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Supporting Information

Transition-Metal-Free Regioselective Hydroamination of Styrenes with Amino-Heteroarenes

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General Experimental

General Method. 1 H NMR (400 MHz) and 13 C NMR (100 MHz) spectra were recorded in CDCl₃/DMSO-d₆. Chemical shifts for protons and carbons are reported in ppm from tetra methyl silane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constants in Hertz and integration. High-resolution mass spectra were recorded on electrospray mass spectrometer. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates and visualized by either UV irradiation or by staining with I_2 . All purchased chemicals were used as received. All melting points are uncorrected.

Scope of Aminopyridine

Scope of Styrene

General Procedure for the Synthesis of N-Heterocyclic amines

N-Heterocyclic amines (1a-n, 1q, 5a,b, 9 and 13) and Alkene (2a-r, 11, and 16) were commercially available from Sigma Aldrich Chemical Co and TCI Chemicals. And 10^1 and $1p^2$ aminopyridine were synthesized.

- 1. S. T. Handy and D. Mayi, Tetrahedron Lett., 2007, 48, 8108–8110.
- 2. B. Clement, M. Weide, U. Wolschendorf and I. Kock, Angew. Chem. Int. Ed., 2005, 44, 635-638.

Table 1. Reaction development^a

Entry	Base(equiv)	Solvent	Time	Temp (°C)	Yield (%) ^b
			(h)		3 a
1	KOH(1.0)	DMSO	3	120	60
2	KOH(1.0)	DMSO	3	100	72
3	KOH(1.0)	DMSO	3	80	85
4	KOH(1.0)	DMSO	3	60	73
5	KOH(0.5)	DMSO	3	80	50
6	KOH(0.2)	DMSO	3	80	Trace
7	KOH(1.5)	DMSO	3	80	57
8	KOH(1.0)	DMSO	1.5	80	70
9	KOH(1.0)	DMSO	1	80	60
10	KOH(1.0)	DCE	3	80	45
11	KOH(1.0)	NMP	3	80	n.r.
12	KOH(1.0)	DMPU	3	80	n.r.
13	KOH(1.0)	DMF	3	80	n.r.
14	KOH(1.0)	Toluene	3	80	n.r.
15	$KO^tBu(1.0)$	DMSO	3	80	25
16	$K_2CO_3(1.0)$	DMSO	3	80	n.r.
17	$K_3PO_4(1.0)$	DMSO	3	80	n.r.

18	$Cs_2CO_3(1.0)$	DMSO	3	80	n.r.
19	KOAc(1.0)	DMSO	3	80	n.r.
20	$Et_3N(1.0)$	DMSO	3	80	n.r.

^aReactions were performed using 0.5 mmol of **1a**, 0.8 mmol of **2a** and base in 2.0 mL of solvent. ^bIsolated yield. n.r. = no reaction. DMSO = Dimethylsulfoxide, DMF = Dimethylformamide, DMPU = N,N'-Dimethylpropylene urea, DCE = Dichloroethane, NMP = N-Methylpyrrolidone.

N-Heterocyclic amines (3–8). In an oven-dried 15 mL reaction vial, a solution of aminopyridine **1** (0.5 mmol), alkene **2** (0.8 mmol) and KOH (1.0equiv) in 2 mL of DMSO was heated in an oil bath at 80 °C for 3 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL X 3) and water (10 mL X 3). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na₂SO₄. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on neutral/basic alumina. The structure and purity of products were confirmed by comparison of their physical and spectral data (¹H NMR, ¹³C NMR, and HRMS).

N-Phenethylpyridin-2-amine (3a). The crude product was purified by column chromatography (hexane/EtOAc = 95/5) to afford 3a as a yellow oil, (84.1 mg, 85%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.03 (d, J = 4.5 Hz, 1H), 7.37–7.33 (m, 1H), 7.31–7.24 (m, 4H), 7.21–7.17 (m, 1H), 6.57 (t, J= 5.5 Hz, 1H), 6.51–6.45 (m, 2H), 3.50 (q, J= 7.2 Hz, 2H), 2.86(t, J= 8.0 Hz, 2H); ¹³C{¹H} NMR (100MHz, (CD₃)₂SO) δ 159.3, 148.2, 140.6, 137.0, 129.2, 128.8, 126.4, 112.0, 108.6, 43.1, 35.8;IR spectrum in film (v_{max}, cm⁻¹) 3338, 1690, 1465, 1341; HRMS (ESI) m/z Calcd for [C₁₃H₁₄N₂] requires [M]⁺198.1157, found 198.1169.

Me *N*-(4-Methylphenethyl)pyridin-2-amine (3b). The crude product was purified by column chromatography (hexane/EtOAc = 95/5) to afford 3b as a brown oil, (84.8 mg, 80%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.02 (dd, J_{I} = 5.0, J_{2} = 1.2 Hz, 1H), 7.37–7.32 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.54 (t, J = 5.6 Hz, 1H), 6.50–6.45 (m, 2H), 3.47 (dd, J_{I} = 14.4, J_{2} = 6.2 Hz, 2H), 2.81 (t, J = 8.0 Hz, 2H), 2.26 (s, 3H); 13 C{ 1 H} NMR

(100 MHz, (CD₃)₂SO) δ 159.3, 148.2, 137.4, 137.0, 135.3, 129.4, 129.1, 112.0, 108.6, 43.2, 35.4, 21.2; IR spectrum in film (v_{max} , cm⁻¹) 3340, 1652, 1463, 1450, 1332; HRMS (ESI) m/z Calcd for [C₁₄H₁₆N₂] requires [M]⁺212.1313, found 212.1331.

N-(4-Diphenylphosphanyl)phenethyl)pyridin-2-amine (3c). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3c as a pale yellow oil, (143.30 mg, 75%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.96–7.94 (m, 1H), 7.64–7.51 (m, 1H), 7.39–7.16 (m,14H), 6.56 (t, J = 5.4 Hz, 1H), 6.46–6.45 (m, 2H), 3.47 (q, J = 7.2 Hz, 2H), 2.91–2.81 (m, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.0, 147.8, 141.6, 137.4 (d, C-P, 3 J_{C-P} = 11.13 Hz),137.0, 134.1 (d, C-P, 3 J_{C-P} = 10.39 Hz), 133.9, 133.7, 133.6 (d, C-P, 3 J_{C-P} = 19.36 Hz), 132.4, 131.9, 131.8, 129.7 (d, C-P, 3 J_{C-P} = 7.12 Hz), 129.3, 129.2 (d, C-P, 3 J_{C-P} = 6.84 Hz), 129.1, 111.9, 108.6, 42.6, 35.4; 31 P NMR (162 MHz, (CD₃)₂SO) δ -7.32–7.55; IR spectrum in film (ν _{max}, cm⁻¹) 3342, 1649, 1464, 1346, 1332; HRMS (ESI) m/z Calcd for [C₂₅H₂₄N₂P] requires [M+H]⁺ 383.1677, found 383.1695.

CI *N*-(4-Chlorophenethyl)pyridin-2-amine (3d). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3d as a brown oil, (102.1 mg, 88%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.02 (d, J = 3.2 Hz, 1H), 7.34–7.21 (m, 5H), 6.50–6.44 (m, 3H), 3.50–3.47 (m, 2H), 2.85–2.82 (m, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.2, 139.6, 137.0, 131.3, 131.0, 128.7, 112.1, 108.7, 42.9, 35.2; IR spectrum in film (ν_{max} , cm⁻¹) 3332, 1690, 1460, 1270, 1332, 850; HRMS (ESI) m/z Calcd for [C₁₃H₁₄ClN₂] requires [M+H]⁺233.0846, found 233.0816.

Br N-(4-Bromophenethyl)pyridin-2-amine (3e). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3e as a brown oil, (124.2 mg, 90%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.00 (d, J = 4.0 Hz, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.37–7.33 (m, 1H), 7.21 (d, J = 8.3 Hz, 2H), 6.52 (t, J = 5.5 Hz, 1H), 6.49–6.45 (m, 2H), 3.47 (dd, J_I = 13.3, J₂ = 7.0 Hz, 2H), 2.82 (t, J = 7.3 Hz, 2H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 159.2, 148.1, 140.0, 137.0, 131.5, 131.4,119.5, 111.9, 108.6, 42.6,

35.0; IR spectrum in film $(v_{\text{max}}, \text{cm}^{-1})$ 3347, 1676, 1465, 1342, 690; HRMS (ESI) m/z Calcd for $[C_{13}H_{14}BrN_2]$ requires $[M+H]^+$ 277.0340, found 277.0351.

by column chromatography (hexane/EtOAc = 90/10) to afford **3f** as a brown oil, (125.5 mg, 91%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.97–7.96 (m, 1H), 7.43 (s, 1H), 7.36–7.30 (m, 2H), 7.22–7.18 (m, 2H), 6.50–6.43 (m, 3H), 3.45 (dd, J_{I} = 12.9, J_{Z} = 7.0 Hz, 2H), 2.82 (t, J = 7.1 Hz, 2H); 13 C{ 1 H} NMR (100 MHz, (CD₃)₂SO) δ 159.2, 148.1, 143.5, 137.1, 132.0, 131.0, 129.4, 128.4, 122.2, 112.1, 108.7, 42.7, 35.2; IR spectrum in film (v_{max} , cm⁻¹) 3341, 1680, 1463, 1340, 650; HRMS (ESI) m/z Calcd for [C₁₃H₁₄BrN₂] requires [M+H]⁺ 277.0340, found 277.0352.

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F *N*-(3-Fluorophenethyl)pyridin-2-amine (3g). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3g as a brown oil, (101.5 mg, 94%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.06 (d, J = 3.7 Hz, 1H), 7.33 (ddd, J_{I} = 22.2, J_{2} = 11.5, J_{3} = 4.9 Hz, 2H), 7.08 (d, J = 7.1 Hz, 2H), 7.00 (dd, J_{I} = 12.0, J_{2} = 5.2 Hz, 1H), 6.56 (dd, J_{I} = 12.6, J_{2} =6.8 Hz, 2H), 6.51 – 6.46 (m, 1H), 3.56 (dd, J_{I} = 13.1, J_{2} =6.8 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 163.9, 161.5 159.2, 148.1, 143.5 (C-F, 3 J_{C-F} = 7.3 Hz), 136.9, 130.3 (C-F, 3 J_{C-F} = 8.1 Hz), 125.2 (C-F, 4 J_{C-F} = 2.5 Hz), 115.8 (C-F, 3 J_{C-F} = 20.4 Hz), 113.0 (C-F, 3 J_{C-F} = 20.7 Hz), 111.9, 108.5, 42.6, 35.3; 19 F NMR (376 MHz, (CD₃)₂SO) δ -113.503 – -113.659; IR spectrum in film (v_{max}, cm⁻¹) 3334, 1673, 1462, 1400, 1341; HRMS (ESI) m/z Calcd for [C₁₃H₁₄FN₂] requires [M+H]⁺217.1141, found 217.1145.

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 $^{\text{CF}_3}$ *N*-(3-(Trifluoromethyl)phenethyl)pyridin-2-amine (3h). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3h as a brown oil, (127.7 mg, 96%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.02 (d, J = 4.5 Hz, 1H), 7.62 (s, 1H), 7.58–7.50 (m, 3H), 7.38–7.35 (m, 1H), 6.63 (t, J = 5.2 Hz, 1H), 6.52–6.47 (m, 2H), 3.55 (dd, J_1 = 12.9, J_2 = 6.7 Hz, 2H), 2.98 (t, J = 7.1 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.2, 148.0, 142.1, 137.0, 133.4, 129.8, 129.6, 129.5, 125.7(C-F, 3 J_{C-F} = 3.8 Hz), 124.4 (C-F, 1 J_{C-F} = 254.9 Hz), 123.2 (C-F, 4 J_{C-F} = 2.9 Hz), 112.0, 108.7, 42.6, 35.3; 19 F NMR (376 MHz,

(CD₃)₂SO) δ -61.061; IR spectrum in film (ν_{max} , cm⁻¹) 3345, 1683, 1460, 1380, 1266; HRMS (ESI) m/z Calcd for [C₁₄H₁₄F₃N₂] requires [M+H]⁺ 267.1109, found 267.1119.

N-(2-([1,1'-Biphenyl]-4-yl)ethyl)pyridin-2-amine (3i). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3i as a brown oil, (120.6 mg, 88%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.05–8.04 (m, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.46–7.42 (m, 2H), 7.38–7.28 (m, 4H), 6.99–6.56 (m, 1H), 6.53–6.47 (m, 2H), 3.54(q, J = 6.64 Hz, 2H), 2.91 (t, J = 7.4 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.2, 140.6, 139.9, 138.4, 137.0, 129.8, 129.4, 127.6, 127.1, 127.0, 112.0, 108.6, 42.9, 35.3; IR spectrum in film (ν_{max} , cm⁻¹) 3336, 1689, 1462, 1342; HRMS (ESI) m/z Calcd for [C₁₉H₁₉N₂] requires [M+H]⁺ 275.1548, found 275.1559.

Me^{Me} *N*-(4-(*tert*-Butyl)phenethyl)pyridin-2-amine (3j). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3j as a brown oil, (105.4 mg, 83%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.02 (d, J = 3.8 Hz, 1H), 7.33–7.28 (m,3H), 7.17 (d, J = 8.1 Hz, 2H), 6.53–6.49(m, 2H), 6.47–6.44 (m, 1H), 3.49 (q, J = 6.8 Hz, 2H), 2.84 (t, J = 7.5 Hz, 2H), 1.26 (s, 9H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.69 148.1, 137.4, 136.8, 128.8, 125.4, 111.9, 108.5, 43.1, 35.2, 34.5, 31.7;IR spectrum in film (ν_{max} , cm⁻¹) 3350, 1690, 1460, 1450, 1340; HRMS (ESI) m/z Calcd for [C₁₇H₂₃N₂] requires [M+H]⁺255.1861, found 255.1868.

H N

N-(2-(Naphthalen-1-yl)ethyl)pyridin-2-amine (3k). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3k as a brown oil, (105.4 mg, 85%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.31 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 3.9 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.55 (dt, J_{I} = 14.6, J_{2} =6.9 Hz, 2H), 7.47 – 7.34 (m, 3H), 6.68 (t, J = 5.4 Hz, 1H), 6.53 – 6.44 (m, 2H), 3.58 (dd, J_{I} = 13.8, J_{2} = 6.9 Hz, 2H), 3.35 – 3.29 (m, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.2, 148.1, 137.1, 136.6, 134.0, 132.2, 129.0, 127.1, 127.0, 126.5, 126.0 (d, J = 2.9 Hz), 124.5, 111.9, 108.8, 42.4, 33.1; IR spectrum in film (v_{max} , cm $^{-1}$) 3343, 1676, 1463, 1333; HRMS (ESI) m/z Calcd for [C₁₇H₁₇N₂] requires [M+H]⁺ 249.1392, found 249.1402.

N-(2,2-Diphenylethyl)pyridin-2-amine (3l). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3l as a brown oil, (123.3 mg, 90%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.00–7.99 (m, 1H), 7.33–7.26 (m, 9H), 7.19–7.15 (m, 2H), 6.46–6.44 (m, 3H), 4.39–4.35 (m, 1H), 3.90 (t, J = 7.1 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.1, 148.0, 143.9, 136.9, 128.9, 128.5, 126.7, 112.0, 108.9, 50.4, 45.9; IR spectrum in film (ν_{max} , cm $^{-1}$) 3350, 1670, 1460, 1339; HRMS (ESI) m/z Calcd for [C₁₉H₁₉N₂] requires [M+H]⁺ 275.1548, found 275.1559.

N-(2-(Pyridin-2-yl)ethyl)pyridin-2-amine (3m). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3m as a brown oil, (74.6 mg, 75%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.54 (d, J = 4.8 Hz, 1H), 8.04 (d, J = 4.9 Hz, 1H), 7.68 (td, J_{1} = 7.6, J_{2} =1.8 Hz, 1H), 7.39–7.35 (m, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.21 (dd, J_{1} = 6.9, J_{2} = 5.3 Hz, 1H), 6.64 (t, J = 5.0 Hz, 1H), 6.53–6.47 (m, 2H), 3.67 (dd, J_{1} = 12.8, J_{2} = 6.9 Hz, 2H), 3.05 (t, J = 7.2 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 160.2, 159.3, 149.5, 148.1, 137.1, 136.8, 123.7, 121.8, 112.0, 108.6, 41.3, 38.0; IR spectrum in film (v_{max} , cm $^{-1}$) 3320, 1689, 1462, 1340; HRMS (ESI) m/z Calcd for [C₁₂H₁₄N₃] requires [M+H]⁺ 200.1188, found 200.1194.

N-(2-Phenylpropyl)pyridin-2-amine (3n). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3n as a brown oil, (86.9 mg, 82%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.99 (d, J = 3.6 Hz, 1H), 7.34–7.25 (m, 5H), 7.21–7.17 (m, 1H), 6.49–6.43 (m, 3H), 3.49–3.34 (m, 2H), 3.07 (td, J_{1} = 14.0, J_{2} =7.0 Hz, 1H), 1.25 (d, J = 6.9 Hz, 3H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.4, 148.1, 146.0, 137.0, 128.8, 127.7, 111.9, 108.7, 48.5, 39.3, 20.0; IR spectrum in film (ν_{max} , cm⁻¹) 3338, 1691, 1465, 1450, 1341; HRMS (ESI) m/z Calcd for [C₁₄H₁₇N₂] requires [M+H]⁺213.1392, found 213.1396.

4-Methyl-*N*-phenethylpyridin-2-amine (4a). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4a as a

brown oil, (90.1 mg, 85%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 6.88 (d, J = 5.4 Hz, 1H), 6.38–6.25 (m, 5H), 5.49 (d, J = 5.2 Hz, 1H), 5.42 (s, 1H), 4.04 (s, 1H), 2.58 (t, J = 7.3 Hz, 2H), 1.97 (t, J = 7.3 Hz, 2H), 1.28 (s, 3H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 151.8, 141.8, 139.0, 132.6, 121.5, 121.0, 118.8, 106.5, 101.2, 35.9, 28.3, 12.8; IR spectrum in film (ν_{max} , cm⁻¹) 3349, 1687, 1462, 1449, 1340; HRMS (ESI) m/z Calcd for [C₁₄H₁₇N₂] requires [M+H]⁺ 213.1392, found 213.1398.

Note that the content of the conten

5-Methyl-*N***-phenethylpyridin-2-amine** (**4c**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **4c** as a brown oil, (76.3 mg, 72%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.81 (s, 1H), 7.30–7.13 (m, 6H), 6.39 (d, J = 8.4 Hz, 1H), 6.26 (t, J = 5.4 Hz, 1H), 3.41 (q, J = 6.8 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.08 (s, 3H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 157.5, 147.4, 140.6, 138.1, 129.1, 128.7, 126.4, 120.0, 108.2, 43.2, 35.7, 17.5; IR spectrum in film (ν_{max} , cm⁻¹) 3310, 1690, 1465, 1442, 1320; HRMS (ESI) m/z Calcd for [C₁₄H₁₇N₂] requires [M+H]⁺213.1392, found 213.1333.

6-Methyl-*N*-phenethylpyridin-2-amine (4d). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4d as a brown oil, (80.6 mg, 76%): 1 H NMR (400 MHz, CDCl₃) δ 7.35–7.29 (m, 3H), 7.25–7.20 (m, 3H), 6.44 (d, J = 7.3 Hz, 1H), 6.19 (d, J = 8.2 Hz, 1H), 4.58 (s, 1H), 3.50 (dd, $J_{I} = 13.0$, $J_{2} = 7.1$ Hz, 2H), 2.91 (t, J = 7.1 Hz, 2H), 2.36 (s, 3H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 158.4, 157.1, 139.3, 138.0, 128.9, 128.7, 126.5, 112.4, 102.9, 43.8, 35.8, 24.4; IR spectrum in film (ν_{max} , cm ${}^{-1}$) 3322, 1685,

1461, 1450, 1340; HRMS (ESI) m/z Calcd for $[C_{14}H_{17}N_2]$ requires $[M+H]^+$ 213.1392, found 213.1401.

6-Methyl-*N*-(4-methylphenethyl)pyridin-2-amine (4e). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4e as a brown oil, (89.3 mg, 79%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 7.83 (d, J = 5.2 Hz, 1H), 7.17–7.06 (m, 4H), 6.47 (t, J = 5.6 Hz, 1H), 6.32 (dd, $J_I = 5.3$, $J_2 = 0.9$ Hz, 1H), 6.29 (s, 1H), 3.41 (q, J = 6.4 Hz, 2H), 2.76(t, J = 8.0 Hz, 2H), 2.26 (s, 3H), 2.14 (s, 3H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 159.2, 147.6, 147.3, 137.4, 135.3, 129.4, 129.1, 113.6, 108.6, 43.2, 35.3, 21.2; IR spectrum in film (ν_{max} , cm⁻¹) 3343, 1633, 1460, 1450, 1259; HRMS (ESI) m/z Calcd for [C₁₅H₁₉N₂] requires [M+H]⁺ 227.1548, found 227.1562.

F **6-Methyl-***N***-(4-fluoromethylphenethyl)pyridin-2-amine** (**4f**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **4f** as a brown oil,(100.1 mg, 87%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.88 (d, J = 4.9 Hz, 1H), 7.32 (dd, J_I = 14.3, J_2 = 7.6 Hz, 1H), 7.09 (d, J = 8.2 Hz, 2H), 7.01 (t, J = 8.9 Hz, 1H), 6.45 (s, 1H), 6.34 – 6.32 (m, 2H), 3.50 (dd, J_I = 12.9, J_2 = 6.7 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H), 2.14 (s, 3H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 163.9, 161.5, 159.4, 147.4 (C-F, ${}^{2}J_{C-F}$ =50.6 Hz), 143.5 (C-F, ${}^{3}J_{C-F}$ =7.5 Hz), 130.4 (C-F, ${}^{3}J_{C-F}$ =8.4 Hz), 125.3, 115.8 (C-F, ${}^{2}J_{C-F}$ =20.6 Hz), 113.6, 113.0 (C-F, ${}^{2}J_{C-F}$ =20.7 Hz), 108.4, 42.6, 35.3, 21.0; 19 F NMR (376 MHz, (CD₃)₂SO) δ -113.766 –-113.836; IR spectrum in film (v_{max} , cm $^{-1}$) 3346, 1654, 1465, 1450, 1400, 1256; HRMS (ESI) m/z Calcd for [C₁₄H₁₆FN₂] requires [M+H] $^{+}$ 231.1298, found 231.1311.

F₃C H N

N-Phenethyl-4-(trifluoromethyl)pyridin-2-amine (4g). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4g as a brown oil,(118.4 mg, 89%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.20 (d, J = 5.2 Hz, 1H), 7.32–7.26 (m, 5H),7.24–7.16 (m, 1H), 6.74 (s, 1H), 6.70 (d, J = 5.1 Hz, 1H), 3.55–3.50(m, 2H), 2.85–2.82 (m, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.4, 150.0, 140.2, 137.8,137.5, 129.1, 128.8, 126.5, 124.0(C-F, 1 1 1 C- 1 F=270.7 Hz), 122.4, 106.2 (C-F, 3 1 1 C- 1 F=5.9 Hz), 104.3, 42.8, 35.4; 19 F NMR (376 MHz, (CD₃)₂SO) δ –64.06; IR spectrum in film (v_{max}, cm⁻¹) 3350, 1683,

1462, 1450, 1350, 1250; HRMS (ESI) m/z Calcd for [C₁₄H₁₄F₃N₂] requires [M+H]⁺ 267.1109, found 267.1119.

N-Phenethylpyridin-3-amine (4h). The crude product was product was purified by column chromatography (hexane/EtOAc = 85/15) to afford 4h as a brown oil, (66.3 mg, 67%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.06 (d, J = 2.3 Hz, 1H), 7.81 (d, J = 3.8 Hz, 1H), 7.33–7.28 (m, 4H), 7.23–7.19 (m, 1H), 7.08 (dd, J_{I} = 8.1, J_{2} = 4.6 Hz, 1H), 6.95 (dd, J_{I} = 8.3, J_{2} = 1.5 Hz, 1H), 5.95 (s, 1H), 3.29 (dd, J_{I} = 11.8, J_{2} = 7.0 Hz, 2H), 2.87 (t, J = 7.5 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 145.2, 140.1, 137.3, 135.9, 129.2, 128.9, 126.5, 124.1, 117.8, 44.6, 35.3; IR spectrum in film (v_{max} , cm $^{-1}$) 3340, 1690, 1465, 1342; HRMS (ESI) m/z Calcd for [C₁₃H₁₅N₂] requires [M+H]⁺ 199.1235, found 199.1243.

Me *N*-(4-Methylphenethyl)pyridin-3-amine (4i). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4i as a brown oil, (67.8 mg, 64%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.05 (s, 1H), 7.80 (s, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.11 – 7.06 (m, 3H), 6.93 (d, J = 8.3 Hz, 1H), 5.92 (s, 1H), 3.26 (t, J = 7.2 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 2.26 (s, 3H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 157.8, 148.7, 138.0, 137.2, 135.6, 129.6, 129.4, 111.9, 106.3, 51.1, 33.5, 21.4; IR spectrum in film (ν max, cm⁻¹) 3350, 1652, 1463, 1452, 1332; HRMS (ESI) m/z Calcd for [C₁₄H₁₇N₂] requires [M+H]⁺ 213.1392, found 213.1390.

ci *N*-(4-Chlorophenethyl)pyridin-3-amine (4j). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4j as a brown oil, (90.5 mg, 78%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.98 (s, 1H), 7.77 (s, 1H), 7.33 (dd, J_{I} = 17.8, J_{2} =8.3 Hz, 4H), 7.09 (dd, J_{I} = 8.1, J_{2} = 4.6 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 5.96 (s, 1H), 3.27 (t, J = 7.1 Hz, 2H), 2.83 (t, J = 7.3 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 145.2, 139.2, 136.9, 135.3, 131.2, 131.1, 128.7, 124.3, 118.2, 44.3, 34.4; IR spectrum in film (ν_{max} , cm⁻¹) 3340, 1672, 1464, 1333, 790; HRMS (ESI) m/z Calcd for [C₁₃H₁₄CIN₂] requires [M+H]⁺ 233.0846, found 233.0844.

Me H

5-Methyl-*N***-phenethylpyridin-3-amine** (**4k**). The crude product was product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **4k** as a brown oil, (83.7 mg, 79%): ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 7.3 Hz, 2H), 7.24–7.20 (m, 3H), 6.98 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 8.2 Hz, 2H), 3.36 (t, J = 7.0 Hz, 2H), 2.89 (t, J = 7.1 Hz, 2H), 2.23 (s, 3H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ 145.9, 139.5, 129.9, 128.9, 128.7, 126.8, 126.5, 113.3, 45.6, 35.7, 20.5; IR spectrum in film (ν_{max} , cm⁻¹) 3345, 1650, 1460, 1449, 1332; HRMS (ESI) m/z Calcd for [C₁₄H₁₇N₂] requires [M+H]⁺ 213.1392, found 213.1401.

2-Chloro-*N***-phenethylpyridin-3-amine** (**4l**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **4l** as a brown oil, (89.3 mg, 77%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.54 (d, J = 4.2 Hz, 1H), 7.32–7.27(m, 2H), 7.24–7.20 (m, 3H), 7.09–7.06 (m, 1H), 6.89 (d, J = 7.9 Hz, 1H), 4.58 (s, 1H), 3.39–3.37(m, 2H), 2.93–2.91 (m, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.5, 148.4, 139.8, 137.2, 131.5, 131.2, 128.9, 112.3, 108.9, 43.1, 35.3; IR spectrum in film (v_{max}, cm $^{-1}$) 3350, 1687, 1461,1256, 749; HRMS (ESI) m/z Calcd for [C₁₃H₁₄ClN₂] requires [M+H]⁺233.0846, found 233.0856.

3-Chloro-*N*-phenethylpyridin-4-amine (4m). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4m as a brown oil, (92.8 mg, 80%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.16 (s, 1H), 8.06 (d, J= 4.5 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.21 (t, J = 6.7 Hz, 1H), 6.73 (d, J = 5.6 Hz, 1H), 6.36 (t, J = 5.1 Hz, 1H), 3.44 (dd, J_{I} = 14.4, J_{2} =6.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 149.3, 148.8, 148.0, 139.6, 129.2, 128.8, 126.7, 106.4, 43.9, 34.8; IR spectrum in film (ν _{max}, cm⁻¹) 3334, 1676, 1465, 1251, 750; HRMS (ESI) m/z Calcd for [C₁₃H₁₄ClN₂] requires [M+H]⁺ 233.0846, found 233.0858.

N-Phenethylpyridin-2-amine (4n). The crude product was purified by column chromatography (hexane/EtOAc = 60/40) to afford 4n as a yellow oil, (74.2 mg, 75%): ¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 2H), 7.26–7.21 (m, 2H), 7.14 (dd, J_I = 19.0, J_2 = 7.1 Hz, 3H), 6.36 (s, 2H), 4.76 (s, 1H), 3.33 (dd, J_I = 12.0, J_2 = 6.5 Hz, 2H), 2.82 (t, J = 7.1 Hz, 2H); ¹³C{1H} NMR (100MHz, CDCl₃) δ 153.5, 149.5, 138.7, 128.8, 128.8, 126.7, 107.7, 43.8, 35.1; IR

spectrum in film (v_{max} , cm⁻¹) 3337, 1693, 1468, 1351; HRMS (ESI) m/z Calcd for [C₁₃H₁₄N₂] requires [M]⁺ 198.1157, found 198.1140.

5-Bromo-*N*-phenethylpyridin-2-amine (4o). The crude product was product was purified by column chromatography (hexane/EtOAc = 95/5) to afford 4o as a brown oil, (117.3 mg, 85%): 1 H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 2.1 Hz, 1H), 7.35 (dd, J_{I} = 8.8, J_{I} = 2.4 Hz, 1H), 7.21 (t, J = 7.3 Hz, 2H), 7.13 (dd, J_{I} = 13.2, J_{I} = 7.2 Hz, 3H), 6.16 (d, J = 8.9 Hz, 1H), 4.62 (s, 1H), 3.43 (d, J = 4.8 Hz, 2H), 2.81 (t, J = 6.9 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 157.0, 148.4, 139.7, 138.9, 128.7, 128.6, 126.4, 108.3, 106.8, 43.3, 35.4; IR spectrum in film (v_{max} , cm $^{-1}$) 3347, 1670, 1465, 1342, 680; HRMS (ESI) m/zCalcd for [C₁₃H₁₄BrN₂] requires [M+H]⁺277.0340, found 277.0357.

6-Bromo-*N***-phenethylpyridin-3-amine** (**4p**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **4p** as a brown oil, (113.1 mg, 82%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 7.74 (d, J = 2.8 Hz, 1H), 7.32 – 7.18 (m, 6H), 6.94 (dd, J_I = 8.8, J_2 = 3.2 Hz, 1H), 6.18 (t, J = 5.6 Hz, 1H), 3.28 – 3.23 (m, 2H), 2.85 – 2.80 (m, 2H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 145.2, 140.0, 135.0, 129.3, 128.8, 128.0, 126.7, 126.1, 122.4, 44.6, 35.1; IR spectrum in film (v_{max} , cm⁻¹) 3350, 1690, 1462, 1340, 687; HRMS (ESI) m/z Calcd for [C₁₃H₁₄BrN₂] requires [M+H]⁺ 277.0340, found 277.0353.

 \bigwedge_{N}^{H}

N-Phenethylquinolin-2-amine (4q). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4q as a brown oil, (71.9 mg, 58%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.83 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.48–7.44 (m, 1H), 7.34–7.29 (m, 4H), 7.24–7.19(m, 1H), 7.16–7.12 (m, 2H), 6.81–6.74 (m, 1H), 3.64–3.59(m, 2H), 2.92 (t, J = 7.6 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.1, 140.6, 139.8, 138.4, 137.0, 129.8, 129.3, 127.6, 127.6, 127.0, 126.9, 111.9, 108.6, 42.9, 35.3; IR spectrum in film (ν_{max} , cm⁻¹) 3346, 1685, 1462, 1340; HRMS (ESI) m/z Calcd for [C₁₇H₁₇N₂] requires [M+H]⁺249.1392, found 249.1403.

N-Phenethylquinolin-8-amine (4r). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4r as a brown oil, (68.2)

mg, 55%): ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.71 (d, J = 4.0, 1H), 8.20 (d, J = 6.8 Hz, 1H), 7.49–7.46 (m, 1H), 7.39–7.23 (m, 6H), 7.06 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.46 (t, J = 5.4 Hz, 1H), 3.52 (q, J = 6.8 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 147.3, 144.7, 140.1, 136.4, 129.2, 128.9, 128.3, 126.6, 122.2, 113.7, 104.8, 44.5, 35.1; IR spectrum in film (ν_{max} , cm⁻¹) 3350, 1690, 1465, 1339; HRMS (ESI) m/z Calcd for [C₁₇H₁₇N₂] requires [M+H]⁺ 249.1392, found 249.1404.

N-Phenethyl-5-phenylpyridin-2-amine (4s). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4s as a brown oil, (106.9 mg, 78%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.34 (d, J = 2.3 Hz, 1H), 7.71 (dd, J_{I} = 8.8, J_{2} =2.5 Hz, 1H), 7.58 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.33–7.19 (m, 6H), 6.79 (t, J = 5.3 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 3.53 (dd, J_{I} = 13.8, J_{2} =6.5 Hz, 2H), 2.87 (t, J = 7.4 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 158.5, 145.8, 140.4, 138.6, 135.6, 129.3, 129.1, 128.8, 126.7, 126.4, 125.8, 124.0, 108.8, 43.0, 35.7; IR spectrum in film (v_{max} , cm⁻¹) 3340, 1695, 1463, 1266; HRMS (ESI) m/z Calcd for [C₁₉H₁₉N₂] requires [M+H]⁺ 275.1548, found 275.1542.

NH N

N-Phenethyl-11-phenylbenzo[*c*]phenanthridine-6-amine (4t). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4t as a brown oil, (148.0 mg, 69%): 1 H NMR (400 MHz, CDCl₃) δ 9.24 (d, J = 7.2 Hz, 1H), 7.78–7.76 (m, 1H), 7.64–7.51 (m, 4H), 7.47 (s, 1H), 7.40–7.28(m, 10H), 7.23–7.12 (m, 2H), 5.46 (t, J = 4.8 Hz, 1H), 4.11 (q, J = 6.8 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 152.9, 145.1, 142.9, 140.0, 137.6, 134.6, 133.0, 130.7, 129.1, 129.0, 128.8, 128.3, 127.4, 127.1, 126.5, 126.1, 125.9, 125.8, 125.2, 121.5, 119.5, 115.2, 43.2, 35.7; IR spectrum in film (v_{max} , cm⁻¹) 3317,1644, 1461, 1331; HRMS (ESI) m/z Calcd for [C₃₀H₂₅N₂] requires [M+H]⁺425.2018, found 425.2029.

N-Benzyl-*N*-phenethylpyridin-2-amine (4u). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 4u as a brown oil, (132.5 mg, 92%): 1 H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 3.5 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.30 – 7.21 (m, 4H), 7.18 (t, J = 7.0 Hz, 6H), 6.58 – 6.48 (m, 1H), 6.44 (d, J = 8.6 Hz, 1H), 4.62 (s, 2H), 3.73(t, J = 5.6 Hz, 2H), 2.90 (t, J = 7.8 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 158.1, 148.3, 139.8, 138.9, 137.3, 129.0, 128.7, 128.6,127.1, 127.0, 126.3, 112.0, 105.9, 52.0, 50.6, 33.9; IR spectrum in film (ν_{max} , cm $^{-1}$) 3346, 1686, 1461, 1341; HRMS (ESI) m/z Calcd for [C₂₀H₂₁N₂] requires [M+H]⁺ 289.1705, found 289.1718.

N-Phenethylpyrimidin-2-amine (6a). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 6a as a brown oil, (78.6 mg, 79%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.28(d, J = 4.2 Hz, 2H), 7.30–7.17 (m, 6H), 6.55 (t, J = 4.7 Hz, 1H), 3.51 (q, J = 6.3 Hz, 2H), 2.85(t, J = 7.6 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 162.7, 158.4, 140.2, 129.1, 128.7, 126.4, 110.4, 42.8, 35.5; IR spectrum in film (ν_{max} , cm $^{-1}$) 3338, 1695, 1460, 1340; HRMS (ESI) m/z Calcd for [C₁₂H₁₄N₃] requires [M+H]⁺ 200.1188, found 200.1192.

Me N

N-(**4-Methylphenethyl)pyrimidin-2-amine** (**6b**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **6b** as a brown oil, (78.8 mg, 74%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.28 (d, J = 3.4 Hz, 2H), 7.21 (t, J = 5.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.55 (t, J = 4.7 Hz, 1H), 3.49 (dd, J_{I} = 14.8, J_{2} = 6.1 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.26 (s, 3H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 162.7, 158.4, 137.1, 135.4, 129.4, 129.0, 110.4, 43.0, 35.1, 21.1; IR spectrum in film (ν_{max} , cm⁻¹) 3350, 1690, 1464, 1449, 1342; HRMS (ESI) m/z Calcd for [C₁₃H₁₆N₃] requires [M+H]⁺214.1344, found 214.1348.

N N

W-(2-(Naphthalen-1-yl)ethyl)pyrimidin-2-amine (6c). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 6c as a brown oil, (105.8 mg, 85%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.28 (s, 2H), 8.18 (d, J = 8.2 Hz,

1H), 7.86 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.55–7.46 (m, 2H), 7.42–7.35 (m, 2H), 6.53 (t, J = 4.8 Hz, 1H), 5.47 (s, 1H), 3.81 (q, J = 6.8 Hz, 2H), 3.39 (t, J = 7.1 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 162.1, 158.1, 135.3, 134.0, 132.1, 129.0, 127.3, 127.0, 126.1, 125.7, 125.6, 123.9, 110.6, 42.1, 33.0; IR spectrum in film (ν_{max} , cm⁻¹) 3350, 1690, 1464, 1449, 1342; HRMS (ESI) m/z Calcd for [C₁₆H₁₆N₃] requires [M+H]⁺ 250.1344, found 250.1350.

N-Phenethylpyrazin-2-amine (7a). The crude product was product was purified by column chromatography (hexane/EtOAc = 85/15) to afford 7a as a brown oil, (74.6 mg, 75%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.96 (s, 2H), 7.66 (d, J = 2.2 Hz, 1H), 7.32–7.16 (m, 6H), 3.52 (q, J = 6.7 Hz, 2H), 2.86(t, J = 7.4 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, (CD₃)₂SO) δ 155.5, 142.0, 140.2, 133.8, 131.1, 129.1, 128.8, 126.5, 42.3, 35.3; IR spectrum in film (ν_{max} , cm⁻¹) 3347, 1687, 1462, 1343; HRMS (ESI) m/z Calcd for [C₁₂H₁₄N₃] requires [M+H]⁺ 200.1188, found 200.1190.

Ne Me Me

N-(4-(*tert*-Butyl)phenethyl)pyrazin-2-amine (7b). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 7b as a brown oil, (88.0 mg, 69%): ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.78 (s, 1H), 7.72 (d, J = 2.6 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 4.57 (s, 1H), 3.55 (q, J = 6.5 Hz, 2H), 2.84 (t, J = 6.9 Hz, 2H), 1.24 (s, 9H); ¹³C{¹H}NMR (100 MHz, (CD₃)₂SO) δ 154.6, 149.6, 142.1, 135.8, 132.9, 132.2, 128.6, 125.7, 42.6, 35.0, 34.5, 31.4;IR spectrum in film (ν max, cm⁻¹) 3350, 1695, 1461, 1452, 1341; HRMS (ESI) m/z Calcd for [C₁₆H₂₂N₃] requires [M+H]⁺ 256.1814, found 256.1819.

N-(**4-Vinylbenzyl)pyridin-2-amine** (**8a**). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **8a** as a brown oil, (71.4 mg, 68%): 1 H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.34 (dd, J_{I} = 25.0, J_{2} = 7.7 Hz, 5H), 6.73–6.55 (m, 2H), 6.34 (d, J = 8.4 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.22 (d, J = 10.9 Hz, 1H), 5.10 (s, 1H), 4.47 (d, J = 5.5 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 158.7, 148.3, 139.0, 137.5, 136.6, 127.6, 126.5, 113.8, 113.2, 106.9, 46.1; IR spectrum in film (v_{max} , cm⁻¹)

3334, 1644, 1458, 1280; HRMS (ESI) m/z Calcd for [C₁₄H₁₅N₂] requires [M+H]⁺ 211.1235, found 211.1220.

$$\begin{array}{c|c} & H & \\ & & \\ & & \end{array}$$

N-(4-Vinylbenzyl)quinolin-2-amine (8b). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 8b as a brown oil, (101.4 mg, 78%): 1 H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.35 – 7.23 (m, 4H), 7.14 (dd, J_{I} = 13.3, J_{2} = 5.7 Hz, 1H), 6.62 (dd, J_{I} = 17.6, J_{2} = 10.9 Hz, 1H), 6.53 (d, J = 8.9 Hz, 1H), 5.65 (d, J = 17.6 Hz, 1H), 5.15 (d, J = 10.9 Hz, 1H), 5.07 (s, 1H), 4.62 (d, J = 5.5 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 156.7, 147.9, 139.0, 137.5, 136.7, 136.5, 129.6, 127.9, 127.5, 126.5, 123.6, 122.2, 113.8, 111.3, 45.6; IR spectrum in film (ν_{max} , cm $^{-1}$) 3342, 1868, 1664, 1464, 1275; HRMS (ESI) m/z Calcd for [C₁₈H₁₇N₂] requires [M+H]⁺261.1392, found 261.1404.

N N

N-(4-Vinylbenzyl)pyrazin-2-amine (8c). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 8c as a brown oil, (86.5 mg, 82%): 1 H NMR (400 MHz, CDCl₃) δ 7.94–7.93 (m, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.76 (d, J = 2.7 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 6.64 (dd, J_{I} =17.6, J_{2} =11.0 Hz, 1H), 5.67 (d, J = 17.6 Hz, 1H), 5.18 (d, J = 10.9 Hz, 1H), 4.90 (s, 1H), 4.48 (d, J = 5.8 Hz, 2H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 163.0, 158.6, 138.5, 137.2, 137.1, 128.4, 127.0, 114.2, 110.7, 49.4; IR spectrum in film (v_{max} , cm $^{-1}$) 3345, 1690, 1642, 1465, 1339; HRMS (ESI) m/z Calcd for [C₁₃H₁₄N₃] requires [M+H]⁺212.1188, found 212.1201.

N,N-bis(4-Vinylbenzyl)pyrazin-2-amine (8d). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 8d as a brown oil, (73.6 mg, 45%): 1 H NMR (400 MHz, CDCl₃) δ 8.09 (dd, J_{I} = 2.5, J_{2} = 1.6 Hz, 1H), 7.97 (d, J = 1.2 Hz, 1H),7.84 (d, J = 2.6 Hz, 1H), 7.36 (d, J = 8.2 Hz, 4H), 7.18 (d, J = 8.1 Hz, 4H), 6.70 (dd, J_{I} = 17.6, J_{2} = 11.0 Hz, 2H), 5.73 (dd, J_{I} = 17.6, J_{2} =0.8 Hz, 2H), 5.23 (dd, J_{I} = 10.9, J_{2} =0.6 Hz, 2H), 4.78 (s, 4H); 13 C{ 1 H}NMR (100 MHz, CDCl₃) δ 154.4, 141.9, 137.0, 136.9, 136.4, 132.5, 130.1, 127.3, 126.6, 113.9, 50.6; IR spectrum in film (v_{max} , cm $^{-1}$) 3332, 1694, 1638, 1462, 1340; HRMS (ESI) m/z Calcd for [C_{22} H $_{22}$ N $_{3}$] requires [M+H] $^{+}$ 328.1814, found 328.1828.

N-(3-Vinylphenethyl)pyridin-2-amine) (12). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 12 as a yellow oil,(91.9 mg, 82%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.98 (d, J = 4.0 Hz, 1H), 7.44–7.11 (m, 5H), 6.77–6.65 (m, 1H), 6.52 (t, J = 5.6 Hz, 1H), 6.45 (dd, J_{I} = 7.0, J_{2} = 4.9 Hz, 2H), 5.79 (dd, J_{I} = 17.0, J_{2} = 14.3 Hz, 1H), 5.22 (dd, J_{I} = 15.2, J_{2} = 11.5 Hz, 1H), 3.54–3.40 (m, 2H), 2.83 (dd, J_{I} = 13.9, J_{2} = 6.6 Hz, 2H); 13 C{ 1 H} NMR (100MHz, (CD₃)₂SO) δ 159.2, 148.0, 140.8, 140.4, 137.5, 137.2, 137.0, 135.4, 129.4, 128.9, 128.8, 126.9, 126.5, 124.3, 114.5, 113.8, 111.9, 108.6, 42.8, 35.6, 35.9; IR spectrum in film (ν_{max} , cm $^{-1}$) 3349, 1690, 1646, 1460, 1340; HRMS (ESI) m/z Calcd for [C₁₅H₁₇N₂] requires [M+H] $^{+}$ 225.1392, found 225.1405.

N-Phenethyl-*N*-(3-vinylphenethyl)pyridin-2-amine (12'). In an oven-dried 15 mL reaction vial, a solution of *N*-(3-Vinylphenethyl)pyridin-2-amine) 12 (0.5 mmol), alkene 2a (0.8 mmol), and KOH (1.0 equiv) in 2 mL of DMSO was heated in an oil bath at 80 °C for 3 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL X 3) and water (10 mL X 3). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na₂SO₄. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on neutral/basic alumina. The structure and purity of products were confirmed by comparison of their physical and spectral data (¹H NMR, ¹³C NMR, and HRMS).

N-Phenethyl-*N*-(3-vinylphenethyl)pyridin-2-amine (12'). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 12' as a brown oil, (68.92 mg, 42%): ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 4.1 Hz, 1H), 7.59–7.56 (m, 1H), 7.48–7.18 (m, 9H), 6.88–6.81 (m, 1H), 6.71–6.65 (m, 2H), 5.87 (dd, J_I = 17.6, J_2 = 13.1 Hz, 1H), 5.36 (dd, J_I = 14.8, J_2 = 10.9 Hz, 1H), 3.76 (t, J = 7.3 Hz, 4H), 3.00–2.97 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ 157.7, 148.7, 140.3, 139.8, 138.0, 137.4, 137.1, 136.9, 135.8, 129.3, 128.9, 128.7, 127.1, 126.6, 124.4, 114.1, 113.5, 111.7, 105.8, 51.5, 34.2, 34.0; IR spectrum in film (ν_{max} , cm⁻¹) 1687, 1660, 1644, 1464, 1342; HRMS (ESI) m/z Calcd for [C₂₃H₂₅N₂] requires [M+H]⁺ 329.2018, found 329.2026.

 H_2N N N

Phenethylpyridin-2,6-diamine (14). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 14 as a yellow oil, (84.1 mg, 79%):
¹H NMR (400 MHz, (CD₃)₂SO) δ 7.33–7.17 (m, 5H), 7.03 (t, J = 7.8 Hz, 1H), 5.90 (t, J = 5.6 Hz, 1H), 5.64–5.61 (m, 2H), 5.37 (s, 2H), 3.33 (q, J = 6.4 Hz, 2H), 2.79 (t, J = 8 Hz, 2H);
¹³C{¹H} NMR (100MHz, (CD₃)₂SO) δ 159.2, 158.6, 140.7, 138.5, 129.2, 128.8, 126.4, 95.3, 95.1, 43.4, 35.9; IR spectrum in film (ν_{max} , cm⁻¹) 3500, 3487, 3338, 1690, 1465, 1341; HRMS (ESI) m/z Calcd for [C₁₃H₁₆N₃] requires [M+H]⁺214.1344, found 214.1354.

 N^2 , N^2 -Diphenethylpyridine-2,6-diamine (14'). In an oven-dried 15 mL reaction vial, a solution of N^2 -Phenethylpyridin-2,6-diamine 14 (0.5 mmol), alkene 2a (0.8 mmol), and KOH (1.0 equiv) in 2 mL of DMSO was heated in an oil bath at 80 °C for 3 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL X 3) and water (10 mL X 3). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na₂SO₄. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on neutral/basic alumina. The structure and purity of products were confirmed by comparison of their physical and spectral data (1 H NMR, 13 C NMR, and HRMS).

 H_2N N N

 N^2 , N^2 -Diphenethylpyridine-2,6-diamine (14'). The crude product was product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 14' as a brown oil, (76.12 mg, 48%): ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.16 (m, 5H), 7.12 (d, J = 6.7 Hz, 6H), 5.79 (dd, J_1 = 56.7, J_2 = 7.9 Hz, 2H), 4.07 (s, 2H), 3.51 – 3.44 (m, 4H), 2.80 – 2.73 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ 157.5, 157.0, 140.1, 139.0, 128.9, 128.5, 126.1, 95.4, 95.1, 51.2, 34.2; IR spectrum in film (ν_{max} , cm⁻¹) 3450, 1686, 1650, 1645, 1465, 1341; HRMS (ESI) m/z Calcd for [C₂₁H₂₄N₃] requires [M+H]⁺318.1970, found 318.1971.

N,*N*-(**Diphenethylpyridin-2-amine**) (**15a-c**). In an oven-dried 15 mL reaction vial, a solution of *N*-Phenethylpyridin-2-amine **3a** (0.5 mmol), alkene **2** (0.8 mmol) and KOH (1.0 equiv) in 2 mL of DMSO was heated in an oil bath at 80 °C for 6 h. Progression of the reaction was

monitored by TLC analysis; after complete consumption of starting material, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL X 3) and water (10 mL X 3). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na₂SO₄. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on neutral/basic alumina. The structure and purity of products were confirmed by comparison of their physical and spectral data (¹H NMR, ¹³C NMR, and HRMS).

N,N-(**Diphenethylpyridin-2-amine**) (**15a**). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **15a** as a yellow oil, (113.3 mg, 75%): 1H NMR (400 MHz, CDCl₃) δ 8.22 (dd, J_1 = 4.9, J_2 = 1.4 Hz, 1H), 7.47–7.43 (m, 1H), 7.31–7.26 (m, 4H), 7.22–7.18 (m, 6H), 6.56–6.51 (m, 2H), 3.59 (t, J = 7.6 Hz, 4H), 2.84 (t, J = 7.6 Hz, 4H); ¹³C{1H} NMR (100MHz, CDCl₃) δ 157.5, 148.4, 139.9, 137.2, 128.9, 128.5, 126.3, 111.4, 105.6, 51.3, 34.0; IR spectrum in film (ν max, cm⁻¹) 3350, 1692, 1465, 1340; HRMS (ESI) m/z Calcd for [C₂₁H₂₃N₂] requires [M+H]⁺ 303.1861, found 303.1875.

N-(4-Chlorophenethyl)-N-phenethylaniline (15b). The crude product was purified by column chromatography (hexane/EtOAc = 98/2) to afford 15b as a yellow oil,

was purified by column chromatography (nexane/EtOAc = 98/2) to afford **15b** as a yellow oil, (139.4 mg, 83%): 1 H NMR (400 MHz, CDCl₃) δ 8.13 (ddd, J_{I} = 4.9, J_{2} = 1.9, J_{3} = 0.8 Hz, 1H), 7.39–7.35 (m, 1H), 7.23–7.10 (m, 6H), 7.04–7.01 (m, 2H), 6.49–6.46 (m, 1H), 6.42 (d, J = 8.7 Hz, 1H), 3.46–3.51 (m, 4H), 2.71–2.78 (m, 4H); 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 157.4, 148.4, 139.7, 138.4, 137.2, 132.0, 130.3, 129.0, 128.6, 126.3, 111.6, 105.7, 51.5, 51.2, 34.0, 33.5; IR spectrum in film (v_{max} , cm ${}^{-1}$) 3354, 1682, 1469, 1345; HRMS (ESI) m/z Calcd for [C₂₁H₂₂ClN₂] requires [M+H] ${}^{+}$ 337.1472, found 337.1475.

N-(2-([1,1'-Bipheny]-4-yl)ethyl)-N-phenethylaniline (15c). The crude product was purified by column chromatography (hexane/EtOAc = 85/5) to afford 15c as a yellow oil, (155.1 mg, 82%): ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J= 3.7 Hz, 1H), 7.50

(d, J = 7.3 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H), 7.40–7.33 (m, 3H), 7.27–7.12 (m, 8H), 6.50–6.45 (m, 2H), 3.56 (t, J = 7.3 Hz, 4H), 2.80 (q, J = 6.3 Hz, 4H); 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 157.4, 148.4, 141.0, 140.0, 139.2, 139.0, 137.1, 129.3, 128.9, 128.7, 128.5, 127.2, 127.1, 127.0, 126.2, 111.4, 105.6, 51.3, 51.2, 34.0, 33.6; IR spectrum in film (ν_{max} , cm⁻¹) 3340, 1695, 1475, 1330; HRMS (ESI) m/z Calcd for [C₂₇H₂₇N₂] requires [M+H]⁺ 379.2174, found 379.2175.

N-(2-Phenethyl-2-*d*)pyridin-2-amine) (3a'). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3a' as a yellow oil, (77.6 mg, 78%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 7.98 (d, J = 2.7 Hz, 1H), 7.36–7.18 (m, 6H), 6.53 (s, 1H), 6.46 (d, J = 7.3 Hz, 2H), 3.44 (t, J = 6.0 Hz, 2H), 2.81 (t, J = 7.1 Hz, 1H); 13 C{ 1 H} NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.1, 140.5, 137.0, 129.2, 128.8, 126.4, 111.9, 108.6, 42.9, 35.7–35.2 (m); HRMS (ESI) m/z Calcd for [C₁₃H₁₃DN₂] requires [M]⁺ 199.1220, found 199.1240.

D D D N

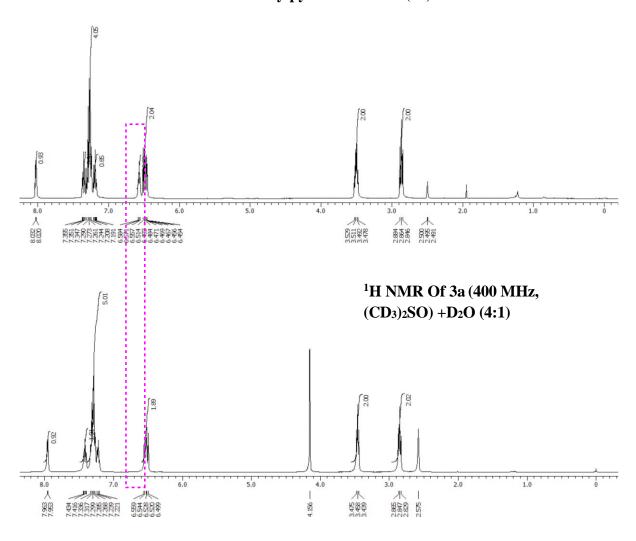
N-(2-(Phenyl-ds)ethyl-1,1,2-ds)pyridin-2-amine) (3a"). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford 3a" as a yellow oil, (76.2 mg, 74%): 1 H NMR (400 MHz, (CD₃)₂SO) δ 8.03 (d, J = 3.8 Hz, 1H), 7.37–7.33 (m, 1H), 6.52–6.46 (m, 3H), 2.86–2.84 (m, 1H); 13 C{ 1 H} NMR (100 MHz, (CD₃)₂SO) δ 159.3, 148.1, 140.3, 137.0, 129.3–128.0 (m), 126.1–125.6 (m), 112.0, 108.5, 42.9–42.0 (m), 35.6–35.0 (m); HRMS (ESI) m/z Calcd for [C₁₃H₆D₈N₂] requires [M]⁺206.1659, found 206.1660.

COPIES OF ¹H NMR, ¹³C NMR, HRMS

¹H NMR

(400 MHz, (CD₃)₂SO)

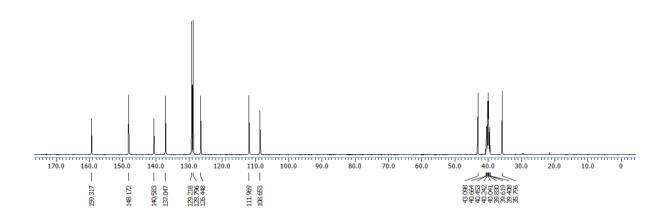
N-Phenethylpyridin-2-amine (3a)



¹³C NMR

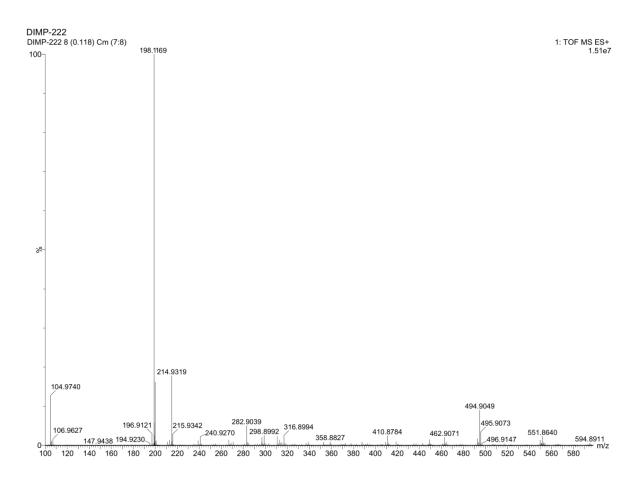
(100 MHz, (CD₃)₂SO)

N-Phenethylpyridin-2-amine (3a)



HRMS

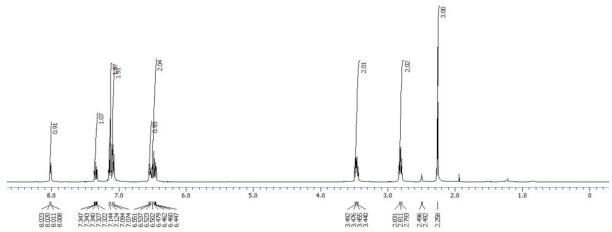
N-Phenethylpyridin-2-amine (3a)



¹H NMR

(400 MHz, (CD₃)₂SO)

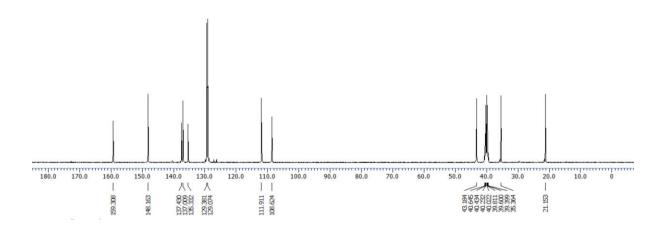
N-(4-Methylphenethyl)pyridin-2-amine (3b)



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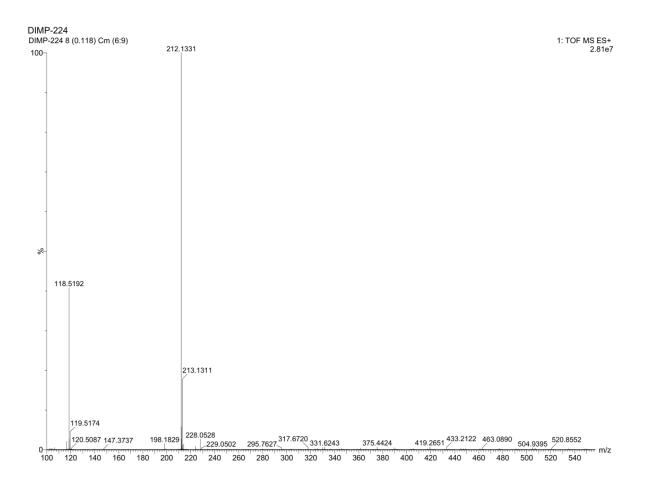
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N-(4-Methylphenethyl)pyridin-2-amine (3b)



HRMS

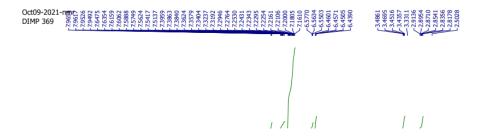
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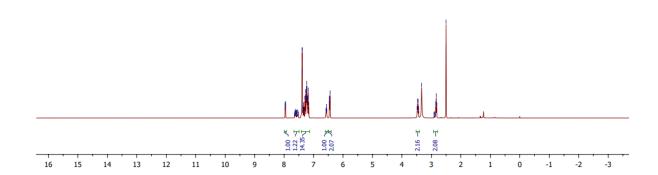


¹H NMR

(400 MHz, (CD₃)₂SO)

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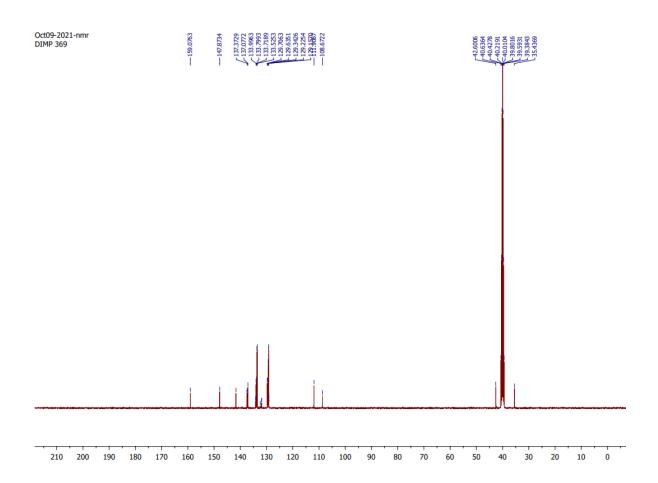




¹³C NMR

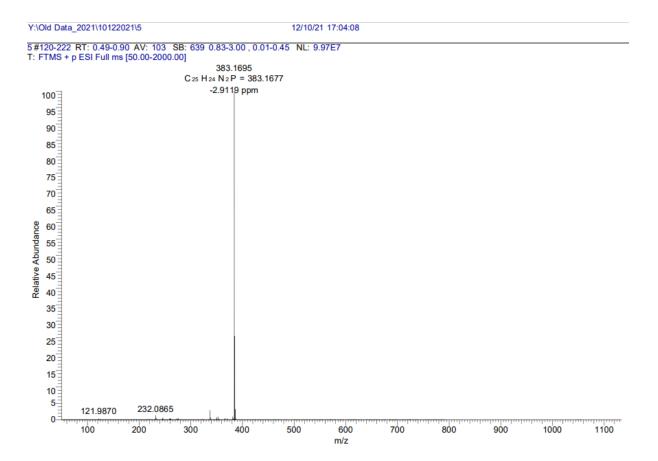
(100 MHz, (CD₃)₂SO)

${\it N-} ({\it 4-diphenylphosphanyl}) phenethyl) pyridin-{\it 2-amine}~({\it 3c})$



HRMS

N-(4-diphenylphosphanyl)phenethyl)pyridin-2-amine (3c)

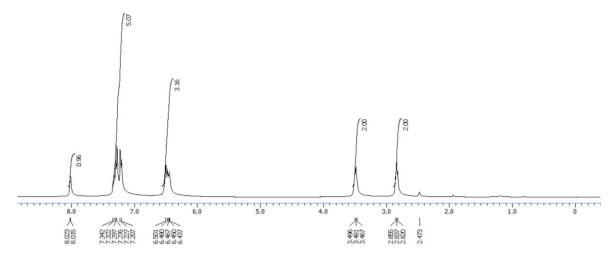


¹H NMR

(400 MHz, (CD₃)₂SO)

$$\bigvee_{N}^{H} \bigvee_{C_{I}}$$

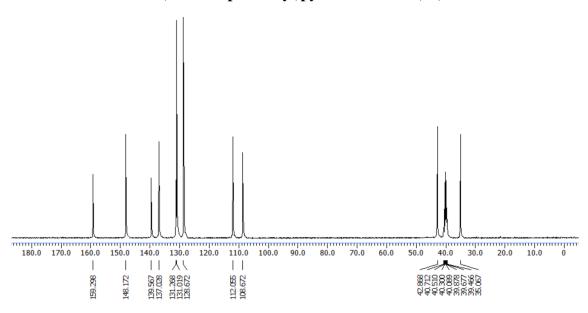
N-(4-Chlorophenethyl)pyridin-2-amine (3d)



¹³C NMR

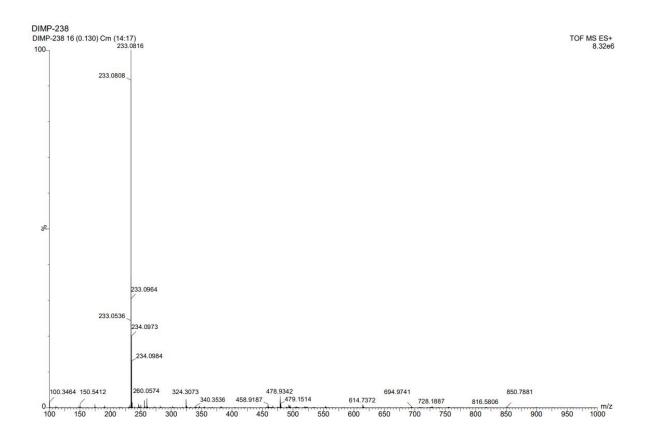
(100 MHz, (CD₃)₂SO)

N-(4-Chlorophenethyl)pyridin-2-amine (3d)



HRMS

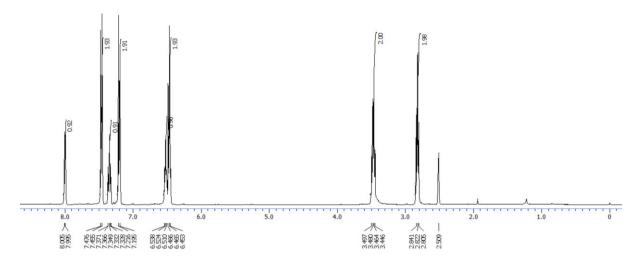
N-(4-Chlorophenethyl)pyridin-2-amine (3d)



¹H NMR

(400 MHz, (CD₃)₂SO)

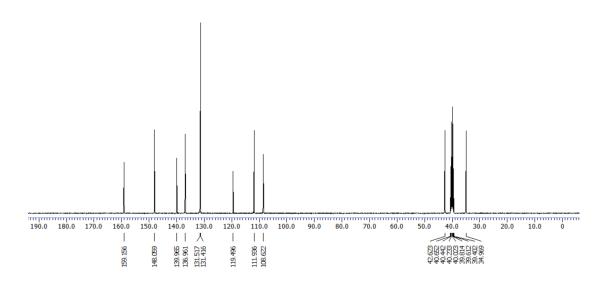
N-(4-Bromophenethyl)pyridin-2-amine (3e)



¹³C NMR

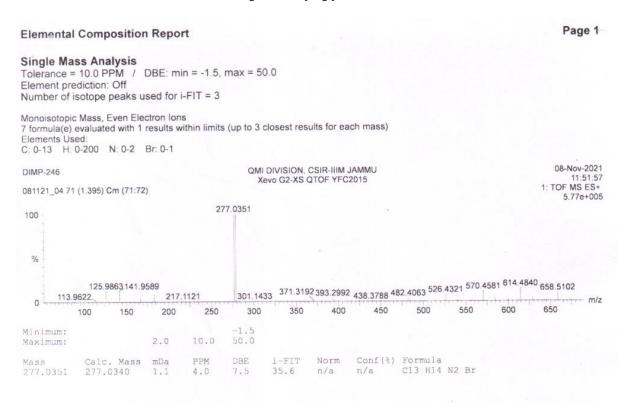
(100 MHz, (CD₃)₂SO)

N-(4-Bromophenethyl)pyridin-2-amine (3e)



HRMS

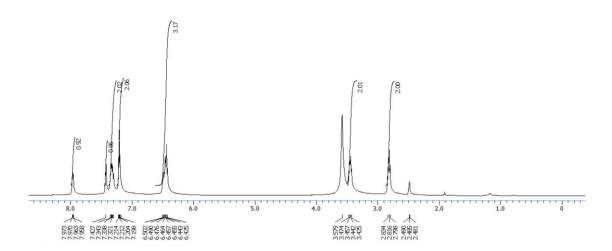
N-(4-Bromophenethyl)pyridin-2-amine (3e)



¹H NMR

(400 MHz, (CD₃)₂SO)

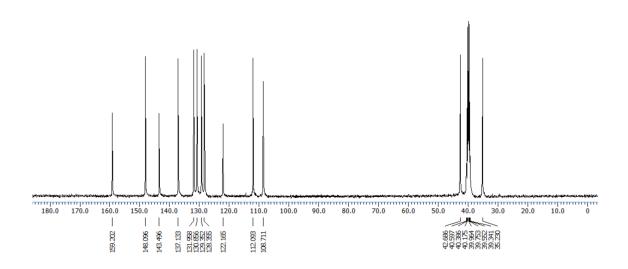
N-(3-Bromophenethyl)pyridin-2-amine (3f)



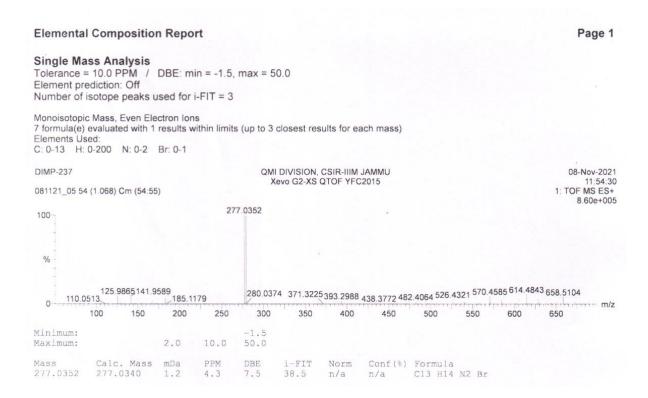
¹³C NMR

(100 MHz, (CD₃)₂SO)

N-(3-Bromophenethyl)pyridin-2-amine (3f)

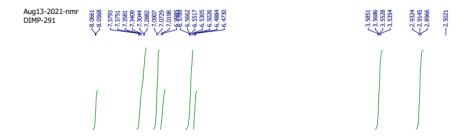


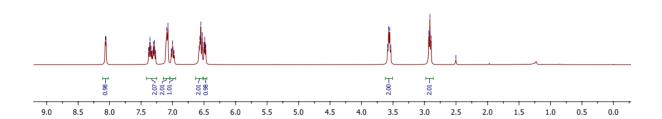
N-(3-Bromophenethyl)pyridin-2-amine (3f)



¹H NMR

N-(3-Fluorophenethyl)pyridin-2-amine (3g)

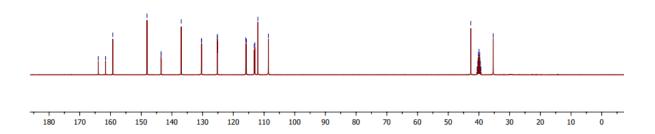




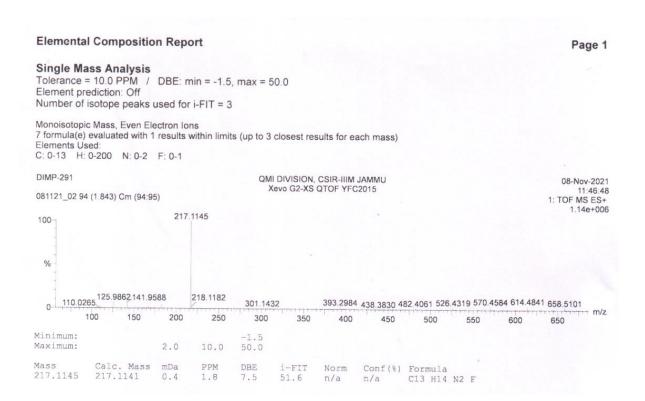
¹³C NMR

N-(3-Fluorophenethyl)pyridin-2-amine (3g)



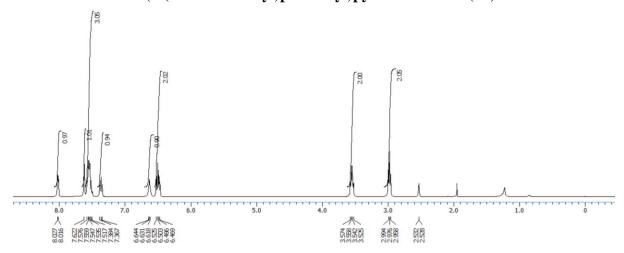


N-(3-Fluorophenethyl)pyridin-2-amine (3g)



¹H NMR

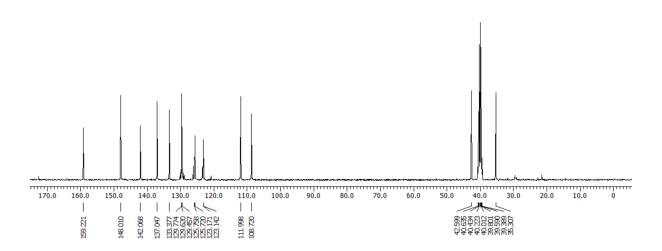
N-(3-(trifluoromethyl)phenethyl)pyridin-2-amine (3h)



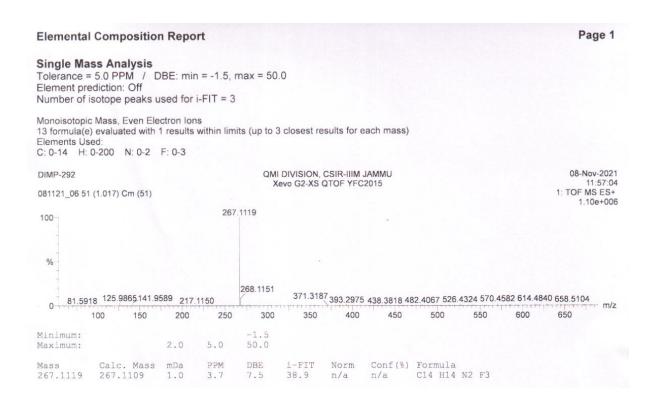
¹³C NMR

(100 MHz, (CD₃)₂SO)

N-(3-(trifluoromethyl)phenethyl)pyridin-2-amine (3h)

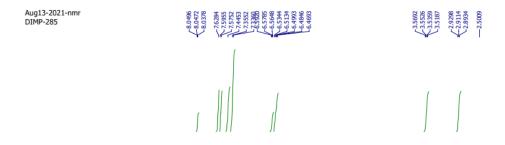


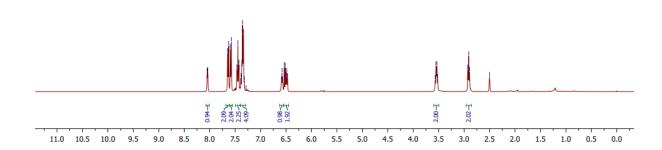
N-(3-(trifluoromethyl)phenethyl)pyridin-2-amine (3h)



¹H NMR

N-(2-([1,1'-biphenyl]-4-yl)ethyl)pyridin-2-amine (3i)

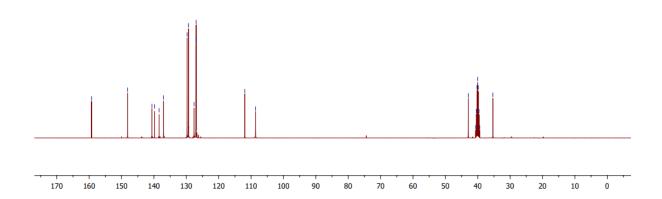




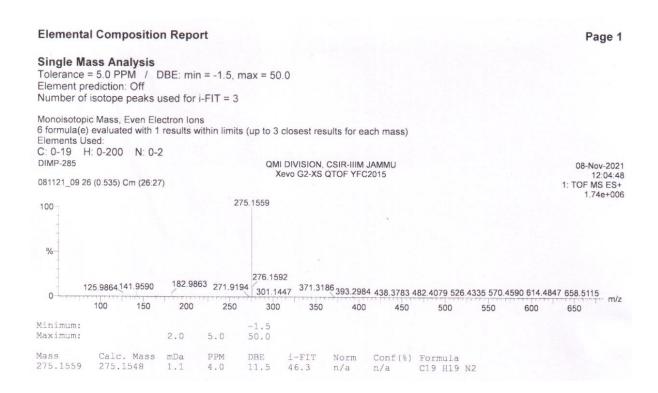
¹³C NMR

N-(2-([1,1'-biphenyl]-4-yl)ethyl)pyridin-2-amine (3i)



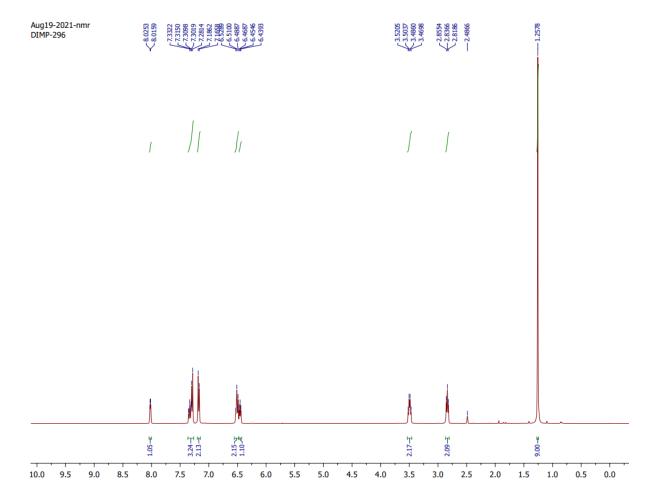


N-(2-([1,1'-biphenyl]-4-yl)ethyl)pyridin-2-amine (3i)



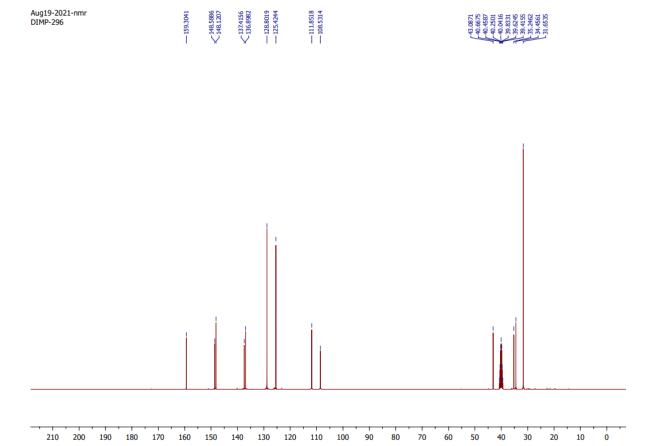
¹H NMR

N-(4-(tert-butyl)phenethyl)pyridin-2-amine (3j)

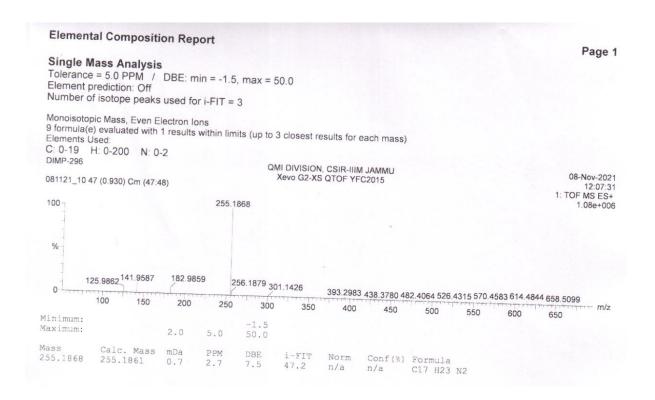


¹³C NMR

N-(4-(*tert*-butyl)phenethyl)pyridin-2-amine (3j)

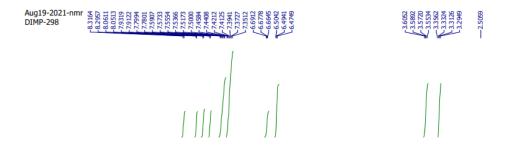


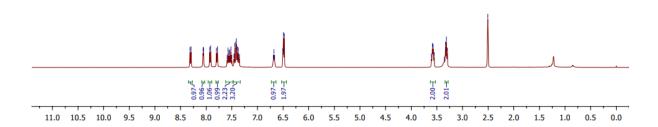
N-(4-(*tert*-butyl)phenethyl)pyridin-2-amine (3j)



¹H NMR

N-(2-(Naphthalen-1-yl)ethyl)pyridin-2-amine (3k)

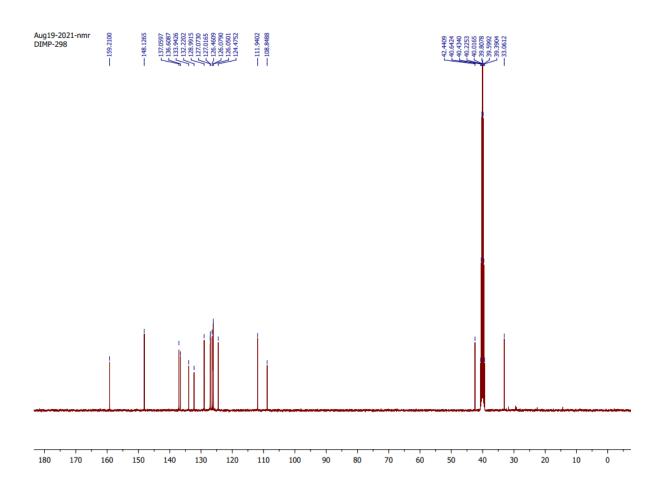




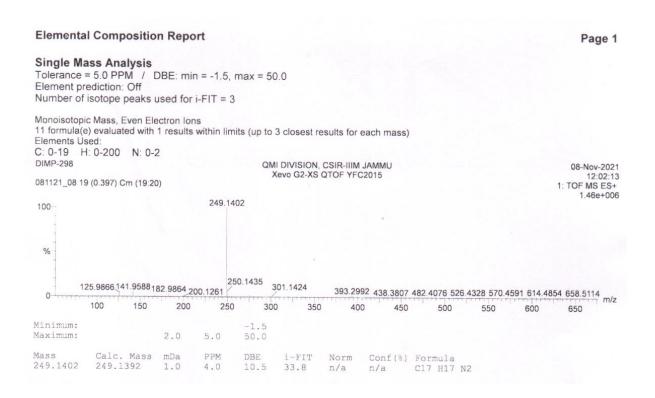
¹³C NMR

$$\bigcup_{N}^{H}$$

N-(2-(Naphthalen-1-yl)ethyl)pyridin-2-amine (3k)

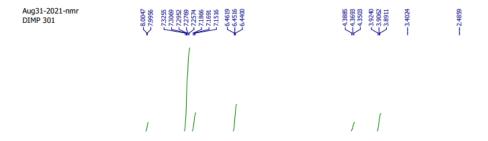


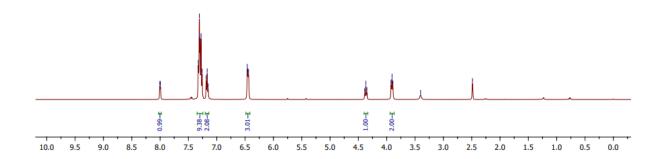
N-(2-(Naphthalen-1-yl)ethyl)pyridin-2-amine (3k)



¹H NMR

N-(2,2-diphenylethyl)pyridin-2-amine (3l)

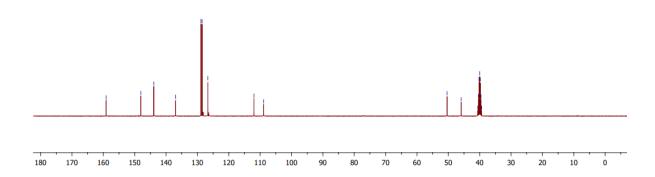




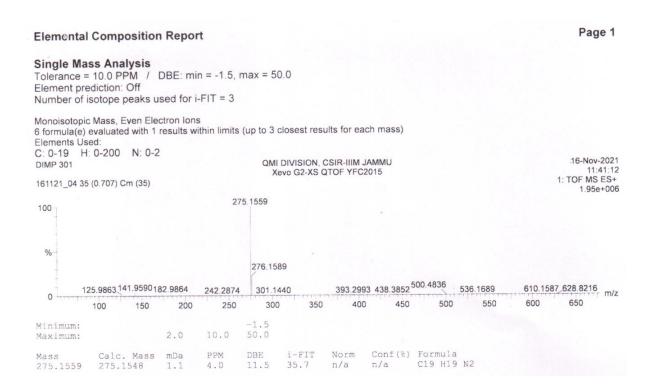
¹³C NMR

N-(2,2-diphenylethyl)pyridin-2-amine (3l)

Aug31-2021-nmr DIMP 301	159.1178	148.0408	143.9098	136.9371	128.8601 128.4923 126.6604	111.9701	50.3950 45.8937 40.4214 40.0041 59.7955 39.5870
	1			1	(ノノ	1.1	

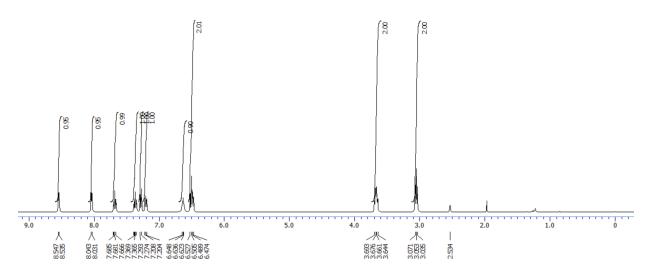


N-(2,2-diphenylethyl)pyridin-2-amine (3l)



¹H NMR

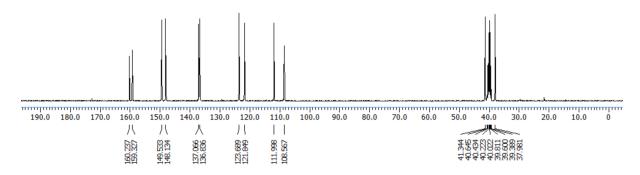
N-(2-(Pyridin-2-yl)ethyl)pyridin-2-amine (3m)



¹³C NMR

(100 MHz, (CD₃)₂SO)

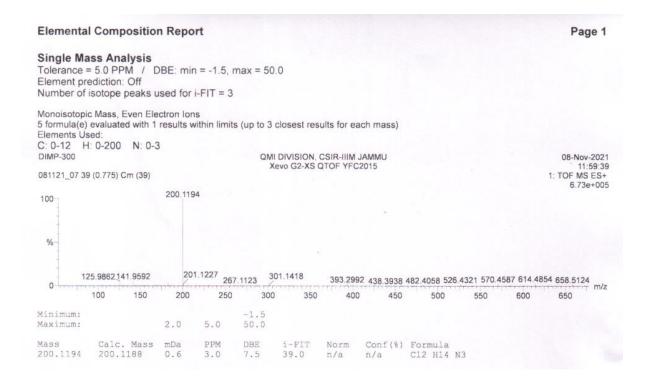
N-(2-(Pyridin-2-yl)ethyl)pyridin-2-amine (3m)



HRMS

$$\bigvee_{N}^{H}\bigvee_{N}$$

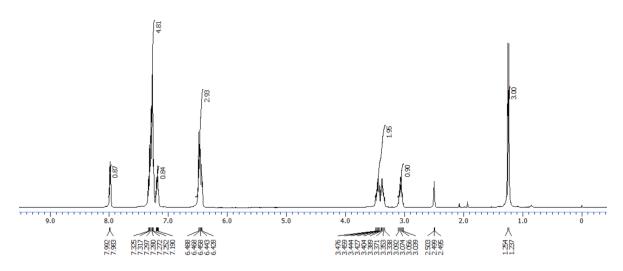
N-(2-(Pyridin-2-yl)ethyl)pyridin-2-amine (3m)



¹H NMR

(400 MHz, (CD₃)₂SO)

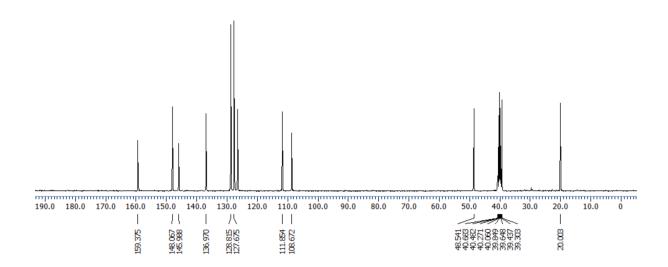
N-(2-Phenylpropyl)pyridin-2-amine (3n)



¹³C NMR

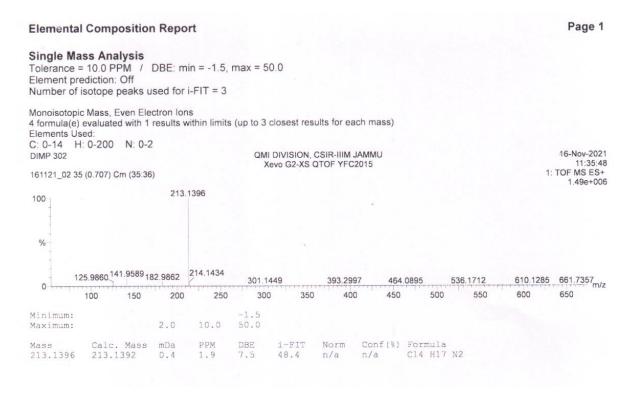
(100 MHz, (CD₃)₂SO)

N-(2-Phenylpropyl)pyridin-2-amine (3n)



HRMS

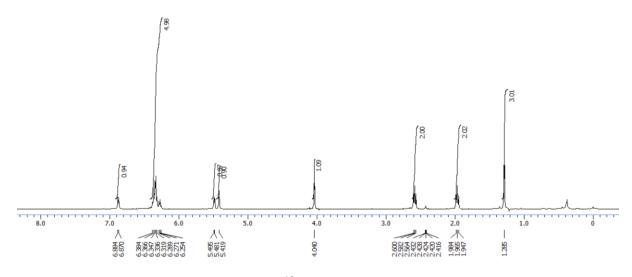
N-(2-Phenylpropyl)pyridin-2-amine (3n)



¹H NMR

(400 MHz, (CD₃)₂SO)

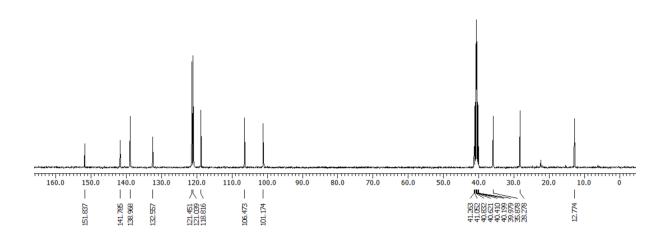
$\hbox{\bf 4-Methyl-} \textit{N-} phenethyl pyridin-\hbox{\bf 2-} amine~(4a)$



¹³C NMR

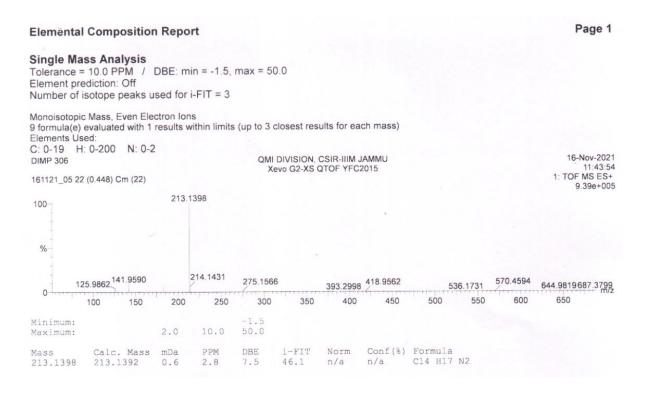
(100 MHz, (CD₃)₂SO)

4-Methyl-N-phenethylpyridin-2-amine (4a)



HRMS

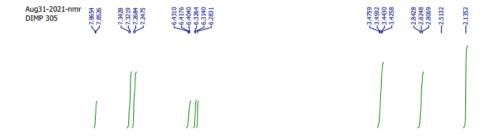
4-Methyl-N-phenethylpyridin-2-amine (4a)

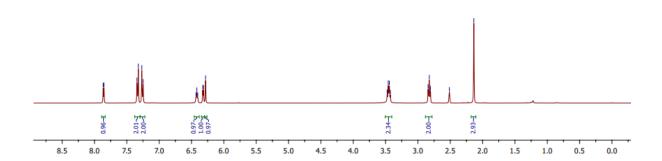


¹H NMR

(400 MHz, (CD₃)₂SO)

N-(4-Chlorophenethyl)-4-methylpyridin-2-amine (4b)



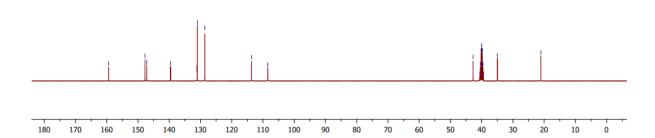


¹³C NMR

$$\stackrel{\mathsf{Me}}{\longleftarrow} \stackrel{\mathsf{H}}{\bigvee} \stackrel{\mathsf{Col}}{\bigvee} \stackrel{\mathsf{Co$$

N-(4-Chlorophenethyl)-4-methylpyridin-2-amine (4b)





N-(4-Chlorophenethyl)-4-methylpyridin-2-amine (4b)

Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Number of isotope peaks used for i-FIT = 3

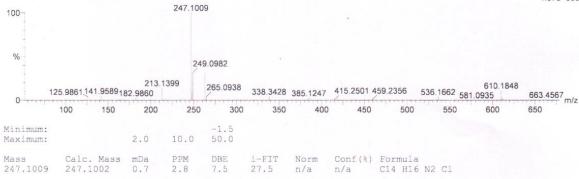
Monoisotopic Mass, Even Electron Ions 7 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass) Elements Used:

C: 0-14 H: 0-200 N: 0-2 CI: 0-1 **DIMP 305**

QMI DIVISION, CSIR-IIIM JAMMU Xevo G2-XS QTOF YFC2015

16-Nov-2021 11:38:29 1: TOF MS ES+ 1.07e+006

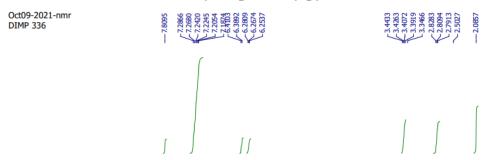
161121_03 7 (0.155) Cm (7)

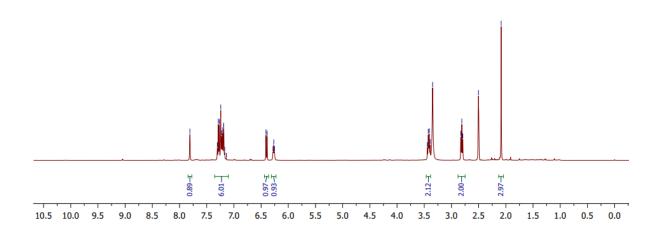


¹H NMR

(400 MHz, (CD₃)₂SO)

5-Methyl-N-phenethylpyridin-2-amine (4c)

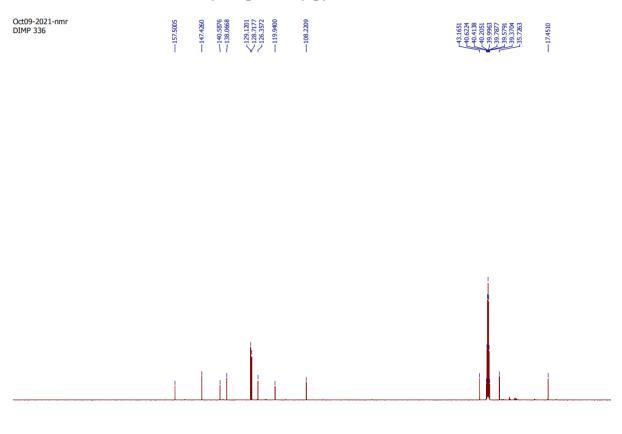




¹³C NMR

(100 MHz, (CD₃)₂SO)

5-Methyl-N-phenethylpyridin-2-amine (4c)



170 160

180

150

140 130

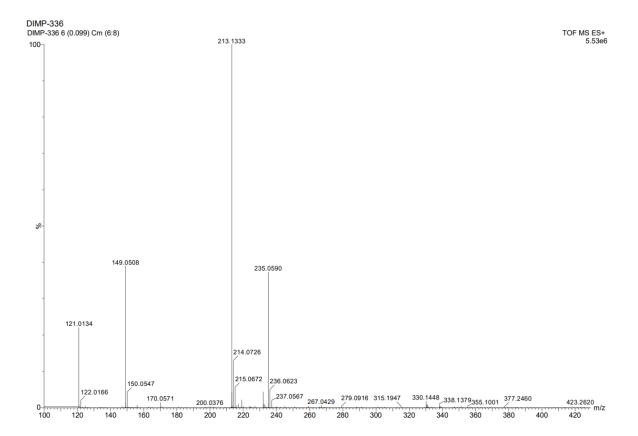
120

110 100

30 20

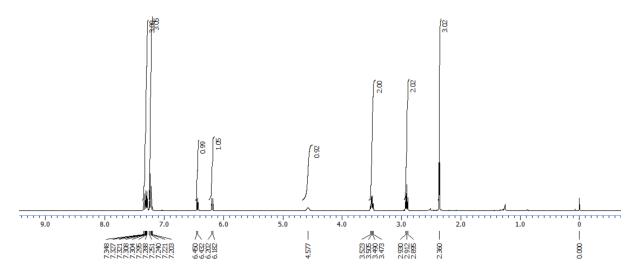
HRMS

 $5-Methyl-\textit{N}-phenethylpyridin-2-amine} \ (4c)$



¹H NMR (400 MHz, CDCl₃)

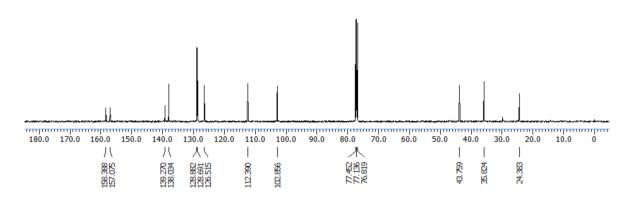
6-Methyl-N-phenethylpyridin-2-amine (4d)



¹³C NMR

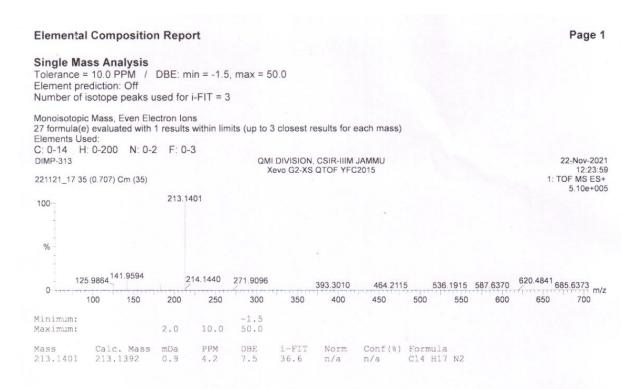
(100 MHz, CDCl₃)

6-Methyl-N-phenethylpyridin-2-amine (4d)



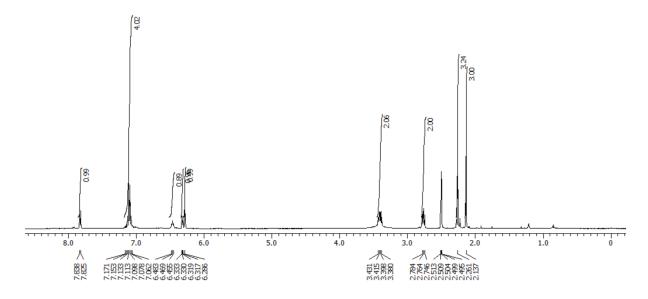
HRMS

6-Methyl-N-phenethylpyridin-2-amine (4d)



¹H NMR

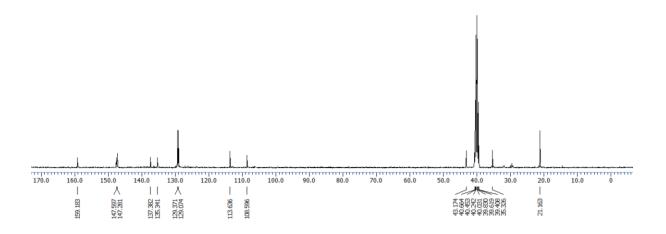
6-Methyl-N-(4-methylphenethyl)pyridin-2-amine (4e)



¹³C NMR

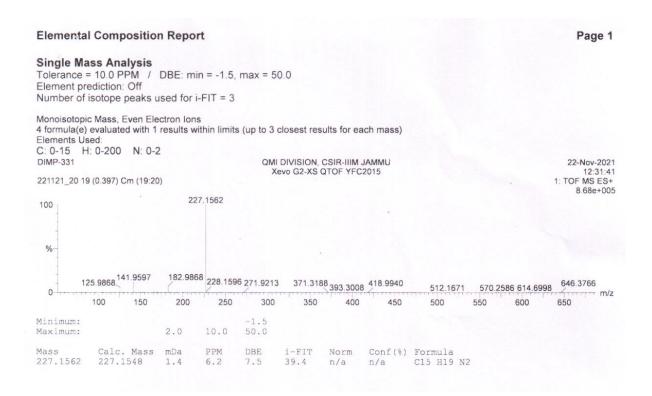
(100 MHz, (CD₃)₂SO)

6-Methyl-N-(4-methylphenethyl)pyridin-2-amine (4e)



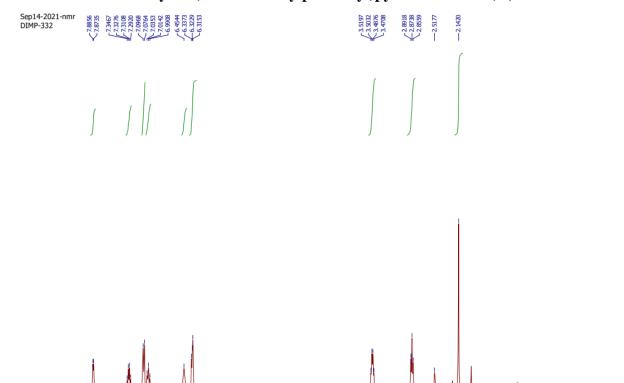
HRMS

6-Methyl-N-(4-methylphenethyl)pyridin-2-amine (4e)



¹H NMR

$6-Methyl-N-(3-fluoromethyl) pyridin-2-amine\ (4f) \\$



3.0

1.0

0.0

9.0

8.5

8.0

7.5

6.0

5.5

5.0

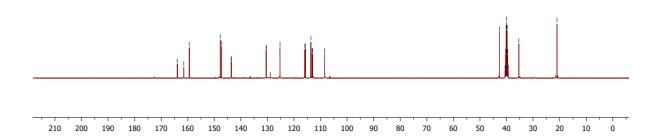
¹³C NMR

$\textbf{6-Methyl-} N \textbf{-} \textbf{(3-fluoromethylphenethyl)} \textbf{pyridin-2-amine} \ \textbf{(4f)}$

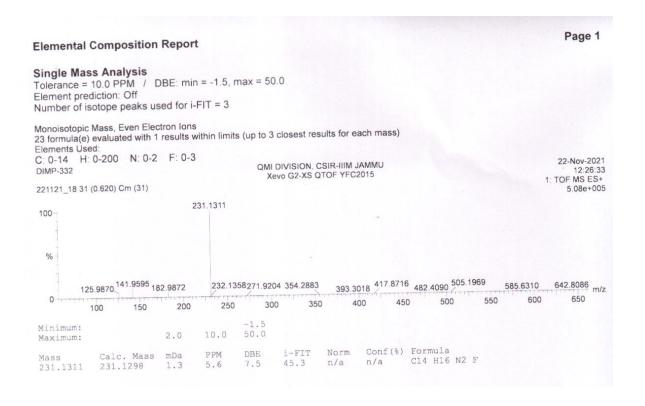
Sep14-2021-nmr DIMP-332





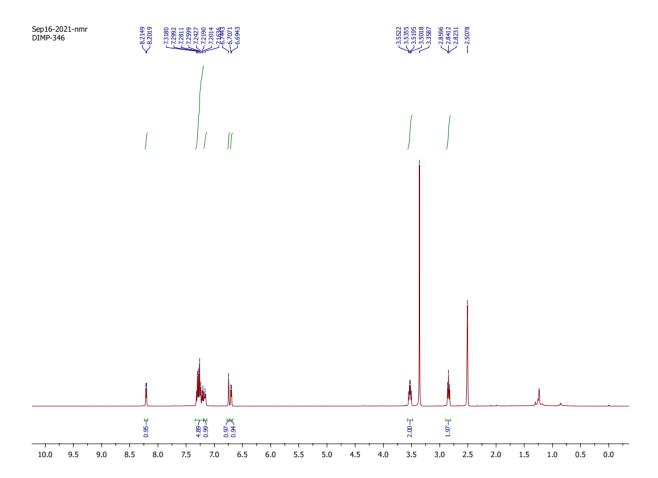


6-Methyl-N-(3-fluoromethylphenethyl)pyridin-2-amine (4f)



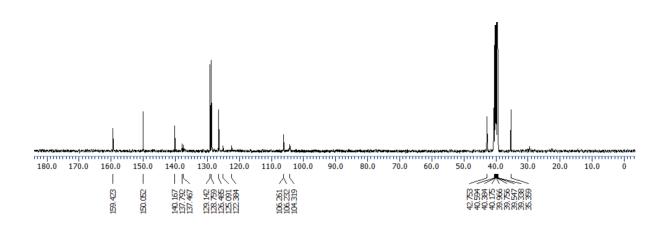
$$F_3C$$
 N
 N

N-Phenethyl-4-(trifluoromethyl)pyridine-2-amine (4g)

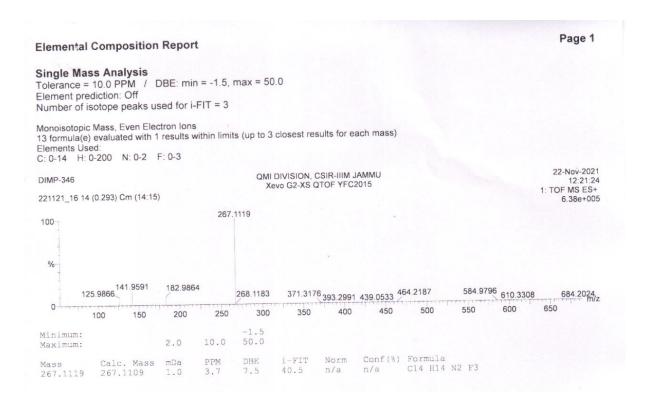


$$F_3C$$
 N
 N

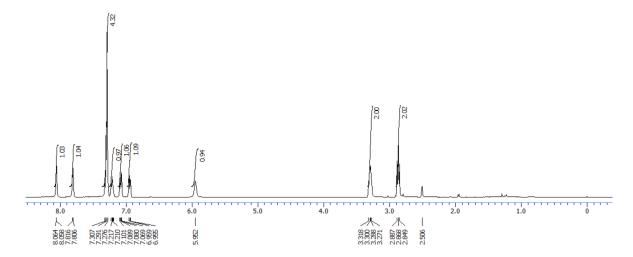
$N\hbox{-} Phenethyl-4-(trifluoromethyl) pyridin-2-amine\ (4g)$



N-Phenethyl-4-(trifluoromethyl)pyridine-2-amine (4g)



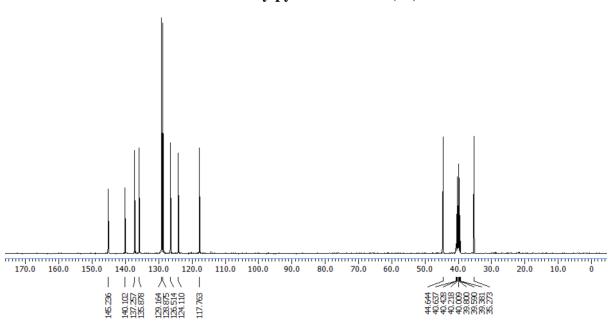
N-Phenethylpyridin-3-amine (4h)



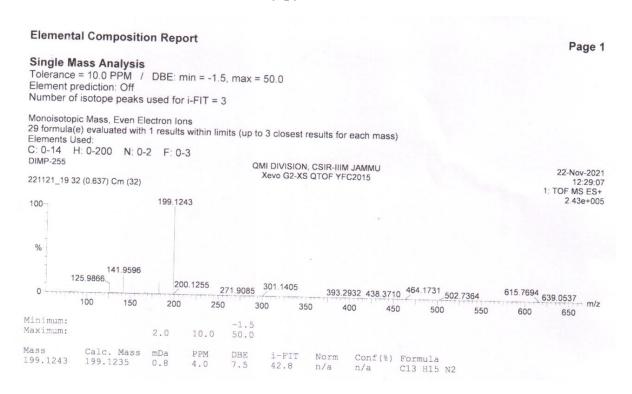
¹³C NMR

(100 MHz, (CD₃)₂SO)

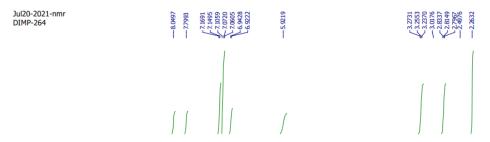
N-Phenethylpyridin-3-amine (4h)

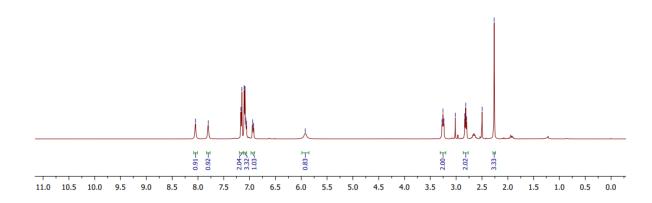


N-Phenethylpyridin-3-amine (4h)

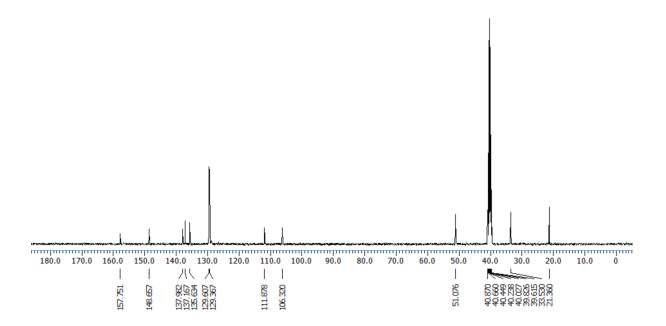


N-(4-Methylphenethyl)pyridin-3-amine (4i)

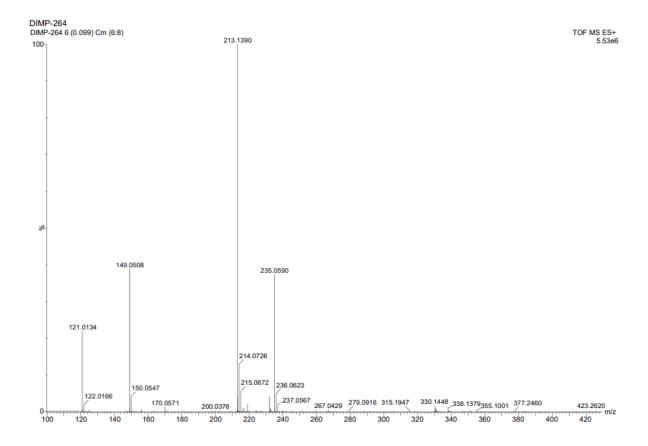




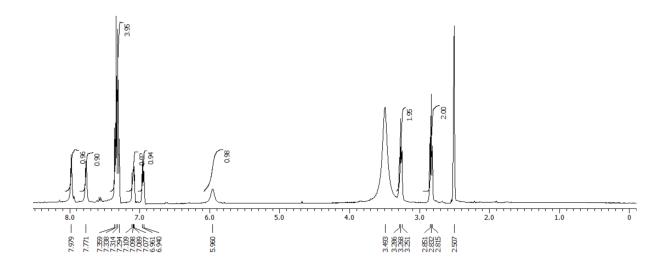
N-(4-Methylphenethyl)pyridin-3-amine (4i)



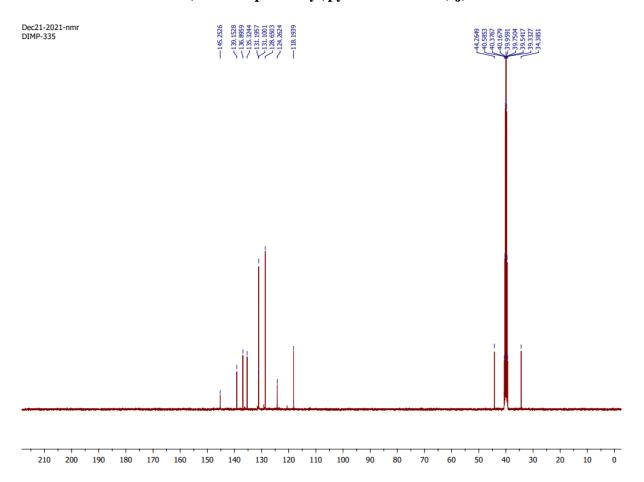
N-(4-Methylphenethyl)pyridin-3-amine (4i)



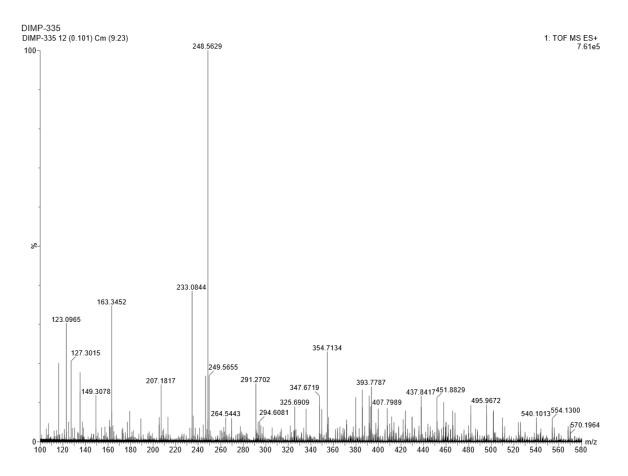
N-(4-Chlorophenethyl)pyridin-3-amine (4j)



N-(4-Chlorophenethyl)pyridin-3-amine (4j)

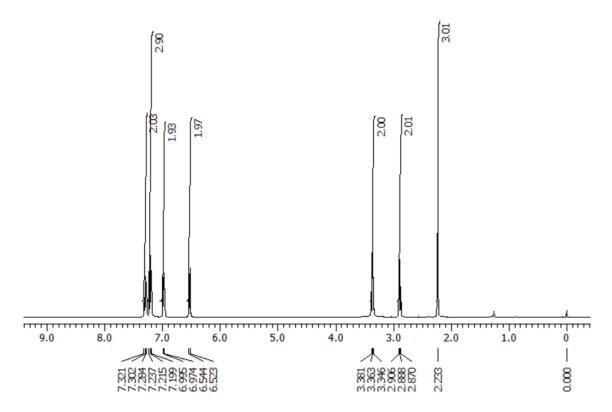


N-(4-Chlorophenethyl)pyridin-3-amine (4j)



(400 MHz, CDCl₃)

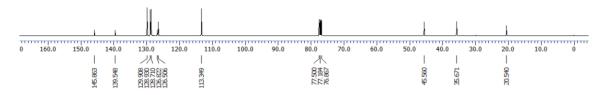
5-Methyl-N-phenethylpyridin-3-amine (4k)



¹³C NMR

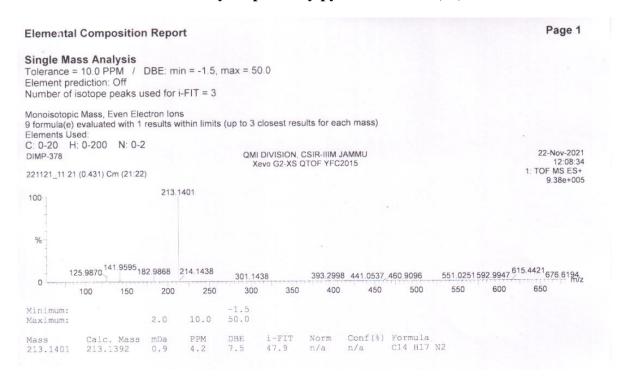
(100 MHz, CDCl₃)

5-Methyl-N-phenethylpyridin-3-amine (4k)

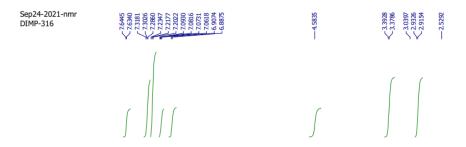


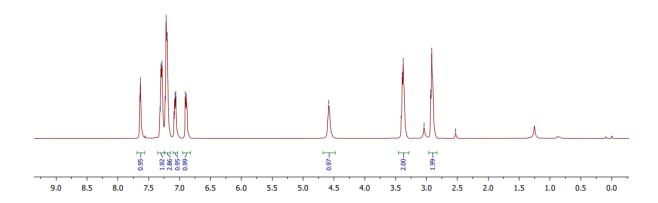
HRMS

$5-Methyl-N-phenethylpyridin-3-amine\ (4k)$

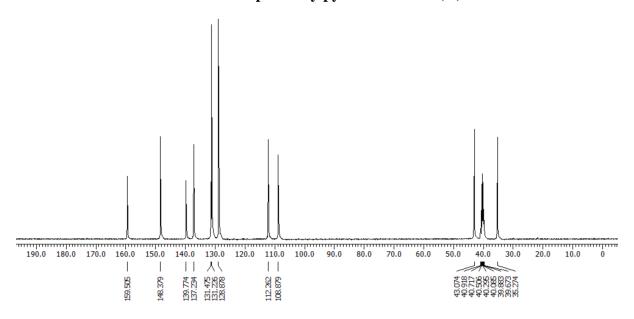


$\hbox{\bf 2-Chloro-} N\hbox{\bf -phenethylpyridin-3-amine (4l)}$

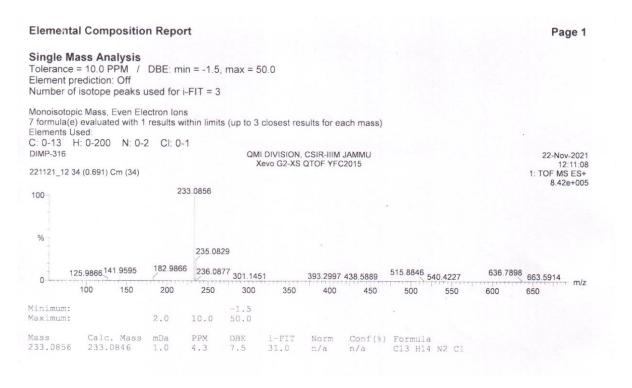




2-Chloro-N-phenethylpyridin-3-amine (4l)



2-Chloro-N-phenethylpyridin-3-amine (4l)

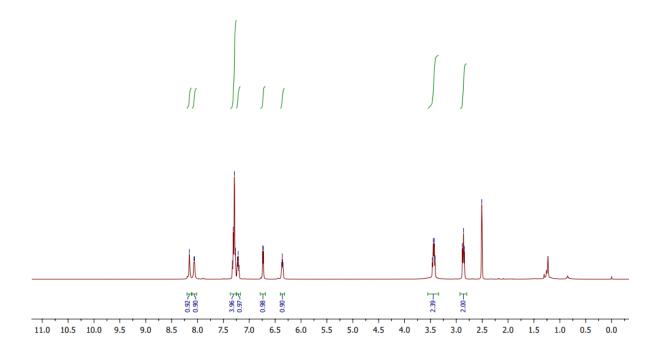


3-Chloro-N-phenethylpyridin-4-amine (4m)

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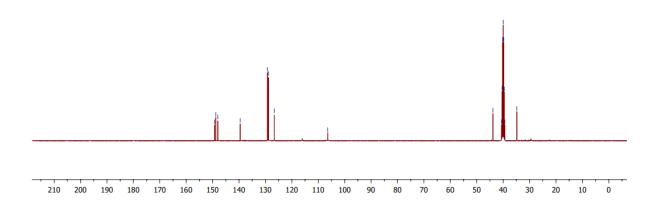




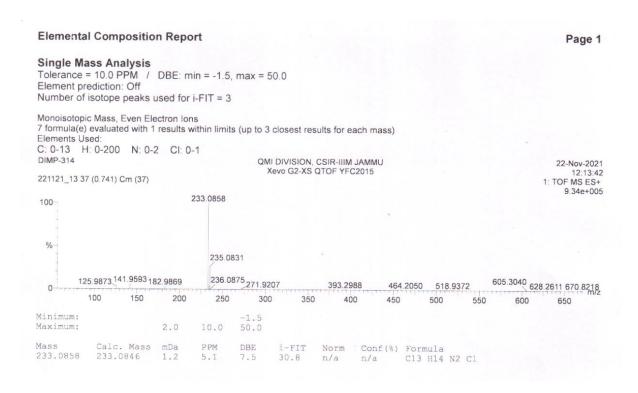
3-Chloro-*N*-phenethylpyridin-4-amine (4m)

Aug31-2021-nmr DIMP 314



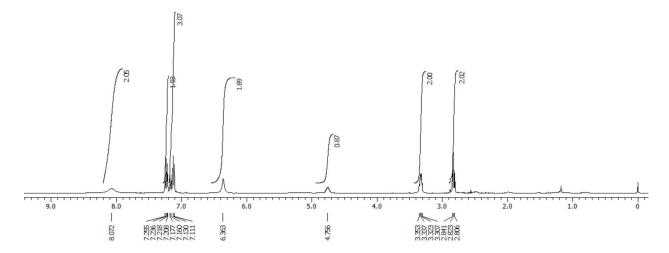


${\bf 3-Chloro-} \textit{N-} \textbf{phenethylpyridin-4-amine} \; \textbf{(4m)}$



(400 MHz, CDCl₃)

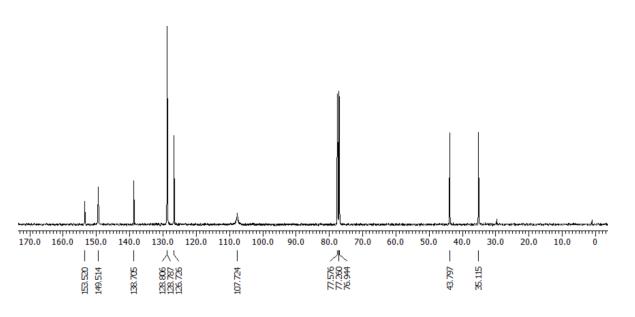
N-Phenethylpyridin-4-amine (4n)



¹³C NMR

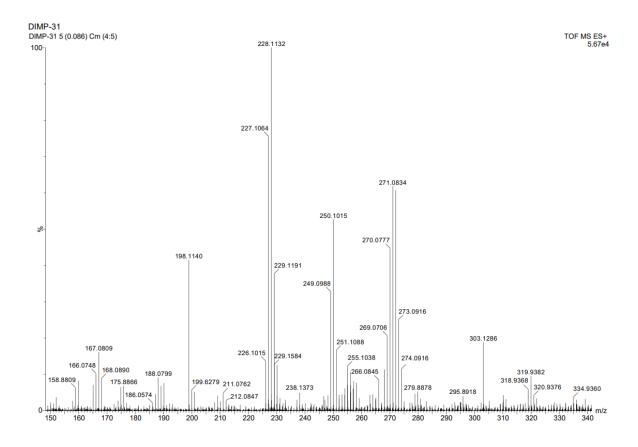
(100 MHz, CDCl₃)

N-Phenethylpyridin-4-amine (4n)



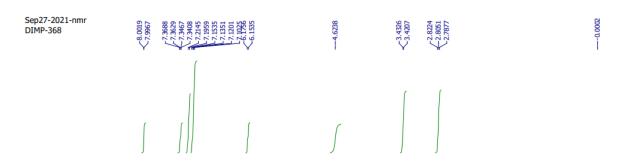
HRMS

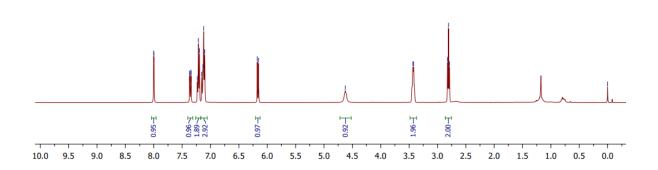
N-Phenethylpyridin-4-amine (4n)



(400 MHz, CDCl₃)

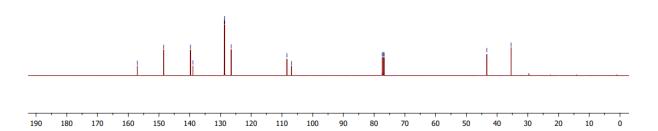
5-Bromo-N-phenethylpyridin-2-amine (40)



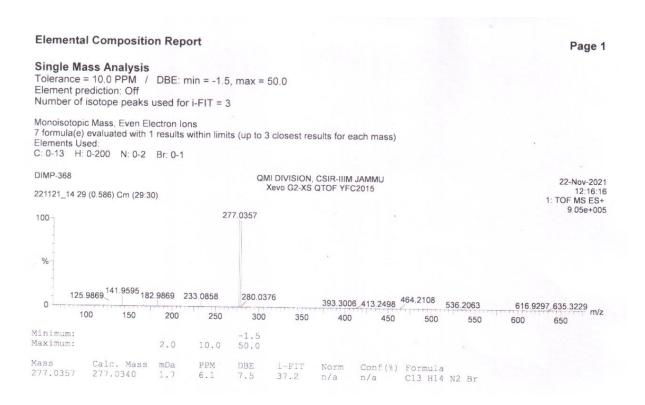


(100 MHz, CDCl₃)

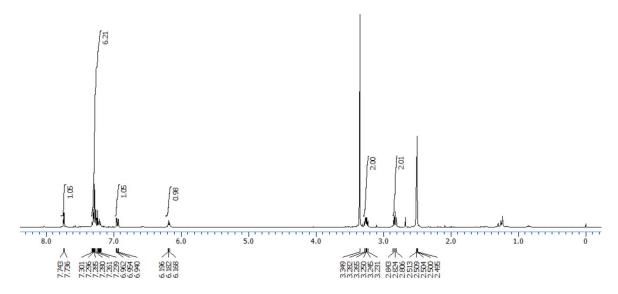
$5\text{-}Bromo\text{-}N\text{-}phenethylpyridin-2-amine} \ (4o)$



5-Bromo-N-phenethylpyridin-2-amine (40)



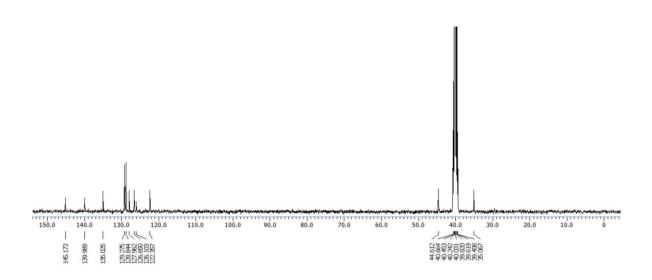
6-Bromo-N-phenethylpyridin-3-amine (4p)



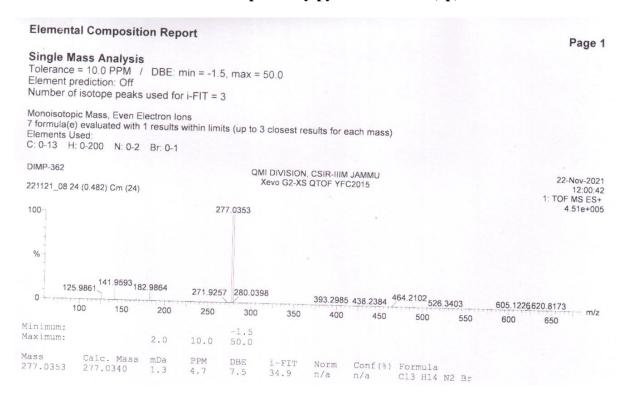
¹³C NMR

(100 MHz, (CD₃)₂SO)

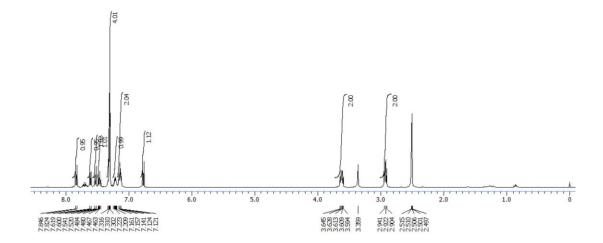
6-Bromo-N-phenethylpyridin-3-amine (4p)



6-Bromo-N-phenethylpyridin-3-amine (4p)



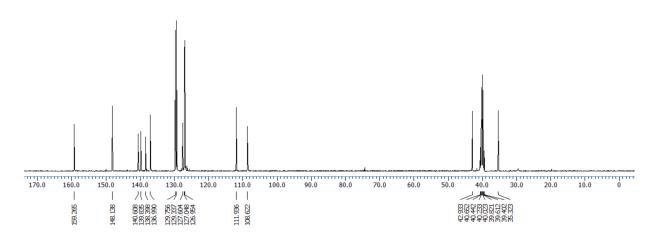
N-Phenethylquinolin-2-amine (4q)



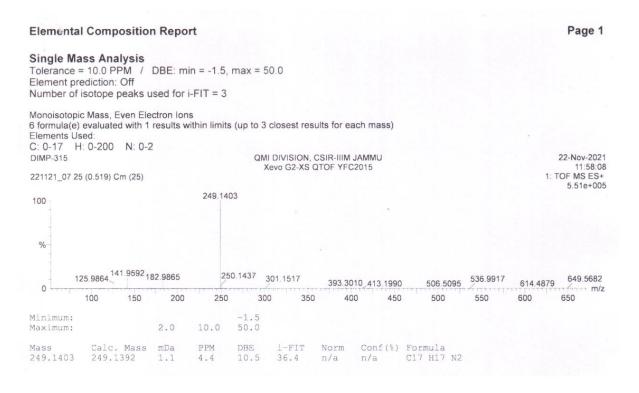
¹³C NMR

(100 MHz, (CD₃)₂SO)

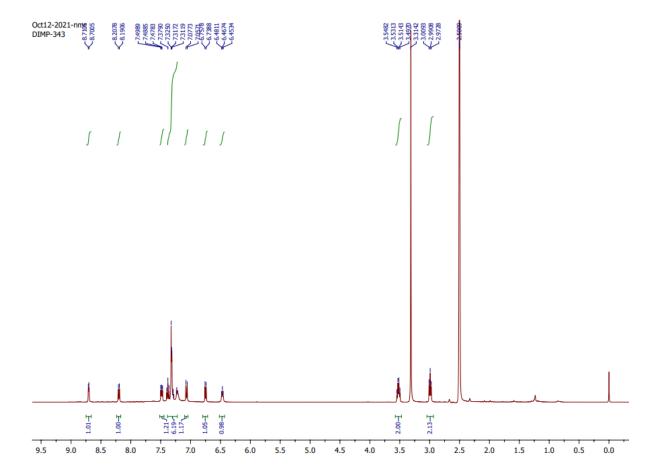
N-Phenethylquinolin-2-amine (4q)



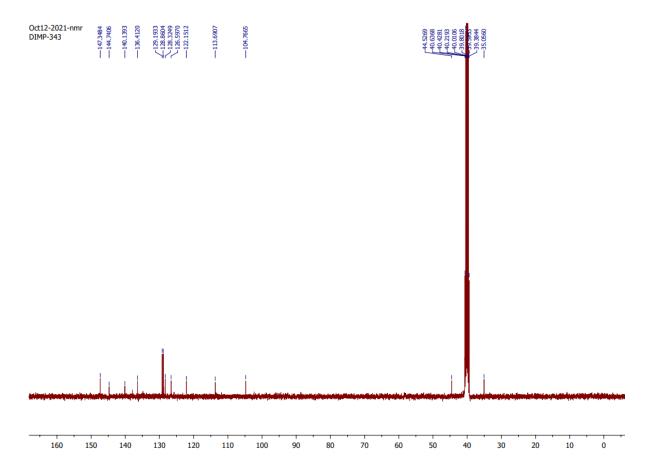
N-Phenethylquinolin-2-amine (4q)



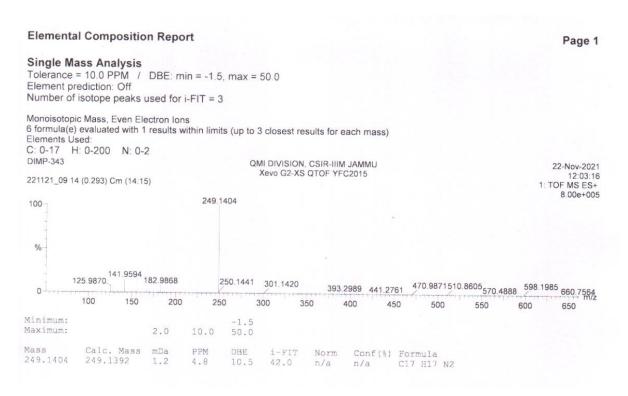
N-Phenethylquinolin-8-amine (4r)



N-Phenethylquinolin-8-amine (4r)

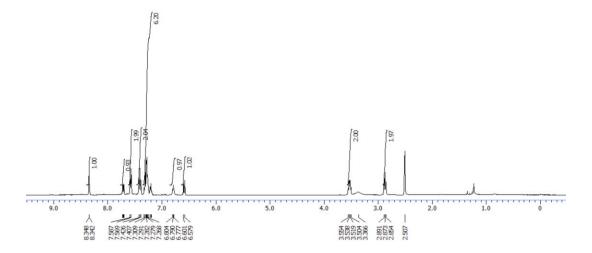


N-Phenethylquinolin-8-amine (4r)



(400 MHz, (CD₃)₂SO)

N-Phenethyl-5-phenylpyridin-2-amine (4s)



¹³C NMR

(100 MHz, (CD₃)₂SO)

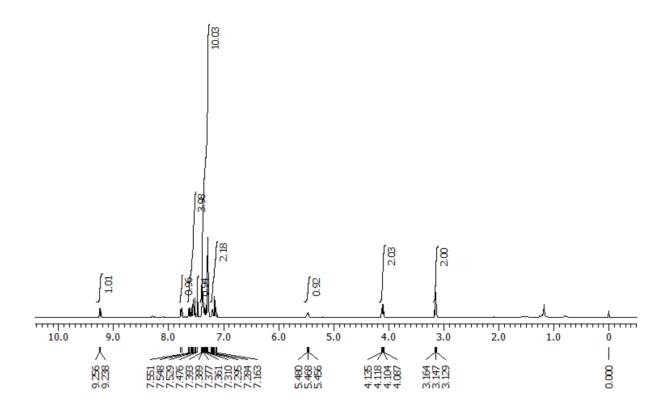
N-Phenethyl-5-phenylpyridin-2-amine (4s)

12/10/21 17:42:16 Y:\Old Data_2021\10122021\15 15 #120-222 RT: 0.49-0.90 AV: 103 SB: 610 0.91-3.00 , 0.01-0.41 NL: 1.85E8 T: FTMS + p ESI Full ms [50.00-2000.00] 275.1542 C₁₉ H₁₉ N₂ = 275.1548 -2.5018 ppm 100∃ 90 = 70= Relative Abundance 30= 25=

m/z

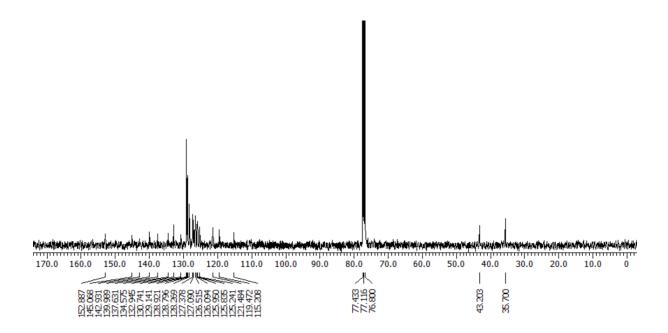
(400 MHz, CDCl₃)

N-Phenethyl-11-phenylbenzo[c]phenanthridine-6-amine (4t)



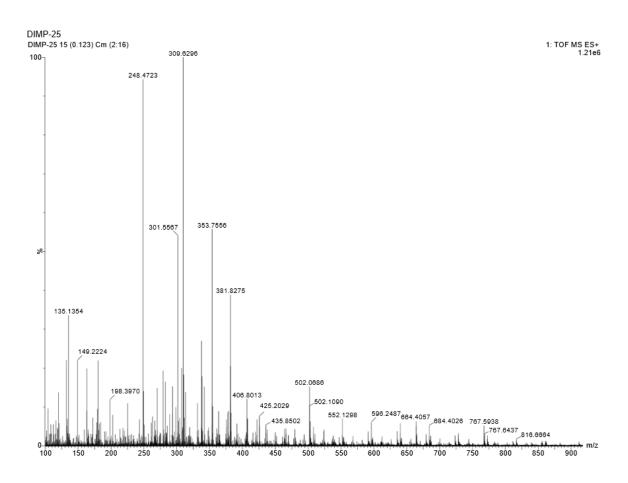
(100 MHz, CDCl₃)

N-Phenethyl-11-phenylbenzo[c]phenanthridine-6-amine (4t)



HRMS

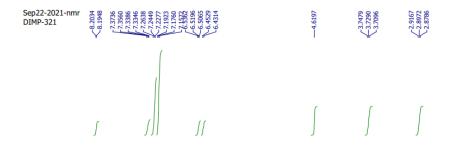
$N\hbox{-} Phenethyl\hbox{-} 11\hbox{-} phenylbenzo [c] phenanthridine\hbox{-} 6\hbox{-} amine \ (4t)$

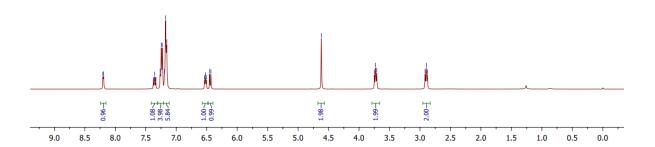


¹H NMR

(400 MHz, CDCl₃)

N-Benzyl-N-phenethylpyridin-2-amine (4u)

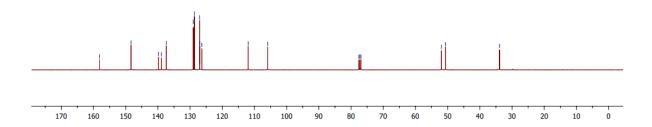




(100 MHz, CDCl₃)

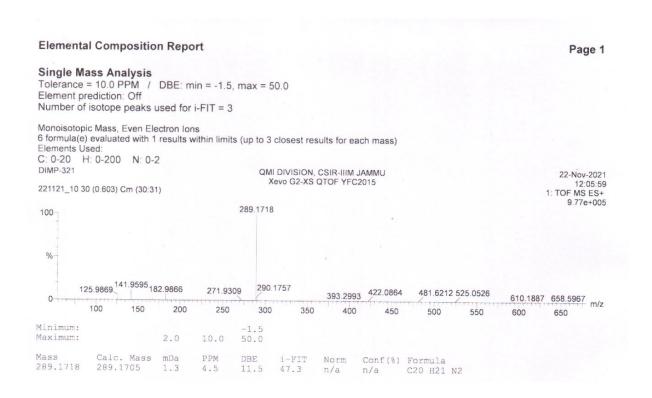
N-Benzyl-N-phenethylpyridin-2-amine (4u)





HRMS

N-Benzyl-N-phenethylpyridin-2-amine (4u)

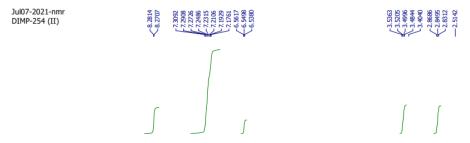


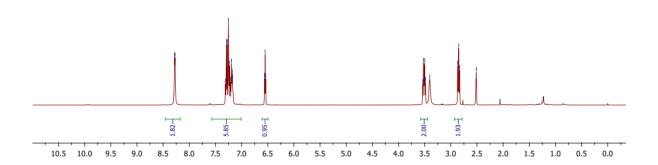
¹H NMR

(400 MHz, (CD₃)₂SO)

$$\bigcap_{N} \bigcap_{H}$$

N-Phenethylpyrimidin-2-amine (6a)

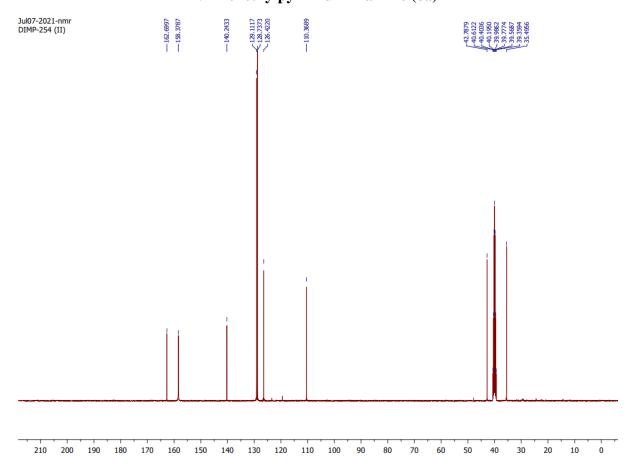




(100 MHz, (CD₃)₂SO)

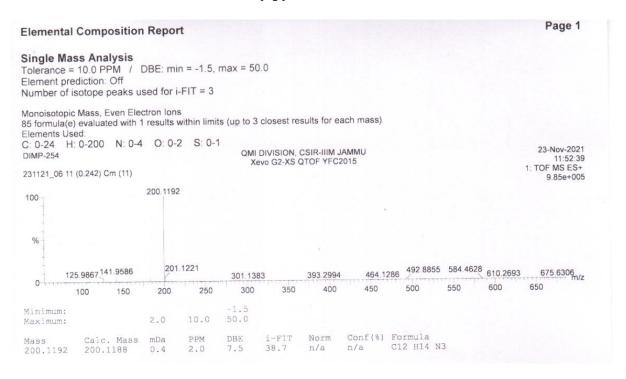
$$\bigcap_{N} \bigcap_{H}$$

N-Phenethylpyrimidin-2-amine (6a)



HRMS

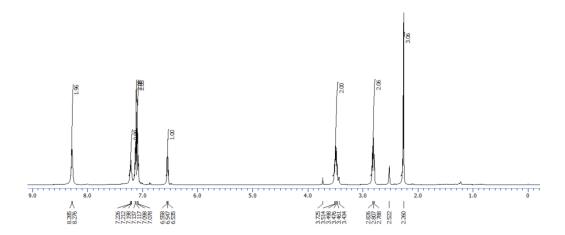
N-Phenethylpyrimidin-2-amine (6a)



¹H NMR

(400 MHz, (CD₃)₂SO)

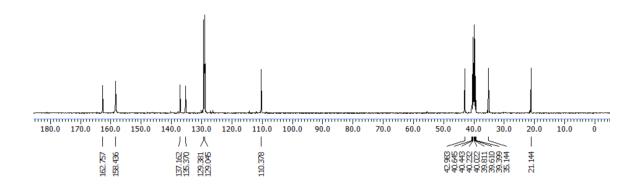
N-(4-Methylphenethyl)pyrimidin-2-amine (6b)



¹³C NMR

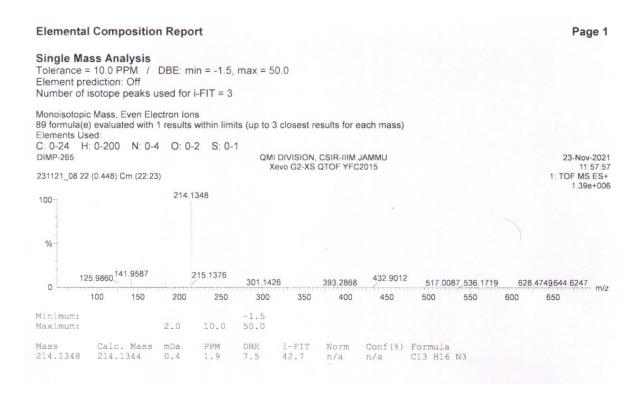
(100 MHz, (CD₃)₂SO)

N-(4-Methylphenethyl)pyrimidin-2-amine (6b)



HRMS

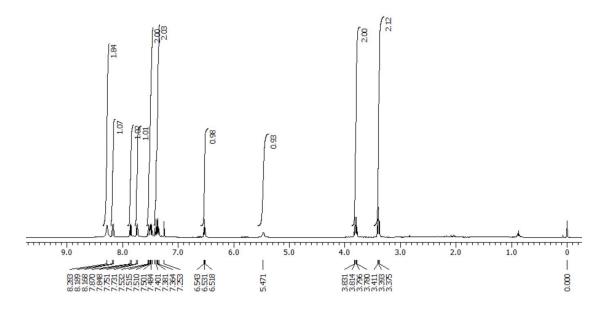
N-(4-Methylphenethyl)pyrimidin-2-amine (6b)



¹H NMR

(400 MHz, (CD₃)₂SO)

N-(2-(Naphthalen-1-yl)ethyl)pyrimidin-2-amine (6c)

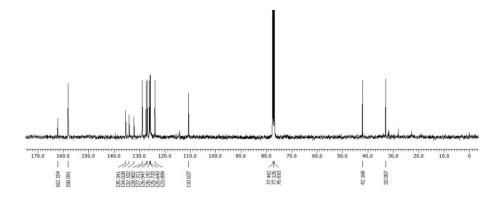


¹³C NMR

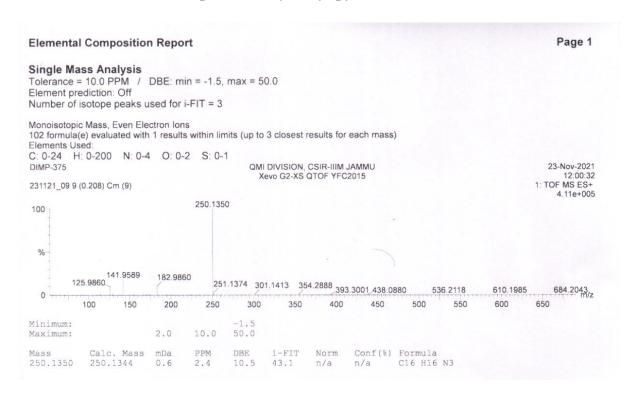
(100 MHz, (CD₃)₂SO)

$$\bigcap_{N} \bigcap_{H}$$

N-(2-(Naphthalen-1-yl)ethyl)pyrimidin-2-amine (6c)



N-(2-(Naphthalen-1-yl)ethyl)pyrimidin-2-amine (6c)

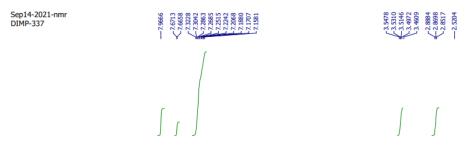


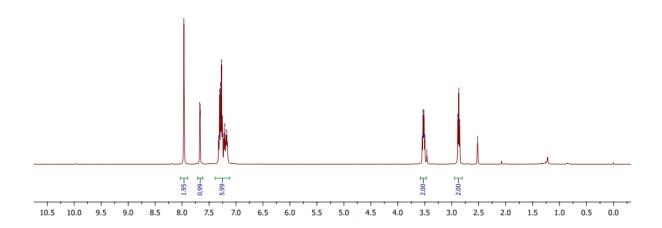
¹H NMR

(400 MHz, (CD₃)₂SO)

$$\binom{N}{N}$$

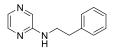
N-Phenethylpyrazin-2-amine (7a)



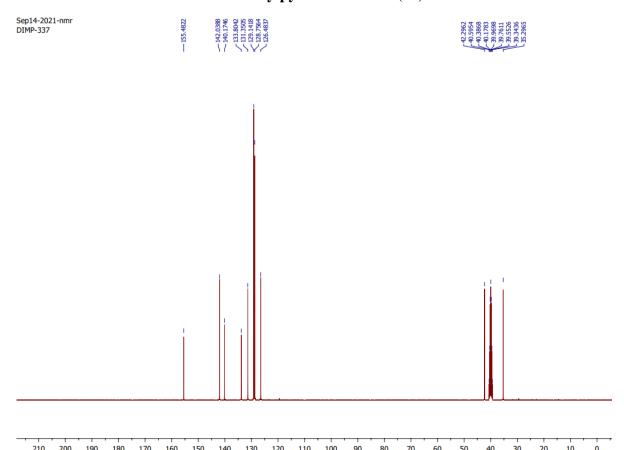


¹³C NMR

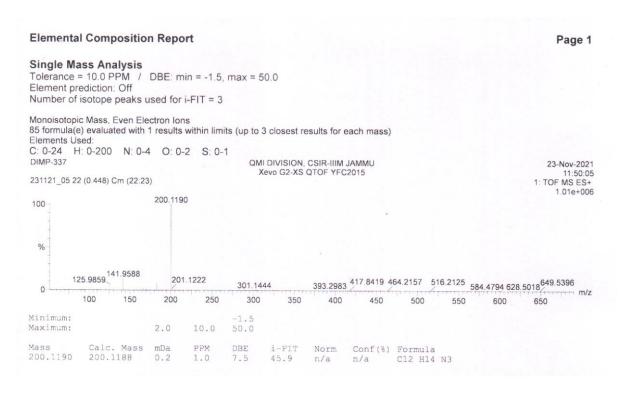
(100 MHz, (CD₃)₂SO)



N-Phenethylpyrazin-2-amine (7a)

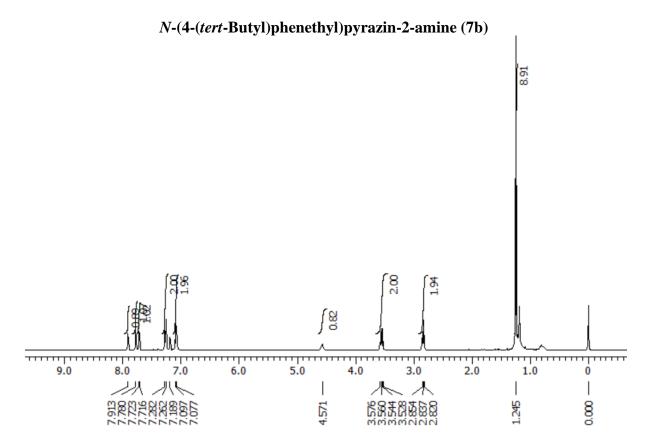


N-Phenethylpyrazin-2-amine (7a)



¹H NMR

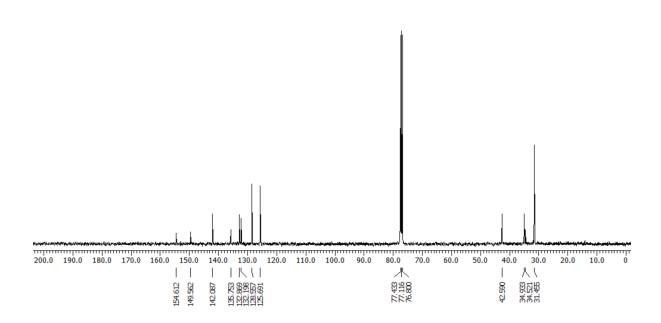
(400 MHz, (CDCl₃)



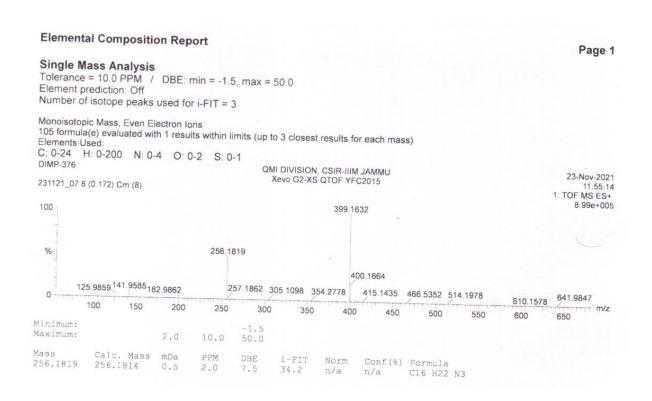
¹³C NMR

(100 MHz, (CD₃)₂SO)

N-(4-(tert-Butyl)phenethyl)pyrazin-2-amine (7b)



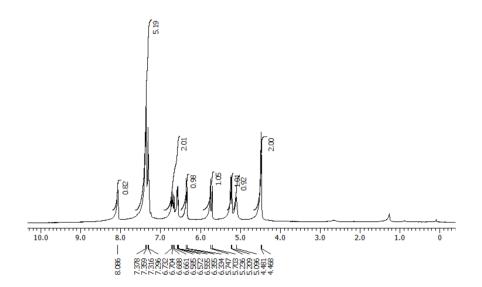
N-(4-(*tert*-Butyl)phenethyl)pyrazin-2-amine (7b)



¹H NMR

(400 MHz, CDCl₃)

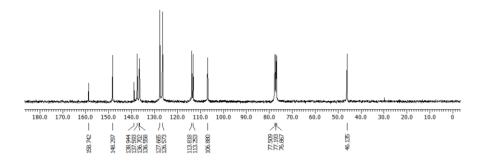
N-(4-Vinylbenzyl)pyridin-2-amine (8a)



¹³C NMR

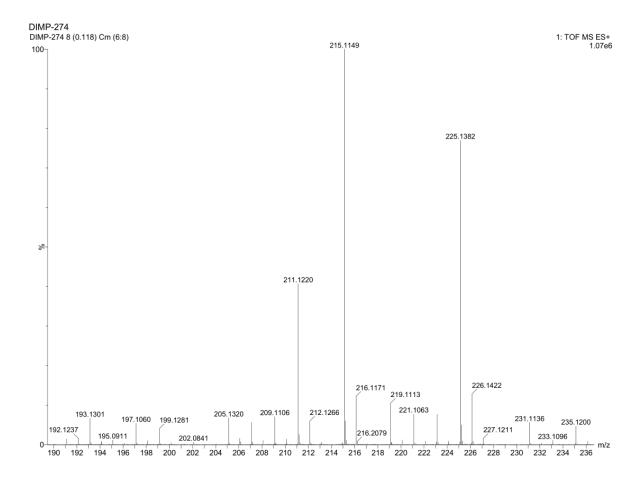
(100 MHz, CDCl₃)

N-(4-Vinylbenzyl)pyridin-2-amine (8a)



HRMS

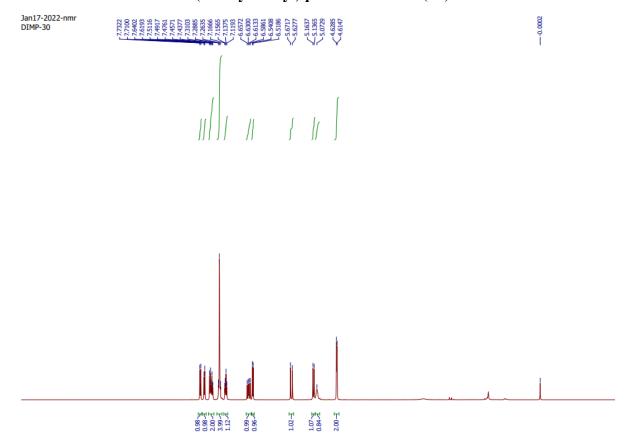
N-(4-Vinylbenzyl)pyridin-2-amine (8a)



¹H NMR

(400 MHz, CDCl₃)

N-(4-Vinylbenzyl)quinolin-2-amine (8b)



11.5

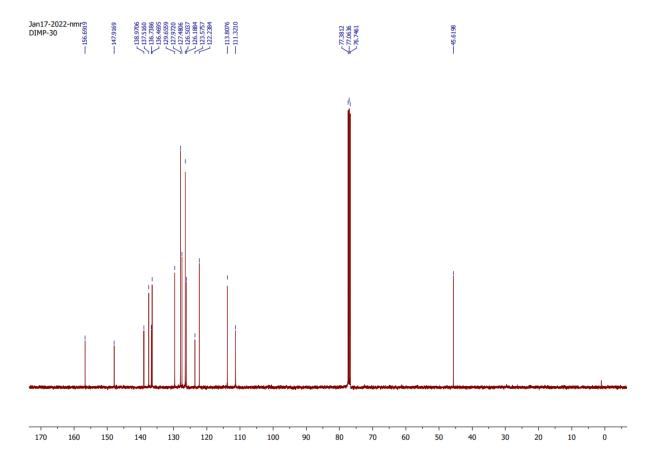
10.5

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

¹³C NMR

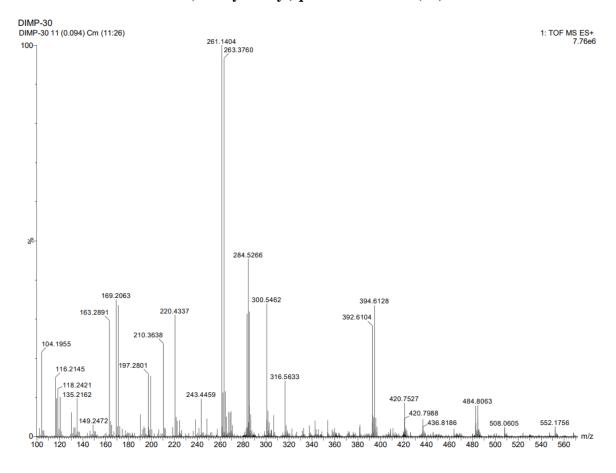
(100 MHz, CDCl₃)

N-(4-Vinylbenzyl)quinolin-2-amine (8b)



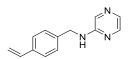
HRMS

N-(4-Vinylbenzyl)quinolin-2-amine (8b)

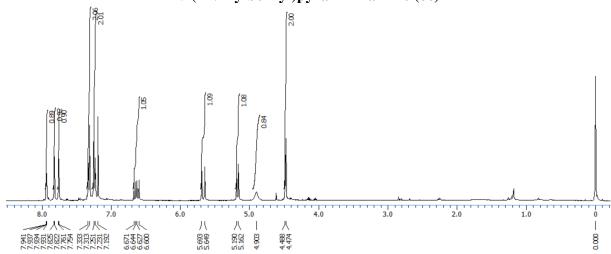


¹H NMR

(400 MHz, CDCl₃)



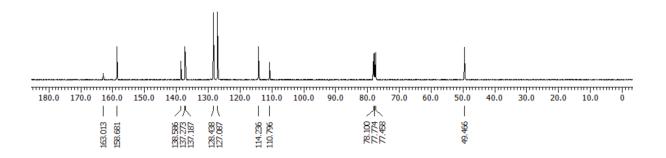
N-(4-Vinylbenzyl)pyrazin-2-amine (8c)



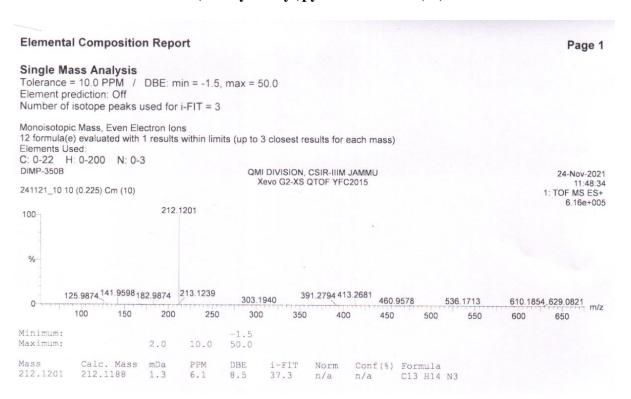
¹³C NMR

(100 MHz, CDCl₃)

N-(4-Vinylbenzyl)pyrazin-2-amine (8c)



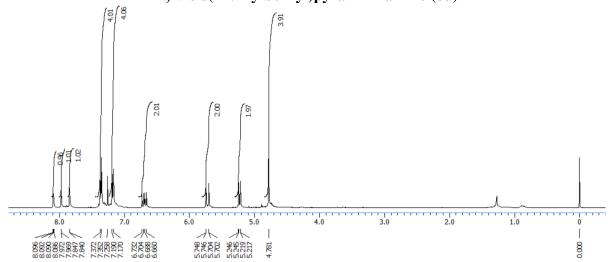
N-(4-Vinylbenzyl)pyrazin-2-amine (8c)



¹H NMR

(400 MHz, CDCl₃)

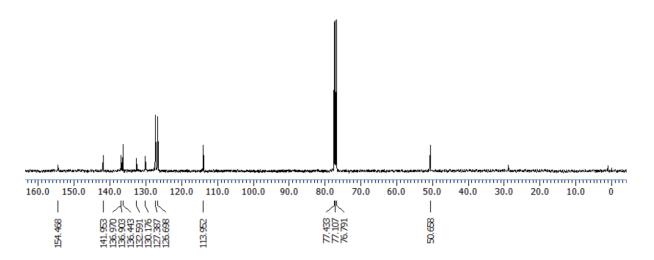
N,N-bis(4-Vinylbenzyl)pyrazin-2-amine (8d)



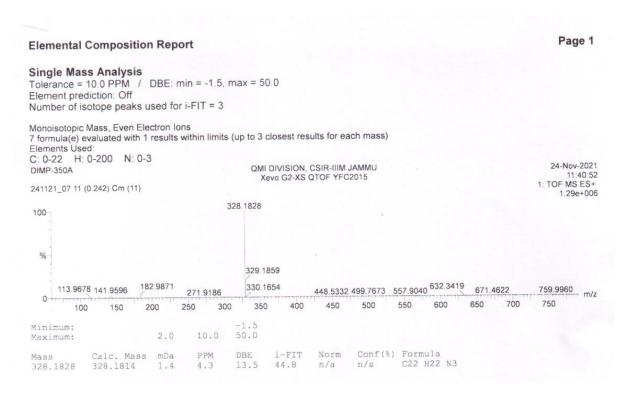
¹³C NMR

(100 MHz, CDCl₃)

N,N-bis(4-Vinylbenzyl)pyrazin-2-amine (8d)



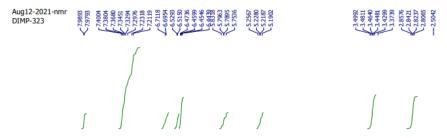
N,N-bis(4-Vinylbenzyl)pyrazin-2-amine (8d)

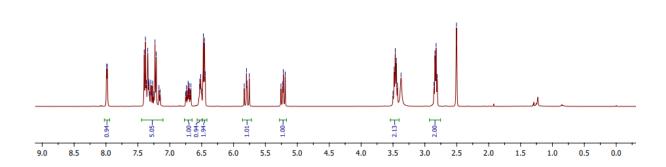


¹H NMR

(400 MHz, (CD₃)₂SO)

N-(3-Vinylphenethyl)pyridin-2-amine) (12)

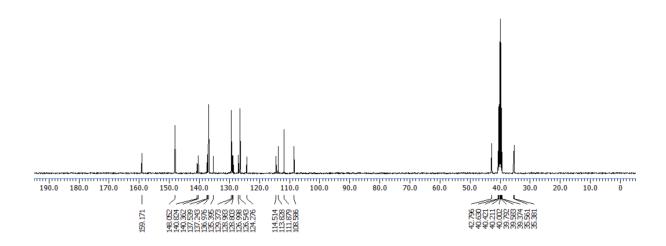




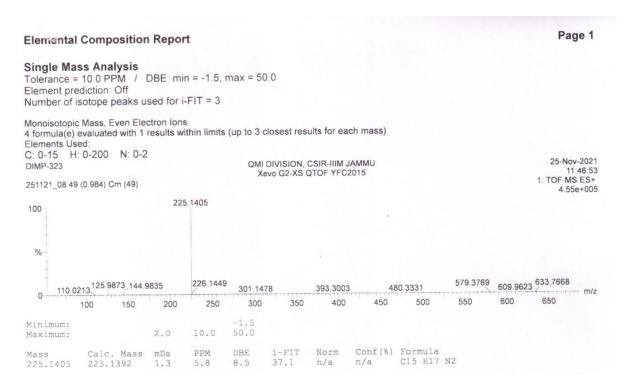
¹³C NMR

(100 MHz, (CD₃)₂SO)

N-(3-Vinylphenethyl)pyridin-2-amine) (12)



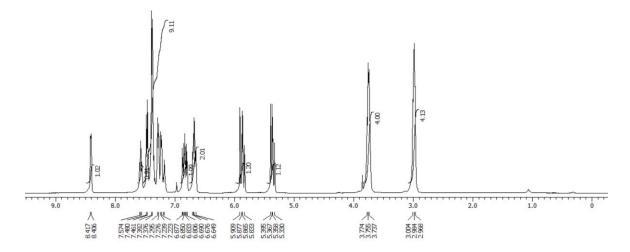
N-(3-Vinylphenethyl)pyridin-2-amine) (12)



¹H NMR

(400 MHz, CDCl₃)

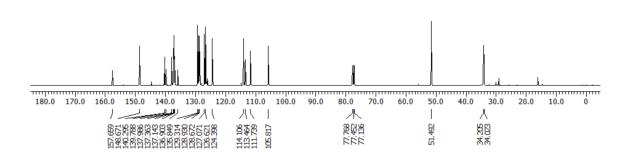
N-Phenethyl-N-(3-vinylphenethyl)pyridin-2-amine (12')



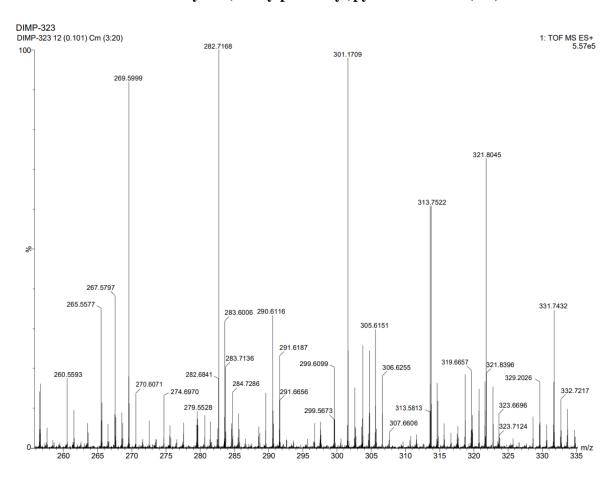
¹³C NMR

(100 MHz, CDCl₃)

N-Phenethyl-N-(3-vinylphenethyl)pyridin-2-amine (12')



$N ext{-}Phenethyl-N ext{-}(3 ext{-}vinylphenethyl)pyridin-2-amine (12')$

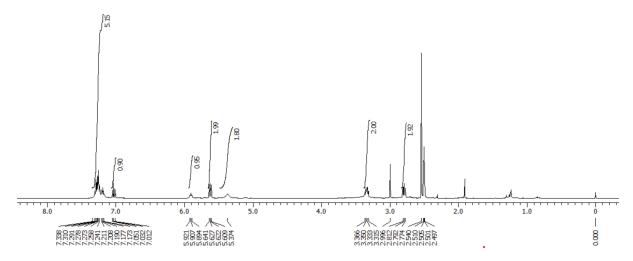


¹H NMR

(400 MHz, (CD₃)₂SO)

$$H_2N \nearrow N \nearrow N$$

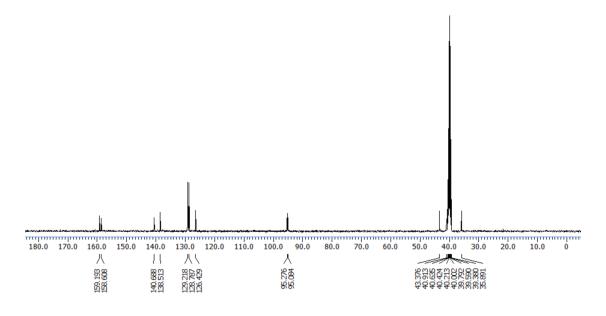
N^2 -Phenethylpyridin-2,6-diamine (14)



¹³C NMR

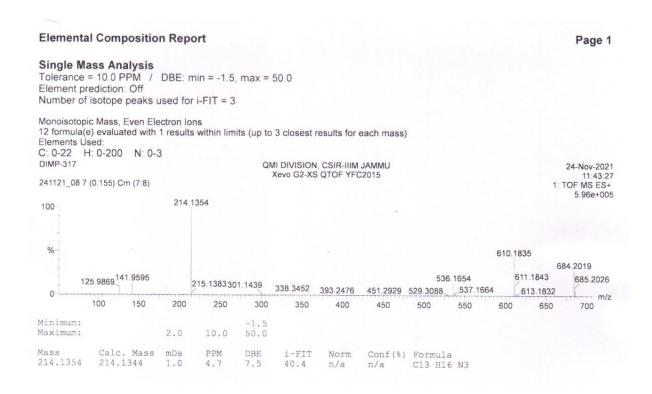
(100 MHz, (CD₃)₂SO)

N^2 -Phenethylpyridin-2,6-diamine (14)



$$H_2N$$
 N N N N

N^2 -Phenethylpyridin-2,6-diamine (14)

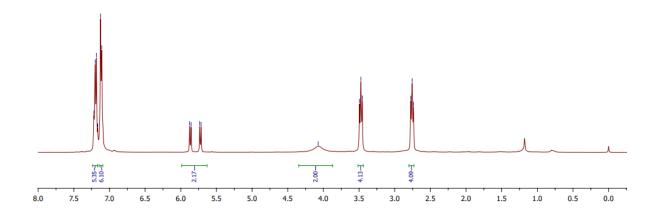


¹H NMR

(400 MHz, (CDCl₃)

N^2 , N^2 -Diphenethylpyridine-2,6-diamine (14')

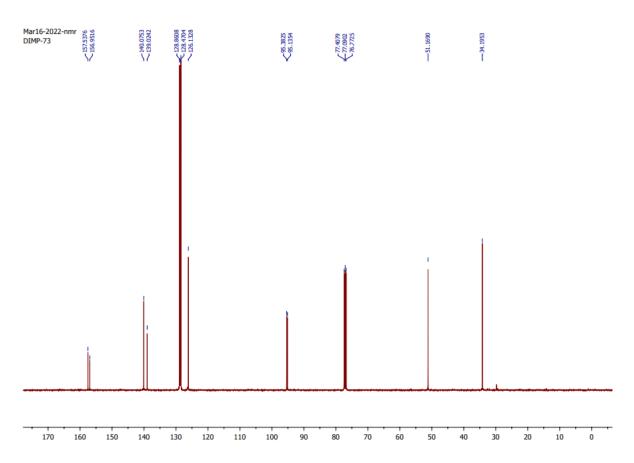




¹³C NMR

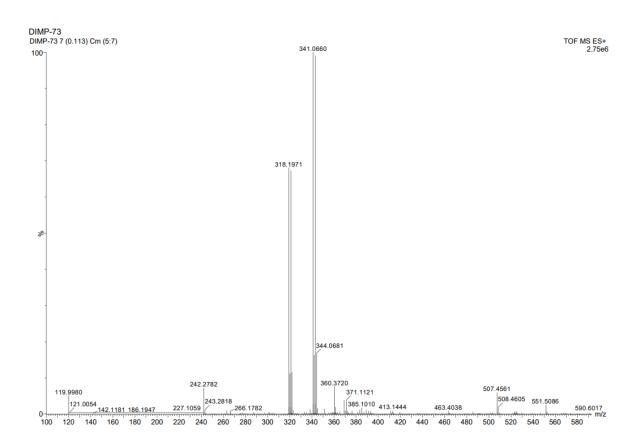
(100 MHz, (CDCl₃)

N^2 , N^2 -Diphenethylpyridine-2,6-diamine (14')



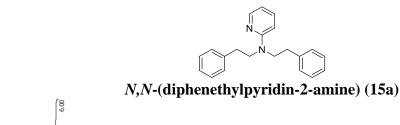
HRMS

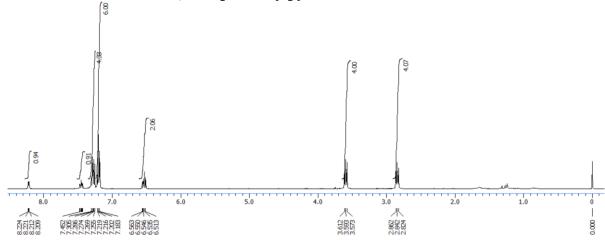
N^2 , N^2 -Diphenethylpyridine-2,6-diamine (14')



¹H NMR

(400 MHz, CDCl₃)

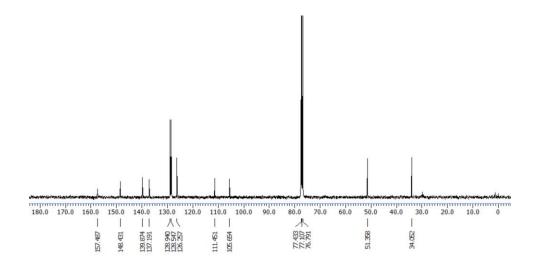




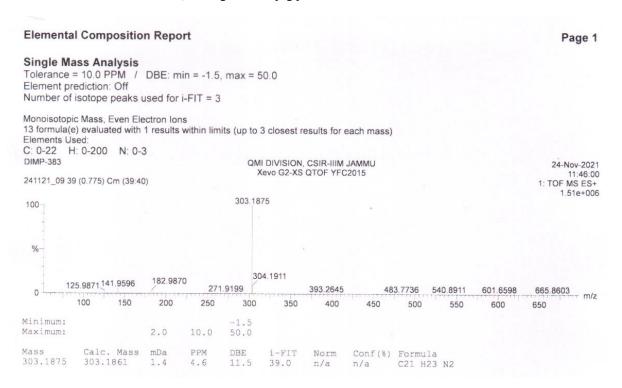
¹³C NMR

(100 MHz, CDCl₃)

N,N-(diphenethylpyridin-2-amine) (15a)

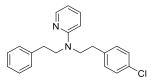


N,N-(diphenethylpyridin-2-amine) (15a)

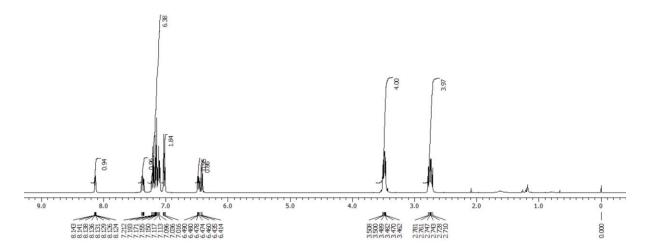


¹H NMR

(400 MHz, CDCl₃)



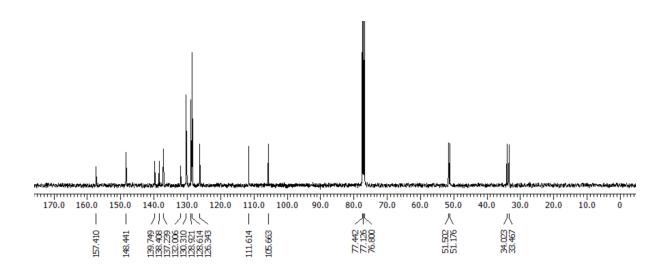
N-(4-Chlorophenethyl)-*N*-phenethylpyridin-2-amine (15b)



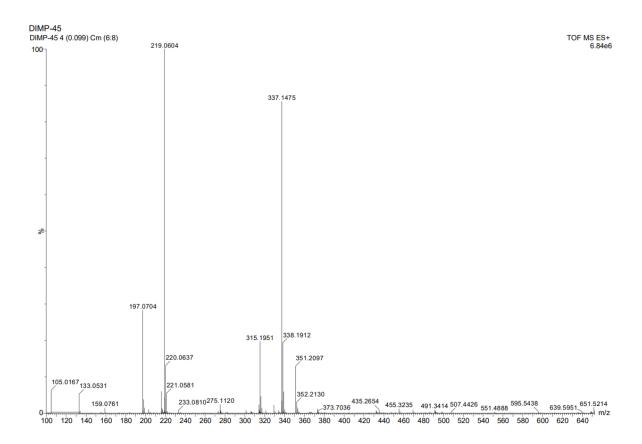
¹³C NMR

(100 MHz, CDCl₃)

N-(4-Chlorophenethyl)-N-phenethylpyridin-2-amine (15b)



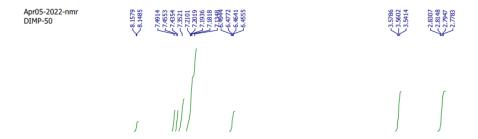
N-(4-Chlorophenethyl)-N-phenethylpyridin-2-amine (15b)

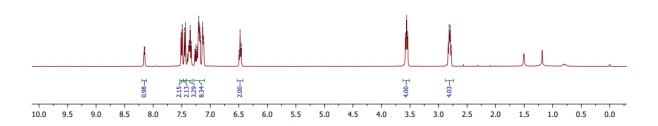


¹H NMR

(400 MHz, CDCl₃)

N-(2-([1,1'-Biphenyl]-4-yl)ethyl)-N-phenethylpyridin-2-amine (15c)

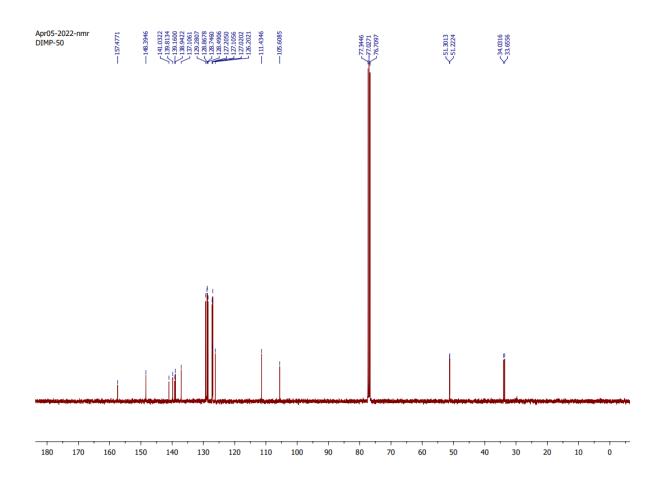




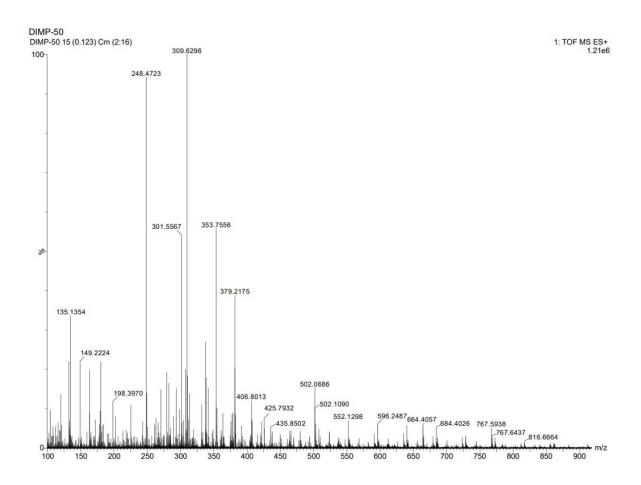
¹³C NMR

(100 MHz, CDCl₃)

N-(2-([1,1'-Biphenyl]-4-yl)ethyl)-N-phenethylpyridin-2-amine (15c)



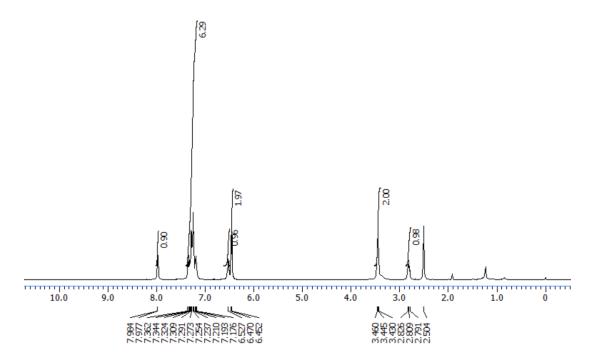
N-(2-([1,1'-Biphenyl]-4-yl)ethyl)-N-phenethylpyridin-2-amine (15c)



¹H NMR

(400 MHz, (CD₃)₂SO)

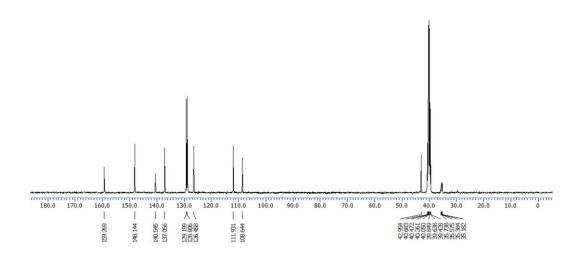
N-(2-Phenethyl-2-d)pyridin-2-amine) (3a')



¹³C NMR

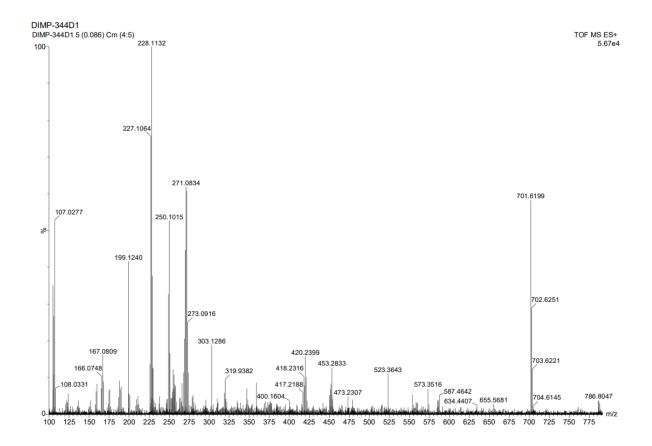
(100 MHz, (CD₃)₂SO)

N-(2-Phenethyl-2-d)pyridin-2-amine) (3a')



HRMS

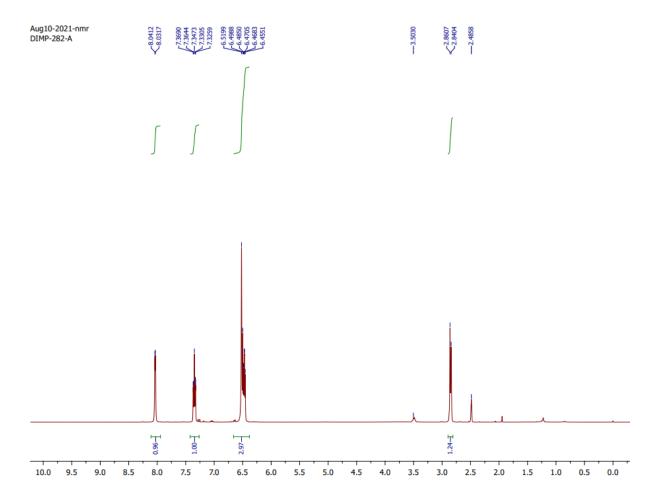
N-(2-Phenethyl-2-d)pyridin-2-amine) (3a')



¹H NMR

(400 MHz, (CD₃)₂SO)

N-(2-(Phenyl-*d*₅)ethyl-1,1,2-*d*₃)pyridin-2-amine) (3a")

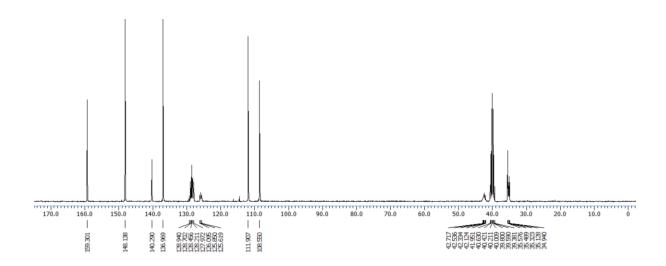


¹³C NMR

(100 MHz, (CD₃)₂SO)

$$\begin{array}{c} D \\ D \\ D \\ D \\ \end{array}$$

N-(2-(Phenyl- d_5)ethyl-1,1,2- d_3)pyridin-2-amine) (3a")



N-(2-(Phenyl- d_5)ethyl-1,1,2- d_3)pyridin-2-amine) (3a")

