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SUPPORTING INFORMATION

A convergent synthesis of vinyloxyimidazopyridine *via* Cu(I)-catalyzed three-component coupling

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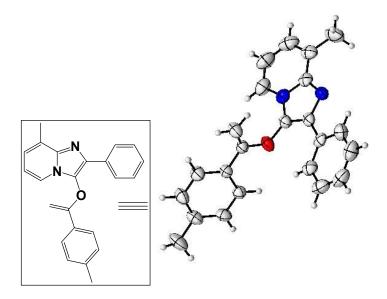
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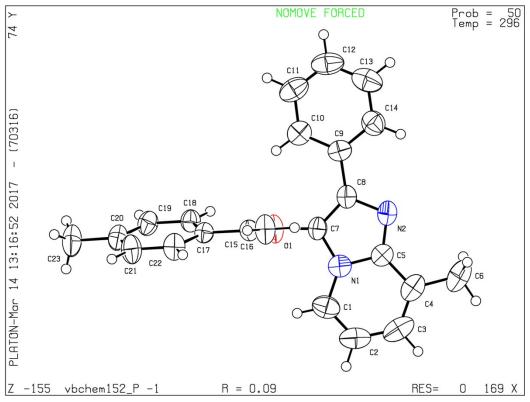
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1. X-ray crystallographic data:

1.1. X-ray crystallographic data for 4b.

The white crystals of $\bf 4b$ were obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical Formula: $C_{23}H_{20}N_2O$.





ORTEP (with 50% probability) diagram for the structure **8-Methyl-2-phenyl-3-((1-(p-tolyl)vinyl)oxy)imidazo[1,2-a]pyridine (4b).**

Wavelength 0.71073 Å

Formula C23H20N2O

Crystal system Triclinic

Space group P -1

Unit cell dimensions a = 9.5942(6) Å $\alpha = 101.242(3) ^{\circ}$

b = 9.7522(7) Å $\beta = 98.692(3) ^{\circ}$

c = 10.4775(6) Å $\gamma = 100.998(3) ^{\circ}$

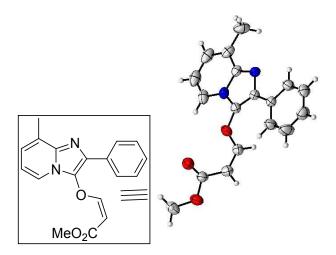
Volume 925.62(10)Å³

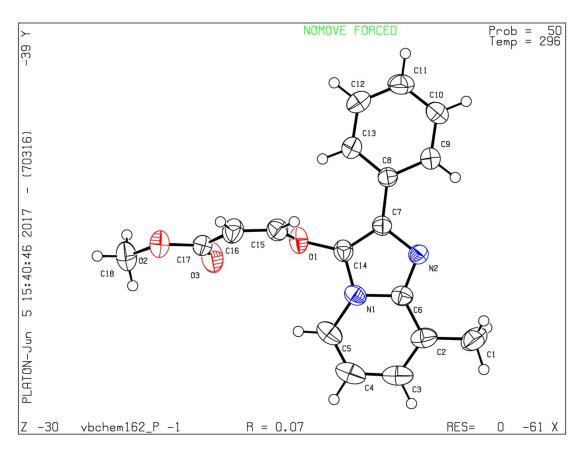
Z 2 **R-factor (%)** 9.23

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centreas supplementary publication with a CCDC reference number CCDC **1566643**.

1.2. Structure Determination (X-ray crystallographic data for 7b).

The white crystals of 7b were obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical Formula: $C_{18}H_{16}N_2O_3$.





ORTEP (with 50% probability) diagram for the structure **Methyl** (**Z**)-3-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)acrylate (7b):

Wavelength 0.71073 Å

Formula C18 H16 N2 O3

Crystal system Triclinic

Space group P-1

Unit cell dimensions a = 8.2376(4) Å $\alpha = 98.745(2) ^{\circ}$

b = 8.7359(4) Å $\beta = 102.654(2) ^{\circ}$

c = 11.8649(6) Å $\gamma = 102.432(2) ^{\circ}$

Volume 795.58(7) Å³

Z 2 R-factor (%) 6.70

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centreas supplementary publication with a CCDC reference number CCDC **1566644**.

2. General information:

All reagents were purchased from commercial sources and used without further purification. ¹H NMR spectra were determined on 400 MHz spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet), dd (double doublet) and coupling constants (J) were given in Hz. ¹³C{1H} NMR spectra were recorded at 100 MHz in CDCl₃ solution. Chemical shifts as internal standard are referenced to CDCl₃ (δ = 7.26 for ¹H and δ = 77.16 for ¹³C{¹H} NMR) as internal standard. TLC was done on silica gel coated glass slide. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. X-ray single crystal data were collected using MoK α (λ = 0.71073 Å) radiation with CCD area detector.

3. Experimental procedures:

3.1. Experimental procedure for the synthesis of 4a.

A mixture of 2-amino-3-methylpyridine (1a) (0.2 mmol, 22 mg) and phenylglyoxal hydrate (2a) (0.21 mmol, 29 mg) were taken in a sealed tube. Then 1,2-dichlorobenzene (2 mL) was added to it and stirred at room temperature for few seconds. Then phenylacetylene (3a) (0.22 mmol, 23 mg) and CuI (10 mol%, 3.8 mg) was added to it and stirred at 120 °C for 5 hours under open atmosphere. After completion of the reaction (TLC) the reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60–120 mesh) using *n*-hexane/ EtOAc (9:1) as the eluent to afford pure 4a as a yellow gummy mass (52 mg, 81% yield).

3.2. Synthesis of 4g on 1 mmol scale.

A mixture of 2-amino-3-methylpyridine (1a) (1 mmol, 109 mg) and phenylglyoxal hydrate (2a) (1.05 mmol, 142 mg) were taken in a sealed tube. Then 1,2-dichlorobenzene (6 mL) was added to it and stirred at room temperature for few seconds. Then ethynylcyclopropane (3g) (1.1 mmol, 73 mg) and CuI (10 mol%, 19 mg) was added to it and stirred at 120 °C for 5 hours under open atmosphere. After completion of the reaction (TLC) the reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over

anhydrous Na_2SO_4 . The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60–120 mesh) using *n*-hexane/ EtOAc (9:1) as the eluent to afford pure **4g** as a brown oil (275 mg, 95% yield).

3.3. Experimental procedure for the synthesis of 5.

A mixture of 2-amino-3-methylpyridine (1a) (0.4 mmol, 44 mg) and phenylglyoxal hydrate (2a) (0.42 mmol, 58 mg) were taken in a sealed tube. Then 1,2-dichlorobenzene (4 mL) was added to it and stirred at room temperature for few seconds. Then 1,8-nonadiyne (3x) (0.22 mmol, 26 mg) and CuI (20 mol%, 7.6 mg) was added to it and stirred at 120 °C for 5 hours under open atmosphere. After completion of the reaction (TLC) the reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60–120 mesh) using *n*-hexane/ EtOAc as the eluent to afford pure 5 as a brown oil.

3.4. Experimental procedure for the synthesis of 7a.

A mixture of 2-amino-3-methylpyridine (1a) (0.2 mmol, 22 mg) and phenylglyoxal hydrate (2a) (0.21 mmol, 29 mg) were taken in a sealed tube. Then 1,2-dichlorobenzene (2 mL) was added to it and stirred at room temperature for few seconds. Then ethylpropiolate (6a) (0.22 mmol, 22 mg) and CuI (10 mol%, 3.8 mg) was added to it and stirred at 120 °C for 5 hours under open atmosphere. After completion of the reaction (TLC) the reaction mixture was cooled to room

temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 . The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60–120 mesh) using *n*-hexane/ EtOAc (4:1) as the eluent to afford pure **7a** as a yellow solid (60 mg, 94% yield).

3.5. Experimental procedure for the synthesis of 9a.

A mixture of 2-amino-3-methylpyridine (1a) (0.2 mmol, 22 mg) and phenylglyoxal hydrate (2a) (0.21 mmol, 29 mg) were taken in a sealed tube. Then 1,2-dichlorobenzene (2 mL) was added to it and stirred at room temperature for few seconds. Then ethylphenylpropiolate (8a) (0.22 mmol, 35 mg) and CuI (10 mol%, 3.8 mg) was added to it and stirred at 120 °C for 5 hours under open atmosphere. After completion of the reaction (TLC) the reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporation of the solvent in vacuum and purified by column chromatography on silica gel (60–120 mesh) using *n*-hexane/ EtOAc (9:1) as the eluent to afford pure 9a as a yellow gummy mass (56 mg, 71% yield).

3.6. General procedure for the synthesis of 2a.¹

SeO₂ (15 mmol), 1,4-dioxane (9 mL) and water (1 mL) were added to a 100 mL three-necked bottle and fitted it with an condenser. The mixture was heated to 50-55 °C and stirred until the solid dissolved. It was followed by addition of Compound A (10 mmol) and the reaction was maintained at reflux temperature. After the reaction was complete, as monitored by TLC, the

mixture was filtered through a pad of celite. The filtrate was evaporated to afford a crude product that was purified by distillation under reduced pressure to give a yellow liquid. This liquid was dissolved in hot water (5 mL) to afford $2a \cdot H_2O$ as a white solid.

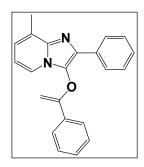
White solid (85%, 1.29 g); 1 H NMR (400 MHz, CDCl₃): δ 8.13-8.11 (m, 2H), 7.69-7.58 (m, 1H), 7.54-7.47 (m, 2H), 5.98 (s, 1H), 4.51 (s, 2H); 13 C NMR (100 MHz): δ 195.0, 189.7, 134.7, 130.6, 130.0, 128.9, 87.3.

3.7. General procedure for the synthesis of 10a.²

To a solution of 2-amino-3-methylpyridine (1a) (108 mg, 1 mmol) in CH₂Cl₂ (4 mL), phenylglyoxal hydrate (2a) (154 mg, 1 mmol) was added portion wise and the reaction mixture was stirred overnight at rt. The reaction mixture was then concentrated under reduced pressure to give 2-phenylimidazo[1,2-a]pyridin-3-ol (203 mg, 91%) as a yellowish amorphous powder.

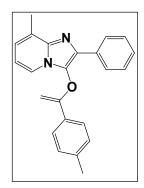
¹H NMR (400 MHz, DMSO- d_6): δ 8.14-8.12 (m, 3H), 7.35 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 6.8 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.96 (t, J = 6.8 Hz, 1H), 2.50 (s, 3H).

4. Characterization data for the products:



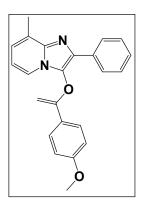
8-Methyl-2-phenyl-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4a):

Yellow gummy mass (81%, 52 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.11-8.08 (m, 2H), 7.91-7.88 (m, 2H), 7.65 (d, J = 6.8 Hz, 1H), 7.51-7.46 (m, 3H), 7.43-7.39 (m, 2H), 7.31-7.27 (m, 1H), 6.98-6.96 (m, 1H), 6.69 (t, J = 7.2 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 4.17 (d, J = 3.6 Hz, 1H), 2.69 (s, 3H); ¹³C NMR (100 MHz): δ 156.3, 140.4, 133.6, 133.0, 130.7, 130.0, 129.5, 128.75, 128.71, 127.8, 127.6, 126.5, 125.5, 123.0, 119.5, 112.3, 88.0, 16.5; HRMS calcd for C₂₂H₁₉N₂O [M +H]⁺: 327.1492; found [M +H]⁺: 327.1494.



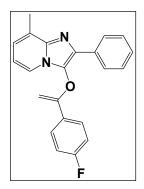
8-Methyl-2-phenyl-3-((1-(p-tolyl)vinyl)oxy)imidazo[1,2-a]pyridine (4b):

White solid (85%, 57 mg); m.p.: 148-149 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.10-8.07 (m, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 6.4 Hz, 1H), 7.41-7.38 (m, 2H), 7.30-7.26 (m, 3H), 6.97-6.95 (m, 1H), 6.68 (t, J = 6.8 Hz, 1H), 4.89 (d, J = 3.6 Hz, 1H), 4.11 (d, J = 3.2 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); 13 C NMR (100 MHz): δ 156.4, 140.4, 139.6, 133.1, 130.9, 130.8, 130.1, 129.4, 128.7, 127.9, 127.6, 126.6, 125.4, 122.9, 119.6, 112.2, 87.2, 21.4, 16.5; Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23%; Found: C, 80.94; H, 5.80; N, 8.09%.



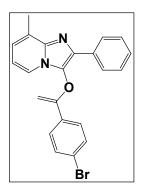
3-((1-(4-Methoxyphenyl)vinyl)oxy)-8-methyl-2-phenylimidazo[1,2-a]pyridine (4c):

Yellow gummy mass (73%, 51 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.08-8.06 (m, 2H), 7.83-7.80 (m, 2H), 7.64 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.01-6.95 (m, 3H), 6.68 (t, J = 7.2 Hz, 1H), 4.81 (d, J = 4.0 Hz, 1H), 4.05 (d, J = 3.6 Hz, 1H), 3.88 (s, 3H), 2.67 (s, 3H); ¹³C NMR (100 MHz): δ 160.7, 156.1, 140.4, 133.1, 130.7, 130.1, 128.7, 127.9, 127.5, 126.9, 126.6, 126.3, 123.0, 119.6, 114.1, 112.2, 86.3, 55.5, 16.5; HRMS calcd for $C_{23}H_{21}N_2O_2$ [M +H]⁺: 357.1598; found [M +H]⁺: 357.1591.



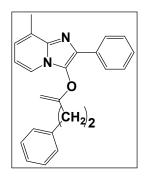
3-((1-(4-Fluorophenyl)vinyl)oxy)-8-methyl-2-phenylimidazo[1,2-a]pyridine (4d):

Yellow gummy mass (81%, 55 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.07-8.05 (m, 2H), 7.87-7.84 (m, 2H), 7.62 (d, J = 6.8 Hz, 1H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 1H), 7.18-7.14 (m, 2H), 6.98-6.96 (m, 1H), 6.70 (t, J = 6.8 Hz, 1H), 4.87 (d, J = 4.0 Hz, 1H), 4.14 (d, J = 3.6 Hz, 1H), 2.68 (s, 3H); ¹³C NMR (100 MHz): δ 163.6 (J_{C-F} = 248 Hz), 155.5, 140.4, 133.0, 130.8, 129.9, 129.8 (J_{C-F} = 4 Hz), 128.7, 127.9, 127.6, 127.4 (J_{C-F} = 8 Hz), 126.6, 123.0, 119.4, 115.7 (J_{C-F} = 22 Hz), 112.4, 87.8, 16.5; Anal. Calcd for C₂₂H₁₇FN₂O: C, 76.73; H, 4.98; N, 8.13%; Found: C, 76.90; H, 5.04; N, 8.21%.



3-((1-(4-Bromophenyl)vinyl)oxy)-8-methyl-2-phenylimidazo[1,2-a]pyridine (4e):

Yellow gummy mass (82%, 66 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.05-8.02 (m, 2H), 7.76-7.72 (m, 2H), 7.62-7.59 (m, 3H), 7.41-7.37 (m, 2H), 7.30-7.27 (m, 1H), 6.98-6.96 (m, 1H), 6.70 (t, J = 6.8 Hz, 1H), 4.94 (d, J = 4.0 Hz, 1H), 4.18 (d, J = 4.0 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (100 MHz): δ 155.5, 140.4, 132.9, 132.5, 131.9, 130.8, 129.8, 128.7, 128.0, 127.7, 127.0, 126.6, 123.8, 123.1, 119.4, 112.4, 88.6, 16.5; Anal. Calcd for $C_{22}H_{17}BrN_2O$: C, 65.20; H, 4.23; N, 6.91%; Found: C, 65.39; H, 4.31; N, 6.79%.

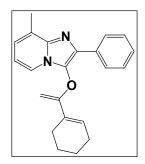


8-Methyl-2-phenyl-3-((4-phenylbut-1-en-2-yl)oxy)imidazo[1,2-a]pyridine (4f):

Yellow solid (95%, 67 mg); m.p.: 93-94 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.02-8.00 (m, 2H), 7.41-7.37 (m, 3H), 7.32-7.26 (m, 5H), 7.23-7.19 (m, 1H), 6.88-6.86 (m, 1H), 6.58 (t, J = 6.8 Hz, 1H), 4.13 (d, J = 3.2 Hz, 1H), 3.79 (d, J = 3.2 Hz, 1H), 3.06 (t, J = 8.0 Hz, 2H), 2.78-2.74 (m, 2H), 2.61 (s, 3H); ¹³C NMR (100 MHz): δ 159.0, 140.7, 140.2, 133.1, 130.4, 130.1, 128.6, 128.58, 128.51, 127.7, 127.4, 126.6, 126.3, 122.7, 119.5, 112.0, 88.0, 35.0, 33.3, 16.4; Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90%; Found: C, 81.15; H, 6.35; N, 8.01%.

3-((1-Cyclopropylvinyl)oxy)-8-methyl-2-phenylimidazo[1,2-a]pyridine (4g):

Brown oil (98%, 56 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.92-7.90 (m, 2H), 7.43 (d, J = 6.8 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.19-7.14 (m, 1H), 6.77-6.75 (m, 1H), 6.52 (t, J = 6.8 Hz, 1H), 4.04 (d, J = 2.8 Hz, 1H), 3.66 (d, J = 2.8 Hz, 1H), 2.51 (s, 3H), 1.64-1.57 (m, 1H), 0.87-0.83 (m, 2H), 0.73-0.70 (m, 2H); ¹³C NMR (100 MHz): δ 159.7, 140.1, 133.0, 130.3, 129.8, 128.5, 127.6, 127.3, 126.5, 122.6, 119.3, 112.0, 85.6, 16.4, 13.6, 5.3; HRMS calcd for C₁₉H₁₉N₂O [M +H]⁺: 291.1492; found [M +H]⁺: 291.1493.



3-((1-(Cyclohex-1-en-1-yl)vinyl)oxy)-8-methyl-2-phenylimidazo[1,2-a]pyridine (4h):

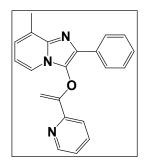
Brown oil (71%, 46 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.06-8.03 (m, 2H), 7.59 (d, J = 6.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.30-7.27 (m, 1H), 6.94-6.92 (m, 1H), 6.72 (t, J = 4.4 Hz, 1H), 6.67 (t, J = 6.8 Hz, 1H), 4.35 (d, J = 3.2 Hz, 1H), 3.90 (d, J = 3.2 Hz, 1H), 2.65 (s, 3H), 2.30-2.24 (m, 4H), 1.80-1.76 (m, 2H), 1.73-1.68 (m, 2H); ¹³C NMR (100 MHz): δ 157.1, 140.4, 133.2, 130.5, 130.1, 128.6, 127.8, 127.4, 127.1, 126.5, 124.3, 122.8, 119.7, 112.0, 86.5, 25.6, 25.2, 22.7, 22.1, 16.5; HRMS calcd for C₂₂H₂₃N₂O [M +H]⁺: 331.1805; found [M +H]⁺: 331.1813.

3-(Hex-1-en-2-yloxy)-8-methyl-2-phenylimidazo[1,2-a|pyridine (4i):

Yellow solid (96%, 58 mg); m.p.: 57-58 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.28-7.24 (m, 1H), 6.87 (d, J = 6.8 Hz, 1H), 4.07 (d, J = 3.2 Hz, 1H), 3.75 (d, J = 2.8 Hz, 1H), 2.61 (s, 3H), 2.41 (t, J = 8.0 Hz, 2H), 1.75-1.68 (m, 2H), 1.50-1.41 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz): δ 159.9, 140.1, 133.1, 130.3, 130.2, 128.5, 127.7, 127.4, 126.6, 122.7, 119.4, 112.0, 87.1, 33.2, 29.2, 22.3, 16.4, 13.9; Anal. Calcd for C₂₀H₂₂N₂O: C, 78.40; H, 7.24; N, 9.14%; Found: C, 78.20; H, 7.36; N, 9.21%.

8-Methyl-3-(oct-1-en-2-yloxy)-2-phenylimidazo[1,2-a]pyridine (4j):

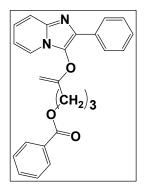
Yellow solid (97%, 64 mg); m.p.: 52-53 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.02-8.00 (m, 2H), 7.52 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.26-7.22 (m, 1H), 6.84 (d, J = 6.8 Hz, 1H), 6.60 (t, J = 6.8 Hz, 1H), 4.06 (d, J = 3.2 Hz, 1H), 3.74 (d, J = 2.8 Hz, 1H), 2.59 (s, 3H), 2.39 (t, J = 8.0 Hz, 2H), 1.75-1.67 (m, 2H), 1.43-1.39 (m, 2H), 1.34-1.30 (m, 4H), 0.91-0.87 (m, 3H); 13 C NMR (100 MHz): δ 159.9, 140.1, 133.2, 130.3, 130.2, 128.4, 127.6, 127.3, 126.6, 122.6, 119.4, 111.9, 87.1, 33.5, 31.7, 28.9, 27.0, 22.6, 16.4, 14.1; Anal. Calcd for C₂₂H₂₆N₂O: C, 79.00; H, 7.84; N, 8.38%; Found: C, 79.19; H, 7.74; N, 8.49%.



8-Methyl-2-phenyl-3-((1-(pyridin-2-yl)vinyl)oxy)imidazo[1,2-a]pyridine (4k):

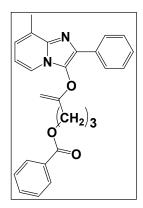
Brown gummy mass (75%, 49 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.70-8.69 (m, 1H), 8.07-8.05 (m, 2H), 8.00 (d, J = 8.0 Hz, 1H), 7.87-7.82 (m, 1H), 7.66 (d, J = 6.8 Hz, 1H), 7.41-7.34 (m, 3H), 7.29-7.26 (m, 1H), 6.98-6.96 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 5.68 (d, J = 3.2 Hz, 1H),

4.33 (d, J = 3.2 Hz, 1H), 2.68 (s, 3H); ¹³C NMR (100 MHz): δ 155.4, 151.3, 149.8, 140.4, 137.1, 132.9, 130.7, 129.9, 128.7, 128.3, 127.9, 127.6, 126.6, 124.0, 123.1, 119.6, 112.3, 91.2, 16.5; Anal. Calcd for C₂₁H₁₇N₃O: C, 77.04; H, 5.23; N, 12.84%; Found: C, 77.21; H, 5.30; N, 12.72%.



4-((2-Phenylimidazo[1,2-a]pyridin-3-yl)oxy)pent-4-en-1-yl benzoate (4l):

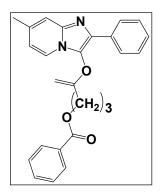
Brown oil (87%, 69 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.08-8.06 (m, 2H), 8.02-7.99 (m, 2H), 7.74-7.72 (m, 1H), 7.59-7.54 (m, 2H), 7.46-7.41 (m, 4H), 7.32-7.28 (m, 1H), 7.16-7.11 (m, 1H), 6.79-6.76 (m, 1H), 4.49 (t, J = 6.4 Hz, 2H), 4.20 (d, J = 3.2 Hz, 1H), 3.86 (d, J = 3.2 Hz, 1H), 2.63 (t, J = 8.0 Hz, 2H), 2.28-2.21 (m, 2H); ¹³C NMR (100 MHz): δ 166.7, 158.7, 139.9, 133.1, 132.8, 130.9, 130.3, 129.77, 129.72, 128.7, 128.5, 127.8, 126.6, 124.2, 121.6, 117.9, 112.3, 88.2, 64.1, 30.3, 26.4; Anal. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03%; Found: C, 75.13; H, 5.66; N, 7.11%.



4-((8-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)pent-4-en-1-yl benzoate (4m):

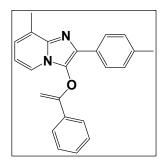
Brown oil (91%, 74 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.03-7.98 (m, 4H), 7.53 (d, J = 6.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.39-7.35 (m, 4H), 7.25-7.21 (m, 1H), 6.85-6.83 (m, 1H), 6.60 (t, J = 6.8 Hz, 1H), 4.41 (t, J = 6.4 Hz, 2H), 4.12 (d, J = 3.2 Hz, 1H), 3.80 (d, J = 2.8 Hz, 1H), 2.58 (s, 3H), 2.55 (t, J = 8.0 Hz, 2H), 2.21-2.14 (m, 2H); ¹³C NMR (100 MHz): δ 166.4, 158.6, 140.1, 133.0, 132.9, 130.2, 130.1, 129.8, 129.5, 128.4, 128.3, 127.6, 127.4, 126.5, 122.7, 119.3, 112.1, 87.9,

63.9, 30.1, 26.2, 16.3; HRMS calcd for $C_{26}H_{25}N_2O_3$ [M +H]⁺: 413.1860; found [M +H]⁺: 413.1867.



4-((7-Methyl-2-phenylimidazo[1,2-a|pyridin-3-yl)oxy)pent-4-en-1-yl benzoate (4n):

Yellow gummy mass (89%, 73 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.06 (m, 2H), 7.99-7.97 (m, 2H), 7.63 (d, J = 6.8 Hz, 1H), 7.59-7.55 (m, 1H), 7.47-7.40 (m, 4H), 7.33 (s, 1H), 7.31-7.26 (m, 1H), 6.63-6.61 (m, 1H), 4.49 (t, J = 6.8 Hz, 2H), 4.20 (d, J = 3.2 Hz, 1H), 3.87 (d, J = 2.8 Hz, 1H), 2.63 (t, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.29-2.22 (m, 2H); ¹³C NMR (100 MHz): δ 166.7, 158.8, 140.4, 135.1, 133.1, 133.0, 130.4, 130.3, 129.7, 129.4, 128.6, 128.5, 127.6, 126.5, 120.9, 116.2, 114.9, 88.1, 64.1, 30.3, 26.4, 21.5; Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; N, 6.79%; Found: C, 75.50; H, 5.79; N, 6.88%.

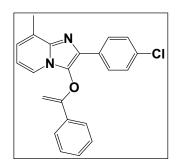


8-Methyl-3-((1-phenylvinyl)oxy)-2-(p-tolyl)imidazo[1,2-a]pyridine (40):

Brown gummy mass (84%, 57 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.4 Hz, 2H), 7.85-7.83 (m, 2H), 7.58 (d, J = 6.8 Hz, 1H), 7.45-7.40 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 6.90-6.88 (m, 1H), 6.60 (t, J = 6.8 Hz, 1H), 4.88 (d, J = 3.6 Hz, 1H), 4.10 (d, J = 3.6 Hz, 1H), 2.64 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz): δ 156.2, 140.2, 137.2, 133.6, 130.8, 130.1, 129.6, 129.4, 129.3, 128.6, 127.6, 126.4, 125.4, 122.8, 119.3, 112.1, 87.9, 21.3, 16.5; Anal. Calcd for C₂₃H₂₀N₂O: C, 81.15; H, 5.92; N, 8.23%; Found: C, 80.97; H, 5.81; N, 8.36%.

2-(4-Methoxyphenyl)-8-methyl-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4p):

Brown gummy mass (81%, 57 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 8.8 Hz, 2H), 7.89-7.87 (m, 2H), 7.63 (d, J = 6.8 Hz, 1H), 7.50-7.45 (m, 3H), 6.96-6.93 (m, 3H), 6.67 (t, J = 6.8 Hz, 1H), 4.94 (d, J = 3.6 Hz, 1H), 4.15 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H), 2.67 (s, 3H); ¹³C NMR (100 MHz): δ 159.2, 156.3, 140.3, 133.7, 130.8, 129.5, 129.2, 128.7, 127.9, 127.6, 125.8, 125.5, 122.9, 119.4, 114.1, 112.1, 88.0, 55.3, 16.5; HRMS calcd for $C_{23}H_{21}N_2O_2$ [M +H]⁺: 357.1598; found [M +H]⁺: 357.1593.

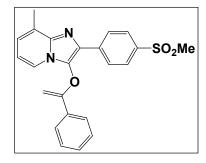


2-(4-Chlorophenyl)-8-methyl-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4q):

Brown gummy mass (91%, 65 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.04-8.00 (m, 2H), 7.89-7.86 (m, 2H), 7.63 (d, J = 6.8 Hz, 1H), 7.51-7.46 (m, 3H), 7.38-7.35 (m, 2H), 6.98-6.96 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 4.95 (d, J = 4.0 Hz, 1H), 4.14 (d, J = 3.6 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (100 MHz): δ 156.2, 140.4, 133.4, 133.3, 131.6, 130.1, 129.7, 129.6, 128.88, 128.80, 127.9, 127.8, 125.4, 123.2, 119.5, 112.4, 88.1, 16.5; Anal. Calcd for C₂₂H₁₇ClN₂O: C, 73.23; H, 4.75; N, 7.76%; Found: C, 73.05; H, 7.66; N, 7.63%.

8-Methyl-2-(3-nitrophenyl)-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4r):

Yellow solid (86%, 63 mg); m.p.: 155-156 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.96 (t, J = 2.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.10-8.08 (m, 1H), 7.89-7.87 (m, 2H), 7.67 (d, J = 6.8 Hz, 1H), 7.54-7.46 (m, 4H), 7.01 (d, J = 6.8 Hz, 1H), 6.73 (t, J = 6.8 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 4.12 (d, J = 3.6 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (100 MHz): δ 156.6, 148.7, 140.6, 134.9, 133.2, 132.0, 130.8, 129.8, 129.5, 128.8, 128.4, 128.2, 125.5, 123.6, 122.0, 121.4, 119.6, 112.8, 88.2, 16.4; HRMS calcd for $C_{22}H_{18}N_3O_3$ [M +H]*: 372.1343; found [M +H]*: 372.1346.

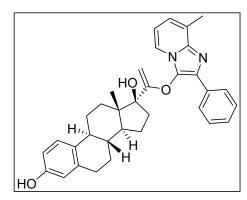


8-Methyl-2-(4-(methylsulfonyl)phenyl)-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4s):

Brown solid (83%, 67 mg); m.p.: 184-185 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.87-7.85 (m, 2H), 7.65 (d, J = 6.4 Hz, 1H), 7.50-7.47 (m, 3H), 7.00 (d, J = 6.8 Hz, 1H), 6.72 (t, J = 6.8 Hz, 1H), 4.96 (d, J = 4.0 Hz, 1H), 4.12 (d, J = 4.0 Hz, 1H), 3.03 (s, 3H), 2.66 (s, 3H); 13 C NMR (100 MHz): δ 156.3, 140.7, 138.7, 138.5, 133.1, 131.3, 129.8, 128.8, 128.7, 128.2, 127.7, 127.0, 125.3, 123.7, 119.6, 112.9, 88.2, 44.6, 16.4; HRMS calcd for $C_{23}H_{21}N_2O_3S$ [M +H]*: 405.1267; found [M +H]*: 405.1273.

8-Methyl-2-(naphthalen-2-yl)-3-((1-phenylvinyl)oxy)imidazo[1,2-a]pyridine (4t):

Brown gummy mass (88%, 66 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.60 (s, 1H), 8.27-8.24 (m, 1H), 7.95-7.93 (m, 2H), 7.89-7.80 (m, 3H), 7.69 (d, J = 6.4 Hz, 1H), 7.54-7.42 (m, 5H), 7.00-6.98 (m, 1H), 6.70 (t, J = 6.8 Hz, 1H), 4.97 (d, J = 3.6 Hz, 1H), 4.21 (d, J = 3.6 Hz, 1H), 2.74 (s, 3H); ¹³C NMR (100 MHz): δ 156.4, 140.5, 133.73, 133.70, 132.9, 130.7, 130.6, 130.5, 130.4, 129.6, 128.7, 128.5, 128.2, 127.8, 127.7, 126.0, 125.9, 125.5, 124.6, 123.1, 119.5, 112.3, 88.2, 16.6; HRMS calcd for $C_{26}H_{21}N_2O$ [M +H]⁺: 377.1648; found [M +H]⁺: 377.1676.



(8R,9S,13S,14S,17S)-13-Methyl-17-(1-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-

yl)oxy)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (4u): White gummy mass (72%, 74 mg); 1 H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 6.8 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 6.98 (d, J = 6.8 Hz, 1H), 6.73 (t, J = 6.8 Hz, 1H), 6.65-6.63 (m, 1H), 6.55 (d, J = 2.4 Hz, 1H), 4.42 (d, J = 4.0 Hz, 1H), 4.23 (d, J = 3.6 Hz, 1H), 2.92 (s, 1H), 2.83-2.76 (m, 2H), 2.65 (s, 3H), 2.34-2.26 (m, 2H), 2.19-2.11 (m, 2H), 1.91-1.85 (m, 2H), 1.75-1.69 (m, 3H), 1.55-1.49 (m, 2H), 1.36-1.25 (m, 2H), 1.04 (s, 3H); 13 C NMR (100 MHz): δ 162.7, 153.8, 140.5, 138.3, 132.7, 132.3, 131.6, 129.6, 128.5, 127.9, 127.6, 126.5, 123.3, 120.1, 115.5, 112.9, 112.5, 91.2, 86.0, 48.8, 47.7, 43.7, 39.6, 36.1, 34.2, 29.7, 27.5, 26.6, 23.0, 16.6, 14.6; HRMS calcd for $C_{34}H_{37}N_2O_3$ [M +H]+: 521.2799; found [M +H]+: 521.2797.

(7-Chloro-3-(4-methylbenzyl)imidazo[1,2-a]pyridin-2-yl)(cyclohexa-2,4-dien-1-

yl)methanone (**4v**): White solid (83%, 60 mg); m.p.: 165-166 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.29-8.27 (m, 2H), 8.04-8.03 (m, 1H), 7.60-7.56 (m, 2H), 7.52-7.48 (m, 2H), 7.28-7.25 (m, 1H), 7.14-7.08 (m, 4H), 4.66 (s, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz): δ 190.8, 142.0, 140.6, 138.0, 136.7, 133.0, 132.7, 130.9, 129.7, 129.2, 128.8, 128.2, 128.1, 123.9, 119.9, 108.7, 29.4, 21.1; Anal. Calcd for C₂₂H₁₉ClN₂O: C, 72.82; H, 5.28; N, 7.72%; Found: C, 73.00; H, 5.19; N, 7.59%.

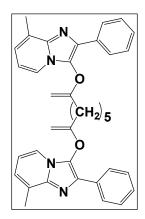
(7-Bromo-3-(4-methylbenzyl)imidazo[1,2-a]pyridin-2-yl)(cyclohexa-2,4-dien-1-

yl)methanone (**4w**): White solid (82%, 66 mg); m.p.: 161-162 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.29-8.27 (m, 2H), 7.93 (d, J = 1.6 Hz, 1H), 7.64-7.57 (m, 2H), 7.53-7.49 (m, 2H), 7.20-7.17 (m, 1H), 7.14-7.08 (m, 4H), 4.66 (s, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz): δ 190.8, 141.9, 140.8, 138.1, 136.7, 133.0, 132.8, 130.9, 129.7, 129.0, 128.3, 128.1, 127.2, 122.1, 121.7, 119.7, 29.4, 21.1; Anal. Calcd for C₂₂H₁₉BrN₂O: C, 64.87; H, 4.70; N, 6.88%; Found: C, 64.65; H, 4.81; N, 7.00%.

$$O$$
 $CH_2/5$

8-Methyl-3-(non-1-en-8-yn-2-yloxy)-2-phenylimidazo[1,2-a]pyridine (5a):

Brown oil (44%, 30 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.03-8.01 (m, 2H), 7.59 (d, J = 6.4 Hz, 1H), 7.44-7.41 (m, 2H), 7.31-7.27 (m, 1H), 6.95-6.93 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 4.13 (d, J = 3.2 Hz, 1H), 3.80 (d, J = 2.8 Hz, 1H), 2.65 (s, 3H), 2.46 (t, J = 8.0 Hz, 2H), 2.27-2.23 (m, 2H), 1.97 (t, J = 2.8 Hz, 1H), 1.83-1.76 (m, 2H), 1.66-1.56 (m, 4H); ¹³C NMR (100 MHz): δ 159.8, 140.2, 133.2, 130.4, 130.2, 128.5, 127.8, 127.5, 126.7, 122.7, 119.5, 112.1, 87.4, 84.5, 68.5, 33.5, 28.3, 26.6, 18.5, 16.5; HRMS calcd for $C_{23}H_{25}N_2O$ [M +H]⁺: 345.1961; found [M +H]⁺: 345.1965.



3,3'-(Nona-1,8-diene-2,8-diylbis(oxy))bis(8-methyl-2-phenylimidazo[1,2-a]pyridine) (5b):

Brown oil (26%, 30 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.06-8.04 (m, 4H), 7.60 (d, J = 6.8 Hz, 2H), 7.44 (t, J = 7.6 Hz, 4H), 7.29 (t, J = 7.6 Hz, 2H), 6.94-6.92 (m, 2H), 6.67 (t, J = 6.8 Hz, 2H), 4.16 (d, J = 2.8 Hz, 2H), 3.84 (d, J = 2.8 Hz, 2H), 2.65 (s, 6H), 2.51 (t, J = 8.0 Hz, 4H), 1.92-1.84 (m, 4H), 1.70-1.60 (m, 2H); ¹³C NMR (100 MHz): δ 159.8, 140.3, 133.2, 130.4, 130.2, 128.6, 127.9, 127.5, 126.7, 122.8, 119.5, 112.1, 87.5, 33.6, 28.8, 27.0, 16.5; HRMS calcd for $C_{37}H_{37}N_4O_2$ [M +H]⁺: 569.2911; found [M +H]⁺: 569.2920.

Ethyl (Z)-3-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)acrylate (7a):

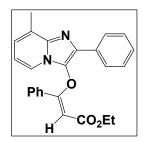
Yellow solid (94%, 60 mg); m.p.: 97-98 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.28-7.25 (m, 1H), 6.92 (d, J = 6.8 Hz, 1H), 6.70 (t, J = 6.8 Hz, 1H), 6.51 (d, J = 6.8 Hz, 1H), 5.22 (d, J = 6.8 Hz, 1H), 4.27 (q, J = 14.0 Hz, J = 7.2 Hz, 2H), 2.58 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz): δ 164.0, 155.7, 139.6, 133.3, 132.2, 128.7, 127.7, 127.6, 126.9, 123.2, 119.2, 112.6, 102.5, 60.3, 16.3, 14.3; Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69%; Found: C, 70.98; H, 5.55; N, 8.81%.

Methyl (Z)-3-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)acrylate (7b):

White solid (93%, 57 mg); m.p.: 94-95 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.00-7.97 (m, 2H), 7.85 (d, J = 6.4 Hz, 1H), 7.43-7.39 (m, 2H), 7.31-7.27 (m, 1H), 6.95-6.93 (m, 1H), 6.72 (t, J = 6.8 Hz, 1H), 6.54 (d, J = 6.8 Hz, 1H), 5.24 (d, J = 6.8 Hz, 1H), 3.82 (s, 3H), 2.60 (s, 3H); 13 C NMR (100 MHz): δ 164.5, 156.0, 139.7, 133.3, 132.2, 128.7, 127.8, 127.7, 127.0, 123.3, 119.2, 112.7, 102.0, 51.5, 16.4; HRMS calcd for $C_{18}H_{17}N_2O_3$ [M +H]⁺: 309.1234; found [M +H]⁺: 309.1242.

Methyl (Z)-3-((2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)oxy)acrylate (7c):

Brown gummy mass (68%, 46 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1H), 8.14-8.11 (m, 1H), 8.08-8.06 (m, 1H), 7.93-7.89 (m, 2H), 7.85-7.83 (m, 1H), 7.63 (d, J = 9.2 Hz, 1H), 7.50-7.47 (m, 2H), 7.25-7.21 (m, 1H), 6.91-6.87 (m, 1H), 6.61 (d, J = 6.8 Hz, 1H), 5.31 (d, J = 6.8 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (100 MHz): δ 164.6, 155.9, 139.7, 133.7, 133.4, 133.1, 129.3, 128.6, 128.5, 127.8, 126.48, 126.43, 126.3, 124.9, 124.7, 121.6, 117.9, 112.9, 102.6, 51.7; Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13%; Found: C, 73.45; H, 4.77; N, 8.02%.



Ethyl (Z)-3-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)-3-phenylacrylate (9a):

Yellow gummy mass (71%, 56 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, J = 6.8 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.19-7.16 (m, 1H), 7.04-6.99 (m, 4H), 6.89 (d, J = 6.8 Hz, 1H), 6.74 (t, J = 6.8 Hz, 1H), 5.55 (s, 1H), 4.23 (q, J = 14.4 Hz, J = 7.2 Hz, 2H), 2.53 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz): δ 164.5, 163.5, 132.9, 132.8, 130.5, 130.2, 128.5, 128.25, 128.22, 127.7, 127.69, 127.65, 127.60, 127.1, 122.6, 119.3, 112.5, 103.3, 60.5, 16.5, 14.4; Anal. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03%; Found: C, 75.56; H, 5.50; N, 6.93%.

Dimethyl 2-((8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)oxy)fumarate (9b):

Brown gummy mass (79%, 57 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J = 6.8 Hz, 1H), 7.87-7.85 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 6.99-6.97 (m, 1H), 6.77 (t, J = 6.8 Hz, 1H), 6.19 (s, 1H), 3.68 (s, 3H), 3.56 (s, 3H), 2.62 (s, 3H); ¹³C NMR (100 MHz): δ 163.7, 161.4, 149.6, 139.8, 132.3, 131.4, 129.5, 128.4, 127.8, 127.6, 127.4, 123.2, 120.3, 112.2, 109.9, 53.2, 52.1, 16.5; HRMS calcd for $C_{20}H_{19}N_2O_5$ [M +H]⁺: 367.1288; found [M +H]⁺: 367.1293.

Diethyl 2-((2-phenylimidazo[1,2-a|pyridin-3-yl)oxy)fumarate (9c):

Brown gummy mass (73%, 55 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, J = 6.8 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 9.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.28-7.24 (m, 1H), 7.21-7.17 (m, 1H), 6.86 (t, J = 6.8 Hz, 1H), 6.19 (s, 1H), 4.17 (q, J = 14.4 Hz, J = 7.2 Hz, 2H), 3.96 (q, J = 14.4 Hz, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz): δ 163.3, 160.8, 149.9, 139.4, 131.7, 131.3, 129.7, 128.4, 127.9, 127.6, 124.7, 122.5, 117.5, 112.3, 110.3, 62.6, 61.3, 14.1, 13.6; Anal. Calcd for C₂₁H₂₀N₂O₅: C, 66.31; H, 5.30; N, 7.36%; Found: C, 66.10; H, 5.21; N, 7.47%.

5. References

- 1. *a*) H. A. Riley and A. R. Gray, *Organic Syntheses*; Wiley & Sons: New York, NY, 1943; Collect. Vol. II, p 509; *b*) P. Wang, W.-J. Tao, X.-L. Sun, S. Liao and Y. Tang, *J. Am. Chem. Soc.*, 2013, **135**, 16849; *c*) S. Batra and H. Batchu, *Eur. J. Org. Chem.*, 2012, 2935.
- 2. a) B. Alcaide, J. Plumet, M. A. Sierra and C. Vicent, J. Org. Chem., 1989, 54, 5763; b) B. Alcaide, R. Pgrez-Ossorio, J. Plumet and M. A. Sierra, Tetrahedron Lett., 1986, 27, 1627.

6. NMR spectra for the synthesized compounds:



