SUPPORTING INFORMATION

_cine_-Substitutions at 5-membered Hetarenes enabled by Sulfonium Salts

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MATERIALS AND METHODS

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 25–40 °C at an appropriate pressure. Purified compounds were further dried under vacuum (10⁻⁶ – 10⁻³ bar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated. Reactions that require heating were performed in sealed glass vials placed inside an aluminium heating block, unless otherwise stated. Temperatures refer to the temperature of the aluminium heating block.

Solvents

Dichloromethane, and methanol were purchased from Sigma-Aldrich and used as received. Anhydrous solvents were obtained from Phoenix Solvent Drying Systems. All deuterated solvents were purchased from Euriso-Top. Anhydrous acetonitrile-d₃ was dried by storage over molecular sieves. The term “hexanes” refers to a mixture of volatile saturated hydrocarbons, mostly 2-methylpentane.

Chromatography

Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250 µm thickness silica gel 60 F₂₅₄ plates and visualized by irradiation UV light or by dipping the TLC plate into a dilute, alkaline, aqueous KMnO₄-solution. Flash chromatography was performed on an Isolera Four from Biotage using silica gel (40–63 µm particle size) purchased from Geduran.

NMR Spectroscopy

NMR spectra were recorded on a Bruker Ascend™ 500 spectrometer operating at 500 MHz, 471 MHz, 203 MHz, and 126 MHz, for ¹H, ¹⁹F, ³¹P, and ¹³C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ¹H NMR: CDCl₃, δ 7.260; CD₃CN, δ 1.940; DMSO-d₆, δ 2.500; For ¹³C NMR: CDCl₃, δ 77.16; CD₃CN, δ 1.32; DMSO-d₆, δ 39.52. ¹⁹F NMR spectra were referenced using a unified chemical shift scale based on the ¹H resonance of tetramethylsilane (1% v/v solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration. Multiplets resulting from coupling to several magnetically non identical atoms with a coincidentally equal (within the limits of detection) coupling constant are indicated with ψ as well as splittings not resulting from a coupling to another spin.

Massspectrometry

High-resolution mass spectra were acquired using a Q Exactive Plus Orbitrap manufactured by Thermo Scientific, Bremen, Germany or a Q Exactive GC Orbitrap manufactured by Thermo Scientific, Bremen, Germany in combination with the gas-chromatograph Trace 1310 manufactured by Thermo Scientific, Bremen, Germany.
Starting materials

All substrates were used as received from commercial suppliers, unless otherwise stated. Chemicals were purchased from Sigma-Aldrich, Chempur, TCI, or Alfa Aesar.
EXPERIMENTAL DATA

Experimental procedures and compound characterization

**Thianthrene-S-oxide**
Thianthrene-S-oxide was prepared as described previously.\(^4a\)

**Dibenzothiophene-S-oxide**
Dibenzothiophene-S-oxide was prepared as described previously.\(^4e\)

**Imidazopyridazine-derived dibenzothiophenium salt S1 (CCDC 1987149)**

\[
\begin{array}{c}
\text{S1} \\
\end{array}
\]

Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with imidazopyridazine (1.07 g, 9.00 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (1.80 g, 9.00 mmol, 1.0 equiv.), and DCM (60 ml, c = 0.15 M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (2.77 mL, 4.16 g, 19.8 mmol, 2.2 eq.) was added. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 1.5 h. Subsequently, the reaction mixture was diluted with water (20 ml). The layers were separated. The aqueous layer was extracted with DCM (20 ml). The combined organic layers were dried over MgSO\(_4\). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 1) to afford 2.88 g (77 %) of compound S1 as brown foam. 

\textbf{NMR Spectroscopy:}

\(^1\text{H} \text{NMR} \ (500 \text{ MHz, CD}_3\text{CN, 298 K, } \delta): 8.81 \ (s, 1H), 8.34 \ (dd, J = 7.8, 1.1 Hz, 2H), 8.16 – 8.07 \ (m, 4H), 7.87 \ (td, J = 7.7, 1.0 Hz, 2H), 7.61 \ (td, J = 7.7, 1.2 Hz, 2H), 7.34 \ (dd, J = 9.1, 4.8 Hz, 1H).}

\(^{13}\text{C} \ {^1\text{H}} \ \text{NMR} \ (128 \text{ MHz, CD}_3\text{CN, 298 K, } \delta): 160.6 \ (q, J = 32 Hz), 147.4, 146.5, 146.4, 141.6, 135.1, 132.0, 128.9, 128.2, 128.0, 124.9, 123.4, 118.6 \ (q, J = 299 Hz), 102.5.}

\(^{19}\text{F} \ \text{NMR} \ (471 \text{ MHz, CD}_3\text{CN, 298 K, } \delta): -75.4.}

\textbf{HRMS-ESI (m/z) calc'd for C}_{18}\text{H}_{12}\text{N}_3\text{S}^+ [M-TFA]^+, 302.0746; found 302.0744; deviation 0.8 ppm.}

\textbf{X-ray crystallography:}

Sample preparation: In a 2 mL GC-vial, a small portion of compound S1 (approx. 5 mg) was dissolved in 0.5 mL chloroform. It was then placed in a 20 mL glass vial filled with 2 mL hexanes. The larger vial was capped.
and the cap was stabbed with a syringe needle. The system was left on a shelf at 20 °C until the formed crystals had sufficient size (approx. one week).

X-ray measurement:
device: Bruker-AXS Kappa Mach3 APEX-II
method: f- and w-scans
radiation: Mo-Kα
wavelength: 0.71073 Å
radiation source: 1mS
Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.

**Fig. S1:** Crystal structure of compound S1. The nonhydrogen atoms are depicted with 50 % probability ellipsoids.

**Table S1.** Crystal data and structure refinement.

| Identification code | 12795 |
|---------------------|-------|
| Empirical formula   | C_{20}H_{14}F_{3}N_{3}O_{3}S |
| Color               | colourless |
| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Formula weight                 | 433.40 g · mol⁻¹                           |
| Temperature                    | 100(2) K                                  |
| Wavelength                     | 0.71073 Å                                 |
| Crystal system                 | TRICLINIC                                  |
| Space group                    | P1, (no. 2)                                |
| Unit cell dimensions           | a = 7.7627(3) Å                           |
|                                | α = 100.4140(10)°.                        |
|                                | b = 9.9150(3) Å                           |
|                                | β = 106.2760(10)°.                        |
|                                | c = 13.0037(5) Å                          |
|                                | γ = 91.2600(10)°.                         |
| Volume                         | 942.12(6) Å                               |
| Z                              | 2                                         |
| Density (calculated)           | 1.528 Mg · m⁻³                            |
| Absorption coefficient         | 0.230 mm⁻¹                                |
| F(000)                         | 444 e                                     |
| Crystal size                   | 0.118 x 0.075 x 0.054 mm³                 |
| θ range for data collection   | 2.742 to 34.845°.                         |
| Index ranges                   | -12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20 |
| Reflections collected          | 37409                                     |
| Independent reflections        | 8122 [R_{int} = 0.0214]                   |
| Reflections with I > 2σ(I)     | 6938                                      |
| Completeness to θ = 25.242°   | 99.9%                                     |
| Absorption correction         | Gaussian                                  |
| Max. and min. transmission     | 0.99 and 0.98                            |
| Refinement method              | Full-matrix least-squares on F²           |
| Data / restraints / parameters | 8122 / 0 / 327                            |
| Goodness-of-fit on F²          | 1.030                                     |
| Final R indices [I > 2σ(I)]    | R₁ = 0.0346, wR² = 0.0888                 |
| R indices (all data)           | R₁ = 0.0433, wR² = 0.0943                 |
| Largest diff. peak and hole    | 0.7 and -0.5 e · Å⁻³                     |
| Bond                        | Length [Å] (E) | Bond                        | Length [Å] (E) |
|-----------------------------|---------------|-----------------------------|---------------|
| S(1)-C(1)                   | 1.7811(8)     | S(1)-C(12)                  | 1.7837(8)     |
| S(1)-C(13)                  | 1.7337(8)     | N(1)-C(14)                  | 1.3564(13)    |
| N(1)-C(15)                  | 1.3389(13)    | N(2)-N(3)                   | 1.3509(11)    |
| N(2)-C(18)                  | 1.3145(13)    | N(3)-C(13)                  | 1.3787(11)    |
| N(3)-C(15)                  | 1.3865(11)    | C(1)-C(2)                   | 1.3842(12)    |
| C(1)-C(6)                   | 1.3991(11)    | C(2)-H(2)                   | 0.941(15)     |
| C(2)-C(3)                   | 1.3949(13)    | C(3)-H(3)                   | 0.961(16)     |
| C(3)-C(4)                   | 1.3920(14)    | C(4)-H(4)                   | 0.970(15)     |
| C(4)-C(5)                   | 1.3941(13)    | C(5)-H(5)                   | 0.960(15)     |
| C(5)-C(6)                   | 1.3936(12)    | C(6)-C(7)                   | 1.4628(12)    |
| C(7)-C(8)                   | 1.3950(12)    | C(7)-C(12)                  | 1.3994(11)    |
| C(8)-H(8)                   | 0.957(14)     | C(8)-C(9)                   | 1.3929(13)    |
| C(9)-H(9)                   | 0.960(14)     | C(9)-C(10)                  | 1.3966(13)    |
| C(10)-H(10)                 | 0.959(14)     | C(10)-C(11)                 | 1.3981(12)    |
| C(11)-H(11)                 | 0.926(14)     | C(11)-C(12)                 | 1.3815(12)    |
| C(13)-C(14)                 | 1.3868(11)    | C(14)-H(14)                 | 0.965(14)     |
| C(15)-C(16)                 | 1.4095(15)    | C(16)-H(16)                 | 0.940(17)     |
| C(16)-C(17)                 | 1.3593(18)    | C(17)-H(17)                 | 0.943(18)     |
| C(17)-C(18)                 | 1.4230(16)    | C(18)-H(18)                 | 0.976(16)     |
| F(1)-C(20)                  | 1.3423(11)    | F(2)-C(20)                  | 1.3240(12)    |
| F(3)-C(20)                  | 1.3262(11)    | O(1)-C(19)                  | 1.2334(11)    |
| O(2)-C(19)                  | 1.2557(10)    | C(19)-C(20)                 | 1.5491(12)    |
| O(3)-H(3A)                  | 0.828(19)     | O(3)-H(3B)                  | 0.846(19)     |
| C(1)-S(1)-C(12)             | 91.59(4)      | C(13)-S(1)-C(1)             | 104.65(4)     |
| C(13)-S(1)-C(12)            | 104.75(4)     | C(15)-N(1)-C(14)            | 105.51(7)     |
| C(18)-N(2)-N(3)             | 113.51(8)     | N(2)-N(3)-C(13)             | 126.42(7)     |
| N(2)-N(3)-C(15)             | 127.11(8)     | C(13)-N(3)-C(15)            | 106.43(7)     |
| C(2)-C(1)-S(1)              | 124.60(6)     | C(2)-C(1)-C(6)              | 124.07(8)     |
| C(6)-C(1)-S(1)              | 111.24(6)     | C(1)-C(2)-H(2)              | 121.1(9)      |
| C(1)-C(2)-C(3)              | 116.61(8)     | C(3)-C(2)-H(2)              | 122.3(9)      |
| C(2)-C(3)-H(3)              | 117.2(9)      | C(4)-C(3)-C(2)              | 120.69(8)     |
| C(4)-C(3)-H(3)              | 122.1(9)      | C(3)-C(4)-H(4)              | 118.6(9)      |
Under an ambient atmosphere, a 250 ml round bottom flask equipped with a teflon coated stir bar and a reflux condenser was charged with hydroxybromonaphthalene (3.00 g, 13.4 mmol, 1.0 equiv.), chlorobutane (2.0 ml, 1.8 g, 19 mmol, 1.4 equiv.), potassium carbonate (1.9 g, 13 mmol, 1.0 equiv.), and DMF (100 ml, c = 0.13 M). The mixture was heated to 100 °C and stirred for 4 h. After cooling to 25 °C, the mixture was diluted
with water (75 ml) and EtOAc (50 ml). The layers were separated. The aqueous layer was extracted with EtOAc (2 × 50 ml). The combined organic layers were washed with water (2 × 50 ml), dried over MgSO4, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography and on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 10 / 1) to afford 2.06 g (55 %) of compound S2 as yellowish liquid.

Rf = 0.73 (hexanes / EtOAc, 4 / 1 (v/v)).

NMR Spectroscopy:

$^1$H NMR (500 MHz, CDCl$_3$, 298 K, δ): 8.27 (dd, J = 8.6, 2.7 Hz, 1H), 7.81 (d, J = 9.1 Hz, 2H), 7.59 (ddt, J = 8.5, 7.0, 1.6 Hz, 1H), 7.42 (ddt, J = 8.3, 6.8, 1.4 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 4.21 (t, J = 6.5 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.71 – 1.56 (m, 2H), 1.05 (t, J = 7.4, 2.5 Hz, 3H).

$^{13}$C ($^1$H) NMR (128 MHz, CDCl$_3$, 298 K, δ): 153.5, 133.3, 129.9, 128.9, 128.1, 127.7, 126.3, 124.4, 115.3, 109.6, 70.0, 31.6, 19.4, 14.0.

HRMS-EI (m/z) calc'd for C$_{14}$H$_{15}$OBr$^+$ [M]+, 278.0301; found 278.0297; deviation 1.2 ppm.

Bromobutoxynapthalin-derived diphenylsulfonium salt S3

Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with bromobutoxynaphthalene (1.02 g, 3.65 mmol, 1.0 equiv.), thianthrene-S-oxide (849 mg, 3.65 mmol, 1.0 equiv.), and DCM (50 ml, c = 0.073 M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (2.5 mL, 3.8 g, 18 mmol, 5.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.5 ml, 0.60 g, 3.7 mmol, 1.0 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 5 h. Subsequently, the reaction mixture was poured onto aqueous NaHCO$_3$ solution (saturated, 50 ml). The layers were separated. The organic layer was washed with aqueous NaBF$_4$ solution (20 % (w/w), 3 × 20 ml), and water (20 ml), and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc / DCM / MeOH (2 / 1 / 0 / 0, then 0 / 0 / 2 / 1) to afford 828 mg (39 %) of compound S3 as dark purple solid.

Rf = 0.52 (DCM / MeOH, 9 / 1 (v/v)).

NMR Spectroscopy:
\[^1\text{H} \text{ NMR} \ (500 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ 8.60 \ (\text{dd, } J = 7.5, \ 1.4 \text{ Hz, } 2\text{H}), \ 8.18 \ (\text{d, } J = 9.3 \text{ Hz, } 1\text{H}), \ 7.99 \ (\text{d, } J = 2.3 \text{ Hz, } 1\text{H}), \ 7.89 - 7.72 \ (\text{m, } 7\text{H}), \ 7.30 \ (\text{d, } J = 9.1 \text{ Hz, } 1\text{H}), \ 7.14 \ (\text{dd, } J = 9.3, \ 2.3 \text{ Hz, } 1\text{H}), \ 4.17 \ (\text{t, } J = 6.4 \text{ Hz, } 2\text{H}), \ 1.89 - 1.77 \ (\text{m, } 2\text{H}), \ 1.62 - 1.48 \ (\text{m, } 2\text{H}), \ 0.98 \ (\text{t, } J = 7.4 \text{ Hz, } 3\text{H}).\]

\[^{13}\text{C} \ {^{1}\text{H} \text{ NMR} \ (128 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ 156.5, \ 136.4, \ 135.5, \ 134.91, \ 134.86, \ 131.4, \ 130.6, \ 130.5, \ 130.2, \ 129.5, \ 129.0, \ 123.6, \ 119.3, \ 118.9, \ 116.7, \ 108.8, \ 69.9, \ 31.3, \ 19.3, \ 13.9.}\]

\[^{19}\text{F \ NMR} \ (471 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ -150.6, \ -150.7.\]

\textbf{HRMS-ESI(m/z) calc'd for } C_{26}\text{H}_{22}\text{O}_{2}\text{S}_{2}\text{Br}^{+} \ [\text{M-BF}_4]^+; \ 493.0290; \text{ found } 493.0285; \text{ deviation } 1.1 \text{ ppm.}\]

\textbf{Thienothiophene-derived dibenzothiophenium salt S4}

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene (400 mg, 2.85 mmol, 1.00 equiv.), thianthrene-S-oxide (571 mg, 2.85 mmol, 1.0 equiv.), and DCM (11 ml, c = 0.26 M). The mixture was cooled to –78 °C, subsequently trifluoroacetic acid anhydride (1.21 ml, 1.80 g, 8.56 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was stirred at –78 °C for 30 min, then allowed to warm to 25 °C, over a period of approximately 1 h. The reaction mixture was stirred at 25 °C for 12 h. Subsequently, the reaction mixture was diluted with DCM (25 ml). The organic phase was washed with aqueous NaHCO\textsubscript{3} solution (saturated, 30 ml). The aqueous layer was extracted with DCM (2 × 20 ml). The combined organic layers were dried with MgSO\textsubscript{4}. The solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 620 mg (51 %) of compound S4 as green-brown solid.

\(R_f = 0.50 \ (\text{DCM / MeOH, 10 / 1 (v/v))}.\)

\textbf{NMR Spectroscopy:}

\[^1\text{H} \text{ NMR} \ (500 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ 9.31 \ (\text{s, } 1\text{H}), \ 8.41 \ (\text{d, } J = 8.0 \text{ Hz, } 2\text{H}), \ 8.11 \ (\text{dd, } J = 7.8, \ 1.1 \text{ Hz, } 2\text{H}), \ 7.84 \ (\text{t, } J = 7.6 \text{ Hz, } 2\text{H}), \ 7.70 \ (\text{d, } J = 5.3 \text{ Hz, } 1\text{H}), \ 7.65 \ (\text{t, } J = 7.7 \text{ Hz, } 2\text{H}), \ 7.11 \ (\text{d, } J = 5.3 \text{ Hz, } 1\text{H}).\]

\[^{13}\text{C} \ {^{1}\text{H} \text{ NMR} \ (126 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ 145.8, \ 139.3, \ 138.2, \ 137.0, \ 134.7, \ 134.4, \ 134.1, \ 131.8, \ 129.4, \ 123.6, \ 121.5, \ 119.5. \text{ C-atoms of trifluoroacetate ion were not detected.}\]

\[^{19}\text{F \ NMR} \ (471 \text{ MHz, } \text{CDCl}_3, \ 298 \text{ K, } \delta): \ -75.3 \ (\text{s}).\]

\textbf{HRMS-ESI(m/z) calc'd for } C_{18}\text{H}_{11}\text{S}_{3}^{+} \ [\text{M-TFA}]^{+}, \ 323.0017; \text{ found } 323.0015; \text{ deviation } 0.8 \text{ ppm.}\]
**2-Phenylthiophene-derived dibenzothiophenium salt S5**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with dibenzothiophene-S-oxide (0.50 g, 2.5 mmol, 1.0 equiv.), 2-phenylthiophene (0.40 g, 2.5 mmol, 1.0 equiv.), and MeCN (5 ml, c = 0.5 M). The mixture was cooled to −78 °C, subsequently trifluoroacetic acid anhydride (0.53 mL, 3.8 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C, over a period of 20 min. Subsequently, the mixture was stirred for 1 h at 25 °C. Subsequently, the reaction mixture was diluted with DCM (30 ml) and washed with water (3 × 30 ml). The organic layer was dried with MgSO$_4$. The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 17 / 3) to afford 1.01 g (89 %) of compound S5 as pale yellow, highly viscous oil.

$R_f = 0.33$ (DCM / MeOH, 9 / 1 (v/v)).

**NMR Spectroscopy:**

$^1$H NMR (500 MHz, CD$_3$CN, 298 K, δ): 8.35 – 8.30 (m, 3H), 8.21 (d, J = 8.1 Hz, 2H), 7.94 (q, J = 7.6 Hz, 2H), 7.73 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 4.0 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H).

$^{13}$C $^1$H NMR (126 MHz, CD$_3$CN, 298 K, δ): 157.9, 144.5, 139.5, 135.7, 134.6, 132.7, 132.5, 131.2, 130.4, 129.0, 127.2, 126.2, 125.5, 120.6. C-atoms of the trifluoroacetate ion were not detected.

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, δ): –76.3 (s).

**HRMS-ESI (m/z)** calc’d for C$_{22}$H$_{15}$S$_2^+$ [M-TFA]$^+$, 343.0610; found 343.0606; deviation 1.0 ppm.

**2-Chlorothiophene-derived dibenzothiophenium salt S6**

Dibenzothiophene-S-oxide (0.50 g, 2.5 mmol, 1.0 equiv.) and 2-chlorothiophene (0.70 ml, 7.5 mmol, 3.0 equiv.) were suspended in acetonitrile (5 ml, c = 0.5 M). At 0 °C, tetrafluoroboric acid diethyl ether complex (0.37 ml, 2.7 mmol, 1.1 equiv.) and trifluoroacetic acid anhydride (0.70 mL, 5.0 mmol, 2.0 eq.) were added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C, and was stirred for 2 h. Subsequently, EtOAc (10 ml) and aqueous NaHCO$_3$ solution (saturated, 10 ml) were added under vigorous stirring. The organic phase was separated, and the aqueous layer was extracted with EtOAc (2 × 20 ml).
combined organic layers were washed with aqueous NaBF₄ solution (10 % (w/w), 2 × 20 mL), dried over MgSO₄, and concentrated under reduced pressure. The resulting solid was washed with DCM (2 ml) to afford 610 mg (63 %) of dibenzothiophenium salt S6 as colorless crystals.

Rₛ = 0.36 (DCM / MeOH, 9 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CD₃CN, 298 K, δ): 8.31 (dd, J = 7.9, 1.2 Hz, 2H), 8.17 – 8.11 (m, 3H), 7.96 (ψtd, J = 7.7, 1.1 Hz, 2H), 7.75 (ddd, J = 8.4, 7.6, 1.2 Hz, 2H), 7.21 (d, J = 4.3 Hz, 1H).

¹³C {¹H} NMR (126 MHz, CD₃CN, 298 K, δ): 143.8, 143.3, 139.5, 136.0, 133.8, 132.9, 130.4, 129.0, 125.7, 120.9.

¹⁹F NMR (471 MHz, CD₃CN, 298 K, δ): –151.2, –151.3.

HRMS-ESI (m/z) calc’d for C₁₆H₁₀S₂Cl⁺ [M-BF₄]⁺, 300.9907; found 300.9904; deviation 1.0 ppm.

Benzothiazol-substituted thiophene-derived thianthrenium salt S7

Under an atmosphere of argon, a 50 ml round bottom flask equipped with a teflon coated stir bar was charged with benzothiazolylthiophen (1.00 g, 4.60 mmol, 1.0 equiv.), thianthrene-S-oxide (1.07 g, 4.60 mmol, 1.0 equiv.), and DCM (10 ml, c = 0.46 M). The mixture was cooled to 0 °C, subsequently trimethylsilyltriflate (0.83 ml, 1.0 g, 4.6 mmol, 1.0 equiv.) and trifluoroacetic acid anhydride (1.6 ml, 2.4 g, 11.5 mmol, 2.5 eq.) were added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C over a period of approximately 30 min. The reaction mixture was stirred at 25 °C. Subsequently, the reaction mixture was washed with aqueous NaHCO₃ solution (saturated, 15 ml), washed with water (15 ml), and washed with aqueous NaBF₄ solution (10 % (w/w), 2 × 15 ml). The resulting precipitate was dissolved by addition of approx. 0.3 L of DCM. The organic layer was washed with aqueous NaBF₄ solution (10 % (w/w), 50 ml). The organic phase was dried over MgSO₄, and loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 2.65 g (95 %) of compound S7·CH₂Cl₂ as yellow crystals.

Rₛ = 0.59 (DCM / MeOH, 9 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CD₃CN, 298 K, δ): 8.34 (dd, J = 8.1, 1.3 Hz, 2H), 8.02 – 7.95 (m, 3H), 7.94 – 7.86 (m, 3H), 7.78 (ddd, J = 8.0, 7.4, 1.3 Hz, 2H), 7.66 (d, J = 4.2 Hz, 1H), 7.63 (d, J = 4.2 Hz, 1H), 7.52 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.45 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 5.44 (s, 2H).

¹³C {¹H} NMR (126 MHz, CD₃CN, 298 K, δ): 159.6, 154.0, 147.5, 139.7, 136.9, 136.4, 136.3, 135.0,
131.5, 131.2, 129.6, 128.2, 127.6, 125.5, 124.2, 123.3, 120.5, 55.3.

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, $\delta$): −151.46, −151.52.

HRMS-ESI (m/z) calc’d for C$_{23}$H$_{14}$NS$_4^{+}$ [M-TFA]$^+$, 432.0004; found 432.0003; deviation 0.1 ppm.

Imidazopyridine-derived dibenzo thiophenium salt S$^8$

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine (590 mg, 5.0 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (1.0 g, 5.0 mmol, 1.0 equiv.), and MeCN (15 ml, c = 0.33 M). The mixture was cooled to −78 °C, subsequently trifluoroacetic acid anhydride (1.0 ml, 1.6 g, 7.5 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C, over a period of 1 h. The reaction mixture was stirred at 25 °C for 24 h. Subsequently, the reaction mixture was diluted with DCM (15 ml) and washed with water (30 ml). The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 4 / 1) to afford 1.50 g (72 %) of compound S$^8$ as colorless crystals.

$R_f = 0.21$ (DCM / MeOH, 10 / 1 (v/v)).

NMR Spectroscopy:

$^1$H NMR (500 MHz, CD$_3$CN, 298 K, $\delta$): 8.75 (s, 1H), 8.43 (dd, $J = 8.1, 1.3$ Hz, 2H), 8.08 (dd, $J = 8.1, 0.8$ Hz, 2H), 7.95 (qd, $J = 7.6, 1.0$ Hz, 2H), 7.79 (d, $J = 9.0$ Hz, 1H), 7.69 (ddd, $J = 8.4, 7.4, 1.2$ Hz, 2H), 7.54 (ddd, $J = 9.0, 7.0, 1.2$ Hz, 1H), 7.06 (d, $J = 7.0$ Hz, 1H), 6.87 (td, $J = 6.9, 1.2$ Hz, 1H).

$^{13}$C {${}^1$H} NMR (126 MHz, CD$_3$CN, 298 K, $\delta$): 160.30 (q, $J = 31$ Hz), 152.7, 150.6, 140.1, 135.5, 132.6, 131.7, 129.1, 127.8, 126.3, 125.8, 120.0, 118.65 (q, $J = 298$ Hz), 117.6, 95.3.

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, $\delta$): −75.3 (s).

HRMS-ESI (m/z) calc’d for C$_{19}$H$_{13}$N$_2$S$^+$ [M-TFA]$^+$, 301.0794; found 301.0792; deviation 0.8 ppm.
BINOL-dimethylether-derived thianthrenium salt S9

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with BINOL-dimethylether (250 mg, 0.80 mmol, 1.0 equiv.), thianthrene-S-oxide (365 mg, 1.6 mmol, 2.0 equiv.), and DCM (3 ml, c = 0.27 M). The mixture was cooled to −78 °C, subsequently trifluoroacetic acid anhydride (0.37 ml, 0.50 g, 2.4 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was stirred at −78 °C for 30 min, then allowed to warm to 25 °C, over a period of approximately 1 h. The reaction mixture was stirred at 25 °C for 12 h. Subsequently, the reaction mixture was diluted with DCM (10 ml). The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 320 mg (45 %) of compound S9 as brown solid.

Rf = 0.67 (DCM / MeOH, 4 / 1 (v/v)).

NMR Spectroscopy:

$^1$H NMR (500 MHz, CDCl₃, 298 K, δ): 8.67 (ddd, J = 8.2, 6.6, 1.7 Hz, 4H), 8.05 (s, 2H), 7.98 (d, J = 9.2 Hz, 2H), 7.80 – 7.67 (m, 12H), 7.44 (d, J = 9.3 Hz, 2H), 6.90 (d, J = 1.5 Hz, 4H), 3.70 (s, 6H).

$^{13}$C ($^1$H) NMR (126 MHz, CDCl₃, 298 K, δ): 157.8, 136.5, 135.5, 135.4, 134.68, 134.66, 131.7, 131.3, 130.3, 130.21, 130.18, 130.1, 128.4, 127.9, 123.1, 119.5, 119.3, 118.3, 117.9, 115.5, 56.6. C-atoms of the trifluoroacetate anion were not detected.

$^{19}$F NMR (471 MHz, CDCl₃, 298 K, δ): −74.8 (s).

HRMS-ESI (m/z) calc’d for C₄₆H₃₂O₃S₄²⁺ [M-2TFA]²⁺, 372.0637; found 372.0630; deviation 1.8 ppm.

3-Phenylthiophen-derived dibenzothiophenium salt S10
Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 3-phenylthiophene (0.50 g, 3.1 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (0.76 g, 82% dibenzothiophen-S-oxide, rest sulfone, 3.1 mmol, 1.0 equiv.), and MeCN (5 ml, c = 0.6 M). The mixture was cooled to –78 °C, subsequently trifluoroacetic acid anhydride (1.3 mL, 2.0 g, 9.4 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C, over a period of 1 h. Subsequently, the reaction mixture was diluted with DCM (10 ml) and washed with water (2 × 30 ml). The organic layer was dried with MgSO₄. The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 4 / 1) to afford 1.17 g (82%) of compound S₁₀ as pale yellow highly viscous oil.

Rₛ = 0.14 (DCM / MeOH, 9 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CDCl₃, 298 K, δ): 8.07 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 7.81 – 7.75 (m, 3H), 7.71 (d, J = 6.8 Hz, 2H), 7.57 (q, J = 7.8 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.21 (d, J = 5.2 Hz, 1H).

¹³C {¹H} NMR (126 MHz, CDCl₃, 298 K, δ): 154.4, 138.4, 136.2, 134.5, 132.9, 131.7, 131.6, 131.5, 129.9, 129.7, 129.2, 128.4, 124.2, 117.1. C-atoms of trifluoroacetate ion were not detected.

¹⁹F NMR (471 MHz, CDCl₃, 298 K, δ): –74.8 (s).

HRMS-ESI (m/z) calc’d for C₂₂H₁₅S₂⁺ [M-TFA]⁺, 343.0610; found 343.0606; deviation 1.2 ppm.

Methoxyquinolin-derived thianthrenium salt S₁₁

A flame-dried, argon-filled Schlenk-tube equipped with a magnetic stir bar was charged with methoxy methyl quinoline (866 mg, 5.00 mmol, 1.00 equiv.), thianthrene S-oxide (1.16 g, 5.00 mmol, 1.00 equiv.), and dry MeCN (20 mL, c = 0.25 M). After cooling to 0 °C, trifluoroacetic anhydride (2.09 mL, 3.16 g, 15.0 mmol, 3.00 equiv.) was added while stirring. Trimethylsilyl trifluoromethanesulfonate (1.81 mL, 2.22 g, 10.0 mmol, 2.00 equiv.) was added dropwise. The mixture was stirred at 0 °C for 1 h, then at ambient temperature for 14 h. The reaction mixture was diluted with DCM. The solution was washed with aqueous NaHCO₃ solution, and subsequently with aqueous NaBF₄ solution. The organic phase was dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM / MeOH (47:3 (v/v)) to afford 1.558 g (66%) of S₁₁ as colorless solid.

Rₛ = 0.58 (DCM / MeOH, 10 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, DMSO-d₆, 298 K, δ): 8.66 (d, J = 9.5 Hz, 1H), 8.59 (d, J = 8.6 Hz, 1H), 8.10 (d, J =
9.6 Hz, 1H), 8.04 (dd, J = 7.9, 1.3 Hz, 2H), 7.76 (t, d, J = 7.6, 1.2 Hz, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.54 (ddd, J = 8.5, 7.3, 1.3 Hz, 2H), 7.40 (dd, J = 8.3, 1.2 Hz, 2H), 3.81 (s, 3H), 2.72 (s, 3H).

$^{13}$C {$^1$H} NMR (126 MHz, DMSO-$d_6$, 298 K, $\delta$): 160.8, 158.7, 143.4, 140.4, 132.8, 131.6, 130.8, 129.8, 129.7, 128.1, 127.9, 125.0, 123.1, 118.4, 96.0, 57.7, 24.4.

$^{19}$F NMR (471 MHz, DMSO-$d_6$, 298 K, $\delta$): –148.2, –148.3.

HRMS-ESI (m/z) calc’d for C$_{23}$H$_{18}$NOS$_2$ $^+$ [M-BF$_4$]$^+$, 388.0824; found 388.0825; deviation 0.3 ppm.

**Methoxynaphthalin-derived diphenylsulfonium salt S12**

Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with 2-methoxynaphthalene (1.58 g, 10.0 mmol, 1.0 equiv.), diphenylsulfoxide (2.02 g, 10.0 mmol, 1.0 equiv.), and DCM (40 ml, c = 0.25 M). The mixture was cooled to 0°C, subsequently, trifluoroacetic acid anhydride (2.82 mL, 4.20 g, 20.0 mmol, 2.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.68 ml, 0.81 g, 5.0 mmol, 0.50 equiv.) was added dropwise at 0°C. The reaction mixture was allowed to warm to 25°C, and stirred at 25°C for 1 h. Subsequently, the reaction mixture was poured onto aqueous NaHCO$_3$ solution (saturated, 120 ml). The reaction mixture was stirred for 5 min. The organic layer was separated and subsequently washed with NaBF$_4$ solution (10 % (w/w), 3 x 50 ml). The organic layer was dried with MgSO$_4$. The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 1 / 1) to afford 2.27 g (53 %) of compound S12 as colorless solid. $R_f = 0.47$ (DCM / MeOH, 9 / 1 (v/v)).

**NMR Spectroscopy:**

$^1$H NMR (500 MHz, CD$_3$CN, 298 K, $\delta$): 8.52 – 8.46 (m, 2H), 8.09 (ddd, J = 8.2, 1.4, 0.7 Hz, 1H), 7.82 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.74 – 7.72 (m, 3H), 7.69 – 7.65 (m, 3H), 7.63 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.58 (d, J = 9.2 Hz, 1H), 7.34 (s, 3H).

$^{13}$C {$^1$H} NMR (128 MHz, CD$_3$CN, 298 K, $\delta$): 161.7, 140.7, 134.8, 134.7, 131.9, 131.6, 131.2, 130.6, 130.4, 126.8, 124.8, 122.5, 115.8, 101.4, 57.6.

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, $\delta$): –151.7, –151.8.

HRMS-ESI (m/z) calc’d for C$_{23}$H$_{18}$OS$^+$ [M-BF$_4$]$^+$, 343.1151; found 343.1148; deviation 0.7 ppm.
Anthracen-derived diphenylsulfonium salt S13

Under an ambient atmosphere, a 250 ml round bottom flask equipped with a teflon coated stir bar was charged with anthracen (2.00 g, 11.2 mmol, 1.0 equiv.), diphenylsulfoxide (2.27 g, 11.2 mmol, 1.0 equiv.), and DCM (100 ml, c = 0.11 M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (4.7 mL, 7.1 g, 33.7 mmol, 3.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.5 mL, 0.60 g, 3.7 mmol, 0.33 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 5 h. Subsequently, the reaction mixture was poured onto aqueous NaHCO₃ solution (saturated, 100 ml), and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography and on silica gel eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 3 / 2). The product containing solutions were washed with aqueous NaBF₄ solution (20 % (w/w), 3 × 25 ml). The organic layer was dried with MgSO₄. The solvent was removed to afford 1.86 g (37 %) of compound S13 as yellow solid.

Rₛ = 0.55 (DCM / MeOH, 9 / 1 (v/v)).

NMR Spectroscopy:

$^1$H NMR (500 MHz, CDCl₃, 298 K, δ): 9.12 (s, 1H), 8.44 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 7.8 Hz, 2H), 7.82 – 7.61 (m, 14H).

$^{13}$C ($^1$H) NMR (128 MHz, CDCl₃, 298 K, δ): 139.6, 134.3, 134.1, 132.1, 131.83, 131.76, 131.0, 129.6, 127.1, 123.4, 122.8, 109.5.

$^{19}$F NMR (471 MHz, CDCl₃, 298 K, δ): −152.91, −152.95.

HRMS-ESI (m/z) calc’d for C$_{26}$H$_{19}$S$^+$ [M-BF$_4$]$^+$, 363.1202; found 363.1197; deviation 1.4 ppm.

Bithiophen-derived dibenzothiophenium salt 1

Under an ambient atmosphere, a 50 ml round bottom flask equipped with a teflon coated stir bar was charged with dibenzothiophene-S-oxide (2.44 g, 82 % (w/w) rest dibenzothiophene sulfone, 10 mmol, 1.0 equiv.),
bithiophene (1.746 g, 10.5 mmol, 1.05 equiv.), and MeCN (15 ml, c = 0.67 M). The mixture was cooled to –78 °C, subsequently trifluoroacetic acid anhydride (2.09 mL, 15 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C, over a period of approximately 20 min, and subsequently stirred for 1 h at 25 °C. Subsequently, the reaction mixture was diluted with DCM (30 ml) and washed with water (2 × 50 ml). The organic layer was dried with MgSO₄. The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 4.05 g (88 %) of compound 1 as a brown solid.

R_f = 0.34 (DCM / MeOH, 9 / 1 (v/v)).

**NMR Spectroscopy:**

^1H NMR (500 MHz, CDCl₃, 298 K, δ): 8.78 (d, J = 4.1 Hz, 1H), 8.43 – 8.39 (m, 2H), 8.11 (dd, J = 7.8, 1.1 Hz, 2H), 7.84 (qqd, J = 7.6, 1.1 Hz, 2H), 7.67 (ddd, J = 8.5, 7.5, 1.2 Hz, 2H), 7.31 (dd, J = 5.0, 1.2 Hz, 1H), 7.18 (d, J = 4.2 Hz, 1H), 7.09 (dd, J = 3.7, 1.2 Hz, 1H), 6.97 (dd, J = 5.1, 3.7 Hz, 1H).

^13C (^1H) NMR (126 MHz, CDCl₃, 298 K, δ): 149.6, 144.9, 138.2, 134.42, 134.38, 134.2, 131.8, 129.2, 128.5, 128.0, 126.8, 125.1, 123.7, 118.7. C-atoms of the trifluoroacetate ion were not detected.

^19F NMR (471 MHz, CDCl₃, 298 K, δ): –75.0 (s).

HRMS-ESI (m/z) calc’d for C_{20}H_{13}S_{3}^+ [M-TFA]^+ , 349.0144; found 349.0171; deviation 1.0 ppm.

**Pyrazole-substituted bithiophene 2**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), K₂CO₃ (250 mg, 1.81 mmol, 3.4 equiv.), pyrazole (100 mg, 1.47 mmol, 2.7 equiv.), and DMSO (10 ml, c = 0.054 M). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 4 / 1 (v/v)) to afford 117 mg (94 %) of compound 2 as yellowish oil.

R_f = 0.92 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**
Methoxymethylbenzoate-derived thianthrenium salt 3

Methoxymethylbenzoate-derived thianthrenium salt was prepared as described previously.\textsuperscript{4b}

Side reaction with the methoxymethylbenzoate-derived thianthrenium salt, compound 4

\[
\begin{align*}
\text{OMe} & \quad \text{O} & \quad \text{OMe} & \quad \text{BF}_4^- \\
\text{S} & \quad \text{S} \\
3 & \quad \xrightarrow{2.0 \text{ equiv. KCN}} \quad \text{DMSO, 60 °C, 20 h} \\
\text{OMe} & \quad \text{CN} & \quad \text{OMe}
\end{align*}
\]

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 2-methoxymethylbenzoate-derived thianthrenium salt 3 (375 mg, 0.80 mmol, 1.0 equiv.), KCN (104 mg, 1.60 mmol, 2.0 equiv.), and DMSO (10 ml, c = 0.08 M). The vial was sealed, and the reaction mixture was subsequently stirred for 20 h at 60 °C. Subsequently, the reaction mixture was diluted aqueous Fe(OAc)\textsubscript{2} solution (200 mg Fe(OAc)\textsubscript{2} in 5 ml H\textsubscript{2}O). The mixture was stirred for 10 min at ambient temperature, and subsequently poured onto a biphasic mixture of EtOAc (150 ml) and water (150 ml). The layers were separated. The aqueous layer was extracted with EtOAc (2 x 50 ml). The combined organic layers were washed with water (50 ml) and subsequently dried over MgSO\textsubscript{4}. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (19 / 1 gradient to 3 / 2 (v/v)) to afford 32 mg (21 %) of compound 4 as colorless oil.

\(R_f = 0.41\) (hexanes / EtOAc, 7 / 3 (v/v)).

**NMR Spectroscopy:**

\(^1\text{H NMR}\) (500 MHz, CDCl\textsubscript{3}, 298 K, \(\delta\)):\n7.70 (d, \(J = 8.6\) Hz, 1H), 7.59 (d, \(J = 2.7\) Hz, 1H), 7.11 (dd, \(J = 8.6, 2.7\) Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H).

\(^{13}\text{C} \{^1\text{H}\} \text{NMR}\) (126 MHz, CDCl\textsubscript{3}, 298 K, \(\delta\)):\n164.5, 162.5, 136.4, 134.4, 118.5, 118.0, 116.6, 104.5, 56.0, 53.0.

NMR data of compound 4 match with the NMR data reported in the literature.\textsuperscript{18}
Pyrazol-substituted imidazopyridazine 5 (CCDC 1987150)

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridazine-derived dibenzothiophenium salt S1 (200 mg, 0.48 mmol, 1.0 equiv.), K$_2$CO$_3$ (266 mg, 1.93 mmol, 4.0 equiv.), pyrazol (98 mg, 1.44 mmol, 3.0 equiv.), and DMSO (10 ml, c = 0.05 M). The vial was sealed and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with water (10 ml). The reaction mixture was extracted with EtOAc (4 × 20 ml). The combined organic layers were dried with MgSO$_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 3 (v/v)) to afford 72 mg (80 %) of compound 5 as colorless solid.

R$_f$ = 0.48 (hexanes / EtOAc, 4 / 1 (v/v)).

**NMR Spectroscopy:**

$^1$H NMR (500 MHz, CDCl$_3$, 298 K, δ): 8.34 (dd, J = 2.6, 0.7 Hz, 1H), 8.31 (dd, J = 4.5, 1.6 Hz, 1H), 8.23 (d, J = 0.6 Hz, 1H), 7.87 (ddd, J = 9.2, 1.7, 0.7 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.06 (dd, J = 9.1, 4.5 Hz, 1H), 6.46 (dd, J = 2.5, 1.7 Hz, 1H).

$^{13}$C ($^1$H) NMR (126 MHz, CDCl$_3$, 298 K, δ): 144.4, 143.2, 142.1, 137.2, 127.4, 124.5, 117.4, 107.5, 104.6.

**HRMS-ESI (m/z)** calc’d for C$_9$H$_8$N$_5$ [M+H]$^+$, 186.0774; found 186.0773; deviation 0.4 ppm.

**X-ray crystallography:**

Sample preparation: Vapor diffusion technique was used to grow the crystals. Compound 5 (approx. 5mg) was dissolved in 1.5 mL DCM in a 4 mL glass vial. The vial with the solution was placed inside a 20 mL glass vial filled with 3 mL pentane. The 20 ml vial was sealed and the vials were left at ambient temperature for three days to yield the crystals that were used for the analysis.

X-ray measurement:

device: Bruker AXS Enraf-Nonius KappaCCD
method: CCD f- and w-scans
radiation: Mo-Kα
wavelength: 0.71073 Å
radiation source: 0.2 x 2 mm$^2$ focus rotating anode

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.
Fig. S2: Crystal structure of compound 5. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S3. Crystal data and structure refinement.

| Property          | Value                                      |
|-------------------|--------------------------------------------|
| Identification code | 12857                                      |
| Empirical formula  | C₉H₇N₅                                      |
| Color             | colourless                                 |
| Formula weight    | 185.20 g·mol⁻¹                              |
| Temperature       | 100(2) K                                   |
| Wavelength        | 0.71073 Å                                  |
| Crystal system    | Monoclinic                                 |
| Space group       | P 2₁/n, (No. 14)                            |
| Unit cell dimensions | a = 5.4868(3) Å  \(\alpha = 90^\circ\).  |
|                    | b = 13.7279(12) Å  \(\beta = 99.788(5)^\circ\).  |
|                    | c = 11.0932(7) Å  \(\gamma = 90^\circ\).  |
| Volume            | 823.40(10) Å³                              |
| Z                 | 4                                          |
| Property                          | Value                  |
|----------------------------------|------------------------|
| Density (calculated)             | 1.494 Mg·m$^{-3}$      |
| Absorption coefficient           | 0.100 mm$^{-1}$        |
| F(000)                           | 384 e                  |
| Crystal size                     | 0.37 x 0.3 x 0.17 mm$^3$ |
| $\theta$ range for data collection | 2.968 to 48.137°.     |
| Index ranges                     | $-11 \leq h \leq 11$, $-28 \leq k \leq 28$, $-23 \leq l \leq 23$ |
| Reflections collected            | 54162                  |
| Independent reflections          | 7910 [$R_{int} = 0.0402$] |
| Reflections with $I > 2\sigma(I)$ | 5629                  |
| Completeness to $\theta = 25.242^\circ$ | 99.0 %         |
| Absorption correction            | Gaussian               |
| Max. and min. transmission       | 0.98426 and 0.96449    |
| Refinement method                | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters   | 7910 / 0 / 149         |
| Goodness-of-fit on $F^2$         | 1.049                  |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0396$        |
|                                  | w$R^2 = 0.1074$        |
| R indices (all data)             | $R_1 = 0.0669$        |
|                                  | w$R^2 = 0.1157$        |
| Extinction coefficient           | n/a                   |
| Largest diff. peak and hole      | 0.544 and -0.285 e·Å$^{-3}$ |
Table S4. Bond lengths [Å] and angles [°].

| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| N(4A)-N(5A)           | 1.3613(6)  | N(4A)-C(7A)           | 1.3619(6)  |
| N(4A)-C(1A)           | 1.3942(6)  | N(2A)-N(3A)           | 1.3508(6)  |
| N(2A)-C(3A)           | 1.3903(6)  | N(2A)-C(2A)           | 1.3718(6)  |
| N(3A)-C(6A)           | 1.3147(7)  | N(5A)-C(9A)           | 1.3272(7)  |
| N(1A)-C(3A)           | 1.3369(6)  | N(1A)-C(1A)           | 1.3583(6)  |
| C(6A)-C(5A)           | 1.4186(7)  | C(3A)-C(4A)           | 1.4096(6)  |
| C(7A)-C(8A)           | 1.3758(7)  | C(5A)-C(4A)           | 1.3686(7)  |
| C(9A)-C(8A)           | 1.4134(8)  | C(1A)-C(2A)           | 1.3783(6)  |
| C(1B)-C(2B)           | 1.330(18)  | C(1B)-N(4B)           | 1.300(14)  |
| C(1B)-N(1B)           | 1.340(16)  | C(3B)-N(2B)           | 1.3900     |
| C(3B)-C(4B)           | 1.3900     | C(3B)-N(1B)           | 1.319(13)  |
| N(2B)-N(3B)           | 1.3900     | N(2B)-C(2B)           | 1.325(15)  |
| N(3B)-C(6B)           | 1.3900     | C(6B)-C(5B)           | 1.3900     |
| C(5B)-C(4B)           | 1.3900     | N(4B)-C(7B)           | 1.4200     |
| N(4B)-N(5B)           | 1.4200     | C(7B)-C(8B)           | 1.4200     |
| C(8B)-C(9B)           | 1.4200     | C(9B)-N(5B)           | 1.4200     |
| N(5A)-N(4A)-C(7A)     | 112.70(4)  | N(5A)-N(4A)-C(1A)     | 119.31(4)  |
| C(7A)-N(4A)-C(1A)     | 127.99(4)  | N(3A)-N(2A)-C(3A)     | 126.50(4)  |
| N(3A)-N(2A)-C(2A)     | 125.43(4)  | C(2A)-N(2A)-C(3A)     | 108.07(4)  |
| C(6A)-N(3A)-N(2A)     | 114.07(4)  | C(9A)-N(5A)-N(4A)     | 104.04(4)  |
| C(3A)-N(1A)-C(1A)     | 104.01(4)  | N(3A)-C(6A)-C(5A)     | 124.95(4)  |
| N(2A)-C(3A)-C(4A)     | 117.60(4)  | N(1A)-C(3A)-N(2A)     | 110.78(4)  |
| N(1A)-C(3A)-C(4A)     | 131.60(4)  | N(4A)-C(7A)-C(8A)     | 106.34(5)  |
| C(4A)-C(5A)-C(6A)     | 119.69(5)  | N(5A)-C(9A)-C(8A)     | 112.20(5)  |
| C(5A)-C(4A)-C(3A)     | 117.18(5)  | N(1A)-C(1A)-N(4A)     | 120.60(4)  |
| N(1A)-C(1A)-C(2A)     | 113.67(4)  | C(2A)-C(1A)-N(4A)     | 125.72(4)  |
| N(2A)-C(2A)-C(1A)     | 103.47(4)  | C(7A)-C(8A)-C(9A)     | 104.73(5)  |
| C(2B)-C(1B)-N(1B)     | 113.3(12)  | N(4B)-C(1B)-C(2B)     | 123.0(12)  |
| N(4B)-C(1B)-N(1B)     | 123.8(11)  | N(2B)-C(3B)-C(4B)     | 120.0      |
| N(1B)-C(3B)-N(2B)     | 107.2(7)   | N(1B)-C(3B)-C(4B)     | 132.8(7)   |
| N(3B)-N(2B)-C(3B)     | 120.0      | C(2B)-N(2B)-C(3B)     | 109.8(8)   |
| C(2B)-N(2B)-N(3B)     | 130.2(8)   | N(2B)-N(3B)-C(6B)     | 120.0      |
| C(5B)-C(6B)-N(3B)     | 120.0      | C(6B)-C(5B)-C(4B)     | 120.0      |
| C(5B)-C(4B)-C(3B)     | 120.0      | N(2B)-C(2B)-C(1B)     | 104.0(11)  |
Benzotriazol-substituted imidazopyridazine 6 (CCDC 1987148)

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridazine-derived dibenzothiophenium salt S1 (200 mg, 0.48 mmol, 1.0 equiv.), K₂CO₃ (266 mg, 1.93 mmol, 4.0 equiv.), benzotriazol (172 mg, 1.44 mmol, 3.0 equiv.), and DMSO (10 ml, c = 0.05 M). The vial was sealed and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with water (10 ml). The reaction mixture was extracted with EtOAc (4 × 20 ml). The combined organic layers were dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 7 / 13 (v/v)) to afford 75 mg (66 %) of compound 6 as colorless solid and 10 mg (9 %) of compound S₁⁴ as colorless solid.

Compound S₁⁴:

\[ R_f = 0.37 \text{ (hexanes / EtOAc, 4 / 1 (v/v)).} \]

NMR Spectroscopy:

\[ ^1H \text{ NMR (500 MHz, CDCl}_3, 298 K, \delta): 8.62 (d, J = 0.6 Hz, 1H), 8.42 (dd, J = 4.5, 1.6 Hz, 1H), 8.08 – 8.03 (m, 1H), 7.96 (dd, J = 6.6, 3.1 Hz, 2H), 7.45 (dd, J = 6.7, 3.0 Hz, 2H), 7.18 (dd, J = 9.2, 4.5 Hz, 1H). \]

\[ ^13C \text{ \{^1H\} NMR (126 MHz, CDCl}_3, 298 K, \delta): 145.3, 144.2, 137.8, 127.7, 125.9, 118.6, 118.4, 107.8. \] One C-atom not detected.

HRMS-ESI (m/z) calc’d for C₁₂H₉N₆ [M+H]⁺, 237.0883; found 237.0881; deviation 0.8 ppm.

Compound 6:

\[ R_f = 0.73 \text{ (hexanes / EtOAc, 4 / 1 (v/v)).} \]

NMR Spectroscopy:

\[ ^1H \text{ NMR (500 MHz, CDCl}_3, 298 K, \delta): 8.57 (d, J = 0.6 Hz, 1H), 8.55 (dt, J = 8.4, 1.0 Hz, 1H), 8.43 (dd, J = 4.5, 1.6 Hz, 1H), 8.15 (dt, J = 8.4, 1.0 Hz, 1H), 8.04 (ddd, J = 9.2, 1.7, 0.7 Hz, 1H), 7.64 (ddd, J = 8.2, 7.0, 1.0 Hz, 1H), 7.47 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.18 (dd, J = 9.2, 4.5 Hz, 1H). \]
$^{13}$C \{H\} NMR (126 MHz, CDCl$_3$, 298 K, $\delta$): 146.2, 143.7, 141.9, 137.3, 131.7, 128.8, 125.1, 124.9, 119.8, 117.7, 113.0, 106.2.

HRMS-El (m/z) calc'd for C$_{12}$H$_9$N$_6$ [M+H]$^+$, 237.0883; found 237.0880; deviation 1.4 ppm.

**X-ray crystallography:**

Sample preparation: Vapor diffusion technique was used to grow the crystals. Compound 6 (approx. 5mg) was dissolved in 1.5 mL DCM in a 4 mL glass vial. The vial with the solution was placed inside a 20 mL glass vial filled with 3 mL pentane. The 20 mL vial was sealed and the vials were left at ambient temperature for three days to yield the crystals that were used for the analysis.

X-ray measurement:

device: Bruker AXS Enraf-Nonius KappaCCD

method: CCD f- and w-scans

radiation: Mo-K\(\alpha\)

wavelength: 0.71073 Å

radiation source: 0.2 x 2 mm$^2$ focus rotating anode

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.
**Fig. S3:** Crystal structure of compound 6. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

**Table S5. Crystal data and structure refinement.**

| Property                  | Value                        |
|---------------------------|------------------------------|
| Identification code       | 12856                        |
| Empirical formula         | C_{12}H_{8}N_{6}             |
| Color                     | colourless                   |
| Formula weight            | 236.24 g · mol\(^{-1}\)      |
| Temperature               | 100(2) K                     |
| Wavelength                | 0.71073 Å                    |
| Crystal system            | MONOCLINIC                   |
| Space group               | P2\(_1\)/n, (no. 14)         |
| Unit cell dimensions      | a = 8.5333(6) Å             |
|                           | \(\alpha = 90^\circ\).      |
| Property                                      | Value                        |
|----------------------------------------------|------------------------------|
| b                                            | 11.275(3) Å                 |
| c                                            | 10.7791(16) Å               |
| Volume                                       | 1037.1(3) Å³                |
| Z                                            | 4                            |
| Density (calculated)                         | 1.513 Mg · m⁻³              |
| Absorption coefficient                       | 0.101 mm⁻¹                  |
| F(000)                                       | 488 e                       |
| Crystal size                                 | 0.40 x 0.33 x 0.16 mm³      |
| θ range for data collection                  | 2.614 to 33.203°            |
| Index ranges                                 | -13 ≤ h ≤ 12, -17 ≤ k ≤ 17, -16 ≤ l ≤ 16 |
| Reflections collected                        | 22379                       |
| Independent reflections                      | 3956 [R_{int} = 0.0646]     |
| Reflections with I>2σ(I)                     | 3019                        |
| Completeness to θ = 25.242°                 | 99.8 %                      |
| Absorption correction                        | Gaussian                    |
| Max. and min. transmission                   | 0.99 and 0.96               |
| Refinement method                            | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 3956 / 0 / 164              |
| Goodness-of-fit on F²                        | 1.057                       |
| Final R indices [I>2σ(I)]                    | R₁ = 0.0487, wR² = 0.1343   |
| R indices (all data)                         | R₁ = 0.0683, wR² = 0.1453   |
| Extinction coefficient                       | 0.054(11)                   |
| Largest diff. peak and hole                  | 0.5 and -0.5 e · Å⁻³       |
Table S6. Bond lengths [Å] and angles [°].

|       | Bond Lengths [Å] |       | Bond Angles [°] |
|-------|------------------|-------|-----------------|
| N(1)-N(2) | 1.3712(11) | N(1)-C(1) | 1.3746(12) |
| N(1)-C(7)  | 1.4040(13) | N(2)-N(3) | 1.3021(12) |
| N(3)-C(6)  | 1.3828(13) | N(4)-N(5) | 1.3572(12) |
| N(4)-C(8)  | 1.3728(13) | N(4)-C(12) | 1.3908(12) |
| N(5)-C(9)  | 1.3153(14) | N(6)-C(7) | 1.3611(13) |
| N(6)-C(12) | 1.3393(13) | C(1)-C(2) | 1.4023(14) |
| C(1)-C(6)  | 1.4026(14) | C(2)-C(3) | 1.3808(15) |
| C(3)-C(4)  | 1.4142(16) | C(4)-C(5) | 1.3829(16) |
| C(5)-C(6)  | 1.4063(14) | C(7)-C(8) | 1.3778(14) |
| C(9)-C(10) | 1.4161(15) | C(10)-C(11) | 1.3679(15) |
| C(11)-C(12) | 1.4121(14) |      |      |

|       | Bond Lengths [Å] |       | Bond Angles [°] |
|-------|------------------|-------|-----------------|
| N(2)-N(1)-C(1) | 110.16(8) | N(2)-N(1)-C(7) | 119.05(8) |
| C(1)-N(1)-C(7)  | 130.77(8) | N(3)-N(2)-N(1) | 108.97(8) |
| N(2)-N(3)-C(6)  | 108.26(8) | N(5)-N(4)-C(8) | 125.15(9) |
| N(5)-N(4)-C(12) | 126.82(9) | C(8)-N(4)-C(12) | 108.02(8) |
| C(9)-N(5)-N(4)  | 113.41(9) | C(12)-N(6)-C(7) | 103.85(8) |
| N(1)-C(1)-C(2)  | 133.99(9) | N(1)-C(1)-C(6) | 103.51(8) |
| C(2)-C(1)-C(6)  | 122.49(9) | C(3)-C(2)-C(1) | 115.60(10) |
| C(2)-C(3)-C(4)  | 122.70(10) | C(5)-C(4)-C(3) | 121.43(10) |
| C(4)-C(5)-C(6)  | 116.72(10) | N(3)-C(6)-C(1) | 109.10(9) |
| N(3)-C(6)-C(5)  | 129.86(10) | C(1)-C(6)-C(5) | 121.04(9) |
| N(6)-C(7)-N(1)  | 120.61(9) | N(6)-C(7)-C(8) | 113.71(9) |
| C(8)-C(7)-N(1)  | 125.67(9) | N(4)-C(8)-C(7) | 103.54(9) |
| N(5)-C(9)-C(10) | 125.50(10) | C(11)-C(10)-C(9) | 119.60(10) |
| C(10)-C(11)-C(12) | 117.30(10) | N(4)-C(12)-C(11) | 117.36(9) |
| N(6)-C(12)-N(4) | 110.86(8) | N(6)-C(12)-C(11) | 131.76(9) |
Cyano-substituted bromobutoxynaphthalene 7

Under an ambient atmosphere, a 25 ml round bottom flask equipped with a teflon coated stir bar and a reflux condenser was charged with bromobutoxynaphthalene-derived thianthrenium salt S3 (200 mg, 0.34 mmol, 1.0 equiv.), KCN (67 mg, 1.0 mmol, 3.0 equiv.), and MeCN (5 ml, c = 0.05 M). The reaction mixture was stirred at 80 °C for 3 d. The solvent was removed under reduced pressure. The residue was dissolved in a biphasic mixture of water (5 ml) and EtOAc (5 ml). The layers were separated. The organic layer was washed with aqueous FeSO₄ solution (10 ml, 0.1 M). The organic layer was dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 10 / 1 (v/v)) to afford 75.5 mg (72 %) of compound 7 as colorless solid.

Rᵣ = 0.37 (hexanes / EtOAc, 10 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CDCl₃, 298 K, δ): 8.48 (dt, J = 8.7, 1.0 Hz, 1H), 8.19 (dd, J = 9.1, 0.9 Hz, 1H), 7.81 (dd, J = 7.1, 1.1 Hz, 1H), 7.58 (dd, J = 8.7, 7.1 Hz, 1H), 7.43 (d, J = 9.1 Hz, 1H), 4.23 (t, J = 6.4 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.67 – 1.54 (m, 3H), 1.02 (t, J = 7.4 Hz, 3H).

¹³C {¹H} NMR (126 MHz, CDCl₃, 298 K, δ): 154.8, 133.1, 131.7, 131.0, 128.5, 126.7, 126.1, 117.8, 117.1, 110.5, 110.0, 70.0, 31.5, 19.4, 14.0.

HRMS-Cl (m/z) calc’d for C₁₅H₁₄NOBr [M]+, 303.0253; found 303.0257; deviation 1.1 ppm.

Benzimidazol-substituted thienothiophene 8 (CCDC 1987147)

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt S4 (100 mg, 0.229 mmol, 1.0 equiv.), K₂CO₃ (63 mg, 0.46 mmol, 2.0 equiv.), benzimidazol (47 mg, 0.40 mmol, 1.7 equiv.), and DMSO (1.5 ml, c = 0.15 M). The
vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was directly loaded onto a column of silica gel and purified by chromatography eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 45 mg (78 %) of compound 8 as colorless solid.

\[ R_f = 0.39 \text{ (hexanes / EtOAc, 1 / 1 (v/v))} \]

**NMR Spectroscopy:**

\[ ^1H \text{ NMR} \ (500 \text{ MHz, CD}_3\text{CN, 298 K, } \delta): \] 8.30 (s, 1H), 7.83 – 7.78 (m, 1H), 7.72 (d, \( J = 1.6 \text{ Hz, 1H} \)), 7.61 (dd, \( J = 5.2, 1.5 \text{ Hz, 1H} \)), 7.58 – 7.53 (m, 1H), 7.45 (d, \( J = 5.2 \text{ Hz, 1H} \)), 7.39 – 7.33 (m, 2H).

\[ ^{13}C \{'^1H}\text{ NMR} \ (126 \text{ MHz, CD}_3\text{CN, 298 K, } \delta): 144.7, 143.7, 140.7, 135.0, 134.4, 129.9, 128.0, 124.7, 123.9, 121.7, 121.5, 121.2, 112.1. \]

**HRMS-EI (m/z) calc’d for C_{13}H_8N_2S_2^+ [M]^+, 256.0123; found 256.0125; deviation 0.5 ppm.**

**X-ray crystallography:**

Sample preparation: Compound 8 was dissolved in warm acetone in a 4 ml vial. The open vial was left standing for 1 d at ambient temperature, resulting in the formation of colorless crystals.

X-ray measurement:

device: Bruker-AXS Kappa Mach3 APEX-II
method: ‘CCD f- and w-scans
radiation: Cu-K\( \alpha \)

wavelength: 1.54178 Å
radiation source: 0.2 x 2 mm\(^2\) focus rotating anode
Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.
**Fig. S4:** Crystal structure of compound 8. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

**Table S7. Crystal data and structure refinement.**

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Identification code           | 12773                                      |
| Empirical formula             | $\text{C}_{13}\text{H}_8\text{N}_2\text{S}_2$ |
| Color                         | colourless                                 |
| Formula weight                | 256.33 g · mol$^{-1}$                      |
| Temperature                   | 100(2) K                                   |
| Wavelength                    | 1.54178 Å                                  |
| Crystal system                | TRICLINIC                                  |
| Space group                   | P1, (no. 2)                                |
| Unit cell dimensions          | $a = 3.86470(10)$ Å, $\alpha = 89.7700(10)^\circ$ |
b = 9.8913(3) Å  \quad \beta = 87.9850(10)^\circ.

c = 14.0495(4) Å  \quad \gamma = 85.984(2)^\circ.

Volume 535.42(3) Å³

Z 2

Density (calculated) 1.590 Mg · m⁻³

Absorption coefficient 4.281 mm⁻¹

F(000) 264 e

Crystal size 0.183 x 0.101 x 0.031 mm³

θ range for data collection 3.147 to 72.410°.

Index ranges -4 ≤ h ≤ 4, -12 ≤ k ≤ 11, -17 ≤ l ≤ 17

Reflections collected 19864

Independent reflections 1985 [R_{int} = 0.0399]

Reflections with I>2σ(I) 1740

Completeness to θ = 67.679° 95.3 %

Absorption correction Gaussian

Max. and min. transmission 0.90 and 0.62

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 1985 / 0 / 154

Goodness-of-fit on F² 1.218

Final R indices [I>2σ(I)]  R₁ = 0.0364 \quad wR² = 0.0947

R indices (all data)  R₁ = 0.0414 \quad wR² = 0.0963

Largest diff. peak and hole 0.4 and -0.4 e · Å⁻³

Table S8. Bond lengths [Å] and angles [°].

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| S(1)-C(2)             | 1.726(2)| S(1)-C(3)             | 1.730(2)|
| S(2)-C(5)             | 1.729(2)| S(2)-C(6)             | 1.724(2)|
| N(1)-C(1)             | 1.411(3)| N(1)-C(7)             | 1.381(3)|
Triazol-substituted thienothiophene 9

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt S4 (100 mg, 0.229 mmol, 1.0 equiv.), K2CO3 (63 mg, 0.46 mmol, 2.0 equiv.), 1,2,4-triazol (48 mg, 0.69 mmol, 3.0 equiv.), and DMSO (1.5 ml, c = 0.15 M). The vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was directly loaded onto a column of silica gel and purified by chromatography eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 34 mg (72 %) of compound 9 as green solid.

\[
\begin{array}{ccc}
N(1)-C(13) & 1.396(3) & N(2)-C(7) & 1.303(3) \\
N(2)-C(8) & 1.396(3) & C(1)-C(2) & 1.426(3) \\
C(1)-C(6) & 1.362(3) & C(2)-C(5) & 1.385(3) \\
C(3)-C(4) & 1.356(3) & C(4)-C(5) & 1.427(3) \\
C(8)-C(9) & 1.393(3) & C(8)-C(13) & 1.406(3) \\
C(9)-C(10) & 1.386(3) & C(10)-C(11) & 1.402(3) \\
C(11)-C(12) & 1.388(3) & C(12)-C(13) & 1.395(3) \\
C(2)-S(1)-C(3) & 90.93(10) & C(6)-S(2)-C(5) & 91.34(10) \\
C(7)-N(1)-C(1) & 125.40(18) & C(7)-N(1)-C(13) & 105.65(17) \\
C(13)-N(1)-C(1) & 128.76(17) & C(7)-N(2)-C(8) & 104.54(17) \\
N(1)-C(1)-C(2) & 122.89(18) & C(6)-C(1)-N(1) & 125.56(19) \\
C(6)-C(1)-C(2) & 111.54(19) & C(1)-C(2)-S(1) & 136.07(17) \\
C(5)-C(2)-S(1) & 110.78(16) & C(5)-C(2)-C(1) & 113.12(19) \\
C(4)-C(3)-S(1) & 113.84(17) & C(3)-C(4)-C(5) & 110.6(2) \\
C(2)-C(5)-S(2) & 110.98(16) & C(2)-C(5)-C(4) & 113.87(19) \\
C(4)-C(5)-S(2) & 135.12(17) & C(1)-C(6)-S(2) & 113.01(16) \\
N(2)-C(7)-N(1) & 114.33(19) & N(2)-C(8)-C(13) & 110.36(18) \\
C(9)-C(8)-N(2) & 129.31(19) & C(9)-C(8)-C(13) & 120.33(19) \\
C(10)-C(9)-C(8) & 118.0(2) & C(9)-C(10)-C(11) & 121.0(2) \\
C(12)-C(11)-C(10) & 122.0(2) & C(11)-C(12)-C(13) & 116.5(2) \\
N(1)-C(13)-C(8) & 105.11(17) & C(12)-C(13)-N(1) & 132.7(2) \\
C(12)-C(13)-C(8) & 122.15(19) \\
\end{array}
\]
\( R_\text{f} = 0.36 \) (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

\(^1\text{H} \text{ NMR} \) (500 MHz, \( \text{CD}_3\text{CN}, 298 \text{ K}, \delta \)): 8.83 (s, 1H), 8.12 (s, 1H), 7.71 (d, \( J = 1.5 \text{ Hz}, 1\text{H} \)), 7.62 (dd, \( J = 5.3, 1.6 \text{ Hz}, 1\text{H} \)), 7.38 (d, \( J = 5.3 \text{ Hz}, 1\text{H} \)).

\(^{13}\text{C} \{' \text{H} \} \text{ NMR} \) (126 MHz, \( \text{CD}_3\text{CN}, 298 \text{ K}, \delta \)): 152.7, 142.9, 140.4, 132.4, 131.0, 129.5, 121.0, 118.3.

**HRMS-ESI (m/z) calc’d for \( \text{C}_8\text{H}_5\text{N}_3\text{S}_2^+ \ [\text{M}^+] \), 206.9919; found 206.9923; deviation 1.9 ppm.

**Diphenylimidazole-substituted bithiophene 10**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), \( \text{K}_2\text{CO}_3 \) (200 mg, 1.45 mmol, 2.7 equiv.), diphenylimidazole (250 mg, 1.14 mmol, 2.1 equiv.), and DMSO (10 ml, \( c = 0.054 \text{ M} \)). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over \( \text{MgSO}_4 \). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (7 / 3 gradient to 0 / 1 (v/v)) to afford 189 mg (91 %) of compound 10 as colorless solid.

\( R_\text{f} = 0.51 \) (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

\(^1\text{H} \text{ NMR} \) (500 MHz, \( \text{CDCl}_3, 298 \text{ K}, \delta \)): 8.13 (s, 1H), 7.52 (dd, \( J = 5.1, 1.2 \text{ Hz}, 1\text{H} \)), 7.47 – 7.40 (m, 5H), 7.34 – 7.30 (m, 3H), 7.27 – 7.22 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 (d, \( J = 1.6 \text{ Hz}, 1\text{H} \)), 7.07 (dd, \( J = 5.1, 3.6 \text{ Hz}, 1\text{H} \)).

\(^{13}\text{C} \{' \text{H} \} \text{ NMR} \) (126 MHz, \( \text{CDCl}_3, 298 \text{ K}, \delta \)): 138.3, 137.9, 136.8, 136.0, 134.84, 134.81, 131.3, 130.5, 129.31, 129.26, 129.0, 128.9, 128.64, 128.55, 127.0, 126.8, 125.1, 121.5, 118.6.

**HRMS-ESI (m/z) calc’d for \( \text{C}_{23}\text{H}_{17}\text{N}_2\text{S}_2^+ \ [\text{M}+\text{H}]^+ \), 385.0828; found 385.0825; deviation 0.8 ppm.
Benzimidazole-substituted bithiophene 11

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), K₂CO₃ (200 mg, 1.45 mmol, 2.7 equiv.), benzimidazole (200 mg, 1.69 mmol, 3.1 equiv.), and DMSO (10 ml, c = 0.054 M). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (7 / 3 gradient to 0 / 1 (v/v)) to afford 133 mg (88 %) of compound 11 as yellowish oil.

Rᵣ = 0.39 (hexanes / EtOAc, 1 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CDCl₃, 298 K, δ): 8.19 (s, 1H), 7.91 – 7.86 (m, 1H), 7.62 – 7.57 (m, 1H), 7.38 – 7.35 (m, 2H), 7.35 (d, J = 1.6 Hz, 1H), 7.31 (dd, J = 5.1, 1.2 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.07 (dd, J = 5.1, 3.6 Hz, 1H).

¹³C {¹H} NMR (126 MHz, CDCl₃, 298 K, δ): 143.3, 142.1, 139.2, 136.2, 134.7, 133.6, 128.2, 125.8, 124.9, 124.2, 123.3, 120.6, 119.2, 115.3, 110.8.

HRMS-ESI (m/z) calc’d for C₁₅H₁₁N₂S₂⁺ [M+H]⁺, 283.0358; found 283.0357; deviation 0.5 ppm.

Benzotriazole-substituted 2-phenylthiophene 12

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 2-phenylthiophene-derived dibenzothiophenium salt S₄ (150 mg, 0.33 mmol, 1.0 equiv.), benzotriazole (78 mg,
0.66 mmol, 2.0 equiv.), K₂CO₃ (132 mg, 1.31 mmol, 4.0 equiv.), and DMSO (5 ml, c = 0.07 M). The vial was sealed, and subsequently stirred for 2 d at 60 °C. Subsequently, the reaction mixture was diluted with EtOAc (30 ml) and washed with water (70 ml). The aqueous layer was extracted with EtOAc (2 × 10 ml). The combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 4 / 1 (v/v)) to afford 50 mg (55 %) of compound 12 as colorless crystals. A second fraction, which based on ¹H NMR spectroscopy is assumed to be 2-(5-phenylthiophen-3-yl)-2H-benzo[d][1,2,3]triazole (S15), was also obtained, but not in pure form.

Rᵣ = 0.65 (hexanes / EtOAc, 7 / 3 (v/v)).

**NMR Spectroscopy:**

¹H NMR (500 MHz, CDCl₃, 298 K, δ): 8.16 (d, J = 8.4 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.71 – 7.67 (m, 2H), 7.63 – 7.56 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.35 (m, 1H).

¹³C {¹H} NMR (126 MHz, CDCl₃, 298 K, δ): 146.3, 146.0, 135.8, 133.4, 132.2, 129.3, 128.7, 128.6, 126.0, 124.6, 120.6, 118.1, 114.3, 110.5.

HRMS-ESI (m/z) calc’d for C₁₆H₁₂N₃S⁺ [M+H]⁺, 278.0746; found 278.0743; deviation 1.4 ppm.

**Phthalimide-substituted 2-chlorothiophene 13**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with chlorothiophene-derived dibenzothiophenium salt S6 (200 mg, 0.51 mmol, 1.0 equiv.), potassium phthalimide (381 mg, 2.06 mmol, 4.0 equiv.), and MeCN (5 ml, c = 0.1 M). The vial was sealed, and subsequently the mixture was stirred for 4 d at 60 °C. Subsequently, the reaction mixture diluted with EtOAc (35 ml) and washed with water (2 × 20 ml) and brine (1 × 10 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 7 / 3 (v/v)) to afford 80 mg (59 %) of compound 13 as colorless crystals.

Rᵣ = 0.66 (hexanes / EtOAc, 7 / 3 (v/v)).

**NMR Spectroscopy:**

¹H NMR (500 MHz, CDCl₃, 298 K, δ): 7.93 (dd, J = 5.5, 3.0 Hz, 2H), 7.79 (dd, J = 5.5, 3.0 Hz, 2H), 7.50 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 1.8 Hz, 1H).
\(^{13}\text{C}\ (^{1}\text{H})\text{ NMR}\) (126 MHz, CDCl\(_3\), 298 K, \(\delta\)): 166.5, 134.8, 131.6, 130.2, 128.8, 124.0, 122.4, 116.1.

\text{HRMS-ESI (m/z) calc'd for C}_{12}\text{H}_{6}\text{NO}_{2}\text{SClNa}^{+} [M+Na]^{+}, 285.97000; found 285.9698; deviation 0.9 ppm.

\textbf{Cyano-substituted 2-chlorothiophene 14}

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with chlorothiophene-derived dibenzothiophenium salt \textbf{S6} (500 mg, 1.29 mmol, 1.00 equiv.), KCN (168 mg, 2.57 mmol, 2.00 equiv.), and MeCN (10 ml, \(c = 0.13\) M). The vial was sealed, and stirred for 24 h at 50 \(^\circ\)C. Subsequently, the reaction mixture was poured onto an aqueous solution of iron(II) acetate (0.2 g in 100 ml water). The mixture was extracted with EtOAc (30 ml). The organic layer was dried over MgSO\(_4\). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 3 / 1 (v/v)) to afford 111 mg (60 \%) of compound 14 as colorless oil, which crystallized after several days.

\(R_f = 0.79\) (hexanes / EtOAc, 7 / 3 (v/v)).

\textbf{NMR Spectroscopy:}

\(^{1}\text{H} \text{NMR}\) (500 MHz, CDCl\(_3\), 298 K, \(\delta\)): 7.72 (d, \(J = 1.5\) Hz, 1H), 7.12 (d, \(J = 1.5\) Hz, 1H).

\(^{13}\text{C} \ (^{1}\text{H})\text{ NMR}\) (126 MHz, CDCl\(_3\), 298 K, \(\delta\)): 134.2, 132.7, 127.1, 114.2, 110.5.

\text{HRMS-ESI (m/z) calc'd for C}_{5}\text{H}_{2}\text{NSClNa}^{+} [M+Na]^{+}, 165.9489; found 165.9490; deviation 0.7 ppm.

\textbf{Triazol-substituted 2-benzothiazolo thiophene 15}

Under an ambient atmosphere, a 20 ml glass-vial was charged with thianthrenium salt \textbf{S7*CH\(_2\)Cl\(_2\)} (200 mg, 0.33 mmol, 1.0 equiv.), K\(_2\)CO\(_3\) (100 mg, 0.72 mmol, 2.2 equiv.), 1,2,4-triazole (50 mg, 0.72 mmol, 2.2 equiv.), and MeCN (10 ml, \(c = 0.033\) M). The vial was sealed, and the reaction mixture was subsequently stirred for 20 h at 80 \(^\circ\)C. Subsequently, the reaction mixture was allowed to cool to 25 \(^\circ\)C, and filtered through a thin layer of silica gel. The solvent was removed, and the residue was purified by column chromatography on
silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 7 / 13 (v/v)) to afford 84 mg (89 %) of compound 15 as yellow solid.

R<sub>f</sub> = 0.22 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, δ): 8.54 (s, 1H), 8.11 (s, 1H), 8.06 (dt, J = 8.3, 0.8 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.63 (d, J = 1.5 Hz, 1H), 7.52 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.42 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H).

<sup>13</sup>C <sup>1</sup>H NMR (126 MHz, CDCl<sub>3</sub>, 298 K, δ): 159.9, 153.6, 152.6, 141.3, 139.0, 136.1, 135.0, 127.0, 126.0, 123.5, 121.8, 120.6, 116.5.

**HRMS-ESI (m/z)** calc’d for C<sub>13</sub>H<sub>9</sub>N<sub>4</sub>S<sub>2</sub> <sup>+</sup> [M+H]<sup>+</sup>, 285.0263; found 285.0260; deviation 1.2 ppm.

**Pyrazolopyridinyl-substituted 2-benzothiazolo thiophene 16**

![Diagram of compound 16](image)

Under an ambient atmosphere, a 20 ml glass-vial was charged with thianthrenium salt S<sup>7</sup>*CH<sub>2</sub>Cl<sub>2</sub> (200 mg, 0.33 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (100 mg, 0.72 mmol, 2.2 equiv.), pyrazolopyridine (100 mg, 0.84 mmol, 2.5 equiv.), and MeCN (10 ml, c = 0.033 M). The vial was sealed, and the reaction mixture was subsequently stirred for 2 d at 80 °C. Subsequently, the reaction mixture was allowed to cool to 25 °C, and filtered through a thin layer of silica gel. The solvent was removed, and the residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 4 / 1 (v/v)) to afford 29 mg (26 %) of compound 16 as yellow solid (> 95 % purity). A sample was further purified by column chromatography on silica gel eluting with DCM / EtOAc, which was used for the acquisition of the <sup>1</sup>H NMR spectrum.

R<sub>f</sub> = 0.66 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, δ): 8.68 (dd, J = 4.5, 1.6 Hz, 1H), 8.51 (d, J = 1.4 Hz, 1H), 8.33 (d, J = 1.5 Hz, 1H), 8.18 (s, 1H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.88 (dd, J = 8.0, 1.2, 0.6 Hz, 1H), 7.49 (dd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.39 (dd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.25 (dd, J = 8.0, 4.5 Hz, 1H).

<sup>13</sup>C <sup>1</sup>H NMR (126 MHz, CDCl<sub>3</sub>, 298 K, δ): 161.3, 153.6, 149.71, 149.65, 138.4, 136.1, 135.0, 134.1, 130.5, 126.7, 125.6, 123.2, 122.3, 121.7, 118.1, 116.9, 114.8.

**HRMS-ESI (m/z)** calc’d for C<sub>17</sub>H<sub>11</sub>N<sub>4</sub>S<sub>2</sub> <sup>+</sup> [M+H]<sup>+</sup>, 335.0420; found 388.0415; deviation 1.3 ppm.
Phthalimide-substituted imidazopyridine 17

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine-derived dibenzothiophenium salt S8 (200 mg, 0.48 mmol, 1.0 equiv.), potassium phthalimide (268 mg, 1.45 mmol, 3.0 equiv.), and MeCN (10 ml, c = 0.05 M). The vial was sealed, and subsequently stirred for 3 d at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (60 ml) and washed with water (50 ml). The aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 3 / 2 (v/v)) to afford 37 mg (29 %) of compound 17 as yellow crystals.

Rᵥ = 0.50 (EtOAc).

NMR Spectroscopy:

¹H NMR (500 MHz, DMSO-dma, 298 K, δ): 8.66 (d, J = 6.7 Hz, 1H), 8.14 (s, 1H), 8.00 (dd, J = 5.5, 3.0 Hz, 2H), 7.93 (dd, J = 5.5, 3.1 Hz, 2H), 7.62 (d, J = 9.0 Hz, 1H), 7.35 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 7.01 (utd, J = 6.8, 0.9 Hz, 1H).

¹³C {¹H} NMR (126 MHz, DMSO-dma, 298 K, δ): 166.6, 143 (only visible in HMBC spectrum), 135.0, 133.9, 131.4, 127.2, 125.4, 123.6, 116.8, 112.8, 109.2.

HRMS-ESI (m/z) calc’d for C₁₅H₁₀N₃O₂ [M+H]⁺, 264.0768; found 264.0765; deviation 1.1 ppm.

Dimethyltriazol-substituted imidazopyridine 18

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine-derived dibenzothiophenium salt S8 (200 mg, 0.48 mmol, 1.0 equiv.), potassium carbonate (266 mg, 1.93 mmol, 4.0 equiv.), diemthyltriazol (141 mg, 1.45 mmol, 3.0 equiv.), and MeCN (10 ml, c = 0.05 M). The vial was sealed, and subsequently stirred for 3 d at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (30 ml) and washed with water (100 ml). The aqueous layer was extracted with EtOAc (2
× 20 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 1 gradient to 0 / 1 (v/v)) to afford 69 mg (67 %) of compound 18 as light green solid.

Rf = 0.17 (EtOAc).

**NMR Spectroscopy:**

**¹H NMR** (500 MHz, CDCl₃, 298 K, δ): 8.13 (d, J = 6.7 Hz, 1H), 7.78 (bs, 1H), 7.59 (dd, J = 9.0, 1.0 Hz, 1H), 7.25 (ddd, J = 9.1, 6.8, 1.2 Hz, 1H), 6.87 (dtd, J = 6.8, 1.1 Hz, 1H), 2.82 (s, 3H), 2.41 (s, 3H).

**¹³C {¹H} NMR** (126 MHz, CDCl₃, 298 K, δ): 160.5, 153.6, 143.2, 142.0, 125.9, 125.4, 117.7, 113.4, 102.7, 14.1, 13.9.

**HRMS-ESI (m/z)** calc’d for C₁₁H₁₂N₅⁺ [M+H]⁺, 214.1087; found 214.1085; deviation 1.2 ppm.

**Cyano BINOL-dimethylether 19**

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with BINOL-dimethylether-derived thianthrenium salt S9 (120 mg, 0.124 mmol, 1.0 equiv.), KCN (24 mg, 0.37 mmol, 3.0 equiv.), and MeCN (0.5 ml, c = 0.25 M). The vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was poured onto a mixture of EtOAc (10 ml) and water (15 ml). The aqueous layer was extracted with EtOAc (3 × 10 ml). Subsequently, the combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 23 mg (51 %) of compound 19 as colorless oil.

Rf = 0.56 (EtOAc / hexanes, 1 / 1 (v/v)).

**NMR Spectroscopy:**

**¹H NMR** (500 MHz, CD₃CN, 298 K, δ): 8.38 (d, J = 9.3 Hz, 1H), 7.85 (d, J = 6.9 Hz, 1H), 7.79 (d, J = 9.3 Hz, 1H), 7.33 (dd, J = 8.7, 6.8 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 3.77 (s, 2H).

**¹³C {¹H} NMR** (126 MHz, CD₃CN, 298 K, δ): 157.2, 134.3, 131.7, 131.0, 128.4, 127.9, 127.0, 119.8, 118.7, 117.4, 111.0, 57.2.
HRMS-ESI (m/z) calc'd for C_{24}H_{16}N_{2}O_{2}Na\(^+\) [M+Na\(^+\)], 387.1104; found 387.1100; deviation 1.0 ppm.

**Phenylurazole-substituted bithiophene 20**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (200 mg, 0.43 mmol, 1.0 equiv.), potassium carbonate (239 mg, 1.73 mmol, 4.0 equiv.), phenylurazole (230 mg, 1.30 mmol, 3.0 equiv.), and DMSO (10 ml, c = 0.04 M). The vial was sealed, and subsequently stirred for 2 d at 80 °C. Subsequently, the reaction mixture was poured onto a biphasic mixture of EtOAc (50 ml), water (50 ml) and sulfuric acid (1M, 10 ml). The layers were separated, and the aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (10 ml), and subsequently dried over MgSO\(_4\). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 6 / 4 (v/v)) to afford 100 mg (68 %) of compound 20 as colorless solid.

R\(_f\) = 0.48 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

\(^1\)H NMR (500 MHz, DMSO-\(d_6\), 298 K, \(\delta\)): 11.66 (bs, 1H), 7.58 – 7.56 (m, 2H), 7.54 – 7.51 (m, 4H), 7.47 – 7.42 (m, 1H), 7.36 (dd, \(J = 3.6, 1.2\) Hz, 1H), 7.31 (d, \(J = 1.6\) Hz, 1H), 7.12 (dd, \(J = 5.1, 3.6\) Hz, 1H).

\(^{13}\)C \(\{^1\)H\} NMR (126 MHz, DMSO-\(d_6\), 298 K, \(\delta\)): 152.5, 149.2, 137.1, 136.3, 134.9, 131.9, 129.4, 129.0, 128.7, 127.0, 126.6, 125.0, 116.5, 108.6.

HRMS-ESI (m/z) calc'd for C\(_{24}\)H\(_{16}\)N\(_2\)O\(_2\)S\(_2\) [M+H\(^+\)], 342.0366; found 342.0363; deviation 0.8 ppm.

**Diphenylhydantoin-substituted bithiophene 21**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), potassium carbonate (299 mg, 2.72 mmol, 5.0 equiv.), and DMSO (10 ml, c = 0.11 M). The vial was sealed, and subsequently stirred for 6 h at 80 °C. The reaction mixture was poured onto a biphasic mixture of EtOAc (50 ml), water (50 ml) and sulfuric acid (1M, 10 ml). The layers were separated, and the aqueous layer was extracted with EtOAc (50 ml). The combined organic layers were washed with water (20 ml), and subsequently dried over MgSO\(_4\). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 6 / 4 (v/v)) to afford 50 mg (28 %) of compound 21 as colorless solid.

R\(_f\) = 0.38 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

\(^1\)H NMR (500 MHz, DMSO-\(d_6\), 298 K, \(\delta\)): 11.71 (bs, 1H), 7.69 – 7.66 (m, 2H), 7.65 – 7.63 (m, 2H), 7.62 – 7.58 (m, 4H), 7.56 – 7.54 (m, 1H), 7.37 (dd, \(J = 3.6, 1.2\) Hz, 1H), 7.31 (d, \(J = 1.6\) Hz, 1H), 7.12 (dd, \(J = 5.1, 3.6\) Hz, 1H).

\(^{13}\)C \(\{^1\)H\} NMR (126 MHz, DMSO-\(d_6\), 298 K, \(\delta\)): 152.5, 149.2, 137.1, 136.3, 134.9, 131.9, 129.4, 129.0, 128.7, 127.0, 126.6, 125.0, 116.5, 108.6.
mg, 2.16 mmol, 4.0 equiv.), diphenylhydantoin (409 mg, 1.62 mmol, 3.0 equiv.), and DMSO (10 ml, c = 0.05 M). The vial was sealed, and subsequently stirred for 19 h at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (40 ml) and washed with water (100 ml). The aqueous layer was extracted with EtOAc (2 × 40 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 7 / 3 (v/v)). The resulting solid was dissolved in 100 ml EtOAc and washed with dilute aqueous NaOH solution (3 × 50 ml), followed by washing with water (2 × 30 ml). Subsequently, the solvent was removed to afford 185 mg (82 %) of compound 21 as colorless crystals. 

Rᵣ = 0.71 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

**¹H NMR** (500 MHz, DMSO-d₆, 298 K, δ): 10.05 (s, 1H), 7.74 (d, J = 1.5 Hz, 1H), 7.60 (d, J = 1.5 Hz, 1H), 7.54 (dd, J = 5.1, 1.2 Hz, 1H), 7.48 – 7.34 (m, 11H), 7.10 (dd, J = 5.1, 3.6 Hz, 1H).

**¹³C {¹H} NMR** (126 MHz, DMSO-d₆, 298 K, δ): 171.6, 153.5, 139.4, 135.8, 135.6, 129.6, 128.7, 128.42, 128.38, 126.8, 126.0, 124.5, 120.2, 118.3, 69.0.

**HRMS-ESI (m/z) calc’d for C₂₃H₁₅N₂O₂S₂⁺ [M-H]⁻, 415.0581; found 415.0582; deviation 0.3 ppm.**

**Dimethyltriazol-substituted bithiophene 22**

![Chemical structure of compound 22](image)

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), potassium carbonate (338 mg, 2.45 mmol, 4.5 equiv.), dimethyltriazole (178 mg, 1.84 mmol, 3.4 equiv.), and DMSO (10 ml, c = 0.05 M). The vial was sealed, and subsequently stirred for 23 h at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (50 ml) and washed with water (50 ml). The aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 1 / 4 (v/v)) to afford 125 mg (88 %) of compound 22 as colorless solid.

Rᵣ = 0.19 (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**
\(^1\)H NMR (500 MHz, CDCl\(_3\), 298 K, \(\delta\)): 7.31 (d, \(J = 1.6\) Hz, 1H), 7.28 (dd, \(J = 5.1, 1.2\) Hz, 1H), 7.24 (dd, \(J = 3.6, 1.2\) Hz, 1H), 7.18 (d, \(J = 1.5\) Hz, 1H), 7.05 (dd, \(J = 5.1, 3.6\) Hz, 1H), 2.57 (s, 3H), 2.41 (s, 3H).

\(^{13}\)C \(^1\)H NMR (126 MHz, CDCl\(_3\), 298 K, \(\delta\)): 160.0, 152.4, 138.5, 136.2, 136.0, 128.1, 125.7, 124.8, 119.6, 115.7, 13.8, 13.4.

HRMS-EI (m/z) calc'd for C\(_{12}\)H\(_{11}\)N\(_3\)S\(_2\) \([\text{M}^+]\), 261.0389; found 261.0391; deviation 0.9 ppm.

Pyridone-substituted bithiophene 23

![Pyridone-substituted bithiophene 23](image)

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt 1 (250 mg, 0.54 mmol, 1.0 equiv.), K\(_2\)CO\(_3\) (150 mg, 1.09 mmol, 2.0 equiv.), pyridone (100 mg, 1.05 mmol, 2.0 equiv.), and DMSO (10 ml, c = 0.054 M). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over MgSO\(_4\). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (7 / 3 gradient to 0 / 1 (v/v)) to afford 128 mg (91 %) of compound 23 as colorless crystals.

R\(_f\) = 0.27 (hexanes / EtOAc, 1 / 1 (v/v)).

NMR Spectroscopy:

\(^1\)H NMR (500 MHz, CDCl\(_3\), 298 K, \(\delta\)): 7.43 (ddd, \(J = 6.9, 2.1, 0.8\) Hz, 1H), 7.38 (ddd, \(J = 9.2, 6.6, 2.1\) Hz, 1H), 7.32 (d, \(J = 1.5\) Hz, 1H), 7.30 (d, \(J = 1.5\) Hz, 1H), 7.25 (dd, \(J = 5.1, 1.1\) Hz, 1H), 7.21 (dd, \(J = 3.6, 1.2\) Hz, 1H), 7.03 (dd, \(J = 5.1, 3.6\) Hz, 1H), 6.67 (d\(\gamma\)t, \(J = 9.3, 1.1\) Hz, 1H), 6.24 (d\(\gamma\)td, \(J = 6.7, 1.4\) Hz, 1H).

\(^{13}\)C \(^1\)H NMR (126 MHz, CDCl\(_3\), 298 K, \(\delta\)): 162.1, 140.0, 138.8, 137.60, 137.59, 136.6, 128.0, 125.4, 124.5, 122.0, 121.4, 118.7, 106.5.

HRMS-ESI (m/z) calc'd for C\(_{13}\)H\(_9\)NOS\(_2\)Na\(^+\) \([\text{M+Na}^+]\), 282.0018; found 282.0016; deviation 0.7 ppm.
Ethoxybithiophene 24

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt 1 (200 mg, 0.43 mmol, 1.0 equiv.), NaOtBu (125 mg, 1.29 mmol, 3.0 equiv.), and EtOH (10 ml, c = 0.04 M). The vial was sealed and the reaction mixture was stirred at 75 °C for 40 h. Subsequently, the solvent was removed under reduced pressure. The residue was dissolved in a biphasic mixture of EtOAc (10 ml) and aqueous HBr solution (0.1 M, 10 ml), and the layers were separated. The organic layer was washed with water (2 × 10 ml), and dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes to afford 67 mg (74 %) of compound 24 as yellowish oil.

\[ R_i = 0.62 \text{ (hexanes / EtOAc, 9 / 1 (v/v))} \]

NMR Spectroscopy:

\[ ^1H \text{ NMR (500 MHz, CDCl}_3, 298 K, \delta): 7.21 (dd, } J = 5.1, 1.2 \text{ Hz, 1H), 7.15 (dd, } J = 3.6, 1.2 \text{ Hz, 1H), 7.00 (dd, } J = 5.1, 3.6 \text{ Hz, 1H), 6.86 (d, } J = 1.3 \text{ Hz, 1H), 6.13 (d, } J = 1.8 \text{ Hz, 1H), 4.02 (q, } J = 7.0 \text{ Hz, 2H), 1.41 (t, } J = 7.0 \text{ Hz, 3H).} \]

\[ ^13C \{^1H\} \text{ NMR (126 MHz, CDCl}_3, 298 K, \delta): 157.5, 137.7, 136.0, 127.9, 124.7, 123.7, 116.2, 96.4, 65.7, 14.9.} \]

HRMS-EI (m/z) calc'd for C₁₀H₁₀OS⁺ [M⁺], 210.0168; found 210.0171; deviation 1.8 ppm.

Cyano-substituted 3-phenylthiophene 25

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 3-phenylthiophene-derived dibenzothiophenium salt S10 (200 mg, 0.44 mmol, 1.0 equiv.), KCN (71 mg, 1.1 mmol, 2.5 equiv.), and DMSO (9 ml, c = 0.05 M). The vial was sealed, and subsequently stirred for 23 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (10 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). The combined organic layers were washed with aqueous Fe(OAc)₂ solution (5 ml). Subsequently, the organic layer was dried over MgSO₄. The solvent was
removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 17 / 3 (v/v)) to afford 40 mg (49 %) of compound 25 as colorless oil, which crystallized after several hours.

R_f = 0.85 (hexanes / EtOAc, 7 / 3 (v/v)).

NMR Spectroscopy:

^1H NMR (500 MHz, CDCl₃, 298 K, δ): 7.87 (d, J = 1.4 Hz, 1H), 7.66 (d, J = 1.5 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.41 – 7.33 (m, 1H).

^13C (^1H) NMR (126 MHz, CDCl₃, 298 K, δ): 143.3, 136.4, 133.8, 129.3, 128.5, 127.0, 126.6, 114.7, 110.8.

HRMS-ESI (m/z) calc'd for C_{11}H_{7}NS⁺ [M⁺], 185.0294; found 185.0296; deviation 1.4 ppm.

Cyano-substituted 6-methoxy-2-methylquinoline 26

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with methoxymethylquinoline-derived thianthrenium salt S11 (98 mg, 0.18 mmol, 1.0 equiv.), KCN (43 mg, 0.66 mmol, 3.6 equiv.), and DMSO (3 ml, c = 0.06 M). The vial was sealed, and the reaction mixture was subsequently stirred for 42 h at 60 °C. Subsequently, the reaction mixture was poured onto a mixture of aqueous Fe(OAc)₂ solution (120 mg Fe(OAc)₂ in 20 ml H₂O) and 20 ml EtOAc. The aqueous layer was extracted with EtOAc (3 × 20 ml). The combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 3 / 2 (v/v)) to afford 6 mg (16 %) of compound 26 as colorless crystals.

R_f = 0.67 (hexanes / EtOAc, 7 / 3 (v/v)).

NMR Spectroscopy:

^1H NMR (500 MHz, CDCl₃, 298 K, δ): 7.98 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 2.8 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 2.8 Hz, 1H), 3.94 (s, 3H), 2.77 (s, 3H).

^13C (^1H) NMR (126 MHz, CDCl₃, 298 K, δ): 159.3, 156.0, 143.2, 135.2, 127.5, 127.3, 124.0, 117.2, 113.6, 111.1, 56.1, 25.4.

HRMS-ESI (m/z) calc’d for C_{12}H_{11}NO⁺ [M+H⁺], 199.0866; found 199.0865; deviation 0.5 ppm.
Cyano-substituted methoxy-naphthalin 27

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with methoxynaphthalene-derived diphenylsulfonium salt S12 (250 mg, 0.50 mmol, 1.0 equiv.), KCN (66 mg, 1.0 mmol, 2.0 equiv.), and MeCN (3 ml, c = 0.17 M). The vial was sealed, and the reaction mixture was subsequently stirred for 6 d at 80 °C. Subsequently, the reaction mixture was diluted with water (50 ml) and extracted with EtOAc (3 × 20 ml). The combined organic layers were washed with aqueous FeSO₄ solution (approx. 20 %, 10 ml). The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 9 / 1 (v/v)) to afford 34 mg (37 %) of compound 27 as colorless crystals.

Rₛ = 0.46 (hexanes / EtOAc, 4 / 1 (v/v)).

NMR Spectroscopy:

¹H NMR (500 MHz, CD₃CN, 298 K, δ): 8.09 – 8.06 (m, 1H), 7.92 – 7.89 (m, 1H), 7.67 (d, J = 2.6 Hz, 1H), 7.63 – 7.55 (m, 3H), 3.93 (s, 3H).

¹³C {¹H} NMR (126 MHz, CD₃CN, 298 K, δ): 157.3, 135.4, 129.0, 128.6, 128.4, 127.2, 126.1, 125.4, 118.0, 113.1, 111.9, 56.6.

HRMS-ESI (m/z) calc’d for C₁₂H₉NONa⁺ [M+Na]⁺, 206.0576; found 206.0575; deviation 0.6 ppm.

Pyrazol-substituted anthracen 28

Under an atmosphere of argon, a flame dried Schlenk tube equipped with a teflon coated stir bar was charged with pyrazol (102 mg, 1.5 mmol, 3.0 equiv.), and K₂CO₃ (276 mg, 2.0 mmol, 4.0 equiv.) and deuterium oxide (2 ml). The mixture was stirred at 25 °C for 45 min. The solvent was removed under reduced pressure and the residue was dried in vacuo. Subsequently, anthracen-derived diphenylsulfonium salt S13 (225 mg, 0.50 mmol, 1.0 equiv.), DMSO-d₆ (5 ml, c = 0.1 M), and D₂O (50 µl) were added. The reaction mixture was stirred at 80 °C for 6 h. The mixture was diluted with water (30 ml). The mixture was extracted with EtOAc (5 × 40 ml). The combined organic layers were washed with water (30 ml). The organic layer was
dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 17 / 3 (v/v)) to afford 110 mg (90%) of compound 28 as yellow solid with a deuterium incorporation of 77% by ¹H NMR by integration of the ¹H-signal at 8.73 ppm.

Rᵣ = 0.37 (hexanes / EtOAc, 5 / 1 (v/v)).

**NMR Spectroscopy:**

¹H NMR (500 MHz, CD₃CN, 298 K, δ): 8.73 (s, 0.23H), 8.17 (dd, J = 8.2, 1.6 Hz, 2H), 7.96 – 7.94 (m, 2H), 7.61 – 7.49 (m, 4H), 7.34 (d, J = 8.6 Hz, 2H), 6.73 (t, J = 2.1 Hz, 1H).

¹³C {¹H} NMR (126 MHz, CD₃CN, 298 K, δ): 141.5, 134.7, 133.5, 132.3, 132.2, 129.9, 129.5, 129.3, 129.22, 129.17 (t, J = 24 Hz), 128.4, 126.8, 123.5, 107.3.

**HRMS-ESI (m/z)** calc'd for C₁₇H₁₂N₂D [M+H]+, 246.1136; found 246.1137; deviation 0.5 ppm.

**REFERENCES**

(18) S. Zheng, C. Yu, Z. Shen Org. Lett. 2012, 14, 3644-3647.
SUPPLEMENTARY INFORMATION

SPECTROSCOPIC DATA

$^1$H NMR of imidazopyridazine-derived dibenzothiophenium salt S1

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of imidazopyridazine-derived dibenzothiophenium salt S1

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of imidazopyridazine-derived dibenzothiophenium salt S1

CDCl$_3$, 471 MHz, 298 K
1H NMR of bromobutoxy naphthalene S2

CDCl₃, 500 MHz, 298 K
$^{13}$C NMR of bromobutoxy naphthalene S2

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of bromobutoxynaphthalene-derived thianthrenium salt S3

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of bromobutoxynaphthalene-derived thianthrenium salt S3

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of bromobutoxynaphthalene-derived thianthrenium salt S3

CDCl$_3$, 471 MHz, 298 K, an impurity of trifluoroacetate ions was detected.
**1H NMR of thienothiophen-derived dibenzothiophenium salt S4**

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of thienothiophen-derived dibenzothiophenium salt S4

CD$_3$CN, 126 MHz, 298 K
$^{19}$F NMR of thienothiophen-derived dibenzothiophenium salt S4

CD$_3$CN, 471 MHz, 298 K
$^1$H NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5

CD$_3$CN, 126 MHz, 298 K

Diagram of the compound and its NMR spectrum.
$^{19}$F NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5

CD$_3$CN, 126 MHz, 298 K
$^1$H NMR of 2-chlorothiophen-derived dibenzothiophenium salt S6

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of 2-chlorothiophen-derived dibenzothiophenium salt S6

CD$_3$CN, 126 MHz, 298 K
$^{19}$F NMR of 2-chlorothiophen-derived dibenzothiophenium salt S6

CD$_3$CN, 471 MHz, 298 K
\(^1\)H NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7

CD\(_3\)CN, 500 MHz, 298 K
$^{13}$C NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7

CD$_3$CN, 126 MHz, 298 K
$^{19}\text{F NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7}$

CD$_3$CN, 471 MHz, 298 K
\(^1\text{H NMR of imidazopyridine-derived dibenzothiophenium salt S8}\)

CD\(_2\)CN, 500 MHz, 298 K
Supplementary Information

$^{13}$C NMR of imidazopyridine-derived dibenzothiophenium salt S8

CD$_3$CN, 126 MHz, 298 K
$^{19}\text{F NMR of imidazopyridine-derived dibenzothiophenium salt S8}$

CD$_3$CN, 471 MHz, 298 K
$^1$H NMR of BINOL dimethylether-derived thianthrenium salt S9

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of BINOL dimethylether-derived thianthrenium salt S9

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of BINOL dimethylether-derived thianthrenium salt S9

CDCl$_3$, 471 MHz, 298 K
\(^1\)H NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10

CDCl\textsubscript{3}, 500 MHz, 298 K
$^{13}$C NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10

CDCl$_3$, 471 MHz, 298 K
$^1$H NMR of methoxyquinolin-derived thianthrenium salt S11

DMSO-$d_6$, 500 MHz, 298 K
$^{13}$C NMR of methoxyquinolin-derived thianthrenium salt S11

DMSO-$d_6$, 126 MHz, 298 K
$^{19}$F NMR of methoxyquinolin-derived thianthrenium salt S11

DMSO-\textit{d}_6, 471 MHz, 298 K
$^1$H NMR of methoxynaphthalin-derived diphenylsulfonium salt S12

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of methoxynaphthalin-derived diphenylsulfonium salt S12

CD$_3$CN, 126 MHz, 298 K
$^{19}$F NMR of methoxynaphthalin-derived diphenylsulfonium salt S12

CD$_3$CN, 471 MHz, 298 K
Supplementary Information

$^1$H NMR of anthracen-derived diphenylsulfonium salt S13

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of anthracen-derived diphenylsulfonium salt S13

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of anthracen-derived diphenylsulfonium salt S13

CDCl$_3$, 471 MHz, 298 K
$^1$H NMR of benzotriazol-substituted imidazopyridazine S14

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of benzotriazol-substituted imidazopyridazine S14

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of bithiophen-derived dibenzothiophenium salt 1

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of bithiophen-derived dibenzothiophenium salt 1

CDCl$_3$, 126 MHz, 298 K
$^{19}$F NMR of bithiophen-derived dibenzothiophenium salt 1

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of pyrazol-substituted bithiophen 2

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of pyrazol-substituted bithiophen 2

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of cyano methoxy methylbenzoate 4

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of cyano methoxy methylbenzoate 4

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of pyrazol-substituted imidazopyridazine 5

CDCl$_3$, 500 MHz, 298 K
$^{13}\text{C} \text{ NMR of pyrazol-substituted imidazopyridazine 5}$

CDCl$_3$, 126 MHz, 298 K
\(^1\)H NMR of benzotriazol-substituted imidazopyridazine 6

CDCl\(_3\), 500 MHz, 298 K
$^{13}$C NMR of benzotriazol-substituted imidazopyridazine 6

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of cyano-substituted butoxynaphthalene 7

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of cyano-substituted butoxynaphthalene 7

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of benzimidazol-substituted thienothiophen 8

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of benzimidazol-substituted thienothiophen 8

CD$_3$CN, 126 MHz, 298 K
$^1$H NMR of triazol-substituted thienothiophen 9

CD$_2$CN, 500 MHz, 298 K
13C NMR of triazol-substituted thienothiophen 9

CD3CN, 126 MHz, 298 K
$^1$H NMR of diphenylimidazol-substituted bithiophen 10

DMSO-$d_6$, 500 MHz, 298 K
$^{13}$C NMR of diphenylimidazol-substituted bithiophen 10

DMSO-$d_6$, 126 MHz, 298 K
$^1$H NMR of benzimidazol-substituted bithiophen 11

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of benzimidazol-substituted bithiophen 11

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of benzotriazol-substituted 2-phenylthiophen 12

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of benzotriazol-substituted 2-phenylthiophen 12

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of phthalimid-substituted 2-chlorothiophen 13

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of phthalimid-substituted 2-chlorothiophen 13

CDCl$_3$, 126 MHz, 298 K
$^{1}H$ NMR of cyano-substituted 2-chlorothiophen 14

CDCl$_3$, 500 MHz, 298 K

[Chemical structure and NMR spectrum image]
\textsuperscript{13}C NMR of phthalimid-substituted 2-chlorothiophen 14

CDCl\textsubscript{3}, 126 MHz, 298 K
SUPPLEMENTARY INFORMATION

\(^1\text{H} \text{NMR of triazol-substituted benzothiazolylthiophen 15}

CDCl\(_3\), 500 MHz, 298 K
$^{13}$C NMR of triazol-substituted benzothiazolylthiophen 15

CDCl$_3$, 126 MHz, 298 K
**1H NMR of pyrazolopyridine-substituted benzothiazolylthiophen 16**

CDCl₃, 500 MHz, 298 K
$^{13}$C NMR of pyrazolopyridine-substituted benzothiazolylthiophen 16

CDCl$_3$, 500 MHz, 298 K
$^1$H NMR of phthalimid-substituted imidazopyridine 17

DMSO-$d_6$, 500 MHz, 298 K
$^{13}$C NMR of phthalimid-substituted imidazopyridine 17

DMSO-$d_6$, 126 MHz, 298 K
$^1$H NMR of dimethyltriazol-substituted imidazopyridine 18

CDCl$_3$, 500 MHz, 298 K
Supplementary Information

$^{13}$C NMR of dimethyltriazol-substituted imidazopyridine 18

CDCl$_3$, 126 MHz, 298 K

![NMR Spectrum]

ppm

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190

144.01
13.78
132.28
122.30
117.69
113.28
102.53
125.90
125.33
117.59
125.98
131.49
130.43
$^1$H NMR of cyano-substituted BINOL diethylether 19

CD$_3$CN, 500 MHz, 298 K
\[^{13}\text{C} \text{NMR of cyano-substituted BINOL diemthylether 19}\]

CD\(_2\)CN, 126 MHz, 298 K
\textit{^1H NMR of phenylurazol-substituted bithiophen 20}

DMSO-$d_6$, 500 MHz, 298 K
$^{13}$C NMR of phenylurazol-substituted bithiophen 20

DMSO-$d_6$, 126 MHz, 298 K
$^1$H NMR of diphenylhydantoin-substituted bithiophen 21

DMSO-$d_6$, 500 MHz, 298 K
$^{13}$C NMR of diphenylhydantoin-substituted bithiophen 21

DMSO-$d_6$, 126 MHz, 298 K
$^1$H NMR of dimethyltriazol-substituted bithiophen 22

CDCl$_3$, 500 MHz, 298 K
\(^{13}\text{C} \text{ NMR of dimethyltriazol-substituted bithiophen 22}\)

CDCl\(_3\), 126 MHz, 298 K
\(^1H\) NMR of pyridon-substituted bithiophen 23

CDCl\(_3\), 500 MHz, 298 K
$^{13}$C NMR of pyridon-substituted bithiophen 23

CDCl$_3$, 126 MHz, 298 K
1H NMR of ethoxy-substituted bithiophen 24

CDCl₃, 500 MHz, 298 K
$^{13}$C NMR of ethoxy-substituted bithiophen 24

CDCl$_3$, 126 MHz, 298 K
$^1$H NMR of cyano-substituted 3-phenylthiophene 25

CDCl$_3$, 500 MHz, 298 K
$^{13}$C NMR of cyano-substituted 3-phenylthiophene 25

CDCl$_3$, 126 MHz, 298 K
\(^1\text{H NMR of cyano-substituted methoxyquinoline 26}\)

CDCl\(_3\), 500 MHz, 298 K
\(^{13}\)C NMR of cyano-substituted methoxyquinoline 26

CDCl\(_3\), 126 MHz, 298 K
$^1$H NMR of cyano-substituted methoxynaphthalene 27

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of cyano-substituted methoxynaphthalene 27

CD$_3$CN, 126 MHz, 298 K
$^1$H NMR of pyrazol-substituted anthracen 28

CD$_3$CN, 500 MHz, 298 K
$^{13}$C NMR of pyrazol-substituted anthracen 28

CD$_3$CN, 126 MHz, 298 K