Supporting Information

Selective photochemical synthesis of primary arylamines and symmetric diarylamines via amination of aryl bromides using Ni(NH₃)₆Cl₂ as a nitrogen source and catalyst

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1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and visualization on TLC was achieved by UV light and the use of ninhydrin and iodine color developer to assist. Flash column chromatography was performed on silica gel 200-300 mesh.

¹H NMR spectra, ¹³C{¹H} NMR spectra and ¹⁹F NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. ¹H NMR spectra was reported in units of parts per million (ppm) relative to tetramethylsilane (δ 0 ppm), CDCl₃ (δ 7.26 ppm) or DMSO-d₆ (δ 2.50 ppm). Multiplicities are given as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet) or m (multiplet). ¹³C{¹H} NMR spectra was reported in ppm relative to tetramethylsilane (δ 0 ppm), CDCl₃ (δ 77.16 ppm) or DMSO-d₆ (δ 39.52 ppm). HRMS (ESI) were performed on fourier transform ion cyclotron resonance mass spectrometer.

The purple LED lamp used in the experiments was assembled by ourselves (Figure S1). Each of lamp include: 9 W purple LED (390-395 nm, 3 LED lamp beads in series), aluminium radiator with fan, electric driver (XC-8W600-OS). The optical power up to 200 ± 10 mw at 1 cm axis distance detected by Thorlabs' Optical Power Meter (PM100D, S120VC). The LED beads were purchased from Zhuhai UV Optoelectronics Co., Ltd. (THUV395T3WL-3535-60).



Figure S1. Pictures of photo device and reaction tube

2. Optimization of reaction conditions

2.1 The reaction conditions for preparation of primary arylamines

Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) DBU (1.5 equiv) solvent (2.0 mL) 390-395 nm, 65-70 °C, 24 h	NH ₂ +	H H
solvent (2.0 mL)	diarylamine	arylamine
DMSO	13%	59%
DMF	16%	51%
DMAc	13%	42%
THF	N.D.	trace
1,4-Dioxane	N.D.	N.D.
CH ₃ CN	N.D.	7%
2-MeTHF	N.D.	N.D.
DMSO:THF=5:1	5%	35%
DMAC:THF=9:1	5%	16%
	Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) DBU (1.5 equiv) solvent (2.0 mL) 390-395 nm, 65-70 °C, 24 h Solvent (2.0 mL) DMSO DMF DMAC THF 1,4-Dioxane CH ₃ CN 2-MeTHF DMSO:THF=5:1 DMAC:THF=9:1	Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) DBU (1.5 equiv) b U (1.5 equiv) solvent (2.0 mL) 390-395 nm, 65-70 °C, 24 h Solvent (2.0 mL) diarylamine DMSO 13% DMF 16% DMAc 13% THF N.D. 1,4-Dioxane N.D. CH ₃ CN N.D. 2-MeTHF N.D. DMSO:THF=5:1 5% DMAC:THF=9:1 5%

Table S1.	The	screening	of	solvents
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Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), DBU (1.5 equiv), solvent (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3-benzodioxole as an internal standard.

Br –	Ni(NH ₃₎₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) base (1.5 equiv) DMSO (2.0 mL) 390-395 nm, 65-70 °C, 24 h	→ NH ₂ +	₩
entry	base (1.5 equiv)	diarylamine	arylamine
1	DBU	13%	59%
2	DBN	7%	31%
3	TBD	23%	40%
4	MTBD	trace	98%
5	DMTHPM	18%	61%
6	DABCO	5%	trace
7	TMG	6%	41%
8	<i>t</i> -BuTMG	trace	86%
9	DIPEA	trace	N.D.
10	Et ₃ N	5%	trace

Table S2. The screening of bases

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), base (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3-benzodioxole as an internal standard.



Reaction conditions: aryl bromide (0.2 mmol), $Ni(NH_3)_6Cl_2$ (35 mol%), ligand (5 mol%), *t*-BuTMG (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. The yields of arylamines were determined by ¹H NMR using 1,3-benzodioxole as an internal standard.

Table S4. The screening of the amount of DMSO

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), *t*-BuTMG (1.5 equiv), DMSO (x mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3-benzodioxole as an internal standard.

Br .	Ni(NH ₃) ₆ X₂ (x mol%) <i>d</i> -Mebpy (5 mol%) <u>t-BuTMG (1.5 equiv)</u> DMSO (2.0 mL) 390-395 nm, 65-70 °C, 24 h	→ ^{NH} 2 +	N N
entry	[Ni]-NH ₃ (x mol%)	diarylamine	arylamine
1	Ni(NH ₃) ₆ Br ₂ (35 mol%)	5%	62%
2	Ni(NH ₃) ₆ I ₂ (35 mol%)	trace	40%
3	Ni(NH ₃) ₆ Cl ₂ (17 mol%)	trace	75%
4	Ni(NH ₃) ₆ Cl ₂ (20 mol%)	trace	74%
5	Ni(NH ₃) ₆ Cl ₂ (25 mol%)	trace	79%
6	Ni(NH ₃) ₆ Cl ₂ (30 mol%)	trace	79%
7	Ni(NH ₃) ₆ Cl ₂ (35 mol%)	trace	83%
8	Ni(NH ₃) ₆ Cl ₂ (40 mol%)	trace	80%

Table S5. The screening of Ni(NH₃)₆X₂ (x mol%)

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆X₂ (x mol%), *d*-Mebpy (5 mol%), *t*-BuTMG (1.5 equiv), DMSO (x mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3-benzodioxole as an internal standard.

Table S6. Control experiments

Br	Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) MTBD (1.5 equiv) DMSO (2 mL) 390-395 nm, 65-70 °C, 24 h	→ NH ₂ +	H H
entry	reaction conditions	diarylamine	arylamine
1	Standard conditions	trace	98%
2	No Ni(NH ₃) ₆ Cl ₂	N.D.	N.D.
3	No ligand	N.D.	11%
4	No base	N.D.	N.D.
5	No light, 70 ^o C	N.D.	N.D.
6	Air instead of Ar	N.D.	31%

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), MTBD (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3-benzodioxole as an internal standard.

2.2 The reaction conditions for preparation of symmetric diarylamines

	Ni(NH ₃) ₆ Cl ₂ (35 mol%) Br d-Mebpy (5 mol%) <u>PS (2.0 mol% / 5. 0 mol%)</u> DBU (1.5 equiv) DMSO:THF=1:1 (2.0 mL) 390-395 nm, 65-70 °C, 24 h	•NH ₂ + 0	H N O
entry	PS (2.0 mol%)	diarylamine	arylamine
1	_	10%	48%
2	BP (5.0 mol%)	23%	49%
3	[lr(dtbbpy)(ppy) ₂][PF ₆] (2.0 mol%)	45%	45%
4	[Ir(dF(CF ₃) ₂ ppy) ₂ (dtbbpy)][PF ₆] (2.0 mol%)	22%	8%
5	Ru(2,2'-bpy) ₃ Cl ₂ ·6H ₂ O (2.0 mol%)	10%	36%

Table S7. The screening of photosensitizers

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), PS (2.0 mol% / 5.0 mol%), DBU (1.5 equiv), DMSO:THF=1:1 (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S8. The	screening	of t	bases
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 Br O	Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) [Ir(dtbbpy)(ppy) ₂][PF ₆] (2.0 mol%) base (1.5 equiv) DMSO:THF=1:1 (2.0 mL) 390-395 nm, 65-70 °C, 24 h	NH ₂ +	
entry	base (1.5 equiv)	diarylamine	arylamine
1	DBU	46%	45%
2	DBN	42%	24%
3	TBD	trace	14%
4	MTBD	5%	6%
5	DMTHPM	31%	46%
6	DABCO	trace	6%
7	TMG	29%	30%
8	<i>t</i> -BuTMG	38%	58%
9	DIPEA	trace	trace
10	DIPA	31%	12%
11	Et ₃ N	trace	7%

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (2.0 mol%), base (1.5 equiv), DMSO:THF=1:1 (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

	Ni(<mark>NH₃)</mark> 6	Cl ₂ (35 mol%)			
	d-Meb	py (5 mol%) ()_][PE_] (2 0 mol%	() NH		н
	Br (IIIUUUUUU) DBU (solver additive light source	(1.5 equiv) (1.5 equiv) (1.0 equiv) (1.0 equiv) (1.0 equiv)			
entry	solvent (2.0 mL)	light source	additive (1.0 equiv)	diarylamine	arylamine
1	DMSO:THF=1:1	390-395 nm	_	45%	45%
2	THF	390-395 nm	—	20%	trace
3	1,4-Dioxane	390-395 nm	—	23%	trace
4	CH ₃ CN	390-395 nm	—	21%	60%
5	2-MeTHF	390-395 nm	—	17%	8%
6	Toulene	390-395 nm	—	15%	trace
7	DMSO	390-395 nm	—	46%	46%
8	DMAc	390-395 nm	—	45%	18%
9	DMF	390-395 nm	—	50%	17%
10	DMF	365-370 nm	—	21%	35%
11	DMF	460-465 nm	—	35%	45%
12	DMF	490-495 nm	—	32%	57%
13	DMF	520-530 nm	—	26%	54%
14	DMF	390-395 nm	TBAC	32%	29%
15	DMF	390-395 nm	TBAB	39%	18%
16	DMF	390-395 nm	TBAI	9%	63%
17	DMF	390-395 nm	NaCl	44%	24%
18	DMF	390-395 nm	NaBr	38%	27%
19	DMF	390-395 nm	KBr	45%	27%
20	DMF	390-395 nm	KI	8%	74%

Table S9. The screening of solvents, light sources and additives

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (2.0 mol%), DBU (1.5 equiv), additive (1.0 equiv), solvent (2.0 mL), light source, 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

	Ni(NH d-M [Ir(dtbbpy)(D 390-395	₃₎₆ Cl ₂ (35 mol%) ebpy (5 mol%) [ppy) ₂][PF ₆] (x mol%) BU (y equiv) MSO (z mL) nm, 65-70 °C, 24 h		NH ₂ + 0	H N O O
entry	DBU (y equiv)	DMSO (z mL)	[lr] (x mol%)	diarylamine	arylamine
1	0.5	2.0 mL	2.0 mol%	32%	11%
2	1.0	2.0 mL	2.0 mol%	61%	21%
3	1.5	2.0 mL	2.0 mol%	47%	38%
4	2.0	2.0 mL	2.0 mol%	48%	39%
5	2.5	2.0 mL	2.0 mol%	42%	46%
6	3.0	2.0 mL	2.0 mol%	39%	48%
7	3.5	2.0 mL	2.0 mol%	36%	51%
8	1.0	1.0 mL	2.0 mol%	63%	11%
9	1.0	1.5 mL	2.0 mol%	59%	17%
10	1.0	2.5 mL	2.0 mol%	55%	17%
11	1.0	3.0 mL	2.0 mol%	54%	20%
12	1.0	1.0 mL	0.5 mol%	36%	39%
13	1.0	1.0 mL	1.0 mol%	50%	32%
14	1.0	1.0 mL	1.5 mol%	61%	17%
15	1.0	1.0 mL	2.5 mol%	65%	24%
16	1.0	1.0 mL	3.0 mol%	65%	25%
17	1.0	1.0 mL	3.5 mol%	72%	15%
18	1.0	1.0 mL	4.0 mol%	69%	15%

Table S10.	The screening	of the amount	of DBU, DMSO	and [Ir(dtbbpy	$(ppy)_2 [PF_6]$
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Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (x mol%), DBU (y equiv), DMSO (z mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S11. The screening of Ni(NH₃)₆X₂

_(D O O	Ni(NH ₃₎₆ X ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) [Ir(dtbbpy)(ppy) ₂][PF ₆] (3.5 mol%) DBU (1.0 equiv) DMSO (1.0 mL) 390-395 nm, 65-70 °C, 24 h	NH ₂ + 0	
	entry	[Ni]-NH ₃ (35 mol%)	diarylamine	arylamine
	1	Ni(NH ₃) ₆ Cl ₂	73%	15%
	2	$Ni(NH_3)_6Br_2$	61%	8%
	3	$Ni(NH_3)_6I_2$	8%	79%

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆X₂ (35 mol%), *d*-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.



Reaction conditions: aryl bromide (0.2 mmol), $Ni(NH_3)_6Cl_2$ (35 mol%), ligand (5 mol%), [Ir(dtbbpy)(ppy)_2][PF_6] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. The yields of diarylamines were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S13. Control experiments

O Br	Ni(NH ₃) ₆ Cl ₂ (35 mol%) <i>d</i> -Mebpy (5 mol%) [Ir(dtbbpy)(ppy) ₂][PF ₆] (3.5 mol%) DBU (1.0 equiv) DMSO (1.0 mL) 390-395 nm, 65-70 °C, 24 h	NH ₂ + 0	
entry	reaction conditions	diarylamine	arylamine
1	Standard conditions	72%	15%
2	No Ni(NH ₃) ₆ Cl ₂	N.D.	N.D.
3	No dmebpy	58%	25%
4	No [lr]	11%	47%
5	No DBU	N.D.	trace
6	No light, 70 ^o C	N.D.	N.D.
7	Air instead of Ar	33%	33%
8	390-395 nm, R.T.	19%	4%

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

3. General procedure for reactions

3.1 Synthesis of [(NH₃)₆Ni]X₂^[2]

NiX₂
$$\xrightarrow{\text{NH}_4\text{X}, \text{ excessive } \text{NH}_3 \cdot \text{H}_2\text{O}}_{\text{ice bath}}$$
 [(NH₃)₆Ni]X₂

In an ice bath, a magnetic stir bar, NiX_2 , NH_4X and excessive ammonia water, were placed into an oven-dried 25 mL dried round-bottomed flask. The reaction mixture for 2-12 h when the reaction is completed. The resulting purplish solution was rinsed with ammonia water and ethanol. The precipitate was filter collected on a frit, rinsed with ethanol and residual solvent was removed under vacuum to give the compound. The compound was used without further purification.

3.2 Standard procedure for exploration of the scope of arylamines



To an oven-dried 10 mL of storage tube were added solid aryl bromides (0.2 mmol) (liquid aryl bromides were added via syringe after purged and evacuated), Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then *t*-BuTMG (1.5 equiv) or MTBD (1.5 equiv) and DMSO (2.0 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with 9 W purple LEDs (390-395 nm, 1 cm away from the tube, optical power: $200 \pm 10 \text{ mw/cm}^2$) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with saturated brine or saturated NH₄Cl (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.3 Standard procedure for exploration of the scope of symmetric diarylamines

 $Ni(NH_3)_6Cl_2$ (35 mol%) d-Mebpy (5 mol%) [lr(dtbbpy)(ppy)₂][PF₆] (3.5 mol%) DBU (1.0 equiv) DMSO (1.0 mL) 390-395 nm, 65-70 °C, 24 h

To an oven-dried 10 mL of storage tube were added solid aryl bromides (0.2 mmol) (liquid aryl bromides were added via syringe after purged and evacuated), Ni(NH₃)₆Cl₂ (35 mol%), (4,4'-dimethyl-2,2'-bipyridine) *d*-Mebpy (5 mol%), $[Ir(dtbbpy)(ppy)_2][PF_6]$ (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then DBU (1.0 equiv) and DMSO (1.0 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with 9 W purple LEDs (390-395 nm, 1 cm away from the tube, optical power: $200 \pm 10 \text{ mw/cm}^2$) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH₄Cl (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.4 Preparation of benzocaine at gram scale



To an oven-dried 200 mL of storage tube were added Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then ethyl 4-bromobenzoate (10 mmol), *t*-BuTMG (1.5 equiv) and DMSO (100 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH₄Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.5 Preparation of antioxidant at gram scale



To an oven-dried 100 mL of storage tube were added Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then 1-bromo-4-octylbenzene (5 mmol), DBU (1.0 equiv) and DMSO (25 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 48 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH₄Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.6 Preparation of bis(4-methoxyphenyl)amine



To an oven-dried 10 mL of storage tube were added Ni(NH₃)₆Cl₂ (35 mol%), *d*-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%), [Ir(dtbbpy)(ppy)₂][PF₆] (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then 4-bromoanisole (2 mmol), DBU (1.0 equiv) and DMSO (4 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH₄Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.



3.7 Preparation of organic hole-transporting material Spiro-OMeTAD

According to literature, Spiro-OMeTAD was synthesized.^[22] To an oven-dried 10 mL of storage tube were added 2,2',7,7'-tetrabromo-9,9'-spirobi[9H-fluorene] (0.2 mmol), 4,4'-dimethoxydiphenylamine (0.9 mmol), sodium tert-butoxide (6.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (5 mol%), tri-tert-butylphosphine (10 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then toluene (2 mL) was added. The tube was sealed with a Teflon screw valve. The reaction mixture was heated at 110 °C for 16 h. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

4. Analytical data of products



Aniline (4): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (t, *J* = 7.6 Hz, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 3.61 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.5, 129.4, 118.6, 115.2. Spectral datas obtained for the compound are in good agreement with the reported datas.^[1]



4-(Methylsulfonyl)aniline (5): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.24 (br, 2H), 2.99 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.5, 129.6, 128.9, 114.2, 45.1. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Aminobenzenesulfonamide (6): yellow solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.50 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 5.82 (s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 151.9, 130.1, 127.5, 112.5. Spectral datas obtained for the compound are in good agreement with the reported datas.^[3]



4-(Trifluoromethyl)aniline (7): light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 8.3 Hz, 1H), 6.69 (d, J = 8.3 Hz, 1H), 3.94 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.5, 126.8 (q, J = 4.0 Hz), 125.0 (q, J = 269.0 Hz), 120.3 (q, J = 32.0 Hz), 114.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.25. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Aminobenzonitrile (8): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.17 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 150.6, 133.9, 120.3, 114.5, 100.2. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



Methyl 4-aminobenzoate (9): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.08 (br, 2H), 3.85 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.3, 150.9, 131.7, 119.9, 113.9, 51.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



1-(4-Aminophenyl)ethan-1-one (10): light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.13 (br, 2H), 2.50 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 196.6, 151.2, 130.9, 128.1, 113.9, 26.2. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



N-(4-Aminophenyl)acetamide (11) : yellow solid; ¹H NMR (400 MHz, DMSO- d_6) δ 9.60 (s, 1H), 7.23 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 4.84 (br, 2H), 1.99 (s, 3H). ¹³C{¹H} NMR (100 MHz, DMSO- d_6) δ 167.8, 145.0, 129.1, 121.3, 114.3, 24.1. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Vinylaniline (12): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, J = 8.3 Hz, 2H), 6.60 (d, J = 8.3 Hz, 2H), 6.58 – 6.56 (m, 1H), 5.52 (d, J = 17.6 Hz, 1H), 5.01 (d, J = 10.9 Hz, 1H), 3.66 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.3, 136.7, 128.5, 127.5, 115.1, 110.1. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -126.85. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Fluoroaniline (13): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.86 (t, J = 8.7 Hz, 1H), 6.63 – 6.60 (m, 1H), 3.53 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.6 (d, J = 235.0 Hz) 142.5, 116.2 (d, J = 7.0 Hz), 115.8 (d, J = 23.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -126.85. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Chloroaniline (14): light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 3.63 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.1, 129.2, 123.2, 116.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Bromoaniline (15): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 3.66 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.5, 132.1, 116.8, 110.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



[1,1'-Biphenyl]-4-amine (16): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.3 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.30 – 7.26 (m, 1H), 6.77 (d, J = 8.5 Hz, 2H), 3.72 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.0, 141.3, 131.7, 128.8, 128.2, 126.5, 126.4, 115.5. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



p-Toluidine (17): white solid; ¹H NMR (400 MHz, CDCl₃) δ 6.98 (d, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 2H), 3.44 (br, 2H), 2.25 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.8, 129.9, 128.0, 115.4, 20.6. Spectral datas obtained for the compound are in good agreement with the reported datas.^[7]



4-Isopropylaniline (18): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 2H), 3.47 (br, 2H), 2.85 (hept, *J* = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.3, 139.3, 127.2, 115.3, 33.3, 24.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Octylaniline (19): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.9 (d, J = 8.3 Hz, 2H), 6.63 (d, J = 8.3 Hz, 2H), 3.48 (br, 2H), 2.50 (t, J = 7.6 Hz, 2H), 1.56 (p, J = 7.2 Hz, 2H), 1.31 - 1.27 (m, 10H), 0.89 (t, J = 6.7 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.1, 133.3, 129.3, 115.4, 35.2, 32.0, 32.0, 29.6, 29.4, 29.4, 22.8, 14.2. Spectral datas obtained for the compound are in good agreement with the reported datas.^[4]



4-Cyclopropylaniline (20): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.91 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 3.27 (br, 2H), 1.85 – 1.78 (m, 1H), 0.86 (q, *J* = 5.1 Hz, 2H), 0.59 (q, *J* = 5.1 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.1, 134.0, 126.9, 115.4, 14.7, 8.4.Spectral datas obtained for the compound are in good agreement

with the reported datas.^[5]



4-(Trifluoromethoxy)aniline (21): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.68 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.4, 141.5, 122.5, 120.8 (d, J = 256.5 Hz), 115.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.48. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



4-Methoxyaniline (22): black solid; ¹H NMR (400 MHz, CDCl₃) δ 6.75 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.32 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.3, 140.5, 116.9, 115.3, 56.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



3,5-Dimethylaniline (2): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.43 (s, 1H), 6.35 (s, 2H), 3.45 (br, 2H), 2.23 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.3, 139.1, 120.7, 113.2, 21.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



o-Toluidine (23): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.11 – 7.07 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.59 (s, 2H), 2.21 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.7, 130.5, 127.0, 122.4, 118.7, 115.0, 17.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[6]



2-Isopropylaniline (24): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (dd, J = 7.7, 1.5 Hz, 1H), 7.04 (td, J = 7.7, 1.5 Hz, 1H), 6.80 (td, J = 7.9, 1.1 Hz, 1H), 6.69 (dd, J = 7.9, 1.1 Hz, 1H), 3.65 (s, 2H), 2.92 (hept, J = 6.8 Hz, 1H), 1.28 (d, J = 6.8 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.4, 132.8, 126.6, 125.5, 119.2, 116.0, 27.8, 22.4. Spectral datas obtained for the compound are in good agreement with the reported datas.[2]



3-Fluoroaniline (25): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.06 (m, 1H), 6.47 – 6.36 (m, 3H), 3.71 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 164.0 (d, J =244.4 Hz), 148.4 (d, J = 11.1 Hz), 130.6 (d, J = 10.1 Hz), 110.8 (d, J = 2.0 Hz), 105.2 (d, J = 21.2 Hz), 102.1 (d, J = 25.3 Hz).¹⁹F NMR (376 MHz,CDCl₃) δ -113.20. Spectral datas obtained for the compound are in good agreement with the reported datas.^[10]



3-Chloroaniline (26): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.67 (t, *J* = 2.0 Hz, 1H), 6.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.67 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.8, 134.9, 130.4, 118.5, 115.0, 113.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[6]



3-(Difluoromethoxy)aniline (27): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.66 – 6.29 (m, 4H), 3.63 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.7, 147.2, 129.6, 115.2 (t, *J* = 259.6 Hz), 111.1, 107.8, 105.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.24 (d, *J* = 71.4 Hz). Spectral datas obtained for the compound are in good agreement with the reported datas.^[12]



Naphthalen-2-amine (28): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.68 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.27 (t, *J* = 9.1 Hz, 1H), 7.00 – 6.96 (m, 2H), 3.86 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.2, 135.1, 129.3, 128.1, 127.8, 126.5, 125.9, 122.6, 118.4, 108.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[8]



Pyridin-2-amine (29): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 4.9

Hz, 1H), 7.36 (td, J = 8.3, 1.8 Hz, 1H), 6.58 (td, J = 4.9, 1.8 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 4.57 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.6, 148.1, 137.7, 113.9, 108.6. Spectral datas obtained for the compound are in good agreement with the reported datas.^[3]



Pyridin-3-amine (30): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 2.7 Hz, 1H), 7.95 (d, *J* = 4.7 Hz, 1H), 7.00 (dd, *J* = 8.1, 4.7 Hz, 1H), 6.91 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.82 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 142.8, 139.8, 137.4, 123.7, 121.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[3]



4-(Trifluoromethyl)pyridin-2-amine (31): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 6.62 (dd, J = 5.5, 1.8 Hz, 1H), 4.65 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.0, 150.4, 149.0 (q, J = 34.0 Hz), 121.8 (q, J = 272.0 Hz), 111.2, 106.4 (q, J = 2.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ - 68.54. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



3-Methylpyridin-2-amine (32): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 6.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.54 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.56 (br, 2H), 2.05 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 157.3, 145.6, 137.6, 116.5, 114.2, 17.1. Spectral datas obtained for the compound are in good agreement with the reported datas.^[9]



6-Methoxypyridin-3-amine (33): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 2.9 Hz, 1H), 7.01 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.59 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 3H), 3.16 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.2, 136.8, 133.0, 127.8, 110.8, 53.4. Spectral datas obtained for the compound are in good agreement with the reported

datas.[9]



5-Chloro-2-methoxypyridin-3-amine (34): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 2.2 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 3.95 (s, 3H), 3.60 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.5, 132.7, 131.8, 124.4, 119.6, 53.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[9]



Dibenzo[b,d]furan-3-amine (35): light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.3 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.84 (s, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.36 (br, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 158.1, 156.1, 146.9, 125.3, 125.0, 122.7, 121.4, 119.5, 115.8, 111.4, 111.3, 97.6. Spectral datas obtained for the compound are in good agreement with the reported datas.^[11]



1H-Indol-5-amine (36): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (br, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.12 (s, 1H), 6.95 (s, 1H), 6.67 (d, J = 8.5 Hz, 1H), 6.38 (s, 1H), 3.50 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 139.7, 130.9, 129.0, 124.8, 113.1, 111.6, 105.7, 101.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



Benzo[b]thiophen-3-amine (37): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 5.4 Hz, 1H), 7.15 (d, J = 5.4 Hz, 1H), 7.10 (d, J = 1.8 Hz, 1H), 6.78 (dd, J = 8.5, 1.8 Hz, 1H), 3.58 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.7, 141.0, 130.6, 127.2, 123.2, 123.1, 115.0, 108.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



2,3-Dihydrobenzo[b][1,4]dioxin-6-amine (38): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.67 (d, *J* = 8.5 Hz, 1H), 6.24 (d, *J* = 2.6 Hz, 1H), 6.20 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.22 – 4.20 (m, 2H), 4.18 – 4.16 (m, 2H), 3.28 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.0, 140.9, 136.5, 117.7, 108.8, 104.3, 64.8, 64.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



5-Aminoisobenzofuran-1(3H)-one (39): yellow solid; ¹H NMR (400 MHz, DMSO d_6) δ 7.48 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.62 (s, 1H), 6.28 (s, 2H), 5.19 (s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO- d_6) δ 170.8, 154.7, 150.2, 126.2, 114.8, 111.1, 104.5, 68.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



Quinolin-2-amine (40): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.55 (td, J = 7.0, 1.3 Hz, 1H), 7.25 (t, J = 7.0 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 4.96 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 157.2, 147.8, 138.2, 129.9, 127.6, 126.1, 123.7, 122.8, 111.8. Spectral datas obtained for the compound are in good agreement with the reported datas.^[9]



Isoquinolin-3-amine (41): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 8.93 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.26 (t, J = 8.2 Hz, 1H), 6.77 (s, 1H), 4.52 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.7, 151.8, 139.0, 130.5, 127.9, 124.8, 124.2, 123.2, 99.7. Spectral datas obtained for the compound are in good agreement with the reported datas.^[9]



4-(9H-Carbazol-9-yl)aniline (42): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 7.7 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.33 – 7.28 (m, 4H), 6.86 (d, J = 8.5 Hz, 2H), 3.80 (br, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.1,

141.7, 128.6, 128.3, 125.9, 123.1, 120.3, 119.6, 116.0, 109.9. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



Ethyl 4-aminobenzoate (76): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.05 (br, 2H), 1.36 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 166.83, 150.84, 131.69, 120.31, 113.92, 76.84, 60.43, 14.56. Spectral datas obtained for the compound are in good agreement with the reported datas.^[2]



Diphenylamine (45): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.7 Hz, 4H), 7.12 (d, *J* = 8.1 Hz, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 5.72 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.3, 129.5, 121.2, 118.0. Spectral datas obtained for the compound are in good agreement with the reported datas.^[13]



Di-*p*-tolylamine (46): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, *J* = 8.2 Hz, 4H), 6.95 (d, *J* = 8.2 Hz, 4H), 5.51 (br, 1H), 2.30 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.3, 130.3, 130.0, 118.1, 20.8. Spectral datas obtained for the compound are in good agreement with the reported datas.^[13]



Bis(4-octylphenyl)amine (47): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 8.4 Hz, 4H), 2.54 (t, J = 7.6 Hz, 4H), 1.59 (p, J = 7.4 Hz, 4H), 1.34 – 1.26 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.7, 29.5, 29.4, 22.8, 14.3. Spectral datas obtained for the compound are in good agreement with the reported datas.^[15]



Bis(4-decylphenyl)amine (48): black solid; ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, J = 8.4 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 2.55 (t, J = 7.6 Hz, 4H), 1.60 (p, J = 7.2 Hz,

4H), 1.32 - 1.28 (m, 28H), 0.90 (t, J = 6.8 Hz, 6H). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) δ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.9, 29.8, 29.8, 29.7, 29.5, 22.8, 14.3. HRMS (ESI) m/z calc. for C₃₂H₅₂N [M+H]⁺: 450.4094, found: 450.4089.



Bis(4-dodecylphenyl)amine (49): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, J = 8.3 Hz, 4H), 6.97 (d, J = 8.3 Hz, 4H), 5.56 (br, 1H), 2.62 – 2.47 (m, 4H), 1.65 – 1.53 (m, 6H), 1.27 (s, 34H), 0.89 (t, J = 6.7 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 22.9, 14.3. HRMS (ESI) m/z calc. for C₃₆H₆₀N [M+H]⁺: 506.4720, found: 506.4716.



Bis(4-cyclohexylphenyl)amine (50): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, J = 8.4 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 2.52 – 2.39 (m, 2H), 1.94 – 1.67 (m, 11H), 1.39 (p, J = 12.0 Hz, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 140.7, 127.5, 43.82, 34.8 27.0, 26.21. HRMS (ESI) m/z calc. for C₂₄H₃₂N [M+H]⁺: 334.2529, found: 334.2529.



N-(**Bicyclo**[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[4.2.0]octa-1(6),2,4-trien-3-amine (51): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.81 (s, 2H), 3.12 (s, 8H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.6, 143.3, 138.2, 123.5, 117.6, 113.2, 29.3, 29.1. HRMS (ESI) m/z calc. for C₁₆H₁₆N [M+H]⁺: 222.1277, found: 222.1275.



Bis(4-phenoxyphenyl)amine (52): gray solid; ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.29 (m, 4H), 7.11 – 6.92 (m, 14H), 5.55 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.4, 150.9, 139.8, 129.8, 122.7, 120.8, 119.5, 118.0. HRMS (ESI) m/z calc. for C₂₄H₂₀NO₂ [M+H]⁺: 354.1489, found: 354.1488.



Bis(4-methoxyphenyl)amine (53): black solid; ¹H NMR (400 MHz, CDCl₃) δ 6.94 (d, J = 8.7 Hz, 4H), 6.83 (d, J = 8.7 Hz, 4H), 5.30 (br, 1H), 3.78 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.4, 138.1, 119.7, 114.8, 55.8. Spectral datas obtained for the compound are in good agreement with the reported datas.^[15]



Bis(4-(methylthio)phenyl)amine (54): black solid; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, *J* = 7.0 Hz, 4H), 6.89 (d, *J* = 7.4 Hz, 4H), 5.56 (br, 1H), 2.36 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 130.0, 129.4, 118.7, 18.0. Spectral datas obtained for the compound are in good agreement with the reported datas.^[16]



Bis(4-(trimethylsilyl)phenyl)amine (55): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.4 Hz, 4H), 7.11 (d, J = 8.4 Hz, 4H), 5.80 (br, 1H). 0.28 (s, 18H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.5, 134.7, 131.9, 117.2, -0.3. HRMS (ESI) m/z calc. for C₁₈H₂₈NSi₂ [M+H]⁺: 314.1760, found: 314.1757.



Bis(4-fluorophenyl)amine (56): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 6.96 (m, 8H), 5.48 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 157.8 (d, *J* = 240.4 Hz), 139.8 (d, *J* = 2.0 Hz), 119.4 (d, *J* = 8.1 Hz), 116.0 (d, *J* = 22.2 Hz) ¹⁹F NMR (376 MHz, CDCl₃) δ -122.63. Spectral datas obtained for the compound are in good agreement with the reported datas.^[13]



Bis(4-(trifluoromethyl)phenyl)amine (57): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.5 Hz, 4H), 7.16 (d, J = 8.5 Hz, 4H), 6.11 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.1, 124.6 (d, J = 271.7 Hz), 127.1 (d, J = 3.0 Hz), 123.9 (d, J = 32.3

Hz), 117.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.78. Spectral datas obtained for the compound are in good agreement with the reported datas.^[13]



1,1'-(Azanediylbis(4,1-phenylene))bis(ethan-1-one) (58): black solid; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.8 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 4H), 2.56 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 196.6, 146.1, 131.0, 130.6, 117.1, 26.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[18]



Dimethyl 4,4'-azanediyldibenzoate (44): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.6 Hz, 4H), 7.12 (d, *J* = 8.6 Hz, 4H), 6.61 (br, 1H), 3.88 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.8, 146.0, 131.6, 123.3, 117.1, 52.0. Spectral datas obtained for the compound are in good agreement with the reported datas.^[18]



4,4'-Azanediyldibenzonitrile (59): brown solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.51 (br, 1H), 7.74 (d, *J* = 7.4 Hz, 4H), 7.30 (d, *J* = 7.4 Hz, 4H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 145.7, 133.7, 119.4, 117.3, 102.1. Spectral datas obtained for the compound are in good agreement with the reported datas.^[19]



Bis(4-chlorophenyl)amine (60): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.7 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 4H), 5.64 (br, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 129.4, 126.1, 112.0. Spectral datas obtained for the compound are in good agreement with the reported datas.^[13]



Di-*o*-tolylamine (61): white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 2H), 5.16 (br, 1H), 2.28 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 142.1, 131.0, 127.1, 126.9, 121.5,

118.4, 17.9. Spectral datas obtained for the compound are in good agreement with the reported datas.^[14]



Bis(2-methoxyphenyl)amine (62): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 7.6 Hz, 2H), 6.95 – 6.84 (m, 6H), 6.52 (br, 1H), 3.91 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.2, 132.7, 120.9, 120.3, 115.7, 110.8, 55.8. HRMS (ESI) m/z calc. for C₁₄H₁₅NNaO₂ [M+Na]⁺: 252.1000, found: 252.0990.



Bis(2-isopropylphenyl)amine (63): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 7.6 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 7.02 – 6.94 (m, 4H), 5.33 (br, 1H), 3.12 (hept, J = 6.8 Hz, 2H), 1.30 (d, J = 6.8 Hz, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.4, 138.2, 126.5, 125.8, 121.8, 119.4, 27.8, 22.8. Spectral datas obtained for the compound are in good agreement with the reported datas.^[14]



Bis(2-isopropoxyphenyl)amine (64): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.8 Hz, 2H), 6.90 (t, J = 7.7 Hz, 4H), 6.81 (m, 2H), 4.55 (hept, J = 5.7 Hz, 2H), 1.39 (d, J = 6.0 Hz, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.9, 134.1, 121.1, 119.7, 115.0, 114.3, 71.4, 22.5. HRMS (ESI) m/z calc. for C₁₈H₂₃NNaO₂ [M+Na]⁺: 308.1626, found: 308.1621.



Bis(3-fluoro-4-methoxyphenyl)amine (65): black solid; ¹H NMR (400 MHz, CDCl₃) δ 6.88 (t, J = 9.0 Hz, 2H), 6.79 (dd, J = 12.8, 2.7 Hz, 2H), 6.68 – 6.71 (m, 2H), 3.86 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.2 (d, J = 246.4 Hz), 142.5 (d, J = 11.11 Hz), 137.9 (d, J = 9.1 Hz), 115.3 (d, J = 3.0 Hz), 113.9 (d, J = 4.0 Hz), 107.3 (d, J = 21.2 Hz), 57.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -132.92. HRMS (ESI) m/z calc. for C₁₄H₁₃F₂NNaO₂ [M+Na]⁺: 288.0807, found: 288.0807.



Bis(3,5-difluoro-4-methoxyphenyl)amine (66): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 6.65 – 6.49 (m, 4H), 5.58 (br, 1H), 3.93 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.8 (dd, J = 248.5, 8.1 Hz), 138.0 (t, J = 12.1 Hz), 131.3 (t, J = 15.2 Hz), (102.5, 102.4, 102.3, 102.2), 62.3 (t, J = 3.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -127.30. HRMS (ESI) m/z calc. for C₁₄H₁₁F₄NNaO₂ [M+Na]⁺: 324.0618, found: 324.0622.



Di(thiophen-2-yl)amine (67): brown solid; ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.30 (m, 2H), 7.21 (dd, *J* = 3.5, 1.2 Hz, 2H), 7.00 – 6.92 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 135.7, 132.9, 129.8, 127.6. Spectral datas obtained for the compound are in good agreement with the reported datas.^[20]



Bis(6-methoxypyridin-3-yl)amine (68): brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 2.9 Hz, 2H), 7.27 (dd, J = 8.8, 2.9 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 5.21 (br, 1H), 3.89 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.8, 137.0, 134.7, 130.5, 111.2, 53.6. HRMS (ESI) m/z calc. for C₁₂H₁₄N₃O₂ [M+H]⁺: 232.1081, found: 232.1078.



Bis(6-methylpyridin-2-yl)amine (69): yellow oil; ¹H NMR (400 MHz, CDCl₃ δ 7.47 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.28 (br, 1H), 6.69 (d, *J* = 7.3 Hz, 2H), 2.46 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.8, 153.6, 138.1, 115.6, 108.4, 24.4. Spectral datas obtained for the compound are in good agreement with the reported datas.^[17]



Bis(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)amine (70): black solid; ¹H NMR (400 MHz, CDCl₃) δ 6.75 (d, *J* = 8.6 Hz, 2H), 6.56 (s, 2H), 6.50 (s, 2H), 4.30 – 4.14 (m, 8H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.0, 138.5, 138.2, 117.7, 111.9, 107.3, 64.7, 64.4. HRMS (ESI) m/z calc. for C₁₆H₁₆NO₄ [M+H]⁺: 286.1074, found: 286.1074.



Bis(4-(9H-carbazol-9-yl)phenyl)amine (71): black oil; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.8 Hz, 4H), 7.63 – 7.45 (m, 13H), 7.37 – 7.34 (m, *J* = 7.9, 4.0 Hz, 7H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 142.6, 141.4, 130.9, 128.5, 126.0, 123.3, 120.4, 119.9, 118.9, 109.9. Spectral datas obtained for the compound are in good agreement with the reported datas.^[21]



N2,N2',N2',N2',N7,N7,N7',N7'-Octakis(4-methoxyphenyl)-9,9'-spirobi[fluorene]-2,2',7,7'-tetraamine (74): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.2 Hz, 4H), 6.92 (d, J = 8.9 Hz, 16H), 6.81 – 6.75 (m, 20H), 6.56 (d, J = 1.7 Hz, 4H), 3.77 (s, 24H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.2, 150.2, 147.3, 141.7, 135.7, 125.2, 122.9, 119.9, 118.3, 114.6, 65.7, 55.6. Spectral datas obtained for the compound are in good agreement with the reported datas.^[22]

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







 $^{13}C\{^1H\}$ NMR (100 MHz, CDCl_3) spectrum of compound $\boldsymbol{7}$





¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 7

¹H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{8}$





¹H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{9}$




 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{10}$





S38



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 12





 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 13





 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 13















S46



S47



 $^{13}C\{^1H\}$ NMR (100 MHz, CDCl_3) spectrum of compound ${\bf 20}$







 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound $\boldsymbol{21}$

 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **22**







 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 23





 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{24}$









 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 25









 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{28}$





¹H NMR (400 MHz, CDCl₃) spectrum of compound **29**





 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **30**





 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **31**





















S68









 $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl_3) spectrum of compound ${\bf 40}$












S75











S80

160 150 140 130 120 110 180 90 80 70 60 50 40 30 f1 (ppm)

210 200 190

180 170

20

10 0

-10







 $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl_3) spectrum of compound $\boldsymbol{52}$













 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 57





 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound $\boldsymbol{57}$





 $^{13}C\{^1H\}$ NMR (100 MHz, CDCl_3) spectrum of compound ${\bf 58}$





























¹H NMR (400 MHz, CDCl₃) spectrum of compound 66





 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 66





 $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of compound **67**













 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **74**