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Electronic Supplementary Information.....

Diamine-functionalized porous graphene oxide sheet decorated with palladium oxide nanoparticles for the oxidative amidation of aldehydes

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Spectral Data of Representative Products

1. 4-nitro-N-phenylbenzamide



Yellow solid

¹H-NMR (400 MHz, CDCl₃): δ 8.55 (s, 1H), 8.32 (d, 2H, J = 8.8 Hz), 8.07 (d, 2H, J = 8.8 Hz), 7.42 (t, 2H, J = 8 Hz), 7.24-7.31 (m, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 157.47, 151.00, 149.37, 141.65, 129.50, 129.43, 127.17, 124.11, 121.05 ppm. HRMS (ES): Calcd: 242.0691. Found: 243.0741 [M+H]⁺ and 244.0721 [MH+2]⁺.



Fig. S1 (b): ¹³C-NMR of 4-nitro-N-phenylbenzamide

2. N-(p-tolyl)benzamide



Orange solid

¹H-NMR (400 MHz, CDCl₃): δ 8.48 (s, 1H), 7.90-7.92 (m, 2H), 7.46-7.50 (m, 3H), 7.15-7.23 (m, 4H), 2.39 (s, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 159.76, 149.53, 136.42, 135.93, 131.34, 129.89, 128.83, 120.94, 21.15 ppm. HRMS (ES): Calcd: 211.0997. Found: 212.1037 [M+H]⁺ and 213.1048 [MH+2]⁺.



3. 4-nitro-N-(p-tolyl)benzamide



¹**H-NMR (400 MHz, CDCl₃):** δ 8.56 (s, 1H), 8.31 (d, 2H, J = 8.8 Hz), 8.06 (d, 2H, J = 8.8 Hz), 7.17-7.24 (m, 4H), 2.38 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 156.46, 149.22, 148.32, 141.85, 137.35, 130.05, 129.37, 124.10, 121.09, 21.20 ppm. **HRMS (ES):** Calcd: 256.0848. Found: 257.0878. [M+H]⁺ and 258.0898 [MH+2]⁺.





Fig. S3 (b): ¹³C-NMR of 4-nitro-N-(p-tolyl)benzamide

4. 2-nitro-N-(p-tolyl)benzamide



¹H-NMR (400 MHz, CDCl₃): δ 8.94 (s, 1H), 8.30 (d, 1H, J = 8 Hz), 8.05 (d, 1H, J = 8.4 Hz), 7.72 (t, 1H, J = 8 Hz), 7.57-7.61 (m, 1H), 7.21(s, 4H), 2.38 (s, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 154.93, 149.33, 148.53, 137.11, 133.65, 131.34, 131.10, 129.99, 129.78, 124.61, 121.29, 21.17 ppm. HRMS (ES): Calcd: 256.0848. Found: 257.0888 [M+H]⁺ and 258.0898 [MH+2]⁺.



5. 4-methyl-N-(p-tolyl)benzamide



¹**H-NMR (400 MHz, CDCl₃):** δ 8.42 (s, 1H), 7.78 (d, 2H, J = 8 Hz), 7.26 (d, 2H, J = 7.6 Hz), 7.11-7.20 (m, 4H), 2.41 (s, 3H), 2.36 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 159.72, 149.70, 141.76, 135.66, 133.85, 129.82, 129.58, 128.79, 120.89, 21.71, 21.09 ppm. **HRMS (ES):** Calcd: 225.1154. Found: 226.1204 [M+H]⁺ and 227.1194 [MH+2]⁺.



Fig. S5 (a): ¹H-NMR 4-methyl-N-(p-tolyl)benzamide



Fig. S5 (b): ¹³C-NMR of 4-methyl-N-(p-tolyl)benzamide

6. 2-methoxy-N-(p-tolyl)benzamide



Orange solid

¹**H-NMR (400 MHz, CDCl₃):** δ 9.01 (s, 1H), 8.23 (d, 1H, J = 8 Hz), 7.45 (t, 1H, J = 7.6 Hz), 7.23 (s, 4H), 7.08 (t, 1H, J = 7.6 Hz), 6.95 (d, 1H, J = 8.4 Hz), 3.88 (s, 3H), 2.41 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 159.56, 155.79, 150.31, 135.65, 132.70, 129.86, 127.57, 124.97, 121.21, 120.99, 111.23, 55.63, 21.18 ppm. **HRMS (ES):** Calcd: 241.1103. Found: 242.1153 [M+H]⁺ and 243.1143 [MH+2]⁺.



Fig. S6 (b): ¹³C-NMR of 2-methoxy-N-(p-tolyl)benzamide

7. 4-chloro-N-(p-tolyl)benzamide



¹H-NMR (400 MHz, CDCl₃): δ 8.42 (s, 1H), 7.82 (d, 2H, J = 8.4 Hz), 7.43 (d, 2H, J = 8.4 Hz), 7.12-7.20 (m, 4H), 2.36 (s, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 158.13, 149.09, 137.24, 136.24, 134.89, 131.02, 129.90, 129.91, 129.14, 120.90, 21.13 ppm. HRMS (ES): Calcd: 245.0607. Found: 246.0647 [M+H]⁺ and 247.0637 [MH+2]⁺.



Fig. S7 (b): ¹³C-NMR of 4-chloro-N-(p-tolyl)benzamide

8. 3-hydroxy-N-(p-tolyl)benzamide



¹H-NMR (400 MHz, CDCl₃): δ 8.33 (s, 1H), 7.40 (s, 1H), 7.30-7.32 (m, 1H), 7.25 (t, 1H, J = 8 Hz), 7.11-7.18 (m, 4H), 6.93 (d, 1H, J = 7.6 Hz), 2.34 (s, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 161.08, 156.84, 148.58, 137.01, 136.42, 130.18, 130.02, 122.02, 121.07, 119.50, 114.61, 21.13 ppm. HRMS (ES): Calcd: 227.0946. Found: 228.0996 [M+H]⁺ and 229.0986 [MH+2]⁺.



9. N-(p-tolyl)thiophene-2-carboxamide



Brown solid

¹**H-NMR (400 MHz, CDCl₃):** δ 8.57 (s, 1H), 7.48 (d, 1H, J = 5.2 Hz), 7.45 (d, 1H, J = 3.6 Hz), 7.17-7.19 (m, 2H), 7.11-7.14 (m, 3H), 2.36 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 152.42, 148.89, 143.06, 136.03, 132.07, 130.16, 129.87, 127.83, 121.02, 21.15 ppm. **HRMS (ES):** Calcd: 217.0561. Found: 218.0601 [M+H]⁺ and 219.0591 [MH+2]⁺.



Fig. S9 (a): ¹H-NMR of N-(p-tolyl)thiophene-2-carboxamide



Fig. S9 (b): ¹³C-NMR of N-(p-tolyl)thiophene-2-carboxamide

10. 5-bromo-2-hydroxy-4-nitro-N-(p-tolyl)benzamide



Yellow solid

¹**H-NMR (400 MHz, CDCl₃):** δ 13.41 (brs, 1H), 8.54 (s, 1H), 7.49 (s, 1H), 7.43 (d, 1H, 8.8 Hz), 7.18-7.24 (m, 4H), 6.92 (d, 1H, J = 8.8 Hz), 2.39 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 160.15, 145.31, 137.50, 135.45, 134.09, 130.12, 121.04, 120.71, 119.23, 110.43, 21.10 ppm. **HRMS (ES):** Calcd: 349.9902. Found: 350.9932 [M+H]⁺ and 351.9942 [MH+2]⁺.



Fig. S10 (a): ¹H-NMR of 5-bromo-2-hydroxy-N-(p-tolyl)benzamide



Fig. S10 (b): ¹³C-NMR of 5-bromo-2-hydroxy-N-(p-tolyl)benzamide

11. 3,5-dichloro-2-hydroxy-N-(p-tolyl)benzamide



Reddish Brown solid

¹**H-NMR (400 MHz, CDCl₃):** δ 14.48 (brs, 1H), 8.55 (s, 1H), 7.43 (d, 1H, J = 2.4 Hz), 7.28 (d, 1H, 2.8 Hz), 7.19-7.23 (m, 4H), 2.38 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 159.22, 156.22, 144.12, 138.26, 132.54, 130.32, 129.64, 123.26, 122.89, 121.13, 120.30, 21.23 ppm. **HRMS (ES):** Calcd: 295.0167. Found: 296.0217 [M+H]⁺ and 297.0197 [MH+2]⁺.



Fig. S11 (a): ¹H-NMR of 3,5-dichloro-2-hydroxy-N-(p-tolyl)benzamide



Fig. S11 (b): ¹³C-NMR of 3,5-dichloro-2-hydroxy-N-(p-tolyl)benzamide

12. N-phenylbenzamide



Yellow Solid

¹H-NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 7.87-7.92 (m, 2H), 7.48 (d, 1H, J = 2 Hz), 7.47 (d, 1H, J = 1.6 Hz) 7.37-7.41 (m, 3H), 7.19-7.23 (m, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 160.53, 152.16, 136.29, 131.47, 129.23, 128.90, 128.86, 126.02, 120.95 ppm. HRMS (ES): Calcd: 197.0841. Found: 198.0881 [M+H]⁺ and 199.0871 [MH+2]⁺.



13. N-(p-tolyl)-[1,1'-biphenyl]-4-carboxamide



Yellow solid

¹H-NMR (400 MHz, CDCl₃): δ 8.49 (s, 1H), 7.95 (d, 2H, J = 8 Hz), 7.69 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 7.2 Hz), 7.45 (t, 2H, J = 8 Hz), 7.37 (t, 1H, J = 7.2 Hz), 7.15-7.21 (m, 4H), 2.37 (s, 3H) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 159.14, 149.52, 143.91, 140.35, 135.88, 135.36, 129.83, 129.23, 128.93, 127.90, 127.46, 127.21, 120.90, 21.07 ppm. HRMS (ES): Calcd: 287.1310. Found: 288.1331 [M+H]⁺ and 289.1342 [MH+2]⁺.



Fig. S13 (a): ¹H-NMR of N-(p-tolyl)-[1,1'-biphenyl]-4-carboxamide



Fig. S13 (b): ¹³C-NMR of N-(p-tolyl)-[1,1'-biphenyl]-4-carboxamide

14. 3,4,5-trimethoxy-N-(p-tolyl)benzamide



Pale Yellow solid

¹**H-NMR (400 MHz, CDCl₃):** δ 8.36 (s, 1H), 7.19 (d, 2H, J = 8 Hz), 7.12-7.15 (m, 4H), 3.94 (s, 6H), 3.91 (s, 3H), 2.37 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 159.10, 153.52, 149.36, 140.84, 135.76, 131.90, 129.79, 120.80, 105.69, 60.99, 56.26, 21.01 ppm. **HRMS (ES):** Calcd: 301.1314. Found: 302.1326 [M+H]⁺ and 303.1321 [MH+2]⁺.



Fig. S14 (b): ¹³C-NMR of 3,4,5-trimethoxy-N-(p-tolyl)benzamide

15. N-(p-tolyl)propionamide

Ö Brownish Liquid

Brownish Liquid

¹H-NMR (400 MHz, CDCl₃): δ 7.11 (s, 1H), 6.94 (d, 2H, J = 7.6 Hz), 6.59 (d, 2H, J = 8 Hz), 2.22 (s, 3H), 2.17 (t, 2H, J = 8.4 Hz), 1.07-1.12 (m, 2H), 0.97 (t, 3H, J = 7.6 Hz) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 163.95, 141.12, 134.84, 129.78, 120.71, 41.94, 20.42, 19.05, 13.78 ppm. HRMS (ES): Calcd: 163.0997. Found: 164.0992 [M+H]⁺ and 165.0998 [MH+2]⁺.





Fig. S15 (b): ¹³C-NMR of N-(p-tolyl)propionamide

16. 4-fluoro-N-propylbenzamide



¹**H-NMR (400 MHz, CDCl₃):** δ 8.21 (s, 1H), 7.68-7.72 (m, 2H), 7.06 (t, 2H, J = 8.8 Hz), 3.54 (t, 2 H, J = 6.8 Hz), 1.67-1.73 (m, 2H), 0.93 (t, 3H, J = 7.2 Hz) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 165.49, 162.99, 132.70, 129.98, 129.89, 115.81, 115.59, 63.46, 24.11, 11.90 ppm. **HRMS (ES):** Calcd: 181.0903. Found: 182.0908 [M+H]⁺ and 183.0914 [MH+2]⁺.



Fig. S16 (b): ¹³C-NMR of 4-fluoro-N-propylbenzamide

17. 2-hydroxy-3-methoxy-N-pentylbenzamide



Yellowish Liquid

¹H-NMR (400 MHz, CDCl₃): δ 8.20 (s, 1H), 6.81 (d, 1H, J = 8 Hz), 6.77 (d, 1H, J = 8 Hz), 6.68 (t, 1H, J = 8 Hz), 3.80 (s, 3H), 3.48 (t, 2H, J = 6.8 Hz), 1.56-1.63 (m, 2H), 1.24-1.32 (m, 4H) 0.83 (t, 3H, J = 7.2 Hz) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 164.56, 153.09, 148.73, 122.82, 118.35, 117.43, 113.71, 58.60, 56.00, 30.52, 29.28, 22.43, 14.02 ppm. HRMS (ES): Calcd: 237.1365. Found: 238.1358 [M+H]⁺ and 239.1362 [MH+2]⁺.



Fig. S17 (b): ¹³C-NMR of 2-hydroxy-3-methoxy-N-pentylbenzamide

18. 4-nitro-N-pentylbenzamide



Yellowish Liquid

¹H-NMR (400 MHz, CDCl₃): δ 8.32 (s, 1H), 8.21 (d, 2H, J = 8.4 Hz), 7.86 (d, 2H, J = 8.8 Hz), 3.63 (t, 2H, J = 7.2 Hz), 1.65-1.72 (m, 2H), 1.31-1.33 (m, 4H), 0.87 (t, 3H, J = 6.8 Hz) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 158.49, 148.92, 141.92, 128.75, 123.90, 62.04, 30.48, 29.60, 22.54, 14.10 ppm. HRMS (ES): Calcd: 236.1161. Found: 237.1155 [M+H]⁺ and 238.1167 [MH+2]⁺.



Fig. S18 (b): ¹³C-NMR of 4-nitro-N-pentylbenzamide

19. 3,4,5-trimethoxy-N-pentylbenzamide



¹**H-NMR (400 MHz, CDCl₃):** δ 7.99 (s, 1H), 6.82-6.85 (m, 2H), 3.69-3.76 (m, 9H), 3.39-3.46 (m, 2H), 1.52-1.55 (m, 2H), 1.17-1.19 (m, 4H), 0.75 (s, 3H) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 160.31, 153.31, 139.91, 131.87, 104.88, 61.54, 60.74, 56.04, 40.78, 30.57, 29.47, 22.45, 14.03 ppm. **HRMS (ES):** Calcd: 281.1627. Found: 282.1632 [M+H]⁺ and 283.1638 [MH+2]⁺.





20. N-pentylthiophene-2-carboxamide



¹H-NMR (400 MHz, CDCl₃): δ 8.32 (s, 1H), 7.34 (d, 1H, J = 4.8 Hz), 7.25 (d, 1H, J = 3.2 Hz), 7.02-7.04 (m, 1H), 3.53 (t, 2H, J = 6.8 Hz), 1.64 (m, 2H), 1.29-1.34 (m, 4H), 0.88 (t, 3H, J = 7.2 Hz) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 153.99, 142.73, 130.10, 128.57, 127.35, 61.50, 30.63, 29.60, 22.58, 14.13 ppm. HRMS (ES): Calcd: 197.0874. Found: 198.0879 [M+H]⁺ and 199.0881[MH+2]⁺.



Fig. S20 (a): ¹H-NMR of N-pentylthiophene-2-carboxamide





^{21. 4-}fluoro-N-octylbenzamide



¹H-NMR (400 MHz, CDCl₃): δ 8.22 (s, 1H), 7.61 (d, 2H, J = 8 Hz), 7.20 (d, 2H, J = 8 Hz), 3.58 (t, 2H, J = 6.8 Hz), 1.67 (m, 2H), 1.27-1.32 (m, 10H), 0.87 (t, 3H, J = 6.4 Hz) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ 160.73, 140.69, 133.73, 129.39, 128.02, 61.78, 31.86, 30.96, 29.43, 29.28, 27.37, 22.67, 21.46, 14.10 ppm. HRMS (ES): Calcd: 251.1685. Found: 252.1692 [M+H]⁺ and 253.1697 [MH+2]⁺.



Fig. S21 (b): ¹³C-NMR of 4-fluoro-N-octylbenzamide

22. 4-methoxy-N-octylbenzamide



Yellowish Liquid

¹**H-NMR (400 MHz, CDCl₃):** δ 8.18 (s, 1H), 7.65 (d, 2H, J = 8.8 Hz), 6.90 (d, 2H, J = 8.8 Hz), 3.82 (s, 3H) 3.55 (t, 2H, J = 7.2 Hz), 1.63-1.68 (m, 2H), 1.25-1.30 (m, 10H), 0.87 (t, 3H, J = 6.8 Hz) ppm. ¹³**C-NMR (75 MHz, CDCl₃):** δ 161.53, 160.18, 129.62, 129.37, 114.02, 61.80, 55.42, 31.94, 31.10, 29.51, 29.36, 27.44, 22.75, 14.19 ppm. **HRMS (ES):** Calcd: 263.1885. Found: 264.1889 [M+H]⁺ and 265.1893 [MH+2]⁺.



Fig. S22 (a): ¹H-NMR of 4-methoxy-N-octylbenzamide



Fig. S22 (b): ¹³C-NMR of ¹H-NMR of 4-methoxy-N-octylbenzamide



Fig. S23: SAED pattern of PGO-NH₂@PdO nano-catalyst.



a) E-factor:

(Total mass of stoichiometric reactant) – (Total mass of

Mass of product

E-factor =
$$(0.151 + 0.107) - (0.251)/0.251$$

= 0.028
b) Atom Economy (AE):
 $[M.W. of product / \sum (M.W. of stoichiometric reactants)]_{X 100}$
 $AE = [256.26 / (151.12 + 107.15)] X 100$
= 99.22%
c) Carbon Efficiency (CE):
 $[(No. of moles of product)(No. of carbon in product)]$
 $\overline{\sum} [(No. of moles of reactant)(No. of carbon in reactant)]_{X 100}}$
 $cE = \overline{[(1 X 7) + (1 X 6)]}_{X 100} = 98 \%$
d) Process Mass Intensity (PMI):
 $Mass of product$
 $Mass of product$
 $Mass of product$
 $Mass of product$
e) Reaction Mass Efficiency (RME):
 $\overline{\sum} (Mass of stoichiometric reactants)}$
 $RME = \overline{(0.151 + 0.107)}_{X 100} = 97.29 \%$

Table S1: CHNS analysis of GO, PGO-COOH, PGO-COCl, PGO-NH₂ and PGO-NH₂@PdO.

Entry	Sample (10 mg)	Nitrogen (wt %)	Carbon (wt %)	Hydrogen (wt %)

1.	GO	0.68	60.31	4.49
2.	PGO-COOH	0.42	49.92	2.89
3.	PGO-COC1	2.49	25.89	3.39
4.	PGO-NH ₂	8.67	40.03	3.74
5.	PGO-NH ₂ @PdO	8.54	41.23	3.15

Table S2: A comparison of the TON and TOF of PGO-NH₂@PdO nano-catalyst with several heterogeneous catalysts previously reported for amide derivative synthesis.

S. N.	Catalyst (amount)	Reactants	Product	Time	TON	TOF	Ref.
1.	SiO ₂ @APTES@Pd-FFR	O 	0	1.5 h	414	276	1
	(20 mg)	H + HN					
2.	[Ru(L ₁)Cl(CO)(PPh ₃) ₂] (1 mol%)	$ \begin{array}{c} 0 & 0 \\ - & H \\ + & NH_2 \end{array} $		12 h	9800	817	2
3.	[Ru(L1)(CO)Cl(AsPh ₃) ₂] (2.98 X 10 ⁻⁴ mol)	O_2N H + NH ₂ OH.HCl	O2N NH2	18 h	188	10.4	3
4.	[(№ -C ₁₀ H ₁₄)-RuCl ₂ (C ₆ H ₅ NH ₂)] (0.017 g, 5 mol%)	$H + NH_2OH.HCl$	NH ₂	5 h	19.60	3.92	4
5.	PGO-NH2@PdO (10mg)	O_2N H + NH_2	O ₂ N H	20 min	445.45	1349.85	This Work

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