2H), 5.30 (d, J = 10.0 Hz, 1H), 5.14-5.02 (m, 3H), 3.61-3.56 (m, 1H), 2.92-2.87 (m, 1H), 2.49-2.43 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 137.1, 133.7, 132.8, 129.8, 129.2, 128.8, 123.8, 118.4, 69.2, 31.5; HRMS (ESI) m/z calcd for C₁₂H₁₃O₂S⁻ [M-H]⁻ 221.0642, found 221.0621.



4-Phenyl-1-(4-(phenylthio)hexa-1,5-dien-2-yl)-1*H***-1,2,3-triazole** (42): According to **General Procedure E**, compound 42 was obtained as a white soild by silica gel flash (*n*-hexane

as eluent, 58.7 mg, 88% yield). m.p.: 106-108 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.88 (s, 1H), 7.85 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.38-7.35 (m, 3H), 7.29-7.19 (m, 3H), 5.77-5.67 (m, 1H), 5.43 (d, J = 1.2 Hz, 1H), 5.08 (s, 1H), 4.96 (d, J = 10.2 Hz, 1H), 4.85 (d, J = 17.4 Hz, 1H), 3.93 (q, J = 7.8 Hz, 1H), 3.22-3.12 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 147.6, 140.5, 137.0, 133.7, 133.0, 130.0, 128.86, 128.78, 128.4, 127.4, 125.8, 117.5, 116.9, 106.8, 49.3, 38.2; HRMS (ESI) m/z calcd for C₂₀H₁₈N₃S⁻ [M-H]⁻ 332.1227, found 332.1204.



(2-Vinylcyclopropane-1,1-diyl)dibenzene (44): According to General Procedure F, compound 44 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 58.2 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.32-7.27 (m, 2H), 7.26-7.20 (m, 3H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.15-7.11 (m, 1H), 5.18 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.12-5.01 (m, 1H), 4.90 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.32-2.26 (m, 1H), 1.61-1.56 (m, 1H), 1.54-1.49 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 146.5, 141.3, 139.2, 130.9, 128.3, 127.3, 126.5, 125.8, 113.8, 37.0, 31.0, 22.2; HRMS (ESI) m/z calcd for C₁₇H₁₇⁺ [M+H]⁺ 221.1325, found 221.1342.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(N,N-dimethylaniline) (**45**): According to **General Procedure F**, compound **45** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 70.8 mg, 77% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.19 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 5.18-5.10 (m, 2H), 4.90-4.84 (m, 1H), 2.92 (s, 6H), 2.87 (s, 6H), 2.21-2.14 (m, 1H), 1.51-1.47 (m, 1H), 1.41-1.36 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 149.0, 148.8, 140.2, 135.7, 131.2, 130.1, 127.8, 112.8, 112.7, 112.4, 40.9, 40.7, 35.5, 31.0, 22.1; HRMS (ESI) m/z calcd for C₂₁H₂₅N₂⁻ [M-H]⁻ 305.2023, found 305.1953.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(N,N-diethylaniline) (**46**): According to **General Procedure F**, compound **46** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 97.9 mg, 90% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.15 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 5.18-5.13 (m, 2H), 4.87-4.85 (m, 1H), 3.33-3.26 (m, 8H), 2.16-2.12 (m, 1H), 1.49 (dd, *J* = 8.5, 4.6 Hz, 1H), 1.35 (t, *J* = 5.1 Hz, 1H), 1.15-1.10 (m, 12H); ¹³C NMR (150 MHz, CDCl₃) δ 146.2, 145.8, 140.6, 134.5, 131.4, 129.0, 128.0, 112.5, 111.7, 111.5, 44.4, 44.3, 35.5, 31.1, 22.1, 12.7, 12.6; HRMS (ESI) m/z calcd for C₂₅H₃₅N₂⁺ [M+H]⁺ 363.2795, found 363.2831.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(methoxybenzene) (**47**): According to **General Procedure F**, compound **47** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 67.3 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 5.17 (d, J = 17.0 Hz, 1H), 5.13-5.02 (m, 1H), 4.90 (d, J = 10.0 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.25-2.17 (m, 1H), 1.55-1.48 (m, 1H), 1.44-1.39 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 158.1, 157.7, 139.5, 139.2, 133.9, 131.6, 128.3, 113.64, 113.62, 113.5, 55.3, 55.2, 35.7, 30.8, 22.0; HRMS (ESI) m/z calcd for C₁₉H₂₁O₂⁺ [M+H]⁺ 281.1536, found 281.1508.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(tert-butylbenzene) (**48**): According to **General Procedure F**, compound **48** was obtained as a white soild by silica gel flash (*n*-hexane as eluent, 68.8 mg, 69% yield). m.p.: 82-84 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.28-7.24 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.13-5.03 (m, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 2.26-2.19 (m, 1H), 1.62-1.58 (m, 1H), 1.46-1.43 (m, 1H), 1.30 (s, 9H), 1.27 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 149.1, 148.4, 143.9, 139.7, 138.2, 130.4, 126.7, 125.10, 125.08, 113.3, 36.1, 34.4, 34.3, 31.4, 31.3, 22.4; HRMS (ESI) m/z calcd for C₂₅H₃₁⁻ [M-H]⁻ 331.2431, found 331.2408.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(methylbenzene) (**49**): According to **General Procedure F**, compound **49** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 59.6 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.13-7.07 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 2H), 5.19 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.14-5.05 (m, 1H), 4.91 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 2.28-2.23 (m, 1H), 1.56-1.53 (m, 1H), 1.49-1.45 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 143.9, 139.5, 138.5, 135.9, 135.3, 130.6, 128.95, 128.93, 127.1, 113.5, 36.4, 30.8, 22.0, 21.1, 20.9; HRMS (ESI) m/z calcd for C₁₉H₁₉⁻ [M-H]⁻ 247.1492, found 247.1472.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(fluorobenzene) (**50**): According to **General Procedure F**, compound **50** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 37.7 mg, 49% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, J = 8.0, 6.0 Hz, 2H), 7.13 (dd, J = 8.5, 5.5 Hz, 2H), 6.99 (t, J = 8.5 Hz, 2H), 6.92 (t, J = 8.5 Hz, 2H), 5.19 (d, J = 17.0 Hz, 1H), 5.08-4.97 (m, 1H), 4.93 (d, J = 10.0 Hz, 1H), 2.24 (td, J = 8.5, 6.0 Hz, 1H), 1.54 (dd, J = 8.5, 5.0 Hz, 1H), 1.45 (t, J = 5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 161.5 (d, J = 245.0 Hz), 161.2 (d, J = 245.0 Hz), 142.1 (d, J = 3.5 Hz), 138.6, 137.0 (d, J = 3.0 Hz), 132.1 (d, J = 8.0 Hz), 128.8 (d, J = 8.0 Hz), 115.2 (d, J = 21.0 Hz), 115.1 (d, J = 21.0 Hz), 114.3, 35.7, 30.7, 22.1; ¹⁹F NMR (470 MHz, CDCl₃) δ (-115.92)-(-116.03) (m, 1F), (-117.01)-(-117.15) (m, 1F); HRMS (ESI) m/z calcd for C₁₇H₁₅F₂⁺ [M+H]⁺ 257.1136, found 257.1121.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(chlorobenzene) (**51**): According to **General Procedure F**, compound **51** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 67.7 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.24 (m, 2H), 7.24-7.20 (m, 2H), 7.21-7.16 (m, 2H), 7.08-7.04 (m, 2H), 5.19 (dd, *J* = 16.5, 1.5 Hz, 1H), 5.05-4.96 (m, 1H), 4.93 (dd, *J* = 10.0, 1.5 Hz, 1H), 2.27-2.21 (m, 1H), 1.54 (dd, *J* = 8.5, 5.5 Hz, 1H), 1.47 (t, *J* = 5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 144.5, 139.4, 138.3, 132.6, 132.1, 131.9, 128.60, 128.58, 128.45, 114.7, 35.9, 30.9, 22.1; HRMS (ESI) m/z calcd for C₁₇H₁₃Cl₂- [M-H]-287.0400, found 287.0376.



4,4'-(2-Vinylcyclopropane-1,1-diyl)bis(bromobenzene) (52): According to **General Procedure F**, compound **52** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 97.6 mg, 86% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 16.5 Hz, 1H), 5.06-4.96 (m, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 2.29-2.21 (m, 1H), 1.58-1.52 (m, 1H), 1.50-1.45 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 144.9, 139.8, 138.2, 132.4, 131.6, 131.4, 129.0, 120.8, 119.9, 114.7, 36.0, 30.9, 22.1; HRMS (ESI) m/z calcd for C₁₇H₁₃Br₂- [M-H]- 374.9390, found 374.9366.



(2-Vinylcyclopropane-1,1-diyl)bis(4,1-phenylene) bis(trifluoromethanesulfonate) (53): According to General Procedure F, compound 53 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 128.6 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J =8.5 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 5.26-5.19 (m, 1H), 5.05-4.96 (m, 2H), 2.34-2.25 (m, 1H), 1.65 (dd, J = 8.5, 5.5 Hz, 1H), 1.54 (t, J =5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 148.4, 147.8, 146.0, 141.0, 137.5, 132.6, 128.9, 121.4, 121.3, 118.6 (q, J = 320.0 Hz), 115.5, 35.7, 31.4, 22.5; ¹⁹F NMR (470 MHz, CDCl₃) δ -72.88 (s, 3F), -72.92 (s, 3F); HRMS (ESI) m/z calcd for C₁₉H₁₃F₆O₆S₂⁻ [M-H]⁻ 515.0063, found 515.0041.



(2-Vinylcyclopropane-1,1-diyl)bis(4,1-phenylene) bis(2,2-dimethylpropanoate) (54): According to General Procedure F, compound 54 was obtained as a white solid by silica gel flash (*n*-hexane as eluent, 107.2 mg, 85% yield). m.p.: 54-56 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.18 (d, *J* = 17.0 Hz, 1H), 5.11-5.00 (m, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 2.29-2.21 (m, 1H), 1.60-1.54 (m, 1H), 1.50-1.45 (m, 1H), 1.35 (s, 9H), 1.33 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 177.12, 177.07, 149.6, 149.1, 143.5, 138.8, 138.4, 131.7, 128.1, 121.3, 121.2, 114.2, 39.1, 39.0, 35.9, 31.2, 27.1, 22.4; HRMS (ESI) m/z calcd for C₂₇H₃₃O₄⁺ [M+H]⁺ 421.2373, found 421.2332.



3,3'-(2-Vinylcyclopropane-1,1-diyl)bis(methylbenzene) (55): According to General **Procedure F**, compound **55** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 52.2 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.21-7.12 (m, 4H), 7.08-6.99 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 1H), 5.20 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.13-5.03 (m, 1H), 4.90 (dd, *J* = 10.0, 1.5 Hz, 1H), 2.31 (s, 3H), 2.30-2.24 (m, 4H), 1.55 (dd, *J* = 8.5, 4.5 Hz, 1H), 1.46 (t, *J* = 5.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 146.6, 141.3, 139.4, 137.8, 137.7, 131.4, 128.1, 128.07, 128.03, 127.8, 127.2, 126.6, 124.6, 113.5, 37.0, 30.7, 21.9, 21.48, 21.45; HRMS (ESI) m/z calcd for C₁₉H₂₁⁺ [M+H]⁺ 249.1638, found 249.1618.



3,3'-(2-Vinylcyclopropane-1,1-diyl)bis(fluorobenzene) (56): According to **General Procedure F**, compound 56 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 46.1 mg, 60% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, J = 8.0, 6.0 Hz, 2H), 7.13 (dd, J = 8.5, 5.5 Hz, 2H), 6.99 (t, J = 8.5 Hz, 2H), 6.92 (t, J = 8.5 Hz, 2H), 5.19 (d, J = 17.0 Hz, 1H), 5.08-4.97 (m, 1H), 4.93 (d, J = 10.0 Hz, 1H), 2.24 (td, J = 8.5, 6.0 Hz, 1H), 1.54 (dd, J = 8.5, 5.0 Hz, 1H), 1.45 (t, J = 5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 161.5 (d, J = 245.0 Hz), 161.2 (d, J = 245.0 Hz), 142.1 (d, J = 3.5 Hz), 138.6, 137.0 (d, J = 3.0 Hz), 132.1 (d, J = 8.0 Hz), 128.8 (d, J = 8.0 Hz), 115.2 (d, J = 21.0 Hz), 115.1 (d, J = 21.0 Hz), 114.3, 35.7, 30.7, 22.1; ¹⁹F NMR (470 MHz, CDCl₃) δ (-115.92)-(-116.03) (m, 1F), (-117.01)-(-117.15) (m, 1F); HRMS (ESI) m/z calcd for C₁₇H₁₅F₂⁺ [M+H]⁺ 257.1136, found 257.1121.



2-(1-(2,4-Dimethylphenyl)-2-vinylcyclopropyl)-1,4-dimethylbenzene (57): According to **General Procedure F**, compound 57 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 38.1 mg, 46% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.46-7.40 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 2.5 Hz, 2H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.07-4.96 (m, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 2.50-2.42 (m, 1H), 2.29 (s, 3H), 2.25 (s, 6H), 2.21 (s, 3H), 1.57-1.53 (m, 1H), 1.29-1.22 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 139.5, 139.0, 138.92, 138.89, 136.0, 135.9, 135.2, 131.73, 131.68, 131.4, 130.5, 125.39, 125.37, 113.9, 35.5, 28.8, 21.3, 21.1, 20.83, 20.78, 20.7; HRMS (ESI) m/z calcd for C₂₁H₂₅⁺ [M+H]⁺ 277.1951, found 277.1941.



(1-Methyl-2-vinylcyclopropyl)benzene (58): According to General Procedure F, compound 58 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 30.4 mg, 64% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.24 (m, major, 5H), 7.21-7.15 (m, minor, 5H), 5.80-5.70 (m, major, 1H), 5.17 (d, *J* = 17.0 Hz, major, 1H), 5.08 (d, *J* = 17.0 Hz, major, 1H), 5.07-5.03 (m, minor, 1H), 4.92-4.83 (m, minor, 1H), 4.80-4.74 (m, minor, 1H), 1.81-1.71 (m, major, 1H), 1.70-1.64 (m, minor, 1H), 1.41(s, minor, 3H), 1.40 (s, major, 3H), 1.37-1.32 (m, major, 1H), 1.28-1.25 (m, minor, 1H), 0.87 (t, *J* = 17.0, minor, 1H), 0.83 (t, *J* = 5.0, major, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 138.73, 138.70, 137.0, 136.5, 134.70, 134.65, 130.4, 128.7, 127.7, 127.0, 116.92, 116.88, 115.7, 115.6, 115.0, 114.9, 47.5, 47.4, 37.4, 36.6, 33.5, 33.4, 31.8, 31.7; HRMS (ESI) m/z calcd for C₁₂H₁₅⁺ [M+H]⁺ 159.1168, found 159.1153.



1-(2-Vinylcyclopropyl)naphthalene (**59**): According to **General Procedure F**, compound **59** was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 31.5 mg, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.72 (m, major, 3H, minor, 3H), 7.64 (s, major, 1H), 7.53 (s, minor, 1H), 7.48-7.38 (m, major, 2H, minor, 2H), 7.37 (d, J = 8.5 Hz, major, 1H), 7.20 (d, J = 7.5 Hz, minor, 1H), 5.63-5.55 (m, minor, 1H), 5.16-5.13 (m, major, 1H, minor, 1H), 5.12-5.06 (m, major, 1H), 4.97 (d, J = 10.0 Hz, minor, 1H), 4.82 (dd, J = 9.0, 2.5 Hz, major, 1H), 2.51 (dd, J = 15.0, 8.0 Hz, major, 1H), 2.13-2.07 (m, minor, 1H), 1.99-1.90 (m, major, 1H), 1.85-1.77 (m, minor, 1H), 1.38-1.30 (m, major, 1H, minor, 1H), 1.23-1.16 (m, major, 1H, minor, 1H); ¹³C NMR (150 MHz, CDCl₃) (major) δ 140.7, 138.1, 133.5, 132.1, 128.2, 127.6, 127.5, 127.0, 125.9, 125.3, 124.8, 123.8, 114.1, 25.5, 23.6, 11.8. (minor) 139.8, 136.5, 133.4, 132.0, 128.0, 127.52, 127.50, 127.3, 126.0, 125.0, 124.6, 112.7, 27.4, 23.1, 16.7. HRMS (ESI) m/z calcd for C₁₅H₁₃⁻ [M-H]⁻ 193.1023, found 193.1002.



2-Vinylspiro[cyclopropane-1,9'-fluorene] (60): According to General Procedure F, compound 60 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 20.9 mg, 32% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.87-7.79 (m, 2H), 7.38-7.26 (m, 4H), 7.20 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.05-5.96 (m, 1H), 5.27 (d, J = 17.0 Hz, 1H), 5.17 (d, J = 10.5 Hz, 1H), 2.65-2.58 (m, 1H), 2.12 (dd, J = 8.5, 5.5 Hz, 1H), 1.94 (dd, J = 7.5, 5.5 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 147.9, 144.2, 140.8, 139.5, 135.2, 126.9, 126.2, 126.1, 126.0, 121.9, 120.1, 119.8, 118.4, 117.2, 36.1, 34.8, 22.9; HRMS (ESI) m/z calcd for C₁₇H₁₃⁻ [M-H]⁻ 217.1023, found 217.1003.



Allyl(methyl)diphenylsilane (63): According to General Procedure G, compound 63 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 29.6 mg, 62% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 6.5 Hz, 4H), 7.37-7.31 (m, 6H), 5.82-5.73 (m, 1H), 4.92-4.83 (m, 2H), 2.06 (d, *J* = 8.0 Hz, 2H), 0.54 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 136.6, 134.6, 134.1, 129.3, 127.8, 114.3, 22.2, -4.8; HRMS (ESI) m/z calcd for C₁₆H₁₉Si⁺ [M+H]⁺ 239.1251, found 239.1233.



Allyldimethyl(phenyl)silane (64): According to General Procedure G, compound 64 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 23.3 mg, 66% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.50 (m, 2H), 7.38-7.34 (m, 3H), 5.81-5.73 (m, 1H), 4.89-4.82 (m,
2H), 1.76 (d, J = 8.0 Hz, 2H), 0.28 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 138.7, 134.6, 133.6, 129.0, 127.7, 113.4, 23.7, 1.0, -3.5; HRMS (ESI) m/z calcd for C₁₁H₁₇Si [M+H]⁺ 177.1074, found 177.1199.



Allyl(benzyl)dimethylsilane (65): According to General Procedure G, compound 65 was obtained as a colorless oil by silica gel flash (*n*-hexane as eluent, 22.8 mg, 40% yield).¹H NMR (600 MHz, CDCl₃) δ 7.22-7.26 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 5.75 - 5.82 (m 1H), 4.91–4.86 (m, 2H), 2.13 (s, 2H), 1.55 (d, *J* = 8.2 Hz, 2H), 0.00 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 140.0 (s), 134.7 (s), 128.2 (s), 128.1 (s), 123.98 (s), 113.21 (s), 25.06 (s), 22.68 (s), -4.03 (s).

VII. X-ray crystallographic data.



AHZ-Tfs



CCDC: 2296818

| Empirical formula | $C_{10}H_9F_3N_2O_2S$ |
|-----------------------------------|---|
| Temperature | 270.17 K |
| Unit cell dimensions | a = 21.146(5) Å |
| | b = 8.147(2) Å |
| | c = 16.078(4) Å |
| | alpha = 90 deg. |
| | beta = 117.284(13) deg. |
| | gamma = 90 deg. |
| Volume | 2461.8(11) Å ³ |
| Z | 8 |
| Calculated density | 1.501 g/cm ³ |
| F(000) | 1136.0 |
| Crystal size | 0.15 x 0.11 x 0.08 mm |
| Theta range for data collection | 11.626 to 127.438 |
| Reflections collected | 5712 |
| Independent reflections | 1944 [$R_{int} = 0.0577, R_{sigma} = 0.0599$] |
| Data / restraints / parameters | 1944/0/172 |
| Goodness-of-fit on F ² | 1.056 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0549, wR_2 = 0.1297$ |
| Rindices (all data) | $R_1 = 0.0693, wR_2 = 0.1411$ |

VIII. Copies of NMR spectra



¹³C NMR spectrum of compound **1a** (125 MHz, DMSO)



S40





¹H NMR spectrum of compound **3** (600 MHz, CDCl₃)



¹H NMR spectrum of compound 4 (500 MHz, CDCl₃)



¹H NMR spectrum of compound **5** (500 MHz, CDCl₃)





 19 F NMR spectrum of compound **6** (564 MHz, CDCl₃)





NMR spectrum of compound 8 (150 MHz, CDCl₃)



 13 C NMR spectrum of compound 9 (125 MHz, CDCl₃)





S51



S52













¹³C NMR spectrum of compound **17** (150 MHz, CDCl₃)







¹³C NMR spectrum of compound **19** (150 MHz, CDCl₃)







S63







¹³C NMR spectrum of compound **26** (125 MHz, CDCl₃)



¹³C NMR spectrum of compound **27** (125 MHz, CDCl₃)



¹³C NMR spectrum of compound **28** (125 MHz, CDCl₃)





¹³C NMR spectrum of compound **31** (125 MHz, CDCl₃)






¹H NMR spectrum of compound **34** (500 MHz, CDCl₃)



S74



¹H NMR spectrum of compound **36** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **37** (600 MHz, CDCl₃)



¹H NMR spectrum of compound **38** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **39** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **40** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **42** (600 MHz, CDCl₃)



¹H NMR spectrum of compound 44 (500 MHz, CDCl₃)



¹H NMR spectrum of compound **45** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **46** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **47** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **48** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **49** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **50** (500 MHz, CDCl₃)



 ^{19}F NMR spectrum of compound **50** (470 MHz, CDCl_3)



¹³C NMR spectrum of compound **51** (125 MHz, CDCl₃)



¹H NMR spectrum of compound **52** (500 MHz, CDCl₃)



¹³C NMR spectrum of compound **52** (125 MHz, CDCl₃)



¹³C NMR spectrum of compound **53** (125 MHz, CDCl₃)



¹H NMR spectrum of compound **54** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **55** (500 MHz, CDCl₃)



¹H NMR spectrum of compound **56** (500 MHz, CDCl₃)



¹³C NMR spectrum of compound **56** (125 MHz, CDCl₃)



S96



¹³C NMR spectrum of compound **58** (150 MHz, CDCl₃)





¹³C NMR spectrum of compound **60** (150 MHz, CDCl₃)



¹³C NMR spectrum of compound **63** (150 MHz, CDCl₃)



¹³C NMR spectrum of compound **64** (150 MHz, CDCl₃)



S102

VIIII. Reference

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