

Supplementary Information

Aminoquinoline-Based Tridentate (NNN)-Copper Catalyst for C–N Bond-Forming Reactions from Aniline and Diazo Compounds

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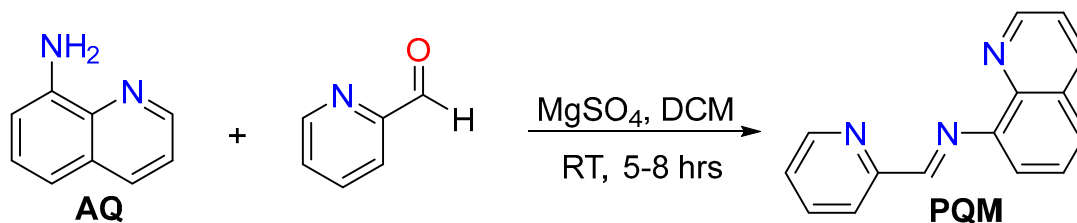
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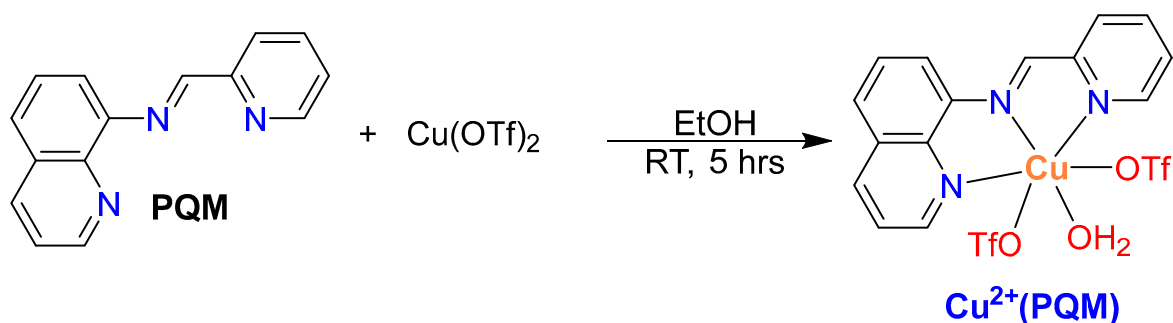
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Procedure for the synthesis of PQM ligand



A 25-mL round-bottom (RB) flask was charged with a magnetic stir bar, 2.0 mmol of 8-aminoquinoline (AQ), 2.2 mmol of 2-pyridine carboxaldehyde, and 10.0 mmol of MgSO_4 . This mixture was solvated in 10.0 mL of dichloromethane (DCM) and the reaction was left to stir for approximately 5-8 hours under an N_2 atmosphere at room temperature in a closed with a septum. After stirring, the reaction progress was monitored through TLC. Upon the completion of the precursors, the reaction mixture was filtered through celite. Evaporation of the solvent and subsequent purification by column chromatography on silica gel afforded the oily product of PQM in 60% yields. This compound is known and ^1H -NMR data matches with reported spectra.[1–3] Yield 60% (320.0 mg), Yellow sticky liquid; ^1H NMR (500 MHz, CDCl_3) δ : 9.24 (d, $J = 10.0$ Hz, 1H), 9.01 (d, $J = 4.0$ Hz, 1H), 8.06 (dd, $J = 2.0, 8.0$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.66–7.40 (m, 4H), 7.19 (dd, $J = 2.4, 7.6$ Hz, 1H), 7.08 (dd, $J = 2.4, 8.4$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H) ppm.

Procedure for the synthesis of PQM ligated copper complex



A 25-mL round-bottom (RB) flask was equipped with a stirring bar and charged with 1.0 mmol of **PQM**, 1.0 mmol of Cu(OTf)₂, and solvated with 5.0 mL of EtOH solvent. The mixture was stirred at ambient temperature for 6h, and then EtOH was removed *in vacuo*. After, the precipitate was washed with methanol to afford the Cu²⁺(PQM) in green color powder. The Cu²⁺(PQM) could be crystallized in EtOH and DCM. Crystallization and evaporation of the solvent afforded the green color product of Cu²⁺(PQM) in 71% yield. Anal. calcd for C₁₇H₁₃CuF₆N₃O₇S₂: C, 33.31; H, 2.14; N, 6.86; S, 10.46. Found: C, 31.46; H, 2.16; N, 6.54; S, 12.46.

Powder X-ray diffraction (PXRD) analysis for the Cu²⁺(PQM) fitted with the LeBail profile fitting.

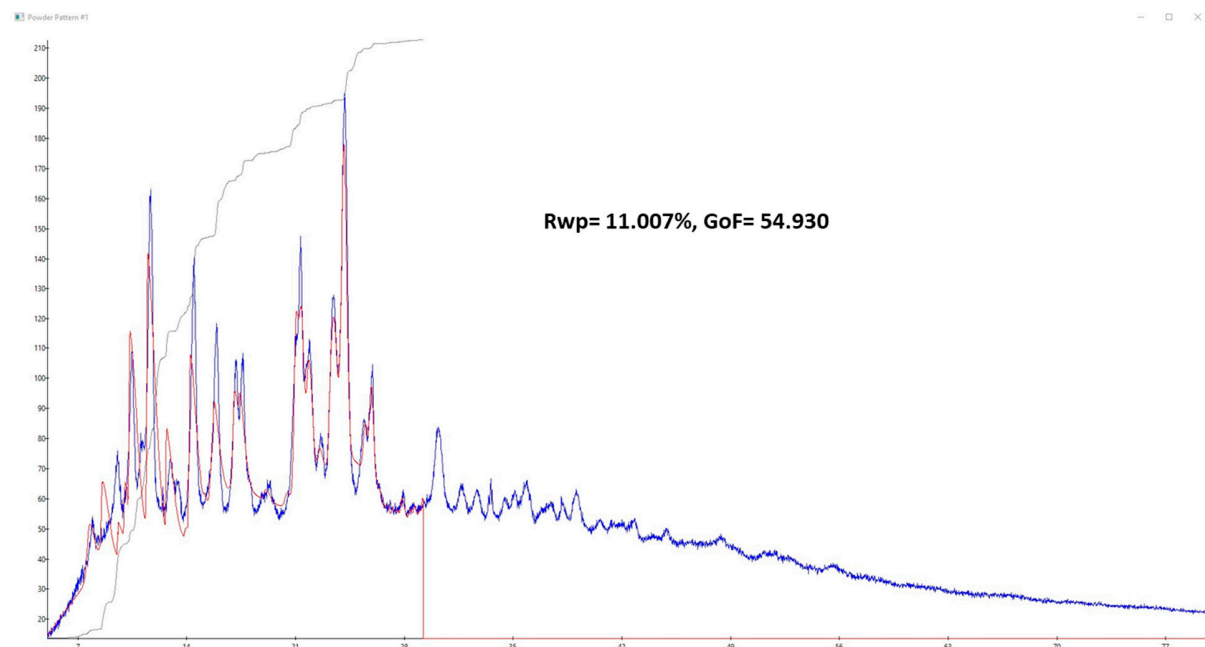
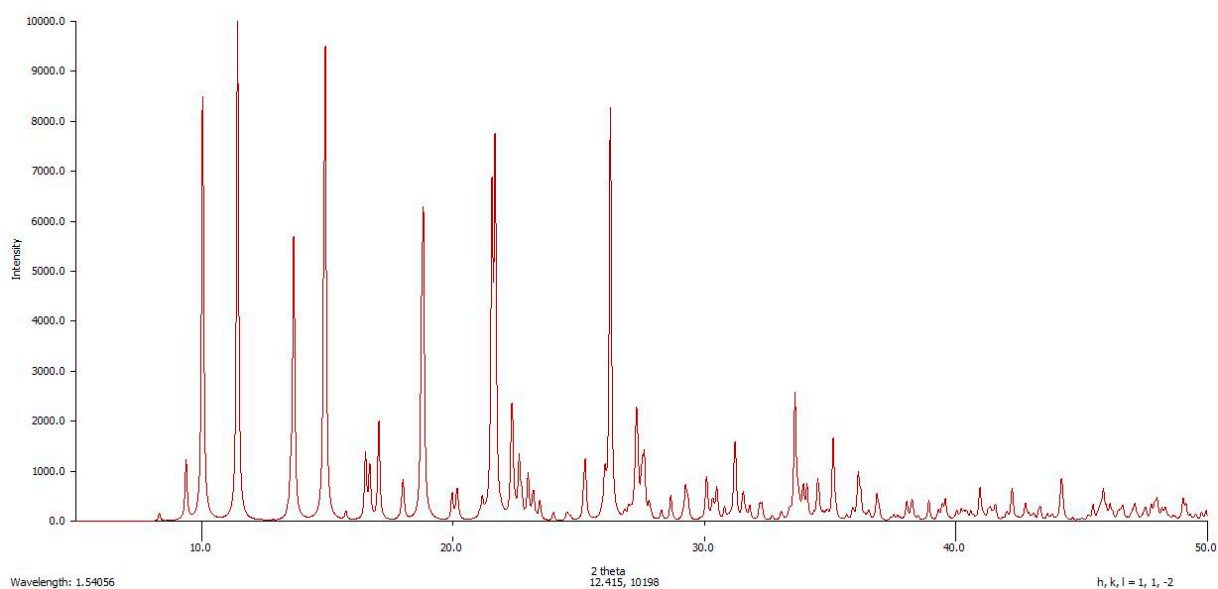


Figure S1. Cu²⁺(PQM) LeBail refinement fitting profile of PXRD and single-XRD [Blue–measured and Red – stimulated].

Powder sample:	Single crystal:
Symmetry_space_group_name_H-M 'C ₂ /m'	Symmetry_space_group_name_H-M 'C ₂ /m'
a = 21.95385 Å	a = 24.0665 Å
b = 10.95825 Å	b = 11.8732 Å
c = 17.17444 Å	c = 17.8506 Å
β = 101.089°	β = 99.940°
volume = 4054.60 Å ³	volume = 5024.2 Å ³



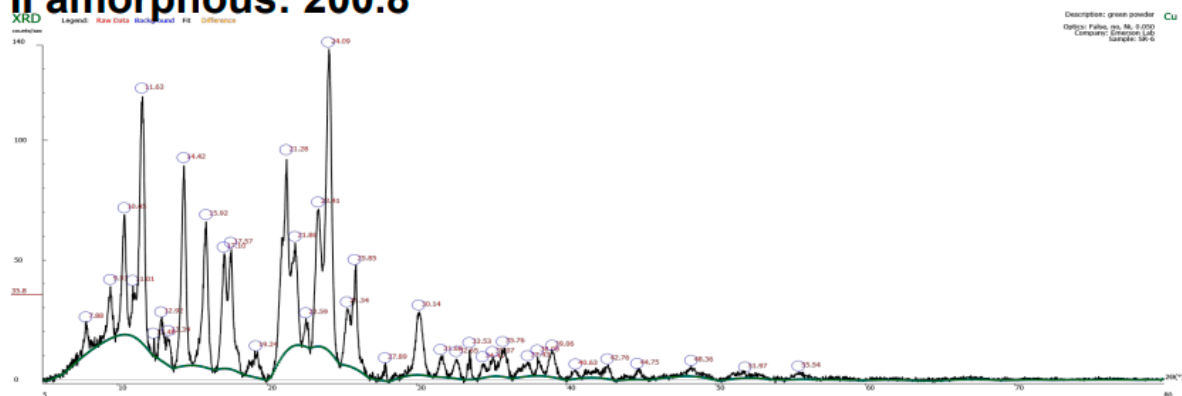
CRYSTALLINITY REPORT

% crystallinity: 69.13

% amorphous: 30.87

|| crystallinity: 449.7

|| amorphous: 200.8



2th Range: 5.00° ... 80.00°

delta 2th: 0.0197°

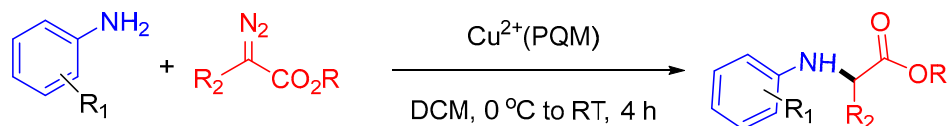
Dwell: 4 sec

Scan time: 00d 03h 11m 23s

HV: 30kV, 20mA

Figure S2. Cu^{2+} (PQM) complex crystalline phase PXRD.

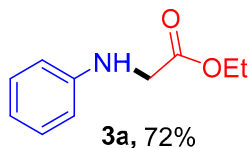
General procedure for C–N bond construction by Cu²⁺(PQM) catalyzed redox-neutral type cross-coupling (3a-3v)



A 10-mL vial was charged with a magnetic stir bar, 0.5 mmol of amine, 1.0 mmol of diazo-compound, and 0.05 mmol of Cu²⁺(PQM). This mixture was solvated in 3.0 mL of dichloromethane (DCM) and the reaction was started at 0 °C to ambient temperature stir for approximately four hours under an N₂ atmosphere. After the completion of the reaction time, the resulting reaction mixture was diluted with ethyl acetate and filtered through a thin pad of celite. The filtrate was evaporated under reduced pressure and subsequent purification by column chromatography on silica gel afforded the desired products.

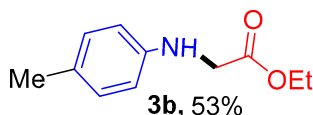
Spectroscopic and physical data of all compounds (3a-3v)

Ethyl phenylglycinate (3a)[4]



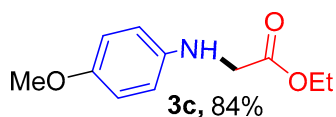
Yield: 72%; Pale brownish sticky solid; mp = 58 °C; ^1H NMR (500 MHz, CDCl_3) δ : 7.21 (t, J = 4.5 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 4.29–4.20 (m, 3H), 3.92 (s, 2H), 1.34 (t, J = 6.4 Hz, 3H) ppm.

Ethyl *p*-tolylglycinate (3b)[5]



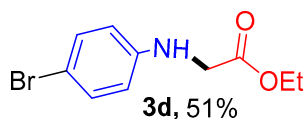
Yield: 53%; Brownish solid; mp = 56–58 °C; ^1H NMR (500 MHz, CDCl_3) δ : 7.01 (d, J = 7.6 Hz, 2H), 6.58 (d, J = 7.8 Hz, 2H), 4.26 (q, J = 6.8 Hz, 2H), 3.90 (s, 2H), 2.28 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H) ppm.

Ethyl (4-methoxyphenyl)glycinate (3c)[5]



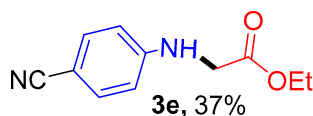
Yield: 84%; Yellow semi-solid; mp = 43 °C; ^1H NMR (500 MHz, CDCl_3) δ : 6.78 (d, J = 8.2 Hz, 2H), 6.54 (d, J = 8.2 Hz, 2H), 4.22 (q, J = 6.8 Hz, 2H), 4.10 (bs, 1H), 3.86 (s, 2H), 3.75 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H) ppm.

Ethyl (4-bromophenyl)glycinate (3d)[6]



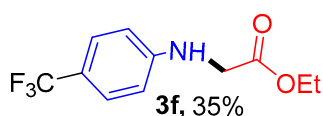
Yield: 51%; Light reddish brown solid; mp = 95–98 °C; ^1H NMR (500 MHz, CDCl_3) δ : 7.30–7.23 (m, 2H), 6.51–6.46 (m, 2H), 4.11 (s, 1H), 4.27 (q, J = 7.0 Hz, 2H), 3.89 (s, 2H), 1.31 (t, J = 7.2 Hz, 3H) ppm.

Ethyl (4-cyanophenyl)glycinate (3e)[7]



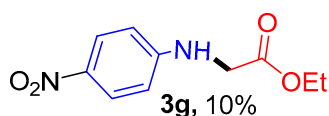
Yield: 37%; Yellowish solid; ^1H NMR (500 MHz, CDCl_3) δ : 7.48 (d, $J = 7.8$ Hz, 2H), 6.59 (d, $J = 7.6$ Hz, 2H), 4.08 (s, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 2H), 1.29 (t, $J = 7.2$ Hz, 3H) ppm.

Ethyl (4-(trifluoromethyl)phenyl)glycinate (3f)[8]



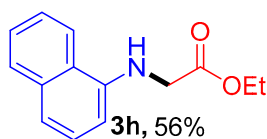
Yield: 35%; Pale white solid; ^1H NMR (500 MHz, CDCl_3) δ : 7.40 (dd, $J = 8.2, 1.2$ Hz, 2H), 6.59 (dd, $J = 8.4, 1.2$ Hz, 2H), 4.60 (s, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 3.89 (s, 2H), 1.28 (t, $J = 7.2$ Hz, 3H) ppm.

Ethyl (4-nitrophenyl)glycinate (3g)[9]



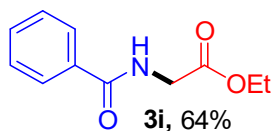
Yield: 10%; Yellow solid; mp = 132-134 °C; ^1H NMR (500 MHz, CDCl_3) δ : 8.14 (d, $J = 8.8$ Hz, 2H), 6.60 (d, $J = 8.8$ Hz, 2H), 5.11 (bs, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 3.40 (s, 2H), 1.33 (t, $J = 7.0$ Hz, 3H) ppm.

Ethyl naphthalen-1-ylglycinate (3h)[10]



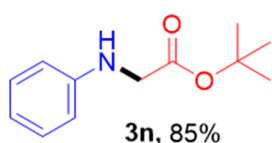
Yield: 56%; White solid; ^1H NMR (500 MHz, CDCl_3) δ : 7.45 (d, $J = 7.2$ Hz, 2H), 7.30 (m, 2H), 7.21 (m, 1H), 7.09 (m, 2H), 4.12 (s, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.89 (s, 2H), 1.28 (t, $J = 7.2$ Hz, 3H) ppm.

Ethyl benzoylglycinate (3i)[11]



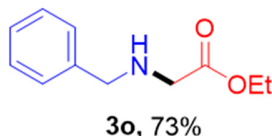
Yield: 64%; Pale white solid; mp = 60 °C; ^1H NMR (500 MHz, CDCl_3) δ : 7.86 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.0 Hz, 1H), 7.45 (dd, J = 8.0, 7.1 Hz, 2H), 6.80 (s, 1H), 4.30–4.22 (s, 4H), 1.34 (t, J = 7.2 Hz, 3H) ppm.

tert-Butyl 2-(phenylamino)acetate (3n)[12]



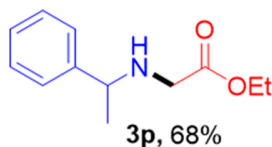
Yield: 85%; Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.18 (dd, J = 7.6 Hz, 2H), 6.73 (t, J = 7.6 Hz, 1H), 6.6 (d, J = 7.6 Hz, 2H), 3.24 (br, 1H), 3.79 (s, 2H), 1.48 (s, 9H) ppm.

Ethyl benzylglycinate (3o)[13]



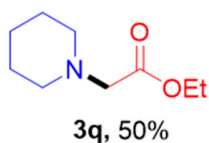
Yield: 73%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.46–7.17 (m, 5H), 4.05 (q, J = 7.1 Hz, 2H), 3.8 (s, 2H), 3.39 (s, 2H), 2.18 (bs, 1H), 1.26 (t, J = 7.1 Hz, 3H) ppm.

Ethyl (1-phenylethyl)glycinate (3p)[14]



Yield: 68%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.32–7.24 (m, 5H), 4.15 (q, J = 7.2 Hz, 2H), 3.79 (q, J = 6.4, 2H), 2.25 (ABq, J_{AB} = 17.4 Hz, 2H), 1.87 (bs, 1H), 1.38 (d, J = 6.4 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H) ppm.

Ethyl 2-(piperidin-1-yl)acetate (3q)[15]



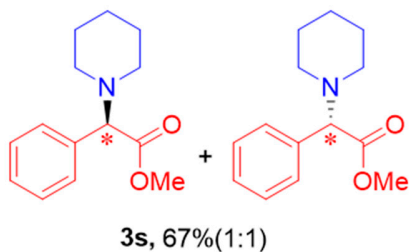
Yield: 50%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 4.18 (q, $J = 7.2$ Hz, 2H), 3.17 (s, 2H), 2.5 (m, 4H), 1.62 (m, 4H), 1.43 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H) ppm.

Ethyl 2-morpholinoacetate (3r)[7]



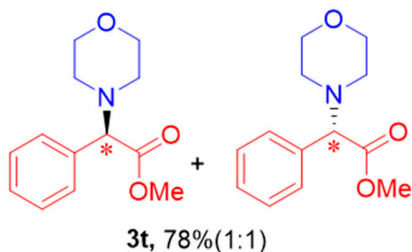
Yield: 66%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 4.10 (q, $J = 7.2$ Hz, 2H), 3.55 (m, 4H), 3.02 (s, 2H), 2.48 (m, 4H), 1.27 (t, $J = 7.2$ Hz, 3H) ppm.

Methyl 2-phenyl-2-(piperidin-1-yl)acetate (3s)[16]



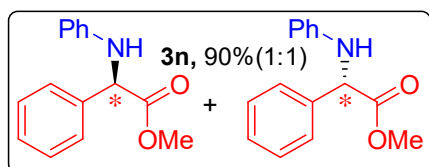
Yield: 67%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.25-7.35 (m, 3H), 7.39-7.44 (m, 2H), 3.97 (s, 1H), 3.66 (s, 3H), 2.28-2.45 (m, 4H), 1.52-1.64 (m, 4H), 1.37-1.47 (m, 2H) ppm.

Methyl 2-morpholino-2-phenylacetate (3t)[16]



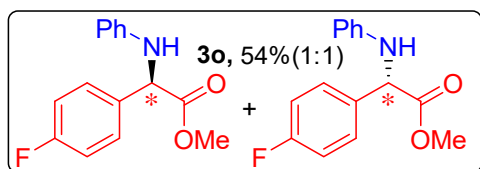
Yield: 78%; Pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.42–7.46 (m, 2H), 7.29–7.38 (m, 3H), 3.98 (s, 1H), 3.73 (t, $J = 5.2$ Hz 4H), 3.69 (s, 3H), 2.45 (t, $J = 4$ Hz 4H) ppm.

Methyl 2-phenyl-2-(phenylamino)acetate (3u)[17]

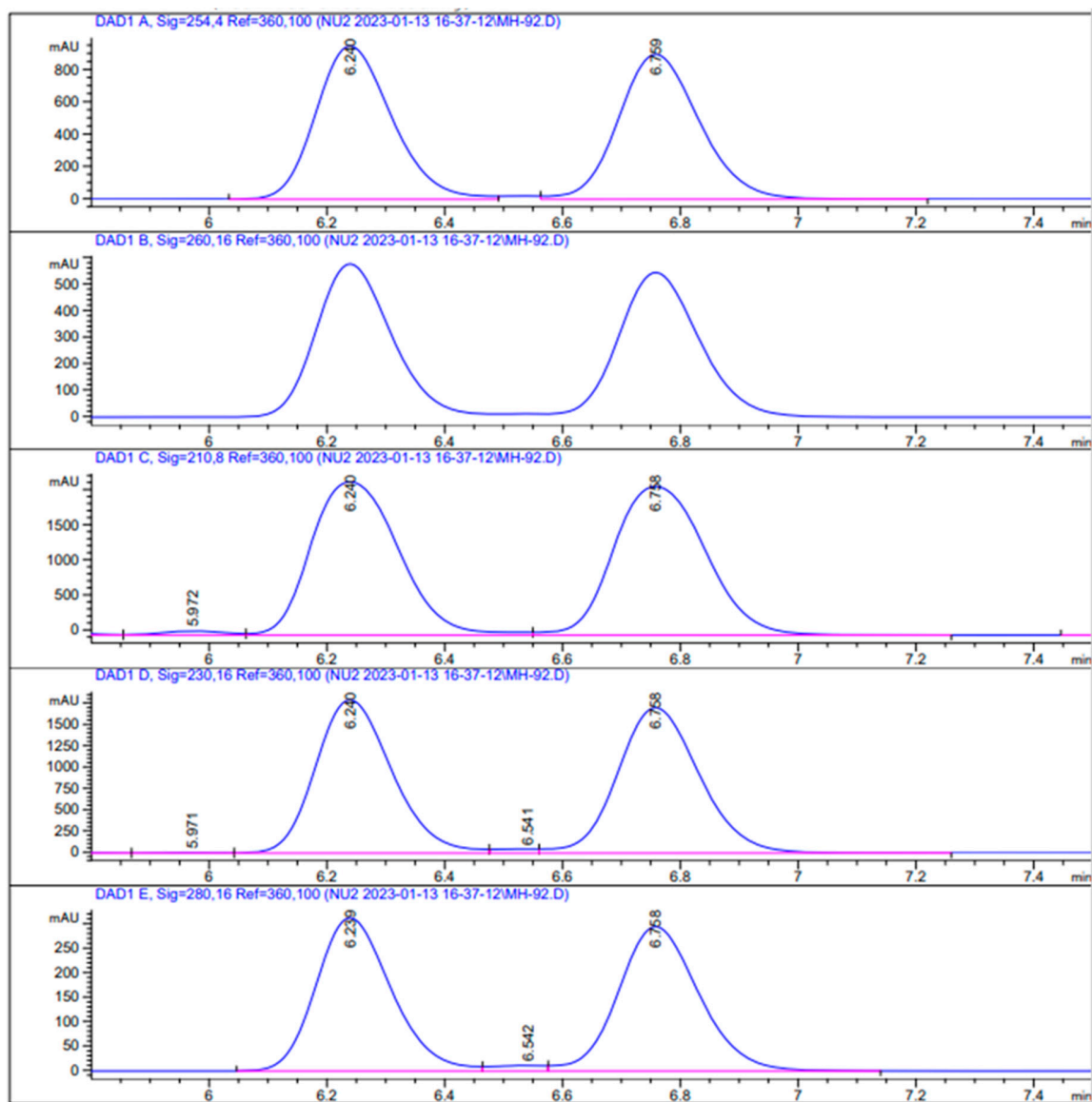


Yield: 90%; Yellowish solid; ^1H NMR (500 MHz, CDCl_3) δ : 7.52 (d, $J = 7.0$ Hz, 2H), 7.40–7.36 (m, 3H), 7.15 (t, $J = 7.6$ Hz, 2H), 6.69 (t, $J = 7.6$ Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 2H), 5.06 (d, $J = 6.0$ Hz, 1H), 4.98 (s, 1H), 4.31–4.20 (s, 2H), 1.25 (t, $J = 7.1$ Hz, 3H) ppm.

Methyl 2-(4-fluorophenyl)-2-(phenylamino)acetate (3v)



Yield: 56%; Yellow sticky solid; IR (neat) 3218, 3051, 2967, 2954, 1684, 1626, 1591, 1447, 1368, 1218, 1030, 785 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ : 7.53–7.47 (m, 2H), 7.15 (t, $J = 8.0$ Hz, 2H), 7.06 (t, $J = 8.5$ Hz, 2H), 6.73 (t, $J = 7.5$ Hz, 2H), 6.51 (d, $J = 3.0$ Hz, 1H), 5.07 (d, $J = 5.5$ Hz, 1H), 4.98 (bs, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ : 172.1, 163.7 ($^1J_{\text{C-F}} = 245.6$ Hz), 145.7, 133.4 ($^4J_{\text{C-F}} = 3.1$ Hz), 129.3, 129.0 7 ($^3J_{\text{C-F}} = 8.3$ Hz), 118.3, 115.9 ($^2J_{\text{C-F}} = 21.5$ Hz), 113.4, 60.0, 52.9 ppm; ^{19}F NMR (500 MHz, CDCl_3) δ : 113.86 ppm; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{FNaNO}_2$: 282.0901 $[\text{M}+\text{H}^+]$; found: 282.0948.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.240	VV	0.1386	8516.69531	950.15955	49.8175
2	6.759	VB	0.1495	8579.08691	897.73230	50.1825

Totals : 1.70958e4 1847.89185

Figure S3. HPLC spectra of compound **3v** and integration data.

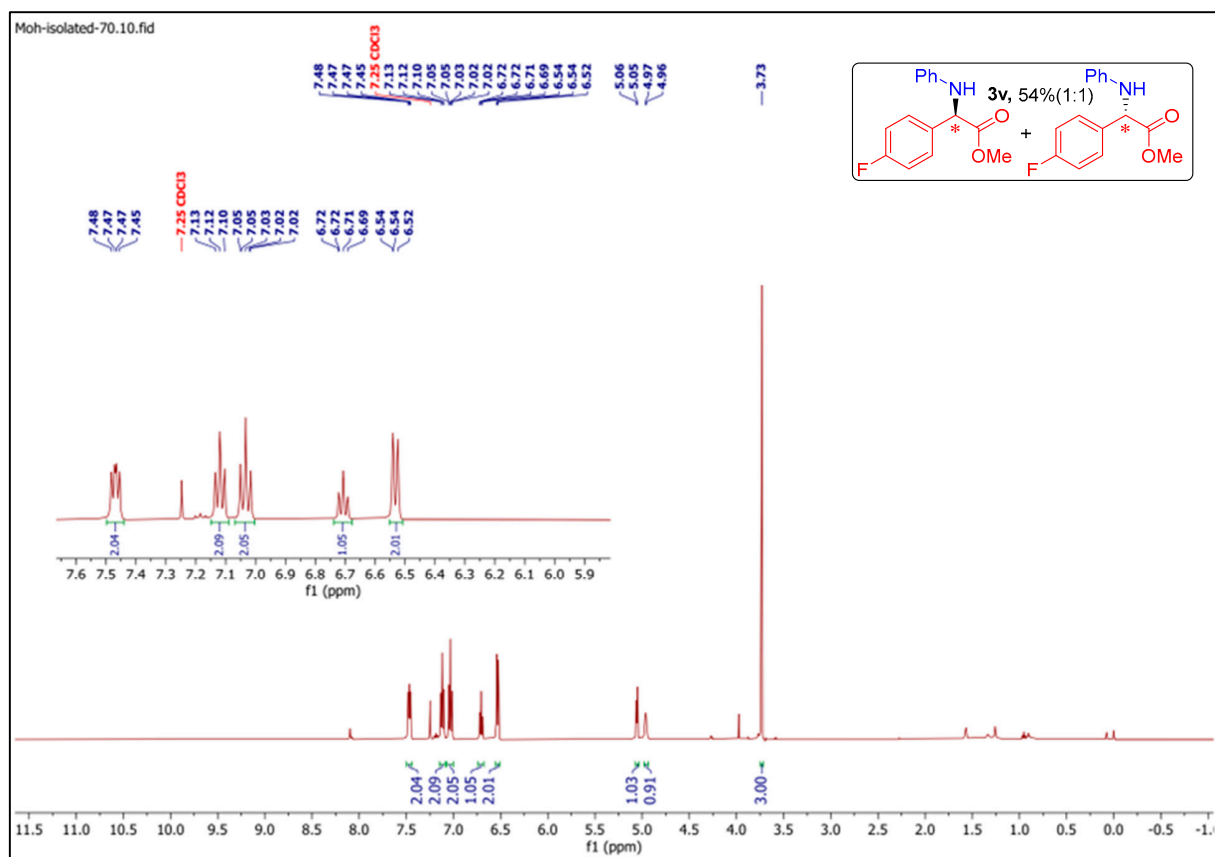


Figure S4. ^1H NMR spectra of compound **3v** (CDCl_3 , 500 MHz)

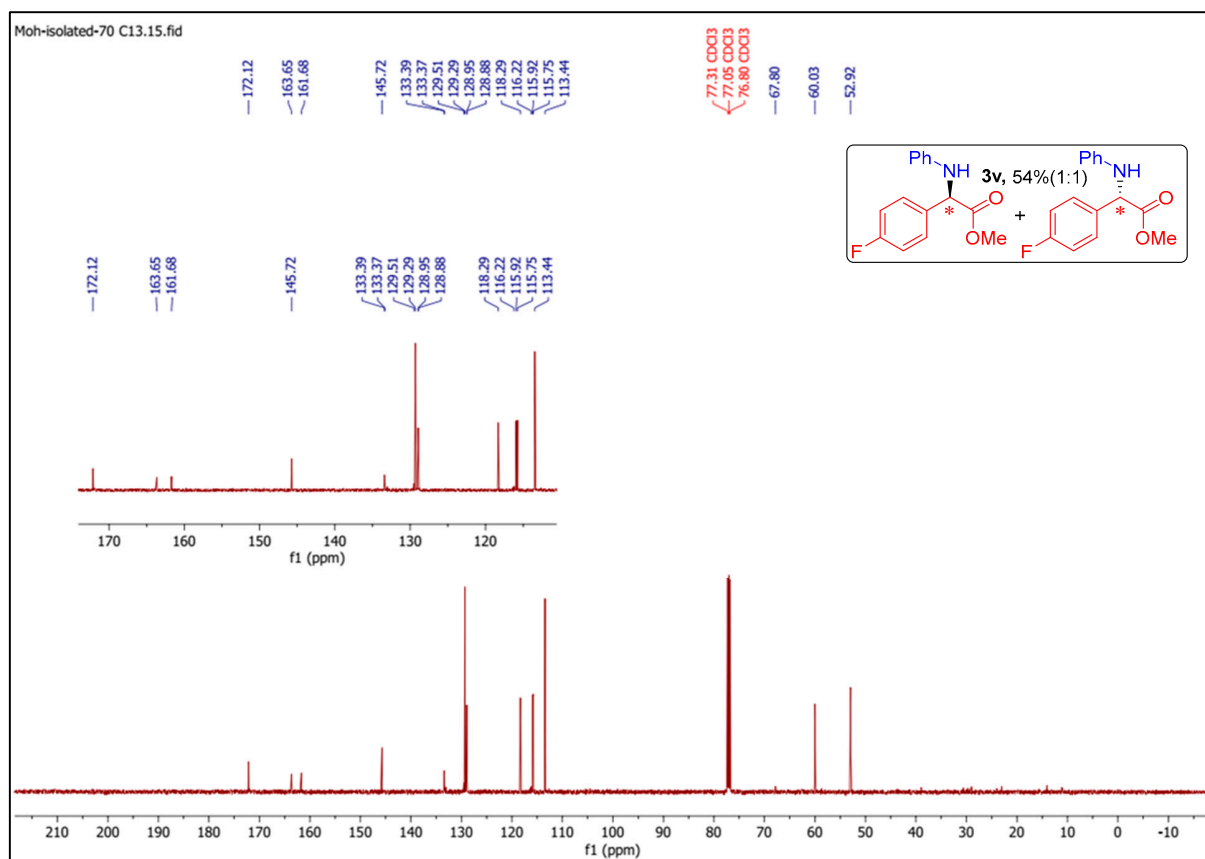


Figure S5. ¹³C NMR spectra of compound **3v** (CDCl₃, 125 MHz)

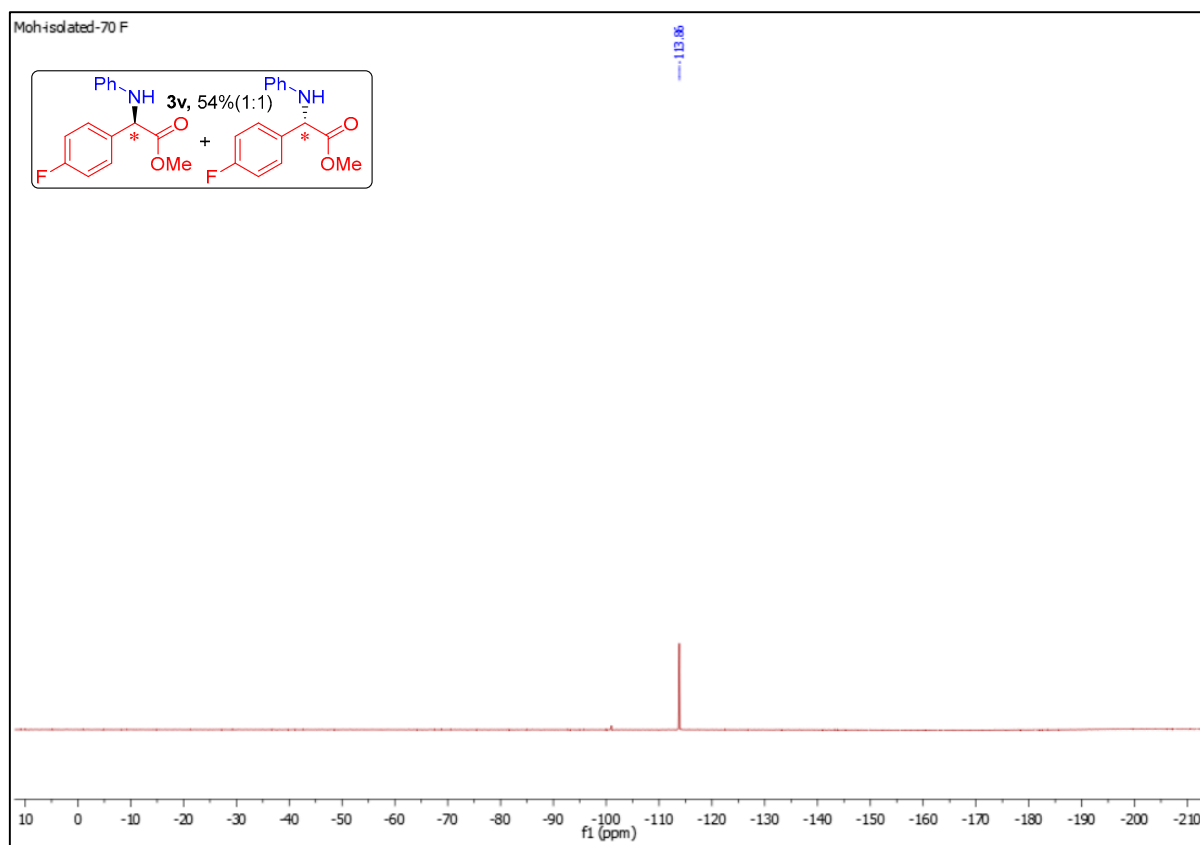


Figure S6. ^{19}F NMR spectra of compound **3v** (CDCl_3 , 40 MHz)

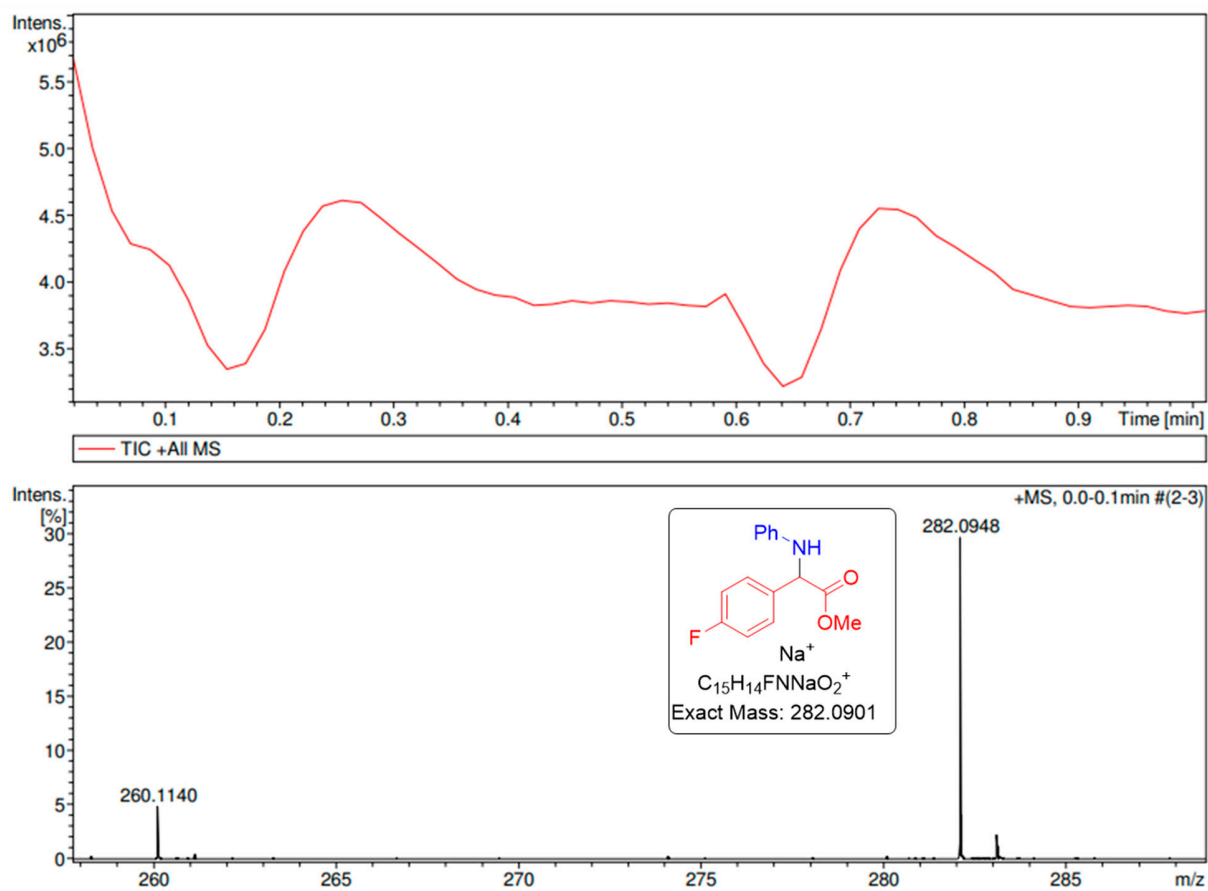
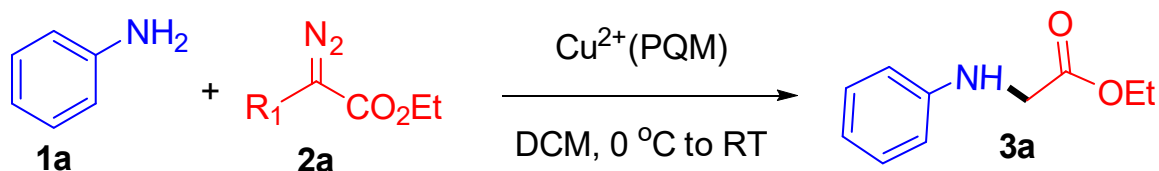


Figure S7. HRMS data for the compound **3o**

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound 3a



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1a**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (min)	30	60	90	120	150	180	210	240	270	300
Yields (%)	12	21	38	47	59	64	70	73	73	74

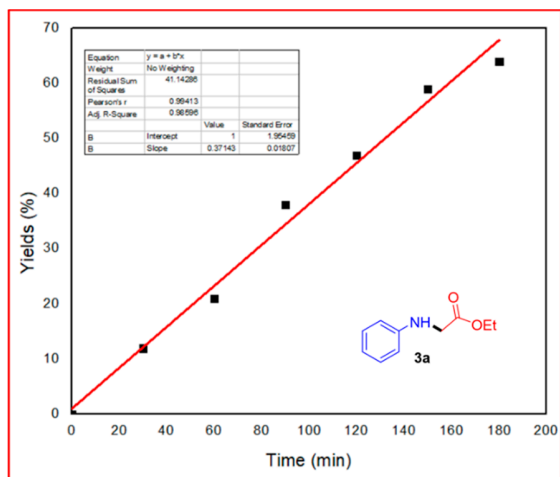
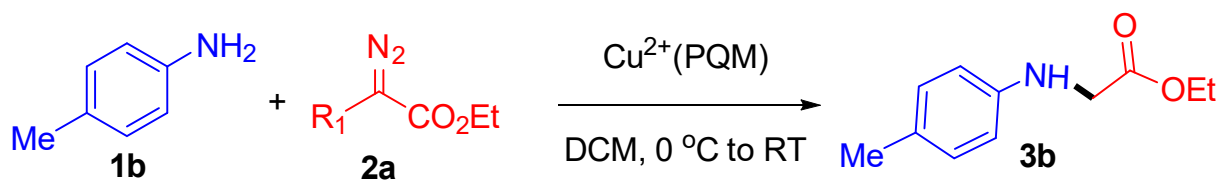


Figure S8. N–H insertion reaction kinetics plot for compound **3a**.

$\text{Cu}^{2+}(\text{PQM})$ catalyst N–H insertion reaction kinetics plot for compound **3b**



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1b**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of $\text{Cu}^{2+}(\text{PQM})$. This mixture was dissolved in 0.5 mL of deuterated dichloromethane ($\text{DCM-}d_2$), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N_2 atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (min)	30	60	90	120	150	180	210	240	270	300
Yields (%)	9	15	23	31	38	43	47	53	53	54

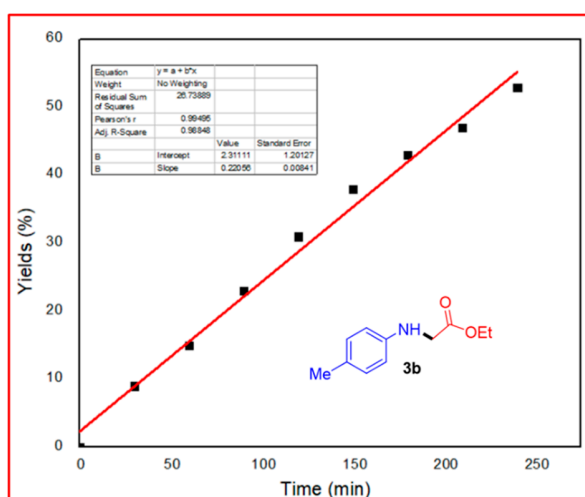
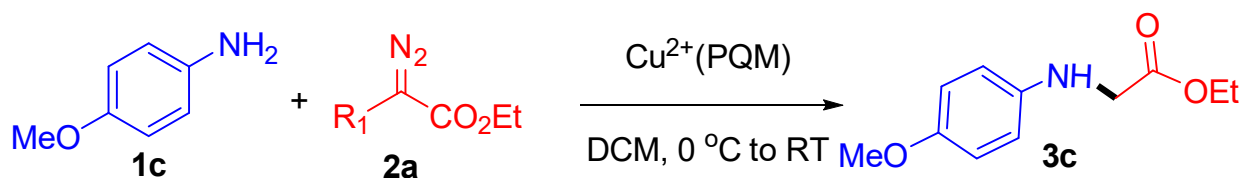


Figure S9. N–H insertion reaction kinetics plot for compound **3b**.

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound 3c



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1c**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (min)	30	60	90	120	150	180	210	240	270	300
Yields (%)	15	31	45	59	65	71	79	83	83	83

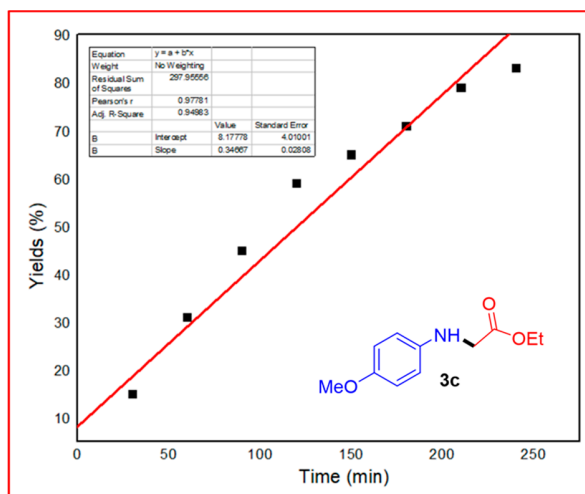
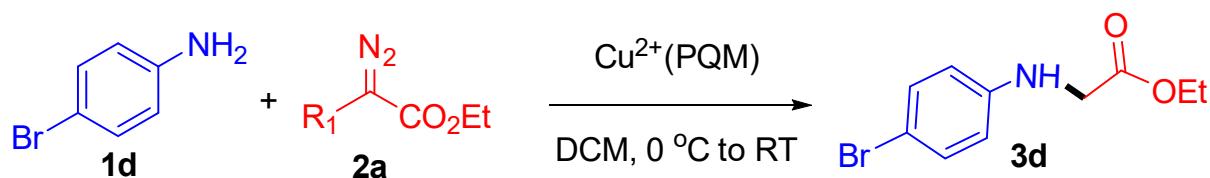


Figure S10. N–H insertion reaction kinetics plot for compound **3c**.

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound **3d**



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1d**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (min)	30	60	90	120	150	180	210	240	270	300
Yields (%)	11	18	23	31	38	45	49	51	51	51

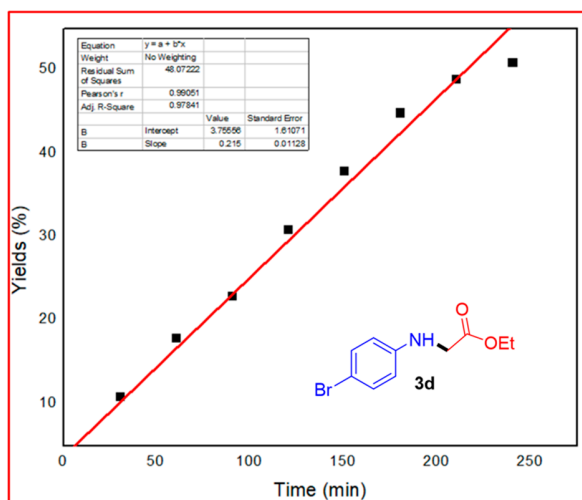
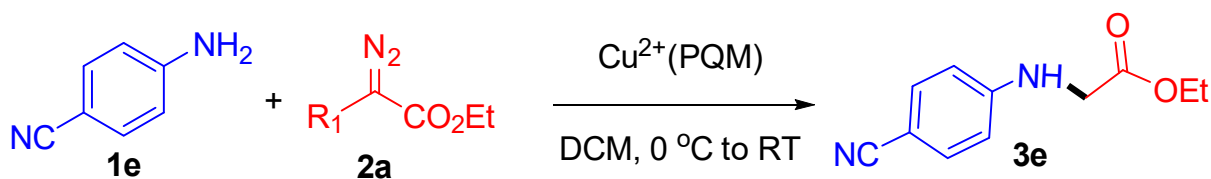


Figure S11. N–H insertion reaction kinetics plot for compound **3d**.

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound **3e**



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1e**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (min)	30	60	90	120	150	180	210	240	270	300
Yields (%)	4	9	14	21	27	30	34	37	38	39

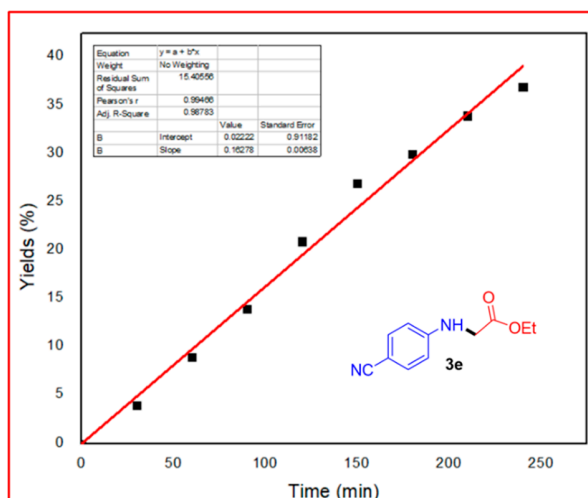
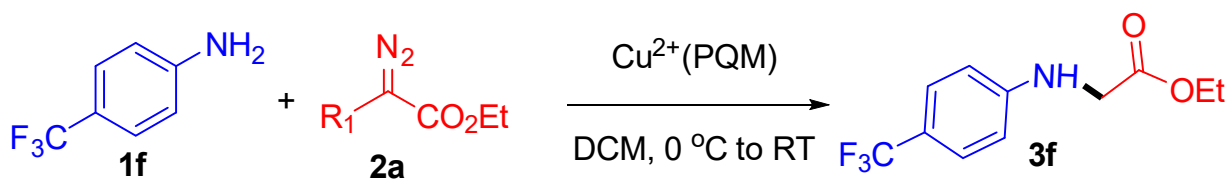


Figure S12. N–H insertion reaction kinetics plot for compound **3e**.

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound **3f**



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1f**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (mints)	30	60	90	120	150	180	210	240	270	300
Yields (%)	4	9	14	21	27	30	34	37	38	39

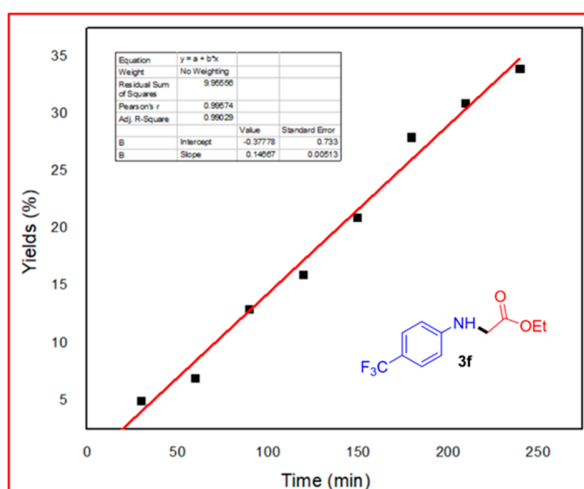
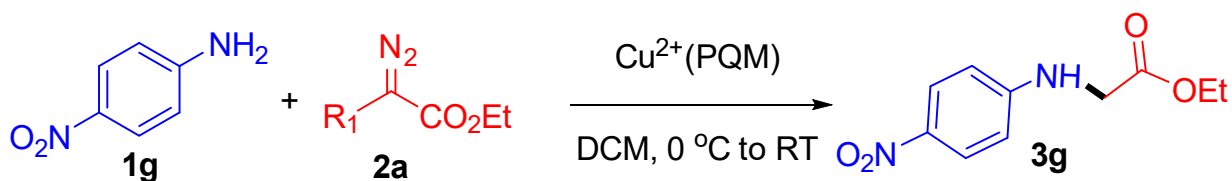


Figure S13. N–H insertion reaction kinetics plot for compound **3f**.

Cu²⁺(PQM) catalyst N–H insertion reaction kinetics plot for compound **3g**



A 1.0 mL NMR tube was charged with 0.5 mmol of anilines (**1g**), 1.0 mmol of ethyl diazo acetate (**2a**), 0.05 mmol of mesitylene (used as an internal standard) and 0.05 mmol of Cu²⁺(PQM). This mixture was dissolved in 0.5 mL of deuterated dichloromethane (DCM-*d*₂), and the reaction was started at 0 °C to ambient temperature stir for approximately five hours under an N₂ atmosphere. The reaction progress was monitored at 10-minute intervals using a 500 MHz NMR instrument.

Time (mints)	30	60	90	120	150	180	210	240	270	300
Yields (%)	0	2	3	5	7	9	10	10	11	11

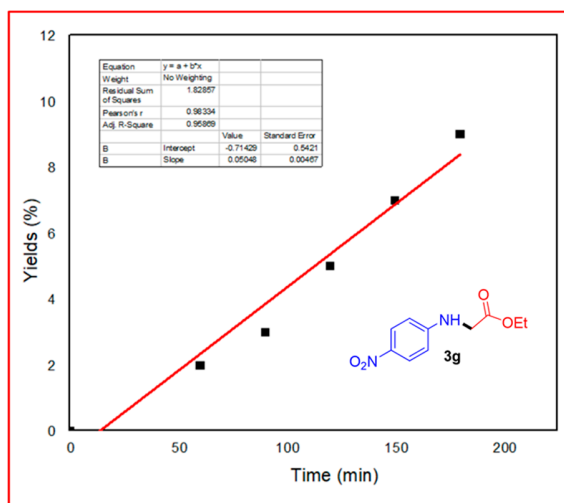


Figure S14. N–H insertion reaction kinetics plot for compound **3g**.

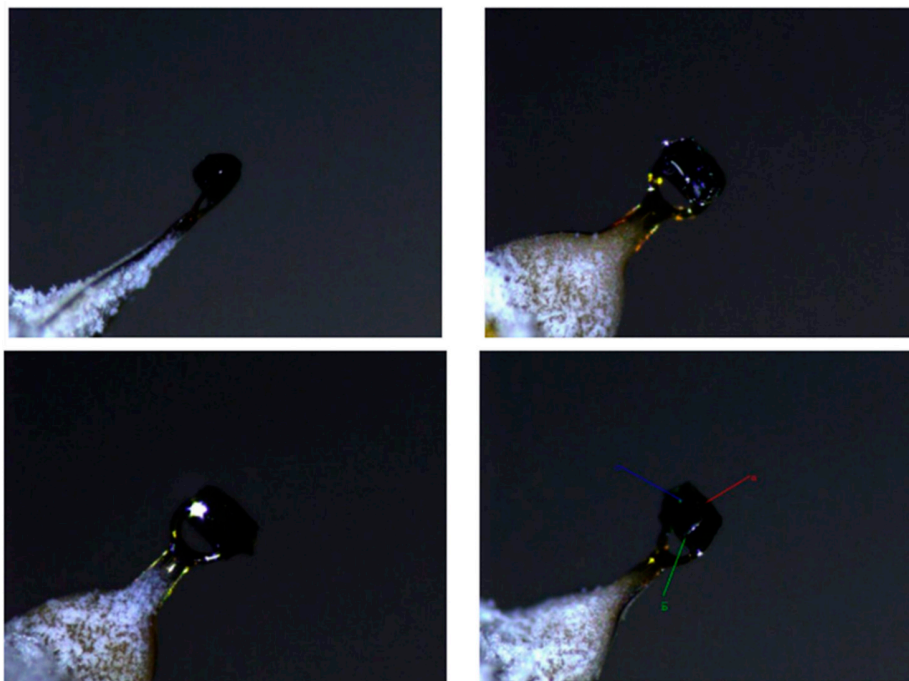


Figure S15: $\text{Cu}^{2+}(\text{PQM})$ complex crystal view on mounted on a cryoLoop.

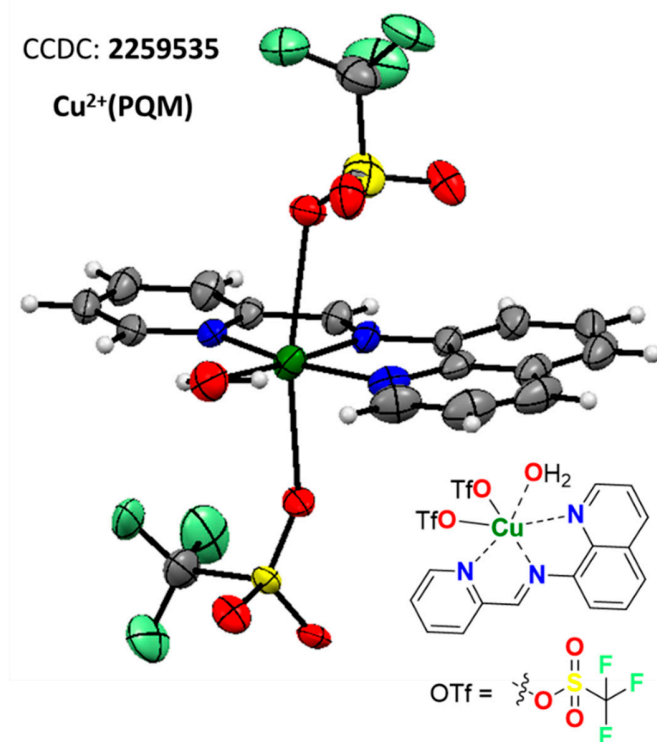


Figure S16. Crystallographic data, structure of $\text{Cu}^{2+}(\text{PQM})$ complex, and related report

Table S1: Sample and crystal data for $\text{Cu}^{2+}(\text{PQM})$ complex.

Identification code	D_JE_014	
Chemical formula	$\text{C}_{17}\text{H}_{19}\text{CuF}_6\text{N}_3\text{O}_{10}\text{S}_2$	
Formula weight	667.01 g/mol	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal size	(0.168 x 0.267 x 0.271) mm ³	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 24.0665(11) Å	$\alpha = 90^\circ$
	b = 11.8732(5) Å	$\beta = 99.940(2)^\circ$
	c = 17.8506(8) Å	$\gamma = 90^\circ$
Volume	5024.2(4) Å ³	
Z	8	
Density (calculated)	1.764 g/cm ³	
Absorption coefficient	3.742 mm ⁻¹	
F(000)	2696	

Table S2. Data collection and structure refinement for $\text{Cu}^{2+}(\text{PQM})$ complex.

Theta range for data collection	3.73 to 74.66°
Index ranges	-30 ≤ h ≤ 30, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	48142
Independent reflections	5136 [R(int) = 0.0327]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.5720 and 0.4300
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)

Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5136 / 585 / 493
Goodness-of-fit on F^2	1.048
	4785
Final R indices	data; $R1 = 0.0803$, $wR2 = 0.2308$ $I > 2\sigma(I)$
	all data $R1 = 0.0837$, $wR2 = 0.2349$
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.1416P)^2 + 35.7616P]$ where $P = (F_o^2 + 2F_c^2) / 3$
Extinction coefficient	0.0004(1)
Largest diff. peak and hole	2.426 and -1.014 eÅ ⁻³
R.M.S. deviation from mean	0.149 eÅ ⁻³

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