Visible-light mediated 3-Component Synthesis of Sulfonylated Coumarins from Sulfur Dioxide

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1. General Information

Reactions

Unless otherwise mentioned, all reactions were carried out under an argon atmosphere in flame dried glassware applying standard Schlenk techniques. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by $^1$H-NMR. Irradiation experiments were performed using commercially available High Power 10 W LED (white 9000-15000K from AVONEC®, maximum $\lambda_{\text{em}} = 458$ nm).¹ For each irradiation reaction the light source was placed ≈ 1-2 cm away from the reaction vessels. A custom-made photoreactor box with an incorporated magnetic stirrer was used with 3 interchangeable heat sinks with mounted LEDs arranged around the reactions vessels (Figure SI1). The temperature inside the box was maintained below 30 °C (internal reaction temperature ≤ 30 °C) with an integrated fan. Experiments under sunlight were performed in an open-air lab.

![Figure S1: Pictures of the custom-made photoreactor box used for reaction performed under visible-light irradiation. Reproduced with permission from Adv. Synth. Catal. 2017, 359, 1308-1319. Copyright 2017 Wiley-VCH.](image)

Chromatography

Column chromatography was performed with Silica 60 (0.04-0.063 mm, 230-400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO$_2$ (TLC silica gel 60 F254). The spots were visualized by ultraviolet light.

Solvents

Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. All anhydrous solvents were purchased from...
commercial suppliers and stored over MS 4Å under an atmosphere of argon. Solvents for column chromatography were technical standard.

Materials.

All starting materials, which were obtained from commercial sources, were used without further purification. SO₂ (sulfur dioxide 3.8) was used directly without further purification. **SO₂ is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution!** 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) was synthesized according to a literature reports either from 1,4-diazabicyclo[2.2.2]octane and sulfur dioxide gas⁷ or from 1,4-diazabicyclo[2.2.2]octane and Karl Fisher solution A.⁸ Commercially available diphenyliodonium salts were purchased. Following diaryliodonium salts were synthesized according to literature: diphenyliodonium tetrafluoroborate,⁴ bis(p-chlorophenyl)iodonium triflate,⁵ bis(2,5-dimethylphenyl)iodonium triflate,⁵ dimesityliodonium triflate,⁵ diphenyliodonium triflate (1a),⁵ mesitylphenyliodonium triflate (4a),⁵ (4-methoxyphenyl)phenyliodonium triflate(4b),⁶ (2,4,6-trimethoxyphenyl)phenyliodonium tosylate (4d),⁷ bis(p-methoxyphenyl) toslylate⁸ and bis(p-tolyl)iodonium triflate.⁵

Diphenyliodonium tosylat was prepared from salt exchange with a sat. aq. NaOTs from diphenyliodonium triflate (1a).⁵ For the synthesis of (2-(2-propenyloxy)phenyl)(2,4,6-trimethylphenyl)iodonium tosylate (4f) instead of a sat. aq. solution of NaBF₄ a sat. aq. solution of NaOTs was used.⁹ (3-trifluoromethylphenyl)(2,4,6-trimethoxyphenyl)iodonium triflate (4e) was synthesized by adapting the literature procedure of Stuart et al.⁷ (2,4-Dimethoxyphenyl)phenyliodonium triflate (4c) was synthesized by adapting the literature protocols.⁶

Propynoates were synthesized by adapting literature procedure.¹⁰ (3-Phenoxy-1-propyn-1-yl)benzene was synthesized by using a different procedure.¹¹

**Analytical Data and Instrumentation**

**NMR spectroscopy**

Proton nuclear magnetic resonance spectra (¹H NMR), carbon spectra (¹³C NMR) and fluorine spectra (¹⁹F) were recorded at 250.13, 500.18 and 600.31 MHz (¹H), 75.44, 125.77 and 150.95 MHz (¹³C), 282.31 and 470.64 (¹⁹F), respectively. Chemical shifts are reported as δ - values relative to the residual CDCl₃ (δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C). Coupling constants (J) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q =
quintet; sextet = sextet; m = multiplet; dd = doublet of doublets, td = triplets of doublets; ddd = doublets of doublets of doublets and ddt = doublet of doublets of triplets.

**Melting points**

Melting points are reported uncorrected. The solvent given in brackets after the melting points is the last solvent the compound was treated with (e.g. for transfer of the compound into a smaller flask).

**Mass spectrometry**

Mass spectra (MS) were measured using electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) were measured using matrix-assisted laser desorption/ionization (MALDI) techniques.

**UV-Vis spectroscopy**

UV-Vis Spectra were recorded at 20 °C.

**Infrared spectroscopy.**

Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm⁻¹) and classified in weak (w), medium (m) and strong (s).

**Crystal structure determination**

Data were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoKα radiation (λ = 0.71073 Å) and were scaled using the frame scaling procedure in the X-AREA program system.

The structures were solved by direct methods using the program SHELXS and refined against F² with full-matrix least-squares techniques using the program SHELXL.

The absolute structure for both structures was determined by refinement of the Flack parameter, 0.08(6) for ma108 (7e) and -0.05(14) for ma109 (7d).

CCDC files 1578047 and 1578048 contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
2. General procedures

TP1: Typical Procedure for visible-light induced sulfone synthesis from diaryliodonium salts, DABSO and aryl propynoate.

A 10-mL tube was charged with a magnetic stirring bar, propynoate (0.3 mmol, 1 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diaryliodonium salt (0.36 mmol, 1.2 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. After the completion of the reaction, the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel (n-hexane/EtOAc) to afford the analytically pure product.
3. **Experimental procedures and Analytical Data**

4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (3a)

![Chemical Structure of 3a]

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (94 mg, 87%).

Analytical data are consistent with the literature.\(^{12}\)

R\(_f\) = 0.6 (n-hexane/EtOAc 7:3)

**m.p.** = 189-191 °C (DCM)

\(^1\)H NMR (250.13 MHz, CDCl\(_3\)) \(\delta\) 8.05–7.98 (m, 2H), 7.68–7.56 (m, 3H), 7.55–7.46 (m, 1H), 7.40–7.31 (m, 2H), 7.23–7.15 (m, 1H), 7.03 (dd, \(J = 8.0, 1.5\) Hz, 1H) ppm.

\(^{13}\)C NMR (75.44 MHz, CDCl\(_3\)) \(\delta\) 159.7, 155.7, 154.0, 140.4, 134.8, 133.8, 132.7, 130.1, 129.4, 129.3, 128.8, 128.3, 127.6, 126.1, 125.0, 120.4, 116.9 ppm.

MS (ESI): m/z calcd. for C\(_{21}\)H\(_{15}\)O\(_4\)S\(_1\) [M+H]\(^+\) = 363.07; found: 363.07.

4-phenyl-3-tosyl-2H-chromen-2-one (3b)

![Chemical Structure of 3b]

Prepared from di(\(p\)-tolyl)iodonium triflate (166 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a light white solid (100 mg, 89%).

Analytical data are consistent with the literature.\(^{12}\)

R\(_f\) = 0.6 (n-hexane/EtOAc 7:3)

**m.p.** = 162-165 °C (decomp., DCM)

\(^1\)H NMR (250.13 MHz, CDCl\(_3\)) \(\delta\) 7.93–7.84 (m, 2H), 7.65–7.53 (m, 4H), 7.39–7.27 (m, 5H), 7.22–7.14 (m, 1H), 7.01 (dd, \(J = 8.1, 1.4\) Hz, 1H), 2.41 (s, 3H) ppm.
$^{13}$C NMR (75.44 MHz, CDCl$_3$) $\delta$ 159.3, 155.7, 154.0, 144.9, 137.4, 134.7, 132.8, 130.1, 129.4, 129.4, 129.4, 128.3, 127.6, 126.4, 124.9, 120.4, 116.9, 21.8 ppm.

**MS (ESI):** m/z calcd. for C$_{22}$H$_{17}$O$_5$S$_1$ [M+H]$^+$ = 377.08; found: 377.02.

3-((4-methoxyphenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3c)

![Chemical structure]

Prepared from di($p$-methoxyphenyl)iodonium triflate (184 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a light white solid (107 mg, 91%).

$R_f$ = 0.4 (n-hexane/EtOAc 7:3)

m.p. = 197-198 °C (decomp., DCM)

$^1$H NMR (250.13 MHz, CDCl$_3$) $\delta$ 8.00–7.89 (m, 2H), 7.67–7.53 (m, 4H), 7.40–7.30 (m, 3H), 7.24–7.13 (m, 2H), 7.04–6.89 (m, 3H), 3.86 (s, 3H) ppm.

$^{13}$C NMR (75.44 MHz, CDCl$_3$) $\delta$ 164.0, 158.8, 155.8, 153.9, 153.9, 153.9, 134.6, 132.9, 131.8, 131.8, 130.0, 129.3, 128.3, 127.6, 126.6, 124.9, 120.5, 116.9, 114.0, 55.8 ppm.

**MS (ESI):** m/z calcd. for C$_{22}$H$_{17}$O$_5$S$_1$ [M+H]$^+$ = 393.08; found: 393.01.

**HRMS: m/z calcd. for C$_{22}$H$_{17}$O$_5$S$_1$ [M+H]$^+$ = 393.07912; found: 393.07877.

**IR (cm$^{-1}$)** 1744 (s), 1602 (w), 1322 (s), 1260 (s), 1019 (m), 830 (s), 802 (s), 701 (s), 556 (s), 542 (s).

3-((4-fluorophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3d)

![Chemical structure]

Prepared from di($p$-fluorophenyl)iodonium triflate (168 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (86 mg, 76%).

Analytical data are consistent with the literature.$^{12}$

$R_f$ = 0.5 (n-hexane/EtOAc 7:3)

m.p. = 164-165 °C (DCM)
$^1$H NMR (250.13 MHz, CDCl$_3$) δ 8.09–7.96 (m, 2H), 7.69 – 7.53 (m, 4H), 7.40–7.29 (m, 3H), 7.24–7.11 (m, 3H), 7.03 (dd, $J = 8.3$, 1.5 Hz, 1H) ppm.

$^{13}$C NMR (125.77 MHz, CDCl$_3$) δ 166.0 (d, $J = 256.5$ Hz), 164.3, 159.8, 155.7, 154.0, 136.3 (d, $J = 3.1$ Hz), 135.0, 132.6, 132.4 (d, $J = 9.7$ Hz), 130.1, 129.5, 128.4, 127.6, 126.0, 125.1, 120.3, 117.0, 116.2, 115.9 ppm.

$^{19}$F NMR (282.31 MHz, CDCl$_3$) δ -103.4 ppm.

MS (ESI): m/z calcd. for C$_{21}$H$_{14}$F$_{1}$O$_{4}$S$_{1}$ [M+H]$^+$ = 381.06; found: 380.84.

3-((4-chlorophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3e)

![3-((4-chlorophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one](image)

Prepared from di(p-chlorophenyl)iodonium triflate (180 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (100 mg, 84%).

Analytical data are consistent with the literature.$^{12}$

$R_f = 0.6$ (n-hexane/EtOAc 7:3)

m.p. = 195-196 °C (DCM)

$^1$H NMR (250.13 MHz, CDCl$_3$) δ 7.98–7.90 (m, 2H), 7.67–7.55 (m, 4H), 7.50–7.43 (m, 2H), 7.38 – 7.30 (m, 2H), 7.24–7.17 (m, 1H), 7.04 (dd, $J = 8.1$, 1.6 Hz, 1H) ppm.

$^{13}$C NMR (75.44 MHz, CDCl$_3$) δ 160.0, 155.7, 154.1, 140.6, 138.8, 135.0, 132.5, 130.9, 130.2, 129.6, 129.1, 128.4, 127.6, 125.8, 125.1, 120.3, 117.0 ppm.

MS (ESI): m/z calcd. for C$_{21}$H$_{14}$Cl$_{1}$O$_{4}$S$_{1}$ [M+H]$^+$ = 397.03; found: 396.94.

3-((4-bromophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3f)

![3-((4-bromophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one](image)
Prepared from di(\(p\)-bromophenyl)iodonium triflate (212 mg, 0.360 mmol, 1.2 equiv.) and phenyl phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (98 mg, 75%).

Analytical data are consistent with the literature.\textsuperscript{12}

\(R_f = 0.5\) (n-hexane/EtOAc 7:3)

\textbf{m.p.} = 188-190 °C (DCM)

\(\textsuperscript{1}H\text{ NMR}\) (250.13 MHz, CDCl\(_3\)) \(\delta\) 7.92–7.80 (m, 2H), 7.69–7.53 (m, 6H), 7.39–7.31 (m, 3H), 7.24–7.16 (m, 1H), 7.04 (dd, \(J = 8.0, 1.5\) Hz, 1H) ppm.

\(\textsuperscript{13}C\text{ NMR}\) (75.44 MHz, CDCl\(_3\)) \(\delta\) 160.0, 155.7, 154.1, 139.3, 135.1, 132.5, 132.1, 131.9, 130.1, 129.6, 129.3, 128.4, 127.6, 125.7, 125.1, 120.3, 117.0 ppm.

\textbf{MS (ESI)}: m/z calcd. for C\(_{21}\)H\(_{14}\)BrO\(_4\)S\(_1\) [M+H]\(^+\) = 442.98; found: 442.77.

\(3-((2,5\text{-dimethylphenyl})\text{sulfonyl})-4\text{-phenyl}-2H\text{-chromen-2-one (3g)}\)

Prepared from di(2,4-dimethylphenyl)iodonium triflate (166 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (77 mg, 66%).

\(R_f = 0.5\) (n-hexane/EtOAc 7:3)

\textbf{m.p.} = 209-210 °C (DCM)

\(\textsuperscript{1}H\text{ NMR}\) (250.13 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 1.3\) Hz, 1H), 7.68–7.58 (m, 1H), 7.57–7.49 (m, 3H), 7.42–7.32 (m, 3H), 7.25–7.17 (m, 2H), 7.10 (dd, \(J = 8.4, 1.6\) Hz, 1H), 7.06 (d, \(J = 7.8\) Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H) ppm.

\(\textsuperscript{13}C\text{ NMR}\) (75.44 MHz, CDCl\(_3\)) \(\delta\) 159.2, 155.5, 154.1, 138.5, 136.1, 134.6, 134.3, 134.2, 132.1, 131.2, 129.8, 129.6, 128.3, 128.3, 126.2, 125.0, 120.2, 117.1, 21.0, 19.7 ppm.

\textbf{MS (ESI)}: m/z calcd. for C\(_{23}\)H\(_{19}\)O\(_4\)S\(_1\) [M+H]\(^+\) = 391.10; found: 390.90.

\textbf{HRMS}: m/z calcd. for C\(_{23}\)H\(_{19}\)O\(_4\)S\(_1\) [M+H]\(^+\) = 391.09986; found: 391.09945.

\textbf{IR (cm\(^{-1}\))}: 2911 (w), 1723 (m), 1603 (m), 1313 (m), 1155 (m), 757 (s), 697 (s), 596 (s), 572 (s), 519 (s).
3-(mesitylsulfonyl)-4-phenyl-2H-chromen-2-one (3h)

Prepared from dimesitylodionium trflate (171 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (40 mg, 33%).

R_f = 0.5 (n-hexane/EtOAc 7:3)

m.p. = 234-235°C (DCM)

^1H NMR (250.13 MHz, CDCl_3) δ 7.67–7.52 (m, 4H), 7.42–7.32 (m, 3H), 7.26–7.12 (m, 2H), 6.88 (s, 2H), 2.59 (s, 6H), 2.26 (s, 3H) ppm.

^13C NMR (75.44 MHz, CDCl_3) δ 157.6, 157.1, 155.9, 154.0, 143.1, 140.0, 135.0, 134.3, 132.1, 132.0, 129.7, 129.7, 128.4, 128.5, 127.2, 125.0, 120.1, 117.1, 22.3, 21.2 ppm.

MS (ESI): m/z calcd. for C_{24}H_{21}O_4S [M+H]^+ = 403.12; found: 404.90.

HRMS: m/z calcd. for C_{24}H_{21}O_4S [M+H]^+ = 403.11551; found: 403.11504.

IR (cm^{-1}) 2982 (w), 1729 (s), 1321 (s), 1151 (s), 991 (m), 757 (s), 669 (s), 640 (s), 597 (s), 513 (s).

3-(Phenylsulfonyl)-4-p-tolyl-2H-chromen-2-one (3l)

Prepared from diphenyldiononium trflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-(p-tolyl)propynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (108 mg, 96%).

Analytical data are inconsistent with the literature.^13

R_f = 0.4 (n-hexane/EtOAc 7:3)

m.p. = 202-203 °C (DCM)

^1H NMR (250.13 MHz, CDCl_3) δ 8.05–7.97 (m, 2H), 7.65–7.56 (m, 2H), 7.54–7.45 (m, 2H), 7.42–7.30 (m, 3H), 7.26–7.15 (m, 3H), 7.08 (dd, J = 8.1, 1.6 Hz, 1H), 2.50 (s, 3H) ppm.
$^{13}$C NMR (75.44 MHz, CDCl$_3$) $\delta$ 160.1, 155.8, 154.0, 140.5, 139.5, 134.7, 133.8, 130.2, 129.7, 129.3, 129.1, 128.7, 127.6, 126.1, 124.9, 120.5, 116.9, 21.7 ppm.

**MS (ESI):** m/z calcld. for C$_{22}$H$_{17}$O$_4$S$_1$ [M+H]$^+$ = 377.08; found: 376.86.

### 3-(phenylsulfonyl)-4-(thiophen-2-yl)-2H-chromen-2-one (3m)

![Chemical Structure](image)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-(thiophen-2-yl)propynoate (69 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (26 mg, 24%).

$R_f$ = 0.4 (n-hexane/EtOAc 7:3)

**m.p.** = 186-188 °C (DCM)

$^1$H NMR (600.31 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J$ = 7.8 Hz, 2H), 7.69 (d, $J$ = 4.8 Hz, 1H), 7.65–7.58 (m, 2H), 7.51 (t, $J$ = 7.8 Hz, 2H), 7.33 (d, $J$ = 8.4 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.29 – 7.21 (m, 3H) ppm.

$^{13}$C NMR (150.95 MHz, CDCl$_3$) $\delta$ 155.4, 153.7, 153.4, 140.3, 135.0, 133.9, 130.9, 129.8, 129.7, 129.4, 128.8, 128.4, 127.4, 125.2, 120.7, 116.9 ppm.

**MS (ESI):** m/z calcld. for C$_{19}$H$_{12}$O$_4$S$_2$ [M+H]$^+$ = 369.03; found: 368.81.

**HRMS:** m/z calcld. for C$_{19}$H$_{12}$O$_4$S$_2$ [M+H]$^+$ = 369.02498; found: 369.02515.

**IR (cm$^{-1}$)** 2982 (w), 1739 (s), 1307 (m), 1159 (s), 738 (m), 708 (s), 682 (s), 634 (s), 608 (s), 562 (s).

### 4-ethyl-3-(phenylsulfonyl)-2H-chromen-2-one (3n)

![Chemical Structure](image)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl pent-2-ynoate (52 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (36 mg, 38%).

$R_f$ = 0.5 (n-hexane/EtOAc 7:3)

**m.p.** = 151-152 °C (DCM)
1H NMR (250.13 MHz, CDCl₃) δ 8.14–8.05 (m, 1H), 7.90 (dd, J = 8.3, 1.5 Hz, 1H), 7.67–7.57 (m, 1H), 7.56–7.47 (m, 1H), 7.43–7.35 (m, 1H), 7.29 (dd, J = 8.3, 1.0 Hz, 1H), 3.69 (q, J = 7.5 Hz, 2H), 1.53 (t, J = 7.5 Hz, 3H) ppm.

13C NMR (75.44 MHz, CDCl₃) δ 163.9, 155.6, 154.0, 141.0, 134.6, 133.7, 128.8, 128.8, 126.7, 125.5, 125.2, 118.5, 117.6, 21.6, 15.6 ppm.

MS (ESI): m/z calcd. for C₁₇H₁₅O₄S₁ [M+H]^+ = 315.07; found: 315.08.

HRMS: m/z calcd. for C₁₇H₁₅O₄S₁ [M+H]^+ = 315.06856; found: 315.06848.

IR (cm⁻¹) 2979 (w), 1733 (m), 1598 (m), 1544 (m), 1308 (m), 1151 (m), 759 (s), 631 (s), 563 (s), 541 (s).

4-Propyl-3-(phenylsulfonyl)-2H-chromen-2-one (3o)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl hexyl-2-ynoate (56 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (38 mg, 39%).

Rᵢ = 0.5 (n-hexane/EtOAc 7:3)

m.p. = 118-120 °C (DCM)

1H NMR (250.13 MHz, CDCl₃) δ 8.13–8.03 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.70–7.46 (m, 4H), 7.42–7.34 (m, 1H), 7.32–7.22 (m, 1H), 3.75–3.41 (m, 2H), 1.89 (sextet, J = 7.3 Hz, 1H), 1.23 (t, J = 7.4 Hz, 2H) ppm.

13C NMR (75.44 MHz, CDCl₃) δ 162.6, 155.6, 153.9, 141.1, 134.6, 133.7, 128.8, 126.7, 125.6, 125.2, 118.9, 117.6, 30.0, 25.2, 14.9 ppm.

MS (ESI): m/z calcd. for C₁₈H₁₇O₂S₁ [M+H]^+ = 329.08; found: 329.09.

HRMS: m/z calcd. for C₁₈H₁₇O₂S₁ [M+H]^+ = 329.08421; found: 329.08428.

IR (cm⁻¹) 2965 (w), 1718 (s), 1534 (s), 1319 (m), 1157 (s), 716 (s), 628 (s), 567 (s), 550 (s), 539 (s).
4-phenyl-3-(phenylsulfonyl)-2H-chromene (3p)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (62 mg, 0.30 mmol, 1.0 equiv.) and isolated as a colourless oil (12 mg, 11%).

Analytical data are consistent with the literature.\(^\text{13}\)

\(R_f = 0.7\) (n-hexane/EtOAc 7:3)

\(^1\text{H NMR}\) (250.13 MHz, CDCl\(_3\)) \(\delta\) 7.53–7.44 (m, 3H), 7.42–7.29 (m, 5H), 7.28–7.20 (m, 2H), 7.06–6.97 (m, 2H), 6.92 (dd, \(J\) = 8.1, 1.1 Hz, 1H), 6.80 (td, \(J\) = 7.6, 1.1 Hz, 1H), 6.61 (dd, \(J\) = 7.8, 1.5 Hz, 1H), 5.22 (s, 2H) ppm.

\(^{13}\text{C NMR}\) (75.44 MHz, CDCl\(_3\)) \(\delta\) 155.0, 145.5, 141.5, 133.4, 133.2, 132.6, 129.8, 129.1, 128.9, 128.8, 128.6, 128.5, 128.0, 127.6, 124.3, 122.1, 116.4, 64.4 ppm.

\(\text{MS (ESI)}\): m/z calcd. for \(C_{21}H_{17}O_3S\) [M+Na]\(^+\) = 371.07; found: 371.02.

7-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7a)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-tolyl 3-phenylpropynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (101 mg, 90%).

Analytical data are inconsistent with the literature.\(^\text{13}\)

\(R_f = 0.4\) (n-hexane/EtOAc 7:3)

\(\text{m.p.} = 219\text{-}220 ^\circ\text{C (DCM)}\)

\(^1\text{H NMR}\) (250.13 MHz, CDCl\(_3\)) \(\delta\) 8.05–7.96 (m, 2H), 7.64–7.54 (m, 4H), 7.49 (ddd, \(J\) = 8.5, 2.6, 1.1 Hz, 2H), 7.38–7.29 (m, 2H), 7.14 (s, 1H), 6.99 (ddd, \(J\) = 8.4, 1.6, 0.5 Hz, 1H), 6.89 (d, \(J\) = 8.3 Hz, 1H), 2.44 (s, 3H) ppm.

\(^{13}\text{C NMR}\) (75.44 MHz, CDCl\(_3\)) \(\delta\) 159.8, 156.0, 154.2, 147.0, 140.6, 133.7, 132.1, 129.8, 129.3, 129.3, 128.7, 128.3, 127.6, 126.3, 124.8, 118.0, 117.0, 22.0 ppm.
**MS (ESI):** m/z calcd. for C\textsubscript{22}H\textsubscript{17}O\textsubscript{5}S_1 [M+H]^+ = 377.08; found: 376.88.

**7- methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7b)**

![Chemical structure of 7b](image)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-anisyl 3-phenylpropynoate (76 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (40 mg, 34%).

Analytical data are consistent with the literature.\textsuperscript{13}

R<sub>f</sub> = 0.3 (n-hexane/EtOAc 7:3)

m.p. = 210-212 °C (DCM)

\textsuperscript{1}H NMR (250.13 MHz, CDCl\textsubscript{3}) δ 8.05–7.96 (m, 2H), 7.63–7.53 (m, 4H), 7.53–7.44 (m, 2H), 7.37–7.28 (m, 2H), 6.91 (d, J = 9.0 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 6.73 (dd, J = 9.0, 2.5 Hz, 1H), 3.87 (s, 1H) ppm.

\textsuperscript{13}C NMR (75.44 MHz, CDCl\textsubscript{3}) δ 165.4, 159.9, 156.3, 156.2, 140.8, 133.6, 133.1, 131.4, 129.3, 129.2, 128.7, 128.2, 127.6, 122.5, 113.8, 113.7, 100.4, 56.2 ppm.

**MS (ESI):** m/z calcd. for C\textsubscript{22}H\textsubscript{17}O\textsubscript{5}S_1 [M+H]^+ = 393.08; found: 392.87.

**7-bromo-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7c)**

![Chemical structure of 7c](image)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-bromophenyl 3-phenylpropynoate (90 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (97 mg, 74%).

R<sub>f</sub> = 0.7 (n-hexane/EtOAc 7:3)

m.p. = 239-240 °C (DCM)

\textsuperscript{1}H NMR (250.13 MHz, CDCl\textsubscript{3}) δ 8.03–7.94 (m, 2H), 7.65–7.56 (m, 4H), 7.55–7.47 (m, 3H), 7.37–7.28 (m, 3H), 6.87 (d, J = 8.5 Hz, 1H) ppm.

\textsuperscript{13}C NMR (75.44 MHz, CDCl\textsubscript{3}) δ 159.0, 155.1, 154.0, 140.1, 134.0, 132.3, 131.0, 129.7, 129.5, 129.3, 128.8, 128.6, 128.5, 127.5, 126.2, 120.2, 119.4 ppm.

**MS (ESI):** m/z calcd. for C\textsubscript{21}H\textsubscript{14}Br\textsubscript{1}O\textsubscript{4}S_1 [M+H]^+ = 442.98; found: 442.78.
HRMS: m/z calcd. for C_{21}H_{14}Br_{1}O_{4}S_{1} [M+H]^+ = 440.97907; found: 440.97877.

IR (cm^{-1}) 1735 (w), 1583 (w), 1170 (w), 777 (m), 688 (s), 607 (s), 556 (s).

7-chloro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7d)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-chlorophenyl 3-phenylpropynoate (77 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (63 mg, 53%).

R_f = 0.7 (n-hexane/EtOAc 7:3)

m.p. = 235-236 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl_3) δ 8.03–7.95 (m, 2H), 7.66–7.56 (m, 4H), 7.55–7.45 (m, 2H), 7.38–7.29 (m, 3H), 7.16 (dd, J = 8.8, 2.0 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H) ppm.

^{13}C NMR (75.44 MHz, CDCl_3) δ 158.9, 155.2, 154.2, 141.2, 140.2, 133.9, 132.3, 131.0, 129.7, 129.4, 128.8, 128.4, 127.5, 126.0, 125.7, 119.0, 117.2 ppm.

MS (ESI): m/z calcd. for C_{21}H_{14}Cl_{1}O_{4}S_{1} [M+H]^+ = 397.03; found: 396.81.

HRMS: m/z calcd. for C_{21}H_{14}Cl_{1}O_{4}S_{1} [M+H]^+ = 397.02958; found: 397.02918.

IR (cm^{-1}) 2982 (w), 1731 (m), 1320 (m), 1156 (m), 1088 (w), 1005 (m), 683 (s), 575 (s), 551 (s), 512 (s).

6-methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7e)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-anisyl 3-phenylpropynoate (76 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (103 mg, 88%).

R_f = 0.3 (n-hexane/EtOAc 7:3)

m.p. = 217-218 °C (DCM)
\( ^1H \) NMR (250.13 MHz, CDCl\(_3\)) \( \delta \) 8.01–7.93 (m, 2H), 7.60–7.50 (m, 4H), 7.50–7.41 (m, 2H), 7.35–7.28 (m, 1H), 7.22 (s, 1H), 7.15 (dd, \( J = 9.1, 2.9 \) Hz, 1H), 6.37 (d, \( J = 2.8 \) Hz, 1H), 3.58 (s, 2H) ppm.

\( ^{13}C \) NMR (75.44 MHz, CDCl\(_3\)) \( \delta \) 159.4, 156.3, 155.9, 148.6, 140.4, 133.8, 132.8, 129.5, 129.3, 128.8, 128.4, 127.5, 126.3, 122.4, 120.8, 118.0, 112.2, 55.8 ppm.

**MS (ESI):** m/z calcd. for \( C_{22}H_{17}O_5S_1 [M+H]^+ \) = 393.08; found: 392.88.

**HRMS:** m/z calcd. for \( C_{22}H_{17}O_5S_1 [M+H]^+ \) = 393.07912; found: 393.07859.

**IR (cm\(^{-1}\))** 2982 (w), 1723 (m), 1156 (m), 1026 (m), 818 (m), 778 (s), 687 (s), 579 (s), 556 (s), 548 (s).

6-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7f) and 8-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7f‘)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-tolyl 3-phenylpropynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a waxy, low-melting white solid in a 5:1 ratio (96 mg, 86%).

Analytical data are inconsistent with the literature.\(^{13}\)

**R\(_f\) = 0.5 \((n\text{-hexane/EtOAc} 7:3)\)**

\( ^1H \) NMR (250.13 MHz, CDCl\(_3\)) \( \delta \) 8.04–7.97 (m), 7.65–7.53 (m), 7.54–7.46 (m), 7.42 (dd, \( J = 8.5, 2.0 \) Hz), 7.36–7.31 (m), 7.24 (d, \( J = 8.5 \) Hz), 7.08 (t, \( J = 7.8 \) Hz), 6.85 (d, \( J = 8.0 \) Hz), 6.77 (d, \( J = 1.3 \) Hz), 2.43 (s), 2.26 (s) ppm.

\( ^{13}C \) NMR (75.44 MHz, CDCl\(_3\)) \( \delta \) 159.7, 155.9, 152.3, 140.5, 136.1 136.0, 134.9, 133.7, 133.0, 132.8, 129.5, 129.4, 129.3, 128.9, 128.7, 128.7, 128.3, 128.2 127.8, 127.7 127.6 125.9, 124.4, 120.1, 116.7, 21.1, 15.5 ppm.

**MS (ESI):** m/z calcd. for \( C_{22}H_{17}O_5S_1 [M+H]^+ \) = 377.08; found: 376.85.

6-acetyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7g)
Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-acetylphenyl 3-phenylpropynoate (1a, 79 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (43 mg, 30%).

R<sub>f</sub> = 0.3 (n-hexane/EtOAc 7:3)

m.p. = 260-263 °C (DCM)

1<sup>H</sup> NMR (250.13 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, J = 7.3, 2.3 Hz, 1H), 8.01–7.96 (m, 2H), 7.65–7.44 (m, 6H), 7.36–7.29 (m, 2H), 7.25–7.13 (m, 2H) 2.77 (s, 3H) ppm.

13<sup>C</sup> NMR (75.44 MHz, CDCl<sub>3</sub>) δ 196.5, 159.4, 154.5, 152.4, 140.1, 135.7, 134.3, 134.1, 129.7, 129.4, 128.9, 128.5, 127.6, 127.5, 126.3, 124.7, 121.1, 32.2 ppm.

MS (ESI): m/z calcd. for C<sub>23</sub>H<sub>16</sub>O<sub>5</sub>S<sub>1</sub> [M+H]<sup>+</sup> = 405.08; found: 404.86.

HRMS: m/z calcd. for C<sub>23</sub>H<sub>16</sub>O<sub>5</sub>S<sub>1</sub> [M+H]<sup>+</sup> = 405.07912; found: 405.07913.

IR (cm<sup>-1</sup>) 2923 (w), 1735 (s), 1315 (s), 1271 (s), 1153 (s), 717 (s), 689 (s), 634 (s), 561 (s), 552 (s).

8-acetyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7g’)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-acetylphenyl 3-phenylpropynoate (79 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (39 mg, 28%).

R<sub>f</sub> = 0.2 (n-hexane/EtOAc 7:3)

m.p. = 277-280 °C (DCM)

1<sup>H</sup> NMR (250.13 MHz, CDCl<sub>3</sub>) δ 8.19 (dd, J = 8.8, 2.0 Hz, 1H), 8.05–7.97 (m, 2H), 7.66–7.58 (m, 5H), 7.56–7.48 (m, 2H), 7.41 (d, J = 8.5 Hz, 1H), 7.39–7.33 (m, 2H), 2.42 (s, 3H) ppm.

13<sup>C</sup> NMR (75.44 MHz, CDCl<sub>3</sub>) δ 195.5, 159.3, 156.6, 155.0, 140.0, 134.1, 134.0, 133.9, 131.9, 130.8, 129.9, 129.4, 128.9, 128.6, 127.6, 127.0, 120.3, 117.5, 26.4 ppm.

MS (ESI): m/z calcd. for C<sub>23</sub>H<sub>16</sub>O<sub>5</sub>S<sub>1</sub> [M+H]<sup>+</sup> = 405.08; found: 404.89.
HRMS: m/z calcd. for C_{23}H_{16}O_{5}S_{1} [M+H]^+ = 405.07912; found: 405.07930.

IR (cm^{-1}) 1730 (w), 1685 (w), 1151 (m), 782 (w), 714 (w), 690 (w), 593 (m), 566 (s), 549 (s), 453 (w).

8-fluoro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7h) and 6-fluoro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7h’)

Prepared from diphenyliodonium triflate (155 mg, 0.360 mmol, 1.2 equiv.) and 3-fluorophenyl 3-phenylpropynoate (72 mg, 0.30 mmol, 1.0 equiv.) and isolated as an inseparable waxy, low-melting solid in a 7.5:1 ratio (93 mg, 82%).

R_f = 0.4 (n-hexane/EtOAc 7:3)

^{1}H NMR (250.13 MHz, CDCl_3) δ 8.07–7.96 (m), 7.68–7.56 (m), 7.56–7.45 (m), 7.43–7.30 (m), 7.12 (td, J = 8.2, 4.7 Hz), 6.81 (dt, J = 8.3, 1.4 Hz), 6.69 (dt, J = 8.8, 1.7 Hz) ppm.

^{13}C NMR (75.44 MHz, CDCl_3) δ 160.5, 158.7, 158.7, 157.2, 155.4, 150.2, 150.2, 140.1, 134.0, 132.4, 132.2, 129.8, 129.6, 129.4, 128.8, 128.6, 128.4, 127.6, 127.5, 127.1, 125.2, 124.5, 122.6, 122.3, 121.4, 121.3, 118.7, 118.6, 115.5, 115.1 ppm.

^{19}F NMR (470.64 MHz, CDCl_3) δ -115.1, 132.7 ppm.

MS (ESI): m/z calcd. for C_{21}H_{14}F_{1}O_{4}S_{1} [M+H]^+ = 381.06; found: 380.85.

HRMS: m/z calcd. for C_{21}H_{14}F_{1}O_{4}S_{1} [M+H]^+ = 381.05913; found: 381.05850.

IR (cm^{-1}) 3074 (w), 1734 (m), 1311 (m), 1155 (m), 1082 (m), 839 (m), 716 (s), 682 (s), 555 (s), 539 (s).

6,8-dimethyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7i)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and 3,5-dimethylphenyl 3-phenylpropynoate (75 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (110 mg, 94%).

R_f = 0.5 (n-hexane/EtOAc 7:3)
m.p. = 204-205 °C (DCM)

\(^1\)H NMR (250.13 MHz, CDCl₃) \(\delta\) 8.04–7.97 (m, 2H), 7.64–7.45 (m, 6H), 7.38–7.27 (m, 3H), 6.60 (s, 1H), 2.39 (s, 3H), 2.21 (s, 3H) ppm.

\(^{13}\)C NMR (75.44 MHz, CDCl₃) \(\delta\) 160.0, 156.0, 150.7, 140.6, 137.4, 134.2, 133.7, 133.0, 129.3, 129.3, 128.7, 128.2, 127.7, 127.3, 126.2, 125.5, 124.8, 119.9, 21.0, 15.5 ppm.

MS (ESI): m/z calcd. for C\(_{24}\)H\(_{18}\)O\(_4\)S\(_1\) \([\text{M}+\text{H}]^+\) = 391.10; found: 390.99.

HRMS: m/z calcd. for C\(_{24}\)H\(_{18}\)O\(_4\)S\(_1\) \([\text{M}+\text{H}]^+\) = 391.09986; found: 391.09961.

IR (cm\(^{-1}\)) 3066 (w), 1727 (m), 1323 (m), 1152 (m), 779 (s), 701 (m), 646 (m), 599 (m), 571 (s), 552 (s).

4-phenyl-3-(phenylsulfonyl)-2H-benzo[h]chromen-2-one (7)

Prepared from diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.2 equiv.) and naphthalen-2-yl 3-phenylpropynoate (82 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (85 mg, 69%).

R\(_f\) = 0.5 (n-hexane/EtOAc 7:3)

m.p. = 259-260 °C (DCM)

\(^1\)H NMR (250.13 MHz, CDCl₃) \(\delta\) 7.92–7.80 (m, 2H), 7.69–7.53 (m, 6H), 7.38–7.31 (m, 3H), 7.24–7.17 (m, 1H), 7.04 (dd, \(J = 8.0, 1.05\) Hz, 1H) ppm.

\(^{13}\)C NMR (75.44 MHz, CDCl₃) \(\delta\) 160.5, 155.8, 152.4, 140.5, 136.1, 133.8, 133.2, 130.6, 129.4, 129.3, 128.8, 128.4, 127.9, 127.9, 127.6, 125.1, 124.8, 123.7, 123.4, 122.5, 115.5 ppm.

MS (ESI): m/z calcd. for C\(_{25}\)H\(_{17}\)O\(_4\)S\(_1\) \([\text{M}+\text{H}]^+\) = 413.08; found: 412.88.

HRMS: m/z calcd. for C\(_{25}\)H\(_{17}\)O\(_4\)S\(_1\) \([\text{M}+\text{H}]^+\) = 413.08421; found: 413.08404.

IR (cm\(^{-1}\)) 2982 (w), 1735 (m), 1537 (m), 1155 (m), 1142 (m), 766 (s), 689 (m), 592 (s), 560 (s), 518 (s).
4. Selectivity studies

4.1 Selectivity studies with sterically differentiated diaryliodonium salts

Prepared from mesitylphenyliodonium triflate (4a, 142 mg, 0.300 mmol, 1.00 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (2a, 62 mg, 0.30 mmol, 1.0 equiv.). 3a was isolated as a white solid (83 mg, 77%).

Analytical data of 3a are in agreement with the data of 3a prepared from the corresponding symmetrical iodonium salt (see page 5).\textsuperscript{12}

4.2 Selectivity studies with methoxybenzenes

Prepared from (4-methoxyphenyl)phenyliodonium triflate (4b, 166 mg, 0.360 mmol, 1.2 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (2a, 62 mg, 0.30 mmol, 1.0 equiv.). 3a (71 mg, 66%) and 3c (24 mg, 17%) were isolated as white solids.

Analytical data of 3a and 3c are in agreement with the data of 3a and 3c prepared from the corresponding symmetrical iodonium salts (see page 5 and 6) and with the literature.\textsuperscript{12}
Prepared from (2,4-dimethoxyphenyl)phenyliodonium triflate (4c, 147 mg, 0.36 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (2a, 62 mg, 0.30 mmol, 1.0 equiv.). 3a was isolated as white solids (70 mg, 65%).

Analytical data of 3a are in agreement with the data of 3a prepared from the corresponding symmetrical iodonium salt (see page 5) and with the literature.\textsuperscript{12}

Prepared from (2,4-dimethoxyphenyl)phenyliodonium triflate (4d, 195 mg, 0.360 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (2a, 62 mg, 0.30 mmol, 1.0 equiv.). 3a was isolated as white solids (94 mg, 87%).

Analytical data of 3a are in agreement with the data of 3a prepared from the corresponding symmetrical iodonium salt (see page 5) and with the literature.\textsuperscript{12}

4.3 Selectivity studies with electronically differentiated diaryliodonium salts

Prepared from (2,4,6-trimethoxyphenyl)(3-trifluoromethylphenyl)liodonium triflate (4e, 183 mg, 0.300 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (2a, 62 mg, 0.30 mmol, 1.0 equiv.). 3i (95 mg, 74%) and 5 (73 mg, 83%) were isolated as white solids.

Analytical Data of 3i

\textbf{R}_f = 0.3 (n-hexane/EtOAc 7:3)

\textbf{m.p.} = 202-203 °C (DCM)
\(^1\)H NMR (250.13 MHz, CDCl\(_3\)) \(\delta\) 8.29 (d, \(J = 7.8\) Hz, 1H), 8.20 (s, 1H), 7.86 (d, \(J = 7.8\) Hz, 1H), 7.72–7.57 (m, 5H), 7.40–7.31 (m, 3H), 7.22 (t, \(J = 7.8\) Hz, 1H), 7.06 (dd, \(J = 8.0, 1.5\) Hz, 1H) ppm.

\(^{13}\)C NMR (125.77 MHz, CDCl\(_3\)) \(\delta\) 160.6, 155.7, 154.1, 141.5, 135.3, 132.9, 132.3, 131.5 (q, \(J = 33.5\) Hz), 130.5 (q, \(J = 3.5\) Hz), 130.2, 129.7, 129.6, 128.5, 127.5, 125.4, 125.2, 123.3 (q, \(J = 272.9\) Hz), 120.2, 117.1.

\(^{19}\)F NMR (282.31 MHz, CDCl\(_3\)) \(\delta\) -62.8 ppm.

MS (ESI): m/z calcd. for C\(_{22}\)H\(_{13}\)F\(_3\)O\(_4\)S\(_1\) [M+H]\(^+\) = 431.06; found: 430.84.

HRMS: m/z calcd. for C\(_{22}\)H\(_{13}\)F\(_3\)O\(_4\)S\(_1\) [M+H]\(^+\) = 431.05594; found: 431.05549.

IR (cm\(^{-1}\)) 1731 (s), 1345 (s), 1324 (s), 1163 (s), 1130 (s), 762 (s), 692 (s), 647 (s), 569 (s), 538 (s).

Analytical data of 5 are in agreement with literature.\(^{14}\)

\(^1\)H NMR (250.13 MHz, CDCl\(_3\)) \(\delta\) 6.15 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H) ppm.

5. Radical trap experiments

\[ \begin{align*}
\text{OTf}^- & \quad \text{TEMPO (2.0 equiv.)} \\
\text{DABSO, 2a} & \quad \text{white} \\
\text{MeOH, N}_2 \quad \text{r.t., 8h} & \quad \text{MeOH, SO}_3 \text{Ph} \\
\text{MeOH, N}_2 \quad \text{r.t., 8h} & \quad \text{3a, -}
\end{align*} \]

A 10-mL tube was charged with a stirring bar, phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.20 equiv.), TEMPO (94 mg, 0.60 mmol, 2.0 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. Afterwards no formation of product 3a was observed.
A 10-mL tube was charged with a stirring bar, phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diphenyliodonium triflate (1a, 155 mg, 0.360 mmol, 1.20 equiv.), BHT (132 mg, 0.600 mmol, 2.00 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. Afterwards no formation of product 3a was observed.

6. Radical clock experiment

Prepared from (2-allyloxyphenyl)[2,4,6-trimethylphenyl]iodonium tosylium (4f, 198 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (2a, 67 mg, 0.30 mmol, 1.0 equiv.). 7k (88 mg, 70%) and 3h (10 mg, 8%) were isolated as a white solids.

Analytical data of 3h are in agreement with the data of 3h prepared from the symmetrical iodonium salt dimesityliodonium triflate (see page 9).

Analytical data of 7k:

R_f = 0.5 (n-hexane/EtOAc 7:3)

m.p. = 174-175 °C (DCM)

^1H NMR (600.31 MHz, CDCl_3) δ 7.73–7.64 (m, 1H), 7.61–7.51 (m, 3H), 7.44 (dd, J = 8.4, 1.1 Hz, 1H), 7.36–7.13 (m, 5H), 7.09 (dd, J = 8.1, 1.4 Hz, 1H), 6.86 (td, J = 7.4, 0.9 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.65 (t, J = 9.4 Hz, 1H), 4.53–4.40 (m, 1H), 4.17–3.96 (m, 2H), 3.75–3.61 ppm.

^13C NMR (75.44 MHz, CDCl_3) δ 160.9, 159.9, 157.3, 153.9, 135.3, 131.9, 130.1, 129.7, 129.4, 128.4, 128.3, 128.0, 127.4, 126.9, 125.4, 124.6, 121.0, 120.1, 117.2, 110.1, 76.1, 59.6, 36.7 ppm.

MS (ESI): m/z calcd. for C_{24}H_{19}O_5S_1 [M+H]^+ = 419.10; found: 418.99.

HRMS: m/z calcd. for C_{24}H_{19}O_5S_1 [M+H]^+ = 419.09477; found: 419.09455.
IR (cm\(^{-1}\)) 1743 (m), 1482 (m), 1318 (m), 1233 (m), 1130 (m), 750 (s), 738 (m), 725 (m), 590 (m), 508 (s).
7. UV-Vis spectra

The UV-Vis absorption spectra of Ph$_2$IOTf (1a), DABSO and propynoate (2a) (in MeOH, 0.02M) were measured independently. Ph$_2$IOTf (1a) show almost no absorption in the visible region. The propynoate 2a absorbs light below 400 nm but a neglectable absorbance in spectral region of sunlight or the used LEDs. Only DABSO displays a low absorbance of visible-light throughout the whole visible region. In the case of a 1:1 mixture of DABSO and Ph$_2$IOTf (1a) a slight decrease in the absorbance was detected, which could indicate some kind of interaction between those two components. Mixing of two components did not lead to significant changes in the UV/VIS spectra.

Contrary to a previous report by Chatani, no (long-lived) charge-transfer complex could be observed.

![Figure S2: All UV-Vis spectra of Ph$_2$IOTf (1a), DABSO, propynoate (2a) independently and of their corresponding mixtures in MeOH.](image)
**Figure S3:** UV-Vis spectra of Ph$_2$IOTf (1a), DABSO, propynoate (2a) independently in MeOH.

**Figure S4:** UV-Vis spectra of Ph$_2$IOTf (1a), DABSO, propynoate (2a) and of their corresponding mixtures in MeOH.
Figure S5: UV-Vis spectra of Ph$_2$IOTf (1a), DABSO, propynoate (2a) and of their corresponding mixtures in MeOH.

Figure S6: UV-Vis spectra of Ph$_2$IOTf (1a), DABSO, propynoate (2a) and of their corresponding mixtures in MeOH.
8. References

1. For the complete emission-spectra, see: https://www.avonec.de/images/10W-Spektrum/10W_9000k-15000k.jpg; Accessed: March 2018.
9. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F NMR Spectra
## 10. X-ray data

<table>
<thead>
<tr>
<th></th>
<th>7d (ma109)</th>
<th>7e (ma108)</th>
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<tbody>
<tr>
<td><strong>CCDC</strong></td>
<td>1578048</td>
<td>1578047</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{21}H_{13}ClO_{4}S</td>
<td>C_{22}H_{16}O_{5}S</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>396.82</td>
<td>392.41</td>
</tr>
<tr>
<td><strong>Temperature [K]</strong></td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td><strong>Wavelength [Å]</strong></td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>Pna2_{1}</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>12.8859(12)</td>
<td>7.7651(6)</td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>5.6317(3)</td>
<td>16.4066(12)</td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>25.025(2)</td>
<td>14.1404(15)</td>
</tr>
<tr>
<td><strong>α [°]</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β [°]</strong></td>
<td>92.804(8)</td>
<td>90</td>
</tr>
<tr>
<td><strong>γ [°]</strong></td>
<td>90</td>
<td>90</td>
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<tr>
<td><strong>V [Å³]</strong></td>
<td>1813.9(2)</td>
<td>1801.5(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>D_{calc} [Mg/m³]</strong></td>
<td>1.453</td>
<td>1.447</td>
</tr>
<tr>
<td><strong>µ [mm⁻¹]</strong></td>
<td>0.351</td>
<td>0.213</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>816</td>
<td>816</td>
</tr>
<tr>
<td><strong>Crystal size [mm³]</strong></td>
<td>0.210 x 0.120 x 0.030</td>
<td>0.280 x 0.120 x 0.120</td>
</tr>
<tr>
<td><strong>Theta range for data collection [°]</strong></td>
<td>2.215 to 25.517</td>
<td>3.240 to 25.639</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-15&lt;=h&lt;=15, -6&lt;=k&lt;=6, -30&lt;=l&lt;=30</td>
<td>-8&lt;=h&lt;=9, -18&lt;=k&lt;=19, -17&lt;=l&lt;=17</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>17139</td>
<td>8840</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>6690 [R(int) = 0.0763]</td>
<td>3312 [R(int) = 0.0313]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 25.000°</strong></td>
<td>99.9 %</td>
<td>99.7 %</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.000 and 0.525</td>
<td>1.000 and 0.592</td>
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<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>6690 / 2 / 487</td>
<td>3312 / 1 / 255</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>0.954</td>
<td>0.976</td>
</tr>
<tr>
<td><strong>R₁, wR₁ [I &gt; 2σ(I)]</strong></td>
<td>0.0708, 0.1858</td>
<td>0.0299, 0.0632</td>
</tr>
<tr>
<td><strong>R₁, wR₁ (all data)</strong></td>
<td>0.0860, 0.1986</td>
<td>0.0359, 0.0647</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole [eÅ⁻³]</strong></td>
<td>0.495 and -0.397</td>
<td>0.173 and -0.205</td>
</tr>
</tbody>
</table>
Figure S7: Perspective view of one of the two molecules in the asymmetric unit of 7d (ma109) with displacement ellipsoids at the 50 % probability level.

Figure S8: Perspective view of 7e (ma108) with displacement ellipsoids at the 50 % probability level.