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Construction of Porphyrin Based Photocatalyst Comprising Pyridinium Ionic Liquid Moiety for Metal-Free Visible Light-Assisted N-Arylation of Amines: Facile Approach to Afford Drug Intermediates

Bhairav Chandroday Mataghare^a, and Pundlik Rambhau Bhagat^{a,b*}

[a] Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632014, India.

[b] Carbon Dioxide Research and Green Technology Centre, Vellore Institute of Technology, Vellore-632014, India. drprbhagat111@gmail.com a,b*

*Corresponding author e-mail address: drprbhagat111@gmail.com (Pundlik Rambhau Bhagat)

Supporting information

Index

| S.N | Content | | | | |
|-----|---|----|------------|--|--|
| 1 | ¹ H NMR spectrum of 2-(4-formylbenzylidene) malononitrile (1A) | 5 | S1 | | |
| 2 | ¹³ C NMR spectrum of 2-(4-formylbenzylidene) malononitrile (1A) | 5 | S2 | | |
| 3 | FT-IR Spectrum of 2-(4-formyl benzylidene) malononitrile (1A) | 6 | S3 | | |
| 4 | ¹ H NMR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridin-1-ium chloride (1B) | 6 | S4 | | |
| 5 | ¹³ CNMR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridin-1-ium chloride (1B) | 7 | S5 | | |
| 6 | FT-IR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridin-1-ium chloride (1B) | 7 | S6 | | |
| 7 | FT-IR Spectrum of PBILFPc Photocatalyst | 8 | S7 | | |
| 8 | ¹ H NMR spectrum of Recycled PBILFPc Photocatalyst | 8 | S 8 | | |
| 9 | HRMS (M + H ⁺) Spectrum of PBILFPc Photocatalyst | 9 | S9 | | |
| 10 | Comparative FT-IR Spectrum of PBILFPc Photocatalyst upto 6th Run | 9 | S10 | | |
| 11 | ¹ H NMR spectrum of 4-(1H-imidazol-1-yl)aniline (A2) | 10 | S11 | | |
| 12 | ¹³ C NMR spectrum of 4-(1H-imidazol-1-yl)aniline (A2) | 10 | S12 | | |
| 13 | ¹ H NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole (A3) | 11 | S13 | | |
| 14 | ¹³ C NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole (A3) | 11 | S14 | | |
| 15 | ¹ H NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole (A4) | 12 | S15 | | |
| 16 | ¹³ C NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole (A4) | 12 | S16 | | |
| 17 | ¹ H NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole (A5) | 13 | S17 | | |
| 18 | ¹³ C NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole (A5) | 13 | S18 | | |
| 19 | ¹ H NMR spectrum of 4-(1H-imidazol-1-yl)phenol (A6) | 14 | S19 | | |
| 20 | ¹³ C NMR spectrum of 4-(1H-imidazol-1-yl)phenol (A6) | 14 | S20 | | |
| 21 | ¹ H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole (A7) | 15 | S21 | | |

| 22 | ¹³ C NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole (A7) | 15 | S22 |
|----|---|----|-----|
| 23 | ¹ H NMR spectrum of 1-phenyl-1H-imidazole (A8) | 16 | S23 |
| 24 | ¹ H NMR spectrum of 1-trityl-1H-imidazole (A9) | 16 | S24 |
| 25 | ¹³ C NMR spectrum of 1-trityl-1H-imidazole (A9) | 17 | S25 |
| 26 | ¹ H NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde (A10) | 17 | S26 |
| 27 | ¹³ C NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde (A10) | 18 | S27 |
| 28 | ¹ H NMR spectrum of 1-(3-nitrophenyl)-1H-1,2,4-triazole (A11) | 18 | S28 |
| 29 | ¹ H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-1,2,4-triazole (A12) | 19 | S29 |
| 30 | ¹ H NMR spectrum of 1-(4-nitrophenyl)-1H-1,2,4-triazole (A13) | 19 | S30 |
| 31 | ¹ H NMR spectrum of 4-(4-nitrophenyl)morpholine (A14) | 20 | S31 |
| 32 | ¹ H NMR spectrum of 4-(3-nitrophenyl)morpholine (A15) | 20 | S32 |
| 33 | ¹ H NMR spectrum of 4-(2,4-dinitrophenyl)morpholine (A16) | 21 | S33 |
| 34 | ¹ H NMR spectrum of 1-(3-nitrophenyl)-1H-indole (A17) | 21 | S34 |
| 35 | ¹³ C NMR spectrum of 1-(3-nitrophenyl)-1H-indole (A17) | 22 | S35 |
| 36 | ¹ H NMR spectrum of 1-(4-nitrophenyl)-1H-indole (A18) | 22 | S36 |
| 37 | ¹ H NMR spectrum of 1-phenyl-1H-indole (A19) | 23 | S37 |
| 38 | ¹ H NMR spectrum of 4-(1H-benzo[d]imidazol-1-yl)benzaldehyde (A20) | 23 | S38 |
| 39 | ¹ H NMR spectrum of 1-(4-nitrophenyl)-1H-benzo[d]imidazole (A21) | 24 | S39 |
| 40 | ¹ H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-benzo[d]imidazole (A22) | 24 | S40 |
| 41 | GCMS spectrum of Reaction Mixture after 5 hours | 25 | S41 |
| 42 | GCMS spectrum of Reaction Mixture after 10 hours | 26 | S42 |
| 43 | GCMS spectrum of Reaction Mixture after 15 hours | 27 | S43 |
| 44 | GCMS spectrum of Reaction Mixture after 20 hours | 28 | S44 |
| 45 | GCMS spectrum of 4-(1H-imidazol-1-yl)benzaldehyde A1 | 29 | S45 |
| 46 | GCMS spectrum of Aryl radical with TEMPO | 30 | S46 |
| 47 | Leaching Test of PBILFPc Photocatalyst. | 31 | S47 |
| 48 | BET Surface Area of PBILFPc Photocatalyst. | 32 | S48 |

| 49 | BET Isotherm Parameters of PBILFPc Photocatalyst. | 33 | S49 |
|----|--|----|-----|
| 50 | BET Adsorption/Desorption Isotherm of PBILFPc Photocatalyst. | 34 | S50 |
| 51 | TON & TOF Calculation as per the reviewer's suggestion | 35 | |
| 52 | Preparation of Stock Solution for UV-visible and Fluorescence Spectroscopy | 35 | |



Fig S1. ¹H NMR spectrum of 2-(4-formylbenzylidene) malononitrile (1A)



Fig S2. ¹³C NMR spectrum of 2-(4-formylbenzylidene) malononitrile (1A)



Fig. S3. FT-IR Spectrum of 2-(4-formyl benzylidene) malononitrile (1A)



Fig S4. ¹H NMR spectrum of 1-(carboxychloromethyl)-4-formyl-

pyridin-1-ium chloride (1B)



Fig S5. ¹³CNMR spectrum of 1-(carboxychloromethyl)-4-formyl-

pyridin-1-ium chloride (1B)



Fig S6. FT-IR spectrum of 1-(carboxychloromethyl)-4-formyl-

pyridine-1-ium chloride (1B)



Fig S7. FT-IR Spectrum of PBILFPc Photocatalyst



Fig S8. ¹H NMR spectrum of Recycled PBILFPc Photocatalyst



Fig S9. HRMS (M + H)+ Spectrum of PBILFPc Photocatalyst



Fig S10. Comparative FT-IR Spectrum of PBILFPc Photocatalyst upto 6th Run



Fig S11. ¹H NMR spectrum of 4-(1H-imidazol-1-yl)aniline (A2)



Fig S12. ¹³C NMR spectrum of 4-(1H-imidazol-1-yl)aniline (A2)



Fig S13. ¹H NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole (A3)



Fig S14. ¹³C NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole (A3)



Fig S15. ¹H NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole (A4)



Fig S16. ¹³C NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole (A4)



Fig S17. ¹H NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole (A5)



Fig S18. ¹³C NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole (A5)



Fig S19. ¹H NMR spectrum of 4-(1H-imidazol-1-yl)phenol (A6)



Fig S20. ¹³C NMR spectrum of 4-(1H-imidazol-1-yl)phenol (A6)



Fig S21. ¹H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole (A7)



Fig S22. ¹³C NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole (A7)



Fig S23. ¹H NMR spectrum of 1-phenyl-1H-imidazole (A8)



Fig S24. ¹H NMR spectrum of 1-trityl-1H-imidazole (A9)



Fig S25. ¹³C NMR spectrum of 1-trityl-1H-imidazole (A9)



Fig S26. ¹H NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde (A10)



Fig S27. ¹³C NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde (A10)



Fig S28. ¹H NMR spectrum of 1-(3-nitrophenyl)-1H-1,2,4-triazole (A11)



Fig S29. ¹H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-1,2,4-triazole (A12)



Fig S30. ¹H NMR spectrum of 1-(4-nitrophenyl)-1H-1,2,4-triazole (A13)



Fig S31. ¹H NMR spectrum of 4-(4-nitrophenyl)morpholine (A14)



Fig S32. ¹H NMR spectrum of 4-(3-nitrophenyl)morpholine (A15)



Fig S33. ¹H NMR spectrum of 4-(2,4-dinitrophenyl)morpholine (A16)



Fig S34. ¹H NMR spectrum of 1-(3-nitrophenyl)-1H-indole (A17)



Fig S35. ¹H NMR spectrum of 1-(3-nitrophenyl)-1H-indole (A17)



Fig S36. ¹H NMR spectrum of 1-(4-nitrophenyl)-1H-indole (A18)



Fig S37. ¹H NMR spectrum of 1-phenyl-1H-indole (A19)



Fig S38. ¹H NMR spectrum of 4-(1H-benzo[d]imidazol-1-yl)benzaldehyde (A20)



Fig S39. ¹H NMR spectrum of 1-(4-nitrophenyl)-1H-benzo[d]imidazole (A21)



Fig S40. ¹H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-benzo[d]imidazole (A22)



Fig S41. GCMS spectrum of Reaction Mixture after 5 hours



Fig S42. GCMS spectrum of Reaction Mixture after 10 hours



Fig S43. GCMS spectrum of Reaction Mixture after 15 hours



Fig S44. GCMS spectrum of Reaction Mixture after 20 hours



Fig S45. GCMS spectrum of 4-(1H-imidazol-1-yl)benzaldehyde [BMCN-IMI-01]A1



Fig S46. GCMS spectrum of Aryl radical with TEMPO

| Time | A* | В | С |
|----------------|--|------------------------------------|--|
| (h) | Under Optimized Reaction | | |
| | conditions | | |
| | | | |
| 0 | R1 + R2 + 20 mg PBILFPc | R1 + R2 + 20 mg PBILFPc | R1 + R2 + 20 mg PBILFPc |
| | + ACN 10 mL | + ACN 10 mL | + ACN 10 mL |
| 5 | Reaction continued | Reaction works up to know | Photocatalyst removed by |
| | | | |
| | | the yield of the product at 5 | filtration and continued |
| | | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 |
| | | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 h |
| | | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 h |
| 10 | Reaction continued | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 h Reaction continued |
| 10 15 | Reaction continued Reaction continued | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 h Reaction continued Reaction continued |
| 10 15 20 | Reaction continued Reaction continued Reaction continued | the yield of the product at 5 h | filtration and continued reaction under 5 W LED for 20 h Reaction continued Reaction continued Reaction continued |



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Quantachrome

| Operator: Sample ID: Sample Desc: Sample Weight: Approx. Outgas Tir Analysis gas: Analysis Time: Analysis Mode: VoldVol. Mode: | VIT Date: PDK-BM-CAT-II-180723 0.0194 g ne:3.6 hrs Nitrogen 1:10 hr:min Standard He Measure | 2023/07/18 O Filename: P Comment: Instrument: A Final Outgas Temp.: Non-Ideality: 6. Bath temp.: 77 Cold Zone V: 3. <u>Multi-Poi</u> | perator: VIT DK-BM-CAT-II-180 utosorb IQ Station 1 200 °C 58e-05 1/Torr 7.35 K 70928 cc nt BET | 1723.qps Extended in CellType: VoldVol Re Warm Zone | Date:2023/07/19 nfo: Available 9mm measure:off V: 13.1482 cc |
|--|--|---|---|---|--|
| Adsorbate model | Dat Thermal Transpiration: Nitrogen Molec. Wt.: 28.013 | a Reduction Pa on Eff. mol. diam Temperature Cross Section | arameters C eter (D): 3.54 A 77.350K : 16.200 A ² | Data Eff. cell ster Liquid Dens | m diam. (d): 4.0000 m |
| | | -Multi-Point | BET Data — | | |
| Relative Pressure [P/Po] | Volume @ STP 1 [cc/g] | / [W((Po/P) - 1)] [1/g] | Relative Pressure [P/Po] | Volume @ STP [cc/g] | 1 / [W((Po/P) - 1)] [1/g] |
| 1.01160e 1.51146e 2.00873e | 01 5.8469 01 8.6003 01 11.4228 | 1.5401e+01 1.6566e+01 1.7607e+01 | 2.51051e-01 2.99693e-01 | 14.2562 19.5383 | 1.8813e+01 1.7525e+01 |
| | Corre | Slope = Intercept = lation coefficient, r = C constant= | 13.116 1/ 1.455e+ 0.80789 1.902 | g 01 1/g 3 | |
| | | Surface Area = | 125.882 m | ²/g | |
| | | | | | |
| | | | | | |

Fig S48. BET Surface Area of PBILFPc Photocatalyst.

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| | | Report | | |
|-----------------------------|---|--|---|--|
| VIT Date: | 2023/07/18 | Operator: VIT | Date | :2023/07/19 |
| PDK-BM-CAT-II-180723 | Filename: | PDK-BM-CAT-II-18072 | 3.qps | |
| | Comment: | | | |
| 0.0194 g | Instrument: | Autosorb iQ Station 1 | | |
| Approx. Outgas Time:3.6 hrs | | mp.:200 °C | Extended info: | Available |
| Nitrogen | Non-ideality: | 6.58e-05 1/Torr | CellType: | 9mm |
| 1:10 hr:min | Bath temp.: | 77.35 K | | |
| Standard | | | VoidVol Remeas | ure:off |
| He Measure | Cold Zone V: | 3 70928 cc | Warm Zone V: | 13 1482 cc |
| | VIT Date: PDK-BM-CAT-II-180723 0.0194 g Ime:3.6 hrs Nitrogen 1:10 hr:min Standard He Measure | VIT Date:2023/07/18 PDK-BM-CAT-II-180723 Filename: Comment: 0.0194 g Instrument: 'ime:3.6 hrs Final Outgas Tei Nitrogen Non-ideality: 1:10 hr:min Bath temp.: Standard He Measure Cold Zene V: | VIT Date:2023/07/18 Operator: VIT PDK-BM-CAT-II-180723 Filename: PDK-BM-CAT-II-180723 Comment: Autosorb iQ Station 1 'ime:3.6 hrs Final Outgas Temp.:200 °C Nitrogen Non-ideality: 6.58e-05 1/Torr 1:10 hr:min Bath temp.: 77.35 K Standard Ha Massure Cald Zaas V. 2.70028 cc | VIT Date:2023/07/18 Operator: VIT Date PDK-BM-CAT-II-180723 Filename: PDK-BM-CAT-II-180723.qps Comment: 0.0194 g Instrument: Autosorb (Q Station 1 Time:3.6 hrs Final Outgas Temp.:200 °C Extended info: Nitrogen Non-ideality: 6.58e-05 1/Torr CellType: 1:10 hr:min Bath temp.: 77.35 K VoldVol Remease bits Moneyurga Cald Zana V: 2.70028 co VoldVol Remease V: |

—Data Reduction Parameters Data -

| Thermal Transpiration: on | Eff. mol. diameter | or (D): 3.54 A | Eff. cell stem dia | m. (d): 4.0000 mm |
|---------------------------|---|---|---|--|
| Nitrogen | Temperature | 77.350K | | |
| Molec. Wt.: 28.013 | Cross Section: | 16.200 A ^a | Liquid Density: | 0.808 g/cc |
| | Thermal Transpiration: on Nitrogen Molec. Wt.: 28.013 | Thermal Transpiration: on Nitrogen Eff. mol. diameter Molec. Wt.: 28.013 Cross Section: | Thermal Transpiration: on Nitrogen Eff. mol. diameter (D): 3.54 Å Molec. Wt.: 28.013 Temperature Cross Section: 77.350K | Thermal Transpiration: on Nitrogen Eff. mol. diameter (D): 3.54 Å Eff. cell stem dia Nolec. Wt.: 28.013 Temperature 77.350K Liquid Density: |

| Isotherm Data | | | | | | |
|---|--|--|---|--|---|--|
| Relative Pressure | Volume @ STP [cc/g] | Relative Pressure | Volume @ STP [cc/g] | Relative Pressure | Volume @ STP [cc/g] | |
| 5.14290e-02 1.01160e-01 1.51146e-01 2.00873e-01 2.51051e-01 2.99693e-01 3.50258e-01 4.00412e-01 4.50805e-01 5.00173e-01 5.50398e-01 6.00149e-01 6.50263e-01 | 3.0293 5.8469 8.6003 11.4228 14.2562 19.5383 23.6354 27.3751 30.7916 34.3641 37.9283 41.4892 45.0035 | 7.50562e-01 8.00023e-01 9.01418e-01 9.94482e-01 9.94422e-01 9.93438e-01 9.50859e-01 8.99781e-01 8.50510e-01 8.00176e-01 7.50897e-01 7.00484e-01 | $\begin{array}{c} 51.9415\\ 55.4085\\ 59.0659\\ 62.8823\\ 66.3261\\ 91.9689\\ 89.6739\\ 70.4747\\ 67.5018\\ 64.6092\\ 61.6616\\ 58.6172\\ 55.5266\end{array}$ | 5.99838e-01 5.49707e-01 4.99487e-01 3.99568e-01 3.49602e-01 2.99576e-01 1.99747e-01 1.49557e-01 9.96401e-02 5.16977e-02 | 49.4972 46.1393 42.6190 39.2034 35.3820 31.5638 27.6544 23.7072 19.5642 15.3359 11.1639 6.8480 | |

Report id:{565228057:20230719 120813235} Page 1 of 1

Fig S49. BET Isotherm Parameters of PBILFPc Photocatalyst.

ion and Reduction @ 1994-2016, Quantachrome Instruments version 5.0

n Data Acquisi



Fig S50. BET Adsorption/Desorption Isotherm of PBILFPc Photocatalyst.

TON & TOF Calculation as per the reviewer's suggestion

The TON of the photocatalyst was found to be 9,33,333 and TOF is 46,666. The detailed calculation are as follows:

Molecular Weight of the Photocatalyst = 1026.071

Quantity of Photocatalyst utilized for the reaction 20mg = 0.02g

Moles of Photocatalyst =
$$(0.02/1026.071) \times 100 =$$

= 0.00195

For TON = (Optimized time of reaction x yield of reaction) / moles of Photocatalyst

$$= (20 \times 91) / 0.00195$$

= 9,33,333.33
For TOF = TON / Reaction Time
= 9,33,333.33 / 20
=46,666.67 h⁻¹

Preparation of Stock Solution for UV-visible and Fluorescence Spectroscopy

A 1mM Stock solution of PBILFPc Photocatalyst was prepared.

A standard working concentration of $2x10^{-5}$ M was used for UV-visible and Fluorescence spectroscopy studies.

$$W = \frac{NEV}{1000} = (10^{-3} \text{ x } 1026.071 \text{ x } 10) / 1000$$

W = 10.26 x 10^{-3} g
W = 10 mg in 10mL DMSO
Stock = 10^{-3} M in DMSO (10mL)

Note: Due to the heterogeneous nature of the Photocatalyst, it is difficult for us to properly dissolve it in DMSO, we gave gentle heating and sonication to the stock solution, and after we took it for analysis.

Now Working Concentration

Stock Solution : Working Solution

$$N1V1 = N2V2$$

 $10^{-3} \times 40\mu L = N2 \times 2mL$
 $N2 = (10^{-3} \times 40 \times 10^{-3} mL) / 2$
 $N2 = 2 \times 10^{-5} M$