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Supporting Information

Selective synthesis of alkyl amines and N-vinylazoles from vinyl

sulfonium salts with N-nucleophiles

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1. General Information

All solvents were dried over molecular sieves. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The products were isolated by column chromatography on silica gel (200-300 mesh) by using petroleum ether (PE, 30-60 °C) and ethyl acetate (EA) as eluents. Silica gel for column chromatography was purchased from AnhuiLiangchen Chemical Co, Lt. All yields described herein are the isolated yields after column chromatography. Reaction progress and product mixtures were routinely monitored by TLC using TLC SiO₂ sheets, and compounds were visualized under ultraviolet light. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer. Chemical shifts are reported in ppm with the residual solvent signal as the internal standard. For ¹H NMR: CDCl₃, δ 7.26; CD₃OD, δ 3.31. For ¹³C NMR: CDCl₃, δ 77.00; CD₃OD, δ 49.15. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), brs (broad singlet). High–Resolution Mass Spectra (HRMS) were recorded on Agilent 1290UPLC-QTOF-MS (6546). Melting points were measured with a melting point instrument (Shanghai Yidian Physical Optical Instrument Co., Ltd., SGW, and X-4A) and were uncorrected.

2. Synthesis of vinyl sulfonium salts



General experimental procedures for the synthesis of vinyl sulfonium salts: Under an argon atmosphere, tetramethylene sulfoxide (0.49 mL, 5.5 mmol) and anhydrous DCM (25 mL) were added to a 100 mL round bottom flask at -40 °C. The Tf₂O (0.93 mL, 5.5 mmol) was added dropwise under argon, then styrene derivative (5.0 mmol) was added gradually. The reaction mixture was stirred at -40 °C for 15 min before warming to 0 °C. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether (100 mL) to precipitate out the vinyl sulfonium salts solid. The solid was collected by recrystallisation (DCM/Et₂O) to afford the sulfonium salts 1.



(E)-1-styryltetrahydro-1H-thiopheN-1-ium trifluoromethanesulfonate^[1]

1a was synthesized following the general procedure on 10.0 mmol scale. Sulfonium salt **1a** was obtained as a white solid in 90% yield (3.15 g). ¹**H NMR** (400 MHz, CD₃OD) δ 7.75–7.64 (m, 3H), 7.52–7.42 (m, 3H), 7.08 (d, *J* = 15.2 Hz, 1H), 3.83–3.76 (m, 2H), 3.60–3.50 (m, 2H), 2.58–2.45 (m, 2H), 2.38–2.27 (m, 2H).



(E)-1-(4-(methylthio)styryl)tetrahydro-1H-thiopheN-1-ium trifluoromethanesulfonate

1b was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt **1b** was obtained as a yellow solid in 80% yield (926.5 mg). M.p. = 94-96 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.62–7.57 (m, 3H), 7.31–7.28 (m, 2H), 6.99 (d, *J* = 15.2 Hz, 1H), 3.81–3.74 (m, 2H), 3.54–3.48 (m, 2H), 2.54–2.46 (m, 5H), 2.34–2.28 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 150.04, 145.90, 130.59, 130.18, 126.90, 121.97(d, *J* = 320.2 Hz), 112.75, 49.01, 29.95, 14.87. HRMS *m/z* (ESI)

calcd for $C_{13}H_{17}S_2$ (M–OTf)⁺ 237.0766, found 237.0766.



(E)-1-(4-Fluorostyryl)tetrahydro-1H-thiopheN-1-ium trifluoromethanesulfonate^[1]

1c was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt **1c** was obtained as a white solid in 95% yield (680.5 mg). ¹H NMR (400 MHz, CD₃OD) δ 7.75–7.71 (m, 2H), 7.67 (d, J = 15.2 Hz, 1H), 7.22–7.17 (m, 2H), 7.04 (d, J = 15.2 Hz, 1H), 3.83–3.76 (m, 2H), 3.57–3.51 (m, 2H), 2.56–2.47 (m, 2H), 2.36–2.27 (m, 2H).





(E)-1-(2-Chlorostyryl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate^[1]

1d was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt 1d was obtained as a white solid in 82% yield (613.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.81 (m, 2H), 7.43–7.27 (m, 3H), 7.19 (d, *J* = 15.3 Hz, 1H), 3.94–3.84 (m, 2H), 3.62–3.50 (m, 2H), 2.66–2.51 (m, 2H), 2.41–2.28 (m, 2H).



(E)-1-(2-phenylprop-1-en-1-yl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate

1e was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt 1e was obtained as a white solid in 83% yield (690.5 mg). M.p. = 128-130 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.64–7.61 (m, 2H), 7.47–7.43 (m, 3H), 6.60 (d, *J* = 1.2 Hz, 1H), 3.84–3.77 (m, 2H), 3.56–3.50 (m, 2H), 2.55 (d, *J* = 1.2 Hz, 3H), 2.53–2.44 (m, 2H), 2.36–2.27 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 159.49, 139.84, 131.76, 130.10, 127.72, 121.96 (d, *J* = 320.2Hz), 113.11, 49.00, 30.08, 19.56. HRMS *m/z* (ESI) calcd for C₁₃H₁₇S (M–OTf)⁺ 205.1045, found 205.1045.



1-(2,2-diphenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate^[2]

If was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt **If** was obtained as a white solid in 93% yield (772.0 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.52–7.47 (m, 3H), 7.44–7.32 (m, 5H), 7.24–7.20 (m, 1H), 6.92 (s, 1H), 3.75–3.68 (m, 2H), 3.63–3.56 (m, 2H), 2.61–2.54 (m, 2H), 2.32–2.24 (m, 2H).



(E)-1-(1-phenylprop-1-en2-yl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate

1g was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt **1g** was obtained as a white solid in 61% yield (431.9 mg). M.p. = 95-97 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.62–7.60 (m, 1H), 7.52–7.40 (m, 5H), 3.84–3.68 (m, 4H), 2.49–2.41 (m, 2H), 2.35 (s, 3H), 2.33–2.27 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 147.12, 134.94, 131.23, 130.84, 130.08, 125.18, 121.95 (d, *J* = 319.2Hz), 44.88, 30.57, 13.96. HRMS *m/z* (ESI) calcd for C₁₃H₁₇S (M–OTf)⁺ 205.1045, found 205.1045.



(E)-1-(1, 2-diphenylvinyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate^[2]

1h was synthesized following the general procedure on 1 mmol scale. Sulfonium salt **1h** was obtained as a white solid in 60% yield (249.6 mg). ¹**H** NMR (400 MHz, CD₃OD) δ 7.77 (s, 1H), 7.69–7.62 (m, 3H), 7.51–7.48 (m, 2H), 7.35–7.31 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.85–3.78 (m, 2H), 3.65–3.58 (m, 2H), 2.11–2.01 (m, 2H), 1.76–1.66 (m, 2H).



1-(1H-inden-2-yl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (1i)

1i was synthesized following the general procedure on 2 mmol scale. Sulfonium salt **1i** was obtained as a white solid in 65% yield (423.0 mg). M.p. = 117-119 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.95– 7.94 (s, 1H), 7.64–7.59 (m, 2H), 7.47–7.38 (m, 2H), 3.95 (s, 2H), 3.91–3.82 (m, 2H), 3.79–3.71 (m, 2H), 2.58–2.47 (m, 2H), 2.43–2.32 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 148.24, 148.16, 146.11, 142.27, 129.96, 128.75, 128.58, 125.55, 124.76, 120.35 (d, *J* = 320.2 Hz), 48.58, 39.38, 30.52. HRMS *m/z* (ESI) calcd for C₁₃H₁₅S (M–OTf)⁺ 203.0889, found 203.0889.



1-(3,4-dihydronaphthalen-2-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate

1j was synthesized following the general procedure on 2 mmol scale. Sulfonium salt 1j was obtained as a white solid in 81% yield (591.8 mg). M.p. = 110-112 °C; ¹H NMR (400 MHz, CD₃OD) δ 7.54 (s, 1H), 7.40–7.24 (m, 4H), 3.83–3.67 (m, 4H), 3.09 (t, *J* = 8.2 Hz, 2H), 2.75–2.69 (m, 2H), 2.51– 2.39 (m, 2H), 2.37–2.25 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 143.87, 136.99, 132.53, 132.30, 130.05, 129.13, 128.51, 124.33, 121.96 (d, *J* = 320.2 Hz), 45.49, 30.64, 28.70, 23.74. HRMS *m/z* (ESI) calcd for C₁₄H₁₇S (M–OTf)⁺ 217.1405, found 217.1406.



1-(benzofuran-2-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate

1k was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt 1k was obtained as a white solid in 56% yield (395.5 mg). M.p. = 102-104 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.92 (d, *J* = 0.9 Hz, 1H), 7.83–7.79 (m, 1H), 7.72–7.69 (m, 1H), 7.62–7.57 (m, 1H), 7.46–7.42 (m, 1H), 4.00–3.93 (m, 4H), 2.77–2.68 (m, 2H), 2.50–2.41 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 159.27, 137.75, 130.14, 127.85, 126.21, 124.27, 121.56, 113.29, 49.94, 31.07. HRMS *m/z* (ESI) calcd for C₁₂H₁₃OS (M–OTf)⁺ 205.0682, found 205.0682.



1-(benzo[b]thiophen-2-yl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate

11 was synthesized following the general procedure on 2.0 mmol scale. Sulfonium salt 11 was obtained as a white solid in 55% yield (406.1 mg). M.p. = 101-102 °C; ¹H NMR (400 MHz, CD₃OD) δ 8.67 (s, 1H), 8.13–8.09 (m, 2H), 7.68–7.57 (m, 2H), 4.09–4.00 (m, 2H), 3.94–3.85 (m, 2H), 2.64–2.54 (m, 2H), 2.52–2.42 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 141.53, 137.08, 135.50, 127.90, 127.58, 124.93, 122.25, 121.94 (d, *J* = 319.2 Hz), 116.94, 49.36, 30.01. HRMS *m/z* (ESI) calcd for C₁₂H₁₃S₂ (M–OTf)⁺ 221.0453, found 221.0453.



1-((E)-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)vinyl) tetrahydro-1H-thiophen-1-ium

trifluoromethan esulfonate

1m was synthesized following the general procedure on 3 mmol scale. Sulfonium salt **1m** was obtained as a white solid in 45% yield (687.0 mg). M.p. = 211-214 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.61 (d, *J* = 15.2 Hz, 1H), 7.44–7.39 (m, 3H), 7.01 (d, *J* = 15.2 Hz, 1H), 3.81–3.76 (m, 2H), 3.55–3.50 (m, 2H), 2.96–2.93 (m, 2H), 2.53–2.47 (m, 4H), 2.35–2.28 (m, 3H), 2.18–2.13 (m, 1H), 2.11–2.05 (m, 2H), 1.93–1.89 (m, 1H), 1.70–1.45 (m, 6H), 0.92 (s, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 223.51, 150.71, 145.66, 139.09, 131.88, 130.38, 127.43, 127.17, 113.12, 51.81, 48.98, 46.06, 39.42, 36.82, 32.89, 30.36, 29.98, 27.49, 26.81, 22.62, 14.37. HRMS *m/z* (ESI) calcd for C₂₄H₃₁OS (M–OTf)⁺ 367.2090, found 367.2091.

3. Experimental Optimization

	S ⁺ OTf	+ Conditions	•	S	
	1a	2a		3aa	
Entry	2a (equiv)	Base (equiv)	Solvent	T (°C)	Yield of 3aa ^b
1	1.5	t-BuOK (2.0)	THF	rt	20%
2	1.5	t-BuONa (2.0)	THF	rt	18%
3	1.5	t-BuOLi (2.0)	THF	rt	30%
4	1.5	K ₃ PO ₄ (2.0)	THF	rt	25%
5	1.5	KOH (2.0)	THF	rt	28%
6	1.5	Cs_2CO_3 (2.0)	THF	rt	30%
7	1.5	NaCO ₃ (2.0)	THF	rt	35%
8	1.5	NaOH (2.0)	THF	rt	35%
9	1.5	NaH (2.0)	THF	rt	32%
10	1.5	Na ₃ PO ₄ (2.0)	THF	rt	38%
11	1.5	Et ₃ N (2.0)	THF	rt	40%
12	1.5	-	THF	rt	32%
13	2.0	-	THF	rt	35%
14	3	-	THF	rt	46%
15	4.0	-	THF	rt	48%
16	3	-	THF	40	50%
17	3	-	THF	60	72%
18	3	-	THF	80	89%
19	3	-	THF	100	86%
20 ^c	2.0	-	THF	80	88%

Table S1: Optimization of the Reaction Conditions for the Synthesis of 3aa

^{*a*} Reaction conditions: **1** (0.3 mmol), amines **2a** (3.0 equiv), THF (2.0 mL), 80 ^oC, 6 h, under an air atmosphere; ^{*b*} Isolated yield after chromatography; ^{*c*} Under an argon atmosphere.

		oTf + ^H _N <u>−</u> Re	action conditions		
	1a	2a'		4aa'	
Entry	2a' (equiv)	Base (equiv)	Solvent	T (°C)	Yield of 4aa' ^b
1	3.0	-	THF	80	15%
2	3.0	-	THF	rt	18%
3	1.5	-	THF	rt	14%
4	1.5	t-BuOK (1.0)	THF	rt	78%
5	1.5	Cs ₂ CO ₃ (1.0)	THF	rt	82%
6	1.5	KOH (1.0)	THF	rt	86%
7	1.5	K ₃ PO ₄ (1.0)	THF	rt	60%
8	1.5	NaH (1.0)	THF	rt	80%
9	1.5	Et ₃ N (1.0)	THF	rt	20%
10	1.5	DBU (1.0)	THF	rt	66%
11	1.5	KOH (2.0)	THF	rt	86%
12	1.5	KOH (3.0)	THF	rt	86%

Table S2: Optimization of the Reaction Conditions for the Synthesis of 4aa'

^{*a*} Reaction conditions: **1a** (0.3 mmol), amines **2a'** (1.5 equiv), KOH (1.0 equiv), THF (2.0 mL), rt, 6 h, under an air atmosphere; ^{*b*} Isolated yield after chromatography.

4. General procedures for the products



General procedure A for the synthesis of alkylamines: A 10.0 mL schlenk tube with a stirring bar was added vinyl sulfonium salts **1** (0.3 mmol, 1.0 equiv), **2** (0.9 mmol, 3.0 equiv) and THF (2.0 mL). The reaction mixture was stirred at 80 °C for 3-6 h. After complete consumption of the vinyl sulfonium salts (monitored by the TLC), the resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel to afford desired product (**3** and **5**).



General procedure B for the synthesis of *N***-vinylazoles:** A 10.0 mL schlenk tube with a stirring bar was added vinyl sulfonium salts **1a** (102 mg, 0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), KOH (16.8 mg, 0.3 mmol, 1.0 equiv) or KOH (50.4 mg, 0.3 mmol, 3.0 equiv) and THF (2.0 mL). The reaction mixture was stirred at room temperature for 3-6 h. After complete consumption of the vinyl sulfonium salts (monitored by the TLC), the resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel to afford desired product (**4 and 6**).

5. Characterization data of products



(*E*)-*N*-(4-(styrylthio)butyl)aniline (3aa). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), **3aa** was obtained as a colorless oil in 89% yield (75.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.29 (m, 4H), 7.22–7.16 (m, 3H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 15.6 Hz, 1H), 3.60 (brs, 1H), 3.17 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 1.87–1.74 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.21, 136.99, 129.24, 128.62, 127.29, 126.88, 125.49, 124.82, 117.31, 112.73, 43.44, 32.39, 28.57, 27.01. HRMS *m*/z (ESI) calcd for C₁₈H₂₁NS (M+H)⁺ 284.1764, found 284.1764.



(*E*)-*N*-(4-(styrylthio)butyl)-[1,1'-biphenyl]-2-amine (3ab). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ab was obtained as a white solid in 88% yield (94.8 mg). M.p. = 39-40 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.37 (m, 4H), 7.33–7.18 (m, 7H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.70–6.65 (m, 2H), 6.44 (d, *J* = 15.5 Hz, 1H), 3.89 (brs, 1H), 3.12 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 1.74–1.64 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 144.92, 139.36, 136.93, 130.19, 129.26, 128.85, 128.67, 128.59, 127.52, 127.15, 127.11, 126.84, 125.44, 124.74, 116.79, 110.23, 43.38, 32.26, 28.34, 26.97. HRMS *m/z* (ESI) calcd for C₂₄H₂₅NS (M+H)⁺ 360.1780, found 360.1782.



(*E*)-*N*-(4-(styrylthio)butyl)naphthalen-1-amine (3ac). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ac was obtained as a colorless

oil in 85% yield (84.9 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.79–7.76 (m, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.41–7.36 (m, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.30–7.27 (m, 4H), 7.23 (d, J = 8.3 Hz, 1H), 7.21–7.17 (m, 1H), 6.72 (d, J = 15.6 Hz, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.50 (d, J = 15.6 Hz, 1H), 4.32 (brs, 1H), 3.32 (t, J = 6.4 Hz, 2H), 2.89 (t, J = 6.7 Hz, 2H), 1.96–1.89 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 143.31, 136.97, 134.28, 128.65, 128.62, 127.40, 126.89, 126.58, 125.68, 125.50, 124.74, 124.68, 123.35, 119.74, 117.34, 104.29, 43.67, 32.42, 28.32, 27.13. HRMS *m*/*z* (ESI) calcd for C₂₂H₂₃NS (M+H)⁺ 334.1624, found 334.1626.



(*E*)-*N*-(4-(styrylthio)butyl)quinolin-8-amine (3ad). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ad was obtained as a yellow solid in 95% yield (95.2 mg). M.p. = 40-42 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, *J* = 3.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.39–7.32 (m, 2H), 7.29–7.23 (m, 4H), 7.21–7.15 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.73–6.65 (m, 2H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.15 (brs, 1H), 3.37–3.33 (m, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 1.94–1.87 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.76, 144.70, 138.13, 137.01, 135.94, 128.63, 128.57, 127.75, 127.15, 126.79, 125.46, 124.89, 121.33, 113.69, 104.46, 42.84, 32.39, 28.29, 27.12. HRMS *m/z* (ESI) calcd for C₂₁H₂₂N₂S (M+H)⁺ 335.1576, found 335.1581.



(*E*)-*N*-benzyl-4-(styrylthio)butan-1-amine (3ae). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ae was obtained as a colorless oil in 66% yield (58.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.15 (m, 10H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.78 (s, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 1.78–1.71 (m, 2H), 1.68–1.61 (m, 2H), 1.41 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.34, 137.04, 128.57, 128.35, 128.06, 126.90, 126.88, 126.76, 125.42, 125.06, 53.96, 48.76, 32.48, 29.13, 27.21. HRMS *m/z* (ESI) calcd for C₁₉H₂₃NS (M+H)⁺ 298.1624, found 298.1625.



(*E*)-*N*-(4-(styrylthio)butyl)cyclohexanamine (3af). Prepared following the general procedure A, after purification by column chromatography using PE/EA (5:1), 3af was obtained as a colorless oil in 64% yield (55.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 4H), 7.21–7.16 (m, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.45–2.39 (m, 1H), 1.90–1.85 (m, 2H), 1.76–1.71 (m, 4H), 1.66–1.60 (m, 3H), 1.26–1.21 (m, 2H), 1.18–1.14 (m, 1H), 1.09–1.02 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.06, 128.58, 126.91, 126.77, 125.43, 125.10, 56.84, 46.41, 33.62, 32.53, 29.64, 27.39, 26.14, 25.06. HRMS *m/z* (ESI) calcd for C₁₈H₂₇NS (M+H)⁺ 290.1937, found 290.1937.



(*E*)-*N*-(tert-butyl)-4-(styrylthio)butan-1-amine (3ag). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ag was obtained as a colorless oil in 74% yield (58.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.27 (m, 4H), 7.21–7.16 (m, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.78–1.71 (m, 2H), 1.64–1.56 (m, 2H), 1.10 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 137.08, 128.59, 126.91, 126.78, 125.44, 125.15, 50.29, 42.07, 32.56, 30.27, 29.01, 27.55. HRMS *m/z* (ESI) calcd for C₁₆H₂₅NS (M+H)⁺ 264.1780, found 264.1780.



(*E*)-*N*-(**prop-2-yn-1-yl**)-4-(styrylthio)butan-1-amine (3ah). Prepared following the general procedure A under argon atmosphere, after purification by column chromatography using PE/EA (10:1), 3ah was obtained as a colorless oil in 71% yield (52.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.26 (m, 4H), 7.21–7.17 (m, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 3.43 (s, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 6.9 Hz, 2H), 2.22 (s, 1H), 1.80–1.72 (m, 2H), 1.68–1.60 (m, 2H), 1.37 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 137.00, 128.57, 126.91, 126.78, 125.41, 124.98, 82.10, 71.31, 47.98, 38.07, 32.39, 28.82, 27.13. HRMS *m/z* (ESI) calcd for C₁₅H₁₉NS



(*E*)-4-(styrylthio)-*N*-(thiophen-2-ylmethyl)butan-1-amine (3ai). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ai was obtained as a colorless oil in 77% yield (70.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 4H), 7.21–7.18 (m, 2H), 6.96–6.91 (m, 2H), 6.71 (d, *J* = 15.5 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 3.99 (s, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 1.80–1.72 (m, 2H), 1.69–1.62 (m, 2H), 1.49 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.20, 137.07, 128.59, 126.99, 126.79, 126.58, 125.46, 125.07, 124.77, 124.28, 48.48, 48.37, 32.49, 29.04, 27.19. HRMS *m/z* (ESI) calcd for C₁₇H₂₁NS₂ (M+H)⁺ 304.1188, found 304.1190.



(*E*)-*N*-benzhydryl-4-(styrylthio)butan-1-amine (3aj). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3aj was obtained as a colorless oil in 95% yield (106.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.34–7.27 (m, 8H), 7.22 (t, *J* = 7.3 Hz, 3H), 6.73 (d, *J* = 15.5 Hz, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 4.83 (s, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 6.9 Hz, 2H), 1.82–1.75 (m, 2H), 1.71–1.64 (m, 2H), 1.53 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.17, 137.07, 128.58, 128.43, 127.21, 126.94, 126.77, 125.44, 125.12, 67.54, 47.56, 32.50, 29.27, 27.19. HRMS *m/z* (ESI) calcd for C₂₅H₂₇NS (M+H)⁺ 374.1937, found 374.1937.



(*E*)-*N*-cyclohexyl-*N*-(4-(styrylthio)butyl)cyclohexanamine(3ak). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ak was obtained as a colorless oil in 70% yield (77.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 4H), 7.20–

7.16 (m, 1H), 6.73 (d, J = 15.6 Hz, 1H), 6.46 (d, J = 15.6 Hz, 1H), 2.81 (t, J = 7.4 Hz, 2H), 2.52 (t, J = 7.4 Hz, 4H), 1.78–1.64 (m, 10H), 1.61–1.48 (m, 4H), 1.26–1.18 (m, 8H), 1.10–1.02 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.14, 128.56, 126.68, 126.60, 125.39, 125.38, 57.87, 45.65, 32.67, 31.68, 30.44, 27.25, 26.43, 26.28. HRMS *m*/*z* (ESI) calcd for C₂₄H₃₇NS (M+H)⁺ 372.2719, found 372.2719.



(*E*)-*N*,*N*-diisopropyl-4-(styrylthio)butan-1-amine (3al). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3al was obtained as a colorless oil in 79% yield (70.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27(m, 4H), 7.21–7.16 (m, 1H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.04–2.97 (m, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.73–1.65 (m, 2H), 1.57–1.49 (m, 2H), 1.00 (d, *J* = 6.5 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 137.13, 128.58, 126.70, 126.64, 125.40, 125.31, 48.25, 44.60, 32.62, 30.29, 27.28, 20.65. HRMS *m/z* (ESI) calcd for C₁₈H₂₉NS (M+H)⁺ 292.2093, found 292.2095.



(*E*)-*N*,*N*-dimethyl-4-(styrylthio)butan-1-amine (3am). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3am was obtained s a colorless oil in 46% yield (32.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.25 (m, 4H), 7.20–7.17 (m, 1H), 6.72 (d, *J* = 15.5 Hz, 1H), 6.47 (d, *J* = 15.5 Hz, 1H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.22 (s, 6H), 1.76–1.69 (m, 2H), 1.65–1.58 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.06, 128.58, 126.82, 126.75, 125.41, 125.07, 59.13, 45.42, 32.47, 27.24, 26.75. HRMS *m/z* (ESI) calcd for C₁₄H₂₁NS (M+H)⁺ 236.1467, found 236.1468



(*E*)-*N*-methyl-*N*-(4-(styrylthio)butyl)aniline (3an). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3an was obtained as a colorless oil in 58% yield (51.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.18 (m, 7H), 6.69 (d, *J* = 8.2 Hz, 4H), 6.47 (d, *J* = 15.6 Hz, 1H), 3.36–3.29 (m, 2H), 2.91 (s, 3H), 2.83–2.77 (m, 2H), 1.75–1.68 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.14, 136.95, 129.14, 128.58, 127.07, 126.82, 125.44, 124.89, 116.06, 112.14, 52.22, 38.30, 32.47, 27.04, 25.92. HRMS *m*/*z* (ESI) calcd for C₁₉H₂₃NS (M+H)⁺ 298.1624, found 298.1624.



(*E*)-*N*-benzyl-*N*-methyl-4-(styrylthio)butan-1-amine (3ao). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), **3ao** was obtained as a colorless oil in 91% yield (83.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.16 (m, 10H), 6.71 (d, *J* = 15.2 Hz, 1H), 6.46 (d, *J* = 15.0 Hz, 1H), 3.47 (s, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.39 (t, *J* = 6.3 Hz, 2H), 2.19 (s, 3H), 1.77–1.61 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 139.14, 137.09, 128.97, 128.58, 128.16, 126.87, 126.77, 126.73, 125.42, 125.16, 62.30, 56.61, 42.18, 32.44, 27.12, 26.39. HRMS *m/z* (ESI) calcd for C₂₀H₂₅NS (M+H)⁺ 312.1780, found 312.1780.



(*E*)-*N*,*N*-dibenzyl-4-(styrylthio)butan-1-amine (3ap). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), **3ap** was obtained as a colorless oil in 89% yield (103.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 7.1 Hz, 4H), 7.30–7.27 (m, 8H), 7.22–7.16 (m, 3H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 3.53 (s, 4H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 6.5 Hz, 2H), 1.73–1.60 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 139.75, 137.09, 128.76, 128.57, 128.14, 126.78, 126.71, 126.68, 125.40, 125.17, 58.28, 52.33,

32.20, 26.74, 25.94. HRMS *m/z* (ESI) calcd for C₂₆H₂₉NS (M+H)⁺ 388.2093, found 388.2095.



(*E*)-*N*-allyl-*N*-benzyl-4-(styrylthio)butan-1-amine (3aq). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3aq was obtained as a colorless oil in 82% yield (83.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.17 (m, 10H), 6.70 (d, *J* = 15.4 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 5.92–5.82 (m, 1H), 5.20–5.11 (m, 2H), 3.55 (s, 2H), 3.06 (d, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 7.1 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 1.74–1.58 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 139.65, 137.12, 135.99, 128.83, 128.58, 128.14, 126.77, 126.74, 125.43, 125.20, 117.22, 58.11, 56.77, 52.51, 32.41, 27.03, 26.06. HRMS *m*/*z* (ESI) calcd for C₂₂H₂₇NS (M+H)⁺ 338.1937, found 338.1938.



(*E*)-1-(4-(styrylthio)butyl)pyrrolidine (3ar). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3ar was obtained as a colorless oil in 71% yield (55.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.25 (m, 4H), 7.20–7.16 (m, 1H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.51–2.44 (m, 6H), 1.79–1.64 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 137.06, 128.57, 126.76, 126.73, 125.40, 125.09, 55.93, 54.17, 32.48, 28.16, 27.50, 23.35. HRMS *m*/*z* (ESI) calcd for C₁₆H₂₃NS (M+H)⁺ 262.1624, found 262.1624.



(*E*)-1-(4-(styrylthio)butyl)piperidine (3as). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), **3as** was obtained as a colorless oil in 93% yield (76.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 4H), 7.21–7.16 (m, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.37–2.30 (m, 6H), 1.74–1.62 (m, 4H), 1.61–1.55 (m, 4H), 1.45–1.40 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.08, 128.56,

126.79, 126.73, 125.41, 125.13, 58.83, 54.58, 32.52, 27.57, 26.08, 25.96, 24.44. **HRMS** *m*/*z* (ESI) calcd for C₁₇H₂₅NS (M+H)⁺ 276.1780, found 276.1780.



(*E*)-4-(4-(styrylthio)butyl)morpholine (3at). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 3at was obtained as a colorless oil in 88% yield (73.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 4H), 7.22–7.16 (m, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 15.5 Hz, 1H), 3.71 (t, *J* = 4.4 Hz, 4H), 2.83 (t, *J* = 7.1 Hz, 2H), 2.46–2.41 (m, 4H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.77–1.70 (m, 2H), 1.68–1.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.06, 128.61, 127.03, 126.83, 125.44, 125.01, 66.98, 58.38, 53.72, 32.51, 27.27, 25.57. HRMS *m/z* (ESI) calcd for C₁₆H₂₃NOS (M+H)⁺ 278.1573, found 278.1573.



(*E*)-1-(4-(styrylthio)butyl)-1*H*-pyrazole (**3aa'**). Prepared following the general procedure A, after purification by column chromatography using PE/EA (5:1), **3aa'** was obtained as a colorless oil in 55% yield (42.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.37 (s, 1H), 7.31–7.25 (m, 4H), 7.19 (s, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 6.23 (s, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.06–1.98 (m, 2H), 1.72–1.64 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.21, 136.92, 128.86, 128.58, 127.32, 126.87, 125.45, 124.61, 105.35, 51.45, 32.00, 29.36, 26.39. HRMS *m/z* (ESI) calcd for C₁₅H₁₈N₂S (M+H)⁺ 259.1263, found 259.1264.



1-(1-phenylvinyl)-1*H*-pyrazole.^[3] (4aa'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 4aa' was obtained as a colorless oil in 86% yield (43.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.72–7.66 (m, 1H), 7.51–7.49 (m, 1H), 7.43–7.37 (m, 5H), 6.36 (t, *J* = 2.1 Hz, 1H), 5.60 (s, 1H), 5.20 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ



1-(1-phenylvinyl)-1*H*-imidazole ^[3] (4ab'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 4aa' was obtained as a colorless oil in 80% yield (40.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.43–7.35 (m, 3H), 7.34–7.31 (m, 2H), 7.13 (s, 1H), 7.02 (s, 1H), 5.32 (s, 1H), 5.29 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.19, 137.12, 135.59, 129.66, 129.60, 128.69, 127.20, 119.25, 106.36.



1-(1-phenylvinyl)-1*H***-pyrrole ^[3] (4ac').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ac'** was obtained as a colorless oil in 79% yield (39.6 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 5H), 6.83–6.80 (m, 2H), 6.27–6.25 (m, 2H), 5.18 (s, 1H), 5.09 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 146.36, 136.97, 129.09, 128.34, 127.86, 121.07, 109.32, 103.24.



2-(1-phenylvinyl)-2*H***-1,2,3-triazole (4ad')**. Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ac'** was obtained as a colorless oil in 46% yield (23.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 2H), 7.41 (s, 5H), 5.91 (s, 1H), 5.40 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 146.05, 135.31, 134.75, 129.31, 128.30, 128.16, 107.51. HRMS *m/z* (ESI) calcd for C₁₀H₉N₃ (M+H)⁺ 172.0869, found 172.0869.



1-(1-phenylvinyl)-1*H***-1,2,4-triazole**^[3] **(4ae').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ae'** was obtained as a colorless oil in 83% yield (42.5 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 8.15 (s, 1H), 8.06 (s, 1H), 7.46–7.30 (m, 5H), 5.69 (s, 1H), 5.36 (s, 1H). ¹³C **NMR** (101 MHz, CDCl₃) δ 152.33, 143.19, 142.73, 134.31, 129.85, 128.80, 127.62, 107.62.



3-chloro-1-(1-phenylvinyl)-1*H***-indazole (4af')**. Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ae'** was obtained as a white solid in 91% yield (69.3 mg). M.p. = 41-42 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.43–7.27 (m, 6H), 7.26–7.19 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 5.57 (s, 1H), 5.56 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.73, 141.01, 135.83, 135.72, 129.39, 128.63, 127.84, 127.23, 122.15, 121.99, 119.79, 111.84, 108.74. HRMS *m/z* (ESI) calcd for C₁₅H₁₁ClN₂ (M+H)⁺ 255.0684, found 255.0684.



1-(1-phenylvinyl)-1*H***-benzo**[*d*]**imidazole**^[3] (**4ag'**). Prepared following the general procedure B, after purification by column chromatography using PE/EA (3:1), **4ag'** was obtained as a colorless oil in 78% yield (51.5 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.43–7.35 (m, 3H), 7.34–7.25 (m, 3H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 5.69 (s, 1H), 5.47 (s, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 143.89, 143.04, 142.15, 135.26, 133.75, 129.74,

128.84, 126.71, 123.38, 122.62, 120.44, 111.71, 109.43.



9-(1-phenylvinyl)-9*H***-carbazole^[3] (4ah')**. Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ah'** was obtained as a colorless oil in 76% yield (61.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.7 Hz, 2H), 7.44–7.29 (m, 11H), 6.12 (s, 1H), 5.64 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.67, 140.78, 136.32, 129.03, 128.70, 126.20, 125.81, 123.38, 120.15, 119.77, 112.87, 110.84.



1-(1-phenylvinyl) pyrrolidin-2-one (4ai'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (2:1), 4ai' was obtained as a colorless oil in 85% yield (47.7 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 5H), 5.39 (s, 1H), 5.28 (s, 1H), 3.53 (t, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 2.14–2.06 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 174.62, 143.42, 136.07, 128.44, 128.37, 126.27, 109.34, 49.47, 31.86, 18.49. HRMS *m/z* (ESI) calcd for C₁₂H₁₃NO (M+H)⁺ 188.1070, found 188.1070.



1-(1-phenylvinyl)piperidin-2-one^[3] (4aj'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (2:1), 4aj' was obtained as a colorless oil in 60% yield (36.1 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.23 (m, 5H), 5.71 (s, 1H), 5.25 (s, 1H), 3.48 (t, J= 5.4 Hz, 2H), 2.55 (t, J= 6.0 Hz, 2H), 1.99– 1.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 169.79, 147.85, 135.44, 128.54, 128.41, 125.30, 111.88, 50.57, 32.60, 23.31, 21.40.



1-(1-phenylvinyl)-1*H***-indole^[3] (4ak').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **4ak'** was obtained as a white solid in 86% yield (56.5 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.65 (m, 1H), 7.46–7.31 (m, 5H), 7.21 (d, J = 3.3 Hz, 1H), 7.18–7.10 (m, 3H), 6.66 (d, J = 3.4 Hz, 1H), 5.62 (s, 1H), 5.41 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.92, 136.99, 136.37, 129.24, 129.13, 128.68, 128.56, 126.92, 121.95, 120.90, 120.15, 111.86, 108.10, 103.05.



1-(1-phenylvinyl)-1*H*-indole-5-carbonitrile (4al'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (3:1), 4al' was obtained as a white solid in 86% yield (67.3 mg). M.p. = 123-124 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 1H), 7.43–7.35 (m, 3H), 7.33–7.28 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 5.79 (s, 1H), 5.50 (s, 1H), 2.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.33, 144.13, 137.24, 135.69, 135.12, 129.64, 128.84, 126.51, 126.38, 123.65, 122.89, 122.57, 118.23, 111.90, 110.67, 27.66. HRMS *m/z* (ESI) calcd for C₁₈H₁₅NO (M+H)⁺ 262.1226, found 262.1227.



1-(1-phenylvinyl)-1*H*-indole-5-carbonitrile (4am'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 4am' was obtained as a colorless

oil in 85% yield (62.2 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.43–7.28 (m, 5H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 3.4 Hz, 1H), 5.71 (s, 1H), 5.41 (s, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 144.19, 137.84, 136.01, 130.94, 129.57, 128.84, 128.79, 126.59, 126.42, 124.92, 120.49, 112.54, 109.77, 103.70, 103.30. **HRMS** *m*/*z* (ESI) calcd for C₁₇H₁₂N₂ (M+H)⁺ 245.1073, found 245.1073.



1-(1-phenylvinyl)-1*H*-pyrrolo[3,2-*b*]pyridine (4an'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (2:1), 4an' was obtained as a colorless oil in 80% yield (52.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 2.7 Hz, 1H), 7.42–7.32 (m, 4H), 7.30–7.26 (m, 2H), 7.02–6.98 (m, 1H), 6.83 (s, 1H), 5.58 (s, 1H), 5.35 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 147.50, 144.49, 143.75, 136.26, 131.67, 129.47, 129.37, 128.69, 126.92, 118.97, 116.75, 108.15, 104.11. HRMS *m*/z (ESI) calcd for C₁₅H₁₂N₂ (M+H)⁺ 221.1073, found 221.1073.



6-bromo-1-(1-phenylvinyl)-1*H***-indole (4ao').** Prepared following the general procedure B. after purification by column chromatography using PE/EA (5:1), **4ao'** was obtained as a white solid in 86% yield (76.6 mg). M.p. = 58-59 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.40–7.31 (m, 4H), 7.28–7.20 (m, 3H), 7.11 (d, *J* = 3.3 Hz, 1H), 6.57 (s, 1H), 5.64 (s, 1H), 5.37 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.37, 136.48, 129.38, 129.22, 128.68, 127.92, 126.74, 123.50, 122.10, 115.65, 114.59, 108.94, 103.12. HRMS *m/z* (ESI) calcd for C₁₂H₁₂BrN (M+H)⁺ 298.0226, found 298.0227.



1-(1-phenylvinyl)-1*H*-pyrrolo[2,3-*b*]pyridine^[3] (4ap'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 4ap' was obtained as a colorless oil in 91% yield (60.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 3.7 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.40-7.27 (m, 5H), 7.18 (d, *J* = 3.2 Hz, 1H), 7.11 (m, 1H), 6.54 (d, *J* = 3.2 Hz, 1H), 5.77 (d, *J* = 12.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.28, 143.50, 142.78, 137.26, 128.93, 128.92, 128.84, 128.43, 126.72, 121.27, 116.49, 110.08, 100.71.



(*E*)-*N*-(4-((4-fluorostyryl)thio)butyl)quinolin-8-amine (5cd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5cd was obtained as a yellow oil in 95% yield (100.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.39–7.32 (m, 2H), 7.23–7.17 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 2H), 6.66–6.59 (m, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.14 (brs, 1H), 3.38–3.31 (m, 2H), 2.90–2.81 (m, 2H), 1.95–1.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 161.76 (d, *J* = 246.2 Hz), 146.74, 144.67, 138.09, 135.94, 133.22 (d, *J* = 3.1 Hz), 128.61, 127.73, 126.87 (d, *J* = 7.8 Hz), 126.03, 124.56 (d, *J* = 2.3 Hz), 121.33, 115.42 (d, *J* = 21.7 Hz), 113.69, 104.44, 42.78, 32.38, 28.23, 27.09. ¹⁹F NMR (376 MHz, CDCl₃) δ –115.40. HRMS *m*/z (ESI) calcd for C₂₁H₂₁FN₂S (M+H)⁺ 353.1482, found 353.1483.



(*E*)–*N*–(4–((2–chlorostyryl)thio)butyl)quinolin–8–amine (5dd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5dd was obtained

as a yellow oil in 96% yield (106.0 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 8.71 (s, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.44–7.34 (m, 4H), 7.19 (t, J = 7.3 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.85–6.75 (m, 2H), 6.68 (d, J = 7.5 Hz, 1H), 6.18 (brs, 1H), 3.41–3.35 (m, 2H), 2.96–2.89 (m, 2H), 1.99–1.89 (m, 4H). ¹³**C NMR** (101 MHz, CDCl₃) δ 146.72, 144.63, 138.06, 135.92, 134.98, 131.83, 129.64, 128.58, 128.07, 127.72, 127.62, 126.77, 125.86, 122.05, 121.31, 113.67, 104.44, 42.80, 32.06, 28.31, 26.85. **HRMS** *m/z* (ESI) calcd for C₂₁H₂₁ClN₂S (M+H)⁺ 369.1187, found 369.1187.



(*E*)-*N*-(4-((2-phenylprop-1-en-1-yl)thio)butyl)quinolin-8-amine (5ed). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5ed was obtained as a yellow oil in 96% yield (100.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.38–7.26 (m, 6H), 7.21–7.18 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 6.14 (brs, 1H), 3.36-3.30 (m, 2H), 2.85–2.81 (m, 2H), 2.12 (s, 3H), 1.92–1.84 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.73, 144.69, 141.96, 138.09, 135.92, 133.68, 128.60, 128.25, 127.73, 126.56, 125.06, 123.42, 121.31, 113.63, 104.43, 42.85, 33.94, 28.09, 17.59. HRMS *m/z* (ESI) calcd for C₂₂H₂₄N₂S (M+H)⁺ 349.1733, found 349.1736.



N-(4-((2,2-diphenylvinyl)thio)butyl)quinolin-8-amine (5fd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5fd was obtained as a yellow oil in 98% yield (120.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.39–7.29 (m, 7H), 7.26–7.17 (m, 5H), 7.01 (d, J = 8.1 Hz, 1H), 6.63 (d, J = 7.3 Hz, 1H), 6.57 (s, 1H), 6.13 (brs, 1H), 3.36–3.29 (m, 2H), 2.84–2.78 (m, 2H), 1.91–1.83 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.73, 144.67, 141.84, 139.51, 138.69, 138.09, 135.91, 129.66, 128.59, 128.24, 128.17, 127.73, 127.42, 126.96, 126.77, 125.85, 121.31, 113.64, 104.43, 42.80, 34.57, 28.08,



(*E*)-*N*-(4-((1-phenylprop-1-en-2-yl)thio)butyl)quinolin-8-amine (5gd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5gd was obtained as a yellow oil in 75% yield (78.3 mg). ¹H NMR (400 MHz, CDCl3) δ 8.68 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.39–7.28 (m, 4H), 7.24–7.16 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.35 (s, 1H), 6.15 (brs, 1H), 3.38–3.31 (m, 2H), 2.88 (t, *J* = 6.9 Hz, 2H), 2.12 (s, 3H), 1.96–1.84 (m, 4H). ¹³C NMR (101 MHz, CDCl3) δ 146.74, 144.67, 138.08, 137.47, 135.94, 134.10, 128.60, 128.51, 128.14, 127.74, 126.05, 123.52, 121.33, 113.65, 104.44, 42.84, 31.09, 28.46, 26.25, 19.59. HRMS *m/z* (ESI) calcd for C₂₂H₂₄N₂S (M+H)⁺ 349.1733, found 349.1736.



(*E*)-*N*-(4-((1,2-diphenylvinyl)thio)butyl)quinolin-8-amine (5hd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5hd was obtained as a yellow oil in 90% yield (110.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.69 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.41–7.29 (m, 7H), 7.11–7.04 (m, 4H), 6.97–6.92 (m, 2H), 6.81 (s, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.13 (brs, 1H), 3.31–3.26 (m, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 1.89–1.74 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.71, 144.66, 138.06, 137.85, 137.83, 136.65, 135.92, 129.57, 128.87, 128.60, 127.98, 127.90, 127.72, 127.32, 126.43, 121.31, 113.58, 104.42, 42.75, 31.43, 28.13, 26.88. HRMS *m*/z (ESI) calcd for C₂₇H₂₆N₂S (M+H)⁺ 411.1889, found 411.1889.



N-(4-((1*H*-inden-2-yl)thio)butyl)quinolin-8-amine (5id). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5id was obtained

as a yellow solid in 82% yield (85.1 mg). M.p. = 79-81 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.39–7.29 (m, 3H), 7.22–7.15 (m, 2H), 7.07–7.02 (m, 2H), 6.65 (d, J = 7.6 Hz, 1H), 6.48 (s, 1H), 6.15 (brs, 1H), 3.45 (s, 2H), 3.38–3.32 (m, 2H), 3.00–2.95 (m, 2H), 1.96–1.89 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.74, 145.01, 144.66, 143.52, 142.12, 138.10, 135.93, 128.60, 127.73, 126.48, 124.62, 123.38, 123.05, 121.32, 118.99, 113.69, 104.45, 42.79, 42.05, 32.28, 28.43, 26.53. HRMS *m*/*z* (ESI) calcd for C₂₂H₂₂N₂S (M+H)⁺ 347.1576, found 347.1576.



N-(4-((3,4-dihydronaphthalen-2-yl)thio)butyl)quinolin-8-amine (5jd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5jd was obtained as a yellow oil in 94% yield (101.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.43–7.35 (m, 2H), 7.17–7.06 (m, 4H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 6.19 (brs, 1H), 3.41–3.35 (m, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.43 (t, *J* = 8.0 Hz, 2H), 1.99–1.88 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.72, 144.64, 138.06, 136.89, 135.92, 134.42, 133.52, 128.58, 127.72, 127.16, 126.54, 125.92, 124.78, 121.31, 119.47, 113.66, 104.44, 42.78, 30.56, 29.05, 28.43, 28.31, 26.13. HRMS *m*/z (ESI) calcd for C₂₃H₂₄N₂S (M+H)⁺ 361.1733, found 361.1736.



N-(4-(benzofuran-2-ylthio)butyl)quinolin-8-amine (5kd). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5kd was obtained as a yellow solid in 94% yield (98.1 mg). M.p. = 64-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.46–7.40 (m, 2H), 7.37–7.31 (m, 2H), 7.26–7.16 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.77 (s, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.12 (brs, 1H), 3.34–3.28 (m, 2H), 2.99 (t, *J* = 6.9 Hz, 2H), 1.94–1.80 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 156.26, 150.29, 146.71, 144.66, 138.10, 135.92, 128.60, 128.56, 127.73, 124.27, 122.80, 121.31, 120.31, 113.65, 111.07, 110.88,

104.44, 42.77, 34.38, 27.95, 27.38. **HRMS** *m*/*z* (ESI) calcd for C₂₁H₂₀N₂OS (M+H)⁺ 349.1369, found 349.1370.



N-(4-(benzo[*b*]thiophen-2-ylthio)butyl)quinolin-8-amine (5ld). Prepared following the general procedure A, after purification by column chromatography using PE/EA (10:1), 5ld was obtained as a yellow oil in 97% yield (105.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.46–7.35 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.15 (brs, 1H), 3.36–3.29 (m, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 1.97–1.90 (m, 2H), 1.85–1.78 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 146.73, 144.67, 139.83, 139.09, 138.11, 135.93, 128.62, 127.74, 126.95, 126.78, 124.73, 124.40, 122.85, 122.54, 121.32, 113.64, 104.44, 42.80, 34.52, 28.06, 27.08. HRMS *m*/z (ESI) calcd for C₂₁H₂₀N₂S₂ (M+H)⁺ 365.1141, found 365.1143.



1-(4-(benzofuran-2-ylthio)butyl)-1*H***-indole (5kp').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (10:1), **5kp'** was obtained as a colorless oil in 74% yield (71.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.32–7.17 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.67 (s, 1H), 6.44 (s, 1H), 4.11 (t, *J* = 7.0 Hz, 2H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.01–1.94 (m, 2H), 1.68–1.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 156.25, 135.76, 128.55, 128.48, 127.67, 124.41, 122.87, 121.39, 120.97, 120.42, 119.24, 111.46, 110.90, 109.25, 101.08, 45.77, 34.10, 28.77, 26.98. HRMS *m/z* (ESI) calcd for C₂₀H₁₉NOS (M+H)⁺ 322.1260, found 322.1260.



1-(4-(benzo[*b*]thiophen-2-ylthio)butyl)-1*H*-pyrrolo[3,2-*b*]pyridine (5lp'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (10:1), 5lp' was obtained as a colorless oil in 85% yield (86.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.44–7.36 (m, 2H), 7.29 (s, 1H), 7.14 (s, 1H), 7.06–7.03 (m, 1H), 6.43 (s, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.05–1.98 (m, 2H), 1.65–1.57 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.34, 142.69, 139.80, 139.04, 128.72, 127.73, 127.27, 126.46, 124.74, 124.40, 122.87, 122.50, 120.49, 115.58, 99.44, 43.91, 34.21, 29.22, 26.64. HRMS *m*/z (ESI) calcd for C₁₉H₁₈N₂S₂ (M+H)⁺ 339.0984, found 339.0985.



1-(1-(4-(methylthio)phenyl)vinyl)-1*H*-indole (6bk'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 6bk' was obtained as a white solid in 88% yield (70.0 mg) when KOH (3.0 equiv) was used in reaction. M.p. = 89-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.1 Hz, 1H), 7.22–7.18 (m, 5H), 7.16–7.07 (m, 3H), 6.63–6.59 (m, 1H), 5.53 (s, 1H), 5.31 (s, 1H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.42, 140.04, 136.30, 133.51, 129.22, 128.64, 127.24, 125.98, 121.96, 120.90, 120.17, 111.88, 107.47, 103.06, 15.33. HRMS *m/z* (ESI) calcd for C₁₇H₁₅NS (M+H)⁺ 266.0998, found 266.0999.



1-(1-(4-fluorophenyl)vinyl)-1*H*-indole^[4] (6ck'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 6ck' was obtained as a white solid in 96% yield (68.3 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 6.3 Hz, 1H), 7.34-7.29 (m, 2H), 7.20-7.14 (m, 4H), 7.06 (t, J = 8.5 Hz, 2H), 6.66 (d, J = 2.8 Hz, 1H), 5.55 (s, 1H), 5.38 (s, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 163.25 (d, J = 249.0 Hz), 143.98, 136.25, 133.11 (d, J = 3.3 Hz), 129.30, 128.76 (d, J = 8.3 Hz), 128.56, 122.06, 120.99, 120.28, 115.59 (d, J = 21.8 Hz), 111.81, 107.83, 103.27. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -112.00.



1-(1-(2-chlorophenyl)vinyl)-1*H*-indole (6dk'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 6dk' was obtained as a white solid in 95% yield (72.1 mg) when KOH (3.0 equiv) was used in reaction. M.p. = 55-57 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.59 (m, 1H), 7.46–7.43 (m, 1H), 7.39–7.28 (m, 3H), 7.23–7.20 (m, 1H), 7.12–7.09 (m, 2H), 7.05–7.02 (m, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 5.58 (s, 1H), 5.33 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.72, 136.37, 135.77, 133.48, 131.40, 130.28, 130.18, 129.59, 127.63, 126.94, 122.23, 121.00, 120.36, 111.56, 108.84, 103.63. HRMS *m*/*z* (ESI) calcd for C₁₆H₁₂ClN (M+H)⁺ 254.0731, found 254.0731.



1-(3,4-dihydronaphthalen-1-yl)-1*H***-pyrazole (6ja').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **6ja'** was obtained as a colorless oil in 79% yield (46.5 mg). ¹**H** NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.62 (s, 1H), 7.22–7.12 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 6.20 (t, *J* = 4.8 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.52–2.47 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.23, 138.27, 136.31, 131.25, 130.15, 128.06, 127.57, 126.55, 123.19, 122.89, 105.85, 27.43, 22.44. HRMS *m*/z (ESI) calcd for C₁₃H₁₂N₂ (M+H)⁺ 197.1073, found 197.1073.



1-(3,4-dihydronaphthalen-1-yl)-1*H*-indole^[4] (6jk'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 6jk' was obtained as a colorless oil in 56% yield (41.1 mg) when KOH (3.0 equiv) was used in reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.65 (m, 1H), 7.23–7.16 (m, 4H), 7.14–7.09 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.66–6.61 (m, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.19 (t, *J* = 4.9 Hz, 1H), 2.96 (t, *J* = 7.9 Hz, 2H), 2.61–2.50 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 136.70, 136.35, 136.23, 132.11, 128.64, 128.50, 128.01, 127.63, 126.63, 125.14, 123.11, 121.76, 120.78, 119.83, 111.13, 102.33, 27.56, 22.78.



1-(3,4-dihydronaphthalen-1-yl)-1*H*-**pyrrolo**[**3,2-***b***]pyridine (6jn').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **6jn'** was obtained as a green oil in 70% yield (51.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.49-8.47 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 3.3 Hz, 1H), 7.25–7.18 (m, 2H), 7.06–7.02 (m, 2H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.19 (t, *J* = 4.7 Hz, 1H), 2.97 (t, *J* = 8.1 Hz, 2H), 2.59–2.55 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 146.86, 143.59, 136.22, 135.85, 131.76, 131.52, 129.67, 128.31, 127.80, 126.69, 125.35, 122.77, 118.21, 116.61, 103.39, 27.42, 22.69. HRMS *m/z* (ESI) calcd for C₁₇H₁₄N₂ (M+H)⁺ 247.1230, found 247.1230.



1-(3,4-dihydronaphthalen-1-yl)-1*H***-indole-4-carbonitrile (6jq').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **6jq'** was obtained as a colorless oil in 52% yield (42.1 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 7.4 Hz, 1H), 7.40–7.36 (m, 2H), 7.26–7.19 (m, 2H), 7.15 (t, J = 8.0 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.87–6.83 (m, 1H), 6.42 (d, J = 7.7 Hz, 1H), 6.24–6.20 (m, 1H), 2.99 (t, J = 8.1 Hz, 2H), 2.62–2.57 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 136.32, 136.10, 135.59, 131.47, 131.25, 129.69, 128.42, 127.85, 126.74, 126.28, 125.36, 122.57, 121.46, 118.67, 115.84, 103.11, 101.29, 27.33, 22.72. HRMS *m/z* (ESI) calcd for C₁₉H₁₄N₂ (M+H)⁺ 271.1230, found 271.1230.



5-chloro-1-(3,4-dihydronaphthalen-1-yl)-1*H***-indole (6jr').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **6jr'** was obtained as a green oil in 60% yield (50.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.23–7.17 (m, 3H), 7.09–7.01 (m, 3H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.20 (t, *J* = 4.7 Hz, 1H), 2.98 (t, *J* = 8.1 Hz, 2H), 2.58–2.53 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 136.19, 136.06, 135.06, 131.76, 129.94, 129.46, 128.19, 127.74, 126.67, 125.53, 125.48, 122.87, 122.07, 120.13, 112.14, 101.96, 27.45, 22.73. HRMS *m/z* (ESI) calcd for C₁₈H₁₄ClN (M+H)⁺ 280.0888, found 280.0888.



6-bromo-1-(3,4-dihydronaphthalen-1-yl)-1*H***-indole (6jo').** Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), **6jo'** was obtained as a green oil in 45% yield (43.6 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.24–7.17 (m, 3H), 7.14 (d, *J* = 2.8 Hz, 1H), 7.04 (t, *J* = 7.1 Hz, 1H), 6.63–6.59 (m, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.19 (t, *J* = 4.6 Hz, 1H), 2.97 (t, *J* = 8.2 Hz, 2H), 2.61–2.53 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 137.52, 136.16, 135.82, 131.79, 129.30, 128.25, 127.76, 127.24, 126.74, 125.90, 123.15, 122.74, 122.01, 115.44, 113.84, 102.48, 27.41, 22.76. **HRMS** *m/z* (ESI) calcd for C₁₈H₁₄BrN (M+H)⁺ 324.0382, found 324.0382.



(8R,9S,13S,14S)-3-(1-(1H-pyrrolo[2,3-b]pyridin-1-yl)vinyl)-13-methyl-

6,7,8,9,11,12,13,14,15,16-decahydro-17*H***-cyclopenta[***a***]phenanthren-17-one (6mp'). Prepared following the general procedure B, after purification by column chromatography using PE/EA (5:1), 6mp'** was obtained as a white solid in 65% yield (75.9 mg). M.p. = 206-208 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.36–8.32 (m, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.13–7.08 (m, 1H), 7.07–7.01 (m, 2H), 6.53 (s, 1H), 5.71 (d, *J* = 22.1 Hz, 2H), 2.90–2.82 (m, 2H), 2.56–2.46 (m, 1H), 2.44–2.37 (m, 1H), 2.35–2.25 (m, 1H), 2.21–1.93 (m, 4H), 1.68–1.38 (m, 6H), 0.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 220.80, 143.47, 142.68, 140.63, 136.58, 134.73, 129.08, 128.89, 127.18, 125.45, 124.16, 121.29, 116.43, 109.43, 100.55, 50.44, 47.91, 44.40, 37.95, 35.80, 31.51, 29.34, 26.37, 25.58, 21.54, 13.80. HRMS *m*/*z* (ESI) calcd for C₂₇H₂₈N₂O (M+H)⁺ 397.2274, found 397.2275.

6. Synthetic Application

5.1 One-pot synthesis of 3aa and 4aa'



General procedure: Under an argon atmosphere, sulfoxide (32.0 μ L, 0.36 mmol, 1.2 equiv) and anhydrous DCM (2.0 mL) were added to a 10 mL schlenk tube at -40 °C. The Tf₂O (76.0 μ L, 0.45 mmol, 1.5 equiv) was added dropwise under argon, then styrene (34.5 μ L, 0.3 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 15 min before warming to 0 °C. After stirring for 2 h, the solvent was removed under reduced pressure. Then KOH (33.6 mg, 0.9 mmol, 2.0 equiv), aniline (82.5 μ L 0.9 mmol, 3.0 equiv) and THF (2 mL) were added. The reaction mixture was stirred at 80 °C for 6 h. The crude product was purified by column chromatography on silica gel (PE/EA=10/1) to afford product **3aa** (79%, 67.0 mg).



General procedure: Under an argon atmosphere, sulfoxide (32.0 μ L, 0.36 mmol, 1.2 equiv) and anhydrous DCM (2.0 mL) were added to a 10 mL schlenk tube at -40 °C. The Tf₂O (76.0 μ L, 0.45 mmol, 1.5 equiv) was added dropwise under argon, then styrene (34.5 μ L, 0.3 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 15 min before warming to room temprature. After stirring for 2 h, the solvent was removed under reduced pressure. Then KOH (50.4 mg, 0.9 mmol, 3.0 equiv), pyrazole (30.6 mg, 0.45 mmol, 1.5 equiv) and THF (2.0 mL) were added. The reaction mixture was stirred at room temperature for 6 h. The crude product was purified by column chromatography on silica gel (PE/EA=5/1) to afford product **4aa'** (73%, 37.2 mg).

5.2 Scale-up reaction



General procedure: To a solution of aniline (1.37 mL, 15.0 mmol, 3.0 equiv) in THF (50.0 mL) was added styrene sulfonium salts (1.7 g, 5.0 mmol, 1.0 equiv). The reaction mixture was stirred at 80 °C for 6 h (under reflux). The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA=10/1) to afford product **3aa** (86%, 1.21 g).

5.3 Product derivatization



Following the relative literature^[5]: A 10 mL schlenk tube with a stirring bar was added **3aa** (56.6 mg, 0.2mmol, 1.0 equiv), TFA (1.0 mL), DCM (1.0 mL) and H₂O₂ (30% aq., 20.4 µL, 0.2 mmol, 1.0 equiv) under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with saturated aqueous NaHCO₃ at 0 °C and the aqueous phase extracted with DCM. The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EA=3/1) to afford product 7 (colorless liquid, 89%, 53.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.44 (m, 2H), 7.41–7.34 (m, 3H), 7.24 (d, *J* = 15.4 Hz, 1H), 7.19–7.14 (m, 2H), 6.81 (d, *J* = 15.5 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.61–6.56 (m, 2H), 3.70 (brs, 1H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.91–2.76 (m, 2H), 1.98–1.74 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.00, 136.96, 133.72, 130.16, 129.65, 129.21, 128.89, 127.56, 117.32, 112.66, 53.50, 43.27, 28.53, 19.68. HRMS *m/z* (ESI) calcd for C₁₈H₂₁NOS (M+H)⁺ 300.1417, found 300.1416.



Following the relative literature^[5]: A 10 mL schlenk tube with a stirring bar was added **3aa** (56.6 mg, 0.2mmol, 1.0 equiv), TFA (1.0 mL), DCM (1.0 mL) and H₂O₂ (30% aq., 102 µL, 1.0 mmol, 5.0 equiv) under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with saturated aqueous NaHCO₃ at 0 °C and the aqueous phase extracted with DCM. The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EA=5/1) to afford product **8** (colorless liquid, 90 %, 56.7 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.61 (d, *J* = 15.4 Hz, 1H), 7.53–7.50 (m, 2H), 7.48–7.41 (m, 3H), 7.20–7.13 (m, 2H), 6.83 (d, *J* = 15.5 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 2H), 3.68 (brs, 1H), 3.17 (t, *J* = 6.8 Hz, 2H), 3.14–3.09 (m, 2H), 2.00–1.93 (m, 2H), 1.81–1.74 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 147.92, 144.98, 132.09, 131.37, 129.23, 129.11, 128.56, 124.50, 117.41, 112.67, 54.74, 43.15, 28.12, 20.35. HRMS *m/z* (ESI) calcd for C₁₈H₂₁NO₂S (M+H)⁺ 316.1366, found 316.1367.



Following the relative literature ^[6]: A 10 mL schlenk tube with a stirring bar was added CF₃SO₂Na (117 mg, 0.75 mmol, 1.5 equiv) and PPh₃ (393.4 mg, 1.5 mmol, 3.0 equiv), compound **8** (157.5 mg, 0.5 mmol) was dissolved in MeCN (2.5 mL), and the solution was added under argon. The resulting mixture was stirred at room temperature for 1 h. After that, AgF (2.25 mmol, 286 mg, 4.5 equiv) was added. Then the reaction mixture was stirred at 50 °C for 5 h. The resulting mixture was concentrated and purified by column chromatography on silica gel (PE/EA=10/1) to afford product **9** (colorless liquid, 70 %, 134.0 mg). ¹H NMR (400 MHz, CDCl₃) *δ* 7.60 (d, *J* = 15.5 Hz, 1H), 7.56–7.51 (m, 2H), 7.50–7.42 (m, 3H), 7.39–7.32 (m, 2H), 7.32–7.23 (m, 3H), 6.82 (d, *J* = 15.4 Hz, 1H), 3.40 (t, *J* = 7.0 Hz, 2H), 3.08–3.01 (m, 2H), 1.94–1.84 (m, 2H), 1.68–1.59 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) *δ* 145.05, 140.28, 132.10, 131.40, 129.27, 129.12, 128.54, 127.26, 127.19, 124.44, 123.30 (d, *J* = 255.2 Hz), 54.48, 48.04, 26.72, 19.74. ¹⁹F NMR (376 MHz, CDCl₃) *δ* -58.23. HRMS *m*/z (ESI) calcd for C₁₉H₂₀F₃NO₂S (M+Na)⁺ 406.1059, found 406.1059.
7. References

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8. ¹H, ¹³C, and ¹⁹F NMR spectra

¹H NMR of 1a



¹H NMR of 1b





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −4 f1 (ppm)

¹H NMR of 1c



¹H NMR of 1d



¹H NMR of 1e







¹H NMR of 1f



¹H NMR of 1g



¹³C NMR of 1g















¹H NMR of 1j





¹H NMR of 1k





¹H NMR of 11





¹H NMR of 1m



¹³C NMR of 1m



¹H NMR of 3aa







¹H NMR of 3ac

(777) (777) (777) (777) (775)





¹H NMR of 3ad







¹H NMR of 3af





¹H NMR of 3ag





S55

4.5 4.0 f1 (ppm) 3.5

3.0

2.5

2.0

1.5

1.0

0.

0.5

6.5

7.0

7.5

6.0

5.5

5.0

8.5

8.0



¹H NMR of 3ai





¹H NMR of 3aj







 $\frac{4.00}{1.00} \tfrac{4}{4}$

7.5

8.5

8.0

F 00.1

F 10.1

7.0





4.5 4.0 f1 (ppm)

5.0

5.5

6.0

F 00.7 2.5

2.00 H

3.5

0.

0.5

2.09 <u>1</u>

2.0



¹H NMR of 3am



¹³C NMR of 3am



¹H NMR of 3an







¹H NMR of 3ap





¹H NMR of 3aq













¹H NMR of 4aa'





¹H NMR of 4ab'





¹H NMR of 4ac'





¹H NMR of 4ad'




¹H NMR of 4ae'





¹H NMR of 4af





¹H NMR of 4ag'





¹H NMR of 4ah'









¹³C NMR of 4ai'



S78



¹H NMR of 4ak'





¹H NMR of 4al'



¹³C NMR of 4al'



¹H NMR of 4am'



¹³C NMR of 4am'



¹H NMR of 4an'





¹H NMR of 4ao'



¹³C NMR of 4ao'



¹H NMR of 4ap'



¹³C NMR of 4ap'



¹H NMR of 5cd





¹⁹F NMR of 5cd





¹H NMR of 5dd



¹³C NMR of 5dd





¹H NMR of 5ed



¹³C NMR of 5ed





¹H NMR of 5fd



¹³C NMR of 5fd





¹H NMR of 5gd





¹H NMR of 5hd



¹³C NMR of 5hd





¹H NMR of 5id



¹³C NMR of 5id





¹H NMR of 5jd



¹³C NMR of 5jd

 $- \frac{146.72}{136.89}$ $- \frac{146.72}{136.89}$ $- \frac{146.72}{135.89}$ $- \frac{144.64}{135.89}$ $- \frac{133.52}{123.52}$ $- \frac{123.52}{123.52}$ $- \frac{123.52}{123.56}$ $- \frac{123.52}{123.56}$ $- \frac{124.44}{113.66}$ $- \frac{124.44}{113.66}$ $- \frac{124.43}{123.56}$ $- \frac{124.43}{123.56}$



¹H NMR of 5kd



¹³C NMR of 5kd







¹³C NMR of 5ld









¹³C NMR of 5kp'





¹H NMR of 5lp'



¹H NMR of 6bk'



¹³C NMR of 6bk'



¹H NMR of 6ck'



¹³C NMR of 6ck'





¹⁹F NMR of 6ck'



70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -1 fl (ppm)

¹H NMR of 6dk'





¹H NMR of 6ja'





¹H NMR of 6jk'





¹H NMR of 6jn'





¹H NMR of 6jq'





¹H NMR of 6jr'





¹H NMR of 6jo'





¹³C NMR of 6mp'



¹H NMR of 7

 $\begin{array}{c} 7.47\\ 7.47\\ 7.45\\ 7.45\\ 7.45\\ 7.45\\ 7.74\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.74\\ 6.53\\$

-3.70 -3.18 -3.17 -3.16




¹H NMR of 8











