SUPPORTING INFORMATION

Iron and Copper based bifunctional catalysts for base & solvent free C-N coupling of amines and aryl/benzyl chlorides under aerobic conditions

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Experimental Details: The ¹H, ¹³C {¹H} NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ¹H and 101 MHz for ¹³C) at room temperature. FTIR spectra in the range 4000–400 cm⁻¹ were recorded on a Perkin Elmer 10.4.00 FT-IR spectrometer as KBr pellets of the sample. Powder XRD was performed on Rikagu (miniflex - 600) equipped with CuK α 1 radiation (λ = 1.5409 Å). ESCA+ (Omicron Nanotechnology Oxford Instruments) was used for recording the X-ray photoelectron spectroscopy (XPS) data.

Chemicals and reagents: LR grade Reactants, reagents, chemicals and solvents available commercially from sigma Aldrich, TCI were purchased within the country were used. LG grade Fe(CO)₅ was purchased from Acros organics.

Procedure for synthesis of $Fe_3E_2(CO)_9$ [E = S, Se, or Te] catalyst

 $Fe_3E_2(CO)_9$ (E = S, Se, or Te) catalyst was synthesised through the earlier known methodology.^{S1, S2}

^{S1} W. Hieber, J. Gruber, *Zeitschrift für anorganische und allgemeine Chemie*, 1958, 296, 91-103.

^{S2}H. Schumann, M. Michael, P. Joachim, *Journal of Organometallic Chemistry* 1982, 240, 407-411.

Procedure for Catalytic Reaction

In a 10 mL reaction tube, amine and arylhalide (1 mmol of each) were considered, to this 2 mol% of $Fe_3Se_2(CO)_9$ and 10 mol% of $Cu(OAc)_2$ were added. The reaction mixture was then heated at 100 °C with continuous stirring for 4 h. After completion of the reaction, the reaction mixture was cool down at room temperature and the product was extracted in organic layer through solvent extraction using the mixture of ethyl acetate and water. Organic layer was dried over anhydrous Na₂SO₄, and then concentrated on rotatory evaporator. If required desired products can be isolated through column chromatography using hexaneethylacetate mixture as eluent.

Control Experiments

Intermolecular competitive experiments were conducted to find the selectivity of the reaction towards various amines and arylchlorides. In this sequence, the very first reaction was performed between *p*-nitrochlorobenzene and *p*-methylchlorobenzene with pyrrolidine, which shows a major selectivity towards the electron withdrawing functionality (Scheme S1).



Scheme S1. Selectivity with donating/withdrawing arylchlorides.

Another reaction of aniline & propylamine with chlorobenzene shows the utmost selectivity of the reaction toward aniline, while the competitive reaction between benzylamine & aniline transformed comparable yield, with both aniline & benzylic amine as products (Schemes S2 and S3).



Scheme S2. Selectivity with aniline or propylamine.



Scheme S3. Selectivity with aniline or benzylamine

Competitive experiments focused on the distinction between primary and secondary aliphatic amines were also executed. Two separate experiments, first consisting of chlorobenzene and a mixture of propylamine and pyrrolidine (cyclic aliphatic amine) while in other experiment, the pyrrolidine was replaced with diethylamine (acyclic aliphatic amine). In both the experiments, the selectivity was dominated with secondary amine, and reaction was found less selective towards primary amine i.e. propylamine (Schemes S4 and S5).





Scheme S5. Selectivity with diethylamine and propylamine.

Further, selectivity order for various secondary aliphatic amines was studied, and excellent selectivity was obtained with cyclic amine (pyrrolidine), while poor selectivity was recorded with acyclic amine (diethylamine) (Scheme S6).



Scheme S6. Selectivity with diethylamine and pyrrolidine.

During the development of substrate scope, a different reactivity order was experienced with heterocyclic arylchloride (4,7-dichloroquinoline). Therefore, some additional reactions has been included in control experiments. Among the aniline & propylamine, good selectivity was obtained with aliphatic amine, which is contrast to the results obtained with chlorobenzene. While similar extent of selectivity was found with benzylic amine and aniline (Schemes S7 and S8).



Scheme S7. Selectivity with aniline and propylamine.



Scheme S8. Selectivity with aniline and benzylamine.

Furthermore, an exclusive selectivity of propylamine was observed over the diethylamine and pyrrolidine (Schemes S9 and S10).



Scheme S9. Selectivity with propylamine and diethylamine.



Scheme S10. Selectivity with propylamine and pyrrolidine.

The selectivity for secondary cyclic & non-cyclic amines were also examined and a significant selectivity was observed with pyrrolidine (Scheme S11).



Scheme S11. Selectivity with diethylamine and pyrrolidine

Characterisation of Recovered Catalyst

The FTIR spectrum does not shows any absorption peaks for Fe, Cu or Se oxides. While, the Raman spectrum reveals the characteristic peaks at 140, 199 and 637 cm⁻¹ which indicated the presence of CuSe, FeSe, and FeCu respectively.^{1,2} The phase composition of the decomposed catalyst was studied through Powder XRD (Figure S3, SI). While closely observing the pattern it is clearly a mix phase. With the help of literature we found the pattern was in close proximity with the JCPDS card no. 00-020-1020 and 85-0735 that represents the CuSe and FeSe phases.³⁻⁵ Moreover, corroboration of few other peaks confirms the presence of FeCu in the composite.⁶ Further, the collected catalyst leftover was characterized through XPS (Figure S4 to S9, SI). The survey scan reveals the presence of Fe, Cu, N, O, and Se atoms in the sample. The recorded quantity Fe, Cu and Se were 34.79, 22.94 and 3.07% respectively, further 27.53 and 14.75% of N and O were also found in the sample. As it is established through FTIR Fe, Cu and Se are not present in the oxide forms. The peak in the region of O (1s) at 531.4 eV corresponds to the organic C=O.⁷ The available N (1s) is in the pyridinic and graphitic form which corresponds to the peaks at 398.3 and 399.6 eV.⁸ The peaks of Se (3d) at 53.5 and 54.9 eV corresponds to the CuSe and FeSe respectively.^{9,10} Two peaks in the region of Cu (2p) corresponding to CuSe can be seen at 932.6 and 952.5 eV which represents 2p (3/2) and 2p (1/2).52 The deconvolution of the XPS spectrum in the region of Fe (2p) shows two peaks each in the region of 2p (1/2) and 2p (3/2). Two peaks with lower values of maxima (710 and 720.3 eV) in both regions correspond to the lower oxidation state (Fe^{2+}). The other two peaks in both the regions with maxima of 713.9 and 723.7 eV are related to the higher oxidation state of (Fe³⁺), the literature suggests these peaks corresponds to FeSe and FeCu.^{10,11}



Figure S1. FTIR spectrum of decomposed catalyst



Figure S2. Raman spectrum of decomposed catalyst



Figure S3. Powder XRD of decomposed catalyst



Figure S4. XPS Survey scan



Figure S5. XPS scan for Cu (2p)



Figure S6. XPS scan for Fe (2p)



Figure S7. XPS scan for Se (3d)



Figure S8. XPS scan for N (1s)



Figure S9. XPS scan for O (1s)

Characterisation Data of Synthesised Compounds

		1-phenylpyrrolidine ¹²
1.		¹ H NMR (400 MHz, CDCl ₃) δ 7.19-7.14 (m, 2H), 6.62- 6.58 (m, 1H), 6.52-6.50 (m, 2H), 3.23-3.20 (m, 4H), 1.96-1.90 (m, 4H).
	×	¹³ C NMR (101 MHz, CDCl ₃) δ 147.97, 129.15, 115.34, 111.63, 47.57, 25.49.
		1-(4-nitrophenyl)pyrrolidine ¹³
2.	O ₂ N	 ¹H NMR (400 MHz, CDCl₃) δ 8.19-8.15 (m, 2H), 6.54- 6.50 (m, 2H), 3.47-3.43 (m, 4H), 2.16-2.10 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 151.87, 136.57, 126.41, 110.41, 47.95, 25.48.
3	F ₃ C	1-(4-(trifluoromethyl)phenyl)pyrrolidine ¹⁴
		¹ H NMR (400 MHz, CDCl ₃) δ 7.47 (d, <i>J</i> = 8.9 Hz, 2H), 6.57 (d, <i>J</i> = 8.7 Hz, 2H), 3.34 (t, <i>J</i> = 6.6 Hz, 4H), 2.09- 2.02 (m, 4H).
		 ¹³C NMR (101 MHz, CDCl₃) δ 149.82, 126.97 (q, J = 3.7 Hz), 125.47 (q, J = 268.6 Hz), 116.64 (q, J = 32.4 Hz), 110.88, 47.56, 25.52.
		19F NMR (400 MHz, CDCl₃) δ -60.62
4.	H ₃ C	1-(p-tolyl)pyrrolidine ¹² ¹ H NMR (400 MHz, CDCl ₃) δ 7.07 (d, <i>J</i> = 7.2 Hz, 2H), 6.55-6.53 (m, 2H), 3.28 (q, <i>J</i> = 4.4 Hz, 4H), 2.29 (s, 3H), 2.04-2.02 (m, 4H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 145.11, 128.64, 123.47, 110.82, 46.86, 24.81, 19.30

		1-(o-tolyl)pyrrolidine ¹²
5.	CH ₃ N	 ¹H NMR (400 MHz, CDCl₃) δ 7.18-7.14 (m, 1H), 6.53 (d, J = 7.4 Hz, 1H), 6.44 (s, 2H), 3.31 (t, J = 6.4 Hz, 4H), 2.36 (s, 3H), 2.06-2.02 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.10, 138.83, 129.04, 116.39, 112.41, 108.93, 47.63, 25.49, 21.90
		1-(o-nitro)phenylpyrrolidine ¹⁵
6.		¹ H NMR (400 MHz, CDCl ₃) δ 7.78 (dd, $J = 8.2$, 1.6 1H), 7.43-7.38 (m, 1H), 6.95 (d, $J = 8.6$ Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 3.27-3.24 (m, 4H), 2.06-2.01 (m, 4H). ¹³ C NMR (101 MHz, CDCl ₃) δ 142.81, 137.09, 133.03,
		126.78, 115.94, 115.49, 50.41, 25.78
7.		 2-(pyrrolidin-1-yl)pyridine¹⁴ ¹H NMR (400 MHz, CDCl₃) δ 8.12 (dd, J = 5.2, 2.0 Hz, 1H), 7.35-7.30 (m, 1H), 6.47 (dd, J = 6.4, 5.1 Hz, 1H), 6.31 (d, J = 8.5 Hz, 1H), 3.43-3.40 (m, 4H), 1.92-1.89 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 157.33, 148.17, 137.05,
		111.11, 106.64, 46.71, 25.62.
8.	H ₂ N Br	2-bromo-5-(pyrrolidin-1-yl)aniline ¹ H NMR (400 MHz, CDCl ₃) δ 7.00 (t, $J = 8.0$ Hz, 1H), 6.03 (dd, $J = 8$, 2.3 Hz, 1H), 5.91 (d, $J = 2.2$ Hz, 1H), 3.28-3.20 (m, 4H), 3.08 (s, 2H), 2.00-1.92 (m, 4H). ¹³ C NMR (101 MHz, CDCl ₃) δ 149.16, 147.42, 130.02, 103.36, 103.12, 98.67, 47.66, 25.51. HRMS (CH ₃ CN) [M + H] ⁺ (m/z) Calc. Value for C ₁₀ H ₁₃ BrN ₂ : 240.0262, observed: 240.0263

	3-(pyrrolidin-1-yl)quinolone ¹⁶
9.	 ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 2.8 Hz, 1H), 7.94-7.92 (m, 1H), 7.59 (dd, J = 7.7, 1.9 Hz, 1H), 7.39- 7.34 (m, 2H), 6.94 (d, J = 2.9 Hz, 1H), 3.40 (t, J = 6.5 Hz, 4H), 2.08-2.03 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 141.46, 140.57, 129.71, 128.87, 126.88, 125.85, 124.39, 111.08, 47.68, 25.50
	7-chloro-4-(pyrrolidin-1-yl)quinolone ¹⁷
10.	¹ H NMR (400 MHz, CDCl ₃) δ 8.43 (s, 1H), 8.12-8.09 (m, 1H), 7.93-7.90 (m, 1H), 7.26-7.21 (m, 1H), 6.40 (dd, J = 5.6, 2.4 Hz, 1H), 3.68-3.63 (m, 4H), 2.06-2.00 (m, 4H). ¹³ C NMR (101 MHz, CDCl ₃) δ 152.53, 151.06, 150.95, 134.34, 128.47, 126.61, 123.68, 102.97, 52.27, 26.07.
	5-(piperidin-1-yl)pyrimidine ¹⁸
11.	 ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.11 (s, 2H), 3.36-3.29 (m, 4H), 2.06 – 2.03 (m, 4H), 1.82-1.79 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 161.34, 146.15, 139.18, 47.82, 46.83, 25.21.
	1-phenylpiperidine ¹⁸
12.	 ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.23 (m, 2H), 6.96-6.93 (m, 2H), 6.84-6.80 (m, 1H), 3.16-3.14 (m, 4H), 1.74-1.68 (m, 4H), 1.62 – 1.53 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 152.37, 129.11, 119.31, 116.67, 50.80, 25.97, 24.41.

		1-(4-nitrophenyl)piperidine ¹⁵
13.	O ₂ N	¹ H NMR (400 MHz, CDCl₃) δ 8.17-8.13 (m, 2H), 6.86- 6.82 (m, 2H), 3.50 (d, J = 5.1 Hz, 4H), 1.74 (s, 6H).
		 ¹³C NMR (101 MHz, CDCl₃) δ 154.93, 137.46, 126.21, 112.35, 48.42, 25.33, 24.29.
		1-(2-nitrophenyl)piperidine ¹⁹
14.		 ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 8.1, 1.5 Hz, 1H), 7.50-7.45 (m, 1H), 7.16 (d, J = 8.3 Hz, 1H), 7.01- 6.79 (m, 1H), 3.06-3.03 (m, 4H), 1.74 (q, J = 5.6 Hz, 4H), 1.63 (q, J = 5.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.25, 142.82, 136.64, 126.21, 121.09, 120.81, 53.15, 26.18, 24.25.
		1-(4-(trifluoromethyl)phenyl)piperidine ²⁰
		¹ H NMR (400 MHz, CDCl ₃) δ 7.50 (d, $J = 8.8$ Hz, 2H),
	F ₃ C	6.96 (d, $J = 8.8$ Hz, 2H), 3.32-3.30 (m, 4H), 1.76-1.63
15.		(m, 6H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 153.84, 126.38 (q, J =
		5.7 Hz, $124.91 (q, 209.1 Hz)$, $119.59 (q, J = 32.5 Hz)$, 114.64, 49.36, 25.47, 24.33,
		19E NMD (400 MHz CDCL) S (1.11)
		r INIVIK (400 IVIHZ, CDCI3) 0 -01.11

		7-chloro-4-(piperidin-1-yl)quinolone ²¹
16.		¹ H NMR (400 MHz, CDCl ₃) δ 8.65 (d, $J = 5.1$ Hz, 1H), 8.00 (d, $J = 2.2$ Hz, 1H), 7.90 (d, $J = 9.0$ Hz, 1H), 7.38 (dd, $J = 9.0$, 2.2 Hz, 1H), 6.78 (d, $J = 5.2$ Hz, 1H), 3.17 – 3.14 (m, 4H), 1.82 (t, $J = 5.6$ Hz, 4H), 1.73 – 1.64 (m, 2H). ¹³ C NMR (101 MHz, CDCl ₃) δ 158.08, 151.55, 149.83, 134.74, 128.44, 125.80, 125.44, 122.00, 108.66, 53.55, 24.96, 24.29.
17.	NC	 4-(propylamino)benzonitrile²² ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.74 (m, 2H), 7.44-7.41 (m, 2H), 6.44 (s, 1H), 3.47-3.42 (m, 2H), 1.68 (t, J = 7.4 Hz, 2H), 1.03 (t, J = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.62, 137.53, 133.22, 128.79, 128.38, 41.90, 22.91, 11.49.
18.	NH CI NH	7-chloro-N-propylquinolin-4-amine²³ ¹ H NMR (400 MHz, CDCl ₃) δ 8.46 (s, 1H), 7.94 (d, $J = 2.7$ Hz, 1H), 7.74 (d, $J = 9.6$ Hz, 1H), 7.38 – 7.29 (m, 1H), 6.40 (d, $J = 5.3$ Hz, 1H), 3.31-3.27 (m, 2H), 1.82-1.76 (m, 2H), 1.08-1.04 (m, 3H). ¹³ C NMR (101 MHz, CDCl ₃) δ 152.06, 149.86, 149.16, 134.90, 128.83, 125.31, 121.01, 117.22, 99.17, 45.08, 22.21, 11.71.

		N,N-diethyl-4-nitroaniline ¹⁹
19.	O ₂ N	 ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.13 (m, 2H), 6.64 – 6.62 (m, 2H), 3.51 (q, J = 7.1 Hz, 4H), 1.28 (t, J = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 152.25, 136.30, 126.57, 109.85, 45.00, 12.45.
		7-chloro-N,N-diethylquinolin-4-amine
20.		¹ H NMR (400 MHz, CDCl ₃) δ 8.61 (d, $J = 5.6$ Hz, 1H), 7.99 (t, $J = 2.2$ Hz, 1H), 7.94 (dd, $J = 9.0$, 2.1 Hz, 1H), 7.36-7.33 (m, 1H), 6.78 (dd, $J = 5.1$, 2.2 Hz, 1H), 3.36- 3.30 (m, 4H), 1.16-1.12 (m, 6H). ¹³ C NMR (101 MHz, CDCl ₃) δ 156.05, 151.17, 150.45, 134.81, 128.58, 125.85, 125.63, 122.97, 110.30, 46.56, 12.20. HRMS (CH ₃ CN) [M + H] ⁺ (m/z) Calc. Value C ₁₃ H ₁₅ ClN ₂ : 235.0997, observed: 235.0994
		7-chloro-N-ethyl-N-propylquinolin-4-amine
21.		¹ H NMR (400 MHz, CDCl ₃) δ 8.62 (d, $J = 5.2$ Hz, 1H), 8.02 (d, $J = 2.2$ Hz, 1H), 7.95 (dd, $J = 9.0$, 1.2 Hz, 1H), 7.38-7.35 (m, 1H), 6.79 (dd, $J = 5.3$ Hz, 1H), 3.40-3.35 (m, 2H), 3.29 – 3.20 (m, 2H), 1.65-1.56 (m, 2H), 1.17- 1.14 (m, 3H), 0.88 (t, $J = 7.4$ Hz, 3H). ¹³ C NMR (101 MHz, CDCl ₃) δ 156.37, 150.78, 150.13, 135.02, 128.32, 125.86, 125.69, 122.77, 110.06, 53.50, 47.88, 20.20, 12.28, 11.66. HRMS (CH ₃ CN) [M + H] ⁺ (m/z) Calc. Value for C ₁₄ H ₁₇ ClN ₂ : 249.1153, observed: 249.1158



		1-(4-nitrophenyl)piperazine ²⁷
26.	O ₂ N NH	 ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 9.0 Hz, 2H), 6.83-6.78 (m, 2H), 3.49-3.46 (m, 4H), 3.02 (t, J = 5.1 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 155.28, 138.49, 126.04, 112.70, 48.17, 45.74
27.	K K	N-Benzylaniline ²⁸ ¹ H NMR (400 MHz, CDCl ₃) δ 7.35 – 7.16 (m, 5H), 7.16-7.03 (m, 2H), 6.67-6.6(m, 1H), 6.59 – 6.51 (m, 2H), 4.24 (s, 2H), 3.94 (s, 1H). ¹³ C NMR (101 MHz, CDCl ₃) δ 148.11, 139.40, 129.25, 128.62, 127.49, 127.21, 117.52, 112.80, 48.27.
28.	H ₃ C	N-benzyl-4-methylaniline ²⁹ ¹ H NMR (400 MHz, CDCl ₃) δ 7.31-7.16 (m, 5H), 6.92 (d, J = 8.1 Hz, 2H), 6.49 (d, J = 8.1 Hz, 2H), 4.24 (s, 2H), 3.78 (s, 1H), 2.18 (s, 3H). ¹³ C NMR (101 MHz, CDCl ₃) δ 145.58, 134.13, 129.79, 128.65, 127.65, 127.56, 127.21, 113.08, 48.73, 20.44.
29.	O ₂ N	N-benzyl-4-nitroaniline ³⁰ ¹ H NMR (400 MHz, CDCl ₃) δ 8.19-8.06 (m, 2H), 7.48- 7.33 (m, 5H), 6.67-6.55 (m, 2H), 4.98 (s, 1H), 4.48 (d, J = 5.6 Hz, 2H). ¹³ C NMR (101 MHz, CDCl ₃) δ 152.07, 136.36, 127.98, 126.88, 126.36, 125.43, 110.34, 98.92, 46.64.

		4-(benzylamino)benzonitrile ³⁰
30.	NC	¹ H NMR (400 MHz, CDCl ₃) δ 7.79-7.76 (m, 2H), 7.46- 7.34 (m, 7H), 6.46 (s, 1H), 4.68 (d, <i>J</i> = 5.6 Hz, 2H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 166.32, 137.95, 137.87, 132.75, 128.91, 128.45, 128.02, 127.81, 44.30.
		N-benzyl-4-(trifluoromethyl)aniline ³¹
		¹ H NMR (400 MHz, CDCl ₃) δ 7.44-7.32 (m, 7H), 6.65 (d, $J = 8.6$ Hz, 2H), 4.40 (s, 3H).
31.		¹³ C NMR (101 MHz, CDCl ₃) δ 150.50, 138.49, 128.84,
	F ₃ C	127.57, 127.40, 126.67 (q, J = 3.7 Hz), 125.02 (q, J =
		269.0 Hz), 119.01 (q, <i>J</i> = 32.4 Hz), 112.00, 47.80
		¹⁹ F NMR (400 MHz, CDCl ₃) δ -61.06
	H ₃ C	N-benzyl-3-methylaniline ²⁹
		¹ H NMR (400 MHz, CDCl ₃) δ 7.43-7.28 (m, 4H), 7.11
22		(t, J = 7.7 Hz, 1H), 6.59 (d, J = 7.4 Hz, 1H), 6.52-6.48
52.		(m, 2H), 4.36 (s, 2H), 4.00 (s, 1H), 2.31 (s, 3H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 138.03, 128.11, 128.03,
		127.78, 127.61, 126.52, 126.17, 117.48, 112.63, 108.95,
		47.23, 20.39.
	H NO ₂	N-benzyl-2-nitroaniline ³⁰
33.		¹ H NMR (400 MHz, CDCl ₃) δ 8.49 (s, 1H), 8.25 (dd, J
		= 8.6, 1.6 Hz, 1H), 7.38-7.31 (m, 6H), 6.88-6.85 (m,
		1H), $6./4-6./2$ (m, 1H), 4.61 (d, $J = 5./$ Hz, 2H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 144.56, 138.26, 137.50,
		130.33, 129.03, 127.795, 127.13, 126.98, 115.83,
		117.27, 77.10

		N-benzylpyridin-2-amine ²⁹
34.	H N N	 ¹H NMR (400 MHz, CDCl₃) δ 8.088 (d, J = 4.8, 1H), 7.41-7.11 (m, 6H), 6.60-6.56 (m, 1H), 6.35 (d, J = 8.4 4.98 (s, 1H), 4.50 (d, J = 5.6 Hz, 2H), ¹³C NMR (101 MHz, CDCl₃) δ 159.17, 148.73, 139.69, 138.03, 129.17, 129.05, 127.92, 113.68, 107.32, 46.84
35.	H CH_3	N-(4-methylbenzyl)pyridin-2-amine ³⁰ ¹ H NMR (400 MHz, CDCl ₃) δ 8.15-8.14 (m, 1H), 7.46- 7.42 (m, 1H), 7.31-7.26 (m, 2H), 7.19 (d, <i>J</i> = 7.9 Hz, 2H), 6.63 (dd, <i>J</i> = 7.0 Hz, 1H), 6.41 (d, <i>J</i> = 8.3 Hz, 1H), 4.93 (s, 1H), 4.50 (d, <i>J</i> = 5.7 Hz, 2H), 2.38 (s, 3H). ¹³ C NMR (101 MHz, CDCl ₃) δ 159.25, 148.79, 138.04,
36.	$(\mathbf{x}_{n},\mathbf{y}_{n})$	N-benzylquinolin-3-amine ³² H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 2.8 Hz, 1H), 7.99 (dd, J = 6.2 Hz, 1H), 7.62-7.59 (m, 1H), 7.45 (q, J = 3.3 Hz, 2H), 7.36-7.32 (m, 4H), 7.31-7.27 (m, 1H), 7.04 (d, J = 2.8 Hz, 1H), 4.52 (t, J = 5.4 Hz, 1H), 4.45 (d, J = 4.7 Hz, 2H). 13C NMR (101 MHz, CDCl₃) δ 141.58, 138.30, 131.25,129.97, 129.57, 128.94, 128.41,127.72, 127.58, 127.22, 126.13, 125.37, 125.17, 48.05



	Diphenylamine ²⁵
	¹ H NMR (400 MHz, CDCl ₃) δ 7.31 (t, $J = 7.9$ Hz, 4H),
	7.12-7.10 (m, 4H), 6.97 (t, <i>J</i> = 7.3 Hz, 2H), 5.74 (s, 1H).
	¹³ C NMR (101 MHz, CDCl ₃) δ 143.13, 129.38, 121.02,
	117.82
	4-methyl-N-phenylaniline ³⁴
	¹ H NMR (400 MHz, CDCl ₃) δ 7.30-7.26 (m, 2H), 7.13
	(d, $J = 8.3$ Hz, 2H), 7.06-7.03 (m, 4H), 6.92 (t, $J = 7.3$
H ₃ C	Hz, 1H), 5.63 (s, 1H), 2.35 (s, 3H).
	¹³ C NMR (101 MHz, CDCl ₃) δ 142.93, 139.27, 129.91,
	128.85, 128.30. 119.28, 117.89, 115.84, 19.69
CH ₃ H	2-methyl-N-phenylaniline ³⁵
	¹ H NMR (400 MHz, CDCl ₃) δ 7.23-7.15 (m, 4H), 7.18
	(t, J = 7.5 Hz, 1H), 7.01-6.92 (m, 4H), 2.30 (s, 3H).
	¹³ C NMR (101 MHz, CDCl ₃) δ 142.84, 140.09, 129.83,
	128.24, 128.22, 128.19, 128.17, 128.16, 127.15, 125.64,
	120.85, 119.35, 117.62. 116.37, 116.36, 116.35, 116.34,
	116.33, 116.32, 116.31, 116.30, 116.29, 16.80.
NO ₂ H	2-nitro-N-phenylaniline ³⁶
	¹ H NMR (400 MHz, CDCl ₃) δ 9.55 (s, 1H), 8.26 (dd, J
	= 8.6, 1.4 Hz, 1H), 7.49-7.40 (m, 3H), 7.33 (d, J = 7.9
	Hz, 2H), 7.28 (d, <i>J</i> = 8.6 Hz, 2H), 6.80-6.75 (m, 1H).
	¹³ C NMR (101 MHz, CDCl ₃) δ 143.16, 138.75, 135.76,
	133.37, 129.80, 126.74, 125.73, 124.46, 117.56, 116.10
	$\begin{split} & (\downarrow \downarrow^{H} \downarrow \downarrow^{H}) \\ & (\downarrow \downarrow^{H} \downarrow \downarrow^{H}) \\ & (\downarrow \downarrow^{H} \downarrow^{H} \downarrow^{H}) \\ & (\downarrow^{H}) \\ & (\downarrow^{H} \downarrow^{H}) \\ & (\downarrow^{H }) \\ & (\downarrow^{H}) \\ & (\downarrow^{H }) \\ & ($

	O ₂ N H	4-nitro-N-phenylaniline ³⁶
44.		 ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 9.1 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.27-7.24 (m, 3H), 6.99 (d, J = 9.1 Hz, 2H), 6.33 (s, 1H).
		 ¹³C NMR (101 MHz, CDCl₃) δ 150.18, 139.86, 139.52, 129.81, 126.30, 124.74, 121.98, 113.74.
		4-methoxy-N-phenylaniline ³⁴
45.	H ₃ C ₀	¹ H NMR (400 MHz, CDCl ₃) δ 7.31 (d, 1H), 7.28-7.24 (m, 2H), 7.14-7.12 (m, 2H), 6.97-6.95 (m, 2H), 6.92-6.88 (m, 2H), 3.85 (s, 3H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 155.31, 145.20, 135.74, 129.36, 122.25, 119.60, 115.66, 114.70, 55.63
	$F_{3}C$	N-phenyl-4-(trifluoromethyl)aniline ³⁴
46.		¹ H NMR (400 MHz, CDCl ₃) δ 7.51 (d, <i>J</i> = 8.4 Hz, 2H), 7.40-7.36 (m, 2H), 7.20-7.18 (m, 2H), 7.12-7.08 (m, 3H), 5.96 (s, 1H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 146.78, 141.16, 126.74
		(q, J = 3.5 Hz), 124.05 (q, J = 209.4 Hz), 122.97, 122.15, 121.66 (q, J = 32.4 Hz), 120.05, 115.36.
		¹⁹ F NMR (400 MHz, CDCl ₃) δ -61.48
		N-phenylpyridin-2-amine ³⁷
47.		 ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 4.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.38 (d, J = 3.8 Hz, 4H), 7.10-7.02 (m 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.79-6.78 (m, 1H), 6.66 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 156.67, 149.13, 141.13,
		138.41, 130.01, 123.55, 121.05, 115.78, 108.92

		N1-(4-methoxyphenyl)benzene-1,4-diamine ³⁸
48.	H ₃ C ₀ NH ₂	¹ H NMR (400 MHz, CDCl₃) δ 7.28 (d, <i>J</i> = 9.0 Hz, 2H), 7.15 (s, 1H), 7.07-6.96 (m, 2H), 6.75-6.72 (m, 4H), 3.67 (s, 2H), 3.68 (s, 3H)
		 ¹³C NMR (101 MHz, CDCl₃) δ 154.54, 144.43, 134.97, 128.58, 121.47, 115.69, 114.89, 113.93, 54.86
		7-chloro-N-phenylquinolin-4-amine ¹⁷
49.	CI NH	 ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 8.05 (s, 2H), 7.44 (t, J = 7.8 Hz, 4H), 7.35 (d, J = 8.3 Hz, 3H), 6.89 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.98, 141.54, 139.46, 135.59, 129.89, 129.08, 126.25, 125.54, 125.13, 122.91,
		121.17, 118.13, 102.53.
		(E)-1-(4-morpholinophenyl)-3-phenylprop-2-en-1- one ³⁹
50.		¹ H NMR (400 MHz, CDCl ₃) δ 7.97-8.01 (m, 2H), 7.76 (d, $J = 8$ Hz, 1H), 7.58 – 7.55 (m, 2H), 7.50-7.48 (m, 2H), 6.90-6.87 (m, 2H), 3.87-3.84 (m, 4H), 3.28-3.25 (m, 4H).
		¹³ C NMR (101 MHz, CDCl ₃) δ 190.95, 152.92,145.14, 139.13, 132.51, 130.23, 128.62, 128.47, 126.36, 118.83, 114.73, 66.73, 40.08
51.		1,4-dibenzylpiperazine ⁴⁰
		¹ H NMR (400 MHz, CDCl ₃) δ 7.30-7.22 (m, 10H), 3.50 (s, 4H), 2.48 (s, 8H)
		¹³ C NMR (101 MHz, CDCl ₃) & 137.18, 128.41, 127.33, 126.17, 62.21, 52.19

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Figure S10: ¹H NMR of Compound 2a



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Figure S11: ¹³C NMR of Compound 2a



Figure S12: ¹H NMR of Compound 2b





Figure S13: ¹³C NMR of Compound 2b



Figure S14: ¹H NMR of Compound 2c





Figure S15: ¹³C NMR of Compound 2c





Figure S16: ¹⁹F NMR of Compound 2c





Figure S17: ¹H NMR of Compound 2d














Figure S20: ¹³C NMR of Compound 2e









NO₂















Figure S25: ¹H NMR of Compound 2i



Figure S26: ¹³C NMR of Compound 2i



Figure S27: ¹H NMR of Compound 2h



Figure S28: ¹³C NMR of Compound 2h





Figure S29: ¹H NMR of Compound 2j



Figure S30: ¹³C NMR of Compound 2j



Figure S31: ¹H NMR of Compound 3a





Figure S32: ¹³C NMR of Compound 3a







Figure S34: ¹³C NMR of Compound 3j



Figure S35: ¹H NMR of Compound 3b









Figure S37: ¹H NMR of Compound 3d



Figure S38: ¹³C NMR of Compound 3d







Figure S40: ¹³C NMR of Compound 3c



Figure S41: ¹⁹F NMR of Compound 3c









Figure S43: ¹³C NMR of Compound 3e









Figure S45: ¹³C NMR of Compound 4a





Figure S46: ¹H NMR of Compound 4c





Figure S47: ¹³C NMR of Compound 4c



Figure S48: ¹H NMR of Compound 4d





Figure S49: ¹³C NMR of Compound 4d





Figure S50: ¹H NMR of Compound 4e



Figure S51: ¹³C NMR of Compound 4e





Figure S52: ¹H NMR of Compound 4f



Figure S53: ¹³C NMR of Compound 4f









Figure S55: ¹³C NMR of Compound 4b


Figure S56: ¹H NMR of Compound 3g











Figure S58: ¹H NMR of Compound 3h



Figure S59: ¹³C NMR of Compound 3h









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 f1 (ppm)

Figure S61: ¹³C NMR of Compound 3i



Figure S62: ¹H NMR of Compound 3f



Figure S63: ¹³C NMR of Compound 3f



Figure S64: ¹H NMR of Compound 5a





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

Figure S65: ¹³C NMR of Compound 4a









Figure S67: ¹³C NMR of Compound 5e









Figure S69: ¹³C NMR of Compound 5b









Figure S71: ¹³C NMR of Compound 5d



CF₃







Figure S73: ¹³C NMR of Compound 5c



Figure S74: ¹⁹F NMR of Compound 5c



Ν́ Η





Figure S76: ¹³C NMR of Compound



H

ΝO₂

Figure S77: ¹H NMR of Compound 5f













Figure S80: ¹³C NMR of Compound 5g



→ H N







Figure S82: ¹³C NMR of Compound 5i









Figure S84: ¹³C NMR of Compound 5l



Figure S85: ¹H NMR of Compound 5k



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 f1 (ppm)

Figure S86: ¹³C NMR of Compound 5k



Figure S87: ¹H NMR of Compound 5j



Figure S88: ¹³C NMR of Compound 5j









Figure S90: ¹³C NMR of Compound 5h





Figure S91: ¹H NMR of Compound 6a


H N

Figure S92: ¹³C NMR of Compound 6b



HN





HN

Figure S94: ¹³C NMR of Compound 6g









Figure S96: ¹³C NMR of Compound 6f





Figure S97: ¹H NMR of Compound 6d





Figure S98: ¹³C NMR of Compound 6d





Figure S99: ¹H NMR of Compound 6b











Figure S101: ¹H NMR of Compound 6e

















Figure S104: ¹³C NMR of Compound 6c





Figure S105: ¹⁹F NMR of Compound 6c





Figure S106: ¹H NMR of Compound 6h





Figure S107: ¹³C NMR of Compound 6h



Figure S108: ¹H NMR of Compound







Figure S110: ¹H NMR of Compound 6i



Figure S111: ¹³C NMR of Compound 6i







Figure S113: ¹³C NMR





Figure S114: ¹H NMR





Figure S115: ¹³C NMR