Supporting Information

Palladium–Catalyzed α-Arylation of Sulfoxonium Ylides with Aryl Fluorosulfates

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General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All sulfoxonium ylides **1** and aryl fluorosulfates **2** were prepared by following reported method.^{1,2,3} Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded in CDCl₃ on Bruker Avance or Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ¹H, ¹³C, and ¹⁹F NMR analysis. High resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier Spectrometer (ESI source).

Experimental procedure

1. Synthesis of sulfoxonium ylides^{1,2} Procedure A:

$$Ar = OH \xrightarrow{O}_{Cl_3CO} OCCl_3 \xrightarrow{O}_{Cl_3CO} OCCl_3 \xrightarrow{V_3 + I^-}_{I_3} O \xrightarrow{V_3 + I^-}_{I_3} O$$

To a 200 mL round-bottom flask was added phenol (15 mmol) and Et_3N (30 mmol). The reaction mixture was stirred at 0 °C under vigorous stirring followed by the dropwise addition of a solution of triphosgene (16.5 mmol) in DCM (80 mL) through pressure-equalized dropping funnel. After stirring the resulting reaction mixture at room temperature for another 3 h, it was washed with ice-cold water (50 mL x 3) and evaporated the organic layer under vacuum to obtain the crude product of chloroformate aryl ester. The crude product was directly used in subsequent steps without further purification.

To a 200 mL round-bottom flask was added potassium *tert*-butoxide (57 mmol, 3.8 equiv.), anhydrous THF (70 mL), and trimethylsulfoxonium iodide (48 mmol, 3.2 equiv.) at room temperature. The resulting solution was heated on an oil bath to reflux for 2 h. The reaction mixture was cooled to 0 °C followed by dropwise addition of the crude chloroformate aryl ester obtained above in THF (10-15 mL). The reaction was allowed to warm to room temperature and stirred for additional 3 h. After completion of reaction as monitored by TLC, water (150 mL) and EtOAc (50 mL) were added to the resulting slurry. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (30 mL x 2). The combined organic extracts were washed with saturated brine and dried over anhydrous Na₂SO₄. The solvents were removed under

reduced pressure and the residue was purified by silica gel column chromatography to obtain the analytically pure product of sulfoxonium ylides.

Procedure B:

$$R \xrightarrow{O} Cl + \underbrace{S}^{O} + I^{-} \xrightarrow{'BuOK} O \xrightarrow{O} O$$

THF, 0 °C to rt R

To a 200 mL round-bottom flask was added potassium *tert*-butoxide (57 mmol, 3.8 equiv.), anhydrous THF (70 mL), and trimethylsulfoxonium iodide (48 mmol, 3.2 equiv.) at room temperature. The resulting solution was heated on an oil bath to reflux for 2 h. The reaction mixture was cooled to 0 °C, followed by dropwise addition of acyl chlorides (15 mmol) in THF (10-15 mL). The reaction was allowed to warm to room temperature and stirred for additional 3 h. After completion of reaction as monitored by TLC, water (150 mL) and EtOAc (50 mL) were added to the resulting slurry. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (30 mL x 2). The combined organic extracts were washed with saturated brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography to obtain the analytically pure product of sulfoxonium ylides.

Except for sulfoxonium ylides **1a** and **1j-n** which were synthesized according to Procedure B, all the other sulfoxonium ylides **1b-i** were synthesized by using Procedure A.

2. Synthesis of aryl fluorosulfates³

Ar=OH
$$\frac{SO_2F_2 \text{ (balloon)}}{DCM, \text{ rt, 12 h}}$$
 Ar=OSO₂F

To a 500 mL single-neck round-bottom flask was sequentially charged with phenol (100 mmol, 1.0 equiv.), dichloromethane (250 mL, 0.4 M), and triethylamine (300 mmol, 3.0 equiv.), and it was then sealed with a rubber septum. The atmosphere above the solution was removed by gentle vacuum, and SO_2F_2 gas was subsequently introduced into the flask by a needle from a balloon filled with SO_2F_2 gas. The reaction mixture was vigorously stirred at room temperature for 12 h. The solvent was evaporated and the residual was purified by silica gel column chromatography using petroleum ether and EtOAc as eluent to afford the pure product of aryl fluorosulfate. Spectral data of the products are in accord with those previously reported.³

3. Typical procedure for the cross-coupling of sulfoxonium ylides with aryl fluorosulfates

$$\begin{array}{c} O & O \\ R & \parallel \\ R & \parallel \\ R & \parallel \\ I (1.5 \text{ equiv.}) \end{array} + Ar - OSO_2F \xrightarrow{Pd_2(dba)_3 (5 \text{ mol}\%)}_{MeCN, N_2, 80 \ ^\circC, 12 \ h} & R & O & O \\ MeCN, N_2, 80 \ ^\circC, 12 \ h & Ar \\ I (1.5 \text{ equiv.}) & I (1 \text{ equiv.}) \end{array}$$

To an oven-dried seal tube equipped with a magnetic stirring bar was added sulfoxonium ylide **1** (0.75 mmol, 1.5 equiv.), $Pd_2(dba)_3$ (0.025 mmol, 22.9 mg), CsF (1 mmol, 151.9 mg), X-Phos (0.1 mmol, 47.7 mg), and anhydrous MeCN (2 mL). The seal tube was backfilled with nitrogen gas for three times. Then aryl fluorosulfate **2** (0.5 mmol, 1 equiv.) was added into the seal tube. The reaction mixture was stirred at 80 °C for 12 h before quenching with saturated NH₄Cl solution (2 mL). Then water (80 mL) were added and extracted with EtOAc (20 mL x 3). The organic layers were combined, washed with saturated brine, and dried over Na₂SO₄. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether or MeOH/DCM as eluents) to yield the product **3** or **4**.

4. 5 mmol scale synthesis



To an oven-dried seal tube equipped with a magnetic stirring bar was added sulfoxonium ylide **1a** (7.5 mmol, 1592 mg), $Pd_2(dba)_3$ (0.25 mmol, 228.9 mg), CsF (10 mmol, 1519 mg), X-Phos (1 mmol, 476.7 mg), and anhydrous MeCN (10 mL). The seal tube was backfilled with nitrogen gas for three times. Then aryl fluorosulfate **2a** (5 mmol, 880.8 mg) was added into the seal tube. The reaction mixture was stirred at 80 °C for 12 h before quenching with saturated NH₄Cl solution (10 mL). Then water (150 mL) was added and extracted with EtOAc (40 mL x 3). The organic layers were combined, washed with saturated brine, and dried over Na₂SO₄. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using MeOH/DCM as eluents) to yield the product **3a** in 80% yield (1154.9 mg)

Optimization of reaction conditions

7

L7

	PhO I a (1.5 equiv.)	+ $\frac{OSO_2F}{Ii}$ $\frac{Pd}{Ii}$ MeC 2a (1 equiv.)	2(dba) ₃ (5 mol ⁴ gand (20 mol% CsF (2 equiv.) ℃N, N ₂ , 80 ℃,	$\begin{array}{c} 2 \\ 2 \\ 0 \\ 0 \\ 0 \\ 12 \\ h \\ 3 \\ 3 \\ a \end{array}$	S S
		O'Pr O'Pr		PCy ₂	P'Bu ₂
	X-Phos L1	RuPhos L2	CyJohnPl L3	nos John L	Phos 4
	$ _{J_3}^{P} P = 0$	$Cl \rightarrow B_3 P$	PPh ₂ Fe PPh ₂ dppf		N N
	MeO-	$\frac{1}{2}$ P $\left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$rac{1}{2}$	Ph ₂ P dppp L11	_PPh ₂
$\begin{array}{c c} & & & & & \\ \hline & & & & \\ PPh_2 & PPh_2 & & & \\ DPEPhos & L13 & L14 \\ L12 & L13 & L14 \end{array}$				\rightarrow N= \langle	
Entry	Ligand	Yield $(\%)^b$	Entry	Ligand	Yield $(\%)^b$
1	L1	82 (84) ^c	8	L8	<5 ^d
2	L2	73	9	L9	6
3	L3	56	10	L10	<5
4	L4	20	11	L11	$<5^d$
5	L5	<5	12	L12	15
6	L6	<5	13	L13	$<5^d$

 Table S1. Optimization of reaction conditions by using different ligands^a

^{*a*} The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.75 mmol), **2a** (0.5 mmol), $Pd_2(dba)_3$ (0.025 mmol), CsF (1 mmol), and ligand (20 mol%) in anhydrous MeCN (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^{*c*} Isolated yield. ^{*d*} Ligand (10 mol%) was used.

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L14

 10^d

 $<5^d$

$\begin{array}{c} O O O O O O O O O O O O O O O O O O O$					
Entry	Base	Yield $(\%)^b$	Entry	Base	Yield $(\%)^b$
1	Et ₃ N	<5	6	K ₂ CO ₃	<5
2	DBU	<5	7	K ₃ PO ₄	71
3	^t BuOK	<5	8	AcONa	<5
4	NaOH	42	9	CsF	82 (84) ^c
5	Cs_2CO_3	32			
<i>a</i> T 1	, •	C 1		C C 10 1	1 1

Table S2. Optimization of reaction conditions by using different bases^a

^{*a*} The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.75 mmol), **2a** (0.5 mmol), Pd₂(dba)₃ (0.025 mmol), base (2 equiv.), and X-Phos (0.1 mmol) in anhydrous MeCN (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^{*c*} Isolated yield.

Table S3. Optimization of reaction conditions by using different solvents^a

$\begin{array}{c} O O O O O O O O O O O O O O O O O O O$					
Entry	Solvent	Yield $(\%)^b$	Entry	Solvent	Yield $(\%)^b$
1	<i>p</i> -Xylene	<5	5	DMA	28
2	THF	72	6	DMSO	<5
3	1,4-dioxane	66	7	MeCN	82 (84) ^c
4	DMF	42	8	H_2O	15

^{*a*} The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.75 mmol), **2a** (0.5 mmol), $Pd_2(dba)_3$ (0.025 mmol), CsF (1 mmol), and X-Phos (0.1 mmol) in solvent (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^{*c*} Isolated yield.

Characterization data of products



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (3a): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 84%, 121.8 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.47–7.42 (m, 2H), 7.40–7.34 (m, 2H), 7.34–7.27 (m, 3H), 7.16–7.11 (m, 1H), 7.10–7.04 (m, 2H), 3.46 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.5, 151.4, 133.7, 131.6, 129.0, 128.4, 127.3, 124.7, 122.3, 70.7, 42.9 ppm. IR (KBr): ν = 3013, 2926, 1643, 1594, 1485, 1416, 1193, 703 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₇O₃S⁺ [M+H]⁺ 289.0893, found: 289.0891.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(4-nitrophenyl)acetate (3b): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 83%, 137.9 mg. Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.19–8.14 (m, 2H), 7.62–7.57 (m, 2H), 7.39–7.33 (m, 2H), 7.21–7.16 (m, 1H), 7.09 (dd, *J* = 8.6, 1.2 Hz, 2H), 3.58 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.4, 150.7, 145.0, 139.4, 132.0, 129.1, 125.0, 123.0, 121.9, 69.4, 43.3 ppm. IR (KBr): *ν* = 3018, 2913, 1679, 1633, 1584, 1504, 1329, 854 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆NO₅S⁺ [M+H]⁺ 334.0744, found: 334.0740.



Phenyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-(3-nitrophenyl)acetate (3c): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 77%, 128.4 mg. Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.34–8.26 (m, 1H), 8.09 (ddd, J = 8.3, 2.3, 1.1 Hz, 1H), 7.76 (ddd, J = 7.7, 1.8, 1.1 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.37–7.32 (m, 2H), 7.20–7.14 (m, 1H), 7.12–7.06 (m, 2H), 3.55

(s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.6, 150.8, 147.8, 139.0, 133.2, 129.0, 128.6, 127.5, 124.9, 122.0, 121.2, 68.0, 43.1 ppm. IR (KBr): ν = 3017, 2923, 1640, 1517, 1398, 1238, 1024, 749 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆NO₅S⁺ [M+H]⁺ 334.0744, found: 334.0745.



Phenyl 2-(4-cyanophenyl)-2-(dimethyl(oxo)-\lambda^6-sulfaneylidene)acetate (3d): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 69%, 107.8 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.38–7.32 (m, 2H), 7.21–7.15 (m, 1H), 7.08 (dd, *J* = 8.6, 1.2 Hz, 2H), 3.55 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.2, 150.7, 137.0, 132.5, 131.4, 128.9, 124.8, 121.9, 119.0, 108.7, 69.5, 43.0 ppm. IR (KBr): *v* = 3008, 2911, 2225, 1648, 1597, 1341, 1189, 958 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₆NO₃S⁺ [M+H]⁺ 314.0845, found: 314.0846.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(4-formylphenyl)acetate (3e): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 86%, 135.9 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 9.94 (s, 1H), 7.84–7.79 (m, 2H), 7.63–7.58 (m, 2H), 7.36–7.30 (m, 2H), 7.18–7.13 (m, 1H), 7.11–7.06 (m, 2H), 3.49 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.8, 163.5, 150.8, 138.7, 134.1, 132.4, 129.2, 129.0, 124.9, 122.0, 70.1, 43.0 ppm. IR (KBr): ν = 3124, 3016, 2928, 1697, 1649, 1401, 1188, 732 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₇O₄S⁺ [M+H]⁺ 317.0842, found: 317.0840.



Phenyl 2-(4-acetylphenyl)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (3f): This product was

purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 72%, 119.2 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.94–7.89 (m, 2H), 7.56–7.51 (m, 2H), 7.35–7.30 (m, 2H), 7.18–7.12 (m, 1H), 7.10–7.04 (m, 2H), 3.47 (s, 6H), 2.57 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197.7, 163.7, 150.9, 137.1, 134.6, 132.0, 129.0, 128.0, 124.8, 122.0, 70.0, 43.0, 26.5 ppm. IR (KBr): ν = 3029, 2927, 1683, 1639, 1595, 1403, 1195, 747 cm⁻¹. HRMS (m/z): calcd for C₁₈H₁₉O₄S⁺ [M+H]⁺ 331.0999, found: 331.0998.



Methyl 4-(1-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenoxyethyl)benzoate (3g): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 2:1). Yield = 92%, 160.2 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.03–7.98 (m, 2H), 7.55–7.49 (m, 2H), 7.36–7.30 (m, 2H), 7.18–7.12 (m, 1H), 7.07 (dd, *J* = 8.6, 1.2 Hz, 2H), 3.89 (s, 3H), 3.45 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 166.7, 163.6, 151.0, 137.0, 132.4, 129.2, 128.9, 127.7, 124.7, 122.0, 70.4, 51.8, 42.8 ppm. IR (KBr): *v* = 3026, 2925, 1713, 1642, 1600, 1337, 1199, 709 cm⁻¹. HRMS (m/z): calcd for C₁₈H₁₉O₅S⁺ [M+H]⁺ 347.0948, found: 347.0948.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(4-(trifluoromethoxy)phenyl)acetate (3h): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 43%, 79.6 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.49–7.44 (m, 2H), 7.36–7.30 (m, 2H), 7.22–7.18 (m, 2H), 7.18–7.13 (m, 1H), 7.07 (d, *J* = 7.4 Hz, 2H), 3.47 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.1, 151.1, 148.1, 134.7, 130.1, 129.0, 124.8, 122.1, 120.6, 120.3 (q, *J* = 255.6 Hz), 69.0, 42.8 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -57.56 (s, 3F) ppm. IR (KBr): *v* = 3029, 2925, 1646, 1508, 1495, 1277, 1197, 746 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₆F₃O₄S⁺ [M+H]⁺ 373.0716, found: 373.0720.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(4-fluorophenyl)acetate (3i): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 88%, 135.1 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.38 (m, 2H), 7.35–7.30 (m, 2H), 7.17–7.12 (m, 1H), 7.10–7.03 (m, 4H), 3.41 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.3, 162.0 (d, *J* = 247.0 Hz), 151.2, 135.4 (d, *J* = 8.2 Hz), 129.0, 127.2, 124.7, 122.1, 115.3 (d, *J* = 21.4 Hz), 69.3, 42.6 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -114.39 (s, 1F) ppm. IR (KBr): ν = 3013, 2929, 1648, 1507, 1400, 1340, 1188, 1008 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆FO₃S⁺ [M+H]⁺ 307.0799, found: 307.0800.



Phenyl 2-(4-chlorophenyl)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (3j): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 300:1). Yield = 52%, 84.7 mg. Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.29 (m, 6H), 7.18–7.11 (m, 1H), 7.09–7.04 (m, 2H), 3.46 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.2, 151.2, 134.8, 133.1, 129.5, 129.0, 128.5, 124.8, 122.1, 69.3, 43.1 ppm. IR (KBr): ν = 3023, 2927, 1656, 1492, 1336, 1233, 1193, 721 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆ClO₃S⁺ [M+H]⁺ 323.0503, found: 323.0515.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(*p*-tolyl)acetate (3k): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 61%, 92.5 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.36– 7.28 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 3.41 (s, 6H), 2.36 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.6, 151.4, 137.2, 133.6, 129.2, 128.9, 124.6, 122.3, 70.5, 42.7, 21.2 ppm. IR (KBr): *ν* = 3021, 2924, 2245, 1645, 1494, 1401, 1177, 727 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₉O₃S⁺ [M+H]⁺ 303.1049, found: 303.1046.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(3,5-dimethylphenyl)acetate (31): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 44%, 69.5 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (t, *J* = 7.3 Hz, 2H), 7.18–7.05 (m, 5H), 6.96 (s, 1H), 3.37 (s, 6H), 2.35 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.4, 151.4, 137.7, 131.4, 129.2, 128.8, 124.4, 122.2, 71.3, 42.4, 21.1 ppm. IR (KBr): ν = 3009, 2920, 1752, 1629, 1596, 1400, 1178, 703 cm⁻¹. HRMS (m/z): calcd for C₁₈H₂₁O₃S⁺ [M+H]⁺ 317.1206, found: 317.1205.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(naphthalen-2-yl)acetate (3m): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 66%, 111.9 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, J = 2.1 Hz, 1H), 7.88–7.82 (m, 3H), 7.56 (dd, J = 8.5, 1.8 Hz, 1H), 7.51–7.47 (m, 2H), 7.36–7.30 (m, 2H), 7.18–7.07 (m, 3H), 3.44 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.4, 151.3, 133.3, 132.3, 131.9, 131.6, 129.0, 127.88, 127.86, 127.5, 126.0, 124.7, 122.2, 71.2, 42.7 ppm. IR (KBr): ν = 3024, 2925, 2247, 1748, 1651, 1493, 1175, 744 cm⁻¹. HRMS (m/z): calcd for C₂₀H₁₉O₃S⁺ [M+H]⁺ 339.1049, found: 339.1045.



Phenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-(pyridin-3-yl)acetate (3n): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 50:1). Yield = 51%, 74.3 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (d, J = 2.3 Hz, 1H), 8.46 (dd, J = 4.8, 1.6 Hz, 1H), 7.79–7.69 (m, 1H), 7.36–7.29 (m, 2H), 7.27 (dd, J = 8.3, 5.2 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.9 Hz, 2H), 3.46 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.6, 153.6, 150.9, 147.4, 140.3, 129.0, 127.8, 124.8, 123.0, 122.0, 66.2, 42.9 ppm. IR (KBr): ν = 3027, 2923, 1644, 1494, 1405, 1240, 748, 719 cm⁻¹. HRMS



Phenyl

2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-((8*R***,9***S***,13***S***,14***S***)-13-methyl-17-oxo-7,8,9,11,12,13,14,1 5,16,17-decahydro-6***H***-cyclopenta[***a***]phenanthren-3-yl)acetate (3t):** This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 240:1). Yield = 54%, 125.3 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.33–7.25 (m, 3H), 7.22–7.11 (m, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 3.42 (s, 6H), 2.92 (d, *J* = 5.7 Hz, 2H), 2.50 (dd, *J* = 18.9, 8.5 Hz, 1H), 2.43–2.38 (m, 1H), 2.33–2.27 (m, 1H), 2.19–2.10 (m, 1H), 2.08–1.92 (m, 3H), 1.70–1.58 (m, 2H), 1.57–1.40 (m, 4H), 0.90 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 221.0, 164.5, 151.4, 138.8, 136.4, 134.1, 131.0, 129.3, 128.9, 125.3, 124.6, 122.3, 70.2, 50.3, 47.8, 44.2, 42.8, 37.8, 35.7, 31.4, 29.2, 26.3, 25.4, 21.4, 13.7 ppm. IR (KBr): *ν* = 3022, 2928, 1735, 1655, 1494, 1400, 1195, 753 cm⁻¹. HRMS (m/z): calcd for C₂₈H₃₃O₄S⁺ [M+H]⁺ 465.2094, found: 465.2100.



4-Fluorophenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (4b): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 200:1). Yield = 69%, 106.3 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.45–7.41 (m, 2H), 7.40–7.34 (m, 2H), 7.33–7.28 (m, 1H), 7.05–6.96 (m, 4H), 3.44 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.4, 159.6 (d, *J* = 242.6 Hz), 147.1, 133.7, 131.3, 128.5, 127.5, 123.6 (d, *J* = 8.5 Hz), 115.5 (d, *J* = 23.2 Hz), 70.9, 42.8 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -118.67 (s, 1F) ppm. IR (KBr): *ν* = 3018, 2934, 1647, 1503, 1401, 1333, 1177, 704 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆FO₃S⁺ [M+H]⁺ 307.0799, found: 307.0803.



4-Chlorophenyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-phenylacetate (4c): This product was

purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 300:1). Yield = 76%, 123.1 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.45–7.40 (m, 2H), 7.40–7.35 (m, 2H), 7.33–7.29 (m, 1H), 7.28–7.25 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.45 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.1, 149.9, 134.7, 133.6, 131.3, 129.8, 128.9, 127.5, 123.6, 71.1, 42.7 ppm. IR (KBr): ν = 3026, 2933, 1640, 1583, 1488, 1401, 1194, 698 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₆ClO₃S⁺ [M+H]⁺ 323.0503, found: 323.0506.



p-Tolyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-phenylacetate (4d): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 200:1). Yield = 96%, 145.4 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.44 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32–7.26 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.43 (s, 6H), 2.30 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.7, 149.0, 134.2, 133.6, 131.7, 129.5, 128.4, 127.2, 122.0, 70.5, 42.8, 20.8 ppm. IR (KBr): *v* = 3025, 2933, 1640, 1511, 1401, 1333, 1193, 697 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₉O₃S⁺ [M+H]⁺ 303.1049, found: 303.1049.



m-Tolyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-phenylacetate (4e): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 200:1). Yield = 72%, 109.6 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.45 (d, *J* = 1.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32–7.26 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 5.9 Hz, 2H), 3.41 (s, 6H), 2.33 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.6, 151.2, 139.0, 133.6, 131.6, 128.7, 128.3, 127.2, 125.5, 122.8, 119.2, 70.7, 42.7, 21.2 ppm. IR (KBr): ν = 3009, 2925, 1641, 1593, 1489, 1206, 1015, 704 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₉O₃S⁺ [M+H]⁺ 303.1049, found: 303.1049.



4-Methoxyphenyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (4f): This product was

purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 90%, 143.4 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (d, J = 7.1 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 3.73 (s, 3H), 3.35 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.6, 156.3, 144.6, 133.5, 131.6, 128.3, 127.2, 122.9, 113.9, 70.7, 55.4, 42.5 ppm. IR (KBr): ν = 3026, 2934, 1640, 1604, 1507, 1329, 1197, 698 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₉O₄S⁺ [M+H]⁺ 319.0999, found: 319.0996.



3,5-Dimethylphenyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-phenylacetate (4g): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 250:1). Yield = 79%, 125.6 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.44 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.79 (s, 1H), 6.72 (s, 2H), 3.36 (s, 6H), 2.29 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.5, 151.0, 138.5, 133.4, 131.7, 128.2, 127.0, 126.3, 119.7, 70.8, 42.4, 21.0 ppm. IR (KBr): *v* = 3022, 2925, 1647, 1591, 1401, 1208, 1032, 707 cm⁻¹. HRMS (m/z): calcd for C₁₈H₂₁O₃S⁺ [M+H]⁺ 317.1206, found: 317.1204.



Benzo[*d*][1,3]dioxol-5-yl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (4h): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 400:1). Yield = 57%, 94.3 mg. Light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.40 (m, 2H), 7.39–7.33 (m, 2H), 7.31–7.26 (m, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 2.3 Hz, 1H), 6.50 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.91 (s, 2H), 3.42 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.6, 147.5, 145.6, 144.4, 133.6, 131.4, 128.4, 127.3, 114.5, 107.6, 104.5, 101.3, 70.7, 42.7 ppm. IR (KBr): *ν* = 3017, 2927, 1648, 1593, 1485, 1400, 1167, 702 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₇O₅S⁺ [M+H]⁺ 333.0791, found: 333.0789.



Naphthalen-1-yl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (4i): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 300:1). Yield = 89%, 150.8 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.93 (d, *J* = 10.3 Hz, 1H), 7.87–7.81 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.61–7.54 (m, 2H), 7.51– 7.48 (m, 2H), 7.44 (t, *J* = 8.1 Hz, 3H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 3.25 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 164.1, 147.2, 134.3, 133.7, 131.7, 128.4, 127.7, 127.6, 127.4, 125.9, 125.8, 125.3, 124.6, 121.6, 118.4, 71.3, 42.1 ppm. IR (KBr): *ν* = 3017, 2927, 1648, 1507, 1489, 1398, 1200, 784 cm⁻¹. HRMS (m/z): calcd for C₂₀H₁₉O₃S⁺ [M+H]⁺ 339.1049, found: 339.1045.



Cyclopentyl 2-(dimethyl(oxo)- λ^6 -sulfaneylidene)-2-phenylacetate (4j): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 200:1). Yield = 29%, 40.2 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.31–7.26 (m, 4H), 7.25–7.18 (m, 1H), 5.17 (tt, *J* = 5.7, 2.8 Hz, 1H), 3.40 (s, 6H), 1.81–1.72 (m, 2H), 1.68–1.49 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 166.0, 133.2, 132.8, 128.0, 126.5, 75.3, 70.5, 43.2, 32.8, 23.6 ppm. IR (KBr): ν = 3005, 2960, 1730, 1618, 1400, 1330, 1156, 700 cm⁻¹. HRMS (m/z): calcd for C₁₅H₂₁O₃S⁺ [M+H]⁺ 281.1206, found: 281.1204.



Benzyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylacetate (4k): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 1:1). Yield = 88%, 133.1 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.33–7.29 (m, 4H), 7.28–7.26 (m, 1H), 7.26–7.20 (m, 5H), 5.10 (s, 2H), 3.27 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 165.5, 137.5, 133.5, 132.3, 128.2, 128.1, 127.1, 126.9, 70.6, 64.1, 42.6 ppm. IR (KBr): ν = 3008, 2931, 1730, 1618, 1400, 1330, 1156, 700 cm⁻¹. HRMS (m/z): calcd for C₁₇H₁₉O₃S⁺ [M+H]⁺ 303.1049, found: 303.1046.



2-(Dimethyl(oxo)-\lambda^6-sulfaneylidene)-1,2-diphenylethan-1-one (4l): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 400:1) Yield = 55%, 75.2 mg. White solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.36 (d, *J* = 7.6 Hz,

2H), 7.25–7.19 (m, 4H), 7.19–7.11 (m, 4H), 3.64 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 183.0, 140.1, 134.7, 131.9, 129.4, 128.6, 128.2, 127.4, 127.3, 86.8, 43.0 ppm. IR (KBr): ν = 3014, 2920, 1583, 1515, 1401, 1372, 1204, 710 cm⁻¹. HRMS (m/z): calcd for C₁₆H₁₇O₂S⁺ [M+H]⁺ 273.0944, found: 273.0944.



1-Cyclohexyl-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-2-phenylethan-1-one (4m): This product was purified by silica gel column chromatography using dichloromethane/methanol as eluent (DCM/MeOH = 100:1). Yield = 36%, 50.6 mg. Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.27 (m, 3H), 7.25–7.19 (m, 2H), 3.41 (s, 6H), 2.22 (tt, *J* = 11.5, 3.3 Hz, 1H), 1.66–1.48 (m, 5H), 1.40 (qd, *J* = 12.8, 3.3 Hz, 2H), 1.17–0.91 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 192.5, 134.5, 132.0, 128.4, 127.7, 85.0, 44.8, 42.9, 29.4, 25.72, 25.68 ppm. IR (KBr): *ν* = 3009, 2926, 2847, 1552, 1342, 1165, 1027, 700 cm⁻¹. HRMS (m/z): calcd for C₁₆H₂₃O₂S⁺ [M+H]⁺ 279.1413, found: 279.1411.

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¹H, ¹³C, and ¹⁹F NMR spectra of products

¹H NMR spectrum of 3a (400 MHz, CDCl₃)



¹³C NMR spectrum of 3a (100 MHz, CDCl₃)







¹³C NMR spectrum of 3b (100 MHz, CDCl₃)



¹H NMR spectrum of 3c (400 MHz, CDCl₃)



¹³C NMR spectrum of 3c (100 MHz, CDCl₃)





¹³C NMR spectrum of 3d (100 MHz, CDCl₃)



¹H NMR spectrum of 3e (400 MHz, CDCl₃)



¹³C NMR spectrum of 3e (100 MHz, CDCl₃)





¹³C NMR spectrum of 3f (100 MHz, CDCl₃)



¹H NMR spectrum of 3g (400 MHz, CDCl₃)



¹³C NMR spectrum of 3g (100 MHz, CDCl₃)





¹³C NMR spectrum of 3h (100 MHz, CDCl₃)









¹⁹F NMR spectrum of 3i (376 MHz, CDCl₃)







¹³C NMR spectrum of 3j (100 MHz, CDCl₃)

64.17	51.24	34.76 33.13 29.04 22.04 22.14 22.14	7.32 CDCl3 7.00 CDCl3 6.68 CDCl3 9.28	3.07
E	41	22222222		- 4
1	1			1



¹H NMR spectrum of 3k (400 MHz, CDCl₃)



¹³C NMR spectrum of 3k (100 MHz, CDCl₃)



¹H NMR spectrum of 3l (400 MHz, CDCl₃)



¹³C NMR spectrum of 3l (100 MHz, CDCl₃)





¹³C NMR spectrum of 3m (100 MHz, CDCl₃)



¹H NMR spectrum of 3n (400 MHz, CDCl₃)



¹³C NMR spectrum of 3n (100 MHz, CDCl₃)



¹H NMR spectrum of 3t (400 MHz, CDCl₃)



¹³C NMR spectrum of 3t (100 MHz, CDCl₃)





¹³C NMR spectrum of 4b (100 MHz, CDCl₃)







¹H NMR spectrum of 4c (400 MHz, CDCl₃)



¹³C NMR spectrum of 4c (100 MHz, CDCl₃)



5.0 4.5 f1 (ppm) 3.5

4.0

3.0

2.5 2.0

9.5

9.0 8.5

8.0 7.5

7.0

6.5 6.0 5.5

0.0 -0.

1.0 0.5

1.5

¹³C NMR spectrum of 4d (100 MHz, CDCl₃)



¹H NMR spectrum of 4e (400 MHz, CDCl₃)



¹³C NMR spectrum of 4e (100 MHz, CDCl₃)



¹H NMR spectrum of 4f (400 MHz, CDCl₃)



¹³C NMR spectrum of 4f (100 MHz, CDCl₃)



¹H NMR spectrum of 4g (400 MHz, CDCl₃)



¹³C NMR spectrum of 4g (100 MHz, CDCl₃)



¹H NMR spectrum of 4h (400 MHz, CDCl₃)





¹H NMR spectrum of 4i (400 MHz, CDCl₃)







¹H NMR spectrum of 4j (400 MHz, CDCl₃)



¹³C NMR spectrum of 4j (100 MHz, CDCl₃)



¹H NMR spectrum of 4k (400 MHz, CDCl₃)



¹³C NMR spectrum of 4k (100 MHz, CDCl₃)



¹H NMR spectrum of 4l (400 MHz, CDCl₃)



¹³C NMR spectrum of 4l (100 MHz, CDCl₃)



¹H NMR spectrum of 4m (400 MHz, CDCl₃)



¹³C NMR spectrum of 4m (100 MHz, CDCl₃)

