Electronic Supplementary Information for

Nickel(II)/Lewis acid catalyzed olefin hydroamination and hydroarylation

under mild conditions

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1. Experimental section

1.1 Materials and analytical methods

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored by TLC with Haiyang GF–254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or KMnO₄ as visualizing agents as needed. Flash column chromatography was performed using 200–300 mesh silica gel under increased pressure. ¹H and ¹³C NMR {¹H} spectra were respectively recorded on a Brüker AV–600 spectrometer. Chemical shifts (δ) were expressed in ppm (parts per million) with TMS as the internal standard, and coupling constants (*J*) were reported in hertz (Hz). High resolution mass spectra were obtained on a mass spectrometer by using ESI FT–ICR mass.

1.2 General procedures for hydroamination of substituted styrene and aniline with the Ni(OAc)₂/Sc(OTf)₃ catalyst in TFE.

In a typical procedure, Ni(OAc)₂ (0.01 mmol, 1.7 mg) and Sc(OTf)₃ (0.02 mmol, 9.96 mg) were dissolved in TFE (1 mL) in a glass tube. After pre–stirring so prepared catalyst solution for 20 min under 60 °C, substituted styrene **1** (0.1 mmol) and aniline **2** (0.5 mmol, 5eq) were added in. The reaction mixtures were stirred at 60 °C for the desired reaction time with an air balloon as the atmosphere. Then, the mixtures were evaporated under reduced pressure, and the residue was purified by column chromatography (petroleum ether/ethyl acetate: 15:1 to 5:1) to give the corresponding hydroamination product **3** and hydroarylation product **4**.

1.3 General procedures for hydroamination of acrylonitrile or acrylate with aniline in TFE.

In a typical procedure, Ni(OAc)₂ (0.01 mmol, 1.7 mg) and Sc(OTf)₃ (0.02 mmol, 9.96 mg) were dissolved in TFE (1 mL) in a glass tube. After pre–stirring so prepared solution for 20 min under 70 °C, acrylonitrile or acrylate **5** (0.1 mmol) and aniline **2** (0.5 mmol, 5eq) were added in. The reaction mixtures were stirred at 70 °C for the desired reaction time with an air balloon as the atmosphere. Then, the mixtures were evaporated under reduced pressure, and the residue was purified by column chromatography (petroleum ether/ethyl acetate: 10:1 to 5:1) to give corresponding hydroamination product **6**.

1.4 General procedures for UV-Vis experiments in TFE.

In a typical UV-vis experiment, 4-methylstyrene (1a, 5.9 mg, 0.05 mmol) and 4-bromoaniline (2a, 8.5 mg, 0.05 mmol) were dissolved in 4 mL of TFE in a glass tube, respectively. Ni(OAc)₂ (8.5 mg, 0.05 mmol) and Sc(OTf)₃ (24.9 mg, 0.05 mmol) were dissolved in 4 mL of TFE in another glass tube, which was pre-stirred for 20 min under 60 °C, then cooled down to room temperature. Next, these solutions were diluted by 250-folds prior to their UV-Vis studies. The UV-Vis scans were carried out for so prepared solution of 1a, 1a with Ni(OAc)₂/Sc(OTf)₃, 2a, 2a with Ni(OAc)₂, 2a with Sc(OTf)₃ at room temperature, respectively.

1.5 General procedures for the bromo trapping experiments with TBAB.

In a typical procedure, Ni(OAc)₂ (0.01 mmol, 1.7 mg) and Sc(OTf)₃ (0.02 mmol, 9.96 mg) were dissolved in TFE (1 mL) in a glass tube. After pre–stirring so prepared solution for 20 min under 60 °C, 4–methylstyrene **1a** (0.1 mmol) or acrylonitrile **5a** (0.1 mmol) and aniline **2** (0.5 mmol, 5eq) were added in, then tetrabutylammonium bromide (TBAB, 0.5 mmol, 5eq) was added to the mixture. The reaction mixtures were stirred at 60 °C for the desired reaction time with an air balloon

as the atmosphere. Then, the yield was determined by GC, 27% for 7 (1–(1–bromoethyl)–4–methylbenzene) and 19% for 8 (3–bromopropanenitrile), respectively.

2. Optimization studies and control experiments of the reaction conditions for the

model reaction of 1a and 2a.

1aa 2aa 3aa 4aa Yield (%)^b Entry Cat. 3 4 5 1 Ni(TFA)2 trace 2 Ni(TFA)₂/Sc(OTf)₃ 32 3 3 Ni(ClO₄)₂ trace ND 4 Ni(ClO₄)₂/Sc(OTf)₃ trace ND

Table S1. Different Ni(II) sources for the model reaction ^a

^a Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Cat., LA, TFE (1 mL), air balloon, 60 °C, 12 h. ^bIsolated yield, n.d. = not detected.

Table S2. Ratio of 1a and 2a for the model reaction ^a

+ 1aa	Br LA LA	- H Br	H H H 2 Br 4aa
	D /: 61 /0	Yield	(%) ^b
Entry	Ratio of Ia/2a —	3	4
1	2:1	25	12
2	1:1	30	20
3	1:2	57	15
4	1:3	62	15
5	1:4	66	16
6	1:5	74	17

^a Conditions: **1a** (0.1 mmol), **2a**, Ni(OAc)₂ (0.10 equiv), Sc(OTf)₃ (0.20 equiv), TFE (1 mL), air balloon, 60 °C, 12 h. ^bIsolated yield.

1aa	+ _{Br}	cat. LA 3aa	Br + 4aa
Yie		Yield	(%) ^b
Entry	Ratio of Cat/ LA	3	4
1	2.5 % : 2.5 %	4	trace
2	2.5 % : 5 %	18	6
3	5 % : 5 %	32	9
4	5 % : 10 %	44	12
5	10 % : 10 %	62	14
6	10 % : 20 %	74	16

Table S3. Ratio and amount of catalyst loading for the model reaction ^a

^a Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol),Ni(OAc)₂, Sc(OTf)₃, TFE (1 mL), air balloon, 60 °C, 12 h. ^bIsolated yield.

Table S4. Control experiments for the model reaction ^a

+ 1aa	Br NH_2 $cat.$ H	Hr Haa	
		Yield (%) ^b	
Entry	Cat. –	3	4
1	Ni(OAc) ₂ (10 mol %) + Sc(OTf) ₃ (20 mol %)	74	16
2	Ni(OAc) ₂ (10 mol %) + HOTf (5 mol %)	22	trace
3	$Ni(OAc)_2 (10 mol \%) + HOTf (10 mol \%)$	32	4
4	$Ni(OAc)_2 (10 mol \%) + HOTf (20 mol \%)$	27	trace
5	Ni(OAc) ₂ (10 mol %) + HOTf (40 mol %)	23	trace
6	Ni(OAc) ₂ (10 mol %) + HOTf (100 mol %)	11	trace

^a Conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), Cat., LA, TFE (1 mL), air balloon, 60 °C, 12 h. ^bIsolated yield.

3. Optimizations and control experiments for the model reaction of 5a and 2a.

<i>∞</i> 0	CN +	NH ₂		~HN
5a		2a		6aa
entry	Catalyst	Lewis acid	Solvent	Yield (%) ^b
1	Ni(OAc) ₂	_	TFE	ND
2	Ni(OAc) ₂	NaOTf	TFE	trace
3	Ni(OAc) ₂	Mg(OTf) ₂	TFE	10
4	Ni(OAc) ₂	Cu(OTf) ₂	TFE	13
5	Ni(OAc) ₂	Zn(OTf) ₂	TFE	15
6	Ni(OAc) ₂	Al(OTf) ₃	TFE	19
7	Ni(OAc) ₂	Y(OTf) ₃	TFE	24
8	Ni(OAc) ₂	Yb(OTf) ₃	TFE	35
9	Ni(OAc) ₂	Sc(OTf) ₃	TFE	43
10	-	Sc(OTf) ₃	TFE	ND
11	Ni(OTf) ₂	-	TFE	11
12	Ni(OAc) ₂	Sc(OTf) ₃	1,4-Dioxane	ND
13	Ni(OAc) ₂	Sc(OTf) ₃	DMF	ND
14	Ni(OAc) ₂	Sc(OTf) ₃	DMSO	ND
15	Ni(OAc) ₂	Sc(OTf) ₃	DCE	trace
16	Ni(OAc) ₂	Sc(OTf) ₃	MeCN	ND
17°	Ni(OAc) ₂	Sc(OTf) ₃	TFE	34
18 ^d	Ni(OAc) ₂	Sc(OTf) ₃	TFE	50
19°	Ni(OAc) ₂	Sc(OTf) ₃	TFE	47

Table S5. Optimization studies of the reaction conditions for the model reaction of 5a and 2a

^aConditions: **5a** (0.1 mmol), **2a** (0.5 mmol), TFE (1.0 mL), catalyst (10 mol %), LA (20 mol %), air balloon, 60 °C, 12 h. ^bIsolated yield. ^c50 °C. ^d70 °C. ^e80 °C.

Entry	Ratio of 6a/ 2a	Yield (%) ^b
1	2:1	10
2	1:1	13
3	1:2	22
4	1:3	33
5	1:4	41
6	1:5	50

Table S6. Ratio of **5a** and **2a** for the model reaction ^a

^a Conditions: **5a** (0.1 mmol), **2a**, Ni(OAc)₂ (0.10 equiv), Sc(OTf)₃ (0.20 equiv), TFE (1 mL), air balloon, 70 °C, 12 h. ^bIsolated yield.

Entry	Cat.	Yield (%) ^b
1	Ni(TFA) ₂	trace
2	$Ni(TFA)_2/Sc(OTf)_3$	12
3	Ni(ClO ₄) ₂	trace
4	$Ni(ClO_4)_2/Sc(OTf)_3$	trace

Table S7. Ratio and amount of catalyst loading for the model reaction ^a

^a Condition: **5a** (0.1 mmol), **2a** (0.5 mmol), Cat. (0.1 equiv.), LA (0.2 equiv.), TFE (1 mL), air balloon, 70 °C, 12 h. ^bIsolated yield.

Entry	Cat.	Ratio of Cat/ LA	Yield (%) ^b
1	Ni(OAc) ₂ /Sc(OTf) ₃	2.5 % : 2.5 %	trace
2	Ni(OAc) ₂ /Sc(OTf) ₃	2.5 % : 5 %	10
3	Ni(OAc) ₂ /Sc(OTf) ₃	5 % : 5 %	10
4	Ni(OAc) ₂ /Sc(OTf) ₃	5 % : 10 %	24
5	Ni(OAc) ₂ /Sc(OTf) ₃	10 % : 10 %	37
6	Ni(OAc) ₂ /Sc(OTf) ₃	10 % : 20 %	50

Table S8. Ratio and amount of catalyst loading for the model reaction ^a

^a Conditions: **5a** (0.1 mmol), **2a** (0.5 mmol), Cat., LA, TFE (1 mL), air balloon, 70 °C, 12 h. ^bIsolated yield.

Table S9. Control experiments for the model reaction ^a

Entry	Cat.	Yield (%) ^b
1	Ni(OAc) ₂ (10 mol %) + Sc(OTf) ₃ (20 mol %)	50
2	Ni(OAc) ₂ (10 mol %) + HOTf (5 mol %)	18
3	$Ni(OAc)_2 (10 \text{ mol } \%) + HOTf (10 \text{ mol } \%)$	30
4	$Ni(OAc)_2 (10 \text{ mol } \%) + HOTf (20 \text{ mol } \%)$	22
5	$Ni(OAc)_2 (10 \text{ mol }\%) + HOTf (40 \text{ mol }\%)$	17
6	Ni(OAc) ₂ (10 mol %) + HOTf (100 mol %)	13

^a Conditions: **5a** (0.1 mmol), **2a** (0.5 mmol), TFE (1 mL), air balloon, 60 °C, 12 h. ^bIsolated yield.

4. UV-Vis studies and control experiments on mechanistic studies.



Fig. S1 UV–vis spectra of 4-methylstyrene (1a) and Ni(OAc)₂/Sc(OTf)₃ with their mixtures in TFE at room temperature.

As shown in Fig. S1, **1a** alone in TFE demonstrated two distinct absorbance bands around 203 nm and 249 nm which could be attributed to the π - π * transition. Adding 1 equiv. of Ni(OAc)₂/Sc(OTf)₃ to **1a** in TFE caused no obvious change, indicating that there was no interaction between **1a** and the catalyst.



Fig. S2 GC-MS spectra of 1-(1-bromoethyl)-4-methylbenzene (7): (a) MS spectrum of 7 from the reaction mixtures; (b) comparison of the MS spectra between the reaction mixtures and the data base; (c) MS spectrum of 7 from the data base.



Fig. S3 GC-MS spectra of 3-bromopropanenitrile (8): (a) MS spectrum of 8 from the reaction mixtures; (b) comparison of the MS spectra between the reaction mixtures and the data base; (c) MS spectrum of 8 from the data base.

5. Experimental characterization data for products

4–bromo–N–(1–(p–tolyl)ethyl)aniline (3aa): Brown oil (74% yield, 21.4 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.31 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), 6.37 (d, J = 7.1 Hz, 1H), 4.41 (t, J = 6.8 Hz, 1H), 1.39 (d, J = 6.7 Hz, 3H), 1.25 (s, 9H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 147.32, 143.01, 135.94, 129.39, 128.78, 126.23, 119.26, 114.58, 52.31, 25.05, 21.07.

4–bromo–N–(1–(4–(tert–butyl)phenyl)ethyl)aniline (3ba): Brown oil (67% yield, 36.1 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.31 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), 6.37 (d, J = 7.1 Hz, 1H), 4.41 (t, J = 6.8 Hz, 1H), 1.39 (d, J = 6.7 Hz, 3H), 1.25 (s, 9H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 149.21, 147.71, 142.91, 131.64, 126.01, 125.55, 115.07, 106.59, 52.04, 34.56, 31.65, 24.93.

4–bromo–N–(1–(4–phenoxyphenyl)ethyl)aniline (3ca): Brown oil (72% yield, 26.3 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (400 MHz, DMSO– d_6) δ 7.22 (d, J = 8.1 Hz, 1H), 7.18–7.03 (m, 2H), 6.44 (d, J = 8.8 Hz, 1H), 4.38 (d, J = 6.8 Hz, 0H), 2.24 (s, 2H), 1.38 (d, J = 6.7 Hz, 2H) ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 157.19, 155.69, 147.59, 141.01, 131.67, 130.46, 127.90, 123.79, 119.00, 118.95, 115.14, 106.77, 51.92, 24.96.

4–bromo–N–(1–(m–tolyl)ethyl)aniline (3da): Brown oil (62% yield, 18.1 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.19–7.09 (m, 5H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.9 Hz, 2H), 6.36 (d, *J* = 6.9 Hz, 1H), 4.38 (t, *J* = 6.8 Hz, 1H), 2.27 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 147.68, 146.05, 137.83, 131.63, 128.73, 127.70, 126.84, 123.38, 115.10, 106.66, 52.49, 25.03, 21.60.

4–bromo–N–(1–(2–methoxyphenyl)ethyl)aniline (3ea): Brown oil (60% yield, 18.2 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.23 (dd, J = 7.6, 1.7 Hz, 1H), 7.20–7.15 (m, 1H), 7.10 (d, J = 8.8 Hz, 2H), 6.99 (dd, J = 8.2, 1.1 Hz, 1H), 6.85 (td, J = 7.4, 1.1 Hz, 1H), 6.36 (dd, J = 11.0, 7.9 Hz, 3H), 4.72 (t, J = 6.9 Hz, 1H), 3.86 (s, 3H), 1.37 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 156.90, 147.54, 133.06, 131.68, 128.08, 125.93, 120.96, 114.82, 111.28, 106.63, 55.94, 46.27, 23.01

4–bromo–N–(1–(3,4,5–trimethylphenyl)ethyl)aniline (3ga): Brown oil (72% yield, 23.0 mg). petroleum ether/ethyl acetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.06 (d, J = 8.8 Hz, 2H), 6.72 (s, 2H), 6.32–6.15 (m, 3H), 4.65 (dd, J = 7.2, 5.9 Hz, 1H), 2.33 (s, 6H), 2.15 (s, 3H), 1.44 (d, J = 7.0 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 147.31, 136.82, 135.31, 135.24, 131.65, 130.63, 113.73, 106.04, 49.13, 20.80, 20.70, 20.38.

4–bromo–N–(1–(naphthalen–2–yl)ethyl)aniline (3ha): Brown oil (43% yield, 13.8 mg). petroleum ether/ethyl acetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.88–7.81 (m, 4H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.50–7.44 (m, 2H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.51 (dd, *J* = 12.0, 7.9 Hz, 3H), 4.61 (t, *J* = 6.7 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 147.64, 143.62, 133.44, 132.65, 131.65, 128.58, 126.52, 125.93, 125.00, 124.53, 115.21, 106.84, 52.72, 24.83.

4–bromo–N–(2–phenylpropan–2–yl)aniline (*3ia*): Brown oil (62% yield, 18.0 mg). petroleum ether/ethyl acetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.44–7.39 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.24 (d, *J* = 9.0 Hz, 2H), 6.20 (s, 1H), 1.55 (s, 6H). ¹³C NMR{¹H} (101 MHz, DMSO–*d*₆) δ 147.81, 146.50, 131.22, 128.92, 126.62, 125.75, 116.80, 106.78, 55.53, 30.40.

4–chloro–N–(1–(p–tolyl)ethyl)aniline (3ab): Brown oil (72% yield, 17.7 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.22 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.7

Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 8.8 Hz, 2H), 6.32 (d, J = 6.9 Hz, 1H), 4.39 (t, J = 6.7 Hz, 1H), 2.25 (s, 3H), 1.38 (d, J = 6.7 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 147.32, 143.01, 135.94, 129.39, 128.78, 126.23, 119.26, 114.58, 52.31, 25.05, 21.07.

3–(tert–butyl)–N–(1–(p–tolyl)ethyl)aniline (3ac): Brown oil (47% yield, 12.4 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.25 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 6.86 (t, J = 7.9 Hz, 1H), 6.59 (t, J = 2.1 Hz, 1H), 6.51–6.44 (m, 1H), 6.22 (dd, J = 7.9, 2.3 Hz, 1H), 5.97 (d, J = 6.7 Hz, 1H), 4.38 (p, J = 6.7 Hz, 1H), 2.25 (s, 4H), 1.38 (d, J = 6.7 Hz, 3H), 1.16 (s, 9H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 147.58, 142.72, 135.35, 131.25, 129.29, 128.77, 128.55, 127.72, 115.94, 114.24, 37.47, 21.56, 21.01.

3-fluoro-N-(1-(p-tolyl)ethyl)aniline (3ad): Brown oil (72% yield, 16.4 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO- d_6) δ 7.24 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 6.97 (q, J = 8.1 Hz, 1H), 6.47 (d, J = 6.9 Hz, 1H), 6.36–6.30 (m, 1H), 6.25–6.16 (m, 2H), 4.41 (t, J = 6.8 Hz, 1H), 2.25 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO- d_6) δ 150.55, 150.44, 143.02, 135.99, 130.45, 130.35, 129.41, 126.21, 109.53, 102.05, 101.84, 99.44, 99.19, 52.22, 24.97, 21.07. ¹⁹F NMR (565 MHz, DMSO- d_6) δ -113.50 (q, J = 9.8, 9.3 Hz).

3-chloro–N–(1–(p–tolyl)ethyl)aniline (3ae): Brown oil (69% yield, 17.0 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.24 (s, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.97 (t, J = 8.0 Hz, 1H), 6.48–6.43 (m, 3H), 6.44–6.41 (m, 1H), 4.42 (t, J = 6.8 Hz, 1H), 2.25 (s, 3H), 1.38 (d, J = 6.7 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 149.92, 142.90, 136.02, 133.77, 130.59, 129.44, 126.20, 115.36, 112.35, 111.87, 52.10, 25.01, 21.07.

3-bromo–N–(1–(p–tolyl)ethyl)aniline (3af): Brown oil (70% yield, 20.1 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.27–7.20 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.64 (t, *J* = 2.1 Hz, 1H), 6.58 (ddd, *J* = 7.8, 1.9, 0.8 Hz, 1H), 6.48–6.42 (m, 2H), 4.42 (t, *J* = 6.8 Hz, 1H), 2.26 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 150.10, 142.88, 136.03, 130.94, 129.45, 126.20, 122.52, 118.24, 115.30, 112.13, 52.07, 25.01, 21.08.

3–iodo–N–(1–(p–tolyl)ethyl)aniline (3ag): Brown oil (64% yield, 21.7 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.26–7.18 (m, 2H), 7.11 (s, 2H), 6.87 (t, J = 1.9 Hz, 1H), 6.79–6.72 (m, 2H), 6.46 (dt, J = 7.6, 2.0 Hz, 1H), 6.36 (d, J = 7.0 Hz, 1H), 4.39 (p, J = 6.8 Hz, 1H), 2.25 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 149.98, 142.91, 136.01, 131.11, 129.43, 126.20, 124.31, 121.46, 112.40, 95.67, 51.99, 25.01, 21.08.

3–((1–(*p*-tolyl)ethyl)amino)benzonitrile (3ah): Brown oil (64% yield, 21.7 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.25 (d, J = 7.8 Hz, 2H), 7.16 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 7.7 Hz, 2H), 6.87–6.83 (m, 1H), 6.81 (dd, J = 8.4, 2.4 Hz, 1H), 6.76 (t, J = 1.9 Hz, 1H), 6.70 (d, J = 7.0 Hz, 1H), 4.48 (t, J = 6.8 Hz, 1H), 2.25 (s, 3H), 1.40 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 148.86, 142.47, 136.17, 130.33, 129.50, 126.23, 119.99, 119.18, 118.03, 115.05, 111.82, 51.93, 24.88, 21.07.

2-methyl–N–(1–(p–tolyl)ethyl)aniline (3ai): Brown oil (51% yield, 11.6 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.27 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.3 Hz, 1H), 6.86–6.76 (m, 1H), 6.43 (t, J = 7.3 Hz, 1H), 6.27 (d, J = 8.1 Hz, 1H), 4.96 (d, J = 6.8 Hz, 1H), 4.48 (t, J = 6.7 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H), 1.47 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 145.82, 143.46, 135.80, 130.11, 129.33, 126.82, 126.23, 122.35, 116.20, 111.23, 52.43, 25.33, 21.08, 18.26.

2–*ethyl–N–(1–(p–tolyl)ethyl)aniline (3aj):* Brown oil (44% yield, 10.4 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.33–7.21 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.94 (dd, J = 7.3, 1.6 Hz, 1H), 6.81 (td, J = 7.7, 1.6 Hz, 1H), 6.47 (td, J = 7.3, 1.2 Hz, 1H), 6.29 (dd, J = 8.2, 1.1 Hz, 1H), 5.02 (d, J = 6.7 Hz, 1H), 4.48 (t, J = 6.7 Hz, 1H), 2.59 (q, J = 7.5 Hz, 2H), 2.24 (s, 3H), 1.47 (s, 3H), 1.20 (t, J = 7.5 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 145.12, 143.53, 135.80, 129.33, 127.98, 127.91, 126.69, 126.23, 116.40, 111.48, 52.44, 25.30, 23.78, 21.07, 13.69. **2**–*phenoxy–N–(1–(p–tolyl)ethyl)aniline (3ak):* Brown oil (31% yield, 9.5 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.38 (dd, J = 8.6, 7.3 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.6 Hz, 3H), 7.01–6.93 (m, 2H), 6.84 (td, J = 7.7, 1.5 Hz, 1H), 6.75 (dd, J = 7.7, 1.5 Hz, 1H), 6.52 (d, J = 8.1 Hz, 2H), 5.23 (d, J = 7.3 Hz, 1H), 4.53 (t, J = 6.9 Hz, 1H), 2.25 (s, 3H), 1.39 (d, J = 6.8 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 157.94, 142.97, 142.93, 140.00, 136.03, 130.23, 129.38, 126.21, 125.18, 123.11, 119.76, 117.73, 116.58, 113.28, 52.18, 24.96, 21.06.

3,4–difluoro–N–(1–(p–tolyl)ethyl)aniline (3am): Brown oil (70% yield, 17.2 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO–d₆) δ 7.24 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.01 (dt, J = 11.0, 9.2 Hz, 1H), 6.42–6.33 (m, 2H), 6.28–6.23 (m, 1H), 4.38 (t, J = 6.8 Hz, 1H), 2.25 (s, 3H), 1.37 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–d₆) δ 146.12, 146.02, 142.82, 136.05, 129.44, 126.23, 117.70, 117.53, 108.77, 101.14, 100.94, 52.53, 24.98, 21.06. ¹⁹F NMR (565 MHz, DMSO-d₆) δ -138.85 (ddd, J = 23.5, 13.8, 9.5 Hz), -159.38 (m).

3,4–dichloro–N–(1–(p–tolyl)ethyl)aniline (3an): Brown oil (71% yield, 20.0 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.63 (dd, *J* = 7.2, 4.7 Hz, 2H), 6.47 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.42 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H), 1.38 (d, *J* = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 148.53, 142.49, 136.15, 131.40, 130.73, 129.49, 126.19, 116.68, 113.90, 113.59, 52.17, 24.89, 21.07.

N–(*1*–(*p*–*tolyl*)*ethyl*)–3,5–*bis*(*trifluoromethyl*)*aniline* (*3ao*): Brown oil (60% yield, 20.7 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.02 (s, 2H), 6.99 (s, 1H), 4.59 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H), 1.43 (d, *J* = 6.7 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO–*d*₆) δ 149.53, 141.80, 136.39, 131.31, 130.99, 129.59, 126.19, 125.40, 122.69, 112.33, 52.00, 24.63, 21.05. ¹⁹F NMR (565 MHz, DMSO-*d*₆) δ -61.90 (s).

4–chloro–2–iodo–N–(1–(p–tolyl)ethyl)aniline (3ap): Brown oil (71% yield, 26.4 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.66 (d, J = 2.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.14–7.08 (m, 3H), 6.36 (d, J = 8.9 Hz, 1H), 4.89 (d, J = 6.7 Hz, 1H), 4.56 (p, J = 6.7 Hz, 1H), 2.25 (s, 3H), 1.49 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 145.89, 141.73, 137.60, 136.40, 129.59, 129.17, 126.13, 120.93, 113.16, 85.98, 53.09, 24.89, 21.07.

3,4,5-trichloro-N-(1-(p-tolyl)ethyl)aniline (3aq): Brown oil (74% yield, 23.2 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO- d_6) δ 7.23 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 7.1 Hz, 1H), 6.68 (s, 2H), 4.47 (t, J = 6.8 Hz, 1H), 2.26 (s, 3H), 1.38 (d, J = 6.7 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO- d_6) δ 148.24, 141.98, 136.34, 133.17, 129.58, 126.17, 114.96, 113.21, 51.99, 24.70, 21.07.

2,4,6-trimethyl–*N*–(*1*–(*p*-tolyl)ethyl)aniline (3ar): Brown oil (55% yield, 13.8 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.19 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.67 (s, 2H), 4.10 (t, *J* = 7.9 Hz, 1H), 3.74 (d, *J* = 10.3 Hz, 1H), 2.25 (s, 3H), 2.11 (s, 3H),

2.07 (s, 6H), 1.41 (d, J = 6.7 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO- d_6) δ 143.44, 143.07, 135.92, 129.76, 129.67, 129.50, 129.03, 126.60, 56.73, 23.57, 21.08, 20.62, 19.07.

5-bromo-N-(1-(p-tolyl)ethyl)pyrazin-2-amine (3as): Brown oil (47% yield, 13.6 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO- d_6) δ 8.03 (d, J = 1.4 Hz, 1H), 7.78–7.72 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.89 (t, J = 7.1 Hz, 1H), 2.26 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO- d_6) δ 153.88, 143.67, 142.11, 138.63, 136.16, 129.33, 126.31, 124.03, 50.01, 23.58, 21.07.

N–(*1*–(*p*–*tolyl*)*ethyl*)*benzo[b]thiophen*–*5*–*amine (3at):* Brown oil (60% yield, 15.9 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz,) δ 7.56 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 5.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 3H), 6.80–6.74 (m, 2H), 6.15 (d, *J* = 7.0 Hz, 1H), 4.48 (t, *J* = 6.8 Hz, 1H), 2.24 (s, 3H), 1.42 (d, *J* = 6.6 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 146.04, 143.41, 140.99, 135.80, 129.34, 127.33, 126.31, 123.82, 122.75, 114.73, 105.17, 52.51, 25.24, 21.07.

N–(*1*–(*p*–*tolyl*)*ethyl*)*quinolin–8–amine (3au):* Brown oil (42% yield, 11.1 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (400 MHz, DMSO–*d*₆) δ 8.78 (q, *J* = 3.5, 2.9 Hz, 1H), 8.36–8.08 (m, 1H), 7.52 (dq, *J* = 7.7, 3.5 Hz, 1H), 7.31 (dd, *J* = 7.7, 4.6 Hz, 2H), 7.21 (td, *J* = 7.8, 2.9 Hz, 1H), 7.10 (dd, *J* = 7.6, 4.6 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.50–6.30 (m, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 2.24 (t, *J* = 3.4 Hz, 3H), 1.66–1.49 (m, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 147.54, 143.67, 142.61, 136.47, 135.94, 129.49, 128.83, 128.71, 128.00, 126.21, 122.18, 113.96, 106.29, 52.22, 25.01, 21.08.

4–bromo–2–(1–(4–(tert–butyl)phenyl)ethyl)aniline (4ba): Brown oil (9% yield, 3.12 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.30 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 2.4 Hz, 1H), 7.04 (dd, J = 8.5, 2.4 Hz, 1H), 6.56 (d, J = 8.5 Hz, 1H), 4.98 (s, 2H), 4.13 (q, J = 7.1 Hz, 1H), 1.47 (d, J = 7.1 Hz, 3H), 1.26 (s, 9H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 148.73, 145.38, 142.39, 132.15, 129.48, 129.45, 127.50, 125.52, 117.30, 107.56, 37.69, 34.52, 31.64, 21.44.

4–bromo–2–(1–(3,4–dimethoxyphenyl)ethyl)aniline (4fa): Brown oil (58% yield, 19.3 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.04 (s, 2H), 6.86 (s, 2H), 6.73 (dd, J = 8.3, 2.1 Hz, 1H), 6.60–6.53 (m, 1H), 4.98 (s, 2H), 4.10 (d, J = 7.1 Hz, 1H), 3.72 (s, 6H), 1.46 (d, J = 7.1 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 149.06, 147.68, 145.37, 137.93, 132.39, 129.46, 119.52, 117.29, 112.38, 107.54, 56.50, 55.99, 37.93, 21.38.

4–bromo–2–(1–(3,4,5–trimethylphenyl)ethyl)aniline (4ga): Brown oil (12% yield, 3.7 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.25 (d, J = 2.4 Hz, 1H), 7.11 (dd, J = 8.4, 2.3 Hz, 1H), 6.80 (s, 2H), 6.55 (d, J = 8.4 Hz, 1H), 4.24 (s, 2H), 4.21 (d, J = 7.2 Hz, 1H), 2.18 (s, 3H), 2.10 (d, J = 4.4 Hz, 6H), 1.51 (d, J = 7.3 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 145.63, 136.91, 136.20, 135.66, 131.31, 130.87, 130.04, 129.51, 117.21, 108.11, 35.94, 21.17, 20.71, 17.77.

4–bromo–2–(1–(naphthalen–2–yl)ethyl)aniline (4ha): Brown oil (30% yield, 9.7 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.89–7.80 (m, 4H), 7.50–7.45 (m, 2H), 7.35 (dd, J = 8.5, 1.8 Hz, 1H), 7.08–7.01 (m, 2H), 6.60 (d, J = 9.2 Hz, 1H), 5.08 (s, 2H), 4.36 (dd, J = 5.8, 2.3 Hz, 1H), 1.58 (d, J = 7.0 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 145.53, 143.02, 133.49, 132.18, 131.96, 129.78, 129.67, 128.30, 128.01, 127.87, 127.14, 126.53, 125.95, 125.49, 117.43, 107.61, 38.36, 21.04.

4–bromo–2–(1–phenylvinyl)aniline (4ja): Brown oil (53% yield, 14.5 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.40–7.28 (m, 5H), 7.21 (dd, J = 8.7, 2.4 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.67 (d, J = 8.6 Hz, 1H), 5.87–5.82 (m, 1H), 5.33–5.27 (m, 1H), 4.73 (s, 2H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 145.78, 145.35, 139.26, 132.31, 131.34, 129.00, 128.54, 128.12, 126.80, 117.25, 117.19, 107.00.

4–chloro–2–(1–(p–tolyl)ethyl)aniline (4ab): Brown oil (5% yield, 1.3 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.15–7.07 (m, 4H), 6.92 (d, J = 7.8 Hz, 2H), 6.65–6.58 (m, 1H), 4.94 (s, 2H), 4.13 (q, J = 7.1 Hz, 1H), 2.26 (s, 3H), 1.45 (d, J = 7.1 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 144.96, 142.41, 135.48, 131.74, 129.37, 127.77, 126.76, 126.61, 120.02, 116.76, 37.88, 21.32, 21.03.

5-chloro-2-(1-(p-tolyl)ethyl)aniline (4ae): Brown oil (14% yield, 3.5 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO- d_6) δ 7.12–7.07 (m, 4H), 6.95 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 2.3 Hz, 1H), 6.53 (dd, J = 8.2, 2.3 Hz, 1H), 5.07 (s, 2H), 4.09 (q, J = 7.1 Hz, 1H), 2.25 (s, 3H), 1.45 (d, J = 7.0 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO- d_6) δ 151.30, 148.15, 143.76,135.72, 129.26, 126.30, 113.14, 110.96, 110.00, 32.60, 25.12, 21.08.

5–bromo–2–(1–(p–tolyl)ethyl)aniline (4af): Brown oil (11% yield, 3.2 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.09 (q, *J* = 8.1 Hz, 4H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 2.2 Hz, 1H), 6.66 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.07 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 2.25 (s, 3H), 1.44 (d, *J* = 7.1 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO–*d*₆) δ 147.87, 142.63, 135.36, 129.30, 129.16, 128.98, 127.73, 119.80, 118.83, 117.11, 37.50, 21.48, 21.01.

5-iodo-2-(1-(p-tolyl)ethyl)aniline (4ag): Brown oil (10% yield, 3.3 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO- d_6) δ 7.09 (q, J = 8.2 Hz, 4H), 6.97 (d, J = 1.9 Hz, 1H), 6.84 (dd, J = 8.1, 1.9 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 4.99 (s, 2H), 4.08 (q, J = 7.1 Hz, 1H), 2.25 (s, 3H), 1.43 (d, J = 7.1 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO- d_6) δ 147.88, 142.62, 135.35, 129.56, 129.41, 129.29, 127.73, 124.95, 123.13, 92.56, 37.56, 21.39, 21.02.

2-methyl-6-(1-(p-tolyl)ethyl)aniline (4ai): Brown oil (6% yield, 1.5 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.15–7.03 (m, 4H), 6.91 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 4.36 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 1H), 2.25 (s, 3H), 2.05 (s, 3H), 1.47 (d, *J* = 7.1 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 143.50, 143.42, 135.21, 129.28, 129.17, 128.32, 127.74, 124.97, 121.88, 116.58, 38.30, 22.09, 21.01, 18.45.

2–ethyl–6–(1–(p–tolyl)ethyl)aniline (4aj): Brown oil (6% yield, 1.2 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) ¹H NMR (600 MHz, DMSO– d_6) δ 7.16–7.04 (m, 4H), 6.93 (dd, J = 7.7, 1.5 Hz, 1H), 6.85 (dd, J = 7.7, 1.5 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 4.35 (s, 2H), 4.14 (t, J = 7.1 Hz, 1H), 2.48–2.37 (m, 3H), 2.25 (s, 3H), 1.47 (d, J = 7.1 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 143.46, 142.88, 135.23, 129.36, 129.32, 127.74, 127.56, 126.22, 124.87, 116.79, 38.42, 24.22, 22.22, 21.01, 13.65.

2–*phenoxy*–**6**–(*1*–(*p*–*tolyl*)*ethyl*)*aniline* (*4ak*): Brown oil (8% yield, 2.3 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 14.8, 8.1 Hz, 3H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.59 (t, *J* = 7.8 Hz, 1H), 4.49 (s, 2H), 4.22 (d, *J* = 7.2 Hz, 1H), 2.25 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO–*d*₆) δ 157.92, 142.96, 142.57, 137.77, 135.36, 131.97, 130.16, 129.34, 127.74, 123.30, 122.81, 118.05, 117.32, 116.69, 38.18, 21.88, 21.03.

2-bromo-6-(1-(p-tolyl)ethyl)aniline (4al): Brown oil (47% yield, 13.6 mg). petroleum ether/ethyl cetate: 8:1 ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.16 (d, *J* = 2.0 Hz, 1H), 7.13–7.03 (m, 4H), 6.94 (dd,

J = 8.3, 2.0 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 5.11 (s, 2H), 3.94 (d, J = 7.2 Hz, 1H), 2.24 (s, 3H), 1.47 (d, J = 7.2 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 144.15, 144.09, 136.35, 135.21, 130.96, 129.31, 127.71, 127.50, 115.86, 107.87, 42.87, 22.08, 21.01.

4,5–difluoro–2–(1–(p–tolyl)ethyl)aniline (4am): Brown oil (11% yield, 2.8 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.14–7.08 (m, 4H), 6.96–6.93 (m, 1H), 6.55 (dd, J = 13.2, 7.5 Hz, 1H), 4.93 (s, 2H), 4.09 (q, J = 7.1 Hz, 1H), 2.26 (d, J = 3.3 Hz, 3H), 1.45 (d, J = 7.1 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 143.71, 142.43, 135.50, 129.36, 129.22, 127.69, 116.13, 114.90, 103.00, 102.80, 37.52, 21.60, 21.02. ¹⁹F NMR (565 MHz, DMSO-d6) δ δ - 142.65 (ddd, J = 22.9, 13.3, 9.3 Hz), -154.69 (m).

4,5–dichloro–2–(1–(p–tolyl)ethyl)aniline (4an): Brown oil (11% yield, 3.2 mg). petroleum ether/ethyl cetate: 15:1 ¹H NMR (600 MHz, DMSO–d₆) δ 7.17–7.08 (m, 4H), 7.04 (s, 1H), 6.80 (s, 1H), 5.26 (s, 2H), 4.12 (q, J = 7.1 Hz, 1H), 2.26 (s, 3H), 1.45 (d, J = 7.0 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–d₆) δ 146.48, 141.98, 135.62, 130.89, 129.41, 128.88, 128.72, 127.74, 117.15, 115.78, 37.46, 21.22, 21.03

4–chloro–2–iodo–6–(1–(p–tolyl)ethyl)aniline (4ap): Brown oil (9% yield, 3.5 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.51 (d, J = 2.4 Hz, 1H), 7.15–7.09 (m, 4H), 7.01 (d, J = 2.5 Hz, 1H), 4.96 (s, 2H), 4.24 (q, J = 7.0 Hz, 1H), 2.26 (s, 3H), 1.46 (d, J = 7.1 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 144.53, 141.78, 135.80, 135.45, 132.00, 129.51, 127.77, 127.36, 121.03, 85.48, 21.45, 21.03.

6–(*1*–(*p*–*tolyl*)*ethyl*)*benzo[b]thiophen–5–amine (4at):* Brown solid (17% yield, 4.6 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.51 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 5.5 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.72 (dd, *J* = 18.9, 11.7 Hz, 3H), 2.26 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 142.95, 142.21, 139.38, 134.91, 129.41, 129.28, 127.33, 126.28, 123.34, 122.89, 121.13, 116.66, 36.23, 21.01, 17.45.

7–(1–(p–tolyl)ethyl)quinolin–8–amine (4au): Brown solid (33% yield, 8.6 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (400 MHz, DMSO–d₆) δ 8.72 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.42 (dd, J = 8.1, 4.1 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.09 (dd, J = 10.8, 8.2 Hz, 3H), 5.72 (s, 2H), 4.45 (t, J = 7.1 Hz, 1H), 2.23 (s, 3H), 1.57 (d, J = 7.1 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO–d₆) δ 147.64, 143.08, 141.32, 138.03, 136.17, 135.26, 129.28, 127.80, 127.14, 126.93, 125.67, 121.38, 114.47, 37.94, 21.24, 21.02.

2,6–dimethyl–4–(1–(p–tolyl)ethyl)aniline (4aB): Brown oil (52% yield, 12.5 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.13–7.02 (m, 4H), 6.67 (s, 2H), 4.32 (s, 2H), 3.86 (d, J = 7.2 Hz, 1H), 2.24 (s, 3H), 2.03 (s, 6H), 1.46 (d, J = 7.3 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 144.95, 142.49, 134.81, 134.17, 129.13, 127.47, 127.08, 120.93, 43.38, 22.35, 20.99, 18.37.

3–((4–bromophenyl)amino)propanenitrile (6aa): Brown oil (50% yield, 11.1 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.30–7.16 (m, 2H), 6.59 (d, J = 8.8 Hz, 2H), 6.16 (t, J = 6.2 Hz, 1H), 3.31 (d, J = 6.5 Hz, 2H), 2.71 (t, J = 6.5 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 147.55, 131.97, 120.08, 114.62, 107.41, 17.69.

3–((4–chlorophenyl)amino)propanenitrile (6ab): Brown oil (51% yield, 9.2 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–d₆) δ 7.12 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 6.13 (t, J = 6.2 Hz, 1H), 3.31 (s, 3H), 2.71 (t, J = 6.5 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO–d₆) δ 147.19, 129.16, 120.08, 120.06, 114.05, 17.73.

3–((3–chlorophenyl)amino)propanenitrile (6ae): Brown oil (43% yield, 7.7 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.10 (t, J = 8.0 Hz, 1H), 6.65 (t, J = 2.2 Hz, 1H), 6.62–6.53 (m, 2H), 6.27 (t, J = 6.1 Hz, 1H), 3.36 (d, J = 6.4 Hz, 2H), 2.71 (t, J = 6.5 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 149.80, 134.25, 130.98, 116.18, 111.79, 111.38, 17.77.

3–((3–bromophenyl)amino)propanenitrile (6af): Brown oil (37% yield, 8.2 mg). petroleum ether/ethyl cetate: 8:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.04 (t, J = 8.0 Hz, 1H), 6.79 (d, J = 2.1 Hz, 1H), 6.72 (ddd, J = 7.8, 1.9, 0.9 Hz, 1H), 6.62 (dd, J = 8.3, 2.2 Hz, 1H), 6.26 (t, J = 6.2 Hz, 1H), 3.33 (s, 2H), 2.71 (t, J = 6.5 Hz, 2H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 149.97, 131.30, 122.94, 120.06, 119.07, 114.71, 111.66, 30.57, 17.77.

3–((3–iodophenyl)amino)propanenitrile (6ag): Brown oil (48% yield, 12.9 mg). petroleum ether/ethyl cetate: 6:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 6.98 (t, *J* = 1.8 Hz, 1H), 6.93–6.84 (m, 2H), 6.63 (dt, *J* = 8.6, 1.6 Hz, 1H), 6.17 (t, *J* = 6.2 Hz, 1H), 3.31 (d, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 6.5 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 149.82, 131.45, 125.20, 120.77, 119.49, 111.98, 96.02, 17.76.

3–(*benzo[b]thiophen–5–ylamino)propanenitrile (6at):* Brown solid (45% yield, 9.0 mg). petroleum ether/ethyl cetate: 6:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.67 (d, J = 8.7 Hz, 1H), 7.62–7.58 (m, 1H), 7.23 (d, J = 5.4 Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 6.80 (dd, J = 8.7, 2.4 Hz, 1H), 5.96 (t, J = 6.3 Hz, 1H), 2.86–2.68 (m, 2H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 145.79, 141.33, 128.19, 127.69, 123.93, 123.16, 120.22, 114.31, 104.31, 17.69.

3–(p–tolylamino)propanenitrile (6av): Brown oil (51% yield, 9.8 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 6.92 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 5.66 (t, *J* = 6.3 Hz, 1H), 3.30 (q, *J* = 6.5 Hz, 2H), 2.69 (t, *J* = 6.5 Hz, 2H), 2.16 (s, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 145.92, 129.92, 125.25, 120.21, 112.84, 20.51, 17.82.

3–((4–(tert–butyl)phenyl)amino)propanenitrile (6aw): Brown oil (66% yield, 13.4 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 5.70 (s, 1H), 3.32–3.28 (m, 2H), 2.70 (t, *J* = 6.5 Hz, 2H), 1.22 (s, 9H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 145.77, 139.07, 126.07, 120.22, 112.43, 33.92, 31.90, 17.88.

3–(*m*–tolylamino)propanenitrile (6ax): Brown oil (57% yield, 9.2 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 6.98 (t, J = 7.7 Hz, 1H), 6.45–6.38 (m, 3H), 5.80 (t, J = 6.2 Hz, 1H), 3.32–3.29 (m, 2H), 2.70 (t, J = 6.5 Hz, 2H), 2.20 (s, 3H). ¹³C NMR {¹H} (101 MHz, DMSO–*d*₆) δ 148.18, 138.54, 129.35, 120.19, 117.76, 113.29, 109.99, 21.78, 17.83.

3–((3–methoxyphenyl)amino)propanenitrile (6ay): Brown oil (63% yield, 11.2 mg). petroleum ether/ethyl cetate: 8:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.02–6.96 (m, 1H), 6.21 (dt, J = 8.2, 1.4 Hz, 1H), 6.17 (dt, J = 7.2, 1.5 Hz, 2H), 5.93 (t, J = 6.2 Hz, 1H), 3.69 (s, 3H), 3.31 (t, J = 6.4 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H). ¹³C NMR{¹H} (101 MHz, DMSO– d_6) δ 160.89, 149.59, 130.23, 120.19, 105.66, 102.47, 98.38, 55.14, 17.84.

3–((1H–indol–5–yl)amino)propanenitrile (6az): Brown soild (53% yield, 9.7 mg). petroleum ether/ethyl cetate: 6:1 ¹H NMR (600 MHz, DMSO– d_6) δ 10.67 (s, 1H), 7.21–7.09 (m, 2H), 6.68 (d, J = 2.2 Hz, 1H), 6.55 (dd, J = 8.6, 2.2 Hz, 1H), 6.20 (td, J = 2.0, 1.0 Hz, 1H), 5.28 (t, J = 6.4 Hz, 1H), 3.34–3.31 (m, 2H), 2.73 (t, J = 6.6 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 141.47, 130.35, 128.92, 125.31, 120.38, 112.32, 111.74, 101.20, 100.55, 17.82.

ethyl 3–((4–bromophenyl)amino)propanoate (6ba): Brown soild (23% yield, 6.2 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.20 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.9

Hz, 2H), 5.88 (t, J = 5.8 Hz, 1H), 4.07 (q, J = 7.1 Hz, 2H), 3.25 (q, J = 6.5 Hz, 2H), 2.55 (d, J = 6.7 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 172.01, 148.18, 131.88, 114.46, 106.88, 60.40, 33.98, 14.53.

butyl 3–((4–bromophenyl)amino)propanoate (6ca): Brown soild (23% yield, 10.7 mg). petroleum ether/ethyl cetate: 12:1 ¹H NMR (600 MHz, DMSO–*d*₆) δ 7.20 (d, *J* = 8.8 Hz, 2H), 6.60–6.50 (m, 2H), 5.87 (t, *J* = 5.8 Hz, 1H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.25 (q, *J* = 6.5 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 1.58–1.50 (m, 2H), 1.35–1.29 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ¹³C NMR{¹H} (101 MHz, DMSO–*d*₆) δ 172.78, 148.18, 131.87, 114.45, 106.01, 64.14, 34.00, 30.61, 19.05, 14.1.

benzyl 3–((4–bromophenyl)amino)propanoate (6da): Brown soild (37% yield, 12.4 mg). petroleum ether/ethyl cetate: 10:1 ¹H NMR (600 MHz, DMSO– d_6) δ 7.41–7.32 (m, 5H), 7.24–7.17 (m, 2H), 6.60–6.51 (m, 2H), 5.91 (t, J = 5.8 Hz, 1H), 5.11 (s, 2H), 3.29 (q, J = 6.5 Hz, 2H), 2.63 (t, J = 6.7 Hz, 2H). ¹³C NMR {¹H} (101 MHz, DMSO– d_6) δ 171.93, 148.16, 136.59, 131.89, 128.87, 128.44, 128.34, 114.48, 106.91, 65.98, 33.97.

6. The ¹H NMR, ¹³C NMR{¹H} and ¹⁹F NMR spectra of the synthesized compounds

compounds

¹H NMR spectrum (600 MHz, DMSO-d₆) of **3aa**







¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ca**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3da**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ea**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ga**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ha**





¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ab**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ac**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ad**

¹⁹F NMR spectrum (565 MHz, DMSO-d₆) of **3ad**




¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ae**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3af**





¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ah**



S41





¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ak**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **3am**



















¹H NMR spectrum (600 MHz, DMSO-d₆) of **3ar**



S52





¹H NMR spectrum (600 MHz, DMSO-d₆) of **3au**







¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ga**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ha**





¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ab**



¹H NMR spectrum (600 MHz, DMSO-d₆) of 4ae







¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ai**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **4aj**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ak**





¹H NMR spectrum (600 MHz, DMSO-d₆) of **4am**







¹H NMR spectrum (600 MHz, DMSO-d₆) of **4an**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **4ap**




¹H NMR spectrum (600 MHz, DMSO-d₆) of 4au



¹H NMR spectrum (600 MHz, DMSO-d₆) of **4aB**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **6aa**



¹H NMR spectrum (600 MHz, DMSO-d₆) of 6ab



¹H NMR spectrum (600 MHz, DMSO-d₆) of **6ae**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **6af**



¹H NMR spectrum (600 MHz, DMSO-d₆) of 6ag



¹H NMR spectrum (600 MHz, DMSO-d₆) of 6at





¹H NMR spectrum (600 MHz, DMSO-d₆) of **6aw**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **6ax**



¹H NMR spectrum (600 MHz, DMSO-d₆) of 6ay





¹H NMR spectrum (600 MHz, DMSO-d₆) of **6ba**



¹H NMR spectrum (600 MHz, DMSO-d₆) of **6ca**



¹H NMR spectrum (600 MHz, DMSO-d₆) of 6da

7. The HRMS spectra of the new compounds





HRMS (ESI-TOF) spectrum of 3ca



HRMS (ESI-TOF) spectrum of 3da



HRMS (ESI-TOF) spectrum of 3ea



HRMS (ESI-TOF) spectrum of 3ga



HRMS (ESI-TOF) spectrum of 3ha



S94

HRMS (ESI-TOF) spectrum of **3ac**



HRMS (ESI-TOF) spectrum of 3ad



HRMS (ESI-TOF) spectrum of 3ae



HRMS (ESI-TOF) spectrum of 3af



HRMS (ESI-TOF) spectrum of 3ag



S99

HRMS (ESI-TOF) spectrum of 3ah



HRMS (ESI-TOF) spectrum of 3ai



HRMS (ESI-TOF) spectrum of 3aj



HRMS (ESI-TOF) spectrum of 3ak



HRMS (ESI-TOF) spectrum of 3am



HRMS (ESI-TOF) spectrum of 3an



HRMS (ESI-TOF) spectrum of 3ao



HRMS (ESI-TOF) spectrum of 3ap



HRMS (ESI-TOF) spectrum of 3aq


HRMS (ESI-TOF) spectrum of 3ar



HRMS (ESI-TOF) spectrum of 3as



HRMS (ESI-TOF) spectrum of 3at



HRMS (ESI-TOF) spectrum of 3au



HRMS (ESI-TOF) spectrum of 4ba



HRMS (ESI-TOF) spectrum of 4fa



HRMS (ESI-TOF) spectrum of 4ga



HRMS (ESI-TOF) spectrum of 4ha



HRMS (ESI-TOF) spectrum of 4ae



HRMS (ESI-TOF) spectrum of 4af



HRMS (ESI-TOF) spectrum of 4ai



HRMS (ESI-TOF) spectrum of 4aj



HRMS (ESI-TOF) spectrum of 4ak



HRMS (ESI-TOF) spectrum of 4al



HRMS (ESI-TOF) spectrum of 4am



HRMS (ESI-TOF) spectrum of 4an



HRMS (ESI-TOF) spectrum of 4ap



HRMS (ESI-TOF) spectrum of 4at



HRMS (ESI-TOF) spectrum of 4au



HRMS (ESI-TOF) spectrum of 6aa



HRMS (ESI-TOF) spectrum of 6ag



HRMS (ESI-TOF) spectrum of 6az



S130

HRMS (ESI-TOF) spectrum of 6ca



HRMS (ESI-TOF) spectrum of 6da

