Supporting information

Transition-Metal-Free Aryl–Heteroatom Bond Formation via C–S Bond Cleavage

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1. General Methods for Experiments

All reactions were carried out under a slightly positive pressure of dry argon by using standard Schlenk line techniques. Liquids and solutions were transferred with syringes. All solvents and chemical reagents were obtained from commercial sources such as Strem Chemicals, Adamas-beta, Sigma-Aldrich, J&K, Accela and TCI, which were used without further purification. ¹H and ¹³C NMR spectra were recorded with tetramethylsilane as an internal reference. Low and high-resolution mass spectra were recorded on EI-TOF (electrospray ionization-time of flight) or ESI-TOF. Normal-phase column chromatography was performed with silica gel 60 (230–400 mesh) from Merck and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

2. Optimization for Reaction Conditions

NC 1a 1.0 eq.	но _~ , f +		base Solven	(m eq.)	O Me 3a
Entry	Base	n	m	solvent	NMR Yield
1	KO ^t Bu	1.5	1.5	DMF	74%
2	Na ₂ CO ₃	1.5	1.5	DMF	trace
4	K_2CO_3	1.5	1.5	DMF	12%
5	KHCO ₃	1.5	1.5	DMF	trace
6	K ₃ PO ₄	1.5	1.5	DMF	45%
7	Cs_2CO_3	1.5	1.5	DMF	88%
8	Cs_2CO_3	1.5	1.5	THF	45%
9	Cs_2CO_3	1.5	1.5	DMSO	46%
10	Cs ₂ CO ₃	1.5	1.5	DCM	50%
11	Cs ₂ CO ₃	1.5	1.5	NMP	25%
12	Cs ₂ CO ₃	1.5	1.5	MeCN	78%
13	Cs ₂ CO ₃	1.1	1.1	DMF	53%
14 ^a	Cs ₂ CO ₃	1.5	1.5	DMF	80%
15 ^b	Cs ₂ CO ₃	1.5	1.5	DMF	79%

 Table S1. Screening of Etherification Conditions

^a performed in darkness

^b add 2.0 eq. TEMPO

O ₂ N	⊕ SMe₂ ⊖OTf (1.0 eq.).	• MeSeSeMe (n eq.).	base (m eq.) ► Solvent, r.t., 3h		N 6a
Entry	Base	n	m	solvent	NMR Yield
1	KO ^t Bu	1.5	1.5	DMF	0%
2	NaH	1.5	1.5	DMF	trace
4	KHMDS	1.5	1.5	DMF+THF	trace
5	NaBH ₄	1.5	3.0	THF+H ₂ O+DMF	75%
6	KBH ₄	1.5	3.0	THF+H ₂ O+DMF	98%
7	KBH ₄	1.0	2.0	THF+H ₂ O+DMF	96%
8	KBH ₄	0.6	1.2	THF+H ₂ O+DMF	48%

Table S2. Screening of Selenation Conditions

Table S3. Screening of Stannylation Conditions

	+ Me ₃ Sn—SnMe ₃	base (n eq.) Solvent, r.t., 8h		NC SnMe ₃
1a (1.0 eq.).	(n eq.).			7a
Entry	Base	n	solvent	NMR Yield
1	KO ^t Bu	2.0	DMF	0%
2	KF	2.0	DMF	21%
3	KOAc	2.0	DMF	0%
4	NaOEt	2.0	DMF	0%
5	TBAF	2.0	DMF	28%
6	CsF	2.0	DMF	66%
7	CsF	2.0	DMSO	39%
9	CsF	2.0	NMP	trace
10	CsF	1.5	DMF	65%

Table S4. Screening of Silylation Conditions



Entry	Base	n	solvent	NMR Yield
1	KF	2.0	DMF	12%
2	CsF	2.0	DMF	44%
3	NaOMe	2.0	DMF	0%
4	TBAF	2.0	DMF	28%
5	CsF	2.0	THF	29%
6	CsF	2.0	DMSO	17%
7	CsF	2.0	CH ₃ CN	18%
8	CsF	2.0	NMP	26%
9	CsF	1.5	DMF	55%
10	CsF	1.1	DMF	33%

3. Details of Experiments

3.1 General Procedure for Preparation of Arylsulfonium Salts

K₂CO₃ (15 mmol), thiolphenol (10 mmol), iodomethane (15 mmol) and acetone (50 mL) were added into a flask. The mixture was stirred at room temperature overnight. After the completion of the reaction as indicated by TLC, the mixture was concentrated under a reduced pressure. H₂O (40 mL) was added to the residue and the resulting mixture was extracted with EA. The combined organic layer was dried over Na₂SO₄, concentrated under a reduced pressure. The residue was purified by silica gel column chromatography to give arylmethylthioether.

To a stirred solution of arylmethylthioether (10 mmol dissolved in 10 ml 1,2-dichloroethane) in a 200 mL flask was added dropwise methyl trifluoromethanesulfonate (1.35 mL, 12.0 mmol) at 25°C for 8 h. Solvent was then removed in vacuum and the residue was washed with Et₂O, dried under vacuum to give arylsulfonium salts solid.

3.2 General Procedure for the Reactions of Arylsulfonium Salts with Alcohols



Alcohol (0.3 mmol), cesium carbonate (0.3 mmol, for **2i-n**: 0.6 mmol) and DMF (1 ml) were added into a 10 ml flask; drop the arylsulfonium salt DMF solution (0.2 mmol in 1 ml DMF) into the

flask, stirred at room temperature for 3 h. The resulting mixture was extracted with ethyl acetate, the combined organic layer was dried over Na₂SO₄, then concentrated under a reduced pressure. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product.

3.3 General Procedure for the Reactions of Arylsulfonium Salts with Thiols



Add thiol (0.3 mmol), cesium carbonate (0.3 mmol, for **4g**, **4h**, **4l**: 0.6 mmol) and DMF (1 ml) into a 10 ml flask; drop the arylsulfonium salt DMF solution (0.2 mmol in 1 ml DMF) into the flask, stirred at room temperature for 3 h. The resulting mixture was extracted with ethyl acetate, the combined organic layer was dried over Na₂SO₄, then concentrated under a reduced pressure. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product.

3.4 General Procedure for the Selenation Reaction of Arylsulfonium Salts



KBH₄ aqueous solution (0.6 mmol in 0.5 ml H₂O) was added dropwise into selenide solution (0.3 mmol dissolved in 0.5 ml THF) in a 10 ml flask, stirred at room temperature for 10 min. Then, arylsulfonium salt solution (0.2 mmol dissolved in 1 ml DMF) was added into the flask, stirred at room temperature for 3 h. The resulting mixture was extracted with ethyl acetate, the combined organic layer was dried over Na₂SO₄, then concentrated under a reduced pressure. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product.

3.5 General Procedure for the Stannylation Reaction of Arylsulfonium Salts



Stannide (0.3 mmol), cesium fluoride (0.3 mmol), DMF (1 ml) were added into a Schlenck with argon protected at room temperature. Arylsulfonium salt (0.2 mmol) was dissolved in 1 ml DMF and added dropwise into the Schlenk. The mixture was stirred at room temperature for 8h. The resulting mixture was extracted with ethyl acetate, the combined organic layer was dried over Na₂SO₄, then concentrated under a reduced pressure. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product.

3.6 General Procedure for the Silylation Reaction of Arylsulfonium Salts



In a 10 ml Schlenck tube, silane (0.3 mmol) and cesium fluoride (0.3 mmol) were dissolved in 1 ml DMF with argon protected at room temperature. Arylsulfonium salt solution (0.2 mmol dissolved in 1 ml DMF) was added dropwise into the Schlenk. The mixture was stirred at room temperature for 8 h. The resulting mixture was extracted with ethyl acetate, the combined organic layer was dried over Na₂SO₄, then concentrated under a reduced pressure. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product.

3.7 Reactions of Arylsulfoiniums Bearing Electron-neutral and Electron-donating Groups

We have examined more etherification and thioetherification reactions with some arylsulfoinium substrates bearing electron-neutral and electron-donating groups as shown below. But these substrates showed little or no reactivity toward alcohol/thiol. Instead, demethylated byproducts were detected.



4. Mechanistic Studies

Additional control experiment was performed with *p*-CN and *p*-NO₂-substituted thioethers as substrates in our reaction conditions. However, no etherification product was obtained. We think the "real" arylation reagents were aryl dimethylsulfonium salts but not arylmethylthioethers.



We found that when the reactions of arylsulfonium salt **1a** with β -citronellol and 1-dodecanethiol were performed in the presence of TEMPO or 1,1-diphenylethylene as radical scavengers, the yields of **3a** and **5a** hardly changed, thus excluding radical involvement. (ref: Org. Lett. 2018, 20, 4749) In addition, co-product dimethyl sulfide was detected in 80% yield after the etherification of sulfonium salt based on ¹H-NMR.





As shown below, treatment of **1a** with Cs₂CO₃ in the absence of nucleophiles at room temperature in 3 hours provided ArSMe in 20% NNR yield. But when this transformation performed in microwave condition at 90°C, ArSMe was obtained in 92% NMR yield. Then metronidazole or 1-dodecanethiol was added and the subsequent reaction performed in one-pot manner in the standard conditions. No S_NAr product was detected. Based on these results, we consider that ArSMe should be a byproduct of this aromatic nucleophilic substitution reaction, and MeOCO₂Cs could not promote the reaction of ArSMe with NuH.



5. Characterization of Products

4-cyanophenyldimethylsulfonium trifluoromethanesulfonate salt (1a)



White solid. **m.p.** 96.5-101.2°C; ¹**H NMR** (400 MHz, CD₃OD) δ 8.22 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H), 3.35 (s, 6H). ¹³C NMR (126 MHz, CD₃OD) δ 152.34, 134.25, 132.40, 126.46, 121.73 (q, J = 316.75 Hz), 29.01. ¹⁹F NMR (471 MHz, CD₃OD) δ -79.95. All spectral data match those previously reported.¹

4-nitrophenyldimethylsulfonium trifluoromethanesulfonate salt (1b)

Yellow solid. **m.p.** 83.2-85.1°C; ¹**H NMR** (400 MHz, CD₃OD) δ 8.56 – 8.49 (d, J = 4.7 Hz, 2H), 8.33 (d, J = 4.7 Hz, 2H), 3.43 – 3.37 (s, 6H). ¹³C **NMR** (126 MHz, CD₃OD) δ 152.34, 134.25, 132.40, 126.46, 125.52, 122.99, 121.72 (q, J = 316.75 Hz), 120.45, 117.92, 29.01. ¹⁹F **NMR** (471 MHz, CD₃OD) δ -80.01. All spectral data match those previously reported.²

dimethyl(4-(methylsulfonyl)phenyl)sulfonium trifluoromethanesulfonate salt (1c)



Yellow solid. **m.p.** 100.2-101.9°C; IR υ_{max}/cm⁻¹ (film): 3430, 2925, 1579, 1297, 1149, 1095, 1081, 958, 777, 567, 526, 462; ¹H NMR (400 MHz, DMSO-d6) δ 8.33 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 8.5 Hz, 2H), 3.35 (s, 3H), 3.32 (s, 6H). ¹³C NMR (151 MHz, DMSO-d6) δ 144.98, 132.89, 131.03, 128.52, 120.68 (q, J = 322.69 Hz), 42.95, 28.02. ¹⁹F NMR (471 MHz, DMSO-d6) δ -77.74. HRMS (ESI) m/z [M⁺] calcd for C₉H₁₃O₂S₂, 217.0351. found, 217.0346.

dimethyl(4-(trifluoromethyl)phenyl)sulfonium sulfoniumtrifluoromethanesulfonate salt (1d)



White solid. **m.p.** 162.3-164.8°C; ¹**H NMR** (400 MHz, CD₃OD) δ 8.26 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H), 3.36 (s, 6H). ¹³C **NMR** (126 MHz, CD₃OD) δ 136.47 (q, J = 33.39 Hz), 131.78, 128.74, 124.33 (q, J = 325.71 Hz), 121.98 (q, J = 372.08 Hz), 29.00. ¹⁹**F NMR** (471 MHz, CD₃OD) δ -64.86, -79.97. All spectral data match those previously reported.³

(2-cyanophenyl)dimethylsulfonium trifluoromethanesulfonate salt (1e)

White solid. **m.p.** 143.2-147.1°C; IR $\upsilon_{\text{max}/\text{cm}^{-1}}$ (film): 3444, 3027, 2237, 1477, 1430, 1257, 1161, 1030, 779, 640, 516; ¹H NMR (400 MHz, CD₃OD) δ 8.27 (d, J = 8.1 Hz, 1H), 8.05 – 7.97 (m, 2H), 7.90 (t, J = 7.7 Hz, 1H), 3.35 (s, 6H). ¹³C NMR (126 MHz, CD₃OD) δ 136.69, 136.35, 135.83, 130.75, 130.03, 121.73 (q, J = 319.16 Hz), 116.82, 115.67, 29.10. ¹⁹F NMR (471 MHz, CD₃OD) δ -79.95. **HRMS** (ESI) m/z [M⁺] calcd for C₉H₁₀NS, 164.0528. found, 164.0532.

(4-acetylphenyl)dimethylsulfonium trifluoromethanesulfonate salt (1f)



White solid. **m.p.** 103.5-105.6°C; ¹**H NMR** (400 MHz, DMSO-d6) δ 8.21 (s, 4H), 2.66 (s, 3H). ¹³**C NMR** (126 MHz, DMSO-d6) δ 197.40, 140.30, 131.50, 130.18, 129.55, 120.69 (q, J = 322.81 Hz), 28.00, 27.07. ¹⁹**F NMR** (471 MHz, DMSO-d6) δ -77.76. All spectral data match those previously reported.³

(4-benzoylphenyl)dimethylsulfonium trifluoromethanesulfonate salt (1g)



Yellow solid. **m.p.** 97.2-99.4°C; IR v_{max} /cm⁻¹ (film): 3431, 3039, 1664, 1597, 1276, 1257, 1161, 1143, 1032, 638; ¹**H NMR** (400 MHz, DMSO-d6) δ 8.25 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 7.2 Hz, 3H), 7.61 (d, J = 7.7 Hz, 2H), 3.36 (s, 6H). ¹³**C NMR** (126 MHz, DMSO-d6) δ 194.68, 141.41, 135.89, 133.57, 130.64, 130.03, 129.84, 128.82, 120.69 (q, J = 322.81 Hz), 28.05. ¹⁹**F NMR** (471 MHz, DMSO-d6) δ -77.73. **HRMS** (ESI) m/z [M⁺] calcd for C₁₅H₁₅OS, 243.0838. found, 243.0831.

(4-formylphenyl)dimethylsulfonium trifluoromethanesulfonate salt (1f)



Brown oil. ¹H NMR (400 MHz, DMSO-d6) δ 9.64 – 9.59 (m, 1H), 7.75 (t, J = 7.8 Hz, 2H), 7.72 – 7.63 (m, 2H), 2.80 (s, 6H). ¹³C NMR (126 MHz, DMSO-d6) δ 192.46, 139.09, 132.80, 130.56, 130.54, 120.67 (q, J = 322.81 Hz), 27.97. ¹⁹F NMR (471 MHz, DMSO-d6) δ -77.75. All spectral data match those previously reported.¹

(4-(methoxycarbonyl)phenyl)dimethylsulfonium trifluoromethanesulfonate salt (1i)

SMe₂ MeOOC

White solid. **m.p.** 109.1-112.1°C; ¹**H NMR** (400 MHz, CD₃OD) δ 8.30 (d, J = 8.7 Hz, 2H), 8.14 (d, J = 8.9 Hz, 2H), 3.97 (s, 3H), 3.33 (s, 6H). ¹³C **NMR** (126 MHz, CD₃OD) δ 166.53, 136.53, 132.70, 132.49, 132.22, 130.95, 121.79 (q, J = 319.16 Hz), 53.33, 28.98. ¹⁹F **NMR** (471 MHz, CD₃OD) δ -80.05. All spectral data match those previously reported.³

(4-(ethoxycarbonyl)phenyl)dimethylsulfonium trifluoromethanesulfonate salt (1j)



White solid. **m.p.** 93.1-99.6°C; IR υ_{max} /cm⁻¹ (film): 3438, 3024, 1730, 1271, 1248, 1155, 1028, 854, 762, 686, 640, 573, 518, 493; ¹H NMR (400 MHz, CD₃OD) δ 8.29 (dd, J = 8.4, 1.6 Hz, 2H), 8.17 – 8.12 (m, 2H), 4.42 (qd, J = 7.1, 1.4 Hz, 2H), 3.34 (s, 6H), 1.44 – 1.37 (m, 3H). ¹³C NMR (126 MHz, CD₃OD) δ 166.03, 136.79, 132.42, 132.11, 130.94, 121.78 (q, J = 319.16 Hz), 63.07, 28.99, 14.46. ¹⁹F NMR (471 MHz, CD₃OD) δ -79.98. HRMS (ESI) m/z [M⁺] calcd for C₁₁H₁₅O₂S, 211.0787. found, 211.0788.

(S)-4-((3,7-dimethyloct-6-en-1-yl)oxy)benzonitrile (3a)



Colorless oil (42.2 mg, 82% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 15:1). ¹**H NMR** (300 MHz, CDCl₃) δ 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.09 (t, *J* = 6.5 Hz, 1H), 4.03 (t, *J* = 6.3 Hz, 2H), 2.09 – 1.94 (m, 2H), 1.89 – 1.79 (m, 1H), 1.69 – 1.59 (m, 7H), 1.46 – 1.14 (m, 3H), 0.95 (d, *J* = 6.4 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 162.57, 134.08, 131.59, 124.62, 119.45, 115.33, 103.81, 66.86, 37.17, 35.94, 29.58, 25.84, 25.54, 19.63, 17.80. All spectral data match those previously reported.⁴

(S)-1-((3,7-dimethyloct-6-en-1-yl)oxy)-4-nitrobenzene (3b)



Colorless oil (43.3 mg, 78% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 15:1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 9.3 Hz, 2H), 6.94 (d, *J* = 9.3 Hz, 2H), 5.09 (t, *J* = 7.1 Hz, 1H), 4.08 (ddd, *J* = 9.1, 6.6, 3.2 Hz, 2H), 2.01 (dq, *J* = 14.7, 7.2 Hz, 2H), 1.93 – 1.81 (m, 1H), 1.68 (s, 3H), 1.66 – 1.62 (m, 1H), 1.61 (s, 3H), 1.44 – 1.16 (m, 3H), 0.96 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.35, 141.43, 131.65, 126.06, 124.57, 114.54, 67.33, 37.17, 35.93, 29.55, 25.88, 25.55, 19.64, 17.83. All spectral data match those previously reported.⁵

2-methyl-1-(2-(4-(methylsulfonyl)phenoxy)ethyl)-5-nitro-1H-imidazole (3c)



Colorless solid (47.5 mg, 73% yield). **m.p.** 157.2-163.1°C; The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 20:1). IR \vee_{max}/cm^{-1} (film): 3423, 2922, 1593, 1533, 1506, 1363, 1333, 1255, 1188, 1107, 1051, 906, 854, 750, 658; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.78 (t, *J* = 4.6 Hz, 2H), 4.42 (t, *J* = 4.6 Hz, 2H), 3.01 (s, 3H), 2.67 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 161.74, 151.48, 133.82, 132.50, 129.94, 114.98, 67.16, 45.95, 44.92, 14.55. HRMS (ESI) m/z [(M+H)⁺] calcd for C₁₃H₁₆N₃O₅S, 326.0805. found, 326.0809.

2-methyl-5-nitro-1-(2-(4-(trifluoromethyl)phenoxy)ethyl)-1H-imidazole (3d)



Colorless solid (38.5 mg, 61% yield). **m.p.** 142.7-148.2°C; The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 20:1). IR v_{max}/cm^{-1} (film): 3364, 2923, 2852, 1614, 1531, 1481, 1430, 1372, 1329, 1314, 1255, 1165, 1127, 1112, 1054, 849, 824, 740,

641, 600; ¹**H** NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.53 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.75 (t, J = 4.8 Hz, 2H), 4.37 (t, J = 4.8 Hz, 2H), 2.63 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 160.08, 151.66, 133.37, 127.15, 127.12, 123.60 (q, J = 133.56 Hz), 114.30, 66.86, 45.83, 29.71, 14.70.. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.67 (m, 3F). **HRMS** (ESI): m/z [(M+H)⁺] calcd for C₁₃H₁₃F₃N₃O₃, 316.0904. found, 316.0908.

(3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-3-(4-nitrophenoxy)hexadecahydro-17H-cyclopenta[a]phenanthren-17-one (3e)



Colorless solid (40.3 mg, 49% yield). **m.p.** 212.3-221.5°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). IR \vee_{max}/cm^{-1} (film): 3463, 2921, 2852, 1738, 1588, 1507, 1494, 1328, 1260, 1111, 1015, 848, 754; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 9.3 Hz, 2H), 6.91 (d, J = 9.3 Hz, 2H), 4.39 – 4.24 (m, 1H), 2.41 (q, J = 7.5 Hz, 1H), 2.06 (dd, J = 19.2, 9.1 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.87 – 1.82 (m, 2H), 1.77 (dd, J = 4.8, 2.5 Hz, 1H), 1.64 (dd, J = 12.5, 2.9 Hz, 4H), 1.57 – 1.44 (m, 2H), 1.42 – 1.33 (m, 3H), 1.30 – 1.20 (m, 3H), 1.11 (dd, J = 13.7, 3.8 Hz, 1H), 1.00 (dd, J = 12.7, 5.2 Hz, 1H), 0.90 (s, 3H), 0.87 (s, 3H), 0.75 (td, J = 12.0, 11.6, 4.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 221.24, 163.18, 141.04, 125.99, 115.24, 54.43, 51.39, 47.81, 44.77, 36.71, 35.88, 35.86, 35.04, 33.97, 31.54, 30.85, 28.34, 27.62, 21.79, 20.54, 13.85, 12.35. HRMS (EI): m/z [M⁺] calcd for C₂₅H₃₃NO₄, 411.2404. found, 411.2397.

4-amino-1-((2S,4S)-2-((4-nitrophenoxy)methyl)-1,3-oxathiolan-4-yl)pyrimidin-2(1H)-one (3f)



Colorless oil (52.5 mg, 75% yield). The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). IR v_{max}/cm^{-1} (film): 3461, 3361, 2921, 2850, 1631, 1469, 1332, 1217, 1126, 1091, 974, 939, 839, 667, 598; ¹H NMR (400 MHz, DMSO-d6) δ

8.22 (d, J = 9.3 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.31 – 7.19 (m, 4H), 6.29 (t, J = 5.7 Hz, 1H), 5.74 (d, J = 7.5 Hz, 1H), 5.54 (t, J = 4.7 Hz, 1H), 4.58 – 4.48 (m, 2H), 3.46 (dd, J = 11.5, 5.4 Hz, 1H), 3.14 (dd, J = 11.5, 5.9 Hz, 1H). ¹³**C NMR** (126 MHz, DMSO-d6) δ 166.08, 163.68, 155.08, 141.66, 141.15, 126.35, 115.72, 94.82, 87.47, 81.67, 70.29, 36.09. **HRMS** (ESI): m/z [(M+Na)⁺] calcd for C₁₄H₁₄N₄NaO₅S, 373.0577. found, 373.0573.

3-((9H-carbazol-1-yl)oxy)-N-(2-(2-methoxyphenoxy)ethyl)-2-(4-nitrophenoxy)propan-1-amine (3g)



Colorless oil (50.6 mg, 48% yield). The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). IR v max/cm⁻¹ (film): 3514, 3313, 2968, 2233, 1606, 1510, 1302, 1261, 1174, 1018, 839, 706, 550; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 7.8 Hz, 1H), 8.21 (s, 1H), 8.00 (d, *J* = 9.4 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.96 (td, *J* = 7.5, 2.3 Hz, 1H), 6.91 – 6.83 (m, 3H), 6.81 (d, *J* = 9.5 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.64 (s, 1H), 4.29 (dddd, *J* = 41.1, 19.9, 9.7, 4.9 Hz, 4H), 4.07 – 3.97 (m, 3H), 3.93 (s, 1H), 3.86 – 3.78 (m, 1H), 3.77 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 154.86, 153.21, 149.35, 147.63, 141.16, 138.91, 137.78, 126.84, 126.15, 125.40, 122.82, 122.42, 122.30, 121.08, 119.88, 113.79, 112.76, 111.81, 111.63, 110.41, 104.38, 101.32, 69.70, 68.71, 65.87, 57.24, 55.73, 51.56. HRMS (ESI): m/z [(M+H)⁺] calcd for C₃₀H₃₀N₃O₆, 528.2129. found, 528.2116.

(E)-N-(3-methoxy-4-(4-nitrophenoxy)benzyl)-8-methylnon-6-enamide (3h)



Colorless oil (70.8 mg, 83% yield). The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 20:1). IR v_{max}/cm^{-1} (film): 3281, 2956, 2927, 2854,

1646, 1588, 1504, 1488, 1343, 1287, 1272, 1238, 1158, 1121, 1038, 846, 747, 637, 492; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 10.4 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.97 (s, 1H), 6.94 – 6.88 (m, 3H), 5.83 (s, 1H), 5.42 – 5.26 (m, 2H), 4.47 (d, *J* = 5.9 Hz, 2H), 3.76 (s, 3H), 2.24 (dt, *J* = 13.1, 7.1 Hz, 3H), 2.00 (q, *J* = 6.9 Hz, 2H), 1.76 – 1.59 (m, 4H), 1.47 – 1.35 (m, 2H), 0.90 (dd, *J* = 37.7, 6.7 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 173.04, 163.49, 151.66, 142.38, 141.76, 138.16, 137.63, 126.40, 125.78, 122.59, 120.37, 115.78, 112.56, 55.88, 43.25, 36.66, 32.22, 30.96, 29.29, 25.26, 22.65. **HRMS** (ESI): m/z [(M+H)⁺] calcd for C₂₄H₃₁N₂O₅, 427.2227. found, 427.2235.

4-(2,2-difluoroethoxy)benzonitrile (3i)



Colorless solid (31.1 mg, 85% yield). **m.p.** 42.7-47.2°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H NMR** (300 MHz, CDCl₃) δ 7.62 (d, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.11 (t, *J* = 54.9 Hz, 1H), 4.23 (td, *J* = 12.9, 2.5 Hz, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 160.77, 134.19, 118.72, 115.31, 115.06, 113.14, 111.21, 105.56, 67.42, 67.18, 66.94. ¹⁹**F NMR** (471 MHz, CDCl₃) δ -125.23, -125.26, -125.29, -125.35, -125.37, -125.40. ¹⁹**F NMR** (471 MHz, CDCl₃) δ -125.26 (t, *J* = 12.8 Hz, 1F), -125.37 (t, *J* = 12.8 Hz, 1F). All spectral data match those previously reported.⁴

4-(2,2,2-trifluoroethoxy)benzonitrile (3j)



Colorless solid (26.5 mg, 66% yield). **m.p.** 59.1-63.1°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 15:1). ¹**H NMR** (300 MHz, CDCl₃) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.41 (q, *J* = 7.9 Hz, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 160.20, 134.19, 126.15, 123.94, 121.73, 119.52, 118.50, 115.47, 106.09, 65.93, 65.64, 65.35, 65.06. ¹⁹**F NMR** (471 MHz, CDCl₃) δ -73.77 (t, *J* = 7.2 Hz, 3F). All spectral data match those previously reported.⁶

4-(2-(2-methyl-5-nitro-1H-imidazol-1-yl)ethoxy)benzonitrile (3k)



Colorless solid (1.2 g, 88% yield). **m.p.** 148.2-151.5°C; The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.57 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 4.74 (t, J = 4.8 Hz, 2H), 4.38 (t, J = 4.8 Hz, 2H), 2.62 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 160.95, 151.64, 138.52, 134.29, 133.41, 118.81, 115.16, 105.39, 67.07, 45.80, 14.77. All spectral data match those previously reported.⁴

4-(dodecylthio)benzonitrile (5a)



Colorless solid (27.7 mg, 85% yield). **m.p.** 48.5-52.2°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 2.96 (t, *J* = 1.2, 0.1 Hz, 2H), 1.69 (p, *J* = 7.3 Hz, 2H), 1.44 (p, *J* = 7.0 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 16H), 0.88 (t, *J* = 6.7 Hz, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 145.33, 132.17, 126.66, 118.95, 107.89, 31.91, 29.62, 29.55, 29.46, 29.33, 29.11, 28.87, 28.57, 22.68, 14.11. All spectral data match those previously reported.⁷

2-(dodecylthio)benzonitrile (5b)

Colorless solid (23.1 mg, 71% yield). **m.p.** 54.3-61.2°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.60 (dd, J = 7.7, 1.1 Hz, 1H), 7.49 (dd, J = 7.8, 1.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.23 (td, J = 7.6, 1.1 Hz, 1H), 3.01 (d, J = 8.7 Hz, 2H), 1.68 (p, J = 7.3 Hz, 2H), 1.48 – 1.38 (m, 2H), 1.25 (s, 16H), 0.88 (t, J = 6.9 Hz, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 142.30, 133.64, 132.71, 128.66,

125.68, 117.18, 113.37, 33.57, 31.91, 29.62, 29.62, 29.56, 29.45, 29.34, 29.12, 28.82, 28.76, 22.69, 14.11. All spectral data match those previously reported.⁸

(4-(dodecylthio)phenyl)(phenyl)methanone (5c)



White solid (19.8 mg, 55% yield). **m.p.** 67.4-71.1°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 8:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.56 (s, 3H), 1.69 (p, *J* = 7.4 Hz, 2H), 1.44 (p, *J* = 7.0 Hz, 2H), 1.35 – 1.19 (m, 16H), 0.88 (t, *J* = 8.1 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 197.15, 145.02, 133.73, 128.73, 126.26, 32.00, 31.91, 29.63, 29.62, 29.56, 29.48, 29.34, 29.15, 28.90, 28.76, 26.41, 22.69, 14.11. All spectral data match those previously reported.⁷

(4-(dodecylthio)phenyl)(phenyl)methanone (5d)



White solid (28.6 mg, 59% yield). **m.p.** 67.4-71.1°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 15:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.79 – 7.75 (m, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.48 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 3.00 (t, *J* = 5.7 Hz, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.46 (p, *J* = 7.1 Hz, 2H), 1.28 (d, *J* = 14.3 Hz, 16H), 0.88 (t, *J* = 8.1 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 195.82, 144.40, 137.86, 133.90, 132.18, 130.64, 129.83, 128.25, 126.15, 32.10, 31.91, 29.64, 29.63, 29.57, 29.50, 29.34, 29.16, 28.92, 28.81, 22.69, 14.12. All spectral data match those previously reported.⁹

4-(ethylthio)benzaldehyde (5e)



Colorless solid (27.3 mg, 82% yield). **m.p.** 34.1-35.7°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 8:1). ¹H NMR (300 MHz, CDCl₃) δ 9.91 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.03 – 2.97 (m, 2H), 1.74 – 1.65 (m, 2H), 1.50 – 1.40 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 191.32, 147.31, 133.26, 130.14, 126.45, 32.05, 31.97, 29.77, 29.76, 29.70, 29.61, 29.47, 29.27, 29.04, 28.79, 22.82, 14.25. All spectral data match those previously reported.⁷

dodecyl(4-nitrophenyl)sulfane (5f)



Colorless solid (32.2 mg, 88% yield). **m.p.** 48.4-51.3°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 3.04 – 2.96 (m, 2H), 1.76 – 1.65 (m, 2H), 1.50 – 1.40 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.16, 144.72, 125.86, 123.84, 31.85, 29.57, 29.50, 29.41, 29.29, 29.06, 28.82, 28.41, 22.64, 14.07. All spectral data match those previously reported.⁷

benzyl(4-nitrophenyl)sulfane (5g)



Colorless oil (34.8 mg, 71% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.28 (m, 5H), 4.25 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.35, 145.42, 135.60, 128.98, 128.84, 127.95, 126.84, 124.07, 37.22. All spectral data match those previously reported.¹⁰

(4-nitrophenyl)(p-tolyl)sulfane (5h)



White solid (38.3 mg, 78% yield). **m.p.** 77.9-80.7°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 9.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 9.1 Hz, 2H), 2.42 (s, 3H). ¹³**C** NMR (126 MHz, CDCl₃) δ 149.32, 145.16, 140.23, 135.07, 130.85, 126.52, 126.15, 123.97, 21.34. All spectral data match those previously reported.¹¹

(4-chlorophenyl)(4-nitrophenyl)sulfane (5i)



White solid (37.7 mg, 71% yield). **m.p.** 85.1-89.8°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 9.1 Hz, 2H), 7.45 (q, *J* = 8.6 Hz, 4H), 7.21 – 7.15 (m, 2H). ¹³**C** NMR (126 MHz, CDCl₃) δ 147.59, 145.66, 136.08, 135.84, 130.29, 129.20, 127.00, 124.17. All spectral data match those previously reported.¹²

5-methyl-2-(2-((4-nitrophenyl)thio)propan-2-yl)cyclohexan-1-one (5j)



White solid (36.8 mg, 60% yield). **m.p.** 113-120.5°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). IR v max/cm⁻¹ (film): 3429, 1593, 1573, 1508, 1475, 1336, 1072, 852, 808, 738, 505; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 2.67 (dq, *J* = 13.2, 3.4 Hz, 1H), 2.40 – 2.27 (m, 2H), 2.01 – 1.87 (m, 3H), 1.70 – 1.57 (m, 2H), 1.44 (d, *J* = 14.8 Hz, 6H), 1.02 (d, *J* = 6.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.97, 148.01, 141.36, 137.48, 123.38, 57.98, 52.93, 52.26, 36.75,

34.54, 29.78, 28.20, 24.67, 22.19. **HRMS** (EI): m/z [M⁺] calcd for C₁₆H₂₁O₃N₁S₁, 307.1237. found, 307.1244.

methyl N-(tert-butoxycarbonyl)-S-(4-nitrophenyl)-L-cysteinate (5k)



Colorless oil (45 mg, 63% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1). ¹**H NMR** (600 MHz, CDCl₃) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 5.34 (d, *J* = 6.7 Hz, 1H), 4.65 (q, *J* = 4.9 Hz, 1H), 3.70 (s, 3H), 3.57 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.44 (dd, *J* = 14.0, 4.8 Hz, 1H), 1.41 (s, 9H). ¹³**C NMR** (151 MHz, CDCl₃) δ 170.68, 155.04, 145.77, 127.76, 124.13, 80.68, 53.32, 52.95, 35.17, 28.37. All spectral data match those previously reported.¹³

(2-((4-nitrophenyl)thio)propanoyl)glycine (5l)



White solid (27.3 mg, 78% yield). **m.p.** 147-155°C; The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). IR v_{max}/cm⁻¹ (film): 2924, 2854, 1658, 1631, 1464, 1377, 1219, 773; ¹H NMR (300 MHz, DMSO-d6) δ 12.61 (s, 1H), 8.61 (t, *J* = 5.9 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 2H), 7.55 (d, *J* = 9.1 Hz, 2H), 4.29 (q, *J* = 7.0 Hz, 1H), 3.79 (dd, *J* = 5.9, 2.2 Hz, 2H), 1.46 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, DMSO-d6) δ 170.96, 170.91, 145.75, 144.95, 127.72, 123.87, 43.80, 40.91, 18.05. HRMS (ESI): m/z calcd for C₁₁H₁₁N₂O₅S [(M-H)⁻], 283.0394. found, 283.0387.

N-acetyl-S-(4-nitrophenyl)-L-cysteine (5m)



Colorless oil (29.5 mg, 52% yield). The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). ¹**H NMR** (500 MHz, DMSO-d6) δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.1 Hz, 1H), 7.54 (d, *J* = 9.1 Hz, 1H), 4.46 (td, *J* = 8.4, 4.9 Hz, 1H), 3.54 (dd, *J* = 13.6, 5.0 Hz, 1H), 3.32 (dd, *J* = 13.7, 8.5 Hz, 1H), 1.83 (s, 2H). ¹³**C NMR** (126 MHz, DMSO-d6) δ 171.57, 169.54, 146.62, 144.70, 126.64, 123.97, 51.17, 32.75, 22.31. All spectral data match those previously reported.¹⁴

((S)-2-methyl-3-((4-nitrophenyl)thio)propanoyl)-L-proline (5n)



Colorless oil (50.7 mg, 75% yield). The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 10:1). ¹**H NMR** (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 4.57 (dd, *J* = 7.8, 3.0 Hz, 1H), 3.57 – 3.53 (m, 1H), 3.43 (dd, *J* = 13.2, 9.0 Hz, 2H), 3.11 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.93 (ddd, *J* = 9.0, 6.9, 5.3 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.08 – 1.98 (m, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 175.83, 172.60, 146.65, 145.54, 126.70, 124.25, 59.88, 47.85, 38.27, 35.29, 27.71, 24.94, 17.71. All spectral data match those previously reported. ¹⁵

methyl(4-nitrophenyl)selane (6a)

Yellow oil (38 mg, 88% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 147.68, 145.22, 130.53, 125.68, 8.61. All spectral data match those previously reported.¹⁶

ethyl(4-nitrophenyl)selane (6b)

Yellow oil (36.3 mg, 79% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 3.06 (q, *J* = 7.5 Hz, 2H), 1.51 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 147.89, 144.12, 131.91, 125.71, 22.61, 16.82. All spectral data match those previously reported.¹⁷

(4-nitrophenyl)(phenyl)selane (6c)



Yellow solid (24 mg, 43% yield). **m.p.** 54.1-59.2°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 3H), 7.36 (d, *J* = 9.0 Hz, 2H). ¹³**C** NMR (126 MHz, CDCl₃) δ 146.35, 144.06, 136.02, 130.19, 129.87, 129.52, 127.37, 124.11. All spectral data match those previously reported.¹⁸

benzyl(4-nitrophenyl)selane (6d)



Yellow solid (39 mg, 67% yield). **m.p.** 95.4-96.8°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.05 (m, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.26 – 7.23 (m, 1H), 4.25 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.98, 138.11, 137.74, 137.67, 137.45, 134.29, 134.16, 132.58, 132.55, 130.23, 130.20, 129.53, 129.18, 128.41, 128.09. All spectral data match those previously reported.¹⁹

4-(trimethylstannyl)benzonitrile (7a)

Colorless oil (26 mg, 55% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 20:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 2.7 Hz, 4H), 0.33 (s, 9H). ¹³**C** NMR (126 MHz, CDCl₃) δ 150.26, 136.30, 130.85, 119.12, 111.84, -9.49. All spectral data match those previously reported.²⁰

methyl 4-(trimethylstannyl)benzoate (7b)

MeOOC

Yellow oil (47.2 mg, 79% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 0.32 (s, 9H). ¹³**C** NMR (126 MHz, CDCl₃) δ 167.84, 150.04, 136.18, 130.22, 128.91, 52.44, -9.14. All spectral data match those previously reported.²⁰

ethyl 4-(trimethylstannyl)benzoate (7c)

EtOOC

Yellow oil (25 mg, 40% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.32 (s, 9H). ¹³**C NMR** (126 MHz, CDCl₃) δ 166.95, 149.45, 135.73, 130.18, 128.48, 60.86, 14.34, -9.55. All spectral data match those previously reported.²⁰

phenyl(4-(trimethylstannyl)phenyl)methanone (7d)

SnMe₃

Colorless oil (42 mg, 61% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 15:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.55 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 0.34 (s, 9H). ¹³**C** NMR (126 MHz, CDCl₃) δ 196.96, 137.70, 137.26, 135.65, 132.33, 130.06, 129.07, 128.27, 128.23, -9.51. All spectral data match those previously reported.²¹

4-(dimethyl(phenyl)silyl)benzonitrile (8a)

C SiMe₂Ph

Colorless oil (20.4 mg, 43% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.60 (s, 4H), 7.49 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.42 – 7.34 (m, 3H), 0.58 (s, 6H). ¹³**C** NMR (126 MHz, CDCl₃) δ 145.52, 136.59, 134.73, 134.22, 131.16, 129.77, 128.21, 119.10, 112.81, -2.60. All spectral data match those previously reported.²²

methyl 4-(dimethyl(phenyl)silyl)benzoate (8b)

Colorless oil (24.3 mg, 45% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.41 – 7.33 (m, 3H), 3.92 (s, 3H), 0.58 (s, 6H). ¹³**C** NMR (126 MHz, CDCl₃) δ 167.24, 144.68, 137.34, 134.16, 134.14, 130.58, 129.37, 128.55, 127.94, 52.12, -2.56. All spectral data match those previously reported.²²

ethyl 4-(dimethyl(phenyl)silyl)benzoate (8c)

EtOOC

Colorless oil (21.6 mg, 38% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). ¹**H NMR** (300 MHz, CDCl₃) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.37 (d, *J* = 5.9 Hz, 3H), 4.38 (q, *J* = 7.1

Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 0.58 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 166.88, 144.63, 137.52, 134.27, 134.26, 131.08, 129.48, 128.65, 128.06, 61.07, 14.47, -2.43. All spectral data match those previously reported.²³

(4-(dimethyl(phenyl)silyl)phenyl)(phenyl)methanone (8d)



Colorless oil (23.4 mg, 37% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1). IR v max/cm⁻¹ (film): 3462, 3066, 2956, 2922, 1658, 1597, 1446, 1386, 1317, 1278, 1251, 1112, 939, 922, 833, 816, 777, 731, 770, 665, 482; ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.80 (m, 3H), 7.77 – 7.74 (m, 2H), 7.66 – 7.62 (m, 2H), 7.57 – 7.52 (m, 2H), 7.50 – 7.47 (m, 3H), 7.40 – 7.37 (m, 2H), 0.60 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 196.73, 137.86, 137.49, 137.41, 137.19, 134.04, 133.91, 132.30, 129.95, 129.27, 128.92, 128.16, 127.84, -2.66. HRMS (EI): m/z [M⁺] calcd for C₂₁H₂₀OSi, 316.1278. found, 316.1267.

4-(3-hydroxy-3-methylbutoxy)benzonitrile (31)



White oil (34.8 mg, 85% yield). The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.01 (t, *J* = 6.5 Hz, 2H), 1.32 (s, 6H). ¹³**C** NMR (126 MHz, CDCl₃) δ 162.11, 134.16, 119.31, 115.36, 104.26, 70.33, 65.47, 41.74, 29.96. All spectral data match those previously reported.²⁴

4-(((1S,2S,5S)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)oxy)benzonitrile (3m)



White solid (50.4 mg, 93% yield). **m.p.** 87.2-91.5°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.64 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.61 (tdd, *J* = 8.0, 4.6, 2.2 Hz, 1H), 2.30 (ddt, *J* = 10.5, 6.0, 3.0 Hz, 1H), 2.10 (t, *J* = 5.8 Hz, 1H), 2.04 (dq, *J* = 5.6, 2.6 Hz, 1H), 1.79 (ddd, *J* = 14.0, 5.3, 2.5 Hz, 1H), 1.63 (d, *J* = 10.5 Hz, 1H), 1.36 (d, *J* = 9.9 Hz, 6H), 1.05 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 160.89, 134.27, 119.09, 116.74, 104.88, 76.31, 73.95, 53.96, 40.53, 38.67, 35.24, 30.67, 28.35, 27.96, 24.59. All spectral data match those previously reported.⁴

4-(((1R,3aS,5aR,5bR,7aR,9S,11aR,11bR,13aR,13bR)-3a-(hydroxymethyl)-5a,5b,8,8,11a-penta methyl-1-(prop-1-en-2-yl)icosahydro-1H-cyclopenta[a]chrysen-9-yl)oxy)benzonitrile (3n)



White solid (65.2 mg, 60% yield). **m.p.** 98-115°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1). IR v_{max}/cm^{-1} (film): 3483, 2927, 1670, 1606, 1510, 1460, 1259, 1219, 1018, 669; ¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 4.71 (s, 1H), 4.61 (s, 1H), 4.10 (d, J = 8.7 Hz, 1H), 3.67 (d, J = 8.8 Hz, 1H), 3.19 (dd, J = 11.5, 4.6 Hz, 1H), 2.46 (td, J = 10.8, 5.7 Hz, 1H), 2.08 (d, J = 13.3 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.70 (s, 3H), 1.01 (d, J = 3.8 Hz, 6H), 0.96 (s, 3H), 0.83 (s, 4H), 0.75 (s, 3H), 0.68 (d, J = 10.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 165.00, 151.92, 135.88, 121.23, 117.08, 111.89, 105.54, 80.84, 68.66, 57.16, 52.24, 50.67, 49.91, 48.93, 44.63, 42.80, 40.76, 40.60, 39.73, 39.05, 36.39, 36.06, 31.59, 29.87, 29.27, 29.00, 27.09, 22.70, 20.98, 20.16, 18.00, 17.96, 17.26, 16.74. HRMS (EI): m/z [M⁺] calcd for C₃₇H₅₃O₂N, 543.4071. found, 543.4075.

(8R,9S,13S,17S)-13-methyl-3-(4-nitrophenoxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclop enta[a]phenanthren-17-ol (30)



Colorless solid (64.5 mg, 82% yield). **m.p.** 200.4-215.4°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1). IR v max/cm⁻¹ (film): 3600, 3467, 2927, 2864, 1589, 1508, 1487, 1344, 1251, 1163, 1112, 922, 850, 752; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 9.2 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 9.2 Hz, 2H), 6.85 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.80 (s, 1H), 3.75 (t, *J* = 8.7 Hz, 1H), 2.98 – 2.82 (m, 3H), 2.39 – 2.22 (m, 2H), 2.19 – 2.08 (m, 1H), 2.01 – 1.87 (m, 2H), 1.76 – 1.17 (m, 11H), 0.81 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.65, 154.21, 144.27, 141.13, 139.60, 129.07, 127.78, 122.43, 119.56, 118.76, 83.72, 51.98, 46.04, 45.14, 40.46, 38.57, 32.49, 31.50, 28.93, 28.14, 25.05, 12.98. HRMS (EI): m/z [M⁺] calcd for C₂₄H₂₇O4N, 393.1935. found, 393.1927.

2-((4-nitrophenyl)thio)ethan-1-ol (50)



Yellow solid (31.8 mg, 80% yield). **m.p.** 79.8-88.4°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1). ¹**H NMR** (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.25 (t, *J* = 6.1 Hz, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 146.41, 145.54, 127.00, 124.19, 60.66, 35.25. All spectral data match those previously reported.²⁵

4-((4-nitrophenyl)thio)phenol (5p)



White solid (37 mg, 75% yield). **m.p.** 147.5-155.7°C; The product was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 8:1). ¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.7

Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 157.41, 150.08, 144.99, 137.41, 125.60, 123.99, 120.31,

117.22. All spectral data match those previously reported.²⁵

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7. Copies of NMR spectra data



¹H, ¹³C and¹⁹F NMR spectra of compound 1a





¹H, ¹³C and ¹⁹F NMR spectra of compound 1b





¹H, ¹³C and ¹⁹F NMR spectra of compound 1c




¹H, ¹³C and ¹⁹F NMR spectra of compound 1d





¹H, ¹³C and ¹⁹F NMR spectra of compound 1e





¹H, ¹³C and ¹⁹F NMR spectra of compound 1f





¹H, ¹³C and¹⁹F NMR spectra of compound 1g





¹H, ¹³C and ¹⁹F NMR spectra of compound 1h





¹H, ¹³C and ¹⁹F NMR spectra of compound 1i





¹H, ¹³C and ¹⁹F NMR spectra of compound 1j





¹H and ¹³C NMR spectra of compound 3a



¹H and ¹³C NMR spectra of compound 3b



$^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 3c



¹H, ¹³C and ¹⁹F NMR spectra of compound 3d





¹H and ¹³C NMR spectra of compound 3e



¹H and ¹³C NMR spectra of compound 3f



¹H and ¹³C NMR spectra of compound 3g



¹H and ¹³C NMR spectra of compound 3h













¹H and ¹³C NMR spectra of compound 5a



¹H and ¹³C NMR spectra of compound 5b



S65



¹H and ¹³C NMR spectra of compound 5d



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 5e



S68





¹H and ¹³C NMR spectra of compound 5h




S72



S73





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of compound 5m





S77





¹H and ¹³C NMR spectra of compound 6c



¹H and ¹³C NMR spectra of compound 6d



¹H and ¹³C NMR spectra of compound 7a



S82





¹H and ¹³C NMR spectra of compound 7d



¹H and ¹³C NMR spectra of compound 8a



¹H and ¹³C NMR spectra of compound 8b









¹H and ¹³C NMR spectra of compound 3m





¹H and ¹³C NMR spectra of compound 30



