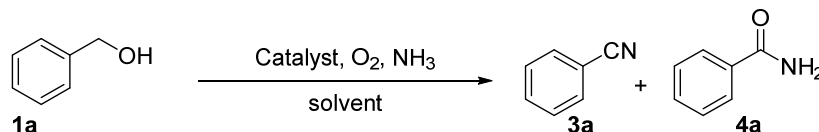


Electronic Supplementary Information (ESI) for

β -MnO₂ nanoparticles as heterogenous catalysts for aerobic oxidative transformation of alcohols to carbonyl compounds, nitriles, and amides

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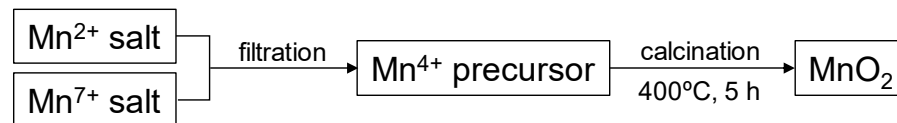
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Table S1. Additive-free aerobic tandem oxidation of benzyl alcohol (**1a**) to benzonitrile (**3a**) and benzamide (**4a**) with heterogeneous catalysts.

entry	catalyst	solvent	temperature (°C)	time (h)	O ₂ (MPa)	yield (%)		remarks	ref.
						3a	4a		
1	β -MnO ₂ nanoparticles	toluene	130	1	0.3	95	–	–	This Work
2 ^a	NCI-Fe/Cu	<i>t</i> -AmOH	130	24	0.5	>99	–	decrease in activity	S1
3	La(OH) ₃ /Fe ₃ O ₄	1,4-dioxane	reflux	2	0.1 (balloon)	95	–	La leaching decrease in activity	S2
4 ^b	Co-[Bmim]Br/C-700	<i>t</i> -AmOH	140	20	0.5	>99	–	–	S3
5 ^c	Co ₃ O ₄ -NGr/C	<i>t</i> -AmOH	130	18	0.5	98	–	–	S4
	Fe ₂ O ₃ -NGr/C	<i>t</i> -AmOH	130	18	0.5	98	–	–	S4
6 ^d	Co-[MCNIm]Cl/C-800	<i>t</i> -AmOH	130	24	0.5	99	–	slight decrease in activity	S5
7 ^e	meso-Co-N/C	<i>t</i> -AmOH	130	18	0.5	95	–	slight decrease in activity	S6
8 ^f	meso-N/C-900	<i>t</i> -AmOH	130	24	0.5	90	–	–	S7
9 ^g	meso-N,B/C	<i>t</i> -AmOH	130	18	0.5	9	83	use of NH ₄ OAc instead of NH ₃ slight decrease in activity	S8
10	amorphous MnO ₂	toluene	100	0.5	0.5	>99	–	use of NH ₃ gas (0.85 MPa) instead of aqueous NH ₃	S9
11	MnO ₂ /graphene oxide	water	150	3	3	–	97	–	S10
12	OMS-2	1,4-dioxane	130	3	0.3	2	95	–	S11
13	Ru/MnO ₂	<i>t</i> -AmOH	100	3	0.5	>99	–	–	S12
14	Ru(OH) _x /Al ₂ O ₃	THF	120	5	0.6 (air)	72	–	–	S13

^aNCI-F/Cu = nitrogen-doped carbon-incarcerated iron/copper bimetallic nanoparticle. *t*-AmOH = *tert*-amyl alcohol. ^bCo-[Bmim]Br/C-700 = C-N-C catalysts prepared by the pyrolysis of carbon-supported Co-[Bmim]Br ([Bmim]Br = 1-butyl-3-methylimidazolium bromide) at 700 °C in N₂. ^cCo₃O₄-NGr/C and Fe₂O₃-NGr/C were prepared by the pyrolysis of carbon-supported Co- and Fe-phenanthroline complexes at 800 °C in Ar. ^dCo-[MCNIm]Cl/C-800 = C-N-C catalysts prepared by the pyrolysis of carbon-supported Co-[MCNIm]Cl ([MCNIm]Cl = 1-methyl-3-cyanomethyl-1H-imidazolium chloride) at 800 °C in N₂. ^eMeso-Co-N/C = mesoporous cobalt-coordinated nitrogen-doped carbon. ^fMeso-N/C-900 = mesoporous nitrogen-doped nanocarbon prepared by the pyrolysis of polypyridyl ligand 4,5-diazafluoren-9-one azine using template assisted synthesis. ^gMeso-N,B/C = metal-free mesoporous nitrogen- and boron-codoped nanocarbon.

Table S2. Effect of the combination of Mn²⁺ and Mn⁷⁺ salts on pH of the reaction solution and MnO₂ formation^a



entry	Mn ²⁺ salt	Mn ⁷⁺ salt	pH ^b	phase ^c	S_{BET}^d (m ² g ⁻¹)	bulk content (wt%)	A/Mn molar ratio (A = Na, K)	AOS
1 ^e	MnSO ₄	NaMnO ₄	0.7	β (β-MnO₂-1)	106	Mn (65.5), Na (0.47), H ₂ O (4.9)	0.017	3.7±0.1
2 ^e	Mn(NO ₃) ₂	NaMnO ₄	0.5	β (β-MnO₂-2)	100	Mn (66.1), Na (0.40), H ₂ O (2.8)	0.014	3.6±0.1
3 ^{e,f}	Mn(OAc) ₂	NaMnO ₄	0.8	β (β-MnO₂-3)	122	Mn (52.8), Na (0.36), H ₂ O (4.4)	0.016	3.8±0.2
4 ^g	Mn(NO ₃) ₂	KMnO ₄	0.8	β (β-MnO₂-4)	124	Mn (58.6), K (0.90), H ₂ O (3.3)	0.022	3.8±0.1
5 ^e	MnSO ₄	KMnO ₄	0.8	α	99	Mn (63.1), K (3.06), H ₂ O (4.3)	0.068	3.6±0.1
6 ^e	Mn(NO ₃) ₂	KMnO ₄	0.5	α	133	Mn (66.0), K (1.94), H ₂ O (7.3)	0.041	3.6±0.1
7 ^e	Mn(OAc) ₂	KMnO ₄	4.6	α	80	Mn (66.3), K (2.65), H ₂ O (3.7)	0.056	3.5±0.1

^a Detailed synthesis conditions are described in the experimental section. The description of hydrates of salts is omitted for clarity. ^b The pH values of the reaction solution were measured after stirring the mixed solution of Mn²⁺ and Mn⁷⁺ salts for 30 min. ^c Determined by XRD analysis for MnO₂. ^d S_{BET} : Specific surface area of MnO₂. ^e Data from reference 56. ^f pH was adjusted by addition of 0.5 M aqueous H₂SO₄. ^g **K-precursor** was treated in 0.1 M HNO₃ aqueous solution.

Table S3. Comparison of surface physicochemical properties of manganese oxides

	β -MnO ₂ -1 ^c	β -MnO ₂ -3 ^c	β -MnO ₂ -4	OMS-2	activated MnO ₂
Oxidation states of surface Mn species ^a	3.5	3.5	3.5	3.3	3.6
Amounts of adsorbed oxygen species (%) ^a	26	28	22	16	21
Reduction rate (mmol g ⁻¹) ^b	1.4	1.7	1.5	1.3	0.7

^a Estimated by XPS analysis. ^b Estimated by H₂-TPR analysis. ^c Data from ref. 56.

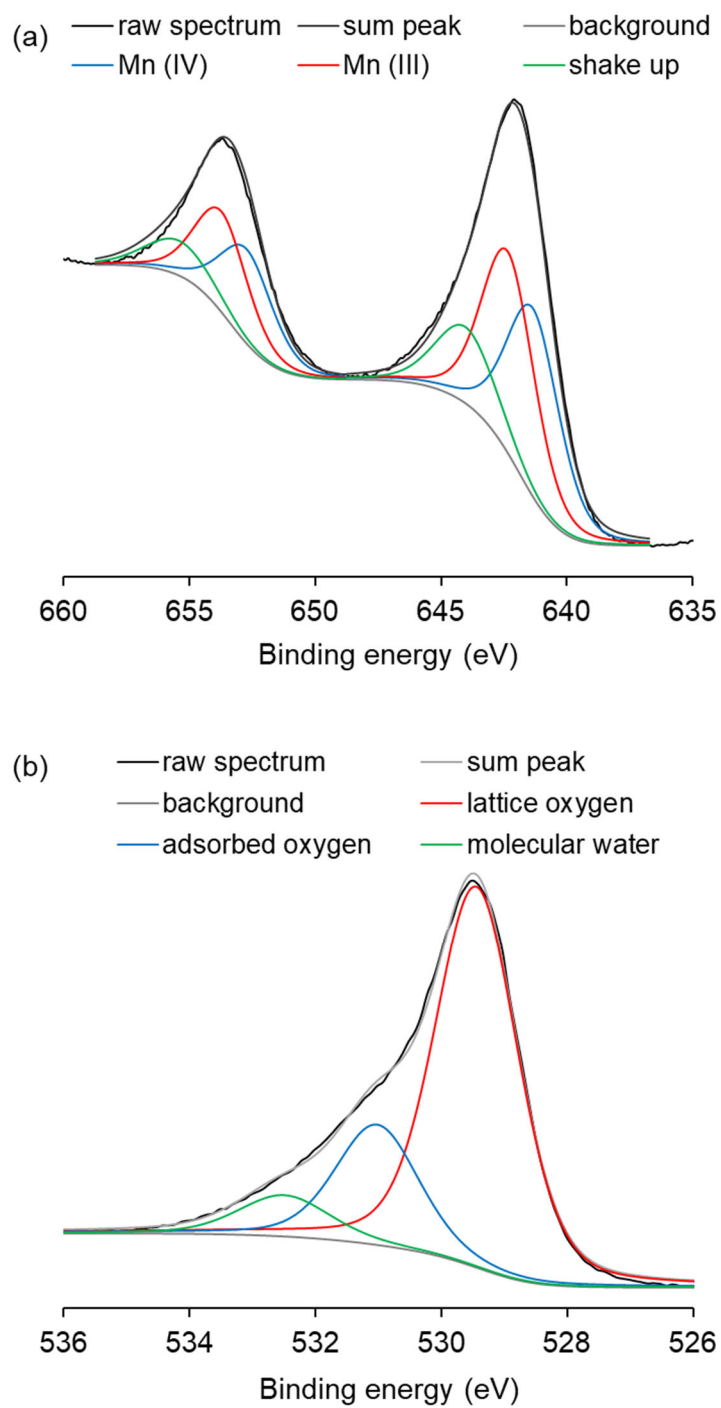


Fig. S1. XPS (a) Mn 2p and (b) O 1s spectra of β -MnO₂-4.

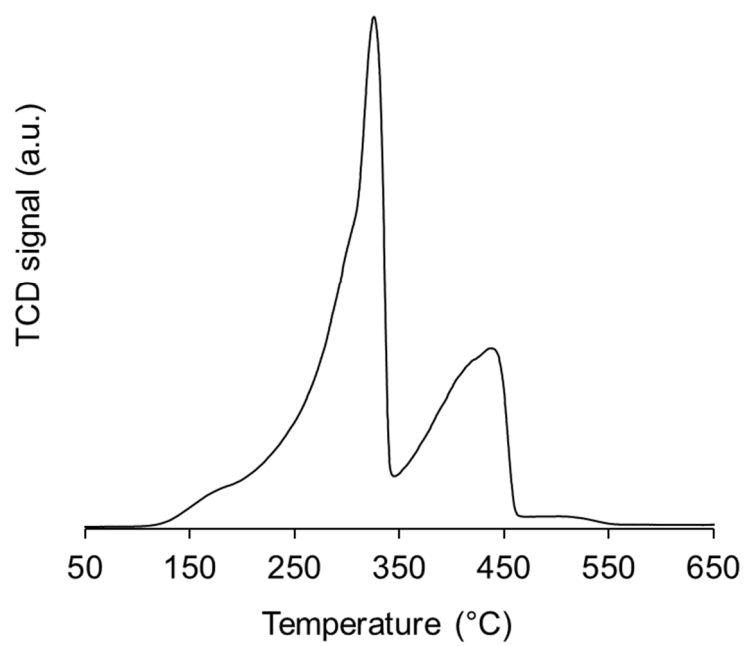


Fig. S2. H₂-TPR profile for β -MnO₂-4.

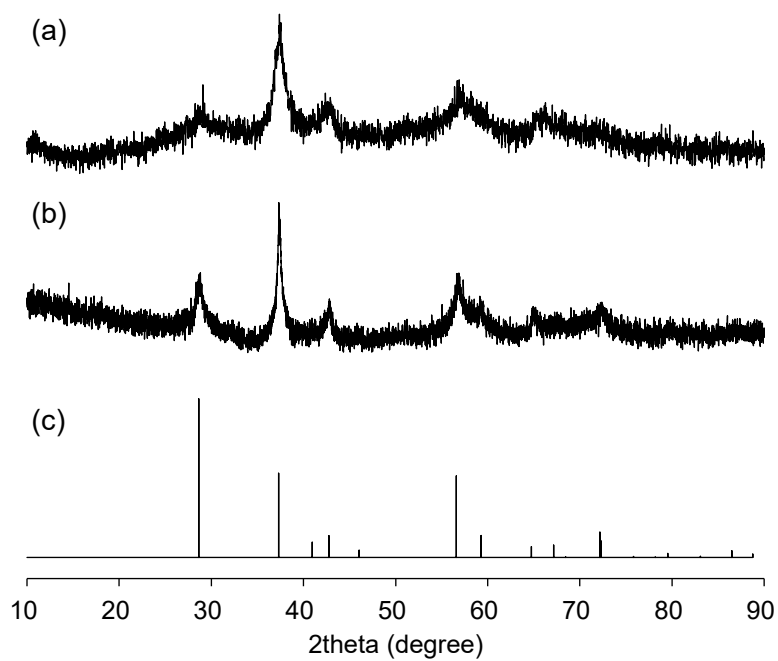


Fig. S3. XRD patterns for (a) fresh $\beta\text{-MnO}_2\text{-1}$, (b) recovered $\beta\text{-MnO}_2\text{-1}$ after the one-pot oxidation of **1a** to **3a** under the conditions of Fig. 6(a), and (c) tetragonal $\beta\text{-MnO}_2$ (JCPDS 01-081-2261).

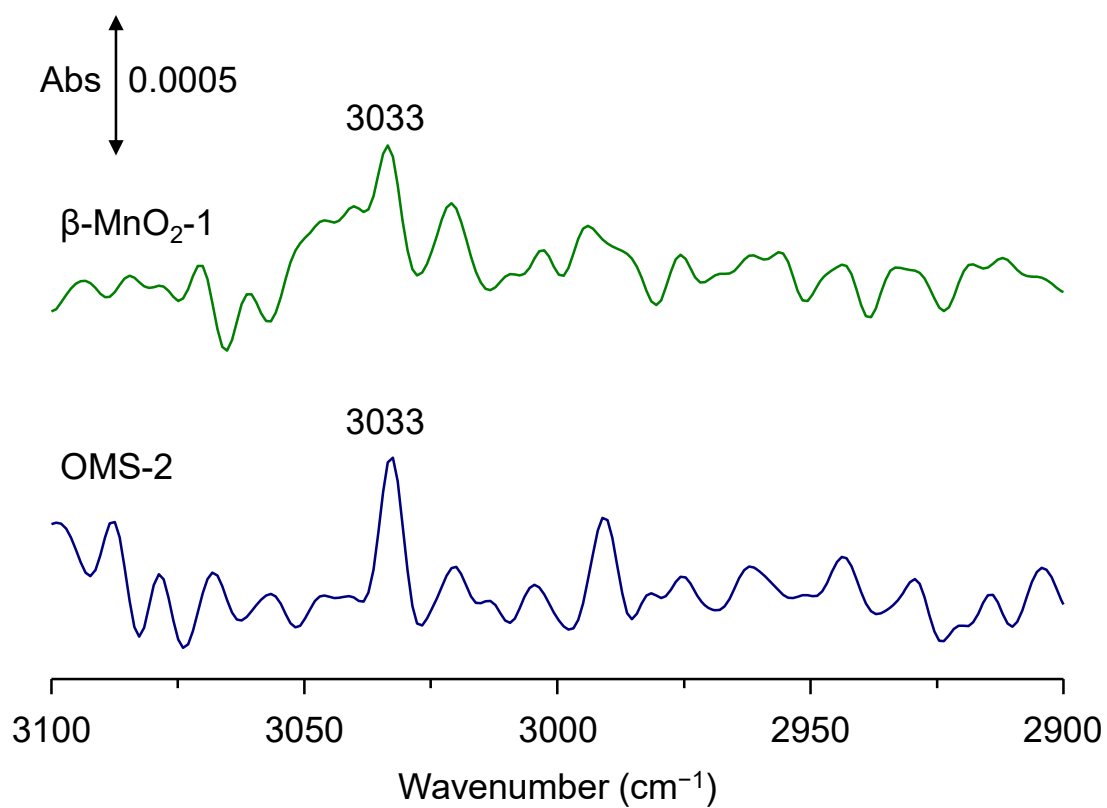


Fig. S4. Difference IR spectra for chloroform-adsorbed $\beta\text{-MnO}_2\text{-1}$ and OMS-2 at $25\text{ }^\circ\text{C}$. Data of $\beta\text{-MnO}_2\text{-1}$ from ref. 59.

Data of products

Benzaldehyde (2a): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 10.03$ (s, 1H), 7.90–7.88 (m, 2H), 7.64–7.62 (m, 1H), 7.56–7.52 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 192.7, 136.8, 134.8, 130.1, 129.3$. MS (EI): m/z (%): 106 ($[M]^+$, 100), 105 (96), 78 (15), 77 (83), 52 (8), 51 (29), 50 (16).

4-Methyl benzaldehyde (2b): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.97$ (s, 1H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 2.44 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 192.1, 145.7, 134.4, 130.0, 129.9, 22.0$. MS (EI): m/z (%): 120 ($[M]^+$, 86), 119 (100), 91 (98), 65 (26), 63 (11), 39 (17).

4-Methoxy benzaldehyde (2c): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.89$ (s, 1H), 7.84 (d, 2H, $J = 8.8$ Hz), 7.01 (d, 2H, $J = 8.8$ Hz), 3.89 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 190.9, 164.8, 132.1, 130.1, 114.5, 55.7$. MS (EI): m/z (%): 136 ($[M]^+$, 70), 135 (100), 107 (19), 92 (16), 77 (35).

4-Chloro benzaldehyde (2d): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.99$ (s, 1H), 7.83 (d, 2H, $J = 8.5$ Hz), 7.52 (d, 2H, $J = 8.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 191.0, 141.1, 137.8, 130.9, 129.4$. MS (EI): m/z (%): 142 ($[M+2]^+$, 22), 141 ($[M+1]^+$, 36), 140 ($[M]^+$, 70), 139 (100), 113 (20), 111 (61), 77 (16), 75 (29), 74 (13), 51 (16), 50 (24).

Methyl terephthalaldehyde (2e): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 10.11$ (s, 1H), 8.20 (d, $J = 8.2$ Hz, 2H), 7.96 (d, $J = 8.2$ Hz, 2H), 3.97 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 191.7, 166.2, 139.3, 135.3, 130.3, 129.7, 52.7$. MS (EI): m/z (%): 164 ($[M]^+$, 39), 163 (14), 133 (100), 105 (34), 77 (27), 76 (11), 51 (19), 50 (13).

4-Nitro benzaldehyde (2f): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 10.17$ (s, 1H), 8.40 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 8.7$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 190.4, 151.3, 140.2, 130.6, 124.5$. MS (EI): m/z (%): 151 ($[M]^+$, 93), 150 (100), 105 (26), 104 (24), 92 (12), 77 (83), 76 (24), 75 (16), 74 (16), 65 (12), 51 (79), 50 (36).

trans-Cinnamaldehyde (2g): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.71$ (d, $J = 7.6$ Hz, 1H), 7.59–7.56 (m, 2H), 7.48 (d, $J = 16.0$ Hz, 1H), 7.46–7.42 (m, 3H), 6.72 (dd, $J = 16.0$ and 7.6 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 193.3, 153.0, 134.4, 131.6, 129.5, 129.0, 128.8$. MS (EI): m/z (%): 132 ($[M]^+$, 77), 131 (100), 104 (29), 103 (67), 102 (12), 78 (40), 77 (48), 51 (31), 50 (12).

2-Pyridinecarboxaldehyde (2h): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 10.09$ (d, $J = 0.8$ Hz, 1H), 8.81–8.79 (m, 1H), 7.99–7.96 (m, 1H), 7.91–7.86 (m, 1H), 7.54–7.51 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 193.7, 153.3, 150.6, 137.4, 128.1, 122.0$. MS (EI): m/z (%): 107 ($[M]^+$, 23), 79 (100), 78 (48), 52 (75), 51 (46), 50 (21).

2-Thiophenecarboxaldehyde (2i): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.50$ (dd, $J =$

1.2 and 0.4 Hz, 1H), 7.78 (ddd, $J = 4.0, 1.2, 0.4$ Hz, 1H), 7.77–7.76 (m, 1H), 7.23–7.21 (m, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 183.2, 144.5, 136.4, 135.3, 128.6$. MS (EI): m/z (%): 113 ($[M+1]^+$, 14), 112 ($[M]^+$, 97), 111 (100), 83 (18), 58 (12), 57 (10).

Furfural (2j): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.67$ (s, 1H), 7.703–7.699 (m, 1H), 7.26 (dd, $J = 3.6, 0.7$ Hz, 1H), 6.61 (dd, $J = 3.6, 1.6$ Hz, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 178.0, 153.2, 148.2, 121.0, 112.7$. MS (EI): m/z (%): 96 ($[M]^+$, 100), 95 (96), 67 (11), 39 (56), 38 (18).

2,5-Diformylfuran (2k): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 9.87$ (s, 1H), 7.34 (s, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 179.3, 154.4, 119.3$. MS (EI): m/z (%): 124 ($[M]^+$, 100), 123 (61), 95 (27), 39 (40), 38 (17).

Acetophenone (2l): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.97$ –7.95 (m, 2H), 7.57–7.55 (m, 2H), 7.48–7.44 (m, 2H), 2.61 (s, 3H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 198.0, 137.2, 133.0, 128.5, 128.3, 26.5$. MS (EI): m/z (%): 120 ($[M]^+$, 29), 105 (100), 77 (65), 51 (17).

Benzophenone (2m): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.82$ –7.79 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.46 (m, 4H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 197.0, 138.0, 132.7, 130.4, 128.6$. MS (EI): m/z (%): 182 ($[M]^+$, 47), 105 (100), 78 (18), 77 (56), 51 (18).

2-Octanone (2n): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 2.42$ (t, $J = 7.6$ Hz, 2H), 2.13 (s, 3H), 1.59–1.55 (m, 2H), 1.31–1.26 (m, 6H), 0.88 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 209.7, 44.2, 31.9, 30.2, 29.2, 24.2, 22.8, 14.3$. MS (EI): m/z (%): 128 ($[M]^+$, 8), 85 (10), 71 (22), 59 (19), 58 (88).

Benzonitrile (3a): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.67$ –7.59 (m, 3H), 7.48 (t, $J = 7.8$ Hz, 2H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 133.1, 132.6, 129.5, 119.2, 112.8$. MS (EI): m/z (%): 103 ($[M]^+$, 100), 76 (38), 50 (14).

4-Methoxybenzonitrile (3b): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.59$ (d, $J = 8.9$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 163.2, 134.3, 119.5, 115.1, 104.4, 55.9$. MS (EI): m/z (%): 133 ($[M]^+$, 100), 90 (48), 103 (47), 63 (18), 64 (15), 104 (13), 76 (13), 39 (12), 118 (10).

4-Methylbenzonitrile (3c): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.55$ –7.26 (m, 4H), 2.42 (s, 3H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 144.0, 132.4, 130.3, 119.5, 109.7, 22.2$. MS (EI): m/z (%): 117 ($[M]^+$, 100), 116 (65), 90 (45), 89 (28), 63 (13), 39 (13).

4-Chlorobenzonitrile (3d): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 7.60$ (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): $\delta = 139.9, 133.7, 130.0, 118.3, 111.2$. MS (EI): m/z (%): 137 ($[M]^+$, 100), 102 (36), 139 ($[M+2]^+$, 31), 75

(17), 50 (16).

Methyl 4-cyanobenzoate (3e): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 8.14 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 3.96 (s, 3H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 165.8, 134.3, 132.6, 130.4, 118.3, 116.8. MS (EI): m/z (%): 130 (100), 102 (48), 161 ($[M]^+$, 17), 75 (15).

4-Nitrobenzonitrile (3f): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 8.37 (d, J = 8.9 Hz, 2H), 7.90 (d, J = 8.9 Hz, 2H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 150.4, 133.8, 124.6, 118.7, 117.1. MS (EI): m/z (%): 102 (100), 75 (43), 148 ($[M]^+$, 42), 51 (25), 90 (24), 76 (22), 50 (20).

Cinnamionitrile (3g): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.46–7.38 (m, 6H), 5.90 (d, J = 16.8 Hz, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 150.9, 133.9, 131.5, 129.5, 127.7, 118.5, 96.7. MS (EI): m/z (%): 130 ($[M+1]^+$, 10), 129 ($[M]^+$, 100), 128 (29), 103 (16), 102 (47), 78 (11), 76 (13), 51 (19), 50 (11).

4-Cyanopyridine (3h): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 8.82 (dd, J = 1.6 Hz and 4.7 Hz, 2H), 7.54 (dd, J = 1.6 Hz and 4.2 Hz, 2H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 151.1, 125.6, 120.8, 116.7. MS (EI): m/z (%): 104 ($[M]^+$, 100), 77 (66), 50 (24), 76 (19), 64 (15), 51 (15).

2-Thiophenecarbonitrile (3i): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.65 (dd, J = 1.1 Hz and 3.8 Hz, 1H), 7.62 (dd, J = 1.1 Hz and 3.8 Hz, 1H), 7.15–7.13 (m, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 137.7, 132.9, 128.0, 114.5, 110.3. MS (EI): m/z (%): 109 ($[M]^+$, 100), 58 (37), 45 (35).

2-Furonitrile (3j): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.63 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 0.9 Hz, 1H), 6.59–6.57 (m, 1H). $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, CDCl_3 , TMS): δ = 147.4, 125.8, 121.2, 111.3. MS (EI): 93 ($[M]^+$, 100), 64 (52), 38 (37), 65 (32), 39 (24), 37 (22).

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