Supplementary Information

Synthesis of I(III)/S(VI) Reagents and Their Reactivity in Photochemical Cycloaddition Reactions with Unsaturated Bonds

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1. Supplementary Notes.

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Anhydrous solvents were dried by passing through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Visualization of the developed chromatogram was performed by irradiation with UV light or treatment with a solution of appropriate stains. Flash column chromatography was performed on silica gel (Qindao Puke Co., China., 200-300 mesh) or neutral silica gel (Bio-Gene Tech. Ltd., 230-400 mesh). Organic solutions were concentrated under reduced pressure on an EYELA rotatory evaporator. Unless otherwise stated, reactions were carried out under an argon atmosphere. Yields refer to purified compounds unless otherwise noted. NMR spectra were recorded at 298 K (unless otherwise stated) on a Bruker AV 400 MHz NMR spectrometer. Chemical shifts (δ) are quoted in ppm relative to residual solvent signals, CDCl₃ referenced at δ 7.26 and 77.16 ppm, DMSO-d₆ referenced at δ 2.50 and 39.52 ppm, CD₃CN referenced at δ 1.94 and 1.39, 118.69 ppm, Acetone-d₆ referenced at δ 2.05 and 29.92, 206.68 ppm. Coupling constants (J) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, p = quintet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sp = septet, m = multiplet, app = apparent. Mass spectra were collected on an Agilent GC/MS 5975C system, a MALDI Micro MX mass spectrometer, or an API QSTAR XL System.
2. Supplementary Methods.

2.1 Synthesis of I(III)/S(VI) Reagents

Supplementary Figure 1. Cyclic and acyclic hypervalent iodine reagents 3a-3w
**General procedure for the synthesis of ylides 2**

According to the literature,[1] the slightly modified method is as follows. Under N₂, acid (5.0 mmol) in CH₂Cl₂ (10 mL) at 0 °C before adding SOCl₂ (7.5 mmol, 1.5 equiv) and one drop of DMF. After 60 minutes stirring at 50 °C, and the volatiles were carefully evaporated under high-vacuum. During that time, trimethylsulfoxonium iodide (3.3 g, 16.5 mmol, 3.0 equiv) was suspended under N₂ in dry THF (40 mL) in a flame-dried 100 mL round bottom flask that was protected from light with aluminium foil. Potassium tertbutoxide (1.8 g, 16.5 mmol, 3.3 equiv) was added, and the mixture was stirred at reflux for 3 hours. After cooling to 0 °C, a solution of acid chloride obtained above in THF (10 mL) was added dropwise to the mixture. The mixture was stirred at room temperature for another hour and then solvents were removed under vacuum. Then 80 ml water were added, extraction with CH₂Cl₂ (50 × 3 mL). Purification by flash chromatography (dichloromethane/MeOH = 30/1) provided the ylide.

**General procedure A for the synthesis of cyclic I, S-ylides 3**

A solution of 1-acetoxy-1,2-benziodoxol-3(1H)-one (1.53 g, 5.0 mmol, 1.0 equiv.) in dichloromethane (10.0 mL, 0.5 M) was treated with trimethylsilyl trifluoromethanesulfonate (0.9 mL, 5.0 mmol, 1.0 equiv.) at room temperature. After 10 minutes, a solution of pyridine (0.44 mL, 5.5 mmol, 1.1 equiv.) in dichloromethane (2.0 mL) was added dropwise over 10 minutes and the resulted suspension was stirred for 30 min at room temperature. A solution of the corresponding sulfoxonium ylides (5.0 mmol, 1.0 equiv.) in dichloromethane (2.0 mL) was added dropwise over 10 minutes and the resulting reaction mixture was stirred until TLC indicated all the ylide was consumed (usually 8 hours). The reaction solution was washed
with distilled water (200 mL × 2) and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the residue was purified by flash column chromatography (DCM/acetone = 10:1) to provide 3 as white solid.

*General procedure B* for the synthesis of acyclic 1, S-ylide 3

A solution of aryliodosodiacetate (5.0 mmol, 1.0 equiv.) in MeOH (5.0 mL, 1.0 M) was treated with corresponding acid HX (5.0 mmol, 1.0 equiv) at room temperature. This clear solution was added dropwise to the ice bath-cooled solution of sulfoxonium ylides (5.0 mmol, 1.0 equiv.) in MeOH (5.0 mL, 1.0 M) over 10 min with stirring. The resulting reaction mixture was stirred at 0 °C for 1 hour. During this period, a large amount of a white precipitate was formed. The solid was collected by filtration, washed successively with MeOH (5 mL × 3) and Et₂O (5 ml × 3), dried under high vacuum and stored at -20 °C. If the hypervalent iodine reagent failed to precipitate, it was subjected to flash column chromatography, eluting with DCM/Acetone mixtures.
1-(1-(dimethyl(5-oxy)-6-sulfanylidene)-2-oxo-2-phenylethyl)-1,2-benziodoxol-3(1H)-one (3a)

Prepared according to the general procedure A using 2-(dimethyl(5-oxy)-6-sulfanylidene)-1-phenylethan-1-one (981.3 mg, 5.0 mmol). Purification by flash chromatography (dichloromethane/acetone = 4/1) provided 3a as a white solid (773.9 mg, 35% yield).

1H NMR (400 MHz, DMSO-d6) δ 8.12 (d, J = 8.1 Hz, 1H), 8.04 (dd, J = 7.4, 1.7 Hz, 1H), 7.82 (ddd, J = 8.3, 7.1, 1.7 Hz, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.31 (dd, J = 8.5, 6.4 Hz, 2H), 4.03 (s, 3H), 3.76 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 188.97, 166.51, 140.48, 134.76, 134.27, 131.69, 130.96, 130.70, 128.47, 127.22, 126.29, 118.76, 66.08, 42.37.

HRMS (ESI) calculated for C17H16IO4S+ [M+H]+ m/z: 442.9808, found: 442.9810.

1-(1-(dimethyl(5-oxy)-6-sulfanylidene)-2-oxododecyl)-1,2-benziodoxol-3(1H)-one (3b)

Prepared according to the general procedure A using 1-(dimethyl(5-oxy)-6-sulfanylidene)tridecan-2-one (823.4 mg, 3.0 mmol). Purification by flash chromatography (dichloromethane/acetone = 4/1) provided 3b as a white solid (1.1 g, 71% yield).

1H NMR (400 MHz, Acetone-d6) δ 8.21 (dd, J = 7.3, 1.7 Hz, 1H), 7.93 (dd, J = 8.1, 1.0 Hz, 1H), 7.73 (td, J = 8.1, 7.6, 1.7 Hz, 1H), 7.66 (td, J = 7.3, 1.0 Hz, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 2.66 (dt, J = 15.0, 7.4 Hz, 1H), 2.48 (dt, J = 15.1, 7.4 Hz, 1H), 1.53 (p, J = 7.4, 6.8 Hz, 2H), 1.32 – 1.15 (m, 16H), 0.86 (t, J = 6.8 Hz, 3H);

13C NMR (101 MHz, Acetone-d6) δ 193.55, 167.48, 136.03, 134.18, 132.69, 131.02, 125.85, 119.02, 64.00, 43.70, 43.10, 40.13, 32.69, 30.41, 29.97, 26.31, 23.39, 14.44.

HRMS (ESI) calculated for C22H34IO4S+ [M+H]+ m/z: 521.1217, found: 521.1213.
The crystal structure of 3b has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2068912.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxo-2-phenylethyl)(phenyl)iodonium hexafluorophosphate (3c)

\[
\begin{align*}
\text{Me}_2(O)S & \quad \text{PF}_6 \\
\end{align*}
\]

Prepared according to the general procedure B using phenylliodoso diacetate (1.6 g, 5.0 mmol), HPF₆ (0.68 ml, 65% w/w, 5.0 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (981.3 mg, 5.0 mmol). After filtration, 3c was collected as a white solid (2.5 g, 90% yield).

\(^1\)H NMR (400 MHz, CD₃CN) δ 7.79 (d, J = 8.5 Hz, 2H), 7.75 – 7.71 (m, 1H), 7.63 – 7.55 (m, 3H), 7.55 – 7.44 (m, 4H), 3.73 (s, 6H).

\(^{13}\)C NMR (101 MHz, CD₃CN) δ 188.84, 138.55, 133.02, 132.57, 132.19, 131.44, 128.59, 127.41, 118.18, 60.83, 42.54.

\(^{19}\)F NMR (376 MHz, CD₃CN) δ -72.40 (d, J = 706 Hz).

\(^{31}\)P NMR (162 MHz, CD₃CN) δ -144.54 (h, J = 706 Hz).

HRMS (ESI) calculated for C₁₆H₁₆IO₂S⁺ [M-PF₆]⁺ m/z: 398.9910, found: 398.9917.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxo-2-phenylethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (3d)

\[
\begin{align*}
\text{Me}_2(O)S & \quad \text{OTf} \\
\end{align*}
\]

Prepared according to the general procedure B using phenylliodoso diacetate (1.6 g, 5.0 mmol), HOTf (0.44 ml, 5.0 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (981.3 mg, 5.0 mmol). After filtration, 3d was collected as a white solid (2.3 g, 85% yield).

\(^1\)H NMR (400 MHz, CD₃CN) δ 7.78 (d, J = 8.1 Hz, 2H), 7.73 – 7.67 (m, 1H), 7.61 – 7.52 (m, 3H), 7.52 – 7.44 (m, 4H), 3.74 (s, 6H).
$^{13}$C NMR (101 MHz, CD$_3$CN) $\delta$ 188.87, 138.77, 132.96, 132.33, 132.02, 131.29, 128.51, 127.41, 120.90 (q, $J = 316.6$ Hz, OSO$_2$CF$_3$), 117.42, 61.47, 42.44.

$^{19}$F NMR (376 MHz, CD$_3$CN) $\delta$ -79.12.

HRMS (ESI) calculated for C$_{16}$H$_{16}$I$_2$S$^+$ [M-OTf]$^+$ m/z: 398.9910, found: 398.9917.

(1-(dimethyl(oxo)-$\lambda^6$-sulfaneylidene)-2-oxo-2-phenylethyl)(phenyl)iodonium tetrafluoroborate (3e)

Prepared according to the general procedure B using phenyliodoso diacetate (1.6 g, 5.0 mmol), HBF$_4$ (0.66 ml, 48% w/w, 5.0 mmol) and 2-(dimethyl(oxo)-$\lambda^6$-sulfaneylidene)-1-phenylethan-1-one (981.3 mg, 5.0 mmol). After filtration, 3e was collected as a white solid (2.2 g, 92% yield).

$^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 7.80 – 7.75 (m, 2H), 7.72 (tt, $J = 6.9$, 1.1 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.53 – 7.43 (m, 4H), 3.74 (s, 6H).

$^{13}$C NMR (101 MHz, CD$_3$CN) $\delta$ 188.90, 138.66, 132.93, 132.48, 132.15, 131.37, 128.57, 127.40, 118.14, 61.00, 42.44.

$^{19}$F NMR (376 MHz, CD$_3$CN) $\delta$ -150.08 (d, $J = 18.8$ Hz).

HRMS (ESI) calculated for C$_{16}$H$_{16}$I$_2$S$^+$ [M-BF$_4$]$^+$ m/z: 398.9910, found: 398.9919.

The crystal structure of 3e has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2068911.

(1-(dimethyl(oxo)-$\lambda^6$-sulfaneylidene)-2-oxo-2-(4-cyclohexylphenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3f)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 1-(4-cyclohexylphenyl)-2-(dimethyl(oxo)-$\lambda^6$-sulfanyliden)ethan-1-one
(834.4 g, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3f was collected as a white solid (1.77 g, 94% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.96 – 7.90 (m, 2H), 7.74 (tt, $J = 6.6, 1.1$ Hz, 1H), 7.66 – 7.60 (m, 2H) 7.52 – 7.45 (m, 2H), 7.38 – 7.32 (m, 2H), 3.91 (s, 6H), 2.65 – 2.59 (m, 1H), 1.89 – 1.82 (m, 4H), 1.79 – 1.71 (m, 1H), 1.54 – 1.38 (m, 4H), 1.35 – 1.27 (m, 1H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 188.76, 151.80, 136.30, 132.61, 132.34, 132.22, 127.86, 126.81, 118.65, 61.45, 44.34, 42.32, 34.08, 26.58, 25.83.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.28 (d, $J = 709$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.12 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{22}$H$_{26}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 481.0693, found: 481.0691.

$^{1}$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.03 – 7.92 (m, 2H), 7.76 (tt, $J = 6.7, 1.1$ Hz, 1H), 7.71 – 7.60 (m, 2H), 7.51 – 7.41 (m, 2H), 7.32 (d, $J = 7.7$ Hz, 2H), 3.94 (s, 6H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 188.76, 141.88, 135.97, 132.66, 132.33, 132.18, 128.96, 127.74, 118.72, 61.33, 42.30, 20.60.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.80 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.19 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{17}$H$_{18}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 413.0067, found: 413.0070.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(p-tolyl)ethyl)(phenyl)iodonium hexafluorophosphate (3g)

Prepared according to the general procedure B using phenyliodosodiacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-1-(p-tolyl)ethan-1-one (630.0 mg, 3.0 mmol). After filtration, 3g was collected as a white solid (1.3 g, 75% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.03 – 7.92 (m, 2H), 7.76 (tt, $J = 6.7, 1.1$ Hz, 1H), 7.71 – 7.60 (m, 2H), 7.51 – 7.41 (m, 2H), 7.32 (d, $J = 7.7$ Hz, 2H), 3.94 (s, 6H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 188.76, 141.88, 135.97, 132.66, 132.33, 132.18, 128.96, 127.74, 118.72, 61.33, 42.30, 20.60.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.80 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.19 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{17}$H$_{18}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 413.0067, found: 413.0070.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(4-chloorophenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3h)
Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 1-(4-chlorophenyl)-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)ethan-1-one (690.0 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3h was collected as a light yellow solid (1.5 g, 87% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.01 (d, $J = 7.8$ Hz, 2H), 7.77 (t, $J = 7.4$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 2H), 7.58 – 7.53 (m, 4H), 3.96 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 187.54, 137.63, 136.67, 132.82, 132.42, 132.25, 129.36, 128.64, 118.67, 61.87, 42.18.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.80 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.20 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{16}$H$_{15}$IClO$_2$S$^+$/[M-PF$_6$]$^+$ m/z: 432.9520, found: 432.9522.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(3-chlorophenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3i)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 1-(3-chlorophenyl)-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)ethan-1-one (690.1 mg, 3.0 mmol). After filtration, 3i was collected as a white solid (1.59 g, 89% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.99 (d, $J = 8.0$ Hz, 2H), 7.82 – 7.75 (m, 1H), 7.66 (t, $J = 7.8$ Hz, 2H), 7.63 – 7.59 (m, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 3.98 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 187.13, 140.97, 133.76, 132.97, 132.45, 132.22, 131.08, 130.50, 127.39, 125.92, 118.74, 62.13, 42.15.
$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.89 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.21 (h, $J = 708$ Hz).

**HRMS** (ESI) calculated for C$_{18}$H$_{20}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 427.0223, found: 427.0232.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(3,4-dimethylphenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3j)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-1-(3,4-dimethylphenyl)ethan-1-one (720.4 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3j was collected as a white solid (1.69 g, 96% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.00 – 7.94 (m, 2H), 7.80 – 7.74 (m, 1H), 7.68 – 7.63 (m, 2H), 7.30 – 7.21 (m, 3H), 3.95 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 189.05, 140.54, 136.66, 136.42, 132.66, 132.30, 132.15, 129.53, 128.73, 125.19, 118.90, 61.36, 42.31, 18.97, 18.85.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.77 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.19 (h, $J = 709$ Hz).

**HRMS** (ESI) calculated for C$_{18}$H$_{20}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 427.0223, found: 427.0232.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylelidene)-2-oxo-2-(5-methylthiophen)ethyl)(phenyl)iodonium hexafluorophosphate (3k)
Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-λ⁶-sulfanylidene)-1-(5-methylthiophen-2-yl)ethan-1-one (648.1 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3k was collected as a white solid (869.9 mg, 50% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.13 – 8.08 (m, 2H), 7.77 – 7.70 (m, 1H), 7.68 – 7.62 (m, 3H), 6.90 (dd, J = 3.8, 1.2 Hz, 1H), 3.92 (s, 6H), 2.53 (s, 3H).

¹³C NMR (101 MHz, Acetone-d₆) δ 178.49, 147.57, 138.61, 132.28, 132.25, 132.25, 132.18, 132.12, 126.65, 118.60, 58.42, 42.90, 14.66.

¹⁹F NMR (376 MHz, Acetone-d₆) δ -71.55 (d, J = 708 Hz).

³¹P NMR (162 MHz, Acetone-d₆) δ -144.17 (h, J = 709 Hz).

HRMS (ESI) calculated for C₁₅H₁₆IO₂S⁺ [M-PF₆⁺] m/z: 418.9631, found: 418.9632.

(1-(dimethyl(oxo)-λ⁶-sulfanylidene)-2-oxo-2-(thiophen-2-yl)ethyl)(phenyl)iodonium hexafluorophosphate (3l)

Prepared according to the general procedure B using phenyliodoso diacetate (1.6 g, 5.0 mmol), HPF₆ (0.68 ml, 65% w/w, 5.0 mmol) and 2-(dimethyl(oxo)-λ⁶-sulfanylidene)-1-(thiophen-2-yl)ethan-1-one (1.0 g, 5.0 mmol). After filtration, 3l was collected as a white solid (2.50 g, 89% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.15 – 8.10 (m, 2H), 7.85 (dd, J = 5.0, 1.1 Hz, 1H), 7.81 (dd, J = 3.8, 1.1 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.69 – 7.63 (m, 2H), 7.22 (dd, J = 5.0, 3.8 Hz, 1H), 3.96 (s, 6H).

¹³C NMR (101 MHz, Acetone-d₆) δ 178.88, 141.05, 132.29, 132.26, 132.10, 131.50, 127.86, 118.61, 59.29, 42.77.

¹⁹F NMR (376 MHz, Acetone-d₆) δ -71.96 (d, J = 707 Hz).

³¹P NMR (162 MHz, Acetone-d₆) δ -144.21 (h, J = 708 Hz).

HRMS (ESI) calculated for C₁₄H₁₄O₂S⁺ [M-PF₆⁺] m/z: 404.9474, found: 404.9481.
(1-(dimethyl(oxo)-λ₆-sulfanylidene)-2-oxo-2-(benzo[b]thiophen-2-yl)ethyl)(phenyl)iodonium hexafluorophosphate (3m)

![Chemical Structure](image)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and 1-(benzo[b]thiophen-2-yl)-2-(dimethyl(oxo)-λ₆-sulfanylidene)ethan-1-one (756.1 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3m was collected as a light yellow solid (1.24 g, 67% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.18 – 8.15 (m, 2H), 8.05 (s, 1H), 8.03 (d, J = 7.4 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.82 – 7.75 (m, 1H), 7.69 – 7.65 (m, 2H), 7.57 – 7.51 (m, 1H), 7.49 (td, J = 7.5, 1.3 Hz, 1H), 3.98 (s, 6H).

¹³C NMR (101 MHz, Acetone-d₆) δ 179.75, 141.03, 140.72, 138.83, 132.60, 132.40, 132.31, 128.22, 127.09, 125.65, 125.30, 122.62, 118.94, 60.77, 42.59.

¹⁹F NMR (376 MHz, Acetone-d₆) δ -71.88 (d, J = 708 Hz).

³¹P NMR (162 MHz, Acetone-d₆) δ -144.18 (h, J = 709 Hz).

HRMS (ESI) calculated for C₁₈H₁₆IO₂S₂⁺ [M-PF₆]⁺ m/z: 454.9631, found: 454.9635.

(1-(dimethyl(oxo)-λ₆-sulfanylidene)-2-oxo-2-(furan-2-yl)ethyl)(phenyl)iodonium hexafluorophosphate (3n)

![Chemical Structure](image)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-λ₆-sulfanylidene)-1-(furan-2-yl)ethan-1-one (558.1 mg, 3.0 mmol). After filtration, 3n was collected as a white solid (1.3 g, 76% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.26 – 8.18 (m, 2H), 7.96 – 7.93 (m, 1H), 7.74 (tt, J = 6.7, 1.2 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.28 (d, J = 3.6 Hz, 1H), 6.73 (dd, J = 3.6, 1.8 Hz, 1H), 3.93 (s, 6H).
$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 172.88, 151.24, 145.88, 133.17, 132.22, 131.93, 119.01, 116.69, 112.55, 57.07, 42.81.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.07 (d, $J$ = 707 Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.22 (h, $J$ = 709 Hz).

HRMS (ESI) calculated for C$_{14}$H$_{14}$IO$_3$S$^+$ [M-PF$_6$]$^+$ m/z: 388.9703, found: 388.9704.

(1-(dimethyl(oxo)-$^{\lambda_6}$-sulfanylidene)-2-oxo-2-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)iodonium hexafluorophosphate (3o)

Prepared according to the general procedure B using phenyliodoso diacetate (644.0 mg, 2.0 mmol), HPF$_6$ (0.28 ml, 65% w/w, 2.0 mmol) and 1-([1,1'-biphenyl]-4-yl)-2-(dimethyl(oxo)-$^{\lambda_6}$-sulfanylidene)ethan-1-one (544.2 mg, 2.0 mmol). After filtration, 3o was collected as a white solid (1.1 g, 89% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 8.11 – 8.00 (m, 2H), 7.85 – 7.81 (m, 2H), 7.81 – 7.74 (m, 3H), 7.73 – 7.63 (m, 4H), 7.57 – 7.49 (m, 2H), 7.49 – 7.39 (m, 1H), 4.00 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 188.40, 143.84, 139.58, 137.60, 132.88, 132.39, 132.21, 129.04, 128.38, 128.18, 127.06, 126.76, 118.86, 61.62, 42.31.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.14 (d, $J$ = 707 Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.22 (h, $J$ = 709 Hz).

HRMS (ESI) calculated for C$_{22}$H$_{20}$O$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 475.0223, found: 475.0227.

(1-(dimethyl(oxo)-$^{\lambda_6}$-sulfanylidene)-2-oxo-2-(o-tolyl)ethyl)(phenyl)iodonium hexafluorophosphate (3p)
Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 1-([1,1'-biphenyl]-2-yl)-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)ethan-1-one (630.2 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3p was collected as a light yellow solid (1.5 g, 91% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.78 – 7.73 (m, 3H), 7.59 (t, $J = 7.7$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 3.98 (s, 6H), 2.13 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 189.70, 139.19, 135.04, 133.48, 132.43, 131.96, 130.89, 130.02, 126.67, 125.53, 118.57, 63.16, 42.31, 17.99.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.77 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.19 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{17}$H$_{18}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 413.0067, found: 413.0063.

(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(phenoxyphenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3q)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-1-(2-phenoxyphenyl)ethan-1-one (864.2 g, 3.0 mmol). After filtration, 3q was collected as a white solid (1.68 g, 88% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.91 – 7.90 (m, 2H), 7.74 (tt, $J = 6.9$, 1.1 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.44 (dd, $J = 7.6$, 1.8 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.15 – 7.09 (m, 1H), 7.05 – 7.03 (m, 1H), 6.81 (d, $J = 7.5$ Hz, 2H), 3.79 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 186.33, 156.82, 152.86, 133.18, 132.36, 132.10, 132.00, 131.61, 129.91, 129.30, 124.10, 123.74, 119.34, 118.43, 118.09, 62.96, 42.15.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.56 (d, $J = 708$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.14 (h, $J = 709$ Hz).

HRMS (ESI) calculated for C$_{22}$H$_{10}$IO$_2$S$^+$ [M-PF$_6$]$^+$ m/z: 491.0172, found: 491.0177.
(1-(dimethyl(oxo)-λ₆-sulfaneylidene)-2-oxo-2-(4-nitrilephenyl)ethyl)(phenyl)iodonium hexafluorophosphate (3r)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and 4-(2-(dimethyl(oxo)-λ₆-sulfanylidene)acetyl)benzonitrile (663.2 mg, 3.0 mmol). After filtration, 3r was collected as a white solid (1.14 g, 65% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.00 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 7.9 Hz, 2H), 7.77 (t, J = 7.4 Hz, 1H), 7.71 (d, J = 7.9 Hz, 2H), 7.65 (t, J = 7.8 Hz, 2H), 3.98 (s, 6H).

¹³C NMR (101 MHz, Acetone-d₆) δ 187.03, 143.19, 133.01, 132.52, 132.50, 132.28, 128.24, 118.66, 117.84, 114.36, 62.44, 42.11.

¹⁹F NMR (376 MHz, Acetone-d₆) δ -71.77 (d, J = 708 Hz).

³¹P NMR (162 MHz, Acetone-d₆) δ -144.20 (h, J = 709 Hz).

HRMS (ESI) calculated for C₁₇H₁₅INO₂S⁺ [M-PF₆]⁺ m/z: 423.9863, found: 423.9864.

(1-(dimethyl(oxo)-λ₆-sulfaneylidene)-2-oxo-2-(naphthalen-1-yl)ethyl)(phenyl)iodonium tetrafluoroborate (3s)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HBF₄ (0.40 ml, 48% w/w, 3.0 mmol) and 2-(dimethyl(oxo)-λ₆-sulfanylidene)-1-(naphthalen-1-yl)ethan-1-one (738.2 g, 3.0 mmol). After filtration, 3s was collected as a white solid (1.24 g, 75% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.05 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.68 – 7.48 (m, 6H), 7.42 – 7.38 (m, 3H), 4.20 – 3.97 (m, 6H).
\[ ^{13}\text{C} \text{ NMR} \ (101 \text{ MHz, Acetone-}d_6) \ \delta \ 189.15, 137.24, 133.59, 132.96, 132.00, 131.66, 130.21, 129.59, 128.44, 127.08, 126.62, 125.07, 125.05, 124.79, 118.36, 64.62, 42.26. \]

\[ ^{19}\text{F} \text{ NMR} \ (376 \text{ MHz, Acetone-}d_6) \ \delta \ -149.05. \]

HRMS (ESI) calculated for C\text{\textsubscript{2}0}H\text{\textsubscript{18}}IO\text{\textsubscript{2}}S\textsuperscript{+} [M-BF\textsubscript{4}\textsuperscript{+}] m/z: 449.0067, found: 449.0065.

(1-(dimethyl(oxo)-\ensuremath{\lambda}\textsuperscript{6}-sulfaneylidene)-2-oxo-2-(3-phenyl)propan)(phenyl)iodonium hexafluorophosphate (3t)

\[
\text{Prepared according to the general procedure B using phenyliodoacetic acid (1.6 g, 5.0 mmol), HPF\textsubscript{6} (0.68 ml, 65\% w/w, 5.0 mmol) and 1-(dimethyl(oxo)-\ensuremath{\lambda}\textsuperscript{6}-sulfaneylidene)-3-phenylpropan-2-one (1.0 g, 5.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3t was collected as a white foamy solid (2.5 g, 91\% yield).} \]

\[ ^{1}\text{H} \text{ NMR} \ (400 \text{ MHz, Acetone-}d_6) \ \delta \ 7.90 \ (d, J = 8.2 \text{ Hz, 2H}), 7.70 \ (t, J = 7.4 \text{ Hz, 1H}), 7.59 – 7.48 \ (m, 2H), 7.35 – 7.21 \ (m, 5H), 4.22 \ (s, 2H), 3.83 \ (s, 6H). \]

\[ ^{13}\text{C} \text{ NMR} \ (101 \text{ MHz, Acetone-}d_6) \ \delta \ 189.36, 135.15, 132.59, 132.05, 131.89, 129.33, 128.58, 126.88, 118.28, 59.43, 45.61, 42.41. \]

\[ ^{19}\text{F} \text{ NMR} \ (376 \text{ MHz, Acetone-}d_6) \ \delta \ -72.18 \ (d, J = 707 \text{ Hz}). \]

\[ ^{31}\text{P} \text{ NMR} \ (162 \text{ MHz, Acetone-}d_6) \ \delta \ -144.22 \ (h, J = 708 \text{ Hz}). \]

HRMS (ESI) calculated for C\text{\textsubscript{17}}H\text{\textsubscript{18}}IO\text{\textsubscript{2}}S\textsuperscript{+} [M-PF\textsubscript{6}\textsuperscript{+}] m/z: 413.0067, found: 413.0082.

(1-(dimethyl(oxo)-\ensuremath{\lambda}\textsuperscript{6}-sulfaneylidene)-2-oxo-2-(4-phenylbutan))(phenyl)iodonium hexafluorophosphate (3u)
Prepared according to the general procedure A using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and 1-(dimethyl(oxo)-λ⁶-sulfanylidene)-4-phenylbutan-2-one (672.3 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3u was collected as a white foamy solid (1.4 g, 81% yield).

**¹H NMR** (400 MHz, CD₃CN) δ 7.83 (d, J = 8.3 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.9 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.25 – 7.21 (m, 3H), 3.58 (s, 6H), 3.07 – 3.03 (m, 2H), 2.94 – 2.90 (m, 2H).

**¹³C NMR** (101 MHz, CD₃CN) δ 190.88, 140.95, 132.70, 132.35, 132.13, 128.49, 126.22, 117.89, 59.13, 42.85, 39.97, 30.77.

**¹⁹F NMR** (376 MHz, CD₃CN) δ -72.45 (d, J = 708 Hz).

**³¹P NMR** (162 MHz, CD₃CN) δ -144.54 (h, J = 707 Hz).

**HRMS (ESI) calculated for C₁₈H₂₀IO₂S⁺ [M-PF₆]⁺ m/z: 427.0223, found: 427.0229.**

(E)(1-(dimethyl(oxo)-λ⁶-sulfanylidene)-2-oxo-2-(6-(p-tolyl)hex-5-en-2-one))(phenyl)iodonium hexafluorophosphate (3v)

Prepared according to the general procedure B using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF₆ (0.41 ml, 65% w/w, 3.0 mmol) and (E)-1-(dimethyl(oxo)-λ⁶-sulfanylidene)-6-(p-tolyl)hex-5-en-2-one (792.3 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3v was collected as a white foamy solid (1.3 g, 70% yield).

**¹H NMR** (400 MHz, Acetone-d₆) δ 8.18 – 8.08 (m, 2H), 7.76 – 7.66 (m, 1H), 7.63 – 7.53 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.37 (d, J = 15.9 Hz, 1H), 6.21 (dt, J = 15.9, 6.8 Hz, 1H), 3.79 (s, 6H), 3.02 (t, J = 7.3 Hz, 2H), 2.48 (dt, J = 6.8, 7.3 Hz, 2H), 2.28 (s, 3H).

**¹³C NMR** (101 MHz, Acetone-d₆) δ 190.86, 136.61, 134.77, 132.74, 132.20, 132.10, 130.63, 129.11, 127.77, 125.92, 118.45, 59.71, 42.57, 38.32, 20.25.

**¹⁹F NMR** (376 MHz, Acetone-d₆) δ -71.94 (d, J = 707 Hz).
$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.21 (h, $J = 708$ Hz).

HRMS (ESI) calculated for $[\text{C}_{21}\text{H}_{24}\text{IO}_2\text{S}]^+$ $\text{m/z}$: 467.0536, found: 467.0538.

$(E)$-(1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2-oxo-2-(non-5-en-2-one))(phenyl)iodonium hexafluorophosphate (3w)

![Diagram of the molecule](image)

Prepared according to the *general procedure B* using phenyliodoso diacetate (966.0 mg, 3.0 mmol), HPF$_6$ (0.41 ml, 65% w/w, 3.0 mmol) and $(E)$-1-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)non-5-en-2-one (648.9 mg, 3.0 mmol). After flash column chromatography, eluting with DCM/Acetone mixtures, 3w was collected as a white foamy solid (1.5 g, 88% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 8.17 – 8.09 (m, 2H), 7.78 – 7.69 (m, 1H), 7.64 – 7.59 (m, 2H), 5.40 (td, $J = 3.7$, 1.8 Hz, 2H), 3.79 (s, 6H), 2.89 (t, $J = 7.3$ Hz, 2H), 2.31 – 2.22 (m, 2H), 1.91 – 1.86 (m, 2H), 1.29 (h, $J = 7.4$ Hz, 2H), 0.83 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 191.02, 132.68, 132.20, 132.09, 131.08, 128.62, 118.41, 59.52, 42.60, 38.53, 34.37, 27.99, 22.37, 13.00.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.97 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.23 (h, $J = 708$ Hz).

HRMS (ESI) calculated for $[\text{C}_{17}\text{H}_{24}\text{IO}_2\text{S}]^+$ $\text{m/z}$: 419.0536, found: 419.0539.
2.2 Light-mediated Tandem [4+2] Cycloaddition: reaction scope.

General Procedure C

To a 10 mL oven-dried tube equipped with a stirring bar was added reagent 3 (0.2 mmol, 1.0 equiv.), alkene 4 (0.8 mmol, 4.0 equiv.), anhydrous MeCN (1.0 mL). The reaction vial was capped with a rubber septum under an argon atmosphere, and it was fixed on a SynLED 4x4 photoreactor (SynLED discover™ 452 nm, 1W, designed and manufactured by Shenzhen SynLED Tech. Ltd., see the picture below for reaction setup) for 5 hours. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography to yield the corresponding products 5.

Supplementary Figure 2. Experimental setup for light-mediated cloaddition reaction.
2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-4-ethyl-3,4-dihydronaphthalen-1(2$H$)-one (5a)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and but-1-ene (0.8 ml, 0.8 mmol, 10% in hexane). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (39.0 mg, 78% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dd, $J = 7.4$, 1.7 Hz, 1H), 7.34 (td, $J = 7.3$, 1.7 Hz, 1H), 7.28 (td, $J = 7.4$, 1.5 Hz, 1H), 7.16 (d, $J = 6.6$ Hz, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 2.80 – 2.71 (m, 2H), 2.70 – 2.62 (m, 1H), 1.64 (p, $J = 7.3$ Hz, 2H), 0.92 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.15, 144.33, 134.55, 130.34, 127.60, 126.51, 124.92, 71.23, 42.65, 42.40, 40.76, 27.18, 23.89, 12.21.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{14}$H$_{19}$O$_2$S]$^+$ m/z: 251.1100, found 251.1092.

2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-4-propyl-3,4-dihydronaphthalen-1(2$H$)-one (5b)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and pent-1-ene (56.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (45.4 mg, 86% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dd, $J = 7.5$, 1.7 Hz, 1H), 7.33 (td, $J = 7.3$, 1.7 Hz, 1H), 7.28 (td, $J = 7.3$, 1.4 Hz, 1H), 7.15 (d, $J = 7.3$ Hz, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 2.86 (tt, $J = 7.5$, 3.9 Hz, 1H), 2.80 – 2.59 (m, 2H), 1.65 – 1.53 (m, 2H), 1.47 – 1.33 (m, 1H), 1.30 – 1.21 (m, 1H), 0.89 (t, $J = 7.3$ Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.26, 144.66, 134.63, 130.42, 127.57, 126.55, 125.01, 71.27, 42.71, 42.49, 38.84, 36.69, 24.34, 20.75, 14.25.

HRMS (ESI-TOF) [M] calculated for [C$_{15}$H$_{20}$O$_2$S] m/z: 264.1184, found 264.1123.

4-butyl-2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)-3,4-dihydronaphthalen-1(2H)-one (5c)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and hex-1-ene (67.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (50.0 mg, 90% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (dd, $J$ = 7.5, 1.6 Hz, 1H), 7.36 (td, $J$ = 7.4, 1.3 Hz, 1H), 7.31 (td, $J$ = 7.4, 1.5 Hz, 1H), 7.17 (dd, $J$ = 7.3, 1.5 Hz, 1H), 3.59 (s, 3H), 3.56 (s, 3H), 2.6 (tt, $J$ = 7.4, 4.0 Hz, 1H), 2.81 – 2.62 (m, 2H), 1.69 – 1.55 (m, 2H), 1.40 – 1.25 (m, 4H), 0.89 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.27, 144.73, 134.61, 130.46, 127.56, 126.55, 124.99, 71.22, 42.71, 42.49, 39.10, 34.11, 29.83, 24.28, 22.86, 14.14.

HRMS (ESI-TOF) [M] calculated for [C$_{16}$H$_{22}$O$_2$S] m/z: 278.1341, found 278.1277.

2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)-4-pentyl-3,4-dihydronaphthalen-1(2H)-one (5d)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and hept-1-ene (79.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH:
30/1) provided the title compound as white solid (53.1 mg, 91% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\)H NMR spectroscopy.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (dd, \(J = 7.5, 1.6\) Hz, 1H), 7.35 (td, \(J = 7.3, 1.7\) Hz, 1H), 7.35 (td, \(J = 7.5, 1.6\) Hz, 1H), 7.17 (dd, \(J = 7.4, 1.5\) Hz, 1H), 3.58 (s, 3H), 3.56 (s, 3H), 2.86 (tt, \(J = 7.4, 4.3\) Hz, 1H), 2.81 – 2.61 (m, 2H), 1.65 – 1.55 (m, 2H), 1.45 – 1.35 (m, 1H), 1.33 – 1.22 (m, 5H), 0.88 (t, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.24, 144.73, 134.60, 130.45, 127.54, 126.53, 124.99, 71.28, 42.71, 42.47, 39.10, 34.36, 31.99, 27.27, 24.26, 22.64, 14.15.

HRMS (ESI-TOF) \([\text{M}+\text{H}]^+\) calculated for \([\text{C}_{17}\text{H}_{25}\text{O}_2\text{S}]^+\) m/z: 293.1570, found 293.1568.

2-(dimethyl(oxo)-\(\lambda^6\)-sulfanylidene)-4-hexyl-3,4-dihydropyridone-1(2H)-one (5e)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and oct-1-ene (89.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (58.2 mg, 95% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\)H NMR spectroscopy.

\(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 7.90 (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.33 (td, \(J = 7.4, 1.6\) Hz, 1H), 7.26 (td, \(J = 7.5, 1.4\) Hz, 1H), 7.20 (d, \(J = 7.5\) Hz, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 2.88 – 2.80 (m, 1H), 2.76 – 2.62 (m, 2H), 1.74 – 1.62 (m, 1H), 1.61 – 1.51 (m, 1H), 1.45 – 1.37 (m, 1H), 1.34 – 1.28 (m, 8H), 0.88 (t, \(J = 6.4\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta\) 174.89, 144.73, 135.49, 129.70, 127.26, 125.92, 125.06, 70.65, 70.61, 41.12, 41.06, 39.04, 34.29, 31.70, 27.43, 24.34, 22.41, 13.47.

HRMS (ESI-TOF) \([\text{M}+\text{Na}]^+\) calculated for \([\text{C}_{18}\text{H}_{26}\text{NaO}_2\text{S}]^+\) m/z: 329.1546, found 329.1543.
2-(dimethyl(oxo)-λ⁶-sulfanylidene)-4-octyl-3,4-dihydronaphthalen-1(2H)-one (5f)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and dec-1-ene (112.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (61.6 mg, 92% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.

¹H NMR (400 MHz, CDCl₃) δ 8.32 (dd, J = 7.5, 1.7 Hz, 1H), 7.75 (td, J = 7.3, 1.7 Hz, 1H), 7.70 (td, J = 7.5, 1.6 Hz, 1H), 7.57 (dd, J = 7.3, 1.5 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.28 – 3.22 (m, 1H), 2.04 – 1.97 (m, 2H), 1.82 – 1.74 (m, 1H), 1.70 – 1.63 (m, 11H), 1.28 (t, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.28, 144.75, 134.62, 130.46, 127.56, 126.54, 124.99, 71.24, 42.73, 42.50, 39.12, 34.42, 31.95, 29.82, 29.62, 29.39, 27.63, 24.27, 22.74, 14.19.

HRMS (ESI-TOF) [M+H]+ calculated for [C₂₀H₃₁O₂S]+ m/z: 335.2039, found 335.2039.

4-decyl-2-(dimethyl(oxo)-λ⁶-sulfanylidene)-3,4-dihydronaphthalen-1(2H)-one (5g)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and dodec-1-ene (134.4 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (65.3 mg, 90% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.
\({ }^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \(\delta \) 7.91 (dd, \(J = 7.6, 1.6 \text{ Hz, 1H}\)), 7.35 (td, \(J = 7.3, 1.7 \text{ Hz, 1H}\)), 7.29 (td, \(J = 7.4, 1.5 \text{ Hz, 1H}\)), 7.16 (dd, \(J = 7.3, 1.5 \text{ Hz, 1H}\)), 3.58 (s, 3H), 3.55 (s, 3H), 2.85 (tt, \(J = 7.4, 3.9 \text{ Hz, 1H}\)), 2.80 – 2.61 (m, 2H), 1.65 – 1.56 (m, 2H), 1.42 – 1.34 (m, 1H), 1.30 – 1.22 (m, 15H), 0.88 (t, \(J = 6.8 \text{ Hz, 3H}\)).

\({ }^{13} \text{C NMR} \) (101 MHz, CDCl\(_3\)) \(\delta \) 176.21, 144.73, 134.58, 130.45, 127.54, 126.53, 124.99, 71.39, 42.71, 42.48, 39.09, 34.40, 34.13, 33.08, 26.64, 26.29, 26.15, 24.27, 22.74, 14.18.

HRMS (ESI-TOF) [M] calculated for [C\(_{22}\)H\(_{34}\)O\(_2\)S] m/z: 362.2280, found 362.2232.

4-(cyclohexylmethyl)-2-(dimethyl(oxo)-\(\lambda^6\)-sulfanylidene)-3,4-dihyronaphthalen-1(2\(H\))-one (5h)

This compound was synthesized following the general procedure C using reagent 3e (108.8 mg, 0.2 mmol), and allylcyclohexane (99.4 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (44.6 mg, 70% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^{1} \text{H NMR} \) spectroscopy.

\({ }^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \(\delta \) 7.91 (dd, \(J = 7.6, 1.6 \text{ Hz, 1H}\)), 7.35 (td, \(J = 7.4, 1.7 \text{ Hz, 1H}\)), 7.30 (td, \(J = 7.4, 1.5 \text{ Hz, 1H}\)), 7.15 (dd, \(J = 7.4, 1.4 \text{ Hz, 1H}\)), 3.58 (s, 3H), 3.56 (s, 3H), 3.06 – 2.95 (m, 1H), 2.80 – 2.57 (m, 2H), 1.78 – 1.64 (m, 5H), 1.57 – 1.50 (m, 1H), 1.44 – 1.40 (m, 1H), 1.33 – 1.12 (m, 5H), 1.01 – 0.83 (m, 2H).

\({ }^{13} \text{C NMR} \) (101 MHz, CDCl\(_3\)) \(\delta \) 176.18, 145.10, 134.56, 130.51, 127.26, 126.42, 124.96, 71.33, 42.67, 42.39, 42.16, 35.69, 34.88, 34.13, 33.08, 26.64, 26.29, 26.15, 24.10.

HRMS (ESI-TOF) [M+H]\(^+\) calculated for [C\(_{19}\)H\(_{27}\)O\(_2\)]\(^+\) m/z: 319.1726, found 319.1680.
4-benzyl-2-(dimethyl(oxo)-\(\lambda^6\)-sulfanylidene)-3,4-dihyronaphthalen-1(2\(H\))-one (5i)

This compound was synthesized following the *general procedure C* using reagent 3c (108.8 mg, 0.2 mmol), and allylbenzene (94.5 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (56.0 mg, 86% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\)H NMR spectroscopy.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (dd, \(J = 7.1, 2.0\) Hz, 1H), 7.36 – 7.31 (m, 2H), 7.29 (dd, \(J = 4.6, 2.1\) Hz, 2H), 7.25 – 7.19 (m, 1H), 7.08 (d, \(J = 7.0\) Hz, 2H), 6.99 (dd, \(J = 7.0, 1.8\) Hz, 1H), 3.65 (s, 3H), 3.54 (s, 3H), 3.19 – 3.11 (m, 1H), 2.98 – 2.85 (m, 2H), 2.73 (dd, \(J = 14.2, 4.9\) Hz, 1H), 2.65 (dd, \(J = 14.3, 3.0\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.16, 143.49, 140.16, 134.53, 130.53, 129.31, 128.38, 127.88, 126.86, 126.24, 125.06, 71.44, 42.88, 42.47, 41.33, 41.15, 23.80.

HRMS (ESI-TOF) [M+H]\(^+\) calculated for [C\(_{19}\)H\(_{21}\)O\(_2\)S]\(^+\) m/z: 313.1257, found 313.1269.

2-(dimethyl(oxo)-\(\lambda^6\)-sulfanylidene)-4-phenethyl-3,4-dihyronaphthalen-1(2\(H\))-one (5j)

This compound was synthesized following the *general procedure C* using reagent 3c (108.8 mg, 0.2 mmol), and but-3-en-1-ylbenzene (105.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (56.0 mg, 86% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\)H NMR spectroscopy.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 (dd, \(J = 7.4, 1.7\) Hz, 1H), 7.42 – 7.26 (m, 4H), 7.24 – 7.10 (m, 4H), 3.59 (s, 3H), 3.55 (s, 3H), 2.93 (tt, \(J = 7.4, 3.8\) Hz, 1H), 2.83 (dd, \(J = 14.2, 4.7\) Hz, 1H), 2.79 – 2.68 (m, 2H), 2.67 – 2.54 (m, 1H), 2.00 – 1.94 (m, 2H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 176.16, 144.12, 142.19, 134.65, 130.51, 128.46, 128.41, 127.64, 126.74, 125.87, 125.12, 71.15, 42.63, 42.56, 38.72, 36.10, 33.82, 24.38.

HRMS (ESI-TOF) [M] calculated for [C$_{20}$H$_{22}$O$_2$S]$^+$ m/z: 326.1341, found 326.1276.

4-((benzyloxy)methyl)-2-(dimethyl(oxo-$\lambda^6$-sulfanylidene)-3,4-dihydronaphthalen-1(2H)-one (5k)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and ((allyloxy)methyl)benzene (118.4 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (47.8 mg, 70% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (dd, $J = 7.4$, 1.8 Hz, 1H), 7.40 – 7.32 (m, 6H), 7.32 – 7.29 (m, 1H), 7.24 (dd, $J = 7.1$, 1.7 Hz, 1H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.41 (d, $J = 12.2$ Hz, 1H), 3.70 – 3.60 (m, 1H), 3.54 (s, 3H), 3.42 (dd, $J = 9.3$, 4.8 Hz, 1H), 3.36 (s, 3H), 3.29 – 3.25 (m, 1H), 3.00 (dd, $J = 14.2$, 3.0 Hz, 1H), 2.74 (dd, $J = 14.2$, 4.9 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.72, 140.33, 138.39, 135.31, 130.72, 128.55, 128.10, 127.74, 127.26, 125.06, 73.12, 71.32, 42.57, 42.18, 39.57, 21.37.

HRMS (ESI-TOF) [M$^+$H]$^+$ calculated for [C$_{20}$H$_{23}$O$_3$S]$^+$ m/z: 343.1362, found 343.1360.

4-(3-(dimethyl(oxo-$\lambda^6$-sulfanylidene)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)butyl benzoate (5l)
This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and hex-5-en-1-yl benzoate (163.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (45.4 mg, 62% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \( ^1H \) NMR spectroscopy.

\[ ^1H \text{NMR} (400 \text{ MHz, Acetone-}d_6) \delta 8.08 – 7.99 (m, 2H), 7.90 (dd, \textit{J} = 7.6, 1.6 \text{ Hz, 1H}), 7.64 (tt, \textit{J} = 6.8, 1.4 \text{ Hz, 1H}), 7.54 – 7.50 (m, 2H), 7.32 (td, \textit{J} = 7.3, 1.6 \text{ Hz, 1H}), 7.26 (td, \textit{J} = 7.4, 1.5 \text{ Hz, 1H}), 7.21 (dd, \textit{J} = 7.4, 1.4 \text{ Hz, 1H}), 4.31 (t, \textit{J} = 6.6 \text{ Hz, 2H}), 3.63 (s, 3H), 3.60 (s, 3H), 2.87 – 2.82 (m, 1H), 2.78 – 2.63 (m, 2H), 1.84 – 1.75 (m, 2H), 1.74 – 1.67 (m, 1H), 1.67 – 1.56 (m, 1H), 1.56 – 1.45 (m, 2H), 1.41 – 1.33 (m, 1H). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, Acetone-}d_6) \delta 174.88, 165.86, 144.59, 135.52, 132.88, 130.60, 129.69, 129.24, 128.50, 127.29, 125.95, 125.07, 70.48, 64.62, 41.11, 41.03, 38.98, 34.19, 27.12, 25.95, 24.42. \]

\[ \text{HRMS (ESI-TOF) } [\text{M+Na}]^{+} \text{ calculated for } [\text{C}_{23}\text{H}_{27}\text{O}_4\text{S}]^{+} \text{ m/z: 399.1625, found 399.1630.} \]

3-(dimethyl(oxo)-\( ^{6} \)-sulfanylidene)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (5m)

![Structure of 3-(dimethyl(oxo)-\( ^{6} \)-sulfanylidene)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (5m)](image)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and vinyl acetate (68.8 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (25.8 mg, 46% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \( ^1H \) NMR spectroscopy.

\[ ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.03 – 7.95 (m, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.39 (m, 1H), 6.07 (dd, \textit{J} = 6.2, 4.6 \text{ Hz, 1H}), 3.61 (s, 3H), 3.59 (s, 3H), 2.95 (dd, \textit{J} = 14.7, 4.6 \text{ Hz, 1H}), 2.87 (dd, \textit{J} = 14.7, 6.2 \text{ Hz, 1H}), 2.08 (s, 3H). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 174.88, 165.86, 144.59, 135.52, 132.88, 130.60, 129.69, 129.24, 128.50, 127.29, 125.95, 125.07, 70.48, 64.62, 41.11, 41.03, 38.98, 34.19, 27.12, 25.95, 24.42. \]

\[ \text{HRMS (ESI-TOF) } [\text{M+Na}]^{+} \text{ calculated for } [\text{C}_{14}\text{H}_{16}\text{NaO}_4\text{S}]^{+} \text{ m/z: 303.0662, found 303.0659.} \]
This compound was synthesized following the *general procedure C* using reagent 3c (108.8 mg, 0.2 mmol), and hex-5-en-1-yl (7,7-dimethylbicyclo[2.2.1]heptan-1-yl)methanesulfonate (240.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (68.8 mg, 70% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 1H), 4.31 – 4.21 (m, 2H), 3.60 (s, 3H), 3.54 (s, 3H) 2.99 (d, $J = 15.1$ Hz, 1H), 2.90 – 2.74 (m, 2H), 2.66 – 2.60 (m, 1H), 2.53 – 2.36 (m, 2H), 2.17 – 2.00 (m, 2H), 1.96 (d, $J = 18.4$ Hz, 1H), 1.76 – 1.70 (m, 2H), 1.67 – 1.60 (m, 3H), 1.48 – 1.38 (m, 4H), 1.34 – 1.27 (m, 1H), 1.12 (s, 3H), 0.89 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.16, 144.32, 134.60, 130.50, 127.56, 126.67, 125.08, 71.24, 70.60, 70.58, 58.02, 48.06, 46.71, 42.82, 42.65, 42.59, 39.02, 34.18, 29.20, 27.08, 26.95, 25.65, 24.94, 24.38, 19.88, 19.78.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{26}$H$_{39}$O$_5$S$_2$]$^+$ m/z: 495.2233, found 495.2239.

3-(3-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)propyl 4-methylbenzenesulfonate (5o)
This compound was synthesized following the *general procedure* C using reagent 3c (108.8 mg, 0.2 mmol), and pent-4-en-1-yl 4-methylbenzenesulfonate (96.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (55.6 mg, 64% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.90 (m, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.30 (m, 4H), 7.08 – 7.06 (m, 1H), 4.07 – 3.94 (m, 2H), 3.59 (m, 3H), 3.54 (m, 3H), 2.84 – 2.73 (m, 2H), 2.62 – 2.58 (m, 1H), 2.44 (s, 3H), 1.82 – 1.67 (m, 2H), 1.65 – 1.52 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.89, 144.77, 143.47, 134.56, 133.00, 130.47, 129.86, 127.87, 127.42, 126.84, 125.15, 70.93, 70.53, 42.58, 42.36, 38.48, 30.02, 26.98, 24.21, 21.64.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{22}$H$_{27}$O$_5$S$_2$]$^+$ m/z: 435.1294, found 435.1299.

2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-4-(trimethylsilyl)-3,4-dihydronaphthalen-1(2H)-one (5p)

This compound was synthesized following the *general procedure* C using reagent 3c (108.8 mg, 0.2 mmol), and trimethyl(vinyl)silane (80.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (29.4 mg, 50% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.30 (td, $J = 7.4$, 1.5 Hz, 1H), 7.20 (td, $J = 7.6$, 1.3 Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 1H), 3.62 (s, 3H), 3.47 (s, 3H), 2.92 (dd, $J = 13.6$, 5.6 Hz, 1H), 2.83 (dd, $J = 13.6$, 1.8 Hz, 1H), 2.49 (dd, $J = 5.6$, 1.8 Hz, 1H), -0.00 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.03, 143.69, 134.25, 130.38, 127.05, 125.03, 124.95, 72.07, 43.10, 42.14, 32.15, 21.25, -1.79.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{15}$H$_{23}$O$_2$SSi]$^+$ m/z: 295.1183, found 295.1187.
2-(3-(dimethyl(oxo)-λ⁶-sulfanylidene)-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)ethyl cinnamate (5q)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and but-3-en-1-yl cinnamate (161.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (44.4 mg, 56% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.

¹H NMR (400 MHz, Acetone-δ6) δ 7.93 (dd, J = 7.5, 1.6 Hz, 1H), 7.76 – 7.68 (m, 3H), 7.49 – 7.43 (m, 3H), 7.36 (td, J = 7.4, 1.6 Hz, 1H), 7.29 (td, J = 7.4, 1.4 Hz, 1H), 7.25 (dd, J = 7.3, 1.4 Hz, 1H), 6.61 (d, J = 16.1 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.70 (d, J = 0.9 Hz, 3H), 3.62 (d, J = 0.9 Hz, 3H), 2.80 (dd, J = 14.2, 4.5 Hz, 1H), 2.74 (dd, J = 14.2, 3.1 Hz, 1H), 2.15 – 2.08 (m, 1H), 2.00 – 1.92 (m, 1H).

¹³C NMR (101 MHz, Acetone-δ6) δ 174.68, 166.22, 144.35, 143.48, 135.59, 134.58, 130.28, 129.90, 128.93, 128.17, 127.39, 126.33, 125.25, 118.29, 70.54, 62.52, 41.07, 40.97, 36.01, 33.05, 24.60.

HRMS (ESI-TOF) [M+H]^+ calculated for [C₂₃H₂₅O₄S]^+: 397.1468, found 397.1475.

2-(dimethyl(oxo)-λ⁶-sulfanylidene)-3,4-diethyl-3,4-dihydronaphthalen-1(2H)-one (5r)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and hex-3-ene (E/Z = 50:50, 67.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as yellow oil (30.6 mg, 55% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.
\[ ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.87 \text{ (dd, } J = 7.4, 1.7 \text{ Hz, 1H}), 7.33 \text{ (td, } J = 7.3, 1.6 \text{ Hz, 1H}), 7.28 \text{ (td, } J = 7.4, 1.6 \text{ Hz, 1H}), 7.13 \text{ (dd, } J = 7.2, 1.5 \text{ Hz, 1H}), 3.60 \text{ (s, 3H)}, 3.55 \text{ (s, 3H)}, 2.76 \text{ (td, } J = 7.3, 1.9 \text{ Hz, 1H}), 2.66 \text{ (td, } J = 7.2, 1.9 \text{ Hz, 1H}), 1.67 – 1.53 \text{ (m, 2H)}, 1.43 – 1.36 \text{ (m, 2H)}, 0.91 \text{ (t, } J = 7.4\text{Hz, 3H}), 0.87 \text{ (t, } J = 7.4\text{Hz, 3H}). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 175.60, 143.14, 133.83, 130.31, 128.99, 126.49, 124.80, 45.83, 43.84, 42.11, 37.87, 29.71, 29.04, 12.34, 12.14. \]

HRMS (ESI-TOF) [M+H]^+ calculated for [C_{16}H_{23}O_{2}S]^+ m/z: 279.1413, found 279.1413.

6-(dimethyl(oxo)-λ^6-sulfanylidene)-6a,7,8,9,10,11,12,13,14,15,16,16a-dodecahydrocyclododeca[a]napthalen-5(6H)-one (5s)

This compound was synthesized following the general procedure C using reagent 3c (54.4 mg, 0.1 mmol), and cyclododecene (E/Z = 63:37, 133.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (32.4 mg, 45% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\text{H NMR}\) spectroscopy.

\[ ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.88 \text{ (dd, } J = 7.6, 1.5 \text{ Hz, 1H}), 7.35 \text{ (td, } J = 7.4, 1.4 \text{ Hz, 1H}), 7.28 – 7.24 \text{ (m, 1H)}, 7.14 \text{ (dd, } J = 7.5, 1.3 \text{ Hz, 1H}), 3.58 \text{ (s, 3H)}, 3.56 \text{ (s, 3H)}, 3.13 – 3.08 \text{ (m, 2H)}, 1.82 – 1.80 \text{ (m, 1H)}, 1.70 – 1.48 \text{ (m, 6H)}, 1.46 – 1.20 \text{ (m, 13H)}. \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 175.29, 144.01, 133.89, 130.86, 128.92, 126.39, 124.54, 44.06, 42.82, 37.88, 35.24, 34.39, 30.17, 26.44, 26.35, 23.06, 22.82, 22.71, 22.37, 22.31, 22.24. \]

HRMS (ESI-TOF) [M+H]^+ calculated for [C_{22}H_{33}O_{2}S]^+ m/z: 361.2196, found 361.2183.
4-(dimethyl(oxo)-λ₆-sulfanylidene)-1,2,3,3a,4,9b-hexahydro-5H-cyclopenta[a]naphthalen-5-one (5t)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and cyclopentene (54.4 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (21.0 mg, 40% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J = 7.7, 1.5 Hz, 1H), 7.40 (td, J = 7.4, 1.5 Hz, 1H), 7.32 – 7.25 (m, 2H), 3.64 (s, 3H), 3.56 (s, 3H), 3.54 – 3.47 (m, 1H), 3.11 (dt, J = 10.2, 8.0 Hz, 1H), 2.31 – 2.16 (m, 2H), 2.03 – 1.95 (m, 1H), 1.68 – 1.57 (m, 2H), 1.46 – 1.36 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 142.49, 133.69, 130.94, 127.07, 125.95, 124.68, 43.54, 42.88, 41.75, 36.57, 35.10, 32.48, 23.45.

HRMS (ESI-TOF) [M+H]+ calculated for [C₁₅H₁₈O₂S]+ m/z: 262.1028, found 262.1025.

10-(dimethyl(oxo)-λ₆-sulfanylidene)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (5u)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and cyclohexene (65.7 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (33.1 mg, 60% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 7.6, 1.5 Hz, 1H), 7.44 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.32 (tt, J = 7.4, 1.2 Hz, 1H), 3.63 (s, 3H), 3.54 (s, 3H), 3.33 – 3.28 (m, 1H), 2.92 – 2.84 (m, 1H), 2.60 – 2.55 (m, 1H), 1.82 (tt, J = 13.7, 4.0 Hz, 1H), 1.61 – 1.45 (m, 3H), 1.42 – 1.27 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.18, 140.40, 135.41, 130.77, 125.88, 125.81, 125.05, 43.66, 43.49, 38.74, 35.07, 31.33, 27.61, 25.75, 20.17.
HRMS (ESI-TOF) [M+H]^+ calculated for [C_{16}H_{21}O_2S]^+ m/z: 277.1257, found 277.1252.

The crystal structure of 5u has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2068911.

10-(dimethyl(oxo)-\lambda^6-sulfanylidene)-2,3,4,4a,10,10a-hexahydro-1,4-methanophenanthren-9(1H)-one (5v)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and bicyclo[2.2.1]hept-2-ene (75.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (46.2 mg, 80% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using ^1H NMR spectroscopy.

^1H NMR (400 MHz, Acetone-d_6) \( \delta \) 7.93 (dd, \( J = 7.7, 1.5 \text{ Hz}, 1\text{H} \)), 7.32 (td, \( J = 7.4, 1.5 \text{ Hz}, 1\text{H} \)), 7.22 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.18 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 3.68 (s, 3H), 3.60 (s, 3H), 3.22 (d, \( J = 9.8 \text{ Hz}, 1\text{H} \)), 3.00 – 2.97 (m, 1H), 2.30 – 2.23 (m, 1H), 2.21 – 2.14 (m, 1H), 1.72 – 1.63 (m, 1H), 1.62 – 1.47 (m, 3H), 1.45 – 1.38 (m, 1H), 1.10 – 1.00 (m, 1H).

^13C NMR (101 MHz, Acetone-d_6) \( \delta \) 172.55, 141.98, 133.76, 129.98, 128.42, 125.19, 123.97, 77.38, 48.46, 47.46, 46.17, 43.65, 41.16, 40.63, 31.74.

HRMS (ESI-TOF) [M+H]^+ calculated for [C_{17}H_{21}O_2S]^+ m/z: 289.1257, found 289.1259.

4-benzyl-2-(dimethyl(oxo)-\lambda^6-sulfanylidene)-4-methyl-3,4-dihydronaphthalen-1(2H)-one (5w)
This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and (2-methylallyl)benzene (105.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as yellow oil (52.8 mg, 81% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (dd, $J = 7.4$, 1.8 Hz, 1H), 7.34 (td, $J = 7.3$, 1.5 Hz, 1H), 7.30 (td, $J = 7.2$, 1.7 Hz, 1H), 7.22 – 7.15 (m, 3H), 6.95 (dd, $J = 7.5$, 1.4 Hz, 1H), 6.82 – 6.80 (m, 2H), 3.67 (s, 3H), 3.55 (s, 3H), 3.03 (d, $J = 13.0$ Hz, 1H), 2.81 (d, $J = 13.0$ Hz, 1H), 2.65 (d, $J = 14.3$ Hz, 1H), 2.59 (d, $J = 14.2$ Hz, 1H), 1.35 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.97, 146.32, 138.13, 134.39, 130.61, 130.44, 127.58, 126.42, 126.08, 125.68, 125.17, 71.89, 46.38, 42.84, 42.39, 38.91, 32.65, 25.09.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{20}$H$_{23}$O$_2$S]$^+$ m/z: 327.1413, found 327.1422.

4-butyl-7-cyclohexyl-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-3,4-dihyronaphthalen-1(2H)-one (5x)

This compound was synthesized following the general procedure C using reagent 3f (125.2 mg, 0.2 mmol), and hex-1-ene (67.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (50.4 mg, 70% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 7.9$ Hz, 1H), 7.15 (dd, $J = 7.9$, 1.8 Hz, 1H), 6.99 (d, $J = 1.8$ Hz, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 2.84 – 2.79 (m, 1H), 2.79 – 2.74 (m, 1H), 2.64 (dd, $J = 13.9$, 3.1 Hz, 1H), 2.55 – 2.48 (m, 1H), 1.90 – 1.83 (m, 3H), 1.80 – 1.72 (m, 1H), 1.64 – 1.55 (m, 2H), 1.48 – 1.37 (m, 4H), 1.37 – 1.21 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.55, 150.80, 144.79, 132.44, 126.07, 125.05, 70.58, 44.74, 42.81, 42.60, 39.29, 34.38, 34.14, 29.89, 26.94, 26.23, 24.31, 22.85, 14.16.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{20}$H$_{33}$O$_2$S]$^+$ m/z: 361.2196, found 361.2186.

4-butyl-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-7-methyl-3,4-dihydnaphthalen-1(2H)-one (5y)

This compound was synthesized following the general procedure C using reagent 3g (111.6 mg, 0.2 mmol), and hex-1-ene (63.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (56.0 mg, 96% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.8$ Hz, 1H), 6.97 (s, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 2.79 – 2.60 (m, 3H), 2.37 (s, 3H), 1.70 – 1.51 (m, 2H), 1.42 – 1.18 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.43, 144.85, 140.67, 132.02, 128.16, 127.31, 125.08, 70.76, 42.75, 42.51, 39.10, 34.06, 29.82, 24.28, 22.83, 21.65, 14.11.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{17}$H$_{25}$O$_2$S]$^+$ m/z: 293.1570, found 293.1579.

4-butyl-7-chloro-2-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-3,4-dihydnaphthalen-1(2H)-one (5z)

This compound was synthesized following the general procedure C using reagent 3h (115.6 mg, 0.2 mmol), and hex-1-ene (63.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH:
30/1) provided the title compound as white solid (34.3 mg, 55% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 8.2$ Hz, 1H), 7.25 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.15 (d, $J = 2.1$ Hz, 1H), 3.56 (s, 3H), 3.54 (s, 3H), 2.84 – 2.78 (m, 1H), 2.74 (dd, $J = 14.1$, 4.8 Hz, 1H), 2.63 (dd, $J = 14.1$, 3.5 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.39 – 1.20 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.11, 146.48, 136.14, 133.18, 127.37, 126.71, 126.66, 71.46, 42.65, 39.06, 33.82, 29.68, 24.14, 22.78, 14.08.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{16}$H$_{22}$ClO$_2$S]$^+$ m/z: 313.1024, found 313.1031.

This compound was synthesized following the general procedure C using reagent 3i (115.6 mg, 0.2 mmol), and hex-1-ene (63.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as a mixture of isomers (white solid, 28.2 mg, 45% yield). Ratio of isomers was determined to be 2:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy. Further purification of mixture by carefully column chromatography on silica gel (DCM/MeOH: 30/1) afforded major product as pure white solid.

Major isomer $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.41 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 3.59 (s, 3H), 3.55 (s, 3H), 3.40 – 3.35 (m, 1H), 2.79 (dd, $J = 14.6$, 2.1 Hz, 1H), 2.65 (dd, $J = 14.6$, 4.8 Hz, 1H), 1.70 – 1.55 (m, 1H), 1.52 – 1.26 (m, 5H), 0.91 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.13, 146.57, 136.65, 132.57, 131.62, 127.15, 123.80, 71.18, 42.49, 42.40, 35.29, 31.54, 29.79, 22.67, 22.22, 14.12.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{16}$H$_{22}$ClO$_2$S]$^+$ m/z: 313.1024, found 313.1024.
4-butyl-2-(dimethyl(oxo)-λ^6-sulfanylidene)-7,8-dimethyl-3,4-dihydronaphthalen-1(2H)-one (5ab)

This compound was synthesized following the *general procedure C* using reagent 3j (114.4 mg, 0.2 mmol), and hex-1-ene (67.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as a mixture of isomers (white solid, 50.2 mg, 82% yield). Ratio of isomers was determined to be 1:1.3 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, $J = 7.8$ Hz, 1.3*1H), 7.69 (s, 1H), 7.11 (d, $J = 7.8$ Hz, 1.3*1H), 6.94 (s, 1H), 3.58 (s, 3.9*3H), 3.54 – 3.53 (m, 3.9*3H, 3H), 3.18 – 3.10 (m, 1.3*1H), 2.82 – 2.71 (m, 1.3*1H, 2H), 2.65 – 2.59 (m, 1.3*1H, 1H), 2.33 (s, 4.1*3H), 2.29 (s, 3H), 2.28 (s, 3H), 2.25 (s, 4.1*3H), 1.67 – 1.53 (m, 1.3*1H, 2H), 1.42 – 1.24 (m, 6.5*5H, 4H), 0.93 – 0.88 (m, 3.9*3H, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.05, 176.65, 143.43, 142.29, 139.90, 139.24, 134.63, 132.63, 128.75, 127.74, 126.03, 122.64, 70.57, 69.47, 42.74, 42.67, 42.51, 38.55, 34.95, 34.11, 32.00, 30.03, 29.79, 24.31, 22.80, 22.74, 22.57, 21.27, 19.87, 19.34, 14.82, 14.08, 14.05.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{18}$H$_{27}$O$_2$S]$^+$ m/z: 307.1726, found 307.1729.

5-(dimethyl(oxo)-λ^6-sulfanylidene)-2-methyl-5a,6,7,8,9,9a-hexahydro-6,9-methanonaphtho[2,1-b]thiophen-4(5H)-one (5ac)

This compound was synthesized following the *general procedure C* using reagent 3k (112.8 mg, 0.2 mmol), and bicyclo[2.2.1]hept-2-ene (75.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (53.0 mg, 86% yield).
**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 6.53 (s, 1H), 3.56 (s, 3H), 3.53 (s, 3H), 3.13 (d, $J = 10.1$ Hz, 1H), 3.02 (d, $J = 10.0$ Hz, 1H), 2.46 (s, 3H), 2.27 (d, $J = 3.6$ Hz, 1H), 2.11 (d, $J = 1.9$ Hz, 1H), 1.71 – 1.61 (m, 2H), 1.56 – 1.38 (m, 3H), 1.16 (dt, $J = 10.0$, 1.6 Hz, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 171.41, 145.84, 143.71, 135.39, 126.16, 48.11, 45.67, 45.49, 44.96, 42.98, 42.71, 33.30, 29.38, 29.14, 16.00.

**HRMS** (ESI-TOF) [M+Na]$^+$ calculated for [C$_{16}$H$_{20}$NaO$_2$S]$^+$ m/z: 331.0797, found 331.0795.

6-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-4-propyl-5,6-dihydrobenzo[b]thiophen-7(4$H$)-one (5ad)

This compound was synthesized following the general procedure C using reagent 3l (110.0 mg, 0.2 mmol), and pent-1-ene (56.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (27.0 mg, 50% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 4.9$ Hz, 1H), 6.93 (d, $J = 4.9$ Hz, 1H), 3.53 (s, 3H), 3.51 (s, 3H), 2.93 – 2.88 (m, 1H), 2.83 (dd, $J = 13.8$, 5.7 Hz, 1H), 2.53 (dd, $J = 13.8$, 6.7 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.58 – 1.47 (m, 1H), 1.46 – 1.38 (m, 1H), 1.37 – 1.28 (m, 1H), 0.92 (t, $J = 7.3$ Hz, 3H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 173.00, 149.03, 143.71, 135.39, 126.16, 69.04, 43.19, 42.79, 36.06, 35.82, 26.50, 20.49, 14.28.

**HRMS** (ESI-TOF) [M] calculated for [C$_{13}$H$_{18}$O$_2$S]$^+$ m/z: 270.0748, found 270.0682.

1-butyl-3-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2,3-dihydrodibenzo[b,d]thiophen-4(1H)-one (5ae)

![Diagram of 1-butyl-3-(dimethyl(oxo)-$\lambda^6$-sulfanylidene)-2,3-dihydrodibenzo[b,d]thiophen-4(1H)-one (5ae)]
This compound was synthesized following the general procedure C using reagent \textit{3m} (120.0 mg, 0.2 mmol), and hex-1-ene (67.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (40.33 mg, 60% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.85 (m, 1H), 7.79 – 7.70 (m, 1H), 7.45 – 7.34 (m, 2H), 3.61 (s, 6H), 3.55 (s, 6H), 3.27 – 3.21 (m, 1H), 2.95 – 2.84 (m, 2H), 1.74 – 1.67 (m, 1H), 1.62 – 1.54 (m, 1H), 1.52 – 1.42 (m, 1H), 1.40 – 1.29 (m, 3H), 0.90 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.16, 143.73, 141.38, 138.63, 138.42, 125.69, 124.27, 123.51, 122.74, 69.27, 43.10, 42.76, 33.95, 31.88, 30.09, 25.01, 22.87, 14.10.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{18}$H$_{23}$O$_2$S]$^+$ m/z: 335.1134, found 335.1123.

5-(dimethyl(oxo)-λ$^6$-sulfanylidene)-5a,6,7,8,9,9a-hexahydro-6,9-methanonaphtho[2,1-b]furan-4(5H)-one (5af)

This compound was synthesized following the general procedure C using reagent \textit{3n} (106.8 mg, 0.2 mmol), and bicyclo[2.2.1]hept-2-ene (75.2 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (33.4 mg, 60% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J$ = 1.8 Hz, 1H), 6.24 (d, $J$ = 1.8 Hz, 1H), 3.55 (s, 3H), 3.53 (s, 3H), 3.13 (d, $J$ = 10.1 Hz, 1H), 3.01 (dd, $J$ = 10.1, 1.7 Hz, 1H), 2.27 – 2.21 (m, 1H), 2.10 – 2.08 (m, 1H), 1.72 – 1.63 (m, 2H), 1.56 – 1.37 (m, 3H), 1.19 (dt, $J$ = 10.0, 1.6 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.82, 147.43, 144.27, 129.80, 110.32, 48.15, 45.64, 44.42, 43.22, 42.66, 42.36, 33.41, 29.33, 29.25.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{15}$H$_{19}$O$_3$S]$^+$ m/z: 279.1049, found 279.1046.
2.3 Light-mediated Tandem [3+2] Cycloaddition: reaction scope.

**General Procedure D**

To a 10 mL oven-dried tube equipped with a stirring bar was added reagent 3 (0.2 mmol, 1.0 equiv.), alkene 6 (0.4 mmol, 2.0 equiv.), anhydrous MeCN (1.0 mL). The reaction vial was capped with a rubber septum under an argon atmosphere, and it was fixed on a blue LED light reaction equipment (1 W, 452 nm) for 3 hours. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography to yield the corresponding products 7.

4-(dimethylethylsulfoxonium)-2,2,5-triphenyl-2,3-dihydrofuran hexafluorophosphate (7a)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (98.8 mg, 95% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.97 – 7.90 (m, 2H), 7.75 (tt, $J$ = 6.6, 1.3 Hz, 1H), 7.68 – 7.58 (m, 6H), 7.51 – 7.44 (m, 4H), 7.40 (tt, $J$ = 6.3, 1.4 Hz, 1H), 4.49 (s, 2H), 4.13 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 171.02, 143.10, 133.01, 129.53, 128.91, 128.82, 128.48, 126.94, 125.57, 99.84, 95.07, 44.14, 40.87.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.20 (d, $J$ = 707 Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.21 (h, $J$ = 708 Hz).

HRMS (ESI-TOF) [M-PF$_6$]$^+$ calculated for [C$_{24}$H$_{23}$O$_2$S]$^+$/m/z: 375.1413, found 375.1417.
5-(4-chlorophenyl)-4-(dimethylethysulfoxonium)-2,2-diphenyl-2,3-dihydrofuran hexafluorophosphate (7b)

This compound was synthesized following the general procedure D using reagent 3h (115.6 mg, 0.2 mmol), and ethene-1,1-diyldibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (95.2 mg, 86% yield).

$^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 8.00 – 7.94 (m, 2H), 7.71 – 7.65 (m, 2H), 7.62 – 7.57 (m, 4H), 7.50 – 7.44 (m, 4H), 7.44 – 7.38 (m, 2H), 4.45 (s, 2H), 4.15 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-d$_6$) $\delta$ 169.84, 142.99, 138.59, 131.46, 129.01, 128.84, 128.53, 125.58, 125.50, 99.78, 95.17, 44.17, 40.90.

$^{19}$F NMR (376 MHz, Acetone-d$_6$) $\delta$ -72.48 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-d$_6$) $\delta$ -144.22 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M- PF$_6$]$^+$ calculated for [$C_{24}H_{22}ClO_2S$]$^+$ m/z: 409.1024, found 409.1022.

5-([1,1'-biphenyl]-4-yl)-4-(dimethylethysulfoxonium)-2,2-diphenyl-2,3-dihydrofuran hexafluorophosph-hate (7c)

This compound was synthesized following the general procedure D using reagent 3o (124.0 mg, 0.2 mmol), and ethene-1,1-diyldibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (93.0 mg, 78% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.00 – 7.89 (m, 4H), 7.82 – 7.75 (m, 2H), 7.58 – 7.52 (m, 6H), 7.50 – 7.44 (m, 5H), 7.44 – 7.37 (m, 2H), 4.28 (s, 2H), 4.04 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 169.00, 144.74, 143.53, 139.09, 130.58, 129.65, 129.32, 129.05, 128.87, 127.49, 127.37, 125.81, 125.76, 100.19, 94.37, 44.22, 40.92.
19F NMR (376 MHz, DMSO-d6) δ -70.11 (d, J = 710 Hz).
31P NMR (162 MHz, DMSO-d6) δ -144.16 (h, J = 712 Hz).

HRMS (ESI-TOF) [M–PF₆]⁺ calculated for [C₃₀H₂₇O₂S]⁺ m/z: 451.1726, found 451.1723.

4-(dimethylethylsulfoxonium)-2,2-diphenyl-5-(o-tolyl)-2,3-dihydrofuran hexafluorophosphate (7d)

This compound was synthesized following the general procedure D using reagent 3p (111.6 mg, 0.2 mmol), and ethene-1,1-diyldibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (70.5 mg, 66% yield).

1H NMR (400 MHz, Acetone-d6) δ 7.66 – 7.55 (m, 6H), 7.54 – 7.38 (m, 8H), 4.49 (s, 2H), 4.02 (s, 6H), 2.33 (s, 3H).

13C NMR (101 MHz, Acetone-d6) δ 171.59, 143.03, 137.42, 132.08, 131.01, 129.66, 128.82, 128.57, 126.63, 126.19, 125.69, 102.70, 96.13, 43.01, 40.56, 18.76.

19F NMR (376 MHz, Acetone-d6) δ -72.21 (d, J = 707 Hz).
31P NMR (162 MHz, Acetone-d6) δ -144.22 (h, J = 708 Hz).

HRMS (ESI-TOF) [M–PF₆]⁺ calculated for [C₂₅H₂₅O₂S]⁺ m/z: 389.1570, found 389.1564.

4-(dimethylethylsulfoxonium)-5-(2-phenoxyphenyl)-2,2-diphenyl-2,3-dihydrofuran hexafluorophosphate (7e)
This compound was synthesized following the general procedure D using reagent 3q (127.2 mg, 0.2 mmol), and ethene-1,1-diyldibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (74.6 mg, 61% yield).

\[^{1}H\] NMR (400 MHz, Acetone-d\textsubscript{6}) \(\delta\) 7.76 (dd, \(J = 7.7, 1.7\) Hz, 1H), 7.66 – 7.62 (m, 1H), 7.58 – 7.51 (m, 4H), 7.50 – 7.44 (m, 2H), 7.43 – 7.33 (m, 7H), 7.7 (tt, \(J = 7.4, 1.1\) Hz, 1H), 7.15 – 7.09 (m, 2H), 7.02 (d, \(J = 8.4\) Hz, 1H), 4.40 (s, 2H), 4.08 (s, 6H).

\[^{13}C\] NMR (101 MHz, Acetone-d\textsubscript{6}) \(\delta\) 167.76, 155.76, 155.65, 143.02, 133.80, 130.92, 130.30, 128.71, 128.42, 125.61, 124.72, 123.37, 119.61, 118.61, 117.96, 101.10, 95.69, 43.66, 40.49.

\[^{19}F\] NMR (376 MHz, Acetone-d\textsubscript{6}) \(\delta\) -72.26 (d, \(J = 707\) Hz).

\[^{31}P\] NMR (162 MHz, Acetone-d\textsubscript{6}) \(\delta\) -144.22 (h, \(J = 708\) Hz).

HRMS (ESI-TOF) [M–PF\textsubscript{6}]\(^{+}\) calculated for [C\textsubscript{30}H\textsubscript{27}O\textsubscript{3}S]\(^{+}\) m/z: 467.1675, found 467.1692.

5-(3,4-dimethylphenyl)-4-(dimethylethylsulfoxonium)-2-phenyl-2,3-dihydrofuran hexafluorophosphate (7f)

\[
\text{5-(3,4-dimethylphenyl)-4-(dimethylethylsulfoxonium)-2-phenyl-2,3-dihydrofuran hexafluorophosphate (7f)}
\]

This compound was synthesized following the general procedure D using reagent 3j (114.4 mg, 0.2 mmol), and styrene (41.6 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (86.8 mg, 92% yield).

\[^{1}H\] NMR (400 MHz, Acetone-d\textsubscript{6}) \(\delta\) 7.63 – 7.58 (m, 4H), 7.54 – 7.43 (m, 3H), 7.37 (d, \(J = 7.7\) Hz, 1H), 6.28 (t, \(J = 10.0\) Hz, 1H), 4.09 (dd, \(J = 13.6, 10.6\) Hz, 1H), 4.02 (s, 3H), 3.98 (s, 3H), 3.68 – 3.62 (m, 1H), 2.36 (s, 3H), 2.34 (s, 3H).

\[^{13}C\] NMR (101 MHz, Acetone-d\textsubscript{6}) \(\delta\) 173.28, 142.67, 139.02, 137.51, 130.14, 129.92, 129.17, 128.99, 127.14, 126.40, 124.57, 98.69, 85.83, 40.92, 40.59, 38.78, 19.12, 18.80.

\[^{19}F\] NMR (376 MHz, Acetone-d\textsubscript{6}) \(\delta\) -72.05 (d, \(J = 707\) Hz).

\[^{31}P\] NMR (162 MHz, Acetone-d\textsubscript{6}) \(\delta\) -144.21 (h, \(J = 708\) Hz).
HRMS (ESI-TOF) [M–PF₆]⁺ calculated for [C₂₀H₂₃O₂S]⁺ m/z: 327.1413, found 327.1412.

4-(dimethylethylsulfoxonium)-5-(4-Cyanophenyl)-2,2-diphenyl-2,3-dihydrofuran hexafluorophosphate (7g)

This compound was synthesized following the *general procedure D* using reagent 3r (113.8 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (30.6 mg, 28% yield).

¹H NMR (400 MHz, Acetone-d₆) δ 8.12 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.62 – 7.56 (m, 4H), 7.50 – 7.45 (m, 4H), 7.44 – 7.39 (m, 2H), 4.49 (s, 2H), 4.20 (s, 6H).

¹³C NMR (101 MHz, Acetone-d₆) δ 168.93, 142.87, 132.35, 131.05, 130.65, 128.86, 128.59, 125.52, 117.53, 115.88, 100.96, 95.70, 44.12, 40.93.

¹⁹F NMR (376 MHz, Acetone-d₆) δ -72.27 (d, J = 707 Hz).

³¹P NMR (162 MHz, Acetone-d₆) δ -144.23 (h, J = 708 Hz).

HRMS (ESI-TOF) [M–PF₆]⁺ calculated for [C₂₅H₂₂NÖ₂S]⁺ m/z: 400.1366, found 400.1362.

4-(dimethylethylsulfoxonium)-5-(naphthalen-1-yl)-2,2-diphenyl-2,3-dihydrofuran tetrafluoroborate (7h)

This compound was synthesized following the *general procedure D* using reagent 3s (107.2 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (51.2 mg, 50% yield).
\[ ^1H \text{NMR} \ (400 \text{ MHz, CD}_3\text{CN}) \ \delta \ 8.20 \ (d, J = 8.3 \text{ Hz, } 1\text{H}), \ 8.06 \ (d, J = 8.2 \text{ Hz, } 1\text{H}), \ 7.80 \ (dd, J = 7.1, 1.2 \text{ Hz, } 1\text{H}), \ 7.74 \ (d, J = 8.4 \text{ Hz, } 1\text{H}), \ 7.70 - 7.63 \ (m, 2\text{H}), \ 7.61 - 7.54 \ (m, 5\text{H}), \ 7.53 - 7.48 \ (m, 4\text{H}), \ 7.47 - 7.42 \ (m, 2\text{H}), \ 4.37 \ (s, 2\text{H}), \ 3.66 \ (s, 6\text{H}). \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz, CD}_3\text{CN}) \ \delta \ 170.88, \ 142.86, \ 133.35, \ 132.51, \ 130.30, \ 128.96, \ 128.82, \ 128.71, \ 127.88, \ 127.25, \ 125.60, \ 125.14, \ 124.33, \ 123.99, \ 103.34, \ 96.45, \ 42.90, \ 40.88. \]

\[ ^{19}F \text{NMR} \ (376 \text{ MHz, CD}_3\text{CN}) \ \delta \ -151.33. \]

\[ \text{HRMS (ESI-TOF)} \ [\text{M} - \text{BF}_4]^+ \ \text{calculated for} \ [\text{C}_{28}\text{H}_{25}\text{O}_2\text{S}]^+ \ m/z: 425.1570, \ \text{found} \ 425.1567. \]

4-(dimethylethylsulfoxonium)-2-phenyl-5-(thiophen-2-yl)-2,3-dihydrofuran hexafluorophosphate (7i)

This compound was synthesized following the general procedure D using reagent 3l (110.0 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (80.1 mg, 89% yield).

\[ ^1H \text{NMR} \ (400 \text{ MHz, Acetone-}d_6) \ \delta \ 8.17 \ (dd, J = 3.9, 1.1 \text{ Hz, } 1\text{H}), \ 8.09 \ (dd, J = 5.0, 1.1 \text{ Hz, } 1\text{H}), \ 7.61 - 7.57 \ (m, 2\text{H}), \ 7.53 - 7.44 \ (m, 3\text{H}), \ 7.37 \ (dd, J = 5.0, 3.9 \text{ Hz, } 1\text{H}), \ 6.26 \ (dd, J = 10.4, 9.3 \text{ Hz, } 1\text{H}), \ 4.20 - 4.18 \ (s, 3\text{H}), \ 4.17 \ (s, 3\text{H}), \ 4.15 \ (dd, J = 13.7, 10.4 \text{ Hz, } 1\text{H}), \ 3.73 \ (dd, J = 13.7, 9.3 \text{ Hz, } 1\text{H}). \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz, Acetone-}d_6) \ \delta \ 165.15, \ 138.74, \ 135.37, \ 134.49, \ 129.24, \ 128.99, \ 128.86, \ 127.57, \ 126.34, \ 96.02, \ 85.46, \ 40.86, \ 40.47, \ 39.40. \]

\[ ^{19}F \text{NMR} \ (376 \text{ MHz, Acetone-}d_6) \ \delta \ -72.28 \ (d, J = 707 \text{ Hz}). \]

\[ ^{31}P \text{NMR} \ (162 \text{ MHz, Acetone-}d_6) \ \delta \ -144.25 \ (h, J = 708 \text{ Hz}). \]

\[ \text{HRMS (ESI-TOF)} \ [\text{M} - \text{PF}_6]^+ \ \text{calculated for} \ [\text{C}_{16}\text{H}_{17}\text{O}_2\text{S}_2]^+ \ m/z: 305.0664, \ \text{found} \ 305.0662. \]

3-(dimethylethylsulfoxonium)-5,5-diphenyl-4,5-dihydro-2,2'-bifuran hexafluorophosphate (7j)
This compound was synthesized following the general procedure D using reagent 3n (106.8 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (77.6 mg, 76% yield).

\[
\begin{align*}
\text{H NMR} & \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.88 \ (d, \ J = 1.8 \text{ Hz, 1H}), \ 7.45 \sim 7.41 \ (m, \ 4H), \ 7.40 \sim 7.35 \ (m, \ 5H), \ 7.34 \sim 7.29 \ (m, \ 2H), \ 6.68 \ (dd, \ J = 3.7, 1.8 \text{ Hz, 1H}), \ 4.09 \ (s, \ 2H), \ 3.80 \ (s, \ 6H). \\
\text{C NMR} & \ (101 \text{ MHz, CDCl}_3) \ \delta \ 157.92, \ 149.49, \ 141.67, \ 141.31, \ 128.89, \ 128.76, \ 125.71, \ 120.13, \ 113.25, \ 95.58, \ 95.55, \ 43.92, \ 42.67.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR} & \ (376 \text{ MHz, CDCl}_3) \ \delta \ -70.53 \ (d, \ J = 712 \text{ Hz}). \\
\text{P NMR} & \ (162 \text{ MHz, CDCl}_3) \ \delta \ -144.17 \ (h, \ J = 713 \text{ Hz}).
\end{align*}
\]

\[
\text{HRMS (ESI-TOF) [M-PF}_6^+] \ \text{calculated for \ [C}_{22}\text{H}_{21}\text{O}_3\text{S]}^+ \ m/z: \ 365.1206, \ \text{found} \ 365.1198.
\]

5-benzyl-4-(dimethylethylsulfoxonium)-2,2-diphenyl-2,3-dihydrofuran hexafluorophosphate (7k)

This compound was synthesized following the general procedure D using reagent 3t (111.6 mg, 0.2 mmol), and ethene-1,1-diyl dibenzene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (53.4 mg, 50% yield).

\[
\begin{align*}
\text{H NMR} & \ (400 \text{ MHz, CD}_3\text{CN}) \ \delta \ 7.41 \sim 7.39 \ (m, \ 4H), \ 7.39 \sim 7.34 \ (m, \ 7H), \ 7.33 \sim 7.30 \ (m, \ 4H), \ 4.12 \ (s, \ 2H), \ 3.91 \ (s, \ 2H), \ 3.71 \ (s, \ 6H). \\
\text{C NMR} & \ (101 \text{ MHz, CD}_3\text{CN}) \ \delta \ 174.69, \ 142.76, \ 133.87, \ 129.47, \ 128.86, \ 128.70, \ 128.46, \ 127.65, \ 125.29, \ 96.36, \ 95.14, \ 42.86, \ 41.47, \ 33.75.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR} & \ (376 \text{ MHz, CD}_3\text{CN}) \ \delta \ -72.78 \ (d, \ J = 705 \text{ Hz}). \\
\text{P NMR} & \ (162 \text{ MHz, CD}_3\text{CN}) \ \delta \ -144.59 \ (h, \ J = 707 \text{ Hz}).
\end{align*}
\]

\[
\text{HRMS (ESI-TOF) [M-PF}_6^+] \ \text{calculated for \ [C}_{25}\text{H}_{25}\text{O}_2\text{S]}^+ \ m/z: \ 389.1570, \ \text{found} \ 389.1570.
\]

2-methyl-4-(dimethylethylsulfoxonium)-2,5-diphenyl-2,3-dihydrofuran hexafluorophosphate (7l)
This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and prop-1-en-2-ylbenzene (47.2 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (69.6 mg, 76% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.92 – 7.88 (m, 2H), 7.74 (tt, $J = 6.6$, 1.3 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.60 – 7.56 (m, 2H), 7.52 – 7.46 (m, 2H), 7.44 – 7.38 (m, 1H), 4.06 (s, 3H), 4.03 (s, 3H), 3.90 (d, $J = 3.0$ Hz, 2H), 2.01 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 171.50, 143.93, 132.85, 129.45, 128.82, 128.81, 127.29, 124.34, 99.07, 92.65, 44.46, 40.88, 40.73.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -72.25 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.24 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M–PF$_6$]$^+$ calculated for [C$_{19}$H$_{21}$O$_2$S] $^+$ m/z: 313.1257, found 313.1256.

4-(dimethylethylsulfoxonium)-5-phenyl-3',4'-dihydro-2'H,3H-spiro[furan-2,1'-naphthalene] hexafluor–ophosphate (7m)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and 1-methylene-1,2,3,4-tetrahydronaphthalene (57.6 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (58.0 mg, 60% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (dd, $J = 7.1$, 1.7 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.57 – 7.48 (m, 3H), 7.31 (td, $J = 7.5$, 1.5 Hz, 1H), 7.26 (td, $J = 7.4$, 1.4 Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 3.67 – 3.64 (m, 1H), 3.57 (s, 3H), 3.56 – 3.54 (m, 1H), 3.51 (s, 3H), 2.91 – 2.78 (m, 2H), 2.41 – 2.28 (m, 2H), 2.09 – 1.99 (m, 1H), 1.98 – 1.86 (m, 1H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.79, 137.37, 136.57, 133.30, 129.21, 129.13, 129.11, 127.35, 126.96, 126.58, 98.50, 92.33, 44.37, 40.85, 40.55, 35.79, 29.06, 19.36.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.57 (d, $J = 712$ Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$) δ -144.25 (h, $J = 713$ Hz).

HRMS (ESI-TOF) [M−PF$_6$]$^+$ calculated for [C$_{21}$H$_{23}$O$_2$S]$^+$ m/z: 339.1413, found 339.1409.

4'-((dimethylethylsulfoxonium)-5'-phenyl-10,11-dihydro-3'H-spiro[dibenzo[a,d][7]annulene-5,2'-furan] hexafluorophosphate (7n)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and 5-methylene-10,11-dihydro-5H-dibenzo[a,d][7]annulene (41.2 mg, 0.2 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (41.5 mg, 76% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 – 7.89 (m, 2H), 7.74 (tt, $J = 6.2$, 1.3 Hz 1H), 7.68 – 7.63 (m, 2H), 7.54 – 7.50 (m, 2H), 7.23 – 7.19 (m, 6H), 3.94 (s, 2H), 3.59 – 3.47 (m, 2H), 3.39 (s, 6H), 3.08 – 2.92 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.68, 140.31, 137.24, 133.53, 131.50, 129.47, 129.36, 128.68, 126.59, 126.26, 123.77, 98.96, 94.36, 48.37, 40.80, 32.40.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.63 (d, $J = 712$ Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$) δ -144.43 (h, $J = 713$ Hz).

HRMS (ESI-TOF) [M−PF$_6$]$^+$ calculated for [C$_{26}$H$_{25}$O$_2$S]$^+$ m/z: 401.1570, found 401.1569.

4-(dimethylethylsulfoxonium)-2,3,5-triphenyl-2,3-dihydrofuran hexafluorophosphate (7o)
This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and (E)-1,2-Diphenylethene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (73.8 mg, 71% yield).

Note: This compound was also synthesized following the general procedure D using (Z)-1,2-Diphenylethene (72.0 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the identical title compound as white solid (67.5 mg, 65% yield).

**1H NMR** (400 MHz, Acetone-d6) δ 8.08 – 8.01 (m, 2H), 7.82 (tt, J = 6.7, 1.4 Hz, 1H), 7.76 – 7.67 (m, 4H), 7.62 – 7.57 (m, 4H), 7.55 – 7.50 (m, 4H), 6.06 (d, J = 6.9 Hz, 1H), 5.14 (d, J = 6.9 Hz, 1H), 3.87 (s, 3H), 3.71 (s, 3H).

**13C NMR** (101 MHz, Acetone-d6) δ 174.50, 139.23, 138.10, 133.50, 130.08, 129.75, 129.58, 129.23, 129.11, 128.16, 126.99, 126.09, 103.32, 94.45, 58.05, 41.29, 41.24.

**19F NMR** (376 MHz, Acetone-d6) δ -72.42 (d, J = 707 Hz).

**31P NMR** (162 MHz, Acetone-d6) δ -144.25 (h, J = 708 Hz).

**HRMS** (ESI-TOF) [M-PF6]+ calculated for [C24H23O2S]+ m/z: 375.1413, found 375.1422.

3-methyl-4-(dimethylethylsulfoxonium)-2,5-diphenyl-2,3-dihydrofuran hexafluorophosphate (7p)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and (E)-β-methyl styrene (47.2 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (77.9 mg, 85% yield).

Note: This compound was also synthesized following the general procedure D using (Z)-β-methyl styrene (47.2 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the identical title compound as white solid (76.1 mg, 83% yield).
1H NMR (400 MHz, Acetone-d6) δ 7.90 (t, J = 1.4 Hz, 1H), 7.88 (t, J = 1.8 Hz, 1H), 7.77 (tt, J = 6.7, 1.3 Hz, 1H), 7.70 – 7.62 (m, 4H), 7.55 – 7.48 (m, 3H), 5.83 (d, J = 5.9 Hz, 1H), 4.17 (s, 3H), 4.02 – 3.96 (m, 1H), 3.90 (s, 3H), 1.80 (d, J = 6.7 Hz, 3H).

13C NMR (101 MHz, Acetone-d6) δ 172.88, 138.50, 133.22, 129.61, 129.34, 129.11, 129.06, 127.37, 125.93, 104.86, 92.75, 47.36, 41.78, 41.12, 20.50.

19F NMR (376 MHz, Acetone-d6) δ -72.43 (d, J = 707 Hz).

31P NMR (162 MHz, Acetone-d6) δ -144.54 (h, J = 713 Hz).

HRMS (ESI-TOF) [M-PF6]+ calculated for [C19H21O2S]+ m/z: 313.1257, found 313.1257.

The crystal structure of 7p has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2128864.

2-cyclopropyl-4-(dimethylsulfoxonium)-2,5-diphenyl-2,3-dihydrofuran hexafluorophosphate (7q)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and (1-cyclopropylvinyl)benzene (57.7 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (79.4 mg, 82% yield).

1H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.68 (m, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.34 (d, J = 7.0 Hz, 1H), 3.75 (d, J = 13.6 Hz, 1H), 3.68 (d, J = 13.6 Hz, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 1.71 – 1.65 (m, 1H), 0.88 (t, J = 6.7 Hz, 1H), 0.75 – 0.71 (m, 1H), 0.65 – 0.61 (m, 1H), 0.48 – 0.44 (m, 2H).

13C NMR (101 MHz, CDCl3) δ 173.07, 141.29, 133.57, 129.38, 129.28, 128.80, 128.64, 126.76, 125.33, 99.13, 95.98, 42.98, 41.35, 40.95, 41.35, 21.30, 2.06, 1.69.

19F NMR (376 MHz, CDCl3) δ -70.89 (d, J = 710 Hz).

31P NMR (162 MHz, CDCl3) δ -144.28 (h, J = 713 Hz).

HRMS (ESI-TOF) [M-PF6]+ calculated for [C21H23O2S]+ m/z: 339.1413, found 339.1420.
2.4 Light-mediated and/or Rh-mediated cycloaddition with nitriles, alkynes and allene: reaction scope.

With nitriles:

![Chemical structure of 1,3 ylide 3](image)

**General Procedure E**

To a 10 mL oven-dried tube equipped with a stirring bar was added reagent 3 (0.2 mmol, 1.0 equiv.), anhydrous nitriles solvent (1.0 mL). The reaction vial was capped with a rubber septum under an argon atmosphere, and it was fixed on a Purple LED light reaction equipment (40 W, 390 nm) for 3 hours. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography to yield the corresponding products 9.

**General Procedure F**

To a 10 mL oven-dried tube equipped with a stirring bar was added reagent 3 (0.2 mmol, 1.0 equiv.), Rh₂(OAc)₄ (2.2 mg, 0.02 equiv.), nitriles solvent (0.5 mL). The reaction vial was vigorously stirred in the open air for ten minutes. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography to yield the corresponding products 9.

2-methyl-4-(dimethylthylsulfoxonium)-5-phenyloxazole hexafluorophosphate (9a)

![Chemical structure of 2-methyl-4-(dimethylthylsulfoxonium)-5-phenyloxazole hexafluorophosphate](image)

This compound was synthesized following the general procedure E using reagent 3c (108.8 mg, 0.2 mmol), and acetonitrile (1.0 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (51.1 mg, 67% yield).

Note: This compound was also synthesized following the general procedure F using reagent 3c (108.8 mg, 0.2 mmol), and acetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (72.4 mg, 95% yield).
\[ ^1H \text{NMR} \ (400 \text{ MHz}, \text{Acetone-}d_6) \delta \ 7.93 \ (d, J = 6.9 \text{ Hz}, 2H), \ 7.72 - 7.67 \ (m, 1H), \ 7.67 - 7.61 \ (m, 2H), \ 4.32 \ (s, 6H), \ 2.69 \ (s, 3H). \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz}, \text{Acetone-}d_6) \delta \ 162.98, \ 158.93, \ 132.33, \ 129.19, \ 129.08, \ 124.52, \ 124.10, \ 40.71, \ 40.64, \ 13.00, \ 12.94. \]

\[ ^{19}F \text{NMR} \ (376 \text{ MHz}, \text{Acetone-}d_6) \delta \ -71.85 \ (d, J = 707 \text{ Hz}). \]

\[ ^{31}P \text{NMR} \ (162 \text{ MHz}, \text{Acetone-}d_6) \delta \ -144.33 \ (h, J = 708 \text{ Hz}). \]

HRMS (ESI-TOF) [M–PF\textsubscript{6}]\textsuperscript{+} calculated for \([C_{12}H_{14}NO_2S]^+\) m/z: 236.0740, found 236.0745.

2-methyl-4-(dimethylethylsulfoxonium)-5-phenyloxazole hexafluorophosphate (9b)

Following the general procedure E using reagent 3u (114.4 mg, 0.2 mmol), and acetonitrile (1.0 mL). According to NMR spectroscopy of crude reaction mixture, trace product was formed.

This compound was synthesized following the general procedure F using reagent 3u (114.4 mg, 0.2 mmol), and acetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (49.9 mg, 61% yield).

\[ ^1H \text{NMR} \ (400 \text{ MHz}, \text{Acetone-}d_6) \delta \ 7.36 - 7.32 \ (m, 2H), \ 7.29 - 7.20 \ (m, 3H), \ 4.07 \ (s, 3H), \ 4.06 \ (s, 3H), \ 3.40 \ (t, J = 7.5 \text{ Hz}, 2H), \ 3.11 \ (t, J = 7.5 \text{ Hz}, 2H), \ 2.62 \ (s, 3H). \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz}, \text{Acetone-}d_6) \delta \ 163.38, \ 162.43, \ 139.55, \ 128.68, \ 128.63, \ 126.77, \ 124.63, \ 40.52, \ 33.28, \ 27.40, \ 12.94. \]

\[ ^{19}F \text{NMR} \ (376 \text{ MHz}, \text{Acetone-}d_6) \delta \ -71.53 \ (d, J = 17.9 \text{ Hz}). \]

\[ ^{31}P \text{NMR} \ (162 \text{ MHz}, \text{Acetone-}d_6) \delta \ -144.30 \ (h, J = 708 \text{ Hz}). \]

HRMS (ESI-TOF) [M–PF\textsubscript{6}]\textsuperscript{+} calculated for \([C_{14}H_{18}NO_2S]^+\) m/z: 264.1053, found 264.1059.

4-(dimethylethylsulfoxonium)-2,5-diphenyloxazole hexafluorophosphate (9c)

53
This compound was synthesized following the *general procedure E* using reagent 3c (108.8 mg, 0.2 mmol), and Benzonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (31.0 mg, 35% yield).

This compound was also synthesized following the *general procedure F* using reagent 3c (108.8 mg, 0.2 mmol), and Benzonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (80.0 mg, 79% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 8.27 – 8.22 (m, 2H), 8.14 – 8.08 (m, 2H), 7.74 – 7.66 (m, 6H), 4.49 (s, 6H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 161.46, 158.75, 132.78, 132.58, 129.46, 129.36, 129.19, 127.17, 126.14, 124.78, 124.04, 40.87.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.40 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.25 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M–PF$_6$]$^+$ calculated for [C$_{17}$H$_{16}$NO$_2$S]$^+$ m/z: 298.0896, found 298.0892.

**2-(tert-butyl)-4-(dimethylethylsulfoxonium)-5-(naphthalen-1-yl)oxazole hexafluorophosphate (9d)**

This compound was synthesized following the *general procedure E* using reagent 3s (118.8 mg, 0.2 mmol), and trimethylacetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (52.0 mg, 55% yield).

This compound was also synthesized following the *general procedure F* using reagent 3s (118.8 mg, 0.2 mmol), and trimethylacetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (89.9 mg, 95% yield).
$^1$H NMR (400 MHz, Acetone-$d_6$) δ 8.29 (d, $J = 8.3$ Hz, 1H), 8.15 – 8.12 (m, 1H), 8.02 – 8.00 (m, 1H), 7.96 – 7.94 (m, 1H), 7.76 – 7.67 (m, 3H), 4.33 (s, 6H), 1.54 (s, 9H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 172.99, 157.96, 133.63, 133.01, 131.47, 131.21, 128.85, 128.14, 127.53, 127.14, 125.06, 124.65, 121.08, 40.44, 34.40, 27.46.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.39 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.27 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M–PF$_6$]$^+$ calculated for [C$_{19}$H$_{22}$NO$_2$S] $^+$ m/z: 328.1366, found 328.1367.

2-($\text{tert}$-butyl)-4-($\text{dimethylethylsulfoxonium}$)-5-phenyloxazole hexafluorophosphate (9e)

This compound was synthesized following the general procedure E using reagent 3c (108.8 mg, 0.2 mmol), and trimethylacetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (52.5 mg, 62% yield).

This compound was also synthesized following the general procedure F using reagent 3c (108.8 mg, 0.2 mmol), and Trimethylacetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (81.2 mg, 96% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 8.00 – 7.92 (m, 2H), 7.73 – 7.67 (m, 1H), 7.67 – 7.62 (m, 2H), 4.35 (brs, 6H), 1.51 (s, 9H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 171.76, 158.66, 132.32, 129.20, 129.10, 124.25, 40.66, 34.21, 27.41.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.29 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.27 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M–PF$_6$]$^+$ calculated for [C$_{15}$H$_{20}$NO$_2$S] $^+$ m/z: 278.1209, found 278.1207.

The crystal structure of 9e has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2152681.

2-($\text{tert}$-butyl)-5-($\text{furan-2-yl}$)-4-($\text{dimethylethylsulfoxonium}$)oxazole hexafluorophosphate (9f)
Following the general procedure E using reagent 3n (106.8 mg, 0.2 mmol), and Trimethylacetonitrile (0.5 mL). According to NMR spectroscopy of crude reaction mixture, trace product was formed.

This compound was synthesized following the general procedure F using reagent 3n (106.8 mg, 0.2 mmol), and Trimethylacetonitrile (0.5 mL). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (49.6 mg, 60% yield).

^1H NMR (400 MHz, Acetone-\textit{d}6) \(\delta\) 8.08 (s, 1H), 7.46 (d, \(J = 3.6\) Hz, 1H), 6.91 – 6.83 (m, 1H), 4.43 (s, 3H), 4.42 (s, 3H), 1.49 (s, 9H).

^13C NMR (101 MHz, Acetone-\textit{d}6) \(\delta\) 170.59, 148.68, 148.00, 139.52, 123.17, 116.74, 113.19, 40.44, 34.19, 27.39.

^19F NMR (376 MHz, Acetone-\textit{d}6) \(\delta\) -72.46 (d, \(J = 707\) Hz).

^31P NMR (162 MHz, Acetone-\textit{d}6) \(\delta\) -144.30 (h, \(J = 708\) Hz).

HRMS (ESI-TOF) [M–PF\textsubscript{6}]\(^+\) calculated for [C\textsubscript{13}H\textsubscript{18}NO\textsubscript{3}S]\(^+\) m/z: 268.1002, found 268.1003.
With alkynes:

\[
\text{3-methyl-4-(dimethylethylsulfoxonium)-2,5-diphenylfuran hexafluorophosphate (10a)}
\]

This compound was synthesized following the *general procedure D* using reagent 3c (108.8 mg, 0.2 mmol), and prop-1-yn-1-ylbenzene (46.4 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/Acetone: 4/1) provided the title compound as white solid (68.4 mg, 75% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using \(^1\)H NMR spectroscopy.

\[^1\text{H NMR\ (400 MHz, Acetone-}d_6\text{) }\delta \ 7.91 \text{ – 7.86 (m, 2H), 7.79 \text{ – 7.75 (m, 2H), 7.74 \text{ – 7.69 (m, 1H), 7.68 \text{ – 7.58 (m, 4H), 7.57 \text{ – 7.52 (m, 1H), 4.35 (s, 6H), 2.67 (s, 3H).}}}
\]

\[^{13}\text{C NMR\ (101 MHz, Acetone-}d_6\text{) }\delta \ 159.17, 152.10, 131.82, 130.44, 129.54, 129.12, 128.85, 128.29, 127.28, 114.60, 114.44, 42.82, 10.07.\]

\[^{19}\text{F NMR\ (376 MHz, Acetone-}d_6\text{) }\delta \ -72.45 \text{ (d, } J = 706 \text{ Hz).}\]

\[^{31}\text{P NMR\ (162 MHz, Acetone-}d_6\text{) }\delta \ -144.27 \text{ (h, } J = 707 \text{ Hz).}\]

\[
\text{HRMS (ESI-TOF) [M–PF}_6\text{]}^+ \text{ calculated for [C}_{19}\text{H}_{19}\text{O}_2\text{S]]} \text{ m/z: 311.1100, found 311.1102.}\]

3-butyl-4-(dimethylethylsulfoxonium)-2,5-diphenylfuran hexafluorophosphate (10b)
This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and hex-1-yn-1-ylbenzene (63.2 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (69.7 mg, 70% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.89 (d, $J = 7.3$ Hz, 2H), 7.80 – 7.76 (m, 2H), 7.24 – 7.22 (m, 1H), 7.69 – 7.65 (m, 2H), 7.61 – 7.57 (m, 2H), 7.55 – 7.51 (m, 1H), 4.27 (s, 6H), 3.10 – 3.01 (m, 2H), 1.81 – 1.73 (m, 2H), 1.53 – 1.45 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 157.97, 151.92, 132.04, 130.48, 129.57, 129.18, 128.61, 127.32, 126.94, 120.75, 114.24, 43.48, 32.44, 23.72, 22.34, 13.02.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -72.32 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.26 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M–PF$_6$]$^+$ calculated for [C$_{22}$H$_{25}$O$_2$S] $^+$/m/z: 353.1570, found 353.1577.

3-cyclohexyl-4-(dimethylethylsulfoxonium)-2,5-diphenylfuran hexafluorophosphate (10c)

This compound was synthesized following the general procedure D using reagent 3c (108.8 mg, 0.2 mmol), and (cyclohexylethynyl)benzene (73.7 mg, 0.4 mmol). Purification by flash chromatography on silica gel (DCM/ Acetone: 4/1) provided the title compound as white solid (65.0 mg, 62% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.87 – 7.81 (m, 2H), 7.73 – 7.69 (m, 1H), 7.69 – 7.62 (m, 4H), 7.62 – 7.57 (m, 3H), 4.26 (s, 3H), 4.25 (s, 3H), 3.05 – 2.98 (m, 1H), 2.05 – 1.97 (m, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.61 (m, 3H), 1.48 – 1.36 (m, 2H), 1.17 – 1.07 (m, 1H).
$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 157.83, 152.94, 131.89, 130.51, 130.17, 129.97, 129.92, 129.08, 128.69, 127.51, 125.48, 113.66, 43.87, 35.62, 32.75, 26.34, 25.41.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -72.40 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) δ -144.26 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M+PF$_6$]$^+$ calculated for [C$_{24}$H$_{27}$O$_2$S]$^+$ m/z: 379.1726, found 379.1721.

4-cyclopentyl-2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)naphthalen-1(2H)-one (11a)

![Structure of 4-cyclopentyl-2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)naphthalen-1(2H)-one (11a)](image)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and ethynylcyclopentane (75.3 mg, 0.8 mmol). Purification by flash chromatography on silica gel DCM/MeOH: 30/1 provided the title compound as light yellow solid (37.5 mg, 65% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.96 (d, $J = 8.3$ Hz, 1H), 7.64 – 7.60 (m, 1H), 7.46 – 7.42 (m, 1H), 7.17 (s, 1H), 3.80 (s, 6H), 3.52 – 3.44 (m, 1H), 2.25 – 2.10 (m, 2H), 1.88 – 1.65 (m, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.59, 138.34, 131.64, 129.79, 125.12, 124.43, 124.35, 124.11, 115.49, 94.38, 40.90, 40.84, 33.01, 25.03.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{17}$H$_{21}$O$_2$S]$^+$ m/z: 289.1257, found 289.1258.

The crystal structure of 11a has been deposited at the Cambridge Crystallographic Data Centre, CCDC 2144537.

4-butyl-2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)naphthalen-1(2H)-one (11b)

![Structure of 4-butyl-2-(dimethyl(oxo)$\lambda^6$-sulfanylidene)naphthalen-1(2H)-one (11b)](image)
This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and 1-Hexyne (67.3 mg, 0.8 mmol). Purification by flash chromatography on silica gel DCM/ MeOH: 30/1 provided the title compound as white solid (37.6 mg, 68% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.46 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.08 (s, 1H) 3.79 (s, 6H), 2.89 – 2.80 (m, 2H), 1.72 – 1.65 (m, 2H), 1.52 – 1.42 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.94, 137.92, 131.68, 129.87, 125.16, 124.46, 123.94, 121.20, 118.71, 94.13, 40.78, 32.50, 32.27, 22.89, 14.08.

HRMS (ESI-TOF) [M+H]$^+$ calculated for $[C_{16}H_{21}O_2S]^+$ m/z: 277.1257, found 277.1263.

2-(dimethyl(oxo)-λ$^6$-sulfanylidene)-4-pentylnaphthalen-1(2H)-one (11c)

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and 1-Heptyne (78.6 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as little yellow oil (36.6 mg, 63% yield). Ratio of isomers was determined to be >20:1 from both the crude reaction mixture and purified products using $^1$H NMR spectroscopy.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.46 (d, $J = 7.4$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.08 (s, 1H) 3.80 (s, 6H), 2.88 – 2.79 (m, 2H), 1.74 – 1.67 (m, 2H), 1.50 – 1.35 (m, 4H), 0.94 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.93, 137.92, 131.66, 129.88, 125.16, 124.46, 123.93, 121.29, 118.68, 94.13, 40.79, 32.57, 32.06, 30.04, 22.64, 14.15.

HRMS (ESI-TOF) [M+H]$^+$ calculated for $[C_{17}H_{23}O_2S]^+$ m/z: 291.1413, found 291.1419.
With allene:

![Chemical Structure](image)

**Mixture of (Z/E)-4-(cyclohexylmethylen)-2-(dimethyl(oxo)-λ⁶-sulfanylidene)-3,4-dihyronaphthalen-1(2H)-one (12)**

This compound was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and 1-Cyclohexylallene (97.8 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/Acetone: 4/1) provided the title compound as little yellow oil (44.3 mg, 70% yield). Ratio of isomers was determined to be 6.3:1 (Z:E) from both the crude reaction mixture and purified products using ¹H NMR spectroscopy.

**major isomer ¹H NMR** (400 MHz, Acetone-d₆) δ 7.95 – 7.93 (m, 1H), 7.53 – 7.50 (m, 1H), 7.41 – 7.35 (m, 1H), 7.32 – 7.27 (m, 1H), 5.77 (d, J = 9.0 Hz, 1H), 3.64 (s, 6H), 3.43 (d, J = 1.8 Hz, 2H), 2.51 – 2.44 (m, 1H), 1.78 – 1.71 (m, 4H), 1.45 – 1.34 (m, 2H), 1.31 – 1.19 (m, 4H).

**¹³C NMR** (101 MHz, Acetone-d₆) δ 173.94, 139.58, 134.80, 132.80, 131.55, 130.13, 126.80, 124.81, 123.59, 41.13, 37.01, 32.84, 25.83, 25.68, 22.64.

**HRMS (ESI-TOF) [M+H]⁺** calculated for [C₁₉H₂₅O₂S]⁺ m/z: 317.1570, found 317.1572.
2.5 Mechanistic experiments.

UV-Visible absorption analysis

Supplementary Figure 3. UV-Vis spectra of I(III)/S(VI) Reagents 3c and 3t at 0.1M in MeCN.

Cation trap experiment

2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-(5-methyl-4,5-dihydrooxazol-5-yl)-1-phenylpropan-1-one, 13:

Compound 13 was synthesized following the general procedure C using reagent 3c (108.8 mg, 0.2 mmol), and N-(2-Methylallyl)benzamide[4] (140.0 mg, 0.8 mmol). Purification by flash chromatography on silica gel (DCM/ MeOH: 30/1) provided the title compound as white solid (35.2 mg, 60% yield). No [4+2] product has been detected in this process.

1H NMR (400 MHz, Acetonitrile-d3) δ 7.89 – 7.80 (m, 2H), 7.75 – 7.70 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.53 – 7.49 (m, 2H), 3.87 (dd, J = 14.4, 6.5 Hz, 1H), 3.80 (dd, J = 14.4, 6.5 Hz, 1H), 3.59 (s, 3H), 3.56 (s, 3H), 3.45 (d, J = 13.7 Hz, 1H), 3.15 (d, J = 13.8 Hz, 1H), 1.70 (s, 3H).

13C NMR (400 MHz, Acetonitrile-d3) δ 172.52, 168.13, 134.18, 132.89, 131.75, 129.39, 128.73, 128.57, 127.24, 98.23, 92.58, 46.22, 41.13, 41.07, 39.54, 23.48.
Intramolecular cyclopropanation

1-dimethylsulfoxonium-6-(p-tolyl)bicyclo[3.1.0]hexan-2-one hexafluorophosphate (14a)

14a was synthesized following the general procedure C using reagent 3v (122.4 mg, 0.2 mmol). Ratio of diastereoisomers was determined to be >20:1 from the crude reaction mixture using $^1$H NMR spectroscopy. Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (13.0 mg, 16% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.55 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 4.29 – 4.20 (m, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 2.85 (dd, $J = 18.2$, 9.3 Hz, 1H), 2.73 (dtd, $J = 12.5$, 9.1, 4.8 Hz, 1H), 2.61 (ddd, $J = 18.2$, 9.4, 1.2 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.34 (s, 3H).

$^{13}$C NMR (400 MHz, Acetone-$d_6$) $\delta$ 203.08, 139.19, 130.05, 129.50, 125.33, 55.00, 40.01, 39.86, 39.47, 33.94, 33.82, 21.11, 20.30.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -72.68 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.26 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{15}$H$_{19}$O$_2$S]$^+$ m/z: 263.1100, found 263.1104.

1-dimethylsulfoxonium-6-propylbicyclo[3.1.0]hexan-2-one hexafluorophosphate (14b)

14b was synthesized following the general procedure C using reagent 3w (112.8 mg, 0.2 mmol). Ratio of diastereoisomers was determined to be >20:1 from the crude reaction mixture using $^1$H NMR spectroscopy.
Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (21.6 mg, 30% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 4.16 (d, $J = 0.9$ Hz, 3H), 4.05 (d, $J = 0.9$ Hz, 3H), 3.38 – 3.45 (m, 1H), 2.52 – 2.71 (m, 2H), 2.61 – 2.46 (m, 2H), 2.35 – 2.26 (m, 1H), 2.16 (dtd, $J = 13.7$, 7.0, 3.7 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.68 – 1.57 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 203.98, 53.28, 40.39, 39.74, 37.85, 37.48, 33.88, 27.96, 22.46, 21.22, 12.94.

$^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -72.36 (d, $J = 707$ Hz).

$^{31}$P NMR (162 MHz, Acetone-$d_6$) $\delta$ -144.28 (h, $J = 708$ Hz).

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{11}$H$_{19}$O$_2$S]$^+$ m/z: 215.1100, found 215.1102.
2.6 Synthetic Application of [4+2] and [3+2] Products.

Large scale experiment.

![Chemical structure](image)

This compound was synthesized following the general procedure C using reagent 3c (544.0 mg, 1.0 mmol), and allylbenzene (945.0 mg, 8.0 mmol). Purification by flash chromatography on silica gel (DCM/MeOH: 30/1) provided the title compound as white solid (296.5 mg, 95% yield).

4-benzyl-3,4-dihydronaphthalen-1(2H)-one (15)

![Chemical structure](image)

This compound was synthesized using following procedure,[2] wet Raney nickel (230 μL of heterogeneous solution) was added to a solution of 5i (62.4 mg, 0.2 mmol) in i-PrOH (3 mL) and the system was then warmed until the reflux temperature. After 1 hour, the crude product is filtered through a pad of celite and washed with 5 mL of i-PrOH. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography to yield the product 15 (34.0 mg, 72%). Its spectra are consistent the reported literature,[3], and this result further serves as a demonstration of the regioselectivity for compound 5i.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.49 (td, $J = 7.5, 1.5$ Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 – 7.26 (m, 1H), 7.24 – 7.18 (m, 3H), 3.29 – 3.23 (m, 1H), 3.17 – 3.12 (m, 1H), 2.94 – 2.80 (m, 2H), 2.64 – 2.56 (m, 1H), 2.22 – 2.13 (m, 1H), 2.01 – 1.94 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.30, 147.46, 139.82, 133.55, 132.03, 129.11, 128.63, 128.47, 127.48, 126.99, 126.52, 41.33, 40.05, 34.81, 26.14.

HRMS (ESI-TOF) [M+H]$^+$ calculated for [C$_{17}$H$_{17}$O]$^+$ m/z: 237.1274, found 237.1278.
4-benzyl-2-(dimethylethylsulfoxonium)-3,4-dihydronaphthalen-1(2H)-one trifluoromethanesulfonate (16)

![Chemical Structure](#)

To a 10 mL oven-dried tube equipped with a stirring bar was added 5i (62.4 mg, 0.2 mmol), HOTf (19.5 μL, 0.22 mmol) and anhydrous MeCN (1.0 mL). The reaction vial was capped with a rubber septum under an air atmosphere for 10 minutes. Solvent was removed under vacuum and the crude mixture was washed with hexane (10 mL) and Et₂O (1 mL) to yield white solid 16 (83.2 mg, 90% yield).

**1H NMR** (400 MHz, CD₃CN) δ 8.09 – 8.06 (m, 2H), 7.90 – 7.79 (m, 2H), 7.70 – 7.60 (m, 2H), 7.58 – 7.46 (m, 3H), 7.44 – 7.37 (m, 7H), 7.34 – 7.30 (m, 7H), 5.63 (dd, J = 14.5, 4.5 Hz, 2H), 5.36 (dd, J = 14.2, 4.3 Hz, 1H), 3.88 (s, 4H), 3.87 (s, 5H), 3.83 – 3.82 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.74 – 3.70 (m, 3H), 3.16 – 3.13 (m, 3H), 2.88 – 2.70 (m, 3H), 2.59 – 2.51 (m, 3H), 2.39 – 2.29 (m, 1H).

**13C NMR** (101 MHz, CD₃CN) δ 188.00, 187.39, 146.59, 146.08, 138.84, 138.24, 136.23, 136.02, 130.91, 129.95, 129.75, 129.38, 129.08, 128.78, 128.68, 128.03, 127.95, 127.82, 127.77, 127.31, 126.92, 126.77, 122.00, 118.83, 68.35, 65.34, 40.53, 39.66, 39.36, 39.29, 39.06, 38.27, 37.86, 37.81, 26.42, 24.36.

**19F NMR** (376 MHz, CD₃CN) δ -79.49.

**HRMS** (ESI-TOF) [M–OTf]⁺ calculated for [C₁₉H₂₁O₂S]⁺ m/z: 313.1257, found 313.1254.

4-benzyl-2-((4-methoxyphenyl)thio)-3,4-dihydronaphthalen-1(2H)-one (17)

![Chemical Structure](#)

To a 15 mL oven-dried tube equipped with a stirring bar was added 5i (31.2 mg, 0.1 mmol), 4-hydroxydinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepine 4-oxide (3.4 mg, 0.01 mmol), 4-methoxybenzenethiol (70.0 mg, 0.5 mmol) and anhydrous DCM (1.0 mL). The reaction vial was capped with a rubber septum under an air atmosphere and it was fixed on oil bath at 80 °C for 10 hours. Solvent
was removed under vacuum and the crude mixture was purified by flash column chromatography (Hexane/EA : 10/1) to provide the title compound as yellow oil (21.0 mg, 56% yield).

\[^1H\text{NMR}\ (400\text{ MHz, CDCl}_3) \delta 8.11\ (dd, \ J = 7.9, 1.5\text{ Hz, 1H}),\ 7.57 - 7.53\ (m, 1H),\ 7.46 - 7.32\ (m, 4H),\ 7.32 - 7.20\ (m, 4H),\ 7.07 - 7.04\ (m, 2H),\ 6.89 - 6.79\ (m, 2H),\ 4.11 - 4.07\ (m, 1H),\ 3.82\ (s, 3H),\ 3.45 - 3.41\ (m, 1H),\ 3.27 - 3.23\ (m, 1H),\ 2.80 - 2.73\ (m, 1H),\ 2.25 - 2.15\ (m, 2H).\]

\[^{13}C\text{NMR}\ (101\text{ MHz, CDCl}_3) \delta 194.04,\ 160.07,\ 146.04,\ 139.14,\ 136.61,\ 133.74,\ 131.30,\ 129.23,\ 128.99,\ 128.58,\ 128.26,\ 127.79,\ 127.08,\ 126.44,\ 122.98,\ 114.63,\ 114.48,\ 55.32,\ 52.64,\ 41.19,\ 38.09,\ 33.16.\]

HRMS (ESI-TOF) [M+Na]⁺ calculated for [C\text{29}H\text{22}NaO2S]⁺ m/z: 411.1719, found 411.1720.

2,2,5-triphenyl-4-(p-tolyl)-2,3-dihydrofuran (18)

To a 15 mL oven-dried tube equipped with a stirring bar was added 7a (52.0 mg, 0.1 mmol), p-tolylboronic acid (27.2 mg, 0.2 mmol), cesium carbonate (65.0 mg, 0.2 mmol), bis(acetonitrile)dichloropalladium(II) (0.5 mg, 0.002 mmol) and anhydrous MeOH (1.0 mL). The reaction vial was capped with a rubber septum and degassed with nitrogen 3 times. The tube was fixed on oil bath at 50 °C for 24 hours. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography (Hexane/EA : 5/1) to provide the title compound as yellow oil (20.2 mg, 52% yield).

\[^1H\text{NMR}\ (400\text{ MHz, CDCl}_3) \delta 7.62\ (dd, \ J = 4.1, 1.9\text{ Hz, 2H}),\ 7.57 - 7.52\ (m, 4H),\ 7.36 - 7.29\ (m, 7H),\ 7.26 - 7.22\ (m, 2H),\ 7.11\ (d, \ J = 8.1\text{ Hz, 2H}),\ 7.02\ (d, \ J = 8.0\text{ Hz, 2H}),\ 3.88\ (s, 2H),\ 2.30\ (s, 3H).\]

\[^{13}C\text{NMR}\ (101\text{ MHz, CDCl}_3) \delta 146.33,\ 135.80,\ 132.48,\ 131.81,\ 128.54,\ 128.23,\ 128.13,\ 128.05,\ 127.24,\ 127.14,\ 125.84,\ 109.42,\ 88.25,\ 50.00,\ 21.13.\]

HRMS (ESI-TOF) [M+Na]⁺ calculated for [C\text{20}H\text{24}NaO]⁺ m/z: 411.1719, found 411.1720.

4-(methylsulfinyl)-2,2,5-triphenyl-2,3-dihydrofuran (19)
To a 10 mL oven-dried flask equipped with a stirring bar was added 7a (52.0 mg, 0.1 mmol), potassium iodide (49.8 mg, 0.3 mmol) and anhydrous acetone (2.0 mL). The reaction mixture was heated until reflux for 2 hours. After cooling down to room temperature, solvent was removed under vacuum and the crude mixture was purified by flash column chromatography (Hexane/EA : 2/1) to provide the title compound as yellow oil (31.7 mg, 88% yield).

\[ \text{1H NMR (400 MHz, CDCl}_3\] } \delta 7.75 – 7.69 (m, 2H), 7.51 – 7.43 (m, 7H), 7.39 – 7.28 (m, 6H), 4.19 (d, J = 14.7 Hz, 1H), 3.74 (d, J = 14.7 Hz, 1H), 2.72 (s, 3H).

\[ \text{13C NMR (101 MHz, CDCl}_3\] } \delta 159.40, 144.94, 144.11, 130.80, 128.59, 128.51, 128.47, 127.89, 127.72, 125.88, 125.50, 111.20, 91.74, 39.98, 38.36.

\[ \text{HRMS (ESI-TOF) [M+Na]}^+ \text{calculated for [C}_{23}\text{H}_{20}\text{NaO}_2\text{S]}^+ \text{m/z: 383.1076, found 383.1081.}

4-(2,2-diphenylvinyl)-2,2,5-triphenyl-2,3-dihydrofuran (20)

To a 15 mL oven-dried tube equipped with a stirring bar was added 7a (52.0 mg, 0.1 mmol), {Ir[dF(CF}_3ppy]_2(dtbbpy)}PF_6 (2.2 mg, 0.002 mmol) and anhydrous MeCN (1.0 mL). 1,1-diphenylethylene (36.0 mg, 0.2 mmol) was added and the reaction tube was capped with a rubber septum and degassed with nitrogen 3 times. The tube was placed close to blue LED and stirred at room temperature for 16 hours. Solvent was removed under vacuum and the crude mixture was purified by flash column chromatography (Hexane/EA : 10/1) to provide the title compound as yellowish solid (33.3 mg, 70% yield).

\[ \text{1H NMR (400 MHz, CDCl}_3\] } \delta 7.83 – 7.77 (m, 2H), 7.49 – 7.30 (m, 14H), 7.25 (m, 9H), 6.98 (s, 1H), 2.99 (d, J = 1.1 Hz, 2H).

\[ \text{13C NMR (101 MHz, CDCl}_3\] } \delta 145.96, 143.13, 140.88, 139.14, 131.32, 130.88, 128.82, 128.35, 128.29, 128.11, 128.08, 127.87, 127.35, 127.08, 126.72, 125.77, 122.16, 110.72, 89.74, 46.55.

\[ \text{HRMS (ESI-TOF) [M+Na]}^+ \text{calculated for [C}_{36}\text{H}_{28}\text{NaO]}^+ \text{m/z: 499.2032, found 499.2035.} \]
2.7 Computational studies and computational details.
All calculations were performed using Gaussian 16, Revision A.03 package.\cite{5} All of the intermediates were optimized by the DFT with the oob97xd functional.\cite{6} For geometry optimizations calculations, we employed LANL2DZ basis set for I with effective core potentials, 6-31G(d) basis sets for H, C, S, F, B, and O. All the stationary structures were characterized with no imaginary frequency. For all intermediates, the Mayer Bond Order and NBO charge of atoms were calculated using Multiwfn.\cite{7} Electrostatic potential maps for each compound were mapped by Gaussview.

**Supplementary Table 1:** Cartesian coordinates of the optimized structures of 3a:

E = -1366.810098 a.u.

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| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| I       | 9.55196900| 3.28473400| 6.33458900|
| S       | 7.35500000| 2.52246000| 4.08451200|
| O       | 5.31103200| 2.50501700| 6.05212300|
| O       | 8.57659300| 2.63194800| 3.27647900|
| C       | 7.55142300| 3.06337300| 5.69252600|
| C       | 6.36221100| 3.00253500| 6.49721500|
| C       | 6.36656700| 3.52438900| 7.90271700|
| C       | 7.00396100| 4.71034700| 8.27461500|
| H       | 7.53531400| 5.30392000| 7.53746200|
| C       | 6.93361500| 5.16117800| 9.58911500|
| H       | 7.42714400| 6.08740500| 9.86653900|
| C       | 6.23375100| 4.42678500| 10.5422100|
| H       | 6.18871400| 4.77420700| 11.57008400|
| C       | 5.58335000| 3.25053900| 10.1737500|
| H       | 5.02841700| 2.68049300| 10.91271300|
| C       | 5.63804400| 2.80926400| 8.85742600|
| H       | 5.11687500| 1.90788300| 8.55159800|
| C       | 6.02583500| 3.43675000| 3.30717100|
Supplementary Figure 4. DFT analysis results of reagent 3a. a) NBO charge distribution; b) Electrostatic potential map; c) Frontier molecular orbital analysis.

Supplementary Table 2: Cartesian coordinates of the optimized structures of 3e:

E = -1603.231248 a.u.

| Bond Length | Mayer Bond Order | ESP | HOMO |
|-------------|------------------|-----|------|
| b_{1(C-I)} = 2.113 | b_{1(C-I)} = 0.902 |  |  |
| b_{2(C-S)} = 1.708 | b_{2(C-S)} = 0.967 |  |  |
|   |   |   |   |
|---|---|---|---|
| C | 6.75474300 | 3.02491300 | 10.24830600 |
| H | 6.59795500 | 2.34016600 | 11.07583500 |
| C | 6.45441800 | 2.62192500 | 8.95164600 |
| H | 6.06388500 | 1.62951600 | 8.75215400 |
| C | 5.33037500 | 3.49836600 | 3.47290300 |
| H | 5.52075200 | 4.57276400 | 3.47790200 |
| H | 4.59576100 | 3.21905300 | 4.22848200 |
| H | 5.05033600 | 3.15812500 | 2.47342000 |
| C | 6.52194900 | 0.96546800 | 3.84767900 |
| H | 5.82624400 | 0.76708900 | 4.66492500 |
| H | 7.47418900 | 0.44419500 | 4.00650200 |
| H | 6.09357600 | 0.73161000 | 2.87034000 |
| C | 9.76504500 | 5.19108400 | 5.47086300 |
| C | 9.70380700 | 5.69125600 | 4.17221900 |
| H | 9.40927400 | 5.04941900 | 3.34743100 |
| C | 10.01286300 | 7.03156700 | 3.95889400 |
| H | 9.96818800 | 7.43742100 | 2.95310400 |
| C | 10.38473900 | 7.84643000 | 5.02676100 |
| H | 10.62856400 | 8.88958200 | 4.85096600 |
| C | 10.44530100 | 7.32921200 | 6.31783300 |
| H | 10.73298900 | 7.96516900 | 7.14914600 |
| C | 10.13222500 | 5.99144200 | 6.55002100 |
| H | 10.16215400 | 5.58832600 | 7.55802700 |
| F | 9.20960400 | -0.34086700 | 4.47502400 |
| F | 8.39499600 | 0.80291500 | 6.28495600 |
| F | 9.29468500 | -1.30662700 | 6.56803000 |
| F | 10.64732800 | 0.49568500 | 6.06339100 |

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Supplementary Figure 5. DFT analysis results of reagent 3e. a) NBO charge distribution; b) Electrostatic potential map; c) Frontier molecular orbital analysis.
3. Supplementary Figures.
3.1 NMR spectra.

Supplementary Figure 6. $^1$H NMR of the 3a (400 MHz, 25 °C in DMSO-$d_6$)

Supplementary Figure 7. $^{13}$C NMR of the 3a (101 MHz, 25 °C in DMSO-$d_6$)
Supplementary Figure 8. $^1$H NMR of the 3b (400 MHz, 25 °C in Acetone-$d_6$).

Supplementary Figure 9. $^{13}$C NMR of the 3b (101 MHz, 25 °C in Acetone-$d_6$).
Supplementary Figure 10. $^1$H NMR of the 3c (400 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 11. $^{13}$C NMR of the 3c (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 12. $^{19}$F NMR of the 3c (376 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 13. $^{31}$P NMR of the 3c (162 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 14. $^1$H NMR of the 3d (400 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 15. $^{13}$C NMR of the 3d (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 16. $^{19}$F NMR of the 3d (376 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 17. $^1$H NMR of the 3e (400 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 18. $^{13}$C NMR of the 3e (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 19. $^{19}$F NMR of the $3e$ (376 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 20. $^1$H NMR of the 3f (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 21. $^{13}$C NMR of the 3f (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 22. $^{19}$F NMR of the 3f (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 23. $^{31}$P NMR of the 3f (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 24. $^1$H NMR of the 3g (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 25. $^{13}$C NMR of the 3g (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 26. $^{19}$F NMR of the 3g (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 27. $^{31}$P NMR of the 3g (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 28. \textsuperscript{1}H NMR of the 3h (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 29. \textsuperscript{13}C NMR of the 3h (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 30. $^{19}$F NMR of the 3h (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 31. $^{31}$P NMR of the 3h (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 32. $^1$H NMR of the 3i (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 33. $^{13}$C NMR of the 3i (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 34. $^{19}$F NMR of the 3i (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 35. $^{31}$P NMR of the 3i (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 36. $^1$H NMR of the 3j (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 37. $^{13}$C NMR of the 3j (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 38. $^{19}$F NMR of the 3j (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 39. $^{31}$P NMR of the 3j (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 40. $^1$H NMR of the 3k (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 41. $^{13}$C NMR of the 3k (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 42. $^{19}$F NMR of the 3k (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 43. $^{31}$P NMR of the 3k (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 44. $^1$H NMR of the 3l (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 45. $^{13}$C NMR of the 3l (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 46. $^{19}$F NMR of the 3l (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 47. $^{31}$P NMR of the 3l (162 MHz, 25 °C in Acetone-$d_6$)
**Supplementary Figure 48.** $^1$H NMR of the 3m (400 MHz, 25 °C in Acetone-$d_6$)

**Supplementary Figure 49.** $^{13}$C NMR of the 3m (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 50. $^{19}$F NMR of the 3m (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 51. $^{31}$P NMR of the 3m (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 52. $^1$H NMR of the 3n (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 53. $^{13}$C NMR of the 3n (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 54. $^{19}$F NMR of the 3n (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 55. $^{31}$P NMR of the 3n (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 56. $^1$H NMR of the 3o (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 57. $^{13}$C NMR of the 3o (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 58. $^{19}$F NMR of the 3o (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 59. $^{31}$P NMR of the 3o (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 60. $^1$H NMR of the 3p (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 61. $^{13}$C NMR of the 3p (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 62. $^{19}$F NMR of the 3p (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 63. $^{31}$P NMR of the 3p (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 64. $^1$H NMR of the 3q (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 65. $^{13}$C NMR of the 3q (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 66. $^{19}$F NMR of the 3q (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 67. $^{31}$P NMR of the 3q (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 68. $^1$H NMR of the 3r (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 69. $^{13}$C NMR of the 3r (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 70. $^{19}$F NMR of the 3r (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 71. $^{31}$P NMR of the 3r (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 72. $^1$H NMR of the 3s (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 73. $^{13}$C NMR of the 3s (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 74. $^{19}$F NMR of the 3s (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 75. $^1$H NMR of the 3t (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 76. $^{13}$C NMR of the 3t (101 MHz, 25 °C in Acetone-$d_6$)
**Supplementary Figure 77.** $^{19}$F NMR of the 3t (376 MHz, 25 °C in Acetone-$d_6$)

**Supplementary Figure 78.** $^{31}$P NMR of the 3t (162 MHz, 25 °C in Acetone-$d_6$)
**Supplementary Figure 79.** $^1$H NMR of the 3u (400 MHz, 25 °C in CD$_3$CN)

**Supplementary Figure 80.** $^{13}$C NMR of the 3u (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 81. $^{19}$F NMR of the 3u (376 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 82. $^{31}$P NMR of the 3u (162 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 83. $^1$H NMR of the 3v (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 84. $^{13}$C NMR of the 3v (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 85. $^{19}$F NMR of the 3v (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 86. $^{31}$P NMR of the 3v (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 87. $^1$H NMR of the 3w (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 88. $^{13}$C NMR of the 3w (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 89. $^{19}$F NMR of the $3w$ (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 90. $^{31}$P NMR of the $3w$ (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 91. $^1$H NMR of the 5a (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 92. $^{13}$C NMR of the 5a (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 93. $^1$H NMR of the 5b (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 94. $^{13}$C NMR of the 5b (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 95. $^1$H NMR of the 5c (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 96. $^{13}$C NMR of the 5c (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 97. $^1$H NMR of the 5d (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 98. $^{13}$C NMR of the 5d (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 99. $^1$H NMR of the 5e (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 100. $^{13}$C NMR of the 5e (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 101. $^1$H NMR of the 5f (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 102. $^{13}$C NMR of the 5f (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 103. $^1$H NMR of the 5g (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 104. $^{13}$C NMR of the 5g (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 105. $^1$H NMR of the 5h (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 106. $^{13}$C NMR of the 5h (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 107. $^1$H NMR of the 5i (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 108. $^{13}$C NMR of the 5i (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 109. $^1$H NMR of the 5j (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 110. $^{13}$C NMR of the 5j (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 111. $^1$H NMR of the 5k (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 112. $^{13}$C NMR of the 5k (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 113. $^1$H NMR of the 51 (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 114. $^{13}$C NMR of the 51 (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 115. $^1$H NMR of the 5m (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 116. $^{13}$C NMR of the 5m (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 117. $^1$H NMR of the 5n (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 118. $^{13}$C NMR of the 5n (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 119. $^1$H NMR of the 5o (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 120. $^{13}$C NMR of the 5o (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 121. $^1$H NMR of the 5p (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 122. $^{13}$C NMR of the 5p (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 123. $^1$H NMR of the 5q (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 124. $^{13}$C NMR of the 5q (101 MHz, 25 °C in Acetone-$d_6$)
**Supplementary Figure 125.** $^1$H NMR of the $5r$ (400 MHz, 25 °C in CDCl$_3$)

**Supplementary Figure 126.** $^{13}$C NMR of the $5r$ (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 127. $^1$H NMR of the 5s (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 128. $^{13}$C NMR of the 5s (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 129. $^1$H NMR of the 5t (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 130. $^{13}$C NMR of the 5t (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 131. $^1$H NMR of the 5u (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 132. $^{13}$C NMR of the 5u (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 133. $^1$H NMR of the 5v (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 134. $^{13}$C NMR of the 5v (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 135. $^1$H NMR of the 5w (400 MHz, 25 °C in CDCl₃)

Supplementary Figure 136. $^{13}$C NMR of the 5w (101 MHz, 25 °C in CDCl₃)
Supplementary Figure 137. $^1$H NMR of the 5x (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 138. $^{13}$C NMR of the 5x (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 139. $^1$H NMR of the 5y (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 140. $^{13}$C NMR of the 5y (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 141. $^1$H NMR of the 5z (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 142. $^{13}$C NMR of the 5z (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 143. $^1$H NMR of the 5aa (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 144. $^{13}$C NMR of the 5aa (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 145. $^1$H NMR of the 5ab (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 146. $^{13}$C NMR of the 5ab (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 147. $^1$H NMR of the 5ac (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 148. $^{13}$C NMR of the 5ac (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 149. $^1$H NMR of the 5ad (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 150. $^{13}$C NMR of the 5ad (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 151. $^1$H NMR of the 5ae (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 152. $^{13}$C NMR of the 5ae (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 153. $^1$H NMR of the 5af (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 154. $^{13}$C NMR of the 5af (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 155. $^1$H NMR of the 7a (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 156. $^{13}$C NMR of the 7a (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 157. $^{19}$F NMR of the 7a (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 158. $^{31}$P NMR of the 7a (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 159. $^1$H NMR of the 7b (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 160. $^{13}$C NMR of the 7b (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 161. $^{19}$F NMR of the 7b (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 162. $^{31}$P NMR of the 7b (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 163. $^1$H NMR of the 7c (400 MHz, 25 °C in DMSO-$d_6$)

Supplementary Figure 164. $^{13}$C NMR of the 7c (101 MHz, 25 °C in DMSO-$d_6$)
Supplementary Figure 165. $^{19}$F NMR of the 7c (376 MHz, 25 °C in DMSO-$d_6$)

Supplementary Figure 166. $^{31}$P NMR of the 7c (162 MHz, 25 °C in DMSO-$d_6$)
Supplementary Figure 167. $^1$H NMR of the 7d (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 168. $^{13}$C NMR of the 7d (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 169. $^{19}$F NMR of the 7d (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 170. $^{31}$P NMR of the 7d (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 171. $^1$H NMR of the $7e$ (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 172. $^{13}$C NMR of the $7e$ (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 173. $^{19}$F NMR of the 7e (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 174. $^{31}$P NMR of the 7e (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 175. $^1$H NMR of the 7f (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 176. $^{13}$C NMR of the 7f (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 177. $^{19}$F NMR of the 7f (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 178. $^{31}$P NMR of the 7f (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 179. $^1$H NMR of the 7g (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 180. $^{13}$C NMR of the 7g (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 181. $^{19}$F NMR of the 7g (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 182. $^{31}$P NMR of the 7g (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 183. $^1$H NMR of the 7h (400 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 184. $^{19}$F NMR of the 7h (376 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 185. $^{13}$C NMR of the 7h (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 186. $^1$H NMR of the 7i (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 187. $^{13}$C NMR of the 7i (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 188. $^{19}$F NMR of the 7i (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 189. $^{31}$P NMR of the 7i (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 190. $^1$H NMR of the 7j (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 191. $^{13}$C NMR of the 7j (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 192. $^{19}$F NMR of the 7j (376 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 193. $^{31}$P NMR of the 7j (162 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 194. $^1$H NMR of the 7k (376 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 195. $^{13}$C NMR of the 7k (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 196. $^{19}$F NMR of the 7k (376 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 197. $^{31}$P NMR of the 7k (162 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 198. $^1$H NMR of the 7l (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 199. $^{13}$C NMR of the 7l (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 200. $^{19}$F NMR of the 7I (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 201. $^{31}$P NMR of the 7I (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 202. $^1$H NMR of the 7m (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 203. $^{13}$C NMR of the 7m (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 204. $^{19}$F NMR of the 7m (376 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 205. $^{31}$P NMR of the 7m (162 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 206. $^1$H NMR of the 7n (400 MHz, 25 °C in CDCl₃)

Supplementary Figure 207. $^{13}$C NMR of the 7n (101 MHz, 25 °C in CDCl₃)
Supplementary Figure 208. $^{19}$F NMR of the 7n (376 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 209. $^{31}$P NMR of the 7n (162 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 210. $^1$H NMR of the 7\textsubscript{o} (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 211. $^{13}$C NMR of the 7\textsubscript{o} (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 212. $^{19}$F NMR of the 7o (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 213. $^{31}$P NMR of the 7o (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 214. $^1$H NMR of the 7p (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 215. $^{13}$C NMR of the 7p (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 216. $^{19}$F NMR of the 7p (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 217. $^{31}$P NMR of the 7p (162 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 218. $^1$H NMR of the 7q (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 219. $^{13}$C-NMR of the 7q (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 220. $^{19}$F-NMR of the 7q ($376$ MHz, $25\,^{\circ}\mathrm{C}$ in CDCl$_3$)

Supplementary Figure 221. $^{31}$P-NMR of the 7q ($162$ MHz, $25\,^{\circ}\mathrm{C}$ in CDCl$_3$)
Supplementary Figure 222. $^1$H NMR of the 9a (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 223. $^{13}$C NMR of the 9a (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 224. $^{31}$P NMR of the 9a (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 225. $^{19}$F NMR of the 9a (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 226. $^1$H NMR of the 9b (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 227. $^{13}$C NMR of the 9b (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 228. $^{31}$P NMR of the 9b (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 229. $^{19}$F NMR of the 9b (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 230. $^1$H NMR of the 9c (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 231. $^{13}$C NMR of the 9c (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 232. $^{31}$P NMR of the 9c (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 233. $^{19}$F NMR of the 9c (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 234. $^1$H NMR of the 9d (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 235. $^{13}$C NMR of the 9d (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 236. $^{31}$P NMR of the 9d (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 237. $^{19}$F NMR of the 9d (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 238. $^1$H NMR of the 9e (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 239. $^{13}$C NMR of the 9e (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 240. $^{31}$P NMR of the 9e (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 241. $^{19}$F NMR of the 9e (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 242. $^1$H NMR of the 9f (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 243. $^{13}$C NMR of the 9f (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 244. $^{31}$P NMR of the 9f (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 245. $^{19}$F NMR of the 9f (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 246. $^1$H NMR of the 10a (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 247. $^{13}$C NMR of the 10a (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 248. $^{31}$P NMR of the 10a (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 249. $^{19}$F NMR of the 10a (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 250. NOE spectra of the 10a (25 °C in Acetone-$d_6$)

Supplementary Figure 251. NOE spectra of the 10a (25 °C in Acetone-$d_6$)
Supplementary Figure 252. $^1$H NMR of the 10b (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 253. $^{13}$C NMR of the 10b (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 254. $^{31}$P NMR of the 10b (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 255. $^{19}$F NMR of the 10b (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 256. $^1$H NMR of the 10c (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 257. $^{13}$C NMR of the 10c (101 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 258. $^{31}$P NMR of the 10c (162 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 259. $^{19}$F NMR of the 10c (376 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 260. $^1$H NMR of the 11a (400 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 261. $^{13}$C NMR of the 11a (101 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 262. $^1$H NMR of the 11b (400 MHz, 25 °C in CDCl₃)

Supplementary Figure 263. $^{13}$C NMR of the 11b (101 MHz, 25 °C in CDCl₃)
**Supplementary Figure 264.** $^1$H NMR of the 11c (400 MHz, 25 °C in CDCl₃)

**Supplementary Figure 265.** $^{13}$C NMR of the 11c (101 MHz, 25 °C in CDCl₃)
**Supplementary Figure 266.** $^1$H NMR of the 12 (400 MHz, 25 °C in Acetone-$d_6$)

**major: Z isomer**

- $5.77$ (dt, $J = 8.9$, 1.8 Hz, $1H^a$)
- $3.43$ (d, $J = 1.8$ Hz, $2H^b$)

$J_{H^a-H^c} = 8.9$ Hz
$J_{H^b-H^a} = 1.8$ Hz

**minor: E isomer**

- $5.47$ (d, $J = 10.2$ Hz Hz, 0.16*$1H^a$)
- $3.20$ (s, 0.32*$2H^b$)

$J_{H^a-H^c} = 10.2$ Hz
$J_{H^b-H^a}$ not detected
Supplementary Figure 267. $^{13}$C NMR of the 12 (101 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 268. $^1$H NMR of the 13 (400 MHz, 25 °C in Acetonitrile-$d_3$)
Supplementary Figure 269. $^{13}$C NMR of the 13 (101 MHz, 25 °C in Acetonitrile-$d_3$)

Supplementary Figure 270. $^1$H-$^{13}$C HSQC of the 13 (101 MHz, 25 °C in Acetonitrile-$d_3$)
Supplementary Figure 271. $^1$H NMR of the 14a (400 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 272. $^{13}$C NMR of the 14a (400 MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 273. $^{19}$F NMR of the 14a (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 274. $^{31}$P NMR of the 14a (162MHz, 25 °C in Acetone-$d_6$)
**Supplementary Figure 275.** \(^1\)H NMR of the 14b (400 MHz, 25 °C in Acetone-\(d_6\))

**Supplementary Figure 276.** \(^{13}\)C NMR of the 14b (400 MHz, 25 °C in Acetone-\(d_6\))
Supplementary Figure 277. $^{19}$F NMR of the 14b (376 MHz, 25 °C in Acetone-$d_6$)

Supplementary Figure 278. $^{31}$P NMR of the 14b (162MHz, 25 °C in Acetone-$d_6$)
Supplementary Figure 279. $^1$H NMR of the 15 (400 MHz, 25 °C in CDCl₃)

Supplementary Figure 280. $^{13}$C NMR of the 15 (101 MHz, 25 °C in CDCl₃)
Supplementary Figure 281. $^1$H NMR of the 16 (400 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 282. $^{13}$C NMR of the 16 (101 MHz, 25 °C in CD$_3$CN)
Supplementary Figure 283. $^{19}$F NMR of the 16 (376 MHz, 25 °C in CD$_3$CN)

Supplementary Figure 284. $^1$H NMR of the 17 (400 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 285. $^{13}$C NMR of the 17 (101 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 286. $^1$H NMR of the 18 (400 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 287. $^{13}$C NMR of the 18 (101 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 288. $^1$H NMR of the 19 (400 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 289. $^{13}$C NMR of the 19 (101 MHz, 25 °C in CDCl$_3$)

Supplementary Figure 290. $^1$H NMR of the 20 (400 MHz, 25 °C in CDCl$_3$)
Supplementary Figure 291. $^{13}$C NMR of the 20 (101 MHz, 25 °C in CDCl$_3$)
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